Supporting Information

Total Synthesis of (±)-Aplykurodinone-1: Traceless Stereochemical Guidance

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General Methods

Unless mentioned otherwise, all non-aqueous reactions were carried out in vacuum-flame-dried glasswares under a balloon-pressure of argon; reagents were commercially available and used as received; anhydrous solvents were purchased as the highest grade from Sigma-Aldrich, or passed through a solvent-purification system, or purified as following: THF was distilled from Nabenzophenone, CH₂Cl₂ was distilled from CaH₂. Reactions were monitored by thin-layer chromatography on Merck silica gel 60-F254 coated 0.25 mm plates. Flash column chromatography was performed using RediSep® pre-packed disposable silica gel columns (normal phase, 230-400 mesh) from Teledyne Isco. And prep-TLC was performed on Merck silica gel 60-F254 coated 0.50 or 1 mm plates. Yields were reported as isolated, spectroscopically pure compounds. NMR spectra were obtained on Bruker DRX 300, or 400 MHz, or Bruker DMX 500 MHz spectrometers. CDCl₃, dried by standing over K₂CO₃, was used and chemical shifts were referenced on residual solvent peaks (TMS δ = 0.0 for ¹H NMR and CHCl₃ δ = 77.00 for ¹³C NMR). Abbreviations for ¹H NMR: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or br = broad. IR spectra were obtained on a Perkin-Elmer Paragon 1000

FTIR spectrometer. And high resolution mass spectra were acquired from the Columbia University Mass Spectral Core facility on a JEOL HX110 spectrometer or from Memorial Sloan-Kettering Cancer Center on a Perkin-Elmer Sciex API 100 in ionspray mode.

Procedures

To a solution of diene **2** (688 mg, 4 mmol) in 80 mL of DME was added Methyl lithium (2.3 mL, 1.6 M in ether) dropwise over 5 min. The mixture was stirred at this temperature for 1 h, then cooled to -78°C . To this mixture was added enone **3** (308 mg, 2 mmol) in 80 mL of THF at -78°C by cannula over 10 min and the reaction was then warmed up to -50°C . The reaction mixture was stirred at -50°C for 2 h before being quenched with 20 mL saturated aqueous Na_2HPO_4 and warmed up to room temperature. The resulting mixture was extracted with DCM and treated with anhydrous MgSO_4 then concentrated to afford a yellow oil. The crude residue was redissolved in 50 mL of toluene and concentrated under vacuum to provide a yellow solid. To this solid in 100 mL of CHCl_3 was added 20 mL TFA. The reaction mixture was refluxed for 15 h before being quenched with 30 mL water. The mixture was washed with aqueous saturated NaHCO_3 , dried over anhydrous MgSO_4 , filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 4:1 to 3:1) afforded the desired product **4** (325 mg, 73%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 6.76 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 3H), 2.67-2.76 (m, 1H), 2.48-2.54 (m, 1H), 2.44 (d, *J* = 16.0 Hz, 1H), 2.41 (d, *J* = 16.0 Hz, 1H), 2.09-2.17 (m, 1H), 1.80-1.87 (m, 1H), 1.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 210.2, 196.7, 168.8, 142.4, 129.7, 65.9, 52.7, 47.0, 45.9, 36.5, 32.7, 23.6; IR (NaCl, cm⁻¹): 2958, 1751, 1727, 1685, 1244; HRMS (FAB+) calcd for C₁₂H₁₅O₄ (M+1): 223.0970, found 223.0971.

To a solution of enone **4** (1.068 g, 4.811 mmol) and 1, 2-ethanedithiol (0.44 mL, 5.292 mmol) in 10 mL AcOH was added p-TSA (548 mg, 2.887 mmol). The reaction mixture was stirred at room temperature for 12 h, then quenched with water. The mixture was extracted with DCM, washed with aqueous saturated NaHCO₃, dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 6:1) afforded the desired product **8** (1.159 g, 81%) as a white solid, m.p. 118-119 °C.

¹H NMR (400 MHz, CDCl₃): δ 6.06 (d, *J* = 10.0 Hz, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 3.71(s, 3H), 3.21-3.39 (m, 4H), 2.56-2.63 (m, 1H), 2.37-2.46 (m, 1H), 2.32 (d, *J* = 14.8 Hz, 1H), 2.27 (d, *J* = 14.8 Hz, 1H), 1.97-1.99 (m, 2H), 1.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 212.9, 170.2, 134.7, 119.7, 63.9, 60.8, 52.3, 47.6, 43.3, 40.3, 39.3, 35.9, 33.0, 23.8; IR (NaCl, cm⁻¹): 2952, 1751, 1729, 1243; HRMS (FAB+) calcd for C₁₄H₁₈O₃S₂ (M⁺): 298.0697, found 298.0711 .

To a solution of ketone **8** (5.830 g, 19.564 mmol) in 120 mL of DCM/MeOH (1:1) at -78 °C was added NaBH₄ in portions. The resulting mixture was stirred while gradually warming up to 0 °C over 4 h, and then quenched with H₂O, extracted with EtOAc, dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. Chromatography

of the residue (hexane/EA = 4:1 to 2:1) afforded the desired product **8'** (5.140 g, 88%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 6.13 (d, J = 10.0 Hz, 1H), 5.67 (d, J = 10.0 Hz, 1H), 4.70 (t, J = 8.4 Hz, 1H), 3.71 (s, 3H), 2.27-3.46 (m, 4H), 2.57 (d, J = 14.8 Hz, 1H), 2.32 (d, J = 14.8 Hz, 1H), 2.29-2.36 (m, 2H), 1.94-2.02 (m, 1H), 1.48-1.58 (m, 1H), 1.30-1.38 (m, 1H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.9, 136.2, 119.8, 75.1, 61.4, 58.1, 52.0, 47.4, 41.7, 40.6, 38.3, 31.3, 28.6, 27.7; IR (NaCl, cm^{-1}): 3476, 2953, 1721, 1248; HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{S}_2$ (M^+): 300.0854, found 300.0859.

To a solution of alcohol **8'** (5.140 g, 17.133 mmol) and DIPEA (17.9 mL, 102.798 mmol) in 50 mL of DCM at 0°C was added MOMCl (3.9 mL, 51.400 mmol) dropwise over 5 min. The mixture was stirred at 0°C for 15 min and at room temperature overnight. The reaction mixture was quenched with water, extracted with DCM, dried over anhydrous MgSO_4 , filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 6:1) afforded the desired product **9** (5.599 g, 95%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 6.10 (d, J = 10.0 Hz, 1H), 5.68 (d, J = 10.0 Hz, 1H), 4.76 (d, J = 6.4 Hz, 1H), 4.61-4.65 (m, 1H), 4.61-4.63 (d, J = 6.4 Hz, 1H), 3.68 (s, 3H), 3.27-3.44 (m, 4H), 3.35 (s, 3H), 2.45 (d, J = 14.8 Hz, 1H), 2.36 (m, 1H), 2.29 (d, J = 14.8 Hz, 1H), 2.05-2.07 (m, 1H), 1.54-1.60 (m, 1H), 1.30-1.38 (m, 1H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.0, 135.0, 121.1, 96.4, 80.7, 61.6, 58.1, 55.3, 51.9, 47.4, 41.9, 40.6, 38.2, 31.9, 28.5, 28.0; IR (NaCl, cm^{-1}): 2950, 1727, 1247, 1045; HRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_4\text{S}_2$ (M^+): 344.1116, found 344.1099.

To a solution of ester **9** (1.006 g, 2.924 mmol) in 20 mL of DCM at -78°C was added Dibal-H (11.7 mL, 1 M in toluene) dropwise over 10 min. The mixture was stirred for 4 h

then quenched carefully with 10 mL H₂O and warmed up to room temperature. To the mixture was added 20 mL 1M aqueous HCl. The mixture was extracted with DCM, washed with saturated aqueous NaHCO₃ solution, dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure to give pure desired product **9'** (5.599 g, quant.) as colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.12 (d, *J* = 10.0 Hz, 1H), 5.63 (d, *J* = 10.0 Hz, 1H), 4.65(d, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 1H), 4.00 (t, *J* = 8.4 Hz, 1H), 3.62-3.66 (br s, 2H), 3.25-3.45 (m, 4H), 3.35 (s, 3H), 2.46 (d, *J* = 14.8 Hz, 1H), 2.29-2.33 (m, 1H), 2.27-2.31 (d, *J* = 14.8 Hz, 1H), 1.97-2.06 (m, 1H), 1.83 (br s, 1H, OH), 1.48-1.58 (m, 1H), 1.24-1.27 (m, 1H), 1.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 136.2, 124.2, 96.1, 81.3, 65.0, 61.8, 55.4, 50.7, 48.5, 41.0, 40.8, 38.1, 31.9, 28.1, 26.5; IR (NaCl, cm⁻¹): 3465, 2954, 1040; HRMS (FAB+) calcd for C₁₅H₂₄O₃S₂ (M⁺): 316.1167, found 316.1180 .

To a solution of thioketal **9'** (200 mg, 0.633 mmol) in 7.5 mL of THF/MeOH/H₂O (2:2:1) was added Tl(NO₃)₃·3H₂O (309 mg, 0.696 mmol) in 3 mL MeOH dropwise. The mixture was stirred at room temperature for 1 h, then quenched with ice-water, extracted with EtOAc, washed with saturated aqueous NaHCO₃ solution, dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 1:1) afforded desired product **10** (144 mg, 95%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.02 (d, *J* = 10.0 Hz, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 4.68 (d, *J* = 6.8 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.17 (t, *J* = 6.3 Hz, 1H), 3.83-3.86 (d, *J* = 11.6 Hz, 1H), 3.79-3.82 (d, *J* = 11.6 Hz, 1H), 3.37 (s, 3H), 2.58-2.62 (d, *J* = 16.4 Hz, 1H), 2.29-2.33 (d, *J* = 16.4 Hz, 1H), 2.10-2.17 (m, 1H), 1.68-1.72 (m, 1H), 1.42-1.52 (m, 2H), 1.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 199.9, 149.9, 131.2, 96.2, 81.8, 64.3, 55.5, 53.4, 47.9, 42.0, 34.3, 28.7, 25.3; IR (NaCl, cm⁻¹): 3454, 2943, 1670, 1040; HRMS (FAB+) calcd for C₁₃H₂₁O₄ (M+1): 241.1440, found 241.1429 .

To a solution of alcohol **10** (186 mg, 0.775 mmol) in 5 mL DCM was added glyoxylic acid chloride tosylhydrazone (378 mg, 1.449 mmol) and N, N-dimethylaniline (0.18 mL, 1.418 mmol) at 0 °C. The dark green solution was stirred for 25 min prior to injection of triethylamine (0.54 mL, 3.875 mmol). The resulting orange suspension was stirred 10 min at 0 °C then for 1 h at room temperature. The mixture was concentrated in vacuo. Chromatography of the residue (hexane/EA = 2:1) afforded desired product **11** (210 mg, 88%) as a light yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 6.94 (d, *J* = 10.4 Hz, 1H), 6.19 (d, *J* = 10.4 Hz, 1H), 4.72 (s, 1H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 6.8 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.26 (d, *J* = 11.2 Hz, 1H), 4.11 (t, *J* = 8.4 Hz, 1H), 3.37 (s, 3H), 2.44 (d, *J* = 16.8 Hz, 1H), 2.35 (d, *J* = 16.8 Hz, 1H), 2.11-2.20 (m, 1H), 1.71-1.78 (m, 1H), 1.46-1.57 (m, 2H), 1.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 199.1, 166.2, 148.5, 131.3, 96.0, 81.0, 65.6, 55.6, 51.9, 47.9, 46.1, 41.9, 34.5, 28.9, 25.5; IR (NaCl, cm⁻¹): 2956, 2113, 1681, 1043; HRMS (FAB+) calcd for C₁₅H₂₁N₂O₅ (M+1): 309.1450, found 309.1468.

A solution of diazoester **11** (204 mg, 0.622 mmol) in 13 mL toluene was added slowly to a stirred refluxing solution of bis-(N-*t*-butylsalicylaldiminato) copper (II) catalyst (14 mg, 0.033 mmol) in 100 mL toluene over 4 h at a constant rate. The solution was held at reflux for 30 min after completion of addition, cooled, concentrated and purified by flash chromatography (Hexane/EA = 2:1 to 1:1) to give the desired product **5** (69 mg, 40%) as a yellow solid, m.p. 109-110 °C.

^1H NMR (400 MHz, CDCl_3): δ 4.69 (d, $J = 6.8$ Hz, 1H), 4.61 (d, $J = 6.8$ Hz, 1H), 4.53 (d, $J = 11.2$ Hz, 1H), 4.38 (d, $J = 11.2$ Hz, 1H), 4.09 (t, $J = 8.4$ Hz, 1H), 3.38 (s, 3H), 2.80 (t, $J = 8.0$ Hz, 1H), 2.20-2.30 (m, 4H), 2.14-2.18 (d, $J = 12.4$ Hz, 1H), 1.70-1.87 (m, 2H), 1.41-1.47 (m, 1H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 204.1, 167.3, 96.0, 78.9, 73.2, 55.7, 47.4, 46.6, 43.0, 34.1, 31.3, 27.4, 25.0, 24.4, 20.6; IR (NaCl, cm^{-1}): 2927, 1742, 1694, 1040; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_5$ ($M+1$): 281.1389, found 281.1371.

To a solution of ketone **5** (60 mg, 0.214 mmol) in 10 mL of DCM/MeOH (1:1) was added $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (90 mg, 0.235 mmol). The resulting mixture was cooled to -78°C . To the mixture was added NaBH_4 (20 mg, 0.429 mmol) in portion. The reaction mixture was stirred at this temperature for 40 min then quenched with H_2O , extracted with DCM , dried over anhydrous MgSO_4 , filtered and concentrated at reduced pressure. The residue was directly used in the next step without further purification. The major epimer **12'** (the more polar one) was obtained for analysis by chromatography (hexane/EA = 1:1 to 1:2).

^1H NMR (400 MHz, CDCl_3): δ 4.67 (d, $J = 6.8$ Hz, 1H), 4.59 (d, $J = 6.8$ Hz, 1H), 4.44 (m, 1H), 4.42 (d, $J = 11.2$ Hz, 1H), 4.23 (d, $J = 11.2$ Hz, 1H), 4.00 (t, $J = 8.4$ Hz, 1H), 3.36 (s, 3H), 2.33 (t, $J = 8.4$ Hz, 1H), 2.14-2.25 (m, 1H), 1.77-1.95 (m, 5H), 1.66-1.73 (m, 1H), 1.19-1.31 (m, 2H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.5, 96.0, 79.6, 73.4, 64.2, 55.6, 43.2, 41.9, 40.2, 32.1, 27.6, 25.9, 24.5, 18.9, 13.4; IR (NaCl, cm^{-1}): 3387, 2955, 1724, 1038; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_4$ ($M-1$): 265.1440, found 265.1451.

To a solution of alcohol **12'** (888 mg, 3.148 mmol) in 60 mL of toluene was added PPh_3 (1.650 g, 6.296 mmol), imidazole (642 mg, 9.444 mmol) and iodine (1.199 g, 4.722

mmol). The resulting mixture was heated to reflux for 1h then cooled to room temperature and concentrated. Chromatography of the residue (hexane/EA = 2:1) afforded both epimers of the desired product **12** as a thick yellow oil (980 mg, 78% from **5**).

The major epimer: ^1H NMR (400 MHz, CDCl_3): δ 4.83-4.89 (m, 1H), 4.66 (d, J = 6.8 Hz, 1H), 4.58 (d, J = 6.8 Hz, 1H), 4.36 (d, J = 11.2 Hz, 1H), 4.24 (d, J = 11.2 Hz, 1H), 3.97 (t, J = 8.4 Hz, 1H), 3.35 (s, 3H), 2.38 (t, J = 8.4 Hz, 1H), 2.17-2.24 (m, 1H), 1.95-2.09 (m, 5H), 1.83-1.87 (dd, J = 10.0, 8.0 Hz, 1H), 1.22-1.27 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.5, 96.0, 79.7, 73.2, 55.6, 43.9, 43.5, 41.6, 30.5, 27.9, 27.6, 25.9, 21.9, 20.1, 16.3; IR (NaCl, cm^{-1}): 2952, 1739, 1039; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{22}\text{IO}_4$ ($M+1$): 393.0563, found 393.0579.

To a solution of iodide **12** (1.250 g, 3.189 mmol) in 40 mL of THF/MeOH (3:1) at room temperature was added SmI_2 (63.8 mL, 0.1 M in THF) dropwise over 15 min. The resulting mixture was stirred for 1h, then quenched with water. The mixture was extracted with EtOAc, washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 3:1) afforded desired product **13** (721 mg, 85%) as a light yellow solid, m.p. 61-63 $^{\circ}\text{C}$.

^1H NMR (500 MHz, CDCl_3): δ 5.65-5.68 (m, 1H), 5.51-5.53 (d, J = 10.0 Hz, 1H), 4.61 (d, J = 7.0 Hz, 1H), 4.60 (d, J = 7.0 Hz, 1H), 4.27 (d, J = 11.5 Hz, 1H), 4.22 (m, 1H), 4.18 (d, J = 11.5 Hz, 1H), 3.36 (s, 3H), 2.86-2.90 (m, 2H), 2.19-2.25 (m, 2H), 1.94-2.00 (m, 2H), 1.85-1.90 (dd, J = 18.0, 5.5 Hz, 1H), 1.62-1.69 (m, 2H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 173.4, 128.5, 124.1, 96.0, 83.5, 70.1, 55.8, 46.1, 40.7, 35.8, 34.4,

34.3, 30.0, 27.3, 25.0; IR (NaCl, cm^{-1}): 2955, 2889, 1755, 1042; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{23}\text{O}_4$ (M+1): 267.1596, found 267.1581.

To a solution of compound **13** (82 mg, 0.308 mmol) in 5 mL THF was added 5 mL of aqueous HCl (1N). The mixture was heated at 55 °C for 17 h then cooled to room temperature. The mixture was diluted between H₂O and EtOAc and extracted with EtOAc. The combined organic phase was washed with saturated aqueous NaHCO₃ solution, dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 1:1) afforded the desired product **13'** (58 mg, 85%) as a white solid, m.p. 113-115 °C.

¹H NMR (400 MHz, CDCl₃): δ 5.66-5.70 (m, 1H), 5.57 (d, J = 6.0 Hz, 1H), 4.46 (dd, J = 8.8, 6.8 Hz), 4.29 (d, J = 9.2 Hz, 1H), 4.23 (d, J = 9.2 Hz, 1H), 2.84-2.92 (m, 2H), 2.41 (br s, 1H, OH), 2.15-2.25 (m, 2H), 1.83-2.01 (m, 3H), 1.55-1.64 (m, 1H), 1.21-1.27 (m, 1H), 1.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 174.2, 128.7, 124.3, 78.2, 70.8, 46.4, 41.1, 35.8, 34.7, 34.3, 29.5, 29.4, 25.1; IR (NaCl, cm^{-1}): 3417, 2957, 1732; HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3$ (M+1): 223.1334, found 223.1326.

To a solution of alcohol **13'** (58 mg, 0.261 mmol) in 5 mL DCM was added DMP (144 mg, 0.340 mmol). The mixture was stirred at room temperature for 1 h then diluted with 5 mL of DCM and washed with 3 mL of saturated aqueous Na₂SO₃ solution and 3 mL of saturated aqueous NaHCO₃ solution. The organic phase was dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 3:1 to 1:1) afforded the desired product **6** (58 mg, quant.) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 5.83-5.88 (m, 1H), 5.47-5.51 (m, 1H), 4.48 (d, $J = 13.2$ Hz, 1H), 4.24 (d, $J = 13.2$ Hz, 1H), 2.74-2.80 (dd, $J = 15.2, 5.6$ Hz, 1H), 2.52-2.66 (m, 2H), 2.34-2.42 (m, 2H), 2.01-2.22 (m, 3H), 1.60-1.70 (m, 1H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.7, 171.8, 127.4, 126.1, 66.2, 53.2, 39.4, 33.4, 33.3, 33.1, 32.5, 30.7, 24.3; IR (NaCl, cm^{-1}): 2960, 1755, 1726, 1139; HRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3$ ($M+1$): 221.1178, found 221.1183.

To a mixture of ketone **6** (56 mg, 0.255 mmol) and 3 mL water was added K_2CO_3 (70 mg, 0.509 mmol). The mixture was sonicated for 5 min to form a milky solution. The mixture was heated at 100°C for 30 min and then cooled to room temperature. To the mixture was added some dry ice and then 5 mL of DCM followed by NIS (114 mg, 0.509 mmol). The resulting mixture was stirring for 14 h then quenched with 3 mL of saturated aqueous Na_2SO_3 solution. The mixture was extracted with DCM, washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA= 3:1 to 1:1) afforded the desired product **15** (64 mg, 75%) as a white solid, m.p. 162°C (dec.).

^1H NMR (400 MHz, CDCl_3): δ 4.48-4.52 (dd, $J = 10.4, 8.0$ Hz, 1H), 4.07-4.14 (m, 1H), 3.18-3.26 (m, 1H), 2.63-2.71 (dd, $J = 17.6, 12.8$ Hz, 1H), 2.53-2.59 (dd, $J = 17.6, 9.6$ Hz), 2.28-2.48 (m, 2H), 2.15-2.21 (m, 2H), 1.78-1.91 (m, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 216.0, 174.0, 84.0, 55.0, 44.0, 41.7, 34.1, 34.0, 33.9, 31.5, 26.3, 22.6; IR (NaCl, cm^{-1}): 3445, 2954, 1782, 1739; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{16}\text{IO}_3$ ($M+1$): 335.0144, found 335.0152.

To a solution of crude acid **14** (2 mg, 0.010 mmol) in 0.4 mL of benzene/MeOH (1:1) was added 0.01 mL TMSCHN₂ (0.02 mmol, 2M in ether). The mixture was stirred at room temperature for 2 h. The mixture was concentrated under vacuo. Chromatography of the residue on preparative TLC (hexane/EA = 2:1) afforded desired product **14'** (1.7 mg, 77%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.62-5.67 (m, 1H), 5.55-5.59 (m, 1H), 3.68 (s, 3H), 2.99-3.03 (m, 1H), 2.46 (d, *J* = 7.6 Hz, 2H), 2.30-2.36 (m, 1H), 2.18-2.27 (m, 1H), 1.91 (t, *J* = 1.2 Hz, 1H), 1.80-1.86 (m, 3H), 1.70-1.75 (m, 1H), 1.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 217.3, 172.5, 127.3, 125.2, 58.0, 51.6, 39.2, 36.4, 34.3, 33.9, 32.2, 29.4, 27.8.

To a mixture of Raney-Ni (~40mg) and 0.2 mL EtOH was added iodide **15** (44 mg, 0.132 mmol) in 6 mL DCM dropwise. The resulting mixture was stirred at room temperature for 4 h then filtered through a pad of silica gel and washed with EtOAc. The filtrate was concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 3:1 to 2:1) afforded the desired product **16** (25 mg, 90%) as a white solid, m.p. 85-87 °C.

¹H NMR (400 MHz, CDCl₃): δ 4.34-4.40 (m, 1H), 3.00-3.04 (m, 1H), 2.61-2.68 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.53-2.60 (dd, *J* = 17.2, 9.2 Hz, 1H), 2.24-2.38 (m, 2H), 1.95-2.04 (m, 2H), 1.70-1.87 (m, 2H), 1.64-1.68 (m, 1H), 1.48-1.53 (m, 1H), 1.30 (s, 3H), 1.23-1.27 (m,

1H); ^{13}C NMR (100 MHz, CDCl_3): δ 217.6, 175.8, 77.2, 55.8, 37.8, 34.3, 33.8, 32.7, 32.5, 29.3, 26.9, 24.2; IR (NaCl, cm^{-1}): 2950, 1776, 1738; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$ (M+1): 209.1178, found 209.1180.

To a solution of Ketone **16** (82 mg, 0.394 mmol) and TEA (0.33 mL, 2.364 mmol) in 5 mL DCM at 0°C was added TMSOTf (0.21 mL, 1.183 mmol) dropwise. The mixture was stirred at 0°C for 1 h and then at room temperature for an additional 3 h. The reaction was quenched with saturated aqueous NaHCO_3 solution, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated at reduced pressure. The residue was dissolved in 10 mL CH_3CN and Pd(OAc)_2 (353 mg, 1.576 mmol) was added to the mixture. The reaction mixture was stirred at room temperature for 14 h then filtered through a silica gel pad and washed with EtOAc. The filtrate was concentrated and redissolved in 5 mL THF, and TBAF (1 mL, 1 M in THF) was added to this mixture. The mixture was stirred at room temperature for 1 h then quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated in vacuo. Chromatography of the residue (hexane/EA = 2:1 to 1:1) afforded the desired product **7** (62 mg, 76%) as a white solid (m.p. $141\text{--}142^\circ\text{C}$), as well as the recovered compound **16** (13 mg); the yield based on recovery of starting material is 90%.

^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, $J = 6.0$ Hz, 1H), 6.17 (d, $J = 6.0$ Hz, 1H), 4.67–4.71 (m, 1H), 3.26–3.34 (m, 1H), 2.81–2.88 (dd, $J = 18.4, 10.8$ Hz, 1H), 2.56–2.63 (dd, $J = 18.4, 8.4$ Hz, 1H), 2.09 (d, $J = 3.6$ Hz, 1H), 1.75–1.81 (m, 1H), 1.62–1.69 (m, 1H), 1.51–1.56 (m, 1H), 1.35–1.45 (m, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 208.9, 176.0, 170.8, 131.0, 77.1, 52.8, 43.8, 33.7, 31.8, 27.9, 27.7, 24.2; IR (NaCl, cm^{-1}): 2961, 1756, 1693, 1192; HRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ (M+1): 207.1021, found 207.1025.

To a solution of bromide **17** (94 mg, 0.336 mmol) in 8 mL ether at -78°C was added *t*-BuLi (0.45 mL, 0.672 mmol, 1.5 M in pentane) dropwise. The yellow solution was stirred at -78°C for 40 min and -30°C for an additional 25 min, then cooled to -78°C again. To the reaction solution at -78°C was added CuCN (33 mg, 0.370 mmol) in one portion. The resulting suspension was stirred at this temperature for 5 min, then at -30°C for 25 min to form a homogeneous solution. The mixture was cooled to -98°C . To the mixture was added a solution of enone **7** (23 mg, 0.112 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (0.043 mL, 0.336 mmol) in 2 mL THF at -30°C by cannula. The resulting orange solution was warmed up to -78°C over 2 h then quenched with a mixture of saturated aqueous NH_4Cl and saturated ammonia (9:1) and warmed up to room temperature. The resulting mixture was extracted with EtOAc, washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated in vacuo. Chromatography of the residue (hexane/EA = 5:1 to 4:1) afforded desired product **18** (30 mg, 66%) as a colorless oil, along with the diastereoisomer (3 mg, 7%); the total yield is 73%.

^1H NMR (400 MHz, CDCl_3): δ 5.24 (t, $J = 7.2$ Hz, 1H), 4.53 (dd, $J = 13.6, 6.0$ Hz, 1H), 3.62 (t, $J = 6.8$ Hz, 2H), 2.77-2.82 (dd, $J = 16.4, 4.0$ Hz, 1H), 2.63-2.70 (m, 2H), 2.57-2.61 (t, $J = 8.4$ Hz, 1H), 2.48-2.55 (dd, $J = 19.6, 9.2$ Hz, 1H), 2.38-2.45 (dd, $J = 19.6, 8.8$ Hz, 1H), 2.26-2.31 (q, $J = 6.8$ Hz, 2H), 2.02-2.10 (m, 1H), 1.96 (d, $J = 8.0$ Hz, 1H), 1.70-1.75 (m, 1H), 1.67 (s, 3H), 1.55-1.63 (m, 1H), 1.38-1.50 (m, 1H), 1.00 (s, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 217.7, 176.0, 134.1, 124.9, 77.9, 62.5, 55.0, 50.3, 41.5, 40.1, 33.4, 31.7, 30.2, 29.6, 25.8, 24.0, 22.8, 18.2, 16.8, -5.3; IR (NaCl, cm^{-1}): 2952, 2927, 1781, 1736; HRMS (FAB+) calcd for $\text{C}_{23}\text{H}_{39}\text{O}_4\text{Si}$ ($\text{M}+1$): 407.2618, found 407.2596.

A solution of compound **18** (17 mg, 0.0419 mmol) and Crabtree catalyst (17 mg, 0.0210 mmol) was stirred under a balloon of H₂ for 36 h. The mixture was filtered through a silica pad and washed with EtOAc. The filtrate was concentrated in vacuo. Chromatography of the residue (hexane/EA = 5:1 to 4:1) afforded the desired product **19** (8.5 mg, 50%) as a white solid.

¹H NMR (400MHz, CDCl₃): δ 4.62 (dd, J = 6.8 Hz, 1H), 3.58 (t, J = 6.0 Hz, 2H), 2.86-2.91 (dd, J = 17.6, 1.6 Hz, 1H), 2.60 (d, J = 8.8 Hz, 1H), 2.54 (dd, J = 10.0, 8.8 Hz, 1H), 2.46-2.51 (m, 1H), 2.06-2.14 (m, 2H), 1.85-1.88 (m, 1H), 1.70-1.75 (m, 2H), 1.58-1.67 (m, 3H), 1.40-1.49 (m, 3H), 1.06-1.10 (m, 1H), 1.03 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 217.8, 176.1, 78.4, 63.1, 57.0, 48.1, 41.6, 41.3, 34.5, 33.4, 32.7, 31.7, 31.6, 29.3, 25.9, 24.2, 21.4, 18.7, 18.3, -5.2; IR (NaCl, cm⁻¹): 2952, 1780, 1732, 1098; HRMS (FAB+) calcd for C₂₃H₄₁O₄Si (M+1): 409.2774, found 409.2749.

To a solution of compound **19** (8 mg, 0.020 mmol) in 3 mL CH₃CN/THF (2:1) was added 0.20 mL of aqueous HF (48%). The mixture was stirred for 1 h then quenched with water, extracted with DCM, washed with saturated aqueous NaHCO₃ solution, dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. The residue was

dissolved in 3 mL DCM and DMP (17 mg, 0.039 mmol) was then added to the solution. The mixture was stirred for 1 h then diluted with 5 mL of DCM and washed with 3 mL of saturated aqueous Na₂SO₃ solution and 3 mL of saturated aqueous NaHCO₃ solution. The organic phase was dried over anhydrous MgSO₄, filtered and concentrated at reduced pressure. Chromatography of the residue (hexane/EA = 2:1 to 1:1) afforded the desired product **20** (5.0 mg, 87%) as colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 9.79 (t, *J* = 1.6 Hz, 1H), 4.64 (q, *J* = 6.8 Hz, 1H), 2.88-2.92 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.42-2.62 (m, 5H), 2.09-2.19 (m, 2H), 1.72-1.91 (m, 4H), 1.61-1.68 (m, 2H), 1.42-1.49 (m, 1H), 1.29-1.35 (m, 1H), 1.03 (s, 3H), 1.00 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 217.1, 201.8, 176.1, 78.3, 57.0, 48.2, 41.6, 41.3, 40.9, 34.4, 33.3, 32.7, 31.5, 27.5, 24.2, 21.3, 18.4; IR (NaCl, cm⁻¹): 2954, 1773, 1728, 1700, 1171; HRMS (EI⁺) calcd for C₁₇H₂₄O₄ (M⁺): 292.1675, found 292.1693.

To a solution of the above sulfone (139mg, 0.55mmol) in 5 mL THF at -78°C was added LiHMDS (0.5 mL, 1M in THF). The resulting yellow solution was stirred at this temperature for 1 h. To the aldehyde **20** (3.5 mg, 0.012 mmol) in 0.6 mL THF at -78°C was added 0.14 mL of the above solution (0.014 mmol). The mixture was stirred at -78°C for 50 min then quenched with saturated aqueous NH₄Cl and warmed up to room temperature. The mixture was extracted with EtOAc, washed with brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. Chromatography of the residue (benzene / ether = 7:3) on preparative TLC afforded the desired product **1a** (2.6 mg, 68%)

¹H NMR (400 MHz, CDCl₃): δ 5.06 (t, *J* = 7.2 Hz, 1H), 4.63 (q, *J* = 6.8 Hz, 1H), 2.86-2.91 (dd, *J* = 18.0, 1.6 Hz, 1H), 2.59-2.61 (dd, *J* = 18.0, 8.4 Hz, 1H), 2.52-2.57 (dd, *J* =

20.0, 8.4 Hz, 1H), 2.45-2.50 (m, 2H), 2.02-2.14 (m, 4H), 1.85-1.94 (m, 2H), 1.71-1.74 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.35-1.50 (m, 2H), 1.06-1.12 (m, 1H), 1.03 (s, 3H), 1.00 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 217.8, 176.1, 131.8, 124.1, 78.5, 57.0, 48.2, 41.6, 41.3, 35.6, 34.4, 33.4, 32.8, 31.5, 25.6, 24.7, 24.2, 21.4, 18.7, 17.6; IR (NaCl, cm^{-1}): 2924, 1780, 1732, 1168; HRMS (EI $^{+}$) calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3$ (M^{+}): 318.2195, found 318.2176.

To a solution of bromide **21** (88 mg, 0.468 mmol) in 5 mL ether at -78°C was added $t\text{-BuLi}$ (0.55 mL, 0.936 mmol, 1.7 M in pentane) dropwise. The yellow solution was stirred at -78°C for 50 min. To the reaction solution at -78°C was added CuCN (46 mg, 0.515 mmol) in one portion. The resulting suspension was stirred at this temperature for 5 min then at -20°C for 20 min to form a homogeneous solution. The mixture was cooled to -78°C . To the mixture was added a solution of enone **7** (24 mg, 0.117 mmol) and $\text{BF}_3\cdot\text{OEt}_2$ (0.059 mL, 0.468 mmol) in 2 mL THF at -78°C by cannula. The resulting orange solution was stirred at -78°C for 2 h then quenched with a mixture of saturated aqueous NH_4Cl and saturated ammonia (9:1) and warmed up to room temperature. The resulting mixture was extracted with EtOAc , washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated in vacuo. Chromatography of the residue (hexane/ $\text{EA} = 5:1$ to $4:1$) afforded the desired product **22** (19 mg, 51%) as a white solid, m.p. $85\text{--}87^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ 5.08-5.11 (m, 1H), 5.02 (s, 1H), 4.80 (s, 1H), 4.53-4.57 (dd, $J = 14.4, 6.0$ Hz, 1H), 2.80-2.84 (dd, $J = 16.0, 3.2$ Hz, 1H), 7.32 (t, $J = 9.2$ Hz, 1H), 2.56-2.66 (m, 2H), 2.49-2.51 (dd, $J = 9.2, 1.2$ Hz, 1H), 2.46 (d, $J = 8.4$ Hz, 1H), 2.01-2.17 (m, 5H), 1.97 (d, $J = 8.4$ Hz, 1H), 1.65-1.75 (m, 1H), 1.69 (s, 3H), 1.61 (s, 3H), 1.40-1.52 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 217.5, 176.0, 147.3, 132.2, 123.4, 111.9, 77.9, 54.9, 47.6, 41.5, 41.0, 36.7, 33.5, 33.4, 30.3, 26.8, 25.6, 24.1,

22.6, 17.7; IR (NaCl, cm^{-1}): 2926, 1780, 1738, 1170; HRMS (EI+) calcd for $\text{C}_{20}\text{H}_{28}\text{O}_3$ (M^+): 316.2038, found 316.2027.

To Wilkinson catalyst (6 mg, 0.006 mmol) was added compound **22** (6 mg, 0.019 mmol) in 3 mL benzene. The mixture was stirred under a balloon of H_2 for 4 h then filtered through a silica pad and washed with EtOAc. The filtrate was concentrated in vacuo. Chromatography of the residue (hexane/EA = 5:1) afforded the desired product **23** (4 mg, 67%).

^1H NMR (400 MHz, CDCl_3): δ 5.08 (t, $J = 7.2$ Hz, 1H), 4.59 (dd, $J = 7.2, 6.4$ Hz, 1H), 2.84 (dd, $J = 21.2, 6.8$ Hz, 1H), 2.54-2.61 (dd, $J = 21.2, 8.4$ Hz, 1H), 2.52-2.58 (m, 1H), 2.40-2.47 (dd, $J = 20.0, 8.8$ Hz, 1H), 1.90-2.19 (m, 6H), 1.81 (d, $J = 9.6$ Hz, 1H), 1.65-1.75 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.35-1.55 (m, 2H), 1.10-1.25 (m, 1H), 1.06 (s, 3H), 0.88 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 217.9, 176.1, 131.8, 124.0, 78.2, 56.5, 47.5, 41.2, 40.2, 36.1, 33.3, 33.2, 32.9, 31.4, 25.7, 25.3, 24.2, 21.7, 17.8, 17.7; IR (NaCl, cm^{-1}): 2924, 1780, 1732, 1169; HRMS (EI+) calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3$ (M^+): 318.2195, found 318.2192.

An alternative route (from compound **9** to compound **29** or **12'**) is shown below:

To a solution of alcohol **9** (3.821 g, 12.093 mmol) in 30 mL DMF was added imidazole (3.289 g, 48.372 mmol) and TBSCl (3.645 g, 24.186 mmol). The mixture was stirred at room temperature for 5 h. The mixture was diluted between EtOAc and water and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated under vacuo. Chromatography of the residue (hexane/EA = 20:1) afforded the desired product **24** (5.16 g, quant.) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 6.01 (d, J = 10.0 Hz, 1H), 5.52 (d, J = 10.0 Hz, 1H), 4.60 (d, J = 6.8 Hz, 1H), 4.56 (d, J = 6.8 Hz, 1H), 3.98 (t, J = 8.0 Hz, 1H), 3.33 (s, 3H), 3.28-3.42 (m, 4H), 2.45 (d, J = 14.4 Hz, 1H), 2.30 (d, J = 14.4 Hz, 1H), 2.20-2.26 (m, 1H), 1.97-2.05 (m, 1H), 1.52-1.62 (m, 1H), 1.22-1.30 (m, 1H), 1.04 (s, 3H), 0.89 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 134.8, 125.5, 96.0, 81.0, 65.2, 62.5, 55.2, 51.2, 49.0, 41.5, 40.2, 38.7, 33.1, 28.9, 26.1, 25.9, 18.2, -5.4, -5.7; IR (NaCl, cm^{-1}): 2953, 2927, 1113, 1044; HRMS (FAB+) calcd for $\text{C}_{21}\text{H}_{39}\text{O}_3\text{SiS}_2$ ($M+1$): 431.2110, found 431.2106.

To a solution of compound **24** (5.160 g, 12 mmol) in 100 mL of THF/MeOH/ H_2O (2:2:1) at room temperature was added a solution of $\text{Ti}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (5.861 g, 13.200 mmol) in

40 mL MeOH. The mixture was stirred at room temperature for 1 h then quenched with water. The mixture was extracted with EtOAc. The organic phase was washed with saturated aqueous NaHCO₃ and brine, dried over anhydrous MgSO₄, filtered and concentrated under vacuo. Chromatography of the residue (hexane/EA = 8:1) afforded the desired product **24'** (3.33 g, 78%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.90 (d, *J* = 10.4 Hz, 1H), 6.15 (d, *J* = 10.4 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 1H), 4.07 (t, *J* = 8.0 Hz, 1H), 3.82 (d, *J* = 6.4 Hz, 1H), 3.69 (d, *J* = 6.4 Hz, 1H), 3.34 (s, 3H), 2.63 (d, *J* = 12.4 Hz, 1H), 2.30 (d, *J* = 12.4 Hz, 1H), 2.10-2.12 (m, 1H), 1.66-1.70 (m, 1H), 1.45-1.51 (m, 2H), 1.09 (s, 3H), 0.84 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 200.4, 150.2, 130.9, 96.0, 81.3, 64.9, 55.4, 53.7, 48.5, 42.3, 34.8, 29.1, 25.7, 25.0, 18.0, -5.6, -5.7; IR (NaCl, cm⁻¹): 2954, 2930, 1679, 1044; HRMS (FAB+) calcd for C₁₉H₃₃O₄Si (M+1): 353.2148, found 353.2158.

To a solution of enone **24'** (3.33 g, 9.407 mmol) in 80 mL of DCM/MeOH (1:1) was added CeCl₃·7H₂O (3.856 g, 10.348 mmol). The mixture was stirred at room temperature for 10 min then cooled to -78 °C. To the mixture was added NaBH₄ (536 mg, 14.110 mmol) in one portion. The mixture was stirred at -78 °C for 1 h then quenched with water and warmed to room temperature. The mixture was extracted with DCM, washed with brine, dried over anhydrous MgSO₄, filtered and concentrated under vacuo. Chromatography of the residue (hexane/EA = 6:1 to 3:1) afforded the desired product **25** (2.52 g, 75%) as a colorless oil and its epimeric compound (487 mg, 15%).

¹H NMR (400 MHz, CDCl₃): δ 5.91 (d, *J* = 10.0 Hz, 1H), 5.62 (d, *J* = 10.0 Hz, 1H), 4.60 (br s, 2H), 4.25 (m, 1H), 3.95 (t, *J* = 8.0 Hz, 1H), 3.64 (d, *J* = 10.0 Hz, 1H), 3.58 (d, *J* = 10.0 Hz, 1H), 3.33 (s, 3H), 1.96-1.98 (m, 1H), 1.80-1.84 (m, 1H), 1.66-1.72 (m, 1H), 1.53-1.59 (m, 1H), 1.42-1.50 (m, 1H), 1.39 (br s, 1H, OH), 1.18-1.25 (m, 1H), 1.04 (s, 3H), 0.88 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 133.1, 130.3, 96.1, 80.2, 65.3, 65.1, 55.2, 51.6, 42.3, 40.2, 33.0, 28.9, 27.4, 25.8, 18.1, -5.4, -5.7;

IR (NaCl, cm^{-1}): 3363, 2953, 2929, 1045; HRMS (FAB+) calcd for $\text{C}_{19}\text{H}_{35}\text{O}_3\text{Si}$ (M-1): 339.2355, found 339.2354.

To a solution of compound **25** (2.52 g, 7.079 mmol) in 20 mL DCM was added Pyridine (3.4 mL, 42.474 mmol), DMAP (1.73 g, 14.158 mmol) and acetic anhydride (2.7 mL, 28.315 mmol). The mixture was stirred at room temperature for 14 h then quenched with water, extracted with DCM, washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated under vacuo. Chromatography of the residue (hexane/EA = 8:1) afforded the desired product **25'** (2.79 g, quant.) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 5.82 (d, J = 10.4 Hz, 1H), 5.73 (d, J = 10.4 Hz, 1H), 5.36 (t, J = 8.0 Hz, 1H), 4.61 (d, J = 6.8 Hz, 1H), 4.58 (d, J = 6.8 Hz, 1H), 3.95 (t, J = 8.0 Hz, 1H), 3.65 (d, J = 10.0 Hz, 1H), 3.58 (d, J = 10.0 Hz, 1H), 3.33 (s, 3H), 2.03 (s, 3H), 1.95-2.01 (m, 1H), 1.79-1.87 (m, 1H), 1.67-1.77 (m, 2H), 1.42-1.53 (m, 1H), 1.22-1.32 (m, 1H), 1.04 (s, 3H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 131.9, 128.7, 96.0, 80.2, 68.6, 65.0, 55.2, 51.7, 40.1, 37.4, 33.0, 28.8, 26.9, 25.8, 21.3, 18.1, -5.5, -5.6; IR (NaCl, cm^{-1}): 2954, 2929, 1736, 1246; HRMS (FAB+) calcd for $\text{C}_{21}\text{H}_{39}\text{O}_5\text{Si}$ (M+1): 399.2567, found 399.2578.

To a solution of compound **25'** (2.790 g, 7.010 mmol) in 14 mL was added 14 mL TBAF (14 mmol, 1 M in THF). The mixture was stirred at room temperature for 1 h then quenched with water and extracted with EtOAc. The organic phase was washed with saturated brine, dried over anhydrous MgSO_4 , filtered and concentrated under vacuo. Chromatography of the residue (hexane/EA = 1:1) afforded the desired product **26** (1.75 g, 88%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 5.96 (d, J = 10.4 Hz, 1H), 5.86 (d, J = 10.4 Hz, 1H), 5.40 (t, J = 8.0 Hz, 1H), 4.66 (d, J = 6.4 Hz, 1H), 4.59 (d, J = 6.4 Hz, 1H), 3.98 (t, J = 8.4 Hz, 1H), 3.70 (br s, 2H), 3.36 (s, 3H), 2.05 (s, 3H), 1.99-2.02 (m, 1H), 1.86-1.91 (m, 2H), 1.77-1.84 (m, 1H), 1.61-1.67 (m, 1H), 1.43-1.48 (m, 1H), 1.24-1.32 (m, 1H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.8, 130.8, 130.6, 96.1, 80.8, 68.4, 65.2, 55.4, 51.5,

40.0, 37.3, 32.4, 28.3, 27.2, 21.2; IR (NaCl, cm^{-1}): 3473, 2953, 1733, 1244, 1041; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{25}\text{O}_5$ ($\text{M}+1$): 285.1702, found 285.1724.

To a solution of alcohol **26** (1.750 g, 6.162 mmol) in 36 mL DCM was added glyoxylic acid chloride tosylhydrazone (3.004 g, 11.523 mmol) and N, N-dimethylaniline (1.43 mL, 11.276 mmol) at 0 °C. The dark green solution was stirred for 25 min prior to injection of triethylamine (4.29 mL, 30.810 mmol). The resulting orange suspension was stirred for 10 min at 0 °C, then for 1 h at room temperature. The mixture was concentrated in vacuo. Chromatography of the residue (hexane/EA = 4:1) afforded the desired product **27** (2.06 g, 95%) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 5.88 (d, J = 10.4 Hz, 1H), 5.79 (dd, J = 10.4, 2.0 Hz, 1H), 5.40 (m, 1H), 4.71 (br s, 1H), 4.63 (d, J = 6.8 Hz, 1H), 4.57 (d, J = 6.8 Hz, 1H), 4.38 (d, J = 11.2 Hz, 1H), 4.13 (d, J = 11.2 Hz, 1H), 3.94 (dd, J = 9.6, 7.6 Hz, 1H), 3.35 (s, 3H), 2.06 (s, 3H), 1.99-2.04 (m, 1H), 1.89-1.94 (dd, J = 8.0, 6.8 Hz, 1H), 1.78-1.85 (m, 1H), 1.47-1.55 (m, 2H), 1.27-1.34 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 166.2, 130.2, 129.7, 96.0, 79.9, 68.1, 66.3, 55.4, 50.0, 46.0, 39.9, 37.4, 32.7, 28.6, 27.2, 21.2; IR (NaCl, cm^{-1}): 2954, 2110, 1733, 1699, 1242, 1042; HRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}_6$ ($\text{M}+1$): 353.1713, found 353.1711.

A solution of diazoester **27** (230 mg, 0.650 mmol) in 20 mL toluene was added slowly to a stirred refluxing solution of bis-(N-*t*-butylsalicylaldiminato) copper (II) catalyst (14 mg, 0.033 mmol) in 100 mL toluene over 4 h at a constant rate. The solution was held at reflux for 30 min after completion of addition, then cooled, concentrated and purified by flash chromatography (Hexane/EA = 1:1) to give desired product **28** (170 mg, 81%) as a yellow solid, m.p. 148-150 °C.

^1H NMR (400 MHz, CDCl_3): δ 5.54 (m, 1H), 4.67 (d, J = 6.8 Hz, 1H), 4.58 (d, J = 6.8 Hz, 1H), 4.36 (d, J = 11.2 Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 4.00 (t, J = 8.4 Hz, 1H), 3.36 (s, 3H), 2.35 (t, J = 8.4 Hz, 1H), 2.17-2.27 (m, 1H), 2.07 (s, 3H), 1.89-2.04 (m, 2H), 1.65-1.81 (m, 3H), 1.41-1.47 (dd, J = 14.4, 10.8 Hz, 1H), 1.25-1.34 (m, 1H), 1.04 (s, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 171.3, 169.6, 96.0, 79.4, 73.0, 67.4, 55.6, 42.8, 41.6, 35.5, 32.0, 27.5, 25.8, 21.7, 21.2, 18.9, 13.8; IR (NaCl, cm^{-1}): 2958, 1738, 1247; HRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_6$ (M+1): 325.1651, found 325.1674.

To a solution of acetate **28** (1.02 g, 3.148 mmol) in 30 mL MeOH was added K_2CO_3 (521 mg, 3.778 mmol). The mixture was stirred at room temperature for 4 h then filtered through a silica gel pad and washed with EtOAc. The filtrate was concentrated to give pure alcohol **29** (**12'**) (0.84 g, 95%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 4.67 (d, J = 6.8 Hz, 1H), 4.59 (d, J = 6.8 Hz, 1H), 4.44 (m, 1H), 4.42 (d, J = 11.2 Hz, 1H), 4.23 (d, J = 11.2 Hz, 1H), 4.00 (t, J = 8.4 Hz, 1H), 3.36 (s, 3H), 2.33 (t, J = 8.4 Hz, 1H), 2.14-2.25 (m, 1H), 1.77-1.95 (m, 5H), 1.66-1.73 (m, 1H), 1.19-1.31 (m, 2H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.5, 96.0, 79.6, 73.4, 64.2, 55.6, 43.2, 41.9, 40.2, 32.1, 27.6, 25.9, 24.5, 18.9, 13.4; IR (NaCl, cm^{-1}): 3387, 2955, 1724, 1038; HRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_4$ (M-1): 265.1440, found 265.1451.

To a solution of alcohol **29** (9.0 mg, 0.032 mmol) in 2 mL was added DMAP (4 mg, 0.032 mmol) and 1, 1'-Thiocarbonyldiimidazole (34 mg, 0.191 mmol). The mixture was refluxed for 12 h then cooled to room temperature. The mixture was quenched with water, extracted with DCM, washed with cold 1N aqueous HCl solution and then saturated aqueous NaHCO_3 solution, dried over anhydrous MgSO_4 , filtered and concentrated under vacuo. Chromatography of the residue on preparative TLC (hexane/EA = 1:4) afforded the desired product **30** (12.5 mg, 82%) as a white solid, m.p. 120-122 $^\circ\text{C}$.

^1H NMR (500 MHz, CDCl_3): δ 8.46 (s, 1H), 7.74 (s, 1H), 7.05 (s, 1H), 6.38 (q, J = 8.0 Hz, 1H), 4.71 (d, J = 6.5 Hz, 1H), 4.63 (d, J = 6.5 Hz, 1H), 4.45 (d, J = 11.0 Hz, 1H), 4.30 (d, J = 11.0 Hz, 1H), 4.07 (t, J = 8.0 Hz, 1H), 3.40 (s, 3H), 2.53 (t, J = 8.5 Hz, 1H), 2.26-2.32 (m, 1H), 2.02-2.12 (m, 3H), 1.92 (t, J = 9.0 Hz, 1H), 1.77 (m, 1H), 1.59-1.64 (dd, J = 14.0, 10.5 Hz, 1H), 1.39-1.45 (m, 1H), 1.11 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 183.9, 169.1, 130.9, 117.9, 115.5, 96.1, 79.3, 73.0, 55.7, 43.2, 41.9, 34.6, 32.2, 29.6, 27.5, 25.5, 20.3, 19.7, 14.5.

NAME zyd-1-244pure
 EXPNO 1
 PROCNO 1
 Date_ 20081016
 Time 16.16
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 84
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 80.6
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200021 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

—210.299
 —196.793
 —168.849
 —142.475
 —129.796
 —65.903
 —52.772
 —47.008
 —45.999
 —36.574
 —32.777
 —23.692

NAME zyd-1-244pure
 EXPNO 2
 PROCNO 1
 Date_ 20081016
 Time 16.22
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 30902
 SOLVENT Aceton
 NS 548
 DS 0
 SWH 28089.887 Hz
 FIDRES 0.908999 Hz
 AQ 0.5501056 sec
 RG 16384
 DN 17.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.69999999 sec
 d11 0.03000000 sec
 DELTA 0.59999996 sec
 TD0 1

***** CHANNEL f1 *****
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 ppm

NAME zy3-2-140
 EXPNO 1
 PROCNO 1
 Date_ 20081226
 Time 10.36
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 24
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 57
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200055 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-140
EXPNO 2
PROCNO 1
Date_ 20081226
Time 10.39
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 598
DS 0
SNH 27173.912 Hz
FIDRES 0.879358 Hz
AQ 0.5686468 sec
RG 16384
DW 18.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyd-2-146-2
 EXPNO 1
 PROCNO 1
 Date_ 20081229
 Time 15.26
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT D2O
 NS 20
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 57
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

***** CHANNEL f1 *****
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200023 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-146-2
EXPNO 2
PROCNO 1
Date_ 20081229
Time 15.28
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 261
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyd-2-148-1
 EXPNO 1
 PROCNO 1
 Date_ 20081230
 Time 11.30
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 37
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 71.8
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

***** CHANNEL f1 *****
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200054 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

6.120
 6.095
 5.698
 5.673
 4.772
 4.756
 4.650
 4.646
 4.631
 4.614
 3.689
 3.449
 3.439
 3.435
 3.427
 3.379
 3.375
 3.369
 3.357
 3.338
 3.327
 3.316
 3.303
 3.293
 3.290
 3.284
 3.278
 2.478
 2.441
 2.372
 2.366
 2.310
 2.273
 2.070
 2.051
 1.601
 1.598
 1.594
 1.590
 1.577
 1.569
 1.549
 1.545
 1.541
 1.386
 1.365
 1.352
 1.343
 1.331
 1.309
 0.933

NAME zyd-2-148-1
EXPNO 2
PROCNO 1
Date_ 20081230
Time 11.33
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 300
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.6291535 MHz

NAME zyd-2-152
 EXPNO 1
 PROCNO 1
 Date_ 20081231
 Time 14.52
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 54
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 64
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200050 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-152
EXPNO 2
PROCNO 1
Date_ 20081231
Time 14.57
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 437
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TDC 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

— 136.267
— 124.222
— 96.153
— 81.329
— 65.043
— 61.821
— 55.485
— 50.776
— 48.505
— 41.042
— 40.828
— 38.196
— 31.991
— 28.150
— 26.577

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

NAME zyd-2-216
 EXPNO 1
 PROCNO 1
 Date_ 20090116
 Time 15.54
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 21
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 71.8
 DW 83.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9199995 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

—199.967

—149.995

—131.223

—96.206

—81.806

—64.373

—55.572

—53.471

—47.956

—42.052

—34.396

—28.700

—25.350

NAME zyd-2-216
EXPNO 2
PROCNO 1
Date_ 20090116
Time 15.56
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 342
DS 0
SMH 26178.010 Hz
PIDRES 0.847130 Hz
AQ 0.5902782 sec
RG 16384
DN 19.100 use
DE 6.00 use
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 use
PL1 -1.00 dB
SFO1 100.5699800 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 use
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599714 MHz
WDW EM
SSB 0

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

NAME zyd-6-126
 EXPNO 1
 PROCNO 1
 Date_ 20100122
 Time 12.35
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 25
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 32
 DW 83.200 usec
 DE 6.50 usec
 TE 294.9 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200038 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-6-126
 EXPNO 2
 PROCNO 1
 Date_ 20100122
 Time 12.38
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 3041
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6816244 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 295.0 K
 D1 0.69999999 sec
 D11 0.03000000 sec
 TD0 1

----- CHANNEL f1 -----
 NUC1 13C
 P1 14.00 usec
 PL1 -4.60 dB
 PL1W 94.90110779 W
 SFO1 100.5710256 MHz

NAME zyd-6-142
 EXPNO 1
 PROCNO 1
 Date_ 20100127
 Time 11.00
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 28
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 90.5
 DW 83.200 usec
 DE 6.50 usec
 TE 295.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200076 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

4.704
4.687
4.622
4.605
4.549
4.521
4.404
4.376
4.118
4.097
4.077
3.381
2.820
2.800
2.780
2.308
2.296
2.288
2.281
2.261
2.252
2.241
2.231
2.204
2.187
2.144
1.879
1.847
1.833
1.814
1.802
1.794
1.787
1.776
1.767
1.764
1.754
1.745
1.734
1.722
1.703
1.476
1.465
1.449
1.442
1.432
1.418
1.411
1.095

carbon 13

NAME syd-6-143
EXPNO 2
PROCNO 1
Date_ 20100127
Time 17.03
INSTRUM spect
PROBHD 5 mm F4001 1H/
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 1270
DS 0
SWH 24018.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 144
CW 18.800 usec
DE 6.50 usec
TE 295.0 K
D1 0.60599999 sec
D11 0.03000000 sec
TDO 1

***** CHANNEL f1 *****
NUC1 13C
P1 14.00 usec
PL1 -4.60 dB
PL1W 94.90118779 W
SFO1 100.5710296 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC1 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 21.88 dB
PL13 120.00 dB
PL2W 12.20776844 W
PL12W 0.07918380 W
PL13W 0.00000000 W
SFO2 399.9215997 MHz
SI 32768
SF 100.5599685 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

NAME zyd-5-18
EXPNO 1
PROCNO 1
Date_ 20090815
Time 17.48
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 26
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 101.6
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200056 MHz
WDW RM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

4.688
4.671
4.600
4.583
4.448
4.415
4.387
4.366
4.256
4.229
4.029
4.008
3.987
3.365
2.359
2.338
2.317
2.256
2.242
2.233
2.221
2.210
2.198
2.187
2.178
2.164
2.144
1.956
1.942
1.924
1.911
1.892
1.877
1.864
1.852
1.845
1.839
1.828
1.818
1.808
1.798
1.773
1.739
1.726
1.718
1.706
1.692
1.687
1.674
1.662
1.034
0.914

NAME zyd-5-18
EXPNO 3
PROCNO 1
Date_ 20090815
Time 17.51
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 281
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DM 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyd-5-22
 EXPNO 1
 PROCNO 1
 Date_ 20090818
 Time 16.58
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 27
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 128
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.920061 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

4.893
 4.879
 4.875
 4.862
 4.848
 4.845
 4.831
 4.676
 4.659
 4.588
 4.571
 4.381
 4.354
 4.256
 4.229
 3.993
 3.972
 3.950
 3.354
 2.408
 2.387
 2.366
 2.245
 2.235
 2.223
 2.212
 2.201
 2.191
 2.178
 2.089
 2.059
 2.043
 2.013
 1.995
 1.878
 1.857
 1.853
 1.833
 1.730
 1.727
 1.718
 1.715
 1.696
 1.694
 1.246
 1.241
 1.237
 1.227
 1.223
 1.212
 1.203
 1.189
 1.038

NAME zyd-5-22
EXPNO 2
PROCNO 1
Date_ 20090818
Time 17.01
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 445
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TDC 1

***** CHANNEL f1 *****
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyd-3-116
 EXPNO 1
 PROCNO 1
 Date_ 20090329
 Time 12.54
 INSTRUM spect
 PROBHD 5 mm TXI 13C 2
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 90
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 64
 DW 83.200 usec
 DE 5.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 TD0 1

----- CHANNEL f1 -----
 NUC1 1H
 P1 3.00 usec
 PL1 3.00 dB
 SFO1 500.1325006 MHz
 SI 16384
 SF 500.1300121 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-3-116
EXPNO 2
PROCNO 1
Date_ 20090329
Time 13.04
INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zgpg30
TD 42038
SOLVENT CDCl3
NS 5916
DS 0
SWH 30030.029 Hz
FIDRES 0.714354 Hz
AQ 0.6999827 sec
RG 32768
DW 16.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
G11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.40 usec
PL1 -4.00 dB
SFO1 125.7703640 MHz

5.704
5.699
5.695
5.690
5.684
5.679
5.674
5.670
5.665
5.660
5.588
5.563
4.487
4.469
4.464
4.447
4.4310
4.281
4.258
4.229
2.924
2.911
2.897
2.866
2.848
2.415
2.253
2.236
2.226
2.218
2.212
2.206
2.201
2.195
2.189
2.178
2.171
2.154
2.010
2.003
1.997
1.976
1.959
1.952
1.945
1.927
1.913
1.896
1.883
1.852
1.839
1.643
1.633
1.626
1.615
1.609
1.603
1.598
1.591
1.586
1.581
1.568
1.561
1.551
1.279
1.269
1.255
1.246
1.236
1.222
1.212
1.004

NAME zyd-4-120
EXPNO 1
PROCNO 1
Date_ 20090615
Time 17.13
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 22
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 71.8
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200056 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

— 174.207

— 128.770
— 124.361

— 78.258
— 70.813

— 46.442
— 41.133
— 35.809
— 34.714
— 34.331
— 29.514
— 29.478
— 25.150

NAME zyd-4-120
EXPNO 2
PROCNO 1
Date_ 20090615
Time 17.14
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 286
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

5.884
5.878
5.871
5.865
5.858
5.852
5.846
5.839
5.833
5.512
5.506
5.501
5.495
5.487
5.481
5.476
5.470
4.504
4.472
4.262
4.230
2.800
2.786
2.762
2.748
2.621
2.614
2.605
2.599
2.555
2.549
2.530
2.524
2.427
2.418
2.395
2.389
2.380
2.371
2.345
2.162
2.154
2.106
2.102
2.094
2.088
2.082
2.048
2.043
1.668
1.662
1.645
1.637
1.629
1.612
1.606
1.042

NAME zyd-4-126
EXPNO 1
PROCNO 1
Date_ 20090617
Time 9.39
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 36
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 80.6
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200052 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

—215.713

—171.813

—127.493
—126.116

—66.247

—53.206

39.486
33.422
33.390
33.166
32.578
30.713
24.384

NAME zyd-4-126
EXPNO 2
PROCNO 1
Date_ 20090617
Time 9.47
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 296
DS 0
SWH 27173.912 Hz
FIDRES 0.879358 Hz
AQ 0.5686468 sec
RG 16384
DW 18.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 ppm

NAME zyd-5-80
EXPNO 1
PROCNO 1
Date_ 20090902
Time 15.29
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 21
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 161.3
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NOC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200081 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

— 216.006

— 174.059

— 84.004

— 55.025
 44.013
 41.707
 34.139
 34.022
 33.920
 31.520
 26.338
 22.639

NAME zyd-5-80
 EXPNO 2
 PROCNO 1
 Date_ 20090902
 Time 15.33
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 30902
 SOLVENT Aceton
 NS 609
 DS 0
 SNH 26178.010 Hz
 FIDRES 0.847130 Hz
 AQ 0.5902782 sec
 RG 16384
 DW 19.100 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.69999999 sec
 d11 0.03000000 sec
 DELTA 0.59999996 sec
 TD0 1

***** CHANNEL f1 *****
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

NAME zyd-4-158
 EXPNO 1
 PROCNO 1
 Date_ 20090625
 Time 18.08
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 38
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 256
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

***** CHANNEL f1 *****
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200105 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-4-158
EXPNO 2
PROCNO 1
Date_ 20090625
Time 22.03
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 28567
DS 0
SWH 27173.912 Hz
FIDRES 0.879358 Hz
AQ 0.5686468 sec
RG 16384
DW 18.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

***** CHANNEL f1 *****
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

ppm

NAME zyd-4-158
 EXPNO 4
 PROCNO 1
 Date_ 20090626
 Time 9.39
 INSTRUM spect
 PROBHD 5 mm TXI 13C 2
 PULPROG noesygpphzz.jd
 TD 1024
 SOLVENT CDCl3
 NS 12
 DS 16
 SWH 3004.808 Hz
 FIDRES 2.934382 Hz
 AQ 0.1704436 sec
 RG 64
 DW 166.400 usec
 DE 6.00 usec
 TE 300.0 K
 d0 0.00015771 sec
 D1 2.00000000 sec
 D8 0.69999999 sec
 D16 0.00010000 sec
 IN0 0.00033325 sec
 ST1CNT 0
 TAU 0.67481601 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.00 usec
 P32 20000.00 usec
 PL1 2.00 dB
 SFO1 500.1317505 MHz
 SF29 34.05 dB
 SFNAM29 chirp_20K_noezq
 SFOAL29 0.500
 SPOFFS29 0.00 Hz

===== GRADIENT CHANNEL =====
 GPNAM1 SINE.100
 GPX0 0.00 %
 GPX1 0.00 %
 GPY0 0.00 %
 GPY1 0.00 %
 GPZ0 20.00 %
 GPZ1 40.00 %
 P31 5000.00 usec
 NDO 1
 TD 256
 SFO1 500.1318 MHz
 FIDRES 11.721681 Hz
 SW 6.000 ppm
 PnMODE States-TPPI
 SI 1024
 SF 500.130088 MHz
 WDW QSINE
 SSB 2
 LB 0.00 Hz
 GB 0
 PC 1.00

4.405
4.389
4.381
4.373
4.365
4.349
4.340
3.034
3.023
3.017
3.008
2.682
2.656
2.639
2.613
2.605
2.582
2.562
2.539
2.385
2.374
2.361
2.348
2.344
2.321
2.299
2.294
2.272
2.249
2.043
2.022
2.008
2.000
1.994
1.986
1.979
1.973
1.965
1.959
1.875
1.853
1.842
1.831
1.825
1.820
1.802
1.792
1.778
1.769
1.745
1.701
1.685
1.677
1.669
1.653
1.644
1.537
1.533
1.529
1.520
1.506
1.501
1.498
1.493
1.488
1.480
1.300
1.277
1.271
1.259
1.242
1.235

NAME zyd-5-76
EXPNO 1
PROCNO 1
Date_ 20090901
Time 15.01
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 42
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 181
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

***** CHANNEL f1 *****
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200076 MHz
WDW RM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

1.000

1.000

2.140

2.181

1.191

1.025

2.180

0.984

1.114

3.434

1.229

NAME zyd-5-76
 EXPNO 2
 PROCNO 1
 Date_ 20090901
 Time 15.05
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 30902
 SOLVENT Aceton
 NS 522
 DS 0
 SWH 26178.010 Hz
 FIDRES 0.847130 Hz
 AQ 0.5902782 sec
 RG 16384
 DW 19.100 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.69999999 sec
 d11 0.03000000 sec
 DELTA 0.59999996 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

NAME ryd-5-116
 EXPNO 1
 PROCNO 1
 Date_ 20091102
 Time 22.48
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 36
 DS 0
 SMH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 256
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

***** CHANNEL f1 *****
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200095 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

— 208.964

— 176.024

— 170.832

— 131.080

— 77.084

— 52.859

— 43.854

— 33.764

— 31.896

— 27.930

— 27.716

— 24.260

carbon NMR

zyd-5-116

NAME zyd-6-178
 EXPNO 1
 PROCNO 1
 Date_ 20100209
 Time 9.52
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 80
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 22.6
 DW 83.200 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200072 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

—217.704

carbon 13

—176.037

—134.171

—124.966

—77.948

—62.587

—55.047

—50.321

41.564

40.139

33.484

31.728

30.227

29.663

25.888

24.023

22.853

18.271

16.864

—5.304

NAME syd-6-178
EXPNO 2
PROCNO 1
Date_ 20100209
Time 16.07
INSTRUM spect
PROBHD 5 mm PABBI LH/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 631
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 201
DE 20.800 usec
TE 6.50 usec
TI 300.0 K
D1 0.6999999 sec
D11 0.0300000 sec
TD0 2

===== CHANNEL f1 =====
NUC1 13C
P1 14.00 usec
PL1 -4.60 dB
PL1W 94.90218779 W
SFO1 100.5718256 MHz

===== CHANNEL f2 =====
CPDPRG2 Maltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 21.88 dB
PL13 120.00 dB
PL2W 12.20776844 W
PL12W 0.87918380 W
PL13W 0.90000000 W
SFO2 399.9215997 MHz
SI 32768
SF 100.5599678 MHz
KCM 0
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

NAME zyd-6-180
 EXPNO 1
 PROCNO 1
 Date_ 20100211
 Time 14.10
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 68
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 114
 DW 83.200 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200105 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

4.654
4.637
4.619
4.602

3.596
3.581
3.565
2.912
2.908
2.868
2.863
2.610
2.588
2.544
2.492
2.490
2.469
2.139
2.115
2.111
2.094
1.883
1.856
1.755
1.724
1.676
1.670
1.647
1.638
1.551
1.455
1.448
1.441
1.436
1.422
1.037
0.889
0.041

NAME zyd-6-180
 EXPNO 2
 PROCNO 1
 Date_ 20100211
 Time 14.24
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 32216
 DS 0
 SWH 27173.912 Hz
 FIDRES 0.829282 Hz
 AQ 0.6029812 sec
 RG 203
 DW 18.400 usec
 DE 6.50 usec
 TE 300.0 K
 D1 0.69999999 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 14.00 usec
 PL1 -4.60 dB
 PL1W 94.90110779 W
 SFO1 100.5710256 MHz

NAME zyd-6-192-1
 EXPNO 1
 PROCNO 1
 Date_ 20100220
 Time 11.13
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 67
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 114
 DW 83.200 usec
 DE 6.50 usec
 TE 295.0 K
 D1 1.00000000 sec
 TD0 1

***** CHANNEL f1 *****
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200092 MHz
 WDW EM
 SSB 0
 LB 0.20 KHz
 GB 0
 PC 1.00

4.673
 4.657
 4.639
 4.622
 2.925
 2.921
 2.880
 2.876
 2.604
 2.559
 2.517
 2.468
 2.447
 2.159
 2.140
 2.115
 1.888
 1.784
 1.758
 1.742
 1.726
 1.653
 1.646
 1.638
 1.631
 1.624
 1.570
 1.460
 1.337
 1.315
 1.301
 1.039
 1.001
 0.985

0.864

1.000

1.032

5.162

2.164

1.987

2.451

2.273

1.438

1.508

2.913

2.806

NAME zyd-6-136
 EXPNO 2
 PROCNO 1
 Date_ 20100125
 Time 17.08
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 23448
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6816244 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 295.6 K
 D1 0.69999999 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 14.00 usec
 PL1 -4.60 dB
 PL1W 94.90110779 W
 SFO1 100.5710256 MHz

NAME zyd-6-170-1
 EXPNO 1
 PROCNO 1
 Date_ 20100206
 Time 10.41
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 212
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 181
 DW 83.200 usec
 DE 6.50 usec
 TE 295.5 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200104 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

5.081
 5.063
 5.046
 4.662
 4.645
 4.627
 4.610

2.915
 2.911
 2.870
 2.867
 2.618
 2.597
 2.573
 2.552
 2.544
 2.523
 2.494
 2.474
 2.458
 2.141
 2.109
 2.091
 2.081
 2.074
 2.060
 2.026
 1.903
 1.881
 1.747
 1.717
 1.687
 1.603
 1.460
 1.448
 1.436
 1.423
 1.386
 1.371
 1.363
 1.031
 1.012
 0.996

Aplykurodinone-1(1)

— 217.846

— 176.181

— 131.829

— 124.150

— 78.492

— 57.080
— 48.227
— 41.682
— 41.333
— 35.688
— 34.420
— 31.410
— 32.833
— 31.565
— 25.686
— 24.752
— 24.258
— 21.415
— 18.717
— 17.671

NAME 2yd-6-242-p
EXPNO 1
PROCNO 1
Date_ 28100120
Time 21.13
INSTRUM spect
PROBHD 5 mm ZABDO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 13669
DS 0
SWH 27173.512 Hz
FIDRES 0.4029802 Hz
AQ 0.6023812 sec
RG 1820
DM 38.400 mmec
DE 6.50 mmec
TE 300.0 K
D0 0.00000000 sec
D01 0.01000000 sec
EDC 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 mmec
PL1 1.20 dB
PL1W 49.53329468 W
SFO1 100.6228295 MHz

===== CHANNEL f2 =====
CROSS2 waltz16
NUC2 1H
PCPD2 99.00 mmec
PL2 -1.00 dB
PL12 16.80 dB
PL13 16.80 dB
PL1W 26.94167927 W
PL1W 0.37150142 W
PL1W 0.37150142 W
SFO2 400.1314885 MHz
S2 12780
SFO 400.1314885 MHz
WCH 0
SFO 0
LB 1.60 Hz
GB 0
PC 1.40

Aplykurodinone-1(1)

NAME zyd-5-204
 EXPNO 1
 PROCNO 1
 Date_ 20091118
 Time 22.36
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 57
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 161.3
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200057 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

5.126
 5.109
 5.097
 5.035
 4.813
 4.589
 4.574
 4.555
 4.540
 2.849
 2.817
 2.810
 2.742
 2.720
 2.678
 2.662
 2.655
 2.650
 2.642
 2.608
 2.588
 2.528
 2.504
 2.488
 2.467
 2.182
 2.162
 2.147
 2.134
 2.111
 2.095
 2.087
 2.075
 2.059
 2.039
 2.021
 1.996
 1.975
 1.704
 1.624
 1.515
 1.508
 1.487
 1.480
 1.472
 1.452
 1.032

NAME zyd-5-204
EXPNO 2
PROCNO 1
Date_ 20091118
Time 23.27
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 24525
DS 0
SWH 27173.912 Hz
FIDRES 0.879358 Hz
AQ 0.5686468 sec
RG 16384
DW 18.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyd-6-208-p
 EXPNO 1
 PROCNO 1
 Date_ 20100310
 Time 14.42
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 256
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 203
 DW 83.200 usec
 DE 6.50 usec
 TE 295.1 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.25 usec
 PL1 0.00 dB
 PL1W 12.20776844 W
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200107 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

5.101
 5.083
 5.065
 4.610
 4.594
 4.576

2.868
 2.832
 2.618
 2.597
 2.585
 2.581
 2.566
 2.561
 2.554
 2.546
 2.476
 2.454
 2.426
 2.405
 2.191
 2.165
 2.142
 1.824
 1.800
 1.696
 1.614
 1.455
 1.419
 1.390
 1.217
 1.203
 1.194
 1.181
 1.171
 1.160
 1.068
 0.894
 0.877

0.885
 1.000
 0.924
 2.286
 1.263
 1.023
 3.222
 2.504
 1.271
 7.080
 5.048
 2.610
 3.050
 3.603
 4.846

—217.972

—176.139

—131.872

—124.059

—78.261

56.539
47.584
41.234
40.252
36.178
33.389
33.298
32.915
31.492
29.693
25.712
25.372
24.258
21.773
17.829
17.722

NAME syd-6-208-p
EXPNO 3
PROCNO 1
Date_ 20100311
Time 1.21
INSTRUM spect
PROBHD 5 mm TANGO HD-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
DS 16581
DS 0
SWH 26041.666 Hz
FIDRES 0.794723 Hz
AQ 0.6291956 sec
RG 1020
RW 19.200 usec
RE 6.50 usec
TE 296.3 K
D1 0.89999999 sec
D11 0.03000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 8.50 usec
PL1 3.30 dB
PL1W 43.53329448 W
SF01 100.6220298 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SF02 400.1316095 MHz
SI 32768
SF 100.6127696 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NAME zyd-2-196
 EXPNO 1
 PROCNO 1
 Date_ 20090111
 Time 12.22
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 29
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 71.8
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200098 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-196
 EXPNO 2
 PROCNO 1
 Date_ 20090111
 Time 12.24
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 30902
 SOLVENT Aceton
 NS 434
 DS 0
 SWH 22075.055 Hz
 FIDRES 0.714357 Hz
 AQ 0.6999803 sec
 RG 16384
 DW 22.650 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.69999999 sec
 d11 0.03000000 sec
 DELTA 0.59999996 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

NAME zyd-2-202
 EXPNO 1
 PROCNO 1
 Date_ 20090114
 Time 9.59
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 30
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 57
 DW 83.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200081 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-202
 EXPNO 2
 PROCNO 1
 Date_ 20090114
 Time 10.02
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 30902
 SOLVENT Aceton
 NS 317
 DS 0
 SWH 27173.912 Hz
 FIDRES 0.879358 Hz
 AQ 0.5686468 sec
 RG 16384
 DW 18.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.69999999 sec
 d11 0.03000000 sec
 DELTA 0.59999996 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

NAME zyd-2-218-1-pure
 EXPNO 1
 PROCNO 1
 Date_ 20090121
 Time 11.17
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 54
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 20.2
 DW 83.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200060 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-218-1-pure
 EXPNO 2
 PROCNO 1
 Date_ 20090121
 Time 11.20
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 30902
 SOLVENT Aceton
 NS 314
 DS 0
 SWH 22075.055 Hz
 FIDRES 0.714357 Hz
 AQ 0.6999803 sec
 RG 128
 DW 22.650 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.69999999 sec
 d11 0.03000000 sec
 DELTA 0.59999996 sec
 TD0 1

----- CHANNEL f1 -----
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 96.25 usec
 PL2 0.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SFO2 399.9215997 MHz
 SI 65536
 SF 100.5599684 MHz
 WDW EM
 SSB 0

NAME zyd-2-240
 EXPNO 1
 PROCNO 1
 Date_ 20090123
 Time 14.26
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 61
 DS 0
 SNH 5995.204 Hz
 PIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 45.3
 DW 83.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200067 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-240
EXPNO 2
PROCNO 1
Date_ 20090123
Time 14.35
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 193
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.69999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyd-2-244
 EXPNO 1
 PROCNO 1
 Date_ 20090126
 Time 12.07
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDC13
 NS 34
 DS 0
 SMH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 90.5
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200022 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-244
EXPNO 2
PROCNO 1
Date_ 20090126
Time 12.09
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 214
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

NAME zyl-2-224
 EXPNO 1
 PROCNO 1
 Date_ 20090118
 Time 11.50
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 99
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 724.1
 DW 83.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200111 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME zyd-2-246
EXPNO 2
PROCNO 1
Date_ 20090127
Time 10.25
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 269
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

— 170.777
— 166.245

— 130.257
— 129.757

— 96.014

— 79.942

— 68.130
— 66.388

— 55.423

— 50.050

— 46.001

— 39.973

— 37.468

— 32.700

— 28.649

— 27.282

— 21.220

NAME zyd-2-250
EXPNO 1
PROCNO 1
Date_ 20090128
Time 12.02
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 37
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 64
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

***** CHANNEL f1 *****
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200031 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

5.567
5.548
5.540
5.533
5.524
5.505
4.688
4.671
4.599
4.582
4.380
4.352
4.244
4.217
4.023
4.002
3.981
3.363
3.377
2.356
2.249
2.236
2.225
2.214
2.202
2.076
2.013
1.999
1.980
1.960
1.936
1.921
1.913
1.898
1.779
1.756
1.734
1.713
1.479
1.451
1.442
1.346
1.333
1.323
1.311
1.299
1.289
1.275
1.048

NAME zyd-2-250
EXPNO 2
PROCNO 1
Date_ 20090128
Time 12.07
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 204
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

171.328
169.633

96.018
79.445
73.078
67.425
55.612
42.852
41.696
35.531
32.086
27.588
25.835
21.744
21.212
18.956
13.842

NAME zyd-2-272
 EXPNO 1
 PROCNO 1
 Date_ 20090205
 Time 12.37
 INSTRUM spect
 PROBHD 5 mm TXI 13C 2
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7263477 sec
 RG 32
 DW 83.200 usec
 DE 5.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.00 usec
 PL1 3.00 dB
 SFO1 500.1325006 MHz
 SI 16384
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NOESY

183.948

169.169

130.901

117.941

115.562

96.115

79.302

73.068

55.728

43.239

41.928

34.607

32.282

29.683

27.539

25.561

20.387

19.748

14.566

Current Data Parameters
NAME zyd-2-272
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20090205
Time 12.39
INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zgpg30
TD 42038
SOLVENT CDCl3
NS 4946
DS 0
SWH 30030.029 Hz
FIDRES 0.714354 Hz
AQ 0.6999827 sec
RG 32768
DN 16.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

***** CHANNEL f1 *****
NUC1 13C
P1 10.40 usec
PL1 -4.00 dB
SFO1 125.7703640 MHz

Comparison of ^1H -NMR spectra of Aplykurodinones (Natural, synthetic and 13-*epi*-). δ from 7.5 to 0.5 ppm in CDCl_3 .

Comparison of ^{13}C -NMR spectra of Aplykurodinones (Natural, synthetic and 13-*epi*-). δ from 190 to 10 ppm in CDCl_3 .

Aplykurodinone-1 (natural)

Aplykurodinone-1 (synthetic)

13-*epi*-Aplykurodinone-1 ((synthetic)