

Total Synthesis of (-)-Rhodomollanol A

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Supporting Information Available

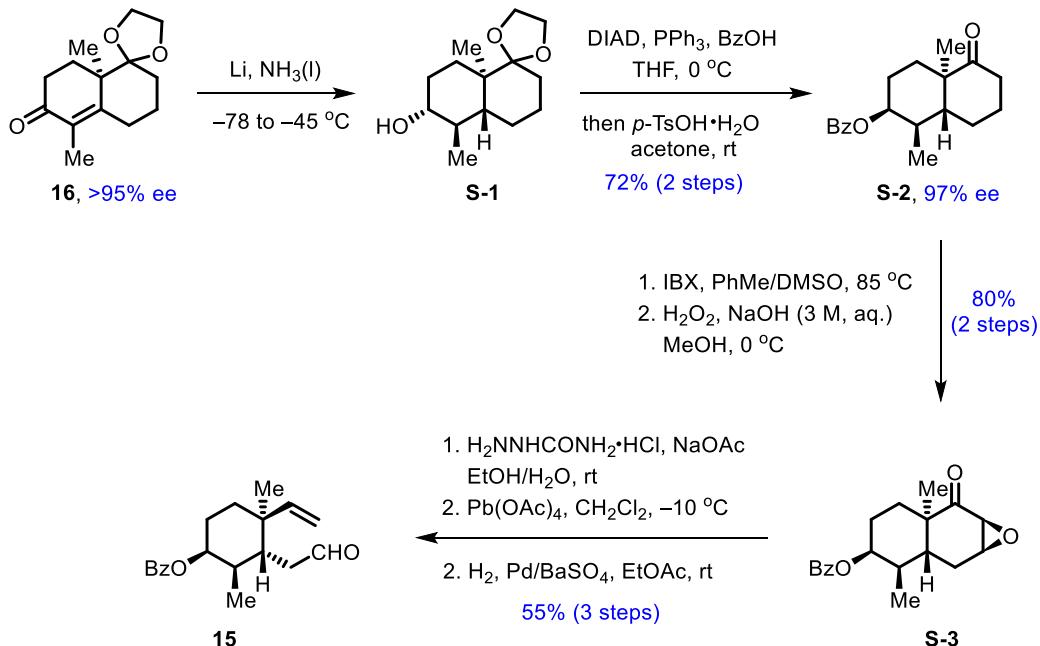
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I) Experimental Procedures and Spectroscopic Data of Compounds

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Anhydrous methylene chloride (CH_2Cl_2) and hexamethyl phosphoryl triamide (HMPA) were distilled before use from calcium hydride. Anhydrous tetrahydrofuran (THF) and toluene were distilled before use from sodium-benzophenone ketyl. Acetic acid (AcOH), acetone, 1,2-dichlorobenzene (*o*-DCB), dimethyl sulfoxide (DMSO), ethanol (EtOH), ethyl acetate (EtOAc), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), isopropanol (*i*-PrOH), methanol (MeOH), triethylamine (Et₃N) and pyridine were purchased at the highest commercial quality and used without further purification. Reactions that required heating were operated on a magnetic stirrer with an oil bath. Solvent degassing was conducted by bubbling with a stream of argon for 15–20 min. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of ammonium molybdate, anisaldehyde, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. Yields refer to chromatographically homogeneous materials. NMR spectra were recorded on a Bruker AV-400 or Agilent DD2-600 and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, m = multiplet. Melting points (m.p.) are uncorrected, and recorded on a Buchi B-540

melting point apparatus. Optical rotation data were obtained on a PerkinElmer Model 341 Polarimeter. High performance liquid chromatography (HPLC) analyses were performed on a Shimadzu LC-20A HPLC system. Detection of eluent was carried out with a photodiode array detector at 210 nm. High-resolution mass spectra (HRMS) were recorded on a Waters MALDI SYNAPT G2-Si High Definition Mass Spectrometry.

Procedures for the Preparation of Aldehyde **15**¹



Scheme S1. Preparation of aldehyde **15**

Preparation of bicyclic ketone **S-2**:

To a stirred solution of liquid ammonia (400 mL) at -78 °C was added Li (9.44 g, 1.34 mol, 4.0 equiv). The resulting mixture was stirred at -78 °C for 30 min before a solution of enone **16**² (>95% ee, 80.0 g, 339 mmol, 1.0 equiv) in THF (200 mL) was added. The resulting mixture was stirred at -45 °C for 4 h before quenched with EtOH (80 mL). The ammonia was evaporated under a stream of nitrogen at 30 °C, and the residue was partitioned between EtOAc (200 mL) and NH₄Cl (200 mL, sat. aq.). The

layers were separated, and the aqueous layer was extracted with EtOAc (3×200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude alcohol **S-1** as a yellow oil, which was used directly without further purification.

To a stirred solution of alcohol **S-1** (crude, obtained above) in THF (250 mL) at 0 °C were sequentially added BzOH (48.8 g, 400 mmol, 1.2 equiv), PPh_3 (105 g, 400 mmol, 1.2 equiv) and DIAD (78.7 mL, 398 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 1 h before a solution of *p*-TsOH• H_2O (76.0 g, 400 mmol, 1.2 equiv) in acetone (300 mL) was added. The resulting mixture was stirred at room temperature for 2 h before diluted with EtOAc (200 mL) and quenched with NaHCO_3 (500 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 20:1) afforded bicyclic ketone **S-2** (91.5 g, 72% over two steps) as a white solid. **S-2**: m.p. 92–94 °C (hexanes/EtOAc); $R_f = 0.50$ (silica gel, hexanes:EtOAc 4:1); 97% ee [Daical Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 97/3, $v = 1.0 \text{ mL}\cdot\text{min}^{-1}$, $\lambda = 210 \text{ nm}$, t (major) = 10.80 min, t (minor) = 13.88 min]; $[\alpha]_D^{20} = +3.2$ ($c = 0.5$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 8.05\text{--}7.92$ (m, 2 H), 7.52 (t, $J = 7.4 \text{ Hz}$, 1 H), 7.41 (t, $J = 7.6 \text{ Hz}$, 2 H), 5.17 (d, $J = 2.4 \text{ Hz}$, 1 H), 2.70–2.60 (m, 1 H), 2.24 (dd, $J = 14.4, 4.3 \text{ Hz}$, 1 H), 2.11–2.04 (m, 1 H), 1.97–1.61 (m, 7 H), 1.58–1.52 (m, 1 H), 1.50–1.40 (m, 1 H), 1.16 (s, 3 H), 0.93 ppm (d, $J = 6.6 \text{ Hz}$, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 215.7$, 166.0, 132.9, 130.7, 129.5 (2C), 128.4 (2C), 74.2, 48.5, 45.5, 37.2, 34.4, 27.3, 26.0 (2C),

23.1, 16.2, 16.1 ppm; HRMS (ESI): calcd for $C_{19}H_{24}O_3Na^+ [M + Na]^+$ 323.1618, found 323.1623.

Preparation of epoxide **S-3**:

To a stirred solution of bicyclic ketone **S-2** (99.0 g, 330 mmol, 1.0 equiv) in DMSO/toluene (3:1, 1 L) at 85 °C was added IBX (185 g, 661 mmol, 2.0 equiv). The resulting mixture was stirred at 85 °C for 12 h before another portion of IBX (185 g, 661 mmol, 2.0 equiv) was added. The reaction was stirred at 85 °C for an additional 12 h before cooled to 0 °C, diluted with EtOAc (1000 mL) and quenched with $Na_2S_2O_3$ (500 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude enone as a white solid, which was used directly without further purification.

To a stirred solution of enone (crude, obtained above) in MeOH (1000 mL) at 0 °C were sequentially added H_2O_2 (30% wt/wt aq., 84.8 mL, 838 mmol, 2.5 equiv) and NaOH (3.0 M aq., 167 mL, 495 mmol, 1.5 equiv). The resulting mixture was stirred at 0 °C for 30 min before diluted with CH_2Cl_2 (500 mL) and quenched with NH_4Cl (500 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 6:1) afforded epoxide **S-3** (82.9 g, 80% over two steps) as a white solid. **S-3**: m.p. 101–103 °C (hexanes/EtOAc); $R_f = 0.50$ (silica gel, hexanes:EtOAc 4:1); $[\alpha]_D^{20} = -3.0$ ($c = 0.5$, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) $\delta = 8.01$ (dd, $J = 8.0, 1.4$ Hz, 2 H), 7.56 (t, $J =$

7.4 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 5.19 (q, J = 2.5 Hz, 1 H), 3.57 (t, J = 2.4 Hz, 1 H), 3.25 (d, J = 3.4 Hz, 1 H), 2.44 (s, 1 H), 2.16 (d, J = 4.2 Hz, 1 H), 2.05–1.96 (m, 1 H), 1.87–1.78 (m, 2 H), 1.72 (d, J = 13.8 Hz, 2 H), 1.65–1.60 (m, 1 H), 1.05 (s, 3 H), 0.98 ppm (d, J = 6.7 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 206.9, 166.2, 133.1, 130.5, 129.7 (2C), 128.6 (2C), 73.7, 52.8, 51.9, 45.6, 34.2, 32.1, 26.7, 25.8, 24.3, 15.8, 15.5 ppm; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na}^+ [\text{M} + \text{Na}]^+$ 337.1410, found 337.1416.

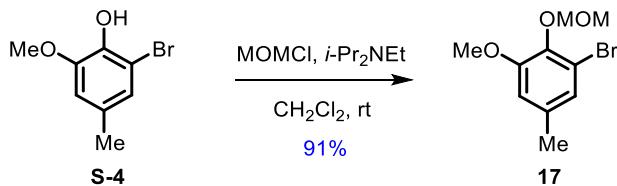
Preparation of aldehyde 15:

To a stirred solution of epoxide **S-3** (78.5 g, 250 mmol, 1.0 equiv) in $\text{EtOH}/\text{H}_2\text{O}$ (2.5:1, 700 mL) at room temperature were sequentially added NaOAc (23.8 g, 290 mmol, 1.2 equiv) and $\text{H}_2\text{NNHCONH}_2\bullet\text{HCl}$ (65.7 g, 587 mmol, 2.3 equiv). The resulting mixture was stirred at room temperature for 1 h before diluted with CH_2Cl_2 (200 mL) and quenched with brine (200 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude hydrazone as a yellow oil, which was used directly without further purification.

To a stirred solution of hydrazone (crude, obtained above) in CH_2Cl_2 (400 mL) at -10°C was added $\text{Pb}(\text{OAc})_4$ (129 g, 291 mmol, 1.2 equiv). The resulting mixture was stirred at -10°C for 30 min before quenched with H_2O (200 mL) and filtered through a short pad of celite. The filtrate was extracted with CH_2Cl_2 (3×200 mL), and the combined organic layers were washed with NaHCO_3 (200 mL, sat. aq.), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 6:1) afforded the corresponding alkyne as a white solid.

To a stirred solution of alkyne (obtained above) in EtOAc (120 mL) at room temperature were sequentially added SiO₂ (12.0 g) and Pd/BaSO₄ (2.2 g). The resulting mixture was stirred at room temperature under hydrogen atmosphere (1 atm) for 30 min before filtered through a short pad of celite. The filtrate was concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 6:1) afforded aldehyde **15** (41.3 g, 55% over three steps) as a white solid. **15**: m.p. 117–119 °C (hexanes/EtOAc); *R*_f = 0.50 (silica gel, hexanes:EtOAc 6:1); [α]_D²⁰ = +2.5 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 9.77 (d, *J* = 2.5 Hz, 1 H), 8.08 (d, *J* = 7.3 Hz, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 5.76 (dd, *J* = 17.4, 10.9 Hz, 1 H), 5.23–5.18 (m, 1 H), 5.08–5.02 (m, 2 H), 2.45–2.35 (m, 2 H), 2.28–2.21 (m, 1 H), 2.00–1.92 (m, 1 H), 1.81 (dd, *J* = 14.0, 9.2 Hz, 3 H), 1.30–1.22 (m, 1 H), 1.02 (s, 3 H), 0.88 ppm (d, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 202.5, 166.2, 148.8, 133.1, 130.8, 129.7 (2C), 128.6 (2C), 112.9, 74.5, 45.2, 40.6, 39.0, 36.3, 33.8, 26.4, 17.3, 15.5 ppm; HRMS (ESI): calcd for C₁₉H₂₄O₃Na⁺ [M + Na]⁺ 323.1618, found 323.1626.

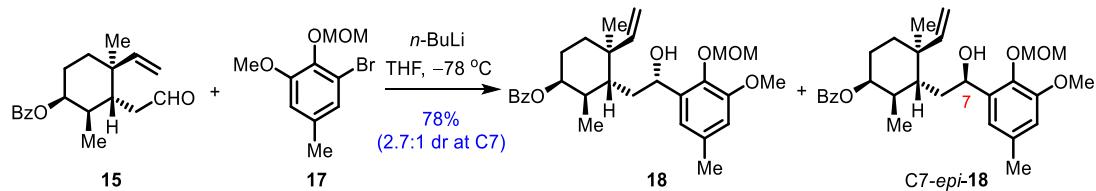
Preparation of phenyl bromide **17**:



To a stirred solution of bromophenol **S-4**³ (10.0 g, 46.3 mmol, 1.0 equiv) in CH₂Cl₂ (100 mL) at room temperature were sequentially added *i*-Pr₂NEt (16.1 mL, 92.6 mmol, 2.0 equiv) and MOMCl (4.20 mL, 55.6 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 2 h before quenched with NaHCO₃ (50 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 50

mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded phenyl bromide **17** (11.0 g, 91%) as a white solid. **17**: m.p. 108–110 °C (hexanes/EtOAc); R_f = 0.50 (silica gel, hexanes:EtOAc 10:1); ^1H NMR (400 MHz, CDCl_3) δ = 6.96 (d, J = 1.0 Hz, 1 H), 6.66 (d, J = 1.2 Hz, 1 H), 5.12 (s, 2 H), 3.82 (s, 3 H), 3.65 (s, 3 H), 2.28 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 153.1, 141.1, 135.4, 125.3, 117.4, 112.7, 98.7, 58.0, 56.1, 21.1 ppm; HRMS (ESI): calcd for $\text{C}_{10}\text{H}_{13}\text{BrO}_3\text{Na}^+ [\text{M} + \text{Na}]^+$ 282.9940, found 282.9946.

Preparation of alcohols **18** and C7-*epi*-**18**:



To a stirred solution of phenyl bromide **17** (27.3 g, 105 mmol, 1.1 equiv) in THF (150 mL) at –78 °C was added *n*-BuLi (45.8 mL, 2.4 M in hexanes, 110 mmol, 1.1 equiv). The resulting mixture was stirred at –78 °C for 10 min before a solution of aldehyde **15** (30.0 g, 100 mmol, 1.0 equiv) in THF (50 mL) was added. The reaction was stirred at –78 °C for an additional 1 h before quenched with NH_4Cl (50 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*.

Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded alcohols **18** (27.5 g, 57%) and C7-*epi*-**18** (11.1 g, 21%) as white solids. **18**: m.p. 122–124 °C (hexanes/EtOAc); R_f = 0.45 (silica gel, hexanes:EtOAc 2:1); $[\alpha]_D^{20} = +28.0$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ = 8.10–8.07 (m, 2 H), 7.58 (t, J = 7.4 Hz, 1 H),

7.47 (t, $J = 7.6$ Hz, 2 H), 6.72 (s, 1 H), 6.64 (s, 1 H), 6.01 (dd, $J = 17.5, 10.8$ Hz, 1 H), 5.20 (d, $J = 1.4$ Hz, 1 H), 5.14–5.04 (m, 4 H), 4.93–4.88 (m, 1 H), 3.80 (s, 3 H), 3.51 (s, 3 H), 2.69 (d, $J = 6.5$ Hz, 1 H), 2.30 (s, 3 H), 1.99–1.81 (m, 6 H), 1.47–1.41 (m, 1 H), 1.27–1.20 (m, 1 H), 1.07 (d, $J = 6.8$ Hz, 3 H), 1.02 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 166.3, 151.6, 150.2, 141.2, 138.7, 134.5, 132.9, 131.0, 129.7 (2C), 128.5 (2C), 119.1, 112.2, 111.7, 99.5, 75.3, 70.2, 57.9, 55.8, 41.2, 41.0, 38.4, 37.3, 34.1, 26.6, 21.6, 16.9, 15.3 ppm; HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{38}\text{O}_6\text{Na}^+$ [M + Na]⁺ 505.2561, found 505.2560.

C7-*epi*-18: m.p. 116–118 °C (hexanes/EtOAc); R_f = 0.50 (silica gel, hexanes:EtOAc 2:1); $[\alpha]_D^{20} = +0.7$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ = 8.11–8.08 (m, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 6.79 (s, 1 H), 6.68 (d, $J = 1.3$ Hz, 1 H), 5.12–5.04 (m, 4 H), 4.98 (d, $J = 6.1$ Hz, 1 H), 4.88 (dd, $J = 17.4, 1.3$ Hz, 1 H), 4.78 (dd, $J = 10.6, 1.3$ Hz, 1 H), 3.88 (s, 3 H), 3.47 (s, 3 H), 2.66 (d, $J = 4.1$ Hz, 1 H), 2.33 (s, 3 H), 1.90–1.63 (m, 5 H), 1.57–1.45 (m, 2 H), 1.19 (d, $J = 6.8$ Hz, 3 H), 1.05–1.00 (m, 1 H), 0.98 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 166.3, 151.4, 149.8, 141.9, 137.2, 133.9, 132.8, 131.0, 129.9 (2C), 128.5 (2C), 120.8, 112.2, 110.8, 99.3, 75.6, 69.0, 57.8, 55.8, 41.0, 39.9, 38.0, 36.9, 33.8, 26.3, 21.6, 17.1, 14.8 ppm; HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{38}\text{O}_6\text{Na}^+$ [M + Na]⁺ 505.2561, found 505.2566.

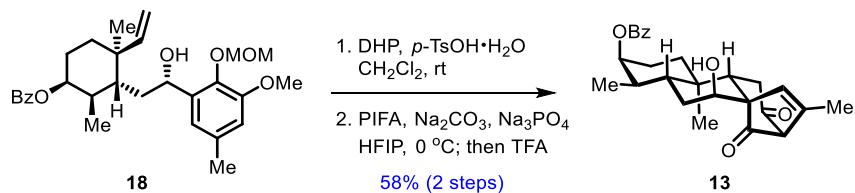
Recycle of alcohol C7-*epi*-18:

To a stirred solution of alcohol C7-*epi*-18 (11.0 g, 22.8 mmol, 1.0 equiv) and silica gel (5.0 g) in CH_2Cl_2 (50 mL) at room temperature was added PDC (17.2 g, 45.6 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 2 h before filtered

through a short pad of celite. The filtrate was concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded the corresponding ketone as a white solid.

To a stirred solution of ketone (obtained above) in EtOH (50 mL) at 0 °C was added NaBH₄ (1.0 g, 27 mmol, 1.0 equiv). The resulting mixture was stirred at 0 °C for 30 min before quenched with acetone (5 mL) and NH₄Cl (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were washed with brine (20 mL, sat. aq.), dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 6:1) afforded **18** (6.7 g, 61% over two steps), along with the recovered C7-*epi*-**18** (2.1 g, 19% over two steps).

Preparation of tetracyclic diketone 13:

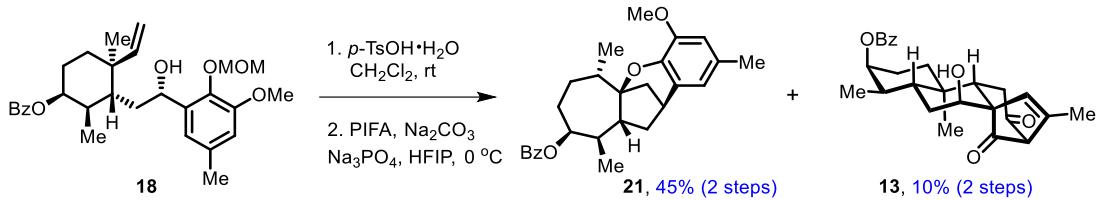


To a stirred solution of alcohol **18** (2.3 g, 5.3 mmol, 1.0 equiv) in CH₂Cl₂ (80 mL) at room temperature were sequentially added DHP (1.2 mL, 13 mmol, 2.5 equiv) and *p*-TsOH•H₂O (1.0 g, 5.3 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 3 h before quenched with NaHCO₃ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude vinylphenol as a yellow oil, which was used directly without further purification.

To a stirred solution of vinylphenol (crude, obtained above) in HFIP (200 mL) at 0

⁰C were added Na₂CO₃ (1.7 g, 16 mmol, 3.0 equiv), Na₃PO₄ (1.7 g, 11 mmol, 2.0 equiv) and PIFA (2.8 g, 6.4 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 20 min before TFA (9.8 mL, 0.13 mol, 25 equiv) was added. The reaction was stirred at room temperature for an additional 30 min before quenched with NaHCO₃ (200 mL, sat. aq.) and Na₂S₂O₃ (120 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 100 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded tetracyclic diketone **13** (1.3 g, 58% over two steps) as a white solid. **13**: m.p. 218–220 °C (hexanes/EtOAc); *R*_f = 0.50 (silica gel, hexanes:EtOAc 2:1); [α]_D²⁰ = +6.4 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 8.02 (d, *J* = 8.0 Hz, 2 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.7 Hz, 2 H), 6.36–6.27 (m, 1 H), 5.21–5.12 (m, 1 H), 4.20 (s, 1 H), 3.51 (s, 1 H), 2.86 (dd, *J* = 17.7, 10.6 Hz, 1 H), 2.43 (d, *J* = 17.7 Hz, 1 H), 2.27 (d, *J* = 10.5 Hz, 1 H), 2.16 (s, 1 H), 2.08 (td, *J* = 12.2, 3.7 Hz, 1 H), 1.88–1.77 (m, 6 H), 1.76–1.62 (m, 2 H), 1.50 (d, *J* = 13.0 Hz, 1 H), 1.30 (td, *J* = 13.2, 3.8 Hz, 1 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.63 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 205.2, 204.5, 166.2, 140.8, 133.0, 132.1, 130.7, 129.6 (2C), 128.5 (2C), 75.3, 74.6, 66.0, 58.0, 42.9, 38.4, 37.4, 35.9, 33.7, 33.6, 29.9, 26.0, 17.5, 16.2, 10.8 ppm; HRMS (ESI): calcd for C₂₆H₃₀NaO₅⁺ [M + Na]⁺ 445.1985, found 445.1991.

Preparation of tricycle **21**:



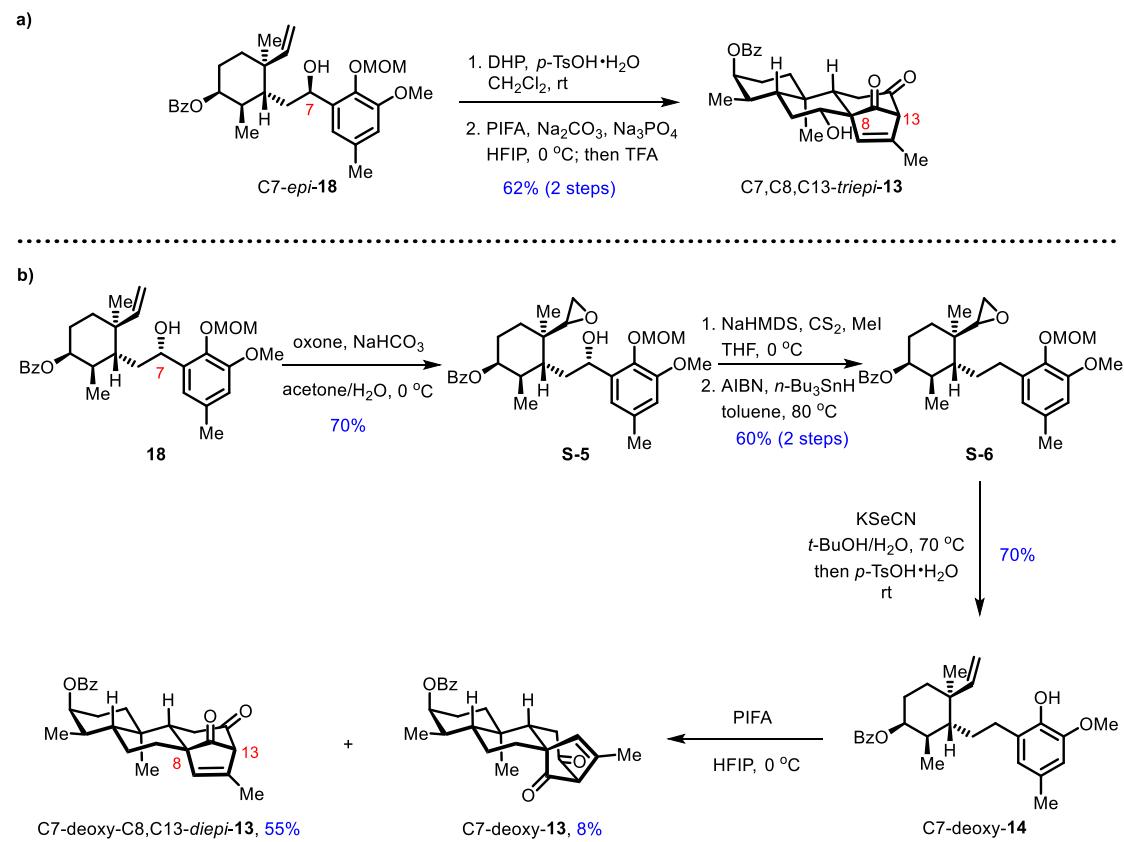
To a stirred solution of alcohol **18** (0.11 g, 0.23 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) at room temperature was *p*-TsOH•H₂O (23 mg, 0.12 mmol, 0.5 equiv). The resulting mixture was stirred at room temperature for 3 h before quenched with NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude vinylphenol as a yellow oil, which was used directly without further purification.

To a stirred solution of vinylphenol (crude, obtained above) in HFIP (10 mL) at 0 °C were added Na₂CO₃ (73 mg, 0.69 mmol, 3.0 equiv), Na₃PO₄ (75 mg, 0.46 mmol, 2.0 equiv) and PIFA (0.15 g, 0.34 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 20 min before quenched with Na₂S₂O₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded tricycle **21** (43 mg, 45% over two steps) as a white solid, along with **13** (8.5 mg, 10% over two steps). **21**: m.p. 141–143 °C (CH₂Cl₂/EtOAc); *R*_f = 0.50 (silica gel, hexanes:EtOAc 5:1); [α]_D²⁰ = +35.0 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 8.08 (d, *J* = 7.1 Hz, 2 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 7.8 Hz, 2 H), 6.60 (d, *J* = 2.0 Hz, 1 H), 6.47 (d, *J* = 1.9 Hz, 1 H), 5.26–5.21 (m, 1 H), 3.88 (s, 3 H), 3.00 (t, *J* = 4.4 Hz, 1 H), 2.70–2.52 (m, 2 H), 2.26 (s,

3 H), 2.26–2.19(m, 1 H) 2.12–1.93 (m, 3 H), 1.93–1.81 (m, 3 H), 1.81–1.69(m, 1 H),
 1.67–1.57 (m, 1 H), 1.15 (d, J = 7.1 Hz, 3 H), 1.04 ppm (d, J = 7.0 Hz, 3 H); ^{13}C NMR
 (100 MHz, CDCl_3) δ = 166.1, 148.2, 140.8, 132.9, 130.9, 130.1, 130.0 (2C), 128.4 (2C),
 120.1, 112.2, 91.0, 76.3, 56.6, 49.5, 45.5, 39.7, 37.6, 37.3 (2C), 34.3, 29.7, 26.4, 21.0,
 18.8, 18.5 ppm; HRMS (ESI): calcd for $\text{C}_{27}\text{H}_{32}\text{NaO}_4^+$ [M + Na]⁺ 443.2193, found
 443.2190.

Investigations on the ODI-(5+2) Cycloaddition/Pinacol-Type 1,2-Acyl Migration

Cascade Reactions of C7-*epi*-18 and C7-Deoxy-14



Scheme S2. Attempts of ODI-(5+2) cascades of **a**) C7-*epi*-**18**, and **b**) C7-deoxy-**14**

Preparation of tetracyclic diketone C7,C8,C13-*triepi*-13:

To a stirred solution of alcohol C7-*epi*-18 (63 mg, 0.13 mmol, 1.0 equiv) in CH₂Cl₂ (5 mL) at room temperature were sequentially added DHP (30 µL, 0.33 mmol, 2.5 equiv) and *p*-TsOH•H₂O (26 mg, 0.13 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 3 h before quenched with NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude vinylphenol as a white solid, which was used directly without further purification.

To a stirred solution of vinylphenol (crude, obtained above) in HFIP (6 mL) at 0 °C were added Na₂CO₃ (42 mg, 0.40 mmol, 3.0 equiv), Na₃PO₄ (43 mg, 0.26 mmol, 2.0 equiv) and PIFA (68 mg, 0.16 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 20 min before TFA (0.25 mL, 3.3 mmol, 25 equiv) was added. The resulting mixture was stirred at room temperature for 30 min before quenched with NaHCO₃ (10 mL, sat. aq.) and Na₂S₂O₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded tetracyclic diketone C7,C8,C13-*triepi*-13 (34 mg, 62% over two steps) as a white solid. **C7,C8,C13-*triepi*-13:** m.p. 150–152 °C (hexanes/EtOAc); *R*_f = 0.25 (silica gel, hexanes:EtOAc 2:1); [α]_D²⁰ = −171.6 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 8.00 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 6.20 (s, 1 H), 5.25–5.16 (m, 1 H), 4.32 (d, *J* = 11.3 Hz, 1 H), 3.58 (s, 1 H), 2.67 (dd, *J* = 16.9, 11.8 Hz, 1 H), 2.38 (dd, *J* = 16.9, 6.1 Hz, 1 H),

2.10–1.97 (m, 2 H), 1.92 (s, 3 H), 1.89–1.78 (m, 2 H), 1.71 (dd, J = 21.4, 12.1 Hz, 1 H), 1.63–1.52 (m, 2 H), 1.44–1.25 (m, 3 H), 0.98 (d, J = 6.7 Hz, 3 H), 0.93 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 205.9, 201.2, 166.1, 138.2, 133.2, 130.7, 129.6 (2C), 128.6 (2C), 128.3, 74.2, 74.1, 67.2, 62.5, 45.9, 44.2, 37.5, 36.1, 34.2, 32.6, 29.7, 26.0, 17.4, 16.4, 12.4 ppm; HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{30}\text{NaO}_5^+$ [M + Na]⁺ 445.1985, found 445.1987.

Preparation of epoxide S-5:

To a stirred solution of alcohol **18** (1.2 g, 2.5 mmol, 1.0 equiv) and NaHCO_3 (1.0 g, 12 mmol, 4.8 equiv) in acetone/ H_2O (1:1, 20 mL) at 0 °C was added oxone (1.5 g, 2.5 mmol, 1.0 equiv). The resulting mixture was stirred at 0 °C for 12 h before diluted with EtOAc (10 mL) and quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded epoxide **S-5** (0.87 g, 70%) as a white solid. **S-5**: m.p. 120–122 °C (hexanes/EtOAc); R_f = 0.30 (silica gel, hexanes:EtOAc 2:1); $[\alpha]_D^{20} = +4.0$ (c = 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ = 8.13 (d, J = 7.3 Hz, 2 H), 7.59 (t, J = 7.3 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H), 6.80 (s, 1 H), 6.66 (s, 1 H), 5.14–5.12 (m, 2 H), 5.07 (dd, J = 10.0, 4.7 Hz, 1 H), 4.94 (d, J = 6.1 Hz, 1 H), 3.86 (s, 3 H), 3.44 (s, 3 H), 2.92 (s, 1 H), 2.67 (dd, J = 4.3, 2.9 Hz, 1 H), 2.47 (t, J = 4.2 Hz, 1 H), 2.31 (s, 3 H), 1.92–1.80 (m, 4 H), 1.75–1.69 (m, 2 H), 1.58–1.49 (m, 2 H), 1.31 (d, J = 13.3 Hz, 1 H), 1.21 (d, J = 6.8 Hz, 3 H), 0.60 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 166.2, 151.5, 141.8, 137.5, 134.1, 132.8, 130.9, 129.9

(2C), 128.5 (2C), 120.1, 112.5, 99.3, 75.1, 69.9, 60.3, 57.8, 55.8, 45.7, 38.9, 38.6, 37.5, 37.1, 30.5, 25.9, 21.6, 16.8, 10.1 ppm; HRMS (ESI): calcd for $C_{29}H_{38}O_7Na^+$ [M + Na]⁺ 521.2510, found 521.2515.

Preparation of MOM ether **S-6**:

To a stirred solution of epoxide **S-5** (0.60 g, 1.2 mmol, 1.0 equiv) and CS₂ (0.73 mL, 12 mmol, 10 equiv) in THF (10 mL) at 0 °C was added NaHMDS (2.0 M in THF, 1.8 mL, 3.6 mmol, 3.0 equiv). The resulting mixture was stirred at 0 °C for 30 min before MeI (0.37 mL, 6.0 mmol, 5.0 equiv) was added. The reaction was stirred at 0 °C for an additional 10 min before quenched with NH₄Cl (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude xanthate as a yellow oil, which was used directly without further purification.

To a stirred solution of xanthate (crude, obtained above) in toluene (10 mL, degassed) at room temperature were sequentially added AIBN (39 mg, 0.24 mmol, 0.2 equiv) and *n*-Bu₃SnH (0.96 mL, 3.6 mmol, 3.0 equiv). The resulting mixture was warmed to 80 °C and stirred for 2 h before cooled to room temperature and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded MOM ether **S-6** (0.35 g, 60% over two steps) as a white solid. **S-6**: m.p. 114–116 °C (hexanes/EtOAc); R_f = 0.55 (silica gel, hexanes:EtOAc 4:1); $[\alpha]_D^{20}$ = +3.1 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 8.12–8.10 (m, 2 H), 7.59 (t, J = 7.4 Hz, 1 H), 7.49 (t, J = 7.5 Hz, 2 H), 6.58 (d, J = 3.4 Hz, 2 H), 5.20 (d, J = 2.2 Hz, 1 H), 5.04 (dd, J = 14.3, 5.7 Hz, 2 H), 3.82 (s, 3 H), 3.52 (s, 3 H), 2.82–2.63 (m, 4 H), 2.51–2.50 (m, 1

H), 2.30 (s, 3 H), 1.95–1.91 (m, 1 H), 1.84–1.61 (m, 5 H), 1.47–1.32 (m, 2 H), 1.15 (d, J = 6.7 Hz, 3 H), 0.68 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 166.3, 151.9, 141.9, 136.3, 133.8, 133.0, 131.0, 129.7 (2C), 128.6 (2C), 122.7, 111.2, 99.1, 74.9, 60.2, 57.7, 55.7, 45.2, 42.5, 37.5, 37.1, 31.9, 31.0, 30.1, 26.0, 21.5, 16.7, 11.2 ppm; HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{38}\text{O}_6\text{Na}^+$ [M + Na]⁺ 505.2561, found 505.2566.

Preparation of vinylphenol C7-deoxy-14:

To a stirred solution of MOM ether **S-6** (0.20 g, 0.41 mmol, 1.0 equiv) in *t*-BuOH/H₂O (9:1, 5 mL) at room temperature was added KSeCN (0.14 g, 1.0 mmol, 2.5 equiv). The resulting mixture was warmed to 70 °C and stirred for 36 h before *p*-TsOH•H₂O (0.19 g, 1.0 mmol, 2.5 equiv) was added. The resulting mixture was stirred at room temperature for 2 h before diluted with EtOAc (5 mL) and quenched with NaHCO₃ (15 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 10:1) afforded vinylphenol C7-deoxy-**14** (0.12 g, 70%) as a white solid. **C7-deoxy-14:** m.p. 107–109 °C (hexanes/EtOAc); R_f = 0.50 (silica gel, hexanes:EtOAc 10:1); $[\alpha]_D^{20}$ = +5.0 (c = 0.5, CHCl₃); ^1H NMR (400 MHz, CDCl_3) δ = 8.12–8.09 (m, 2 H), 7.60 (t, J = 7.4 Hz, 1 H), 7.50 (t, J = 7.6 Hz, 2 H), 6.55 (d, J = 4.1 Hz, 2 H), 5.71 (dd, J = 17.5, 10.7 Hz, 1 H), 5.50 (s, 1 H), 5.22 (d, J = 2.2 Hz, 1 H), 5.03–4.96 (m, 2 H), 3.86 (s, 3 H), 2.73 (ddd, J = 13.1, 11.4, 4.7 Hz, 1 H), 2.52 (ddd, J = 13.2, 10.7, 6.7 Hz, 1 H), 2.29 (s, 3 H), 1.92 (dd, J = 13.4, 2.9 Hz, 1 H), 1.88–1.73 (m, 3 H), 1.70–1.63 (m, 1 H), 1.58–1.52 (m, 1 H), 1.38 (ddd, J = 19.1, 10.7, 5.3 Hz, 1 H), 1.20 (d, J = 2.9 Hz, 1 H), 1.16 (d,

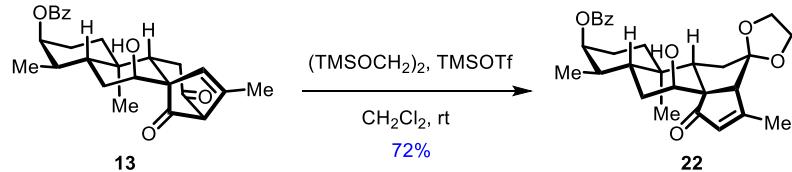
$J = 6.8$ Hz, 3 H), 1.01 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.3, 149.7, 146.2, 141.2, 132.9, 131.1, 129.7$ (2C), 128.6, 128.5 (2C), 128.3, 122.8, 111.2, 109.3, 75.4, 56.1, 44.4, 41.2, 37.0, 34.1, 31.4, 30.4, 26.5, 21.3, 17.0, 15.5 ppm; HRMS (ESI): calcd for $\text{C}_{27}\text{H}_{34}\text{O}_4\text{Na}^+ [\text{M} + \text{Na}]^+$ 445.2349, found 445.2355.

Preparation of tetracyclic diketones C7-deoxy-13 and C7-deoxy-C8,C13-diepi-13:

To a stirred solution of vinylphenol C7-deoxy-**14** (0.10 g, 0.24 mmol, 1.0 equiv) in HFIP (10 mL) at 0 °C was added PIFA (0.12 g, 0.29 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 20 min before diluted with Et_2O (5 mL) and quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded tetracyclic diketones C7-deoxy-**13** (7.8 mg, 8%) and C7-deoxy-C8,C13-diepi-**13** (54 mg, 55%) as white solids. **C7-deoxy-13:** m.p. 196–198 °C (hexanes/EtOAc); $R_f = 0.45$ (silica gel, hexanes:EtOAc 4:1); $[\alpha]_D^{20} = +5.5$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) $\delta = 8.07\text{--}8.02$ (m, 2 H), 7.60–7.55 (m, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 5.84 (d, $J = 1.6$ Hz, 1 H), 5.17 (d, $J = 2.6$ Hz, 1 H), 3.52 (s, 1 H), 2.92 (dd, $J = 17.8, 10.7$ Hz, 1 H), 2.48 (d, $J = 17.8$ Hz, 1 H), 2.20 (dd, $J = 9.8, 2.2$ Hz, 1 H), 1.90 (d, $J = 10.7$ Hz, 2 H), 1.83 (d, $J = 1.5$ Hz, 3 H), 1.80–1.69 (m, 3 H), 1.59–1.44 (m, 4 H), 1.32–1.23 (m, 1 H), 0.94 (d, $J = 6.7$ Hz, 3 H), 0.70 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 206.7, 204.3, 166.2, 140.3, 135.6, 133.0, 131.0, 129.6$ (2C), 128.5 (2C), 75.3, 74.8, 53.9, 47.9, 45.6, 38.5, 36.5, 34.4, 34.0, 29.0, 26.1, 21.4, 17.4, 16.3, 11.2 ppm; HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{30}\text{O}_4\text{Na}^+ [\text{M} + \text{Na}]^+$ 429.2036, found 429.2042.

C7-deoxy-C8,C13-diepi-13: m.p. 164–166 °C (hexanes/EtOAc); R_f = 0.40 (silica gel, hexanes:EtOAc 4:1); $[\alpha]_D^{20} = -150.0$ (c = 0.5, CHCl₃); ¹H NMR (400 MHz, acetone-*d*₆) δ = 8.11–8.07 (m, 2 H), 7.65–7.61 (m, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 6.28 (d, *J* = 1.6 Hz, 1 H), 5.18 (q, *J* = 2.7 Hz, 1 H), 3.39 (s, 1 H), 2.73 (dd, *J* = 16.7, 12.0 Hz, 1 H), 2.32 (dd, *J* = 16.7, 5.9 Hz, 1 H), 2.00 (dd, *J* = 13.9, 4.8 Hz, 1 H), 1.90–1.79 (m, 7 H), 1.66–1.57 (m, 2 H), 1.54 (dd, *J* = 12.0, 6.0 Hz, 1 H), 1.46–1.37 (m, 3 H), 1.01 (s, 3 H), 0.96 ppm (d, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, acetone-*d*₆) δ = 207.3, 201.9, 166.3, 138.0, 133.7, 132.1, 131.8, 130.2 (2C), 129.4 (2C), 75.3, 74.9, 57.0, 47.6, 46.6, 38.3, 36.7, 34.9, 33.3, 27.5, 26.6, 21.3, 16.8, 16.6, 12.5 ppm; HRMS (ESI): calcd for C₂₆H₃₀O₄Na⁺ [M + Na]⁺ 429.2036, found 429.2033.

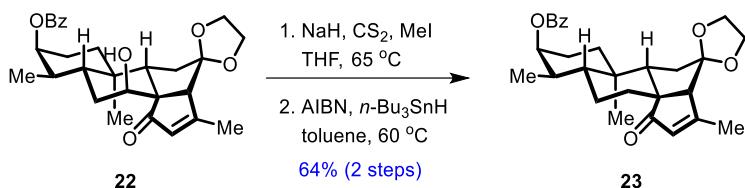
Preparation of tetracycle 22:



To a stirred solution of diketone **13** (4.8 g, 11 mmol, 1.0 equiv) in CH₂Cl₂ (110 mL) at room temperature were sequentially added (CH₂OTMS)₂ (8.3 mL, 34 mmol, 3.1 equiv) and TMSOTf (2.2 mL, 13 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 5 min before quenched with NaHCO₃ (50 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded tetracycle **22** (3.8 g, 72%) as a white solid. **22**: m.p. 185–187 °C (hexanes/EtOAc); *R*_f = 0.20 (silica gel,

8.04 (d, $J = 7.7$ Hz, 2 H), 7.55 (t, $J = 7.4$ Hz, 1 H), 7.45 (t, $J = 7.6$ Hz, 2 H), 5.85 (s, 1 H), 5.27–5.20 (m, 1 H), 4.10–4.01 (m, 1 H), 3.90 (s, 3 H), 3.70 (s, 1 H), 3.21 (s, 1 H), 2.20 (dd, $J = 13.3$, 3.0 Hz, 2 H), 2.14 (s, 3 H), 2.06–1.83 (m, 5 H), 1.67 (dd, $J = 11.9$, 4.3 Hz, 1 H), 1.60 (dd, $J = 14.2$, 2.9 Hz, 1 H), 1.55–1.41 (m, 2 H), 1.38–1.31 (m, 1 H), 1.10 (s, 3 H), 0.88 ppm (d, $J = 6.7$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 208.6, 174.8, 166.3, 132.8, 131.8, 130.8, 129.6 (2C), 128.4 (2C), 116.2, 75.4, 67.9, 65.2, 64.1, 63.6, 60.9, 48.3, 39.2, 35.7, 34.8, 33.9, 33.1, 28.7, 26.2, 19.9, 16.0, 12.3 ppm; HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{34}\text{NaO}_6^+$ [M + Na]⁺ 489.2248, found 489.2261.

Preparation of enone 23:

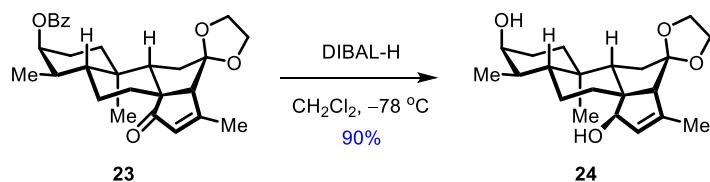


To a stirred solution of tetracycle **22** (6.5 g, 14 mmol, 1.0 equiv) and CS_2 (8.4 mL, 0.14 mol, 10 equiv) in THF (100 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 1.7 g, 42 mmol, 3.0 equiv). The resulting mixture was warmed to 65 °C and stirred for 5 h before cooled to room temperature and MeI (4.4 mL, 70 mmol, 5.0 equiv) was added. The resulting mixture was stirred at room temperature for 10 min before quenched with NH_4Cl (50 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×50 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude xanthate as a yellow oil, which was used directly without further purification.

To a stirred solution of xanthate (crude, obtained above) in toluene (100 mL, degassed) at room temperature were sequentially added AIBN (0.46 g, 2.8 mmol, 0.2

equiv) and *n*-Bu₃SnH (11 mL, 42 mmol, 3.0 equiv). The resulting mixture was warmed to 60 °C and stirred for 2 h before cooled to room temperature and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded enone **23** (4.0 g, 64% over two steps) as a white solid. **23**: m.p. 167–169 °C (hexanes/EtOAc); *R*_f = 0.45 (silica gel, hexanes:EtOAc 3:1); [α]_D²⁰ = −1.8 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 8.04 (d, *J* = 8.0 Hz, 2 H), 7.54 (t, *J* = 7.3 Hz, 1 H), 7.45 (t, *J* = 7.1 Hz, 2 H), 5.77 (s, 1 H), 5.20 (s, 1 H), 4.01 (s, 1 H), 3.87 (s, 3 H), 2.63 (s, 1 H), 2.10 (s, 3 H), 1.98–1.76 (m, 5 H), 1.69 (ddd, *J* = 21.8, 15.6, 3.9 Hz, 2 H), 1.59–1.43 (m, 4 H), 1.42–1.30 (m, 2 H), 1.13 (s, 3 H), 0.89 ppm (d, *J* = 6.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 210.0, 173.0, 166.2, 132.8, 131.3, 131.0, 129.6 (2C), 128.4 (2C), 116.9, 75.5, 66.8, 65.2, 64.0, 58.7, 55.4, 47.3, 36.0, 35.7, 35.0, 34.6, 33.6, 26.3, 20.7, 19.9, 16.1, 12.5 ppm; HRMS (ESI): calcd for C₂₈H₃₄NaO₅⁺ [M + Na]⁺ 473.2298, found 473.2305.

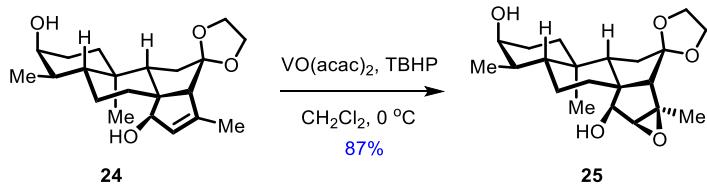
Preparation of diol **24**:



To a stirred solution of enone **23** (3.3 g, 7.4 mmol, 1.0 equiv) in CH₂Cl₂ (100 mL) at −78 °C was added DIBAL-H (1.5 M in toluene, 17 mL, 26 mol, 3.5 equiv). The resulting mixture was stirred at −78 °C for 30 min before diluted with EtOAc (10 mL) and quenched with Rochelle's salt (50 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel,

hexanes:EtOAc 3:1) afforded diol **24** (2.3 g, 90%) as a white solid. **24**: m.p. 171–172 °C (CH₂Cl₂); R_f = 0.50 (silica gel, hexanes:EtOAc 1:1); $[\alpha]_D^{20}$ = +1.6 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 5.35 (s, 1 H), 4.83 (d, J = 6.5 Hz, 1 H), 3.94 (dd, J = 6.4, 3.7 Hz, 1 H), 3.88–3.78 (m, 3 H), 3.77 (s, 1 H), 2.34 (s, 1 H), 2.01–1.94 (m, 1 H), 1.84 (ddd, J = 17.7, 8.7, 3.7 Hz, 1 H), 1.74 (s, 3 H), 1.70–1.63 (m, 3 H), 1.59 (dd, J = 13.1, 3.5 Hz, 1 H), 1.56–1.45 (m, 4 H), 1.44–1.29 (m, 3 H), 1.27–1.16 (m, 2 H), 0.94 (s, 3 H), 0.90 ppm (d, J = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 140.9, 130.0, 118.2, 77.9, 72.3, 71.2, 65.2, 64.0, 57.7, 55.2, 45.5, 35.9, 35.3, 34.8, 34.6, 33.1, 28.8, 23.9, 17.3, 16.4, 10.9 ppm; HRMS (ESI): calcd for C₂₁H₃₂NaO₄⁺ [M + Na]⁺ 371.2193, found 371.2201.

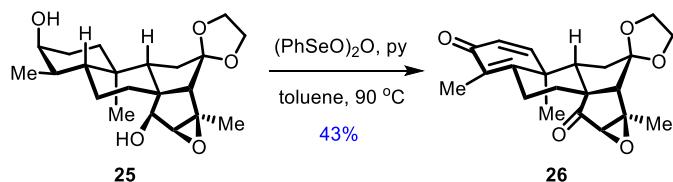
Preparation of epoxide 25:



To a stirred solution of diol **24** (1.6 g, 4.5 mmol, 1.0 equiv) in CH₂Cl₂ (50 mL) at 0 °C were sequentially added 4 Å molecular sieves (1.5 g), VO(acac)₂ (0.29 g, 1.1 mmol, 0.2 equiv) and TBHP (5.5 M in decane, 2.5 mL, 14 mmol, 3.0 equiv). The resulting mixture was stirred at 0 °C for 6 h before quenched with Na₂S₂O₃ (30 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded epoxide **25** (1.4 g, 87%) as a white solid. **25**: m.p. 180–182 °C (hexanes/EtOAc); *R*_f = 0.45 (silica gel,

4.29 (d, $J = 10.7$ Hz, 1 H), 4.02–3.94 (m, 1 H), 3.92–3.85 (m, 1 H), 3.84–3.76 (m, 2 H), 3.74 (s, 1 H), 3.47 (s, 1 H), 2.21 (d, $J = 17.3$ Hz, 2 H), 2.13 (s, 1 H), 1.80 (t, $J = 14.2$ Hz, 1 H), 1.73 (d, $J = 6.9$ Hz, 1 H), 1.65 (t, $J = 13.8$ Hz, 1 H), 1.60–1.45 (m, 4 H), 1.42 (d, $J = 8.1$ Hz, 6 H), 1.30–1.21 (m, 2 H), 1.16 (d, $J = 11.6$ Hz, 1 H), 0.92 (s, 3 H), 0.87 ppm (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 116.3, 73.4, 72.1, 68.5, 66.1, 64.5, 63.5, 62.3, 54.8, 50.2, 45.2, 37.0, 35.9, 35.6, 34.7, 33.1, 28.8, 23.9, 17.4, 16.2, 10.2 ppm; HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{32}\text{NaO}_5^+ [\text{M} + \text{Na}]^+$ 387.2142, found 387.2149.

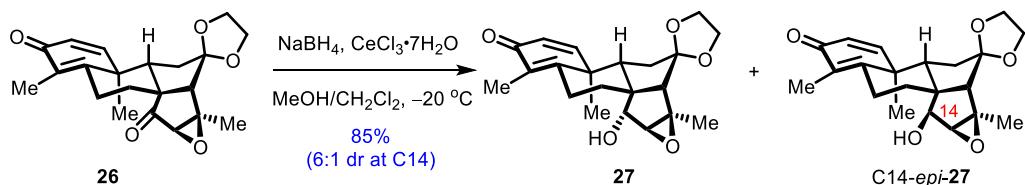
Preparation of cyclohexadienone **26**:



To a stirred solution of epoxide **25** (1.2 g, 3.3 mol, 1.0 equiv) in toluene (50 mL) at room temperature were sequentially added pyridine (1.3 mL, 17 mmol, 5.0 equiv) and $(\text{PhSeO})_2\text{O}$ (5.9 g, 17 mol, 5.0 equiv). The resulting mixture was warmed to 90 °C and stirred for 12 h before cooled to room temperature and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 6:1) afforded cyclohexadienone **26** (0.51 g, 43%) as a white solid. **26**: m.p. 187–189 °C (hexanes/EtOAc); R_f = 0.45 (silica gel, hexanes:EtOAc 2:1); $[\alpha]_{D}^{20} = -10.8$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ = 6.82 (d, $J = 9.9$ Hz, 1 H), 6.15 (d, $J = 9.9$ Hz, 1 H), 4.04–3.97 (m, 1 H), 3.92 (td, $J = 7.0, 4.6$ Hz, 1 H), 3.86 (q, $J = 7.1$ Hz, 1 H), 3.79 (q, $J = 7.0$ Hz, 1 H), 3.32 (s, 1 H), 2.73–2.63 (m, 1 H), 2.49 (s, 1 H), 2.47–2.41 (m, 1 H), 2.35 (dd, $J = 14.0, 3.1$ Hz, 1 H), 1.88 (s, 3 H), 1.83 (d, $J = 25.9$ Hz, 1 H), 1.58 (d, $J = 6.6$ Hz, 5 H), 1.44 (s, 3 H), 1.44–1.38 ppm (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 211.0, 185.8, 160.5, 154.9, 129.8,

125.8, 114.9, 64.9, 63.7, 63.4, 62.8, 61.2, 58.2, 50.6, 42.6, 37.5, 36.9, 25.2, 21.7, 17.3, 10.8 ppm; HRMS (ESI): calcd for $C_{21}H_{24}NaO_5^+ [M + Na]^+$ 379.1516, found 379.1526.

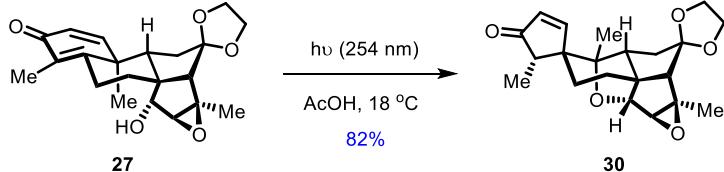
Preparation of alcohols **27 and C14-*epi*-**27**:**



To a stirred solution of cyclohexadienone **26** (0.61 g, 1.7 mmol, 1.0 equiv) in MeOH/CH₂Cl₂ (1:1, 40 mL) at -20 °C were sequentially added CeCl₃•7H₂O (1.3 g, 3.4 mmol, 2.0 equiv) and NaBH₄ (96 mg, 2.6 mmol, 1.5 equiv). The resulting mixture was stirred at -20 °C for 15 min before quenched with acetone (5 mL) and H₂O (20 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 2:1) afforded alcohol **27** (0.44 g, 73%) and C14-*epi*-**27** (73 mg, 12%) as white solids. **27**: m.p. 163–165 °C (hexanes/EtOAc); *R*_f = 0.30 (silica gel, hexanes:EtOAc 1:1); [α]_D²⁰ = -3.4 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 6.72 (d, *J* = 9.9 Hz, 1 H), 6.26–6.11 (m, 1 H), 4.25 (d, *J* = 11.6 Hz, 1 H), 4.11–4.03 (m, 1 H), 3.98 (t, *J* = 6.4 Hz, 2 H), 3.87 (q, *J* = 7.4 Hz, 1 H), 3.42 (s, 1 H), 3.07 (dd, *J* = 11.6, 2.1 Hz, 1 H), 2.72 (d, *J* = 16.0 Hz, 1 H), 2.43 (t, *J* = 12.7 Hz, 1 H), 2.32–2.23 (m, 1 H), 2.18 (d, *J* = 15.1 Hz, 2 H), 1.96–1.79 (m, 2 H), 1.89 (s, 3 H), 1.45 (s, 3 H), 1.29 (s, 3 H), 1.18 ppm (t, *J* = 13.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ = 186.0, 161.3, 154.7, 128.9, 126.6, 117.0, 76.0, 64.9, 64.1, 64.0, 63.1, 61.0, 54.2, 52.4, 43.3, 40.5, 38.8, 25.0, 21.6, 16.5, 10.8 ppm; HRMS (ESI): calcd for $C_{21}H_{26}NaO_5^+ [M + Na]^+$ 381.1672, found 381.1679.

C14-*epi*-27: m.p. 155–157 °C (hexanes/EtOAc); $R_f = 0.25$ (silica gel, hexanes:EtOAc 1:1); $[\alpha]_D^{20} = -32.8$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) $\delta = 6.77$ (d, $J = 9.9$ Hz, 1 H), 6.20 (d, $J = 9.9$ Hz, 1 H), 4.49 (dd, $J = 10.1, 1.3$ Hz, 1 H), 4.03–3.90 (m, 2 H), 3.87–3.81 (m, 1 H), 3.81–3.75 (m, 1 H), 3.55 (s, 1 H), 2.95–2.82 (m, 1 H), 2.70 (ddd, $J = 14.6, 4.6, 2.5$ Hz, 1 H), 2.43 (ddd, $J = 13.7, 5.1, 2.5$ Hz, 1 H), 2.26 (dd, $J = 10.3, 2.5$ Hz, 1 H), 2.22 (s, 1 H), 1.89 (d, $J = 1.1$ Hz, 3 H), 1.86 (s, 1 H), 1.69–1.56 (m, 2 H), 1.46 (s, 3 H), 1.33 (s, 3 H), 1.29 ppm (dd, $J = 13.7, 4.6$ Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 186.0, 161.8, 154.9, 129.1, 126.6, 115.7, 73.4, 68.1, 64.8$ (2C), 63.7, 62.3, 50.6, 50.4, 43.0, 37.0, 36.9, 27.1, 18.2, 17.3, 10.9 ppm; HRMS (ESI): calcd for C₂₁H₂₆NaO₅⁺ [M + Na]⁺ 381.1672, found 381.1683.

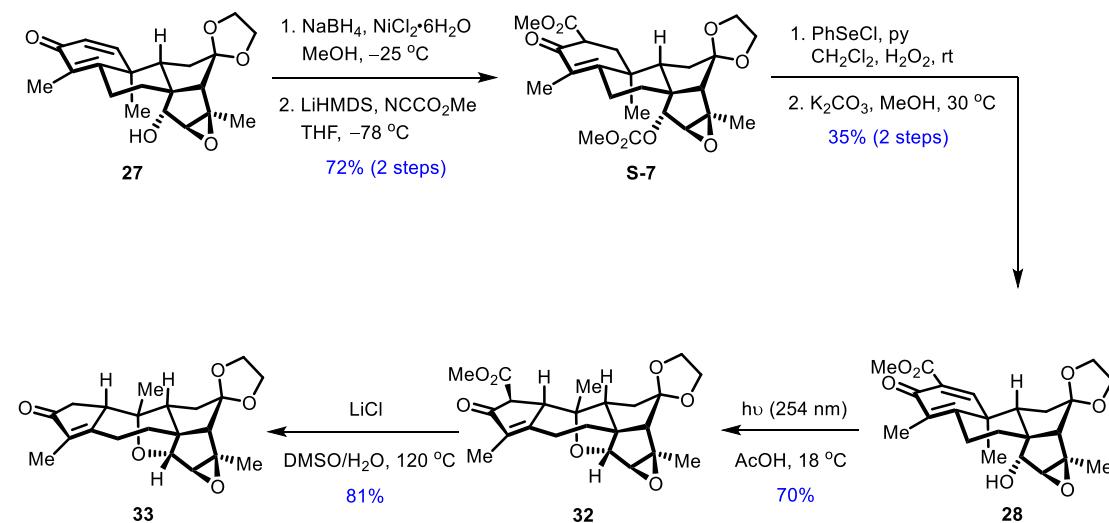
Preparation of spirocycle **30**:



A stirred solution of alcohol **27** (10 mg, 0.028 mmol) in AcOH (3 mL) at 18 °C was irradiated with a 254 nm lamp (300 W) for 20 min before concentrated *in vacuo*. The residue was partitioned between CH₂Cl₂ (5 mL) and NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded spirocycle **30** (8.2 mg, 82%) as a white solid. **30**: m.p. 130–132 °C (CH₂Cl₂/Et₂O); $R_f = 0.40$ (silica gel, hexanes:EtOAc 2:1); $[\alpha]_D^{20} = -22.9$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) $\delta = 7.50$ (d, $J = 6.0$ Hz, 1 H), 6.17 (d, $J = 6.0$ Hz, 1 H), 4.40 (s, 1 H), 4.01–3.95 (m, 2 H),

3.94–3.87 (m, 2 H), 3.23 (s, 1 H), 2.26–2.16 (m, 1 H), 2.15 (d, J = 1.4 Hz, 1 H), 2.14–2.04 (m, 2 H), 2.04–1.94 (m, 1 H), 1.80–1.71 (m, 3 H), 1.57 (ddd, J = 11.9, 6.2, 2.0 Hz, 1 H), 1.51 (s, 3 H), 1.35 (d, J = 7.4 Hz, 3 H), 0.91 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 209.6, 166.3, 132.3, 116.8, 89.0, 85.5, 71.2, 65.6, 64.2, 64.1, 63.2, 57.0, 56.2, 55.7, 54.9, 33.8, 33.4, 33.3, 19.3, 18.0, 9.6 ppm; HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{26}\text{O}_5^+$ [M + H]⁺ 359.1853, found 359.1859.

Photo-Nazarov Cyclization of Cyclohexadienone 28



Scheme S3. Photo-Nazarov cyclization of cyclohexadienone **28**

Preparation of ester S-7:

To a stirred solution of dienone **27** (50 mg, 0.14 mmol, 1.0 equiv) in MeOH (5 mL) at -25 °C were sequentially added $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (50 mg, 0.21 mmol, 1.5 equiv) and NaBH_4 (7.9 mg, 0.21 mmol, 1.5 equiv). The resulting mixture was stirred at -25 °C for 30 min before diluted with CH_2Cl_2 (5 mL), and quenched with acetone (1 mL) and H_2O (5 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*.

Flash column chromatography (silica gel, hexanes:EtOAc 2:1) afforded the corresponding enone as a white solid.

To a stirred solution of enone (obtained above) in THF (5 mL) at -78 °C were sequentially added LiHMDS (1.0 M in THF, 0.38 mL, 0.38 mmol, 2.7 equiv) and NCCO₂Me (30 μL, 0.35 mmol, 2.5 equiv). The resulting mixture was stirred at -78 °C for 1 h before quenched with NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded ester **S-7** (48 mg, 72% over two steps) as a white solid. **S-7**: m.p. 168–170 °C (hexanes/EtOAc); *R*_f = 0.40 (silica gel, hexanes:EtOAc 2:1); [α]_D²⁰ = -27.2 (c = 0.15, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 5.14 (s, 1 H), 4.04–3.95 (m, 2 H), 3.88 (q, *J* = 6.8 Hz, 1 H), 3.81 (s, 3 H), 3.81–3.74 (m, 1 H), 3.77 (s, 3 H), 3.56 (s, 1 H), 3.51 (dd, *J* = 14.7, 4.7 Hz, 1 H), 2.71–2.62 (m, 1 H), 2.36–2.22 (m, 3 H), 2.20–2.13 (m, 1 H), 2.09 (t, *J* = 14.0 Hz, 1 H), 1.94–1.83 (m, 2 H), 1.81–1.72 (m, 4 H), 1.55 (s, 3 H), 1.41 (td, *J* = 13.7, 3.5 Hz, 1 H), 1.06 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 193.2, 171.6, 162.2, 155.3, 128.4, 116.3, 80.8, 65.0, 64.3, 64.2, 64.1, 63.6, 56.0, 55.3, 52.8, 52.4, 49.8, 39.2, 38.4, 38.3, 38.2, 24.9, 18.1, 16.6, 11.4 ppm; HRMS (ESI): calcd for C₂₅H₃₂NaO₉⁺ [M + Na]⁺ 499.1939, found 499.1946.

Preparation of cyclohexadienone **28**:

To a stirred solution of ester **S-7** (48 mg, 0.10 mmol, 1.0 equiv) in CH₂Cl₂ (5 mL) at room temperature were sequentially added pyridine (11 μL, 0.14 mmol, 1.4 equiv) and PhSeCl (21 mg, 0.11 mmol, 1.1 equiv). The resulting mixture was stirred at room

temperature for 1 h before cooled to 0 °C and added H₂O₂ (30% wt/wt aq., 96 µL, 0.95 mmol, 9.5 equiv). The resulting mixture was stirred for 20 min before quenched with Na₂S₂O₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude dienone as a yellow oil, which was used directly without further purification.

To a stirred solution of dienone (crude, obtained above) in MeOH (5 mL) at 30 °C was added K₂CO₃ (19 mg, 0.14 mmol, 1.4 equiv). The resulting mixture was stirred at 30 °C for 12 h before diluted with CH₂Cl₂ (5 mL) and quenched with NH₄Cl (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 2:1) afforded cyclohexadienone **28** (15 mg, 35% over two steps) as a white solid. **28**: m.p. 181–183 °C (hexanes/EtOAc); *R*_f = 0.30 (silica gel, hexanes:EtOAc 1:2); [α]_D²⁰ = −1.9 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 7.36 (s, 1 H), 4.27 (d, *J* = 11.7 Hz, 1 H), 4.13–4.06 (m, 1 H), 4.04–3.97 (m, 2 H), 3.90 (q, *J* = 7.4 Hz, 1 H), 3.84 (s, 3 H), 3.44 (s, 1 H), 3.04 (d, *J* = 11.8 Hz, 1 H), 2.79–2.67 (m, 1 H), 2.45 (td, *J* = 14.3, 4.0 Hz, 1 H), 2.33–2.25 (m, 1 H), 2.21 (d, *J* = 16.2 Hz, 2 H), 1.99 (dd, *J* = 12.4, 8.9 Hz, 1 H), 1.92 (s, 4 H), 1.47 (s, 3 H), 1.36 (s, 3 H), 1.21 ppm (td, *J* = 13.7, 3.7 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ = 181.5, 166.4, 159.8, 158.7, 129.8, 129.7, 116.9, 76.1, 64.8, 64.2, 64.1, 63.1, 61.0, 54.4, 52.5, 51.9, 43.1, 40.4, 38.7, 25.0, 21.3, 16.5, 11.1 ppm; HRMS (ESI): calcd for C₂₃H₂₈NaO₇⁺ [M + Na]⁺ 439.1727, found 439.1736.

Preparation of pentacyclic ester 32:

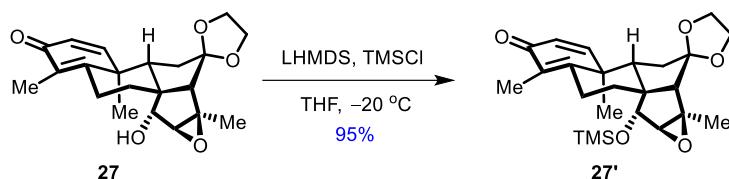
A stirred solution of cyclohexadienone **28** (12 mg, 29 μmol) in AcOH (3 mL) at 18 °C was irradiated with a 254 nm mercury lamp (300 W) for 20 min before concentrated *in vacuo*. The residue was partitioned between CH₂Cl₂ (5 mL) and NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 \times 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded pentacyclic ester **32** (8.4 mg, 70%) as a white solid. **32**: m.p. 203–205 °C (hexanes/EtOAc); R_f = 0.60 (silica gel, hexanes:EtOAc 1:2); $[\alpha]_D^{20} = -27.9$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 4.01–3.89 (m, 4 H), 3.75 (s, 3 H), 3.65 (s, 2 H), 3.19 (s, 1 H), 3.06 (s, 1 H), 2.86 (dd, J = 13.0, 6.8 Hz, 1 H), 2.68 (dd, J = 11.0, 7.9 Hz, 1 H), 2.49 (q, J = 12.1 Hz, 1 H), 2.08–1.99 (m, 2 H), 1.82 (ddd, J = 25.2, 11.8, 6.0 Hz, 3 H), 1.70 (s, 3 H), 1.46 (s, 3 H), 1.20 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 200.8, 172.7, 170.4, 136.7, 115.5, 90.0, 86.8, 68.4, 67.3, 65.6, 65.4, 63.3, 61.4, 57.5, 53.7, 52.9, 49.5, 37.0, 35.1, 27.2, 22.3, 17.1, 8.5 ppm; HRMS (ESI): calcd for C₂₃H₂₈NaO₇⁺ [M + Na]⁺ 439.1727, found 439.1732.

Preparation of pentacycle 33:

To a stirred solution of pentacyclic ester **32** (8.3 mg, 19 μmol , 1.0 equiv) in DMSO (2 mL) at room temperature was added LiCl (8.1 mg, 0.19 mmol, 10 equiv). The resulting mixture was warmed to 120 °C and stirred for 16 h before cooled to room temperature, diluted with Et₂O (5 mL) and quenched with H₂O (5 mL). The layers were separated, and the aqueous layer was extracted with Et₂O (3 \times 5 mL). The combined

organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 2:1) afforded pentacycle **33** (5.8 mg, 81%) as a white solid. **33**: m.p. 212–214 °C (hexanes/EtOAc); R_f = 0.50 (silica gel, hexanes:EtOAc 1:1); $[\alpha]_D^{20} = -17.5$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ = 4.02–3.90 (m, 4 H), 3.67 (s, 1 H), 3.20 (d, $J = 1.0$ Hz, 1 H), 2.84 (dd, $J = 13.0, 6.8$ Hz, 1 H), 2.67 (dd, $J = 11.5, 7.4$ Hz, 1 H), 2.67–2.63 (m, 1 H), 2.59 (dd, $J = 18.5, 2.7$ Hz, 1 H), 2.41 (dd, $J = 18.4, 6.5$ Hz, 1 H), 2.48–2.37 (m, 1 H), 2.06 (s, 1 H), 2.05–1.98 (m, 1 H), 1.89 (dd, $J = 23.68, 12.1$ Hz, 2 H), 1.83–1.75 (m, 1 H), 1.68 (d, $J = 1.9$ Hz, 3 H), 1.46 (s, 3 H), 1.22 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 208.0, 172.1, 138.4, 115.7, 89.9, 86.9, 68.4, 67.5, 65.6, 65.5, 63.3, 61.4, 53.2, 49.8, 37.0, 36.8, 35.3, 27.2, 22.5, 17.1, 8.2 ppm; HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{27}\text{O}_5^+ [\text{M} + \text{H}]^+$ 359.1853, found 359.1858.

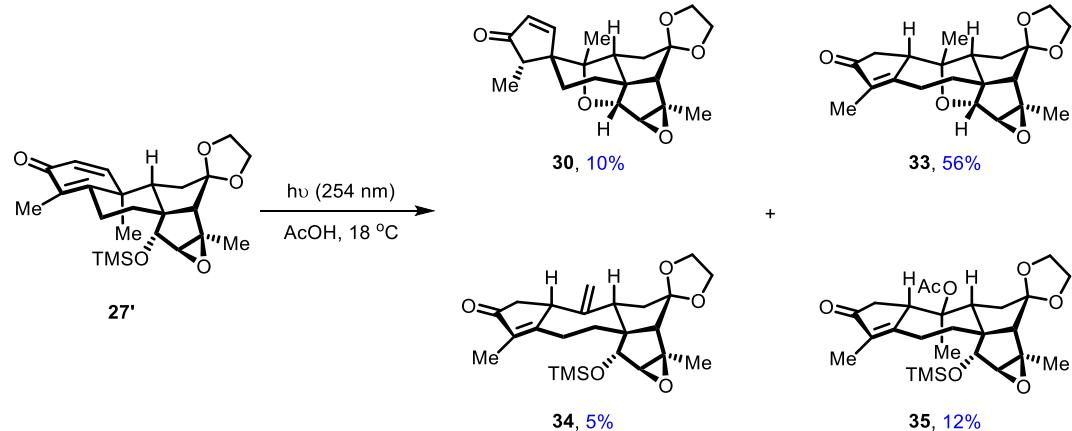
Preparation of cyclohexadienone **27'**:



To a stirred solution of the alcohol **27** (0.50 g, 1.4 mmol, 1.0 equiv) in THF (20 mL) at –20 °C were sequentially added LiHMDS (1.0 M in THF, 2.1 mL, 2.1 mmol, 1.5 equiv) and TMSCl (0.27 mL, 2.1 mmol, 1.5 equiv). The resulting mixture was stirred at –20 °C for 30 min before quenched with NaHCO_3 (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 10:1) afforded cyclohexadienone **27'** (0.57

g, 95%) as a white solid. **27'**: m.p. 159–161 °C (hexanes/EtOAc); R_f = 0.55 (silica gel, hexanes:EtOAc 3:1); $[\alpha]_D^{20} = -19.4$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 6.79 (d, $J = 9.9$ Hz, 1 H), 6.17 (d, $J = 9.9$ Hz, 1 H), 4.37 (s, 1 H), 3.97–3.87 (m, 2 H), 3.86–3.79 (m, 1 H), 3.73 (q, $J = 6.9$ Hz, 1 H), 3.39 (s, 1 H), 2.73–2.67 (m, 1 H), 2.60–2.50 (m, 1 H), 2.45–2.34 (m, 1 H), 2.11 (s, 1 H), 2.10–2.05 (m, 1 H), 1.88 (d, $J = 0.9$ Hz, 3 H), 1.73–1.64 (m, 2 H), 1.50 (s, 3 H), 1.19 (s, 3 H), 1.22–1.13 (m, 1 H), 0.19 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ = 186.0, 161.6, 155.2, 128.8, 126.5, 116.5, 77.4, 66.2, 64.7, 64.2, 63.5, 63.4, 54.7, 52.5, 43.4, 39.9, 39.4, 25.2, 22.7, 16.8, 10.7, 1.1 ppm (3C); HRMS (ESI): calcd for C₂₄H₃₄NaO₅Si⁺ [M + Na]⁺ 453.2068, found 453.2073.

Photo-Nazarov cyclization of cyclohexadienone **27'**:

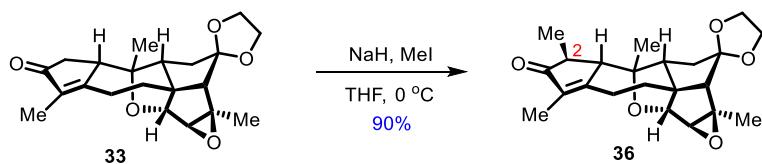


A stirred solution of dienone **27'** (0.55 g, 1.3 mmol) in AcOH (64 mL) at 18 °C was irradiated with a 254 nm lamp (300 W) for 40 min before concentrated *in vacuo*. The residue was partitioned between CH₂Cl₂ (20 mL) and NaHCO₃ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1 to 4:1) afforded

pentacycle **33** (0.26 g, 56%) and spirocycle **30** (46 mg, 10%), along with alkene **34** (28 mg, 5%) and acetate **35** (75 mg, 12%) as white solids. **34**: m.p. 146–148 °C (hexanes/EtOAc); R_f = 0.50 (silica gel, hexanes:EtOAc 3:1); $[\alpha]_D^{20} = -25.3$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 4.95 (s, 1 H), 4.85 (s, 1 H), 4.11 (s, 1 H), 4.04–3.93 (m, 2 H), 3.92–3.82 (m, 2 H), 3.49 (d, $J = 6.1$ Hz, 1 H), 3.22 (s, 1 H), 2.91 (ddd, $J = 18.3, 12.2, 4.8$ Hz, 1 H), 2.84–2.68 (m, 2 H), 2.68–2.58 (m, 1 H), 2.58–2.48 (m, 2 H), 2.31 (s, 1 H), 2.22 (m, 1 H), 1.89 (ddd, $J = 14.6, 12.5, 4.8$ Hz, 1 H), 1.82–1.74 (m, 1 H), 1.64 (d, $J = 1.7$ Hz, 3 H), 1.61 (s, 3 H), 0.03 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ = 208.4, 174.3, 144.6, 134.8, 115.0, 110.1, 74.6, 67.8, 66.3, 65.1(2C), 63.5, 57.3, 55.3, 49.1, 43.0, 40.0, 37.8, 27.3, 17.6, 8.2, 0.1 ppm (3C); HRMS (ESI): calcd for C₂₄H₃₅O₅Si⁺ [M + H]⁺ 431.2248, found 431.2250.

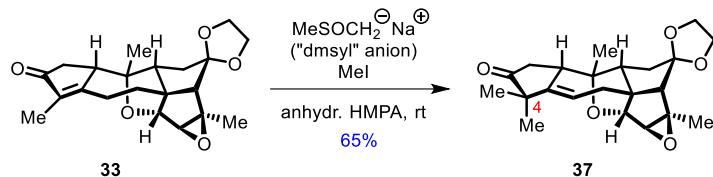
35: m.p. 154–156 °C (hexanes/EtOAc); R_f = 0.50 (silica gel, hexanes:EtOAc 2:1); $[\alpha]_D^{20} = +0.9$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 4.38–4.31 (m, 1 H), 4.25 (s, 1 H), 4.01–3.95 (m, 1 H), 3.92–3.87 (m, 1 H), 3.87–3.81 (m, 1 H), 3.81–3.75 (m, 1 H), 3.37 (s, 1 H), 3.33 (dd, $J = 14.9, 6.6$ Hz, 1 H), 2.80–2.57 (m, 2 H), 2.53 (dd, $J = 14.88, 12.04$ Hz, 1 H), 2.49–2.41 (m, 1 H), 2.35 (s, 1 H), 2.34 (s, 1 H), 2.33 (s, 1 H), 1.97 (s, 3 H), 1.79–1.70 (m, 1 H), 1.67 (d, $J = 1.76$, 3 H), 1.55 (s, 3 H), 1.53–1.46 (m, 1 H), 0.95 (s, 3 H), 0.15 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ = 207.9, 173.1, 170.2, 138.0, 115.1, 87.7, 74.5, 66.7, 64.6, 64.5, 64.0, 63.6, 56.9, 55.2, 49.7, 41.4, 37.3, 36.0, 26.7, 22.3, 20.0, 17.2, 8.3, 1.1 (3C) ppm; HRMS (ESI): calcd for C₂₆H₃₈NaO₇Si⁺ [M + Na]⁺ 513.2279, found 513.2284.

Preparation of 2-methyl cyclopentenone **36:**



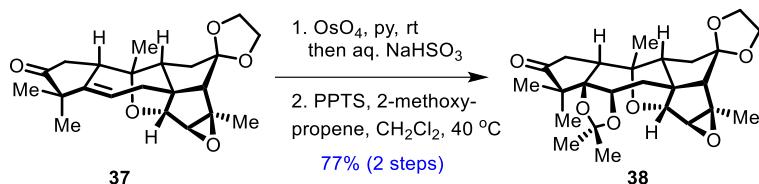
To a stirred solution of pentacycle **33** (11 mg, 30 µmol, 1.0 equiv) in THF (2 mL) at 0 °C were sequentially added NaH (60% dispersion in mineral oil, 2.4 mg, 60 µmol, 2.0 equiv) and MeI (3.7 µL, 60 µmol, 2.0 equiv). The resulting mixture was stirred at 0 °C for 20 min before quenched with NH₄Cl (2 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 2 mL). The combined organic layers were washed dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded 2-methyl cyclopentenone **36** (10 mg, 90%) as a white solid. **36:** m.p. 198–200 °C (hexanes/EtOAc); *R*_f = 0.50 (silica gel, hexanes:EtOAc 3:1); [α]_D²⁰ = −7.5 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 4.02–3.91 (m, 4 H), 3.67 (s, 1 H), 3.19 (s, 1 H), 2.86 (dd, *J* = 12.9, 6.8 Hz, 1 H), 2.65 (dd, *J* = 11.7, 7.3 Hz, 1 H), 2.55–2.47 (m, 1 H), 2.44–2.33 (m, 1 H), 2.18 (t, *J* = 2.1 Hz, 1 H), 2.06 (t, *J* = 1.6 Hz, 1 H), 2.04–1.98 (m, 1 H), 1.91 (dd, *J* = 23.9, 12.2 Hz, 1 H), 1.87–1.83 (m, 1 H), 1.83–1.75 (m, 1 H), 1.69 (d, *J* = 1.6 Hz, 3 H), 1.46 (s, 3 H), 1.28 (s, 3 H), 1.19 ppm (d, *J* = 7.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 210.8, 170.6, 137.0, 115.7, 90.0, 87.3, 68.4, 67.5, 65.6 (2C), 63.3, 62.4, 61.4, 49.9, 41.8, 37.0, 35.2, 27.2, 22.3, 18.0, 17.2, 8.3 ppm; HRMS (ESI): calcd for C₂₂H₂₉O₅⁺ [M + H]⁺ 373.2010, found 373.2019.

Preparation of 4,4-dimethyl cyclopentanone 37:



To a stirred solution of pentacycle **33** (20 mg, 56 µmol, 1.0 equiv) in freshly distilled HMPA (2 mL) at room temperature were sequentially added “dmsyl” anion⁴ (0.5 M in DMSO, 0.16 mL, 84 µmol, 1.5 equiv) and MeI (6.8 µL, 0.11 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 5 min before quenched with H₂O (2 mL) and diluted with Et₂O (2 mL). The layers were separated, and the aqueous layer was extracted with Et₂O (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded 4,4-dimethyl cyclopentanone **37** (14 mg, 65%) as a white solid. **37**: m.p. 221–223 °C (hexanes/EtOAc); *R*_f = 0.40 (silica gel, hexanes:EtOAc 2:1); [α]_D²⁰ = +55.1 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 5.49–5.40 (m, 1 H), 4.07 (s, 1 H), 4.03–3.96 (m, 2 H), 3.96–3.91 (m, 2 H), 3.26 (s, 1 H), 2.82–2.71 (m, 1 H), 2.64–2.49 (m, 3 H), 2.39–2.25 (m, 2 H), 2.09–2.05 (m, 1 H), 1.97 (t, *J* = 12.2 Hz, 1 H), 1.86 (ddd, *J* = 12.2, 7.0, 2.4 Hz, 1 H), 1.51 (s, 3 H), 1.21 (s, 3 H), 1.12 (s, 3 H), 1.06 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 220.0, 146.7, 119.7, 115.8, 85.9, 85.0, 69.3, 67.0, 65.7, 64.9, 63.3, 60.0, 54.4, 52.5, 49.7, 40.5, 40.0, 37.2, 27.0, 23.6, 22.8, 17.4 ppm; HRMS (ESI): calcd for C₂₂H₂₉O₅⁺ [M + H]⁺ 373.2010, found 373.2021.

Preparation of acetonide 38:

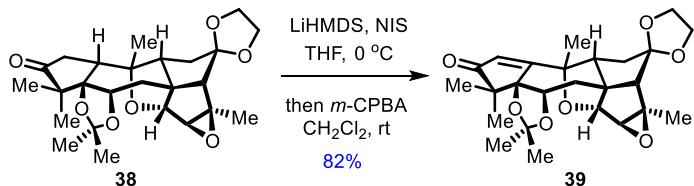


To a stirred solution of 4,4-dimethyl cyclopentanone **37** (0.14 g, 0.38 mmol, 1.0 equiv) in pyridine (5 mL) at room temperature was added OsO_4 (0.11 g, 0.41 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature for 8 h before diluted with Et_2O (5 mL) and quenched with NaHSO_3 (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 2:1) afforded the corresponding diol as a white solid.

To a stirred solution of diol (obtained above) in CH_2Cl_2 (5 mL) at room temperature were sequentially added 2,2-methoxypropene (0.11 mL, 1.1 mmol, 3.0 equiv) and PPTS (19 mg, 0.075 mmol, 0.2 equiv). The resulting mixture was warmed to 40 °C and stirred for 12 h before cooled to room temperature and quenched with NaHCO_3 (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 6:1) afforded acetonide **38** (0.13 g, 77% over two steps) as a white solid. **38**: m.p. 233–235 °C (hexanes/EtOAc); $R_f = 0.45$ (silica gel, hexanes:EtOAc 3:1); $[\alpha]_D^{20} = -10.9$ ($c = 0.5$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 4.18$ (dd, $J = 6.1, 1.3$ Hz, 1 H), 4.14 (s, 1 H), 4.01–3.93 (m, 4 H), 3.41 (dd, $J = 12.2, 7.3$ Hz, 1 H), 3.26 (s, 1 H), 2.83 (dd, $J =$

17.9, 7.9 Hz, 1 H), 2.64–2.55 (m, 2 H), 2.45 (dd, J = 17.9, 10.4 Hz, 1 H), 2.11 (s, 1 H), 2.09 (dd, J = 15.9, 6.1 Hz, 1 H), 1.87 (dd, J = 24.2, 12.1 Hz, 1 H), 1.86–1.78 (m, 1 H), 1.50 (s, 3 H), 1.44 (s, 3 H), 1.26 (s, 3 H), 1.18 (s, 3 H), 1.13 (s, 3 H), 1.08 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 217.9, 115.8, 105.7, 92.5, 89.5, 87.7, 76.1, 69.7, 67.7, 65.5, 64.0, 63.6, 61.9, 57.0, 52.2, 49.1, 40.2, 36.6, 35.8, 28.3, 26.2, 24.7, 22.8, 18.5, 17.5 ppm; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{34}\text{NaO}_7^+$ [M + Na]⁺ 469.2197, found 469.2202.

Preparation of enone **39**:

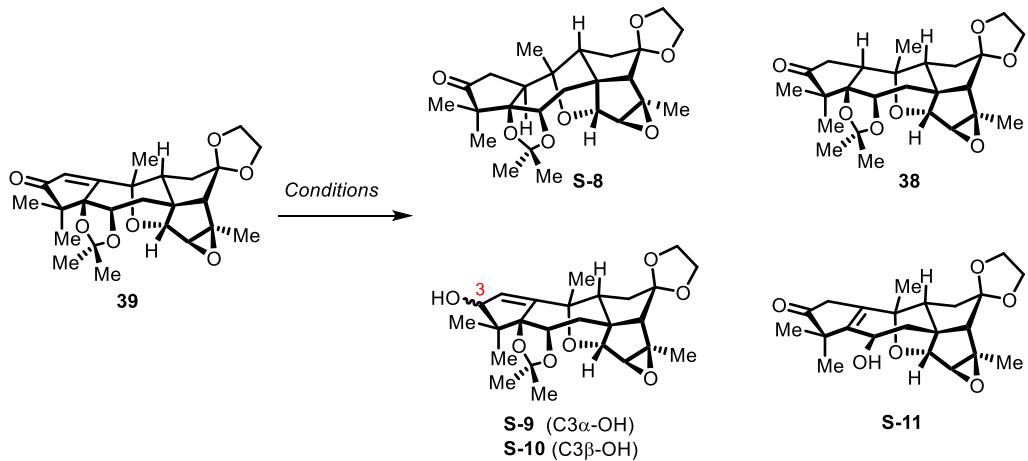


To a stirred solution of acetonide **38** (95 mg, 0.21 mmol, 1.0 equiv) in THF (4 mL) at 0 °C were sequentially added LiHMDS (1.0 M in THF, 0.25 mL, 0.25 mmol, 1.2 equiv) and NIS (72 mg, 0.32 mmol, 1.5 equiv). The resulting mixture was stirred at 0 °C for 1 h before CH_2Cl_2 (8 mL), NaHCO_3 (0.18 g, 2.1 mmol, 10 equiv) and *m*-CPBA (85% wt/wt, 0.21 g, 1.1 mmol, 5.0 equiv) were sequentially added. The resulting mixture was stirred at room temperature for 6 h before quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded enone **39** (103 mg, 82%) as a white solid. **39**: m.p. 216–218 °C (hexanes/EtOAc); R_f = 0.45 (silica gel, hexanes:EtOAc 3:1); $[\alpha]D^{20} = -12.5$ ($c = 0.1$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ = 6.40 (s, 1 H), 4.50 (dd, J = 4.2, 2.2 Hz, 1 H), 4.09 (dd, J = 11.5, 7.1 Hz, 1 H), 4.00–3.91 (m, 4 H), 3.85 (s, 1 H), 3.30 (s, 1 H), 2.44 (dd, J = 16.4, 2.3 Hz, 1 H),

2.14 (s, 1 H), 1.96 (dd, $J = 16.3, 4.1$ Hz, 1 H), 1.83 (dd, $J = 23.6, 11.9$ Hz, 1 H), 1.82–1.75 (m, 1 H), 1.52 (s, 3 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.35 (s, 3 H), 1.14 ppm (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 210.1, 179.2, 132.1, 116.1, 107.8, 92.5, 90.8, 85.4, 77.4, 69.1, 66.1, 65.6, 64.2, 63.6, 63.0, 52.2, 44.9, 39.3, 35.7, 27.7, 26.5, 24.7, 23.3, 19.4, 17.1$ ppm; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{32}\text{NaO}_7^+ [\text{M} + \text{Na}]^+$ 467.2040, found 467.2057.

Failed Attempts on the Inversion of the Stereochemistry at C-1 of Enone 39

Table S1. Attempted hydrogenation and 1,4-reduction of enone **39^a**



Entry	Reagents	Solvent	Temp. (°C)	Products (Yield) ^b
1	Pd/C, H_2 (1 atm)	MeOH	25	– ^c
2	Pd/C, H_2 (50 atm)	MeOH	25	– ^c
3	Crabtree's cat., H_2 (50 atm)	CH_2Cl_2	25	– ^c
4	PtO_2 , H_2 (50 atm)	EtOAc	25	S-10 (96%)
5	NaBH_4	MeOH	25	S-9 (30%), S-10 (45%)
6	NaBH_4 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	MeOH	–20	S-9 (24%), S-10 (72%)
7	L-Selectride	THF	–40	S-9 (62%), S-10 (31%)
8	LiAlH_4 , CuI , HMPA	THF	0	– ^c
9	HSiCl_3 , HMPA	CH_2Cl_2	40	– ^c
10	$[(\text{Ph}_3\text{P})\text{CuH}]_6$	toluene	60	– ^c

11	(Ph ₃ P) ₃ RhCl, Et ₃ SiH	toluene	60	^{-c}
12	Mn(dpm) ₃ , TBHP, PhSiH ₃	<i>i</i> -PrOH	25	38 (80%)
13	PhSiH ₃ , <i>n</i> -Bu ₃ SnH (O- <i>t</i> -Bu) ₂	toluene	120	^{-d}
14	SmI ₂	MeOH/THF	rt	S-11 (10%)
15	Li, naphthalene	THF	-78	S-11 (53%)
16	Li, NH ₃ (l)	THF	-78	^{-d}

^aReactions were performed on 0.02 mmol scale. ^bIsolated yields. ^cRecovery of **39**. ^dDecomposition.

Preparation of allylic alcohols **S-9** and **S-10** (entry 7):

To a stirred solution of enone **39** (8.9 mg, 20 µmol, 1.0 equiv) in THF (5 mL) at $-40\text{ }^{\circ}\text{C}$ was added L-Selectride (1.0 M in THF, 0.10 mL, 0.10 mmol, 5.0 equiv). The resulting mixture was stirred at $-40\text{ }^{\circ}\text{C}$ for 30 min before quenched with NH₄Cl (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 \times 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 2:1) afforded allylic alcohols **S-9** (5.5 mg, 62%) and **S-10** (2.8 mg, 31%) as white solids. **S-9**: m.p. 222–224 °C (hexanes/EtOAc); *R*_f = 0.40 (silica gel, hexanes:EtOAc 1:1); [α]_D²⁰ = -8.6 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 6.18 (d, *J* = 1.5 Hz, 1 H), 4.57 (dd, *J* = 8.4, 1.5 Hz, 1 H), 4.19 (dd, *J* = 4.2, 2.0 Hz, 1 H), 4.00 (s, 1 H), 3.99–3.91 (m, 4 H), 3.87 (dd, *J* = 11.7, 7.0 Hz, 1 H), 3.32 (s, 1 H), 2.39 (dd, *J* = 16.3, 2.0 Hz, 1 H), 2.12 (s, 1 H), 2.01 (dd, *J* = 16.1, 4.2 Hz, 1 H), 1.83 (t, *J* = 11.9 Hz, 1 H), 1.75 (ddd, *J* = 12.2, 7.0, 2.0 Hz, 1 H), 1.51 (s, 3 H), 1.47 (s, 3 H), 1.42 (s, 3 H), 1.33 (s, 3 H), 1.15 (s, 3 H), 0.94 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 151.9, 137.8, 116.2, 106.7, 96.1, 89.7, 84.3, 81.3, 77.3, 68.9, 66.7, 65.5, 64.3, 63.6, 63.5, 51.3, 45.9, 39.4, 36.1, 28.6, 26.8, 24.4, 20.4, 19.3, 17.2 ppm; HRMS (ESI): calcd for C₂₅H₃₄NaO₇⁺ [M + Na]⁺ 469.2197, found

469.2205.

S-10: m.p. 229–230 °C (hexanes/EtOAc); R_f = 0.45 (silica gel, hexanes:EtOAc 1:1); $[\alpha]_D^{20} = +8.5$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 6.45 (d, J = 3.2 Hz, 1 H), 4.30 (dd, J = 4.3, 1.9 Hz, 1 H), 4.00–3.93 (m, 4 H), 3.92–3.86 (m, 1 H), 3.89 (s, 1 H), 3.83 (dd, J = 11.5, 3.2 Hz, 1 H), 3.30 (s, 1 H), 2.40 (dd, J = 16.3, 2.0 Hz, 1 H), 2.12 (s, 1 H), 1.95 (dd, J = 16.2, 4.3 Hz, 1 H), 1.82 (t, J = 11.7 Hz, 1 H), 1.76 (ddd, J = 12.1, 7.1, 2.2 Hz, 1 H), 1.51 (s, 3 H), 1.47 (s, 3 H), 1.45 (s, 3 H), 1.34 (s, 3 H), 1.13 (s, 3 H), 0.99 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 155.4, 136.8, 116.2, 107.0, 95.9, 89.8, 84.3, 81.7, 76.3, 68.9, 66.7, 65.5, 64.2, 63.6, 63.4, 48.2, 45.6, 39.6, 36.0, 28.5, 27.0, 25.5, 24.2, 19.1, 17.2 ppm; HRMS (ESI): calcd for C₂₅H₃₄NaO₇⁺ [M + Na]⁺ 469.2197, found 469.2205.

Conversion of enone 39 to acetonide 38 (entry 12):

To a stirred solution of enone **39** (8.9 mg, 20 μmol, 1.0 equiv) in *i*-PrOH (4 mL, degassed) at room temperature were sequentially added Mn(dpm)₃ (7.3 mg, 10 μmol, 0.5 equiv) and TBHP (5.5 M in decane, 22 μL, 0.12 mmol, 6.0 equiv). The resulting mixture was stirred at room temperature for 10 h before concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded acetonide **38** (7.1 mg, 80%).

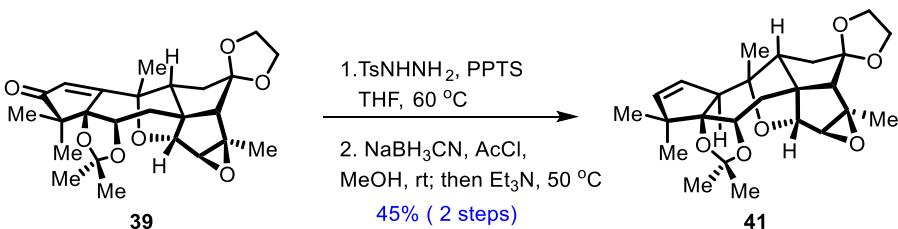
Preparation of alcohol S-11 (entry 15):

Preparation of the stock solution of Li/naphthalene (1.0 M in THF): To a stirred solution of naphthalene (0.28 g, 2.2 mmol, 1.1 equiv) in THF (2 mL) at room

temperature was added Li (14 mg, 2.0 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 1 h before use.

To a solution of enone **39** (8.9 mg, 20 μ mol, 1.0 equiv) in THF (5 mL) at -78°C was added a solution of Li/naphthalene (1.0 M in THF, 0.20 mL, 0.20 mmol, 10 equiv). The resulting mixture was stirred at -78°C for 10 min before quenched with NH₄Cl (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded alcohol **S-11** (4.1 mg, 53%) as a white solid. **S-11**: m.p. 217–219 $^{\circ}\text{C}$ (hexanes/EtOAc); $R_f = 0.30$ (silica gel, hexanes:EtOAc 1:1); $[\alpha]_D^{20} = -22.0$ ($c = 0.1$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 4.38 (s, 1 H), 4.05–3.93 (m, 4 H), 3.80 (s, 1 H), 3.56 (dd, $J = 11.6, 7.2$ Hz, 1 H), 3.35 (s, 1 H), 3.23 (d, $J = 23.1$ Hz, 1 H), 3.01 (d, $J = 23.0$ Hz, 1 H), 2.27 (d, $J = 15.3$ Hz, 1 H), 2.18–2.10 (m, 2 H), 1.97–1.82 (m, 2 H), 1.53 (s, 3 H), 1.34 (s, 3 H), 1.18 (s, 3 H), 1.08 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 219.5, 144.5, 135.9, 116.1, 88.5, 84.7, 68.7, 66.8, 65.6, 64.6, 64.3, 63.5, 61.7, 54.0, 48.9, 47.7, 42.0, 37.0, 23.7, 22.3, 20.3, 17.2 ppm; HRMS (ESI): calcd for C₂₂H₂₈NaO₆⁺ [M + Na]⁺ 411.1778, found 411.1786.

Preparation of alkene **41**:



To a stirred solution of enone **39** (62 mg, 0.14 mmol, 1.0 equiv) in THF (5 mL) at

room temperature were sequentially added TsNHNH₂ (50 mg, 0.27 mmol, 2.0 equiv) and PPTS (7.5 mg, 30 µmol, 0.2 equiv). The resulting mixture was warmed to 60 °C and stirred for 6 h before cooled to room temperature and quenched with NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude hydrazone as a white solid, which was used directly without further purification.

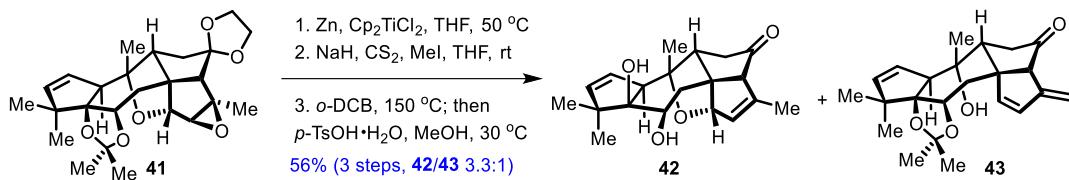
To a stirred solution of hydrazone (crude, obtained above) in MeOH (5 mL) at room temperature were sequentially added NaBH₃CN (26 mg, 0.41 mmol, 1.5 equiv) and AcCl (10 µL, 0.14 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 1 h before Et₃N (0.11 mL, 0.82 mmol, 6.0 equiv) was added. The resulting mixture was degassed and warmed to 50 °C and stirred for 1 h before cooled to room temperature and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 10:1) afforded alkene **41** (27 mg, 45% over two steps) as a white solid. **41**: m.p. 243–245 °C (hexanes/EtOAc); *R*_f = 0.40 (silica gel, hexanes:EtOAc 4:1); [α]_D²⁰ = −3.3 (c = 0.5, CHCl₃); ¹H NMR (400 MHz, acetone-*d*₆) δ = 5.88 (dd, *J* = 6.2, 1.8 Hz, 1 H), 5.52 (dd, *J* = 6.2, 3.6 Hz, 1 H), 4.38 (t, *J* = 3.0 Hz, 1 H), 4.07 (s, 1 H), 3.96–3.91 (m, 4 H), 3.85 (dd, *J* = 11.1, 7.8 Hz, 1 H), 3.44–3.42 (m, 1 H), 3.19 (d, *J* = 1.1 Hz, 1 H), 2.36 (dd, *J* = 16.1, 2.7 Hz, 1 H), 2.09 (d, *J* = 1.6 Hz, 1 H), 1.88 (dd, *J* = 16.1, 3.3 Hz, 1 H), 1.72 – 1.67 (m, 2 H), 1.46 (s, 3 H), 1.46 (d, *J* = 0.8 Hz, 3 H), 1.30–1.29 (m, 3 H), 1.21 (s, 3 H), 1.13 (s, 3 H), 1.03 ppm (s, 3 H); ¹³C NMR (100 MHz, acetone-*d*₆) δ = 141.0, 127.7, 117.0, 108.5, 99.6, 94.1, 87.2, 78.6, 70.2, 66.0 (2C), 65.5,

64.1, 63.8, 55.2, 51.2, 46.1, 43.8, 35.9, 29.2, 28.2, 24.2, 22.4, 20.0, 18.0 ppm; HRMS

(ESI): calcd for $C_{25}H_{34}NaO_6^+$ [M + Na]⁺ 453.2248, found 453.2257.

Of note, without the solvent degassing manipulations, the reaction on the same scale as described above afforded a mixture of alkene **41** (15 mg, 25%) and alcohol **S-10** (14 mg, 23%).

Preparation of diene **42** and triene **43**:



To a stirred solution of alkene **41** (22 mg, 50 μ mol, 1.0 equiv) in THF (5 mL, degassed) at room temperature were sequentially added Cp_2TiCl_2 (19 mg, 75 μ mol, 1.5 equiv) and Zn dust (12 mg, 0.19 mmol, 3.8 equiv). The resulting mixture was warmed to 50 °C and stirred for 6 h before filtered through a short pad of celite. The filtrate was washed with NH₄Cl (5 mL, sat. aq.) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded the corresponding alcohol as a white solid.

To a stirred solution of the alcohol (obtained above), CS_2 (12 μ L, 0.20 mmol, 4.0 equiv) in THF (5 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 8.0 mg, 0.20 mmol, 4.0 equiv). The resulting mixture was stirred at room temperature for 5 h before MeI (12 μ L, 0.20 mmol, 4.0 equiv) was added. The reaction was stirred for an additional 10 min before quenched with NH₄Cl (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* to afford the crude

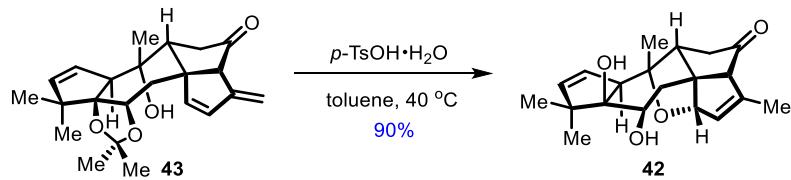
xanthate as a white solid, which was used directly without further purification.

A stirred solution of xanthate (crude, obtained above) in *o*-DCB (5 mL) was warmed to 150 °C and stirred for 20 h before cooled to room temperature and MeOH (5 mL) and *p*-TsOH•H₂O (19 mg, 0.10 mmol, 2.0 equiv) were added. The resulting mixture was warmed to 30 °C and stirred for 36 h before diluted with EtOAc (5 mL) and quenched with NaHCO₃ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded diene **42** (7.1 mg, 43% over three steps) and triene **43** (2.4 mg, 13% over three steps) as white solids. **42**: m.p. 230–232 °C (hexanes/EtOAc); R_f = 0.40 (silica gel, hexanes:EtOAc 1:1); $[\alpha]_D^{20} = +145.0$ (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 5.80 (dd, J = 6.0, 1.8 Hz, 1 H), 5.56 (q, J = 1.7 Hz, 1 H), 5.53 (dd, J = 6.0, 3.6 Hz, 1 H), 4.82 (s, 1 H), 4.29 (q, J = 8.3 Hz, 1 H), 3.76 (dd, J = 11.6, 7.9 Hz, 1 H), 3.21 (dd, J = 3.6, 1.8 Hz, 1 H), 2.67 (dd, J = 16.4, 11.6 Hz, 1 H), 2.60 (s, 1 H), 2.17 (d, J = 1.5 Hz, 1 H), 2.15–2.13 (m, 1 H), 2.13–2.06 (m, 1 H), 1.93 (d, J = 1.3 Hz, 1 H), 1.75 (q, J = 1.3 Hz, 3 H), 1.51 (d, J = 9.1 Hz, 1 H), 1.32 (s, 3 H), 1.26 (s, J = 2.2 Hz, 3 H), 1.15 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 214.8, 144.3, 141.0, 127.8, 127.7, 88.8, 87.9, 87.8, 72.7, 69.7, 58.9, 58.7, 54.0, 46.1, 41.9, 39.2, 23.1, 22.6, 21.2, 15.2 ppm; HRMS (ESI): calcd for C₂₀H₂₆NaO₄⁺ [M + Na]⁺ 353.1723, found 353.1728.

43: m.p. 174–176 °C (hexanes/EtOAc); R_f = 0.40 (silica gel, hexanes:EtOAc 2:1); $[\alpha]_D^{20} = +20.0$ (c = 0.1, CHCl₃); ¹H NMR (600 MHz, acetone-*d*₆) δ = 6.58 (d, J = 5.5 Hz, 1H),

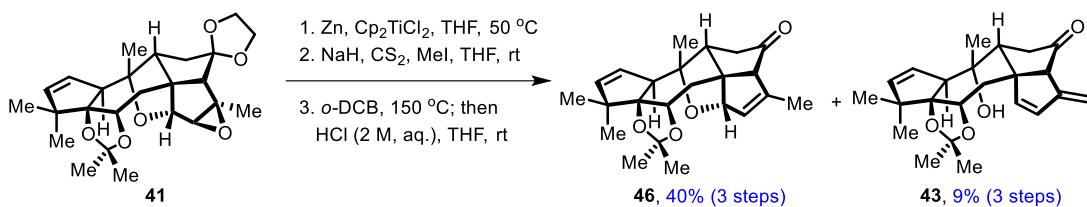
6.07 (dd, $J = 5.5$, 0.8 Hz, 1 H), 5.96 (dd, $J = 6.2$, 1.7 Hz, 1 H), 5.57 (dd, $J = 6.1$, 3.3 Hz, 1 H), 4.94 (q, $J = 1.1$ Hz, 1 H), 4.90 (d, $J = 1.2$ Hz, 1 H), 4.45 (dd, $J = 4.5$, 1.8 Hz, 1 H), 3.38–3.36 (m, 1 H), 3.59 (dd, $J = 14.5$, 6.3 Hz, 1 H), 3.37 (s, 1 H), 2.88 (d, $J = 1.4$ Hz, 1 H), 2.47 (ddd, $J = 16.5$, 14.6, 0.8 Hz, 1 H), 2.32 (dd, $J = 16.4$, 4.5 Hz, 1 H), 2.17 (ddd, $J = 16.4$, 6.3, 1.6 Hz, 1 H), 1.75 (dd, $J = 16.3$, 1.7 Hz, 1 H), 1.46 (d, $J = 0.8$ Hz, 3 H), 1.35 (s, 3 H), 1.33 (d, $J = 0.8$ Hz, 3 H), 1.15 (s, 3 H), 1.02 ppm (s, 3 H); ^{13}C NMR (150 MHz, acetone- d_6) δ = 214.0, 150.7, 146.8, 141.0, 132.1, 128.4, 108.6, 106.5, 97.7, 77.0, 73.9, 68.9, 59.8, 58.4, 51.3, 45.1, 38.3, 38.1, 28.1, 27.5, 25.0, 23.6, 23.0; HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{30}\text{NaO}_4^+ [\text{M} + \text{Na}]^+$ 393.2036, found 393.2048.

Conversion of triene **43** to diene **42**:



To a stirred solution of triene **43** (4.0 mg, 11 μmol , 1.0 equiv) in toluene (2 mL) at room temperature was added p -TsOH·H₂O (2.1 mg, 11 μmol , 1.0 equiv). The resulting mixture was warmed to 40 °C and stirred for 10 h before cooled to room temperature and quenched with NaHCO₃ (2 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 \times 2 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded diene **42** (3.3 mg, 90%).

Preparation of diene **46**:



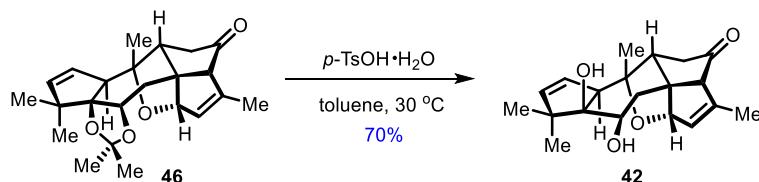
To a stirred solution of alkene **41** (5.2 mg, 12 μmol , 1.0 equiv) in THF (2 mL, degassed) at room temperature were sequentially added Cp_2TiCl_2 (3.5 mg, 14 μmol , 1.2 equiv) and Zn dust (3.8 mg, 58 μmol , 4.8 equiv). The resulting mixture was warmed to 50 °C and stirred for 6 h before cooled to room temperature and filtered through a short pad of celite. The filtrate was washed with NH_4Cl (5 mL, sat. aq.) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes: EtOAc 3:1) afforded the alcohol as a white solid.

To a stirred solution of alcohol (obtained above), CS_2 (3.5 μL , 58 μmol , 4.8 equiv) in THF (2 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 1.9 mg, 47 μmol , 3.9 equiv). The resulting mixture was stirred at room temperature for 5 h before MeI (3.6 μL , 58 μmol , 4.8 equiv) was added. The reaction was stirred for an additional 10 min before quenched with NH_4Cl (2 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3×2 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude xanthate as a white solid, which was used directly without further purification.

A stirred solution of xanthate (crude, obtained above) in *o*-DCB (2 mL) was warmed to 150 °C and stirred for 20 h before cooled to room temperature and THF (2 mL) followed by HCl (2.0 M aq., 0.20 mL, 0.40 mmol, 33 equiv) were added. The resulting mixture was stirred at room temperature for 24 h before diluted with EtOAc .

(2 mL) and quenched with NaHCO₃ (2 mL, sat. aq.). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 2 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded diene **46** (1.8 mg, 40% over three steps) as a white solid, along with triene **43** (0.4 mg, 9% over three steps). **46**: m.p. 195–197 °C (hexanes/EtOAc); *R*_f = 0.40 (silica gel, hexanes:EtOAc 2:1); [α]_D²⁰ = −272.0 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 5.99 (dd, *J* = 6.2, 1.7 Hz, 1 H), 5.65 (dd, *J* = 6.1, 3.5 Hz, 1 H), 5.51 (s, 1 H), 4.84 (s, 1 H), 4.48 (t, *J* = 3.0 Hz, 1 H), 4.05 (dd, *J* = 11.5, 7.9 Hz, 1 H), 3.62 (s, 1 H), 2.75–2.68 (m, 2 H), 2.55 (dd, *J* = 16.3, 2.9 Hz, 1 H), 2.14 (dd, *J* = 16.1, 3.1 Hz, 1 H), 2.07–2.00 (m, 1 H), 1.75–1.72 (m, 3 H), 1.50 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 3 H), 1.19 (s, 3 H), 1.06 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 214.1, 144.5, 140.4, 127.2, 126.9, 108.4, 99.6, 98.6, 88.2, 72.2, 58.4, 54.7, 50.5 (2C), 42.5, 41.4, 36.3, 28.4, 27.9, 23.9, 22.1, 19.4, 15.1 ppm; HRMS (ESI): calcd for C₂₃H₃₀NaO₄⁺ [M + Na]⁺ 393.2036, found 393.2030.

Conversion of diene **46** to diene **42**:



To a stirred solution of the diene **46** (3.7 mg, 10 μmol, 1.0 equiv) in toluene (2 mL) at room temperature was added *p*-TsOH·H₂O (0.8 mg, 4.0 μmol, 0.4 equiv). The resulting mixture was warmed to 30 °C and stirred for 10 h before cooled to room temperature and quenched with NaHCO₃ (2 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 2 mL). The combined organic

layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 8:1) afforded diene **42** (2.3 mg, 70%).

Preparation of (-)-rhodomollanol A (7):

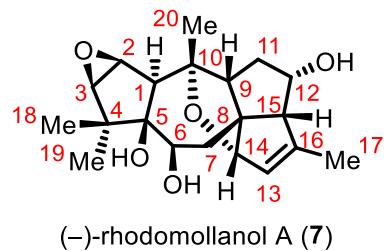


To a stirred solution of diene **42** (10 mg, 30 μmol , 1.0 equiv) in CH_2Cl_2 (4 mL) at 0 °C were sequentially added 4 Å molecular sieve (10 mg), $\text{VO}(\text{acac})_2$ (4.0 mg, 15 μmol , 0.5 equiv) and TBHP (5.5 M in decane, 27 μL , 0.15 mmol, 5.0 equiv). The resulting mixture was stirred at 0 °C for 2 h before quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (4 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×4 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded the corresponding epoxide as a white solid.

To a stirred solution of epoxide (obtained above) in MeOH (4 mL) at 0 °C was added NaBH_4 (4.6 mg, 0.12 mmol, 4.0 equiv). The resulting mixture was stirred at 0 °C for 15 min before diluted with CH_2Cl_2 (4 mL), quenched with acetone (1 mL) and H_2O (4 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×4 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Reversed-phase HPLC purification [Ultimate XB-C18 (5 μM , 10 x 250 mm column), $\text{MeCN}/\text{H}_2\text{O} = 30:70$, $v = 1.5 \text{ mL } \text{min}^{-1}$, $\lambda = 210 \text{ nm}$, $t = 12.5\text{--}15.0 \text{ min}$] afforded (-)-rhodomollanol A (**7**, 7.8 mg, 74% over two steps) as a white solid. **(-)-7:** m.p. 185–186 °C ($\text{H}_2\text{O}/\text{MeOH}$) [Lit. m.p. 187–188 °C (MeOH)],⁵ $R_f = 0.25$ (silica gel, hexanes:EtOAc

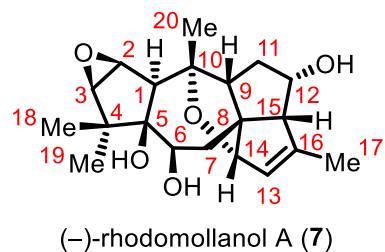
1:2); $[\alpha]_D^{20} = -64.0$ ($c = 0.1$, MeOH) [Lit. $[\alpha]_D^{20} = -44.9$ ($c = 0.1$, MeOH)];⁵ ^1H NMR (400 MHz, CD₃OD) $\delta = 5.49$ (s, 1 H), 4.53 (dd, $J = 2.5, 1.3$ Hz, 1 H), 4.20 (ddd, $J = 11.7, 7.7, 5.4$ Hz, 1 H), 3.86 (dd, $J = 10.5, 5.8$ Hz, 1 H), 3.83 (dd, $J = 3.3, 1.0$ Hz, 1 H), 3.46 (dd, $J = 11.8, 6.4$ Hz, 1 H), 3.17 (d, $J = 3.2$ Hz, 1 H), 2.46 (d, $J = 7.7$ Hz, 1 H), 2.29 (d, $J = 1.0$ Hz, 1 H), 2.06 (dd, $J = 13.2, 10.5$ Hz, 1 H), 1.88 (s, 3 H), 1.87 (dd, $J = 13.2, 5.8$ Hz, 1 H), 1.73 (ddd, $J = 11.8, 6.4, 5.4$ Hz, 1 H), 1.62 (q, $J = 11.5$ Hz, 1 H), 1.44 (s, 3 H), 1.29 (s, 3 H), 1.10 ppm (s, 3 H); ^{13}C NMR (100 MHz, CD₃OD) $\delta = 148.3$, 127.9, 88.4, 88.2, 82.6, 74.8, 73.9, 64.6, 64.4, 61.7, 59.5, 55.9, 48.8, 48.4, 43.1, 35.4, 22.4, 20.7, 20.6, 18.1 ppm; HRMS (ESI): calcd for C₂₀H₂₈NaO₅⁺ [M + Na]⁺ 371.1829, found 371.1834 [Lit. found 371.1825].⁵

Table S2. ^1H NMR Spectroscopic (CD_3OD , 25 °C) Comparison of Natural⁵ and Synthetic (–)-Rhodomollanol A (7).



No.	Natural δ ^1H [ppm, mult, J (Hz)]	Synthetic δ ^1H [ppm, mult, J (Hz)]
1	2.29, d (J = 0.6 Hz)	2.29, d (J = 1.0 Hz)
2	3.82, dd (J = 3.2, 0.6 Hz)	3.83, dd (J = 3.3, 1.0 Hz)
3	3.17, d (J = 3.2 Hz)	3.17, d (J = 3.2 Hz)
4		
5		
6	3.86, dd (J = 10.6, 5.8 Hz)	3.86, dd (J = 10.5, 5.8 Hz)
7	1.87, dd (J = 13.2, 5.8 Hz) 2.05, dd (J = 13.2, 10.6 Hz)	1.87, dd (J = 13.2, 5.8 Hz) 2.06, dd (J = 13.2, 10.5 Hz)
8		
9	3.46, dd (J = 12.0, 6.4 Hz)	3.46, dd (J = 11.8, 6.4 Hz)
10		
11	1.72, ddd (J = 12.0, 6.4, 5.6 Hz) 1.63, q (J = 12.0 Hz)	1.73, ddd (J = 11.8, 6.4, 5.4 Hz) 1.62, q (J = 11.5 Hz)
12	4.20, ddd (J = 12.0, 7.8, 5.6 Hz)	4.20, ddd (J = 11.7, 7.7, 5.4 Hz)
13	5.49, s	5.49, s
14	4.53, s	4.53, dd (J = 2.5, 1.3 Hz)
15	2.46, d (J = 7.8 Hz)	2.46, d (J = 7.7 Hz)
16		
17	1.88, s	1.88, s
18	1.29, s	1.29, s
19	1.10, s	1.10, s
20	1.44, s	1.44, s

Table S3. ^{13}C NMR (CD_3OD , 25 °C) Spectroscopic Comparison of Natural⁵ and Synthetic (–)-Rhodomollanol A (7).



No.	Natural δ ^{13}C (ppm)	Synthetic δ ^{13}C (ppm)
1	55.9	55.9
2	59.5	59.5
3	64.7	64.6
4	48.4	48.4
5	82.6	82.6
6	73.9	73.9
7	43.1	43.1
8	61.7	61.7
9	49.0	48.8
10	88.2	88.2
11	35.4	35.4
12	74.8	74.8
13	128.0	128.0
14	88.4	88.4
15	64.4	64.4
16	148.3	148.3
17	18.1	18.1
18	20.7	20.7
19	20.6	20.6
20	22.4	22.4

III) Abbreviations

acac	acetylacetone
AIBN	azodi <i>isobutyl</i> onitrile
Bz	benzoyl
Cp	cyclopentadienyl
DHP	3,4-dihydro-2 <i>H</i> -pyran
DIAD	di <i>isopropyl</i> azodicarboxylate
DIBAL-H	di <i>isobutyl</i> aluminium hydride
DMSO	dimethyl sulfoxide
dpm	tris(2,2,6,6-tetramethyl-3,5-heptanedionato)
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol
HMPA	hexamethylphosphoric triamide
IBX	2-iodoxybenzoic acid
LiHMDS	lithium bis(trimethylsilyl)amide
<i>m</i> -CPBA	3-chloroperbenzoic acid
MOMCl	chloromethyl methyl ether
NaHMDS	sodium bis(trimethylsilyl)amide
NIS	<i>N</i> -iodosuccinimide
<i>o</i> -DCB	1,2-dichlorobenzene
oxone	potassium peroxymonosulfate
PDC	pyridinium dichromate
PIFA	[bis(trifluoroacetoxy)iodo]benzene

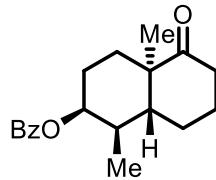
PPTS	pyridinium 4-toluenesulfonate
<i>p</i> -TsOH	4-toluenesulfonic acid
py	pyridine
TBHP	<i>tert</i> -butyl hydroperoxide
TESCl	triethyl chlorosilane
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TMSCl	trimethyl chlorosilane
TMSOTf	trimethylsilyl trifluoromethanesulfonate

IV) References

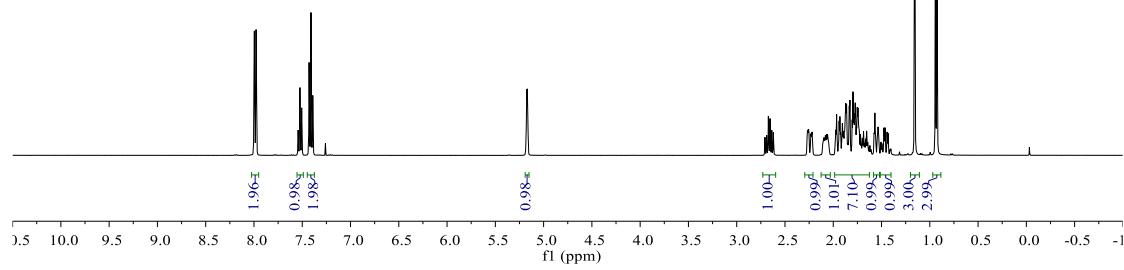
- (1) He, C.; Hu, J.; Wu, Y.; Ding, H. *J. Am. Chem. Soc.* **2017**, *139*, 6098–6101.
- (2) **16** is commercially available, and could also be prepared according to the procedures reported by Shenvi and coworkers: Wan, K. K.; Iwasaki, K.; Umotoy, J. C.; Wolan, D. W.; Shenvi, R. A. *Angew. Chem., Int. Ed.* **2015**, *54*, 2410–2415.
- (3) For the preparation of the known bromophenol **S-4**, see: Börger, C.; Schmidt, A. H.; Knölker, H. -J. *Synlett* **2014**, *25*, 1381–1384.
- (4) For the preparation of “dmsyl” anion, see: Stork, G.; Niu, D.; Fujimoto, A.; Koft, E. R.; Balkovec, J. M.; Tata, J. R.; Dake, G. R. *J. Am. Chem. Soc.* **2001**, *123*, 3239–3242.
- (5) Zhou, J.; Zhan G.; Zhang, H.; Zhang, Q.; Li, Y.; Xue, Y.; Yao, G. *Org. Lett.* **2017**, *19*, 3935–3938.

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

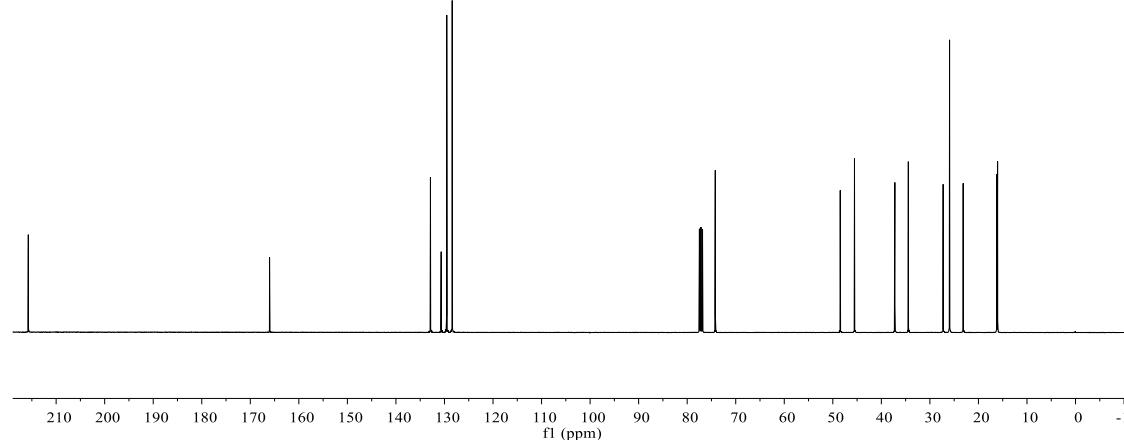
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7.3907
5.1745
5.1685
2.6898
2.6720
2.6547
2.6369
2.6200
2.2665
2.2559
2.2307
2.2197
2.0814
2.0647
1.9735
1.9652
1.9391
1.9312
1.9242
1.8958
1.8840
1.8775
1.8699
1.8621
1.8342
1.8270
1.7517
1.7445
1.7180
1.7783
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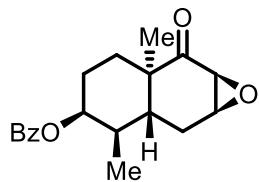


^1H NMR spectrum (400 MHz, CDCl_3)

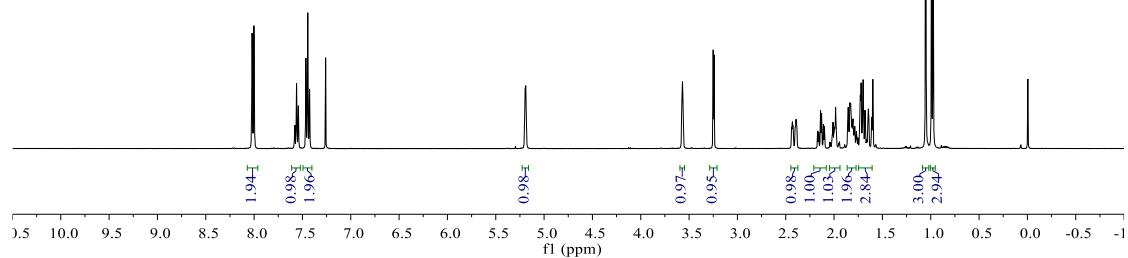


^{13}C NMR spectrum (100 MHz, CDCl_3)

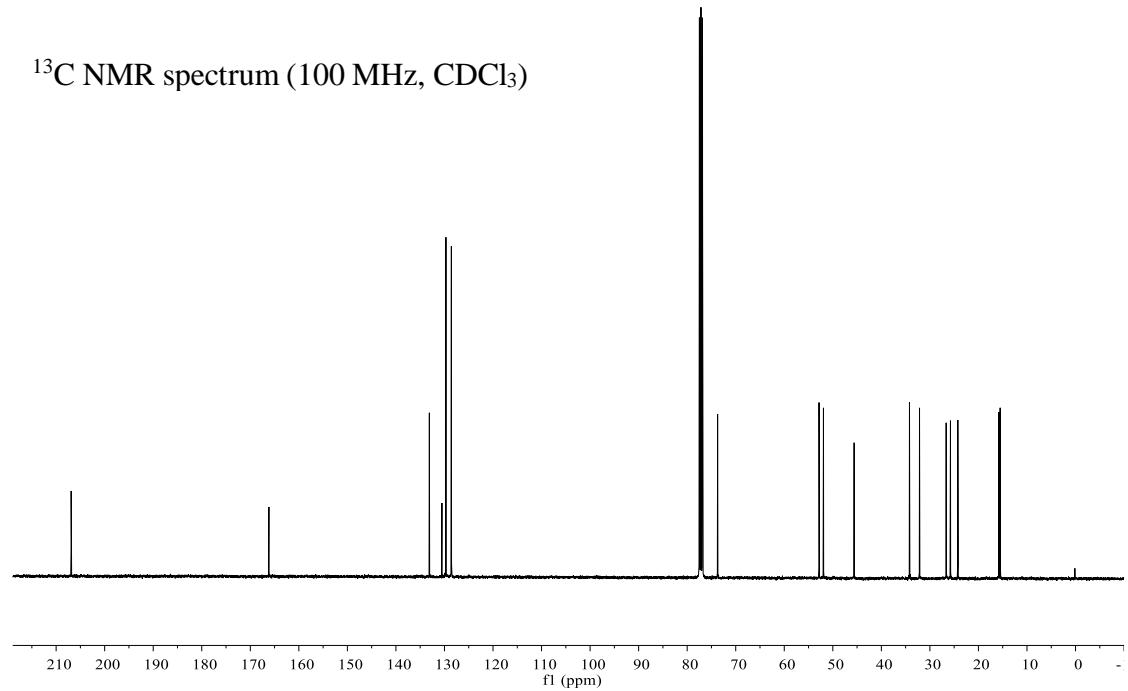


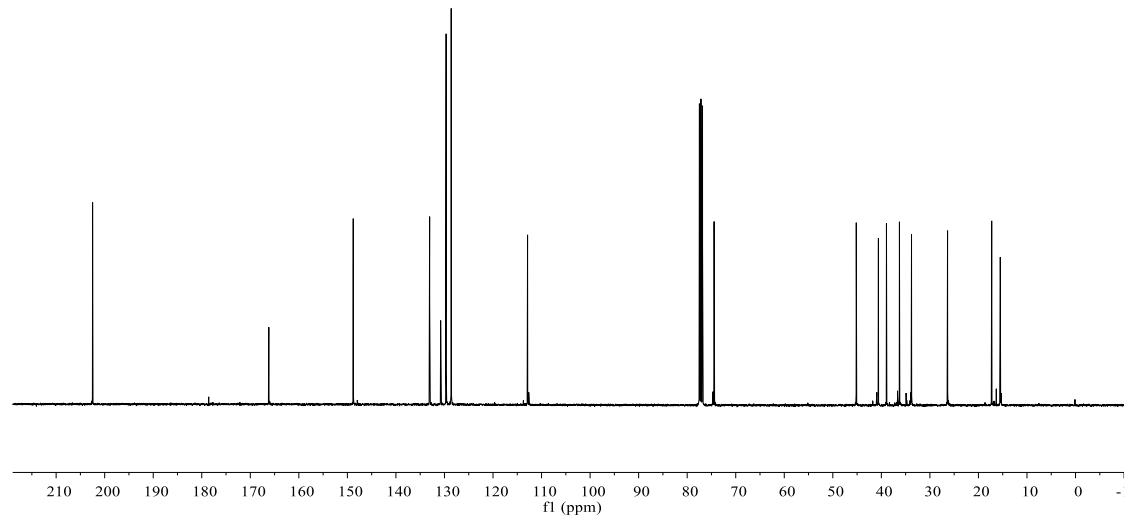
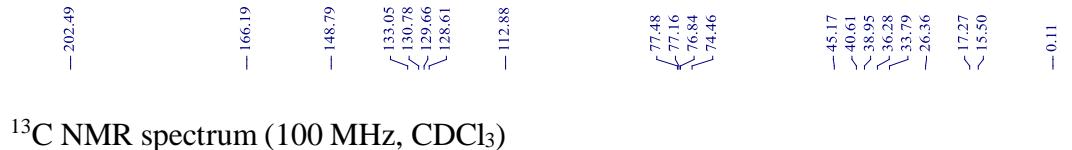
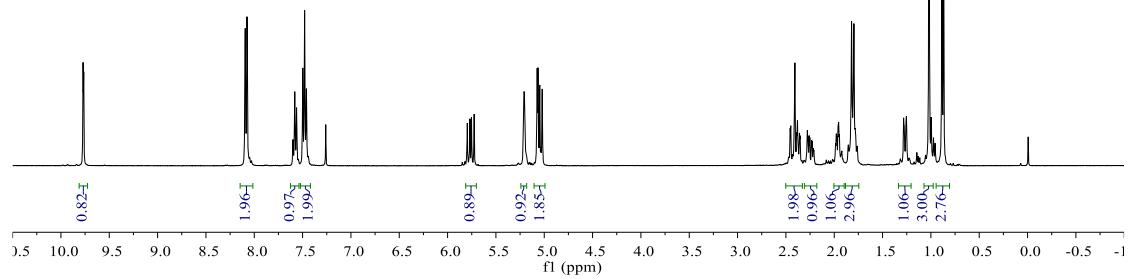
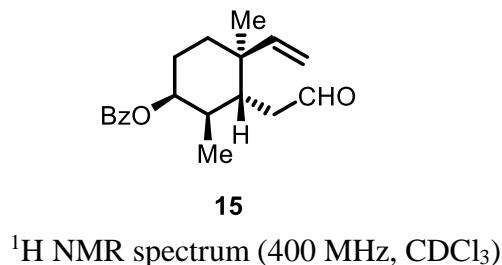


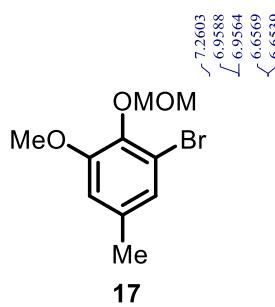
^1H NMR spectrum (400 MHz, CDCl_3)



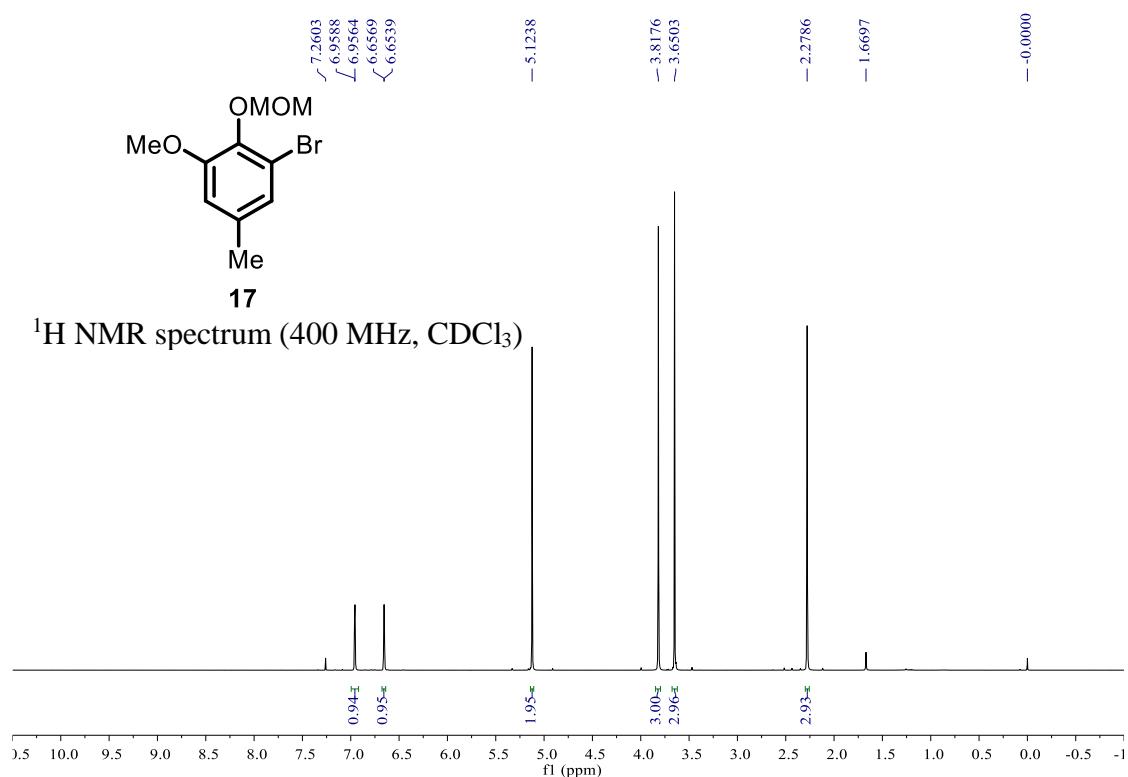
^{13}C NMR spectrum (100 MHz, CDCl_3)



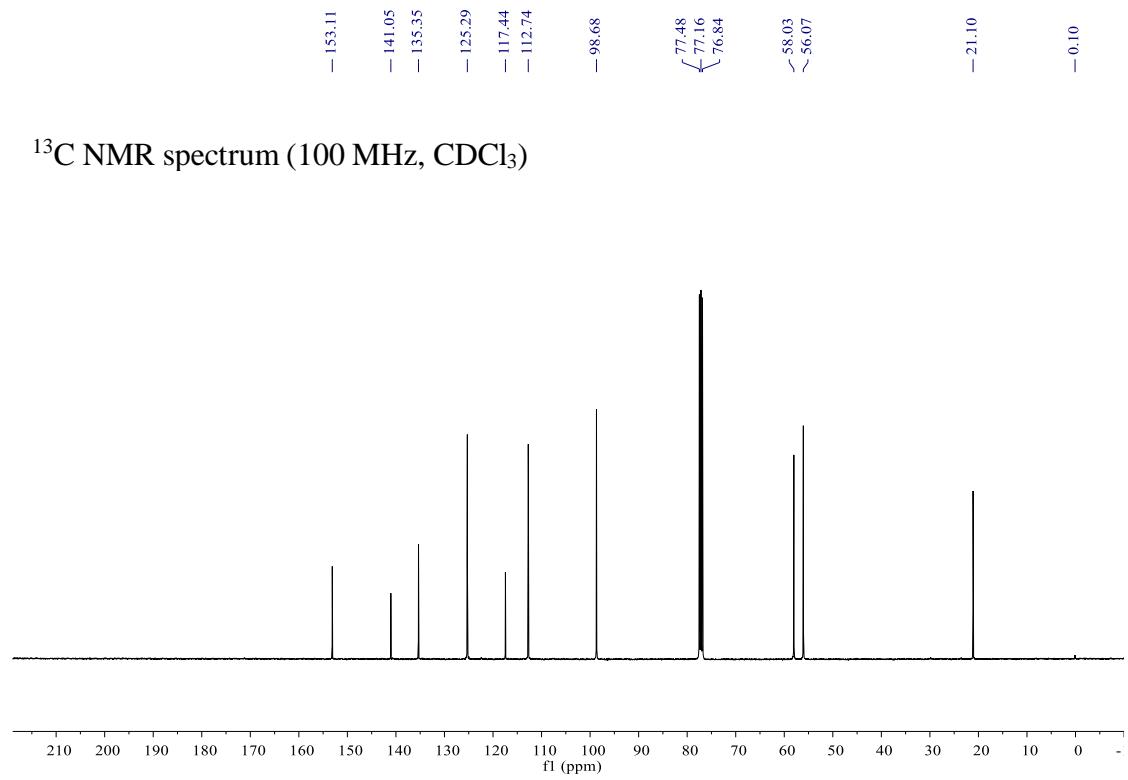


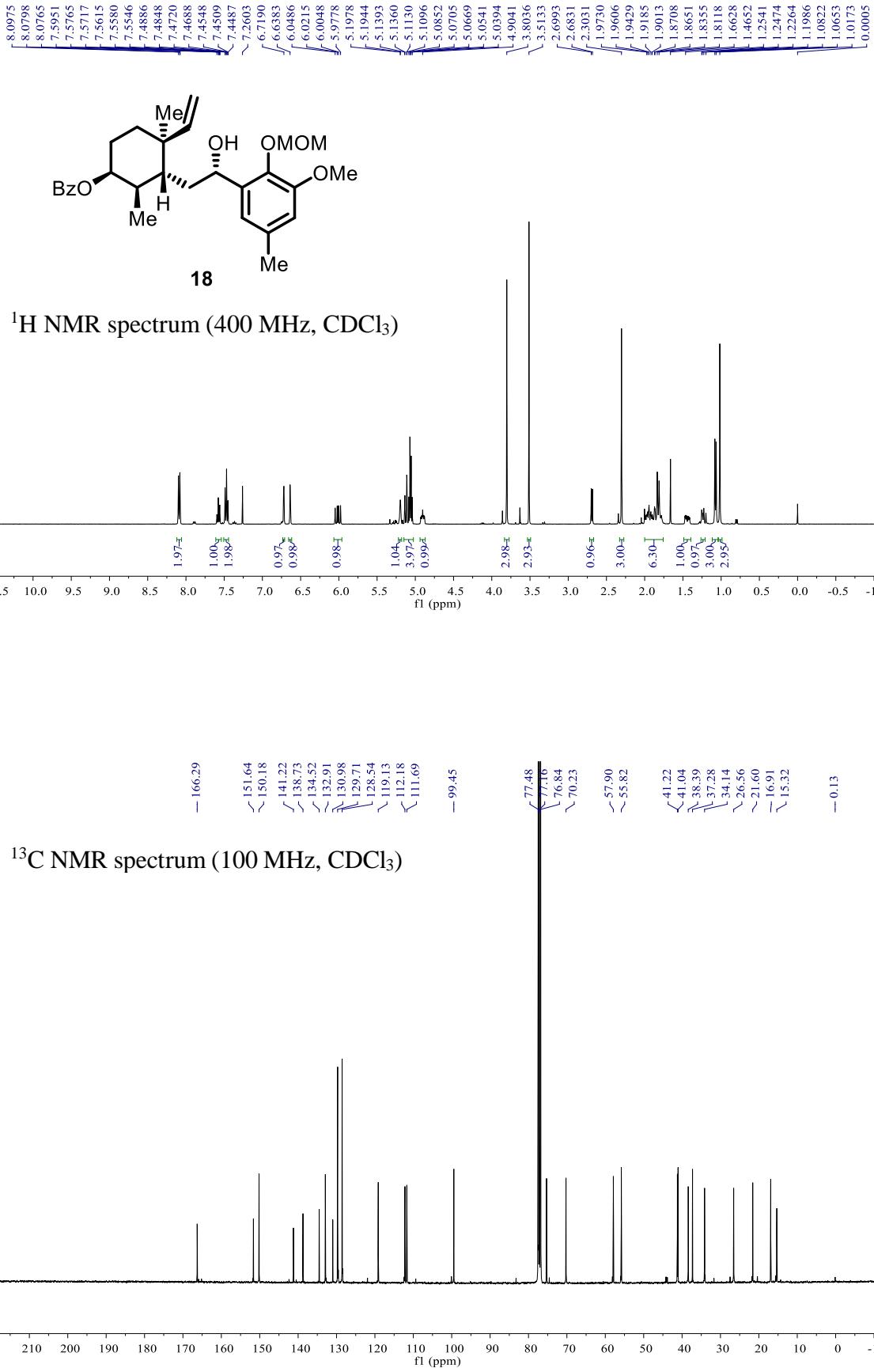


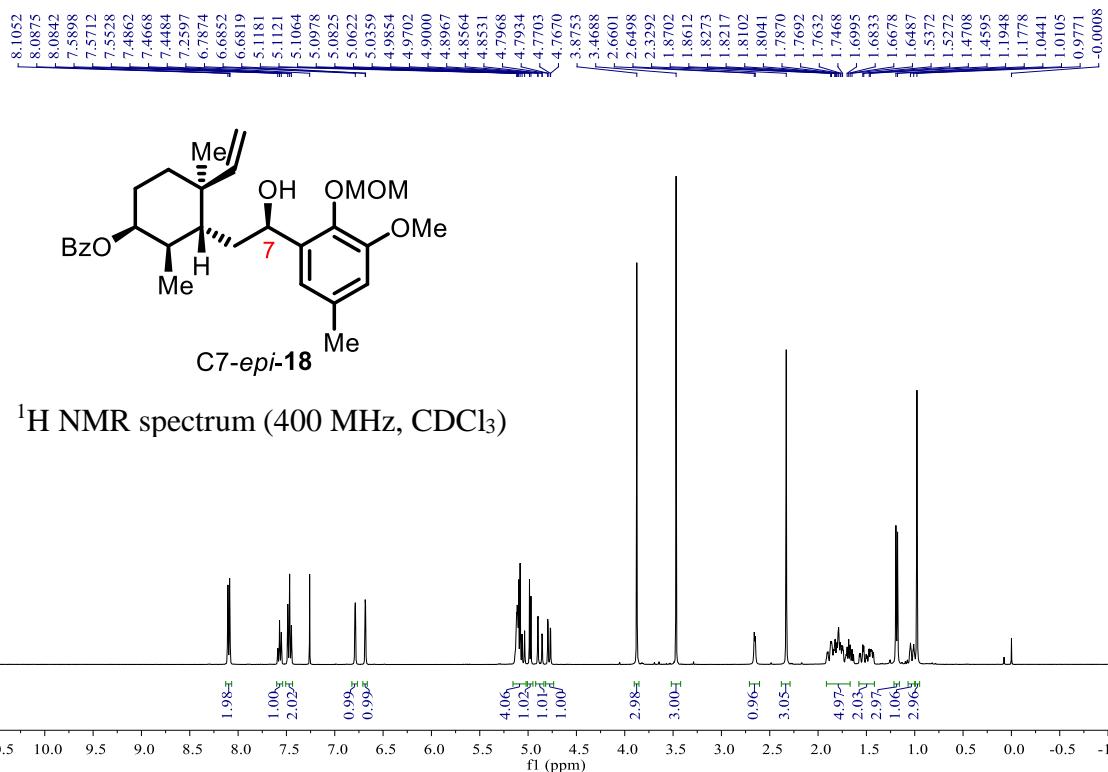
^1H NMR spectrum (400 MHz, CDCl_3)



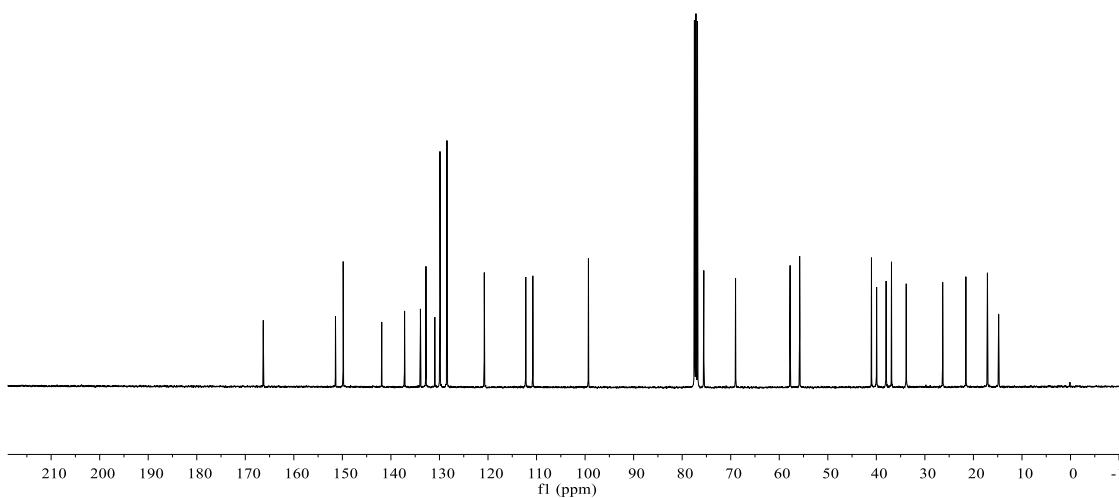
^{13}C NMR spectrum (100 MHz, CDCl_3)

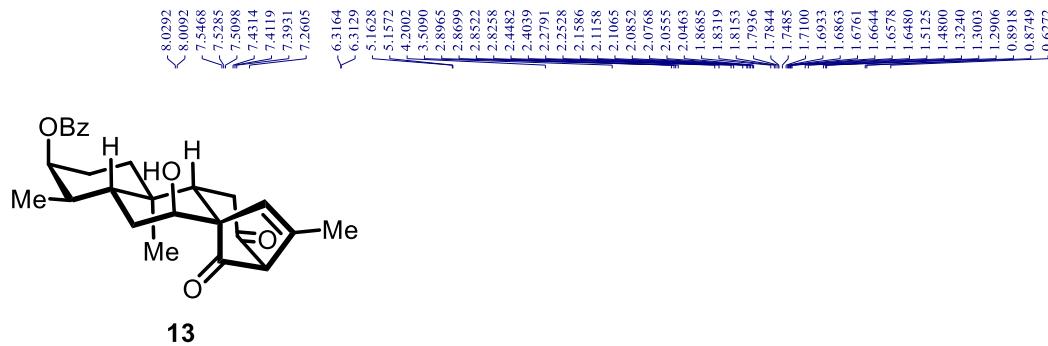




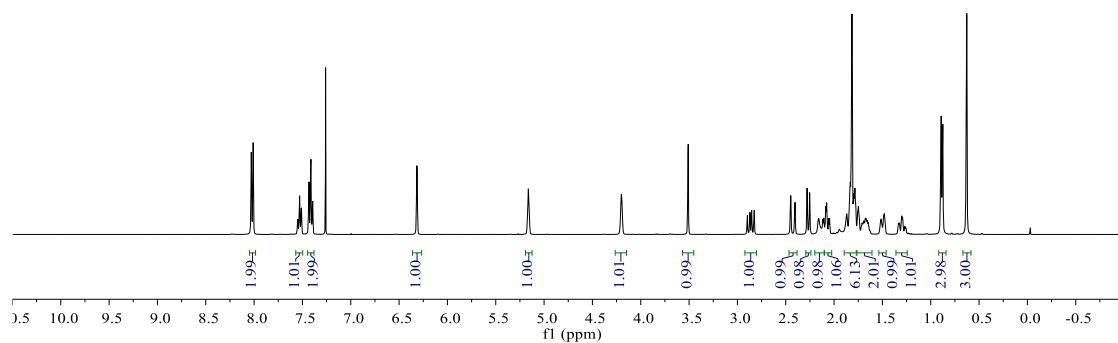


¹³C NMR spectrum (100 MHz, CDCl₃)

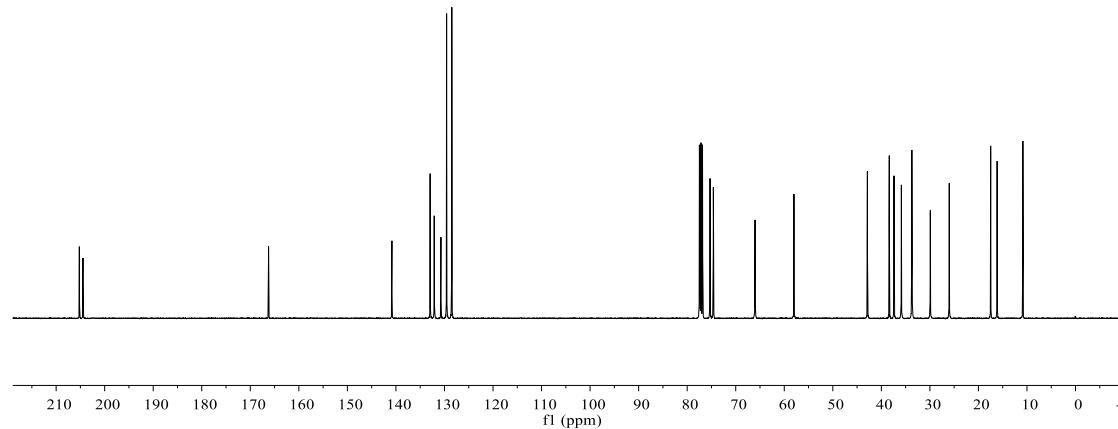




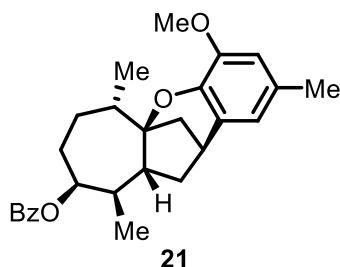
¹H NMR spectrum (400 MHz, CDCl₃)



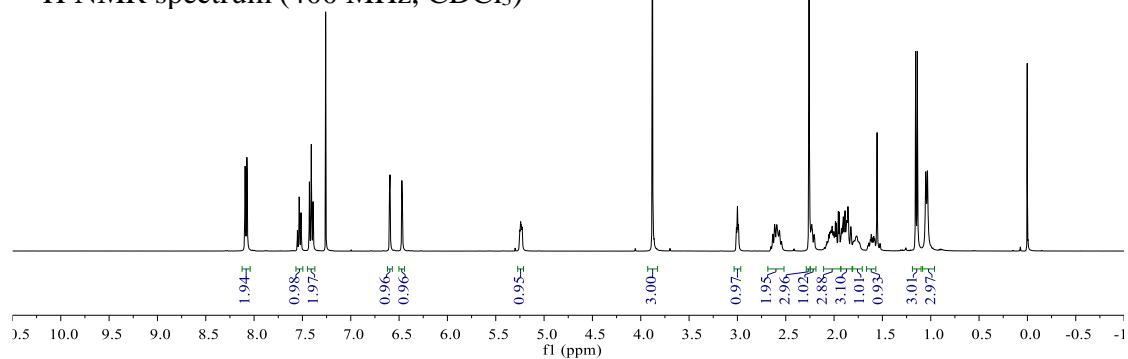
¹³C NMR spectrum (100 MHz, CDCl₃)



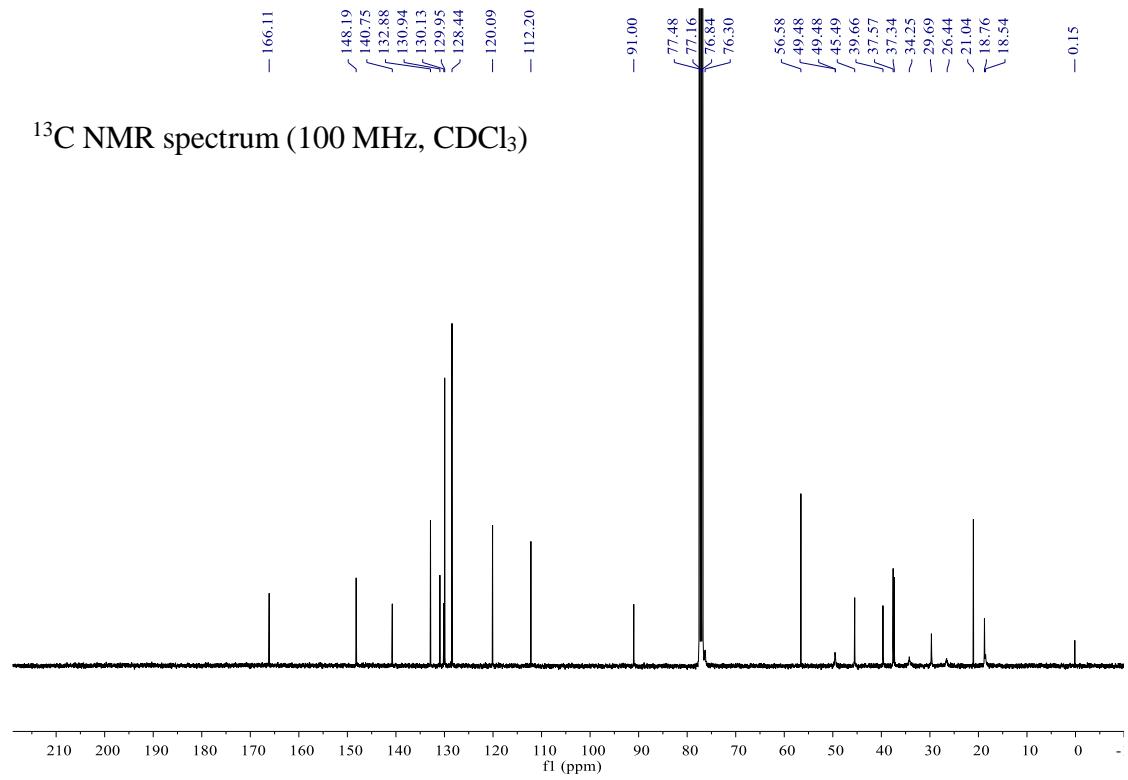
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 7.5519
 7.5333
 7.5117
 7.4278
 7.4082
 7.3895
 7.2595
 6.5987
 6.5938
 6.4722
 6.4674
 5.2538
 5.2506
 5.2451
 5.2420
 5.2376
 5.2346
 5.2283
 5.2251
 3.8795
 3.0106
 2.9997
 2.9888
 2.6533
 2.6347
 2.6157
 2.6101
 2.5968
 2.5923
 2.5849
 2.5644
 2.5428
 2.2588
 2.2391
 2.2307
 2.2229
 2.2091
 2.2028
 1.9857
 1.9560
 1.9459
 1.9044
 1.8864
 1.8864
 1.8597
 1.8563
 1.8528
 1.6151
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 1.5554
 1.1563
 1.1385
 1.0515
 1.0340
 0.0020

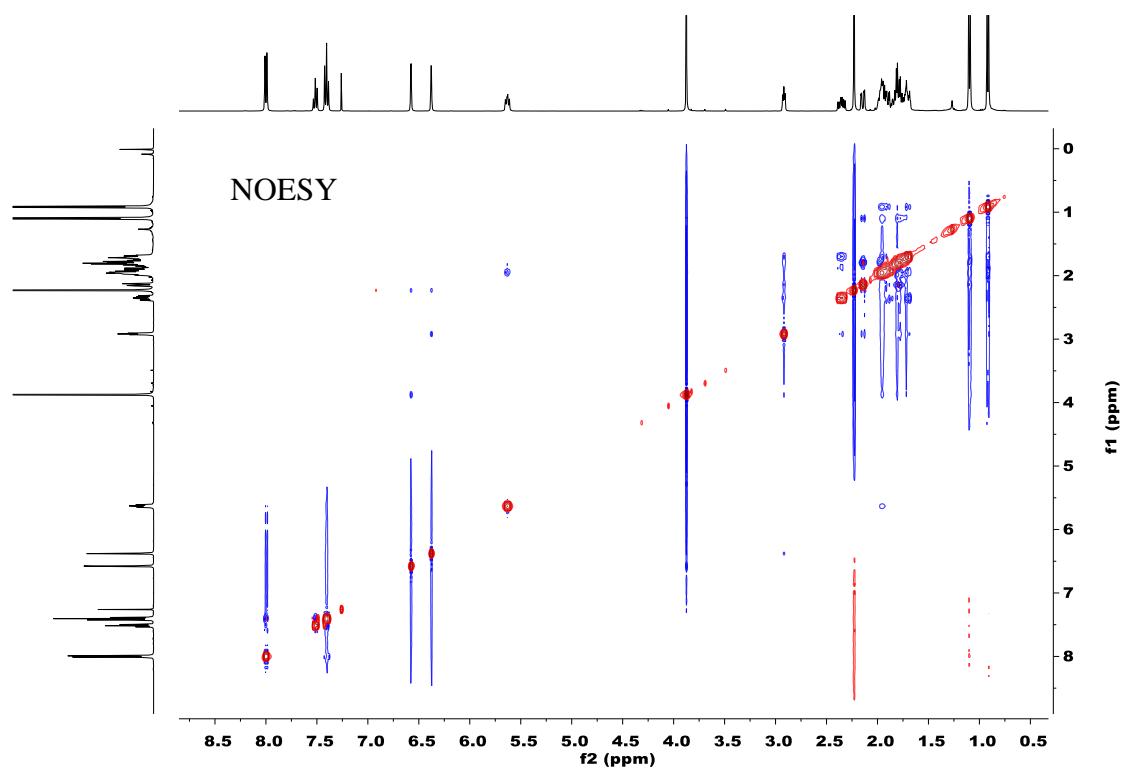
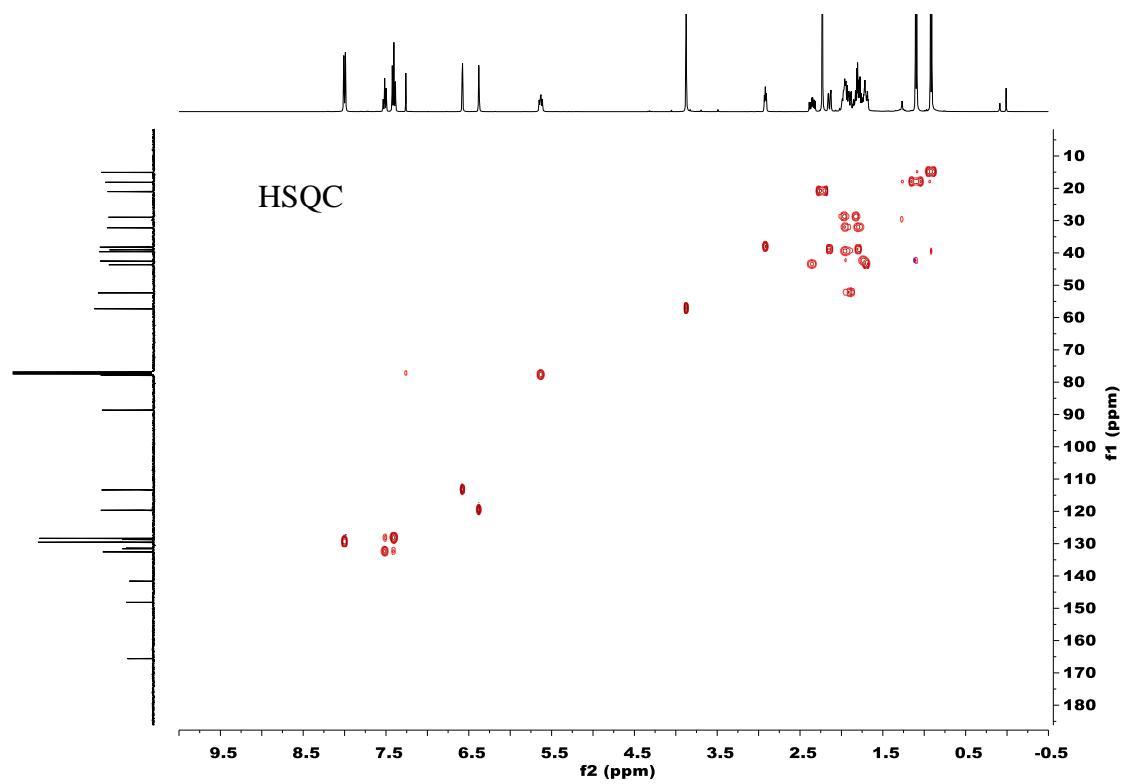


¹H NMR spectrum (400 MHz, CDCl₃)

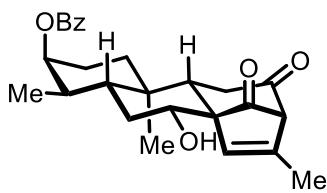


¹³C NMR spectrum (100 MHz, CDCl₃)



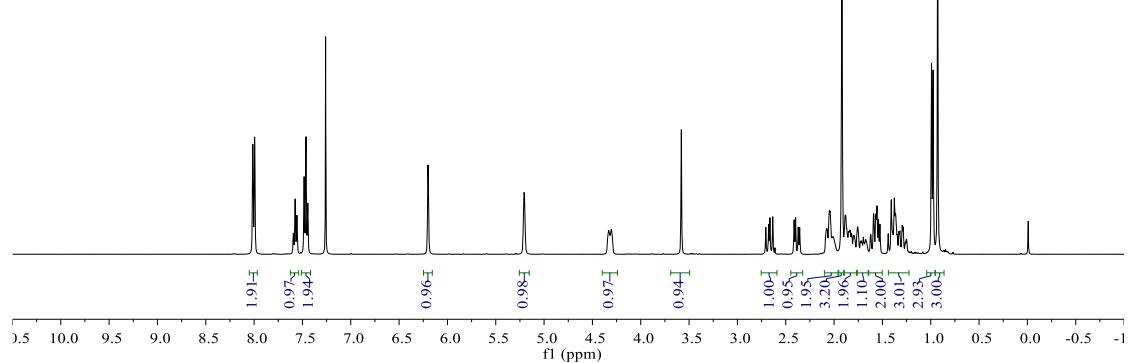


8.0133
 7.9944
 7.5932
 7.5751
 7.5565
 7.4823
 7.4633
 7.4442
 7.2601
 6.2008
 5.2079
 5.2030
 4.3325
 4.3042
 3.5802
 2.7061
 2.6767
 2.6638
 2.6344
 2.4132
 2.3980
 2.3708
 2.3556
 2.0799
 2.0742
 2.0485
 2.0092
 1.9191
 1.8851
 1.8379
 1.8211
 1.7909
 1.7560
 1.7204
 1.6970
 1.6724
 1.6196
 1.5911
 1.5691
 1.5555
 1.5405
 1.5252
 1.4395
 1.4082
 1.3767
 1.3644
 1.3287
 1.3191
 1.2954
 1.2857
 1.2621
 1.2508
 1.09920
 1.09753
 0.9282
 -0.0088



C7,C8,C13-triepi-13

¹H NMR spectrum (400 MHz, CDCl₃)



- 205.89
- 201.24

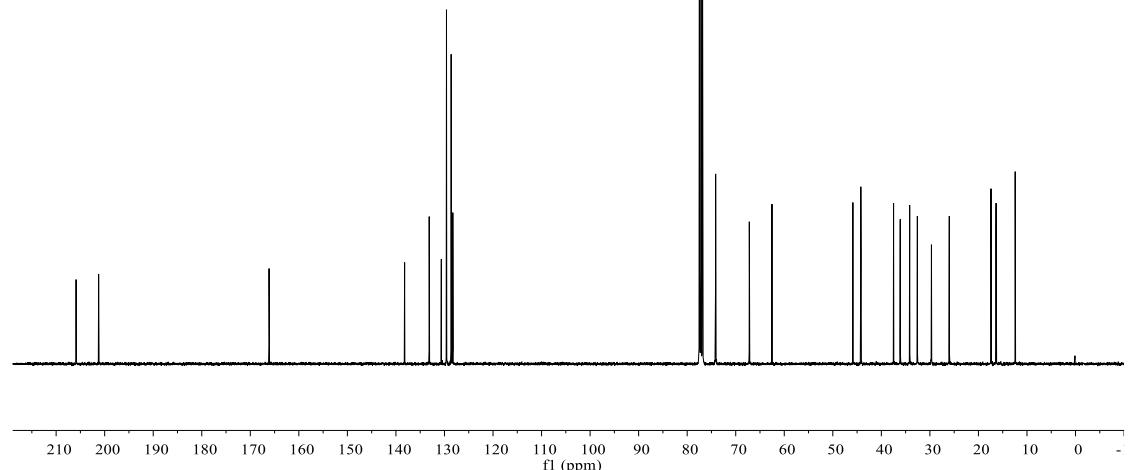
- 166.13

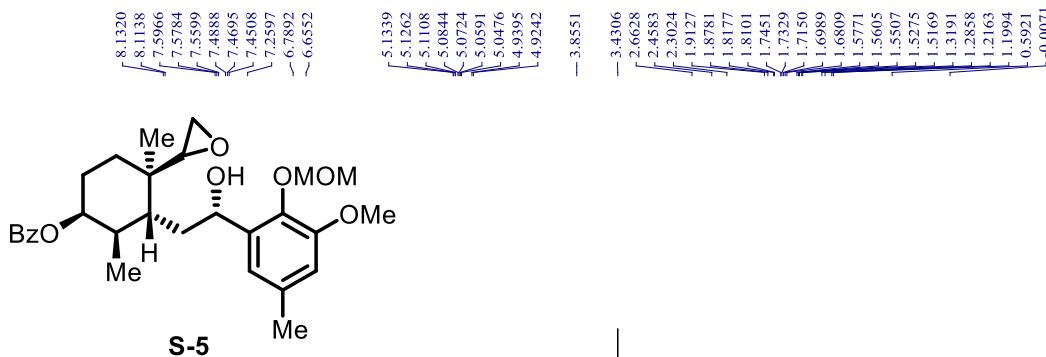
138.21
133.15
130.65
129.58
128.62
128.28

77.48
75.46
76.84
74.15
74.13
67.20
62.53
45.87
44.33
37.48
36.11
34.16
32.58
29.68
26.00
17.41
16.36
12.43

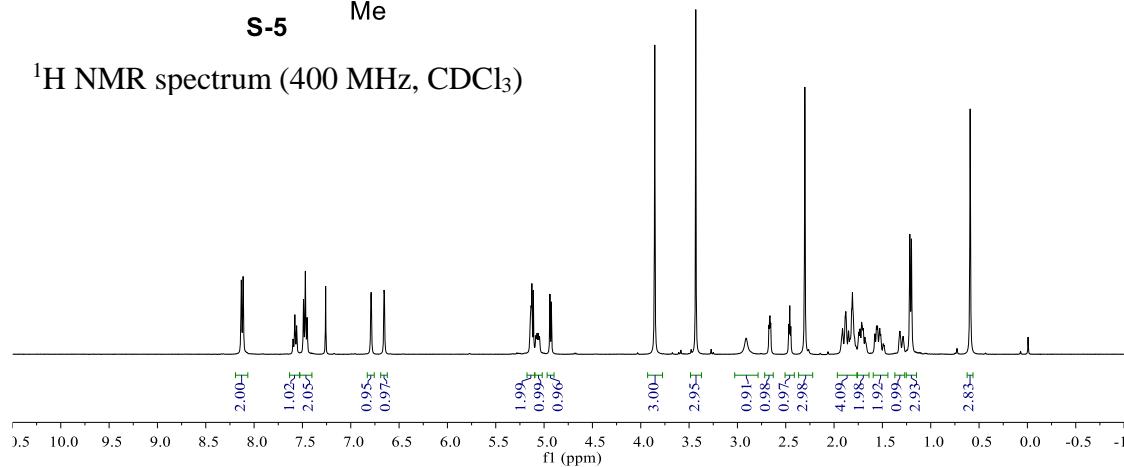
- 0.12

¹³C NMR spectrum (100 MHz, CDCl₃)

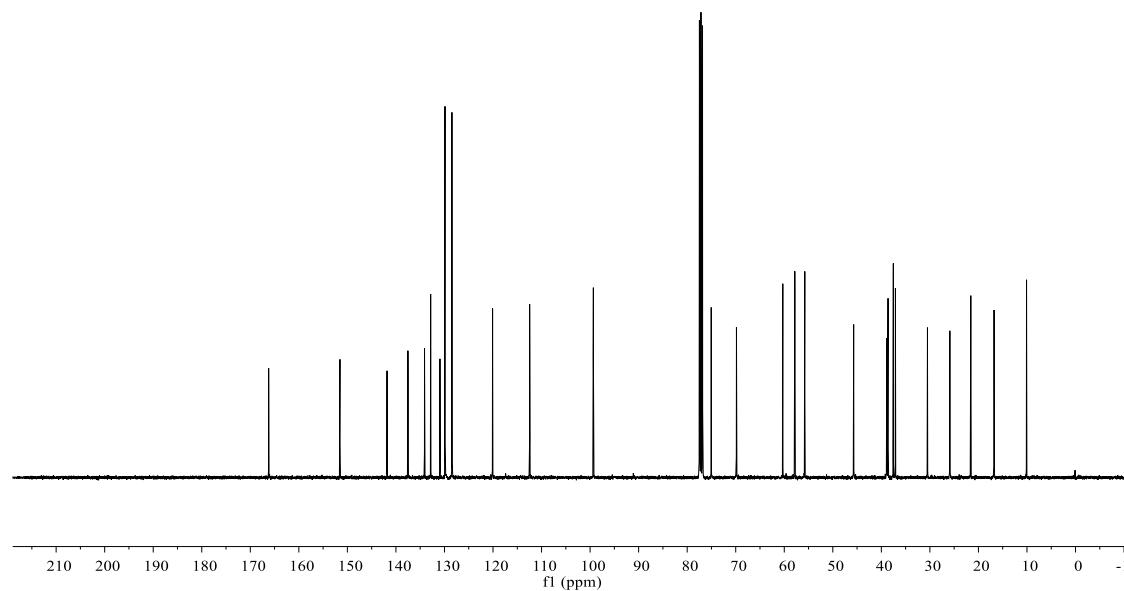


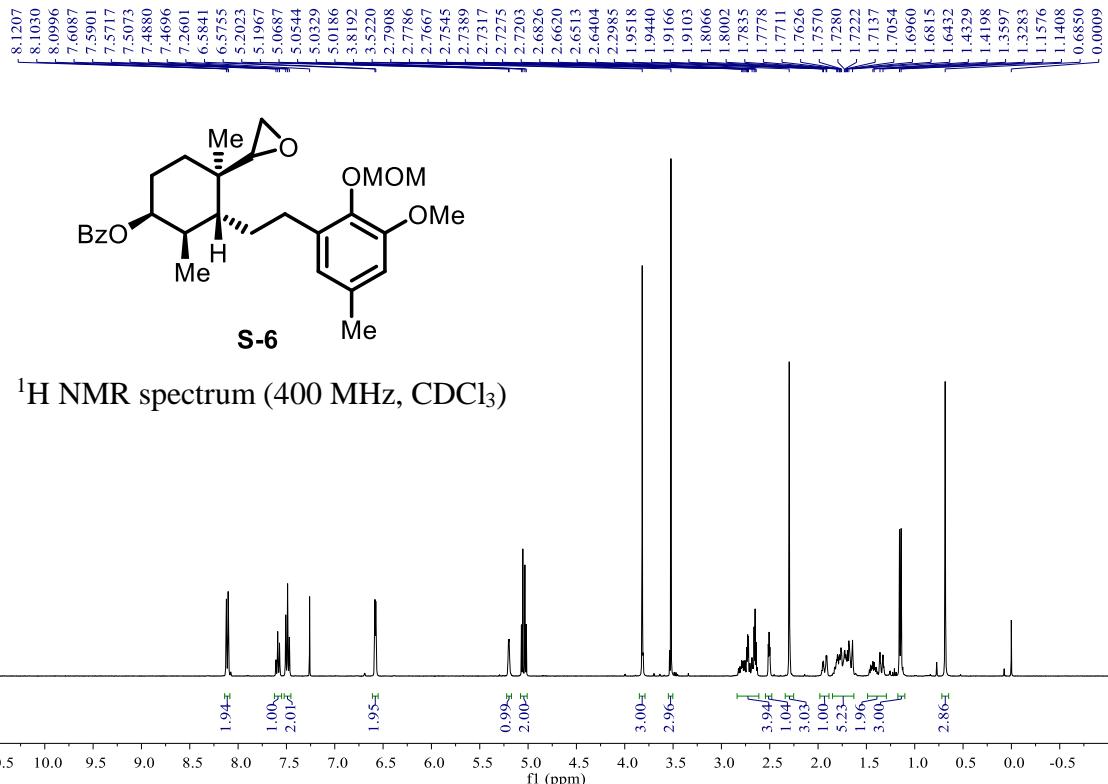


¹H NMR spectrum (400 MHz, CDCl₃)

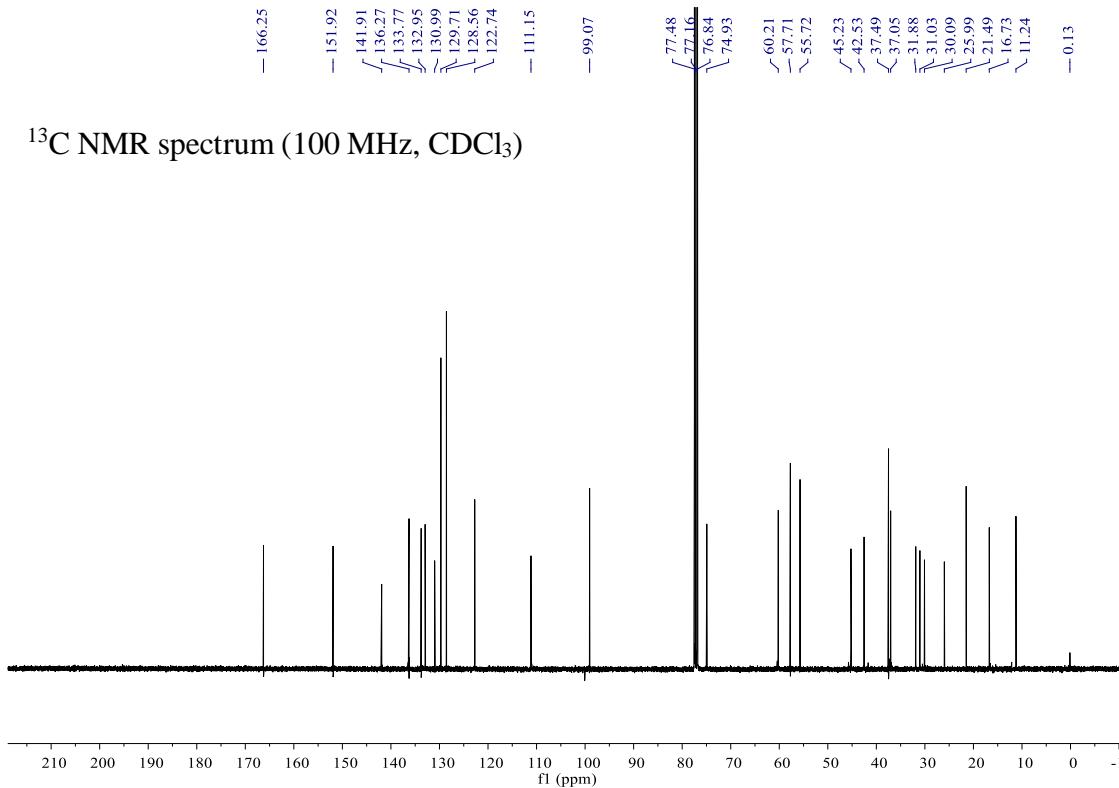


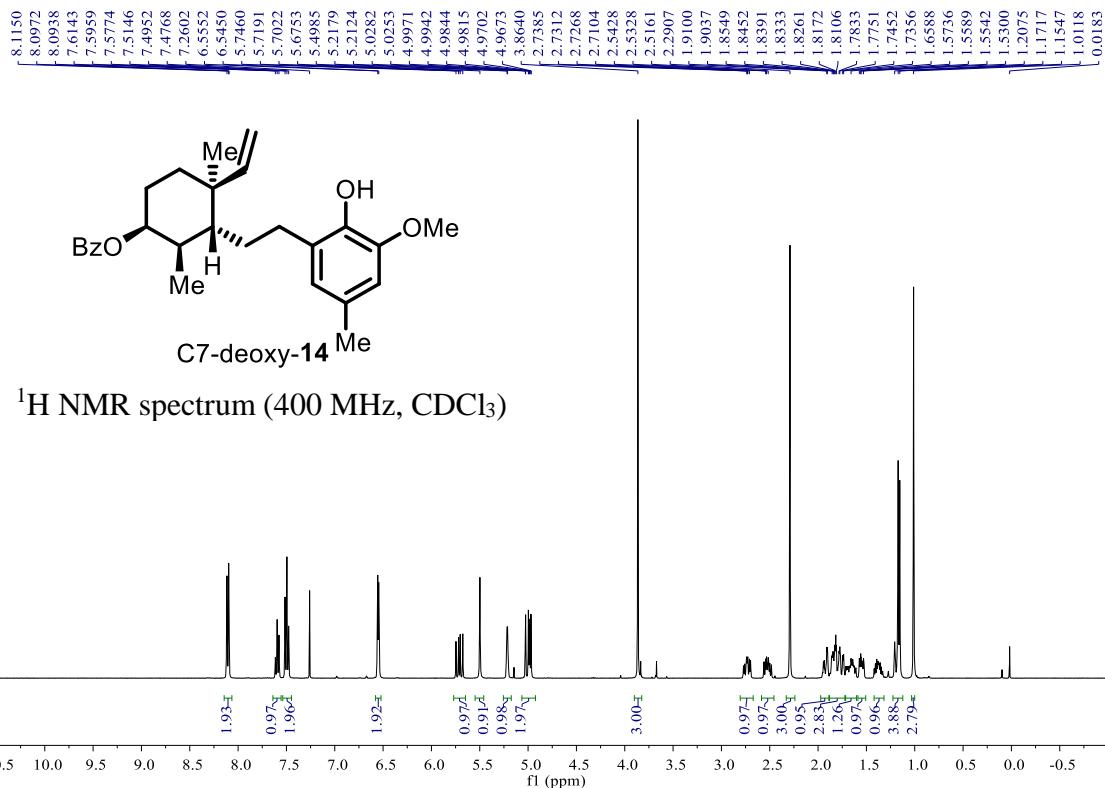
¹³C NMR spectrum (100 MHz, CDCl₃)



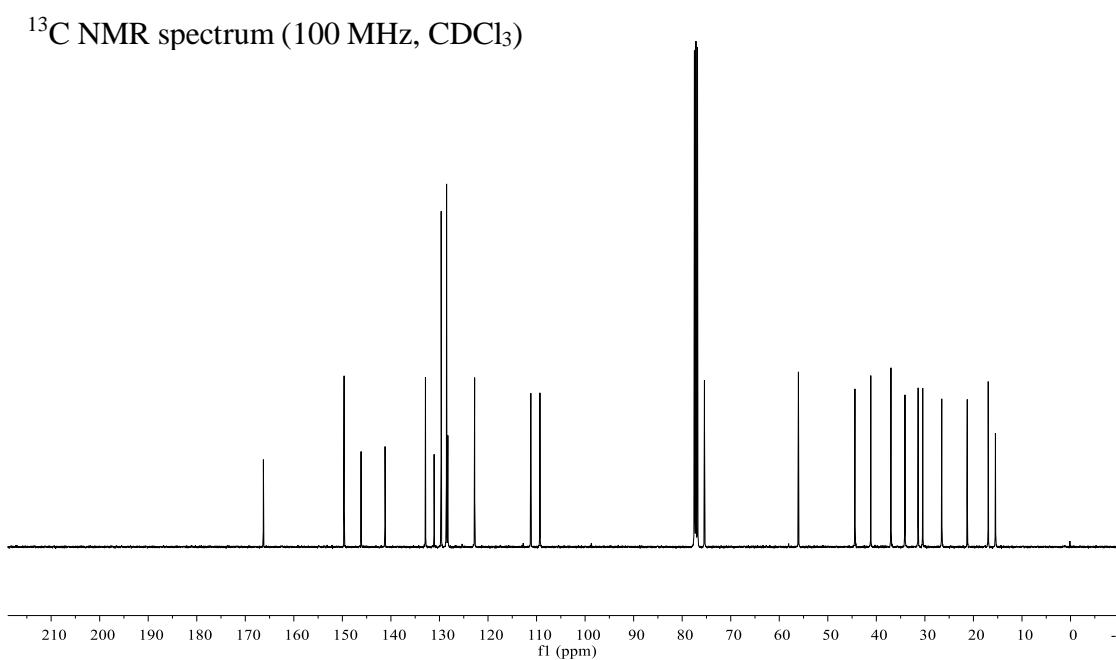


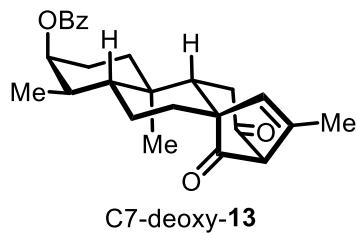
¹³C NMR spectrum (100 MHz, CDCl₃)



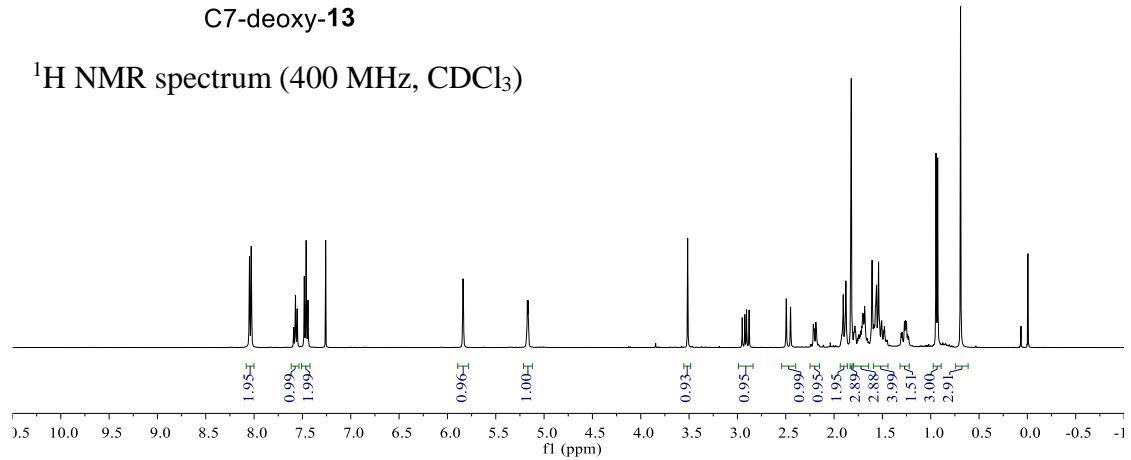


¹³C NMR spectrum (100 MHz, CDCl₃)





¹H NMR spectrum (400 MHz, CDCl₃)



> 206.66
 ~ 204.27

- 166.18

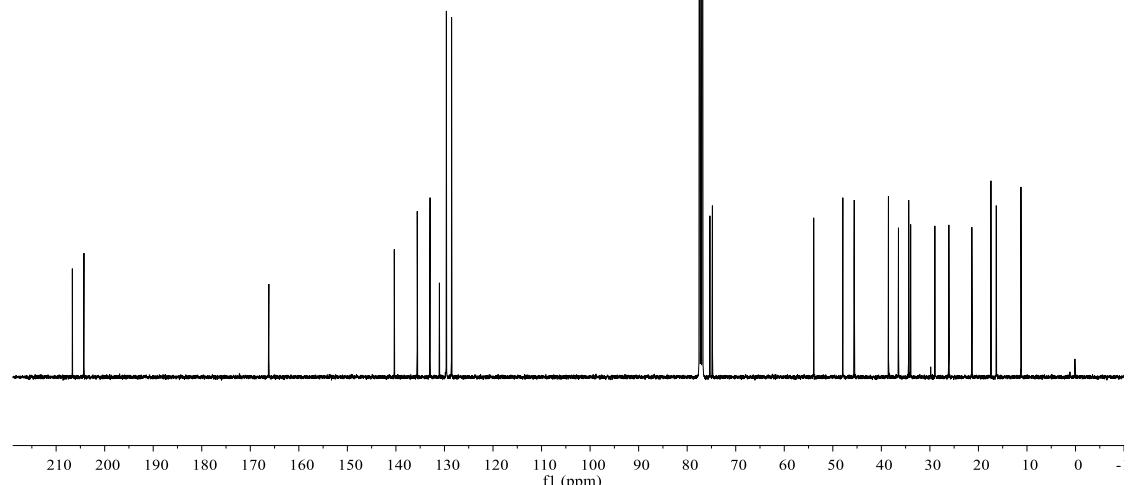
140.34
 135.61
 132.97
 131.04
 > 129.61
 128.53

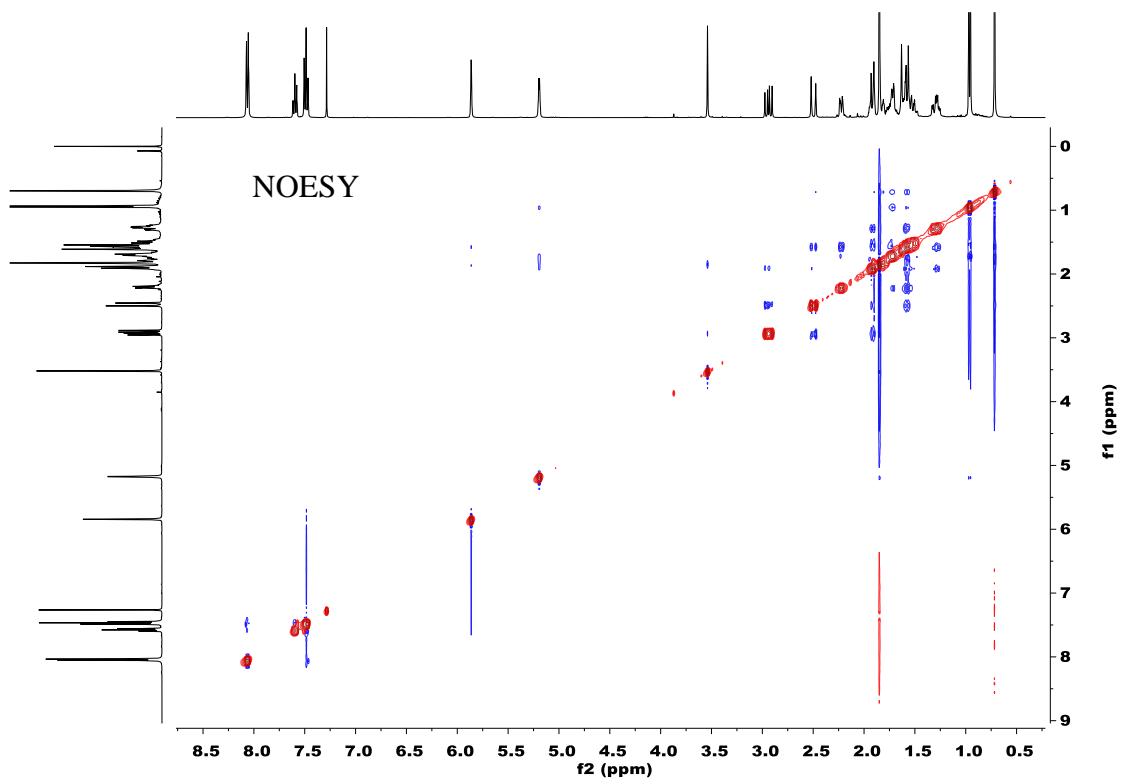
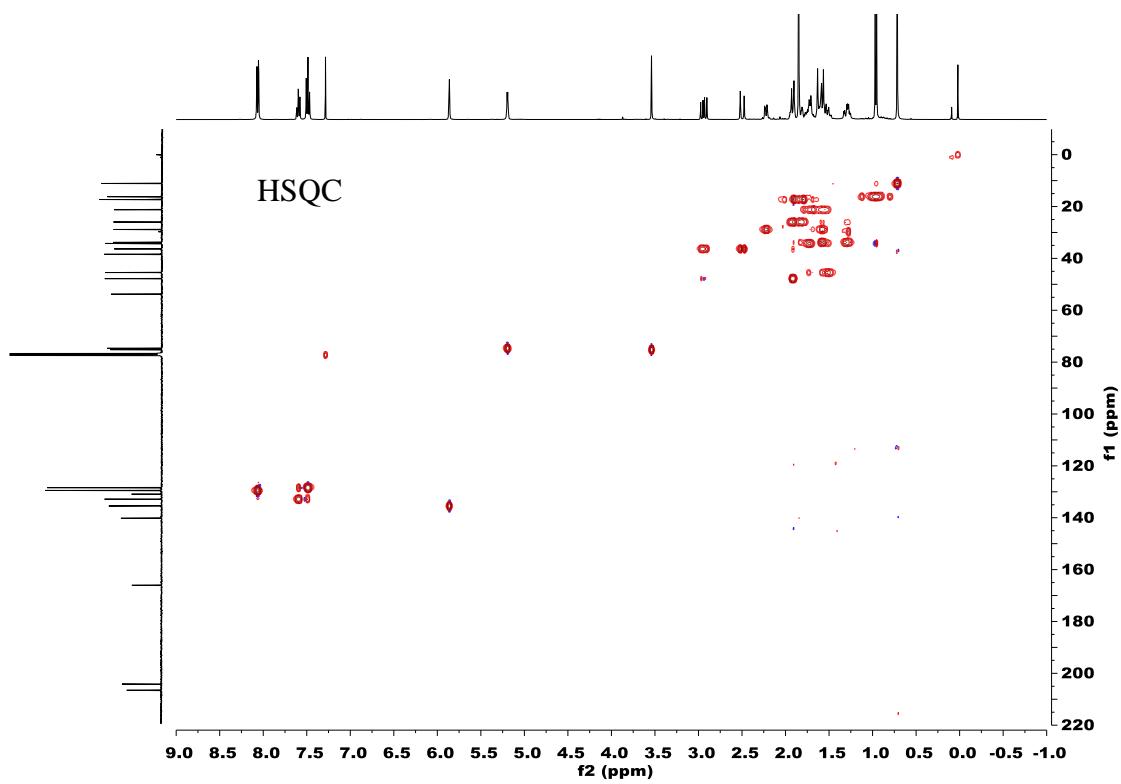
77.48
 77.16
 76.89
 75.32
 74.80

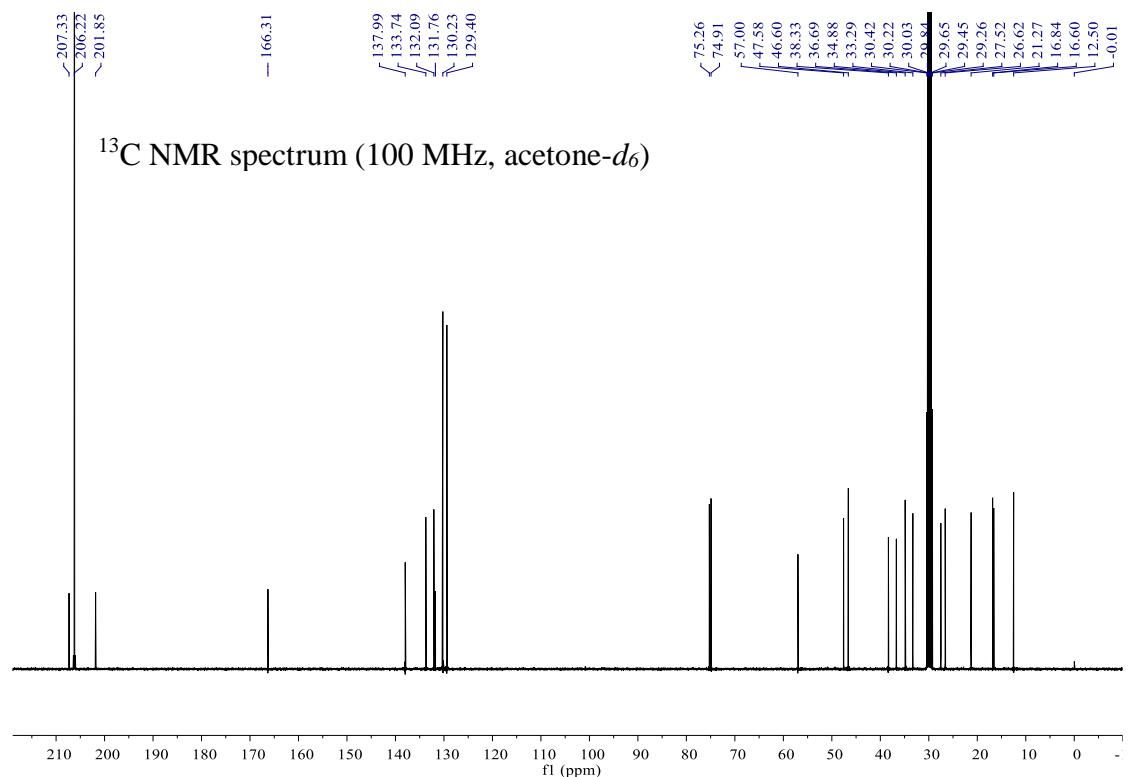
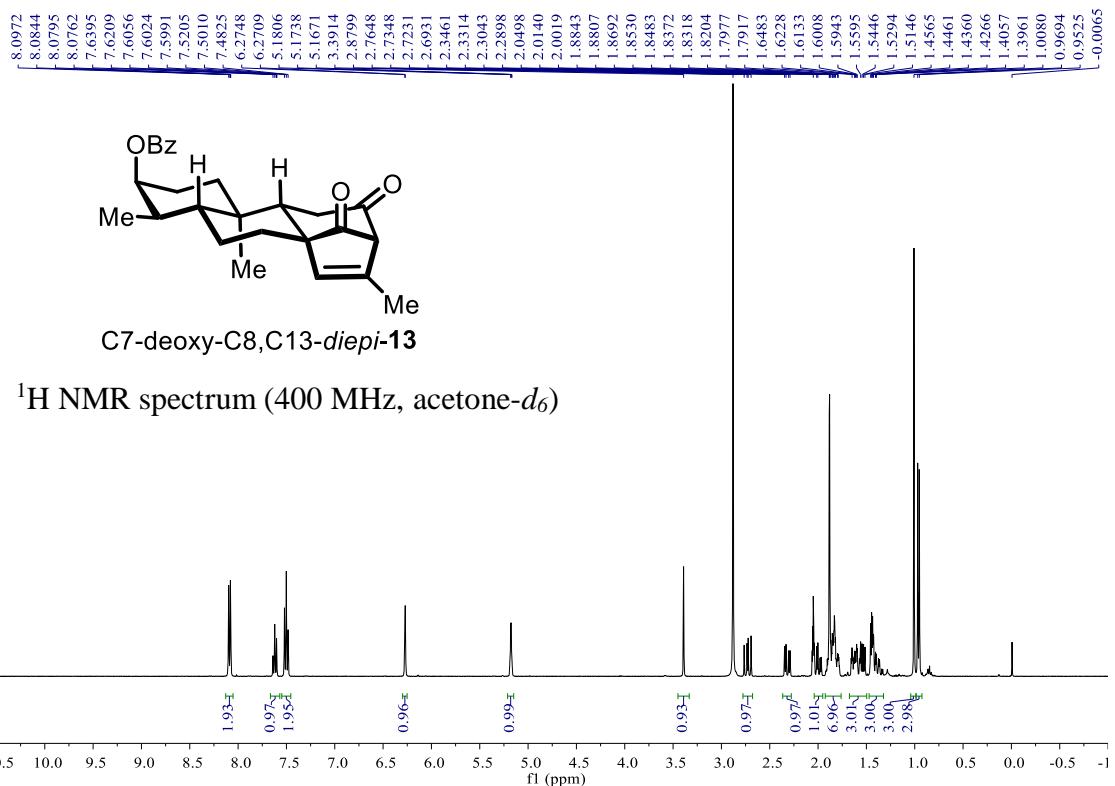
53.94
 47.93
 45.58
 38.54
 36.47
 34.36
 33.96
 - 28.97
 > 26.09
 - 21.36
 17.42
 > 16.32
 > 11.24

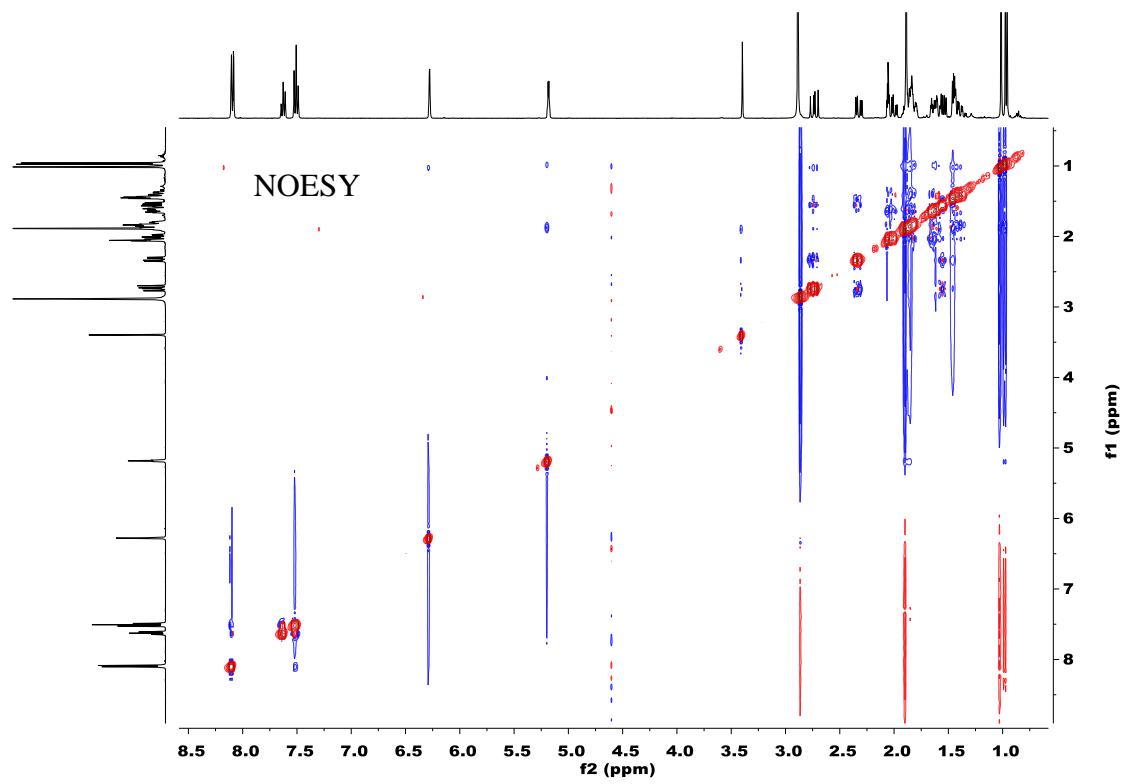
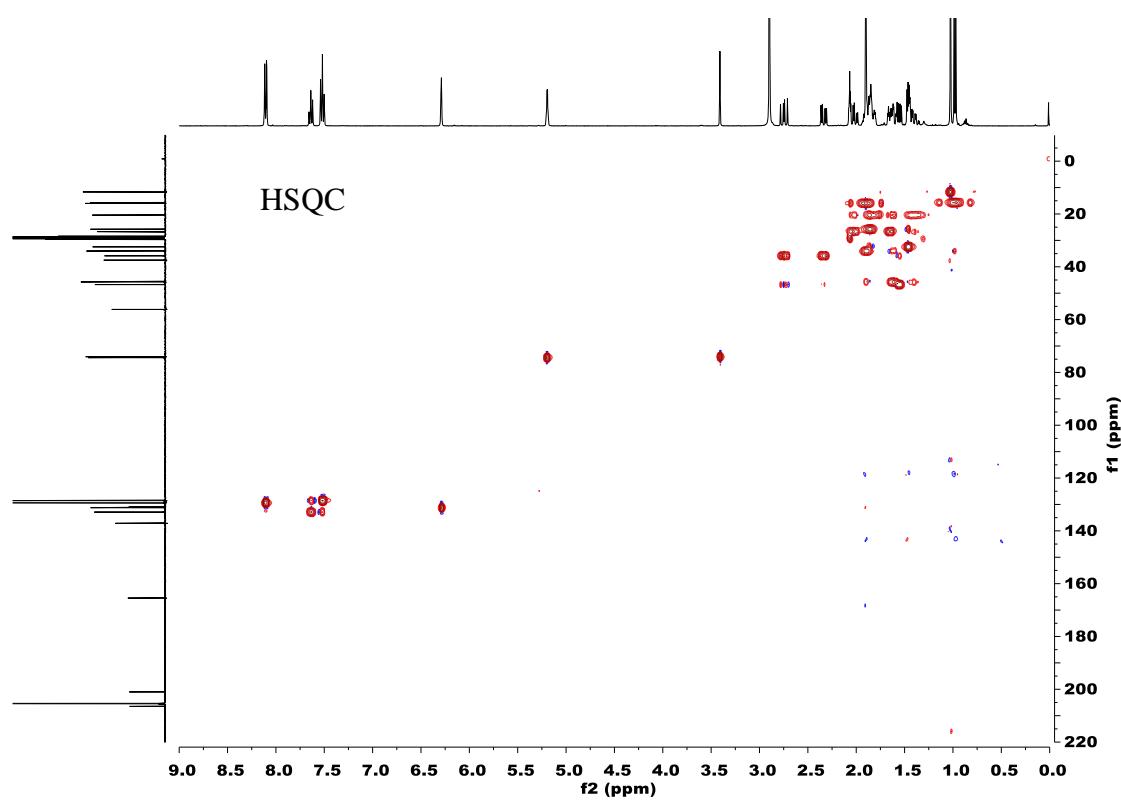
- 0.13

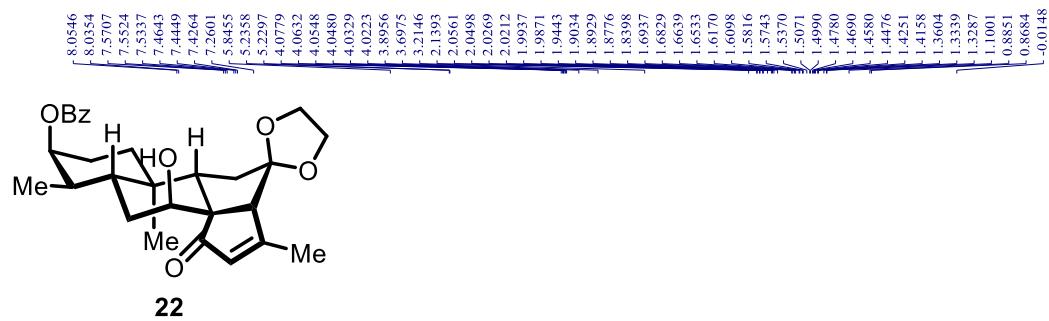
¹³C NMR spectrum (100 MHz, CDCl₃)



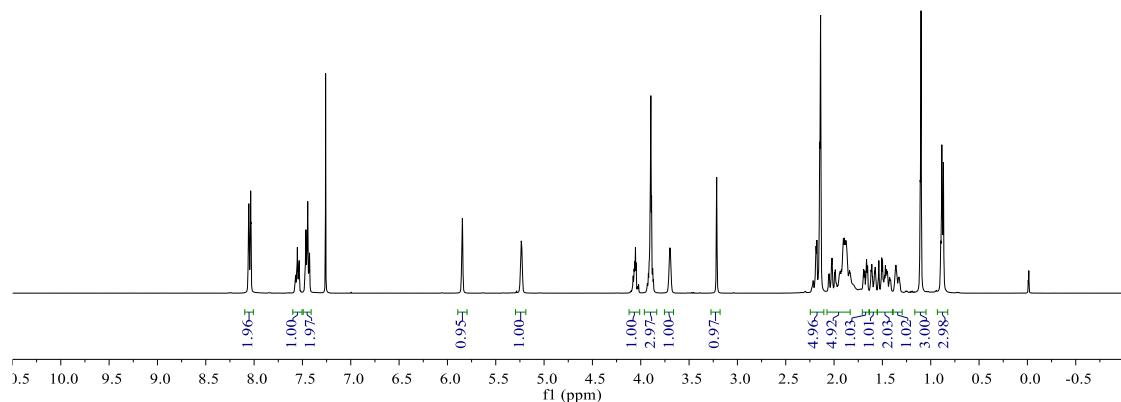




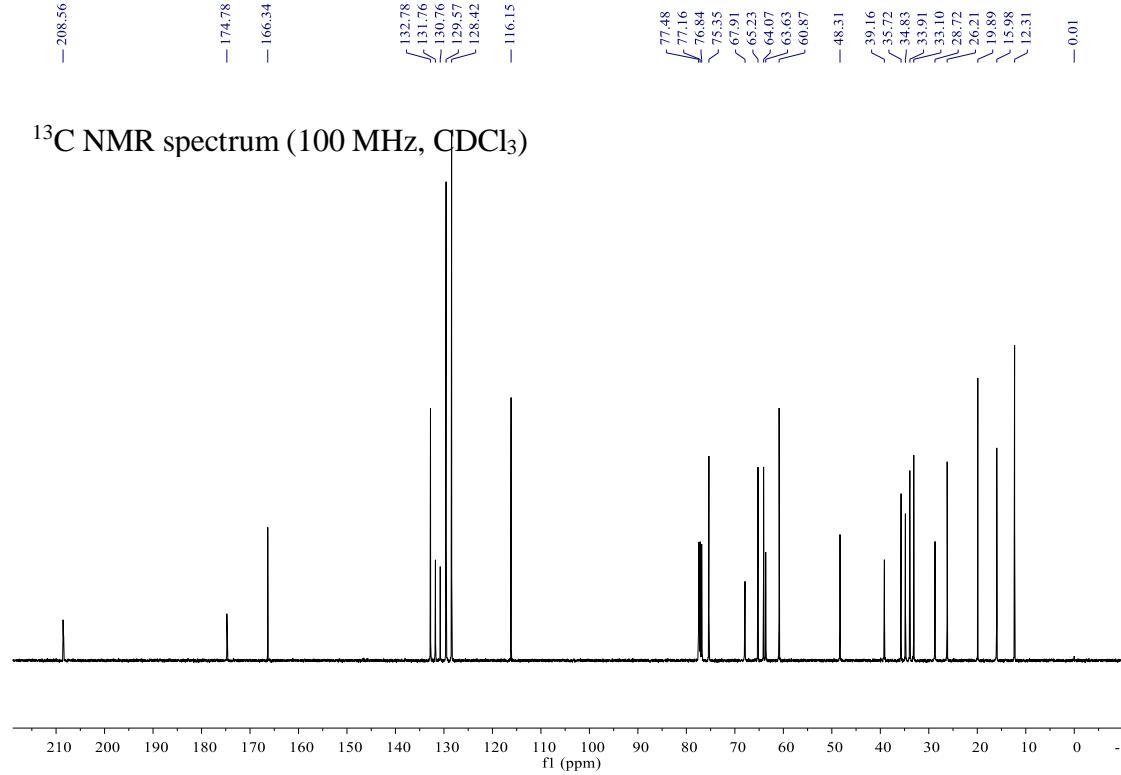


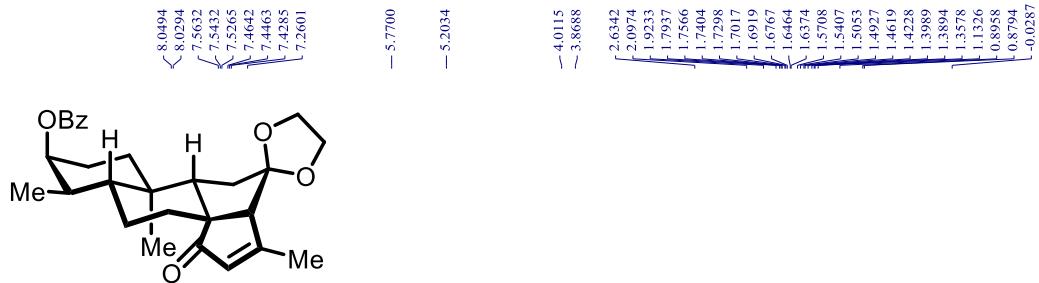


¹H NMR spectrum (400 MHz, CDCl₃)



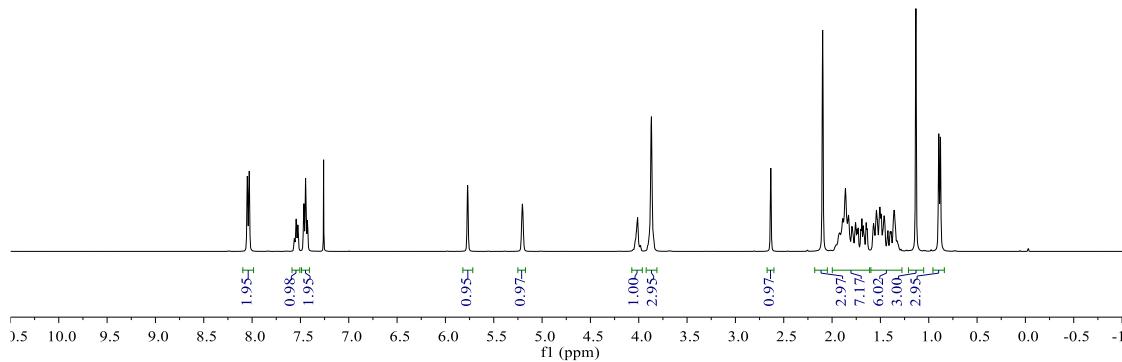
¹³C NMR spectrum (100 MHz, CDCl₃)



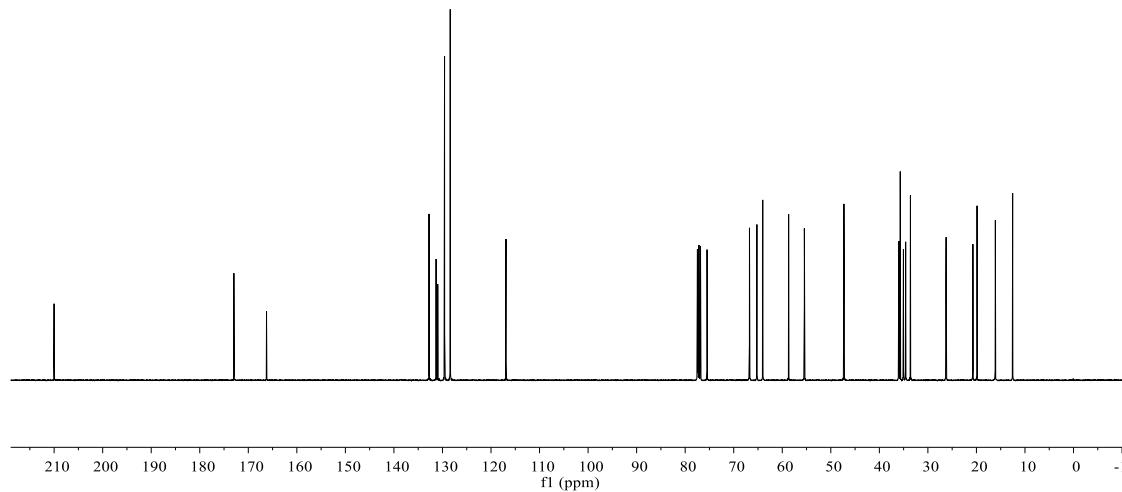


23

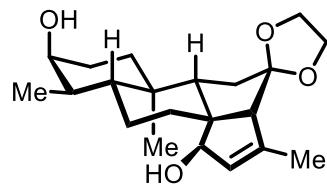
¹H NMR spectrum (400 MHz, CDCl₃)



¹³C NMR spectrum (100 MHz, CDCl₃)

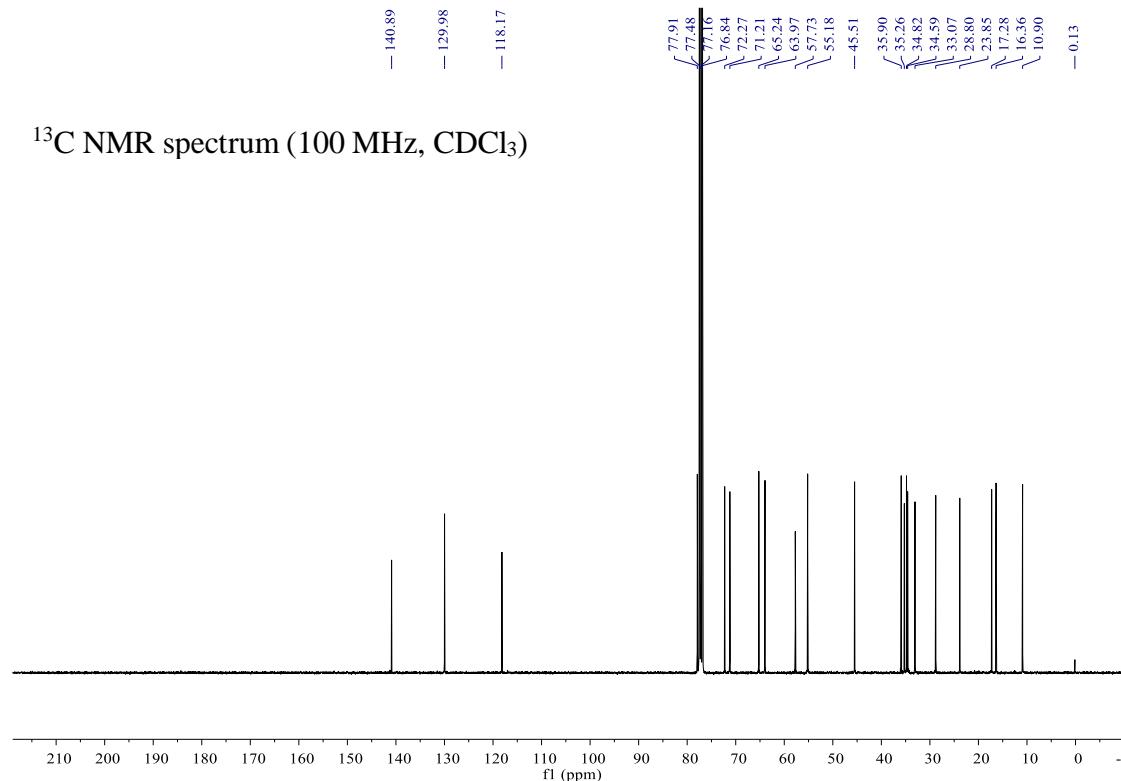
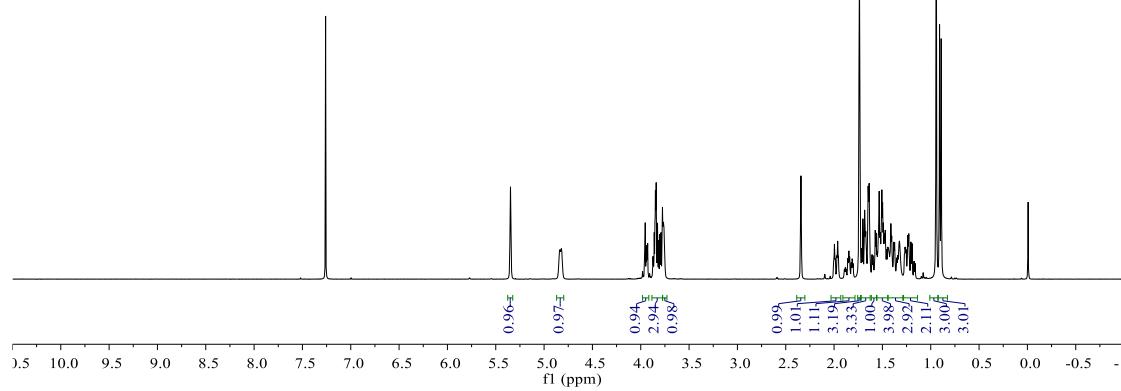


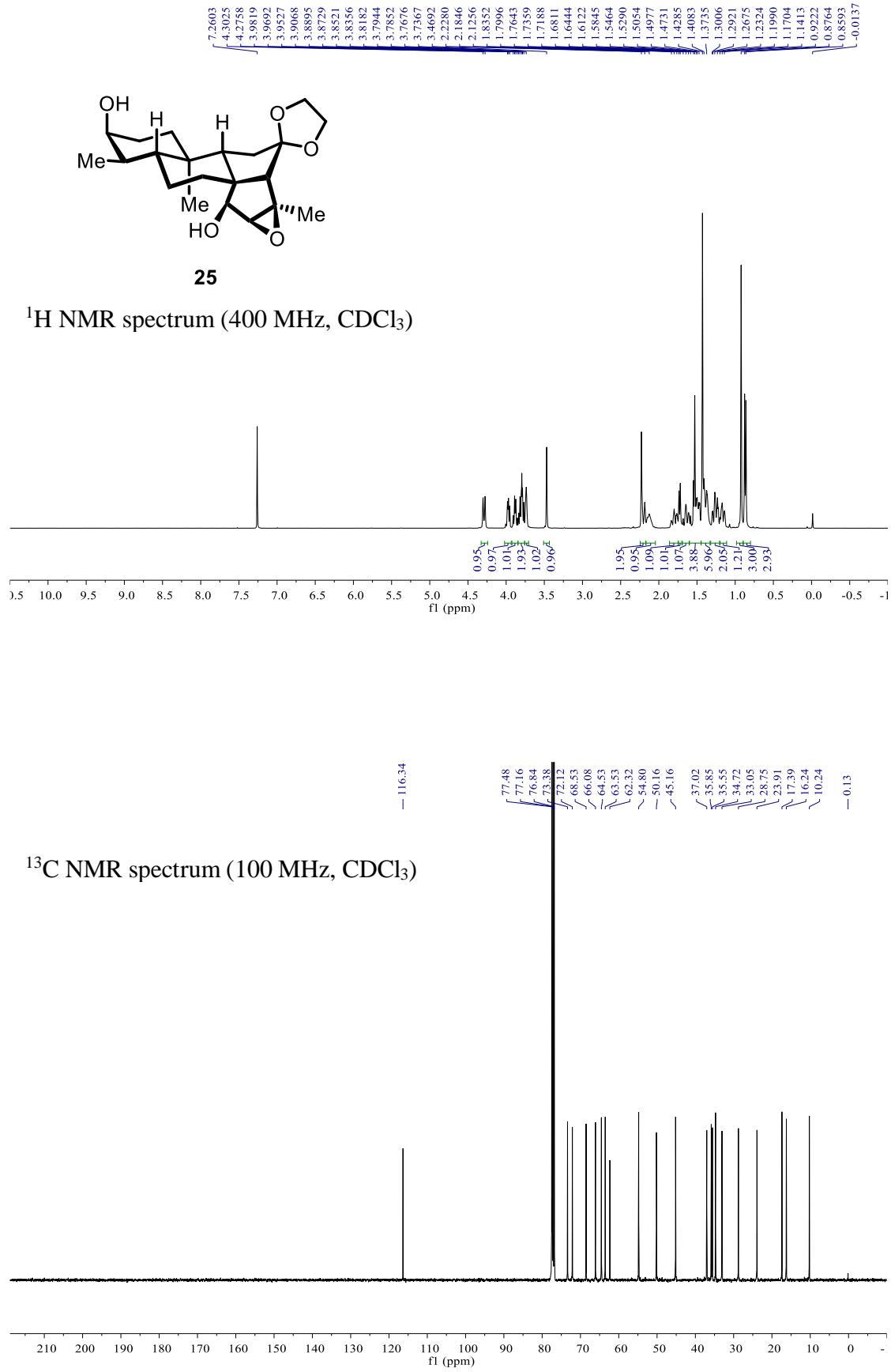
7.2604
5.3473
4.8372
4.8210
3.9535
3.9436
3.9370
3.9282
3.8731
3.8602
3.8483
3.8446
3.8139
3.8026
3.7905
3.7751
3.7653
3.2429
2.0033
1.9962
1.9882
1.9701
1.9627
1.9549
1.8575
1.8472
1.8385
1.7377
1.7020
1.6835
1.6716
1.6476
1.6372
1.6071
1.5979
1.5741
1.5656
1.5333
1.5057
1.4980
1.4901
1.4781
1.4701
1.4557
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1.2054
1.1938
1.09435
1.09086
0.8914
-0.0077

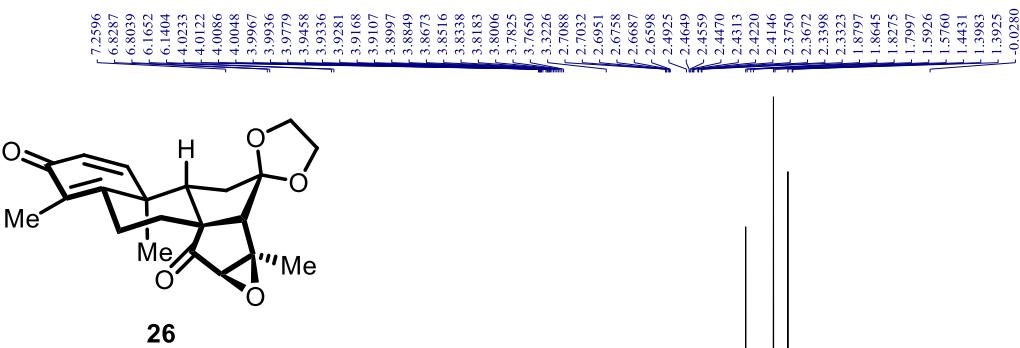


24

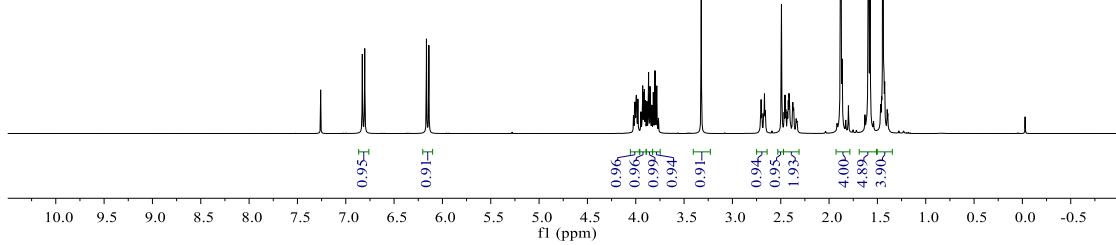
¹H NMR spectrum (400 MHz, CDCl₃)



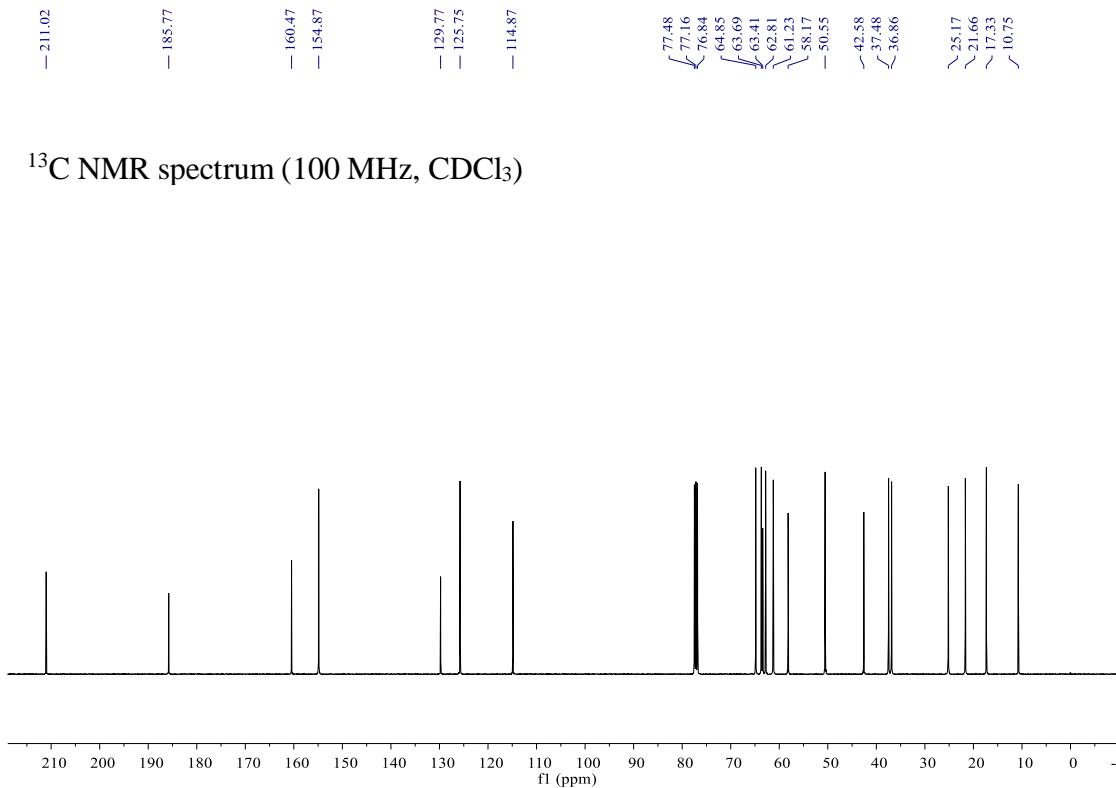




^1H NMR spectrum (400 MHz, CDCl_3)

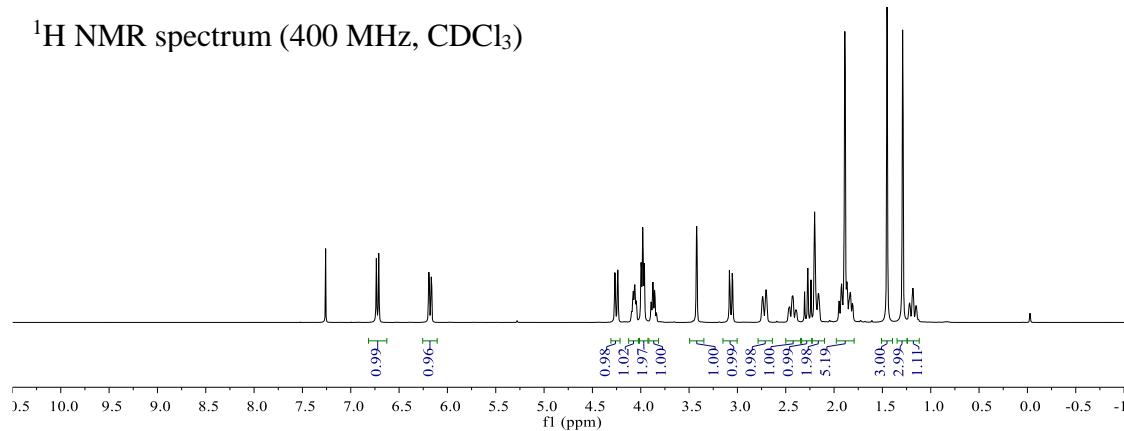


^{13}C NMR spectrum (100 MHz, CDCl_3)

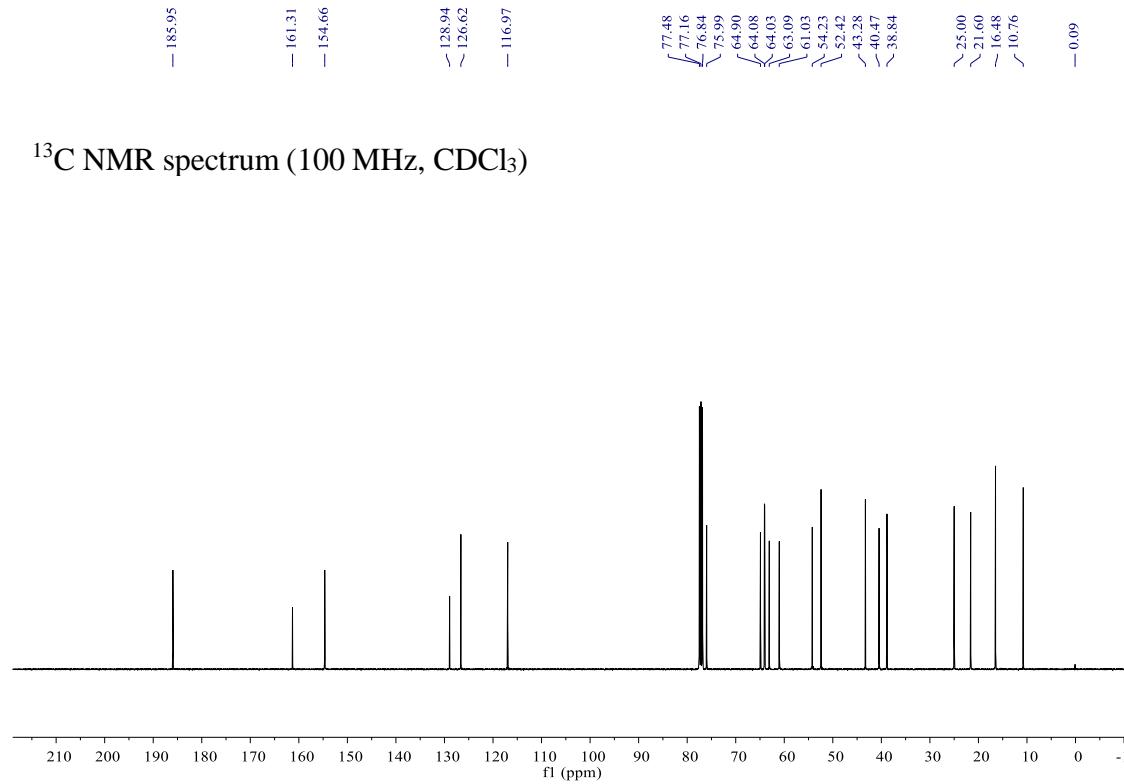


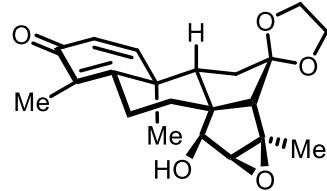


¹H NMR spectrum (400 MHz, CDCl₃)



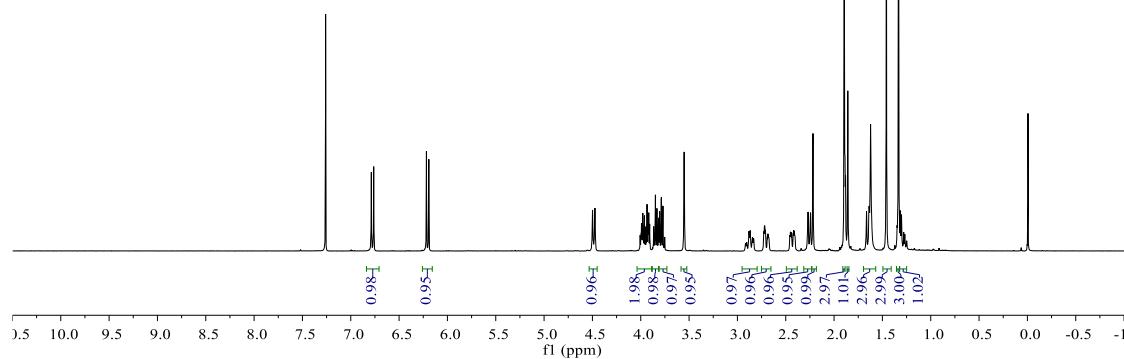
¹³C NMR spectrum (100 MHz, CDCl₃)





C14-epi-27

¹H NMR spectrum (400 MHz, CDCl₃)



- 185.98

— 161.76

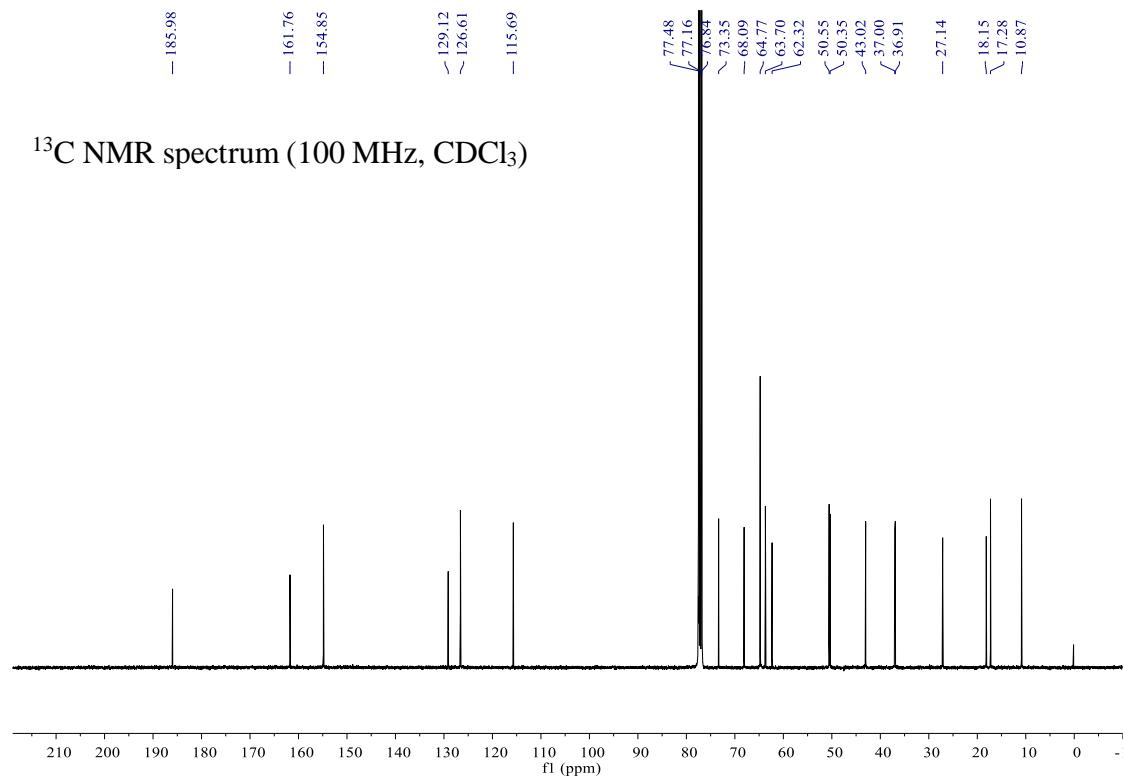
129.12

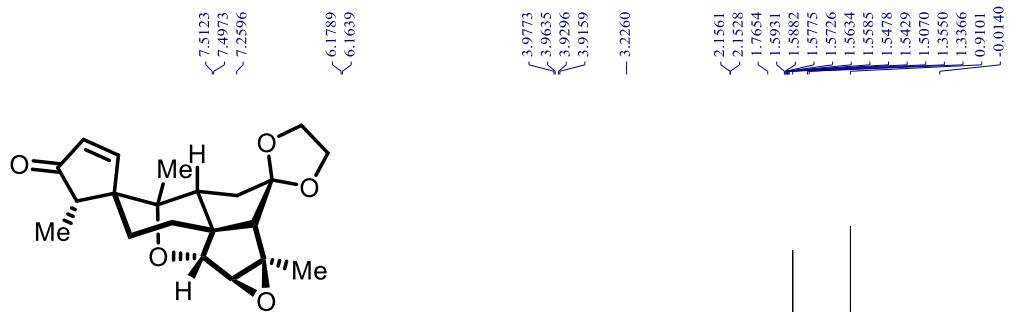
— 115.69

77.48
77.16
76.84
~ 73.35
- 68.09
~ 64.77
~ 63.70
62.32
50.55
50.35
~ 43.02
~ 37.00
~ 26.01

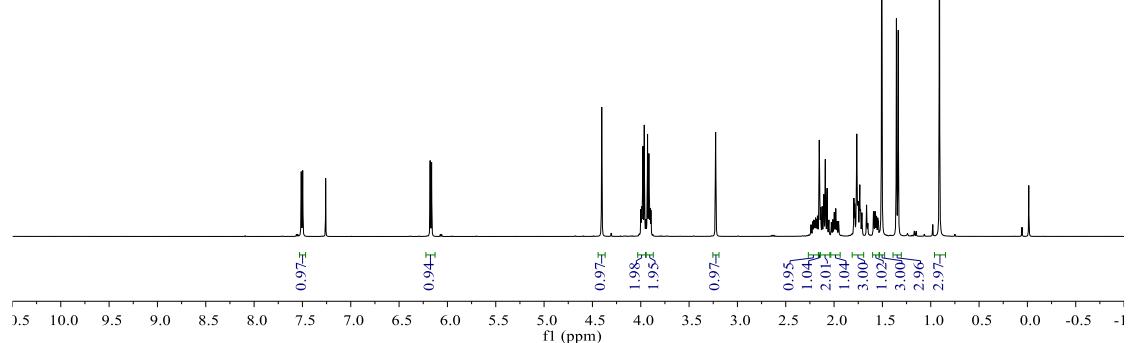
— 27.14
— 18.15
— 17.28
— 10.87

¹³C NMR spectrum (100 MHz, CDCl₃)

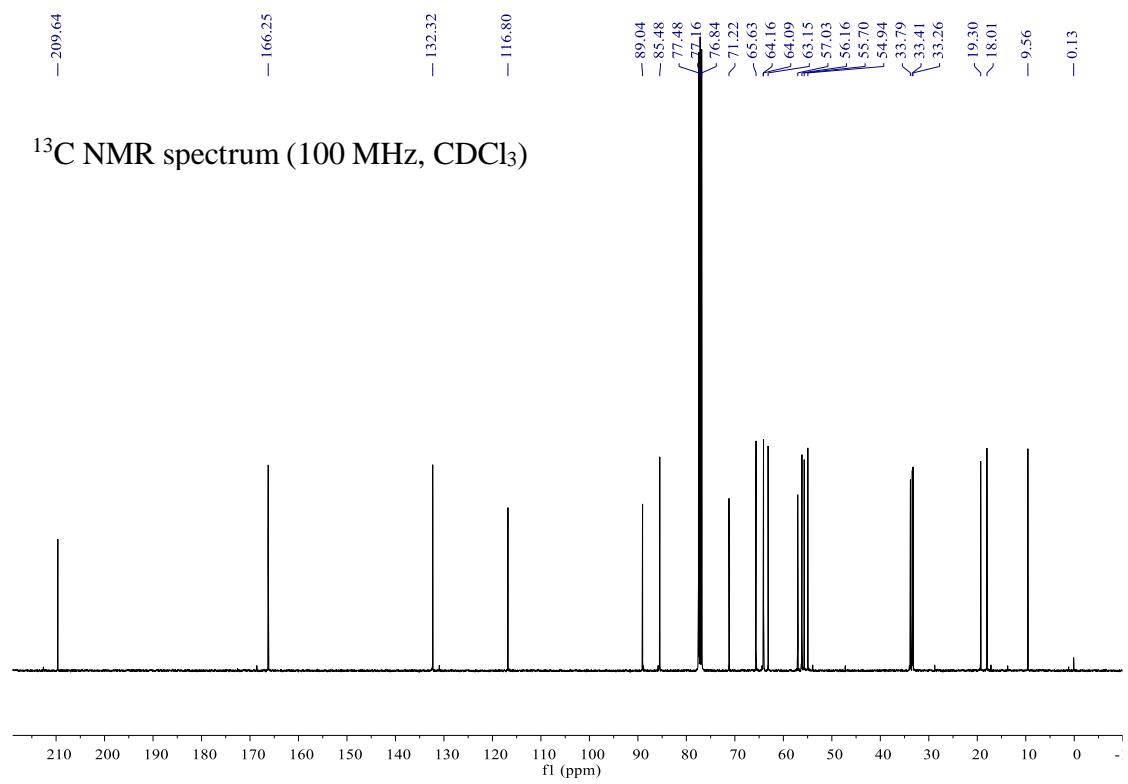


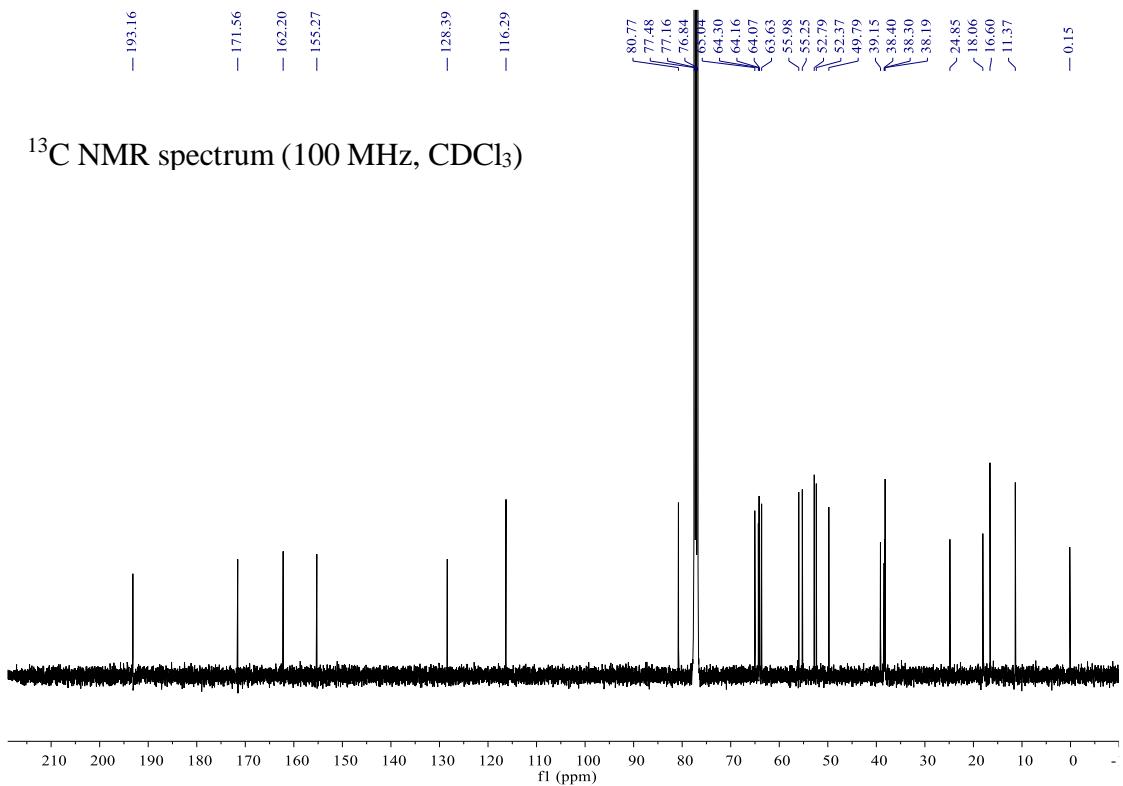
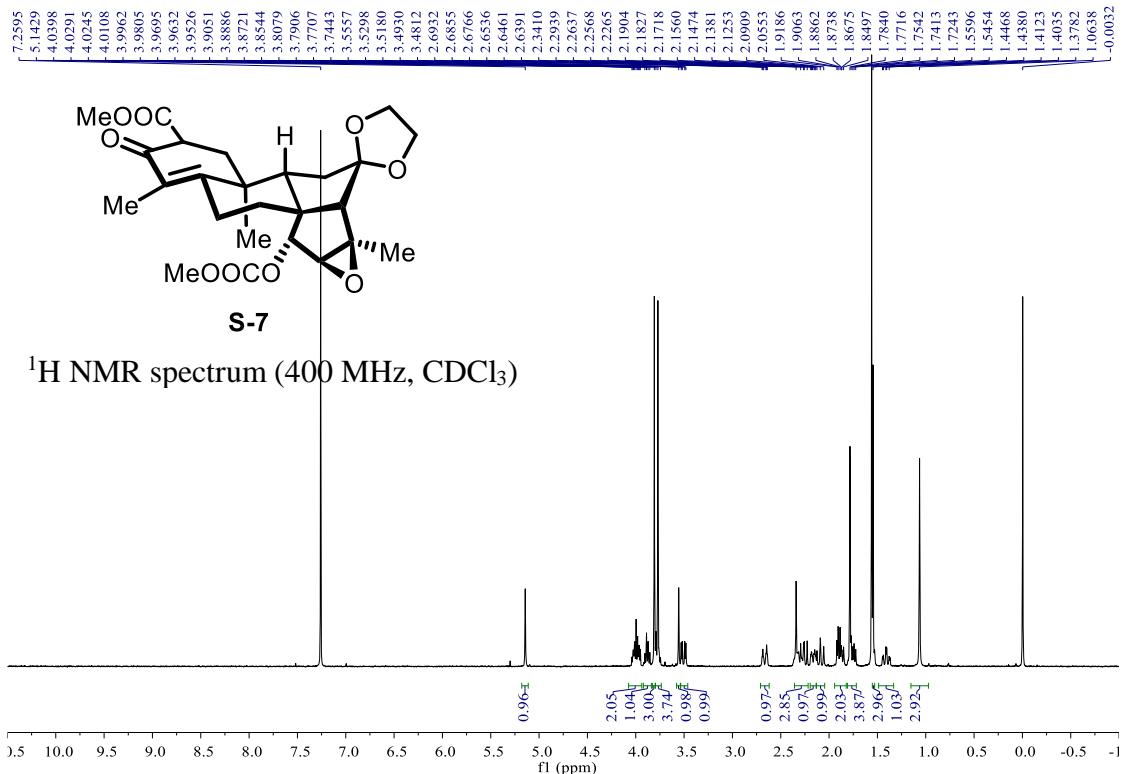


¹H NMR spectrum (400 MHz, CDCl₃)

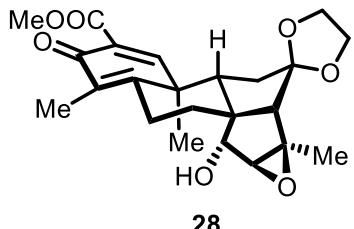


¹³C NMR spectrum (100 MHz, CDCl₃)

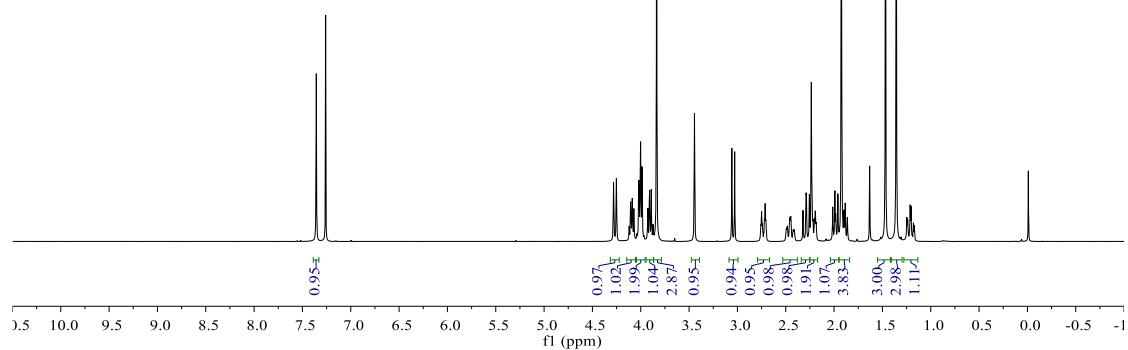




7.3563
 7.2598
 4.2810
 4.2517
 4.1195
 4.1053
 4.0867
 4.0714
 4.0204
 4.0014
 3.9868
 3.9269
 3.9081
 3.8908
 3.8728
 3.8354
 3.4441
 3.0578
 3.0283
 2.7577
 2.7497
 2.7415
 2.7207
 2.7127
 2.7049
 2.4939
 2.4839
 2.4586
 2.4481
 2.4222
 2.4121
 2.3216
 2.2899
 2.2869
 2.2552
 2.2352
 2.2030
 2.1947
 2.1847
 2.0139
 1.9916
 1.9830
 1.9605
 1.9244
 1.8976
 1.8847
 1.8623
 1.6318
 1.4682
 1.3563
 1.2471
 1.2381
 1.2131
 1.2037
 1.1789
 1.1695
 -0.0100



¹H NMR spectrum (400 MHz, CDCl₃)



- 181.50

- 166.35
- 159.83
- 158.65

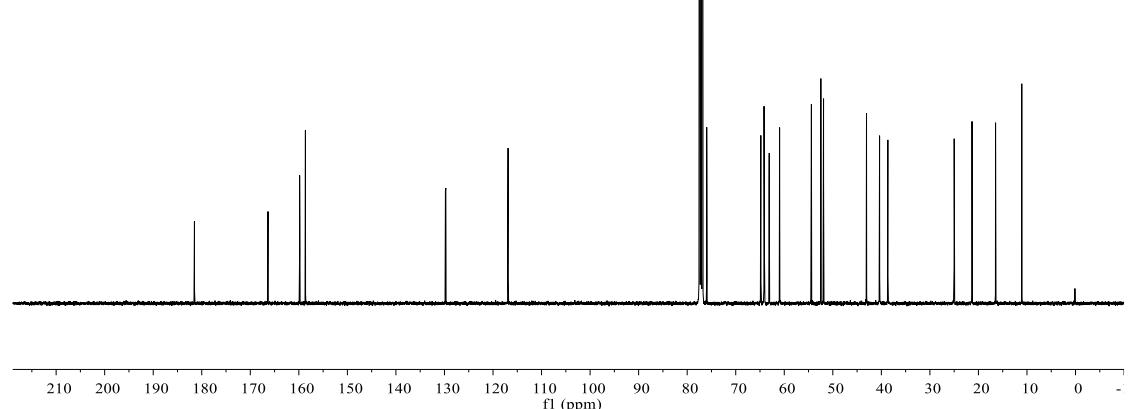
- 116.90

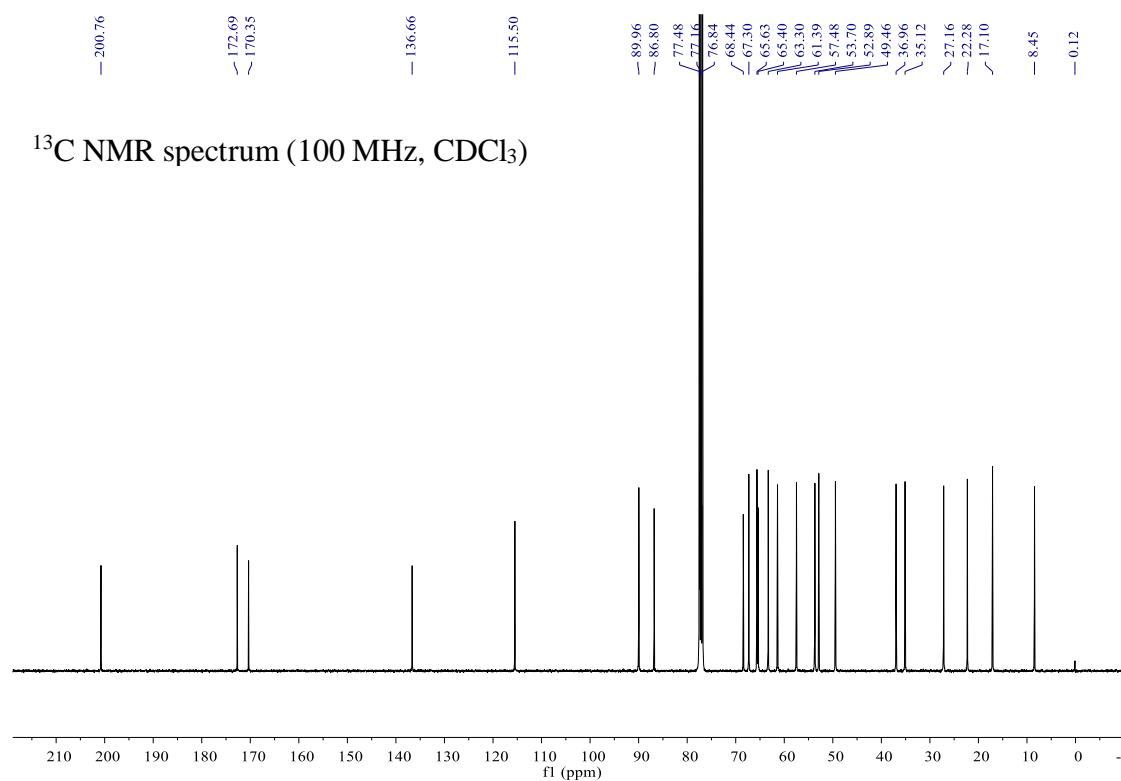
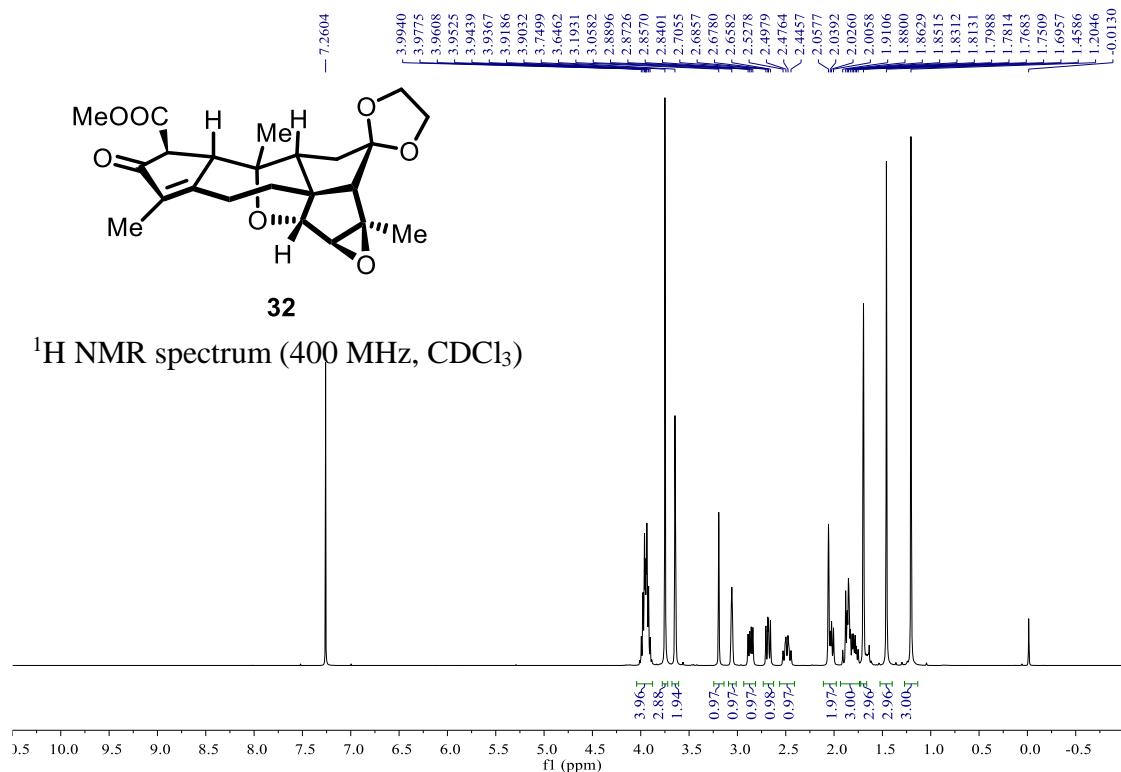
77.48
77.16
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64.82
64.17
64.09
63.10
60.97
54.41
52.46
51.91
43.06
40.37
38.66

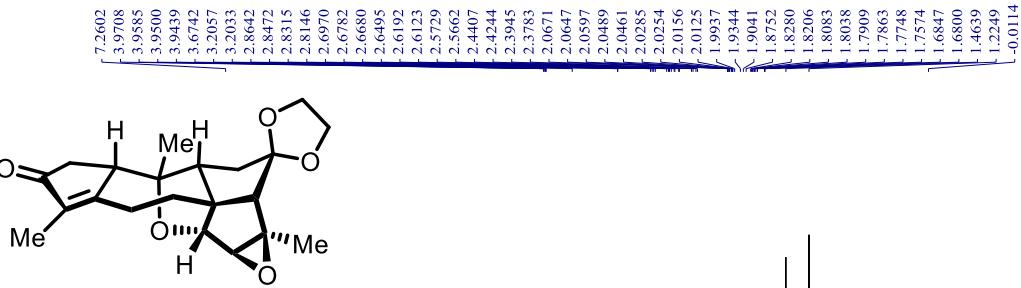
25.00
25.32
16.47
11.07

- 0.12

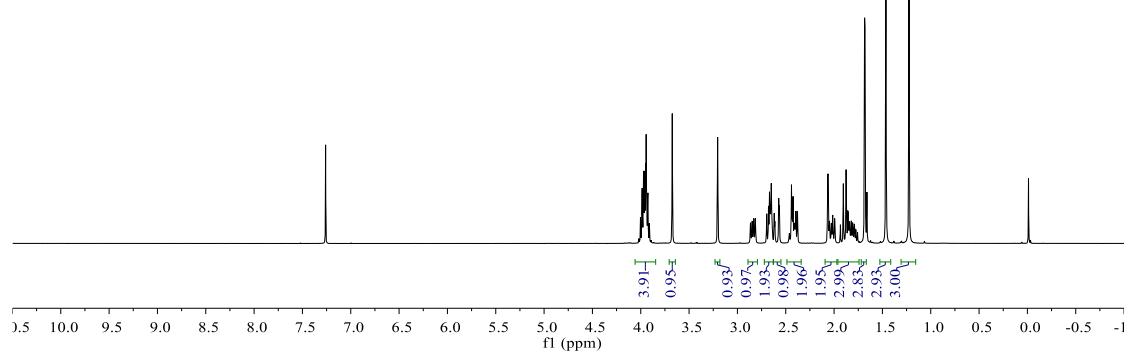
¹³C NMR spectrum (100 MHz, CDCl₃)



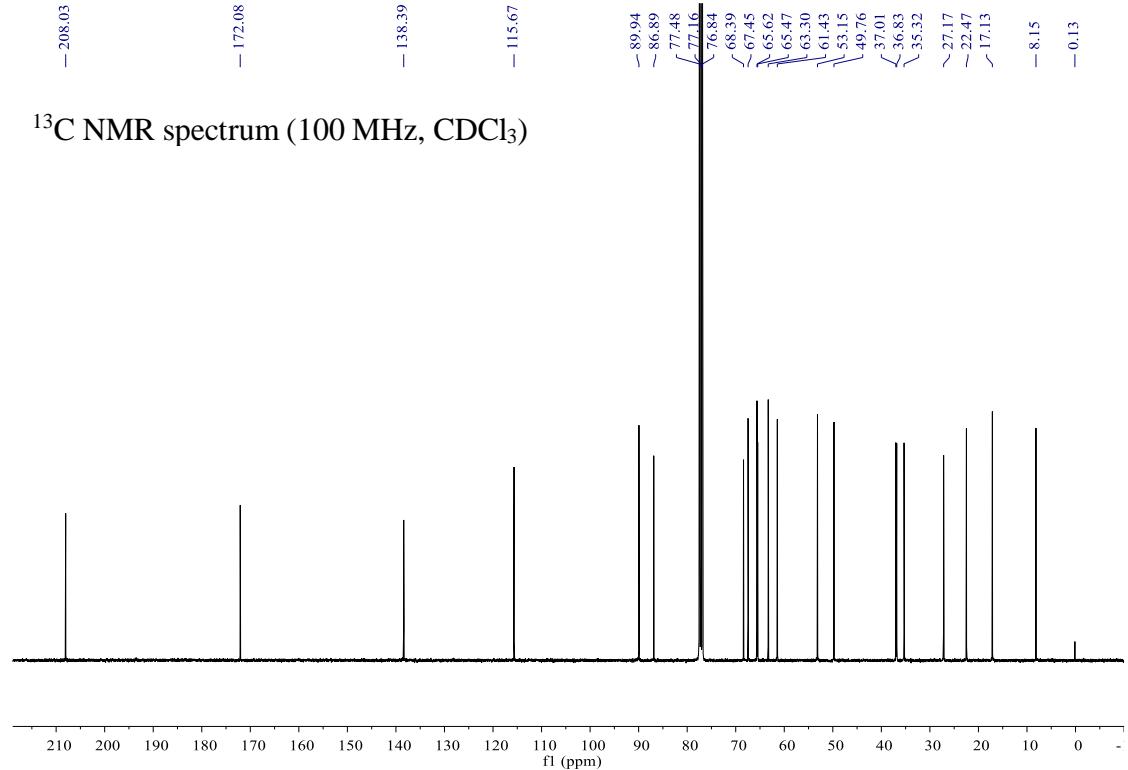


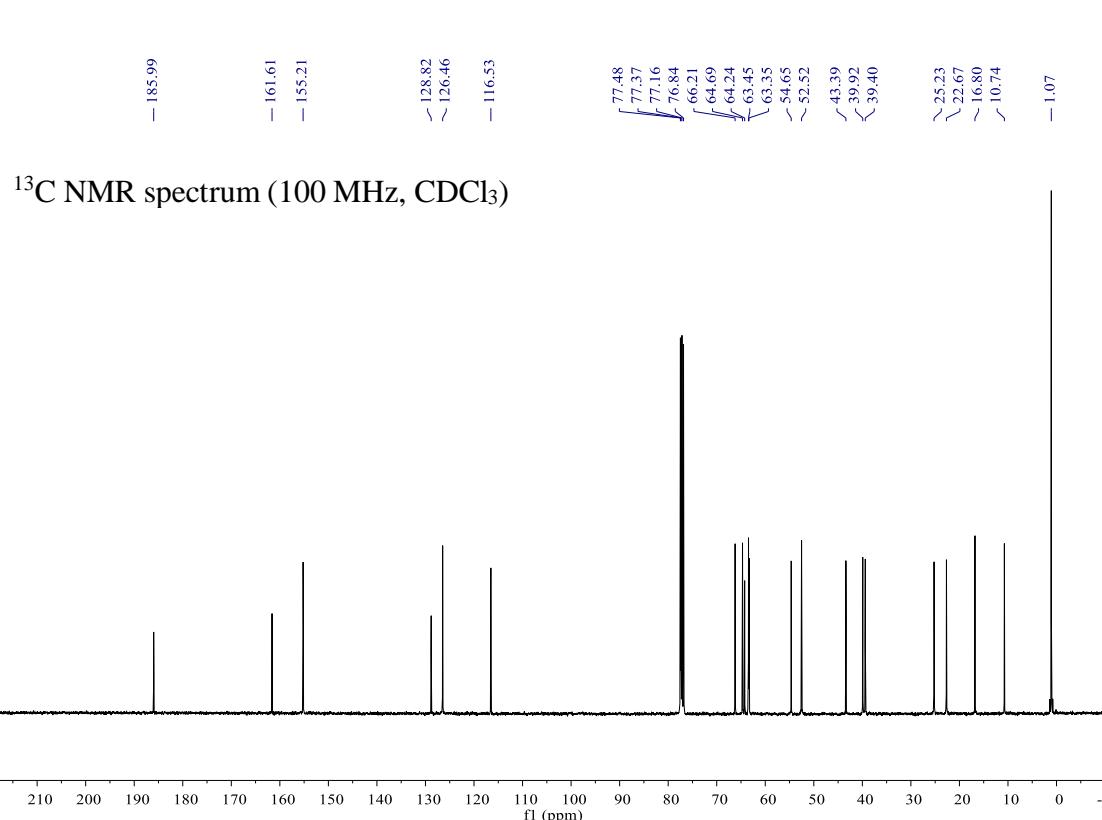
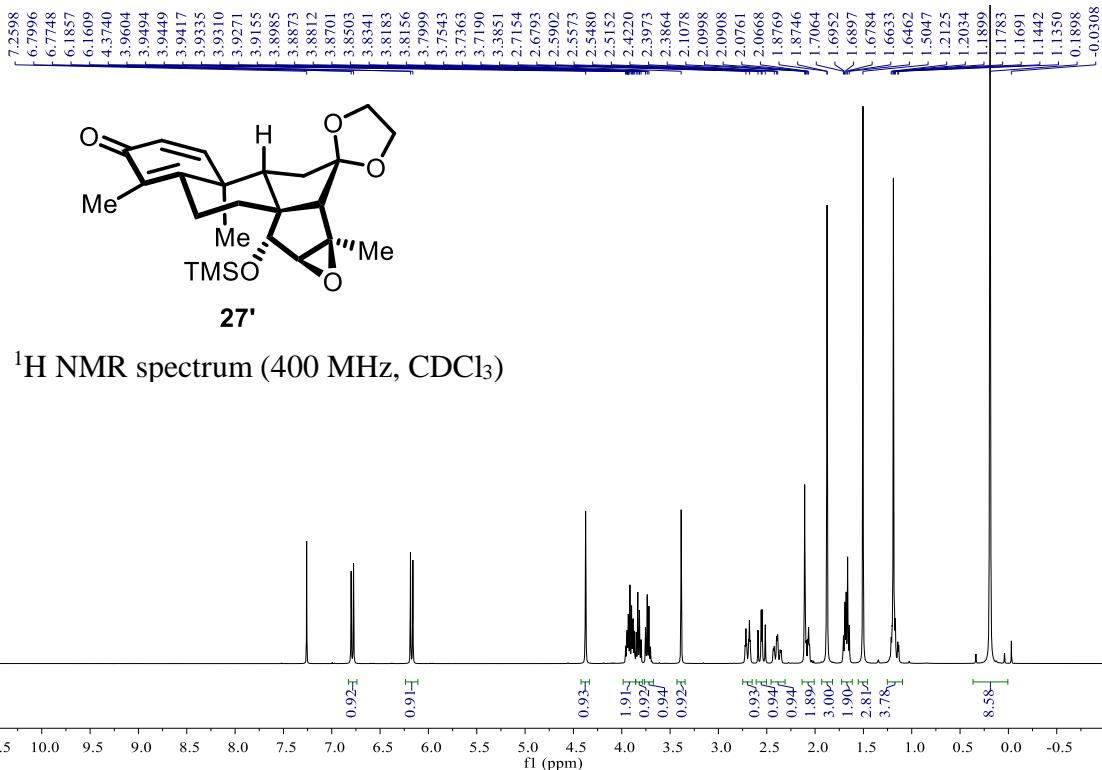


¹H NMR spectrum (400 MHz, CDCl₃)

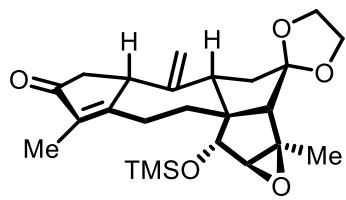


¹³C NMR spectrum (100 MHz, CDCl₃)

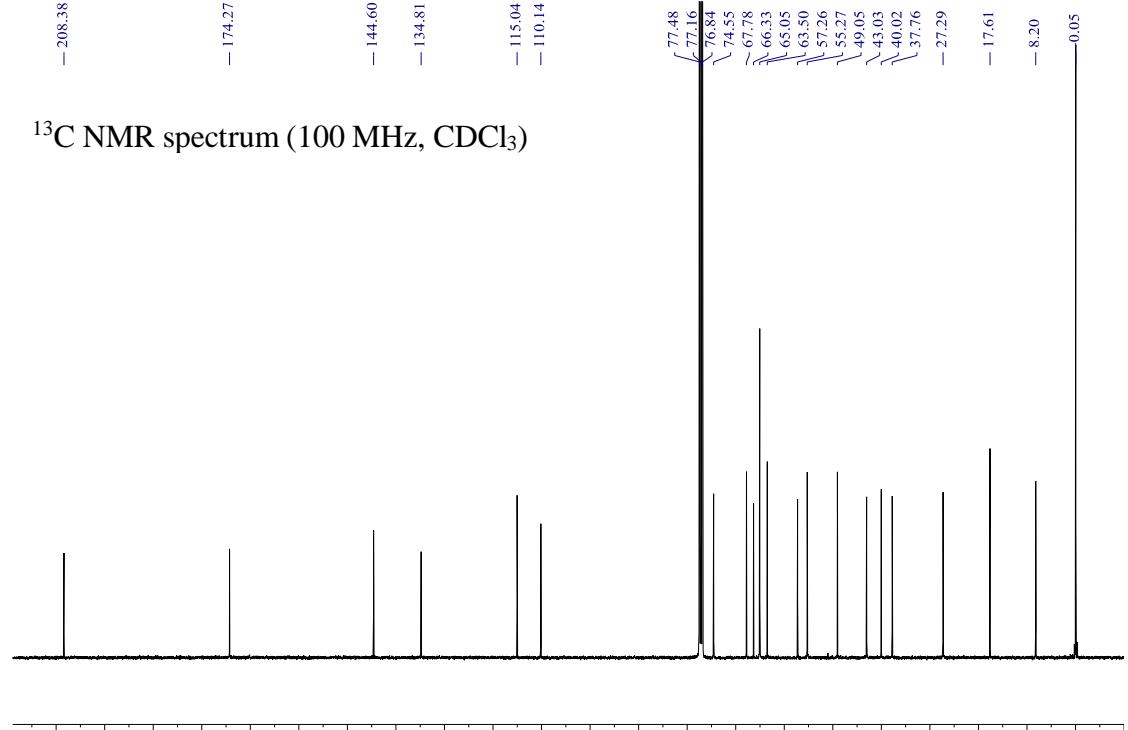
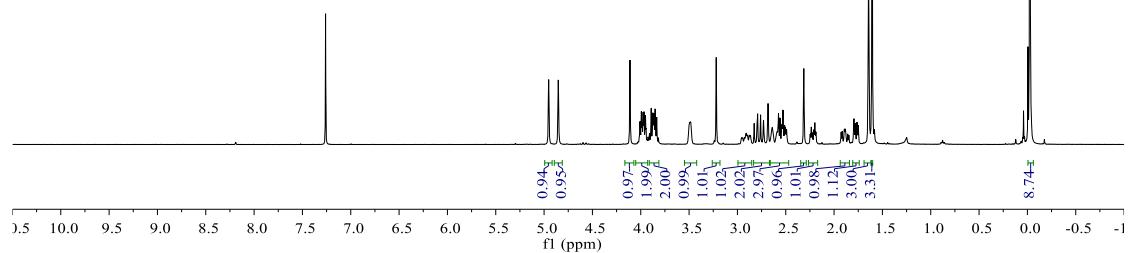


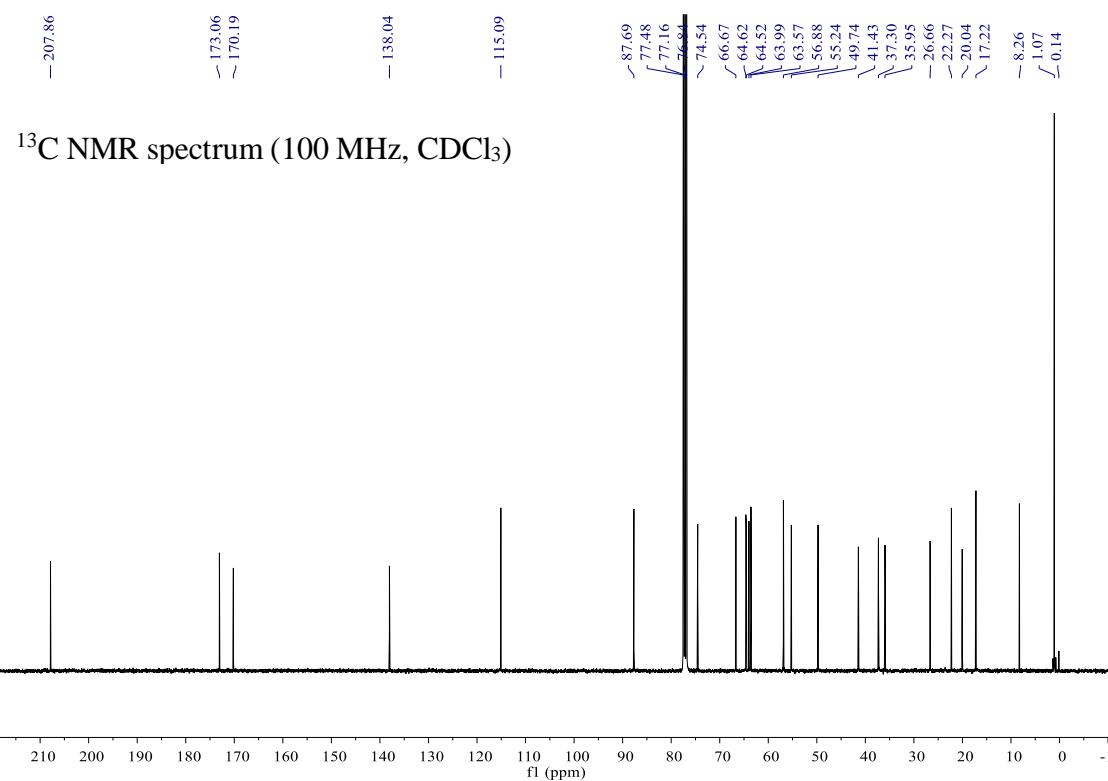
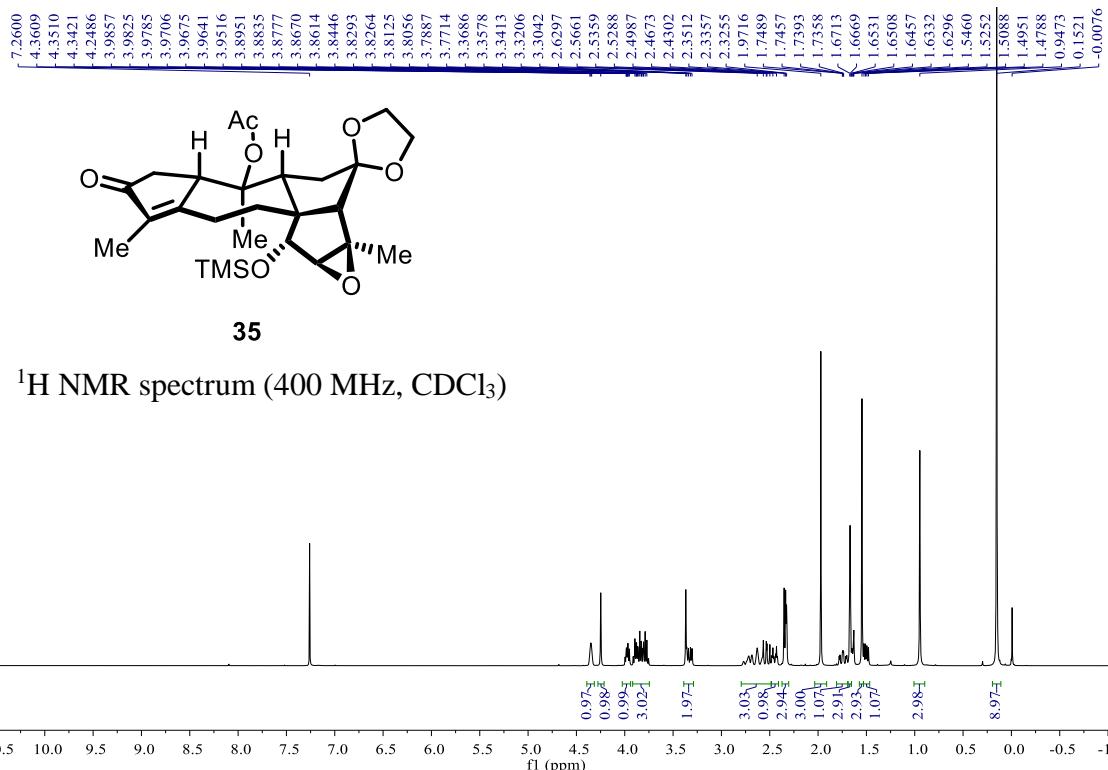


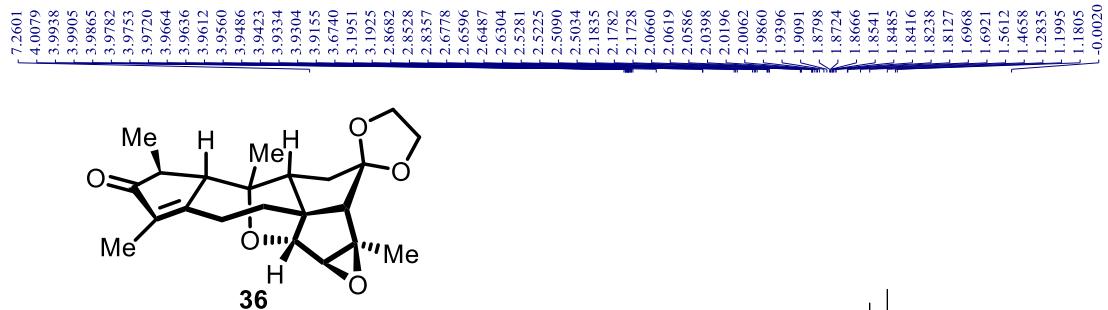
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-4.1114
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-3.9922
-3.9853
-3.9757
-3.9686
-3.9661
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-3.9509
-3.9447
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-3.8509
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-2.1993
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-1.8902
-1.8834
-1.7944
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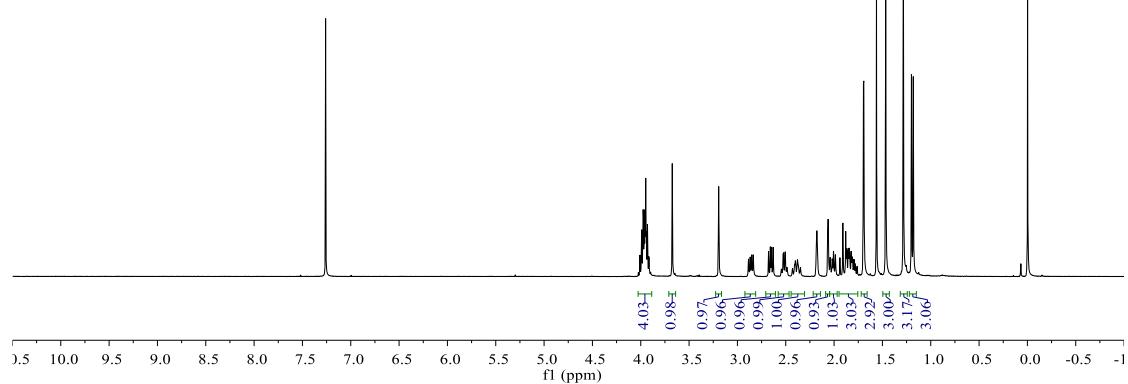
¹H NMR spectrum (400 MHz, CDCl₃)



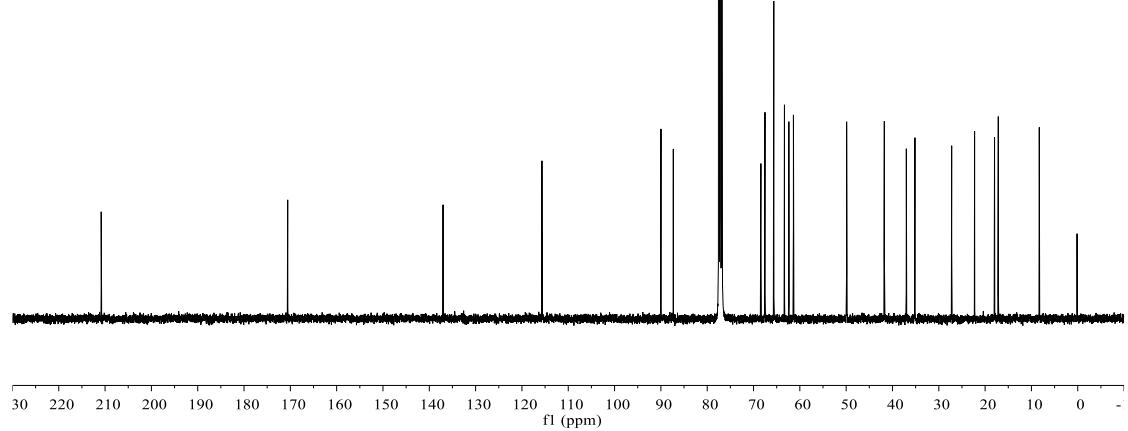




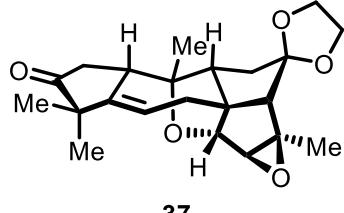
¹H NMR spectrum (400 MHz, CDCl₃)



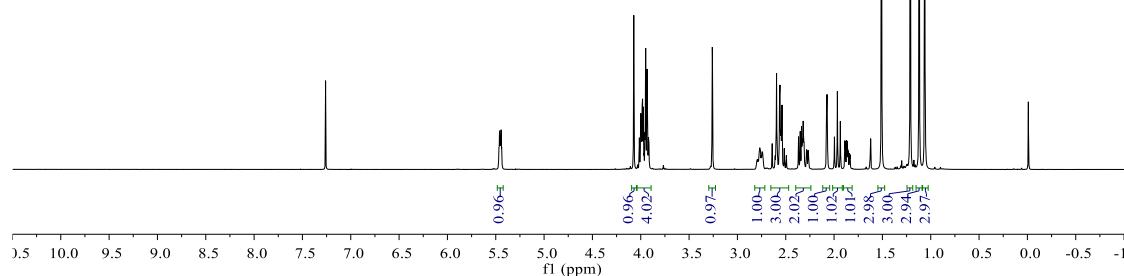
¹³C NMR spectrum (100 MHz, CDCl₃)



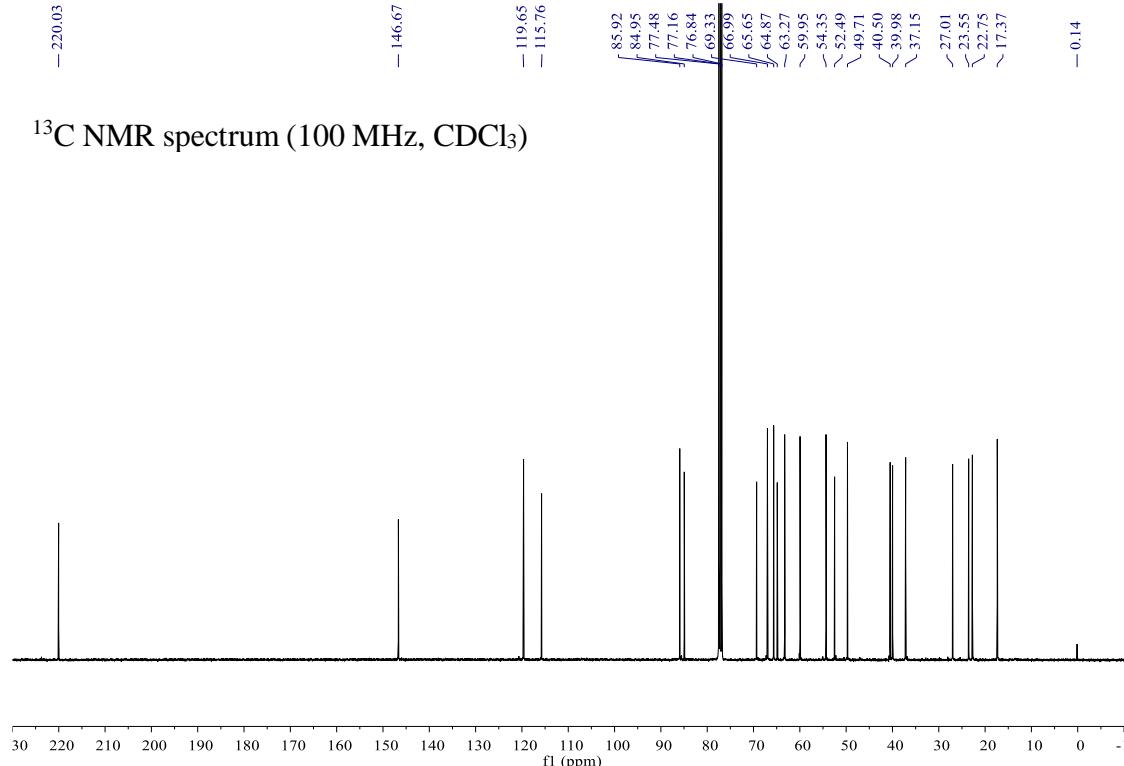
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3.9474
3.9364
3.9337
3.9300
3.9206
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2.6401
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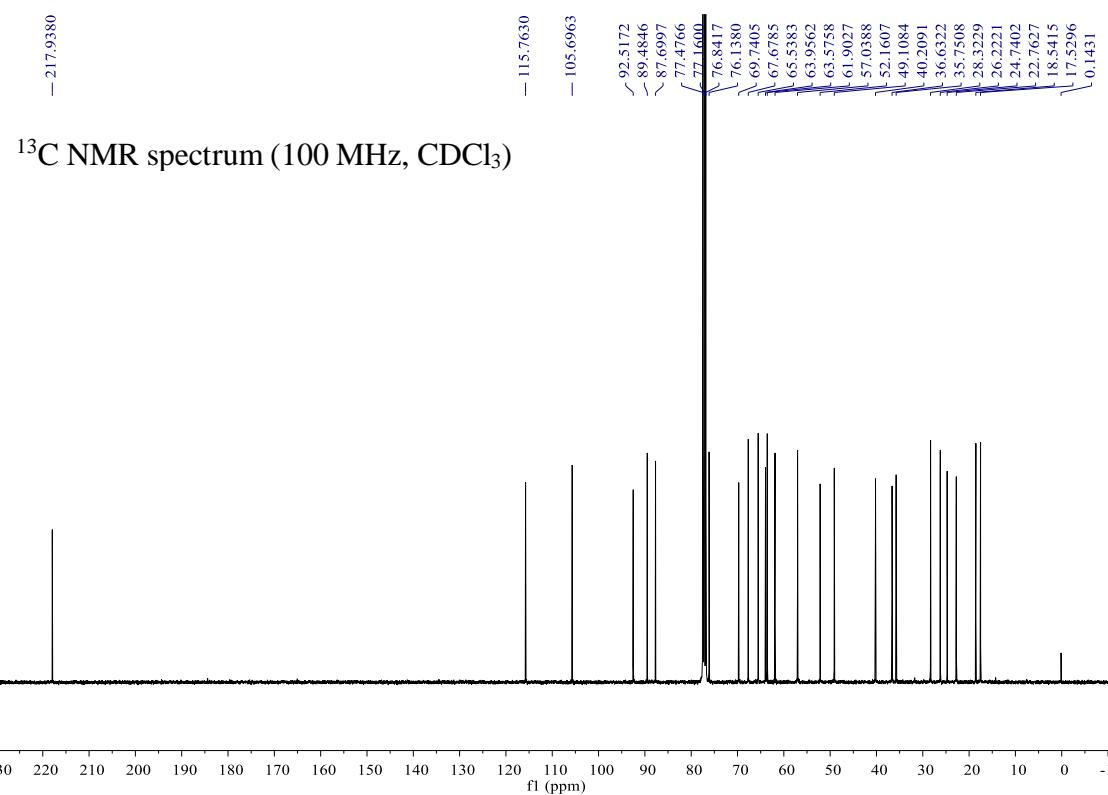
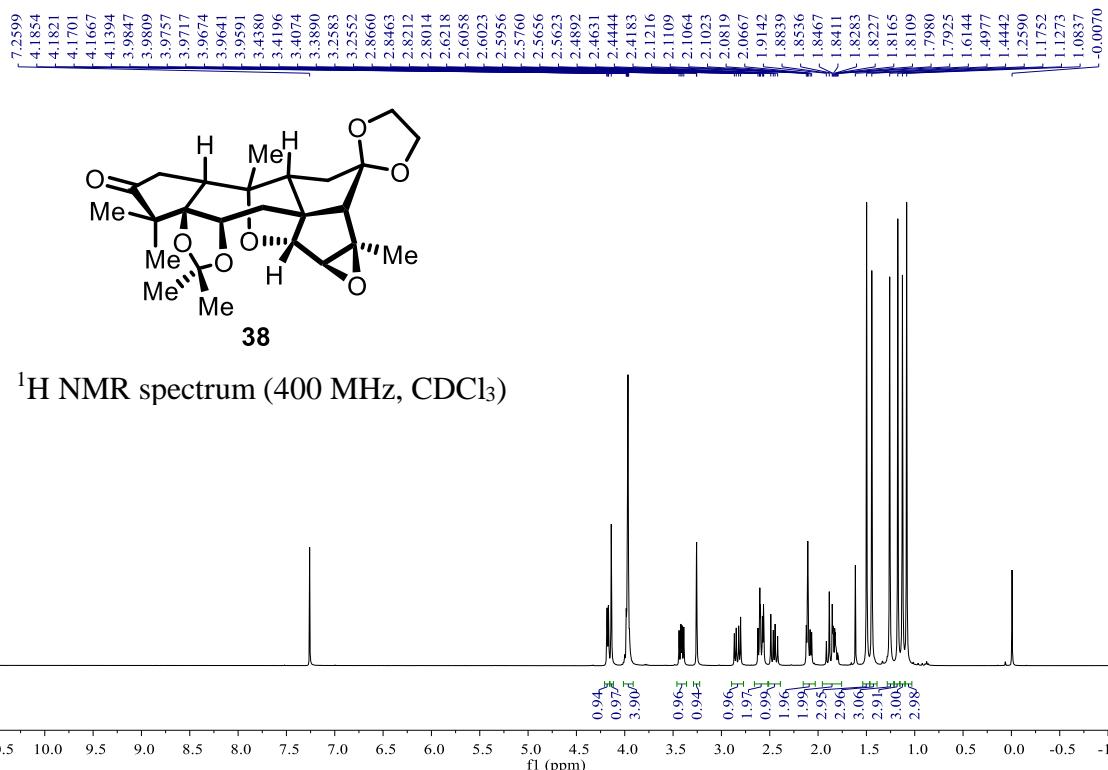


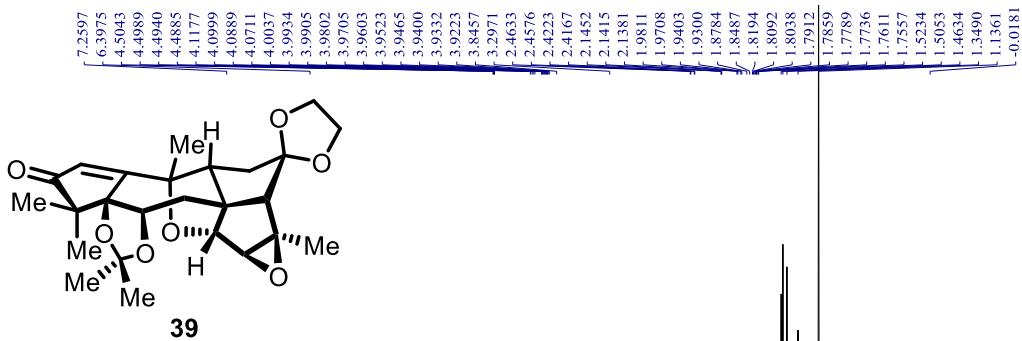
¹H NMR spectrum (400 MHz, CDCl₃)



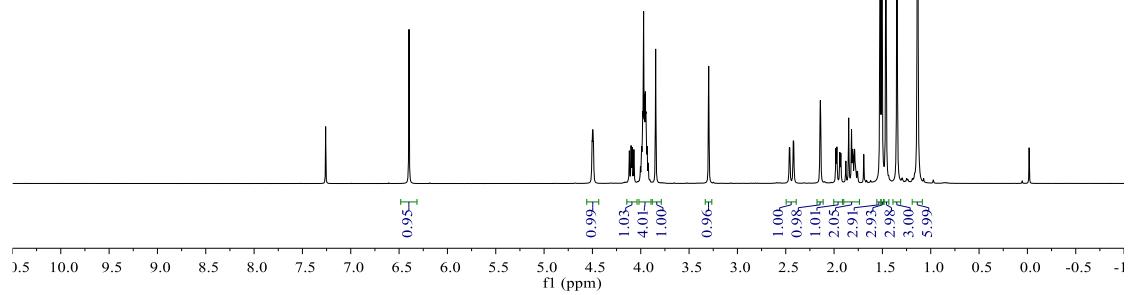
¹³C NMR spectrum (100 MHz, CDCl₃)



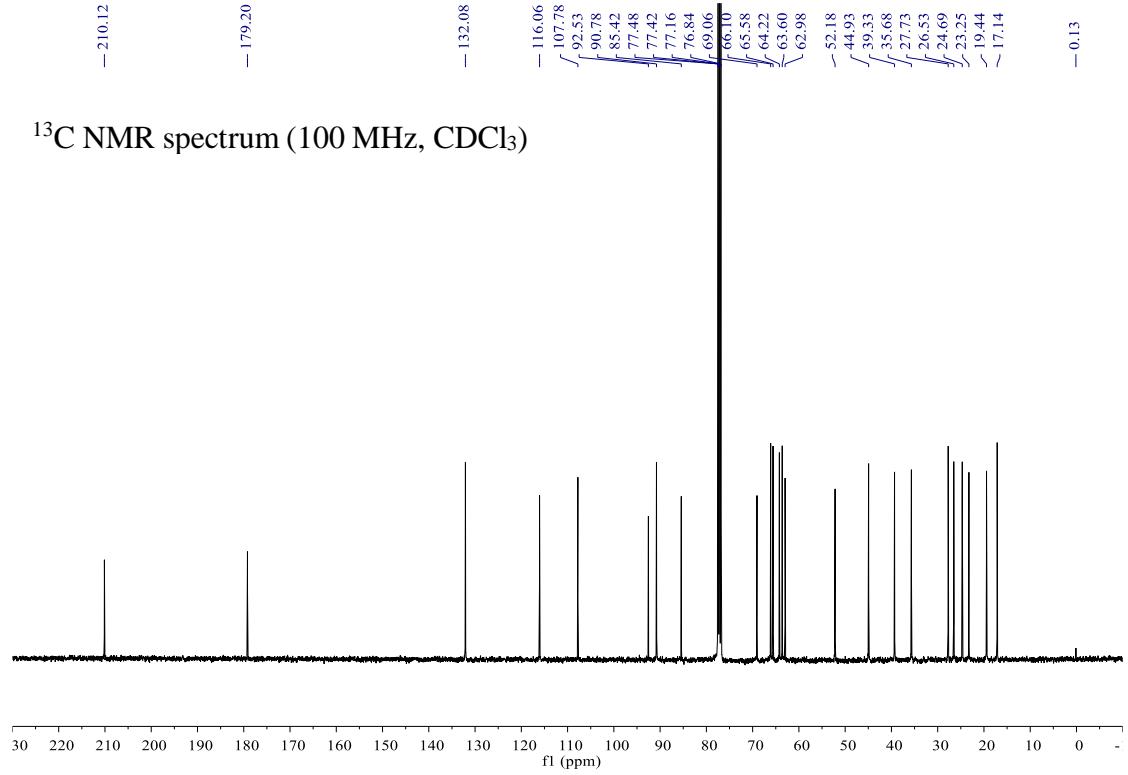


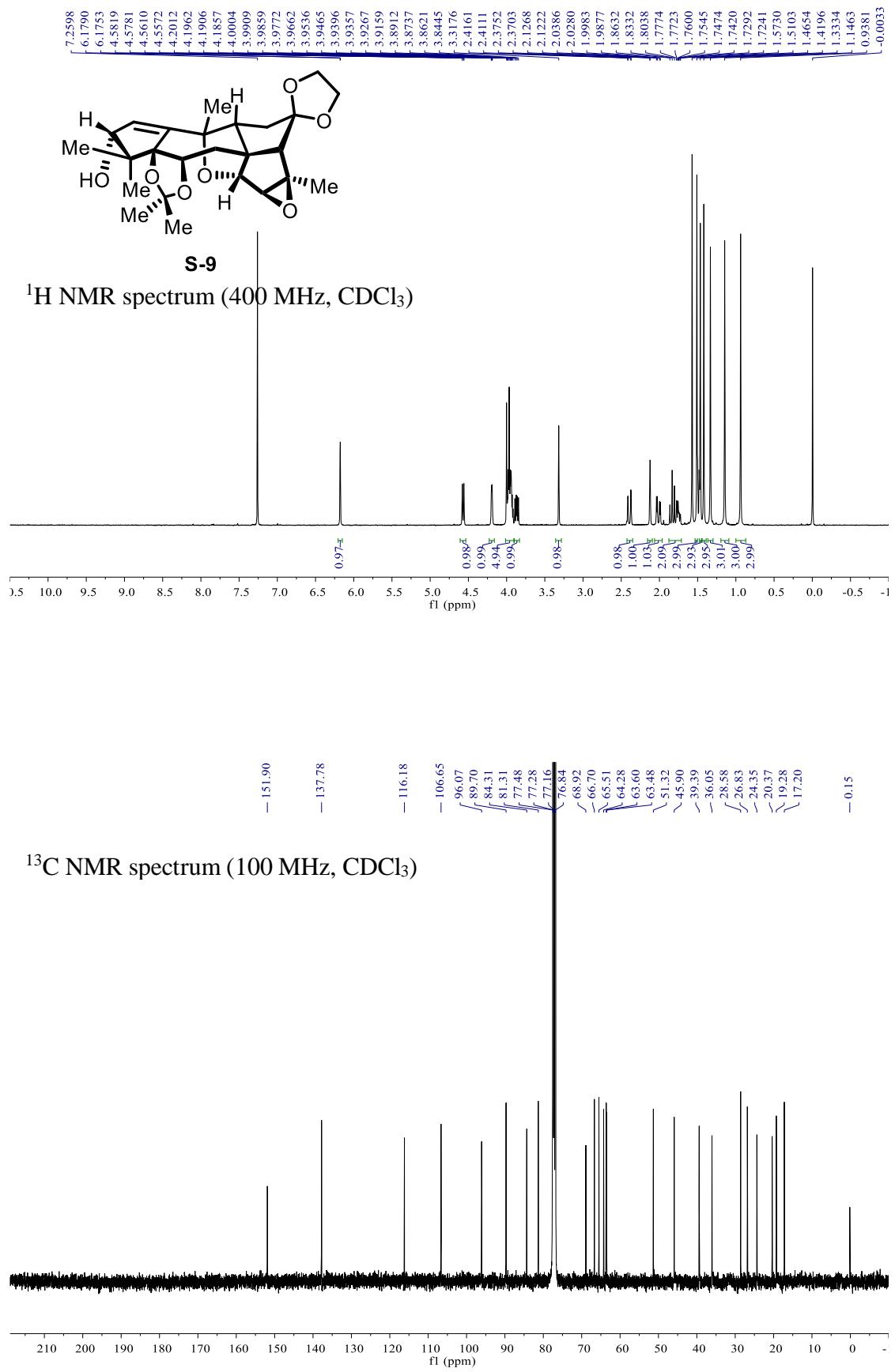


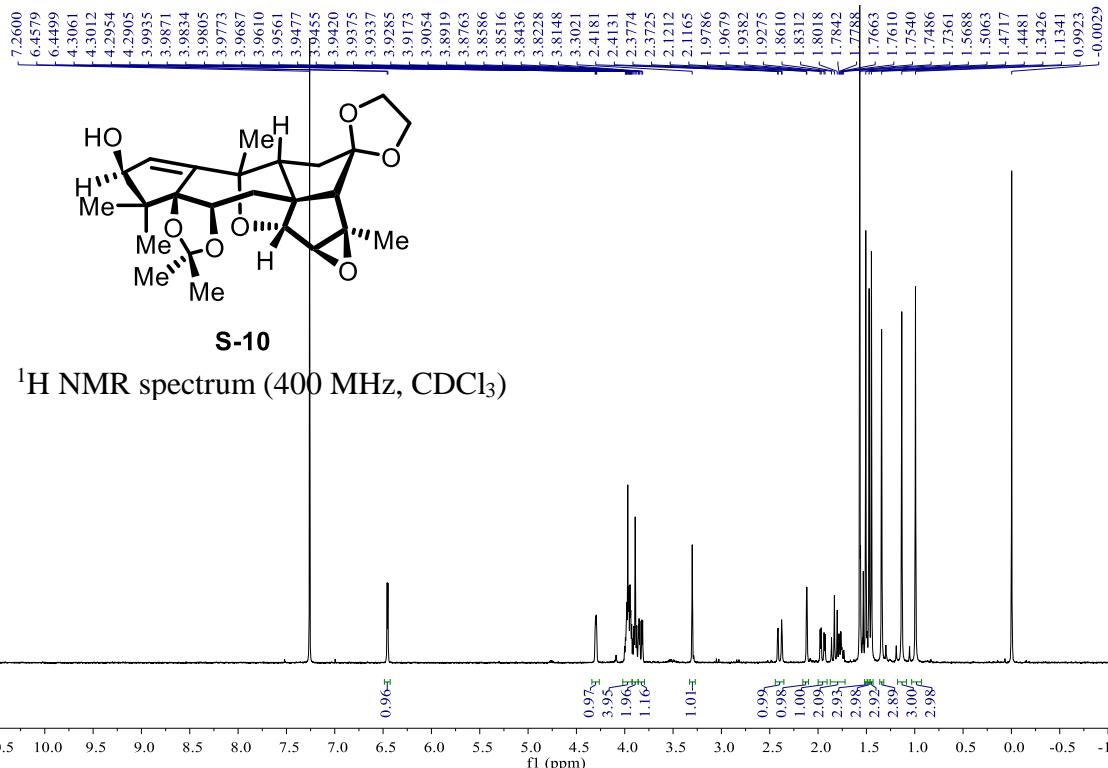
^1H NMR spectrum (400 MHz, CDCl_3)



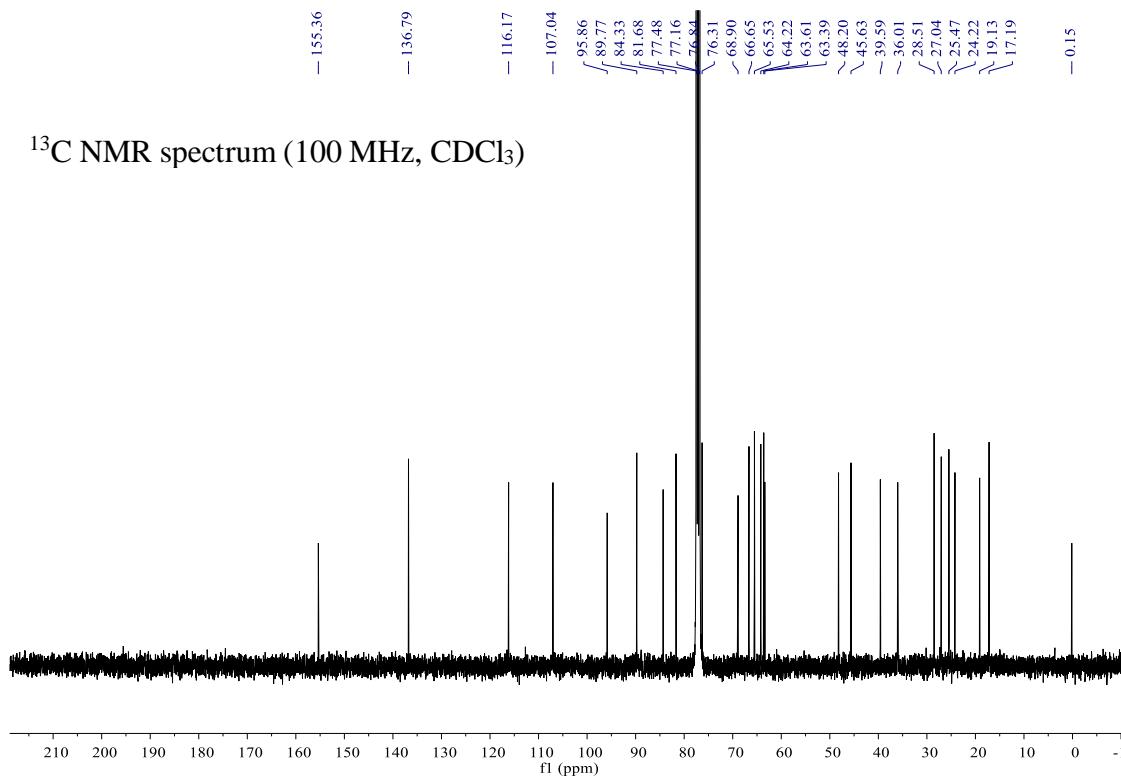
^{13}C NMR spectrum (100 MHz, CDCl_3)

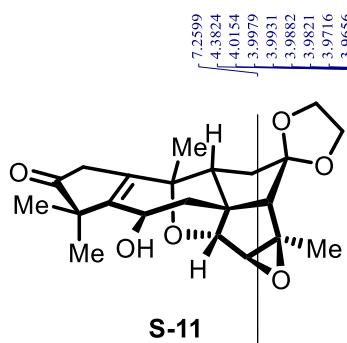




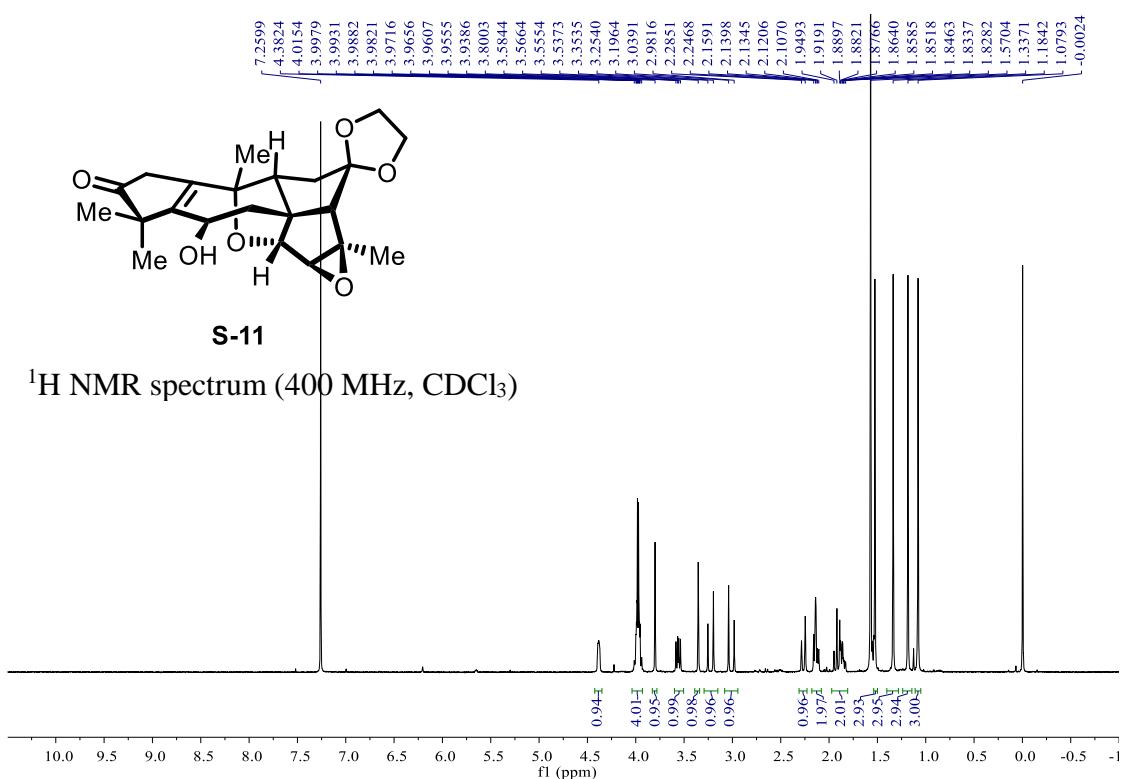


¹³C NMR spectrum (100 MHz, CDCl₃)

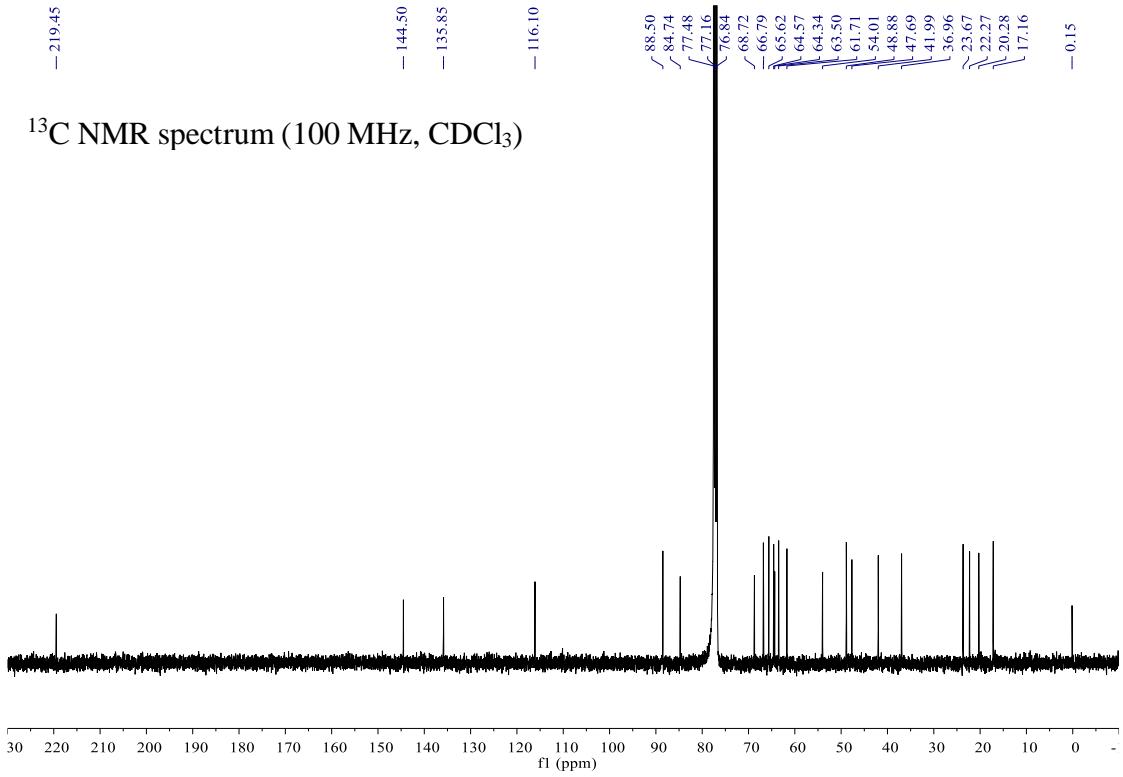


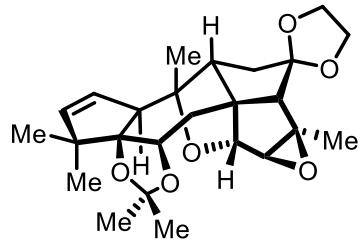


¹H NMR spectrum (400 MHz, CDCl₃)



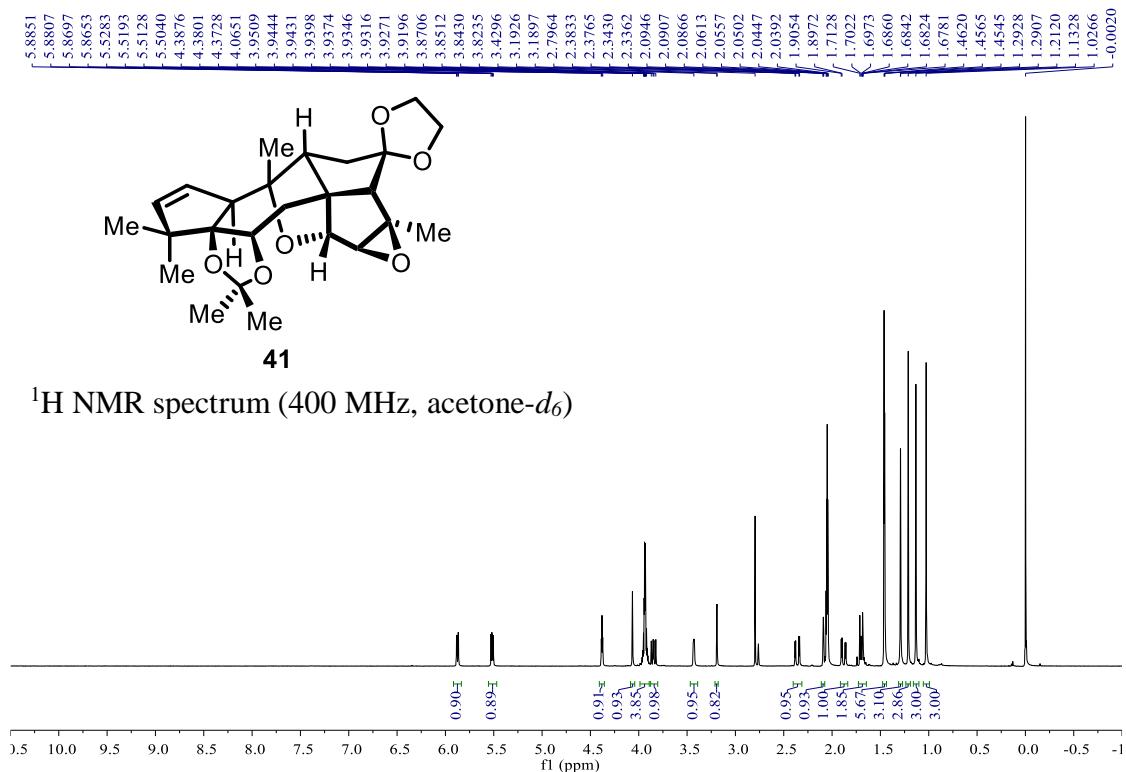
¹³C NMR spectrum (100 MHz, CDCl₃)



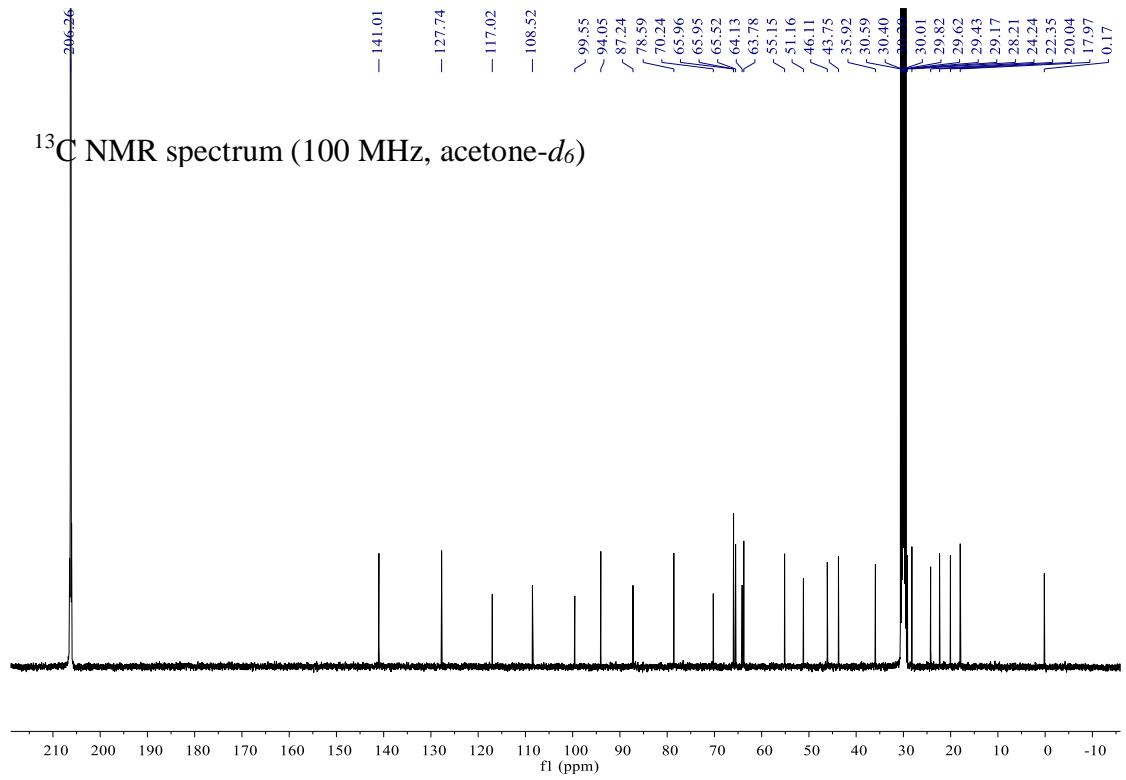


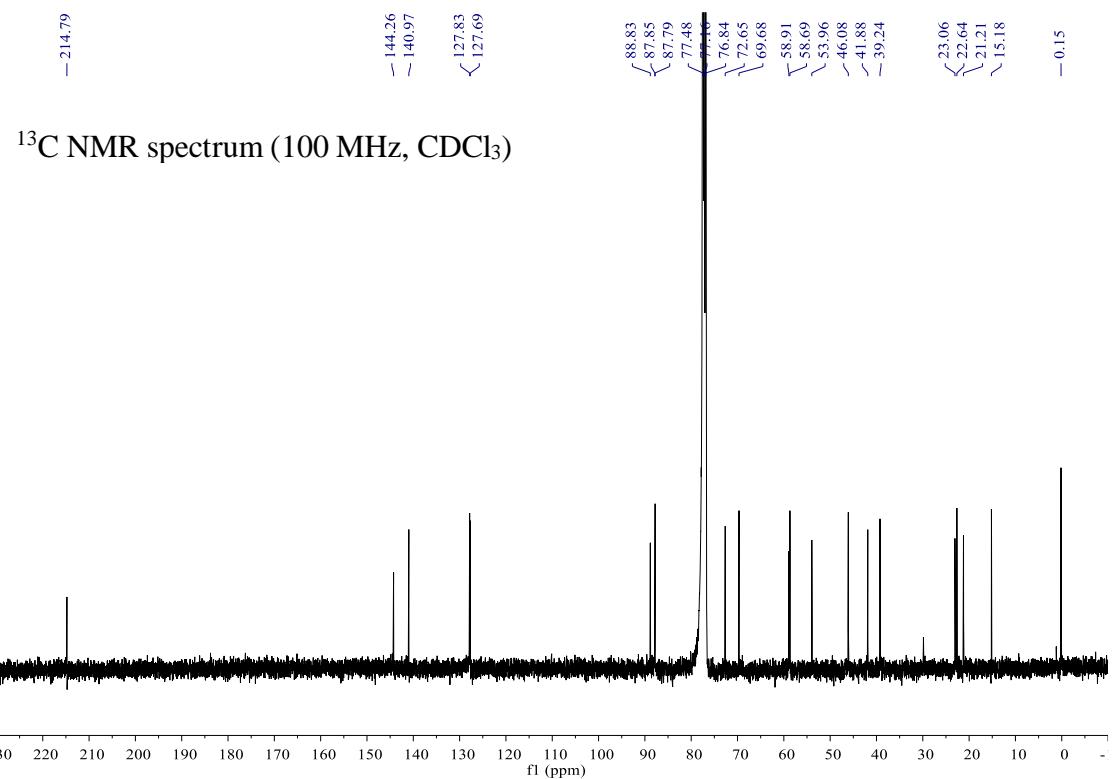
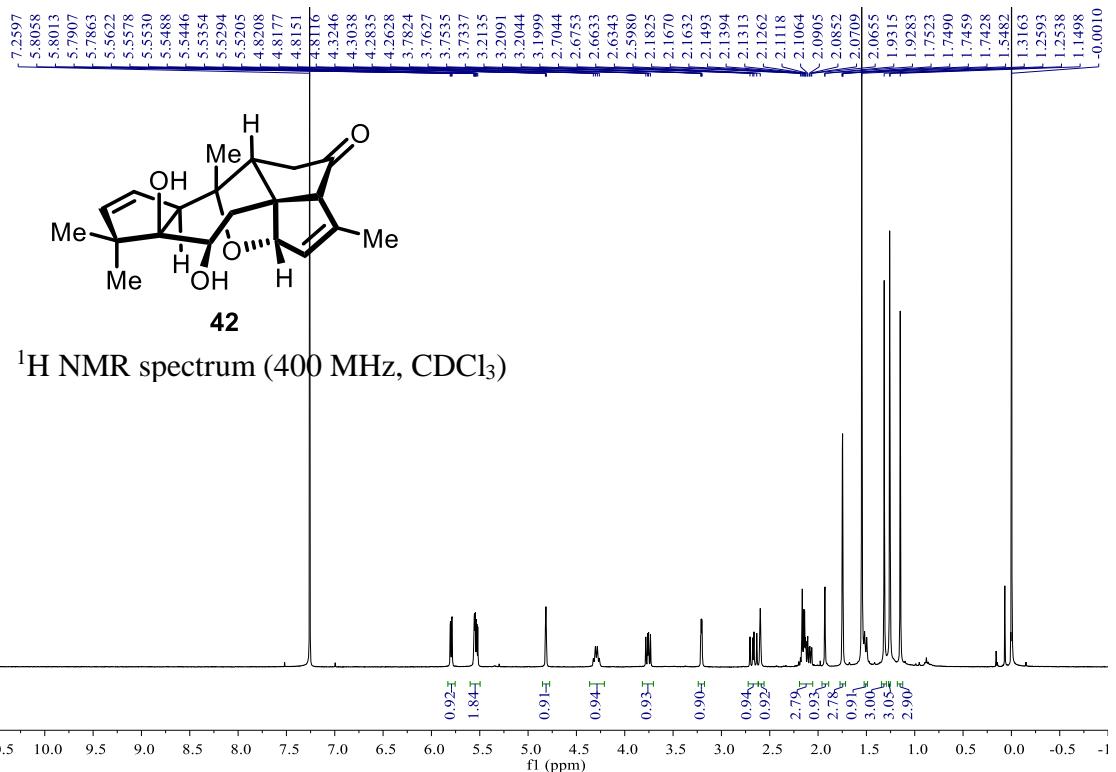
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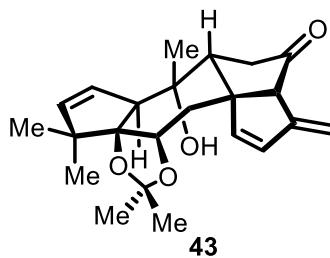
¹H NMR spectrum (400 MHz, acetone-*d*₆)



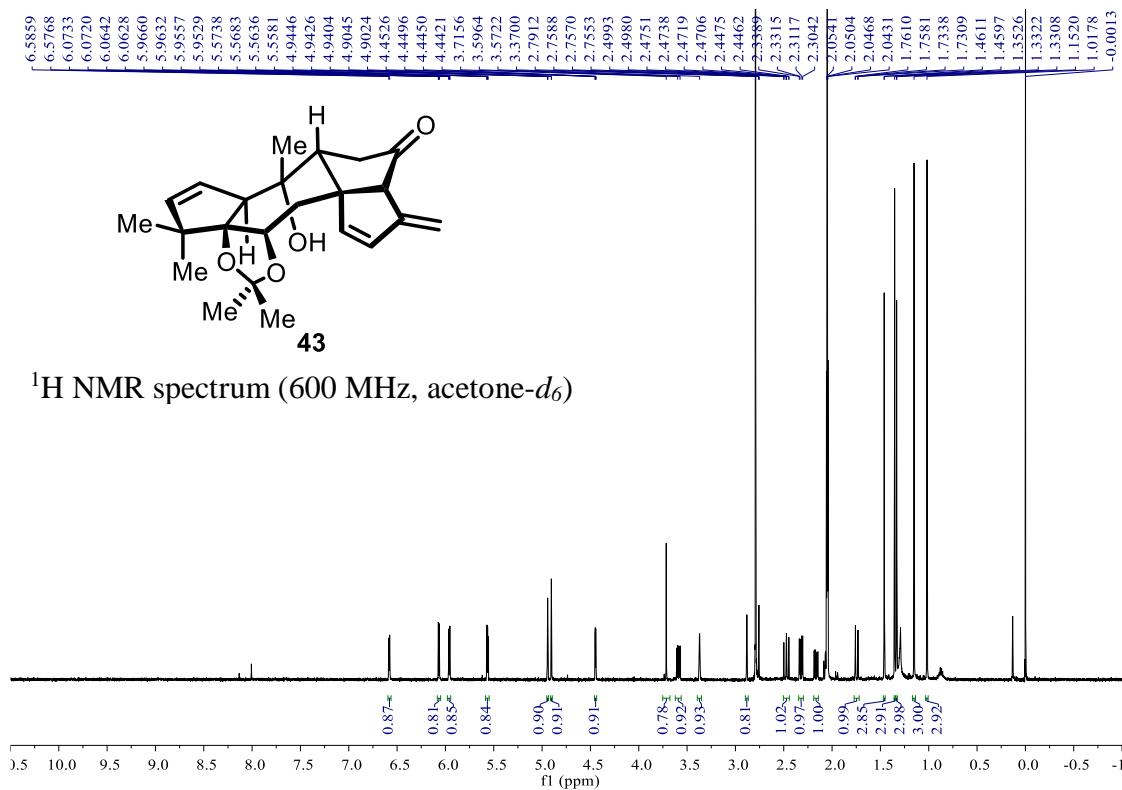
¹³C NMR spectrum (100 MHz, acetone-*d*₆)



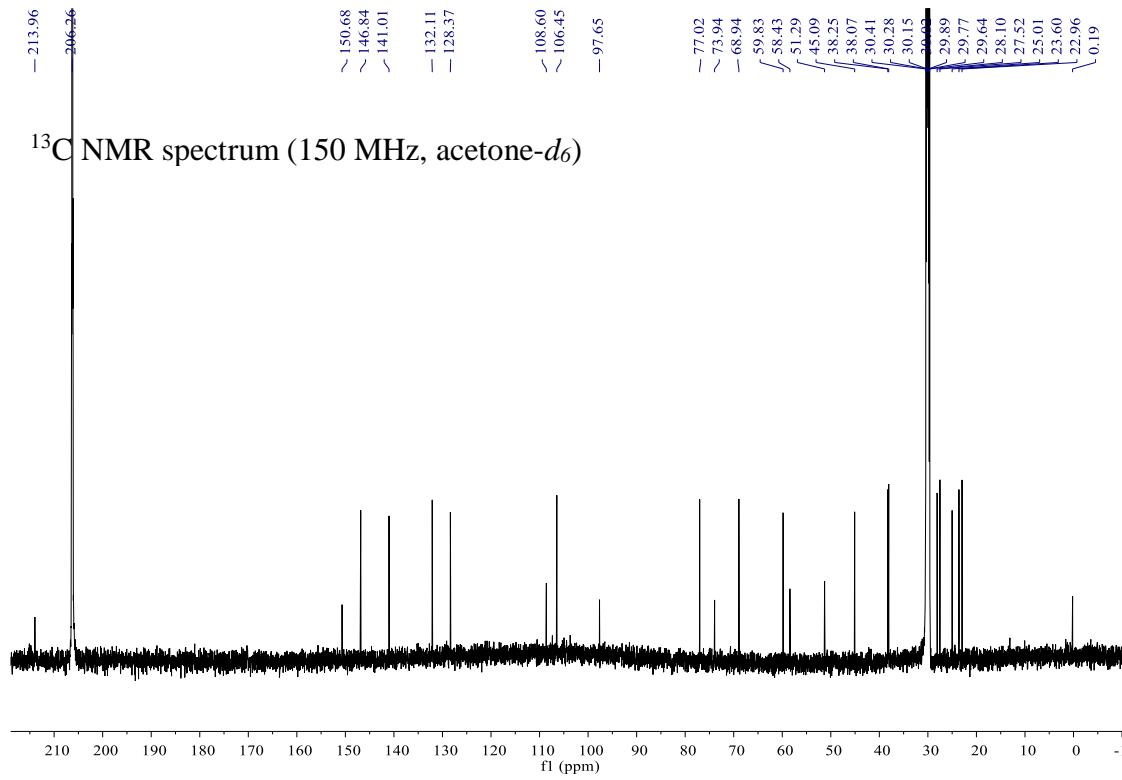


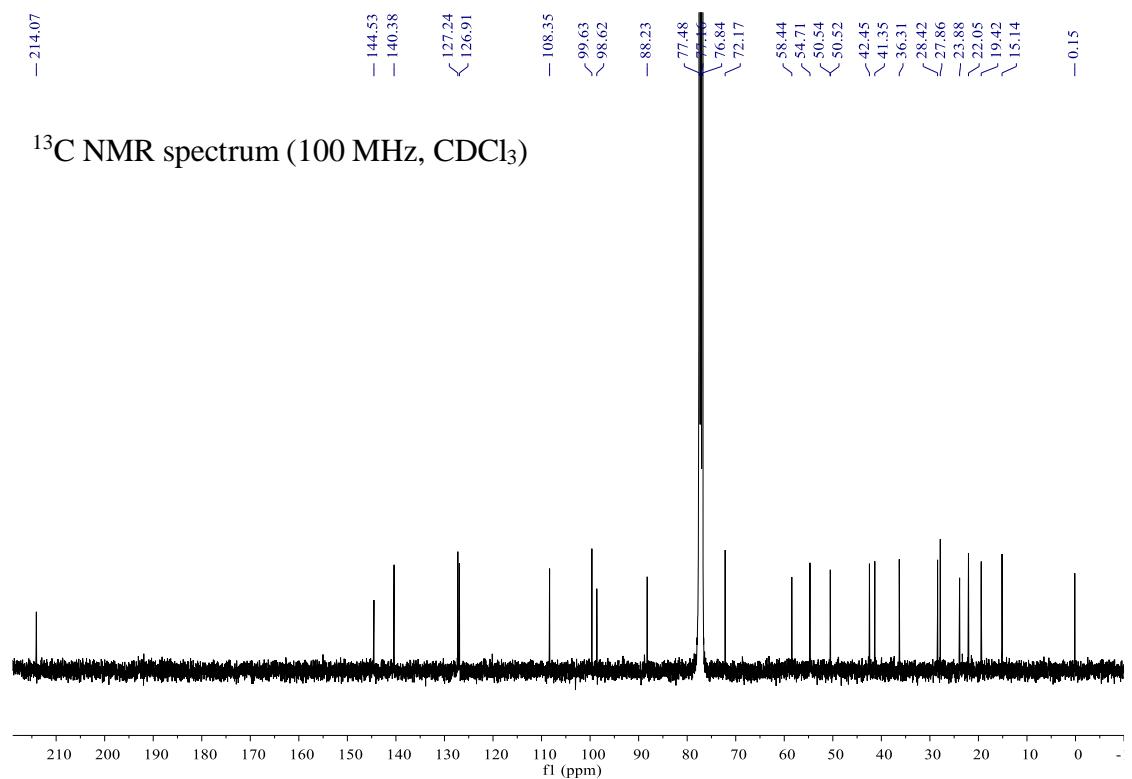
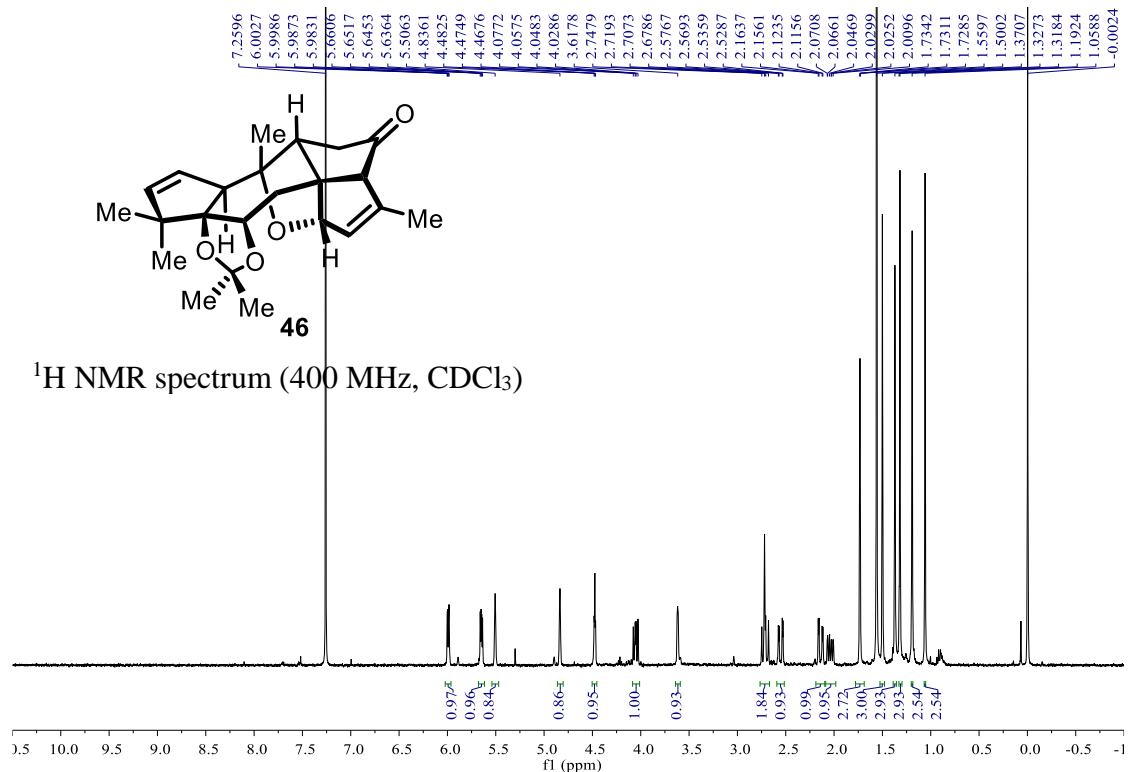


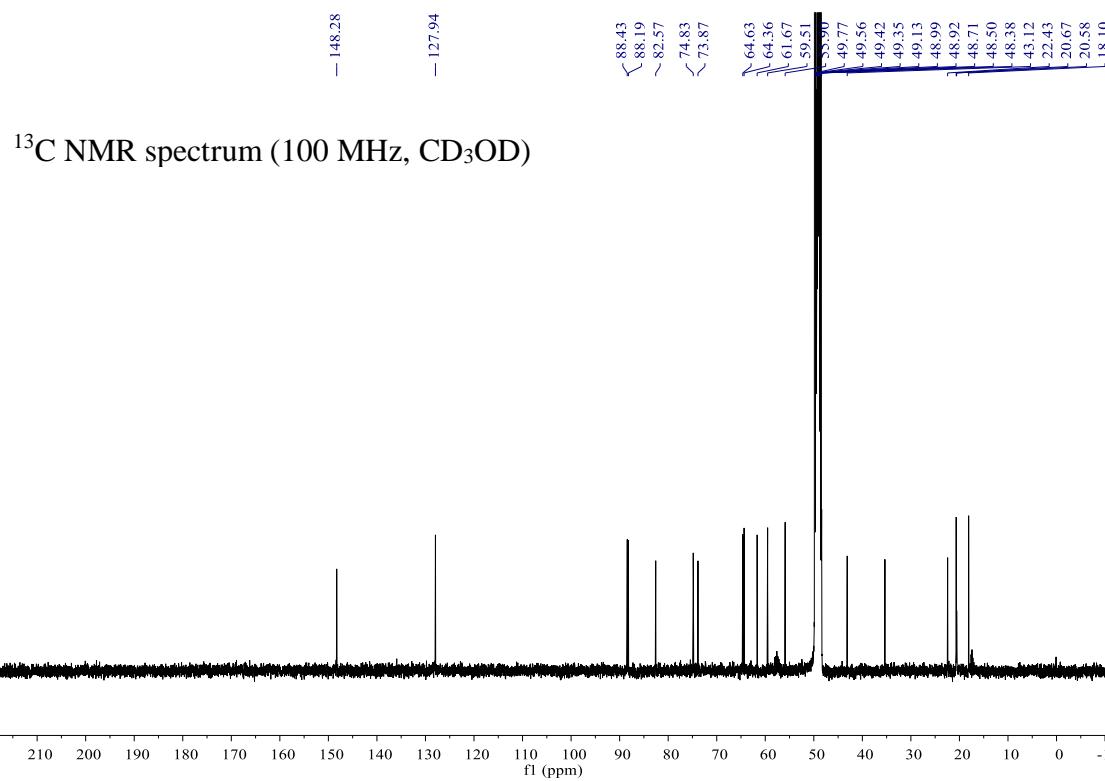
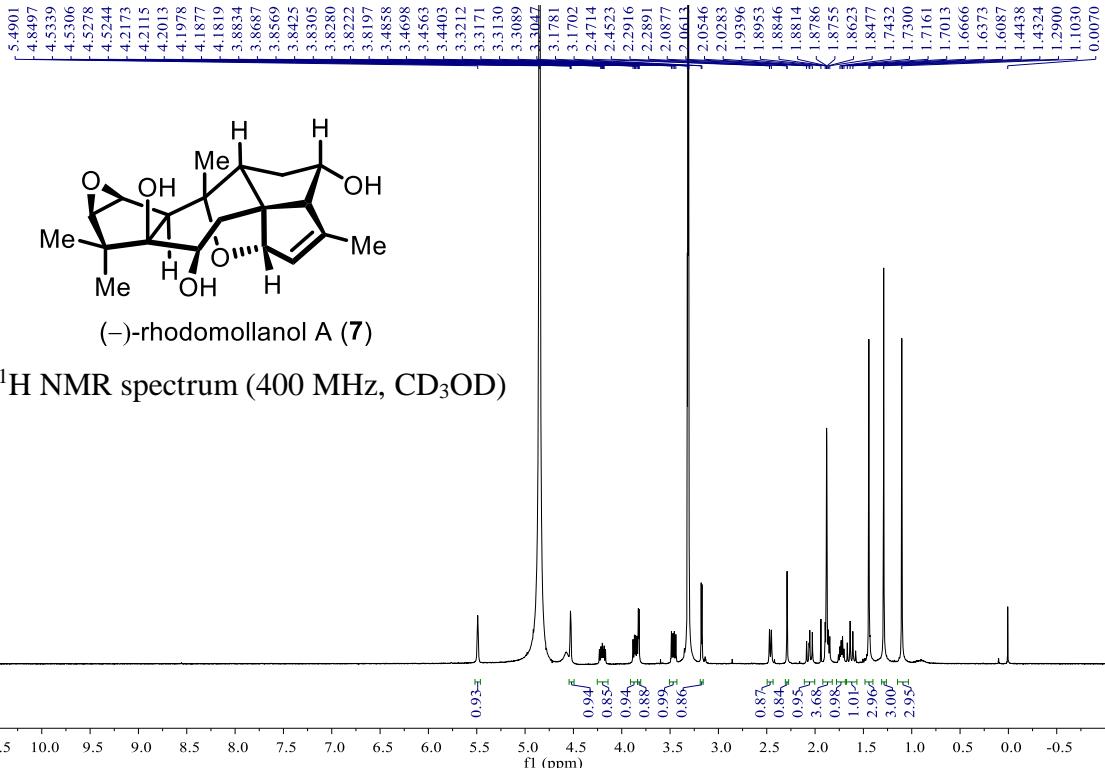
¹H NMR spectrum (600 MHz, acetone-*d*₆)



¹³C NMR spectrum (150 MHz, acetone-*d*₆)







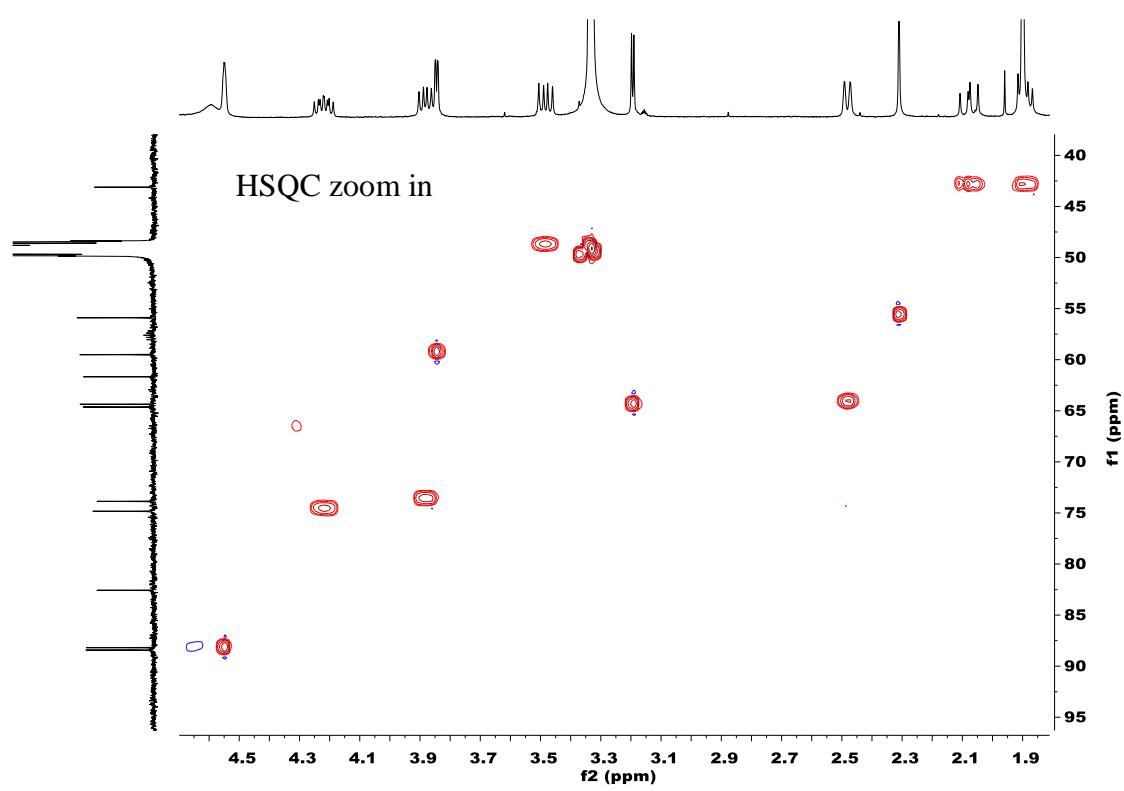
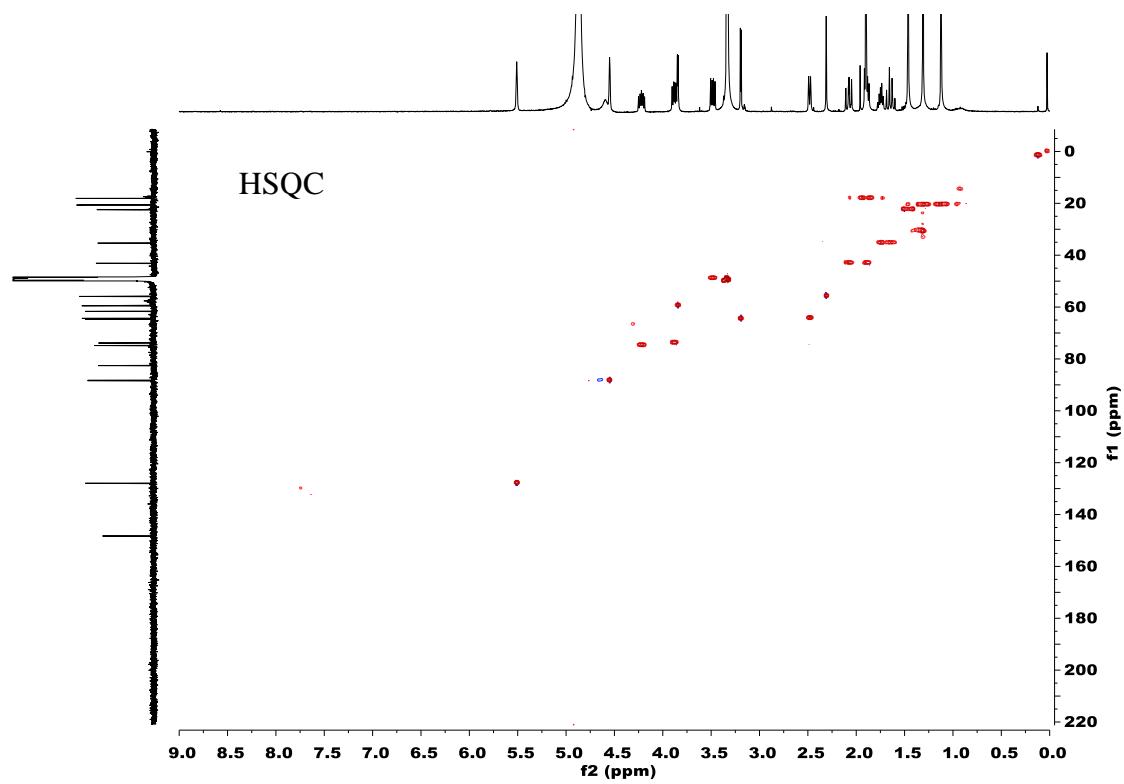


Figure S1. Comparison of ^1H NMR Spectra of Synthetic and Natural (-)-Rhodomollanol A (CD_3OD , 25 °C)

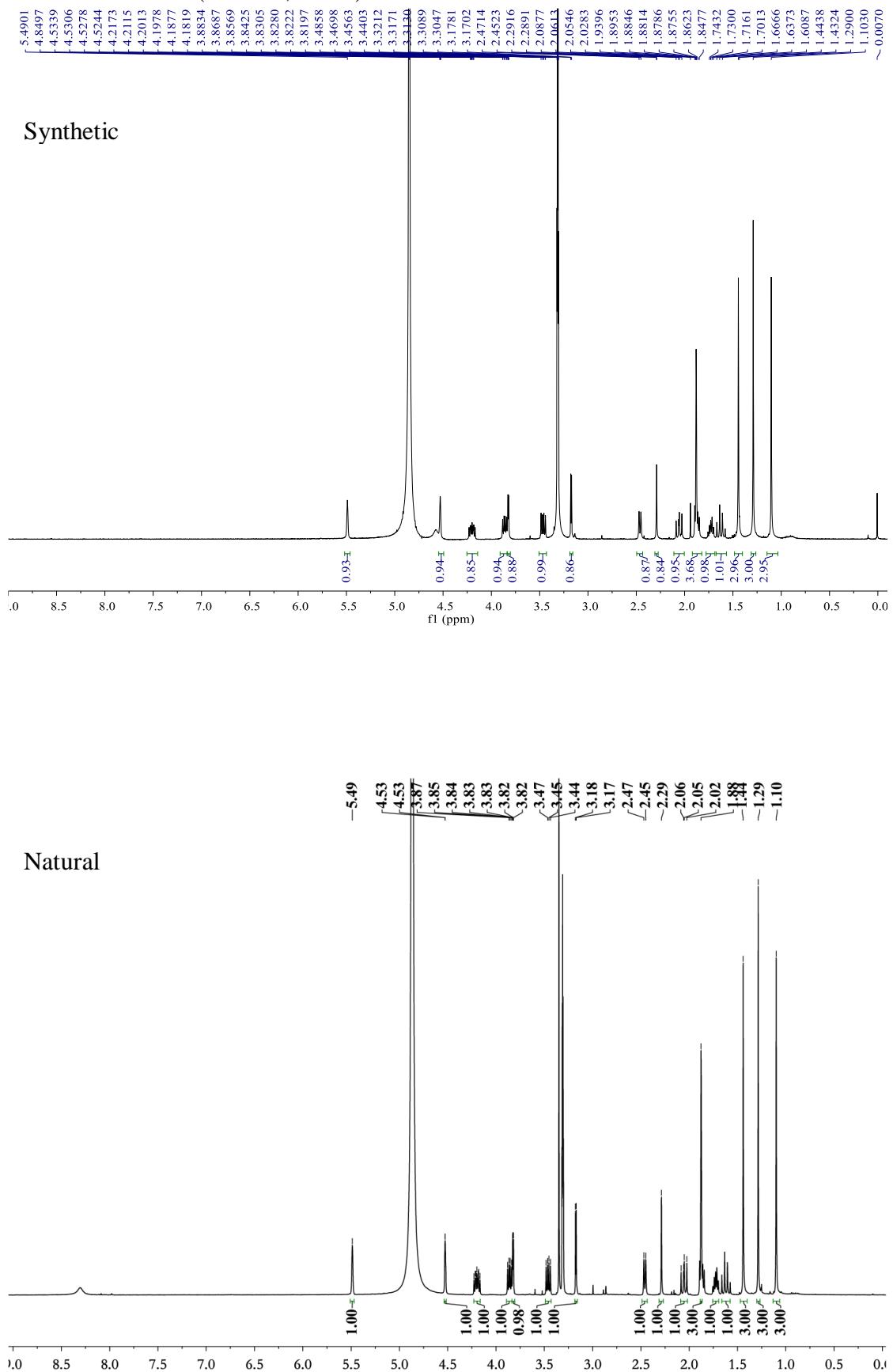
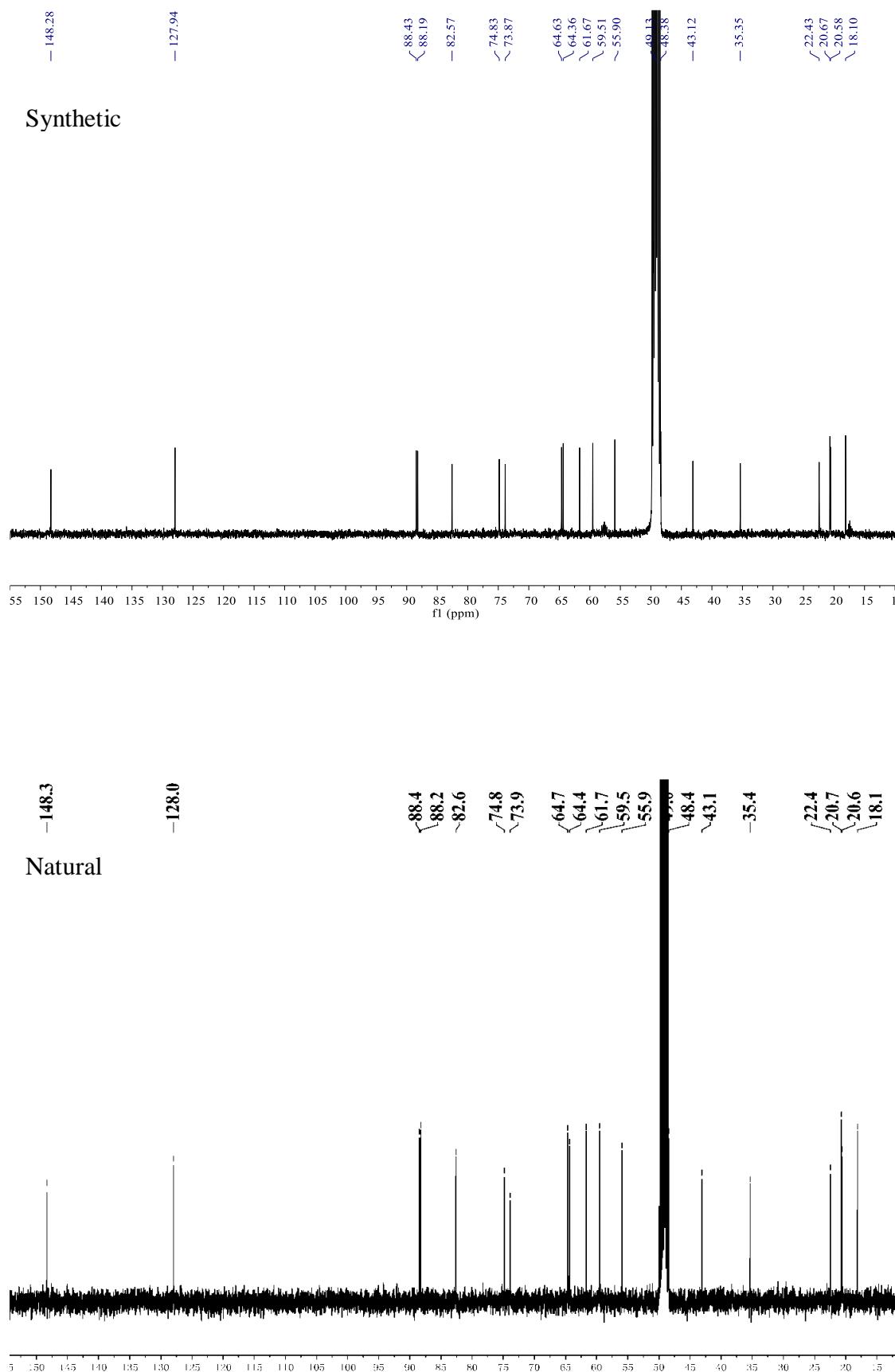


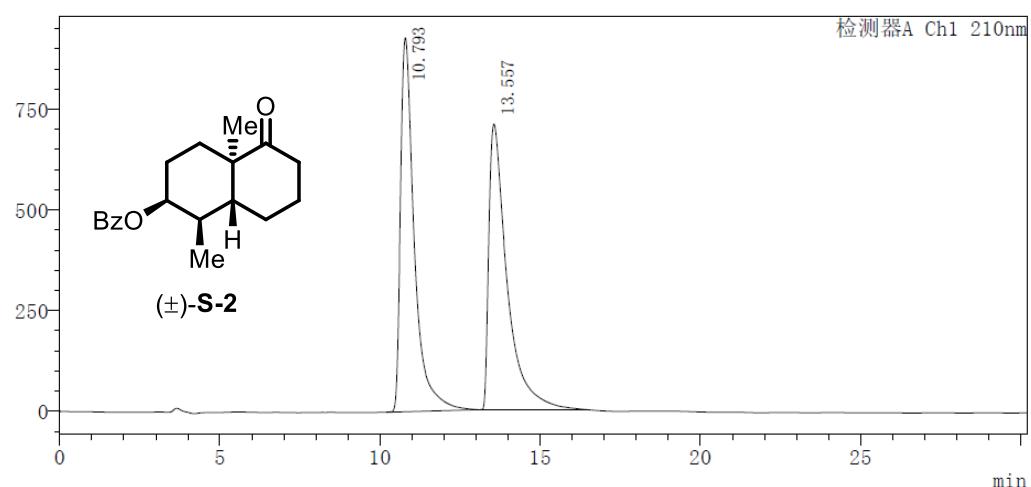
Figure S2. Comparison of ^{13}C NMR Spectra of Synthetic and Natural (-)-Rhodomollanol A (CD_3OD , 25 °C)



V) HPLC Chromatographs

Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL · min⁻¹, λ = 210 nm.

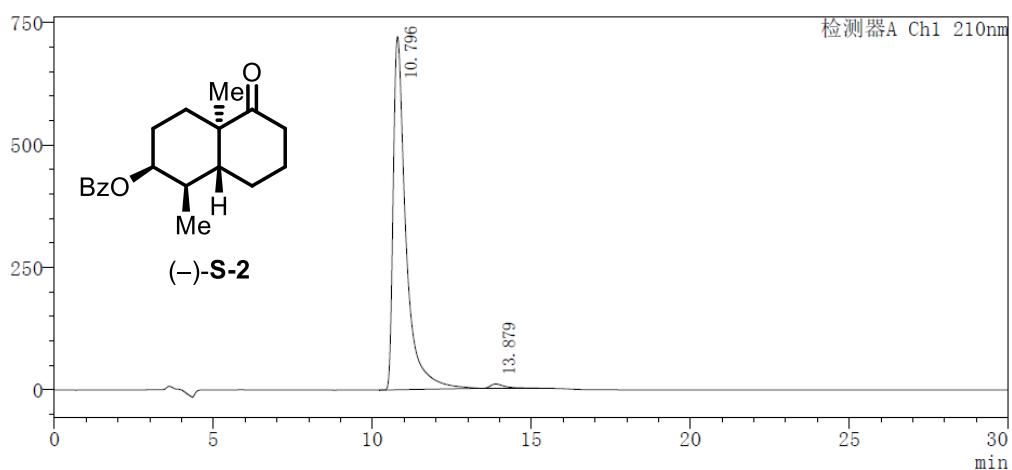
mV



检测器A Ch1 210nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.793	27848972	928332	49.793		M	
2	13.557	28080034	708858	50.207		M	
总计		55929006	1637189				

mV



检测器A Ch1 210nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.796	20134236	721025	98.543		M	
2	13.879	297625	8764	1.457		M	
总计		20431862	729789				