Supporting Information

on

Diastereoselective Aldol Reactions of Enolates Generated from Vicinally Substituted Trimethylsilylmethyl Cyclopropyl Ketones

by

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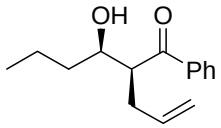
General

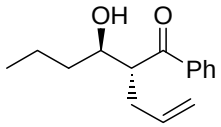
^{1}H and ^{13}C spectra were recorded in $CDCl_3$ solutions. The ^{1}H and ^{13}C spectra were referred, respectively, to TMS used as an internal standard and the central line for $CDCl_3$. Elemental (C, H, N) analyses were done on Perkin-Elmer 240-C automatic elemental analyzer. All the reactions were carried out using freshly distilled and dry solvents (CH_2Cl_2 and benzene) from solvent stills. Column chromatography was performed over silica gel (100-200 mesh) from Acme Chemicals using hexanes and ethyl acetate mixtures as eluent. The separation of isomers and their rigorous purification were achieved by radial chromatography using plates coated with silica gel PF_{254} (E-Merck). Except few compounds all the compounds could be separated by radial chromatography. Solvents were removed under reduced pressure on a rotovap. Organic extracts were dried with anhydrous Na_2SO_4.

Typical procedure for the $TiCl_4$-assisted reaction of the cyclopropane derivative 1a with benzaldehyde

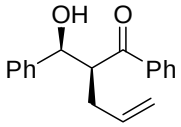
A freshly prepared solution of $TiCl_4$ (0.114 g, 0.75 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added to a solution of **1a** (0.116 g, 0.5 mmol) in anhydrous CH_2Cl_2 (2 mL). The contents were stirred for 30 min that resulted in a red color solution. A solution of PhCHO (0.080 g, 0.75 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added. Decoloration commenced as the reaction proceeded. It was stirred for 1 h and then quenched with a solution of cold 2% HCl (5 mL). Ether (20 mL) was added to it and the layers were separated. The organic layer was washed with cold 2% HCl solution (5 mL). The combined aqueous layers were extracted with ether (2x5 mL). The combined organic extracts were washed with water and brine, and dried. Removal of the solvents furnished the crude product that was purified by column chromatography (EtOAc/hexanes) to isolate 2-allyl-1,3-diphenyl-3-hydroxy-1-propanone, 0.1 g, 75%, colorless viscous oil. Separation of the *syn* and *anti* isomers was achieved by radial chromatography.



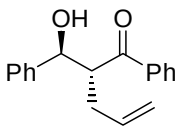
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (2H, m), 7.59-7.57 (1H, m), 7.50-7.46 (2H, m), 5.81-5.71 (1H, tdd, *J* = 17.1, 10.0, 7.1 Hz), 5.06-5.00 (1H, qd, *J* = 16.8, 1.5 Hz), 4.93 (1H, d, *J* = 10.0 Hz), 3.98-3.94 (1H, m), 3.62-3.58 (1H, m), 2.65-2.52 (2H, m), 1.60-1.32 (4H, m), 0.91 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.4, 137.2, 135.9, 133.4, 128.7, 128.5, 116.8, 71.7, 50.6, 37.1, 31.8, 19.3, 13.9. Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found C, 77.46; H, 8.55.



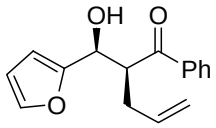
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (2H, m), 7.60-7.57 (1H, m), 7.51- 7.58 (2H, m), 5.81-5.71 (1H, tdd, *J* = 17.1, 10.0, 7.1 Hz), 5.11-5.05 (1H, qd, *J* = 17.1, 1.5 Hz), 5.00 (1H, d, *J* = 10.0 Hz), 3.91-3.87 (1H, m), 3.61-3,56 (1H, dt, *J* = 6.8, 4.6 Hz), 2.54 (2H, t, *J* = 7.1 Hz), 1.60-1.32 (4H, m), 0.89 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 137.5, 134.9, 133.5, 128.8, 128.3, 117.4, 72.3, 50.2, 37.9, 34.5, 19.2, 13.9. Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found C, 77.38; H, 8.50.



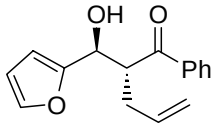
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (2H, d, *J* = 7.3 Hz), 7.55-7.52 (1H, m), 7.43-7.37 (4H, m), 7.31-7.28 (2H, m), 7.23-7.19 (1H, m), 5.65-5.54 (1H, tdd, *J* = 17.1, 9.9, 7.1 Hz), 5.10 (1H, d, *J* = 4.6 Hz), 4.94-4.89 (1H, dd, *J* = 17.1, 1.2 Hz), 4.86-4.83 (1H, dd, *J* = 10.0, 1.0 Hz), 3.88-3.83 (1H, td, *J* = 8.9, 4.5 Hz), 3.26 (1H, s), 2.68-2.61 (1H, m), 2.52-2.46 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.2, 141.7, 137.0, 135.4, 133.3, 128.6, 128.4, 128.3, 127.5, 126.2, 116.9, 73.7, 52.7, 31.7. Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found C, 81.08; H, 6.73.



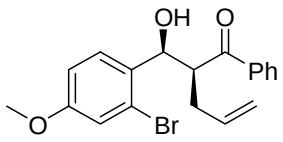
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.86 (2H, m), 7.56-7.52 (1H, m), 7.45-7.31 (6H, m), 7.27-7.23 (1H, m), 5.67-5.57 (1H, tdd, *J* = 17.1, 10.0, 7.1 Hz), 5.02 (1H, t, *J* = 6.1 Hz), 4.96 (1H, d, *J* = 17.1 Hz), 4.93 (1H, d, *J* = 10.0 Hz), 3.93-3.88 (1H, m), 3.18 (1H, d, *J* = 5.6 Hz), 2.47-2.40 (1H, m), 2.32-2.26 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.8, 142.4, 137.9, 134.4, 133.2, 128.6, 128.5, 128.3, 127.9, 126.4, 117.6, 75.5, 52.6, 34.7. Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found C, 81.04; H, 6.71.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.89 (2H, m), 7.58-7.53 (1H, m), 7.46-7.42 (2H, m), 7.28 (1H, t, *J* = 1.3 Hz), 6.25 (2H, s), 5.72-5.61 (1H, tdd, *J* = 17.1, 10.0, 7.1 Hz), 5.10 (1H, d, *J* = 5.4 Hz), 5.00-4.96 (1H, dd, *J* = 17.1, 1.6 Hz), 4.92-4.89 (1H, dd, *J* = 10.0, 0.9 Hz), 4.10-4.05 (1H, m), 3.09 (1H, broad s), 2.69-2.56 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.0, 154.0, 141.7, 136.7, 135.0, 134.0, 133.4, 128.6, 128.4, 117.1, 110.3, 107.4, 107.1, 68.4, 50.2, 32.4. Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found C, 74.90; H, 6.13.

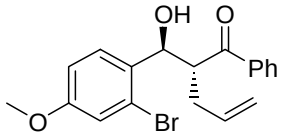


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.90 (2H, m), 7.60-7.55 (1H, m), 7.49-7.44 (2H, m), 7.33-7.32 (1H, dd, *J* = 1.7, 1.0 Hz), 6.29-6.27 (2H, m), 5.67-5.65 (1H, tdd, *J* =17.2, 10.0, 7.2 Hz), 5.04 (1H, t, *J* = 6.3 Hz), 5.04-4.96 (2H, m), 4.12-4.07 (1H, q, *J* = 6.7 Hz), 3.43 (1H, d, *J* = 7.3 Hz), 2.45-2.40 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.4, 154.8, 142.0, 137.2, 134.0, 133.4, 128.7, 128.4, 117.8, 110.3, 107.4, 68.9, 49.4, 34.3. Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found C, 74.87; H, 6.16.

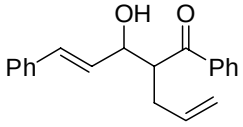


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.01 (2H, m), 7.62-7.58 (2H, m), 7.51-7.47 (2H, m), 7.11- 7.10 (1H, m), 6.92-6.89 (1H, m), 5.55-5.44 (1H, m), 5.32 (1H, s), 4.88-4.83 (1H, dd, *J* = 16.9, 1.5 Hz), 4.79 (1H, d, *J* = 10.2 Hz), 4.08-4.03 (1H, m), 3.95 (1H, broad s), 3.80 (3H,

s), 2.62-2.54 (1H, m), 2.32-2.56 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 159.4, 136.8, 135.3, 133.7, 131.7, 129.5, 128.7, 121.5, 118.0, 116.9, 113.3, 71.7, 55.5, 48.4, 30.4. Anal. Calcd. for $C_{19}H_{19}BrO_3$: C, 60.81; H, 5.10. Found C, 60.85; H, 5.01.



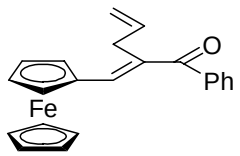
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (2H, d, *J* = 7.3 Hz), 7.60-7.57 (1H, m), 7.51-7.45 (2H, m), 7.36 (1H, d, *J* = 8.1 Hz), 7.12-7.10 (1H, m), 6.98 (1H, d, *J* = 1.7 Hz), 5.60-5.50 (1H, tdd, *J* = 17.1, 10.2, 7.1 Hz), 5.20 (1H, t, *J* = 3.3 Hz), 4.90-4.86 (1H, dd, *J* = 17.1, 1.5 Hz), 4.83-4.80 (1H, dd, *J* = 10.2, 1.0 Hz), 4.05-4.01 (1H, td, *J* = 9.6, 3.8 Hz), 3.87 (3H, s), 3.45 (1H, d, *J* = 3.7 Hz), 2.67-2.58 (1H, m), 2.34-2.27 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.6, 156.3, 137.0, 135.7, 133.4, 129.2, 128.8, 128.6, 128.5, 123.8, 121.7, 116.6, 113.9, 69.6, 55.6, 49.4, 30.7. Anal. Calcd. for $C_{19}H_{19}BrO_3$: C, 60.81; H, 5.10. Found C, 60.73; H, 4.97.



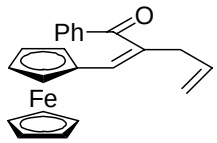
Characteristic ^{1}H signals for the *syn* isomer: δ 6.69-6.65 (1H, dd, *J* = 15.9, 0.7 Hz), 6.26-6.21 (1H, dd, *J* = 15.9, 6.4 Hz), 5.04-5.00 (1H, dd, *J* = 17.1, 1.5 Hz), 4.96-4.93 (1H, dd, *J* = 10.0, 1.0 Hz), 4.69 (1H, t, *J* = 5.0 Hz), 2.91 (1H, s)

Characteristic ^{1}H signals for the *anti* isomer: δ 6.65 (1H, d, *J* = 15.6 Hz), 6.26-6.20 (1H, dd, *J* = 15.9, 6.8 Hz), 5.09-5.04 (1H, dd, *J* = 16.8, 1.2 Hz), 5.01-4.98 (1H, dd, *J* = 10.0, 1.0 Hz), 4.64-4.60 (1H, broad m), 3.03 (1H, broad d, *J* = 4.8 Hz).

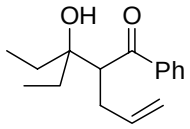
^{13}C NMR (100 MHz, $CDCl_3$) of the mixture: δ 204.5, 203.8, 137.5, 137.2, 136.5, 136.4, 135.5, 134.6, 133.4, 134.9, 131.4, 130.0, 129.1, 128.7, 128.5, 128.4, 127.8, 127.7, 126.5, 117.6, 117.1, 73.8, 72.8, 51.1, 51.0, 34.3, 32.1.



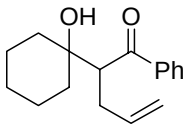
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (2H, m), 7.56-7.52 (1H, m), 7.49-7.45 (2H, m), 7.08 (1H, s), 6.07-5.97 (1H, m), 5.22-5.17(1H, dd, *J* = 17.3, 1.7 Hz), 5.25-5.12 (1H, dd, *J* = 10.0, 1.7 Hz), 4.50-4.49 (2H, t, *J* = 1.8 Hz), 4.43-4.42 (2H, t, *J* = 1.8 Hz), 4.16 (5H, s), 3.45-3.43 (2H, td, *J* = 5.6, 1.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 145.1, 139.5, 135.3, 134.5, 131.4, 129.2, 128.1, 115.3, 78.5, 70.9, 70.7, 69.4, 31.5. Anal. Calcd. for $C_{22}H_{20}FeO$: C, 74.17; H, 5.66. Found C, 74.10; H, 5.55.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.89 (2H, m), 7.50-7.44 (1H, m), 7.41-7.37 (2H, m), 6.42 (1H, s), 5.93-5.85 (1H, m), 5.15-5.08 (2H, m), 4.08 (5H, d, *J* = 1.0 Hz), 4.03 (4H, s), 3.11-3.09 (2H, dd, *J* = 6.8, 1.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.4, 137.3, 136.1, 134.7, 133.2, 129.4, 128.5, 128.0, 117.3, 80.3, 69.11, 69.08, 68.9, 40.1. Anal. Calcd. for $C_{22}H_{20}FeO$: C, 74.17; H, 5.66. Found C, 74.04; H, 5.52.

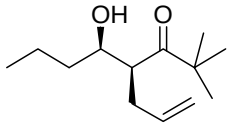


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (2H, d, *J* = 7.6 Hz), 7.62-7.58 (1H, m), 7.50-7.47 (2H, m), 5.70-5.60 (1H, tdd, *J* = 17.1, 10.0, 7.3 Hz), 5.04-5.00 (1H, dd, *J* = 17.1, 1.4 Hz), 4.89-4.86 (1H, dd, *J* = 10.0, 1.0 Hz), 3.74-3.70 (1H, dd, *J* = 10.1, 4.3 Hz), 3.67 (1H, s), 2.67-2.60 (1H, m), 2.56-2.50 (1H, m), 1.76-1.29 (4H, m), 0.90 (3H, t, *J* = 7.4 Hz), 0.80 (3H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.1, 138.6, 135.7, 133.6, 128.7, 128.4, 117.1, 76.6, 49.5, 32.8, 30.4, 26.8, 7.9, 7.7. Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found C, 77.95; H, 8.88.

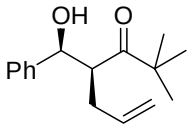


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (2H, m), 7.60-7.56 (1H, m), 7.49-7.46 (2H, m), 5.71-5.61 (1H, tdd, *J* = 16.9, 10.0, 7.2 Hz), 5.04-4.98 (1H, qd, *J* = 16.8, 1.6 Hz), 4.89-4.86 (1H, td, *J* = 10.0, 1.0 Hz), 3.65-3.62 (1H, dd, *J* = 9.0, 5.4 Hz), 3.44 (1H, s), 2.66-2.56 (2H,

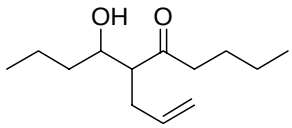
m), 1.89-1.16 (10 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 138.6, 135.9, 133.5, 128.7, 128.4, 117.0, 73.1, 53.2, 37.6, 35.3, 32.4, 25.7, 21.8, 21.7. Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found C, 78.92; H, 8.40.



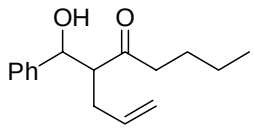
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72-5.62 (1H, tdd, *J* = 17.1, 10.0, 7.3 Hz), 5.01-4.97 (1H, dd, *J* = 17.1, 1.5 Hz), 4.94-4.91 (1H, dd, *J* = 10.0, 1.0 Hz), 3.68-3.65 (1H, m), 3.09-3.04 (1H, m), 2.85 (1H, s), 2.41-2.27 (2H, m), 1.56-1.40 (2H, m), 1.35-1.25 (2H, m), 1.09 (9H, s), 0.87 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.3, 136.4, 116.8, 71.2, 49.3, 44.7, 36.7, 30.9, 26.1, 19.3, 13.9. Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found C, 73.46; H, 11.29.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (5H, m), 5.65-5.54 (1H, m), 4.97-4.89 (3H, m), 3.39-3.35 (1H, td, *J* = 8.7, 4.4 Hz), 3.22 (1H, broad s), 2.51-2.43 (1H, m), 2.30-2.24 (1H, m), 1.02 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.4, 141.7, 136.0, 127.2, 127.5, 126.2, 116.9, 73.6, 52.3, 44.8, 31.8, 26.0. Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found C, 77.90; H, 8.86.



Characteristic ^{1}H signals for the *syn* isomer: δ 3.85-3.82 (1H, m), 0.92 (3H, t, *J* = 7.1 Hz). Characteristic ^{1}H signals for the *anti* isomer: δ 3.74-3.71 (1H, m), 0.95 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) of the mixture: δ 216.2, 215.1, 136.0, 135.0, 117.3, 116.9, 72.1, 71.1, 56.1, 56.0, 44.8, 44.2, 37.7, 36.6, 33.8, 31.1, 25.1, 25.0, 22.2, 19.2, 19.0, 13.9, 13.8.



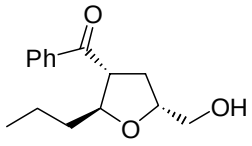
Characteristic ^{1}H signals for the *syn* isomer: δ 4.88 (1H, d, *J* = 5.8 Hz), 3.03 (1H, s), 0.82 (3H, t, *J* = 7.3 Hz).

Characteristic ^{1}H signals for the *anti* isomer: δ 4.80 (1H, t, *J* = 6.2 Hz), 3.15 (1H, d, *J* = 5.6 Hz), 0.86 (3H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) of the mixture: δ 215.4, 214.4, 142.3, 141.8, 135.5, 134.5, 128.3, 127.7, 126.2, 117.5, 117.0, 75.2, 73.8, 58.6, 57.9, 45.2, 44.7, 34.0, 31.9, 24.8, 22.0, 13.8, 13.7.

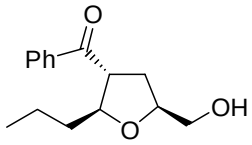
Conversion of *syn*-2-allyl-1-phenyl-3-hydroxy-1-hexanone into tetrahydrofuranylmethanol derivatives

To a stirred solution of *syn*-2-allyl-1-phenyl-3-hydroxy-1-hexanone (0.05 g, 0.22 mmol) in anhydrous benzene (2 mL), *m*-CPBA (0.095 g, 0.33 mmol, 60%) was added in portions at 0-5 ºC. The reaction mixture was stirred at the same temperature for 3 h and then warmed to room temperature. After stirring for 20 h at room temperature, the reaction mixture was quenched with saturated aqueous Na_2SO_3 solution (5 mL). Et_2O (15 mL) was added and the layers were separated. The organic solution was washed with saturated aq $NaHCO_3$ (2 x 5mL). The combined aqueous washings were extracted with Et_2O (2 x5 mL) and the combined organic extracts were washed with brine, dried, and concentrated to obtain the crude product. This was purified by silica gel column chromatography (EtOAc/hexanes) to furnish a mixture of the corresponding tetrahydrofuranylmethanol derivatives, 0.038 g, 71%. Separation of the diastereomers was achieved by radial chromatography.

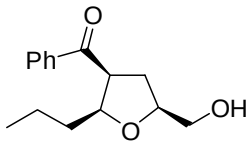


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (2H, m), 7.61-7.58 (1H, m), 7.51-7.47 (2H, m), 4.39-4.34 (1H, m), 4.32-4.26 (1H, dq, *J* = 7.6, 3.4 Hz), 3.79-3.73 (1H, dt, *J* = 8.6, 6.8 Hz), 3.71-3.67 (1H, dd, *J* = 11.7, 3.3 Hz), 3.66-3.61 (1H, dd, *J* = 11.7, 6.1 Hz), 2.41-2.34 (1H, ddd, *J* = 12.4, 8.6, 7.1 Hz), 2.08-2.00 (1H, td, *J* = 12.7, 8.2 Hz), 1.68-1.58 (1H, m), 1.56-1.42 (2H, m), 1.36-1.28 (1H, m), 0.90 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9,

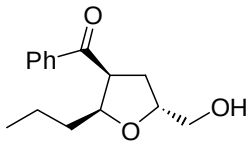
136.6, 133.4, 128.8, 128.4, 81.2, 78.9, 64.6, 51.9, 37.0, 33.0, 29.7, 19.4, 14.0. Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found C, 72.38; H, 7.98.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (2H, m), 7.60-7.57 (1H, m), 7.51-7.47 (2H, m), 4.32-4.27 (1H, dt, *J* = 7.6, 4.6 Hz), 4.22-4.16 (1H, m), 3.83-3.80 (1H, dd, *J* = 11.7, 3.0 Hz), 3.69-3.63 (1H, dt, *J* = 9.8, 7.3 Hz), 3.57-3.53 (1H, dd, *J* = 11.8, 4.5 Hz), 2.27-2.20 (1H, ddd, *J* = 12.4, 10.0, 7.3 Hz), 2.19-2.12 (1H, td, *J* = 12.4, 7.3 Hz), 1.68-1.30 (4H, m), 0.90 (3H, t, *J* = 7.13 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.4, 136.7, 133.4, 128.8, 128.4, 82.1, 78.8, 64.3, 51.6, 37.2, 33.1, 19.4, 14.1. Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found C, 72.44; H, 8.03.

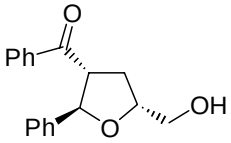


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (2H, m), 7.62-7.58 (1H, m), 7.51-7.48 (2H, m), 4.30-4.25 (1H, m), 4.23-4.17 (1H, q, *J* = 7.6 Hz), 4.21-4.14 (1H, m), 3.92-3.89 (1H, dd, *J* = 11.6, 6.6 Hz), 3.72-3.67 (1H, dd, *J* = 11.7, 4.9 Hz), 2.65 (1H, broad s), 2.41-2.34 (1H, ddd, *J* = 13.0, 8.8, 7.1 Hz), 2.15-2.08 (1H, td, *J* = 13.0, 7.3 Hz), 1.49-1.07 (4H, m), 0.77 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 137.5, 133.5, 128.9, 128.3, 81.1, 79.2, 64.8, 49.1, 34.2, 30.1, 19.8, 13.8. Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found C, 72.59; H, 8.06.

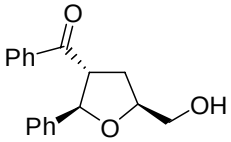


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (2H, d, *J* = 8.3 Hz), 7.61-7.57 (1H, m), 7.49 (2H, t, *J* = 7.7 Hz), 4.49-4.44 (1H, m), 4.41-4.35 (1H, m), 4.22-4.16 (1H, q, *J* = 7.5 Hz), 3.77-3.73 (1H, dd, *J* = 11.5, 2.9 Hz), 3.59-3.55 (1H, dd, *J* = 11.5, 5.5 Hz), 2.68-2.61 (1H, m), 1.97 (1H, broad s), 1.95-1.88 (1H, ddd, *J* = 13.0, 8.3, 5.4 Hz), 1.49-1.15 (3H, m), 1.01-0.93 (1H, m), 0.78 (3H, t, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 137.4, 133.3, 128.8, 128.2,

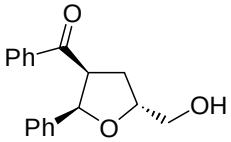
80.8, 77.7, 65.3, 49.9, 33.1, 29.4, 19.4, 13.8. Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found C, 72.40; H, 7.96.



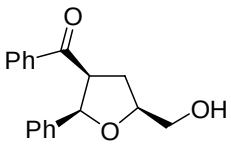
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.78 (2H, m), 7.55-7.51 (1H, m), 7.41-7.23 (7H, m), 5.42 (1H, d, *J* = 7.8 Hz), 4.60-4.54 (1H, m), 4.10-4.03 (1H, td, *J* = 9.8, 8.2 Hz), 3.80-3.76 (1H, dd, *J* = 11.8, 3.3 Hz), 3.74-3.70 (1H, dd, *J* = 11.7, 6.1 Hz), 2.54-2.47 (1H, ddd, *J* = 12.6, 8.3, 6.7 Hz), 2.25-2.17 (1H, ddd, *J* = 12.6, 9.8, 8.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 141.1, 137.0, 133.4, 128.63, 128.56, 128.4, 127.9, 125.8, 82.7, 80.3, 64.7, 55.5, 33.8. Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found C, 76.42; H, 6.31.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.78 (2H, m), 7.55-7.50 (1H, m), 7.44-7.24 (7H, m), 5.30 (1H, d, *J* = 7.6 Hz), 4.38-4.32 (1H, m), 4.07-3.92 (2H, m), 3.74-3.70 (1H, dd, *J* = 11.8, 4.8 Hz), 2.44-2.29 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 140.6, 136.4, 133.4, 128.61, 128.56, 128.5, 128.1, 126.2, 83.7, 79.4, 64.5, 54.7, 33.4. Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found C, 76.45; H, 6.33.

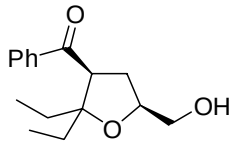


Characteristic ^{1}H signals: δ 5.47 (1H, d, *J* = 7.3 Hz), 4.86-4.80 (1H, m), 3.85-3.81 (1H, dd, *J* = 11.7, 3.2 Hz), 3.69-3.65 (1H, dd, *J* = 11.6, 5.8 Hz), 2.71-2.65 (1H, ddd, *J* = 13.0, 7.8, 4.9 Hz), 2.13-2.06 (1H, ddd, *J* = 13.0, 7.1, 6.1 Hz).

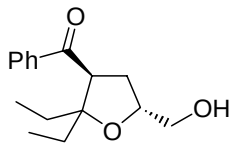


Characteristic ^{1}H signals: δ 5.29 (1H, d, *J* = 8.1 Hz), 4.36-4.30 (1H, m), 4.10-4.07 (1H, dd, *J* = 11.9, 2.5 Hz), 3.94-3.90 (1H, dd, *J* = 11.7, 4.9 Hz), 2.64-2.57 (1H, ddd, *J* = 13.0, 8.6, 6.1 Hz), 2.29-2.22 (1H, td, *J* = 13.0, 7.7 Hz).

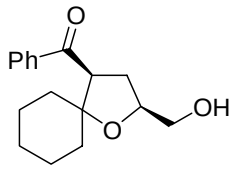
^{13}C NMR (100 MHz, $CDCl_3$) of the mixture: δ 200.4, 199.1, 138.3, 137.5, 132.7, 132.6, 128.2, 128.12, 128.07, 128.04, 127.9, 127.8, 127.7, 126.8, 126.4, 83.5, 83.3, 80.2, 79.6, 65.3, 64.3, 51.5, 51.1, 30.5, 30.1.



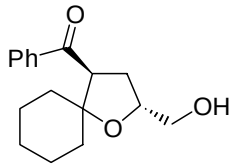
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.90 (2H, m), 7.59-7.57 (1H, m), 7.50-46 (2H, m), 4.25-4.19 (1H, m), 4.10 (1H, t, *J* = 7.7 Hz), 3.88-3.85 (1H, dd, *J* = 11.6, 2.8 Hz), 3.70-3.66 (1H, dd, *J* = 11.5, 4.9 Hz), 2.46-2.39 (1H, m), 2.20-2.13 (1H, td, *J* = 12.9, 7.4 Hz), 1.80-1.71 (1H, sextet, *J* = 7.3 Hz), 1.72 (1H, broad s), 1.59-1.46 (2H, m), 1.35-1.26 (1H, sextet, *J* = 7.3 Hz), 1.00 (3H, t, *J* = 7.3 Hz), 0.73 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 138.2, 133.2, 128.7, 128.2, 88.1, 77.9, 65.0, 50.9, 31.5, 28.4, 27.9, 8.24, 8.18. Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found C, 73.15; H, 8.33.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.88 (2H, m), 7.58-7.55 (1H, m), 7.49-7.45 (2H, m), 4.33-4.28 (1H, m), 4.07-4.03 (1H, dd, *J* = 9.0, 6.8 Hz), 3.80-3.77 (1H, dd, *J* = 11.5, 3.2 Hz), 3.58-3.54 (1H, dd, *J* = 11.5, 5.0 Hz), 2.62-2.55 (1H, td, *J* = 12.8, 7.3 Hz), 2.08 (1H, broad s), 2.04-1.97 (1H, ddd, *J* = 12.7, 8.8, 6.8 Hz), 1.82-1.73 (1H, sextet, *J* = 7.3 Hz), 1.71-1.62 (1H, sextet, *J* = 7.3 Hz), 1.51-1.42 (1H, sextet, *J* = 7.3 Hz), 1.23-1.14 (1H, sextet, *J* = 7.3 Hz), 0.97 (3H, t, *J* = 7.3 Hz), 0.77 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 138.3, 133.0, 128.7, 128.0, 87.8, 77.1, 65.2, 51.2, 31.5, 29.0, 26.7, 8.1, 7.7. Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found C, 73.11; H, 8.30.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (2H, m), 7.60-7.57 (1H, m), 7.51-7.47 (2H, m), 4.25-4.19 (1H, m), 3.97-3.93 (1H, dd, *J* = 7.8, 7.1 Hz), 3.91-3.88 (1H, dd, *J* = 11.9, 2.9 Hz), 3.74-3.70 (1H, dd, *J* = 11.5, 4.9 Hz), 2.47-2.40 (1H ddd, *J* = 12.9, 8.5, 6.8 Hz), 2.20-2.13 (1H, td, *J* = 12.9, 7.5 Hz), 1.92- 1.87 (1H, m), 1.69-1.26 (6H, m), 1.10-1.02 (2H, m), 0.90-0.82 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 137.9, 133.3, 128.7, 128.4, 84.5, 76.9, 64.9, 53.9, 36.7, 34.2, 30.8, 25.3, 22.7, 22.4. Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found C, 74.28; H, 7.97.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (2H, m), 7.59-7.57 (1H, m), 7.50-7.46 (2H, m), 4.38-4.32 (1H, m), 3.92-3.88 (1H, dd, *J* = 8.6, 7.0 Hz), 3.80-3.76 (1H, dd, *J* = 11.5, 3.2 Hz), 3.57-3.53 (1H, dd, *J* = 11.5, 4.9 Hz), 2.65-2.58 (1H, m), 2.20 (1H, broad s), 2.04-1.97 (1H, ddd, *J* = 12.7, 8.8, 6.6 Hz), 1.80-1.38 (8H, m), 1.04-0.88 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 137.9, 133.1, 128.6, 128.4, 84.4, 77.0, 65.2, 54.8, 38.8, 31.8, 30.9, 25.3, 23.1, 21.9. Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found C, 74.36; H, 7.99.