Supporting Information

Asymmetric Total Synthesis of Propindilactone G

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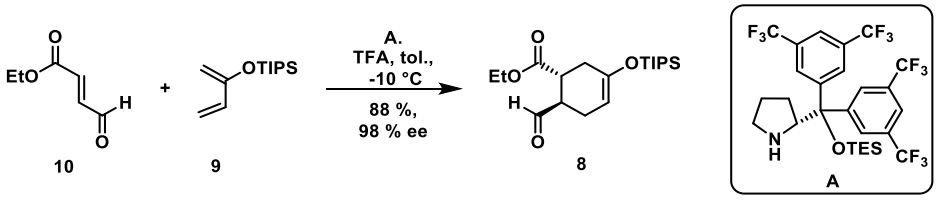
I: Experimental Procedures and Spectroscopic Data of the Synthesized Compounds

General Procedure. Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

Reactions were monitored by Thin Layer Chromatography on plates (GF254) supplied by Yantai Chemicals (China) visualized by UV or stained with ethanolic solution of phosphomolybdic acid and cerium sulfate, basic solution of $KMnO_4$, and iodine vapor. If not specially mentioned, flash column chromatography was performed using E. Merck silica gel (60, particle size 0.040–0.063 mm). NMR spectra were recorded on Bruker AV400, Bruker AV500 instruments and calibrated by using residual undeuterated chloroform (δH = 7.26 ppm) and $CDCl_3$ (δC = 77.0 ppm), or undeuterated pyridine (δ_H = 8.71 ppm) and pyridine-d5 (δ_C = 150.1 ppm) as internal references. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, td = triple doublet, dt = double triplet, dq = double quartet, m = multiplet. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) as ionization method.

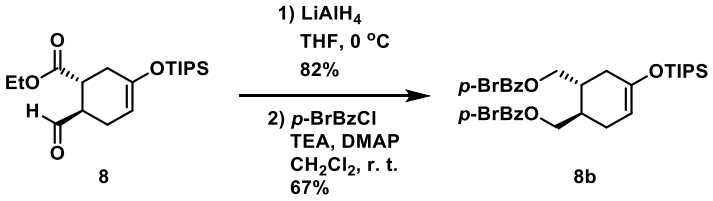
Synthesis of compound **8**:



10 9 8

To a solution of dienophile **10** (50 g, 390 mmol) and catalyst **A** (25 g, 39 mmol) in toluene (80 mL) was added a solution of trifluoromethanesulfonic acid (8.9 g, 78 mmol) in toluene (160 mL), and the mixture was then cooled to - 10 ^{o}C. To this solution was added diene **9** 106 g, 468 mmol) slowly during 15 min. and the resultant mixture was stirred at - 10 ^{o}C for 7 h. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ (200 mL) at - 10 ^{o}C, and the mixture was then extracted with petroleum ether (3× 250 mL). The combined organic layers were washed with brine (250 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to give product **8** (121.5 g, 88% yield, 98% *e.e.*) as yellow oil; R_f = 0.60 (silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = - 16.1 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2944, 2867, 1731, 1673, 1465, 1368, 1204 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.67 (d, *J* = 1.1 Hz, 1H), 4.84 (td, *J* = 3.3, 1.6 Hz, 1H), 4.15 (qd, *J* = 7.1, 4.9 Hz, 2H), 3.01 – 2.92 (q, *J* = 8.0 Hz, 1H), 2.82 (tdd, *J* = 9.0, 5.6, 1.0 Hz, 1H), 2.40 – 2.29 (m, 3H), 2.15 (ddt, *J* = 17.2, 8.6, 2.6 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.15 – 1.08 (m, 3H), 1.04 (d, *J* = 6.4 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 173.8, 149.3, 99.9, 61.0, 47.3, 39.9, 22.8, 17.9, 14.1, 12.6 ppm; HRMS (ESI): *m/z* calcd for $C_{19}H_{35}O_4Si$ $[M + H]^+$: 355.2299, found 355.2310.

Synthesis of compound **8b** for the *ee* value detection of compound **8**:

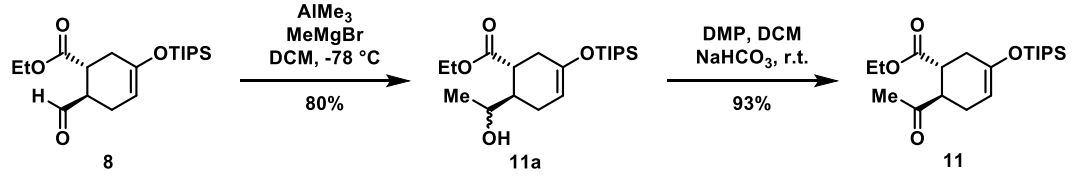


8 8b

To a solution of compound **8** (217 mg, 0.61 mmol) in THF (2 mL) was added lithium aluminum hydride (1.5 mL, 2.4 M, 3.6 mmol) at 0 ^{o}C, and the mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with a saturated solution of NH_4Cl (3 mL) and Rochelle salt (3 mL), and the mixture was extracted with EtOAc (3×3 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, 1% TEA) to give alcohol **8a** (157 mg, 82% yield) as colorless oil.

To a solution of alcohol **8a** (51 mg, 0.16 mmol) in CH_2Cl_2 (1 mL) was added TEA (37 mg, 0.37 mmol), *p*-BrBzCl (86 mg, 0.39 mmol) and DMAP (7 mg, 0.06 mmol) at room temperature. After stirring at room temperature for 17 h, the reaction mixture was quenched with a saturated solution of NH_4Cl (1 mL), and the mixture was extracted with CH_2Cl_2 (3×2 mL). The combined organic layers were washed with brine (2 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1, 1% TEA) to give product **8b** (73 mg, 67% yield, 98% *e.e.*) as colorless oil. R_f = 0.70 (silica gel, petroleum ether/ethyl acetate = 1:1); $[\alpha]_D^{25}$ = - 43.5 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2942, 2864, 1720, 1590, 1267, 1199, 1113, 1102, 1012, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 4H), 7.53 (dd, *J* = 8.5, 3.9 Hz, 4H), 4.86 (s, 1H), 4.37 (d, *J* = 5.2 Hz, 4H), 2.30 – 2.27(m, 3H), 2.19 – 2.06 (m, 3H), 1.18 – 1.12 (m, 3H), 1.08 (d, *J* = 6.4 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 148.9, 131.8, 131.2, 131.2, 129.1, 129.1, 128.3, 128.3, 100.9, 67.2, 67.1, 35.7, 34.7, 31.9, 26.2, 18.1, 12.8 ppm; HRMS (ESI): *m/z* calcd for $C_{31}H_{40}Br_2O_5Si$ $[M + H]^+$: 679.1084, found 679.1080.

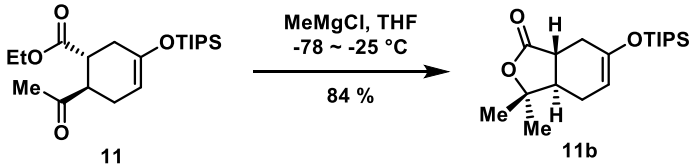
Synthesis of compound **11:**



To a solution of $AlMe_3$ (90.0 mL, 25% w/w in hexane, 228 mmol) was added methylmagnesium bromide (50.6 mL, 3.0 M, 152 mmol) in a drop-wise manner over 20 min at 0 ^oC, and the resultant gray suspension was first stirred for an additional 15 min. The formed mixture was first cooled to - 78 ^oC, and then stirred at the same temperature for 90 min. To this suspension was slowly added a solution of compound **8** (35.9 g, 101 mmol) in CH_2Cl_2 (500 mL), and the resultant light-yellow solution was then stirred at the same temperature for another 40 min. The reaction mixture was quenched with a saturated solution of Rochelle salt (500 mL) at -78 ^oC, and the mixture was extracted with EtOAc (3×200 mL). The combined organic layers were washed with saturated solution of Rochelle salt (100 mL) and brine (200 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give compound **11a** (30 g, 80 % yield) as colorless oil.

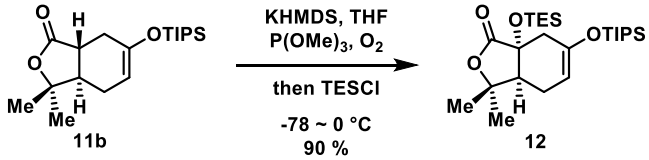
To a solution of compound **11** (30.0 g, 81 mmol) in CH_2Cl_2 (400 mL) was added $NaHCO_3$ (54.4 g, 648 mmol) and Dess-Martin periodinane (37.8 g, 89.1 mmol) at room temperature, and resultant mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with a saturated solution of $Na_2S_2O_3$ (400 mL), and the mixture was extracted with Et_2O (3×1 L). The combined organic layers were washed with brine (800 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give the product **11** (27.6g, 93% yield) as a colorless oil; R_f = 0.60 (Silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = - 17.7 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2949, 2866, 2339, 2358, 1739, 1733, 1716, 1204 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.85 – 4.84 (m, 1H), 4.13 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.01 – 2.78 (m, 2H), 2.45 – 2.33 (m, 2H), 2.28 – 2.19 (m, 4H), 1.95 – 2.07 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 – 1.11 (m, 3H), 1.07 (d, *J* = 6.4 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.9, 174.6, 149.0, 100.4, 60.7, 48.3, 41.8, 32.1, 29.1, 26.3, 17.9, 17.7, 14.1, 12.6 ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{37}O_4Si$ $[M + H]^+$: 369.2456, found 369.2456.

Synthesis of compound **11b**:



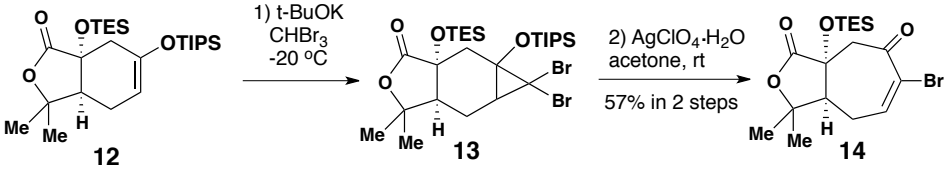
To a solution of compound **11** (27.5 g, 74.6 mmol) in THF (750 mL) was slowly added methylmagnesium chloride (37.3 mL, 3.0 M, 112 mmol) at - 78 ^oC, and the resultant mixture was warmed up - 25 ^oC, and stirred at the same temperature for 8 h. The reaction mixture was quenched with a saturated solution of NH_4Cl (750 mL), and the mixture was extracted with Et_2O (3× 500 mL). The combined organic layers were washed with brine (500 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (dichloromethane) to give product **11b** (21.2 g, 84% yield) as white solids; R_f = 0.70 (Silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = - 50.8 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2970, 2867, 1739, 1365, 1230, 1217, 1205 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.93 – 4.94 (m, 1H), 2.67 – 2.55 (m, 1H), 2.46 (dd, *J* = 10.8, 5.2 Hz 1H), 2.35 – 2.23 (m, 1H), 2.16 – 1.93 (m, 3H), 1.48 (s, 3H), 1.30 (s, 3H), 1.20 – 1.11 (m, 3H), 1.07 (d, *J* = 6.3 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 150.6, 102.4, 85.7, 47.9, 41.2, 30.5, 27.6, 23.3, 21.1, 18.0, 12.6 ppm; HRMS (ESI): *m/z* calcd for $C_{19}H_{35}O_3Si$ $[M + H]^+$: 339.2350, found 339.2342.

Synthesis of compound **12**:



To a solution of compound **11b** (501 mg, 1.48 mmol) in THF (9 ml) was added potassium bis(trimethylsilyl)amide (1.0 M solution in THF, 2.95 ml, 2.95 mmol) in drop-wise manner at -78 °C under nitrogen atmosphere, and the resultant mixture was stirred at the same temperature for 10 min. After warming up to 0 °C, the reaction mixture was stirred at the same temperature for 30 min, and then cooled back to -78 °C. To this solution was added $P(OMe)_3$ (0.35 ml, 3.0 mmol) in one portion, and the resultant mixture was degassed with O_2 for 3 times, and stirred at -78 °C for 20 min under oxygen atmosphere, and then stirred 0 °C for 1 h. After changing the reaction atmosphere from oxygen to nitrogen, the reaction mixture was treated with TESCl (0.30 ml, 1.8 mmol), and the formed mixture was stirred at 0 °C for 1 h. The reaction mixture was quenched with a saturated solution of NH_4Cl (10 mL), and the mixture was extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4. The solvent was removed under vacuum (warning: the remaining $P(OMe)_3$ is poisonous), and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200:1 – 120:1) to give product **12** (626 mg, 90% yield) as thick clear colorless oil; R_f = 0.60 (silica gel, petroleum ether/ethyl acetate = 12:1); $[\alpha]_D^{25}$ = + 42.3 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2948, 2892, 2868, 1779, 1680, 1465, 1390, 1374, 1363, 1211, 1137, 1104, 1003, 904, 883, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.85 (dt, *J* = 4.9, 2.4 Hz, 1H), 2.44 (ddt, *J* = 17.6, 8.4, 2.9 Hz, 1H), 2.37 (d, *J* = 1.9 Hz, 2H), 2.31 (d, *J* = 8.4 Hz, 1H), 2.03 (ddd, *J* = 17.8, 3.9, 1.6 Hz, 1H), 1.43 (s, 3H), 1.26 (s, 3H), 1.18 – 1.09 (m, 3H), 1.06 (d, *J* = 6.5 Hz, 18H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 8.5 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.0, 146.9, 99.6, 83.7, 49.2, 38.7, 30.5, 22.6, 20.7, 18.1, 12.7, 7.1, 6.2 ppm; HRMS (ESI): *m/z* calcd for $C_{25}H_{49}O_4Si_2^+$ $[M + H]^+$: 469.3164, found 469.3152.

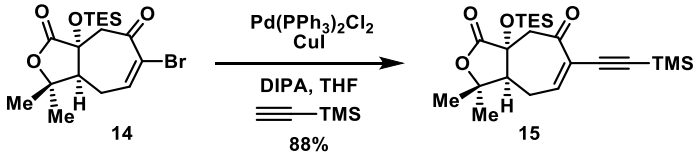
Synthesis of compound **14**:



To a solution of compound **12** (17.2 g, 36.7 mmol) in dry petroleum ether (680 mL) was added potassium *tert*-butoxide (41.2 g, 367 mmol), and the mixture was cooled to - 20 °C. To this solution was added a solution of bromoform (69.5 g, 275 mmol) in petroleum ether (220 mL) in a drop-wise manner over 1 h, and the resultant mixture was stirred at - 20 °C for another 45 min. The reaction mixture was filtered with a short pad of silica gel, and eluted with petroleum ether/ethyl acetate = 4:1. The eluent was removed under vacuum to afford unstable red-brown oil.

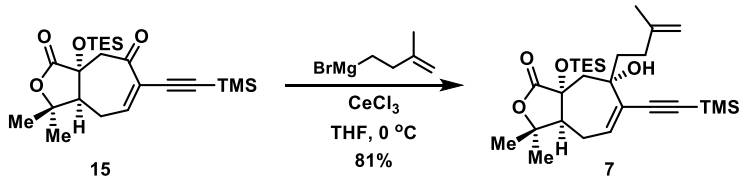
To a solution of the above oil in acetone (350 mL) was added $CaCO_3$ (36.7 g, 367 mmol) and silver perchlorate monohydrate (20.7 g, 91.7 mmol), the mixture was stirred at 30 °C for 2 h. The reaction mixture was quenched with TEA (85 mL), followed by addition of silica gel (85 g), and the solvent in the mixture was removed under vacuum. The residue absorbed on silica gel was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give the product **14** (8.4 g, 57% yield) as a white solid; R_f = 0.50 (Silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = + 83.5 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2954, 2875, 1753, 1683, 1269, 1192, 1069, 848, 749, 740, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.36 (m, 1H), 3.39 (d, *J* = 15.1 Hz, 1H), 2.83 (d, *J* = 15.1 Hz, 1H), 2.56 – 2.49 (m, 3H), 1.56 (s, 3H), 1.35 (s, 3H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.67 (q, *J* = 8.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.4, 174.3, 143.2, 129.5, 83.4, 78.6, 55.4, 48.9, 30.0, 27.8, 24.9, 6.8, 5.7 ppm; HRMS (ESI): *m/z* calcd for $C_{17}H_{27}BrO_4Si$ $[M + H]^+$: 403.0935, found 403.0945.

Synthesis of compound **15**:



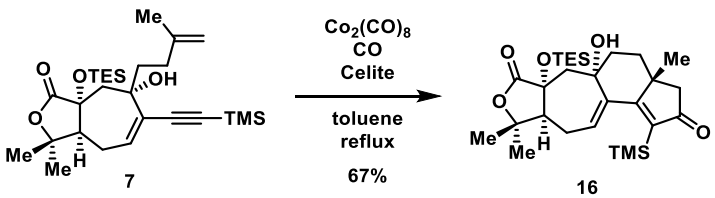
To a solution of compound **14** (29.40 g, 72.9 mmol) in THF (750 mL) was added $Pd(PPh_3)_2Cl_2$ (3.27 g, 4.7mmol) , copper(I) iodide (2.85 g, 15.0mmol) and diisopropylamine (30 mL, 214 mmol), and the resultant mixture was degassed with nitrogen while stirring at room temperature for 40 min. To this mixture was slowly added a solution of ethynyltrimethylsilane (9 g, 91.6 mmol) in THF (50 mL) at same temperature over 40 min, and the resultant mixture was quenched with a saturated solution of NH_4Cl (800 mL), and the mixture was extracted with EtOAc (3×500 mL). The combined organic layers were washed with Na_2EDTA (aq. 500 mL), brine (500 mL) and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give product **15** (26.8 g, 88% yield) as a white solid; R_f = 0.40 (silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = + 28.4 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2947, 2358, 2329, 1769, 1673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.12-7.09 (m, 1H), 3.23 (d, *J* = 15.6 Hz, 1H), 2.78 (d, *J* = 15.6 Hz, 1H), 2.58-2.45 (m, 3H), 1.55 (s, 3H), 1.35 (s, 3H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.71-0.64 (m, 6H), 0.19 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 174.5, 146.6, 130.3, 100.4, 96.4, 83.3, 78.4, 55.3, 49.7, 29.8, 26.6, 24.7, 6.7, 5.6, -0.4 ppm; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{36}NaO_4Si_2$ $[M + Na]^+$: 443.2044, found 443.2046.

Synthesis of compound **7**:



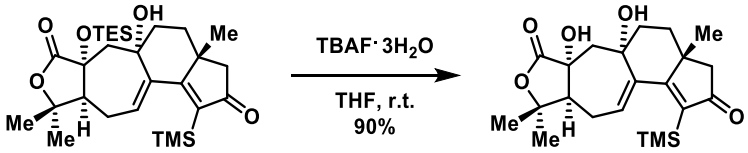
To an anhydrous cerium (III) chloride (44.4 g, 180 mmol) was added THF (900 mL) at 0 °C, and the resultant mixture was stirred at room temperature for 12 h. To this mixture was added fresh Grignard reagent (72 mL, 1.5M, 108 mmol) at 0 °C, and the resultant mixture was stirred at the same temperature for 1 h. After addition of a solution of compound **15** (25.1 g, 60 mmol) in THF (300 mL) to the above prepared reaction mixture at 0 °C, the resultant mixture was stirred for 15 min, and quenched with a 10% solution of AcOH (250 mL), and the mixture was extracted with EtOAc (3×500 mL). The combined organic layers were washed with brine (500 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give product **7** (23.7 g, 81% yield) as a colorless oil; R_f = 0.75 (Silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = -6.3 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2957, 2880, 2361, 2341, 1772, 1064, 858, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.22 (dd, *J* = 9.3, 5.2 Hz, 1H), 4.71 (s, 2H), 3.94 (s, 1H), 2.49 (dd, *J* = 13.0, 4.3 Hz, 1H), 2.39 (d, *J* = 15.1 Hz, 1H), 2.28-2.25 (m, 1H), 2.14-1.94 (m, 5H), 1.81-1.77 (m, 1H), 1.74 (s, 3H), 1.52 (s, 3H), 1.29 (s, 3H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.79 (m, 6H), 0.17 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.7, 145.4, 133.4, 131.9, 109.8, 104.9, 93.0, 83.3, 80.8, 75.2, 55.0, 41.9, 40.2, 31.8, 29.6, 25.0, 24.5, 22.4, 6.7, 5.7, -0.1 ppm; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{47}O_4Si_2$ $[M + H]^+$: 491.3007, found 491.3003.

Synthesis of compound **16**:



To a suspension of dry celite (1 g, 10 wt) in toluene (5 mL) was added a solution of compound **7** (100 mg, 0.2 mmol) in toluene (1 mL) and octacarbonyldicobalt (34 mg, 0.1 mmol) at room temperature, and the resultant mixture was first stirred at the same temperature for 12h under nitrogen atmosphere to form a substrate-Co complex, and then stirred at 110 ^{o}C under balloon pressure of CO for 2 days to proceed the Pauson-Khand reaction. The reaction was worked up by filtered of the reaction mixture through a pad of celite, and washed with EtOAc (3×15 mL). The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to give product **16** (71.8 mg, 67% yield) as white solids and its diastereomoer (26.0 mg, 24% yield); R_f = 0.35 (Silica gel, petroleum ether/ethyl acetate = 4:1); $[\alpha]_D^{25}$ = - 222.4 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2989, 2955, 2900, 1766, 1688, 1684, 1241, 1066, 845, 841cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.57 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.86 (s, 1H), 2.70 (dd, *J* = 12.6, 4.0 Hz, 1H), 2.43 (d, *J* = 15.6 Hz, 1H), 2.34-2.26 (m, 1H), 2.29 (s, 2H), 2.23 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.10 (d, *J* = 15.6 Hz, 1H), 2.00 (dd, *J* = 12.3, 5.6 Hz, 1H), 1.89-1.77 (m, 2H), 1.75-1.69 (m, 1H), 1.6 (s, 3H), 1.37 (s, 3H), 1.10 (s, 3H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.84-0.72 (m, 6H), 0.22 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.2, 192.0, 174.6, 142.5, 138.1, 124.1, 85.0, 82.5, 75.7, 56.4, 52.6, 45.3, 42.8, 38.2, 34.1, 30.4, 25.5, 24.9, 24.7, 6.9, 5.7, 0.3 ppm; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{47}O_5Si_2$ $[M + H]^+$: 519.2957, found 519.2956.

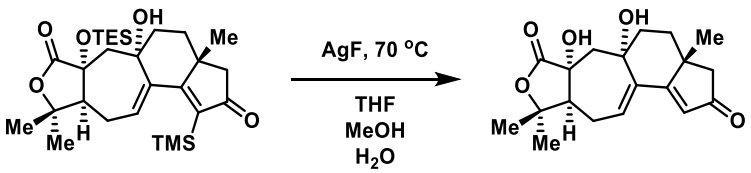
Synthesis of compound **17a**:



16 **17a**

To a solution of compound **16** (50 mg, 0.096 mmol) in THF (2 mL) was added tetrabutylammonium fluoride trihydrate (45.6 mg, 0.145 mmol), and the resultant mixture was stirred at room temperature for 30 min. The reaction was quenched with a saturated solution of $NaHCO_3$ (2 mL), and the mixture was extracted with EtOAc (3× 5 mL), and the combined organic layers were washed with brine (5 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product **17a** (35 mg, 90%) as a white solid; R_f = 0.55 (silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = - 216.0 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 3411, 2946, 2274, 1768, 1660, 1557, 1362, 1258, 1250, 839 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.63 (dd, *J* = 9.3, 3.7 Hz, 1H), 4.99 (d, br. *J* = 8.1 Hz, 1H), 3.70 (d, br. *J* = 7.2 Hz, 1H), 2.71 (dd, *J* = 13.2, 3.8 Hz, 1H), 2.42 (d, *J* = 15.4 Hz, 1H), 2.36-2.24 (m, 4H), 2.21 (d, *J* = 15.4 Hz, 1H), 1.99-1.90 (m, 2H), 1.88-1.81 (m, 1H), 1.79-1.71 (m, 1H), 1.58 (s, 3H), 1.36 (s, 3H), 1.10 (s, 3H), 1.36 (s, 3H), 0.2 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.3, 191.4, 176.1, 140.9, 138.6, 125.2, 85.1, 80.1, 76.9, 54.9, 52.5, 45.4, 42.8, 38.0, 33.9, 30.4, 25.3, 24.7, 24.4, 0.2 ppm; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{33}O_5Si$ $[M + H]^+$: 405.2092, found 405.2095. CCDC 1407538 contains the supplementary crystallographic data for compound **17a** and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of compound **17**:

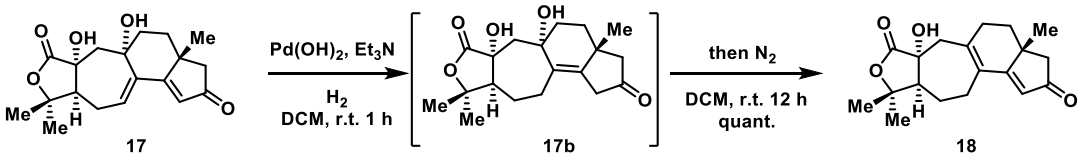


16 **17**

To a solution of compound **16** (12.47 g, 24 mmol) in a mixed solvent of THF (75 mL), MeOH (67.5 mL) and H_2O (7.5 mL) was added silver (I) fluoride (30.5 g, 240 mmol), and the resultant mixture was stirred at 80 ^{o}C for 2 days. The

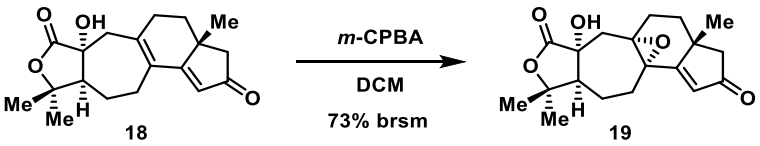
reaction was quenched with a saturated solution of $NaHCO_3$ (150 mL), and the mixture was first filtered through a pad of celite, and then washed with EtOAc (3×100mL), and the filtrate was finally extracted with EtOAc (3× 200mL). The combined organic layers were washed with brine (200 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 2:2:1) to give product **17** (6.8g, 85% yield) as a white solid; R_f = 0.40 (silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = - 363.7 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2989, 2900, 1766, 1701, 1685, 1670, 1419, 1263, 1066, 1058, 760, 754, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.96 (dd, *J* = 9.2, 3.6 Hz, 1H), 5.91 (s, 1H), 4.74 (s, 1H), 3.64 (s, 1H), 2.62 (dd, *J* = 13.0, 3.3 Hz, 1H), 2.42 (d, *J* = 15.5 Hz, 1H), 2.36 (d, *J* = 5.3 Hz, 2H), 2.33-2.27 (m, 1H), 2.22 (d, *J* = 15.4 Hz, 1H), 2.16 (s, 1H), 2.02-1.71 (m, 4H), 1.64 (s, 3H), 1.39 (s, 3H), 1.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.8, 184.9, 175.4, 140.2, 127.7, 127.7, 85.5, 80.4, 75.6, 54.7, 52.2, 43.4, 42.9, 37.5, 32.7, 30.1, 25.8, 25.4, 24.5 ppm; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}O_5$ $[M + H]^+$: 333.1696, found 333.1692.

Synthesis of compound **18**:



To a solution of compound **17** (6.8g, 20.5 mmol) in CH_2Cl_2 (350 mL) was added triethylamine (17.2 mL, 122.8 mmol), and the mixture was stirred at room temperature for 10 min, followed by addition of Pearlman catalyst (4.8g, 20% w/w, 0.7 wt), and the resultant mixture was first degassed with hydrogen, and then stirred at room temperature for 1h. After the substrate **17** was converted completely to **17b** monitored by TLC, the reaction mixture was stirred overnight under nitrogen. The reaction was quenched by filtration of the mixture through a pad of celite, and washed with EtOAc (3 × 150mL). The filtrate was concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel (ethyl acetate/dichloromethane = 1:1) to give product **18** (6.5g, quant.) as white solid; data for **17b**: R_f = 0.35 (silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = + 3.2 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2953, 2359, 2340, 1763, 1751, 1457, 1275, 1083, 1035, 761, 751, 708, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.50 (s, 1H), 3.29 (s, 1H), 3.05 (d, *J* = 22.2 Hz, 1H), 2.91 (d, *J* = 22.1 Hz, 1H), 2.65 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.54-2.40 (m, 3 H), 2.33 (d, *J* = 17.2 Hz, 1H), 2.22 (d, *J* = 17.1 Hz, 1H), 2.16-2.07 (m, 1H), 2.02-1.87 (m, 2H), 1.77 (m, 2H), 1.70 (d, *J* = 15.4 Hz, 1H), 1.51 (s, 3H), 1.27 (s, 3H), 1.09 (s, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.8, 177.2, 138.0, 135.2, 84.0, 80.1, 73.3, 56.8, 55.7, 43.5, 40.4, 40.1, 36.9, 31.6, 29.9, 26.3, 26.0, 24.8, 24.4, 1.0, -0.03 ppm; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}O_4$ $[M + Na]^+$: 357.1672, found 357.1673. Data for **18**: R_f = 0.42 (Silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = - 99.4 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2977, 2918, 1762, 1700, 1684, 1662, 1653, 1571, 1275, 1057 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.77 (s, 1H), 3.46 (s, 1H), 2.91 (d, *J* = 16.1 Hz, 1H), 2.62-2.40 (m, 5H), 2.34 (d, *J* = 17.8 Hz, 1H), 2.29-2.20 (m, 2H), 2.20 (d, *J* = 17.8 Hz, 1H), 1.99-1.66 (m, 4H), 1.51 (s, 3H), 1.37 (s, 3H), 1.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.1, 180.9, 178.1, 139.4, 129.1, 121.9, 84.6, 78.9, 54.4, 51.8, 40.3, 40.3, 34.0, 33.0, 29.9, 28.6, 25.3, 24.3, 23.8 ppm; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}O_4$ $[M + H]^+$: 317.1747, found 317.1754.

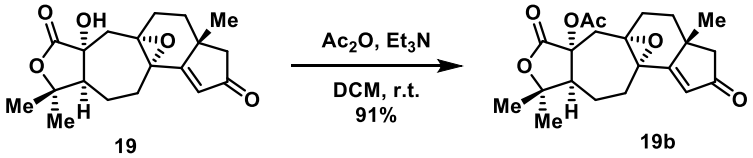
Synthesis of compound **19**:



To a stirred solution of compound **18** (6.5 g, 20.5 mmol) in CH_2Cl_2 (200 mL) was added 3-chloroperbenzoic acid (7.8g, 70%, 51.0 mmol) at 0 ^oC, and the resultant mixture was stirred at room temperature for 2 days. The reaction mixture

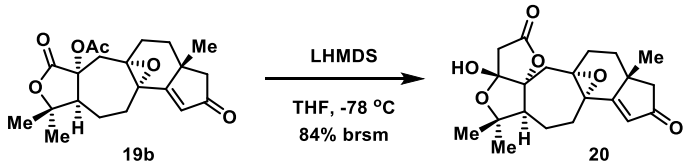
was quenched with a saturated solution of $NaHSO_3$ (150 mL) and $NaHCO_3$ (150 mL), and resultant mixture was stirred for 1 h. The mixture was extracted with EtOAc (3×150 mL), and the combined organic layers were washed with brine (150 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1.5:1) to give product **19** (4.2 g, 62% yield, 73% b.r.s.m. yield) as a white solid; R_f = 0.45 (silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = + 18.8 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 3452, 2927, 1761, 1704, 1700, 1271, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.18 (s, 1H), 4.25 (br, 1H), 2.63 (d, *J* = 15.8 Hz, 1H), 2.64-2.55 (m, 1H), 2.45-2.37 (m, 3H), 2.33 (d, *J* = 18.0 Hz, 1H), 2.20 (d, *J* = 18.0 Hz, 1H), 2.11-2.04 (m, 2H), 1.87-1.57 (m, 4H), 1.54 (s, 3H), 1.33 (s, 3H), 1.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.1, 181.7, 175.3, 129.8, 84.4, 78.0, 64.9, 61.3, 54.7, 50.7, 40.6, 37.9, 30.3, 29.4, 29.2, 28.8, 24.6, 24.3, 22.4 ppm; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{25}O_5$ $[M + H]^+$: 333.1696, found 333.1697.

Synthesis of compound **19b**:



To a solution of compound **19** (4.2 g, 12.6 mmol) in CH_2Cl_2 (126 mL) was added 4-(dimethylamino)pyridine (926mg, 7.6 mmol), triethylamine (17.6 mL, 126.4 mmol) and acetic anhydride (3.9 g, 37.9 mmol) at 0 °C, and the resultant mixture was stirred at room temperature overnight. The reaction mixture was quenched with a saturated solution of NH_4Cl (150 mL), and the mixture was extracted with EtOAc (3×100mL). The combined organic layers were washed with brine (100 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give product **19b** (4.3g, 91% yield) as white solid; R_f = 0.50 (Silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = - 11.9 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2976, 2956, 2872, 1773, 1740, 1734, 1707, 1700, 1696, 1279, 1243, 1229, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.18 (s, 1H), 2.93 (dd, *J* = 16.8, 11.0 Hz, 1H), 2.42-2.28 (m, 2H), 2.34 (d, *J* = 17.8 Hz, 1H), 2.31 (d, *J* = 15.9 Hz, 1H), 2.21 (d, *J* = 17.9 Hz, 1H), 2.17-2.07 (m, 2H), 2.12 (s, 3H), 2.01-1.88 (m, 1H), 1.81-1.71 (m, 1H), 1.64-1.55 (m, 2H), 1.53 (s, 3H), 1.43 (s, 3H), 1.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 182.3, 173.0, 169.8, 129.9, 84.8, 82.7, 62.3, 59.7, 51.3, 49.2, 40.6, 37.8, 29.6, 29.4, 29.0, 27.4, 25.0, 24.8, 21.5, 20.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{27}O_6$ $[M + H]^+$: 375.1802, found 375.1798.

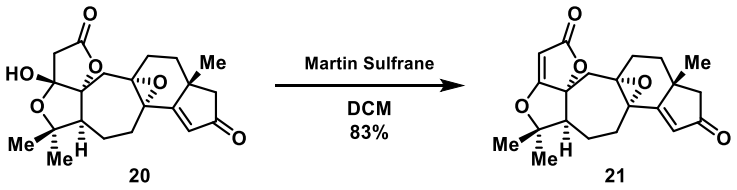
Synthesis of compound **20**:



To a solution of compound **19b** (4.3g, 11.5 mmol) in THF (200 mL) was slowly added lithium bis(trimethylsilyl)amide (28.6 mL, 1M, 28.6 mmol) at -78 °C for 2h, and the reaction mixture was then warmed up to -40 °C, and the mixture was then stirred at the same temperature for 12h. The reaction mixture was quenched with a saturated solution of NH_4Cl (200 mL), and the formed mixture was then extracted with EtOAc (3×100mL). The combined organic layers were washed with brine (100 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give product **20** [3.3 g, 76% yield; 84% yield (brsm)] as white solid; R_f = 0.32 (silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = - 52.5 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 3374, 2969, 2931, 1780, 1772, 1700, 1684, 1675, 1669, 1247, 1089, 1021, 1025, 981 cm^{-1};

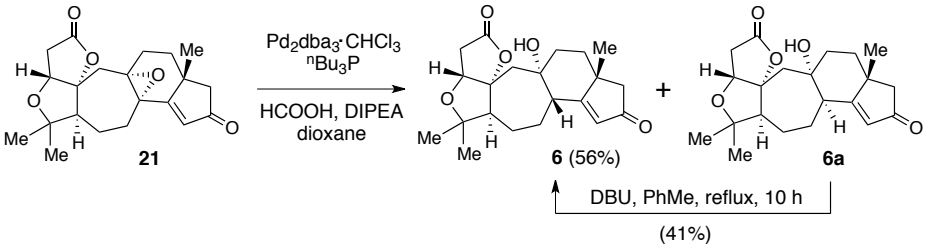
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.14 (s, 1H), 3.37 (br, 1H), 3.07 (d, *J* = 16.1 Hz, 1H), 2.89 (d, *J* = 17.1 Hz, 1H), 2.74 (d, *J* = 17.2 Hz, 1H), 2.65-2.51 (m, 2H), 2.30 (d, *J* =17.9 Hz, 1H), 2.19 (d, *J* = 19.0 Hz, 1H), 2.06-1.95 (m, 3H), 1.93-1.78 (m, 1H), 1.77-1.63 (m, 2H), 1.60-1.48 (m, 2H), 1.30 (s, 3H), 1.26 (s, 3H), 1.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 183.0, 172.2, 128.9, 107.9, 97.2, 87.2, 62.7, 57.9, 52.2, 50.8, 42.0, 40.9, 36.1, 31.5, 29.6, 29.5, 29.2, 26.1, 24.7, 23.6 ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{27}O_6$ $[M + H]^+$: 375.1802, found 375.1795.

Synthesis of compound **21**:



To a solution of compound **20** (3.3 g, 8.8 mmol) in CH_2Cl_2 (450 mL) was added Martin sulfurane dehydrating agent (10.8g, 16.0 mmol) at 0 °C, and the resultant mixture was stirred at room temperature overnight. The reaction mixture was quenched with a saturated solution of NH_4Cl (450 mL), and the formed mixture was extracted with CH_2Cl_2 (3×200 mL). The combined organic layers were washed with brine (200 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (dichloromethane/ethyl acetate = 15:1) to give product **21** (2.6g, 83% yield) as white solid; R_f = 0.47 (Silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = -53.4 (c = 1.0 in CH_2Cl_2); IR (neat): ν_{max} = 2970, 2929, 1761, 1709, 1695, 1653, 1650, 1166, 885 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.21 (s, 1H), 4.98 (s, 1H), 2.63 (d, *J* = 15.6 Hz, 1H), 2.45-2.28 (m, 3H), 2.33 (d, *J* = 17.8 Hz, 1H), 2.21 (d, *J* = 17.9 Hz, 1H), 2.18-2.03 (m, 3H), 1.97-1.85 (m, 1H), 1.77 (br, 1H), 1.72-1.62 (m, 1H), 1.59 (s, 3H), 1.58-1.52 (m, 2H), 1.46 (s, 3H), 1.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 187.0, 182.3, 173.4, 130.6, 100.5, 88.0, 86.6, 61.8, 51.0, 41.0, 40.5, 31.0, 29.3, 28.4, 26.6, 25.3, 24.9, 20.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{25}O_5$ $[M + H]^+$: 357.1696, found 357.1700. CCDC 1407537 contains the supplementary crystallographic data for compound **21** and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of compound **6**:

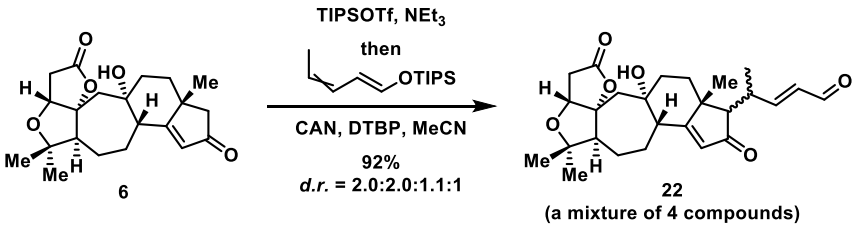


To a solution of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (29.0 mg, 0.028 mmol) in dioxane (1.0 mL) was added ^{n}Bu$_3$P (113.4 mg, 10% w/w in hexane, 0.056 mmol) and a mixture solution of formic acid (64.0 mg, 1.4 mmol) and Hunig's base (72.0 mg, 0.56 mmol) in dioxane (0.5 mL), and stirred at room temperature for 10 min. To this mixture was added a solution of compound **21** (100.0 mg, 0.28 mmol) in dioxane (4 mL) at the same temperature. Then the mixture was stirred at 45 °C for 10 h. The reaction mixture was filtered through a pad of celite and washed with EtOAc (3×10 mL). The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give the product **6** (56.2 mg, 56% yield) as a white solid and diastereoisomer **6a** (22.0 mg, 22% yield) as a white solid.

To a solution of **6a** (22.0 mg, 0.06 mmol) in toluene was added 1,8-Diazabicyclo[5.4.0]undec-7-ene (91 mg, 0.6 mmol) and stirred for 10 h at 110 °C. The reaction mixture was directly purified by a flash column chromatography on silica gel

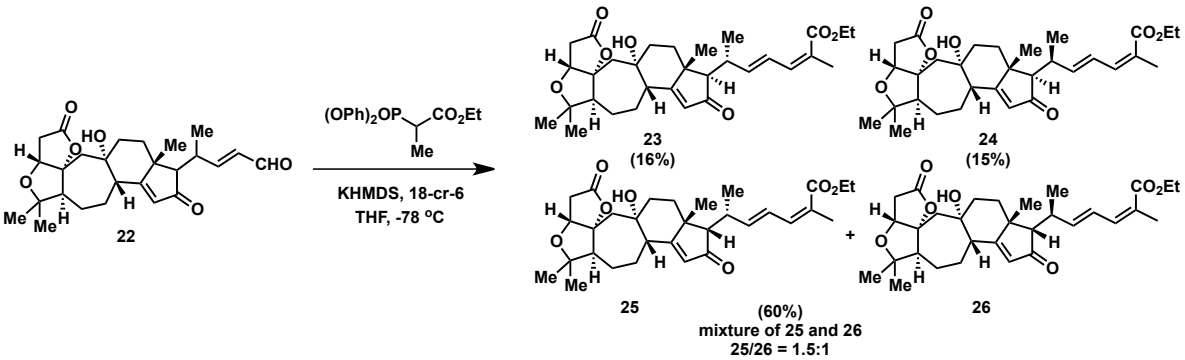
(petroleum ether/ethyl acetate = 3:1) to give the product **6** (9.0 mg, 41% yield) as a white solid. Data for **6**:R_f = 0.25 (Silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = + 42.0 (c = 0.54 in CH_2Cl_2); IR (neat): ν_{max} = 3588, 2959, 2929, 2853, 2365, 2323, 1779, 1691, 1230, 1200, 1063, 906 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.80 (d, *J* = 1.3 Hz, 1H), 4.18 (dd, *J* = 4.5, 1.2 Hz, 1H), 3.34 (s, 1H), 2.71 (dd, *J* = 5.1, 2.9 Hz, 2H), 2.40 (dd, *J* = 13.3, 4.6 Hz, 2H), 2.31 (s, 2H), 2.08 (d, *J* = 15.1 Hz, 1H), 2.04-1.95, (m, 1H), 1.95-1.86 (m, 2H), 1.90 (d, *J* = 15.3 Hz, 1H), 1.86-1.79 (m, 1H), 1.75-1.68 (m, 1H), 1.63-1.55 (m, 3H), 1.35 (s, 3H), 1.26 (s, 3H), 1.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.6, 188.1, 173.4, 127.3, 98.8, 84.6, 80.8, 75.4, 59.9, 52.2, 50.3, 45.2, 42.8, 38.2, 35.2, 34.8, 28.3, 26.7, 25.3, 24.6, 21.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{29}O_5$ $[M + H]^+$: 361.2010, found 361.2006. Data for **6a**: R_f = 0.20 (Silica gel, petroleum ether/ethyl acetate = 1:3); $[\alpha]_D^{25}$ = + 14.5 (c = 0.5 in CH_2Cl_2); IR (neat): ν_{max} = 3588, 2967, 2871, 2336, 1769, 1689, 1192, 1055, 905 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.91 (s, 1H), 4.16 (d, *J* = 4.9 Hz, 1H), 3.21 (dd, *J* = 13.3, 5.6 Hz, 1H), 2.77 (dd, *J* = 18.3, 5.0 Hz, 1H), 2.69 (d, *J* = 18.3 Hz, 1H), 2.53 (d, *J* = 2.4 Hz, 1H), 2.44 (dd, *J* = 13.3, 3.8 Hz, 1H), 2.38 (d, *J* = 18.0 Hz, 1H), 2.29 (d, *J* = 17.9 Hz, 1H), 2.09-2.20 (m, 1H), 2.07 (d, *J* = 15.2 Hz, 1H), 2.01 (dd, *J* = 13.6, 4.2 Hz, 1H), 1,96 (d, *J* = 15.2 Hz, 1H), 1.70-1.86 (m, 3H), 1.67 (d, *J* = 13.6 Hz, 1H), 1.50-1.65 (m, 2H), 1.36 (s, 3H), 1.35 (s, 3H), 1.07 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.6, 186.6, 174.0, 130.5, 97.9, 84.8, 79.9, 74.5, 54.4, 54.3, 47.6, 44.5, 42.5, 35.3, 33.9, 31.1, 28.8, 28.3, 26.4, 23.1, 21.5 ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{29}O_5$ $[M + H]^+$: 361.2010, found 361.2003.

Synthesis of compound **22**:



To a solution of compound **6** (54 mg, 0.15 mmol) in CH_2Cl_2 (2.0 mL) was added TEA (63.0 μL, 0.45 mmol) and triisopropylsilyl trifluoromethanesulfonate (60 μL, 0.225 mmol) at 0 °C, and the resultant mixture stirred at room temperature for 1 h. The reaction mixture was worked up by removal of the solvent under vacuum and the residue was dissolved in MeCN (10 mL), followed by addition of triisopropyl(((1E)-penta-1,3-dien-1-yl)oxy)silanes (100 mg, 0.45 mmol). To this solution was slowly added a solution formed by mixing ammonium cerium(IV) nitrate (373 mg, 0.68 mmol) in MeCN (10 mL) with 2,6-di-tert-butylpyridine (0.33 mL, 1.5 mmol) at -50 °C, and the result mixture was first warmed to -30 °C, and then stirred at the same temperature for 30 min. The reaction mixture was quenched with a saturated solution of NH_4Cl (3 mL), and the formed mixture was then extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give the mixed compound **22** (60.9 mg, 92%, *dr* = 1.98:1.98:1.1:1) as two pairs of diastereoisomers; R_f = 0.42 (silica gel, dichloromethane /acetone = 5:1); $[\alpha]_D^{25}$ = + 10.5 (c = 0.25 in CH_2Cl_2); IR (neat): ν_{max} = 3564, 2971, 2929, 2867, 2341, 1772, 1685, 1378, 1059, 910, 931 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.70-9.39 (m, 2 H), 9.53 (d, *J* = 7.8 Hz, 1H), 9.48 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 15.6, 8.3 Hz, 1H), 7.06 (dd, *J* = 15.8, 7.4 Hz, 1H), 7.04 (dd, *J* = 15.6, 7.5 Hz, 1H), 6.92 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.17-5.99 (m, 4H), 5.89-5.77 (m, 4H), 4.28-4.15 (m, 4H), 3.54-3.32 (m, 4H), 3.04-2.85 (m, 4H), 2.80-2.63 (m, 8H), 2.51-2.23 (m, 16H), 2.21-1.71 (m, 36H), 1.62 (s, 12H), 1.39-1.17 (m, 24H), 1.13 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 207.1, 194.4, 194.2, 187.8, 187.1, 173.4, 162.4, 161.5, 132.0, 131.3, 131.2, 126.9, 126.7, 126.5, 98.8, 98.7, 98.7, 84.6, 84.6, 80.8, 75.4, 75.4, 62.8, 61.7, 60.0, 59.9, 59.9, 50.3, 47.0, 46.8, 46.1, 45.9, 45.0, 44.9, 37.9, 35.9, 35.7, 35.5, 35.3, 35.2, 35.1, 30.0, 29.0, 28.3, 28.3, 27.3, 26.7, 26.6, 26.3, 25.2, 25.2, 21.9, 21.8, 21.8, 21.8, 20.0, 17.4, 16.4 ppm; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{35}O_6$ $[M + H]^+$: 443.2428, found 443.2434.

Synthesis of compounds of **23, 24, 25 and 26**:



To a solution of 18-crown-6 (460 mg, 1.74 mmol) in THF (10 mL) was added potassium bis(trimethylsilyl)amide (0.57 mL, 0.91 M, 0.522 mmol) at - 78 ^{o}C, and the resulting mixture was stirred at the same temperature for 10 min. To this mixture was added a solution of ethyl 2-(diphenoxyphosphoryl)propanoate (174.5 mg, 0.522 mmol) in THF (1.74 mL) at - 78 ^{o}C, and resulting mixture was then stirred at the same temperature for 10 min. followed by addition of a solution of compound **22** (77 mg, 0.174 mmol) in THF (1.5 mL) at - 78 ^{o}C, and the resulting mixture was stirred for 1.5 h. The reaction mixture was quenched with a saturated solution of NH_4Cl (10 mL) at - 78 ^{o}C, and the formed mixture was then extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give product **23** (14.7 mg, 16% yield), **24** (13.7 mg, 15%), and **25** and **26** (55.0 mg, 60% yield) as a inseparable mixture; Data for **23**: R_f = 0.75 (Silica gel, dichloromethane /acetone = 5:1); $[\alpha]_D^{25}$ = + 15.1 (c = 0.3 in CH_2Cl_2); IR (neat): ν_{max} = 3556, 2982, 2925, 2878, 2353, 1767, 1693, 1621, 1445, 1373, 1231, 1172, 1143, 920, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.39 (d, *J* = 11.1 Hz, 1H), 5.90 (dd, *J* = 15.2, 8.2 Hz, 1H), 5.80 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.17 (d, *J* = 3.6 Hz, 1H), 3.32 (s, 1H), 2.82 (h, *J* = 7.1 Hz, 1H), 2.72-2.68 (m, 2H), 2.43-2.35 (m, 2H), 2.21 (d, *J* = 7.8 Hz, 1H), 2.06 (d, *J* = 15.6 Hz, 1H), 1.95 (s, 3H), 1.86 (d, *J* = 15.4 Hz, 1H), 1.82-1.72 (m, 3H), 1.59-1.52 (m, 2H), 1.35-1.33 (m, 6H), 1.31 (d, *J* = 7.1 Hz, 3H), 1.26 (s, 3H), 1.18 (s, 3H), 1.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.6, 185.3, 173.4, 167.7, 145.9, 140.6, 126.6, 126.3, 124.8, 98.8, 84.6, 80.8, 74.8, 64.5, 60.2, 59.9, 49.8, 46.9, 45.1, 38.0, 35.6, 35.2, 34.8, 29.7, 28.4, 26.7, 25.2, 21.8, 20.7, 19.0, 14.3 ppm; HRMS (ESI): *m/z* calcd for $C_{31}H_{43}O_7$ $[M + H]^+$: 527.3003, found 527.3009. Data for **24**: R_f = 0.74 (Silica gel, dichloromethane /acetone = 5:1); $[\alpha]_D^{25}$ = + 12.7 (c = 0.3 in CH_2Cl_2); IR (neat): ν_{max} = 3551, 2953, 2920, 2854, 2334, 1769, 1678, 1603, 1450, 1369, 1238, 1113, 1172, 921, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (dd, *J* = 15.4, 11.0 Hz, 1H), 6.41 (d, *J* = 11.1 Hz, 1H), 6.15 (dd, *J* = 15.4, 8.1 Hz, 1H), 5.79 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.17 (dd, *J* = 3.6, 1.3 Hz, 1H), 3.31 (s, 1H), 2.88-2.78 (m, 1H), 2.72-2.69 (m, 2H), 2.47-2.33 (m, 2H), 2.28 (d, *J* = 4.3 Hz, 1H), 2.07 (d, *J* = 15.1 Hz, 1H), 2.03-1.97 (m, 1H), 1.93 (s, 3H), 1.87 (d, *J* = 15.3 Hz, 1H), 1.91-1.84 (m, 1H), 1.84-1.76 (m, 3H), 1.59-1.50 (m, 3H), 1.34 (s, 3H), 1.33-1.28 (m, 6H), 1.19 (s, 3H), 1.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.5, 185.9, 173.3, 167.8, 145.2, 140.9, 127.0, 126.8, 124.2, 98.8, 84.6, 80.8, 75.0, 64.6, 60.1, 59.9, 50.0, 47.1, 45.2, 37.9, 35.6, 35.4, 35.2, 28.4, 26.7, 25.2, 21.8, 21.7, 21.2, 20.6, 14.3 ppm; HRMS (ESI): *m/z* calcd for $C_{31}H_{43}O_7$ $[M + H]^+$: 527.3003, found 527.3013. Data for the mixture of **25** and **26:** R_f = 0.77 (Silica gel, dichloromethane /acetone = 5:1); $[\alpha]_D^{25}$ = + 43.5 (c = 0.5 in CH_2Cl_3); IR (neat): ν_{max} = 3564, 2975, 2929, 2867, 2345, 1772, 1685, 1606, 1453, 1362, 1221, 1188, 1158, 914, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 15.3, 11.1 Hz, 2H), 6.43 (d, *J* = 11.1 Hz, 1H), 6.37 (d, *J* = 11.1 Hz, 1H), 6.13 (dd, *J* = 15.3, 8.0 Hz, 1H), 6.02 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.79 (s, 1H), 5.77 (s, 1H), 4.25-4.15 (m, 6H), 3.33 (s, 1H), 3.21 (s, 1H), 2.90-2.73 (m, 2H), 2.73-2.67 (m, 4H), 2.38 (d, *J* = 9.6 Hz, 4H), 2.27-2.20 (m, 2H), 2.19-2.02 (m, 4H), 2.01-1.74 (m, 16H), 1.66-1.54 (m, 6H), 1.38-1.24 (m, 24H), 1.13 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.0, 208.6, 187.2, 186.8, 173.4, 173.4, 167.8, 167.7, 146.1, 144.2, 140.9, 127.3, 126.9, 126.9, 125.9, 124.6, 124.4, 98.7, 84.6, 84.5, 80.8, 75.4, 67.1, 63.1, 62.5, 60.1, 60.0, 59.9, 59.9, 50.2, 46.4, 45.9, 45.1, 45.0, 38.0, 36.0, 35.9, 35.2, 35.1, 30.1, 29.7, 28.9, 28.3, 28.3, 27.1, 26.7, 26.7,

26.1, 25.2, 21.9, 21.8, 21.0, 20.7, 20.6, 17.4, 14.3, 12.6 ppm; HRMS (ESI): *m/z* calcd for $C_{31}H_{43}O_7$ $[M + H]^+$: 527.3003, found 527.3010.

^{1}H NMR Assignments of Compound **23** and **24**[a]

No.	**23** δH [ppm, mult, *J* (Hz)] 500 MHz	**24** δH [ppm, mult, *J* (Hz)] 500 MHz
1β	4.17 (d, 4.5)	4.17 (d, 4.8)
2α	2.70 (s)	2.69 (s)
2β	2.71 (d, 4.8)	2.71 (d, 4.8)
5α	2.38-2.41 (m)	2.38-2.41 (m)
6	1.83-1.91 (m)	1.84-1.90 (m)
7α	1.99-2.04 (m)	1.97-2.02 (m)
7β	1.77-1.83 (m)[b]	1.78-1.83 (m)[b]
8β	2.35-2.38 (m)	2.35-2.37 (m)
11α	1.77-1.83 (m)[b]	1.78-1.83 (m)[b]
11β	1.50-1.58 (m)	1.52-1.63 (m)
12α	1.92-1.97 (m)[b]	1.91-1.96 (m)[b]
12β	1.71-1.77 (m)[b]	1.76-1.80 (m)[b]
15	5.81 (s)	5.79 (s)
17α	2.21 (d, 7.8)	2.28 (d, 4.4)
18	1.18 (s)	1.19 (s)
19α	2.06 (d, 15.1) ABd	2.06 (d, 15.1) ABd
19β	1.86 (d, 15.5) ABd	1.87 (d, 15.2) ABd
20	2.77-2.87 (m)	2.77-2.89 (m)
21	1.34 (d, 6.3)[b]	1.29 (d, 7.1)[b]
22	5.90 (dd, 15.3, 8.3)	6.14 (dd, 15.3, 8.1)
23	7.10 (dd, 15.3, 11.1)	7.12 (dd, 15.3, 11.0)
24	6.39 (d, 11.1)	6.41 (d, 11.1)
27	1.95 (s)	1.93 (s)
29	1.12 (s)	1.12 (s)
30	1.35 (s)	1.34 (s)
31	4.22 (q, 7.1)	4.21 (q, 7.1)
32	1.32 (t, 7.0)[b]	1.32 (t, 7.0)[b]

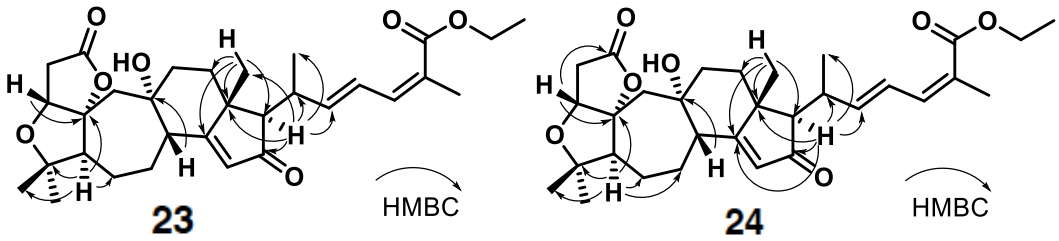
[a] Data were determined at 500 MHz in $CDCl_3$ with δ in ppm and *J* in Hz. [b] Overlapped.

^{13}C NMR Assignments of Compound **23** and **24**[a]

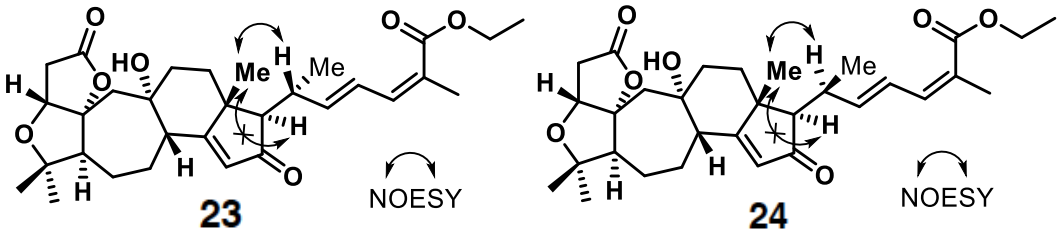
No.	**23** δC (ppm) 126 MHz	**24** δC (ppm) 126 MHz
1	80.8	80.8
2	35.2	35.2
3	173.4	173.4
4	84.6	84.6
5	59.9	59.9
6	26.7	26.7
7	25.2	25.2
8	49.8	50.0
9	74.8	75.0
10	98.8	98.8
11	38.0	37.9
12	34.9	35.4
13	46.9	47.1
14	185.3	186.0
15	126.6	127.0
16	207.6	207.5
17	64.5	64.6
18	21.7	21.7
19	45.1	45.2
20	35.6	35.6
21	18.9	21.2
22	145.9	145.2
23	126.3	126.8
24	140.5	140.9
25	124.8	124.3
26	167.7	167.8
27	20.7	20.6
29	21.8	21.8
30	28.4	28.4
31	60.2	60.0
32	14.3	14.3

[a] Data were determined at 125 MHz in $CDCl_3$ with δ in ppm.

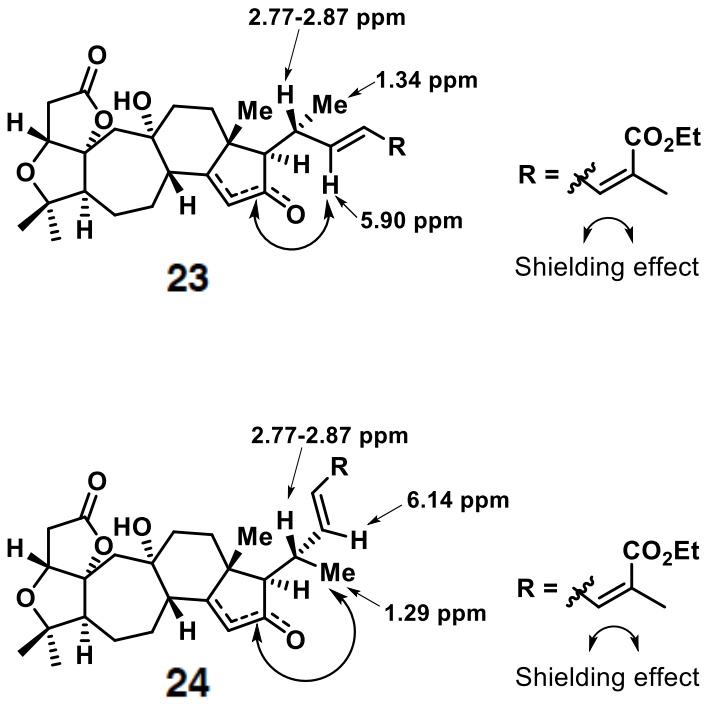
Structure of compound **23** and **24** was confirmed by NMR spectrums and shielding effect.



Selected HMBC correlations of **23** and **24**.

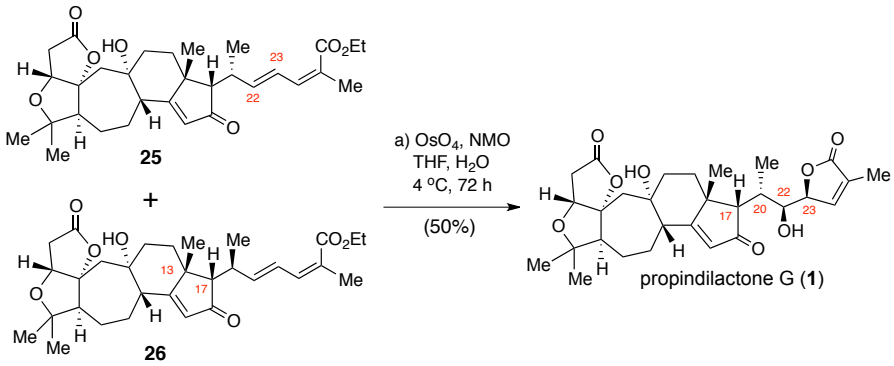


Selected NOESY correlations of **23** and **24**.



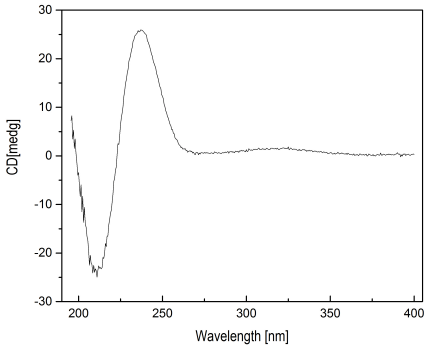
Shielding effect of **23** and **24**.

Synthesis of compound **1**:

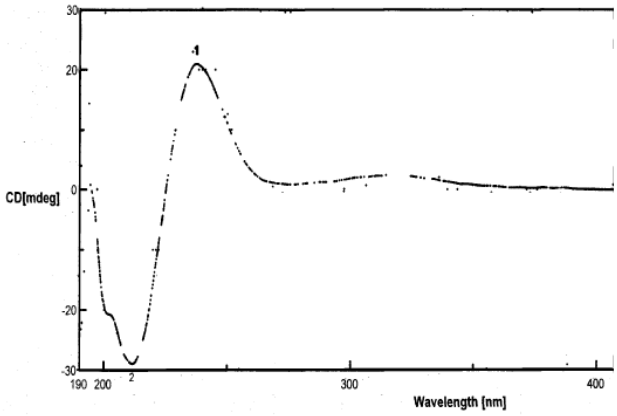


To a solution of mixed compound **25** and **26** (5 mg, 0.0095 mmol) in THF (0.5 mL) and water (0.5 mL) was added NMO (2.2 mg, 0.019 mmol) and osmium tetroxide (0.17 mg, 0.00067 mmol) at 4 °C. The reaction mixture was stirred at 4 °C for 3 d. The reaction mixture was quenched with a saturated solution of $Na_2S_2O_3$ (1 mL) and $NaHCO_3$ (1 mL), and the mixture was extracted with EtOAc (3× 3 mL). The combined organic layers were washed with brine (3 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:4) to give the propindilactone G **1** (2.5 mg, 81 % yield based on the amount of substrate of **25** in the mixture of **25**/**26**) as a white solid; R_f = 0.15 (Silica gel, Dichloromethane /Acetone = 8:1); $[\alpha]_D^{25}$ = + 39.0 (c = 0.15 in MeOH); IR (neat): ν_{max} = 3427, 2975, 2917, 2361, 1743, 1681, 1615, 1378, 1067, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.11-7.12 (m, 1H), 6.08 (d, *J* = 1.1 Hz, 1H), 5.26 (d, *J* = 8.3 Hz, 1H), 4.71 (d, *J* = 8.3 Hz, 1H), 4.25 (d, *J* = 5.0 Hz, 1H), 3.39 (d, *J* = 1.3 Hz, 1H), 3.01 (dd, *J* = 18.0, 5.1 Hz, 1H), 2.75 (d, *J* = 18.0 Hz, 1H), 2.55-2.63 (m, 1H), 2.47-2.52 (m, 1H), 2.46 (dd, *J* = 13.5, 3.9 Hz, 1H), 2.34-2.43 (m, 1H), 2.22 (Abd, *J* = 15.3 Hz, 1H), 2.08 (Abd, *J* = 15.3 Hz, 1H), 1.92-1.97 (m, 1H), 1.88-1.92 (m, 1H), 1.85-1.96 (m, 1H), 1.83 (s, 3H), 1.63-1.69 (m, 1H), 1.61-1.64 (m, 1H), 1.59-1.63 (m, 1H), 1.33-1.38 (m, 1H), 1.29 (s, 1H), 1.26 (d, *J* = 6.7 Hz, 1H), 1.24 (s, 1H), 1.09 (s, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 211.0, 191.0, 175.2, 175.2, 149.3, 130.2, 127.4, 99.4, 84.8, 82.4, 81.9, 75.8, 72.4, 60.2, 57.9, 50.3, 45.8, 45.8, 38.2, 36.6, 36.2, 29.2, 28.5, 28.0, 26.9, 26.7, 22.6, 14.3, 10.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{29}H_{39}O_8$ $[M + H]^+$: 515.2639, found 515.2641. CCDC 1411952 contains the supplementary crystallographic data for propindilactone G and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Circular Dichroism Spectra (CD) were measured on a MOS 450 AF/CD (Biologic, France) at room temperature, using 1 mm quartz cuvettes for the UV region (195 nm to 400 nm). Band width and scan speed were set as 0.5 nm and 30 nm/min. Sample was dissolved to a final concentration of 0.45 mg/mL in MeOH.

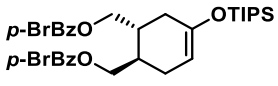


CD spectrum of Natural propindilactone G



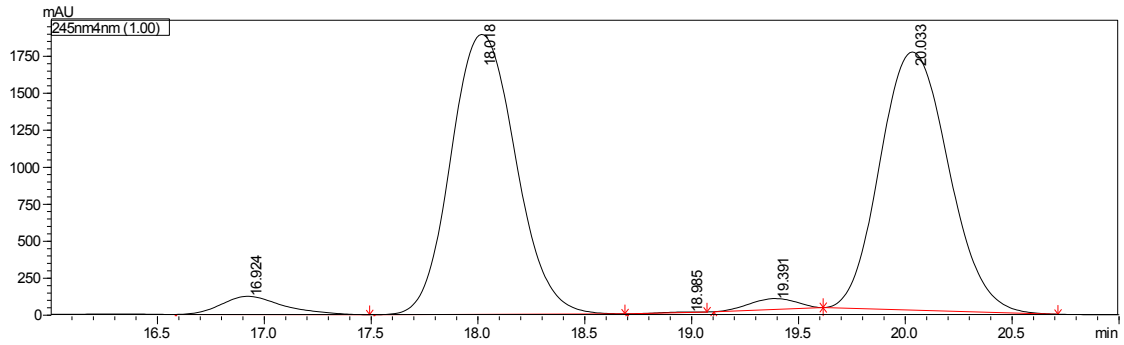
CD spectrum of synthetic revised propindilactone G (1)

II HPLC Traces for Measuring Enantiomeric Excess

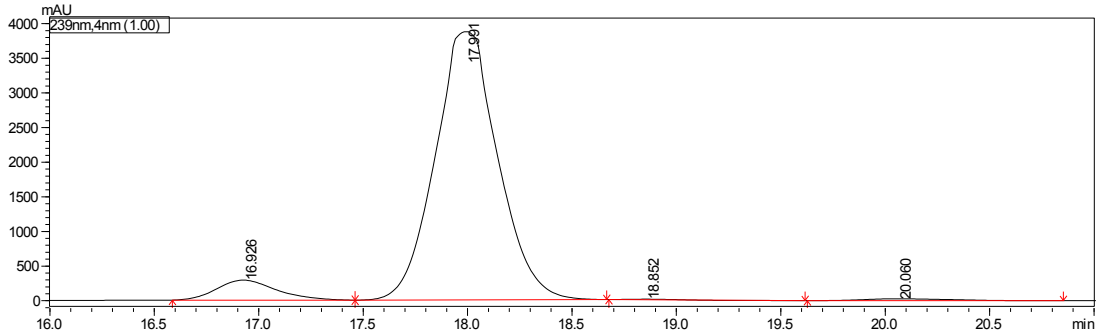


8b

A racemic sample of compound **8b** was obtained through (D/L)-Hayashi catalyst promoted Diels-Alder reaction, followed by reduction and protection reaction. The racemic and optically active **8b** were analyzed with HPLC (CHIRALPAK AD-H column, ^{i}PrOH : hexane = 3 : 97, 0.3 mL/min) and a 245 nm UV detector to determine the retention time and enantiomeric excess. For compound **8b**, *e.e.* = 98%.

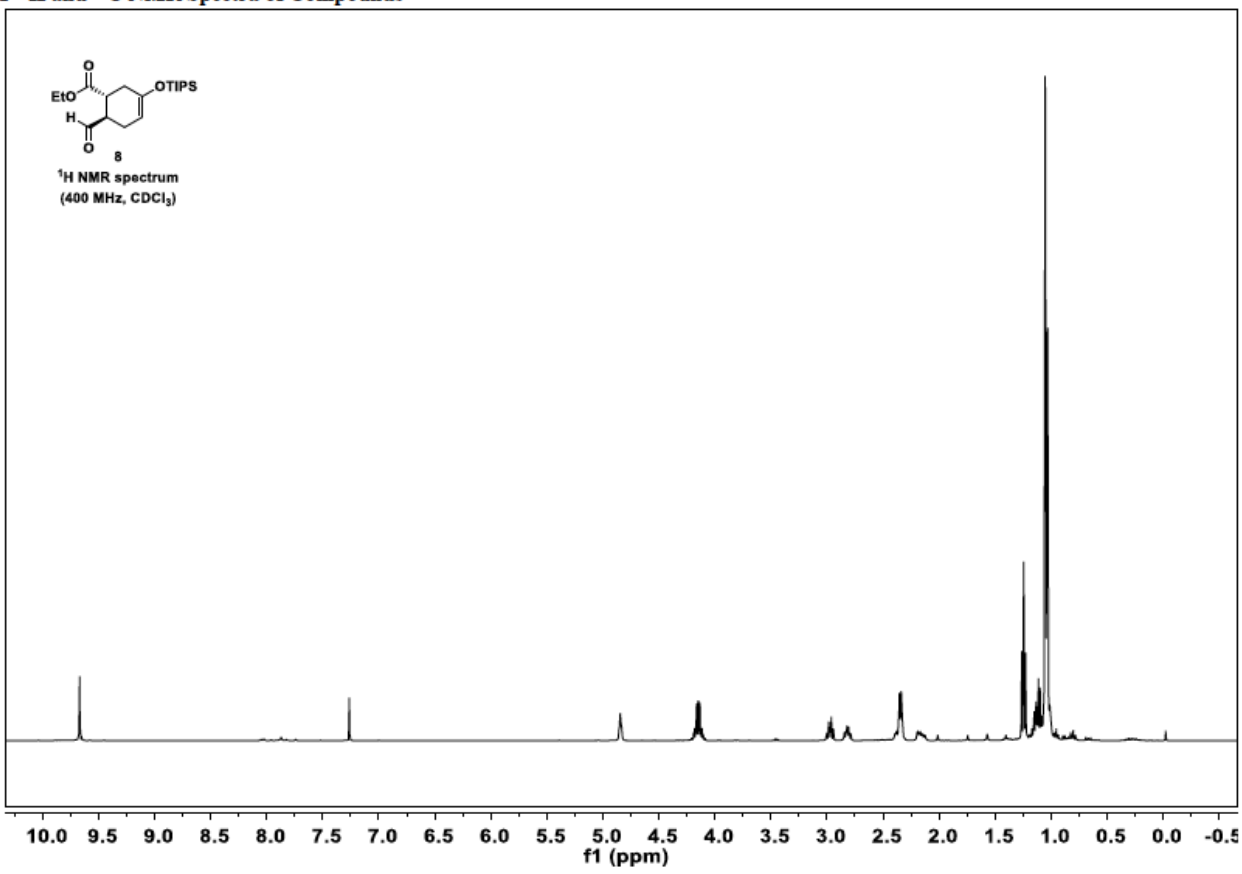


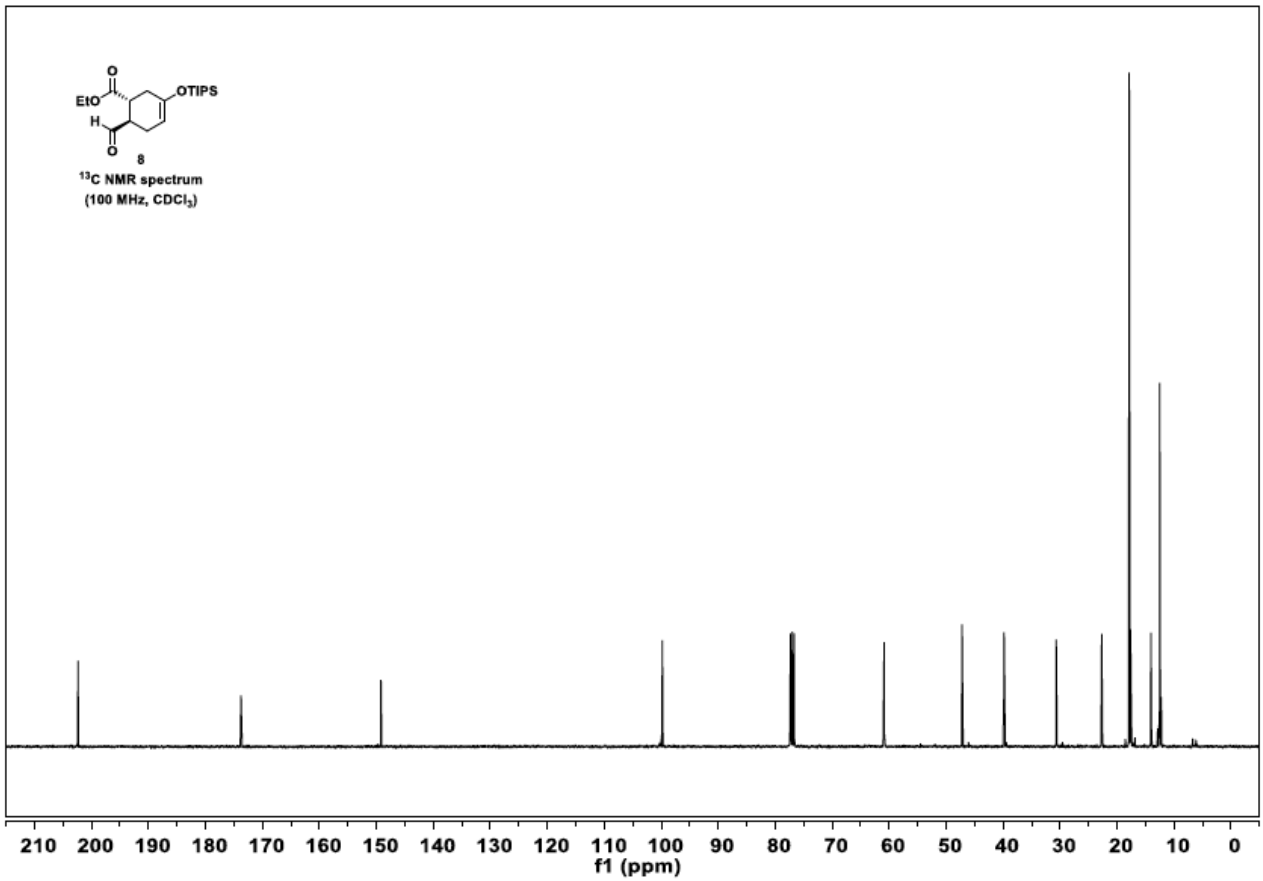
No.	Ret. Time	Area	Height	Rel. Area
1	18.018	39841523	1891884	50.591
2	20.033	38911256	1744604	49.409
Total:		78752779	3636489	100

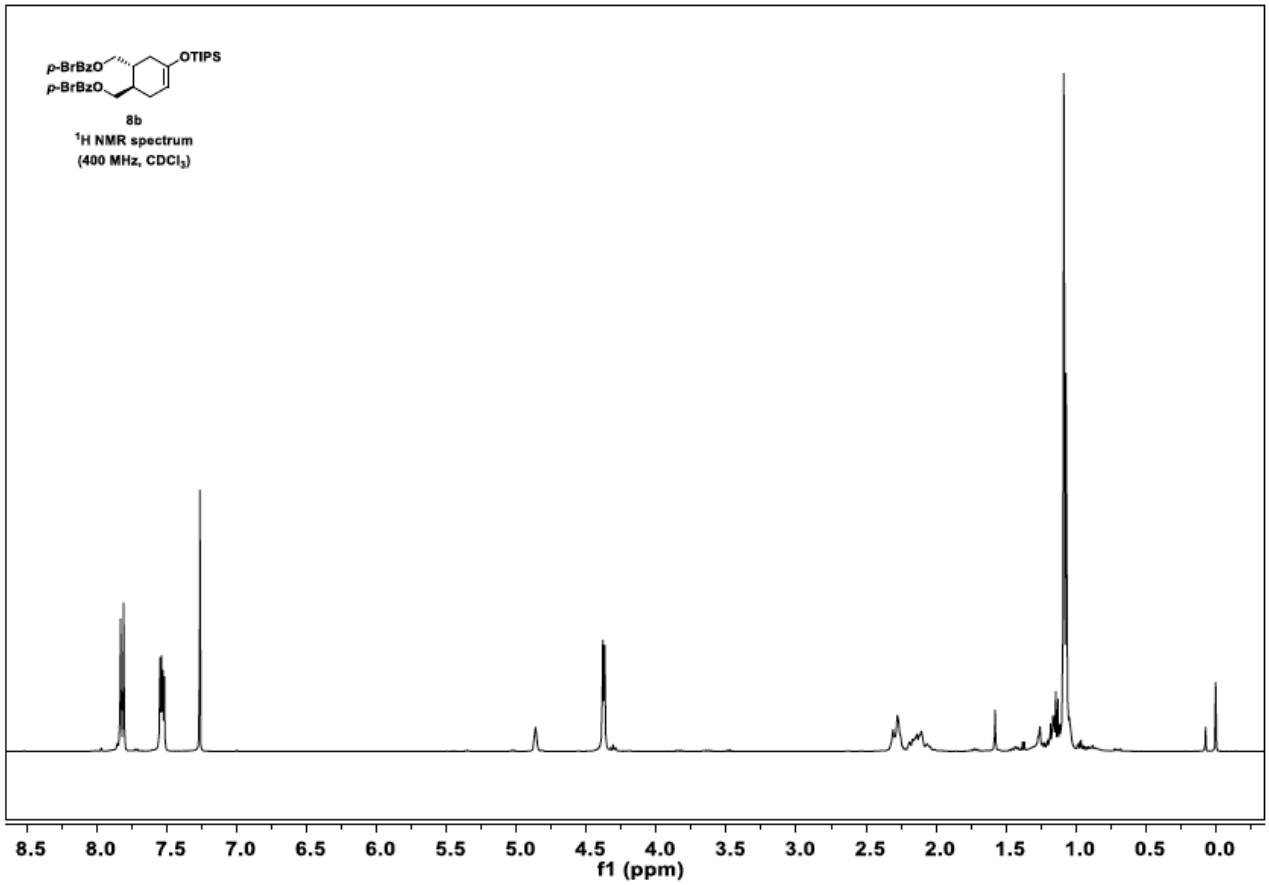


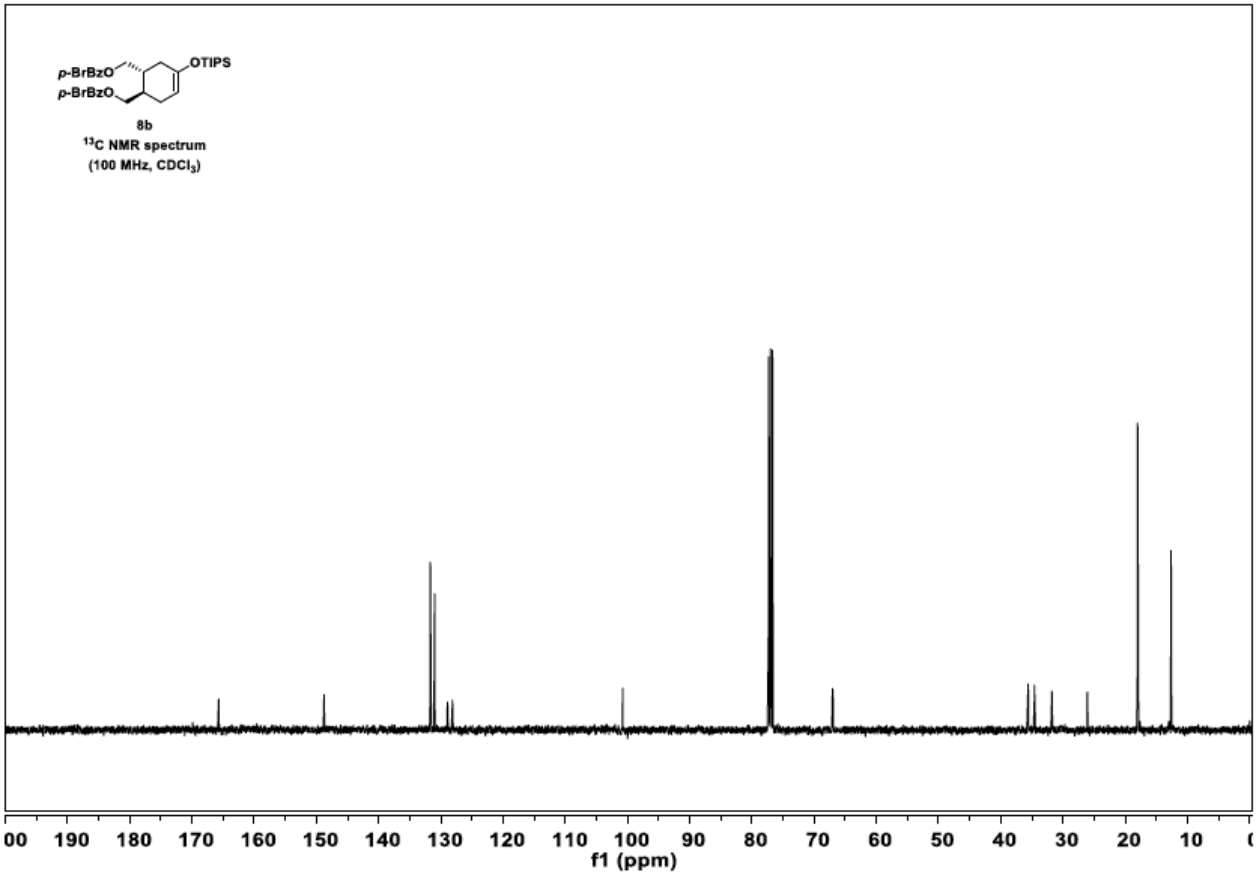
No.	Ret. Time	Area	Height	Rel. Area
1	17. 991	80787729	3871216	99. 08
2	20. 06	750356	26765	0. 92
Total:		81538085	3897981	100

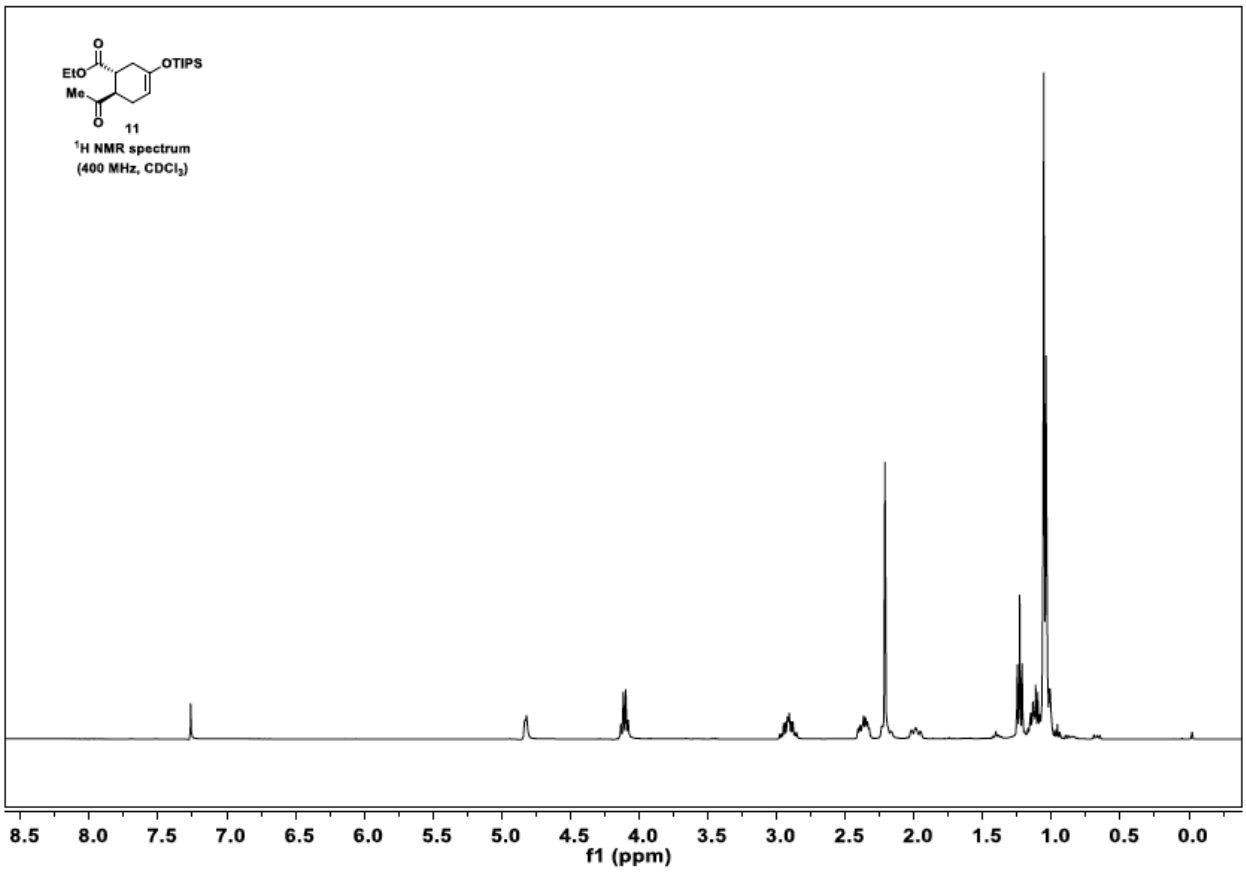
III ^{1}H and ^{13}C NMR Spectra of Compounds

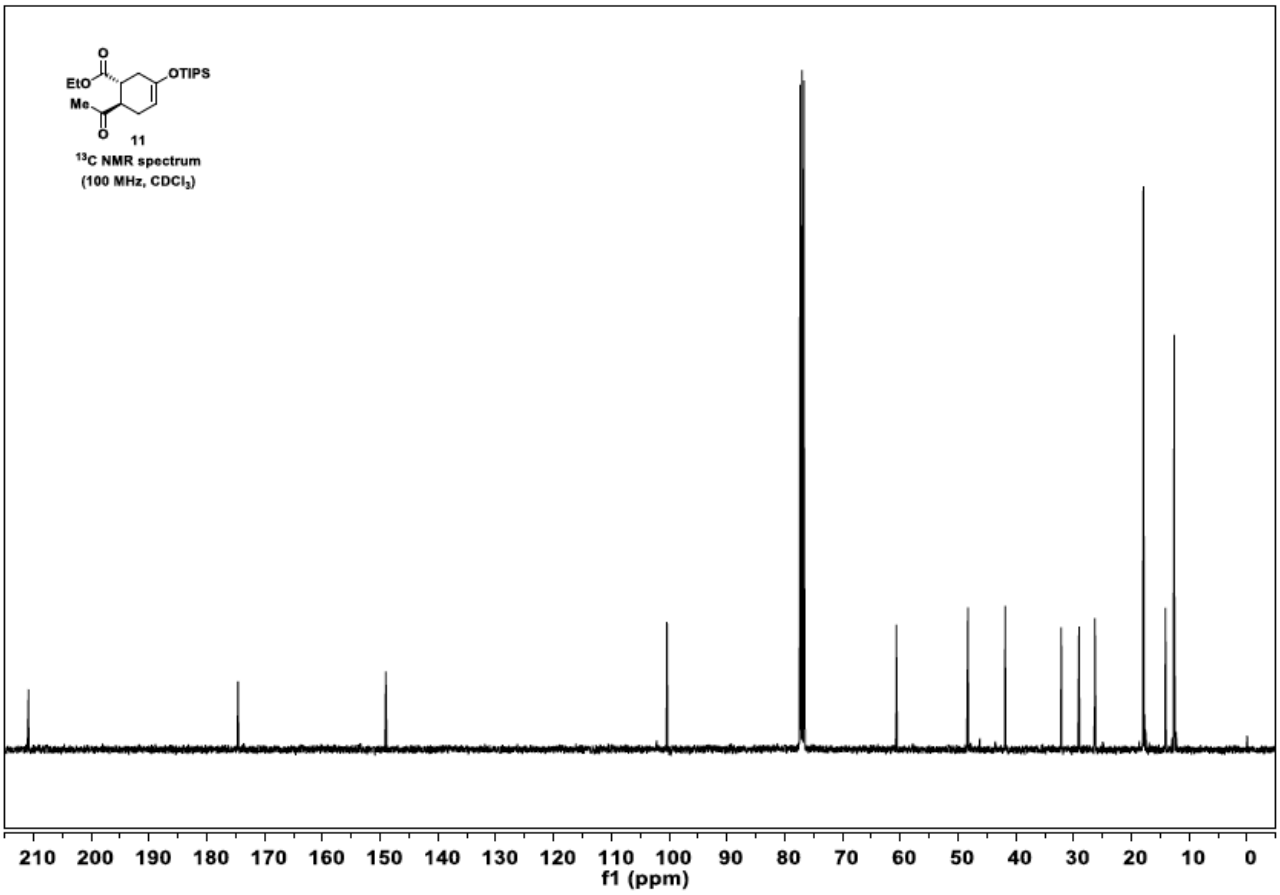


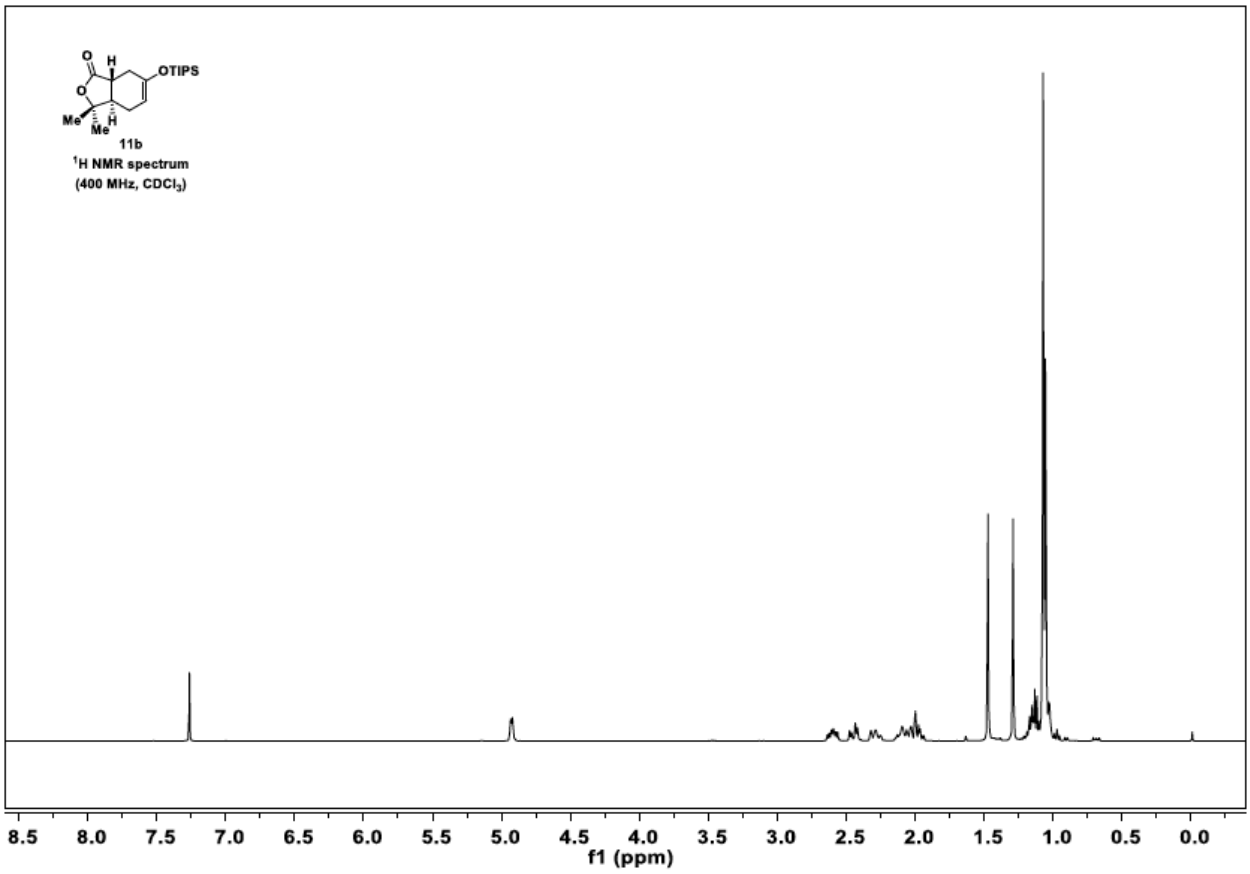


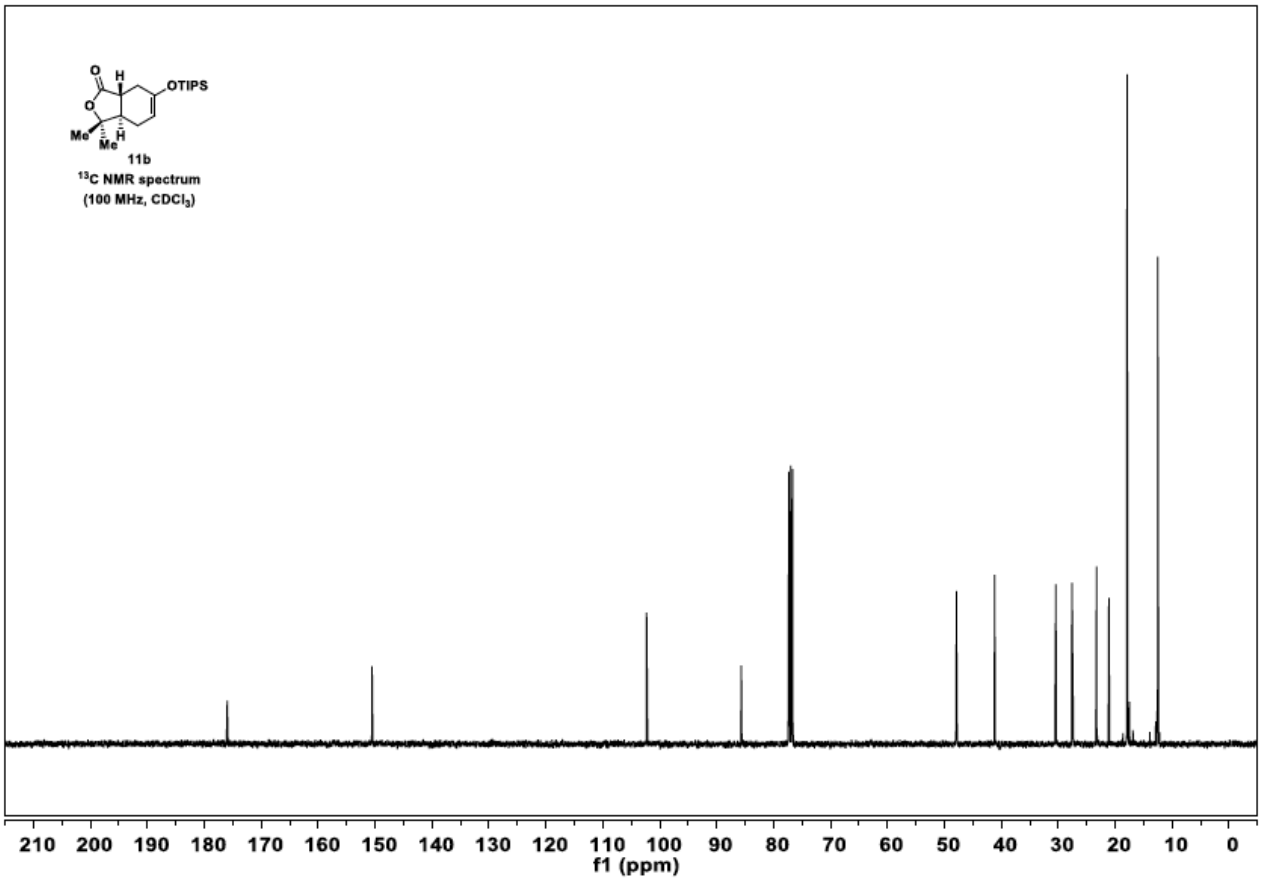

p-BrBzO
p-BrBzO
OTIPS
8b
1H NMR spectrum
(400 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

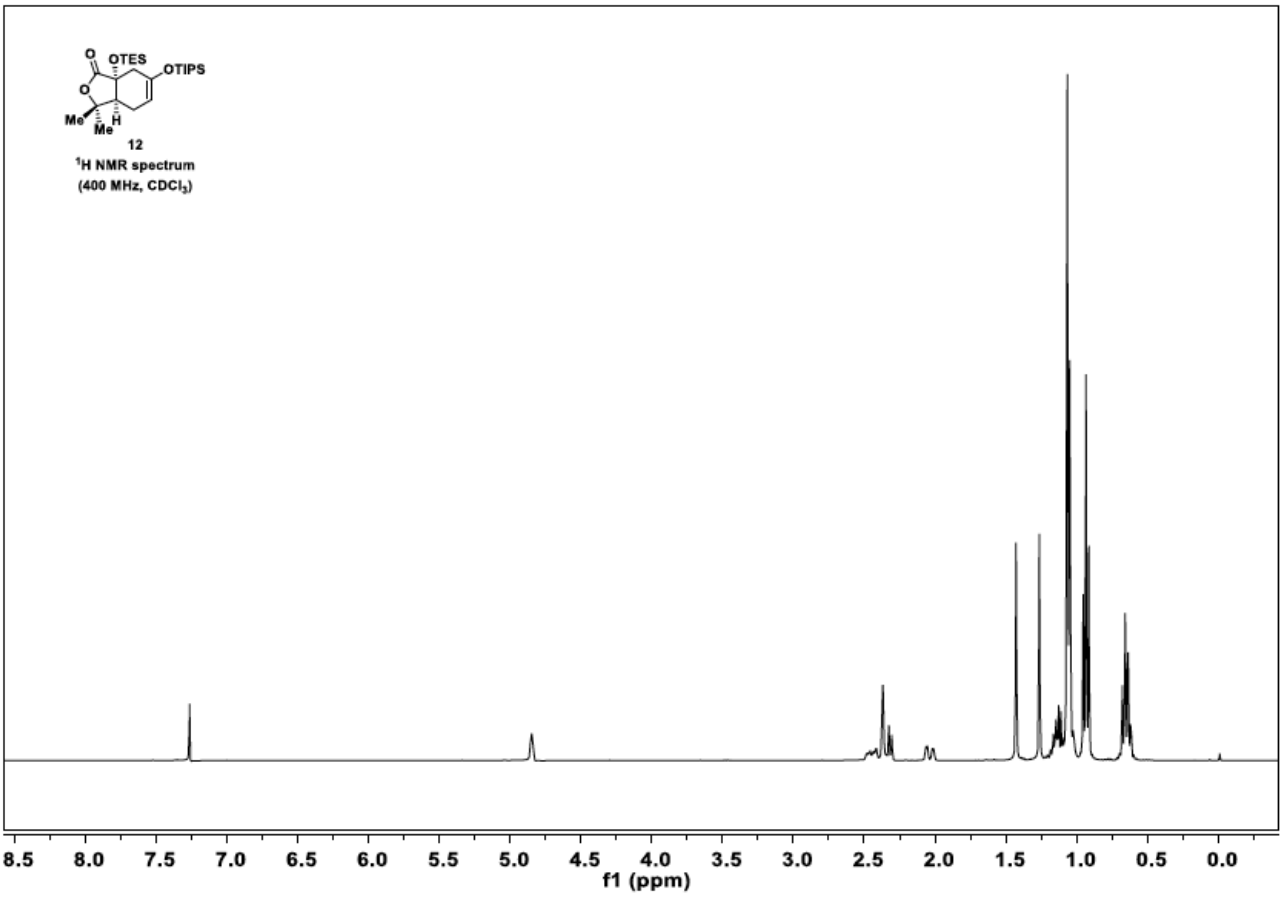

p-BrBzO
p-BrBzO
OTIPS
8b
13C NMR spectrum
(100 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

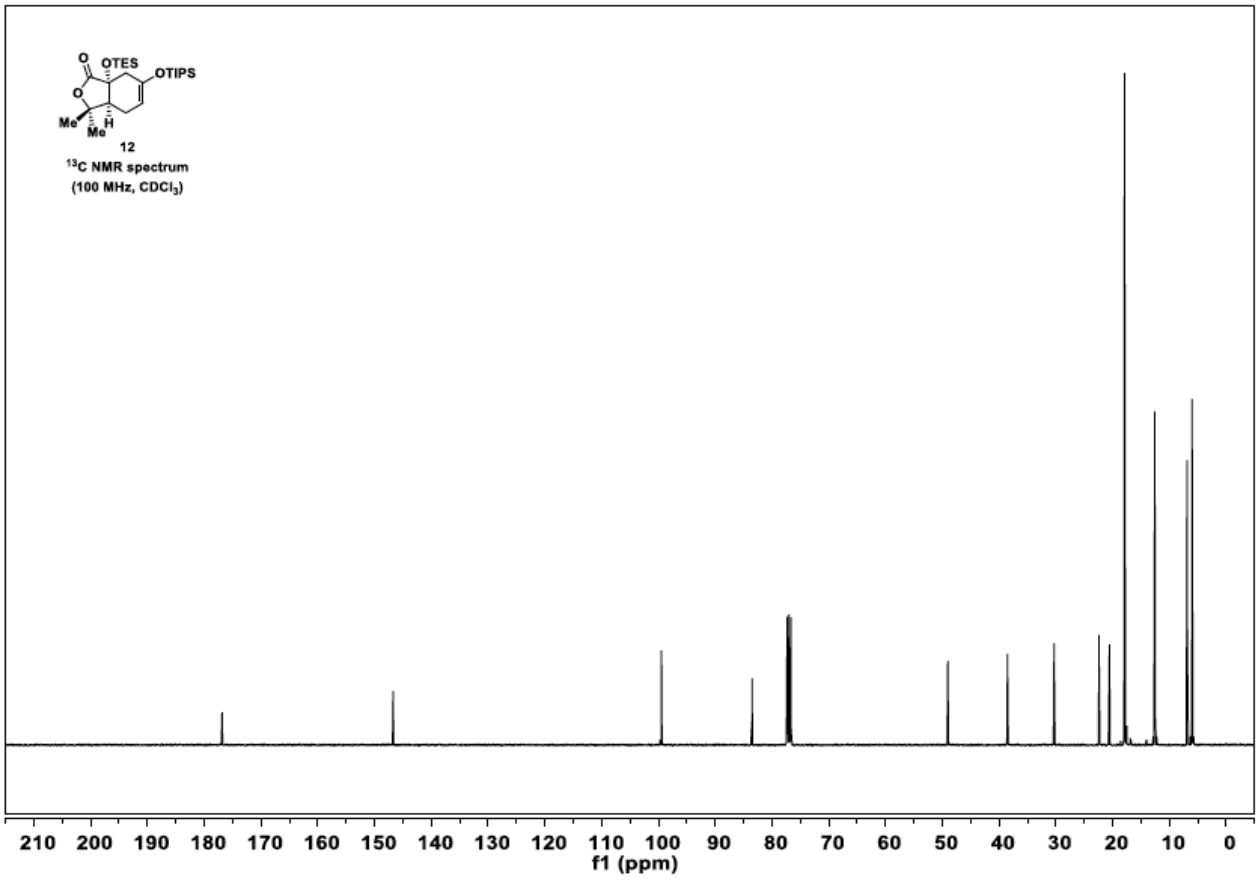

EtO
Me
OTIPS
11
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

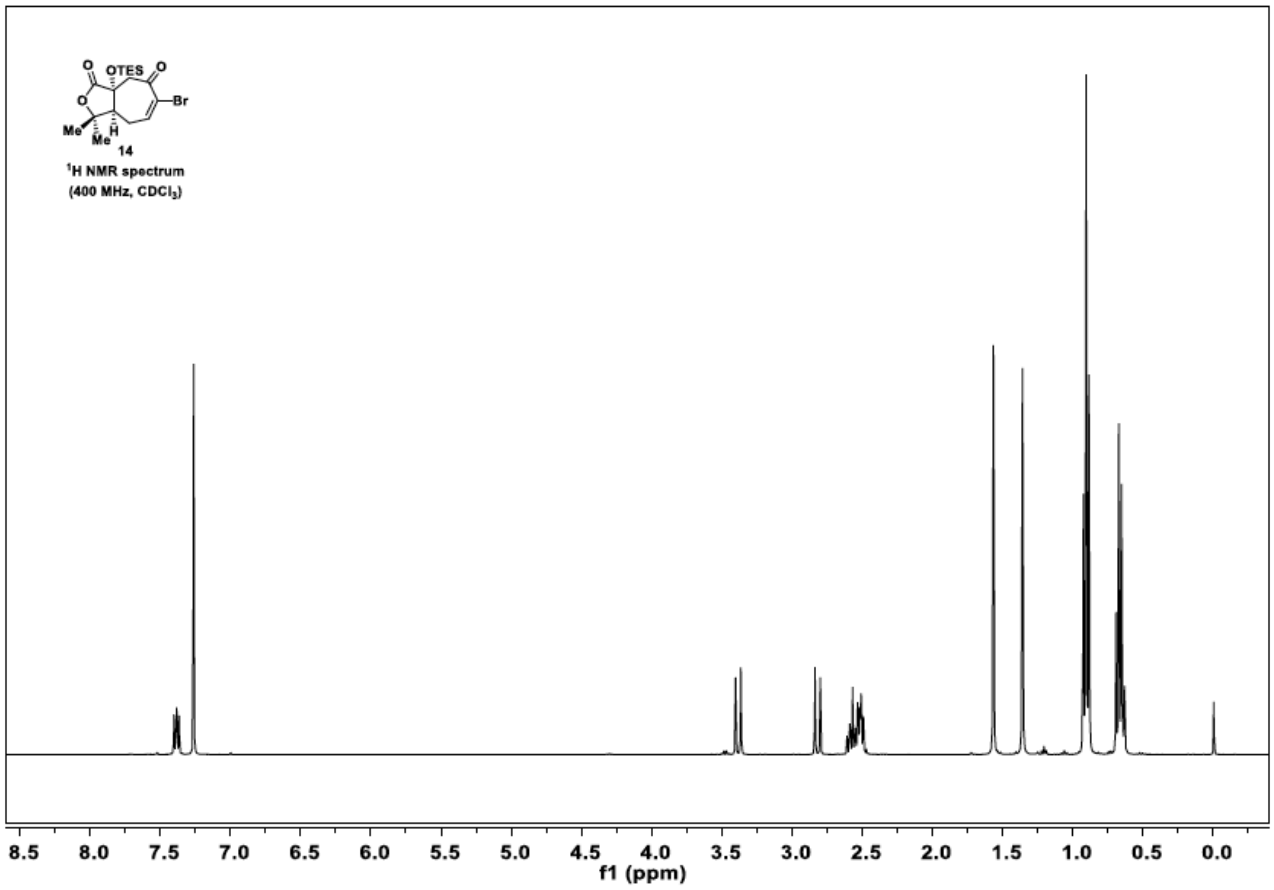

EtO
Me
OTIPS
11
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

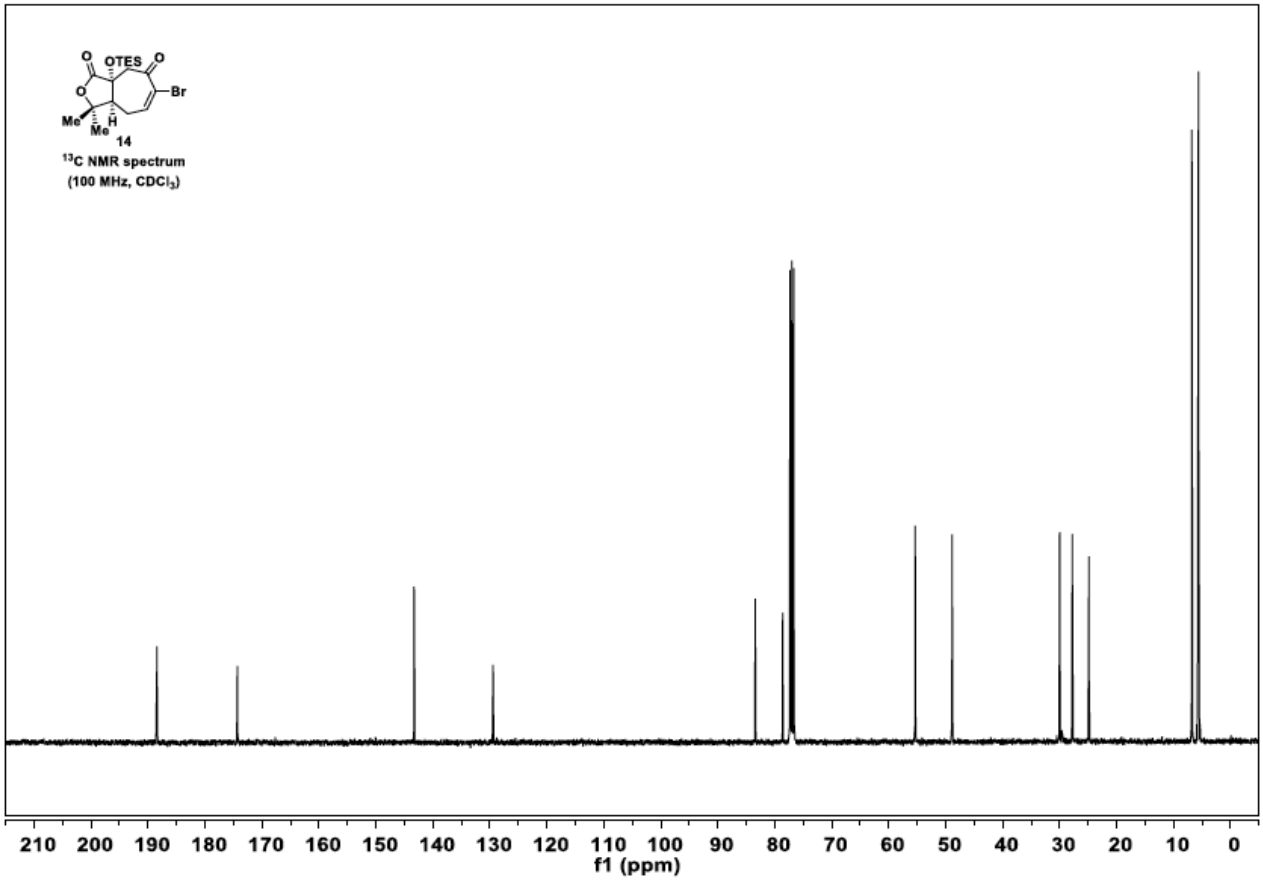

OTIPS
11b
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

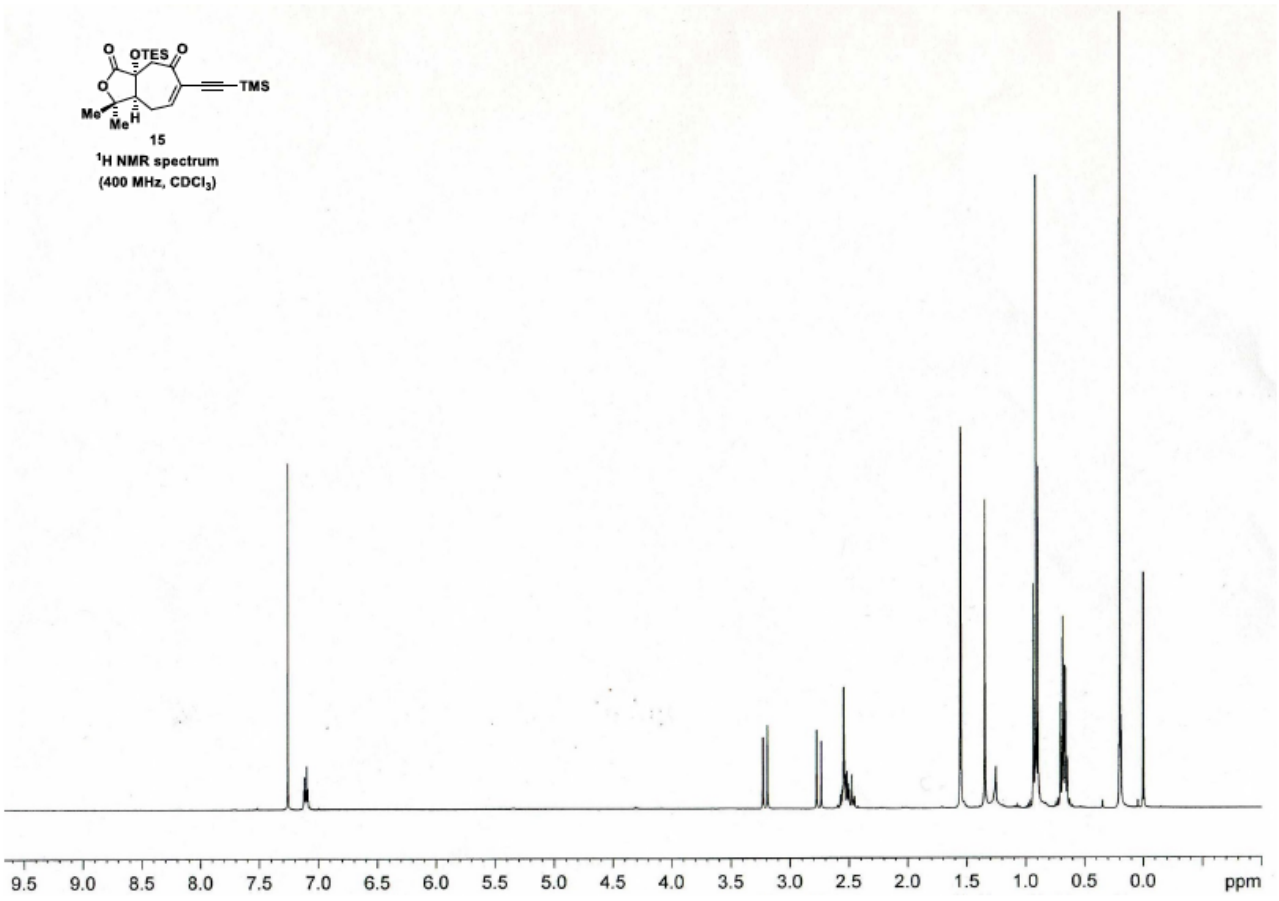

OTIPS
11b
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

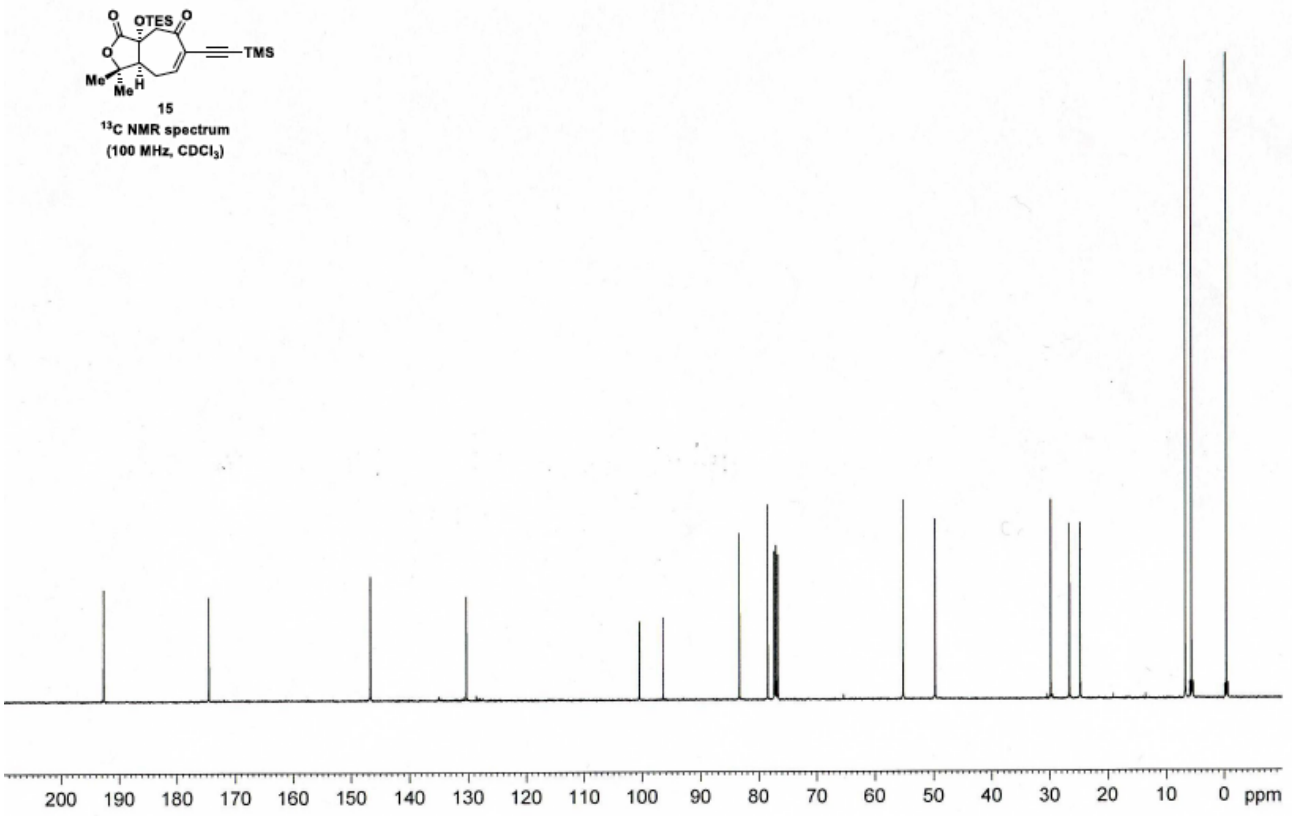

OTES
OTIPS
Me
Me
H
12
1H NMR spectrum
(400 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

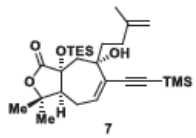

OTES
OTIPS
Me
Me
H
12
13C NMR spectrum
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTES
O
O
O
Br
Me
H
Me
14
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OTES
O
O
O
Br
Me
H
Me
14
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

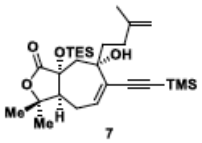

OTES
TMS
Me
Me
H
15
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


OTES
TMS
Me
Me
H
15
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



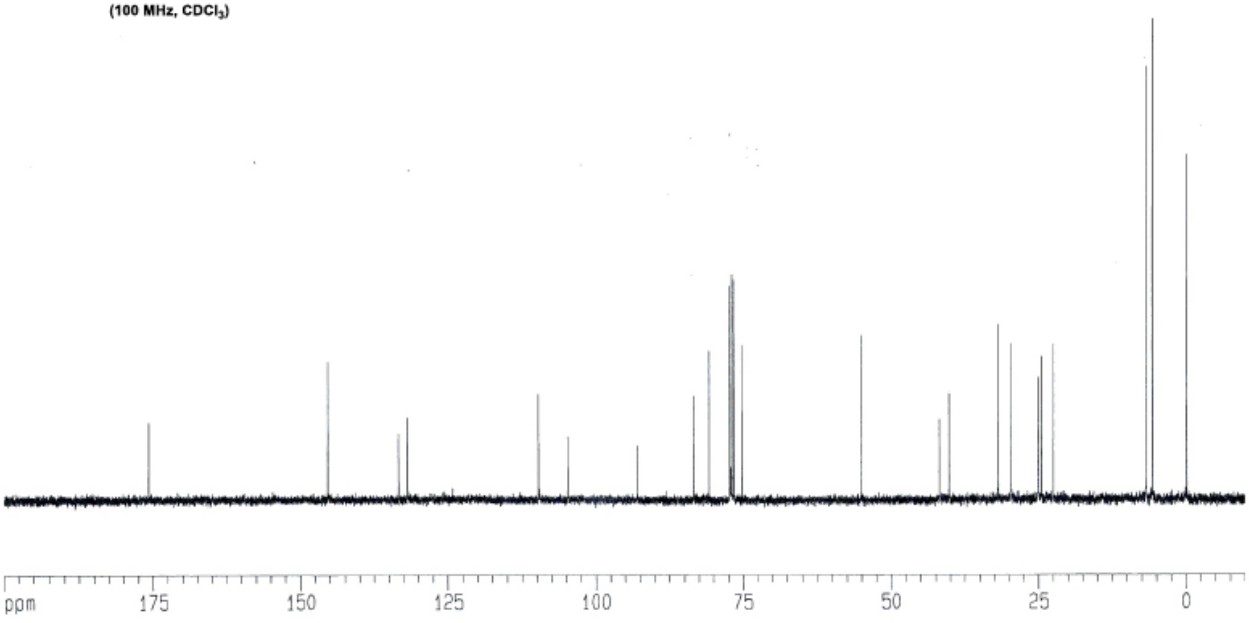
7

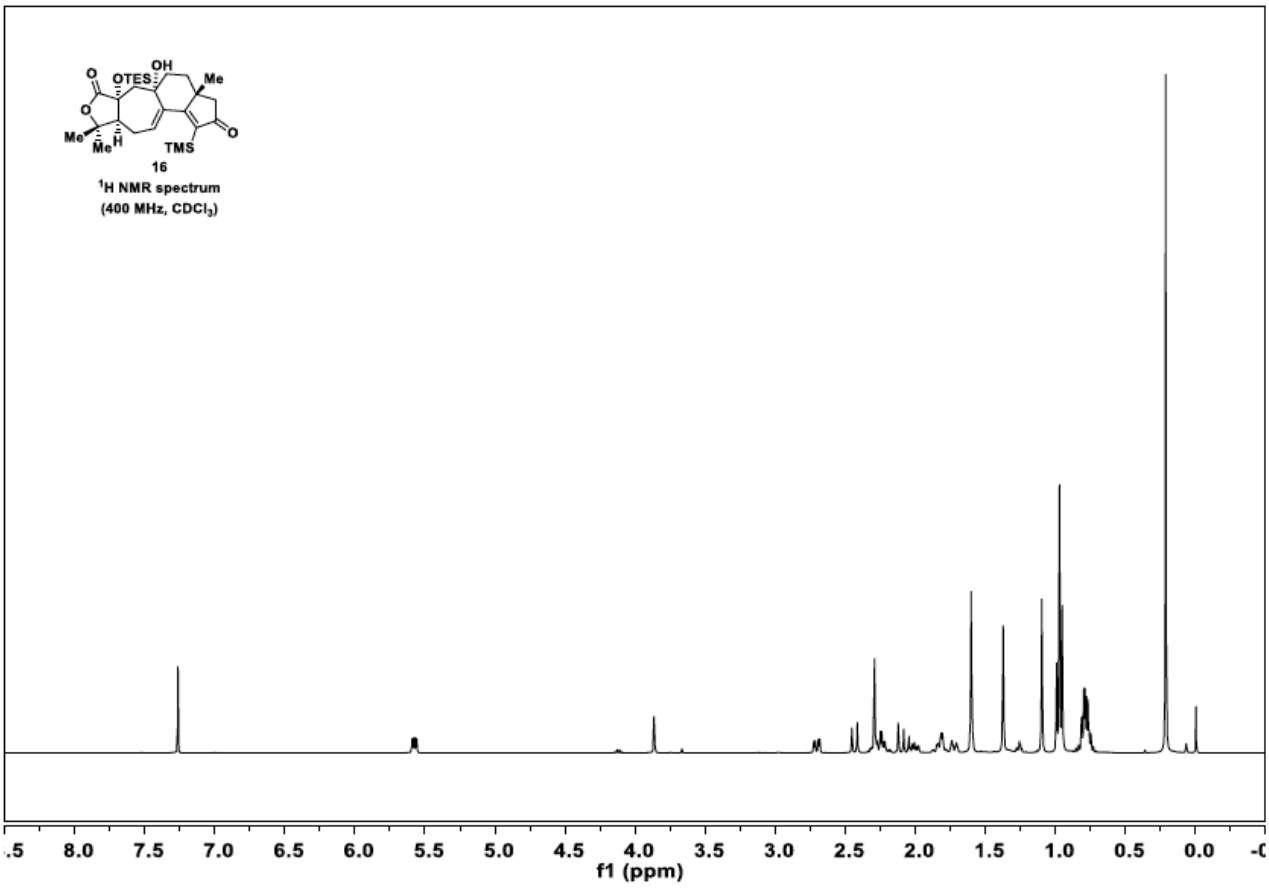
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)

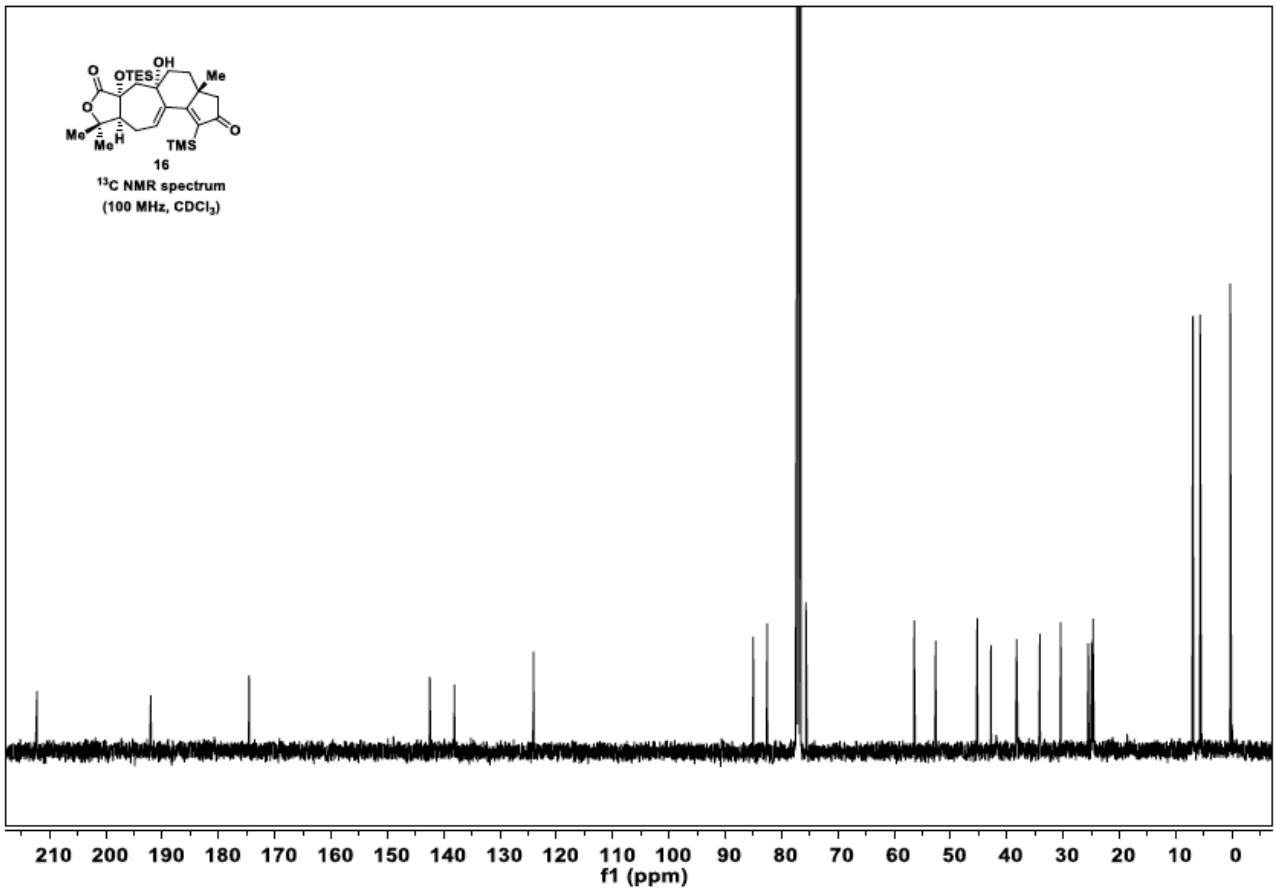


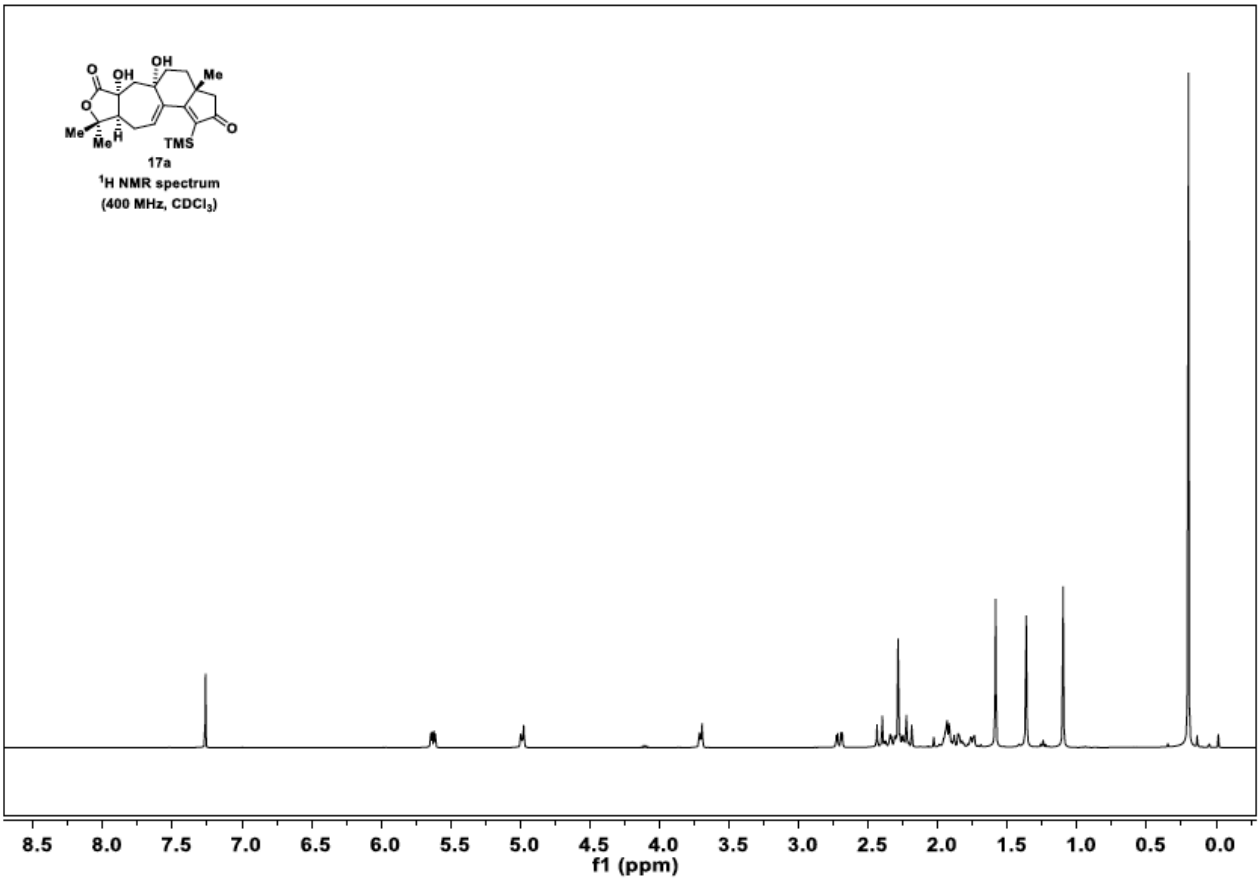
7

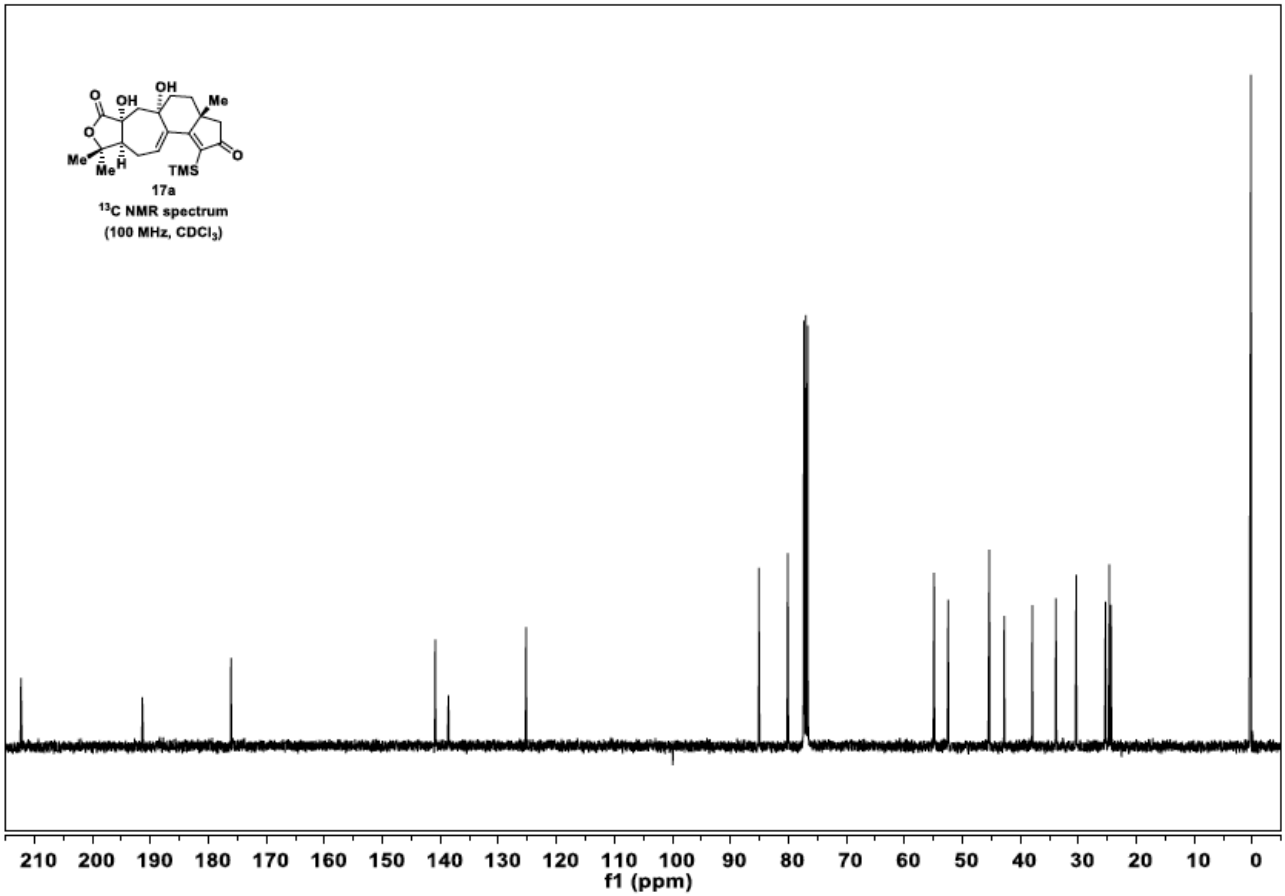
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)

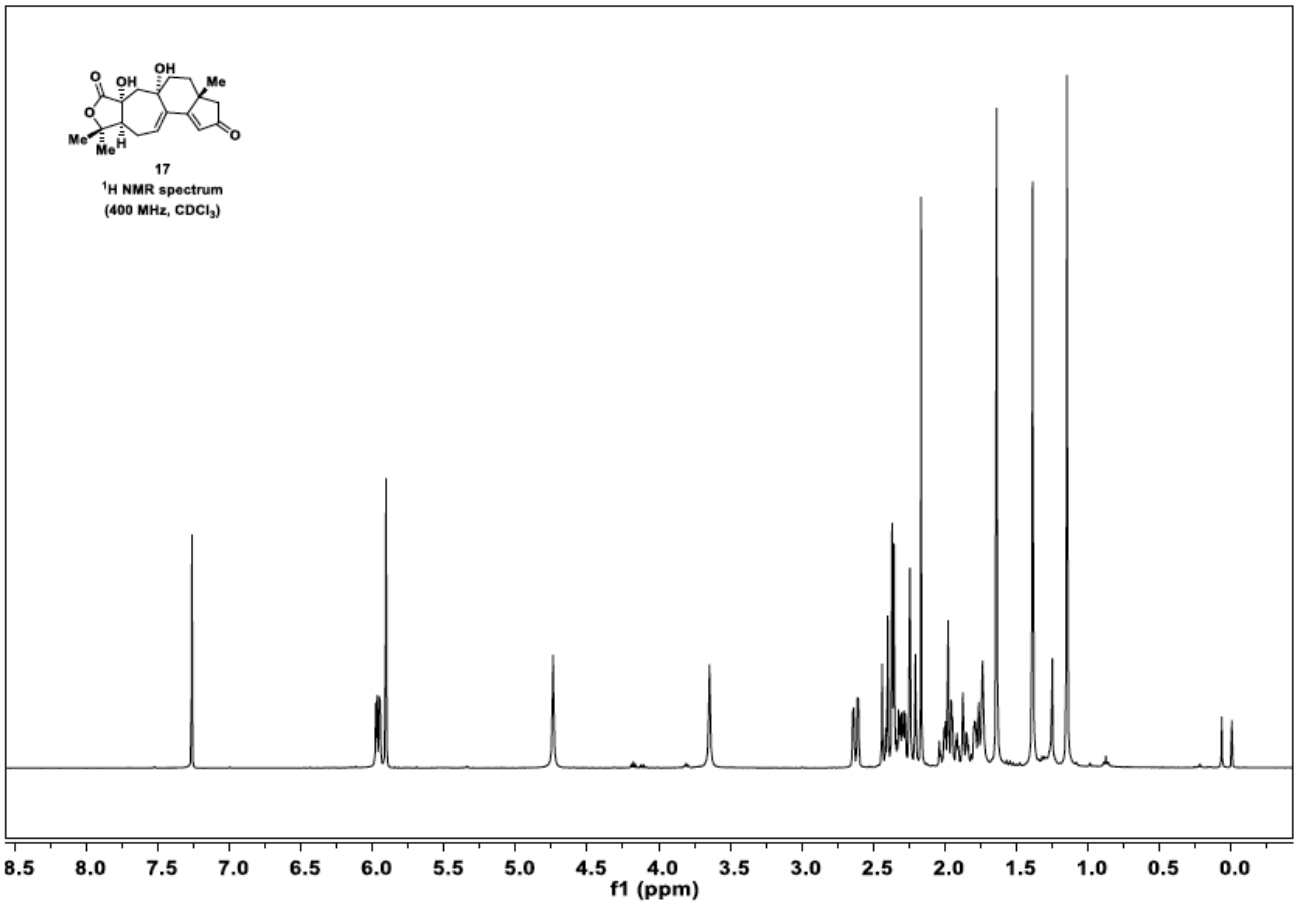


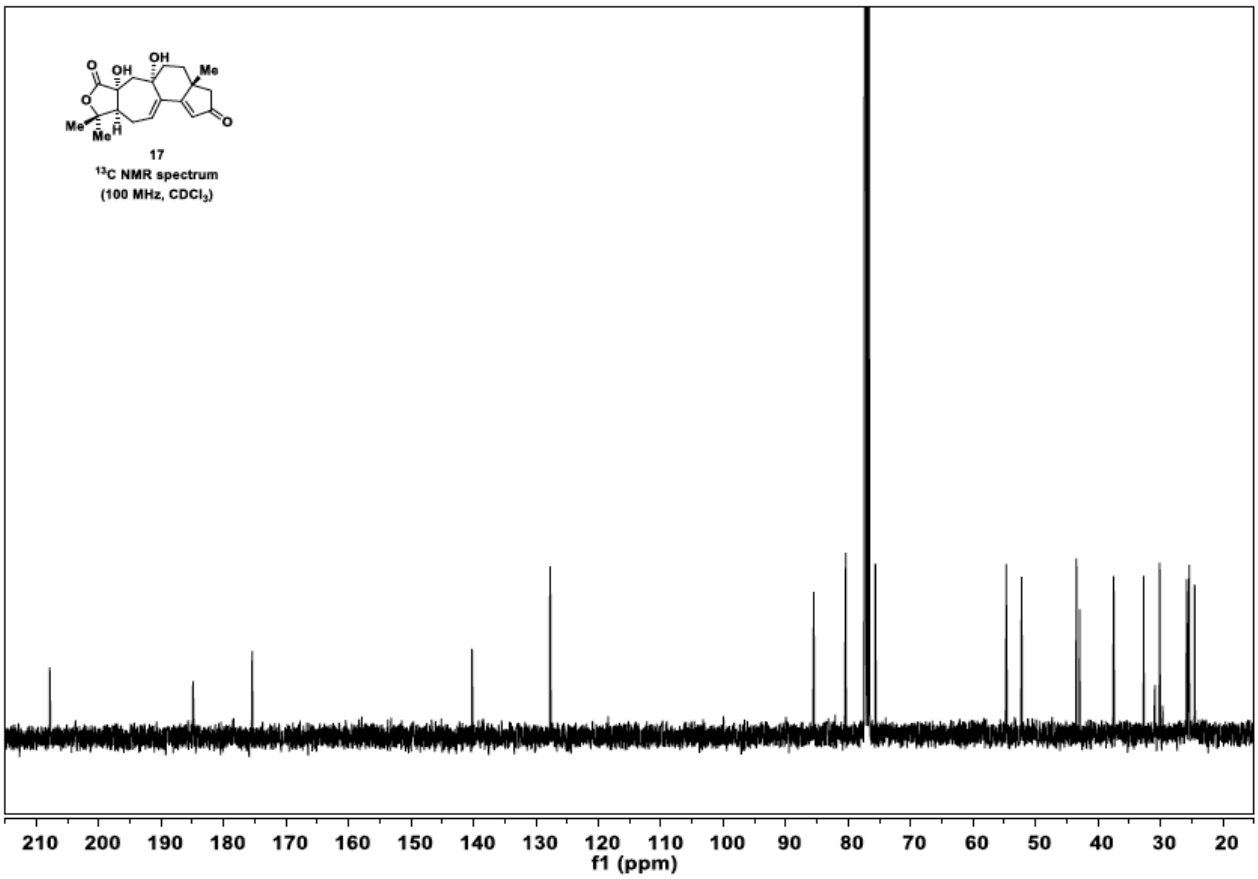

OH
OTES
Me
O
O
Me
Me
H
TMS
O
16
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

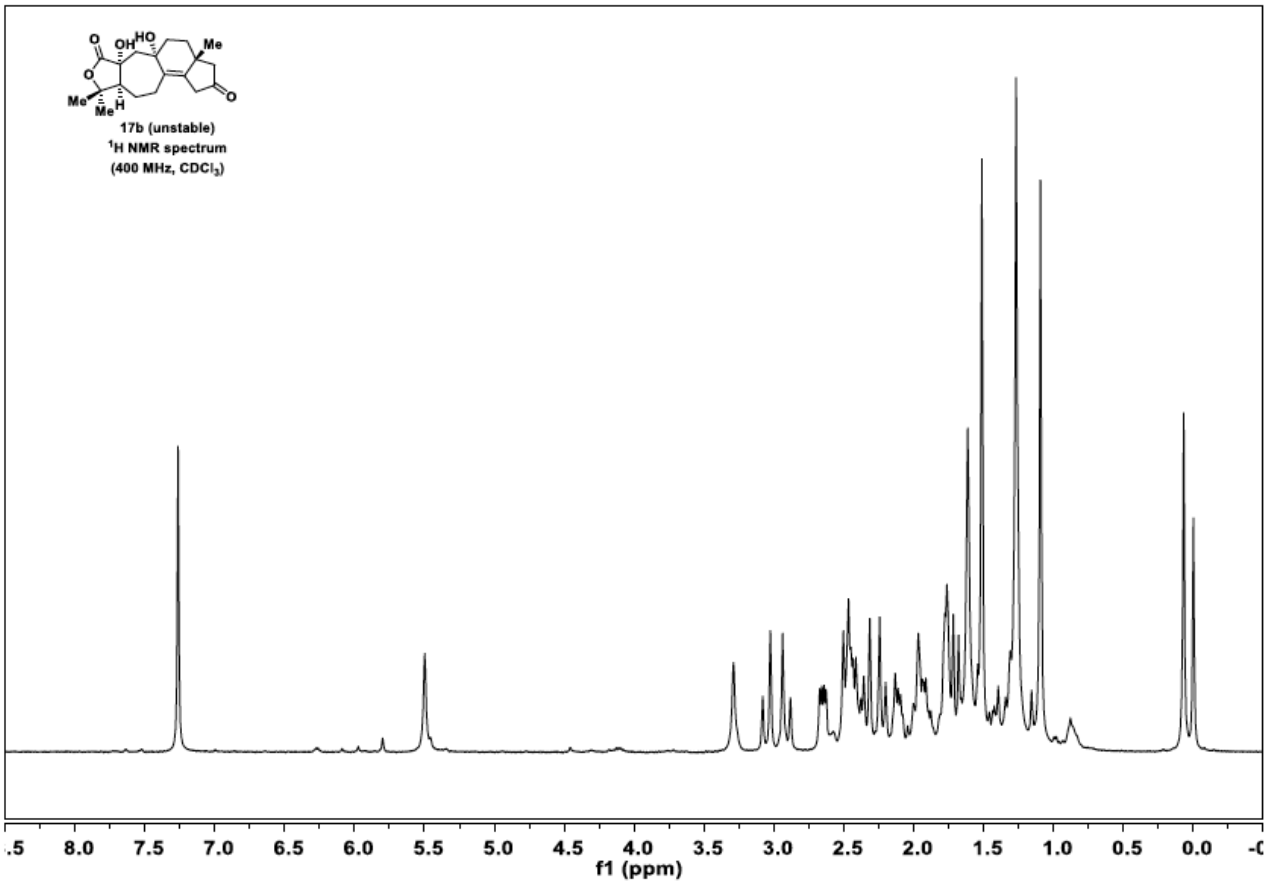

OH
OTES
Me
O
O
Me
Me
H
TMS
O
16
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

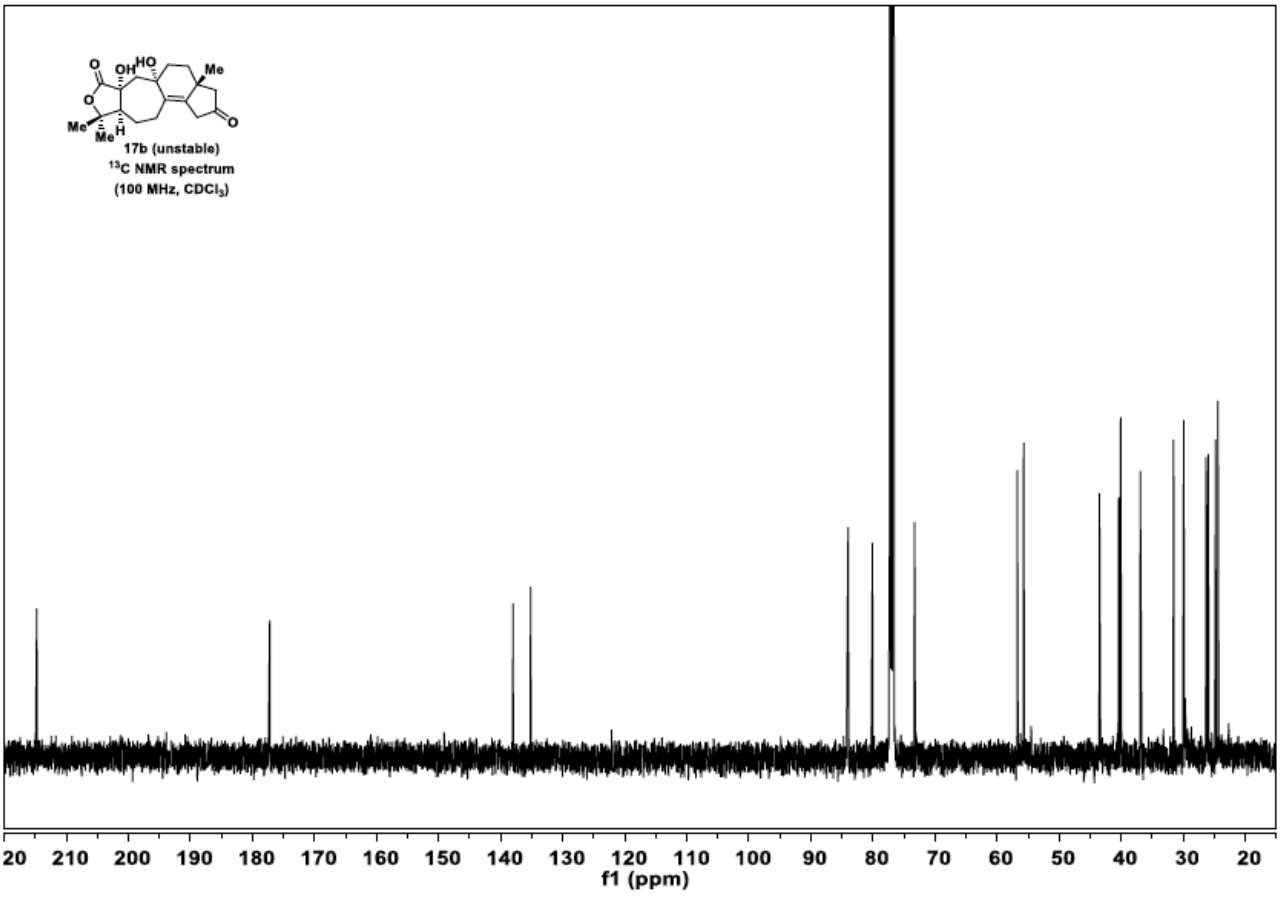

17a
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

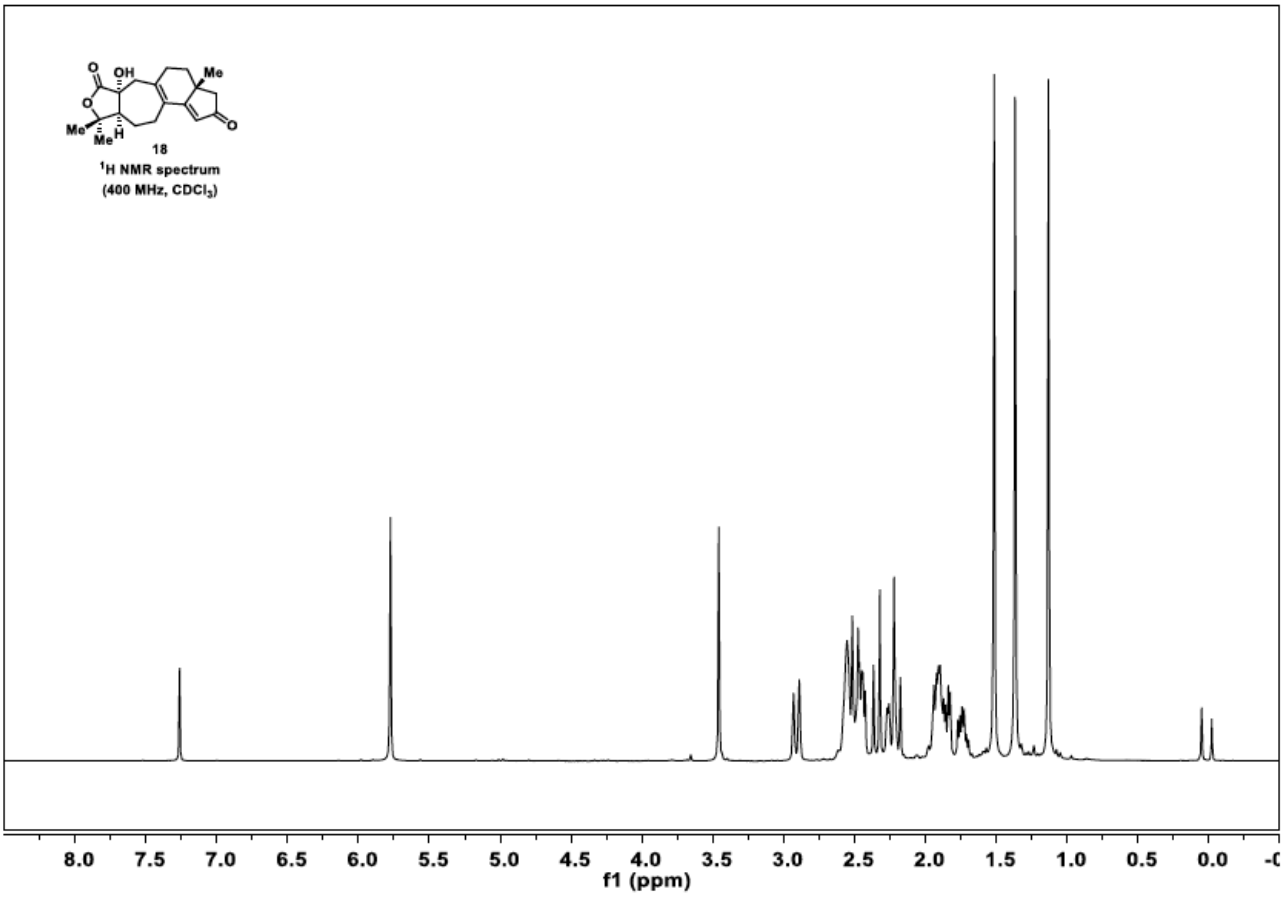

17a
^{13}C NMR spectrum
(100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

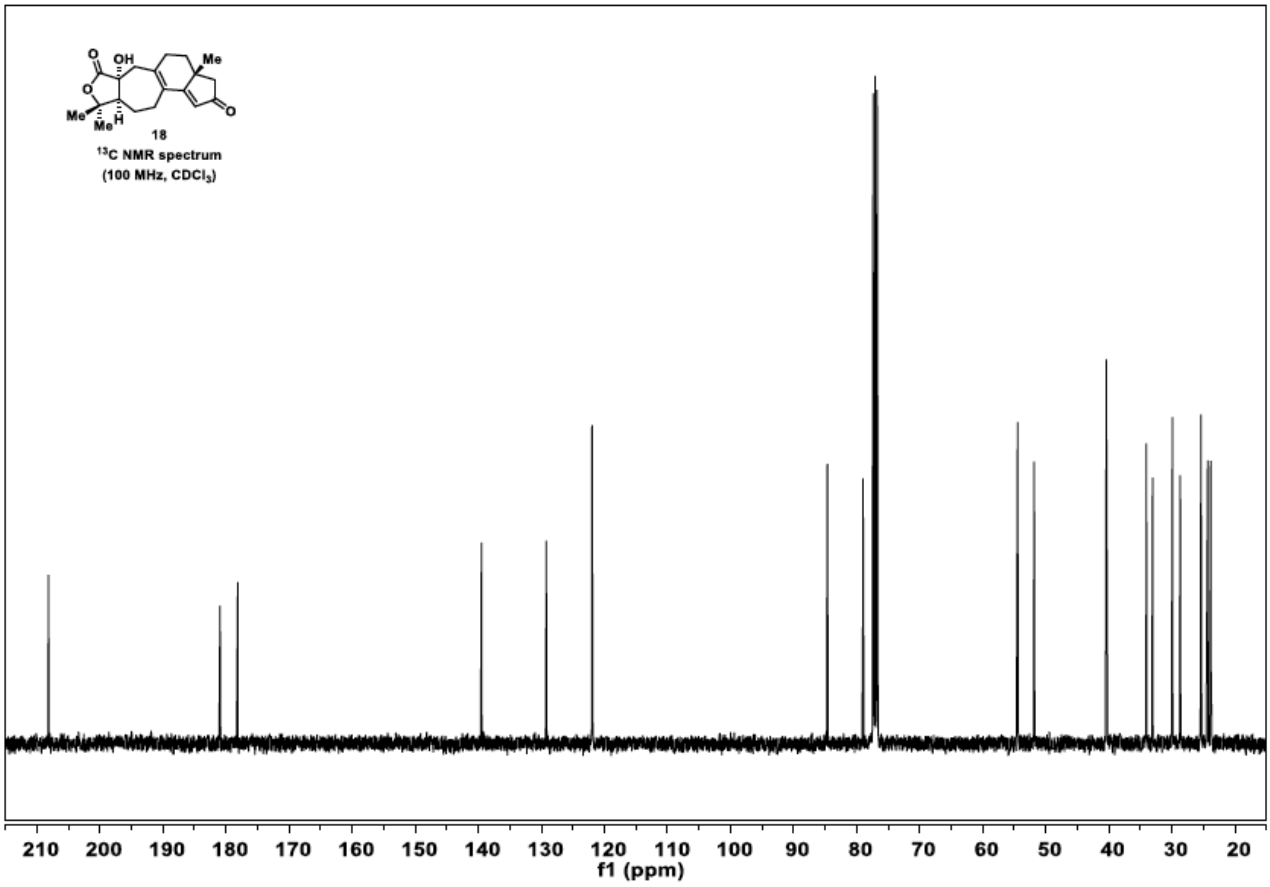

17
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

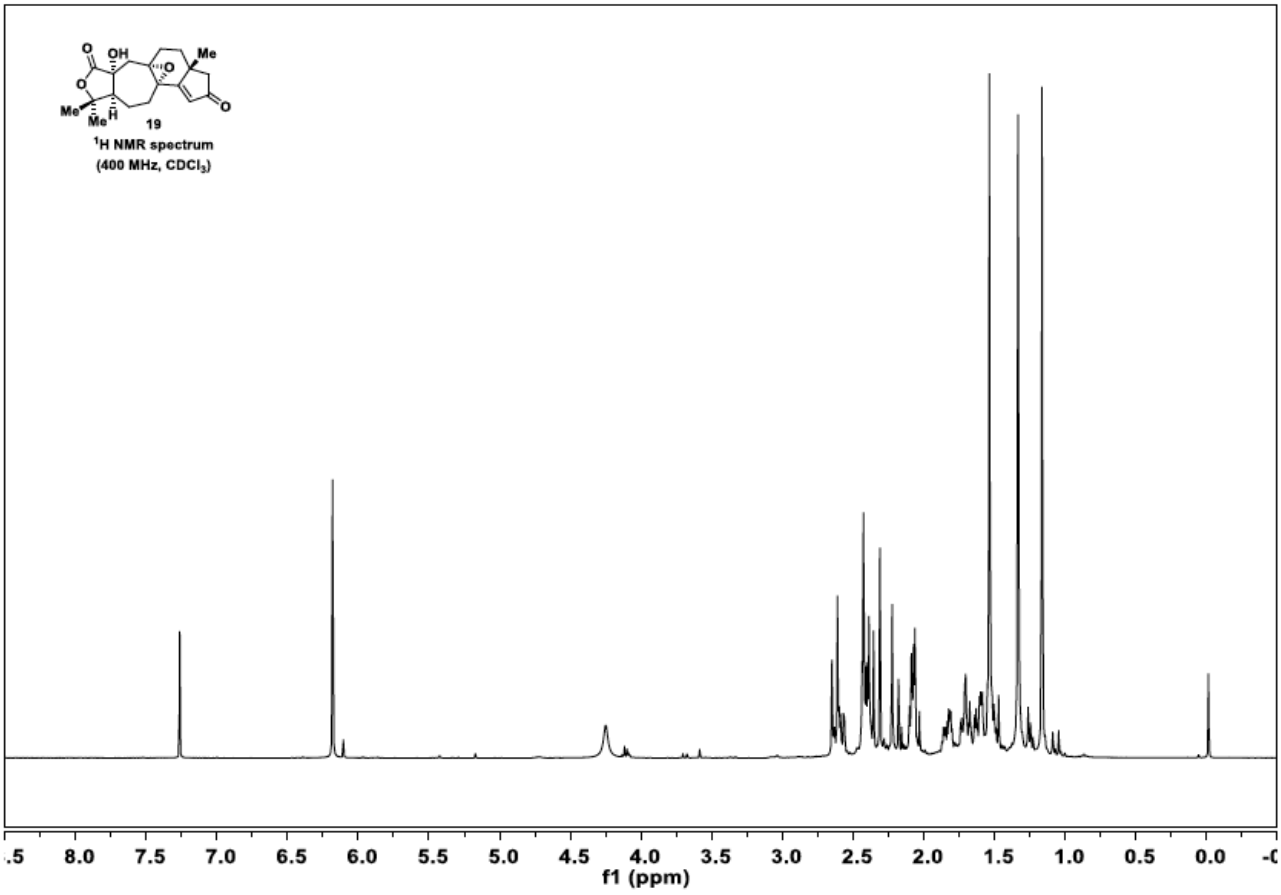

17
^{13}C NMR spectrum
(100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

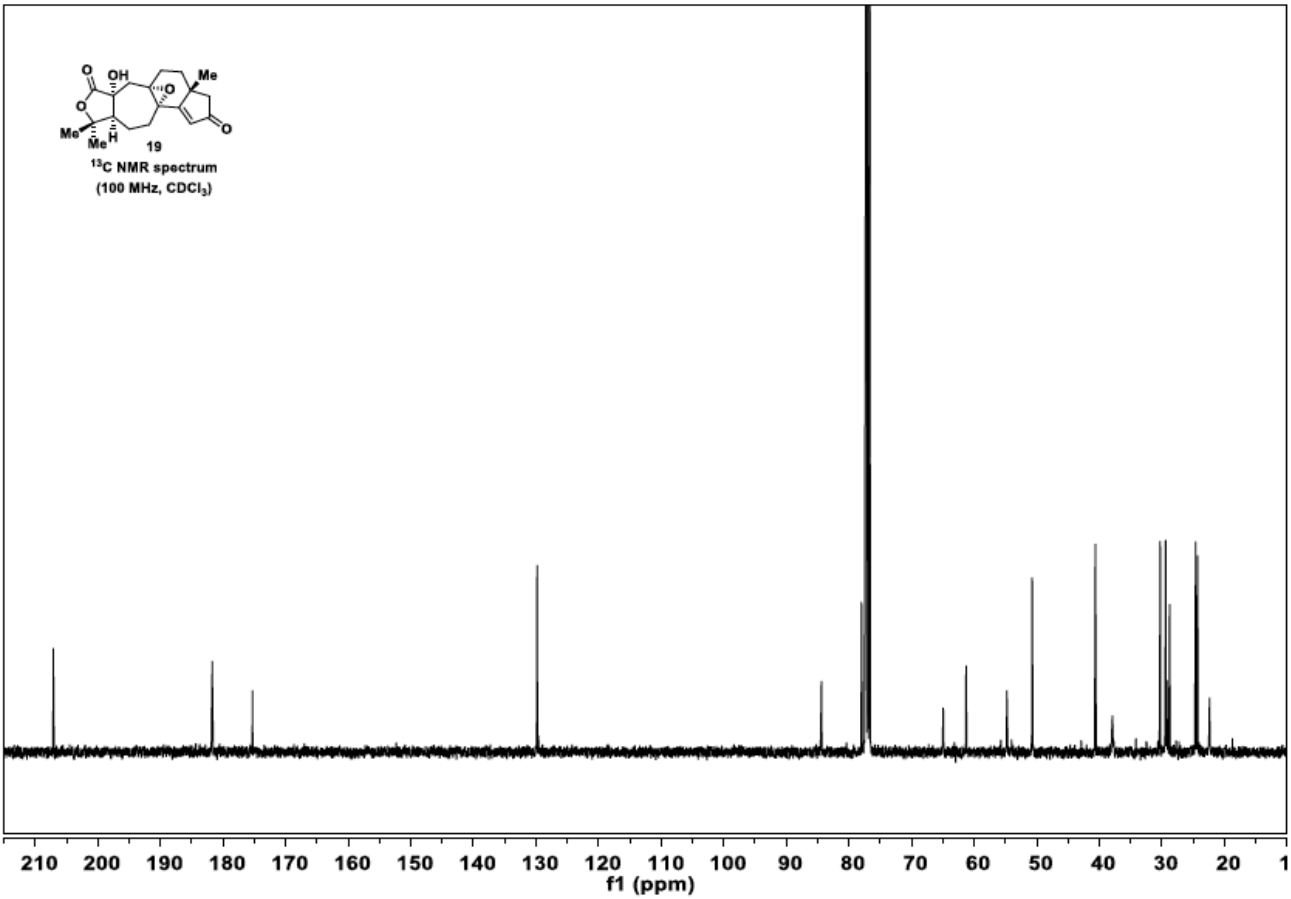

17b (unstable)
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
f1 (ppm)

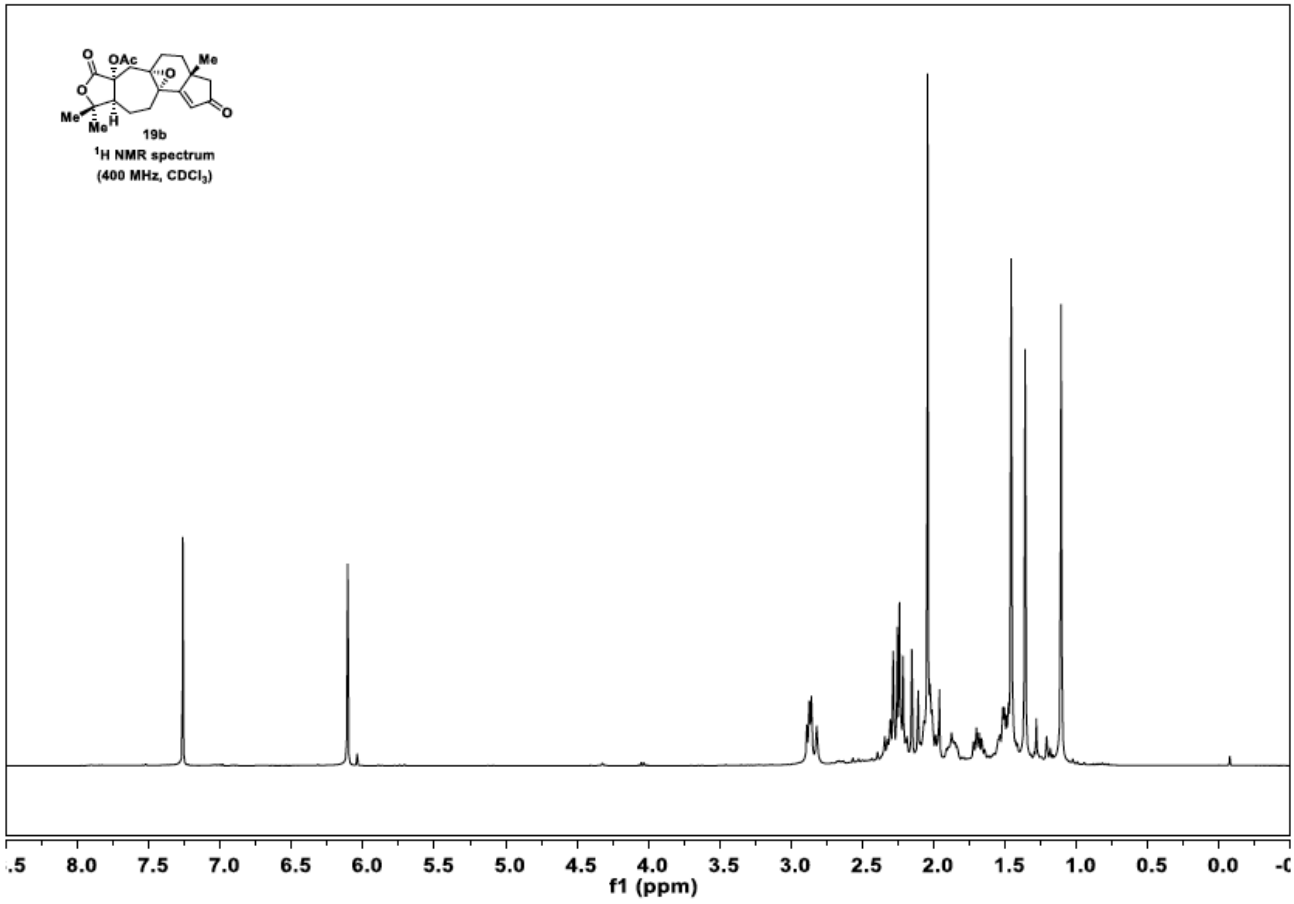

17b (unstable)
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
f1 (ppm)

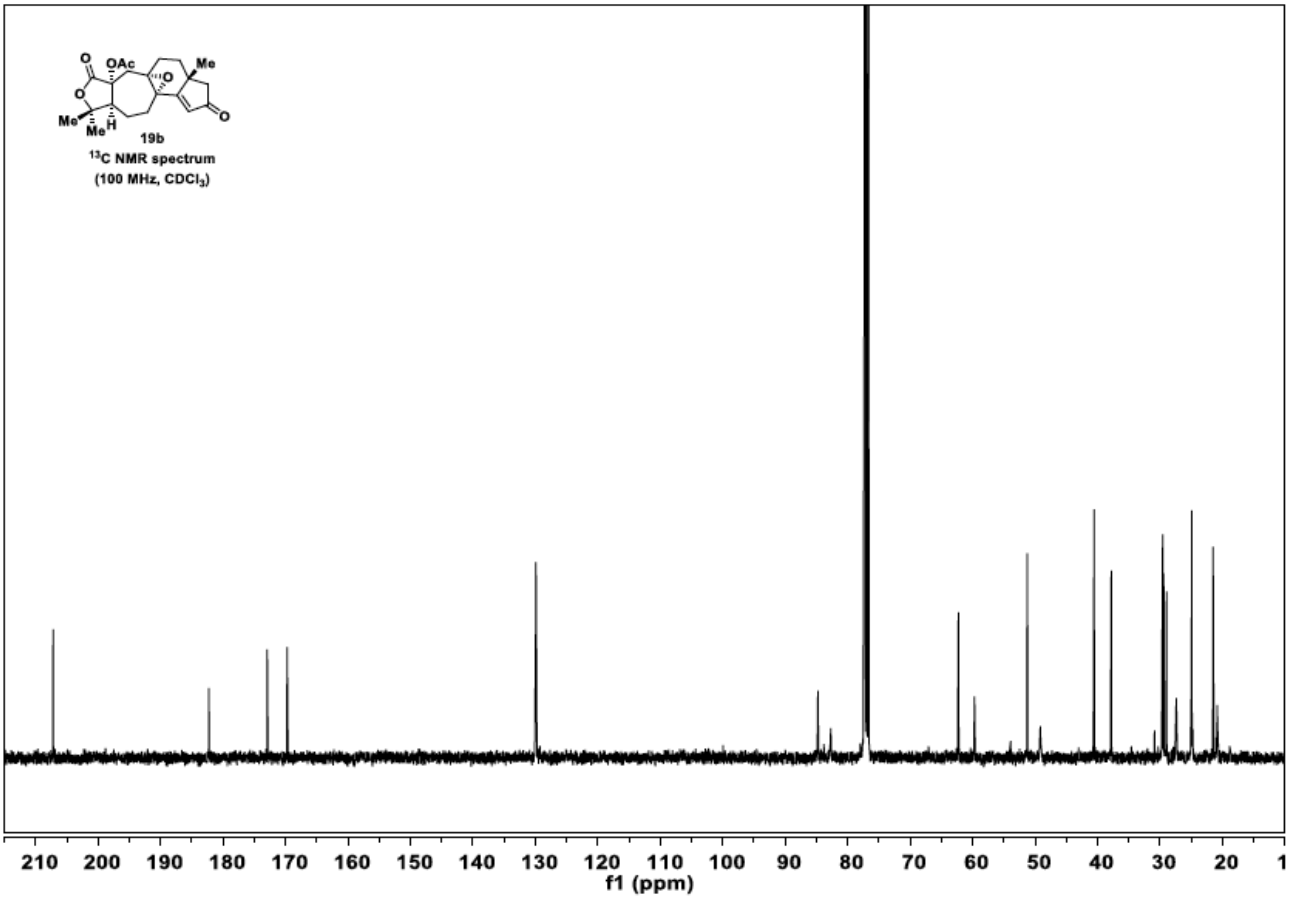

18
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

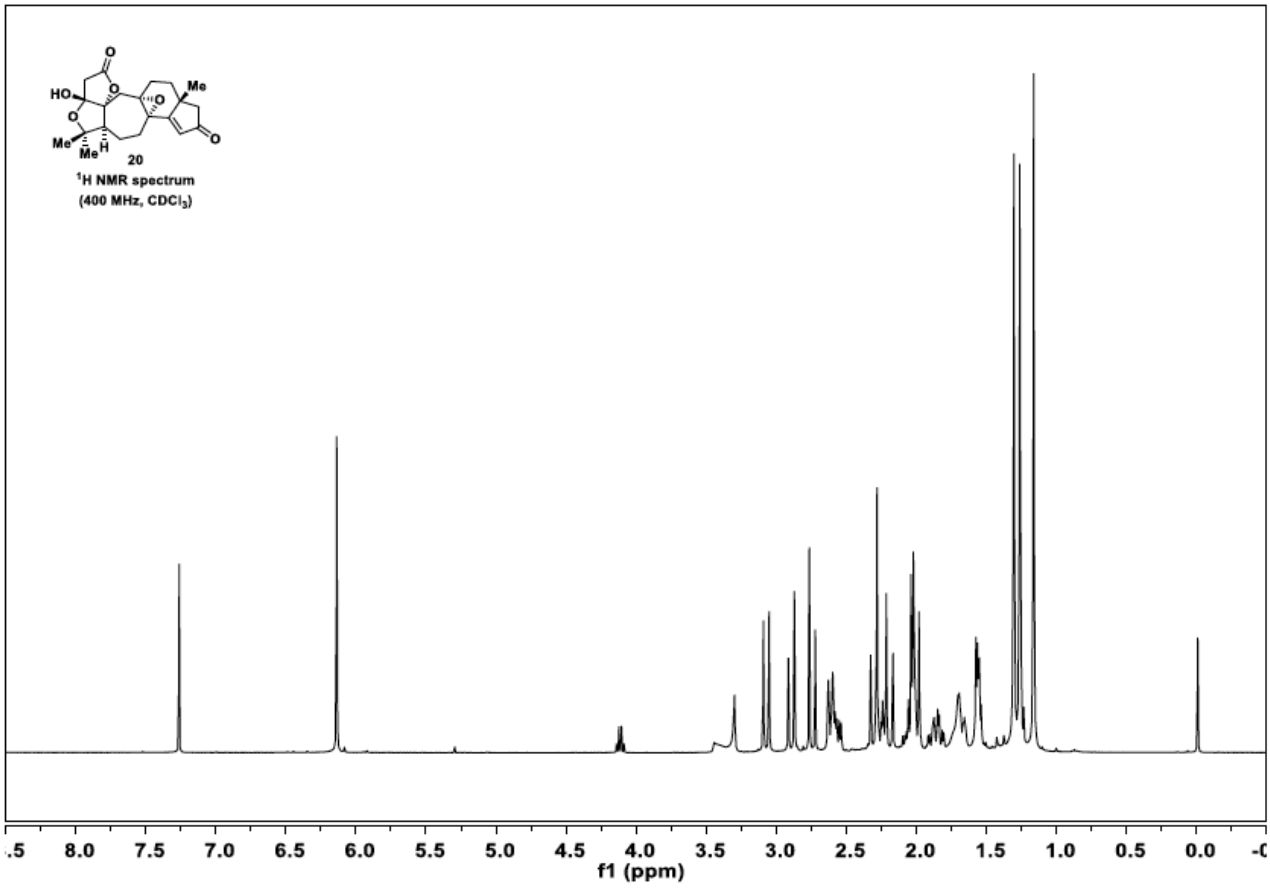

18
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

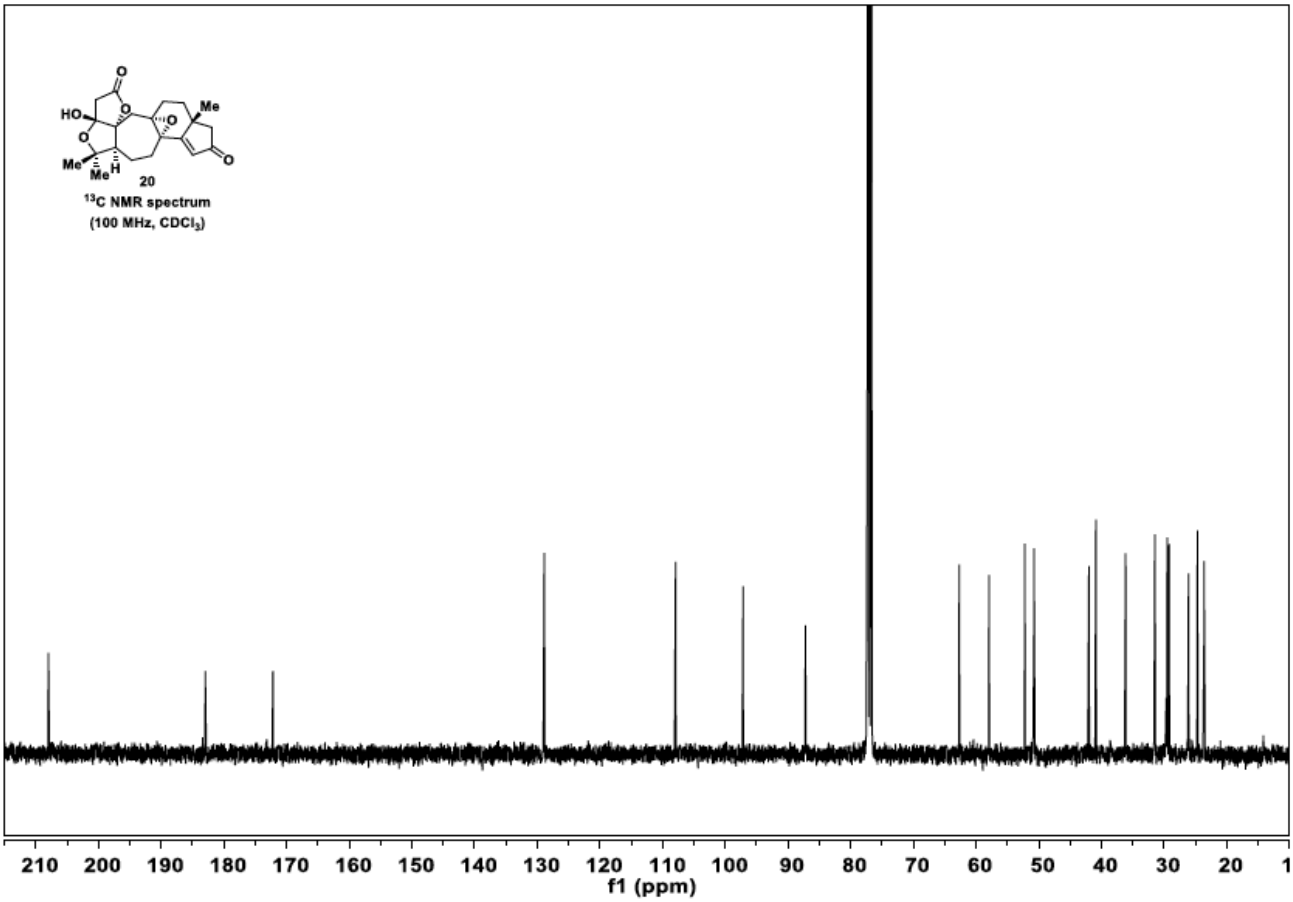

19
1H NMR spectrum
(400 MHz, CDCl3)
f1 (ppm)

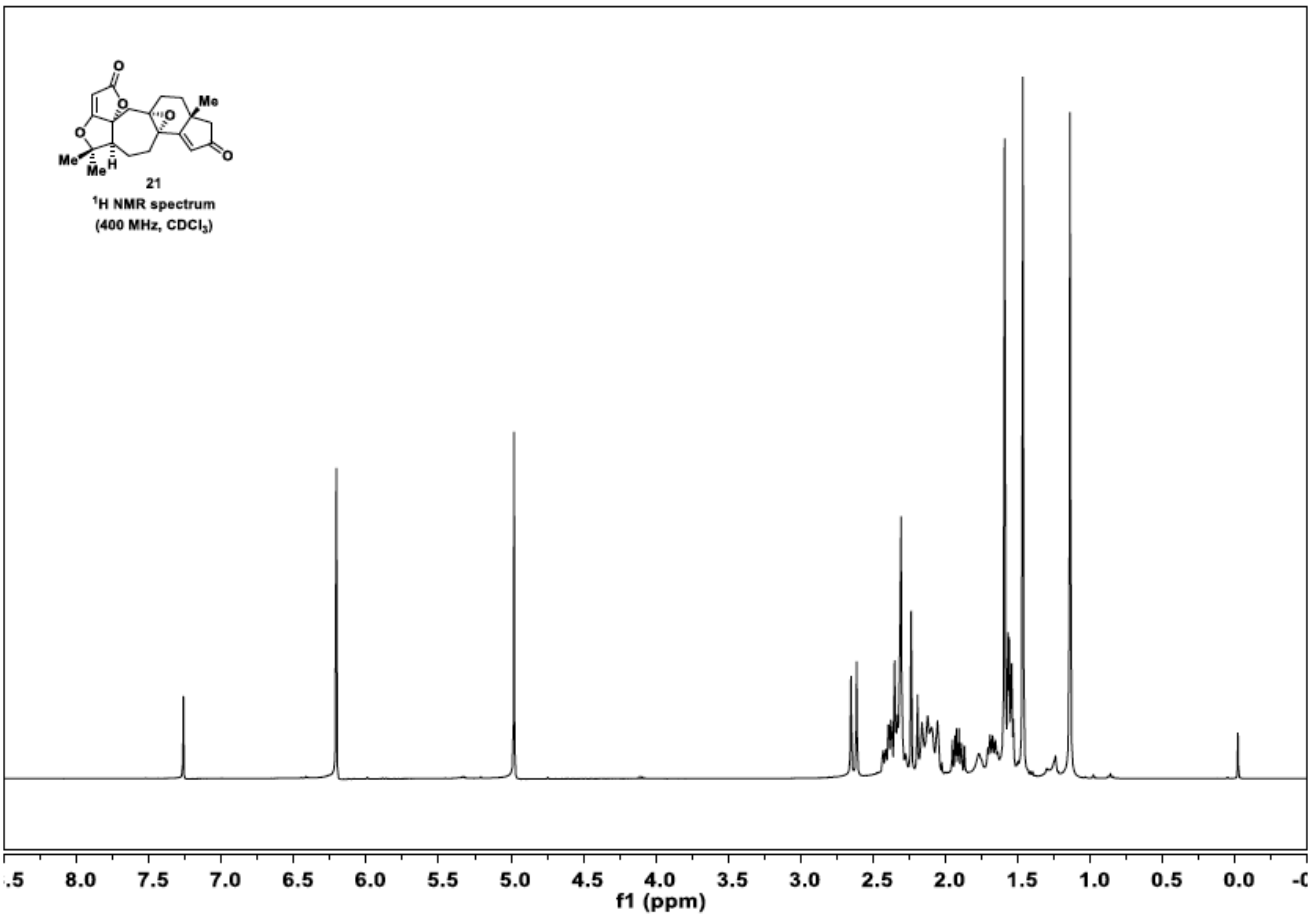

19
13C NMR spectrum
(100 MHz, CDCl3)
f1 (ppm)

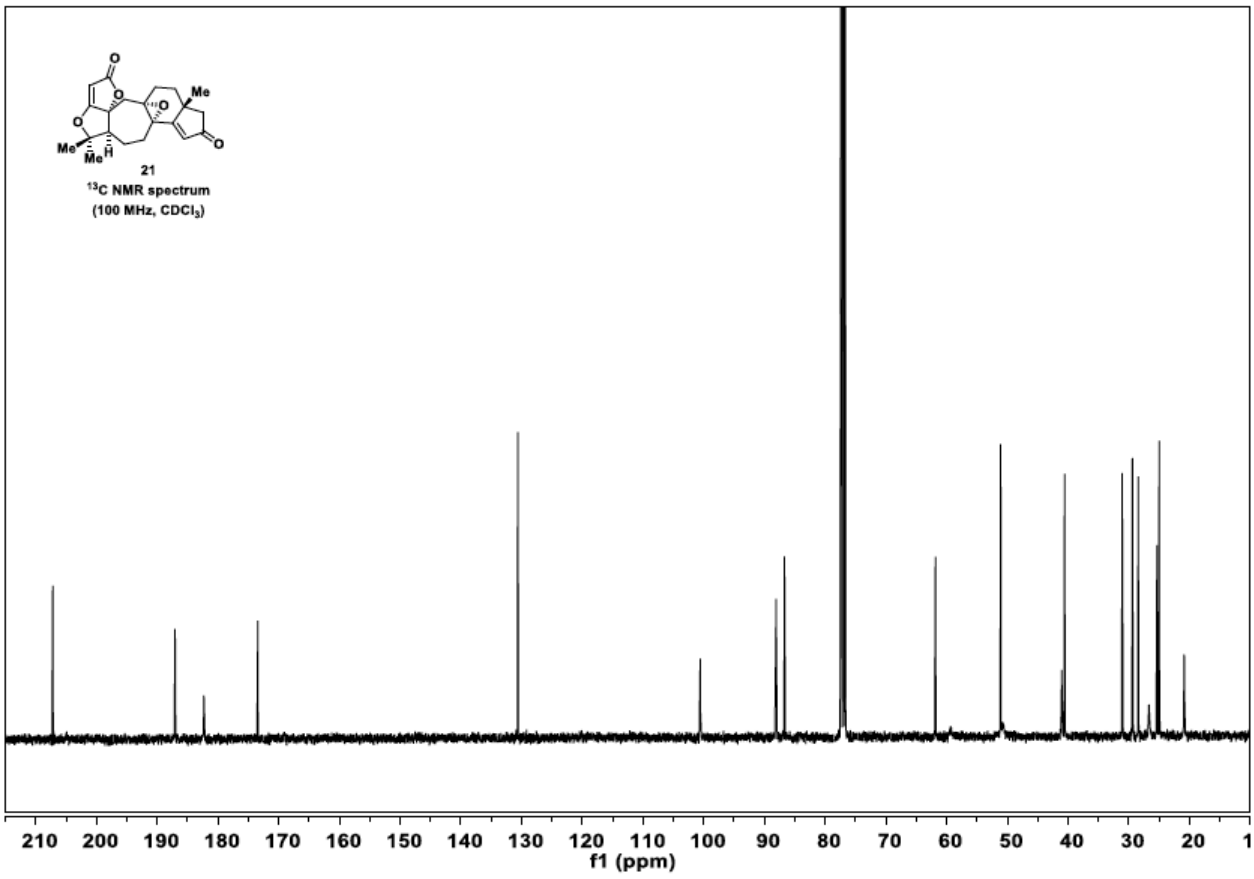

19b
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
f1 (ppm)

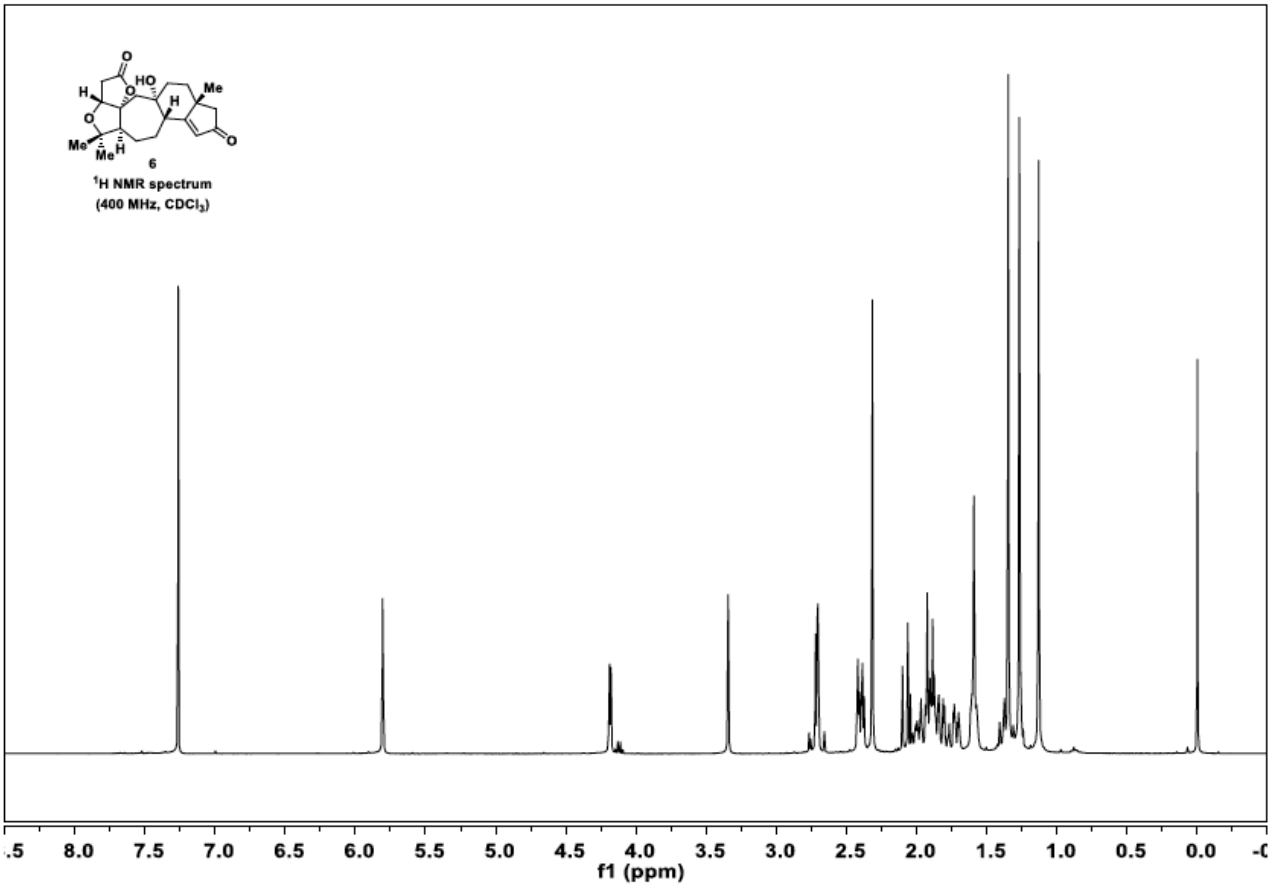

19b
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
f1 (ppm)

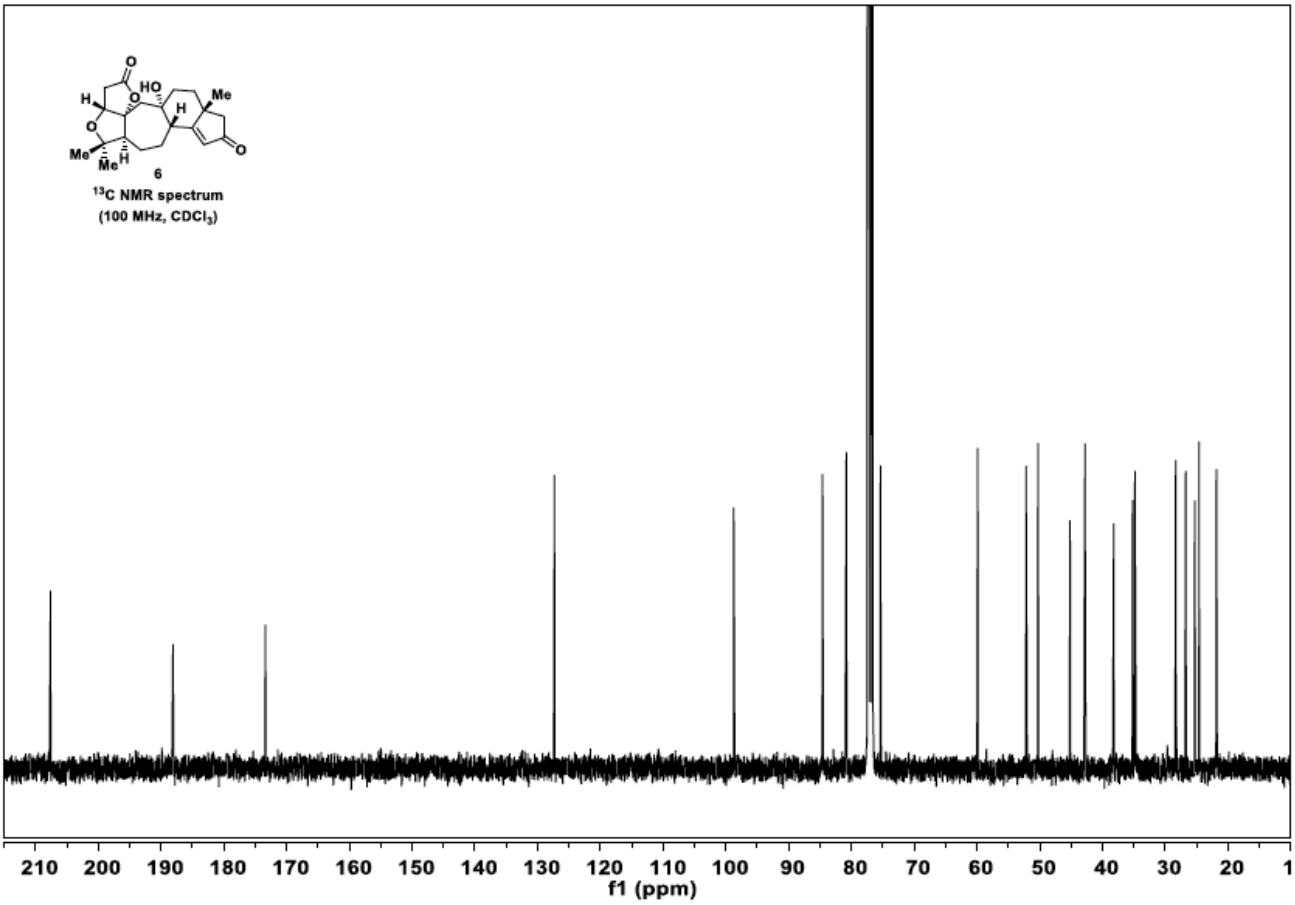

HO
O
O
O
Me
Me
H
Me
O
O
20
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

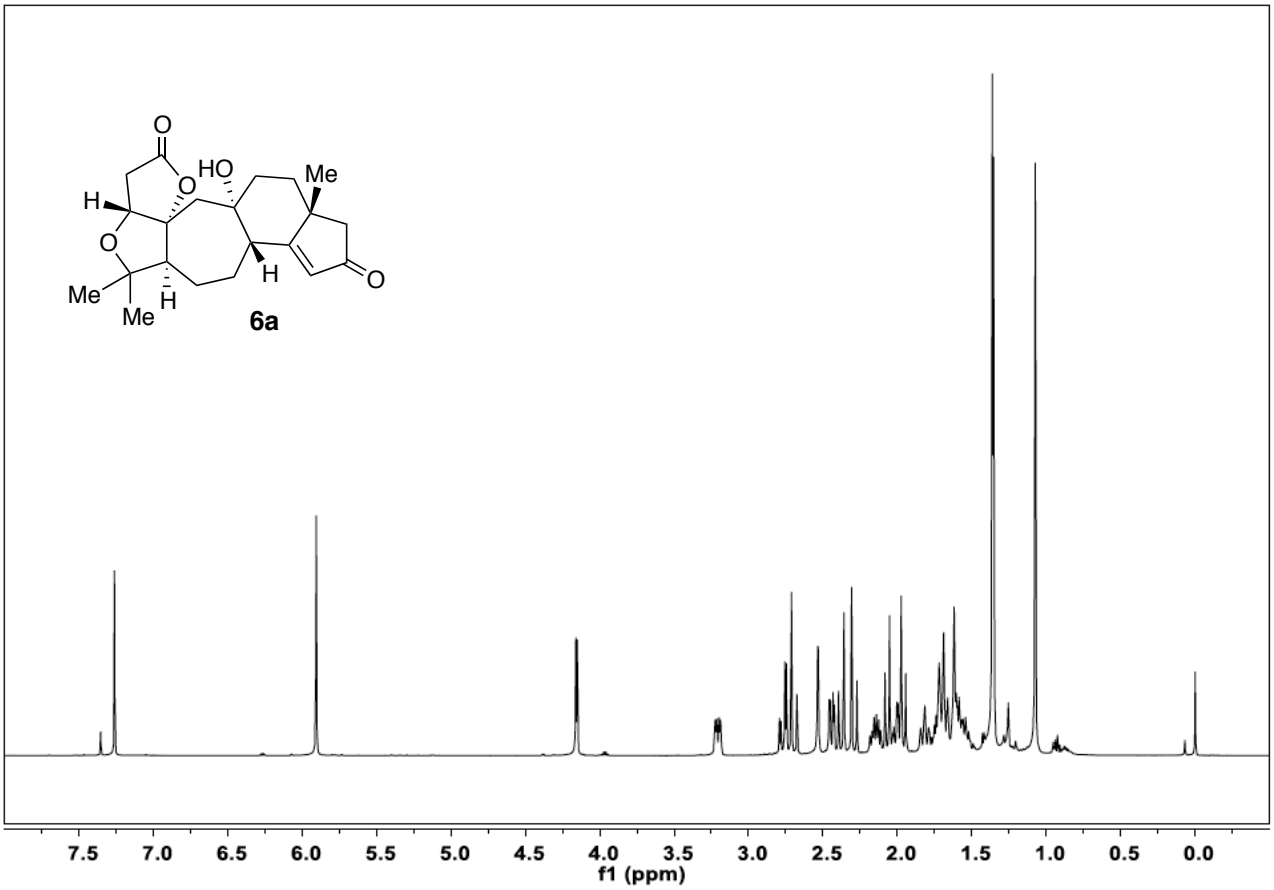

HO
O
O
O
Me
Me
H
Me
O
O
20
^{13}C NMR spectrum
(100 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

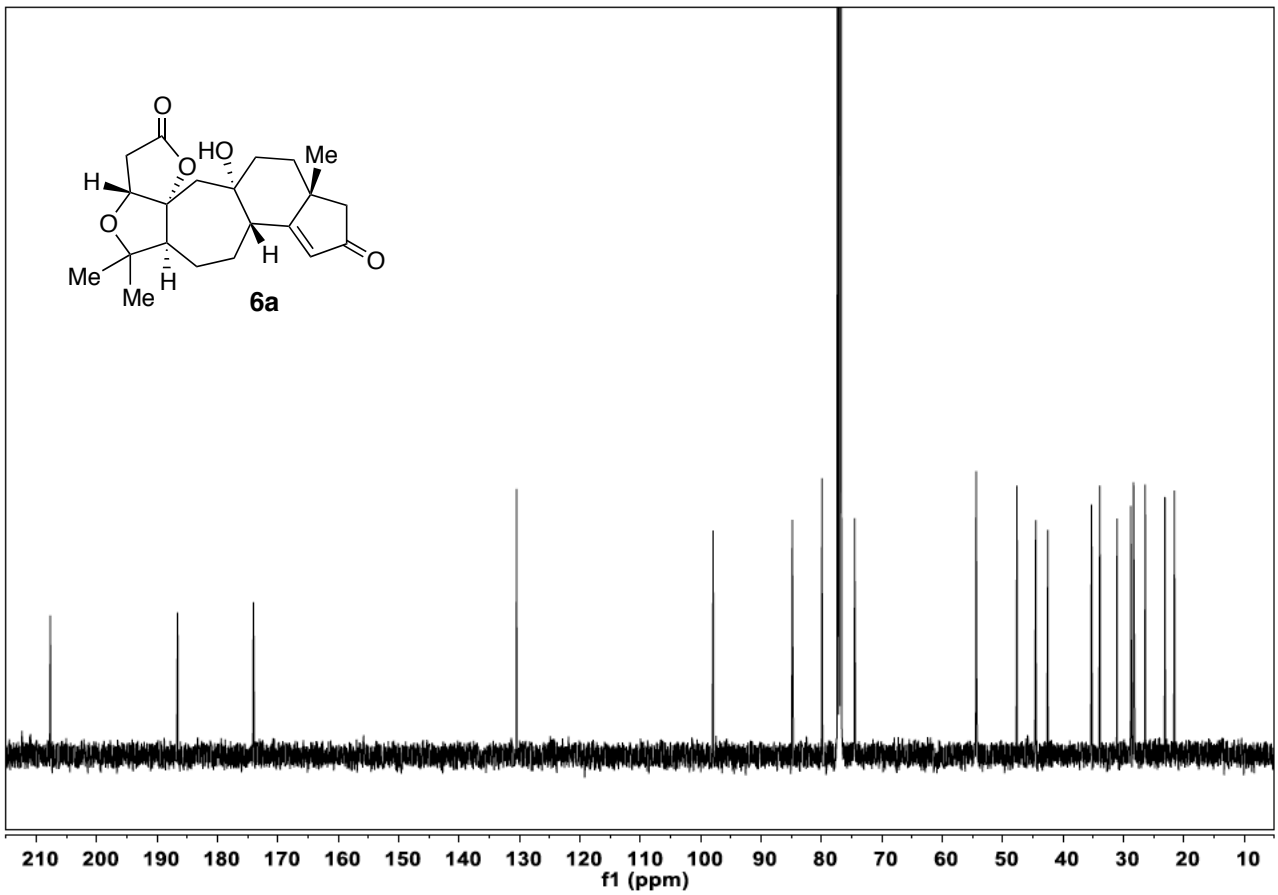

21
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
f1 (ppm)

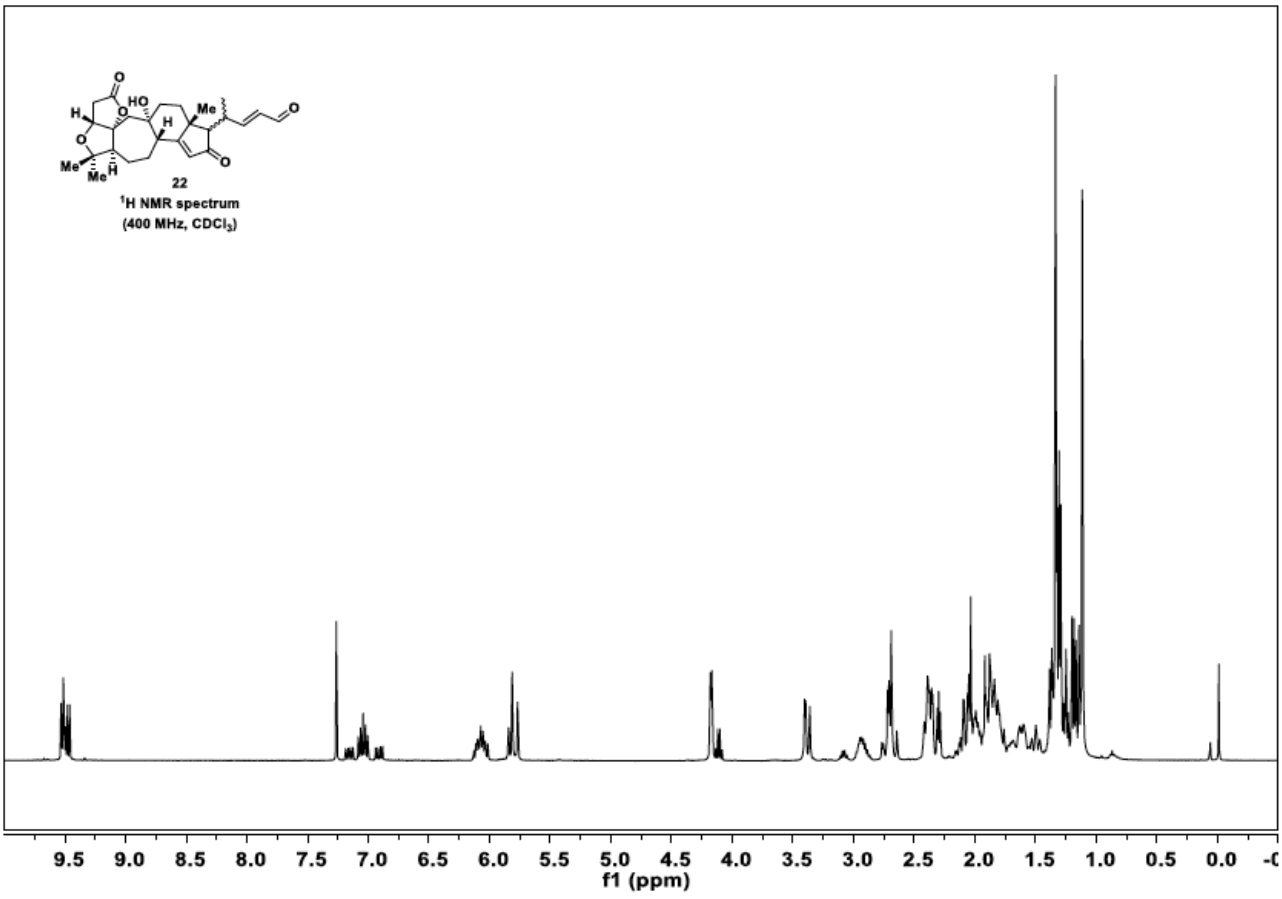

21
^{13}C NMR spectrum
(100 MHz, $CDCl_3$)
f1 (ppm)

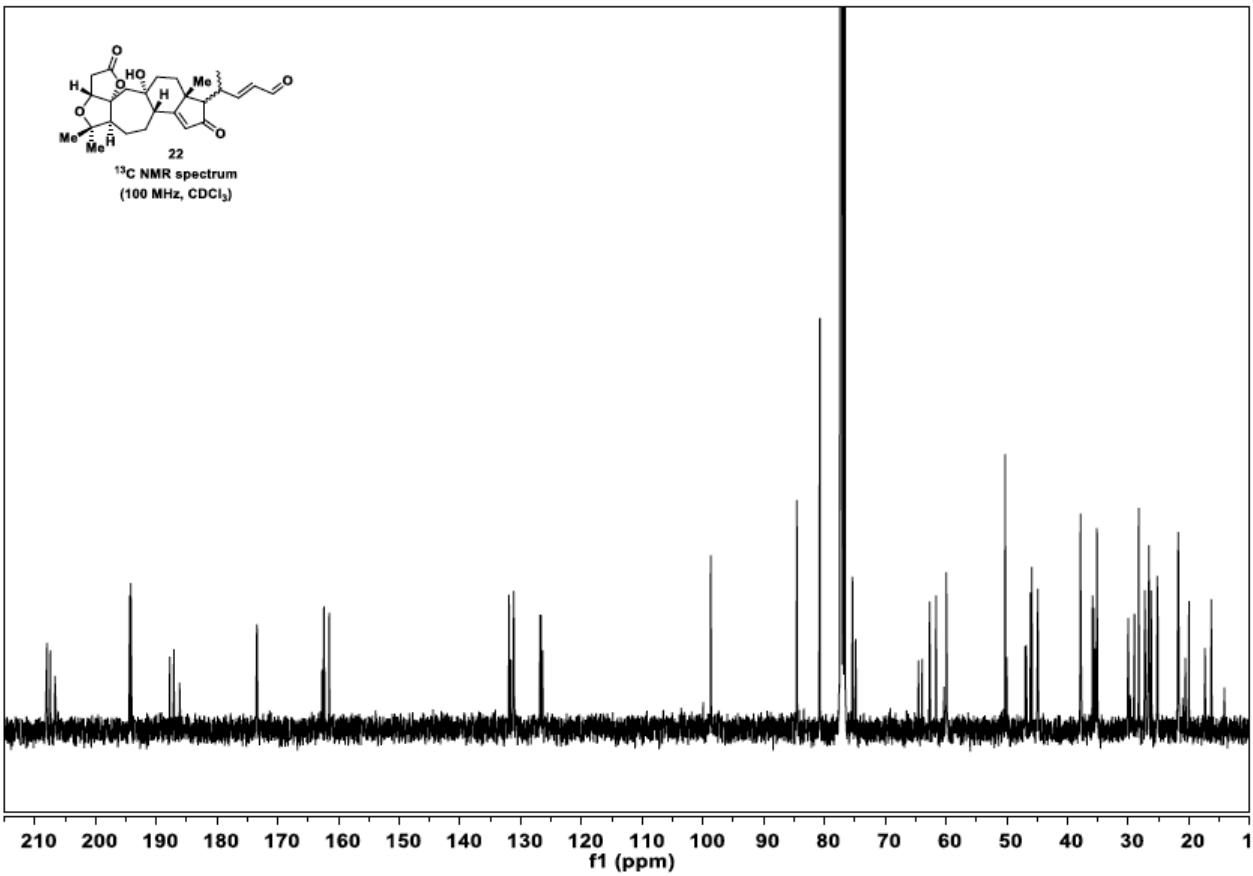

6
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)
f1 (ppm)

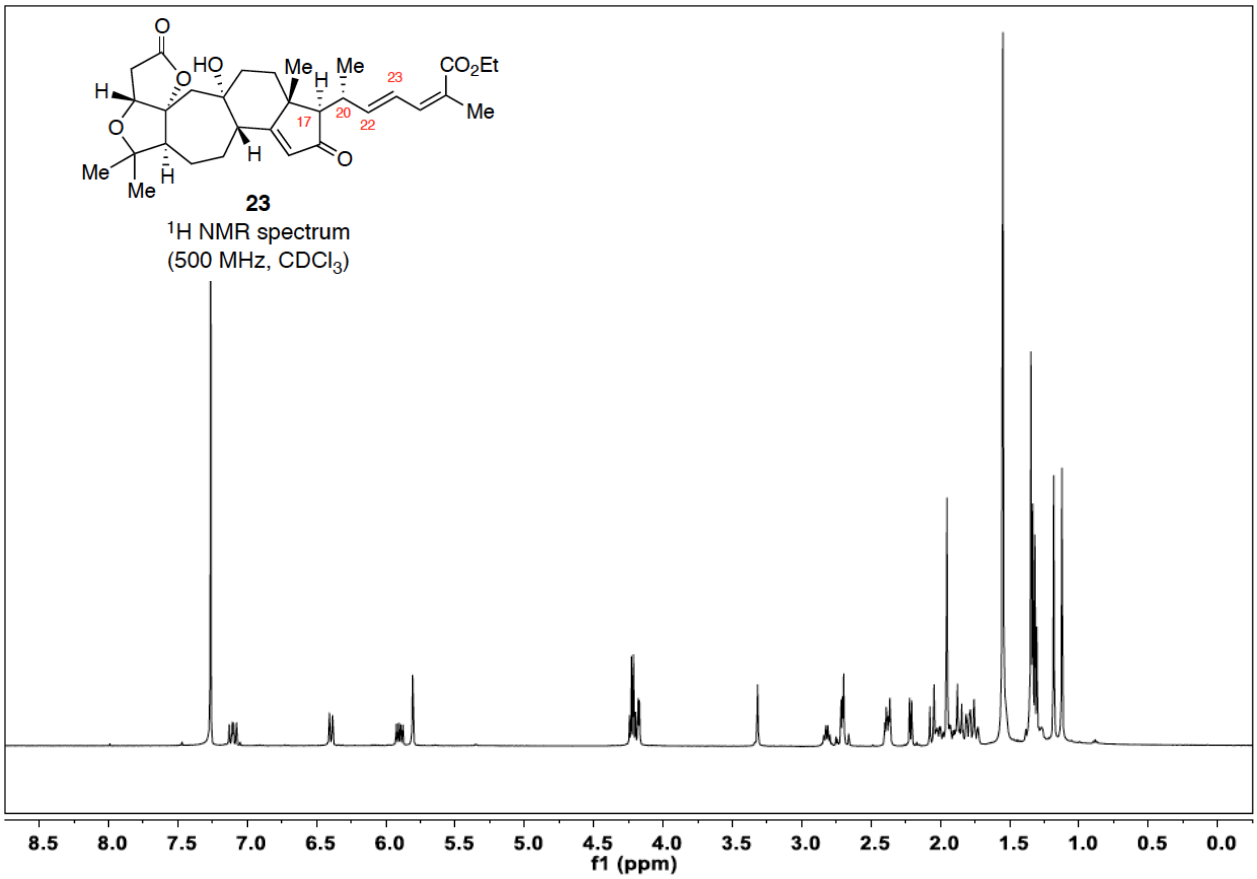

6
^{13}C NMR spectrum
(100 MHz, CDCl$_3$)
f1 (ppm)

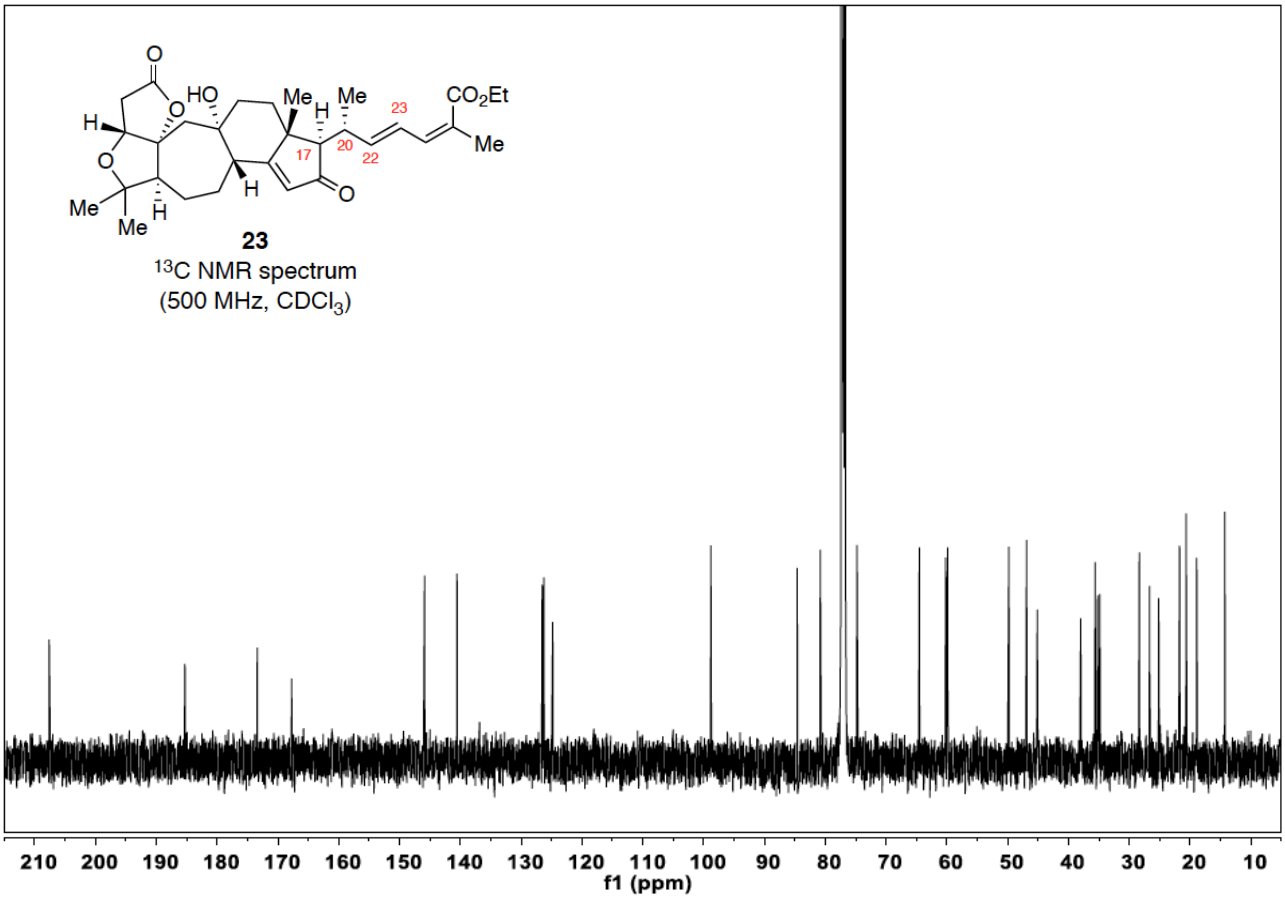

O
HO
Me
H
O
O
H
Me
Me
H
O
6a
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

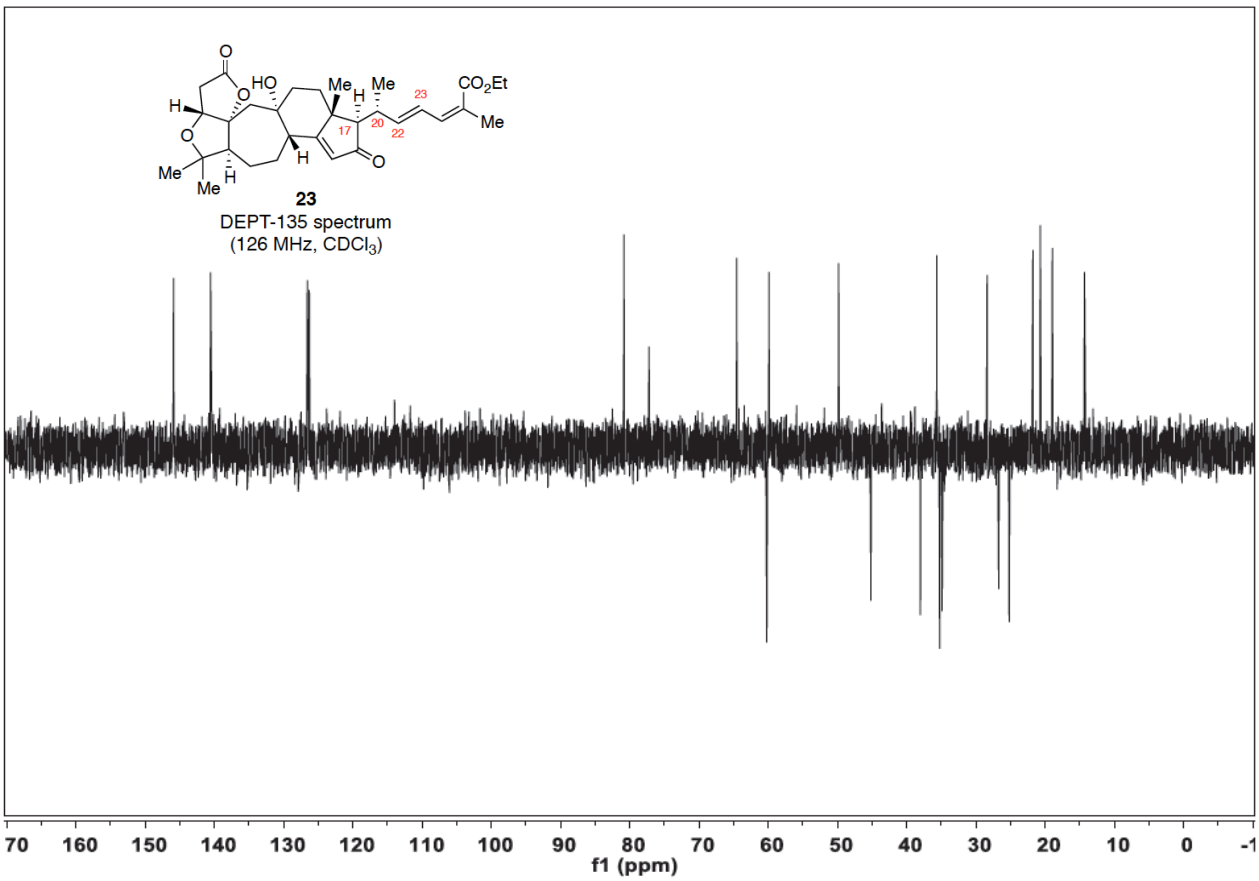

O
HO
Me
H
O
O
H
Me
Me
H
O
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

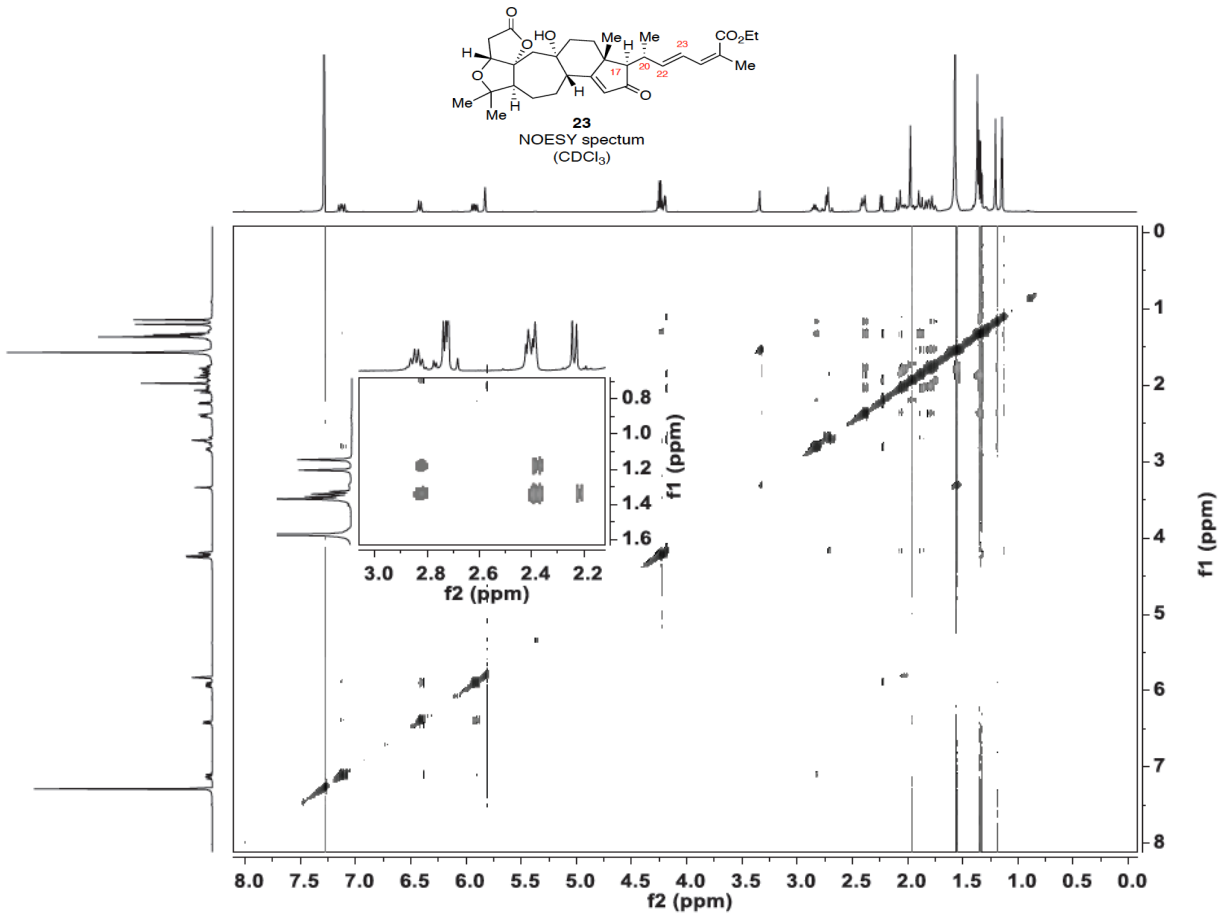

22
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

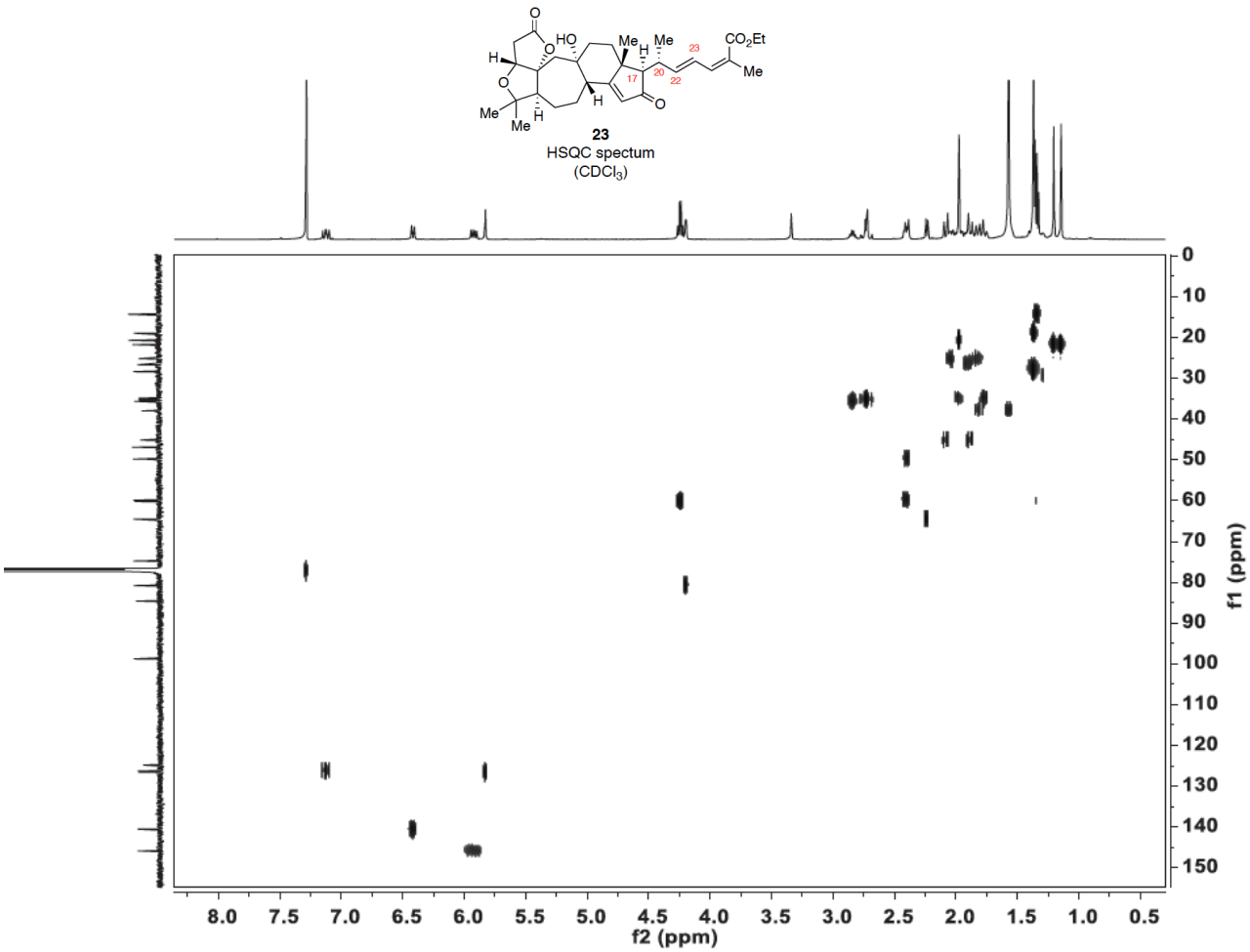

22
^{13}C NMR spectrum
(100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

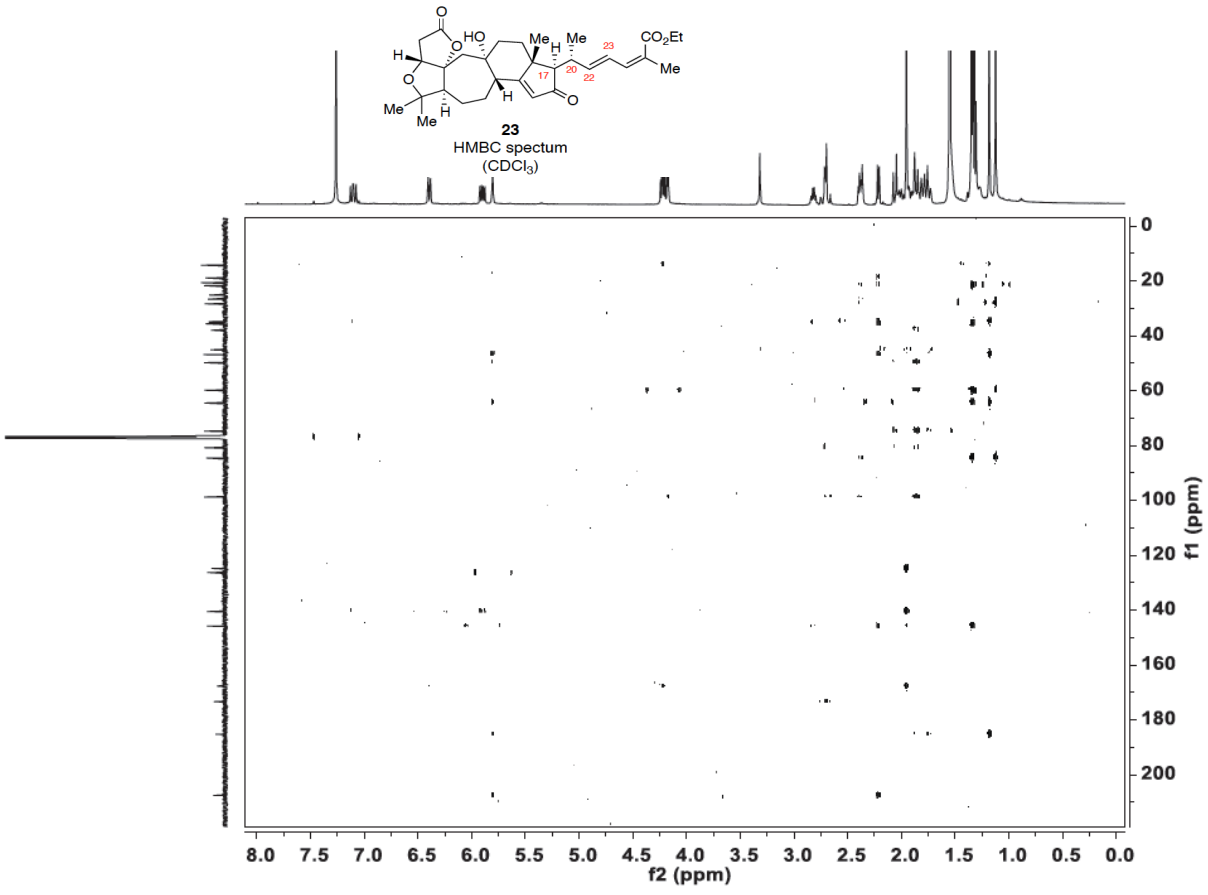

23
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

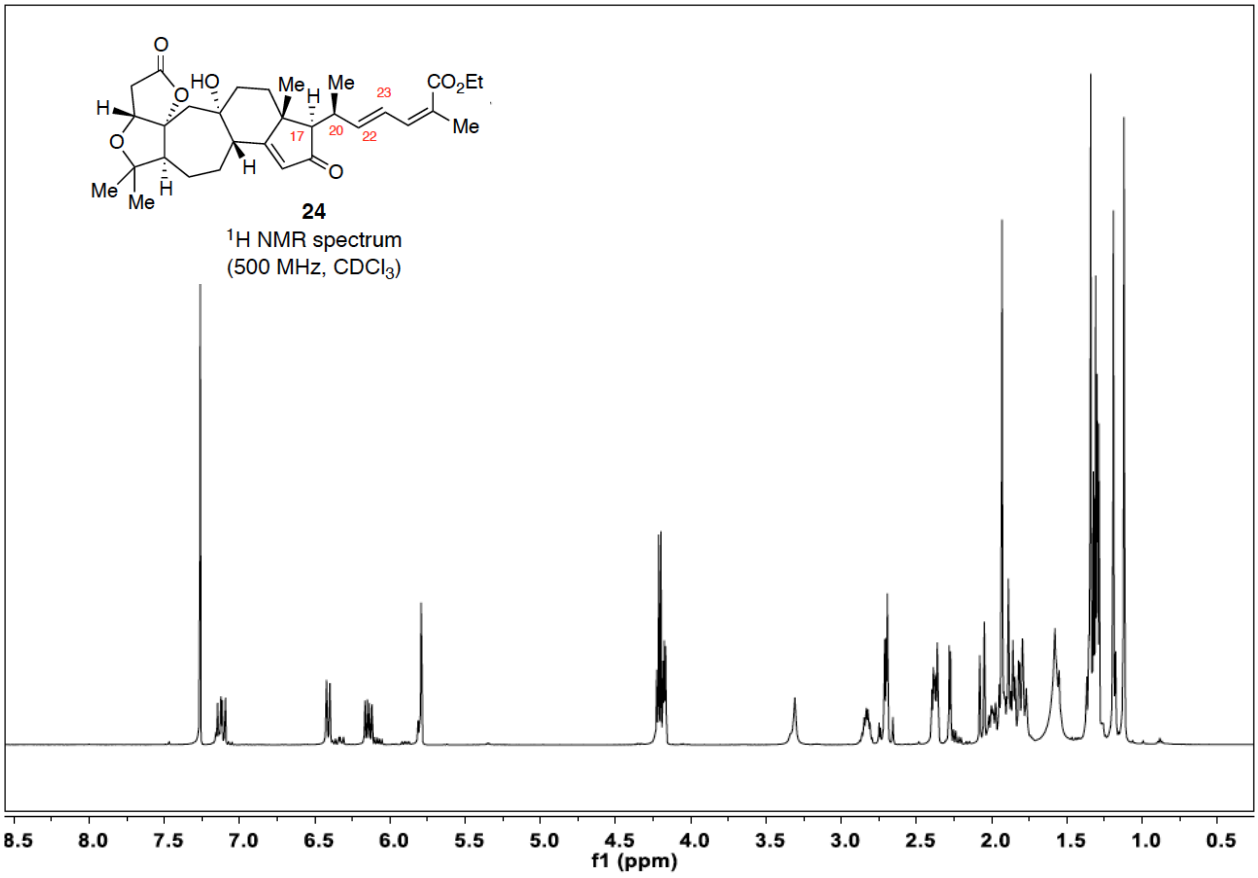

23
^{13}C NMR spectrum
(500 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


23
DEPT-135 spectrum
(126 MHz, CDCl3)
f1 (ppm)


23
NOESY spectum
(CDCl3)
f2 (ppm)
f1 (ppm)

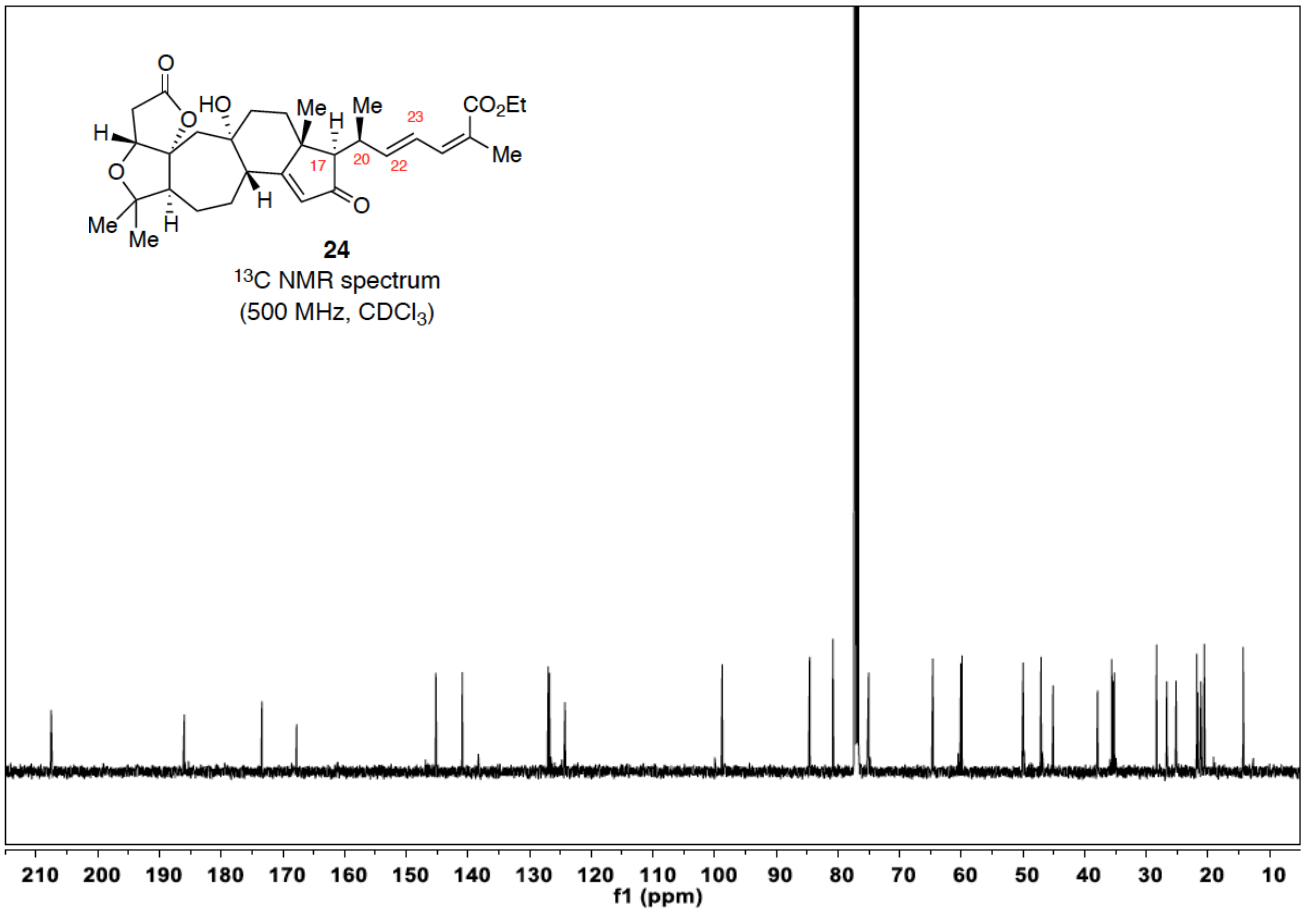

23
HSQC spectum
(CDCl3)
f2 (ppm)
f1 (ppm)


23
HMBC spectum
(CDCl3)
f2 (ppm)
f1 (ppm)



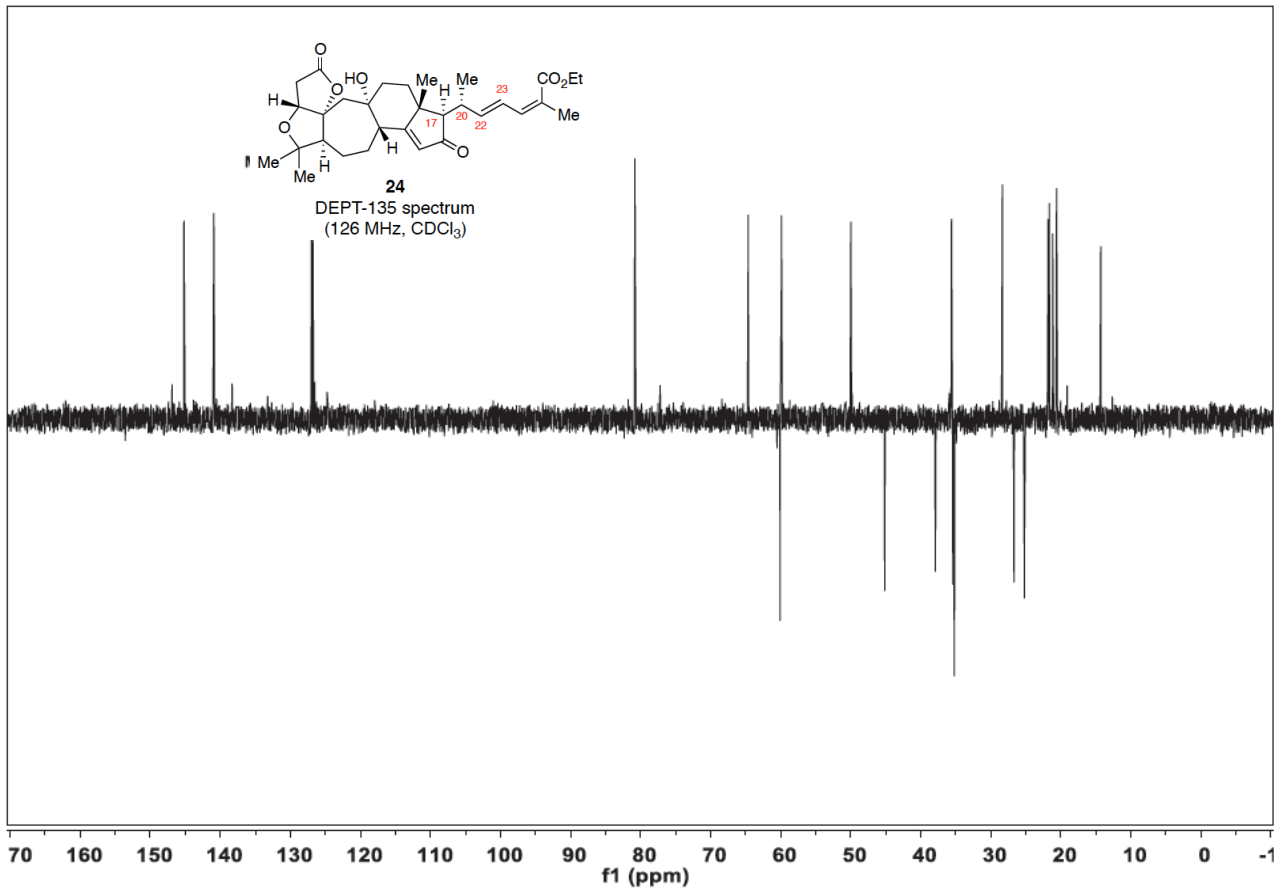
24

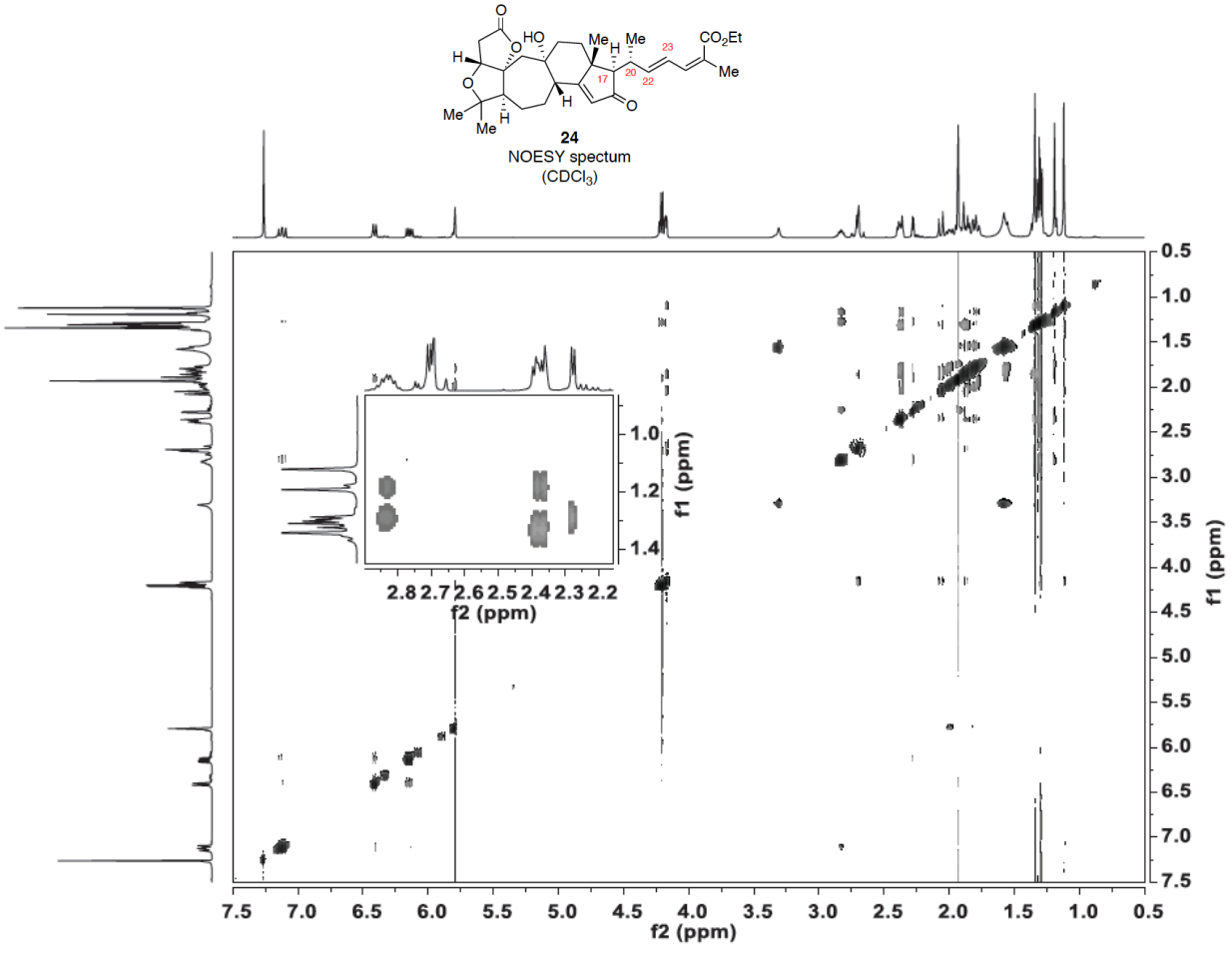
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)

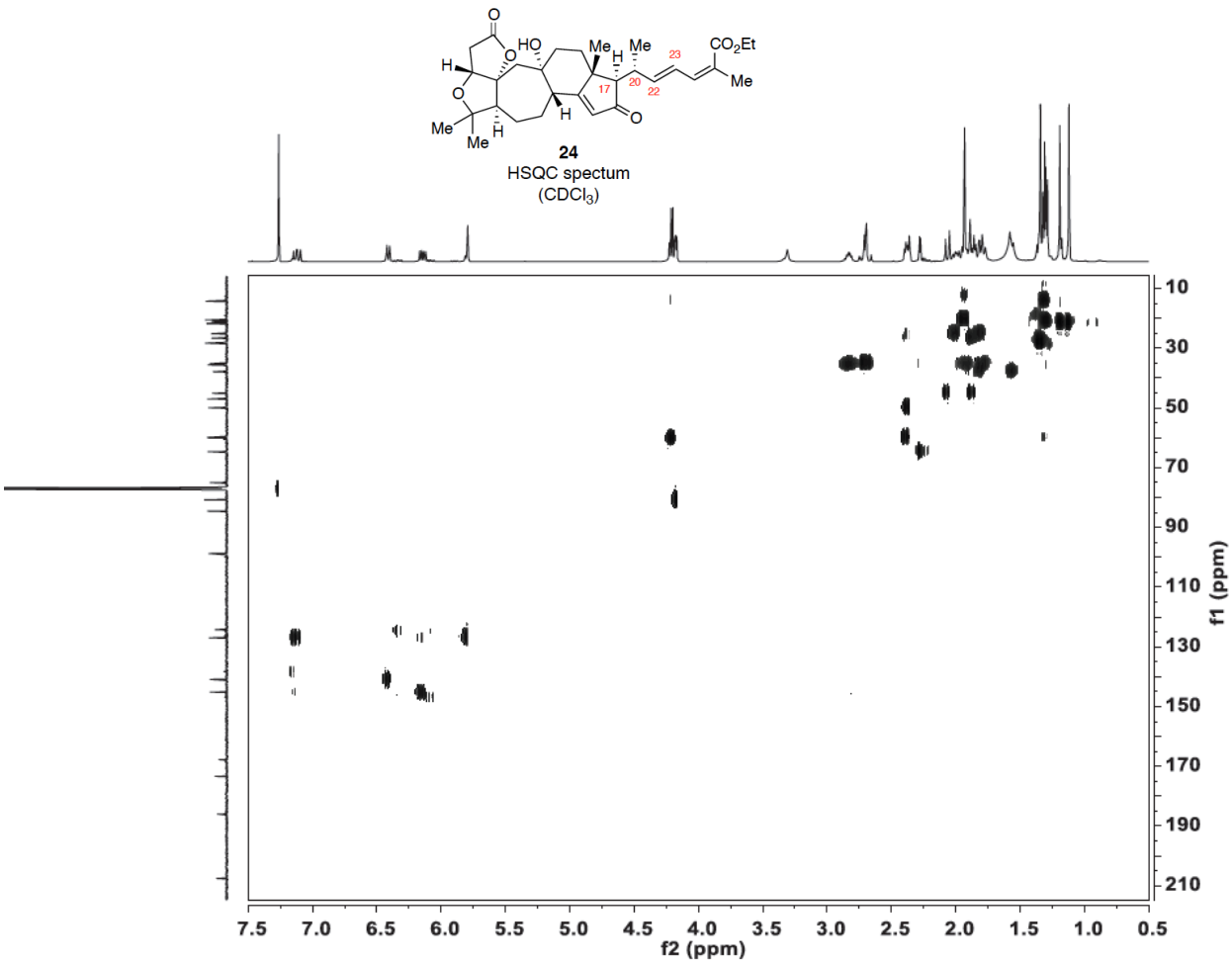


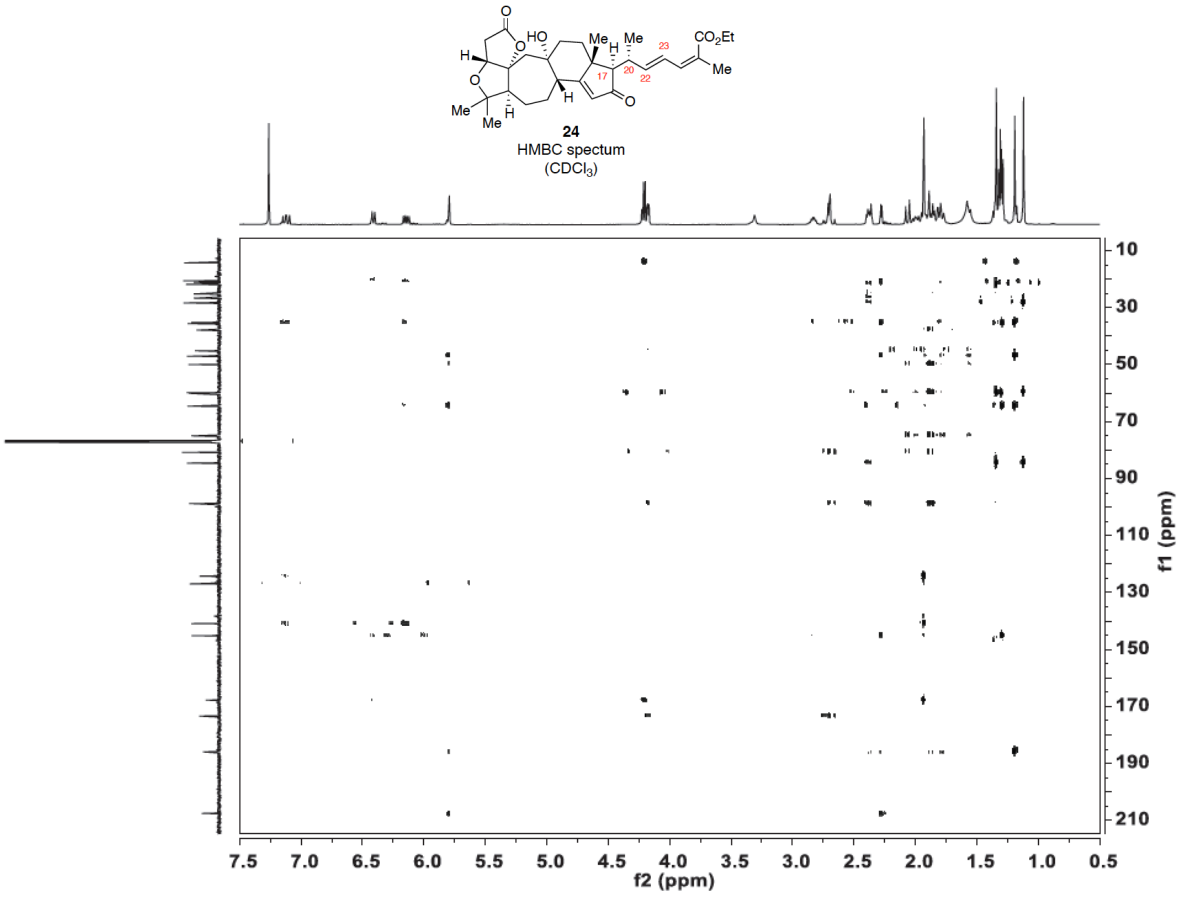
24

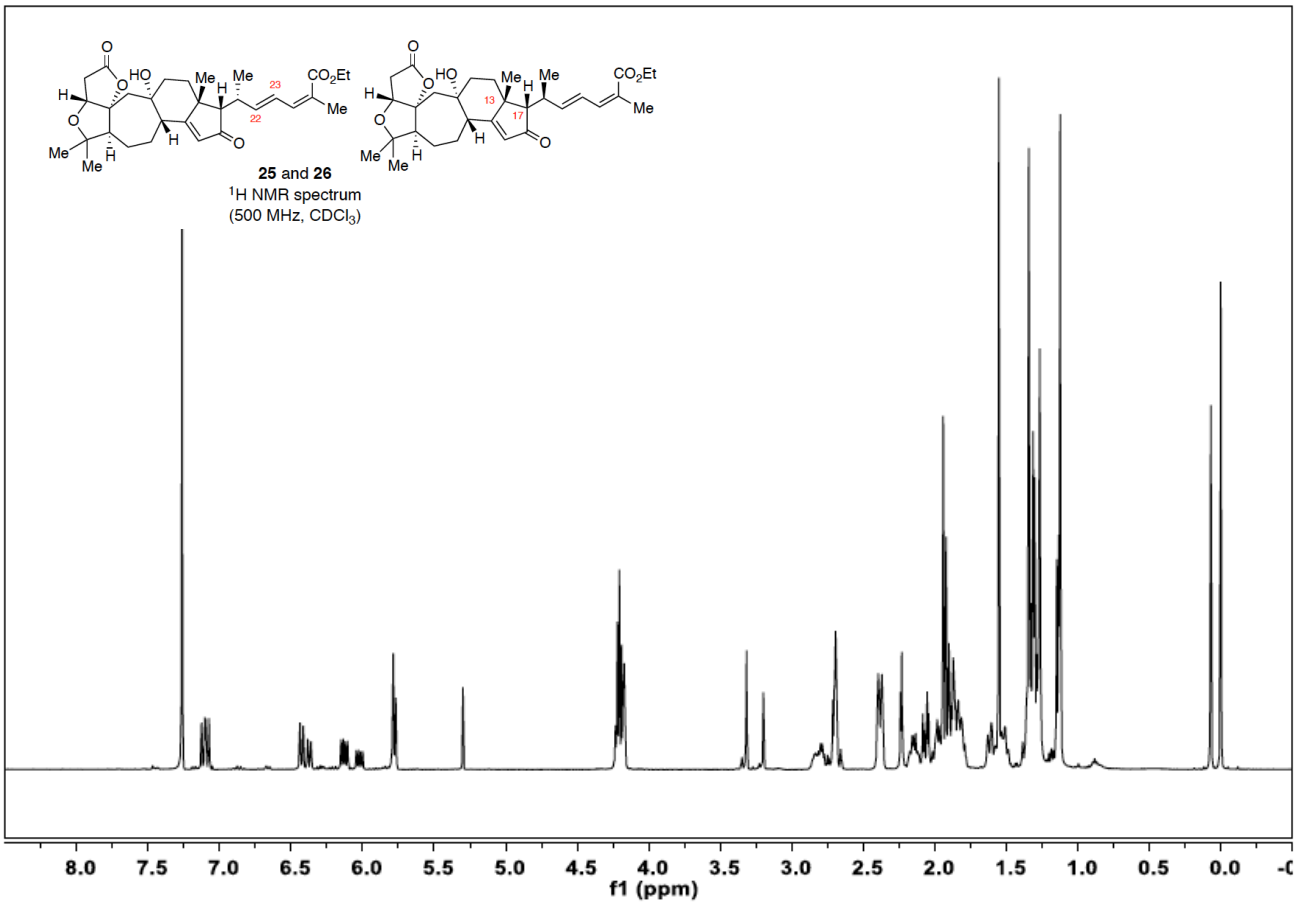
^{13}C NMR spectrum
(500 MHz, $CDCl_3$)

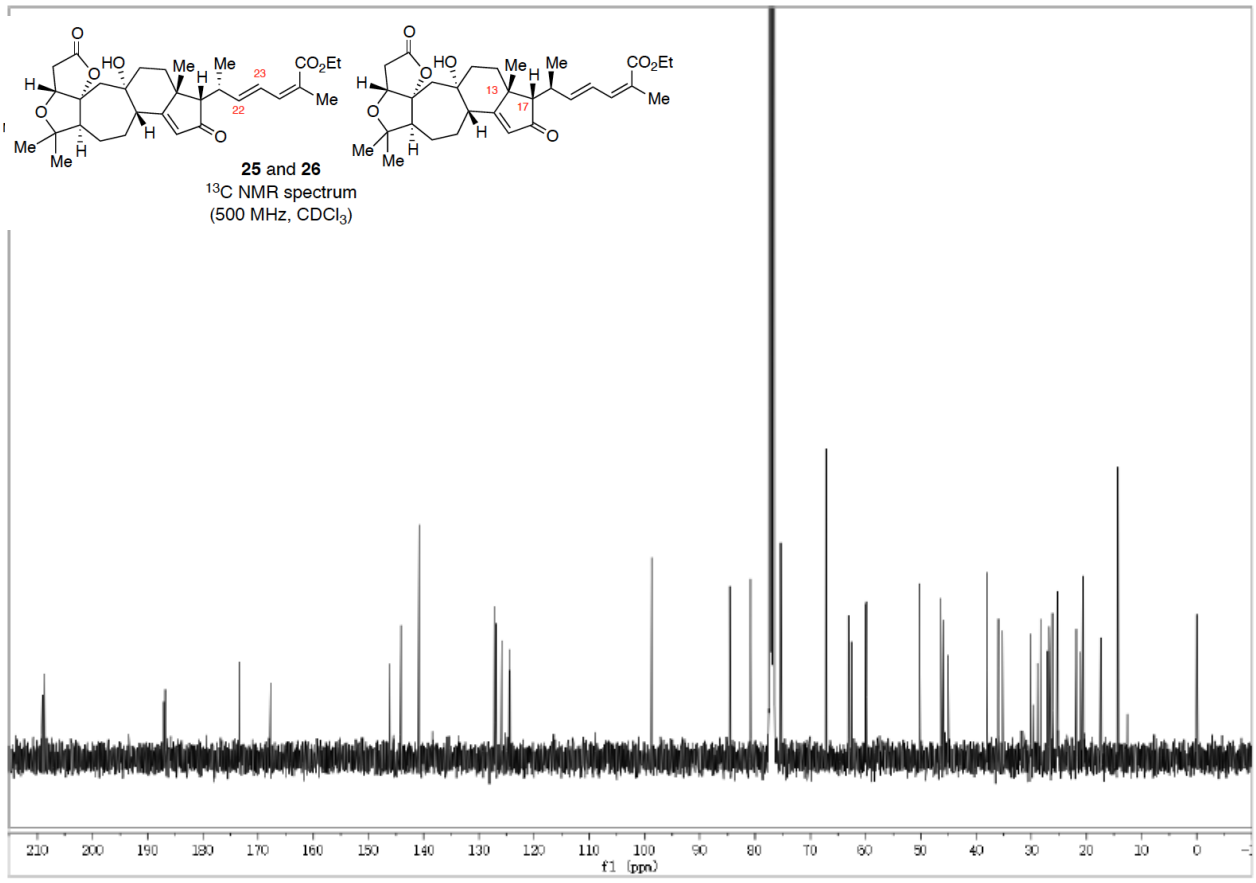

24
DEPT-135 spectrum
(126 MHz, CDCl3)
f1 (ppm)

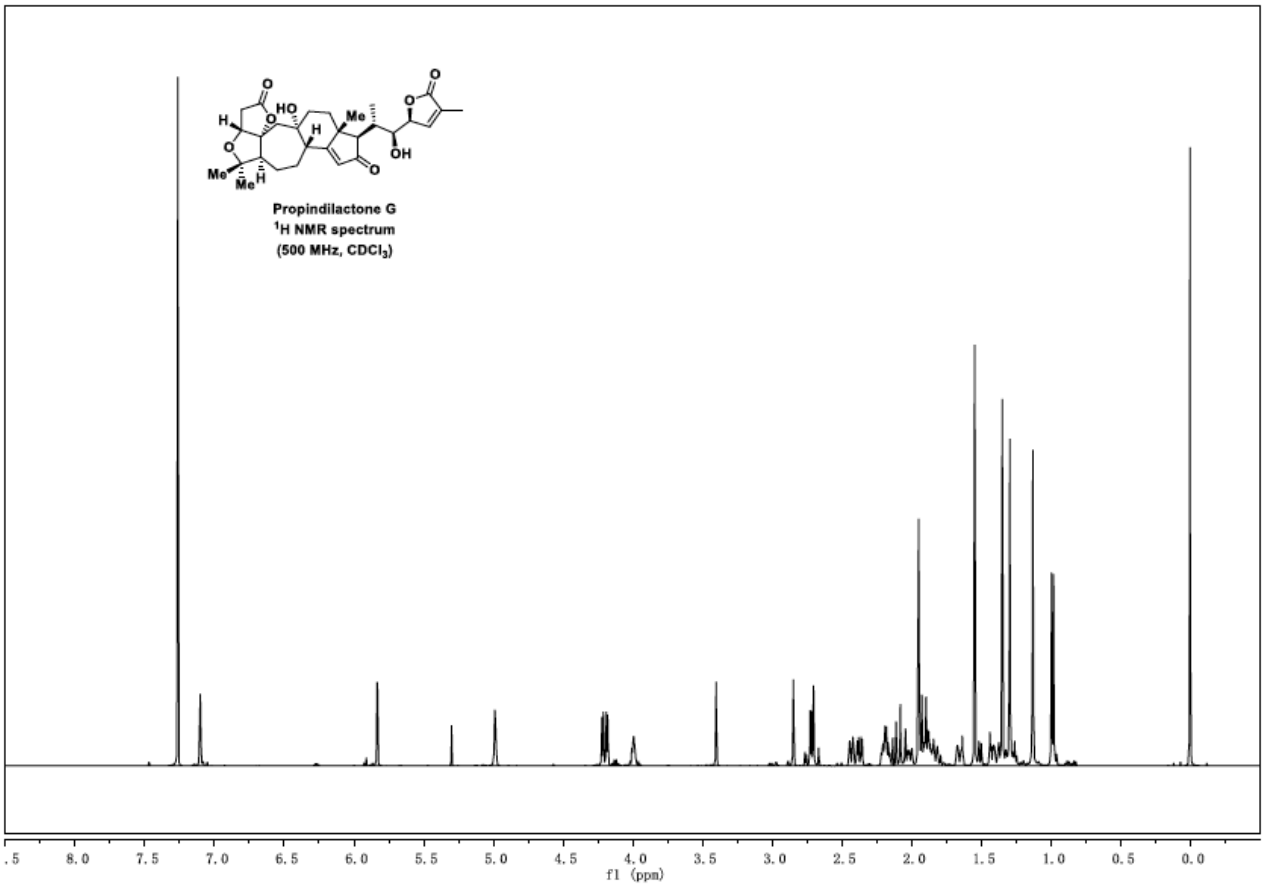

24
NOESY spectum
(CDCl3)
f1 (ppm)
f2 (ppm)

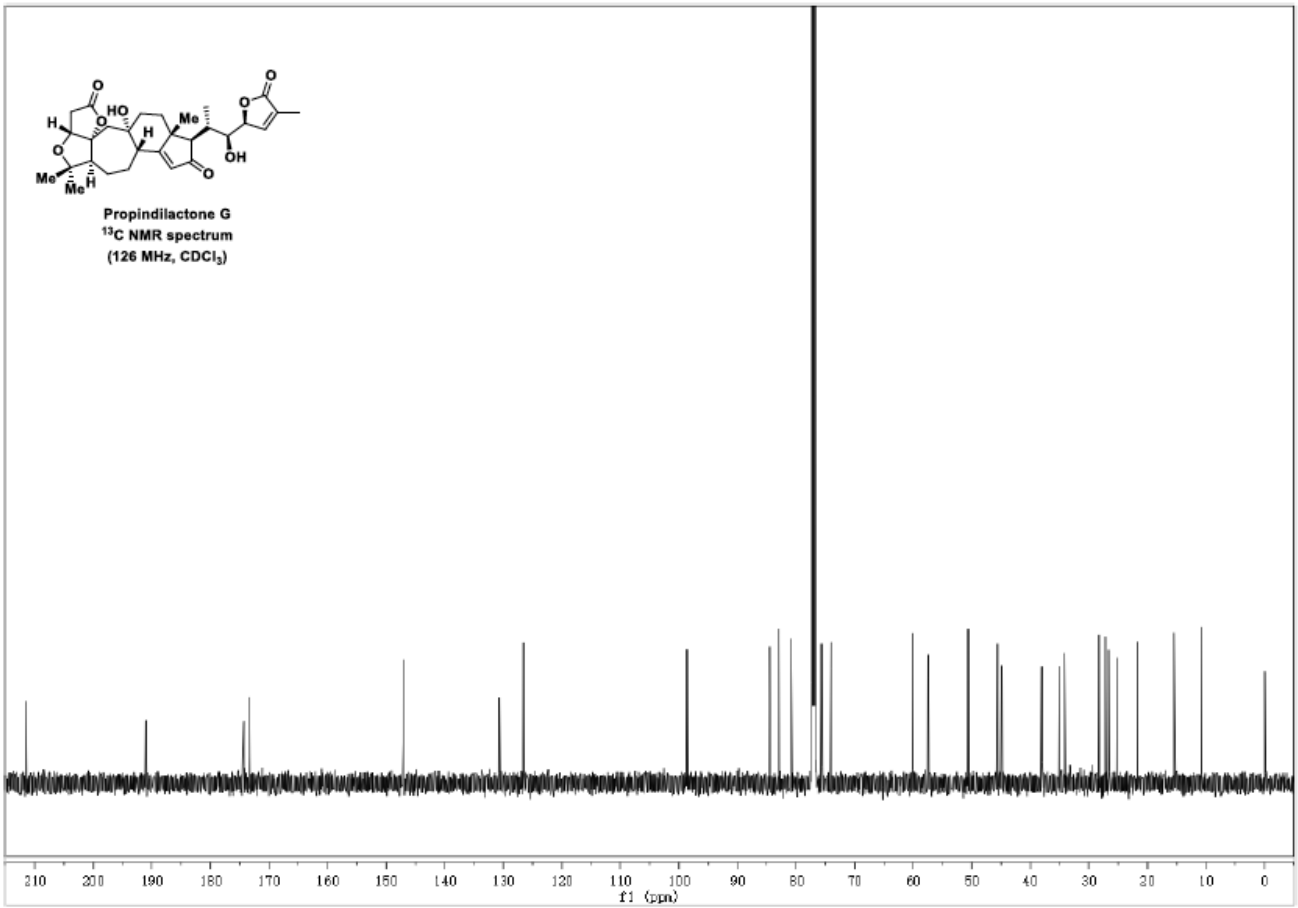

24
HSQC spectum
(CDCl3)
f2 (ppm)
f1 (ppm)


24
HMBC spectum
(CDCl3)
f2 (ppm)
f1 (ppm)

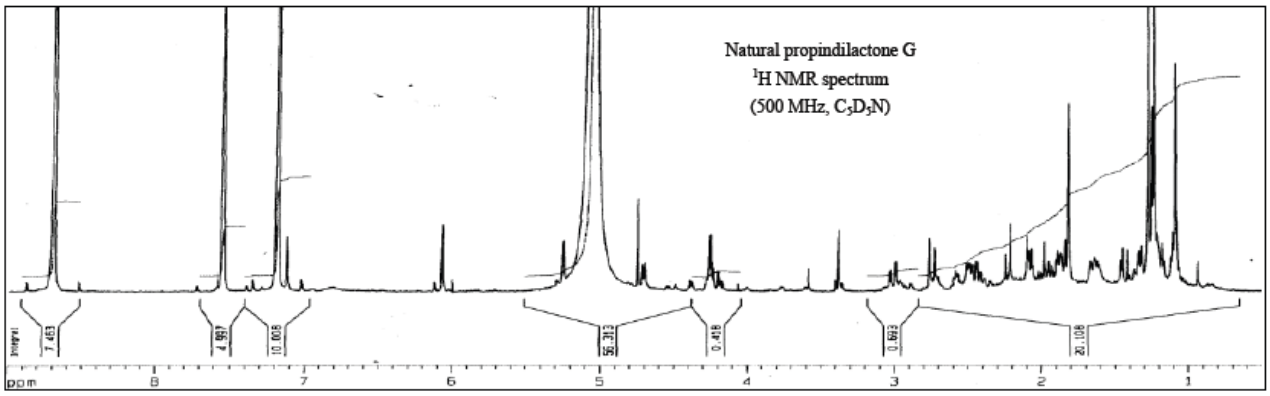

25 and 26
1H NMR spectrum
(500 MHz, CDCl3)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

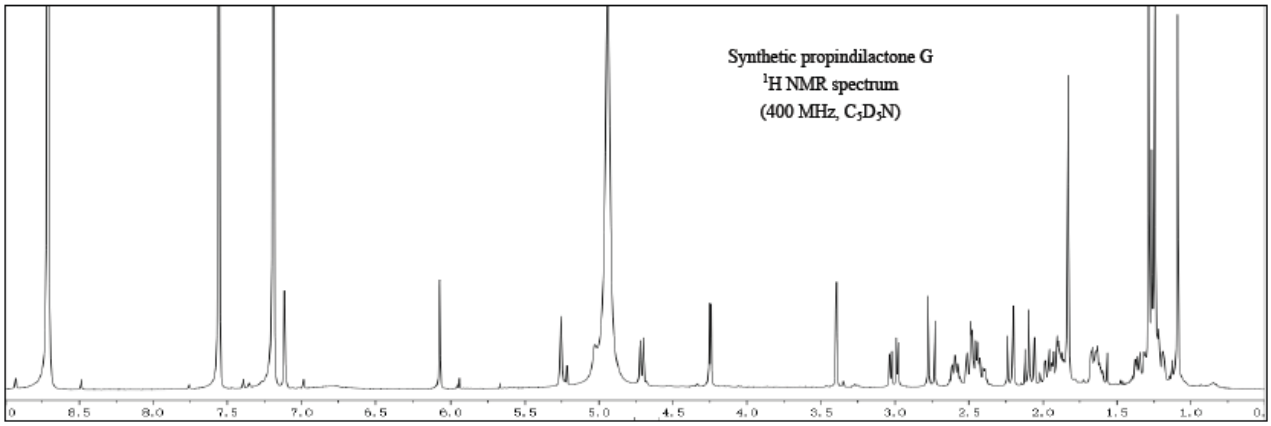

25 and 26
13C NMR spectrum
(500 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

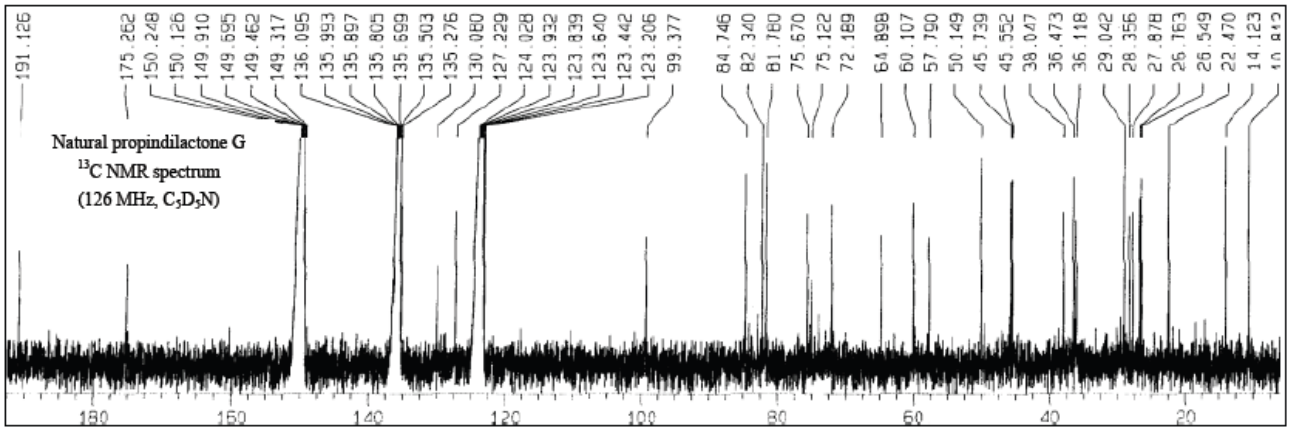

Propindilactone G
1H NMR spectrum
(500 MHz, CDCl3)
f1 (ppm)

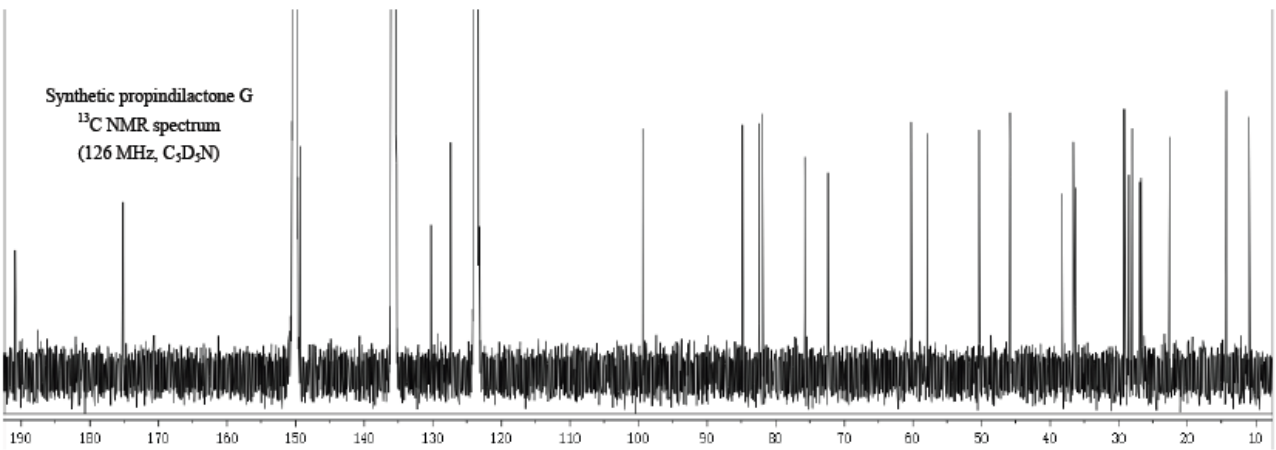

Propindilactone G
13C NMR spectrum
(126 MHz, CDCl3)
f1 (ppm)

IV Comparison of the Spectra of Natural and Synthetic Propindilactone G







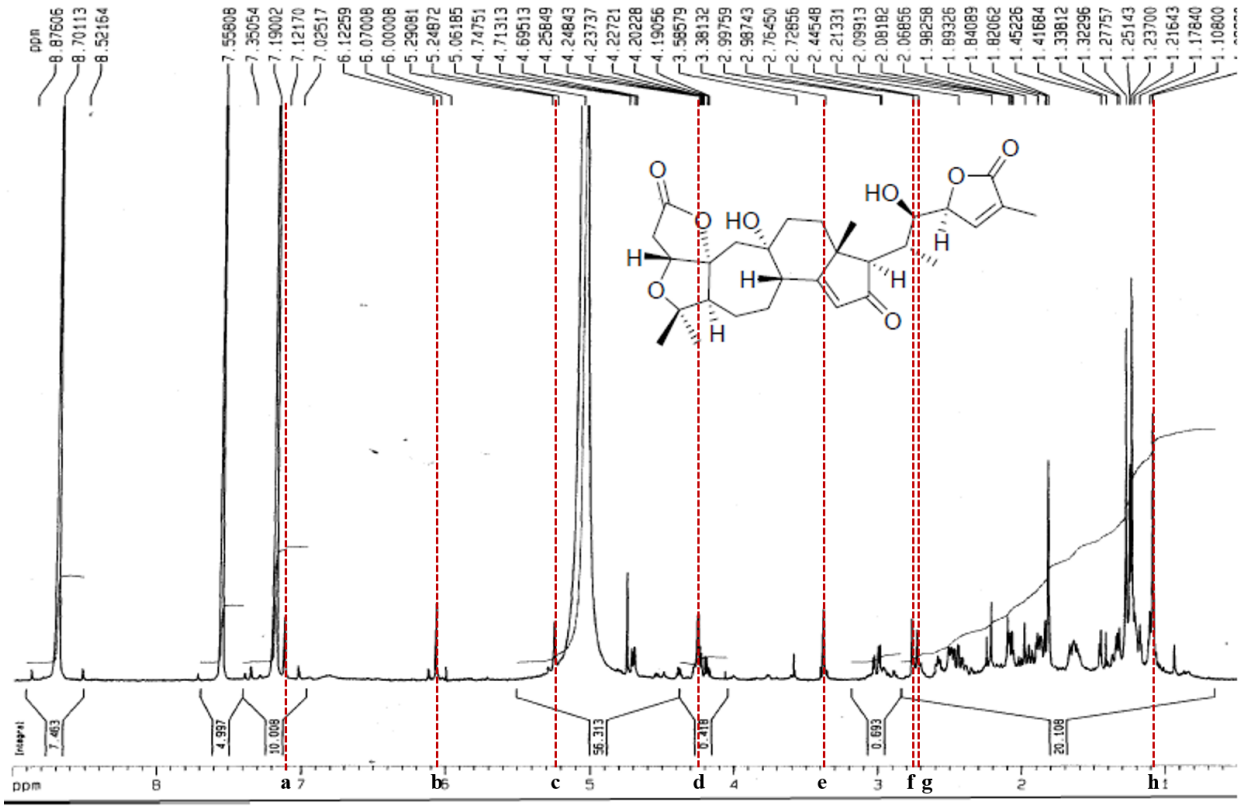


Comparison of ^{1}H NMR data for Propindilactone G

No	Listed* δH [ppm, mult, *J* (Hz)] 500 MHz	Natural (Spectrum) δH [ppm, mult, J (Hz)] 500 MHz	Synthetic δH [ppm, mult, J (Hz)] 400 MHz	Err (Natural - Synthetic) Δδ (ppm)
1β	4.33 (d, 4.5)	4.25 (d, 4.5)	4.25 (d, 5.0)	0
2α	2.79 (d, 17.5)	2.75 (d, 17.5)	2.75 (d, 18.0)	0
2β	3.09 (dd, 4.5, 17.5)	3.01 (dd, 4.5, 17.5)	3.01 (dd, 5.1, 18.0)	0
5α	2.49 (dd, 4.0, 13.5)	2.45 (dd, 4.0, 13.5)	2.46 (dd, 3.9, 13.5)	-0.01
6α	1.63-1.71	1.55-1.63	1.59-1.63	—
6β	1.40 (m)	1.32-1.34	1.33-1.38	—
7α	2.00 (m)	1.92 (m)	1.92-1.97	—
7β	1.90 (m)	1.88 (m)	1.88-1.92	—
8β	2.54-2.59	2.46-2.51	2.47-2.52	—
11α	1.91-1.99	1.83-1.91	1.85-1.96	—
11β	1.68-1.74	1.60-1.66	1.63-1.69	—
12α	2.42 (m)	2.34 (m)	2.34-2.43	—
12b	1.67-1.72	1.61-1.64	1.61-1.64	—
15α	6.11 (s)	6.07 (s)	6.08 (d, 1.1)	-0.01
17	3.40 (brs)	3.38 (s)	3.39 (d, 1.3)	-0.01
18	1.28 (s)	1.24 (s)	1.24 (s)	0
19α	2.32 (ABd, 15.5)	2.20 (ABd, 15.5)	2.22 (ABd, 15.3)	-0.02
19β	2.16 (ABd, 15.5)	2.10 (ABd, 15.5)	2.08 (ABd, 15.3)	-0.02
20	2.60 (m)	2.55-2.6	2.55-2.63	—
21	1.27 (d, 7.5)	1.25 (d, 7.5)	1.26 (d, 6.7)	-0.01
22	4.74 (d, 9.0)	4.72 (d, 9.0)	4.71 (d, 8.3)	0.01
23	5.29 (brs)	5.26 (brs)	5.26 (d, 8.3)	0
24	7.17 (brs)	7.12 (brs)	7.11-7.12	—
27	1.86 (s)	1.83 (s)	1.83 (s)	0
29	1.14 (s)	1.09 (s)	1.09 (s)	0
30	1.31 (s)	1.28 (s)	1.29 (s)	-0.01

* The chemical shift values listed in the isolation paper (*J. Nat. Prod.* **2008**, *71*, 1228.) don't match the ^{1}H NMR spectrum attached in its supporting information (shown below). We therefore utilized the data derived from the ^{1}H NMR spectrum of the isolation paper for the comparison purpose.

The highlighted peaks indicate the inconsistency of the chemical shift values listed in the isolation paper with the ^{1}H NMR spectrum provided in the supporting information.



Peaks	Listed	Spectrum	Synthetic
a	7.17 (brs)	7.12 (brs)	7.11-7.12
b	6.11 (s)	6.07 (s)	6.08 (d)
c	5.29 (brs)	5.26 (brs)	5.26 (d)
d	4.33 (d)	4.25 (d)	4.25 (d)
e	3.40 (brs)	3.38 (s)	3.39 (d)
f/g	2.79 (d)	2.75 (d)	2.75 (d)
h	1.14 (s)	1.09 (s)	1.09 (s)

Comparison of ^{13}C NMR data for Propindilactone G

No	Natural δC (ppm) 126 MHz	Synthetic δC (ppm) 126 MHz	Err (Natural - Synthetic) Δδ (ppm)
1	81.8	81.9	-0.1
2	36.1	36.2	-0.1
3	175.3	175.2	0.1
4	84.7	84.8	-0.1
5	60.1	60.2	-0.1
6	26.5	26.7	-0.2
7	26.8	26.9	-0.1
8	50.1	50.3	-0.2
9	75.7	75.8	-0.1
10	99.4	99.4	0
11	38.0	38.2	-0.2
12	28.4	28.5	-0.1
13	45.7	45.8	-0.1
14	191.1	191.0	0.1
15	127.2	127.4	-0.2
16	211.2	211.0	0.2
17	57.8	57.9	-0.1
18	27.9	28.0	-0.1
19	45.6	45.8	-0.2
20	36.5	36.6	-0.1
21	14.1	14.3	-0.2
22	72.2	72.4	-0.2
23	82.3	82.4	-0.1
24	149.3	149.3	0
25	130.1	130.2	-0.1
26	175.3	175.2	0.1
27	10.8	10.9	-0.1
29	22.5	22.6	-0.1
30	29.0	29.2	-0.2

DFT calculation for the djhydroxylation of substrates **25** and **26**.

1. Complete Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

2. Absolute Calculation Energies, Enthalpies, and Free Energies

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3-LYP[1] with 3-21G(d) basis set (lanl2dz basis set for Os) was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. M11-L functional, recently proposed by Truhlar group, which could give more accurate energy information, is used to calculate single point energies. The larger basis set 6-311G(d) (SDD basis set for Os) is used in the single point energy calculations.

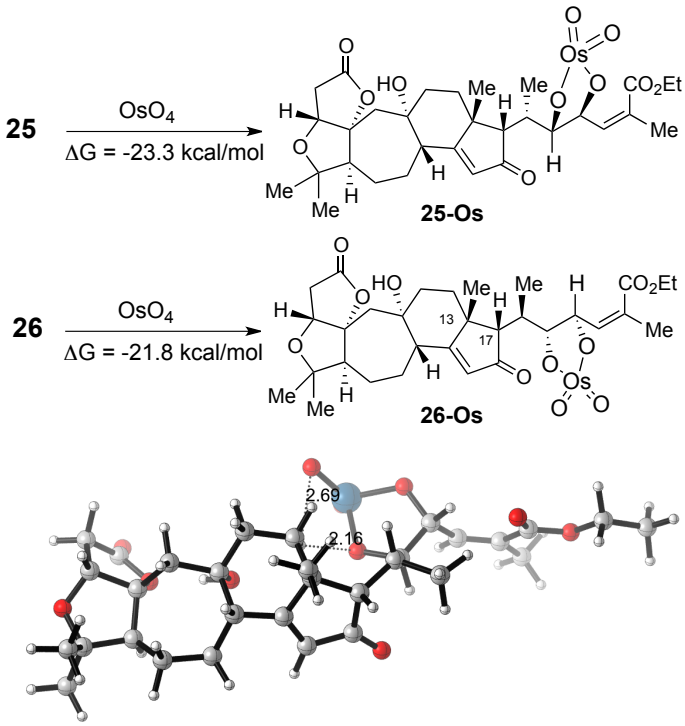


Figure S1. Calculated Gibbs free energy for the formation of **25-Os**.

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$H_{(corr\text{-}B3LYP)}$[3]	$E_{(M11\text{-}L)}$[4]	IF[5]
25	-1723.706215	0.620761	0.729543	-1733.112994	-
25-Os	-2114.080595	0.632078	0.752308	-2124.821976	-
26	-1723.703338	0.619913	0.729256	-1733.111083	-
26-Os	-2114.075080	0.631141	0.752065	-2124.817572	-
OsO_4	-390.302010	-0.015308	0.018571	-391.645222	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M11-L in n,n-DiMethylAcetamide (DMA) solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.

3: Optimized geometries for all the compounds

Substrate 25

C	6.26217200	1.48636100	-0.69062400
C	6.43840500	2.65588600	0.26299800
C	5.81893600	2.17486700	1.57165400
C	5.01881900	0.69615400	-0.17417600
C	3.71098200	1.14356100	-0.82392600

C	2.38252700	0.57996000	-0.23017400
C	1.25668100	1.58256100	-0.59655700
C	-0.10654000	1.11910100	-0.05183200
C	-0.50842700	-0.25770400	-0.64530500
C	-1.73865000	-0.96403700	0.02880000
C	-1.15384900	-2.20288500	0.73875200
C	0.28187200	-2.25936500	0.41402000
C	0.65443100	-1.21029100	-0.34025600
C	2.04251800	-0.84135000	-0.80620400
C	3.08020400	-1.89081900	-0.36626300
C	4.47852800	-1.73292300	-1.01131000
C	5.42642100	-0.79964200	-0.23954900
C	6.90193400	-0.78795400	-0.78298000
C	7.81648500	-1.73693900	-0.00621500
C	7.01570800	-1.01022600	-2.29940800
C	-0.76221900	-0.15169900	-2.17216000
C	-2.70633700	-0.14999100	0.95267800
C	-2.19432400	0.01932100	2.41027700
C	-4.02584600	-0.89060400	0.99688300
C	-5.20855500	-0.37526700	0.62059000
C	-7.95496000	0.58540300	-0.20978200
C	-7.68287700	-0.76509800	0.32500500
C	-6.43513400	-1.15027900	0.68525600
C	-8.87138500	-1.69552200	0.44887700
O	7.38529200	0.58379700	-0.46996800
O	4.95687700	1.08819600	1.27876800
O	5.93903400	2.59749500	2.69897300
O	2.40367200	0.44538000	1.21659000
O	-1.79229200	-2.98357200	1.45975400
O	-9.30533400	0.72405400	-0.49990400
H	6.15127700	1.77456300	-1.74136600
H	7.49074500	2.90136900	0.40650400
H	5.89518500	3.54601100	-0.07505300
H	3.74605800	0.91431900	-1.89457600
H	3.67333900	2.23761500	-0.72743300
H	1.51418300	2.54261600	-0.13227700
H	1.22898500	1.72864600	-1.68249800
H	-0.87998700	1.86624100	-0.26402900
H	0.01445700	1.02000900	1.02829300
H	-2.36326500	-1.35527900	-0.78678100
H	0.91966800	-3.04179200	0.79543200
H	2.03352500	-0.76011300	-1.90333900
H	3.15073400	-1.82355000	0.72483800
H	2.69481200	-2.88346000	-0.62458400

H	4.37258100	-1.40379400	-2.05204800
H	4.95766300	-2.72034300	-1.04167200
H	5.46626900	-1.13095900	0.80306700
H	7.80824800	-1.46202400	1.05226200
H	8.84182900	-1.65944200	-0.38057300
H	7.47487100	-2.77152300	-0.11649300
H	8.05002400	-0.81629600	-2.59853500
H	6.36301200	-0.33038200	-2.85709000
H	6.75569000	-2.03779500	-2.56905100
H	-0.98712100	-1.14144400	-2.58463600
H	0.10077600	0.25384600	-2.70761700
H	-1.62030000	0.50528400	-2.35650000
H	-2.86622000	0.83819700	0.50377900
H	-1.22511800	0.52228100	2.44138200
H	-2.09763100	-0.96197400	2.88126900
H	-2.91515500	0.61349100	2.98131400
H	-3.94094600	-1.91372300	1.35976200
H	-5.29406900	0.63864100	0.24923300
H	-6.32464800	-2.16409600	1.06920400
H	-8.55802100	-2.66306700	0.85158200
H	-9.34433600	-1.85075400	-0.52666200
H	-9.63290100	-1.26439400	1.10734300
H	3.29294000	0.75852400	1.55621100
O	-7.16389800	1.51598500	-0.40500800
C	-9.70463700	2.04338300	-1.04276500
H	-9.46282100	2.82025900	-0.31167800
H	-9.13271500	2.24564600	-1.95283900
C	-11.20319400	1.93976200	-1.30698000
H	-11.73200100	1.71193300	-0.37735700
H	-11.58278200	2.88403200	-1.71090600
H	-11.40177700	1.13964300	-2.02546000

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C	7.55232600	0.09061900	-1.28547600
C	7.63103300	1.14328300	-2.37750800
C	6.82500600	2.31614700	-1.82797700
C	6.21942400	0.36561800	-0.52268800
C	5.03074700	-0.40962300	-1.08635500
C	3.61444400	-0.04556800	-0.54102400
C	2.58660000	-0.46052400	-1.62582900
C	1.14453200	-0.14528500	-1.18888100
C	0.77687300	-0.90582900	0.11344400
C	-0.54788200	-0.45065100	0.81246200
C	-0.11144700	0.28310500	2.08864400

C	1.34721100	0.11727900	2.20817600
C	1.85175900	-0.52830800	1.14040700
C	3.30030000	-0.78900500	0.80726100
C	4.23145500	-0.32062600	1.94121600
C	5.71076400	-0.75434000	1.79410600
C	6.57017400	0.23028700	0.98256000
C	8.11233100	-0.07687200	1.00632000
C	8.85679000	0.76036300	2.04821100
C	8.45814400	-1.56924000	1.13292800
C	0.71553600	-2.43781500	-0.12944700
C	-1.62232000	0.31904900	-0.00583900
C	-1.39901200	1.85275900	-0.06361400
C	-3.00861300	0.05686900	0.63079800
C	-4.16671000	0.37913800	-0.30843100
C	-5.53738900	3.05308900	-0.08585100
C	-6.07829300	1.81489400	0.54314100
C	-5.45571100	0.63252900	0.41355600
C	-7.36765900	1.96514900	1.32138200
O	8.59407100	0.40618600	-0.31622400
O	5.97780600	1.82709700	-0.80264700
O	6.80419000	3.47914600	-2.16150900
O	3.44066700	1.37340700	-0.27919800
O	-0.87333700	0.89934800	2.85036600
O	-3.15877000	-1.41843200	0.94595600
O	-4.34982600	-0.84495600	-1.18108400
O	-6.37622700	4.11543600	0.14882600
H	7.60804800	-0.94093500	-1.64857100
H	8.66016600	1.44490000	-2.57268700
H	7.16359200	0.80237200	-3.30870300
H	5.20089800	-1.48227100	-0.94283200
H	5.02264400	-0.22465300	-2.16953100
H	2.81724000	0.11764100	-2.52933500
H	2.70954200	-1.52332100	-1.86408200
H	0.44000700	-0.39846600	-1.98977100
H	1.10792200	0.92956400	-0.99808900
H	-1.04524200	-1.36265400	1.16600400
H	1.90256500	0.52552700	3.03855800
H	3.43372900	-1.86634200	0.63091900
H	4.15634700	0.77165400	1.97582600
H	3.84785300	-0.72095200	2.88651700
H	5.76316700	-1.76228500	1.36585000
H	6.15224200	-0.81494300	2.79747200
H	6.43057000	1.23281900	1.39955500
H	8.68561700	1.82214200	1.85004800

H	9.93126800	0.56163500	1.98963800
H	8.50431200	0.51637900	3.05583800
H	9.53386600	-1.68628800	0.97185200
H	7.93114800	-2.17255300	0.38635300
H	8.20552100	-1.95091400	2.12621000
H	0.58660900	-2.96068700	0.82527700
H	1.62130400	-2.81965100	-0.60927500
H	-0.14458300	-2.67563500	-0.76656000
H	-1.64699300	-0.09247200	-1.02448400
H	-0.48979200	2.08621600	-0.62141200
H	-1.29555900	2.23836800	0.95299200
H	-2.24085000	2.36648900	-0.53744700
H	-3.05697400	0.54500200	1.60577100
H	-3.93879800	1.18754500	-0.99655900
H	-5.89320100	-0.24102800	0.89319600
H	-7.68093500	1.00152600	1.73156200
H	-8.15877400	2.35514500	0.67352500
H	-7.23959900	2.67985600	2.14053200
H	4.28500900	1.85189300	-0.52907700
Os	-3.84791300	-2.52245200	-0.44147000
O	-2.51732700	-3.24696800	-1.28523400
O	-5.27736800	-3.36729900	0.05123100
O	-4.49681600	3.18418700	-0.74476800
C	-5.94479100	5.42013800	-0.42403700
H	-4.93258600	5.63944600	-0.07495700
H	-5.92210900	5.33393500	-1.51373400
C	-6.96963500	6.43812800	0.06112600
H	-6.97642600	6.47229400	1.15392500
H	-6.72118200	7.43235300	-0.32396900
H	-7.96862100	6.16195600	-0.28702600

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C	6.54143000	1.12633400	-0.53867700
C	6.77603500	2.32985700	0.35733500
C	6.04678900	1.97814400	1.65098900
C	5.19153300	0.50405600	-0.07059500
C	3.97457100	1.07094000	-0.79624800
C	2.57220200	0.64144500	-0.26083600
C	1.56826200	1.75828600	-0.64460700
C	0.12553400	1.42119800	-0.21908300
C	-0.37433800	0.10867700	-0.89592000
C	-1.71154000	-0.46421600	-0.29119700
C	-1.22458800	-1.55867100	0.70390600
C	0.19184800	-1.81943600	0.40046800

C	0.67568900	-0.93047500	-0.48037900
C	2.11360400	-0.72710700	-0.88475500
C	3.00187400	-1.88815100	-0.40042100
C	4.45736700	-1.86524700	-0.92612000
C	5.42130400	-1.02984400	-0.06326500
C	6.94173300	-1.20555300	-0.43522600
C	7.66281500	-2.17346300	0.50533500
C	7.19626200	-1.56034000	-1.90930200
C	-0.47856300	0.24160500	-2.43390400
C	-2.76143600	0.54128100	0.28785800
C	-3.94399200	-0.23078200	0.85336300
C	-5.23681500	-0.03864800	0.53392700
C	-8.19970200	0.22268100	-0.00862300
C	-7.61983700	-0.76351800	0.92604100
C	-6.28400400	-0.84441400	1.13812400
C	-8.59710000	-1.67660100	1.63674400
O	7.53947700	0.13082800	-0.16868300
O	5.10550300	0.95840400	1.36397700
O	6.14718400	2.44908800	2.76105300
O	2.52766800	0.46527800	1.18014500
O	-1.88461100	-2.11946000	1.58990500
O	-9.58268900	0.10113600	-0.03925700
H	6.53946600	1.35041200	-1.61072400
H	7.83744800	2.48712000	0.54947500
H	6.33706900	3.24453500	-0.05775200
H	4.04102900	0.82250800	-1.86112400
H	4.04099500	2.16454300	-0.71319100
H	1.88527100	2.67019400	-0.12336400
H	1.62436900	1.94996400	-1.72300500
H	-0.53154700	2.26143200	-0.46021500
H	0.13699900	1.27198100	0.86544300
H	-2.21814000	-1.01523800	-1.09895900
H	0.74523700	-2.58844600	0.91687200
H	2.17577800	-0.63321600	-1.97775500
H	2.99922300	-1.84720600	0.69363800
H	2.53437500	-2.82949700	-0.71172500
H	4.47620500	-1.52696300	-1.96911500
H	4.83635100	-2.89548200	-0.92311500
H	5.30109100	-1.33501600	0.98097700
H	7.56186100	-1.82077100	1.53557300
H	8.72665600	-2.21682600	0.25256300
H	7.23598000	-3.17836600	0.42059900
H	8.27282800	-1.50152700	-2.09434600
H	6.69245800	-0.86253200	-2.58629900

H	6.85285100	-2.57306400	-2.13779100
H	-0.76101400	-0.72222000	-2.87217700
H	0.46863500	0.55476200	-2.88255500
H	-1.24200000	0.97804600	-2.70104800
H	-5.94152400	-1.60006300	1.84437900
H	-8.06363700	-2.36371500	2.29996400
H	-9.17999000	-2.25756200	0.91415400
H	-9.31144300	-1.09309200	2.22726300
H	3.40732100	0.75145200	1.56571200
O	-7.62197800	1.06859500	-0.70254600
C	-10.28124400	1.04265200	-0.94461400
H	-10.06877200	2.06839500	-0.62957600
H	-9.89849200	0.91501000	-1.96114900
C	-11.76209800	0.69500000	-0.83126800
H	-12.09536600	0.81201700	0.20361200
H	-12.35619900	1.35304200	-1.47388500
H	-11.92662200	-0.34262700	-1.13466500
C	-3.22188600	1.57148600	-0.76833700
H	-3.69417400	1.06088200	-1.61483400
H	-3.95531200	2.25706900	-0.33188400
H	-2.38688400	2.16597600	-1.14197000
H	-2.28270000	1.07405900	1.12330300
H	-5.56278900	0.71166400	-0.17233100
H	-3.66758700	-1.01562200	1.55000200

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C	-6.78279000	-0.71649700	-0.76775400
C	-6.63882100	-2.22793800	-0.71669200
C	-5.67206100	-2.48249500	0.43580000
C	-5.46912300	-0.13847700	-0.14917000
C	-4.40256400	0.16375500	-1.20157800
C	-2.96873400	0.52058100	-0.70281900
C	-1.99236400	0.24632900	-1.87622100
C	-0.54075200	0.58661200	-1.49955500
C	-0.37955700	2.07631800	-1.11058600
C	0.97998300	2.43662200	-0.41543500
C	0.65008500	2.52086000	1.08959600
C	-0.81612600	2.51555800	1.20667100
C	-1.39893300	2.29146100	0.01487200
C	-2.85597600	2.03100500	-0.26775700
C	-3.73664100	2.33620100	0.95740500
C	-5.25669900	2.35314600	0.66222000
C	-5.93332600	0.98197700	0.82060600
C	-7.49687200	1.00865300	0.68124900

C	-8.20279700	1.13416200	2.03268800
C	-8.02029200	2.04498600	-0.32625600
C	-0.61530000	3.01374500	-2.31857700
C	2.31126300	1.69289700	-0.75502000
C	2.69739600	0.58271300	0.24995400
C	3.91554400	-0.25039000	-0.17070900
C	6.81438100	0.62743600	0.15803300
C	6.09107500	-0.19330600	1.16669300
C	4.81379000	-0.56632000	0.98906100
C	6.88120800	-0.59788800	2.39341300
O	-7.82864000	-0.35153300	0.17991900
O	-4.96503900	-1.28059500	0.69267100
O	-5.44305300	-3.49382400	1.05878200
O	-2.54028000	-0.27993400	0.43089500
O	1.48529700	2.59766300	2.00379600
O	8.13142000	0.78122900	0.51822500
H	-6.96543700	-0.31675100	-1.77076800
H	-7.59552700	-2.71445800	-0.52594600
H	-6.19892300	-2.62957300	-1.63680500
H	-4.76194100	0.96831700	-1.85273300
H	-4.31131800	-0.73921300	-1.82105900
H	-2.04184800	-0.82572300	-2.10157800
H	-2.32085300	0.79970800	-2.76470400
H	0.13389300	0.32147800	-2.32138100
H	-0.28410100	-0.00227900	-0.62263500
H	1.16026500	3.48748700	-0.69075400
H	-1.31158000	2.60924400	2.16063400
H	-3.17341100	2.64575300	-1.12198900
H	-3.49968300	1.57743000	1.71155600
H	-3.44648400	3.31531300	1.35522600
H	-5.43450900	2.76068200	-0.34020900
H	-5.74317100	3.03588700	1.37136500
H	-5.70501300	0.59902300	1.82050200
H	-7.89881100	0.30560800	2.67849300
H	-9.28735400	1.08991900	1.89368100
H	-7.94445000	2.08391000	2.51253900
H	-9.08793300	1.86435100	-0.48248900
H	-7.51165800	1.96239300	-1.29268900
H	-7.88449900	3.06325500	0.04940500
H	-0.57650700	4.06273700	-2.00291100
H	-1.58386200	2.83450200	-2.79394300
H	0.16617500	2.84799300	-3.07007100
H	4.34083300	-1.17055700	1.76206300
H	6.26076000	-1.19414400	3.06746400

H	7.24292400	0.28674300	2.92725800
H	7.75983200	-1.18168100	2.10219500
H	-3.29970000	-0.86891600	0.71424600
O	6.36827300	1.13156400	-0.88266600
C	8.96884100	1.58317400	-0.41472000
H	8.96450000	1.09916200	-1.39488300
H	8.52525600	2.57675400	-0.51986400
C	10.35635600	1.62203100	0.21419600
H	10.74697600	0.60690700	0.32529600
H	11.03887900	2.19843300	-0.41860200
H	10.30828300	2.08860400	1.20184900
C	3.45091200	2.75246500	-0.71860000
H	3.43087900	3.23473900	0.26532400
H	4.44129200	2.32133800	-0.88454400
H	3.27126500	3.51353400	-1.48591700
H	2.23817000	1.25047600	-1.75667900
H	4.47320600	0.18426200	-0.99548900
H	2.82518300	1.04252000	1.23093200
O	1.54898800	-0.37549400	0.44962000
Os	1.67461500	-2.14379800	-0.23291100
O	3.43102600	-1.59019800	-0.68302500
O	0.68586900	-2.29044500	-1.64885500
O	1.72147100	-3.31878200	1.03736200

OsO_4

Os	0.00000000	0.00000000	0.00000000
O	-1.00314000	-1.00314000	1.00314000
O	1.00314000	1.00314000	1.00314000
O	-1.00314000	1.00314000	-1.00314000
O	1.00314000	-1.00314000	-1.00314000