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Supporting Information

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Radical Additions of Xanthates to Vinyl Epoxides and Related Derivatives: A Powerful Tool for the Modular Creation of Quaternary Centres

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General experimental procedures.

All commercially available reagents and solvents were used without further purification unless otherwise noted. Methylene chloride was dried by distillation from calcium hydride. Et2O was distilled from Na with benzophenone as an indicator. Flash column chromatography was carried out on silica gel. TLC was conducted on silica gel 200 micron, 60F254 plates. ^{1}H NMR spectra were recorded on Brucker 400 MHz NMR instruments. Chemical shifts are reported in ppm with the solvent as internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent as internal standard (CDCl3: 77.0 ppm). Mass spectrometry were performed on a Hewlett Packard HP 5989 spectrometer with a Hewlett Packard HP 5890 (NH_3 CI) chromatograph. High-resolution mass spectrometry were recorded on a JEOL JMS-Gcmate II, GC/MS at the Ecole Polytechnique.

Characterization of the compounds prepared by radical addition using BEt_3/O_2:

5 6-Hydroxy-hex-4-enoic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 5.64-5.56 (m, 2 H), 4.23 (d, *J* = 7.2 Hz, 0.2 H, *cis* isomer), 4.08 (q, *J* = 16.4 Hz, 2 H), 4.03 (d, *J*= 9,8 Hz, 1.8 H, *trans* isomer), 2.36-2.30 (m, 4 H), 1.23 (t, *J*= 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.15, 129.39, 129.00, 63.69, 60.33, 33.75, 27.42, 14.18. MS, m/z: 176 ($M+NH_4^+$).

7 6-Hydroxy-hex-4-enoic acid methoxy-methyl-amide

^{1}H NMR ($CDCl_3$) δ 5.68-5.64 (m, 2 H), 4.13 (d, *J* = 8.3 Hz, 0.4 H, *cis* isomer), 4.03 (d, *J* = 16.0 Hz, 1.6 H, *trans* isomer), 3.65 (s, 3 H), 3.14 (s, 3 H), 2.63-2.47 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 208.15, 132.78,

127.76, 63.45, 56.09, 40.32, 38.15, 32.28, 27.27, 23.11, 14.10. MS, m/z: 174 ($M+H^+$).

9 8-Hydroxy-4,4-dimethyl-oct-6-en-2-one

^{1}H NMR ($CDCl_3$) δ 5.47-5.63 (m, 2 H), 4.26 (d, *J* = 10.1 Hz, 0.8 H, *cis* isomer), 4.05 (d, *J* = 15.1 Hz, 1.2 H, *trans* isomer), 2.26 (s, 2 H), 2.06 (s, 2 H), 0.95 (s, 6 H), 0.87 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.35, 132.16, 128.32, 63.71, 53.16, 44.50, 33.66, 31.70, 27.04. MS, m/z: 153 ($M+H^+-H_2O$).

11 4-(7-Methyl-1,4-dioxa-spiro[4.5]dec-7-yl)-but-2-en-1-ol

^{1}H NMR ($CDCl_3$) δ 5.71-5.59 (m, 2 H), 4.29 (d, *J* = 9.3 Hz, 0.5 H, *cis* isomer), 4.10 (d, *J* = 16.4 Hz, 1.5 H, *trans* isomer), 3.90 (s, 4 H), 2.10-1.98 (m, 2 H), 1.63-1.30 (m, 10 H), 0.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 131.71, 129,31, 109.39, 63.90, 63.72, 36.90, 36.77, 34.87, 34.74, 25.92, 19.59. MS, m/z: 229 ($M+H^+$).

16 3-Butyl-3-(4-hydroxy-but-2-enyl)-cyclobutanone

^{1}H NMR ($CDCl_3$) δ 5.77-5.64 (m, 2 H), 4.32 (d, *J* = 11.4 Hz, 0.5 H, *cis* isomer), 4.13 (d, *J* = 15.1s Hz, 1.5 H, *trans* isomer), 2.81-2.68 (m, 4 H), 2.33 (d, 2 H), 1.23-1.37 (m, 6 H), 0.92 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.15, 132.78, 127.76, 63.45, 56.09, 40.32, 38.15, 32.28, 27.27, 23.11, 14.10. MS, m/z: 214 ($M+NH_4^+$).

17 6-(1-Butyl-3-oxo-cyclobutyl)-3-hydroxy-hex-4-enoic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 5.80-5.61 (m, 2 H), 4.25 (d, *J* = 6.9 Hz, 0,4 H, *cis* isomer), 4.15 (d, *J* = 7.1 Hz, 1.6 H, *trans* isomer), 3.79 (q, *J* = 7.15 Hz, 2 H), 2.55 (m, 4 H), 2.42 (d, *J* = 7.03 Hz, 1 H), 1.65 (m, 2 H), 1.40-1.21 (m, 9 H), 0.95 (t, *J* = 7.45, 3 H); ^{13}C NMR ($CDCl_3$) δ 207.98, 172.33, 134.36, 127.35, 68.55, 68.02, 56.12, 56.09, 41.50, 40.28, 38.09, 32.26, 30.37, 29.76, 25.66, 14.23. MS, m/z: 283 ($M+H^+$).

18 3-Butyl-3-(3-hydroxy-3,5,5-trimethyl-cyclohex-1-enylmethyl)-cyclobutanone

^{1}H NMR ($CDCl_3$) δ 5.43 (s, 1 H), 3.01-2.70 (m, 2 H), 2.38-2.27 (m, 2 H), 1.67-1.48 (m, 6 H), 1.43 (s, 3H), 1.53-1.33 (m, 4 H), 1.11 (s, 3 H), 0.98 (s, 3H), 0.81 (t, *J* = 6.82 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.29, 135.43, 125.58, 69.39, 57.45, 57.32, 49.98, 45.88, 43.80, 37.92, 31.50, 31.17, 30.46, 30.37, 29.76, 27.64, 27.22, 23.15. MS, m/z: 261 ($M+H^+-H_2O$).

22 Acetic acid (E)-8-benzyloxy-6-hydroxy-2-methyl-2-(3-oxo-butyl)-oct-4-enyl ester

^{1}H NMR ($CDCl_3$) δ 7.37-7.26 (m, 5 H), 5.72-5.70 (m, 2 H), 4.52 (s, 2 H), 4.37 (m, *J* = 8.6 Hz, 0.5 H, *cis* isomer), 4,30 (m, *J* = 11.2 Hz, 1.5 H, *trans* isomer), 3.72-3.63 (m, 2 H), 2.96 (m, 1 H), 2.90 (m, 1 H), 2.51 (m, 1H), 2.21-2.01 (m, 2 H) 1.90-1.83 (m, 2H), 1.43 (s, 3 H), 1.29-1.23 (m, 5 H), 0.80-0.92 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 207.61, 170.20, 131.38, 130.55, 127.42, 127.39, 126.68, 126.62, 111.89, 72.27, 70.79, 67.83, 67.41, 40.01, 35.79, 33.27, 31.05, 28.94, 26.06, 21.32, 19.95, 15.67, 12.68. MS, m/z: 307 ($M+H^+$).

25 5-[(S)-4-(5-Hydroxy-1,1-dimethyl-pent-3-enyl)-cyclohex-1-enyl]-3-oxo-pentanoic acid ethyl ester

^{1}H NMR ($CDCl_3$) δ 5.74-5.60 (m, 2 H), 5.39 (d, *J* = 3.02 Hz, 1 H), 4.29 (d, *J* = 7.29 Hz , 0.4 H, *cis* isomer), 4.20 (q, *J* = 7.14 Hz, 2 H), 4.12 (d, *J* 8.35 Hz, 1.6 H, *trans* isomer), 3.44 (s, 2 H), 2.64 (t, *J* = 7.23 Hz, 2 H), 2.23 (m, 3 H), 2.01-1.95 (m, 6 H), 1.81-1.77 (m, 2 H), 1.28 (t, *J* = 7.13 Hz, 3 H), 0.82 (s, 3 H), 0.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 202.64, 167.21, 135.72, 131.29, 129.81, 121.72, 63.78, 61.34, 49.29, 43.02, 41.78, 41.35, 35.17, 30.90, 29.71, 26.32, 24.23, 24.19, 23.71, 14.09. MS, m/z: 337 ($M+H^+$).

28 2,2-Dimethyl-propionic acid 1-[3-(4-bromo-phenyl)-3-oxo-propyl]-5-hydroxy-pent-3-enyl ester

^{1}H NMR ($CDCl_3$) δ 7.84 (d, *J*= 8.60Hz, 2 H), 7.64 (d, *J* = 8.59 Hz, 2 H), 5.70-5.75 (m, 2 H), 5.04-4.99 (m, 1 H), 4.24 (m, 0,8 H), 4.14 (d, *J* = 5.16Hz, 1,2 H), 2.98 (t, *J* = 7.37 Hz, 2 H), 2.41 (t, *J* = 5.52 Hz, 2 H), 2.11-2.00 (m, 2H), 1.23 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 198.04, 178.11, 135.32, 132.59, 131.87,

129.42, 128.24, 126.82, 72.18, 63.23, 38.82, 37.34, 34.33, 27.90, 27.11. MS, m/z: 395 - 397 ($M+H^+$).

32 N-{2,2,2-Trifluoro-1-[(4R,5R)-5-(4-hydroxy-but-2-enyl)-2-oxo-[1,3]dioxolan-4-yl]-ethyl}-benzamide

^{1}H NMR ($CDCl_3$) δ 6.78 (d, *J* = 9.98Hz, 1 H), 5.92-5.86 (m, 1 H), 5.63-5.57 (m, 1 H), 5.01-4.95 (m, 1 H), 4.66-4.54 (m, 1 H), 4.54 (t, *J* = 5.56 Hz, 1 H), 4.18 (t, *J* = 5.35 Hz, 0.2H, *cis* isomer), 4.15 (t, *J* = 6.28 Hz, 1.8 H, *trans* isomer), 2.74-2.65 (m, 1 H), 2.54-2.47 (m, 1 H), 1.99 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.65, 153.12, 136.07, 133.32, 124.86, 122.42, 62.60, 51.61, 51.31, 36.75, 35.36, 29.69, 22.70. MS, m/z: 282 ($M+H^+$).

36 5-[2-(2-Hydroxy-cyclohexylidene)-vinyl]-5-methyl-dihydro-furan-2-one

^{1}H NMR ($CDCl_3$) δ 4.75 (s, 1H), 3.45 (m, 1H), 2.81 (t, *J* = 9.40 Hz, 2H), 2.63 (t, *J*= 9,25 Hz, 2H), 2.25 (s, 3 H), 1.73-1.21 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 209.87, 195.45, 180.30, 176.50, 142.24, 136.11, 126.20, 124.49, 99.81, 79.43, 66.97, 38.79, 31.00, 30.66, 30.03, 29.85, 28.80, 23.14, 21.26, 17.98. MS, m/z: 337 ($M+H^+$). HRMS calculated for $C_{13}H_{18}O_3$: 336.2301; found: 336.2306.

38 Acetic acid (E)-6-benzoylamino-2-methyl-2-(3-oxo-butyl)-hex-4-enyl ester

^{1}H NMR ($CDCl_3$) δ 8.02-7.99 (m, 2 H), 7.55-7.44 (m, 3 H), 6.05-5.97 (m, 1 H), 5.43 (d, *J* = 10.31 Hz, 0.2 H, *cis* isomer), 5.30 (d, *J* = 10.77 Hz, 1.8 H, *trans* isomer), 5.20-5.14 (m, 1 H), 3.83 (dd, *J* = 14.63, 9.88 Hz, 1H), 4.27 (dd, *J* = 14.64, 7.92 Hz, 1 H), 2.60 (m, 2 H), 2.20 (s, 3 H), 2.10 (s, 3 H), 1.67 (m, 2H), 1.44 (m, 2H) 0.98 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.64, 171.24, 163.99, 142.70, 136.43, 131.40, 128.39, 128.23, 117.41, 80.55, 68.88, 66.88, 60.58, 41.07, 32.11, 29.99, 27.13, 21.00, 16.73. MS, m/z: 346 ($M+H^+$).

Preparation and description of the precursors

12 3-Butyl-cyclobut-2-enone

3-Butyl-cyclobut-2-enone was prepared from 3-Butyl-4,4-dichloro-cyclobut-2-enone.

Preparation of 3-Butyl-4,4-dichloro-cyclobut-2-enone:

To a solution of 1-hexyne (3.44 mL, 30 mmol, 1 eq) and activated zinc powder (5.9 g, 90 mmol, 3 eq) in 110 mL of dey Et_2O, under N2, was added over 30 min a solution containing trichloroacetyl chloride (8.1 mL, 72 mmol, 2.4eq) and $POCl_3$ (6.4 mL, 69 mmol, 2.3 eq) in 60 mL of dry Et_2O. The mixture was stirred at room temperature for 3h30. The solution was decanted and the etherated phase separated. Zinc was washed twice with Et_2O. The combined organic phases were washed with cold ice, diluted $NaHCO_3$, brine, then dried over $MgSO_4$, filtered and concentrated. The crude brown oil (5.6g, 97%) was used in the next step without any further purification.

^{1}H NMR ($CDCl_3$) δ 6.26 (t, *J* = 1.6 Hz, 1 H), 3.57 (q, *J* = 7.0 Hz, 2 H), 2.75 (td, *J* = 7.6, 1.5 Hz, 2 H), 1.82-1.74 (m, 2 H), 1.56-1.47 (m, 2 H), 1.26 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 186.26, 179.48, 135.69, 91.97, 27.64, 26.06, 22.41, 13.67. MS, m/z: 194 ($M+H^+$).

Preparation of 3-Butyl-cyclobut-2-enone:

To a solution of TMEDA (4.5 mL, 29.6 mmol, 5.7 eq), Zn(Ag) (2.1 g, 29.6 mmol, 5.7 eq, prepared according to J. Org. Chem., 1973, 3658-3660) in 26 mL of EtOH under N2 at 0°C, was added dropwise 1.7 mL of acetic acid and then 3-Butyl-4,4-dichloro-cyclobut-2-enone (1g, 5.2 mmol, 1 eq) in 7.3 mL of dry Et2O. The mixture was stirred at 0°C for 15 min the at room temperature. After 6 hours, the mixture was filtered through celite. 150 mL of Et2O : pentane 1:1 was passed through. The combined organic phases were washed with 50 mL of 1N aqueuous HCl, 50 mL of water; 80 mL of saturated NaHCO3, 50 mL of brine, dried over MgSO4, filtered and concentrated at 0°C under vacuum. 580 mg (90%) of a

yellow oil was obtained.

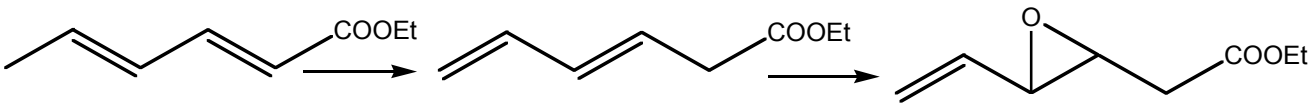
^{1}H NMR ($CDCl_3$) δ 5.89 (s, 1 H), 3.16 (s, 2 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 1.68-1.56 (m, 2 H), 1.47-1.38 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 186.97, 180.36, 133.14, 49.72, 30.83, 27.23, 21.42, 12.75. MS, m/z: 125 ($M+H^+$).

13 Dithiocarbonic acid (1-butyl-3-oxo-cyclobutyl) ester ethyl ester

To a solution of 12 (100 mg, 0.81 mmol, 1 eq) in 6 mL of anhydrous DCM at 0°C was added trifluoroacetic acid (602 μL, 8.1 mmol, 10 eq) and ethyl xanthic acid potassium salt (658 mg, 4.1 mmol, 5 eq). The solution was strirred at 0°C for 20 hours. The resulting solution was partitionned between Et2O and water. The organic phase was washed with brine, dried over MgSO4, filtered and concentrated in vacuo. The residue was chromatographed (Petroleum Ether : Diethyl Ether 95:5 to 90:10). 162 mg (81%) of a yellow oil was isolated.

^{1}H NMR ($CDCl_3$) δ 4.65 (q, *J* = 14.3 Hz, 2 H), 3.39-3.20 (m, 4 H), 2.11 (m, 2 H), 1.43-1.33 (m, 7 H), 0.92 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 211.78, 203.80, 69.62, 59.66, 45.39, 38.57, 28.35, 22.67, 14.02, 13.83. MS, m/z: 247 ($M+H^+$).

14 (3-Vinyl-oxiranyl)-acetic acid ethyl ester



A **B** **14**

Compound **14** was prepared in two steps starting from ethyl sorbate **A**. The latter was isomerised into **B** according to the procedure described in *J. Am. Chem. Soc*. **1996**, 10971. The epoxidation was done as described below:

To a solution of **B** (300 mg, 2.14mmol, 1 eq) in 20 mL of dichloromethane at 0°C was added solid Na_2CO_3 (915 mg, 8.6 mmol, 4 eq) and peracetic acid 32 % WT in acetic acid pretreated with a catalytic amount of sodium acetate. The solution was stirred at room temperature for 18 hours. The mixture was washed twice with Na_2CO_3 saturated and once with brine, dried over $MgSO_4$, filtered and evaporated. The residue was chromatographed (Petroleum Ether : Diethyl Ether 95:5 to 85:15) yielding 44 mg (15%) of **14**.

^{1}H NMR ($CDCl_3$) δ 5.48-5.63 (m, 2 H), 5.31 (d, *J* = 9.7 Hz, 1 H), 4.18 (q, *J* = 7.0 Hz, 2 H), 3.20 (t, *J* = 6.9 Hz, 2 H), 2.65-2.54 (m, 2 H), 1.27 (t, *J* = 7.0 Hz, 3 H) ; ^{13}C NMR ($CDCl_3$) δ 170.21, 134.80, 119.97, 60.97, 58.35, 55.73, 37.65, 14.21. MS, m/z: 157 ($M+H^+$).

15 1,3,3-Trimethyl-5-methylene-7-oxa-bicyclo[4.1.0]heptane

Compound **15** was prepared in two steps starting from isophorone. The epoxidation was described in *Eur. J. Org. Chem.* **2000**, 1905. The product was transformed into **15** using a Wittig reaction as described in *Synthesis* **1980**, 872.

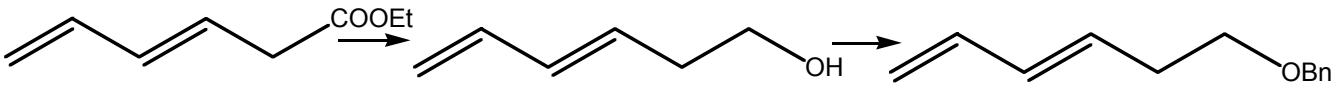
20 Acetic acid 2-ethoxythiocarbonylsulfanyl-2-methyl-5-oxo-hexyl ester

To a deoxygenated solution of dithiocarbonic acid ethyl ester (2-oxo-propyl) ester (prepared from chloroacetone (2.7 mL, 33.5 mmol, 1 eq) and ethylxanthic acid potassium salt (5.9 g, 36.9 mmol, 1.1 eq) in 40 mL of acetone) and methallyle acetate (228 mg, 2 mmol, 1 eq) in 6 mL of 1,2-dichloroethane was added dilauroyl peroxide (DLP) (5% each 1.5 hour) until the reaction was finished (15%). The reaction mixture was concentrated in vacuo and purified by flash chromatography (Petroleum Ether : Diethyl Ether 75:25 to 50:50) to afford 20 as a yellow oil (348mg, 60%).

^{1}H NMR ($CDCl_3$) δ 4.65 (q, *J* = 7.1 Hz, 2 H), 4.40 (d, *J* = 11.3 Hz, 1 H), 4.31 (d, *J* = 11.3 Hz, 1 H), 2.60

(m, 2 H), 2.22 (ddd, *J* = 15.05, 10.28, 5.49 Hz, 1 H), 2.17 (s, 3 H), 2.08 (s, 3 H), 1.95 (ddd, *J* = 14.89, 10.53, 5.48 Hz, 1 H), 1.46 (t, *J* = 7.18 Hz, 3H), 1.36 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 221.64, 207.26, 170.61, 70.12, 68.54, 56.27, 30.16, 29.95, 22.30, 20.87, 13.70. MS, m/z: 310 ($M+NH_4^+$).

21 2-(2-Benzyloxy-ethyl)-3-vinyl-oxirane



B **C** **21**

B was reduced using $LiAlH_4$ as described in *J. Am. Chem. Soc.***1996**, 10971 to give C, which was then protected using the method described in *Org. Lett.* **2003**, 1923 to yield **21**.

24 5-[(S)-4-(1-Ethoxythiocarbonylsulfanyl-1-methyl-ethyl)-cyclohex-1-enyl]-3-oxo-pentanoic acid ethyl ester

To a deoxygenated solution of 4-Ethoxythiocarbonylsulfanyl-3-oxo-butyric acid ethyl ester (1g, 4mmol, 1 eq) and (-)-β-pinene (1.09g, 8 mmol, 2 eq) in 12 mL of 1,2-dichloroethane was added dilauroyl peroxide (DLP) (5% each 1.5 hour) until the reaction was finished (15%). The reaction mixture was concentrated in vacuo and purified by flash chromatography (Petroleum Ether : Diethyl Ether 100:0 to 85:15) to afford **24** as a yellow oil (1.23g, 80%).

^{1}H NMR ($CDCl_3$) δ 5.37 (d, *J* = 3.5 Hz, 1 H), 4.66 (q, *J* = 7.1 Hz, 2 H), 4.18 (q, *J* = 7.1 Hz, 2 H), 3.42 (s, 2 H), 2.63 (dt, *J* = 7.26, 1.13 Hz, 2 H), 2.44-1.80 (m, 9 H), 1.46 (s, 6 H), 1.43 (t, *J* = 7.14 Hz, 3 H), 1.26 (t, *J* = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 214.17, 202.32, 167.08, 135.76, 120.74, 69.25, 61.27, 58.94, 49.20, 42.61, 41.16, 30.60, 29.50, 26.96, 25.06, 24.70, 24.46, 14.02, 13.68. MS, m/z: 403 ($M+NH_4^+$).

27 2,2-Dimethyl-propionic acid 4-(4-bromo-phenyl)-1-ethoxythiocarbonylsulfanyl-4-oxo-butyl ester

To a deoxygenated solution of dithiocarbonic acid ethyl ester (2-oxo-2-phenyl-ethyl) ester (2 g, 6.3 mmol, 1 eq) and vinyl pivalate (1.9 mL, 12.6 mmol, 2 eq) in 6 mL of 1,2-dichloroethane was added dilauroyl peroxide (DLP) (5% each 1.5 hour) until the reaction was finished (30%). The reaction mixture was concentrated in vacuo and purified by flash chromatography (Petroleum Ether : Diethyl Ether 100:0 to 85:15) to afford **27** as a yellow oil (2.02g, 72%).

^{1}H NMR ($CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 6.70 (t, *J* = 6.5 Hz, 1 H), 4.63 (q, *J* = 7.1 Hz, 2 H), 3.42 (td, *J* = 7.1, 2.8 Hz, 2 H), 2.45-2.36 (m, 2 H), 1.41 (t, *J* = 7.13 Hz, 3 H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 210.04, 196.87, 176.77, 135.28, 132.03, 129.57, 128.51, 80.27, 70.30, 38.93, 34.20, 28.53, 27.02, 13.72. MS, m/z: 446-448.

31 2,2-Dimethyl-propionic acid (E)-1-[3-(4-bromo-phenyl)-3-oxo-propyl]-5-hydroxy-pent-3-enyl ester

To a deoxygenated solution of dithiocarbonic acid (1-acetylamino-2,2,2-trifluoro-ethyl) ester ethyl ester (1 g, 3.7 mmol, 1 eq) and 1,3-dioxol-2-one (955 mg, 11.1 mmol, 3 eq) in 7.5 mL of 1,2-dichloroethane was added dilauroyl peroxide (DLP) (5% each 1.5 hour) until the reaction was finished (25%). The reaction mixture was concentrated in vacuo and purified by flash chromatography (Petroleum Ether : Diethyl Ether 60:40 to 40:60) to afford **27** as two diastereomers (948 mg, 1:1, 74%).

First diastereomer: yellow oil

^{1}H NMR ($CDCl_3$) δ 7.38 (d, *J* = 10.0 Hz, 1 H), 6.04 (d, *J* = 5.3 Hz, 1H), 5.17 (qd, *J* = 10.0, 7.6 Hz, 1H), 5.12 (d, *J* = 5.3 Hz, 1 H), 4.69 (q, *J* =7.0 Hz, 2 H), 2.16 (s, 3 H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 205.7, 171.9, 152.9, 123.2, 83.5, 77.7, 71.5, 51.2, 22.6, 13.6. MS, m/z: 348 ($M+H^+$).

Second diastereomer : yellowish cristals

^{1}H NMR ($CDCl_3$) δ 6.35 (d, *J* = 5.3 Hz, 1 H), 6.06 (d, *J* = 10.0 Hz, 1H), 5.19 (qdd, *J* = 10.0, 7.6, 5.3 Hz, 1H), 4.85 (dd, *J* = 5.3, 5.3 Hz, 1 H), 4.72 (q, *J* =7.0 Hz, 2 H), 2.13 (s, 3 H), 1.48 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 208.7, 173.7, 153.7, 125.0, 85.6, 77.3, 72.7, 52.9, 22.4, 13.9. MS, m/z: 348 ($M+H^+$).

35 1-Ethynyl-7-oxa-bicyclo[4.1.0]heptane

Compound 35 was prepared according to the procedure described by Piotti and Halper in *J. Org. Chem.* **1997**, 8484.