Supporting Information

A General Enantioselective and Stereochemically Divergent Four-Stage Approach to Fused Tetracyclic Terpenoid Systems

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1. Materials and Methods

A. Stereochemical Relationships

All stereochemical relationships depicted for products generated are the result of interpretation of both 1D and 2D NMR spectra. The relative stereochemistry between the C9 and 13 substituents was established via 1D nOe experiments, unless otherwise indicated.

B. Experimental Setups

All reactions were conducted in flame-dried glassware under an atmosphere of nitrogen and in anhydrous solvents unless otherwise indicated. Later examples utilized silylated glassware, azeotropically dried starting materials, and vacuum-dried BINOL. All reagents and starting materials were purchased from commercial sources and used as received, unless otherwise indicated. Anhydrous dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), tetrahydrofuran (THF), and toluene (PhMe) were obtained by passing commercially available HPLC grade solvents through a column of activated alumina using a Glass Contour Solvent Purification System by Pure Process Technology LLC. Titanium isopropoxide ($Ti(O\textit{i}\text{-}Pr)_4$) was distilled prior to use and stored in a foil-wrapped round bottom flask under an atmosphere of nitrogen. Said flask was stored in a desiccator when not in use. *n*-BuLi was purchased from Sigma-Aldrich as a 2.5 M solution in hexanes and was titrated against N-benzylbenzamide according to a literature procedure[1] to accurately determine the titer before use. Percent yields correspond to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Flash chromatography was performed on a Biotage® Automated Liquid Chromatography System Isolera One® using Biotage® SNAP KP-Sil 10-25 g or Biotage® SNAP Ultra 25 μm HP-Sphere 10-50 g silica gel cartridges or performed using a forced flow of the indicated solvent system on Sorbent Technologies TM silica gel 60Å (40–63 μm particle size). Thin phase chromatography (TLC) analyses were performed on EMD TLC silica gel 60 F_{234} glass plates and the compounds were visualized by exposure to UV light (254 nm) followed by staining with *p*-anisaldehyde, cerium ammonium molybdate, or $KMnO_4$.

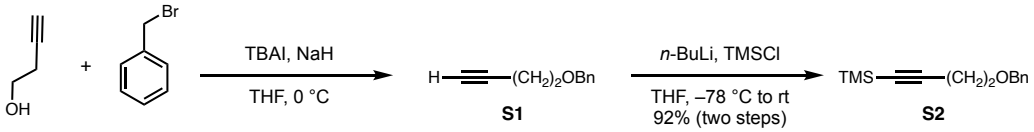
C. Spectral Analysis Information

^{1}H NMR spectra were recorded on a Bruker Avance III 500 MHz (TBI probe) or a 600 MHz (BBFO probe) spectrometer using chloroform-*d* ($CDCl_3$) as solvent for all samples. All signals are reported in parts per million (ppm) and calibrated to the residual protium signal of chloroform ($CHCl_3$, 7.26 ppm). Signals are reported as δ chemical shifts in ppm (multiplicity, coupling constants in Hz, integration). ^{13}C{1H} NMR spectra were recorded on a Bruker Avance III 600 MHz (BBFO probe) spectrometer measured at 150 MHz or a Bruker Avance III 500 MHz (TBI probe) spectrometer measured at 125 MHz. All signals are reported in ppm and are calibrated to the central line of the residual solvent signal of $CHCl_3$ (77.2 ppm). Signals are reported as δ chemical shift(s) in ppm. Two-dimensional NMR spectra, including COSY, HSQC, HMBC, and NOESY were recorded on a Bruker Avance III 600 MHz spectrometer (BBFO probe), or a Bruker Avance III 500 MHz spectrometer (TBI probe). Infrared spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer. IR absorption is reported as strong (s), medium (m), weak (w), and/or broad (br). ESI-TOF high-resolution mass spectroscopy (HRMS) analyses were performed at the mass spectrometry laboratory of the University of Illinois at Urbana-Champaign. Optical rotations ($[\boldsymbol{\alpha}]$) were obtained on a JASCO P-2000 polarimeter equipped with tungsten-halogen lamp (WI) and interface filter set to 589 nm, using a sample cell with a pathlength

of 100 mm. Specific rotations are reported as: $[\alpha]_{589}^{T\,(°C)}$: (c, solvent) and are based on the equation $[\alpha]_{589}^{T\,(°C)}$= (100•[α])/(l•c), where the concentration (c) is reported as g/2 mL and the pathlength (l) is in decimeters.

2. Experimental Procedures

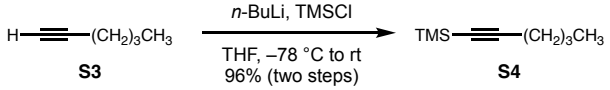
A. Synthesis of TMS Alkynes:



Synthesis of TMS-Alkyne S2: Alkyne **S1** was generated by the reported procedure described by Sarpong *et al*.[2] To a stirring solution of 3-butynol (5 mL, 66 mmol, 1.2 equiv.) in THF (55 mL) at 0 °C was sequentially added NaH (60% in oil, 2.6 g, 66 mmol, 1.2 equiv.), TBAI (2.03 g, 5.5 mmol. 0.1 equiv), and benzyl bromide (6.5 mL, 55 mmol, 1 equiv). The reaction mixture was stirred for 30 min at 0 ºC, before being warmed to rt and stirred overnight (about 16 h). The reaction was then quenched by the addition of saturated aqueous NH_4Cl and extracted with Et_2O (3 x 100 mL). The combined organic phases were washed with DI water (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Column chromatography (0–5% EtOAc in hexanes) afforded benzyl ether (**S1**) as a light-yellow oil which was used in a subsequent silylation reaction.

To a stirring solution of alkyne **S1**, in THF at –78 ºC was added *n*-BuLi (26.4 mL, 66 mmol, 1.2 equiv, 2.5 M in hexanes) dropwise. The reaction mixture was stirred at –78 ºC for 15 mins before the addition of TMSCl (8.37 mL, 66 mmol, 1.2 equiv) dropwise. The reaction mixture was then warmed to rt and stirred for 1 h after which time the reaction was quenched with saturated aqueous NH_4Cl (100 mL) and extracted with Et_2O (3 x 100 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford the desired silylated alkyne **S2** (12.0 g, 51.6 mmol, 92% yield) as a clear oil.

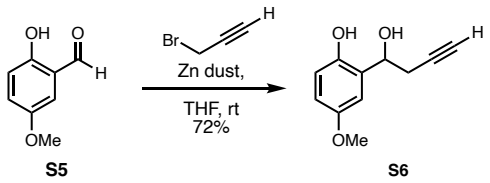
Spectral Data for Compound S2: The spectral data for **S2** matched previously reported data by Shaw *et al*.[3]



Synthesis of TMS-Alkyne S4: Alkyne **S4** was generated by the reported procedure described by Tonks *et al*.[4] To a stirring solution of alkyne **S3** (4.5 mL, 39.1 mmol, 1 equiv), in THF at –78 ºC was added *n*-BuLi (16.8 mL, 42 mmol, 1.1 equiv, 2.5 M in hexanes) dropwise. The reaction mixture was stirred at –78 ºC for 15 mins before the addition of TMSCl (5.35 mL, 42 mmol, 1.1 equiv) dropwise. The resulting solution was warmed to rt and stirred for 1 h after which time the reaction was quenched with saturated aqueous NH_4Cl (100 mL) and extracted with Et_2O (3 x 100 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford the desired silylated alkyne **S4** (5.8 g, 37.58 mmol, 96% yield) as a clear oil.

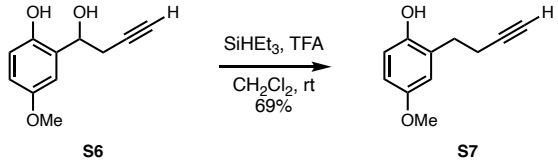
Spectral Data for Compound S4: The spectral data for **S4** matched previously reported data by Tonks *et al*.[4]

B. Synthesis of Enynes:



Synthesis of Diol S6: To a stirring solution of zinc dust (4.71g, 72.1 mmol, 3 equiv) in anhydrous THF (47 mL) at rt was added propargyl bromide (8.0 mL, 72.1 mmol, 3 equiv). The resulting solution was stirred for 2 h at rt. Then, 2-hydroxy-5-methoxybenzaldehyde **S5** (3 mL, 24.0 mmol, 1 equiv) was added dropwise. The reaction mixture was stirred for 17 h at rt, and progress was monitored by TLC. The reaction was quenched by the slow addition of saturated aqueous NH_4Cl. The biphasic solution was transferred to a separatory funnel and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 50 mL), and the combined organic phase was washed with brine (2 x 50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 25 g cartridge and a gradient from 10–25% EtOAc in hexanes to afford **S6** (3.35g, 17.4 mmol, 72%) as an orange oil.

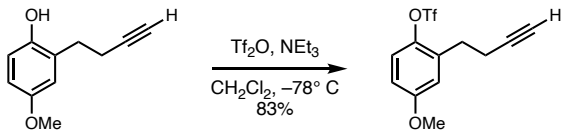
Data for Compound S6: The spectral data for **S6** matched previously reported data by Xiang *et al*.[5] For NMR Spectra of **S6** see page S69. **TLC:** R_f = 0.19 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 6.80 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 4.96 (dd, *J* = 8.9, 4.4 Hz, 1H), 3.75 (s, 3H), 2.80 (ddd, *J* = 16.9, 9.0, 2.5 Hz, 1H), 2.68 (ddd, *J* = 17.0, 4.5, 2.7 Hz, 1H), 2.15 (app. t, *J* = 2.4 Hz, 1H); **^{13}C{1H} NMR** (151 MHz, $CDCl_3$): δ 153.2, 149.1, 126.2, 118.1, 114.6, 112.9, 80.3, 73.5, 71.0, 55.9, 28.0.



Synthesis of Phenol S7: To a solution of the diol **S6** (0.20g, 1.04 mmol, 1 equiv) in CH_2Cl_2 (2.1 mL) at rt was added triethylsilane (0.3 mL, 2.08 mmol, 2 equiv). Then, trifluoroacetic acid (0.3 mL, 4.16 mmol, 4 equiv) was added dropwise and the reaction was stirred at rt for 1 h and the progress of the reaction was monitored by TLC (20% EtOAc in hexanes). Upon completion, the reaction was quenched with saturated aqueous $NaHCO_3$, and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Sfär Silica HC D 10 g cartridge and a gradient from 0–20% EtOAc in hexanes to afford the phenol **S7** (0.128g, 0.726 mmol, 69%) as a white solid.

Data for Compound S7: The spectral data for **S7** matched previously reported data by Xiang *et al*.[5] For NMR Spectra of **S7** see page S70. **TLC:** R_f = 0.44 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.79 – 6.69 (m, 2H), 6.66 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.76 – 4.65 (br, 1H), 3.76 (s, 3H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.51 (td, *J* = 7.3, 2.6 Hz, 2H), 2.01 (app. t, *J* = 2.7 Hz,

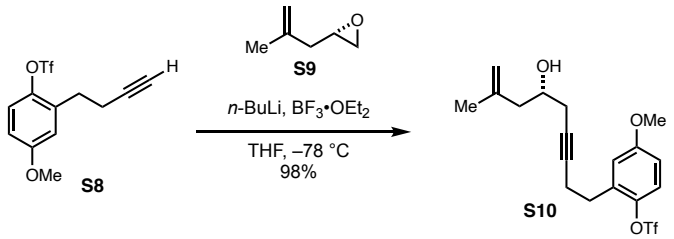
1H). **^{13}C{1H} NMR** (151 MHz, $CDCl_3$) δ 153.9, 147.6, 128.2, 116.6, 116.3, 112.67, 84.5, 69.3, 55.9, 30.0, 19.3.



S7 **S8**

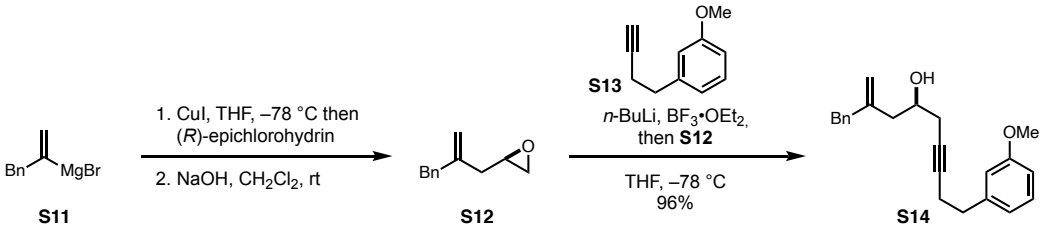
Synthesis of Aryl Triflate S8: To anhydrous CH_2Cl_2 (61 mL) was added the phenol S**7** (1.31 g, 7.45 mmol, 1 equiv), and the solution was cooled to –78 °C. Triethylamine (1.24 mL, 8.94 mmol, 1.2 equiv) was added dropwise, and the reaction mixture became bright yellow. Then, a solution of triflic anhydride (1.25 mL, 7.45 mmol, 1 equiv) in CH_2Cl_2 (14 mL) was added dropwise, and the solution became clear. The reaction mixture was stirred at –78 °C, and progress of the reaction was monitored by TLC (30% EtOAc in hexanes). The reaction was complete after 10 min and was quenched with saturated aqueous $NaHCO_3$. The organic phase was removed, and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® KP-Sil 50 g cartridge and a gradient from 0–20% EtOAc in hexanes to afford the aryl triflate **S1** (1.91g, 6.20 mmol, 83%) as an off-white oil.

Data for Compound S8: The spectral data for **S8** matched previously reported data by Millham *et al*.[6] For NMR Spectra of **S8** see page S71. **TLC:** R_f = 0.56 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.18 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 3.0 Hz, 1H), 6.80 (dd, *J* = 9.0, 3.1 Hz, 1H), 3.82 (s, 3H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.53 (td, *J* = 7.4, 2.6 Hz, 2H), 2.00 (app. t, *J* = 2.7 Hz, 1H); **^{13}C{1H} NMR** (151 MHz, $CDCl_3$): δ 159.0, 141.4, 134.4, 122.5, 121.9, 119.8, 117.7, 116.5, 115.3, 113.2, 82.8, 69.8, 55.8, 29.3, 19.0.



Synthesis of Enyne S10: To a round bottom flask was added the aryl triflate **S8** (0.42 g, 1.39 mmol, 2.5 equiv) in THF (4.6 mL). The solution was cooled to –78 °C, then *n*-BuLi (0.45 mL, 1.11 mmol, 2 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was stirred for 30 min at –78 °C, then BF_3•OEt_2 (0.14 mL, 1.17 mmol, 2.1 equiv) was added dropwise, and the mixture was stirred an additional 30 min at –78 °C. The epoxide **S9**[7] (52 µL, 0.56 mmol, 1 equiv) was added dropwise, and the reaction mixture was stirred for 2 h at –78 °C, and progress was monitored by TLC (30% EtOAc in hexanes). The reaction was quenched at –78 °C with saturated aqueous $NaHCO_3$. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® KP-Sil 25 g cartridge and a gradient from 0–20% EtOAc in hexanes to afford the enyne **S10** (0.222 g, 0.546 mmol, 98%) as an off-white oil.

Data for Compound S10: The spectral data for **S10** matched previously reported data by Millham *et al*.[6] For NMR Spectra of **S10** see page S72. **TLC:** R_f = 0.42 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.17 (d, *J* = 9.0 Hz, 1H), 6.90 (d, *J* = 3.1 Hz, 1H), 6.78 (dd, *J* = 9.0, 3.1 Hz, 1H), 4.86 (s, 1H), 4.77 (s, 1H), 3.84 – 3.78 (m, 4H), 2.88 (app. t, *J* = 7.3 Hz, 2H), 2.54 – 2.51 (m, 2H), 2.39 – 2.28 (m, 2H), 2.23 (dd, *J* = 13.8, 4.6 Hz, 1H), 2.15 (dd, *J* = 13.8, 8.5 Hz, 1H), 1.92 (d, *J* = 3.8 Hz, 1H), 1.74 (s, 3H); **^{13}C{1H} NMR** (151 MHz, $CDCl_3$): δ 159.0, 142.5, 141.5, 134.8, 122.4, 121.9, 119.8, 117.7, 116.6, 115.6, 113.6, 113.0, 81.3, 77.8, 67.8, 55.8, 44.9, 29.7, 27.3, 22.6, 19.3.



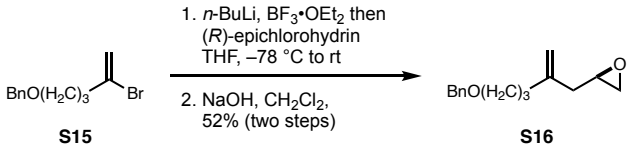
Synthesis of Epoxide S12: To a solution of Grignard reagent **S11**[8] (275 mL, 71.5 mmol, 0.26 M in THF, 1.15 equiv) at –78 °C was added CuI (2.72 g, 14.3 mmol, 0.23 equiv) with vigorous stirring. Then, (*R*)-epichlorohydrin (5.61 mL, 62.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred at –78 °C for 10 mins, and the cooling bath was removed. Upon reaching rt, the reaction was quenched with saturated aqueous NH_4Cl, and diluted with Et_2O and water. The phases were separated, and the aqueous phase was extracted with Et_2O (2 x 30 mL). The combined organic extracts were washed with H_2O (50 mL) and half saturated brine (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude chlorohydrin was taken on to the next step without further purification.

The crude intermediate chlorohydrin was dissolved in CH_2Cl_2 (65 mL) and crushed NaOH (5.80 g, 145 mmol, 2.3 equiv) was added. The reaction mixture was stirred vigorously at rt for 24 h, and then filtered through a short pad of sand and filter paper in a Büchner funnel, using additional CH_2Cl_2 to wash forward. The filtrate was concentrated *in vacuo* to afford the crude epoxide **S12**, which was split into portions and used in the next step without further purification.

Synthesis of Enyne S14: Alkyne **S13**[9] (6.78g, 42.3 mmol, 3.0 equiv) was dissolved in THF (45 mL) and cooled to –78 °C. *n*-BuLi (11.0 mL, 28.2 mmol, 2.5 M in hexanes, 2.0 equiv) was added dropwise, and the resulting solution was stirred at –78 °C for 30 mins. Then, BF_3•OEt_2 (4.35 mL, 35.3 mmol, 2.5 equiv) was added dropwise, and the reaction mixture was stirred at –78 °C for another 30 mins. Then, a solution of the epoxide **S12** (2.45 g, 14.1 mmol, 1 equiv) in THF (14 mL) was added dropwise. The resulting reaction mixture was stirred for another 1 h at –78 °C and was then quenched with saturated aqueous $NaHCO_3$ (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (4 x 25 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography (5–40% EtOAc in hexanes) to afford enyne **S14** (4.06 g, 13.5 mmol, 96%).

Data for Compound S14: For NMR Spectra of **S14** see page S73. **TLC:** R_f 0.38 (40% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 7.5 Hz, 2H), 7.24 – 7.18 (m, 4H), 6.82–6.76 (m, 3H), 4.95 (s, 1H), 4.90 (s, 1H), 3.88 – 3.83 (m, 1H), 3.80 (s, 3H), 3.40 (d, *J* = 15.1 Hz, 1H), 3.37 (d, *J* = 15.1 Hz, 1H), 2.78 (app. t, *J* = 7.5 Hz, 2H), 2.49 – 2.46 (m, 2H), 2.40 – 2.30 (m,

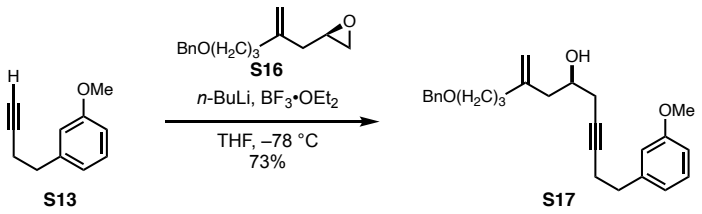
2H), 2.25 (dd, J = 14.2, 4.9 Hz, 1H), 2.14 (dd, J = 14.2, 8.2 Hz, 1H), 1.99 (d, J = 3.82 Hz 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.7, 145.7, 142.5, 139.3, 129.4, 129.2, 128.5, 126.4, 120.9, 114.6, 114.4, 111.6, 82.5, 77.0, 68.1, 55.2, 43.1, 42.4, 35.4, 27.3, 20.9; **IR** (thin film, cm^{-1}): 3446 (br, m), 3061 (w), 3026 (m), 3000 (w), 2933 (s), 2911 (s), 2835 (m), 1644 (m), 1602 (s), 1584 (s), 1492 (s), 1453 (s), 1436 (s), 1261 (s), 1153 (s), 1075 (m), 1052 (s), 898 (m), 778 (m), 742 (s), 698 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{27}O_2$ 335.2011; found, 335.2009, $[\alpha]_{589}^{21.2}$ = –11.5 (*c* 1.03, $CHCl_3$).



Synthesis of Epoxide S16: To a stirring solution of vinyl bromide **S15**[10] (5.00 g, 19.6 mmol, 1.0 equiv) in THF (70 mL) at –78 °C in a 200 mL round-bottom flask was added *n*-BuLi (11.8 mL, 29.4 mmol, 1.5 equiv, 2.5 M in hexanes). The solution was stirred for 30 min before the dropwise addition of BF_3•OEt_2 (2.67 mL, 21.6 mmol, 1.1 equiv) then (*R*)-epichlorohydrin (1.69 mL, 21.6 mmol, 1.10 equiv) as a solution in THF (8 mL). The resulting mixture was stirred at –78 °C for 5 min before being warmed to rt, then was stirred for 1 h before addition of saturated aqueous NH_4Cl (20 mL). The phases were separated, the aqueous phase was extracted with EtOAc (3 x 30 mL), and the combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude material was used in the next step without purification.

To the crude material was added CH_2Cl_2 (40 mL) and NaOH (1.57 g, 39.2 mmol, 2.0 equiv) and the solution was stirred at rt overnight. The reaction was quenched with H_2O (20 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic phase was dried over Na_2SO_4, filtered through celite, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Sfär 50 g cartridge and a gradient from 5–35% EtOAc in hexanes to afford epoxide **S16** (2.34 g, 10.1 mmol, 52%) as a pale, yellow oil.

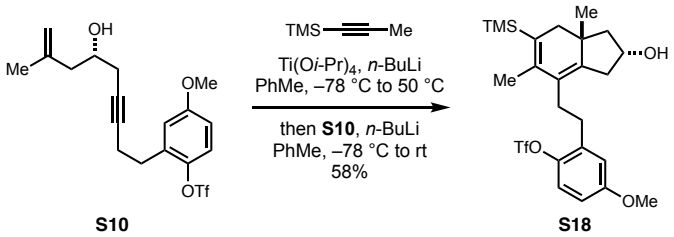
Data for Compound S16: For NMR Spectra of **S16** see page S74. **TLC**: R_f = 0.38 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.36 – 7.32 (m, 4H), 7.30 – 7.27 (m, 1H), 4.90 (s, 1H), 4.86 (s, 1H), 4.50 (d, J = 2.4 Hz, 2H), 3.49 (td, J = 6.4, 2.1 Hz, 2H), 3.05 – 3.00 (m, 1H), 2.80 – 2.78 (m, 1H), 2.51 – 2.47 (m, 1H), 2.31 – 2.25 (m, 1H), 2.23 – 2.14 (m, 3H), 1.81 – 1.75 (m, 2H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 145.4, 138.7, 128.5, 127.8, 127.7, 111.5, 73.1, 69.9, 51.3, 47.1, 39.4, 33.2, 27.9; **IR** (neat, cm^{-1}): 3031 (m), 2987 (m), 2923 (s), 2855 (s), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{21}O_2$ 233.1542; found, 233.1534; $[\alpha]_{589}^{22.1}$**:** +7.7 (*c* 0.0023, $CHCl_3$).



Synthesis of Enyne S17: To a stirring solution of **S13**[9] (4.05 g, 25.3 mmol, 2.5 equiv) in THF (70 mL) in a 200 mL round-bottom flask was added *n*-BuLi (6.10 mL, 15.2 mmol, 1.5 equiv, 2.5 M in hexanes). The solution was stirred for 30 min before BF_3•OEt_2 (2.54 mL, 20.2 mmol, 2.0 equiv), was added. After an additional 30 min **S16** (2.34 g, 10.1 mmol, 1.0 equiv) was added as a solution in THF (10 mL). The resulting mixture was stirred at –78 °C for 45 min before being quenched with saturated aqueous $NaHCO_3$ (20 mL) and then warmed to rt. The reaction mixture was diluted with EtOAc (30 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (3 x 30 mL), and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a gradient from 5–35% EtOAc in hexanes to afford enyne **S17** (2.88 g, 7.34 mmol, 73%) as an orange oil.

Data for Compound S17: For NMR Spectra of **S17** see page S75. **TLC**: R_f = 0.15 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.20 (app. t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.77 – 6.73 (m, 2H), 4.87 (s, 1H), 4.83 (s, 1H), 4.50 (s, 2H), 3.83 – 3.77 (m, 4H), 3.48 (app. t, *J* = 6.4 Hz, 2H), 2.78 (app. t, *J* = 7.4 Hz, 2H), 2.49 – 2.46 (m, 2H), 2.39 – 2.24 (m, 3H), 2.18 – 2.09 (m, 3H), 1.95 (d, *J* = 4.0 Hz, 1H), 1.81 – 1.73 (m, 2H), 1.53 (s, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.7, 145.8, 142.5, 138.6, 129.5, 128.5, 127.8, 127.7, 120.9, 114.4, 112.6, 111.6, 82.4, 77.1, 73.1, 69.9, 68.0, 55.2, 43.3, 35.5, 32.5, 27.9, 27.3, 20.9; **IR** (neat, cm^{-1}): 3445 (w), 3030 (w), 2934 (s), 2858 (m), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{33}O_3$ 393.2430; found, 393.2417; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$**:** –2.4 (*c* 0.0033, $CHCl_3$).

C. Synthesis of Hydrindanes:

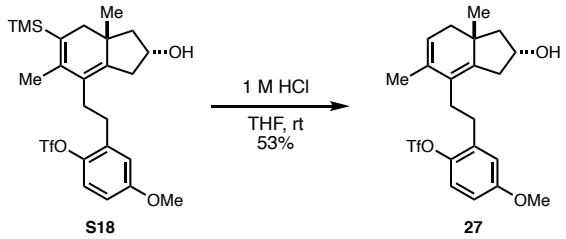


Synthesis of Hydrindane S18: Trimethylsilyl propyne (130 µL, 0.90 mmol, 3.3 equiv) and Ti(O*i*-Pr)$_4$ (0.27 mL, 0.901 mmol, 3.3 equiv) in anhydrous toluene (3.0 mL) were stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (0.72 mL, 1.80 mmol, 6.6 equiv) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S10** (111 mg, 0.273 mmol, 1.0 equiv) was diluted with anhydrous toluene (0.9 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.11 mL, 0.273 mmol, 1.0 equiv). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-propyne, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (1.5 mL) and stirred for 30 mins. The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Sfär Silica HC D 10 g cartridge and a gradient from 0–35% EtOAc in hexanes to afford hydrindane **S18** (82 mg, 0.158 mmol, 58%) as an orange oil.

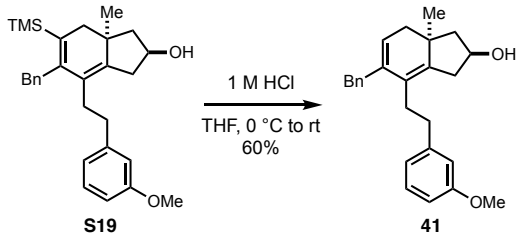
Data for Compound S18: For NMR Spectra of **S18** see page S76. **TLC**: R_f = 0.42 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.9 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.72 (s, 1H), 4.40 (app. p, *J* = 6.3 Hz, 1H), 3.79 (s, 3H), 2.75 (app. dt, *J* = 14.0, 7.2 Hz, 1H), 2.63 (m, 2H), 2.51 – 2.42 (m, 1H), 2.41 – 2.32 (m, 1H), 2.17 (d, *J* = 15.9 Hz, 1H), 2.05 – 1.94 (m, 3H), 1.89 (s, 3H), 1.38 (dd, *J* = 12.0, 8.0 Hz, 1H), 0.79 (s, 3H), 0.15 (s, 9H); **^{13}C{1H} NMR** (151 MHz, $CDCl_3$): δ 158.8, 145.3, 141.9, 140.9, 136.1, 128.8, 128.6, 122.1, 121.9, 119.8, 117.7, 117.2, 115.6, 112.5, 72.0, 55.8, 51.0, 41.5, 39.5, 38.4, 30.3, 30.0, 21.2, 19.1, 0.1.



S18 27

Synthesis of Hydrindane 27: To a stirring solution of hydrindane **S18** (23 mg, 0.044 mmol, 1 equiv) at 0 °C in THF (0.9 mL) was added 1 M HCl (0.56 mL), slowly. The reaction mixture was warmed to rt and stirred for 6 h (reaction progress was monitored by TLC (30% EtOAc in hexanes). Upon completion, the reaction mixture was diluted with EtOAc (1.5 mL) and the organic phase was separated and extracted with EtOAc (3 x 5 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography on a Biotage® Sfar Silica HC D 10 g cartridge and a gradient from 0–35% EtOAc in hexanes to afford protodesilylated hydrindane **27** (10.5 mg, 0.024 mmol, 53%) as a clear oil.

Data for Compound 27: The spectral data for **27** matched previously reported data by Millham *et al*.[6] For NMR Spectra of **27** see page S77. **TLC:** R_f = 0.35 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.15 (d, *J* = 9.0 Hz, 1H), 6.77 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.74 (d, *J* = 3.1 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 1H), 4.43 – 4.35 (m, 1H), 3.80 (s, 3H), 2.77 (ddd, *J* = 14.1, 8.2, 6.1 Hz, 1H), 2.67 – 2.56 (m, 2H), 2.44 – 2.31 (m, 2H), 2.12 (app. d, *J* = 16.5 Hz, 1H), 2.07 – 2.00 (m, 2H), 1.91 (dd, *J* = 17.8, 6.2 Hz, 1H), 1.82 (s, 3H), 1.39 (dd, *J* = 12.2, 7.9 Hz, 1H), 1.28 (d, *J* = 5.8 Hz, 1H), 0.87 (s, 3H); **^{13}C{1H} NMR** (151 MHz, $CDCl_3$): δ 158.8, 143.8, 141.9, 136.1, 132.4, 127.0, 122.2, 121.9, 120.4, 119.8, 117.7, 117.3, 115.7, 112.5, 72.0, 55.8, 51.1, 40.4, 38.0, 37.7, 30.2, 30.2, 22.3, 19.3.

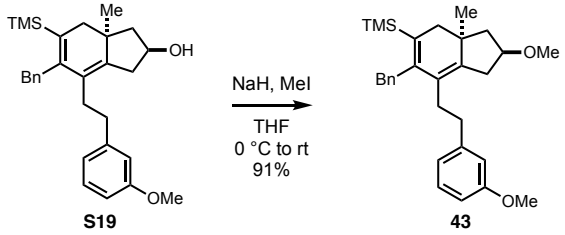


S19 41

Synthesis of Hydrindane 41: To a stirring solution of hydrindane **S19**[6] **(**284 mg, 0.636 mmol, 1.0 equiv) at 0 °C in THF (4 mL) was slowly added 1 M HCl (4 mL). The reaction mixture was warmed to rt over 4 h. Once reaction was judged to be complete by TLC analysis (20% EtOAc in hexanes) the mixture was cooled to 0 °C and saturated aqueous $NaHCO_3$ (3 mL) was added. The resulting solution was further diluted with EtOAc (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with EtOAc (3 x 15 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 10 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford **41** (144 mg, 0.384 mmol, 60%) as a pale-yellow oil.

Data for Compound 41: For NMR Spectra of **41** see page S94. **TLC**: R_f = 0.23 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.29 – 7.25 (m, 2H), 7.21 – 7.16 (m, 4H), 6.74 – 6.71

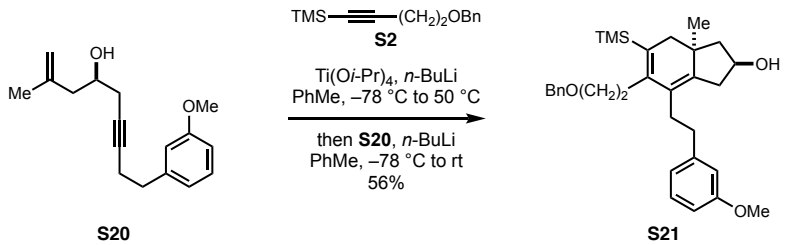
(m, 2H), 6.65 (s, 1H), 5.46 (d, J = 6.14 Hz, 1H), 4.39 – 4.36 (m, 1H), 3.80 (s, 3H), 3.54 – 3.47 (m, 2H), 2.65 (dd, J = 17.7, 7.4 Hz, 2H), 2.45 (app. dt, J = 8.2, 7.6 Hz, 1H), 2.33 – 2.31 (m, 1H), 2.23 – 2.19 (m, 2H), 2.13 (dd, J = 16.6, 6.6 Hz, 1H), 2.06 – 2.03 (m, 1H), 1.89 (dd, J = 17.9, 6.4 Hz, 1H), 1.43 (dd, J = 8.0, 4.3 Hz, 1H), 1.26 (m, 1H), 0.94 (s, 3H), **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.5, 143.8, 143.7, 140.6, 135.7, 130.3, 129.1, 128.7, 128.3, 127.2, 125.9, 122.5, 121.2, 114.7, 110.9, 71.8, 55.2, 51.2, 40.1, 39.4, 38.0, 37.7, 35.5, 31.4, 22.2; **IR** (neat, cm^{-1}): 3348 (s), 2921 (m), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{31}O_2$ 375.2324; found, 375.2314; $[\alpha]_{589}^{21.0}$**:** –10.3 (*c* 0.210, $CHCl_3$).



S19 **43**

Synthesis of Hydrindane 43: To a solution of **S19** (1.00 g, 2.24 mmol, 1.0 equiv) in THF (11 mL) at 0 °C was added NaH (270 mg, 6.72 mmol, 3 equiv), and the resulting mixture was stirred for 10 min before the addition of MeI (0.836 mL, 13.43 mmol, 6 equiv). The solution was warmed to rt and stirred overnight. When the reaction was judged to be complete by TLC analysis, the reaction mixture was cooled to 0 °C and a saturated aqueous solution of $NaHCO_3$ (3 mL) was added. The resulting biphasic mixture was separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography with a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford **43** (931 mg, 2.02 mmol, 91%) as a pale-yellow oil.

Data for Compound 43: For NMR Spectra of **43** see page S95. **TLC**: R_f = 0.50 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.25 (d, J = 7.2 Hz, 2H), 7.17 – 7.14 (m, 4H), 6.71 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 7.4 Hz, 1H), 6.58 (s, 1H), 4.02 – 3.96 (m, 1H), 3.78 (s, 3H), 3.56 (d, J = 16.1 Hz, 1H), 3.31 (s, 3H), 2.71 (dd, J = 18.1, 7.7 Hz, 1H), 2.50 – 2.45 (m, 1H), 2.38 (m, 1H), 2.32 (d, J = 16.0 Hz, 1H), 2.20 (m, 1H), 2.15 – 2.08 (m, 5H), 1.44 (dd, J = 10.5, 2.8 Hz, 1H), 0.93 (s, 3H), 0.15 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.5, 145.1, 143.8, 143.0, 141.0, 131.4, 129.1, 128.8, 128.3, 128.3, 125.8, 120.8, 114.3, 80.1, 57.0, 55.1, 48.0, 41.6, 38.9, 38.4, 35.6, 35.0, 31.6, 21.0, 0.2; **IR** (neat, cm^{-1}): 2947 (m), 1601 (m), **HRMS** (ESI-TOF) (*m/z*): $[M+Na]^+$ calcd for $C_{30}H_{40}O_2SiNa$ 483.2695; found, 483.2672; $[\alpha]_{589}^{21.0}$**:** +53.0 (*c* 0.605, $CHCl_3$).



S20 **S21**

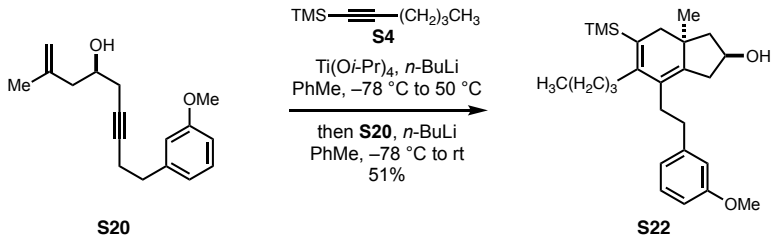
Synthesis of Hydrindane S21: A solution of TMS-alkyne **S2** (1.50 g, 6.45 mmol, 3.3 equiv), Ti(O*i*-Pr)$_4$ (1.9 mL, 6.45 mmol, 3.3 equiv), in anhydrous toluene (21.5 mL) was stirred in a round

bottom flask at –78 °C. Then, *n*-BuLi (5 mL, 12.7 mmol, 6.4 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S20**[7] (506 mg, 1.96 mmol, 1.0 equiv) was diluted with anhydrous toluene (6.5 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.78 mL, 1.96 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne **S2**, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (6.45 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (15 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–40% EtOAc in hexanes to afford hydrindane **S21** (542 mg, 1.10 mmol, 56%) as a pale, yellow oil.

Data for Compound S21: For NMR Spectra of **S21** see page S101. **TLC**: R_f = 0.19 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.33 – 7.31 (m, 4H), 7.29 – 7.27 (m, *J* = 4.33 Hz, 1H), 7.17 (app. t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 2H), 6.66 (s, 1H), 4.49 (s, 2H), 4.34 – 4.31 (m, 1H), 3.78 (s, 3H), 3.43 (td, *J* = 10.0, 4.9 Hz, 1H), 3.32 (td, *J* = 6.3, 3.3 Hz, 1H), 2.78 (ddd, *J* = 6.3, 4.5, 2.4 Hz, 1H), 2.67 – 2.58 (m, 3H), 2.49 – 2.42 (m, 2H), 2.34 – 2.31 (m, 1H), 2.15 (d, *J* = 16.0 Hz, 1H), 1.98 – 2.92 (m, 2H), 1.90 (dd, *J* = 11.3, 6.3 Hz, 1H), 1.35 (dd, *J* = 7.7, 4.8 Hz, 1H), 1.09 (d, *J* = 6.4 Hz, 1H), 0.74 (s, 3H), 0.16 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.3, 145.3, 143.3, 141.8, 138.3, 131.4, 129.0, 128.2, 127.9, 127.4, 127.3, 121.0, 114.6, 110.8, 72.9, 71.6, 70.8, 55.0, 50.8, 41.3, 39.0, 38.3, 35.3, 32.6, 31.2, 21.0; **IR** (neat, cm^{-1}): 3398 (s), 2921 (m), 1601 (m), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{31}H_{43}O_3Si$ 491.2981; found, 491.2975; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.8}}$**:** –1.4 (*c* 0.15, $CHCl_3$).

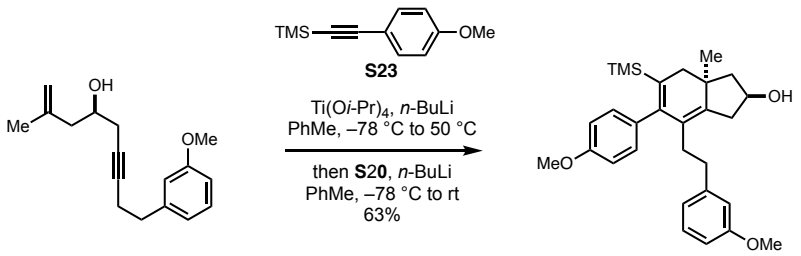


Synthesis of Hydrindane S22: A solution of TMS-alkyne **S4** (0.515 mL, 2.55 mmol, 3.3 equiv), Ti(O*i*-Pr)$_4$ (0.755 mL, 2.55 mmol, 3.3 equiv), in anhydrous toluene (8.5 mL) was stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (2 mL, 5.03 mmol, 6.5 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S20**[7] (200 mg, 0.774 mmol, 1.0 equiv) was diluted with anhydrous toluene (2.6 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.31 mL, 0.774 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne **S4**, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (270 µL, 2.55 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (5 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–25% EtOAc in hexanes to afford hydrindane **S22** (161 mg, 0.390 mmol, 51%) as a pale, yellow oil.

Data for Compound S22: For NMR Spectra of **S22** see page S104. **TLC**: R_f = 0.13 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.18 (app. t, *J* = 7.8 Hz, 1H), 6.76 – 6.72 (m, 2H), 6.67 (s, 1H), 4.38 – 4.31 (m, 1H), 3.79 (s, 3H), 2.72 – 2.62 (m, 2H), 2.50 – 2.43 (m, 1H), 2.43 – 2.31 (m, 3H), 2.21 – 2.17 (m, 1H), 2.13 (d, *J* = 16.0 Hz, 1H), 2.01 – 1.91 (m, 3H), 1.41 – 1.31 (m, 4H), 1.21 – 1.13 (m, 1H), 1.10 (d, *J* = 6.4 Hz, 1H), 0.92 (t, *J* = 6.7 Hz, 3H), 0.79 (s, 3H), 0.16 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 146.9, 145.2, 143.9, 129.3, 128.5, 128.4, 121.3, 114.8, 111.1, 72.0, 55.3, 51.2, 41.5, 39.4, 38.6, 35.7, 33.4, 32.5, 31.6, 23.2, 21.4, 14.2, 0.4; **IR** (neat, cm^{-1}): 3384 (m, br), 2952 (s), 2858 (s), 1740 (w); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{41}O_2Si$ 413.2876; found, 413.2870; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.0}}$**:** –7.2 (*c* 0.0025, $CHCl_3$).

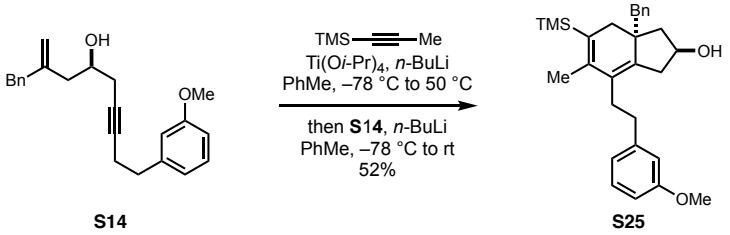


Synthesis of Hydrindane S24: A solution of TMS-alkyne **S23** (521 mg, 2.55 mmol, 3.3 equiv), Ti(O*i*-Pr)4 (0.755 mL, 2.55 mmol, 3.3 equiv), in anhydrous toluene (8.5 mL) was stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (2 mL, 5.03 mmol, 6.5 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S20**[7] (200 mg, 0.774 mmol, 1.0 equiv) was diluted with anhydrous toluene (2.6 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.31 mL, 0.774 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne **S23**, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (260 µL, 2.55 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (15 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–40% EtOAc in hexanes to afford hydrindane **S24** (224 mg, 0.484 mmol, 63%) as a pale, yellow oil.

Data for Compound S24: For NMR Spectra of **S24** see page S107. **TLC**: R_f = 0.27 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.10 (app. t, *J* = 7.8 Hz, 2H), 6.95 (s, 1H), 6.85 (s, 2H), 6.70 – 6.64 (m, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 2.5 Hz, 1H), 4.48 – 4.40 (m, 1H), 3.83 (d, *J* = 1.1 Hz, 3H), 3.73 (d, *J* = 1.1 Hz, 3H), 2.69 (dd, *J* = 17.9, 7.6 Hz, 1H), 2.38 – 2.30 (m, 2H), 2.25 – 2.21 (m, 2H), 2.17 (d, *J* = 15.8 Hz, 2H), 2.14 – 2.08 (m, 3H), 2.05 –2.00 (m, 1H), 1.49 (dd, *J* = 12.3, 7.9 Hz, 1H), 1.33 (br, 1H), 0.95 (s, 3H), -0.23 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.4, 158.5, 147.4, 144.6, 143.9, 134.7, 131.7, 129.0, 128.6, 121.0, 114.1, 111.1, 72.0, 55.2, 55.1, 51.1, 41.1, 39.5, 38.3, 35.3, 32.3, 21.3, 21.2, 0.6; **IR** (neat, cm^{-1}): 3366 (s), 2950 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{29}H_{39}O_3Si$ 463.2668; found, 463.2651; $[\alpha]_{589}^{21.6}$**:** +50.2 (*c* 0.145, $CHCl_3$).



S14 **S25**

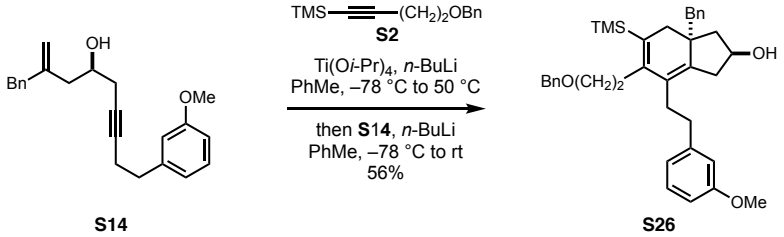
Synthesis of Hydrindane S25: A solution of TMS propyne (0.333 mL, 2.25 mmol, 3.3 equiv), Ti(O*i*-Pr)$_4$ (0.666 mL, 2.25 mmol, 3.3 equiv), in anhydrous toluene (7.5 mL) was stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (1.95 mL, 4.875 mmol, 6.4 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S14** (250 mg, 0.75 mmol, 1.0 equiv) was diluted with anhydrous toluene (2.5 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.3 mL, 0.967 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne **S2**, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (0.076 mL, 0.75 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (8 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic

phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–40% EtOAc in hexanes to afford hydrindane **S25** (176 mg, 0.394 mmol, 52%) as a pale, yellow oil.

Data for Compound S25: For NMR Spectra of **S25** see page S110. **TLC**: R_f = 0.24 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.24 (app. t, *J* = 7.42 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.05 (d, *J* = 7.41 Hz, 2H), 6.75 (dd, *J* = 7.5, 8.2 Hz, 2H), 6.70 (s, 1H), 4.12 – 4.06 (m, 1H), 3.79 (s, 3H), 2.72 – 2.67 (m, 1H), 2.59 – 2.51 (m, 3H), 2.43 – 2.35 (m, 3H), 2.31 – 2.25 (m, 2H), 2.03 (s, 2H), 1.96 (dd, *J* = 17.4, 5.3 Hz, 2H), 1.88 (d, *J* = 16.7 Hz, 1H), 1.21 (dd, *J* = 6.9, 6.1 Hz, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.5, 143.8, 143.6, 142.1, 139.2, 130.3, 130.1, 129.2, 128.9, 127.8, 125.9, 121.1, 114.7, 110.9, 71.7, 55.1, 47.3, 44.4, 39.5, 39.2, 38.5, 35.6, 31.6, 19.3, 0.3; **IR** (neat, cm^{-1}): 3349 (s), 2948 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+Na]^+$ calcd for $C_{29}H_{38}O_2SiNa$ 469.2641; found, 469.2531; $[\alpha]_{589}^{20.8}$**:** –100.6 (*c* 0.51, $CHCl_3$).



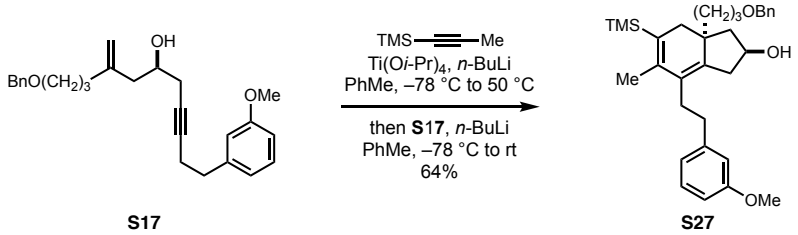
Synthesis of Hydrindane S26: A solution of TMS-alkyne **S2** (335 mg, 1.44 mmol, 3.3 equiv), Ti(O*i*-Pr)$_4$ (0.426 mL, 1.44 mmol, 3.3 equiv), in anhydrous toluene (6 mL) was stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (1.1 mL, 2.84 mmol, 6.4 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S14** (146 mg, 0.436 mmol, 1.0 equiv) was diluted with anhydrous toluene (1.5 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.175 mL, 0.436 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne **S2**, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (1.44 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (5 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–40% EtOAc in hexanes to afford hydrindane **S26** (140 mg, 0.244 mmol, 56%) as a pale, yellow oil.

Data for Compound S26: For NMR Spectra of **S26** see page S113. **TLC**: R_f = 0.19 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 5H), 7.20 – 7.15 (m, 4H), 6.99 (d, *J*

= 7.1 Hz, 2H), 6.74 (dd, *J* = 8.2, 2.9 Hz, 2H), 6.67 (s, 1H), 4.54 – 4.48 (m, 2H), 3.90 (s, 1H), 3.77 (s, 3H), 3.55 (td, *J* = 5.0, 4.5 Hz, 1H), 3.42 (td, *J* = 6.4, 2.9 Hz, 1H), 2.88 – 2.84 (m, 1H), 2.74 – 2.69 (m, 2H), 2.62 (d, *J* = 13.0 Hz, 1H), 2.56 – 2.48 (m, 2H), 2.41 – 2.37 (m, 1H), 2.29 – 2.17 (m, 4H), 1.89 (d, *J* = 16.7 Hz, 1H), 1.82 (dd, *J* = 17.4, 5.2 Hz, 1H), 1.20 (dd, *J* = 6.6, 6.5 Hz, 1H), 0.91 (s, 1H), 0.21 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.0, 144.4, 142.9, 142.7, 138.8, 131.9, 129.6, 128.6, 128.5, 127.8, 127.7, 127.3, 127.2, 127.0, 125.4, 120.7, 114.3, 110.5, 72.6, 71.0, 70.6, 54.6, 46.7, 43.8, 39.4, 39.1, 38.3, 34.9, 32.8, 31.0, 0.0; **IR** (neat, cm^{-1}): 3397 (s), 3060 (m), 3027 (m), 2949 (m), 2856 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+Na]^+$ calcd for $C_{37}H_{46}O_3SiNa$ 589.3216; found, 589.3116; $[\alpha]_{589}^{21.5}$**:** –57.2 (*c* 0.15, $CHCl_3$).



S17 **S27**

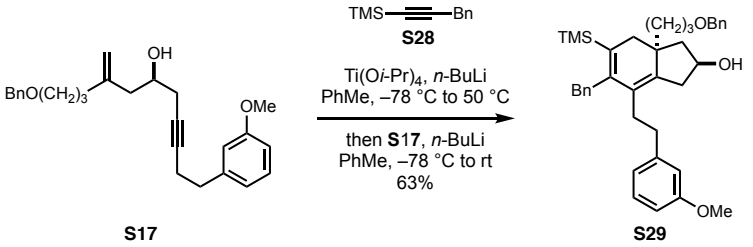
Synthesis of Hydrindane S27: A solution of TMS-propyne (707 mg, 6.30 mmol, 3.3 equiv), Ti(O*i*-Pr)$_4$ (1.87 mL, 6.30 mmol, 3.3 equiv), in anhydrous toluene (42 mL) was stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (4.89 mL, 12.2 mmol, 6.4 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S17** (750 mg, 1.91 mmol, 1.0 equiv) was diluted with anhydrous toluene (6.4 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.764 mL, 1.91 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne TMS-propyne, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (0.640 mL, 6.3 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (10 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–40% EtOAc in hexanes to afford hydrindane **S27** (622 mg, 1.23 mmol, 64%) as a pale, yellow oil.

Data for Compound S27: For NMR Spectra of **S27** see page S116. **TLC**: R_f = 0.10 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 5H), 7.18 (app. t, *J* = 7.8 Hz, 1H), 6.75 – 6.72 (m, 2H), 6.67 (s, 1H), 4.46 (s, 2H), 4.32 – 4.27 (m, 1H), 3.78 (s, 3H), 3.41 – 3.30 (m, 2H), 2.73 – 2.60 (m, 1H), 2.60 – 2.43 (m, 3H), 2.39 – 2.29 (m, 2H), 2.13 (dd, *J* = 12.8, 5.9 Hz, 1H), 2.07 – 2.00 (m, 1H), 1.92 (s, 3H), 1.87 (d, *J* = 16.5 Hz, 1H), 1.53 (s, 1H), 1.48 – 1.38 (m, 2H), 1.38 – 1.31 (m, 1H), 1.31 – 1.23 (m, 1H), 1.10 – 1.01 (m, 2H), 0.15 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.6, 144.8, 143.8, 142.1, 138.7, 129.7, 129.3, 128.5, 128.4, 127.7, 127.6,

121.3, 114.8, 111.1, 72.9, 72.3, 71.1, 55.3, 47.6, 42.5, 38.8, 38.3, 35.8, 31.5, 29.2, 25.7, 19.2, 0.3; **IR** (neat, cm^{-1}): 3398 (w), 2947 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{32}H_{45}O_3Si$ 505.3138; found, 505.3145; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.3}}$**:** –34.7 (*c* 0.002, $CHCl_3$).



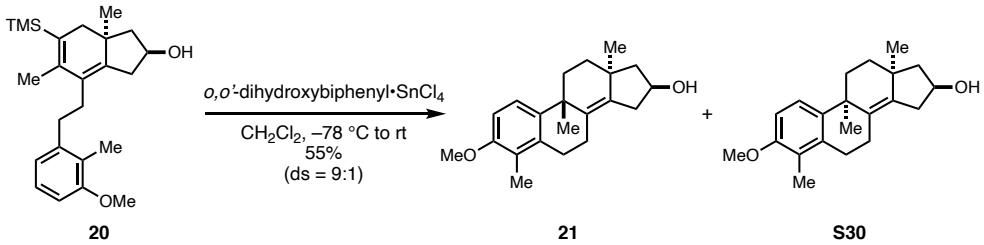
Synthesis of Hydrindane S29: A solution of TMS-alkyne **S28** (1.19 g, 6.30 mmol, 3.3 equiv), Ti(O*i*-Pr)4 (1.87 mL, 6.30 mmol, 3.3 equiv), in anhydrous toluene (42 mL) was stirred in a round bottom flask at –78 °C. Then, *n*-BuLi (4.89 mL, 12.2 mmol, 6.4 equiv, 2.5 M in hexanes) was added dropwise. The resulting solution was warmed to rt, then was heated in an oil bath to 50 °C for 1 h. The reaction mixture was then cooled to rt.

In a separate flask the enyne **S17** (750 mg, 1.91 mmol, 1.0 equiv) was diluted with anhydrous toluene (6.4 mL) and cooled to –78 °C prior to the dropwise addition of *n*-BuLi (0.764 mL, 1.91 mmol, 1.0 equiv, 2.5 M in hexanes). The resulting mixture was stirred for 10 min at –78 °C, then was warmed to rt.

The solution containing the enyne was then added dropwise into the flask containing TMS-alkyne **S28**, and the entire mixture was stirred overnight (18 h). Progress of the desired annulation was monitored by TLC (30% EtOAc in hexanes) and the reaction was quenched with benzaldehyde (0.64 mL, 6.3 mmol, 3.3 equiv), which was stirred for 30 min before the addition of saturated aqueous $NaHCO_3$ (15 mL). The organic phase was decanted, and the aqueous phase was extracted with copious amounts of EtOAc by repeatedly rinsing the reaction flask and decanting the organic phase into a separate flask. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on a Biotage® Snap Ultra 25 g cartridge and a gradient from 0–40% EtOAc in hexanes to afford hydrindane **S29** (699 mg, 1.20 mmol, 63%) as a pale, yellow oil.

Data for Compound S29: For NMR Spectra of **S29** see page S119. **TLC**: R_f = 0.15 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.35 – 7.11 (m, 12H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 4.50 (s, 2H), 4.34 – 4.27 (m, 1H), 3.82 (d, *J* = 16.3 Hz, 1H), 3.78 (s, 3H), 3.59 (d, *J* = 16.0 Hz, 1H), 3.40 (app. t, *J* = 5.9 Hz, 1H), 2.59 – 2.52 (m, 2H), 2.45 (d, *J* = 16.4 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.29 – 2.23 (m, 1H), 2.20 – 2.15 (m, 2H), 2.07 – 1.99 (m, 2H), 1.55 (s, 1H), 1.53 – 1.48 (m, 1H), 1.47 – 1.43 (m, 2H), 1.35 (dd, *J* = 13.2, 5.9 Hz, 1H), 1.29 – 1.25 (m, 1H), 1.08 (d, *J* = 5.5 Hz, 1H), 0.17 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.6, 146.0, 144.1, 143.8, 140.9, 138.8, 132.1, 129.3, 129.3, 128.5, 128.5, 128.4, 128.3, 127.7, 127.6, 127.2, 127.1, 126.0, 121.2, 114.7, 111.1, 73.1, 72.1, 71.1, 55.3, 47.8, 42.4, 39.4, 39.3, 38.8, 35.8, 31.5, 29.1, 25.8, 0.7; **IR** (neat, cm^{-1}): 3394 (b), 2946 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{38}H_{49}O_3Si$ 581.3451; found, 581.3443; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.3}}$**:** –7.3 (*c* 0.0005, $CHCl_3$).

D. Initial studies on C9,C13 *Anti*/*Syn* Selective Reactions and Oxidative Shift



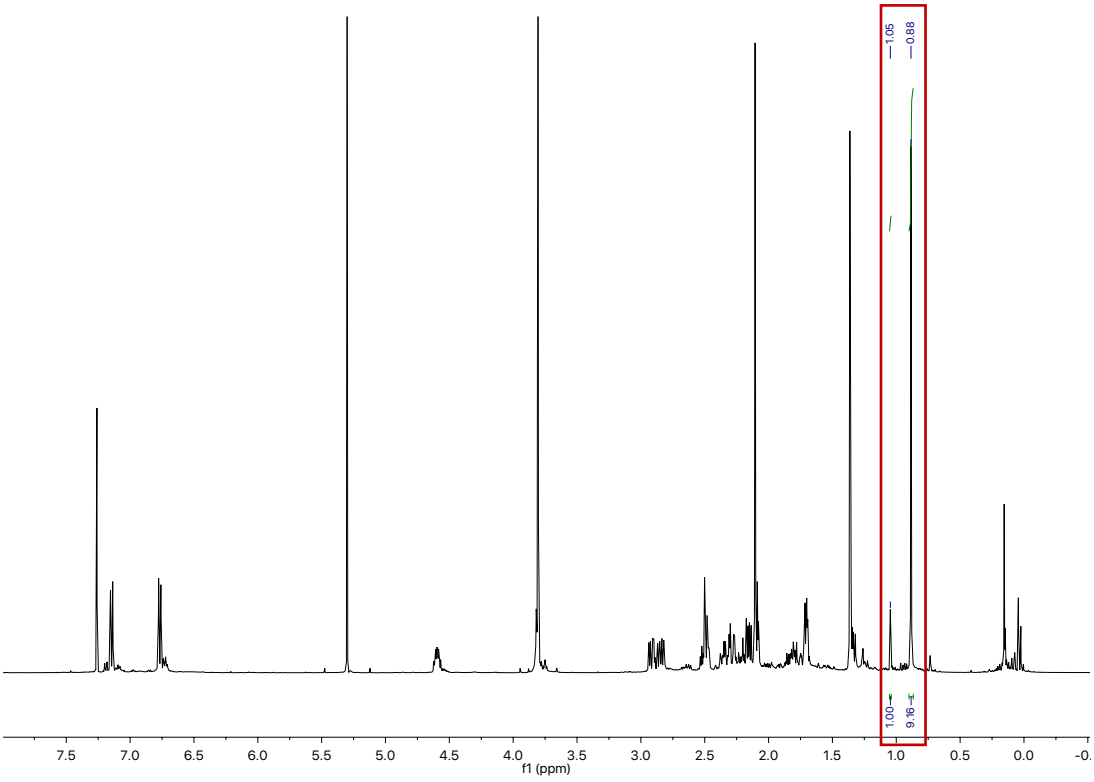
20 **21** **S30**

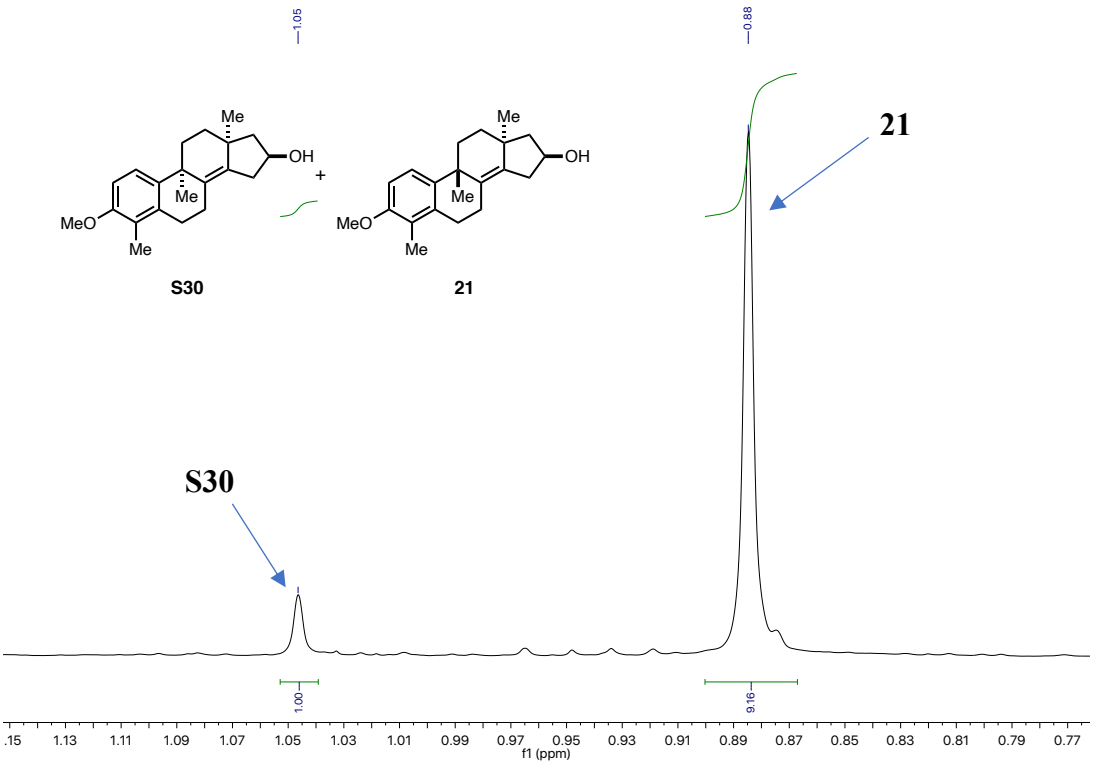
Synthesis of Tetracycle 21: To a stiring solution of *o,o*–dihydroxybiphenyl (0.12 g, 0.64 mmol, 5.4 equiv) in CH_2Cl_2 (6 mL) at –78 °C was added a solution of $SnCl_4$ (1.0 M in CH_2Cl_2, 0.60 mL, 0.60 mmol, 5.0 equiv) dropwise via syringe. The resulting mixture was stirred for 30 min at –78 °C, and then a solution of **20**[7] (47 mg, 0.12 mmol, 1.0 equiv) in 2 mL CH_2Cl_2 was added dropwise via syringe. The resulting mixture was stirred for 1.5 h at –78 °C, and then warmed to rt over 9 min. At this point, the reaction was judged to be complete by TLC analysis. The reaction was quenched with a saturated solution of $NaHCO_3$, and then further diluted with CH_2Cl_2. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered, and and concentrated *in vacuo*. Subsequent purification by SiO_2 flash column chromatography afforded **21** and **S30** as an amorphous white solid (21 mg, 0.066 mmol, 55% combined yield).

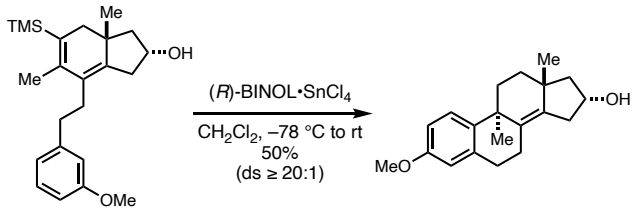
Data for Compound 21: For NMR Spectra of **21** see page S78. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 4.15 – 4.11 (m, 1H), 3.80 (s, 3H), 3.33 (s, 3H), 2.95 – 2.88 (m, 1H), 2.77 (ddd, *J* = 16.9, 8.8, 1.6 Hz, 1H), 2.55 – 2.46 (m, 2H), 2.38 – 2.32 (m, 2H), 2.15 (dd, *J* = 11.7, 6.7 Hz, 1H), 2.12 – 2.07 (m, 4H), 1.83 – 1.76 (m, 1H), 1.72 – 1.68 (m, 2H), 1.36 – 1.30 (m, 4H), 0.88 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 155.0, 140.5, 136.0, 135.7, 131.5, 124.1, 123.7, 108.7, 80.4, 56.9, 55.7, 48.7, 41.2, 38.3, 34.9, 34.2, 33.5, 31.5, 29.6, 25.8, 24.7, 11.5; **IR** (thin film, cm^{-1}): 2933, 2831; **HRMS** (ESI-TOF): calculated for $C_{22}H_{31}O_2$ $[M+H]^+$ 327.2324, found 327.2315. $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.3}}$: –203.4 (*c* 0.010, $CHCl_3$).

Data for Compound S30: For spectral data of **S30** see Kim et al.[7]

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **21** and **S30**



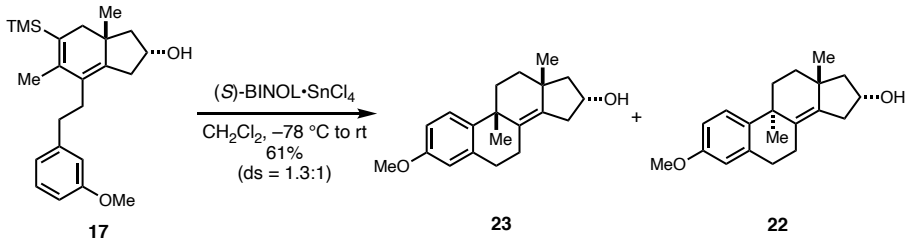




17 **22**

Synthesis of Tetracycle 22: To a solution of (*R*)-BINOL (55 mg, 0.192 mmol, 1.2 equiv) in CH_2Cl_2 (1.5 mL) at –78 °C was added $SnCl_4$ (0.166 mL, 1.0 equiv, 1.0 M in CH_2Cl_2) and the resulting mixture was stirred for 30 min at –78 °C before the addition of **17**[7] (62 mg, 0.160 mmol, 1.0 equiv) in CH_2Cl_2 (1.5 mL). The reaction mixture was the stirred for 2 h at –78 °C before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic phase was washed with 5 mol% NaOH (3 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 25 g column and a gradient from 0-5% EtOAc in hexanes with 10% CH_2Cl_2 as an additive to afford **22** (25 mg, 0.096 mmol, 50%) as a white foam.

Data for Compound 22: For and NMR Spectra of **22** see page S79. **TLC**: Rf = 0.30 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.7 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.59 (d, *J* = 2.3 Hz, 1H), 4.16 – 4.10 (m, 1H) 3.78 (s, 3H), 3.34 (s, 3H), 2.91 – 2.85 (m, 1H), 2.81 – 2.68 (m, 2H), 2.46 – 2.41 (m, 1H), 2.39 – 2.30 (m, 2H), 2.16 (dd, *J* = 11.7, 6.7 Hz, 1H), 2.10 – 2.07 (m, 1H), 1.88 – 1.81 (m, 1H), 1.74 – 1.69 (m, 2H), 1.14 – 1.13 (m, 4H), 0.90 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 140.2, 137.3, 136.1, 131.7, 127.2, 113.1, 112.5, 80.3, 56.9, 55.3, 48.7, 41.2, 38.1, 34.4, 33.3, 32.3, 31.3, 29.8, 25.8, 25.0; **IR** (neat, cm^{-1}): 3391 (s), 2931 (s), 2833 (m), 1608 (m); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{21}H_{29}O_2$ 313.2168; found, 313.2165; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$**:** +135.9 (c 0.002, $CHCl_3$).



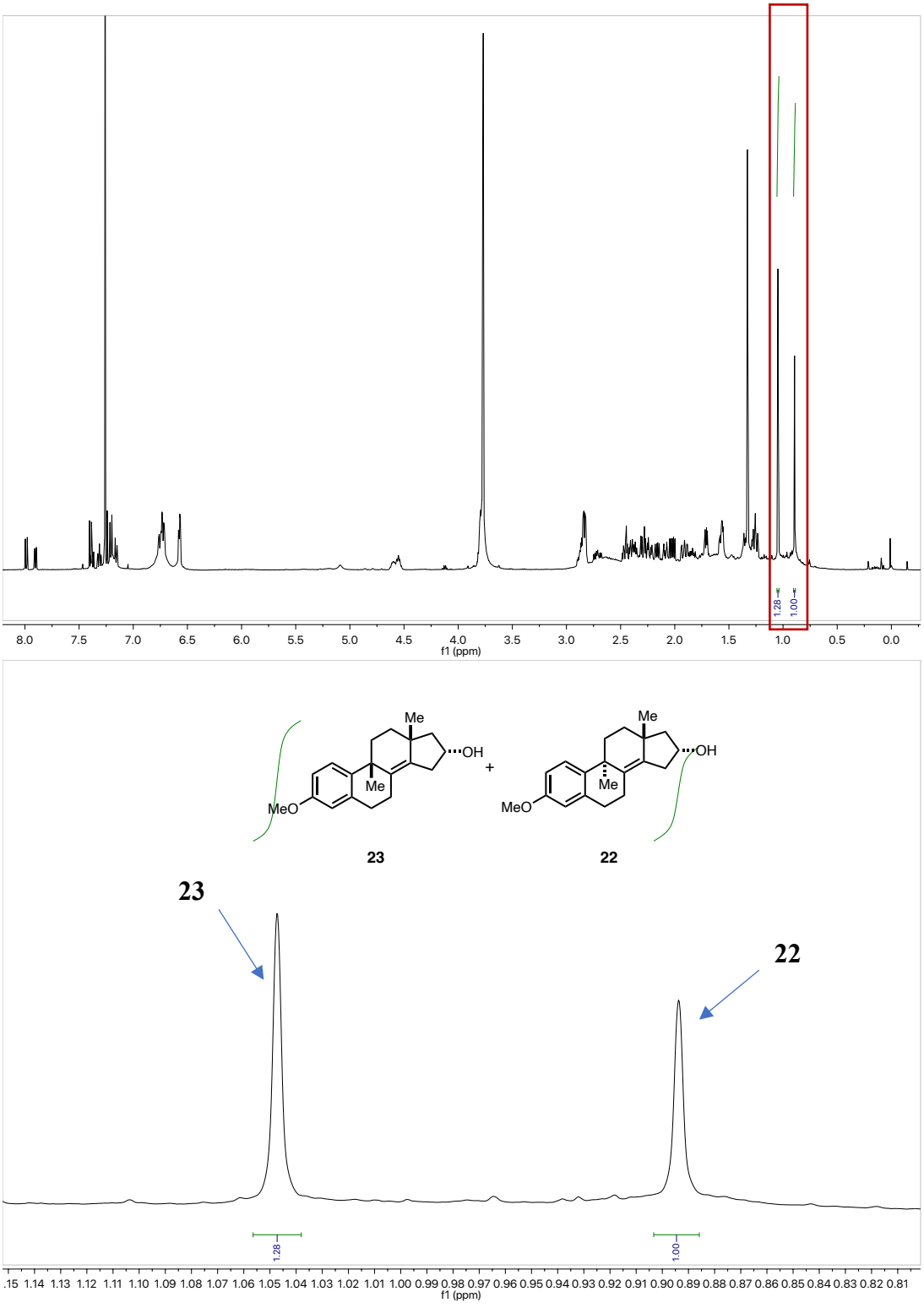
17 23 22

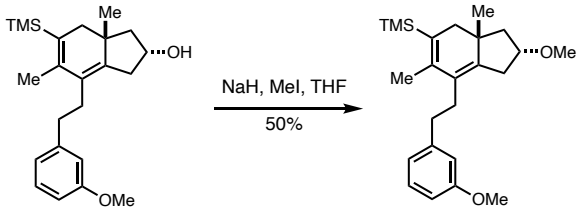
Synthesis of Tetracycles 23 and 22: To a solution of (*S*)–BINOL (16 g, 56mmol, 1.2 equiv) in CH_2Cl_2 (280 mL) at –78 °C was added $SnCl_4$ (0.166 mL, 1.0 equiv, 1.0 M in CH_2Cl_2) and the resulting mixture was stirred for 30 min at –78 °C before the addition of **17**[7] (17 g, 46 mmol, 1.0 equiv) in 230 mL CH_2Cl_2. The reaction mixture was the stirred for 2 h at –78 °C before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (500 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 300 mL) and the combined organic phase was washed with 5 mol% NaOH (500 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was obtained as a 1.3:1 mixture of **23** and **22** (8.35 g of **23** and **22,** 61% combined yield). A subsequent purification by SiO_2 flash column chromatography with a gradient from 0-5% EtOAc in hexanes with 10% CH_2Cl_2 as an additive afforded **23** (5.4 g of **23**, 39% isolated yield,) as yellow solid.

Data for Compound 22: For spectral data of **22** please see previous page.

Data for Compound 23: For NMR Spectra of **23** see page S80. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 4.62 – 4.48 (m, 1H), 3.77 (s, 3H), 2.90 – 2.81 (m, 3H), 2.46 (app. dt, *J* = 13.3, 4.5 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.29 (dd, *J* = 16.7, 5.1 Hz, 1H), 2.23 (ddd, *J* = 14.3, 5.6, 3.5 Hz, 1H), 2.02 (dd, *J* = 12.1, 6.5 Hz, 1H), 1.91 (ddd, *J* = 14.7, 12.3, 3.6 Hz, 1H), 1.57 (ddd, *J* = 12.9, 5.6, 3.5 Hz, 1H), 1.39 (s, 1H), 1.33 (s, 3H), 1.30 – 1.23 (m, 2H), 1.05 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.3, 138.9, 138.6, 137.1, 133.6, 126.4, 113.6, 112.1, 71.1, 55.3, 51.5, 41.3, 39.1, 38.1, 34.4, 34.2, 33.0, 31.9, 25.9, 24.9; **IR** (thin film, cm^{-1}): 3320, 2954, 2912, 2846, 1598; **HRMS** (ESI-TOF): calculated for $C_{20}H_{27}O_2$ $[M+H]^+$ 299.2013, found 299.2; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$**:** –117.2 (*c* 0.0086, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **22** and **23**

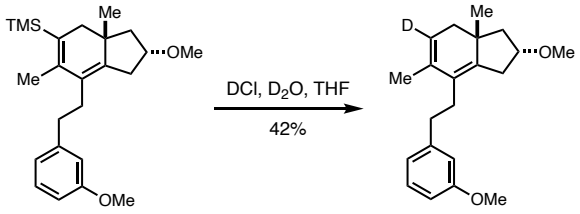




17 **S31**

Synthesis of Hydrindane S31: To a solution of **17**[7] (586 mg, 1.58 mmol, 1 equiv) in THF (8 mL) at 0 °C was added NaH (190 mg, 4.74 mmol, 3 equiv), and the resulting mixture was stirred for 10 min before the addition of MeI (0.590 mL, 9.48 mmol, 6 equiv). The mixture was warmed to rt and stirred overnight. The reaction was quenched with H_2O (12 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography with a Biotage® Snap Ultra 25 g column and a gradient from 1–5% EtOAc in hexanes to afford **S31** (292 mg, 0.788 mmol, 50%) as a yellow oil.

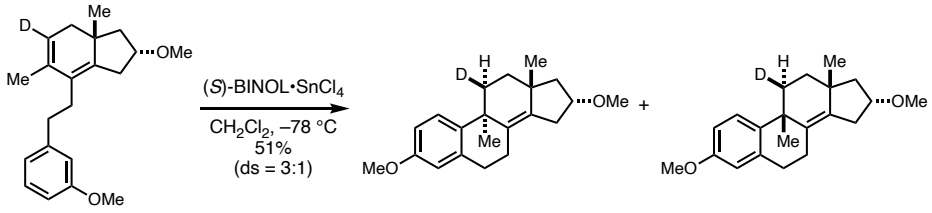
Data for Compound S31: For NMR Spectra of **S31** see page S81. **TLC**: Rf = 0.41 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 – 7.17 (m, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.73 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.72 – 6.70 (m, 1H), 3.98 (app. p, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 3.31 (s, 3H), 2.69 (dd, *J* = 18.0, 8.1 Hz, 1H), 2.63 – 2.51 (m, 2H), 2.45 – 2.38 (m, 1H), 2.37 – 2.30 (m, 1H), 2.21 – 2.13 (m, 2H), 2.07 – 2.02 (m, 2H), 1.93 (d, *J* = 15.9 Hz, 1H), 1.90 (d, *J* = 2.5 Hz, 3H), 1.39 (dd, *J* = 11.7, 8.4 Hz, 1H), 0.80 (s, 3H), 0.15 (s, 9H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.7, 144.0, 141.2, 129.3, 128.0, 121.2, 121.1, 114.6, 111.1, 80.4, 57.1, 55.3, 47.8, 41.4, 35.8, 35.7, 35.0, 31.7, 21.2, 21.0, 19.1, 0.1; **IR** (neat, cm^{-1}): 2949 (s), 2832 (m), 1739 (m); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{24}H_{37}O_2Si$ 385.2563; found, 385.2551; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$: +30.1 (*c* 0.001, $CHCl_3$).



S31 **24**

Synthesis of Deuterated Hydrindane 24: To a solution of hydrindane **S31**[6] **(**64.9 mg, 0.0.169 mmol, 1.0 equiv) at 0 °C in THF (1 mL) was slowly added 2M DCl (1 mL). The reaction mixture was warmed to rt and stirred over 20 h, then cooled to 0 °C and quenched with the addition of D_2O (2 mL). The biphasic solution was separated, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 10 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford **24** (22.1 mg, 0.0705 mmol, 42%) as a pale-yellow oil.

Data for Compound 24: For NMR Spectra of **24** see page S82. **TLC**: R_f = 0.40 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 (app. t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 3.99 (app. p, *J* = 7.4 Hz, 1H), 3.80 (s, 3H), 3.30 (s, 3H), 2.66 (dd, J = 18.3, 7.7 Hz, 1H), 2.62 – 2.53 (m, 2H), 2.40 – 2.29 (m, 2H), 2.15 – 2.01 (m, 4H), 1.82 (s, 3H), 1.41 (app. t, *J* = 10.4 Hz, 1H), 0.88 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.6, 144.0, 142.3, 132.6, 129.3, 127.7, 121.1, 114.6, 111.1, 80.4, 57.0, 55.3, 47.8, 40.0, 37.5, 35.6, 34.6, 31.8, 22.2, 19.3; **IR** (neat, cm^{-1}): 2944 (s), 2819 (m), 1737 (w); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{28}O_2D$ 314.2230; found, 314.2221; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.3}}$**:** +54.0 (*c* 0.265, $CHCl_3$).

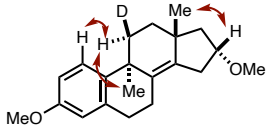


24 **25** **26**

Synthesis of Tetracycles 25 and 26: To a solution of (*S*)-BINOL (39.0 mg, 0.136 mmol, 1.2 equiv) in CH_2Cl_2 (1.3 mL) at –78 °C was added $SnCl_4$ (0.114 mL, 0.114 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) and the resulting mixture was stirred for 30 min at –78 °C before the addition of **24** (35.6 mg, 0.114 mmol, 1.0 equiv) in CH_2Cl_2 (1.5 mL). The reaction mixture was the stirred for 1 h at –78 °C before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic phase was washed with 3 M NaOH (1 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material containing a 3:1 mixture of C9 diastereomers was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-5% EtOAc in hexanes with 10% CH_2Cl_2 as an additive to afford a mixture of tetracycles **25** and **26** (18.1 mg, 0.0577 mmol, 51% combined

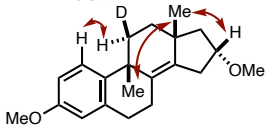
yield) as a white foam. The mixture was purified by HPLC with a gradient from 0-15% EtOAc in hexanes to afford the isolated diastereomers **25** and **26** as white foams.

Data for Compound 25: For NMR Spectra of **25** see page S83. **TLC**: R_f = 0.45 (10% EtOAc, 10% CH_2Cl_2 in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 4.15 – 4.10 (m, 1H), 3.77 (s, 3H), 3.33 (s, 3H), 2.87 (ddd, *J* = 16.1, 5.9, 2.6 Hz, 1H), 2.79 – 2.68 (m, 2H), 2.42 (ddd, *J* = 13.9, 8.1, 3.3 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.15 (dd, *J* = 11.7, 6.6 Hz, 1H), 2.06 (app t, *J* = 2.6 Hz, 1H), 1.71 – 1.68 (m, 2H), 1.37 – 1.31 (m, 4H), 0.91 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 156.9, 140.1, 137.2, 136.0, 131.5, 127.1, 112.9, 112.3, 80.3, 56.8, 55.1, 48.5, 41.1, 37.9, 34.1, 33.1, 32.1, 31.1, 25.7, 24.8; **IR** (neat, cm^{-1}): 2925 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{29}O_2D$ 314.2230; found, 314.2227; $[\alpha]_{589}^{20.7}$**:** +81.9 (*c* 0.145, $CHCl_3$).



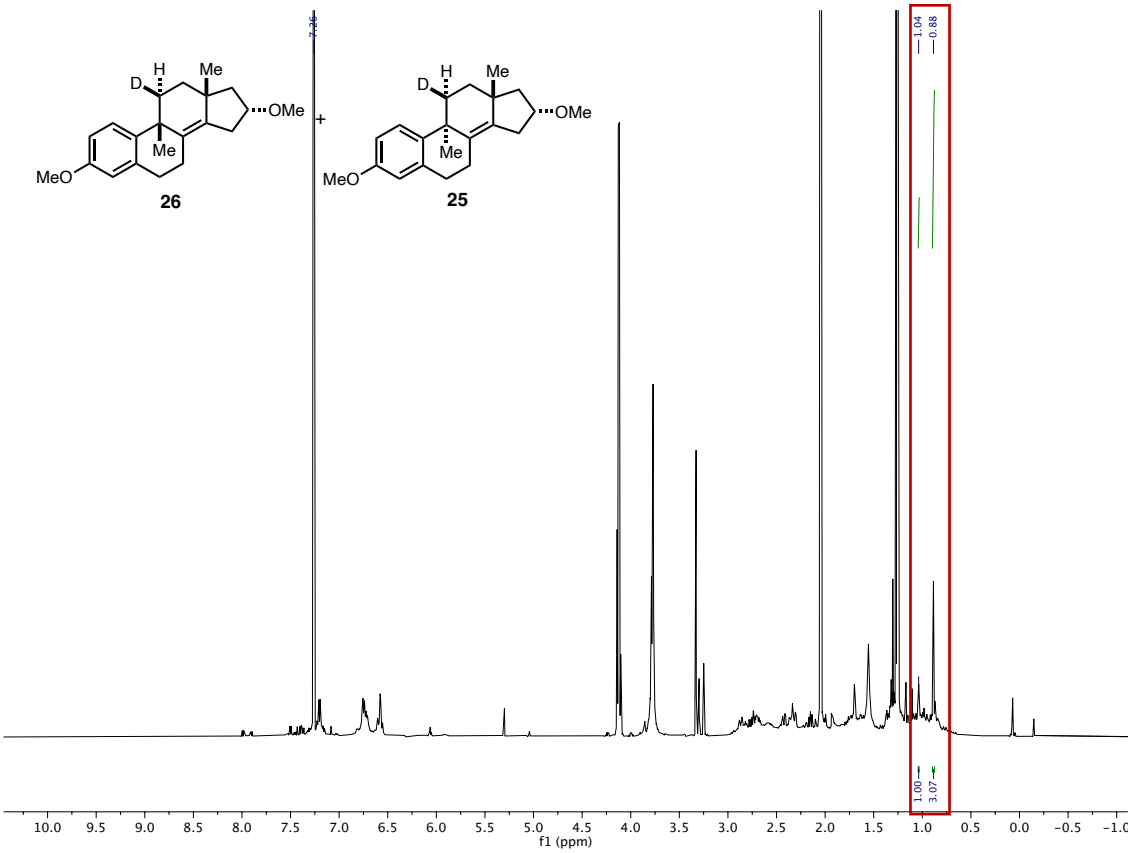
25
Key nOe interactions

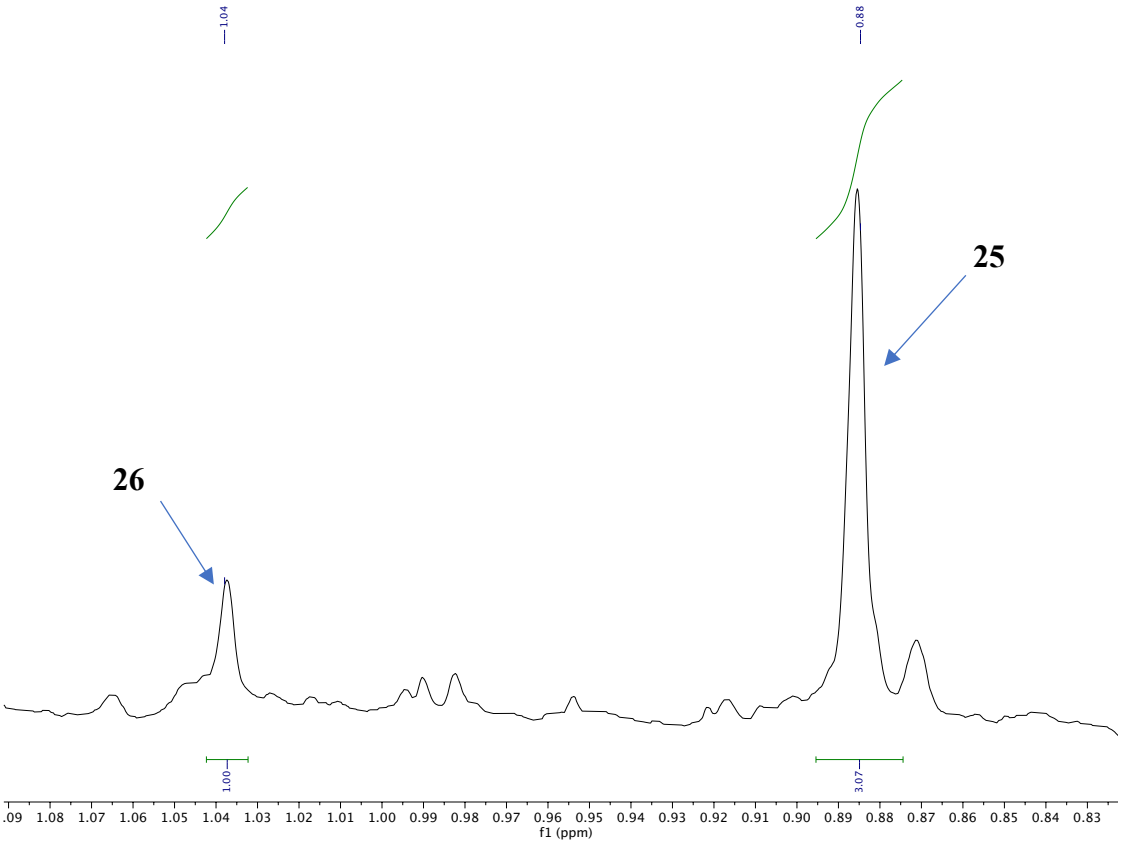
Data for Compound 26: For NMR Spectra of **26** see page S84. **TLC:** R_f = 0.45 (10% EtOAc, 10% CH_2Cl_2 in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.56 (d, *J* = 2.9 Hz, 1H), 4.13 – 4.06 (m, 1H), 3.76 (s, 3H), 3.30 (s, 3H), 2.86 – 2.77 (m, 3H), 2.45 (ddd, *J* = 13.2, 5.9, 3.7 Hz, 1H), 2.39 – 2.34 (m, 1H), 2.32 (dd, *J* = 16.9, 5.5 Hz, 1H), 2.18 (app t, *J* = 3.7 Hz, 1H), 2.00 (dd, *J* = 11.7, 6.6 Hz, 1H), 1.57 – 1.55 (m, 1H), 1.32 (s, 3H), 1.27 – 1.20 (m, 2H), 1.04 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.2, 138.9, 138.7, 136.8, 133.2, 126.4, 113.6, 112.0, 79.7, 56.9, 55.3, 47.9, 41.1, 39.0, 34.7, 33.9, 32.9, 31.7, 29.8, 25.8, 24.8; **IR** (neat, cm^{-1}): 2926 (s), 1710 (w); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{29}O_2D$ 314.2230; found, 314.2220; $[\alpha]_{589}^{20.9}$**:** –10.8 (*c* 0.065, $CHCl_3$).

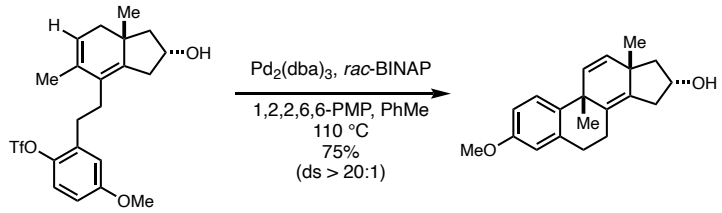


26
Key nOe interactions

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **25** and **26**



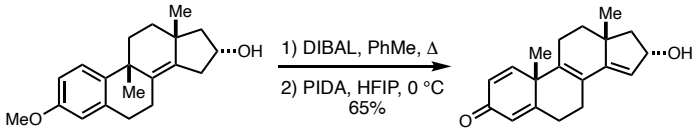




27 29

Synthesis of Tetracycle 29: A flask containing $Pd_2(dba)_3$ (95 mg, 0.104 mmol, 0.20 equiv) and *rac*-BINAP (259 mg, 0.415 mmol, 0.80 equiv) was sparged with N_2 for 5 min before the addition of **27** (for preparation see page S11) (232 mg, 0.519 mmol, 1.0 equiv) in PhMe (21 mL). 1,2,2,6,6-pentamethylpiperidine (PMP) (0.380 mL, 2.07 mmol, 4.0 equiv) was added, the N_2 inlet was removed from the septum, and vinyl tape was used to further seal the flask prior to partial immersion in a pre-heated oil bath at 110 °C until the reaction was deemed complete by TLC analysis. Upon completion, the flask was cooled to rt and concentrated *in vacuo*. The crude residue was then purified by flash chromatography using a gradient of 0–30% EtOAc in hexanes to afford **29** (23 mg, 0.078 mmol, 75%) as a clear oil.

Data for Compound 29: For NMR Spectra of **29** see page S85. **TLC**: Rf = 0.09 (45% EtOAc in 45% hexanes with 10% CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.7 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 6.02 (d, *J* = 9.6 Hz, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 4.59 – 4.53 (m, 1H), 3.77 (s, 3H), 2.91 (ddd, *J* = 16.5, 8.2, 2.2 Hz, 1H), 2.81 – 2.74 (m, 2H), 2.60 – 2.57 (m, 1H), 2.41 (dd, *J* = 16.5, 4.2 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.08 (dd, *J* = 12.4, 6.6 Hz, 1H), 1.58 (s, 1H), 1.51 – 1.43 (m, 4H), 1.11 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 137.9, 136.7, 135.6, 134.3, 132.5, 132.1, 128.0, 113.2, 112.8, 70.7, 55.2, 49.1, 42.7, 40.6, 37.3, 33.3, 31.6, 28.1, 25.3; **IR** (neat, cm^{-1}): 3358 (b), 2953 (s); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{20}H_{25}O_2$ 297.1855; found, 297.1845; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$**:** –217.6 (*c* 0.0012, $CHCl_3$).



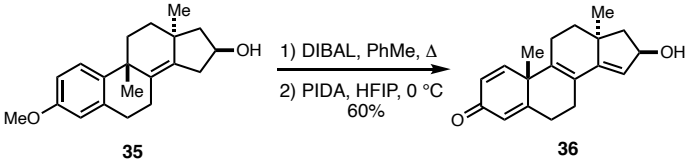
23 34

Synthesis of Tetracycle 34: To a stirring solution of **23**[7] (0.89 g, 2.9 mmol, 1.0 equiv) in 34 mL toluene at rt under N_2 atmosphere was added DIBAL-H (1.0 M in toluene, 34 mL, 34 mmol, 12 equiv). The resulting mixture was heated in an oil bath to 100 °C, refluxed overnight (approx. 20 h), and then cooled to rt. The reaction was slowly quenched by the addition of a saturated aqueous solution of Rochelle's salt, and the resulting mixture was stirred until biphasic. The organic phase was separated, the aqueous phase was acidified with 1 M aqueous HCl and extracted with EtOAc (3 x 200 mL), and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford 1.2 g of a crude amorphous yellow solid.

This crude material was then dissolved in 45 mL HFIP and cooled to 0 °C under N_2 atmosphere, and stirred for 20 min. PIDA (1.3 g, 4.2 mmol, 0.95 equiv) was added, and the resulting reaction mixture was stirred for 1 min at the same temperature (until PIDA is fully dissolved). Then, 30 mL of a saturated solution of $NaHCO_3$ was added. HFIP was subsequently removed from the reaction mixture under vacuum, and the mostly aqueous remains was diluted with 75 mL EtOAc. The organic phase was separated, the aqueous phase was extracted with 3 x 100 mL EtOAc, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude

product was purified with SiO_2 flash column chromatography to afford **34** as an amorphous tan solid (0.55 g, 1.88 mmol, 65% isolated yield over two steps).

Data for Compound 34: For NMR Spectra of **34** see page S86. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 10.2 Hz, 1H), 6.26 (d, *J* = 10.2 Hz, 1H), 6.14 (s, 1H), 5.45 (d, *J* = 1.7 Hz, 1H), 5.09 – 5.01 (m, 1H), 2.80 – 2.71 (m, 1H), 2.58 – 2.47 (m, 4H), 2.36 – 2.32 (m, 2H), 1.83 – 1.79 (m, 1H), 1.61 (s, 1H), 1.54 (td, *J* = 12.2, 5.9 Hz, 1H), 1.46 (s, 3H), 1.37 (dd, *J* = 12.4, 7.5 Hz, 1H), 1.00 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 185.8, 166.3, 153.5, 150.4, 137.2, 128.1, 125.5, 124.3, 123.7, 76.5, 51.6, 44.7, 43.4, 35.9, 30.1, 29.9, 29.0, 24.1, 23.8; **IR** (thin film, cm^{-1}): 3376, 2958, 2914, 2854, 1743, 1722, 1701, 1660; **HRMS** (ESI-TOF): $[M+H]^+$ calcd for $C_{19}H_{22}O_2$ 283.1686, found 283.1698; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$**:** –153.3 (*c* 0.008, $CHCl_3$).



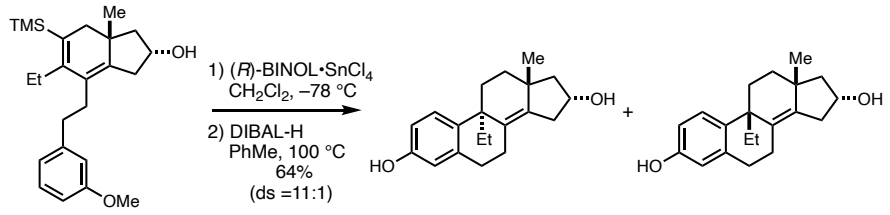
35 **36**

Synthesis of Tetracycle 36: To a stirring solution of **35**[7] (70 mg, 0.23 mmol, 1.0 equiv) in 3 mL toluene at rt under N_2 atmosphere was added DIBAL-H (1.0 M in hexanes, 2.3 mL, 2.3 mmol, 10 equiv). The resulting mixture was heated in an oil bath to 100 °C, refluxed overnight (approx. 16 h), and then cooled to rt. The reaction was slowly quenched by the addition of a saturated aqueous solution of Rochelle's salt, and the resulting mixture was stirred until biphasic. The organic phase was separated, the aqueous phase was acidified with 1 M aqueous HCl and extracted with EtOAc (3 x 15 mL), and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the crude phenol as an amorphous yellow solid.

This crude material was then dissolved in 2 mL HFIP and cooled to 0 °C under N_2 atmosphere, and stirred for 20 min. PIDA (70 mg, 0.22 mmol, 1.0 equiv) was added, and the resulting reaction mixture was stirred for 1 min at the same temperature (until PIDA is fully dissolved). Then, 30 mL of a saturated solution of $NaHCO_3$ was added. HFIP was subsequently removed from the reaction mixture under vacuum, and the mostly aqueous remains was diluted with 20 mL EtOAc. The organic phase was separated, the aqueous phase was extracted with 3 x 15 mL EtOAc, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified with SiO_2 flash column chromatography to afford **36** (40 mg, 0.14 mmol, 60% isolated yield over two steps) as an amorphous white solid. (Caution: Prolonged stirring of more than 30 min after PIDA addition resulted in a significantly lower yield).

Data for Compound 36: For NMR Spectra of **36** see page S87. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 10.1 Hz, 1H), 6.24 (d, *J* = 10.1 Hz, 1H), 6.13 (s, 1H), 5.50 (s, 1H), 5.09 – 5.01 (m, 1H), 2.78 – 2.67 (m, 2H), 2.55 – 2.50 (m, 1H), 2.46 – 2.39 (m, 1H), 2.32 (dd, *J* = 12.1, 6.5 Hz, 2H), 2.28 – 2.17 (m, 1H), 1.86 – 1.78 (m, 2H), 1.57 (app. td, *J* = 12.4, 5.5 Hz, 1H), 1.46 (s, 3H), 1.40 (dd, *J* = 12.1, 7.6 Hz, 1H), 0.88 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$) δ 185.9, 166.6, 152.6, 149.5, 136.9, 128.2, 125.1, 124.7, 123.6, 76.4, 51.5, 44.7, 43.2, 36.1, 29.7, 29.0, 28.6, 24.5, 23.5; **IR** (thin film, cm^{-1}): 3388, 2952, 2923, 2851, 1662, 887, 731; **HRMS** (ESI–TOF): Calculated for $C_{19}H_{23}O_2$ $[M+H]^+$ 283.1698, found 283.1693; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$**:** +128.0 (*c* 0.042, $CHCl_3$).

E. Studies on the Effects of Substitution in the Friedel–Crafts Cyclization



37 **38** **62**

Synthesis of Tetracycles 38 and 62: To a stirring solution of (*R*)-BINOL (146 mg, 0.512 mmol, 1.2 equiv) in CH_2Cl_2 (6 mL) at –78 °C was added $SnCl_4$ (0.426 mL, 1.0 M in CH_2Cl_2, 1.0 equiv) and the resulting solution was stirred for 30 min at –78 °C before the addition of **37**[6] (164 mg, 0.426 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL). The reaction mixture was then stirred at –78 °C for 1 h before being warmed to rt. After stirring for an additional 1 h at rt, saturated aqueous NH_4Cl (1 mL) was added. The biphasic solution was stirred for 1 h before being transferred to a separatory funnel. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 5% NaOH (2 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

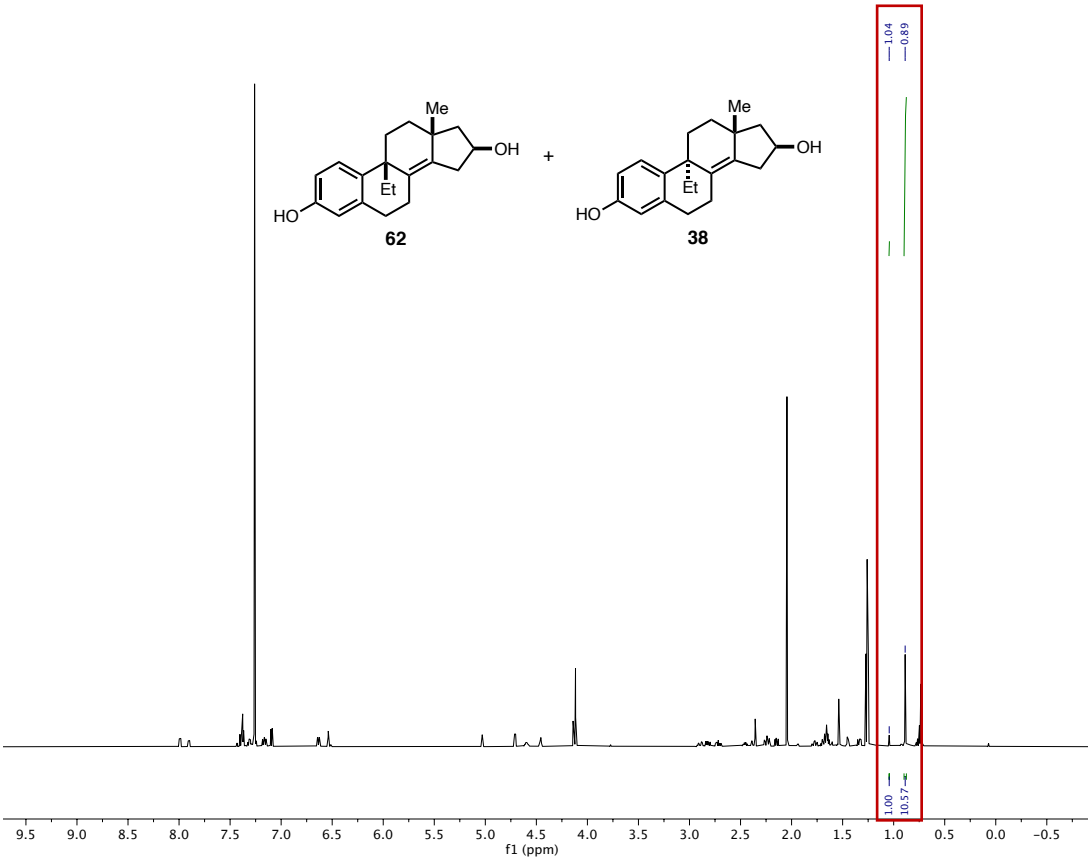
The resulting crude product was dissolved in PhMe (4 mL) at rt under N_2 atmosphere. DIBAL-H (4.23 mL, 10 equiv, 1.0 M in PhMe) was added and the resulting reaction mixture was heated in an oil bath to reflux and stirred overnight. When the reaction was complete, as judged by TLC analysis, the reaction mixture was cooled to 0 °C where it was quenched slowly with ice then 2 M HCl (3 mL). The biphasic solution was separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 20–70% EtOAc in hexanes with an additive of 10% CH_2Cl_2 to afford the corresponding tetracycles **38** and **62** (81 mg, 0.273 mmol, 64% combined yield, 11:1 *anti*:*syn*) as white foams.

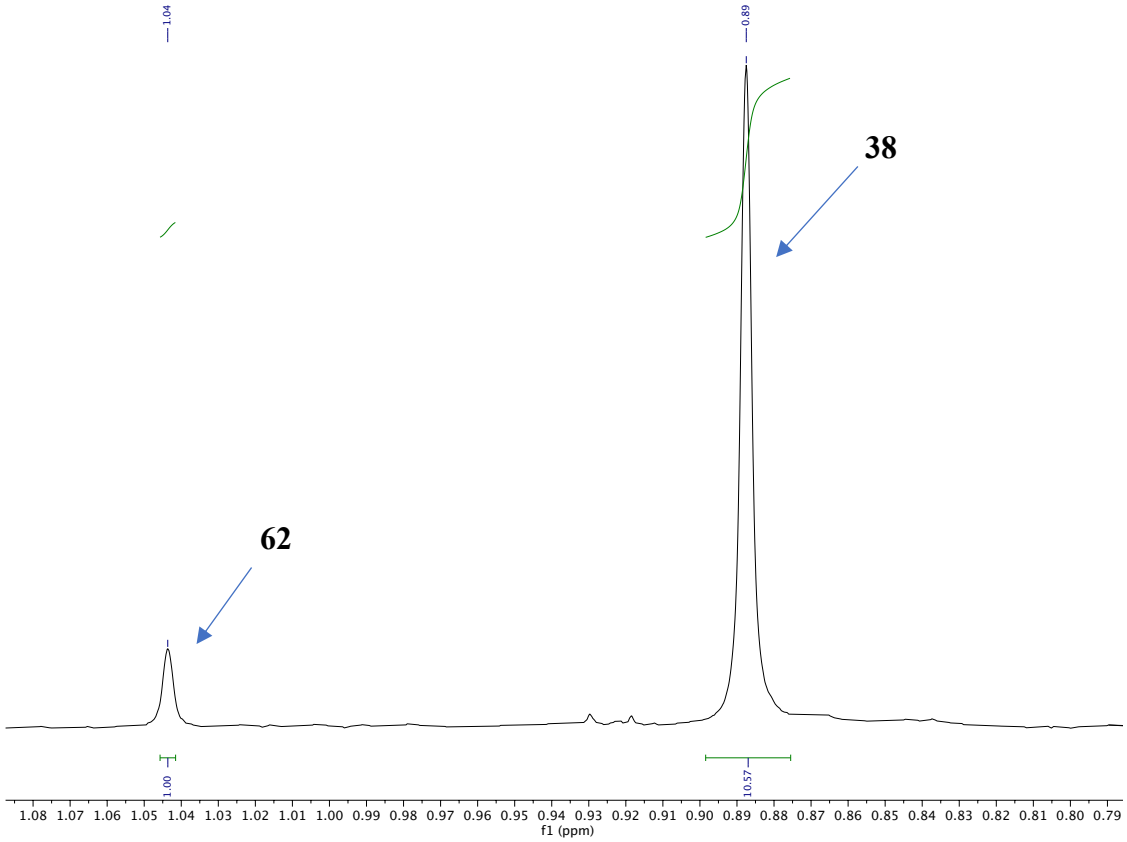
Data for Compound 38: For NMR Spectra of **38** see page S88. For nOe data of compound **38** see Millham et al.[6] **TLC:** Rf = 0.32 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.5 Hz, 1H), 6.63 (app. dd, *J* = 8.5, 2.8 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 4.63 – 4.57 (m, 1H), 4.45 – 4.43 (m, 1H), 2.93 – 2.87 (m, 1H), 2.85 – 2.79 (m, 1H), 2.76 – 2.68 (m, 1H), 2.50 – 2.43 (m, 1H), 2.40 – 2.35 (m, 1H), 2.28 – 2.20 (m, 2H), 2.15 (dd, *J* = 11.9, 6.6 Hz, 1H), 1.81 – 1.74 (m, 1H), 1.73 – 1.60 (m, 4H), 1.54 (s, 1H), 1.45 (d, *J* = 5.4 Hz, 1H), 1.34 (dd, *J* = 11.9, 8.1 Hz, 1H), 0.89 (s, 3H), 0.73 (t, *J* = 7.5 Hz, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 153.1, 138.6, 138.0, 137.3, 131.3, 128.5, 128.0, 120.7, 114.8, 112.7, 71.6, 52.0, 41.5, 41.1, 37.9, 34.0, 33.5, 30.7, 30.1, 26.0, 24.8, 10.1; **IR** (neat, cm^{-1}): 3408 (s), 2954 (m), 2928 (m), 2871 (w), 1704 (w), 1658 (w), 1610 (m), **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{20}H_{27}O_2$ 299.2011; found, 299.2011; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$: +84.1 (*c* 0.0033, $CHCl_3$).

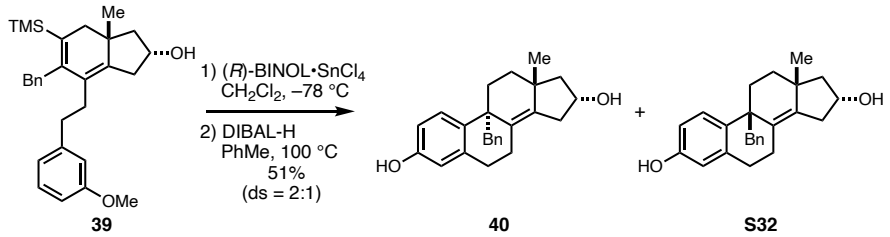
Data for Compound 62: For NMR Spectra of **62** see page S89. For nOe data of compound **62** see Millham et al.[6] **TLC:** Rf = 0.54 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.6 Hz, 1H), 6.71 (app. dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 4.15 – 4.08 (m, 1H), 3.77 (s, 3H), 3.33 (s, 3H), 2.96 – 2.90 (m, 1H), 2.78 – 2.71 (m, 2H), 2.5 – 2.43 (m, 1H), 2.41 – 2.35 (m, 1H), 2.32 – 2.21 (m, 2H), 2.16 – 2.12 (m, 1H), 1.80 – 1.74 (m, 1H), 1.71 – 1.60 (m, 4H),

1.33 – 1.29 (m, 1H), 0.88 (s, 3H), 0.72 (t, J = 7.5 Hz, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.2, 138.3, 137.8, 137.0, 131.0, 127.8, 113.3, 111.4, 80.2, 57.0, 55.2, 48.7, 41.1, 34.5, 33.7, 33.3, 30.9, 30.0, 25.8, 24.8, 10.0; IR (neat, cm^{-1}): 2934 (s), 1608 (m), 865 (w), 815 (w); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{22}H_{31}O_2$ 327.2324; found, 327.2312; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$: –93.5 ($c$ 0.0015, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **38** and **62**







39 **40** **S32**

Synthesis of Tetracycles 40 and S32: To a stirring solution of (*R*)-BINOL (110 mg, 0.384 mmol, 1.2 equiv) in CH_2Cl_2 (2 mL) at –78 °C was added $SnCl_4$ (0.320 mL, 1.0 M in CH_2Cl_2, 1.0 equiv) and the resulting solution was stirred for 30 min at –78 °C before the addition of **39**[6] (143 mg, 0.320 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL). The reaction mixture was then stirred at –78 °C for 1 h before being warmed to rt. After stirring for an additional 1 h, saturated aqueous NH_4Cl (1 mL) was added. The biphasic solution was stirred for 1 h before being transferred to a separatory funnel. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 5% NaOH (2 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

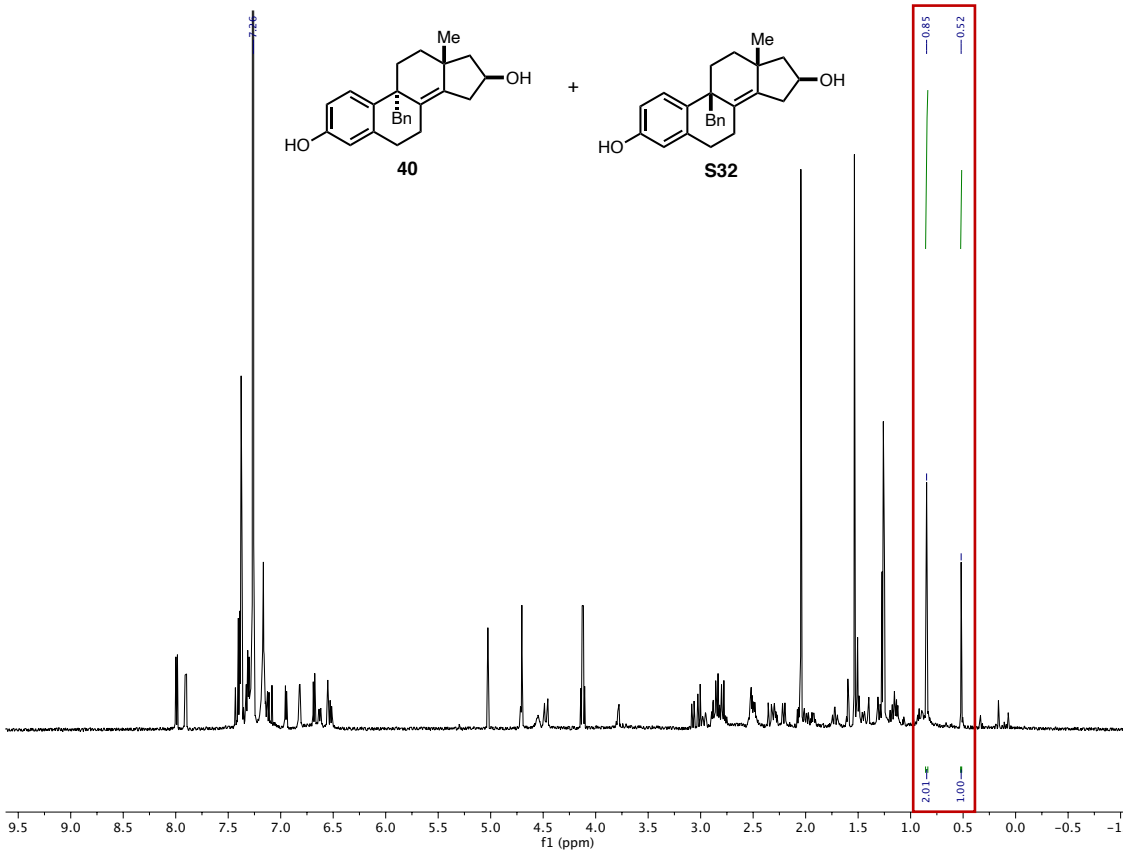
The resulting crude product was dissolved in PhMe (3 mL) at rt under N_2 atmosphere. DIBAL-H (3.2 mL, 10 equiv, 1.0 M in PhMe) was added and the resulting reaction mixture was heated in an oil bath to reflux and stirred overnight. When the reaction was complete, as judged by TLC analysis, the reaction mixture was cooled to 0 °C where it was quenched slowly with ice then 2 M HCl (3 mL). The biphasic solution was separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 20–70% EtOAc in hexanes with an additive of 10% CH_2Cl_2 to afford the corresponding tetracycles **40** and **S32** (69 mg, 0.192 mmol, 50% combined yield, 2:1 *anti*:*syn*) as white foams.

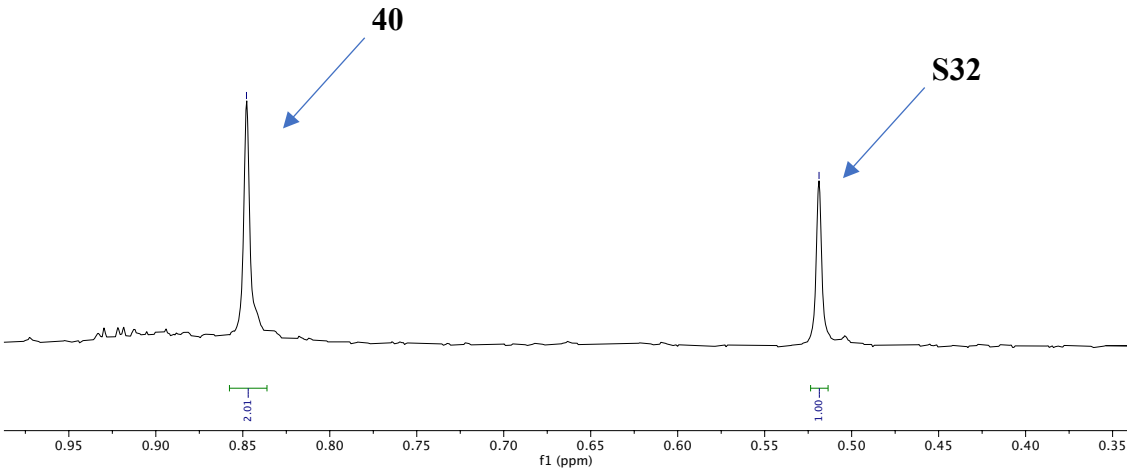
Data for Compound 40: For NMR Spectra of **40** see page S90. For nOe data of compound **40** see Millham et al.[6] **TLC**: Rf = 0.13 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 – 7.17 (m, 3H), 6.84 – 6.79 (m, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.56 – 6.50 (m, 2H), 6.08 (s, 1H), 4.58 – 4.52 (m, 1H), 3.04 – 2.93 (m, 2H), 2.88 – 2.75 (m, 3H), 2.56 – 2.45 (m, 2H), 2.31 (dd, *J* = 16.8, 4.3 Hz, 1H), 2.23 – 2.19 (m, 1H), 2.08 – 2.03 (m, 1H), 1.72 (td, *J* = 14.1, 3.3 Hz, 1H), 1.53 – 1.47 (m, 1H), 1.41 (d, *J* = 6.0 Hz, 1H), 1.32 – 1.14 (m, 1H), 1.14 (dd, *J* = 12.0, 7.7 Hz, 1H), 0.85 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 153.2, 139.2, 138.8, 138.0, 137.9, 130.8, 130.1, 128.7, 128.5, 127.6, 126.2, 114.6, 112.8, 71.6, 51.9, 47.8, 42.5, 41.2, 38.1, 32.9, 31.2, 30.8, 26.2, 24.9; **IR** (neat, cm^{-1}): 3338 (m), 2951 (s), 2850 (s), 1724 (w), 700 (m); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{25}H_{29}O_2$ 361.2168; found, 361.2158; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$: +161.0 (*c* 0.0014, $CHCl_3$).

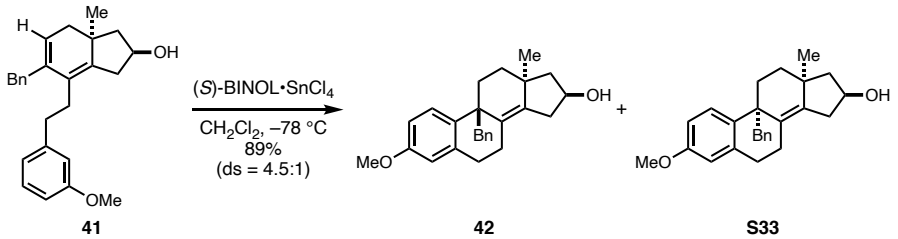
Data for Compound S32: For NMR Spectra of **S32** see page S91. For nOe data of compound **S32** see Millham et al.[6] **TLC**: Rf = 0.13 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 – 7.09 (m, 4H), 6.95 (d, *J* = 6.9 Hz, 2H), 6.62 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 4.99 (s, 1H), 4.52 – 4.45 (m, 1H), 3.07 (d, *J* = 13.4 Hz, 1H), 2.90 – 2.86 (m, 2H), 2.85 – 2.77 (m, 2H), 2.55 – 2.46 (m, 2H), 2.29 (dd, *J* = 16.9, 5.4 Hz, 1H), 2.04 – 1.90 (m, 3H), 1.50 (s, 2H), 1.45 (td, *J* = 12.9, 4.2 Hz, 1H), 1.32 (d, *J* = 5.7 Hz, 1H), 1.20 – 1.12 (m, 1H), 0.52 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 153.5, 139.8, 139.3, 139.0, 137.5, 130.8, 127.5, 127.3, 126.1, 115.4, 113.0, 71.2, 51.4, 49.0, 44.6, 41.2, 38.2, 33.7, 31.6, 29.4, 25.1, 25.0; **IR** (neat, cm^{-1}): 3388 (s),

2948 (m), 2921 (m), 2846 (w), 1703 (m), 701 (m); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{25}H_{29}O_2$ 361.2168; found, 361.2158; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.2}}$: +161.0 (*c* 0.0014, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **40** and **S32**







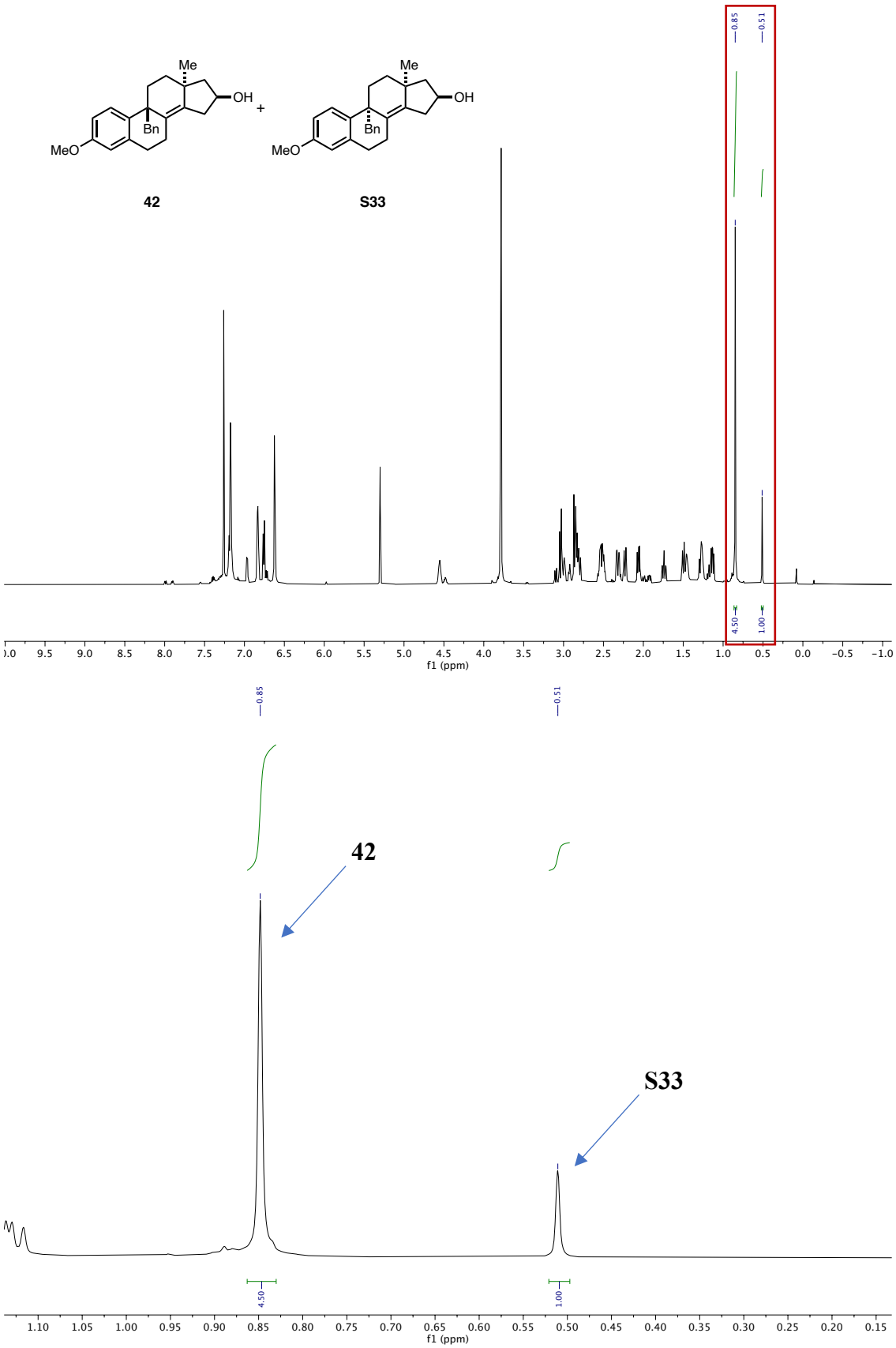
41 **42** **S33**

Synthesis of Tetracycles 42 and S33: To a stirring solution of (*S*)-BINOL (38 mg, 0.112 mmol, 1.1 equiv) in CH_2Cl_2 (2 mL) at –78 °C was added $SnCl_4$ (0.101 mL, 0.101 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at –78 °C before the addition of **41** (see page S11 for preparation) (32 mg, 0.244 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL). The reaction mixture was then stirred at –78 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, saturated aqueous NH_4Cl (4 mL) was added. The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude material containing the 4.5:1 mixture of C9 diastereomers was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0–40% EtOAc in hexanes to afford **42** and **S33** (33 mg, 0.226 mmol, 89% combined yield) as a white foam. An additional purification with a Biotage® Snap Ultra 10 g column and a gradient from 0–25% EtOAc in hexanes was required to isolate each diastereomer, both of which were white foams.

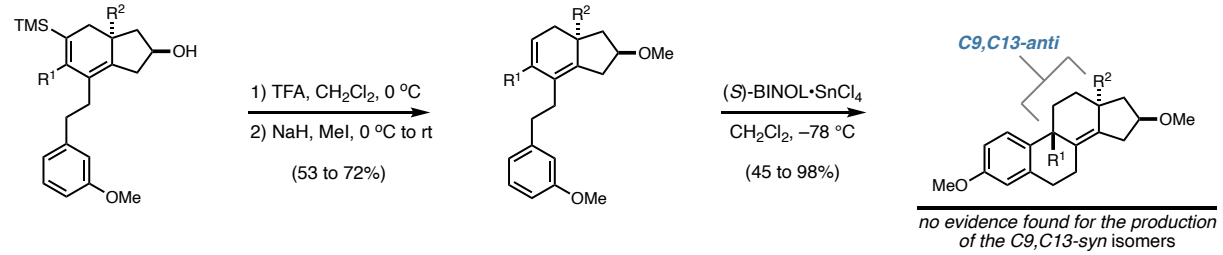
Data for Compound 42: For NMR Spectra of **42** see page S92. **TLC**: R_f = 0.23 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.21 – 7.14 (m, 3H), 6.83 (dd, *J* = 6.4, 3.2 Hz, 2H), 6.78 – 6.73 (m, 1H), 6.64 – 6.59 (m, 2H), 4.57 – 4.54 (m, 1H), 3.78 (s, 3H), 3.06 – 2.97 (m, 2H), 2.88 – 2.78 (m, 3H), 2.55 – 2.49 (m, 2H), 2.32 (dd, *J* = 16.7, 4.3 Hz, 1H), 2.24 – 2.21 (m, 1H), 2.09 – 2.03 (m, 1H), 1.74 (td, *J* = 14.1, 3.4 Hz, 1H), 1.51 – 1.48 (m, 1H), 1.30 – 1.26 (m, 1H), 1.13 (dd, *J* = 12.0, 7.7 Hz, 1H), 0.85 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.37, 139.35, 138.88, 137.95, 137.61, 130.87, 130.21, 128.54, 127.68, 127.62, 126.24, 113.03, 111.70, 77.41, 77.20, 76.99, 71.61, 55.32, 51.93, 48.00, 42.52, 41.24, 38.18, 33.01, 31.69, 30.96, 26.29, 25.08. **IR** (neat, cm^{-1}): 3349 (b), 3026 (s), 2934 (s), 1607 (s), 736 (s), 701 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{30}O_2$ 374.5240; found, 374.5245; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.9}}$**:** –141.4 (*c* 0.650, $CHCl_3$).

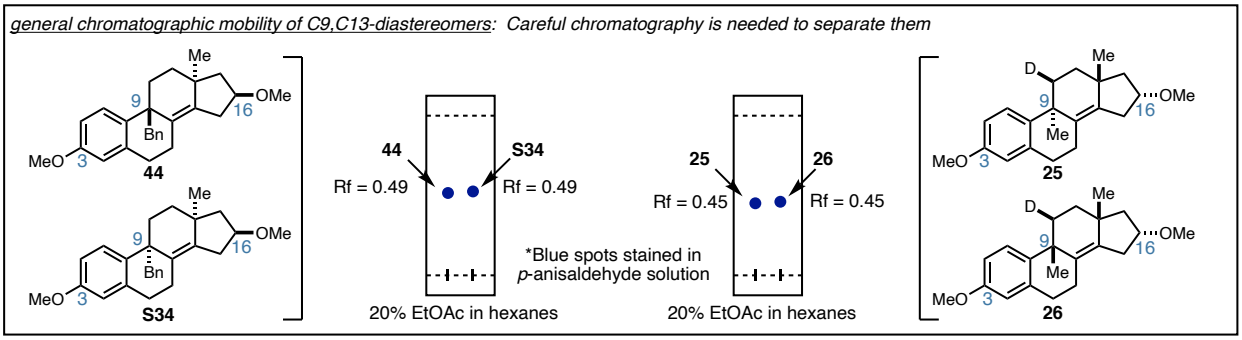
Data for Compound S33: For and NMR Spectra of **S33** see page S93. **TLC**: R_f = 0.23 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.22 – 7.12 (m, 4H), 6.99 – 6.92 (m, 2H), 6.72 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.61 (d, *J* = 2.9 Hz, 1H), 4.49 – 4.45 (m, 1H), 3.79 (s, 3H), 3.09 (d, *J* = 13.4 Hz, 1H), 2.92 (dd, *J* = 8.2, 5.3 Hz, 2H), 2.86 – 2.76 (m, 2H), 2.56 – 2.51 (m, 2H), 2.30 (dd, *J* = 16.9, 5.5 Hz, 1H), 2.04 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.96 – 1.89 (m, 1H), 1.45 (d, *J* = 12.8, 1H), 1.30 – 1.21 (m, 2H), 1.22 – 1.11 (m, 2H), 0.50 (s, 3H).; **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.5, 140.0, 139.2, 137.7, 130.9, 130.8, 127.6, 127.2, 126.1, 113.8, 111.9, 77.4, 77.2, 77.0, 71.2, 55.3, 53.6, 51.7, 49.1, 44.7, 41.3, 38.4, 33.9, 32.0, 29.5, 25.2, 25.0; **IR** (neat, cm^{-1}): 3338 (b), 2920 (m), 1606 (s), 700 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{30}O_2$ 374.5240; found, 374.5243; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.0}}$**:** +30.0 (*c* 0.205, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **42** and **S33**

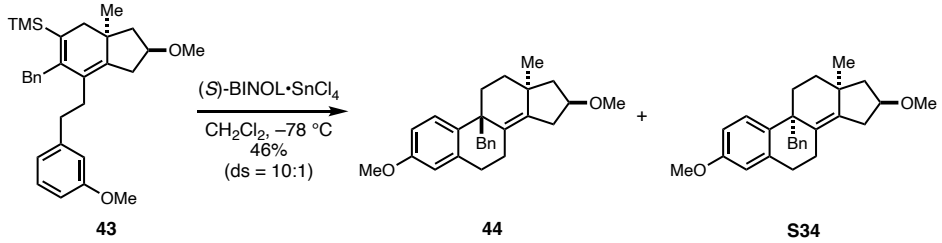


General chromatographic mobility of C9,C13-diastereomers



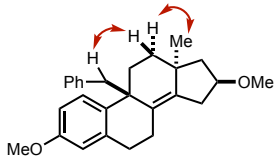


******It is important to note that all observed C9-diastereomers of tetracycles with OMe groups at C3 and C16 have very similar Rf values and could only be separated by HPLC. As a result, isolated yield of all the following C9,C13-anti tetracycles was determined after silica plug or Biotage® column purification with no indication of C9,C13-syn isomers unless otherwise noted.***



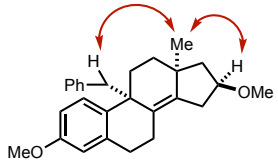
Synthesis of Tetracycles 44 and S34: To a stirring solution of (*S*)-BINOL (23 mg, 0.0788 mmol, 1.1 equiv) in CH_2Cl_2 (2 mL) at –78 °C was added $SnCl_4$ (0.072 mL, 0.0716 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **43** (see page S12 for preparation) (33 mg, 0.0716 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL), and the solution was kept at that temperature for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (4 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product containing the 10:1 mixture of C9 diastereomers was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0–20% EtOAc in hexanes to afford **44** and **S34** as a mixture of diastereomers (14 mg, 0.0360 mmol, 46% combined yield) as a white foam. The mixture was purified by HPLC with a gradient from 0–15% EtOAc in hexanes to afford the isolated diastereomers **44** and **S34** as white foams.

Data for Compound 44: For NMR Spectra of **44** see page S97. **TLC**: R_f = 0.49 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.16 – 7.14 (m, 3H), 6.78 – 6.76 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.9, 2.8 Hz, 1H), 4.14 – 4.10 (m, 1H), 3.78 (s, 3H), 3.34 (s, 3H), 3.02 – 2.98 (m, 2H), 2.86 (d, *J* = 13.4 Hz, 1H), 2.82 – 2.78 (m, 2H), 2.53 – 2.45 (m, 2H), 2.34 (dd, *J* = 17.4, 4.5 Hz, 1H), 2.20 (d, *J* = 13.8 Hz, 1H), 2.07 (dd, *J* = 6.6, 5.5 Hz, 1H), 1.71 (td, *J* = 14.5, 3.5 Hz, 1H), 1.55 – 1.52 (m, 1H), 1.40 – 1.36 (m, 1H), 1.18 (app. t, *J* = 10.0 Hz, 1H), 0.86 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.2, 139.0, 138.1, 137.6, 137.4, 130.7, 129.8, 128.4, 127.4, 125.9, 112.8, 111.3, 80.0, 56.8, 55.1, 48.2, 47.2, 42.3, 40.9, 34.5, 32.6, 31.2, 30.3, 25.8, 24.7; **IR** (neat, cm^{-1}): 2954 (m), 1733 (s), 1607 (s), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_2$ 389.2481; found, 389.2472; $[\alpha]_{589}^{20.8}$**:** –192.7 (*c* 0.845, $CHCl_3$).



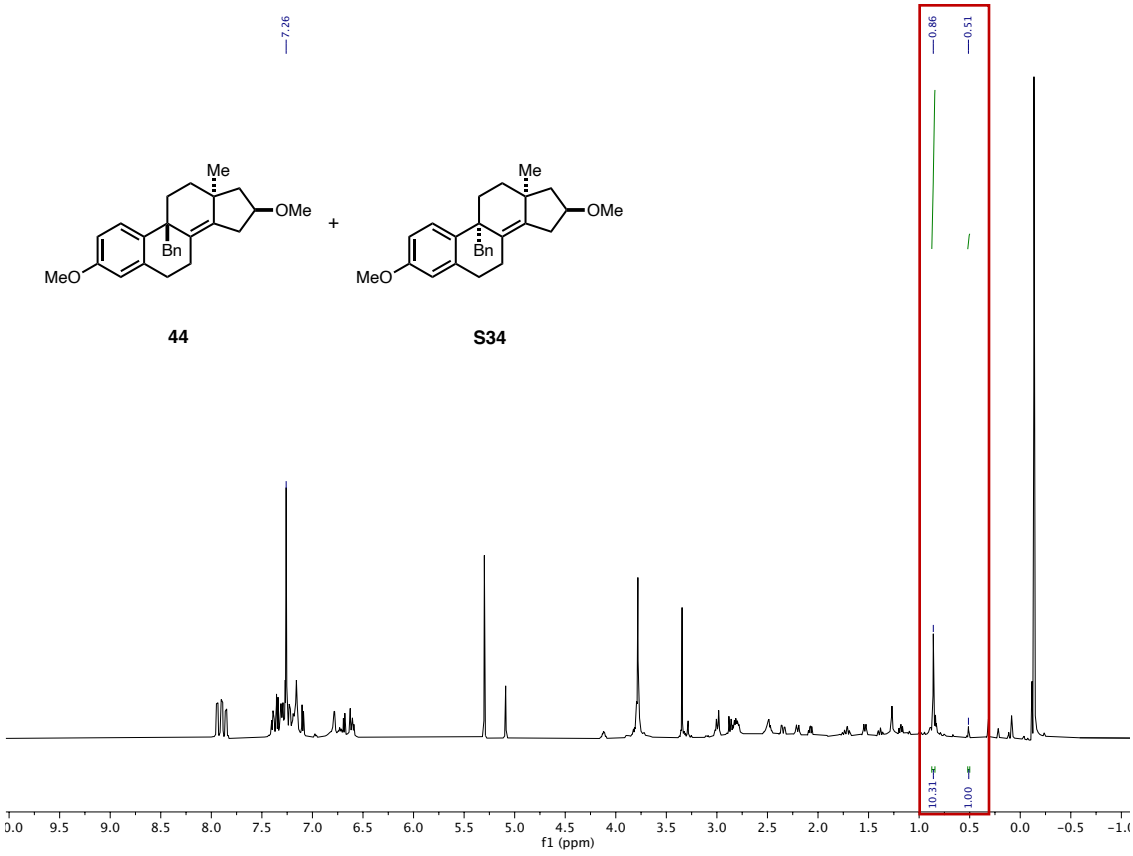
44
Key nOe Interactions

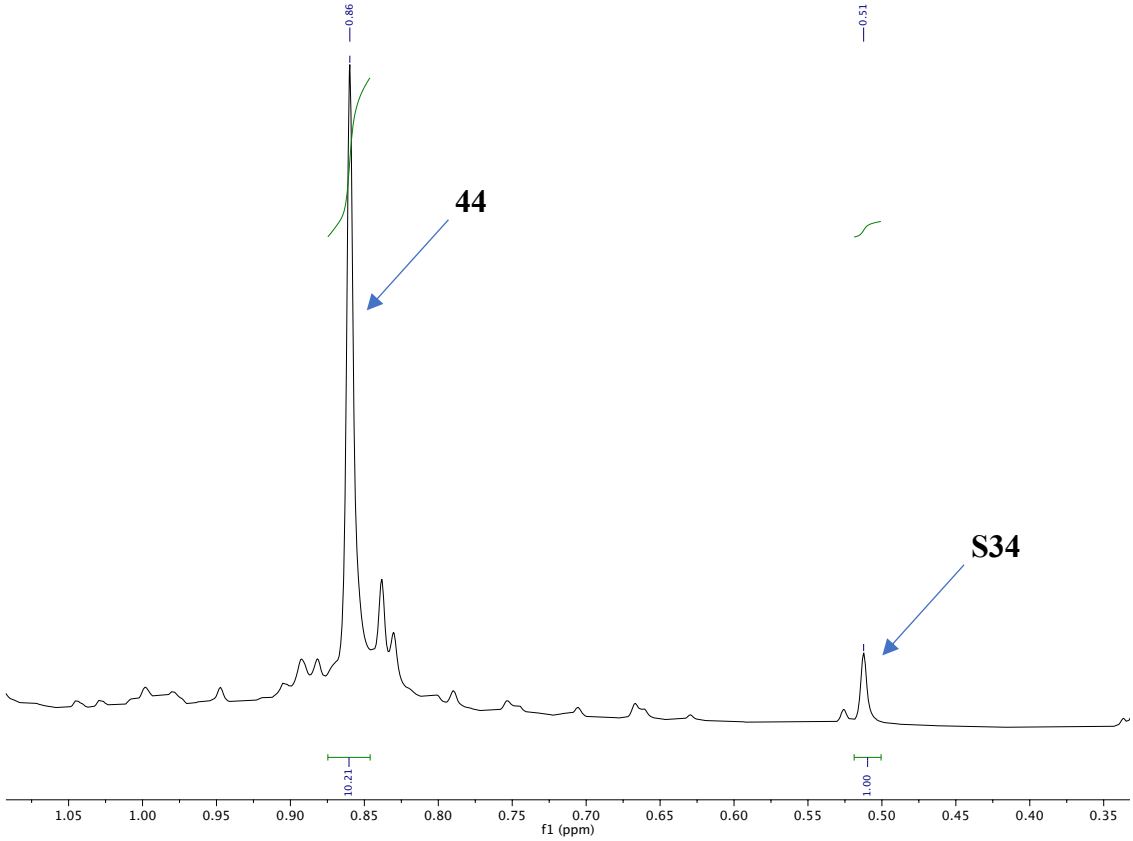
Data for Compound S34: For NMR Spectra of **S34** see page S98. **TLC**: R_f = 0.49 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 4H), 6.97 – 6.94 (m, 2H), 6.71 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 4.03 – 4.00 (m, 1H), 3.79 (s, 3H), 3.28 (s, 3H), 3.09 (d, *J* = 13.4 Hz, 1H), 2.92 – 2.88 (m, 2H), 2.81 – 2.76 (m, 2H), 2.55 – 2.48 (m, 2H), 2.32 (dd, *J* = 17.0, 5.7 Hz, 1H), 2.05 – 2.01 (m, 1H), 1.98 (dd, *J* = 12.7, 3.5 Hz, 1H), 1.91 (dd, *J* = 11.8, 6.4 Hz, 1H), 1.46 – 1.42 (m, 1H), 1.17 – 1.12 (m, 2H), 0.50 (s, 3H).; **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.6, 139.8, 139.3, 137.8, 130.9, 130.9, 127.7, 127.2, 126.2, 113.8, 111.9, 79.8, 77.5, 77.3, 77.1, 57.1, 55.4, 49.1, 48.2, 44.8, 41.1, 35.1, 33.8, 31.9, 29.6, 25.3, 25.0. **IR** (neat, cm^{-1}): 3082 (s), 2920 (w), 1608 (s), 757 (w); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_2$ 389.2481; found, 389.2468; $[\alpha]_{589}^{20.8}$**:** +87.7 (*c* 3.125, $CHCl_3$).

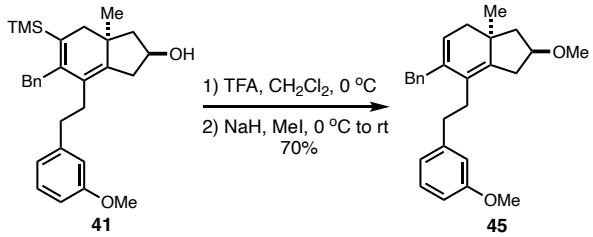


S34
Key nOe Interactions

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **44** and **S34**



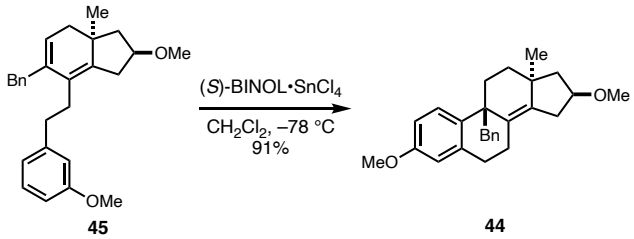




Synthesis of Hydrindane 45: To a stirring solution of hydrindane **41** (for preparation see page S11) **(**58 mg, 0.1298 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (13 µL, 0.168 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 1 h (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once the reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (19 mg, 0.348 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (57 µL, 0.696 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with saturated aqueous $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **45** as a clear oil (35.1 mg, 0.0903 mmol, 70% over two steps).

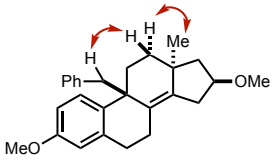
Data for Compound 45: For NMR Spectra of **45** see page S96. **TLC**: R_f = 0.40 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.17 (app. t, *J* = 7.5 Hz, 2H), 7.11 – 7.04 (m, 4H), 6.65 – 6.59 (m, 2H), 6.54 (d, *J* = 2.5 Hz, 1H), 5.31 (d, *J* = 6.3 Hz, 1H), 3.89 (app. p, *J* = 7.5 Hz, 1H), 3.68 (s, 3H), 3.43 – 3.33 (m, 2H), 3.20 (s, 3H), 2.60 (dd, *J* = 18.1, 8.0 Hz, 1H), 2.44 (ddd, *J* = 15.0, 10.1, 5.7 Hz, 1H), 2.34 (ddd, *J* = 13.4, 9.6, 6.8 Hz, 1H), 2.23 – 2.08 (m, 3H), 2.06 – 1.97 (m, 3H), 1.34 (dd, *J* = 11.9, 9.1 Hz, 1H), 0.85 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.5, 143.8, 143.3, 140.7, 135.7, 129.2, 128.7, 128.3, 128.3, 127.3, 125.9, 122.1, 120.9, 114.4, 111.0, 80.2, 56.9, 55.1, 47.7, 39.7, 39.4, 37.6, 35.4, 34.6, 31.5, 22.1; **IR** (neat, cm^{-1}): 2922 (m), 1601 (m), 697 (m); **HRMS** (ESI-TOF) (*m/z*): $[M-H]^+$ calcd for $C_{27}H_{31}O_2$ 387.2324; found, 387.2308; $\boldsymbol{[\alpha]_{589}^{20.9}}$**:** – 12.7 (*c* 1.56, $CHCl_3$).



45 **44**

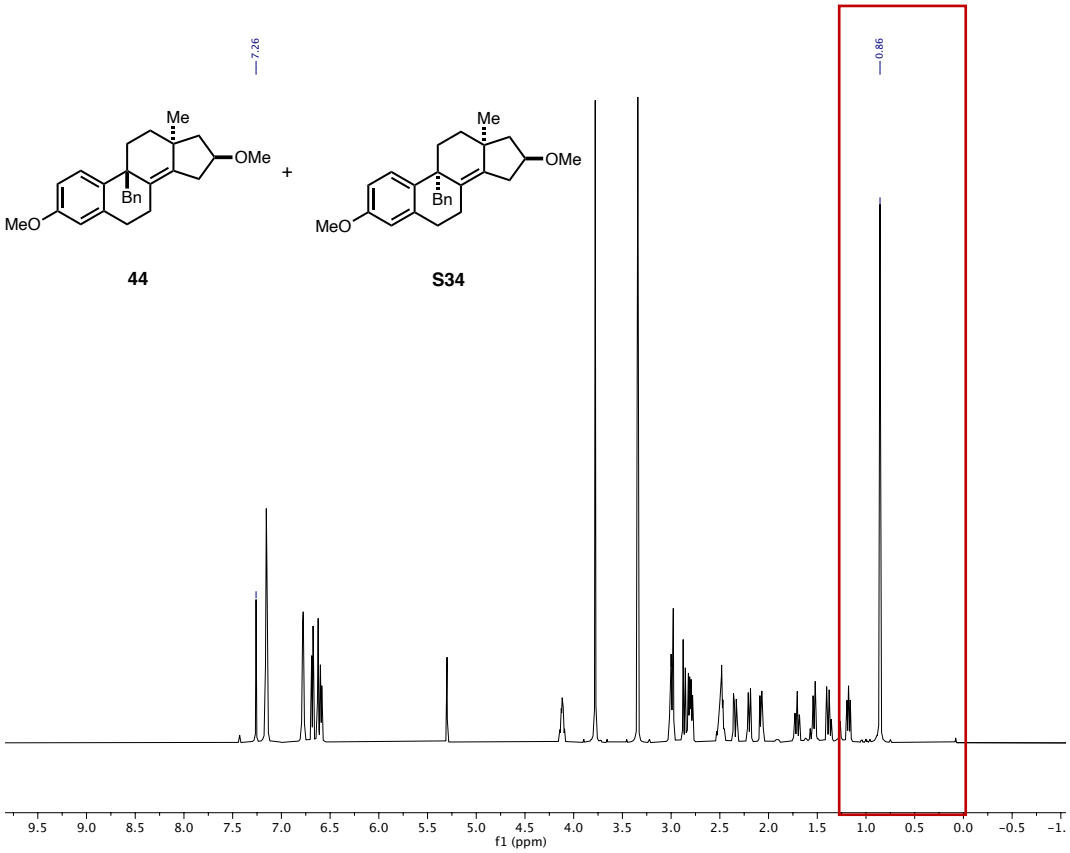
Synthesis of Tetracycle 44: To a stirring solution of (*S*)-BINOL (77 mg, 0.268 mmol, 1.1 equiv) in CH_2Cl_2 (2 mL) at –78 °C was added $SnCl_4$ (0.031 mL, 0.250 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **45** (93 mg, 0.244 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL), and the solution was kept at –78 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (4 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-15% EtOAc in hexanes to afford **44** isolated as a single diastereomer (see note on page S36) (88 mg, 0.226 mmol, 91%) as a white foam.

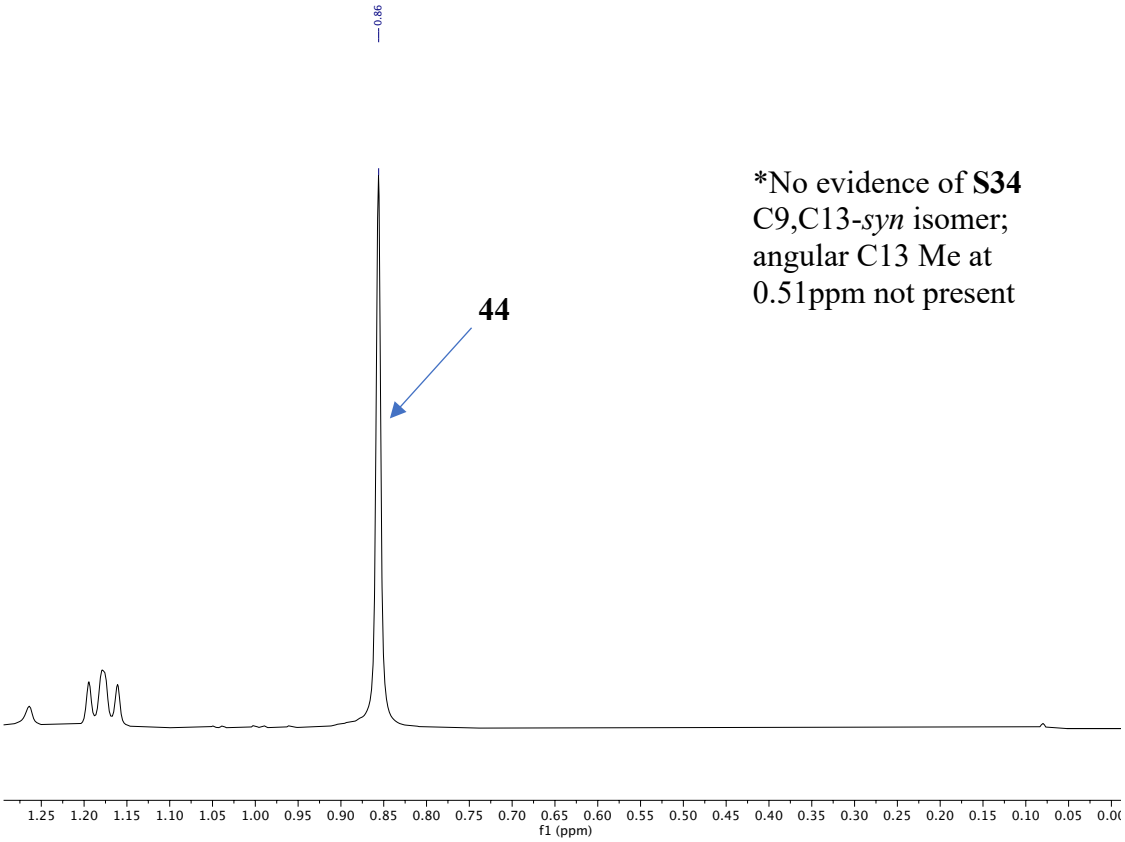
Data for Compound 44: For NMR Spectra of **44** see page S97. **TLC**: R_f = 0.49 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.16 – 7.14 (m, 3H), 6.78 – 6.76 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.9, 2.8 Hz, 1H), 4.14 – 4.10 (m, 1H), 3.78 (s, 3H), 3.34 (s, 3H), 3.02 – 2.98 (m, 2H), 2.86 (d, *J* = 13.4 Hz, 1H), 2.82 – 2.78 (m, 2H), 2.53 – 2.45 (m, 2H), 2.34 (dd, *J* = 17.4, 4.5 Hz, 1H), 2.20 (d, *J* = 13.8 Hz, 1H), 2.07 (dd, *J* = 6.6, 5.5 Hz, 1H), 1.71 (td, *J* = 14.5, 3.5 Hz, 1H), 1.55 – 1.52 (m, 1H), 1.40 – 1.36 (m, 1H), 1.18 (app. t, *J* = 10.0 Hz, 1H), 0.86 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.2, 139.0, 138.1, 137.6, 137.4, 130.7, 129.8, 128.4, 127.4, 125.9, 112.8, 111.3, 80.0, 56.8, 55.1, 48.2, 47.2, 42.3, 40.9, 34.5, 32.6, 31.2, 30.3, 25.8, 24.7; **IR** (neat, cm^{-1}): 2954 (m), 1733 (s), 1607 (s), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_2$ 389.2481; found, 389.2472; $[\alpha]_{589}^{20.8}$**:** –192.7 (*c* 0.845, $CHCl_3$).



44
Key nOe Interactions

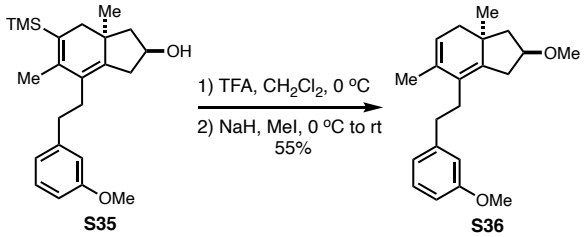
^{1}H NMR (600 MHz, $CDCl_3$) of **44** after Biotage® column purification





*No evidence of **S34** C9,C13-*syn* isomer; angular C13 Me at 0.51ppm not present

F. Synthesis of C9,C13-*Anti*-Substituted Tetracycle

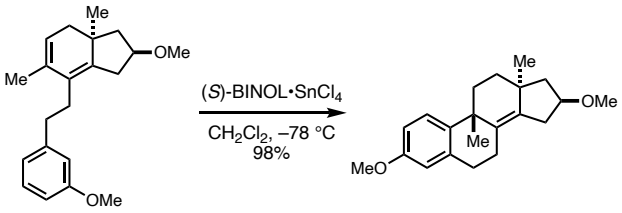


S35 **S36**

Synthesis of Hydrindane S36: To a stirring solution of hydrindane **S35**[7] **(**43 mg, 0.116 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (10 µL, 0.128 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 2 min (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once the reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (14 mg, 0.348 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (43 µL, 0.696 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0-15% EtOAc in hexanes to afford hydrindane **S36** as a clear oil (20 mg, 0.064 mmol, 55% over two steps).

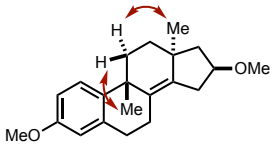
Data for Compound S36: For NMR Spectra of **S36** see page S99. **TLC**: R_f = 0.29 (5% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 (app. t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.75 – 6.69 (m, 2H), 5.39 (d, *J* = 6.1 Hz, 1H), 4.01 – 3.96 (m, *J* = 7.4 Hz, 1H), 3.79 (s, 3H), 3.30 (s, 3H), 2.66 (dd, *J* = 17.3, 7.9 Hz, 1H), 2.62 – 2.53 (m, 2H), 2.39 – 2.28 (m, 2H), 2.15 – 2.01 (m, 4H), 1.82 (s, 3H), 1.41 (app. t, *J* = 10.3 Hz, 1H), 0.88 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.7, 144.0, 142.4, 132.7, 129.3, 127.7, 121.1, 119.8, 114.6, 111.1, 80.4, 57.0, 55.3, 47.8, 40.0, 37.7, 35.6, 34.6, 31.8, 22.3, 19.4; **IR** (neat, cm^{-1}): 3376 (m, br), 2935 (s), 2834 (w), 1734 (m), 756 (m), 698 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{29}O_2$ 313.2168; found, 313.2154; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.5}}$**:** –3.8 (*c* 0.00135, $CHCl_3$).



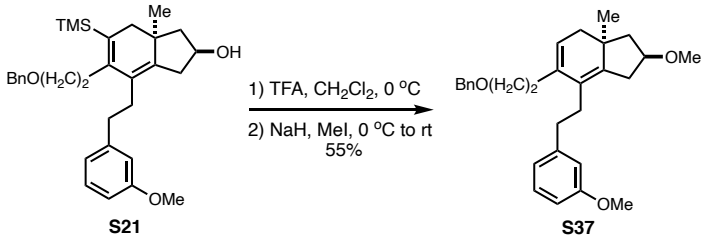
S36 **46**

Synthesis of Tetracycle 46: To a stirring solution of (*S*)-BINOL (28.3 mg, 0.0987 mmol, 1.2 equiv) in CH_2Cl_2 (1.0 mL) at –78 °C was added $SnCl_4$ (0.82 mL, 0.0823 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S36** (25.7 mg, 0.0823 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 mL), and the solution was kept at –78 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 2 M NaOH (1 mL), was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude product was filtered through silica to afford **46** (25.3 mg, 0.0810 mmol, 98%) as a clear oil.

Data for Compound 46: For NMR Spectra of **46** see page S100. **TLC**: R_f= 0.30 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.22 (d, *J*= 8.7 Hz, 1H), 6.76 (d, *J*= 8.4 Hz, 1H), 6.59 (d, *J* = 2.3 Hz, 1H), 4.16 – 4.10 (m, 1H) 3.78 (s, 3H), 3.34 (s, 3H), 2.91 – 2.85 (m, 1H), 2.81 – 2.68 (m, 2H), 2.46 – 2.41 (m, 1H), 2.39 – 2.30 (m, 2H), 2.16 (dd, *J*= 11.7, 6.7 Hz, 1H), 2.10 – 2.07 (m, 1H), 1.88 – 1.81 (m, 1H), 1.74 – 1.69 (m, 2H), 1.14 – 1.13 (m, 4H), 0.90 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 140.2, 137.3, 136.1, 131.7, 127.2, 113.1, 112.5, 80.3, 56.9, 55.3, 48.7, 41.2, 38.1, 34.4, 33.3, 32.3, 31.3, 29.8, 25.8, 25.0; **IR** (neat, cm^{-1}): 2931 (s), 1608 (m); **HRMS** (ESI-TOF) (*m/z*): [$[M+H]^+$ calcd for $C_{21}H_{29}O_2$ 313.2168; found, 313.2159; $[\alpha]_{589}^{22.6}$: –154.1 (*c* 0.00007, $CHCl_3$).



46
Key nOe Interactions

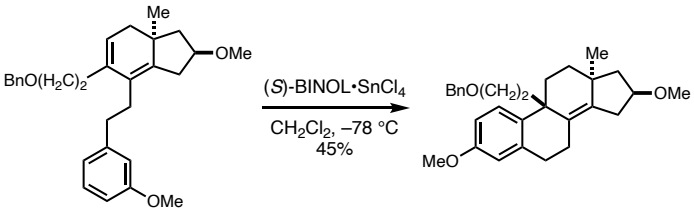


S21 **S37**

Synthesis of Hydrindane S37: To a stirring solution of hydrindane **S21** (for preparation see page S12) **(**43 mg, 0.0876 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (7.4 µL, 0.0964mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 30 mins (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (11 mg, 0.263 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (33 µL, 0.526 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S37** as a clear oil (21 mg, 0.0485 mmol, 55% over two steps).

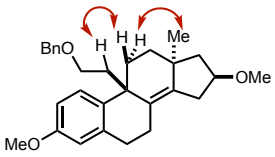
Data for Compound S37: For NMR Spectra of **S37** see page S102. **TLC**: R_f = 0.37 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 – 7.29 (m, 5H), 7.20 – 7.17 (m, 1H), 6.81 – 6.75 (m, 2H), 6.73 (d, *J* = 2.3 Hz, 1H), 5.49 (dd, *J* = 6.7, 2.5 Hz, 1H), 4.54 (d, *J* = 1.7 Hz, 2H), 4.02 – 3.96 (m, 1H), 3.81 (d, *J* = 1.0 Hz, 3H), 3.56 – 3.47 (m, 2H), 3.35 – 3.29 (m, 3H), 2.72 (dd, *J* = 17.9, 7.9 Hz, 1H), 2.63 – 2.59 (m, 1H), 2.54 – 2.46 (m, 3H), 2.41 – 2.31 (m, 2H), 2.15 – 2.06 (m, 3H), 1.41 (dd, *J* = 11.8, 9.1 Hz, 1H), 0.89 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 143.7, 143.0, 133.6, 129.2, 128.4, 127.6, 127.5, 127.0, 121.0, 120.9, 114.5, 111.0, 80.2, 43.0, 70.5, 56.9, 55.2, 47.6, 37.4, 35.5, 34.7, 32.9, 31.5, 22.0; **IR** (neat, cm^{-1}): 3029 (s), 2923 (m), 2858 (m), 776 (m), 697 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{29}H_{37}O_3$ 433.2664; found, 433.2702; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.1}}$**:** –26.2 (*c* 0.15, $CHCl_3$).



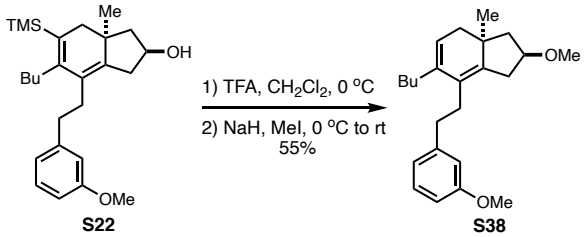
S37 **47**

Synthesis of Tetracycle 47: To a stirring solution of (*S*)-BINOL (22 mg, 0.074 mmol, 1.1 equiv) in CH_2Cl_2 (1 mL) at –78 °C was added $SnCl_4$ (0.067 mL, 0.067 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S37** (29 mg, 0.067 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL), and the solution was warmed to –40 °C and kept at that temperature for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-15% EtOAc in hexanes to afford **47** (13 mg, 0.018 mmol, 45%) as a white foam.

Data for Compound 47: For NMR Spectra of **47** see page S103. **TLC**: R_f = 0.37 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.32 – 7.30 (m, 2H), 7.27 – 7.25 (m, 3H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 4.40 – 4.33 (m, 2H), 4.12 (ddd, *J* = 14.5, 10.4, 6.5 Hz, 1H), 3.77 (s, 3H), 3.40 – 3.31 (m, 5H), 2.95 – 2.90 (m, 1H), 2.77 – 2.71 (m, 2H), 2.41 – 2.37 (m, 2H), 2.34 – 2.25 (m, 2H), 2.14 (dd, *J* = 11.7, 6.6 Hz, 1H), 2.01 – 1.97 (m, 2H), 1.86 – 1.80 (m, 1H), 1.72 – 1.66 (m, 2H), 1.34 – 1.28 (m, 1H), 0.87 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.2, 138.6, 137.7, 137.7, 137.6, 130.1, 128.3, 127.5, 127.4, 127.3, 113.1, 111.6, 80.0, 72.8, 68.3, 56.8, 55.1, 48.5, 41.0, 40.4, 40.1, 34.4, 33.2, 31.6, 30.7, 25.7, 24.8; **IR** (neat, cm^{-1}): 2921 (s), 2850 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+Na]^+$ calcd for $C_{29}H_{36}O_3Na$ 455.2664; found, 455.2562; $[\alpha]_{589}^{21.6}$**:** –138.6 (*c* 0.04, $CHCl_3$).



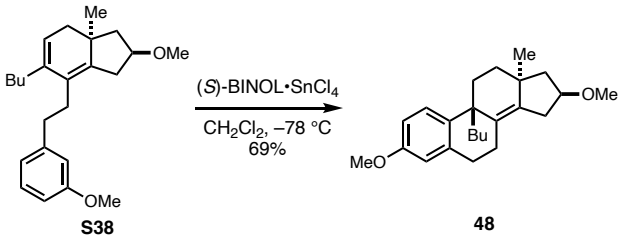
47
Key nOe Interactions



Synthesis of Hydrindane S38: To a stirring solution of hydrindane **S22** (for preparation see page S13) **(**43 mg, 0.104 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (9 µL, 0.094 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 5 mins (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (12.5 mg, 0.312 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (40 µL, 0.624 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S38** as a clear oil (20.2 mg, 0.0570 mmol, 55% over two steps).

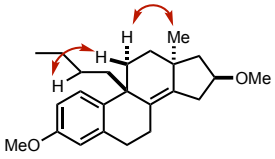
Data for Compound S38: For NMR Spectra of **S38** see page S105. **TLC**: R_f = 0.46 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 (app. t, *J* = 7.9 Hz, 1H), 6.78 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 5.40 (d, *J* = 5.5 Hz, 1H), 4.00 – 3.98 (m, 1H), 3.80 (s, 3H), 3.31 (s, 3H), 2.73 (dd, *J* = 18.0, 7.7 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.55 – 2.49 (m, 1H), 2.38 – 2.29 (m, 2H), 2.21 – 2.15 (m, 1H), 2.14 – 2.05 (m, 5H), 1.48 – 1.27 (m, 5H), 0.91 (t, *J* = 6.6 Hz, 3H), 0.89 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.7, 144.1, 142.7, 137.3, 129.4, 127.6, 121.1, 119.1, 114.6, 111.1, 80.4, 57.1, 55.3, 47.8, 39.8, 37.6, 35.7, 34.8, 32.6, 31.9, 31.6, 22.7, 22.2, 14.2; **IR** (neat, cm^{-1}): 2926 (s), 2871 (m), 776 (w), 696 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{35}O_2$ 355.2637; found, 355.2631; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.5}}$**:** –23.4 (*c* 0.0020, $CHCl_3$).



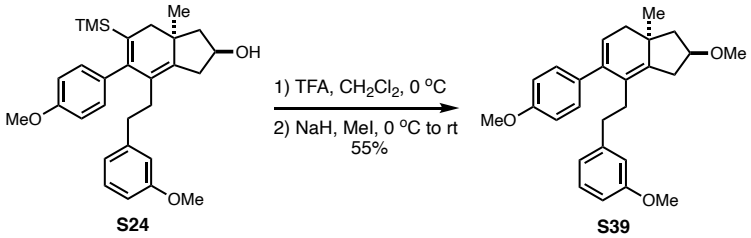
S38 **48**

Synthesis of Tetracycle 48: To a stirring solution of (*S*)-BINOL (18 mg, 0.0620 mmol, 1.1 equiv) in CH_2Cl_2 (1.0 mL) at –78 °C was added $SnCl_4$ (56 µL, 0.0564 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S38** (20 mg, 0.0564 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 mL), and the solution was kept at –78 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 2 M NaOH (1 mL), was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude product was filtered through silica to afford **48** (13.8 mg, 0.0389 mmol, 69%) as a clear oil.

Data for Compound 48: For NMR Spectra of **48** see page S106. **TLC**: R_f = 0.37 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.60 (d, *J* = 2.6 Hz, 1H), 4.15 – 4.09 (m, 1H), 3.77 (s, 3H), 3.33 (s, 3H), 2.93 (dt, *J* = 16.1, 5.7 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.50 – 2.42 (m, 1H), 2.41 – 2.34 (m, 1H), 2.29 (dd, *J* = 17.2, 4.4 Hz, 1H), 2.24 (dt, *J* = 11.4, 6.6 Hz, 1H), 2.14 (dd, *J* = 11.4, 6.6 Hz, 1H), 1.80 (td, *J* = 13.4, 4.0 Hz, 1H), 1.71 – 1.53 (m, 4H), 1.31 (dd, *J* = 11.4, 8.8 Hz, 1H), 1.20 – 1.10 (m, 3H), 1.08 – 1.00 (m, 1H), 0.87 (s, 3H), 0.80 (t, *J* = 7.0 Hz, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 138.9, 137.7, 136.9, 131.0, 127.7, 113.2, 111.5, 80.3, 57.0, 55.2, 48.7, 41.7, 41.1, 41.0, 34.5, 33.5, 31.0, 30.9, 29.8, 27.8, 25.8, 24.8, 23.6, 41.2; **IR** (neat, cm^{-1}): 2931 (s), 1739 (w), 865 (w), 816 (w), 757 (m), **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{35}O_2$ 355.2637; found, 355.2634 ; $[\alpha]_{589}^{22.6}$**:** –154.1 (*c* 0.0007, $CHCl_3$).



48
Key nOe Interactions

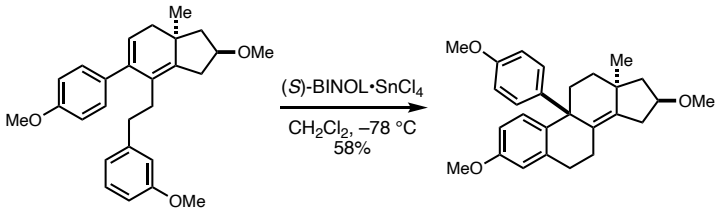


S24 **S39**

Synthesis of Hydrindane S39: To a stirring solution of hydrindane **S24** (for preparation see page S14) (80 mg, 0.173 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (15 µL, 0.190 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 5 mins (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (21 mg, 0.519 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (65 µL, 1.038 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S39** as a clear oil (38.5 mg, 0.095 mmol, 55% over two steps).

Data for Compound S39: For NMR Spectra of **S39** see page S108. **TLC**: R_f = 0.43 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.4, 2H), 7.08 (app. t, *J* = 7.7, 1H), 6.9 (d, *J* = 8.3 Hz, 2H), 6.66 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.49 (d, 7.5 Hz, 1H), 6.34 (s, 1H), 5.61 (app t, *J* = 4.6 Hz, 1H), 4.07 – 4.02 (m, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.34 (s, 3H), 2.82 (dd, *J* = 18.0, 7.8 Hz, 1H), 2.36 – 2.22 (m, 6H), 2.18 (dd, *J* = 18.4, 7.4 Hz, 1H), 2.12 (dd, 12.0, 6.1 Hz, 1H), 1.46 (app. t, *J* = 10.5 Hz, 1H), 0.99 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.3, 158.4, 143.8, 143.4, 139.5, 134.1, 129.1, 127.0, 126.9, 122.8, 120.8, 113.9, 113.3, 111.1, 80.2, 56.9, 55.2, 55.0, 47.5, 39.7, 37.8, 34.9, 34.7, 32.4, 22.2; **IR** (neat, cm^{-1}): 2923 (m), 836 (s), 697 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_3$ 405.2430; found, 405.2427; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.7}}$**:** +24.8 (*c* 0.145, $CHCl_3$).

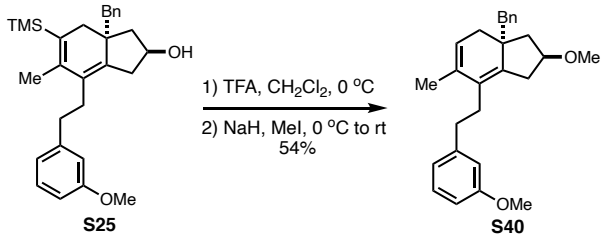


S39 **49**

Synthesis of Tetracycle 49: To a stirring solution of (*S*)-BINOL (10 mg, 0.034 mmol, 1.1 equiv) in CH_2Cl_2 (1 mL) at –78 °C was added $SnCl_4$ (0.031 mL, 0.031 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S39** (12.5 mg, 0.031 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL), and the solution was kept at –78 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and

concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-15% EtOAc in hexanes to afford **49** (7.2 mg, 0.018 mmol, 58%) as a white foam.

Data for Compound 49: For NMR Spectra of **49** see page S109. **TLC**: R_f = 0.40 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 1H), 6.94 (d, 8.5 Hz, 2H), 6.84 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.64 (s, 1H), 4.20 – 4.17 (m, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.39 (s, 3H), 2.73 (dd, *J* = 17.4, 8.7 Hz, 1H), 2.51 (dd, *J* = 16.2, 7.1 Hz, 1H), 2.44 – 2.41 (m, 2H), 2.36 (dd, *J* = 17.2, 4.5 Hz, 1H), 2.25 – 2.10 (m, 3H), 2.07 (d, *J* = 12.9 Hz, 1H), 1.54 – 148 (m, 2H), 1.40 (app. t, *J* = 10.1Hz, 1H), 0.96 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.8, 157.4, 140.6, 139.8, 139.4, 137.7, 128.6, 113.6, 112.9, 110.7, 80.1, 56.0, 55.2, 55.1, 48.5, 47.1, 41.3, 34.6, 47.1, 41.3, 34.6, 31.3, 28.2, 26.8, 25.6; **IR** (neat, cm^{-1}): 2926 (m), 1733 (s), 1717 (m), 1698 (m), 829 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_3$ 405.2430; found, 405.2418; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.8}}$**:** +103.7 (*c* 0.15, $CHCl_3$).
***Stereochemistry at C9 of compound **49** was assigned by analogy. The chemical shift of the C13 angular methyl on compound **49** (0.96 ppm) was nearly identical to the C13 angular methyl (0.97 ppm) of the *anti*-isomer of a similar substrate with aryl functionality at C9 reported by Millham *et al.*[6]

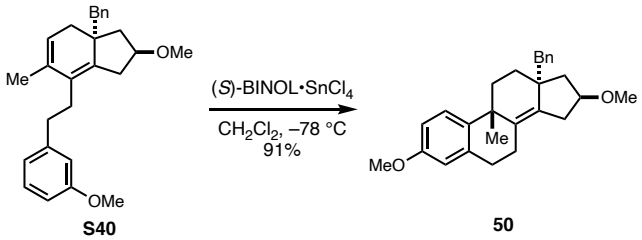


S25 **S40**

Synthesis of S40: To a stirring solution of hydrindane **S25** (for preparation see page S15) **(**38 mg, 0.085 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (7 µL, 0.094 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 5 mins (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (10 mg, 0.255 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (32 µL, 0.510 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S40** as a clear oil (18 mg, 0.0463 mmol, 55% over two steps).

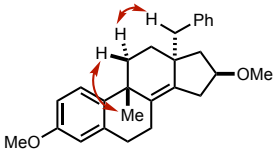
Data for Compound S40: For NMR Spectra of **S40** see page S111. **TLC**: R_f = 0.43 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.28 – 7.25 (m, 2H), 7.20 (app. t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 1H), 6.81 – 6.74 (m, 2H), 5.50 (d, *J* = 5.9 Hz, 1 H), 3.90 – 3.85 (m, 1H), 3.80 (s, 3H), 3.27 (s, 3H), 2.65 – 2.56 (m, 4H), 2.45 – 2.36 (m, 3H), 2.30 (dd, *J* = 6.6, 6.0 Hz, 1H), 2.14 (dd, *J* = 17.8, 6.3 Hz, 2H), 1.91(s, 1H), 1.89 (s, 3H), 1.19 (dd, *J* = 10.7, 3.9 Hz, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.8, 157.4, 140.6, 139.8, 139.4, 137.7, 128.6, 113.6, 112.1, 110.7, 80.1, 57.0, 55.2, 55.1, 48.5, 47.1, 41.3, 34.6, 47.1, 41.3, 34.6, 31.3, 28.2, 26.8, 25.6; **IR** (neat, cm^{-1}): 2926 (m), 1733 (s), 1717 (m), 1698 (m), 829 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_3$ 389.2481; found, 389.2465; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.8}}$**:** +103.7 (*c* 0.15, $CHCl_3$).



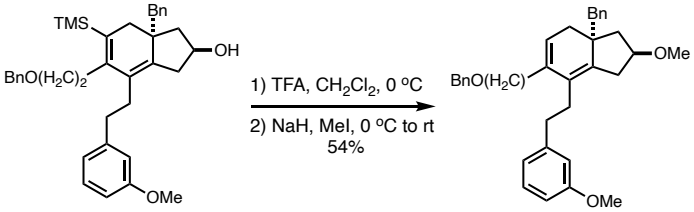
S40 **50**

Synthesis of 50: To a stirring solution of (*S*)-BINOL (37 mg, 0.127 mmol, 1.1 equiv) in CH_2Cl_2 (1 mL) at –78 °C was added $SnCl_4$ (0.116 mL, 0.116 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S40** (45 mg, 0.116 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL), and the solution was kept at –78 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-15% EtOAc in hexanes to afford **50** (41 mg, 0.105 mmol, 91%) as a white foam.

Data for Compound 50: For NMR Spectra of **50** see page S112. **TLC**: R_f = 0.40 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.27 – 7.21 (m, 3H), 7.21 – 7.19 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 1H), 4.22 – 4.19 (m, 1H), 3.80 (s, 3H), 3.35 (s, 3H), 2.93 (dd, *J* = 16.6, 4.9 Hz, 1H), 2.82 – 2.76 (m, 2H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.48 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.43 – 2.35 (m, 4H), 2.10 (d, *J* = 13.2 Hz, 1H), 2.01 (app. t, *J* = 13.6 Hz, 1H), 1.89 (d, *J* = 13.7 Hz, 1H), 1.44 (app t, *J* = 13.3 Hz, 1H), 1.34 (s, 3H), 1.09 (dd, *J* = 3.9, 8.5 Hz, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.0, 140.0, 139.0, 137.1, 136.1, 132.8, 130.4, 127.9, 127.1, 126.0, 113.0, 112.4, 80.0, 56.8, 55.1, 45.5, 43.9, 41.2, 38.2, 34.5, 33.8, 32.2, 31.6, 28.7, 25.0; **IR** (neat, cm^{-1}): 3025 (m), 2929 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{33}O_2$ 389.2481; found, 389.2480; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.0}}$**:** –70.8 (*c* 1.495, $CHCl_3$).



50
Key nOe Interactions

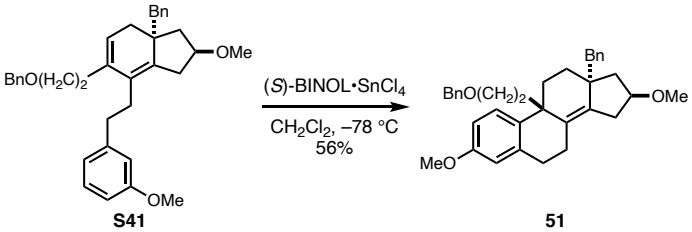


S26 **S41**

Synthesis of S41: To a stirring solution of hydrindane **S26** (for preparation see page S16) **(**46 mg, 0.0811 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (7 µL, 0.094 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 5 h (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (10 mg, 0.243 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (30 µL, 0.487 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S41** as a clear oil (22.2 mg, 0.0436 mmol, 54% over two steps).

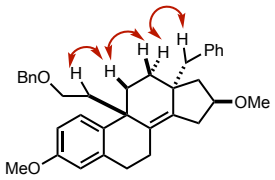
Data for Compound S41: For NMR Spectra of **S41** see page S114. **TLC**: R_f = 0.43 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.36 – 7.29 (m, 4H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.09 – 7.04 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.77 – 6.71 (m, 2H), 4.56 – 4.51 (m, 2H), 3.79 (s, 4H), 3.62 – 3.53 (m, 2H), 3.25 (s, 3H), 2.67 – 2.63 (m, 1H), 2.61 – 2.51 (m, 5H), 2.48 – 2.37 (m, 3H), 2.31 (dd, *J* = 12.6, 6.2 Hz, 1H), 2.15 (dd, *J* = 16.6, 6.5 Hz, 1H), 2.09 (dd, *J* = 18.0, 6.7 Hz, 1H), 1.92 (d, *J* = 16.6 Hz, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.5, 143.6, 143.1, 138.7, 138.4, 134.5, 130.3, 129.2, 128.3, 128.1, 127.8, 127.6, 127.5, 125.9, 121.1, 120.9, 114.5, 111.0, 80.0, 73.0, 70.5, 56.8, 55.1, 44.4, 43.5, 38.4, 35.4, 35.2, 34.3, 32.9, 31.6; **IR** (neat, cm^{-1}): 3025 (m), 2926 (s), 2858 (m), 736 (m), 698 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{41}O_3$ 509.2977; found, 509.3056; $[\alpha]_{589}^{21.4}$**:** –59.9 (*c* 0.105, $CHCl_3$).



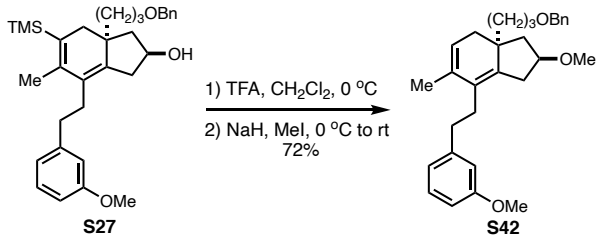
S41 **51**

Synthesis of 51: To a stirring solution of (*S*)-BINOL (11 mg, 0.039 mmol, 1.1 equiv) in CH_2Cl_2 (1 mL) at –78 °C was added $SnCl_4$ (0.035 mL, 0.035 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S41** (15 mg, 0.035 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL), and the solution was kept at –40 °C for 2 h before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phase was washed with 3 M NaOH (3 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0–15% EtOAc in hexanes to afford **51** (10 mg, 0.0196 mmol, 56%) as a white foam.

Data for Compound 51: For NMR Spectra of **51** see page S115. **TLC**: R_f = 0.40 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 6H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.63 (s, 1H), 4.38 – 4.36 (m, 2H), 4.22 – 4.19 (m, 1H), 3.79 (s, 3H), 3.38 – 3.34 (m, 5H), 2.97 (td, *J* = 16.1, 5.4 Hz, 1H), 2.82 – 2.76 (m, 2H), 2.52 (d, *J* = 13.7 Hz, 1H), 2.48 – 2.45 (m, 2H), 2.37 – 2.32 (m, 4H), 2.05 – 1.97 (m, 3H) 1.87 (d, *J* = 13.7 Hz, 1H), 1.42 (app. t, *J* = 13.7 Hz, 1H), 1.08 (dd, *J* = 8.6, 3.8 Hz, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.3, 139.0, 138.5, 137.8, 137.8, 137.6, 131.4, 130.4, 128.3, 127.9, 127.5, 127.4, 126.1, 113.2, 111.7, 79.8, 68.2, 56.9, 55.1, 45.3, 43.9, 41.2, 41.0, 40.2, 34.8, 31.3, 31.0, 28.8, 24.9; **IR** (neat, cm^{-1}): 2923 (m), 2851 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{41}O_3$ 509.2977; found, 509.3056; $[\alpha]_{589}^{21.4}$**:** –19.9 (*c* 0.135, $CHCl_3$).



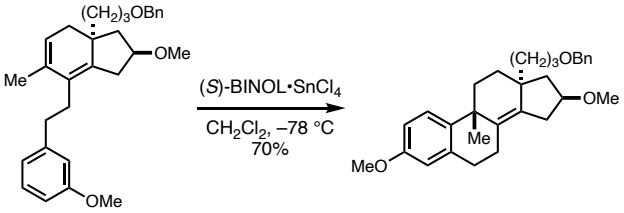
51
Key nOe Interactions



Synthesis of Hydrindane S42: To a stirring solution of hydrindane **S27** (for preparation see page S17) **(**215 mg, 0.426 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (36 µL, 0.4686 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 30 mins (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (5 mL), followed by dilution with CH_2Cl_2 (7 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 10 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (51 mg, 1.28 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (159 µL, 2.56 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S42** as a clear oil (137 mg, 0.306 mmol, 72% over two steps).

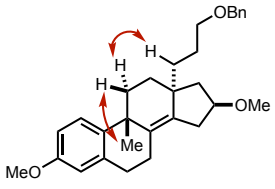
Data for Compound S42: For NMR Spectra of **S42** see page S117. **TLC**: R_f = 0.23 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.19 (app. t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.75 – 6.69 (m, 2H), 5.34 (d, *J* = 5.5 Hz, 1H), 4.48 (s, 2H), 3.94 (m, 1H), 3.79 (s, 3H), 3.45 – 3.36 (m, 1H), 3.27 (s, 3H), 2.66 – 2.52 (m, 3H), 2.40 – 2.29 (m, 2H), 2.26 – 2.13 (m, 3H), 2.03 – 1.97 (m, 1H), 1.80 (s, 3H), 1.55 – 1.40 (m, 3H), 1.31 (dd, *J* = 12.4, 8.4 Hz, 1H), 1.12 – 1.05 (m, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.6, 143.9, 142.4, 138.7, 133.1, 129.3, 128.4, 128.2, 127.7, 127.6, 121.0, 119.6, 114.6, 111.0, 80.5, 73.0, 71.2, 56.9, 55.2, 44.4, 43.2, 35.7, 34.7, 34.2, 31.8, 29.7, 25.5, 19.4; **IR** (neat, cm^{-1}): 2936 (s), 2859 (m), 779 (w), 737 (m), 697 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{39}O_3$ 447.2899; found, 447.2894; $\boldsymbol{[\alpha]_{589}^{22.4}}$**:** –133.8 (*c* 0.00014, $CHCl_3$).



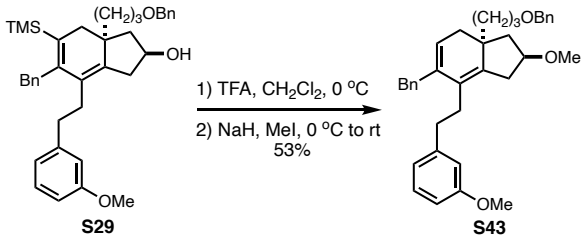
S42 **52**

Synthesis of Tetracycle 52: To a stirring solution of (*S*)-BINOL (36 mg, 0.104 mmol, 1.2 equiv) in CH_2Cl_2 (1.1 mL) at –78 °C was added $SnCl_4$ (0.104 mL, 0.104 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S42** (46.6 mg, 0.104 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL), and the solution was kept at that temperature for 15 min before being transferred to a –40 °C bath. The reaction mixture was the stirred for 2 h at –40 °C before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 5 mol% NaOH (1 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-5% EtOAc in hexanes to afford **52** (32.5 mg, 0.0728 mmol, 70%) as a clear oil.

Data for Compound 52: For NMR Spectra of **52** see page S118. **TLC**: R_f = 0.20 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 – 7.25 (m, 5H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.60 (s, 1H), 4.47 (s, 2H), 4.07 – 4.05 (m, 1H), 3.79 (s, 3H), 3.24 – 3.35 (m, 2H), 3.33 (s, 3H), 2.90 (dd, *J* = 15.8, 2.9 Hz, 1H), 2.81 – 2.69 (m, 2H), 2.48 – 2.42 (m, 1H), 2.41 – 2.30 (m, 3H), 2.04 (d, *J* = 13.2 Hz, 1H), 1.92 (d, *J* = 13.3 Hz, 1H), 1.80 (app. t, *J* = 13.6 Hz, 1H), 1.59 – 1.50 (m, 3H), 1.33 (s, 3H), 1.32 – 1.24 (m, 1H), 1.21 – 1.13 (m, 2H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 140.2, 138.6, 137.3, 136.7, 131.9, 128.4, 127.6, 127.2, 113.0, 112.5, 80.1, 73.0, 71.0, 56.9, 55.2, 44.1, 44.0, 38.0, 34.4, 34.0, 32.3, 31.8, 31.5, 29.0, 25.0, 25.0; **IR** (neat, cm^{-1}): 2932 (s), 2859, 736 (w), 698 (w); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{39}O_3$ 447.2899; found, 447.2892; $[\alpha]_{589}^{22.6}$**:** –97.1 (*c* 0.0019, $CHCl_3$).



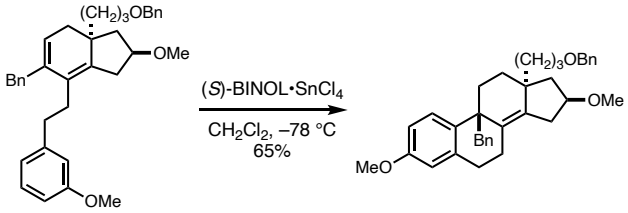
52
Key nOe Interactions



Synthesis of Hydrindane S43: To a stirring solution of hydrindane **S29** (for preparation see page S18) **(**50 mg, 0.086 mmol, 1.0 equiv) at 0 °C in CH_2Cl_2 (2 mL) was slowly added TFA (7.2 µL, 0.095 mmol, 1.1 equiv). The reaction mixture was stirred at 0 °C for 2 h (reaction progress was monitored by TLC, 30% EtOAc in hexanes). Once reaction was complete by TLC the mixture was quenched with DI water (3 mL), followed by dilution with CH_2Cl_2 (5 mL), the biphasic solution was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford the protodesilylated hydrindane as a clear oil which was immediately used in the next reaction.

To a stirring solution of the protodesilylated hydrindane in THF (2 mL) at 0 °C was added NaH in a 60% oil suspension (10.5 mg, 0.258 mmol, 3 equiv), and the solution was stirred for 10 min before the addition of MeI (32 µL, 0.516 mmol, 6 equiv). The solution was warmed to rt and stirred overnight (~ 14 h). Upon completion, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude oil was purified by flash chromatography with a Biotage® Snap Ultra 5 g cartridge and a gradient from 0–15% EtOAc in hexanes to afford hydrindane **S43** as a clear oil (24 mg, 0.0459 mmol, 53% over two steps).

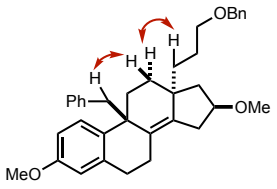
Data for S43: For NMR Spectra of **S43** see page S120. **TLC**: R_f = 0.15 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 4H), 6.74 – 6.68 (m, 2H), 6.63 (s, 1H), 5.37 (d, *J* = 6.6 Hz, 1H), 4.50 (s, 3H), 3.93 (app. p, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.50 – 3.36 (m, 4H), 3.27 (s, 3H), 2.64 (dd, *J* = 18.0, 7.3 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.46 – 2.39 (m, 1H), 2.33 – 2.21 (m, 4H), 2.17 (dd, *J* = 18.0, 6.2 Hz, 1H), 2.08 (d, *J* = 16.5 Hz, 1H), 1.55 – 1.47 (m, 3H), 1.35 (dd, *J* = 12.8, 8.4 Hz, 1H), 1.22 – 1.15 (m, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.6, 143.9, 143.6, 140.7, 138.7, 136.4, 129.5, 129.4, 129.3, 128.8, 128.5, 128.4, 128.1, 128.0, 127.7, 127.6, 126.0, 122.1, 121.0, 114.5, 111.1, 80.5, 73.1, 71.2, 56.9, 55.3, 44.4, 43.1, 39.5, 35.6, 35.0, 34.5, 31.7, 29.7, 25.6; **IR** (neat, cm^{-1}): 2924 (s), 2854 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{43}O_3$ 523.3212; found, 523.3192; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.3}}$**:** –13.9 (*c* 0.0006, $CHCl_3$).



S43 **53**

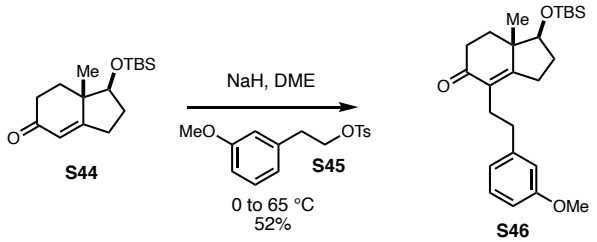
Synthesis of Tetracycle 53: To a stirring solution of (*S*)-BINOL (11.0 mg, 0.0358 mmol, 1.1 equiv) in CH_2Cl_2 (1 mL) at –78 °C was added $SnCl_4$ (33 µL, 0.0325 mmol, 1.0 equiv, 1.0 M in CH_2Cl_2) which was stirred for 30 min at that temperature before the addition of **S43** (17 mg, 0.0325 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL), and the solution was kept at that temperature for 15 min before being transferred to a –40 °C bath. The reaction mixture was the stirred for 2 h at –40 °C before being warmed to rt. After stirring for an additional 1 h, the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The biphasic solution was stirred for 1 h before being transferred to a separatory funnel where the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with 2 M NaOH (1 mL), was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 0-15% EtOAc in hexanes to afford **53** (11 mg, 0.00210 mmol, 65%) as a clear oil.

Data for Compound 53: For NMR Spectra of **53** see page S121. **TLC**: R_f = 0.22 (20% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.32 – 7.22 (m, 5H), 7.15 (app s, 3H), 6.78 (app s, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.62 – 6.57 (m, 2H), 4.41 (s, 2H), 4.04 – 3.98 (m, 1H), 3.77 (s, 3H), 3.36 – 3.28 (m, 5H), 3.03 – 2.95 (m, 2H), 2.84 (d, *J* = 13.6 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.55 – 2.44 (m, 2H), 2.33 (dd, *J* = 16.7, 4.4 Hz, 1H), 2.23 (dd, *J* = 11.8, 6.3 Hz, 1H), 2.13 (d, *J* = 13.6 Hz, 1H), 1.72 – 1.56 (m, 2H), 1.49 – 1.43 (m, 2H), 1.23 – 1.16 (m, 1H), 1.14 – 1.06 (m, 2H), 1.00 – 0.95 (m, 1H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.3, 139.1, 139.0, 138.6, 137.7, 137.6, 130.8, 130.1, 128.5, 128.4, 127.7, 127.7, 127.6, 127.6, 126.1, 112.9, 111.5, 79.9, 73.0, 70.9, 56.9, 55.2, 47.3, 43.8, 42.3, 34.8, 34.9, 31.5, 30.2, 28.4, 24.9, 24.8; **IR** (neat, cm^{-1}): 2931 (s), 2860 (m), 736 (w), 700 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{43}O_3$ 523.3212; found, 523.3210; $[\alpha]_{589}^{22.5}$**:** –121.2 (*c* 0.0004, $CHCl_3$).



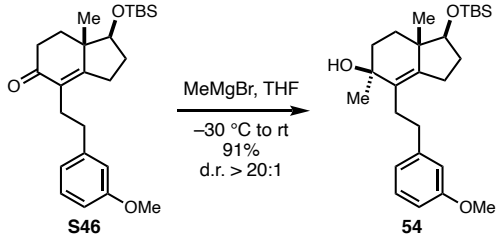
53
Key nOe Interactions

G. Synthesis of Tetracycle from Hajos–Parrish Ketone Derivative



Synthesis of Alkylated Hydrindane S46: To a stirring solution of TBS-protected Hajos–Parrish ketone **S44**[12] (508.7 mg, 1.8 mmol, 1.0 equiv) in DME (1.8 mL) was added NaH (60% dispersion in mineral oil, 108.9 mg, 2.7 mmol, 1.5 equiv) at rt. The reaction mixture was heated in an oil bath to 65 °C and let stir for 20 h. After, tosylate **S45** (611.2 mg, 2.0 mmol, 1.1 equiv) was dissolved in DME (1.8 mL) and added dropwise to the reaction mixture over 15 min at 65 °C. The reaction mixture was let stir for 1 h at 65 °C and then cooled to 0 °C and quenched by the addition of a saturated aqueous solution of NaH_2PO_4 (2 mL). The reaction mixture was warmed to rt before the two phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude concentrate was purified by flash chromatography with a Biotage® Sfär Silica HC D 50 g column and a gradient from 0–12% EtOAc in hexanes with an additive of 5% CH_2Cl_2 to afford alkylated hydrindane **S46** (388.7 mg, 0.9 mmol, 52%) as a yellow oil.

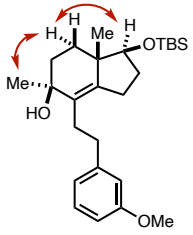
Data for Compound S46: For NMR Spectra of **S46** see page S122. **TLC**: R_f = 0.32 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.16 (app. t, *J* = 7.8 Hz, 1H), 6.73 – 6.71 (m, 2H), 6.66 (s, 1H), 3.78 (s, 3H), 3.59 (dd, *J* = 7.6, 7.9 Hz, 1H), 2.62 (app. t, *J* = 7.4 Hz, 2H), 2.60 – 2.51 (m, 1H), 2.46 – 2.36 (m, 3H), 2.20 – 2.10 (m, 1H), 2.06 – 1.95 (m, 2H), 1.82 – 1.74 (m, 1H), 1.71 – 1.60 (m, 2H), 1.01 (s, 3H), 0.89 (s, 9H), 0.03 (d, *J* = 3.5 Hz, 6H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 198.6, 169.4, 159.6, 143.9, 132.1, 129.2, 121.5, 114.8, 111.2, 81.0, 55.3, 45.7, 34.8, 34.3, 33.8, 29.9, 27.9, 25.9, 25.2, 18.2, 15.5, –4.3, –4.8; **IR** (neat, cm^{-1}): 2957 (s), 2925 (s), 2860 (m), 1658 (s), 868 (w), 837 (m), 781 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{39}O_3Si$ 415.2668; found, 415.2661; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.1}}$: +18.4 (*c* = 0.85, $CHCl_3$).



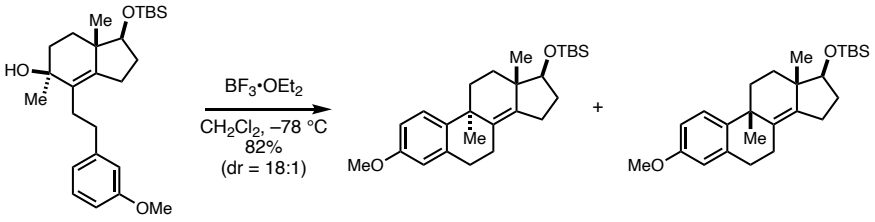
Synthesis of alcohol 54: To a stirring solution of alkylated hydrindane **S46** (132.8 mg, 0.3 mmol, 1.0 equiv) in THF (2.9 mL) was added MeMgBr (0.2 mL, 0.6 mmol, 2.0 equiv, 3.1 M in diethyl ether) dropwise at –30 °C. The reaction mixture was stirred at –30 °C for 2 h and then warmed to rt. After stirring at rt for 23 h, the reaction mixture was quenched by the slow addition of a saturated aqueous solution of NH_4Cl (0.5 mL). H_2O (1 mL) was added, the two phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude concentrate was purified by

flash chromatography with a Biotage® Sfär Silica HC D 25 g column. The column was deactivated with a 5% triethylamine in hexanes (by volume) solution before use and then purification was done with a gradient from 5–20% EtOAc in hexanes to afford alcohol **54** (125.5 mg, 0.3 mmol, 91%) as a colorless oil. There was no detectable presence of the other diastereomer in the ^{1}H NMR of the crude material.

Data for Compound 54: For NMR Spectra of **54** see page S123. **TLC**: R_f = 0.28 (15% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.20 (app. t, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 6.4 Hz, 2H), 3.80 (s, 3H), 3.52 (dd, *J* = 9.8, 7.8 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.41 – 2.34 (m, 1H), 2.34 – 2.25 (m, 2H), 2.18 – 2.13 (m, 1H), 1.88 (ddd, *J* = 17.2, 12.9, 7.8 Hz, 1H), 1.81 (dd, *J* = 14.5, 2.6 Hz, 1H), 1.77 – 1.65 (m, 3H), 1.32 (app. t, *J* = 13.0 Hz, 1H), 1.22 (s, 3H), 0.99 (s, 3H), 0.89 (s, 9H), 0.03 (s, 6H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 159.8, 144.5, 142.2, 134.4, 129.4, 121.2, 114.6, 111.3, 81.6, 73.8, 55.3, 45.0, 37.6, 36.3, 34.2, 30.5, 29.8, 27.7, 26.0, 24.1, 18.2, 17.4, –4.2, –4.6; **IR** (neat, cm^{-1}): 3451 (br), 2957 (s), 2933 (s), 2846 (m), 838 (s), 786 (m); **HRMS** (ESI-TOF) (*m/z*): $[M\text{-}OH]^+$ calcd for $C_{26}H_{41}O_2Si$ 413.2876; found, 413.2867; $[\alpha]_{589}^{22.2}$: +14.0 (c = 0.23, $CHCl_3$).



54
Key nOe Interactions

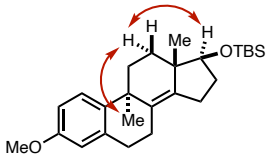


54 **55** **S47**

Synthesis of Tetracycles 55 and S47: To a stirring solution of alcohol **54** (72.6 mg, 0.2 mmol, 1.0 equiv) in CH_2Cl_2 (1.7 mL) was added BF_3•OEt_2 (62.3 µL, 0.5 mmol, 3.0 equiv) dropwise at –78 °C. The reaction mixture was stirred at –78 °C for 15 min and then warmed to –30 °C and quenched by the addition of saturated aqueous $NaHCO_3$ (2 mL). The reaction mixture was let warm to rt before the two phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with water and brine then dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude concentrate was purified by flash chromatography with a Biotage® Sfär Silica HC Duo 10 g column and a gradient from 0-10% EtOAc in hexanes to afford tetracycles **55** and **S47** (57.0 mg, 0.1 mmol, 82%, d.r. 18:1 **54**:**S47**) as an inseparable mixture of yellow oils.

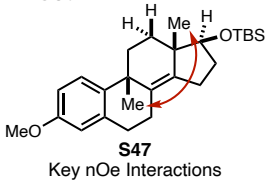
Data for Compound 55: For NMR Spectra of **55** see page S124. **TLC**: R_f = 0.62 (10% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.8 Hz, 1H),

6.57 (s, 1H), 3.77 (s, 3H), 3.62 (dd, *J* = 9.7, 7.8 Hz, 1H), 2.85 (ddd, *J* = 16.1 Hz, 5.9, 2.6 Hz, 1H), 2.71 (ddd, *J* = 16.4, 12.3, 5.7 Hz, 1H), 2.46 (ddd, *J* = 13.1, 5.8, 2.6 Hz, 1H), 2.36 – 2.21 (m, 3H), 2.10 – 2.07 (m, 1H), 1.94 – 1.88 (m, 1H), 1.88 – 1.80 (m, 1H), 1.74 – 1.65 (m, 2H), 1.52 – 1.44 (m, 1H), 1.29 (s, 3H), 0.91 (s, 9H), 0.84 (s, 3H), 0.06 (d, *J* = 7.9 Hz, 6H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 140.3, 137.4, 136.0, 132.9, 127.4, 113.1, 112.5, 82.1, 55.3, 44.2, 38.4, 34.7, 32.3, 32.1, 31.4, 30.6, 26.0, 24.1, 23.8, 18.2, 17.7, –4.2, –4.6; **IR** (neat, cm^{-1}): 2964 (s), 2925 (s), 2857 (s), 840 (s), 809 (w), 774 (s); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{41}O_2Si$ 413.2876; found, 413.2861; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{21.9}}$: +98.5 (c = 0.295, $CHCl_3$).



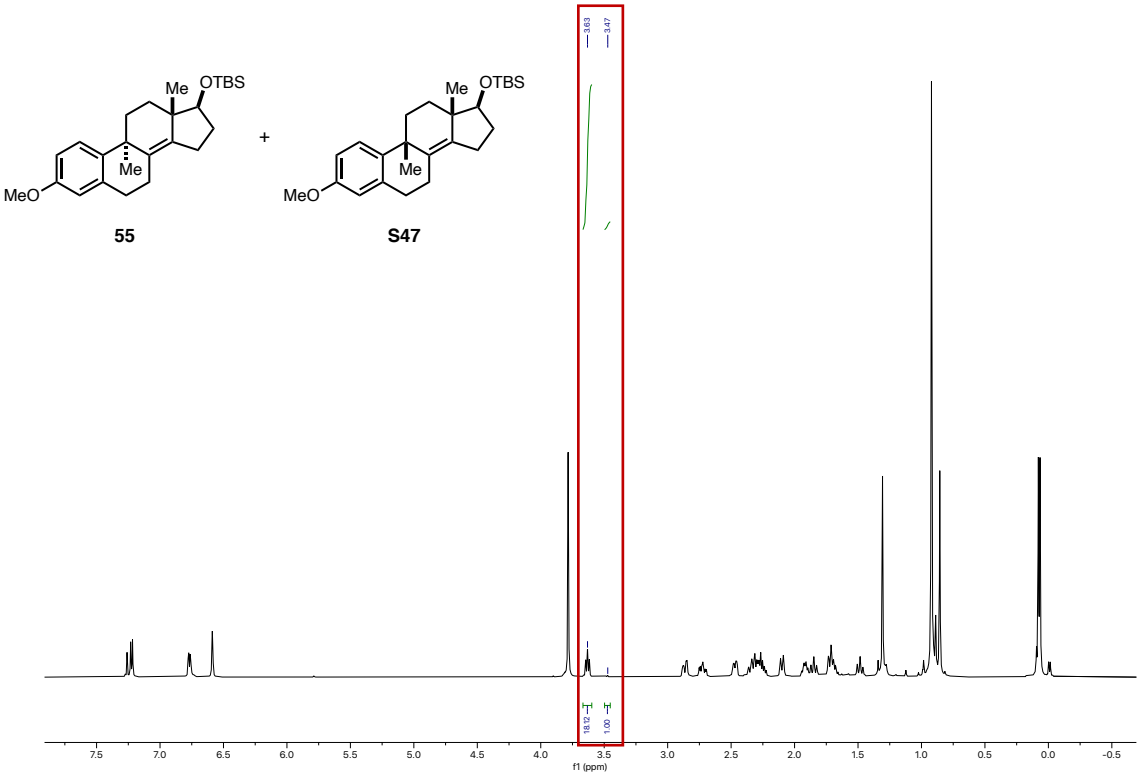
55
Key nOe Interactions

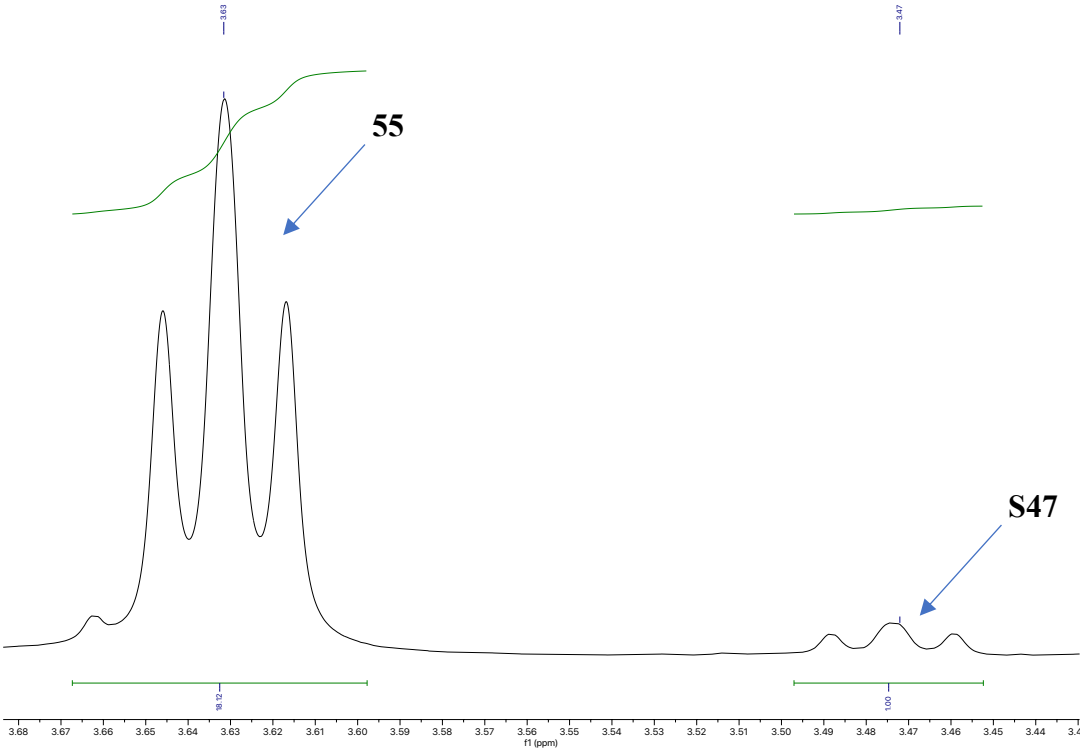
Data for Compound S47: For NMR Spectra of **S47** see page S125. **TLC**: R_f = 0.62 (10% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25 (s, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 3.77 (s, 3H), 3.46 (dd, *J* = 9.9, 7.6 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.48 (ddd, *J* = 13.3, 6.0, 3.0 Hz, 1H), 2.38 – 2.30 (m, 2H), 2.26 – 2.20 (m, 1H), 2.12 – 2.03 (m, 1H), 1.88 (ddd, *J* = 14.2, 11.0, 3.7 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.72 – 1.64 (m, 1H), 1.61 – 1.55 (m, 1H), 1.33 (s, 3H), 1.22 – 1.13 (m, 1H), 0.97 (s, 3H), 0.87 (s, 9H), -0.03 (d, *J* = 6.6 Hz, 6H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.2, 139.1, 138.6, 136.6, 134.3, 126.5, 113.6, 112.0, 80.4, 55.2, 43.8, 39.2, 34.4, 32.3, 32.0, 31.7, 30.2, 26.0, 24.1, 23.8, 18.4, 18.2, –4.3, –4.7; **IR** (neat, cm^{-1}): 3410 (br), 2961 (s), 2926 (s), 2853 (s), 834 (s), 768 (m); **HRMS** (ESI-TOF) (*m/z*): $[M-C_6H_{15}OSi]^+$ calcd for $C_{20}H_{25}O$ 281.1905; found, 281.1895; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –94.9 (c = 0.49, $CHCl_3$).



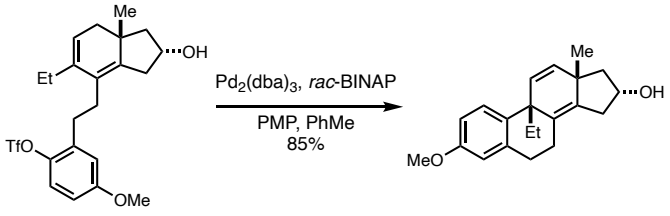
S47
Key nOe Interactions

^{1}H NMR (600 MHz, $CDCl_3$) of crude material containing **55** and **S47**





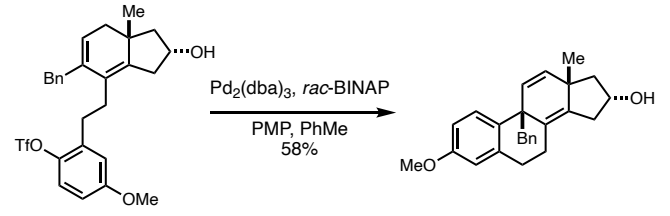
H. Synthesis of C9,C13-*Syn*-Substituted Tetracycles and Oxidative Shift



56 **57**

Synthesis of Tetracycle 57: A flask containing $Pd_2(dba)_3$ (79 mg, 0.087 mmol, 0.20 equiv) and *rac*-BINAP (215 mg, 0.346 mmol, 0.80 equiv) was sparged with N_2 for 5 min before the addition of **56**[6] (199 mg, 0.432 mmol, 1.0 equiv) in PhMe (17 mL). 1,2,2,6,6-pentamethylpiperidine (PMP) (0.310 mL, 1.73 mmol, 4.0 equiv) was added, the N_2 inlet was removed from the septum, and vinyl tape was used to further seal the flask prior to partial immersion in a pre-heated oil bath at 110 °C until the reaction was deemed complete by TLC analysis. Upon completion, the flask was cooled to rt and concentrated *in vacuo*. The crude residue was then purified by flash chromatography using a gradient of 0-30% EtOAc in hexanes to afford **57** (23 mg, 0.074 mmol, 85%) as a clear oil.

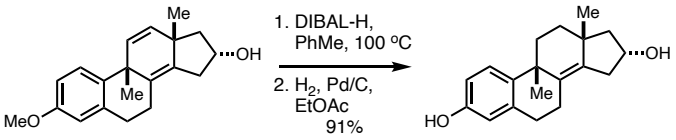
Data for Compound 57: For NMR Spectra of **57** see page S126. **TLC:** Rf = 0.30 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.7 Hz, 1H), 6.76 (app. dd, *J* = 8.7, 2.9 Hz, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 5.88 (d, *J* = 9.8 Hz, 1H), 5.80 (d, *J* = 9.8 Hz, 1H), 4.58 – 4.52 (m, 1H), 3.77 (s, 3H), 2.93 (ddd, *J* = 16.4, 8.4, 2.0 Hz, 1H), 2.81 (dd, *J* = 8.4, 3.7 Hz, 2H), 2.54 (dt, *J* = 13.5, 4.2 Hz, 1H), 2.40 (dd, *J* = 16.4, 3.8 Hz, 1H), 2.32 – 2.24 (m, 1H), 2.08 (dd, *J* = 12.3, 6.8 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.67 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.43 (s, 1H), 1.38 (dd, *J* = 12.3, 7.1 Hz, 1H), 1.11 (s, 3H), 0.80 (t, *J* = 7.5 Hz, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.1, 137.9, 137.0, 136.6, 132.8, 131.2, 129.1, 127.6, 113.5, 112.4, 70.4, 55.2, 49.6, 45.0, 42.6, 37.3, 36.8, 31.6, 28.2, 25.2, 10.7; **IR** (neat, cm-1): 3359 (b), 2957 (m), 1708 (s), 813 (m), 750 (m); **HRMS** (ESI-TOF) (m/z): [M+H]+ calcd for $C_{21}H_{27}O_2$ 311.2011; found, 311.2003; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –95.1 (*c* 0.0013, $CHCl_3$).



58 **59**

Synthesis of Tetracycle 59: A flask containing $Pd_2(dba)_3$ (25 mg, 0.027 mmol, 0.20 equiv) and *rac*-BINAP (68 mg, 0.110 mmol, 0.80 equiv) was sparged with N_2 for 5 min before the addition of **58**[6] (72 mg, 0.137 mmol, 1.0 equiv) in PhMe (5.5 mL). 1,2,2,6,6-pentamethylpiperidine (PMP) (0.099 mL, 0.055 mmol, 4.0 equiv) was added, the N_2 inlet was removed from the septum, and vinyl tape was used to further seal the flask prior to partial immersion in a pre-heated oil bath at 110 °C until the reaction was deemed complete by TLC analysis. Upon completion, the flask was cooled to rt and concentrated *in vacuo*. The crude residue was then purified by flash chromatography using a gradient of 0-30% EtOAc in hexanes to afford **59** (6.0 mg, 0.016 mmol, 58%) as a clear oil.

Data for Compound 59: For NMR Spectra of **59** see page S127. **TLC**: Rf = 0.30 (30% EtOAc in hexanes); **^{1}H NMR** (600 MHz, CDCl3): δ 7.32 (d, *J* = 8.7 Hz, 1H), 7.19 – 7.09 (m, 3H), 6.95 – 6.92 (m, 2H), 6.78 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 5.99 (d, *J* = 9.8 Hz, 1H), 5.69 (d, *J* = 9.8 Hz, 1H), 4.47 – 4.41 (m, 1H), 3.78 (s, 3H), 3.15 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 2.86 – 2.77 (m, 3H), 2.55 (dt, *J* = 13.4, 4.1 Hz, 1H), 2.35 (dd, *J* = 16.5, 3.9 Hz, 1H), 2.27 – 2.19 (m, 1H), 1.95 (dd, *J* = 12.3, 6.7 Hz, 1H), 1.30 (dd, *J* = 12.3, 7.2 Hz, 1H), 1.26 – 1.24 (m, 1H), 0.28 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 157.5, 138.7, 138.3, 137.7, 135.9, 133.3, 131.0, 131.0, 128.6, 128.3, 127.5, 126.3, 113.6, 112.6, 70.5, 55.4, 50.6, 49.6, 46.6, 42.7, 37.4, 31.8, 26.7, 25.5; **IR** (neat, cm^{-1}): 3411 (b), 3026 (s), 2923 (m), 1712 (s), 845 (m), 803 (m), 745 (m), 701 (m); **HRMS** (ESI-TOF) (m/z): [M+H]+ calcd for $C_{26}H_{29}O_2$ 373.2168; found, 373.2161; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –31.0 (*c* 0.0011, $CHCl_3$).

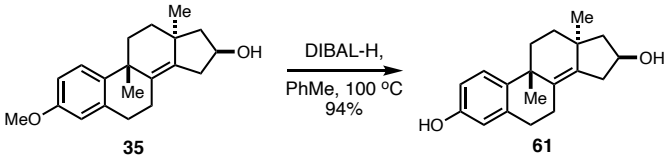


29 **60**

Synthesis of Tetracycle 60: To a stirring solution of **29** (for preparation see page S28) (100 mg, 0.338 mmol, 1.0 equiv) in toluene (4 mL) was added DIBAL-H (1.0 M in hexanes, 3.4 mL, 3.40 mmol, 10 equiv) at rt under N_2 atmosphere. The resulting mixture was heated in an oil bath to 100 °C and refluxed overnight (approx. 12 h). When the reaction was complete, as judged by TLC analysis, the reaction mixture was cooled to 0 °C where it was quenched slowly with ice then 2 M HCl (5 mL). The biphasic solution was separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the crude product as an amorphous yellow oil.

The crude residue was then diluted with 4 ml EtOAc under an atmosphere of N_2 at rt. Pd/C (10 mg, 10% by mass) was then added to the solution. The atmosphere of N_2 was exchanged for H_2 by bubbling H_2 gas into the reaction mixture. The reaction mixture was stirred under a positive pressure of H_2 overnight (approx. 12 h) before the solution was filtered and concentrated *in vacuo*. The resulting crude residue was purified by flash chromatography with a Biotage® Snap Ultra 5 g column and a gradient from 10-30% EtOAc in CH_2Cl_2 to afford **60** (0.87 g, 0.308 mmol, 91% over 2 steps) as a crystalline solid.

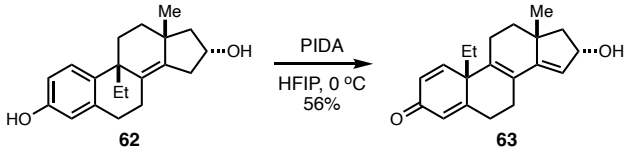
Data for Compound 60: For NMR Spectra of **60** see page S128. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.5 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.50 – 6.49 (m, 1H), 4.59 – 4.53 (m, 1H), 2.88 – 2.82 (m, 1H), 2.81 – 2.76 (m, 2H), 2.46 – 2.43 (dt, *J* = 13.4, 4.6 Hz, 1H), 2.39 – 2.33 (m, 1H), 2.29 (dd, *J* = 16.7, 5.1 Hz, 1H), 2.21 (ddd, *J* = 14.2, 5.7, 3.5 Hz, 1H), 2.02 (dd, *J* = 12.1, 6.5 Hz, 1H), 1.90 (ddd, *J* = 14.2, 12.3, 3.5 Hz, 1H), 1.59 – 1.54 (m, 1H), 1.32 (s, 3H), 1.28 – 1.21 (m, 2H), 1.04 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 153.1, 139.0, 138.9, 137.0, 133.5, 126.6, 115.2, 113.2, 71.1, 51.4, 41.3, 39.0, 38.0, 34.3, 34.1, 32.9, 31.6, 25.9, 24.7; **IR** (neat, cm^{-1}): 3597 (s), 2956 (b), 2930 (b), 2861 (m); **HRMS** (ESI-TOF) (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{25}O_2$ 285.1855; found, 285.1844. $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{22.4}}$**:** –18.2 (*c* 0.0030, $CHCl_3$).



35 **61**

Synthesis of Tetracycle 61: To a stirring solution of **35**[7] (0.17 g, 0.57 mmol, 1.0 equiv) in toluene (5 mL) at rt under N_2 atmosphere was added DIBAL-H (1.0 M in hexanes, 5.7 mL, 5.7 mmol, 10 equiv). The resulting mixture was heated in an oil bath to 100 °C and refluxed overnight (approx. 20 h). When the reaction was complete, as judged by TLC analysis, the reaction mixture was cooled to 0 °C where it was quenched slowly with ice then 2 M HCl (5 mL). The biphasic solution was separated, and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and then the filtrate was concentrated *in vacuo*. The resulting crude product was purified by flash chromatography with a Biotage® Snap Ultra 10 g column and a gradient from 10-30% EtOAc in CH_2Cl_2 to afford **61** (0.15 g, 0.54 mmol, 94% isolated yield) as an amorphous white solid.

Data for Compound 61: For NMR Spectra of **61** see page S129. **^{1}H NMR** (500 MHz, MeOD) δ 7.09 (d, *J* = 8.6 Hz, 1H), 6.60 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.44 (d, *J* = 2.6 Hz, 1H), 4.55 – 4.52 (m, 1H), 2.87 – 2.77 (m, 2H), 2.61 (ddd, *J* = 15.9, 11.8, 5.7 Hz, 1H), 2.41 (ddd, *J* = 12.8, 5.7, 2.5 Hz, 1H), 2.32 (td, *J* = 13.4, 12.8, 5.1 Hz, 1H), 2.23 (dd, *J* = 16.9, 4.5 Hz, 1H), 2.12 – 2.04 (m, 2H), 1.79 (td, *J* = 12.8, 4.0 Hz, 1H), 1.74 – 1.63 (m, 2H), 1.34 – 1.26 (m, 4H), 0.89 (s, 3H); **^{13}C{1H} NMR** (150 MHz, MeOD) δ 155.4, 140.0, 138.0, 137.5, 133.2, 128.1, 115.4, 114.6, 71.7, 52.4, 42.5, 39.0, 38.0, 35.5, 34.4, 33.0, 31.7, 26.1, 26.0; **IR** (thin film, cm^{-1}): 3314, 2932, 2857, 737; **HRMS** (ESI-TOF): calcd for $C_{19}H_{25}O_2$ $[M+H]^+$ 285.1855, found 285; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$; –229.4 (*c* 0.024, MeOH).

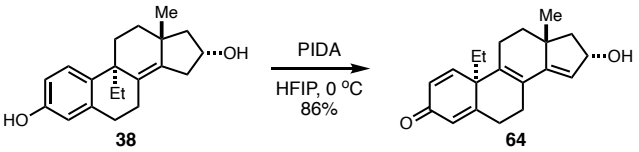


62 **63**

Synthesis of Tetracycle 63: A solution of tetracycle **62** (for preparation see page S30) (24 mg, 0.0791 mmol, 1.0 equiv) in HFIP (2 mL) at 0 °C under N_2 atmosphere was stirred for 10 min before the addition of PIDA (24 mg, 0.0751 mmol, 0.95 equiv). The solution was stirred for no more than 1 min before being quenched with saturated aqueous $NaHCO_3$ (1 mL). HFIP was subsequently removed from the reaction mixture under vacuum, and the mostly aqueous remains was diluted with EtOAc (2 mL). The organic phase was separated, the aqueous phase was extracted with 3 x 20 mL EtOAc, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography using a gradient of 20–60% EtOAc in hexanes to afford **63** (13 mg, 0.0443 mmol, 56%) as a white solid.

Data for Compound 63: For NMR Spectra of **63** see page S130. **TLC:** Rf = 0.23 (45% EtOAc in 45% hexanes with 10% CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.10 (d, *J* = 1.03 Hz, 1H), 6.38 (dd, *J* = 11.0, 1.8 Hz, 1H), 6.24 (s, 1H), 5.44 (s, 1H), 5.06 – 5.03 (m, 1H), 4.43 – 4.36 (m, 1H), 2.66 – 2.49 (m, 5H), 2.37 – 2.28 (m, 2H), 2.10 – 2.05 (m, 1H), 1.90 – 1.76 (m, 4H), 1.55 – 1.49 (m, 1H), 1.36 (dd, *J* = 12.5, 7.3 Hz, 1H), 1.00 (s, 3H), 0.60 (t, *J* = 7.5 Hz, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 186.2, 164.1, 152.1, 150.5, 138.3, 130.5, 125.8, 125.1, 124.1, 76.5, 51.6,

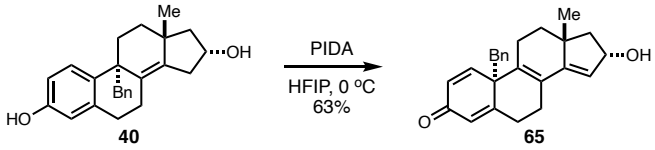
49.5, 43.4, 35.9, 33.9, 30.0, 29.5, 29.1, 24.5, 24.0, 8.1; **IR** (neat, cm^{-1}): 3383 (m), 2925 (s), 2853 (s), 1662 (s), 887 (m), 816 (w), 754 (m); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{20}H_{25}O_2$ 297.1855; found, 297.1849; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –39.6 (*c* 0.0008, $CHCl_3$).



38 64

Synthesis of Tetracycle 64: A solution of tetracycle **38** (for preparation see page S30) (21 mg, 0.0704 mmol, 1.0 equiv) in HFIP (2 mL) at 0 °C under N_2 atmosphere was stirred for 10 min before the addition of PIDA (22 mg, 0.0669 mmol, 0.95 equiv). The solution was stirred for no more than 1 min before being quenched with saturated aqueous $NaHCO_3$ (2 mL). HFIP was subsequently removed from the reaction mixture under vacuum, and the mostly aqueous remains was diluted with EtOAc (2 mL). The organic phase was separated, the aqueous phase was extracted with 3 x 20 mL EtOAc, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography using a gradient of 20–60% EtOAc in hexanes to afford **64** (18 mg, 0.061 mmol, 86%) as a white solid.

Data for Compound 64: For NMR Spectra of **64** see page S131. **TLC:** Rf = 0.09 (45% EtOAc in 45% hexanes with 10% CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.01 (d, *J* = 10.2 Hz, 1H), 6.37 (d, *J* = 9.9 Hz, 1H), 6.24 (s, 1H), 5.49 (s, 1H), 5.08 – 5.05 (m, 1H), 2.80 – 2.71 (m, 1H), 2.62 – 2.53 (m, 1H), 2.52 – 2.42 (m, 2H), 2.37 – 2.21 (m, 3H), 2.09 – 2.04 (m, 2H), 1.88 – 1.78 (m, 2H), 1.62 – 1.54 (m, 1H), 1.43 – 1.35 (m, 1H), 0.88 (s, 3H), 0.59 (t, *J* = 7.4 Hz, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 186.3, 164.4, 151.1, 149.7, 137.9, 130.6, 125.8, 124.7, 124.5, 76.4, 51.5, 49.3, 43.2, 36.2, 32.9, 29.4, 29.0, 25.0, 23.5, 8.1; **IR** (neat, cm^{-1}): 3389 (s), 2924 (s), 2853 (s), 1734 (w), 1661 (s); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ Calcd for $C_{20}H_{25}O_2$ 297.1855; found, 297.1845; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –14.8 (*c* 0.0005, $CHCl_3$).

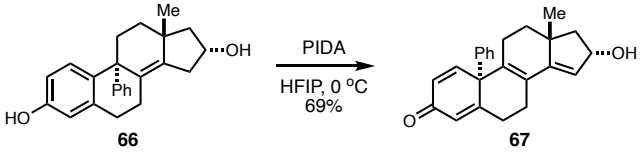


40 65

Synthesis of Tetracycle 65: A solution of tetracycle **40** (for preparation see page S33) (18 mg, 0.064 mmol, 1.0 equiv) in HFIP (2 mL) at 0 °C under N_2 atmosphere was stirred for 10 min before the addition of PIDA (20 mg, 0.061 mmol, 0.95 equiv). The solution was stirred for no more than 1 min before being quenched with saturated aqueous $NaHCO_3$ (2 mL). HFIP was subsequently removed from the reaction mixture under vacuum, and the mostly aqueous remains was diluted with EtOAc (2 mL). The organic phase was separated, the aqueous phase was extracted with 3 x 20 mL EtOAc, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography using a gradient of 20–60% EtOAc in hexanes to afford **65** (11 mg, 0.040 mmol, 63%) as a white solid.

Data for Compound 65: For NMR Spectra of **65** see page S132. **TLC**: Rf = 0.16 (45% EtOAc in 45% hexanes with 10% CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19 – 7.13 (m, 4H), 6.98 – 6.90

(m, 2H), 6.16 (dd, J = 11.1, 1.4 Hz, 1H), 6.06 (s, 1H), 5.55 (s, 1H), 5.10 – 5.08 (m, 1H), 3.26 (d, J = 13.4 Hz, 1H), 3.11 (d, J = 13.4 Hz, 1H), 2.92 – 2.80 (m, 2H), 2.59 – 2.54 (m, 1H), 2.49 (d, J = 17.5 Hz, 1H), 2.39 – 2.26 (m, 3H), 1.84 (dd, J = 12.4, 4.1 Hz, 1H), 1.68 – 1.55 (m, 2H), 1.44 (dd, J = 11.9, 7.7, 1H), 0.91 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 185.6, 163.3, 150.4, 149.6, 136.4, 135.1, 130.1, 129.9, 127.9, 127.2, 126.1, 126.0, 125.0, 76.5, 51.6, 50.3, 46.6, 43.2, 36.1, 29.8, 29.1, 25.2, 23.6; **IR** (neat, cm^{-1}): 3367 (m), 3007 (w), 2924 (m), 2852 (m), 1662 (s); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{25}H_{27}O_2$ 359.2011; found 359.2002; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –17.5 (*c* 0.0001, $CHCl_3$).

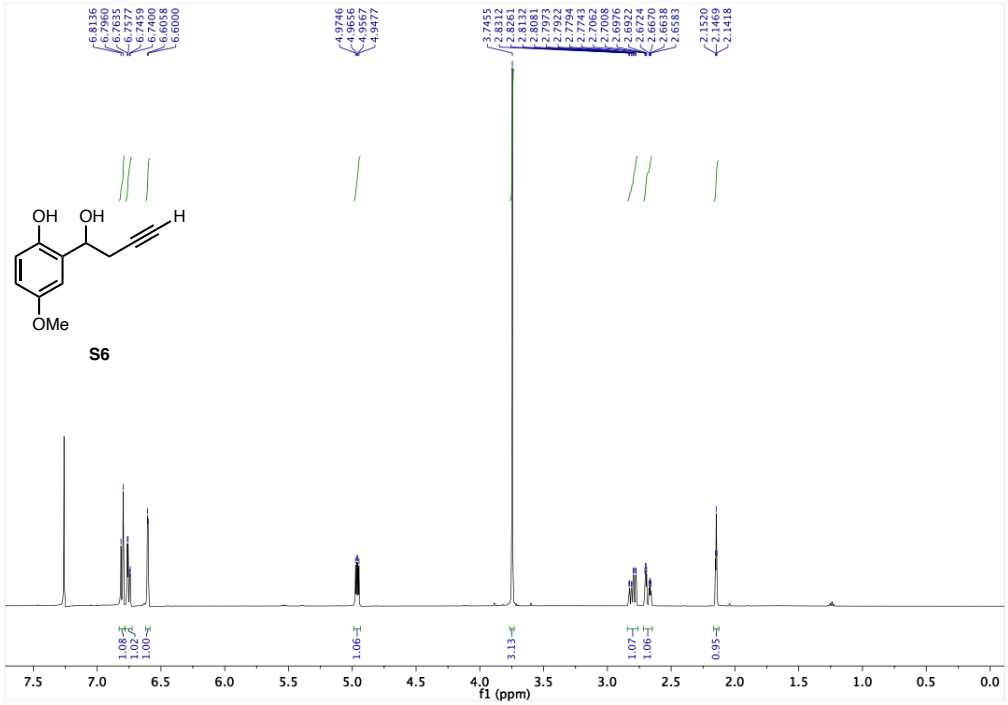


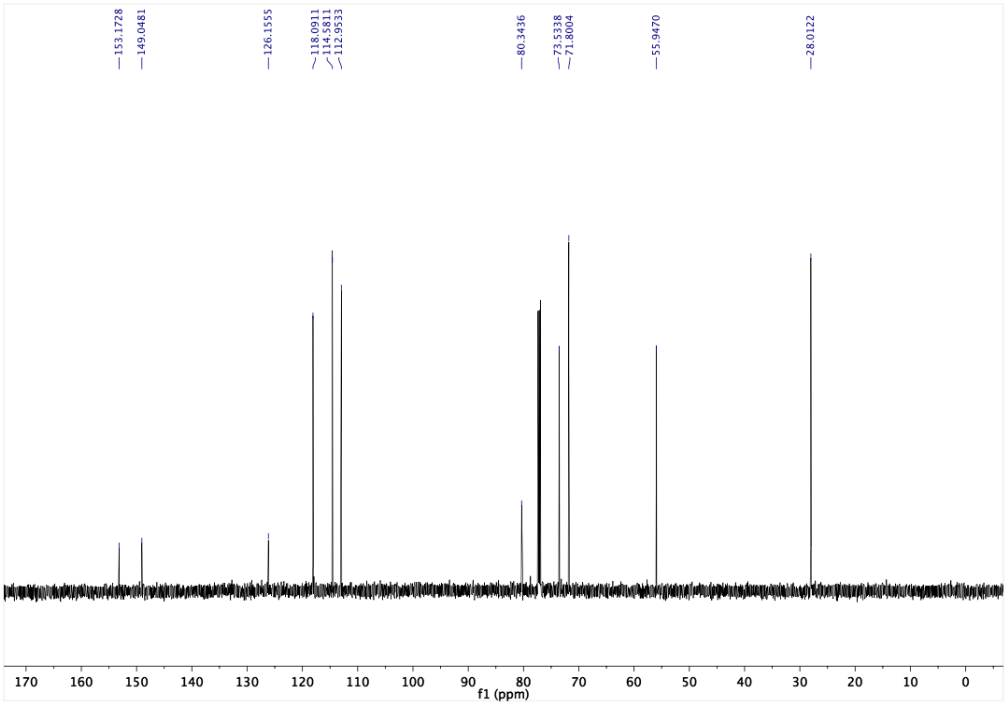
Synthesis of Tetracycle 67: A solution of tetracycle **66**[6] (16 mg, 0.0462 mmol, 1.0 equiv) in HFIP (2 mL) at 0 °C under N_2 atmosphere was stirred for 10 min before the addition of PIDA (14 mg, 0.0439 mmol, 0.95 equiv). The solution was stirred for no more than 1 min before being quenched with saturated aqueous $NaHCO_3$ (2 mL). HFIP was subsequently removed from the reaction mixture under vacuum, and the mostly aqueous remains was diluted with EtOAc (2 mL). The organic phase was separated, the aqueous phase was extracted with 3 x 20 mL EtOAc, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography using a gradient of 20–60% EtOAc in hexanes to afford **67** (11 mg, 0.032 mmol, 69%) as a white solid.

Data for Compound 67: For NMR Spectra of **67** see page S133. **TLC**: Rf = 0.29 (45% EtOAc in 45% hexanes with 10% CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.33 – 7.30 (m, 2H), 7.27 – 7.24 (m, 1H), 7.21 (d, J = 10.1 Hz, 1H), 7.15 (d, J = 7.3 Hz, 2H), 6.47 (dd, J = 10.3, 2.2 Hz, 1H), 6.12 (s, 1H), 5.61 (s, 1H), 5.15 (app. t, J = 7.0 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.46 – 2.37 (m, 2H), 2.37 – 2.27 (m, 3H), 2.24 – 2.17 (m, 1H), 1.86 – 1.81 (m, 1H), 1.73 (dt, J = 12.8, 5.2 Hz, 1H), 1.52 (dd, J = 12.1, 7.7 Hz, 1H), 0.98 (s, 3H); **^{13}C{1H} NMR** (150 MHz, $CDCl_3$): δ 186.3, 165.7, 150.8, 149.4, 139.8, 134.7, 129.1, 129.0, 128.9, 127.7, 127.7, 127.6, 125.3, 122.9, 76.5, 53.8, 51.5, 43.5, 36.0, 29.4, 29.3, 26.7, 23.7; **IR** (neat, cm^{-1}): 3392 (m), 3011 (m), 2924 (s), 2852 (m), 1732 (w), 1666 (s); **HRMS** (ESI-TOF) (m/z): $[M+H]^+$ calcd for $C_{24}H_{25}O_2$ 345.1855; found, 345.1847; $[\boldsymbol{\alpha}]_{\mathbf{589}}^{\mathbf{20.9}}$: –60.8 (*c* 0.0004, $CHCl_3$).

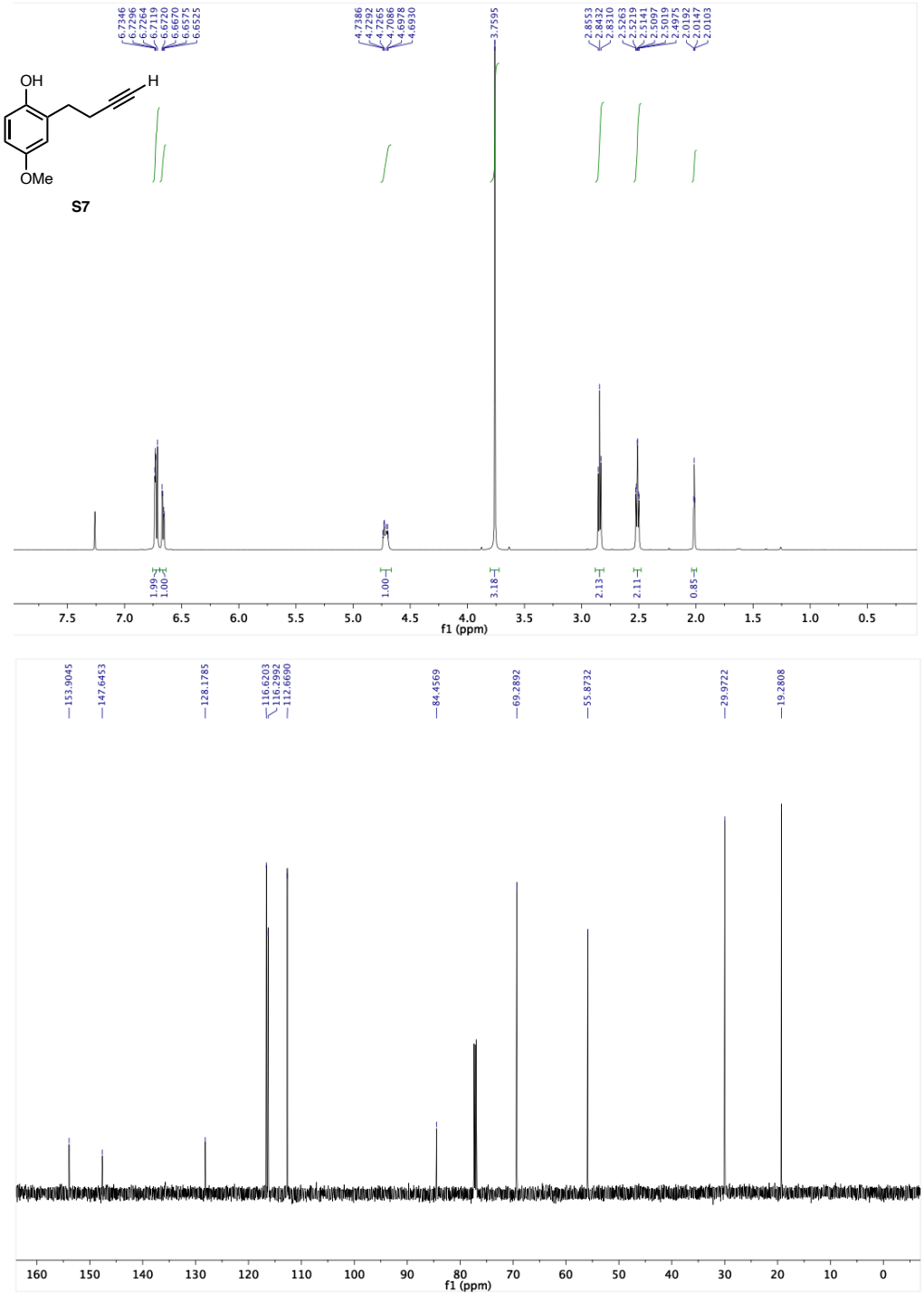
3. NMR Spectra

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of diol **S6**

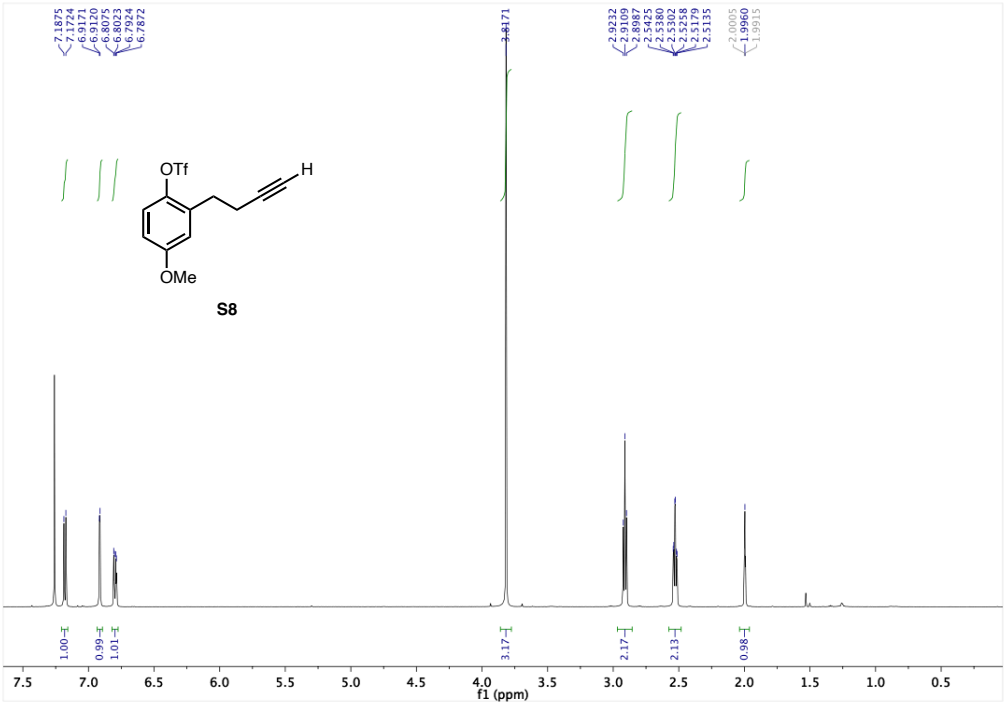


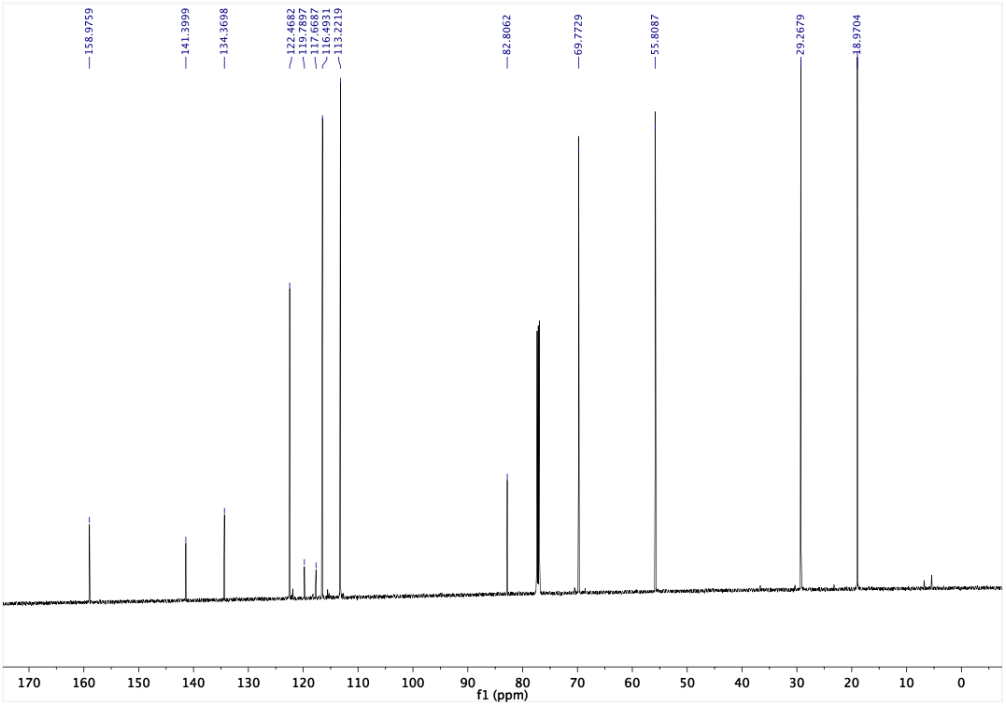


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of phenol **S7**

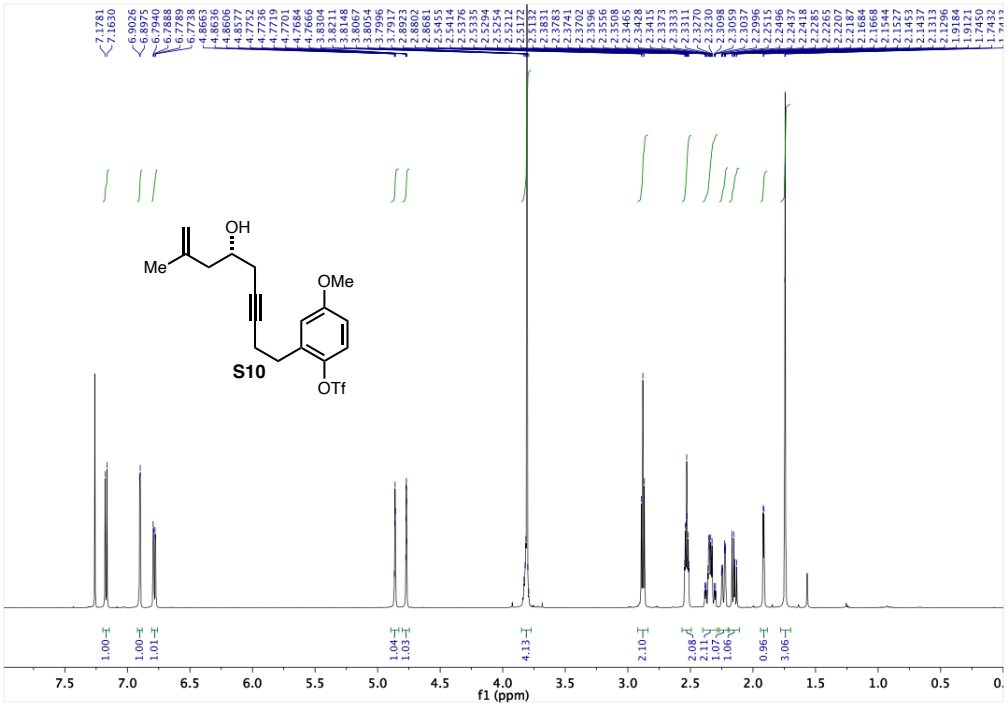


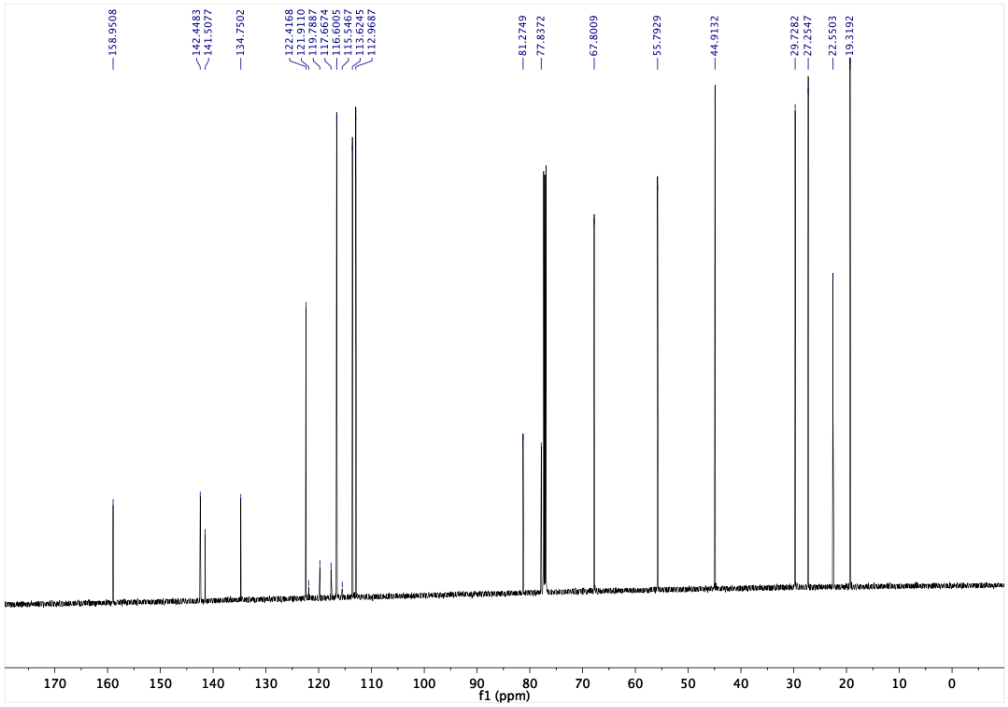
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of aryl triflate **S8**



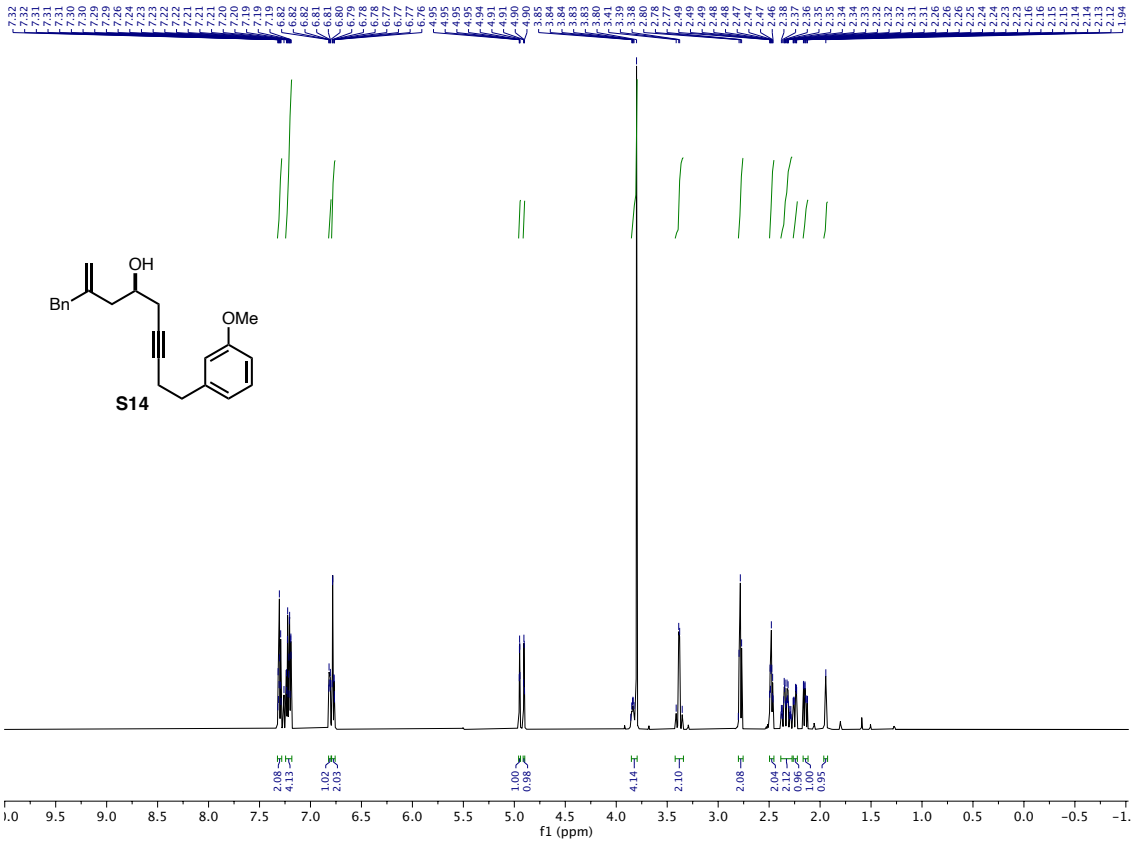


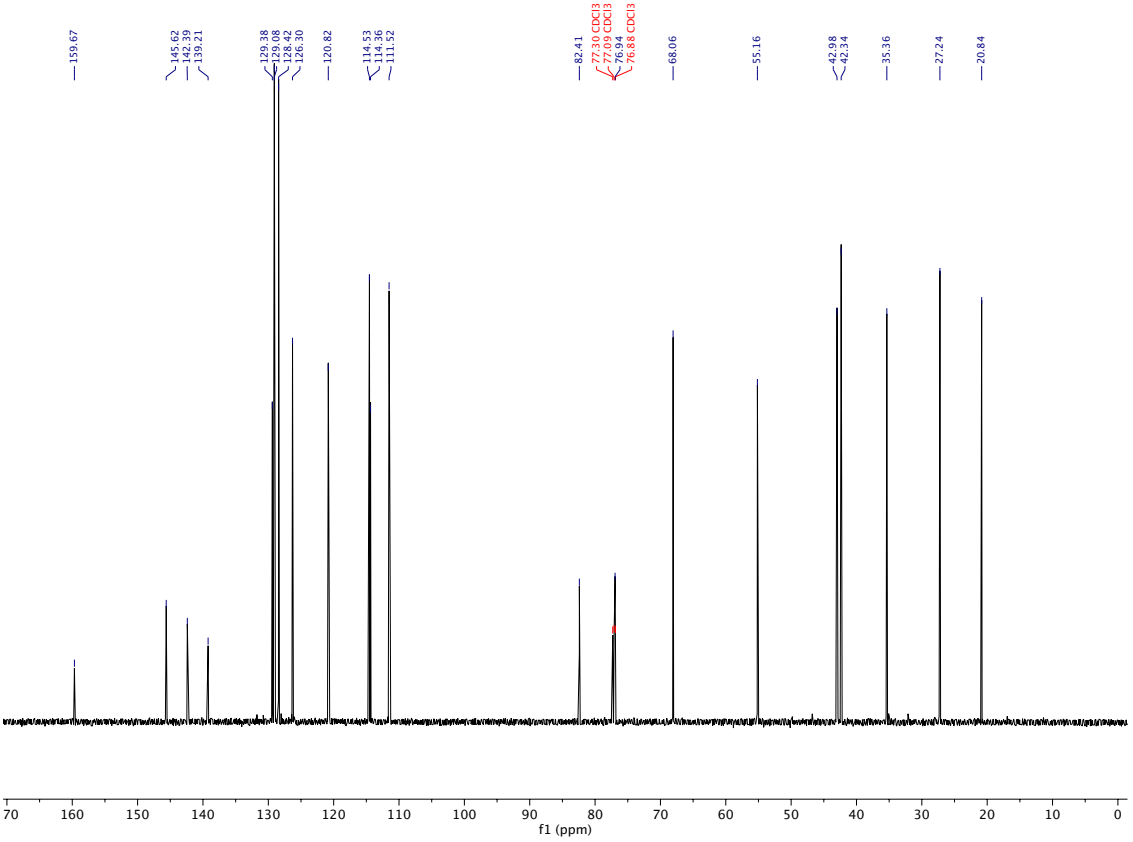
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of enyne **S10**



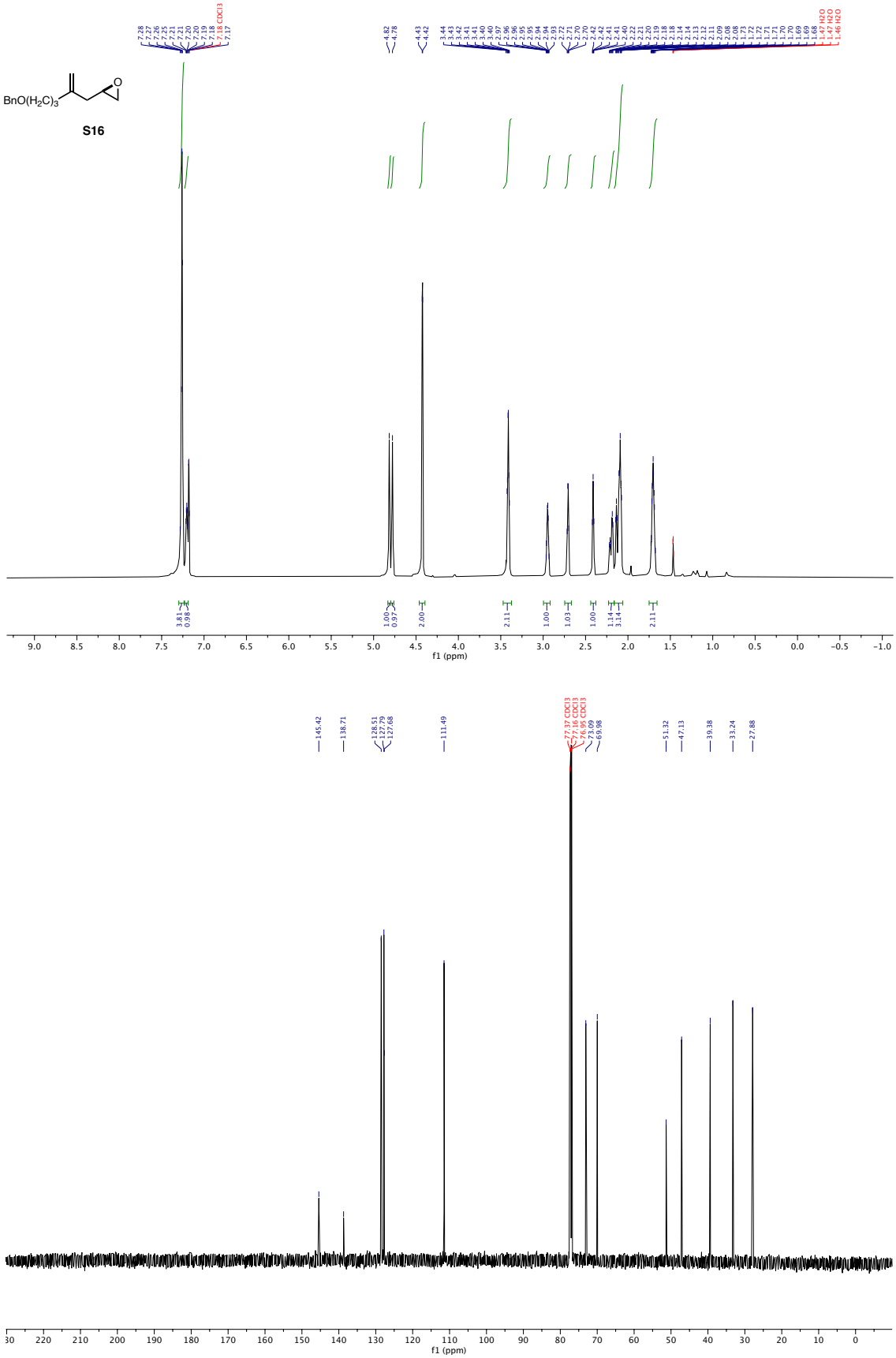


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S14**

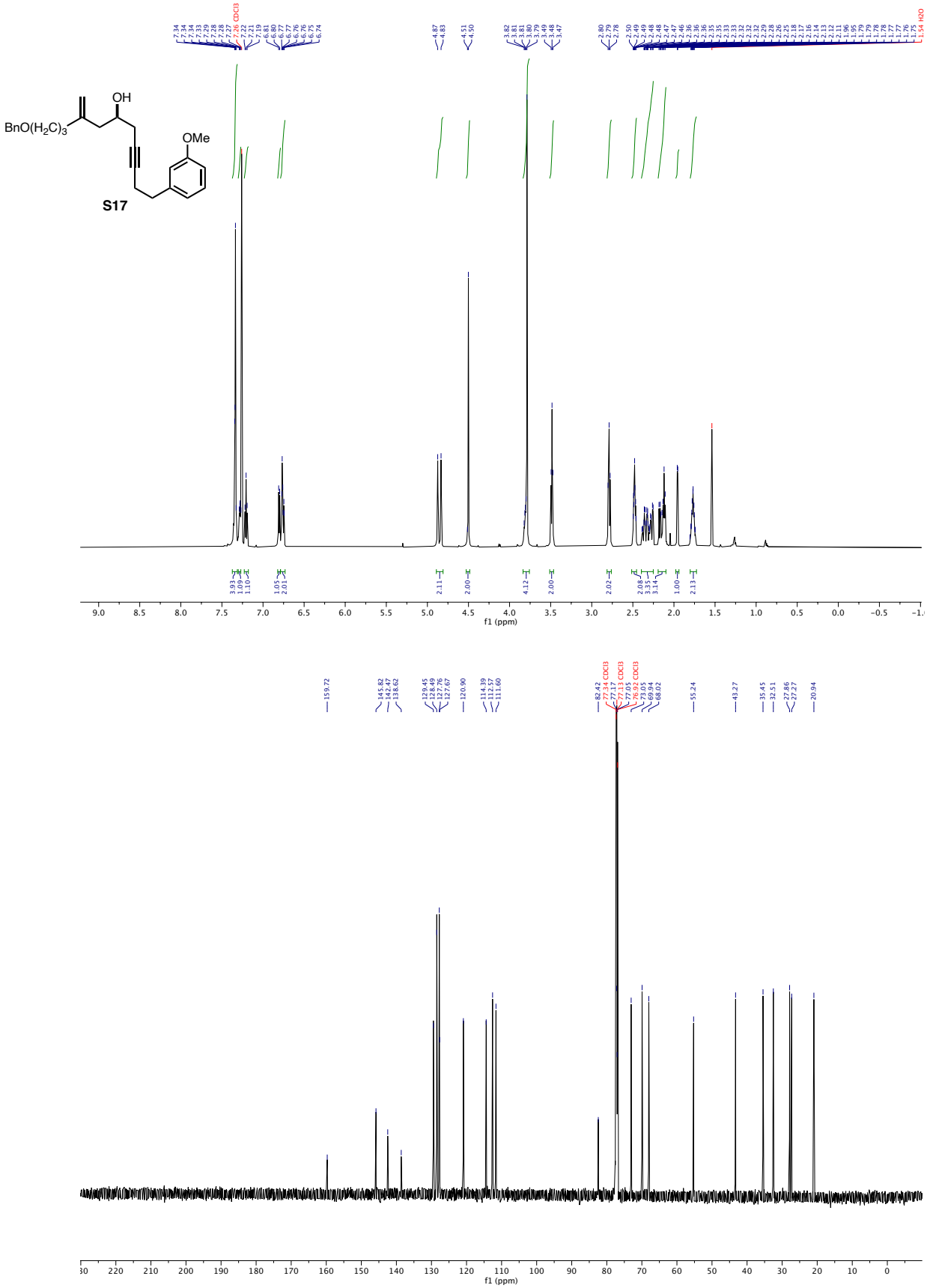




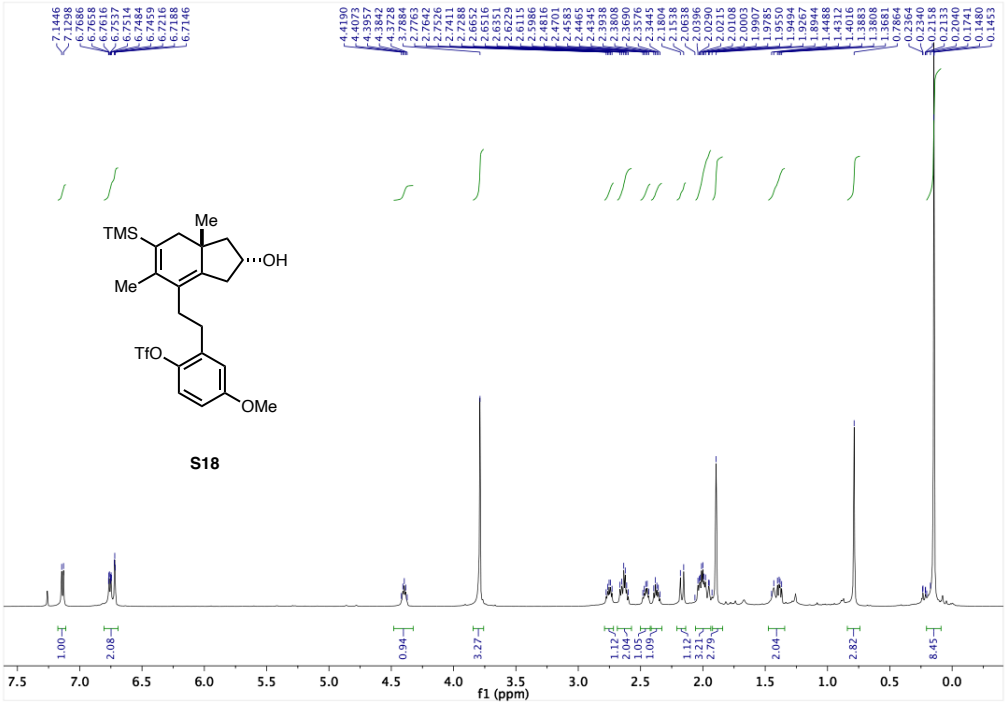
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S16**

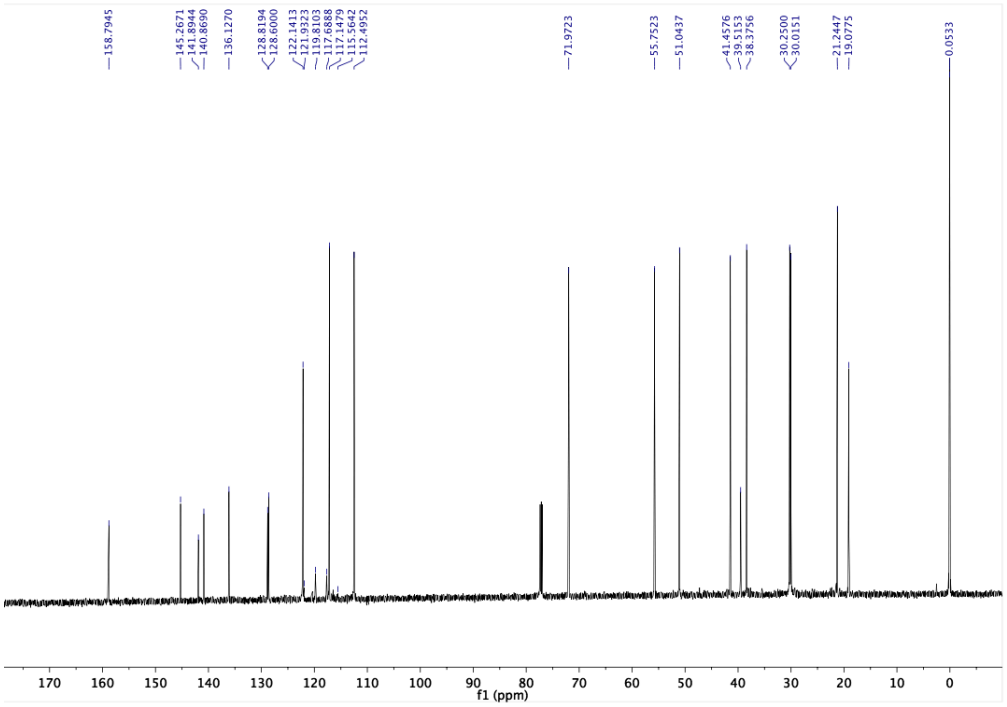


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S17**

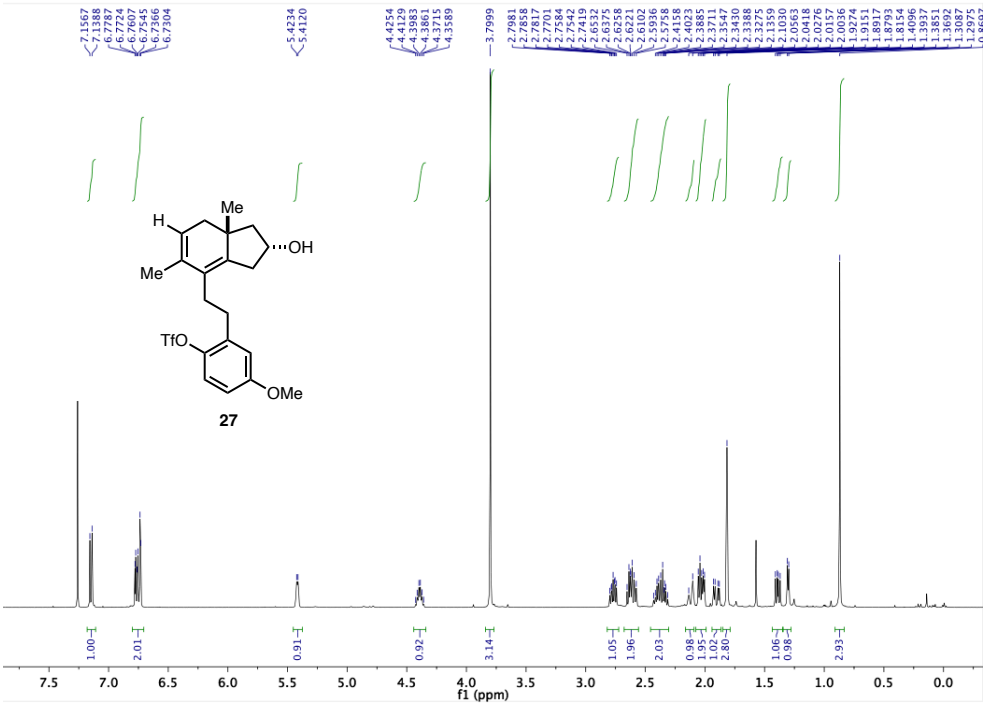


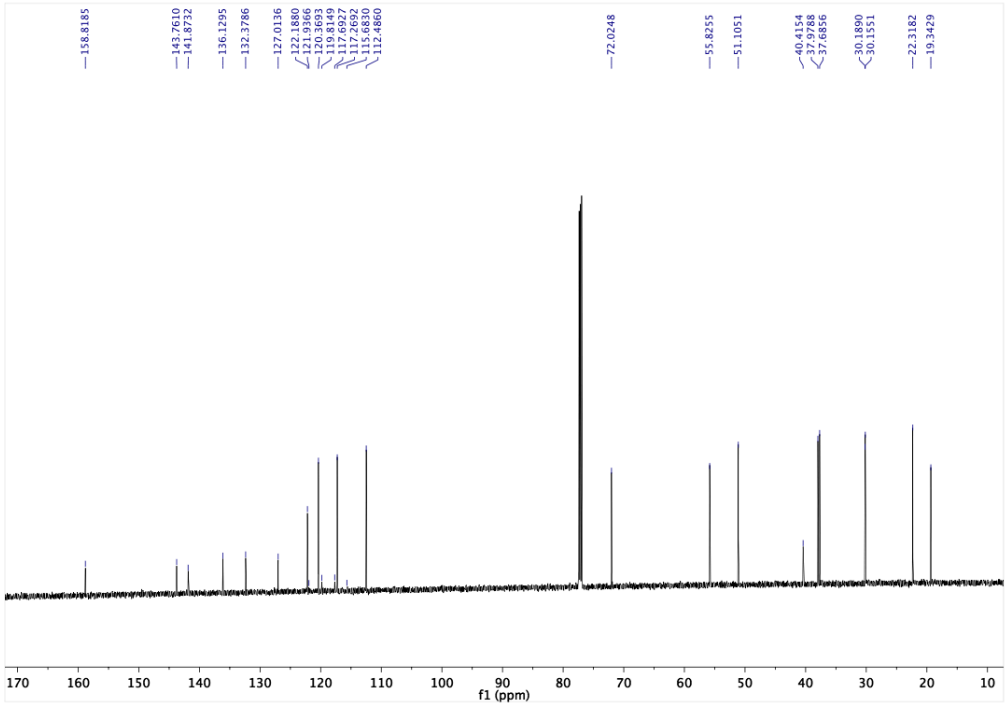
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of hydrindane **S18**



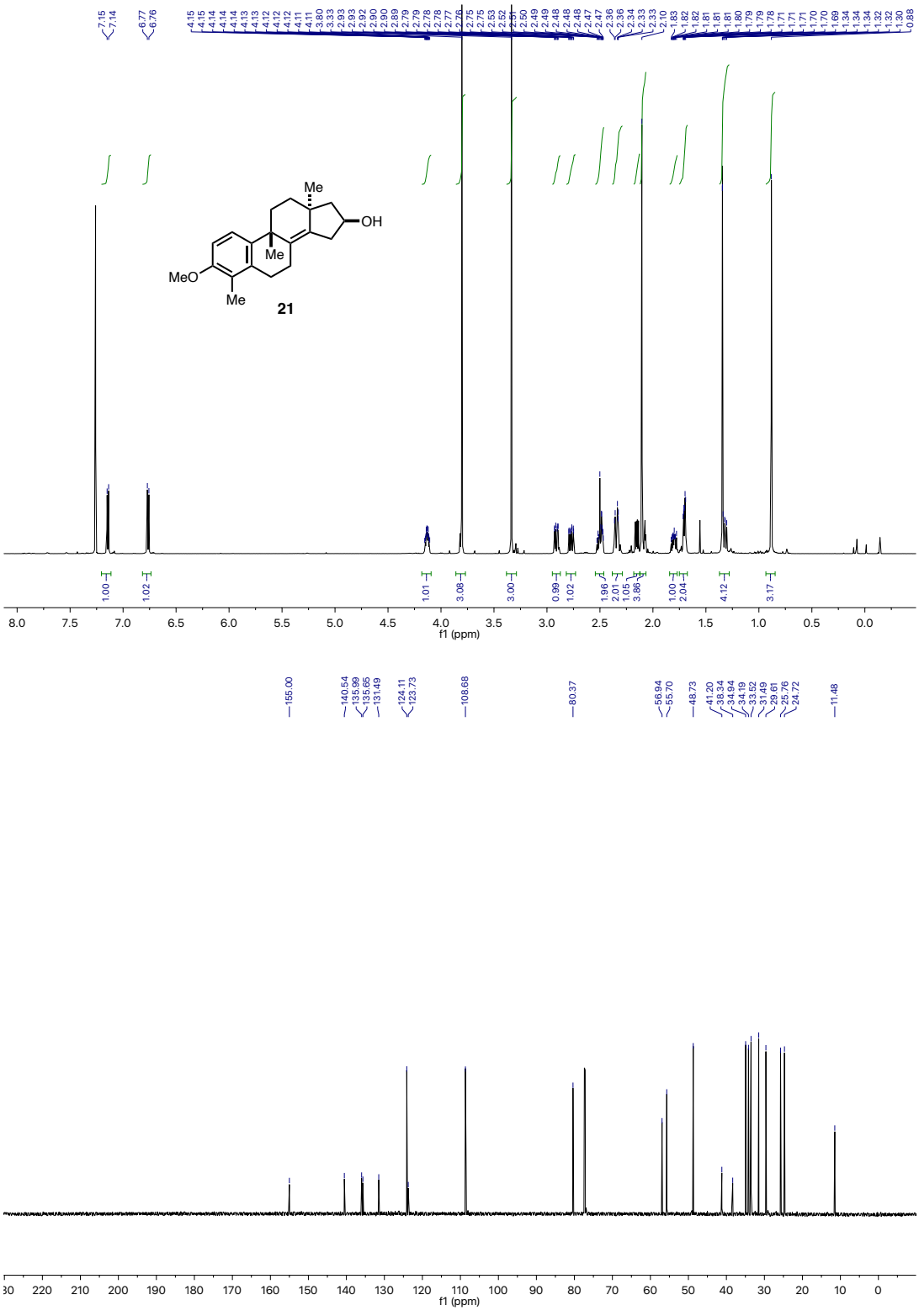


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of hydrindane **27**

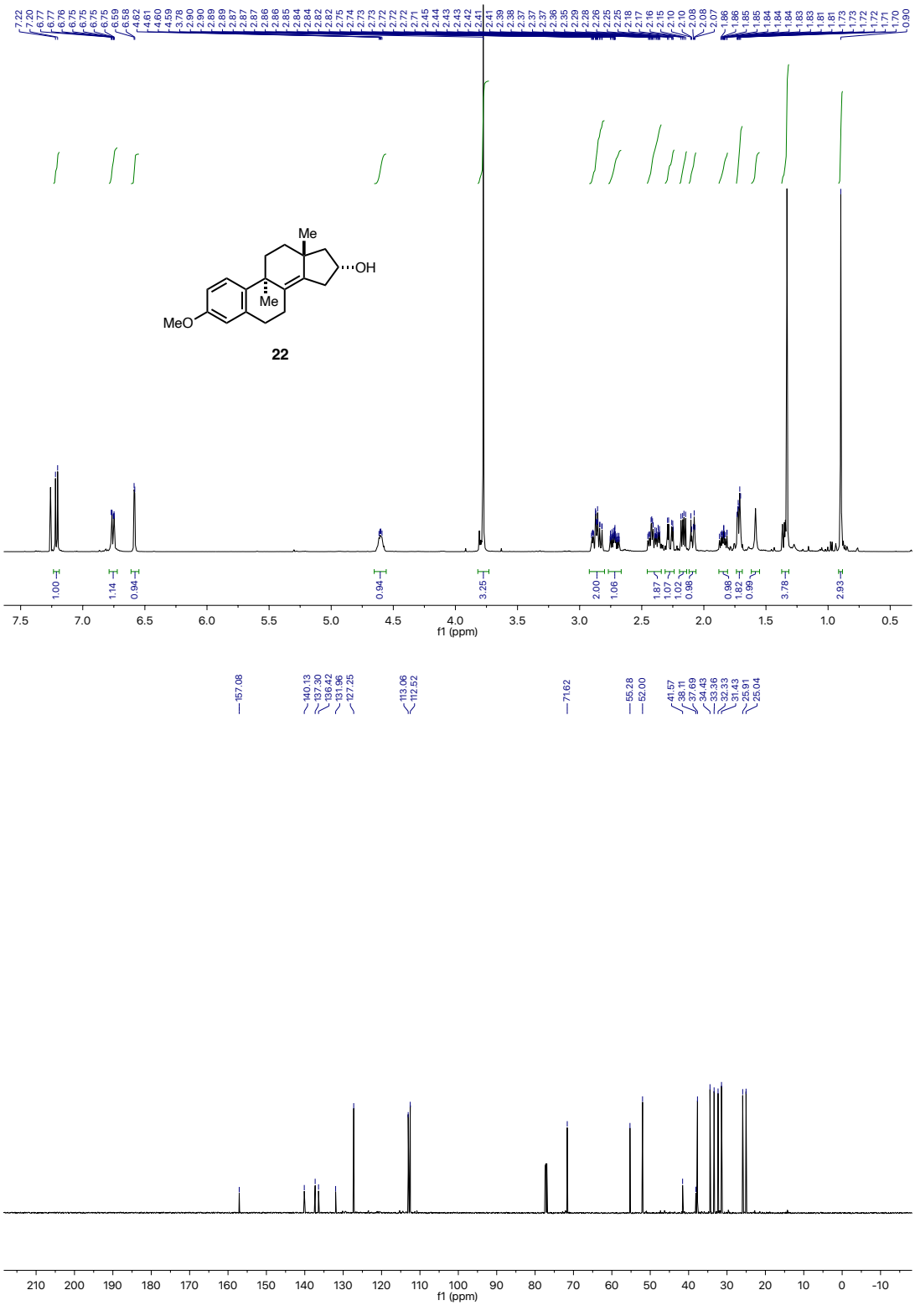




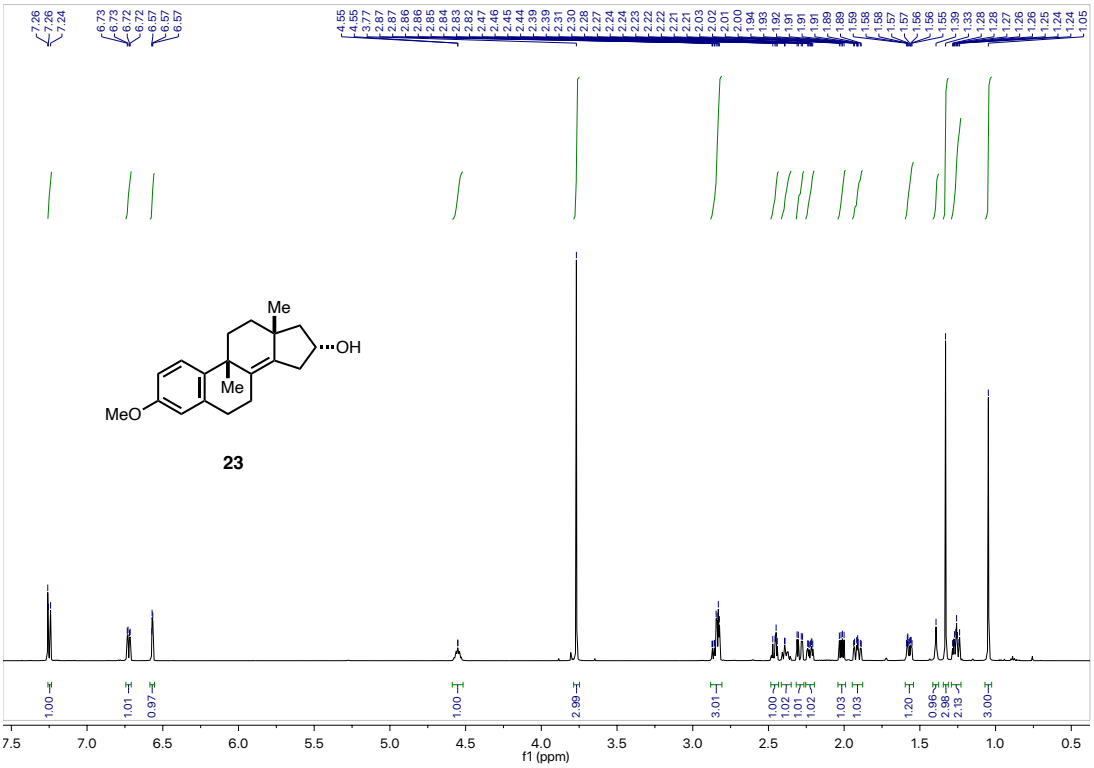
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **21**

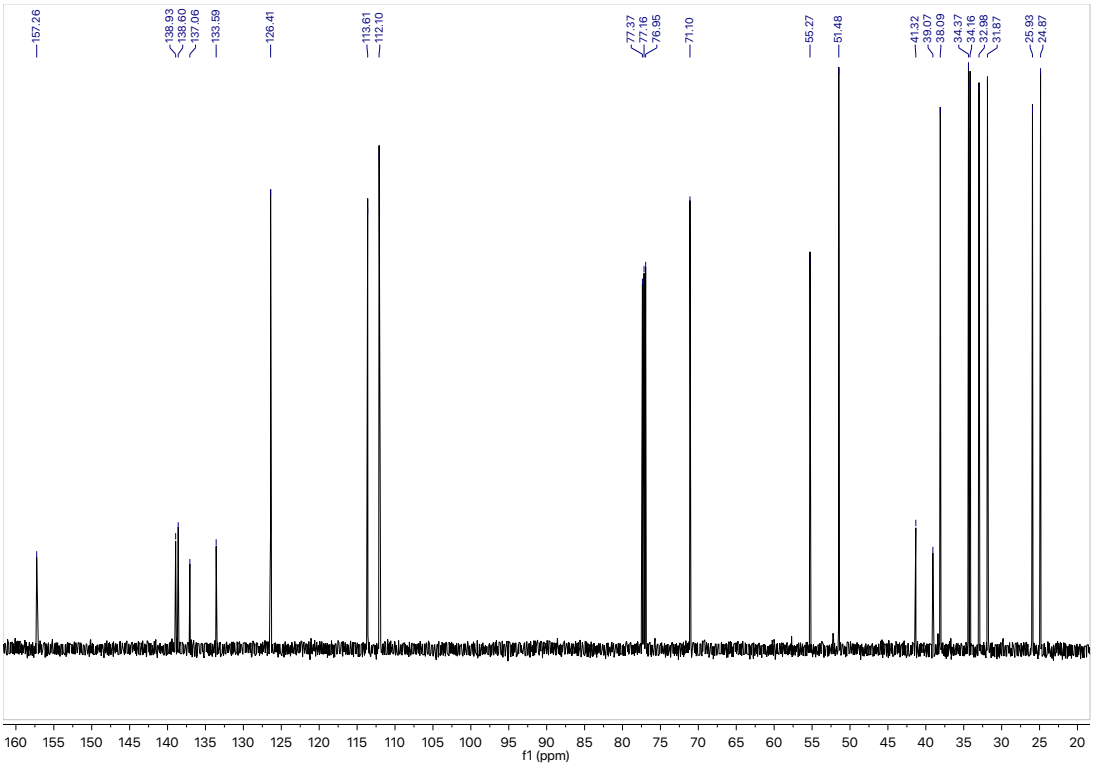


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **22**

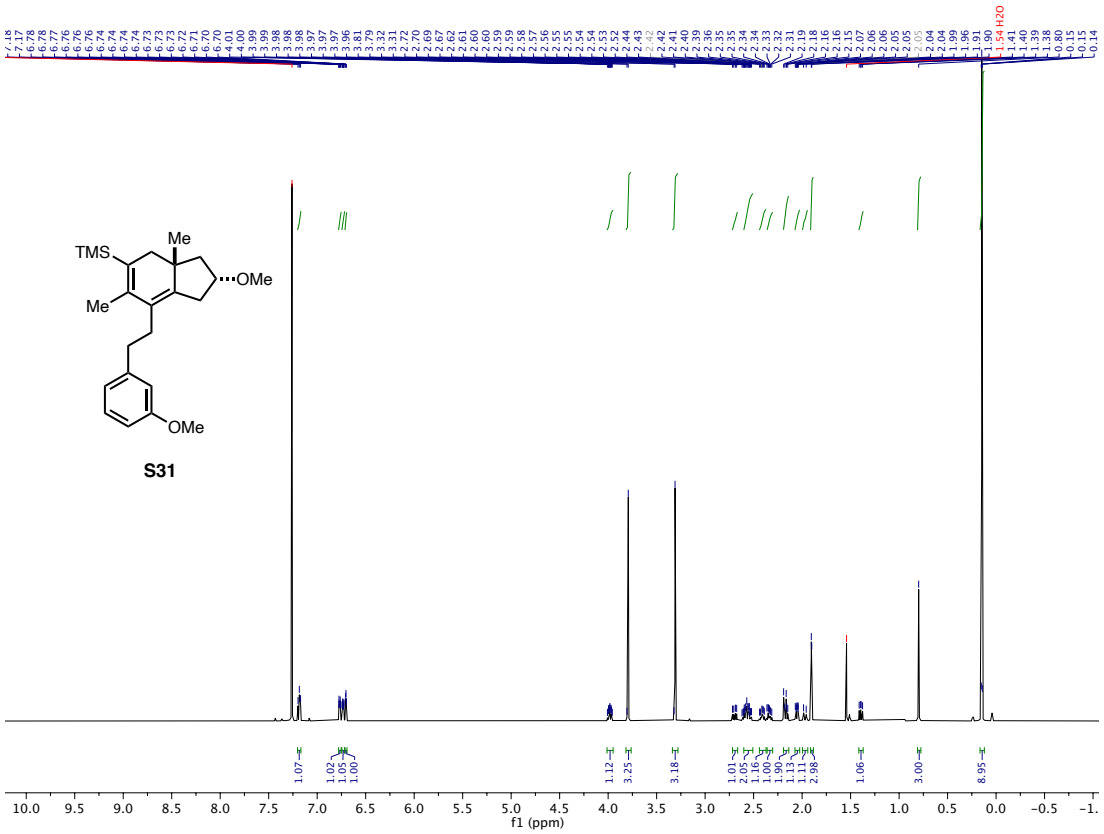


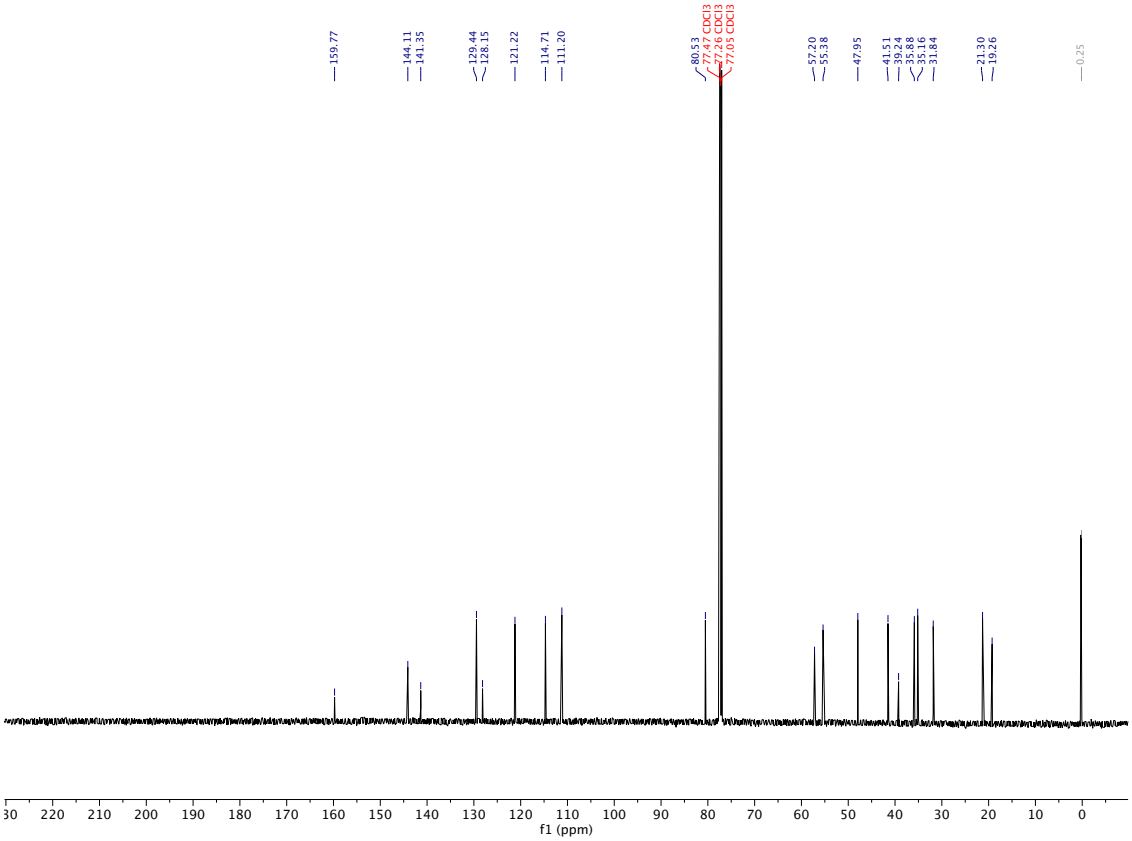
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **23**



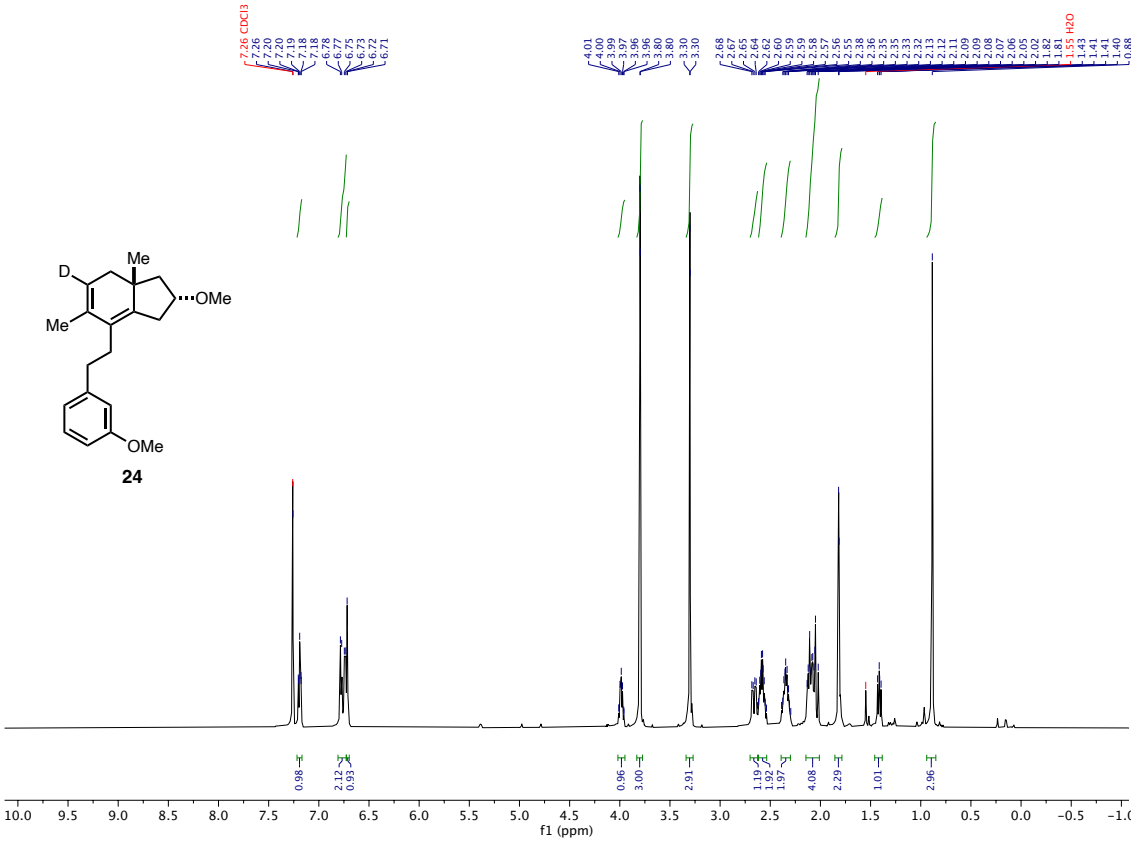


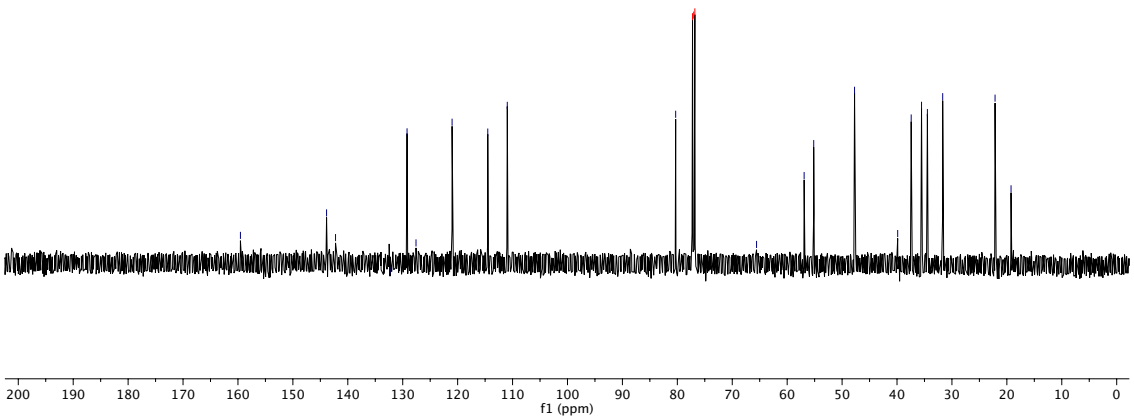
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S31**



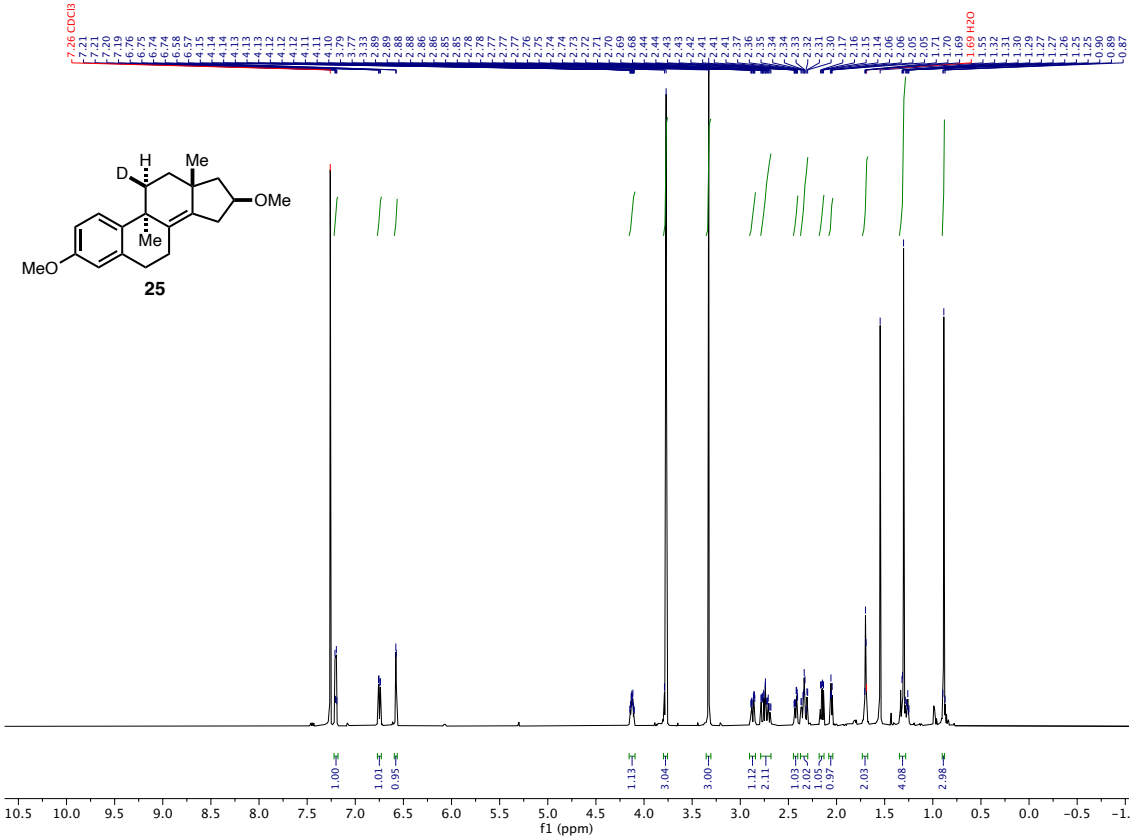


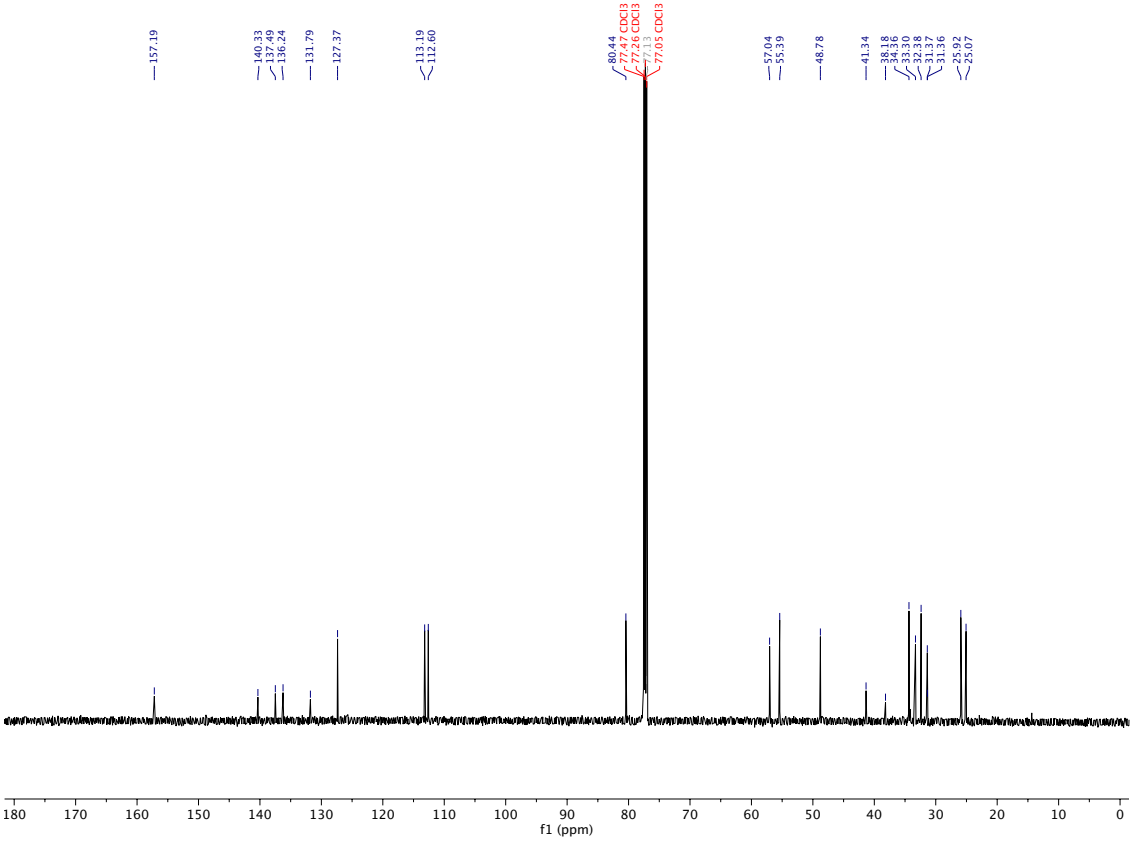
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **24**



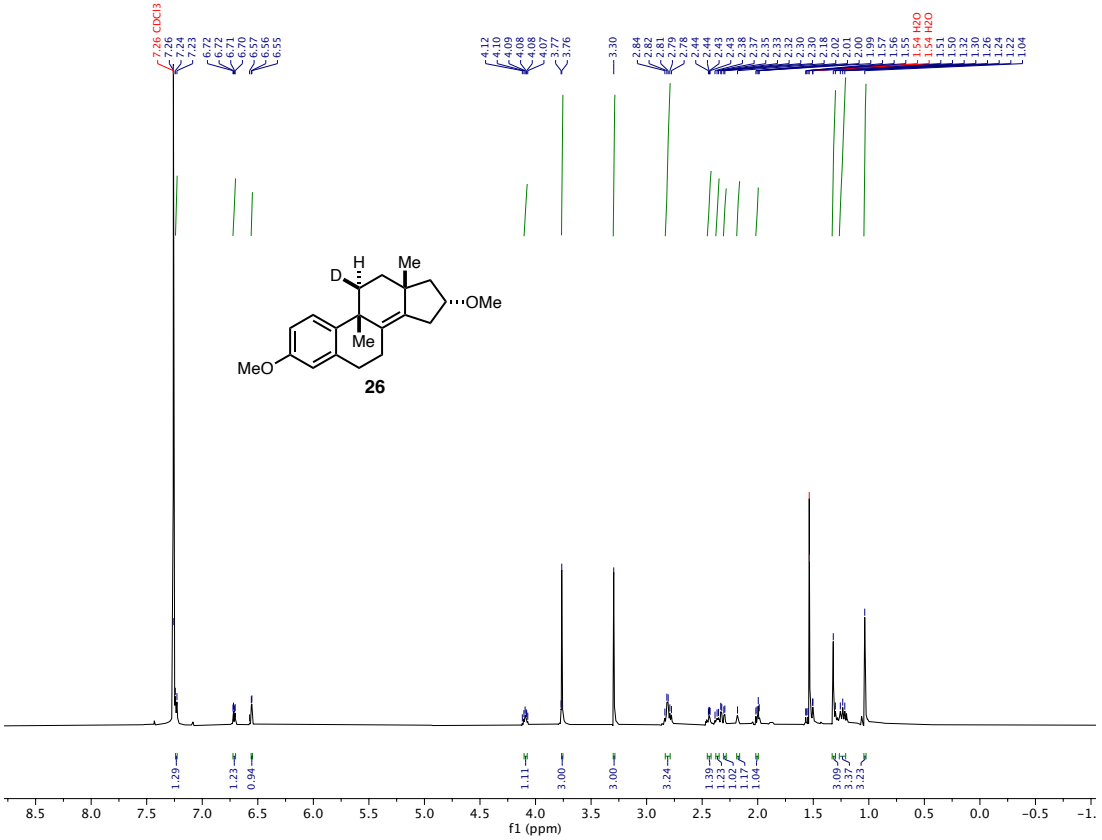


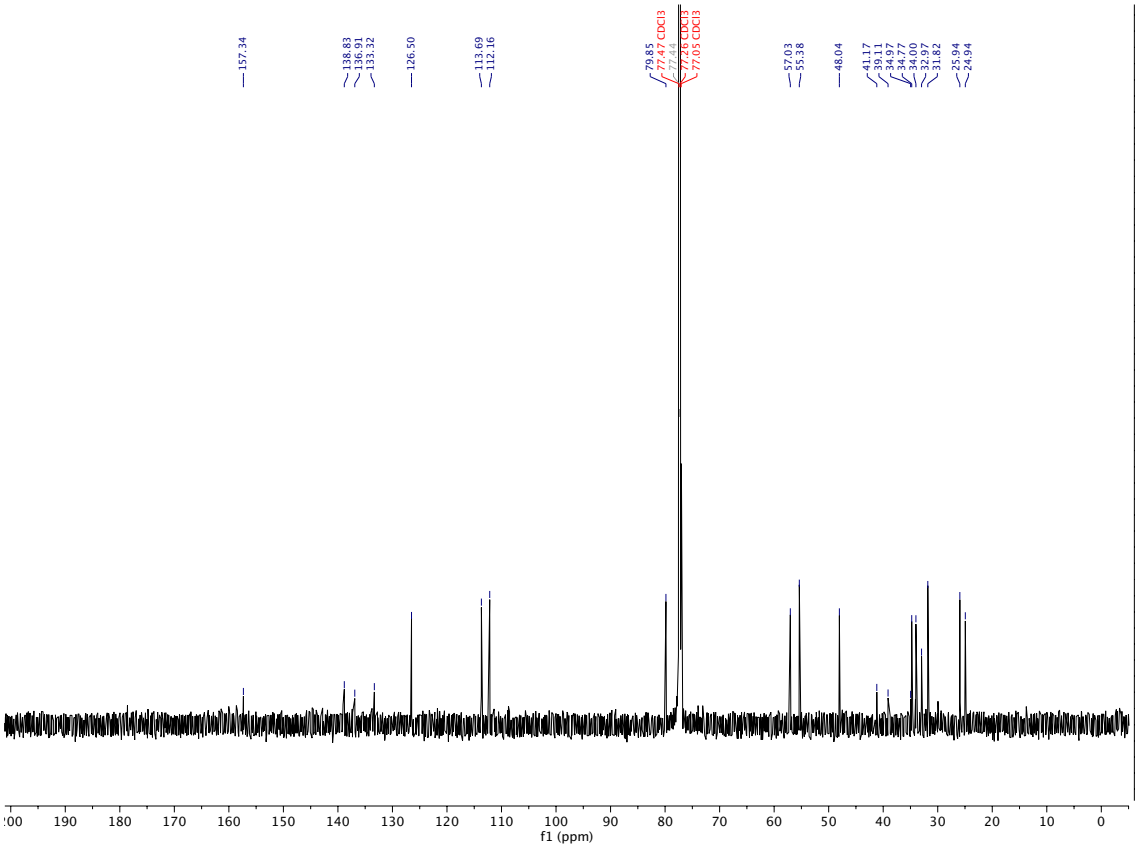
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **25**



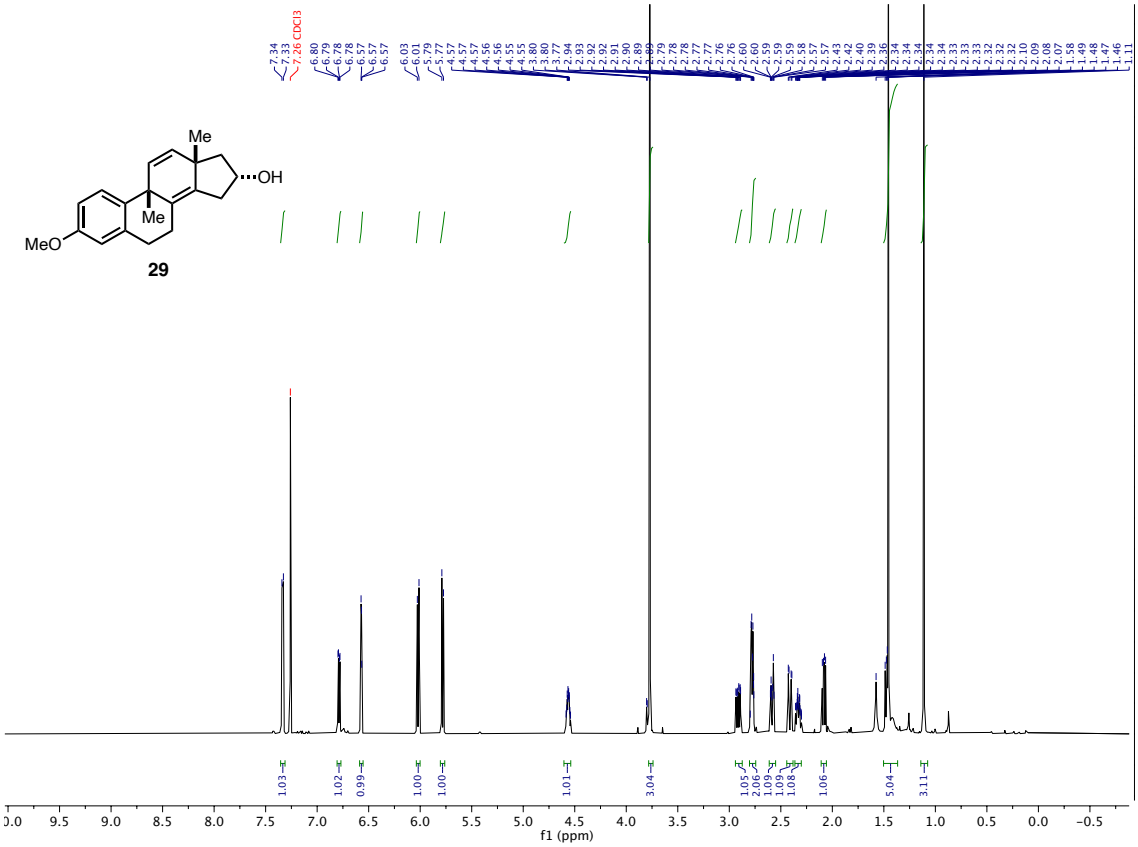


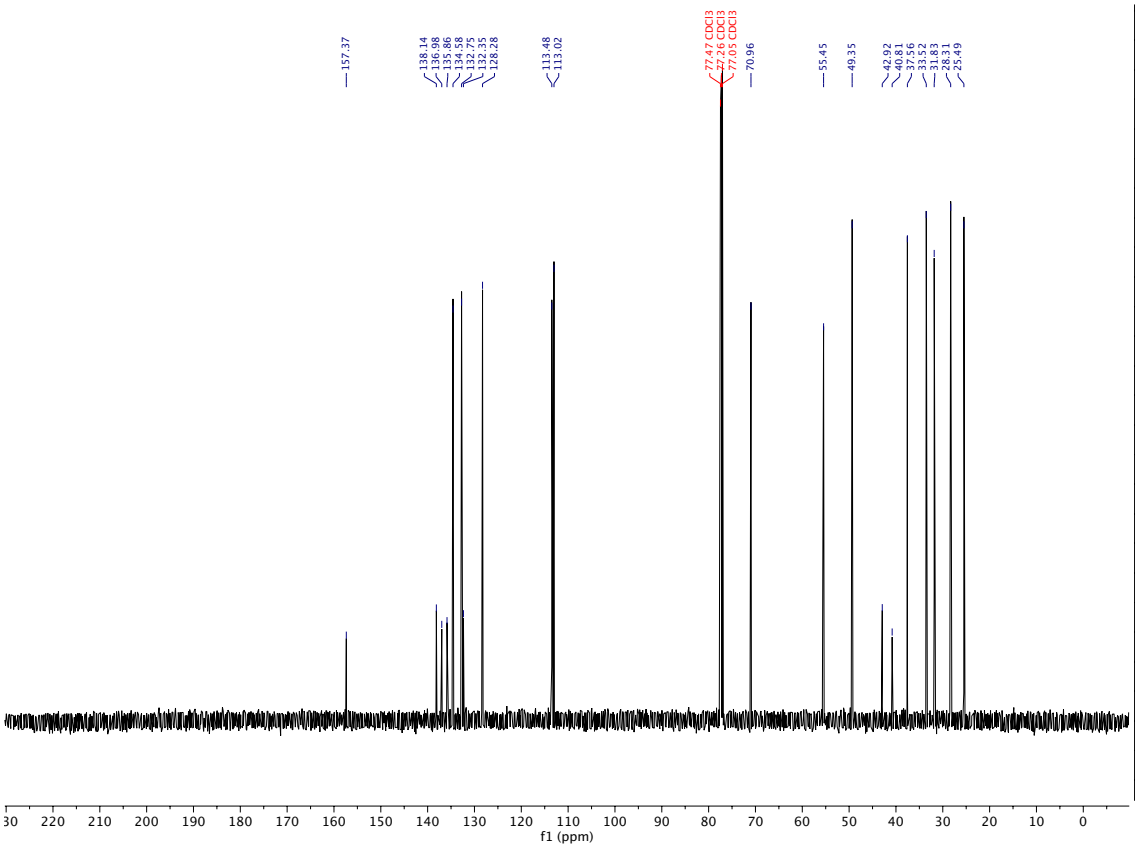
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **26**



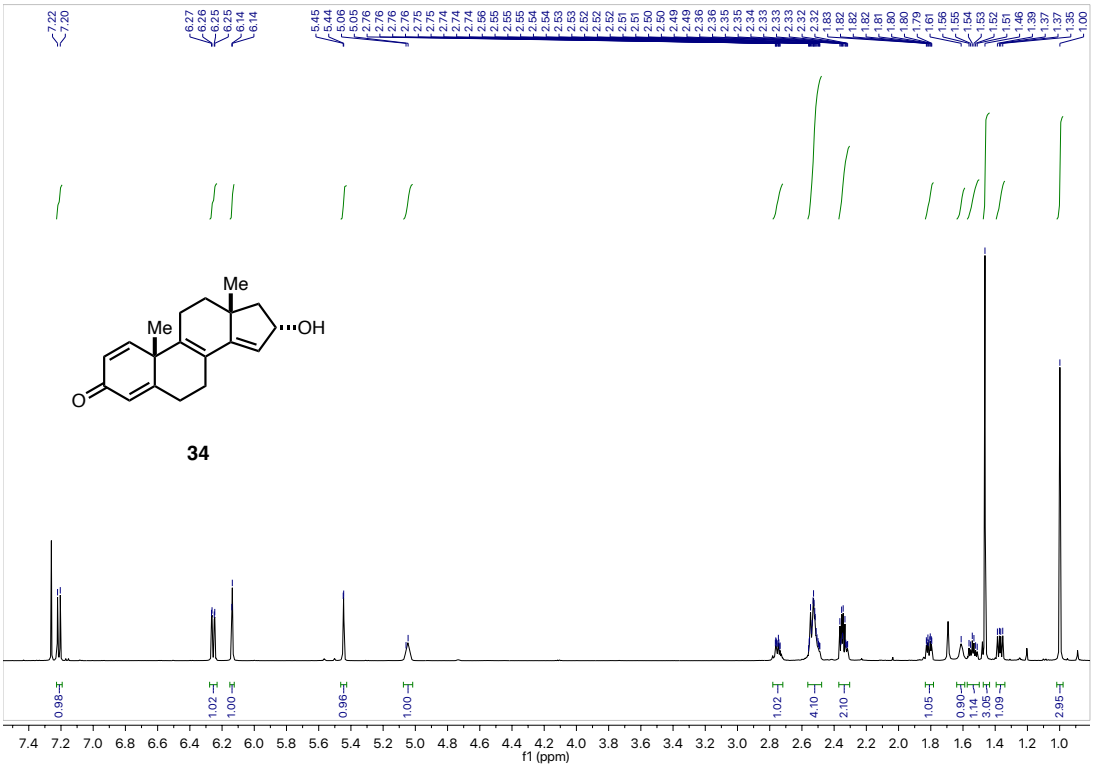


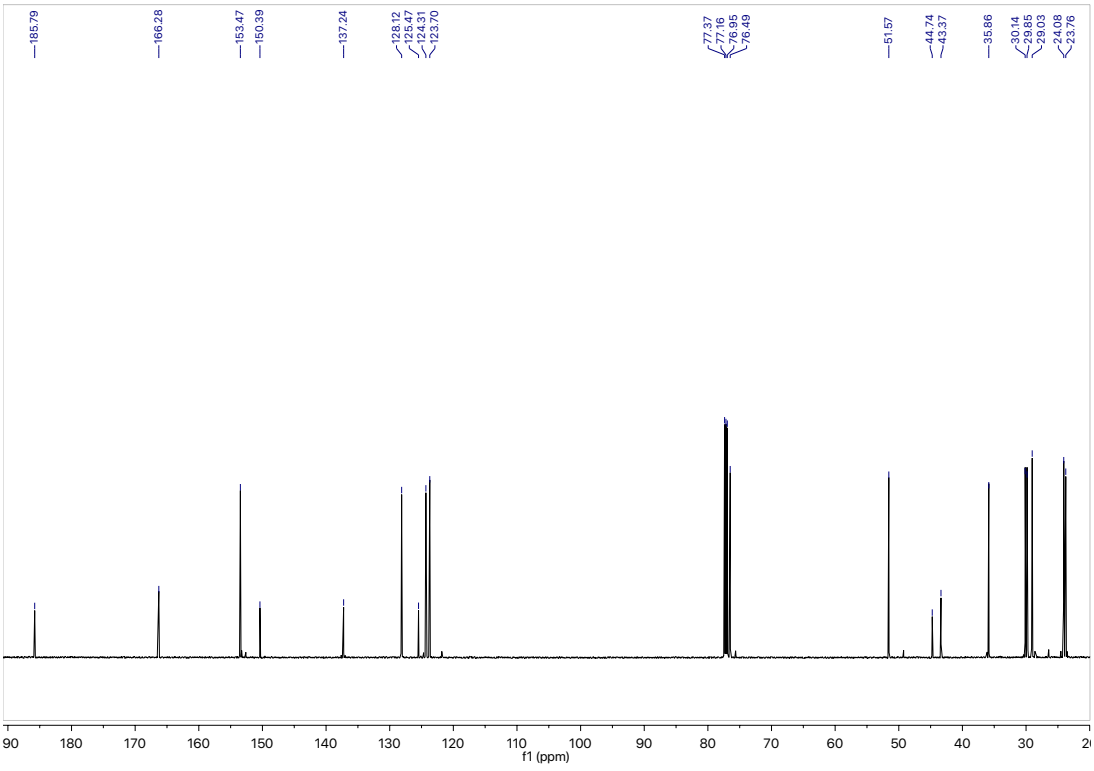
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **29**



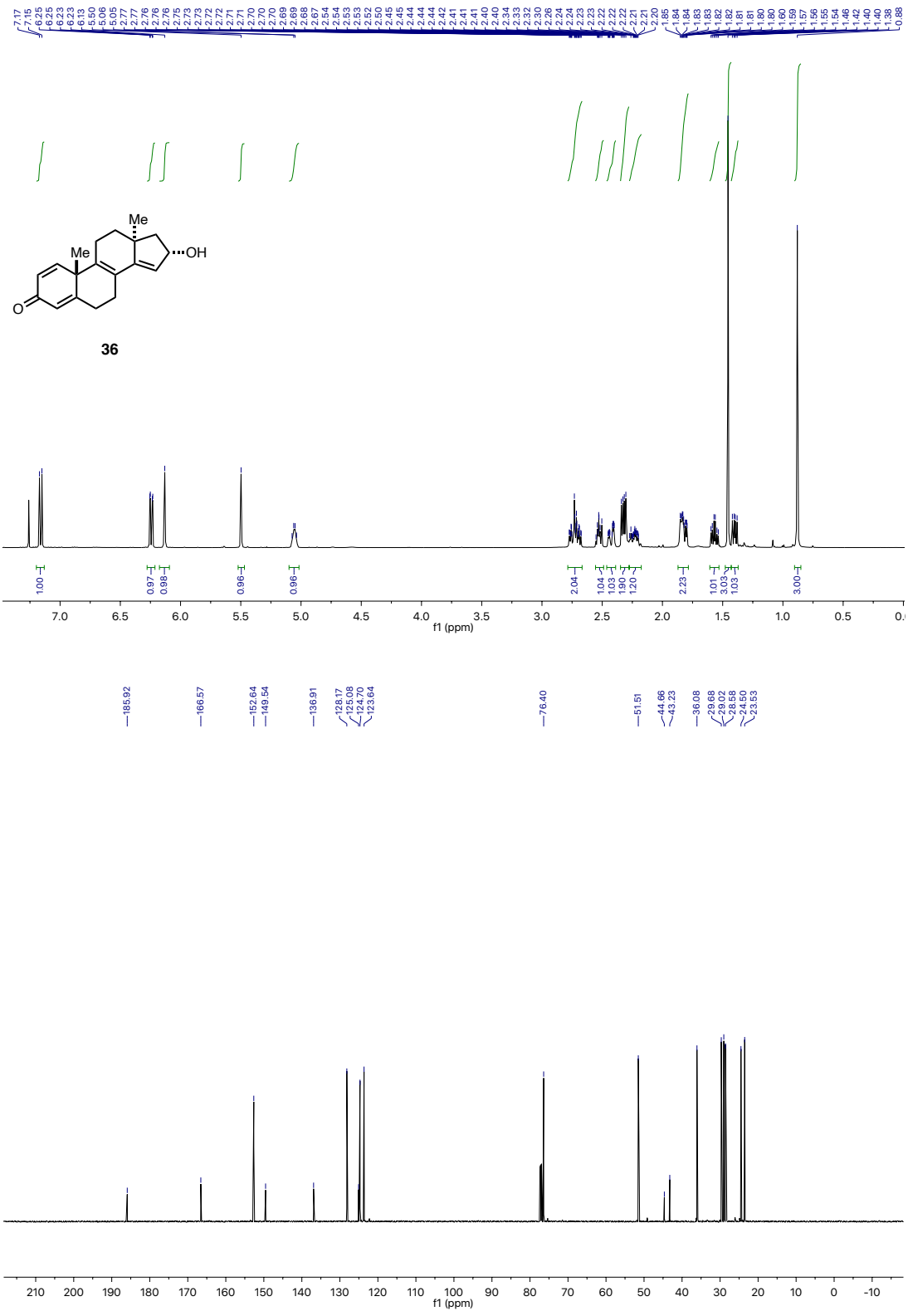


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **34**

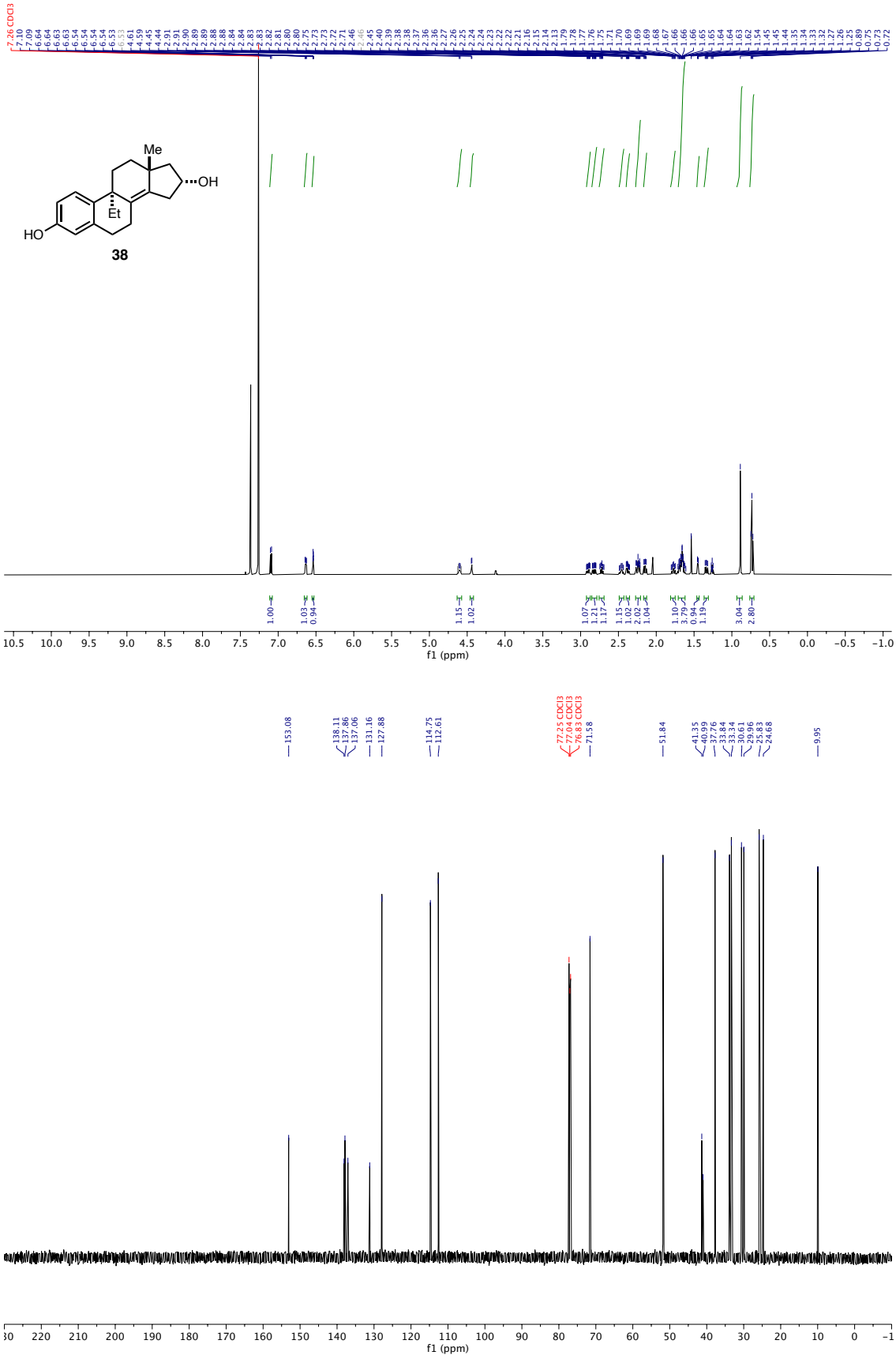




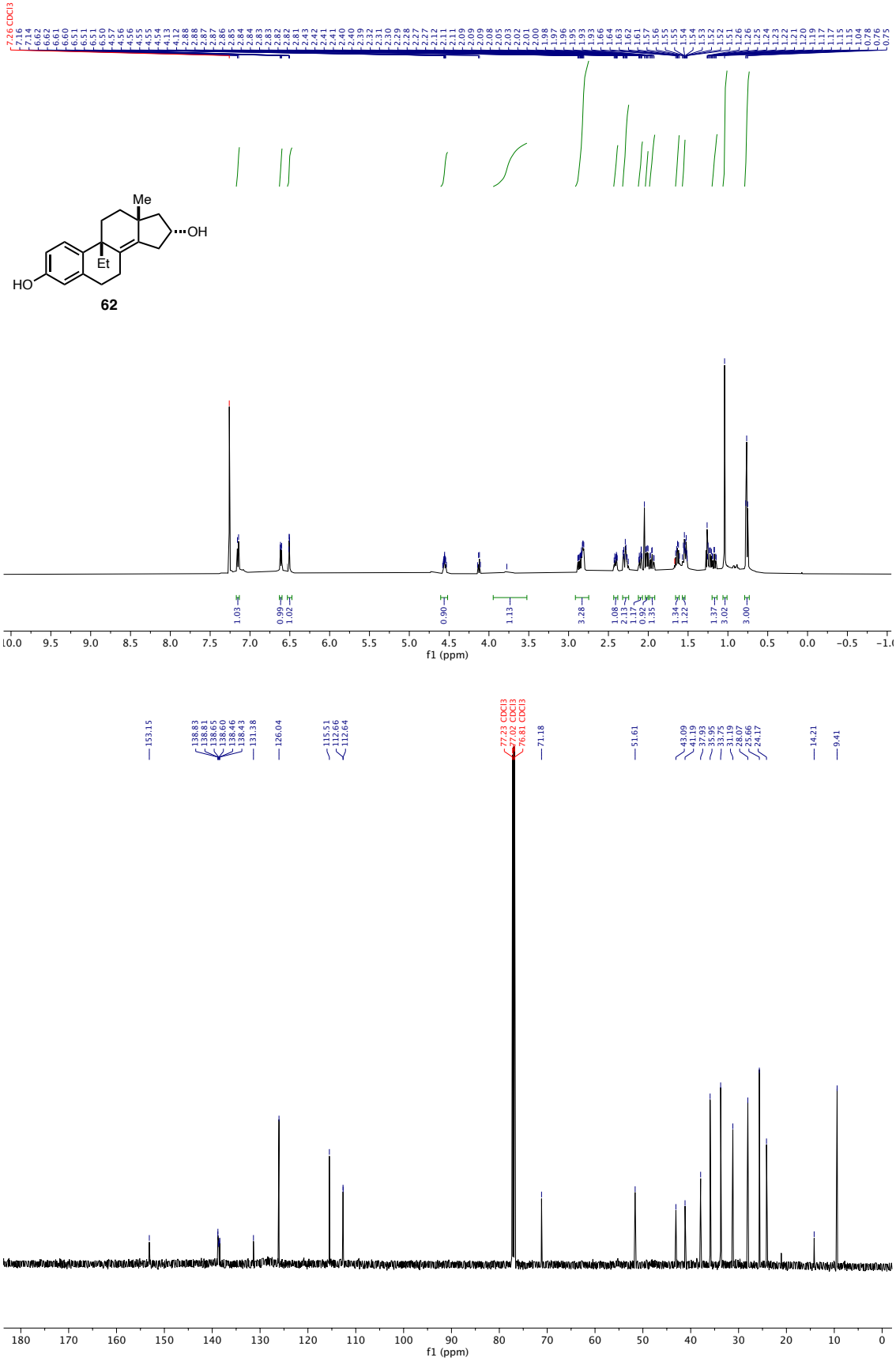
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **36**



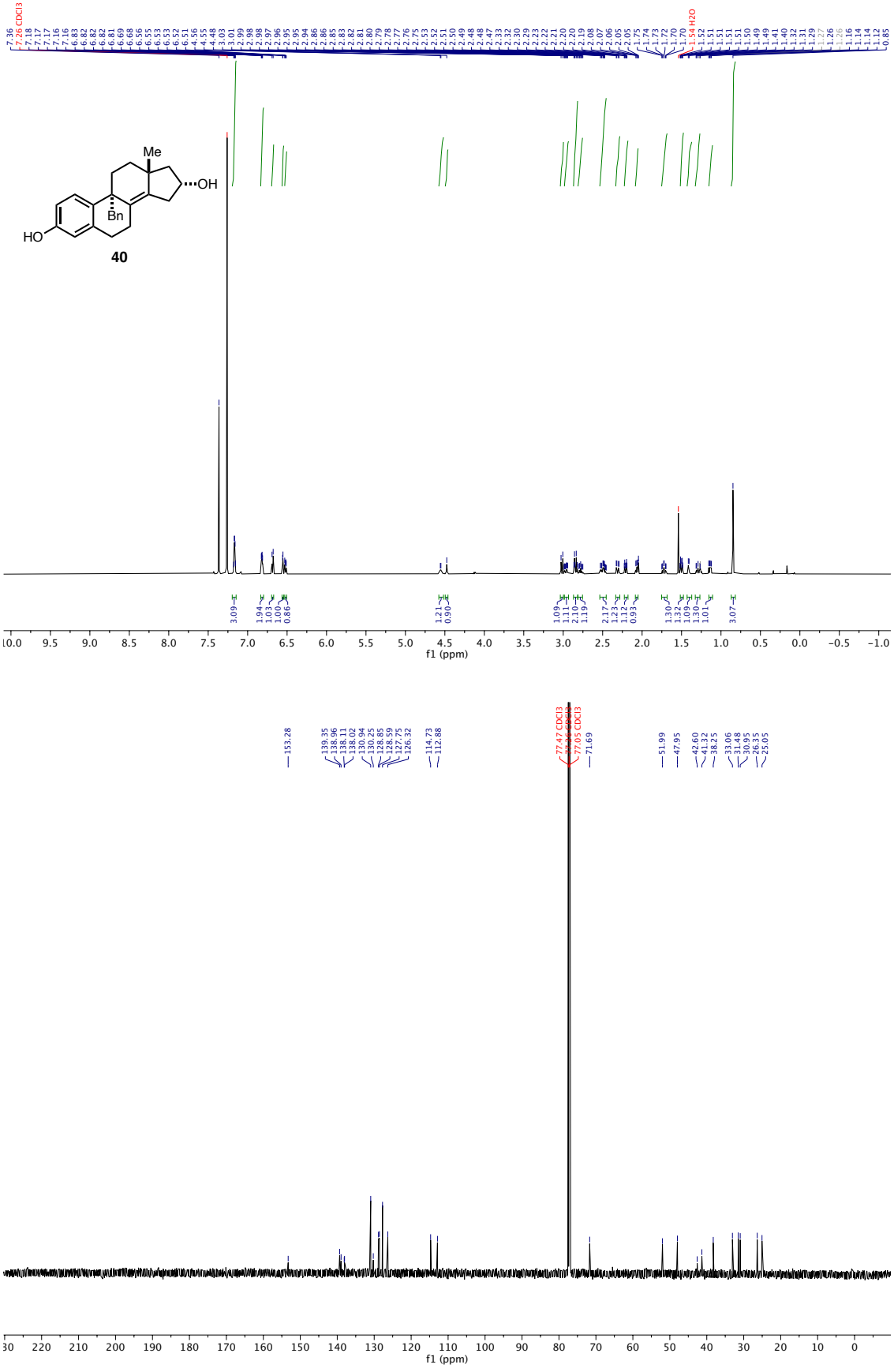
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **38**



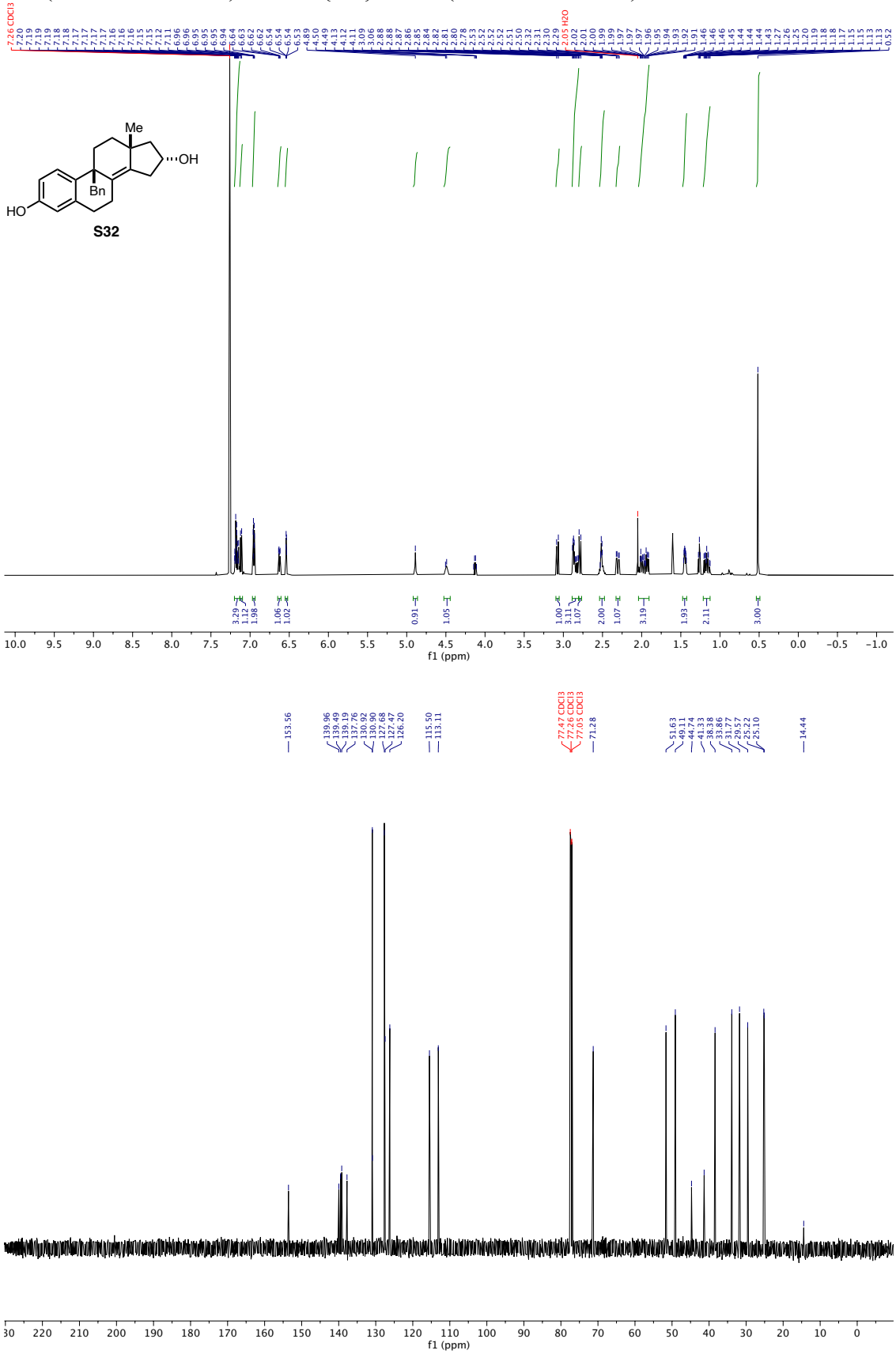
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **62**



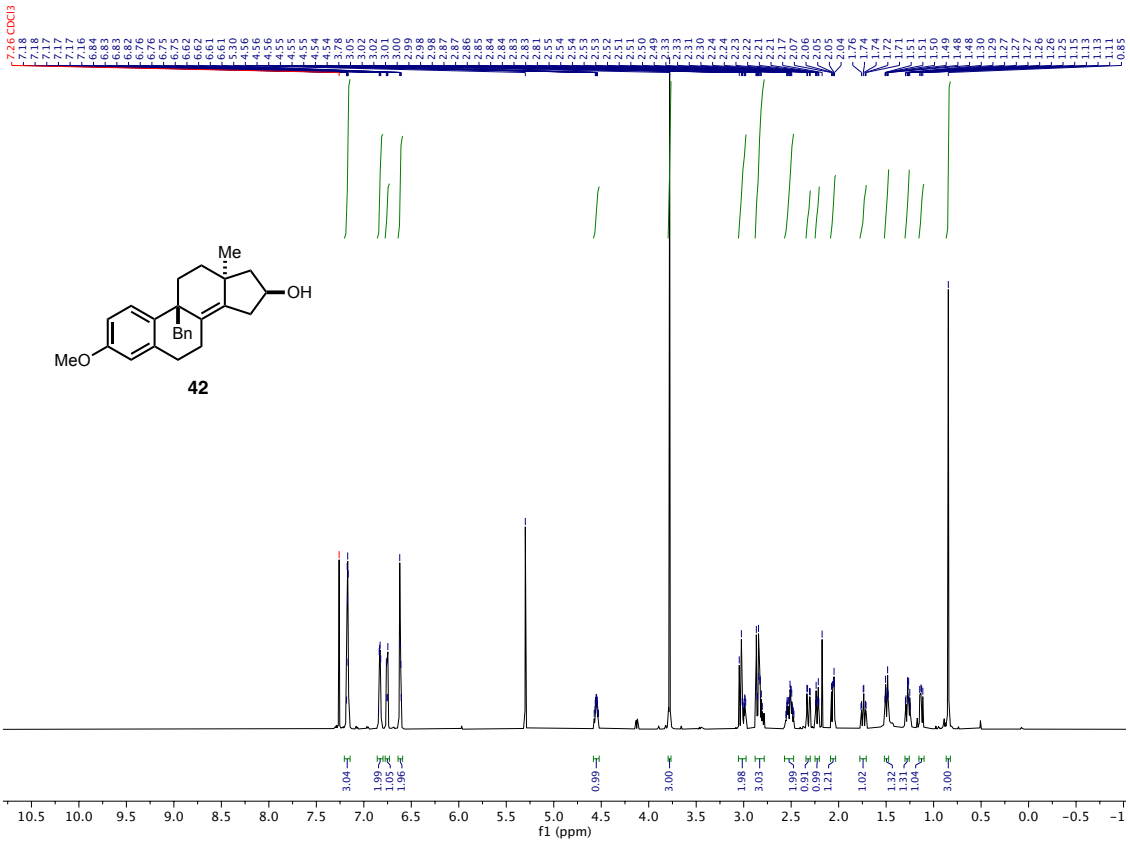
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **40**

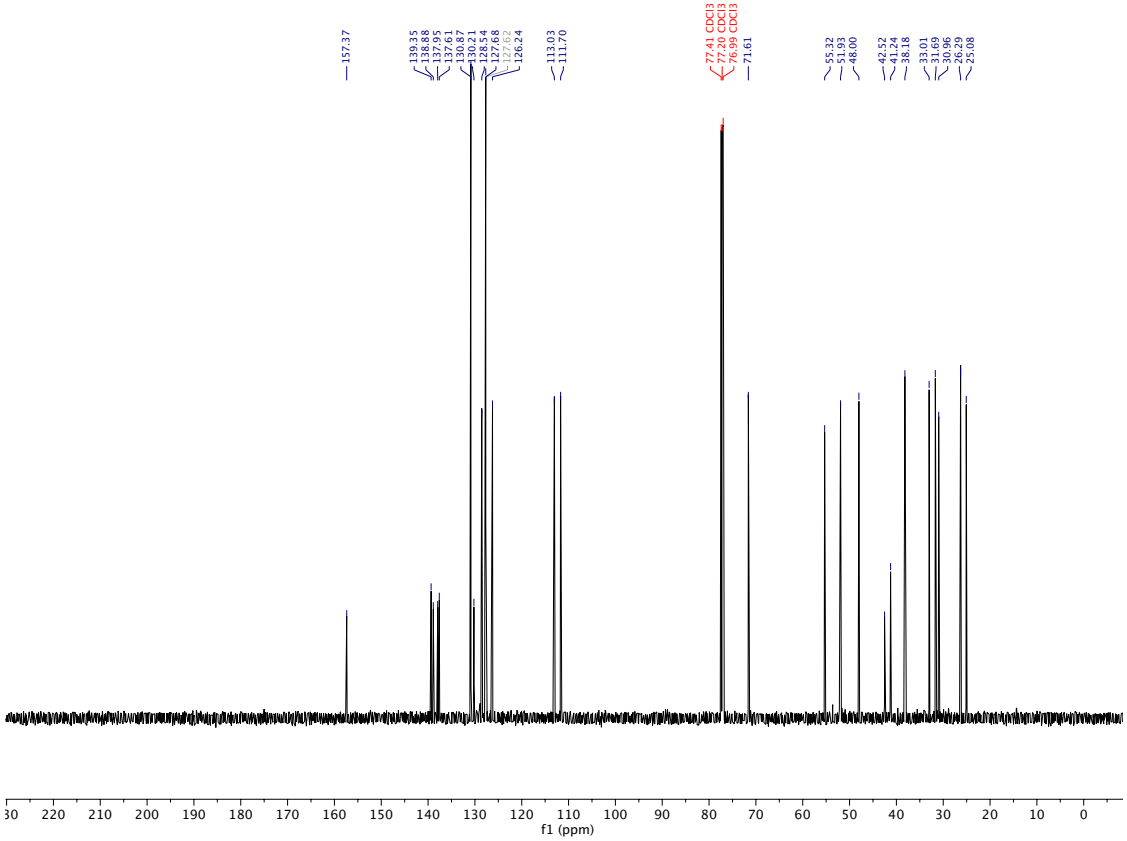


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S32**

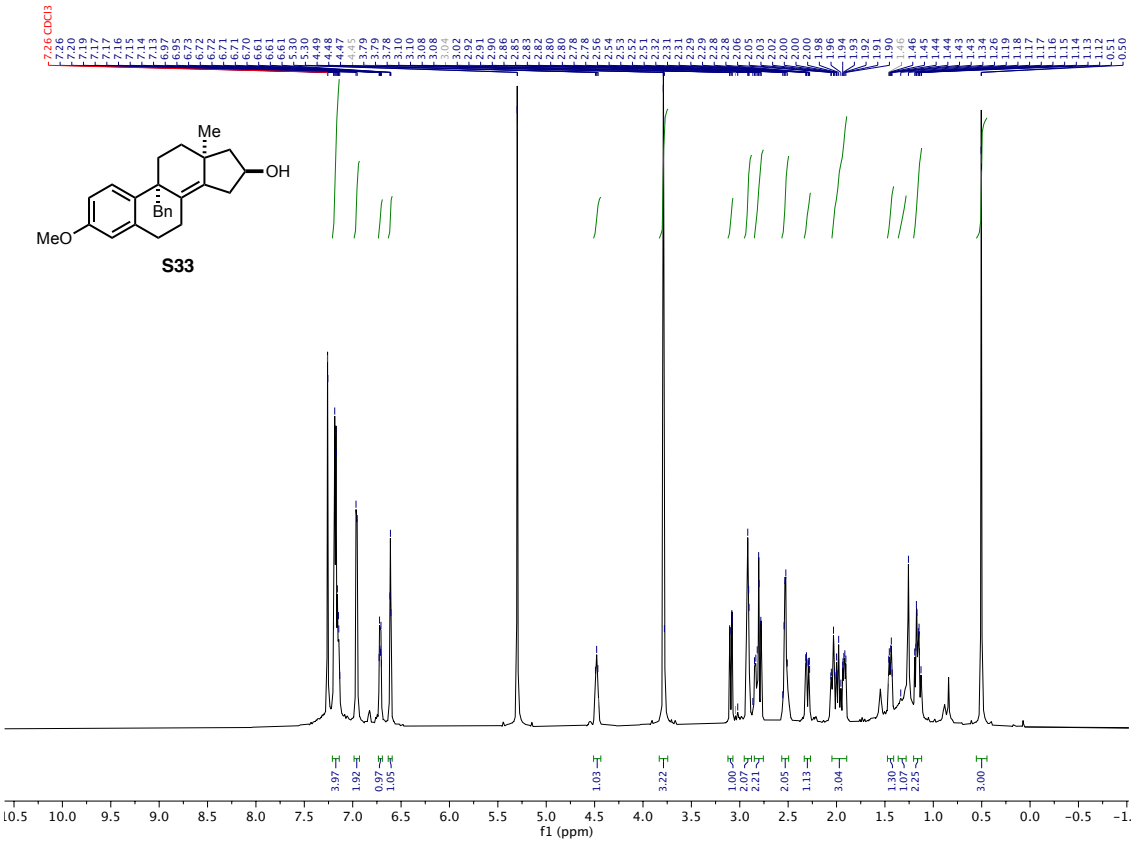


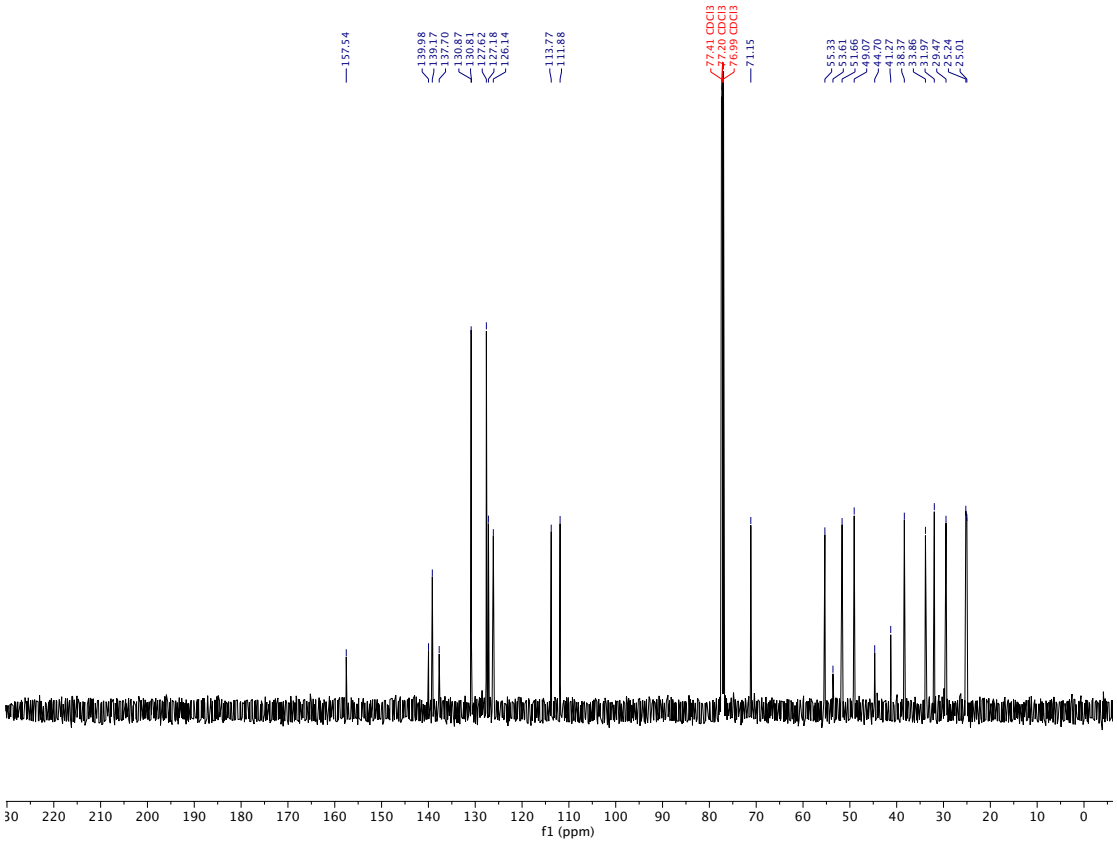
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **42**



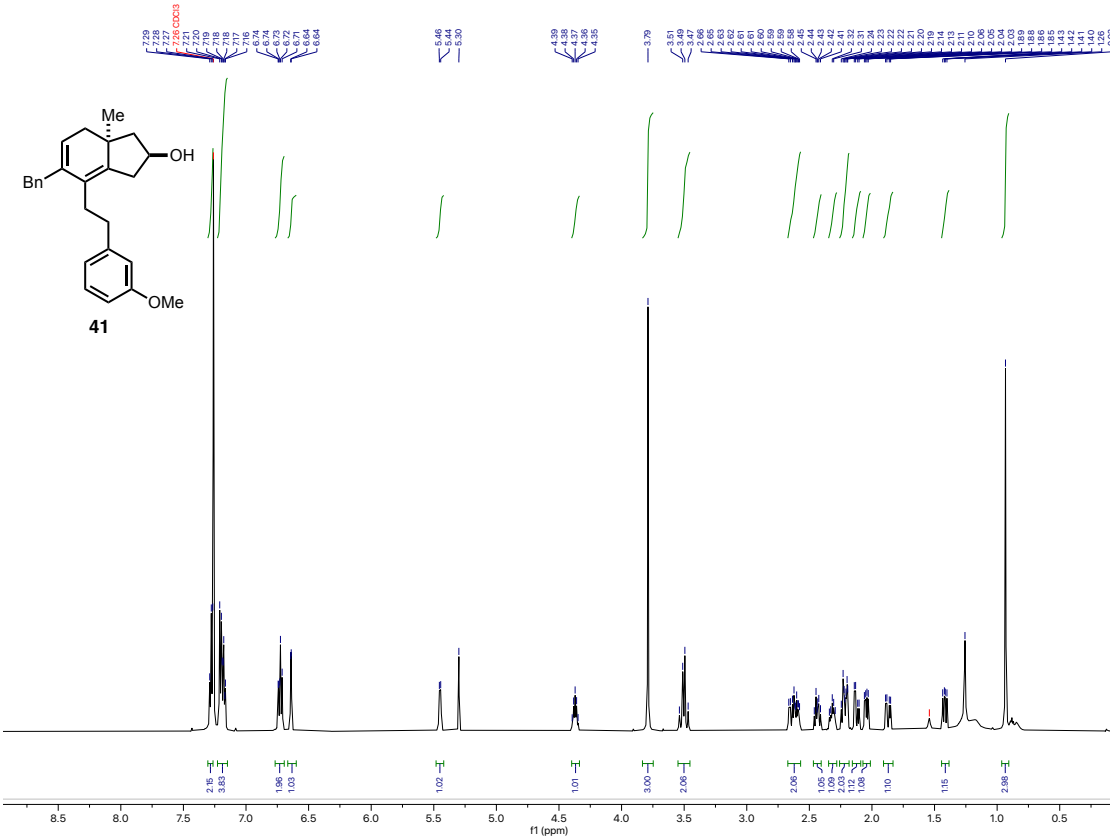


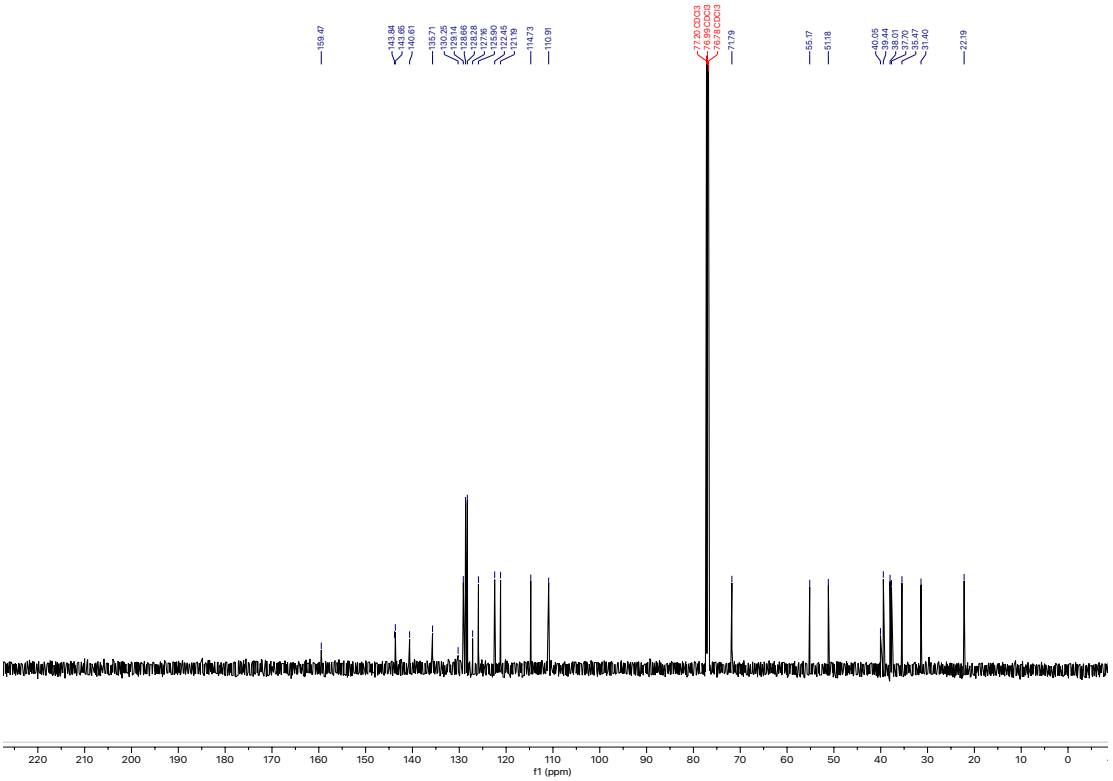
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S33**



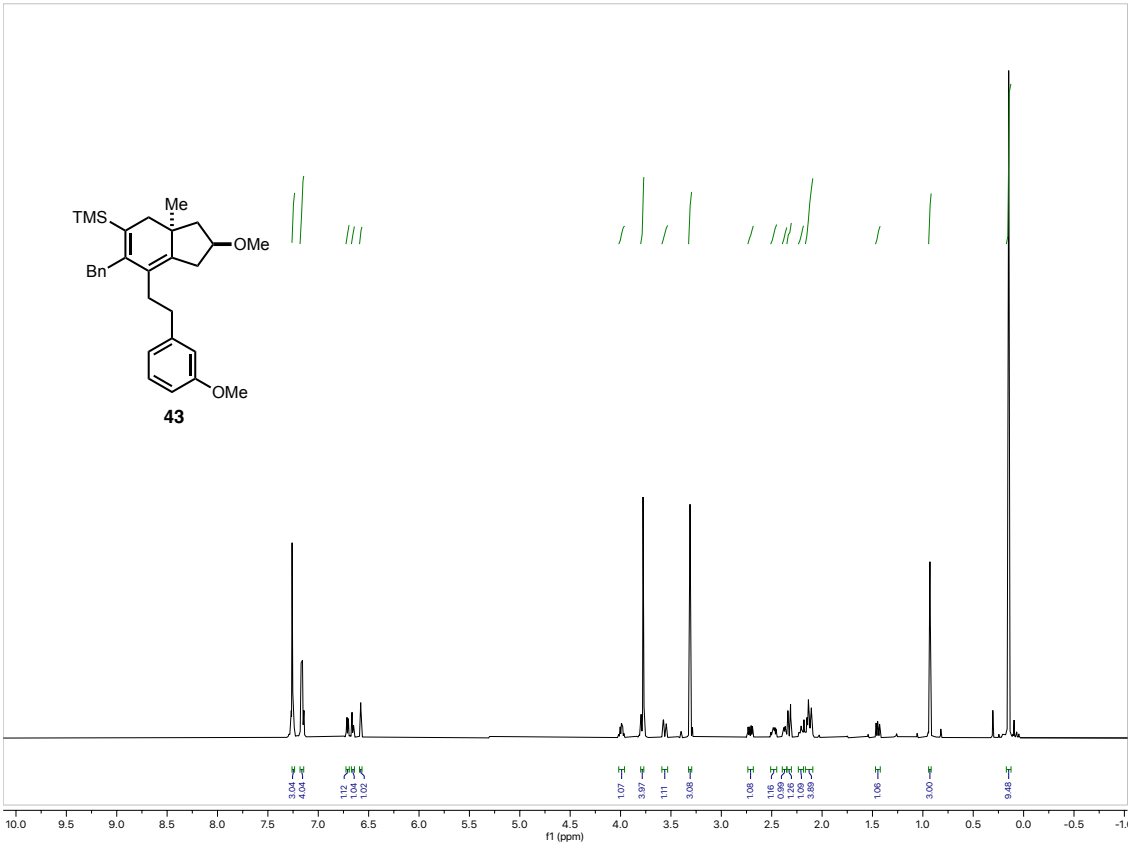


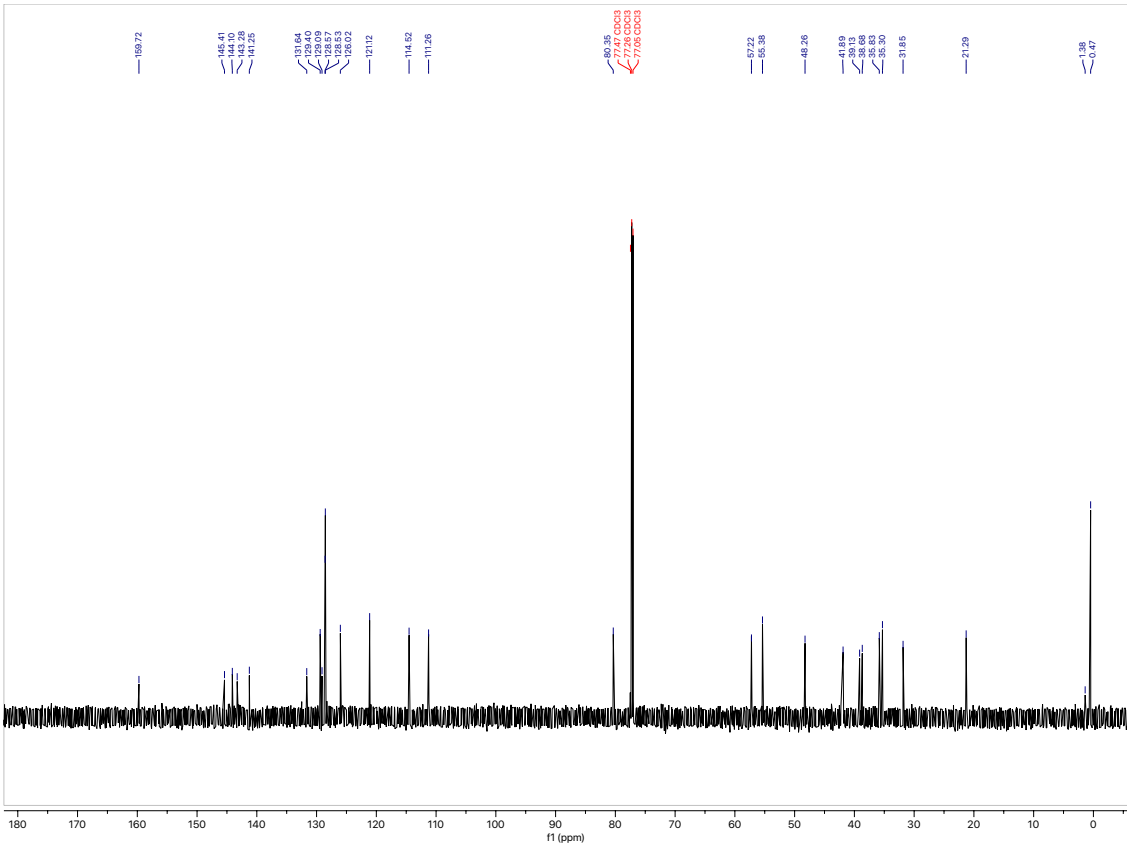
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **41**



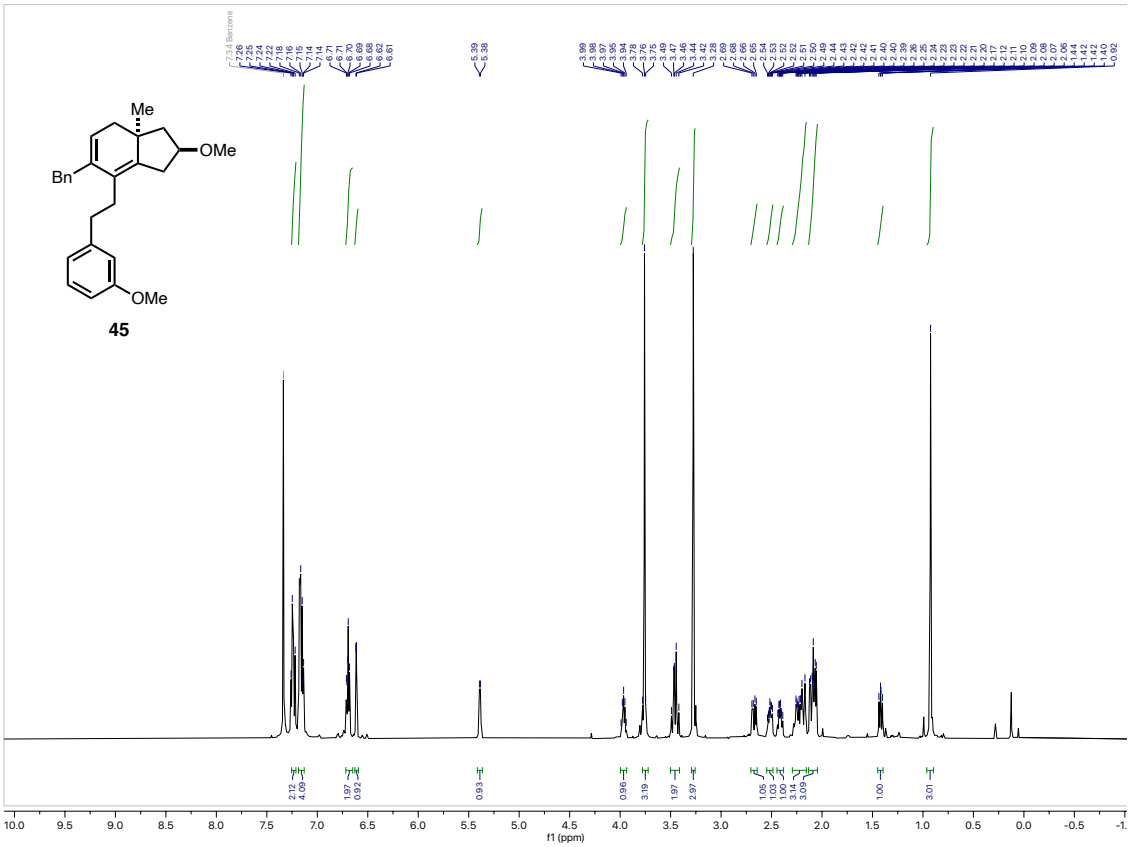


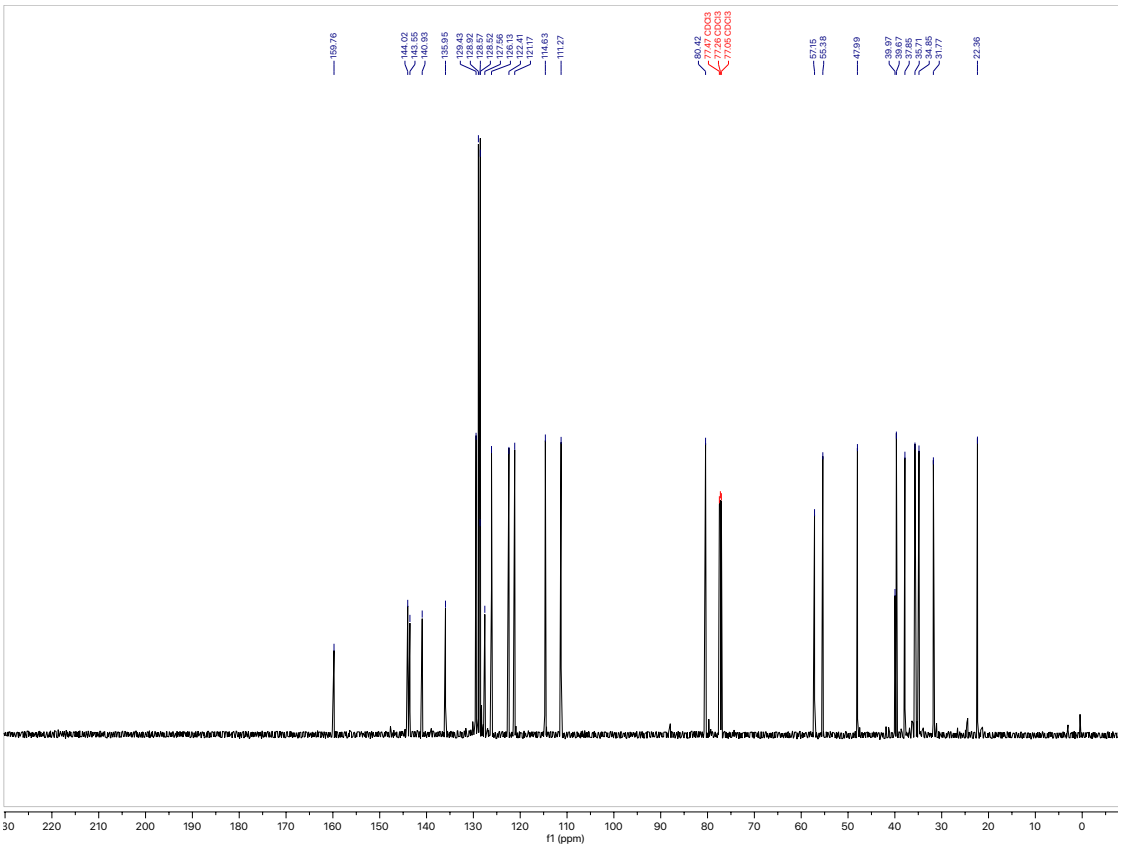
H NMR (600 MHz, $CDCl_3$) and $^{13}C\{1H\}$ NMR (150 MHz, $CDCl_3$) of **43**



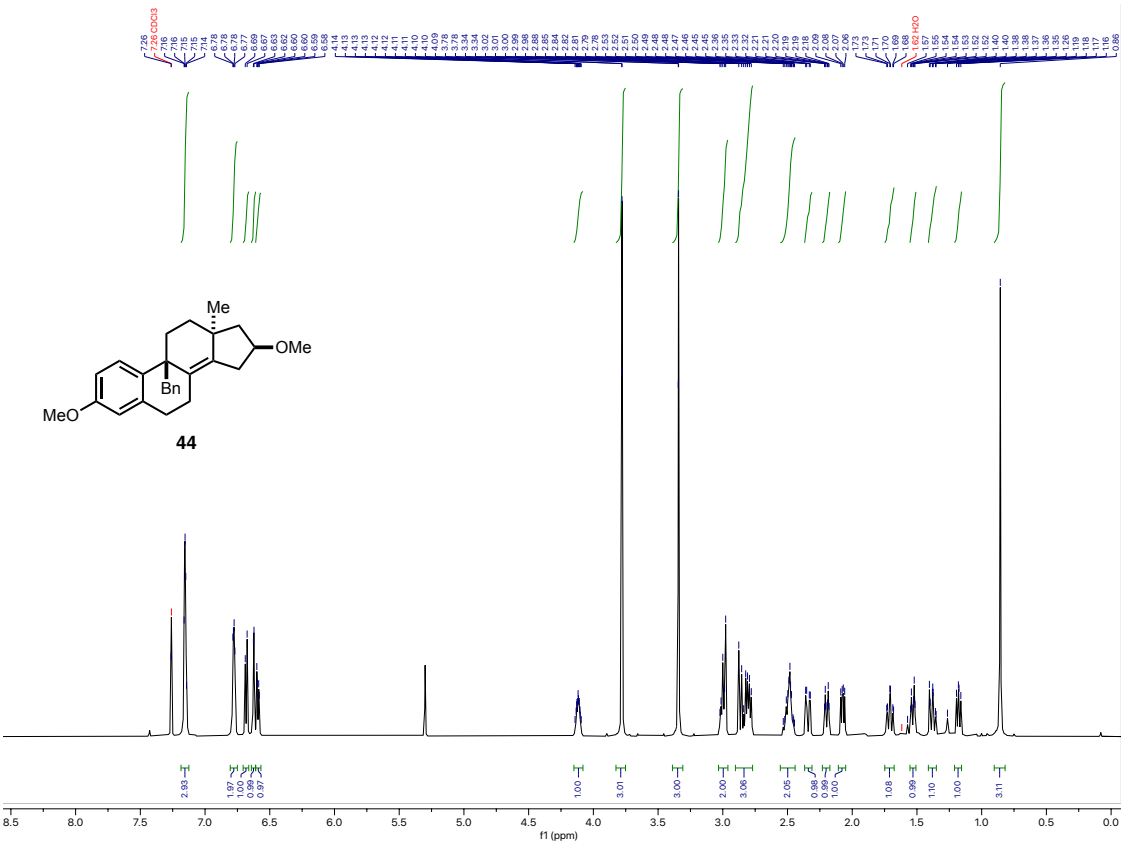


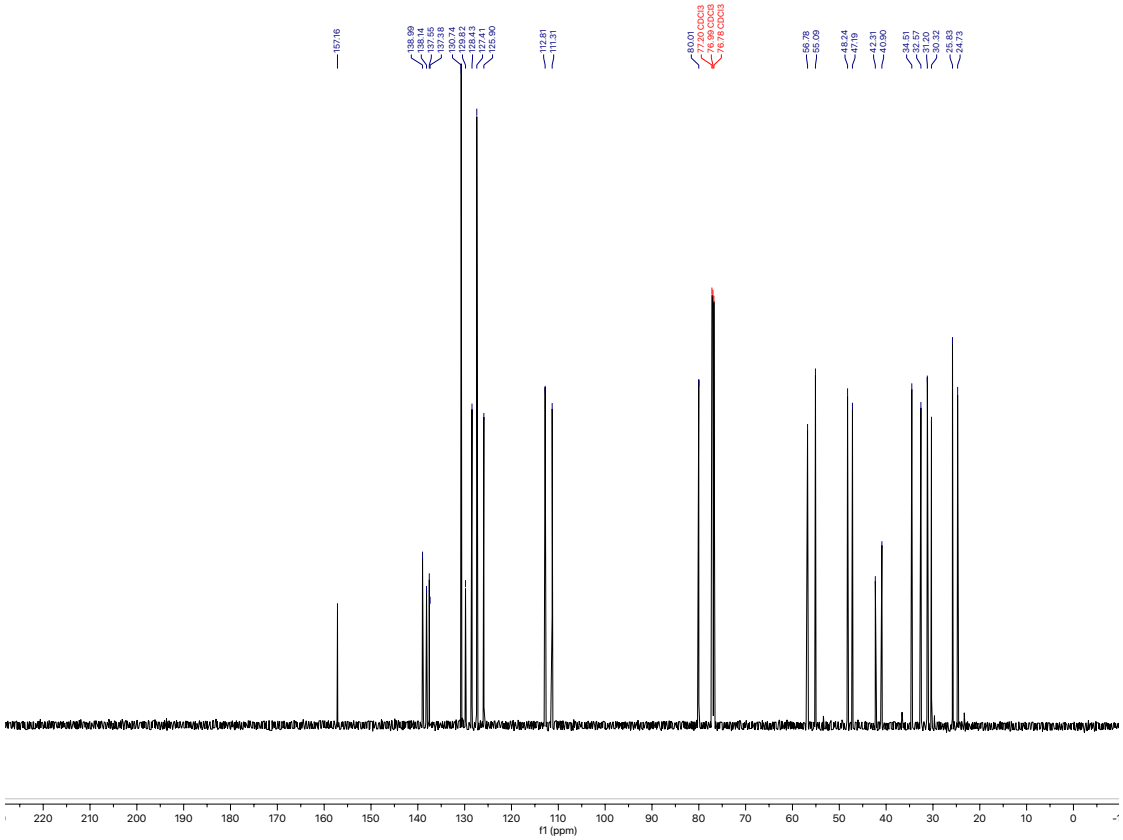
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **45**



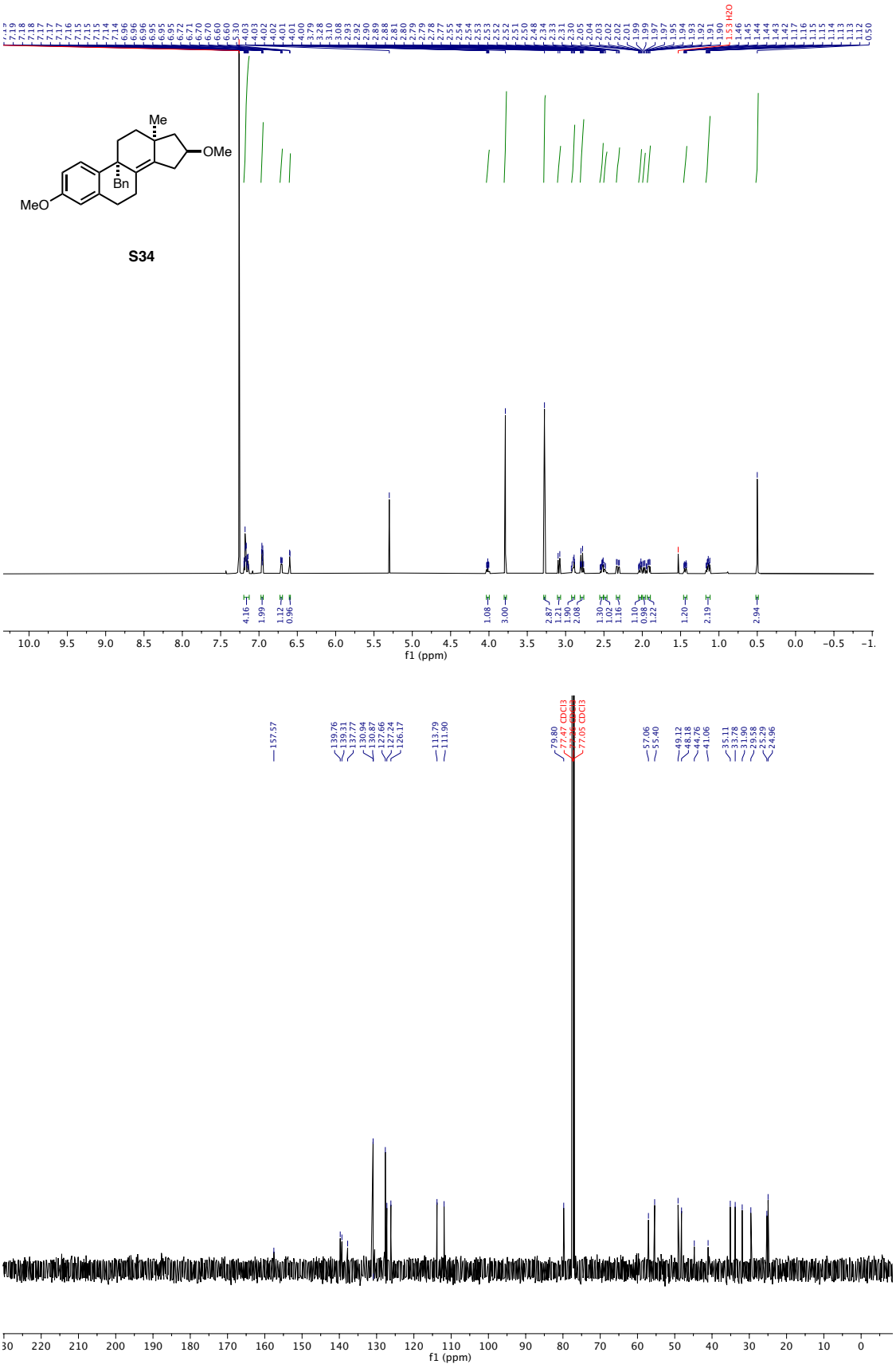


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **44**

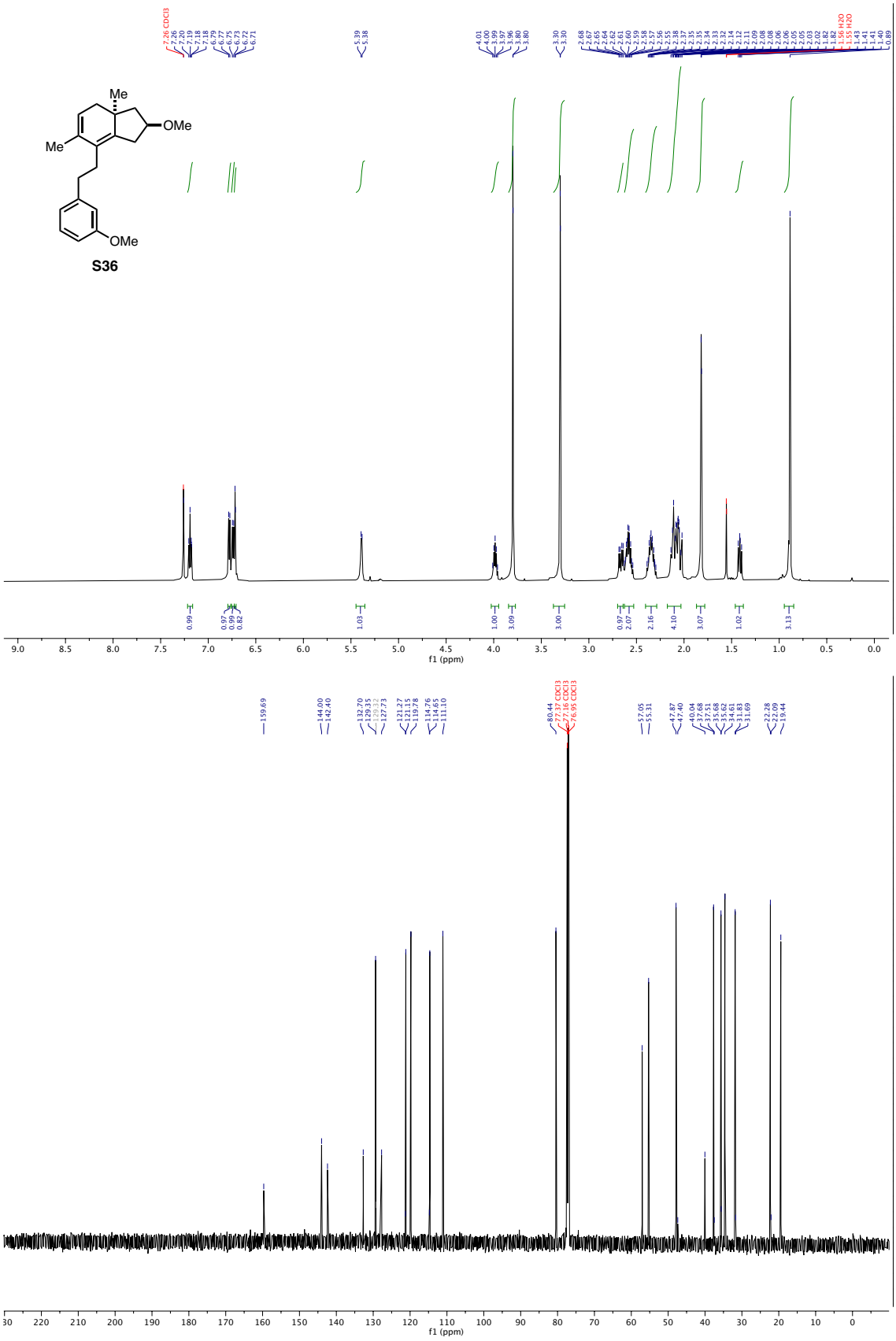




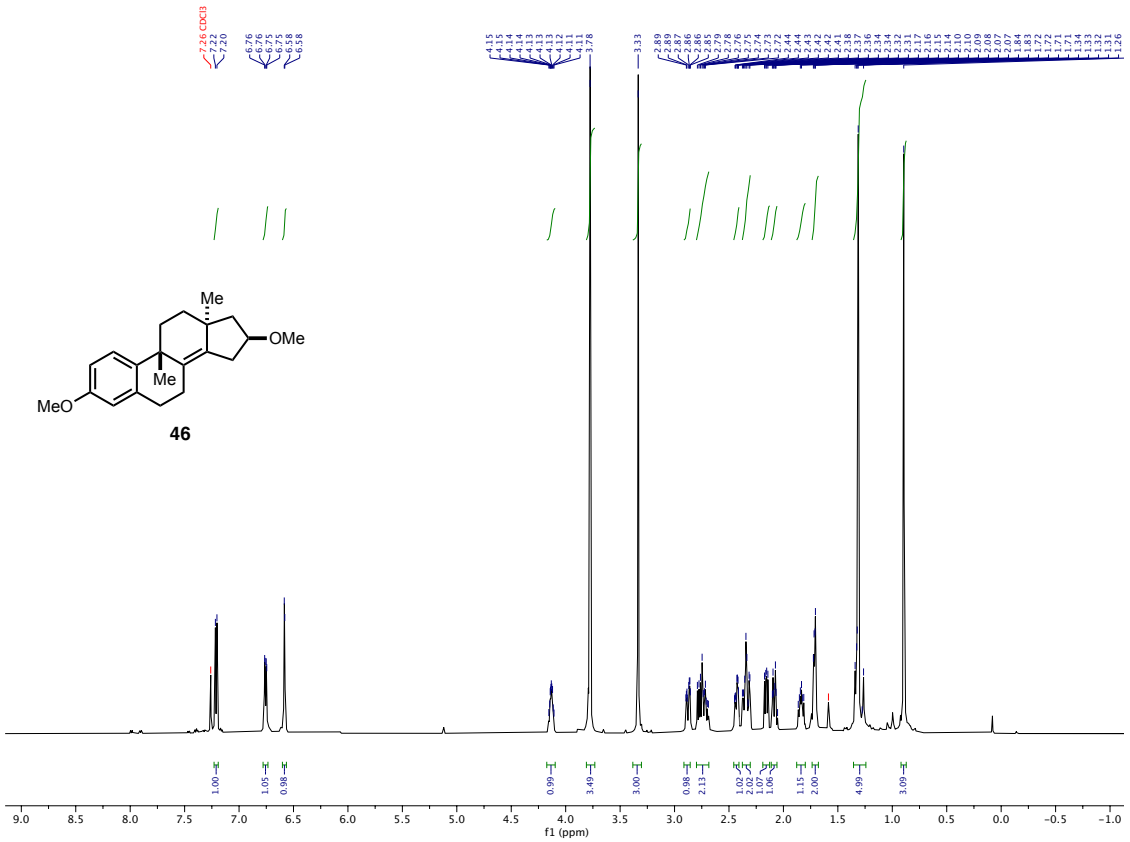
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S34**

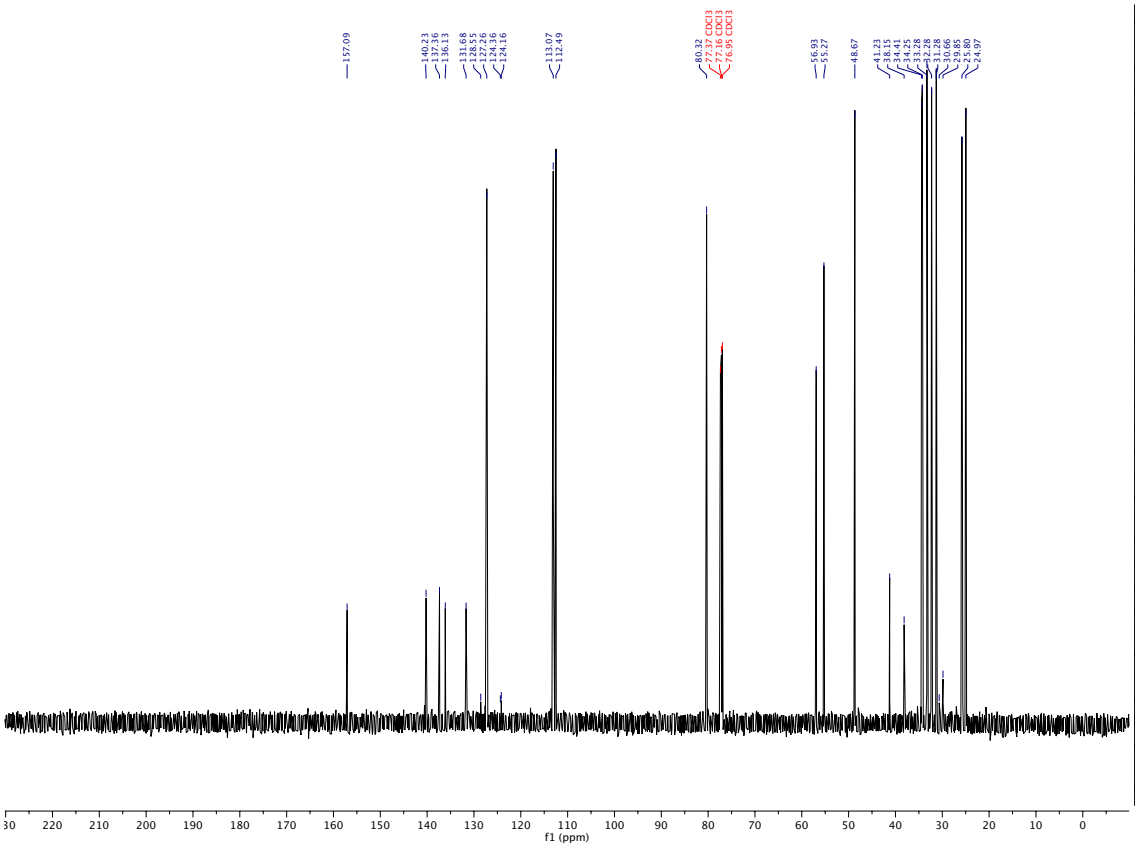


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S36**

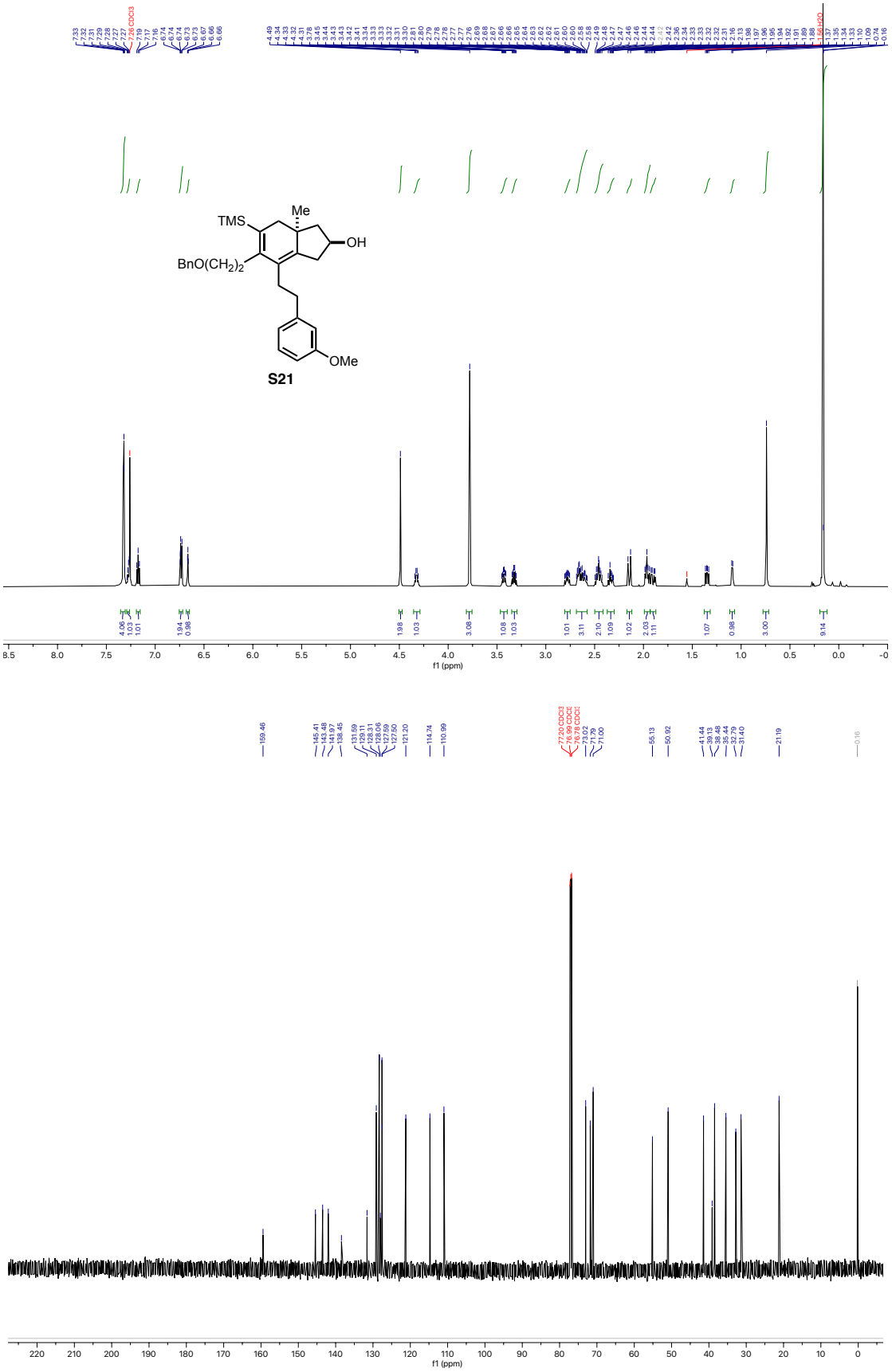


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **46**

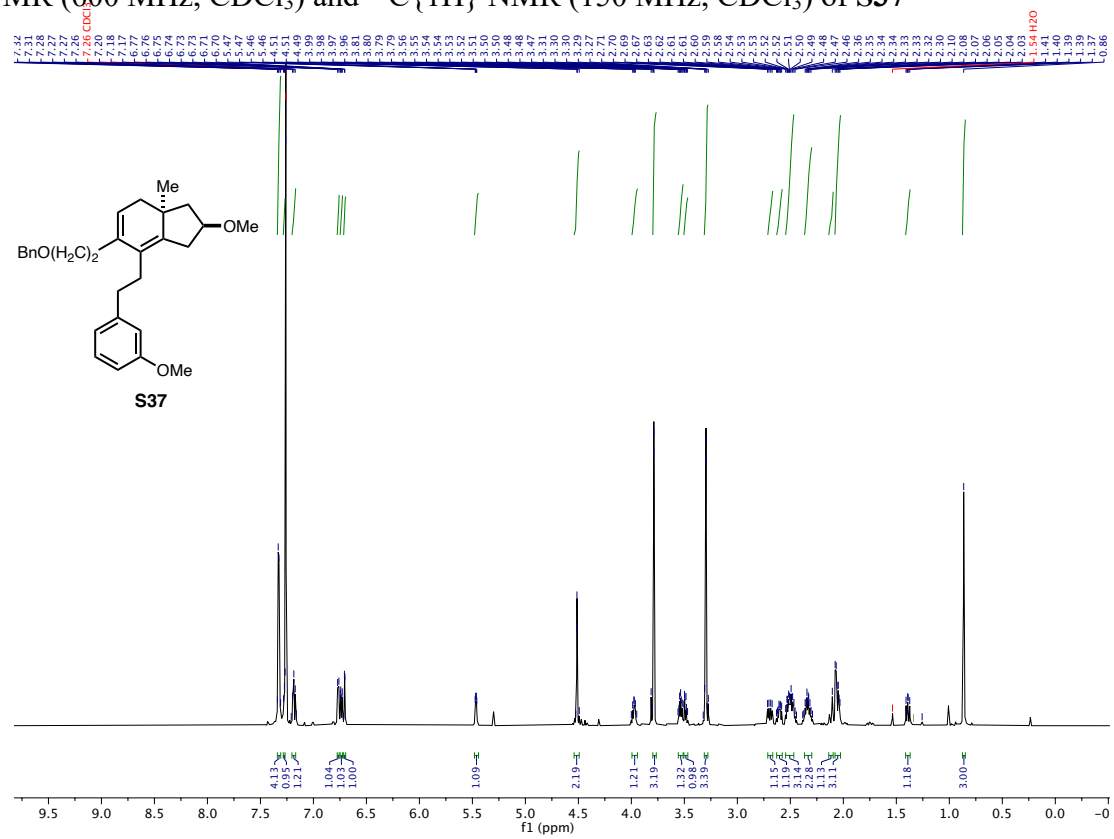


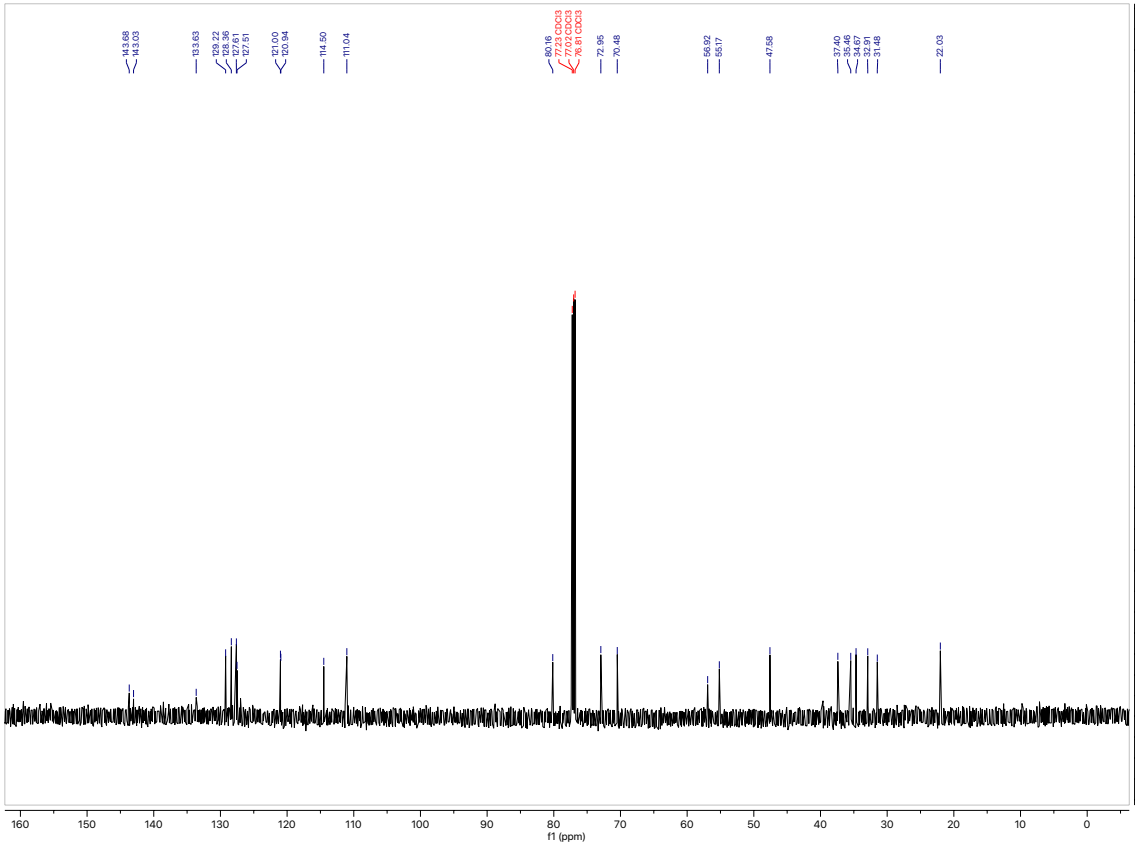


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S21**

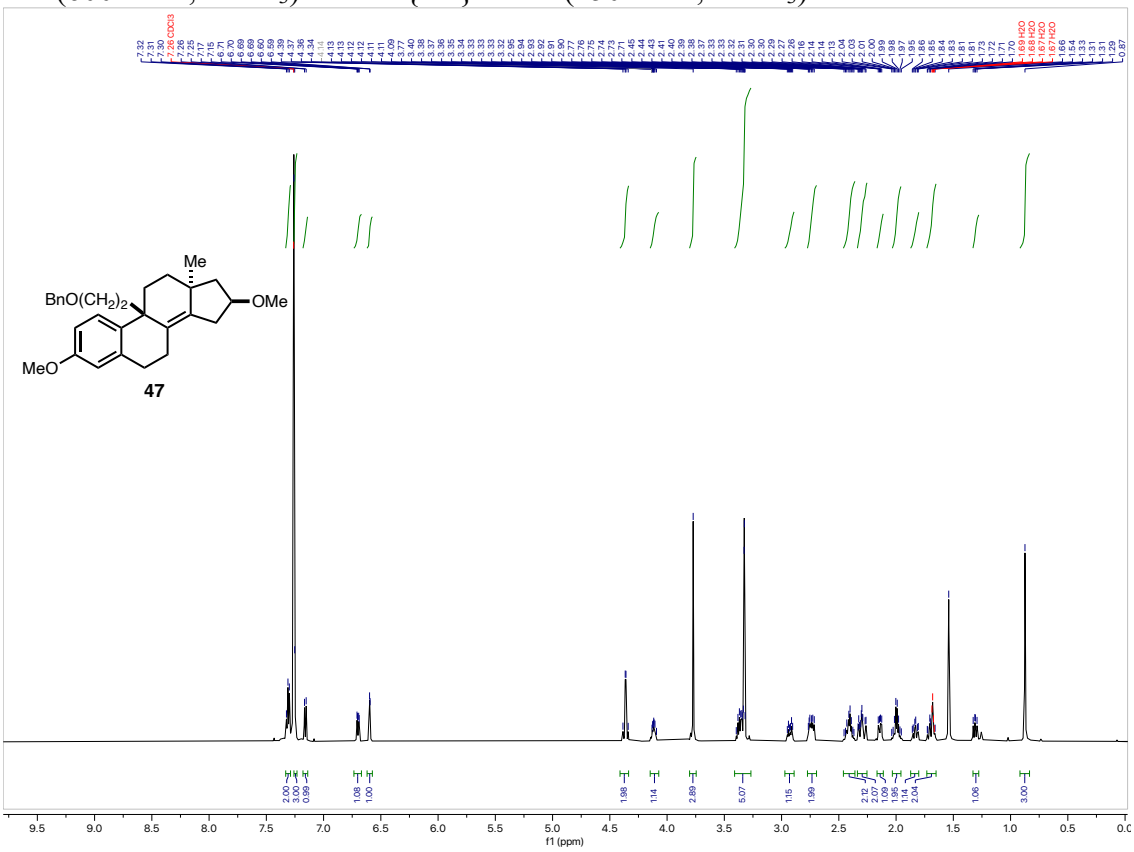


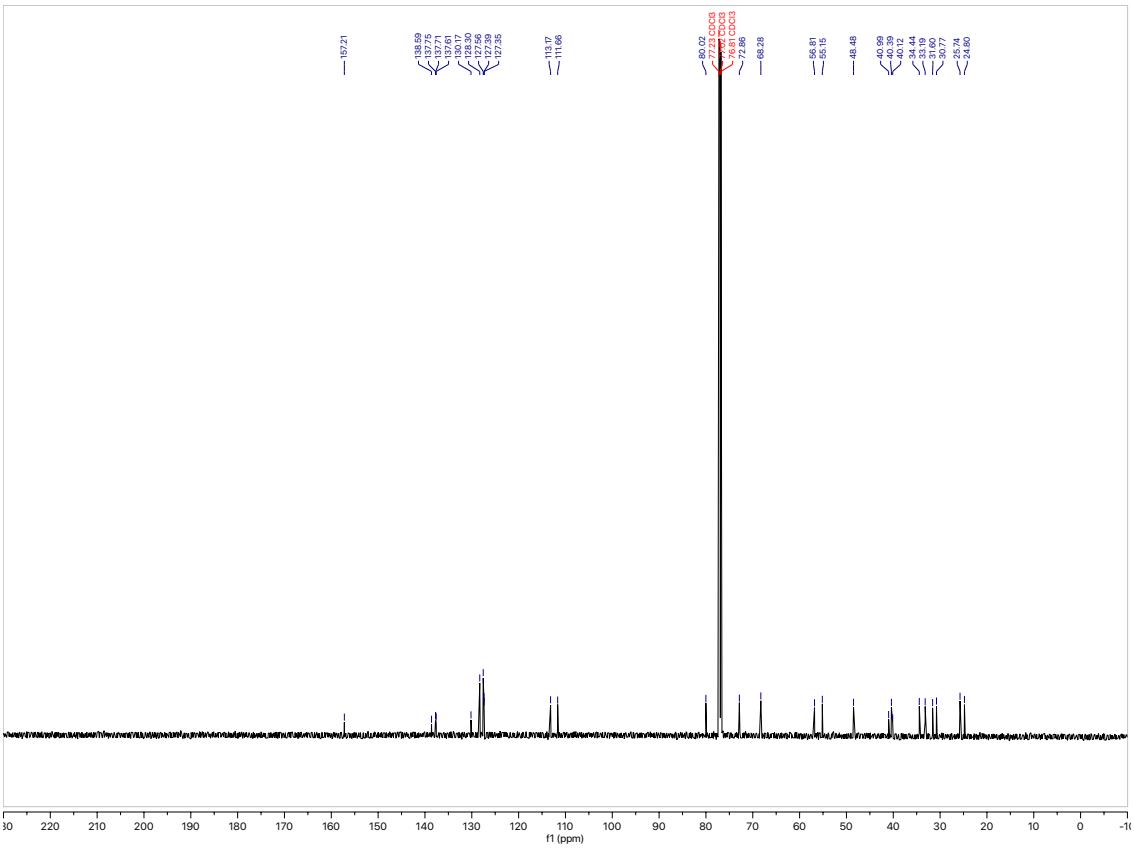
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S37**



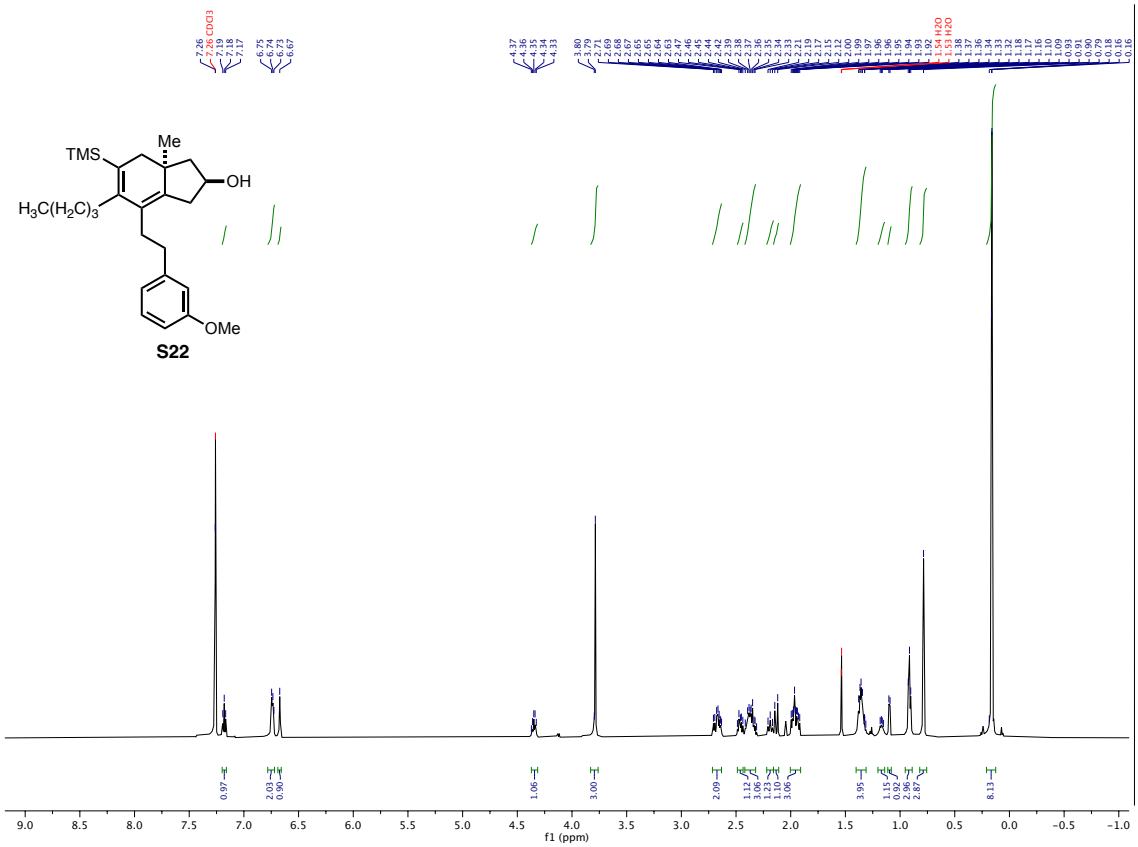


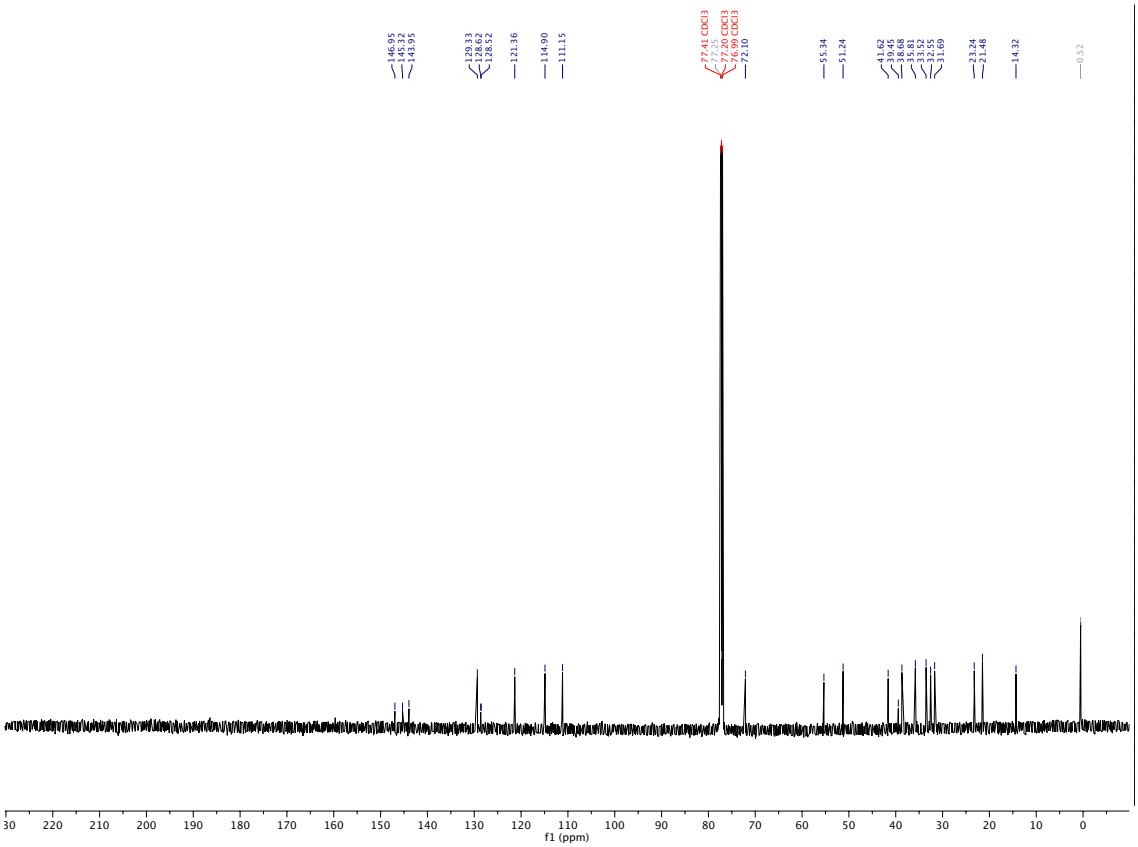
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **47**



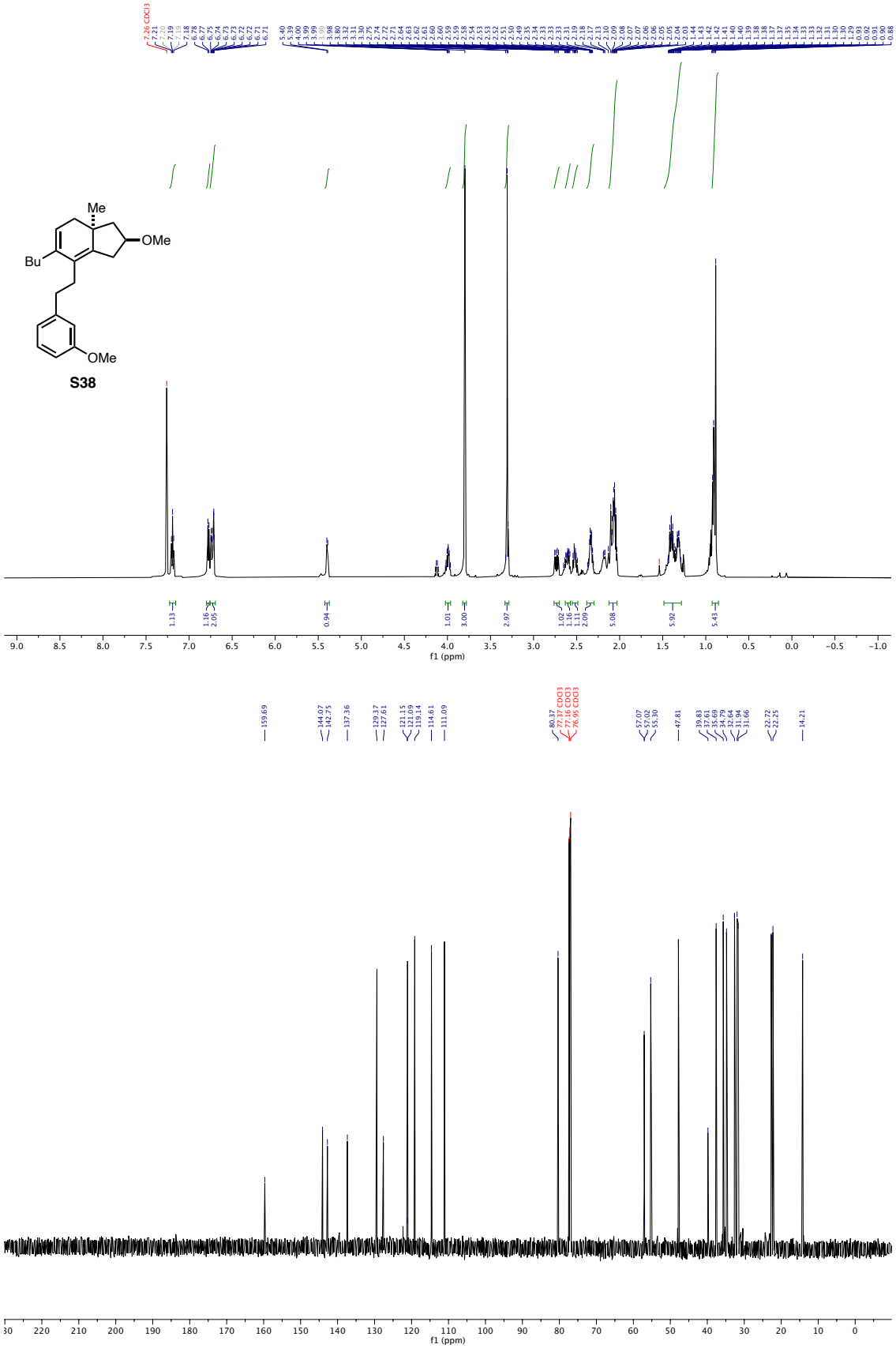


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S22**

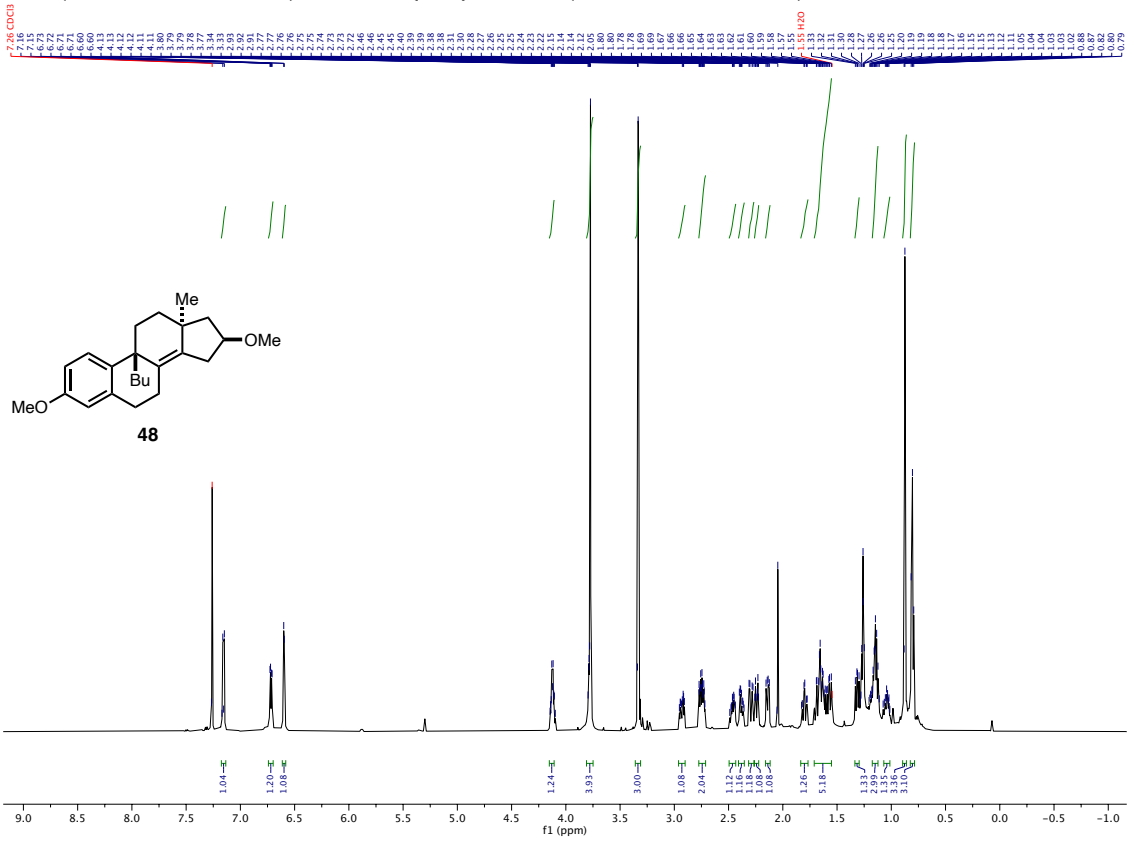


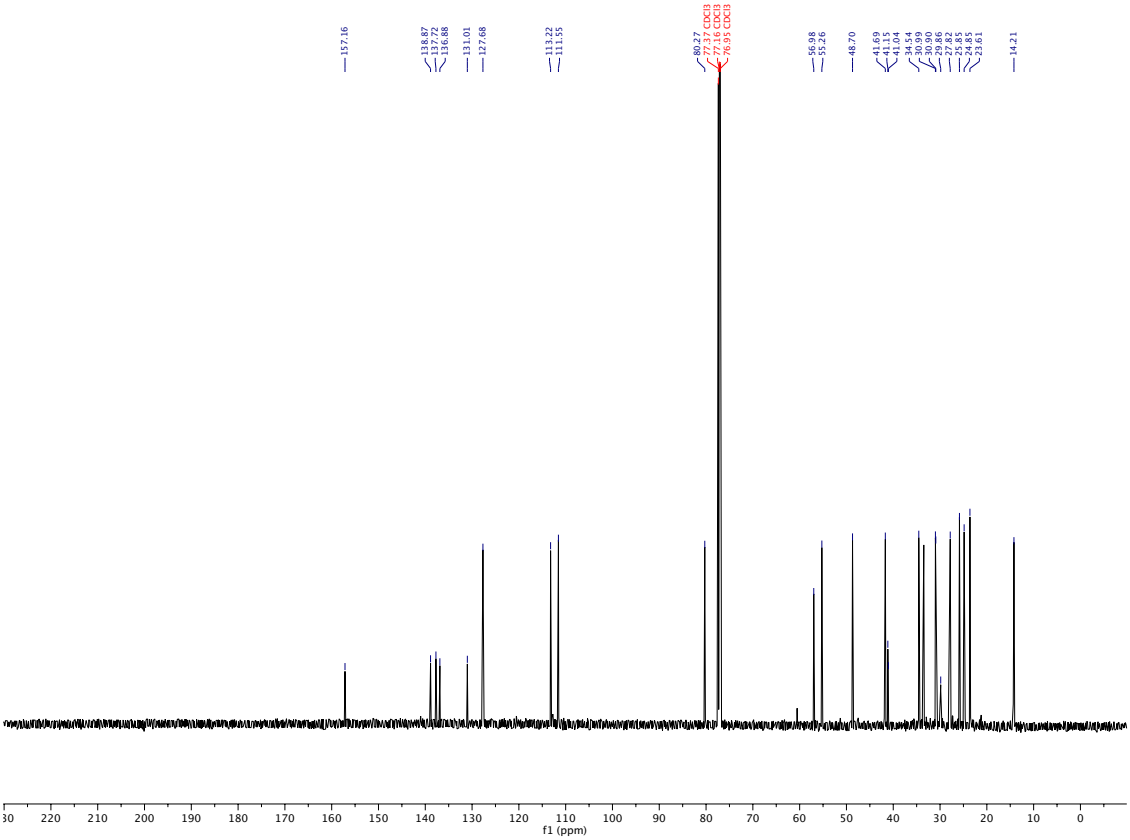


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S38**

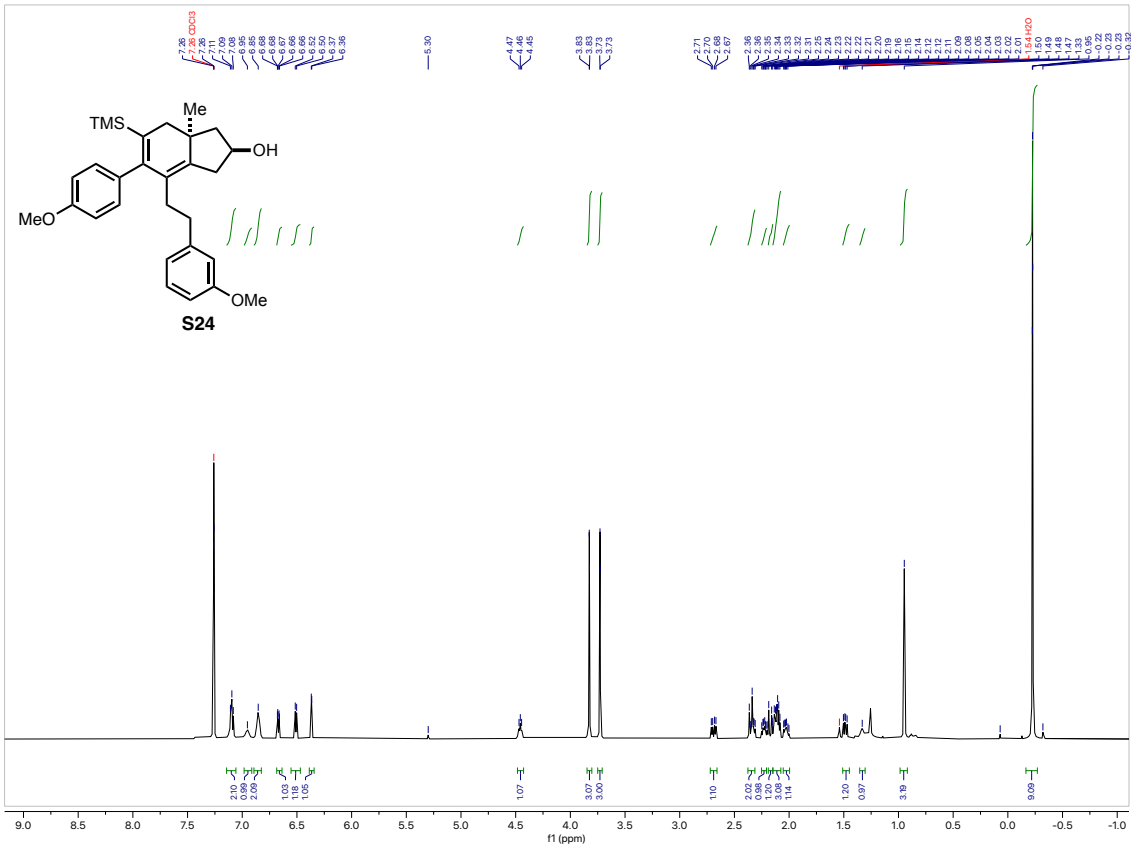


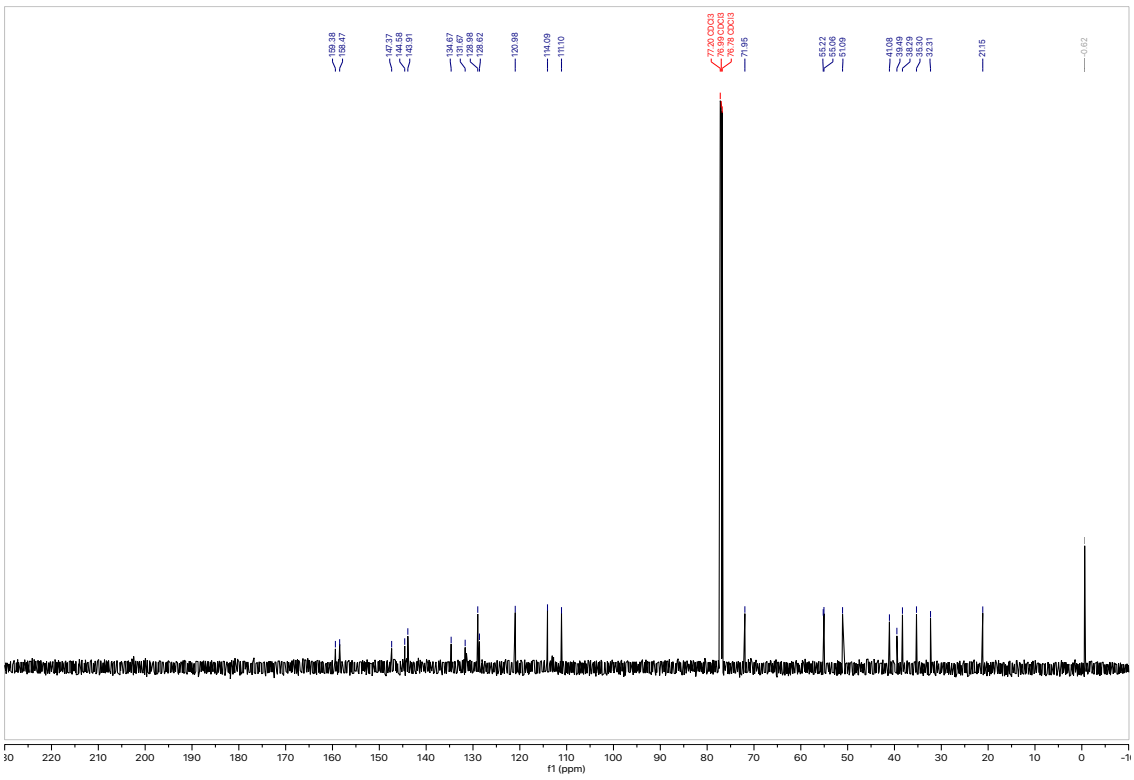
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **48**



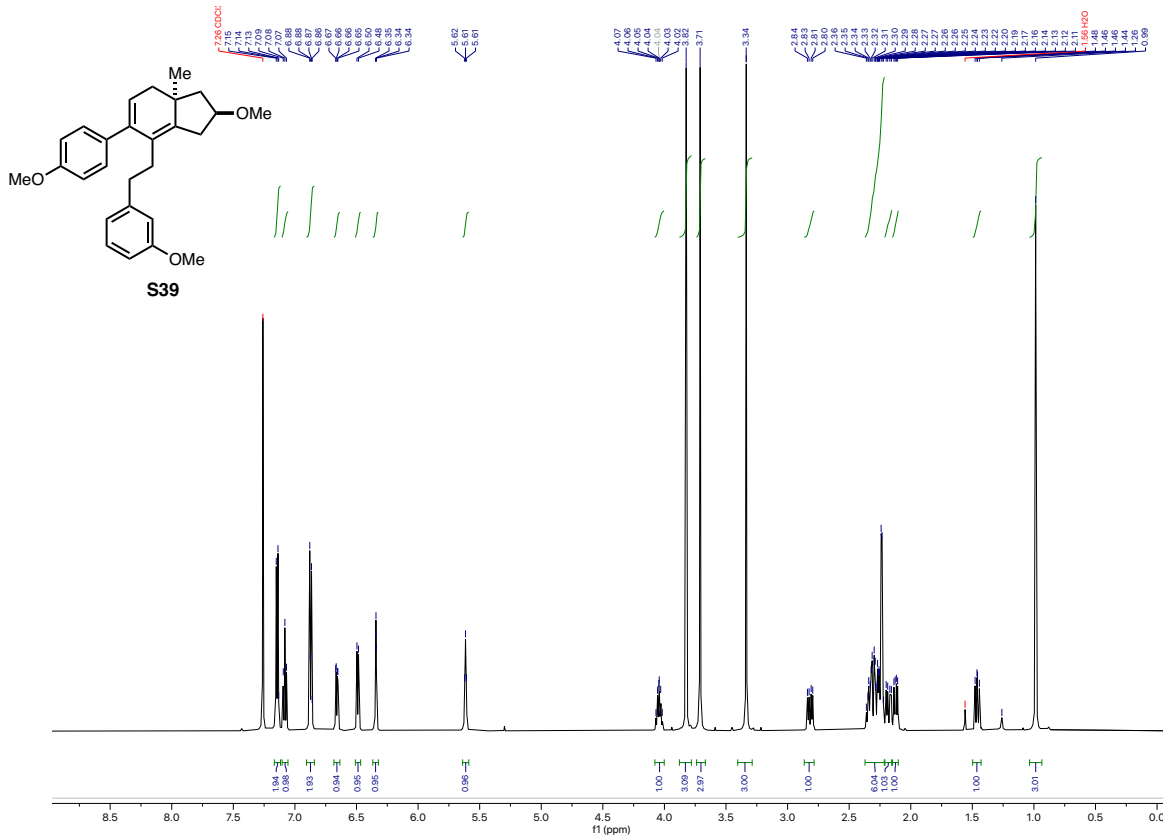


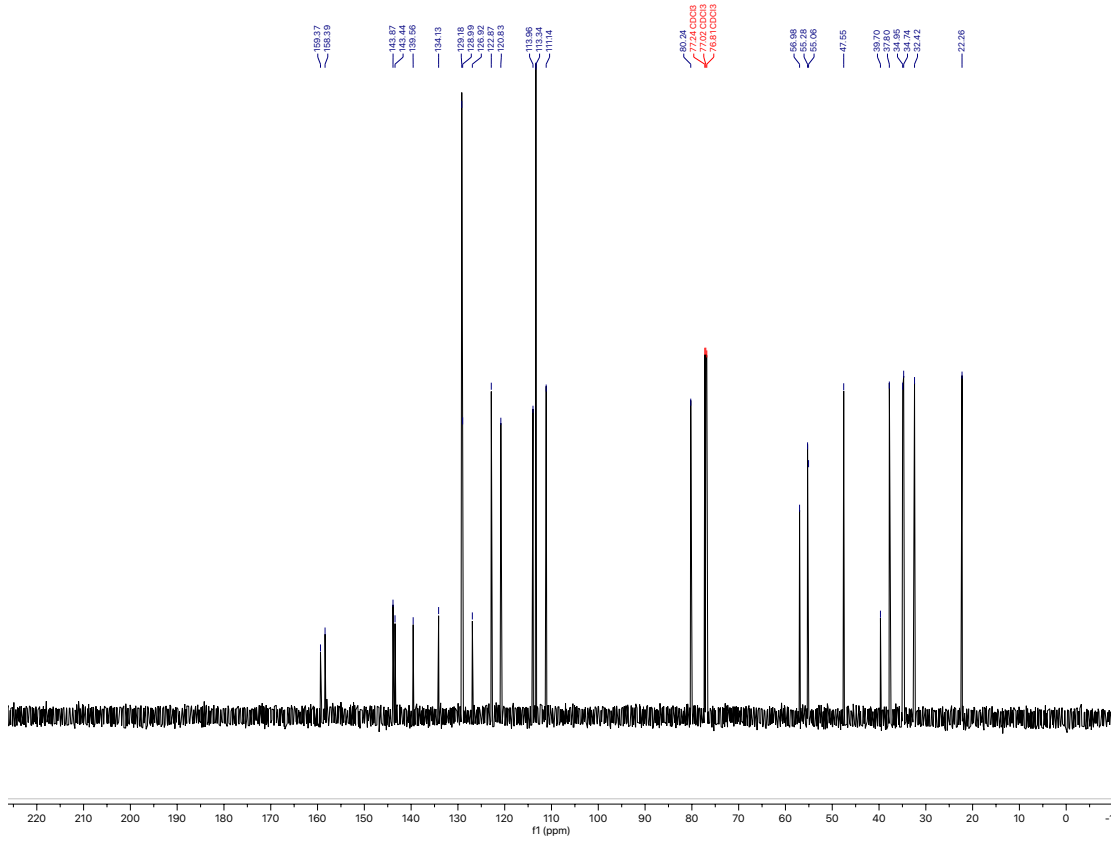
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S24**



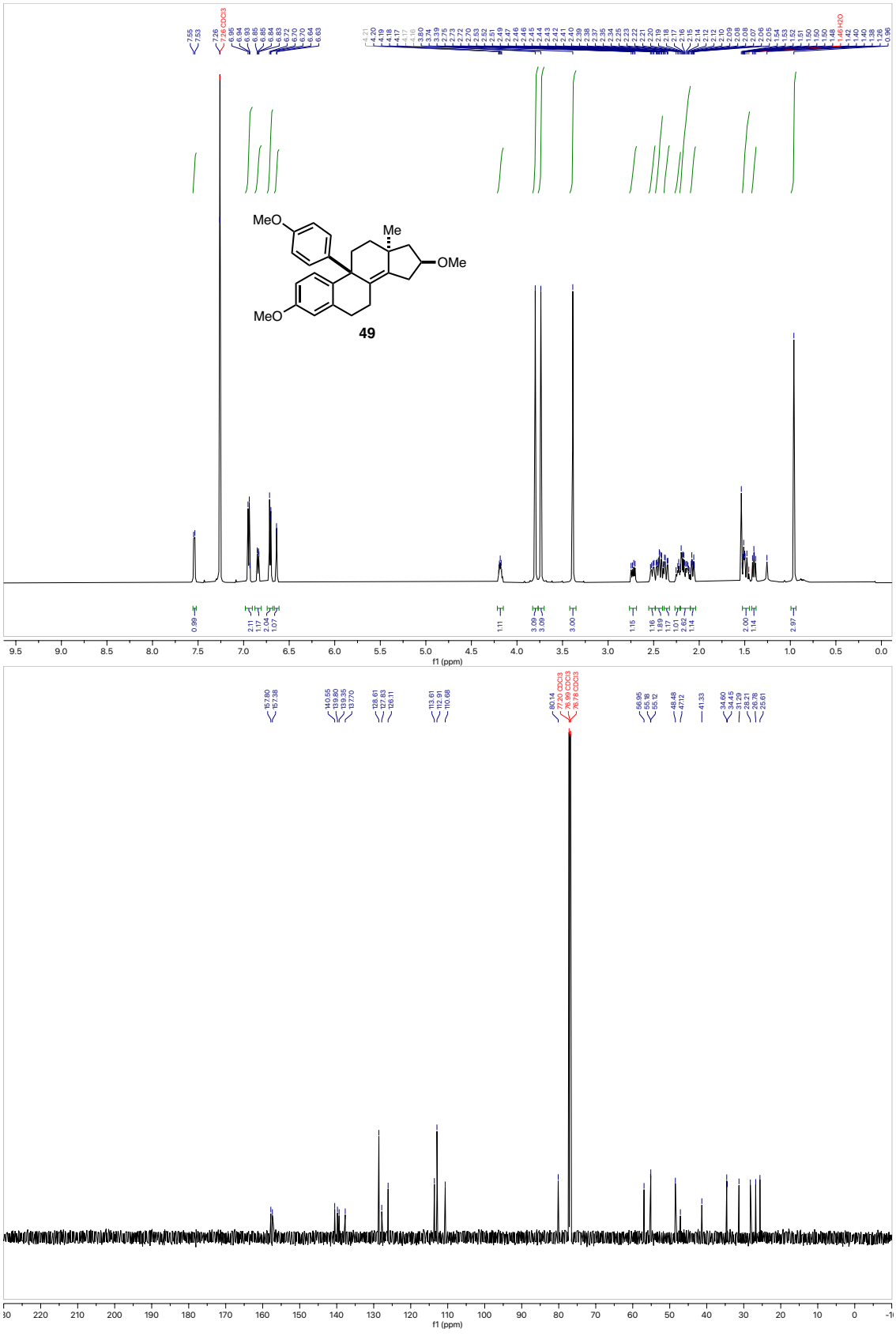


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S39**

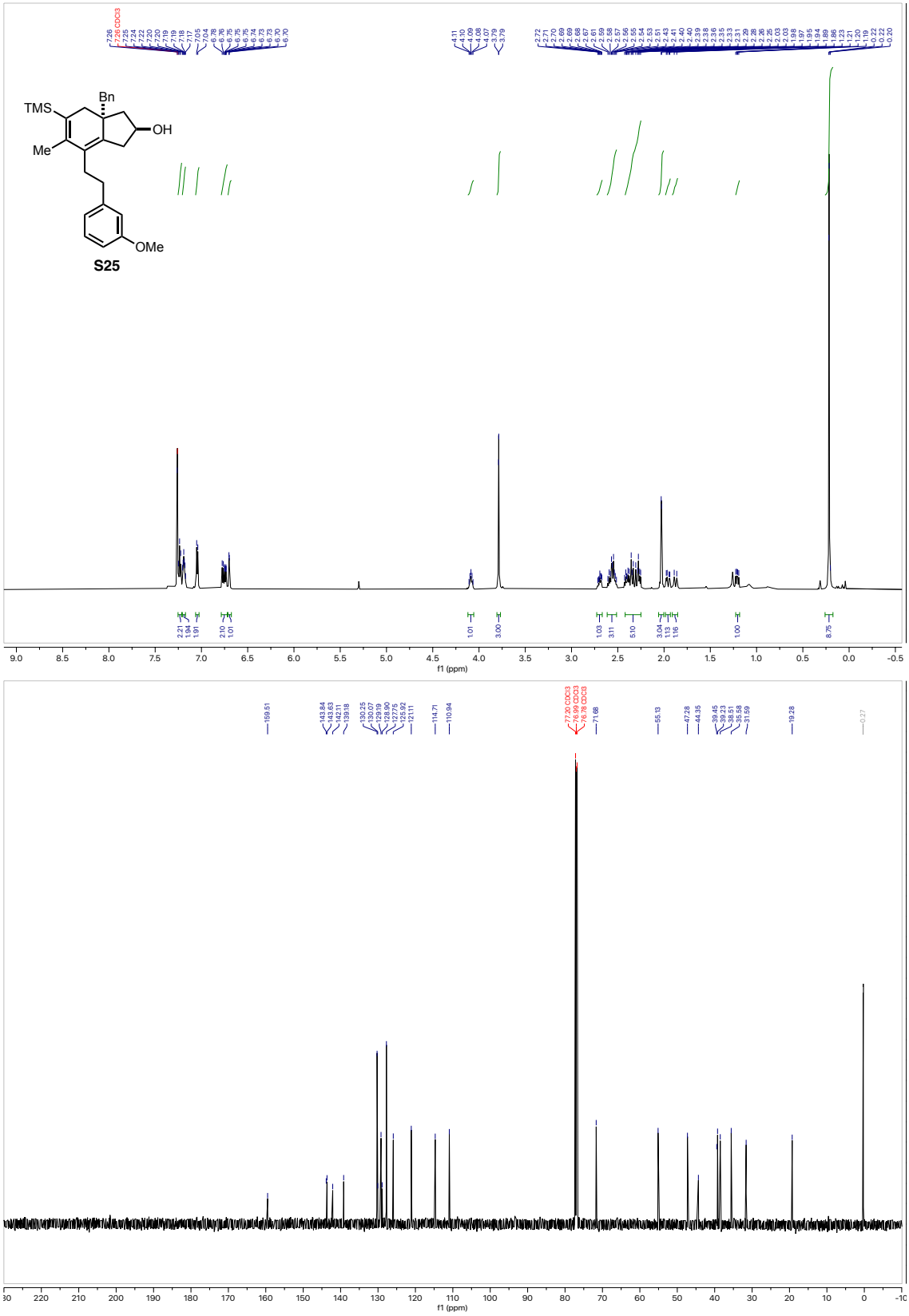




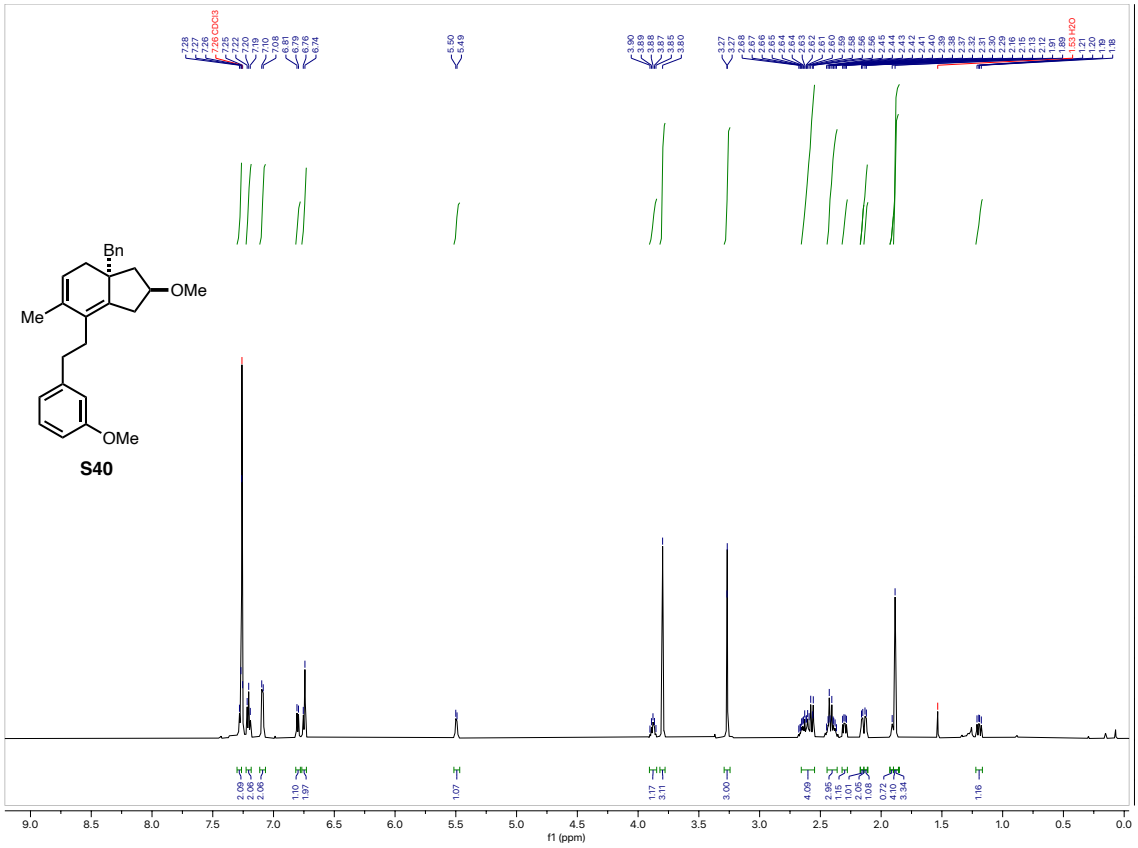
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **49**

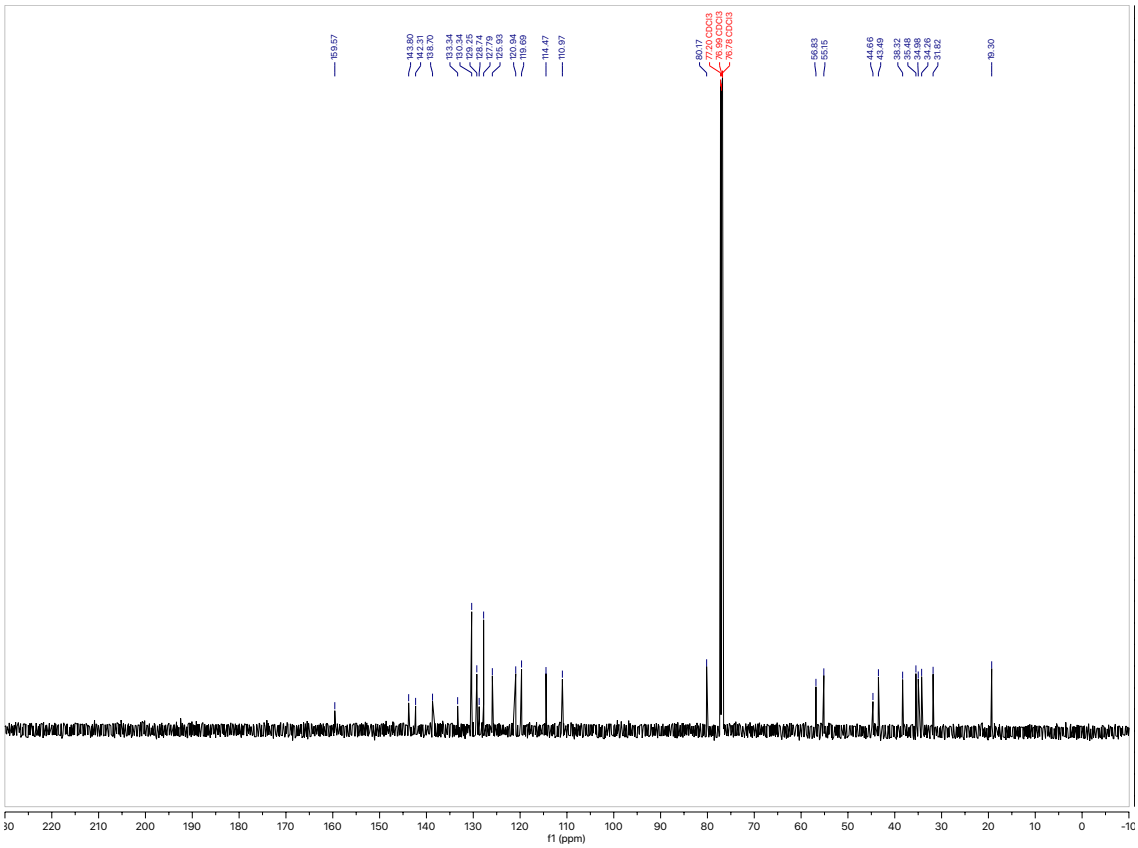


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S25**

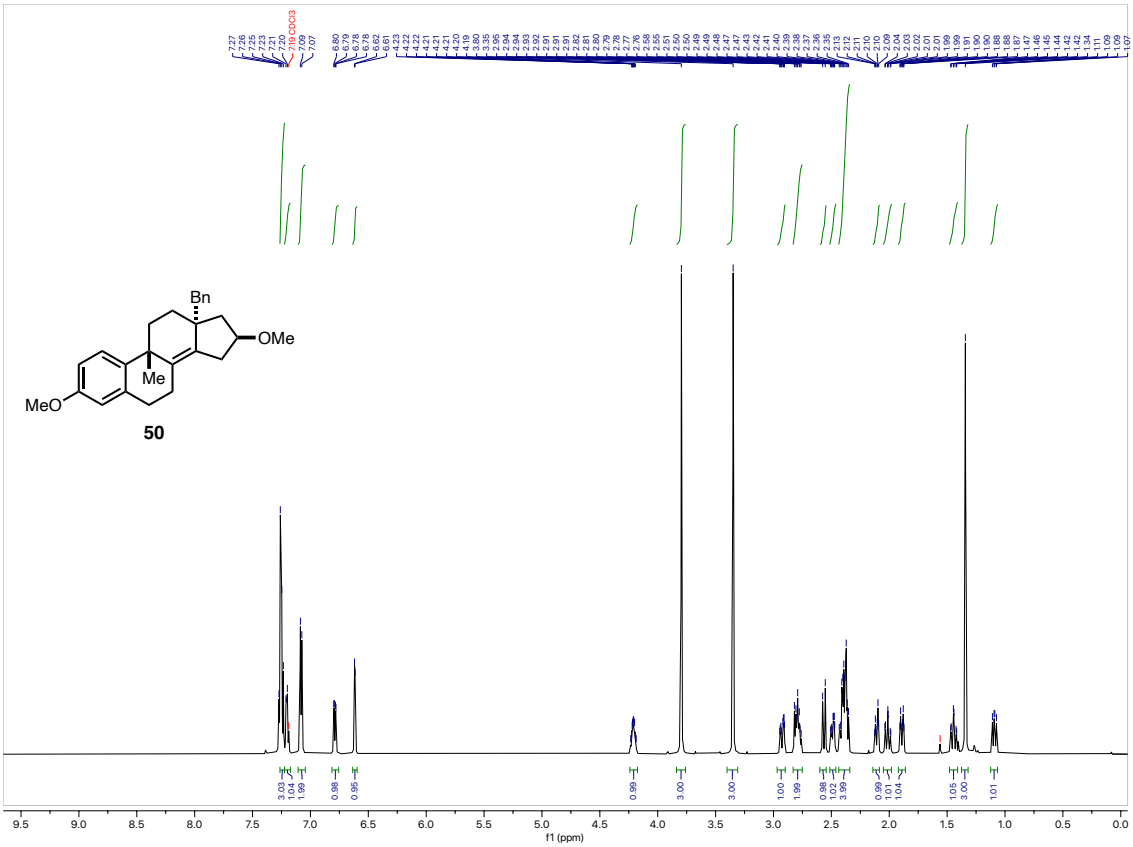


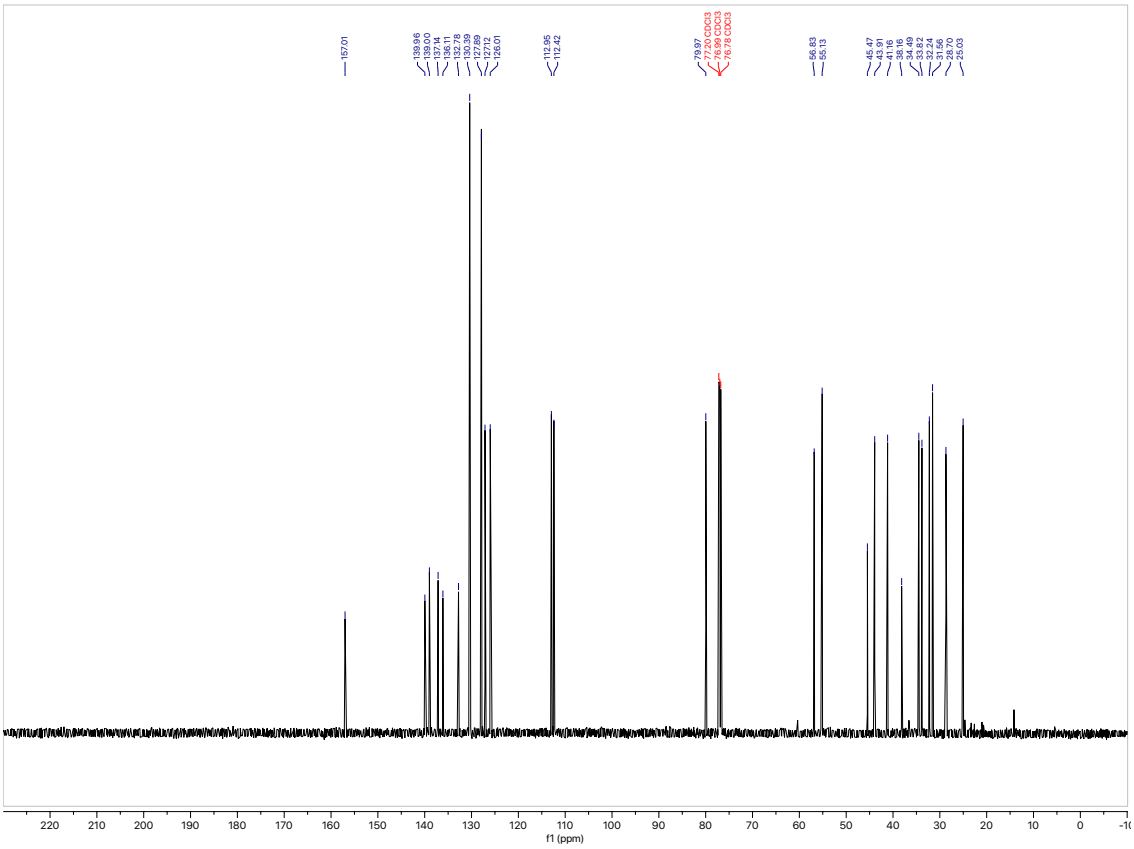
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S40**



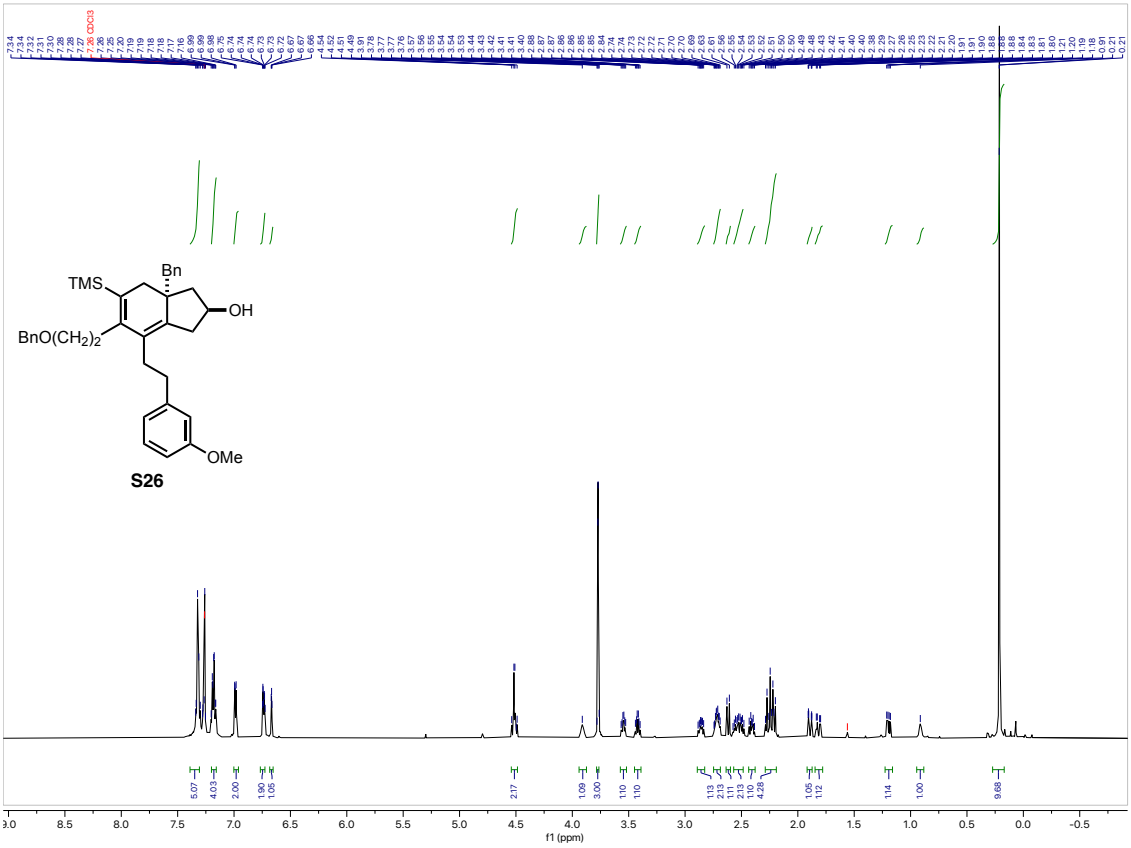


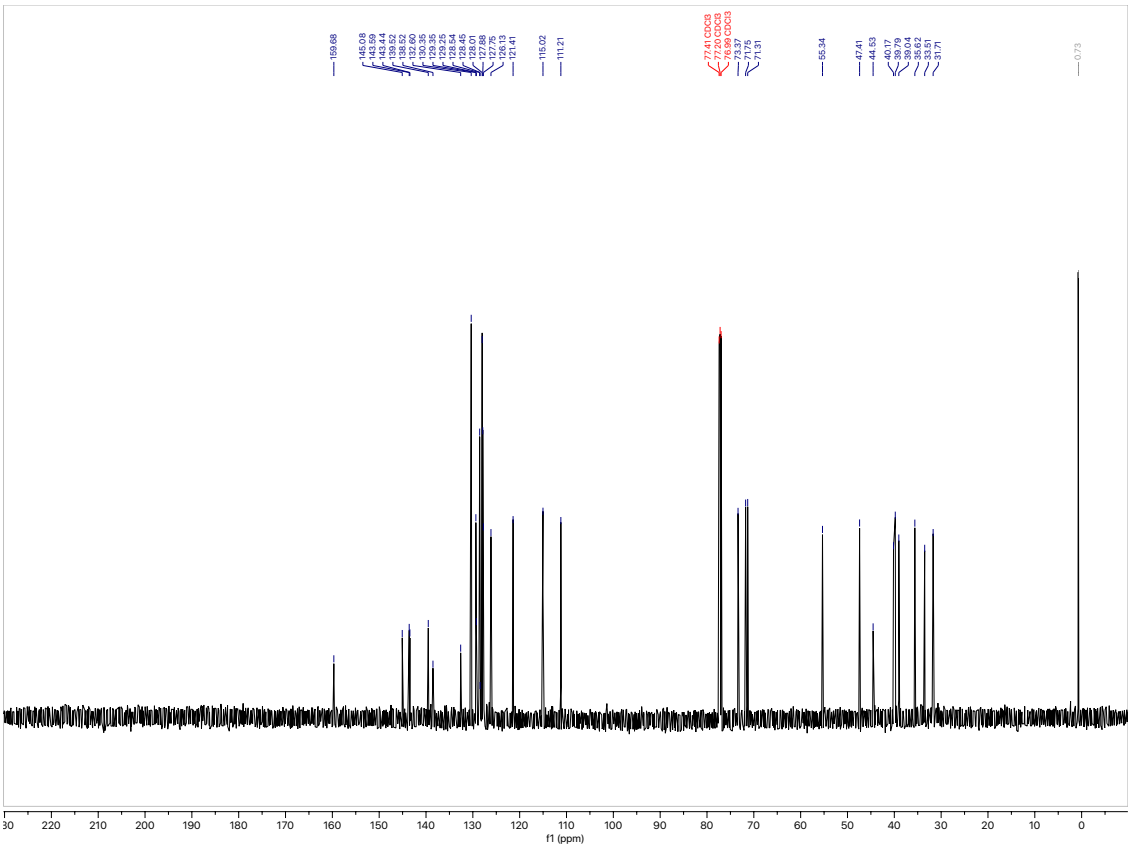
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **50**



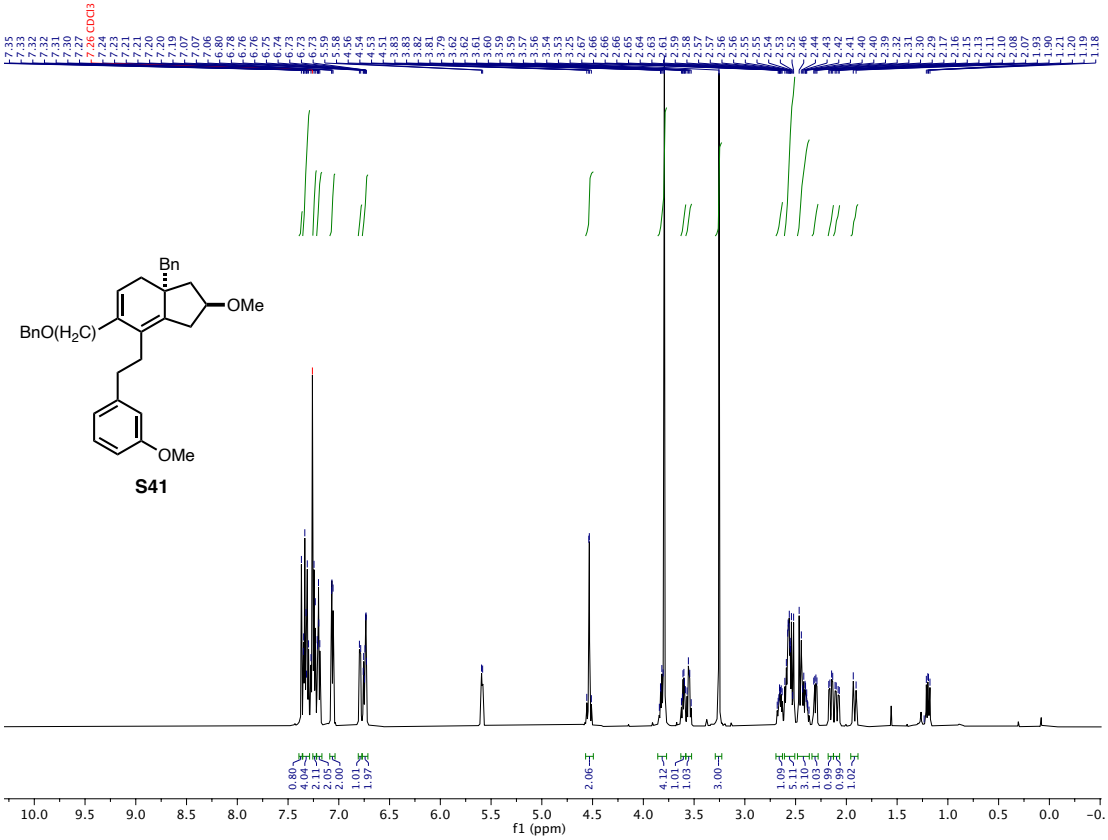


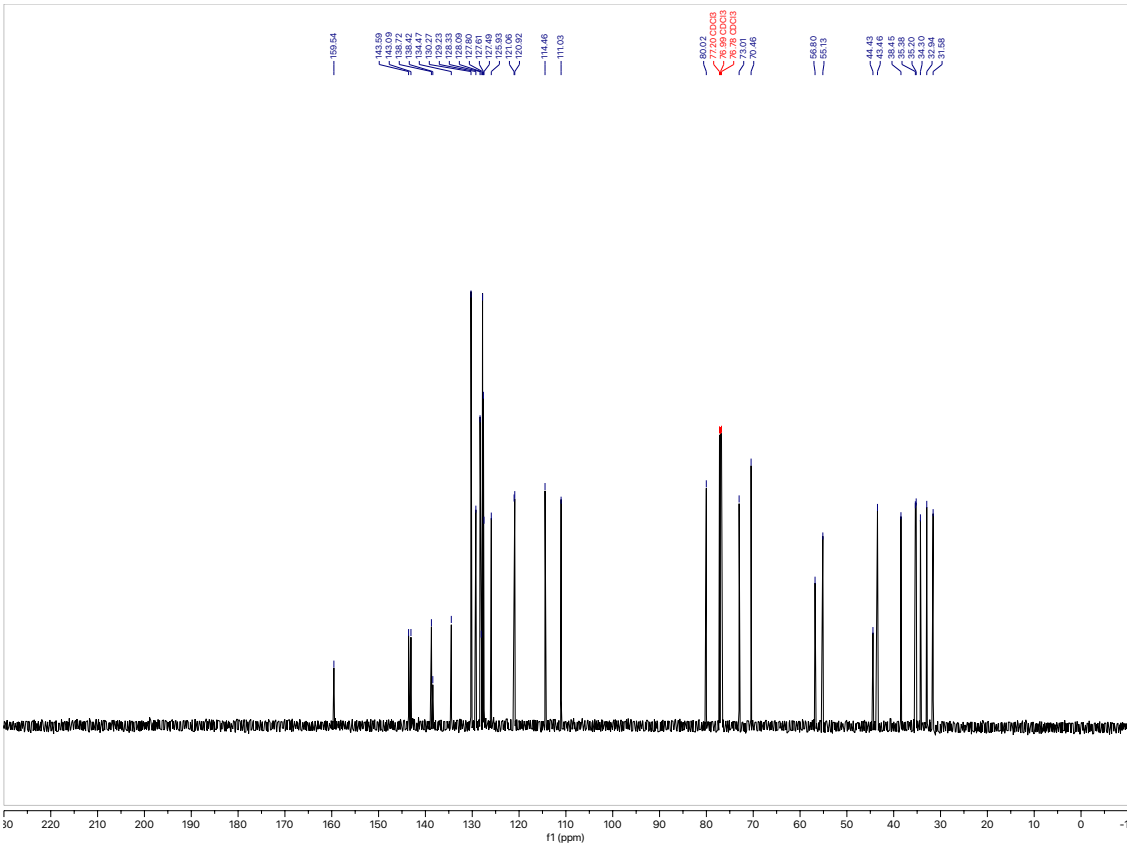
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S26**



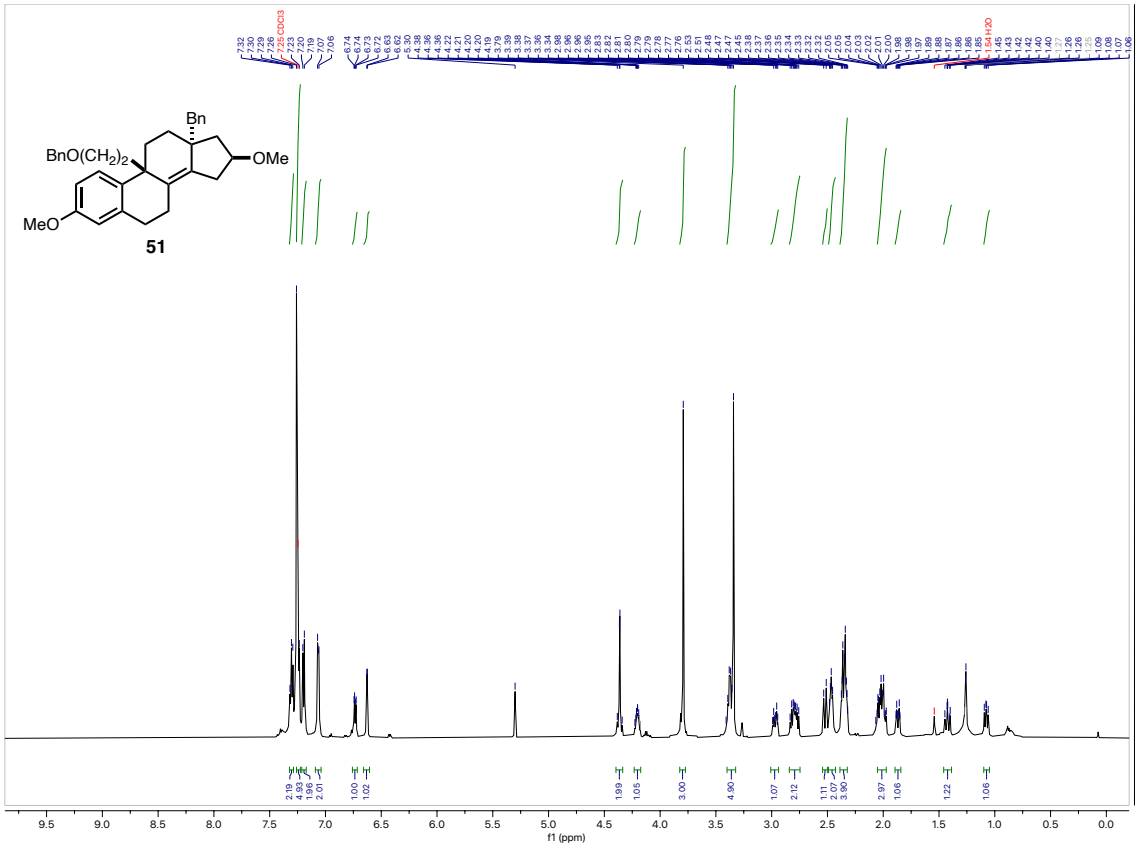


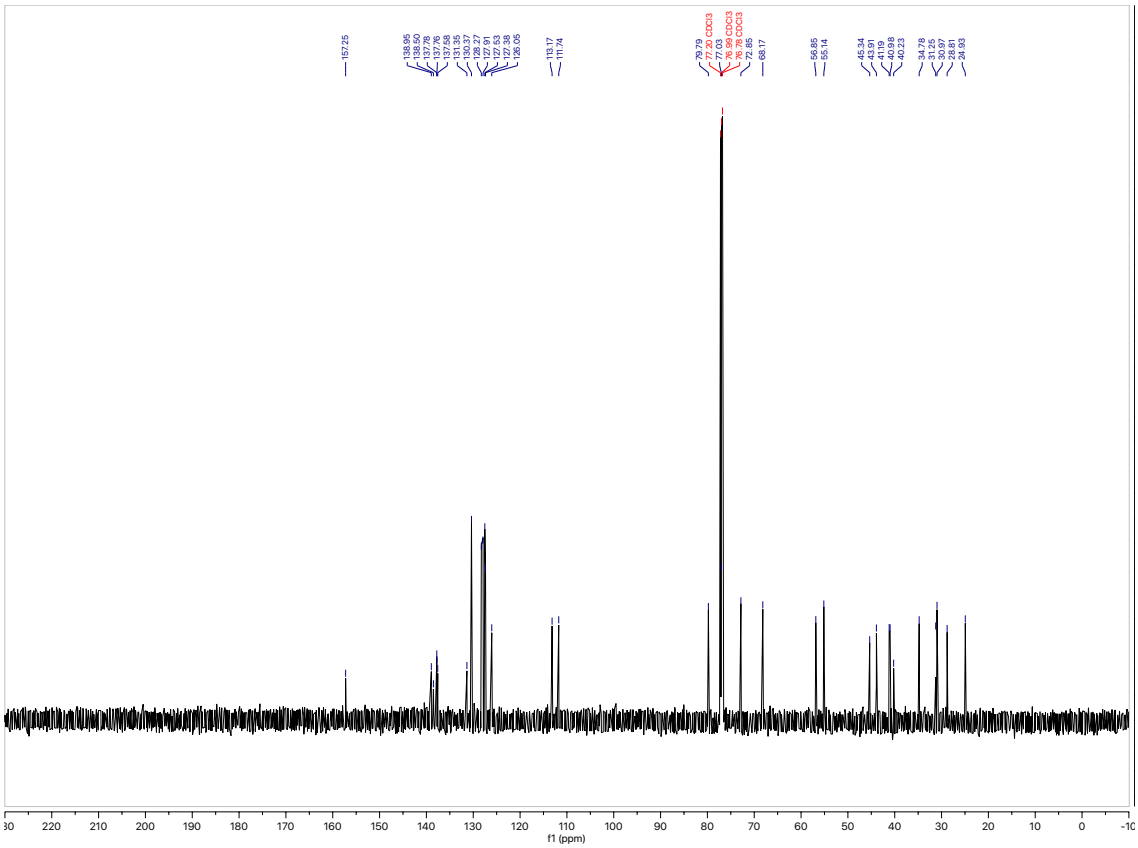
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S41**



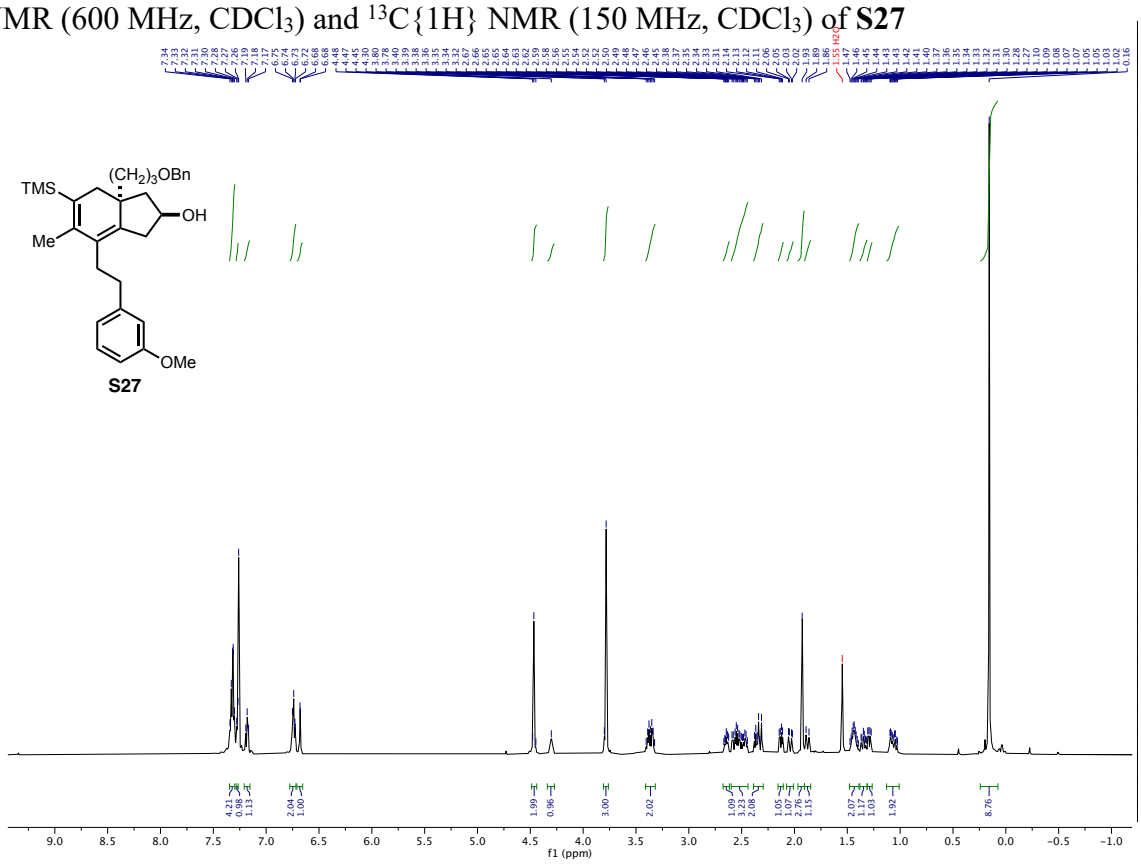


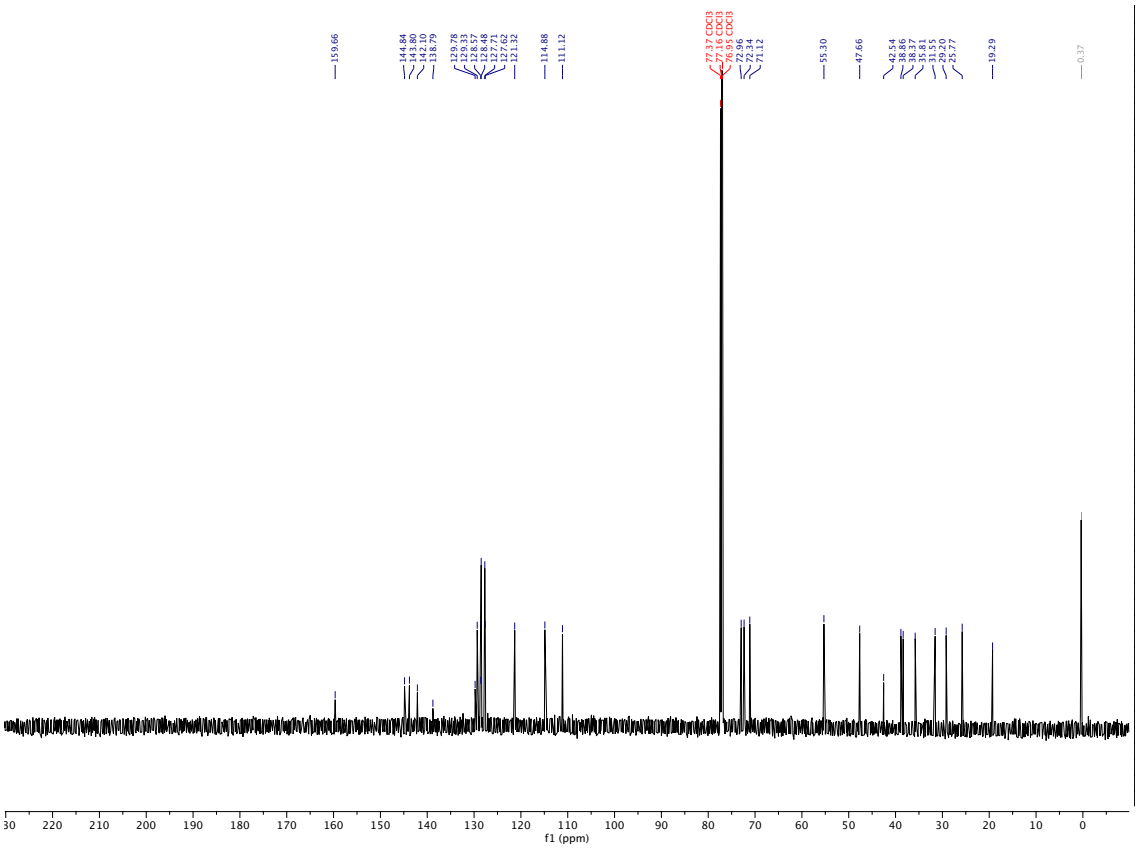
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **51**



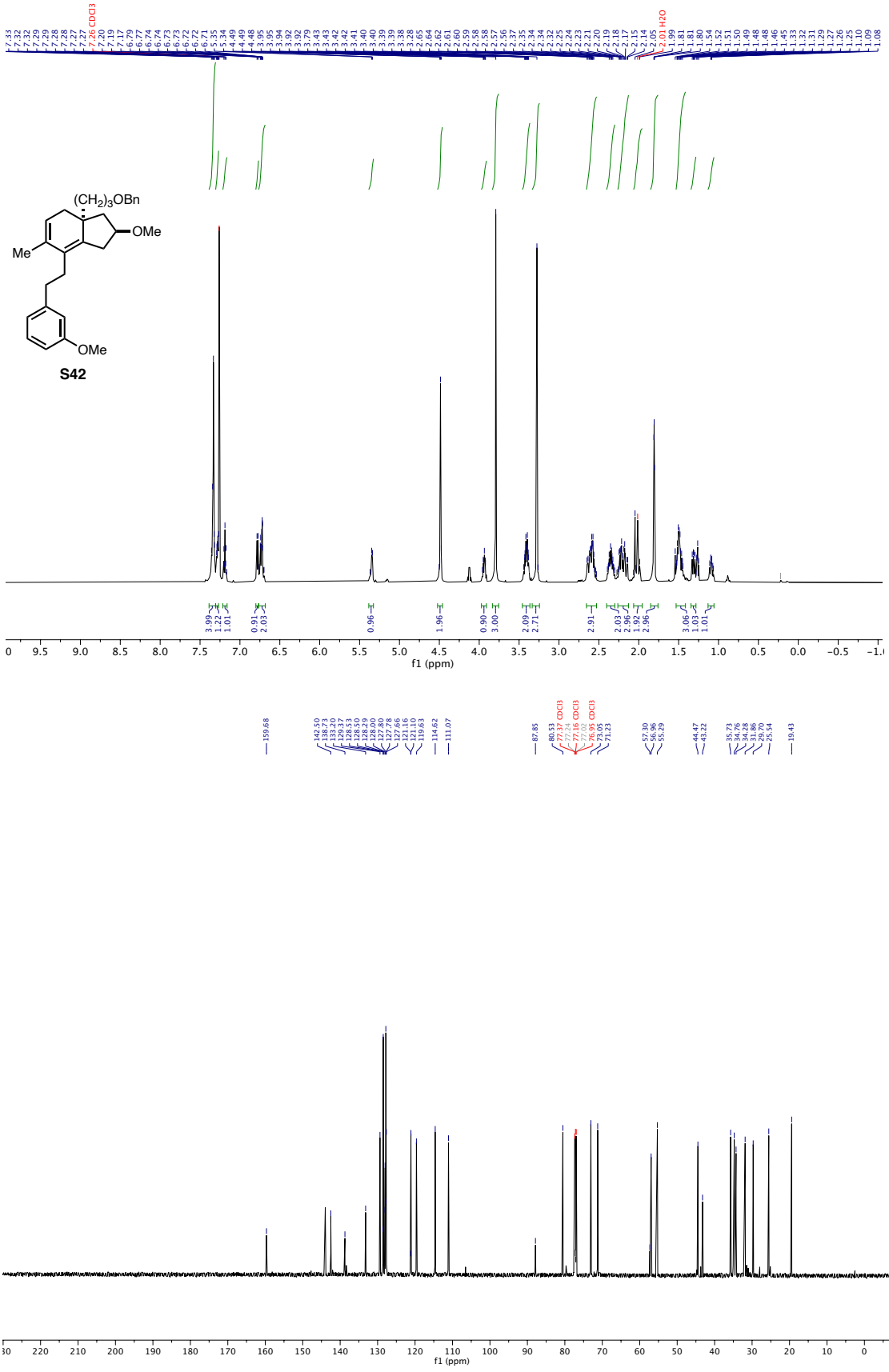


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S27**

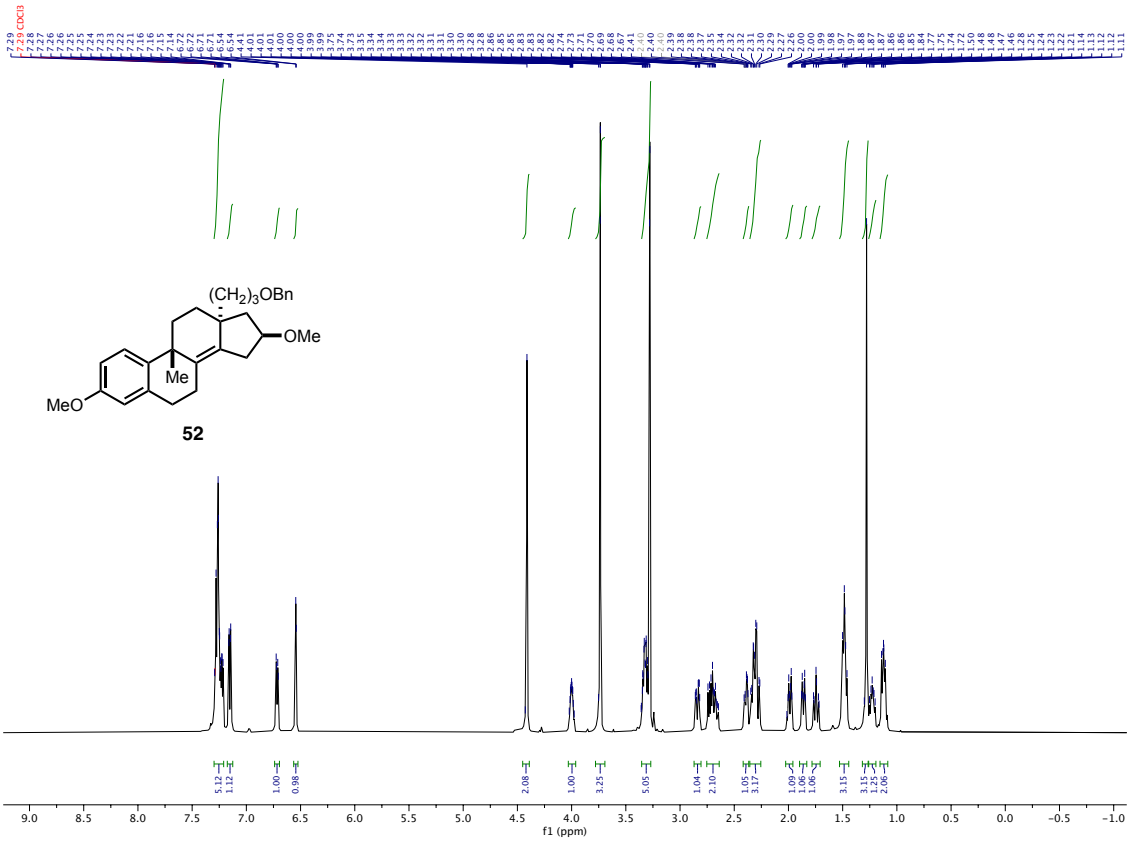




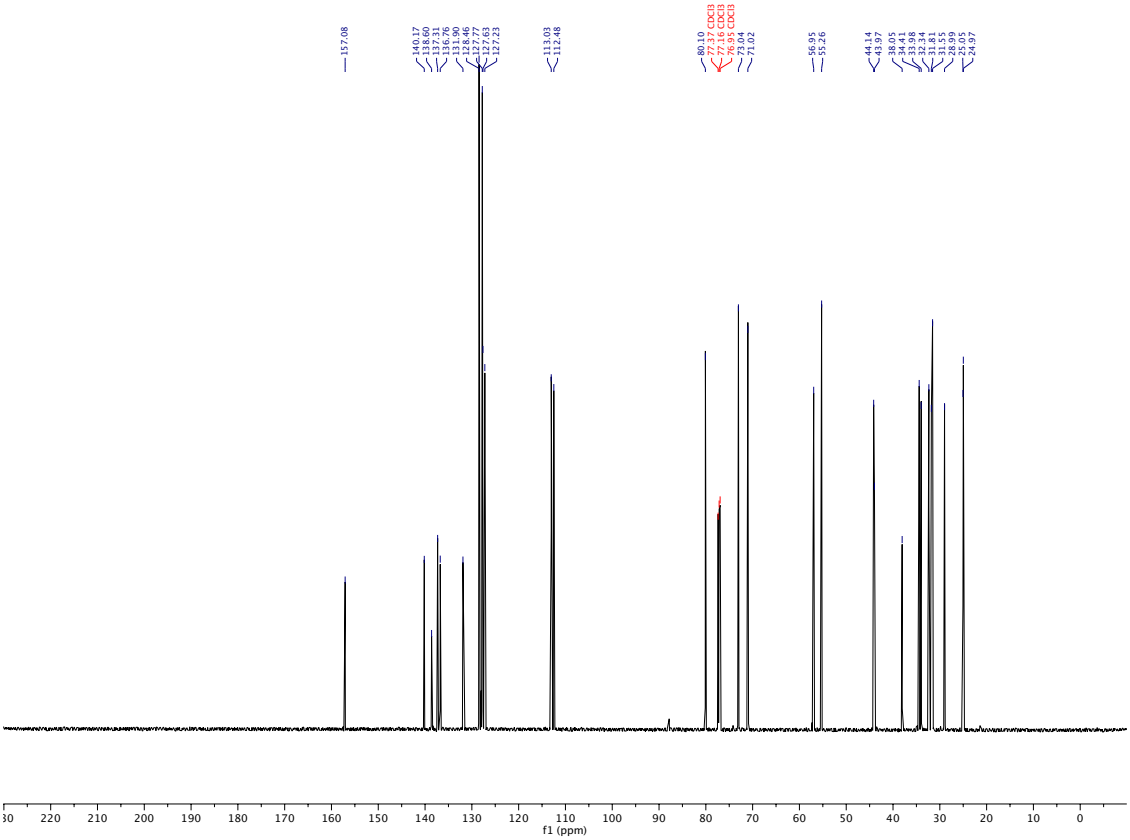
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S42**



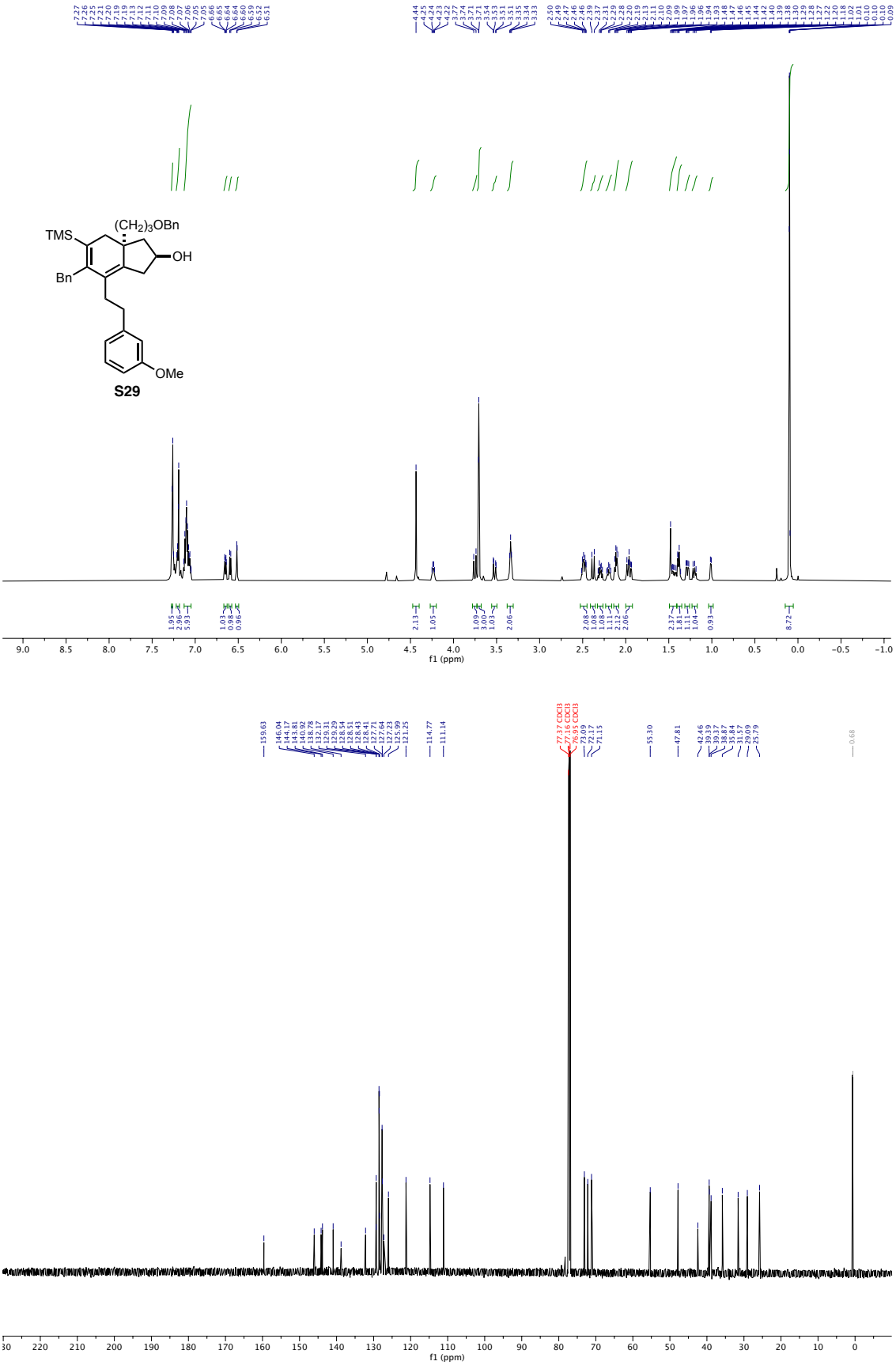
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **52**



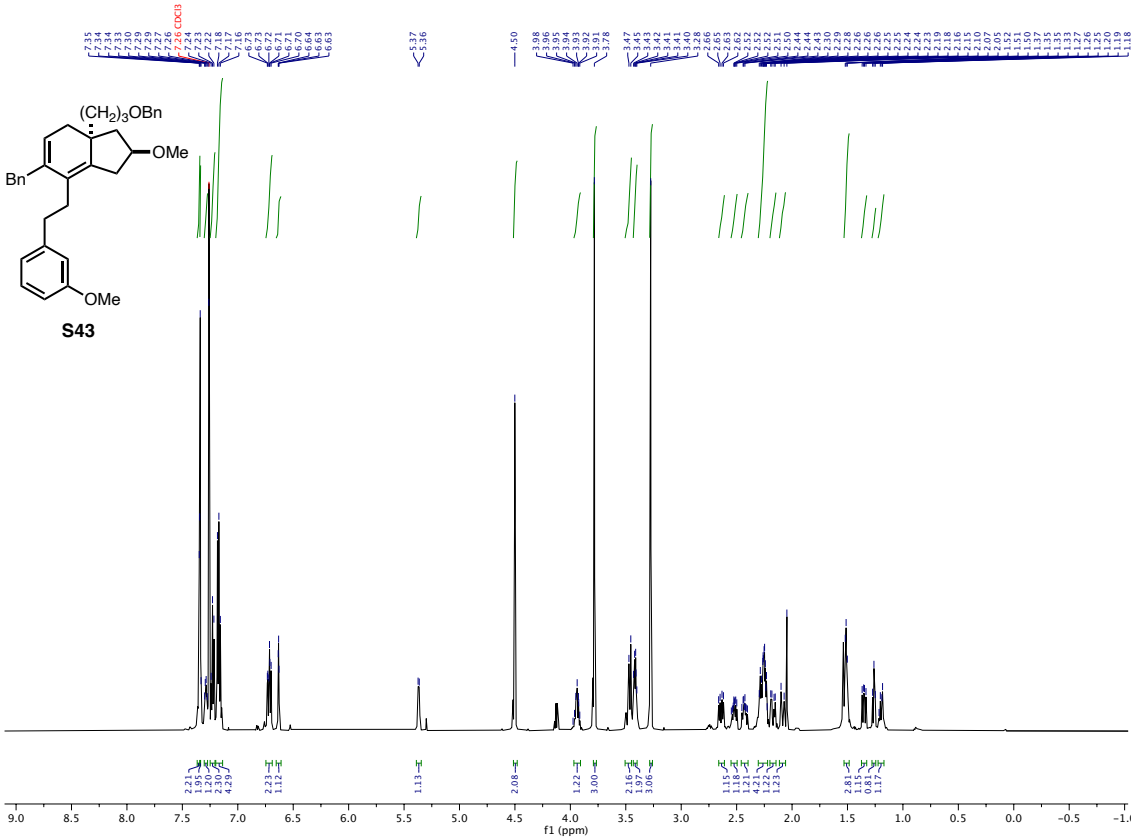
52

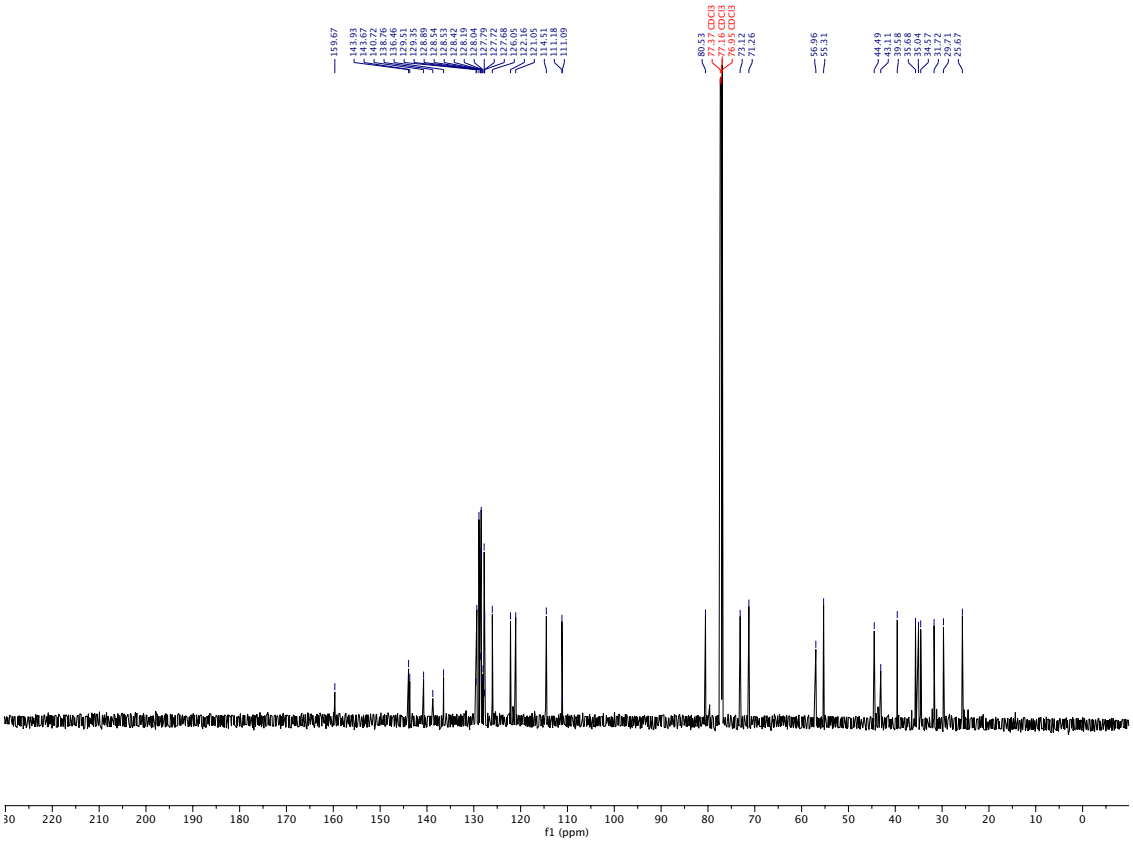


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S29**

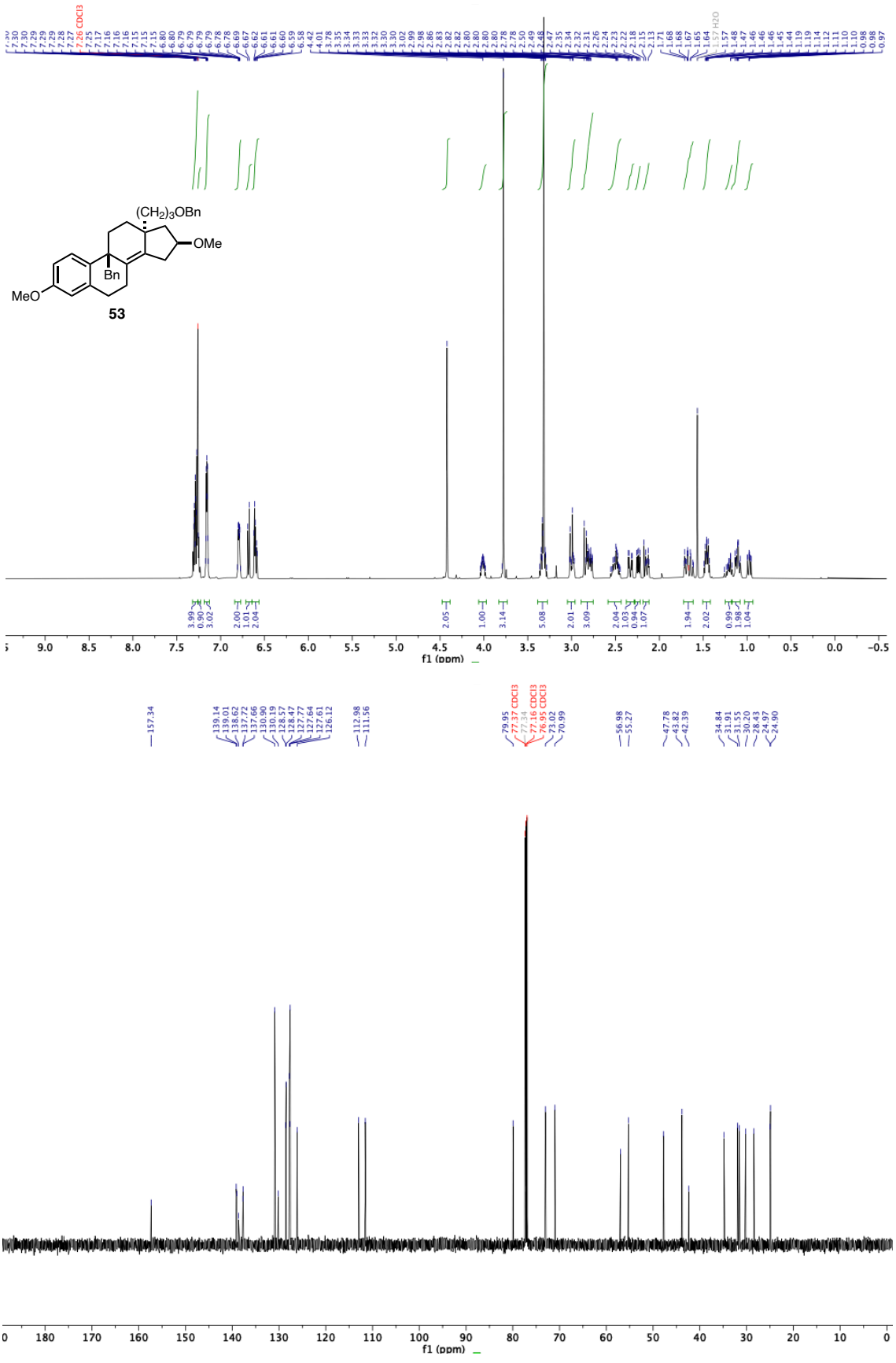


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S43**

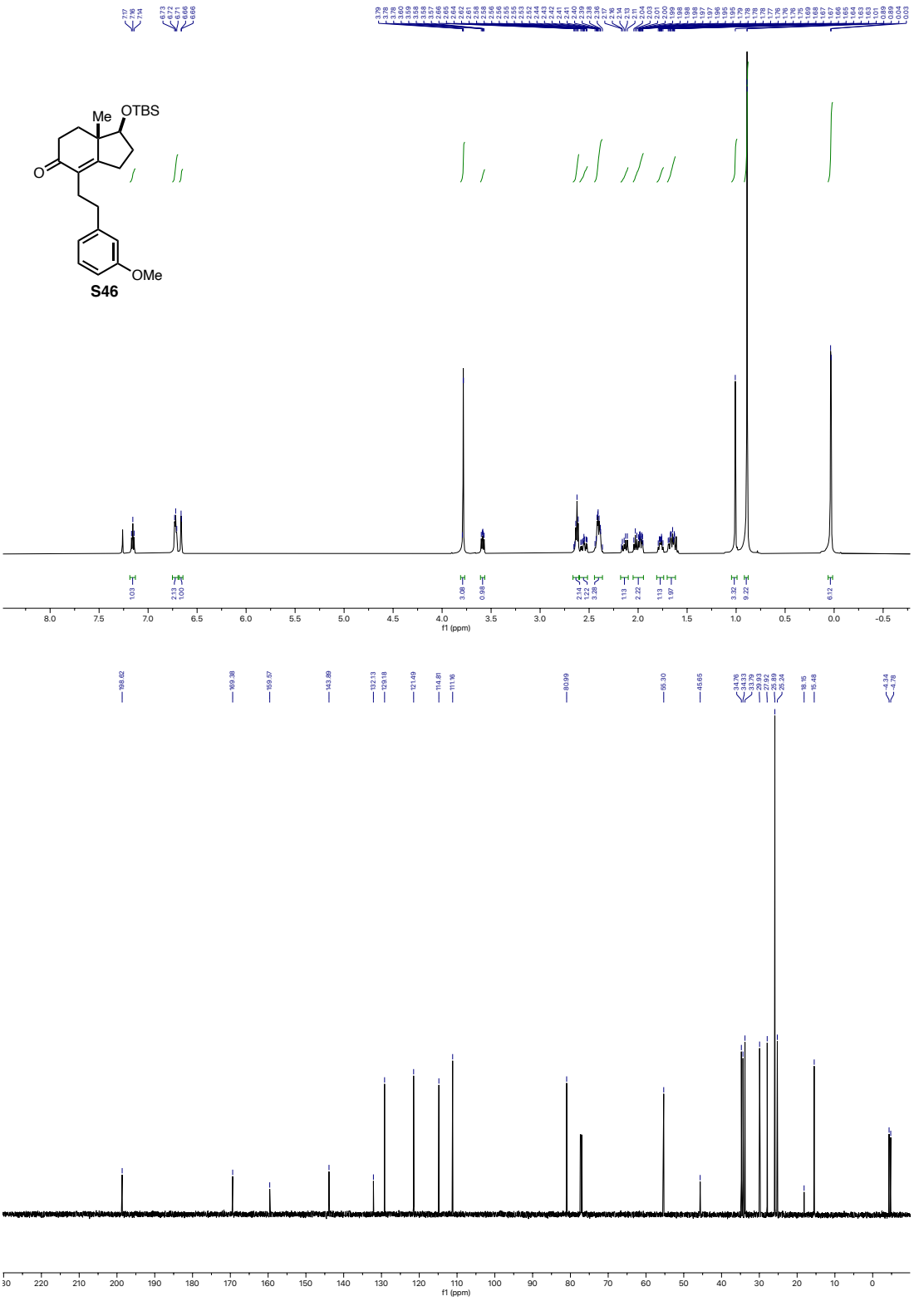




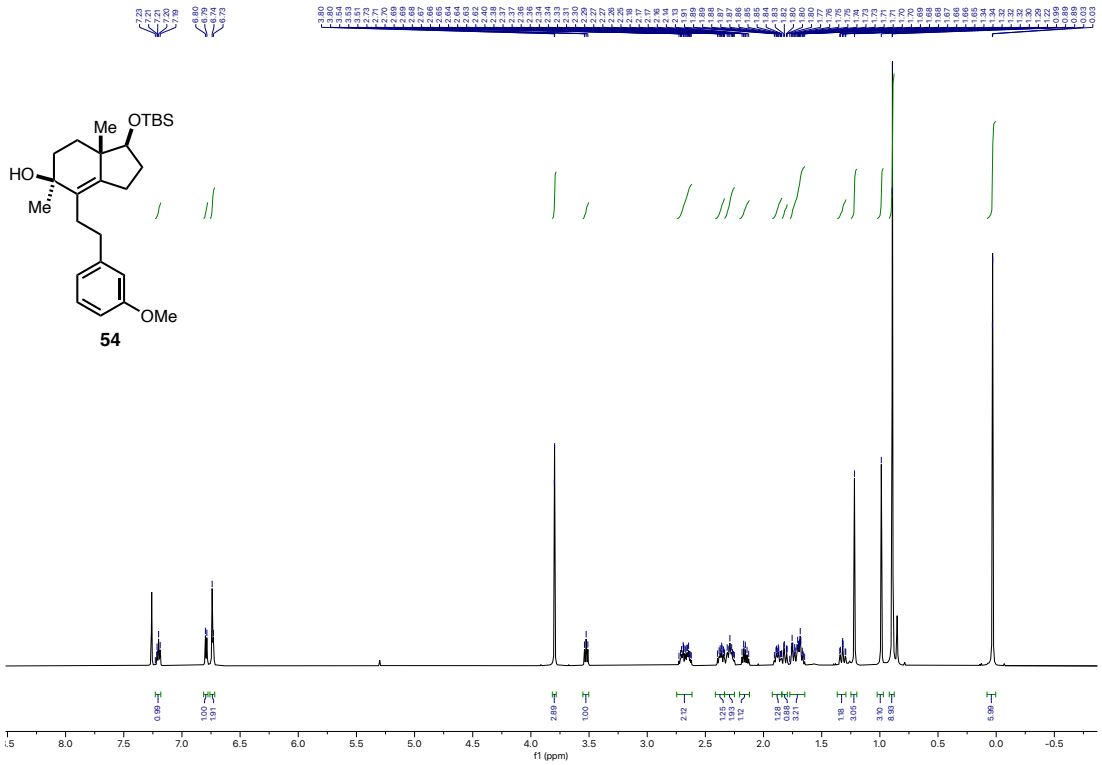
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **53**

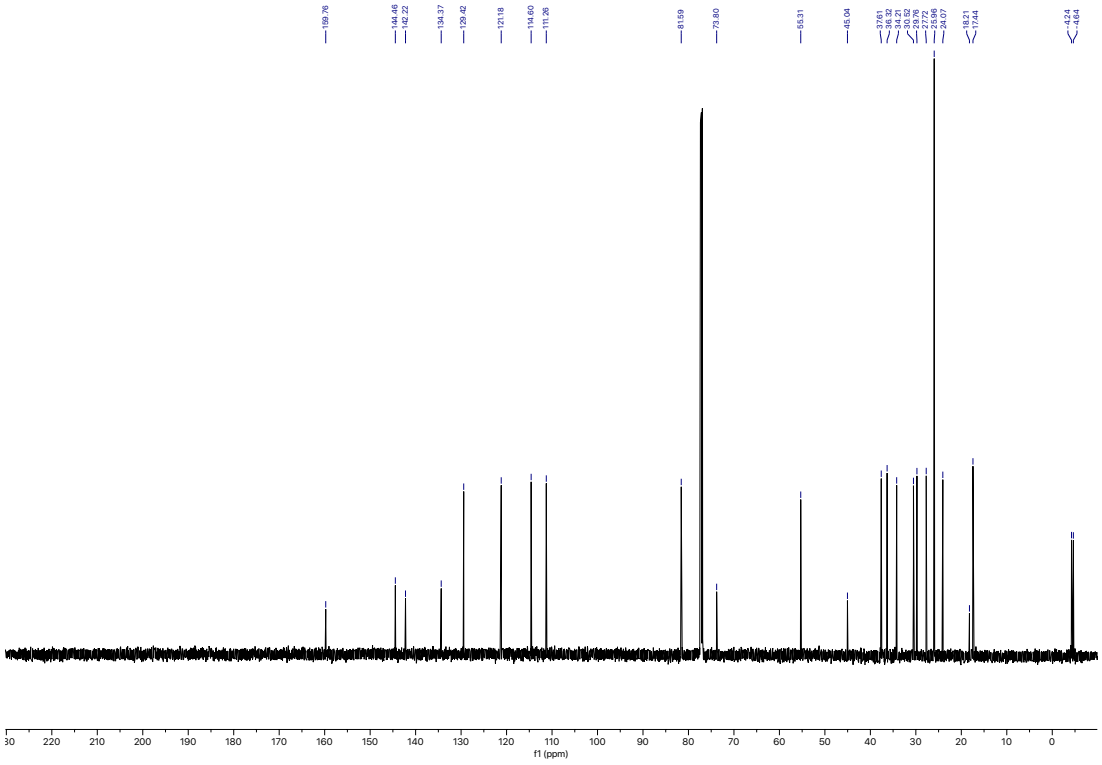


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S46**

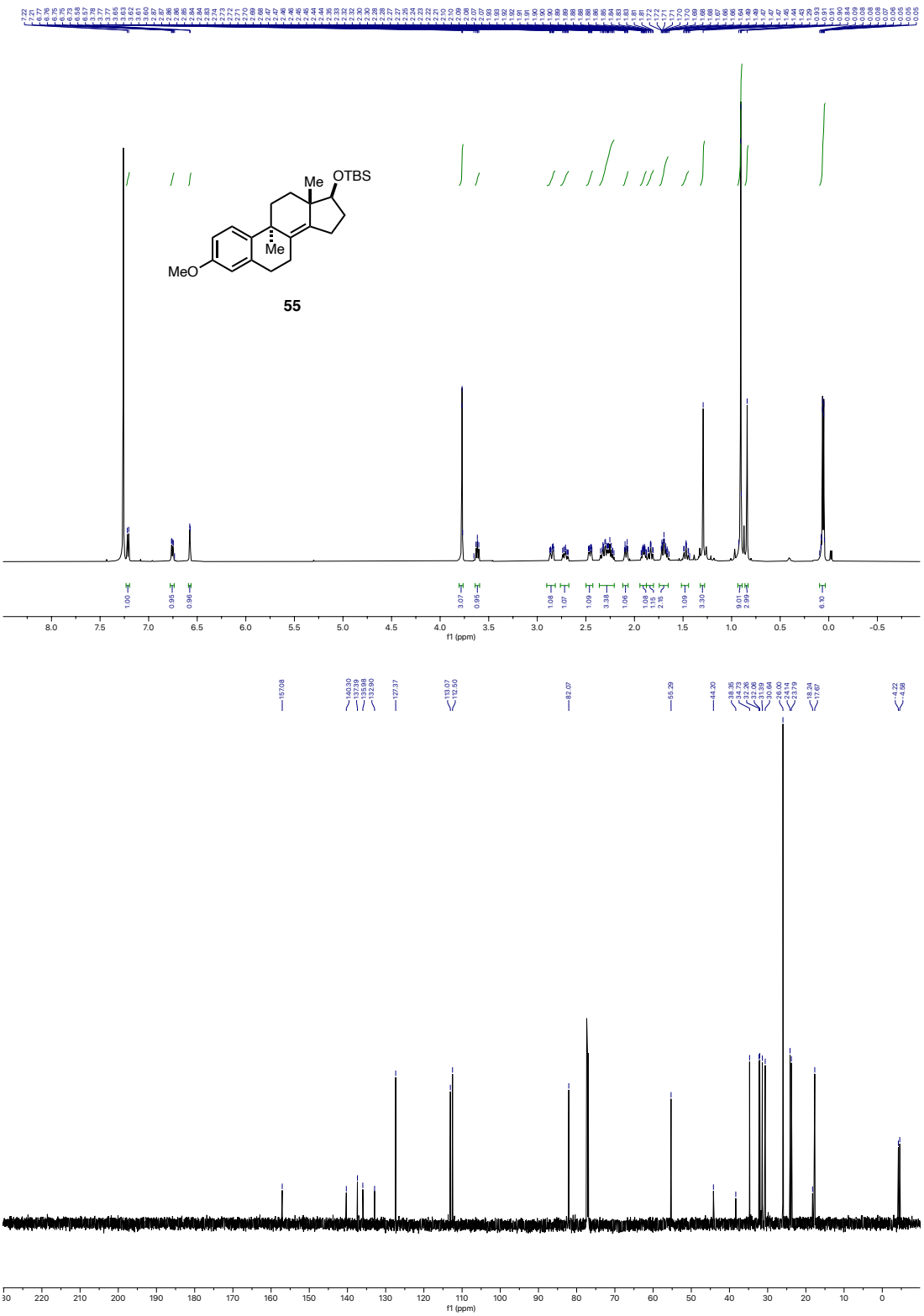


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **54**

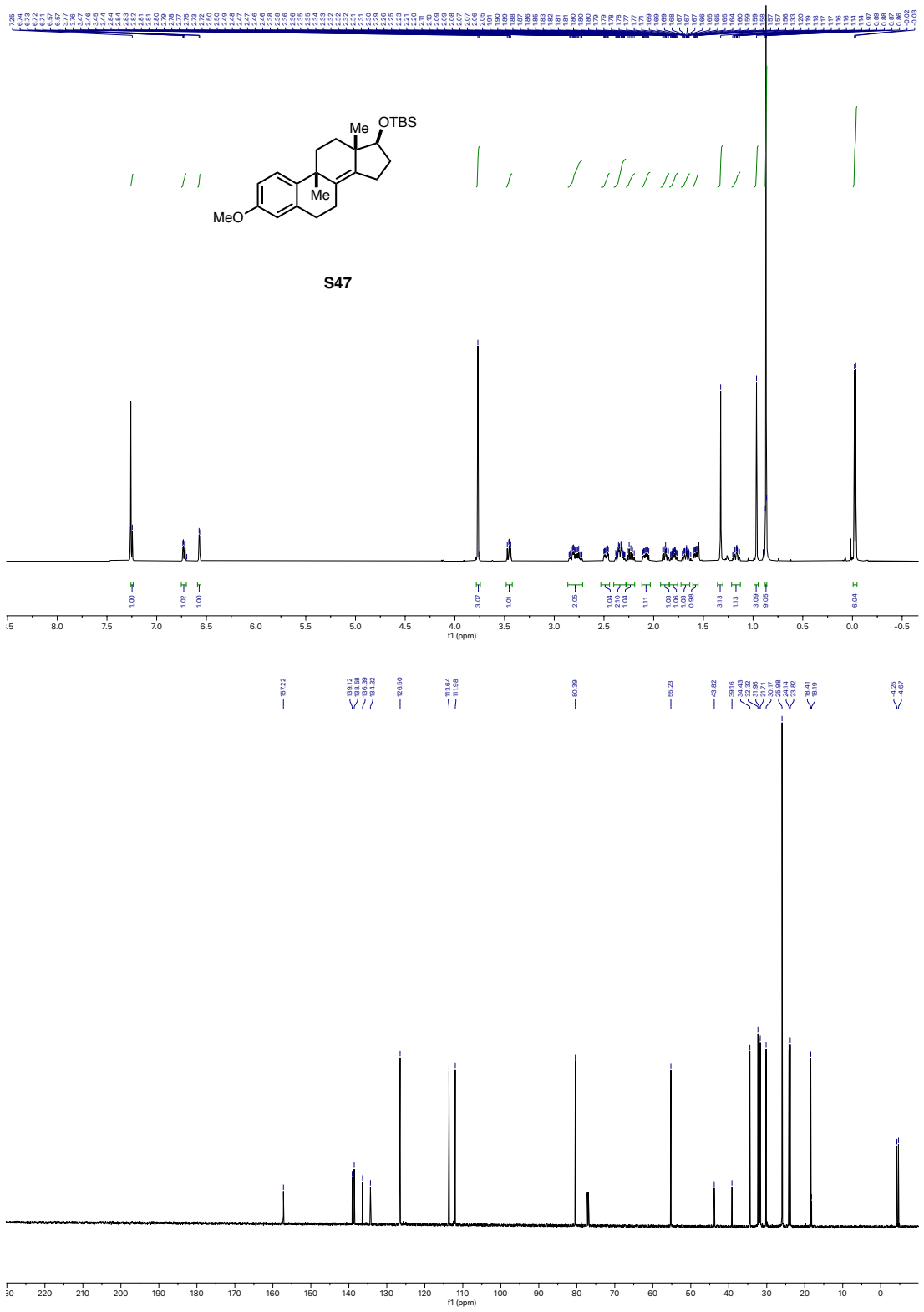




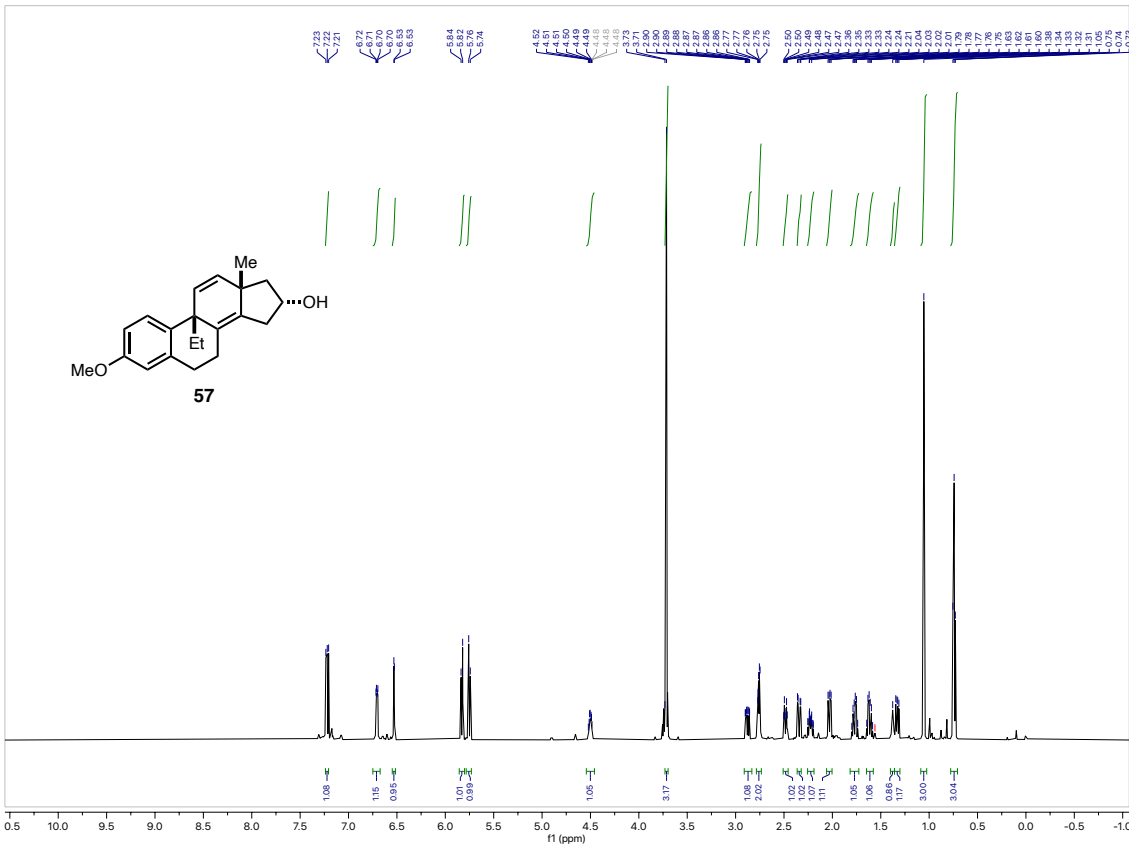
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **55**

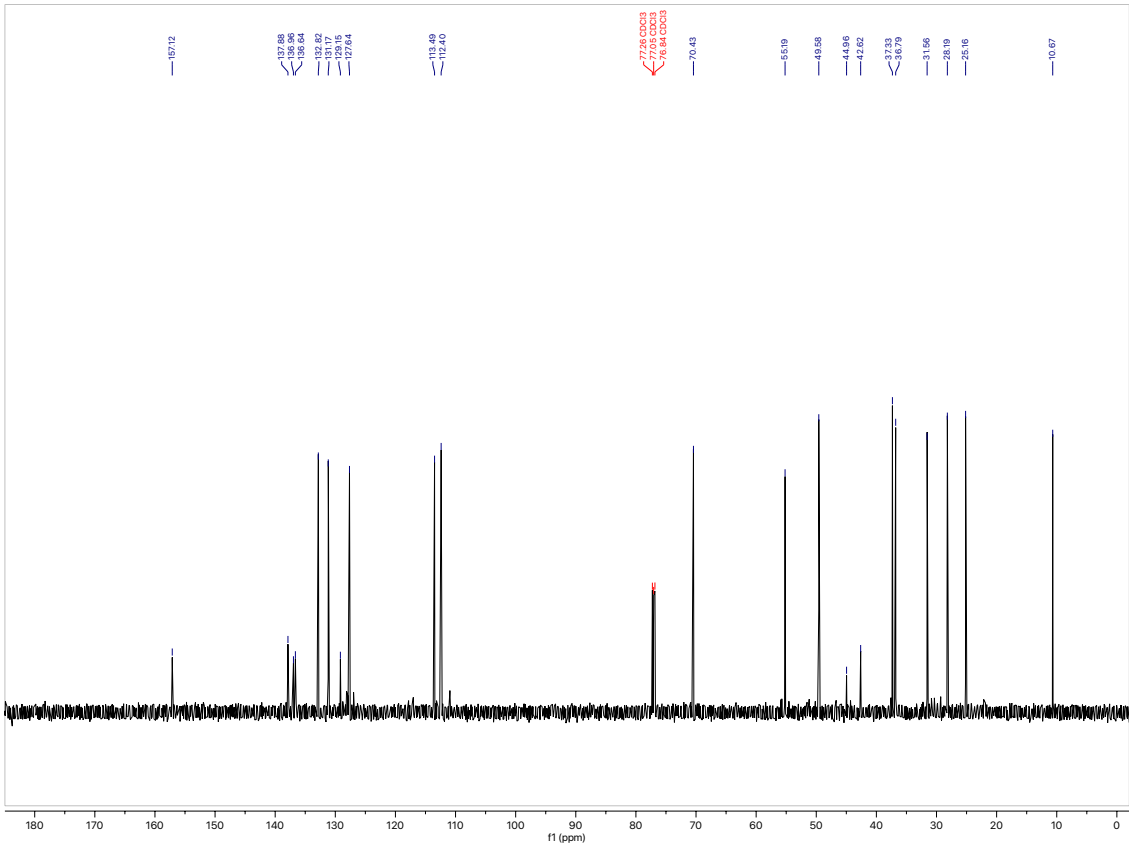


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **S47**

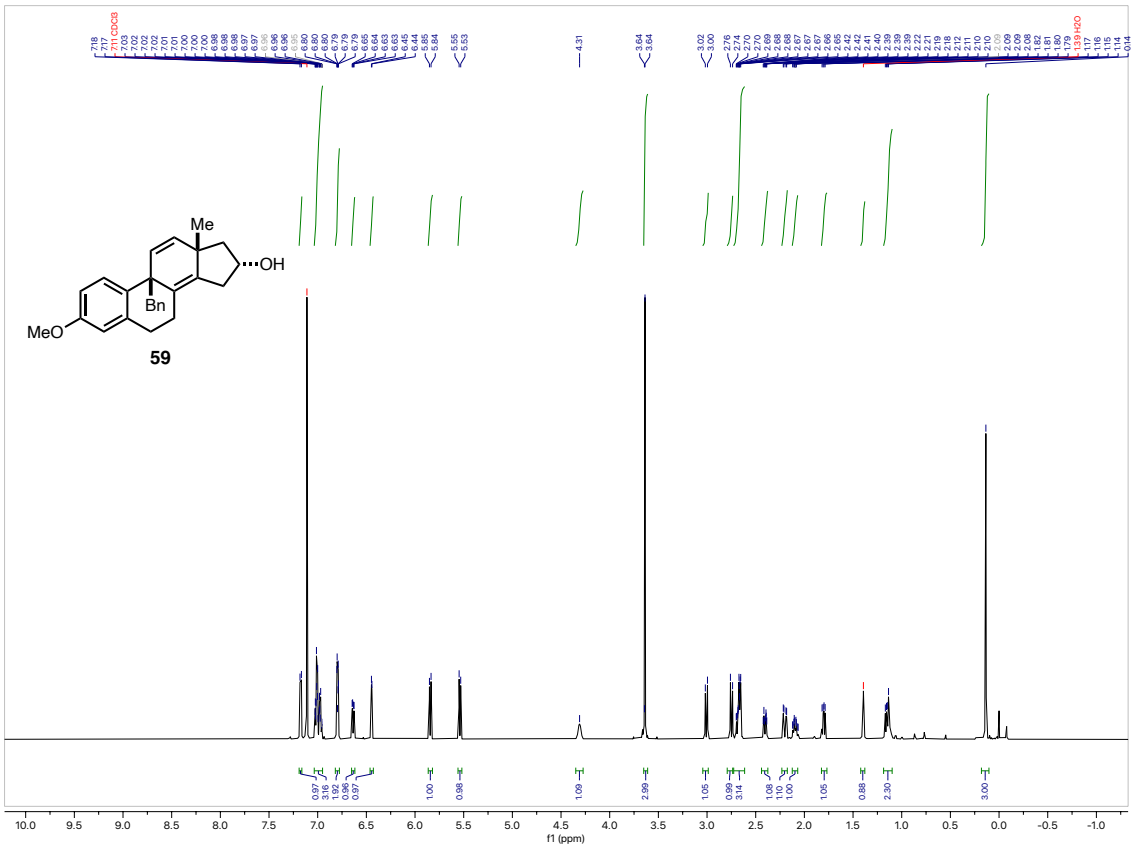


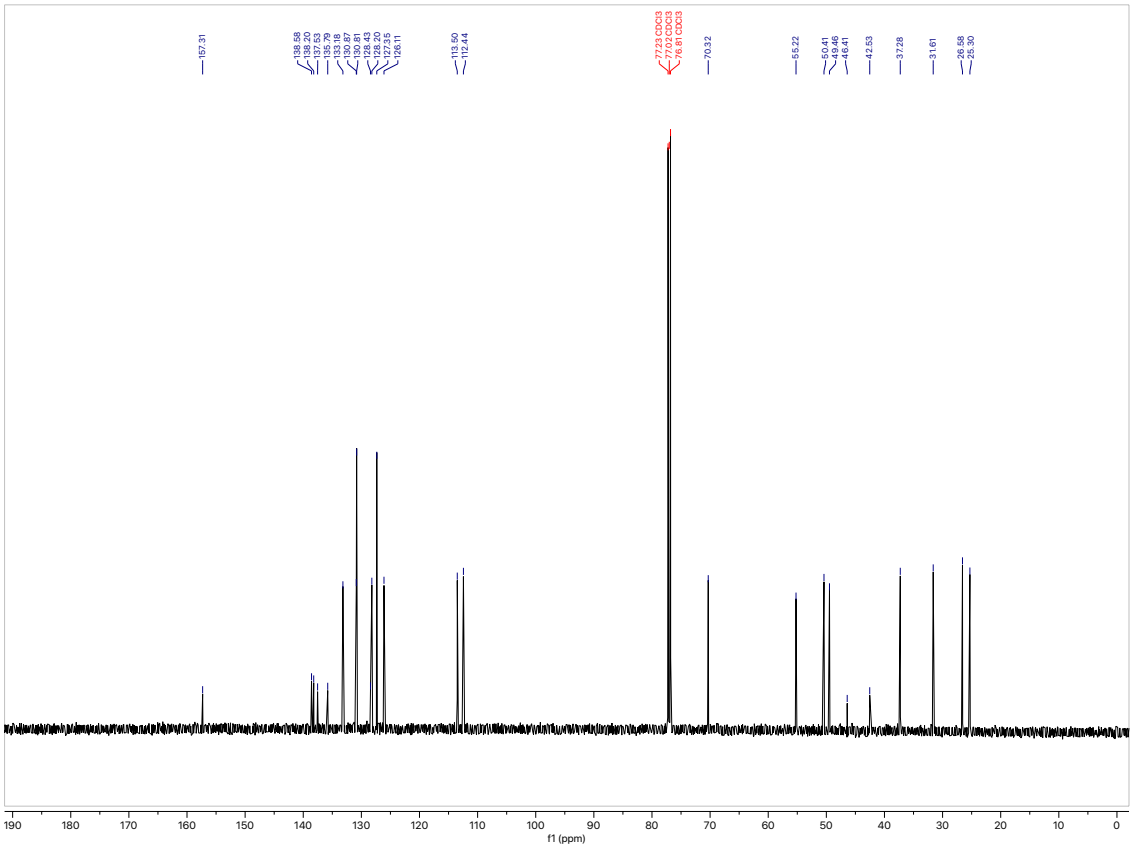
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **57**



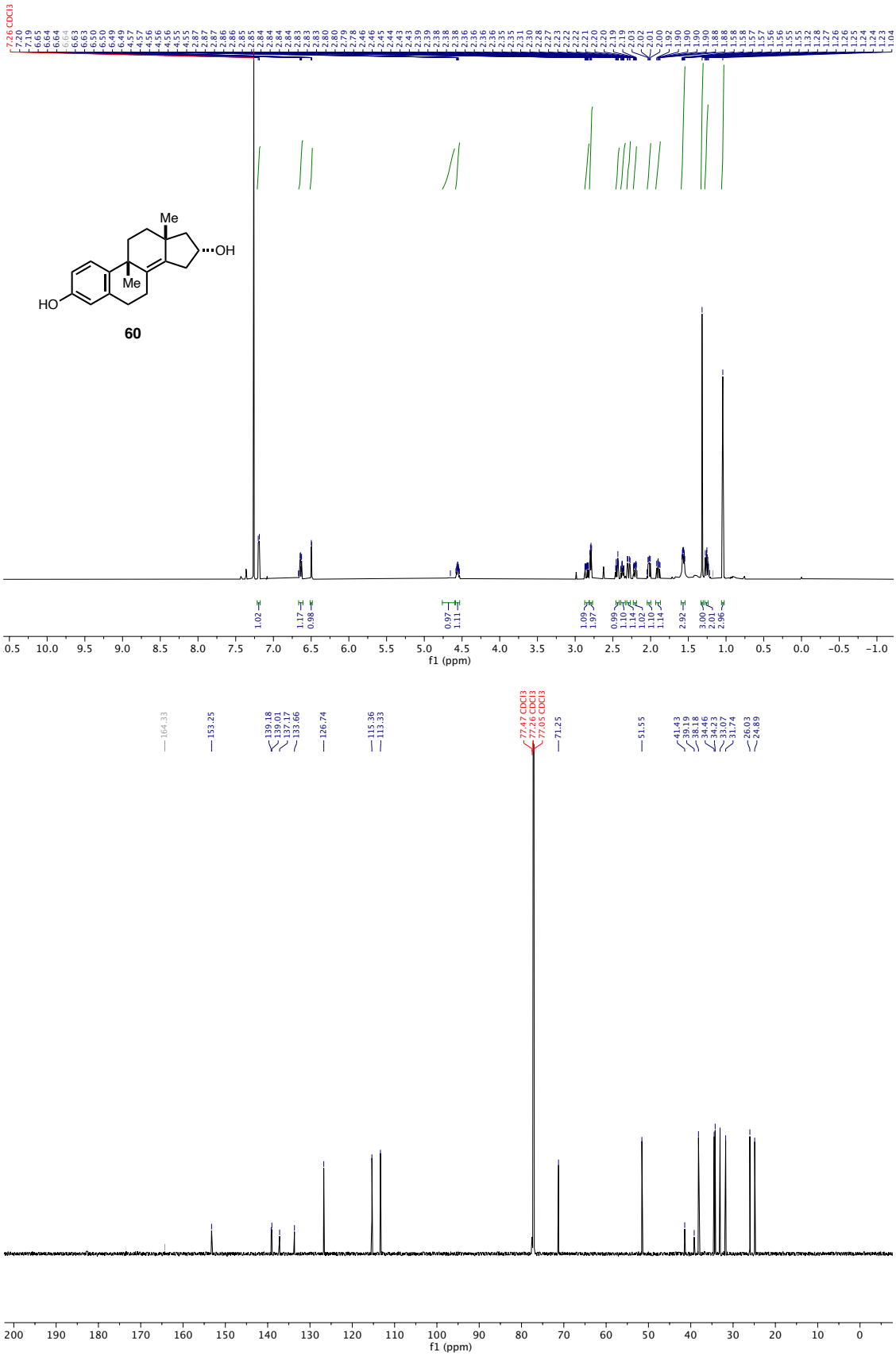


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **59**

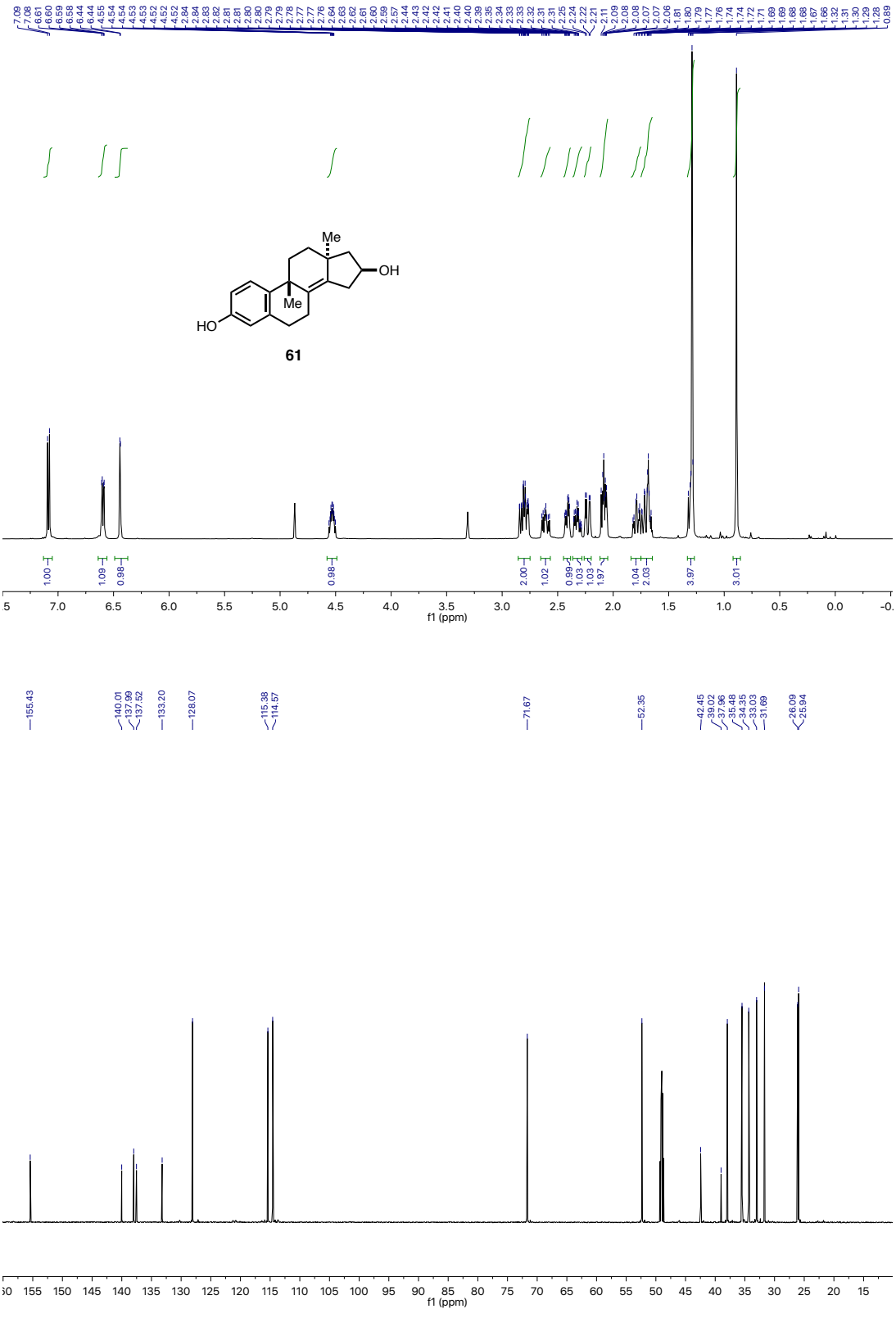




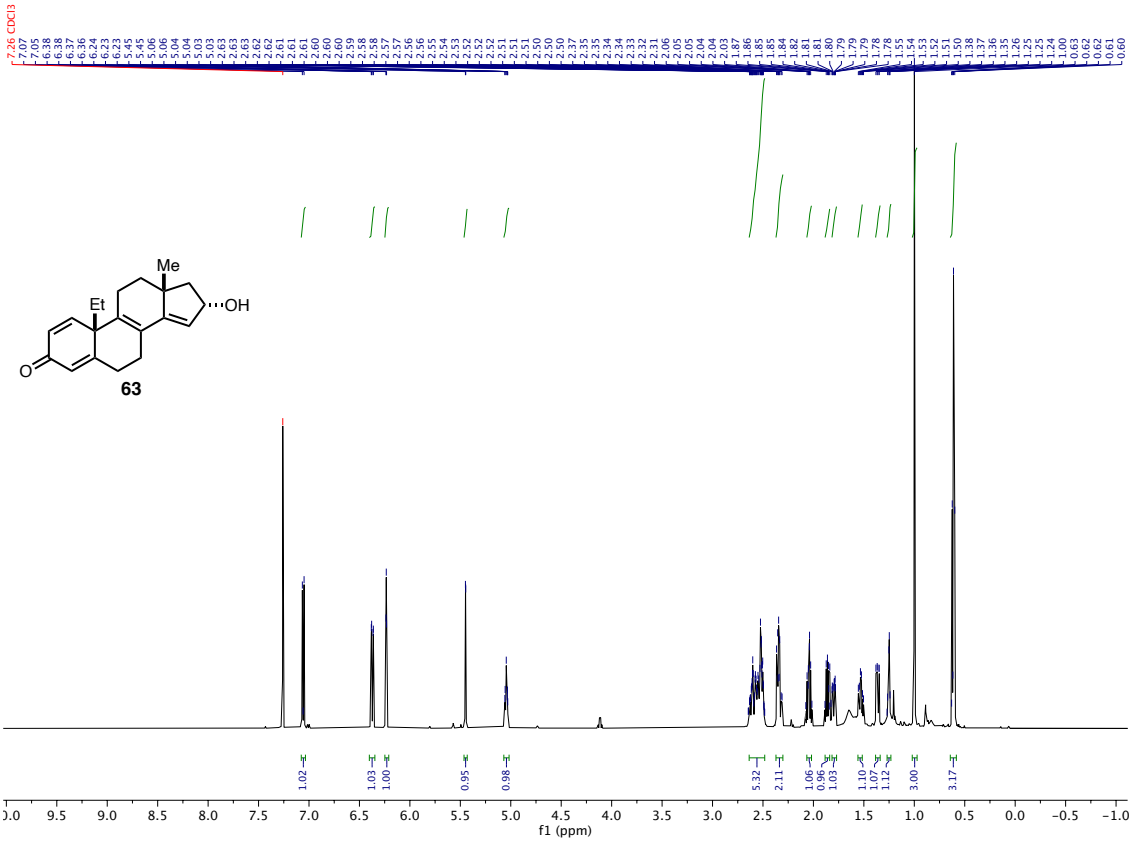
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **60**

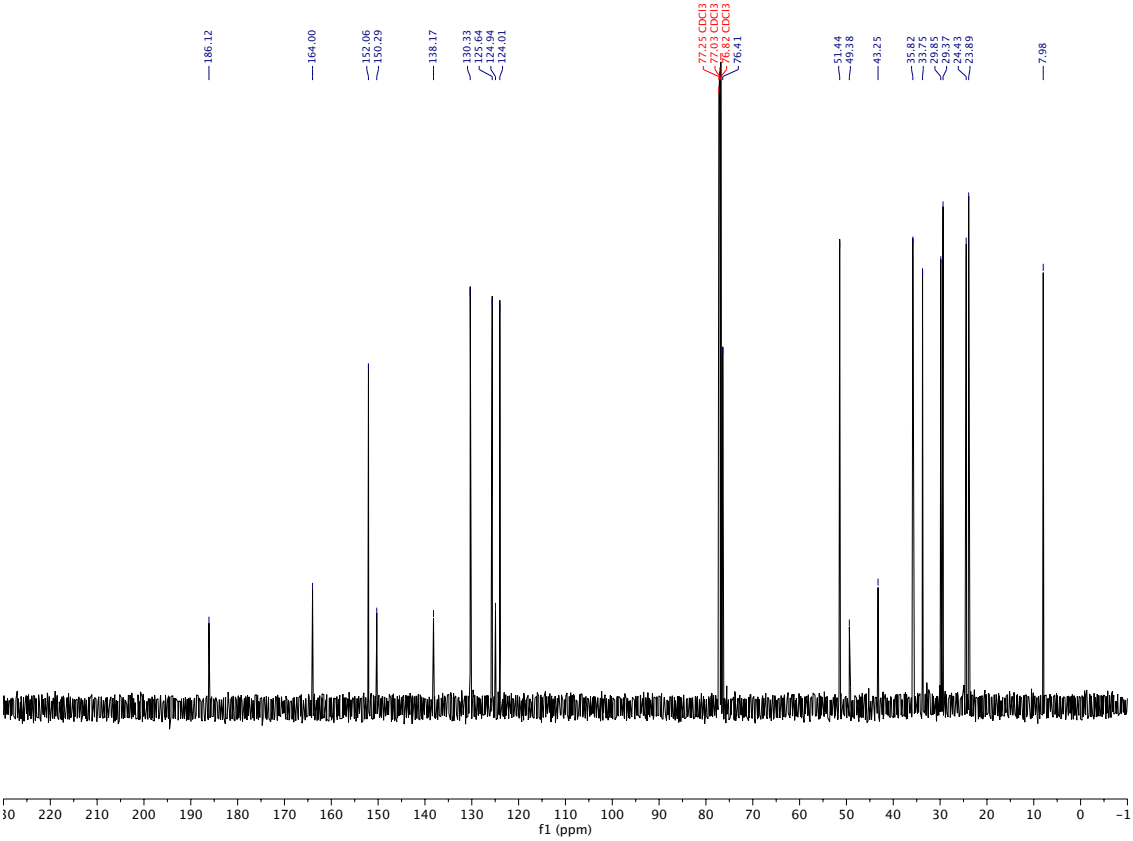


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **61**

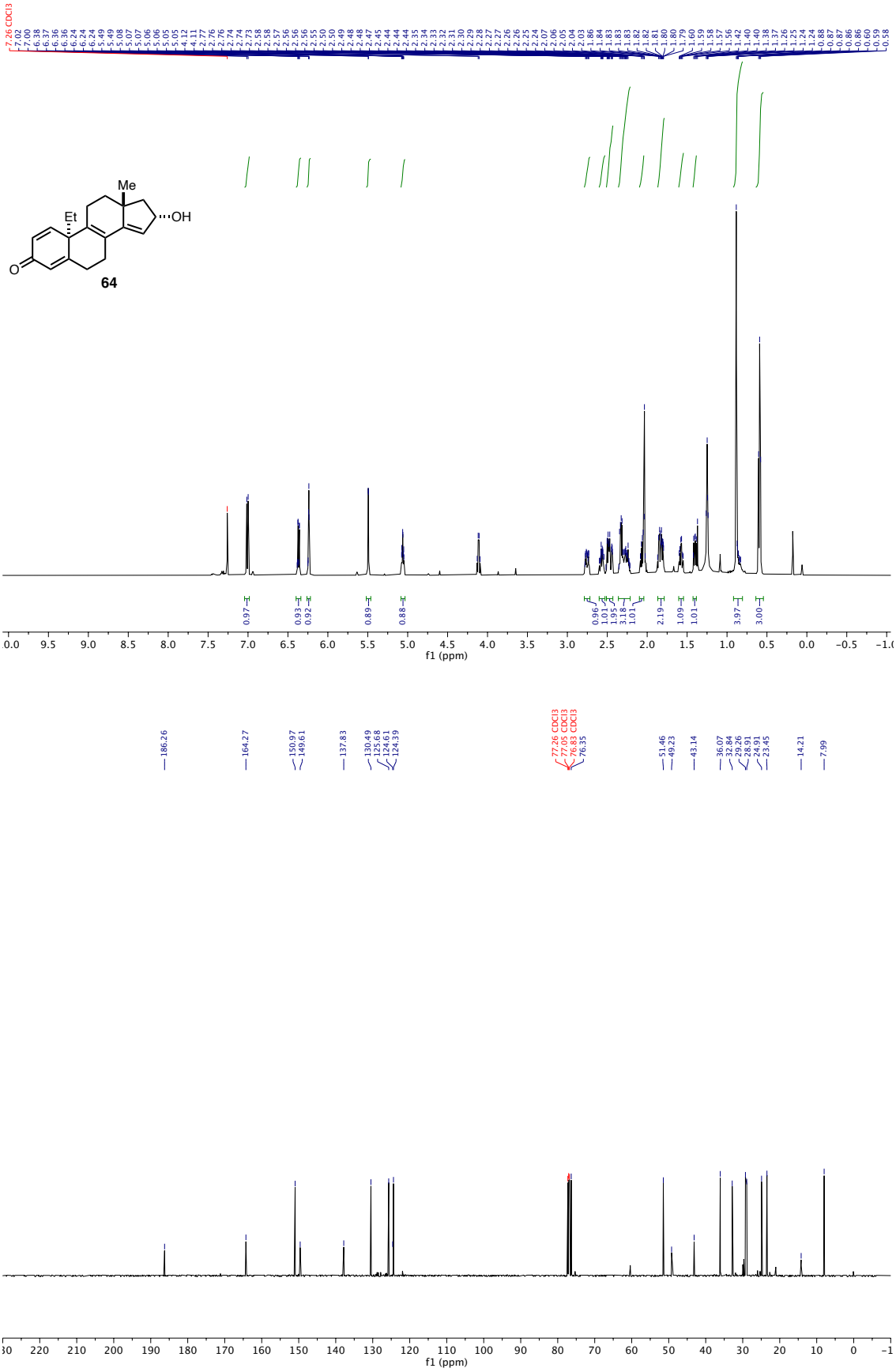


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **63**

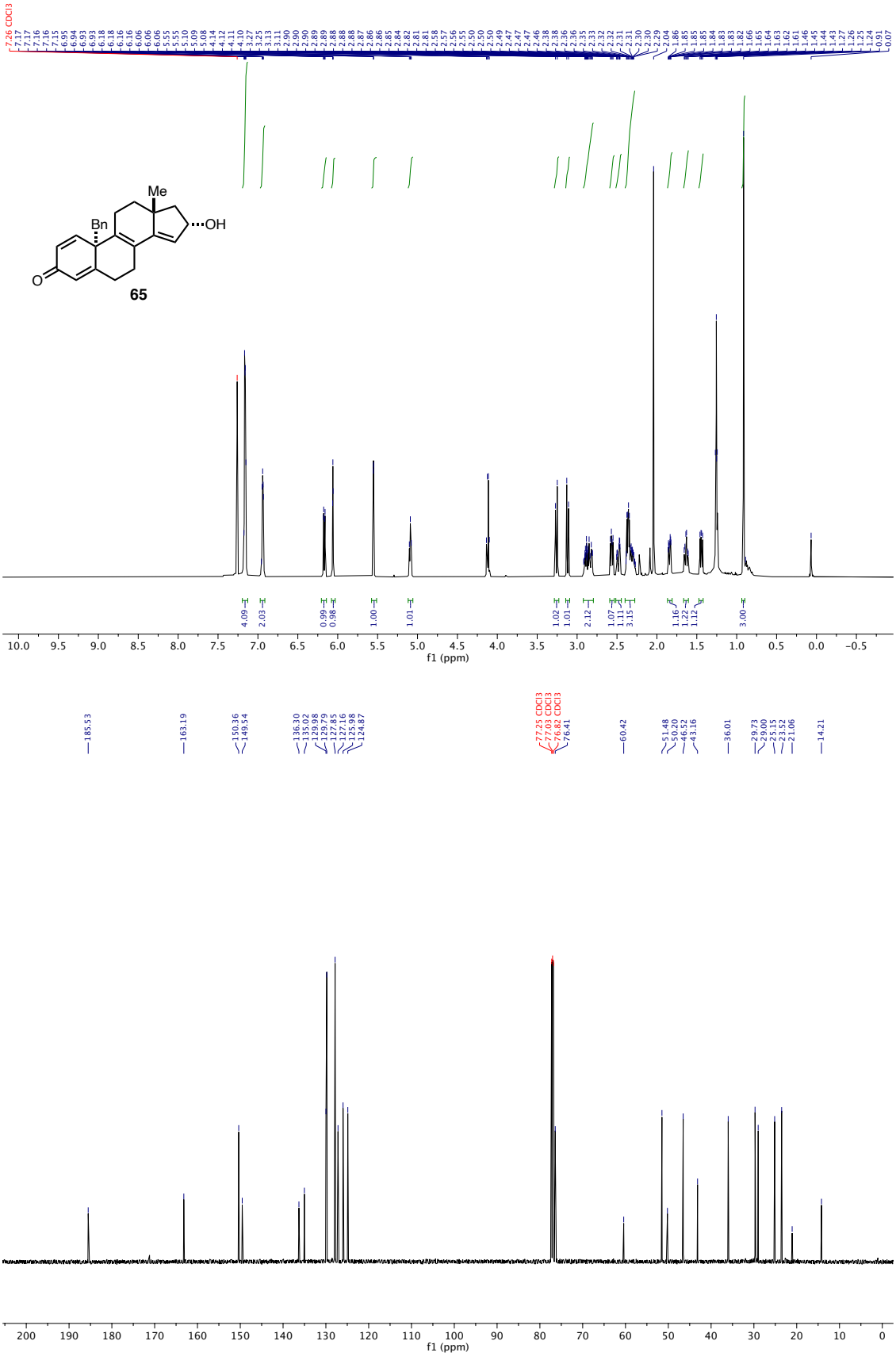




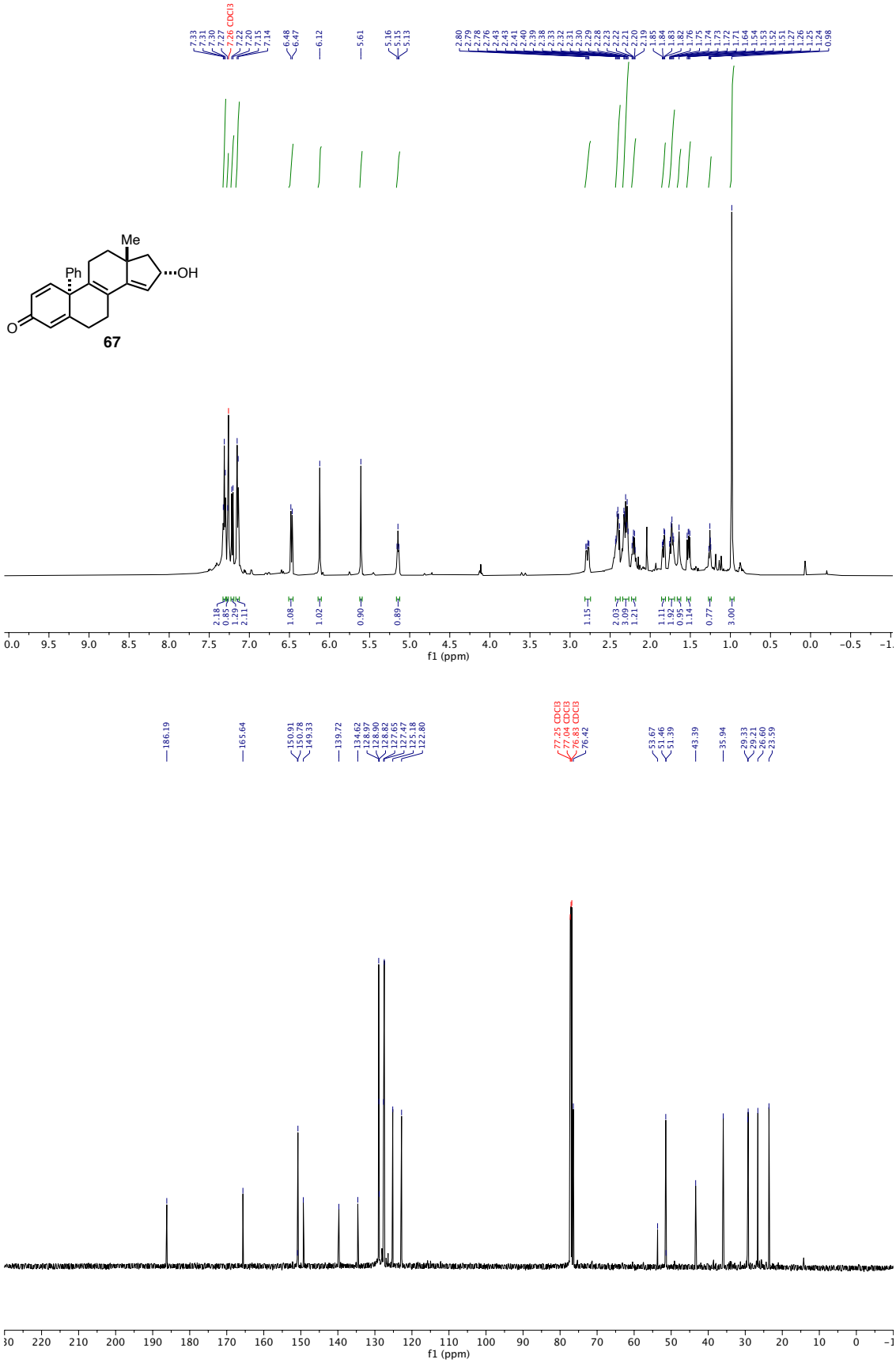
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **64**



^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **65**



^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C{1H} NMR (150 MHz, $CDCl_3$) of **67**



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