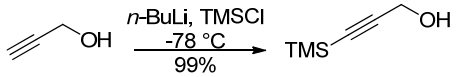
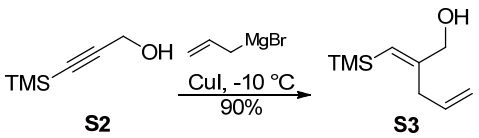
General Information: All reactions were performed using flame-dried glassware under an atmosphere of nitrogen with dry solvents, unless otherwise stated. Dry tetrahydrofuran (THF), diethyl ether, dichloromethane (CH_2Cl_2), toluene (PhMe), methanol (MeOH) were obtained by passing these previously degassed solvents through activated alumina columns. Benzene (PhH) was distilled from sodium/benzophenone. All other commercial reagents were used as provided. Reactions were monitored by thin layer chromatography (TLC) carried out on EMD silica gel 60-F254 plates. Visualization was performed by UV light irradiation and ceric ammonium molybdate, or anisaldehyde, or potassium permanganate stain and heat. SiliaFlash F60 silica (particle size 40-63μm) was used for flash column chromatography. Preparative thin layer chromatography (PTLC) separations were also carried out on EMD silica gel 60-F254 plates. ^{1}H and ^{13}C NMR data was acquired on Bruker DRX 400, Bruker DRX 500, or Bruker DRX 600 and the spectra were calibrated using residual solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Infrared spectra were recorded on a Shimadzu Prestige FT-IR. High resolution mass spectra were acquired at the University of Arizona Mass Spectral Facility.

Experimental Procedures:



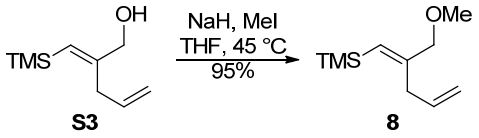
S1 **S2**

A solution of propargyl alcohol (12.0 mL, 203.1 mmol) in THF (775 mL) was cooled to -78 °C, and *n*-BuLi (2.5 M in hexanes, 170.6 mL, 426.5 mmol) was added slowly. After stirring for 30 min at -78 °C, trimethylsilyl chloride (57.1 mL, 446.8 mmol) was added dropwise. Once the addition was completed, the cold bath was removed, and the reaction was stirred at r.t. for 2.0 h. The reaction was cooled to 0 °C, quenched with water (100 mL) and then 1 N HCl solution (300 mL) was added to the crude reaction mixture and stirred at r.t. for 1.5h. The complete consumption of the TMS ether was observed by TLC (R_f 0.90 in 10% ethyl acetate/hexanes). The reaction mixture was poured into a separatory funnel, the organic layer was separated and the aqueous layer was extracted with diethyl ether (4 × 150 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by vacuum distillation (15 mtor, 50 °C) provided the desired alcohol (25.9 g, 99%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 (d, J = 6.1 Hz, 2H), 1.53 (t, J = 6.1 Hz, 1H), 0.18 (s, 9H). The spectrum data is consistent with the reported literature data[1].



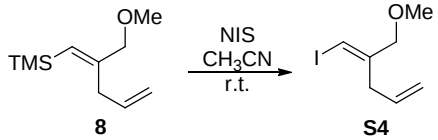
S2 **S3**

A mixture of 3-(trimethylsilyl)prop-2-ynol (11.9 g, 93.0 mmol), diethyl ether (200 mL), and copper iodide (1.92 g, 10.1 mmol) was stirred and cooled at -10 °C (salt/ice bath) and freshly prepared allylmagnesium bromide (0.085M, 300 mL) was added slowly via a cannula. The reaction turned from grey to brown to black. After addition was completed, the reaction was warmed to r.t. naturally and stirred for 12 h totally. The reaction mixture was cooled to 0 °C and quenched with saturated NH_4Cl solution (100 mL) and diluted with water (300 mL). After phase separation, the aqueous phase was filtered over a Celite pad to remove the precipitate. The solution was then extracted with diethyl ether (3 × 150 mL). All organic phases were combined and washed with brine (200 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude product was distilled under vacuum (15 mtor, 72-73 °C) to give a light yellow oil (14.2 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 17.1, 10.1, 6.5 Hz, 1H), 5.62 (t, *J* = 1.6 Hz, 1H), 5.08 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.04 (dq, *J* = 10.1, 1.5 Hz, 1H), 4.06 (dd, *J* = 6.2, 1.5 Hz, 2H), 2.93 (dt, *J* = 6.5, 1.6 Hz, 2H), 1.57 (t, *J* = 6.2 Hz, 1H), 0.14 (s, 9H). The spectrum data is consistent with the reported literature data[2].



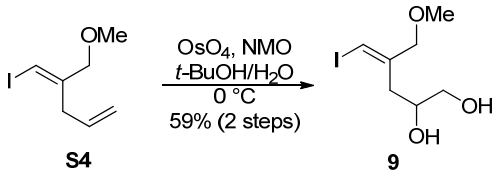
S3 **8**

To a suspension of NaH (60 wt%, 5.36 g, 133.9 mmol) and iodomethane (25.1 mL, 401.9 mmol) in THF (160 mL), alcohol (15.2 g, 89.3 mmol) in THF (20 mL) was added dropwise. The mixture was then stirred at 45 °C for 16 h. After this period of time, the starting material was still present by TLC analysis. More NaH (3.56 g, 89.3 mmol) and iodomethane (5.6 mL, 89.3 mmol) were added and the stirring continued for 5.0 h. The reaction was then cooled to 0 °C and quenched with saturated NH_4Cl solution (50 mL) and diluted with water (50 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 80 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated. Purification by column chromatography (5% diethyl ether/pentane) gave a light yellow oil (15.6 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 17.1, 10.1, 6.5 Hz, 1H), 5.61 (t, *J* = 1.5 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.03 (dq, *J* = 10.1, 1.5 Hz, 1H), 3.83 (d, *J* = 1.4 Hz, 1H), 3.33 (s, 3H), 2.90 (dt, *J* = 6.5, 1.5 Hz, 1H), 0.13 (s, 9H). The spectrum data is consistent with the reported literature data[2].



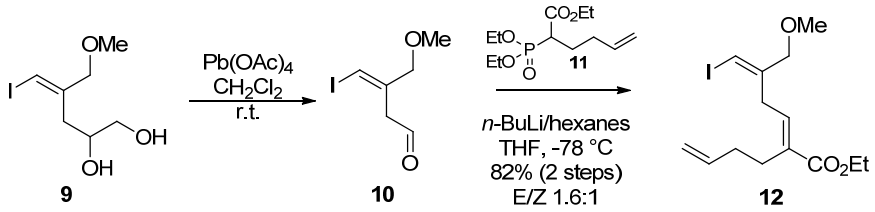
8 **S4**

To the solution of TMS-diene (12.1 g, 65.6 mmol) in acetonitrile (230 mL) was added *N*-iodosuccinimide (17.1g, 76.0 mmol) in portions at 0 °C. After stirring at 0 °C for 40 min the reaction mixture was warmed to r.t., covered with aluminum foil and stirred for 40 h. After that, the reaction was quenched with 10% $Na_2S_2O_3$ solution (200 mL). The two phases were separated and the aqueous phase was extracted with pentane (3 × 150 mL) and the organic phase was also extracted with pentane (6 × 200 mL). The combined extracts were washed with brine (200 mL), dried over anhydrous Na_2SO_4 and carefully concentrated in vacuo. The crude product with residual pentane was used in next step without any further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (tt, *J* = 1.4, 0.5 Hz, 1 H), 5.75 (ddt, *J* = 17.1, 10.0, 6.6 Hz, 1 H), 5.15 (dq, *J* = 17.1, 1.6 Hz, 1 H), 5.09 (ddt, *J* = 10.0, 1.8, 1.3 Hz, 1 H), 3.91 (d, *J* = 1.4 Hz, 2 H), 3.30 (s, 3 H), 2.98 (dt, *J* = 6.6, 1.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.11, 133.26, 117.06, 79.49, 74.80, 58.12, 39.43; IR (film) 3059, 2980, 2928, 2926, 2820, 1639, 1211, 1095, 993, 916, 781 cm^{-1} ; HRMS (EI) *m/z* calcd. for $C_7H_{11}IO$ $[M]^+$: 237.9855, found: 237.9861.



S4 **9**

N-Methylmorpholine *N*-oxide monohydrate (9.34 g, 69.1 mmol) was dissolved in water (140 mL) and cooled to 0 °C, and then the crude iododiene from previous step in *tert*-butanol (140 mL) was added, followed by *tert*-butanol solution of osmium tetroxide (2.5 wt%, 12.0 mL, 1.73 mmol). The reaction was stirred at 0 °C for 8 h then quenched with 15% $NaHSO_3$ solution (250 mL) and extracted with ethyl acetate (6 × 200 mL). The combined extracts were washed with brine (2 × 200 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (60% ethyl acetate/hexanes) to give a light brown oil (10.5 g, 59% yield over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (td, *J* = 1.1, 0.7 Hz, 1H), 4.00 (d, *J* = 1.1 Hz, 2H), 3.93 (ddtd, *J* = 8.8, 6.5, 3.8, 3.3 Hz, 1H), 3.70 (ddd, *J* = 11.2, 6.8, 3.3 Hz, 1H), 3.61 (d, *J* = 3.9 Hz, 1H), 3.53 (ddd, *J* = 11.2, 6.5, 5.4 Hz, 1H), 3.37 (s, 3H), 2.69 (dd, *J* = 6.8, 5.4 Hz, 1H), 2.51 (ddd, *J* = 13.9, 3.9, 0.7 Hz, 1H), 2.40 (dd, *J* = 13.9, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.17, 83.47, 76.70, 70.57, 66.63, 58.28, 39.84; IR (film) 3358, 2926, 2885, 2821, 1610, 1192, 1087, 1033, 910, 783 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_7H_{13}INaO_3$ $[M+Na]^+$: 294.9802, found: 294.9807.



9 **10** **12**

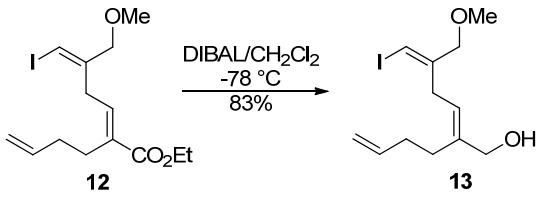
To an ice-water cooled solution of diol (2.03 g, 7.47 mmol) in CH_2Cl_2 (30.0 mL) was added lead (IV) acetate (3.64 g, 8.21 mmol) in portions. After addition completed, the reaction mixture was allowed to warm to r.t. and stirred for 1.0 h. The mixture was then poured directly over a silica gel pad, filtered and

the filter cake was washed with ethyl acetate. After the filtrate was concentrated on rotovap, the residue was taken up in ether and filtered over a Celite pad and washed with ethyl ether. The filtrate was concentrated again on rotovap and then placed under high vacuum briefly to remove the residual solvents and formaldehyde. The resulting aldehyde crude product was used immediately.

To a THF (10 mL) solution of phosphonate[3] (11.43 g, 41.1 mmol), *n*-BuLi (2.5 M in hexane, 14.9 mL, 37.4 mmol) was added dropwise at -78 °C while stirring. After 2.0 h, the aforementioned aldehyde in THF (5.0 mL) was added dropwise and the stirring was continued for 6.0 h. Saturated NH_4Cl solution (5 mL) was then added to quench the reaction. After warmed to r.t. the mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (10% ethyl acetate/hexanes to straight ethyl acetate) to give the desired product mixture (colorless oil, 2.24 g, E/Z 1.6:1, yield 82%) and recovered phosphonate. The E/Z mixture was further separated by column chromatography (5% ethyl ether/hexanes): high R_f fraction, Z isomer, colorless oil, 0.86 g; low R_f fraction, E isomer, colorless oil, 1.38 g.

Z isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (td, *J* = 1.4, 0.7 Hz, 1H), 5.85 – 5.71 (m, 2H), 5.01 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1H), 4.96 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 1.4 Hz, 2H), 3.39 (dq, *J* = 7.5, 0.8 Hz, 2H), 3.31 (s, 3H), 2.37 (ddt, *J* = 8.7, 6.2, 1.0 Hz, 2H), 2.23 – 2.13 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.78, 146.41, 137.81, 136.17, 133.71, 115.29, 79.41, 75.10, 60.48, 58.24, 35.79, 34.12, 33.31, 14.44; IR (film) 2980, 2927, 1708, 1639, 1448, 1377, 1201, 1095, 1026, 912, 785 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{14}H_{21}INaO_3$ $[M+Na]^+$: 387.0428, found: 387.0429.

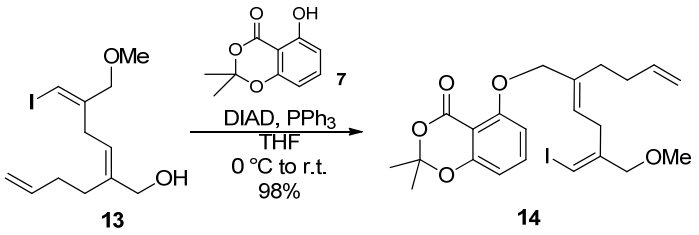
E isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (tt, *J* = 7.5, 0.6 Hz, 1H), 6.40 (td, *J* = 1.3, 0.6 Hz, 1H), 5.84 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.04 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.0, 1.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 1.3 Hz, 2H), 3.31 (s, 3H), 3.14 (dd, *J* = 7.5, 0.6 Hz, 2H), 2.54 – 2.45 (m, 2H), 2.25 – 2.15 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.51, 145.69, 137.97, 137.21, 134.03, 115.25, 80.49, 74.98, 60.66, 58.11, 34.70, 33.37, 26.72, 14.37; IR (film) 2978, 2929, 2819, 1708, 1639, 1448, 1371, 1261, 1199, 1095, 912, 783 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}IO_3$ $[M+H]^+$: 365.0608, found: 365.0603.



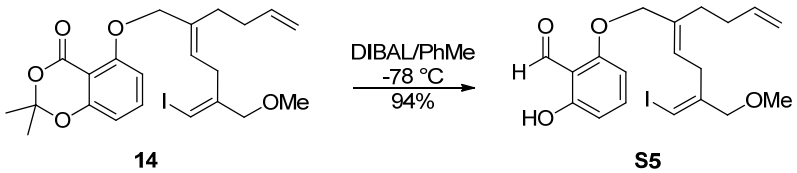
12 **13**

To a solution of ester (10.1 g, 27.8 mmol) in CH_2Cl_2 (200 mL) was added DIBAL (1.0 M in CH_2Cl_2, 69.5 mL) dropwise at -78 °C. The reaction was stirred at -78 °C for 6.5 h then quenched with 10% Rochelle's salt solution (150 mL). The mixture was diluted with CH_2Cl_2 (200 mL), warmed to r.t. and stirred vigorously until two clear layers formed. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column

chromatography (10-25% ethyl acetate/hexanes) to provide a colorless oil (7.54 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (td, *J* = 1.4, 0.6 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.2, 6.5 Hz, 1H), 5.39 (dddt, *J* = 7.3, 6.7, 1.2, 0.8 Hz, 1H), 5.06 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1H), 4.98 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H), 4.07 (dq, *J* = 6.1, 1.2 Hz, 2H), 3.89 (d, *J* = 1.4 Hz, 2H), 3.30 (s, 3H), 3.02 (dq, *J* = 7.3, 0.8 Hz, 2H), 2.34 – 2.25 (m, 2H), 2.20 (dddt, *J* = 8.3, 6.5, 5.7, 1.4 Hz, 2H), 1.33 (t, *J* = 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.03, 141.10, 138.31, 121.76, 115.11, 79.12, 74.90, 66.85, 58.08, 33.71, 32.70, 27.84; IR (film) 3385, 2926, 2856, 2819, 1639, 1448, 1087, 1064, 912 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{12}H_{19}INaO_2$ $[M+Na]^+$: 345.0322, found: 345.0318.

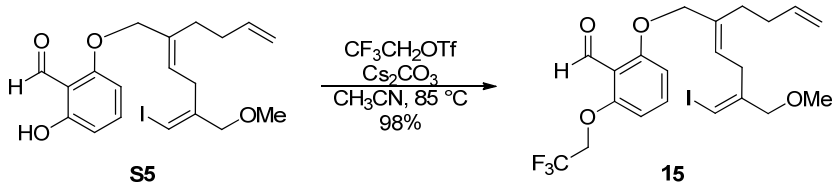


To an ice-water cooled solution of alcohol (2.39g, 7.42 mmol), phenol[4] (1.57 g, 8.90 mmol) and triphenylphosphine (2.33 g, 8.90 mmol) in THF (50 mL) was added diisopropyl azodicarboxylate (1.73 mL, 8.90 mmol) slowly. After the addition was completed, stirring continued for 1.0 h at 0 °C and then the reaction mixture was warmed to r.t. naturally and stirred overnight. The reaction was concentrated and the residue was taken up in ethyl acetate. After the solid was filtered off, the filtrate was concentrated again and the residue was purified by column chromatography (20% ethyl acetate/hexanes) to provide a light yellow oil (3.61 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.4 Hz, 1H), 6.59 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.54 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.31 – 6.26 (m, 1H), 5.87 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.65 (ddt, *J* = 8.4, 7.3, 1.1 Hz, 1H), 5.07 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H), 4.58 (q, *J* = 1.1 Hz, 2H), 3.90 (d, *J* = 1.4 Hz, 2H), 3.30 (s, 3H), 3.07 (d, *J* = 7.3 Hz, 2H), 2.41 (dd, *J* = 9.2, 6.3 Hz, 2H), 2.34 – 2.20 (m, 2H), 1.70 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.55, 157.89, 157.85, 146.88, 138.29, 136.23, 136.14, 124.26, 115.13, 109.30, 106.96, 105.23, 103.73, 79.06, 74.86, 72.67, 58.14, 33.85, 32.38, 27.83, 25.74 (2C); IR (film) 3074, 2993, 2927, 2821, 1735, 1606, 1583, 1479, 1330, 1259, 1203, 1080, 918, 802, 761, 690 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{22}H_{28}IO_5$ $[M+H]^+$: 499.0976, found: 499.0982.

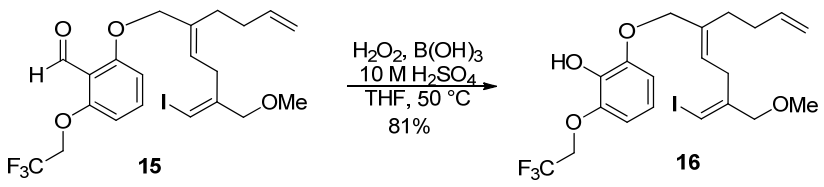


To a solution of acetonide (4.19 g, 8.41 mmol) in toluene (70 mL) cooled at -78 °C, DIBAL/PhMe (1.2M, 14.7 mL, 17.7 mmol) was added dropwise. After stirring at -78 °C for 3 h, the reaction was quenched with 10% Rochelle's salt solution (100 mL) and then diluted with ethyl acetate (200 mL). The mixture was warmed to r.t. and vigorously stirred overnight. The organic layer was separated and the aqueous

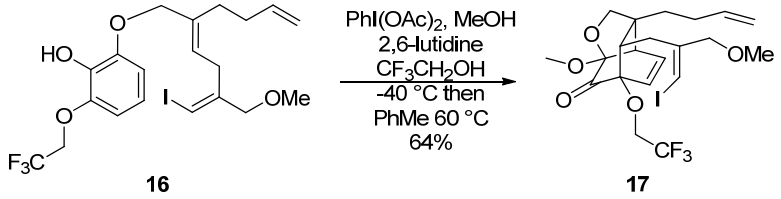
layer was extracted with ethyl acetate (5 × 100 mL). The combined organic layers were washed with brine (200 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration, the crude product was purified by column chromatography (10% ethyl acetate/hexanes) to give a light yellow oil (3.48g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 10.37 (d, *J* = 0.6 Hz, 1H), 7.38 (t, *J* = 8.4, 1H), 6.52 (dt, *J* = 8.4, 0.8 Hz, 1H), 6.37 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.33 (dq, *J* = 1.3, 0.7 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.54 (ddt, *J* = 7.3, 6.4, 1.0 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.01 (ddt, *J* = 10.2, 1.9, 1.2 Hz, 1H), 4.52 (q, *J* = 1.0 Hz, 2H), 3.88 (d, *J* = 1.3 Hz, 2H), 3.29 (s, 3H), 3.07 (d, *J* = 7.3 Hz, 2H), 2.42 – 2.33 (m, 2H), 2.31 – 2.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.32, 163.80, 161.75, 146.60, 138.45, 137.84, 136.17, 125.64, 115.49, 111.18, 110.05, 102.27, 79.70, 75.01, 72.65, 58.10, 33.86, 32.45, 28.00; IR (film) 3074, 3061, 2926, 2887, 1639, 1618, 1456, 1240, 1074, 914, 783, 717 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}INaO_4$ $[M+Na]^+$: 465.0533, found: 465.0542.



In a high pressure flask was charged phenol (9.94 g, 22.5 mmol), cesium carbonate (7.33 g, 22.5 mmol), 2, 2, 2-trifluoroethyl trifluoromethanesulfonate (4.86 mL, 33.7 mmol) and dry acetonitrile (112 mL). The flask was flushed with N_2 for 5 minutes, capped and heated to 85 °C (bath temperature). The reaction mixture was stirred at 85 °C for 2.0 h; the reaction solution gradually turned from light yellow to colorless. After cooling to r.t., the reaction mixture was diluted with ethyl acetate (150 mL) and filtered through a Celite pad. The filtrate was washed with saturated $NaHCO_3$ solution (3 × 100 mL) and brine (150 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (15% ethyl acetate/hexanes) to give a light yellow oil (11.5 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 8.4, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.31 (td, *J* = 1.4, 0.6 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H), 5.58 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.99 (ddt, *J* = 10.2, 1.9, 1.2 Hz, 1H), 4.54 (q, *J* = 1.1 Hz, 2H), 4.42 (q, *J* = 8.1 Hz, 2H), 3.88 (d, *J* = 1.4 Hz, 2H), 3.29 (s, 3H), 3.06 (d, *J* = 7.3 Hz, 2H), 2.42 – 2.34 (m, 2H), 2.29 – 2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.30, 161.38, 159.50, 146.70, 138.00, 136.15, 135.58, 125.07, 123.25 55 (q, *J* = 278.72 Hz), 116.08, 115.31, 107.77, 106.89, 79.37, 74.92, 72.84, 67.37 (q, *J* = 35.8 Hz), 58.09, 33.84, 32.36, 27.84; IR (film) 3076, 2978, 2927, 2877,2823, 2779, 1693, 1598, 1473, 1288, 1246, 1166, 1122, 777 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}F_3INaO_4$ $[M+Na]^+$: 547.0564, found: 547.0566.

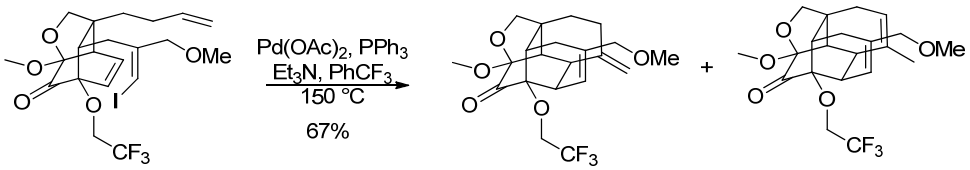


In a high-pressure flask, 10 M sulfuric acid (3.9 mL, 39.3 mmo) was added to a suspension of boric acid (1.21 g, 19.6 mmol) in THF (30 mL) with stirring. Heat was generated during addition. After the flask had been cooled to r.t. in the air, hydrogen peroxide (30 wt% in water, 0.98 mL, 8.65 mmol) was added slowly. After stirring at r.t. for 1.0 h, phenyl aldehyde (2.06 g, 3.93 mmol) in THF (10 mL) was added. The high-pressure flask was then capped and immersed in 50 °C oil bath and heated for 4.0h. The reaction mixture turned from colorless to light yellow gradually. After the reaction was cooled to r.t., ethyl acetate (100 mL) was added and the mixture was washed with water (3 × 50 mL) and brine (50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (10% ethyl acetate/hexanes) to yield a colorless oil (1.63 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 8.3, 8.3 Hz, 1H), 6.65 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.62 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.31 (td, *J* = 1.3, 0.6 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.2, 6.5 Hz, 1H), 5.57 (s, 1H), 5.51 (tt, *J* = 7.3, 1.0 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.00 (ddt, *J* = 10.2, 1.9, 1.1 Hz, 1H), 4.52 (q, *J* = 1.0 Hz, 2H), 4.43 (q, *J* = 8.3 Hz, 2H), 3.84 (d, *J* = 1.3 Hz, 2H), 3.27 (s, 3H), 3.05 (d, *J* = 7.3, 2H), 2.40 – 2.31 (m, 2H), 2.30 – 2.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.99, 146.65, 145.27, 138.00, 136.78, 136.64, 125.52, 123.55 (q, *J* = 278.72 Hz), 119.21, 115.38, 110.01, 108.54, 79.46, 74.90, 73.42, 67.84 (q, *J* = 35.3 Hz), 58.03, 33.87, 32.52, 27.90; IR (film) 3535, 3076, 2978, 2931, 2823, 1612, 1479, 1280, 1163, 1087, 1031, 966, 914, 777, 717 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}F_3INaO_4$ $[M+Na]^+$: 535.0564, found: 535.0570.



16 17

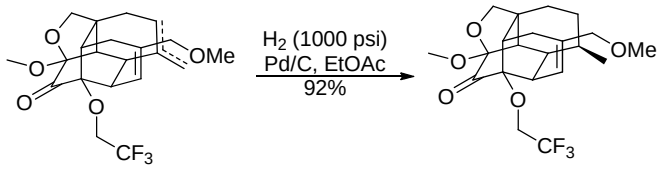
To a solution of phenol (440.7 mg, 0.860 mmol) and 2,6-lutidine (0.5 mL, 4.30 mmol) in 2,2,2-triflouroethanol (76 mL) was added a solution of iodobenzene diacetate (290.9 mg, 0.903 mmol) in MeOH (10 mL) dropwise at -40 °C (acetonitrile/dry ice bath). After addition, the reaction was stirred for 1.0 h at the same temperature then transferred via a cannula to pre-heated (70 °C) toluene (340 mL) in a 1 L 3-neck round-bottom flask equipped with a condenser. The resulting solution was stirred at 60 °C for 16 h while the reaction solution turned from yellow to light yellow gradually. After that time, the reaction was cooled to r.t., the solvent was evaporated and the residue was placed under vacuum for a few hours to remove any residual 2, 6-lutidine. Purification of the crude product by column chromatography (10-15% ethyl acetate/hexanes) gave a light yellow oil, 298.2 mg (64% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.27 (m, 2H), 5.77 (ddt, *J* = 17.1, 10.2, 6.3 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.00 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.31 (dq, *J* = 11.3, 8.6 Hz, 1H), 4.13 (dq, *J* = 11.3, 8.6 Hz, 1H), 4.09 (d, *J* = 8.3 Hz, 1H), 4.04 (dd, *J* = 12.2, 0.9 Hz, 1H), 3.99 (dd, *J* = 12.2, 1.3 Hz, 1H), 3.85 (d, *J* = 8.3 Hz, 1H), 3.53 (s, 3H), 3.26 (s, 3H), 3.14 (dd, *J* = 5.5, 3.0 Hz, 1H), 2.81 (t, *J* = 7.1 Hz, 1H), 2.47 (ddd, *J* = 15.6, 6.6, 1.3 Hz, 1H), 2.35 (ddd, *J* = 15.6, 7.7, 1.1 Hz, 1H), 2.11 (dddt, *J* = 13.1, 7.8, 6.3, 1.5 Hz, 2H), 1.63 – 1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.95, 146.95, 137.48, 129.97, 128.60, 123.64 (q, *J* = 277.5 Hz), 115.50, 99.64, 86.83, 80.72, 78.18, 75.50, 63.59 (q, *J* = 35.1 Hz), 57.68, 51.93, 50.24, 47.04, 45.38, 32.53, 30.73, 29.48; IR (film) 3074, 2976, 2937, 2893, 1755, 1641, 1454, 1284, 1161, 1093, 968, 889, 783, 688 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}F_3IO_5$ $[M+H]^+$: 543.0850, found: 543.0841.



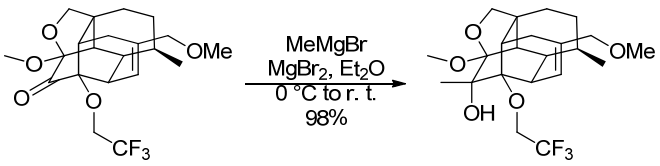
In a high-pressure flask charged with vinyl iodide (600 mg, 1.11 mmol) in trifluorotoluene (110 mL) was added triphenylphosphine (349.4 mg, 1.33 mmol) and triethylamine (0.77 mL, 5.55 mmol). After purging the solution with N_2 for 30 min, palladium (II) acetate (24.8 mg, 0.111 mmol) was added. Purged with N_2 again for 30 min then the vessel was capped and immersed in 150 °C oil bath. The reaction solution was stirred at 150 °C for 2 h and turned from light yellow to yellow. After cooling to r.t. the reaction mixture was filtered over a Celite pad and the filtrate was concentrated. The residue was purified by column chromatography (10-15% ethyl acetate/hexanes) to give two white solids, the higher R_f product being exo-olefin (257.6 mg, 56% yield) and the lower R_f product being endo-olefin (50.6 mg, 11% yield).

Exo-olefin: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dq, *J* = 7.1, 1.5 Hz, 1H), 4.83 (m, 1H), 4.77 (tt, *J* = 1.7, 0.9 Hz, 1H), 4.10 (dq, *J* = 10.7, 8.6 Hz, 1H), 3.89 (d, *J* = 12.3 Hz, 1H), 3.86 (dq, *J* = 10.7, 8.6 Hz, 1H), 3.83 (d, *J* = 7.4 Hz, 1H), 3.75 (d, *J* = 12.3 Hz, 1H), 3.71 (d, *J* = 7.4 Hz, 1H), 3.59 (s, 3H), 3.29 (s, 3H), 3.21 (dd, *J* = 11.3, 2.8 Hz, 1H), 2.79 (ddd, *J* = 10.9, 7.1, 3.0 Hz, 1H), 2.51 (dt, *J* = 5.7, 2.5 Hz, 1H), 2.42 – 2.26 (m, 3H), 2.21 (dd, *J* = 17.1, 8.1 Hz, 1H),), 2.08 (dd, *J* = 13.7, 7.7 Hz, 1H), 1.91 (d, *J* = 2.8 Hz, 1H), 1.48 (ddd, *J* = 13.7, 12.3, 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.99, 145.34, 137.70, 123.82 (q, *J* = 277.6 Hz), 119.42, 113.29, 103.14, 82.85, 80.05, 76.02, 63.05 (q, *J* = 34.8 Hz), 58.23, 52.19, 48.39, 45.45, 40.15, 37.72, 36.11, 28.24, 28.03, 24.88; IR (film) 3072, 2978, 2922, 2873, 1749, 1639, 1462, 1284, 1161, 1107, 972, 896, 734, 682 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{21}H_{26}F_3O_5$ $[M+H]^+$: 415.1727, found: 415.1729.

Endo-olefin: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (dt, *J* = 6.5, 1.6 Hz, 1H), 5.35 (ddd, *J* = 4.3, 2.8, 1.5 Hz, 1H), 4.14 (dq, *J* = 10.7, 8.5 Hz, 1H), 3.89 (d, *J* = 7.3 Hz, 1H), 3.88 (dq, *J* = 10.7, 8.5 Hz, 1H), 3.84 (d, *J* = 7.3 Hz, 1H), 3.79 (s, 2H), 3.61 (s, 3H), 3.24 (s, 3H), 2.85 – 2.71 (m, 2H), 2.45 – 2.34 (m, 2H), 2.24 (d, *J* = 2.8 Hz, 1H), 2.26 – 2.16 (m, 1H), 2.11 – 2.01 (m, 2H), 1.54 (dt, *J* = 2.8, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.66, 138.57, 137.60, 123.82 (q, *J* = 277.6 Hz), 121.09, 117.78, 103.15, 82.36, 79.61, 76.01, 63.10 (q, *J* = 34.8 Hz), 57.33, 52.17, 45.61, 44.51, 38.24, 36.84, 36.09, 30.43, 25.01, 24.83; IR (film) 2929, 2845, 1749, 1454, 1284, 1157, 1107, 1066, 993, 883, 844, 736 cm^{-1} ; HRMS (MALDI) *m/z* calcd. for $C_{21}H_{25}F_3O_5Li$ $[M+Li]^+$: 421.1809, found: 421.1804.



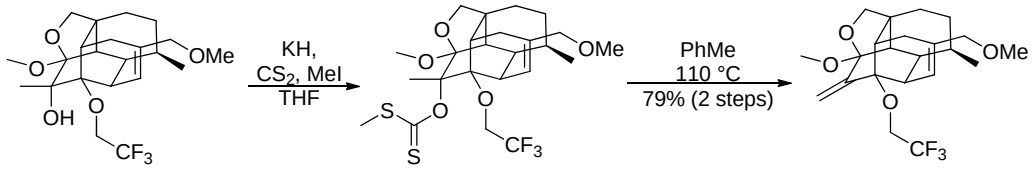
In a 4-mL clear vial, palladium on carbon (10 wt%, 6.9 mg, 0.00647 mmol) was added to a solution of diene (exo- or endo-olefin form previous step, 26.8 mg, 0.0647 mmol) in ethyl acetate (2.0 mL). Six of this vial were placed in a hydrogenation bomb and stirred at r.t. under 1000 psi H_2 for 8.0 h. The reaction mixtures were filtered over a Celite pad and the filtrates were combined and concentrated to give a white solid (161.0 mg, 92% yield). This solid was used without further purification. (Note: The hydrogenation of the endo-olefin usually requires high pressure, however for the exo-olefin, the pressure requirement varies depending on the suppliers and batches of the palladium catalyst. In some cases the reaction was conducted under a hydrogen balloon.) ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.76 (dt, *J* = 7.0, 1.7 Hz, 1H), 4.10 (dq, *J* = 10.7, 8.6 Hz, 1H), 3.88 (d, *J* = 12.8, 1H), 3.79 (dq, *J* = 10.7, 8.6 Hz, 1H), 3.79 (d, *J* = 7.3 Hz, 1H), 3.77 (d, *J* = 12.8, 1H), 3.71 (d, *J* = 7.3 Hz, 1H), 3.61 (s, 2H), 3.32 (s, 3H), 2.76 (ddd, *J* = 10.7, 7.3, 3.1 Hz, 1H), 2.50 – 2.43 (m, 2H), 2.29 (dd, *J* = 19.0, 7.7 Hz, 1H), 2.20 (dt, *J* = 19.0, 1.1 Hz, 1H), 2.09 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.83 (d, *J* = 2.4 Hz, 1H), 1.67 (dddd, *J* = 12.8, 7.0, 5.8, 3.7 Hz, 1H), 1.63 – 1.54 (m, 1H), 1.47 – 1.42 (m, 1H), 1.42 – 1.35 (m, 2H), 1.12 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.88, 137.96, 123.87 (d, *J* = 277.6 Hz), 118.91, 103.09, 82.92, 80.72, 76.00, 63.08 (q, *J* = 34.7 Hz), 58.48, 52.44, 51.13, 45.58, 37.76, 37.52, 35.94 (2C), 28.87, 25.77, 24.59, 21.18; IR (film) 2980, 2914, 2875, 2827, 1751, 1284, 1157, 1103, 1070, 975, 885, 732 cm^{-1} ; HRMS (MALDI) *m/z* calcd. for $C_{21}H_{27}F_3O_5Li$ $[M+Li]^+$: 423.1965, found: 423.1954.



19 **20**

Magnesium bromide diethyl etherate (1.59 g, 6.16 mmol) in a flask was dried by heating gently under vacuum. After the flask was cooled to r.t., anhydrous diethyl ether (15 mL) was added. Magnesium bromide dissolved in ether and two layers of liquid were resulted. Ketone (854.8 mg, 2.05 mmol) in diethyl ether (25 mL) was then added. A white cloudy suspension was formed with a sticky layer of oil on the bottom of the flask. The mixture was cooled to 0 °C with vigorous stirring. Grignard reagent (3.0 M, 2.06 mL, 6.18 mmol) was added dropwise while the suspension turned to a clear solution and the oil layer still existed. After the addition was completed, the reaction mixture was warmed to r.t. and stirred for 1.5 h, during this period of time a white precipitate formed again and the oil layer gradually disappeared. While the reaction was completed it was cooled to 0 °C, quenched by saturated NH_4Cl solution (30 mL) and diluted with water (30 mL) and ethyl acetate (50 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (10% ethyl acetate/hexanes) to give a colorless oil (868.8 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dt, *J* = 7.2, 1.6 Hz, 1H), 4.17 (dq, *J* = 10.8, 8.8 Hz, 1H), 3.86 (ddd, *J* = 12.5, 1.5, 0.7 Hz, 1H), 3.75 (ddd, *J* = 12.5, 1.5, 0.7 Hz, 1H), 3.57 (d, *J* = 6.8 Hz, 1H), 3.48 (dq, *J* = 10.8, 8.8 Hz, 1H), 3.42 (d, *J* = 6.8 Hz, 1H), 3.34 (s, 3H), 3.31 (s, 3H), 3.12 (ddt, *J* = 10.6, 7.4, 3.1 Hz, 1H), 2.91 (s, 1H), 2.40 – 2.25 (m, 2H), 2.11 – 1.89 (m, 3H), 1.76 – 1.51 (m, 2H), 1.48 (d, *J* = 2.2 Hz, 1H), 1.34 – 1.20 (m, 2H), 1.23 (s, 3H), 1.11 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.88, 124.50 (q, *J* = 277.5 Hz), 120.44, 106.63, 82.18, 80.98, 78.53, 76.30, 62.82 (q, *J* = 33.9

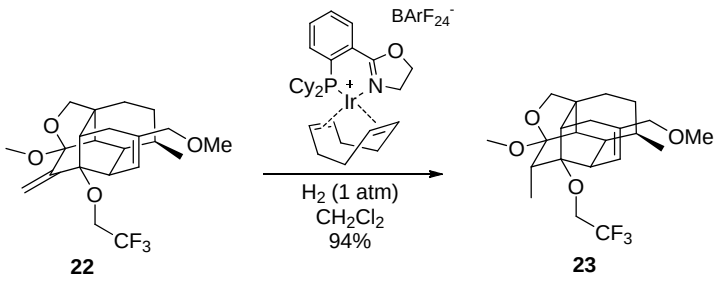
Hz), 58.44, 49.59, 44.29, 44.04, 40.40, 37.87, 36.15, 28.75, 28.55, 26.12, 25.60, 21.45, 16.92; IR (film) 3552, 2981, 2933, 2912, 2872, 1463, 1375, 1282, 1165, 1147, 989, 862 cm^{-1} ; HRMS (MALDI) *m/z* calcd. for $C_{22}H_{31}F_3O_5Li$ $[M+Li]^+$: 439.2278, found: 439.2275.



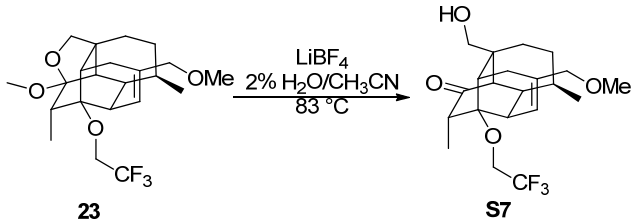
20 **21** **22**

Potassium hydride (30 wt% in mineral oil, 1.06 g, 7.95 mmol) was washed with dry pentane three times under N_2 then suspended in THF (10 mL). Alcohol (0.86 g, 1.99 mmol) in THF (10 mL) was added dropwise at 0 °C. After stirring at 0 °C for 2.0 h, freshly distilled carbon disulfide (1.20 mL, 19.9 mmol) was added dropwise. The reaction was stirred at 0 °C for 1.0 h and r.t. 6.0h. After that time, it was cooled to 0 °C again and methyl iodide (1.24 mL, 19.9 mmol) was added dropwise. The resulting mixture was allowed to warm up to r.t. and stirred for 12 h. The reaction was then quenched by water (10 mL) at 0 °C and diluted with ethyl acetate (20 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated.

The crude product from previous operation was dissolved in toluene (200 mL, 0.01 M) and heated at 110 °C for 2.0 h. After cooling to r.t. the reaction mixture was concentrated. The residue was purified by column chromatography (10% ethyl acetate/hexanes) to give a light yellow solid (0.65 g, 79% yield over 2 steps). (Note: To assure the success of the subsequent iridium catalyzed hydrogenation, this solid should be further purified by tituration with hexanes and filtration to remove the tiny amount of colored impurities.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (dt, *J* = 7.5, 1.4 Hz, 1H), 5.53 (d, *J* = 1.1 Hz, 1H), 5.14 (t, *J* = 0.9 Hz, 1H), 3.94 (dq, *J* = 10.8, 8.8 Hz, 1H), 3.91 (d, *J* = 12.5 Hz, 1H), 3.75 (d, *J* = 12.5Hz, 1H), 3.70 (dq, *J* = 10.8, 8.8 Hz, 1H), 3.66 (d, *J* = 7.1 Hz, 1H), 3.52 (d, *J* = 7.1 Hz, 1H), 3.39 (s, 3H), 3.30 (s, 3H), 2.48 – 2.39 (m, 1H), 2.32 – 2.12 (m, 4H), 2.03 (dd, *J* = 13.2, 5.5 Hz, 1H), 1.71 (d, *J* = 2.2 Hz, 1H), 1.68 – 1.50 (m, 2H), 1.44 – 1.25 (m, 2H),1.07 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 149.23, 135.85, 124.15 (q, *J* = 277.3 Hz), 122.80, 106.65, 105.52, 82.11, 79.29, 76.29, 61.60 (q, *J* = 34.3 Hz), 57.82, 49.53, 46.57, 44.69, 41.17, 38.40, 37.42, 36.78, 29.00, 26.06, 24.84, 21.30; IR (film) 2980, 2916, 2873, 1276, 1161, 1103, 1083, 964, 866 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{22}H_{30}F_3O_4$ $[M+H]^+$: 415.2091, found: 415.2086.

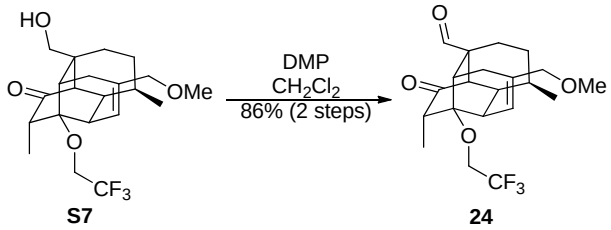


To a solution of diene (464.0 mg, 1.12 mmol) in CH_2Cl_2 (11.2 mL), catalyst[5] (16.9 mg, 0.0112 mmol) was added in one portion. Hydrogen was then bubbled into the resulting pink solution for 5.0 min. The color was quickly discharged and the solution turned to light yellow. The reaction was stirred at r.t. under H_2 balloon for 22 h. After concentration, the residue was purified by column chromatography (15% ethyl acetate/hexanes) to give a white solid (439.4 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (dt, *J* = 7.2, 1.5 Hz, 1H), 3.88 (d, *J* = 12.1 Hz, 1H), 3.74 (d, *J* = 12.1 Hz, 1H), 3.72 (dq, *J* = 10.8, 8.8 Hz, 1H), 3.63 (dq, *J* = 10.8, 8.8 Hz, 1H), 3.58 (d, *J* = 6.9 Hz, 1H), 3.40 (d, *J* = 6.9 Hz, 1H), 3.33 (s, 3H), 3.29 (s, 3H), 2.56 (ddd, *J* = 10.5, 7.2, 2.8 Hz, 1H), 2.28 (ddd, *J* = 11.3, 3.5, 2.1 Hz, 1H), 2.19 (q, *J* = 7.2 Hz, 1H), 2.15 – 2.08 (m, 3H), 1.95 (dd, *J* = 13.4, 6.3 Hz, 1H), 1.74 – 1.62 (m, 1H), 1.58 (dddd, *J* = 12.5, 7.0, 5.5, 3.5 Hz, 1H), 1.41 (d, *J* = 2.1 Hz, 1H), 1.37 – 1.18 (m, 2H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.87, 124.18 (q, *J* = 277.7 Hz), 123.50, 107.97, 81.39, 79.85, 76.45, 60.58 (q, *J* = 34.4 Hz), 57.83, 49.98, 46.49, 44.15, 43.46, 39.06, 37.46, 36.06, 33.16, 28.19, 26.21, 25.25, 21.40, 9.02; IR (film) 2980, 2926, 2875, 1463, 1384, 1280, 1161, 1109, 1020, 862, 678 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{22}H_{32}F_3O_4$ $[M+H]^+$: 417.2247, found: 417.2250.



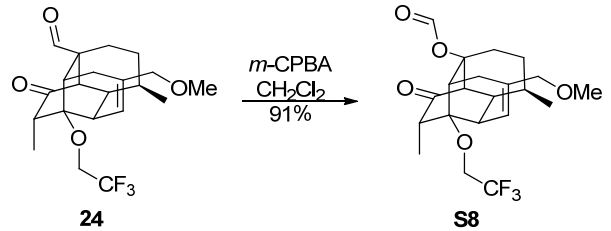
A mixture of acetal (0.35 g, 0.841 mmol) and lithium tetrafluoroborate (0.39 g, 4.160 mmol) in 2% H_2O/CH_3CN (42 mL) was heated at 83 °C for 24 h. The reaction mixture was cooled to r.t., diluted with ethyl acetate (100 mL) and washed with saturated $NaHCO_3$ solution (3 × 30 mL) and brine (30 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting solid was triturated with 15% ethyl acetate/hexanes to give a white solid (0.34 g), which was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (dt, *J* = 7.3, 1.6 Hz, 1H), 3.91 (d, *J* = 12.2 Hz, 1H), 3.79 (d, *J* = 12.2 Hz, 1H), 3.80 – 3.66 (m, 2H), 3.32 (s, 3H), 3.29 (d, *J* = 4.0 Hz, 2H), 2.71 (ddd, *J* = 10.7, 7.1, 3.1 Hz, 1H), 2.62 (q, *J* = 7.3 Hz, 1H), 2.35 (dt, *J* = 4.8, 3.3 Hz, 1H), 2.22 – 2.18 (m, 2H), 2.10 (ddd, *J* = 11.2, 3.7, 1.9 Hz, 1H), 1.94 – 1.77 (m, 3H), 1.68 (m, 2H), 1.34 (dt, *J* = 13.4, 6.8 Hz, 1H), 1.23 (ddd, *J* = 14.3, 12.2, 7.6 Hz, 1H), 1.16 (d, *J* = 7.3 Hz, 3H), 1.09 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.02, 136.75, 124.06 (q, *J* = 277.6 Hz), 122.65, 79.48, 76.42, 72.44, 60.94 (q, *J* = 34.6 Hz), 58.14, 56.97, 46.05, 40.63, 39.46, 35.76, 35.45, 34.17, 29.23, 26.14, 25.25, 21.32, 9.92; IR (film) 3425, 3390,

2943, 2914, 2873, 2812, 1705, 1278, 1153, 1105, 1074, 958, 906, 727, 617 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}F_3O_4$ $[M+H]^+$: 403.2091, found: 403.2089.



S7 **24**

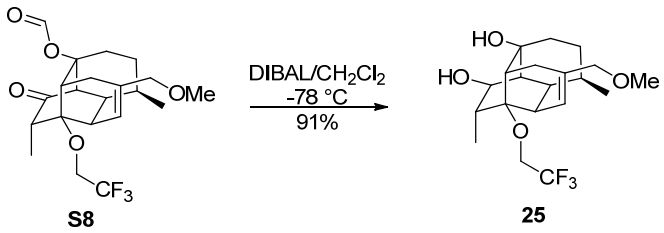
To a solution of alcohol (0.40 g, 0.99 mmol) in dichloromethane (50 mL), Dess-Martin periodinane (505.9 mg, 1.19 mmol) were added at r.t. in portions. After stirring for 2 h, the reaction mixture was diluted with ethyl acetate (100 mL), washed with a 1:1 mixture of saturated $NaHCO_3$ solution and 10% $Na_2S_2O_3$ solution (4 × 30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (30% ethyl acetate/hexanes) to give a white solid (0.34 g, 86% over 2 steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.28 (s, 1H), 5.84 (dt, *J* = 7.1, 1.6 Hz, 1H), 3.90 (d, *J* = 12.2 Hz, 1H), 3.79 (d, *J* = 12.2 Hz, 1H), 3.79 (dq, *J* = 10.6, 8.3 Hz, 1H), 3.71 (dq, *J* = 10.6, 8.3 Hz, 1H), 3.32 (s, 3H), 2.94 (dd, *J* = 7.2, 3.2 Hz, 1H), 2.75 (ddd, *J* = 10.7, 7.1, 3.2 Hz, 1H), 2.33 (q, *J* = 7.3 Hz, 1H), 2.28 (dd, *J* = 19.5, 7.4 Hz, 1H), 2.21 (ddd, *J* = 11.1, 3.8, 2.1 Hz, 1H), 2.15 (d, *J* = 19.5 Hz, 1H), 2.10 (d, *J* = 2.1 Hz, 1H), 1.99 – 1.85 (m, 2H), 1.80 – 1.72 (m, 1H), 1.69 (ddd, *J* = 13.6, 12.1, 7.4 Hz, 1H), 1.49 (ddd, *J* = 13.3, 7.4, 6.0 Hz, 1H), 1.14 (d, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.03, 202.52, 136.57, 123.89 (d, *J* = 277.5 Hz), 122.02, 78.93, 76.15, 61.03 (q, *J* = 34.8 Hz), 58.31, 53.93, 50.22, 46.56, 38.30, 35.27, 34.49, 31.88, 26.79, 25.24, 24.87, 21.25, 9.73; IR (film) 2980, 2924, 2877, 2823, 1728, 1452, 1280, 1163, 1124, 1109, 966, 727 cm^{-1} ; HRMS (ESI) *m/z* calcd. for $C_{21}H_{28}F_3O_4$ $[M+H]^+$: 401.1934, found: 401.1934.



24 **S8**

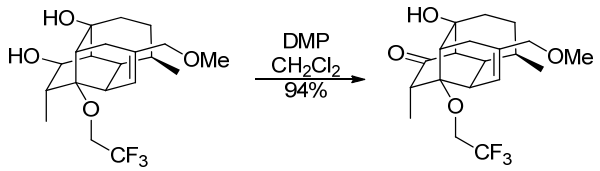
To a solution of aldehyde (150.0 mg, 0.374 mmol) in CH_2Cl_2 (7.5 mL), *meta*-chloroperoxybenzoic acid (70-75 wt%, with benzoic acid and water, 98.0 mg, 0.412 mmol) were added at r.t. in one portion. After stirring for 17 h, the reaction mixture was diluted with ethyl acetate (20 mL), washed with 10% $NaHSO_3$ solution (10 mL), saturated $NaHCO_3$ solution (3 × 10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (20% ethyl acetate/hexanes) to give a white foam (141.2 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 0.9 Hz, 1H), 5.79 (ddd, *J* = 7.1, 2.0, 1.2 Hz, 1H), 3.91 (ddd, *J* = 12.4, 1.5, 0.7 Hz, 1H), 3.80 (ddd, *J* = 12.4, 1.5, 0.7 Hz, 1H), 3.73 – 3.63 (m, 2H), 3.33 (s, 3H), 3.04 – 2.97 (m, 1H), 2.82 – 2.69 (m, 2H), 2.52 – 2.47 (m, 1H), 2.49 (q, *J* = 7.3 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.31 (d, *J* = 2.1 Hz, 1H), 2.27 –

2.18 (m, 1H), 1.95 – 1.70 (m, 2H), 1.59 – 1.41 (m, 2H), 1.20 (d, *J* = 7.3 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.28, 159.77, 137.18, 123.67 (q, *J* = 277.8 Hz), 120.85, 85.02, 78.82, 75.69, 61.11 (q, *J* = 34.8 Hz), 58.61, 58.24, 46.65, 43.09, 39.14, 35.14, 33.49, 31.70, 27.02, 24.95, 20.30, 9.93; IR (film) 2980, 2929, 2877, 2823, 2249, 1712, 1452, 1375, 1282, 1165, 968, 867, 734 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}F_3NaO_5$ $[M+Na]^+$: 439.1703, found: 439.1706.



S8 **25**

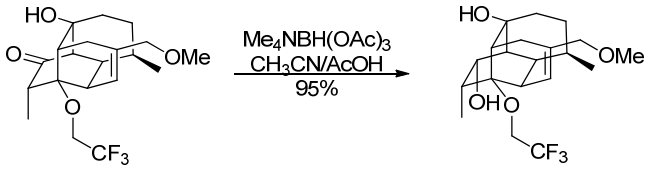
To a solution of keto-ester (488.4 mg, 1.17 mmol) in CH_2Cl_2 (10 mL) was added DIBAL (1.0 M in CH_2Cl_2, 3.51 mL) dropwise at -78 °C. The reaction was stirred at -78 °C for 2.0 h then quenched with 10% Rochelle's salt solution (20 mL). The mixture was diluted with ethyl acetate (40 mL), warmed to r.t. and stirred vigorously until two clear layers formed. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (60% ethyl acetate/hexanes) to give a white solid (415.7 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.72 (d, *J* = 7.1 Hz, 1H), 3.86 (d, *J* = 12.2 Hz, 1H), 3.78 (br s, 1H), 3.74 (d, *J* = 12.2 Hz, 1H), 3.72 (dq, *J* = 10.8, 8.5 Hz, 1H), 3.64 (dq, *J* = 10.8, 8.5 Hz, 1H), 3.51 (s, 1H), 3.29 (s, 3H), 3.14 (br s, 1H), 2.47 (ddd, *J* = 10.8, 7.1, 3.1 Hz, 1H), 2.30 (dd, *J* = 7.4, 3.1 Hz, 1H), 2.25 (d, *J* = 18.9 Hz, 1H), 2.20 – 2.08 (m, 2H), 1.98 (tt, *J* = 7.2, 3.5 Hz, 1H), 1.94 (dt, *J* = 11.0, 2.7 Hz, 1H), 1.82 – 1.62 (m, 2H), 1.53 – 1.42 (m, 2H), 1.35 (dt, *J* = 13.5, 6.3 Hz, 1H), 1.09 (d, *J* = 7.2 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.06, 124.15 (q, *J* = 277.6 Hz), 123.19, 79.79, 78.60, 78.32, 76.25, 60.69 (q, *J* = 34.5 Hz), 57.97, 48.17, 45.58, 42.56, 41.29, 37.51, 36.76, 32.77, 27.37, 24.79, 20.88, 15.16; IR (film) 3346, 2980, 2914, 2875, 1452, 1379, 1282, 1155, 1001, 966, 920, 854, 734 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}F_3NaO_4$ $[M+Na]^+$: 413.1910, found: 413.1916.



25 **26**

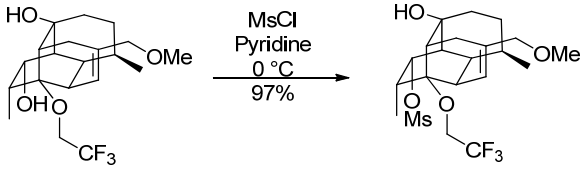
To a solution of diol (349.6 mg, 0.895 mmol) in water-saturated dichloromethane (18 mL), Dess-Martin periodinane (455.7 mg, 1.07 mmol) were added at r.t. in one portion. After stirring for 2 h, another portion of Dess-Martin periodinane (380 mg, 0.895 mmol) was added and the reaction was stirred for further 7 h. The reaction mixture was diluted with ethyl acetate (120 mL), washed with a 1:1 mixture of saturated $NaHCO_3$ solution and 10% $Na_2S_2O_3$ (4 × 30 mL) solution and brine (30 mL), dried over

anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was triturated with 50% ethyl acetate/hexanes and the white solid was collected by filtration. Purification of the filtrate by column chromatography (35% ethyl acetate/hexanes) gave another crop of desired product. Combined white solid weighed 326.8 mg (94% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.78 (d, *J* = 7.1 Hz, 1H), 3.91 (d, *J* = 12.3 Hz, 1H), 3.78 (d, *J* = 12.3 Hz, 1H), 3.71 (q, *J* = 8.4 Hz, 2H), 3.32 (s, 3H), 2.71 (ddd, *J* = 10.6, 7.1, 2.9 Hz, 1H), 2.53 (q, *J* = 7.4 Hz, 1H), 2.39 – 2.17 (m, 6H), 2.04 (d, *J* = 2.1 Hz, 1H), 1.87 – 1.64 (m, 2H), 1.52 – 1.38 (m, 2H), 1.16 (d, *J* = 7.3 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.19, 136.66, 123.93 (d, *J* = 277.6 Hz), 122.16, 79.14, 76.08, 74.03, 61.89, 61.06 (q, *J* = 34.7 Hz), 58.17, 45.91, 43.56, 40.33, 37.03, 35.38, 33.65, 27.57, 24.83, 20.70, 9.79; IR (film) 3396, 2981, 2927, 2879, 2825, 1712, 1456, 1280, 1161, 1120, 1020, 966, 920, 732 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}F_3NaO_4$ $[M+Na]^+$: 411.1754, found: 411.1756.



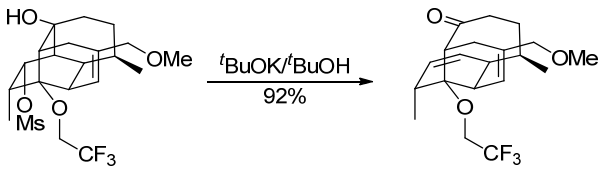
26 **S9**

To a solution of keto-alcohol (173.4 mg, 0.446 mmol) in acetonitrile (5 mL) and acetic acid (10 mL), was added a suspension of tetramethylammonium triacetoxyborohydride (587.4 mg, 2.23 mmol) in acetonitrile (5 mL) at r.t. The reaction mixture was stirred for 3 h before it was quenched by saturated NH_4Cl solution (5 mL). After effervescence had ceased, the solution was diluted with water (10 mL) and ethyl acetate (30 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na2SO4, filtered and concentrated in vacuo. The crude product was triturated with hexanes and the white solid was collected by filtration. Purification of the filtrate by column chromatography (75% ethyl acetate/hexanes) gave another crop of desired product. The combined white solid weighed 165.4 mg (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (dt, *J* = 7.0, 1.5 Hz, 1H), 4.58 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.87 (d, *J* = 12.2 Hz, 1H), 3.74 (d, *J* = 12.2 Hz, 1H), 3.73 (dq, *J* = 10.8, 8.5 Hz, 1H), 3.61 (dq, *J* = 10.8, 8.5 Hz, 1H), 3.29 (s, 3H), 2.60 (ddd, *J* = 10.4, 7.0, 2.9 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.33 (dq, *J* = 10.4, 7.3 Hz, 1H), 2.27 – 2.03 (m, 4H), 1.80 (m, 1H), 1.67 (m, 1H), 1.44 – 1.33 (m, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.87, 124.23 (d, *J* = 277.8 Hz), 123.76, 79.02, 76.44, 74.78, 64.27, 60.58 (q, *J* = 34.3 Hz), 58.03, 51.29, 43.78, 38.46, 36.55, 36.45, 35.46, 33.52, 28.11, 24.82, 21.12, 7.74; IR (film) 3373, 2981, 2926, 2833, 1448, 1280, 1161, 1105, 1002, 966, 916, 864, 732 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}F_3NaO_4$ $[M+Na]^+$: 413.1910, found: 413.1909.



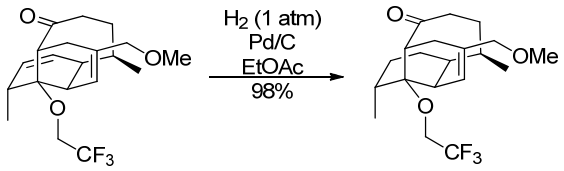
S9 **27**

To a solution of diol (276.0 mg, 0.707 mmol) in anhydrous pyridine (12.0 mL), methanesulfonyl chloride (0.55 mL, 7.07 mmol) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 15 h then quenched with 1 N HCl solution (10 mL) and diluted with ethyl acetate (200 mL). The mixture was washed with 1 N HCl solution (3 × 50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was triturated with 10% ethyl acetate/hexanes and the white solid was collected by filtration. Purification of the filtrate by column chromatography (60% ethyl acetate/hexanes) gave another crop of white solid. The combined white solids weighed 321.3 mg (97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (dt, *J* = 6.9, 1.5 Hz, 1H), 5.48 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.86 (dd, *J* = 12.2, 1.1 Hz, 1H), 3.74 (dd, *J* = 12.2, 1.1 Hz, 1H), 3.72 (dq, *J* = 10.6, 8.4 Hz, 1H), 3.62 (dq, *J* = 10.6, 8.4 Hz, 1H), 3.29 (s, 3H), 3.05 (s, 3H), 2.62 (ddd, *J* = 10.6, 7.0, 2.9 Hz, 1H), 2.52 (dq, *J* = 11.0, 7.5 Hz, 1H), 2.47 (ddd, *J* = 11.4, 3.7, 2.1 Hz, 1H), 2.25 (d, *J* = 18.0 Hz, 1H), 2.20 (dd, *J* = 12.8, 6.3 Hz, 1H), 2.16 – 2.06 (m, 2H), 2.00 (s, 1H), 1.84 – 1.74 (m, 1H), 1.69 (m, 1H), 1.62 (dd, *J* = 3.4, 2.1 Hz, 1H), 1.47 – 1.34 (m, 2H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.13, 124.03 (d, *J* = 277.6 Hz), 122.96, 78.48, 77.01, 76.24, 74.28, 60.70 (q, *J* = 34.6 Hz), 58.13, 49.80, 43.53, 38.17, 38.01, 36.86, 36.09, 34.61, 33.23, 27.85, 24.70, 20.97, 8.91; IR (film) 3412, 2983, 2926, 1448, 1350, 1330, 1282, 1168, 1107, 966, 927, 918, 871, 732, 528 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{31}F_3NaO_6S$ $[M+Na]^+$: 491.1686, found: 491.1684.



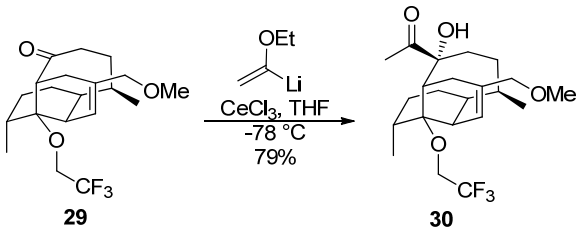
27 **28**

To a solution of mesylate (220.8 mg, 0.471 mmol) in anhydrous *tert*-butanol (44 mL), potassium *tert*-butoxide (1.0 M in THF, 1.41 mL) was added dropwise at r.t. The solution became cloudy and turned yellow. After stirring for 1.5 h, the reaction was quenched with saturated NH_4Cl solution (10 mL) and diluted with ethyl acetate (50 mL) and water (50 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was triturated with hexanes and the white solid was collected by filtration. Purification of the filtrate by column chromatography (15% ethyl acetate/hexanes) gave another crop of white solid. Combined white solids weighed 161.4 mg (92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (dt, *J* = 5.7, 1.5 Hz, 1H), 5.58 – 5.47 (m, 2H), 3.99 (d, *J* = 11.8, 1H), 3.85 (d, *J* = 11.8 Hz, 1H), 3.82 – 3.67 (m, 2H), 3.33 (s, 3H), 2.95 (d, *J* = 7.2 Hz, 1H), 2.83 – 2.78 (m, 1H), 2.74 (ddd, *J* = 14.9, 7.1, 4.0 Hz, 1H), 2.65 (qd, *J* = 7.0, 3.4 Hz, 1H), 2.60-2.53 (m, 1H), 2.46 – 2.38 (m, 1H), 2.25 (d, *J* = 18.6 Hz, 1H), 2.30-2.17 (m, 1H), 1.90 – 1.72 (m, 2H), 1.72 – 1.54 (m, 1H), 1.09 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 211.79, 132.60, 131.32, 130.87, 125.45, 124.84 (d, *J* = 277.8 Hz), 78.93, 76.65, 60.91 (q, *J* = 33.8 Hz), 57.99, 54.19, 44.17, 38.23, 38.10, 37.56, 34.86, 29.76, 25.92, 23.46, 16.33; IR (film) 2927, 2875, 1676, 1280, 1155, 1105, 968, 856 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{28}F_3O_3$ $[M+H]^+$: 373.1985, found: 373.1983.



28 **29**

To a solution of diene (247.3 mg, 0.664 mmol) in ethyl acetate (13.3 mL) was added palladium on carbon (10 wt%, 35.3 mg, 0.0332 mmol). The mixture was bubbled with H_2 for 5 min. then stirred at r.t. under H_2 balloon for 3.0 h. After that time the reaction mixture was filtered through a Celite pad and the filtrate was concentrated and then purified by column chromatography (15% ethyl acetate/hexanes) to give a colorless oil (243.6 mg, 98% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 4.6, 2.4, 1.2 Hz, 1H), 3.97 (d, *J* = 11.9 Hz, 1H), 3.91 – 3.76 (m, 3H), 3.36 (s, 3H), 2.99 (dq, *J* = 5.9, 1.4 Hz, 1H), 2.73 (ddd, *J* = 12.1, 8.4, 3.9 Hz, 1H), 2.60 (q, *J* = 4.1 Hz, 1H), 2.44 (ddt, *J* = 18.2, 5.7, 2.7 Hz, 1H), 2.25 – 2.11 (m, 2H), 1.99 – 1.83 (m, 3H), 1.82 – 1.71 (m, 1H), 1.68 – 1.57 (m, 1H), 1.53 – 1.28 (m, 4H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.76, 132.95, 127.03, 124.25 (q, *J* = 278.3 Hz), 78.93, 76.60, 61.98 (q, *J* = 34.0 Hz), 58.45, 54.04, 42.15, 38.83, 37.96, 37.44, 33.88, 31.44, 27.70, 27.09, 25.95, 24.03, 14.69; IR (film) 2933, 2873, 2821, 1674, 1454, 1377, 1280, 1153, 1103, 972, 850, 667, 536 cm^{-1}; HRMS (MALDI) *m/z* calcd. for $C_{20}H_{29}F_3O_3Li$ $[M+Li]^+$: 381.2224, found: 381.2235.

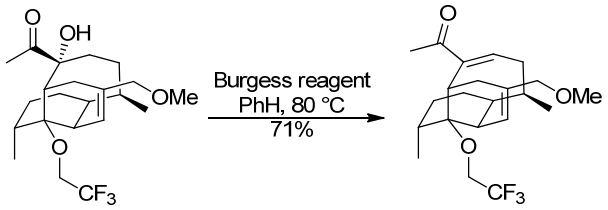


29 **30**

Cerium (III) chloride heptahydrate[6](190 mg, 0.510 mmol) was grounded to a fine powder and placed in a flask equipped with a stir bar. The flask was heated slowly to 90 °C with evacuation and maintained at 90 °C for 3.5 h. After that period of time, the temperature was increased to 140 °C and the flask was heated at 140 °C for 15 h. The flask was then cooled to r.t., nitrogen was introduced and THF (2.5 mL) was added. The resulting slurry was stirred vigorously under N_2 for 2 h. In a separate flask, *t*-BuLi (1.7 M in pentane, 1.5 mL, 2.5 mmol) was added dropwise to a solution of ethyl vinyl ether (0.57 mL, 6.0 mmol) in THF (3.0 mL) at -78 °C. The solution turned yellow and a precipitate formed. After the addition was completed, the cooling bath was removed and the mixture was allowed to warm to 0 °C over an ice-water bath and then stirred at 0 °C for 15 min. while the yellow color was gradually discharged.

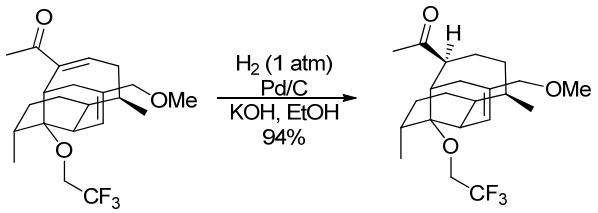
The resulting colorless 1-Ethoxyvinyllithium solution (0.80 mL) was added via a syringe to the $CeCl_3$ suspension (cooled to -78 °C before the addition). A canary yellow mixture was formed and stirred for 1.0 h before ketone (45.0 mg, 0.134 mmol) in THF (0.50 mL) was added. The reaction mixture was stirred at -78 °C for 45 min. and quenched by saturated NH_4Cl solution (3 mL) and extracted with ethyl acetate (5 × 6 mL). The combined organic layers were washed with brine (6 mL) and split into two portions; each was diluted with ethyl acetate to 50 mL and washed with cold 1N HCl solution (10 mL) one time and brine (5 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated.

The residue was purified by column chromatography (15% ethyl acetate/hexanes) to give a colorless oil (44.3 mg, 79% yield). (Note: Prolonged exposure of the allylic alcohol intermediate to acid could destroy the molecule.) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (t, *J* = 3.2 Hz, 1H), 3.92 – 3.67 (m, 4H), 3.30 (s, 3H), 2.85 (ddt, *J* = 13.4, 11.4, 6.8 Hz, 1H), 2.64 (s, 1H), 2.57 (s, 1H), 2.37 (d, *J* = 8.1 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.33 (s, 3H), 2.27 – 2.20 (m, 1H), 2.20 – 2.11 (m, 1H), 2.07 (ddt, *J* = 15.4, 7.5, 2.3 Hz, 1H), 1.97 (ddd, *J* = 15.6, 7.9, 2.2 Hz, 1H), 1.81 – 1.72 (m, 2H), 1.55 (d, *J* = 17.9 Hz, 1H), 1.48 – 1.36 (m, 3H), 1.32 – 1.23 (m, 1H), 1.08 (d, *J* = 7.4 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.45, 132.02, 126.42, 124.49 (q, *J* = 278.7 Hz), 82.45, 82.30, 76.80, 62.07 (q, *J* = 33.8 Hz), 58.20, 43.08, 41.02, 39.38, 36.82, 36.27, 30.63, 27.79, 25.82, 25.31, 24.71, 22.22, 22.19, 15.42; IR (film) 3441, 2931, 2872, 2825, 1703, 1456, 1377, 1357, 1280, 1157, 1107, 972, 910, 734 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{33}F_3O_4Li$ $[M+Li]^+$: 425.2485, found: 425.2486.



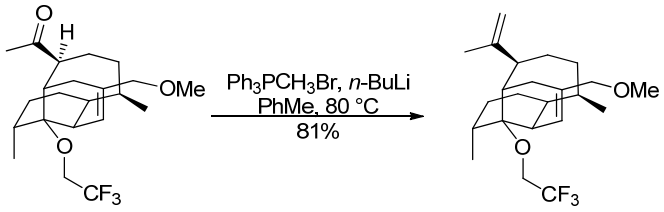
30 **31**

In a high-pressure tube, Burgess's reagent (37.8 mg, 0.159 mmol) was added to a solution of hydroxyl ketone (33.2 mg, 0.0793 mmol) in benzene (8.0 mL) under N_2. The tube was then capped and heated at 80 °C for 1.0 h. The reaction solution turned from colorless to light yellow. After cooling to r.t. the reaction was concentrated and then diluted with diethyl ether (30 mL) and washed with brine (3 × 10 mL). The aqueous phase was back-extracted with ether (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (10% ethyl acetate/hexanes) to give a white solid (22.4 mg, 71% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (t, *J* = 9.0 Hz, 1H), 5.72 (dt, *J* = 5.1, 1.6 Hz, 1H), 4.05 (d, *J* = 9.8 Hz, 1H), 3.97 – 3.79 (m, 3H), 3.77 (d, *J* = 12.1 Hz, 1H), 3,29 – 3.22 (m, 1H), 3.27 (s, 3H), 2.59 (t, *J* = 6.1 Hz, 1H), 2.46 (ddt, *J* = 19.1, 10.2, 2.4 Hz, 1H), 2.39 (s, 3H), 2.03 – 1.93 (m, 2H), 1.90 – 1.83 (m, 1H), 1.81 (d, *J* = 19.1 Hz, 1H), 1.72 (ddd, *J* = 13.0, 9.2, 2.6 Hz, 1H), 1.70 – 1.62 (m, 1H), 1.56 – 1.47 (m, 1H), 1.29 (dq, *J* = 13.7, 5.4 Hz, 1H), 1.14 (dtd, *J* = 13.7, 5.1, 2.4 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.08, 146.73, 145.62, 136.10, 125.76, 124.58 (q, *J* = 278.2 Hz), 81.97, 76.71, 60.94 (q, *J* = 33.8 Hz), 57.70, 42.64, 41.24, 41.10, 33.22, 31.63, 31.52, 30.86, 28.51, 28.48, 27.79, 26.03, 15.43; IR (film) 2954, 2927, 2875, 1662, 1448, 1375, 1274, 1244, 1157, 1109, 968, 856 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{31}F_3O_3Na$ $[M+Na]^+$: 423.2118, found: 423.2113.



31 **32**

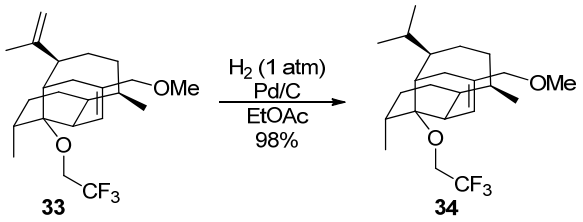
Enone (70.0 mg, 0.175 mmol) was dissolved in absolute ethanol (8.8 mL) containing potassium hydroxide (28.0 mg), to which palladium on carbon (10 wt%, 18.6 mg, 0.0175 mmol) was added. The mixture was bubbled with H_2 for 5 min. then stirred at r.t. under H_2 balloon for 27 h. The reaction was then filtered through a Celite pad and washed with ethyl acetate. Brine (20 mL) was added to the filtrate and the mixture was extracted with ethyl acetate (3 × 15 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (15% ethyl acetate/hexanes) to give a colorless oil (66.2 mg, 94% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.64 (m, 1H), 3.93 – 3.85 (m, 2H), 3.82 – 3.75 (m, 2H), 3.33 (s, 3H), 2.78 (d, J = 11.7 Hz, 1H), 2.44 (s, 1H), 2.35 (d, J = 6.8 Hz, 1H), 2.23 – 2.12 (m, 2H), 2.20 (s, 3H), 2.02 – 1.94 (m, 1H), 1.91 (d, J = 18.0 Hz, 1H), 1.68 – 1.43 (m, 6H), 1.34 (m, 3H), 1.03 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.07, 133.68, 124.48 (q, J = 276.8 Hz), 124.66, 81.42, 76.14, 62.56 (q, J = 33.9 Hz), 58.34, 49.86, 42.62, 38.13, 37.23, 36.60, 33.29, 30.73, 29.16, 28.23, 26.88, 24.18, 24.04, 21.93, 14.53; IR (film) 2956, 2933, 2872, 2821, 1708, 1460, 1377, 1354, 1280, 1157, 1126, 1105, 972, 927, 850 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{33}F_3O_3Na$ $[M+Na]^+$: 425.2274, found: 425.2270.



32 **33**

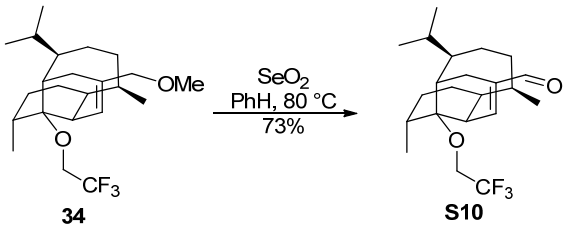
In a high-pressure tube, *n*-BuLi (1.6 M in hexanes, 0.39 mL, 0.624 mmol) was added dropwise to a suspension of methyltriphenylphosphonium bromide (277.4 mg, 0.739 mmol) in toluene (3.5 mL) at 0 °C. The mixture turned to light yellow gradually. After stirring for 15 min., ketone (99.2 mg, 0.246 mmol) in toluene (1.0 mL) was added and the reaction was then warmed to r.t. The tube was then sealed and heated to 80 °C and stirred for 20 h at 80 °C. The reaction was cooled to r.t., quenched with saturated NH_4Cl solution (5.0 mL), and extracted with ethyl acetate (3 × 10 mL). The combined extracts were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was loaded on a silica gel plug and eluted with 5% ethyl acetate/hexanes. To remove the trace amount of triphenylphosphine, the eluate was concentrated, to which acetone (9.0 mL), sodium iodide (540 mg) and Merrifield resin (600 mg) were added. The slurry was stirred at r.t. for 24 h then filtered over a Celite pad and washed with small amount of ethyl acetate. The filtrate was concentrated, re-dissolved in ethyl acetate, washed with water and brine and concentrated again. The residue was purified by column chromatography (5% ethyl ether/hexanes) to give a colorless oil (79.8 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62 (m, 1H), 4.76 (t, J = 1.5 Hz, 1H), 4.62 (d, J = 1.3 Hz, 1H), 3.95 – 3.83 (m, 2H), 3.83

– 3.72 (m, 2H), 3.33 (s, 3H), 2.42 (s, 1H), 2.32 – 2.17 (m, 2H), 2.17 – 2.08 (m, 1H), 2.06 (d, J = 7.0 Hz, 1H), 2.03 – 1.89 (m, 2H), 1.83 – 1.78 (s, 3H), 1.62 (m, 1H), 1.56 – 1.28 (m, 8H), 0.99 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.22, 134.01, 124.63 (q, J = 278.4 Hz), 125.25, 110.04, 81.89, 76.65, 62.56 (q, J = 33.8 Hz), 58.25, 42.88, 42.02, 38.88, 38.39, 36.75, 32.99, 31.78, 28.34, 27.04, 25.98, 24.43, 24.21, 23.78, 14.58; IR (film) 2933, 2870, 1280, 1155, 1124, 1105, 1089, 974, 891 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{35}F_3O_2Li$ $[M+Li]^+$: 407.2744, found: 407.2739.



33 **34**

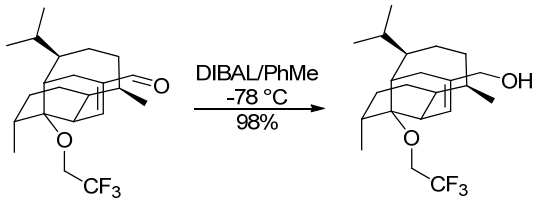
To a solution of alkene (89.0 mg, 0.222 mmol) in ethyl acetate (2.2 mL) was added palladium on carbon (10 wt%, 23.6 mg, 0.0222 mmol). The mixture was bubbled with H_2 for 5 min. then stirred at r.t. under H_2 balloon for 36 h. After that time the reaction mixtures were filtered through a Celite pad and washed with ethyl acetate. The filtrate was concentrated to give a colorless oil (87.8 mg, 98% yield), which solidified in freezer to a white solid. (Note: The R_f of the product is the same as that of the starting material in ethyl acetate/hexanes solvent system, thus the reaction was monitored by ^{1}H-NMR.) ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.60 (m, 1H), 3.92 – 3.83 (m, 2H), 3.81 – 3.72 (m, 2H), 3.31 (s, 3H), 2.41 (m, 1H), 2.24 (m, 1H), 2.19 – 2.09 (m, 2H), 2.00 – 1.94 (m, 1H), 1.91 (d, J = 17.8 Hz, 1H), 1.75 – 1.63 (m, 1H), 1.54 – 1.25 (m, 9H), 1.25 – 1.14 (m, 1H), 0.96 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.1 Hz, 3H), 0.90 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.11, 124.72 (d, J = 278.5 Hz), 125.63, 82.09, 76.81, 62.38 (q, J = 33.7 Hz), 58.07, 42.62, 40.98, 38.21, 37.75, 37.48, 36.14, 33.12, 31.73, 28.85, 27.59, 25.47, 25.43, 24.44, 22.18, 20.94, 14.64; IR (film) 2956, 2933, 2872, 2819, 1463, 1456, 1375, 1280, 1155, 1122, 1101, 975, 850, 659 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}F_3O_2Li$ $[M+Li]^+$: 409.2900, found: 409.2900.



34 **S10**

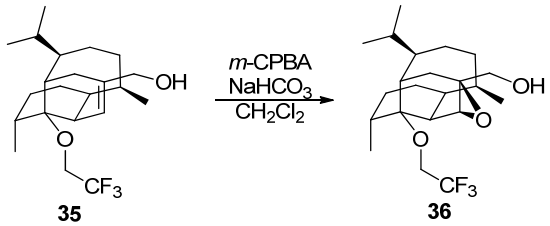
In a high-pressure tube, a mixture of vinylether (18.0 mg, 0.0447 mmol), selenium dioxide (24.8 mg, 0.224 mmol) and benzene (1.0 mL) was heated at 80 °C for 60 h. The reaction was cooled to r.t., filtered over a Celite pad and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (10% ethyl acetate/hexanes) to give a white solid (12.6 mg, 73% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.50 (s, 1H), 6.77 (m, 1H), 3.85 (dq, J = 10.8, 8.4 Hz, 1H), 3.75 (dq, J = 10.8, 8.4 Hz, 1H), 2.70 (m, 1H), 2.40 (d, J = 17.8 Hz, 1H), 2.35 – 2.24 (m, 2H), 2.21 (ddp, J = 13.8, 6.9, 3.7 Hz, 1H),

2.06 (dtt, *J* = 12.2, 6.0, 2.9 Hz, 1H), 1.75 (td, *J* = 9.2, 4.4 Hz, 1H), 1.63 –1.32 (m, 10H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.65, 152.46, 139.88, 124.19 (q, *J* = 278.7 Hz), 82.21, 62.01 (q, *J* = 34.0 Hz), 43.28, 40.84, 40.18, 37.26, 36.71, 35.88, 33.00, 32.19, 28.60, 27.55, 25.30, 24.19, 22.13, 20.92, 20.61, 14.68; IR (film) 2956, 2933, 2872, 1681, 1649, 1278, 1157, 1118, 972 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{33}F_3O_2Li$ $[M+Li]^+$: 393.2587, found: 393.2581.



S10 **35**

To a solution of aldehyde (53.3 mg, 0.138 mmol) in toluene (10 mL) was added DIBAL (1.0 M in toluene, 0.21 mL) dropwise at -78 °C. The reaction was stirred at -78 °C for 1.5 h then quenched with 10% Rochelle's salt solution (5 mL). The mixture was diluted with ethyl acetate (5 mL), warmed to r.t. and stirred vigorously until two clear layers formed. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (10% ethyl acetate/hexanes) to give a colorless oil (52.5 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.62 (m, 1H), 4.06 (q, *J* = 13.1 Hz, 2H), 3.86 (dq, *J* = 10.7, 8.6 Hz, 1H), 3.76 (dq, *J* = 10.7, 8.6 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.29 (ddt, *J* = 17.8, 6.5, 2.9 Hz, 1H), 2.21 – 2.09 (m, 2H), 2.03 – 1.90 (m, 2H), 1.76 – 1.62 (m, 1H), 1.62 – 1.15 (m, 11H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.37, 124.72 (d, *J* = 278.6 Hz), 124.29, 82.12, 67.15, 62.31 (q, *J* = 33.7 Hz), 42.62, 40.86, 38.06, 37.71, 37.49, 36.19, 33.11, 31.77, 28.83, 27.58, 25.52, 25.16, 24.47, 22.14, 20.90, 14.66; IR (film) 3342, 2956, 2933, 2872, 2358, 2341, 1466, 1278, 1155, 1124, 975, 734 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{35}F_3O_2Li$ $[M+Li]^+$: 395.2744, found: 395.2730.



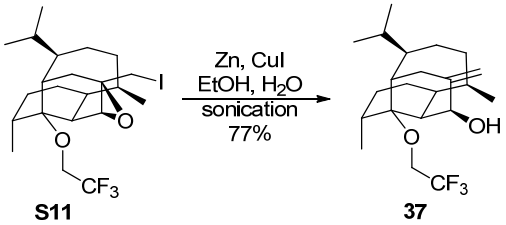
35 **36**

A mixture of allylic alcohol (40.0 mg, 0.103 mmol) and $NaHCO_3$ (43.3 mg, 0.515 mmol) in CH_2Cl_2 (2.0 mL) was cooled to 0 °C, to which *meta*-Chloroperoxybenzoic acid (70-75 wt% in water, 36.8 mg, 0.154 mmol) was added in one portion. The mixture was allowed to warm to r.t. naturally and stirred for 18 h totally. After water (2 mL) and ethyl acetate (10 mL) were added to the mixture, the organic phase was separated and washed with saturated $NaHSO_3$ solution (3 × 2 mL), saturated $NaHCO_3$ solution (3 × 2 mL)

and brine (2 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting solid (43.4 mg) was used in the next step without further purification. An analytical sample was obtained by triturating the solid with hexanes. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.19 (m, 1H), 3.81 – 3.70 (m, 2H), 3.65 (dd, *J* = 12.3, 9.7 Hz, 1H), 3.38 (s, 1H), 2.69 (d, *J* = 3.9 Hz, 1H), 2.26 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.14 (dqd, *J* = 13.7, 7.2, 3.9 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.97 (d, *J* = 8.0 Hz, 1H), 1.75 (d, *J* = 9.2 Hz, 1H), 1.69 (td, *J* = 9.8, 4.0 Hz, 1H), 1.63 – 1.43 (m, 7H), 1.43 – 1.23 (m, 4H), 0.95 – 0.89 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 124.75 (q, *J* = 278.3 Hz), 80.78, 62.59, 61.89 (q, *J* = 33.6 Hz), 60.63, 59.00, 42.25, 40.77, 37.44, 36.90, 35.35, 34.74, 33.23, 29.93, 28.78, 28.29, 26.37, 24.59, 23.25, 21.87, 21.16, 14.23; IR (film) 3431, 2954, 2937, 2873, 1456, 1278, 1155, 1122, 974 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{35}F_3O_3Li$ $[M+Li]^+$: 411.2693, found: 411.2693.

36 **S11**

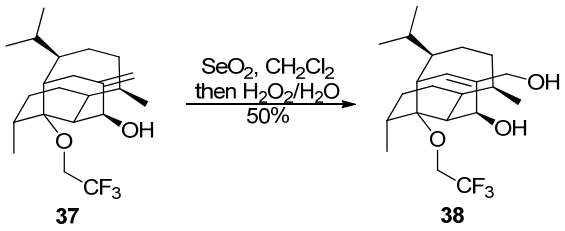
In a high-pressure tube, a mixture of triphenylphosphine (32.6 mg, 0.124 mmol), imidazole (11.2 mg, 0.165 mmol), iodine (31.5 mg, 0.124 mmol) and alcohol (33.5 mg, 0.0828 mmol) in THF (1.5 mL) was heated to 65 °C and stirred for 5.0 h. The reaction was then cooled to r.t., diluted with ethyl acetate (5 mL), washed with 10% $Na_2S_2O_3$ solution (2 × 3 mL) and brine (3 mL), dried over anhydrous Na_2SO_4, filtered and concentrated on rotovap. The residue was loaded on a silica gel column and eluted with 5% diethyl ether/hexanes. The eluate was collected and concentrated on rotovap then briefly on high vacuum to give a white solid (27.8 mg, 68% for two steps). This product was used immediately afterward. (Note: The product was unstable when concentrated; partial decomposition was observed after it was dried on high vacuum overnight at room temperature.)



S11 **37**

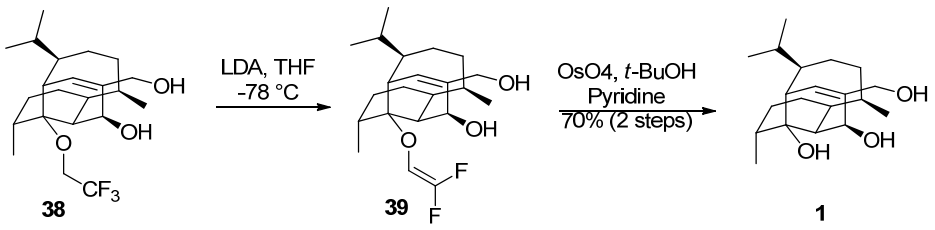
Commercial zinc powder was stirred with 1 N HCl solution for 5 min, and then the acid solution was removed by a pipette. The zinc residue was washed with water (3 ×), absolute ethanol (3 ×) and dry diethyl ether (3 ×). (The wash solutions were removed each time by a pipette.) The material was then dried on high vacuum overnight. The pre-treated zinc powder (73.4 mg, 1.12 mmol) and copper(I) iodide (106.6 mg, 0.560 mmol) are sonicated under N_2 in aqueous ethanol (4.5 ml, 40% H_2O, v/v) for 5 min. A mixture of iodide (28.8 mg, 0.0560 mmol) in ethanol (2.0 ml) was added to the resulting black suspension and the sonication was continued for 1.5 h. The reaction was quenched with saturated NH_4Cl solution (1.0

mL) then filtered over a Celite pad and washed with diethyl ether. The filtrate was extracted with ether (3 × 5 mL), and the combined extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (10% diethyl ether/hexanes) to give a colorless oil (16.7 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.09 (s, 1H), 5.03 (s, 1H), 4.26 (d, *J* = 7.9 Hz, 1H), 4.05 (dq, *J* = 10.3, 8.3 Hz, 1H), 3.81 (dq, *J* = 10.3, 8.3 Hz, 1H), 2.75 (d, *J* = 7.8 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.41 (d, *J* = 4.8 Hz, 1H), 2.31 (d, *J* = 16.2 Hz, 1H), 2.16 (pd, *J* = 7.1, 4.1 Hz, 1H), 2.06 (d, *J* = 7.6 Hz, 1H), 1.93 (dq, *J* = 13.6, 7.0 Hz, 1H), 1.84 (dtd, *J* = 14.0, 6.8, 4.3 Hz, 1H), 1.78 (m, 1H), 1.71 (m, 1H), 1.68 – 1.46 (m, 4H), 1.46 – 1.21 (m, 4H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.97 – 0.91 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.36, 124.50 (q, *J* = 277.9 Hz), 113.11, 84.37, 75.62, 60.78 (q, *J* = 33.8 Hz), 47.92, 44.98, 40.61, 38.69, 36.02, 36.00, 33.35, 31.23, 29.04, 28.89, 28.56, 26.67, 25.36, 21.66, 20.76, 15.87; IR (film) 3417, 2954, 2931, 2875, 1454, 1393, 1276, 1159, 1118, 972, 906, 879, 734 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{35}F_3O_2Li$ [M+Li]$^+$: 395.2744, found: 395.2734.



37 **38**

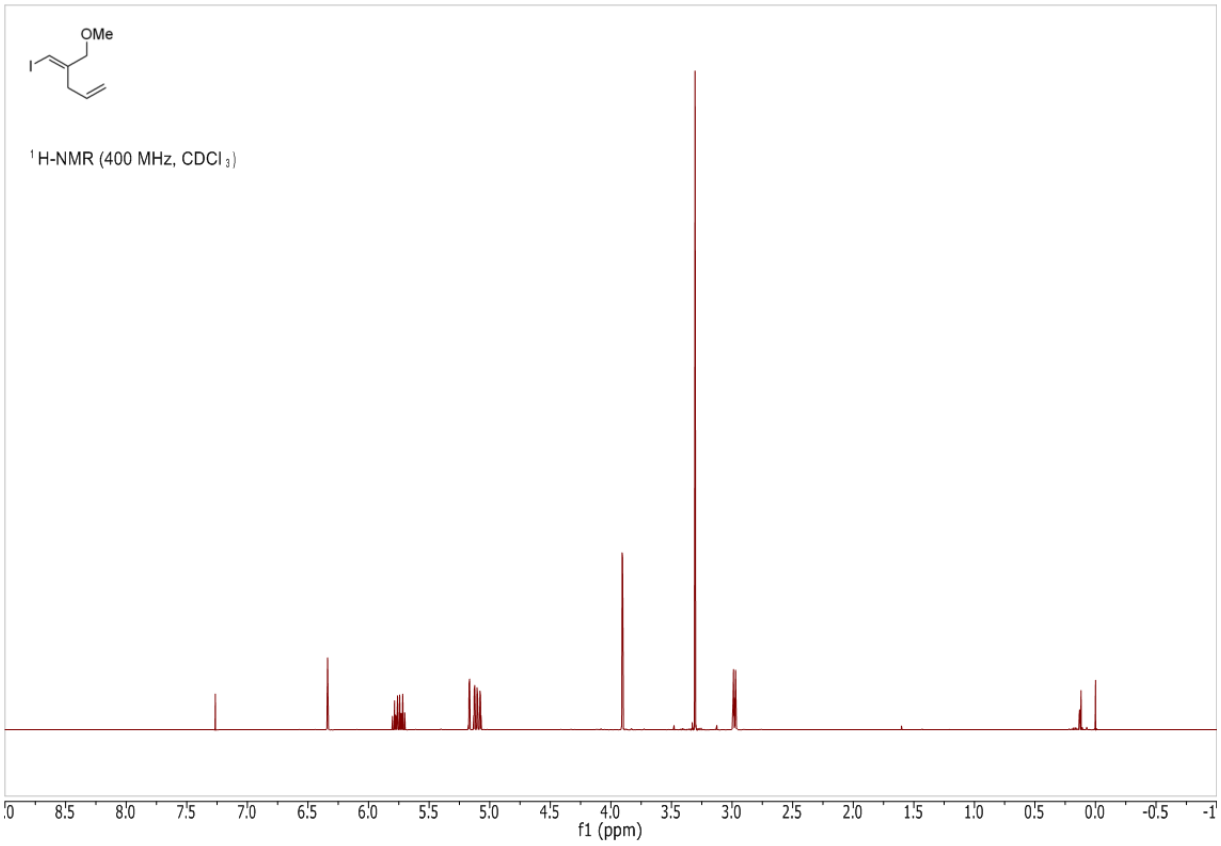
A mixture of olefin (12.0 mg, 0.0309 mmol) and selenium dioxide (17.1 mg, 0.154 mmol) in CH_2Cl_2 (3.0 mL) was stirred at r.t. for 6 h then hydrogen peroxide (30 wt% in water, 0.035 mL, 0.309 mmol) was added and stirred for 16 h. The reaction was diluted with ethyl acetate (6 mL) and washed with 10% $NaHSO_3$ solution (2 mL), saturated $NaHCO_3$ solution (2 mL) and brine (2 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (15% ethyl acetate/hexanes) to give a colorless oil (6.3 mg, 50% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.72 (d, *J* = 5.8 Hz, 1H), 4.34 – 4.16 (m, 2H), 4.06 (d, *J* = 11.1 Hz, 1H), 3.71 – 3.52 (m, 2H), 2.84 (d, *J* = 11.2 Hz, 1H), 2.60 (s, 1H), 2.40 (d, *J* = 4.6 Hz, 1H), 2.27 (d, *J* = 5.7 Hz, 1H), 2.22 – 2.07 (m, 2H), 2.06 – 1.96 (m, 1H), 1.88 (ddt, *J* = 25.5, 12.9, 4.8 Hz, 2H), 1.66 (pd, *J* = 6.8, 3.9 Hz, 1H), 1.60 – 1.49 (m, 1H), 1.49 – 1.31 (m, 4H), 1.31 – 1.12 (m, 2H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.93, 124.47, 124.38 (q, *J* = 278.3 Hz), 83.60, 72.61, 66.83, 59.81 (q, *J* = 33.8 Hz), 50.87, 45.86, 40.27, 37.64, 35.85, 33.80, 33.28, 30.63, 29.82, 28.91, 28.46, 26.52, 21.14, 19.73, 17.54; IR (film) 3429, 2953, 2927, 2358, 2345, 1269, 1161, 1111, 1006, 974, 894 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{35}F_3O_3Li$ [M+Li]$^+$: 411.2693, found: 411.2682.



38 **39** **1**

Trifluoroethyl ether (0.7 mg, 0.0017 mmol) was dissolved in THF (0.15 mL) and cooled to -78 °C, and freshly prepared LDA (0.5 M in THF, 0.27 mL, 0.136 mmol) was added slowly. After addition was completed, the reaction was stirred at -78 °C for 30 min. then quenched with saturated NH_4Cl solution (0.5 mL) and extracted with ethyl acetate (3 × 1.0 mL). The combined extracts were washed with brine (1.5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. ^{1}H-NMR analysis of the crude product indicated 25% conversion of starting material to the product. The crude product was then purified by prep-TLC (60% diethyl ether/hexanes) to give the unreacted starting material and the desired product. The isolated starting material was re-subjected to the reaction condition. After three iterations, approximate 0.6 mg of desired product was obtained (judging by the integration of the ^{1}H-NMR peaks of solvent and product).

The resulting difluorovinyl ether was dissolved in pyridine (0.30 mL) and osmium tetroxide (2.5 wt% in tert-butanol, 0.05 mL, 0.0039 mmol) was added at r.t. After stirring for 30 min., the reaction was quenched by saturated $NaHSO_3$ solution (1.5 mL), diluted with THF (1.0 mL) and stirred vigorously at r.t. for 8.0 h. The reaction mixture was extracted with ethyl acetate (3 × 2.0 mL), washed with brine (2.0 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by a short column (50% acetonitrile/benzene) to give approximate 0.4 mg of desired product (judging by the integration of the ^{1}H-NMR peaks of solvent and product, 70% yield for two steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (d, *J* = 5.6 Hz, 1H), 4.30 (AB q, *J* = 12.0 Hz, 2H), 4.19 (s, 1H), 3.30 (bs, 1H), 2.45 (bs, 1H), 2.30 (d, *J* = 5.6 Hz, 1H), 2.26 (d, *J* = 3.9 Hz, 1H), 2.15 – 2.09 (m, 1H), 2.03 – 1.93 (m, 2H), 1.81 – 1.71 (m, 2H), 1.66 – 1.53 (m, 3H), 1.40 – 1.10 (m, 6H), 1.00 – 0.95 (m, 9H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (extracted from HSQC and HMBC spectra) δ 136.8, 128.4, 75.6, 72.8, 67.9, 51.3, 45.8, 44.2, 40.4, 35.9, 34.7, 33.1, 29.6, 29.0, 28.7, 27.3, 24.9, 21.5, 20.6, 15.4; IR (film) 3405, 2954, 2925, 2869, 2855, 1559, 1462, 1386, 1106, 1017, 998, 904, 736, 701 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{34}O_3Li$ $[M+Li]^+$: 329.2662, found: 329.2662.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7.5
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6.0
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5.0
4.5
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3.0
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2.0
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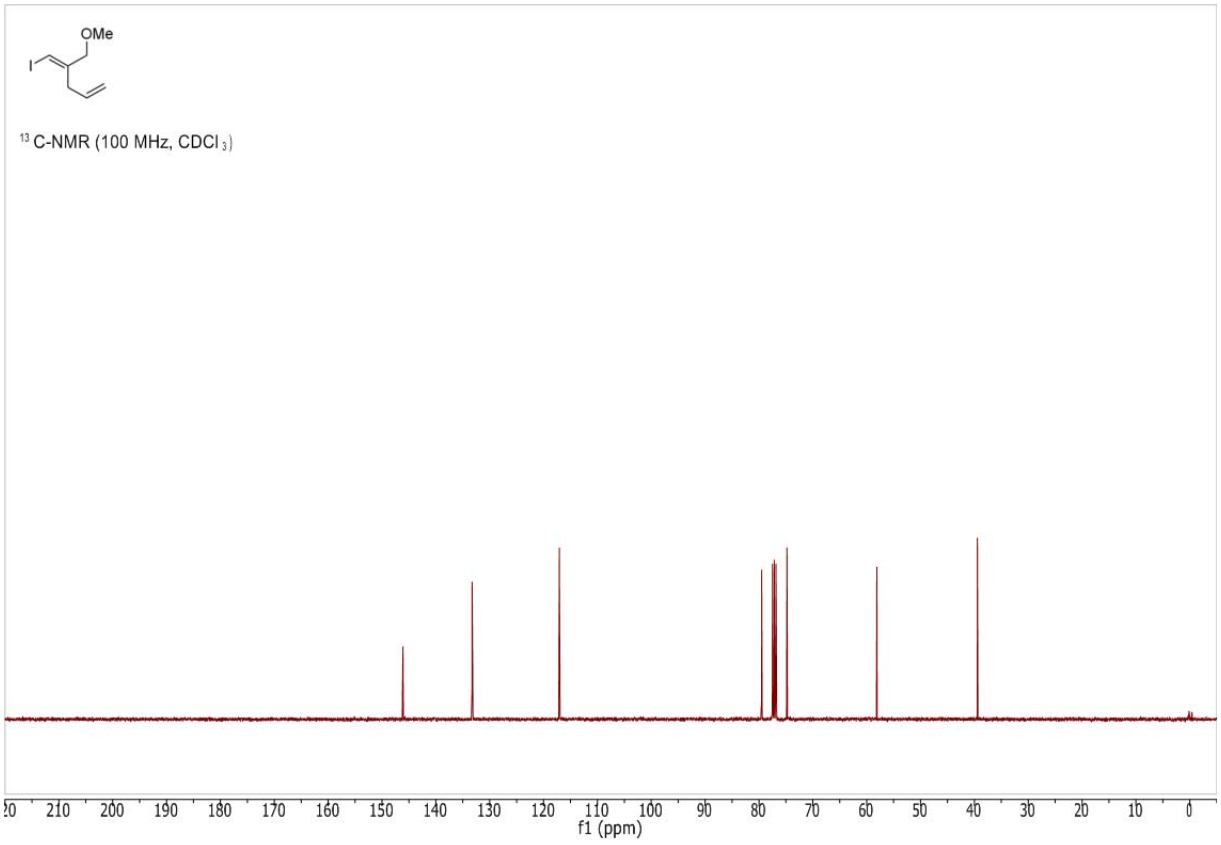
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180
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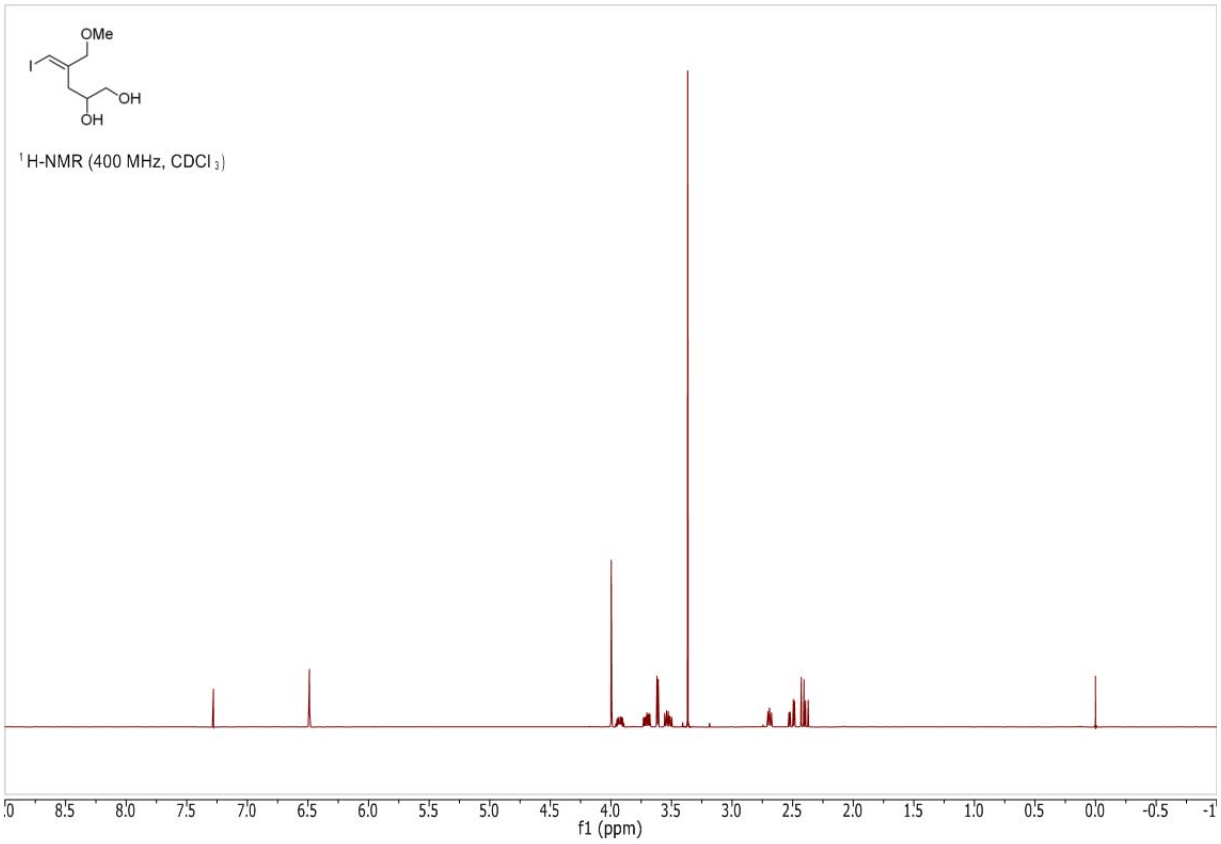
40
30
20
10
0
f1 (ppm)


OMe
I
OH
OH
1 H-NMR (400 MHz, CDCl 3)
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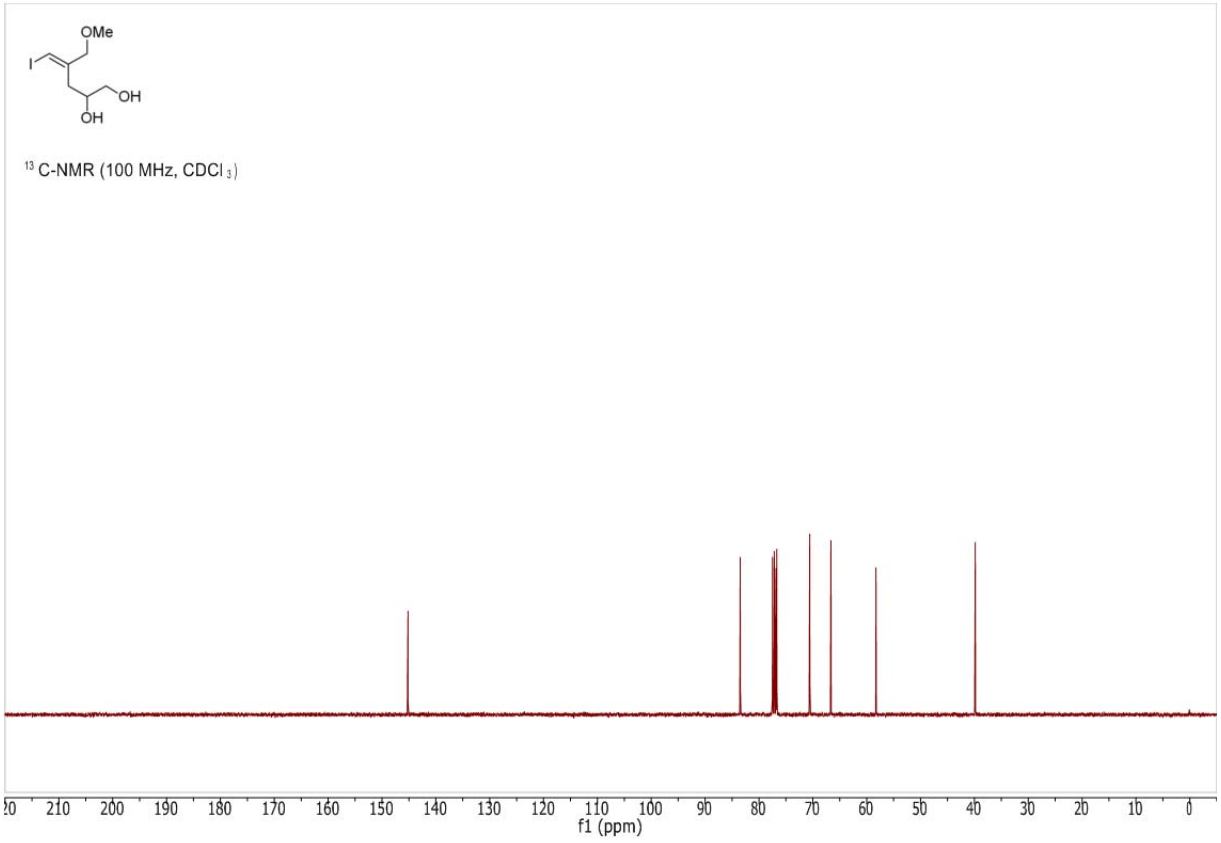
f1 (ppm)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OH
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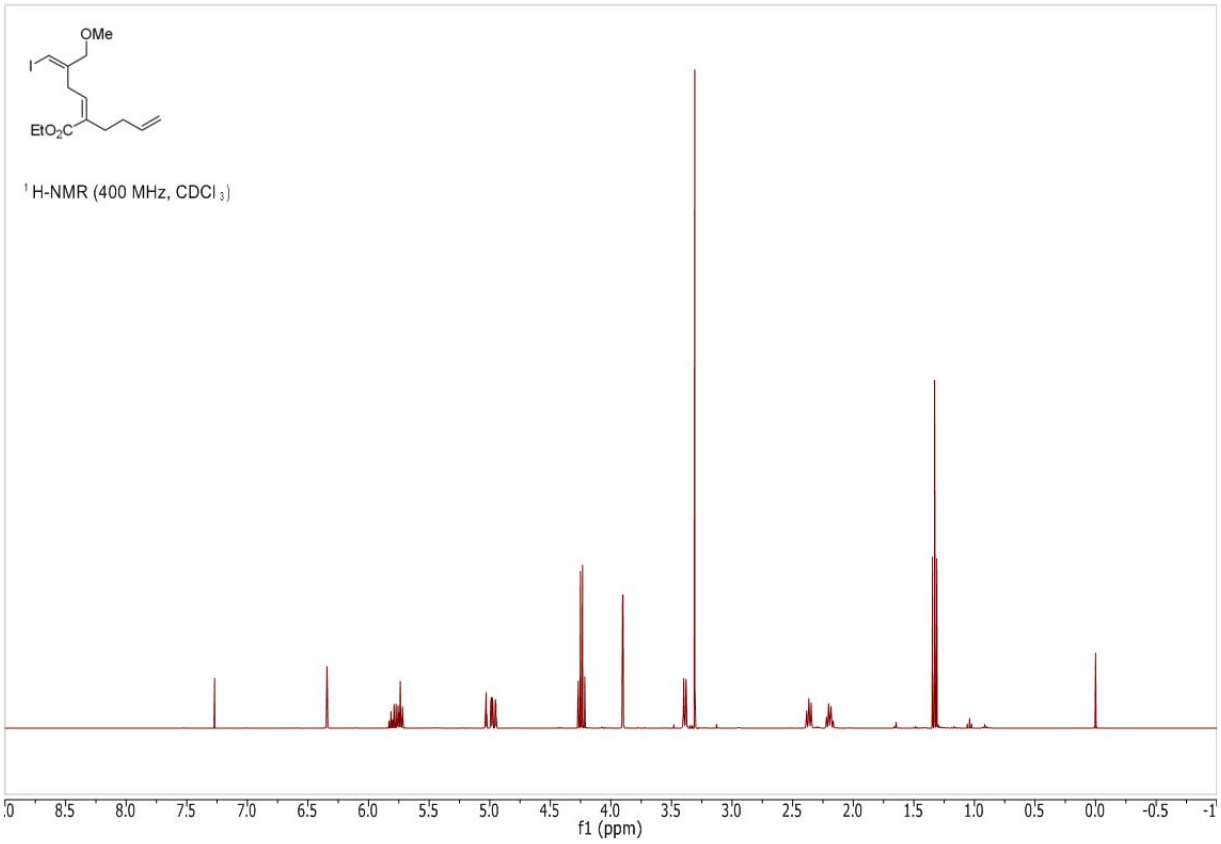
f1 (ppm)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EtO2C
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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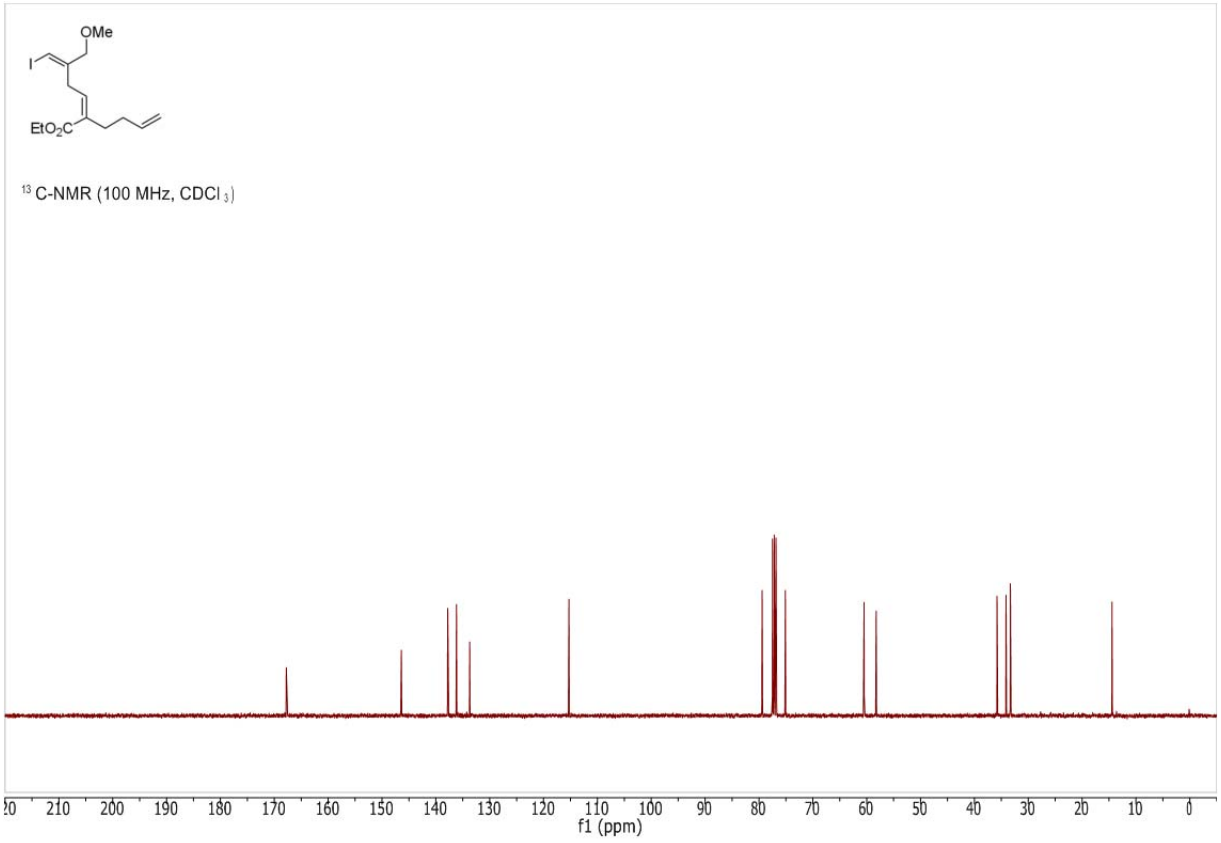
-0.5
f1 (ppm)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I
EtO2C
13 C-NMR (100 MHz, CDCl 3)
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200
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180
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100
90
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60
50
40
30
20
10
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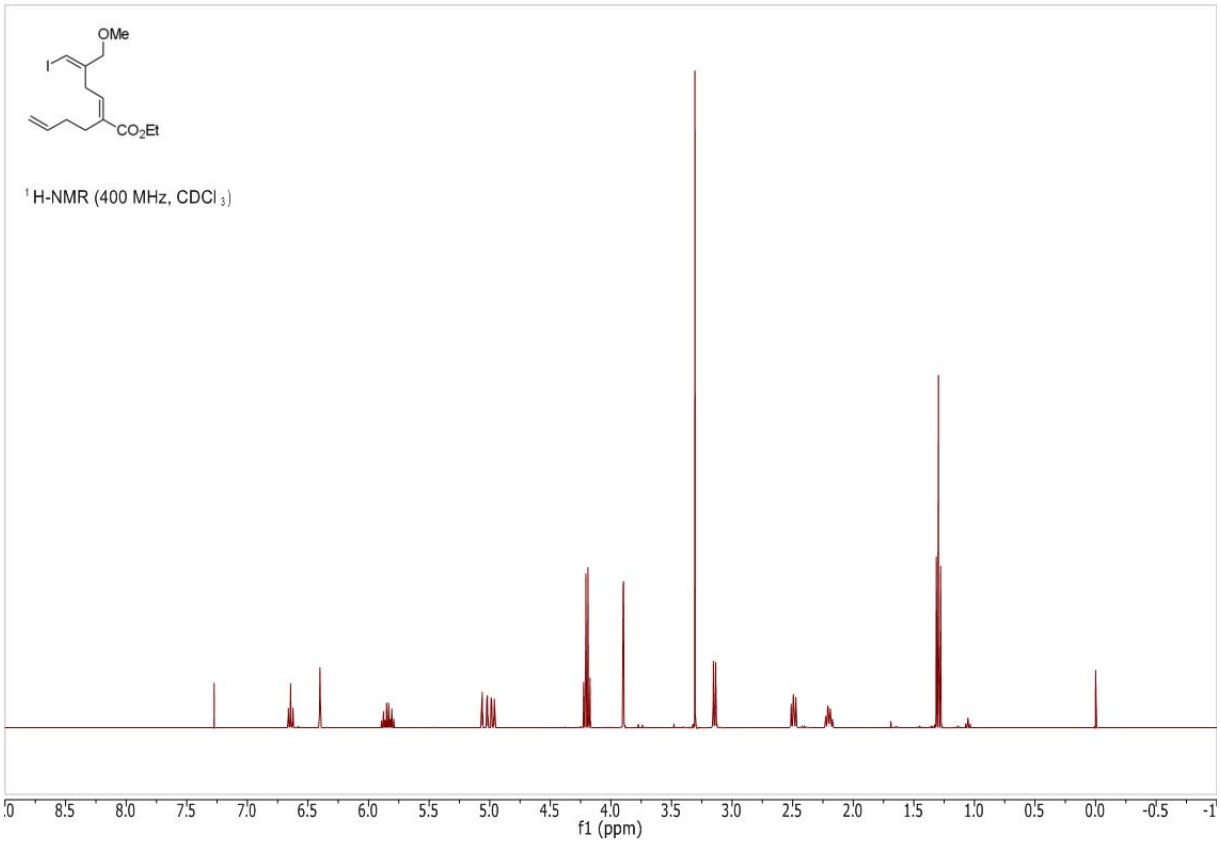
f1 (ppm)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5.0
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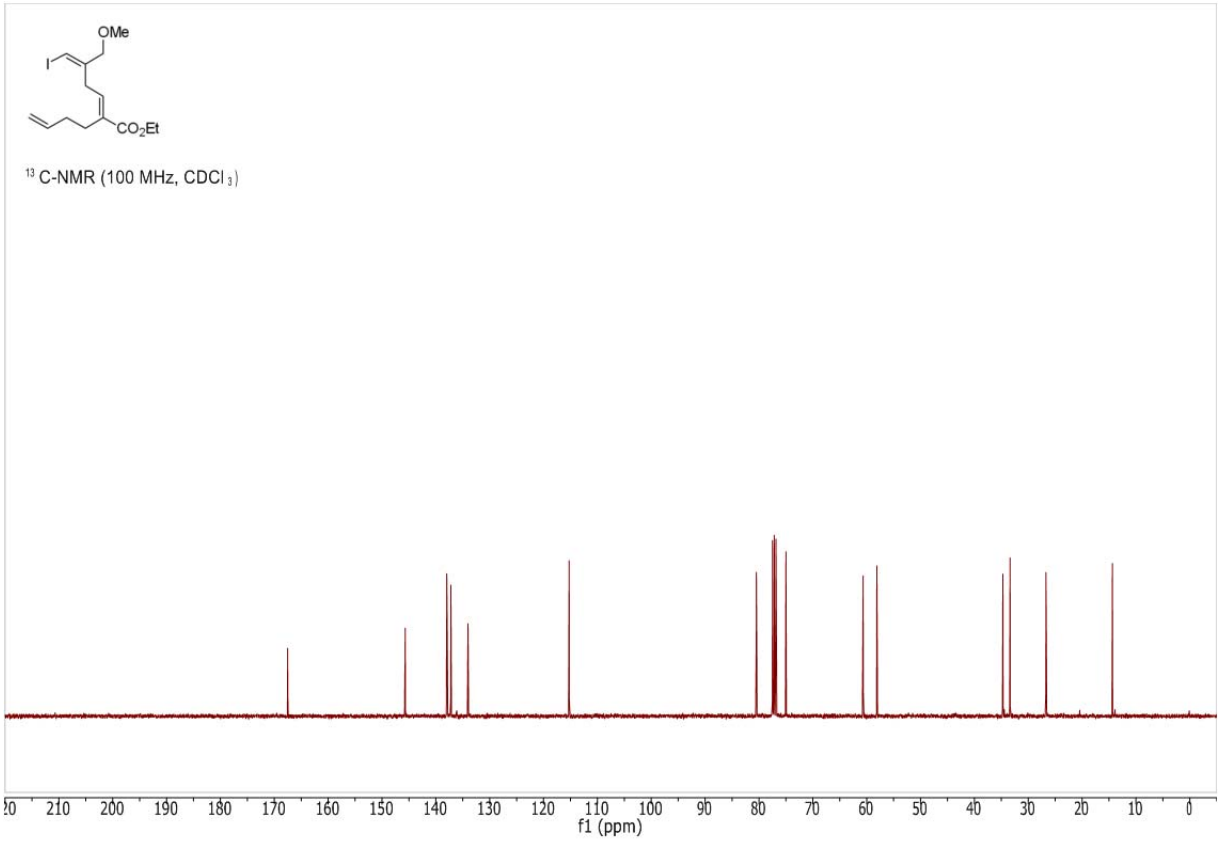
f1 (ppm)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CO2Et
13 C-NMR (100 MHz, CDCl 3)
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180
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10
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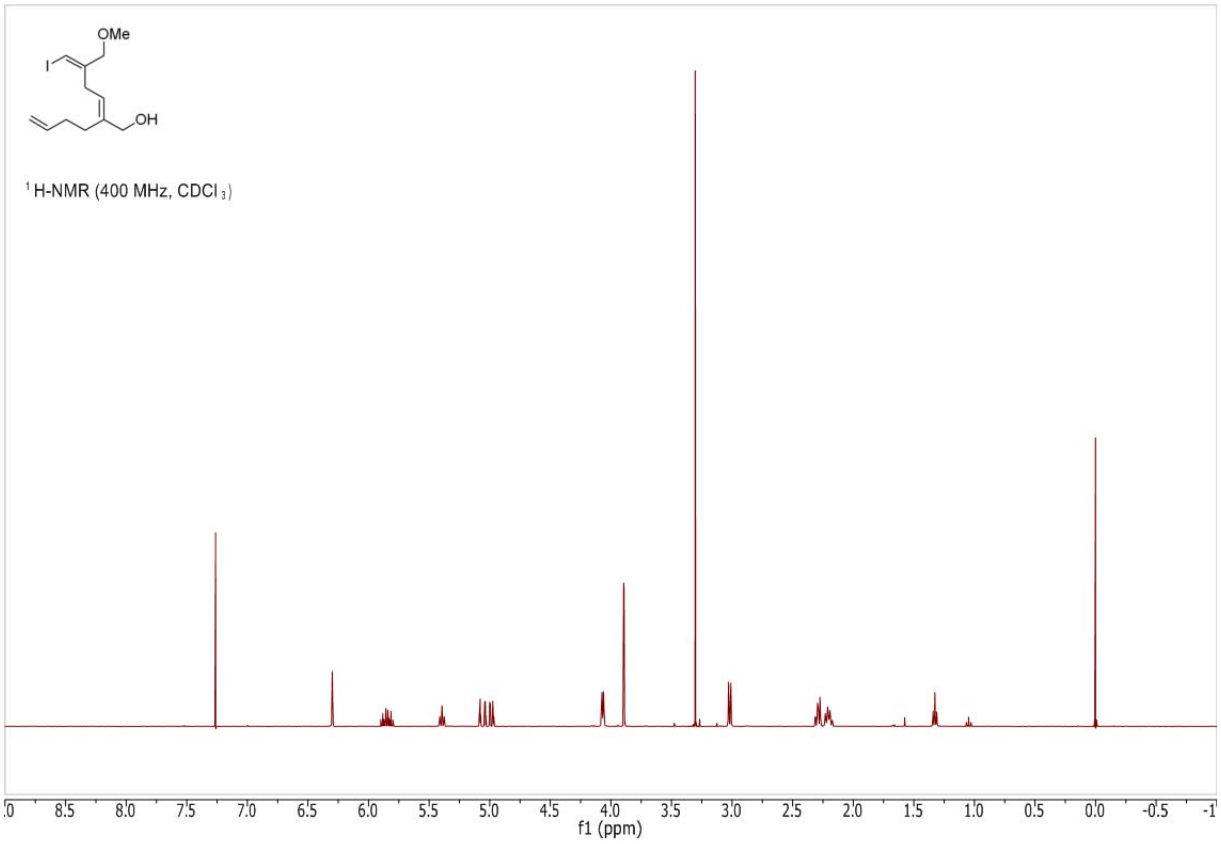
f1 (ppm)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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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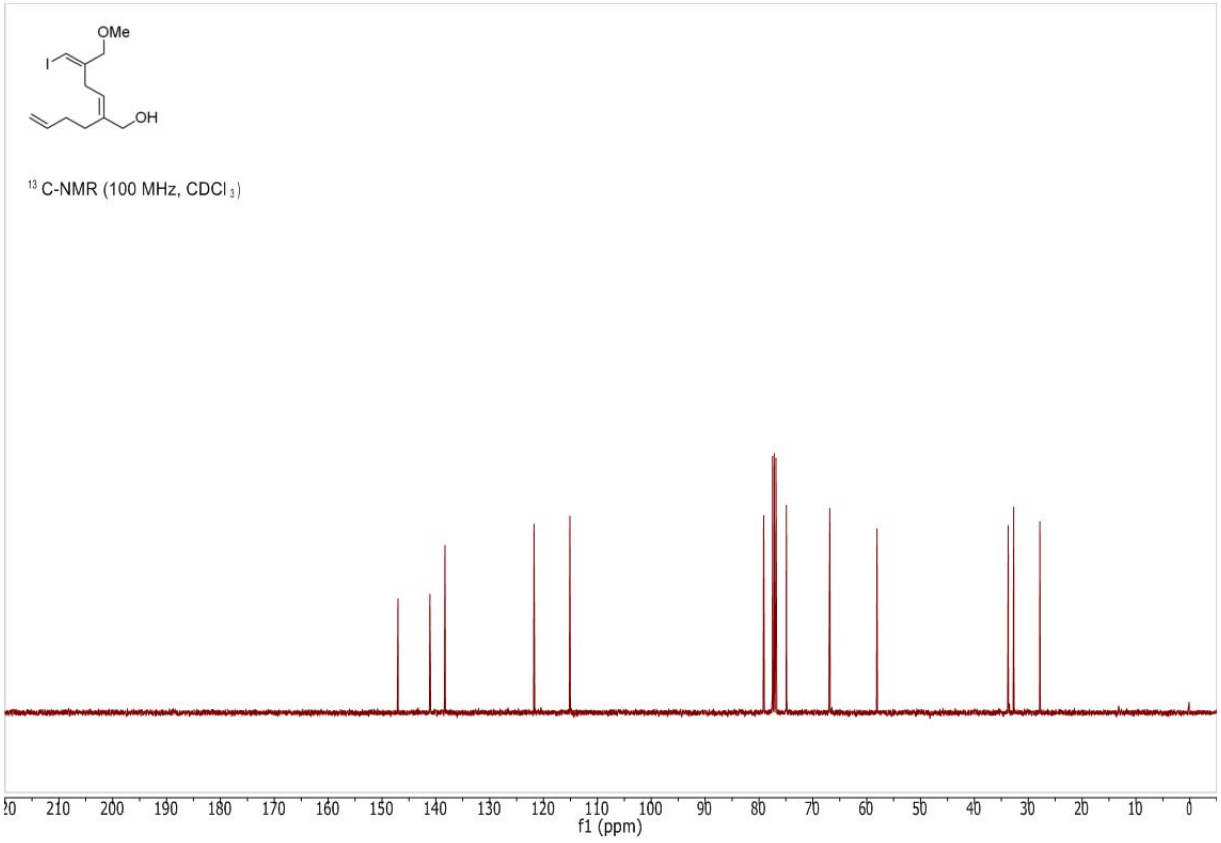
-0.5
f1 (ppm)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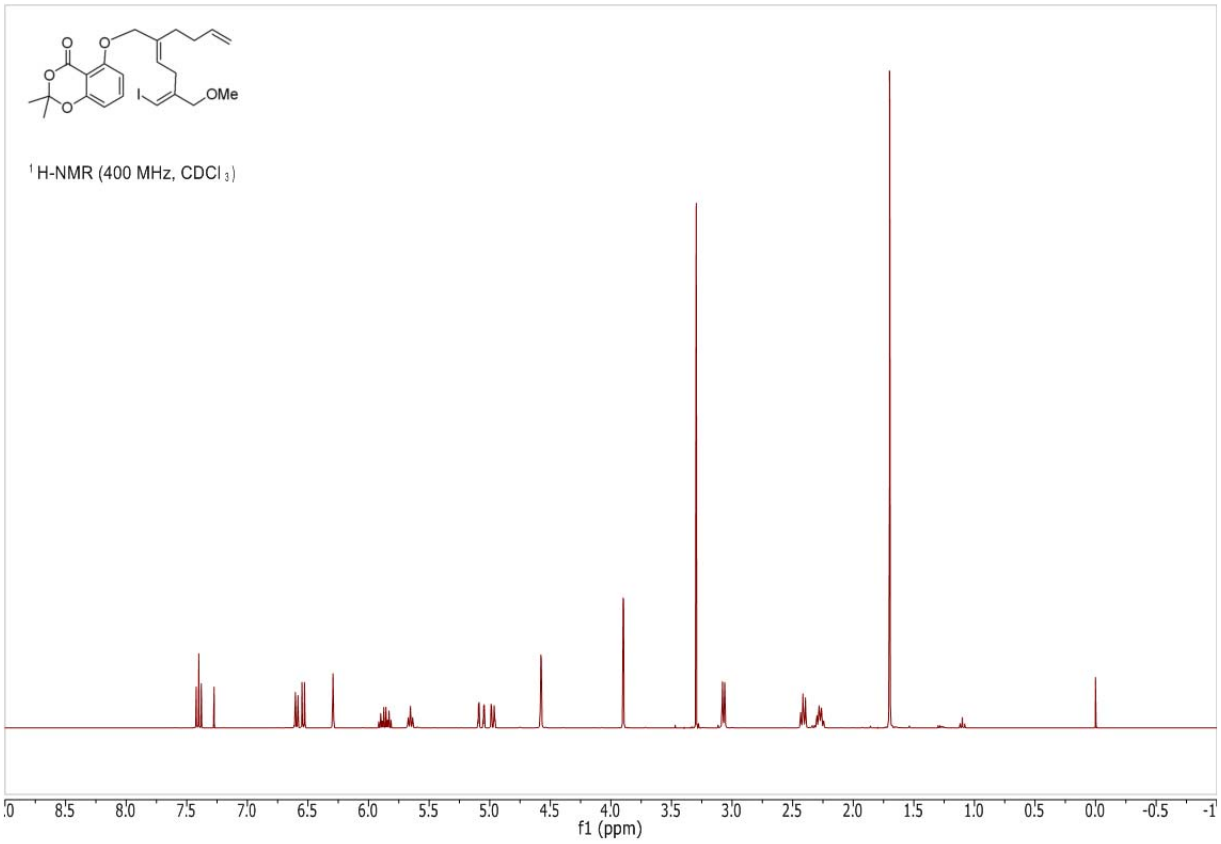
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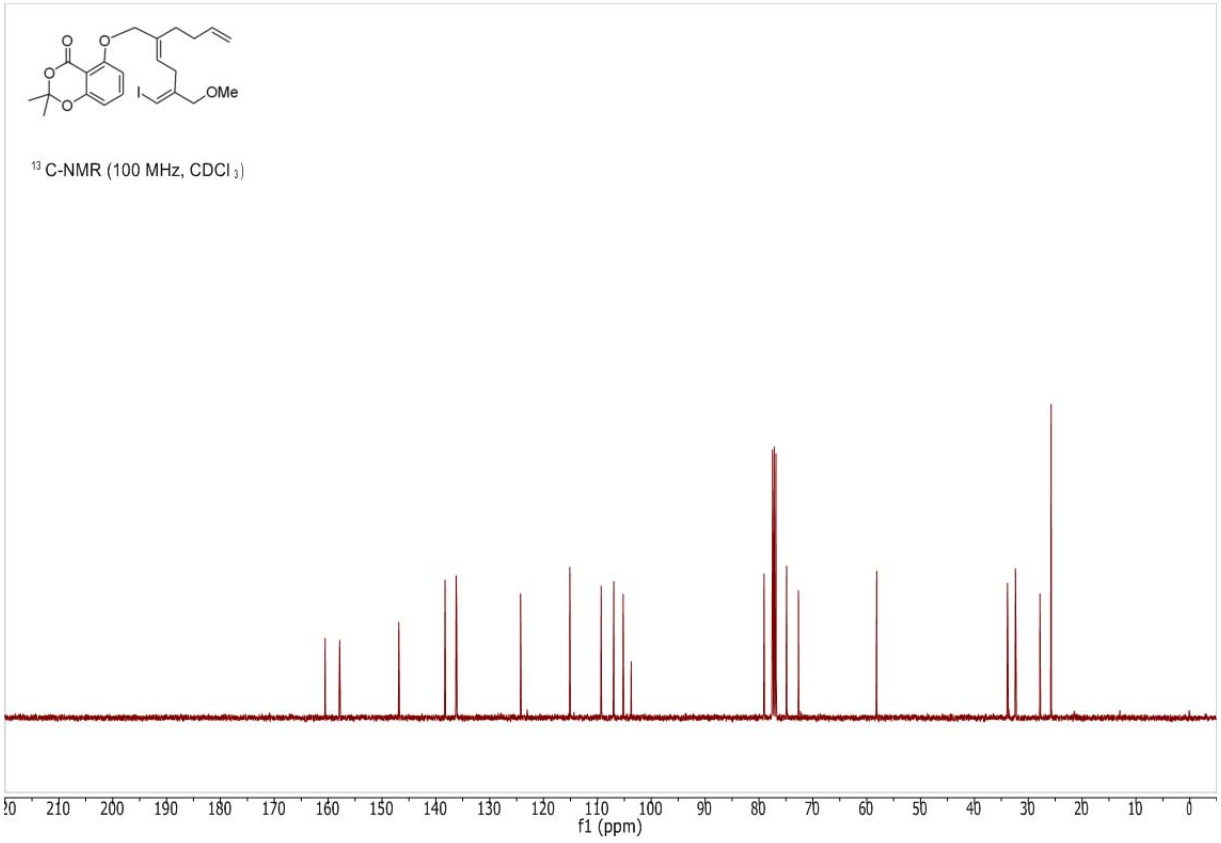
f1 (ppm)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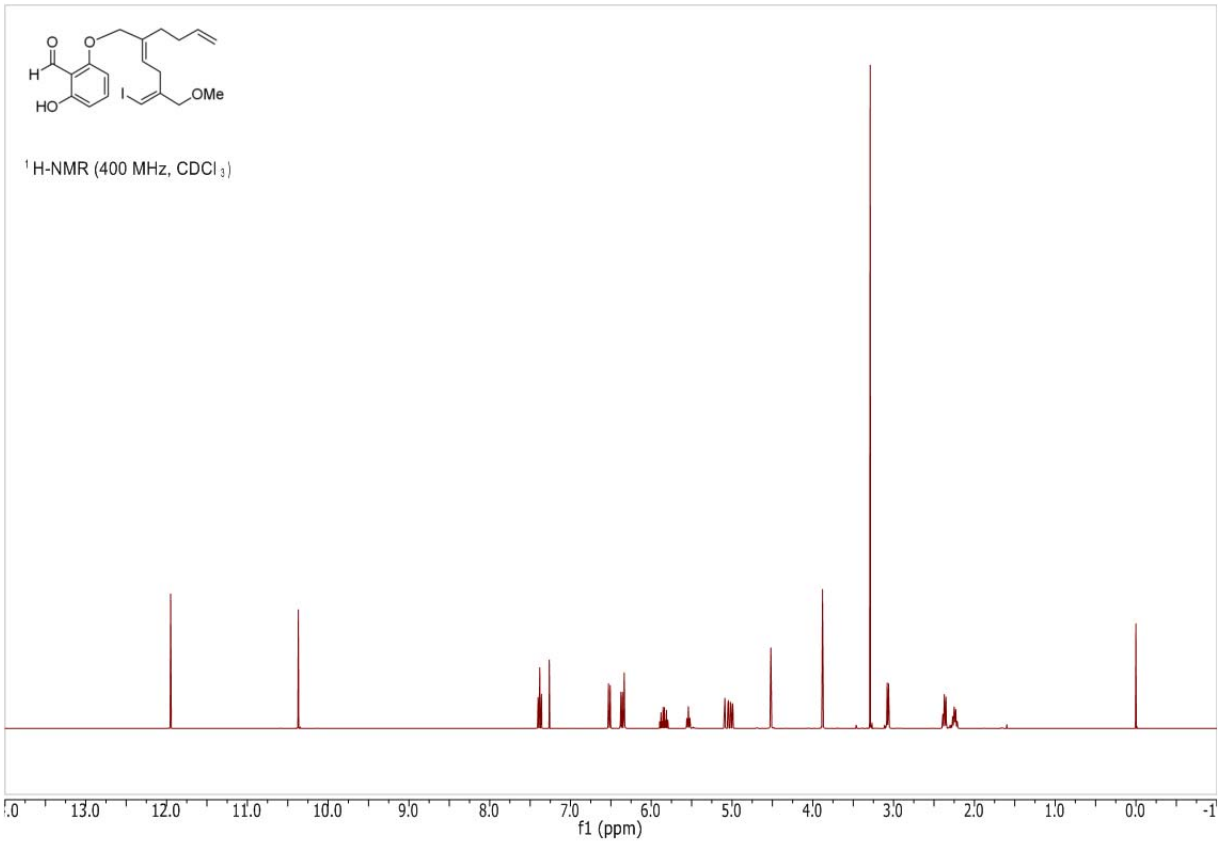
f1 (ppm)


O
H
HO
O
I
OMe
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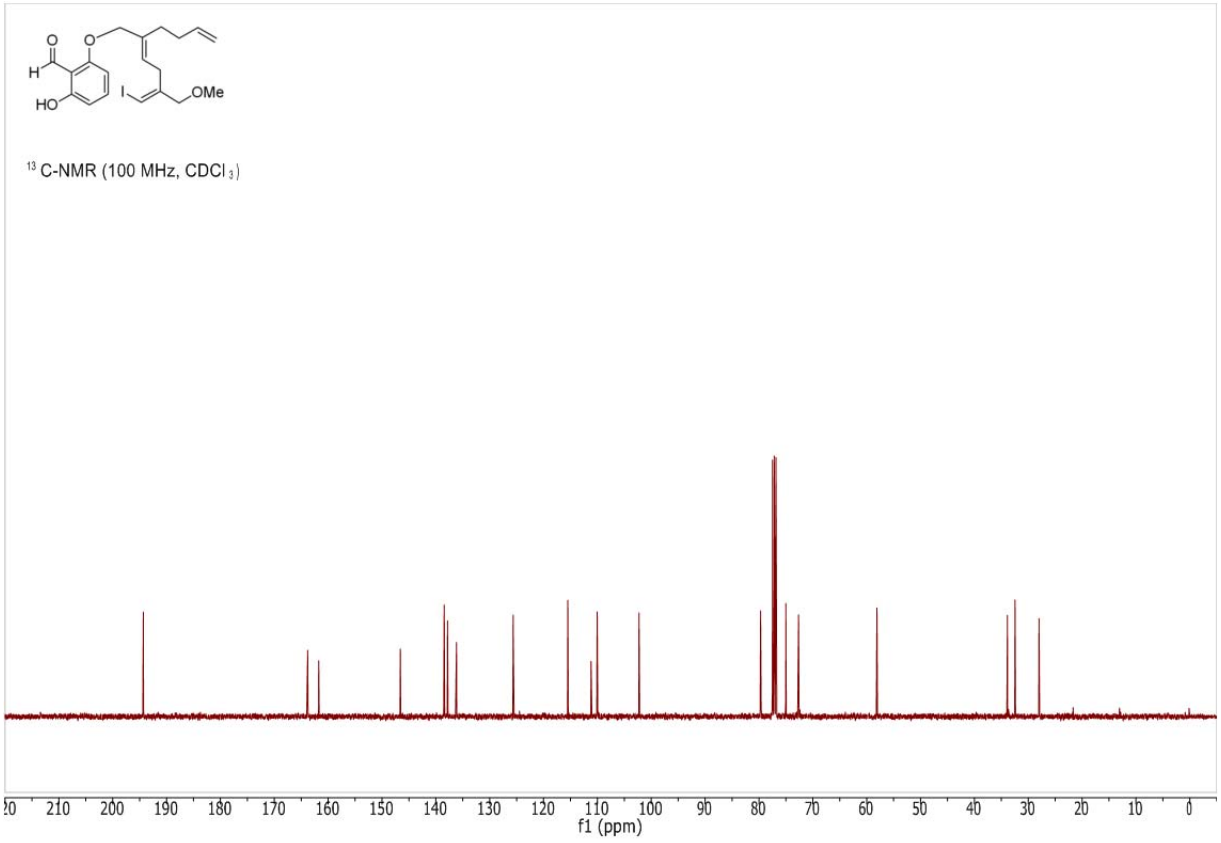
f1 (ppm)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H
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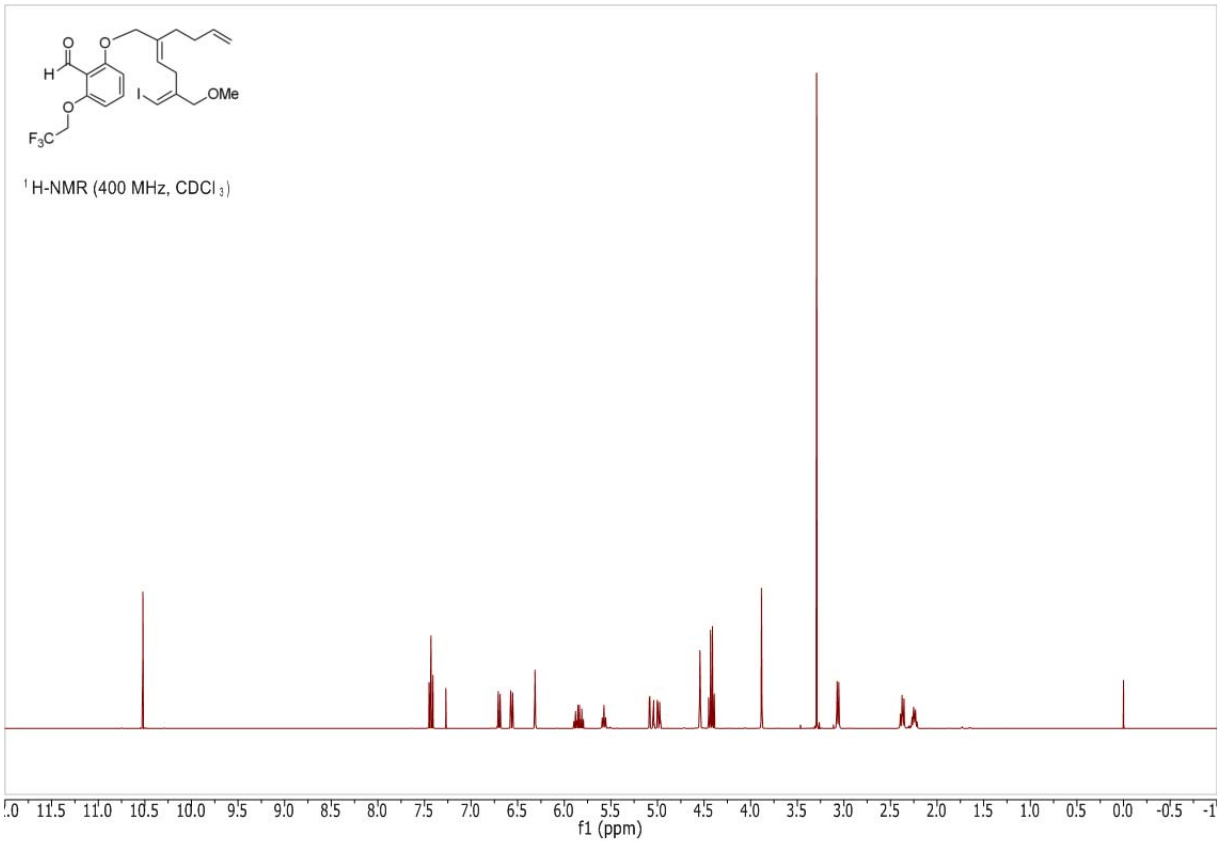
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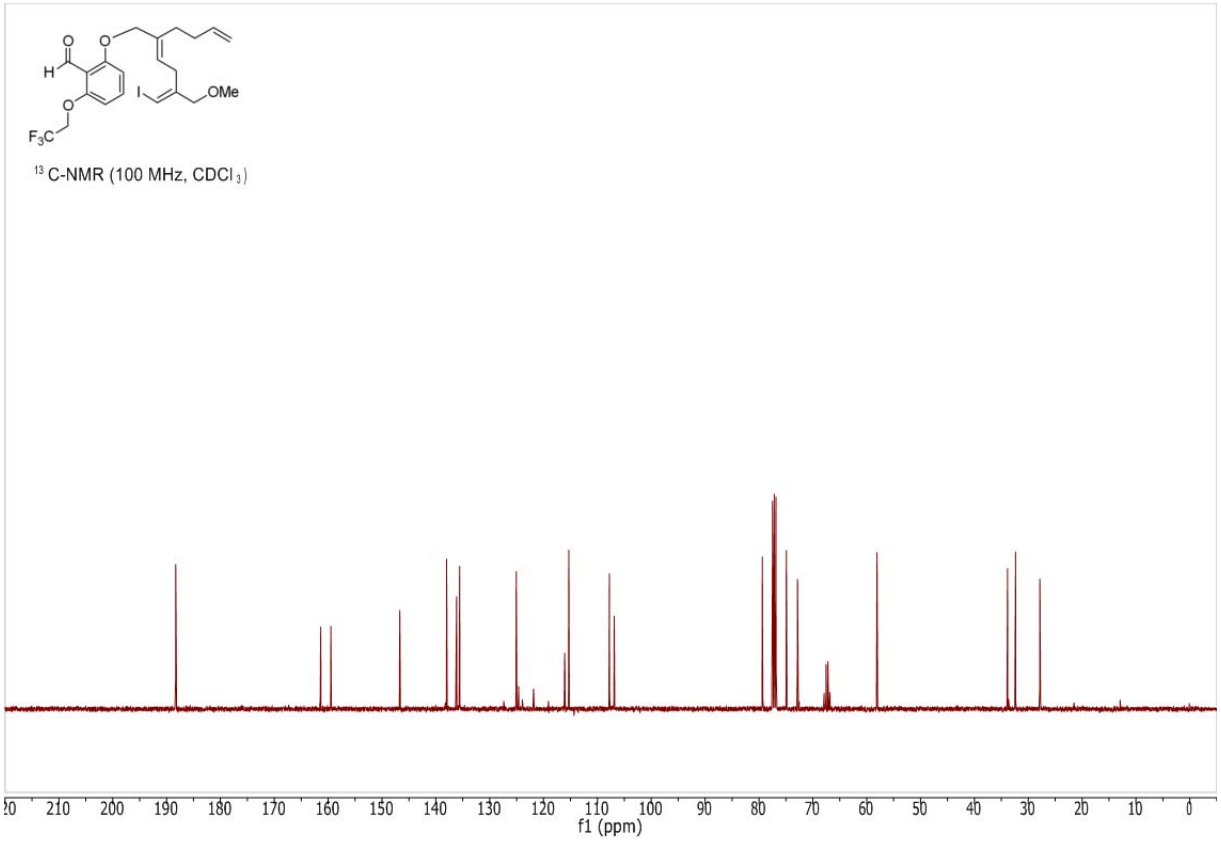
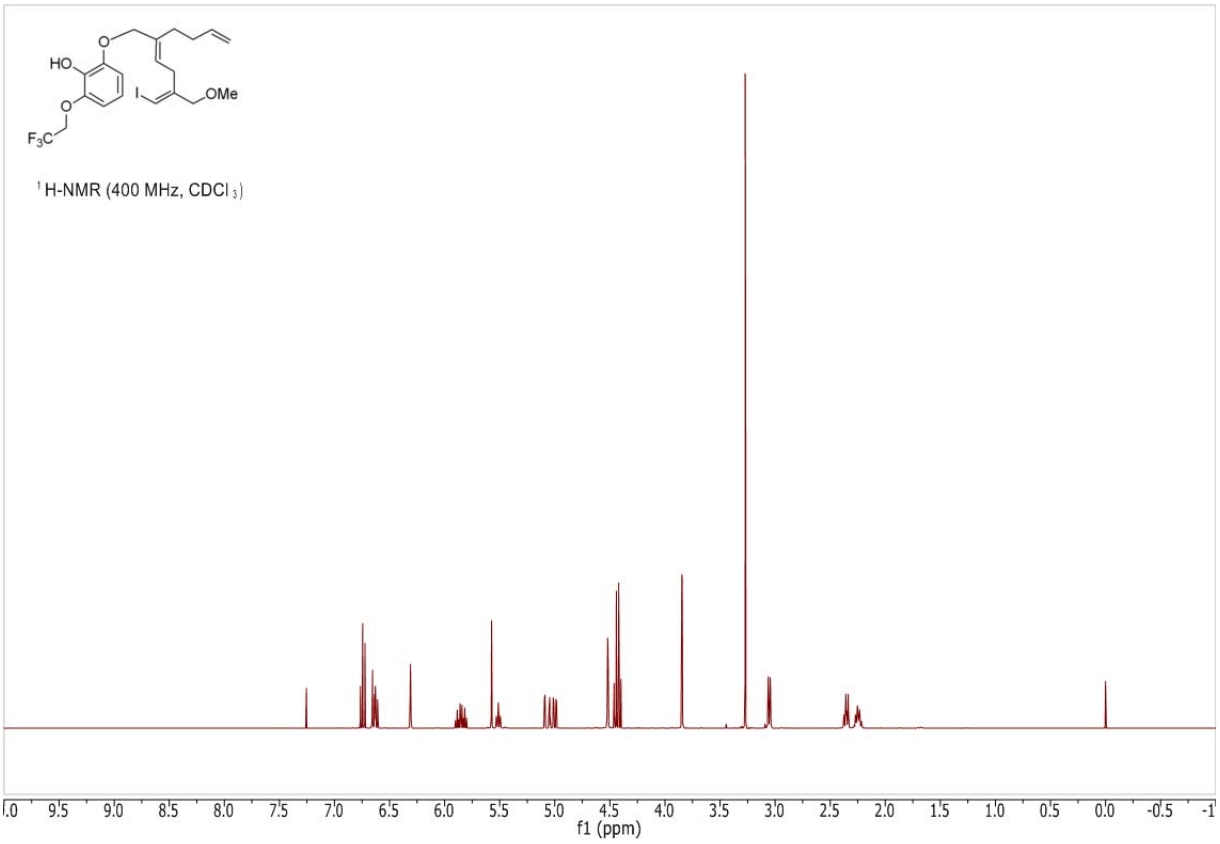
O
O
I
OMe
O
F3C
1 H-NMR (400 MHz, CDCl 3)
f1 (ppm)


H
O
O
I
OMe
O
F3C
13 C-NMR (100 MHz, CDCl 3)
f1 (ppm)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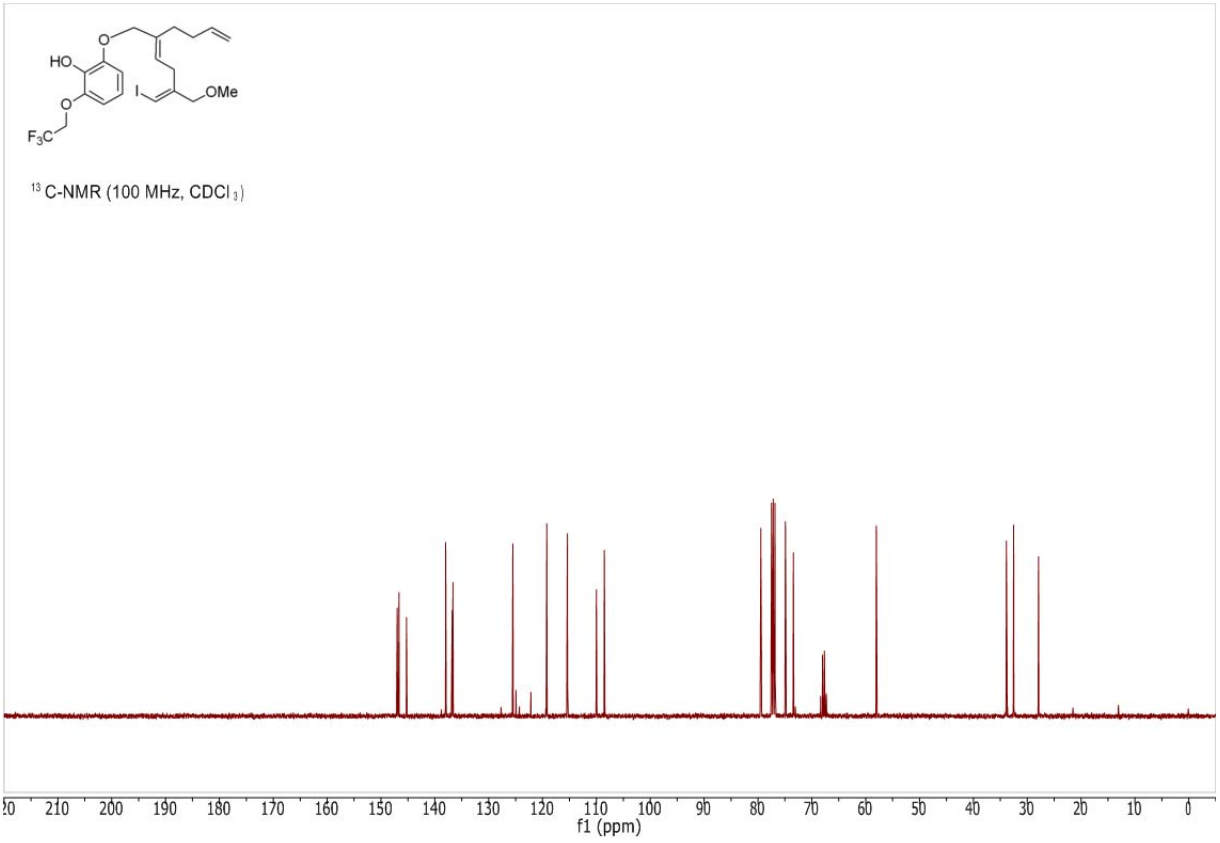
OMe
F3C
1 H-NMR (400 MHz, CDCl 3)
f1 (ppm)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O
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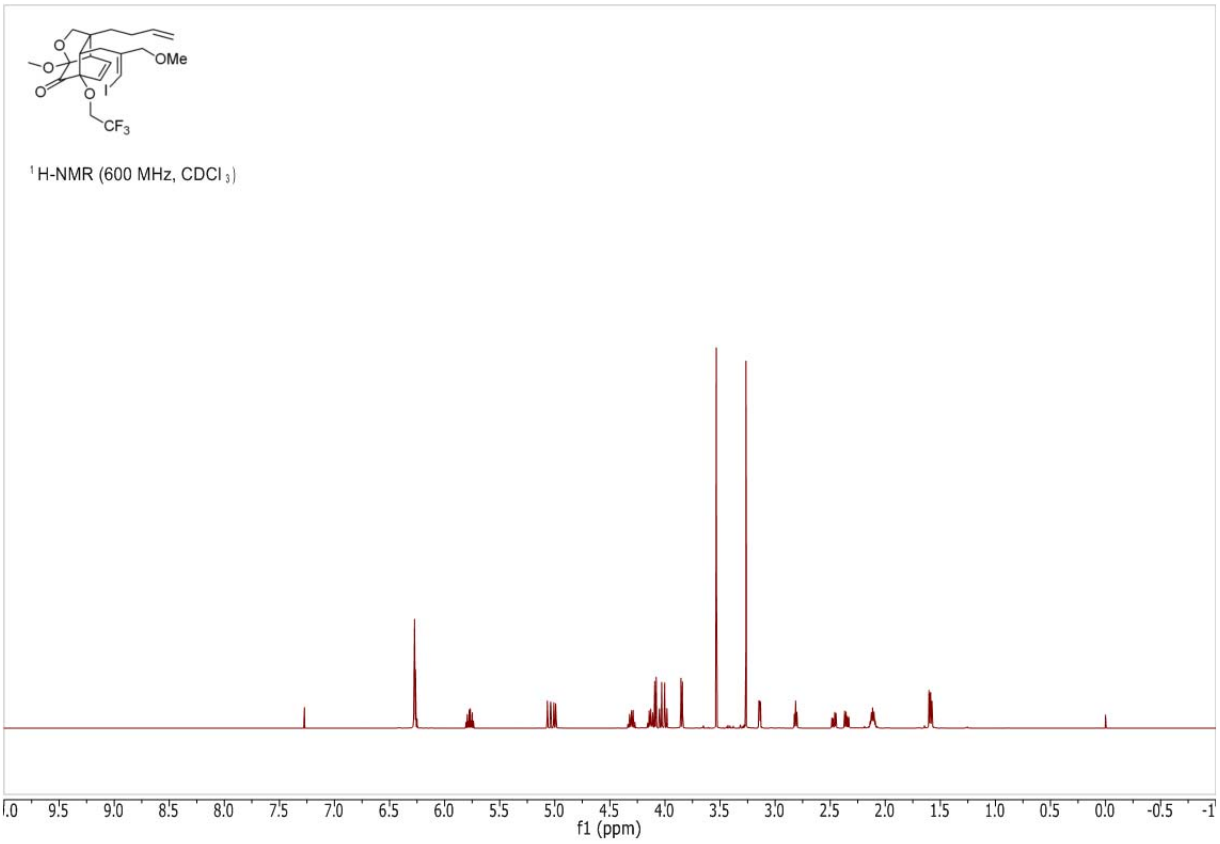
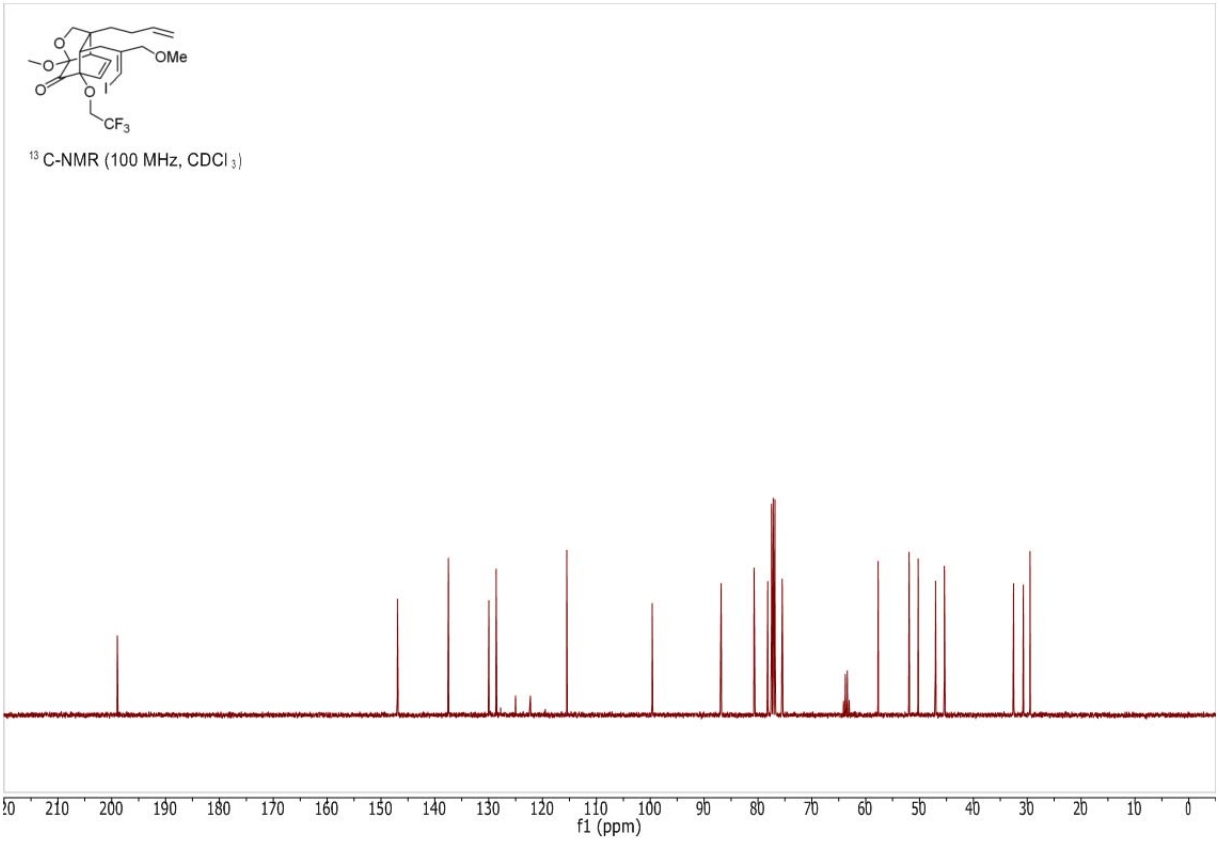
OMe
F3C
13 C-NMR (100 MHz, CDCl 3)
f1 (ppm)


OMe
CF3
1 H-NMR (600 MHz, CDCl 3)
f1 (ppm)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CF3
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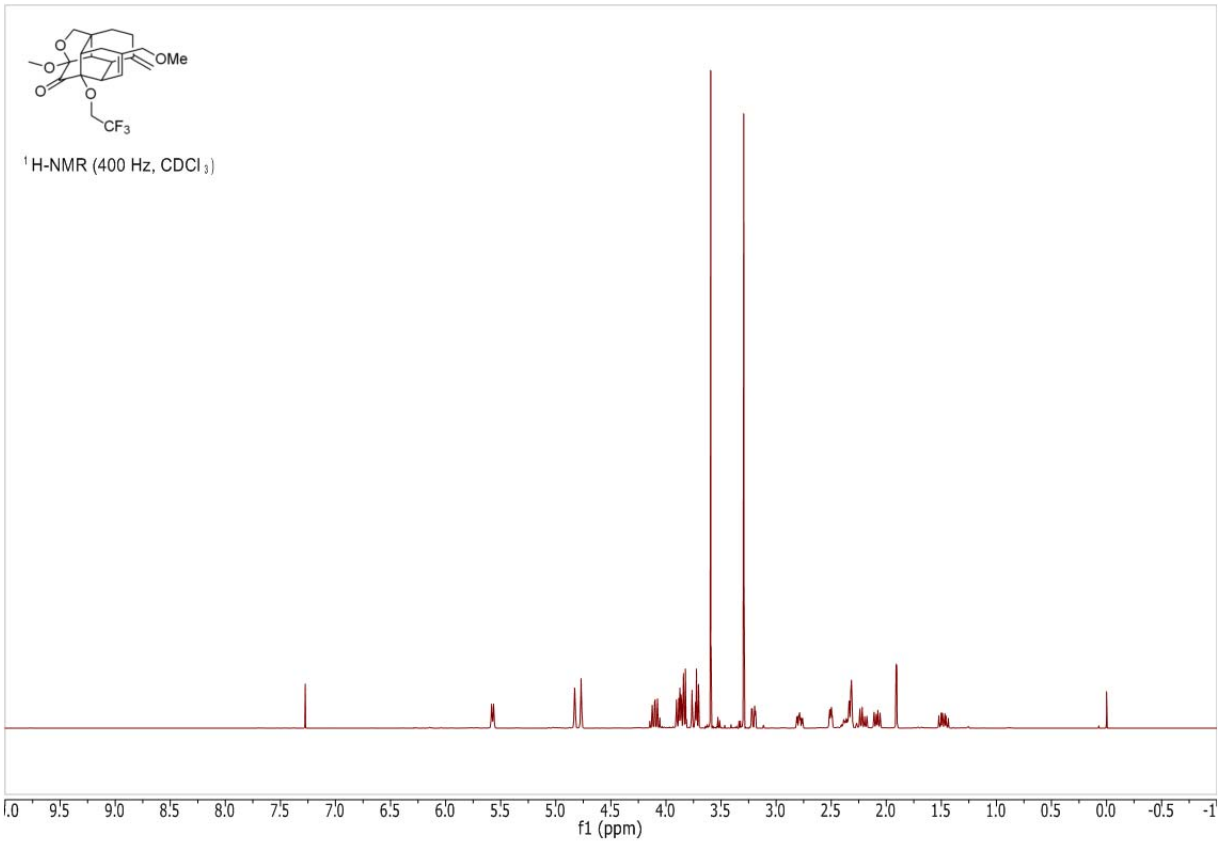
f1 (ppm)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CF3
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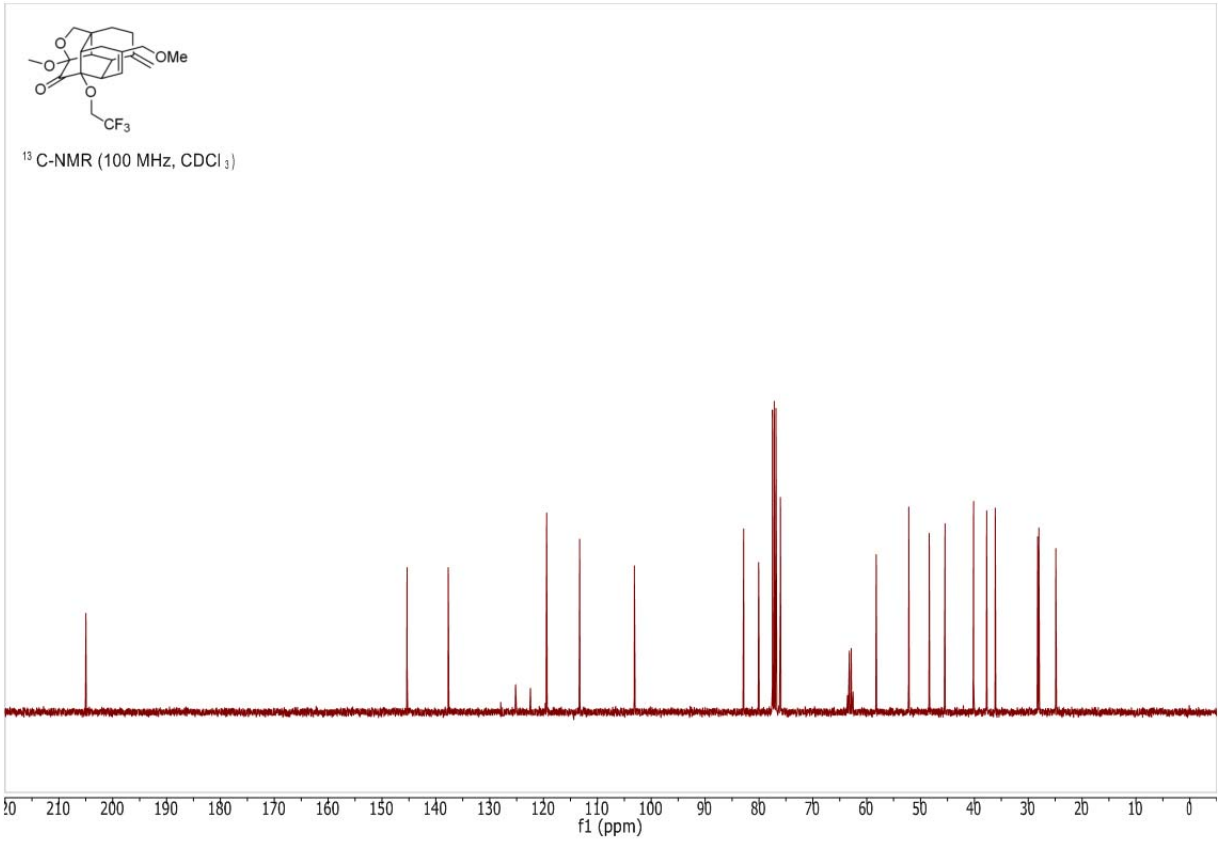
f1 (ppm)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CF3
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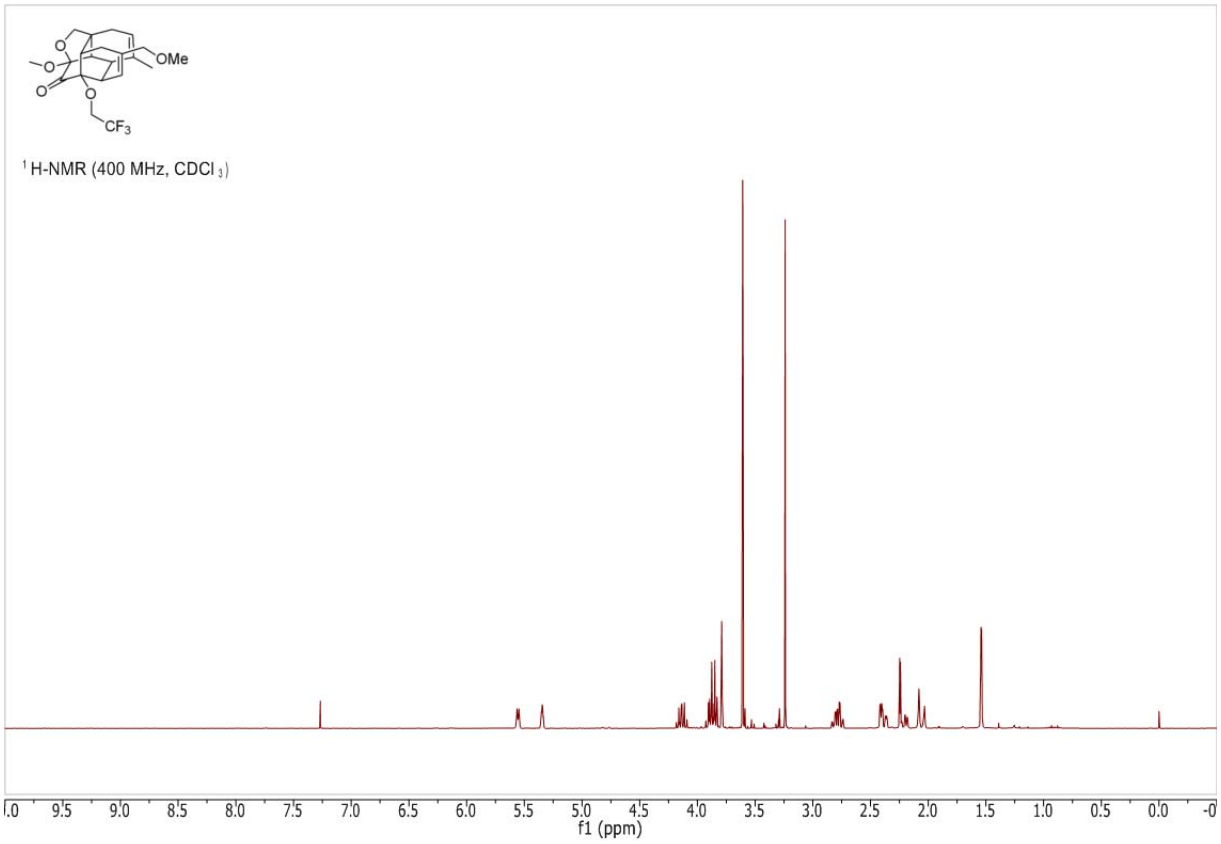
f1 (ppm)


OMe
O
O
O
CF3
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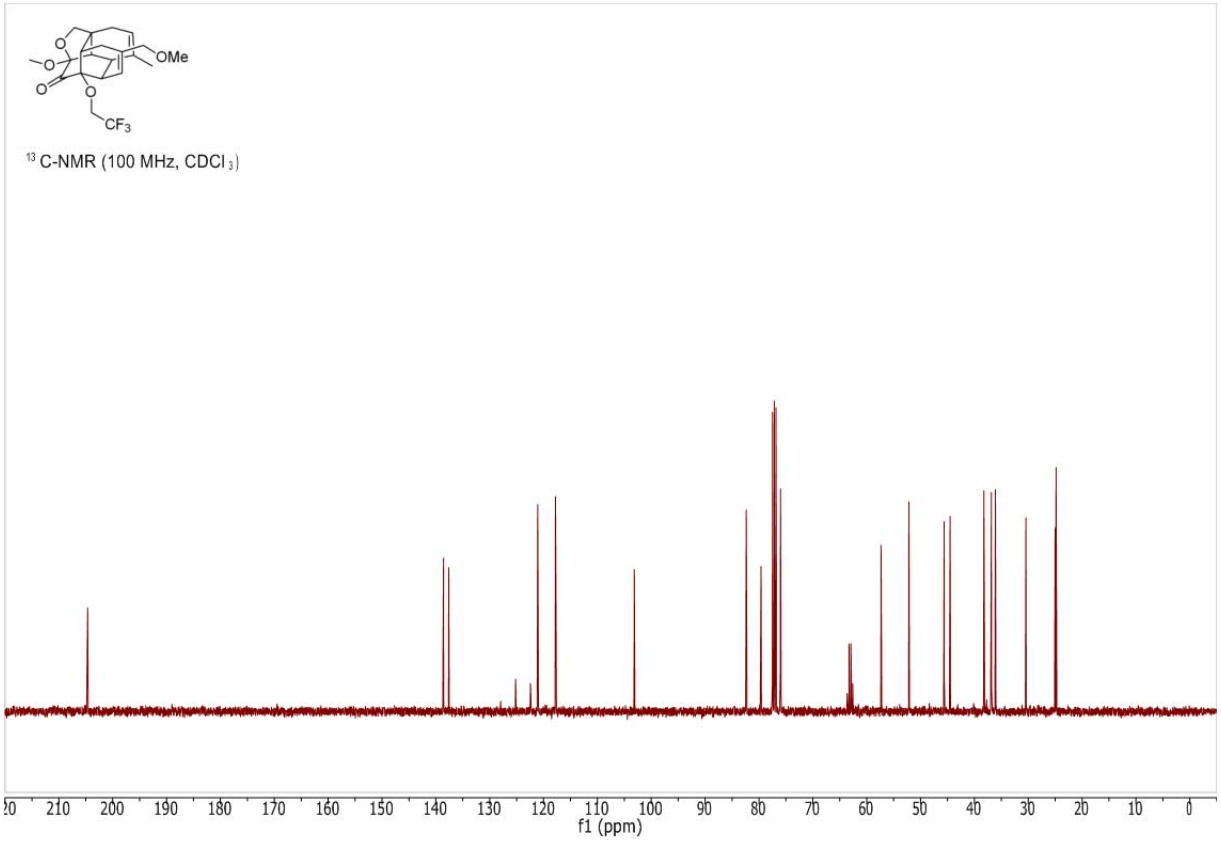
f1 (ppm)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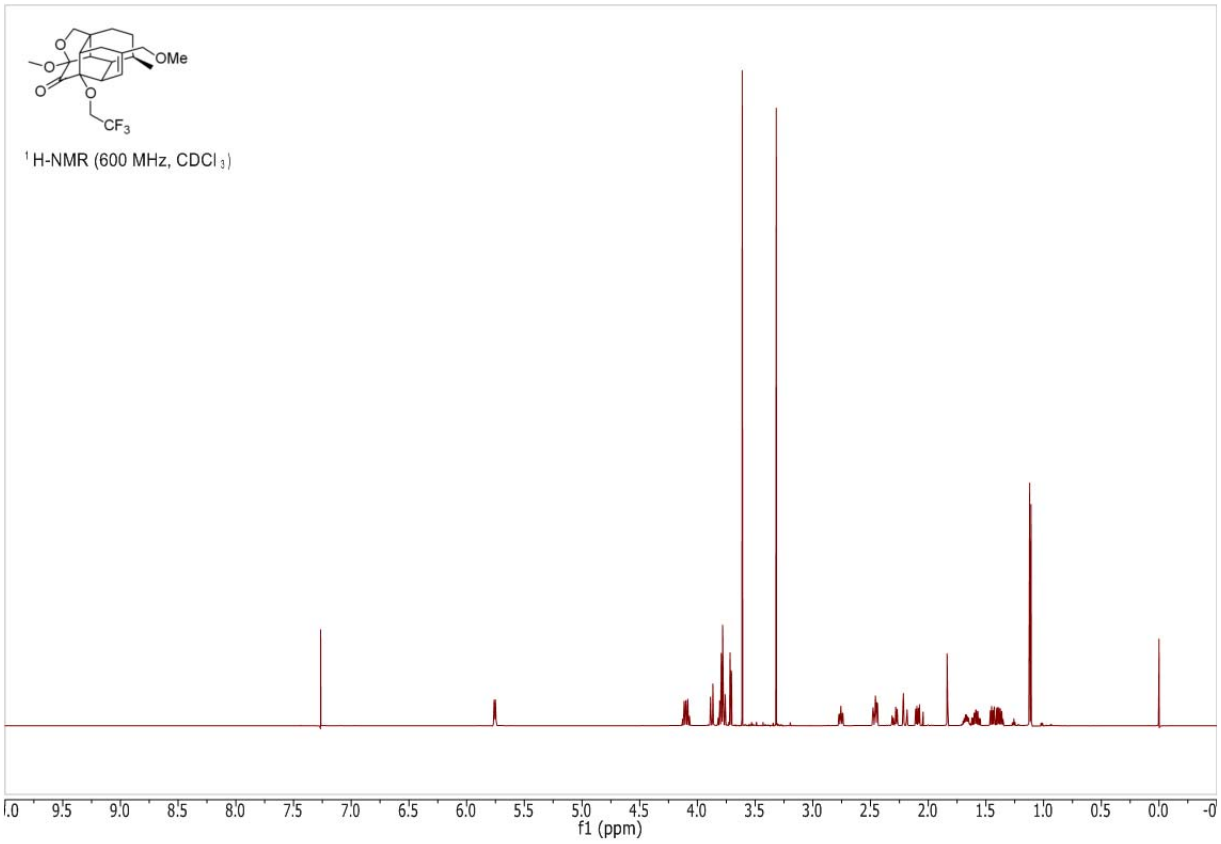
CF3
13 C-NMR (100 MHz, CDCl 3)
f1 (ppm)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O
CF3
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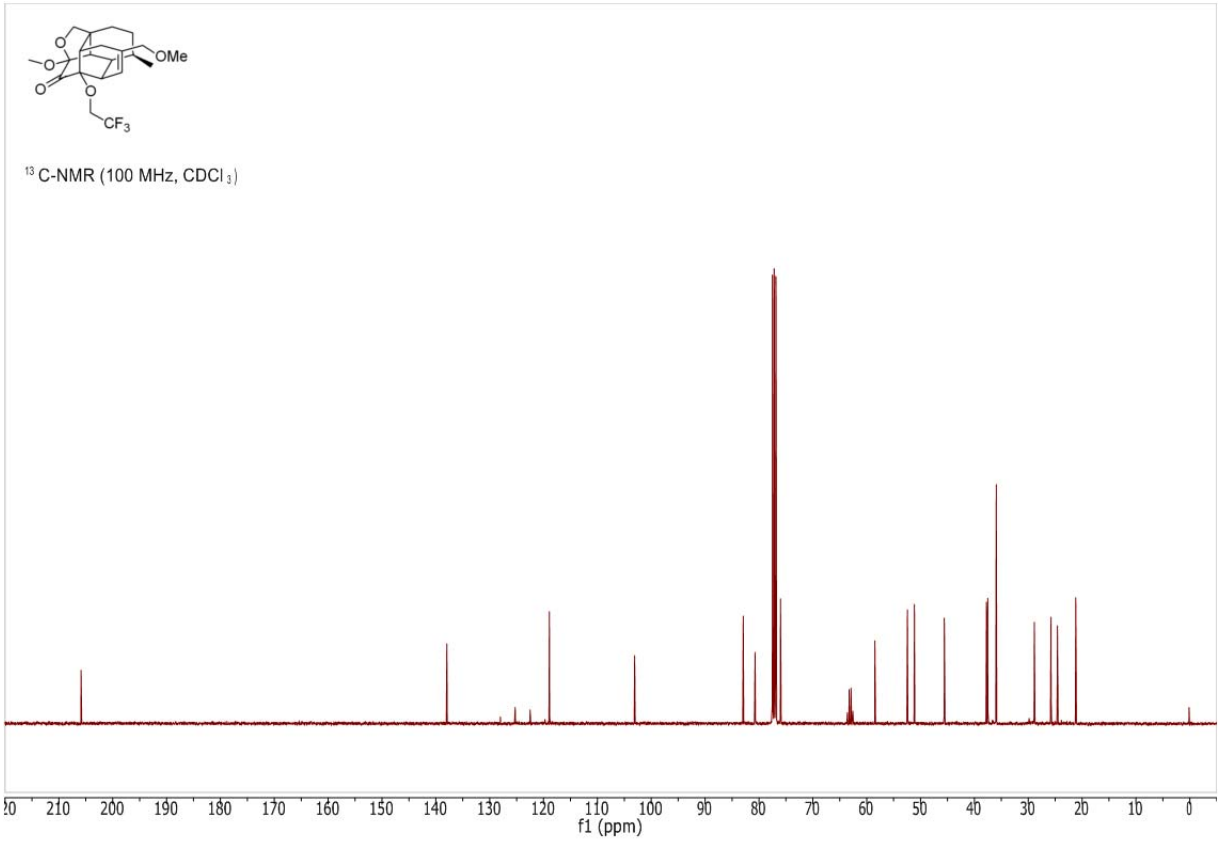
f1 (ppm)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CF3
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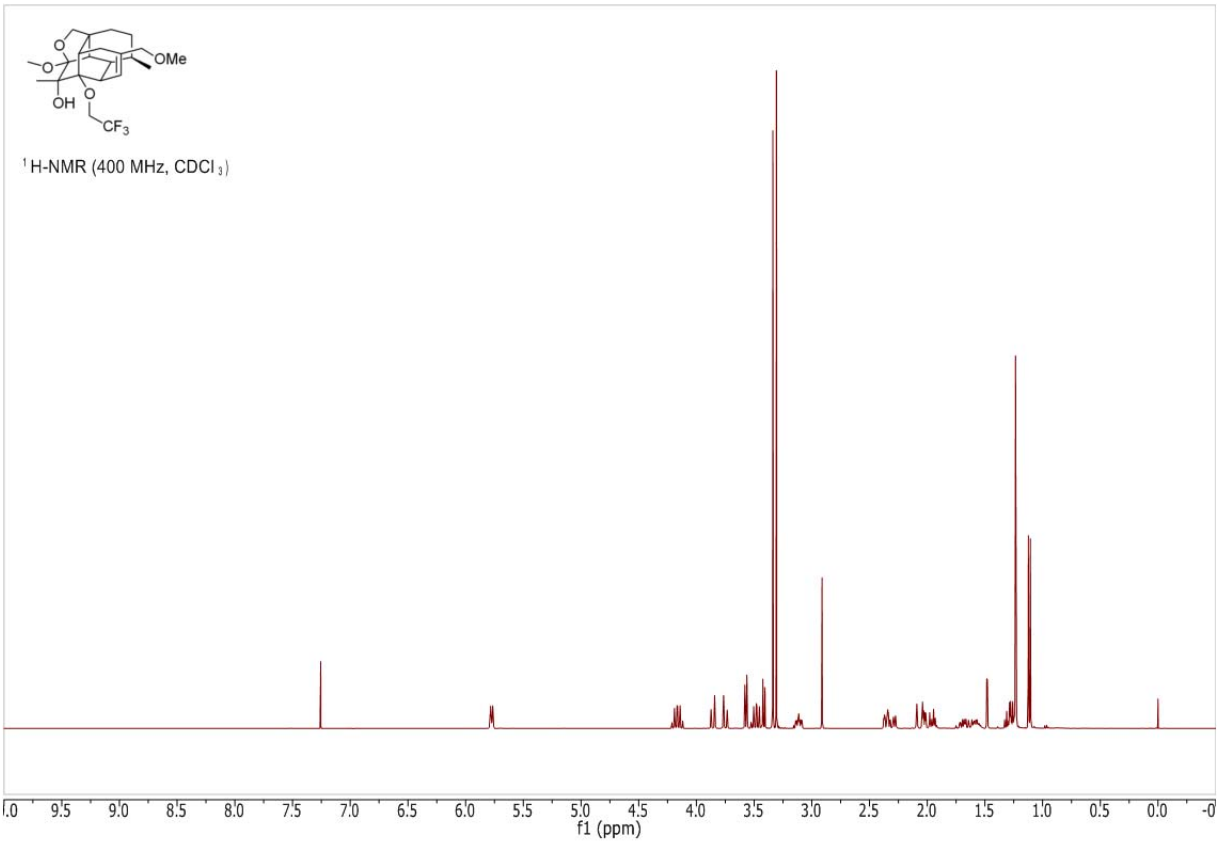
f1 (ppm)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CF3
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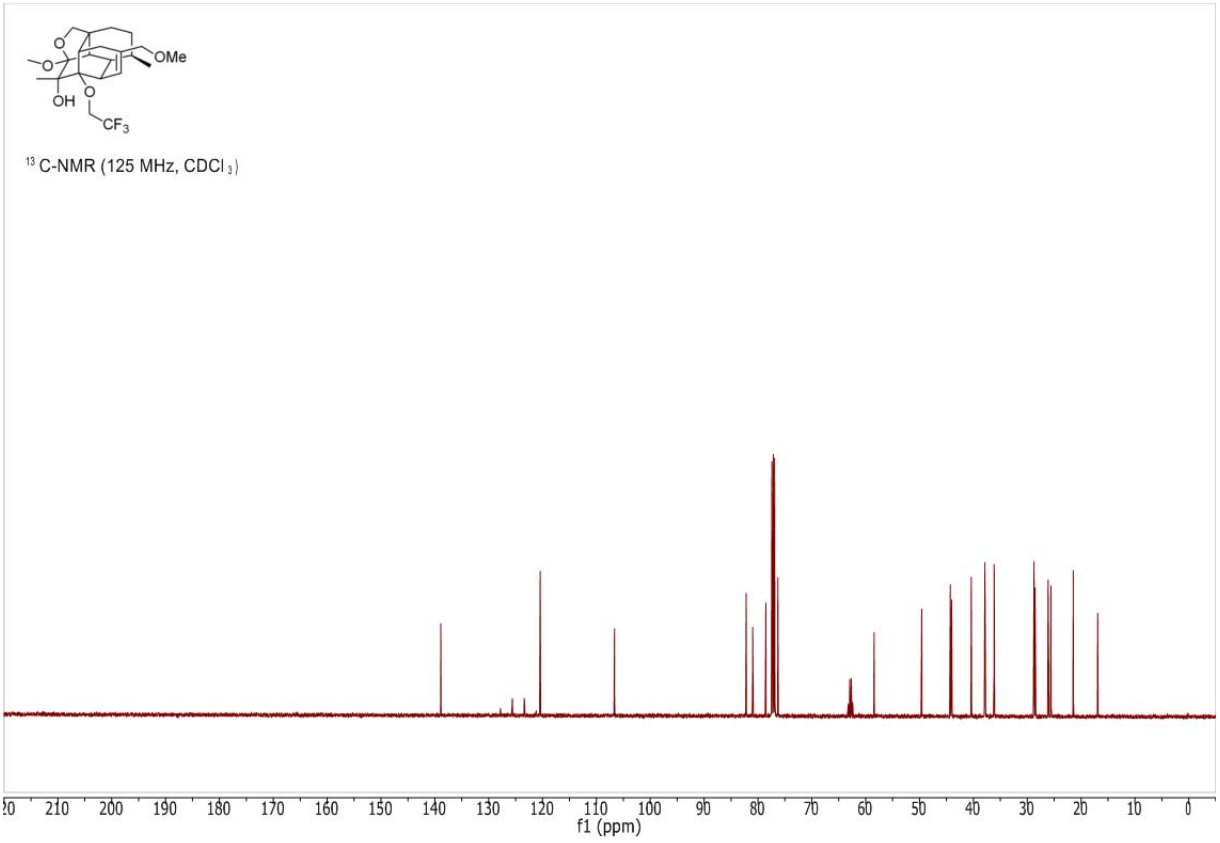
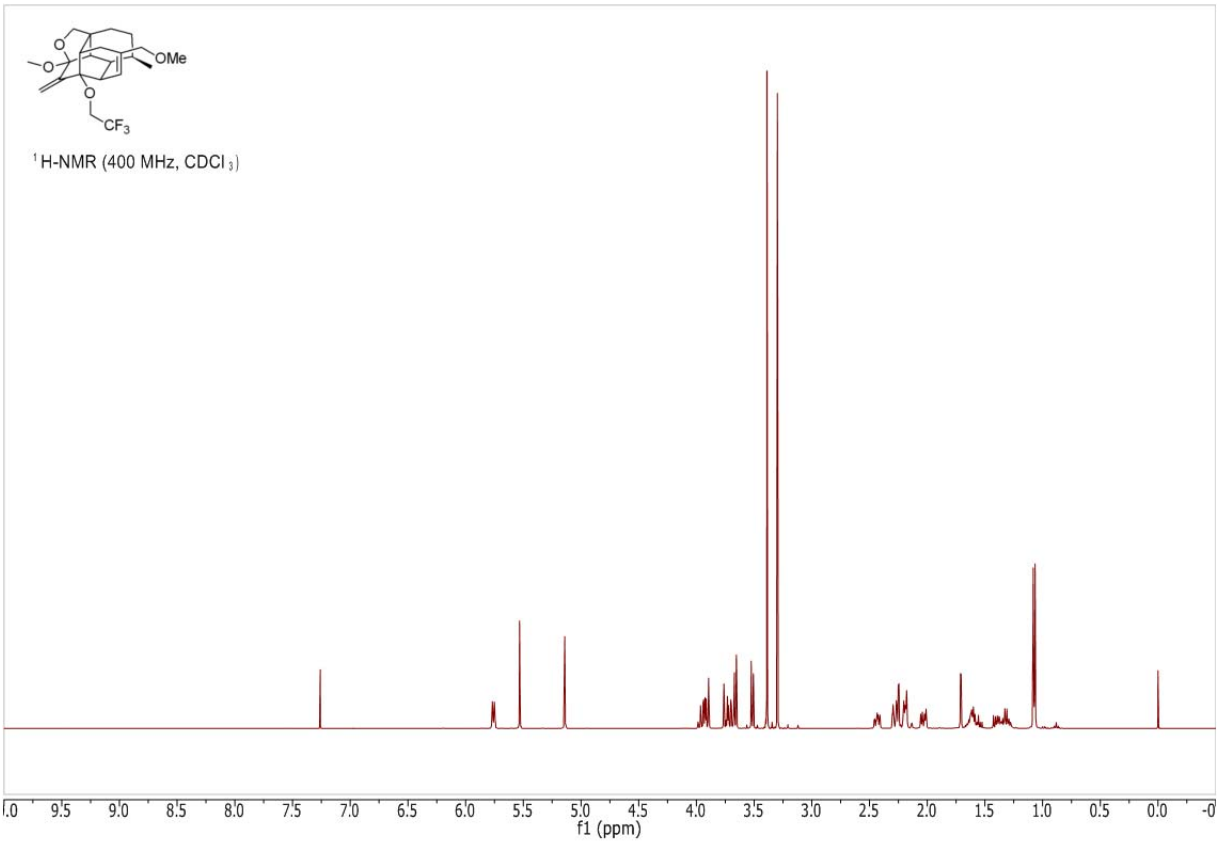
f1 (ppm)


OMe
OH
O
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)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O
O
CF3
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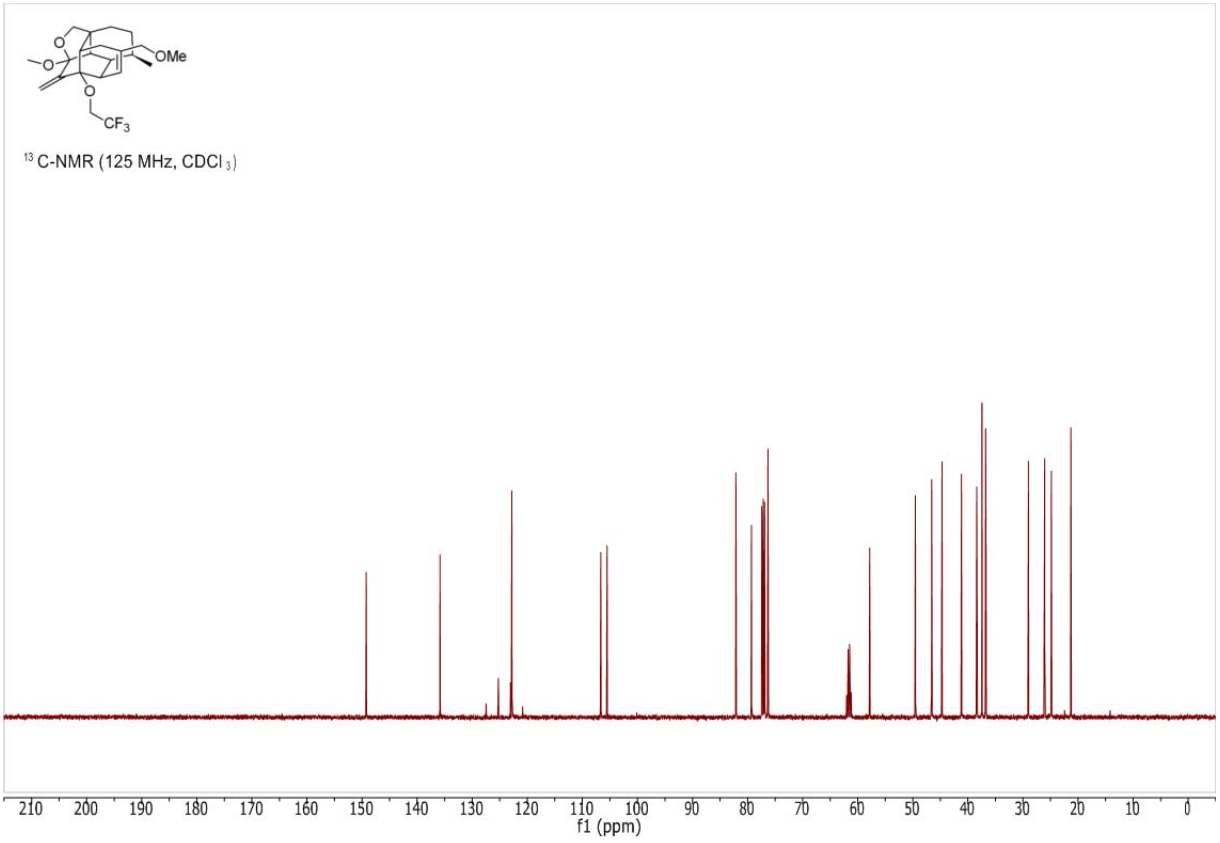
f1 (ppm)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O
O
CF3
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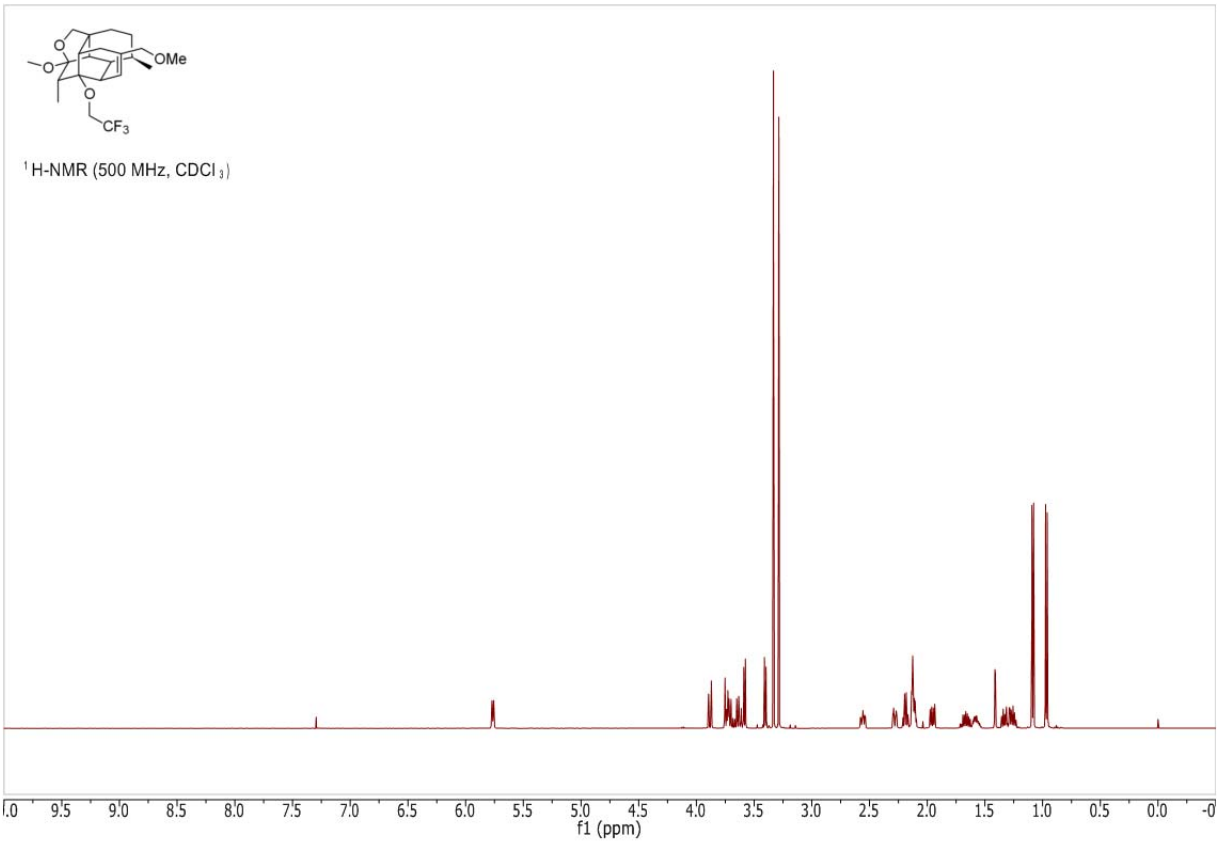
f1 (ppm)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O
O
CF3
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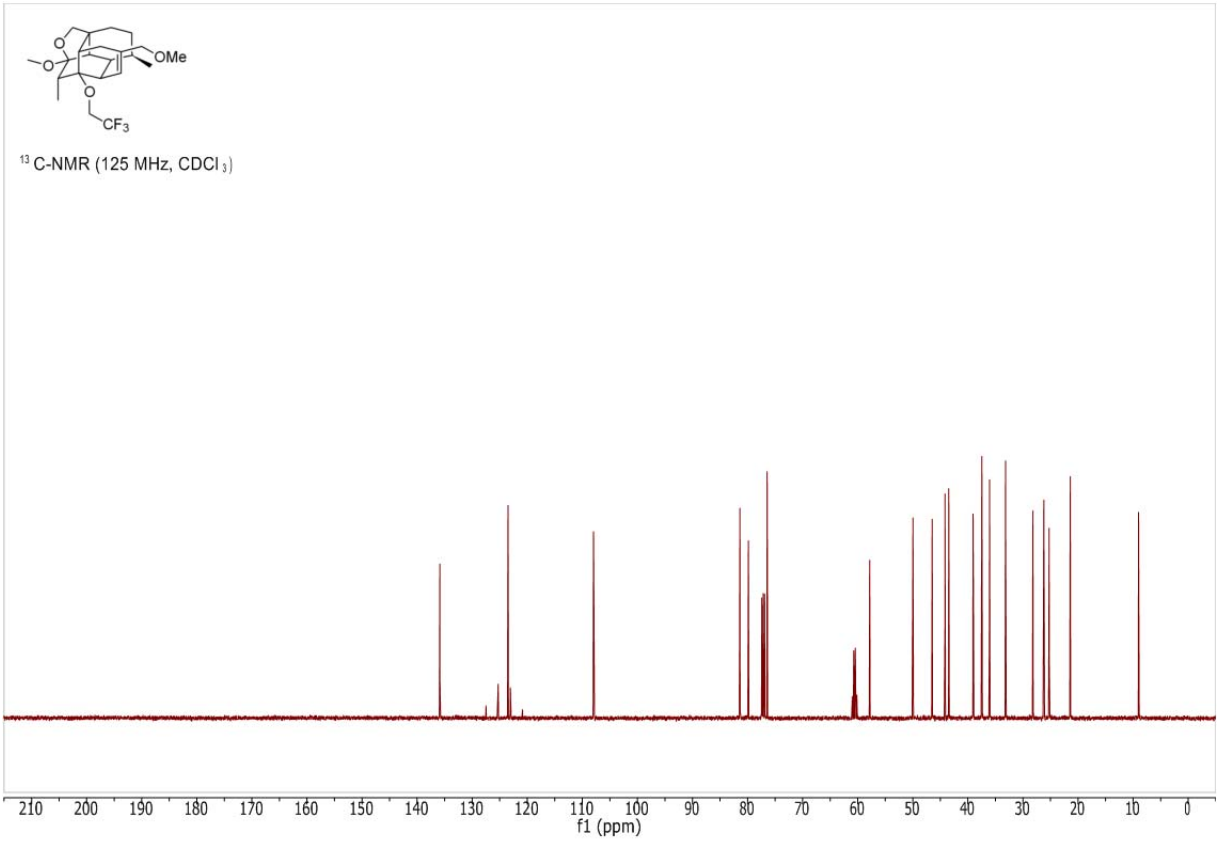
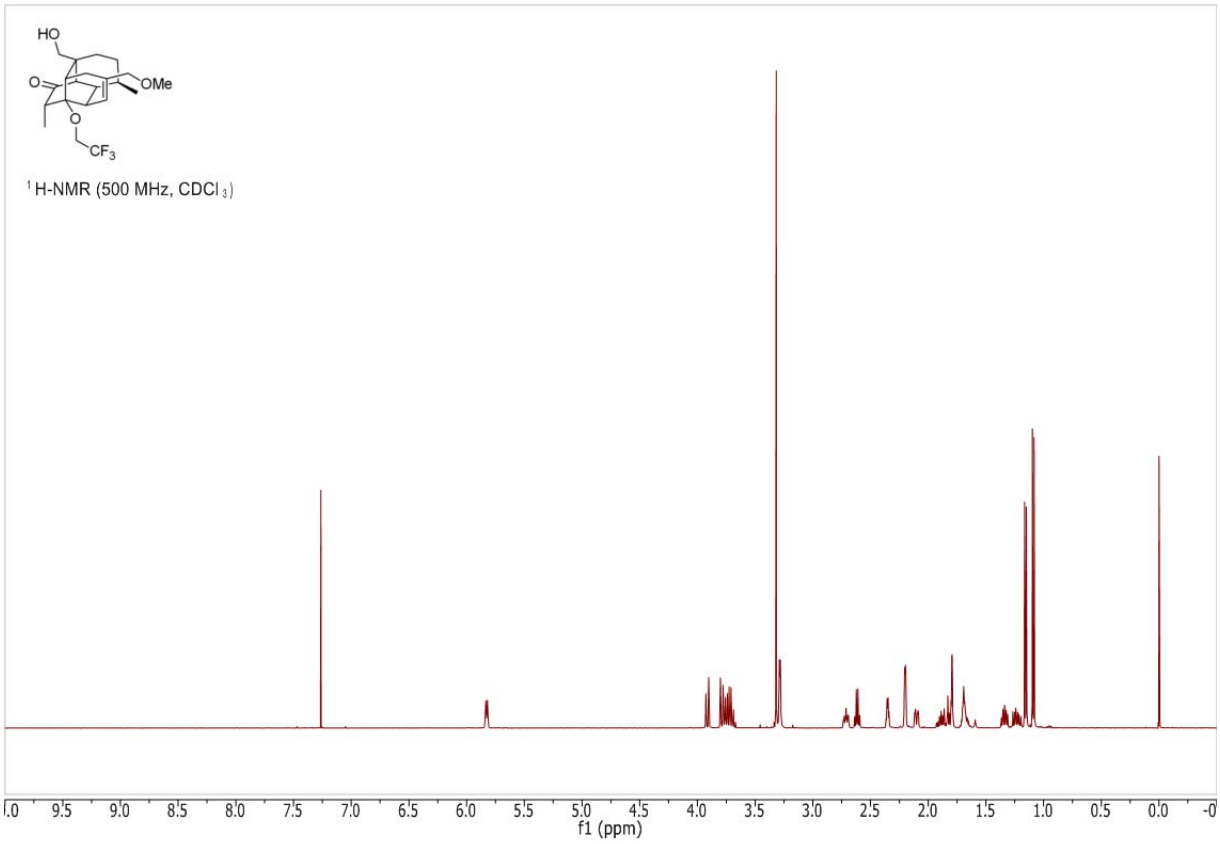
f1 (ppm)


OMe
O
O
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)


HO
O
OMe
O
CF3
1 H-NMR (500 MHz, CDCl 3)
9.5
9.0
8.5
8.0
7.5
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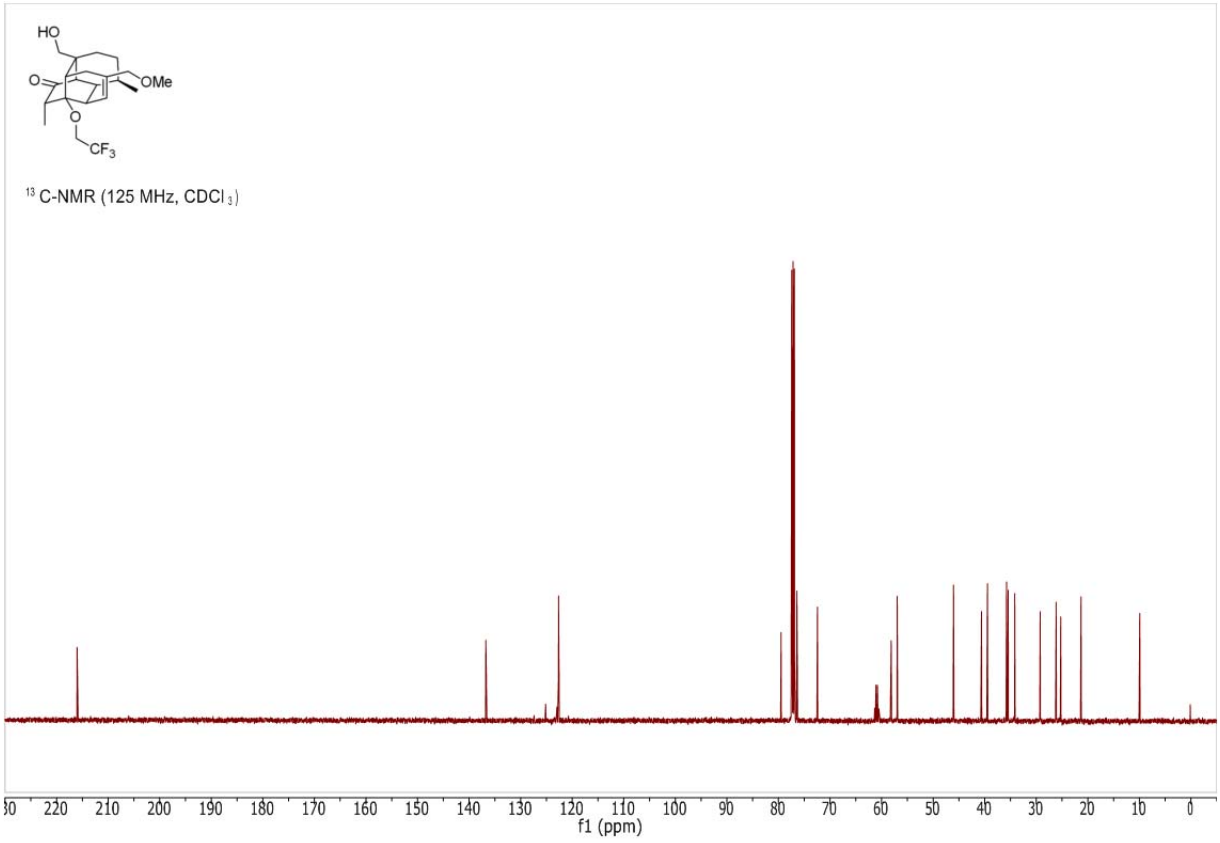
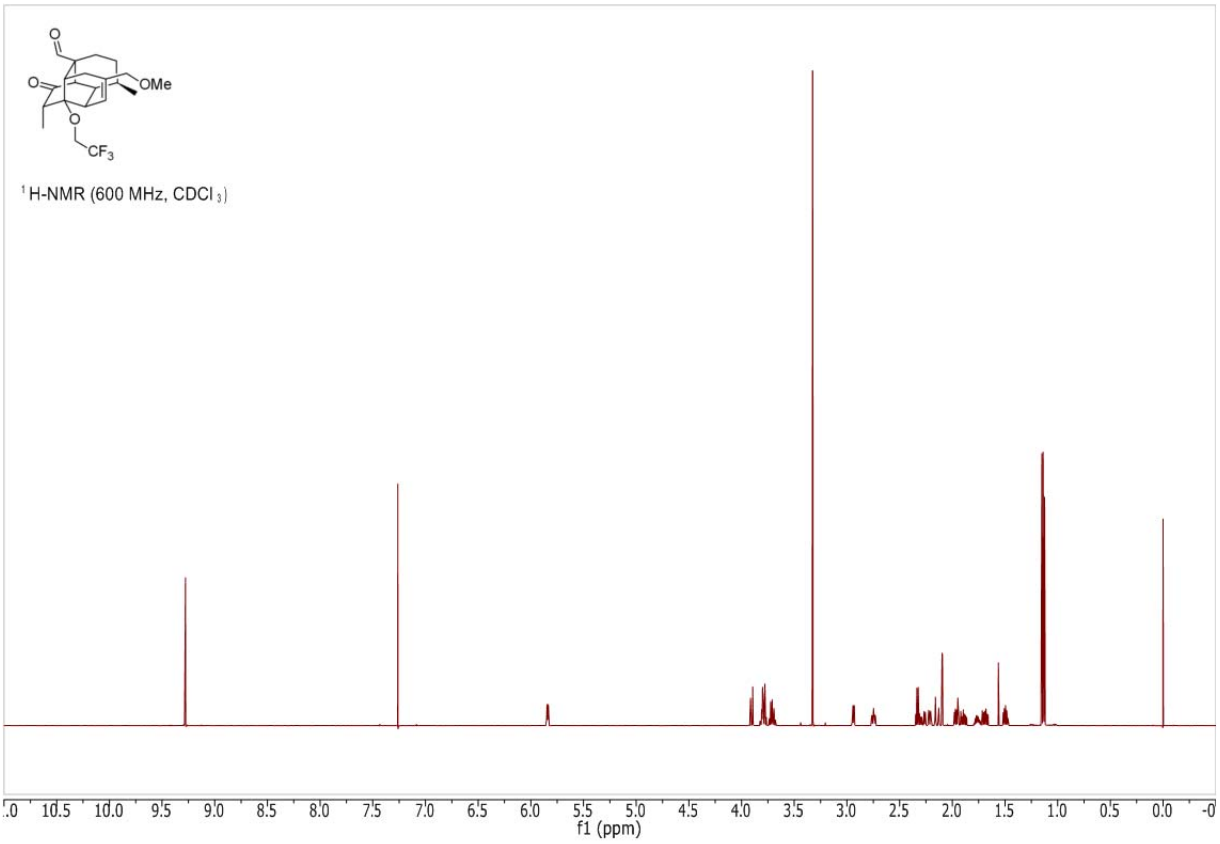
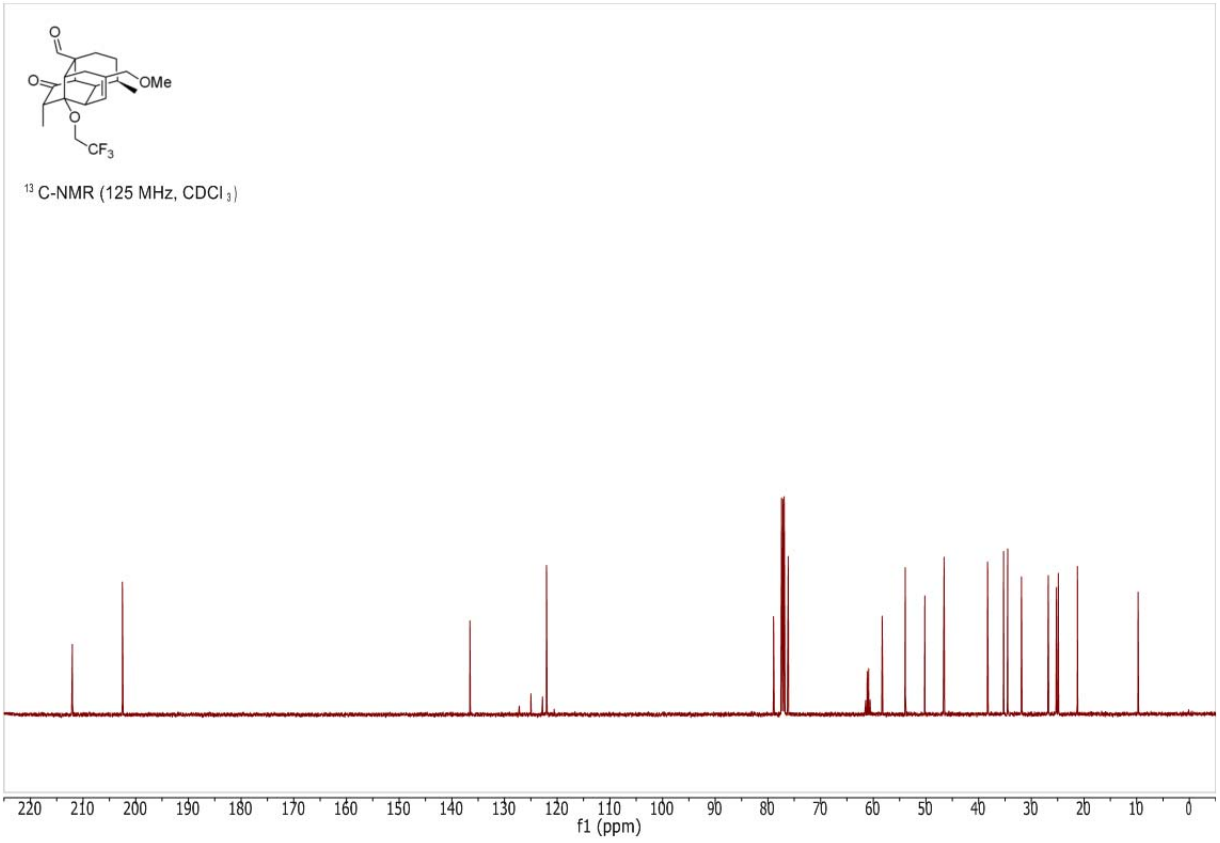
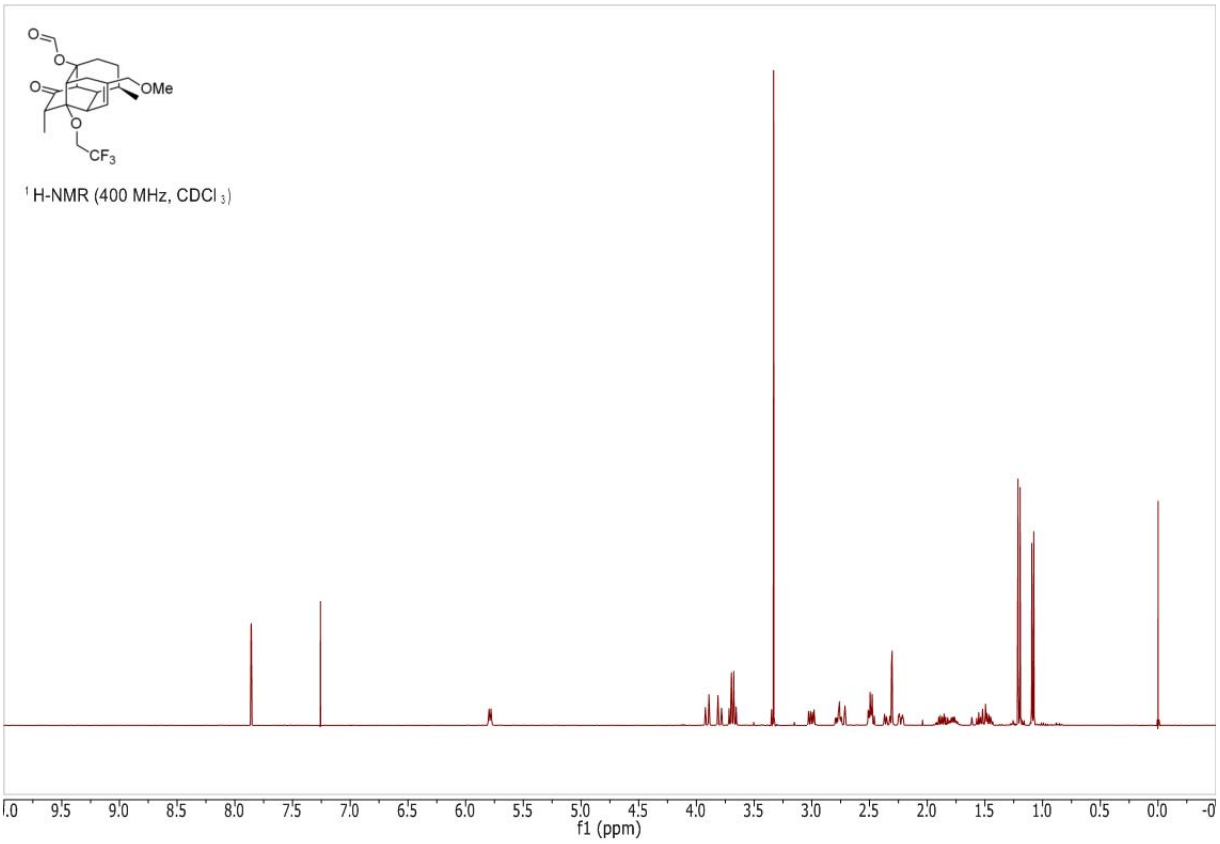
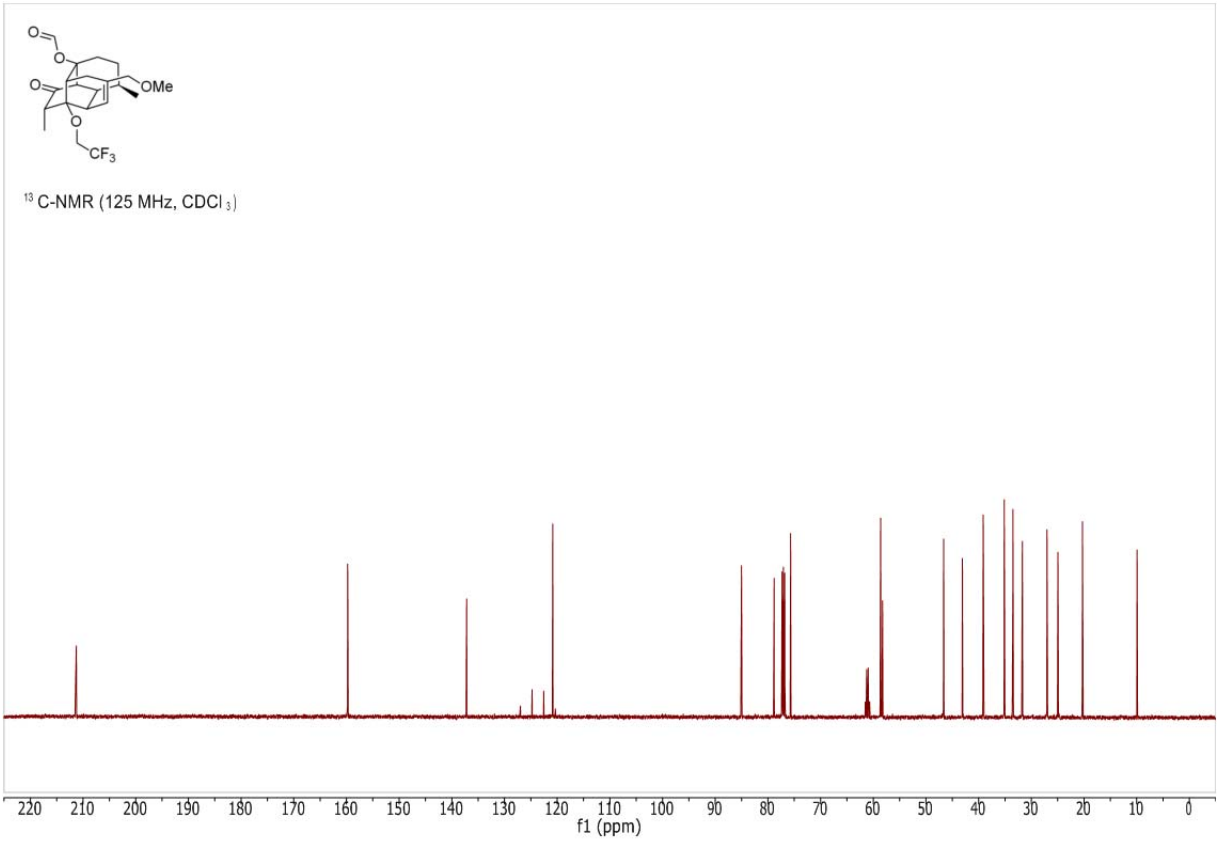
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
O
OMe
O
CF3
13 C-NMR (125 MHz, CDCl 3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
CF3
1H-NMR (600 MHz, CDCl3)
f1 (ppm)


OMe
CF3
13C-NMR (125 MHz, CDCl3)
f1 (ppm)


OMe
CF3
1 H-NMR (400 MHz, CDCl 3)
f1 (ppm)


OMe
CF3
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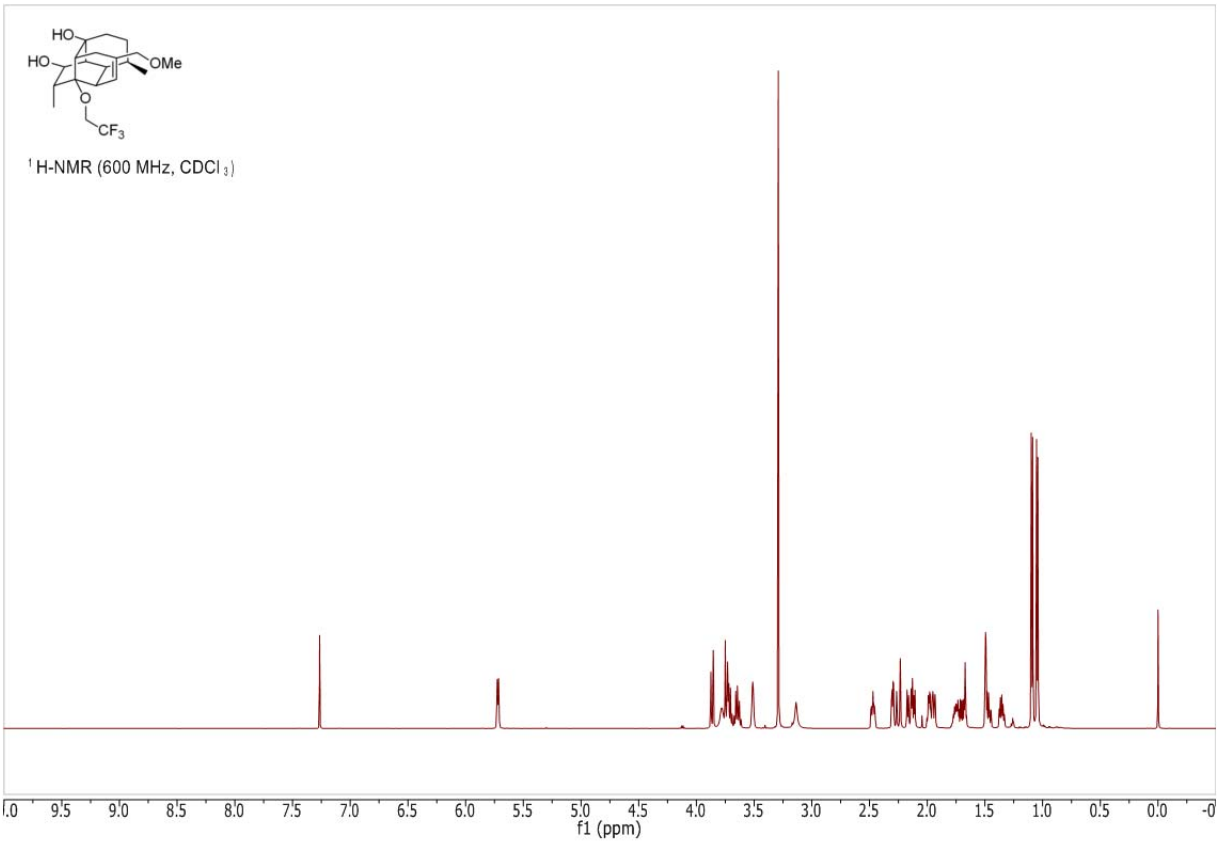
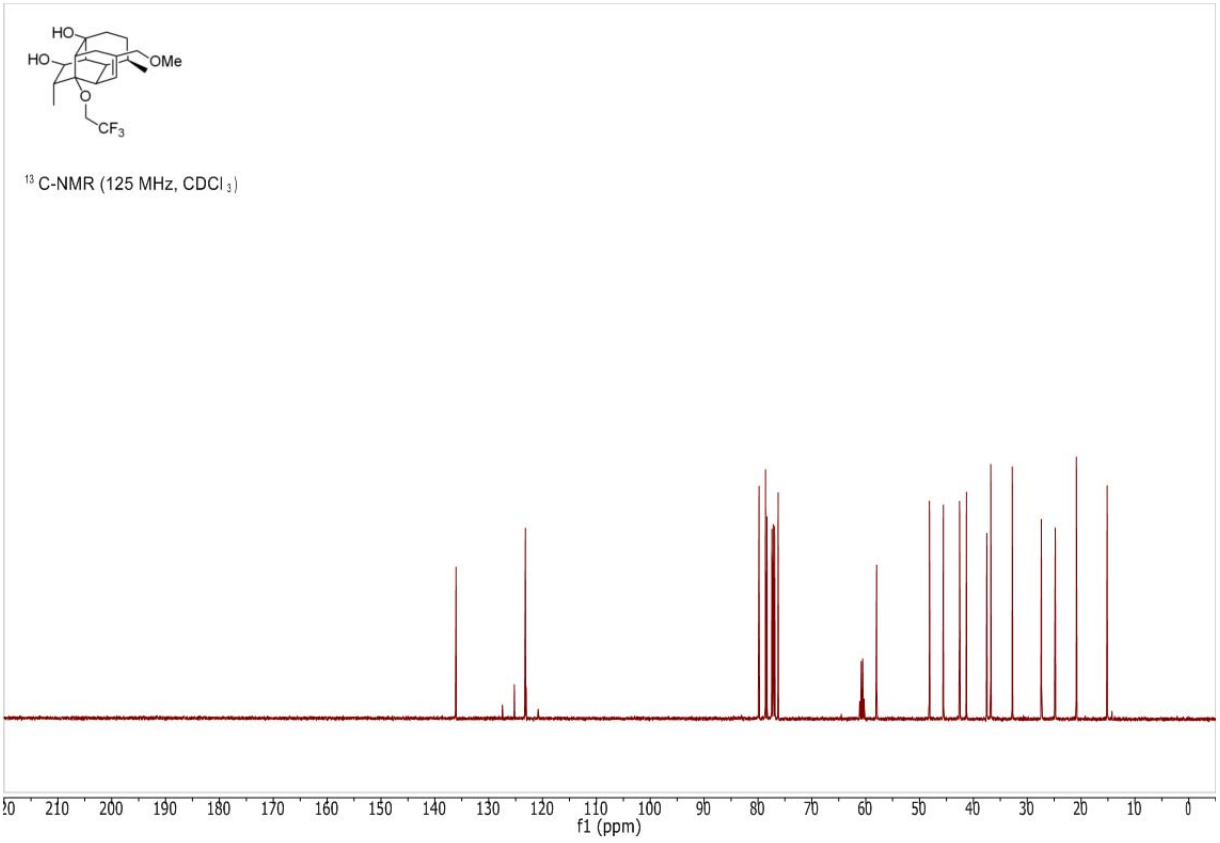
f1 (ppm)


HO
HO
OMe
O
CF3
1 H-NMR (600 MHz, CDCl 3)
f1 (ppm)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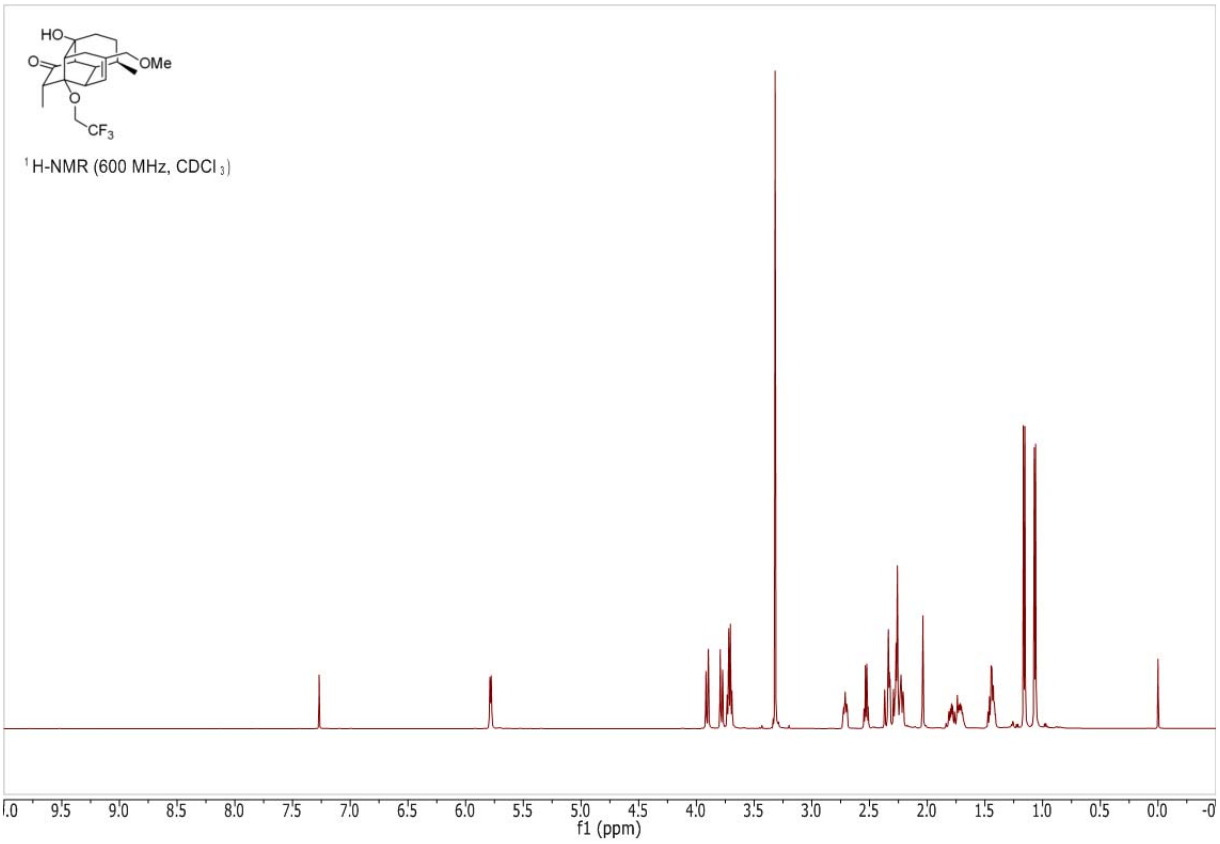
HO
OMe
O
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)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OMe
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CF3
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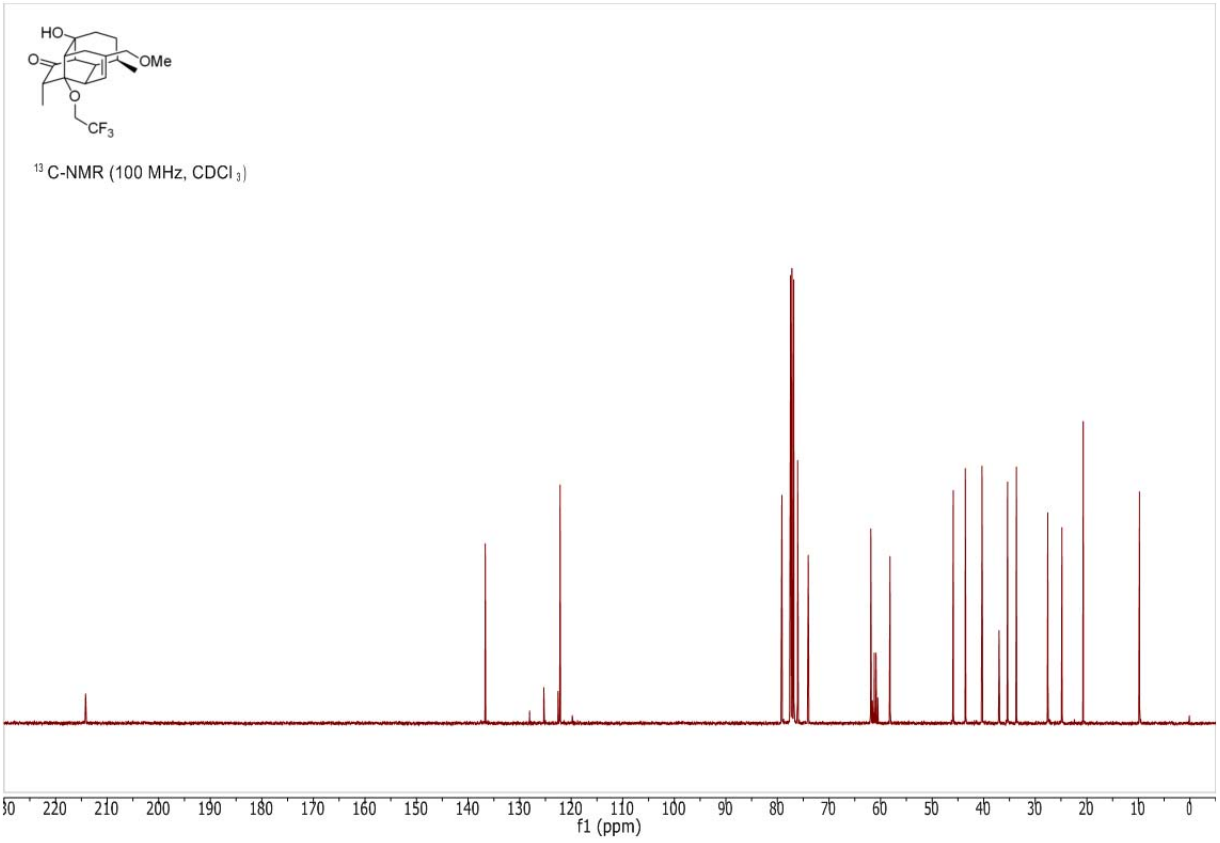
f1 (ppm)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OMe
O
CF3
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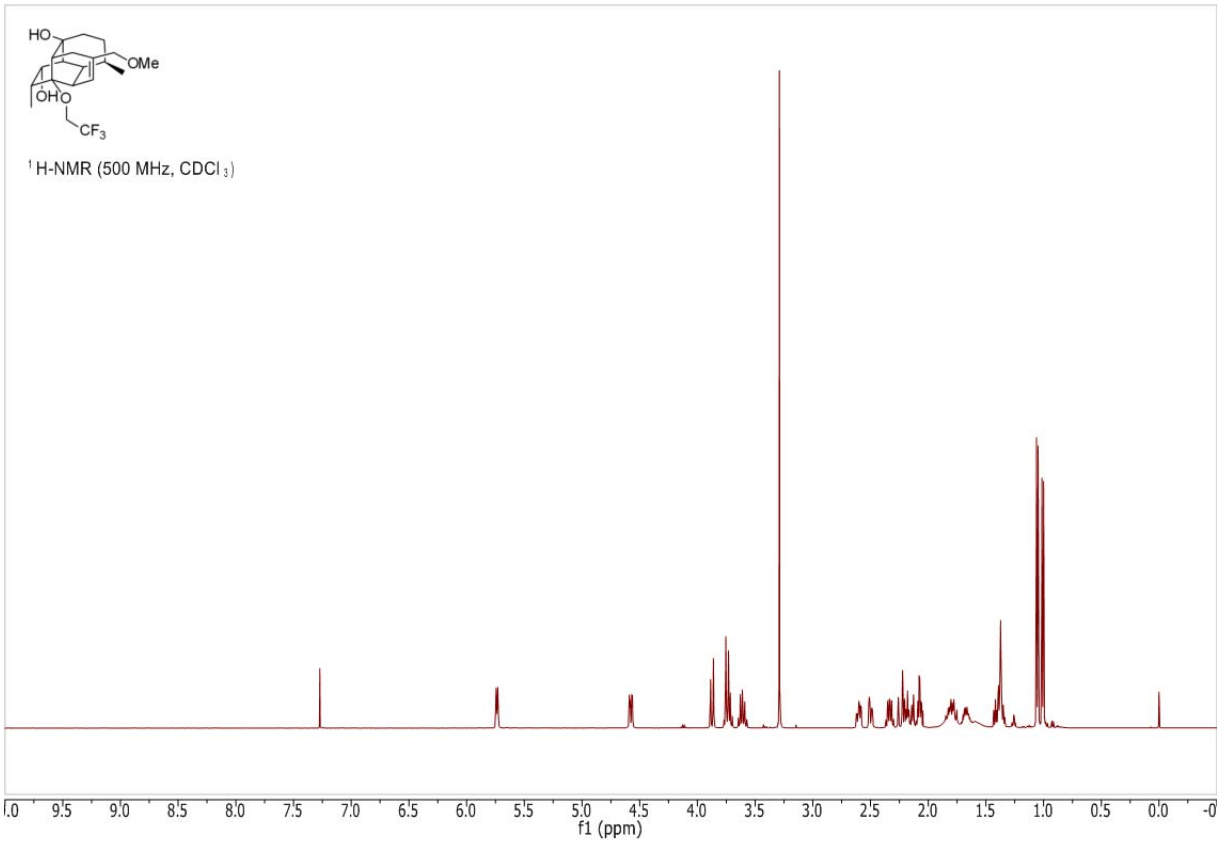
f1 (ppm)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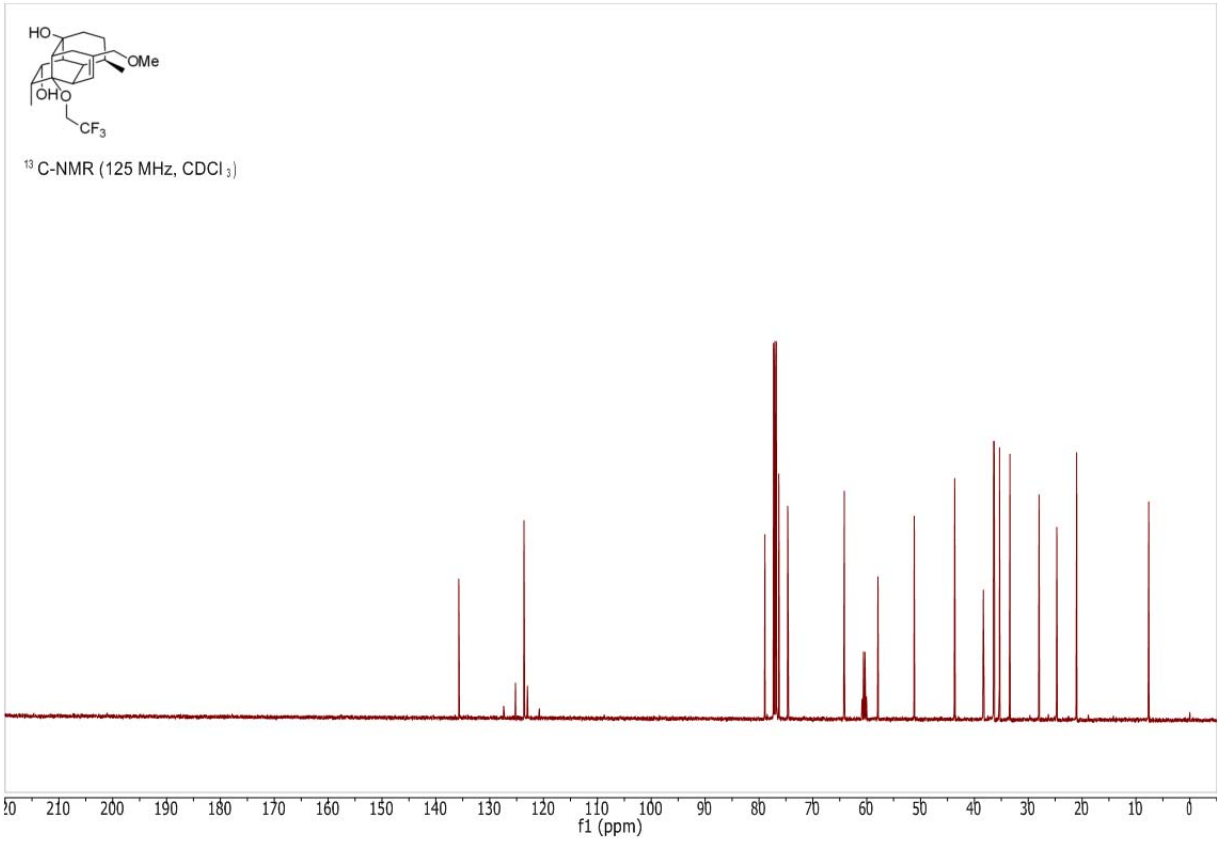
OMe
OH
O
CF3
1 H-NMR (500 MHz, CDCl 3)
f1 (ppm)


HO
OMe
OH
O
CF3
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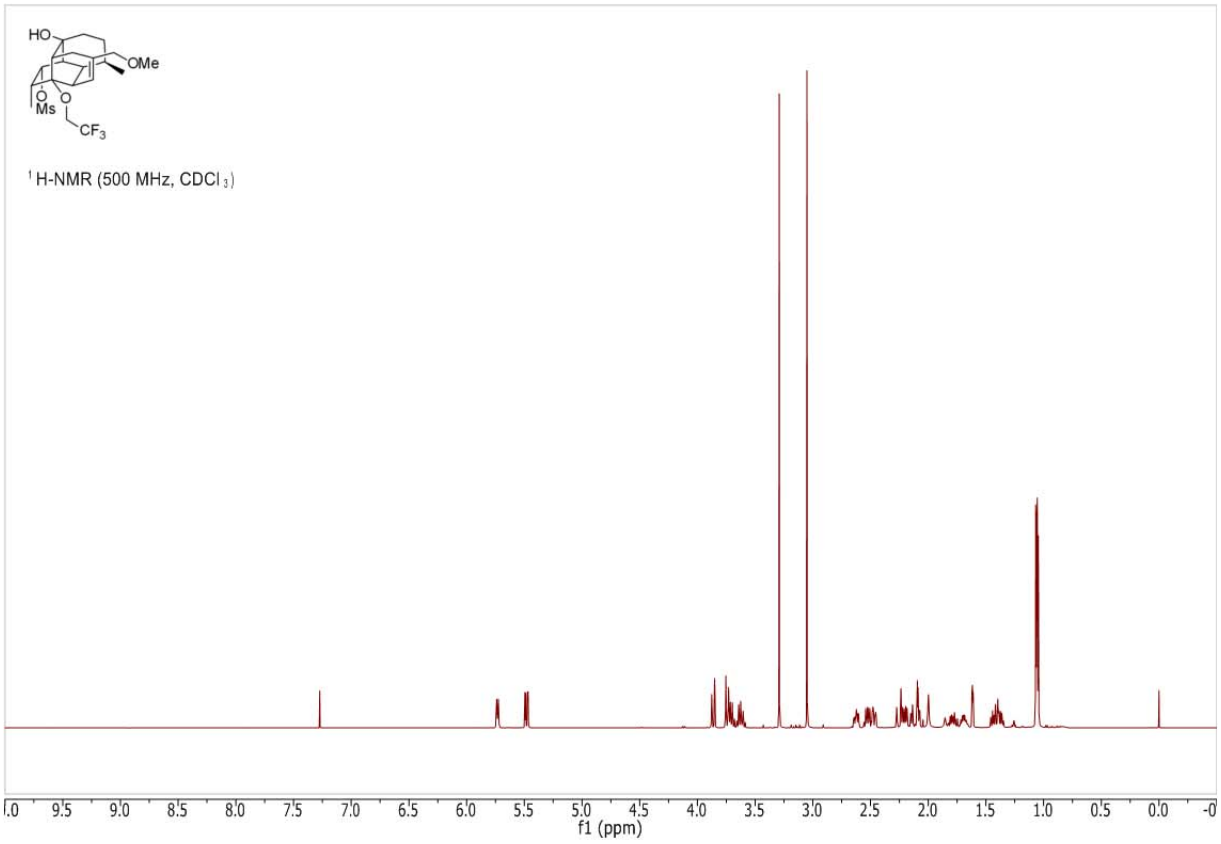
f1 (ppm)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O
CF3
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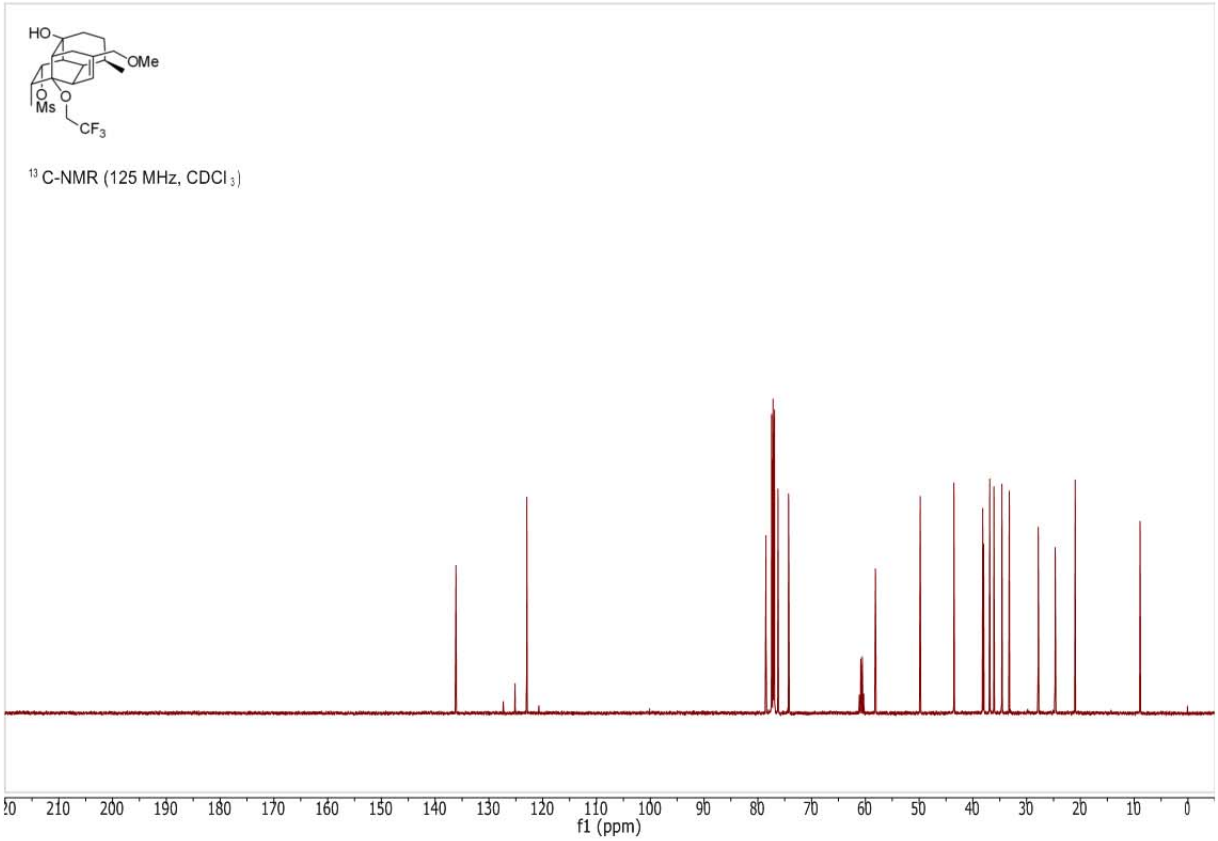
f1 (ppm)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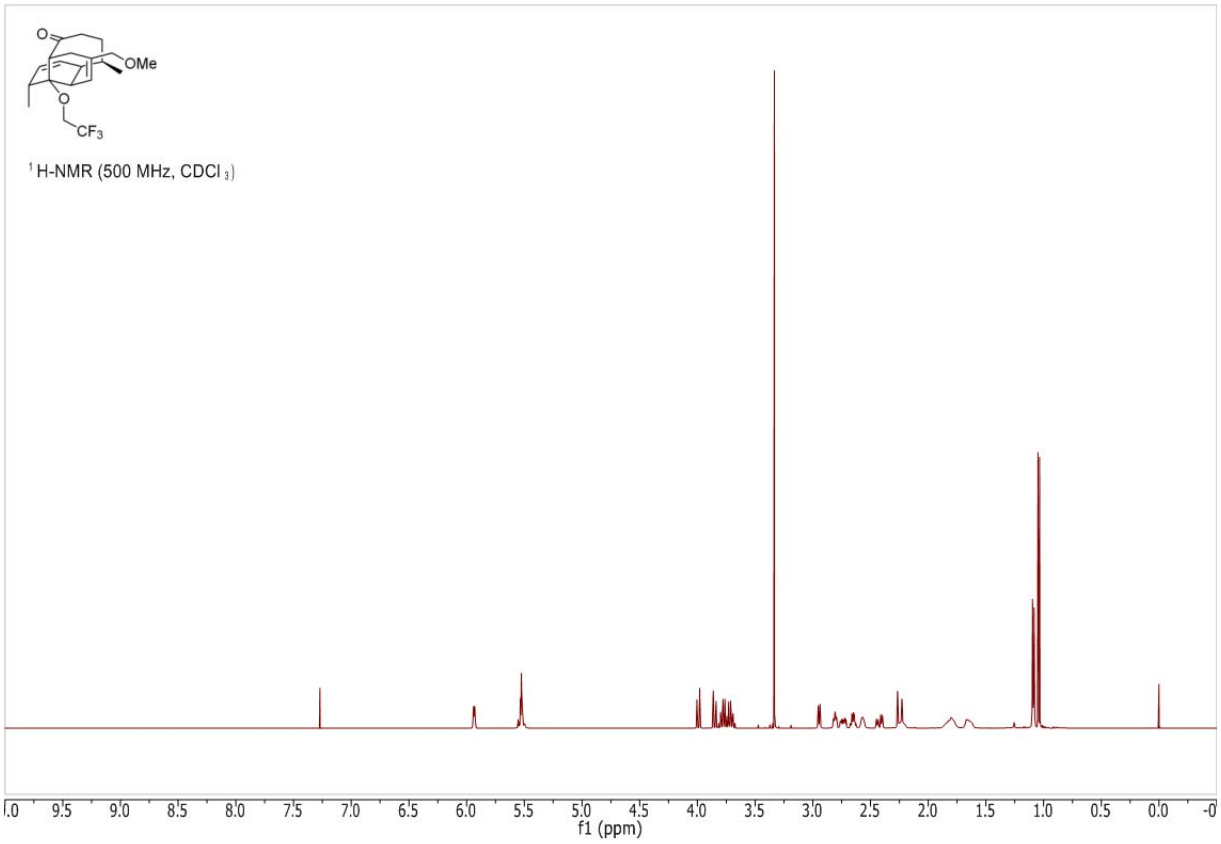
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)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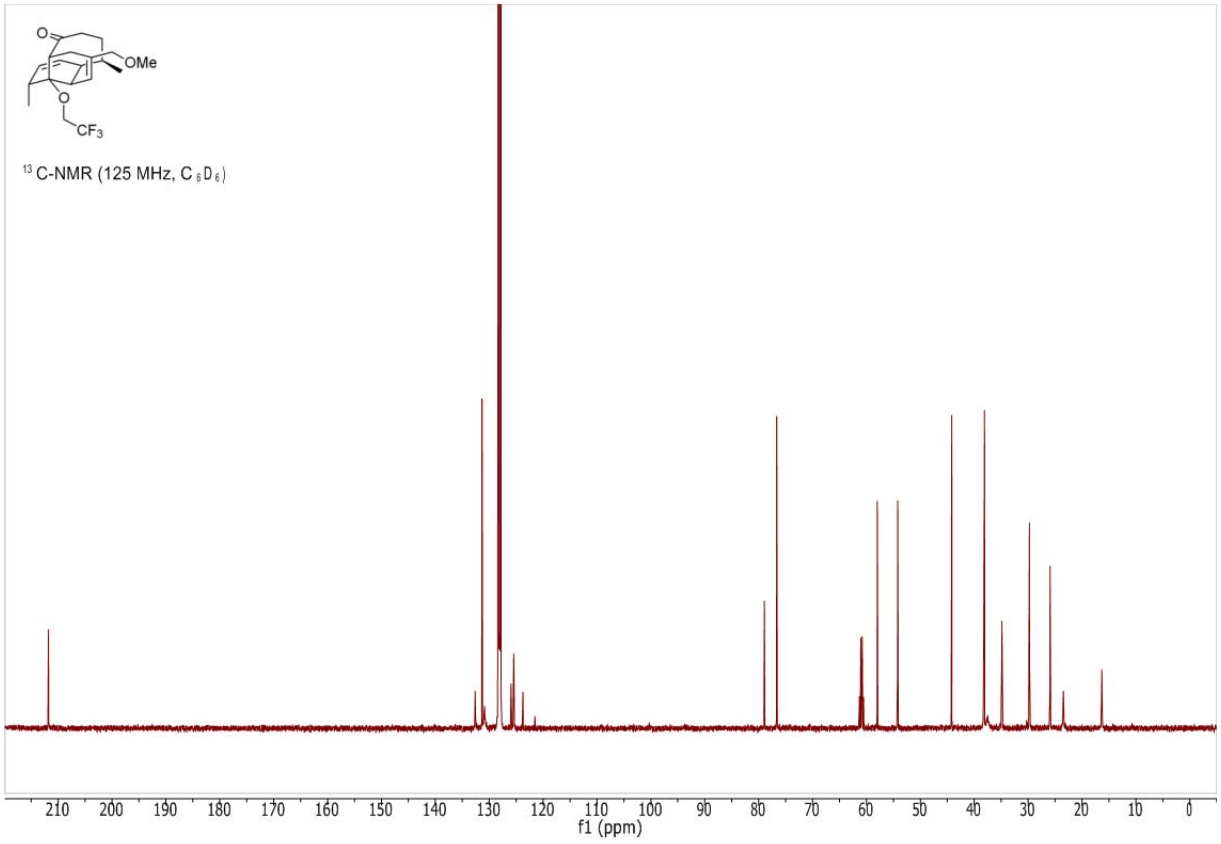
1 H-NMR (500 MHz, CDCl 3)
f1 (ppm)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CF3
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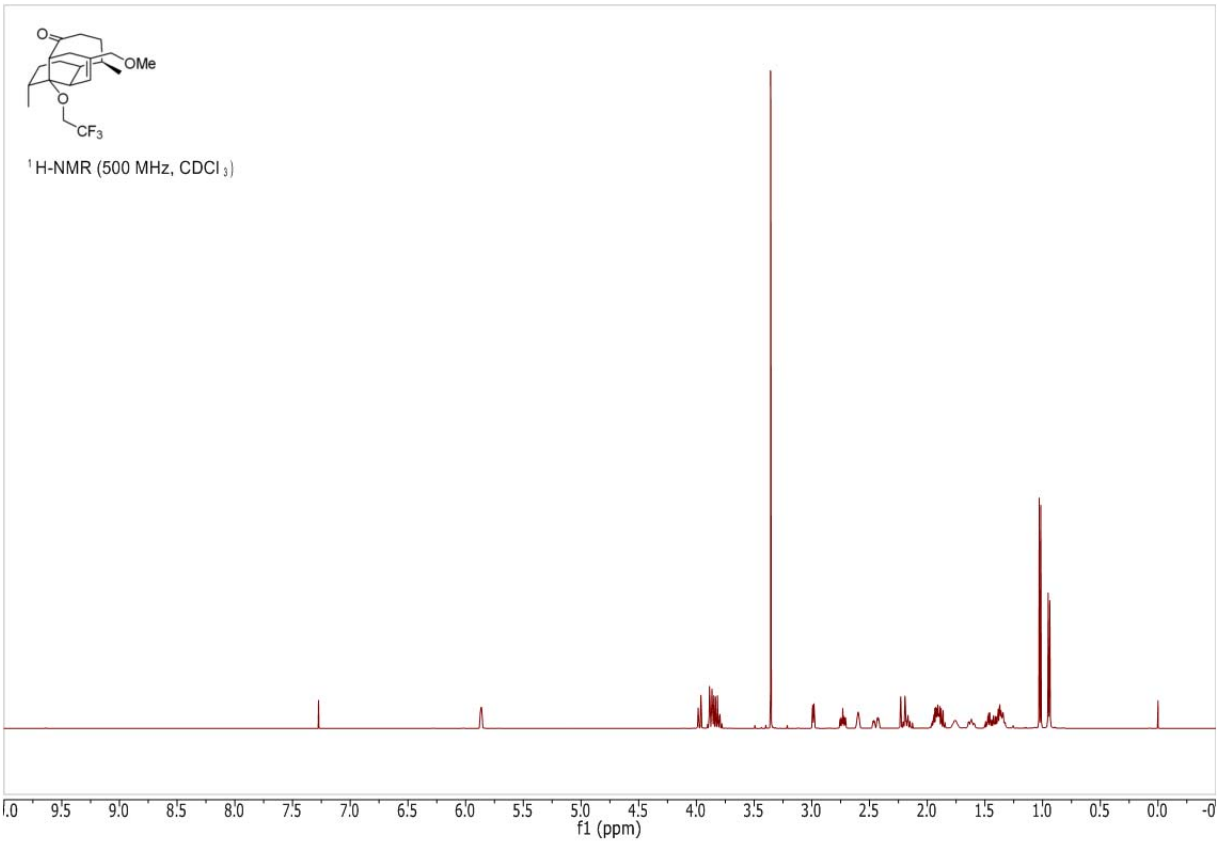
f1 (ppm)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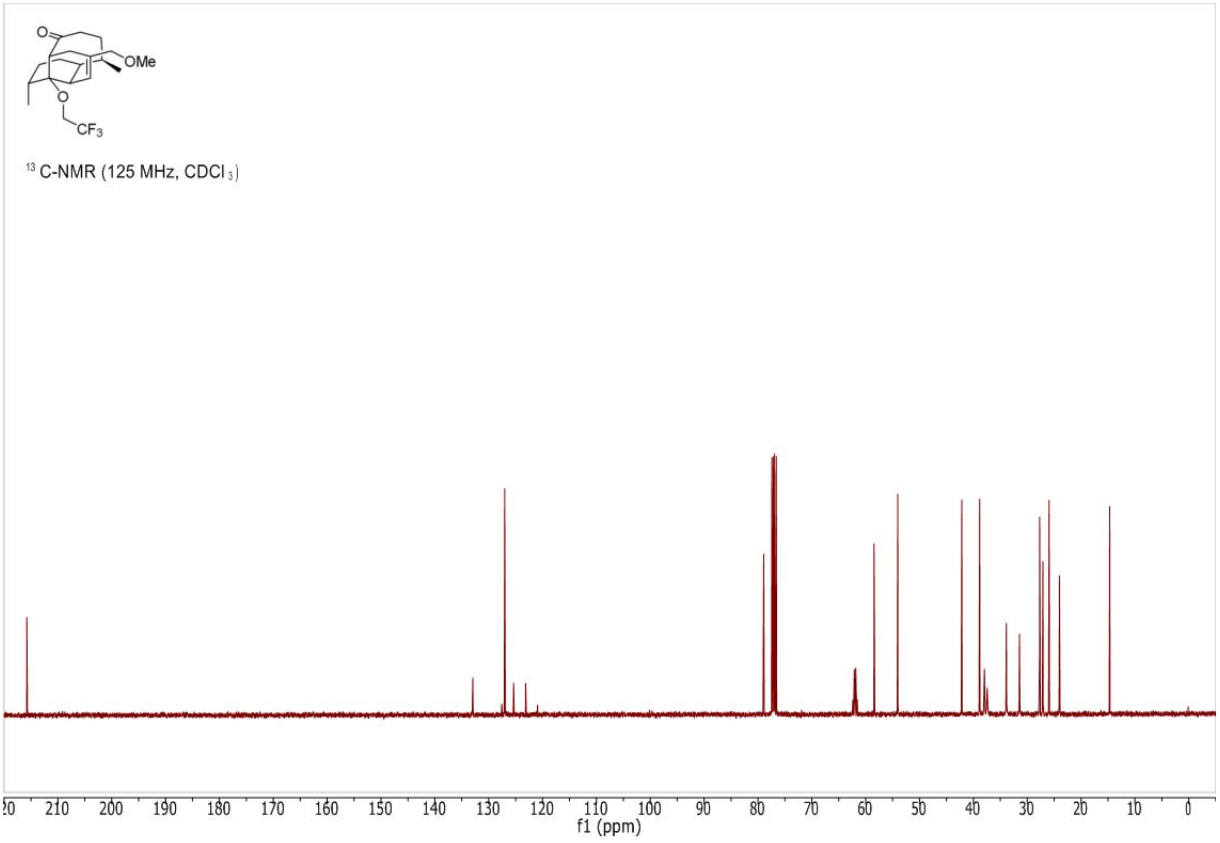
CF3
1 H-NMR (500 MHz, CDCl 3)
f1 (ppm)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CF3
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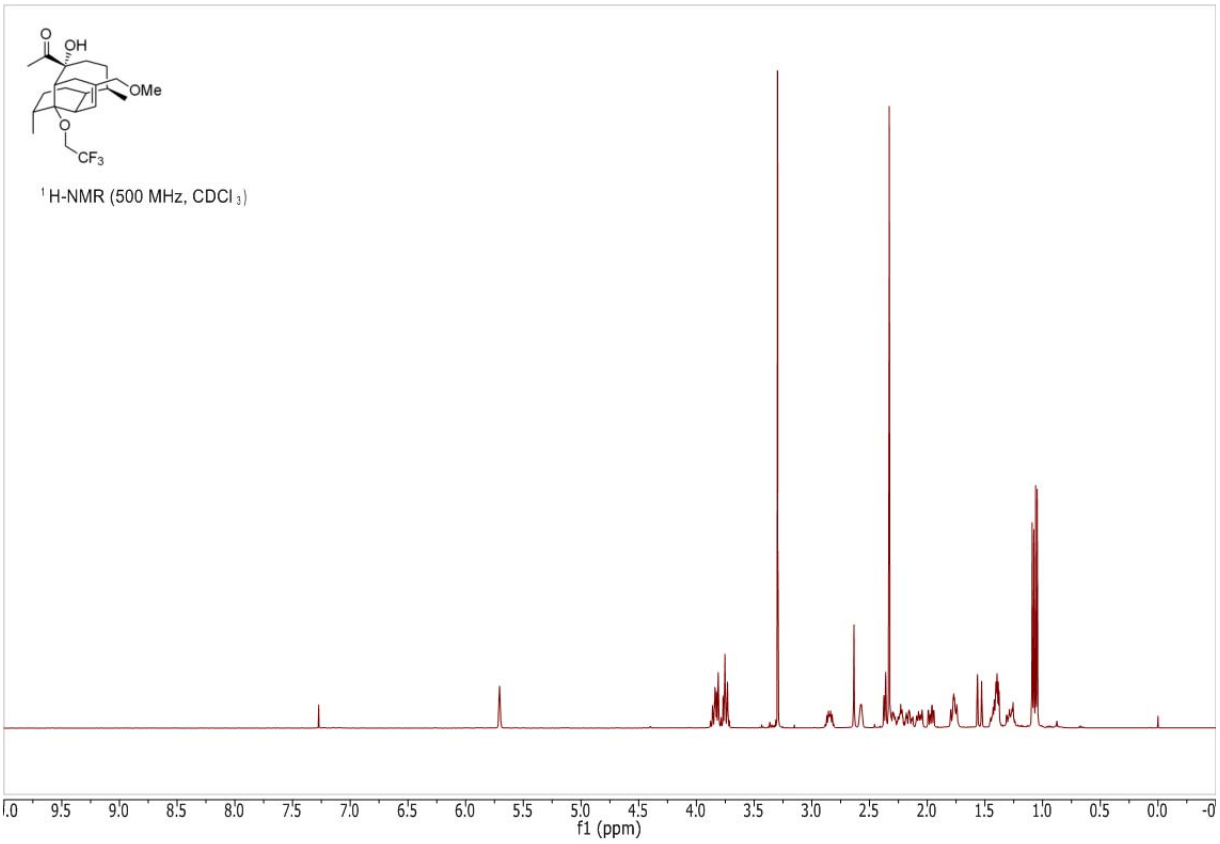
f1 (ppm)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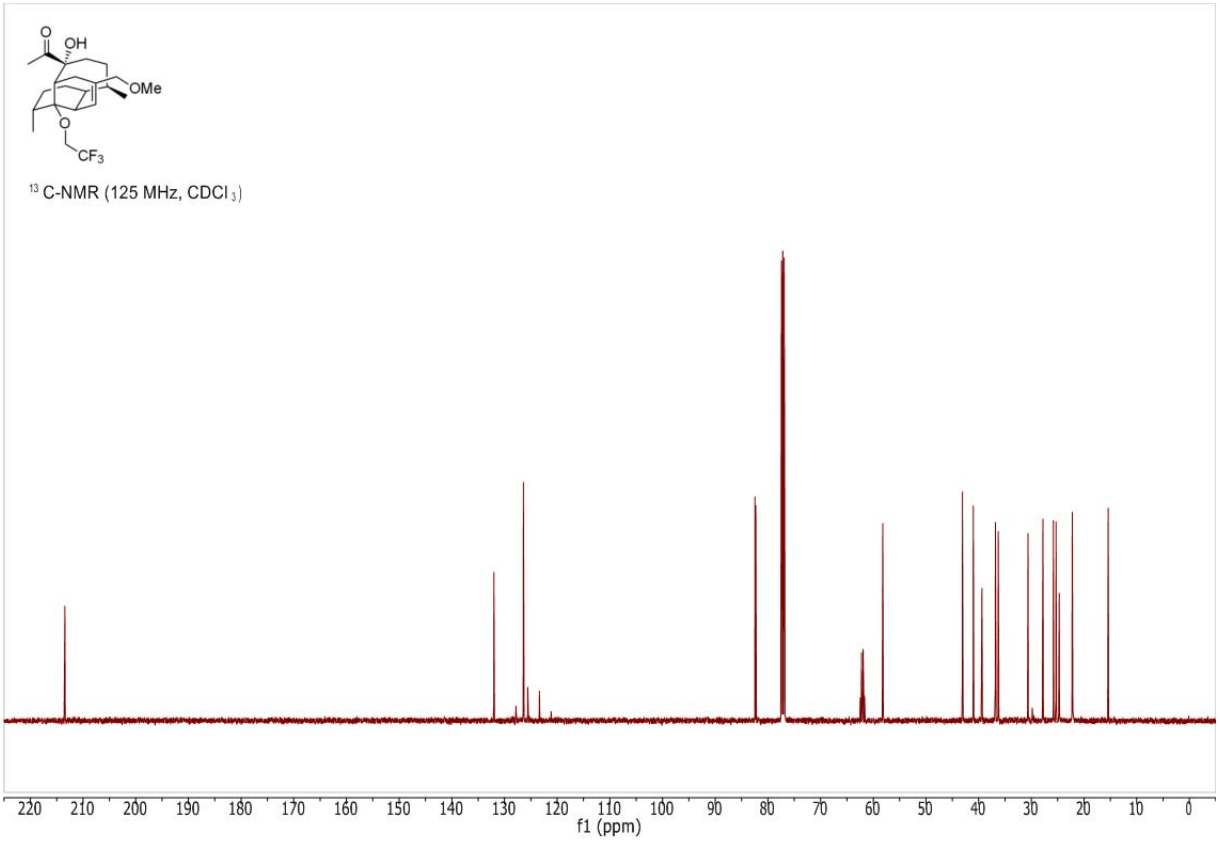
CF3
1 H-NMR (500 MHz, CDCl 3)
f1 (ppm)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CF3
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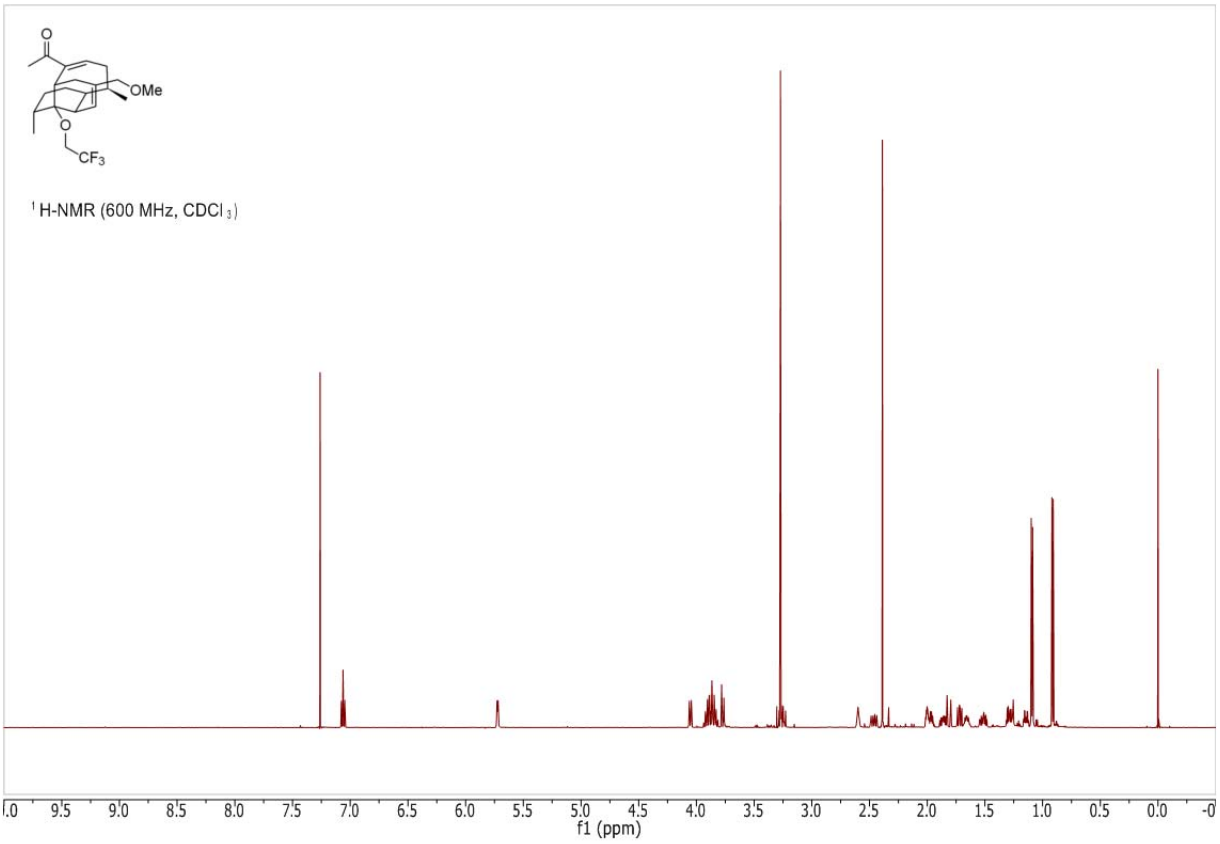
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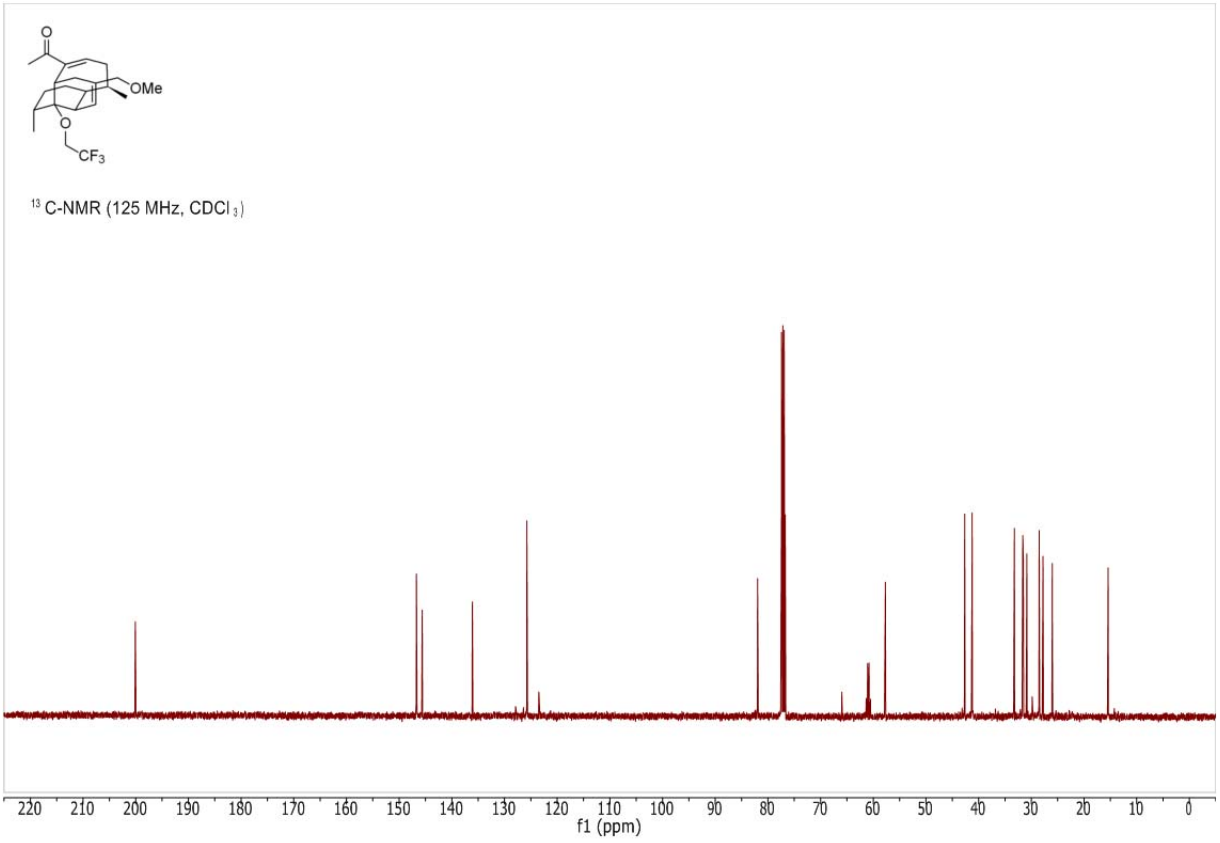
OMe
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CF3
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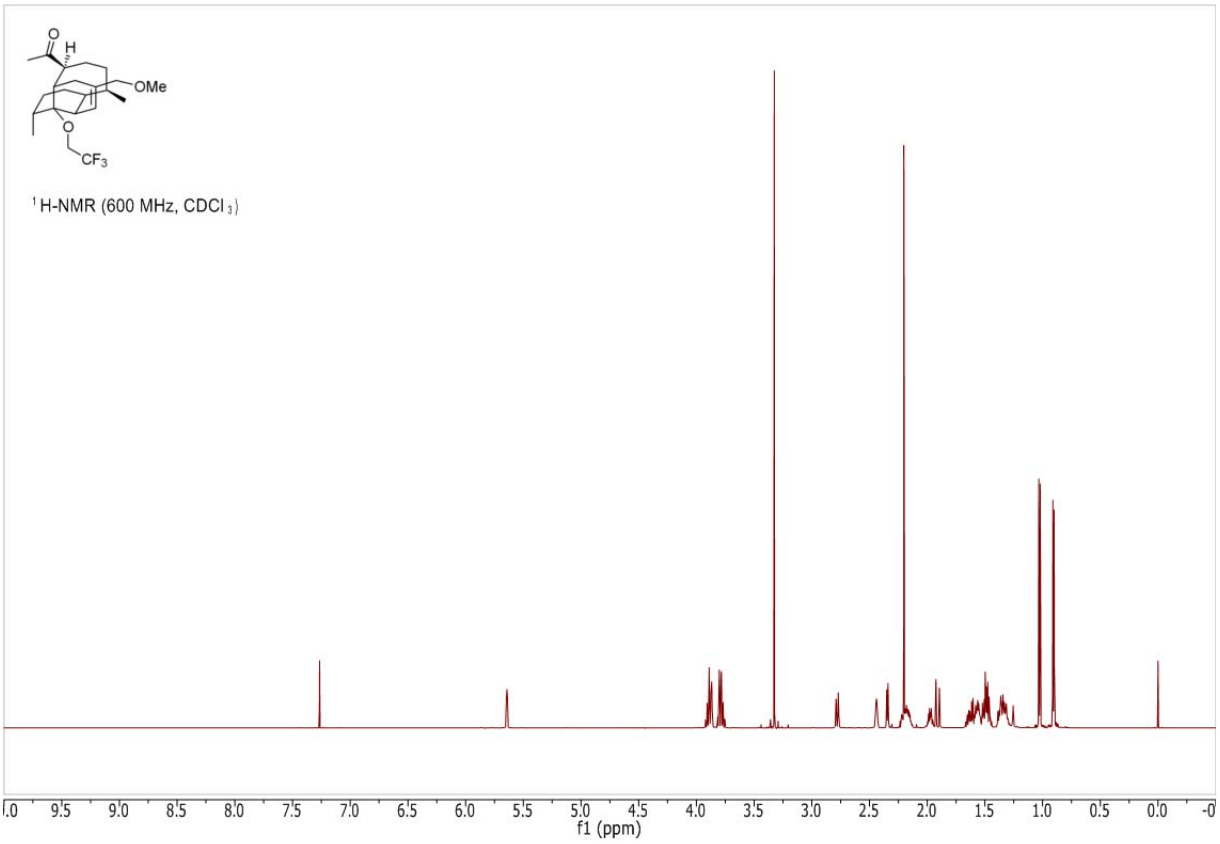
f1 (ppm)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CF3
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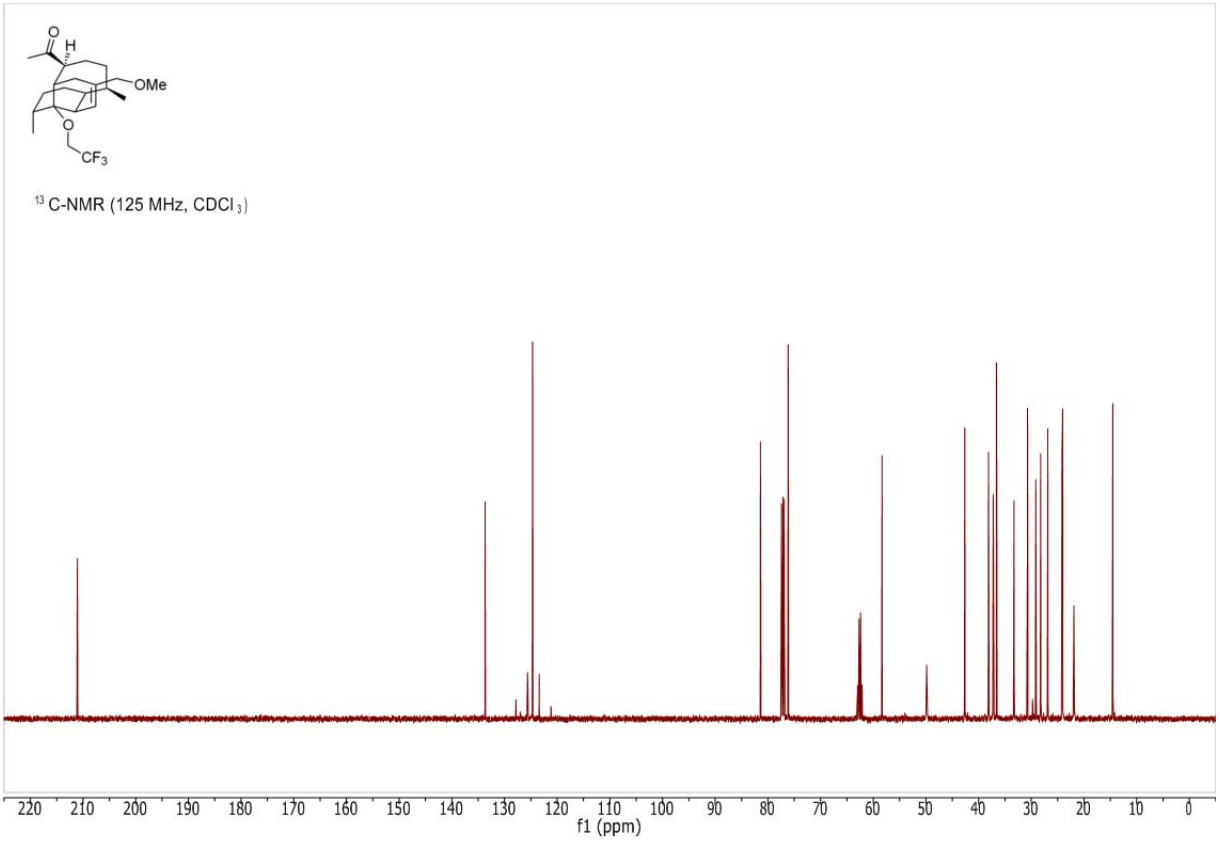
f1 (ppm)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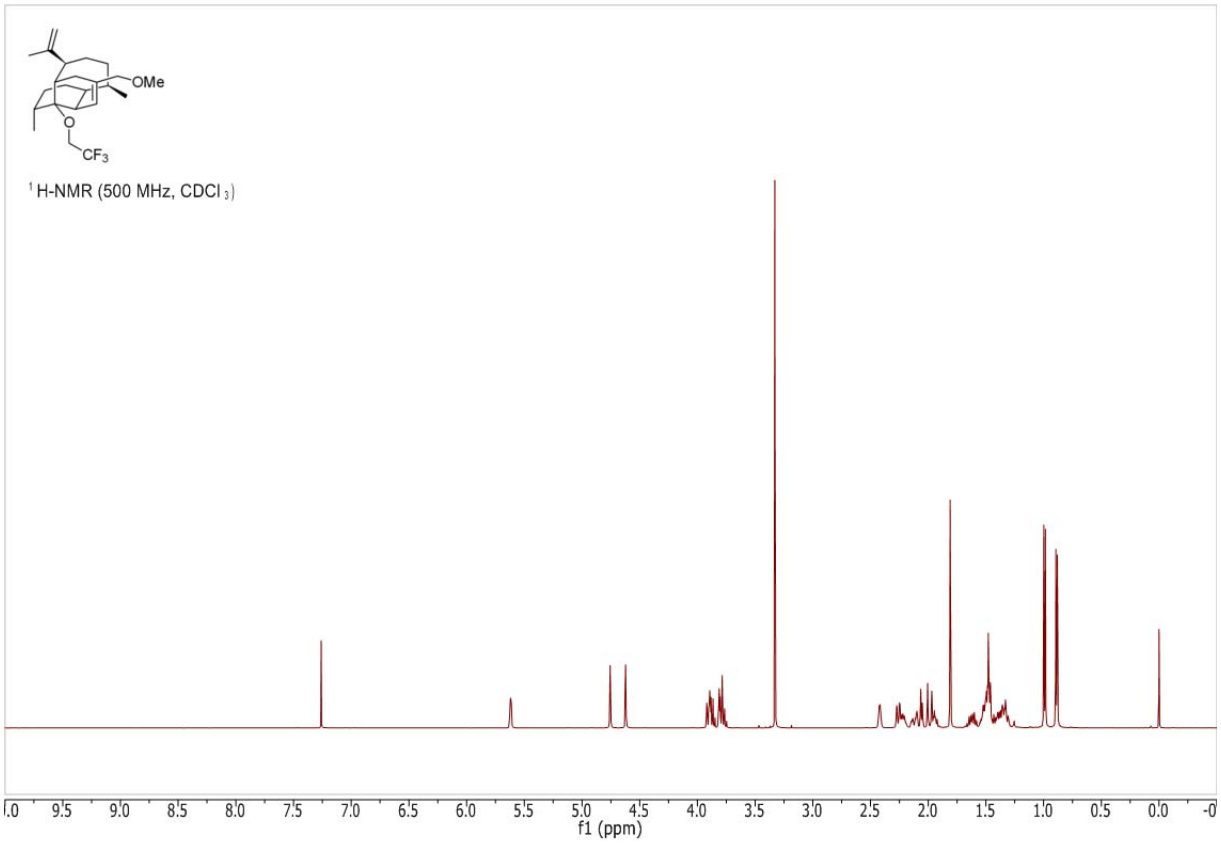
CF3
13C-NMR (125 MHz, CDCl3)
f1 (ppm)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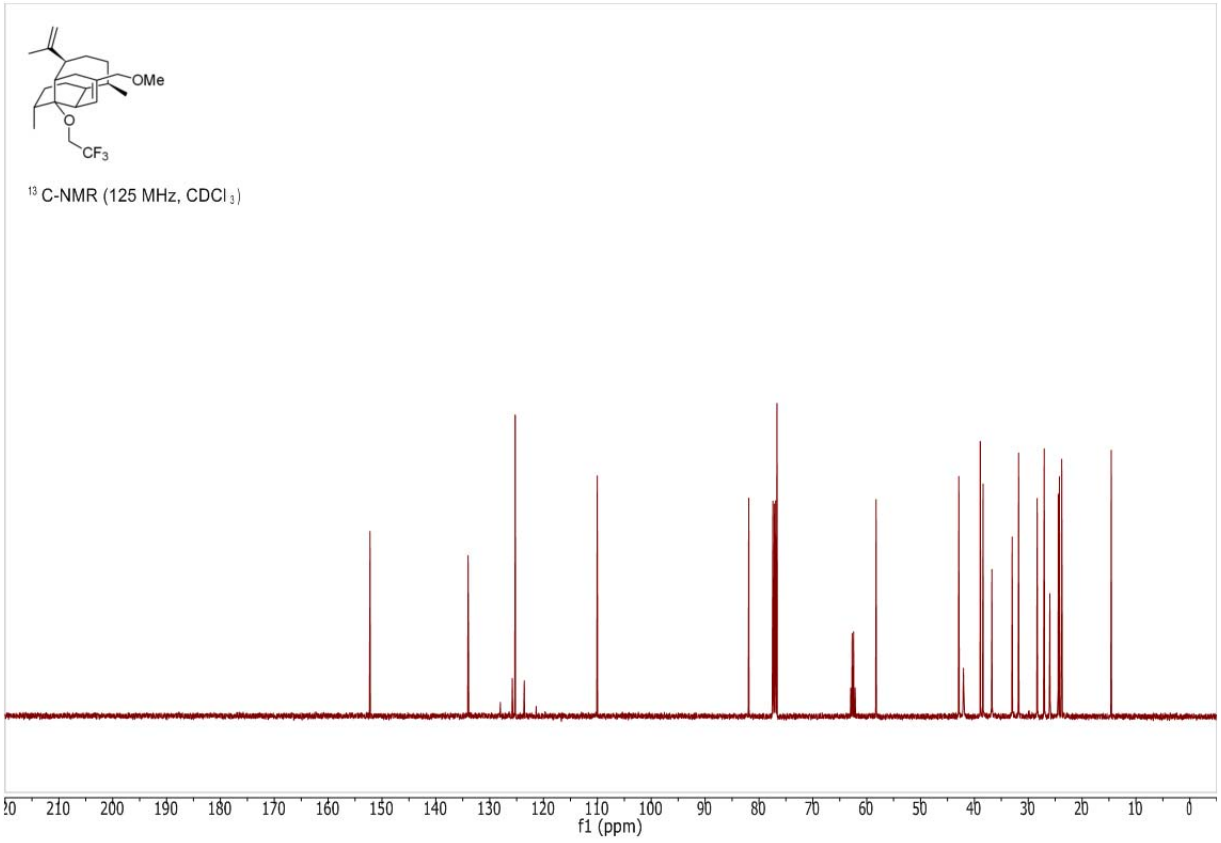
CF3
1 H-NMR (500 MHz, CDCl 3)
f1 (ppm)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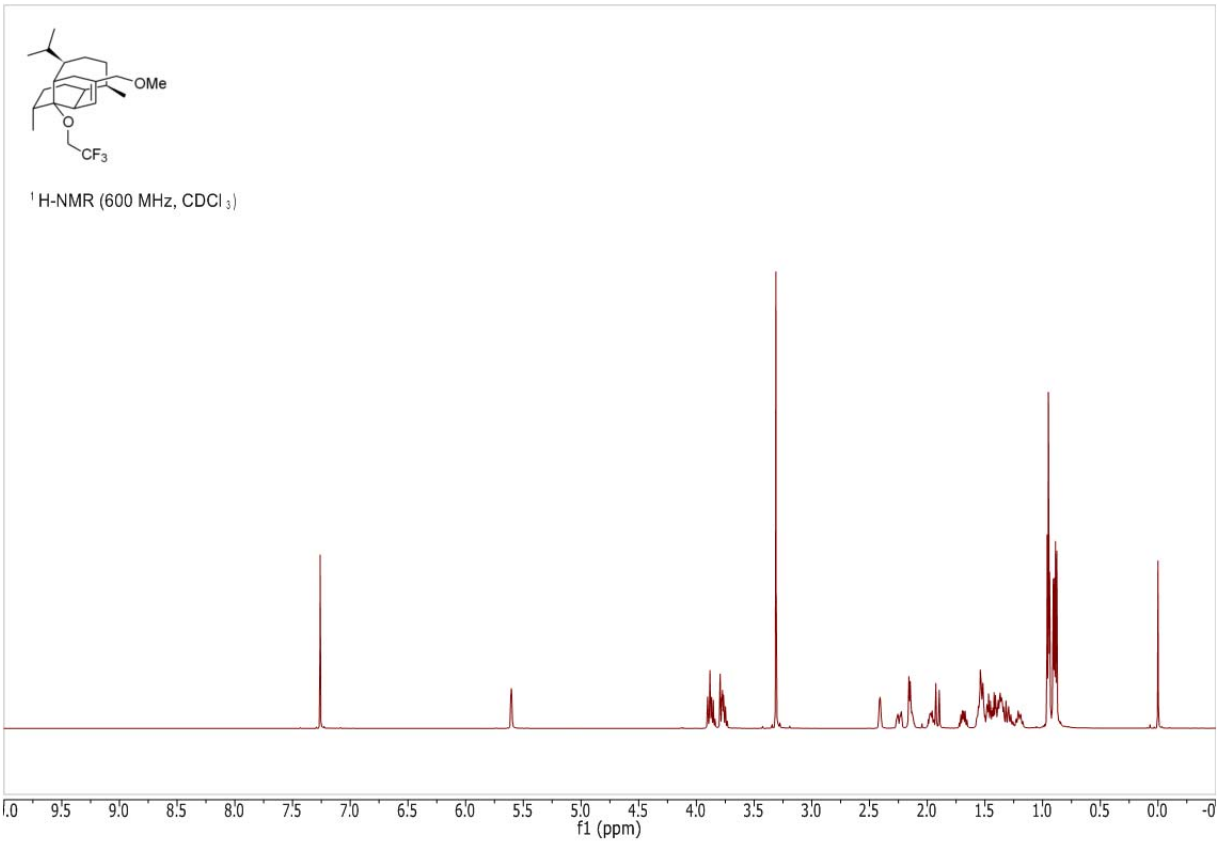
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)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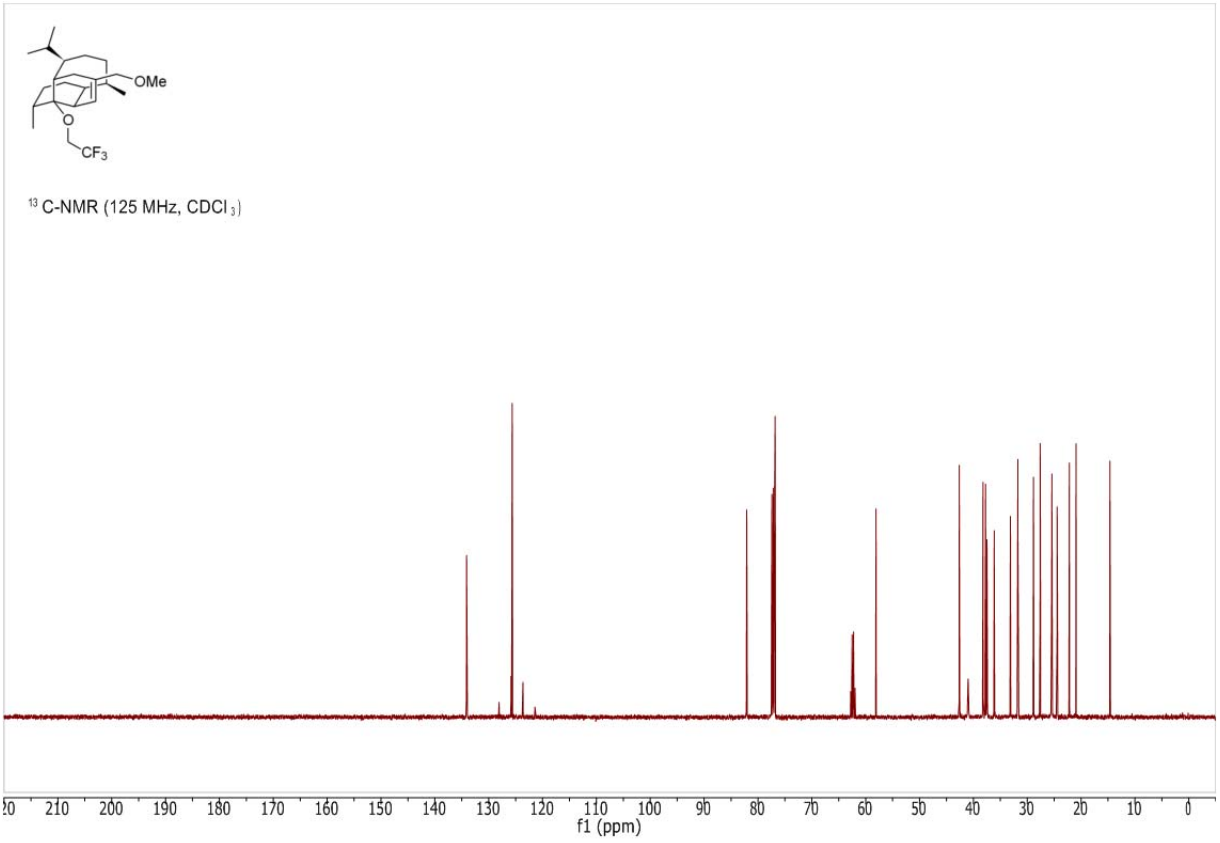
O
CF3
1 H-NMR (600 MHz, CDCl 3)
f1 (ppm)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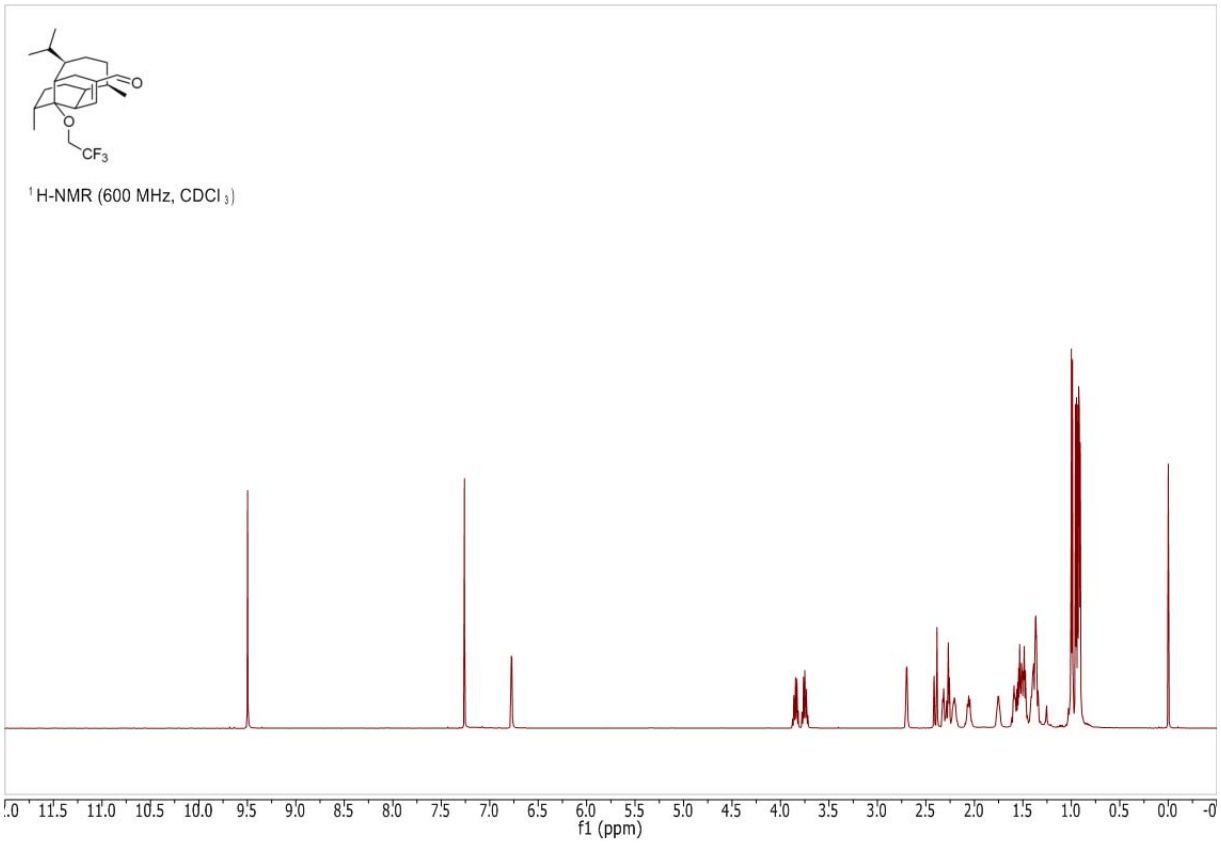
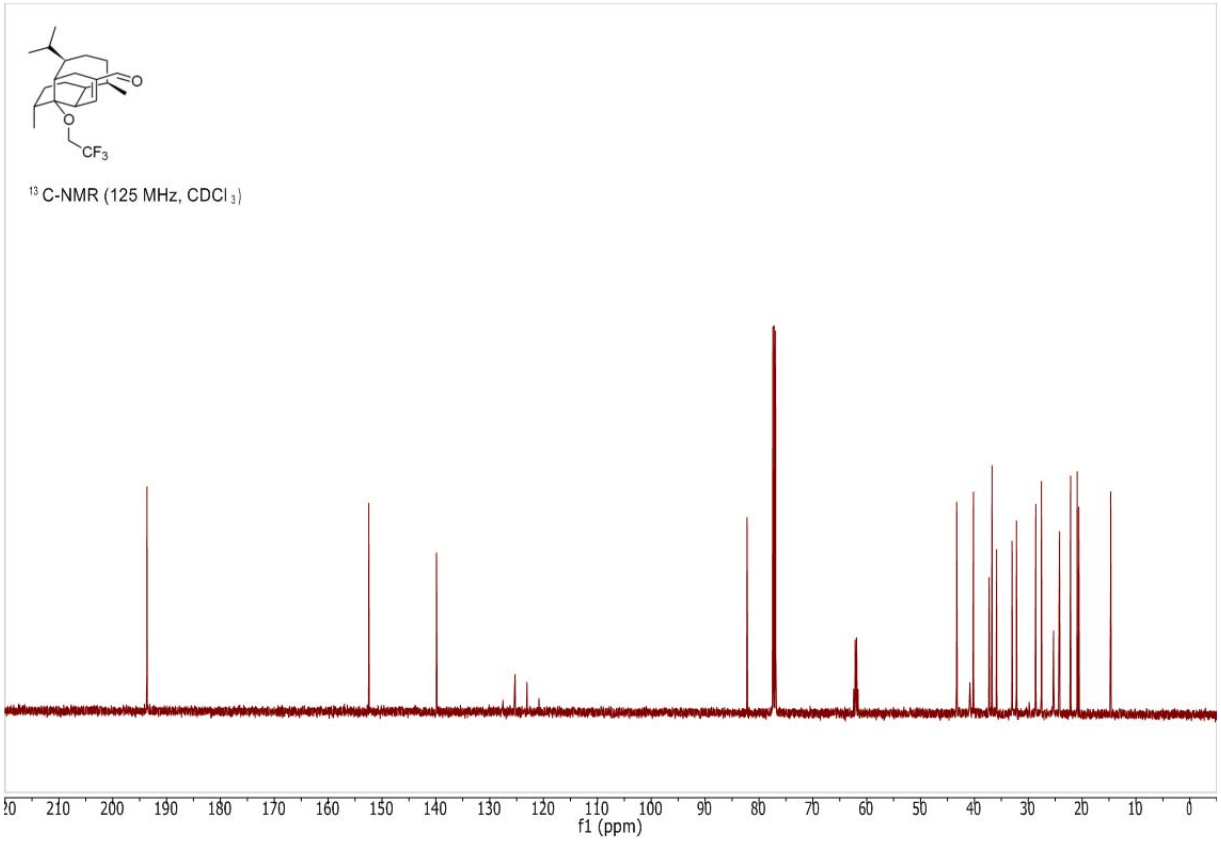
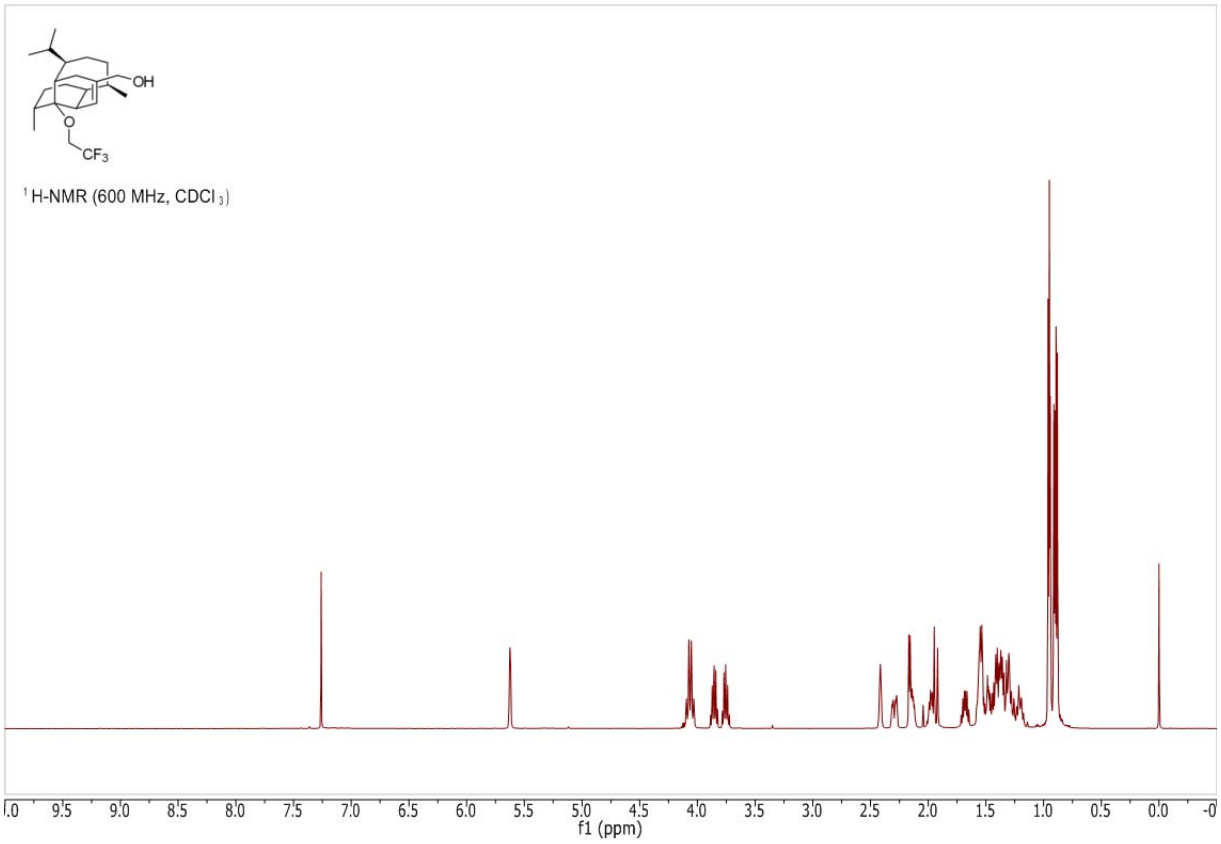
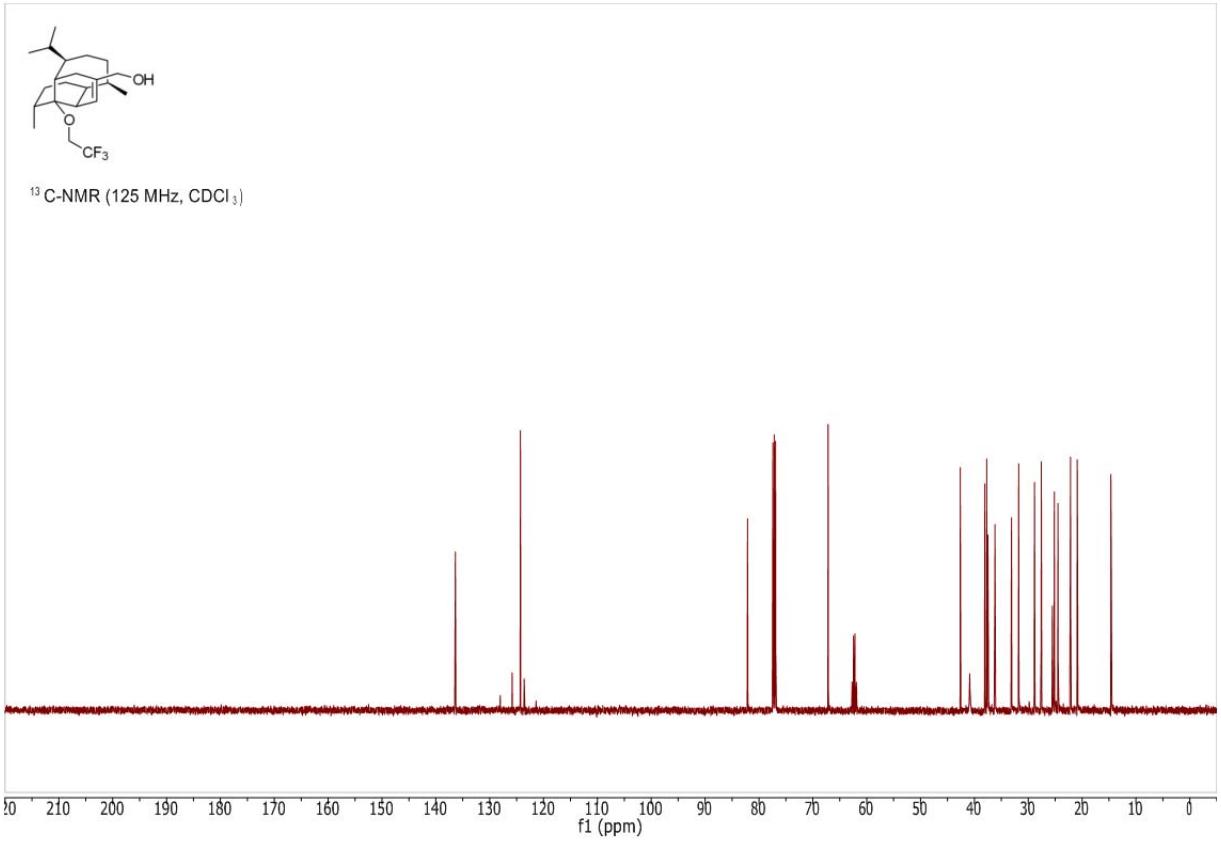
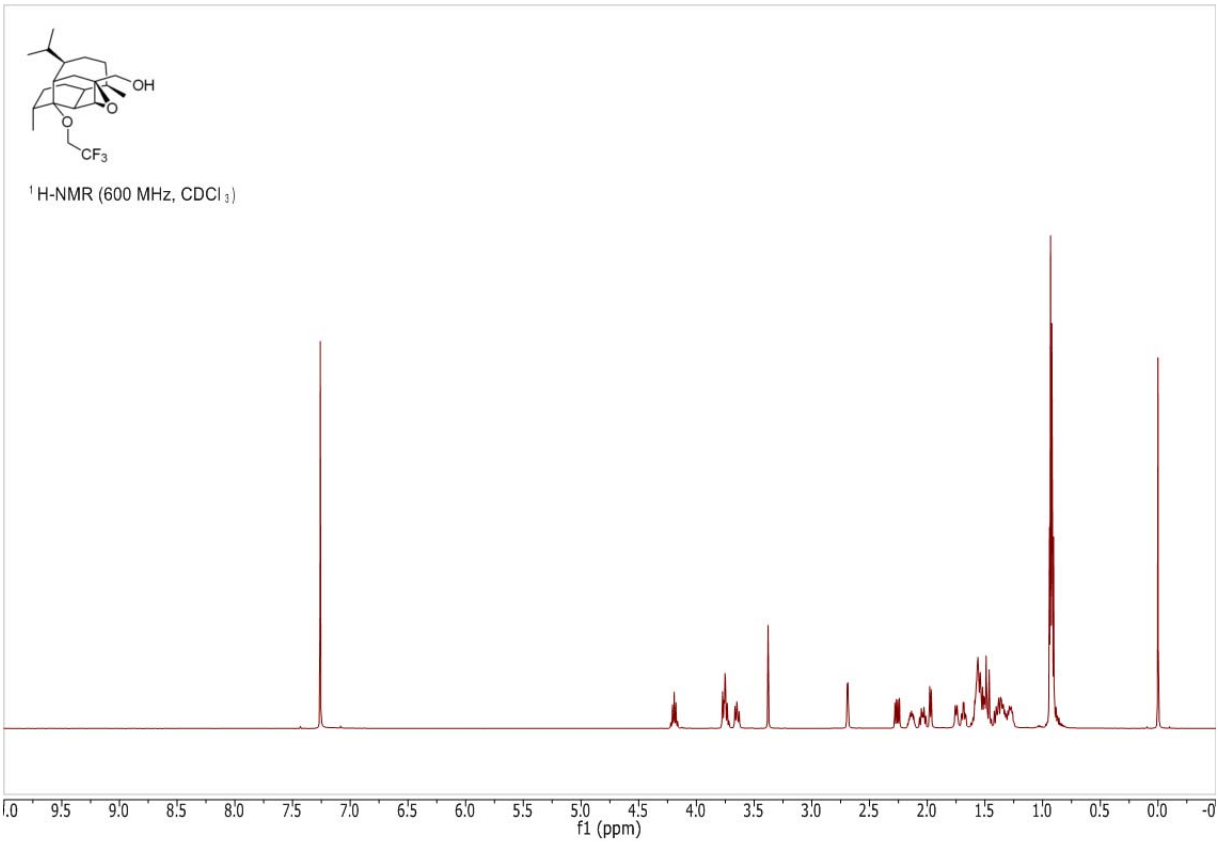
O
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)

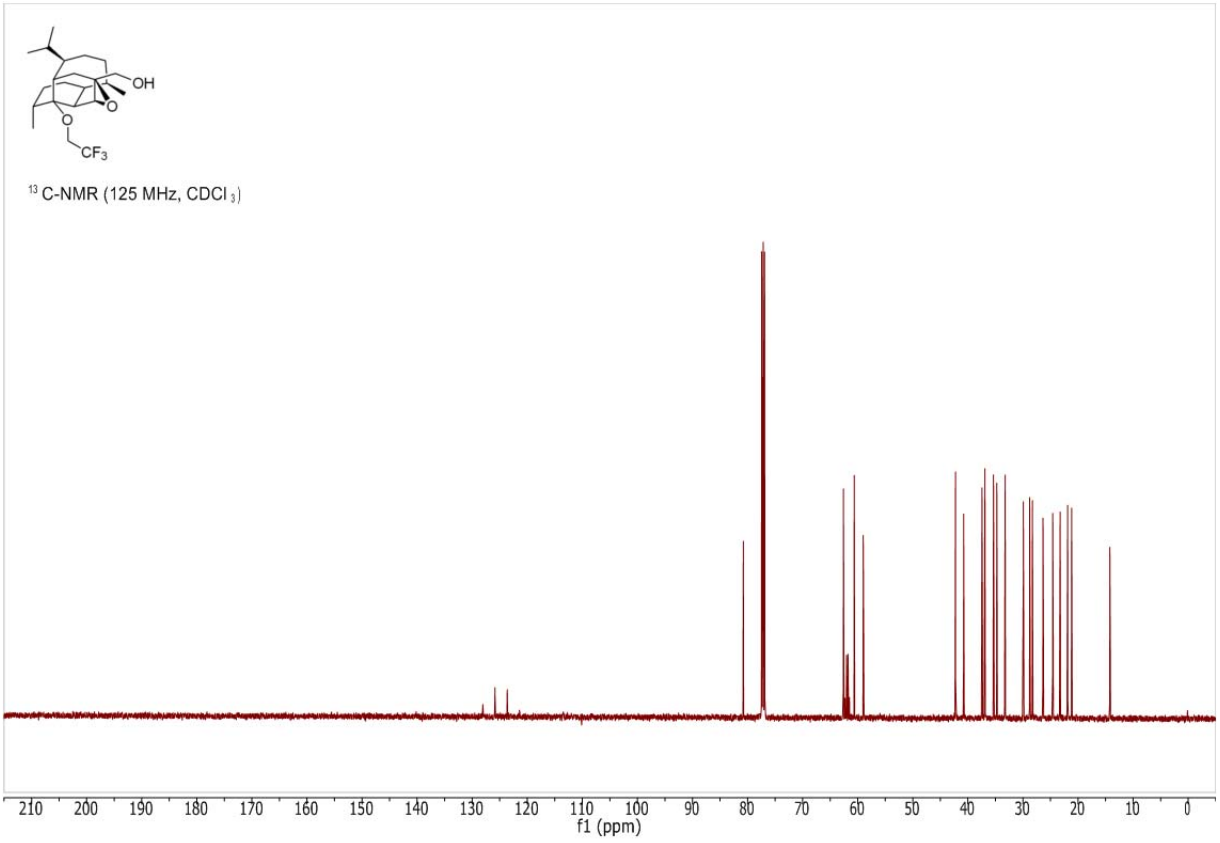

O
O
CF3
1H-NMR (600 MHz, CDCl3)
f1 (ppm)

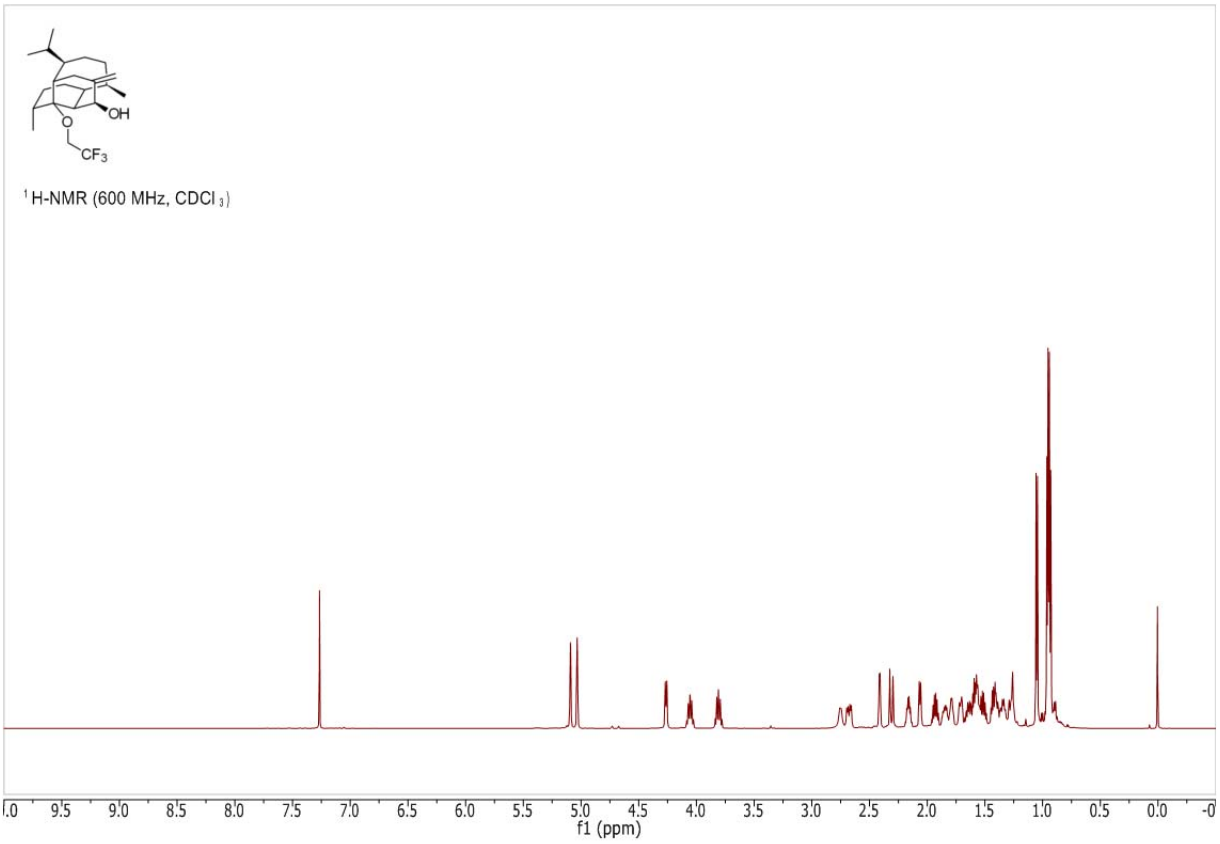

O
O
CF3
13C-NMR (125 MHz, CDCl3)
f1 (ppm)

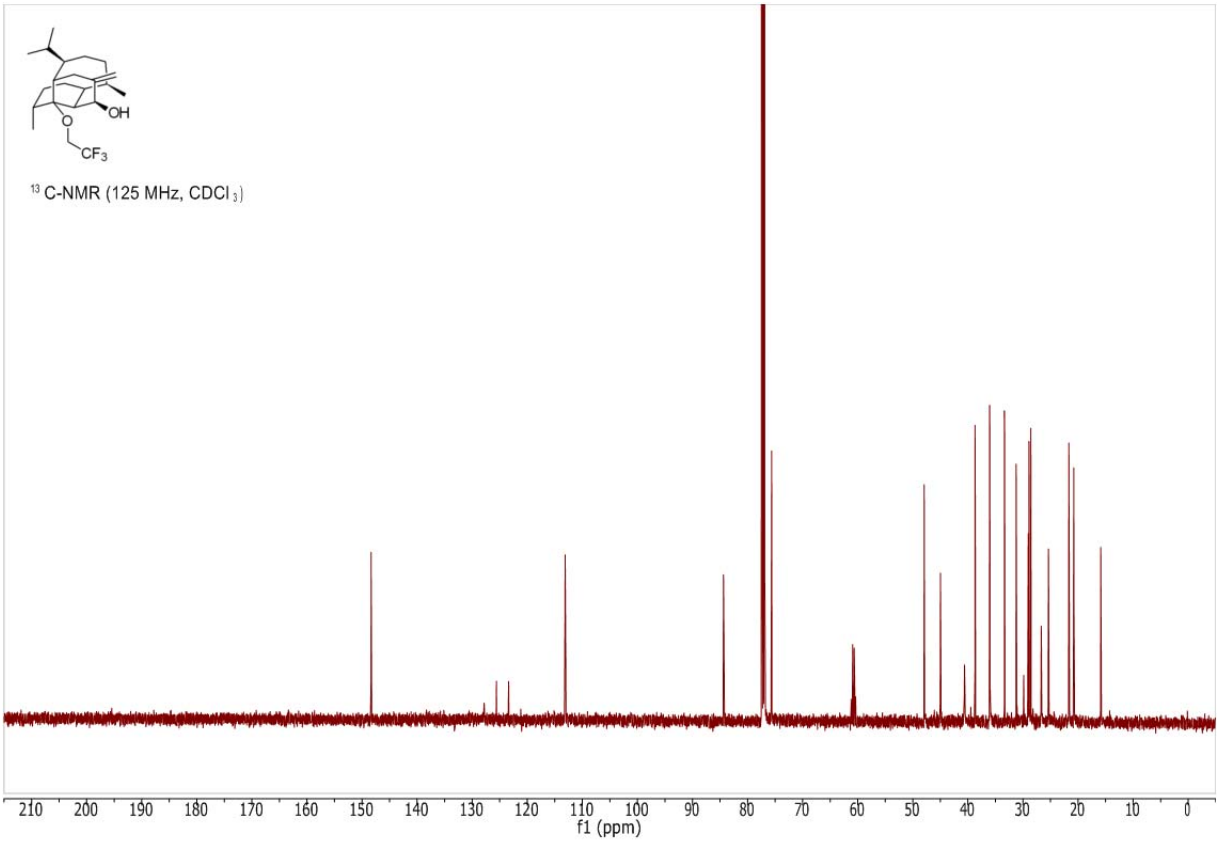

OH
O
CF3
1 H-NMR (600 MHz, CDCl 3)
f1 (ppm)

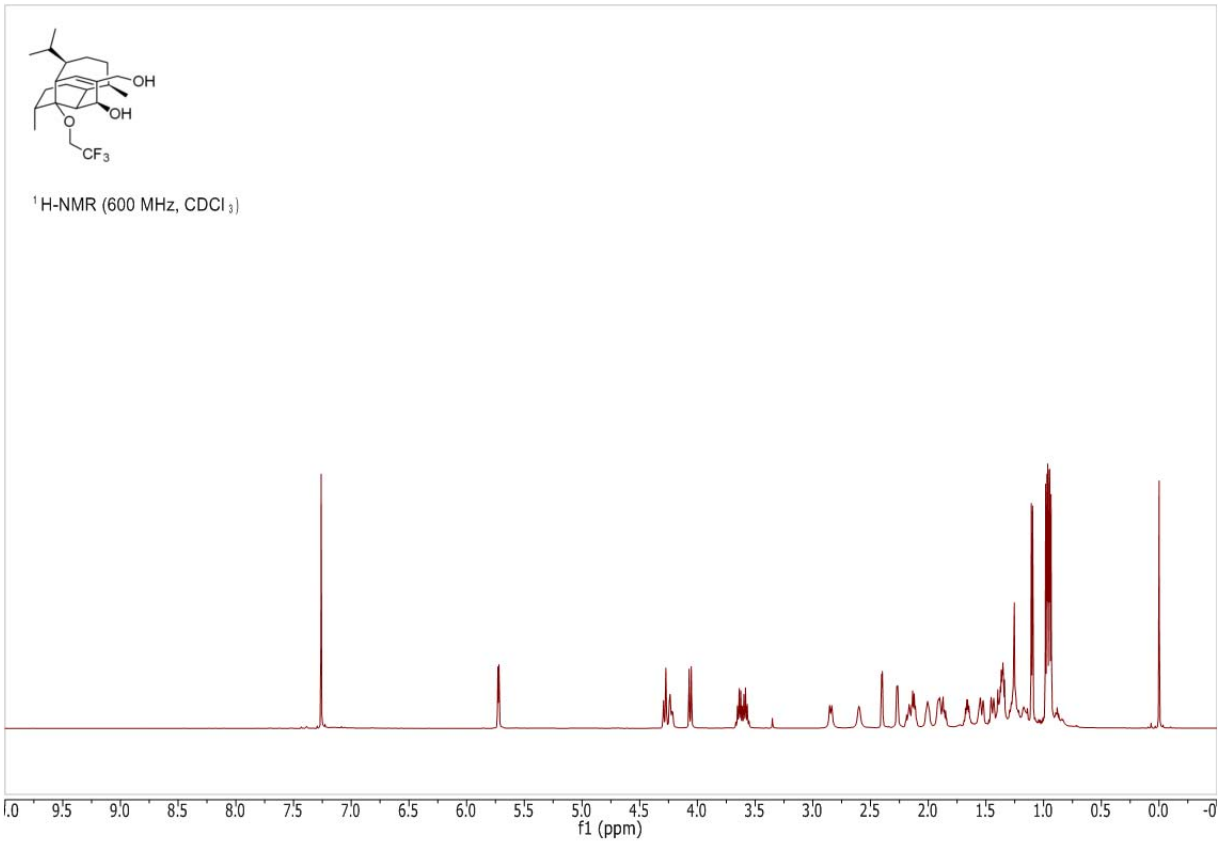

OH
O
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)

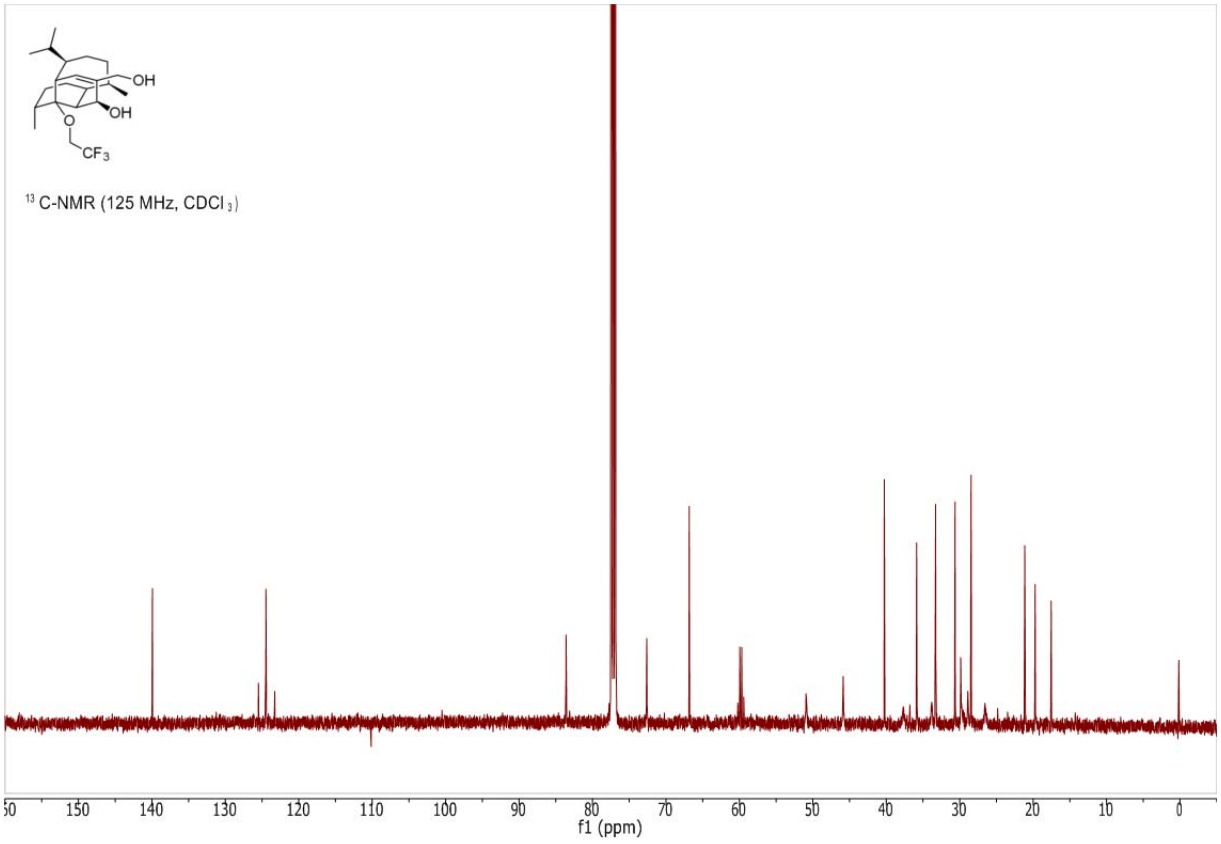

OH
O
O
CF3
1 H-NMR (600 MHz, CDCl 3)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

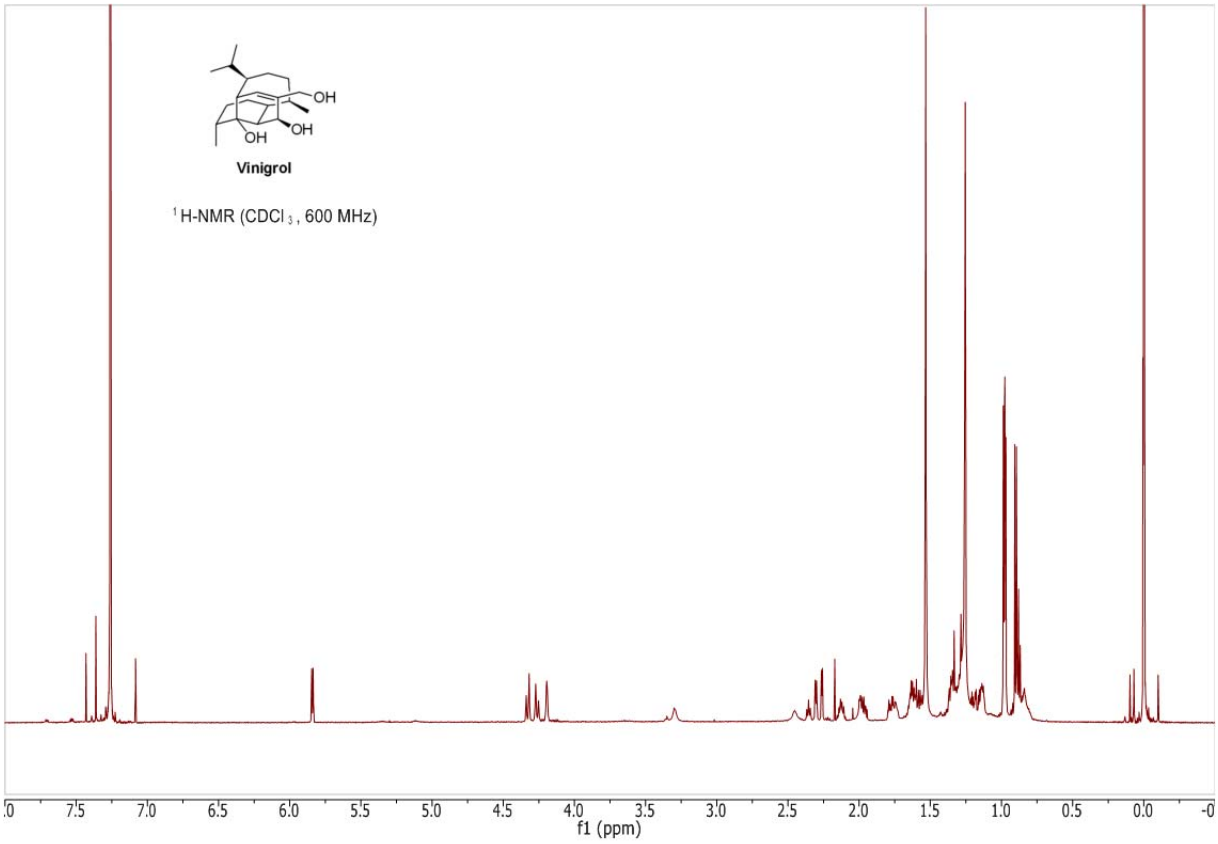

OH
O
O
CF3
13 C-NMR (125 MHz, CDCl 3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
O
CF3
1 H-NMR (600 MHz, CDCl 3)
f1 (ppm)

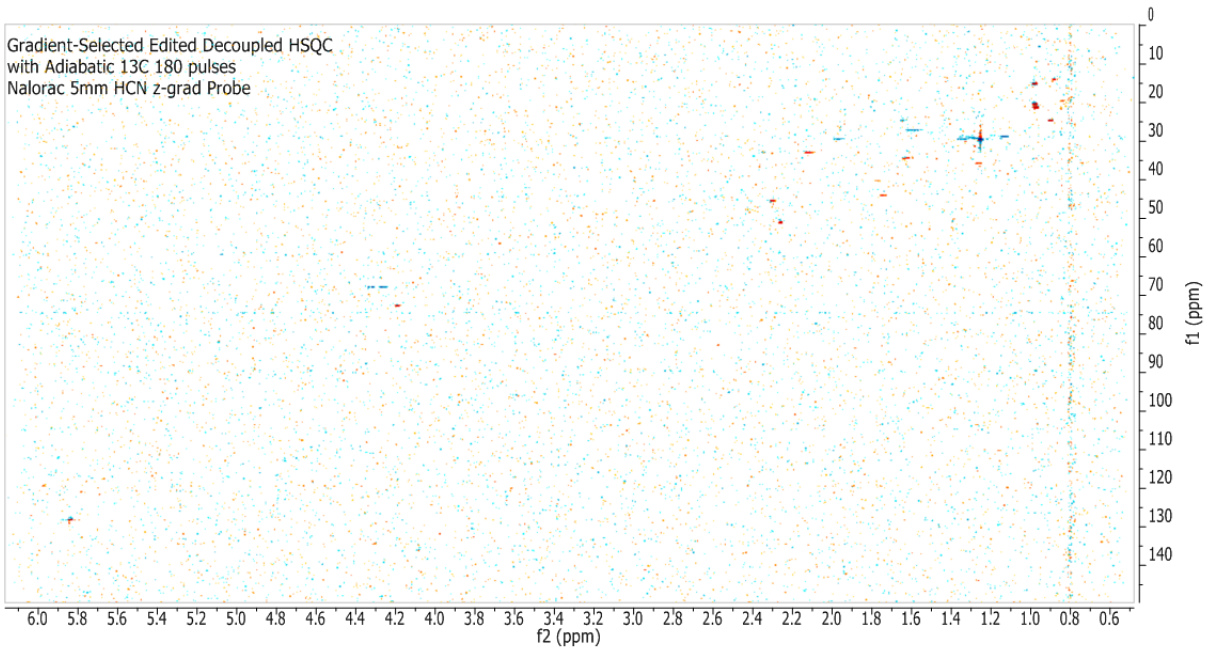

OH
O
CF3
13 C-NMR (125 MHz, CDCl 3)
f1 (ppm)


OH
OH
O
CF3
1H-NMR (600 MHz, CDCl3)
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)


OH
OH
O
CF3
13C-NMR (125 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OH
OH
Vinigrol
1H-NMR (CDCl3, 600 MHz)
f1 (ppm)


OH
OH
OH


Gradient-Selected Edited Decoupled HSQC
with Adiabatic 13C 180 pulses
Nalorac 5mm HCN z-grad Probe
f2 (ppm)
f1 (ppm)

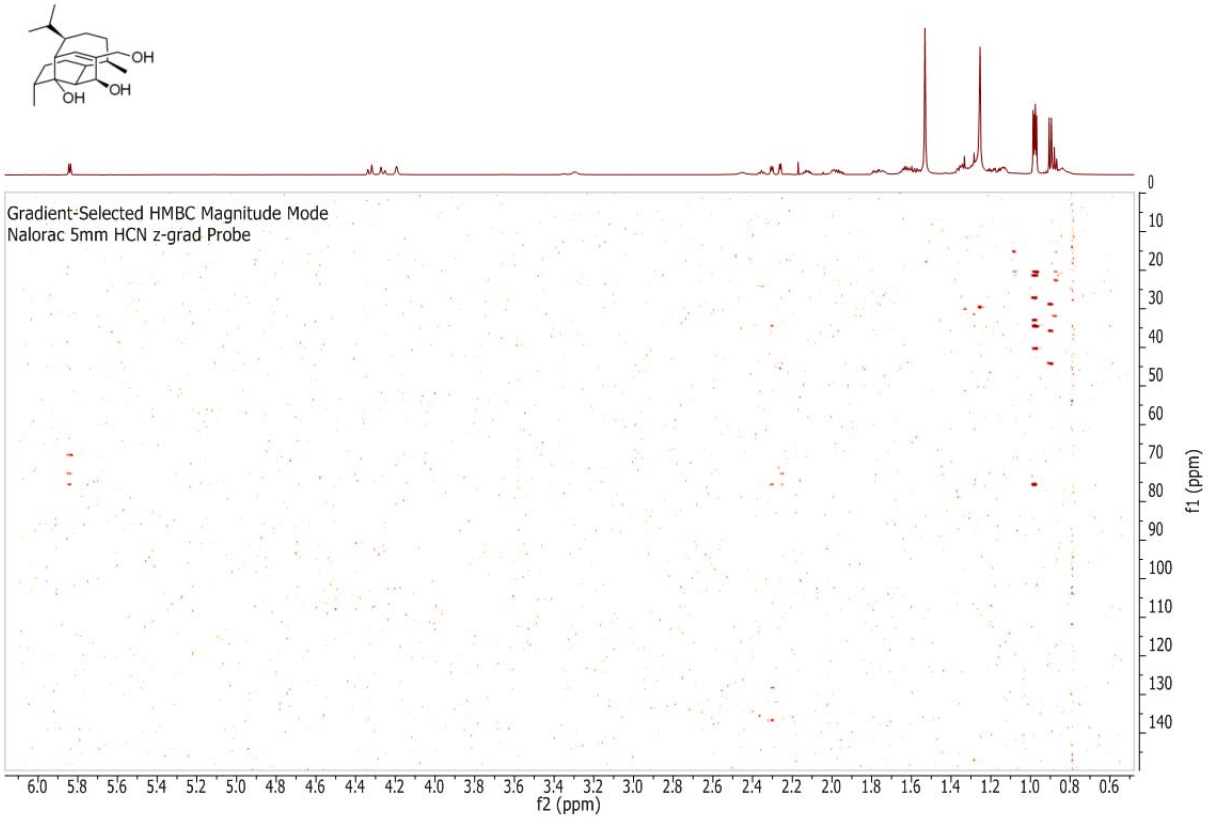


Table 1. Carbon chemical shifts of vinigrol extracted from HSQC and HMBC spectra

^{13}C (δ ppm)	^{1}H correlation from HSQC (δ ppm)	^{1}H correlation from HMBC (δ ppm)
136.8		2.30
128.4	5.84	2.30
75.6		5.84, 2.30, 0.98
72.8	4.19	5.84, 2.26
67.9	4.33, 4.26	5.84
51.3	2.26	
45.8	2.30	2.26
44.2	1.74	0.90
40.4	1.77	0.98
35.9	1.26	0.90
34.7	1.63	2.30, 0.98
33.1	2.12	0.98
29.6	1.97, 1.35	
29.0	1.34, 1.13	0.90
28.7	1.35, 1.19	
27.3	1.59	0.98
24.9	0.90	
21.5	0.98	0.98
20.6	0.98	0.98
15.4	0.98	

Table 2. ^{1}H NMR data comparison between **1** and Baran's vinigrol[7]

^{1}H NMR ($CDCl_3$, 600 MHz) δ of **1** in ppm (multiplicity, coupling constant)	^{1}H NMR ($CDCl_3$ 600 MHz) δ in ppm (as reported in ref. 7) (multiplicity, coupling constant)
5.84 (d, 5.6 Hz)	5.83 (d, 5.5 Hz)
4.30 (AB q, 12.0 Hz)	4.30 (AB q, 12.0 Hz)
4.19 (s)	4.20 (s)
3.30 (bs)	3.40 (bs)
2.45 (bs)	2.65 (bs)
2.30 (d, 5.6 Hz)	2.30 (d, 5.4 Hz)
2.26 (d, 3.9 Hz)	2.25 (d, 3.7 Hz)
2.15 – 2.09 (m)	2.15– 2.09 (m)
2.03 – 1.93 (m)	1.99 – 1.93 (m)
1.81 – 1.71 (m)	1.80 – 1.70 (m)
1.66 – 1.53 (m)	1.65 – 1.50 (m)
1.40 – 1.10 (m)	1.40 – 1.05 (m)
1.00 – 0.95 (m)	1.00 – 0.95 (m)
0.90 (d, 6.8 Hz)	0.9 (d, 6.8)

Table 3. ^{13}C NMR data comparison between **1** and Baran's vinigrol[7]

^{13}C NMR δ of **1** in ppm	^{13}C NMR ($CDCl_3$ 150 MHz) δ in ppm (as reported in ref. 7)
136.8	136.5
128.4	128.4
75.6	75.5
72.8	72.8
67.9	67.9
51.3	51.1
45.8	45.5
44.2	44.2
40.4	40.2
35.9	35.8
34.7	34.5
33.1	33.0
29.6	29.6
29.0	28.9
28.7	28.6
27.3	27.2
24.9	24.8
21.5	21.5
20.6	20.5
15.4	15.3

Reference

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