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 (CDCl$_3$: 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,
9 8-Hydroxy-4,4-dimethyl-oct-6-en-2-one

\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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, 3 H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 209.35, 132.16, 128.32, 63.71, 53.16, 44.50, 33.66, 31.70, 27.27, 23.11, 14.10. MS, m/z: 153 (M+H\(^+\)-H\(_2\)O).

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

\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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, 3 H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 5.77-5.64 (m, 2 H), 4.32 (d, \(J = 11.4\) Hz, 0.5 H, cis isomer), 4.13 (d, \(J = 15.1\)s 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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
1H NMR (CDCl₃) 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, 3 H), 1.53-1.33 (m, 4 H), 1.11 (s, 3 H), 0.98 (s, 3 H), 0.81 (t, J = 6.82 Hz, 3 H); 13C NMR (CDCl₃) 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⁺-H₂O).

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

1H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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

1H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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

1H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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-{(4R,5R)-5-(4-hydroxy-but-2-enyl)-2-oxo-[1,3]dioxolan-4-yl}-benzamide

¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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

¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₃H₁₈O₃: 336.2301; found: 336.2306.

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

¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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
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 dry Et₂O, under N₂, was added over 30 min a solution containing trichloroacetyl chloride (8.1 mL, 72 mmol, 2.4 eq) and POCl₃ (6.4 mL, 69 mmol, 2.3 eq) in 60 mL of dry Et₂O. The mixture was stirred at room temperature for 3h30. The solution was decanted and the etherated phase separated. Zinc was washed twice with Et₂O. The combined organic phases were washed with cold ice, diluted NaHCO₃, brine, then dried over MgSO₄, filtered and concentrated. The crude brown oil (5.6g, 97%) was used in the next step without any further purification.

¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 then 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 \(\mu\)L, 8.1 mmol, 10 eq) and ethyl xanthic acid potassium salt (658 mg, 4.1 mmol, 5 eq). The solution was stirred at 0°C for 20 hours. The resulting solution was partitionned between Et\(_2\)O and water. The organic phase was washed with brine, dried over MgSO\(_4\), 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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

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, 2.14 mmol, 1 eq) in 20 mL of dichloromethane at 0°C was added solid Na₂CO₃ (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 Na₂CO₃ saturated and once with brine, dried over MgSO₄, filtered and evaporated. The residue was chromatographed (Petroleum Ether : Diethyl Ether 95:5 to 85:15) yielding 44 mg (15%) of 14.

¹H NMR (CDCl₃) 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) ; ¹³C NMR (CDCl₃) 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 dithiocarboxonic 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%).

¹H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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+NH₄⁺).

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

B was reduced using LiAlH₄ 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%).

1H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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+NH₄⁺).

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%).

1H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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 ethyl ester (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

1H NMR (CDCl₃) 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); 13C NMR (CDCl₃) 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$_3$) $\delta$ 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$_3$) $\delta$ 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.