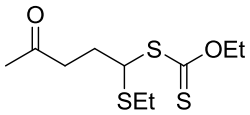
Applications de la Chimie Radicalaire des Xanthates : Synthèse d'Alpha Céto Vinyl Carbinols, Synthèse stéréosélective de Sulfones Vinyliques et d'Alcènes, Induction de la Chiralité sur des Systèmes Cycliques, Approche à la Synthèse des Sesquiterpènes de type eudesmane, Approche à la Synthèse du (+)-Maritimol - Synthèse du fragment C16-C30 du dolabélide C

Marie-Gabrielle Braun

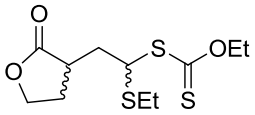
PARTIE EXPERIMENTALE

I. Récapitulatif des Molécules Citées dans la Partie Expérimentale

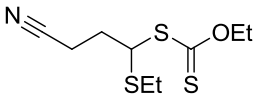
A. Chapitre III : Synthèse d'α-Céto Carbinols Vinyliques



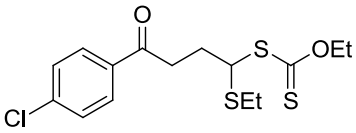
III-16a, p 386



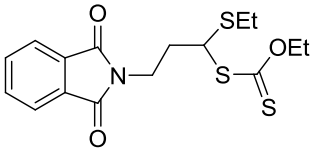
III-16b, p 387



III-16c, p 388



III-16d, p 389



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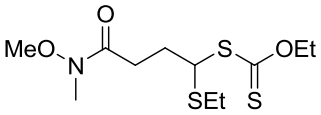
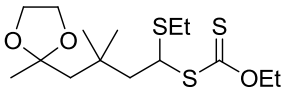
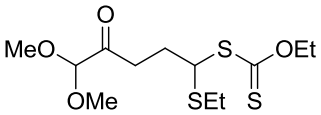


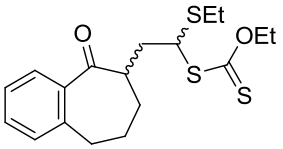
III-16f, p 391



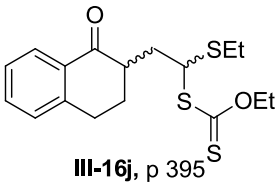
III-16g, p 392



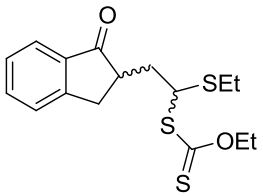
III-16h, p 393



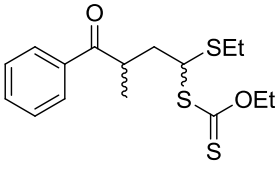
III-16i, p 394



III-16j, p 395



III-16k, p 396



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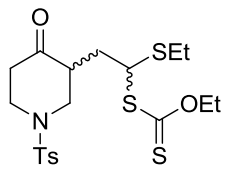
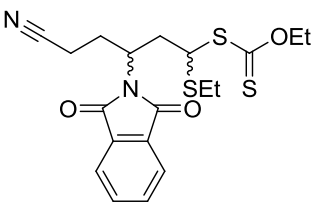


III-16m, p 398



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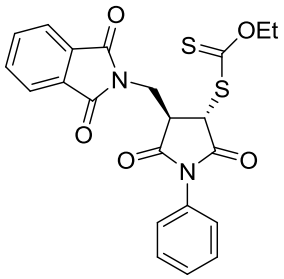
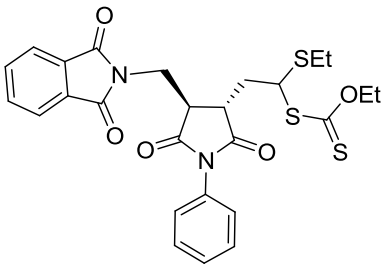
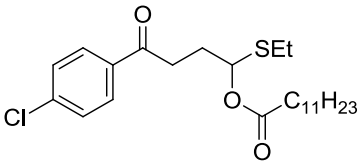


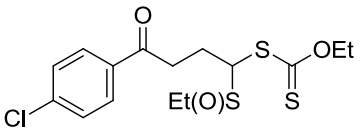
III-7o, p 400



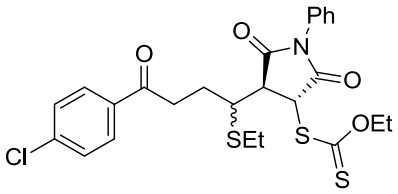
III-16o, p 401



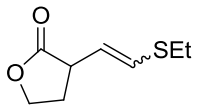
III-20, p 402



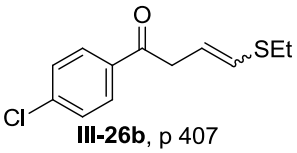
III-23, p 403



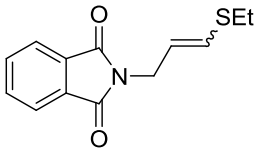
III-25, p 404



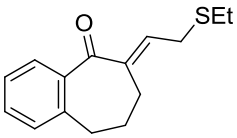
III-26a, p 405



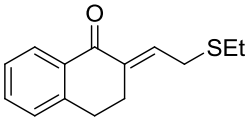
III-26b, p 407



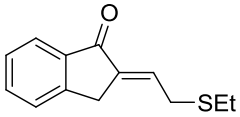
III-26c, p 408



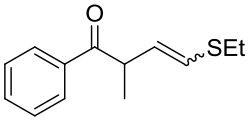
III-27d, p 409



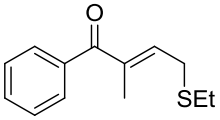
III-27e, p 410



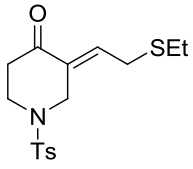
III-27f, p 411



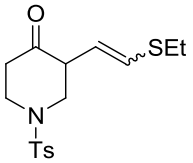
III-26g, p 412



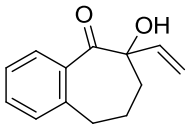
III-27g, p 412



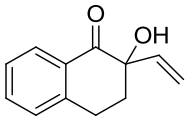
III-27h, p 414



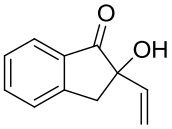
III-26h, p 414



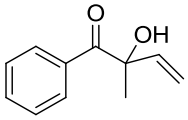
III-32a, p 416



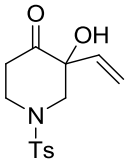
III-32b, p 417



III-32c, p 418

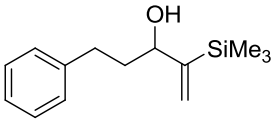


III-32d, p 419

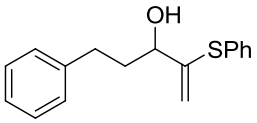


III-32e, p 420

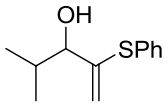
B. Chapitre IV : Synthèse Stéréosélective d'Oléfines



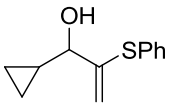
IV-7a, p 421



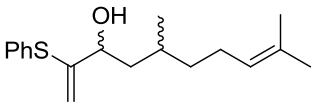
IV-13a, p 422



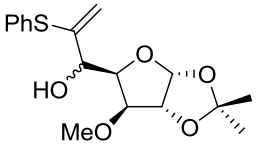
IV-13b, p 423



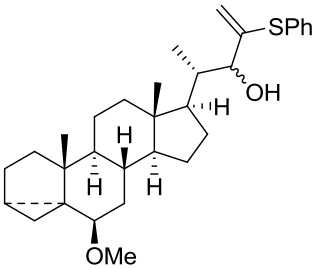
IV-13c, p 424



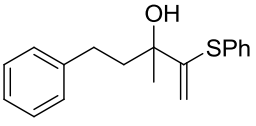
IV-13d, p 425



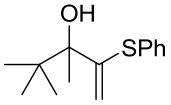
IV-13e, p 426



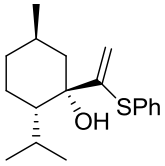
IV-13f, p 427



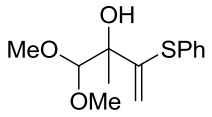
IV-13g p 429



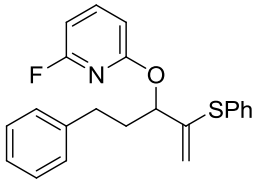
IV-13h, p 430



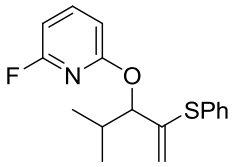
IV-13i, p 431



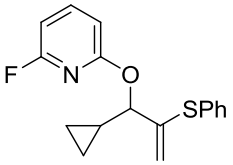
IV-13j, p 432



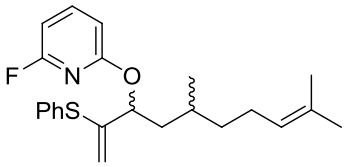
IV-11a, p 434



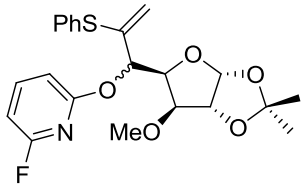
IV-11b, p 435



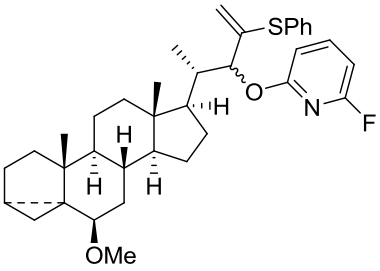
IV-11c, p 436



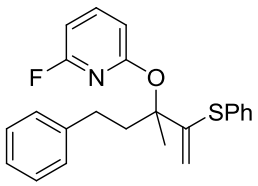
IV-11d, p 437



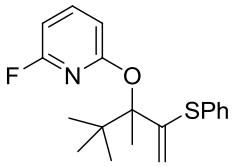
IV-11e, p 438



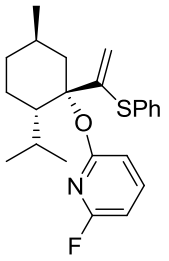
IV-11f, p 440



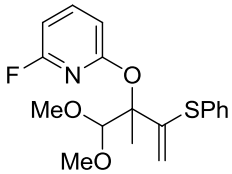
IV-11g, p 442



IV-11h, p 443



IV-11i, p 444



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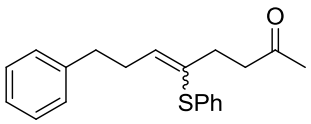
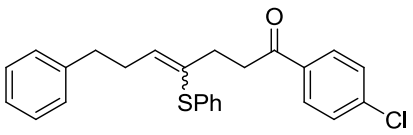
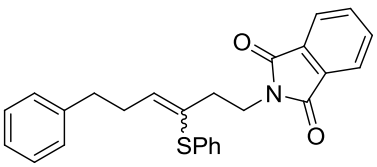


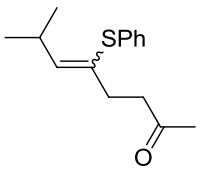
IV-10a, p 446



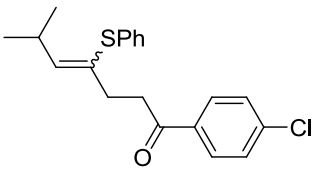
IV-10b, p 447



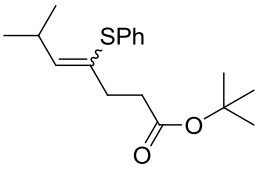
IV-10c, p 448



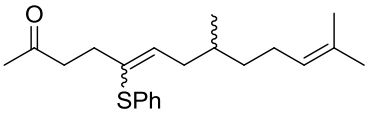
IV-10d, p 449



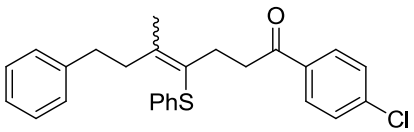
IV-10e, p 450



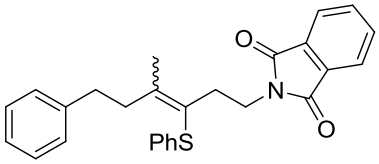
IV-10f, p 451



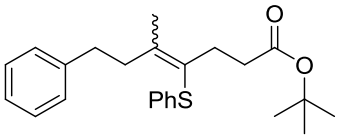
IV-10g, p 452



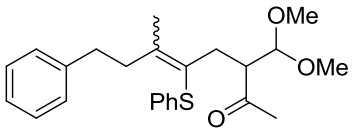
IV-10h, p 453



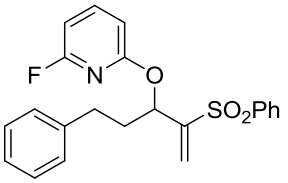
IV-10i, p 454



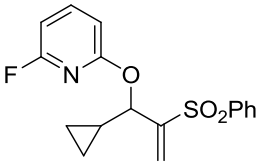
IV-10j, p 455



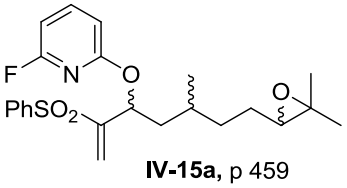
IV-10k, p 456



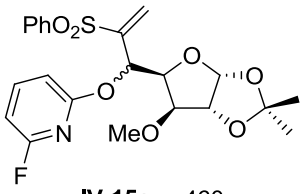
IV-15a, p 457



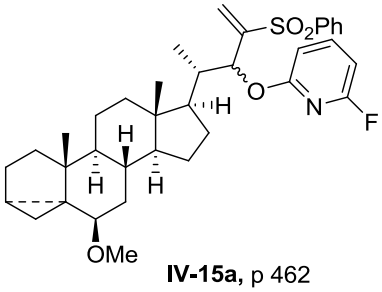
IV-15a, p 458



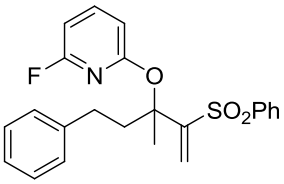
IV-15a, p 459



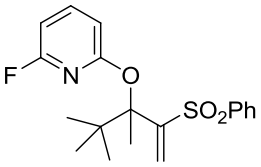
IV-15a, p 460



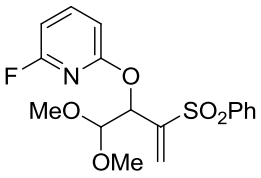
IV-15a, p 462



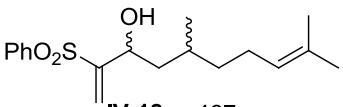
IV-15a, p 464



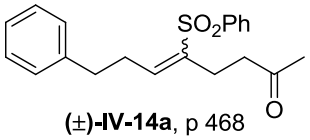
IV-15a, p 465



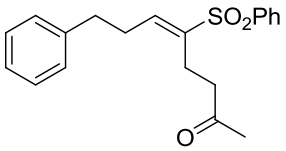
IV-15a, p 466



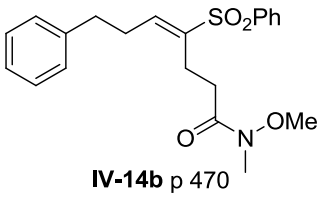
IV-18, p 467



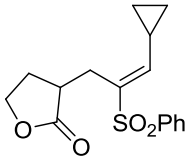
(±)-IV-14a, p 468



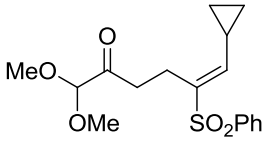
IV-14a, p 469



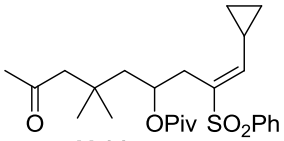
IV-14b p 470



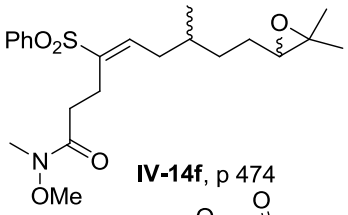
IV-14c, p 471



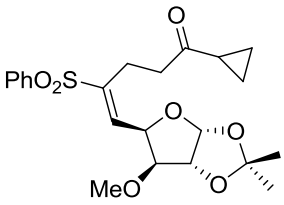
IV-14d, p 472



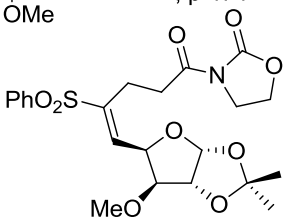
IV-14e, p 473



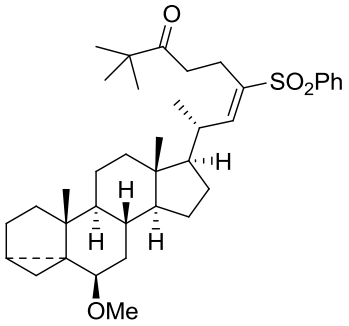
IV-14f, p 474



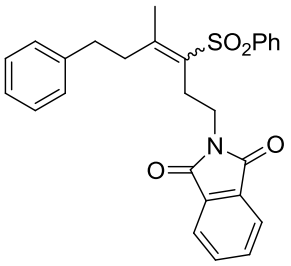
IV-14g, p 475



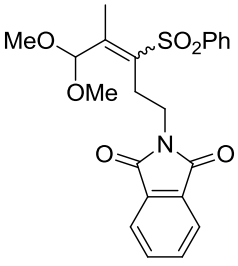
IV-14h, p 476



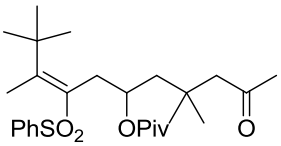
IV-14i, p 477



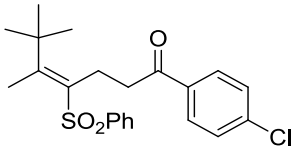
IV-14j, p 479



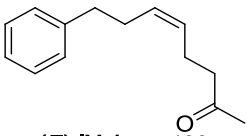
IV-14k, p 480



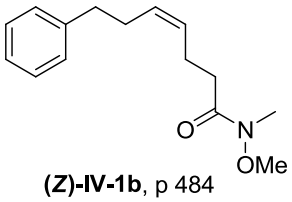
IV-14l, p 481



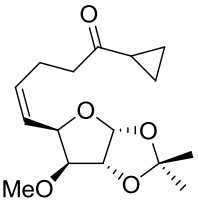
IV-14m, p 482



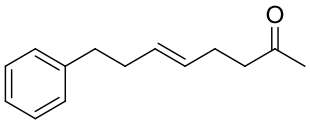
(*Z*)-IV-1a, p 483



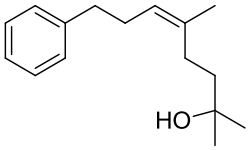
(*Z*)-**IV-1b**, p 484



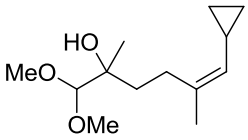
(*Z*)-**IV-1c**, p 485



(*E*)-**IV-1b**, p 486



IV-21a, p 487



IV-21b, p 488

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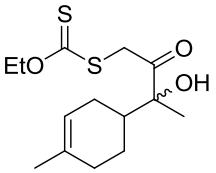
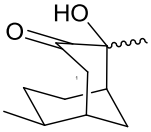
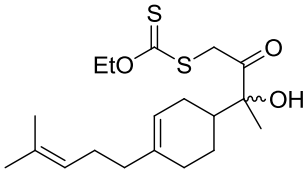


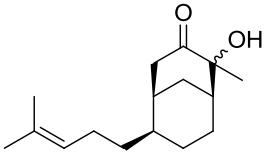
RH2, p 490



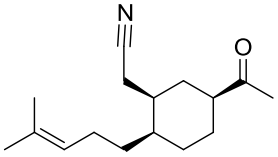
RH4, p 492



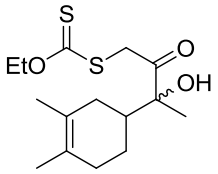
V-2, p 494



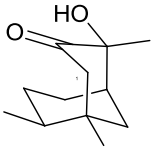
V-3, p 495



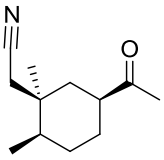
V-4, p 496



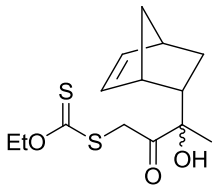
V-6, p 497



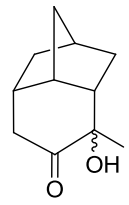
V-7, p 498



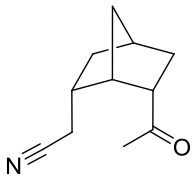
V-8, p 500



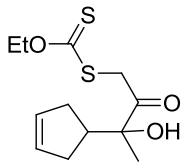
V-10, p 501



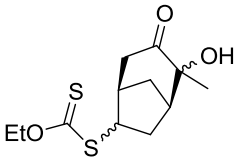
V-11, p 502



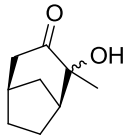
V-12, p 504



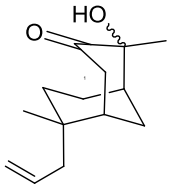
V-17, p 505



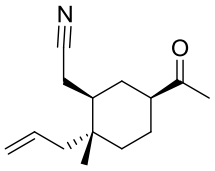
V-18, p 506



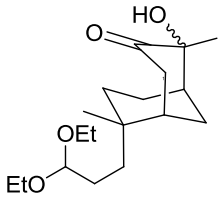
V-19, p 507



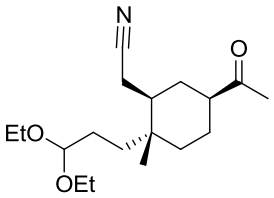
V-24, p 508



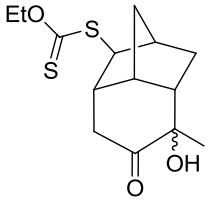
V-25, p 510



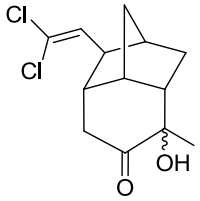
V-26, p 512



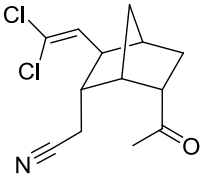
V-27, p 514



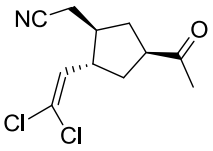
V-22, p 515



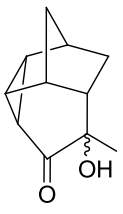
V-29, p 516



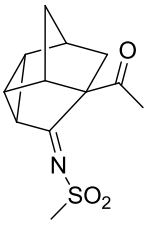
V-30, p 518



V-32, p 519

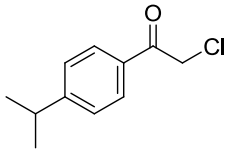


V-35, p 520

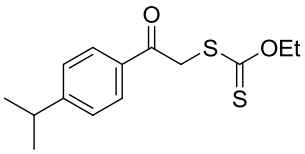


V-38, p 522

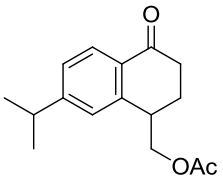
D. Chapitre VI : Approche à la Synthèse des Eudesmanes



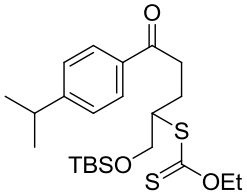
VI-4, p 523



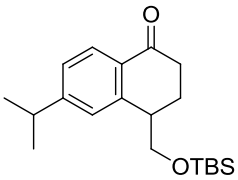
VI-3, p 524



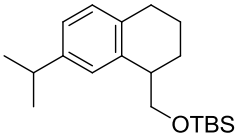
VI-2a, p 525



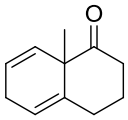
VI-5 p 526



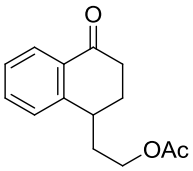
VI-2b, p 527



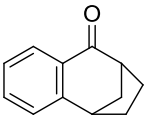
VI-8, p 528



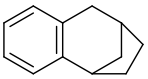
VI-10, p 529



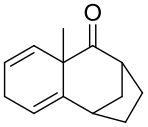
VI-14, p 530



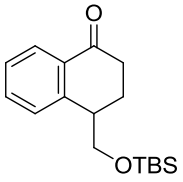
CO1, p 531



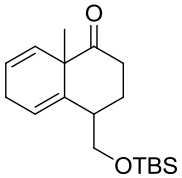
VI-15, p 532



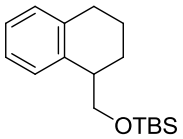
VI-16, p 533



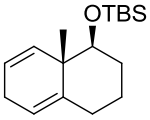
VI-19, p 534



VI-18, p 535

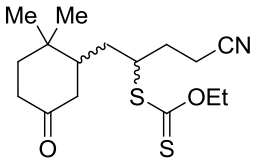


VI-21, p 536

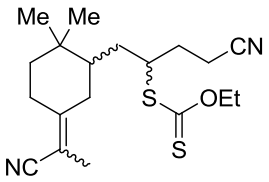


VI-23, p 537

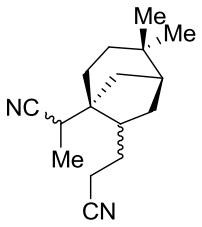
E. Chapitre VII Approche à la Synthèse du (+)-Maritimol



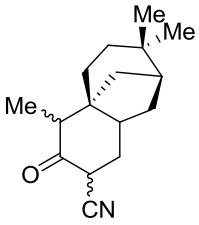
MC8, p 539



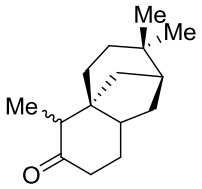
MC5, p 540



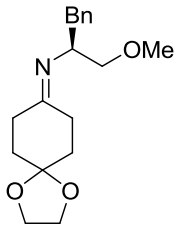
MC4, p 541



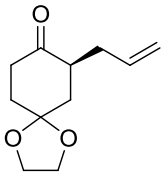
MC10, p 542



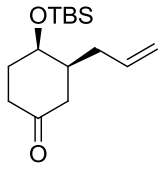
MC3, p 543



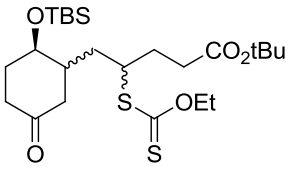
MC25, p 544



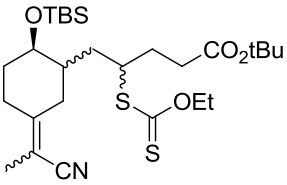
MC26, p 545



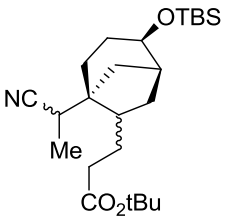
VII-9, p 546



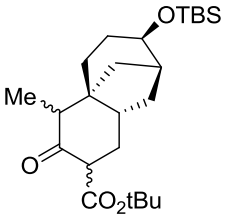
VII-12, p 547



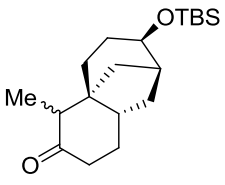
VII-13, p 548



VII-8, p 549

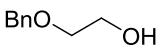


VII-16, p 550

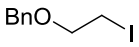


VII-7, p 551

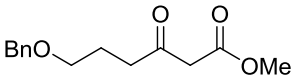
F. Chapitre VIII : Synthèse du Fragment C16-C30 du Dolabélide C



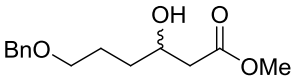
AV16, p 552



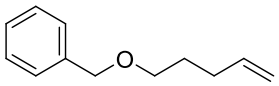
AV17, p 553



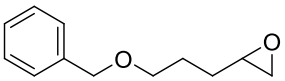
AV18, p 554



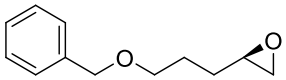
(±)-AV16, p 555



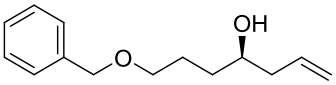
VIII-8, p 556



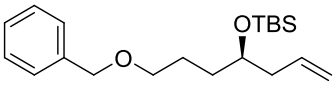
(±)-VIII-6, p 557



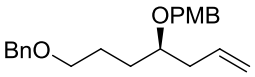
VIII-6, p 558



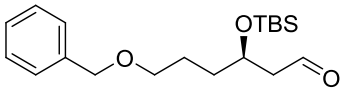
VIII-10, p 559



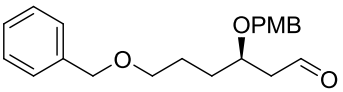
VIII-11a, p 560



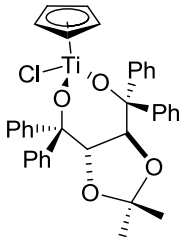
VIII-11b, p 561



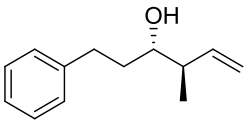
VIII-5a, p 562



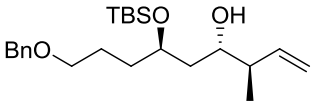
VIII-5b, p 563



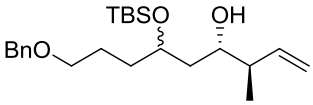
(*S*,*S*)-DU2, p 564



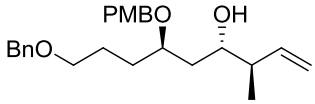
VIII-12, p 565



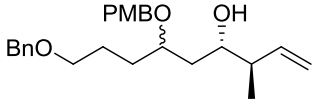
VIII-4a, p 566



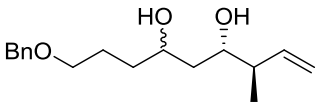
***anti*-VIII-4a,** p 567
***syn*-VIII-4a,** p 567



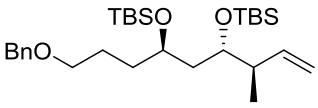
VIII-4b, p 568



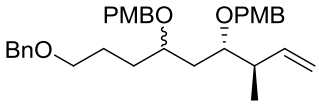
***anti*-VIII-4b,** p 569
***syn*-VIII-4b,** p 569



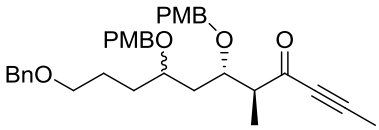
***anti*-VIII-13b,** p 570
***syn*-VIII-13b,** p 570



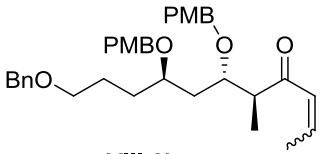
VIII-15a, p 573



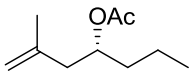
***anti*-VIII-15b,** p 575
***syn*-VIII-15b,** p 575



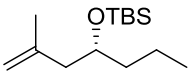
***anti*-VIII-18b,** p 578
***syn*-VIII-18b,** p 578



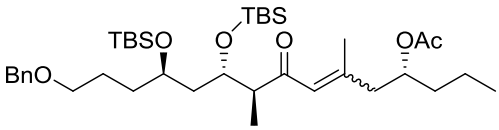
VIII-2b, p 582



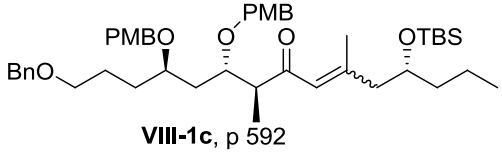
VIII-3a, p 585



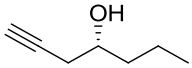
VIII-3c, p 587



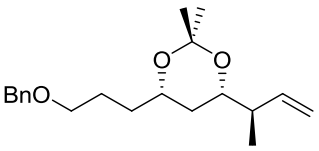
VIII-1a, p 589



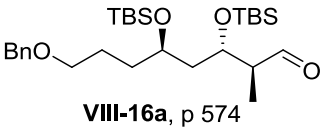
VIII-1c, p 592



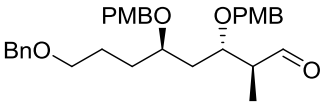
LE5, p 594



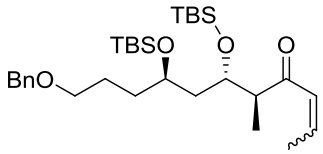
VIII-14, p 572



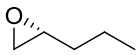
VIII-16a, p 574



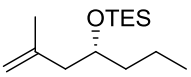
VIII-16b, p 576



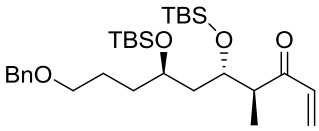
VIII-2a, p 580



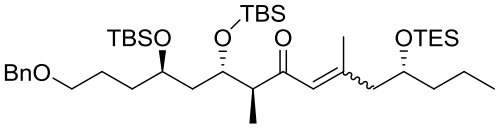
VIII-20, p 584



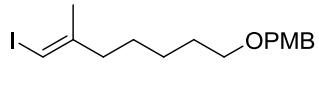
VIII-3b, p 586



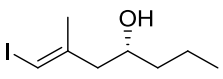
VIII-22, p 588



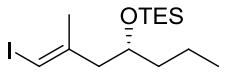
VIII-1b, p 591



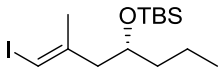
VIII-26, p 593



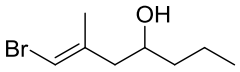
HA12, p 595



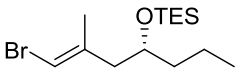
VIII-24a, p 596



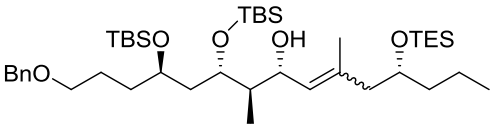
VIII-24b, p 597



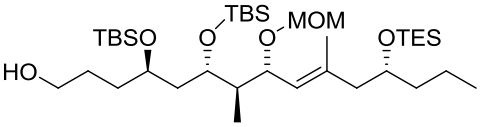
VIII-27, p 598



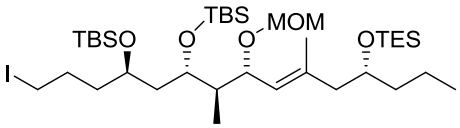
VIII-28, p 599



VIII-23a, p 600



VIII-32, p 601



AV2, p 603

II. Généralités

A. Abréviations

1. Unités

°C	degré Celsius
h	heure
Hz, MHz	hertz, mégahertz
g, mg	gramme, milligramme
min	minutes
mL, µL	millilitre, microlitre
mmol	millimole
ppm	partie par million

2. Autres

ar	aromatique
cat.	catalytique
TLC (CCM)	chromatographie sur couche mince
d	doublet
δ	déplacement chimique
equiv	nombre d'équivalents
HRMS	spectrométrie de masse haute résolution
IR	infra-rouge
J	constante de couplage
MP	point de fusion
quant.	quantitatif
q	quadruplet
RMN	résonance magnétique nucléaire
s	singulet
σ	nombre d'ondes

B. Purification des solvants et réactifs

Le dichlorométhane est distillé sur hydrure de calcium. L'éther et le tétrahydrofurane sont distillés sur sodium en présence de benzophénone comme indicateur.

Les réactifs sont généralement utilisés sans purification préalable, leur pureté étant vérifiée par RMN du proton.

Toutes les réactions sensibles à l'eau ou à l'air sont réalisées sous flux d'azote.

C. Chromatographie

Les chromatographies sur couche mince (CCM) ont été effectuées sur des plaques de silice sur aluminium 60 F_{254} (Merck ou SDS).

Les CCM sont observées en lumière ultraviolette à 254 ou 366 nm. Elles sont généralement immergées dans un révélateur à la vanilline, à l'anisaldéhyde, ou au permanganate de potassium, puis chauffées au pistolet à décapage.

Les chromatographies flash sur gel de silice ont été réalisées avec de la silice SDS 60 A C.C. (40-63 µm).

D. Appareillage d'analyse utilisé

Les spectres de résonance magnétique nucléaire ont été réalisés sur un appareil Bruker AMX 400 (400 MHz).

En RMN du proton (RMN ^{1}H), les déplacements chimiques (δ) sont exprimés en partie par million (ppm) par rapport au proton du chloroforme (δ = 7.26 ppm). Les constantes de couplage (J) sont exprimées en Hertz (Hz).

En RMN du carbone (RMN ^{13}C), les déplacements chimiques (δ) sont exprimés en partie par million (ppm) en prenant la raie centrale du chloroforme deutéré (δ=77.0 ppm) comme référence interne. Pour chaque produit, un spectre a été enregistré « Broad Band » (découplage par bruit de protons) et un autre en séquence Jmod ou DEPT pour déterminer la parité du nombre de protons portés par le carbone.

Dans certains cas, l'attribution des signaux a été complétée par des expériences à deux dimensions (COSY, HSQC).

Les spectres infra-rouge (IR) ont été réalisés sur un appareil Perkin-Elmer FT-IR 2000 à transformée de Fourier en solution dans le tétrachlorure de carbone, dans une cuve de chlorure de sodium ou de fluorure de calcium. Les spectres sont réalisés en absorption et les nombres d'onde σ des bandes d'absorption sont exprimés en cm^{-1}.

Les spectres de masse à haute résolution (HRMS) ont été réalisés sur un spectromètre JEOL JMS-GCmate II, GS/MS à l'Ecole Polytechnique.

Les molécules ont été nommées selon la nomenclature IUPAC par le logiciel Autonom 1.1 (Beilstein Institut).

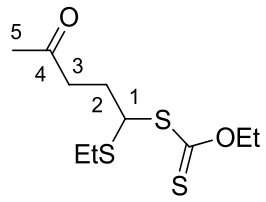
III. Modes opératoires et analyses

A. Chapitre III : Synthèse d'α-Céto Carbinols Vinyliques

GENERAL PROCEDURE III-A : INTERMOLECULAR RADICAL ADDITION

A solution of **xanthate** (1.0 equiv) and **olefin** (2.0 equiv) in **ethyl acetate** (AcOEt) (1 mL/mmol of xanthate) was refluxed for 15 min under a nitrogen flow. **Dilauroyl peroxide** (DLP) (5 mol %) was then added and additional DLP (5 mol %) was added every 90 min until total consumption of the starting xanthate or until no evolution could be detected by TLC analysis. The reaction mixture was then cooled to 20 °C and evaporated to dryness under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired xanthate adduct.

***O*-Ethyl *S*-1-(ethylthio)-4-oxopentyl carbonodithioate** **III-16a**

	$C_{10}H_{18}O_2S_3$ M= 266.4 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out using xanthate **III-7a**[1] (178 mg, 1.0 mmol) and ethyl vinyl sulfide **III-15** (203 µL, 2.0 mmol), and needed 20 mol% of DLP to go to completion (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16a** (216 mg, 81%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 4.80 (dd, *J*= 7.5, 5.9 Hz, 1H, C***H***-1), 4.64 (q, *J*= 7.1 Hz, 2H, OC***H***$_2$), 2.58-2.79 (m, 4H, C***H*****$_2$**-3, SC***H*****$_2$**), 2.18-2.29 (m, 2H, C***H*****$_2$**-2), 2.01 (s, 3H, C***H*****$_3$**-5). 1.43 (t, *J*= 7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.28 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**).

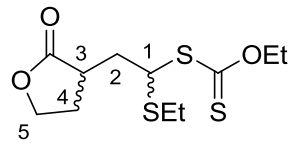
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 214.0 (C=S), 207.3 (C-4), 70.1 (OCH_2), 55.0 (C-1), 40.8 (C-3), 30.1 (CH_3-5), 29.8 (C-2), 25.9 (SCH_2), 14.5 (SCH_2***C***H_3), 13.8 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 2961, 2928, 2872, 2856, 1722, 1443, 1365, 1291, 1266, 1220, 1147, 1111, 1049.

HRMS (EI) Calcd. for $C_{10}H_{18}O_2S_3$: 266.0469 Found : 266.0478

[1] Charrier, N; Gravestock, D; Zard, S. Z. *Angew. Chem. Int. Ed.* **2006**, *39*, 6520.

_O_-Ethyl _S_-1-(ethylthio)-2-(2-oxotetrahydrofuran-3-yl)ethyl carbonodithioate **III-16b**

	$C_{11}H_{18}O_3S_3$ M= 294.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7b**[2] (618 mg, 3.0 mmol) and ethyl vinyl sulfide **III-15** (608 µL, 6.0 mmol), and needed 10 mol % of DLP to go to completion (3 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford radical adduct **III-16b** (777 mg, 88%) as a yellow oil and as a mixture of two diasteromers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.06 (t, *J*= 7.2 Hz, 0.5H, C***H***-1), 4.72 (dd, *J*= 10.1, 4.0 Hz, 0.5H, C***H***-1), 4.60-4.67 (m, 2H, OC***H***$_2$), 4.32-4.41 (m, 1H, C***H***-5), 4.15-4.24 (m, 1H, C***H***-5), 2.48-2.97 (m, 5H, C***H***-3, C***H***-4, SC***H*****$_2$**, C***H***-2), 2.02-2.19 (m, 2H, C***H***-2, C***H***-4), 1.39-1.43 (m, 3H, OCH_2C***H*****$_3$**), 1.23-1.29 (m, 3H, SCH_2C***H*****$_3$**).

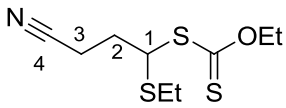
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.8, 213.4 (C=S), 178.4, 178.1 (C=O), 70.2, 70.0 (OCH_2), 66.5, 66.4 (C-5), 53.6, 53.4 (C-1), 37.4, 37.4 (C-3), 36.9, 36.5 (C-2), 29.7, 28.4 (C-4), 25.9, 25.5 (SCH_2), 14.5, 14.4 (SCH_2***C***H_3), 13.7, 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 2980, 2931, 2874, 1781, 1455, 1372, 1220, 1146, 1111, 1049, 1031.

HRMS (EI) Calcd. for $C_{11}H_{18}O_3S_3$: 294.0418 Found : 294.0409

[2] Engler, E. M.; Patel, V. V.; Andersen, J. R.; Schumaker, R. R.; Fukushima, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 3769

_S_-3-Cyano-1-(ethylthio)propyl _O_-ethyl carbonodithioate **III-16c**

	$C_9H_{15}NOS_3$ M= 249.4 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7c**[3] (323 mg, 2.0 mmol) and ethyl vinyl sulfide **III-15** (406 µL, 4.0 mmol), and needed 15 mol % of DLP to go to completion (4 h 30 min). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 1:9) to afford radical adduct **III-16c** (434 mg, 87%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.79 (dd, *J*= 8.8, 4.9 Hz, 1H, C***H***-1), 4.67 (q, *J*= 7.1 Hz, 2H, OC***H***$_2$), 2.64-2.79 (m, 2H, SC***H*****$_2$**), 2.62 (t, *J*= 7.3 Hz, 2H, C***H*****$_2$**-3), 2.41-2.50 (m, 1H, C***H***-2), 2.14-2.23 (m, 1H, C***H***-2), 1.45 (t, *J*= 7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.31 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**).

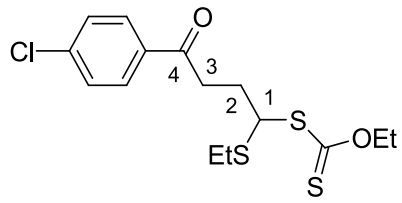
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.0 (C=S), 118.5 (C-4), 70.3 (OCH_2), 53.6 (C-1), 31.8 (C-2), 26.1 (SCH_2), 15.2 (C-3), 14.5 (SCH_2***C***H_3), 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2979, 2930, 2873, 2856, 2251, 1711, 1443, 1424, 1379, 1364, 1291, 1266, 1215, 1147, 1111, 1055.

HRMS (EI): Calcd. for $C_9H_{15}NOS_3$: 249.0316 Found : 249.0312

[3] Dinizo, S.E. et al. *J. Org. Chem.* **1976**, *17*, 2846.

_S_-4-(4-Chlorophenyl)-1-(ethylthio)-4-oxobutyl _O_-ethyl carbonodithioate **III-16d**



$C_{15}H_{19}ClO_2S_3$
M= 363.0
$g.mol^{-1}$

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7**[4] (1.37 g, 5.0 mmol) and ethyl vinyl sulfide **III-15** (1.01 mL, 10.0 mmol), and needed 15 mol % of DLP to go to completion (3 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16d** (1.63 g, 90%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.90 (d, *J*= 8.5 Hz, 2H, C***H***-ar), 7.43 (d, *J*= 8.5 Hz, 2H, C***H***-ar), 4.89 (dd, *J*= 7.3, 5.9 Hz, 1H, C***H***-1), 4.58-4.66 (m, 2H, OC***H***$_2$), 3.26 (ddd, *J*= 17.1, 8.9, 5.9 Hz, 1H, C***H***-3), 3.14 (ddd, *J*= 17.1, 8.9, 6.0 Hz,, 1H, C***H***-3), 2.61-2.80 (m, 2H, SC***H$_2$***), 2.32-2.50 (m, 2H, C***H$_2$***-2), 1.41 (t, *J*= 7.1 Hz, 3H, OCH_2C***H$_3$***), 1.28 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

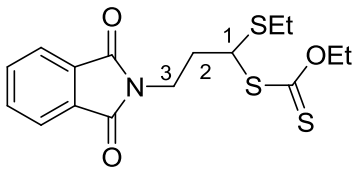
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.8 (C=S), 197.4 (C-4), 139.5, 135.0, 129.4, 128.9 (C-ar), 70.0 (OCH_2), 55.0 (C-1), 35.8 (C-3), 30.3 (C-2), 25.9 (SCH_2), 14.4 (SCH_2***C***H_3), 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 2979, 2929, 2872, 2856, 1692, 1591, 1401, 1364, 1265, 1221, 1110, 1094.

HRMS (EI) Calcd. for $C_{15}H_{19}ClO_2S_3$: 362.0236 Found : 362.0242

[4] Liard, A. unpublished results.

_S_-3-(1,3-Dioxoisoindolin-2-yl)-1-(ethylthio)propyl _O_-ethyl carbonodithioate **III-16e**



$C_{16}H_{19}NO_3S_3$
M= 369.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7e**[5] (563 mg, 2.0 mmol) and ethyl vinyl sulfide (406 µL, 4.0 mmol), and needed 15 mol % of DLP to go to completion (4 h 30). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 3:7) to afford radical adduct **III-16e** (600 mg, 81%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.85 (dd, *J*= 5.4, 3.1 Hz, 2H, C***H***-ar), 7.72 (dd, *J*= 5.4, 3.0 Hz, 2H, C***H***-ar), 4.68 (dd, *J*= 9.9, 3.9 Hz, 1H, C***H***-1), 4.56 (q, *J*= 7.1 Hz, 2H, OC***H***$_2$), 4.00 (ddd, *J*= 14.0, 7.7, 6.3 Hz, 1H, C***H***-3), 3.89 (dt, *J*= 14.0, 6.1 Hz, 1H, C***H***-3), 2.77 (dq, *J*= 12.6, 7.4 Hz, 1H, SC***H***), 2.67 (dq, *J*= 12.6, 7.4 Hz, 1H, SC***H***), 2.45 (dddd, *J*= 11.6, 7.7, 6.1, 3.9 Hz, 1H, C***H***-2), 2.17 (dddd, *J*= 11.6, 9.9, 6.3, 6.1 Hz, 1H, C***H***-2), 1.36 (t, *J*= 7.1 Hz, 3H, OCH_2C***H$_3$***), 1.28 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

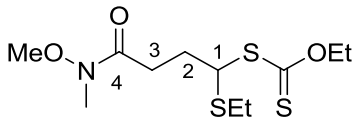
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.0 (C=S), 168.3 (C=O), 139.9, 132.2, 123.2 (C-ar), 69.8 (OCH_2), 53.1 (C-1), 35.8 (C-3), 35.4 (C-2), 26.3 (SCH_2), 14.4 (SCH_2***C***H_3), 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2980, 2930, 2872, 1775, 1720, 1469, 1437, 1393, 1367, 1219, 1111, 1050.

HRMS (EI): Calcd. for M-Xa : $C_{13}H_{14}NO_2S$: 248.0745 Found : 248.0735

[5] Quiclet-Sire, B.; Zard, S. Z. *Org. Lett.* **2008**, *10*, 3279.

_O_-Ethyl _S_-1-(ethylthio)-4-(methoxy(methyl)amino)-4-oxobutyl carbonodithioate **III-16f**

	$C_{11}H_{21}NO_3S_3$ M= 311.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7f**[6] (223 mg, 1.0 mmol) and ethyl vinyl sulfide **III-15** (203 µL, 2.0 mmol), and needed 15 mol % of DLP to go to completion (4 h 30). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 3:7) to afford radical adduct **III-16f** (265 mg, 85%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.85 (dd, *J*= 7.5, 5.8 Hz, 1H, C***H***-1), 4.64 (q, *J*= 7.1 Hz, 2H, OC***H***$_2$), 3.67 (s, 3H, OC***H*****$_3$**), 3.17 (s, 3H, NC***H*****$_3$**), 2.60-2.77 (m, 4H, C***H*****$_2$**-3, SC***H*****$_2$**), 2.23-2.39 (m, 2H, C***H*****$_2$**-2), 1.42 (t, *J*= 7.1Hz, 3H, OCH_2C***H*****$_3$**), 1.27 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**).

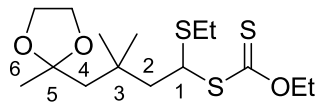
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.8 (C=S), 173.2 (C-4), 69.9 (OCH_2), 61.2 (OCH_3), 55.1 (C-1), 32.3 (NCH_3), 30.8 (C-2), 29.4 (C-3), 25.8 (SCH_2), 14.4 (SCH_2***C***H_3), 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2964, 2931, 2872, 2856, 1676, 1461, 1443, 1413, 1384, 1221, 1148, 1112, 1053.

HRMS (EI) Calcd. for $C_{11}H_{21}NO_3S_3$: 311.0684 Found : 311.0689

[6] Briggs, M. E.; Zard, S. Z. *Synlett* **2005**, 334.

_O_-Ethyl _S_-1-(ethylthio)-4,4-dimethyl-5-(2-methyl-1,3-dioxolan-2-yl)pentyl carbonodithioate **III-16g**

	$C_{16}H_{30}O_3S_3$ M= 366.6 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7g**[7] (430 mg, 1.6 mmol) and ethyl vinyl sulfide **III-15** (330 µL, 3.2 mmol), and showed no evolution after the addition of 20 mol% of DLP (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16g** (305 mg, 52%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.95 (dd, *J*= 7.2, 5.4 Hz, 1H, C***H***-1), 4.65 (q, *J*= 7.1 Hz, 2H, OC***H***$_2$), 3.93 (s, 4H, OC***H*****$_2$**C***H*****$_2$**O), 2.57-2.78 (m, 2H, SC***H*****$_2$**), 2.13 (dd, *J*= 14.9, 5.4 Hz, 1H, C***H***-2), 1.99 (dd, *J*= 14.9, 7.2 Hz, 1H, C***H***-2), 1.74-1.84 (m, 2H, C***H*****$_2$**-4), 1.43 (t, *J*= 7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.34 (s, 3H, C***H*****$_3$**-6), 1.28 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**), 1.12, 1.11 (2s, 6H, (C***H*****$_3$**)$_2$-3).

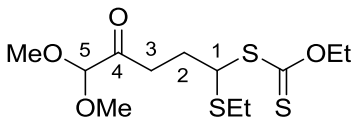
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.1 (C=S), 110.5 (C-5), 69.8 (OCH_2), 63.8 (CH_2-O)$_2$, 52.8 (C-1), 49.1 (C-4), 48.8 (C-2), 34.1 (C-3), 28.6 ((CH_3)$_2$-3), 26.2 (C-6), 26.0 (SCH_2), 14.4 (SCH_2***C***H_3), 13.8 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2960, 2929, 2874, 1449, 1364, 1216, 1146, 1111, 1047.

HRMS (EI): Calcd. for $C_{16}H_{30}O_3S_3$: 366.1357 Found : 366.1349

[7] Corbet, M. Thesis *Ecole Polytechnique*, **2009**.

_O_-Ethyl _S_-1-(ethylthio)-5,5-dimethoxy-4-oxopentyl carbonodithioate **III-16h**

	$C_{12}H_{22}O_4S_3$ M= 326.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7h**[8] (200 mg, 0.84 mmol) and ethyl vinyl sulfide **III-15** (170 µL, 1.68 mmol), and needed 15 mol % of DLP to go to completion (4 h 30 min). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford radical adduct **III-16h** (208 mg, 76%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.79 (dd, *J*= 7.9, 5.6 Hz, 1H, C***H***-1), 4.64 (q, *J*= 7.1 Hz, 2H, OC***H***$_2$), 4.48 (s, 1H, C***H***-5), 3.40 (s, 6H, (OC***H***$_3$)$_2$), 2.62-2.94 (m, 4H, C***H***$_2$-3, SC***H***$_2$), 2.15-2.35 (m, 2H, C***H***$_2$-2), 1.41 (t, *J*= 7.1 Hz, 3H, OCH_2C***H***$_3$), 1.27 (t, *J*= 7.4 Hz, 3H, SCH_2C***H***$_3$).

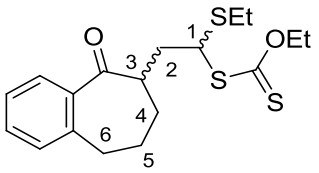
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.8 (C=S), 204.3 (C-4), 103.9 (C-5), 70.0 (OCH_2), 54.9 (C-1), 54.8 ($(OCH_3)_2$), 34.9 (C-2), 29.2 (C-3), 25.8 (SCH_2), 14.4 (SCH_2***C***H_3), 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2963, 2933, 2872, 2834, 1732, 1443, 1366, 1292, 1266, 1223, 1147, 1111, 1051.

HRMS (EI): Calcd. for $C_{12}H_{22}O_4S_3$: 326.0680 Found : 326.0683

[8] Mougin, C.; Sanion, J., Zard, S. Z. *Heterocycles* **2007**, *74*, 211.

_8O_-Ethyl _S_-1-(ethylthio)-2-(5-oxo-6,7,8,9-tetrahydro-5H-benzo[7] annulen-6-yl)ethyl carbonodithioate **III-16i**



$C_{18}H_{24}O_2S_3$
M= 368.6 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7i**[9] (500 mg, 1.78 mmol) and ethyl vinyl sulfide **III-15** (270 µL, 3.56 mmol), and needed 15 mol% of DLP to go to completion (4 h 30). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16i** (578 mg, 88%) as a yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.65-7.68 (m, 1H, C***H***-ar), 7.20-7.37 (m, 3H, C***H***-ar), 4.96 (dd, *J*= 8.2, 7.0 Hz, 0.5H, C***H***-1), 4.82 (dd, *J*= 8.9, 6.3 Hz, 0.5H, C***H***-1), 4.52-4.68 (m, 2H, OC***H***$_2$), 3.17-3.26 (m, 1H, C***H***-3), 2.90-3.08 (m, 2H,C***H*****$_2$**-6), 2.56-2.84 (m, 3H, C***H***-2, SC***H*****$_2$**), 1.96-2.18 (m, 3H, C***H*****$_2$**-5, C***H***-2), 1.61-1.74 (m, 2H, C***H*****$_2$**-4), 1.45 (t, *J*= 7.1 Hz, 1.5H, OCH_2C***H*****$_3$**), 1.37 (t, *J*= 7.1 Hz, 1.5H, OCH_2C***H*****$_3$**), 1.27 (t, *J*= 7.4 Hz, 1.5H, OCH_2C***H*****$_3$**), 1.21 (t, *J*= 7.4 Hz, 1.5H, SCH_2C***H*****$_3$**).

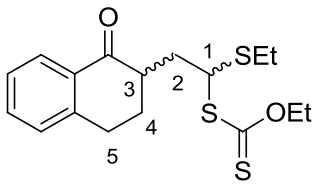
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.8 (C=S), 205.8, 205.7 (C=O), 142.2, 142.0, 139.9, 136.7, 131.3, 129.9, 129.9, 128.8, 128.5, 126.4, 126.3 (C-ar), 70.1, 70.0 (OCH_2), 54.2, 54.0 (C-1), 47.5, 47.5 (C-3), 37.5, 36.8 (C-2), 33.7, 33.6 (C-6), 30.8, 30.0 (C-4), 25.8, 25.7 (SCH_2), 25.6, 25.6 (C-5), 14.6, 14.5 (SCH_2***C***H_3), 13.7 (O***C***H_2CH_3).

IR (ν, cm^{-1}, CCl_4) 3070, 3022, 2929, 2857, 1821, 1687, 1599, 1449, 1378, 1265, 1233, 1112, 1051.

HRMS (EI) Calcd. for $C_{18}H_{24}O_2S_3$: 368.0938 Found : 368.0922

[9] Tetard, T. Unpublished results.

_O_-Ethyl _S_-1-(ethylthio)-2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl carbonodithioate **III-16j**

	$C_{17}H_{22}O_2S_3$ M= 354.6 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7j**[10] (1.33 g, 5.0 mmol) and ethyl vinyl sulfide **III-15** (1.01 mL, 10.0 mmol), and needed 25 mol% of DLP to go to completion (7 h 30). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16j** (1.61 g, 91%) as a slightly yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.02 (t, *J*= 7.3 Hz, 1H, C***H***-ar), 7.44-7.48 (m, 1H, C***H***-ar), 7.22-7.32 (m, 2H, C***H***-ar), 5.15 (dd, *J*= 7.7, 7.5 Hz, 0.5H, C***H***-1), 4.96 (dd, *J*= 10.4, 5.3 Hz, 0.5H, C***H***-1), 4.63 (q, *J*= 7.1 Hz, 1H, OC***H***$_2$), 4.62 (q, *J*= 7.1 Hz, 1.H, OC***H***$_2$), 2.64-3.08 (m, 6H, C***H***-2, C***H*****$_2$**-5, C***H***-3, SC***H*****$_2$**), 2.32-2.42 (m, 1H, C***H***-4), 2.05 (ddd, *J*= 14.3, 8.7, 5.2 Hz, 0.5H, C***H***-2), 1.88-2.00 (m, 1.5H, C***H***-2, C***H***-4), 1.40 (t, *J*= 7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.31 (t, *J*= 7.5 Hz, 1.5H, SCH_2C***H*****$_3$**), 1.29 (t, *J*= 7.4 Hz, 1.5H, SCH_2C***H*****$_3$**).

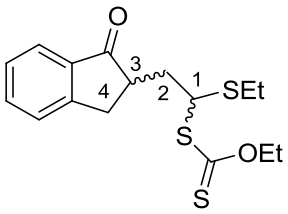
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.0, 213.9 (C=S), 199.0, 198.9 (C=O), 143.8, 143.7, 133.3, 133.2, 132.3, 128.6, 127.4, 127.4, 126.6 (C-ar), 70.0, 69.9 (OCH_2), 54.1, 53.8 (C-1), 45.4 (C-3), 36.5, 35.7 (C-2), 29.4, 28.8 (C-4), 28.6, 28.1 (C-5), 25.8, 25.4 (SCH_2), 14.5, 14.4 (SCH_2**C**H_3), 13.7, 13.7 (OCH_2**C**H_3).

IR (ν, cm^{-1}, CCl_4): 2958, 2930, 2857, 1688, 1602, 1455, 1435, 1364, 1297, 1221, 112, 1049.

HRMS (EI): Calcd. for $C_{17}H_{22}O_2S_3$: 354.0782 Found : 354.0797

[10] Pothier, J. Thesis, *Ecole Polytechnique*, **1999**.

_O_-Ethyl-_S_-1-(ethylthio)-2-(1-oxo-2,3-dihydro-1_H_-inden-2-yl)ethyl carbonodithioate **III-16k**



$C_{16}H_{20}O_2S_3$
M= 340.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7k**[9] (1.0 g, 4.0 mmol) and ethyl vinyl sulfide **III-15** (812 µL, 8.0 mmol), and needed 15 mol% of DLP to go to completion (4 h 30 min). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16k** (1.21 g, 89%) as a yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

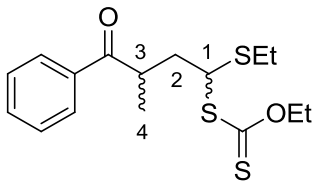
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.75 (d, *J*= 7.6 Hz, 1H, C***H***-ar), 7.60 (m, 1H, C***H***-ar), 7.50 (d, *J*= 7.6 Hz, 0.5H, C***H***-ar), 7.46 (d, *J*= 7.7 Hz, 0.5H, C***H***-ar), 7.37 (m, 1H, C***H***-ar), 5.23 (dd, *J*= 7.3, 7.3 Hz, 0.5H, C***H***-1), 4.91 (dd, *J*= 10.9, 4.2 Hz, 0.5H, C***H***-1), 4.64 (q, *J*= 7.1 Hz, 1H, OC***H₂***), 4.63 (q, *J*= 7.1 Hz, 1H, OC***H₂***), 3.40-3.49 (m, 1H, C***H***-3), 2.55-3.15 (m, 5H, C***H***-2, C***H₂***-4, SC***H₂***), 2.00-2.16 (m, 1H, C***H***-2), 1.41 (t, *J*= 7.1 Hz, 3H, OCH_2C***H₃***), 1.29-1.35 (m, 3H, SCH_2C***H₃***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 214.2, 213.9 (C=S), 207.3, 207.2 (C=O), 153.3, 136.5, 136.4, 134.8, 134.8, 127.5, 127.5, 126.6, 126.5, 124.0 (C-ar), 70.1, 70.0 (OCH_2), 54.4, 54.2 (C-1), 45.7, 45.4 (C-3), 38.0, 37.3 (C-2), 33.9, 32.5 (C-4), 26.0, 25.5 (SCH_2), 14.6, 14.5 (SCH_2***C***H_3), 13.8, 13.7 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 3076, 3034, 2979, 2930, 2873, 2849, 1717, 1610, 1590, 1474, 1464, 1455, 1434, 1378, 1363, 1342, 1326, 1295, 1277, 1220, 1111, 1050.

HRMS (EI) Calcd. for $C_{16}H_{20}O_2S_3$: 340.0625 Found : 340.0614

_O_-Ethyl _S_-1-(ethylthio)-3-methyl-4-oxo-4-phenylbutyl carbonodithioate **III-16l**



$C_{16}H_{22}O_2S_3$
M= 342.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7l**[9] (1.27 g, 5.0 mmol) and ethyl vinyl sulfide **III-15** (1.0 mL, 10.0 mmol), and needed 15 mol % of DLP to go to completion. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16l** (1.61 g, 94%) as a yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

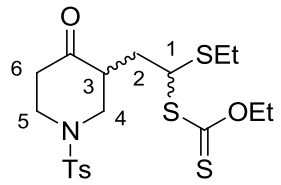
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.93-8.00 (m, 2H, C***H***-ar), 7.42-7.56 (m, 3H, C***H***-ar), 4.81 (dd, *J*= 8.9, 6.4 Hz, 0.5H, C***H***-1), 4.77 (dd, *J*= 8.7, 6.5 Hz, 0.5H, C***H***-1), 4.36-4.62 (m, 2H, OC***H***$_2$), 3.80-3.91 (m, 1H, C***H***-3), 2.37-2.73 (m, 3H, C***H***-2, SC***H$_2$***), 2.09 (ddd, *J*= 13.6, 6.6, 6.6 Hz, 0.5H, C***H***-2), 1.90-1.97 (m, 0.5H, C***H***-2), 1.40 (t, *J*= 7.1 Hz, 1.5H, OCH$_2$C***H$_3$***), 1.32 (t, *J*= 7.1 Hz, 1.5H, OCH$_2$C***H$_3$***), 1.27 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***) 1.27 (d, *J*= 7.0 Hz, 1.5H, C***H$_3$***-4), 1.23 (d, *J*= 7.0 Hz, 1.5H, C***H$_3$***-4), 1.12 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.2 (C=S), 202.9, 202.6 (C=O), 136.5, 135.9, 133.0, 133.0, 128.6, 128.6, 128.3, 128.3 (C-ar), 70.0, 69.8 (OCH_2), 53.6 (C-1), 39.8, 39.1 (C-3), 38.6, 38.4 (C-2), 25.8, 25.6 (SCH_2), 18.4, 17.1 (C-4), 14.4, 14.3 (SCH_2***C***H_3), 13.6, 13.6 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 3089, 3067, 3029, 2983, 2932, 2900, 2870, 1745, 1688, 1597, 1583, 1449, 1389, 1374, 1326, 1291, 1220, 1149, 1112, 1054.

HRMS (EI) Calcd. for $C_{16}H_{22}O_2S_3$: 342.0782 Found : 342.0782

_O_-Ethyl _S_-1-(ethylthio)-2-(4-oxo-1-tosylpiperidin-3-yl)ethyl carbonodithioate **III-16m**



$C_{19}H_{27}NO_4S_4$
M= 461.7 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7m**[9] (1.87 g, 5.0 mmol) and ethyl vinyl sulfide **III-15** (1.01 mL, 10.0 mmol), and needed 15 mol % of DLP to go to completion (4 h 30). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford radical adduct **III-16m** (2.01 g, 80%) as a yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

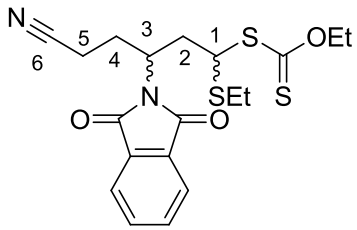
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.69 (d, *J*= 8.1 Hz, 1H, C***H***-ar), 7.66 (d, *J*= 8.1 Hz, 1H, C***H***-ar), 7.34 (d, *J*= 8.1 Hz, 1H, C***H***-ar), 7.34 (d, *J*= 8.1 Hz, 1H, C***H***-ar), 4.82 (dd, *J*= 9.0, 6.2 Hz, 0.5H, C***H***-1), 4.71 (dd, *J*= 9.7, 5.7 Hz, 0.5H, C***H***-1), 4.59-4.68 (m, 2H, OC***H***$_2$), 4.17 (ddd, *J*= 11.8, 6.1, 2.5 Hz, 0.5H, C***H***-5), 3.99 (dtd, *J*= 8.8, 5.9, 2.7 Hz, 0.5H, C***H***-4), 3.85 (ddd, *J*= 11.9, 5.6, 2.0 Hz, 0.5H, C***H***-5), 3.70-3.76 (m, 0.5H, C***H***-4), 2.47-3.04 (m, 7.5H, C***H***-3, C***H***-5, C***H***-4, C***H$_2$***-6, C***H***-2, SC***H$_2$***), 2.42 (s, 3H, C***H$_3$***-ar), 2.36-2.54 (m, 0.5H, C***H***-2), 1.82 (ddd, *J*= 14.5, 7.7, 5.7 Hz, 0.5H, C***H***-2), 1.71 (ddd, *J*= 14.7, 9.1, 5.6 Hz, 0.5H, C***H***-2), 1.43 (t, *J*= 7.1 Hz, 1.5H, OCH$_2$C***H$_3$***), 1.41 (t, *J*= 7.1 Hz, 1.5H, OCH$_2$C***H$_3$***), 1.30 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***), 1.25 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 214.2, 213.3 (C=S), 206.3, 206.2 (C=O), 144.1, 144.1, 133.3, 133.2, 129.9, 129.9, 127.5, 127.4 (C-ar), 70.2, 70.1 (OC*H*$_2$), 53.2, 53.0 (C-1), 51.2, 50.7 (C-4), 47.4, 46.9 (C-3), 46.5, 46.4 (C-5), 40.3, 40.0 (C-2), 33.8, 32.9 (C-6), 25.9, 25.9 (SCH$_2$), 21.5, 21.5 (CH$_3$-ar), 14.5 14.4 (SCH$_2$***C****H$_3$*), 13.7, 13.7 (OCH$_2$***C***H$_3$).

IR (ν, cm^{-1}, CCl_4) 2979, 2928, 2872, 2854, 1722, 1599, 1494, 1470, 1452, 1443, 1368, 1220, 1170, 1111, 1048.

HRMS (EI) Calcd. for M-Xa : $C_{16}H_{22}NO_3S_2$: 340.1041 Found : 340.1059

_S_-5-Cyano-3-(1,3-dioxoisoindolin-2-yl)-1-(ethylthio)pentyl _O_-ethyl carbonodithioate **III-16n**



$C_{19}H_{22}O_3S_3$
M= 422.6 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with a solution of the xanthate **III-7n**[11] (668 mg, 2.0 mmol) and ethyl vinyl sulfide **III-15** (406 µL, 4.0 mmol), and needed 15 mol % of DLP to go to completion (4 h 30). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 3:7) to afford the radical adduct **III-16n** (752 mg, 89%) as a colorless oil and as a mixture of two diastereomers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.88-7.93 (m, 2H, C***H***-ar), 7.78-7.81 (m, 2H, C***H***-ar), 4.53-4.89 (m, 4H, C***H***-1, OC***H***$_2$, C***H***-3), 2.06-2.80 (m, 8H, SC***H$_2$***, C***H$_2$***-2, C***H$_2$***-4, C***H$_2$***-5), 1.45 (t, *J*= 7.1 Hz, 1.5H, $OCH_2C\boldsymbol{H_3}$), 1.36 (t, *J*= 7.1 Hz, 1.5H, $OCH_2C\boldsymbol{H_3}$), 1.28 (t, *J*= 7.4 Hz, 1.5H, $SCH_2C\boldsymbol{H_3}$), 1.17 (t, *J*= 7.4 Hz, 1.5H, $SCH_2C\boldsymbol{H_3}$).

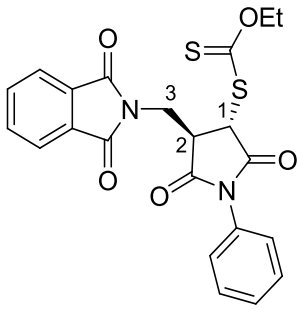
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 214.1, 213.4 (C=S), 168.5, 168.5 (C=O), 134.3, 134.2, 131.7, 131.6, 123.4, 123.4 (C-Ar), 118.7, 118.5,(CN), 69.9 (OCH_2), 53.0, 52.8 (C-3), 49.0, 48.8 (C-1), 39.6, 39.4 (C-2), 28.6, 27.9 (C-4), 26.5, 25.8 (SCH_2), 14.8, 14.6 (C-5), 14.3, 14.2 ($SCH_2\boldsymbol{C}H_3$), 13.7, 13.6 ($OCH_2\boldsymbol{C}H_3$).

IR (ν, cm^{-1}, CCl_4) 2976, 2930, 2872, 2251, 1775, 1716, 1470, 1451, 1392, 1372, 1265, 1220, 1146, 1111, 1088, 1049.

HRMS (EI) Calcd. for $C_{19}H_{22}O_3S_3$: 422.0793 Found : 422.0809

[11] Quiclet-Sire, B.; Revol, G.; Zard, S. Z. *Tetrahedron* **2010**, *66*, 6656.

_S_-4-((1,3-Dioxoisoindolin-2-yl)methyl)-2,5-dioxo-1-phenylpyrrolidin-3-yl _O_-ethyl carbonodithioate **III-7o**



$C_{22}H_{18}N_2O_5S_2$
M= 454.5 g.mol^{-1}

A solution of *N*-phenylmaleimide **III-18** (173 mg, 1.0 mmol, 1.0 equiv) and xanthate **III-7e** (562 mg, 2.0 mmol, 2.0 equiv) in ethyl acetate (1 mL) was refluxed for 15 min under a nitrogen flow. Dilauroyl peroxide (DLP) (5 mol %) was then added and the reaction mixture was refluxed for 1 h 30. The reaction mixture was then cooled to 20 °C and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 3:7) to afford the radical adduct **III-7m** (350 mg, 77%) as a colorless oil which solidified upon standing.

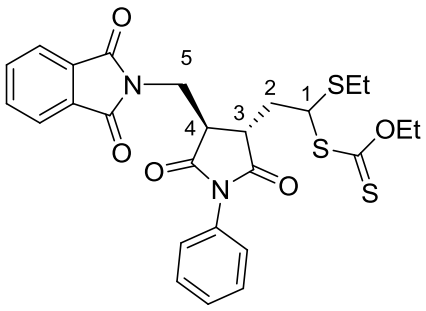
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.94 (dd, *J*= 5.4, 3.1 Hz, 2H, C***H***-ar), 7.82 (dd, *J*= 5.4, 3.1 Hz, 2H, C***H***-ar), 7.40-7.56 (m, 5H, C***H***-ar), 4.58-4.68 (m, 2H, OC***H***$_2$), 4.47 (dd, *J*= 14.1, 6.2 Hz, 1H, C***H***-3), 4.41 (d, *J*= 6.3 Hz, 1H, C***H***-1), 4.24 (dd, *J*= 14.1, 8.9 Hz,, 1H, C***H***-3), 3.92 (td, *J*= 8.9, 6.3 Hz, 1H, C***H***-2), 1.40 (t, *J*= 7.1 Hz, 3H, OCH$_2$C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 209.2 (C=S), 173.2, 171.1 (C=O), 168.2 (C=O), 134.4, 131.7, 131.6, 129.2, 128.9, 126.1, 123.7 (C-ar), 71.0 (OCH$_2$), 49.3 (C-1), 45.2 (C-2), 37.7 (C-3), 13.6 (OCH$_2$***C***H$_3$).

IR (ν, cm^{-1}, CCl_4) 2957, 2927, 2855, 1777, 1720, 1599, 1501, 1467, 1383, 1370, 1292, 1261, 1240, 1199, 1166, 1114, 1047.

HRMS (EI) Calcd. for M-Xa : $C_{19}H_{13}N_2O_4$: 333.0875 Found : 333.0884

_S_-2-(4-((1,3-Dioxoisoindolin-2-yl)methyl)-2,5-dioxo-1-phenyl pyrrolidin-3-yl)-1-(ethylthio)ethyl _O_-ethyl carbonodithioate **III-16o**



$C_{26}H_{26}N_2O_5S_3$
M= 542.7 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with xanthate **III-7o** (400 mg, 0.88 mmol) and ethyl vinyl sulfide **III-15** (178 µL, 1.76 mmol), and needed 15 mol % of DLP to go to completion (4 h 30 min). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 3:7) to afford the radical adduct **III-16o** (267 mg, 56%) as a mixture of two epimers at C-1 in a 1:1 ratio and as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.87-7.89 (m, 2H, C***H***-ar), 7.73-7.75 (m, 2H, C***H***-ar), 7.30-7.49 (m, 5H, ***H***-ar), 5.09 (dd, *J*= 10.9, 4.3 Hz, 0.5H, C***H***-1), 4.96 (dd, *J*= 10.8, 4.5 Hz, 0.5H, C***H***-1), 4.56-4.67 (m, 2H, OC***H***$_2$), 4.25-4.31 (m, 1H, C***H***-5), 4.06-4.13 (m, 1H, C***H***-5), 3.55-3.60 (m, 0.5H, C***H***-4), 3.31-3.36 (m, 0.5H, C***H***-4), 3.10-3.22 (m, 1H, C***H***-3), 2.41-2.82 (m, 4H, SC***H$_2$***, C***H$_2$***-2), 1.42 (t, *J*= 7.1 Hz, 1.5H, OCH$_2$C***H$_3$***), 1.37 (t, *J*= 7.1 Hz, 1.5H, OCH$_2$C***H$_3$***), 1.27 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***), 1.17 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.4 (C=S), 176.4, 176.3, 175.4, 175.1 (C=O), 168.1, 168.0 (C=O), 134.2, 134.2, 131.8, 131.8, 129.1, 129.1, 128.6, 126.3, 123.6, 123.6 (C-ar), 70.2, 70.1 (OCH_2), 53.0, 52.5 (C-1), 43.5, 43.4 (C-4), 42.3, 42.0 (C-3), 38.2, 38.2 (C-5), 36.6, 36.5 (C-2), 26.3, 25.9 (SCH_2), 14.4, 14.4 (SCH_2***C***H_3), 13.8, 13.7 (OCH_2***C***H_3).

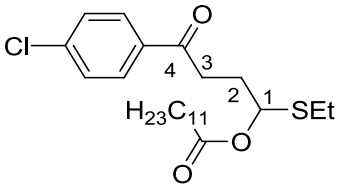
IR (ν, cm^{-1}, CCl_4) 3070, 2929, 1777, 1721, 1599, 1501, 1385, 1365, 1220, 1189, 1111, 1049.

HRMS (EI) Calcd. For $C_{26}H_{26}N_2O_5S_3$: 542.1004 Found : 542.0992

GENERAL PROCEDURE III-B : RADICAL CYCLIZATION

A solution of **xanthate** (1.0 equiv) in **ethyl acetate** (AcOEt) (10 mL/mmol of xanthate) was refluxed for 20 min under a nitrogen flow. Dilauroyl peroxide (**DLP**) (20 mol %) was then added and additional DLP (20 mol %) was added every 60 min until total consumption of the starting xanthate or until no evolution could be detected by TLC analysis. The reaction mixture was then cooled to 20 °C and evaporated to dryness under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the tetralone.

4-(4-Chlorophenyl)-1-(ethylthio)-4-oxobutyl dodecanoate — III-20

	$C_{24}H_{37}ClO_3S$ M= 440.2 g.mol^{-1}

Following general procedure **III-B** for radical cyclisation, the reaction was carried out with xanthate **III-16d** (363 mg, 1.0 mmol) and needed 140 mol % of DLP to go to completion. The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 3:7) to afford radical adduct **III-20** (185 mg, 42%) as a colorless oil which solidified upon standing.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.89 (d, *J*= 8.6 Hz, 2H, C***H***-ar), 7.43 (d, *J*= 8.6 Hz, 2H, C***H***-ar), 6.10 (t, *J*= 8.6 Hz, 1H, C***H***-1), 3.01-3.16 (m, 2H, C***H***$_2$-3), 2.51-2.77 (m, 3H, C***H***-CO, SC***H$_2$***), 2.25-2.33 (m, 3H, C***H$_2$***-2, C***H***-CO), 1.57-1.64 (m, 2H, $COCH_2C$***H$_2$***), 1.24-1.28 (m, 19H, C_8***H$_{16}$***, SCH_2C***H$_3$***), 0.87 (t, *J*= 7.8 Hz, 3H, C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 197.2 (C-4), 173.2 (C=O), 139.6, 134.9, 129.4, 128.9 (C-ar), 77.9 (C-1), 34.6 (C-3), 34.5 (***C***OCH_2), 31.9 (C-2), 29.6, 29.4, 29.3, 29.2, 29.1 (C_7H_{14}), 24.9 (SCH_2), 24.8 ($COCH_2$***C***H_2), 22.7 (***C***H_2CH_3), 15.0 (SCH_2***C***H_3), 14.1 (CH_3).

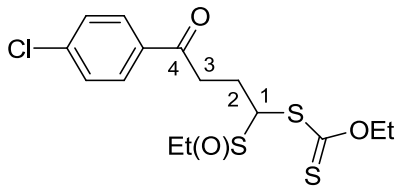
IR (ν, cm^{-1}, CCl_4): 2958, 2928, 2872, 2856, 1738, 1692, 1591, 1488, 1466, 1456, 1415, 14000, 1368, 1313, 1266, 1223, 1202, 1175, 1150, 1094.

HRMS (EI): Calcd. for $C_{22}H_{25}ClO_3S$: 440.2152 — Not found

GENERAL PROCEDURE III-C : OXIDATION OF SULFIDES TO SULFOXIDES

An **aqueous** solution (1.8 mL/mmol of sulfide) of **$NaIO_4$** (1.0 equiv) was added to a **methanolic** solution (8.5 mL/mmol of sulfide) of **sulfide** (1.0 equiv) at 20 °C. The mixture was stirred at 20 °C overnight, then filtered and the filtrate was concentrated *in vacuo*. The residue was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

_S_-4-(4-Chlorophenyl)-1-(ethylsulfinyl)-4-oxobutyl _O_-ethyl carbonodithioate **III-23**



$C_{15}H_{19}ClO_3S_3$
M= 379.0 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out with sulfide **III-16d** (72 mg, 0.20 mmol) and $NaIO_4$ (43 mg, 0.20 mmol). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 7:3) afforded the sulfoxide **III-23** (57 mg, 75%) as a yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

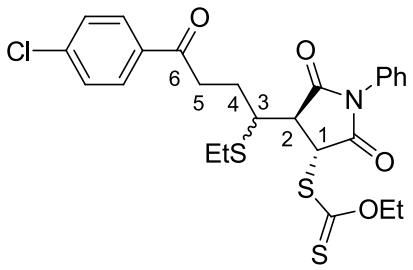
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.89 (d, *J*= 8.5 Hz, 2H, C***H***-ar), 7.44 (d, *J*= 8.5 Hz, 2H, C***H***-ar), 5.05 (dd, *J*= 10.3, 4.7 Hz, 0.5H, C***H***-1), 4.99 (dd, *J*= 10.3, 3.9 Hz, 0.5H, C***H***-1), 4.50-4.66 (m, 2H, OC***H***$_2$), 3.24-3.30 (m, 2H, C***H*****$_2$**-3), 2.68-3.06 (m, 3H, C***H***-3, SC***H*****$_2$**), 2.20-2.41 (m, 1H, C***H***-3), 1.35-1.45 (m, 6H, OCH_2C***H*****$_3$**, SCH_2C***H*****$_3$**).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 211.4, 210.6 (C=S), 197.9, 196.0 (C-4), 139.8, 134.8 129.4, 129.0 (C-ar), 71.6, 71.5 (OCH_2), 67.3, 66.2 (C-1), 43.8, 43.0 (SCH_2), 35.2, 34.6 (C-3), 23.7, 21.5 (C-2), 13.7 (OCH_2***C***H_3), 7.7, 7.4 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2983, 2961, 2935, 2877, 1691, 1592, 1453, 1401, 1364, 1292, 1230, 1148, 1111, 1045.

HRMS (EI): Calcd. for $C_{15}H_{19}ClO_3S_3$: 378.0185 Found : 378.0183

_S_-4-(4-Chlorophenyl)-1-(ethylsulfinyl)-4-oxobutyl _O_-ethyl carbonodithioate **III-25**



$C_{25}H_{26}ClNO_4S_3$
M= 536.1 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with the xanthate **III-16d** (726 mg, 2.0 mmol) and *N*-phenylmaleimide **III-18** (173 mg, 1.0 mmol), and needed 5 mol % of DLP to go to completion. The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 3:7) to afford the radical adduct **III-25** (311 mg, 58%) as a mixture of two epimers at C-3 in a 1:1 ratio and as a yellow solid.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.94 (d, *J*= 8.6 Hz, 1H, C***H***-ar), 7.94 (d, *J*= 8.7 Hz, 1H, C***H***-ar), 7.41-7.51 (m, 5H, C***H***-ar), 7.34 (d, *J*= 8.6 Hz, 1H, C***H***-ar), 7.34 (d, *J*= 8.7 Hz, 1H, C***H***-ar), 4.60-4.71 (m, 2H, OCH_2), 4.53 (dd, *J*= 5.7, 4.2 Hz, 1H, C***H***-1), 3.71 (dd, *J*= 6.1, 2.8 Hz, 0.5H, C***H***-2), 3.59-3.66 (m, 1H, C***H***-2, C***H***-3), 3.34-3.41 (m, 0.5H, C***H***-3), 3.31 (t, *J*= 7.2 Hz, 2H, C***H$_2$***-5), 2.56-2.68 (m, 2H, SC***H$_2$***), 2.22-2.39 (m, 1.5H, C***H$_2$***-4), 1.95-2.05 (m, 0.5H C***H***-4), 1.41 (t, *J*= 7.1 Hz, 3H, OCH_2C***H$_3$***), 1.28 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 210.3, 209.8 (C=S), 197.9, 197.7 (C-6), 174.7, 174.2 (CO-C2), 172.2, 171.8 (CO-C1), 139.7, 139.7, 135.0, 134.9, 131.9, 131.7, 129.4, 129.2, 129.2, 129.0, 129.0 128.9, 126.3, 126.2 (C-ar), 71.1 (OCH_2), 51.9, 51.1 (C-2), 49.0, 47.2 (C-1), 46.1, 45.8 (C-3), 36.1, 35.9 (C-5), 27.6, 26.6 (C-4), 24.7, 22.7 (SCH_2), 15.2, 14.9 (SCH_2***C***H_3), 14.1, 13.7 (OCH_2***C***H_3).

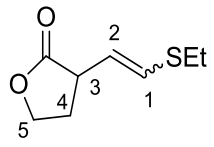
IR (ν, cm^{-1}, CCl_4) 3065, 2970, 2930, 2860, 1775; 1720, 1690, 1405, 1363, 1220, 1110.

HRMS (EI) Calcd.for $C_{25}H_{26}ClNO_4S_3$: 535.0712 Found : 535.0710

GENERAL PROCEDURE III-D : SELECTIVE ELIMINATION OF THE XANTHATE

A solution of **xanthate** (1.0 equiv) in **diphenylether** (2 mL/mmol of xanthate) was heated at 190 °C under a nitrogen flow until total consumption of the starting material or until no evolution could be detected by TLC analysis. The reaction mixture was then cooled to 20 °C. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

3-(2-(Ethylthio)vinyl)dihydrofuran-2(3H)-one **III-26a**



$C_8H_{12}O_2S$
M= 172.2 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with xanthate **III-16b** (390 mg, 1.32 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (59:5, 3:7) to afford (*Z*)-vinylsulfide **III-26a** (82 mg, 36%) and (*E*)-vinylsulfide **III-26a** (88 mg, 39%) as two colorless oils.

(*E*) isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 6.21 (dd, *J*= 15.3, 1.3 Hz, 1H, C***H***-1), 5.53 (dd, *J*= 15.3, 6.6 Hz, 1H, C***H***-2), 4.36 (dt, *J*= 9.0, 3.3 Hz, 1H, C***H***-5), 4.23 (dt, *J*= 9.0, 6.6 Hz, 1H, C***H***-5), 3.28 (dddd, *J*= 10.0, 8.3, 6.6, 1.3 Hz, 1H, C***H***-3), 2.71 (q, *J*= 7.4 Hz, 2H, SC***H*****$_2$**), 2.46 (dddd, *J*= 12.4, 8.3, 6.6, 3.3 Hz, 1H, C***H***-4), 2.16 (dtd, *J*= 12.4, 9.5, 8.4 Hz, 1H, C***H***-4), 1.29 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 176.9 (C=O), 128.4 (C-1), 121.1 (C-2), 66.5 (C-5), 42.8 (C-3), 29.2 (C-4), 26.1 (SCH_2), 14.2 (SCH_2***C***H_3).

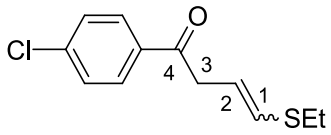
IR (ν, cm^{-1}, CCl_4) 2973, 2929, 2874, 1783, 1712, 1678, 1613, 1558, 1541, 1454, 1371, 1262, 1211, 1151, 1031.

HRMS (EI) Calcd. for $C_8H_{12}O_2S$: 172.0558 Found : 172.0550

(*Z*) isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	6.31 (d, *J*= 9.4 Hz, 1H, C***H***-1), 5.59-5.63 (m, 1H, C***H***-2), 4.39-4.42 (m, 1H, C***H***-5), 4.24-4.32 (m, 1H, C***H***-5), 3.52-3.58 (m, 1H, C***H***-3), 2.72 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 2.52-2.57 (m, 1H, C***H***-4), 2.00-2.08 (m, 1H, C***H***-4), 1.30 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	177.2 (C=O), 130.9 (C-1), 123.3 (C-2), 66.8 (C-5), 40.0 (C-3), 29.5 (C-4), 28.0 (SCH_2), 15.4 (SCH_2***C***H_3).
IR (ν, cm^{-1}, CCl_4)	2977, 2929, 2874, 1781, 1668, 1608, 1558, 1541, 1484, 1454, 1370, 1266, 1211, 1147, 1030.
HRMS (EI)	Calcd. for $C_8H_{12}O_2S$: 172.0558 Found : 172.0562

1-(4-Chlorophenyl)-4-(ethylthio)but-3-en-1-one **III-26b**

	$C_{12}H_{13}ClOS$ M= 240.7 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with xanthate **III-16d** (724 mg, 2.0 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford (*E*)-vinylsulfide **III-26b** (171 mg, 36%) and (*Z*)-vinylsulfide **III-26b** (178 mg, 37%) as two yellow oils.

(*E*) isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.89 (dd, *J*= 8.6, 1.9 Hz, 2H, C***H***-ar), 7.43 (d, *J*= 8.6, 3.0 Hz, 2H, C***H***-ar), 6.14 (dt, *J*= 15.2, 1.2 Hz, 1H, C***H***-1), 5.75 (dt, *J*= 15.2, 6.9 Hz, 1H, C***H***-2), 3.74 (dd, *J*= 6.9, 1.2 Hz, 2H, C***H$_2$***-3), 2.71 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 1.28 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 196.3 (C-4), 139.6, 134.7, 129.7, 129.4 (C-ar), 127.7 (C-1), 119.7 (C-2), 42.6 (C-3), 26.2 (SCH_2), 14.3 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2973, 2929, 2873, 1691, 1591, 1572, 1488, 1450, 1400, 1377, 1335, 1264, 1205, 1094, 1052.

HRMS (EI): Calcd. for $C_{12}H_{13}ClOS$: 240.0376 Found : 240.0370

(*Z*) isomer

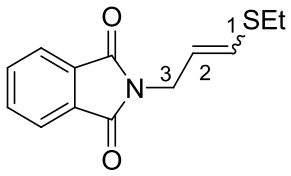
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.94 (d, *J*= 8.6 Hz, 2H, C***H***-ar), 7.42 (d, *J*= 8.6 Hz, 2H, C***H***-ar), 6.21 (dt, *J*= 9.5, 1.4 Hz, 1H, C***H***-1), 5.75 (dt, *J*= 9.5, 6.7 Hz, 1H, C***H***-2), 3.78 (dd, *J*= 6.7, 1.4 Hz,, 2H, C***H$_2$***-3), 2.74 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 1.32 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 196.1 (C-4), 139.6, 134.8, 129.7, 128.9 (C-ar), 128.5 (C-1), 120.8 (C-2), 39.0 (C-3), 27.9 (SCH_2), 15.6 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2969, 2929, 2873, 1692, 1590, 1572, 1488, 1400, 1355, 1314, 1266, 1217, 1084, 1051.

HRMS (EI): Calcd. for $C_{12}H_{13}ClOS$: 240.0376 Found : 240.0386

2-(3-(Ethylthio)allyl)isoindoline-1,3-dione **III-26c**

	$C_{13}H_{13}NO_2S$ M= 247.3 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with xanthate **III-16e** (120 mg, 0.32 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 2:8) to afford vinylsulfide **III-26c** (67 mg, 85%) as a yellow oil and as a mixture of geometric isomers in a 1:1 ratio.

(*E*) isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.84 (dd, *J*= 5.4, 3.0 Hz, 2H, C***H***-ar), 7.71 (dd, *J*= 5.4, 3.0 Hz, 2H, C***H***-ar), 6.38 (dt, *J*= 15.1, 1.0 Hz, 1H, C***H***-1), 5.58 (dt, *J*= 15.1, 6.8 Hz, 1H, C***H***-2), 4.28 (dd, *J*= 6.8, 1.0 Hz, 2H, C***H$_2$***-3), 2.69 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 1.27 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 167.9 (C=O), 133.9, 132.1, 123.3 (C-ar), 130.0 (C-1), 119.7 (C-2), 39.6 (C-3), 26.0 (S***C***H_2), 14.3 (SCH_2***C***H_3).

(*Z*) isomer

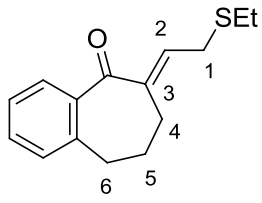
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.90 (dd, *J*= 5.4, 3.0 Hz, 2H, C***H***-ar), 7.76 (dd, *J*= 5.4, 3.0 Hz, 2H, C***H***-ar), 6.19 (dt, *J*= 9.6, 1.4 Hz, 1H, C***H***-1), 5.58 (dt, *J*= 9.6, 6.5 Hz, 1H, C***H***-2), 4.39 (dd, *J*= 6.5, 1.4 Hz, 2H, C***H$_2$***-3), 2.67 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 1.32 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 167.9 (C=O), 133.9, 132.2, 123.3 (C-ar), 129.4 (C-1), 122.3 (C-2), 36.3 (C-3), 28.2 (S***C***H_2), 15.4 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 2975, 2929, 2874, 1774, 1717, 1616, 1468, 1430, 1391, 1345, 1117, 1058.

HRMS (EI) Calcd. for $C_{13}H_{13}NO_2S$: 247.0667 Found : 247.0670

(*E*)-6-(2-(Ethylthio)ethylidene)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one **III-27d**

	$C_{15}H_{18}OS$ M= 246.4 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with xanthate **III-16i** (510 mg, 1.38 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford allylsulfide **III-27d** (230 mg, 67%) as a yellow oil.

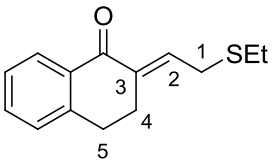
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.71-7.73 (m, 1H, C***H***-ar), 7.15-7.46 (m, 3H, C***H***-ar), 6.90 (t, *J*= 8.2 Hz, 1H, C***H***-2), 3.34 (d, *J*= 8.2 Hz, 2H, C***H*****$_2$**-1), 2.79 (t, *J*= 6.9 Hz, 2H, C***H*****$_2$**-6), 2.58 (q, *J*= 7.4 Hz, SC***H*****$_2$**), 2.37 (t, *J*= 6.9 Hz, 2H, C***H*****$_2$**-4), 1.91 (p, *J*= 6.9 Hz, 2H, C***H*****$_2$**-5), 1.26 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 197.2 (C=O), 139.4, 139.4, 135.7, 132.4, 129.0, 129.0, 126.9 (C-ar, C-3), 138.3 (C-2), 31.2 (C-6), 28.5 (C-1), 26.1 (C-5), 25.6 (SCH_2), 23.7 (C-4), 14.7 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 3070, 3023, 2942, 2864, 1677, 1619, 1599, 1451, 1296, 1264, 1252.

HRMS (EI) Calcd. for $C_{15}H_{18}OS$: 246.1078 Found : 246.1076

(*E*)-2-(2-(Ethylthio)ethylidene)-3,4-dihydronaphthalen-1(2*H*)-one **III-27e**



$C_{14}H_{16}OS$
M= 232.3 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with xanthate **III-16j** (900 mg, 2.53 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford allylsulfide **III-27e** (394 mg, 67%) as a yellow oil and vinylsulfide **III-26e** (108 mg, 18%) as a yellow oil.

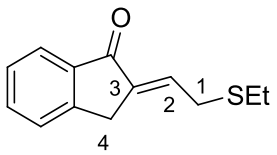
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 8.09 (dd, *J*= 7.8, 1.1 Hz, 1H, C***H***-ar), 7.47 (ddd, *J*= 7.5, 7.5, 1.1 Hz, 1H, C***H***-ar), 7.33 (dd, *J*= 7.5, 7.5 Hz, 1H, C***H***-ar), 7.24 (d, *J*= 7.8, Hz, 1H, C***H***-ar), 6.95 (tt, *J*= 8.1, 1.4 Hz, 1H, C***H***-2), 3.35 (d, *J*= 8.1 Hz, 2H, C***H$_2$***-1), 2.97-3.00 (m, 2H, C***H$_2$***-4), 2.83-2.86 (m, 2H, C***H$_2$***-5), 2.53 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 1.26 (t, *J*= 7.4 Hz, 3H, SCH_2C***H$_3$***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 187.0 (C=O), 143.4, 133.3, 133.2, 128.2, 128.2, 127.0 (C-ar), 136.3 (C-3) 134.5 (C-2), 29.0 (C-4), 28.2 (C-1), 25.6 (SCH_2), 25.3 (C-5), 14.6 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 3072, 3029, 2965, 2931, 2872, 2849, 1780, 1621, 1600, 1456, 1436, 1376, 1314, 1296, 1249, 1223, 1157, 1127, 1055.

HRMS (EI) Calcd. for $C_{14}H_{16}OS$: 232.0922 Found : 232.0923

(*E*)-2-(2-(Ethylthio)ethylidene)-2,3-dihydro-1*H*-inden-1-one **III-27f**

	$C_{13}H_{14}OS$ M= 218.3 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with a solution of xanthate **III-16k** (409 mg, 1.2 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford allylsulfide **III-27f** (261 mg, 67%) as a yellow oil.

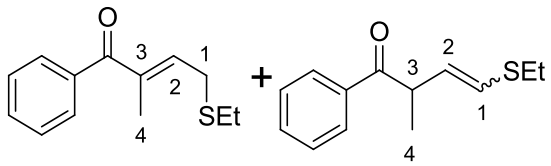
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.66 (dd, *J*= 7.7, 1.1 Hz, 1H, C***H***-ar), 7.60 (ddd, *J*= 7.7, 7.6, 1.1 Hz, 1H, C***H***-ar), 7.50 (d, *J*= 7.6 Hz, 1H, C***H***-ar), 7.40 (dd, *J*= 7.7, 7.6 Hz, 1H, C***H***-ar), 6.90 (tt, *J*= 8.1, 2.1 Hz, 1H, C***H***-2), 3.71 (t, *J*= 2.1 Hz, 2H, C***H***$_2$-4), 3.38 (d, *J*= 8.1 Hz, 2H, C***H*****$_2$**-1), 2.55 (q, *J*= 7.4 Hz, 2H, SC***H*****$_2$**), 1.27 (t, *J*= 7.4 Hz, 3H, SCH_2C***H*****$_3$**).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 193.0 (C=O), 149.1, 137.5, 134.7, 126.3, 124.5 (C-ar), 138.6 (C-3), 133.0 (C-2), 30.0 (C-1), 29.8 (C-4), 25.6 (SCH_2), 14.6 (SCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 2927, 2855, 1716, 1608, 1466, 1264, 1208, 1168, 1046, 1009.

HRMS (EI) Calcd. for $C_{13}H_{14}OS$: 218.0765 Found : 218.0766

(*E*)-4-(Ethylthio)-2-methyl-1-phenylbut-2-en-1-one	**III-26g**
4-(Ethylthio)-2-methyl-1-phenylbut-3-en-1-one	**III-27g**

	$C_{13}H_{16}OS$ M= 220.3 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out with xanthate **III-16l** (1.39 g, 4.05 mmol). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford allylsulfide **III-27g** (280 mg, 31%) as a yellow oil and vinylsulfide **III-26g** (440 mg, 49%) as a yellow oil and as a mixture of geometric isomers in a 1:1 ratio.

Allylsulfide **III-27g**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.64-7.66 (m, 2H, C***H***-ar), 7.50-7.53 (m, 1H, C***H***-ar), 7.40-7.44 (m, 2H, C***H***-ar), 6.32 (td, *J*= 7.9, 1.0 Hz, 1H, C***H***-2), 3.36 (d, *J*= 7.9 Hz, 2H, C***H₂***-1), 2.53 (q, *J*= 7.4 Hz,, 2H, SC***H₂***), 2.01 (d, *J*= 1.0 Hz, 3H, C***H₃***-4), 1.27 (t, *J*= 7.4 Hz, 3H, SCH_2C***H₃***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 198.4 (C=O), 140.9 (C-2), 138.1, 137.5 (C-ar, C-3), 137.5, 131.7, 129.3, 128.1 (C-ar), 29.3 (C-1), 25.6 (SCH_2), 14.7 (SCH_2***C***H_3), 12.6 (CH_3-4).

IR (ν, cm^{-1}, CCl_4): 3066, 2974, 2929, 2873, 1655, 1598, 1578, 1447, 1382, 1353, 1316, 1278, 1220, 1176, 1005.

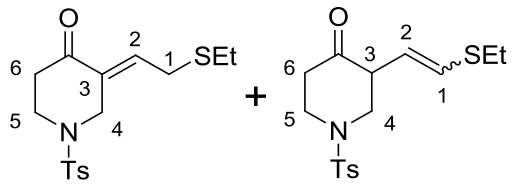
HRMS (EI): Calcd. for $C_{13}H_{12}OS$: 220.0922 Found : 220.0916

Vinylsulfide **III-26g**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.99-8.09 (m, 2H, C***H***-ar), 7.48-7.63 (m, 3H, C***H***-ar), 6.17 (dd, *J*= 15.3, 0.8 Hz, 0.5H, C***H***-1 *E* isomer), 6.10 (d, *J*= 9.3 Hz, 0.5H, C***H***-1 *Z* isomer), 5.73 (dd, *J*= 15.3, 8.2 Hz, 0.5H, C***H***-2 *E* isomer), 5.61-5.64 (m, 0.5H, C***H***-2 *Z* isomer), 4.48 (dq, *J*= 13.7, 6.8 Hz,, 0.5H, C***H***-3 *Z* isomer), 4.25 (m, 0.5H, C***H***-3 *E* isomer), 2.79 (q, *J*= 7.4 Hz, 1H, SC***H₂*** *Z* isomer), 2.71 (q, *J*= 7.4 Hz, 1H, SC***H₂*** *E* isomer), 1.28-1.39 (m, 6H, C***H₃***-4, SCH_2C***H₃***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	(*Z*) isomer 201.3 (C=O), 136.2, 133.0, 128.5, 128.5 (C-ar), 129.2 (C-2), 126.6 (C-1), 42.2 (C-3), 27.9 (SCH_2), 16.6 (C-4), 15.7 (SCH_2***C***H_3). (*E*) isomer 200.7 (C=O), 136.3, 133.0, 128.6, 128.5 (C-ar), 129.3 (C-2), 125.9 (C-1), 45.0 (C-3), 26.2 (SCH_2), 17.6 (C-4), 14.3 (SCH_2***C***H_3).
IR (ν, cm^{-1}, CCl_4)	2977, 2933, 2875, 1722, 1686, 1598, 1580, 144, 1369, 1265, 1222, 1170, 1111, 1065.
HRMS (EI)	Calcd. for $C_{13}H_{12}OS$: 220.0922 Found : 220.0925

(*E*)-3-(2-(Ethylthio)ethylidene)-1-tosylpiperidin-4-one	**III-27h**
3-(2-(Ethylthio)vinyl)-1-tosylpiperidin-4-one	**III-26h**

	$C_{16}H_{21}NO_3S_2$ M= 339.5 g.mol^{-1}

Following general procedure **III-D**, the reaction was carried out xanthate **III-16m** (1.7 g, 3.68 mmol). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (95:5, 2:8) to afford allylsulfide **III-27h** (775 mg, 62%) as a yellow oil and vinylsulfide **III-26h** (200 mg, 16%) as a yellow oil and as a 1:1 mixture of geometric isomers.

Allylsulfide **III-27h**

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.70 (d, *J*= 8.2 Hz, 2H, C***H***-ar), 7.35 (d, *J*= 8.2 Hz, 2H, C***H***-ar), 6.78 (tt, *J*= 8.3, 2.0 Hz, 1H, C***H***-2), 4.04 (s, 2H, C***H$_2$***-4), 3.42 (t, *J*= 6.3 Hz, 2H, C***H***$_2$-5), 3.18 (d, *J*= 8.3 Hz, 2H, C***H$_2$***-1), 2.60 (t, *J*= 6.3 Hz, 2H, C***H$_2$***-6), 2.50 (q, *J*= 7.4 Hz, 2H, SC***H$_2$***), 2.44 (s, 3H, C***H$_3$***-ar), 1.24 (t, *J*= 7.4 Hz, 3H, SCH$_2$C***H$_3$***).

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz): 194.4 (C=O), 144.2, 133.1, 131.2, 129.9 (C-ar), 136.9 (C-3), 127.6 (C-2), 45.7 (C-5), 43.5 (C-4), 38.5 (C-6), 27.8 (C-1) 25.7 (SCH$_2$), 21.5 (CH$_3$-ar), 14.6 (SCH$_2$***C***H$_3$).

Vinylsulfide **III-26h**

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.64-7.70 (m, 2H, C***H***-ar), 7.32-7.34 (m, 2H, C***H***-ar), 6.27 (dd, *J*= 9.6, 0.8 Hz, 0.5H, C***H***-1), 6.18 (dd, *J*= 15.5, 0.9 Hz, 0.5H, C***H***-1), 5.62 (dd, *J*= 9.6, 8.4 Hz, 0.5H, C***H***-2 *Z*), 5.53 (dd, *J*= 15.5, 7.7 Hz, 0.5H, C***H***-2 *E*), 3.76-3.87 (m, 1H, C***H***-4), 3.63-3.69 (m, 1H, C***H***-5), 3.52-3.58 (m, 0.5H, C***H***-3), 3.28-3.34 (m, 0.5H, C***H***-3), 3.00-3.10 (m, 1H, C***H***-5), 2.89 (dd, *J*= 11.8, 9.3 Hz, 0.5H, C***H***-4), 2.78 (dd, *J*= 12.0, 9.5 Hz, 0.5H, C***H***-4), 2.71 (q, *J*= 7.4 Hz, 1H, SC***H$_2$***), 2.70 (q, *J*= 7.4 Hz, 1H, SC***H$_2$***), 2.48-2.60 (m, 2H, C***H$_2$***-6), 2.42 (s, 3H, C***H$_3$***-ar), 1.29 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***), 1.28 (t, *J*= 7.4 Hz, 1.5H, SCH$_2$C***H$_3$***).

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz): (*E*) isomer: 205.1 (C=O), 144.1, 131.1, 129.9, 127.5 (C-ar), 129.4 (C-1), 119.6 (C-2), 52.8 (C-3), 49.9 (C-4), 46.3 (C-5), 39.8 (C-6), 26.1 (SCH$_2$), 21.5 (CH$_3$-ar), 14.6 (SCH$_2$***C***H$_3$).

(*Z*) isomer

204.6 (C=O), 144.6, 133.7, 129.9, 127.5 (C-ar), 129.9 (C-1), 120.7 (C-2), 51.1 (C-3), 49.9 (C-4), 46.3 (C-5), 40.0 (C-6), 28.0 (SCH_2), 21.5 (CH_3-ar), 15.4 ($SCH_2\boldsymbol{C}H_3$).

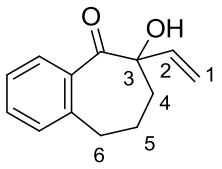
IR (ν, cm^{-1}, CCl_4) 2973, 2928, 2852, 1724, 1598, 1495, 1467, 1367, 1169, 1100.

HRMS (EI) Calcd. for $C_{16}H_{21}NO_3S_2$: 339.0963 Found : 339.0959

GENERAL PROCEDURE III-E : FORMATION OF VINYL CARBINOLS

To a solution of the crude **sulfoxide** (1.0 equiv) in **toluene** (5 mL/mmol), was added **triphenylphosphine** (2.0 equiv) at 20 °C. The mixture was refluxed overnight. The reaction mixture was then cooled to 20 °C and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield desired tertiary alcohols.

6-Hydroxy-6-vinyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one III-32a

	$C_{13}H_{14}O_2$ M= 202.2 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out with allyl sulfide **III-27d** (74 mg, 0.30 mmol) and $NaIO_4$ (64 mg, 0.30 mmol). Crude sulfoxide was directly used in the next step without further purification.

Following general procedure **III-E**, the reaction was carried out with crude sulfoxide and triphenylphosphine (157 mg, 0.60 mmol). Flash chromatography on silica gel (petroleum ether/ether, 8:2) afforded tertiary alcohol **III-32a** (31 mg, 51% over 2 steps) as a yellow oil.

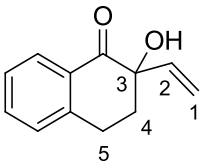
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.18-7.42 (m, 4H, C***H***-ar), 5.93 (dd, *J*= 16.9, 10.6 Hz, 1H, C***H***-2), 5.46 (dd, *J*= 16.9, 1.4 Hz, 1H, C***H***-1), 5.09 (dd, *J*= 10.6, 1.4 Hz, 1H, C***H***-1), 4.37 (s, 1H, O***H***), 2.91-2.94 (m, 2H, C***H***$_2$-6), 2.00-2.25 (m, 4H, C***H*****$_2$**-4, C***H*****$_2$**-5).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 208.0 (C=O), 139.0, 137.8, 131.8, 129.9, 129.2, 126.7 (C-ar), 138.0 (C-2), 115.7 (C-1), 81.9 (C-3), 41.4 (C-4), 36.2 (C-6), 24.0 (C-5).

IR (ν, cm^{-1}, CCl_4) 3504, 2959, 2929, 2856, 1701, 1686, 1600, 1450, 1263, 1147, 1104, 1072.

HRMS (EI) Calcd. for $C_{13}H_{14}O_2$: 202.0994 Found : 202.0990

2-Hydroxy-2-vinyl-3,4-dihydronaphthalen-1(2*H*)-one **III-32b**

	$C_{12}H_{12}O_2$ M= 188.2 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out with a mixture of allylsulfide **III-27e** and vinylsulfide **III-26e** (140 mg, 0.60 mmol) and $NaIO_4$ (128 mg, 0.60 mmol). Crude sulfoxide was directly used in the next step without further purification.

Following general procedure **III-D**, the reaction was carried out with crude sulfoxide and triphenylphosphine (315 mg, 1.2 mmol). Flash chromatography on silica gel (petroleum ether/ether, 8:2) afforded tertiary alcohol **III-32b** (73 mg, 65% over 2 steps) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 8.04 (dd, *J*= 7.9, 1.2 Hz, 1H, C***H***-ar), 7.53 (ddd, *J*= 7.6, 7.5, 1.2 Hz, 1H, C***H***-ar), 7.35 (ddd, *J*= 7.9, 7.5, 1.2 Hz, 1H, C***H***-ar), 7.27 (dd, *J*= 7.6, 1.2 Hz, 1H, C***H***-ar), 6.06 (dd, *J*= 17.3, 10.7 Hz, 1H, C***H***-2), 5.31 (dd, *J*= 17.3, 0.9 Hz, 1H, C***H***-1), 5.21 (dd, *J*= 10.7, 0.9 Hz, 1H, C***H***-1), 3.96 (s, 1H, O***H***), 3.14 (ddd, *J*= 17.7, 12.5, 5.4 Hz, 1H, C***H***-5), 3.00 (ddd, *J*= 17.7, 5.1, 2.5 Hz,, 1H, C***H***-5), 2.23-2.36 (m, 2H, C***H***$_2$-4).

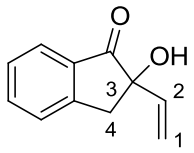
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 199.4 (C=O), 143.8, 134.2, 130.6, 129.0, 127.9, 126.9 (C-ar), 136.7 (C-2), 117.1 (C-1), 35.4 (C-4), 26.4 (C-5).[12]

IR (ν, cm^{-1}, CCl_4) 3508, 2935, 1693, 1604, 1456, 1286, 1222, 1158, 1084.

HRMS (EI) Calcd. for $C_{12}H_{12}O_2$: 188.0837 Found : 188.0842

[12] The quaternary carbon of the alcool C-3 cannot be seen because of the carbons of the chloroform.

2-Hydroxy-2-vinyl-2,3-dihydro-1*H*-inden-1-one **III-32c**

	$C_{11}H_{10}O_2$ M= 174.2 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out with the allylsulfide **III-27f** (150 mg, 0.69 mmol) and $NaIO_4$ (148 mg, 0.69 mmol). The crude sulfoxide was directly used in the next step without further purification.

Following general procedure **III-E**, the reaction was carried out with crude sulfoxide and triphenylphosphine (362 mg, 1.38 mmol). Flash chromatography on silica gel (petroleum ether/petroleum, 8:2) afforded tertiary alcohol **III-32c** (85 mg, 71% over 2 steps) as a yellow oil.

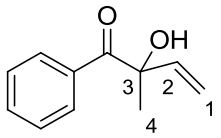
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.79 (d, *J*= 7.6Hz, 1H, C***H***-ar), 7.65-7.67 (m, 1H, C***H***-ar), 7.37-7.48 (m, 2H, C***H***-ar), 5.89 (dd, *J*= 17.2, 10.6 Hz, 1H, C***H***-2), 5.41 (d, *J*= 17.2 Hz, 1H, C***H***-1), 5.22 (d, *J*= 10.6 Hz, 1H, C***H***-1), 3.42-3.48 (m, 2H, C***H*****$_2$**-4), 2.92 (s, 1H, O***H***).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 205.4 (C=O), 150.9, 136.0, 128.1, 126.7, 125.0 (C-ar), 138.0 (C-2), 115.1 (C-1), 81.0 (C-3), 41.2 (C-4).

IR (ν, cm^{-1}, CCl_4) 3554, 3480, 2928, 2856, 1728, 1611, 1558, 1542, 1466, 1323, 1298, 1211, 1138.

HRMS (EI) Calcd. for $C_{11}H_{10}O_2$: 174.0681 Found : 174.0683

2-Hydroxy-2-methyl-1-phenylbut-3-en-1-one **III-32d**

	$C_{11}H_{12}O_2$ M= 176.2 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out with a mixture of allylsulfide **III-27g** and vinylsulfide **III-26g** (420 mg, 1.9 mmol) and $NaIO_4$ (408 mg, 1.9 mmol). Crude sulfoxide was directly used in the next step without further purification.

Following general procedure **III-E**, the reaction was carried out with sulfoxide and triphenylphosphine (996 mg, 3.8 mmol). Flash chromatography on silica gel (petroleum ether/ether, 8:2) afforded tertiary alcohol **III-32d** (224 mg, 67 % over 2 steps) as a colorless oil.

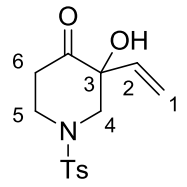
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 8.02 (d, *J*= 8.4 Hz, 2H, C***H***-ar), 7.42-7.56 (m, 3H, C***H***-ar), 6.22 (dd, *J*= 17.3, 10.6 Hz, 1H, C***H***-2), 5.55 (dd, *J*= 17.3, 0.5 Hz, 1H, C***H***-1), 5.34 (dd, *J*= 10.6, 0.5 Hz,, 1H, C***H***-1), 4.46 (s, 1H, O***H***), 1.67 (s, 3H, C***H*****$_3$**-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 202.1 (C=O), 140.3 (C-2), 133.6, 133.3, 130.1, 128.5 (C-ar), 116.6 (C-1), 78.3 (C-3), 26.0 (C-4).

IR (ν, cm^{-1}, CCl_4) 3502, 2929, 2856, 1687, 1601, 1455, 1364, 1264, 1223, 1112, 1049.

HRMS (EI) Calcd. for $C_{11}H_{12}O_2$: 176.0837 Found : 176.0832

3-Hydroxy-1-tosyl-3-vinylpiperidin-4-one **III-32e**

	$C_{14}H_{17}NO_4S$ M= 295.4 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out with allylsulfide **III-27h** and vinylsufide **III-26h** (340 mg, 1.0 mmol) and $NaIO_4$ (214 mg, 1.0 mmol). Crude sulfoxide was directly used in the next step without further purification.

Following general procedure **III-E**, the reaction was carried out with crude sulfoxide and triphenylphosphine (524 mg, 2.0 mmol). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 8:2) afforded tertiary alcohol **III-32e** (165 mg, 56% over 2 steps) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.65 (d, *J*= 8.1 Hz, 2H, C***H***-ar), 7.34 (d, *J*= 8.1 Hz, 2H, C***H***-ar), 6.32 (dd, *J*= 17.1, 10.6 Hz, 1H, C***H***-2), 5.60 (d, *J*= 17.1 Hz, 1H, C***H***-1), 5.39 (d, *J*= 10.6 Hz, 1H, C***H***-1), 4.15-4.20 (m, 1H, C***H***-5), 4.10 (ddd, *J*= 11.4, 2.9 Hz, 1H, C***H***-4), 2.99 (ddd, *J*= 14.2, 12.8, 7.1 Hz,, 1H, C***H***-5), 2.59-2.66 (m, 1H, C***H***-6), 2.51 (ddd, *J*= 14.3, 2.6, 2.0 Hz, 1H, C***H***-6), 2.04 (s, 3H, C***H$_3$***-ar), 2.03 (d, *J*= 11.4 Hz, 1H, C***H***-4).

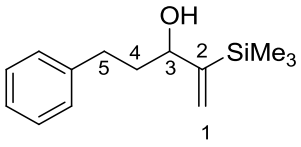
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 206.6 (C=O), 144.3, 132.9, 130.0, 127.5 (C-ar), 135.2 (C-2), 118.3 (C-1), 77.6 (C-3), 56.7 (C-4), 46.9 (C-5), 37.3 (C-6), 21.5 (CH_3-ar).

IR (ν, cm^{-1}, CCl_4) 3491, 2927, 2854, 1726, 1598, 1495, 1467, 1401, 1368, 1293, 1224, 1184, 1171, 1095.

HRMS (EI) Calcd. for $C_{14}H_{17}NO_4S$: 295.0878 Found : 295.0884

B. Chapitre IV : Synthèse Stéréosélective de Sulfones Vinyliques et d'Oléfines

5-Phenyl-2-(trimethylsilyl)pent-1-en-3-ol[184] **IV-7a**

	$C_{14}H_{22}OSi$ M= 234.4 g.mol^{-1}

To a solution of (1-bromovinyl) trimethylsilane **IV-6** (431 µL, 2.8 mmol, 1.0 equiv) in ether (8 mL), was added dropwise a 1.5 M solution of *tert*-butyllithium in hexane (2.27 mL, 3.4 mmol, 1.2 equiv) at -78 °C. After 2 h at -78 °C, hydrocynnamaldehyde **IV-5a** (195 µL, 2.8 mmol) was added dropwise and the mixture was then stirred for 1 h at 20 °C. The reaction mixture was slowly quenched with water. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 8:2) to afford the corresponding alcohol **IV-7a** (426 mg, 65%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.21-7.27 (m, 2H, C***H***-ar), 7.17-7.22 (m, 3H, C***H***-ar), 5.82 (dd, *J*= 2.4, 1.4 Hz, 1H, C***H***-1), 5.45 (dd, *J*= 2.4, 0.8 Hz, 1H, C***H***-1), 4.31 (dd, *J*= 7.9, 4.6 Hz, 1H, C***H***-3), 2.76 (dd, *J*= 13.9, 9.7, 5.6 Hz, 1H, C***H***-5), 2.67 (dd, *J*= 13.9, 9.7 Hz, 1H, C***H***-5), 2.62 (s, 1H, O***H***), 1.78-1.94 (m, 2H, C***H$_2$***-4), 0.13 (s, 9H, $Si(CH_3)_3$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 155.3 (C-2), 142.1, 128.5, 128.3, 125.8 (C-ar), 124.0 (C-1), 75.5 (C-3), 39.0 (C-5), 32.1 (C-4), -0.58 ($Si(CH_3)_3$.

IR (ν, cm^{-1}, CCl_4): 3621, 3086, 3064, 3029, 2956, 2861, 1941, 1870, 1715, 1691, 1603, 1496, 1455, 1407, 1250, 1184, 1120, 1048.

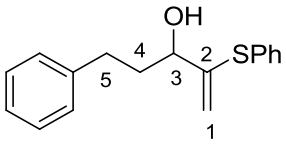
HRMS (EI): Calcd. for $C_{14}H_{22}OSi$: 234.1440 Found : 234.1442

[184] Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem* **1978**, *43*, 1526.

GENERAL PROCEDURE IV-A : PREPARATION OF VINYLSULFIDE DERIVATIVES[185]

To a 1.6 M solution of ***n*-butyllithium** in hexane (1.2 equiv) and TMEDA (1.0 equiv) in THF (3 mL/mmol of phenyl vinyl thioether) at -78 °C was added **phenyl vinyl thioether IV-12** (1.0 equiv) allowing the temperature to rise to 20 °C during 30 min. The **electrophile IV-5** (1.2 equiv) was then added at -78 °C to the yellow reaction mixture. After completion, the reaction mixture was slowly quenched with water. The aqueous phase was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding alcohol **IV-13**.

5-Phenyl-2-(phenylthio)pent-1-en-3-ol IV-13a



$C_{17}H_{18}OS$
M= 270.4 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether (2.4 mL, 20 mmol), hydrocinnamaldehyde (3.2 mL, 24 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford alcohol **IV-13a** (4.5 g, 78%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.54-7.56 (m, 2H, C***H***-ar), 7.29-7.42 (m, 8H, C***H***-ar), 5.56 (s, 1H, C***H***-1), 5.05 (s, 1H, C***H***-1), 4.31-4.34 (m, 1H, C***H***-3), 2.74-2.90 (m, 2H, C***H$_2$***-5), 2.11-2.24 (m, 2H, C***H$_2$***-4).

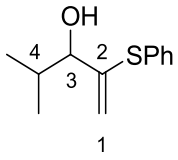
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 149.0 (C-2), 141.6, 133.4, 129.2, 128.4, 128.3, 128.3, 128.0, 125.8 (C-Ar), 113.0 (C-1), 73.9 (C-3), 37.6 (C-4), 31.7 (C-5).

IR (ν, cm^{-1}, CCl_4): 3527, 3514, 3086, 3065, 2958, 2931, 2863, 1713, 1604, 1583, 1496, 1478, 1454, 1440, 1374, 1356.

HRMS (EI): Calcd for $C_{17}H_{18}OS$: 270.1078 Found : 270.1085

[185] Foubelo, F.; Gutierrez, A.; Yus, M. *Tetrahedron Lett*. **1999**, *40*, 8173.

4-Methyl-2-(phenylthio)pent-1-en-3-ol **IV-13b**

	$C_{12}H_{16}OS$ M= 208.3 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether **IV-12** (2.4 mL, 20 mmol) and *iso*-butyraldéhyde (3.0 mL, 24 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford alcohol **IV-13b** (2.41 g, 58%) as a yellow oil.

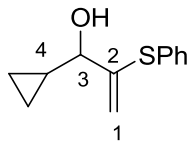
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.47-7.49 (m, 2H, C***H***-ar), 7.31-7.37 (m, 3H, C***H***-ar), 5.39 (s, 1H, C**H**-1), 4.87 (s, 1H, C***H***-1), 3.92 (d, *J*= 6.8 Hz, 1H, C***H***-3), 2.04 (sextd, *J*= 13.5, 6.7 Hz, 1H, C***H***-4), 0.98 (d, *J*= 6.8 Hz, 3H, C***H$_3$***-C4), 0.92 (d, *J*= 6.8 Hz, 3H, C***H$_3$***-C4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 148.5 (C-2), 133.7, 132.3, 129.3, 128.1 (C-ar), 112.9 (C-1), 80.4 (C-3), 32.1 (C-4), 19.5, 17.2 ($(CH_3)_2$-4).

IR (ν, cm^{-1}, CCl_4): 3612, 3378, 2962, 2931, 2873, 1606, 1584, 1476, 1468, 1440, 1386, 1367, 1301, 1233, 1173.

HRMS (EI): Calcd. for $C_{12}H_{16}OS$: 208.0922 Found : 208.0915

1-Cyclopropyl-2-(phenylthio)prop-2-en-1-ol **IV-13c**

	$C_{12}H_{14}OS$ M= 206.3 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether **IV-12** (4.8 mL, 40 mmol), cyclopropanecarboxaldehyde **IV-5c** (3.6 mL, 48 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford alcohol **IV-13c** (6.9 g, 82%) as a yellow oil.

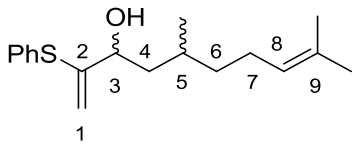
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.43-7.45 (m, 2H, C***H***-ar), 7.22-7.31 (m, 3H, C***H***-ar), 5.52 (s, 1H, C***H***-1), 4.93 (s, 1H, C***H***-1), 3.52 (d, *J*= 8.1 Hz, 1H, C***H***-3), 2.88 (brs, 1H, O***H***), 1.19-1.27 (m, 1H, C***H***-4), 0.62-0.64 (m, 2H, C$\boldsymbol{H_2}$-C4), 0.41-0.45 (m, 2H, C$\boldsymbol{H_2}$-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 148.3 (C-2), 133.1, 132.9, 129.2, 127.7 (C-ar), 113.7 (C-1), 78.4 (C-3), 17.0 (C-4), 3.3, 3.2 ((***C***H_2)$_2$-C4).

IR (ν, cm^{-1}, CCl_4) 3616, 3495, 3080, 3008, 2959, 2930, 2873, 2860, 1717, 1584, 1479, 1440, 1401, 1044.

HRMS (EI) Calcd for $C_{12}H_{14}OS$: 206.0765 Found : 206.0697

5,9-Dimethyl-2-(phenylthio)deca-1,8-dien-3-ol **IV-13d**

	$C_{18}H_{26}OS$ M= 290.4 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether **IV-12** (2.4 mL, 20 mmol), (±)-citronellal **IV-5d** (4.3 mL, 24 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 8:2) to afford alcohol **IV-13d** (5.1 g, 85%) as a mixture of two diastereomers in a 1:1 ratio and as a yellow oil.

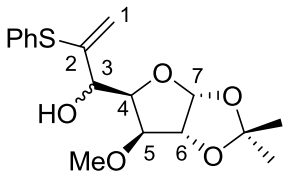
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.46-7.48 (m, 2H, C***H***-ar), 7.29-7.35 (m, 3H, C***H***-ar), 5.47, 5.41 (2s, 1H, C***H***-1), 5.10 (t, *J*= 7.1 Hz, 1H, CH-8), 4.85, 4.92 (2s, 1H, C***H***-1), 4.25-4.34 (m, 1H, C***H***-3), 2.21-2.29 (m, 1H, O***H***), 1.96-2.07 (m, 2H, C***H$_2$***-7), 1.05-1.93 (m, 5H, C***H$_2$***-4, C***H***-5, C***H$_2$***-6), 1.68, 1.60 (s, 6H, (C***H$_3$*)$_2$**-9), 0.94 (d, *J*= 6.5 Hz, 1.5H, C***H$_3$***-5), 0.92 (d, *J*= 6.6 Hz, 1.5H, C***H$_3$***-5).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 150.0, 149.8, 133.5, 133.2, 129.2, 129.2, 127.9, 127.9 (C-ar), 132.6, 132.5 (C-2), 131.0 (C-9), 124.8, 124.7 (C-8), 112.4 (C-1), 73.3, 69.9 (C-3), 43.8, 43.6 (C-4), 37.4, 36.6 (C-6), 29.3, 29.2 (C-5), 25.6, 25.2(CH_3-C9), 25.4, 25.3 (C-7), 20.3, 20.0 (CH_3-C9), 17.6 (CH_3-C5).

IR (ν, cm^{-1}, CCl_4): 3614, 3489, 2959, 2929, 2873, 1716, 1583, 1479, 1457, 1440, 1378, 1086.

HRMS (EI): Calcd. for $C_{18}H_{26}OS$: 290.1704 Found : 290.1705

1-((*3aR,5R,6S,6aR*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,2-d][1,3]dioxol-5-yl)-2-(phenylthio)prop-2-en-1-ol **IV-13e**

	$C_{17}H_{22}O_5S$ M= 338.4 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether **IV-12** (2.2 mL, 18 mmol) and (3*aR*,5S,6*S*,6a*R*)-6-Methoxy-2,2-dimethyl tetrahydrofuro[3,2-d][1,3]dioxole-5-carbaldehyde[15] (4.4 g, 21.5 mmol), giving crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 2:1) to afford alcohol **IV-13e** (5.4 g, 69%) as a yellow oil and as a mixture of epimers at C3 in a 3:1 ratio.

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.47-7.49 (m, 2H, C***H***-ar), 7.29-7.38 (m, 3H, C***H***-ar), 6.02 (d, *J*= 3.3 Hz, 0.75H, C***H***-7 dia1), 5.99 (d, *J*= 3.3 Hz, 0.25H, C***H***-7 dia2), 5.77 (s, 0.25H, C***H***-1 dia2), 5.72 (s, 0.75H, C***H***-1 dia1), 5.26 (s, 0.75H, C***H***-1 dia1), 5.21 (s, 0.25H, C***H***-1 dia2), 4.59-5.62 (m, 2H, C***H***-3, C***H***-4), 4.44-4.48 (m, 1H, C***H***-6), 3.96 (d, *J*= 3.7 Hz, 0.75H, C***H***-5 dia1), 3.42 (d, *J*= 3.2 Hz, 0.25H, C***H***-5 dia1), 3.42 (s, 2.25H, OC***H$_3$*** dia 1), 3.40 (s, 0.75H, OC***H$_3$*** dia2), 1.52, 1.36 (2s, 6H, (C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz)

Major diastereomer (1)

145.0 (C-2), 132.5, 132.5, 129.2, 127.8 (C-Ar), 116.6 (C-1), 112.1 (***C***-(CH$_3$)$_2$), 105.0 (C-7), 85.3 (C-5), 81.1 (C-6), 79.4 (C-4), 72.9 (C-3), 57.7 (OCH$_3$), 26.7, 26.3 ((CH$_3$)$_2$).

Minor diastereomer (2)

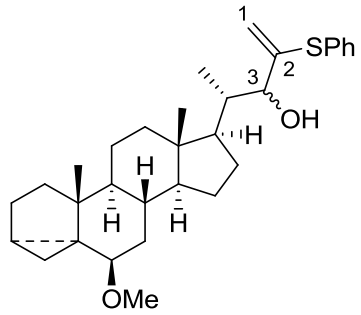
143.2 (C-2), 132.9, 132.3, 129.2, 127.6 (C-Ar), 117.2 (C-1), 111.7 (***C***-(CH$_3$)$_2$), 104.9 (C-7), 85.0 (C-5), 81.5 (C-6), 80.9 (C-4), 72.1 (C-3), 57.6 (OCH$_3$), 26.8, 26.3 ((CH$_3$)$_2$).

IR (ν, cm^{-1}, CCl$_4$): 3592, 3541, 2992, 2935, 2832, 1731, 1609, 1583, 1558, 1541, 1478, 1440, 1383, 1373, 1249, 1217, 1194, 1165, 1114, 1084, 1025.

HRMS (EI): Calcd. for $C_{17}H_{22}O_5S$: 338.1188 Found : 338.1193

[15] The aldehyde was prepared from diacetone D-glucose in three steps according to literature procedures : (a) Yan, S.; Klemm, D. *Tetrahedron* **2002**, *58*, 10065. (b) Petitou, M.; Sinay, P. Eur. *J. Org. Chem.* **2002**, *67*, 3595.

4-(*S*)-4-((2a*R*,4a*R*,4b*S*,6a*S*,7*R*,9a*S*,9b*S*,11*R*,11a*R*)-11-Methoxy-4a,6a dimethylhexadecahydrocyclopenta[*a*]cyclopropa[2,3]cyclopenta[1,2-*f*]naphthalen-7-yl)- 2-(phenylthio)pent-1-en-3-ol **IV-13f**



$C_{31}H_{44}O_2S$
M= 480.7 g.mol^{-1}

To a 2.2 M solution of *n*-butyllithium in hexane (1.74 mL, 3.82 mmol, 1.2 equiv) and TMEDA (500 µL, 3.32 mmol, 1.0 equiv) in THF (9.5 mL) at -78 °C was added phenyl vinyl thioether **IV-12** (500 µL, 3.82 mmol, 1.2 equiv) allowing the temperature to rise to 20 °C during 30 min. Aldehyde **IV-5f**[16] (1.15 g, 3.32 mmol, 1.0 equiv) was added at -78 °C. After completion, the reaction mixture was slowly quenched with water. The aqueous phase was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 8:2) to afford alcohol **IV-13f** (1.20 g, 75%) as two colorless oils corresponding to the two epimers at C-3. (1.0 g, 50%) of the major diastereomer and (200 mg, 25%) as of the other diasteromer were obtained.

Major diastereomer (1)

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.47-7.48 (m, 2H, C***H***-ar), 7.33-7.35 (m, 3H, C***H***-ar), 5.58 (s, 1H, C***H***-1), 5.24 (s, 1H, C***H***-1), 4.26 (brs, 1H, C***H***-3), 3.36 (s, 3H, OCH_3), 2.80 (brs, 1H, C***H***-OCH_3), 1.00-2.00 (m, 15H), 1.07 (s, 3H, C***H*****$_3$**), 0.78-0.99 (m, 5H), 0.94 (d, *J*= 6.8 Hz, 3H, C***H***$_3$-C4), 0.76 (s, 3H, C***H*****$_3$**), 0.67-0.70 (m, 1H), 0.44-0.47 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 147.4, 132.9, 132.7, 129.1, 127.7, 113.6, 82.3, 74;8, 56.5, 56.4, 52.6, 47.9, 43.3, 42.6, 40.0, 38.2, 35.1, 35.0, 30.5, 27.3, 24.0, 22.7, 21.4, 19.2, 13.0, 12.2, 11.1.

IR (ν, cm^{-1}, CCl_4): 3621, 3491, 3063, 2939, 2869, 2850, 2820, 1713, 1608, 1584, 1475, 1456, 1441, 1382, 1325,1295, 1270, 1200, 1184, 1099.

[16] The aldehyde was prepared from stigmasterol in three steps according to litterature procedures : Izgu, E. C.; Burns, A. C.; Hoye, T. R. *Org. Lett.* **2011**, *13*, 703.

HRMS (EI) Calcd. for $C_{31}H_{44}O_2S$: 480.3062 Found : 480.3070

Minor diastereomer (2)

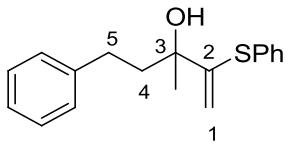
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.49-7.51 (m, 2H, C***H***-Ar), 7.34-7.39 (m, 3H, C***H***-Ar), 5.50 (s, 1H, C***H***-1), 5.02 (s, 1H, C***H***-1), 4.36 (brs, 1H, C***H***-3), 3.37 (s, 3H, OCH_3), 2.82 (brs, 1H, C***H***-OCH_3), 1.07-2.04 (m, 15H), 1.07 (s, 3H, C***H*****$_3$**), 0.92 (d, *J*= 6.8 Hz, 3H, C***H***$_3$-C4), 0.81 (s, 3H, C***H*****$_3$**), 0.75-0.8.90 (m, 5H), 0.66-0.71 (m, 1H), 0.45-0.48 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 147.0, 132.2, 132.9, 129.2, 127.8, 114.7, 82.3, 76.6, 56.5, 56.1, 52.6, 47.9, 43.3, 43.3, 42.6, 40.1, 35.2, 35.0, 33.3, 30.5, 28.5, 24.9, 24.4, 22.7, 21.4, 19.2, 14.3, 13.0, 12.1.

IR (ν, cm^{-1}, CCl_4) 3615, 3489, 3063, 2935, 2870, 2851, 2820, 1710, 1472, 1456, 1441, 1382, 1374, 1325, 1270, 1246, 1185, 1099, 1024.

HRMS (EI) Calcd. for $C_{31}H_{44}O_2S$: 480.3062 Found : 480.3061

3-Methyl-5-phenyl-2-(phenylthio)pent-1-en-3-ol **IV-13g**

	$C_{18}H_{20}OS$ M= 284.4 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether (2.4 mL, 20 mmol) and the 4-phenyl-2-butanone **IV-5g** (3.59 mL, 24 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 8:2) to afford alcohol **IV-13g** (4.55 g, 80%) as a yellow oil.

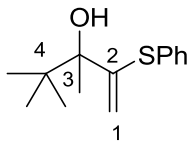
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.51-7.53 (m, 2H, C***H***-ar), 7.20-7.40 (m, 8H, C***H***-ar), 5.47 (s, 1H, C***H***-1), 4.75 (s, 1H, C***H***-1), 2.67-2.71 (m, 2H, C***H$_2$***-4), 2.01-2.18 (m, 2H, C***H$_2$***-5), 1.54 (s, 3H, C***H$_3$***-3).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 153.6 (C-2), 142.2, 134.2, 133.0, 129.4, 128.4, 128.3, 125.8 (C-ar), 110.5 (C-1), 76.2 (C-3), 43.3 (C-5), 30.4 (C-4), 28.5 (CH_3-C3).

IR (ν, cm^{-1}, CCl_4) 3614, 3482, 3076, 3063, 2957, 2928, 1713, 1477, 1455, 1441, 1377, 1209, 1171, 1086, 1024.

HRMS (EI) Calcd. for $C_{18}H_{20}OS$: 284.1235 Found : 284.1239

3,4,4-Trimethyl-2-(phenylthio)pent-1-en-3-ol **IV-13h**

	$C_{14}H_{20}OS$ M= 236.4 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether (4.8 mL, 40 mmol) and 3,3-dimethylbutan-2-one **IV-5h** (6.0 mL, 48 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 90:10) to afford alcohol **IV-13h** (6.62 g, 70%) as a colorless oil.

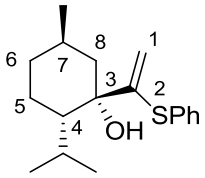
^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz) 7.49-7.51 (m, 2H, C***H***-ar), 7.30-7.38 (m, 3H, C***H***-ar), 5.40 (s, 1H, C***H***-1), 4.96 (s, 1H, C***H***-1), 2.38 (s, 1H, O***H***), 1.52 (s, 3H, C***H$_3$***-3), 1.11 (s, 9H, (C***H$_3$***)$_3$-4).

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz) 152.8 (C-2), 134.7, 133.2, 129.2, 127.8 (C-ar), 114.9 (C-1), 80.0 (C-3), 35.4 (C-4), 26.0 (CH$_3$)$_3$-4, 20.7 (CH$_3$-3).

IR (ν, cm^{-1}, CCl$_4$) 3629, 3608, 3482, 3076, 3064, 2960, 2874, 1701, 1583, 1478, 1440, 1396, 1370, 1355, 1230, 1132, 1114, 1084, 1025.

HRMS (EI) Calcd for $C_{14}H_{20}OS$: 236.1235 Found : 236.1236

(1S,2S,5R)-2-Isopropyl-5-methyl-1-(1-(phenylthio)vinyl)cyclohexanol **IV-13i**

	$C_{18}H_{26}OS$ M= 290.4 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether (2.4 mL, 20 mmol) and L-menthone **IV-5i** (4.14 mL, 24 mmol), giving the crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 95:5) to afford alcohol **IV-13i** (4.94 g, 85%) as a clear oil.

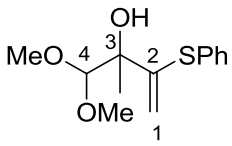
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.49-7.51 (m, 2H, C***H***-ar), 7.33-7.38 (m, 3H, C***H***-ar), 5.46 (s, 1H, C***H***-1), 4.61 (s, 1H, C***H***-1), 2.02-2.09 (m, 1H, C***H***-C4), 1.79-1.82 (m, 2H, C***H***-6, C***H***-7), 1.51-1.69 (m, 5H, C***H$_2$***-5, C***H$_2$***-8, C***H***-4), 0.95-9.98 (m, 1H, C***H***-6), 0.95 (d, *J*= 7.0 Hz, 3H, C***H$_3$***-7), 0.90 (d, *J*= 4.7 Hz, (***C***H$_3$)-CH), 0.89 (d, 3H, *J*= 4.5 Hz, (***C***H$_3$)-CH).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 155.2 (C-2), 134.6, 133.2, 129.3, 128.3 (C-ar), 108.5 (C-1), 80.3 (C-3), 48.8 (C-4), 47.3 (C-8), 34.9 (C-6), 28.2 (***C***H(CH$_3$)$_2$), 26.7 (***C***H$_3$-C7), 23.8, 18.4 ((***C***H$_3$)$_2$-CH), 22.2 (C-7).

IR (ν, cm^{-1}, CCl_4) 3600, 3077, 3063, 2940, 2928, 2870, 2846, 1600, 1583, 1477, 1456, 1440, 1385, 1376, 1366, 1238, 1178, 1118, 1024.

HRMS (EI) Calcd for $C_{18}H_{26}OS$: 290.1704 Found : 290.1698

1,1-Dimethoxy-3-(phenylthio)but-3-en-2-ol **IV-13j**

	$C_{12}H_{16}O_3S$ M= 254.3 g.mol^{-1}

Following general procedure **IV-A**, the reaction was carried out using phenyl vinyl thioether (2.4 mL, 20 mmol) and the 1,1-dimethoxyacetone **IV-5j** (2.9 mL, 24 mmol), giving crude alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford alcohol **IV-13j** (3.51 g, 69%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.41-7.43 (m, 2H, C***H***-Ar), 7.23-7.30 (m, 3H, C***H***-Ar), 5.58 (s, 1H, C***H***-1), 4.80 (s, 1H, C***H***-1), 4.42 (s, 1H, C***H***-4), 3.49, 3.36 (s, 6H, ((OC***H*****$_3$**$)_2$), 1.39 (s, 2H, C***H*****$_3$**-3).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 149.7 (C-2), 133.5, 129.2, 128.0 (C-Ar), 113.6 (C-1), 107.9 (C-4), 77.9 (C-3), 58.0, 57.7 ($(OCH_3)_2$), 22.6 (CH_3-3).

IR (ν, cm^{-1}, CCl_4) 3643, 3579, 3467, 3076, 3063, 2958, 2934, 2874, 2834, 1715, 1582, 1478, 1440, 1375, 1355, 1198, 1146, 1110, 1086.

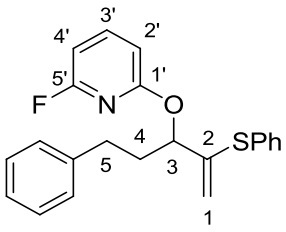
HRMS (EI) Calcd for $C_{12}H_{16}O_3S$: 254.0977 Found : 254.0981

GENERAL PROCEDURE IV-B : PREPARATION OF THE FLUOROPYRIDINE DERIVATIVES[17]

To a stirred solution of alcohol **IV-13** (1.0 equiv) in anhydrous dimethylsulfoxide (1 mL per mmol of alcohol) was added portwise **sodium hydride** (60% in mineral oil, 1.2 equiv). The resulting mixture was stirred for 20 min. **2,6-Difluoropyridine** (1.2 equiv) was then added dropwise. The reaction was monitored by TLC. After completion, the reaction mixture was slowly quenched with water. The aqueous phase was extracted with diethylether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding fluoropyridine derivative.

[17] Charrier, N.; Quiclet-Sire, B.; Zard, S. Z. *J. Am. Chem. Soc.* **2008**, *130*, 8898.

2-Fluoro-6-(5-phenyl-2-(phenylthio)pent-1-en-3-yloxy)pyridine **IV-11a**

	$C_{22}H_{20}FNOS$ M= 365.5 g.mol^{-1}

Alcohol **IV-13a** (4.47 g, 16.5 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (2.8 mL, 19.8 mmol), to give the crude fluoropyridine derivative (rt, 2 h). The residue was purified by silica gel column chromatography (petroleum ether/ether 98:2) to afford fluoropyridine derivative **IV-11a** (6.43 g, 88%) as a colorless oil.

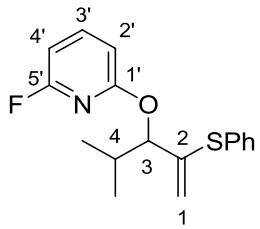
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.65 (dd, *J*= 8.0, 7.8 Hz, 1H, C***H***-3'), 7.51-7.53 (m, 2H, C***H***-ar), 7.22-7.36 (m, 8H, C***H***-ar), 6.62 (dd, *J*= 8.0, 1.1 Hz, 1H, C***H***-2'), 6.48 (dd, *J*= 7.8, 2.6 Hz, 1H, C***H***-4'), 5.56 (t, *J*= 5.8 Hz, 1H, C***H***-3), 5.54 (s, 1H, C***H***-1), 5.11 (s, 1H, C***H***-1), 2.68-2.84 (m, 2H, C***H$_2$***-5), 2.29-2.42 (m, 2H, C***H$_2$***-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 162.1 (d, *J*= 13.6 Hz, C-1'), 162.0 (d, *J*= 237.1 Hz, C-5'), 144.3 (C-2), 142.7 (d, *J*= 8.0 Hz, C-3'), 141.5, 133.1, 132.4, 129.1, 128.4, 128.3, 127.8, 125.9, C-Ar), 115.5 (C-1), 107.4 (d, *J*= 5.1 Hz, C-2'), 100.5 (d, *J*= 35.7 Hz, C-4'), 76.9 (C-3), 35.7 (C-4), 31.6 (C-5).

IR (ν, cm^{-1}, CCl_4) 3065, 3029, 2928, 2858, 1612, 1574, 1452, 1442, 1323, 1232, 1017.

HRMS (EI) Calcd. for $C_{22}H_{20}FNOS$: 365.1250 Found : 365.1245

2-Fluoro-6-(4-methyl-2-(phenylthio)pent-1-en-3-yloxy)pyridine **IV-11b**

	$C_{17}H_{18}FNOS$ M= 303.4 g.mol^{-1}

Alcohol **IV-13b** (2.13 g, 10.2 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (1.07 mL, 11.7 mmol), to give the crude fluoropyridine derivative (rt, 1 h). The residue was purified by silica gel column chromatography (petroleum ether/ether 98:2) to afford fluoropyridine derivative **IV-11b** (2.5 g, 82%) as a colorless oil.

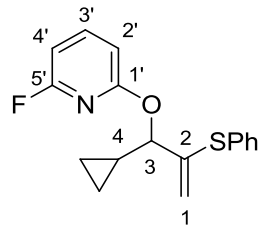
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.63 (dd, *J*= 8.0, 7.8 Hz, 1H, C***H***-3'), 7.48-7.50 (m, 2H, C***H***-Ar), 7.28-7.34 (m, 3H, C***H***-Ar), 6.61 (d, *J*= 8.0 Hz, 1H, C***H***-2'), 6.45 (dd, *J*= 7.8, 2.6 Hz, 1H, C***H***-4'), 5.45 (s, 1H, C***H***-1), 5.32 (d, J= 6.1 Hz, 1H, C***H***-3), 5.04 (s, 1H, C***H***-1), 2.35 (dsext, *J*= 13.5, 6.7 Hz, 1H, C***H***-4), 1.03 (d, *J*= 6.8 Hz, 3H, C***H$_3$***-4), 1.00 (d, *J*= 6.8 Hz, 3H, C***H$_3$***-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 162.5 (d, *J*= 13.6 Hz, C-1'), 162.0 (d, *J*= 240.3 Hz, C-5'), 143.7 (C-2), 142.6 (d, *J*= 8.0 Hz, C-3'), 133.1, 132.6, 129.1, 127.8 (C-ar), 115.9 (C-1), 107.4 (d, *J*= 5.1 Hz, C-2'), 100.2 (d, *J*= 35.8 Hz, C-4'), 82.2 (C-3), 30.7 (C-4), 19.3, 17.2 (CH_3-4).

IR (ν, cm^{-1}, $CDCl_3$) 3077, 3063, 2967, 2936, 2911, 2875, 1611, 1574, 1477, 1452, 1386, 1367, 1323, 1272, 1231, 1142, 1099, 1068, 1023.

HRMS (EI) Calcd. for $C_{17}H_{18}FNOS$: 303.1093 Found : 303.1092

2-Fluoro-6-(1-cyclopropyl-2-(phenylthio)allyloxy)pyridine **IV-11c**

	$C_{17}H_{16}FNOS$ M= 301.4 g.mol^{-1}

Alcohol **IV-13c** (6.8 g, 33.0 mmol) was then transformed following general procedure **IV-B**, using 2,6-difluoropyridine (3.6 mL, 39.6 mmol), to give the crude fluoropyridine derivative (1 h 30 min). The residue was purified by silica gel column chromatography (petroleum ether/ether 98:2) to afford fluoropyridine derivative (8.75 g, 88%) **IV-11c** as a colorless oil.

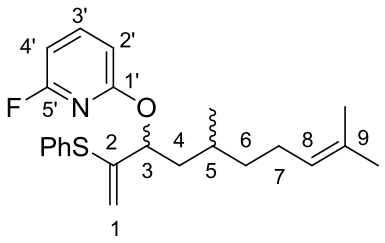
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.62 (dd, *J*= 8.0, 7.8 Hz, 1H, C***H***-3'), 7.42-7.49 (m, 2H, C***H***-ar), 7.25-7.33 (m, 3H, C***H***-ar), 6.61 (dd, *J*= 8.0, 1.5 Hz, 1H, C***H***-2'), 6.45 (dd, *J*= 7.8, 2.6 Hz, 1H, C***H***-4'), 5.57 (s, 1H, C***H***-1), 5.06 (s, 1H, C***H***-1), 5.03 (d, *J*= 8.6 Hz, 1H, C***H***-3), 1.36-1.45 (m, 1H, C***H***-4), 0.58-0.71 (m, 2H, C***H$_2$***-4), 0.46-0.56 (m, 2H, C***H$_2$***-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 161.9 (d, *J*= 13.5 Hz, C-1'), 161.8 (d, *J*= 240.5 Hz, C-5'), 145.0 (C-2), 142.6 (d, *J*= 8.0 Hz, C-3'), 133.0, 132.8, 129.0, 127.0 (C-Ar), 115.4 (C-1), 107.5 (d, *J*= 5.1 Hz, C-2'), 100.3 (d, *J*= 35.7 Hz, C-4'), 81.0 (C-3), 15.3 (C-4), 3.9, 3.6 ($(CH_2)_2$-4).

IR (ν, cm^{-1}, CCl_4) 3079, 3064, 2932, 1618, 1574, 1478, 1441, 1328, 1273, 1231, 1142, 1069, 1016.

HRMS (EI) Calcd. for $C_{17}H_{16}FNOS$: 301.0937 Found : 301.0934

2-Fluoro-6-(5,9-Dimethyl-2-(phenylthio)deca-1,8-dien-3-yloxy)pyridine IV-11d

	$C_{23}H_{28}FNO_3S$ M= 385.5 g.mol^{-1}

Alcohol **IV-13d** (5.0 g, 17.2 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (1.9 mL, 20.6 mmol), to give the crude fluoropyridine derivative (rt, 2 h). The residue was purified by silica gel column chromatography (petroleum ether/ether 98:2) to afford fluoropyridine derivative **IV-11d** (5.3 g, 79%) as a colorless oil.

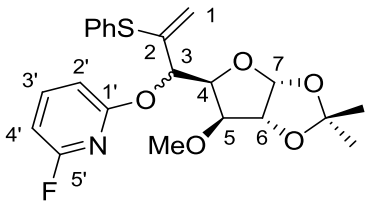
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.67 (dd, *J*= 7.9, 7.8 Hz, 1H, C***H***-3'), 7.52-7.56 (m, 2H, ***H***-ar), 7.32-7.38 (m, 3H, 3***H***-ar), 6.63 (d, *J*= 7.9, 1.6 Hz, 1H, C***H***-2'), 6.50 (dd, *J*= 7.8, 2.4 Hz, 1H, C***H***-4'), 5.65 (dd, *J*= 8.5, 5.3 Hz, 0.5H, C***H***-3), 5.61 (dd, *J*= 10.3, 3.9 Hz, 0.5H, C***H***-3), 5.54, 5.53 (s, 1H, C***H***-1), 5.14 (t, *J*= 7.1 Hz, 0.5H, C***H***-8), 5.07 (t, *J*= 7.0 Hz, 0.5H, C***H***-8), 5.09, 5.04 (s, 1H, C***H***-1), 1.95-2.07 (m, 2H, C***H$_2$***-7), 1.60-1.82 (m, 4H, C***H$_2$***-4, C***H***-5), 1.72, 1.68, 1.65, 1.61 (s, 6H, (C***H$_3$***)$_2$-9), 1.00 (d, *J*= 6.7 Hz, 1.5H, C***H$_3$***-5), 0.88 (d, *J*= 6.5 Hz, 1.5H, C***H$_3$***-5).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 162.0 (d, *J*= 240.6 Hz, C-5'), 162.1 (d, *J*= 13.4 Hz, C-1'), 145.5, 145.5, 133.3, 133.1, 129.1, 129.0, 127.8, 127.8 (C-ar), 142.6 (d, *J*= 8.1 Hz, C-3'), 132.5 (C-2), 131.2 (C-9), 124.8, 124.7 (C-8), 114.9, 114.7 (C-1), 107.4 (d, *J*= 5.0 Hz, C-2'), 107.0 (d, *J*= 5.4 Hz, C-2'), 107.0 (d, *J*= 5.4 Hz, C-2'), 100.3 (d, *J*= 35.8 Hz, C-4'), 100.3 (d, *J*= 35.7 Hz, C-4'), 76.4, 75.7 (C-3), 41.7, 41.4 (C-4), 37.5, 36.5 (C-6), 29.3, 29.1 (C-5), 25.7, 25.6 (CH_3-9), 25.5, 25.2 (C-7), 20.0, 19.1 (CH_3-9), 17.7, 17.6 (CH_3-5).

IR (ν, cm^{-1}, CCl_4) 2961, 2929, 2857, 1611, 1573, 1451, 1324, 1231, 1019.

HRMS (EI) Calcd. for $C_{23}H_{28}FNOS$:385.1876 Found : 385.1884

2-Fluoro-6-(1-((3a*R*,5*S*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydro furo [3,2-d][1,3]dioxol-5-yl)-2-(phenylthio)allyloxy)pyridine **IV-11e**

	$C_{22}H_{24}FNO_5S$ M= 433.5 g.mol^{-1}

Alcohol **IV-13e** (2.35 g, 6.95 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (634 µL, 8.00 mmol), to give crude fluoropyridine derivative rt, 3 h). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 80:20) to afford fluoropyridine derivative **IV-11e** (2.74 g, 91%) as two epimers at C-3 in a 3:1 ratio which could be separated.

Major diastereomer (1)

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.60 (dd, *J*= 8.0, 7.8 Hz, 1H, C***H***-3'), 7.40-7.42 (m, 2H, C***H***-ar), 7.19-7.25 (m, 3H, C***H***-ar), 6.51 (d, *J*= 8.0 Hz, 1H, C***H***-2'), 6.46 (dd, *J*= 7.8, 2.6 Hz, 1H, C***H***-4'), 5.94 (d, *J*= 3.6 Hz, 1H, C***H***-7), 5.86 (d, *J*= 9.4 Hz, 1H, C***H***-3), 5.81 (s, 1H, C***H***-1), 5.17 (s, 1H, C***H***-1), 4.68 (dd, *J*= 9.5, 3.0 Hz, 1H, C***H***-4), 4.57 (d, *J*= 3.6 Hz, 1H, C***H***-6), 3.93 (d, *J*= 3.0 Hz, 1H, C***H***-5), 3.17 (s, 3H, OC***H*****$_3$**), 1.51, 1.33 (s, 6H, (C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 161.7 (d, *J*= 240.9 Hz, C-1'), 161.1 (d, *J*= 13.8 Hz, C-5'), 142.7 (d, *J*= 7.8 Hz, C-3'), 142.4 (C-2), 133.2, 133.0, 129.0, 127.5 (C-Ar), 120.6 (C-1), 111.9 (***C***-$(CH_3)_3$), 107.0 (d, *J*= 5.0 Hz, C-2'), 105.3 (C-7), 100.8 (d, *J*= 35.6 Hz, C-4'), 83.4 (C-5), 81.6 (C-6), 79.4 (C-4), 75.4 (C-3), 57.9 (OCH_3), 26.9, 26.5 ($(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4) 3063, 2992, 2933, 2829, 1615, 1576, 1451, 1383, 1373, 1329, 1231, 1165, 1120, 1085, 1024.

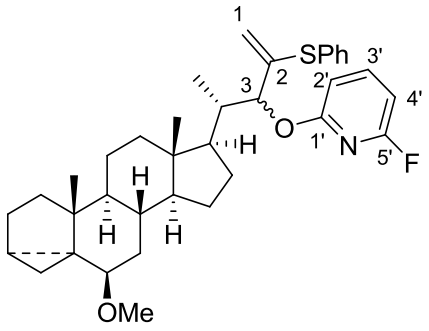
HRMS (EI) Calcd. for $C_{22}H_{24}FNO_5S$: 433.1359 Found : 433.1362

Minor diastereomer (2)

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.59 (dd, *J*= 7.8, 7.8 Hz, 1H, C***H***-3'), 7.41-7.44 (m, 2H, C***H***-ar), 7.22-7.32 (m, 3H, C***H***-ar), 6.61 (dd, *J*= 7.8, 1.0 Hz, 1H, C***H***-2'), 6.44 (dd, *J*= 7.8, 2.6 Hz, 1H, C***H***-4'), 5.97 (d, *J*= 3.2 Hz, 1H, C***H***-7), 5.96 (d, *J*= 7.9 Hz, 1H, C***H***-3), 5.67 (s, 1H, C***H***-1), 4.99 (s, 1H, C***H***-1), 4.68 (dd, *J*= 8.6, 3.3 Hz, 1H, C***H***-4), 4.60 (d, *J*= 3.3 Hz, 1H, C***H***-6), 3.42 (d, *J*= 3.2 Hz, 1H, C***H***-5), 3.18 (s, 3H, OC***H*****$_3$**), 1.51, 1.35 (s, 6H, (C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	161.7 (d, *J*= 244.4 Hz, C-1'), 161.6 (d, *J*= 13.7 Hz, C-5'), 142.5 (d, *J*= 7.7 Hz, C-3'), 142.2 (C-2), 133.9, 133.9, 129.2, 128.2 (C-Ar), 117.2 (C-1), 112.0 (***C***-$(CH_3)_3$), 108.0 (d, *J*= 5.0 Hz, C-2'), 105.4 (C-7), 100.5 (d, *J*= 35.8 Hz, C-4'), 83.8 (C-5), 81.4 (C-6), 80.9 (C-4), 76.4 (C-3), 57.5 (OCH_3), 26.9, 26.4 ($(CH_3)_2$).
IR (ν, cm^{-1}, CCl_4)	3063, 2992, 2933, 2829, 1615, 1576, 1451, 1383, 1373, 1329, 1231, 1165, 1120, 1085, 1024.
HRMS (EI)	Calcd. for $C_{22}H_{24}FNO_5S$: 433.1359 Found : 433.1362

2-Fluoro-6-(((*S*)-4-((2a*R*,4a*R*,4b*S*,6a*S*,7*R*,9a*S*,9b*S*,11*R*,11a*R*)-11-methoxy-4a,6a dimethylhexadecahydrocyclopenta[*a*]cyclopropa[2,3] cyclopenta[1,2-*f*]naphthalen-7-yl)- 2-(phenylthio)pent-1-en-3-yloxy) pyridine **IV-11f**



$C_{36}H_{46}FNO_2S$
M= 575.8 g.mol^{-1}

Alcohol **IV-13f** (1.14 g, 2.36 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (257 µL, 3.24 mmol), to give crude fluoropyridine derivative. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 98:2) to afford fluoropyridine derivative **IV-11f** (1.09 g, 80%) as a mixture of two epimers at C-3 in a 4:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.57-7.63 (m, 2.2H, C***H***-3', C***H***-ar), 7.45-7.47 (m, 0.8H, C***H***-ar), 7.25-7.36 (m, 3H, C***H***-ar), 6.59 (dd, *J*= 8.0, 1.2 Hz, 1H, C***H***-2'), 6.43 (dd, *J*= 7.8, 2.4 Hz, 1H, C***H***-4'), 5.57 (d, *J*= 3.7 Hz, 0.2H, C***H***-3 dia2), 5.48 (s, 0.8H, C***H***-1 dia1), 5.44 (s, 0.2H, C***H***-1 dia2), 5.32 (d, *J*= 1.2 Hz, 0.8H, C***H***-3 dia1), 5.32 (s, 0.8H, C***H***-1 dia1), 5.00 (s, 0.2H, C***H***-1 dia2), 3.31 (s, 0.6H, OCH_3 dia2), 3.29 (s, 2.4H, OCH_3 dia1), 2.76 (brs, 0.2H), 2.71 (brs, 0.8H), 1.33-2.10 (m, 15H), 1.12 (d, *J*= 6.8 Hz, 0.6H, C***H$_3$***-4 dia2), 1.01 (d, *J*= 6.9 Hz, 2.4H, C***H$_3$***-4 dia1), 1.01 (s, 3H), 0.83-0.89 (m, 5H), 0.76 (s, 0.6H dia2), 0.70 (s, 2.4H dia1), 0.61-0.65 (m, 1H), 0.38-0.44 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

<u>Major diastereomer (1)</u>

162.1 (d, *J*= 240.6 Hz, C-1'), 162.4 (d, *J*= 13.7 Hz, C-5'), 142.7 (d, *J*= 7.9 Hz, C-3'), 141.9 (C-2), 132.9, 132.3, 128.9, 127.4 (C-Ar), 116.2 (C-1), 106.8 (d, *J*= 5.1 Hz, C-2'), 100.1 (d, *J*= 35.7 Hz, C-4'), 82.2, 78.4, 56.4, 56.3, 52.5, 47.9, 43.3, 42.6, 40.0, 37.1, 35.2, 34.8, 33.3, 30.4, 27.2, 24.9, 23.9, 22.7, 21.4, 19.2, 13.0, 12.3, 12.2.

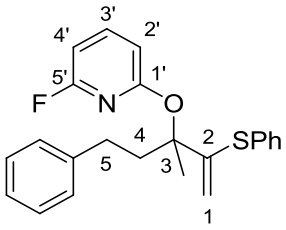
<u>Minor diastereomer (2)</u>

162.0 (d, *J*= 240.4 Hz, C-1'), 161.8 (d, *J*= 13.7 Hz, C-5'), 142.5 (d, *J*= 7.9 Hz, C-3'), 149.0 (C-2), 133.1, 132.5, 129.0, 127.6 (C-Ar), 116.2 (C-1), 107.4 (d, *J*= 5.1 Hz, C-2'), 100.2 (d, *J*= 35.7 Hz, C-4'), 82.2, 79.9, 56.5, 56.1, 52.7, 43.3, 43.3, 40.5, 40.1, 37.1, 35.2, 34.9, 33.3, 30.4, 28.3, 24.9, 24.4, 22.7, 19.2, 15.1, 13.0, 12.2, 12.0.

IR (ν, cm^{-1}, CCl_4) 3060, 2946, 2865, 2845, 2819, 1612, 1572, 1442, 1380, 1323, 1232, 1178, 1141, 1100, 1080, 1021.

HRMS (EI) Calcd. for $C_{36}H_{46}FNO_2S$: 575.3233 Found : 575.3228

2-Fluoro-6-(3-methyl-5-phenyl-2-(phenylthio)pent-1-en-3-yloxy)pyridine **IV-11g**



$C_{23}H_{22}FNOS$
M= 379.5 g.mol^{-1}

Alcohol **IV-13g** (4.27 g, 15 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (1.64 mL, 18 mmol), to give the crude fluoropyridine derivative (rt, 3 h). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the corresponding fluoropyridine derivative **IV-11g** (4.44 g, 78%) as a colorless oil.

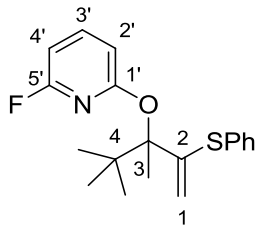
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.70 (dd, *J*= 7.9, 7.7 Hz, 1H, C***H***-3'), 7.53-7.55 (m, 2H, C***H***-ar), 7.34-7.40 (m, 5H, C***H***-ar), 7.26-7.28 (m, 3H, C***H***-ar), 6.72 (d, *J*= 7.9 Hz, 1H, C***H***-2'), 6.54 (d, *J*= 7.7 Hz, 1H, C***H***-4'), 5.52 (s, 1H, C***H***-1), 4.86 (s, 1H, C***H***-1), 2.76-2.79 (m, 2H, C***H$_2$***-5), 2.51-2.59 (m, 2H, C***H$_2$***-4), 1.97 (s, 3H, C***H$_3$***-3).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 161.6 (d, *J*= 14.6 Hz, C-1'), 161.5 (d, *J*= 239.3 Hz, C-5'), 142.2 (d, *J*= 8.0 Hz, C-3'), 150.8 (C-2), 142.2, 134.4, 132.9, 129.2, 128.4, 128.4, 128.2, 125.8 (C-ar), 111.7 (C-1), 108.9 (d, *J*= 5.1 Hz, C-2'), 100.4 (d, *J*= 36.0 Hz, C-4'), 85.2 (C-3), 42.2 (C-5), 30.3 (C-4), 24.2 (CH_3-3).

IR (ν, cm^{-1}, CCl_4): 2928, 2855, 1612, 1574, 1441, 1326, 1231, 1209, 1172, 1086, 1024.

HRMS (EI): Calcd. for $C_{23}H_{22}FNOS$: 379.1406 Found : 379.1400

2-Fluoro-6-(3,4,4-trimethyl-2-(phenylthio)pent-1-en-3-yloxy)pyridine IV-11h

	$C_{19}H_{22}FNOS$ M= 331.4 g.mol^{-1}

Alcohol **IV-13h** (6.38 g, 27 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (3.0 mL, 32.4 mmol), to give crude fluoropyridine derivative (rt, 3 h). The residue was purified by silica gel column chromatography (petroleum ether/ether 99:1) to afford fluoropyridine derivative **IV-11h** (5.6 g, 63%) as a colorless oil.

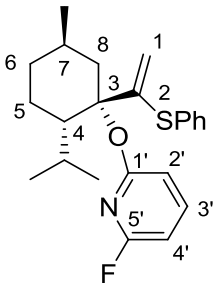
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.58-7.62 (m, 3H, C***H***-ar, C***H***-3'), 7.27-7.35 (m, 3H, C***H***-ar), 6.63 (dd, *J*= 8.0, 1.4 Hz, 1H, C***H***-2'), 6.43 (dd, *J*= 7.6, 2.7 Hz, 1H, C***H***-4'), 5.24 (s, 1H, C***H***-1), 4.97 (s, 1H, C***H***-1), 1.90 (s, 3H, C***H$_3$***-3), 1.16 (s, 9H, (C***H$_3$***)$_3$-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 162.0 (d, *J*= 14.6 Hz, C-1'), 161.4 (d, *J*= 238.5 Hz, C-5') , 142.0 (d, *J*= 8.0 Hz, C-3'), 135.1 (C-2), 133.3, 129.1, 128.8, 127.6 (C-ar), 116.3 (C-1), 108.9 (d, *J*= 5.2 Hz, C-2'), 99.9 (d, *J*= 36.2 Hz, C-4'), 89.4 (C-3), 39.5 (C-4), 26.0 ($(CH_3)_3$-4), 20.2 (CH_3-3).

IR (ν, cm^{-1}, CCl_4) 3063, 2962, 2931, 2875, 1616, 1601, 1573, 1478, 1439, 1397, 1373, 1330, 1232, 1126, 1105, 1073, 1015.

HRMS (EI) Calcd. for $C_{19}H_{22}FNOS$: 331.1406 Found : 331.1400

2-Fluoro-6-((1*S*,2*S*,5*R*)-2-isopropyl-5-methyl-1-(1-(phenylthio)vinyl) cyclohexyloxy)pyridine **IV-11i**

	$C_{23}H_{28}FNOS$ M= 385.5 g.mol^{-1}

Alcohol **IV-13i** (4.80 g, 16.5 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (1.83 mL, 20 mmol), to give crude fluoropyridine derivative (rt, 4 h). The residue was purified by silica gel column chromatography (petroleum ether/ether 99:1) to afford the corresponding fluoropyridine derivative **IV-11i** (3.95 g, 62%) as a colorless oil.

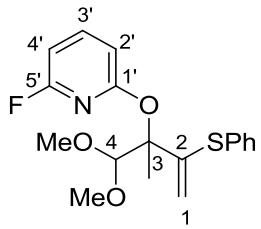
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.60 (dd, *J*= 7.9, 7.8 Hz, 1H, C***H***-2'), 7.56-7.58 (m, 2H, C***H***-ar), 7.26-7.38 (m, 3H, C***H***-Ar), 6.63 (dd, *J*= 7.9, 1.5 Hz, 1H, C***H***-2'), 6.43 (dd, *J*= 7.8, 2.8 Hz, 1H, C***H***-4'), 5.26 (s, 1H, C***H***-1), 4.96 (s, 1H, C***H***-1), 3.23 (dt, *J*= 14.0, 2.3, 1H, C***H***-4), 2.22-2.32 (m, 1H, C***H***-C4), 1.55-1.78 (m, 6H, C***H***-6, C***H$_2$***-5, C***H***-7, C***H$_2$***-8), 0.95-1.08 (m, 1H, C***H***-6), 0.99 (d, *J*= 7.0 Hz, 3H, C***H$_3$***-7), 0.96 (d, *J*= 7.2 Hz, 3H, (***C***H_3)-CH), 0.77 (d, *J*= 6.7 Hz, 3H, (***C***H_3)-CH).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 161.7 (d, *J*= 14.6 Hz, C-1'), 161.4 (d, *J*= 238.9 Hz, C-5') , 142.0 (d, *J*= 8.0 Hz, C-3'), 134.0 (C-2), 133.4, 129.2, 127.2 (C-ar), 108.7 (d, *J*= 5.2 Hz, C-4'), 100.1 (d, *J*= 36.3 Hz, C-2'), 90.3 (C-3), 40.1 (C-8), 34.9 (C-6), 27.7 (***C***H_3-C7), 26.5 (C-4), 23.8, 17.7 ((***C***H_3)$_2$-CH), 22.2 (C-7), 20.7 (C-5).

IR (ν, cm^{-1}, CCl_4) 3063, 2957, 2871, 2848, 1611, 1573, 1477, 1440, 1385, 1368, 1330, 1302, 1230, 1141, 1128, 1011, 1024.

HRMS (EI) Calcd for $C_{23}H_{28}FNOS$: 385.1876 Found : 385.1867

2-Fluoro-6-(1,1-dimethoxy-3-(phenylthio)but-3-en-2-yloxy)pyridine IV-11j

	$C_{18}H_{20}FNO_3S$ M= 349.4 g.mol^{-1}

Alcohol **IV-13j** (4.80 g, 17 mmol) was transformed following general procedure **IV-B**, using 2,6-difluoropyridine (1.7 mL, 18.7 mmol), to give crude protected alcohol. The residue was purified by silica gel column chromatography (petroleum ether/ether 99:1) to afford protected alcohol **IV-11j** (5.10 g, 86%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.62 (dd, *J*= 8.0, 7.8 Hz, 1H, C***H***-3'), 7.41-7.43 (m, 2H, C***H***-Ar), 7.26-7.33 (m, 3H, C***H***-ar), 6.64 (dd, *J*= 8.0 Hz, 1.5 Hz, 1H, C***H***-2'), 6.47 (dd, *J*= 7.8, 2.8 Hz, 1H, C***H***-4'), 5.53 (s, 1H, C***H***-1), 4.91 (s, 1H, C***H***-1), 4.66 (s, 1H, C***H***-4), 3.67, 3.55 (s, 6H, (OC***H*****$_3$**$)_2$), 1.86 (s, 3H, C***H*****$_3$**-3).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 161.1 (d, *J*= 239.4 Hz, C-5'), 160.8 (d, *J*= 14.6 Hz, C-1'), 147.4 (C-2), 142.1 (d, *J*= 7.9 Hz, C-3'), 133.6, 133.1, 128.9, 127.8 (C-Ar), 114.6 (C-1), 108.7 (d, *J*= 5.1 Hz, C-2'), 108.5 (C-4), 100.4 (d, *J*= 35.9 Hz, C-4'), 86.5 (C-3), 58.5, 57.5 ($(OCH_3)_2$), 17.0 (CH_3-3).

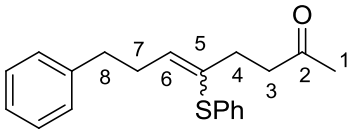
IR (ν, cm^{-1}, CCl_4): 3076, 2995, 2931, 2833, 1614, 1575, 1456, 1376, 1327, 1273, 1231, 1207, 1187, 1089, 1023.

HRMS (EI): Calcd for $C_{18}H_{20}FNO_3S$: 349.1148 Found : 349.1150

GENERAL PROCEDURE IV-C : OLEFINATION REACTION

A solution of **xanthate** (1.0 equiv) and the desired **olefin** (2.0 equiv) in ethyl acetate (1 mL /mmol of starting xanthate) was refluxed for 20 min under nitrogen. Lauroyl peroxide (DLP) (20% mol) was then added to the refluxing solution, followed by additional portions (20% mol) every hour until starting the xanthate was completely consumed. The mixture was then cooled to 20 °C, concentrated *in vacuo* and purified by flash chromatography on silica gel.

8-Phenyl-5-(phenylthio)oct-5-en-2-one IV-10a



$C_{20}H_{22}OS$
M= 310.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11a** (800 mg, 2.0 mmol) and xanthate **IV-4a**[1] (180 mg, 1.0 mmol). The reaction needed 140 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 10:90) to afford vinylsulfide **IV-10a** (200 mg, 64%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.13-7.33 (m, 10H, C***H***-ar), 5.98 (t, *J*= 6.8 Hz, 0.67H, C***H***-6 *Z* isomer), 5.92 (t, *J*= 7.6 Hz, 0.33H, C***H***-6 *E* isomer), 2.65-2.76 (m, 3.33H, C***H$_2$***-7, C***H$_2$***-8 *Z* isomer), 2.57-2.61 (m, 2H, C***H$_2$***-4), 2.48-2.53 (m, 0.67H, C***H$_2$***-8 *E* isomer), 2.39-2.43 (m, 1.33H, C***H$_2$***-3 *Z* isomer), 2.32-2.35 (m, 0.67H, C***H$_2$***-3 *E* isomer), 2.05 (s, 2H, C***H$_3$***-1 *Z* isomer), 2.04 (s, 1H, C***H$_3$***-1 *E* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

<u>*Z* isomer</u>

208.0 (C-2), 141.4 (C-5), 137.1 (C-6), 134.7, 132.7, 129.3, 128.6, 128.5, 128.3, 126.1, 125.9 (C-ar), 42.6 (C-3), 35.4 (C-8), 31.6 (C-7, C-4), 30.0 (C-1).

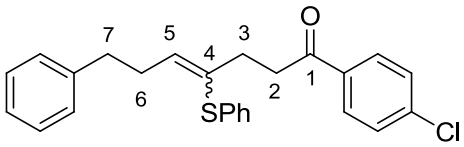
<u>*E* isomer</u>

207.9 (C-2), 141.3 (C-5), 136.8 (C-6), 135.0, 132.9, 130.2, 129.8, 128.9, 128.4, 126.4, 126.0 (C-ar), 42.0 (C-3), 35.4 (C-8), 31.1 (C-4), 30.3 (C-7), 29.9 (C-1).

IR (ν, cm^{-1}, CCl_4): 3065, 3029, 3005, 2927, 2857, 1718, 1606, 1584, 1496, 1362, 1053.

HRMS (EI): Calcd. for $C_{20}H_{22}OS$: 310.1391 Found : 310.1403

1-(4-Chlorophenyl)-7-phenyl-4-(phenylthio)hept-4-en-1-one **IV-10b**



$C_{25}H_{23}ClOS$
M= 407.0 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11a** (800 mg, 2.0 mmol) and xanthate **IV-4b**[4] (275 mg, 1.0 mmol). The reaction needed 140 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford vinylsulfide **IV-10b** (244 mg, 60%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

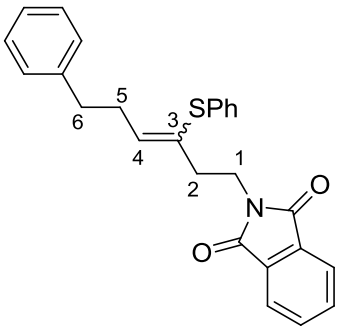
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.79 (d, *J*= 8.6 Hz, C***H***-ar *Z* isomer, 1.33H), 7.78 (d, *J*= 8.7 Hz, C***H***-ar *E* isomer, 0.67H), 7.40 (d, *J*= 8.6 Hz, 0.67H, C***H***-ar *E* isomer), 7.39 (d, *J*= 8.6 Hz, 1.33H, C***H***-ar *Z* isomer), 7.16-7.32 (m, 10H, C***H***-ar), 6.05 (t, *J*= 6.8 Hz, 0.67 H, C***H***-5 *Z* isomer), 5.98 (t, *J*= 7.5 Hz, 0.33H, C***H***-5 *E* isomer), 3.09 (dd, *J*= 7.8, 6.7 Hz, 1.33H, C***H$_2$***-2 *Z* isomer), 2.90 (dd, *J*= 8.4, 6.8 Hz, 0.67H, C***H$_2$***-2 *E* isomer), 2.81-2.84 (m, 0.67H, C***H$_2$***-7 *E* isomer), 2.76-2.52 (m, 5.33H, C***H$_2$***-6 *Z* isomer, C***H$_2$***-7, C***H$_2$***-3).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 198.1 (C=O *Z* isomer), 198.0 (C=O *E* isomer), 141.3, 141.2, 139.4, 139.3, 137.4, 137.1, 134.7, 134.6, 133.0, 132.8, 130.2, 129.9, 129.4, 129.4, 129.0, 129.0, 128.8, 128.8, 128.6, 128.5, 128.3, 128.3, 126.5, 126.2, 126.0, 125.9 (C-ar, C-4, C-5), 37.9 (C-2 *Z* isomer), 37.3 (C-2 *E* isomer), 35.4 (C-7 *Z* isomer), 35.4 (C-7 *E* isomer), 32.2 (C-3 *Z* isomer), 31.6 (C-6 *E* isomer), 31.1 (C-3 *E* isomer), 25.5 (C-6 *Z* isomer).

IR (ν, cm^{-1}, CCl_4) 3064, 3029, 2927, 2857, 1690, 1590, 1478, 1440, 1401, 1290, 1202, 1093, 1025, 1013.

HRMS (EI) Calcd. for $C_{25}H_{23}ClOS$: 406.1158 Found : 406.1160

2-(4-Methyl-6-phenyl-3-(phenylthio)hex-2-enyl)isoindoline-1,3-dione **IV-10c**

	$C_{26}H_{23}NO_2S$ M= 413.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11a** (800 mg, 2.0 mmol) and xanthate **IV-4c**[5] (281 mg, 1.0 mmol). The reaction needed 120 mol% of DLP to go to completion (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 2:8) to afford the corresponding vinylsulfide **IV-10c** (318 mg, 77%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

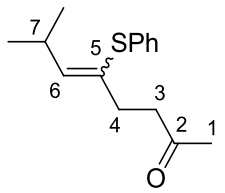
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.81-7.83 (m, 2H, C***H***-ar), 7.69-7.71 (m, 2H, C***H***-ar), 7.09-7.26 (m, 10H, C***H***-ar), 5.93 (t, *J*= 7.6 Hz, 0.33H, C***H***-4 *E* isomer), 5.91 (t, *J*= 6.9 Hz, C***H***-4, 0.67H *Z* isomer), 3.83 (t, *J*= 6.9 Hz, 1.33H, C***H$_2$***-1 *Z* isomer), 3.79 (t, *J*= 7.2 Hz, 0.67H, C***H$_2$***-1 *E* isomer), 2.56-2.67 (m, 3.33H, C***H$_2$***-6, C***H$_2$***-5 *Z* isomer), 2.41-2.51 (m, 2.67H, C***H$_2$***-2, C***H$_2$***-5 *E* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 168.1, 168.1 (C=O), 141.4, 141.0 (C-3), 137.9, 137.9 (C-4), 134.8, 134.7, 133.9, 133.8, 132.1, 132.1, 131.1, 130.5, 129.9, 128.9, 128.5, 128.4, 128.4, 128.3, 126.6, 126.3, 126.0, 125.9, 123.2, 123.1 (C-ar), 37.2, 36.7 (C-1), 36.0, 29.8 (C-5), 35.4, 35.3 (C-2), 31.6, 30.8 (C-6).

IR (ν, cm^{-1}, CCl_4) 3064, 3029, 2927, 2856, 1775, 1718, 1614, 1583, 1454, 1440, 1393, 1360, 1236, 1224, 1024.

HRMS (EI) Calcd. for $C_{26}H_{23}NO_2S$: 413.1449 Found : 413.1450

7-Methyl-5-(phenylthio)oct-5-en-2-one **IV-10d**

	$C_{15}H_{20}OS$ M= 248.4 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11b** (607 mg, 2.0 mmol) and xanthate **IV-4a**[1] (178 mg, 1.0 mmol). The reaction needed 120 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford vinylsulfide **IV-10d** (164 mg, 66%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.15-7.27 (m, 5H, C***H***-ar), 5.80 (d, *J*= 11.3 Hz, 0.33H, C***H***-6 *E* isomer), 5.78 (d, *J*= 9.2 Hz, 0.67H, C***H***-6 *Z* isomer), 2.93-3.06 (m, 0.67H, C***H***-7 *Z* isomer), 2.60-2.77 (m, 0.33H, C***H***-7 *E* isomer), 2.62 (t, *J*= 7.5 Hz, 2H, C***H$_2$***-3), 2.46 (t, *J*= 7.4 Hz, 0.67H, C***H$_2$***-4 *E* isomer), 2.41 (t, *J*= 7.5 Hz, 1.33H, C***H$_2$***-4 *Z* isomer), 2.09 (s, 1H, C***H$_3$***-1 *E* isomer), 2.07 (s, 2H, C***H$_3$***-1 *Z* isomer), 1.02 (d, *J*= 6.7 Hz, 2H, (C***H$_3$***)$_2$-7 *E* isomer), 1.00 (d, *J*= 6.7 Hz, 4H, (C***H$_3$***)$_2$-7 *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

<u>*Z* isomer</u>

207.9 (C=O), 145.4 (C-6), 133.0 (C-5), 129.2, 129.1, 128.9, 126.0 (C-ar), 42.7 (C-3), 31.6 (C-2), 30.0 (C-7), 29.3 (C-1), 22.7 ((CH$_3$)$_2$-7).

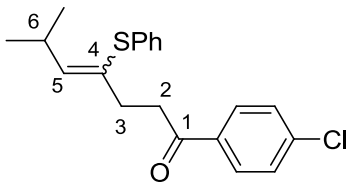
<u>*E* isomer</u>

207.8 (C=O), 146.6 (C-6), 135.5 (C-5), 129.3, 129.1, 128.9, 126.3 (C-ar), 42.5 (C-3), 31.9 (C-2), 29.7 (C-7), 28.6 (C-1), 22.8 ((CH$_3$)$_2$-7).

IR (ν, cm^{-1}, CCl_4) 3075, 2964, 2930, 2868, 1731, 1584, 1478, 1441, 1367, 1258, 1233, 1152, 1052.

HRMS (EI) Calcd. for $C_{20}H_{22}OS$: 248.1235 Found : 248.1230

1-(4-Chlorophenyl)-6-methyl-4-(phenylthio)hept-4-en-1-one **IV-10e**

	$C_{20}H_{21}ClOS$ M= 344.9 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11b** (607 mg, 2.0 mmol) and xanthate **IV-4b**[4] (275 mg, 1.0 mmol). The reaction needed 140 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford vinylsulfide **IV-10e** (203 mg, 59%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

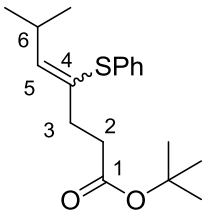
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)
7.66-7.71 (m, 2H, C***H***-ar), 7.23-7.27 (m, 2H, C***H***-ar), 7.03-7.24 (m, 5H, C***H***-ar), 5.73 (d, *J*= 9.8 Hz, 0.33H, C***H***-5 *E* isomer), 5.70 (d, *J*= 9.2 Hz, 0.67H, C***H***-5 *Z* isomer), 2.97-3.03 (m, 2H, C***H$_2$***-2), 2.83-2.92 (m, 0.67H, C***H***-6 *Z* isomer), 2.63-2.73 (m, 0.33H, C***H***-6 *E* isomer), 2.50 (t, *J*= 7.5 Hz, 0.67H, C***H$_2$***-3 *E* isomer), 2.44 (t, *J*= 7.4 Hz, 1.33H, C***H$_2$***-3 *Z* isomer), 0.91 (d, *J*= 6.6 Hz, 2H, (C***H$_3$***)$_2$-6 *E* isomer), 0.87 (d, *J*= 6.7 Hz, 4H, (C***H$_3$***)$_2$-6 *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)
<u>*Z* isomer</u>
198.3 (C=O), 145.8 (C-6), 139.3, 135.2, 135.0, 129.5, 129.2, 129.0 128.8, 128.6, 126.1 (C-ar, C-5), 38.0 (C-2), 32.2 (C-2), 29.3 (C-6), 22.7 ($(CH_3)_2$-6).
<u>*E* isomer</u>
198.1 (C=O), 147.0 (C-6), 139.4, 135.4, 134.8, 129.6, 129.4, 128.9, 128.8, 128.6, 126.3 (C-ar), 37.7 (C-2), 32.2 (C-3), 28.7 (C-6), 22.8 ($(CH_3)_2$-6).

IR (ν, cm^{-1}, CCl_4)
3064, 3029, 2927, 2856, 1719, 1583, 1478, 1454, 1439, 1360, 1219, 1159, 1054, 1025.

HRMS (EI) Calcd. for $C_{20}H_{21}ClOS$: 344.1002 Found : 344.0997

tert-Butyl 6-methyl-4-(phenylthio)hept-4-enoate **IV-10f**

	$C_{18}H_{26}O_2S$ M= 306.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11b** (607 mg, 2.0 mmol) and xanthate **IV-4d**[18] (236 mg, 1.0 mmol). The reaction needed 120 mol% of DLP to go to completion (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford vinylsulfide **IV-10f** (218 mg, 71%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.29 (m, 3H, C***H***-ar), 7.16-7.21 (m, 2H, C***H***-ar), 5.80 (d, J= 9.2 Hz, 0.67H, C***H***-5 *Z* isomer), 3.00 (ddt, *J*= 13.3, 9.1, 6.7 Hz, 0.67H, C***H***-6 *Z* isomer), 2.71 (ddt, *J*= 13.2, 9.7, 6.6 Hz, 0.33H, C***H***-6 *E* isomer), 2.40-2.51 (m, 4H, C***H₂***-2, C***H₂***-1), 1.42 (s, 3H, $(CH_3)_3$ *E* isomer), 1.41 (s, 6H, $(CH_3)_3$ *Z* isomer), 1.03 (d, *J*= 6.6 Hz, 2H, (C***H₃***)$_2$-5 *E* isomer), 1.00 (d, *J*= 6.7 Hz, 4H, (C***H₃***)$_2$-5), *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

<u>*Z* Isomer</u>

172.1 (C-1), 145.3 (C-5), 135.4 (C-4), 129.4, 129.1, 128.9, 126.2 (C-ar), 80.2 (C-O), 34.7 (C-2), 32.8 (C-3), 29.4 (C-6), 28.1 ($(CH_3)_3$), 22.7 ($(CH_3)_2$-6).

<u>*E* Isomer</u>

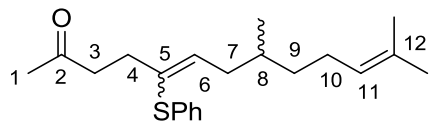
172.2 (C-1), 146.7 (C-5), 135.8 (C-4), 129.7, 129.1, 128.9, 125.9 (C-ar), 80.3 (C-O), 34.6 (C-2), 32.8 (C-3), 28.7 (C-6), 28.0 ($(CH_3)_3$), 22.9 ($(CH_3)_2$-6).

IR (ν, cm^{-1}, CCl_4): 2927, 2857, 1733, 1608, 1585, 1452, 1440, 1233, 1156, 1025.

HRMS (EI): Calcd. for $C_{18}H_{26}O_2S$: 306.1654 Found : 306.1660

[18] Woulfe, S. R., Miller M. J. *J. Org. Chem*. **1986**, *51*, 3133.

8,12-Dimethyl-5-(phenylthio)trideca-5,11-dien-2-one **IV-10g**



$C_{21}H_{30}OS$
M= 330.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11b** (771 mg, 2.0 mmol) and xanthate **IV-4d**[1] (178 mg, 1.0 mmol). The reaction needed 140 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford vinylsulfide **IV-10g** (218 mg, 66%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)
7.17-7.28 (m, 5H, C***H***-ar), 5.97 (t, *J*= 8.0 Hz, 0.33H, C***H***-6 *E* isomer), 5.95 (t, *J*= 7.6 Hz, 0.67H, C***H***-6 *Z* isomer), 5.09 (t, *J*= 6.0 Hz, 1H, C***H***-11), 2.57-2.65 (m, 3H, C***H***-7, C***H$_2$***-3), 2.43-2.47 (m, 2H, C***H$_2$***-4), 1.97-2.06 (m, 2H, C***H$_2$***-10), 1.70-1.79 (m, 1H, C***H***-7), 1.69, 1.60 (s, 6H, (C***H$_3$***)$_2$-9), 1.30-1.43 (m, 3H, C***H$_2$***-9, C***H***-8), 0.91 (d, *J*= 6.7 Hz, 2H, C***H$_3$***-5), 0.86 (d, *J*= 6.5 Hz, 1H, C***H$_3$***-8).

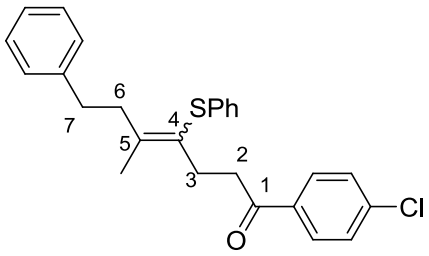
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)
<u>*Z* isomer :</u>
208.0 (C-2), 136.9 (C-6), 135.0 (C-5), 132.4 (C-12), 131.2, 129.3, 128.9, 126.0 (C-ar), 124.7 (C-11), 42.7 (C-3), 37.0 (C-9), 36.8 (C-7), 32.9 (C-3), 30.0 (C-1), 26.7 (C-8), 24.6 (CH_3-12), 22.7 (C-10), 19.6 (CH_3-8), 17.7 (CH_3-12).

<u>*E* isomer :</u>
207.9 (C-2), 137.9 (C-6), 135.4 (C-5), 132.4 (C-12), 131.2, 129.3, 129.0, 126.4 (C-ar), 124.6 (C-11), 42.2 (C-3), 36.7 (C-9), 36.3 (C-7), 34.3 (C-3), 29.9 (C-1), 25.6 (C-8), 25.2 (CH_3-12), 21.0 (C-10), 19.6 (CH_3-8), 17.7 (CH_3-12).

IR (ν, cm^{-1}, CCl_4)
3075, 2958, 2856, 1774, 1720, 1607, 1584, 1478, 1449, 1377, 1359, 1326, 1292, 1231, 1219, 1160, 1103.

HRMS (EI) Calcd. for $C_{21}H_{30}OS$: 330.2017 Found : 330.2015

1-(4-Chlorophenyl)-5-methyl-7-phenyl-4-(phenylthio)hept-4-en-1-one IV-10h



$C_{26}H_{25}ClOS$
M= 421.0 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11d** (759 mg, 2.0 mmol) and xanthate **IV-4b**[4] (178 mg, 1.0 mmol). The reaction needed 120 mol% of DLP to go to completion (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford vinylsulfide **IV-10h** (265 mg, 63%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

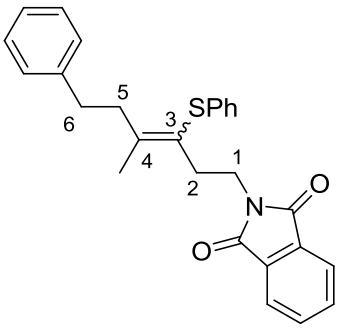
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.82 (d, *J*= 8.6 Hz, 1.33H, C***H***-ar *Z* isomer), 7.76 (d, *J*= 8.6 Hz, 0.67H, C***H***-ar *E* isomer), 7.39 (d, *J*= 8.6 Hz, 1.33H, C***H***-ar *Z* isomer), 7.37 (d, *J*= 8.6 Hz, 0.67H, C***H***-ar *E* isomer), 7.05-7.28 (m, 10H, C***H***-ar), 3.08 (dd, *J*= 8.4, 7.0 Hz, 1.33H, C***H$_2$***-2 *Z* isomer), 2.42-2.90 (m, 6.67H, C***H$_2$***-2 *E* isomer, C***H$_2$***-6, C***H$_2$***-7, C***H$_2$***-3), 2.09 (s, 1H, C***H$_3$***-C5 *E* isomer), 1.97 (s, 2H, C***H$_3$***-C5 *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 198.5, 198.5 (C-1), 144.6, 144.5, 141.6, 141.2, 139.3, 139.3, 136.3, 136.3, 135.1, 135.1, 129.5, 129.5, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.8, 126.0, 125.9, 125.6, 125.4 (C-ar, C-4, C-5), 39.0, 37.9 (C-2), 37.6, 36.8 (C-6), 34.7, 34.3 (C-5), 27.9, 27.6 (C-3), 19.3, 21.2 (CH_3-5).

IR (ν, cm^{-1}, CCl_4): 3064, 3029, 2928, 2856, 1774, 1689, 1589, 1449, 1441, 1231, 1093, 1014.

HRMS (EI): Calcd. for $C_{26}H_{25}ClOS$: 420.1315 Found : 420.1300

2-(4-Methyl-6-phenyl-3-(phenylthio)hex-3-enyl)isoindoline-1,3-dione IV-10i

	$C_{27}H_{25}NO_2S$ M= 427.6 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11d** (759 mg, 2.0 mmol) and xanthate **IV-4c**[5] (281 mg, 1.0 mmol). The reaction needed 120 mol% of DLP to go to completion (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 1:9) to afford vinylsulfide **IV-10i** (334 mg, 74%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.80-7.83 (m, 2H, C***H***-ar), 7.67-7.71 (m, 2H, C***H***-ar), 7.01-7.32 (m, 10H, C***H***-ar), 3.85 (t, *J*= 7.5 Hz, 1.33H, C***H*****$_2$**-1 *Z* isomer), 3.77 (t, *J*= 7.5 Hz, 0.67H, C***H*****$_2$**-1 *E* isomer), 2.81 (t, *J*= 7.6 Hz, 0.67H, C***H*****$_2$**-6 *E* isomer), 2.72-2.77 (m, 1.33H, C***H*****$_2$**-6 *Z* isomer), 2.65-2.68 (m, 2H, C***H*****$_2$**-5 *Z* isomer), 2.58-2.62 (m, 2H, C***H*****$_2$**-5 *E* isomer, C***H*****$_2$**-2 *Z* isomer), 2.48 (t, *J*= 7.5 Hz, 0.67H, C***H*****$_2$**-2 *E* isomer), 2.05 (s, 1H, C***H*****$_3$**-4 *E* isomer), 1.90 (s, 2H, C***H*****$_3$**-4 *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

<u>*Z* isomer</u>

168.2 (C=O), 145.8, 136.3, 133.8, 132.1, 128.9, 128.8, 128.4, 128.3, 125.8, 125.7, 123.1 (C-ar), 141.7 (C-3), 124.0 (C-4), 39.1 (C-1), 36.7 (C-6), 34.7 (C-5), 31.9 (C-2), 22.7 (CH_3-6).

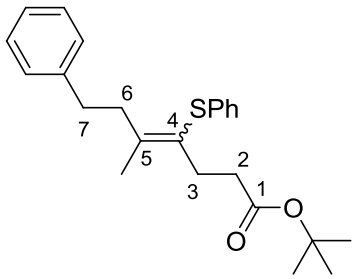
<u>*E* isomer</u>

168.2 (C=O), 145.8, 136.3, 133.8, 132.1, 128.8, 128.6, 128.4, 128.3, 126.0, 125.4, 123.1 (C-ar), 141.1 (C-3), 124.2 (C-4), 37.1 (C-1), 36.4 (C-6), 34.3 (C-5), 31.9 (C-2), 21.0 (CH_3-6).

IR (ν, cm^{-1}, CCl_4): 3064, 3029, 2928, 2856, 1775, 1718, 1615, 1604, 1583, 1468, 1454, 1439, 1393, 1358, 1120.

HRMS (EI): Calcd. for $C_{27}H_{25}NO_2S$: 427.1606 Found : 427.1611

tert-Butyl 5-methyl-7-phenyl-4-(phenylthio)hept-4-enoate **IV-10j**



$C_{24}H_{30}O_2S$
M= 382.6 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-11d** (759 mg, 2.0 mmol) and xanthate **IV-4d**[18] (236 mg, 1.0 mmol). The reaction needed 120 mol% of DLP to go to completion (6 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 1:9) to afford vinylsulfide **IV-10j** (230 mg, 60%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.02-7.33 (m, 10H, C***H***-ar), 2.81-2.84 (m, 0.67H, C***H*****$_2$**-7 *E* isomer), 2.68-2.78 (m, 2.67H, C***H*****$_2$**-7 *Z* isomer, C***H*****$_2$**-6 *Z* isomer), 2.59-2.63 (m, 0.67H, C***H*****$_2$**-6 *E* isomer), 2.49-2.52 (m, 1.33H, C***H*****$_2$**-3 *Z* isomer), 2.36-2.44 (m, 2H, C***H*****$_2$**-3 *E* isomer, C***H*****$_2$**-2 *Z* isomer), 2.24-2.28 (m, 0.67H, C***H*****$_2$**-2 *E* isomer), 2.03 (s, 1H, C***H*****$_3$**-5 *E* isomer), 1.95 (s, 2H, C***H*****$_3$**-5 *Z* isomer), 1.41 (s, 6H, (C***H*****$_3$**)$_3$ *Z* isomer), 1.40 (s, 3H, (C***H*****$_3$**)$_3$ *E* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

<u>*Z* isomer</u>

172.5 (C-1), 144.7, 136.6, 128.8, 128.4, 128.3, 128.2, 125.9, 125.4, (C-ar), 141.7 (C-4), 126.1 (C-5), 80.1 (C-O), 39.1 (C-7), 34.8 (C-6), 34.5 (C-2), 28.7 (C-3), 28.1 ((CH_3)$_3$), 19.3 (CH_3-5).

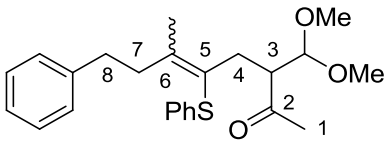
<u>*E* isomer</u>

172.4 (C-1), 144.5, 136.7, 128.8, 128.5, 128.4, 127.6, 126.0, 125.2 (C-ar), 141.3 (C-4), 128.1 (C-5), 80.1 (C-O), 36.8 (C-7), 34.7 (C-6), 34.4 (C-2), 28.6 (C-3), 28.1 ((CH_3)$_3$), 21.2 (CH_3-5).

IR (ν, cm^{-1}, CCl_4): 3060, 3020, 2928, 2856, 1731, 1610, 1583, 1441, 1231, 1150, 1024.

HRMS (EI): Calcd. for $C_{24}H_{30}O_2S$: 382.1967 Found : 382.1973

3-(Dimethoxymethyl)-6-methyl-8-phenyl-5-(phenylthio)oct-5-en-2-one IV-10k

	$C_{24}H_{30}O_3S$ M= 398.6 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using the olefin **IV-11d** (759 mg, 2.0 mmol) and the xanthate **IV-4e**[19] (252 mg, 1.0 mmol). The reaction needed 140 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 1:9) to afford vinylsulfide **IV-10k** (298 mg, 78%) as a colorless oil and as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the (*Z*) isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.11-7.33 (m, 10H, C***H***-ar), 4.30 (d, *J*= 8.0 Hz, 0.67H, C***H***-C3 *Z* isomer), 4.29 (d, *J*= 7.0 Hz, 0.33H, C***H***-C3 *E* isomer), 3.31-3.38 (m, 1H, C***H***-3), 3.25 (s, 3H, OCH_3), 2.71 (s, 1H, OCH_3 *E* isomer), 2.70 (s, 2H, OCH_3 *Z* isomer), 2.63-2.86 (m, 4.67 H, C$\boldsymbol{H_2}$-8, C***H***-4, C$\boldsymbol{H_2}$-7 *Z* isomer, C***H***-7 *E* isomer), 2.44-2.51 (m, 0.33H, C***H***-7 *E* isomer), 2.26 (dd, *J*= 14.4, 4.0 Hz, 0.67H, C***H***-4 *Z* isomer), 2.13-2.17 (m, 0.33H, C***H***-4 *E* isomer), 2.13 (s, 1H, C$\boldsymbol{H_3}$-1 *E* isomer), 2.12 (s, 2H, C$\boldsymbol{H_3}$-1 *Z* isomer), 2.04 (s, 1H, C$\boldsymbol{H_3}$-6 *E* isomer), 1.92 (s, 2H, C$\boldsymbol{H_3}$-6 *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 209.8, 209.7 (C-2), 145.5, 145.3, 135.8, 135.8, 128.9, 128.8, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 1260.0, 125.8, 125.7, 125.5 (C-ar), 141.5, 141.3 (C-5), 124.5, 124.4 (C-6), 104.8 (***C***H$(OCH_3)_2$), 55.5, 55.4, 52.2, 52.8 ($(OCH_3)_2$), 39.1, 36.5 (C-8), 34.8, 34.1 (C-6), 32.9, 32.8 (C-4), 30.5 (C-1), 21.3, 19.5 (C-6).

IR (ν, cm^{-1}, CCl_4) 3064, 3043, 2932, 2860, 2834, 1716, 1583, 1558, 1478, 1440, 1354, 1119, 1060.

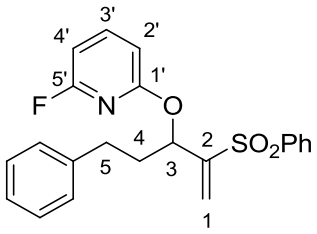
HRMS (EI) Calcd. for $C_{24}H_{30}O_3S$: 398.1916 Found : 398.1911

[19] El Qacemi, M. ; Ricard, L.; Zard, S. Z. *Chem. Commun.* **2006**, 4422.

GENERAL PROCEDURE IV-D : OXIDATION OF VINYLSULFIDES

To a stirred solution of the vinylsulfide **IV-11** (1.0 equiv) in CH_2Cl_2 (10 mL/mmol of vinysulfure) at 0 °C, was added in small portions 70% ***m*-CPBA** (2.5 equiv) and the reaction was stirred overnight at 20 °C. It was then filtered and diluted with CH_2Cl_2. The solution was washed twice with a 10% $Na_2S_2O_3$ and a saturated aqueous $NaHCO_3$ then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding vinylsulfone.

2-Fluoro-6-(5-phenyl-2-(phenylsulfonyl)pent-1-en-3-yloxy)pyridine **IV-15a**

	$C_{22}H_{20}FNO_3S$ M= 397.5 g.mol^{-1}

Vinylsulfide **IV-11ca** (5.75 g, 15.7 mmol) was oxidized following general procedure **IV-D** using 70% *m*-CPBA (6.78 g, 39.3 mmol), giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford sulfone **IV-15a** (5.55 g, 83%) as a colorless oil which solidified upon standing.

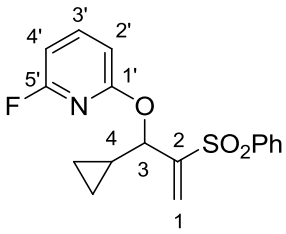
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.77-7.79 (m, 2H, C***H***-ar), 7.43-7.60 (m, 4H, C***H***-ar, C***H***-3'), 7.20-7.27 (m, 3H, C***H***-ar), 7.12-7.14 (m, 2H, C***H***-ar), 6.49 (s, 1H, C***H***-1), 6.40 (dd, *J*= 7.9, 1.2 Hz, 1H, C***H***-2'), 6.35 (dd, *J*= 7.8, 2.5 Hz, 1H, C***H***-4'), 6.07 (s, 1H, C***H***-1), 5.53 (m, 1H, C***H***-3), 2.78 (ddd, *J*= 14.0, 9.6, 5.0 Hz, 1H, C***H***-5), 2.69 (ddd, *J*= 14.0, 9.2, 7.3 Hz, 1H, C***H***-5), 2.37-2.46 (m, 1H, C***H***-4), 2.21 (dtd, *J*= 14.0, 9.4, 5.0 Hz, 1H, C***H***-4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 161.6 (d, *J*= 242.4 Hz, C-5'), 161.0 (d, *J*= 13.5 Hz, C-1'), 150.5 (C-2), 142.7 (d, *J*= 7.8 Hz, C-3'), 140.8, 139.1, 133.4, 129.0, 128.6, 128.4, 128.4, 126.0 (C-ar), 125.5 (C-1), 106.9 (d, *J*= 5.2 Hz, C-2'), 100.9 (d, *J*= 35.3 Hz, C-4'), 71.8 (C-3), 36.7 (C-4), 31.6 (C-5).

IR (ν, cm^{-1}, CCl_4) 3067, 3029, 2930, 2863, 1614, 1578, 1497, 1451, 1322, 1274, 1232, 1232, 1142, 1084.

HRMS (EI) Calcd. for $C_{22}H_{20}FNO_3S$: 397.1148 Found : 397.1152

2-Fluoro-6-(1-cyclopropyl-2-(phenylsulfonyl)allyloxy)pyridine **IV-15b**

	$C_{17}H_{16}FNO_3S$ M= 333.4 g.mol^{-1}

Vinylsulfide **IV-11c** (4.0 g, 13.3 mmol) was oxidized following general procedure **IV-D** using 70% *m*-CPBA (8.2 g, 33.2 mmol), giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford sulfone **IV-15b** (4.0 g, 91%) as a colorless oil which solidified upon standing.

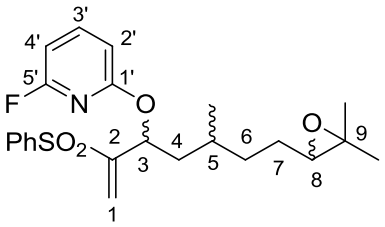
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.81-7.83 (m, 2H, C***H***-Ar), 7.25-7.33 (m, 4H, C***H***-ar, C***H***-3'), 6.58 (s, 1H, C***H***-1), 6.35 (dd, *J*= 7.8, 2.5 Hz, 1H, C***H***-2'), 6.27 (s, 1H, C***H***-1), 6.22 (dd, *J*= 7.9, 1.3 Hz, 1H, C***H***-4'), 5.31 (d, *J*= 8.6 Hz, 1H, C***H***-3), 1.37-1.45 (m, 1H, C***H***-4), 0.56-0.62 (m, 3H, C***H*$_2$**-C4, C***H***-C4), 0.40-0.43 (m, 1H, C***H***-C4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 161.4 (d, *J*= 236.4 Hz, C-5'), 160.9 (d, *J*= 13.3 Hz, C-1'), 150. 3 (C-2), 142.6 (d, *J*= 7.9 Hz, C-3'), 139.8, 133.2, 128.8, 128.1 (C-ar), 127.2 (C-1), 107.1 (d, *J*= 5.1 Hz, C-2'), 100.6 (d, *J*= 35.3 Hz, C-4'), 75.1 (C-3), 15.2 (C-4), 4.4, 3.3 ((***C***H$_2$)$_2$-4).

IR (ν, cm^{-1}, CCl_4) 3071, 3013, 2959, 1614, 1576, 1444, 1324, 1232, 1158, 1147, 1030, 1018.

HRMS (EI) Calcd. for $C_{17}H_{16}FNO_3S$: 333.0835 Found : 333.0840

2-Fluoro-6-(7-(3,3-dimethyloxiran-2-yl)-5-methyl-2-(phenylsulfonyl)hept-1-en-3-yloxy)pyridine **IV-15c**



$C_{23}H_{28}FNO_4S$
M= 433.5 g.mol^{-1}

To a stirred solution of vinylsulfide **IV-11d** (3.9 g, 10 mmol) in CH_2Cl_2 (100 mL) at 0 °C, was added in small portions 70% *m*-CPBA (8.6 g, 35 mmol, 3.5 equiv) and the reaction was stirred overnight at 20 °C. The reaction mixture was diluted with CH_2Cl_2 and filtered. The solution was washed twice with a 10% aqueous $Na_2S_2O_3$, once with a saturated aqueous $NaHCO_3$ then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford vinylsulfone **IV-15c** (3.3 g, 76%) as a colorless oil which solidified upon standing as a mixture of 4 diastereomers.

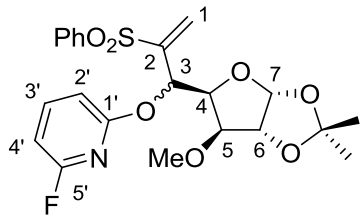
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.87-7.91 (m, 2H, C***H***-ar), 7.46-7.59 (m, 4H, C***H***-ar, C***H***-3'), 6.47, 6.45, 6.43 (s, 1H, C***H***-1), 6.38-6.41 (m, 1H, C***H***-2'), 6.31-6.34 (m, 1H, C***H***-4'), 6.10, 6.08, 6.06 (s, 1H, C***H***-1), 5.64-5.73 (m, 1H, C***H***-3), 2.62-2.69 (m, 1H, C***H***-8), 1.23-2.04 (m, 7H, C***H$_2$***-4, C***H***-5, C***H$_2$***-6, C***H$_2$***-7), 1.29, 1.28, 1.26, 1.25, 1.24, 1.22 (s, 6H, (C***H$_3$***)$_2$-9), 0.92-0.95 (m, 3H, C***H$_3$***-5).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 161.6 (d, *J*= 242.3 Hz, C-5'), 161.0 (d, *J*= 13.4 Hz, C-1'), 160.9 (d, *J*= 13.4 Hz, C-1'), 160.9 (d, *J*= 13.4 Hz, C-1'), 151.5, 151.5, 151.1, 151.0 (C-2), 142.7 (d, *J*= 7.9 Hz, C-3'), 142.7 (d, *J*= 7.8 Hz, C-3'), 139.3, 139.2, 139.2, 139.2, 133.5, 133.5, 129.0, 129.0, 128.2, 128.2 (C-Ar), 125.7, 125.7, 125.2, 125.1 (C-1), 107.0 (d, *J*= 5.2 Hz, C-2'), 107.0 (d, *J*= 5.4 Hz, C-2'), 101.0 (d, *J*= 35.7 Hz, C-4'), 100.8 (d, *J*= 35.3 Hz, C-4'), 100.8 (d, *J*= 35.2 Hz, C-4'), 70.8, 79.5, 70.5 (C-3), 64.5, 64.4, 64.4, 64.4 (C-8), 58.3, 58.3, 58.2, 58.1 (C-9), 42.9, 42.8, 42.5, 42.3 (C-4), 33.8, 33.8, 32.4, 32.4 (C-6), 29.7, 29.6, 29.5, 29.4 (C-5), 26.3, 26.0, 25.9 (C-7), 24.9, 24.9, 24.8, 24.8 (CH_3-9), 19.9, 19.8 (CH_3-5), 18.9, 18.7, 18.6, 18.6 (CH_3-9).

IR (ν, cm^{-1}, CCl_4) 3070, 2962, 928, 2874, 1614, 1575, 1444, 1378, 1322, 1274, 1018.

HRMS (EI) Calcd. for $C_{23}H_{28}FNO_4S$: 433.1723 Found : 433.1719

2-Fluoro-6-(1-((3a*R*,5*S*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydro furo [3,2-d][1,3]dioxol-5-yl)-2-(phenylsulfonyl)allyloxy)pyridine **IV-15d**

	$C_{22}H_{24}FNO_7S$ M= 465.5 g.mol^{-1}

Vinylsulfide **IV-11e** (1.75 g, 4.0 mmol) was oxidized following general procedure **IV-D** giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 7:3) to afford sulfone **IV-15d** (1.58 g, 85%) as two colorless oils which solidified upon standing. 590 mg of the less polar diastereomer and 990 mg of a mixture (3:1) of the two diastereomers were obtained.

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz)

Major diastereomer

7.75-7.77 (m, 2H, C***H***-ar), 7.29-7.45 (m, 4H,C***H***-ar, C***H***-3'), 6.79 (s, 1H, C***H***-1), 6.43 (s, 1H, C***H***-1), 6.28 (dd, *J*= 7.8, 2.5 Hz, 1H, C***H***-2'), 6.05 (d, *J*= 8.0 Hz, 1H, C***H***-3), 5.97 (dd, *J*= 8.0, 1.4 Hz, 1H, C***H***-4'), 5.95 (d, *J*= 4.0 Hz, 1H, C***H***-7), 5.05 (dd, *J*= 8.1, 3.7 Hz, 1H, C***H***-4), 4.59 (d, *J*= 4.0 Hz, 1H, C***H***-6), 3.87 (d, *J*= 3.7 Hz, 1H, C***H***-5), 3.31 (s, 3H, OC***H$_3$***), 1.58, 1.34 (s, 6H, (C***H$_3$***)$_2$).

Minor diastereomer

7.75-7.79 (m, 2H, C***H***-ar), 7.29-7.44 (m, 4H, C***H***-ar, C***H***-3'), 6.71 (s, 1H, C***H***-1), 6.38 (s, 1H, C***H***-1), 6.33 (dd, *J*= 7.8, 2.5 Hz, 1H, C***H***-2'), 6.15 (dd, *J*= 8.0, 0.9 Hz, 1H, C***H***-4'), 5.96 (d, *J*= 9.4 Hz, 1H, C***H***-3), 5.83 (d, 1H, *J*= 3.6 Hz, C***H***-7), 4.87 (dd, *J*= 9.4, 3.2 Hz, 1H, C***H***-4), 4.52 (d, *J*= 3.6 Hz, 1H, C***H***-6), 3.77 (d, *J*= 3.2 Hz, 1H, C***H***-5), 3.10 (s, 3H, OC***H$_3$***), 1.54, 1.32 (s, 6H, (C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz)

Major diastereomer

161.3 (d, *J*= 241.1 Hz, C-5'), 160.6 (d, *J*= 11.5 Hz, C-1'), 145.6 (C-2), 142.2 (d, *J*= 7.8 Hz, C-3'), 140.3, 133.0, 128.7, 128.0 (C-ar), 132.6 (C-1), 112.3 (***C***-(CH$_3$)$_2$), 107.2 (d, *J*= 5.1 Hz, C-2'), 105.4 (C-7), 100.5 (d, *J*= 35.5 Hz, C-4'), 84.0 (C-5), 81.9 (C-6), 80.0 (C-4), 73.7 (C-3), 57.5 (OCH$_3$), 27.1, 26.6 ((CH$_3$)$_2$).

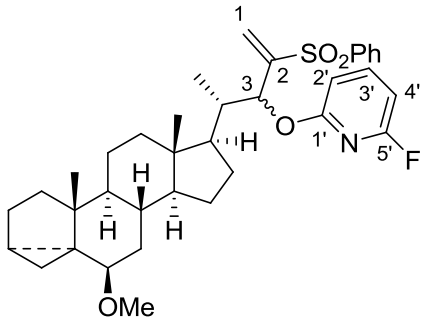
Minor diastereomer

161.4 (d, *J*= 241.7 Hz, C-5'), 160.5 (d, *J*= 11.7 Hz, C-1'), 145.9 (C-2), 142.5 (d, *J*= 7.8 Hz, C-3'), 140.6, 132.7, 128.5, 127.9 (C-ar), 131.8 (C-1), 112.4 (***C***-(CH$_3$)$_2$), 106.6 (d, *J*= 5.1 Hz, C-2'), 105.3 (C-7), 100.9 (d, *J*= 35.4 Hz, C-4'), 83.2 (C-5), 81.7 (C-6), 79.8 (C-4), 71.7 (C-3), 57.7 (OCH$_3$), 27.0, 26.6 ((CH$_3$)$_2$).

IR (ν, cm^{-1}, CCl_4) 3070, 2990, 2933, 2832, 1618, 1577, 1444, 1383, 1373, 1323, 1232, 1147, 1086, 1029.

HRMS (EI) Calcd. for $C_{22}H_{24}FNO_7S$: 465.1258 Found : 465.1269

2-Fluoro-6-(((*S*)-4-((2a*R*,4a*R*,4b*S*,6a*S*,7*R*,9a*S*,9b*S*,11*R*,11a*R*)-11-methoxy-4a,6a dimethylhexadecahydrocyclopenta[*a*]cyclopropa[2,3] cyclopenta[1,2-*f*]naphthalen-7-yl)- 2-(phenylsulfonyl)pent-1-en-3-yloxy) pyridine **IV-15e**



$C_{36}H_{46}FNO_4S$
M= 607.8 g.mol^{-1}

Vinylsulfide **IV-11e** (1.00 g, 1.74 mmol) was oxidized following general procedure **IV-D** giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 8:2) to afford sulfone **IV-15e** (813 mg, 77%) as a 4:1 mixture of epimers at C3 and as a solid.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.98-7.98 (m, 1.6H, C***H***-ar dia1), 7.87-7.88 (m, 0.4H, C***H***-ar dia2), 7.35-7.64 (m, 4H, C***H***-ar, C***H***-3'), 6.51 (s, 0.2H, C***H***-1 dia2), 6.50 (d, *J*= 8.1 Hz, 0.8H, C***H***-2' dia1), 6.43 (s, 0.8H, C***H***-1 dia1), 6.31 (dd, *J*= 7.8, 2.3 Hz, 1H, C***H***-4'), 6.23 (d, *J*= 7.6 Hz, 0.2H, C***H***-2' dia2), 6.17 (s, 0.2H, C***H***-1 dia2), 5.83 (s, 0.8H, C***H***-1 dia1), 5.73 (d, *J*= 4.5 Hz, 0.2H, C***H***-3 dia2), 5.65 (s, 0.8H, C***H***-3 dia1), 3.29 (s, 3H), 2.74 (brs, 0.2H), 2.72 (brs, 0.8H), 2.24-2.27 (m, 0.2H), 2.03-2.07 (m, 0.8H), 1.81-1.94 (m, 2H), 1.65-1.75 (m, 3H), 1.34-1.54 (m, 7H), 1.06-1.18 (m, 3H), 0.99 (s, 3H), 0.94 (d, *J*= 6.8 Hz, 3H), 0.74-0.86 (m, 4H), 0.72 (s, 0.6H, CH_3 dia2), 0.71 (s, 2.4H, CH_3 dia1), 0.60-0.62 (m, 1H), 0.39 (dd, *J*= 7.8, 5.0 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

Major diastereomer 1

161.6 (d, *J*= 242.4 Hz, C-1'), 161.2 (d, *J*= 13.4 Hz, C-5'), 149.0 (C-2), 142.7 (d, *J*= 7.9 Hz, C-3'), 139.3, 133.5, 129.0, 128.2 (C-ar), 125.8 (C-1), 106.7 (d, *J*= 5.1 Hz, C-2'), 100.7 (d, *J*= 35.4 Hz, C-4'), 82.2, 74.3, 56.4, 56.3, 52.5, 47.9, 43.2, 42.6, 39.9, 38.2, 35.1, 34.9, 33.2, 30.4, 27.4, 24.8, 23.9, 22.7, 21.3, 19.2, 13.0, 12.1, 11.6.

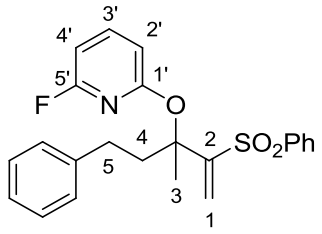
Minor diastereomer 2

161.5 (d, *J*= 241.3 Hz, C-1'), 160.8 (d, *J*= 13.2 Hz, C-5'), 149.2 (C-2), 142.5 (d, *J*= 8.0 Hz, C-3'), 139.7, 133.0, 128.7, 128.0 (C-ar), 125.8 (C-1), 107.0 (d, *J*= 5.1 Hz, C-2'), 100.4 (d, *J*= 36.7 Hz, C-4'), 82.2, 75.6, 56.4, 55.8, 52.6, 47.8, 43.4, 40.2, 40.0, 38.2, 35.1, 34.9, 33.2, 30.4, 28.9, 27.5, 24.4, 22.5, 21.3, 19.2, 15.8, 12.0, 11.3.

IR (ν, cm^{-1}, CCl_4) 3063, 2945, 2870, 2849, 2819, 1616, 1576, 1443, 1383, 1323, 1232, 1178, 1141, 1099, 1981, 1021, 958.

HRMS (EI) Calcd. for $C_{36}H_{46}FNO_4S$: 607.3132 Found : 607.3130

2-Fluoro-6-(3-methyl-5-phenyl-2-(phenylsulfonyl)pent-1-en-3-yloxy)pyridine **IV-15f**



$C_{23}H_{22}FNO_3S$
M= 411.5 g.mol^{-1}

Vinylsulfide **IV-11g** (3.04 g, 8.0 mmol) was oxidized following general procedure **IV-D** using 70% *m*-CPBA (4.8 g, 20 mmol), giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford sulfone **IV-15f** (2.83 g, 86%) as a colorless oil which solidified upon standing.

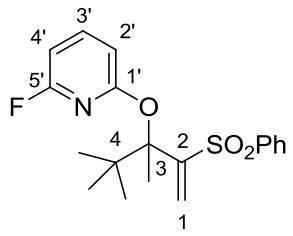
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.88-7.90 (m, 2H, C***H***-ar), 7.51 (dd, *J*= 7.9, 7.8 Hz, 1H, C***H***-3'), 7.42-7.50 (m, 3H, C***H***-ar), 7.14-7.28 (m, 5H, C***H***-ar), 6.74 (s, 1H, C***H***-1), 6.39 (dd, *J*= 7.9, 1.2 Hz, 1H, C***H***-2'), 6.35 (d, *J*= 7.8, 2.6 Hz, 1H, C***H***-4'), 6.12 (s, 1H, C***H***-1), 2.41-2.74 (m, 4H, C***H$_2$***-5, C***H$_2$***-4), 1.73 (s, 3H, C***H$_3$***-3).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 160.9 (d, *J*= 240.5 Hz, C-5'), 160.6 (d, *J*= 14.0 Hz, C-1'), 151.4 (C-2), 142.3 (d, *J*= 7.8 Hz, C-3'), 141.4, 140.6, 132.9, 128.7, 128.4, 128.3, 128.0, 126.5 (C-Ar), 125.8 (C-1), 108.8 (d, *J*= 5.3 Hz, C-2'), 100.6 (d, *J*= 35.6 Hz, C-4'), 82.8 (C-3), 42.9 (C-4), 29.8 (C-5), 24.2 (CH_3-3).

IR (ν, cm^{-1}, CCl_4) 3062, 3020, 2930, 2860, 1612, 1580, 1497, 1451, 1320, 1274, 1232, 1080.

HRMS (EI) Calcd. for $C_{23}H_{22}FNO_3S$: 411.1304 Found : 411.1308

2-Fluoro-6-(3,4,4-trimethyl-2-(phenylsulfonyl)pent-1-en-3-yloxy)pyridine **IV-15g**

	$C_{19}H_{22}FNO_3S$ M= 363.4 g.mol^{-1}

Vinylsulfide **IV-11h** (3.3 g, 10 mmol) was transformed following general procedure **IV-D** using 70% *m*-CPBA (6.0 g, 25 mmol), giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ether 85:15) to afford sulfone **IV-15g** (2.94 g, 81%) as a colorless oil which solidified upon standing.

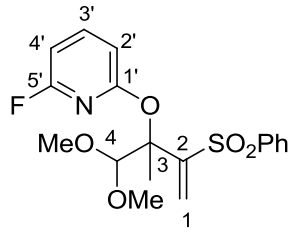
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.97-8.00 (m, 2H, C***H***-Ar),), 7.50-7.61 (m, 4H, C***H***-Ar, C***H***-3'), 6.58 (s, 1H, C***H***-1), 6.53 (d, *J*= 7.9 Hz, 1H, C***H***-2'), 6.30 (dd, *J*= 7.7, 2.2 Hz, 1H, C***H***-4'), 6.00 (s, 1H, C***H***-1), 1.86 (s, 3H, C***H*****$_3$**-3), 1.18 (s, 9H, (C***H*****$_3$)$_3$**-C4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 160.9 (d, *J*= 241.1 Hz, C-5'), 160.6 (d, *J*= 14.1 Hz, C-1'), 151.4 (C-2), 142.2 (d, *J*= 7.9 Hz, C-3'), 142.0, 132.7, 128.8, 128.0 (C-Ar), 132.3 (C-1), 108.9 (d, *J*= 5.2 Hz, C-4'), 100.3 (d, *J*= 35.5 Hz, C-2'), 87.0 (C-3), 40.6 (C-4), 25.3 ($(CH_3)_3$-4), 18.4 (CH_3-3).

IR (ν, cm^{-1}, CCl_4) 3068, 2928, 2856, 1634, 1618, 1574, 1538, 1483, 1464, 1446, 1320, 1234, 1144, 1073, 1016.

HRMS (EI) Calcd. for $C_{19}H_{22}FNO_3S$: 363.1304 Found : 363.1319

2-Fluoro-6-(1,1-dimethoxy-3-(phenylsulfonyl)but-3-en-2-yloxy) pyridine **IV-15h**

	$C_{18}H_{20}FNO_5S$ M= 381.4 g.mol^{-1}

Vinylsulfide **IV-11j** (3.49 g, 10 mmol) was transformed following general procedure **IV-D** using 70% *m*-CPBA (6.0 g, 25 mmol), giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ether 85:15) to afford sulfone **IV-15h** (2.94 g, 77%) as a white solid.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.72-7.74 (m, 2H, C***H***-Ar), 7.36 (dd, *J*= 8.0, 7.7 Hz, 1H, C***H***-3'), 7.18-7.27 (m, 3H, C***H***-ar), 6.81 (s, 1H, C***H***-1), 6.28 (d, *J*= 8.0 Hz, 1H, C***H***-2'), 6.25 (s, 1H, C***H***-1), 6.20 (dd, *J*= 7.8, 2.1 Hz, 1H, C***H***-4'), 5.13 (s, 1H, C***H***-4), 3.65, 3.49 (s, 6H, (OC***H*****$_3$**$)_2$), 1.70 (s, 3H, C***H*****$_3$**-3).

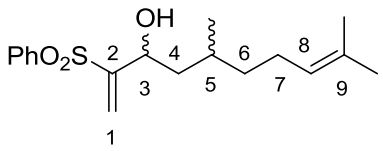
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 160.6 (d, *J*= 236.5 Hz, C-5'), 160.3 (d, *J*= 14.2 Hz, C-1'), 149.8 (C-2), 142.0 (d, *J*= 8.0 Hz, C-3'), 140.1, 132.5, 128.2, 128.2 (C-Ar), 130.8 (C-1), 109.0 (d, *J*= 5.3 Hz, C-2'), 107.0 (C-4), 100.7 (d, *J*= 35.7 Hz, C-4'), 84.6 (C-3), 59.3, 57.3 ($(OCH_3)_2$), 17.3 (CH_3-3).

IR (ν, cm^{-1}, CCl_4): 3070, 2998, 2955, 2937, 2911, 2837, 1617, 1603, 1575, 1446, 1439, 1316, 1232, 1154, 1120, 1088, 1023.

HRMS (EI): Calcd for $C_{18}H_{20}FNO_5S$: 381.1046 Found : 381.1040

MP: 88-89 °C

5,9-Dimethyl-2-(phenylsulfonyl)deca-1,8-dien-3-ol[20] **IV-18**

	$C_{18}H_{26}O_3S$ M= 322.4 g.mol^{-1}

To a solution of phenyl vinyl sulfone (1.70 g, 10 mmol) and (±)-citronellal (7.71 g, 50 mmol, 5.0 equiv) was added DABCO (1.12 g, 10 mmol, 1.0 equiv). The solution was stirred at 20 °C for 6 weeks. The mixture was quenched with a saturated aqueous NH_4Cl solution, and the aqueous phase was then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was then purified by flash chromatography on silica gel (petroleum ether/AcOEt 8:2) to afford the alcohol **IV-18** (2.22 g, 69%) as a mixture of two diastereomers in a 1:1 ratio and as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.86-7.88 (m, 2H, C***H***-Ar), 7.52-7.64 (m, 3H, ***H***-Ar), 6.42, 6.41 (s, 1H, C***H***-1), 6.10, 6.07 (s, 1H, C***H***-1), 4.98-5.00 (m, 1H, C***H***-8), 4.39-4.44 (m, 1H, C***H***-3) 2.53-2.61 (m, 1H, OH), 1.83-1.93 (m, 2H, C***H$_2$***-7), 1.66, 1.64, (s, 3H, C***H$_3$***-9), 1.56, 1.55(s, 3H, C***H$_3$***-9), 1.40-1.47 (m, 2H, C***H$_2$***-4), 0.93-1.27 (m, 3H, C***H$_2$***-6, C***H***-5), 0.79 (d, *J*= 6.5 Hz , 1.5H, C***H$_3$***-5), 0.72 (d, *J*=6.3 Hz , 1.5H, C***H$_3$***-5).

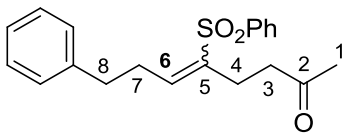
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 153.9, 153.3 (C-2), 139.1, 139.0, 133.7, 129.2, 128.1, 128.1 (C-ar), 131.3, 131.2 (C-9), 124.7, 124.5 (C-1), 124.4 (C-8), 66.8, 66.5 (C-3), 42.5, 43.0 (C-4), 37.4, 36.1 (C-6), 29.1, 28.8 (C-5), 25.7, 17.6, 17.6 (CH_3-9), 25.2, 25.0 (C-7), 19.7, 18.5 (CH_3-5).

IR (ν, cm^{-1}, CCl_4) 3612, 3534, 3070, 2964, 2915, 2873, 2854, 1447, 1378, 1319, 1307, 1171, 1140, 1081, 1025.

HRMS (EI) Calcd. for $C_{18}H_{26}O_3S$: 322.1603 Found : 322.1600

[20] Weichert, A.; Hoffmann, H. M. R. *J. Org. Chem*. **1991**, *56*, 4098

8-Phenyl-5-(phenylsulfonyl)oct-5-en-2-one **(±)-IV-14a**

	$C_{20}H_{22}O_3S$ M= 342.5 g.mol^{-1}

Following general procedure **IV-D**, the reaction was carried out using vinylsulfide **IV-11a** (155 mg, 0.5 mmol), giving crude sulfone. The residue was purified by silica gel column chromatography (petroleum ether/ether 7:3) to afford the corresponding sulfone **(±)-IV-14a** (146 mg, 85%) as a mixture of *Z/E* isomers in a 2:1 ratio in favor of the *Z* isomer and as a colorless oil which solidified upon standing.

^{1}H NMR (δ, ppm) <u>*Z* isomer</u>

($CDCl_3$, 400 MHz) 6.94-7.81 (m, 10H, C***H***-ar), 6.16 (t, *J*= 7.7 Hz, 1H, C***H***-6), 2.99-3.03 (m, 2H, C***H$_2$***-7), 2.73-2.77 (m, 4H, C***H$_2$***-8, C***H$_2$***-4), 2.54-2.57 (m, 2H, C***H$_2$***-3), 2.12 (s, 3H, C***H$_3$***-1).

<u>*E* isomer</u>

6.94-7.73 (m, 10H, C***H***-ar), 6.94 (t, *J*= 7.7 Hz, 1H, C***H***-6), 2.80-2.83 (m, 2H, C***H$_2$***-7), 2.50-2.55 (m, 2H, C***H$_2$***-8), 2.34-2.39 (m, 2H, C***H$_2$***-3), 2.24-2.28 (m, 2H, C***H$_2$***-4), 2.01 (s, 3H, C***H$_3$***-1).

^{13}C NMR (δ, ppm) <u>*Z* isomer</u>

($CDCl_3$, 100 MHz) 206.3 (C-2), 143.9 (C-6), 141.1, 140.5, 133.2, 129.2, 128.5, 128.5, 127.1, 126.2 (C-ar), 139.6 (C-5), 43.0 (C-3), 35.0 (C-7), 30.1 (C-8), 29.3 (C-1), 27.6 (C-4).

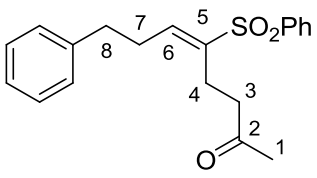
<u>*E* isomer</u>

206.9 (C-2), 142.0 (C-6), 140.5, 140.2, 133.1, 129.1, 128.6, 128.5, 127.9, 126.4 (C-ar), 139.3(C-5), 42.1 (C-3), 34.4 (C-7), 30.3 (C-8), 29.7 (C-1), 20.1 (C-4).

IR (ν, cm^{-1}, CCl_4) 3066, 3029, 2929, 2860, 1720, 1640, 1604, 1586, 1497, 1479, 1447, 1359, 1317, 1148, 1085, 1030.

HRMS (EI) Calcd. for $C_{20}H_{22}O_3S$: 342.1290 Found : 342.1278

(*E*)-8-Phenyl-5-(phenylsulfonyl)oct-5-en-2-one **IV-14a**

	$C_{20}H_{22}O_3S$ M= 342.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15a** (1.6 g, 4.0 mmol) and xanthate **IV-4a**[1] (356 mg, 2.0 mmol). The reaction needed 200 mol% of DLP to go to completion (10 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 30:70) to afford (*E*)-vinylsulfone **IV-14a** (500 mg, 73%) as a colorless oil which solidified upon standing.

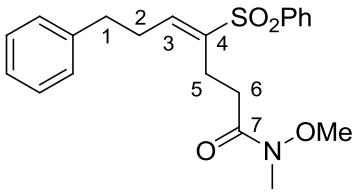
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 6.94-7.73 (m, 10H, C***H***-ar), 6.94 (t, *J*= 7.7 Hz, 1H, C***H***-6), 2.80-2.83 (m, 2H, C***H$_2$***-7), 2.50-2.55 (m, 2H, C***H$_2$***-8), 2.34-2.39 (m, 2H, C***H$_2$***-3), 2.24-2.28 (m, 2H, C***H$_2$***-4), 2.01 (s, 3H, C***H$_3$***-1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 206.9 (C-2), 142.0 (C-6), 140.5, 140.2, 133.1, 129.1, 128.6, 128.5, 127.9, 126.4 (C-ar), 239.3 (C-5), 42.1 (C-3), 34.4 (C-7), 30.3 (C-8), 29.7 (C-1), 20.1 (C-4).

IR (ν, cm^{-1}, CCl_4) 3066, 3029, 2928, 2859, 1720, 1644, 1613, 1576, 1497, 1446, 1359, 1317, 1232, 1148, 1085, 1023.

HRMS (EI) Calcd. for $C_{20}H_{22}O_3S$: 342.1290 Found : 342.1291

(E)-*N*-Methoxy-*N*-methyl-7-phenyl-4-(phenylsulfonyl)hept-4-enamide IV-14b

	$C_{21}H_{25}O_4S$ M= 387.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15a** (790 g, 2.0 mmol) and xanthate **IV-4f**[6] (223 mg, 1.0 mmol). The reaction needed 180 % of DLP to go to completion (9 h). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (10:90, 30:70, 50:50) to afford (*E*)-vinylsulfone **IV-14b** (248 mg, 64%) as a colorless oil which solidified upon standing.

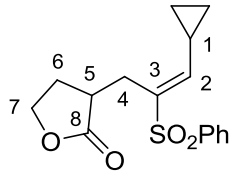
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.71-7.73 (m, 2H, ***H***-ar), 7.45-7.56 (m, 3H, ***H***-ar), 7.12-7.25 (m, 5H, ***H***-ar), 6.97 (t, *J*= 7.6 Hz, 1H, C***H***-3), 3.58 (s, 3H, OC***H$_3$***), 3.11(s, 3H, NC***H$_3$***), 2.86 (t, *J*= 7.3 Hz, 2H, C***H$_2$***-1), 2.54-2.59 (m, 2H, C***H$_2$***-2), 2.45-2.48 (m, 2H, C***H$_2$***-6), 2.36-2.39 (m, 2H, C***H$_2$***-5).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 172.8 (C-7), 142.4, 140.2, 139.5, 129.1, 128.6, 128.4, 127.9, 126.3 (C-ar), 140.5 (C-4), 133.1 (C-3), 61.2 (OCH_3), 34.5 (C-1), 32.2 (NCH_3), 31.1 (C-6), 30.1 (C-2), 21.4 (C-5).

IR (ν, cm^{-1}, CCl_4): 3067, 3029, 2938, 2860, 1669, 1613, 1497, 1446, 1415, 1386, 1316, 1307, 1232, 1178, 1147, 1085.

HRMS (EI): Calcd. for $C_{21}H_{25}O_4S$: 387.1504 Found : 387.1491

(*E*)-3-(3-Cyclopropyl-2-(phenylsulfonyl)allyl)dihydrofuran-2(3H)-one IV-14c

	$C_{16}H_{18}O_4S$ M= 306.4 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15b** (667 mg, 2.0 mmol) and xanthate **IV-4g**[2] (220 mg, 1.0 mmol). The reaction needed 160 mol% of DLP to go to completion (8 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (1:9, 3:7) to afford the corresponding (*E*)-vinylsulfone **IV-14c** (223 mg, 73%) as a colorless oil which solidified upon standing.

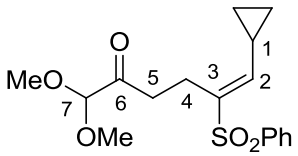
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.83-7.85 (m, 2H, C***H***-ar), 7.52-7.64 (m, 3H, C***H***-ar), 6.41 (d, *J*= 10.9 Hz, 1H, C***H***-2), 4.32-4.34 (m, 1H, C***H***-7), 4.17 (ddd, *J*= 10.6, 9.1, 6.2 Hz, 1H, C***H***-7), 3.08 (tdd, *J*= 11.3, 8.5, 4.3 Hz, 1H, C***H***-5), 2.82 (dd, *J*= 15.2, 4.3 Hz, 1H, C***H***-4), 2.40-2.45 (m, 2H, C***H***-4, C***H***-6), 2.03-2.13 (m, 1H, C***H***-6), 1.57-1.65 (m, 1H, C***H***-1), 1.05-1.10 (m, 2H, C***H$_2$***-C1), 0.72-0.77 (m, 2H, C***H$_2$***-C1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 172.3 (C-8), 149.5 (C-2), 139.3 (C-3), 134.9, 133.3, 129.3, 127.9 (C-ar), 66.6 (C-7), 39.5 (C-5), 28.9 (C-6), 26.8 (C-4), 11.7 (C-1), 9.4, 9.1 ($(CH_2)_2$-1).

IR (ν, cm^{-1}, CCl_4): 3069, 2928, 2856, 1778, 1708, 1615, 1577, 1446, 1372, 1306, 1232, 1149, 1027.

HRMS (EI): Calcd. for $C_{16}H_{18}O_4S$: 306.0929 Found : 306.0935

(*E*)-6-Cyclopropyl-1,1-dimethoxy-5-(phenylsulfonyl)hex-5-en-2-one **IV-14d**



$C_{17}H_{22}O_5S$
M= 338.4 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15b** (667 mg, 2.0 mmol) and xanthate **IV-4h**[8] (238 mg, 1.0 mmol). The reaction needed 180 mol% of DLP to go to completion (9 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 3:7) to afford (*E*)-vinylsulfone **IV-14d** (257 mg, 76%) as a colorless oil which solidified upon standing.

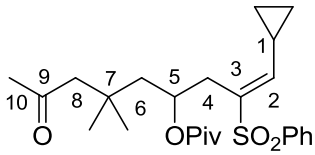
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.81-7.83 (m, 2H, C***H***-ar), 7.51-7.59 (m, 3H, C***H***-ar), 6.29 (d, *J*= 10.8 Hz, 1H, C***H***-2), 4.44 (s, 1H, C***H***-7), 3.37 (s, 6H, (OC***H*****$_3$**)$_2$), 2.79-2.84 (m, 2H, C***H*****$_2$**-5), 2.51-2.55 (m, 2H, C***H*****$_2$**-4), 1.53-1.59 (m, 1H, C***H***-1), 1.00-1.05 (m, 2H, C***H*****$_2$**-1)., 0.70-0.74 (m, 2H, C***H*****$_2$**-1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 204.4 (C-6), 148.1 (C-2), 139.7 (C-3), 136.3, 133.0, 129.1, 127.9 (C-ar), 103.7 (C-7), 54.7 ((OCH$_3$)$_2$), 37.0 (C-5), 19.9 (C-4), 11.4 (C-1), 8.9 ((CH$_2$)$_2$-1).

IR (ν, cm^{-1}, CCl_4) 3069, 3010, 2932, 2856, 2834, 1732, 1639, 1616, 1574, 1446, 1318, 1221, 1142, 1089.

HRMS (EI) Calcd. for $C_{17}H_{22}O_5S$: 338.1188 Found : 338.1181

_(E)_-1-Cyclopropyl-7,7-dimethyl-9-oxo-1-(phenylsulfonyl)dec-1-en-4-yl pivalate **IV-14e**

	$C_{25}H_{36}O_5S$ M= 448.6 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15b** (333 mg, 1.0 mmol) and xanthate **IV-4i**[21] (174 mg, 0.5 mmol). The reaction needed 160 mol% of DLP to go to completion (8 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (10:90, 30:70) to afford vinylsulfone **IV-14e** (159 mg, 71%) as a mixture of *E/Z* isomers in a 92:8 ratio in favor of the *E* isomer and as a colorless oil which solidified upon standing.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.86-7.88 (m, 2H, C***H***-ar), 7.51-7.59 (m, 3H, C***H***-ar), 6.39 (d, 1H, *J*= 10.9 Hz, C***H***-2), 5.15-5.21 (m, 1H, C***H***-5), 2.58 (dd, *J*= 14.4, 5.6 Hz, 1H, C***H***-4), 2.39 (dd, *J*= 14.4, 9.0 Hz, 1H, C***H***-4), 2.42 (s, 2H, C***H$_2$***-8), 2.09 (s, 3H, C***H$_3$***-10), 1.60 (d, *J*= 3.8 Hz, 2H, C***H$_2$***-6), 1.14-1.18 (m, 1H, C***H***-1), 1.14 (s, 9H, O(C***H$_3$***)$_3$), 0.92-0.98 (m, 2H, C***H$_2$***-1), 0.92, 0.89 (s, 6H, (C***H$_3$***)$_2$-6), 0.72-0.77 (m, 2H, C***H$_2$***-1).

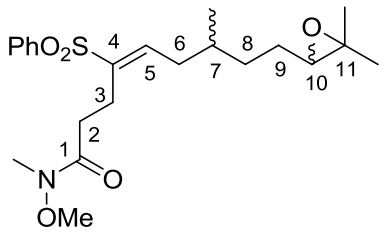
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 208.2 (C-9), 177.9 (C=O), 150.6 (C-2), 140.0 (C-3), 133.7, 133.0, 129.1, 128.1 (C-ar), 69.9 (C-5), 53.9 (C-8), 43.8 (C-6), 38.6 (C-O), 32.6 (C-8), 32.3 (C-4), 32.1 (C-10), 27.5, 27.2 ((CH$_3$)$_2$-7), 27.1 ((CH$_3$)$_3$), 11.9 (C-1), 9.5, 9.3 ((CH$_2$)$_2$-1).

IR (ν, cm^{-1}, CCl_4) 3068, 2958, 2931, 2873, 1720, 1636, 1479, 1446, 1364, 1319, 1307, 1148, 1088, 1031.

HRMS (EI) Calcd. for $C_{25}H_{36}O_5S$: 448.2283 Found : 448.2296

[21] Tournier, L. Thesis *Ecole Polytechnique* **2005**.

(*E*)-9-(3,3-Dimethyloxiran-2-yl)-*N*-methoxy-*N*,7-dimethyl-4-(phenylsulfonyl)non-4-enamide **IV-14f**



$C_{22}H_{33}NO_5S$
M= 423.6 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15c** (867 mg, 2.0 mmol) and xanthate **IV-4f**[6] (223 mg, 1.0 mmol). The reaction needed 200 mol% of DLP to go to completion (10 h). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether petroleum (10:90, 30/70, 50:50) to afford (*E*)-vinylsulfone **IV-14f** (296 mg, 70%) as a mixture of diastereomers in a 1:1 ratio and as a colorless oil which solidified upon standing.

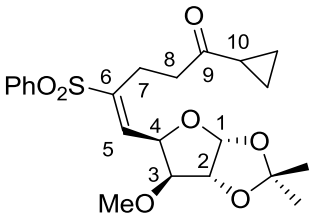
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.84-7.86 (m, 2H, C***H***-ar), 7.50-7.60 (m, 3H, C***H***-ar), 6.99 (t, *J*= 7.5 Hz, 1H, C***H***-5), 3.64 (s, 3H, OC***H*****$_3$**), 3.15 (s, 3H, NC***H*****$_3$**), 2.61-2.68 (m, 3H, C***H***-10, C***H*****$_2$**-2), 2.49 (dd, *J*= 9.9, 6.0 Hz, 2H, C***H*****$_2$**-3), 2.22-2.31 (m, 1H, C***H***-6), 2.07-2.16 (m, 1H, C***H***-6), 1.69-1.76 (m, 1H, C***H***-7), 1.37-1.56 (m, 4H, C***H*****$_2$**-8, C***H*****$_2$**-9), 1.30, 1.25 (s, 6H, (C***H*****$_3$**)$_2$-11), 0.93 (d, *J*= 6.7 Hz, 1.5H, C***H*****$_3$**-7), 0.92 (d, *J*= 6.7 Hz, 1.5H, C***H*****$_3$**-7).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 172.8 (C-1), 142.2 (C-4), 140.6 (C-5), 139.6, 133.2, 129.2, 128.0 (C-ar), 64.2, 64.2 (C-10), 61.3 (OCH_3), 58.3, 58.1 (C-11), 35.5, 35.2 (C-6), 33.4, 33.4 (C-7), 32.8, 32.8 (C-8), 32.2 (NCH_3), 31.2, 30.8 (C-2), 26.5, 26.5 (C-9), 24.9 (CH_3-11), 21.4 (C-3), 19.6, 19.4 (CH_3-7), 18.7, 18.7 (CH_3-11).

IR (ν, cm^{-1}, CCl_4) 3069, 2962, 2929, 1667, 1614, 1574, 1446, 1385, 1318, 1232, 1143, 1085, 1023.

HRMS (EI) Calcd. for $C_{22}H_{33}NO_5S$: 423.2079 Found : 423.2066

(*E*)-1-Cyclopropyl-5-((3a*R*,5*R*,6a*R*)-6-methoxy-2,2-dimethyltetra hydrofuro[3,2-d][1,3]dioxol-5-yl)-4-(phenylsulfonyl)pent-4-en-1-one **IV-14g**

	$C_{22}H_{28}O_7S$ M= 436.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15d** (466 mg, 1.0 mmol) and xanthate **IV-4g**[22] (102 mg, 0.5 mmol). The reaction needed 180 mol% of DLP to go to completion (9 h). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (10:90, 30:70) to afford (*E*)-vinylsulfone **IV-14g** (175 mg, 80%) and as a colorless oil which solidified upon standing.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.85-7.87 (m, 2H, C***H***-ar), 7.50-7.61 (m, 3H, C***H***-ar), 6.98 (d, *J*= 7.2 Hz, 1H, C***H***-5), 5.93 (d, *J*= 3.7 Hz, 1H, C***H***-1), 4.91 (dd, *J*= 7.2, 3.2 Hz, 1H, C***H***-4), 4.62 (d, *J*= 3.7 Hz, 1H, C***H***-2), 3.79 (d, *J*= 3.2 Hz, 1H, C***H***-3), 3.37 (s, 3H, OC***H$_3$***), 2.80-2.95 (m, 2H, C***H$_2$***-8), 2.61 (ddd, *J*= 15.2, 9.5, 6.2 Hz, 1H, C***H***-7), 2.47 (ddd, *J*= 15.2, 9.2, 5.8 Hz, 1H, C***H***-7), 1.81-1.87 (m, 1H, C***H***-10), 1.48, 1.32 (s, 6H, (C***H$_3$***)$_2$), 0.96-1.00 (m, 2H, C***H$_2$***-10), 0.84-0.87 (m, 2H, C***H$_2$***-10).

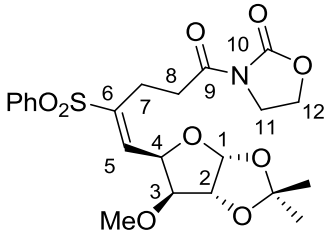
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 208.8 (C-9), 143.7, 133.4, 129.2, 128.2 (C-ar), 138.9 (C-6), 136.0 (C-5), 112.0 (**C**$(CH_3)_2$), 105.1 (C-1), 85.9 (C-3), 81.9 (C-2), 76.8 (C-4), 59.3 (OCH_3), 42.2 (C-8), 26.8, 26.2 ($(CH_3)_2$), 21.2 (C-10), 20.5 (C-7), 10.8, 10.7 ($(CH_2)_2$-10).

IR (ν, cm^{-1}, CCl_4): 3069, 2991, 2934, 2856, 1702, 1614, 1577, 1446, 1384, 1374, 1321, 1232, 1145, 1115, 1084.

HRMS (EI): Calcd. for $C_{22}H_{28}O_7S$: 436.1556 Found : 436.1558

[22] Charrier, N. Thesis *Ecole Polytechnique* **2008**.

3-*((E)*-5-((3a*R*,5*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,2-d][1,3]dioxol-5-yl)-4-(phenylsulfonyl)pent-4-enoyl)oxazolidin-2-one **IV-14h**

	$C_{22}H_{27}NO_9S$ M= 481.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15d** (466 mg, 1.0 mmol) and xanthate **IV-4h**[23] (125 mg, 0.5 mmol). The reaction needed 180 mol% of DLP to go to completion (9 h). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in toluene (10:90, 25:75, 50:50) to afford (*E*)-vinylsulfone **IV-14h** (123 mg, 51%) and as a colorless oil which solidified upon standing.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.91-7.93 (m, 2H, C***H***-ar), 7.56-7.66 (m, 3H, C***H***-ar), 7.04 (d, 1H, *J*= 6.9 Hz, C***H***-5), 5.94 (d, 1H, *J*= 3.7 Hz, C***H***-1), 4.97 (dd, 1H, *J*= 6.9, 3.2 Hz, C***H***-4) , 4.62 (d, 1H, *J*= 3.7 Hz, C***H***-2), 4.39 (t, 2H, *J*= 8.0Hz, C***H$_2$***-12), 3.97 (td, 2H, *J*= 8.0, 1.5 Hz, C***H$_2$***-11), 3.85 (d, 1H, *J*= 3.2Hz, C***H***-3) , 3.41 (s, 3H, OC***H$_3$***), 3.13-3.18 (m, 2H, C***H$_2$***-8), 2.60-2.77 (m, 2H, C***H$_2$***-7), 1.54, 1.37 (s, 6H, (C***H$_3$***)$_2$).

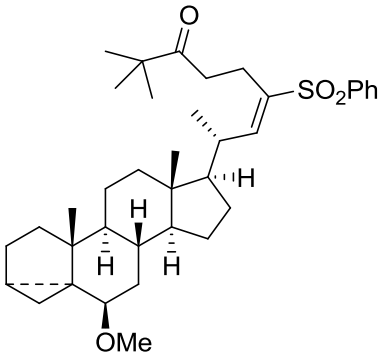
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 171.0 (C-9), 153.2 (C=O), 142.5, 133.3, 129.1, 128.2 (C-ar), 138.9 (C-6), 136.9 (C-5), 111.9 (***C***$(CH_3)_2$), 105.1 (C-1), 85.9 (C-3), 81.8 (C-2), 76.4 (C-4), 62.1 (C-12), 58.2 (OCH_3), 42.3 (C-11), 34.5 (C-8), 26.7, 26.1 ($(CH_3)_2$), 21.6 (C-7).

IR (ν, cm^{-1}, CCl_4): 3069, 2942, 2933, 1791, 1701, 1614, 1540, 1480, 1446, 1384, 1322, 1231, 1153, 1114, 1084, 1024.

HRMS (EI): Calcd. for M–CH_3 : $C_{21}H_{24}NO_9S$: 466.1171 Found : 466.1161

[23] Pautrat, F. Thesis *Ecole Polytechnique* **2002**.

(6*E*,8*S*)-8-[(4a*R*,4b*S*,6a*R*,7*R*,9a*S*,9b*S*,11*R*,11a*R*)-11-Methoxy-4a,6a-dimethylhexadecahydro cyclopenta[*a*]cyclopropa[2,3]cyclopenta [1,2-*f*]naphthalen-7-yl]-2,2-dimethyl-6-(phenylsulfonyl)non-6-en-3-one **IV-14i**

	$C_{37}H_{54}O_4S$ M= 594.9 g.mol^{-1}

A solution of olefin **IV-15e** (456 mg, 0.75 mmol) and xanthate **IV-4i**[24] (235 mg, 1.5 mmol, 2.0 equiv) in ethyl acetate (750 µL) was refluxed for 20 min under nitrogen. Lauroyl peroxide (DLP) (20% mol) was then added to the refluxing solution, followed by additional portions (20% mol) every hour until starting xanthate was completely consumed. The reaction needed 120 mol% of DLP to go to completion (6 h). The mixture was then cooled to 20 °C, concentrated *in vacuo* and purified by flash chromatography on silica gel with a gradient of ether in petroleum ether (2:98, 10:90, 30:70) to afford the corresponding (*E*)-vinylsulfone **IV-14i** (214 mg, 48%) and xanthate **IV-20** (224 mg, 36%).

A solution of xanthate **IV-20** (224 mg, 0.27 mmol) in ethyl acetate (300 µL) was refluxed for 20 min under nitrogen. Lauroyl peroxide (DLP) (20% mol) was then added to the refluxing solution, followed by additional portions (20% mol) every hour until starting xanthate was completely consumed. The reaction needed 120 mol% of DLP to go to completion (6 h). The mixture was then cooled to 20 °C, concentrated *in vacuo* and purified by flash chromatography on silica gel with a gradient of ether in petroleum ether (2:98, 10:90, 30:70) to afford (*E*)-vinylsulfone **IV-14i** (98 mg, 22% from **IV-15e**).

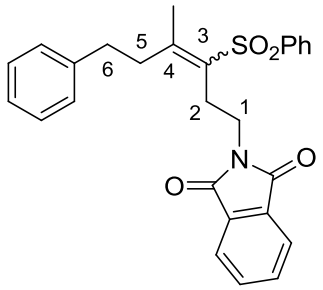
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	7.80-7.82 (m, 2H, C***H***-ar), 7.50-7.59 (m, 3H, C***H***-ar), 6.77 (d, *J*= 10.8 Hz, 1H), 3.32 (s, 3H), 2.73-2.78 (m, 2H), 2.62-2.68 (m, 1H), 2.42-2.50 (m, 2H), 2.28-2.35 (m, 1H), 1.84-1.95 (m, 2H), 1.05-1.80 (m, 12H), 1.09 (s, 9H), 1.06 (d, *J*= 6.6 Hz, 3H), 1.02 (s, 3H), 0.83-0.90 (m, 5H), 0.71 (s, 3H), 0.64-0.66 (m, 1H), 0.44 (dd, *J*= 7.6, 5.2 Hz, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	214.5, 148.4, 139.8, 137.0, 133.1, 129.1, 127.8, 82.2, 56.6, 56.2, 55.6, 48.0, 44.0, 43.4, 43.1, 40.1, 36.1, 35.6, 35.1, 33.3, 27.7, 26.3, 24.9, 24.2, 22.7, 21.4, 21.0, 19.4, 19.2, 13.1, 12.7.

[24] Brunet, E.; Garcia Ruano, J. L.; Rodriguez, J. H.; Alcudia, F. *Tetrahedron* **1984**, *40*, 4433.

IR (ν, cm^{-1}, CCl_4) 2934, 2870, 1708, 1446, 1368, 1316, 1144, 1086, 1017.

HRMS (EI) Calcd. for $C_{37}H_{54}O_4S$: 594.3743 Found : 594.3740

2-(4-Methyl-6-phenyl-3-(phenylsulfonyl)hex-3-enyl)isoindoline-1,3-dione **IV-14j**



$C_{27}H_{25}NO_4S$
M= 459.6 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using the olefin **IV-15f** (823 mg, 2.0 mmol) and the xanthate **IV-4c**[5] (281 mg, 1.0 mmol). The reaction needed 140 mol% of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 3:7) to afford the corresponding vinylsulfone **IV-14j** (262 mg, 57%) as a colorless oil which solidified upon standing and as a mixture of geometric isomers in a 2:1 ratio in favor of the *E* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)
7.80-7.89 (m, 4H, C***H***-ar), 7.70-7.72 (m, 2H, C***H***-ar), 7.48-7.59 (m, 3H, C***H***-ar), 7.09-7.31 (m, 5H, C***H***-ar), 3.75-3.82 (m, 2H, C***H$_2$***-6), 2.64-2.98 (m, 4H, C***H$_2$***-1, C***H$_2$***-2), 2.64-2.68 (m, 1.33H, C***H$_2$***-5 *E* isomer), 2.53-2.57 (m, 0.67H, C***H$_2$***-5 *Z* isomer), 2.24 (s, 1H, C***H$_3$***-4 *Z* isomer), 2.09 (s, 2H, C***H$_3$***-4 *E* isomer).

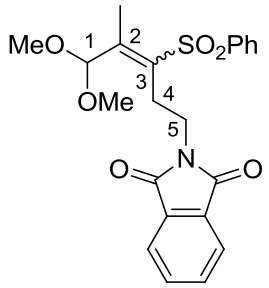
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)
E isomer
168.1 (C=O), 154.2, 141.7, 141.3, 134.0, 133.0, 132.7, 132.1, 129.2, 128.5, 127.4, 126.4, 123.3 (C-ar, C-3, C-4), 37.9 (C-1), 36.7 (C-6), 35.1 (C-5), 29.1 (C-2), 22.4 (CH_3-C4).

Z isomer
168.0 (C=O), 152.9, 141.8, 140.1, 133.9, 133.7, 132.1, 132.9, 129.1, 128.6, 127.3, 126.2, 123.3 (C-ar, C-3, C-4), 39.0 (C-1), 37.6 (C-6), 33.5 (C-5), 28.4 (C-2), 20.2 (CH_3-C4).

IR (ν, cm^{-1}, CCl_4)
3087, 3066, 2929, 2857, 1776, 1719, 1616, 1496, 1446, 1394, 1361, 1317, 1308, 1149, 1086.

HRMS (EI)
Calcd. for $C_{27}H_{25}NO_4S$: 459.1504 Found : 459.1498

(*E*)-2-(5,5-Dimethoxy-4-methyl-3-(phenylsulfonyl)pent-3-enyl) isoindoline-1,3-dione **IV-14k**



$C_{22}H_{23}NO_6S$
M= 429.5 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15h** (762 mg, 2.0 mmol) and xanthate **IV-4c**[5] (281 mg, 1.0 mmol). The reaction needed 160 mol% of DLP to go to completion (8 h). The residue was purified by silica gel column chromatography with a gradient of ethyl acetate in petroleum ether (5:95, 2:8, 3:7) to afford vinylsulfone **IV-14k** (279 mg, 65%) as a yellow oil and as a mixture of geometric isomers in a 2:1 ratio in favor of the *E* isomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.88-7.94 (m, 2H, C***H***-ar), 7.79-7.82 (m, 2H, C***H***-ar), 7.67-7.70 (m, 2H, C***H***-ar), 7.31-7.61 (m, 3H, C***H***-ar), 6.20 (s, 0.33H, C***H***-1 *Z* isomer), 5.11 (s, 0.67H, C***H***-1 *E* isomer), 3.76-3.80 (m, 2H, C***H$_2$***-5), 3.38 (s, 2H, (OC***H$_3$***)$_2$ *Z* isomer), 3.33 (s, 4H, (OC***H$_3$***)$_2$ *E* isomer), 2.84-2.88 (m, 1.33H, C***H$_2$***-4 *E* isomer), 2.67-2.71 (m, 0.67H, C***H$_2$***-4 *Z* isomer), 2.00 (s, 2H, C***H$_3$***-2 *E* isomer), 1.99 (s, 1H, C***H$_3$***-2 *Z* isomer).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

<u>*E* isomer</u>

167.9 (C=O), 149.1 (C-2), 141.2, 136.8, 133.9, 132.0, 129.2, 127.4, 123.2 (C-ar, C-3), 103.0 (C-1), 55.1 ((OCH$_3$)$_2$-1), 37.8 (C-5), 27.8 (C-4), 13.5 (CH$_3$-2).

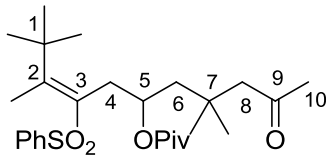
<u>*Z isomer*</u>

167.9 (C=O), 150.2 (C-2), 141.0, 135.5, 134.0, 132.0, 129.2, 127.4, 123.2 (C-ar, C-3), 100.1 (C-1), 55.7 ((OCH$_3$)$_2$), 36.2 (C-5), 29.0 (C-4), 14.1 (CH$_3$-2).

IR (ν, cm^{-1}, CCl_4): 3069, 2932, 1776, 1719, 1617, 1468, 1446, 1395, 1361, 1320, 1152, 1109, 1085.

HRMS (EI): Calcd. for $C_{22}H_{23}NO_6S$: 429.1246 Found : 429.1239

(*E*)-2,2,3,8,8-Pentamethyl-10-oxo-4-(phenylthioperoxy)undec-3-en-6-yl pivalate **IV-14l**

	$C_{27}H_{42}O_5S$ M= 478.7 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15g** (700 mg, 2.0 mmol) and xanthate **IV-4i**[21] (349 mg, 1.0 mmol). The reaction needed 160 mol% of DLP to go to completion (8 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 3:7) to afford (*E*)-vinylsulfone **IV-14l** (297 mg, 62%) as a colorless oil which solidified upon standing.

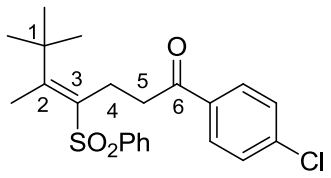
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.74-7.77 (m, 2H, C***H***-ar), 7.44-7.53 (m, 3H, C***H***-ar), 5.50-5.57 (m, 1H, C***H***-5), 3.34 (dd, *J*= 14.8, 6.9 Hz, 1H, C***H***-4), 3.07 (dd, *J*= 14.8, 5.8 Hz, 1H, C***H***-4), 2.48 (s, 2H, C***H*****$_2$**-8), 2.13 (s, 3H, C***H*****$_3$**-10), 1.79-1.83 (m, 2H, C***H*****$_2$**-6), 1.80 (s, 3H, C***H*****$_3$**-2), 1.23 (s, 9H, (C***H*****$_3$**)$_3$(OPiv)), 1.18 (s, 9H, (C***H*****$_3$**)$_3$-1), 1.06, 1.05 (s, 6H, (C***H*****$_3$**)$_2$-7).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 208.8 (C-9), 177.7 (C=O Piv), 160.1 (C-2), 144.2, 132.3, 128.8, 126.4 (C-ar), 137.0 (C-3), 70.7 (C-5), 53.9 (C-8), 46.2 (C-6), 39.0 (C-O (Piv)), 38.8 (C-1), 37.0 (C-4), 33.0 (C-10), 32.4 (C-7), 30.6((CH$_3$)$_3$-1), 28.0, 27.9 ((CH$_3$)$_2$-7), 27.2 ((CH$_3$)$_3$(OPiv)), 20.3 (CH$_3$-C2).

IR (ν, cm^{-1}, CCl_4) 3068, 2959, 2931, 2874, 1720, 1608, 1583, 1479, 1446, 1366, 1303, 1154, 1085, 1034.

HRMS (EI) Calcd. for $C_{27}H_{42}O_5S$: 478.2753 Found : 478.2758

(*E*)-1-(4-Chlorophenyl)-5,6,6-trimethyl-4-(phenylthioperoxy)hept-4-en-1-one **IV-14m**



$C_{22}H_{25}ClO_3S$
M= 405.0 g.mol^{-1}

Following general procedure **IV-C**, the reaction was carried out using olefin **IV-15g** (700 mg, 2.0 mmol) and xanthate **IV-4b**[4] (275 mg, 1.0 mmol). The reaction needed 160 mol% of DLP to go to completion (8 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 2:8) to afford (*E*)-vinylsulfone **IV-14m** (250 mg, 62%) as a white solid.

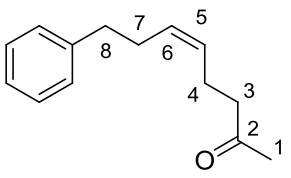
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.97-8.00 (m, 2H, C***H***-ar), 7.80-7.83 (m, 2H, C***H***-ar), 7.44-7.58 (m, 5H, C***H***-ar), 3.43-3.47 (m, 2H, C***H*****$_2$**-5), 3.22-3.25 (m, 2H, C***H*****$_2$**-4), 1.92 (s, 3H, C***H*****$_3$**-2), 1.21 (s, 9H, (C***H*****$_3$**)$_3$-1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 197.8 (C-6), 160.1 (C-2), 143.6, 139.7, 138.8, 134.8, 132.6, 129.7, 1290, 128.9, 126.1 (C-ar, C-3), 39.5 (C-5), 38.7 (C-1), 30.0 ($(CH_3)_3$-1), 26.5 (C-4), 19.8 (CH_3-2).

IR (ν, cm^{-1}, CCl_4) 3069, 2959, 2928, 2858, 1711, 1688, 1590, 1467, 1447, 132, 1307, 1150, 1089.

HRMS (EI) Calcd. for $C_{22}H_{25}ClO_3S$: 404.1213 Found : 404.1219

(*Z*)-8-Phenyloct-5-en-2-one[25] **(*Z*)-IV-1a**

	$C_{14}H_{18}O$ M= 202.3 g.mol^{-1}

$Na_2S_2O_4$ (1.14 g, 6.57 mmol, 15.0 equiv) and $NaHCO_3$ (1.10 g, 13.1 mmol, 30.0 equiv) were added to a solution of a solution of sulfone **IV-14a** (150 mg, 0.44 mmol) in H_2O/EtOH 1:1 (10 mL) and the resulting mixture was refluxed for 4 h. Ethanol was removed *in vacuo* and the aqueous residue was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 9:1) to afford (*Z*)-alkene **(*Z*)-IV-1a** (63 mg, 71%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.18-7.30 (m, 5H, C***H***-ar), 5.43 (ddd, *J*= 12.1, 9.5, 7.2 Hz, 1H, C***H***-5), 5.32 (ddd, *J*= 12.1, 9.5, 7.0 Hz, 1H, C***H***- 6), (t, *J*= 7.6 Hz, 2H, C***H$_2$***-8), 2.21-2.38 (m, 6H, C***H$_2$***-4, C***H$_2$***-7, C***H$_2$***-3), 2.09 (s, 3H, C***H$_3$***-1).

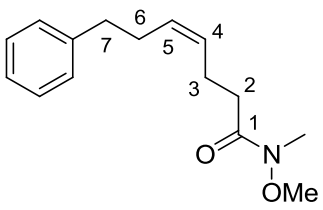
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 208.4 (C-2), 141.9, 128.5, 128.2, 125.8 (C-ar), 129.8 (C-6), 129.5 (C-5), 43.3 (C-3), 35.8 (C-8), 29.9 (C-1), 29.1 (C-7), 21.6 (C-4).

IR (ν, cm^{-1}, CCl_4) 3065, 3028, 2926, 2857, 1721, 1604, 1496, 1454, 1360, 1158.

HRMS (EI) Calcd. for $C_{14}H_{18}O$: 202.1358 Found : 202.1348

[25] Kim, T. H. ; Park, K. M. *Tetrahedron Lett.* **1995**, *36*, 4833.

(*Z*)-*N*-Methoxy-*N*-methyl-7-phenylhept-4-enamide[25] **IV-1b**

	$C_{15}H_{21}NO_2$ M= 247.3 g.mol^{-1}

$Na_2S_2O_4$ (472 mg, 2.71 mmol, 15.0 equiv) and $NaHCO_3$ (455 mg, 5.42 mmol, 30.0 equiv) were added to a solution of sulfone **IV-14b** (70 mg, 0.18 mmol) in H_2O/EtOH 1:1 (4 mL) and the resulting mixture was refluxed for 4 h. Ethanol was removed *in vacuo* and the aqueous residue was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 6:4) to afford (*Z*)-alkene **IV-1b** (34 mg, 76%) as a colorless oil.

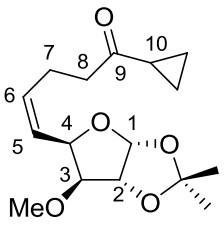
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.17-7.29 (m, 5H, C***H***-ar), 5.37-5.49 (m, 2H, C***H***-4, C***H***-5), 3.66 (s, 3H, OC***H₃***), 3.17 (s, 3H, NC***H₃***), 2.67 (t, *J*= 7.7 Hz, 2H, C***H₂***-7), 2.33-2.65 (m, 6H, C***H₂***-3, C***H₂***-6, C***H₂***-2).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 141.9, 128.5, 128.2, 125.7 (C-ar), 129.9 (C-5), 128.9 (C-4), 61.2 (OCH_3), 35.9 (C-7), 31.8 (NCH_3), 29.7 (C-2), 29.1 (C-6), 22.4 (C-3).
The quartenary carbon C-1 cannot be seen in the NMR.

IR (ν, cm^{-1}, CCl_4) 3059, 2942, 2929, 2857, 1673, 1612, 1558, 1454, 1382, 1305, 1176.

HRMS (EI) Calcd. for $C_{15}H_{21}NO_2$: 247.1572 Found : 247.1579

(*Z*)-1-Cyclopropyl-5-((3a*R*,5*R*,6a*R*)-6-methoxy-2,2-dimethyl tetrahydrofuro[3,2-d][1,3]dioxol-5-yl)pent-4-en-1-one[25] **IV-1c**

	$C_{16}H_{24}O_5$ M= 296.4 g.mol^{-1}

$Na_2S_2O_4$ (392 mg, 2.25 mmol, 15.0 equiv) and $NaHCO_3$ (378 mg, 4.5 mmol, 30.0 equiv) were added to a solution of a solution of sulfone **IV-14f** (65 mg, 0.15 mmol) in H_2O/EtOH 1:1 (4 mL) and the resulting mixture was refluxed for 4 h. Ethanol was removed *in vacuo* and the aqueous residue was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 90:10) to afford (*Z*)-alkene **IV-1c** (36 mg, 82%) as a colorless oil.

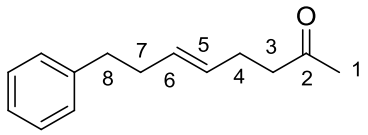
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.91 (d, *J*= 3.9 Hz, 1H, C***H***-1), 5.57-5.69 (m, 2H, C***H***-5, C***H***-6), 4.94 (dd, *J*= 7.7, 3.1 Hz, 1H, C***H***-4), 4.60 (d, *J*= 3.9 Hz, 1H, C***H***-2), 3.64 (d, *J*= 3.1 Hz, 1H, C***H***-3), 3.40 (s, 3H, OC***H*****$_3$**), 2.67 (td, *J*= 7.2, 4.1 Hz, 2H, C***H*****$_2$**-7), 2.43 (dd, *J*= 14.2, 7.2 Hz, 2H, C***H*****$_2$**-8), 1.91 (tt, *J*= 7.8, 4.6 Hz, 1H, C***H***-10), 1.52, 1.33 (s, 6H, (C***H*****$_3$**)$_2$), 1.00-1.04 (m, 2H, C***H*****$_2$**-C10), 0.85-0.89 (m, 2H, C***H*****$_2$**-C10).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 209.8 (C-9), 133.4 (C-6), 124.2 (C-5), 111.4 (**C**$(CH_3)_2$), 104.6 (C-1), 85.8 (C-3), 82.2 (C-2), 75.6 (C-4), 59.2 (OCH_3), 42.8 (C-8), 26.8, 26.2 ($(CH_3)_2$), 22.5 (C-10), 20.5 (C-7), 10.8, 10.8 ($(CH_2)_2$-10).

IR (ν, cm^{-1}, CCl_4): 2991, 2930, 2856, 2830, 1705, 1559, 1540, 1454, 1383, 1373, 1255, 1216, 1194, 1165, 1115.

HRMS (EI) Calcd. for $C_{16}H_{24}O_5$: 296.1624 Found : 296.1609

(*E*)-8-Phenyloct-5-en-2-one[26] **(*E*)-IV-1a**

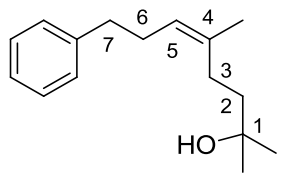
	$C_{14}H_{18}O$ M= 202.3 g.mol^{-1}

To a stirred solution of (*E*)-vinylsulfone **IV-14a** (34 mg, 0.10 mmol) in THF/MeOH 4:1 (10 mL) , was added at -30 °C few crystals of KH_2PO_4 and the amalgam Na/Hg (276 mg, 1.38 g, 0.6 mmol, 6.0 equiv). The reaction mixture was stirred at -30 °C for 4 h and then quenched with a pH 7 buffer solution. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 90:10) to afford alkene (***E*)-IV-1a** (13 mg, 64%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	7.16-7.30 (m, 5H, C***H***-ar), 5.38-5.22 (m, 2H, C***H***-6, C***H***-5), 2.64-2.67 (m, 2H, C***H$_2$***-8), 2.46 (t, *J*= 7.3 Hz, 2H, C***H$_2$***-3), 2.23-2.32 (m, 4H, C***H$_2$***-4, C***H$_2$***-7), 2.12 (s, 3H, C***H$_3$***-1).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	208.5 (C-2), 141.9, 130.5, 128.4, 128.2 (C-ar), 129.0 (C-6), 125.7 (C-5), 43.4 (C-3), 35.9 (C-8), 34.3 (C-7), 29.9 (C-1), 26.8 (C-4).
IR (ν, cm^{-1}, CCl_4)	3065, 3029, 2935, 2858, 1721, 1604, 1496, 1454, 1358, 1158.
HRMS (EI)	Calcd. for $C_{20}H_{22}O_3S$: 202.1358 Found : 202.1348

[26] Chen, S.-H. ; Horvath, R. F. ; Joglar, J. ; Fisher, M. J. ; Danishefsky, S. J. *J. Org. Chem.* **1991**, *56*, 5834.

(*Z*)-2,5-Dimethyl-8-phenyloct-5-en-2-ol[27] **IV-21a**

	$C_{16}H_{24}O$ M= 232.4 g.mol^{-1}

To a stirred solution of sulfone **IV-14a** (34 mg, 0.1 mmol) in THF (1 mL), was added $Ni(acac)_2$ (5 mg, 5 mol%) at 20 °C. To the resulting green solution, was added methylmagnesium bromide (1.4 M THF solution, 214 µL, 0.3 mmol, 3.0 equiv) dropwise at 20 °C. After stirring overnight, the reaction mixture was stirred under reflux for 4 h and then quenched with saturated aqueous NH_4Cl, filtered and extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 7:3) to afford trisubstituted (*Z*)-alkene **IV-21a** (18 mg, 78%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.29 (m, 2H, C***H***-ar), 7.17-7.19 (m, 3H, C***H***-ar), 5.18 (t, *J*=7.0 Hz, 1H, C***H***-5), 2.64 (t, *J*= 7.7 Hz, 2H, C***H$_2$***-7), 2.30-2.34 (m, 2H, C***H$_2$***-6), 2.00-2.04 (m, 2H, C***H$_2$***-3), 1.69 (s, 3H, C***H$_3$***-4), 1.37-1.41 (m, 2H, C***H$_2$***-2), 1.20 (s, 6H, (C***H$_3$***)$_2$-1).

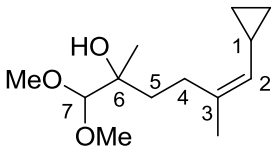
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 142.3, 128.5, 128.2, 125.7 (C-ar), 136.1 (C-4), 124.2 (C-5), 70.9 (C-1), 41.9 (C-2), 36.3 (C-7), 29.9 (C-6), 29.1 ($(CH_3)_2$-1), 26.6 (C-3), 23.4 (CH_3-4).

IR (ν, cm^{-1}, CCl_4): 3617, 3570, 3491, 3086, 3065, 3028, 2968, 2929, 2858, 1604, 1496, 1454, 1370, 1328, 1218, 1121.

HRMS (EI): Calcd. for $C_{16}H_{24}O$: 232.1827 Found : 232.1819

[27] Arjona, O.; Iradier, F.; Plumet, J.; Martínez-Alcázar, M. P.; Hernández-Cano, F.; Fonseca, I. *Tetrahedron Lett.* **1998**, *39*, 6741.

(*Z*)-6-Cyclopropyl-1,1-dimethoxy-2,5-dimethylhex-5-en-2-ol[27] **IV-21b**

	$C_{13}H_{24}O_3$ M= 228.3 g.mol^{-1}

To a stirred solution of sulfone **IV-14d** (80 mg, 0.23 mmol) in THF (2 mL), was added $Ni(acac)_2$ (11 mg, 5 mol%) at 20°C. To the green solution, was added methylmagnesium bromide (1.4 M THF solution, 490 µL, 0.69 mmol, 3.0 equiv) dropwise at 20 °C. After stirring at 20 °C overnight, the reaction was stirred under reflux for 3 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, filtered and extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford trisubstituted (*Z*)-alkene **IV-21b** (37 mg, 71%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 4.52 (d, *J*= 9.3 Hz, 1H, C***H***-2), 4.06 (s, 1H, C***H***-7), 3.57, 3.54 (s, 6H, (OC***H*****$_3$**$)_2$), 2.17-2.31 (m, 2H, C***H*****$_2$**-4), 1.67 (d, *J*= 1.2 Hz, 3H, C***H*****$_3$**-3), 1.60-1.64 (m, 2H, C***H*****$_2$**-5), 1.40-1.50 (m, 1H, C***H***-1), 1.17 (s, 3H, C***H*****$_3$**-6), 0.64-0.67 (m, 2H, C***H*****$_2$**-1), 0.23-0.27 (m, 2H, C***H*****$_2$**-1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 134.6 (C-3), 129.0 (C-2), 111.0 (C-7), 74.7 (C-6), 58.3, 58.1 (($CH_3O)_2$), 35.1 (C-5), 25.9 (C-4), 23.2 (CH_3-3), 21.2 (CH_3-6), 9.7 (C-1), 6.6 (($CH_2)_2$-1).

IR (ν, cm^{-1}, CCl_4) 3590, 3082, 2931, 2856, 2833, 1639, 1616, 1446, 1377, 1319, 1189, 1145, 1107, 1078.

HRMS (EI) Calcd. for $C_{13}H_{24}O$: 228.1726 Found : 228.1719

C. Chapitre V : Induction de la stéréochimie sur des systèmes cycliques

GENERAL PROCEDURE V-A : ADDITION OF THE VINYL ETHYL ETHER

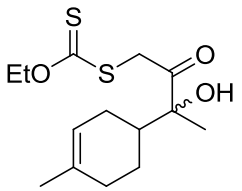
To a stirred solution of **ethyl vinyl ether** (5.0 equiv) in **THF** (2 mL/ mmol of ketone) under nitrogen and at – 78 °C, was added dropwise over 10 minutes ***tert*-butyl lithium** (~1.35 M in pentane, 2.0 equiv). After 15 more minutes, the acetone/dry ice bath was replaced by a water/ice bath, and the solution was then stirred for 15 min. The flask was cooled back to -78 °C, and a solution of the **ketone** (1.0 equiv) in **THF** (2 mL/mmol) was then added dropwise over 10 min. The mixture was then allowed to warm up to 20 °C, and stirred for an additional 2 h. Saturated NH_4Cl and ether were added to quench the reaction. The aqueous layer was then extracted with ether, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and then concentrated *in vacuo* to afford the corresponding ethyl vinyl ether adduct.

GENERAL PROCEDURE V-B : XANTHATE FORMATION FROM THE VINYL ETHYL ETHER ADDUCT

To a stirred solution of the **ethyl vinyl ether adduct** (1.0 equiv) in a mixture of acetonitrile/water (9:1) (2 mL/mmol) under nitrogen in an ice water bath, was added a solution of ***N*-bromosuccinimide** (1.1 equiv) in **acetonitrile/water** (9:1) (2 mL/mmol). The resulting solution was stirred for 20 more minutes, and the mixture was then partitioned between ether and water. The organic layer was then washed with brine, and dried over anhydrous $MgSO_4$, filtered and the solvent were removed *in vacuo* to afford the **α-bromo ketone**. IR and ^1H NMR analysis could be used to see the formation of the carbonyl group.

The previous crude **bromo ketone** (1.0 equiv) was then stirred in **acetone** (1.5 mL/mmol) under nitrogen at 0 °C, and **potassium *O*-ethyl xanthate** (1.2 equiv) was then added. After one hour at 0 °C, the mixture was partitioned between ether and water. Brine was added to the aqueous layer, and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and were removed *in vacuo.* The residue was purified by silica gel column chromatography to afford the **xanthate**.

_O_-Ethyl _S_-3-hydroxy-3-(4-methylcyclohex-3-enyl)-2-oxobutyl carbonodithioate **RH2**

	$C_{14}H_{22}O_3S_2$ M= 302.5 g.mol^{-1}

Following general procedure **V-A**, the reaction was carried out using 1-(4-methyl-cyclohex-3-enyl)-ethanone **RH1** (2.2 mL, 15.0 mmol). The adduct obtained was transformed following general procedure **V-B** to give the crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford xanthate **RH2** (2.77 g, 61% over 3 steps) as a yellow oil as a mixture of two epimers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.27-5.41 (m, 1H), 4.63 (q, *J*= 7.1 Hz, 2H), 4.27-4.40 (m, 2H), 3.28 (brs, 1H), 1.80-2.15 (m, 6H), 1.56-1.66 (m, 1H), 1.63 (s, 3H), 1.45, 1.40 (2s, 3H), 1.41 (t, *J*= 7.1 Hz, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.3, 213.1, 207.4, 207.1, 133.8, 133.7, 119.9, 119.5, 81.2, 80.8, 70.8, 70.8, 42.0, 41.1, 40.8, 30.2, 30.2, 25.8, 24.9, 23.6, 23.2, 23.2, 23.1, 22.1, 13.7.

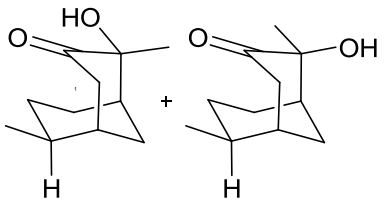
IR (ν, cm^{-1}, CCl_4) 3618, 3503, 1715, 1227, 1055.

HRMS (EI) Calcd. for $C_{14}H_{22}O_3S_2$: 302.1011 Found : 302.1009

GENERAL PROCEDURE V-C : REDUCTION OF XANTHATE WITH HYPOPHOSPHOROUS ACID

A solution of **xanthate** (1.0 equiv), **triethylamine** (5.5 equiv) and **hypophosphorous acid** (50% in water) (5.0 equiv) in dioxane (12.5 mL/mmol of xanthate) was refluxed under nitrogen for 15 minutes. **AIBN** (0.15 mL/mmol of xanthate) was then added to the solution, and reflux was kept for an additional 1 h under N_2. The resulting mixture was partitioned between ethyl acetate and water. The organic layer was then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography to afford the **reduced product**.

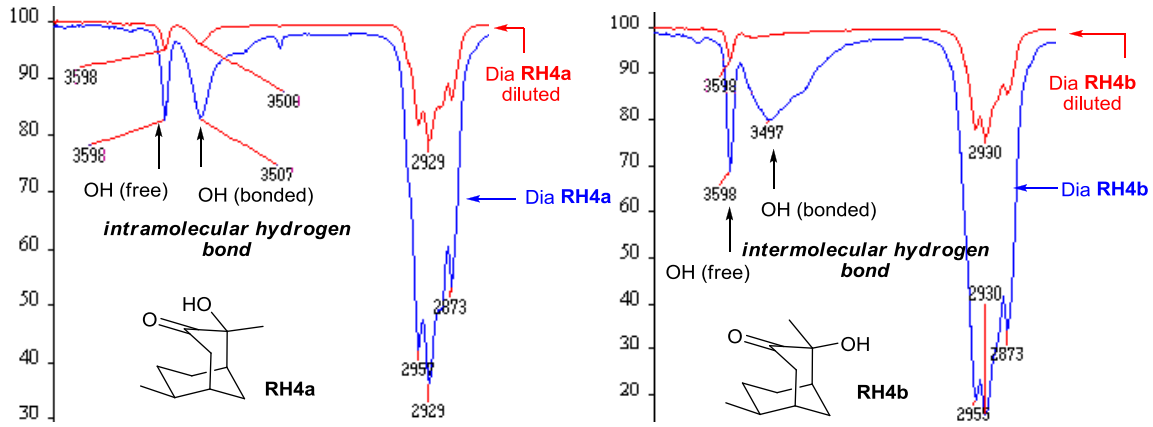
2-Hydroxy-2,6-dimethylbicyclo[3.3.1]nonan-3-one **RH4**



RH4a **RH4b**

$C_{11}H_{18}O_2$
M= 182.3 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **RH6** (150 mg, 0.5 mmol) and needed 10 mol % of DLP to go to completion (3 h). Crude xanthate was then transformed following general procedure **V-C**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford α-hydroxyketone **RH4** (73 mg, 80% over 2 steps) as a mixture of two epimers at C-3 in a 1:1 ratio and as two colorless oils. The diastereomers **RH4a** and **RH4b** were separated at this step and mixed together after characterization for the next step. By analyzing the infrared data, we can determine the structure of the diastereomer **RH4a** which has an intramolecular hydrogen bond and the structure of the diastereomer **RH4b** which has an intermolecular hydrogen bond.



Diastereomer **RH4a**

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 2.77 (dd, *J*= 16.2, 6.1 Hz, 1H), 2.52 (ddd, *J*= 13.1, 6.0, 3.2 Hz, 1H), 2.40 (dt, *J*= 16.2, 2.1 Hz, 1H), 2.22-2.30 (m, 1H), 2.05-2.11 (m, 1H), 2.01-2.05 (m, 1H), 1.66-1.80 (m, 2H), 1.45-1.60 (m, 2H), 1.34-1.44 (m, 1H), 1.30 (s, 3H), 0.87 (d, *J*= 6.9 Hz, 3H), 0.74-0.87 (m, 1H).

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz): 212.4, 76.6, 41.8, 38.0, 37.4, 35.7, 30.8, 27.8, 27.0, 21.9, 19.7.

IR (ν, cm^{-1}, CCl_4) 3598, 3497, 1712.

HRMS (EI) Calcd. for $C_{11}H_{18}O_2$: 182.1307 Found : 182.1315

Diastereomer **RH4b**

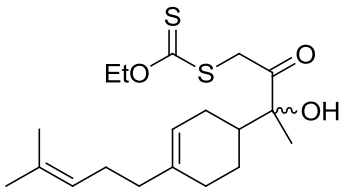
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 2.56 -2.62 (m, 1H), 2.49 (dd, *J*= 16.2, 6.0 Hz, 1H), 2.10- 2.25 (m, 4H), 1.60-1.82 (m, 2H), 1.71 (s, 1H), 1.23-1.41 (m, 2H), 1.40 (s, 3H), 0.88 (d, *J*= 6.9Hz, 3H), 0.77-0.90 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 217.1, 77.7, 42.2, 38.0, 37.9, 35.9, 33.4, 27.9, 26.9, 26.4, 19.6.

IR (ν, cm^{-1}, CCl_4) 3528, 1741, 1709.

HRMS (EI) Calcd. for $C_{11}H_{18}O_2$: 182.1307 Found : 182.1315

_O_-Ethyl _S_-3-hydroxy-3-(4-(4-methylpent-3-enyl)cyclohex-3-enyl)-2-oxobutyl carbonodithioate **V-2**

	$C_{19}H_{30}O_3S_2$ M= 370.6 g.mol^{-1}

Following general procedure **V-A**, the reaction was carried out using 1-(4-(4-methylpent-3-enyl)cyclohex-3-enyl)ethanone[28] **V-1** (7.5 mmol 1.55 g). The adduct obtained was transformed following general procedure **V-B** to give the crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford xanthate **V-2** (2.14 g, 77% over 3 steps) as a yellow oil as a mixture of two epimers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.46-5.48 (m, 0.5H), 5.35-5.37 (m, 0.5H), 5.11-5.35 (m, 1H), 4.70 (q, *J*= 7.1 Hz, 1H), 4.69 (q, *J*= 7.1 Hz, 1H), 4.31-4.44 (m, 2H), 3.31 (brs, 1H), 1.94-2.11 (m, 9H), 1.72 (s, 3H), 1.64 (s, 3H), 1.35-1.40 (m, 2H), 1.52 (s, 3H), 1.47 (t, *J*= 7.1 Hz, 1.5H), 1.48 (t, *J*= 7.1 Hz, 1.5H).

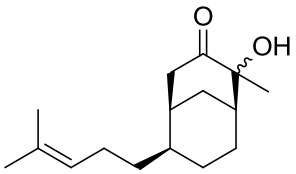
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.4, 213.3, 207.5, 207.5, 137.7, 137.6, 131.3, 131.5, 124.2, 119.6, 119.3, 81.3, 81.0, 71.0, 70.9, 42.1, 41.4, 41.1, 37.5, 37.5, 28.7, 28.7, 26.5, 26.5, 25.9, 25.8, 25.0, 23.8, 22.3, 17.8, 13.8.

IR (ν, cm^{-1}, CCl_4) 3618, 3505, 3155, 2983, 2914, 1816, 1795, 1717, 1469, 1383, 1228, 1097, 1054.

HRMS (EI) Calcd. for $C_{19}H_{30}O_3S_2$: 370.1637 Found : 370.1630

[28] The ketone was prepared from methylvinyl ketone and myrcene in one step according to literature procedures: Veselovsky, V. V.; Gybin, A. S.; Lozanova, A. M.; Moiseenkov, A. M.; Smit, W. A. *Tetrahedron Lett.* **1988**, *29*, 175.

2-Hydroxy-2-methyl-6-(4-methylpent-3-enyl)bicyclo[3.3.1]nonan-3-one V-3

	$C_{16}H_{26}O_2$ M= 250.4 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **V-2** (741 mg, 2.0 mmol) and needed 10 mol % of DLP to go to completion (3 h). Crude xanthate was then transformed following general procedure **V-C**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford α-hydroxyketone **V-3** (351 mg, 70% over 2 steps) as a mixture of two epimers in a 1:1 ratio and as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.06 (t, *J*= 7.1 Hz, 1H), 3.83 (s, 0.5H), 2.78 (dd, *J*= 16.1, 6.1 Hz, 0.5H), 1.89-2.53 (m, 3.5H), 1.67 (s, 3H), 1.23-1.66 (m, 9H), 1.57 (s, 3H), 1.41 (s, 1.5H), 1.32 (s, 1.5H), 0.77-0.89 (m, 2H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

Diastereomer **V-3a**

212.2, 131.6, 124.4, 77.3, 42.4, 40.3, 38.3, 35.5, 34.2, 30.8, 28.0, 25.8, 25.8, 25.4, 22.1, 17.7.

Diastereomer **V-3b**

217.3, 131.5, 124.3, 77.8, 42.7, 40.5, 38.2, 36.2, 34.1, 33.4, 27.9, 26.4, 25.7, 25.3, 25.1, 17.6.

IR (ν, cm^{-1}, CCl_4): 3598, 3504, 2930, 2858, 1709, 1646, 1461, 1415, 1376, 1316, 1239, 1166, 1126.

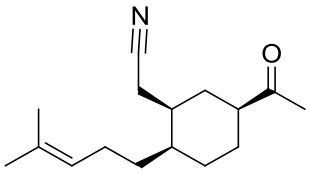
HRMS (EI): Calcd. for $C_{16}H_{26}O_2$: 250.1933 Found : 250.1933

GENERAL PROCEDURE V-D : CLEAVAGE OF HYDROXYCETONES

To a solution of **hydroxyketone** (1.0 equiv) in **ethanol** (1.25 mL/mmol), was added **water** (225 µL/ mmol), **hydroxylamine hydrochloride** (3.0 equiv), and **sodium hydroxide** (8.0 equiv). After being refluxed for 3 h, the mixture was then partitioned between ethyl acetate and water. The aqueous layer was then extracted with ethyl acetate, and the combined organic layers were washed with water, brine, dried over $MgSO_4$ and the solvent were removed *in vacuo*, giving oxime.

The crude product was then dissolved in **pyridine** (1.2 mL/mmol), and **methanesulfonyl chloride** (2.0 equiv) was added. The reaction mixture was stirred overnight at 20 °C. Water was then added, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford nitrile.

2-(5-Acetyl-2-(4-methylpent-3-enyl)cyclohexyl)acetonitrile **V-4**



$C_{16}H_{25}NO$
M= 247.4 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using hydroxyketone **V-3** (87 mg, 0.35 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford nitrile **V-4** (65 mg, 75% over 2 steps) as a colorless oil.

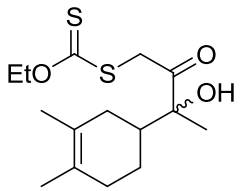
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.07 (t, *J*= 7.1 Hz, 1H), 2.37-2.45 (m, 1H), 2.28 (dd, *J*= 7.9, 2.4 Hz, 2H), 2.15 (s, 3H), 1.71-2.06 (m, 7H), 1.68 (s, 3H), 1.59 (s, 3H), 1.29-1.42 (m, 4H), 1.08-1.16 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 210.8, 132.2, 123.7, 118.8, 50.8, 37.2, 35.0, 28.2, 28.2, 27.8, 25.7, 25.7, 24.1, 22.0, 21.8, 17.7.

IR (ν, cm^{-1}, CCl_4): 2936, 2863, 2248, 1713, 1451, 1427, 1376, 1353, 1162, 1176.

HRMS (EI): Calcd. for $C_{16}H_{25}NO$: 247.1936 Found : 247.1940

_S_-3-(3,4-Dimethylcyclohex-3-enyl)-3-hydroxy-2-oxobutyl _O_-ethyl carbonodithioate **V-6**

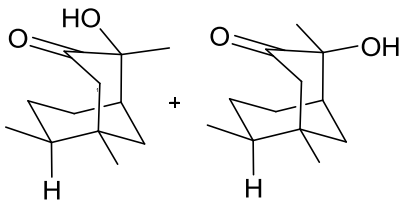
	$C_{15}H_{24}O_3S_2$ M= 316.5 g.mol^{-1}

Following general procedure **V-A**, the reaction was carried out using 1-(3,4-dimethylcyclohex-3-enyl)ethanone[29] **V-5** (6.09 g, 40 mmol). The adduct obtained was transformed following general procedure **V-B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford xanthate **V-6** (8.48 g, 67% over 3 steps) as a yellow oil and as a mixture of two epimers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.65 (q, *J*= 7.1 Hz, 1H), 4.64 (q, *J*= 7.1 Hz, 2H), 4.28-4.38 (m, 2H), 3.24 (brs, 1H), 1.89-2.06 (m, 5H), 1.63, 1.60, 1.56 (3s, 6H), 1.38-1.50 (m, 1H), 1.47, 1.40 (2s, 3H), 1.42 (t, *J*= 7.1 Hz, 3H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	213.3, 213.2, 207.3, 207.3, 125.5, 125.4, 124.5, 124.2, 81.2, 80.9, 70.9, 70.9, 42.0, 41.9, 41.7, 32.1, 31.9, 31.2, 24.0, 23.3, 23.1, 22.5, 19.2, 19.1, 18.7, 13.7
IR (ν, cm^{-1}, CCl_4)	3598, 3513, 2979, 2937, 1711, 1459, 1375, 1221, 1113, 1053.
HRMS (EI)	Calcd. for $C_{15}H_{24}O_3S_2$: 316.1167 Found : 316.1160

[29] The ketone was prepared from but-3-en-2-one and 2,3-dimethylbuta-1,3-diene in one step according to literature procedures: Kreiser, W.; Haumesser, W.; Thomas, A. F. *Helvitica Chem. Acta* **1974**, *57*, 164.

4-Hydroxy-1,4,8-trimethylbicyclo[3.3.1]nonan-3-one **V-7**

 **V-7a** **V-7b**	$C_{12}H_{20}O_2$ M= 196.3 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **V-6** (870 mg, 2.75 mmol) and needed 10 mol % of DLP to go to completion (3 h). Crude xanthate was then transformed following general procedure **V-C**. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 9:1) to afford the α-hydroxyketone **V-7** (372 mg, 69% over 2 steps) as a mixture of two diastereomers in a 1:1 ratio of the two epimers and as two colorless oils. The diastereomers **V-7a** and **V-7b** were separated at this step and mixed together after characterization for the next step.

Diastereomer **V-7a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 2.43 (d, *J*= 16.2 Hz, 1H), 2.27-2.35 (m, 2H), 2.07-2.10 (m, 1H), 1.77-1.71 (m, 1H), 1.49-1.56 (m, 1H), 1.33-1.42 (m, 3H), 1.31 (s, 3H), 0.96 (s, 3H), 0.83 (d, *J*= 6.6 Hz, 3H), 0.80 -0.86 (m, 2H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.2, 75.5, 44.3, 42.8, 41.2, 38.6, 38.1, 28.8, 28.5, 28.0, 21.6, 15.6.

IR (ν, cm^{-1}, CCl_4): 3598, 3487, 2955, 928, 2870, 1711, 1456, 1443, 1375, 1318, 1215, 1157, 1123, 1073, 1025.

HRMS (EI): Calcd. for $C_{12}H_{20}O_2$: 196.1463 Found : 196.1460

Diastereomer **V-7b**

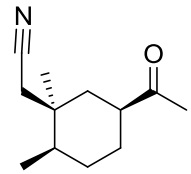
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.80 (s, 1H), 2.50 (dd, *J*= 16.1, 3.3 Hz, 1H), 2.20- 2.23 (m, 1H), 2.15 (d, *J*= 16.1 Hz, 1H), 1.96-2.01 (m, 1H), 1.62 (dt, *J*= 13.8, 3.2 Hz, 1H), 1.33-1.44 (m, 3H), 1.38 (s, 3H), 0.98 (s, 3H), 0.83 (d, *J*= 6.6 Hz, 3H), 0.80-0.86 (m, 2H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.2, 75.5, 44.3, 42.8, 41.2, 38.6, 38.1, 28.8, 28.5, 28.0, 21.6, 15.6.

IR (ν, cm^{-1}, CCl_4) 3507, 2959, 2927, 2873, 1707, 1462, 1453, 1373, 1241, 1162, 1147, 1125, 1106, 1024.

HRMS (EI) Calcd. for $C_{12}H_{20}O_2$: 196.1463 Found : 196.1460

5-Acetyl-1,2-dimethylcyclohexyl)acetonitrile **V-8**

	$C_{12}H_{19}NO$ M= 193.3 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using the hydroxyketone **V-7** (90 mg, 0.47 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford nitrile **V-8** (75 mg, 83% over 2 steps) as a colorless oil.

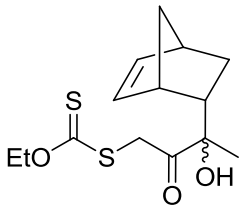
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 2.55 (tt, *J*= 11.7, 4.0 Hz, 1H), 2.13-2.26 (m, 2H), 2.13 (s, 3H), 1.66-1.85 (m, 3H), 1.40-1.53 (m, 4H), 1.20 (s, 3H), 0.94 (d, *J*= 7.1 Hz, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 211.1, 117.9, 46.6, 35.6, 34.7, 33.3, 29.9, 28.1, 28.1, 24.5, 22.3, 14.6.

IR (ν, cm^{-1}, CCl_4) 2960, 2874, 2249, 1712, 1558, 1541, 1455, 1434, 1359, 1320, 1302, 1175, 1127.

HRMS (EI) Calcd. for $C_{12}H_{19}NO$: 193.1467 Found : 193.1460

_S_-(_S_)-3-((1_S_,2_S_,4_S_)-Bicyclo[2.2.1]hept-5-en-2-yl)-3-hydroxy-2-oxobutyl O-ethyl carbonodithioate **V-10**

	$C_{14}H_{20}O_3S_2$ M= 300.4 g.mol^{-1}

Following general procedure **V-A**, the reaction was carried out using endo-2-acetyl-5-norbornene **V-9** (5.4 mL, 40 mmol). The adduct obtained was transformed following general procedure **V-B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether/ether 9:1) to afford xanthate **V-10** (7.57 g, 63% over 3 steps) as a yellow oil and as a mixture of two epimers in a 9:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 6.28-6.30 (m, 0.1H), 6.25-6.28 (m, 0.9H), 6.08-6.10 (m, 0.9H), 6.06-6.09 (m, 0.1H), 4.57-4.65 (m, 2H), 4.21-4.42 (m, 2H), 3.04 (brs, 1H), 2.82 (brs, 1H), 2.57-2.67 (m, 1H), 2.56 (s, 0.1H), 2.45 (s, 0.9H), 1.93 (ddd, *J*= 11.8, 9.6, 3.9 Hz, 0.1H), 1.76 (ddd, *J*= 11.7, 9.6, 3.9 Hz, 0.9H), 1.30-1.40 (m, 6H), 1.24-1.28 (m, 2H), 1.12 (ddd, *J*= 11.8, 5.1, 2.3 Hz, 0.1H), 0.92 (ddd, *J*= 11.7, 5.3, 2.4 Hz, 0.9H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

Major diastereomer

213.4, 207.3, 138.5, 132.2, 80.9, 70.4, 50.3, 45.6, 43.8, 43.1, 42.4, 27.6, 25.8, 13.7.

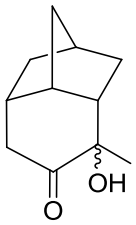
Minor diastereomer

213.4, 208.0, 139.2, 131.3, 81.1, 70.6, 51.4, 45.9, 44.4, 43.1, 42.2, 27.0, 26.3, 13.7.

IR (ν, cm^{-1}, CCl_4) 3558, 3311, 2980, 2901, 2873, 1716, 1445, 1367, 1263, 1227, 1114, 1053.

HRMS (EI) Calcd. for $C_{14}H_{20}O_3S_2$: 300.0854 Found : 300.0869

5-Hydroxy-5-methyloctahydro-6*H*-2,4-methanoinden-6-one **V-11**

	$C_{11}H_{16}O_2$ M= 180.2 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **V-10** (901 mg, 3.0 mmol), and needed 10 mol % of DLP to go to completion (3 h). Crude xanthate was then transformed following general procedure **V-C**. The residue was purified by silica gel column chromatography (petroleum ether/ether 9:1) to afford α-hydroxyketone **V-11** (454 mg, 84% over 2 steps) as a mixture of diastereomers in a 9:1 ratio of the two epimers at C-3 and as two colorless oils. The diastereomers **V-11a** and **V-11b** were separated at this step in order to characterize them and then combined for the next step.

Major diastereomer **V-11a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.22 (dd, *J*= 13.4, 5.8 Hz, 1H), 2.63-2.66 (m, 1H), 2.41-2.46 (m, 1H), 2.24-2.30 (m, 1H), 2.10-2.14 (m, 2H), 1.67-1.81 (m, 2H), 1.37-1.47 (m, 2H), 1.23 (s, 3H), 0.73 (ddd, *J*= 12.5, 4.2, 2.5 Hz, 1H), 0.62 (ddd, *J*= 12.9, 5.1, 2.3 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.0, 76.7, 51.3, 40.5, 40.4, 38.9, 37.7, 37.3, 36.0, 32.2, 22.4.

IR (ν, cm^{-1}, CCl_4): 3604, 3494, 2949, 2873, 1720, 1453, 1421, 1376, 1353, 1309, 1198, 1114, 1098, 1047.

HRMS (EI): Calcd. for $C_{11}H_{16}O_2$: 180.1150 Found : 180.1156

Minor diastereomer **V-11b**

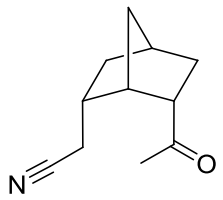
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.97 (s, 1H), 2.81 (dd, *J*= 14.2, 5.6 Hz, 1H), 2.36-2.51 (m, 4H) 2.14-2.16 (m, 1H), 1.79-1.87 (m, 1H), 1.64-1.73 (m, 1H), 1.46-1.49 (m, 2H), 1.45 (s, 3H), 0.81-0.86 (m, 1H), 0.72-0.76 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 215.4, 77.3, 51.6, 41.1, 40.9, 40.5, 38.2, 36.7, 36.4, 31.8, 26.5.

IR (ν, cm^{-1}, CCl_4) 3499, 2953, 2874, 1714, 1558, 1541, 1454, 1377, 1366, 1323, 1197, 1174, 1098.

HRMS (EI) Calcd. for $C_{11}H_{16}O_2$: 180.1150 Found : 180.1157

2-((1*S*,2*S*,4S,6*S*)-6-Acetylbicyclo[2.2.1]heptan-2-yl)acetonitrile **V-12**

	$C_{11}H_{15}NO$ M= 177.2 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using hydroxyketone **V-11** (220 mg, 1.22 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 8:2) to afford nitrile **V-12** (195 mg, 90% over 2 steps) as a colorless oil.

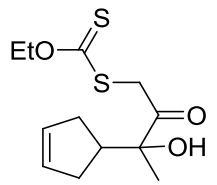
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 2.88-2.95 (m, 2H), 2.23-2.36 (m, 4H), 2.30 (s, 3H), 1.95-2.03 (m, 1H), 1.79 (ddd, *J*= 12.8, 6.2, 1.7 Hz, 1H), 1.53-1.69 (m, 3H), 0.88-0.92 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 211.1, 119.5, 54.7, 43.9, 42.8, 38.4, 37.5, 36.4, 30.2, 30.0, 19.9.

IR (ν, cm^{-1}, CCl_4) 2960, 2874, 2249, 1712, 1558, 1541, 1455, 1434, 1359, 1320, 1302, 1175, 1127.

HRMS (EI) Calcd. for $C_{11}H_{15}NO$: 177.1154 Found : 177.1155

S-3-(Cyclopent-3-enyl)-3-hydroxy-2-oxobutyl O-ethyl carbonodithioate V-17

	$C_{12}H_{18}O_3S_2$ M= 274.4 g.mol^{-1}

Following general procedure **V-A**, the reaction was carried out using 1-(cyclopent-3-enyl)ethanone **V-16** (770 mg, 7.0 mmol). The adduct obtained was transformed following general procedure **V-B** to give crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford xanthate **V-17** (1.02 g, 53% over 3 steps) as a colorless oil.

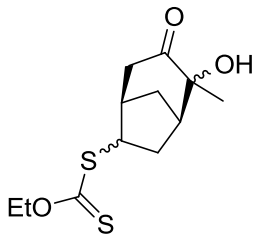
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.63-5.69 (m, 2H), 4.64 (q, *J*= 7.1 Hz, 2H), 4.30-4.41 (m, 2H), 2.73-2.82 (m, 1H), 2.47-2.51 (m, 1H), 2.25-2.37 (m, 2H), 2.04-2.29 ((m, 2H), 1.46 (s, 3H), 1.42 (t, *J*= 7.1 Hz, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.3, 206.9, 129.6, 129.5, 80.4, 71.0, 45.0, 42.0, 33.4, 33.3, 24.6, 13.8.

IR (ν, cm^{-1}, CCl_4) 3616, 3505, 3059, 2984, 2934, 2853, 1717, 1444, 1358, 1228, 1149, 1114, 1053, 1027.

HRMS (EI) Calcd. for $C_{12}H_{18}O_3S_2$: 274.0697 Found : 274.0705

2-Hydroxy-2-methylbicyclo[3.2.1]octan-3-one **V-18**



$C_{12}H_{18}O_3S_2$
M= 274.4 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **V-17** (870 mg, 2.75 mmol) and needed 10 mol % of DLP to go to completion (3 h). The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford xanthate **V-18** (551 mg, 73%) as a mixture of two diastereomers in a 10:1 ratio and as two yellow oils. The diastereomers **V-18a** and **V-18b** were separated at this step and mixed together after characterization for the next step.

Major diastereomer **V-18a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.58-4.64 (m, 2H), 3.77 (s, 1H), 3.60 (ddd, *J*= 9.1, 5.2, 1.6 Hz, 1H), 2.74 (dd, *J*= 15.7, 4.4 Hz, 1H), 2.64-2.69 (m, 2H), 2.47 (t, *J*= 5.1 Hz, 1H), 2.38 (ddd, *J*= 15.3, 9.1, 2.0 Hz, 1H), 2.06-2.10 (m, 1H), 1.92-1.97 (m, 1H), 1.49 (ddd, *J*= 15.3, 6.8, 5.2 Hz, 1H), 1.41 (t, *J*= 7.1 Hz, 3H), 1.39 (s, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.2, 213.7, 79.1, 69.7, 49.2, 47.7, 45.5, 44.6, 33.1, 29.9, 25.5, 13.8.

IR (ν, cm^{-1}, CCl_4): 3601, 3510, 2984, 2958, 2935, 2872, 1720, 1452, 1413, 1377, 1294, 1218, 1146, 1113, 1054.

HRMS (EI): Calcd. for $C_{12}H_{18}O_3S_2$: 274.0697 Found : 274.0696

Minor diastereomer **V-18b**

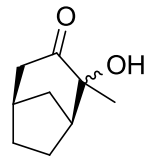
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.58-4.67 (m, 2H), 3.67 (ddd, *J*= 8.8, 5.1, 1.5 Hz, 1H), 2.94 (dd, *J*= 15.5, 4.4 Hz, 1H), 2.41-2.60 (m, 4H), 1.99 (ddd, *J*= 15.5, 8.8, 1.9, 1H), 1.65-1.76 (m, 2H), 1.41 (t, *J*= 7.1 Hz, 3H), 1.31 (s, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.0, 209.8, 77.6, 69.7, 49.8, 47.1, 46.1, 43.4, 30.8, 30.4, 21.9, 13.8.

IR (ν, cm^{-1}, CCl_4) 3512, 2985, 2937, 2877, 1717, 1452, 1419, 1372, 1361, 1340, 1295, 1219, 1145, 1112, 1053.

HRMS (EI) Calcd. for $C_{12}H_{18}O_3S_2$: 274.0697 Found : 274.0695

2-Hydroxy-2-methylbicyclo[3.2.1]octan-3-one **V-19**

	$C_9H_{14}O_2$ M= 154.2 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **V-17** (274 mg, 1.0 mmol), and needed 10 mol % of DLP to go to completion 3 h). Crude xanthate was then transformed following general procedure **V-C**. The residue was purified by silica gel column chromatography (petroleum ether/ether 9:1) to afford α-hydroxyketone **V-19** (106 mg, 69% over 2 steps) as a colorless oil.

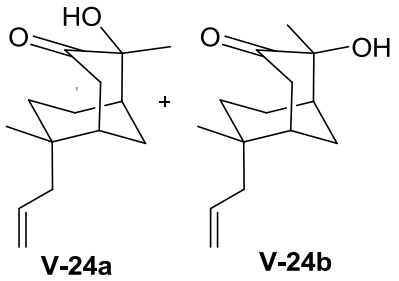
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 3.80 (s, 1H), 2.61 (ddd, *J*= 14.9, 3.5, 2.1 Hz, 1H), 2.52-2.56 (m, 1H), 2.38 (t, *J*= 5.6 Hz, 1H), 2.31 (dt, *J*= 14.9, 3.0 Hz, 1H), 2.07-2.11 (m, 1H), 1.54-1.81 (m, 4H), 1.38 (s, 3H), 1.30-1.38 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 215.2, 79.4, 48.1, 46.1, 36.9, 36.1, 28.0, 25.7, 23.7.

IR (ν, cm^{-1}, CCl_4) 3604, 3501, 2960, 2928, 2855, 1731, 1466, 1377, 1261, 1097.

HRMS (EI) Calcd. for $C_9H_{14}O_2$: 154.0994 Found : 154.0997

6-(3,3-Diethoxypropyl)-2-hydroxy-2,6-dimethylbicyclo[3.3.1]nonan-3-one **V-24**



V-24a **V-24b**

$C_{14}H_{22}O_2$
M= 222.3 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using xanthate **RH2** (303 mg, 2.0 mmol) and needed 10 mol % of DLP to go to completion (3 h). Allyltrimethylsilane (305 µL, 2.0 equiv) was added to the reaction mixture. The reaction needed 20 mol% to go to completion (6 h). The solvent was then removed *in vacuo*. To a solution of xanthate **V-23** in THF (7 mL) was added TBAF (4 mL, 4.0 mmol). The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 85:15) to afford the α-hydroxyketone **V-24** (144 mg, 32% over 3 steps) and α-hydroxyketone **V-24a** (190 mg, 32% over 3 steps) as two colorless oils. The diastereomers **V-24a** and **V-24b** were separated at this stage and mixed together after characterization for the next step.

Diastereomer **V-24a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.72-5.82 (m, 1H), 5.02-5.06 (m, 2H), 2.86 (dd, *J*= 15.9, 5.9 Hz, 1H), 2.47-2.53 (m, 1H), 2.25-2.31 (m, 1H), 2.22-2.30 (m, 1H), 1.90-1.93 (m, 1H), 1.86 (ddd, *J*= 13.9, 6.2, 3.1 Hz, 1H), 1.53-1.75 (m, 3H), 1.32 (s, 3H), 1.16-1.28 (m, 3H), 0.97 (td, *J*= 14.8, 4.8 Hz, 1H), 0.87 (s, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.0, 134.7, 117.4, 76.4, 42.4, 42.0, 40.7, 39.7, 35.7, 30.3, 25.6, 25.3, 23.5, 22.0.

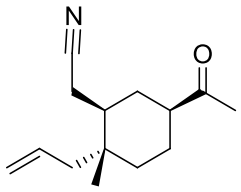
IR (ν, cm^{-1}, CCl_4): 3595, 3503, 2975, 2931, 2874, 1711, 1455, 1444, 1376, 1264, 1238, 1125, 1063.

HRMS (EI) Calcd. for $C_{14}H_{22}O_2$: 222.1620 Found : 222.1616

Diastereomer **V-24b**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	5.76 (dddd, *J*= 17.0, 10.4, 8.0, 7.0 Hz, 1H), 5.01-5.06 (m, 2H), 3.83 (s, 1H), 2.65-2.71 (m, 1H), 2.51-2.58 (m, 2H), 2.31 (dd, *J*= 13.8, 8.1 Hz, 1H), 1.91-2.21 (m, 5H), 1.44-1.50 (m, 1H), 1.40 (s, 3H), 0.87 (s, 3H), 0.98-1.25 (m, 2H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	217.0, 134.6, 117.4, 77.4, 42.5, 42.3, 40.5, 40.2, 36.0, 30.3, 27.9, 27.9, 25.5, 22.1.
IR (ν, cm^{-1}, CCl_4)	3509, 2975, 2931, 2872, 1709, 1455, 1445 1378, 1264, 1238, 1125, 1065.
HRMS (EI)	Calcd. for $C_{14}H_{22}O_2$: 222.1620 Found : 222.1622

5-Acetyl-2-allyl-2-methylcyclohexyl)acetonitrile **V-25**

	$C_{14}H_{21}NO$ M= 219.3 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using hydroxyl ketone **V-24** (233 mg, 1.0 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 85:15) to afford nitrile **V-25** (178 mg, 81% over 2 steps) as a colorless oil.

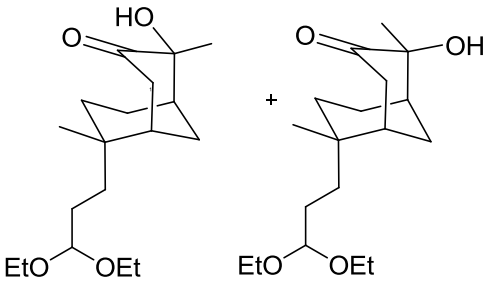
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.72-5.83 (m, 1H), 5.04-5.13 (m, 2H), 2.54 (tt, *J*= 11.6, 3.4 Hz, 1H), 2.32-2.41 (m, 2H), 2.16 (s, 3H), 1.97-2.09 (m, 3H), 1.69-1.81 (m, 2H), 1.37-1.51 (m, 4H), 0.81 (s, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 210.6, 133.1, 119.4, 118.6, 50.7, 46.0, 40.3, 36.6, 35.6, 29.0, 28.3, 23.8, 18.6, 17.8.

IR (ν, cm^{-1}, CCl_4) 3079, 2978, 2937, 2870, 2248, 1713, 1639, 1468, 1444, 1425, 1355, 1212, 1175, 1148.

HRMS (EI) Calcd. for $C_{14}H_{21}NO$: 219.1623 Found : 219.1625

6-(3,3-Diethoxypropyl)-2-hydroxy-2,6-dimethylbicyclo[3.3.1]nonan-3-one **V-26**



V-26a **V-26b**

$C_{18}H_{32}O_4$
M= 312.4 g.mol^{-1}

Following general procedure **III-C**, the reaction was carried out using xanthate **RH2** (605 mg, 2.0 mmol) and needed 10 mol % of DLP to go to completion (3 h). Acrolein diethyl acetal (475µL, 2.0 equiv) was added to the reaction mixture and the reaction needed 15 mol% to go to completion (4 h 30 min). Crude xanthate was then transformed following general procedure **V-C**. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9:1) to afford α-hydroxyketone **V-26a,b** (312 mg, 50% over 3 steps) as a mixture of two epimers in a 1:1 ratio and as two colorless oils. The diastereomers **V-26a** and **V-26b** were separated at this stage and mixed together after characterization for the next step.

Diastereomer **V-26a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.45 (t, *J*= 5.5 Hz, 1H), 3.59-3.68 (m, 2H), 3.39-3.45 (m, 2H), 2.85 (dd, *J*= 15.9, 6.0 Hz, 1H), 2.48-2.53 (m, 1H), 2.24-2.28 (m, 1H), 1.81-2.04 (m, 4H), 1.49-1.59 (m, 4H), 1.32 (s, 3H), 1.20 (t, *J*= 7.3 Hz, 3H), 1.20 (t, *J*= 7.3 Hz, 3H), 1.18-1.39 (m, 3H), 0.84 (s, 3H), 0.74-0.87 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.0, 103.4, 76.5, 61.0, 60.8, 42.1, 40.7, 39.7, 35.1, 32.5, 30.7, 27.8, 25.6, 25.5, 23.6, 22.0, 15.4.

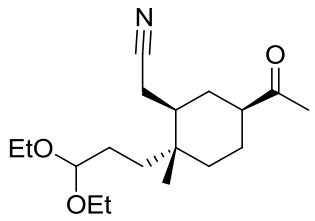
IR (ν, cm^{-1}, CCl_4): 3598, 3502, 2976, 2931, 2876, 1710, 1465, 1455, 1444, 1417, 1375, 1343, 1238, 1126, 1063.

HRMS (EI) Calcd. for $C_{18}H_{32}O_4$: 312.2301 Found : 312.2292

Diastereomer **V-26b**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	4.45 (t, *J*= 5.5 Hz, 1H), 3.61-3.66 (m, 2H), 3.41-3.44 (m, 2H), 2.65-2.71 (m, 1H), 2.54 (dd, *J*= 16.0, 5.8 Hz, 1H), 2.16- 2.19 (m, 1H), 2.06-2.11 (m, 1H), 1.90-1.96 (m, 3H), 1.46-1.65 (m, 4H), 1.40 (s, 3H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.12-1.26 (m, 3H), 0.84 (s, 3H), 0.78-0.90 (m, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	217.0, 103.3, 77.4, 61.0, 60.8, 43.3, 40.4, 40.2, 35.2, 32.5, 30.5, 28.0, 27.9, 27.7, 25.4, 22.1, 15.3.
IR (ν, cm^{-1}, CCl_4)	3509, 2975, 2930, 2875, 1709, 1467, 1455, 1444, 1421, 1376, 1344, 1241, 1124, 1063.
HRMS (EI)	Calcd. for $C_{18}H_{31}O_3$: 295.2273 Found : 295.2275

5-Acetyl-2-allyl-2-methylcyclohexyl)acetonitrile **V-27**

	$C_{18}H_{31}NO_3$ M= 309.4 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using hydroxyketone **V-26** (222 mg, 0.71 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 8:2) to afford nitrile **V-27** (154 mg, 70% over 2 steps) as a yellow oil.

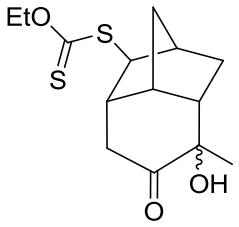
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 4.42 (t, *J*= 5.4 Hz, 1H), 3.58-3.66 (m, 2H), 3.45-3.52 (m, 2H), 2.52 (dd, *J*= 16.7, 3.4 Hz, 1H), 2.32-2.40 (m, 1H), 2.16 (s, 3H), 1.97-2.09 (m, 2H), 1.65-1.74 (m, 4H), 1.48-1.58 (m, 2H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.20 (t, *J*= 7.4 Hz, 3H), 1.18-1.29 (m, 4H), 0.78 (s, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 210.6, 119.5, 103.1, 61.4, 61.2, 50.7, 40.9, 36.3, 36.1, 34.7, 29.0, 28.2, 27.2, 23.8, 18.7, 17.6, 15.3.

IR (ν, cm^{-1}, CCl_4) 2976, 2931, 2873, 2249, 1714, 1467, 1444, 1375, 1354, 1127, 1062.

HRMS (EI) Calcd. for $C_{18}H_{31}NO_3$: 309.2304 Found : 309.2300

_O_-Ethyl _S_-(5-hydroxy-5-methyl-6-oxooctahydro-1_H_-2,4-methanoinden-1-yl) dithiocarbonate **V-22**

	$C_{14}H_{20}O_3S_2$ M= 300.4 g.mol^{-1}

Following general procedure **III-A**, the reaction was carried out using the xanthate **V-10** (7.00 g, 23.3 mmol) and needed 10 mol% of DLP to go to completion (3 h). The residue was purified by silica gel column chromatography (petroleum ether/ether 85:15) to afford the xanthate **V-22** (6.30 g, 90%) as a mixture of two diastereomers in a 9:1 ratio and as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 4.55-4.68 (m, 2H), 3.24 (dd, *J*= 13.8, 5.8 Hz, 0.9H), 3.05-3.08 (m, 1H), 2.83 (dd, *J*= 14.7, 6.2 Hz, 0.1H) 2.76-2.78 (m, 1H) 2.30-2.40 (m, 4H), 1.87-1.95 (m, 1H), 1.64-1.73 (m, 1H), 1.68-1.71 (m, 1H), 1.41 (t, *J*= 7.1 Hz, 3H), 1.42, 1.27 (2s, 3H), 1.20-1.25 (m, 1H), 1.03 (ddd, *J*= 14.1, 4.7, 2.7 Hz, 0.1H), 0.83 (ddd, *J*= 14.1, 4.7, 2.7, 0.9H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

Major diastereomer **V-22a**

213.6, 210.9, 76.9, 69.7, 55.7, 50.1, 44.7, 43.8, 39.0, 38.9, 38.0, 31.3, 22.4, 13.8.

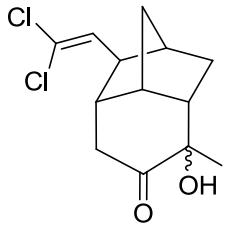
Minor diastereomer **V-22b**

213.2, 210.9, 76.9, 69.7, 55.7, 50.1, 44.7, 43.8, 39.0, 38.9, 38.0, 31.3, 22.4, 13.8.

IR (ν, cm^{-1}, CCl_4) 3603, 3503, 2978, 2958, 2900, 2877, 1722, 1453, 1421, 1377, 1294, 1215, 1113, 1061, 1018.

HRMS (EI) Calcd. for $C_{14}H_{20}O_3S_2$: 300.0854 Found : 300.0869

1-(2,2-Dichlorovinyl)-5-hydroxy-5-methyloctahydro-6*H*-2,4-methanoinden-6-one **V-29**



$C_{13}H_{16}Cl_2O_2$
M= 275.2 g.mol^{-1}

A solution of the xanthate **V-22** (601 mg, 2.0 mmol) and dichlorovinyl ethyl sulfone (756 mg, 4.0 mmol, 2.0 equiv.) in chlorobenzene (2 mL) was heated to reflux under N_2 atmosphere for 10 min. 3 drops of DTBP were added to the solution at intervals of 4 h. After refluxing for 12 h, the reaction mixture was allowed to cool to 20 °C. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ether 7:3) to afford the dichlorovinyl adduct **V-29** (336 mg, 61%) as a mixture of diastereomers in a 9:1 ratio and as two colorless oils. The diastereomers **V-29a** and **V-29b** were separated at this step and mixed together after characterization for the next step.

Major diastereomer **V-29a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.71 (d, *J*= 9.0 Hz, 1H), 3.22 (dd, *J*= 13.7, 5.9 Hz, 1H), 2.71-2.75 (m, 1H), 2.27-2.35 (m, 2H), 2.19-2.23 (m, 1H), 2.07 (d, *J*= 4.5 Hz, 1H), 2.00 (ddd, *J*= 9.0, 4.1, 1.5 Hz, 1H), 1.77-1.85 (m, 1H), 1.58-1.61 (m, 1H), 1.42-1.45 (m, 1H), 1.26 (s, 3H), 0.73 (ddd, *J*= 13.4, 5.1, 2.5 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 211.4, 133.6, 119.6, 76.8, 50.5, 48.6, 46.4, 42.7, 39.7, 39.0, 38.2, 31.8, 22.4.

IR (ν, cm^{-1}, CCl_4): 3604, 3497, 2958, 1716, 1646, 1615, 1455, 1421, 1377, 1114, 1068.

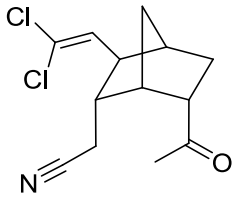
HRMS (EI): Calcd. for $C_{13}H_{16}Cl_2O_2$: 274.0527 Found : 274.0527

Minor diastereomer **V-29b**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.72 (d, *J*= 9.1 Hz, 1H), 3.96 (s, 1H), 2.84 (dd, *J*= 14.6, 6.0 Hz, 1H), 2.59-2.55 (m, 2H), 2.41-2.47 (m, 1H), 2.22-2.24 (m, 1H), 2.06 (d, *J*= 4.4 Hz, 1H), 1.99 (ddd, *J*= 9.0, 4.2, 1.4 Hz, 1H), 1.77 (ddd, *J*= 13.8, 2.6, 4.6 Hz, 1H), 1.58-1.62 (m, 1H), 1.50 (dd, *J*= 10.4, 1.3 Hz, 1H), 1.46 (s, 3H), 0.95 (ddd, *J*= 13.8, 4.6, 2.6 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	214.5, 133.4, 119.9, 77.3, 50.8, 48.9, 46.8, 42.2, 41.2, 39.9, 38.6, 31.5, 26.6.
IR (ν, cm^{-1}, CCl_4)	3501, 2956, 2881, 1715, 1644, 1614, 1570, 1455, 1339, 1139.
HRMS (EI)	Calcd. for $C_{13}H_{16}Cl_2O_2$: 274.0527 Found : 274.0515

2-((1*S*,2S,3*S*,4*S*,6*S*)-6-Acetyl-3-(2,2-dichlorovinyl)bicyclo[2.2.1]heptan-2-yl)acetonitrile **V-30**

	$C_{13}H_{15}Cl_2NO$ M= 272.2 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using hydroxyketone **V-29** (210 mg, 0.81 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 85:15) to afford nitrile **V-30** (165 mg, 75% over 2 steps) as a colorless oil.

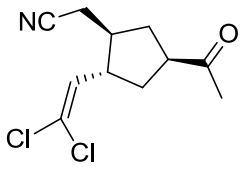
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.63 (d, *J*= 9.5 Hz, 1H), 2.97-2.99 (m, 2H), 2.44 (dd, *J*= 17.4, 6.3 Hz, 1H), 2.35 (dd, *J*= 17.4, 10.7 Hz, 1H), 2.36 (s, 3H), 2.15-2.23 (m, 2H), 1.93-2.05 (m, 2H), 1.58-1.74 (m, 3H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 210.8, 132.1, 120.9, 118.8, 53.6, 48.9, 46.7, 43.9, 43.4, 40.7, 30.3, 30.1, 18.6.

IR (ν, cm^{-1}, CCl_4) 2962, 2928, 2885, 2250, 1712, 1616, 1467, 1455, 1434, 1350, 1194, 1175, 1167.

HRMS (EI) Calcd. for $C_{13}H_{15}Cl_2NO$: 271.0531 Found : 271.0527

2-(4-Acetyl-2-(2,2-dichlorovinyl)cyclopentyl)acetonitrile **V-32**

	$C_{11}H_{13}ClNO$ M= 246.1 g.mol^{-1}

A solution of xanthate **V-22** (162 mg, 0.67 mmol) and dichlorovinyl ethyl sulfone (253 mg, 1.34 mmol, 2.0 equiv.) in chlorobenzene (670 µL) was heated to reflux under N_2 atmosphere for 10 min. 3 drops of DTBP was added to the solution at intervals of 4 h. After refluxing for 12 h, the reaction mixture was allowed to cool to 20 °C. The solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether /ether 8:2) to afford the dichlorovinyl adduct **V-31** (100 mg, 60%) as a mixture of two epimers in a 10:1 ratio of and as a colorless oil.

Following general procedure **V-D**, the reaction was carried out using hydroxyketone **V-31** (86 mg, 0.34 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 8:2) to afford nitrile **V-32** (58 mg, 69% over 2 steps) as a colorless oil.

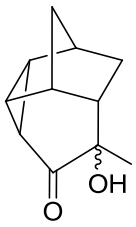
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.69 (d, *J*= 9.5 Hz, 1H), 3.09 (dtd, *J*= 10.3, 8.4, 4.5 Hz, 1H), 2.57-2.66 (m, 1H), 2.53 (dd, *J*= 16.9, 4.8 Hz, 1H), 2.34 (dd, *J*= 16.9, 8.4 Hz, 1H), 2.25-2.37 (m, 2H), 2.19 (s, 3H), 1.97-2.07 (m, 1H), 1.63-1.76 (m, 2H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 208.5, 130.3, 122.7, 118.1, 49.2, 45.1, 43.1, 38.9, 33.4, 28.8, 20.6.

IR (ν, cm^{-1}, CCl_4) 2934, 2873, 2251, 1716, 1621, 1455, 1424, 1361, 1327, 1154, 1063.

HRMS (EI) Calcd. for $C_{11}H_{13}ClNO$: 245.0374 Found : 245.0383

_O_-Ethyl _S_-(5-hydroxy-5-methyl-6-oxooctahydro-1_H_-2,4-methanoinden -1-yl) dithiocarbonate[30] **V-35**

	$C_{11}H_{14}O_2$ M= 178.2 g.mol^{-1}

A stirred solution of xanthate **V-22** (601 mg, 2.0 mmol) and ethyl 2-bromo-2-methylpropionate **V-33** (1.96 g, 10.0 mol, 5.0 equiv) in chlorobenzene (28 mL) was refluxed for 15 min under a nitrogen flow. Dicumyl peroxide (272 mg, 20 mol%) was then added and additional dicumyl peroxide (20 mol %) was added every 2 h. The reaction needed 140 mol% of dicumyl peroxide to go to completion. The reaction mixture was then cooled to 20 °C and evaporated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 8:2) to afford the corresponding bromide **V-34** (368 mg, 71%) as a mixture of epimers in a 9:1 ratio as a yellow oil.

To a stirred solution of bromide **V-34** (500 mg, 1.4 mmol) in THF (10 mL) was added *t*-BuOK at 0 °C (340 mg, 3.0 mmol, 2.2 equiv). The reaction mixture was allowed to warm to 20 °C and stirred for 2 h. Saturated NH_4Cl and ether were added to quench the reaction. The aqueous layer was then extracted with ether, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and then concentrated *in vacuo.* The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 7:3) to afford tetracycle **V-35a** (192 mg, 77%) as a white solid and the tetracycle **V-35b** a colorless oil (20 mg, 8%). The diastereomers **V-35a** and **V-35b** were separated at this step and mixed together after characterization for the next step.

Major diastereomer **V-35a**

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	2.64-2.67 (m 1H), 2.40-2.49 (m, 1H), 2.18-2.34 (m, 4H), 1.99-2.03 (m, 1H), 1.71-1.79 (m, 2H), 1.29 (s, 3H), 0.81-0.86 (m, 1H), 0.64 (td, *J*= 12.9, 3.0 Hz, 1H).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	209.7, 72.5, 54.4, 42.7, 38.9, 38.0, 37.8, 36.1, 35.9, 30.9, 22.3.
IR (ν, cm^{-1}, CCl_4)	3597, 3474, 3035, 2956, 2878, 1701, 1454, 1373, 1315, 1225, 1119, 1100, 1056.

[30] Barbier, F.; Pautrat, F.; Quiclet-Sire, B.; Zard, S. Z. *Synlett* **2002**, 811.

HRMS (EI) Calcd. for $C_{11}H_{14}O_2$: 178.0994 Found : 178.0990

TF (°C) 99-100 °C

Minor diastereomer **V-35b**

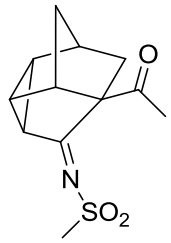
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 3.24 (dd, *J*= 13.4, 5.8 Hz, 1H), 2.65-2.67 (m 1H), 2.43-2.48 (m, 1H), 2.27-2.32 (m, 1H), 2.14-2.18 (m, 2H), 1.69-1.83 (m, 2H), 1.41-1.50 (m, 2H), 1.24 (s, 3H), 0.76 (ddd, *J*= 12.4, 4.1, 2.5 Hz, 1H), 0.65 (ddd, *J*= 12.9, 5.1, 2.3 Hz, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 212.6, 51.4, 40.6, 40.4, 38.9, 37.7, 37.3, 36.0, 32.3, 22.5.
The quaternary carbon of the alcool cannot be seen because of the carbons of the chloroforme.

IR (ν, cm^{-1}, CCl_4) 3604, 2952, 2873, 1721, 1453, 1376, 1264, 1198, 114, 1088, 1046.

HRMS (EI) Calcd. for $C_{11}H_{14}O_2$: 178.0994 Found : 178.0999

6-Acetyltricyclo[3.2.1.0^{2,4}]octane-3-carbonitrile **V-38**

	$C_{12}H_{15}NO_3S$ M= 253.3 g.mol^{-1}

Following general procedure **V-D**, the reaction was carried out using hydroxyketone **V-35** (178 mg, 1.0 mmol). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 7:3) to afford imine **V-38** (152 mg, 60% over 2 steps) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 3.14 (ddd, *J*= 7.0, 4.9, 2.1 Hz, 1H), 3.08-3.10 (m, 1H), 3.06 (s, 3H), 2.88 (dt, *J*= 7.5, 4.5 Hz, 1H), 2.64-2.67 (m, 1H), 2.44-2.49 (m, 1H), 2.28 (s, 3H), 2.15-2.19 (m, 1H), 2.06-2.08 (m, 1H), 1.73 (ddd, *J*= 12.3, 2.3, 1.8 Hz, 1H), 1.54-1.57 (m, 1H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 203.5, 196.1, 65.6, 49.2, 46.3, 44.1, 42.0, 40.9, 39.3, 37.6, 36.4, 28.5.

IR (ν, cm^{-1}, CCl_4) 3054, 2973, 2876, 1713, 1626, 1469, 1449, 1319, 1285, 1238, 1213, 1150, 1073.

HRMS (EI) Calcd. for $C_{12}H_{15}NO_3S$: 253.0773 Found : 253.0769

D. Chapitre VI : Approche à la Synthèse des Sesquiterpènes de type eudesmane

La numérotation des carbones et des hydrogènes de chaque composé décrit dans ce chapitre correspondant à la nomenclature des composés de type eudesmane.

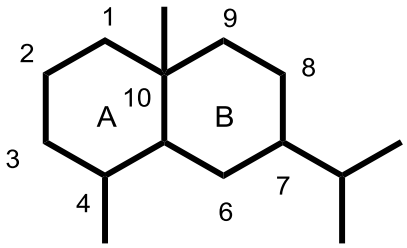
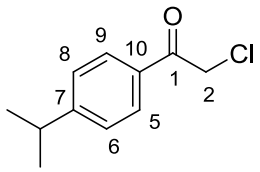


Figure 1 *– Structure des composés de type eudesmane*

2-Chloro-1-(4-*iso*propylphenyl)ethanone **VI-4**

	$C_{11}H_{13}ClO$ M = 196.7 g.mol^{-1}

To a solution of aluminium trichloride (1.73 g, 58 mmol, 1.4 equiv) in carbone disulfide (7 mL) was added dropwise at -10 °C a solution of cumene (5.0 g, 42 mmol, 1.0 equiv) in 2-choroacetylchloride (7.06 g, 63 mmol, 1.5 equiv). The reaction mixture was allowed to warm at 20 °C and was stirred overnight. Ice and concentrated chlorhydric acid (6 mL) were then added carefully, and the mixture was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford α-chloroketone **VI-4** (8.1 g, 98%) as a yellow oil.

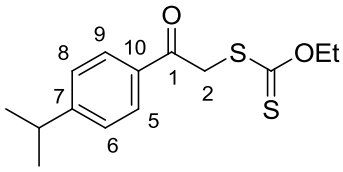
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.89 (d, *J*= 8.2 Hz, 2H, C***H***-8, C***H***-6), 7.35 (d, *J*= 8.2 Hz, 2H, C***H***-9, C***H***-5), 4.68 (s, 2H, C***H*****$_2$**-2), 2.93-3.03 (m, 1H, C***H***-$(CH_3)_2$), 1.28 (d, *J*= 6.9 Hz, 6H, (C***H*****$_3$**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 190.7 (C-1), 155.7 (C-7), 132.2 (C-10), 128.8 (C-9, C-5), 126.9 (C-8, C-6), 45.8 (C-2), 34.3 (***C***H-$(CH_3)_2$), 23.6 ($(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4) 2963, 2928, 2856, 1709, 1688, 1607, 1464, 1282, 1056.

HRMS (EI) Calcd. for $C_{11}H_{13}ClO$: 196.0655 Found : 190.0656

***O*-Ethyl *S*-2-(4-isopropylphenyl)-2-oxoethyl carbonodithioate** **VI-3**



$C_{14}H_{18}O_2S_2$
M= 282.4 $g.mol^{-1}$

Chloro ketone **VI-4** (8.0 g, 40.7 mmol, 1.0 equiv) was stirred in acetone (60 mL) under nitrogen at 0 °C, and potassium *O*-ethyl xanthate (7.82 g, 48.8 mmol, 1.2 equiv) was then added. After 1 h at 0 °C, the mixture was partitioned between ether and water. Brine was then added to the aqueous layer, and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and the solvent were removed *in vacuo* to afford crude xanthate. The residue was purified by silica gel column chromatography (petroleum ether /ether 9:1) to afford xanthate **VI-3** (11.3 g, 98%) as a yellow oil.

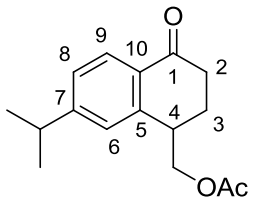
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.96 (d, *J*= 8.3 Hz, 2H, C***H***-8, C***H***-6), 7.35 (d, *J*= 8.3 Hz, 2H, C***H***-9, C***H***-5), 4.65 (s, 2H, C$\boldsymbol{H_2}$-2), 4.63 (q, *J*= 7.1 Hz, 2H, OC$\boldsymbol{H_2}$), 2.93-3.05 (m, 1H, C***H***-$(CH_3)_2$), 1.40 (t, *J*= 7.1 Hz, 3H, $OCH_2C\boldsymbol{H_3}$), 1.28 (d, *J*= 6.9 Hz, 6H, $(C\boldsymbol{H_3})_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.4 (C=S), 191.9 (C-1), 155.4 (C-7), 133.7 (C-10), 128.7 (C-9, C-5), 126.9 (C-8, C-6), 70.6 (OCH_2), 43.5 (C-2), 34.3 (***C***H-$(CH_3)_2$), 23.6 ($(CH_3)_2$), 13.7 ($OCH_2\boldsymbol{C}H_3$).

IR (ν, cm^{-1}, CCl_4) 2964, 2928, 2872, 1686, 1607, 1463, 1417, 1288, 1229, 1149, 1113, 1054.

HRMS (EI) Calcd. for $C_{14}H_{18}O_2S_2$: 282.0748 Found : 282.0749

(7-Isopropyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate **VI-2a**

	$C_{16}H_{20}O_3$ M= 260.3 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with a solution of xanthate **VI-3** (2.82 g, 10 mmol) and allyl acetate (2.17 mL, 20 mmol), and needed 15 mol% of DLP to go to completion (4 h 30 min). After completion, the reaction mixture was then cooled to 20 °C and evaporated *in vacuo*. Crude xanthate was directly used in the next step of cyclization.

Following general procedure **III-B** for radical cyclisation, the reaction was carried out with a solution of crude xanthate and needed 140 mol % of DLP to go to completion (7 h). The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 3:7) to afford tetralone **VI-2a** (2.40 g, 63% over 2 steps) as a colorless oil.

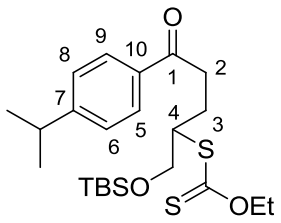
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.95 (d, *J*= 8.1 Hz, 1H, C***H***-9), 7.20 (d, *J*= 8.1 Hz, 1H, C***H***-8), 7.15 (s, 1H, C***H***-6), 4.26-4.36 (m, 2H, C***H*****$_2$**-O), 3.26 (dq, *J*= 9.9, 4.9 Hz, 1H, C***H***-4), 2.86-2.96 (m, 1H, C***H***-$(CH_3)_2$), 2.70-2.78 (m, 1H, C***H***-2), 2.56 (ddd, *J*= 17.7, 6.9, 3.2 Hz, 1H, C***H***-2), 2.20-2.32 (m, 1H, C***H***-3), 2.09-2.17 (m, 1H, C***H***-3), 2.05 (s, 3H, C***H*****$_3$**-CO), 1.23 (d, *J*= 6.8 Hz, 6H, (C***H*****$_3$**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 197.0 (C-1), 170.6 (C=O), 155.1 (C-7), 143.1 (C-5), 130.5 (C-10), 127.6 (C-6), 126.2 (C-9), 125.7 (C-8), 65.9 (OCH_2), 37.4 (C-4), 34.7 (C-2), 34.3 (***C***H-$(CH_3)_2$), 24.6 (C-3), 23.5, 23.5 ($(CH_3)_2$), 20.7 (***C***H_3-CO).

IR (ν, cm^{-1}, CCl_4): 2955, 2935, 2859, 1745, 1691, 1613, 1513, 1464, 1455, 1361, 1302, 1234, 1172, 1099, 1040.

HRMS (EI): Calcd. for $C_{16}H_{20}O_3$: 260.1412 Found : 260.1410

_S_-1-(_tert_-Butyldimethylsilyloxy)-5-(4-isopropylphenyl)-5-oxopentan-2-yl _O_-ethyl carbonodithioate **VI-5**



$C_{23}H_{38}O_3S_2Si$
M= 454.8 g.mol^{-1}

Following general procedure **III-B** for radical addition, the reaction was carried out with a solution of xanthate **VI-3** (2.82 g, 10 mmol) and allyloxy(*tert*-butyl)dimethylsilane (3.44 g, 20 mmol), and needed 20 mol% of DLP to go to completion (6 h). After completion, the reaction mixture was then cooled to 20 °C and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (98:2, 95:5) to afford radical adduct **VI-5** (3.91 g, 86%) as a colorless oil.

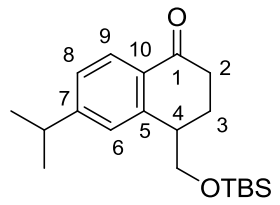
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.89 (d, *J*= 8.4 Hz, 2H, C***H***-8, C***H***-6), 7.30 (d, *J*= 8.1 Hz, 2H, C***H***-9, C***H***-5), 4.54-4.67 (m, 2H, OC***H*****$_2$**CH_3), 3.90-3.96 (m, 2H, C***H***-4, OC***H***), 3.78 (dd, *J*= 11.5, 7.5 Hz, 1H, OC***H***), 3.14 (t, *J*= 7.5 Hz, 2H, C***H*****$_2$**-2), 2.91-3.00 (m, 1H, C***H***-$(CH_3)_2$), 2.32-2.40 (m, 1H, C***H***-3), 1.98-2.07 (m, 1H, C***H***-3), 1.38 (t, *J*= 7.1 Hz, 3H, OCH_2C***H*****$_3$**), 1.26 (d, *J*= 6.9 Hz, 6H, (C***H*****$_3$**$)_2$), 0.96 (s, 9H, SiC(C***H*****$_3$**$)_3$), 0.07, 0.07 (s, 6H, Si(C***H*****$_3$**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.3 (C=S), 198.9 (C-1), 154.5 (C-7), 134.8 (C-10), 128.4 (C-8, C-6), 126.7 (C-9, C-5), 69.9 (O***C***H_2CH_3), 65.3 (OCH_2), 52.6 (C-4), 35.9 (C-2), 34.3 (***C***H-$(CH_3)_2$), 25.9 (SiC(***C***$H_3)_3$, 24.6 (C-3), 23.7 $(CH_3)_2$, 18.3 (SiC), 13.8 (OCH_2***C***H_3), -5.3, -5.4 (Si$(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4): 2964, 2929, 2872, 1685, 1607, 1462, 1416, 1365, 1268, 1219, 1183, 1146, 1054, 1018.

HRMS (EI): Calcd. for $C_{23}H_{38}O_3S_2Si$: 454.2032 Found : 454.2034

4-((*tert*-Butyldimethylsilyloxy)methyl)-6-*iso*propyl-3,4-dihydronaphthalen-1(*2H*)-one **VI-2b**



$C_{20}H_{32}O_4Si$
M= 332.6 g.mol^{-1}

Following general procedure **III-B** for radical cyclisation, the reaction was carried out with a solution of xanthate **VI-5** (3.91 g, 8.6 mmol) and needed 120 mol % of DLP to go to completion. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford tetralone **VI-2b** (1.69 g, 59%) as a colorless oil.

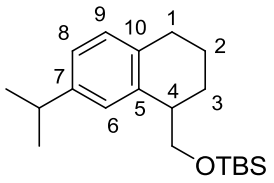
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.97 (d, *J*= 8.0 Hz, 1H, C***H***-9), 7.18-7.21 (m, 2H, C***H***-6, C***H***-8), 3.86 (dd, *J*= 11.5, 6.1 Hz, 1H, OC***H***), 3.80 (dd, *J*= 10.1, 7.9 Hz, 1H, OC***H***), 3.07 (tt, *J*= 9.8, 7.4 Hz, 1H, C***H***-4), 2.91-2.94 (m, 1H, C***H***-$(CH_3)_2$), 2.77 (ddd, *J*= 17.7, 11.5, 6.1 Hz, 1H, C***H***-2), 2.56 (dt, *J*= 17.7, 4.7 Hz, 1H, C***H***-2), 2.20-2.27 (m, 2H, C***H*****$_2$**-3), 1.23 (d, *J*= 6.8 Hz, 6H, (C***H*****$_3$**)$_2$), 0.87 (s, 9H, SiC(C***H*****$_3$**)$_3$), 0.02, -0.01 (s, 6H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 198.0 (C-1), 154.8 (C-7), 144.9 (C-5), 130.8 (C-10), 127.5 (C-6), 126.7 (C-9), 125.3 (C-8), 66.0 (OCH_2), 40.8 (C-4), 34.9 (C-2), 34.4 (***C***H-$(CH_3)_2$), 25.8 (SiC(***C***$H_3)_3$), 24.6 (C-3), 23.5, 23.5 ($(CH_3)_2$), 18.2 (SiC), -5.4, -5.6 ($Si(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4) 2963, 2929, 1687, 1606, 1455, 1279, 1038.

HRMS (EI) Calcd. for $C_{20}H_{32}O_4Si$: 332.2172 Found : 332.2176

tert-Butyl((7-_iso_propyl-1,2,3,4-tetrahydronaphthalen-1-yl)methoxy)dimethylsilane **VI-8**



$C_{20}H_{34}OSi$
M= 318.6 g.mol^{-1}

To a solution of tetralone **VI-2b** (40 mg, 0.116 mmol) in THF (3 mL) at -78 °C, was condensed ammonia (5 mL). Small pieces of lithium were quickly added to the reaction mixture. The resulting blue solution was stirring for 1 h at -78 °C. Then, ammonia was slowly removed at 0 °C and iodomethane (0.02 mL, 0.232 mmol, 2.0 equiv) was added. The reaction mixture was stirred at 0 °C for 2 h and then quenched with NH_4Cl (solid) until the solution became colorless. The resulting mixture was partitioned between CH_2Cl_2 and water. The combined organic extracts were then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford reduced compound **VI-8** (26 mg, 70%) as a colorless oil.

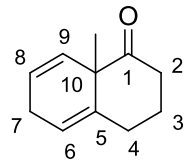
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 6.99-7.16 (m, 3H, C***H***-9, C***H***-6, C***H***-8), 3.80 (dd, *J*= 10.0, 5.1 Hz, 1H, OC***H***), 3.65 (t, *J*= 9.7 Hz, 1H, OC***H***), 2.92-2.98 (m, 1H, C***H***-4), 2.83-2.89 (m, 1H, C***H***-$(CH_3)_2$), 2.73 (t, *J*= 5.9 Hz, 2H, C***H*****$_2$**-1), 1.72-2.00 (m, 4H, C***H*****$_2$**-3, C***H*****$_2$**-2), 1.25 (d, *J*= 6.9 Hz, 6H, (C***H*****$_3$**$)_2$), 0.93(s, 9H, SiC(C***H*****$_3$**$)_3$), 0.08, 0.06 (s, 6H, Si(C***H*****$_3$**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 144.9 (C-7), 137.2 (C-5), 135.2 (C-10), 129.0 (C-9), 127.3 (C-6), 124.0 (C-8), 67.5 (OCH_2), 40.5 (C-4), 33.8 (***C***H-$(CH_3)_2$), 29.4 (C-1), 26.0 (SiC$(CH_3)_3$), 24.7 (C-3), 24.2, 24.0 ($(CH_3)_2$, 19.3 (C-2), 18.3 (SiC), -5.3, -5.4 (Si$(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4): 2963, 2934, 2873, 1462, 1384, 1235, 1227, 1027.

HRMS (EI): Calcd. for $C_{20}H_{34}O$ Si : 318.2379 Found : 318.2378

8a-Methyl-3,4,6,8a-tetrahydronaphthalen-1(*2H*)-one **VI-10**

	$C_{11}H_{14}O$ M= 162.2 g.mol^{-1}

Ammonia (85 mL) was condensed at -78 °C. Then, a solution of tetralone **VI-9** (20 mmol, 2.92 g) and *t*BuOH (2.5 mL, 24 mmol, 1.2 equiv) in ether (10 mL) was added dropwise. Potassium (1.7 g, 2.0 equiv) in small pieces was then added to the solution. After stirring at -78 °C for 15 min, lithium bromide (3.83 g, 40 mmol, 2.0 equiv) was added. The reaction mixture was stirred vigorously at -78 °C for 30 min. Then, iodomethane (2.5 mL, 20 mmol, 2.0 equiv) was added dropwise to the solution. After 15 min at -78 °C, the reaction mixture was allowed to warm to 20 °C. Water and ether were added. A solution of HCl 1M was then added, until the pH reached 7. The aqueous phase was extracted with ether, and the combined organic extracts were washed with water, brine, and dried over anhydrous $MgSO_4$. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford diene **VI-10** (2.92 g, 90%) as a colorless oil.

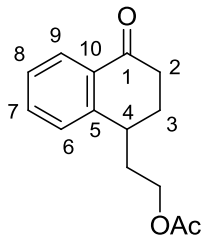
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.94-5.99 (m, 1H, C***H***-9), 5.72-5.74 (m, 1H, C***H***-8), 5.53 (brs, 1H, C***H***-6), 2.63-2.76 (m, 4H, C***H$_2$***-7, C***H***-2, C***H***-4), 2.35-2.41 (m, 1H, C***H***-4), 2.22-2.27 (m, 1H, C***H***-2), 1.99-2.06 (m, 1H, C***H***-3), 1.64 (qd, *J*= 13.0, 4.6 Hz, 1H, C***H***-3), 1.36 (s, 3H, C***H$_3$***-10).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 212.4 (C-1), 138.5 (C-5), 128.5 (C-9), 123.1 (C-8), 120.2 (C-6), 50.8 (C-10), 38.1 (C-2), 31.0 (C-4), 27.0 (***C***H$_3$-10), 26.6 (C-7), 25.2 (C-3).

IR (ν, cm^{-1}, CCl_4) 2956, 2930, 2886, 2858, 1711, 1471, 1463, 1412, 1389, 1361, 1256, 1103.

HRMS (EI) Calcd. for $C_{11}H_{14}O$: 162.1045 Found : 162.1043

2-(4-Oxo-1,2,3,4-tetrahydronaphthalen-1-yl)ethyl acetate VI-14



$C_{14}H_{16}O_3$
M= 232.3 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with a solution of xanthate **VI-13** (3.24 g, 13.5 mmol) and but-3-enyl (3.08 g, 27 mmol), and needed 20 mol% of DLP to go to completion (6 h). Following general procedure **III-B** for radical cyclisation, the reaction was carried out with a solution of the crude xanthate and needed 140 mol % of DLP to go to completion. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 7:3) to afford tetralone **VI-14** (1.38 g, 44% over 2 steps) as a yellow oil.

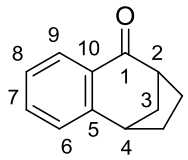
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.01 (d, *J*= 7.6 Hz, 1H, C***H***-9), 7.47 (t, *J*= 7.6 Hz, 1H, C***H***-7), 7.29 (t, *J*= 7.6 Hz, 1H, C***H***-8), 7.24 (d, *J*= 7.6 Hz, 1H, C***H***-8), 4.18 (td, *J*= 7.5, 2.5 Hz, 2H, OC***H$_2$***), 3.04-3.10 (m, 1H, C***H***-4), 2.74 (ddd, *J*= 17.5, 12.0, 5.0 Hz, 1H, C***H***-2), 2.58 (dt, *J*= 17.5, 4.9 Hz, 1H, C***H***-2), 2.22-2.31 (m, 2H, C***H$_2$***-3), 2.05 (s, 3H, OC***H$_3$***), 1.97-2.05 (m, 2H, C***H$_2$***-C4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 197.7 (C-1), 170.9 (C=O), 146.8 (C-10), 133.5 (C-7), 131.8 (C-5), 128.1 (C-6), 127.4 (C-8), 126.9 (C-9), 61.2 (***C***H_2-OAc), 34.7 (C-4), 34.6 (C-2), 33.1 (***C***H_2-C4), 26.8 (C-3), 20.8 (CH_3).

IR (ν, cm^{-1}, CCl_4): 3071, 3026, 2935, 2872, 1744, 1691, 1601, 1479, 1455, 1417, 1388, 1367, 1328, 1284, 1234, 1159, 1118, 1042.

HRMS (EI): Calcd. for $C_{14}H_{16}O_3$: 232.1099 Found : 232.1103

5,6,7,8-Tetrahydro-9*H*-5,8-methanobenzo[7]annulen-9-one **CO1**

	$C_{12}H_{12}O$ M= 172.2 g.mol^{-1}

To a solution of tetralone **VI-14** (1.20 g, 7.0 mmol) in methanol (30 mL) was added a aqueous 1M NH_4OH solution (30 mL). The reaction mixture was stirred for 4 h at 20 °C. The resulting mixture was partitioned between CH_2Cl_2 and water. The organic layer was then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*, giving alcohol.
To a solution of crude alcohol in CH_2Cl_2 (30 mL), was added at 0 °C, Et_3N (1.02 mL, 10.5 mmol, 1.5 equiv) and tosyl chloride (1.33 g, 1.0 equiv, 7.0 mmol). The reaction mixture was then stirred overnight at 20 °C. The resulting mixture was partitioned between CH_2Cl_2 and water. The organic layer was then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 9:1) to afford the protected alcohol (2.07 g, 86% over 2 steps) as a white solid.
To a solution of protected alcohol (800 mg, 2.32 mmol) in ethanol (40 mL) was added a 1M KOH solution (80 mL). The reaction mixture was stiring for 2 h at reflux, cooled to 20 °C and neutralized with a 1M HCl solution. The resulting mixture was extracted with CH_2Cl_2. The combined organic extracts were then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 9:1) to afford tricycle **CO1** (331 mg, 83%) as a yellow oil.

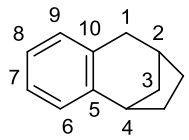
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.98 (d, *J*= 7.5 Hz, 1H, C***H***-9), 7.46 (t, *J*= 7.5 Hz, 1H, C***H***-7), 7.29 (t, *J*= 7.5 Hz, 1H, C***H***-8), 7.25 (d, *J*= 7.5 Hz, 1H, C***H***-6), 3.38 (t, *J*= 5.0 1H, C***H***-2), 3.14 (dd, *J*= 6.6, 5.0 Hz, 1H, C***H***-4), 2.12-2.24 (m, 3H, C***H*****$_2$**-C2, C***H***-3), 1.85 (dt, *J*= 11.7, 4.4 Hz, 1H, C***H***-3), 1.59-1.72 (m, 2H, C***H*****$_2$**-C4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 201.7 (C-1), 151.0 (C-5), 133.7 (C-7), 130.4 (C-10), 127.5, 126.7, 126.6 (C-6, C-8, C-9), 50.0 (C-2), 42.3 (C-4), 39.5 (C-3), 31.7 (***C***H_2-C2), 24.7 (***C***H_2-C4).

IR (ν, cm^{-1}, CCl_4) 3073, 3026, 2951, 2873, 1693, 1604, 1478, 1457, 1448, 1325, 1280, 1242, 1152, 1099, 1010.

HRMS (EI) Calcd. for $C_{12}H_{12}O$: 172.0888 Found : 172.0890

6,7,8,9-Tetrahydro-5*H*-5,8-methanobenzo[7]annulene **VI-15**

	$C_{12}H_{14}$ M= 158.2 g.mol^{-1}

To a solution of the tetralone **CO1** (20 mg, 0.116 mmol) in THF (3 mL) at -78 °C, was condensed ammonia (5 mL). Small pieces of lithium were quickly added to the reaction mixture. The resulting blue solution was stirred for 1 h at -78 °C. Then, ammonia was slowly removed at 0 °C and iodomethane (0.02 mL, 0.232 mmol, 2.0 equiv) was added. The reaction mixture was stirred at 0 °C for 2 h and then quenched with NH_4Cl (solid) until the solution became colorless. The resulting mixture was partitioned between CH_2Cl_2 and water. The aqueous phase was extracted with CH_2Cl_2 and the combined organic extracts was then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 10:90) to afford the reduced compound **VI-15** (14 mg, 76%) as a colorless oil.

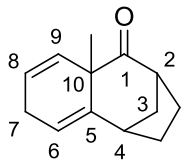
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.00-7.10 (m, 4H, C***H***-9, C***H***-6, C***H***-7, C***H***-8), 3.10 (dd, *J*= 18.8, 4.5 Hz, 1H, C***H***-1), 3.02-3.06 (m, 1H, C***H***-4), 2.65 (d, *J*= 16.8 Hz, 1H, C***H***-1), 2.54-2.58 (m, 1H, C***H***-2), 1.92-1.96 (m, 2H, C***H***-C4, C***H***-3), 1.72-1.82 (m, 3H, C***H***-3, C***H$_2$***-C2), 1.46-1.50 (m, 1H, C***H***-C4).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 145.3 (C-5), 134.5 (C-10), 129.3 (C-9), 126.9 (C-6), 125.7, 125.4 (C-8, C-7), 41.2 (C-4), 39.4 (C-1), 36.4 (C-3), 35.5 (***C***H$_2$-C2), 33.6 (C-2), 29.6 (***C***H$_2$-C4).

IR (ν, cm^{-1}, CCl_4): 3072, 2955, 2873, 1574, 1457, 1447, 1439, 1325, 1280, 1230, 1148, 1133, 1023.

HRMS (EI): Calcd. for $C_{12}H_{14}$: 158.1096 Found : 158.1096

9a-Methyl-3,5,6,7,8,9a-hexahydro-9*H*-5,8-methanobenzo[7]annulen-9-one **VI-16**

	$C_{13}H_{16}O$ M= 188.3 g.mol^{-1}

Ammonia (10 mL) was condensed at -78 °C. Then, a solution of the tetralone **CO1** (1.0 mmol, 146.2 mg) and *t*BuOH (120µL, 1.2 mmol, 1.2 equiv) in ether (1 mL) was added dropwise. Potassium (80 mg, 2.0 equiv) was then added to the solution in small pieces. After stirring at -78 °C for 15 min, lithium bromide (200 mg, 2 mmol, 2.0 equiv) was added. The reaction mixture was stirred vigorously at -78 °C for 30 min. Iodomethane (125 µL, 2 mmol, 2.0 equiv) was then added dropwise to the solution. After 15 min at -78 °C, the reaction mixture was allowed to warm to 20 °C. Water and ether were added and a solution of HCl 1M was added, until the pH reached 7. The aqueous phase was then extracted with ether and the combined organic extracts was then washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford the diene **VI-16** (122 mg, 65%) as a colorless oil and as a mixture of diasteromers in a 8:2 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 6.29-6.25 (m, 1H, C***H***-9), 5.68-5.75 (m, 1.8H, C***H***-8, C***H***-6 dia1), 5.55 (brs, 0.2H, C***H***-6 dia2), 3.12 (brs, 0.8H, C***H***-2 dia1), 3.01 (brs, 0.2H, C***H***-2 dia2), 2.84-2.86 (m, 1H, C***H***-4), 2.64 (brs, 1.6H, C***H$_2$***-7 dia1), 2.59 (brs, 0.4H, C***H$_2$***-7 dia2), 2.22 (d, *J*= 12.4 Hz, 0.8H, C***H***-C4 dia1), 1.89-1.98 (m, 1.8H, C***H***-C2, C***H***-3 dia1), 1.75 (brs, 0.4H, C***H***-3), 1.41-1.56 (m, 3H, C***H***-3 dia1, C***H***-C2, C***H***-C4, C***H***-C4 dia2), 1.26 (d, *J*= 1.6 Hz, 0.6H, C***H$_3$***-10 dia2), 1.22 (d, *J*= 1.6 Hz, 2.4H, C***H$_3$***-10 dia2).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz):

Major diastereomer 1

215.1 (C-1), 144.0 (C-5), 132.5 (C-9), 124.0 (C-8), 121.6 (C-6), 48.7 (C-2), 47.3 (C-10), 41.3 (C-4), 36.1 (***C***H_2-C3), 31.3 (***C***H_2-C4), 30.7 (***C***H_3-10), 27.3 (C-7), 25.2 (***C***H_2-C2).

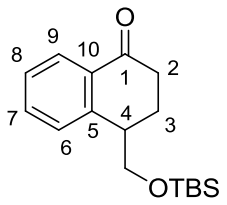
Minor diastereomer 2

214.9 (C-1), 145.8 (C-5), 132.1 (C-9), 124.1 (C-8), 118.1 (C-6), 51.4 (C-2), 49.3 (C-10), 44.9 (C-4), 37.0 (***C***H_2-C3), 30.5 (***C***H_3-10), 28.2 (***C***H_2-C4), 28.1 (C-7), 26.3 (***C***H_2-C2).

IR (ν, cm^{-1}, CCl_4): 3039, 2959, 2874, 2817, 1712, 1604, 1587, 1504, 1457, 1450, 1424, 1325, 1280, 1250, 1229, 1154, 1072, 1017.

HRMS (EI): Calcd. for $C_{13}H_{16}O$: 188.1201 Found : 188.1194

4-((*tert*-Butyldimethylsilyloxy)methyl)-3,4-dihydronaphthalen-1(*2H*)-one **VI-19**



$C_{17}H_{26}O_2Si$
M= 290.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with a solution of the xanthate **VI-20** (4.8 g, 20.0 mmol) and allyloxy(*tert*-butyl)dimethylsilane (6.89 g, 40.0 mmol), and needed 15 mol% of DLP to go to completion. The reaction mixture was then cooled to 20°C and evaporated *in vacuo*. The crude xanthate was directly used in the next step of cyclization. A solution of xanthate in ethyl acetate (100 mL) was refluxed for 15 min under a nitrogen flow. Dilauroyl peroxide (DLP) (20 mol %) was then added and additional DLP (20 mol %) was added every 90 min until total consumption of the starting material. The reaction needed 160 mol% of DLP to go to completion. The reaction mixture was then cooled to 20 °C and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 3:7) to afford the tetralone **VI-19** (2.38 g, 41% over 2 steps) as a colorless oil.

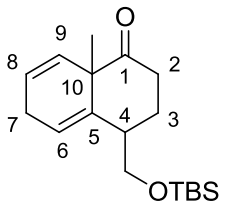
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 8.03 (d, *J*= 8.0 Hz, 1H, C***H***-9), 7.48 (t, *J*= 8.1 Hz, 1H, C***H***-7), 7.30-7.34 (m, 2H, C***H***-6, C***H***-8), 3.86 (dq, *J*= 9.5, 4.8 Hz, 1H, OC***H***), 3.78 (dd, *J*= 10.1, 6.9 Hz, 1H, OC***H***), 3.07 (td, *J*= 9.8, 4.8 Hz, 1H, C***H***-4), 2.80 (ddd, *J*= 17.6, 11.1, 6.5 Hz, 1H, C***H***-2), 2.56 (dt, *J*= 17.6, 4.9 Hz, 1H, C***H***-2), 2.22-2.28 (m, 2H, C***H$_2$***-3), 0.87 (s, 9H, SiC(C***H$_3$***)$_3$), 0.02, -0.01 (s, 6H, Si(C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 198.2 (C-1), 144.6 (C-5), 133.3 (C-7), 132.7 (C-10), 128.7 (C-6), 127.2 (C-8), 127.0 (C-9), 65.9 (OCH_2), 40.6 (C-4), 34.9 (C-2), 25.8 (SiC(***C***H$_3$)$_3$), 24.4 (C-3), 18.2 (SiC), -5.5, -5.6 (Si(***C***H$_3$)$_2$).

IR (ν, cm^{-1}, CCl_4): 2928, 2856, 2873, 1690, 1600, 1454, 1329, 1285, 1234, 1158, 1116, 1047, 1034.

HRMS (EI): Calcd. for $C_{17}H_{26}O_2Si$: 290.1702 Found : 290.1701

4-((*tert*-Butyldimethylsilyloxy)methyl)-8a-methyl-3,4,6,8a-tetrahydronaphthalen-1(*2H*)-one **VI-18**



$C_{18}H_{30}O_2Si$
M= 306.5 g.mol^{-1}

Ammonia (10 mL) was condensed at -78 °C. Then, a solution of the tetralone **VI-19** (1 mmol, 146.2 mg) and *t*BuOH (120 µL, 1.2 mmol, 1.2 equiv) in ether (1 mL) was added dropwise. Potassium (80 mg, 2.0 equiv) in small pieces was then added the solution. After stirring at -78°C for 15 min, lithium bromide (200 mg, 2.0 mmol, 2.0 equiv) was added. The reaction mixture was stirred vigorously at -78 °C for 30 min. Then, iodomethane (125 µL, 2.0 mmol, 2.0 equiv) was added dropwise to the solution. After 15 min at -78 °C, the reaction mixture was allowed to warm at 20 °C. Water and ether were added and a solution of HCl 1M was added, until the pH reached 7. The aqueous phase was then extracted with ether and the combined organic extracts were washed with water, brine, and dried over anhydrous $MgSO_4$. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford the diene **VI-18** (110 mg, 36%) as a colorless oil.

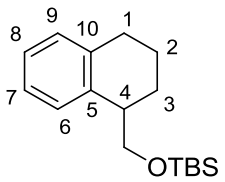
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.95 (dt, *J*= 10.2, 1.9 Hz, 1H, C***H***-9), 5.75 (dtd, *J*= 10.2, 3.5, 1.3 Hz, 1H, C***H***-8), 5.36 (brs, 1H, C***H***-6), 3.96 (dd, *J*= 9.7, 4.6 Hz, 1H, OC***H***), 3.56 (dd, *J*= 9.6, 8.0 Hz, 1H, OC***H***), 2.62-2.76 (m, 4H, C***H$_2$***-7, C***H***-2, C***H***-4), 2.43 (ddd, J= 15.4, 5.1, 3.0 Hz, 1H, C***H***-2), 2.24-2.30 (m, 1H, C***H***-3), 1.34-1.40 (m, 1H, C***H***-3), 1.37 (s, 3H, C***H$_3$***-10), 0.91 (s, 9H, SiC(C***H$_3$***)$_3$), 0.08 (s, 6H, Si(C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.8 (C-1), 138.9 (C-5), 128.9 (C-9), 122.9 (C-8), 117.5 (C-6), 64.7 (OCH_2), 50.3 (C-10), 39.3 (C-4), 37.3 (C-2), 28.4 (C-7), 27.7 (CH_3-10), 26.5 (C-3), 25.9 (SiC(***C***H_3)$_3$), 18.3 (SiC), -5.3 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, CCl_4): 2956, 2930, 2886, 2858, 1711, 1471, 1463, 1412, 1389, 1361, 1256, 1103, 1005.

HRMS (EI): Calcd. for $C_{18}H_{30}O_2Si$: 306.2015 Found : 306.2008

tert-Butyldimethyl((1,2,3,4-tetrahydronaphthalen-1-yl)methoxy)silane VI-21

	$C_{17}H_{28}OSi$ M= 276.5 g.mol^{-1}

To a solution of the tetralone **VI-19** (34 mg, 0.116 mmol) in THF (3 mL) at -78 °C, was condensed ammonia (5 mL). Small pieces of lithium were quickly added to the reaction mixture. The resulting blue solution was stirred for 1 h at -78 °C. Then, ammonia was slowly removed at 0 °C and iodomethane (0.02 mL, 0.232 mmol, 2.0 equiv) was added. The reaction mixture was stirred at 0°C for 2 h and then quenched with NH_4Cl (solid) until the solution became colorless. The resulting mixture was partitioned between CH_2Cl_2 and water. The combined organic extracts were then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*, giving crude reduced product. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford the reduced compound **VI-21** (22 mg, 69%) as a colorless oil.

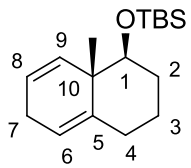
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.06-7.27 (m, 4H, C***H***-6, C***H***-7, C***H***-8, C***H***-9), 3.79 (dd, *J*= 10.0, 5.1 Hz, 1H, OC***H***), 3.69 (t, *J*= 9.7 Hz, 1H, OC***H***), 2.96 (td, *J*= 9.1, 4.7, 1H, C***H***-4), 2.75 (t, *J*= 6.0 Hz, 2H, C***H*****$_2$**-1), 1.95-2.00 (m, 1H, C***H***-3), 1.72-1.83 (m, 3H, C***H***-3, C***H*****$_2$**-2), 0.91 (s, 9H, SiC(C***H*****$_3$**)$_3$), 0.06, 0.04 (s, 6H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 137.9, 137.4 (C-5, C-10), 129.3, 129.1, 125.9, 125.4 (C-6, C-7, C-8, C-9), 67.4 (OCH_2), 40.4 (C-4), 29.8 (C-1), 26.0 (SiC(***C***H$_3$)$_3$), 24.5 (C-3), 19.2 (C-2), 18.4 (SiC), -5.3, -5.4 ($Si(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4): 2930, 2860, 2873, 1600, 1454, 1329, 1285, 1234, 1160, 1116, 1038.

HRMS (EI): Calcd. for $C_{17}H_{28}OSi$: 276.1909 Found : 276.1912

tert-Butyldimethyl((1S,8aS)-8a-methyl-1,2,3,4,6,8a-hexahydro naphthalen-1-yloxy)silane **(±)-VI-23**



$C_{17}H_{30}OSi$
M= 278.5 g.mol^{-1}

To a solution of dienone **VI-10** (1.62 g, 10 mmol) in methanol (20 mL) was added portionwise at -78 °C $NaBH_4$ (454 mg, 1.2 equiv). The reaction mixture was stirred for 1 h at-78 °C and quenched with water. The methanol was removed *in vacuo*. The aqueous phase was then extracted with ether, and the combined organic extracts were washed with water, brine, and dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 1:9) to afford the desired alcohol (1.46 g, 89%) as a colorless oil.

To a stirred suspension of the previous alcohol (1.23 g, 7.5 mmol) in CH_2Cl_2 (30 mL) was added imidazole (1.53 g, 22.5 mmol, 3.0 equiv) and TBSCl (2.26 g, 15 mmol, 2.0 equiv) at 20 °C. After stirring at 20°C overnight, the reaction was quenched with saturated aqueous NH_4Cl and extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (98:2 petroleum ether/ether) to afford the protected alcohol **(±)-VI-23** (1.9 g, 91%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.77 (dt, *J*= 10.1, 1.9 Hz, 1H, C***H***-9), 5.58 (dtd, *J*= 10.1, 3.3, 1.6 Hz, 1H, C***H***-8), 5.39 (brs, 1H, C***H***-6), 3.47 (dd, *J*= 10.6, 5.2 Hz, 1H, C***H***-1), 2.61-2.64 (m, 2H, C***H*****$_2$**-7), 2.22 (ttd, *J*= 13.4, 4.5, 2.1 Hz, 1H, C***H***-4), 1.90-1.94 (m, 1H, C***H***-4), 1.59-1.74 (m, 3H, C***H***-3, C***H*****$_2$**-2), 1.19-1.32 (m, 1H, C***H***-3), 1.08 (s, 3H, C***H*****$_3$**-10), 0.90 (s, 9H, SiC(C***H*****$_3$**)$_3$), 0.04, 0.03 (s, 6H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 141.0 (C-5), 133.7 (C-9), 120.9 (C-8), 118.2 (C-6), 77.0 (C-1), 41.6 (C-10), 31.7 (C-4), 31.4 (C-2), 26.9 (C-7), 25.9 (SiC(***C***H_3)$_3$), 24.9 (C-2), 18.8 (***C***H_3-10), 18.3 (SiC), -4.0, -4.6 (Si(***C***H_3)$_2$).

IR (ν, cm^{-1}, CCl_4): 3031, 2930, 2885, 2857, 1471, 1463, 1439, 1388, 1361, 1254, 1055.

HRMS (EI): Calcd. for $C_{17}H_{30}OSi$: 278.2066 Found : 278.2065

E. Chapitre VII : Approche à la Synthèse Totale du (+)-Maritimol

La numérotation des carbones et des hydrogènes de chaque composé décrit dans ce chapitre correspondant à celle du (+)-maritimol.

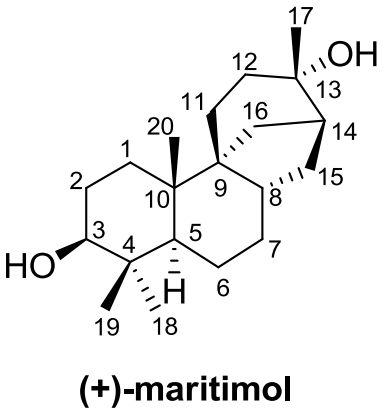
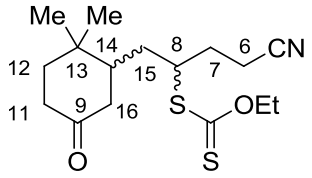


Figure 2 *– Structure du maritimol.*

_S_-(3-Cyano-1-((2,2-dimethyl-5-oxocyclohexyl)methyl)propyl) _O_-ethyl dithiocarbonate **MC8**



$C_{16}H_{25}NO_2S_2$
M= 327.5 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with a solution of olefin **MC7** (1.67 g, 10 mmol) and xanthate **MC6** (1.94 g, 12 mmol, 1.2 equiv) in ethyl acetate, and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ether/petroleum ether, 3:2) afforded radical adduct **MC8** (3.11 g, 95%) as a viscous pale yellow oil and as an inseparable mixture of two diastereoisomers (dr = 2:1).

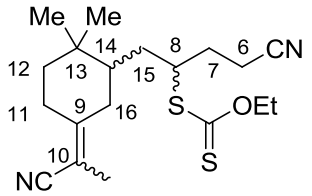
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.57-4.65 (m, 2H, OC***H*₂***), 3.69-3.78 (m, 1H,C***H***-8), 2.30-2.55 (m, 4H), 2.20-2.30 (m, 1H), 1.96-2.20 (m, 2H), 1.47-1.87 (m, 5H), 1.32-1.44 (m, 4H), 1.02 (s, 1H, C***H*₃***-13 dia2), 1.00 (s, 2H, C***H*₃***-13 dia1), 0.98 (s, 1H, C***H*₃***-13 dia2), 0.97 (s, 2H, C***H*₃***-13 dia1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 212.4 (C=S), 210.5, 210.4 (C=O), 118.9, 118.8 (CN), 70.5, 70.3 (OCH_2), 48.2, 47.7 (C-8), 43.9, 43.4 (C-14), 43.1, 42.7 (C-12), 40.0 39.7 (C-16), 38.0, 37.9 (C-11), 36.0, 34.7 (C-7), 32.8 (C-13), 32.3, 28.9 (C-15), 28.5, 28.4, 19.6, 19.2 (($\boldsymbol{C}H_3)_2$-13), 14.7 (C-6), 13.7, 13.6 ($OCH_2\boldsymbol{C}H_3$).

IR (ν, cm^{-1}, CCl_4): 3050, 2963, 2932, 2868, 1717, 1446, 1424, 1388, 1366, 1261, 1223, 1147, 1111, 1051, 902.

HRMS (EI) Calcd. for $C_{16}H_{25}NO_2S_2$ -Xa: 206.1545 Found : 206.1551

_S_-(3-Cyano-1-(((5_E_)-5-(1-cyanoethylidene)-2,2dimethyl cyclohexyl) methyl)propyl) _O_-ethyldithiocarbonate **MC5**



$C_{19}H_{28}N_2OS_2$
M= 364.6 g.mol^{-1}

To a solution of diethyl 1-cyanoethylphosphonate **MC9** (382 mg, 2.0 mmol, 2.0 equiv) in THF (1 mL) was added LiH (16 mg, 2.0 mmol, 2.0 equiv) at 20 °C. The resulting heterogeneous solution was then refluxed for 30 min, and a solution of ketone **MC8** (328 mg, 1.0 mmol, 1.0 equiv) in THF (1 mL) was transferred *via* cannula. After 14 h, LiH (8 mg, 0.5 mmol, 0.5 equiv) was added and the resulting mixture refluxed for another 2 h. It was then hydrolyzed, and the resulting aqueous layer was extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Flash chromatography on silica gel (petroleum ether/ether, 2:1) afforded nitrile **MC5** (350 mg, 96%) as a very viscous pale yellow oil consisting of an inseparable mixture of 4 diastereomers (dr not determined).

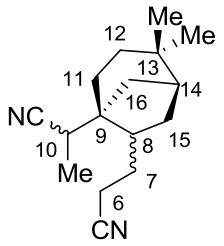
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.58-4.68 (m, 2H, OC***H*₂**), 3.74-3.95 (m, 1H, C***H***-8), 2.57-2.93 (m, 1.7H), 2.32-2.56 (m, 2.7H), 1.96-2.29 (m, 3.3H), 1.65-1.90 (m, 4.3H), 1.44-1.59 (m, 2H), 1.37-1.43 (m, 3H, OCH_2C***H*₃**), 1.20-1.33 (m, 2H), 0.93, 0.92, 0.89, 0.87, 0.86, 0.85 (s, 6H, (C***H***$_3)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 213.8, 212.6, 212.3, 212.2 (C=S), 157.4, 157.3, 157.3, 156.9 (C-9), 119.5, 119.5, 119.4, 119.3, 119.1, 119.0, 118.9, 118.8 (CN), 100.9, 100.7, 100.6, 100.5 (C-10), 70.6, 70.4, 70.3, 70.2 (OCH_2), 48.9, 48.8, 48.3, 48.1 (C-8), 44.9, 44.7, 44.0, 43.7 (C-14), 41.3, 41.2, 40.7, 40.0 (C-12), 35.9, 35.8, 35.2, 35.2 (C-16), 34.1, 33.8, 32.6, 31.3 (C-11), 33.2, 33.1, 32.8, 32.8 (C-13), 32.8, 30.6, 30.6, 30.5, 29.3, 28.9, 25.9, 25.9 (C-15, C-7), 28.9, 28.8, 28.8, 28.6 (CH_3-10), 20.3, 19.5, 19.4 , 19.3 (CH_3-13), 15.4, 14.4, 15.3, 15.3 (CH_3-13), 14.9, 14.8, 14.7, 14.6 (C-6), 13.6 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4): 2962, 2929, 2870, 2250, 2212, 1447, 1388, 1367, 1222, 1147, 1111, 1051, 890.

HRMS (EI) Calcd. for $C_{19}H_{28}N_2OS_2$: 364.1643 Found : 364.1460

2-(7-(2-Cyanoethyl)-4,4-dimethylbicyclo[3.2.1]oct-1-yl)propanenitrile **MC4**



$C_{16}H_{24}N_2$
M= 244.4 g.mol^{-1}

A magnetically stirred solution of xanthate **MC5** (2.0 g, 5.5 mmol, 1.0 equiv), hypophosphorous acid (50% solution in water, 3.0 mL, 28.6 mmol, 5.2 equiv), and triethylamine (4.60 mL, 32.9 mmol, 6.0 equiv) in 1,4-dioxane (70 mL), was refluxed under a nitrogen atmosphere for 20 min. AIBN (181 mg, 1.1 mmol, 0.2 equiv) was then added, and the reaction mixture was refluxed for 2 h. AIBN (181 mg, 1.1 mmol, 0.2 equiv) was added again, and the reaction mixture was refluxed for a further 2 h, time after which the reaction mixture was cooled to 20 °C and diluted with water. The resulting aqueous phase was extracted with ether and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and removed *in vacuo*. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 2:8) afforded bicycle **MC4** (1.18 g, 88%) as a very viscous pale yellow oil and as an inseparable mixture of 4 diastereomers (dr not determined).

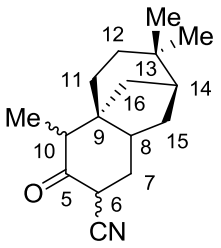
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 2.50–2.61 (m, 1H, C***H***-10), 2.36-2.49 (m, 1H, C***H***-6), 2.20-2.35 (m, 1H, C***H***-6), 2.00-2.13 (m, 1.5H), 1.94–1.84 (m, 0.7H), 1.50-1.82 (m, 4.3H), 1.36-1.46 (m, 1H), 1.20-1.35 (m, 6H), 1.08-1.20 (m, 1.5H), 0.95, 0.94, 0.91, 0.85, 0.85, 0.83 (s, 6H, (C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 122.2, 121.8, 121.6 (CN-10), 119.5, 119.4, 119.3, 119.2 (CN-6), 46.2, 46.2, 45.9, 45.5 (C-9), 45.6 45.4, 44.5, 44.2 (C-14), 42.5, 42.3, 41.3, 39.6 (C-8), 36.9, 36.7, 36.1, 35.4 (C-15), 34.3, 34.1, 34.1, 32.8 (C-12), 33.2, 32.6, 32.4, 32.1 (C-13), 32.3, 32.2, 32.0, 31.5 (C-16), 31.5, 31.5, 29.0, 28.9 (C-11), 31.0, 30.9, 29.3, 29.0 (CH_3-10) 27.0, 26.9, 25.2, 25.0 (C-7), 26.2, 26.1, 25.4, 25.3 (CH_3-13), 16.7, 16.6, 15.3, 15.2 (C-6), 14.3, 14.3, 14.1 14.1 (CH_3-13), 13.9 (OCH_2***C***H_3).

IR (ν, cm^{-1}, CCl_4) 2955, 2867, 2242, 2213, 1713, 1461, 1385.

HRMS (EI) Calcd. for $C_{16}H_{24}N_2$: 244.1940 Found : 244.1936

4,7,7-Trimethyl-3-oxodecahydro-4a,8-methanobenzocycloheptene-2-carbonitrile **MC10**

	$C_{16}H_{23}NO$ M= 245.4 g.mol^{-1}

To a solution of bicycle **MC4** (1.34 g, 5.5 mmol) in THF (130 mL), was added *t*-BuOK (926 mg, 8.3 mmol) at -15 °C. After 1 h, the reaction mixture was hydrolyzed with 1 N HCl and was further stirred for 1 h at 20 °C. The aqueous layer was then extracted 3 times with ethyl acetate, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) to afford tricycle **MC10** (1.05 g, 78%) as a very viscous pale yellow oil, which solidified upon standing and as a mixture of 4 diastereomers (dr = 48:42:6:4). An aliquot was submitted to another flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) and it was possible to isolate a mixture of two diastereomers (dr = 70:30). ^{1}H and ^{13}C NMR spectra were greatly simplified.

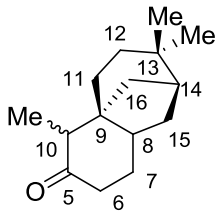
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 3.56 (dd, *J* = 13.6, 4.4 Hz, 0.7H, C***H***-6 dia1), 3.30 (dd, *J* = 8.0, 4.2 Hz, 0.3H, C***H***-6 dia2), 2.74 (q, *J* = 6.7 Hz, 0.3H, C***H***-10 dia2), 2.49 (ddd, *J* = 13.7, 5.6, 4.6 Hz, 0.7H, C***H***-7 dia1), 2.24-2.39 (m, 1.4H, C***H***-10 dia1+ 0.7H), 2.15 (ddd, *J* = 13.7, 8.5, 2.2 Hz, 0.3H), 1.98-2.11 (m, 1.3H), 1.90 (dt, *J* = 13.5, 13.2, 6.0 Hz, 0.7H), 1.74-1.85 (m, 1.3H), 1.67-1.73 (m, 1H), 1.66-1.59 (m, 1H), 1.48-1.36 (m, 1H), 1.13-1.31 (m, 4H), 1.10 (d, *J* = 6.7 Hz, 2.1H, C***H***$_3$-10 dia1), 1.09 (d, *J* = 6.7 Hz, 0.9H, C***H***$_3$-10 dia2), 0.91 (s, 0.9H, C***H***$_3$-13 dia2), 0.90 (s, 2.1H, C***H***$_3$-13 dia1), 0.86 (s, 0.9H, C***H***$_3$-13 dia2), 0.82 (s, 2.1H, C***H***$_3$-13 dia1).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 203.9, 202.4 (C-5), 117.4, 116.5 (CN), 52.4, 48.9 (C-9), 51.5, 48.8 (C-10), 45.8, 45.7 (C-8), 41.9, 39.3 (C-14), 38.9, 36.2 (C-6), 38.2, 36.0 (C-15), 35.1, 34.3 (C-12), 34.3, 34.0 (C-16), 33.3, 32.6 (C-11), 32.4, 32.3 (C-13), 32.2, 31.3 (C-7), 29.2, 28.9 (CH_3-13), 25.8, 25.2 (CH_3-13), 10.4, 9.8 (CH_3-10).

IR (ν, cm^{-1}, CCl_4): 2942, 2868, 2361, 2246, 1731, 1460, 1384.

HRMS (EI): Calcd. for $C_{16}H_{23}NO$: 245.1780 Found : 245.1782

4,7,7-Trimethyloctahydro-4a,8-methanobenzocyclohepten-3-one **MC3**

	$C_{15}H_{24}O$ M= 220.4 g.mol^{-1}

A solution of nitrile **MC10** (601 mg,2.45 mmol) and 50% sulfuric acid (22 mL) in acetic acid (110 mL) was refluxed for 12 h. Acetic acid was then removed *in vacuo* and a saturated aqueous solution of sodium bicarbonate was carefully added. The resulting layer was extracted ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to give a yellow oil. Flash chromatography on silica gel (petroleum ether/ ether, 9:1) afforded ketone **MC3** (500 mg, 92%) as a very viscous colorless oil, which crystallized upon standing and as an inseparable mixture of 2 diastereomers (dr = 70:30).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)

2.46 (q, *J* = 6.7 Hz, 0.7H, C***H***-10 dia1), 2.34 (q, *J* = 6.9 Hz, 0.3H, C***H***-10 dia2), 2.29 (dd, *J* = 4.1, 3.1 Hz, 0.3H, C***H***$_2$-6 dia2), 2.17-2.28 (m, 1H), 1.98-2.09 (m, 2H), 1.89-1.94 (m, 0.7H), 1.69-1.76 (m, 1.7H), 1.66 (t, *J* = 5.4 Hz, 0.7H), 1.61 (t, *J* = 5.8 Hz, 0.3H), 1.45-1.57 (m, 1.3H), 1.35-1.44 (m, 1.3H), 1.16-1.29 (m, 2.7H), 1.07-1.16 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 0.9H, C***H$_3$***-10 dia2), 0.95 (d, *J* = 6.7 Hz, 2.1H, C***H$_3$***-10 dia2), 0.91 (dd, *J* = 5.2, 3.0 Hz, 0.3H), 0.88 (s, 2.1H, C***H$_3$***-13 dia1), 0.87 (s, 0.9H, C***H$_3$***-13 dia2), 0.82 (s, 0.9H, C***H$_3$***-13 dia2), 0.81 (s, 2.1H, C***H$_3$***-13 dia1), 0.71-0.78 (m, 0.7H).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

Major diastereoisomer (1)

215.6 (C-5), 50.1 (C-10), 47.5 (C-9), 45.9 (C-8), 41.1 (C-14), 39.1 (C-6), 38.9 (C-16), 34.6 (C-15), 32.6 (C-13), 32.3 (C-12), 29.9 (C-11), 29.4 (CH_3-13), 27.3 (C-7), 26.1 (CH_3-13), 9.1 (CH_3-10).

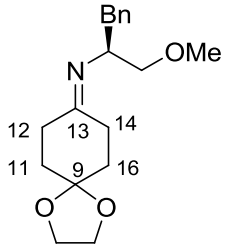
Minor diastereoisomer (2)

214.6 (C-5), 50.3 (C-10), 47.5 (C-9), 45.9 (C-8), 37.9 (C-14), 36.6 (C-6), 35.1 (C-16), 34.7 3.7 (C-15), 33.7 (C-13), 32.9 (C-12), 32.4 (C-11), 29.4 (CH_3-13), 28.8 (C-7), 26.1 (CH_3-13), 9.6 (CH_3-10).

IR (ν, cm^{-1}, CCl_4) 2939, 2865, 1713, 1460, 1380, 1168, 1051.

HRMS (EI) Calcd. for $C_{15}H_{24}O$: 220.1827 Found : 220.1822

(2*S*)-1-Methoxy-3-phenyl-*N*-(1,4-dioxaspiro[4.5]decan-8-ylidene) propan-2-amine **MC25**

	$C_{18}H_{25}NO_3$ M= 303.4 g.mol^{-1}

A solution of 1,4-dioxaspiro[4.5]decan-8-one **MC23** (10.0 g, 64 mmol) and the amine **MC24** (10.6 g, 64 mmol)[31] in toluene (120 mL) was refluxed overnight with azeotropic removal of water using a Dean–Stark apparatus. Removal of toluene afforded the imine **MC25** as a viscous colorless oil which was sufficiently pure for further reaction.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.20-7.26 (m, 2H, C***H***-ar), 7.10-7.19 (m, 3H, C***H***-ar), 3.83-3.97 (m, 5H, O(C***H*****$_2$**$_2$O + NC***H***Bn), 3.51 (dd, *J*= 9.3, 5.1 Hz, 1H, C***H***$_2$OMe), 3.42 (dd, *J*= 9.2, 6.9 Hz, 1H, C***H***$_2$OMe), 3.34 (s, 3H, OC***H*****$_3$**), 2.95 (dd, *J* = 13.2, 4.1 Hz, 1H, C***H***$_2$Ph), 2.63 (dd, *J*= 13.2, 9.3 Hz, 1H, C***H***$_2$Ph), 2.38-2.46 (m, 1H, C***H***-12 or C***H***-14), 2.30-2.38 (m,1H, C***H***-12 or C***H***-14), 2.09 (ddd, *J*= 14.6, 9.8, 5.1 Hz, 1H, C***H***-12 or C***H***-14), 1.94-2.02 (m, 1H, C***H***-12 or C***H***-14), 1.78 (dddd, *J*= 12.4, 7.2, 5.2, 2.1 Hz, 1H, C***H***-11 or C***H***-16), 1.65 (dddd, *J*= 13.1, 9.6, 5.1, 1.3 Hz, 1H, C***H***-11 or C***H***-16), 1.48 (dddd, *J*= 13.0, 7.2, 5.1, 2.1 Hz, 1H, C***H***-11 or C***H***-16), 0.92 (dddd, *J*= 13.4, 9.8, 4.9, 1.3 Hz, 1H, C***H***-11 or C***H***-16).

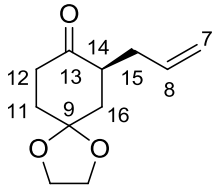
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 171.0 (CN), 139.1, 129.6, 128.1, 126.1 (C-ar), 107.9 (C-9), 76.6 (CH_2), 64.3 (CH_2), 64.2 (CH_2), 60.8 (OCH_3), 59.0 (CH-N), 39.3 (CH_2), 36.5 (CH_2), 34.9 (CH_2), 33.9 (CH_2), 25.3 (CH_2).

IR (ν, cm^{-1}, CCl_4): 3064, 3027, 2926, 2883, 2360, 1663, 1447, 1357, 1268, 1125, 1095, 1034, 953, 899.

HRMS (EI): Calcd. for $C_{18}H_{25}NO_3$: 303.1834 Found : 303.1836

[31] Chen, K.; Richter, J. M.; Baran, P. S. *J. Am. Chem. Soc.* **2008**, *130*, 7247.

(*S*)-7-Allyl-1,4-dioxaspiro[4.5]decan-8-one **MC26**

	$C_{11}H_{16}O_3$ M= 196.2 g.mol^{-1}

To a magnetically stirred solution of diisopropylamine (10 mL, 70.4 mmol) in THF (120 mL), was added *n*-BuLi (2.2 M in hexanes, 30.5 mL, 67.2 mmol, 1.05 equiv) at 0 °C. After 15 min at this temperature, the reaction mixture was cooled down to -40 °C and a solution of imine **MC25** (19.4 g, 64 mmol) in THF (60 mL) was added *via* a cannula. After 90 min at this temperature, the reaction mixture was cooled down to -78 °C and allyl bromide (6.4 mL, 70.4 mmol, 1.1 equiv) was added dropwise. After 90 min of stirring at this temperature, the reaction mixture was hydrolyzed and extracted with ether. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and removed *in vacuo*. The residue was dissolved in ether, and a buffered solution made of water (195 mL), acetic acid (46 mL) and sodium acetate (18.4 g) was added. The resulting biphasic mixture was vigourously stirred for 30 min at 20°C. The aqueous phase was then extracted with ether, and the combined organic phases were washed with a saturated bicarbonate solution, brine, dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. Flash chromatography on silica gel (petroleum ether/ ether, 3:1) afforded olefin **MC26** (9.42 g, 75% from the commercially available 1,4-dioxaspiro[4.5]decan-8-one) as a pale yellow liquid.

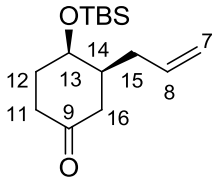
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.68 (dddd, *J*= 16.8, 10.3, 7.8, 6.4 Hz, 1H, C***H***-8), 4.93-5.00 (m, 2H, C***H₂***-7), 3.92-4.02 (m, 4H, O(C***H₂***)₂O), 2.54-2.69 (m, 2H, C***H***-14 C***H***-12), 2.46 (tddd, *J*= 14.3, 6.5, 5.1, 1.4 Hz, 1H, C***H***-15), 2.32 (ddd, *J*= 14.3, 5.1, 3.2 Hz, 1H, C***H***-12), 2.04 (ddd, *J*= 13.1, 5.7, 3.5 Hz, 1H,C***H***-16), 1.85-2.01 (m, 3H, C***H₂***-11, C***H***-15), 1.63 (t, *J*= 13.2 Hz, 1H, C***H***-16).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 210.6 (C-13), 135.7 (C-8), 116.6 (C-7), 107.3 (C-9), 64.6, 64.4 (O(***C***H_2)$_2$O), 45.7 (C-14), 39.8 (C-16), 38.0 (C-11), 34.4 (C-15), 33.1 (C-12),

IR (ν, cm^{-1}, CCl_4): 3080, 2956, 2937, 2884, 1719, 1642, 1454, 1438, 1418, 1365, 1346, 1307, 1265, 1223, 1142, 1118, 1051.

HRMS (EI) Calcd. for $C_{11}H_{16}O_3$: 196.1099 Found : 196.1097

(3*S*,4*R*)-3-Allyl-4-(*tert*-butyldimethylsilyloxy)cyclohexanone **VII-9**



$C_{15}H_{28}O_2Si$
M= 268.5 g.mol^{-1}

To a solution of ketone **MC26** (2.43 g, 12.4 mmol, 1.0 equiv) in ether (25 mL) at -78 °C was added lithium aluminium tri-*tert*-butoxyde hydride (1M in CH_2Cl_2, 17.4 mL, 17.4 mmol, 1.4 equiv) very slowly. The resulting solution was stirred for 1 h at -78 °C. 10 mL of AcOEt, 20 mL of a saturated aqueous Rochelle's salt solution and 20 mL of ether were added and the mixture was stirred for 2 h at 20 °C. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford alcohol **VII-10**.
A solution of alcohol **VII-10** (12.4 mmol) in THF (100 mL) and 1 N HCl (40 mL) was refluxed for 2 h. THF was then removed *in vacuo* and the resulting aqueous phase was extracted with ether. The combined organic phases were washed with a saturated bicarbonate solution, brine, dried over $MgSO_4$, filtered and removed *in vacuo* to afford crude ketone **VII-11**.
To a solution of alcohol **VII-11** (12.4 mmol) in CH_2Cl_2 (25 mL) was added imidazole (2.53 g, 37.1 mmol, 3.0 equiv) and TBSCl (3.73 g, 24.8 mmol, 2.0 equiv) at 0 °C. The reaction mixture was stirring at 20 °C overnight and was then quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (98:2 petroleum ether/ether) to afford protected alcohol **VII-9** (2.83 g, 85% over 3 steps) as a colorless oil.

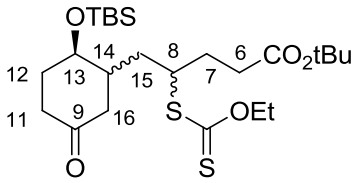
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.68 (ddt, *J*= 17.2, 10.3, 7.0 Hz, 1H, C***H***-8), 4.99-5.04 (m, 2H, C***H$_2$***-7), 3.79 (dd, *J*= 8.7, 5.8 Hz, 1H, C***H***-13), 2.66 (dd, *J*= 13.6, 4.5 Hz, 1H, C***H***-16), 2.51-2.59 (m, 1H, C***H***-11), 1.77-2.26 (m, 7H, C***H$_2$***-16, C***H$_2$***-15, C***H$_2$***-12, C***H***-14), 0.90 (s, 9H, SiC(C***H$_3$***)$_3$, 0.08 (s, 6H, Si(C*H*$_3$)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 211.2 (C-9), 135.3 (C-8), 117.1 (C-7), 70.1 (C-13), 44.2 (C-14), 42.2 (C-16), 37.4 (C-11), 36.9 (C-15), 31.3 (C-12), 25.7 (SiC(***C***H$_3$)$_3$), 18.0 (SiC), -4.5, -4.8 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, CCl_4) 3081, 2956, 2930, 2897, 2858, 1720, 1642, 1471, 1462, 1431, 1418, 1361, 1324, 1304, 1284, 1254, 1103, 1063.

HRMS (EI) Calcd. for $C_{15}H_{28}O_2Si$ -*t*Bu : 211.1154 Found : 211.1150

(*R*)-*tert*-Butyl 5-(2-(*tert*-butyldimethylsilyloxy)-5-oxocyclohexyl)-4-(ethoxycarbonothioylthio)pentanoate **VII-12**



$C_{24}H_{44}O_5S_2Si$
M= 504.8 g.mol^{-1}

Following general procedure **III-A** for radical addition, the reaction was carried out with a solution of olefin **VII-9** (1.90 g, 7.1 mmol, 1.0 equiv) and xanthate **BH3**[18] (2.51 g, 10.6 mmol, 1.5 equiv) in ethyl acetate, and needed 15 mol% of DLP to go to completion (4 h 30 min). Flash chromatography on silica gel (petroleum ether/ether 9:1) afforded radical adduct **VII-12** (3.04 g, 85%) as a viscous pale yellow oil and as an inseparable mixture of two diastereomers in a 2:1 ratio.

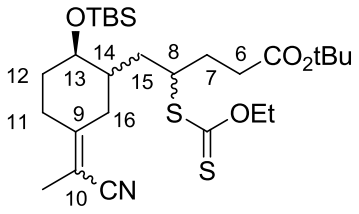
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 4.60-4.67 (m, 2H, OC***H*₂**), 3.73-3.83 (m, 2H, C***H***-13, C***H***-8), 2.78-2.87 (m, 2H), 2.56-2.64 (m, 1H), 2.32-2.38 (m, 2H), 2.18-2.27 (m, 2H), 1.94-2.12 (m, 3H), 1.70-1.88 (m, 2H), 1.51-1.60 (m, 1H), 1.43 (s, 9H, CO_2tBu), 1.41 (t, *J*= 7.1 Hz, 3H, OCH_2C***H*₃**), 0.91, 0.90, 0.81 (3s, 9H, $SiC(C$***H*₃**$)_3$), 0.09, 0.07, 0.07 (4s, 6H, $Si(C$***H*₃**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 213.9, 213.8 (C=S), 172.1, 172.0 (C=O), 80.5, 80.5 (O***C***$(CH_3)_3$), 70.2, 69.5 (C-13), 70.1, 70.1 (OCH_2), 48.4, 48.3 (C-8), 42.8, 42.2, (C-16), 42.1, 41.9 (C-14), 37.4, 37.2 (C-11), 32.6, 32.4 (C-7), 31.2, 31.0 (C-6), 29.5, 29.0 (C-15), 28.1 ($OC(CH_3)_3$), 25.8, 25.7 ($SiC($***C***$H_3)_3$), 25.6, 25.6 (C-12), 18.0, 18.0 (SiC), 13.8, 13.8 (OCH_2CH_3), -3.6, -4.6, -4.7, -4.8 ($Si(CH_3)_2$).

IR (ν, cm^{-1}, CCl_4) 2980, 2956, 2930, 2902, 1728, 1471, 1462, 1391, 1367, 1254, 1219, 1149, 1111, 1054.

HRMS (EI) Calcd. for $C_{24}H_{44}O_5S_2Si$: 504.2399 Found : 504.2391

tert-Butyl 5-((1*R*,2*R*)-2-(_tert_-butyldimethylsilyloxy)-5-(1-cyanoethyli dene) cyclohexyl)-4-(ethoxycarbonothioylthio)pentanoate **VII-13**



$C_{27}H_{47}NO_4S_2Si$
M= 541.9 g.mol^{-1}

To a magnetically stirred solution of diethyl 1-cyanoethylphosphonate **MC6** (2.8 g, 14.7 mmol, 3.0 equiv) in THF (25 mL) was added LiH (118 mg, 14.7 mmol, 3.0 equiv) at 20 °C. The resulting heterogeneous solution was then refluxed for 15 min, and a solution of ketone **VII-12** (2.48 g, 4.91 mmol) in THF (25 mL) was transferred *via* cannula. It was then carefully hydrolyzed, and the resulting aqueous layer was extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and removed *in vacuo*. Flash chromatography on silica gel (petroleum ether/ether, 1:1) afforded nitrile **VII-13** (3.92 g, 70%) as a very viscous pale yellow oil consisting of an inseparable mixture of 4 diastereomers (dr not determined).

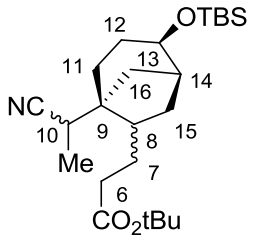
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.60-4.66 (m, 2H, OC***H*₂***), 3.86-3.98 (m, 1H, C***H***-13), 3.52-3.75 (m, 1H, C***H***-8), 2.66-2.95 (m, 2H), 2.00-2.47 (m, 5H), 1.92, 1.88, 1.86 (3s, 3H, C***H*₃***-C11), 1.70-1.90 (m, 4H), 1.52-1.58 (m, 1H), 1.41-1.43 (m, 9H, CO_2tBu), 1.39-1.42 (m, 3H, OCH_2C***H*₃***), 1.19-1.37 (m, 1H), 0.88, 0.87 (2s, 9H, SiC(C***H*₃***)$_3$), 0.05, 0.04, 0.04, 0.03 (4s, 6H, SiC(C***H*₃***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 214.9, 214.1, 213.9, 213.6 (C=S), 172.2, 172.2, 172.1, 172.1 (C=O), 156.3, 156.1 (C-9), 119.6, 119.6, 119.6, 119.6 (CN), 102.0, 101.8, 101.7 (C-11), 80.4, 80.4 (OC(CH_3)$_3$), 72.1, 71.6, 71.1, 70.3 (C-13), 70.2, 70.0, 70.0, 69.9 (OCH_2), 49.4, 48.9, 48.6, 48.5 (C-8), 42.2, 42.0, 41.9, 41.8 (C-14), 37.2, 36.6, 36.3, 36.2 (C-12), 35.8, 34.9, 33.4, 33.1, 32.7, 32.5, 32.4, 32.1, 31.8, 31.7, 31.4, 31.3, 31.0, 30.9, 30.9, 30.7 (C-16, C-7, C-6, C-15, C-12), 29.6, 28.9, 25.2 (C-11), 28.0 (OC(CH_3)$_3$), 25.8 (SiC(CH_3)$_3$), 25.2 (CH_2), 18.0, 17.9 (SiC), 15.7, 15.7, 15.6, 15.6 (CH_3-C11), 13.8, 13.8 (OCH_2CH_3), -4.3, -4.4, -4.6, -4.8 (SiC(CH_3)$_2$).

IR (ν, cm^{-1}, CCl_4): 2979, 2957, 2930, 2858, 2212, 1730, 1637, 1471, 1462, 1391, 1367, 1255, 1217, 1148, 1112, 1052, 1004.

HRMS (EI): Calcd. for $C_{27}H_{47}NO_4S_2Si$: 541.2716 Found : 541.2710

_S_-1-((1_R_,2_R_)-2-(_tert_-butyldimethylsilyloxy)-5-(1-cyanoethylidene) cyclohexyl)-4-cyanobutan-2-yl _O_-ethyl carbonodithioate **VII-8**

	$C_{24}H_{43}NO_3Si$ M= 421.7 g.mol^{-1}

A solution of xanthate **VII-13** (329 mg, 0.61 mmol), hypophosphorous acid (50% solution in water, 313 µL, 3.04 mmol), and triethylamine (467 µL, 3.34 mmol) in 1,4 dioxane (7.6 mL), was refluxed under a nitrogen atmosphere for 20 min. AIBN (20 mg, 0.12 mmol) was then added, and the reaction mixture was refluxed for 2 h. AIBN (20 mg, 0.12 mmol) was added again, and the reaction mixture was refluxed for a further 2 h. The reaction mixture was then cooled to 20 °C and diluted with water. The resulting aqueous phase was extracted with ether and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and removed *in vacuo*. Flash chromatography on silica gel (petroleum ether/ether, 7:3) afforded bicycle **VII-8** (220 mg, 86%) as a very viscous colorless oil and as an inseparable mixture of 4 diastereomers (dr not determined).

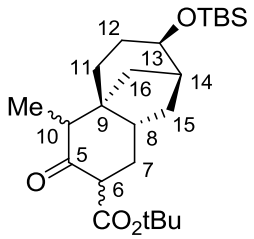
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 3.67-3.69 (m, 1H, C***H***-13), 2.59-2.69 (m, 1H, C***H***-10), 1.59-2.34 (m, 11H), 1.44, 1.44 (2s, 9H, CO_2tBu), 1.25-1.32 (m, 6H), 0.88, 0.87 (2s, 9H, SiC(C***H*****$_3$**)$_3$), 0.02, 0.01 (2s, 6H, Si(CH_3)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 172.8, 172.7 (C=O), 122.6, 122.3 (CN), 80.4, 80.3 (C-O), 69.8, 69.6 (C-13), 46.2, 45.8 (C-9), 41.7 (CH), 41.5 (CH), 41.1 (CH), 39.6 (CH), 35.4 (CH_2), 35.0 (2×CH_2), 33.7 (2×CH_2), 33.3 (CH_2), 31.4 (CH), 31.3 (CH), 28.3 (CH_2), 28.2 (CH_2), 28.1, 28.1 (OC(***C***H_3)$_3$), 27.1 (CH_2), 27.0 (CH_2), 25.8 (SiC(***C***H_3)$_3$), 18.0 (SiC), 14.4, 13.9 (CH_3-10), -4.8, -4.8, -4.8, -4.9 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, CCl_4) 2951, 2932, 2859, 1728, 1471, 1462, 1454, 1392, 1368, 1255, 1151, 1090, 1059.

HRMS (EI) Calcd.for $C_{24}H_{43}NO_3Si$: 421.3012 Found : 421.3016

tert-Butyl (4a*R*,7*R*,8*S*)-7-{[_tert_-butyl(dimethyl)silyl]oxy}-4-methyl-3-oxodecahydro-4a,8-methanobenzo[7]annulene-2-carboxylate **VII-16**



$C_{24}H_{42}O_4Si$
M= 422.7 g.mol^{-1}

To a solution of bicycle **VII-8** (708 mg, 1.68 mmol) in freshly distilled THF (20 mL), was added dropwise freshly prepared LiHMDS in THF (2 equiv, approximately 1M) at -10 °C. The reaction mixture was stirred for 40 min and a 1M HCl solution (20 mL) was added. The mixture was allowed warm to 20 °C and was vigorously stirred for a further 1 h, then ethyl acetate (50 mL) was then added. The resulting solution was extracted with AcOEt and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and removed *in vacuo*. Flash chromatography on silica gel (petroleum ether/ether, 7:3) afforded tricycle **VII-16** (440 mg, 62%) as a very viscous colorless oil consisting of an inseparable mixture of 2 diastereomers in 7:3 ratio.

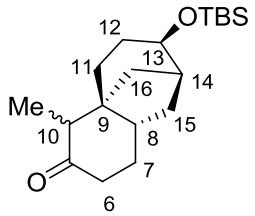
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 3.66-3.69 (m, 0.3H, C***H***-13 dia2), 3.60-3.64 (m, 0.7H, C***H***-13 dia1), 3.32 (dd, *J*= 14.4, 4.0 Hz, 0.7H, C***H***-6 dia1), 3.12 (dd, *J*= 9.1, 4.7 Hz, 0.3H, C***H***-6 dia2), 2.59 (q, *J*= 6.7 Hz, 0.3H, C***H***-10 dia2), 2.33 (q, *J*= 6.7 Hz, 0.7H, C***H***-10 dia1), 2.30-2.40 (m, 0.3H), 1.99-2.24 (m, 3.7H), 1.62-1.89 (m, 5H), 1.45,1.45 (2s, 9H, CO_2*t*Bu), 1.07 (d, *J*= 6.8 Hz, 0.9H, C***H*****$_3$**-10 dia2), 1.08-1.30 (m, 3H), 1.06 (d, *J*= 6.7 Hz, 2.1H, C***H*****$_3$**-10 dia1), 0.87, 0.87 (s, 9H, SiC(C***H*****$_3$**)$_3$), 0.02, 0.00 (2s, 6H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 209.1, 208.2 (C-5), 169.8, 168.4 (C=O), 81.5, 81.1 (C-O), 70.0, 69.8 (C-13), 56.0, 53.7 (C-6), 52.8, 52.3 (C-9), 49.5, 47.8 (C-10), 42.1, 41.7 (C-8), 38.9, 36.7 (C-6), 35.8, 35.6 (C-16), 35.6, 35.4 (C-15), 34.5, 32.3 (C-11), 31.6, 30.3 (C-11), 28.6, 27.6 (C-7), 28.0, 27.9 (OC(***C***H$_3$)$_3$), 25.8 (SiC(***C***H$_3$)$_3$), 18.0 (SiC), 10.3, 9.6 (CH_3-10), -4.8, -4.8, -4.9, -4.9 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, CCl_4) 2955, 2931, 2857, 1739, 1715, 1471, 1461, 1392, 1368, 1286, 1255, 1158, 1122, 1058, 1024, 1001.

HRMS (EI) Calcd. for $C_{24}H_{42}O_4Si$: 422.2852 Found : 422.2847

(4aR,7R,8S)-7-{[*tert*-Butyl(dimethyl)silyl]oxy}-4-methyloctahydro-4a,8-methanobenzo[7]annulen-3-one **VII-7**

	$C_{19}H_{34}O_2Si$ M= 322.6 g.mol^{-1}

A solution of the keto ester **VII-16** (16 mg, 0.05 mmol) in DMSO (400 µL) was refluxed for 1 h. The reaction mixture was then cooled to 20°C. Flash chromatography on silica gel (ether/petroleum ether, 8:2) afforded **VII-7** (13 mg, 80%) as a very viscous colorless oil and as an inseparable mixture of 2 diastereomers in a 7:3 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)

3.52-3.53 (m, 1H, C***H***-13), 2.55 (q, *J*= 6.7 Hz, 0.7H, C***H***-10 dia1), 2.41 (q, *J*= 6.8 Hz, 0.3H C***H***-10 dia2), 2.05-2.32 (m, 4H), 1.91-1.98 (m, 1H), 1.23-1.86 (m, 9H), 0.90 (d, *J*= 6.8 Hz, 0.9H, C***H$_3$***-10 dia2), 0.85 (d, *J*= 6.7 Hz, 2.1H, C***H$_3$***-10 dia1), 0.84 (s, 9H, SiC(C***H$_3$***)$_3$), 0.05 (s, 6H, Si(C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

Major diastereomer 1

214.3 (C-5), 68.1 (C-13), 49.4 (C-10), 45.5 (C-9), 42.5 (C-8), 40.3 (C-14), 38.6 (C-6), 36.5 (C-16), 34.8 (C-15), 29.2 (C-12), 27.0 (C-11), 26.6 (C-7), 25.8 (SiC(***C***H$_3$)$_3$), 17.8 (SiC), 9.1 (CH_3-10), -3.2 (Si(CH_3)$_2$).

Minor diastereomer 2

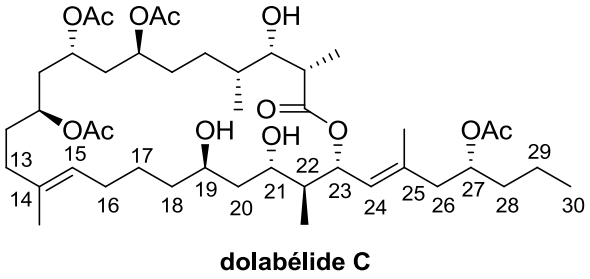
214.3 (C-5), 68.0 (C-13), 49.7 (C-10), 47.3 (C-9), 42.5 (C-8), 41.3 (C-14), 37.1 (C-6), 36.3 (C-16), 35.1 (C-15), 28.6 (C-12), 27.1 (C-11), 25.5 (C-7), 25.8 (SiC(***C***H$_3$)$_3$), 17.8 (SiC), 9.6 (CH_3-10), -3.2 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, CCl_4) 2931, 2858, 1715, 1461, 1407, 1375, 1360, 1254, 1226, 1134, 1093, 1049.

HRMS (EI) Calcd. for $C_{19}H_{34}O_2Si$: 322.2328 Found : 322.2330

F. Chapitre VIII : Synthèse du Fragment C16-C30 du Dolabélide C

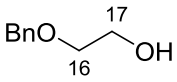
La numérotation des carbones et des hydrogènes de chaque composé décrit dans ce chapitre correspondant à celle de la nomenclature du fragment C16-C30 du dolabélide C (***Figure III***).



dolabélide C

Figure 3 *– Structure du dolabélide C.*

2-Benzyloxyethanol[32] **AV16**

	$C_9H_{12}O_2$ M= 152.2 g.mol^{-1}

A suspension of NaH (60% dispersion in mineral oil, 3.27 g, 80.6 mmol, 1.0 equiv) in 700 mL of THF was treated with 1,2 ethanediol (5 g, 80.6 mmol) dropwise. The reaction was stirred at 20 °C for 30 min, and a solution of benzylbromide (13.8 g, 80.6 mmol, 1.0 equiv) dissolved in a small amount of THF was added dropwise. The reaction was stirred for 48 hours, cooled and diluted with 400 mL of water. The mixture was extracted three times with portions of ether, the combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 80:20, then ether) to provide 2-benzyloxyethanol **AV16** (6.9 g, 56%) as a clear oil.

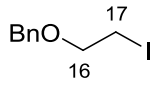
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.36-7.22 (m, 5H, ***H***-ar), 4.54 (s, 2H, C***H*****$_2$**-Ph), 3.72 (t, *J* = 4.4 Hz, 2H, C***H*****$_2$**-16), 3.56 (t, *J* = 4.4 Hz, 2H, C***H*****$_2$**-17).

[32] Cadwell, J. J.; Colman, R.; Kerr, W. J.; Magennis, E. J. *Synlett* **2001**, 1428.

^{13}C NMR (δ, ppm) (CDCl$_3$, 100 MHz) 137.8, 128.3, 127.7, 127.6 (C-ar), 73.1 (CH_2Ph), 71.3 (C-16), 61.6 (C-17).

MS (DI, CI, NH_3) 108, 153 ($M+H^+$), 170 ($M+NH_4^+$).

2-Benzyloxyethyl iodide[33] AV17

	$C_9H_{11}IO$ M= 262.1 g.mol^{-1}

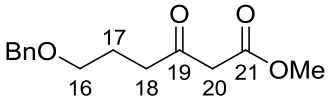
To a solution of 2-benzyloxyethanol **AV16** (8.60 g, 56.5 mmol) in THF (300 mL) were added imidazole (7.7 g, 113 mmol, 2.0 equiv), triphenylphosphine (26.7 g, 102 mmol, 1.8 equiv) and diode (27.3 g, 107 mmol, 1.9 equiv) at 20 °C. The reaction was stirred for 2 hours at 20 °C. The reaction mixture was quenched with sodium thiosulfate, and extracted with ethyl acetate. The organic phase was washed with water, then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 85:15) to provide 2-benzyloxyethyl iodide **AV17** (14.0 g, 94%) as a clear liquid.

^{1}H NMR (δ, ppm) (CDCl$_3$, 400 MHz) 7.36-7.27 (m, 5H, C***H***-ar), 4.58 (s, 2H, C***H*****$_2$**-Ph), 3.74 (t, *J* = 6.8 Hz, 2H, C***H*****$_2$**-16), 3.29 (t, *J* = 6.8 Hz, 2H, C***H*****$_2$**-17).

MS (DI, CI, NH_3) 263 ($M+H^+$), 280 ($M+NH_4^+$).

[33] Berlage, U.; Schmidt, J.; Peters, U.; Welzel, P. *Tetrahedron Lett.* **1987**, *28*, 3091.

Methyl 6-benzyloxy-3-oxohexanoate[33] AV18

	$C_{14}H_{18}O_4$ M= 250.3 g.mol^{-1}

To a stirred suspension of NaH (60% dispersion in mineral oil, 3.16 g, 79 mmol, 1.2 equiv) in THF (80 mL) at 0 °C was added dropwise methyl acetoacetate (7.1 mL, 66 mmol). After 10 min, *n*-butyllithium (1.41 M hexane solution, 57.4 mL, 81 mmol, 1.23 equiv) was added dopwise. After the mixture had been stirred at 0 °C for 10 min, a solution of 2-benzyloxyethyl iodide **AV17** (13.8 g, 53 mmol, 0.8 equiv) in THF (40 mL) was added dropwise. The solution was stirred at 20 °C for 1 h then quenched with a saturated aqueous NH_4Cl solution, filtered and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford ester **AV18** (9.93 g, 76%) as a yellow oil.

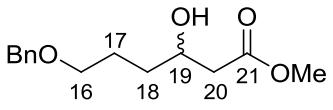
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.22-7.33 (m, 5H, C***H***-ar), 4.46 (s, 2H, C***H*****$_2$**Ph), 3.70 (s, 3H, OC***H*****$_3$**), 3.47 (t, *J* = 6.1 Hz, 2H, C***H*****$_2$**-16), 3.43 (s, 2H, C***H*****$_2$**-20), 2.64 (t, *J* = 7.1 Hz, 2H, C***H*****$_2$**-18), 1.90 (tt, *J* = 7.1, 6.1 Hz, 2H, C***H*****$_2$**-17).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 202.3 (C-19), 167.6 (C-21), 138.2, 128.3, 127.8, 127.6 (C-ar), 72.8 (CH_2Ph), 69.1 (C-16), 52.3 (OCH_3), 49.0 (C-20), 39.8 (C-18), 23.6 (C-17).

IR (ν, cm^{-1}, $CDCl_3$): 3030, 2952, 2863, 1747, 1716 (C=O), 1497, 1456, 1438, 1408, 1362, 1323, 1267, 1202, 1103.

MS (DI, CI, NH_3): 144, 251 ($M+H^+$), 268 ($M+NH_4^+$).

Methyl (*R*)-6-benzyloxy-3-hydroxyhexanoate[34] **(±)-AV19**

	$C_{14}H_{20}O_4$ M= 252.3 g.mol^{-1}

For the preparation of the catalyst, complex $[RuCl_2C_6H_6]_2$ (67 mg, 0.102 mmol, 0.35 mol%) and (*R*)-BINAP (140 mg, 0.223 mmol, 0.8 mol%) were dissolved in DMF (10 mL) and stirred at 110 °C for 10 min. A solution of ketone **AV18** (7.0 g, 28.0 mmol) in degassed methanol (20 mL) was added to the catalyst solution and this mixture was transferred to the hydrogenation reactor. The solution was treated with 10 bar hydrogen at 95 °C and vigorous stirring for 20 h. After cooling to 20 °C the dark red solution was concentrated *in vacuo* and purified by silica gel column chromatography (petroleum ether/ether 70:30) to afford racemic β-hydroxyester **AV19** (6.71 g, 95%) as a pale yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.27-7.36 (m, 5H, C***H***-ar), 4.51 (s, 2H, C***H*****$_2$**Ph), 4.03 (tq, *J* = 8.2, 4.1 Hz, 1H, C***H***-19), 3.70 (s, 3H, OC***H*****$_3$**), 3.51 (t, *J* = 6.2 Hz, 2H, C***H*****$_2$**-16), 3.29 (d, *J* = 3.9 Hz, 1H, O***H***), 2.51 (dd, *J* = 16.2, 4.1 Hz, 1H, C***H***-20), 2.45 (dd, *J* = 16.2, 8.2 Hz, 1H, C***H***-20), 1.70-1.82 (m, 2H, C***H*****$_2$**-18), 1.48-1.69 (m, 2H, C***H*****$_2$**-17).

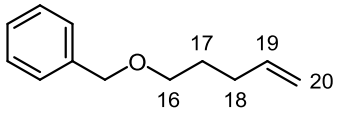
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 173.1 (C-21), 138.2, 128.3, 127.6, 127.5 (C-ar), 72.9 (CH_2Ph), 70.1 (C-16), 67.7 (C-19), 51.2 (OCH_3), 41.3 (C-20), 33.6 (C-18), 25.8 (C-17).

IR (ν, cm^{-1}, $CDCl_3$): 3442 (OH), 2952, 2856, 1735, 1440, 1205, 1170, 1100, 741, 697.

HRMS (EI): Calcd. for $C_{14}H_{20}O_4$: 252.1362 Found : 252.1360

[34] Hoppen, S.; Baurle, S.; Koert, U. *Chem. Eur. J.* **2000**, *6*, 2382.

1-Benzyloxy-4-pentene[35] **VIII-8**



$C_{12}H_{16}O$
M= 176.3 g.mol^{-1}

tetra-Butylammonium iodide (500 mg, 1.3 mmol, 10% wt) was added to a stirred suspension of NaH (50% dispersion in mineral oil, 5.28 g, 110 mmol, 1.9 equiv) in THF (40 mL). After cooling to 0 °C, 4-penten-1-ol **VIII-7** (6.0 mL, 58 mmol) was added dropwise and the mixture was stirred at 20 °C for 30 min. Benzyl bromide (11.2 mL, 94 mmol, 1.6 equiv) was slowly added at 0 °C and the reaction mixture was stirred at 20 °C for 3 h. The reaction was quenched by careful addition of water and the solution was extracted with ether. The combined organic extracts were washed with water then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 90:10) to afford protected alcohol **VIII-8** (10.2 g, quant.) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.32-7.40 (m, 5H, C***H***-ar), 5.86 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, C***H***-19), 5.07 (dd, *J* = 17.0, 2.0 Hz, 1H, C***H***-20), 5.01 (dd, *J* = 10.4, 2.0 Hz, 1H, C***H***-20), 4.55 (s, 2H, C***H*****$_2$**Ph), 3.52 (t, *J* = 6.5 Hz, 2H, C***H*****$_2$**-16), 2.19 (q, *J* = 7.0 Hz, 2H, C***H*****$_2$**-18), 1.76 (quint, *J* = 6.5 Hz, 2H, C***H*****$_2$**-17).

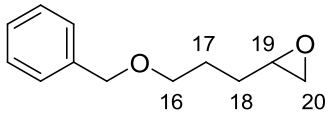
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 138.6, 128.3, 127.5, 127.4 (C-ar), 138.2 (C-19), 114.6 (C-20), 72.8 (CH_2Ph), 69.6 (C-16), 30.3 (C-18), 28.9 (C-17).

IR (ν, cm^{-1}, $CHCl_3$): 3067, 3030, 3017, 3011, 2978, 2941, 2863, 1640, 1496, 1454, 1364, 1227, 1098.

MS (DI, CI, NH_3): 177 ($M+H^+$), 194 ($M+NH_4^+$).

[35] Chow, S.; Kitching, W. *Tetrahedron: Asymmetry* **2002**, *13*, 779.

2-(3-Benzyloxypropyl)oxirane[36] (±)-VIII-6

	$C_{12}H_{16}O_2$ M= 192.3 g.mol^{-1}

1-Benzyloxy-4-pentene **VIII-8** (8.5 g, 48 mmol) was dissolved in CH_2Cl_2 (200 mL). *m*-CPBA 70% (20 g, 81 mmol, 1.4 equiv) was added in small portions and the reaction was stirred overnight at 20 °C. It was then filtered and diluted with CH_2Cl_2. The solution was washed twice with 10% aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$ then with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 80:20) to afford epoxide **(±)-VIII-6** (7.9 g, 86%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.26-7.35 (m, 5H, C***H***-ar), 4.51 (s, 2H, C***H*****$_2$**Ph), 3.47-3.56 (m, 2H, C***H*****$_2$**-16), 2.92-2.96 (m, 1H, C***H***-19), 2.74-2.76 (m, 1H, C***H***-20), 2.47 (dd, *J* = 5.0, 2.7 Hz, 1H, C***H***-20), 1.56-1.83 (m, 4H, C***H*****$_2$**-17, C***H*****$_2$**-18).

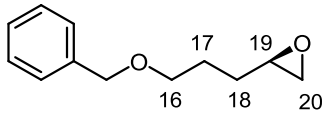
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 138.5, 128.4, 127.6, 127.5 (C-ar), 72.9 (CH_2Ph), 69.8 (C-16), 52.1 (C-19), 47.1 (C-20), 29.3 (C-18), 26.2 (C-17).

IR (ν, cm^{-1}, $CHCl_3$) 3036, 3027, 3015, 3010, 2957, 2856, 1452, 1315, 1278, 1259, 1222, 1202, 1177, 1109, 1071, 1027.

MS (DI, CI, NH_3) 193 ($M+H^+$), 210 ($M+NH_4^+$).

[36] Lowik, D. W. P. M.; Liskamp, R. M. J. *Eur. J. Org. Chem.* **2000**, 1219.

(R)-2-(3-Benzyloxypropyl)oxirane[37] **VIII-6**

	$C_{12}H_{16}O_2$ M= 192.3 g.mol^{-1}

Preparation of the active catalyst:

(R,R)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt (II) (200 mg, 0.3 mmol) and acetic acid (23 µL) were stirred in toluene (1 mL) under air for 1 h. The solvent was removed *in vacuo* to afford the catalyst.

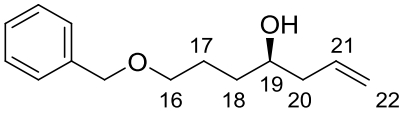
Hydrolytic kinetic resolution of the racemic epoxide **(±)** :

Racemic epoxide **(±)-VIII-6** (7.9 g, 41 mmol), H_2O (0.44 mL, 25 mmol, 0.6 equiv) and the previous catalyst (136 mg, 0.20 mmol, 0.5 mol%) were mixed at 0 °C and stirred at 20 °C for 19 h. The residue was purified by silica gel column chromatography (petroleum ether/ether 95:5) to afford (*R*)-epoxide **VIII-6** (3.83 g, 97%)[38] as a colorless oil. Spectral data were identical with those of racemate **(±)-VIII-6**. The epoxide **VIII-6** was analysed by chiral HPLC using a Chiral OD cel column with a flow rate of 1.0 mL/min and solvent system of 0.5% isopropanol/hexane. The *ee* was determined to be > 98%.

$[\alpha]^{25}_D$ + 8.7 (*c* 1.0, $CHCl_3$)

[37] Chow, S.; Kitching, W. *Tetrahedron: Asymmetry* **2002**, *13*, 779.
[38] The kinetic resolution yield is expressed as a percentage of the theoretical maximum yield of 50%.

(R)-7-Benzyloxyhept-1-en-4-ol **VIII-10**



$C_{14}H_{20}O_2$
M= 220.3 g.mol^{-1}

To a stirred suspension of copper (I) iodide (2.38 g, 12.5 mmol, 0.5 equiv) in THF (100 mL) was added vinylmagnesium bromide (1M THF solution, 125 mL, 125 mmol, 5.0 equiv) dropwise at -30 °C. After 30 min, epoxide **VIII-6** (4.8 g, 25 mmol) in THF (25 mL) was slowly added to the mixture. After stirring at –30 °C for 2 h, the reaction was quenched with saturated aqueous NH_4Cl, filtered and extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 80:20) to afford homoallylic alcohol **VIII-10** (5.23 g, 95%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.25-7.37 (m, 5H, C***H***-ar), 5.78-5.89 (m, 1H, C***H***-21), 5.12 (dm, *J* = 16.1 Hz, 1H, C***H***-22), 5.12 (dm, *J* = 11.2 Hz, 1H, C***H***-22), 4.52 (s, 2H, C***H$_2$***Ph), 3.63 (m, 1H, C***H***-19), 3.52 (t, *J*= 6.0 Hz, 2H, C***H$_2$***-16), 2.34 (d, *J*= 3.9 Hz, 1H, O***H***), 2.17-2.31 (m, 2H, C***H$_2$***-20), 1.71-1.78 (m, 2H, C***H$_2$***-17), 1.62-1.69 (m, 1H, C***H***-18), 1.46-1.55 (m, 1H, C***H***-18).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 138.2, 128.4, 127.7, 127.6 (C-ar), 138.2 (C-21), 117.8 (C-22), 73.0 (CH_2Ph), 70.6 (C-19), 70.4 (C-16), 42.0 (C-20), 34.0 (C-18), 26.2 (C-17).

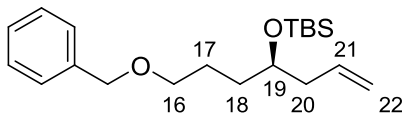
IR (ν, cm^{-1}, $CHCl_3$): 3593, 3413, 3080, 3021, 3014, 3009, 2931, 2864, 1640, 1496, 1454, 1364, 1240, 1095, 1028.

MS (DI, CI, NH_3): 221 ($M+H^+$), 238 ($M+NH_4^+$).

$[\alpha]^{25}_D$: + 6.8 (*c* 1.3, $CHCl_3$)

HRMS (EI): Calcd. for $C_{20}H_{34}O_2Si$: 220.1463 Found : 220.1460

(R)-7-Benzyloxy-4-*tert*-butyldimethylsilyloxyhex-1-ene **VIII-11a**



$C_{20}H_{34}O_2Si$
M= 334.6 g.mol^{-1}

To a stirred suspension of alcohol **VIII-10** (3.6 g, 16 mmol) in CH_2Cl_2 (160 mL) was added imidazole (3.3 g, 49 mmol, 3.0 equiv) and TBSCl (4.9 g, 33 mmol, 2.0 equiv) at 0 °C. After stirring at 20 °C overnight, the reaction was quenched with saturated aqueous NH_4Cl and extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (98:2 petroleum ether/ether) to afford protected alcohol **VIII-15a** (5.0 g, 91%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.27-7.34 (m, 5H, C***H***-ar), 5.81 (ddt, *J*= 17.6, 10.5, 7.2 Hz, 1H, C***H***-21), 5.03 (dm, *J* = 16.8 Hz, 1H, C***H***-22), 5.02 (dm, *J* = 10.6 Hz, 1H, C***H***-22), 4.50 (s, 2H, C***H$_2$***Ph), 3.69-3.74 (m, 1H, C***H***-19), 3.46 (t, *J* = 6.6 Hz, 2H, C***H$_2$***-16), 2.22 (t, *J*= 6.4 Hz, 2H, C***H$_2$***-20), 1.58-1.74 (m, 2H, C***H$_2$***-17), 1.42-1.55 (m, 2H, C***H***-18), 0.88 (s, 9H, SiC(C***H$_3$***)$_3$), 0.04, 0.04 (2s, 6H, Si(C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 138.6, 128.3, 127.6, 127.4 (C-ar), 135.2 (C-21), 116.7 (C-22), 72.8 (CH_2Ph), 71.7 (C-19), 70.5 (C-16), 41.9 (C-20), 33.2 (C-18), 25.9 (SiC(CH_3)$_3$), 25.6 (C-17), 18.1 (SiC), -4.4, -4.5 (Si(CH_3)$_2$).

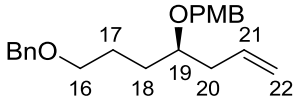
IR (ν, cm^{-1}, $CHCl_3$): 3078, 3029, 3023, 3017, 2955, 2930, 2858, 1640 (C=C), 1496, 1472, 1463, 1454, 1409, 1389, 1362, 1256, 1226, 1215, 1211, 1202, 1092.

MS (DI, CI, NH_3): 335 (M+H$^+$), 352 (M+NH_4^+).

$[\alpha]^{25}_D$: + 13.6 (*c* 1.0, $CHCl_3$)

HRMS (EI): Calcd. for $C_{20}H_{34}O_2Si$: 334.2328 Found : 334.2317

(R)-7-Benzyloxy-4-(4-methoxybenzyloxy)-hex-1-ene **VIII-11b**

	$C_{22}H_{28}O_3$ M= 340.5 g.mol^{-1}

tetra-Butylammonium iodide (200 mg, 0.54 mmol, 10% wt) was added to a stirred suspension of NaH (60% dispersion in mineral oil, 783 mg , 19.6 mmol, 2.2 equiv) in THF (40 mL). After cooling to 0 °C, alcohol **VIII-10** (1.96 g, 8.9 mmol) was added dropwise and the mixture was stirred at 20 °C for 30 min. PMBBr (2.86 g, 14.4 mmol, 1.6 equiv) was slowly added at 0 °C and the reaction mixture was stirred at reflux overnight. The reaction was quenched by careful addition of water and the solution was extracted with ether. The combined organic extracts were washed with water then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (90:10 petroleum ether/ether) to afford protected alcohol **VIII-11b** (2.52 g, 83%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.35 (m, 5H, C***H***-ar), 7.25-7.27 (m, 2H, C***H***-ar), 6.85-6.88 (m, 2H, C***H***-ar), 5.84 (ddt, *J*= 17.2, 10.2, 7.1 Hz, 1H, C***H***-21), 5.04-5.11 (m, 2H, C***H***-22), 4.49 (s, 2H, C***H$_2$***Ph(Bn)), 4.50 (d, *J*= 11.2 Hz, 1H, C***H***Ph(PMB)), 4.41 (d, *J*= 11.2 Hz, 1H, C***H***Ph(PMB)), 3.43-3.48 (m, 3H, C***H$_2$***-16, C***H***-19), 2.26-2.38 (m, 2H, C***H$_2$***-20), 1.56-1.80 (m, 4H, C***H$_2$***-17, C***H$_2$***-18).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 159.1, 138.6, 130.9, 129.3, 128.3, 127.6, 127.5, 113.7 (C-ar), 134.9 (C-21), 116.9 (C-22), 77.9 (C-19), 72.8 (), 70.5 (C-16), 70.4 (CH_2Ph(PMB)), 55.3 (OCH_3), 38.3(C-20), 30.4 (C-18), 25.7 (C-17).

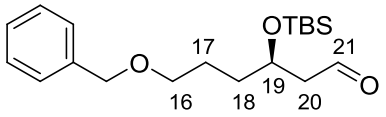
IR (ν, cm^{-1}, $CHCl_3$): 3006, 2937, 2863, 1640 (C=C), 1612, 1514, 1465, 1454, 1442, 1362, 1302, 1249, 1174, 1091, 1036.

MS (DI, CI, NH_3): 341 ($M+H^+$), 358 ($M+NH_4^+$).

$[\alpha]^{25}_D$: + 15.7 (*c* 1.0 , $CHCl_3$)

HRMS (EI): Calcd. for $C_{22}H_{28}O_3$: 340.2039 Found : 340.2032

(R)-6-Benzyloxy-3-*tert*-butyldimethylsilyloxyhexanal **VIII-5a**



$C_{19}H_{32}O_3Si$
M= 336.6 g.mol^{-1}

Through a solution of alkene **VIII-11a** (3.9 g, 12 mmol) in CH_2Cl_2 (100 mL) and methanol (25 mL) in presence of some drops of pyridine, was bubbled ozone at -78 °C for 30 min. After flushing with oxygen, dimethyl sulfide (5 mL) was added at -78 °C and the reaction was stirred overnight at 20 °C. The reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (90:10 petroleum ether/ether) to afford aldehyde **VIII-5a** (3.5 g, 90%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.81 (t, *J* = 2.4 Hz, 1H, C***H***-21), 7.37-7.27 (m, 5H, C***H***-ar), 4.50 (s, 2H, C***H₂***Ph), 4.22 (quint, *J*= 5.6 Hz, 1H, C***H***-19), 3.47 (t, *J* = 5.9 Hz, 2H, C***H₂***-16), 2.52-2.54 (m, 2H, C***H₂***-20), 1.62-1.65 (m, 4H, C***H₂***-17, C***H***-18), 0.87 (s, 9H, SiC(C***H₃***)$_3$), 0.07, 0.05 (2s, 6H, Si(C***H₃***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 202.1 (C-21), 138.5, 128.3, 127.6, 127.5 (C-ar), 72.9 (CH_2Ph), 70.1 (C-16), 67.9 (C-19), 50.8 (C-20), 34.4 (C-18), 25.7 (SiC(CH_3)$_3$), 25.6 (C-17), 18.0 (SiC), -4.5, -4.7 (Si(CH_3)$_2$).

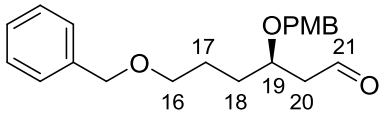
IR (ν, cm^{-1}, $CHCl_3$): 3031, 3022, 3010, 3006, 2956, 2931, 2886, 2858, 1714 (C=O), 1472, 1463, 1453, 1389, 1362, 1315, 1278, 1257, 1230, 1227, 1215, 1211, 1098, 1043.

MS (DI, CI, NH_3): 337 (M+H$^+$), 354 (M+NH_4^+).

$[\alpha]^{25}_D$: - 2.7 (*c* 1.5, $CHCl_3$)

HRMS (EI): Calcd. for (M-*t*Bu): $C_{15}H_{23}O_3Si$: 279.1417 Found : 279.1430

(R)-6-Benzyloxy-3-(4-methoxybenzyloxy)hexanal **VIII-5b**



$C_{21}H_{26}O_4$
M= 342.4 g.mol^{-1}

Through a solution of alkene **VIII-11b** (2.52 g, 7.40 mmol) in CH_2Cl_2 (80 mL) and methanol (20 mL) in presence of some drops of pyridine, was bubbled ozone at -78 °C for 30 min. After flushing with oxygen, dimethyl sulfide (3 mL) was added at -78 °C and the reaction was stirred overnight at 20 °C. The reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (70:30 petroleum ether/ether) to afford the aldehyde **VIII-5b** (2.13 g, 84%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.77 (t, *J* = 2.1 Hz, 1H, C***H***-21), 7.26-7.32 (m, 5H, C***H***-ar), 6.85-6.87 (m, 2H, C***H***-ar), 6.85-6.87 (m, 2H, C***H***-ar), 4.49 (s, 2H, C***H$_2$***Ph(Bn)), 4.48 (d, *J*= 11.1 Hz, 1H, C***H***Ph(PMB)), 4.41 (d, *J*= 11.1 Hz, 1H, C***H***Ph(PMB)), 3.93-3.99 (m, 1H, C***H***-19), 3.80 (s, 3H, OC***H$_3$***(PMB)), 3.47 (t, *J* = 6.1 Hz, 2H, C***H$_2$***-16), 2.67 (ddd, *J*= 16.3, 7.2, 2.6 Hz, 1H, C***H***-20), 2.54 (ddd, *J*= 16.3, 4.8, 1.9 Hz, 1H, C***H***-20), 1.66-1.74 (m, 4H, C***H$_2$***-17, C***H$_2$***-18).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 201.6 (C-21), 159.3, 138.5, 130.2, 129.4, 128.4, 127.6, 127.6, 113.8 (C-ar), 73.6 (C-19), 72.9, 70.9 (CH_2Ph(PMB), CH_2Ph(Bn), C-16), 55.3 (OCH_3(PMB)), 48.3 (C-20), 31.0 (C-18), 25.4 (C-17).

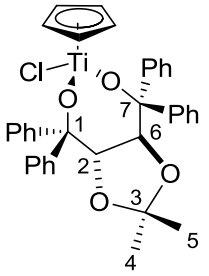
IR (ν, cm^{-1}, $CHCl_3$): 3031, 2936, 2862, 1720 (C=O), 1606, 1514, 1250, 1173, 1096, 1034.

MS (DI, CI, NH_3): 343 ($M+H^+$), 360 ($M+NH_4^+$).

$[\alpha]^{25}_D$: - 6.0 (*c* 1.0, $CHCl_3$)

HRMS (EI): Calcd. for ($M-H_2O$) : $C_{21}H_{24}O_3$: 324.1726 Found : 324.1719

Cyclopentadienyl[(4*S*, *trans*)-2,2-dimethyl- *α,α,α',α'*-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O,O'*]titanium Chloride **(*S,S*)-DU2**

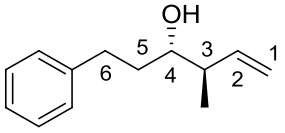
	$C_{36}H_{33}ClO_4Ti$ M= 612.5 g.mol^{-1}

To a solution of $CpTiCl_3$ **DU1** (1.0 g, 4.57 mmol) in freshly distilled toluene (40 mL), was added at 110 °C the ligand **(*S,S*)-TADDOL**[39] (2.17 g, 4.66 mmol, 1.02 equiv). The reaction mixture was stirred overnight at 110 °C under argon and for one day at rt. The solvent was evaporated, and the yellow residue was dissolved in ether (12 mL) followed by the addition of hexane (40 mL); the suspension was stirred for 2 h and filtered to give yellow crystals **(*S,S*)-DU2** (2.13 g, 76%).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.55-7.65 (m, 20H, C***H***-ar), 6.39 (s, 5H, Cp), 5.12 (d, *J* = 7.2 Hz, 1H, C***H***-2 or C***H***-6), 4.92 (d, *J* = 7.2 Hz, 1H, C***H***-2 or C***H***-6), 0.93 (s, 3H, C***H*****$_3$**-4 or C***H*****$_3$**-5), 0.44 (s, 3H, C***H*****$_3$**-4 or C***H*****$_3$**-5).

[39] Beck, A. K.; Gysi, P.; Vecchia, L. L.; Seebach, D. *Organic Syntheses* **2004**, 10, 349.

(3*R*,4*S*)-4-Methyl-1-phenyl-hex-5-en-3-ol[40] VIII-12

	$C_{13}H_{18}O$ M= 190.3 g.mol^{-1}

Crotylmagnesium chloride in THF (3.88 mL of a 0.5M solution, 1.94 mmol, 1.3 equiv) was added dropwise over 10 min at 0 °C to a solution of **(*S*,*S*)-DU2** (1.46 g, 2.38 mmol, 1.6 equiv). After stirring for 3 h at 0 °C, the slightly orange suspension was cooled to -78°C, and hydrocinnamaldehyde (200 mg, 1.5 mmol, dissolved in 2 mL of ether) was added over 2 min. Stirring at -78°C was continued for 4 h. The reaction mixture was then treated with 5 mL of water, stirred for 12 hours at 20 °C, filtered through Celite, and extracted twice with ether (15 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The solid residue was stirred with 15 mL of pentane. Subsequent filtration furnished white crystalline (*S*,*S*)-TADDOL. The residue was purified by silica gel column chromatography (90:10 petroleum ether/ether) to afford alcohol **VIII-12** (240 mg, 84%) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.20-7.28 (m, 5H, C***H***-ar), 5.76 (ddd, *J* = 16.9, 10.6, 8.2 Hz, 1H, C***H***-2), 5.14 (m, 2H, C***H₂***-1), 3.41 (s, 1H, O***H***), 2.88-2.91 (m, 2H, C***H₂***-6), 2.76-2.79 (m, 1H, C***H***-4), 2.27-2.30 (m, 1H, C***H***-3), 1.82-1.85 (m, 2H, C***H₂***-5), 1.04 (d, *J* = 6.7 Hz, 3H, C***H₃***-3).

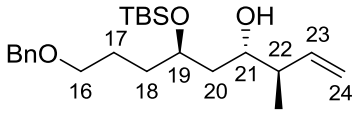
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 142.2, 127.5, 127.5, 125.7 (C-Ar), 140.1 (C-2), 116.5 (C-1), 74.0 (C-4), 44.2(C-6), 36.0 (C-3), 32.1 (C-5), 16.2 (CH_3-3)

$[\alpha]^{25}_D$: -12.5 (*c* 1.0, $CHCl_3$) [41]

[40] Hafner, A.; Duthaler, R. O.; Marti, R.; Rihs, G.; Rothe-Streit, P.; Schwarzenbach, F. *J. Am. Chem. Soc.* **1992**, *114*, 2321

[41] Lachance, H.; Lu, X. ; Gravel, M. ; Hall, D. G. *J. Am. Chem. Soc*. **2003**, *125*, 10160. **$[\alpha]^{25}_D$**= -14.7 (*c* 1.42, $CHCl_3$)

(3*R*,4*S*,6*R)*-9-Benzyloxy-6-(*tert*-butyldimethylsilanyloxy)-3-methyl-non-1-en-4-ol[40] **VIII-4a**

	$C_{23}H_{40}O_3Si$ M= 392.6 g.mol^{-1}

Crotylmagnesium chloride in THF (773 µL of a 0.5 M solution, 0.39 mmol, 1.3 equiv) was added dropwise over 10 min at 0 °C to a solution of **(*S*,*S*)-DU2** (290 mg, 0.48 mmol, 1.6 equiv) in ether (6 mL). After stirring for 3 h at 0 °C, the slightly orange suspension was cooled to -78 °C, and aldehyde **VIII-5a** (100 mg, 0.30 mmol, dissolved in 1 mL of ether) was added over 2 min. Stirring at -78 °C was continued for 20 min, the reaction mixture was then treated with 5 mL of water, stirred for 12 h at 20 °C, filtered through Celite, and extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The solid residue was stirred with 15 mL of pentane. Subsequent filtration furnished white crystalline (*S*,*S*)-TADDOL. The residue was purified by silica gel column chromatography (90:10 petroleum ether/ether) to afford alcohol **VIII-4a** (346 mg, 88%) as a slightly yellow oil. Analysis of the ^{1}H NMR of both the crude and the isolated product showed a ratio of diastereomers > 95:5.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.33-7.26 (m, 5H, C***H***-ar), 5.79 (ddd, *J*= 17.0, 11.1, 7.8 Hz, 1H, C***H***-23), 5.11 (brd, *J*= 11.1 Hz, 1H, C***H***-24), 5.11 (brd, *J*= 17.0 Hz, 1H, C***H***-24), 4.50 (s, 2H, C***H*****$_2$**-Ph (Bn)), 4.04-4.10 (m, 1H, C***H***-19), 3.85 (ddt, *J*= 9.9, 5.0, 2.2 Hz, 1H, C***H***-21), 3.52 (t, *J* = 6.1 Hz, 2H, C***H*****$_2$**-16), 3.18 (d, *J*= 2.2 Hz, 1H, O***H***), 2.19-2.27 (m, 1H, C***H***-22), 1.59-1.72 (m, 5H, C***H*****$_2$**-20, C***H*****$_2$**-18, C***H***-17), 1.26-1.32 (m, 1H, C***H***-17), 1.08 (d, *J* = 6.9 Hz, 3H, C***H*****$_3$**-22), 0.89 (s, 9H, SiC(C***H*****$_3$**)$_3$), 0.09, 0.07 (2s, 6H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 140.7 (C-23), 138.5, 128.3, 127.6, 127.5 (C-ar), 115.2 (C-24), 72.9 (CH_2Ph), 71.3, 71.2 (C-19, C-21), 70.3 (C-16), 44.1 (C-22), 38.6 (C-20), 33.0 (C-18), 26.0 (C-17), 25.8 (Si(CH_3)$_3$), 18.0 (SiC), 15.7 (CH_3-C22), -4.6, -4.7 (Si(CH_3)$_2$).

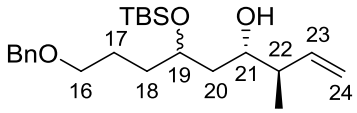
IR (ν, cm^{-1},$CHCl_3$): 3672, 3475, 3084, 3068, 3013, 3009, 2954, 2931, 2884, 2859, 1639 (C=C), 1496, 1471, 1463, 1454, 1434, 1420, 1389, 1362, 1310, 1256, 1095, 1028.

[α]$^{25}_D$: -1.0 (*c* 1.0, $CHCl_3$)

HRMS (EI): Calcd. for (M-*t*Bu) : 335.2043 Found : 335.2044

(3*R*,4*S*,6*R*)-9-Benzyloxy-6-(*tert*-butyldimethylsilanyloxy)-3-methyl-non-1-en-4-ol[40] ***anti*-VIII-4a**

(3*R*,4*S*,6*S*)-9-Benzyloxy-6-(*tert*-butyldimethylsilanyloxy)-3-methyl-non-1-en-4-ol[40] ***syn*-VIII-4a**



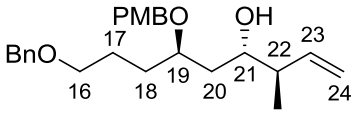
$C_{23}H_{40}O_3Si$
M= 392.6 g.mol^{-1}

Crotylmagnesium chloride in THF (600 µL of a 0.5 M solution, 0.30 mmol, 1.3 equiv) was added dropwise over 10 min at 0 °C to a solution of **(*S*,*S*)-DU2** (225 mg, 0.48 mmol, 1.6 equiv) in ether (4 mL). After stirring for 3 h at 0 °C, the slightly orange suspension was cooled to -78 °C, and aldehyde **(±)-VIII-5a** (77 mg, 0.30 mmol, dissolved in 1 mL of ether) was added over 2 min. Stirring at -78 °C was continued for 20 min, the reaction mixture was then treated with 5 mL of water, stirred for 12 h at 20 °C, filtered through Celite, and extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The solid residue was stirred with 15 mL of pentane. Subsequent filtration furnished white crystalline (*S*,*S*)-TADDOL. The residue was purified by silica gel column chromatography (90:10 petroleum ether/ether) to afford the alcohols ***anti*-VIII-4a** and ***syn*-VIII-4a** (73 mg, 81%) as a slightly yellow oil. Analysis of the ^{1}H NMR of both the crude and the isolated product showed a 1:1 ratio of diastereomers.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.33-7.26 (m, 5H, C***H***-ar), 5.76-5.86 (m, 1H, C***H***-23), 5.11 (brd, *J*= 11.1 Hz, 1H, C***H***-24), 5.11 (brd, *J*= 17.0 Hz, 1H, C***H***-24), 4.50 (s, 2H, C***H$_2$***-Ph (Bn)), 4.04-4.10 (m, 0.5H, C***H***-19), 3.99-4.04 (m, 0.5H, C***H***-19), 3.85 (ddt, *J*= 9.9, 5.0, 2.2 Hz, 0.5H, C***H***-21), 3.60-3.63 (m, 0.5H, C***H***-21), 3.52 (t, *J* = 6.1 Hz, 2H, C***H$_2$***-16), 3.14, 2.92 (brs, 1H, O***H***), 2.14-2.28 (m, 1H, C***H***-22), 1.57-1.72 (m, 5H, C***H$_2$***-20, C***H$_2$***-18, C***H***-17), 1.26-1.32 (m, 1H, C***H***-17), 1.08 (d, *J* = 6.9 Hz, 1.5H, C***H$_3$***-22), 1.08 (d, *J* = 6.9 Hz, 1.5H, C***H$_3$***-22), 0.90, 0.89 (s, 9H, SiC(C***H$_3$***)$_3$), 0.11, 0.09, 0.07, 0.06 (2s, 6H, Si(C***H$_3$***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 140.7, 140.4 (C-23), 138.5, 138.5, 128.3, 128.3, 127.6, 127.5, 127.5, 127.5 (C-ar), 115.3, 115.2 (C-24), 72.9, 72.8 (CH_2Ph), 72.8, 72.6, 71.3, 71.2 (C-19, C-21), 70.4, 70.3 (C-16), 44.1, 43.9 (C-22), 39.8, 38.6 (C-20), 34.2, 33.0 (C-18), 26.0, 25.7 (C-17), 25.8, 25.8 (Si(CH_3)$_3$), 18.0, 17.9 (SiC), 15.7, 15.4 (CH_3-C22), -4.1, -4.6, - 4.7, -4.9 (Si(CH_3)$_2$).

(3*R*,4*S*,6*R*)-9-Benzyloxy-6-(4-methoxybenzyloxy)-3-methyl-non-1-en-4-ol[40] **VIII-4b**



$C_{25}H_{34}O_4$
M= 398.5 g.mol^{-1}

Crotylmagnesium chloride in THF (12.8 mL of a 0.5 M solution, 6.40 mmol, 1.3 equiv) was added dropwise over 10 min at 0 °C to a solution of **(*S*,*S*)-DU2** (4.51 g, 7.36 mmol, 1.6 equiv) in ether (90 mL). After stirring for 20 min at 0°C, the slightly orange suspension was cooled to -78 °C, and aldehyde **VIII-5b** (1.57 g, 4.6 mmol, dissolved in 10 mL of ether) was added over 2 min. Stirring at -78 °C was continued for 4 h. The reaction mixture was then treated with water, stirred for 12 h at 20°C, filtered through Celite, and extracted twice with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filterded and concentrated *in vacuo*. The solid residue was stirred with 15 mL of pentane. Subsequent filtration furnished white crystalline (*S*,*S*)-TADDOL. The residue was purified by silica gel column chromatography (70:30 petroleum ether/ether) to afford the alcohol **VIII-4b** (1.47 g, 80%) as a slightly yellow oil. Analysis of the ^{1}H NMR of both the crude and the isolated product showed a 9:1 ratio of two diastereomers.

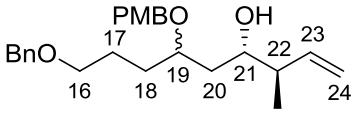
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.25-7.36 (m, 7H, C***H***-ar), 6.86-6.88 (m, 2H, C***H***-ar), 5.81 (ddd, *J*= 17.0, 10.8, 8.0 *Hz*, 1H, C***H***-23), 5.08 (dm, *J*= 10.8 Hz, 1H, C***H***-24), 5.08 (dm, *J*= 17.0 Hz, 1H, C***H***-24), 4.51 (s, 2H, C***H*****$_2$**-Ph (Bn)), 4.48-4.51 (m, 2H, C***H*****$_2$**Ph(PMB)), 3.80 (s, 3H, OC***H*****$_3$**(PMB)), 3.70-3.78 (m, 2H, C***H***-19, C***H***-21), 3.48 (t, *J* = 6.0 Hz, 2H, C***H*****$_2$**-16), 2.59 (s, 1H, O***H***), 2.15-2.24 (m, 1H, C***H***-22), 1.56-1.77 (m, 6H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20), 1.03 (d, *J* = 6.9 Hz, 3H, C***H*****$_3$**-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 159.2 (C-23), 140.6, 138.6, 130.6, 129.4, 128.3, 127.6, 127.5, 113.8 (C-ar), 115.4 (C-24), 76.4 (C-21), 72.9, 71.0, 70.3 (CH_2Ph(Bn), CH_2Ph(PMB), CH_2-16), 71.4 (C-19), 55.2 (OCH_3(PMB)), 44.2 (C-22), 37.3 (C-20), 30.3 (C-18), 25.8 (C-17), 15.9 (CH_3-C22).

IR (ν, cm^{-1}, $CDCl_3$) 3670, 3608, 3471, 3067, 3036, 2937, 2868, 2840, 1639, 1613, 1606, 1514, 1464, 1455, 1363, 1303, 1234, 1075, 1035.

HRMS (EI) Calcd. for $C_{25}H_{34}O_4$: 398.2457 Found : 398.2456

(3*R*,4*S*, 6*R*)-9-Benzyloxy-6-(4-methoxybenzyloxy)-3-methyl-non-1-en-4-ol[40]	***anti*-VIII-4b**
(3*R*,4*S*, 6*S*)-9-Benzyloxy-6-(4-methoxybenzyloxy)-3-methyl-non-1-en-4-ol[40]	***syn*-VIII-4b**

	$C_{25}H_{34}O_4$ M= 398.5 g.mol^{-1}

Crotylmagnesium chloride in THF (2.12 mL of a 0.5 M solution, 1.06 mmol, 1.3 equiv) was added dropwise over 10 min at 0 °C to a solution of **(*S*,*S*)-DU2** (798 mg, 1.30 mmol, 1.6 equiv). After stirring for 3 h at 0 °C, the slightly orange suspension was cooled to -78 °C, and aldehyde (±)-**VIII-5a** (279 mg, 0.814 mmol, dissolved in 2 mL of ether) was added over 2 min. Stirring at -78 °C was continued for 4 h. The reaction mixture was then treated with 5 mL of water, stirred for 12 h at 20 °C, filtered through Celite, and extracted twice with ether (15 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The solid residue was stirred with 15 mL of pentane. Subsequent filtration furnished (*S*,*S*)-TADDOL). The residue was purified by silica gel column chromatography (70:30 petroleum ether/ether) to afford alcohols ***anti*-VIII-4b** and ***syn*-VII-4b** (237 mg, 73%) as a slightly yellow oil. Analysis of the ^{1}H NMR of both the crude and the isolated product showed a 1:1 ratio of two diastereomers.

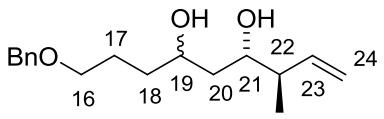
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)

7.26-7.38 (m, 7H, C***H***-ar), 6.93-6.95 (m, 2H, C***H***-ar), 5.84-5.94 (m, 1H, C***H***-23), 5.10-5.17 (m, 2H, C***H₂***-24), 4.57 (s, 2H, C***H₂***-Ph (Bn)), 4.55 (d, *J* = 3.6 Hz, 2H, C***H₂***-Ph (PMB)), 3.84 (s, 3H, OC***H₃***(PMB)), 3.74-3.83 (m, 1H, C***H***-19, C***H***-21), 3.58 (t, *J* = 5.4 Hz, 2H, C***H₂***-16), 2.77 (s, 1H, O***H***), 2.24-2.28 (m, 1H, C***H***-22), 1.65-1.84 (m, 6H, C***H₂***-17, C***H₂***-18, C***H₂***-20), 1.12 (d, *J* = 6.8 Hz, 1.8H, C***H₃***-22), 1.11 (d, *J* = 6.9 Hz, 1.2H, C***H₃***-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

159.2, 159.1, 140.5, 140.2 (C-23), 138.5, 138.5, 131.5, 131.1, 130.5, 130.0, 129.5, 129.4, 128.3, 127.6, 127.5, 127.5, 113.8, 113.8 (C-ar), 115.4, 115.1 (C-24), 76.2, 74.6 (CH_2Ph(PMB)), 72.9 (CH_2Ph(Bn)), 71.3, 71.0, 70.3, 70.2 (C-19, C-21, C-16), 55.2 (O-CH_3), 44.1, 43.9 (C-22), 37.5, 37.2 (C-20), 30.3, 29.9 (C-18), 25.7, 24.8 (C-17), 15.9, 15.4 (CH_3-C22).

***(3R,4S,6R)*-9-(Benzyloxy)-3-methylnon-1-ene-4,6-diol**	***anti*-VIII-13**
***(3R,4S,6S)*-9-(Benzyloxy)-3-methylnon-1-ene-4,6-diol**	***syn*-VIII-13**

	$C_{17}H_{26}O_3$ M= 278.4 g.mol^{-1}

To alcohols ***anti*-VIII-4a** and ***syn*-VIII-4a** (112 mg, 0.28 mmol) was added a solution of HF/acetonitrile 5:95 (10 mL). The solution was stirred at 20 °C for 3 days.The mixture was quenched with a saturated aqueous solution of sodium carbonate.The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 10:90) to afford diol ***syn*-VIII-13** (39 mg, 48%) and ***anti*-VIII-13** (38 mg, 48%) as two colorless oils.

<u>*Syn* diastereomer</u>

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.27-7.36 (m, 5H, C***H***-ar), 5.77 (ddd, *J*= 17.5, 10.8, 7.9 Hz, 1H, C***H***-23), 5.07 (dm, *J*= 10.8 Hz, 1H, C***H***-24), 5.07 (dm, *J*= 17.5 Hz, 1H, C***H***-24), 4.51 (s, 2H, C***H$_2$***-Ph), 3.29 (brs, 1H, O***H***), 3.81-3.85 (m, 1H, C***H***-19), 3.66-3.71 (m, 1H, C***H***-21), 3.51 (t, *J* = 6.0 Hz, 3H, C***H$_2$***-16, O***H***), 2.21 (app sext, 1H, C***H***-22), 1.69-1.76 (m, 2H, C***H$_2$***-20), 1.41-1.64 (m, 4H, C***H$_2$***-18, C***H$_2$***-17), 1.02 (d, *J* = 6.9 Hz, 3H, C***H$_3$***-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 140.2 (C-23), 138.0, 128.3, 127.7, 127.6 (C-ar), 115.7 (C-24), 75.7, 72.5 (C-19, C-21), 73.0 (CH_2Ph), 70.4 (C-16), 44.4 (C-22), 39.5 (C-20), 35.3 (C-18), 25.9 (C-17), 15.4 (CH_3-C22).

IR (ν,cm^{-1}, $CHCl_3$)**:** 3630, 3529, 3068, 3033, 2930, 2860, 1638, 1454, 1420, 1363, 1207, 1099.

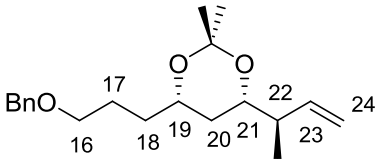
HRMS (EI): Calcd. for $C_{17}H_{26}O_3$: 278.1882 Found : 278.1880

<u>*Anti* diastereomer</u>

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.28-7.35 (m, 5H, ***H***-ar), 5.71-5.80 (m, 1H, C***H***-23), 5.11 (dm, *J*= 11.8 Hz, 1H, C***H***-24), 5.11 (dm, *J*= 15.9 Hz, 1H, C***H***-24), 4.52 (s, 2H, C***H$_2$***-Ph), 3.90-3.97 (m, 1H, C***H***-19), 3.70-3.75 (m, 1H, C***H***-21), 3.52 (td, *J* = 6.2, 1.9 Hz, 2H, C***H$_2$***-16), 3.29 (d, *J*= 3.7 Hz, 1H, O***H***), 2.47 (d, *J*= 3.0 Hz, 1H, O***H***), 2.23 (sextapp, 1H, C***H***-22), 1.71-1.79 (m, 2H, C***H$_2$***-20), 1.57-1.64 (m, 4H, C***H$_2$***-18, C***H$_2$***-17), 1.01 (d, *J* = 6.8 Hz, 3H, C***H$_3$***-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	140.6 (C-23), 138.1, 128.4, 127.7, 127.7 (C-Ar), 116.3 (C-24), 73.1 (CH_2Ph), 71.9, 69.0 (C-19, C-21), 70.6 (C-16), 44.4 (C-22), 39.6 (C-20), 34.8 (C-18), 26.5 (C-17), 16.1 (CH_3-C22).
HRMS (EI)	Calcd. for $C_{17}H_{26}O_3$: 278.1882 Found: 278.1877

(4*R*,6*S*)-4-(3-(Benzyloxy)propyl)-6-((*R*)-but-3-en-2-yl)-2,2-dimethyl-1,3-dioxane **VIII-14**



$C_{20}H_{30}O_3$
M= 318.5 g.mol^{-1}

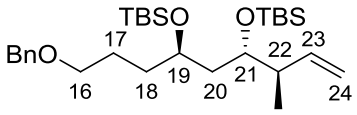
To diol ***syn*-VIII-13** (31 mg, 0.111 mmol) was added 2,2-dimethoxypropane (5 mL) then a catalytic amount of CSA at 20 °C, then the reaction mixture was stirred overnight. The reaction was quenched by addition of saturated aqueous sodium hydrogen carbonate. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give crude dioxolane**VIII-14**.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.34 (m, 5H, C***H***-ar), 5.80-5.88 (m, 1H, C***H***-23), 5.02 (dm, *J*= 16.2 Hz, 1H, C***H***-24), 5.02 (dm, *J*= 11.7 Hz, 1H, C***H***-24), 4.50 (s, 2H, C***H*$_2$**-Ph), 3.76-3.81 (m, 1H, C***H***-19), 3.67-3.71 (m, 1H, C***H***-21), 3.46-3.50 (m, 2H, C***H*$_2$**-16), 2.23 (app sext, 1H, C***H***-22), 1.50-1.76 (m, 6H, C***H*$_2$**-20, C***H*$_2$**-18, C***H*$_2$**-17), 1.37, 1.39 (s, $(CH_3)_2$), 1.00 (d, *J* = 6.9 Hz, 3H, C***H*$_3$**-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 140.6 (C-23), 138.6, 128.3, 127.6, 127.5 (C-ar), 114.3 (C-24), 98.3 (***C***$(CH_3)_2$), 72.9 (CH_2Ph), 72.3, 68.7 (C-19, C-21), 70.2 (C-16), 42.3 (C-22), 33.4 (C-20), 33.0 (C(***C***H_3)), 30.2 (C-18), 25.4 (C-17), 19.7 (C(***C***H_3)), 14.8 (CH_3-C22).

HRMS (EI) Calcd. for $C_{20}H_{30}O_3$: 318.4504 Found : 318.4504

(3*R*,4*S*,6*R*)-9-Benzyloxy-4,6-bis(*tert*-butyldimethylsilyloxy)-3-methyl-non-1-ene **VIII-15a**

	$C_{29}H_{54}O_3Si_2$ M= 506.9 g.mol^{-1}

To a solution of alcohol **VIII-4a** (982 mg, 2.5 mmol) in CH_2Cl_2 (25 mL) at –78 °C were added dropwise Et_3N (1.05 mL, 7.5 mmol, 3.0 equiv) and TBSOTf (1.15 mL, 5 mmol, 2.0 equiv). The reaction mixture was stirred for 1 h at -78 °C and was quenched by saturated aqueous NH_4Cl. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (98:2 petroleum ether/ether) to afford protected alcohol **VIII-15a** (1.23 g, 97%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.25-7.35 (m, 5H, C***H***-ar), 5.79 (ddd, *J*= 17.3, 10.7 7.4 Hz, 1H, C***H***-23), 5.01 (dm, *J* = 17.3 Hz, 1H, C***H***-24), (dm, *J* = 10.7 Hz, 1H, C***H***-24), 4.51 (s, 2H, C***H*****$_2$**Ph), 3.71-3.76 (m, 2H, C***H***-19, C***H***-21), 3.46 (t, *J* = 6.6 Hz, 2H, C***H*****$_2$**-16), 3.71-3.78 (m, 1H, C***H***-22), 1.41-1.70 (m, 6H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20), 0.98 (d, *J*= 6.9 Hz, 3H, C***H*****$_3$**-C22), 0.89, 0.87 (2s, 18H, SiC(C***H*****$_3$**)$_3$), 0.08, 0.07, 0.04, 0.04 (4s, 12H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 140.4 (C-23), 138.6, 128.3, 127.6, 127.5 (C-ar), 114.7 (C-24), 73.3 (C-21), 72.8 (CH_2Ph), 70.5 (C-16), 69.9 (C-19), 43.4 (C-22), 41.5, 34.2 (C-20, C-18), 25.9, 25.9 (SiC(CH_3)$_3$), 25.3 (C-17), 18.1, 18.1 (SiC), 15.0 (CH_3-C22), -3.9, -4.1, -4.2, -4.3 (Si(CH_3)$_2$).

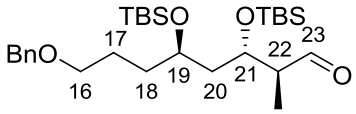
IR (ν, cm^{-1}, $CHCl_3$) 3070, 3034, 3028, 3023, 3017, 3005, 2957, 2930, 2886, 2857, 1638 (C=C), 1586, 1495, 1472, 1463, 1408, 1361, 1257, 1230, 1227, 1219, 1210, 1203, 1188, 1074, 1005.

MS (DI, CI, NH_3) 243 (M-2×OTBS), 375 (M-OTBS), 507 (M+H$^+$), 524 (M+NH_4^+).

[α]$^{25}_D$ - 6.0 (*c* 0.9, $CHCl_3$)

HRMS (EI) Calcd. for (M-*t*Bu) : 449.2907 Found : 449.2912

(2*R*,3*S*,5*R*)-8-Benzyloxy-3,5-bis-(*tert*-butyldimethylsilyloxy)-3-2-methyl-octanal **VIII-16a**



$C_{28}H_{52}O_4Si_2$
M= 508.9 g.mol^{-1}

Through a solution of alkene **VIII-15a** (1.1 g, 2.2 mmol) in CH_2Cl_2 (20 mL) and methanol (5 mL) in presence of some drops of pyridine, was bubbled ozone at -78 °C for 20 min. After flushing with oxygen, dimethyl sulfide (1 mL) was added at -78 °C and the reaction was stirred overnight at 20 °C. The reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (90:10 petroleum ether/ether) to afford aldehyde **VIII-16a** (917 mg, 83%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 9.74 (d, *J* = 1.9 Hz, 1H, C***H***-23), 7.27-7.34 (m, 5H, C***H***-ar), 4.50 (s, 2H, C***H*****$_2$**Ph), 4.06-4.10 (m, 1H, C***H***-21), 3.82 (dq, *J* = 7.2, 5.4 Hz, 1H, C***H***-19), 3.46 (t, *J* = 6.6 Hz, 2H, C***H*****$_2$**-16), 2.50 (qdd, *J*= 6.9, 3.2, 1.9 Hz, 1H, C***H***-22), 1.51-1.67 (m, 6H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20), 1.10 (d, *J* = 6.9 Hz, 3H, C***H*****$_3$**-22), 0.87, 0.88 (2s, 18H, SiC(C***H*****$_3$**)$_3$), 0.08, 0.07, 0.07, 0.06 (4s, 12H, Si(C***H*****$_3$**)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 204.4 (C-23), 138.6, 128.3, 127.6, 127.5 (C-ar), 72.9 (CH_2Ph), 71.3 (C-21), 70.3 (C-16), 69.7 (C-19), 52.1 (C-22), 43.1 (C-20), 34.3 (C-18), 25.9, 25.8 (SiC(CH_3)$_3$), 25.2 (C-17), 18.0, 18.0 (SiC), 10.2 (CH_3-22), -3.9, -4.1, -4.2, -4.4 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, $CHCl_3$): 3673, 3450, 3029, 3023, 3014, 2955, 2931, 2885, 2858, 2338, 1715 (C=O), 1603, 1471, 1463, 1362, 1257, 1239, 1235, 1231, 1223, 1219, 1215, 1211, 1207, 1203, 1177, 1087, 1043, 1006.

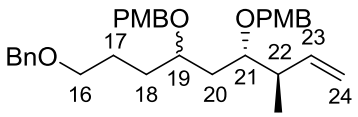
MS (DI, CI, NH_3): 245 (M-2×OTBS), 262 (M-2×OTBS+NH_4^+), 377 (M-OTBS), 394 (M-OTBS+H^+), 509 (M+H^+), 526 (M+NH_4^+).

[α]$^{25}_D$: + 16.0 (*c* 1.2, $CHCl_3$)

HRMS (EI): Calcd. for (M-*t*Bu) :$C_{24}H_{43}O_4Si_2$: 451.2700 Found : 451.2680

(3*R*,4*S*,6*R*)-9-Benzyloxy-4,6-bis-(4-methoxybenzyloxy)-3-methyl-non-1-ene[42] ***anti*-VIII-15b**

(3*R*,4*S*,6*S*)-9-Benzyloxy-4,6-bis-(4-methoxybenzyloxy)-3-methyl-non-1-ene ***syn*-VIII-15b**



$C_{33}H_{42}O_5$
M= 518.7 g.mol^{-1}

To a solution of alcohols ***syn*-VIII-4b** and ***anti*-VII-4b** (210 mg, 0.53 mmol) in DMF (1.5 mL) at 0 °C was added PMBBr (190 mg, 0.95 mmol, 1.8 equiv) in DMF (1 mL, 1 mL rinse) followed by NaH (60% dispersion in mineral oil, 36 mg, 0.90 mmol, 1.70 equiv). After stirring at 0 °C for 90 min, the reaction mixture was poured into water and the solution was extracted with ether. The combined organic extracts were washed with water then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (20:80, 40:60) to afford protected alcohols ***anti*-VIII-15b** and ***syn*-VIII-15b** (229 mg, 83%) as a colorless oil in a 1:1 of two diastereomers.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.25-7.37 (m, 9H, C***H***-ar), 6.87-6.90 (m, 4H, C***H***-ar), 5.78-5.87 (m, 1H, C***H***-23), 5.07-5.11 (m, 2H, C***H*$_2$**-24), 4.56 (s, 2H, C***H*$_2$**-Ph (Bn)), 4.52 (d, *J* = 3.5 Hz, 2H, C***H*$_2$**-Ph (PMB)), 4.49 (d, *J* = 3.7 Hz, 2H, C***H*$_2$**-Ph (PMB)), 3.80 (s, 3H, OC***H*$_3$**(PMB)), 3.79 (s, 3H, OC***H*$_3$**(PMB)), 3.72-3.79 (m, 2H, C***H***-19, C***H***-21), 3.49 (t, *J* = 5.9 Hz, 2H, C***H*$_2$**-16), 2.17-2.20 (m, 1H, C***H***-22), 1.59-1.77 (m, 6H, C***H*$_2$**-17, C***H*$_2$**-18, C***H*$_2$**-20) 1.05 (d, *J* = 6.8 Hz, 3H, C***H*$_3$**-22).

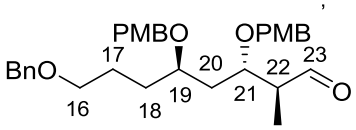
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 159.1, 159.0, 138.6, 138.6, 131.1, 131.1, 131.0, 131.0, 130.4, 129.4, 129.4, 129.3, 129.2, 128.3, 127.6, 127.4, 113.8, 113.7 (C-ar), 140.7, 140.5 (C-23), 115.7, 115.3 (C-24), 77.2, 75.5, 75.1 (CH_2Ph(PMB)×2), 72.8, 72.8 (CH_2Ph(Bn)), 71.3, 70.9 (C-21), 70.5, 70.4 (C-16), 70.2, 70.1 (C-19), 55.2 , 55.2 (O-CH_3×2), 40.2, 40.0 (C-22), 36.0, 34.9 (C-20), 30.5, 30.3 (C-18), 25.5, 25.2 (C-17), 14.6, 13.7 (CH_3-C22).

IR (ν, cm^{-1}, $CDCl_3$) 3032, 3016, 2957, 2934, 2861, 2840, 1611, 1586, 1465, 1455, 1302, 1249, 1173, 1095, 1035.

HRMS (EI) Calcd. for $C_{33}H_{42}O_5$: 518.3032 Found : 518.3029

[42] Clark, D. L.; Heathcock, C. H. *J. Org. Chem.* **1993**, *58*, 5878.

(2*R*,3*S*,5*R)*-8-Benzyloxy-3,5-bis(4-methoxybenzyloxy)-2-methyloctanal **VIII-16b**

	$C_{32}H_{40}O_6$ M= 520.7 g.mol^{-1}

To a solution of alcohol **VIII-4b** (1.3 g, 3.3 mmol) and freshly prepared *p*-methoxybenzyltrichloroacetimidate (1.8 g, 6.6 mmol, 2.0 equiv) in ether (16 mL) at 20 °C was added camphorsulfonic acid (77 mg, 0.30 mmol, 0.1 equiv) in ether (1 mL). The clear solution turned cloudy within 5 min after the addition of acid. The reaction mixture was stirred for 1 h at 20 °C and was then quenched with saturated aqueous $NaHCO_3$ and diluted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (70:30 petroleum ether/ether) to afford protected alcohol **VIII-15b** (1.39 g, 81%) as a colorless oil.

Through a solution of alkene **VIII-15b** (1.39 g, 2.67 mmol) in CH_2Cl_2 (20 mL) and methanol (5 mL) in presence of some drops of pyridine, was bubbled ozone at -78 °C for 45 min. After flushing with oxygen, dimethyl sulfide (2.0 mL) was added at -78 °C and the reaction was stirred overnight at 20 °C. The reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (60:40 petroleum ether/ether) to afford aldehyde **VIII-16b** (1.04 g, 75%) as a colorless oil and as a mixture of two diastereomers in a 9:1 ratio. Only the major diastereomer is decribed.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 9.70 (d, *J*= 1.6 Hz, 1H, C***H***O), 7.26-7.35 (m, 5H, C***H***-ar(Bn)), 7.16-7.23 (m, 4H, C***H***-ar (PMB)), 6.83-6.87 (m, 4H, C***H***-ar(PMB)), 4.50 (C***H$_2$***Ph(Bn)), 4.50 (d, *J*= 11.1 Hz, 1H, C***H***Ph(PMB)), 4.47 (d, *J*= 11.0 Hz, 1H, C***H***Ph(PMB)), 4.34 (d, *J*= 11.0 Hz, 1H, C***H***Ph(PMB)), 4.30 (d, *J*= 11.1 Hz, 1H, C***H***Ph(PMB)), 4.00 (ddd, *J*= 9.4, 4.7, 2.8 Hz, 1H, C***H***-21), 3.78 (s, 6H, OC***H$_3$***(PMB)), 3.66-3.69 (m, 1H, C***H***-19), 3.47 (t, *J*= 6.9 Hz, 2H, C***H$_2$***-16), 2.69-2.76 (m, 1H, C***H***-21), 1.50-1.72 (m, 6H, C***H$_2$***-17, C***H$_2$***-18, C***H$_2$***-20), 1.09 (d, *J*= 6.7 Hz, 3H, C***H$_3$***-C22).

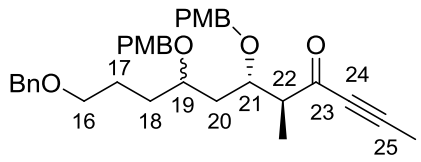
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 204.0 (C=O), 159.2, 159.1, 138.6, 130.8, 130.3, 129.3, 129.3, 128.3, 127.6, 127.5, 113.8, 113.8 (C-ar), 75.7, 74.7 (C-19, C-16), 72.9, 71.6, 70.3, 70.1 (CH_2Ph(PMB), CH_2Ph(PMB), CH_2Ph(Bn), C-16), 55.3 (OCH_3(PMB)), 49.9 (C-22), 37.5 (C-20), 30.3 (C-18), 25.0 (C-17), 9.1 (CH_3-C22).

IR(ν, cm^{-1}, $CHCl_3$) 2955, 2938, 2865, 2840, 1727, 1611, 1513, 1464, 1456, 1361, 1302, 1250, 1174, 1161, 1095, 1035.

MS (DI, CI, NH_3) 381, 400, 520 (M+), 539 ($M+NH_4^+$).

HRMS (EI) Calcd. for $C_{32}H_{40}O_6$: 520.2825 Found : 520.2810

(5*S*,6*S*, 8*R*)-11-Benzyloxy-6,8-bis-(4-methoxybenzyloxy)-5-methylundec-2-yn-4-one	***anti*-VIII-18b**
(5*S*,6*S*,8*S*)-11-Benzyloxy-6,8-bis-(4-methoxybenzyloxy)-5-methylundec-2-yn-4-one	***syn*-VIII-18b**

	$C_{35}H_{42}O_6$ M= 558.3 g.mol^{-1}

To a solution of ***anti*-VIII-15b** and ***syn*-VIII-15b** (896 mg, 1.73 mmol) in dichloromethane (38 mL) and methanol (10 mL) in presence of some drops of pyridine, was bubbled ozone at -78 °C for 30 min. Dimethyl sulfide (1 mL) was added at -78 °C and the reaction was stirred overnight at 20 °C. The reaction mixture was concentrated *in vacuo* and directly used in the next step.

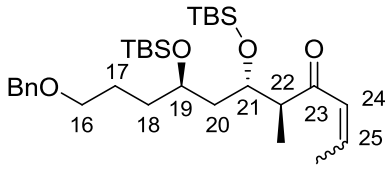
To a stirred solution of crude aldehyde in anhydrous THF (20 mL) at -78 °C was added propynylmagnesium bromide (0.5 M in THF, 10.4 mL, 5.2 mmol, 3 equiv) dropwise. After 1 h stirring, the reaction mixture was quenched by adding a saturated aqueous solution of NH_4Cl (10 mL). The layers were separated and the aqueous phase was extracted 3 times with Et_2O (10mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (30:70, 50:50) to afford the alcohol as a yellow oil as a mixture of diastereomers.

To a stirred solution of 2-iodoxybenzoic acid (1.45g, 5.2 mmol, 3 equiv) in DMSO (20 mL) was added a solution of alcohol in THF (10 mL) at 20 °C. After the solution had been stirred overnight, 30 mL of water and 30 mL of ether were added. The mixture was stirred for 2 h to form a white precipitate, which was then filtered off. The aqueous phase was extracted with ether 3 times. The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (20:80, 40:60) to afford alcohols ***anti*-VIII-18b** and **s*yn*-VIII-18b** (260 mg, 52% for 3 steps) as a yellow oil and as a mixture of two diastereomers in a 1:1 ratio.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.24-7.35 (m, 9H, C***H***-ar), 6.84-6.86 (m, 4H, C***H***-ar), 4.52 (s, 2H, C***H*$_2$**-Ph (Bn)), 4.47 (d, *J* = 3.5 Hz, 2H, C***H*$_2$**-Ph (PMB)), 4.45 (d, *J* = 3.7 Hz, 2H, C***H*$_2$**-Ph (PMB)), 4.20-4.23 (m, 0.5H, C***H***-21), 4.00-4.02 (m, 0.5H, C***H***-21), 3.79, 3.79, 3.77, 3.77 (s, 6H, OC***H*$_3$**(PMB)×2), 3.62-3.66 (m, 0.5H, C***H***-19), 3.53-3.58 (m, 0.5H, C***H***-19), 3.49 (t, *J* = 5.6 Hz, 1H, C***H*$_2$**-16) 3.49 (t, *J* = 6.1 Hz, 1H, C***H*$_2$**-16), 2.99-3.05 (m, 1H, C***H***-22), 1.95 (s, 1.5H , C***H*$_3$**-C22), 1.93 (s, 1.5H , C***H*$_3$**-C22), 1.52-1.76 (m, 6H, C***H*$_2$**-17, C***H*$_2$**-18, C***H*$_2$**-20), 1.05 (t, *J* = 7.2 Hz, 3H, C***H*$_3$**-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	189.6, 189.4 (C-23), 159.1, 158.9, 158.8, 138.5, 138.5, 131.0, 130.7, 130.2, 130.1, 129.4, 129.4, 129.2, 129.0, 128.2, 127.4, 127.3, 113.6, 113.6, 113.5, 113.5 (C-ar), 91.4, 91.3 (C-24), 79.8, 79.7 (C-25), 76.1, 75.7, 75.1, 74.6 (2×(CH_2Ph(PMB)), 72.7, 72.7 (CH_2Ph(Bn)), 71.0, 70.8 (C-21), 70.3, 70.3 (C-16), 70.0, 69.8 (C-19), 55.1 (2×O-CH_3(PMB)), 51.2, 51.2 (C-22), 36.3, 34.6 (C-20), 30.8, 30.3 (C-18), 25.7, 25.4 (C-17), 10.2, 9.7 (CH_3-C22), 4.0 (C-26).
IR (ν, cm^{-1}, $CDCl_3$)	3685, 3599, 3068, 3047, 2986, 2929, 2859, 2360, 2216, 1732,1666, 1608, 1513, 1450, 1362, 1299, 1269, 1035
HRMS (EI)	Calcd. for $C_{27}H_{33}O_5$: (M -PMB) : 437.2328 Found : 437.2325

(5*S*,6*S*,8*R*)-11-Benzyloxy-6,8-bis(*tert*-butyldimethylsilyloxy)-5-methyl-undec-2-en-4-one **VIII-2a**



$C_{31}H_{56}O_4Si_2$
M= 548.9 g.mol^{-1}

A solution of (*Z*)-1-bromo-1-propene (600 µL, 7.0 mmol, 7 equiv) in THF (7 mL) was added dropwise to a solution of magnesium (190 mg, 7.7 mmol, 7.7 equiv) and few crystals of I_2 in THF (7 mL). The reaction mixture was refluxed for 1 h then diluted with ether (7 mL) and cooled to -78 °C. Aldehyde **VIII-16a** (509 mg, 1.0 mmol) in THF (1 mL) was added dropwise and the mixture was stirred at -78 °C for 1 h. Saturated aqueous NH_4Cl was added and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Alcohol **VIII-19a** was directly used in the next step without further purification.

To a stirred suspension of 2-iodoxybenzoic acid (840 mg, 3.0 mmol, 3.0 equiv) in DMSO (18 mL) was added a solution of alcohol **VIII-19a** in THF (9 mL) at 20 °C. After the solution had been stirred overnight, 10 mL of water and 10 mL of ether were added. The mixture was stirred for 2 h to form a white precipitate, which was then filtered off. The aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ether 95:5) to afford the two separable geometric isomers of alkene **VIII-2a** (297 mg, 54% over 2 steps, *Z*/*E*= 4:1) as two yellow oils.

(*Z*) Isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.34 (m, 5H, C***H***-ar), 6.15-6.27 (m, 2H, C***H***-24, C***H***-25), 4.49 (s, 2H, C***H*****$_2$**Ph), 4.18 (dt, *J*= 7.2, 3.3 Hz, 1H, C***H***-21), 3.79 (dt, *J*= 5.4, 8.9 Hz, 1H, C***H***-19), 3.44 (t, *J* = 6.6 Hz, 2H, C***H*****$_2$**-16), 2.75 (qd, *J*= 8.9, 5.4 Hz, 1H, C***H***-22), 2.09 (d, *J*= 5.9 Hz, 3H, C***H*****$_3$**-C25), 1.58-1.63 (m, 2H, C***H*****$_2$**-17), 1.47-1.54 (m, 3H, C***H*****$_2$**-17, C***H***-20), 1.28-1.34 (m, 1H, C***H***-20), 1.05 (d, *J*= 6.8 Hz, 3H, C***H*****$_3$**-C22), 0.89, 0.85 (2s, 18H, SiC(C***H*****$_3$**$)_3$), 0.11, 0.10, 0.05, 0.03 (4s, 12H, Si(C***H*****$_3$**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 202.3 (C-23), 143.5 (C-25), 138.6, 128.3, 127.6, 127.4 (C-24, C-ar), 72.8 (CH_2Ph), 70.5 (C-16), 70.1 (C-21), 69.6 (C-19), 54.1 (C-22), 41.0 (C-20), 34.6 (C-18), 25.9, 25.8 (SiC(CH_3)$_3$), 25.2 (C-17), 18.0, 18.0 (SiC), 16.0 (CH_3-C25), 9.4 (CH_3-C22), -3.8, -4.2, -4.2, -4.3(Si(CH_3)$_2$).

IR (ν, cm^{-1}, $CHCl_3$): 3034, 3028, 3022, 3010, 2957, 2929, 2857, 1688 (C=O), 1627, 1471, 1463, 1378, 1362, 1258, 1221, 1209, 1203, 1095, 1006.

HRMS (EI) Calcd. for $C_{31}H_{56}O_4Si_2$: 548.3717 Found : 548.3722

$[\alpha]^{25}_D$ + 3.9 (*c* 1.5, $CHCl_3$)

(*E*) Isomer

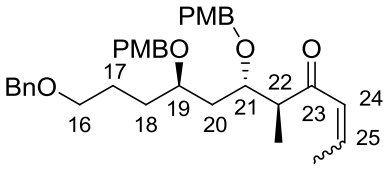
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.26-7.34 (m, 5H, C***H***-ar), 6.87 (dq, *J* = 15.4, 6.9 Hz, 1H, C***H***-25), 6.25 (dq, *J* = 15.3, 1.5 Hz, 1H, C***H***-24), 4.49 (s, 2H, C***H*****$_2$**Ph), 4.17 (ddd, *J* = 8.3, 4.3, 2.9 Hz, 1H, C***H***-21), 3.75-3.81 (m, 1H, C***H***-19), 3.44 (td, *J* = 6.5, 1.3 Hz, 2H, C***H*****$_2$**-16), 2.90 (qd, *J* = 6.8, 4.4 Hz, 1H, C***H***-22), 1.87 (dd, *J* = 6.9, 1.5 Hz, 3H, C***H*****$_3$**-25), 1.46-1.62 (m, 5H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H***-20), 1.30-1.38 (m, 1H, C***H***-20), 1.05 (d, *J* = 6.8 Hz, 3H, C***H*****$_3$**-22), 0.88, 0.84 (2s, 18H, SiC(C***H*****$_3$**$)_3$), 0.11, 0.10, 0.04, 0.03 (4s, 12H, Si(C***H*****$_3$**$)_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 200.7 (C-23), 142.1 (C-25), 130.8 (C-24), 138.6, 128.3, 127.6, 127.4 (C-ar), 72.8 (CH_2Ph), 70.5 (C-16), 70.2, 69.6 (C-19, C-21), 51.6 (C-22), 41.0 (C-20), 34.6 (C-18), 25.8, 25.8 (SiC(CH_3)$_3$), 25.2 (C-17), 18.2 (CH_3-25), 18.0, 18.0 (SiC), 9.7 (CH_3-22), -3.6, -4.1, -4.2, -4.3 (Si(CH_3)$_2$).

$[\alpha]^{25}_D$ + 24.0 (*c* 0.5, $CHCl_3$)

HRMS (EI) Calcd. for $C_{31}H_{56}O_4Si_2$: 548.3717 Found : 548.3703

(5*S*,6*S*,8*R*)-11-Benzyloxy-6,8-bis(4-methoxy-benzyloxy)-5-methylundec-2-en-4-one **VIII-2b**

	$C_{35}H_{44}O_6$ M= 560.7 g.mol^{-1}

A solution of (*Z*)-1-bromo-1-propene (850 µL, 10 mmol, 5.0 equiv) in THF (10 mL) was added dropwise to a suspension of magnesium (267 mg, 11 mmol, 5.5 equiv) and few crystals of I_2 in THF (10 mL). The reaction mixture was refluxed for 1 h then diluted with ether (5 mL) and cooled to -78 °C. Aldehyde **VIII-16b** (1.04 g, 2.0 mmol) in THF (2 mL) was added dropwise and the mixture was stirred at -78 °C for 1 h. Saturated NH_4Cl solution was added and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Alcohol **VIII-19b** was directly used in the next step without further purification.

To a stirred solution of 2-iodoxybenzoic acid (1.68 g, 6.0 mmol, 3.0 equiv) in DMSO (36 mL) was added a solution of alcohol **VIII-19b** in THF (18 mL) at 20 °C. After the solution had been stirred overnight, 20 mL of water and 20 mL of ether were added. The mixture was stirred for 2 h to form a white precipitate, which was then filtered off. The aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ether 90:10) to afford the two separable geometric isomers of alkene **VIII-2b** (639 mg, 57% for 2 steps, *Z/E*= 4:1) as two yellow oils.

(*Z*) Isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.27-7.35 (m, 5H, ***H***-ar), 7.17-7.22 (m, 4H, ***H***-ar), 6.82-6.86 (m, 4H, ***H***-ar), 6.14-6.30 (m, 2H, C***H***-24, C***H***-25), 4.50 (s, 2H, C***H$_2$***Ph(Bn)), 4.44-4.47 (m, 2H, C***H$_2$***Ph(PMB)), 4.22-4.27 (m, 2H, C***H$_2$***Ph(PMB)), 3.99 (ddd, *J*= 8.9, 5.8, 3.0 Hz, 1H, C***H***-21), 3.78 (s, 3H, OC***H$_3$***(PMB), 3.77 (s, 3H, OC***H$_3$***(PMB), 3.60-3.66 (m, 1H, C***H***-19), 3.47 (t, *J* = 5.7 Hz, 2H, C***H$_2$***-16), 2.96 (quint, *J*= 6.6 Hz, 1H, C***H***-22), 2.09 (d, *J*= 6.2 Hz, 3H, C***H$_3$***-C25), 1.52-1.68 (m, 6H, C***H$_2$***-17, C***H$_2$***-18, C***H$_2$***-20), 1.06 (d, *J*= 6.6 Hz, 3H, C***H$_3$***-C22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 203.2 (C-23), 143.4 (C-25), 159.1, 159.0, 138.6, 131.0, 130.5, 129.3, 129.1, 128.3, 127.5, 127.5, 127.4, 113.7, 113.6 (C-24, C-ar), 76.3 (C-21), 74.8 (C-19), 72.8, 71.6, 70.4, 69.9 (CH_2Ph(Bn), CH_2Ph(PMB), CH_2Ph(PMB), C-16), 55.2, 55.2 (OCH_3(PMB)×2), 50.3 (C-22), 36.8 (C-20), 30.4 (C-18), 25.2 (C-17), 16.0 (CH_3-C25), 10.4 (CH_3-C22).

IR (ν, cm^{-1}, $CHCl_3$) 3032, 2957, 2930, 2857, 1709, 1608, 1514, 1464, 1455, 1360,1315, 1302, 1250, 1233, 1172, 1097, 1034.

HRMS (EI) Calcd. for (M-OPMB) :$C_{27}H_{35}O_5$: 439.2484 Found : 439.2493

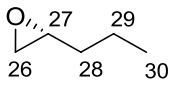
(*E*) Isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.26-7.34 (m, 5H, ***H***-ar), 7.15-7.22 (m, 4H, C***H***-ar), 6.81-6.86 (m, 5H, C***H***-ar, C***H***-25), 6.17-6.22 (m, 2H, C***H***-24), 4.49 (s, 2H, C***H$_2$***Ph(Bn)), 4.46 (d, *J*= 11.2 Hz, 1H, C***H***Ph(PMB)), 4.43 (d, *J*= 10.9 Hz, 1H, C***H***Ph(PMB)), 4.25 (d, *J*= 10.9 Hz, 1H, C***H***Ph(PMB)), 4.24 (d, *J*= 11.2 Hz, 1H, C***H***Ph(PMB)), 3.94-3.99 (m, 1H, C***H***-21), 3.78 (s, 3H, OC***H$_3$***(PMB), 3.77 (s, 3H, OC***H$_3$***(PMB)), 3.62-3.66 (m, 1H, C***H***-19), 3.47 (t, *J* = 5.9 Hz, 2H, C***H$_2$***-16), 3.12 (p, *J*= 6.8 Hz, 1H, C***H***-22), 1.86 (dd, *J*= 6.9, 1.6 Hz, 3H, C***H$_3$***-C25), 1.54-1.68 (m, 6H, C***H$_2$***-17, C***H$_2$***-18, C***H$_2$***-20), 1.06 (d, *J*= 6.9 Hz, 3H, C***H$_3$***-C22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 201.7 (C-23), 142.6 (C-25), 159.1, 159.0, 131.2, 131.0, 130.5, 129.4, 129.1, 128.3, 127.5, 127.4, 113.7, 113.6 (C-24, C-ar), 76.6 (C-21), 74.7 (C-19), 72.8, 71.8, 70.3, 69.7 (CH_2Ph(Bn), CH_2Ph(PMB), CH_2Ph(PMB), C-16), 55.2, 55.2 (OCH_3(PMB)×2), 47.5 (C-22), 36.8 (C-20), 30.4 (C-18), 25.2 (C-17), 18.2 (CH_3-C25), 11.0 (CH_3-C22).

HRMS (EI) Calcd. for: $(M\text{-}OPMB)^+$: $C_{27}H_{35}O_5^+$: 439.2484 Found : 439.2498

(R)-1,2-Epoxypentane[36] **VIII-20**

	$C_5H_{10}O$ M= 86.1 g.mol^{-1}

Preparation of the active catalyst :

(R,R)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt (II) (200 mg, 0.30 mmol) and acetic acid (23 µL) were stirred in toluene (1 mL) under air for 1 h at 20 °C. The solvent was removed *in vacuo*, to afford the catalyst.

Hydrolytic kinetic resolution of the epoxide:

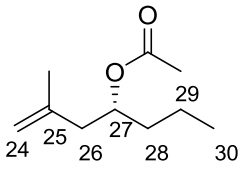
Racemic 1,2-epoxypentane **(±)-VIII-20** (3.0 g, 35.0 mmol), H_2O (0.38 mL, 21.0 mmol, 0.6 equiv) and the above catalyst (115 mg, 0.174 mmol, 0.5 mol%) were mixed at 0°C and stirred at 20 °C for 17 h. $MgSO_4$ was then added and the mixture was distilled (89-90°C, 760 mm Hg to give (*R*)-1,2-epoxypentane **VIII-20** (1.34 g , 89%)[43] as a colorless liquid.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	2.83-2.88 (m, 1H, C***H***-27), 2.69 (td, *J* = 5.0, 4.1 Hz, 1H, C***H***-26), 2.41 (dd, *J* = 5.0, 2.8 Hz, 1H, C***H***-26), 1.41-1.49 (m, 4H, C***H$_2$***-28, C***H$_2$***-29), 0.92 (t, *J* = 7.2 Hz, 3H, C***H$_3$***-30).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	52.0 (C-27), 46.8 (C-26), 34.4 (C-28), 19.2 (C-29), 13.8 (C-30).
IR (ν**,** cm^{-1}, $CHCl_3$**)**	3610, 3308, 2977, 1495, 1470, 1450, 1382, 1145, 1026.
MS (DI, CI, NH_3)	87 ($M+H^+$).
$[\alpha]^{25}_D$	+ 13.6 (*c* 1.0, $CHCl_3$) [44]

[43] The kinetic resolution yield is expressed as a percentage of the theoretical maximum yield of 50%.

[44] MacMillan, J.B.; Molinski, T. F. *J. Am. Chem. Soc*. **2004**, *126*, 9944. **$[\alpha]^{25}_D$**= + 11.1 (*c* 1.0, $CHCl_3$)

(*4R*)-2-Methylhept-1-en-4-yl Acetate **VIII-3a**

	$C_{10}H_{18}O_2$ M= 170.3 g.mol^{-1}

To a stirred suspension of copper (I) iodide (0.68 g, 3.6 mmol, 0.5 equiv) in THF (30 mL) was added isopropenylmagnesium bromide (0.5M THF solution, 43.2 mL, 21.6 mmol, 3.0 equiv) dropwise at -30 °C. After 30 min, (*R*)-1,2-epoxypentane **VIII-20** (0.62 g, 7.2 mmol) in THF (4 mL) was slowly added to the mixture. After stirring at -30 °C for 2 h, the reaction was quenched with saturated aqueous NH_4Cl, filtered and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Alcohol **VIII-21** was directly used in the next step without further purification.

To a stirred solution of allylic alcohol **VIII-21** with DMAP (1.1 g, 9.0 mmol) in CH_2Cl_2 (12 mL) at 0 °C was slowly added acetic anhydride (2.9 mL, 30 mmol). The reaction mixture was allowed to warm to 20 °C and stirred overnight. The mixture was diluted by addition of ether (60 mL) and quenched with saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel chromatography (petroleum ether and then petroleum ether/ether 98:2) to afford protected alcohol **VIII-3a** (1.20 g, 7.1 mmol, 98%) as a colorless oil.

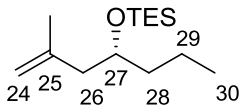
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.04 (ddd, *J* = 12.9, 7.3, 5.7 Hz, 1H, C***H***-27), 4.76 (s, 1H, C***H***-24), 4.70 (s, 1H, C***H***-24), 2.26 (dd, *J* = 13.9, 7.8 Hz, 1H, C***H***-26), 2.17 (dd, *J* = 13.9, 5.3 Hz, 1H, C***H***-26), 2.01 (s, 3H, C***H*****$_3$**-CO), 1.73 (s, 3H, C***H*****$_3$**-25), 1.48-1.53 (m, 2H, C***H*****$_2$**-28), 1.25-1.42 (m, 2H, C***H*****$_2$**-29), 0.90 (t, *J* = 7.3 Hz, 3H, C***H*****$_3$**-30).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 170.7 (C=O), 141.9 (C-25), 113.1 (C-24), 71.9 (C-27), 42.9 (C-26), 36.2 (C-28), 22.4 (CH_3-25), 21.1 (CH_3-CO), 18.6 (C-23), 13.9 (C-30).

IR (ν, cm^{-1}, $CHCl_3$**)** 2963, 2935, 2875, 1728, 1651, 1465, 1376, 1255, 1023.

HRMS (EI) Calcd. for $C_{10}H_{18}O_6$: 170.1307 Found : 170.1303

(4*R*)-2-Methyl-4-(triethylsilyloxy)-hept-1-en-4-yl **VIII-3b**

	$C_{14}H_{30}OSi$ M= 242.5 g.mol^{-1}

To a stirred suspension of copper (I) iodide (0.68 g, 3.6 mmol, 0.5 equiv) in THF (30 mL) was added isopropenylmagnesium bromide (0.5M THF solution, 43.2 mL, 21.6 mmol, 3 equiv) dropwise at -30 °C. After 30 min, (*R*)-1,2-epoxypentane **VIII-20** (0.62 g, 7.2 mmol) in THF (4 mL) was slowly added to the mixture. After stirring at -30 °C for 2 h, the reaction was quenched with saturated aqueous NH_4Cl, filtered and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Alcohol **VIII-21** was directly used in the next step without further purification.

To a solution of alcohol **VIII-21** in CH_2Cl_2 (70 mL) at –78 °C was added dropwise Et_3N (3.1 mL, 22 mmol, 3.0 equiv) and TESOTf (3.2 mL, 14 mmol, 2.0 equiv). The reaction mixture was stirred for 1 h at -78 °C and was quenched with saturated aqueous NH_4Cl. The mixture was warmed to 20 °C. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (1:99, 5:95) to afford product **VIII-3b** (1.70 g, 99%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.76 (s, 1H, C***H***-24), 4.70 (s, 1H, C***H***-24), 3.78-3.84 (m, 1H, C***H***-27), 2.14 (dd, *J* = 13.6, 5.8 Hz, 1H, C***H***-26), 2.14 (dd, *J*= 13.4, 7.0 Hz, 1H, C***H***-26), 1.73 (s, 3H, C***H*****$_3$**-25), 1.28-1.45 (m, 4H, C***H*****$_2$**-28), 0.96 (t, *J*= 7.9 Hz, 9H, Si(CH_2C***H*****$_3$**)$_3$), 0.90 (t, *J*= 6.8 Hz, 3H, C***H*****$_3$**-30), 0.60 (q, *J*= 7.9 Hz, 6H, Si(C***H*****$_2$**CH_3)$_3$).

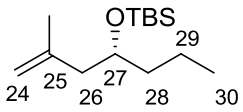
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 143.0 (C-25), 112.6 (C-24), 70.7 (C-27), 46.3 (C-26), 39.2 (C-28), 23.0 (CH_3-25), 18.6 (C-29), 14.2 (C-30), 6.9 (Si(CH_2***C***H_3)$_3$), 5.2 (Si(***C***H_2CH_3)$_3$).

IR (ν, cm^{-1}, $CHCl_3$)**:** 3034, 3029, 3023, 3013, 2958, 2913, 2876, 1646, 1458, 1416, 1363, 1075, 1005.

HRMS (EI): Calcd. for (M-Et): $C_{12}H_{25}OSi$: 213.1675 Found : 213.1682

[α]$^{25}_D$: + 5.4 (*c* 2.0, $CHCl_3$)

(4*R*)-4-(*tert*-Butyldimethylsilyloxy)-2-methylhept-1-ene **VIII-3c**

	$C_{14}H_{30}OSi$ M= 242.5 g.mol^{-1}

To a stirred suspension of copper (I) iodide (0.68 g, 3.6 mmol, 0.5 equiv) in THF (30 mL) was added isopropenylmagnesium bromide (0.5M THF solution, 43.2 mL, 21.6 mmol, 3.0 equiv) dropwise at -30 °C. After 30 min, (*R*)-1,2-epoxypentane **VIII-20** (0.62 g, 7.2 mmol) in THF (4 mL) was slowly added to the mixture. After stirring at -30 °C for 2 h, the reaction was quenched with saturated aqueous NH_4Cl, filtered and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Alcohol **VIII-21** was directly used in the next step without further purification.

To a solution of alcohol **VIII-21** in CH_2Cl_2 (70 mL) at –78 °C were added dropwise Et_3N (3.1 mL, 22 mmol, 3.0 equiv) and TBSOTf (3.3 mL, 14 mmol, 2.0 equiv). The reaction mixture was stirred for 1 h at -78 °C and was quenched with saturated aqueous NH_4Cl. The mixture was warmed to 20 °C. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (1:99, 5:95) to afford product **VIII-3c** (1.70 g, 98%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.76 (s, 1H, C***H***-24), 4.72 (s, 1H, C***H***-24), 3.77-3.83 (m, 1H, C***H***-27), 2.20 (dd, *J* = 13.5, 5.8 Hz, 1H, C***H***-26), 2.13 (dd, *J* = 13.5, 6.8 Hz, 1H, C***H***-26), 1.73 (s, 3H, C$\boldsymbol{H_3}$-25), 1.35-1.42 (m, 4H, C$\boldsymbol{H_2}$-28), 0.88-0.90 (m, 12H, C$\boldsymbol{H_3}$-30, Si(C$\boldsymbol{H_3}$)$_3$), 0.05 (s, 6H, Si(C$\boldsymbol{H_3}$)$_2$).

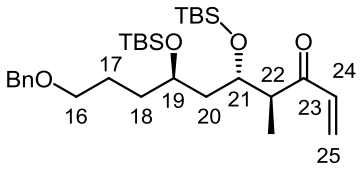
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 143.0 (C-25), 112.7 (C-24), 70.8 (C-27), 46.2 (C-26), 39.2 (C-28), 25.9 (SiC$(CH_3)_3$), 23.0 (CH_3-25), 18.6 (C-29), 18.1 (SiC), 14.2 (C-30), -4.4, -4.5 (Si$(CH_3)_2$).

IR (ν, cm^{-1}, $CHCl_3$**)** 2959, 2931, 2858, 1472, 1463, 1376, 1362, 1255, 1125, 1107, 1088, 1039, 1006.

HRMS (EI) Calcd. for $C_{14}H_{30}OSi$: 242.2066 Found : 242.2057

$[\alpha]^{25}_D$ + 13.2 (*c* 2.0, $CHCl_3$)

(4*R*,5*R*)-10-(Benzyloxy)-5,7-*bis*(tert-butyldimethylsilyloxy)-4-methyldec-1-en-3-one **VIII-22**



$C_{30}H_{54}O_6Si_2$
M= 534.9 g.mol^{-1}

To a stirred solution of aldehyde **VIII-16a** (115 mg, 0.22 mmol) in THF (2 mL) at -78°C was added vinylmagnesium bromide (1.6 M in THF, 490 µL, 0.77 mmol, 3.5 equiv) dropwise. After 2 h stirring, the reaction mixture was quenched with saturated aqueous NH_4Cl. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (30:70, 50:50) to afford alcohol (2 diastereomers) as a yellow oil.

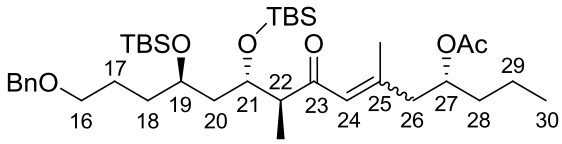
To a stirred suspension of 2-iodoxybenzoic acid (216 mg, 0.77 mmol, 3.5 equiv) in DMSO (20 mL) was added a solution of alcohol in THF (10 mL) at 20 °C. After the solution had been stirred overnight, 3 mL of water and 3 mL of ether were added. The mixture was stirred for 2 h to form a white precipitate, which was then filtered off. The aqueous phase was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 95:5) to afford enone **VIII-22** (59 mg, 50% for 2 steps) as a yellow oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.34 (m, 5H, C***H***-ar), 6.50 (dd, *J*= 17.4, 10.5 Hz, 1H, C***H***-24), 6.24 (dd, *J*= 17.4, 1.3 Hz, 1H, C***H***-25), 5.70 (dd, *J*= 10.5, 1.3 Hz, 1H, C***H***-25), 4.49 (s, 2H, C***H$_2$***-Ph), 4.15-4.19 (m, 1H, C***H***-21), 3.76-3.81 (m, 1H, C***H***-19), 3.44 (t, *J* = 6.8 Hz, 2H, C***H$_2$***-16) 2.97 (qd, *J*= 6.9, 4.7 Hz, 1H, C***H***-22), 1.57-1.62 (m, 6H, C***H$_2$***-17, C***H$_2$***-18, C***H$_2$***-20), 1.08 (d, *J* = 6.8 Hz, 3H, C***H$_3$***-22).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 201.3 (C-23), 138.6, 128.3, 127.7, 127.6 (C-ar), 135.5 (C-24), 127.5 (C-25), 72.8 (CH_2Ph), 70.4 (C-19), 70.2 (C-16), 69.6 (C-21), 51.3 (C-22), 41.2 (C-20), 34.6 (C-18), 25.9, 25.9 (SiC(CH_3)$_3$), 25.2 (C-17), 18.1 (SiC), 10.0 (CH_3-22), -3.7, -4.1, -4.2, -4.2 .

HRMS (EI) Calcd. for $C_{30}H_{54}O_6Si_2$: 534.3561 Found : 534.3559

(1*R*,6*S*,7*S*,9*R*)-12-Benzyloxy-7,9-bis(*tert*-butyldimethylsilyloxy)-3,6-dimethyl-5-oxo-1-propyl-dodec-3-enyl Acetate **VIII-1a**



$C_{38}H_{68}O_6Si_2$
M= 677.1 g.mol^{-1}

Hoveyda Grubbs'second generation catalyst (17 mg, 15 mol%) was added to a stirred solution of enone **VIII-2a** (100 mg, 0.18 mmol) and acetate **VIII-3a** (153 mg, 0.90 mmol, 5.0 equiv) in degassed CH_2Cl_2 (1 mL) under argon. The reaction mixture was heated at reflux for three days. The mixture was then cooled to 20 °C, concentrated *in vacuo* and directly purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95, 10:90) to afford 32 mg of *E* isomer **VIII-1a** and 8 mg of *Z* isomer (33%, *E/Z* = 4:1) as two colorless oils.

(*E*) Isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.25-7.36 (m, 5H, C***H***-ar), 6.19 (s, 1H, C***H***-24), 5.06-5.09 (m, 1H, C***H***-27), 4.50 (s, 2H, C***H₂***Ph), 4.10 (dt, *J* = 8.0, 4.0 Hz, 1H, C***H***-21), 3.79 (dq, *J* = 7.6, 5.4 Hz, 1H, C***H***-19), 3.45 (t, *J* = 6.4 Hz, 2H, C***H₂***-16), 2.68 (qd, *J* = 6.9, 4.6 Hz, 1H, C***H***-22), 2.41 (dd, *J* = 13.6, 7.0 Hz, 1H, C***H***-26), 2.28 (dd, *J* = 13.6, 6.2 Hz, 1H, C***H***-26), 2.14 (s, 3H, C***H₃***COO), 2.03 (s, 3H, C***H₃***-25), 1.24-1.65 (m, 10H, C***H₂***-17, C***H₂***-18, C***H₂***-20, C***H₂***-28, C***H₂***-29), 1.05 (d, *J* = 6.9 Hz, 3H, C***H₃***-22), 0.91 (t, *J*= 7.3 Hz, 3H, C***H₃***-30), 0.88, 0.84 (2s, 18H, SiC(C***H₃***)$_3$), 0.11, 0.10, 0.04, 0.04 (4s, 12H, Si(C***H₃***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 201.7 (C-23), 170.5 ($COCH_3$), 154.2 (C-25), 138.6, 128.3, 127.6, 127.4 (C-ar), 125.4 (C-24), 72.8 (CH_2Ph), 71.7 (C-27), 70.6 (C-21), 70.4 (C-16), 69.6 (C-19), 54.1 (C-22), 46.1 (C-26), 41.5 (C-20), 36.1 (C-18), 34.4 (C-28), 25.9 (SiC(CH_3)$_3$), 25.2 (C-17), 21.2 (CH_3-25), 19.8 ($COCH_3$), 18.5 (C-29), 18.1, 18.0 (SiC),13.8 (C-30), 10.5 (CH_3-22), -3.9, -4.1, -4.2, -4.2 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, $CHCl_3$) 2930, 2957, 2857, 1728, 1683, 1614, 1495, 1471, 1463, 1377, 1363, 1256, 1219, 1093, 1027, 1006.

HRMS (EI) Calcd. for $C_{38}H_{68}O_6Si_2$: 676.4555 Found : 676.4567

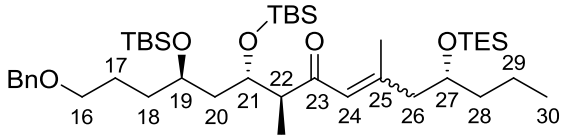
$[\alpha]^{25}_D$ + 13.0 (*c* 0.5, $CHCl_3$)

(*Z*) Isomer

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.25-7.36 (m, 5H, C***H***-ar), 6.22 (s, 1H, C***H***-24), 5.08-5.12 (m, 1H, C***H***-27), 4.50 (s, 2H, C***H₂***Ph), 4.16 (dt, *J* = 7.6, 3.4 Hz, 1H, C***H***-21), 3.79-3.82 (m, 1H, C***H***-19), 3.45 (t, *J* = 6.4 Hz, 2H, C***H₂***-16), 3.04 (dd, *J* = 13.1, 8.4 Hz, 1H, C***H***-26), 2.76 (dd, *J* = 13.1, 4.4 Hz, 1H, C***H***-26), 2.70 (qd, *J* = 6.9, 4.3 Hz, 1H, C***H***-22), 1.99 (s, 3H, C***H₃***COO), 1.91 (s, 3H, C***H₃***-25), 1.18-1.60 (m, 10H, C***H₂***-17, C***H₂***-18, C***H₂***-20, C***H₂***-28, C***H₂***-29), 1.04 (d, *J* = 6.9 Hz, 3H, C***H₃***-22), 0.85-0.91 (m, 18H, SiC(C***H₃***)$_3$), 0.11, 0.10, 0.06, 0.04 (4s, 12H, Si(C***H₃***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 201.0 (C-23), 170.7 ($COCH_3$), 154.8 (C-25), 138.7, 128.4, 127.6, 127.5 (C-ar), 125.8 (C-24), 73.1 (C-27), 72.9 (CH_2Ph), 70.5 (C-21), 70.3 (C-16), 69.7 (C-19), 54.2 (C-22), 41.1 (C-20), 38.0 (C-26), 36.6 (C-18), 34.5 (C-28), 26.0 (CH_3-25), 25.9 ($SiC(CH_3)_3$), 25.3 (C-17), 21.3 ($COCH_3$), 18.7 (C29), 18.1, 18.0 (SiC),14.1 (C-30), 9.9 (CH_3-22), -3.6, -4.1, -4.2, -4.2 ($Si(CH_3)_2$).

(5*R*,9*R*,10*R*,11*S*,13*R*,*E*)-13-(3-(Benzyloxy)propyl)-11-(*tert*-butyldimethyl silyloxy)-2,2,3,3,7,10,15,15,16,16-decamethyl-5-propyl-4,14-dioxa-3,15-disilaheptadec-7-en-9-ol **VIII-1b**



$C_{42}H_{80}O_5Si_3$
M= 749.4 g.mol^{-1}

Hoveyda-Grubbs' second generation catalyst (51 mg, 45 mol%) was added to a stirred solution of enone **VIII-2a** (100 mg, 0.18 mmol) and alkene **VIII-3b** (218 mg, 0.90 mmol, 5.0 equiv) in degassed CH_2Cl_2 (1 mL) under argon. The reaction mixture was heated at reflux for 3 days. The mixture was then cooled to 20 °C, concentrated *in vacuo* and directly purified by silica gel column chromatography with a gradient of ether in petroleum ether (1:99, 3:97, 5:95) to afford *E* isomer **VIII-1b** (47%, 64 mg) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 7.26-7.34 (m, 5H, C***H***-ar), 6.16 (s, 1H, C***H***-24), 4.49 (s, 2H, C***H*****$_2$**Ph), 4.10-4.15 (m, 1H, C***H***-21), 3.79-3.90 (m, 2H, C***H***-19, C***H***-27), 3.44 (t, *J* = 6.4 Hz, 2H, C***H*****$_2$**-16), 2.66-2.74 (m, 1H, C***H***-22), 2.34 (dd, *J* = 12.8, 5.3 Hz, 1H, C***H***-26), 2.15 (dd, *J* = 12.8, 7.8 Hz, 1H, C***H***-26), 2.12 (s, 3H, C***H*****$_3$**-25), 1.26-1.63 (m, 10H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20, C***H*****$_2$**-28, C***H*****$_2$**-29,), 1.04 (dd, *J* = 6.9, 1.6 Hz, 3H, C***H*****$_3$**-22), 0.96 (t, *J*= 7.9 Hz, 9H, Si(CH_2C***H*****$_3$**$)_3$), 0.89 (m, 21H, SiC(C***H*****$_3$**$)_3$, C***H*****$_3$**-30), 0.64 (q, *J*= 7.9 Hz, 6H, Si(C***H*****$_2$**$CH_3)_3$), 0.10, 0.07, 0.05 (3s, 12H, Si(C***H*****$_3$**$)_2$).

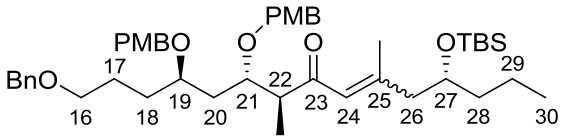
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 201.6 (C-23), 156.0 (C-25), 138.7, 128.3, 127.6, 127.4 (C-ar), 125.2 (C-24), 72.8, 70.6, 70.6, 70.5, 69.7 (C-19, C-21, C-23, C-27, C-16), 54.2 (C-22), 50.1 (C-26), 41.2 (C-20), 39.2 (C-18), 34.6 (C-28), 25.9, 25.9 (SiC$(CH_3)_3$), 25.3 (C-17), 20.2 (CH_3-25), 18.5 (C-29), 18.0, 18.0 (SiC), 14.1 (C-30), 10.0 (CH_3-22), 6.9 (Si(CH_2***C***$H_3)_3$), 5.1 (Si(***C***$H_2CH_3)_3$), -4.3, -4.2 (Si$(CH_3)_2$).

IR (ν, cm^{-1}, $CHCl_3$): 3010, 2958, 2932, 2878, 2858, 1722, 1679, 1608, 1472, 1463, 1412, 1379, 1257, 1238, 1092, 1035

HRMS (EI): Calcd. for $C_{42}H_{80}O_5Si_3$: 748.5314 Found : 748.5307

[α]$^{25}_D$: + 11.5 (*c* 1.0, $CHCl_3$)

(4*R*, 9*S*, 10*S*,12*R*, *E*)-15-(Benzyloxy)-4-(*tert*-butyldimethylsilyloxy)-10,12-bis(4-methoxybenzyloxy)-6,9-dimethylpentadec-6-en-8-one **VIII-1c**



$C_{46}H_{68}O_7Si$
M= 761.1 g.mol^{-1}

Hoveyda Grubbs' second generation catalyst (34 mg, 30 mol%) was added to a stirred solution of enone **VIII-2b** (101 mg, 0.18 mmol) and alkene **VIII-3c** (218 mg, 0.18 mmol, 5 equiv) in degased CH_2Cl_2 (1 mL) under argon. The reaction mixture was heated at reflux for 3 days. The mixture was then cooled to 20 °C, concentrated *in vacuo* and directly purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 10:90, 80:20) to afford *E* isomer **VIII-1c** (61 mg, 45%) as a colorless oil.

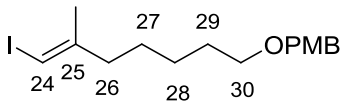
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.26-7.34 (m, 5H, C***H***-ar), 7.15-7.21 (m, 4H, C***H***-ar), 6.80-6.85 (m, 4H, ***H***-ar), 6.11 (s, 1H, C***H***-24), 4.48 (s, 2H, C***H₂***Ph), 4.42-4.46 (m, 2H, C***H₂***-Ph (PMB)), 4.23-4.27 (m, 2H,C***H₂***-Ph(PMB)), 3.94-3.98 (m, 1H, C***H***-21), 3.81-3.86 (m, 1H, C***H***-27), 3.77, 3.76 (2s, 6H, OC***H₃***(PMB)), 3.62-3.65 (m, 1H, C***H***-19), 3.45 (t, *J* = 5.9 Hz, 2H, C***H₂***-16), 2.86-2.93 (m, 1H, C***H***-22), 2.27 (dd, *J* = 12.9, 6.0 Hz, 1H, C***H***-26), 2.19 (dd, *J* = 12.9, 6.7 Hz, 1H, C***H***-26), 2.12 (d, *J*= 0.9 Hz, 3H, C***H₃***-25), 1.54-1.66 (m, 6H, C***H₂***-28, C***H₂***-18, C***H₂***-20), 1.39-1.54 (m, 4H, C***H₂***-17, C***H₂***-29), 1.05 (d, *J* = 7.0 Hz, 3H, C***H₃***-22), 0.88-0.90 (m, 12H, SiC(C***H₃***)$_3$, C***H₃***-30), 0.04, 0.02 (2s, 6H, Si(C***H₃***)$_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 202.4 (C=O), 156.6 (C-25), 159.0, 159.0, 141.9, 138.7, 132.3, 129.3, 129.1, 128.3, 127.6, 127.5, 125.5, 113.8, 113.7 (C-ar, C-24), 74.9, 72.8, 71.7, 70.7, 70.5, 69.9, (C-19, C-21, C-23, C-27, C-16, CH_2Ph ×2), 55.2 (OMe), 50.7 (C-26), 49.6 (C-22), 39.3 (C-20), 30.6 (C-28), 25.9 (C-18), 25.3 (SiC(CH_3)$_3$), 22.3(CH_3-25), 20.3 (C-17), 18.4 (C-29), 18.1 (SiC), 14.2 (C-30), 11.1 (CH_3-22), -4.4, -4.5 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, $CHCl_3$) 2958, 2932, 2877, 2858, 1731, 1679, 1603, 1496, 1471, 1463, 1412, 1379, 1362, 1257, 1095, 1072, 1040.

HRMS (EI) Calcd. for $C_{46}H_{68}O_7Si$: 760.4734 Found : 760.4730

(*E*)-1-((7-Iodo-6-methylhept-6-enyloxy)methyl)-4-methoxybenzene **VIII-26**

	$C_{16}H_{23}IO_2$ M= 374.3 g.mol^{-1}

To a stirred solution of dicyclopentadienylzirconocene dichloride (63 mg, 0.44 mmol, 2.0 equiv) in DCE (1 mL) was added dropwise trimethylaluminium (2 M hexane solution, 660 µL, 1.32 mmol, 6.0 equiv). Stirring was continued for 30 min at 20 °C then a solution of alkyne **LE5** (50 mg, 0.22 mmol) in DCE was added (1 mL) *via* cannula to the mixture. The reaction was stirred at 20 °C overnight and cooled to -30 °C. A solution of iodine (234 mg, 0.66 mmol, 3.0 equiv) in THF was added dropwise and the mixture was stirred at 20 °C for 2 h, quenched carefully by the addition of a saturated aqueous $NaHCO_3$ solution and diluted with ether. The aqueous phase was extracted with ether and the combined organic extracts were washed with water then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ether petroleum ether 5:95) to afford the (*E*)-vinyliodide **VIII-26** (54 mg, 66%) as a colorless oil.

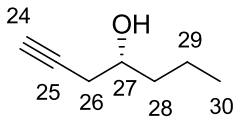
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.25-7.27 (m, 2H, C***H***-ar), 6.87-6.89 (m, 2H, C***H***-ar), 5.87 (s, 1H, C***H***-24), 4.42 (s, 2H, C***H*****$_2$**(Ph)), 3.81 (s, 3H, OC***H*****$_3$**), 3.43 (t, *J*= 6.5 Hz, 2H, C***H*****$_2$**-30), 2.20 (t, *J*= 7.4 Hz, 2H, C***H*****$_2$**-26), 1.81 (s, 3H, C***H*****$_3$**-25), 1.56-1.62 (m, 2H, C***H*****$_2$**-29), 1.40-1.48 (m, 2H, C***H*****$_2$**-27), 1.31-1.37 (m, 2H, C***H*****$_2$**-28)

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 159.1, 130.6, 129.2, 113.7 (C-ar), 148.1 (C-25), 74.5 (C-24), 72.5 (CH_2-Ph), 69.9 (C-30), 55.3 (OCH_3), 39.5 (C-26), 29.5 (C-29), 27.5 (C-27), 25.6 (C-28), 23.8 (CH_3-25).

IR (ν, cm^{-1}, $CHCl_3$**)** .2936, 2859, 2838, 1732, 1717, 1612, 1513, 1464, 1376, 1362, 1392, 1273, 1248, 1171, 1100, 1041.

HRMS (EI) Calcd. for $C_{16}H_{23}IO_2$: 374.0743 Found : 374.0740

(*R*)-Hept-1-yn-4-ol LE5

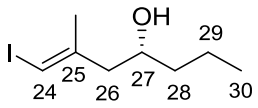
	$C_7H_{12}O$ M= 112.2 g.mol^{-1}

To a stirred solution of (*R)*-epoxypentane **VIII-20** (1.33 g, 15.4 mmol) in DMSO (25 mL) was added lithium acetylide-ethylenediamine at 20 °C. After the solution had been stirred overnight, the resulting mixture was quenched with brine, filtered and extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 80:20) to afford alcohol **LE5** (1.6 g, 93%).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)	3.74-3.76 (m, 1H, C***H***-27), 2.40 (ddd, *J*= 16.7, 4.8, 2.7 Hz, 1H, C***H***-26), 2.29 (ddd, *J*= 16.7, 6.7, 2.7 Hz, 1H, C***H***-26), 2.05 (brs, 1H, O***H***), 2.03 (t, *J*= 2.7 Hz, 1H, C***H***-24), 1.20-1.52 (m, 4H, C***H$_2$***-28, C***H$_2$***-29), 0.92 (t, *J*= 7.2 Hz, 3H, C***H$_3$***-30).
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)	80.9 (C-24), 70.6 (C-27), 69.5 (C-25), 38.3 (C-28), 34.1 (C-26), 18.8 (C-29), 13.9 (C-30).
$[\alpha]^{25}_D$	+0.5 (*c* 2.5, $CHCl_3$)[45]

[45] Schwartz, B. D.; Hayes, P.; Kitching, W.; De Voss, J. J. *J. Org. Chem.* **2005**, *70*, 3054. **$[\alpha]^{25}_D$** = -0.47 (*c* 2.5, $CHCl_3$ for the enantiomer 4*S*)

(R,E)-1-Iodo-2-methylhept-1-en-4-ol[46] **HA12**

	$C_8H_{15}IO$ M= 254.1 g.mol^{-1}

To a stirred solution of dicyclopentadienylzirconocene dichloride (1.46 g, 5.0 mmol, 2.0 equiv) in DCE (25 mL) was added dropwise trimethylaluminium (2 M hexane solution, 7.50 mL, 15 mmol, 6.0 equiv). Stirring was continued for 30 min at 20 °C then a solution of alkyne **LE5** (440 mg, 2.5 mmol) in DCE (10 mL) was added *via* cannula to the mixture. The reaction was stirred at 20 °C overnight and cooled to -30 °C. A solution of iodine (1.9 g, 7.5 mmol, 3.0 equiv) in THF was added dropwise and the mixture was stirred at 20 °C for 2 h, quenched carefully by the addition of saturated aqueous $NaHCO_3$ and diluted with ether. The aqueous phase was extracted with ether and the combined organic extracts were washed with water then brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (0:100, 5:95) to afford vinyliodide **HA12** (560 mg, 88%).

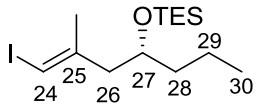
^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 6.0 (s, 1H, C***H***-24), 3.70-3.76 (m, 1H, C***H***-27, 3.70-3.76), 2.33 (dq, *J*= 6.2, 13.9 Hz, 2H, C***H$_2$***-26), 1.87 (s, 3H, C***H$_3$***-25), 1.60 (brs, 1H, O***H***), 1.33-1.48 (m, 4H, C***H$_2$***-28, C***H$_2$***-29), 0.92 (t, *J*= 7.1 Hz, 3H, C***H$_3$***-30).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 145.1 (C-25), 77.1 (C-24), 68.8 (C-27), 47.6 (C-26), 39.1 (C-28), 24.1 (CH_3-C25), 18.8 (C-29), 14.0 (C-30).

$[\alpha]^{25}_D$: -2.5 (*c* 1.0, $CHCl_3$)

[46] Roche, C.; Desroy, N.; Haddad, M.; Phansavath, P.; Genêt, J. P. *Org. Lett.* **2008**, *10*, 3911.

(R,E)-Triethyl(1-iodo-2-methylhept-1-en-4-yloxy)silane **VIII-24a**

	$C_{14}H_{29}IOSi$ M= 368.4 g.mol^{-1}

To a solution of alcohol **HA12** (3 g, 11.8 mmol) in CH_2Cl_2 (50 mL) at –78 °C were added dropwise Et_3N (5.0 mL, 35.4 mmol, 3.0 equiv) and TESOTf (5.34 mL, 23.6 mmol, 2.0 equiv). The reaction mixture was stirred for 1 h at -78 °C and was quenched by a saturated aqueous NH_4Cl solution. The mixture was warmed to 20 °C. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 99:1) to afford product **VIII-24a** (4.0 g, 92%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 5.91 (s, 1H, C***H***-24), 3.73-3.81 (m, 1H, C***H***-27), 2.33 (d, *J*= 6.2 Hz, 2H, C***H*****$_2$**-26), 1.84 (s, 3H, CH_3-25), 1.29-1.40 (m, 4H, C*H*$_2$-28, C*H*$_2$-29), 0.93 (t, *J*= 7.9 Hz, 9H, Si(CH_2C***H*****$_3$**)$_3$), 0.90 (t, *J*= 7.0 Hz, 3H, C***H*****$_3$**-30), 0.58 (q, *J*= 8.0 Hz, 6H, Si(CH_2C***H*****$_3$**)$_3$).

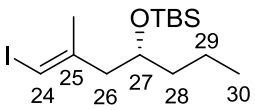
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 145.1 (C-25), 77.1 (C-24), 70.2 (C-27), 47.5 (C-26), 39.5 (C-28), 24.4 (CH_3-25), 18.5 (C-29), 14.2 (C-30), 6.9 (Si(CH_2***C***H_3)$_3$), 5.1 (Si(***C***H_2CH_3)$_3$).

IR (ν,cm^{-1}, $CHCl_3$**)** 3016, 2958, 2936, 2913, 2876, 1616, 1458, 1415, 1378, 1265, 1239, 1075.

HRMS (EI) Calcd. for $C_{14}H_{29}IOSi$-Et : 339.0642 Found : 339.0650

$[\alpha]^{25}_D$ + (*c* 1.0, $CHCl_3$)

(*R,E*)-*tert*-Butyl(1-iodo-2-methylhept-1-en-4-yloxy)dimethylsilane VIII-24b

	$C_{14}H_{29}IOSi$ M= 368.4 g.mol^{-1}

To a solution of alcohol **HA12** (4.0 g, 15.7 mmol) in CH_2Cl_2 (70 mL) at –78 °C were added dropwise Et_3N (6.61 mL, 47.1 mmol, 3.0 equiv) and TBSOTf (5.4 mL, 23.6 mmol, 1.5 equiv). The reaction mixture was stirred for 1 h at -78 °C and was quenched by a saturated aqueous NH_4Cl solution. The mixture was warmed to 20 °C. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 99:1) to afford vinyliodide **VIII-24b** (5.43 g, 94%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.90 (s, 1H, C***H***-24), 3.73-3.79 (m, 1H, C***H***-27, 3.70-3.76), 2.27-2.37 (m, 2H, C***H$_2$***-26), 1.83 (d, *J*= 1.0 Hz, 3H, C***H$_3$***-C25), 1.29-1.39 (m, 4H, C***H$_2$***-28, C***H$_2$***-29), 0.90 (t, *J*= 5.8 Hz, 3H, C***H$_3$***-30), 0.88 (s, 9H, SiC(C***H$_3$***)$_3$), 0.03, 0.02, (s, 6H, Si(C***H$_3$***)$_2$).

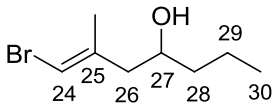
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 145.1 (C-25), 77.1 (C-24), 70.2 (C-27), 47.4 (C-26), 39.5 (C-28), 25.9 (SiC(CH_3)$_3$), 24.5 (CH_3-C25), 18.4 (C-29), 18.1 (SiC), 14.2 (C-30), -4.4, -4.5 (Si(CH_3)$_2$).

IR (ν,cm^{-1}, $CHCl_3$**)**: 3010, 2959, 2858, 1617, 1471, 1463, 1435, 1377, 1362, 1275, 1256, 1144, 1124, 1107, 1087, 1039.

HRMS (EI): Calcd. for $C_{14}H_{29}IOSi$-CH_3 : 353.0799 Found : 353.0797

[α]$^{25}_D$: -23.6 (*c* 3.0, $CHCl_3$)

1-Iodo-2-methylhept-1-en-4-ol **VIII-27**

	$C_8H_{15}BrO$ M= 207.1 g.mol^{-1}

To a stirred suspension of copper (I) iodide (175 mg, 0.92 mmol, 0.5 equiv) in THF (30 mL) was added isopropenylmagnesium bromide (0.5M THF solution, 11 mL, 5.52 mmol, 3 equiv) dropwise at -30 °C. After 30 min, (*R*)-1,2-epoxypentane **VIII-20** (158 mg, 1.84 mmol) in THF (1 mL) was slowly added to the mixture. After stirring at -30 °C for 2 h, the reaction was quenched with saturated aqueous NH_4Cl, filtered and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The alcohol **VIII-21** was directly used in the next step without further purification.

To a stirred solution of alcohol **VIII-21,** in CCl_4 (9 mL) was added a solution of bromine (125 µL, 2.4 mmol, 1.05 equiv) in CCl_4 (3 mL) at 0 °C. The resulting solution was stirred for 1 h, and the solvent and excess bromine was removed *in vacuo*. The residual brown oil was treated with a 5 M solution of KOH in MeOH (5 mL) at 20 °C for 3 h. The reaction mixture was quenched with water and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 9:1) to afford vinylbromide **VIII-27** (152 mg, 40% over 3 steps) as a colorless oil ans as a 9:1 mixture of *E* and *Z* isomers.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz)

6.01 (s, 0.1H, C***H***-24 *Z* isomer), 6.00 (s, 0.9H, C***H***-24 *E* isomer), 3.80-3.85 (m, 0.1H, C***H***-27 *Z* isomer), 3.71-3.77 (m, 0.9H, C***H***-27 *E* isomer), 2.47 (dd, *J*= 13.5, 8.8 Hz, 0.1H, C***H***-26 *Z* isomer), 2.31 (dd, *J*= 13.5, 4.3 Hz, 0.1H, C***H***-26 *Z* isomer), 2.27 (dd, *J*= 13.8, 8.8 Hz, 0.9H, C$\boldsymbol{H_2}$-26 *E* isomer), 2.20 (dd, *J*= 13.8, 8.6 Hz, 0.9H, C$\boldsymbol{H_2}$-26 *E* isomer), 1.85 (s, 0.3H, C$\boldsymbol{H_3}$-25 *Z* isomer), 1.83 (s, 2.7H, C$\boldsymbol{H_3}$-25 *E* isomer), 1.34-1.52 (m, 5H, O***H***, C$\boldsymbol{H_2}$-28, C$\boldsymbol{H_2}$-29), 0.93 (t, *J*= 7.1 Hz, 3H, C$\boldsymbol{H_3}$-30).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz)

(*E*) Isomer

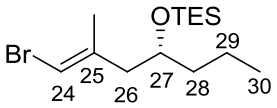
138.9 (C-25), 103.4 (C-24), 68.7 (C-27), 46.4 (C-26), 39.2 (C-28), 19.4 (CH_3-C25), 18.8 (C-29), 14.0 (C-30).

(*Z*) Isomer

139.1 (C-25), 102.8 (C-24), 69.8 (C-27), 42.2 (C-26), 39.8 (C-28), 23.1 (CH_3-C25), 18.8 (C-29), 14.0 (C-30).

HRMS (EI) Calcd. for $C_8H_{15}BrO$: 206.0306 Found : 203.0300

(E)-Triethyl(1-bromo-2-methylhept-1-en-4-yloxy)silane **VIII-28**

	$C_{14}H_{29}BrOSi$ M= 321.4 g.mol^{-1}

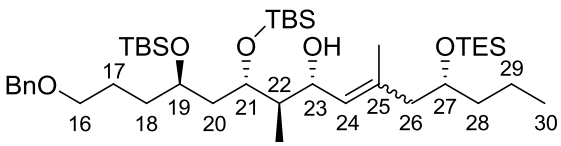
To a solution of alcohol **VIII-27** (140 mg, 0.68 mmol) in CH_2Cl_2 (7 mL) at –78 °C were added dropwise Et_3N (274 µL, 2.03 mmol, 3.0 equiv) and TESOTf (305 µL, 1.35 mmol, 2.0 equiv). The reaction mixture was stirred for 1 h at -78 °C and was quenched by a saturated aqueous NH_4Cl solution. The mixture was warmed to 20 °C. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/ether 99:1) to afford vinylbromide **VIII-28** (177 mg, 81%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 5.91 (s, 1H, C***H***-24), 3.76-3.80 (m, 1H, C***H***-27), 2.16-2.23 (m, 2H, C***H₂***-26), 1.80 (s, 3H, CH_3-25), 1.30-1.43 (m, 4H, C***H₂***-28, C***H₂***-29), 0.93 (t, *J*= 7.9 Hz, 9H, $Si(CH_2C\boldsymbol{H_3})_3$), 0.90 (t, *J*= 7.0 Hz, 3H, C***H₃***-30), 0.58 (q, *J*= 8.0 Hz, 6H, $Si(CH_2C\boldsymbol{H_3})_3$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 138.9 (C-25), 103.2 (C-24), 70.1 (C-27), 46.2 (C-26), 39.5 (C-28), 19.7 (CH_3-25), 18.5 (C-29), 14.2 (C-30), 6.9 ($Si(CH_2\boldsymbol{C}H_3)_3$), 5.1 ($Si(\boldsymbol{C}H_2CH_3)_3$).

HRMS (EI) Calcd. for $C_{14}H_{29}BrOSi$: 320.1171 Found : 320.1165

(5*R*,9*R*,10*R*,11*S*,13*R*,*E*)-13-(3-(Benzyloxy)propyl)-11-(*tert*-butyl dimethyl silyloxy)-2,2,3,3,7,10,15,15,16,16-decamethyl-5-propyl -4,14-dioxa-3,15-disilaheptadec-7-en-9-ol **VIII-23a**



$C_{42}H_{82}O_5Si_3$
M= 751.4 g.mol^{-1}

To a solution of ketone **VIII-1b** (50 mg, 0.067 mmol) in THF (2 mL), was added L-Selectride (1M in THF, 120 µL, 0.12 mmol, 1.8 equiv). After stirring for 5 h at -78 °C, the reaction was quenched by successive addition of methanol and saturated aqueous NH_4Cl. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (2:98, 5:95) to afford alcohol **VIII-23a** (36 mg, 71%) as a colorless oil as a single diastereomer.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 7.26-7.34 (m, 5H, C***H***-ar), 5.19 (d, *J*= 8.8 Hz, 1H, C***H***-24), 4.51 (s, 2H, C***H*****$_2$**Ph), 4.10-4.16 (m, 2H, C***H***-21, C***H***-23), 3.79-3.86 (m, 2H, C***H***-19, C***H***-27), 3.47 (t, *J* = 6.4 Hz, 2H, C***H*****$_2$**-16), 2.23 (dd, *J* = 13.2, 5.3 Hz, 1H, C***H***-26), 2.15 (dd, *J* = 13.2, 7.9 Hz, 1H, C***H***-26), 1.84 (brs, 1H, O***H***), 1.69 (s, 3H, C***H*****$_3$**-25), 1.24-1.74 (m, 11H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20, C***H*****$_2$**-28, C***H*****$_2$**-29, C***H***-22), 0.96 (t, *J*= 7.9 Hz, 9H, Si(CH_2C***H*****$_3$**$)_3$), 0.89 (m, 21H, SiC(C***H*****$_3$**$)_3$, C***H*****$_3$**-30), 0.73 (d, *J* = 6.9 Hz, 3H, C***H*****$_3$**-22), 0.60 (q, *J*= 7.9 Hz, 6H, Si(C***H*****$_2$**$CH_3)_3$), 0.09, 0.08, 0.07 (3s, 12H, Si(C***H*****$_3$**$)_2$).

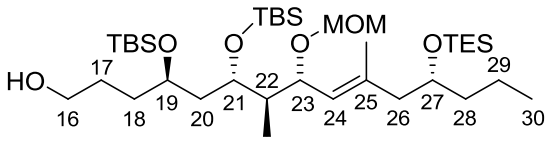
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 138.7, 128.3, 127.6, 127.4 (C-ar), 135.8 (C-25), 129.9 (C-24), 72.9 (CH_2Ph), 71.2, 70.8, 70.6, 70.6, 70.5 (C-19, C-21, C-23, C-27, C-16), 48.3 (C-22), 45.5 (C-26), 41.0 (C-20), 39.0 (C-18), 34.9 (C-28), 26.0, 25.9 (SiC$(CH_3)_3$), 25.4 (C-17), 18.4 (C-29), 18.1, 18.1 (SiC), 17.4 (CH_3-25), 14.2 (C-30), 10.9 (CH_3-22), 6.9 (Si(CH_2***C***$H_3)_3$), 5.2 (Si(***C***$H_2CH_3)_3$), -3.9, -4.1, -4.2, -4.2 (Si$(CH_3)_2$).

IR (ν, cm^{-1}, $CHCl_3$) 3616, 3478, 2958, 2932, 2877, 2858, 1685, 1610, 1471, 1463, 1413, 1379, 1362, 1256, 1073.

HRMS (EI) Calcd. for $C_{42}H_{82}O_5Si_3$: 750.5470 Found : 750.5473

[α]$^{25}_D$ + 4.5 (*c* 1.5, $CHCl_3$)

(4*R*,6*S*,7*R*,8*R*,12*R*)-4,6-bis(*tert*-Butyldimethylsilyloxy)-8-(methoxy methoxy)-7,10-dimethyl-12-(triethylsilyloxy)pentadec-9-en-1-ol **VIII-32**



$C_{37}H_{80}O_6Si_3$
M= 705.3 g.mol^{-1}

Secondary alcohol **VIII-23a** (63 mg, 84 µmmol) was dissolved in DCE (420 µL) followed by the addition of diisopropylethylamine (150 µL, 840 µmol, 10 equiv) and MOMCl (32 µL, 420 µmol, 5.0 equiv) at 20 °C. After stirring for 5 h at 50 °C, the reaction was quenched with successive addition of ether and 10% aqueous HCl solution. The aqueous phase was extracted with ether and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (5:95, 10:90) to afford protected alcohol **VIII-31**(57 mg, 85%) as a slightly yellow oil.

A solution of the benzyl ether **VIII-31** (20 mg, 25 µmmol) and an excess of Raney nickel in absolute ethanol (1 mL) was stirred at 20 °C under 1 atmosphere of H_2. After the reaction was complete, the catalyst was removed by filtration and the solution concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient of ether in petroleum ether (10:90, 20:80) to afford alcohol **VIII-32** (14 mg, 77%) as a colorless oil.

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz) 4.98 (d, *J*= 9.6 Hz, 1H, C***H***-24), 4.62 (d, *J*= 6.5 Hz, 1H, OC***H***-CH_3), 4.42 (d, *J*= 6.5 Hz, 1H, OC***H***-CH_3), 4.10-4.17 (m, 2H, C***H***-21, C***H***-23), 3.88-3.93 (m, 1H, C***H***-19), 3.80-3.85 (m, 1H, C***H***-27), 3.58-3.66 (m, 2H, C***H*****$_2$**-16), 3.34 (s, 3H, OC***H*****$_3$**), 2.27 (dd, *J* = 13.2, 4.6 Hz, 1H, C***H***-26), 2.17 (dd, *J* = 13.2, 8.3 Hz, 1H, C***H***-26), 1.78-1.86 (m, 1H, C***H***-22), 1.63 (s, 3H, C***H*****$_3$**-25), 1.26-1.73 (m, 10H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20, C***H*****$_2$**-28, C***H*****$_2$**-29), 0.96 (t, *J*= 7.9 Hz, 9H, Si(CH_2C***H*****$_3$**)$_3$), 0.89 (s, 18H, SiC(C***H*****$_3$**)$_3$), 0.86 (t, *J*= 6.8 Hz, 3H, C***H*****$_3$**-25), 0.76 (d, *J* = 7.1 Hz, 3H, C***H*****$_3$**-22), 0.60 (q, *J*= 7.9 Hz, 6H, Si(C***H*****$_2$**CH_3)$_3$), 0.09, 0.08, 0.07 (3s, 12H, Si(C***H*****$_3$**)$_2$).

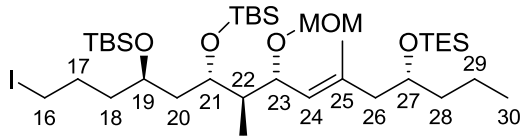
^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz) 137.6 (C-25), 127.1 (C-24), 93.4 (CH_2(MOM)), 73.4 (C-23), 70.7, 70.5, 70.3 (C-21, C-16, C-19), 63.2 (C-16), 55.7 (CH_3-O), 48.3 (C-26), 44.0 (C-22), 39.4 (C-20), 38.7 (C-28), 34.7 (C-18), 28.1 C-17), 26.0 (SiC(CH_3)$_3$), 18.4 (C-29), 18.2, 18.1 (SiC), 17.4 (CH_3-25), 14.2 (C-30), 10.9 (CH_3-22), 7.0 (Si(CH_2***C***H_3)$_3$), 5.1 (Si(***C***H_2CH_3)$_3$), -3.9, -4.1, -4.2, -4.3 (Si(CH_3)$_2$).

IR (ν, cm^{-1}, $CHCl_3$) 3690, 3623, 3397, 2957, 2932, 2884, 2858, 1664, 1602, 1471, 1463, 1412, 1387, 1362, 1256, 1144, 1086, 1034.

$[\alpha]^{25}_D$ - 25.0 (*c* 0.5, $CHCl_3$)

HRMS (EI) Calcd. for $C_{37}H_{80}O_6Si_3$: 704.5263 Found : 704.5191

(5*R*,9*R*,10*R*,11*S*,13*R*)-11-(*tert*-Butyldimethylsilyloxy)-3,3-diethyl-13-(3-iodopropyl)-9-(methoxymethoxy)-7,10,15,15,16,16-hexamethyl-5-propyl-4,14-dioxa-3,15-disilaheptadec-7-ene **AV2**



$C_{37}H_{79}IO_5Si_3$
M= 815.2 g.mol^{-1}

Primary alcohol **VIII-32** (10 mg, 13.6 µmmol) was stirred in THF (300 µL) at 20 °C, followed by the addition of imidazole (2.3 mg, 34 µmol, 2.5 equiv) and Ph_3P (8 mg, 30 µmol, 2.2 equiv). The reaction was cooled to 0 °C and I_2 (7 mg, 27 µmol, 2.0 equiv) was added. The reaction mixture was stirred for 45 min, concentrated and purified by flash chromatography (99:1 petroleum ether/ether) to afford primary iodide **AV2** (8.0 mg, 72%).

^{1}H NMR (δ, ppm) ($CDCl_3$, 400 MHz): 4.98 (d, *J*= 9.6 Hz, 1H, C***H***-24), 4.62 (d, *J*= 6.4 Hz, 1H, OC***H***-CH_3), 4.43 (d, *J*= 6.4 Hz, 1H, OC***H***-CH_3), 4.11-4.17 (m, 2H, C***H***-21, C***H***-23), 3.81-3.90 (m, 2H, C***H***-27, C***H***-19), 3.35 (s, 3H, OC***H*****$_3$**), 3.16-3.21 (m, 2H, C***H*****$_2$**-16), 2.27 (dd, *J* = 13.2, 4.4 Hz, 1H, C***H***-26), 2.17 (dd, *J* = 13.3, 8.3 Hz, 1H, C***H***-26), 1.69 (s, 3H, C***H*****$_3$**-25), 1.28-1.93 (m, 11H, C***H*****$_2$**-17, C***H*****$_2$**-18, C***H*****$_2$**-20, C***H*****$_2$**-28, C***H*****$_2$**-29, C***H***-22), 0.97 (t, *J*= 7.9 Hz, 9H, $Si(CH_2C\boldsymbol{H_3})_3$), 0.90, 0.88 (2s, 18H, $SiC(C\boldsymbol{H_3})_3$), 0.87 (t, *J*= 6.7 Hz, 3H, C***H*****$_3$**-30), 0.77 (d, *J* = 7.1 Hz, 3H, C***H*****$_3$**-22), 0.61 (q, *J*= 7.9 Hz, 6H, $Si(C\boldsymbol{H_2}CH_3)_3$), 0.09, 0,09, 0.08, 0.07 (4s, 12H, $Si(C\boldsymbol{H_3})_2$).

^{13}C NMR (δ, ppm) ($CDCl_3$, 100 MHz): 137.7 (C-25), 127.1 (C-24), 93.4 (CH_2(MOM)), 73.3 (C-23), 70.7, 70.4, 69.5 (C-21, C-16, C-19), 55.7 (CH_3-O), 48.3 (C-26), 44.0 (C-22), 39.9 (C-18), 39.2 (C-20), 38.7 (C-28), 29.1 (C-17), 26.0 ($SiC(CH_3)_3$), 18.4 (C-29), 18.1, 18.1 (SiC), 17.4 (CH_3-25), 14.2 (C-30), 10.9 (CH_3-22), 7.3 (C-16), 6.9 ($Si(CH_2\boldsymbol{C}H_3)_3$), 5.1 ($Si(\boldsymbol{C}H_2CH_3)_3$), -3.9, -4.0, -4.2, -4.2 ($Si(CH_3)_2$).

IR(ν, cm^{-1}, $CHCl_3$): 3690, 3623, 3397, 2957, 2932, 2884, 2858, 1664, 1602, 1471, 1463, 1412, 1387, 1362, 1256, 1144, 1086, 1034.

$[\alpha]^{25}_D$: - 22.0 (*c* 0.5, $CHCl_3$)

HRMS (EI): Calcd. for ($C_{37}H_{79}IO_5Si_3$-I) : 687.5235 Found : 687.5239