Approach to the Synthesis of Cladiell-11-ene-3,6,7-triol

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Supporting Information

Contents

Acid 3. KHMDS (162.3 mL, 0.5 M in toluene, 81.1 mmol) was added dropwise to a solution of ester **2** (10.14 g, 27.0 mmol) and TIPSOTf (24.86 g, 81.1 mmol) in ether (500 mL) at –78 °C. After slowly warm to –20 °C over a 5 h period, the reaction mixture was quenched with saturated $NaHCO_3$ solution. Following extractive work-up, the crude material was dissolved in 25 mL of a 5% solution of 48% aqueous HF in CH_3CN and stirred for 1 h at rt. The reaction mixture was concentrated in vacuo, diluted with ether, washed with a 1 N HCl solution, and isolated by extractive work-up. The crude product was then dissolved in 1 mL NEt_3 and purified by flash chromatography over silica gel eluting with ether, then 1% acetic acid in ether. Removal of excess acetic acid in vacuo gave acid **3** (8.37g, 83%) as a yellow oil. IR (film) 1715 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.79 (s, 3H), 1.81 (s, 3H), 2.15 (m, 1H), 2.46 (m, 2H) 2.81 (dd, 1H, J=7.0, 15.5 Hz), 3.00 (dd, 1H, J=8.1, 15.5 Hz), 4.60 (s, 2H), 4.86 (s, 1H), 4.98 (s, 1H), 5.20 (s, 1H), 5.67 (t, 1H, J=7.5 Hz), 5.75 (d, 1H, J=5.5 Hz), 7.36 (m, 5H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 19.9, 21.8, 21.8, 25.3, 35.7, 45.5, 57.1, 66.8, 80.5, 112.3, 120.7, 126.5, 127.8, 127.9, 128.5, 129.8, 137.9, 139.7, 144.3, 179.1

Lactone 4. Ag_2O (15.11 g, 65.2 mmol) was added to a solution of acid **3** (9.78 g, 26.1 mmol) in DMF (250 mL) and allowed to stir at rt for 15 h. The reaction mixture was then filtered through a plug of silica gel with ether, washed with water, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes to give lactone **4** (7.42 g, 84%) as a clear oil. IR (film) 2933, 1778, 1455, 1211, 1134 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.73 (s, 3H), 1.84 (d, 3H, J=1.6 Hz), 2.14 (m, 2H), 2.37 (dd, 1H, J=6.4, 13.0 Hz), 2.48 (dd, 1H, J=9.1, 13.0 Hz), 2.89 (m, 1H), 4.56 (d, 1H, J=10.9 Hz), 4.71 (d, 1H, J=10.9 Hz), 4.76 (s, 2H), 5.0 (t, 1H, J=7.7 Hz), 5.65 (s, 1H), 5.81 (d, 1H, J=3.5 Hz), 7.31 (m, 5H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 19.40, 21.02, 22.00, 27.74, 40.36, 41.49, 66.80, 75.61, 78.62, 111.01, 124.45, 126.96, 127.82, 127.86, 128.48, 129.72, 135.33, 137.95, 146.90, 176.24.

MOM ether 5. *n*-BuLi (41.0 mL, 2.77 M in hexane, 113.5 mmol) was added dropwise to a solution of tri-n-butyl-[(methoxymethoxy)methyl]stannane (37.73 g, 103.3 mmol) in THF (200 mL) at –78 °C. After 30 min, the reaction mixture was cannulated into a solution of $ZnBr_2$ (23.27 g, 103.3 mmol) in THF (200 mL) at –78 °C. After 25 min, the resulting mixture was cannulated to a solution of CuCN (9.25 g, 103.3 mmol) and LiCl (8.80 g, 206.7 mmol) in THF (200 mL) at –78 °C. The reaction mixture was allowed to stir for 45 min at –78 °C, after which a solution of lactone **4** (8.74 g, 25.8 mmol) in THF (100 mL) was added dropwise. Following slow warming to rt over 18 h, the reaction mixture was poured into a 1:1 NH_4OH/ saturated NH_4Cl solution, extracted with ether, and washed with saturated NaCl solution. The crude product was dried over $MgSO_4$, and concentrated in vacuo. The crude product was then dissolved in 4.5 mL NEt_3 and purified by flash chromatography over silica gel eluting with ether, then 1% acetic acid in ether to give the acid (9.74 g**,** 91%) as a yellow oil. IR (film) 1716 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 3H), 1.70 (s, 3H), 1.75 (s, 3H), 2.14 (dd, 1H, J=5.5, 18.9 Hz), 2.43 (m, 1H), 2.65 (d, 1H, J=6.3 Hz), 2.79 (m, 2H), 3.10 (m, 1H), 3.35 (s, 3H), 3.44 (m, 2H), 4.52 (s, 2H), 4.59 (s, 2H), 4.67 (s, 2H), 5.49 (d, 1H, J=4.3 Hz), 5.58 (t, 1H, J=6.9 Hz), 7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.19, 21.75, 22.52, 25.68, 35.46, 38.70, 39.11,

55.30, 66.65, 69.66, 80.40, 96.60, 110.17, 119.43, 123.80, 127.81, 127.82, 128.47, 131.82, 137.46, 137.96, 147.77, 177.91. Anal Calcd for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.17; H, 8.27.

The acid (9.74 g, 23.5 mmol) was then dissolved in ether (20 mL) and treated with an ethereal solution of diazomethane at rt until the reaction was complete (monitored by TLC). Excess diazomethane was quenched with a few drops of acetic acid and the reaction mixture was concentrated in vacuo. The product was purified by flash chromatography over silica gel using 5/95 ethyl acetate/hexanes to give MOM ether **5** (9.61 g, 95%) as a clear oil. IR (film) 2929, 1735, 1455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3H), 1.64 (s, 3H), 1.68 (s, 3H), 2.07 (dd, 1H, J=5.3, 19.0 Hz), 2.36 (d, 1H, J=19.0 Hz), 2.59 (d, 1H, J=6.3 Hz), 2.67 (d, 2H, J=7.0 Hz), 3.03 (m, 1H), 3.27 (s, 3H), 3.27 (m, 1H), 3.39 (t, 1H, J=9.9 Hz), 3.68 (s, 3H), 4.41 (s, 2H), 4.52 (s, 2H), 4.61 (s, 2H), 5.41 (d, 1H, J=4.0 Hz), 5.52 (t, 1H, J=6.9 Hz), 7.23 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.19, 21.69, 22.49, 25.54, 35.39, 38.56, 38.88, 52.06, 55.22, 66.90, 69.36, 80.34, 96.56, 110.07, 120.00, 123.41, 127.50, 127.62, 128.32, 131.87, 136.91, 138.53, 147.73, 174.65; Anal Calcd for $C_{26}H_{36}O_5$: C, 72.87; H, 8.47. Found: C, 72.61; H, 8.52.

Alcohol 6. $Rh(PPh_3)_3Cl$ (0.96 g, 10% wt of **5**) and MOM ether **5** (9.61 g, 22.4 mmol) in dry benzene (100 mL) was placed in a pressure vessel and shaken under 35 psi of H_2 for 22 h. The reaction mixture was then filtered through a pad of silica gel with ether. The filtrate was then concentrated in vacuo and the residue purified by flash chromatography over silica gel using 5/95ethyl acetate/hexanes to give the diene (9.47 g, 98%) as a yellow oil. IR (film) 2950, 1735, 1455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, 6H, J= 6.5 Hz), 1.45 (m, 1H), 1.52 (s, 3H), 1.61 (m, 1H), 1.78 (s, 3H), 2.12 (dd, 1H, J=5.5, 18.7 Hz), 2.28 (d, 1H, J=19.0 Hz), 2.80 (d, 2H, J=7.1 Hz), 3.11 (m, 1H), 3.36 (s, 3H), 3.36 (m, 1H), 3.49 (t, 1H, J=9.5 Hz), 3.78 (s, 3H), 4.52 (s, 2H), 4.60 (s, 2H), 5.44 (d, 1H, J=4.3 Hz), 5.61 (t, 1H, J= 6.8Hz), 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.06, 21.10, 21.73, 21.87, 24.33, 28.38, 36.04, 37.85, 39.46, 52.06, 55.17, 66.91, 69.51, 80.37, 96.55, 119.84, 123.68, 127.50, 127.63, 128.32, 132.13, 137.06, 138.54, 174.36; Anal Calcd for $C_{26}H_{38}O_5$: C, 72.53; H, 8.90. Found: C, 72.41; H, 9.08.

Five drops of concentrated HCl was added to a solution of the reduced MOM ether (9.47 g, 24.5 mmol) in iPrOH (70 mL) and heated to 65 °C. After12 h, the reaction mixture was concentrated in vacuo, dissolved in ether, washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes to give alcohol **6** (7.65 g, 90%) as a yellow oil. IR (film) 3447, 2952, 1735, 1455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, 6H, J=6.1 Hz), 1.35 (m, 2H), 1.45 (s, 3H), 1.71 (s, 3H), 2.00 (dd, 1H, J=5.4, 19.0 Hz), 2.12 (m, 1H), 2.61 (dd, 1H, J=6.7, 15.7 Hz), 2.80 (dd, 1H, J=7.3, 15.7 Hz), 2.93 (t, 1H, J=7.0 Hz), 3.43 (d, 2H, J=7.4 Hz), 3.69 (s, 3H), 4.44 (s, 2H), 5.34 (s, 1H), 5.60 (t, 1H, J=7.0 Hz), 7.24 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.15, 21.05, 21.50, 21.57, 24.71, 28.66, 36.60, 40.43, 40.44, 52.18, 65.53, 66.98, 80.44, 120.21, 123.96, 127.53, 127.56, 128.32, 131.81, 137.35, 138.48, 174.77; Anal Calcd for $C_{24}H_{34}O_4$: C, 74.58; H, 8.87. Found: C, 74.30; H, 8.93.

***E*-Vinylsulfone 7.** DMSO (1.51 g, 19.4 mmol) was added dropwise to a solution of oxalyl chloride (1.97 g, 15.5 mmol) in CH_2Cl_2 (100 mL) at –78 °C. After 30 min, alcohol **6** (3.00 g, 7.8 mmol) in CH_2Cl_2 (20 mL) was added dropwise. After 30 min, NEt_3 (3.96 g, 38.8 mmol) was added and the solution allowed to warm to rt over 1 h. After 1 h, the reaction mixture was washed with saturated $NaHCO_3$ solution, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes to give the aldehyde (2.84 g, 95 %) as a clear oil. IR (film) 2956, 1728, 1600, 1445 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, 6H, J=6.8 Hz), 1.42 (s, 3H), 1.43 (m, 1H), 1.76 (s, 3H), 1.84 (m, 1H), 2.07 (m, 2H), 2.61 (m, 2H), 3.46 (s, 1H), 3.67 (s, 3H), 4.41 (s, 2H), 5.42 (s, 1H), 5.76 (t, 1H, J=7.0 Hz), 7.24 (m, 5H), 9.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.95, 20.99, 21.10, 21.89, 25.44, 28.58, 36.58, 39.62, 52.02, 52.16, 66.99, 80.24, 122.16, 124.92, 127.55, 127.65, 128.33, 132.58, 132.75, 138.38, 174.31, 202.77.

KHMDS (7.50 mL, 0.5 M in toluene, 3.75 mmol) was added dropwise to a solution of the α-methyl sulfonyl phosphonate (1.24 g, 4.1 mmol) and 18-crown-6 (1.65 g, 6.2 mmol) in THF (75 mL) at –78 °C. After 1 hr, the aldehyde (1.20 g, 3.1 mmol) in THF (15 mL) was added dropwise at –78 °C and the reaction mixture was allowed to warm to rt. After 48 h, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes to give *E*-Vinylsulfone **7** (1.14 g, 68%) as a clear oil. IR (film) 2956, 1738, 1304, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.76 (d, 3H, J=6.6 Hz), 0.79 (d, 3H, J= 6.6Hz), 1.17 (m, 1H), 1.30 (s, 3H), 1.41 (m, 1H), 1.74 (s, 3H), 1.85 (d, 3H, J= 1.2Hz), 2.10 (m, 2H), 2.38 (dd, 1H, J=7.1, 15.7 Hz), 2.51 (dd, 1H, J=6.8, 15.7 Hz), 3.57 (dd, 1H, J=2.1, 9.8 Hz), 3.65 (s, 3H), 4.32 (s, 2H), 5.50 (t, 2H, J=6.3 Hz), 6.75 (dd, 1H, J=1.3, 9.6 Hz), 7.23 (m, 5H), 7.47 (m, 3H), 7.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.50, 20.05, 21.05, 21.18, 21.88, 25.12, 28.39, 36.37, 37.58, 44.60, 52.18, 66.98, 80.16, 120.75, 124.67, 127.60, 127.68, 127.95, 128.35, 129.12, 131.63, 133.09, 135.60, 136.56, 138.28, 139.44, 143.05, 174.21.

Diol 8. OsO_4 (0.37 mL, 0.16 M in H_2O, 0.06 mmol) was added to a solution of $(DHQ)_2PYR$ (0.10 g, 0.12 mmol), $K_3Fe(CN)_6$ (1.16 g, 3.5 mmol) and K_2CO_3 (0.49 g, 3.5 mmol) in a 1:1 *t*-BuOH/H_2O (30 mL) solution at rt. After 5 min, methanesulfonamide (0.11 g, 1.8 mmol) was added directly. After 5 min, *E*-vinylsulfone **7** (0.63 g, 1.8 mmol) in *t*-BuOH (5 mL) was added and the reaction mixture was allowed to stir for 12 h. Saturated $Na_2S_2O_3$ solution was then added to the reaction mixture. After stirring for 30 min, the crude mixture was extracted with ethyl acetate, dried with $MgSO_4$, and concentrated in vacuo. The crude mixture was purified by flash chromatography over silica gel using 30/70 ethyl acetate/hexanes to give diol **8** (0.56 g, 84%) as a white foam. IR (film) 3492, 2956, 1736, 1300, 1138 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.70 (d, 3H, J=6.5 Hz), 0.80 (d, 3H, J=6.4 Hz), 1.32 (s, 3H), 1.34 (s, 3H), 1.43 (m, 2H), 1.59 (td, 1H, J=5.1, 10.8 Hz), 1.75 (m, 1H), 1.81 (d, 3H, J=1.1 Hz), 2.42 (d, 2H, J=7.1 Hz), 2.55 (s, 1H), 3.37 (m, 2H), 3.64 (s, 3H), 4.32 (s, 2H), 5.72 (t, 1H, J=6.8 Hz), 7.21 (m, 6H), 7.44 (m, 3H), 7.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.46, 18.73, 21.97, 22.05, 24.30, 27.45, 28.87, 36.77, 38.98, 44.22, 52.25, 66.96, 71.90, 74.62, 79.95, 123.56, 127.60, 127.64, 128.00, 128.34, 129.10, 133.08, 134.61, 138.29, 139.41, 141.09, 144.67, 174.19.

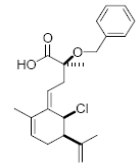
Hydroxy ketone 9. DMSO (0.19 g, 2.4 mmol) was added dropwise to a solution of oxalyl chloride (0.25 g, 1.9 mmol) in CH_2Cl_2 (30 mL) at –78 °C. After 30 min, diol **8** (0.56 g, 0.99 mmol) in CH_2Cl_2 (20 mL) was added dropwise. After 30 min, NEt_3 (0.50 g, 4.9 mmol) was added and the solution was allowed to warm to rt over 1 h. After 1 h, the reaction mixture was washed with saturated $NaHCO_3$ solution, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated in vacuo. The crude mixture was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes togive hydroxy ketone **9** (0.37 g, 65 %) as a white foam. IR (film) 3466, 2959, 1727, 1303, 1114 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.62 (d, 3H, J=6.8 Hz), 0.76 (d, 3H, J=6.8 Hz), 1.38 (s, 3H), 1.40 (s, 3H), 1.55 (m, 1H), 1.83 (d, 3H, J=1.4 Hz), 2.05 (m, 1H), 2.12 (dd, 1H, J=12.4, 14.6 Hz), 2.41 (m, 3H), 2.98 (s, 1H), 3.37 (t, 1H, J=9.6 Hz), 3.65 (s, 3H), 4.31 (s, 2H), 5.85 (t, 1H, J=7.0 Hz), 6.98 (dd, 1H, J=1.3, 10.4 Hz), 7.22 (m, 5H), 7.41 (m, 2H), 7.51 (m, 1H), 7.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.85, 15.92, 21.10, 21.83, 23.48, 28.58, 36.13, 36.83, 40.37, 44.17, 52.20, 67.02, 77.93, 79.87, 124.63, 127.64, 127.71, 128.08, 128.34, 129.16, 133.28, 136.24, 138.23, 139.16, 140.02, 141.83, 174.05, 210.44.

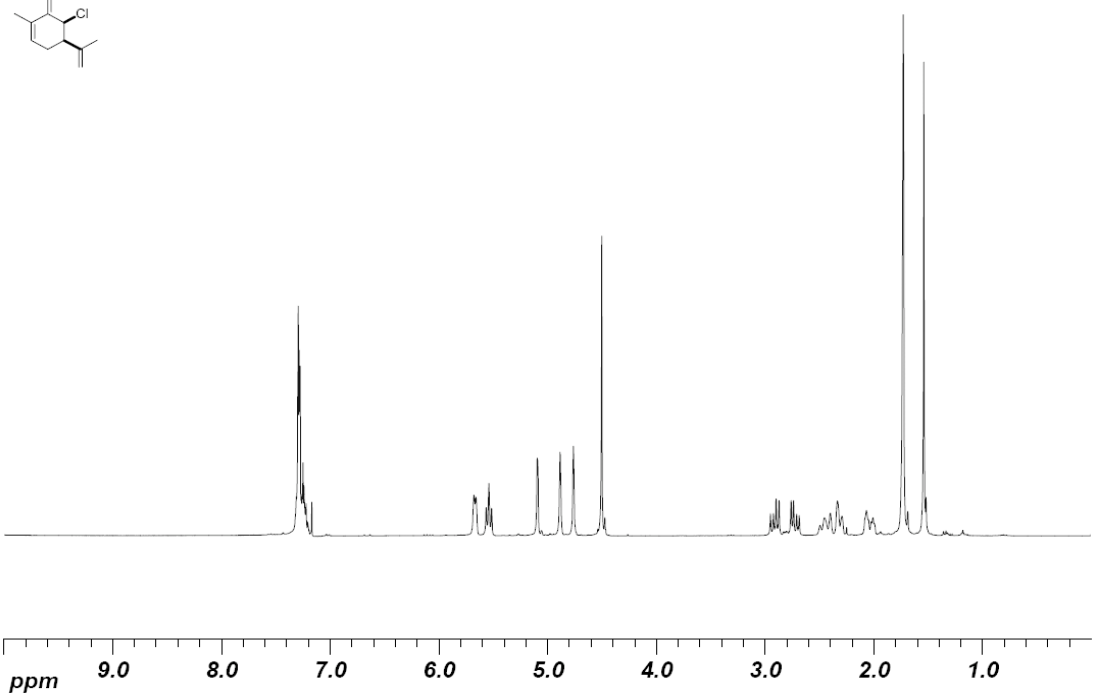
Hydroxy enone 10. Hydroxy ketone **9** (0.86 g, 1.51 mmol) in dry benzene (20 mL) was transferred to a solution of methyltrioxorhenium (0.038 g, 0.15 mmol) in dry benzene (60 mL) at rt. After 48 h, the reaction mixture was filtered thru pad of silica gel with ether and then concentrated to give hydroxy enone **10** (0.86 g, 99%) as a white foam. IR (film) 3498, 2959, 1738, 1665, 1301, 1133 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, 3H, J=6.2 Hz), 0.88 (d, 3H, J=6.2 Hz), 1.46 (m, 2H), 1.59 (s, 3H), 1.70 (s, 3H), 1.76 (d, 3H, J=1.2 Hz), 2.06 (dd, 1H, J=10.4, 14.3 Hz), 2.45 (d, 1H, J=17.2 Hz), 2.58 (dd, 1H, J=4.4, 17.2 Hz), 3.03 (d, 1H, J=2.0 Hz), 3.49 (d, 1H, J=9.3 Hz), 3.66 (s, 3H), 4.45 (d, 1H, J=10.6 Hz), 4.53 (d, 1H, J=10.6 Hz), 5.07 (d, 1H, J=10.4 Hz), 6.91 (dd, 1H, J=1.3, 9.3 Hz), 7.26 (m, 5H), 7.34 (t, 2H, J=7.7Hz), 7.47 (m, 1H), 7.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.43, 11.71, 20.34, 20.86, 21.60, 28.65, 37.34, 37.61, 44.27, 47.07, 52.43, 67.34, 67.40, 79.84, 127.70, 127.82, 127.90, 128.53, 129.00, 130.87, 133.04, 136.31, 137.73, 139.12, 143.87, 156.43, 174.07, 197.66.

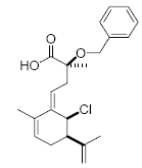
Isobenzofuranone 11. Hydroxy enone **10** (0.86 g, 1.5 mmol) was dissolved in 15 mL of a saturated K_2CO_3 methanol solution and stirred for 3 h at rt. The reaction mixture was then diluted with ether, washed with 1 N HCl solution, extracted, dried over $MgSO_4$ and concentrated in vacuo. The crude mixture was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes to give isobenzofuranone **11** (0.77 g, 90%) as a white foam. IR (film) 2959, 1732, 1666, 1305, 1128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.71 (d, 3H, J=6.8 Hz), 0.83 (d, 3H, J=6.7 Hz), 1.16 (s, 3H), 1.33 (d, 3H, J=7.0 Hz), 1.61 (s, 3H), 1.68-1.96 (m, 4H), 2.04 (d, 1H, J=13.5 Hz), 2.34 (d, 1H, J=15.5 Hz), 2.48 (m, 1H), 3.25 (q, 1H, J=7.0 Hz), 3.70 (s, 3H), 4.31 (d, 1H, J=10.0 Hz), 4.37 (d, 1H, J=11.2 Hz), 4.40 (d, 1H, J=11.2 Hz), 4.79 (d, 1H, J=9.3 Hz), 7.21 (m, 5H), 7.48 (t, 2H, J=7.5 Hz), 7.58 (m, 1H), 7.83 (d, 2H, J=7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.03, 10.58, 15.46, 20.76, 21.72, 27.76, 35.90, 45.16, 45.25, 45.76, 52.39, 64.10, 66.67, 75.69, 79.10, 79.79, 127.36, 127.49, 127.62, 128.29, 129.05, 129.42, 133.77, 137.65, 138.44, 161.91, 173.63, 199.07; Anal Calcd for $C_{32}H_{40}O_7S$: C, 67.58; H, 7.09. Found: C, 67.58; H, 6.99.

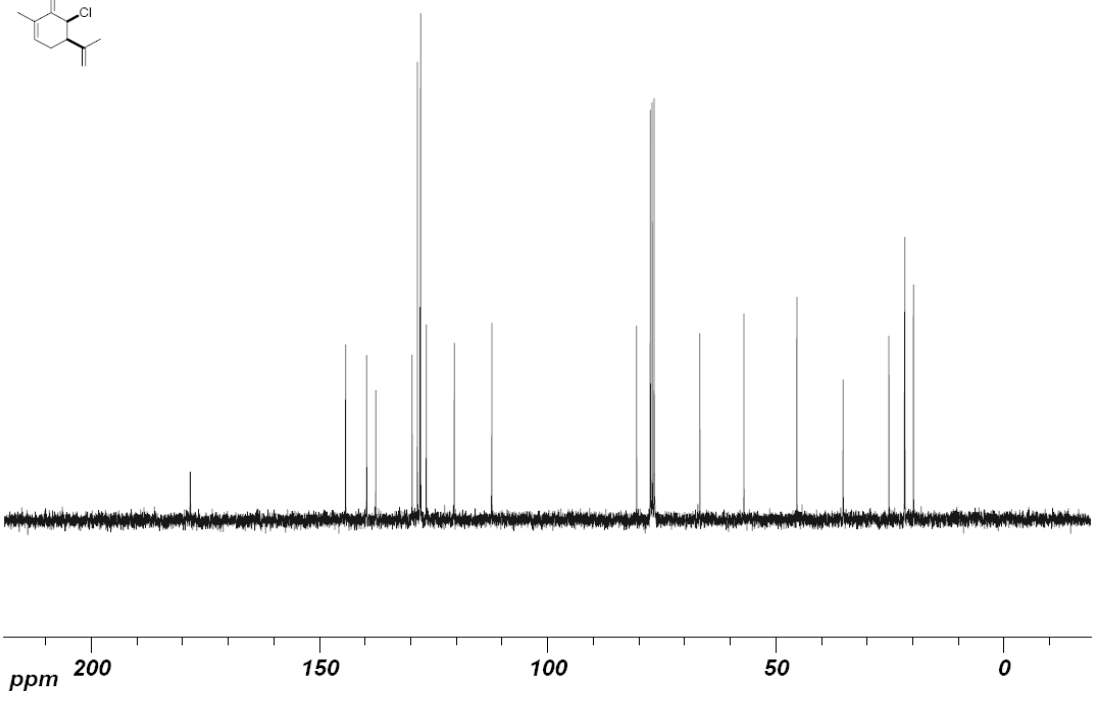
Isobenzofuran 13. Tosylhydrazide (0.12 g, 0.65 mmol) was added to a solution of isobenzofuranone **11** (0.19 g, 0.33 mmol) in absolute ethanol (5 mL). The reaction mixture was heated under reflux for 3 h. The solvent was removed in vacuo to afford a pale yellow foam. The foam was dissolved in anhydrous $CHCl_3$ (15 mL) and catecholborane (0.079 g, 0.66 mmol) was added dropwise at 0 °C. The reaction mixture was allowed to warm to rt over 1.5 h and then cooled to 0 °C. $NaOAc.3H_2O$ (0.13 g, 0.98 mmol) was added in one portion and the reaction mixture was maintained at 0 °C for 1 h. Following the addition of 10 mL of $CHCl_3$, the reaction mixture was heated under reflux for 1 h, cooled to rt and filtered through a pad of Celite. The filtrate was concentrated in vacuo and crude mixture was purified by flash chromatography over silica gel using 10/90 ethyl acetate/hexanes to give isobenzofuran **13** (0.14 g, 77%) as a white foam. IR (film) 2955, 2876, 1737, 1304, 1136 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.72 (d, 3H, J=6.7 Hz), 0.78 (d, 3H, J=6.7 Hz), 1.12 (m, 1H), 1.22 (d, 3H, J=7.0 Hz), 1.24 (s, 3H), 1.46 (dq, 1H, J=6.6, 13.2 Hz), 1.56 (s, 3H), 1.78 (s, 2H), 1.88 (dd, 1H, J=9.0, 14.2 Hz), 1.96 (m, 1H), 2.06 (m, 1H), 2.18 (dd, 1H, J=1.8, 14.2 Hz), 3.01 (dq, 1H, J=1.3, 7.0 Hz), 3.64-3.70 (m, 1H), 3.67(s, 3H), 4.20 (d, 1H, J=7.5 Hz), 4.33 (d, 1H, J=11.2 Hz), 4.40 (d, 1H, J=11.2 Hz), 5.29 (s, 1H), 7.20 (m, 5H), 7.44 (t, 2H, J=7.5 Hz), 7.53 (m, 1H), 7.81 (d, 2H, J=7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.26, 19.09, 21.30, 21.94, 22.41, 23.24, 28.28, 38.42, 43.25, 46.88, 47.60, 52.13, 63.43, 66.49, 79.39, 79.72, 121.72, 127.36, 127.43, 128.24, 128.96, 129.32, 131.88, 133.47, 137.82, 138.75, 173.92.

Acid 3

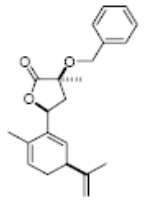


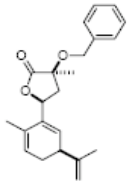




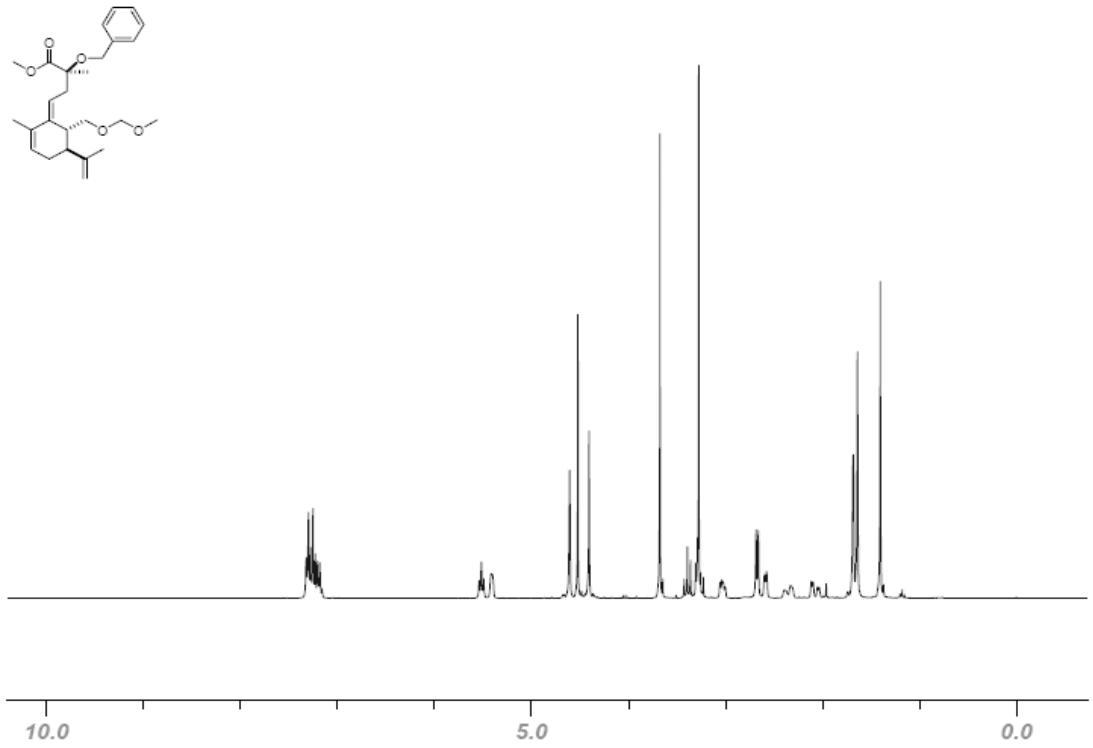


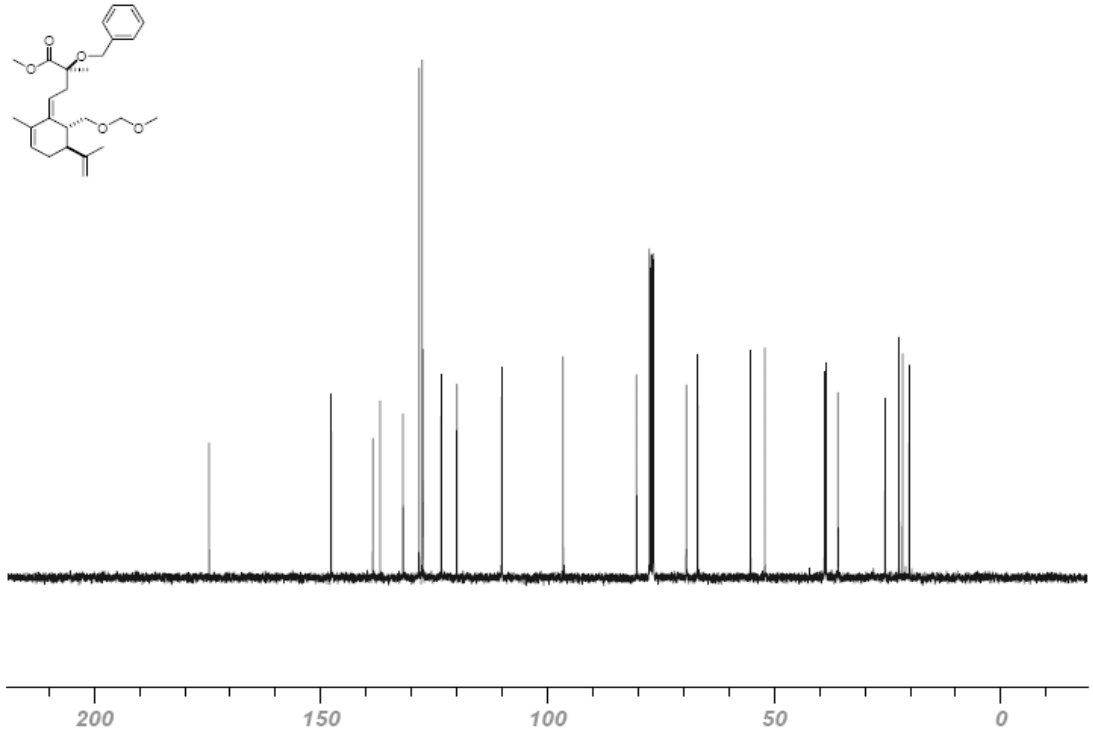
Lactone 4



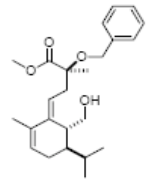


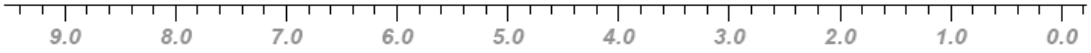
MOM ether 5

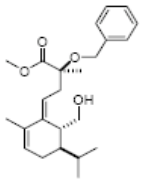




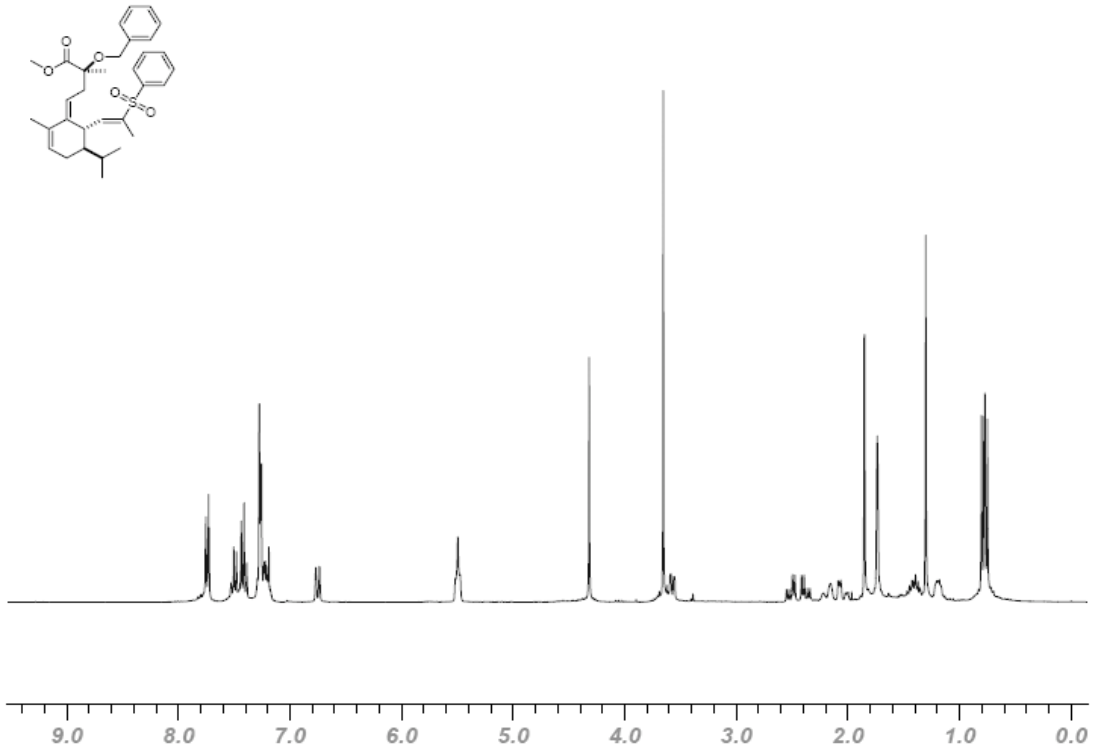
Alcohol 6

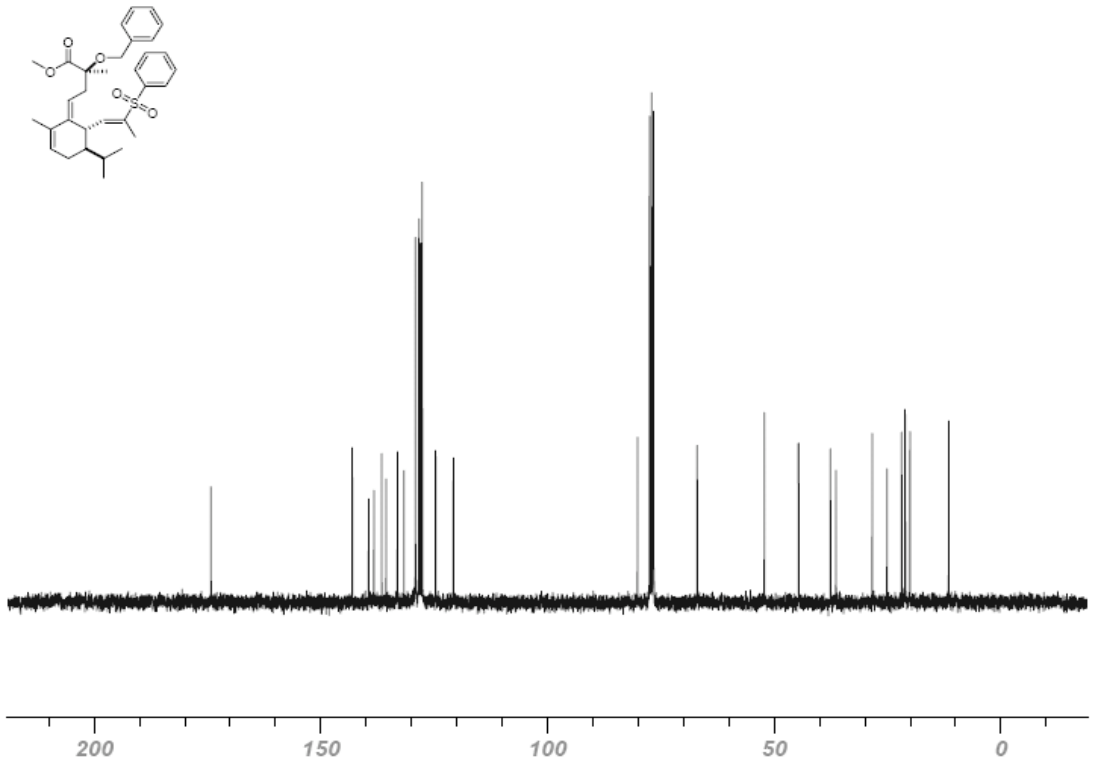




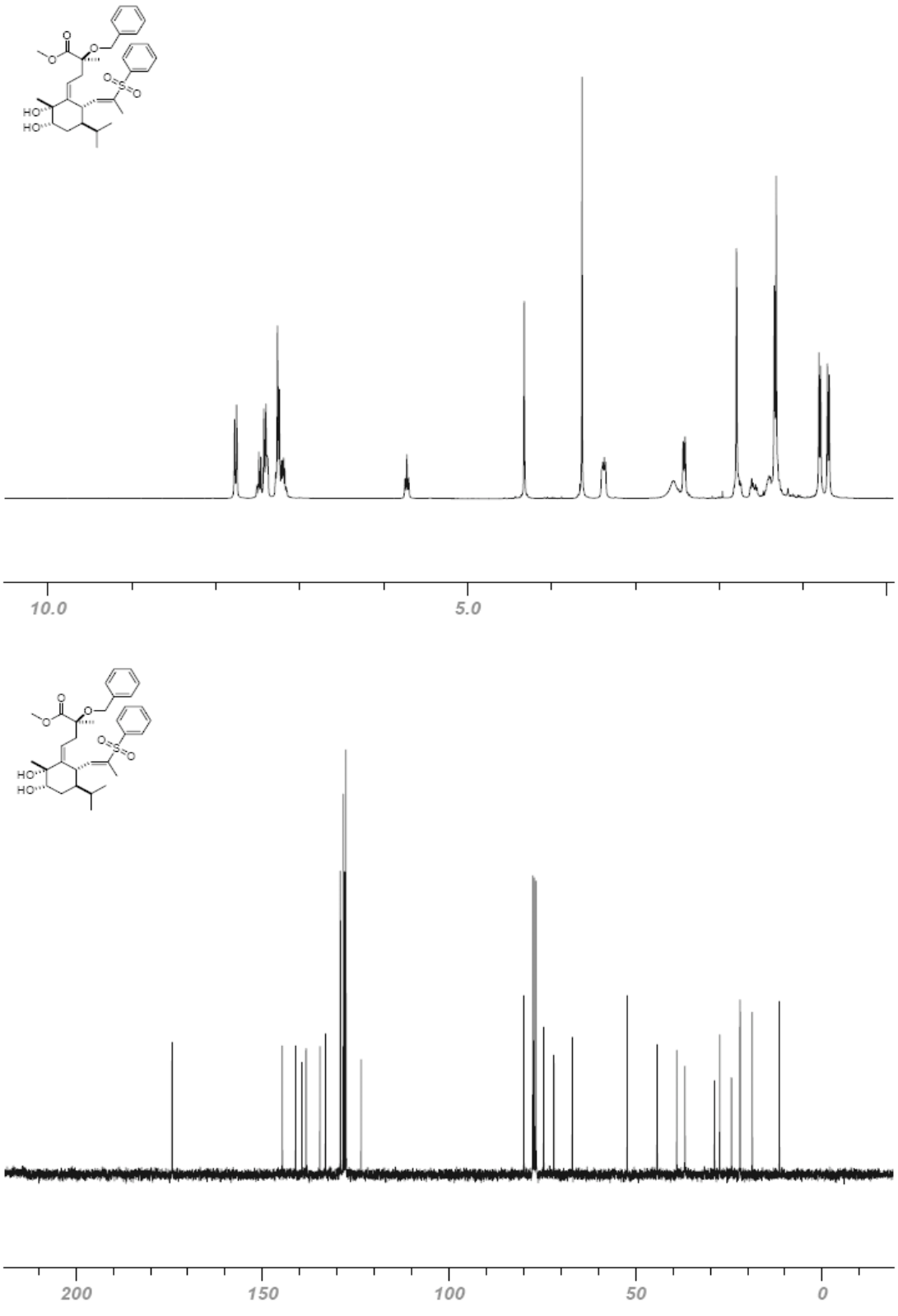


***E*-Vinylsulfone** 7

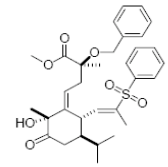


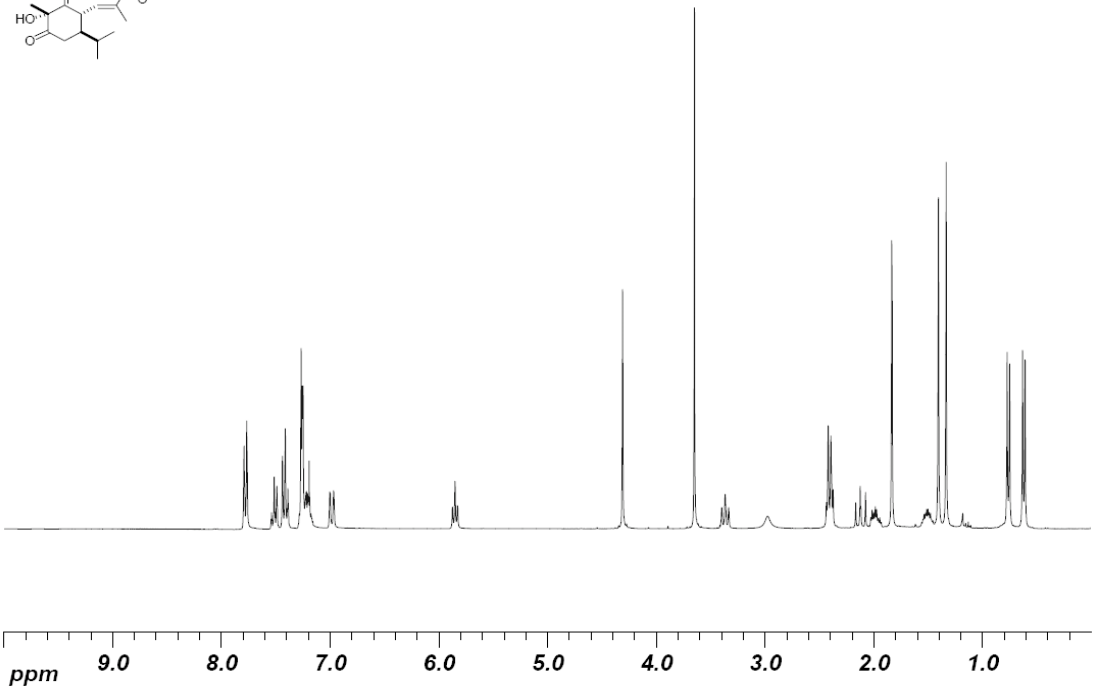


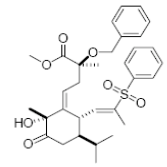
Diol 8

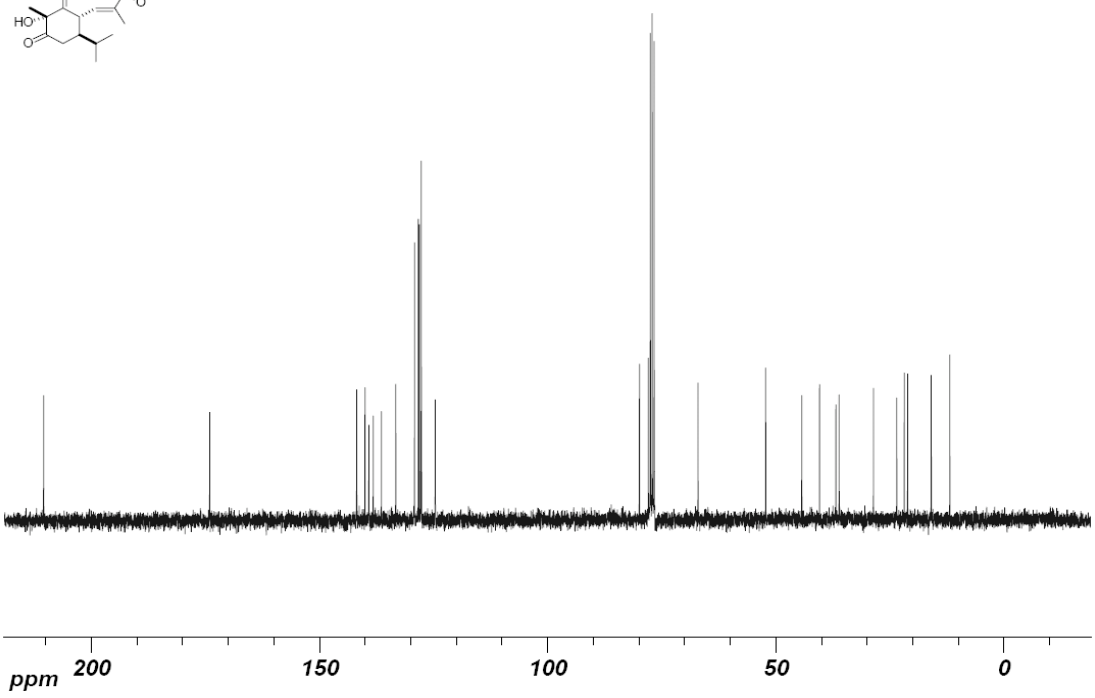


Hydroxy ketone 9

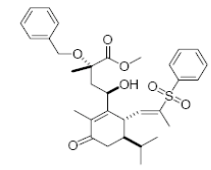


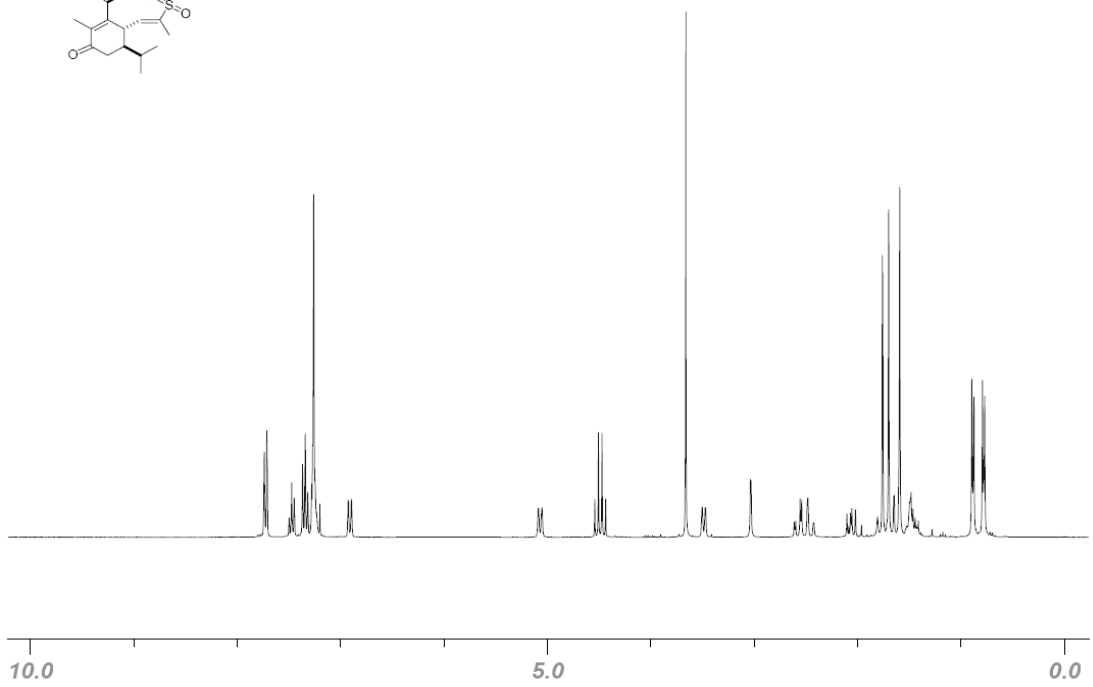


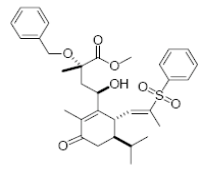


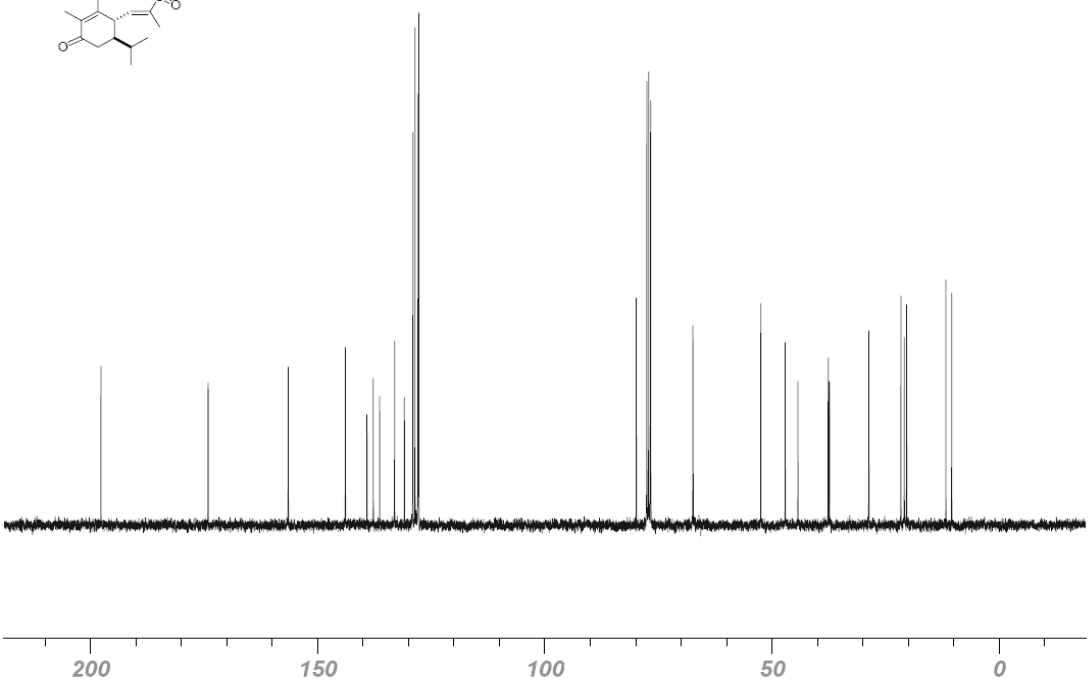


Hydroxy enone 10

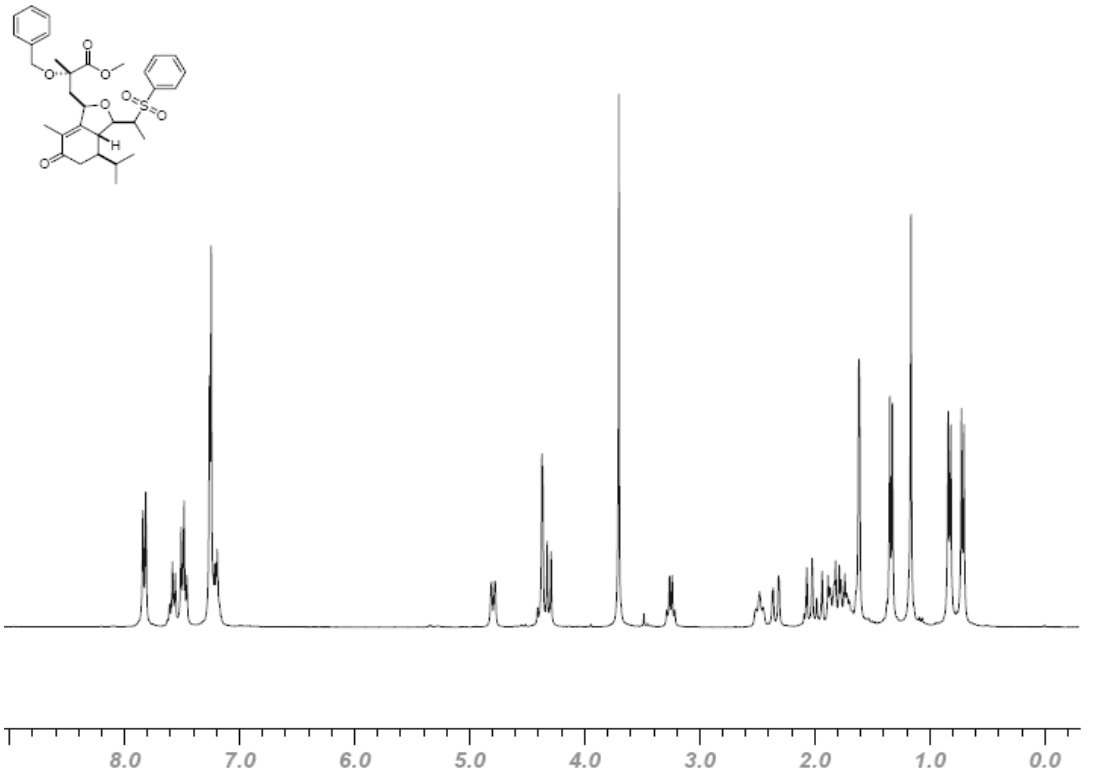


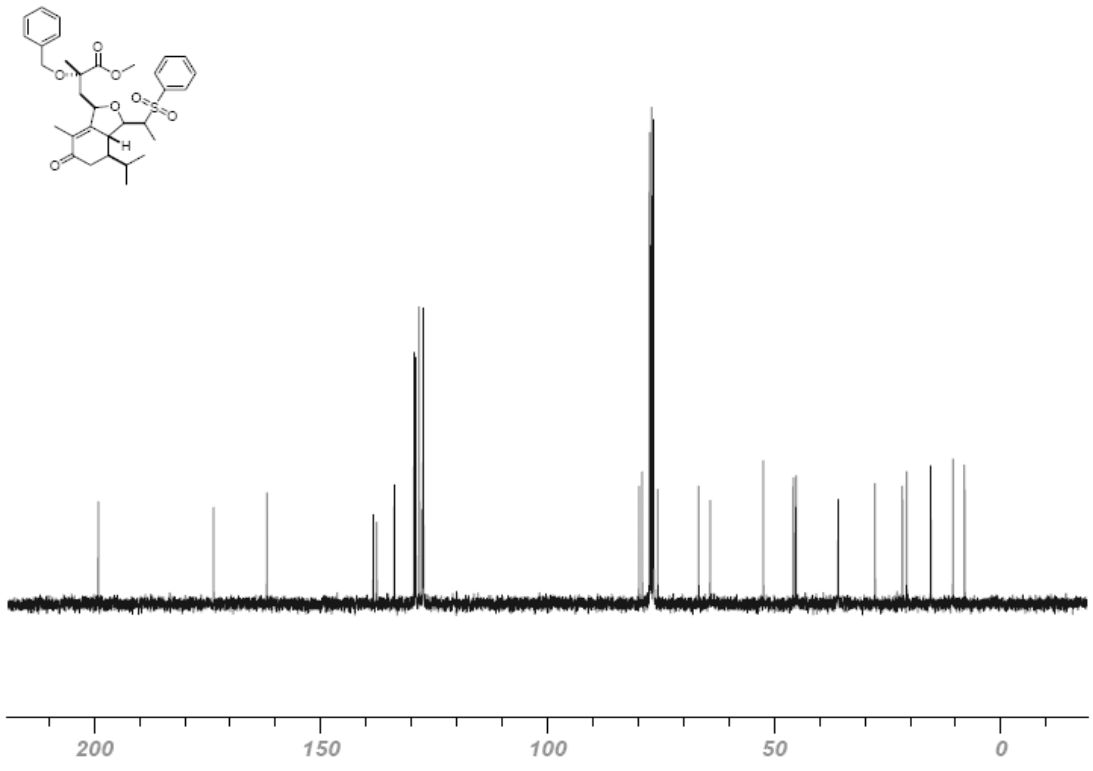




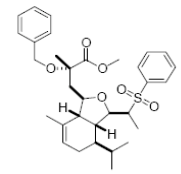


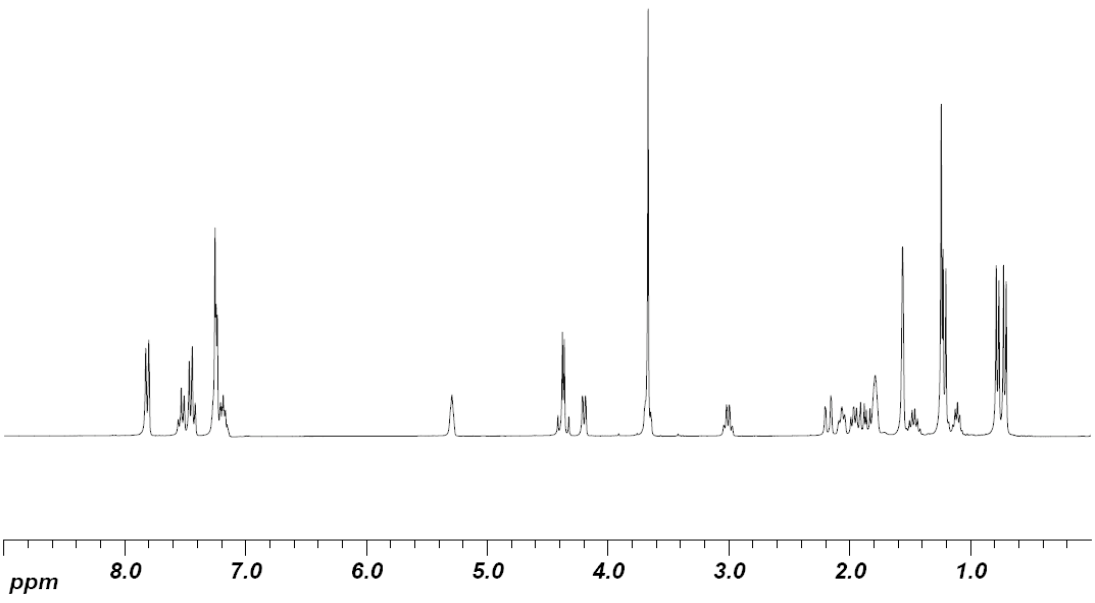
Isobenzofuranone 11

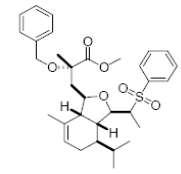


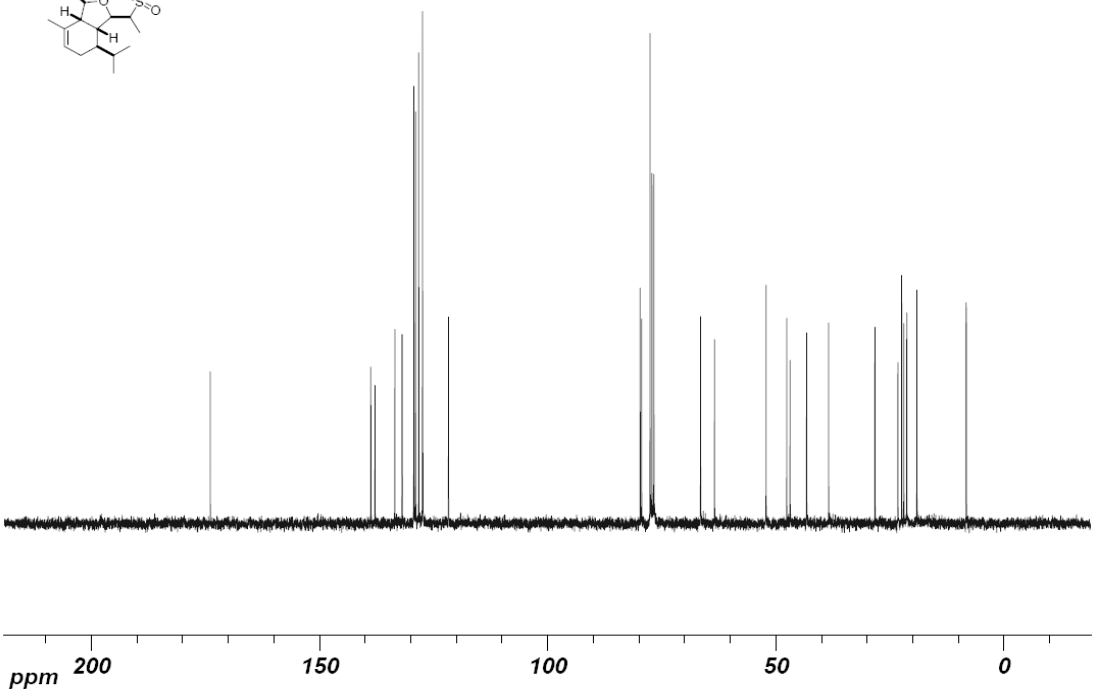


Isobenzofuran 13









Isobenzofuran 13