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Electronic Supporting Information

Rapid Construction of the ABD Tricyclic Skeleton in Meliacarpinin B from Carvone Enabled by an INOC Strategy

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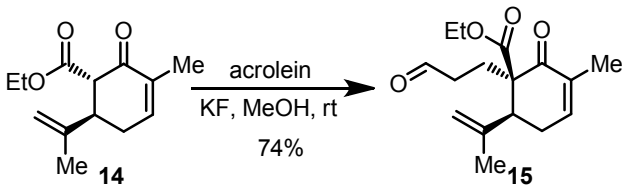
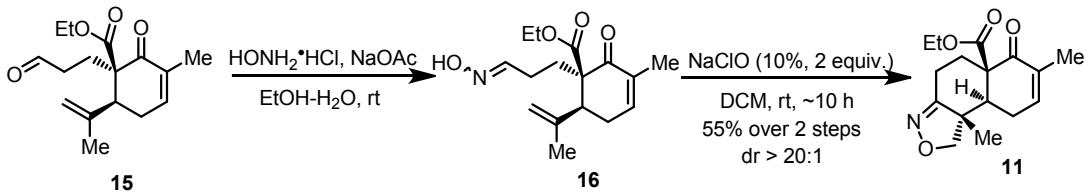
General Procedures

All reactions involving air- and moisture-sensitive reagents were carried out under argon atmosphere using standard syringe-septum cap techniques. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene were distilled from sodium/benzophenone ketyl before use. Methylene chloride (DCM) and triethylamine (Et_3N) were distilled from calcium hydride before use. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel GF254 plates using UV light or basic aqueous potassium permanganate as visualizing agent. For reactions at low temperature, ice/water or CO_2/acetone systems were used. For reactions at evaluated temperature, heating mantle was used. All the temperature refers to external temperature unless otherwise noted. Column chromatography was performed on silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded on Bruker AMX-400 spectrometers (at 400 MHz and 101 MHz respectively) and calibrated by using residual undeuterated chloroform (δ H = 7.26 ppm) and $CDCl_3$ (δ C = 77.16 ppm) as internal references. ^{19}F NMR spectra was recorded on Bruker AMX-400 spectrometers (at 376 MHz) and calibrated by using benzotrifluoride (δ F = –62.80 ppm) as external references. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a Bruker 550 spectrometer. Melting points (m.p.) were recorded on a RY-1A apparatus. High-resolution mass spectra (HRMS) were acquired using Varian 7.0T FTMS or Agilent 6520 Q-TOF LC/MS with electrospray ionization (ESI) source. Optical rotations were recorded on a Perkin–Elmer 341 polarimeter (using the sodium D line; 589nm). X-Ray diffraction crystallographic analysis was performed with a rigaku007 diffractometer on monocrystal of pure recrystallized compound.

Experimental Procedures



To a stirred solution of **14**[1] (55.0 g, 247 mmol, 1.0 equiv.) in MeOH (330 mL) was added KF (28.6 g, 494 mmol, 2.0 equiv.) and acrolein (22 mL, 322 mmol, 1.3 equiv.) at 20–25 °C. Additional acrolein (5 mL, 74 mmol, 0.3 equiv.) was added every 8~10 h untill TLC indicated the consumption of starting material. The reaction was quenched with saturated aq. NH_4Cl solution (300 mL) and H_2O (1000 mL), and the mixture was extracted with EtOAc (3×330 mL). The combined organic layer was washed with brine (330 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 10:1) to afford **15** (51.0 g, 183 mmol, 74%) as a white solid. R_f 0.44 (4:1 Hexane: EtOAc). m.p. 60.1–62.3 °C. IR: 2979, 2926, 2726, 1728, 1663, 1445, 1370, 1211, 1023, 903, 761 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 9.71 (s, 1H), 6.78 (brs, 1H), 4.87 (s, 1H), 4.79 (s, 1H), 4.17–4.05 (m, 2H), 2.88 (dd, J = 9.4, 4.8 Hz, 1H), 2.81–2.71 (m, 1H), 2.60–2.31 (m, 4H), 2.10–2.01 (m, 1H), 1.80 (s, 3H), 1.67 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 195.8, 170.4, 144.8, 144.0, 134.6, 115.6, 61.2, 59.0, 49.0, 39.2, 29.0, 24.4, 20.6, 16.3, 13.8. HRMS (ESI) for $[C_{16}H_{23}O_4]^+$ ($[M+H]^+$): calcd. 279.1591, found 279.1591. [α]15 D = +56.2 (c = 1.0, $CHCl_3$).

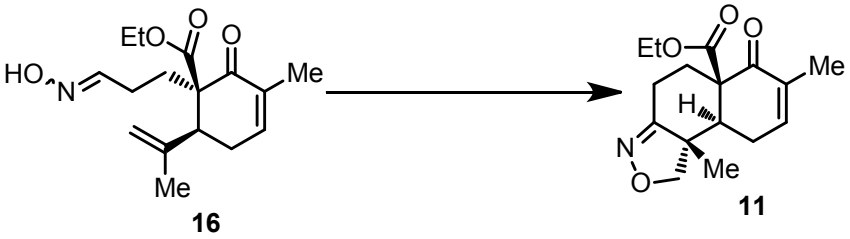


To a stirred solution of **15** (31.7 g, 114 mmol, 1.0 equiv.) in EtOH (200 mL) was added H_2O (100 mL), hydroxylamine hydrochloride (11.9 g, 171 mmol, 1.5 equiv.) and NaOAc (14.0 g, 171 mmol, 1.5 equiv.) at 20–25 °C, and the mixture was stirred for 0.5 h at same temperature. The reaction was diluted with H_2O (500 mL) and extracted with DCM (3×200 mL). The combined organic layer was washed with brine (200 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was used for next step without purification. A small sample was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 5:1) to afford **16** as a colourless oil.

R_f 0.51, 0.43 (2:1 Hexane: EtOAc). IR: 3443, 3275, 2977, 2925, 1730, 1662, 1444, 1369, 1210, 1024, 902, 766 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38 (t, *J* = 5.8 Hz, 0.6 H), 6.83–6.77 (m, 1H), 6.74–6.66 (m, 0.4H), 4.92–4.88 (m, 1H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.18–4.03 (m, 2H), 2.92–3.03 (m, 1H), 2.89–2.75 (m, 1H), 2.56–2.15 (m, 3H), 2.11–1.87 (m, 2H), 1.81 (s, 3H), 1.69 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 195.9, 170.8, 170.7, 151.7, 151.7, 145.4, 145.1, 144.1, 143.9, 135.0, 134.9, 115.7, 115.7, 61.4, 61.3, 59.8, 59.7, 48.1, 47.5, 29.2, 29.2, 28.7, 28.1, 24.9, 20.9, 20.8, 20.3, 16.6, 14.0. HRMS (ESI) for $[C_{16}H_{24}NO_4]^+$ ($[M+H]^+$): calcd. 294.1700, found 294.1706. [α]15 D = +69.5 (*c* = 1.0, $CHCl_3$).

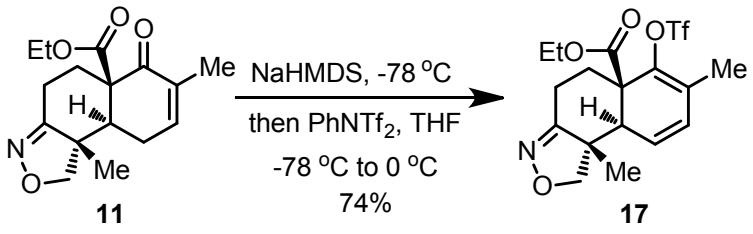
To a stirred solution of crude **16** in DCM (1.14 L) at 20–25 °C, was added dropwise an *aq.* NaClO solution (10%, 170 mL, 228 mmol, 2.0 equiv.) within 2 h. The resulting mixture was stirred at room temperature for 8 h before it was diluted with brine (200 mL) and stand to separated. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 10:1 to 5:1) to afford **11** (18.3 g, 62.4 mmol, 55% over 2 steps) as a white solid. R_f 0.46 (2:1 Hexane: EtOAc). m.p. 68.2–70.0 °C. IR: 2976, 2929, 2867, 1724, 1668, 1447, 1361, 1257, 1202, 1099, 1017, 854, 769 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 6.86 (d, *J* = 5.7 Hz, 1H), 4.22–4.10 (m, 3H), 3.82 (d, *J* = 7.9 Hz, 1H), 3.11–2.93 (m, 2H), 2.76–2.68 (m, 2H), 2.29 (dd, *J* = 11.8, 4.6 Hz, 1H), 2.03–1.93 (m, 1H), 1.82–1.76 (m, 3H), 1.41 (ddd, *J* = 14.1, 12.0, 6.7 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 169.4, 162.9, 145.4, 133.6, 81.4, 61.8, 56.2, 54.2, 50.7, 30.6, 26.3, 19.9, 17.0, 16.6, 13.9. HRMS (ESI) for $[C_{16}H_{22}NO_4]^+$ ($[M+H]^+$): calcd. 292.1543, found 292.1540. [α]27 D = +1.45 (*c* = 3.0, $CHCl_3$).

Condition screening for the INOC reaction[a]



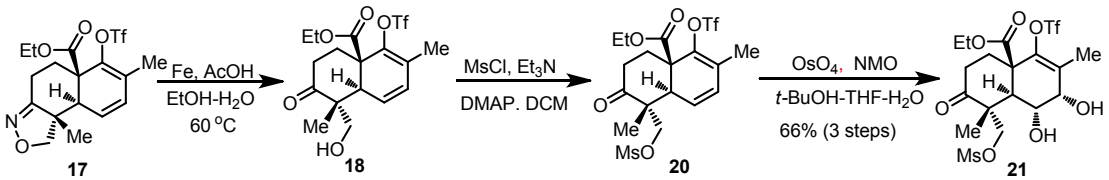
Entry	Conditions	Temperature	Reaction time	Yield[b]
1	NaClO (1.2 equiv.), DCM	20–25 °C	10 h	50%
2	NaClO (1.2 equiv.), DCM	37 °C	6 h	47%
3	Chloramine-T (2.0 equiv.), EtOH	50 °C	3 h	20%
4	*t*-BuOCl (1.2 equiv.), DCM	20–25 °C	3 h	decompose
5	*t*-BuOCl (1.2 equiv.), toluene	20–25 °C	3 h	decompose
6	$PhI(OAc)_2$, CF_3CH_2OH	50 °C	3 h	decompose
7	NaClO (1.2 equiv.), toluene	20–25 °C	10 h	53%[c]
8	NaClO (1.2 equiv.), toluene	80 °C	4 h	46%
9	NaClO (1.2 equiv.), MeCN	20–25 °C	10 h	44%
10	NaClO (1.2 equiv.), THF	20–25 °C	10 h	46%
11	NaClO (2.0 equiv.), DCM	20–25 °C	10 h	54%
12	NaClO (2.0 equiv.), DCM[d]	20–25 °C	10 h	55%
13	NaClO (2.0 equiv.), DCM[d,e]	20–25 °C	10 h	55%

[a] All the reactions were performed on a 1 mmol scale at 0.02 M concentration unless otherwise noted. [b] Isolated yield. [c] Contain impurity, diifficult to be fully removed from the product. [d] Reaction was performed at 16 g scale. [e] Reaction was performed at 0.1 M concentration.



To a stirred solution of **11** (10.0 g, 34.3 mol, 1.0 equiv.) in THF (100 mL) was added NaHMDS (2.0 M in THF, 22 mL, 44.6 mmol, 1.3 equiv.) dropwise at –78 °C. The mixture was stirred for 3 min at –78 °C before $PhNTf_2$ (17.1 g, 48.0 mmol, 1.4 equiv.) was added. The resulting mixture was warmed up to 0 °C and stirred for 0.5 h before it was quenched with saturated aq. NH_4Cl (60 mL) solution. The mixture was

diluted with H_2O (100 mL) and extracted with EtOAc (3×60 mL). The combined organic layer was washed with brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 7:1) to afford **17** (10.8 g, 25.4 mmol, 74%) as a white solid. R_f 0.41 (3:1 Hexane: EtOAc). m.p. 120.4–122.5 °C. IR: 2986, 2932, 2883, 1716, 1443, 1409, 1223, 1135, 959, 842 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 5.97 (dd, *J* = 9.5, 3.4 Hz, 1H), 5.73 (dd, *J* = 9.5, 2.7 Hz, 1H), 4.26 (d, *J* = 7.9 Hz, 1H), 4.22–4.02 (m, 2H), 3.82 (d, *J* = 7.9 Hz, 1H), 3.18 (t, *J* = 3.1 Hz, 1H), 2.80–2.75 (m, 2H), 2.74–2.68 (m, 1H), 1.92 (s, 3H), 1.65–1.56 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 162.4, 144.0, 128.9, 128.4, 127.2, 118.5 (q, *J* = 320.3 Hz), 81.7, 61.7, 54.5, 53.7, 48.8, 30.7, 19.8, 18.1, 16.2, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –72.92. HRMS (ESI) for $[C_{17}H_{21}F_3NO_6S]^+$ ($[M+H]^+$): calcd. 424.1036, found 424.1044. [α]18 D = +247.9 (*c* = 1.0, $CHCl_3$).



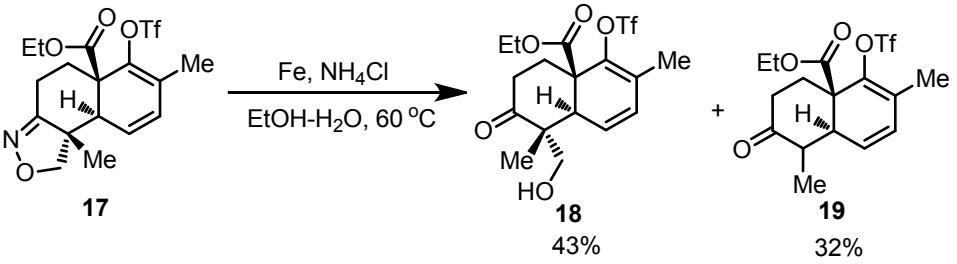
To a stirred solution of **17** (6.0 g, 14.2 mmol, 1.0 equiv.) in EtOH (60 mL) was added H_2O (60 mL) and Fe powder (7.9 g, 142 mmol, 10.0 equiv.) at 20-25 oC, and the mixture was warmed up to 60 °C. AcOH (8.52 g, 142 mmol, 10 equiv.) was added dropwise and stirred for 3 h at same temperature. The reaction was cooled down to 20–25 °C and quenched with saturated aq. $NaHCO_3$ (60 mL), the resulting mixture was passed through a pad of celite and the filtercake was washed with EtOAc. The filtrate was concentrated to remove most of EtOH and EtOAc. The residue was diluted with H_2O (60 mL) and extracted with EtOAc (3×40 mL). The combined organic layer was washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was used for next step without purification. A small sample was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 6:1) to afford **18** as a light yellow solid. R_f 0.67 (3:2 Hexane: EtOAc). m.p. 66.3–68.4 °C. IR: 2984, 2953, 2879, 1718, 1406, 1215, 1138, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 5.95 (dd, *J* = 9.6, 3.1 Hz, 1H), 5.88 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.20-4.09 (m, 2H), 3.85 (d, *J* = 11.4 Hz, 1H), 3.65 (t, *J* = 2.7 Hz, 1H), 3.43 (d, *J* = 11.5 Hz, 1H), 2.89 (ddd, *J* = 16.5, 12.0, 7.0 Hz, 1H), 2.61 (ddd, *J* = 13.4, 7.0, 2.8 Hz, 1H), 2.47 (ddd, *J* = 16.5, 6.3, 2.9 Hz, 1H), 2.17 (brs, 1H), 2.02–1.94 (m, 1H), 1.91 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.3, 171.0, 143.8, 128.2,

127.9, 127.0, 118.6 (q, J = 320.1 Hz) 66.2, 61.8, 51.7, 47.9, 47.2, 35.7, 28.8, 17.2, 15.9, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.36. HRMS (ESI) for $[C_{17}H_{22}F_3O_7S]^+$ ($[M+H]^+$): calcd. 427.1033, found 427.1032. [α]18 D = +168.2 (c = 1.0, $CHCl_3$).

To a stirred solution of crude **18**, Et_3N (2.87 g, 28.4 mmol, 2.0 equiv.) and DMAP (169 mg, 1.42 mmol, 0.1 equiv.) in DCM (60 mL) was added MsCl (2.44 g, 21.3 mmol, 1.5 equiv.) at 0 °C, and the mixture was stirred for 0.5 h at the same temperature. The reaction was quenched with saturated aq. $NaHCO_3$ solution (40 mL) and extracted with DCM (2×30 mL). The combined organic layer was washed with 1M HCl (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was used for next step without purification. A small sample was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 6:1) to afford **20** as a colorless oil. R_f 0.71 (3:2 Hexane: EtOAc). IR: 2965, 1720, 1408, 1359, 1216, 1174, 1136, 965, 847, 811, 749 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.00 (dd, J = 9.7, 3.3 Hz, 1H), 5.86 (dd, J = 9.6, 2.7 Hz, 1H), 4.43 (d, J = 9.8 Hz, 1H), 4.21–4.09 (m, 2H), 4.03 (d, J = 9.8 Hz, 1H), 3.62 (t, J = 3.0 Hz, 1H), 3.02 (s, 3H), 2.92 (ddd, J = 17.4, 12.3, 7.0 Hz, 1H), 2.61 (ddd, J = 13.6, 7.0, 2.4 Hz, 1H), 2.52 (ddd, J = 17.3, 6.2, 2.5 Hz, 1H), 2.01–1.94 (m, 1H), 1.93 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 170.7, 143.6, 129.0, 128.1, 125.6, 118.6 (q, J = 320.1 Hz), 71.1, 62.0, 49.9, 47.9, 46.7, 36.9, 35.2, 28.5, 17.6, 15.9, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –74.15. HRMS (ESI) for $[C_{18}H_{24}F_3O_9S_2]^+$ ($[M+H]^+$): calcd. 505.0808, found 505.0809. [α]18 D = +161.8 (c = 1.0, $CHCl_3$).

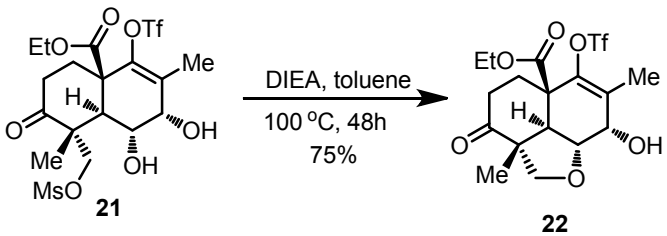
To a stirred solution of crude **20** in THF (40 mL), t-BuOH (40 mL) and H_2O (8 mL) was added NMO (2.49 g, 21.3 mmol, 1.5 equiv.) and OsO_4 (0.16 M in THF, 4.4 mL, 0.71 mmol, 0.05 equiv.) at 0 °C, and the mixture was stirred overnight at 20–25 °C. The reaction was quenched with saturated aq. $Na_2S_2O_3$ solution (30 mL) and the stirring was continued for 0.5 h. The mixture was diluted with H_2O (30 mL) and extracted with EtOAc (3×30 mL). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 4:1 to 1:1) to afford **21** (5.05 g, 9.38 mmol, 66% over 3 steps) as a white foam. R_f 0.65 (1:2 Hexane: EtOAc). IR: 3500, 2990, 2946, 1725, 1407, 1352, 1218, 1175, 1138, 958, 848, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.93 (d, J = 9.3 Hz, 1H), 4.45–4.38 (m, 1H), 4.25–4.15 (m, 2H), 4.14–4.06 (m, 1H), 4.03 (d, J = 9.3 Hz, 1H), 3.00 (s, 3H), 2.99–2.94 (m, 2H), 2.93–2.83 (m, 1H), 2.82 (d, J = 7.5 Hz, 1H), 2.60–2.50 (m, 2H), 2.01 (s, 3H), 2.05–1.94 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.12 (s, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 212.3, 171.4, 145.1, 129.5, 118.4 (q, J = 319.7 Hz), 70.4, 67.1, 63.0, 50.0, 49.4, 41.1, 37.2, 36.4, 28.0, 15.4, 14.2, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.36. HRMS (ESI) for $[C_{18}H_{29}F_3NO_{11}S_2]^+$ ($[M+NH_4]^+$): calcd. 556.1129, found 556.1131. [α]18 D = +136.3 (c = 1.0, $CHCl_3$).



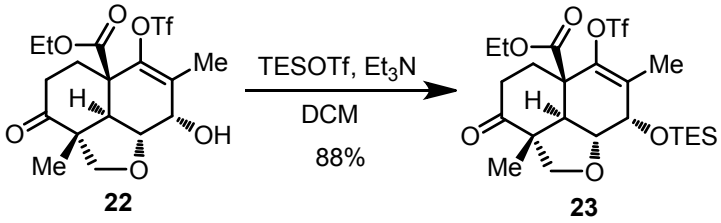
To a stirred solution of **17** (100 mg, 0.24 mmol, 1.0 equiv.) in EtOH (3 mL) was added H_2O (3 mL), NH_4Cl (126 mg, 2.36 mmol, 10.0 equiv.) and Fe powder (131 mg, 2.36 mmol, 10.0 equiv.) at 20–25 °C, the mixture was warmed up to 60 °C and stirred for 5 h. The reaction was cooled down to 20–25 °C and passed through a pad of celite, the filtercake was washed with EtOAc and the filtrate was concentrated to remove most of EtOH and EtOAc. The residue was diluted with H_2O (4 mL) and extracted with EtOAc (3×3 mL). The combined organic layer was washed with brine (3 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 10:1 to 6:1) to afford **19** (30 mg, 0.076 mmol, 32%) and **18** (43 mg, 0.10 mmol, 43%) sequentially.

Compound **19**: colourless oil. R_f 0.49 (6:1 Hexane: EtOAc). IR: 2967, 2932, 1716, 1402, 1214, 1137, 1020, 912, 742 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 5.99 (dd, J = 9.5, 2.3 Hz, 1H), 5.89 (dd, J = 9.5, 3.1 Hz, 1H), 4.27–4.13 (m, 2H), 3.35–3.25 (m, 1H), 2.69–2.63 (m, 1H), 2.58–2.36 (m, 3H), 2.03 (td, J = 13.3, 5.2 Hz, 1H), 1.90 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 170.5, 143.6, 131.5, 127.5, 127.1, 118.8 (q, J = 319.7 Hz), 61.8, 50.3, 50.3, 43.5, 37.2, 30.0, 15.8, 14.1, 12.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.48. HRMS (ESI) for $[C_{16}H_{20}F_3O_6S]^+$ ($[M+H]^+$): calcd. 397.0927, found 397.0923. [α]18 D = +55.2 (c = 1.0, $CHCl_3$).



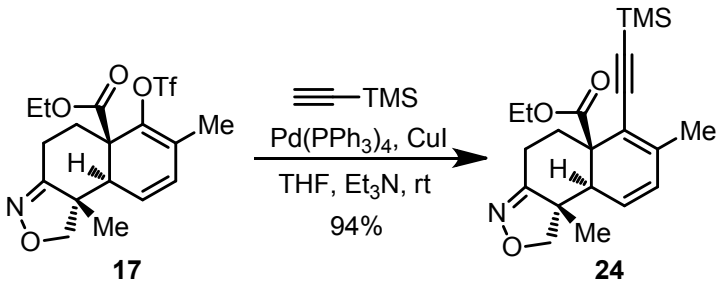
To a stirred solution of **21** (448 mg, 0.83 mmol, 1.0 equiv.) in toluene (10 mL) was added DIEA (537 mg, 4.16 mmol, 5.0 equiv.) at 20–25 °C, the mixture was

warmed up to 100 °C and stirred for 48 h. After cooled to 20–25 °C, the mixture was directly concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 4:1) to afford **22** (276 mg, 0.62 mmol, 75%) as a colourless oil. R_f 0.43 (3:2 Hexane: EtOAc). IR: 3420, 2971, 2894, 1726, 1410, 1218, 1138, 1109, 1038, 870, 845 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 4.53 (dd, *J* = 12.0, 4.6 Hz, 1H), 4.47 (d, *J* = 4.6 Hz, 1H), 4.31–4.16 (m, 2H), 4.04 (d, *J* = 8.5 Hz, 1H), 3.83 (d, *J* = 8.5 Hz, 1H), 3.10 (ddd, *J* = 15.8, 13.0, 6.7 Hz, 1H), 2.82 (dd, *J* = 13.2, 6.5 Hz, 1H), 2.76 (brs, 1H), 2.47–2.36 (m, 2H), 2.02 (s, 3H), 1.79 (td, *J* = 13.1, 5.3 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 169.8, 146.7, 133.0, 118.5 (q, *J* = 319.9 Hz), 77.6, 72.2, 68.8, 62.7, 51.5, 50.8, 48.5, 36.8, 33.5, 16.6, 15.9, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.57. HRMS (ESI) for $[C_{17}H_{25}F_3NO_8S]^+$ ($[M+NH_4]^+$): calcd. 460.1247, found 460.1249. [α]18 D = +120.0 (*c* = 1.0, $CHCl_3$).

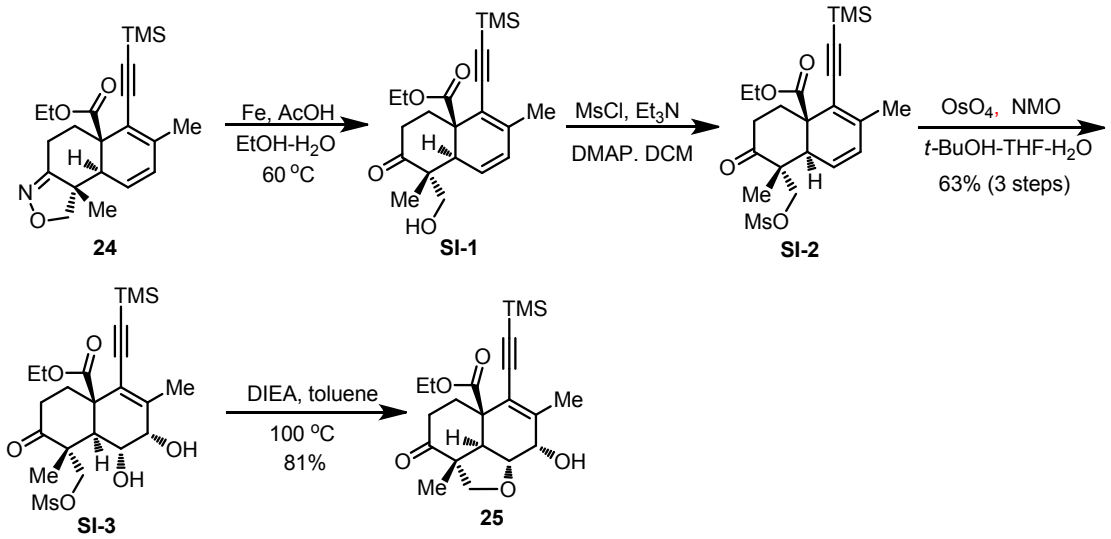


22 **23**

To a stirred solution of **22** (284 mg, 0.64 mmol, 1.0 equiv.) and Et_3N (185 μL, 1.29 mmol, 2.0 equiv.) in DCM (10 mL) was added TESOTf (254 mg, 0.96 mmol, 1.5 equiv.) dropwise at 0 °C, the mixture was stirred for 0.5 h at same temperature. The reaction was quenched with saturated aq. $NaHCO_3$ solution (5 mL) and separated, the aqueous phase was extracted with DCM (2×4 mL). The combined organic layer was washed with brine (3 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 10:1) to afford **23** as a white solid. R_f 0.47 (6:1 Hexane: EtOAc). m.p. 90.5–92.3 °C. IR: 2958, 2883, 1727, 1458, 1410, 1217, 1138, 1100, 1042, 1013, 953, 874, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.49–4.43 (m, 2H), 4.30–4.13 (m, 2H), 3.91 (d, *J* = 8.3 Hz, 1H), 3.76 (d, *J* = 8.3 Hz, 1H), 3.10 (ddd, *J* = 15.9, 12.9, 6.8 Hz, 1H), 2.79 (dd, *J* = 13.1, 6.5 Hz, 1H), 2.53–2.46 (m, 1H), 2.40 (dd, *J* = 16.0, 4.0 Hz, 1H), 1.93 (s, 3H), 1.80 (td, *J* = 13.0, 5.3 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.71–0.62 (m, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 209.7, 170.2, 146.2, 133.7, 118.6 (q, *J* = 319.7 Hz), 77.2 72.6, 71.2, 62.3, 51.7, 50.8, 48.8, 37.1, 33.8, 16.8, 15.8, 13.9, 7.0, 5.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.61. HRMS (ESI) for $[C_{23}H_{36}F_3O_8SSi]^+$ ($[M+H]^+$): calcd. 557.1847, found 557.1844. [α]18 D = +109.3 (*c* = 1.0, $CHCl_3$).



To a stirred solution of **17** (4.0 g, 9.44 mmol, 1.0 equiv) in THF (48 mL) and Et_3N (12 mL) was added trimethylsilylacetylene (2.0 mL, 14.16 mmol, 1.5 equiv), CuI (180 mg, 0.94 mmol, 0.1 equiv), $Pd(PPh_3)_4$ (436 mg, 0.38 mmol, 0.04 equiv) sequentially at 20–25 °C, and the mixture was stirred for 3 h at same temperature. The reaction was quenched with H_2O (100 mL), and the mixture was extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 10:1) to afford **24** (3.3 g, 8.88 mmol, 94%) as a light yellow solid. R_f 0.42 (5:1 Hexane: EtOAc). m.p. 108.6–110.2 °C. IR: 2964, 2864, 2131, 1720, 1446, 1401, 1252, 1214, 1020, 848, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.00 (dd, J = 9.5, 3.2 Hz, 1H), 5.77 (d, J = 9.5 Hz, 1H), 4.26 (d, J = 7.8 Hz, 1H), 4.16–4.02 (m, 2H), 3.80 (d, J = 7.8 Hz, 1H), 2.98–2.86 (m, 2H), 2.77–2.69 (m, 1H), 2.57–1.45 (m, 1H), 1.98 (s, 3H), 1.50 (td, J = 13.7, 4.4 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H), 1.17 (s, 3H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 163.5, 142.0, 129.5, 128.2, 118.7, 104.4, 101.3, 81.9, 60.8, 54.2, 51.9, 46.5, 34.2, 20.9, 20.6, 18.8, 14.0, 0.2. HRMS (ESI) for $[C_{21}H_{30}NO_3Si]^+$ ($[M+H]^+$): calcd. 372.1989, found 372.1995. [α]18 D = +133.0 (c = 1.0, $CHCl_3$).



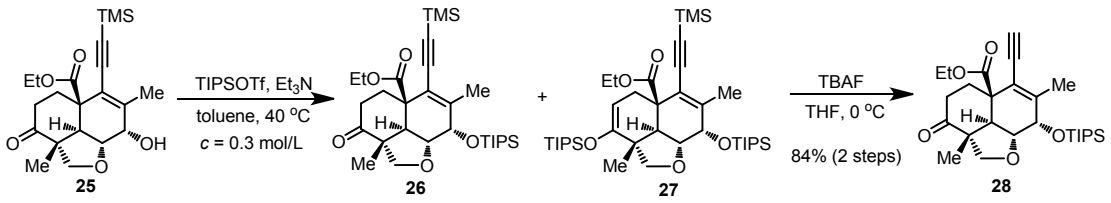
To a stirred solution of **24** (3.3 g, 8.88 mmol, 1.0 equiv.) in EtOH (25 mL) was added H_2O (25 mL) and Fe powder (4.96 g, 88.8 mmol, 10.0 equiv.) at 20–25 °C, and

the mixture was warmed up to 60 °C. AcOH (5.33 g, 88.8 mmol, 10 equiv.) was added dropwise and stirred for 2 h at same temperature. The reaction was quenched with saturated aq. $NaHCO_3$ (50 mL), the resulting mixture was passed through a pad of celite and the filtercake was washed with EtOAc. The filtrate was concentrated to remove most of EtOH and EtOAc. The residue was diluted with H_2O (50 mL) and extracted with EtOAc (3×15 mL). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was used for next step without purification. A small sample was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 6:1) to afford **SI-1** as a colourless oil. R_f 0.55 (2:1 Hexane: EtOAc). IR: 2963, 2133, 1716, 1455, 1404, 1254, 1214, 1137, 1045, 848, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.03–5.93 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.85 (dd, *J* = 11.6, 5.1 Hz, 1H), 3.45 (dd, *J* = 11.5, 7.1 Hz, 1H), 3.27 (s, 1H), 2.93–2.84 (m, 1H), 2.77–2.65 (m, 1H), 2.44–2.27 (m, 2H), 1.99 (s, 3H), 1.80 (td, *J* = 13.9, 4.4 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.07 (s, 3H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9, 172.1, 142.3, 129.0, 128.5, 118.7, 103.7, 101.5, 65.6, 60.9, 52.4, 46.2, 45.0, 36.7, 33.2, 20.6, 17.9, 14.1, 0.2. HRMS (ESI) for $[C_{21}H_{31}O_4Si]^+$ ($[M+H]^+$): calcd. 375.1986, found 375.1980. [α]18 D = +68.4 (*c* = 1.0, $CHCl_3$).

To a stirred solution of crude **SI-1**, Et_3N (2.3 mL, 16.0 mmol, 1.8 equiv.) and DMAP (107 mg, 0.89 mmol, 0.1 equiv.) in DCM (60 mL) was added MsCl (1.32 g, 11.5 mmol, 1.3 equiv.) at 0 °C, and the mixture was stirred for 30 min at the same temperature. The reaction was quenched with saturated aq. $NaHCO_3$ solution (20 mL) and extracted with DCM (2×15 mL). The combined organic layer was washed with 1M HCl (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was used for next step without purification. A small sample was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 6:1) to afford **SI-2** as a colorless oil. R_f 0.60 (2:1 Hexane: EtOAc). IR: 2963, 2132, 1717, 1358, 1254, 1215, 1176, 969, 849, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (dd, *J* = 9.7, 3.2 Hz, 1H), 5.93 (dd, *J* = 9.7, 2.7 Hz, 1H), 4.50 (d, *J* = 9.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.03 (d, *J* = 9.8 Hz, 1H), 3.31 (t, *J* = 2.9 Hz, 1H), 3.02 (s, 3H), 2.87 (ddd, *J* = 13.8, 5.9, 2.4 Hz, 1H), 2.68 (ddd, *J* = 16.6, 14.2, 6.0 Hz, 1H), 2.47 (ddd, *J* = 16.6, 4.4, 2.6 Hz, 1H), 2.00 (s, 3H), 1.84 (td, *J* = 14.0, 4.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 3H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 171.9, 142.3, 129.5, 127.1, 118.7, 104.2, 101.3, 70.5, 61.0, 50.6, 46.1, 44.0, 37.0, 36.2, 32.4, 20.7, 18.5, 14.1, 0.2. HRMS (ESI) for $[C_{22}H_{33}O_6SSi]^+$ ($[M+H]^+$): calcd. 453.1762, found 453.1762. [α]18 D = +70.6 (*c* = 1.0, $CHCl_3$).

To a stirred solution of crude **SI-2** in THF (20 mL), *t*-BuOH (20 mL) and H_2O (4 mL) was added NMO (1.24 g, 10.7 mmol, 1.2 equiv.) and OsO_4 (0.16 M in THF, 2.8 mL, 0.44 mmol, 0.05 equiv.) at 0 °C, and the mixture was stirred overnight at 20–25 °C. The reaction was quenched with saturated aq. $Na_2S_2O_3$ solution (20 mL) and the stirring was continued for 30 min. The mixture was diluted with H_2O (20 mL) and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 5:1 to 2:1) to afford **SI-3** (2.72 g, 5.59 mmol, 63% over 3 steps) as a brown oil. R_f 0.47 (1:1 Hexane: EtOAc). IR: 3502, 2961, 2906, 2143, 1720, 1350, 1254, 1213, 1176, 958, 848, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ4.91 (d, *J* = 9.0 Hz, 1H), 4.50–4.42 (m, 1H), 4.17–4.01 (m, 4H), 3.03 (d, *J* = 9.5 Hz, 1H), 2.98 (s, 3H), 2.90–2.72 (m, 3H), 2.69 (d, *J* = 11.9 Hz, 1H), 2.59–2.50 (m, 1H), 2.08 (s, 3H), 1.83–1.76 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 173.2, 142.2, 122.6, 102.0, 100.4, 77.1, 70.9, 67.6, 61.8, 50.0, 49.8, 40.0, 37.3, 37.2, 31.2, 20.5, 14.7, 14.0, 0.0. HRMS (ESI) for $[C_{22}H_{35}O_8SSi]^+$ ($[M+H]^+$): calcd. 487.1816, found 487.1818. [α]18 D = +217.6 (*c* = 1.0, $CHCl_3$).

To a stirred solution of **SI-3** (2.72 g, 5.59 mmol, 1.0 equiv.) in toluene (50 mL) was added DIEA (3.38 g, 28.0 mmol, 5.0 equiv.) at 20–25 °C, the mixture was warmed up to 100 °C and stirred for 24 h. After cooled to 20–25 °C, the mixture was directly concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 4:1) to afford **25** (276 mg, 0.62 mmol, 75%) as a brown solid. R_f 0.45 (2:1 Hexane: EtOAc). m.p. 85.4–87.0 °C. IR: 3452, 2964, 2898, 2141, 1720, 1408, 1263, 1216, 910, 848, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.49 (dd, *J* = 12.2, 4.5 Hz, 1H), 4.36 (d, *J* = 4.4 Hz, 1H), 4.27–4.15 (m, 2H), 4.02 (d, *J* = 8.4 Hz, 1H), 3.80 (d, *J* = 8.4 Hz, 1H), 3.06–2.86 (m, 2H), 2.61 (brs, 1H), 2.36 (dd, *J* = 15.4, 4.8 Hz, 1H), 2.22 (d, *J* = 12.2 Hz, 1H), 2.11 (s, 3H), 1.66–1.55 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 171.9, 144.7, 122.2, 102.6, 99.9, 76.8, 73.1, 68.8, 61.7, 51.9, 49.3, 48.0, 37.3, 35.8, 21.4, 16.5, 14.2, 0.0. HRMS (ESI) for $[C_{21}H_{34}NO_5Si]^+$ ($[M+NH_4]^+$): calcd. 408.2201, found 408.2196. [α]18 D = +181.6 (*c* = 1.0, $CHCl_3$).



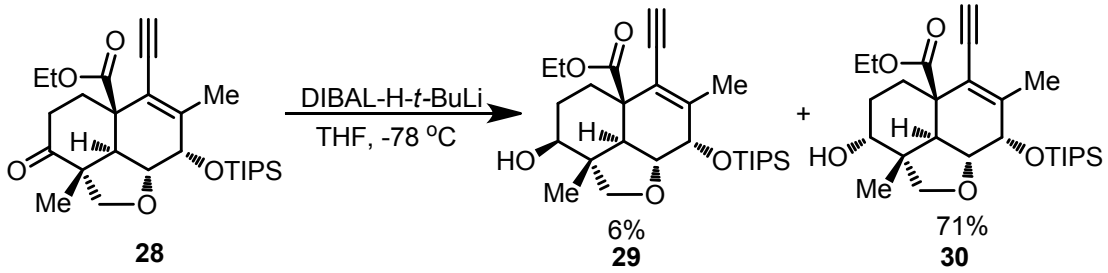
To a stirred solution of **25** (3.50 g, 8.96 mmol, 1.0 equiv.) and Et_3N (3.4 mL, 23.2 mmol, 2.6 equiv.) in toluene (30 mL) was added TIPSOTf (6.04 g, 19.7 mmol, 2.2 equiv.) dropwise at 20–25 °C, and the mixture was warmed to 40 °C and stirred overnight. The reaction was quenched with saturated aq. $NaHCO_3$ solution (40 mL) and extracted with Et_2O (2×15 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue (**27**:**28**= 7.8:1 by ^1H NMR) was used for next step without purification. A small sample was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 80:1 to 40 :1) to afford **27** and **26** sequentially.

Compound **26**: white solid. R_f 0.42 (12:1 Hexane: EtOAc). m.p. 88.3–90.0 °C. IR: 3471, 2955, 2868, 2143, 1723, 1646, 1461, 1260, 1187, 1099, 1041, 846, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 4.54 (d, *J* = 4.2 Hz, 1H), 4.43 (dd, *J* = 12.1, 4.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.95 (d, *J* = 8.3 Hz, 1H), 3.72 (d, *J* = 8.3 Hz, 1H), 3.02 (ddd, *J* = 15.6, 13.0, 6.7 Hz, 1H), 2.89 (dd, *J* = 13.1, 6.5 Hz, 1H), 2.40–2.30 (m, 2H), 2.06 (s, 3H), 1.62–1.53 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 1.16–1.11 (m, 3H), 1.10–1.04 (m, 18H), 0.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0, 172.4, 146.0, 121.1, 102.1, 100.5, 76.3, 73.7, 71.3, 61.6, 52.0, 49.2, 48.4, 37.6, 36.3, 21.8, 18.6, 18.4, 16.5, 14.2, 13.4, 0.1. HRMS (ESI) for $[C_{30}H_{50}NaO_5Si_2]^+$ ($[M+Na]^+$): calcd. 569.3089, found 569.3094. [α]21 D = +198.4 (*c* = 1.0, $CHCl_3$).

Compound **27**: white solid. R_f 0.66 (15:1 Hexane: EtOAc). m.p. 99.6–101.2 °C. IR: 3440, 2950, 2868, 2144, 1732, 1633, 1463, 1191, 1094, 1026, 855, 801, 651 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.61–4.56 (m, 1H), 4.54 (d, *J* = 4.1 Hz, 1H), 4.27 (dd, *J* = 12.6, 4.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.74–3.67 (m, 2H), 3.08 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.59 (d, *J* = 12.7 Hz, 1H), 2.11–2.03 (m, 1H), 2.05 (s, 3H), 1.24–1.12 (m, 9H), 1.12–0.96 (m, 39H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 156.2, 144.9, 122.0, 101.4, 101.0, 99.9, 79.3, 73.9, 71.4, 61.0, 47.7, 47.5, 43.5, 34.8, 21.8, 18.6, 18.4, 18.2, 18.2, 17.8, 14.2, 13.4, 12.8, 0.1. HRMS (ESI) for $[C_{39}H_{71}O_5Si_3]^+$ ($[M+H]^+$): calcd. 703.4604, found 703.4614. [α]21 D = +135.9 (*c* = 1.0, $CHCl_3$).

To a stirred solution of crude mixture from previous step in THF (50 mL) was added TBAF (1.0 M in THF, 10.8 mL, 10.75 mmol, 1.2 equiv.) at 0 °C. The reaction mixture was stirred for 5 min before it was quenched with saturated aq. NH_4Cl solution (50 mL) and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 30 :1) can afford **28** (3.57 g, 7.52 mmol, 84% over 2 steps) as a

colorless oil. R_f 0.35 (12:1 Hexane: EtOAc). IR: 3274, 2946, 2868, 1723, 1461, 1189, 1101, 1041, 1007, 918, 883, 678 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.56 (d, *J* = 4.2 Hz, 1H), 4.44 (dd, *J* = 12.1, 4.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 8.3 Hz, 1H), 3.73 (d, *J* = 8.3 Hz, 1H), 3.21 (s, 1H), 3.09–2.98 (m, 1H), 2.97–2.90 (dd, *J* = 12.9, 6.6 Hz, 1H), 2.40–2.33 (m, 2H), 2.09 (s, 3H), 1.59 (td, *J* = 12.9, 5.2 Hz, 1H), 1.31–1.24 (m, 3H), 1.19–1.11 (m, 6H), 1.11–1.03 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 172.4, 147.2, 119.9, 84.4, 79.2, 76.3, 73.7, 71.2, 61.7, 51.9, 49.1, 48.4, 37.5, 36.3, 21.7, 18.5, 18.4, 16.4, 14.2, 13.3. HRMS (ESI) for $[C_{27}H_{42}NaO_5Si]^+$ ($[M+Na]^+$): calcd. 497.2694, found 497.2697. [α]21 D = +186.7 (*c* = 1.0, $CHCl_3$).



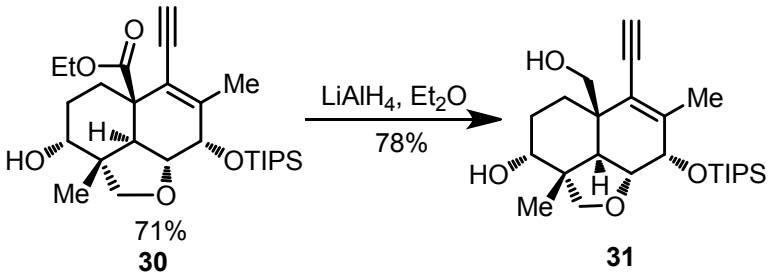
28 **29** **30**

To a solution of DIBAL-H (1.5 M in toluene, 2.2 mL, 3.3 mmol, 1.5 equiv.) was added *t*-BuLi (1.3 M in hexane, 2.5 mL, 3.3 mmol, 1.5 equiv.) slowly at 0 °C. The clear solution was stirred at 0 °C for 5 min before it was added to a solution of **28** (1.04 g, 2.2 mmol, 1.0 equiv.) in THF (15 mL) at −78 °C dropwise. The mixture was stirred for 0.5 h before it was quenched with saturated aq. solution of Rochelle salt (20 mL), The mixture was stirred at room temperature for 1 h and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 15:1 to 6:1) to afford **30** (749 mg, 1.57 mmol, 71%) and **29** (63 mg, 0.13 mmol, 6%) sequentially.

Compound **30**: white solid. R_f 0.52 (5:1 Hexane: EtOAc). m.p. 124.8–126.3 °C. IR: 3301, 2947, 2870, 1724, 1460, 1186, 1100, 1027, 879, 800, 677 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.52 (d, *J* = 4.2 Hz, 1H), 4.39 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 7.3 Hz, 1H), 3.87 (brs, 1H), 3.56 (d, *J* = 7.3 Hz, 1H), 3.17 (s, 1H), 2.63 (d, *J* = 12.5 Hz, 1H), 2.49–2.40 (m, 1H), 2.28–2.16 (m, 1H), 2.06 (s, 3H), 1.78–1.70 (m, 1H), 1.51–1.37 (m, 2H), 1.24–1.06 (m, 24H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 147.1, 121.2, 84.0, 79.5, 73.9, 71.8, 77.2, 70.2, 61.1, 49.2, 43.6, 41.8, 29.3, 28.4, 21.7, 18.6, 18.5, 18.0, 14.2, 13.5. HRMS (ESI) for $[C_{27}H_{44}NaO_5Si]^+$ ($[M+Na]^+$): calcd. 499.2850, found 499.2855. [α]21 D = +191.0 (*c* = 1.0, $CHCl_3$).

Compound **29**: colourless oil. R_f 0.28 (5:1 Hexane: EtOAc). IR: 3305, 2945,

2869, 1725, 1460, 1385, 1210, 1154, 1106, 1025, 881, 803, 679 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.54 (d, *J* = 4.2 Hz, 1H), 4.43 (dd, *J* = 12.2, 4.1 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.88 (d, *J* = 7.7 Hz, 1H), 3.62–3.55 (m, 2H), 3.17 (s, 1H), 2.69–2.62 (m, 1H), 2.06 (s, 3H), 1.97–1.81 (m, 3H), 1.52 (brs, 1H), 1.28–1.05 (m, 25H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 146.9, 120.9, 84.1, 83.0, 79.5, 77.7, 74.2, 71.8, 61.3, 48.3, 47.8, 44.2, 34.0, 30.8, 21.7, 18.6, 18.4, 14.2, 13.4, 11.8. HRMS (ESI) for $[C_{27}H_{44}NaO_5Si]^+$ ($[M+Na]^+$): calcd. 499.2850, found 499.2855. [α]21 D = +161.6 (*c* = 1.0, $CHCl_3$).

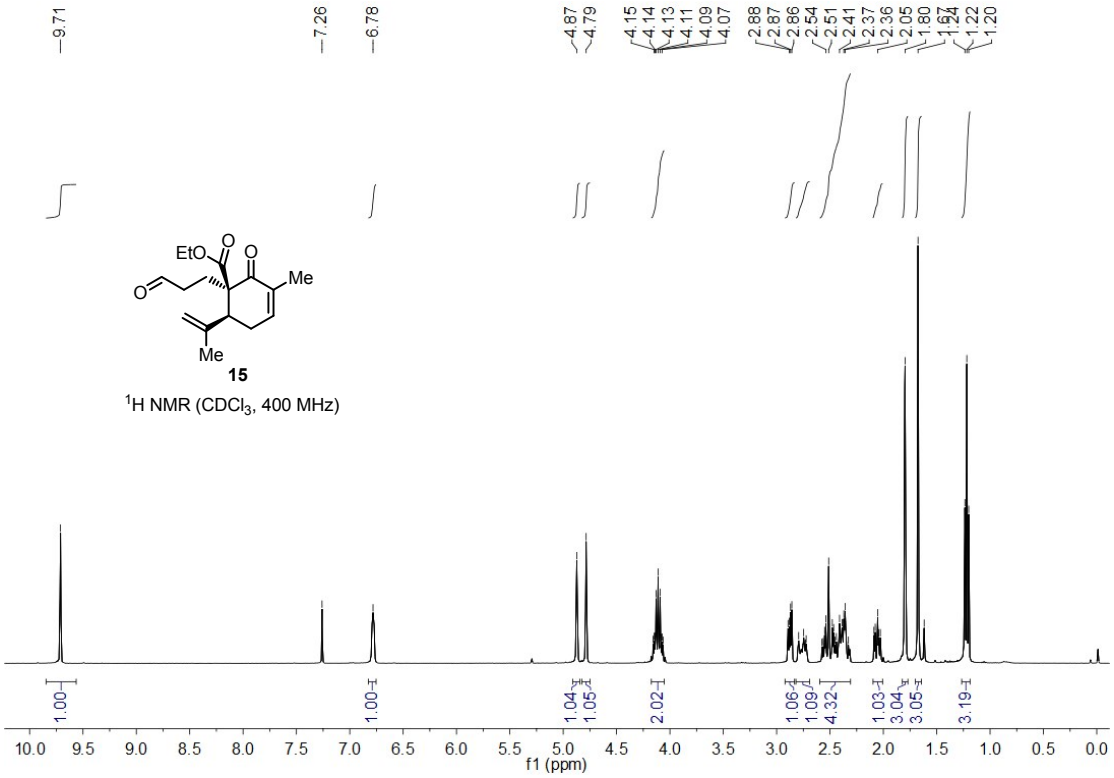


To a suspension of $LiAlH_4$ (66 mg, 1.74 mmol, 5.0 equiv.) in Et_2O (5 mL) was added a solution of **30** (166 mg, 0.35 mmol, 1.0 equiv.) slowly at 0 °C. The reaction mixture was stirred for 6 h at 20–25 °C before it was quenched with H_2O (66 μL), 15% *aq.* NaOH (132 μL) and H_2O (198 μL) sequentially. The resulting mixture was dried over $MgSO_4$ and stirred for 10 min. The solid was removed by filtration through a pad of silica gel, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, petroleum ether:EtOAc, 4:1) to afford **31** (118 mg, 0.27 mmol, 78%) as a white syrup. R_f 0.35 (2:1 Hexane: EtOAc). IR: 3410, 3307, 2942, 2868, 1461, 1384, 1261, 1101, 1037, 1009, 876, 802, 734, 676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.49 (d, *J* = 4.5 Hz, 1H), 4.28 (dd, *J* = 12.8, 4.5 Hz, 1H), 3.98–3.89 (m, 3H), 3.79 (d, *J* = 11.8 Hz, 1H), 3.56 (d, *J* = 7.1 Hz, 1H), 3.22 (s, 1H), 2.44 (d, *J* = 12.8 Hz, 1H), 2.11 (s, 3H), 2.08–1.98 (m, 1H), 1.77–1.67 (m, 2H), 1.59–1.49 (m, 2H), 1.35 (brs, 1H), 1.24 (s, 3H), 1.22–1.14 (m, 3H), 1.14–1.07 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 123.4, 84.0, 80.6, 78.2, 73.5, 71.8, 70.3, 64.5, 44.1, 43.8, 41.6, 28.1, 27.9, 21.6, 19.7, 18.6, 18.5, 13.5. HRMS (ESI) for $[C_{25}H_{42}NaO_4Si]^+$ ($[M+Na]^+$): calcd. 457.2745, found 457.2748. [α]21 D = +49.2 (*c* = 1.0, $CHCl_3$).

Reference

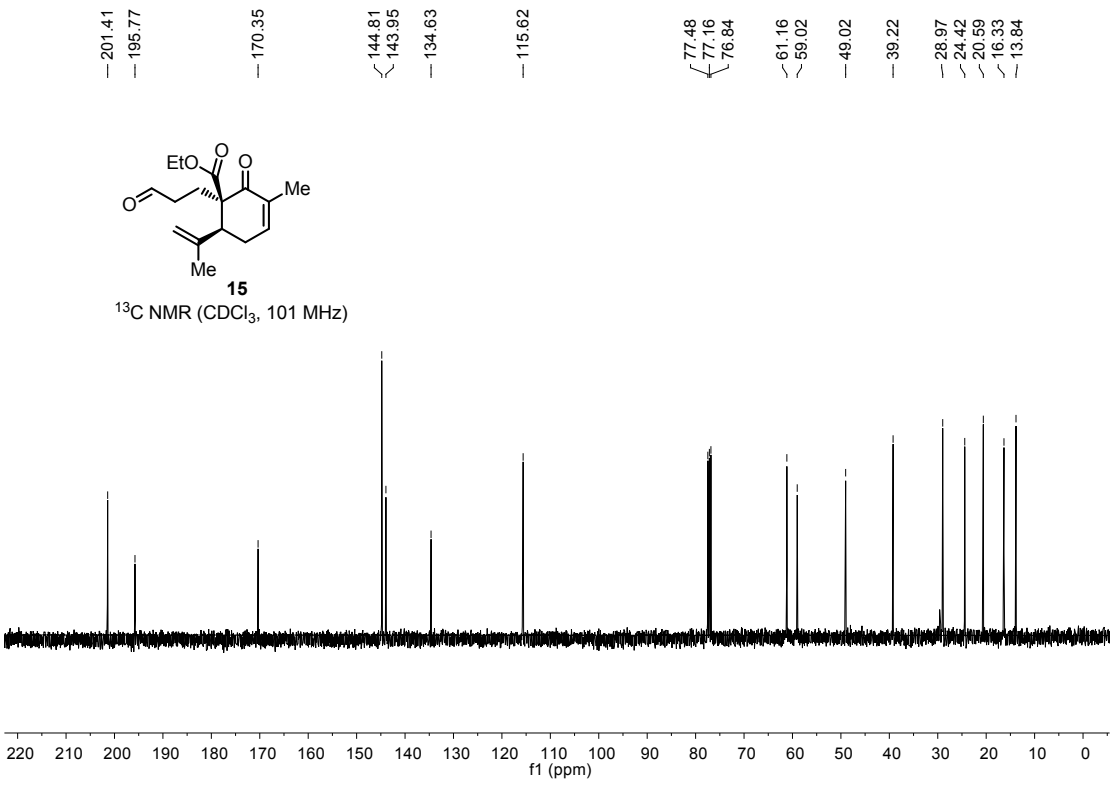
1 [1] J. D. Cuthbertson, A. A. Godfrey, R. J. K. Taylor, A Tandem Amination/Lactamisation Route to 2-Azabicyclo[2.2.2]ocatanones, *Synlett* 2010, 2805.

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



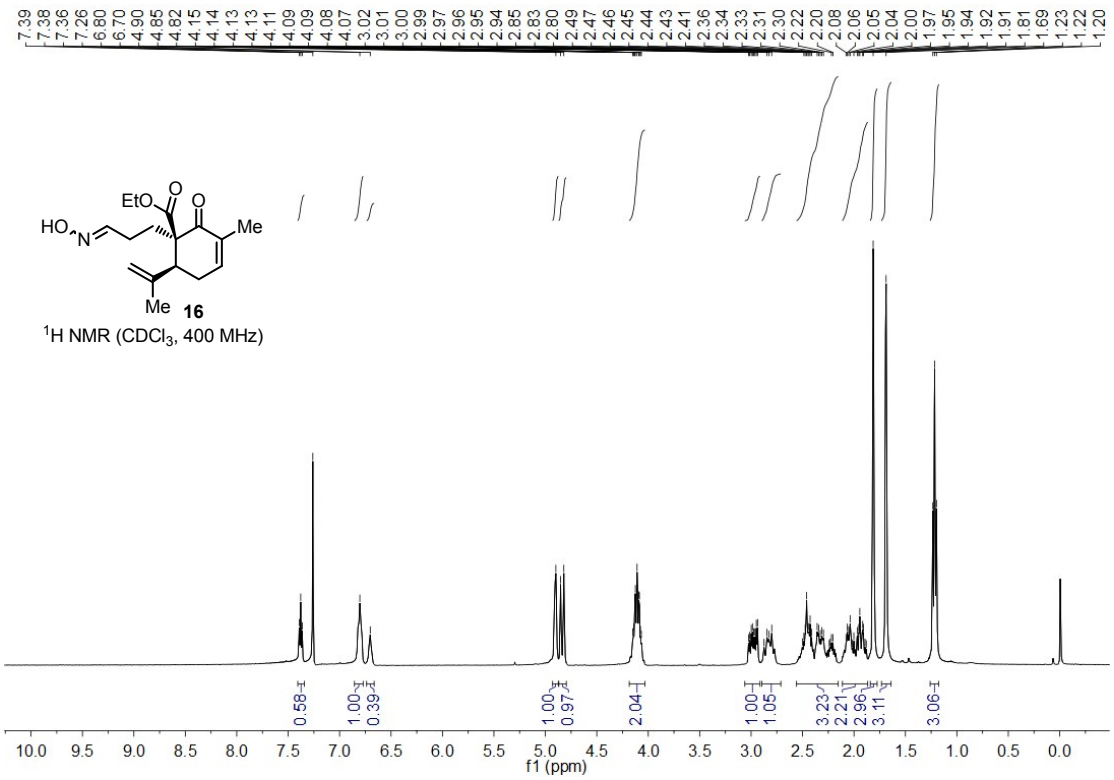
15

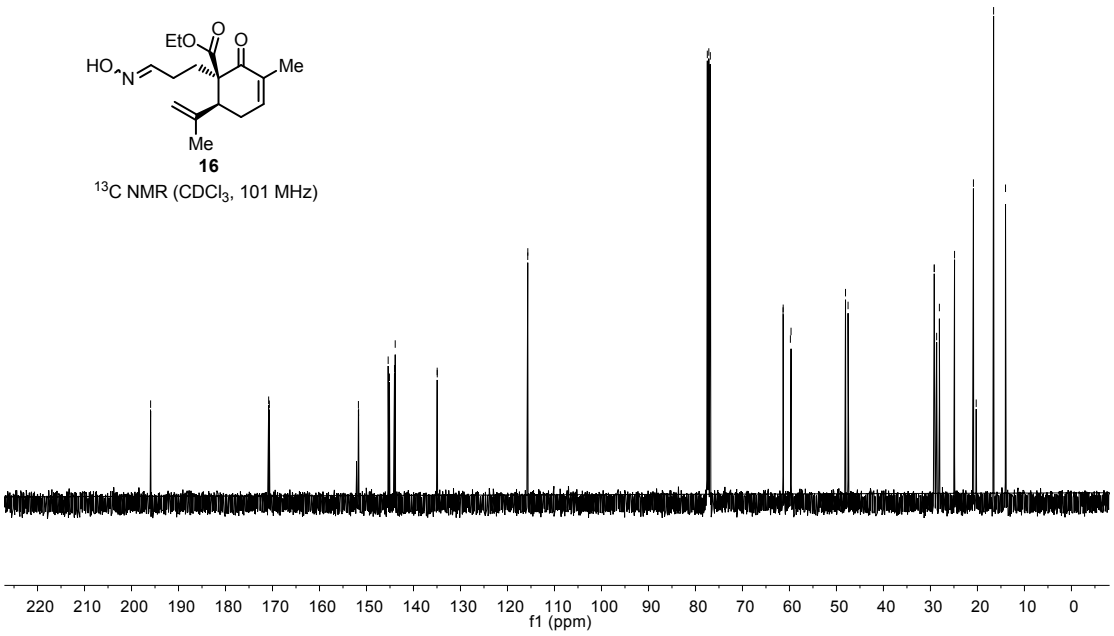
^{1}H NMR ($CDCl_3$, 400 MHz)

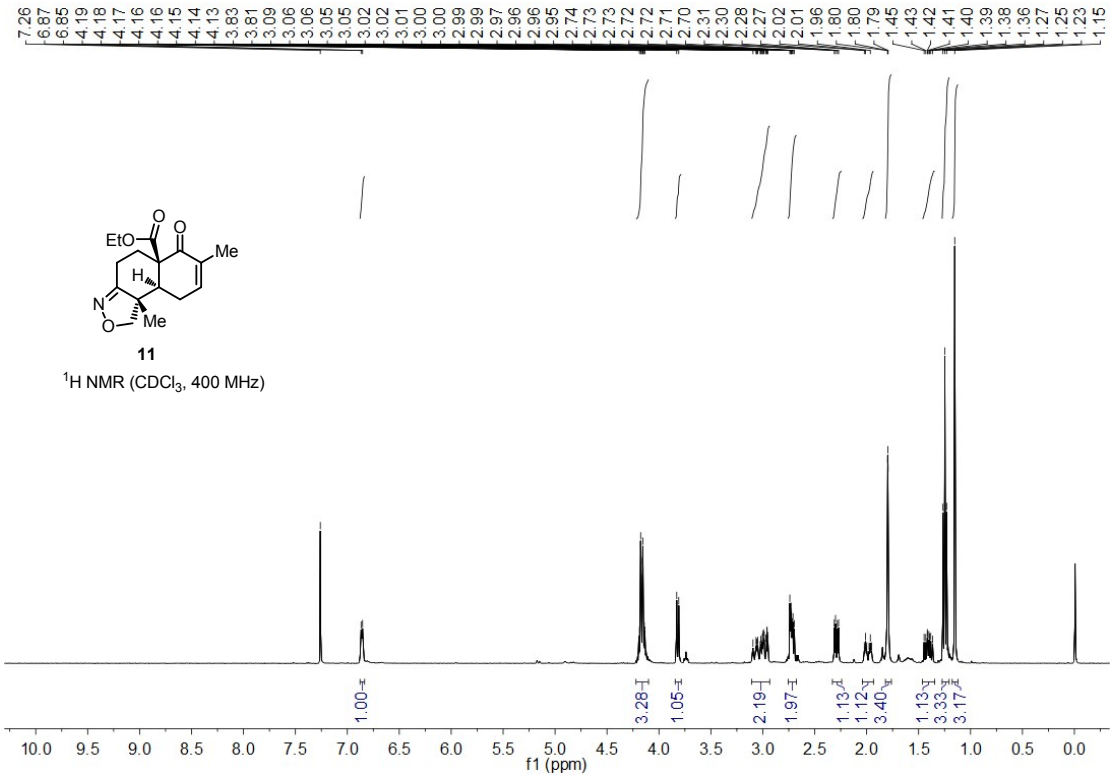


15

^{13}C NMR ($CDCl_3$, 101 MHz)

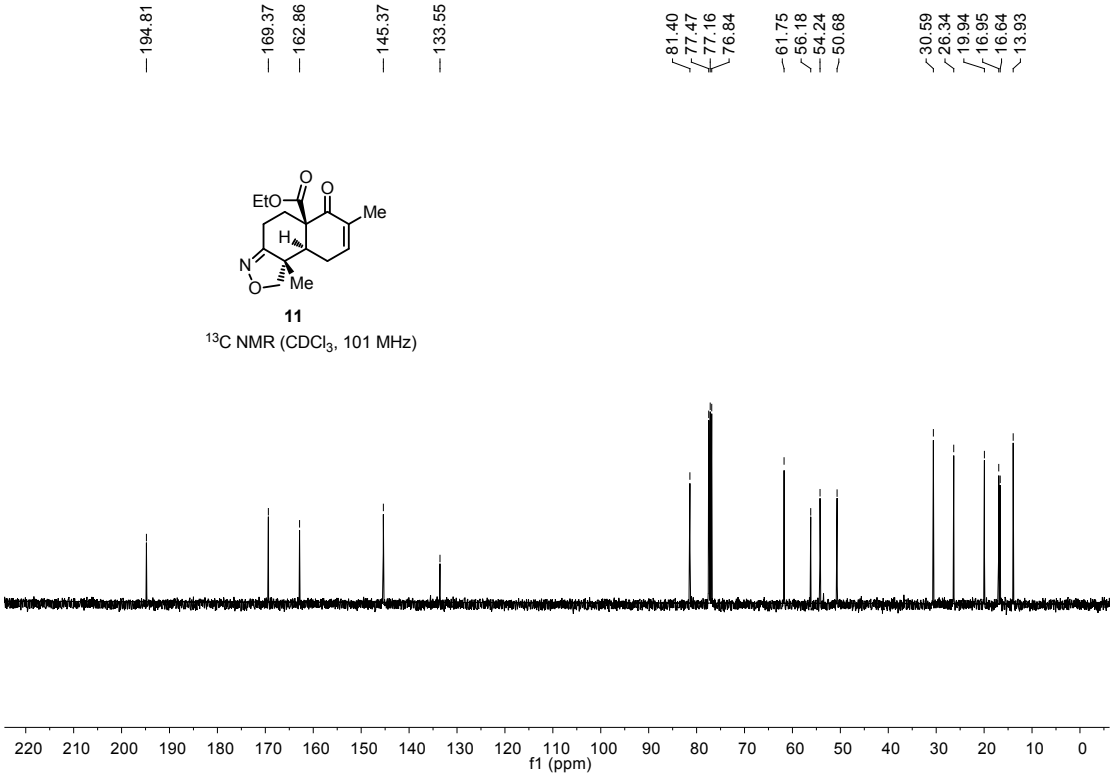

EtO
O
O
HO
N
Me
Me
16
1H NMR (CDCl3, 400 MHz)
f1 (ppm)


EtO
O
O
HO
N
Me
Me
16
13C NMR (CDCl3, 101 MHz)
f1 (ppm)



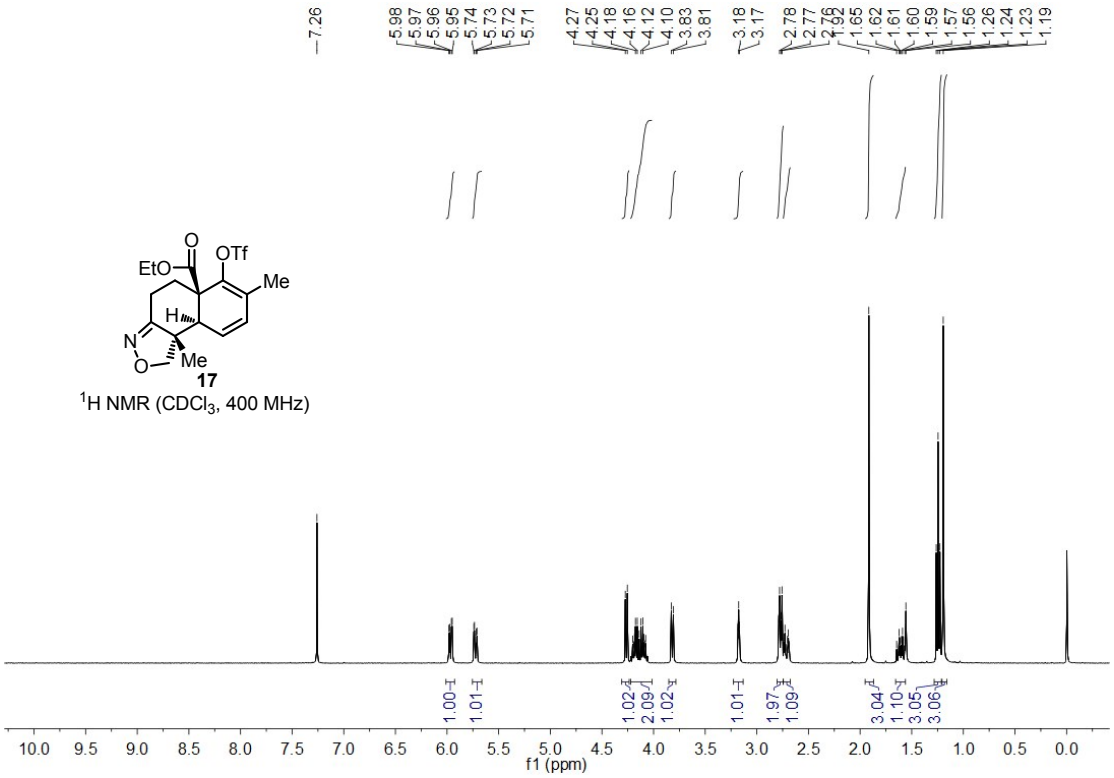
11

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



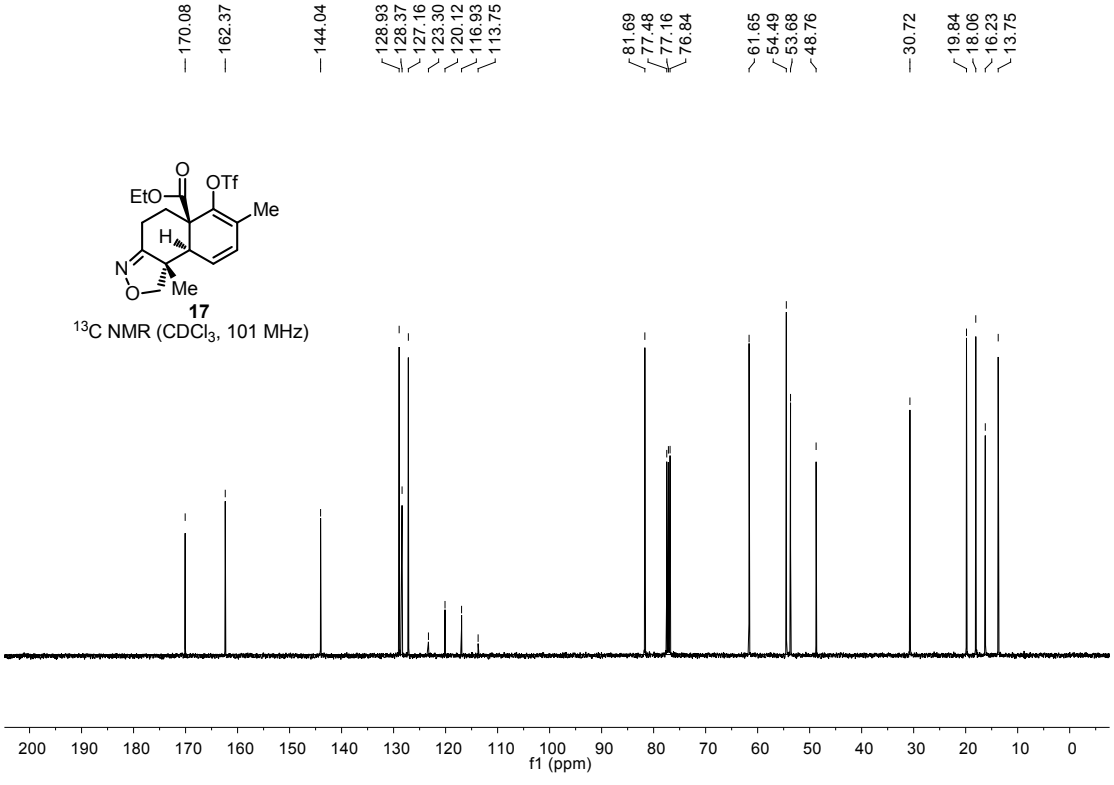
11

^{13}C NMR ($CDCl_3$, 101 MHz)



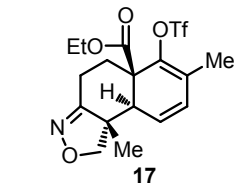
17

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



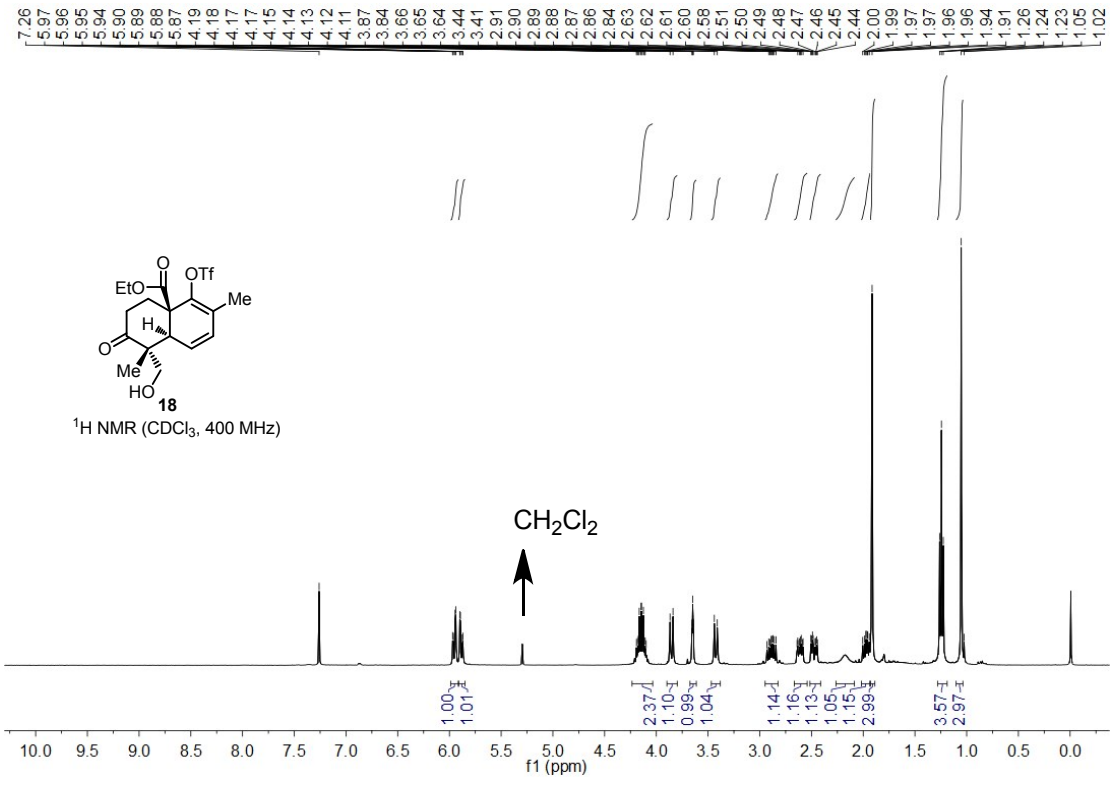
17

^{13}C NMR ($CDCl_3$, 101 MHz)



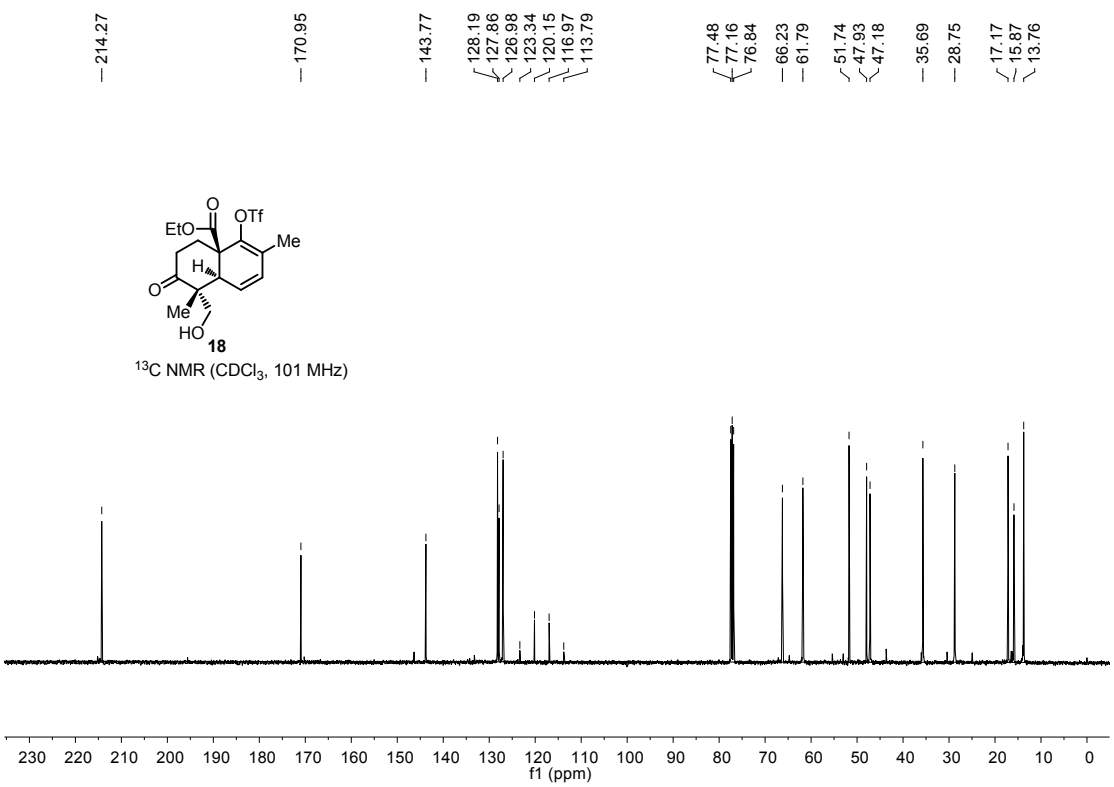
17

^{19}F NMR ($CDCl_3$, 376 MHz)

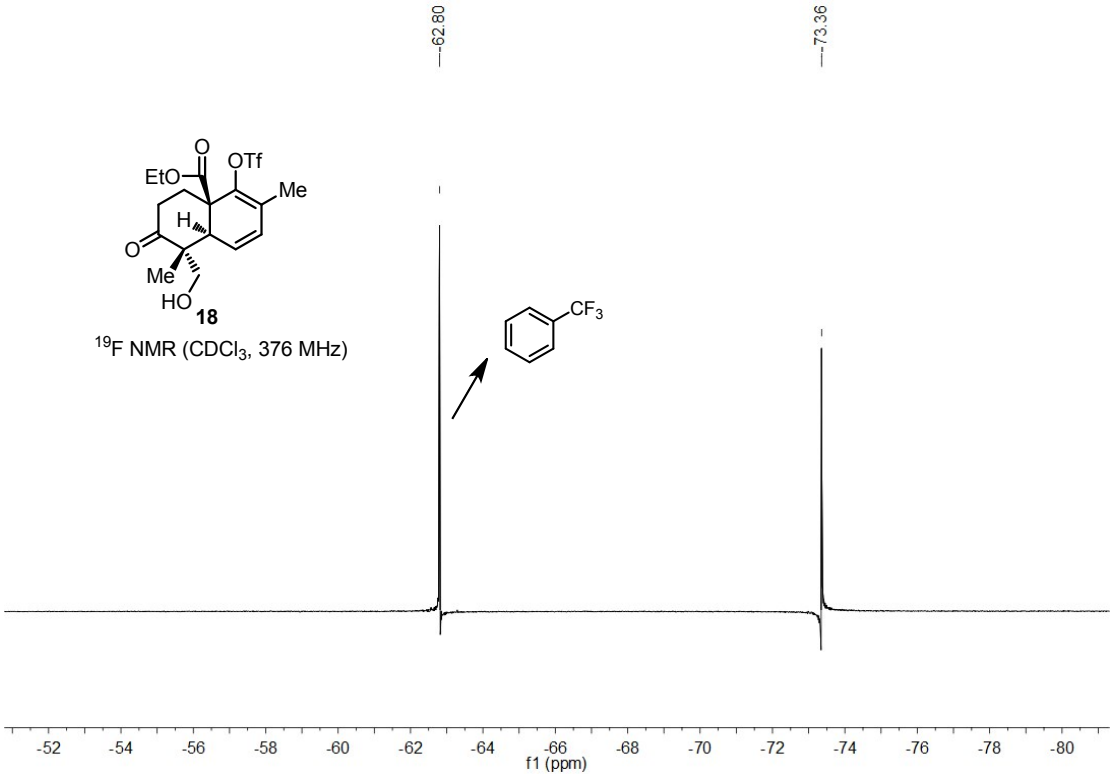


18

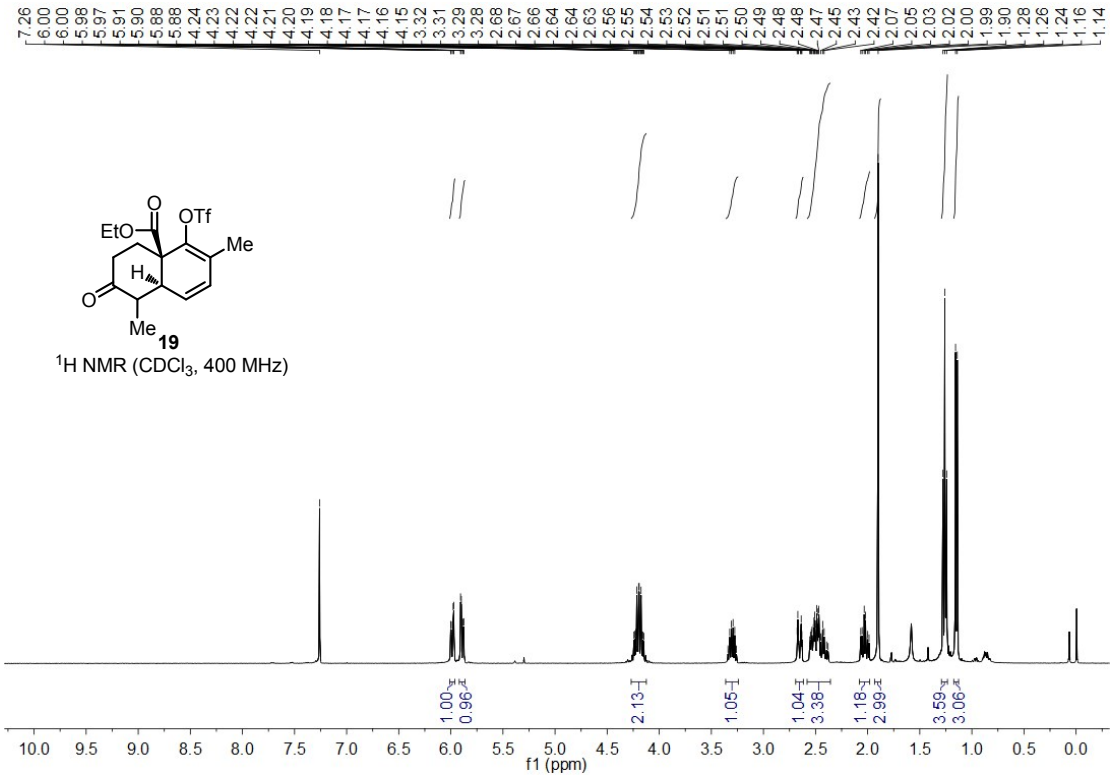
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

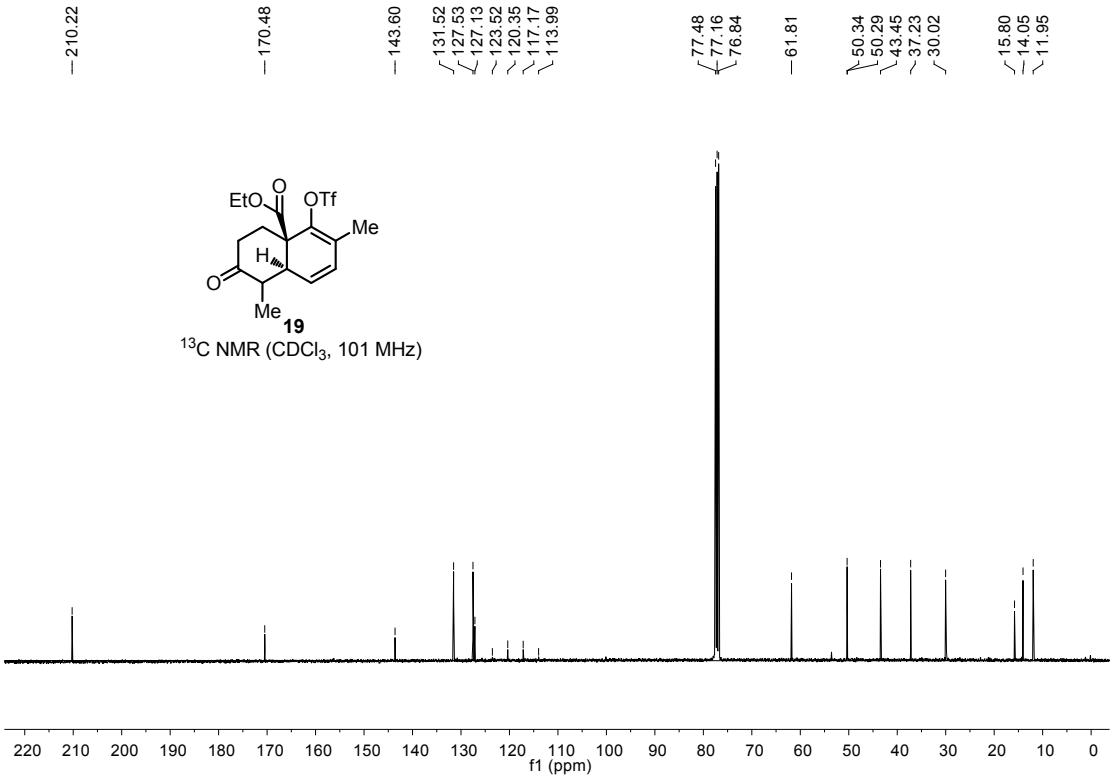


^{19}F NMR ($CDCl_3$, 376 MHz)



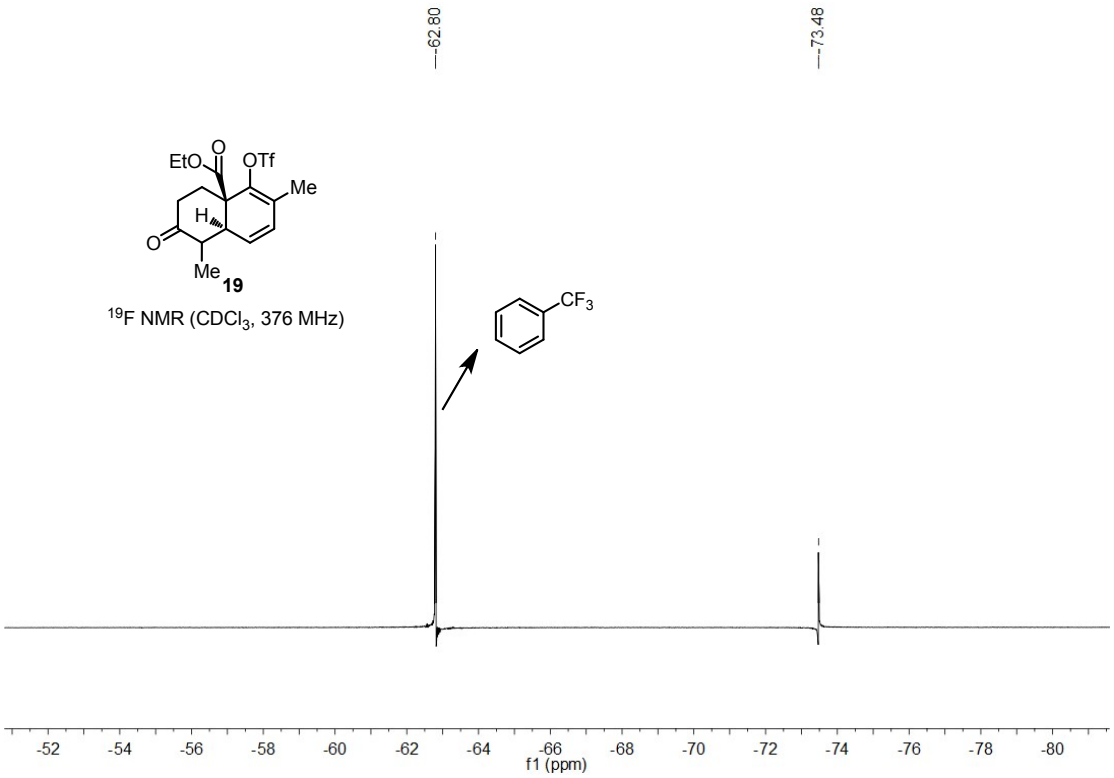
19

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

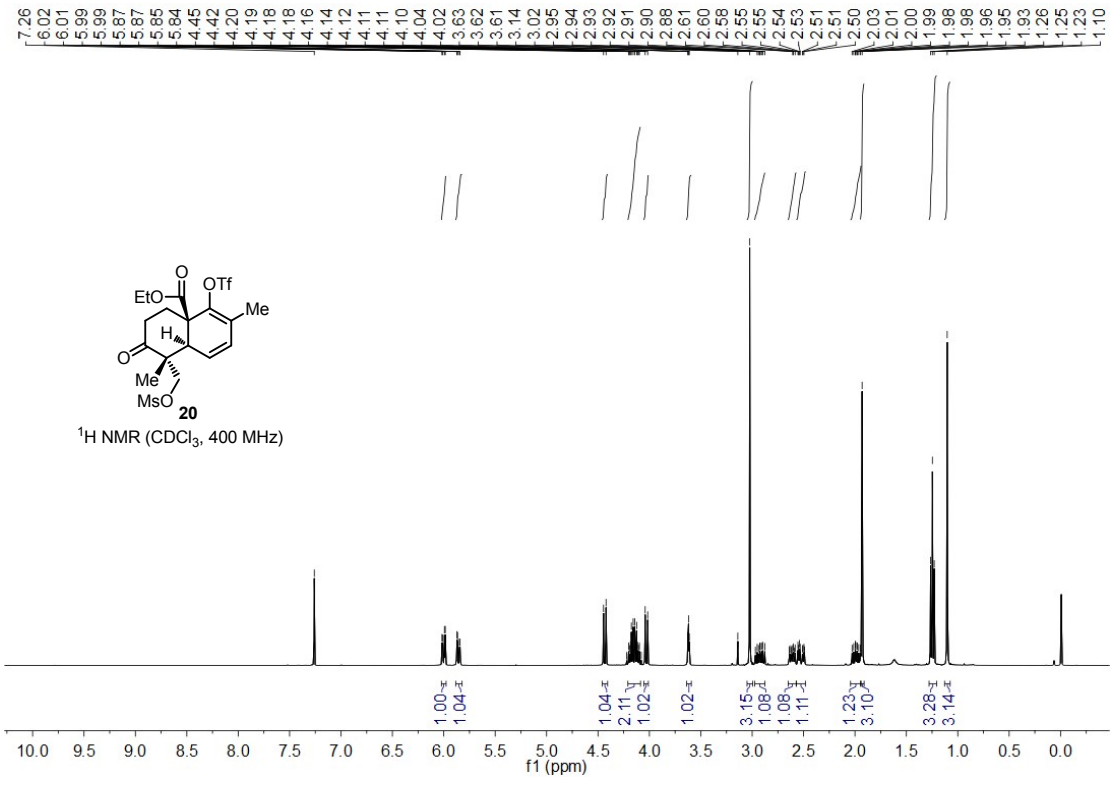


19

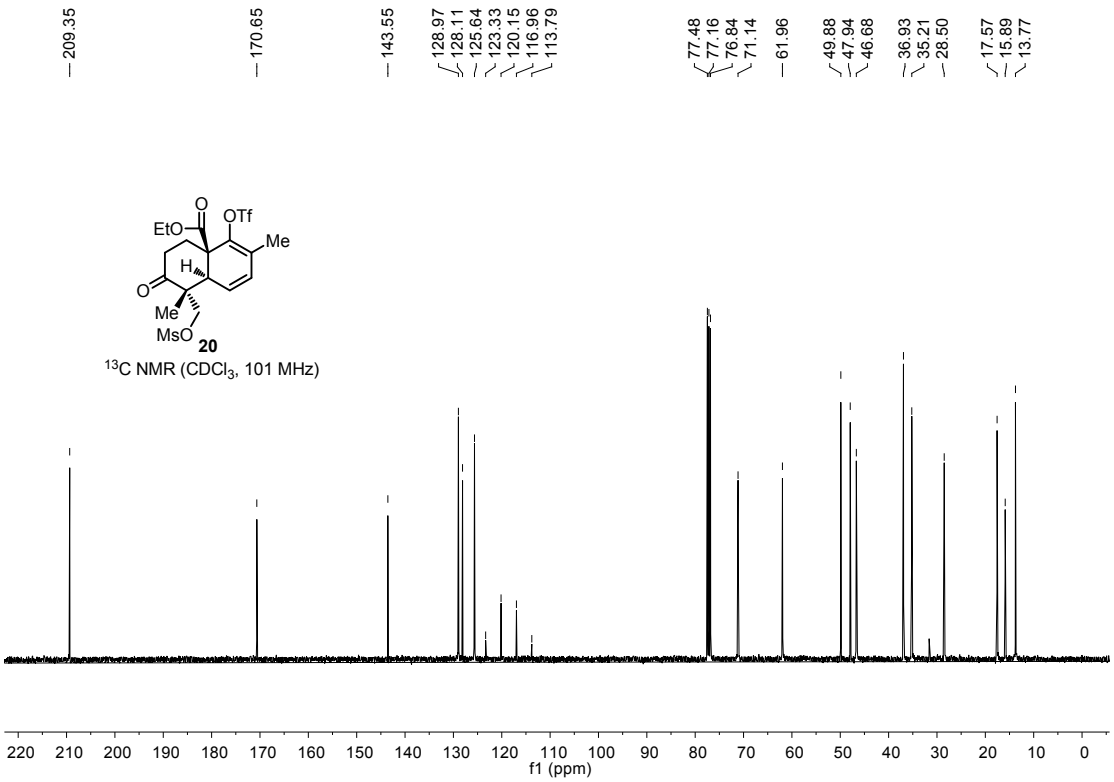
^{13}C NMR ($CDCl_3$, 101 MHz)



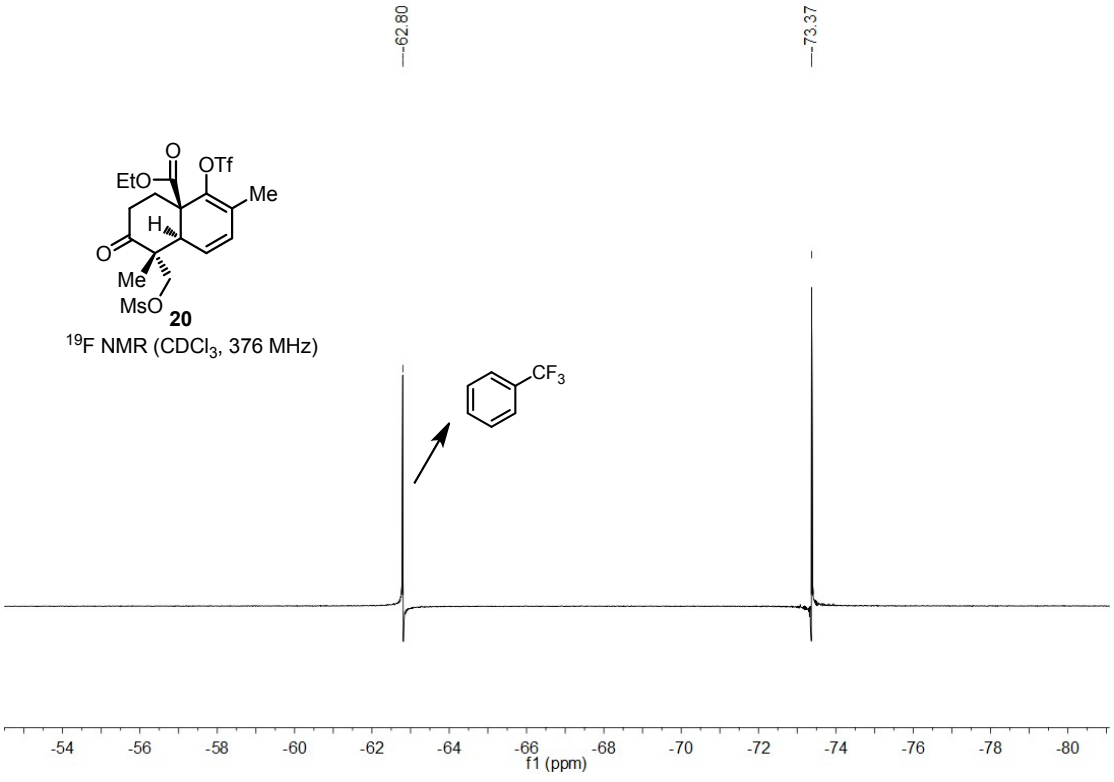
^{19}F NMR ($CDCl_3$, 376 MHz)



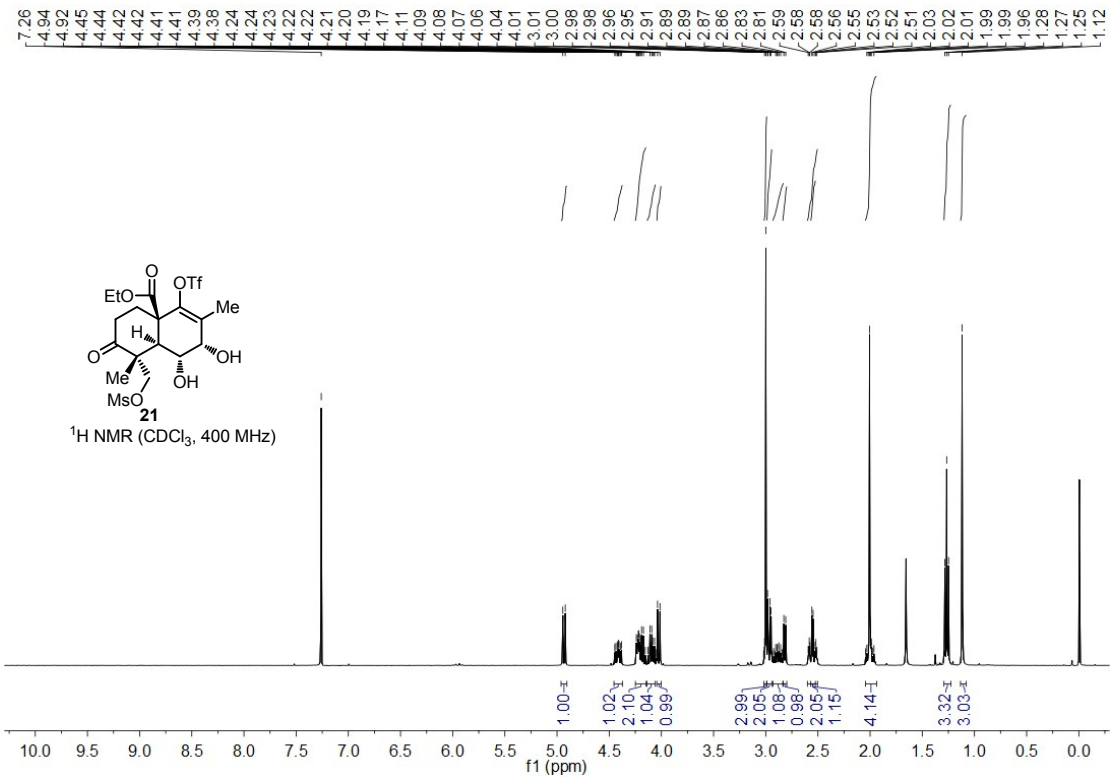
^{1}H NMR ($CDCl_3$, 400 MHz)

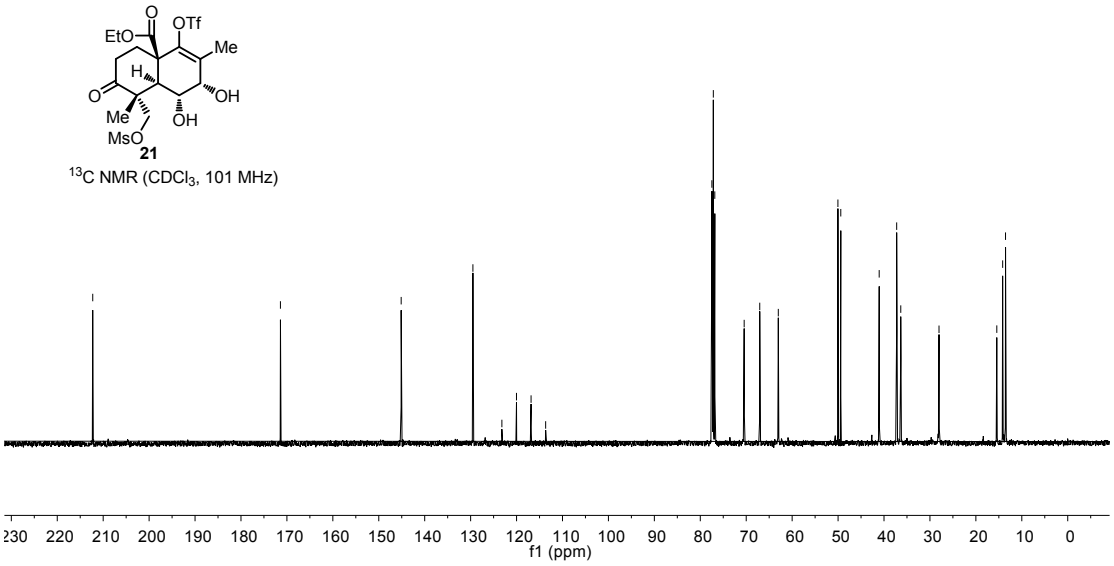


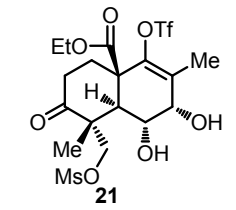
^{13}C NMR ($CDCl_3$, 101 MHz)



^{19}F NMR ($CDCl_3$, 376 MHz)

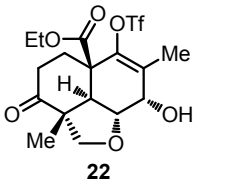

EtO
OTf
Me
H
O
OH
Me
OH
MsO
21
1H NMR (CDCl3, 400 MHz)
f1 (ppm)


EtO
OTf
Me
H
O
OH
Me
OH
MsO
21
13C NMR (CDCl3, 101 MHz)
f1 (ppm)



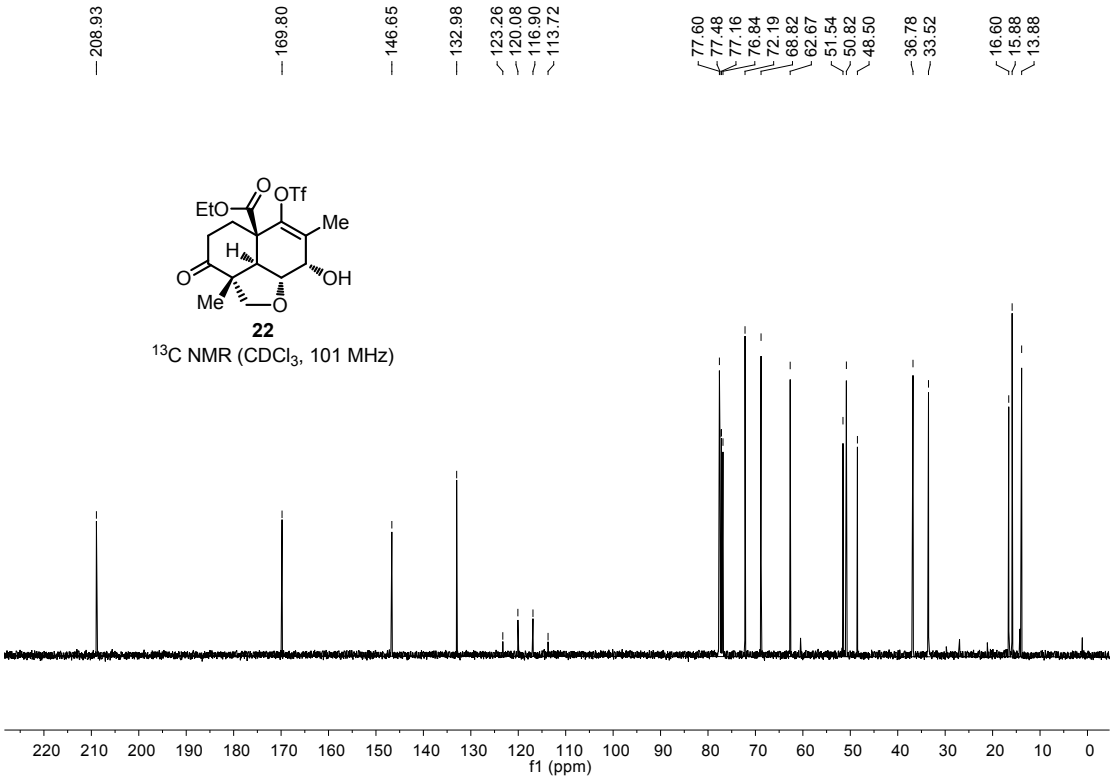
21

^{19}F NMR ($CDCl_3$, 376 MHz)



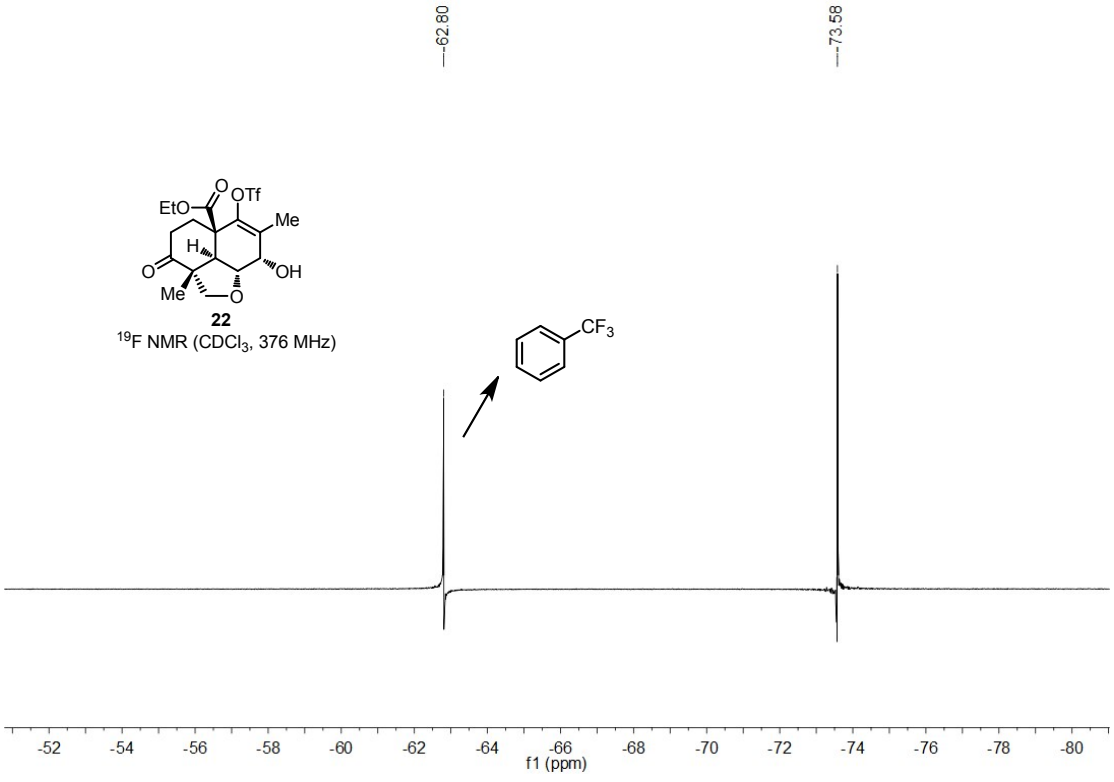
22

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



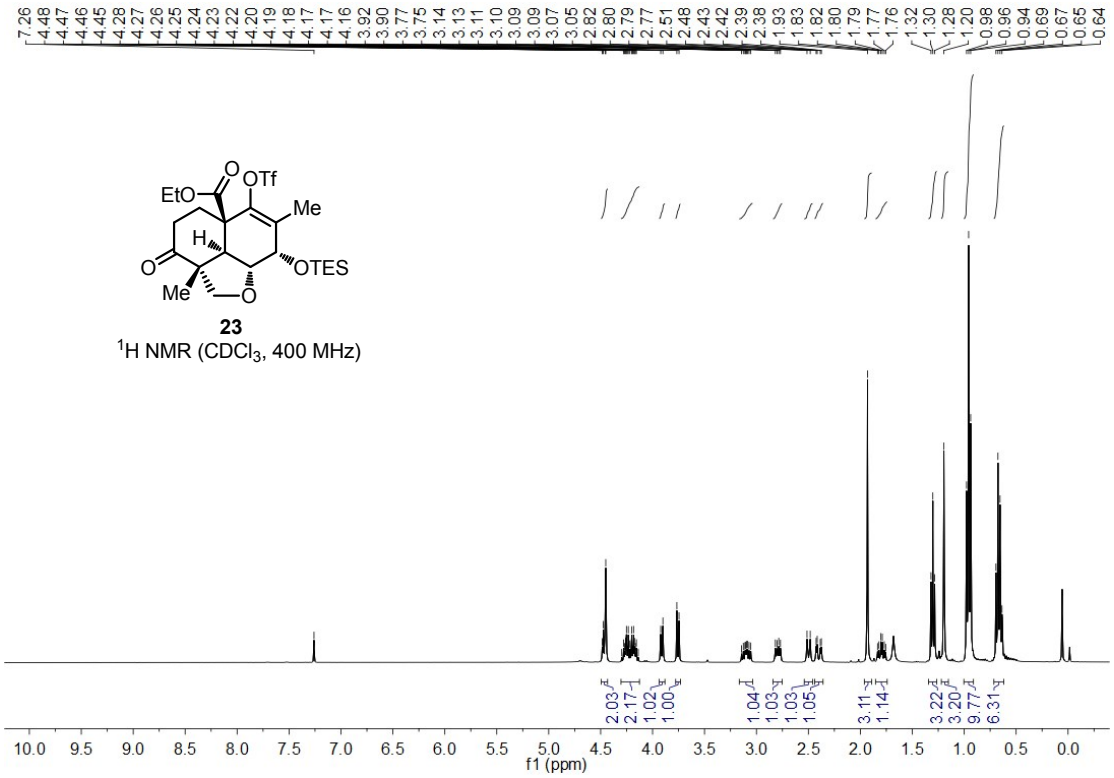
22

^{13}C NMR ($CDCl_3$, 101 MHz)



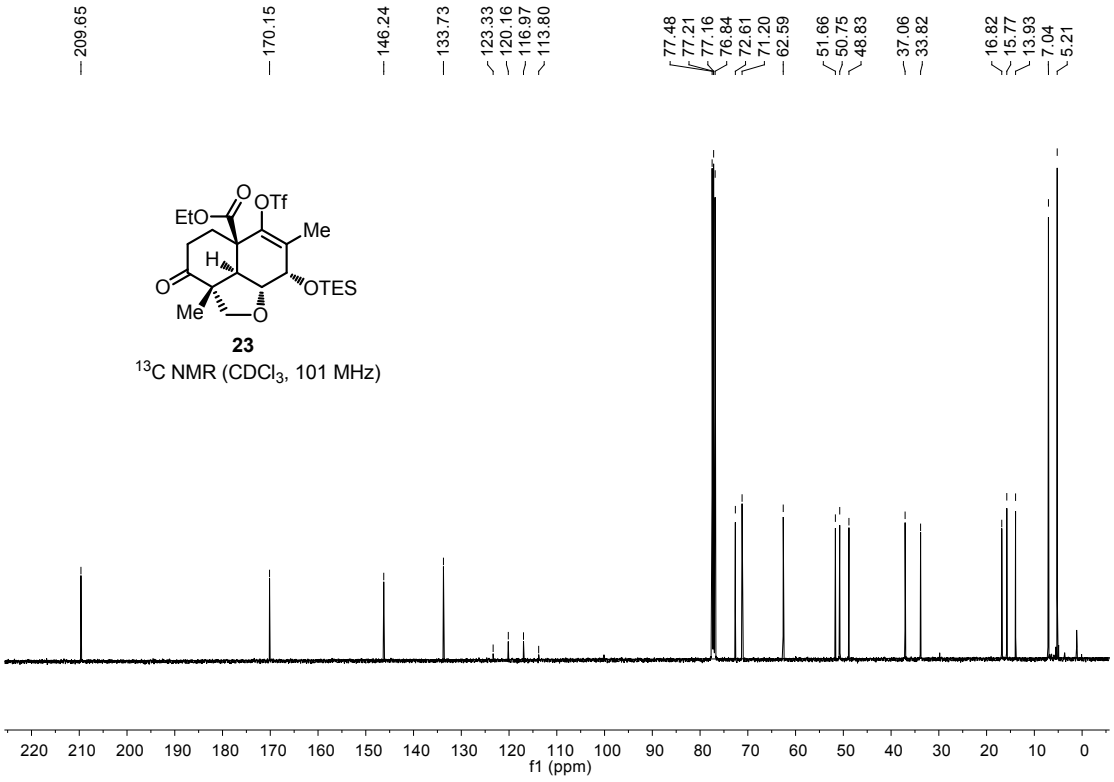
22

^{19}F NMR ($CDCl_3$, 376 MHz)



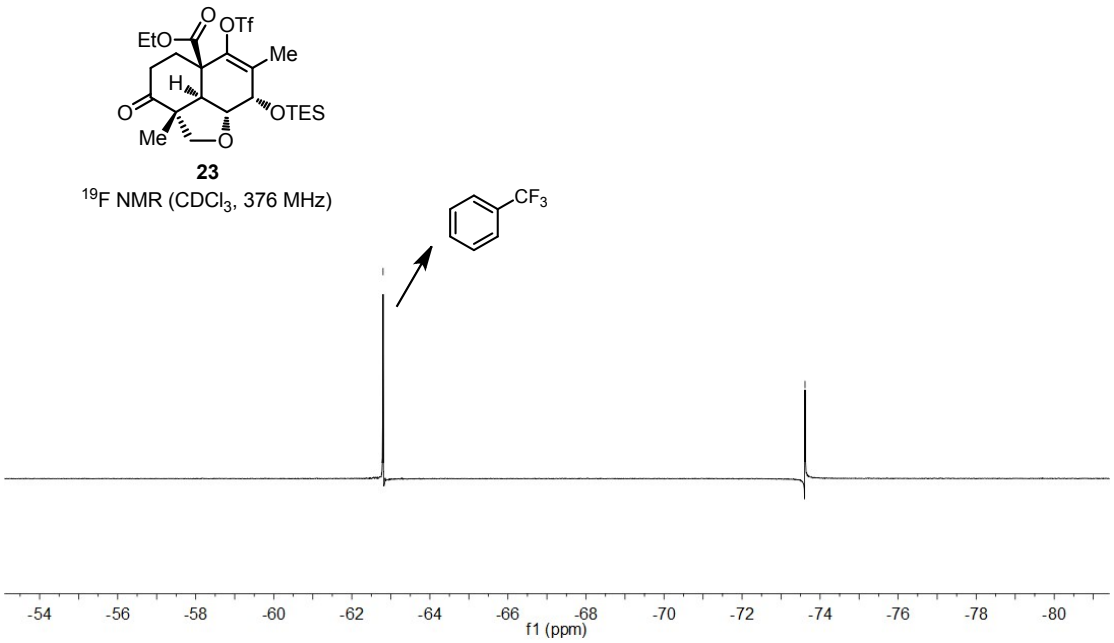
23

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



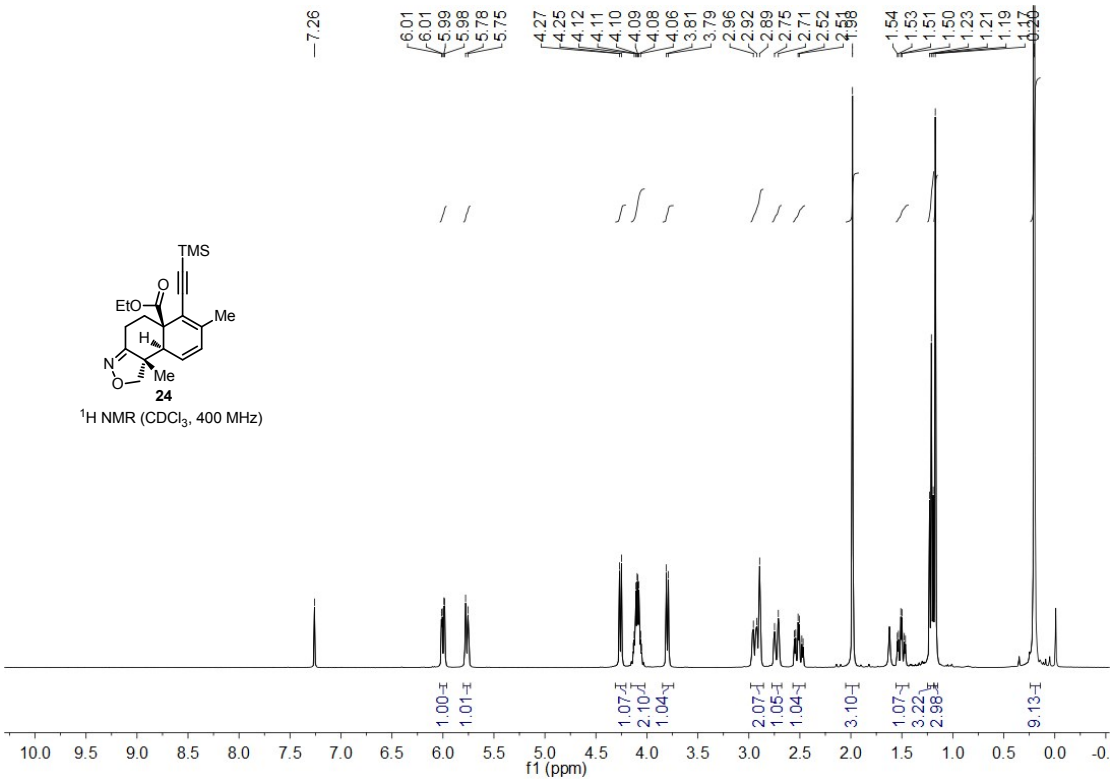
23

^{13}C NMR ($CDCl_3$, 101 MHz)



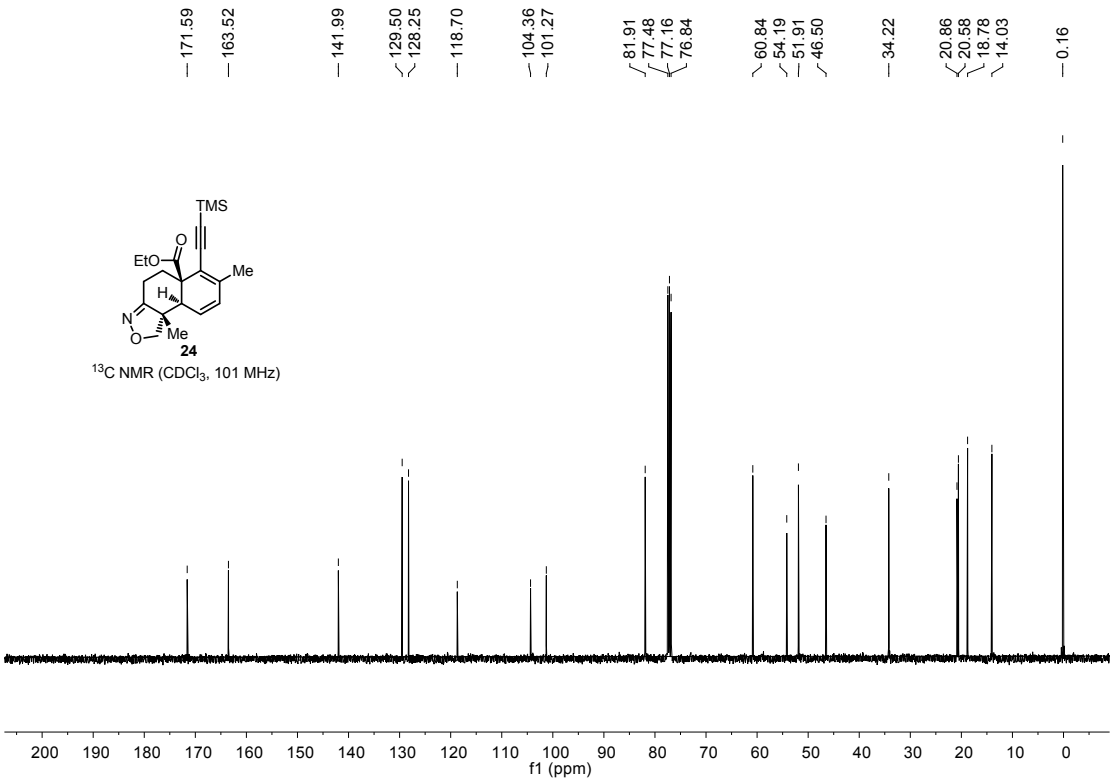
23

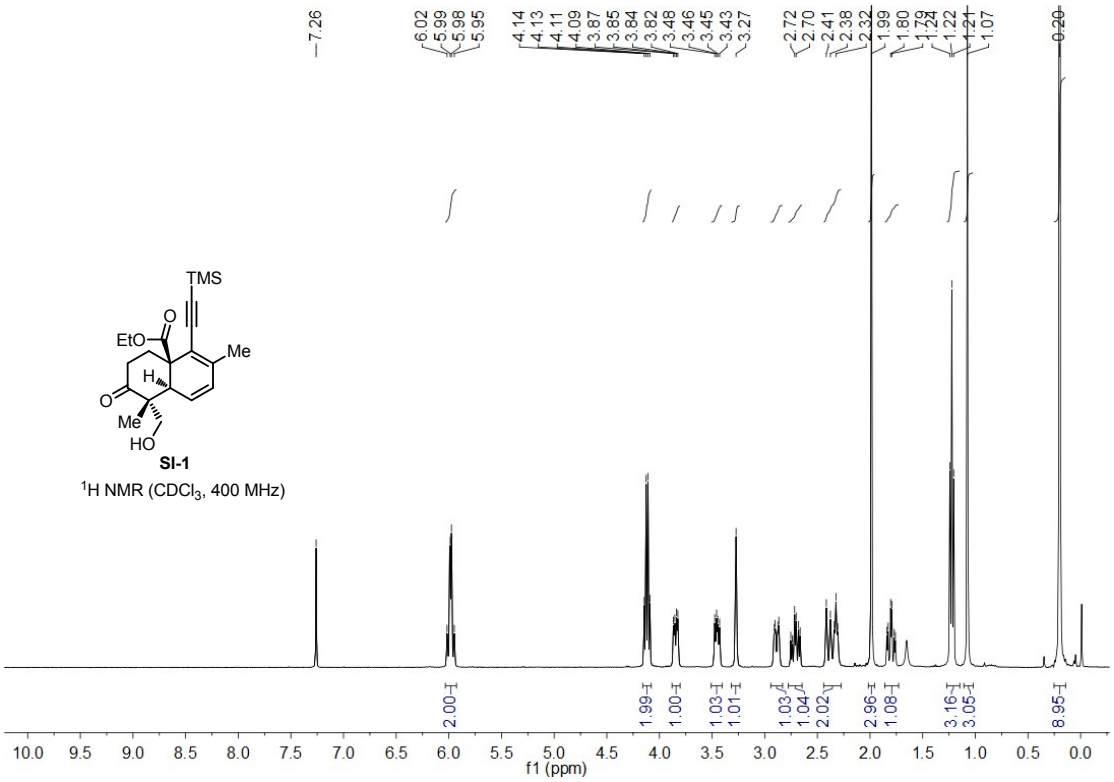
^{19}F NMR ($CDCl_3$, 376 MHz)

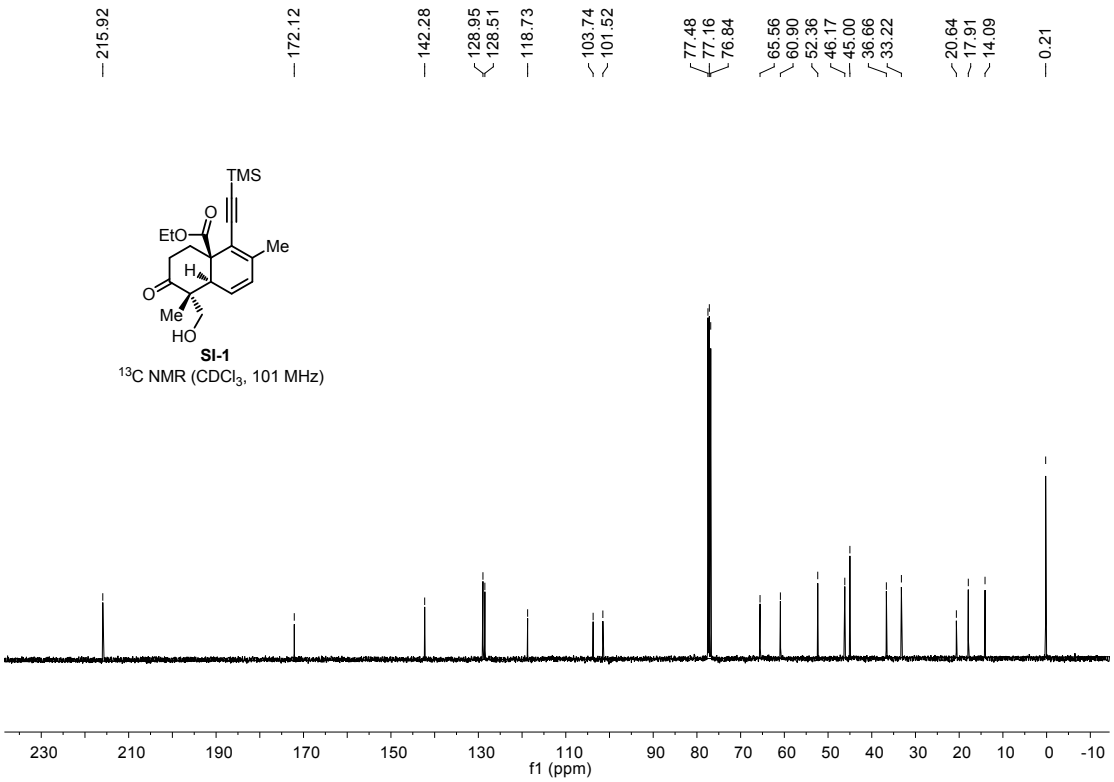


24

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

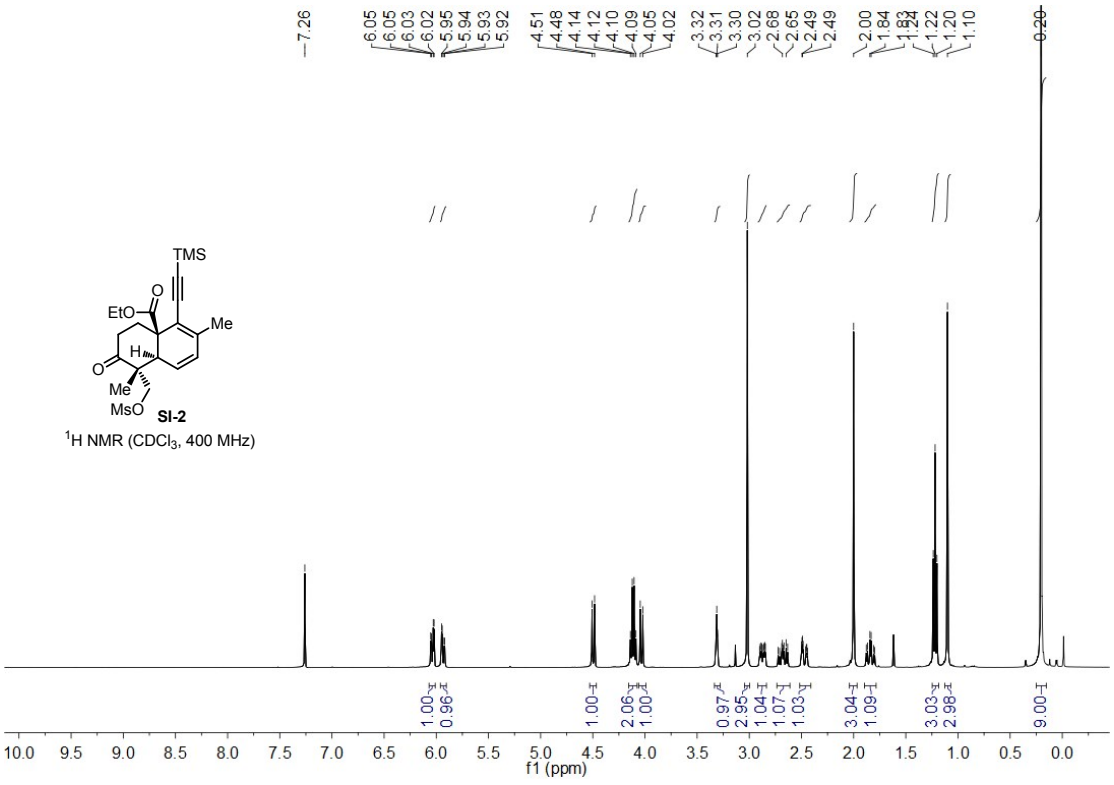

171.59
163.52
141.99
129.50
128.25
118.70
104.36
101.27
81.91
77.48
77.16
76.84
60.84
54.19
51.91
46.50
34.22
20.86
20.58
18.78
14.03
0.16
TMS
EtO
O
Me
H
N
O
Me
24
13C NMR (CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
6.02
5.99
5.98
5.95
4.14
4.13
4.11
4.09
3.87
3.85
3.84
3.82
3.48
3.46
3.45
3.43
3.27
2.72
2.70
2.41
2.38
2.32
1.99
1.80
1.79
1.24
1.22
1.21
1.07
0.20
TMS
EtO
O
Me
H
O
Me
HO
SI-1
1H NMR (CDCl3, 400 MHz)
2.00
1.99
1.00
1.03
1.01
1.03
1.04
2.02
2.96
1.08
3.16
3.05
8.95
10.0 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)



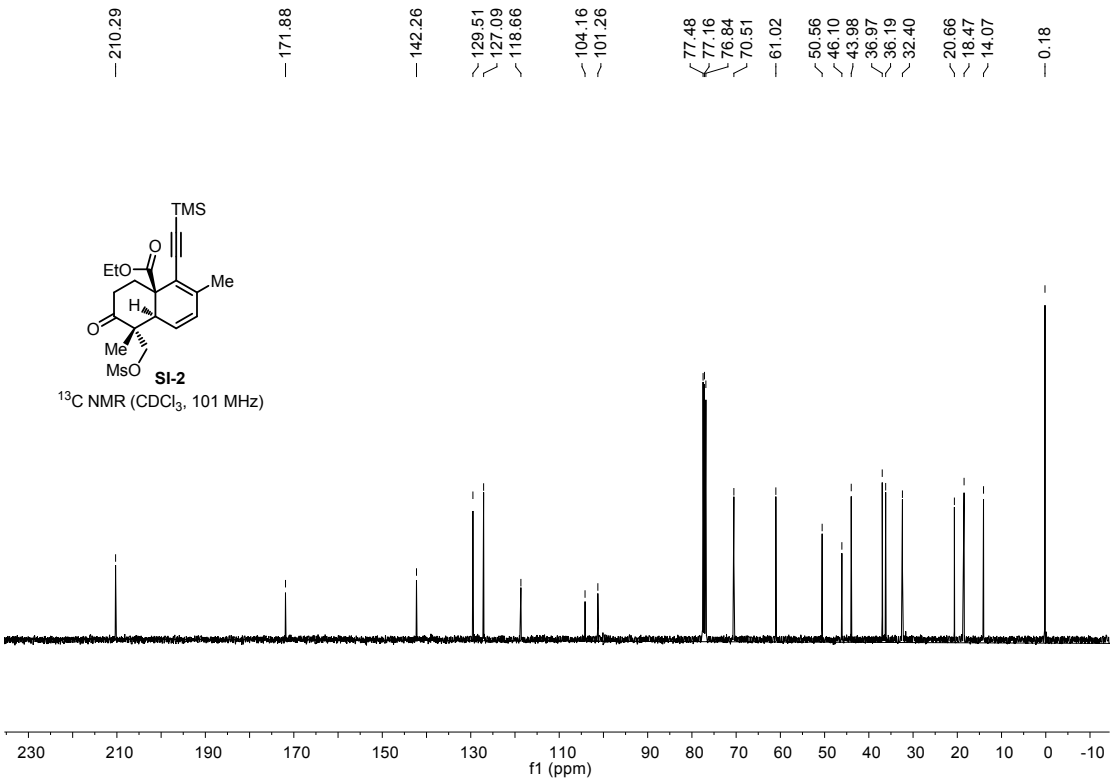
SI-1

^{13}C NMR ($CDCl_3$, 101 MHz)



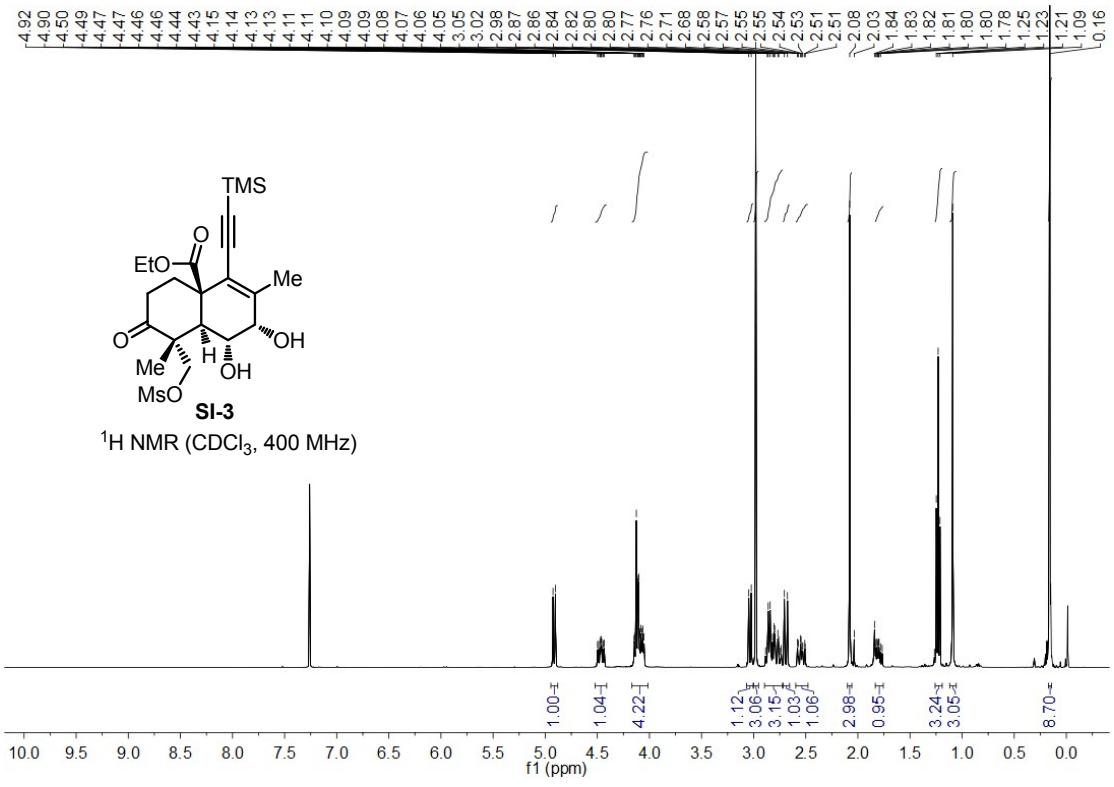
SI-2

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



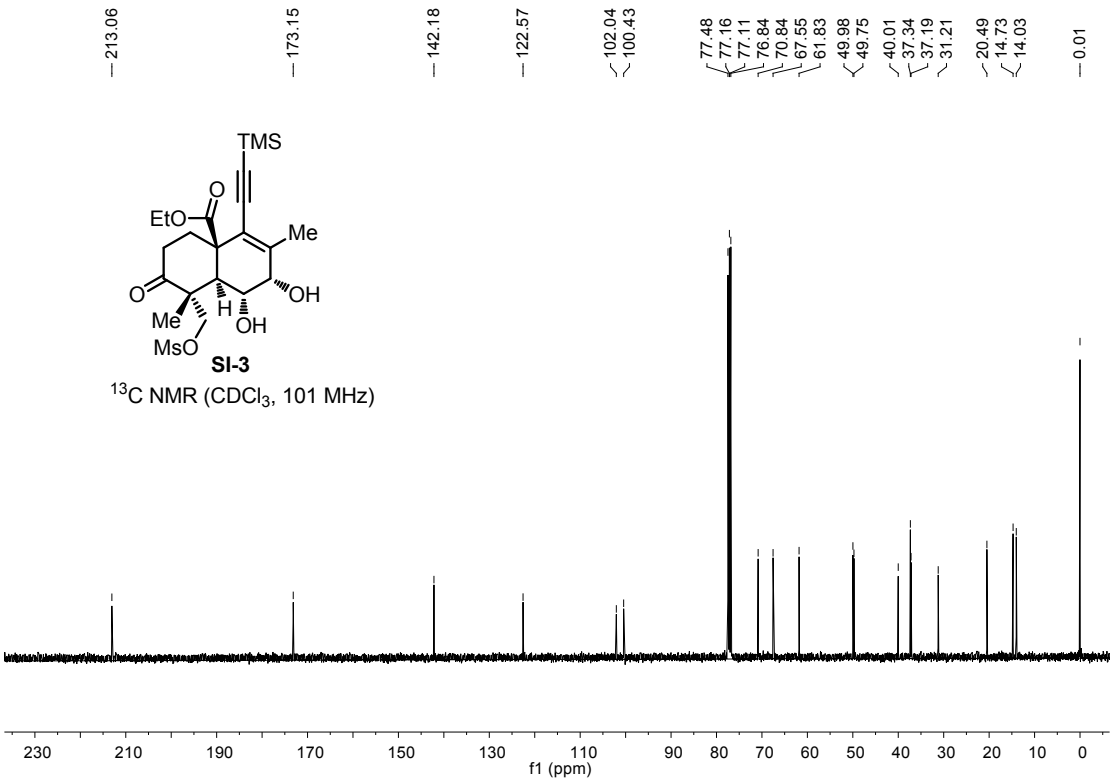
SI-2

^{13}C NMR ($CDCl_3$, 101 MHz)



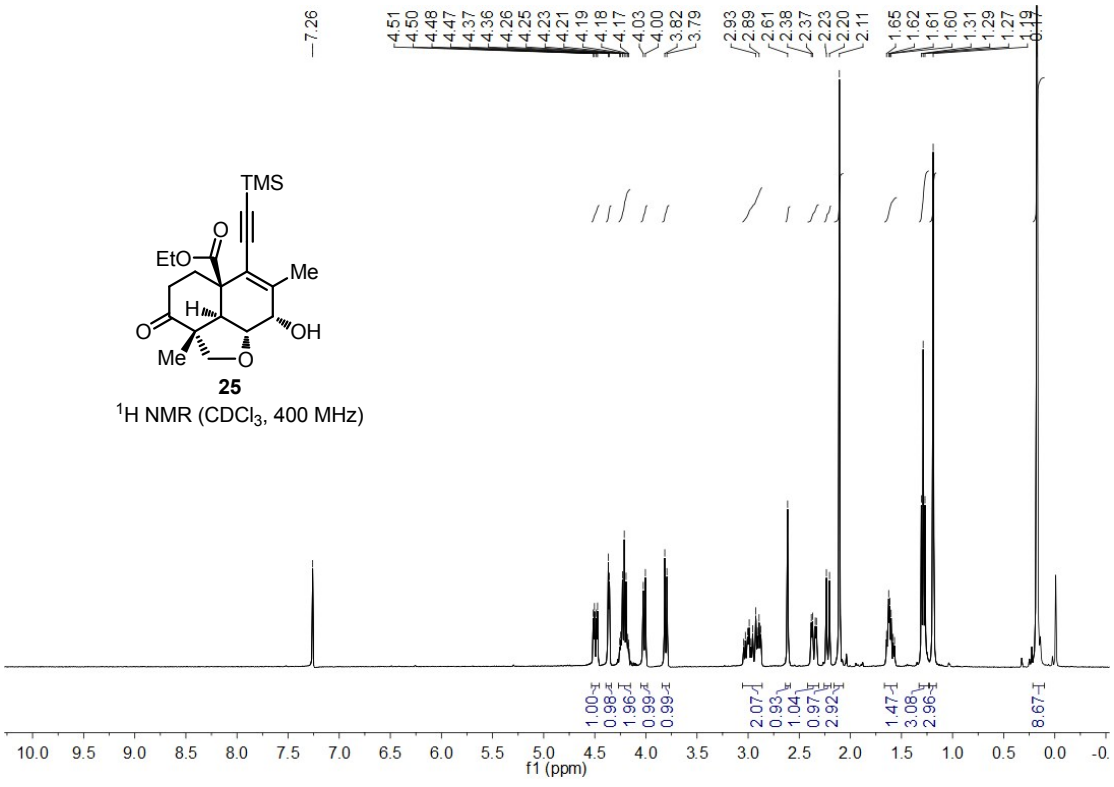
SI-3

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



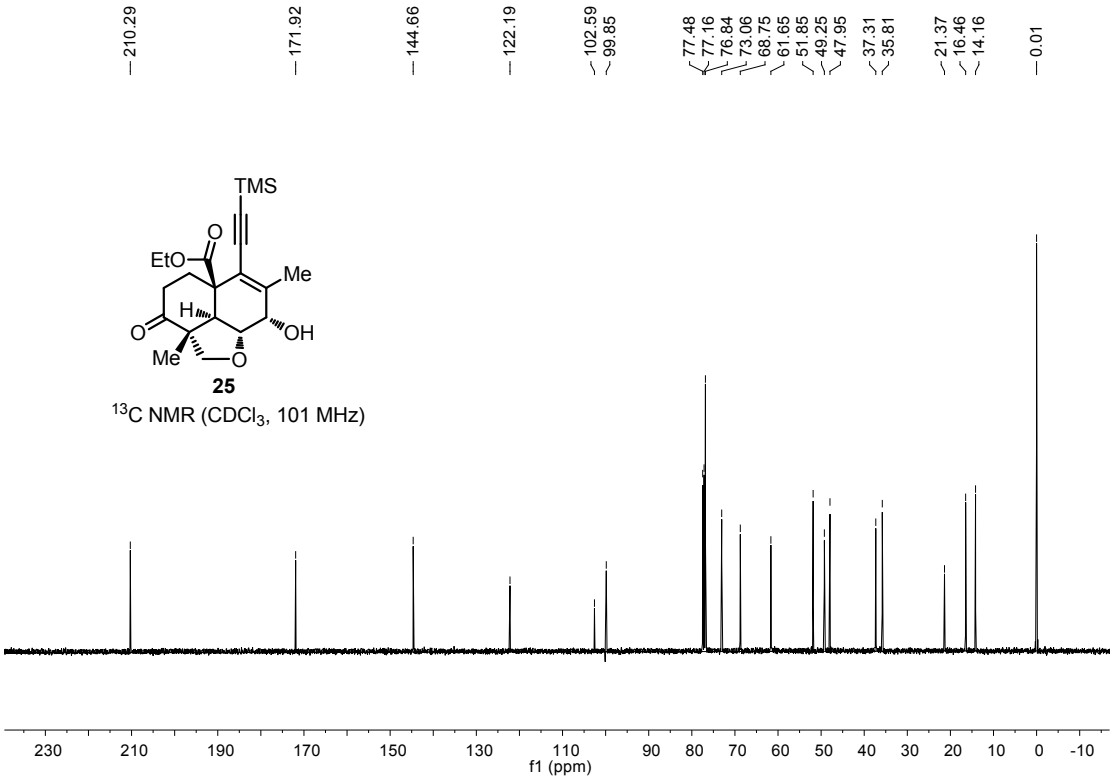
SI-3

^{13}C NMR ($CDCl_3$, 101 MHz)



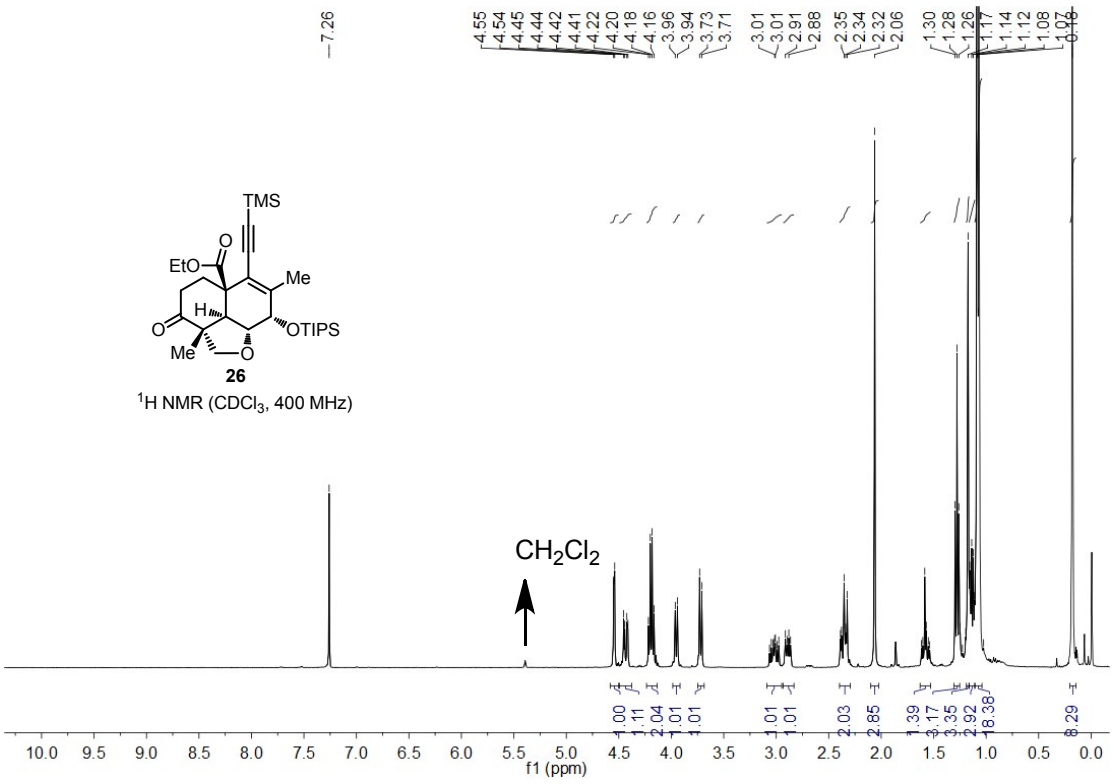
25

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



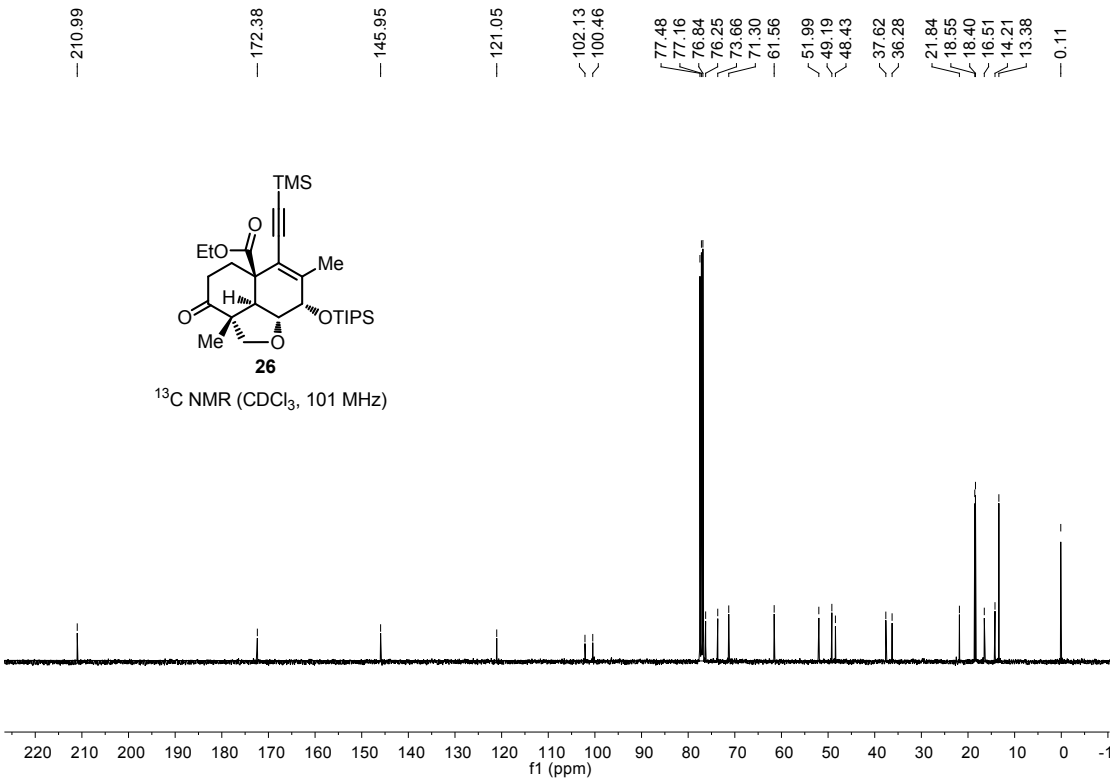
25

^{13}C NMR ($CDCl_3$, 101 MHz)



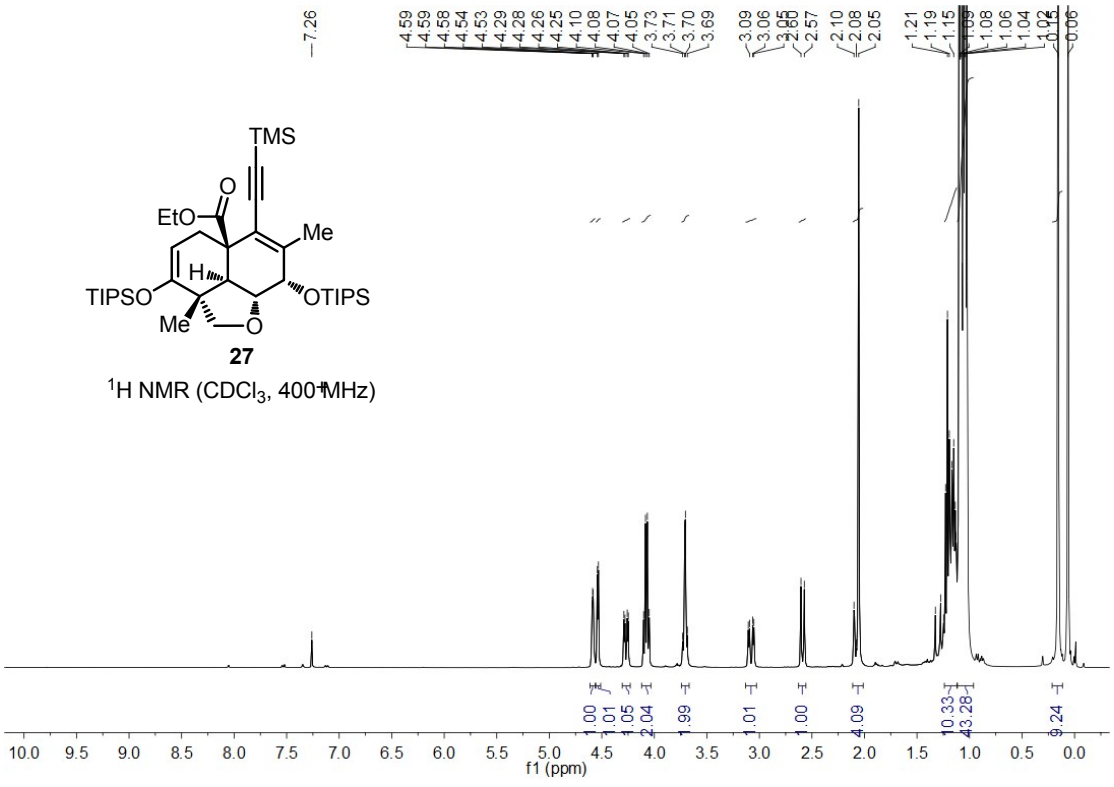
26

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



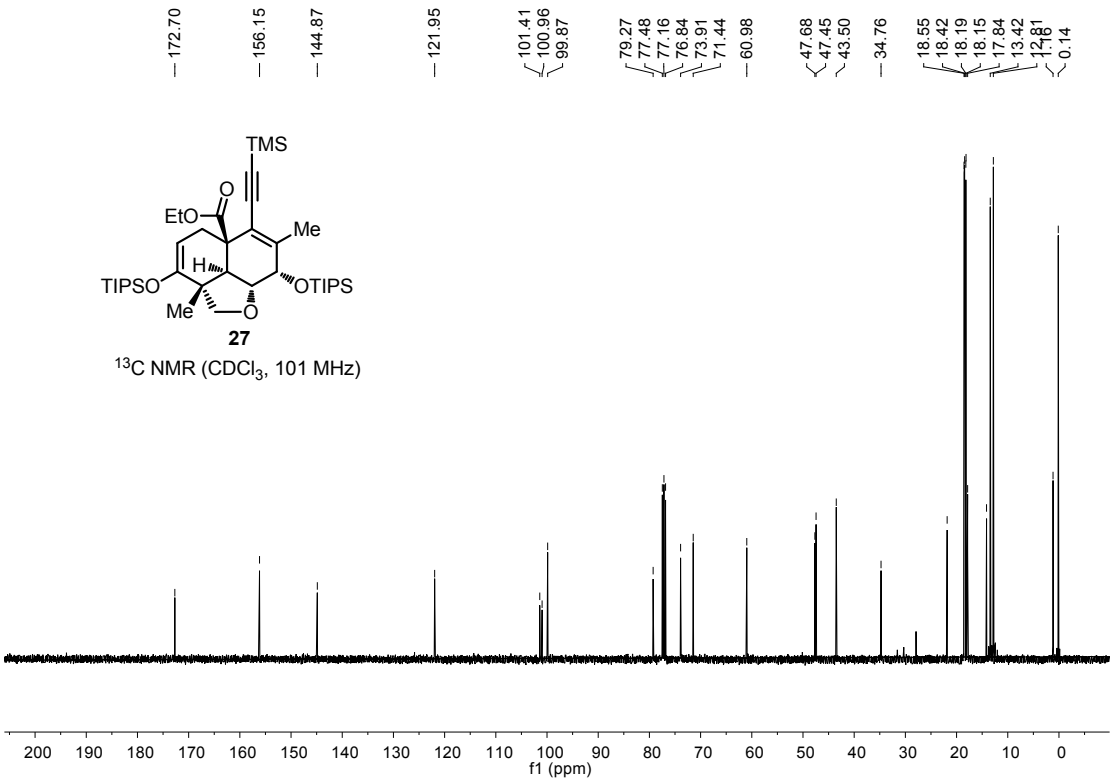
26

^{13}C NMR ($CDCl_3$, 101 MHz)



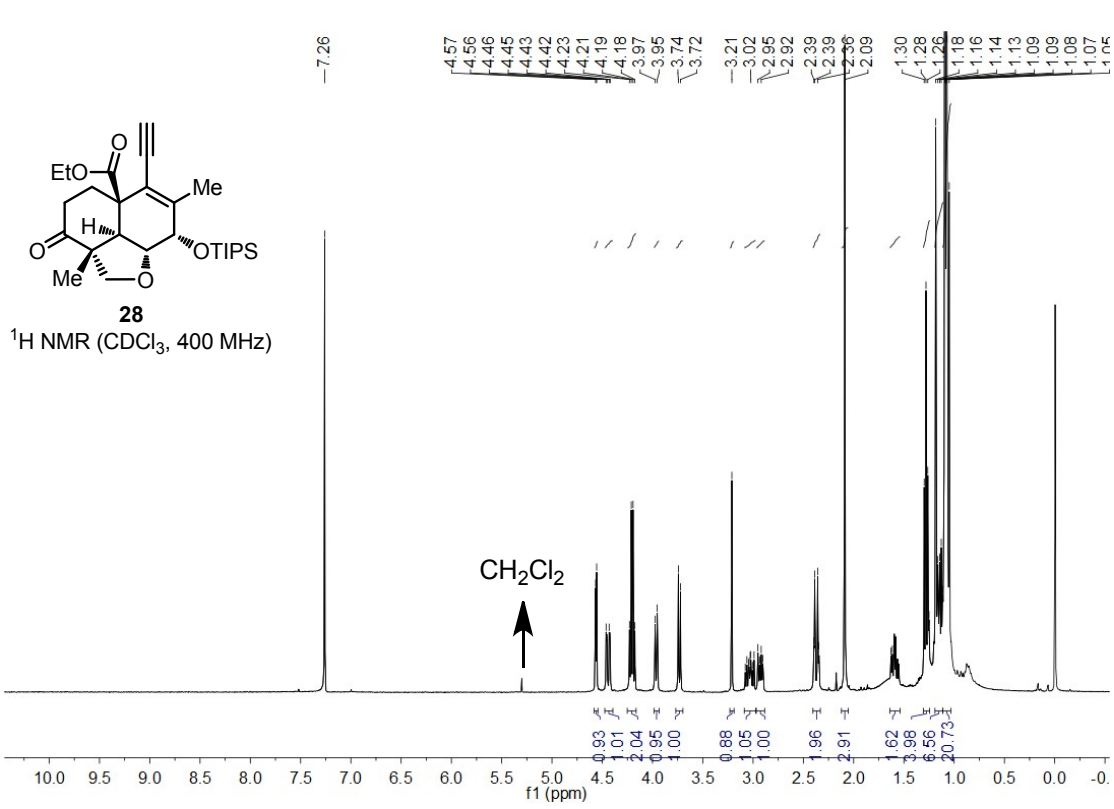
27

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



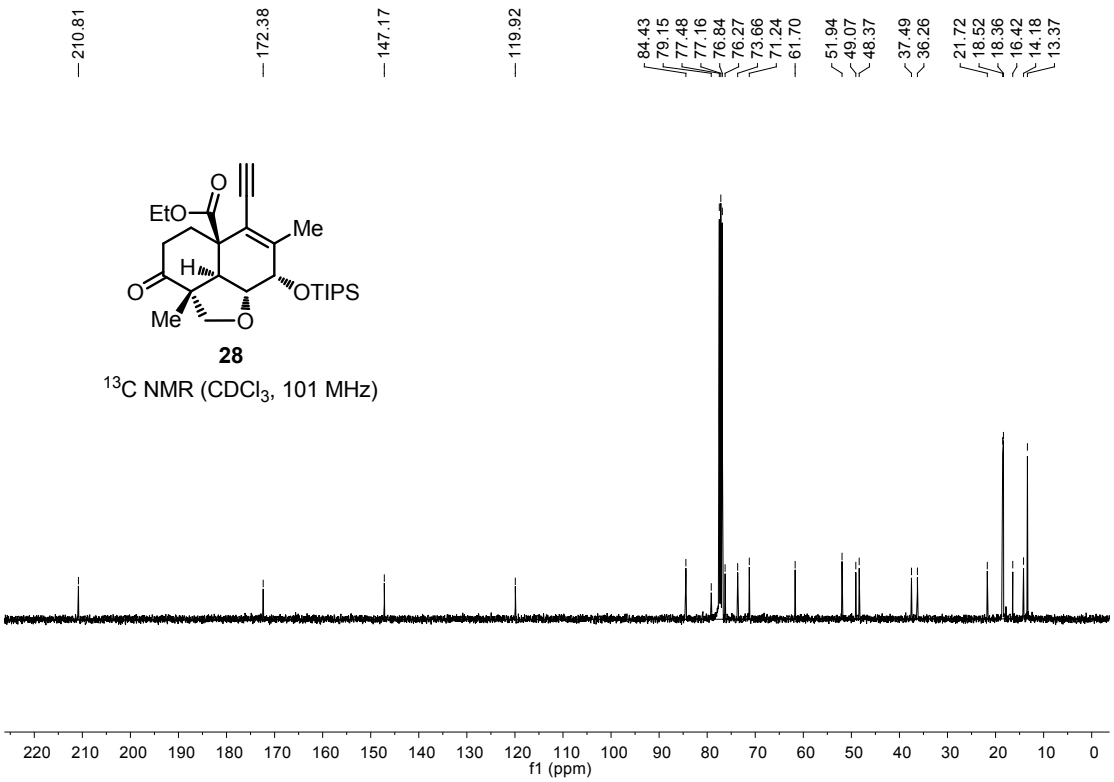
27

^{13}C NMR ($CDCl_3$, 101 MHz)



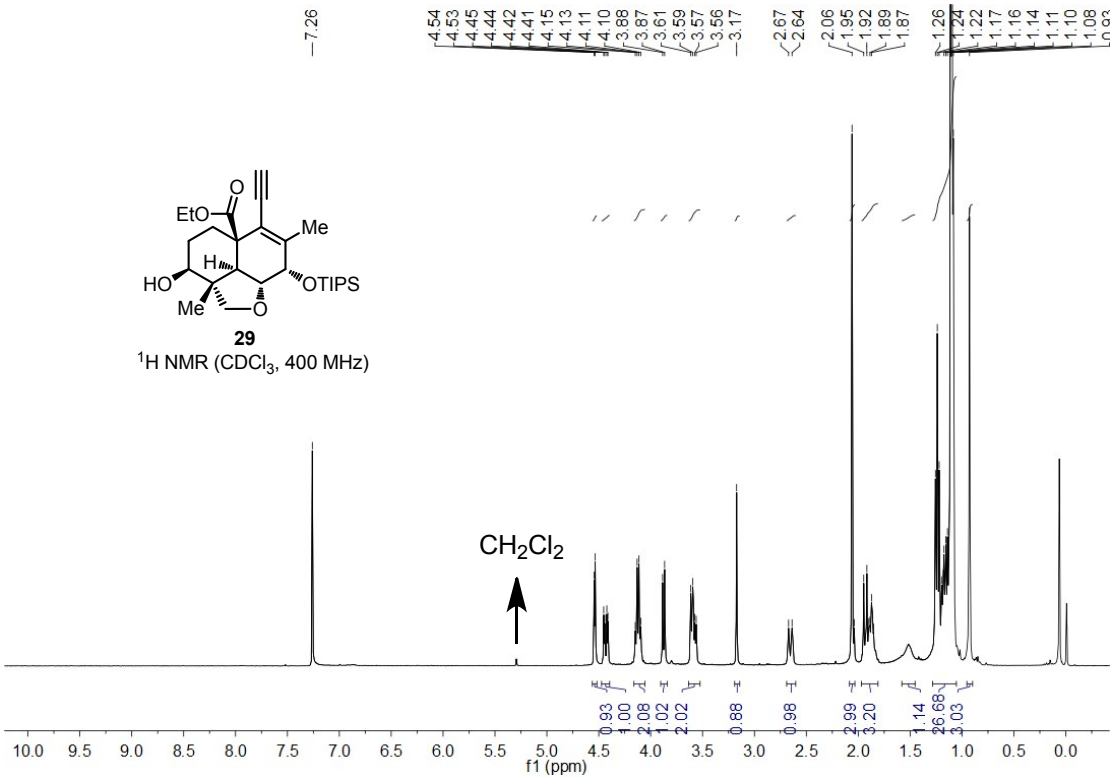
28

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



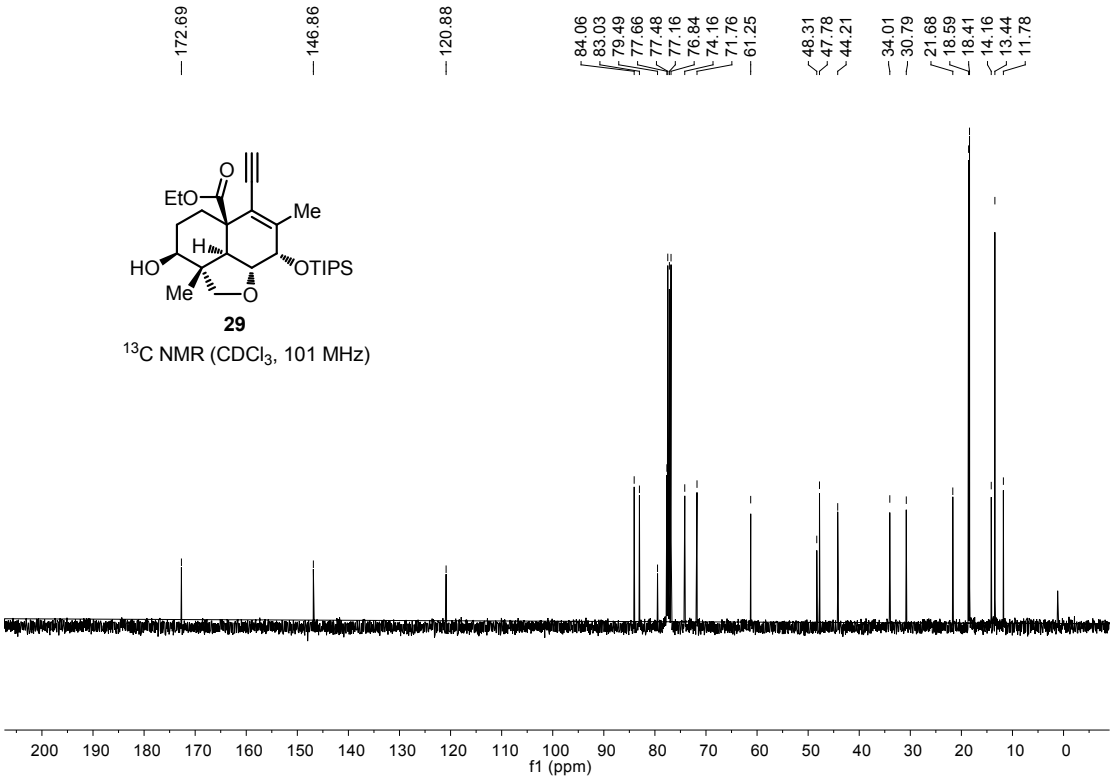
28

^{13}C NMR ($CDCl_3$, 101 MHz)



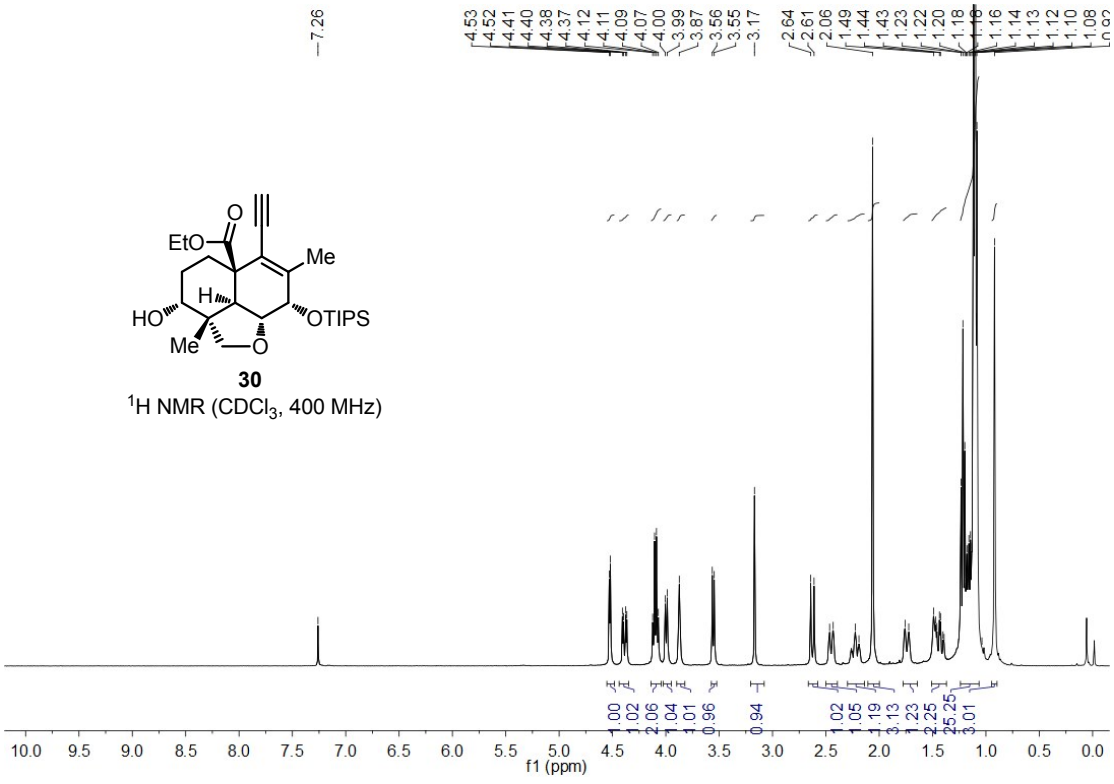
29

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



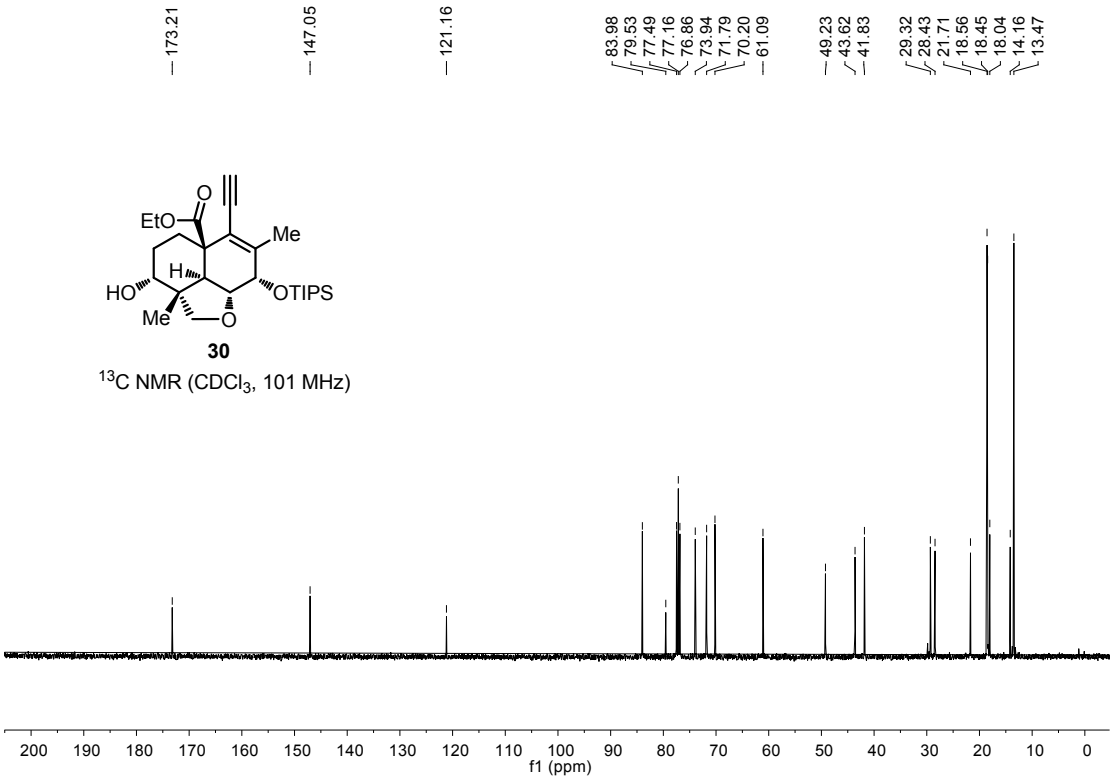
29

^{13}C NMR ($CDCl_3$, 101 MHz)



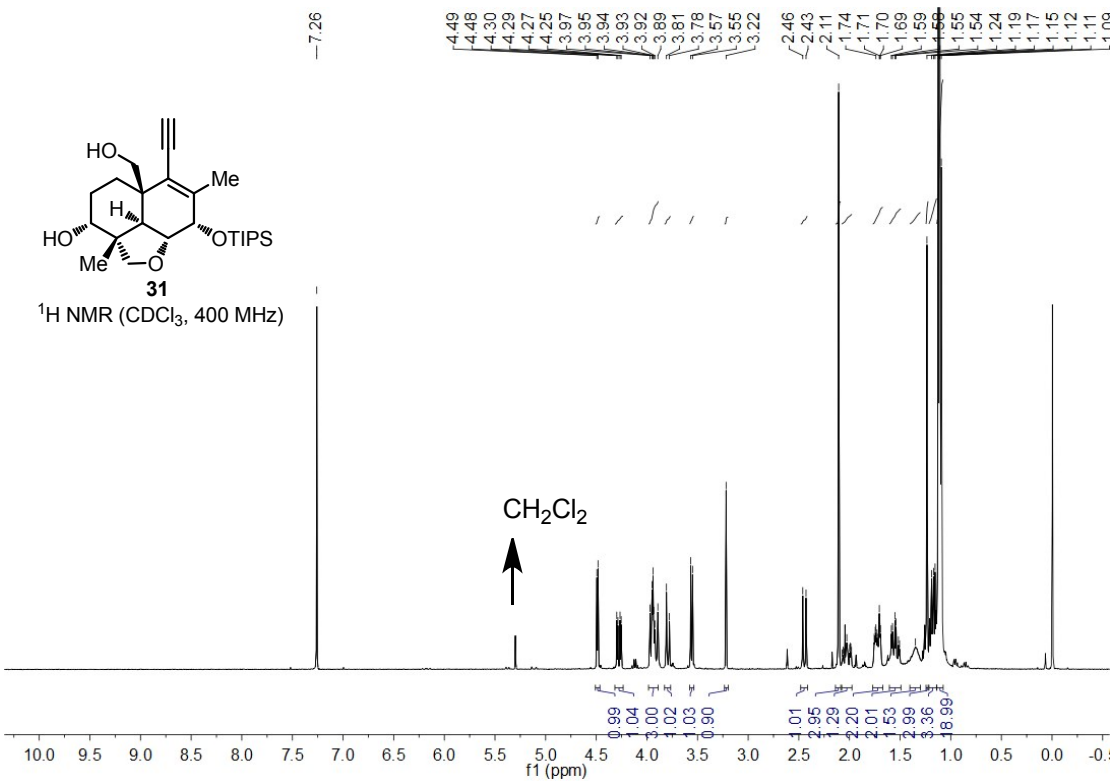
30

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



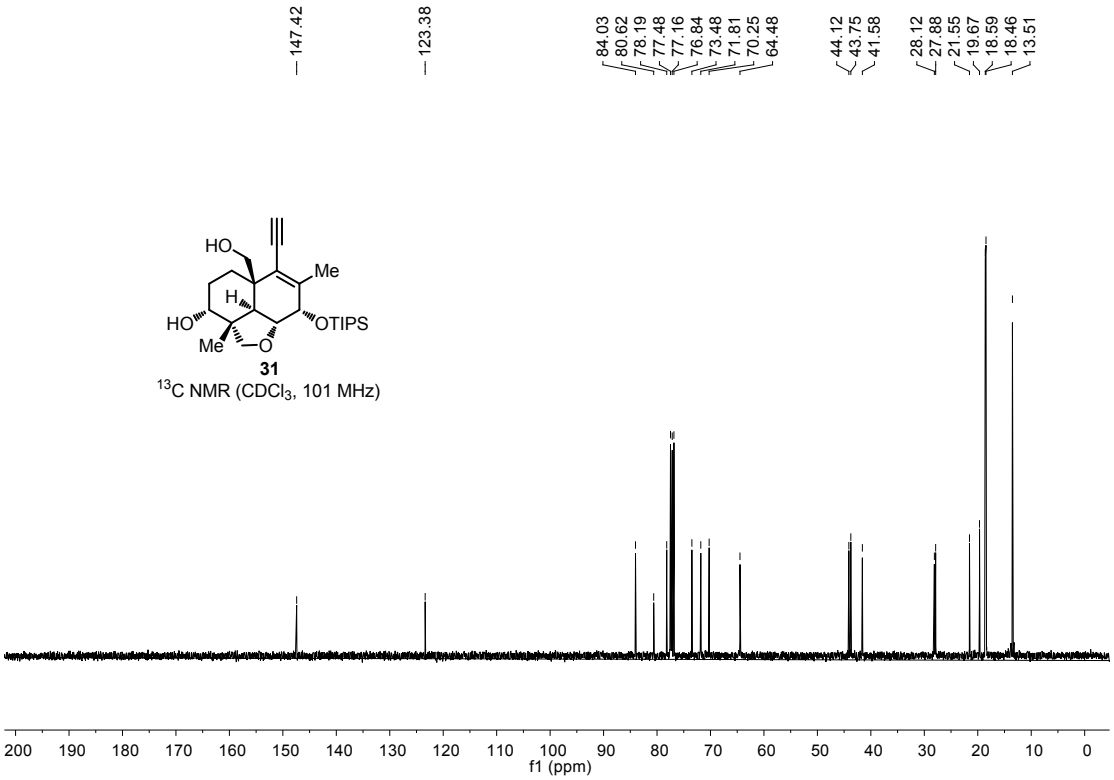
30

^{13}C NMR ($CDCl_3$, 101 MHz)



31

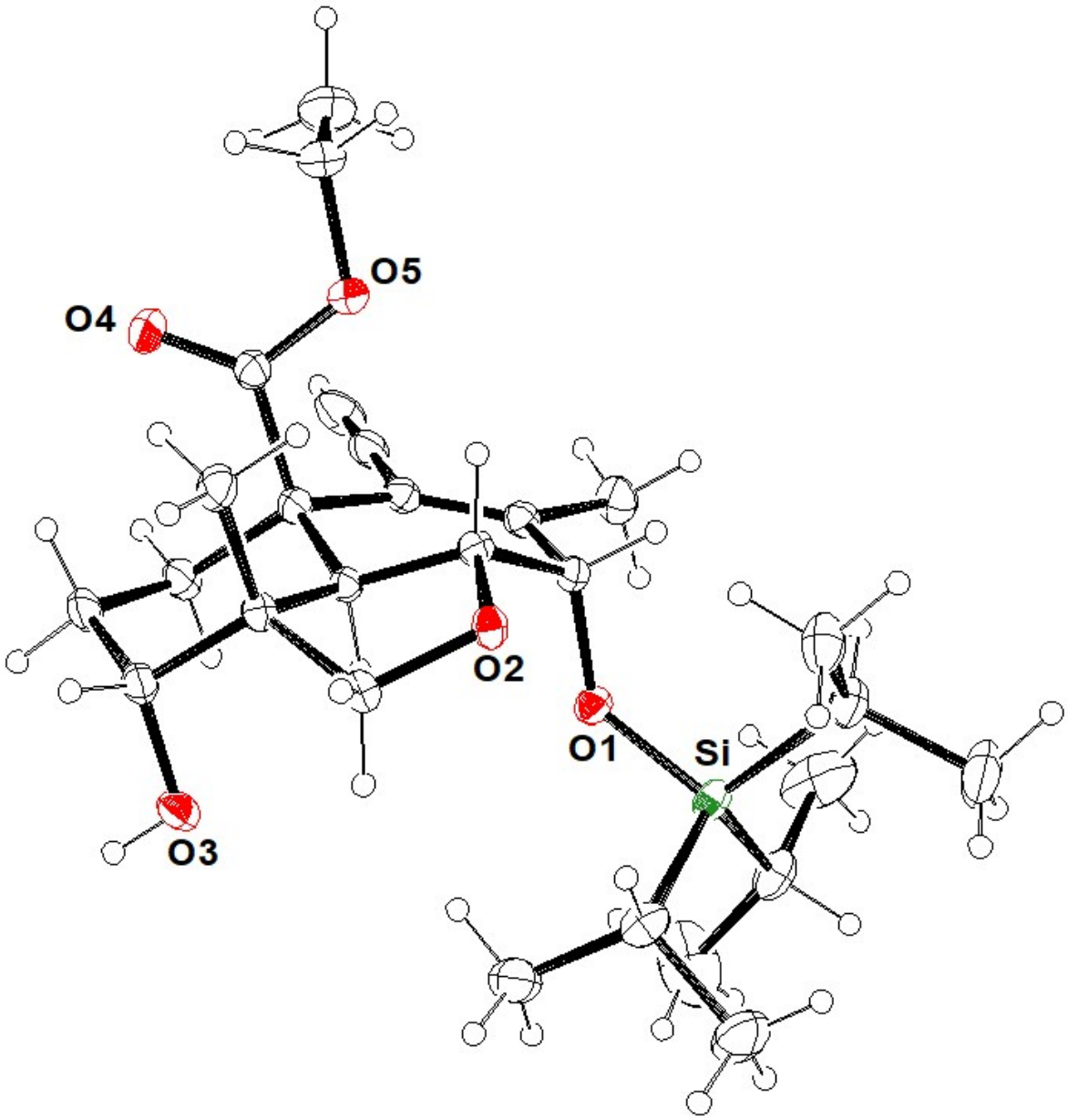
^{1}H NMR ($CDCl_3$, 400 MHz)



31

^{13}C NMR ($CDCl_3$, 101 MHz)

Crystallographic Data of Compound 30



ORTEP of **30** (ellipsoid contour probability = 15%)
(CCDC 1916175)

Single crystal cultivation:

In a 10 mL test tube, ~50 mg pure compound **30** was dissolved in 1 mL DCM, then 5 mL hexane was carefully added to get a biphase mixture, the tube mouth was covered by sealing film. The mixture was left in a place without disturbance to let the solvent volatilize, a needle-like crystal was obatined within 3~5 days.

Crystal data:

Empirical formula	$C_{27}\ H_{44}\ O_5\ Si$
Formula weight	476.71
Temperature/K	113(2)
Wavelength	0.71073
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.5716(19) A alpha = 90 deg. b = 12.164(2) A beta = 90 deg. c = 23.632(5) A gamma = 90 deg.
Volume/$Å^3$	2751.4(9)
Z, $\rho_{calc}g/cm^3$	4, 1.151
μ/mm^{-1}	0.118
F(000)	1040
Crystal size/mm^3	0.200 ×0.180 ×0.120
2Θ range for data collection/°	1.723 to 27.880
Index ranges	-12<=h<=11, -15<=k<=15, -31<=l<=23
Reflections collected	27842
Independent reflections	14214 [R_{int} = 0.0212, R_{sigma} = 0.0130]
Data/restraints/parameters	6559 / 0 / 309
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0519, wR_2 = 0.1260
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1333
Largest diff. peak/hole / e $Å^{-3}$	0.204/-0.233
Flack parameter	0.09(7)