

Supporting Information

for

Total Synthesis of (±)-(1β,4β,4aβ,8aα)-4,8a-Dimethyl-octahydro-naphthalene-1,4a(2H)-diol

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Table of Contents

General Experimental Procedures	S2
Experimental Procedures	S3-S25
NMR spectra	S26-S79
The comparison of ¹H-NMR and ¹³C-NMR spectra between 1 and (1β,4β,4aβ,8aα)-4,8a-Dimethyl-octahydronaphthalene-1,4a(2H)-diol	S80

General Experimental Procedures.

Reactions requiring anhydrous conditions were carried out under a nitrogen atmosphere. THF were freshly distilled from sodium/benzophenone ketyl and transferred via syringe. Dichloromethane was freshly distilled from P₂O₅. Pyridine was freshly distilled over KOH. Commercially available reagents were used as received. IR spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer (film). 1D and 2D NMR spectra were collected on a Bruker AV-600 spectrometer. The solvent used for NMR spectroscopy was deuteriated dimethyl sulfoxide unless stated otherwise, using tetramethylsilane as the internal reference. Chemical shifts are given in parts per million, and *J* values are given in Hertz. HRESIMS were measured with an Agilent G6230 TOF mass spectrometer. All chromatographic manipulations used silica gel (100-200 mesh, 200-300 mesh, Qingdao Marine Chemical Ltd., Qingdao, China) as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminum. TLC plates were visualized by UV radiation at a wavelength of 254 nm or stained by exposure to an ethanolic solution of concentrated sulfuric acid and anisaldehyde, followed by charring where appropriate. The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Experimental Procedures

General Procedure I for Reduction of Enones

To a solution of an enone (1.0 mmol) and CeCl_3 (1.0 mmol) in DCM/MeOH (1:1, 10 mL) was added NaBH_4 (2.0 mmol) over 10 min in portions at $-60\text{ }^\circ\text{C}$. After stirring for 1.5 h at $-60\text{ }^\circ\text{C}$, the reaction mixture was quenched by addition of saturated NH_4Cl solution. The mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4 . Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:6) gave the products.

General Procedure II for Reduction of Enones

To a solution of an enone (1.0 mmol) in THF (10 mL) was added DABIL-H (1.5 mL of a 1.0 M solution in hexane, 1.5 mmol) at $-78\text{ }^\circ\text{C}$. After stirring for 5 min at $-78\text{ }^\circ\text{C}$, the reaction mixture was quenched with MeOH (1.0 mL). The mixture was diluted with EtOAc, washed with sat. aq. sodium potassium tartrate, and dried over anhydrous Na_2SO_4 . Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:10) gave the products.

General Procedure III for Etherification of Allylic Alcohols

A solution of an allylic alcohol (1.0 mmol) in DCM (10 mL) was treated with imidazole (3.0 mmol) and tert-butyldimethylsilyl chloride (1.5 mmol) at room temperature and the mixture was stirred overnight. The reaction mixture was diluted with DCM, washed with sat. aq. NH_4Cl solution and brine, and dried over anhydrous Na_2SO_4 . Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:50) gave the products.

General Procedure IV for Cracking of tert-Butyldimethylsilyl Ether

To a stirred solution of tert-butyldimethylsilyl ether (1.0 mmol) and AcOH (0.4 mmol) in THF (5.0 mL) was added dropwise tetra(n-butyl)ammonium fluoride (1.5 mL of a 1.0 M solution, 1.5 mmol) at $0\text{ }^\circ\text{C}$, and then the reaction solution was transferred to room temperature. After stirring overnight, the reaction mixture was diluted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4 . Filtration, concentration,

and silica gel column chromatography (EtOAc/petroleum ether = 1:5) gave the products.

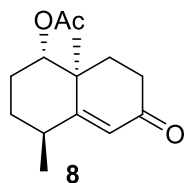
General Procedure V for Methanesulfonylation of Epoxy Alcohols

To a mixture of epoxy alcohol (1.0 mmol) and Et₃N (2.0 mmol) in DCM (5.0 mL) was added methanesulfonyl chloride (1.2 mmol) at 0 °C. After the reaction had been completed, the mixture was diluted with DCM and washed with sat. aq. NH₄Cl and brine, and dried over anhydrous Na₂SO₄. Filtration, concentration, and the products were obtained without further purification.

General Procedure VI for Hydrogenolysis of Mesylates

A solution of mesylate (1.0 mmol) in THF (8.0 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (3.0 mmol) in THF (1.0 mL) at 0 °C. Then, the reaction mixture was refluxed for 4 h and excess reagent was hydrolyzed by dropwise addition of water, followed by 2 N NaOH. The mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:8) gave the products.

(±)-(1S,4S,8aS)-4,8a-Dimethyl-6-oxo-1,2,3,4,6,7,8,8a-octahydronaphthalen-1-yl Acetate (**8**).

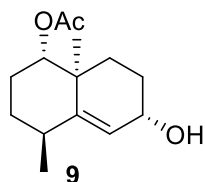


A mixture of the alcohol **7** (2.0 g, 10.29 mmol), pyridine (20 mL), acetic anhydride (7.35 mL, 77.75 mmol) and dimethylaminopyridine (126.75 mg, 0.1 mmol) was stirred for 8 h at room temperature. The pyridine was removed by distillation, the residue was dissolved in

DCM and washed with 10% HCl solution, water and brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification of the crude product on silica gel column chromatography (EtOAc/petroleum ether = 1:4) afforded the ester **8** (2.35 g, 97%) as a light yellowish oil, *R_f* = 0.43 (EtOAc/petroleum ether = 1:2); ¹H NMR (600 MHz, DMSO-*d*₆) δ 5.66 (s, 1H), 4.55 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.39 (ddd, *J* = 16.8, 13.7, 5.1 Hz, 1H), 2.21 (dt, *J* = 16.8, 4.4 Hz, 1H), 2.05 (s, 1H), 1.87 (dt, *J* = 13.6, 4.7 Hz, 2H), 1.83 – 1.77 (m, 1H), 1.77 – 1.71 (m, 1H), 1.67 (td, *J* = 13.6, 4.5 Hz, 1H), 1.24 (s, 3H), 1.13 (qd, *J* = 12.7, 3.9 Hz, 1H), 1.02

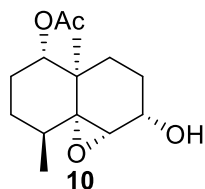
(d, $J = 6.4$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 198.4, 170.4, 170.2, 122.9, 78.6, 40.7, 34.1, 33.3, 33.1, 31.8, 26.8, 21.3, 17.9, 17.7.

(\pm)-(1S,4S,6S,8aS)-6-Hydroxy-4,8a-dimethyl-1,2,3,4,6,7,8,8a-octahydronaphthalen-1-yl Acetate (9**)**



Followed general procedure I, **8** as the material, gave the compound **9** (yield: 96%) as a colorless oil, $R_f = 0.40$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3401, 2939, 2870, 1736, 1676, 1458, 1373, 1240, 1031, 988. ^1H NMR (600 MHz, DMSO- d_6) δ 5.30 (brs, 1H), 4.69 (d, $J = 5.3$ Hz, 1H), 4.36 (dd, $J = 11.3, 5.0$ Hz, 1H), 3.98 (m, 1H), 2.17 (m, 1H), 2.01 (s, 3H), 1.79 – 1.62 (m, 4H), 1.57 (ddd, $J = 13.1, 5.3, 2.4$ Hz, 1H), 1.30 (dddd, $J = 14.4, 11.6, 9.1, 2.3$ Hz, 1H), 1.22 (td, $J = 13.3, 2.5$ Hz, 1H), 1.09 (s, 3H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.92 (qd, $J = 12.8, 4.4$ Hz, 1H). ^{13}C NMR (150 MHz, DMSO- d_6) δ 170.4, 144.8, 126.0, 80.2, 66.4, 39.6, 34.0, 33.2, 31.7, 28.2, 27.3, 21.4, 19.1, 18.5; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 261.1467, found 261.1466.

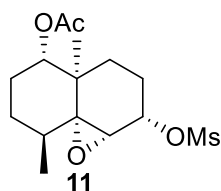
(\pm)-(1aS,2S,4aR,5S,8S,8aR)-2-Hydroxy-4a,8-dimethyloctahydro-3H-naphtho-[1,8a-b]oxiren-5-yl Acetate (10**)**



75% *m*-Chloroperbenzoic acid (725 mg, 3.15 mmol) was added in portions to a solution of **9** (500 mg, 2.10 mmol) in DCM (20 mL) at 0 °C. The resultant mixture was stirred for 12 h at 0 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:5) to give **10** (512 mg, 96%) as a colorless oil, $R_f = 0.32$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3433, 2940, 2877, 1735, 1461, 1373, 1240, 1032. ^1H NMR (600 MHz, DMSO- d_6) δ 4.76 (dd, $J = 11.2, 4.9$ Hz, 1H), 4.65 (d, $J = 5.9$ Hz, 1H), 3.91 (m, 1H), 3.16 (d, $J = 3.6$ Hz, 1H), 2.06 – 2.01 (m, 1H), 2.00 (s, 3H), 1.74 – 1.59 (m, 3H), 1.50 (dddd, $J = 13.9, 11.9, 5.8, 3.6$ Hz, 1H), 1.38 (ddd, $J = 13.7, 11.8, 3.2$ Hz, 1H), 1.20 – 1.26 (m, 1H), 1.09 (qd, $J = 12.8, 4.0$ Hz, 1H), 1.02 (s, 3H), 1.01 – 0.97 (m, 1H), 0.64 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 170.3, 74.5, 66.7, 63.6, 57.8, 38.6, 30.7, 29.6, 28.4,

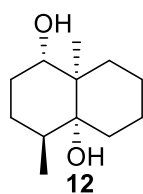
26.8, 25.8, 21.3, 18.1, 14.4; **HRMS** (ESI) m/z calcd for $C_{14}H_{23}O_4$ $[M + H]^+$ 255.1596, found 255.1585.

(±)-(1*S*,2*S*,4*aR*,5*S*,8*S*,8*aR*)-4*a*,8-Dimethyl-2-((methylsulfonyl)oxy)octahydro-3H-naphtho[1,8*a-b*]oxiren-5-yl Acetate (11**)**



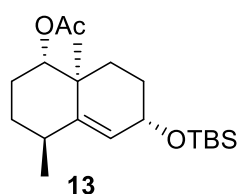
Followed general procedure V, compound **10** as the material, gave the compound **11** (yield: quant.) as a colorless oil, R_f = 0.38 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/ cm^{-1} 2942, 2879, 1732, 1452, 1353, 1244, 1173, 1031, 933, 894. **¹H NMR** (600 MHz, DMSO- d_6) δ 5.13 (dt, J = 6.4, 3.5 Hz, 1H), 4.83 (dd, J = 11.1, 4.8 Hz, 1H), 3.36 (d, J = 3.9 Hz, 1H), 3.22 (s, 3H), 2.06 – 2.12 (m, 1H), 2.02 (s, 3H), 1.80 (dddd, J = 15.5, 12.6, 5.9, 3.7 Hz, 1H), 1.64 – 1.74 (m, 3H), 1.54 (ddt, J = 15.1, 6.2, 3.3 Hz, 1H), 1.34 (td, J = 13.0, 3.4 Hz, 1H), 1.11 – 1.18 (m, 2H), 1.05 (s, 3H), 0.65 (d, J = 6.6 Hz, 3H). **¹³C NMR** (150 MHz, DMSO- d_6) δ 170.4, 76.2, 73.4, 67.1, 54.8, 38.5, 38.3, 30.4, 29.3, 27.1, 26.8, 23.4, 21.3, 18.2, 14.2; **HRMS** (ESI) m/z calcd for $C_{15}H_{24}O_6SNa$ $[M + Na]^+$ 355.1191, found 355.1194.

(±)-(1*S*,4*S*,4*aR*,8*aR*)-4,8*a*-Dimethyloctahydronaphthalene-1,4*a*(2H)-diol (12**)**



Followed general procedure VI, compound **11** or **50** as the material, gave the compound **12** (corresponding yield: 87% and 84%) as a colorless oil, R_f = 0.28 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/ cm^{-1} 3439, 2937, 2865, 1451, 1064, 1021. **¹H NMR** (600 MHz, DMSO- d_6) δ 4.18 (d, J = 5.2 Hz, 1H), 3.75 (dt, J = 11.5, 4.8 Hz, 1H), 3.70 (s, 1H), 1.70 – 1.74 (m, 1H), 1.60 – 1.49 (m, 3H), 1.47 – 1.34 (m, 5H), 1.34 – 1.21 (m, 3H), 1.05 (qd, J = 13.4, 3.9 Hz, 1H), 0.74 (d, J = 7.1 Hz, 3H), 0.73 (s, 3H); **¹³C NMR** (150 MHz, DMSO- d_6) δ 73.6, 67.6, 43.6, 36.4, 30.7, 30.6, 29.0, 26.1, 21.3, 20.8, 15.8, 15.4; **HRMS** (ESI) m/z calcd for $C_{12}H_{22}O_2Na$ $[M + Na]^+$ 221.1517, found 221.1510.

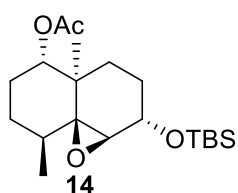
(±)-(1*S*,4*S*,6*S*,8*aS*)-6-((tert-Butyldimethylsilyl)oxy)-4,8*a*-dimethyl-1,2,3,4,6,7,8,8*a*-octahydronaphthalen-1-yl Acetate (13**)**



Followed general procedure III, compound **9** as the material, gave the compound **13** (yield: 95%) as a colorless oil, R_f = 0.55 (EtOAc/petroleum ether = 1:10); **IR** ν_{max} (thin film)/ cm^{-1} 2931,

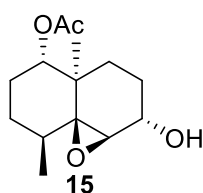
2856, 1739, 1463, 1373, 1240, 1088, 1030, 836. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 5.18 (brs, 1H), 4.32 (dd, *J* = 11.3, 5.0 Hz, 1H), 4.16 (ddd, *J* = 9.2, 4.6, 2.0 Hz, 1H), 2.13 (m, 1H), 1.96 (s, 3H), 1.78 – 1.59 (m, 5H), 1.58 – 1.49 (m, 1H), 1.41 – 1.27 (m, 1H), 1.22 (m, 1H), 1.04 (s, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.82 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 170.4, 145.7, 125.1, 80.1, 68.5, 33.7, 33.1, 31.6, 28.5, 27.2, 26.3 (3×C), 21.4, 19.0, 18.4, 18.3, -3.9, -4.1; **HRMS** (ESI): *m/z* calcd for C₂₀H₃₆O₃SiNa [M + Na]⁺ 375.2331, found 375.2317.

(±)-(1aR,2S,4aR,5S,8S,8aS)-2-((tert-Butyldimethylsilyl)oxy)-4a,8-dimethylocta-hydro-3H-naphtho[1,8a-b]oxiren-5-yl Acetate (14)



75% *m*-Chloroperbenzoic acid (490 mg, 3.15 mmol) was added in portions to a solution of **13** (500 mg, 1.42 mmol) in DCM (20 mL) at -30 °C. The resultant mixture was stirred for 15 h at -30 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and brine, dried with anhydrous Na₂SO₄ and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:50) to give **14** (491 mg, 94%) as a colorless oil, *R_f* = 0.48 (EtOAc/petroleum ether = 1:10); **IR** ν_{max} (thin film)/cm⁻¹ 2952, 2859, 1741, 1465, 1366, 1240, 1092, 838. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 4.53 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.82 (dd, *J* = 9.2, 7.7 Hz, 1H), 2.81 (s, 1H), 2.04 – 2.10 (m, 1H), 1.92 (s, 3H), 1.74 – 1.59 (m, 3H), 1.52 (dt, *J* = 13.4, 3.7 Hz, 1H), 1.23 – 1.08 (m, 2H), 1.07 (s, 3H), 1.05 (m, 2H), 0.81 (s, 9H), 0.52 (d, *J* = 6.6 Hz, 3H), 0.02 (s, 3H), 0.00 (s, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 170.4, 77.7, 67.1, 66.8, 60.0, 38.3, 29.7, 28.6, 27.9, 27.0, 26.8, 26.2 (3×C), 21.3, 18.3, 16.6, 14.1, -4.2, -4.5; **HRMS** (ESI) *m/z* calcd for C₂₀H₃₇O₄Si [M + H]⁺ 369.2461, found 369.2481.

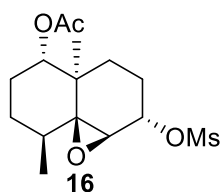
(±)-(1aR,2S,4aR,5S,8S,8aS)-2-Hydroxy-4a,8-dimethyloctahydro-3H-naphtho-[1,8a-b]oxiren-5-yl Acetate (15)



Followed general procedure IV, compound **14** as the material, gave the compound **15** (yield: 86%) as a colorless oil, *R_f* = 0.31 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/cm⁻¹ 3442, 2943, 2877, 1737, 1461, 1374, 1241, 1029, 989. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 5.09 (d, *J* = 5.4 Hz, 1H), 4.60 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.69 (td, *J* = 8.3,

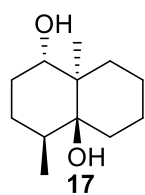
5.4 Hz, 1H), 2.92 (s, 1H), 2.08 – 2.14 (m, 1H), 1.99 (s, 3H), 1.81 – 1.73 (m, 1H), 1.73 – 1.65 (m, 2H), 1.58 (dq, $J = 13.4, 3.9$ Hz, 1H), 1.25 – 1.16 (m, 2H), 1.13 (s, 3H), 1.13 – 1.06 (m, 2H), 0.59 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 170.5, 77.7, 67.1, 64.6, 60.2, 38.4, 29.8, 28.7, 28.1, 27.0, 26.1, 21.3, 16.5, 14.1; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{23}\text{O}_4$ $[\text{M} + \text{H}]^+$ 255.1596, found 255.1603.

(±)-(1aR,2S,4aR,5S,8S,8aS)-4a,8-Dimethyl-2-((methylsulfonyl)oxy)octahydro-3H-naphtho[1,8a-b]oxiren-5-yl Acetate (16)



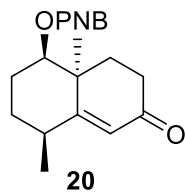
Followed general procedure V, compound **15** as the material, gave the compound **16** (yield: quant.) as a colorless oil, $R_f = 0.37$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 2942, 2879, 1732, 1452, 1352, 1244, 1173, 1031, 933, 894. ^1H NMR (600 MHz, DMSO- d_6) δ 4.82 (t, $J = 8.8$ Hz, 1H), 4.60 (dd, $J = 11.5, 5.1$ Hz, 1H), 3.28 (s, 3H), 3.17 (s, 1H), 2.17 (ddd, $J = 12.7, 6.5, 4.2$ Hz, 1H), 2.01 (s, 3H), 1.96 (ddd, $J = 12.3, 8.3, 3.9$ Hz, 1H), 1.83 – 1.68 (m, 2H), 1.61 (dq, $J = 13.4, 3.9$ Hz, 1H), 1.48 (tdd, $J = 13.7, 9.5, 4.3$ Hz, 1H), 1.26 – 1.17 (m, 3H), 1.17 (s, 3H), 0.62 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 170.5, 77.4, 74.5, 67.3, 56.9, 38.1, 37.9, 29.7, 28.5, 27.2, 26.8, 23.3, 21.3, 16.3, 14.0; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{24}\text{O}_6\text{SNa}$ $[\text{M} + \text{Na}]^+$ 355.1191, found 355.1207.

(±)-(1S,4S,4aS,8aR)-4,8a-Dimethyloctahydronaphthalene-1,4a(2H)-diol (17).



Followed general procedure VI, compound **16** or **41** as the material, gave the compound **17** (corresponding yield: 90% and 85%) as a white solid, $R_f = 0.26$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3456, 2940, 2868, 1458, 1379, 1334, 1180, 1014. ^1H NMR (600 MHz, DMSO- d_6) δ 3.93 (d, $J = 5.4$ Hz, 1H), 3.60 – 3.56 (m, 1H), 3.40 (s, 1H), 1.68 – 1.59 (m, 1H), 1.59 – 1.49 (m, 2H), 1.48 – 1.41 (m, 3H), 1.41 – 1.33 (m, 5H), 1.28 (dd, $J = 13.4, 4.4$ Hz, 1H), 1.26 – 1.20 (m, 1H), 0.81 (s, 3H), 0.68 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 74.1, 71.3, 42.2, 34.0, 30.8, 30.4, 30.3, 29.0, 21.0, 20.7, 15.1, 14.0; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 221.1517, found 221.1521.

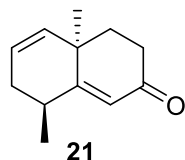
(±)-(1R,4S,8aS)-4,8a-Dimethyl-6-oxo-1,2,3,4,6,7,8,8a-octahydronaphthalen-1-yl 4-Nitrobenzoate (20)



Diethyl azodicarboxylate (1.09 g, 6.2 mmol) were added dropwise to a -10 °C solution of **7** (1.0 g, 5.2 mmol), *p*-nitrobenzoic acid (1.04 g, 6.2 mmol), Ph₃P (2.73 g, 10.4 mol) and 3A molecular sieve in dry THF (20 mL) under N₂ atmosphere. Then the mixture was stirred for 15 h at r.t. and solvent evaporated under reduced pressure.

Redissolved with dichloromethane, Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:15) gave the product **20** (1.02 g, 58%) as a light yellow solid, *R_f* = 0.40 (EtOAc/petroleum ether = 1:2); **IR** *v*_{max} (thin film)/cm⁻¹ 2941, 2871, 1721, 1670, 1608, 1528, 1342, 1271, 1099, 974, 873, 720. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 5.81 (brs, 1H), 5.08 (brs, 1H), 2.63 (dt, *J* = 13.1, 6.7 Hz, 1H), 2.56 – 2.52 (m, 1H), 2.28 – 2.15 (m, 2H), 2.09 (td, *J* = 14.0, 4.7 Hz, 1H), 1.88 (dq, *J* = 14.6, 3.3 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.58 (ddd, *J* = 13.4, 5.2, 3.2 Hz, 1H), 1.50 (qd, *J* = 13.2, 4.0 Hz, 1H), 1.39 (s, 3H), 1.11 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 198.4, 170.1, 163.8, 150.8, 135.5, 131.0 (2×C), 124.6 (2×C), 123.7, 79.6, 40.5, 33.7, 32.9, 31.3, 29.9, 25.9, 22.4, 18.3; **HRMS** (ESI) *m/z* calcd for C₁₉H₂₂O₅N [M + H]⁺ 344.1498, found 344.1489.

(±)-(4aR,8S)-4a,8-Dimethyl-4,4a,7,8-tetrahydronaphthalen-2(3H)-one (21)

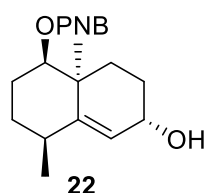


To a solution of 200 mg (0.91 mmol) of cyclopropyl ketal **27** in 25 mL of dichloromethane cooled to 0 °C was added dropwisely, 0.65 mL (0.65 mmol) of 70% perchloric acid over 10 min. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 5 h.

Excess perchloric acid was separated from the reaction mixture followed by evaporation of dichloromethane. The residue was redissolved with ethyl acetate and was washed with 10% aqueous sodium thiosulfate, a saturated solution of sodium bicarbonate, and brine. The organic layers were dried over anhydrous Na₂SO₄. Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:12) gave the **21** as a colorless oil with a 85% yield, *R_f* = 0.51 (EtOAc/petroleum ether = 1:3); **IR** *v*_{max} (thin film)/cm⁻¹ 2952, 2926, 1665, 1618, 1456, 1246. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 5.66 (s, 1H), 5.63 (ddd, *J* = 9.7, 5.6, 2.0 Hz, 1H), 5.44 (dd, *J* = 9.7, 2.7 Hz, 1H), 2.64 (m, 1H), 2.56 (ddd, *J* = 17.5, 14.8, 5.3 Hz, 1H), 2.35 (dt, *J* = 17.2, 5.5 Hz, 1H), 2.24 (ddd, *J* = 17.5, 4.6, 2.3 Hz, 1H), 1.85 – 1.69

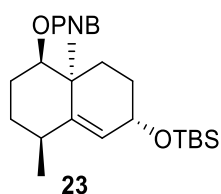
(m, 3H), 1.26 (s, 3H), 1.07 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 198.6, 173.0, 136.2, 124.1, 120.7, 37.9, 35.9, 35.8, 33.8, 31.9, 25.2, 17.2; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{17}\text{O}$ $[\text{M} + \text{H}]^+$ 177.1279, found 177.1269.

(±)-(1R,4S,6S,8aS)-6-Hydroxy-4,8a-dimethyl-1,2,3,4,6,7,8,8a-octahydronaphthalen-1-yl 4-Nitrobenzoate (22)



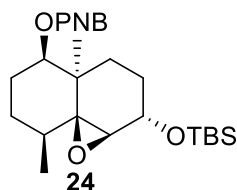
Followed general procedure I, compound **20** as the material, gave the compound **22** (yield: 95%) as a white solid, $R_f = 0.37$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3339, 2936, 2867, 1720, 1528, 1343, 1167, 1074, 720. ^1H NMR (600 MHz, DMSO- d_6) δ 8.38 (d, $J = 8.8$ Hz, 2H), 8.11 (d, $J = 8.8$ Hz, 2H), 5.43 (brs, 1H), 4.90 (brs, 1H), 4.70 (d, $J = 5.4$ Hz, 1H), 4.04 (m, 1H), 2.34 (m, 1H), 2.09 (brt, $J = 14.2$ Hz, 1H), 1.80 (brd, $J = 14.7$ Hz, 1H), 1.77 – 1.70 (m, 1H), 1.69 – 1.60 (m, 2H), 1.44 – 1.36 (m, 1H), 1.32 – 1.24 (m, 2H), 1.23 (s, 3H), 1.03 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 163.9, 150.8, 143.1, 135.9, 130.9 (2×C), 126.8, 124.6 (2×C), 79.6, 66.8, 39.3, 31.7, 31.1, 31.0, 28.9, 26.2, 24.3, 19.0; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5\text{N}$ $[\text{M} + \text{H}]^+$ 346.1654, found 346.1626.

(±)-(1R,4S,6S,8aS)-6-((tert-Butyldimethylsilyl)oxy)-4,8a-dimethyl-1,2,3,4,6,7,8,8a-octahydronaphthalen-1-yl 4-Nitrobenzoate (23)



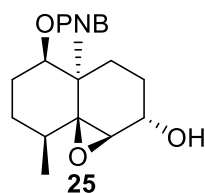
Followed general procedure III, compound **22** as the material, gave the compound **23** (yield: 95%) as a white solid, $R_f = 0.51$ (EtOAc/petroleum ether = 1:10); IR ν_{max} (thin film)/ cm^{-1} 2951, 2858, 1723, 1530, 1344, 1274, 1099, 886, 859, 777, 720. ^1H NMR (600 MHz, DMSO- d_6) δ 8.32 (d, $J = 8.8$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 5.31 (brs, 1H), 4.86 (brs, 1H), 4.19 (m, 1H), 2.31 (m, 1H), 2.05 (brt, $J = 14.2$ Hz, 1H), 1.78 – 1.65 (m, 2H), 1.65 – 1.53 (m, 2H), 1.40 (brq, $J = 13.4$ Hz, 1H), 1.32 – 1.21 (m, 2H), 1.18 (s, 3H), 0.97 (d, $J = 6.4$ Hz, 3H), 0.82 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 163.9, 150.8, 144.1, 135.9, 130.9 (2×C), 125.7, 124.6 (2×C), 79.6, 68.9, 39.2, 31.7, 31.0, 30.9, 29.2, 26.3 (3×C), 26.2, 24.4, 18.9, 18.3, -3.8, -4.0; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{37}\text{NO}_5\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 482.2339, found 482.2342.

(±)-(1aR,2S,4aR,5R,8S,8aS)-2-((tert-Butyldimethylsilyl)oxy)-4a,8-dimethylocta-hydro-3H-naphtho[1,8a-b]oxiren-5-yl 4-Nitrobenzoate (24)



75% *m*-Chloroperbenzoic acid (254 mg, 1.64 mmol) was added in portions to a solution of **23** (500 mg, 1.09 mmol) in DCM (20 mL) at -30 °C. The resultant mixture was stirred for 18 h at -30 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and brine, dried with anhydrous Na₂SO₄ and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:50) to give **24** (476 mg, 92%) as a white solid, *R_f* = 0.38 (EtOAc/petroleum ether = 1:10); **IR** *v*_{max} (thin film)/cm⁻¹ 2933, 2859, 1723, 1530, 1454, 1346, 1275, 1099, 838, 778, 720. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H), 4.91 (brs, 1H), 3.87 (t, *J* = 8.5 Hz, 1H), 2.77 (s, 1H), 2.23 (m, 1H), 2.14 (m, 1H), 1.77 – 1.64 (m, 2H), 1.57 (td, *J* = 13.9, 3.3 Hz, 1H), 1.52 – 1.44 (m, 2H), 1.35 – 1.25 (m, 1H), 1.20 (s, 3H), 0.82 (s, 9H), 0.75 (dt, *J* = 13.2, 3.7 Hz, 1H), 0.62 (d, *J* = 6.6 Hz, 3H), 0.02 (s, 3H), 0.00 (s, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 164.0, 150.8, 135.9, 131.1 (2×C), 124.5 (2×C), 78.1, 66.7, 65.5, 57.7, 37.9, 29.1, 27.8, 26.9, 26.5, 26.2 (3×C), 25.8, 21.0, 18.3, 14.3, -4.2, -4.5; **HRMS** (ESI) *m/z* calcd for C₂₅H₃₇O₆NSiNa [M + Na]⁺ 498.2288, found 498.2279.

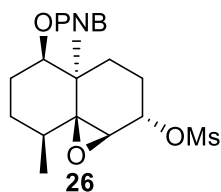
(±)-(1aR,2S,4aR,5R,8S,8aS)-2-Hydroxy-4a,8-dimethyloctahydro-3H-naphtho-[1,8a-b]oxiren-5-yl 4-Nitrobenzoate (25)



Followed general procedure IV, compound **24** as the material, gave the compound **25** (yield: 89%) as a white solid, *R_f* = 0.23 (EtOAc/petroleum ether = 1:2); **IR** *v*_{max} (thin film)/cm⁻¹ 3412, 2940, 2872, 1720, 1528, 1345, 1275, 1108, 909, 720. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 5.08 (d, *J* = 5.5 Hz, 1H), 4.97 (brs, 1H), 3.75 (td, *J* = 8.8, 5.5 Hz, 1H), 2.89 (s, 1H), 2.27 (m, 1H), 2.21 (m, 1H), 1.82 – 1.75 (m, 1H), 1.75 – 1.67 (m, 1H), 1.62 (brt, *J* = 13.3 Hz, 1H), 1.55 (qd, *J* = 13.2, 4.0 Hz, 1H), 1.50 – 1.45 (m, 1H), 1.37 – 1.29 (m, 1H), 1.26 (s, 3H), 0.78 (dt, *J* = 13.0, 3.6 Hz, 1H), 0.68 (d, *J* = 6.6 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 164.0, 150.8, 136.0, 131.1 (2×C), 124.5 (2×C), 78.3, 65.5, 64.7, 57.9, 38.0, 29.1, 27.8,

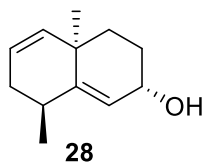
26.5, 26.2, 26.1, 21.0, 14.4; **HRMS** (ESI) m/z calcd for $C_{19}H_{23}O_6NNa$ $[M + Na]^+$ 384.1423, found 384.1420.

(±)-(1aR,2S,4aR,5R,8S,8aS)-4a,8-Dimethyl-2-((methylsulfonyl)oxy)octahydro-3H-naphtho[1,8a-b]oxiren-5-yl 4-Nitrobenzoate (26)



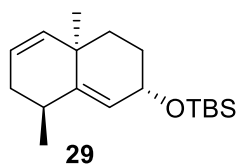
Followed general procedure V, compound **25** as the material, gave the compound **26** (yield: quant.) as a white solid, $R_f = 0.35$ (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/ cm^{-1} 2922, 2854, 1721, 1528, 1451, 1350, 1275, 1175, 1108, 951, 873. **¹H NMR** (600 MHz, DMSO- d_6) δ 8.41 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H), 5.00 (brs, 1H), 4.85 (t, $J = 8.7$ Hz, 1H), 3.27 (s, 3H), 3.14 (s, 1H), 2.33 (m, 1H), 2.22 (m, 1H), 1.97 (m, 1H), 1.81 (dq, $J = 14.8, 3.2$ Hz, 1H), 1.72 – 1.49 (m, 4H), 1.30 (s, 3H), 0.94 (dt, $J = 12.3, 3.4$ Hz, 1H), 0.70 (d, $J = 6.6$ Hz, 3H); **¹³C NMR** (150 MHz, DMSO- d_6) δ 164.0, 150.9, 135.8, 131.1(2×C), 124.5(2×C), 78.0, 74.7, 65.8, 54.8, 37.9, 37.6, 28.9, 27.7, 26.3, 25.2, 23.3, 20.7, 14.3; **HRMS** (ESI) m/z calcd for $C_{20}H_{25}O_8NSNa$ $[M + Na]^+$ 462.1199, found 462.1197.

(±)-(2S,4aR,8S)-4a,8-Dimethyl-2,3,4,4a,7,8-hexahydronaphthalen-2-ol (28)



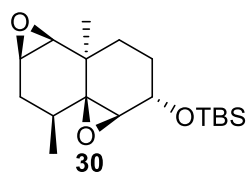
Followed general procedure II, compound **21** as the material, gave the compound **28** (yield: 98%) as a colorless oil, $R_f = 0.36$ (EtOAc/petroleum ether = 1:3); **IR** ν_{max} (thin film)/ cm^{-1} 3314, 3013, 2969, 2936, 2911, 2876, 1661, 1455, 1066, 1037, 1002, 723. **¹H NMR** (600 MHz, DMSO- d_6) δ 5.48 (ddd, $J = 9.7, 5.2, 1.9$ Hz, 1H), 5.32 (dd, $J = 9.7, 2.4$ Hz, 1H), 5.22 (brs, 1H), 4.65 (d, $J = 5.6$ Hz, 1H), 4.02 (m, 1H), 2.37 (m, 1H), 2.20 (dt, $J = 17.1, 5.4$ Hz, 1H), 1.78 (m, 1H), 1.60 (ddt, $J = 17.1, 11.2, 2.4$ Hz, 1H), 1.53 – 1.43 (m, 2H), 1.35 (brt, $J = 13.7$ Hz, 1H), 1.12 (s, 3H), 1.00 (d, $J = 6.6$ Hz, 3H); **¹³C NMR** (150 MHz, DMSO- d_6) δ 146.1, 138.0, 123.6, 122.5, 67.1, 37.3, 36.7, 35.6, 30.4, 28.6, 27.2, 17.8; **HRMS** (ESI): m/z calcd for $C_{12}H_{18}ONa$ $[M + Na]^+$ 201.1255, found 201.1251.

(±)-tert-Butyl(((2S,4aR,8S)-4a,8-dimethyl-2,3,4,4a,7,8-hexahydronaphthalen-2-yl)oxy)-dimethylsilane (29)



Followed general procedure III, compound **28** as the material, gave the compound **29** (yield: 95%) as a colorless oil, $R_f = 0.82$ (EtOAc/petroleum ether = 1:10); **IR** ν_{\max} (thin film)/ cm^{-1} 3014, 2955, 2933, 2857, 1453, 1252, 1088, 881, 833, 775. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 5.42 (ddd, $J = 9.8, 5.3, 2.0$ Hz, 1H), 5.27 (dd, $J = 9.8, 2.5$ Hz, 1H), 5.10 (brs, 1H), 4.20 (brt, $J = 8.0$ Hz, 1H), 2.32 (m, 1H), 2.16 (dt, $J = 17.2, 5.3$ Hz, 1H), 1.74 (m, 1H), 1.62 – 1.42 (m, 3H), 1.33 (td, $J = 13.9, 2.7$ Hz, 1H), 1.06 (s, 3H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.82 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); **^{13}C NMR** (150 MHz, $\text{DMSO}-d_6$) δ 146.0, 136.7, 122.6, 120.5, 68.3, 36.2, 35.5, 34.2, 29.2, 27.8, 26.1, 25.3, (3 \times C), 17.3, 16.6, -4.9, -5.1; **HRMS** (ESI) m/z calcd for $\text{C}_{18}\text{H}_{32}\text{OSiNa}$ [$\text{M} + \text{Na}$] $^+$ 315.2120, found 315.2127.

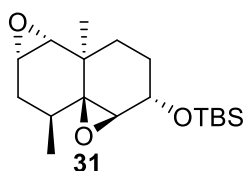
(\pm)-tert-Butyl(((1aS,1bR,4S,4aR,5aS,6S,7aR)-1b,6-dimethyloctahydro-3H-naphtho-[1,2-b:4a,5-b']bis(oxirene)-4-yl)oxy)dimethylsilane (30**)**



A. 75% *m*-Chloroperbenzoic acid (629 mg, 2.74 mmol) was added in portions to a solution of **29** (200 mg, 0.68 mmol) in DCM (15 mL) at -30°C . The resultant mixture was stirred for 18 h at -30°C , and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:50) to give **30** (91 mg, 41%); B. 75% *m*-Chloroperbenzoic acid (201 mg, 0.88 mmol) was added in portions to a solution of **35** (180 mg, 0.58 mmol) in DCM (12 mL) at -30°C . The resultant mixture was stirred for 12 h at -30°C , and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:50) to give **30** (174 mg, 92%) as a colorless oil, $R_f = 0.38$ (EtOAc/petroleum ether = 1:10); **IR** ν_{\max} (thin film)/ cm^{-1} 2954, 2931, 1465, 1253, 1069, 1060, 1006, 873, 835, 775. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 3.89 (t, $J = 8.3$ Hz, 1H), 3.07 (dd, $J = 5.4, 3.9$ Hz, 1H), 2.71 (d, $J = 3.8$ Hz, 1H), 2.59 (s, 1H), 2.16 – 2.04 (m, 1H), 1.96 (dt, $J = 15.0, 6.4$ Hz, 1H), 1.75 (m, 1H), 1.60 (td, $J = 13.5, 3.9$ Hz, 1H), 1.37 (dd, $J = 15.1, 11.7$ Hz, 1H), 1.33 – 1.22 (m, 1H), 1.15 (s, 3H), 1.05 (dt, $J = 12.8, 3.8$ Hz, 1H), 0.81 (s, 9H), 0.46 (d, $J = 6.6$ Hz,

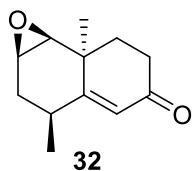
3H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 66.3, 64.6, 60.4, 56.2, 51.1, 34.8, 30.8, 26.7, 26.6, 26.2 (3 \times C), 24.8, 21.0, 18.3, 14.1, -4.2, -4.5; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{33}\text{O}_3\text{Si}$ $[\text{M} + \text{H}]^+$ 325.2199, found 325.2198.

(\pm)-tert-Butyl(((1aR,1bR,4S,4aR,5aS,6S,7aS)-1b,6-dimethyloctahydro-3H-naphtho-[1,2-b:4a,5-b']bis(oxirene)-4-yl)oxy)dimethylsilane (31**)**



A. 75% *m*-Chloroperbenzoic acid (629 mg, 2.74 mmol) was added in portions to a solution of **29** (200 mg, 0.68 mmol) in DCM (15 mL) at -30 °C. The resultant mixture was stirred for 18 h at -30 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:50) to give **31** (115 mg, 52%); B. 75% *m*-Chloroperbenzoic acid (201 mg, 0.88 mmol) was added in portions to a solution of **39** (180 mg, 0.58 mmol) in DCM (12 mL) at -30 °C. The resultant mixture was stirred for 12 h at -30 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:50) to give **31** (176 mg, 93%) as a colorless oil, R_f = 0.30 (EtOAc/petroleum ether = 1:10); IR ν_{max} (thin film)/ cm^{-1} 2955, 2931, 2857, 1465, 1253, 1092, 874, 836, 776. ^1H NMR (600 MHz, DMSO- d_6) δ 3.98 (t, J = 7.7 Hz, 1H), 3.16 (brs, 1H), 2.84 (s, 1H), 2.62 (d, J = 3.7 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.82 (ddt, J = 13.1, 8.1, 3.6 Hz, 1H), 1.53 (td, J = 13.6, 4.3 Hz, 1H), 1.48 – 1.41 (m, 1H), 1.36 (tdd, J = 14.0, 7.1, 4.8 Hz, 1H), 1.11 (s, 3H), 1.08 – 1.00 (m, 1H), 0.80 (s, 9H), 0.51 (d, J = 6.5 Hz, 3H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 66.3, 65.8, 60.7, 59.0, 53.4, 33.4, 32.0, 28.2, 27.4, 26.2 (3 \times C), 23.8, 19.4, 18.2, 13.8, -4.3, -4.5; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 347.2018, found 347.2013.

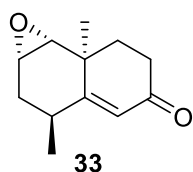
(\pm)-(1aR,3S,7aS,7bS)-3,7a-Dimethyl-2,3,6,7,7a,7b-hexahydronaphtho[1,2b]-oxiren-5(1aH)-one (32**)**



75% *m*-Chloroperbenzoic acid (470 mg, 2.04 mmol) was added in portions to a solution of **21** (240 mg, 1.36 mmol) in DCM (18 mL) at

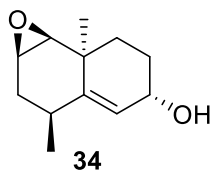
0 °C. The resultant mixture was stirred for 12 h at 0 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and brine, dried with anhydrous Na₂SO₄ and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:10) to give **32** (170 mg, 65%) as a white solid, *R_f* = 0.32 (EtOAc/petroleum ether = 1:2); **IR** *v*_{max} (thin film)/cm⁻¹ 2961, 2916, 2872, 1657, 1613, 1456, 1269, 837. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 5.52 (s, 1H), 3.35 (brs, 1H), 2.87 (d, *J* = 3.9 Hz, 1H), 2.62 (ddd, *J* = 17.7, 14.5, 5.5 Hz, 1H), 2.52 – 2.43 (m, 1H), 2.36 – 2.23 (m, 2H), 1.93 (td, *J* = 13.8, 4.9 Hz, 1H), 1.84 (ddd, *J* = 13.1, 5.5, 2.1 Hz, 1H), 1.48 (ddd, *J* = 14.4, 12.1, 1.2 Hz, 1H), 1.27 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 198.3, 171.8, 120.6, 60.1, 53.4, 35.2, 34.6, 34.2, 33.6, 27.6, 21.1, 16.7; **HRMS** (ESI) *m/z* calcd for C₁₂H₁₇O₂ [M + H]⁺ 193.1229, found 193.1231.

(±)-(1aS,3S,7aS,7bR)-3,7a-Dimethyl-2,3,6,7,7a,7b-hexahydronaphtho[1,2-b]-oxiren-5(1aH)-one (33)



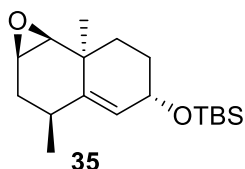
75% *m*-Chloroperbenzoic acid (470 mg, 2.04 mmol) was added in portions to a solution of **21** (240 mg, 1.36 mmol) in DCM (18 mL) at 0 °C. The resultant mixture was stirred for 12 h at 0 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and brine, dried with anhydrous Na₂SO₄ and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:10) to give **33** (73 mg, 28%) as a colorless oil, *R_f* = 0.28 (EtOAc/petroleum ether = 1:2); **IR** *v*_{max} (thin film)/cm⁻¹ 2966, 2933, 2875, 1667, 1459, 1268, 834. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 5.63 (s, 1H), 3.35 (dd, *J* = 5.1, 4.0 Hz, 1H), 2.96 (d, *J* = 4.0 Hz, 1H), 2.65 – 2.50 (m, 2H), 2.35 (ddd, *J* = 15.1, 7.4, 5.5 Hz, 1H), 2.32 – 2.17 (m, 2H), 2.16 – 2.01 (m, 1H), 1.91 – 1.79 (m, 1H), 1.65 (m, 1H), 1.48 – 1.35 (m, 1H), 1.33 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 198.2, 171.0, 1241, 62.2, 53.1, 37.5, 33.9, 33.4, 33.1, 29.4, 21.1, 17.7; **HRMS** (ESI) *m/z* calcd for C₁₂H₁₇O₂ [M + H]⁺ 193.1229, found 193.1232.

(±)-(1aR,3S,5S,7aS,7bS)-3,7a-Dimethyl-1a,2,3,5,6,7,7a,7b-octahydronaphtho[1,2-b]oxiren-5-ol (34)



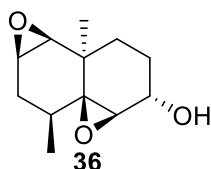
Followed general procedure II, compound **32** as the material, gave the compound **34** (yield: 90%) as a colorless oil, $R_f = 0.28$ (EtOAc/petroleum ether = 1:2); **IR** ν_{\max} (thin film)/ cm^{-1} 3417, 2959, 2930, 2870, 1663, 1457, 1283, 1128, 1071, 846. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 5.12 (s, 1H), 4.66 (d, $J = 5.7$ Hz, 1H), 4.00 (m, 1H), 3.20 (d, $J = 3.7$ Hz, 1H), 2.69 (d, $J = 3.7$ Hz, 1H), 2.12 – 2.20 (m, 2H), 1.86 (m, 1H), 1.50 – 1.65 (m, 3H), 1.27 (m, 1H), 1.12 (s, 3H), 0.91 (d, $J = 6.6$ Hz, 3H). **^{13}C NMR** (150 MHz, $\text{DMSO}-d_6$) δ 145.4, 122.4, 66.7, 60.9, 53.7, 36.8, 34.7, 33.9, 28.8, 26.5, 22.8, 17.4; **HRMS** (ESI): m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 195.1385, found 195.1369.

(\pm)-tert-Butyl(((1aR,3S,5S,7aS,7bS)-3,7a-dimethyl-1a,2,3,5,6,7,7a,7b-octahydro-naphtho[1,2-b]oxiren-5-yl)oxy)dimethylsilane (35**)**



Followed general procedure III, compound **34** as the material, gave the compound **35** (yield: 95%) as a colorless oil, $R_f = 0.45$ (EtOAc/petroleum ether = 1:10); **IR** ν_{\max} (thin film)/ cm^{-1} 2956, 2929, 2856, 1730, 1453, 1254, 1081, 882, 834. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 5.00 (brs, 1H), 4.20 (brt, $J = 8.4$ Hz, 1H), 3.15 (brd, $J = 3.8$ Hz, 1H), 2.64 (d, $J = 3.8$ Hz, 1H), 2.12 (m, 2H), 1.87 – 1.77 (m, 1H), 1.63 – 1.44 (m, 3H), 1.29 – 1.13 (m, 1H), 1.07 (s, 3H), 0.86 (d, $J = 6.5$ Hz, 3H), 0.81 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); **^{13}C NMR** (150 MHz, $\text{DMSO}-d_6$) δ 146.3, 121.5, 69.0, 60.9, 53.7, 36.7, 34.4, 33.9, 29.1, 26.4, 26.3 (3 \times C), 22.7, 18.3, 17.2, -3.9, -4.0; **HRMS** (ESI) m/z calcd for $\text{C}_{18}\text{H}_{33}\text{O}_2\text{Si}$ $[\text{M} + \text{H}]^+$ 309.2250, found 309.2264.

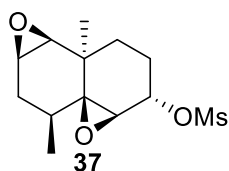
(\pm)-(1aS,1bR,4S,4aR,5aS,6S,7aR)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-ol (36**)**



Followed general procedure IV, compound **30** as the material, gave the compound **36** (yield: 89%) as a colorless oil, $R_f = 0.32$ (EtOAc/petroleum ether = 1:1); **IR** ν_{\max} (thin film)/ cm^{-1} 3473, 2962, 2877, 1461, 1268, 1078, 1045, 1055, 936, 830. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 5.03 (d, $J = 5.4$ Hz, 1H), 3.75 (td, $J = 8.6, 5.4$ Hz, 1H), 3.12 (dd, $J = 5.4, 3.9$ Hz, 1H), 2.76 (d, $J = 3.9$ Hz, 1H), 2.69 (s, 1H), 2.13 (dt, $J = 11.7, 6.7$ Hz, 1H), 2.02 (ddd, $J = 15.0, 6.8, 5.5$ Hz, 1H), 1.84 – 1.70 (m, 1H), 1.64 (ddd, $J = 14.6, 12.9, 3.6$ Hz, 1H), 1.42 (dd, $J = 15.1, 11.7$ Hz, 1H), 1.30 (m, 1H), 1.21 (s, 3H), 1.08

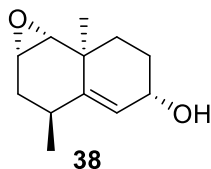
(dt, $J = 12.8, 3.7$ Hz, 1H), 0.52 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 64.6, 64.4, 60.5, 56.5, 51.0, 34.9, 30.8, 27.0, 25.8, 24.9, 21.1, 14.1; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3$ $[\text{M} + \text{H}]^+$ 211.1334, found 211.1337.

(\pm)-(1aS,1bR,4S,4aR,5aS,6S,7aR)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-yl Methanesulfonate (37)



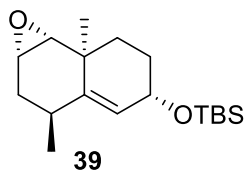
Followed general procedure V, compound **36** as the material, gave the compound **37** (yield: quant.) as a colorless oil, $R_f = 0.40$ (EtOAc/petroleum ether = 1:1); IR ν_{max} (thin film)/ cm^{-1} 2970, 2936, 1352, 1174, 944, 874, 843. ^1H NMR (600 MHz, DMSO- d_6) δ 4.85 (t, $J = 8.4$ Hz, 1H), 3.27 (s, 3H), 3.16 (dd, $J = 5.4, 4.0$ Hz, 1H), 2.96 (s, 1H), 2.82 (d, $J = 4.0$ Hz, 1H), 2.19 (dt, $J = 11.7, 6.7$ Hz, 1H), 2.11 – 2.00 (m, 2H), 1.69 (td, $J = 13.5, 3.6$ Hz, 1H), 1.58 (m, 1H), 1.44 (dd, $J = 15.1, 11.8$ Hz, 1H), 1.24 (s, 3H), 1.22 (m, 1H), 0.55 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 74.4, 64.9, 60.2, 53.3, 51.2, 37.9, 34.6, 30.7, 26.0, 24.6, 23.0, 20.7, 14.0; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{21}\text{O}_5\text{S}$ $[\text{M} + \text{H}]^+$ 289.1110, found 289.1112.

(\pm)-(1aS,3S,5S,7aS,7bR)-3,7a-Dimethyl-1a,2,3,5,6,7,7a,7b-octahydronaphtho[1,2-b]oxiren-5-ol (38)



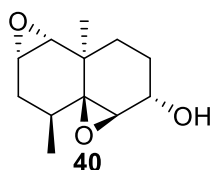
Followed general procedure II, compound **33** as the material, gave the compound **38** (yield: 93%) as a colorless oil, $R_f = 0.25$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3493, 2959, 2931, 2870, 1458, 1283, 1127, 1073. ^1H NMR (600 MHz, DMSO- d_6) δ 5.23 (s, 1H), 4.66 (d, $J = 5.5$ Hz, 1H), 3.98 (m, 1H), 3.19 (t, $J = 4.4$ Hz, 1H), 2.76 (d, $J = 3.7$ Hz, 1H), 2.28 – 2.13 (m, 2H), 1.80 (m, 1H), 1.68 (m, 1H), 1.52 (brd, $J = 13.0$ Hz, 1H), 1.43 (m, 1H), 1.27 (dd, $J = 14.2, 13.0$ Hz, 1H), 1.17 (s, 3H), 0.87 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 143.2, 126.6, 66.8, 62.3, 52.8, 36.2, 34.5, 32.9, 28.2, 27.8, 23.0, 18.2. HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 195.1385, found 195.1366.

(\pm)-tert-Butyl(((1aS,3S,5S,7aS,7bR)-3,7a-dimethyl-1a,2,3,5,6,7,7a,7b-octahydronaphtho[1,2-b]oxiren-5-yl)oxy)dimethylsilane (39)



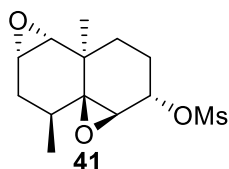
Followed general procedure III, compound **38** as the material, gave the compound **39** (yield: 96%) as a colorless oil, $R_f = 0.40$ (EtOAc/petroleum ether = 1:10); **IR** ν_{\max} (thin film)/ cm^{-1} 2958, 2928, 2858, 1728, 1461, 1382, 1127, 1074, 835, 781. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 5.28 (d, $J = 6.0$ Hz, 1H), 5.15 (brs, 1H), 4.15 (m, 1H), 4.07 (m, 1H), 2.86 (dd, $J = 10.1, 6.1$ Hz, 1H), 2.34 – 2.21 (m, 1H), 2.12 (dq, $J = 12.3, 4.1$ Hz, 1H), 1.74 – 1.64 (m, 2H), 1.33 – 1.26 (m, 1H), 1.23 – 1.15 (m, 1H), 0.93 (s, 3H), 0.90 (d, $J = 6.4$ Hz, 3H), 0.81 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); **^{13}C NMR** (150 MHz, $\text{DMSO}-d_6$) δ 145.4, 124.7, 81.9, 68.6, 63.4, 49.1, 44.2 (2 \times C), 34.6, 31.9, 28.9, 26.3 (3 \times C), 18.3, 17.9, -3.9, -4.1; **HRMS** (ESI) m/z calcd for $\text{C}_{18}\text{H}_{32}\text{O}_2\text{SiNa}$ [$\text{M} + \text{Na}$] $^+$ 331.2069, found 331.2081.

(\pm)-(1aR,1bR,4S,4aR,5aS,6S,7aS)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-ol (40**)**



Followed general procedure IV, compound **31** as the material, gave the compound **40** (yield: 88%) as a white solid, $R_f = 0.29$ (EtOAc/petroleum ether = 1:1); **IR** ν_{\max} (thin film)/ cm^{-1} 3427, 2964, 2879, 1462, 1271, 1079, 1045, 1005, 939, 830. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 5.07 (d, $J = 5.3$ Hz, 1H), 3.83 (td, $J = 8.0, 5.3$ Hz, 1H), 3.21 (brs, 1H), 2.96 (brs, 1H), 2.68 (d, $J = 3.8$ Hz, 1H), 2.03 – 1.89 (m, 2H), 1.82 (m, 1H), 1.66 – 1.46 (m, 2H), 1.38 (tdd, $J = 14.1, 8.1, 4.6$ Hz, 1H), 1.17 (s, 3H), 1.08 (ddd, $J = 12.9, 4.6, 3.1$ Hz, 1H), 0.57 (d, $J = 6.6$ Hz, 3H); **^{13}C NMR** (150 MHz, $\text{DMSO}-d_6$) δ 66.5, 64.0, 61.2, 59.1, 53.4, 33.5, 32.1, 28.5, 26.6, 23.9, 19.5, 13.9; **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 211.1334, found 211.1335.

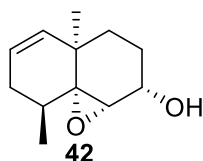
(\pm)-(1aR,1bR,4S,4aR,5aS,6S,7aS)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-yl Methanesulfonate (41**)**



Followed general procedure V, compound **40** as the material, gave the compound **41** (yield: quant.) as a colorless oil, $R_f = 0.32$ (EtOAc/petroleum ether = 1:1); **IR** ν_{\max} (thin film)/ cm^{-1} 2967, 2937, 2881, 1461, 1430, 1350, 1320, 1171, 927, 878, 831, 797. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 4.93 (brt, $J = 8.4$ Hz, 1H), 3.28 (s, 3H), 3.25 (brs, 1H), 3.21 (brs, 1H), 2.73 (d, $J = 3.8$ Hz, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 1.97 (m, 2H),

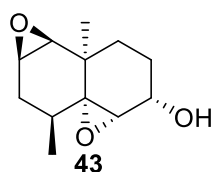
1.74 – 1.57 (m, 2H), 1.53 (m, 1H), 1.22 (ddd, $J = 12.7, 4.3, 2.5$ Hz, 1H), 1.19 (s, 3H), 0.60 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 74.0, 66.6, 58.8, 57.7, 53.3, 37.9, 33.1, 32.0, 27.5, 23.8, 23.7, 19.2, 13.7; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{SNa}$ $[\text{M} + \text{Na}]^+$ 311.0929, found 311.0928.

(±)-(1aS,2S,4aR,8S,8aR)-4a,8-Dimethyl-1a,2,4,4a,7,8-hexahydro-3H-naphtho-[1,8a-b]oxiren-2-ol (42)



75% *m*-Chloroperbenzoic acid (232 mg, 1.01 mmol) was added in portions to a solution of **28** (150 mg, 0.84 mmol) in DCM (8 mL) at -30 °C. The resultant mixture was stirred for 10 h at -30 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:8) to give **42** (147 mg, 90%) gave the compound **42** (yield: 95%) as a colorless oil, $R_f = 0.40$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3396, 3015, 2960, 2934, 2834, 1684, 1659, 1458, 1277, 1063, 858. ^1H NMR (600 MHz, DMSO- d_6) δ 5.54 (ddd, $J = 9.8, 5.7, 1.8$ Hz, 1H), 5.38 (dd, $J = 9.8, 2.7$ Hz, 1H), 4.84 (d, $J = 5.5$ Hz, 1H), 3.74 (m, 1H), 3.17 (d, $J = 1.8$ Hz, 1H), 2.21 – 2.01 (m, 2H), 1.87 – 1.74 (m, 1H), 1.38 – 1.27 (m, 3H), 1.02 (s, 3H), 1.01 – 0.97 (m, 1H), 0.72 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 138.0, 123.2, 67.7, 67.6, 58.7, 35.6, 35.1, 33.8, 30.3, 25.5, 23.4, 13.4; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 195.1385, found 195.1391.

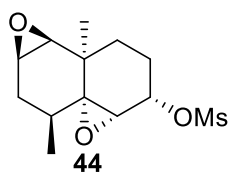
(±)-(1aS,1bR,4S,4aS,5aR,6S,7aR)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,5-b']bis(oxirene)-4-ol (43)



75% *m*-Chloroperbenzoic acid (248 mg, 1.08 mmol) was added in portions to a solution of **42** (140 mg, 0.72 mmol) in DCM (5 mL) at 0 °C. The resultant mixture was stirred for 8 h at 0 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:5) to give **43** (61 mg, 40%) as a white solid, $R_f = 0.36$ (EtOAc/petroleum ether = 1:1); IR ν_{max} (thin film)/ cm^{-1} 3422, 2960, 2934,

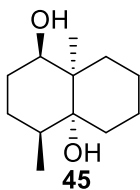
2876, 1459, 1049, 928, 830. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 4.80 (d, *J* = 5.5 Hz, 1H), 3.70 (m, 1H), 3.25 (dd, *J* = 5.7, 3.8 Hz, 1H), 3.07 (d, *J* = 1.8 Hz, 1H), 2.88 (d, *J* = 3.7 Hz, 1H), 2.18 (dt, *J* = 15.2, 6.0 Hz, 1H), 2.03 (m, 1H), 1.49 (m, 2H), 1.43 – 1.27 (m, 3H), 1.09 (s, 3H), 0.59 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 66.8, 65.9, 62.7, 58.9, 53.2, 33.9, 32.6, 32.4, 27.8, 25.5, 20.6, 13.9; **HRMS** (ESI): *m/z* calcd for C₁₂H₁₉O₃ [M + H]⁺ 211.1334, found 211.1329.

(±)-(1aS,1bR,4S,4aS,5aR,6S,7aR)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-yl Methanesulfonate (44)



Followed general procedure V, compound **43** as the material, gave the compound **44** (yield: quant.) as a colorless oil, *R_f* = 0.26 (EtOAc/petroleum ether = 1:2); **IR** *v*_{max} (thin film)/cm⁻¹ 2968, 2939, 2881, 1351, 1173, 930, 879. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 4.95 (ddd, *J* = 7.6, 5.4, 2.5 Hz, 1H), 3.32 (brs, 1H), 3.26 (s, 3H), 3.26 (brs, 1H), 2.96 (d, *J* = 3.7 Hz, 1H), 2.22 (dt, *J* = 15.2, 6.0 Hz, 1H), 2.13 (m, 1H), 1.84 (m, 1H), 1.69 – 1.56 (m, 2H), 1.52 – 1.42 (m, 2H), 1.13 (s, 3H), 0.61 (d, *J* = 6.7 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 78.6, 66.8, 62.4, 55.6, 52.6, 38.2, 34.0, 32.3, 31.5, 27.5, 23.6, 20.6, 13.7; **HRMS** (ESI) *m/z* calcd for C₁₃H₂₀O₅SNa [M + Na]⁺ 311.0929, found 311.0924.

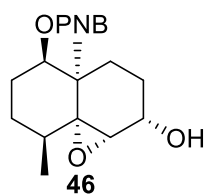
(±)-(1R,4S,4aR,8aR)-4,8a-Dimethyloctahydronaphthalene-1,4a(2H)-diol (45)



Dess-Martin periodinane (640 mg, 1.52 mmol) was added in portions to a solution of **12** (200 mg, 1.01 mmol) in dichloromethane (2.0 mL) at 0 °C, then warmed to room temperature. The resultant mixture was stirred for overnight, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and with brine, dried with anhydrous Na₂SO₄ and concentrated. The crude product was redissolved with THF, and added NaBH₄ (80 mg, 2.1 mmol) over 5 min in portions at 0 °C. After stirring for 3.0 h at 0 °C, the reaction was quenched by addition of saturated NH₄Cl solution. The mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:15) gave **45** (138 mg, 69%) as a white solid, *R_f* = 0.52 (EtOAc/petroleum ether = 1:2); **IR** *v*_{max} (thin film)/cm⁻¹ 3467,

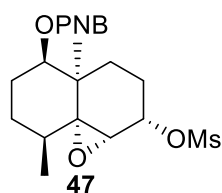
2963, 2932, 2865, 1448, 1374, 1120, 1010. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 4.29 (d, *J* = 4.0 Hz, 1H), 3.53 (s, 1H), 3.52 (m, 1H), 2.06 (m, 1H), 1.85 (td, *J* = 13.1, 4.1 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.63 – 1.41 (m, 3H), 1.38 – 1.19 (m, 6H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.76 (s, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 78.1, 73.3, 41.3, 37.8, 36.8, 31.1, 27.2, 27.2, 24.4, 23.5, 20.5, 15.8; **HRMS** (ESI) *m/z* calcd for C₁₂H₂₂O₂Na [M + Na]⁺ 221.1517, found 221.1518.

(±)-(1aS,2S,4aR,5R,8S,8aR)-2-Hydroxy-4a,8-dimethyloctahydro-3H-naphtho[1,8a-b]oxiren-5-yl 4-Nitrobenzoate (46)



75% *m*-Chloroperbenzoic acid (210 mg, 0.91 mmol) was added in portions to a solution of **46** (210 mg, 0.61 mmol) in DCM (5 mL) at 0 °C. The resultant mixture was stirred for 15 h at 0 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and brine, dried with anhydrous Na₂SO₄ and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:5) to give **46** (207 mg, 94%) as a white solid, *R*_f = 0.30 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/cm⁻¹ 3364, 2940, 2873, 1720, 1605, 1527, 1344, 1268, 1099, 720. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 8.39 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 2H), 5.02 (brd, *J* = 3.3 Hz, 1H), 4.89 (d, *J* = 5.4 Hz, 1H), 3.77 (m, 1H), 3.32 (brs, 1H), 2.17 (m, 1H), 1.92 (m, 1H), 1.78 (m, 1H), 1.67 (m, 1H), 1.51 – 1.39 (m, 3H), 1.38 – 1.32 (m, 1H), 1.23 – 1.17 (m, 1H), 1.14 (s, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 164.0, 150.8, 135.7, 131.1 (2×C), 124.6 (2×C), 80.2, 67.4, 66.5, 60.4, 36.8, 31.5, 31.2, 27.7, 25.4, 25.1, 22.1, 15.1; **HRMS** (ESI) *m/z* calcd for C₁₉H₂₄NO₆ [M + H]⁺ 362.1604, found 362.1603.

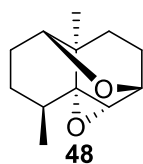
(±)-(1aS,2S,4aR,5R,8S,8aR)-4a,8-Dimethyl-2-((methylsulfonyl)oxy)octahydro-3H-naphtho[1,8a-b]oxiren-5-yl 4-Nitrobenzoate (47)



Followed general procedure V, compound **46** as the material, gave the compound **47** (yield: quant.) as a white solid, *R*_f = 0.37 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/cm⁻¹ 2939, 2875, 1721, 1528, 1347, 1274, 1196, 1178, 1104, 938, 879, 720. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H),

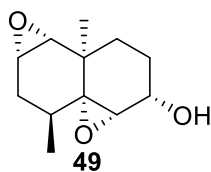
5.08 (dd, $J = 5.2, 1.8$ Hz, 1H), 5.00 (brt, $J = 7.0$ Hz, 1H), 3.55 (brs, 1H), 3.25 (s, 3H), 2.24 (m, 1H), 2.02 – 1.88 (m, 1H), 1.87 – 1.76 (m, 1H), 1.71 (m 3H), 1.57 (m, 1H), 1.49 (qd, $J = 12.3, 5.0$ Hz, 1H), 1.35 (dt, $J = 14.5, 4.5$ Hz, 1H), 1.18 (s, 3H), 0.76 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 163.9, 150.8, 135.6, 131.2 (2 \times C), 124.5 (2 \times C), 80.1, 79.4, 67.9, 56.9, 38.5, 36.7, 30.8, 30.5, 27.6, 25.0, 23.3, 22.0, 14.8; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_8\text{S}$ $[\text{M} + \text{H}]^+$ 440.1379, found 440.1386.

(\pm)-(1aS,2R,4aR,5R,8S,8aR)-4a,8-Dimethyloctahydro-3H-2,5-epoxynaphtho-[1,8a-b]oxirene (48**)**



Followed general procedure VI, compound **44** or **47** as the material, gave the compound **48** (yield: 82%) as a colorless oil, $R_f = 0.55$ (EtOAc/petroleum ether = 1:2); IR ν_{max} (thin film)/ cm^{-1} 3371, 2929, 2861, 1458, 1377, 1274, 1194, 1113. ^1H NMR (600 MHz, DMSO- d_6) δ 4.09 (brt, $J = 3.5$ Hz, 1H), 3.72 (brs, 1H), 3.31 (d, $J = 4.5$ Hz, 1H), 2.38 (m, 1H), 1.57 – 1.75 (m, 3H), 1.53 (dd, $J = 12.5, 4.2$ Hz, 1H), 1.48 – 1.38 (m, 2H), 1.32 (m, 1H), 1.09 (td, $J = 12.0, 4.0$ Hz, 1H), 1.03 (s, 3H), 0.57 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 78.1, 67.9, 63.6, 52.2, 36.7, 32.3, 29.4, 28.2, 27.6, 24.4, 20.2, 13.6; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 195.1385, found 195.1376.

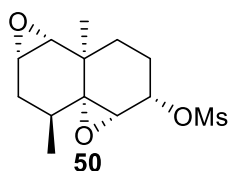
(\pm)-(1aR,1bR,4S,4aS,5aR,6S,7aS)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-ol (49**)**



75% *m*-Chloroperbenzoic acid (248 mg, 1.08 mmol) was added in portions to a solution of **42** (140 mg, 0.72 mmol) in DCM (5 mL) at 0 °C. The resultant mixture was stirred for 8 h at 0 °C, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO_3 and brine, dried with anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (EtOAc/petroleum ether = 1:5) to give **49** (79 mg, 52%) as a white solid, $R_f = 0.31$ (EtOAc/petroleum ether = 1:1); IR ν_{max} (thin film)/ cm^{-1} 3411, 2962, 2931, 2853, 1459, 1216, 860. ^1H NMR (600 MHz, DMSO- d_6) δ 4.89 (s, 1H), 3.73 (dd, $J = 9.7, 5.3$ Hz, 1H), 3.25 (t, $J = 3.2$ Hz, 1H), 3.03 (s, 1H), 2.72 (d, $J = 3.9$ Hz, 1H), 2.12 (dt, $J = 14.6, 3.3$ Hz, 1H), 2.02 (m, 1H), 1.60 (dd, $J = 13.5, 12.3$ Hz, 1H), 1.45 – 1.39 (m, 1H), 1.35 (m, 1H), 1.29 – 1.16 (m, 2H), 1.04 (s, 3H), 0.60 (d, $J = 6.8$ Hz, 3H); ^{13}C

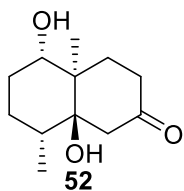
NMR (150 MHz, DMSO-*d*₆) δ 67.8, 66.6, 60.6, 58.3, 53.0, 34.4, 32.9, 32.0, 25.2, 24.6, 19.2, 12.9; **HRMS** (ESI) *m/z* calcd for C₁₂H₁₉O₃ [M + H]⁺ 211.1334, found 211.1333.

(±)-(1aR,1bR,4S,4aS,5aR,6S,7aS)-1b,6-Dimethyloctahydro-3H-naphtho[1,2b:4a,-5-b']bis(oxirene)-4-yl Methanesulfonate (50)



Followed general procedure V, compound **49** as the material, gave the compound **50** (yield: quant.) as a colorless oil, *R_f* = 0.35 (EtOAc/petroleum ether = 1:1); **IR** *v*_{max} (thin film)/cm⁻¹ 2971, 2938, 1461, 1352, 1174, 944, 874, 843. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 5.02 (ddd, *J* = 10.5, 5.7, 1.7 Hz, 1H), 3.28 (t, *J* = 3.3 Hz, 1H), 3.26 (brs, 1H), 3.26 (s, 3H), 2.76 (d, *J* = 3.9 Hz, 1H), 2.14 (dt, *J* = 14.4, 3.3 Hz, 1H), 2.07 (m, 1H), 1.78 – 1.58 (m, 3H), 1.39 – 1.32 (m, 2H), 1.07 (s, 3H), 0.61 (d, *J* = 6.9 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 79.7, 68.0, 60.2, 55.4, 53.0, 38.3, 33.4, 32.6, 31.9, 25.2, 22.4, 19.0, 12.7; **HRMS** (ESI) *m/z* calcd for C₁₃H₂₁O₅S [M + H]⁺ 289.1110, found 289.1101.

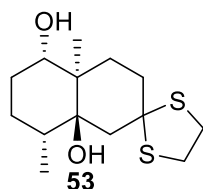
(±)-(4aR,5R,8S,8aR)-5,8a-Dihydroxy-4a,8-dimethyloctahydronaphthalen-2(1H)-one (52)



To a solution of (200.00 mg, 0.94 mmol) of ketal **51** in 5 mL of acetone was added a mixture of 0.536 mL of water and 65 μ L of concentrated sulfuric acid. After having been refluxed for 45 min, the solution was concentrated under reduced pressure. The resulting mixture was extracted with ethyl acetate. The extracts were washed with saturated sodium bicarbonate solution and brine, dried over anhydrous Na₂SO₄. Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:12) to afford ketol **52** (160.34 mg, 80%) as a white solid, *R_f* = 0.22 (EtOAc/petroleum ether = 1:1); **IR** *v*_{max} (thin film)/cm⁻¹ 3397, 2943, 2875, 1700, 980. **¹H NMR** (600 MHz, DMSO-*d*₆) δ 4.29 (d, *J* = 5.2 Hz, 1H), 4.23 (s, 1H), 3.65 (dt, *J* = 11.7, 4.8 Hz, 1H), 2.91 (d, *J* = 14.4 Hz, 1H), 2.33 (ddd, *J* = 15.4, 13.3, 7.2 Hz, 1H), 2.07 (ddt, *J* = 15.4, 5.3, 1.9 Hz, 1H), 2.01 (tt, *J* = 13.7, 4.8 Hz, 1H), 1.93 (dd, *J* = 12.9, 5.2 Hz, 1H), 1.88 (dd, *J* = 14.4, 2.2 Hz, 1H), 1.68 – 1.53 (m, 3H), 1.41 (m, 1H), 1.19 (brd, *J* = 13.2 Hz, 1H), 1.09 (s, 3H), 0.96 (d, *J* = 7.7 Hz, 3H); **¹³C NMR** (150 MHz, DMSO-*d*₆) δ 211.7,

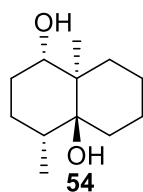
79.7, 72.5, 50.4, 42.0, 38.0, 34.2, 26.6, 26.6, 26.6, 17.6, 15.3; **HRMS** (ESI) m/z calcd for $C_{12}H_{20}O_3Na$ $[M + Na]^+$ 235.1310, found 235.1322.

(±)-(4aR,5R,8S,8aR)-4a,8-Dimethylhexahydro-1H-spiro[naphthalene-2,2'-[1,3]-dithi-olane]-5,8a(3H)-diol (53)



A solution of the ketol **52** (150.00 mg, 0.71 mmol), ethanedithiol (75 μ L, 0.89 mmol), boron trifluoride etherate (500 μ L) in AcOH (15 mL) and 3A Molecular sieve was stirred at r.t. for 4h, under nitrogen atmosphere. After this time, the reaction mixture was diluted with ethylacetate, washed with saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4 . Solvent removal followed by chromatography with EtOAc/petroleum ether (1:12) gave compound **53** (160.00 mg, 78%) as a white solid, R_f = 0.35 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/ cm^{-1} 3444, 2929, 2888, 1019. **1H NMR** (600 MHz, $DMSO-d_6$) δ 4.07 (d, J = 5.4 Hz, 1H), 3.73 (s, 1H), 3.66 (dt, J = 11.5, 5.0 Hz, 1H), 3.24 – 3.15 (m, 2H), 3.13 – 3.05 (m, 2H), 2.63 (d, J = 14.2 Hz, 1H), 2.06 (tt, J = 13.7, 5.1 Hz, 1H), 1.95 – 1.82 (m, 3H), 1.64 (d, J = 14.2 Hz, 1H), 1.61 – 1.51 (m, 2H), 1.39 (m, 1H), 1.28 (m, 1H), 1.11 (brd, J = 12.9 Hz, 1H), 0.90 (d, J = 7.7 Hz, 3H), 0.86 (s, 3H); **^{13}C NMR** (150 MHz, $DMSO-d_6$) δ 76.2, 71.6, 67.2, 46.5, 41.4, 40.8, 39.1, 39.1, 36.5, 32.9, 26.8, 26.7, 17.1, 16.2; **HRMS** (ESI) m/z calcd for $C_{14}H_{24}O_2S_2Na$ $[M + Na]^+$ 311.1115, found 311.1102.

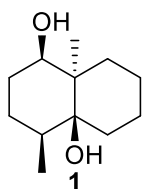
(±)-(1R,4S,4aR,8aR)-4,8a-Dimethyloctahydronaphthalene-1,4a(2H)-diol (54)



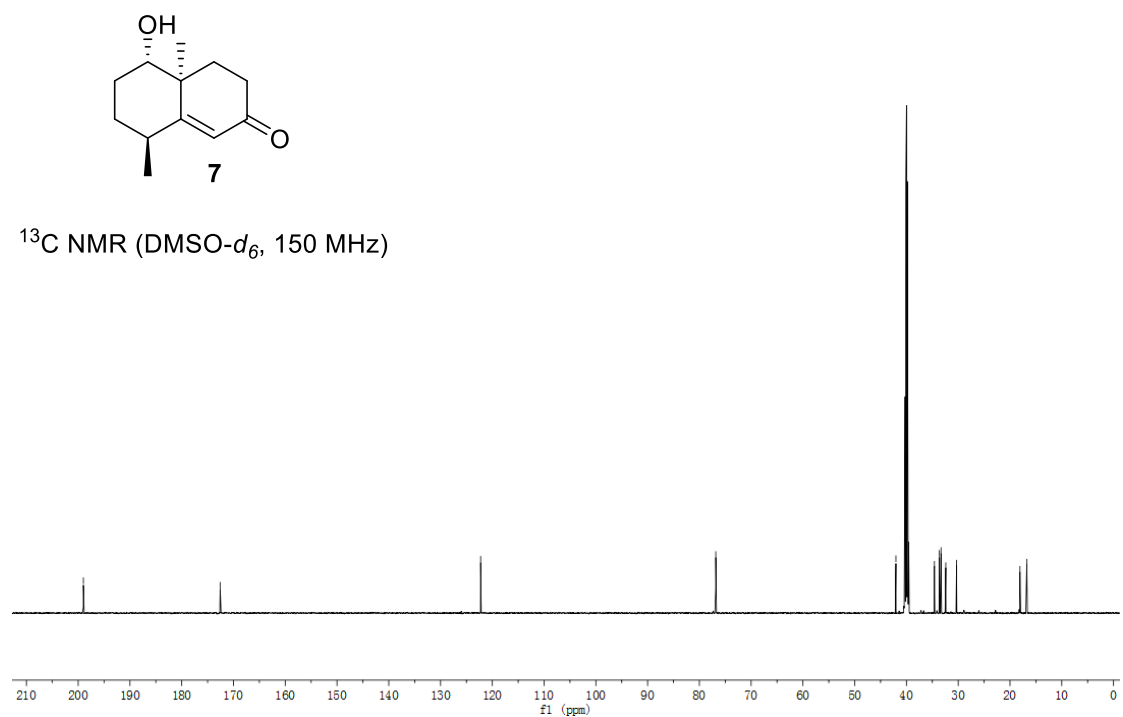
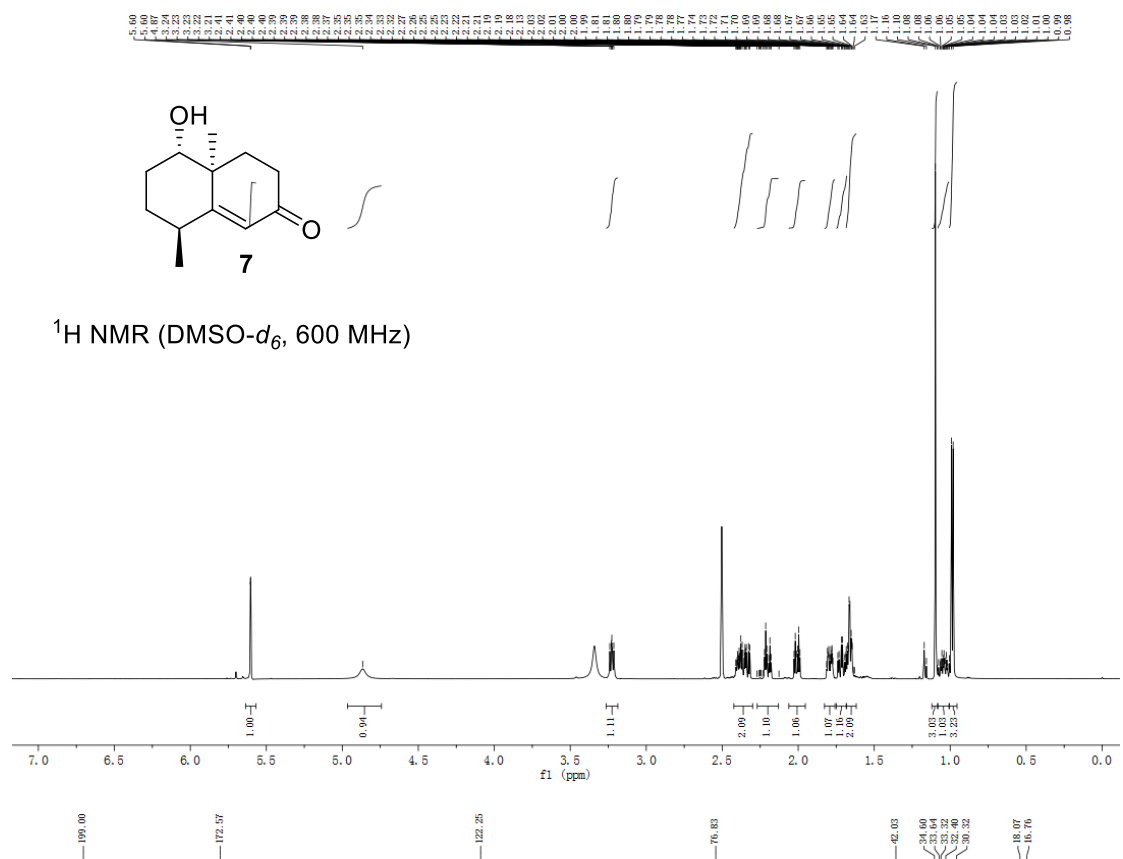
A solution of compound **53** (100.00 mg, 0.50 mmol) in Ethanol (10 mL) was treated with W-2 Raney Ni (80 mg) for 8 h under reflux. After this time, Vacuum filtration was performed to remove the residue, and the filtrate was concentrated under reduced pressure. And purified by silica gel column chromatography with EtOAc/hexane (1:10) to yield compound **54** (65 mg, 66%) as a white solid, R_f = 0.25 (EtOAc/petroleum ether = 1:2); **IR** ν_{max} (thin film)/ cm^{-1} 3366, 2928, 2865, 1019, 957, 921. **1H NMR** (600 MHz, $DMSO-d_6$) δ 3.93 (d, J = 5.3 Hz, 1H), 3.64 (dt, J = 11.6, 4.9 Hz, 1H), 3.39 (s, 1H), 2.11 (tt, J = 13.7, 5.1 Hz, 1H), 1.83 (td, J = 13.2, 4.0 Hz, 1H), 1.77-1.69 (m, 1H), 1.60 (dd, J = 12.1, 5.3 Hz, 1H), 1.54 (m, 1H), 1.45 (m, 1H), 1.37 (m, 4H), 1.27 (brd, J = 12.7 Hz, 1H), 1.13 (brd, J = 13.0 Hz, 1H), 1.02 (brd, J = 12.5 Hz), 0.92 (d, J = 7.7 Hz, 3H), 0.87 (s, 3H); **^{13}C**

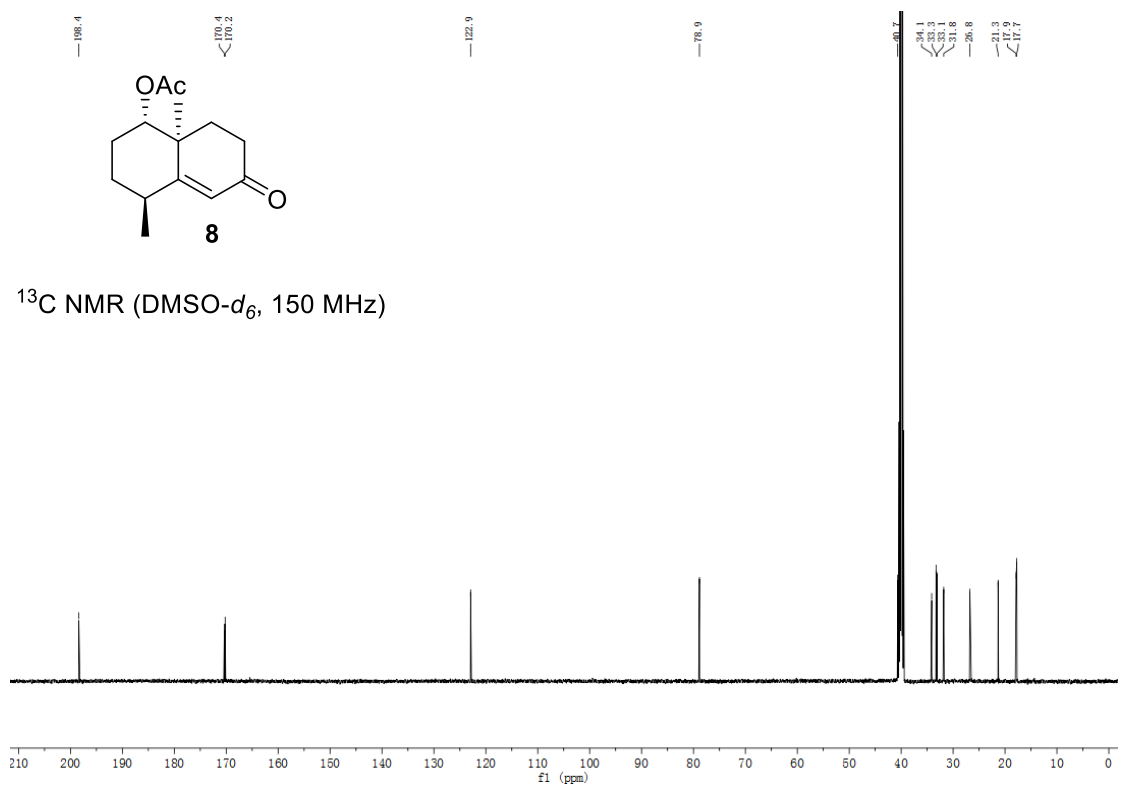
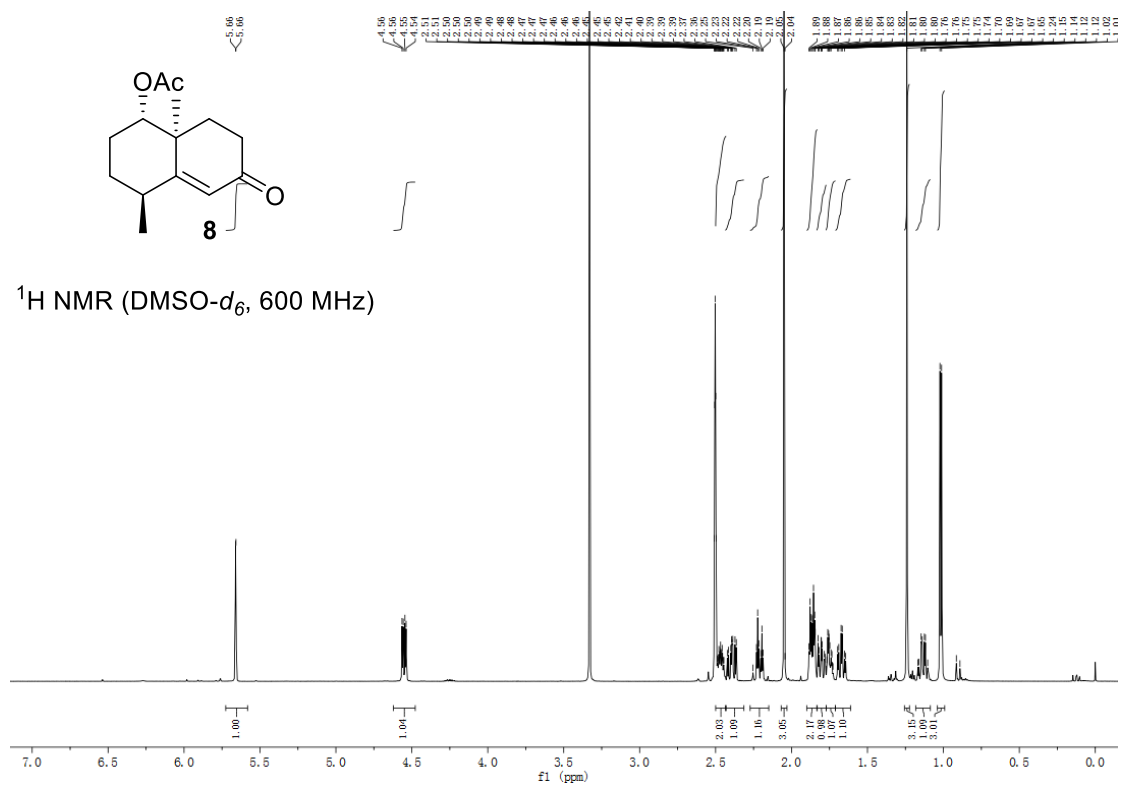
NMR (150 MHz, DMSO-*d*₆) δ 75.2, 72.2, 42.1, 40.4, 33.2, 32.4, 27.0, 26.8, 21.3, 21.1, 17.2, 15.9. **HRMS** (ESI) *m/z* calcd for C₁₂H₂₂O₂Na [M + Na]⁺ 211.1517, found 211.1518.

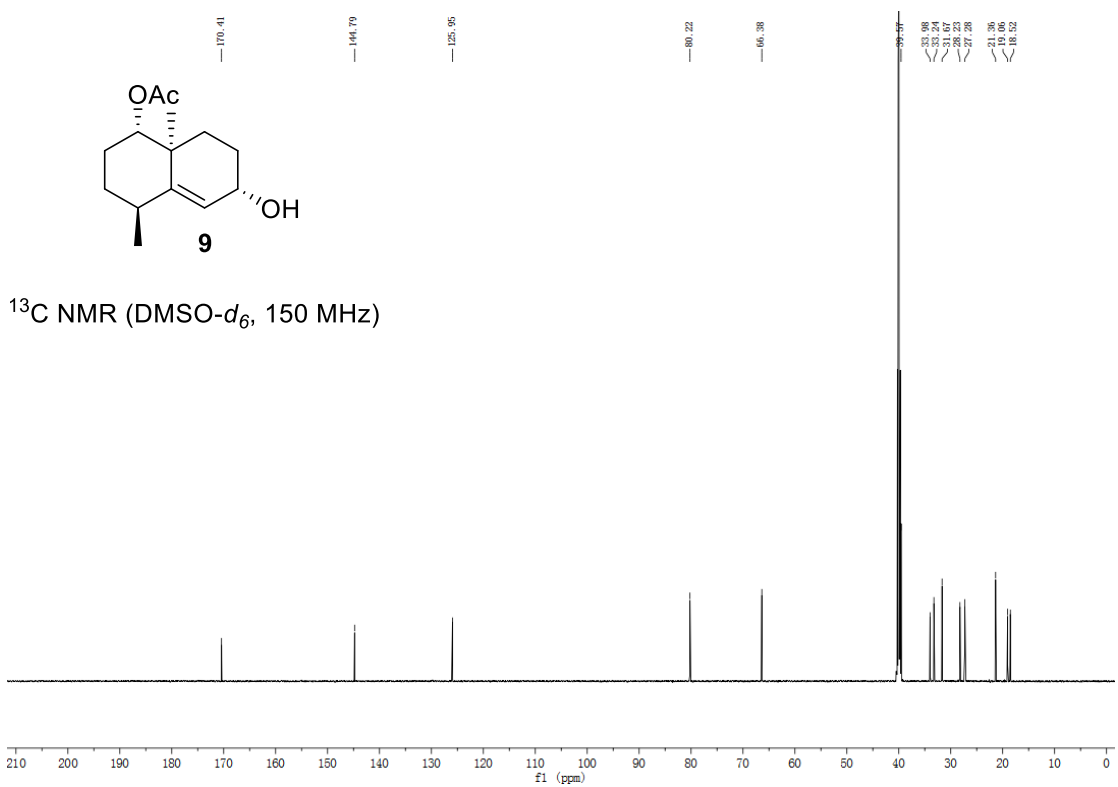
(±)-(1R,4S,4aS,8aR)-4,8a-Dimethyloctahydronaphthalene-1,4a(2H)-diol (1)

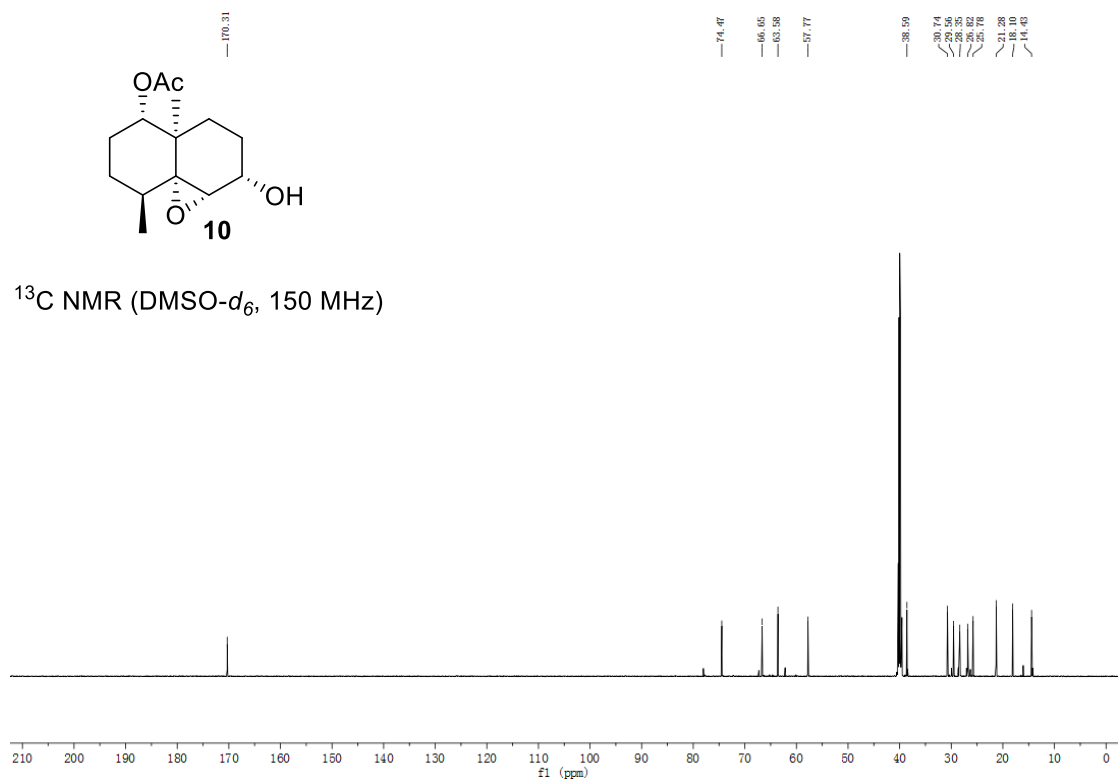
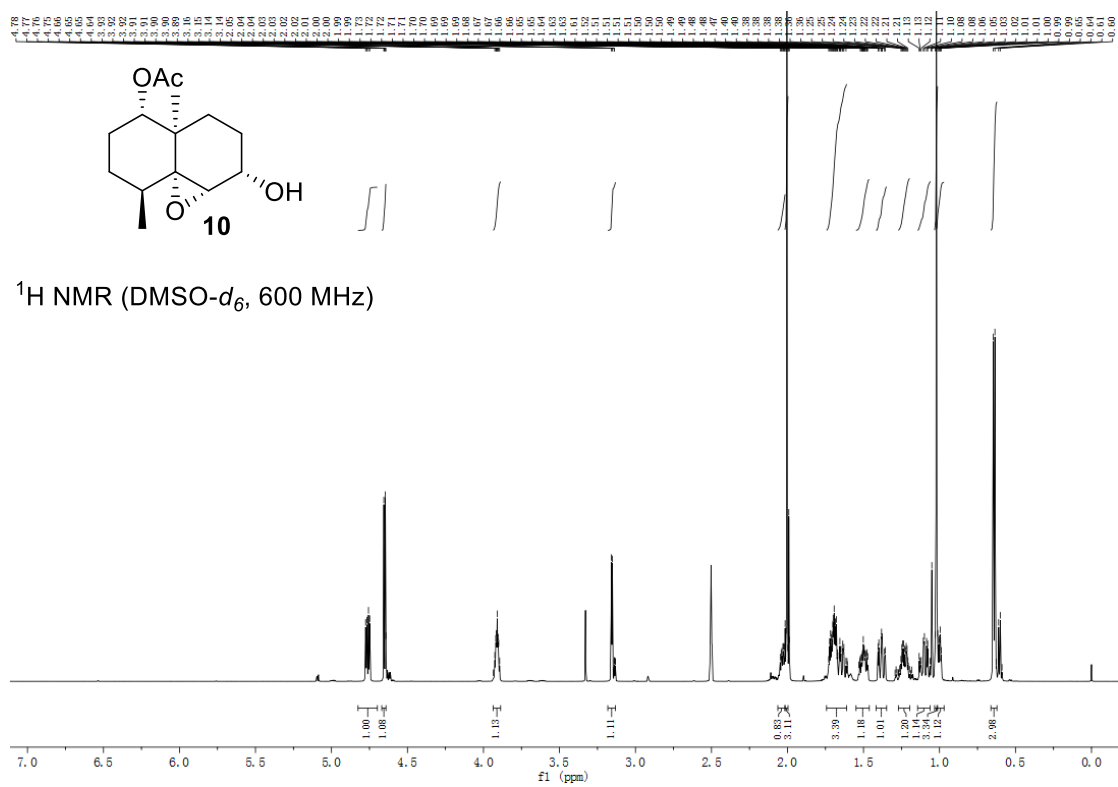


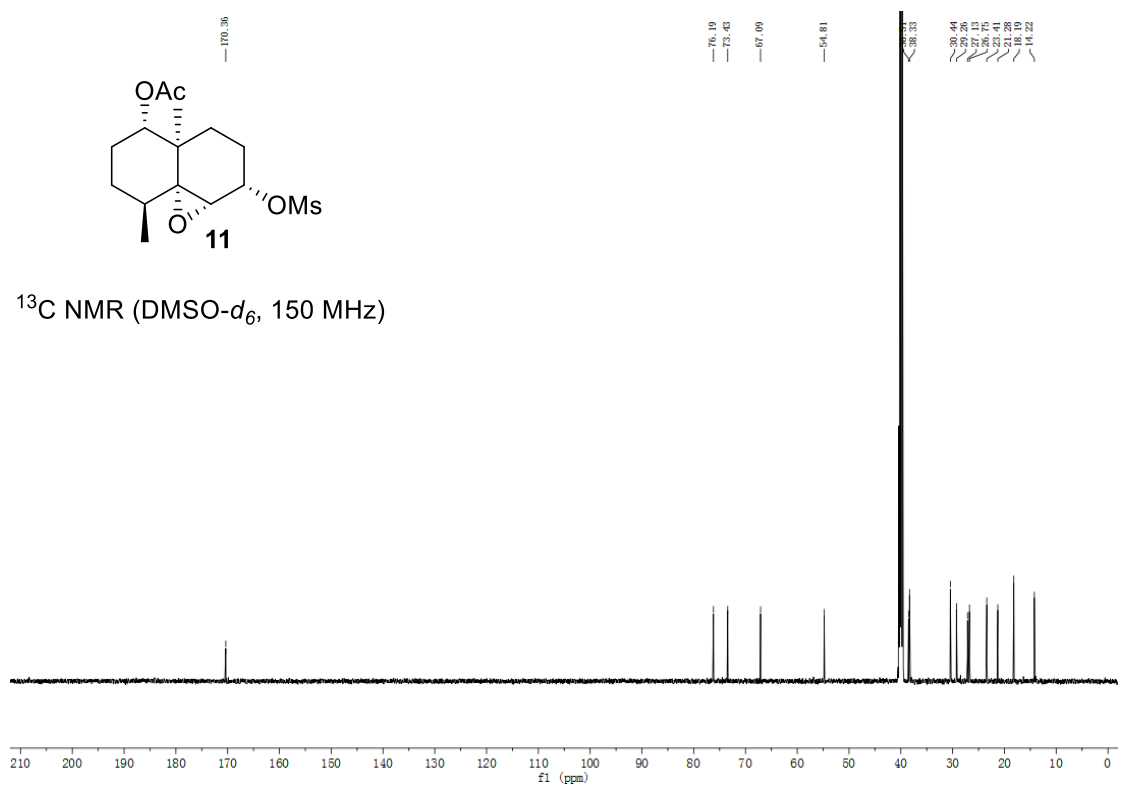
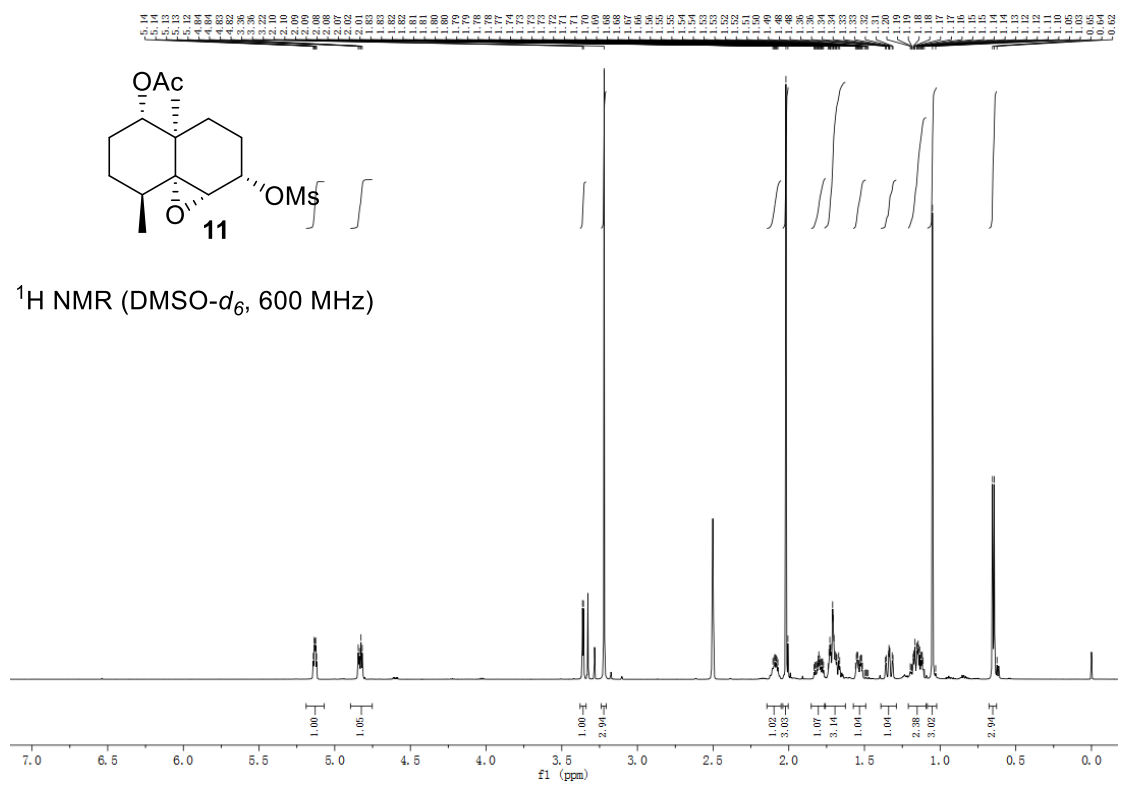
A. Dess-Martin periodinane (320 mg, 0.76 mmol) was added in portions to a solution of **17** (100 mg, 1.01 mmol) in dichloromethane (2.0 mL) at 0 °C, then warmed to room temperature. The resultant mixture was stirred for overnight, and then poured into a 10% solution of sodium bisulfite. The organic layer was separated and washed with 5% solution of NaHCO₃ and with saturated NaCl solution, dried with anhydrous Na₂SO₄ and concentrated. The crude product was redissolved with THF, and added NaBH₄ (40 mg, 1.05 mmol) over 5 min in portions at 0 °C. After stirring for 3.5 h at 0 °C, the reaction was quenched by addition of saturated NH₄Cl solution. The mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. Filtration, concentration, and silica gel column chromatography (EtOAc/petroleum ether = 1:15) gave **1** (78 mg, 78%); B. Followed General procedure VI, compound **26** or **37** as the material, gave the compound **1** (corresponding yield: 85% and 84%) as a colorless oil, *R*_f = 0.50 (EtOAc/petroleum ether = 1:2); ¹H NMR (600 MHz, DMSO-*d*₆) δ 5.38 (d, *J* = 4.5 Hz, 1H), 4.76 (brs, 1H), 3.27 (m, 1H), 2.21 (td, *J* = 13.0, 4.7 Hz, 1H), 1.89 (m, 1H), 1.67 (dt, *J* = 13.2, 4.9 Hz, 1H), 1.61 (m, 1H), 1.60 (m, 1H), 1.51 (m, 1H), 1.49 (m, 1H), 1.44 (m, 1H), 1.40 (m, 1H), 1.36 (m, 1H), 1.19 (m, 1H), 1.13 (brt, *J* = 13.5 Hz, 1H), 0.89 (s, 3H), 0.78 (brd, *J* = 13.0 Hz, 1H), 0.70 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 76.0, 75.1, 39.6, 34.3, 30.6, 30.1, 28.8, 25.5, 21.2, 20.6, 20.3, 15.3.













C[C@H]1[C@@H](O)[C@H]2CCCC[C@@H]1C2

¹H NMR (DMSO-*d*₆, 600 MHz)

Chemical shift (ppm): 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0




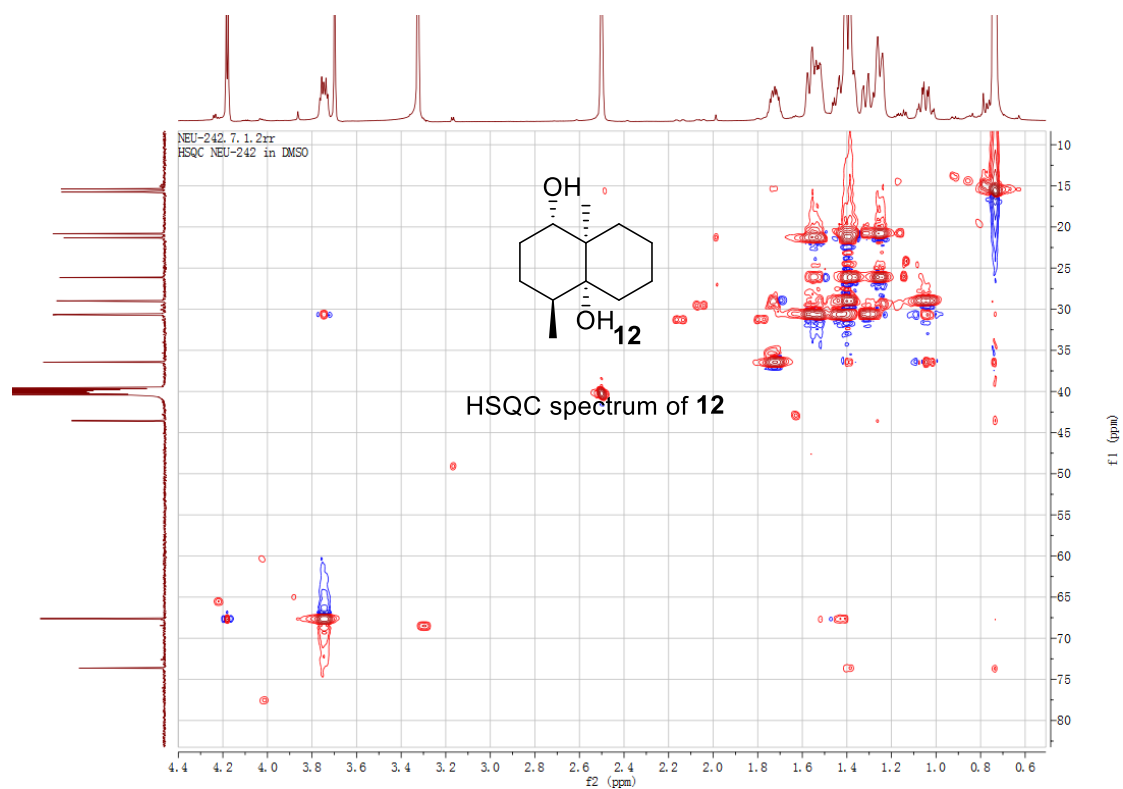
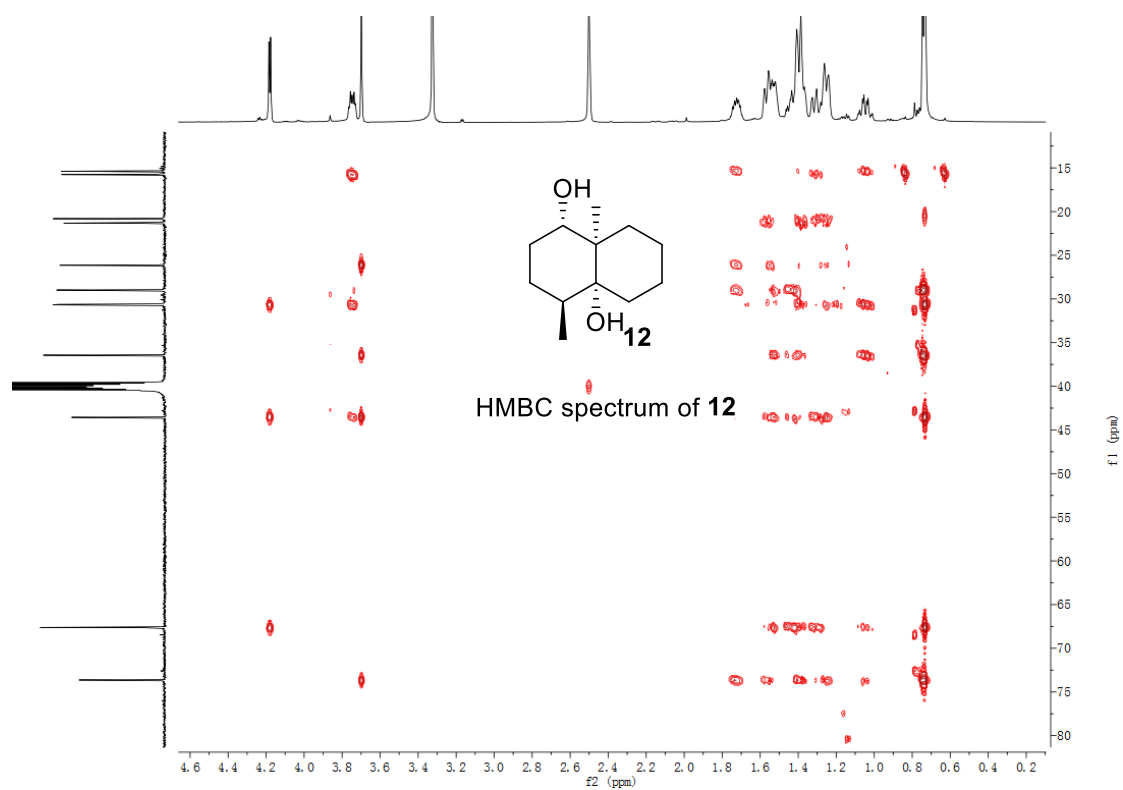
13C NMR (DMSO-*d*₆, 150 MHz)

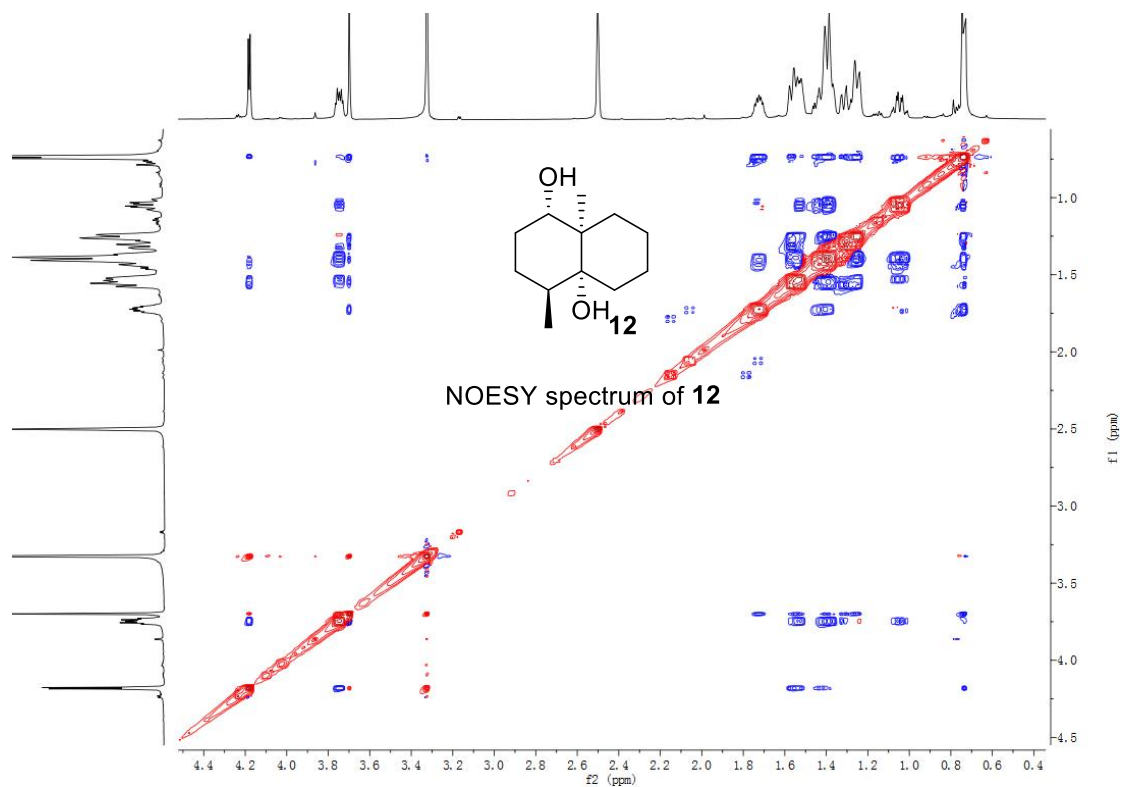
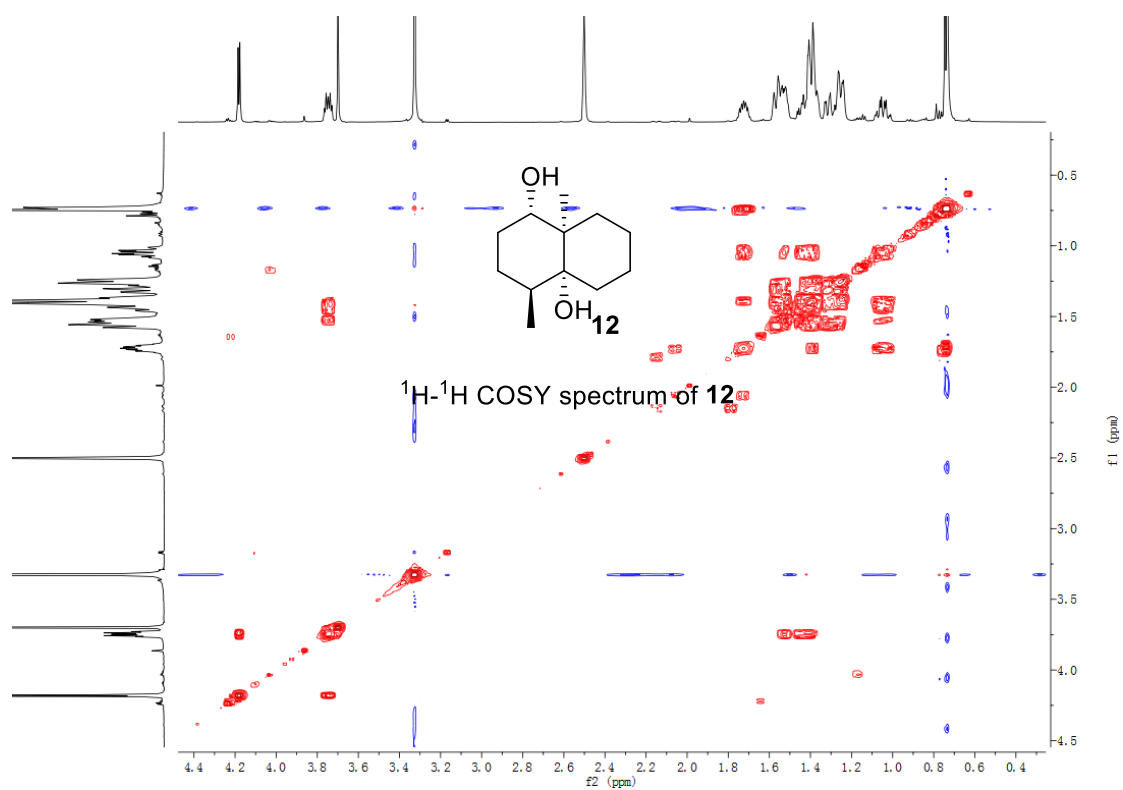
Chemical structure of **12** is shown above the spectrum.

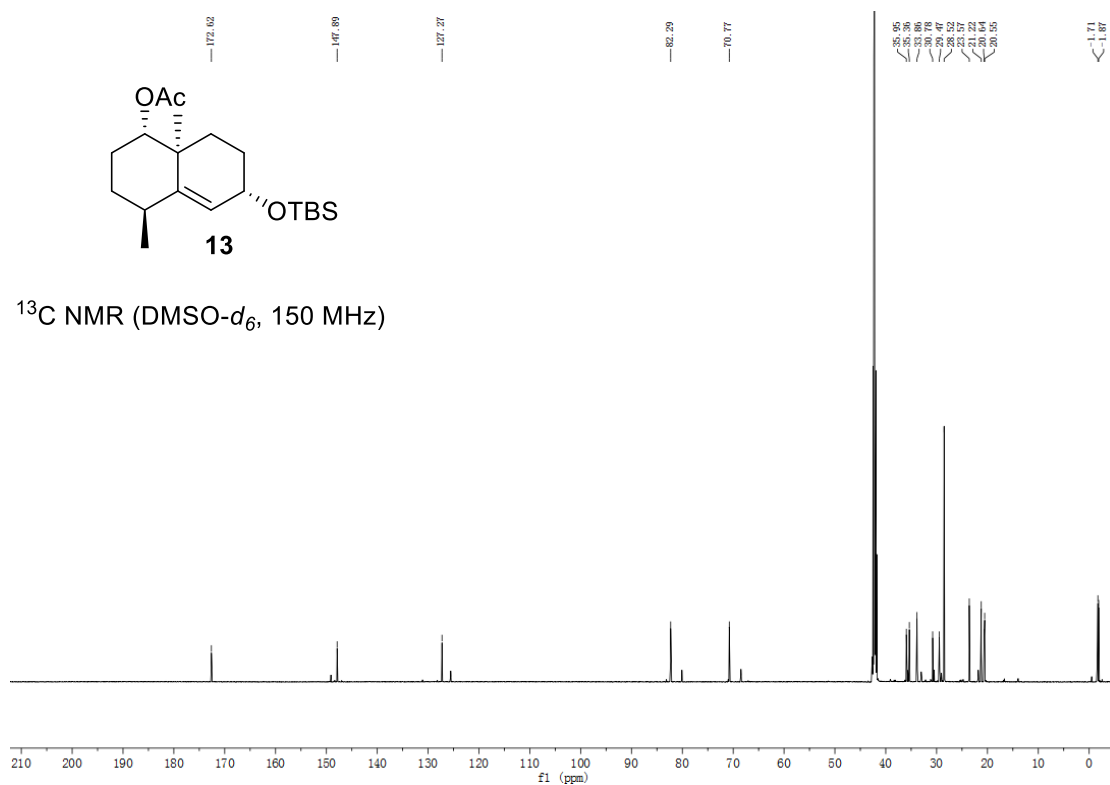
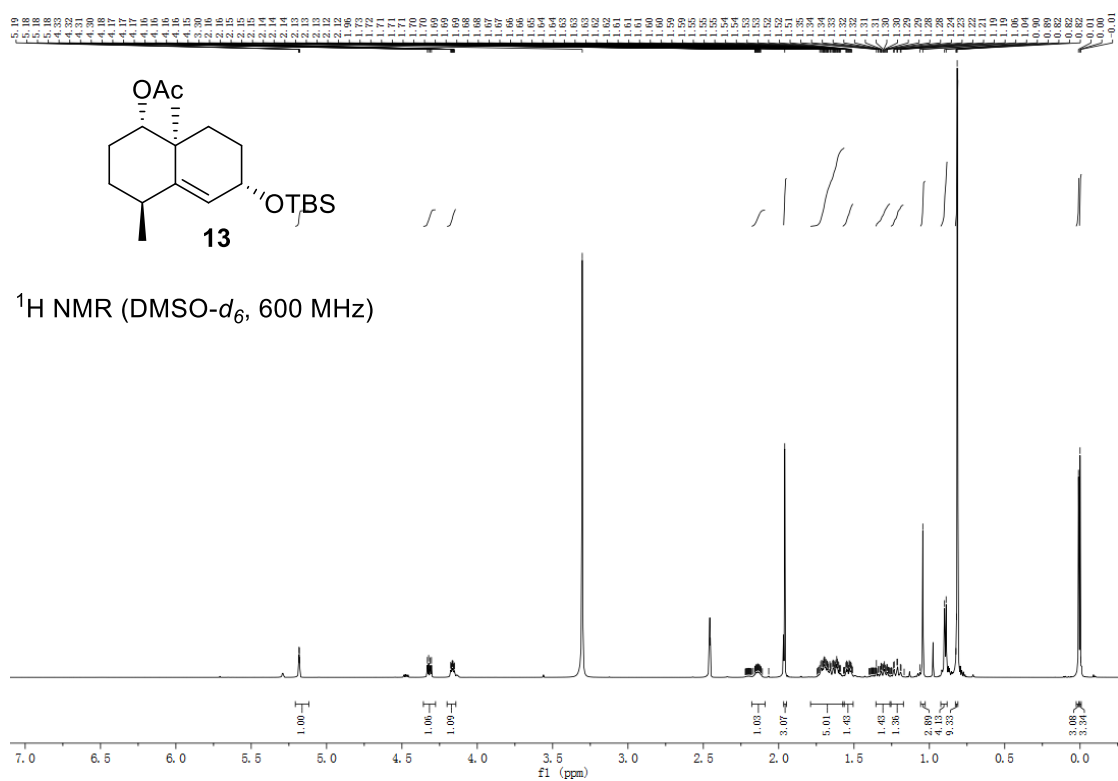
The spectrum displays the following chemical shifts (ppm):

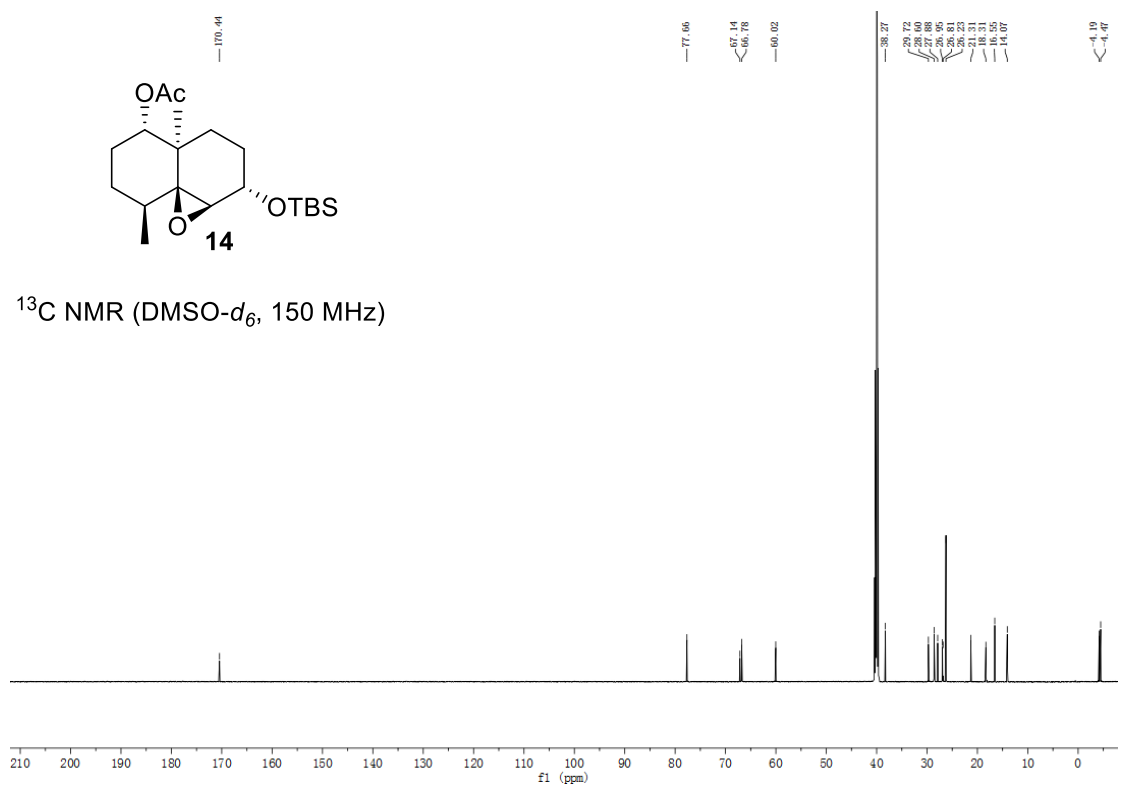
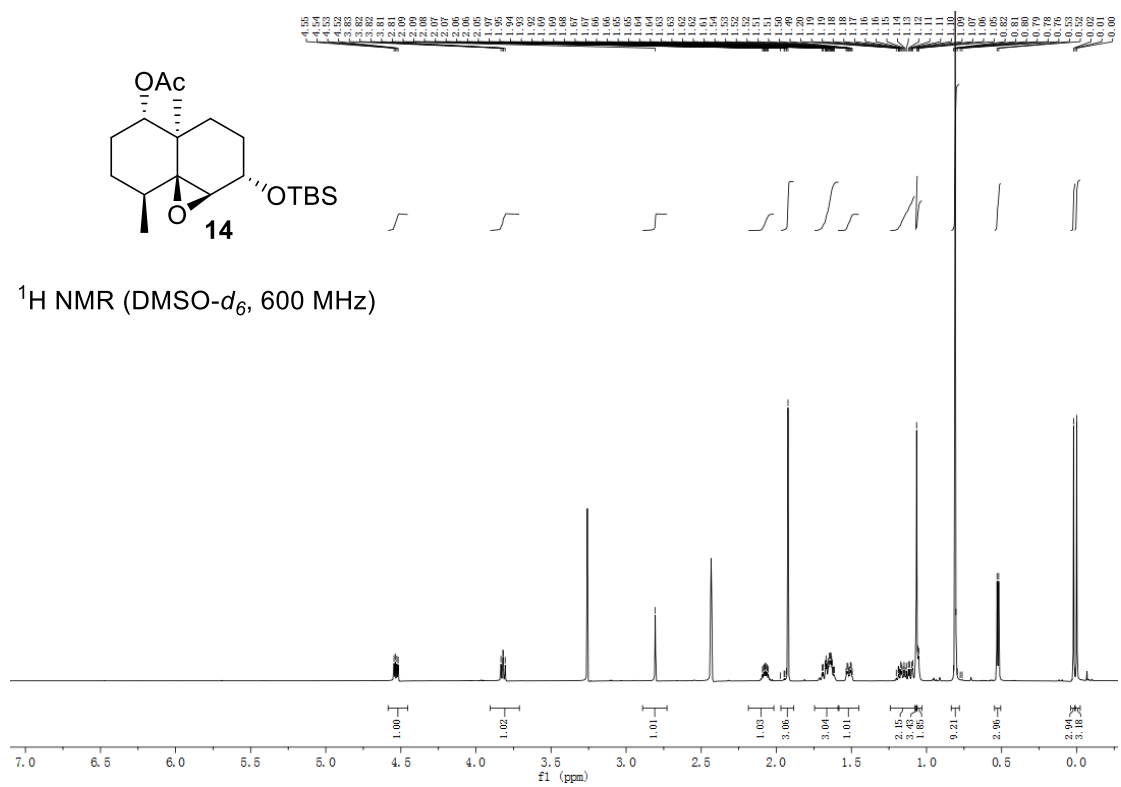
- 73.63
- 67.62
- 41.55
- 36.44
- 30.68
- 29.62
- 29.98
- 28.14
- 21.52
- 20.81
- 15.76
- 15.39

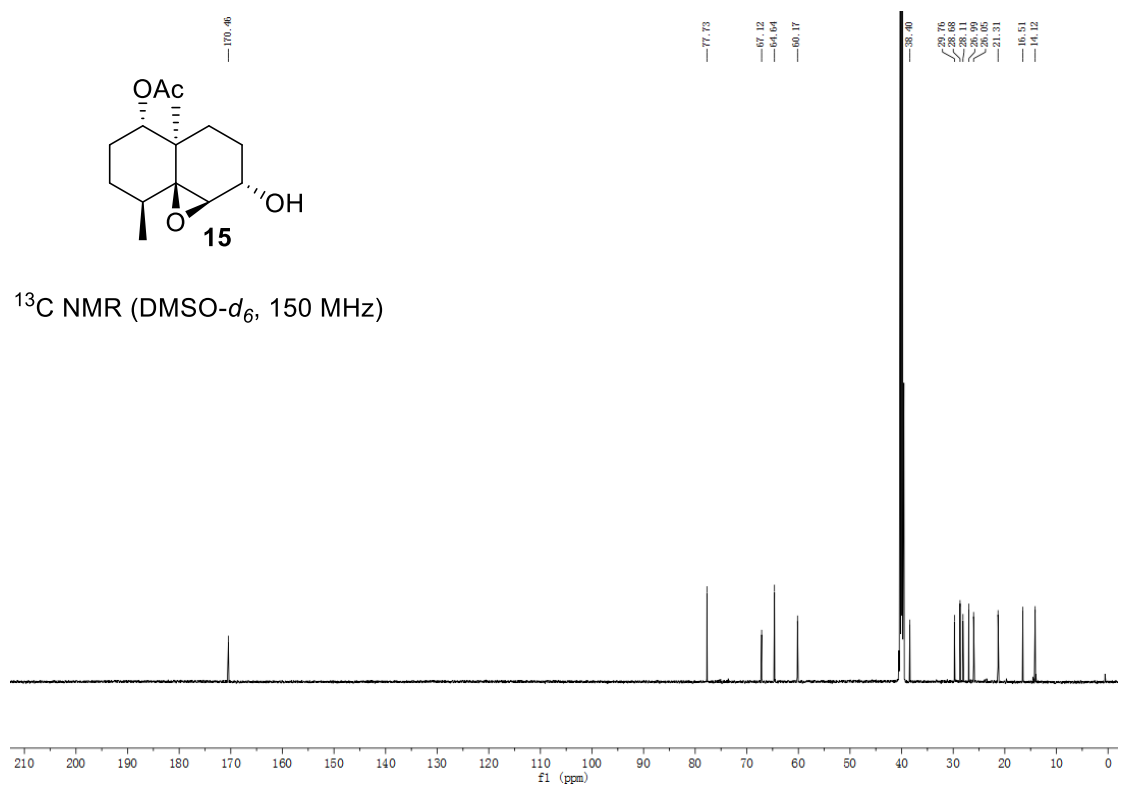
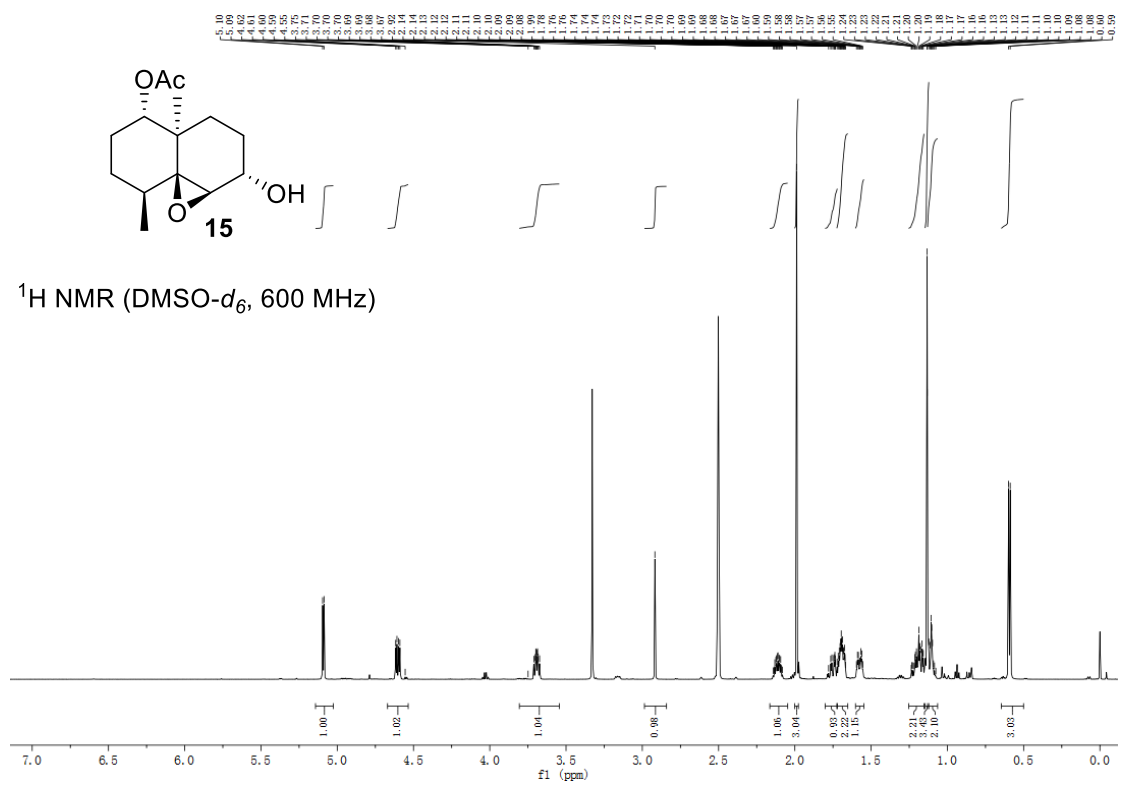


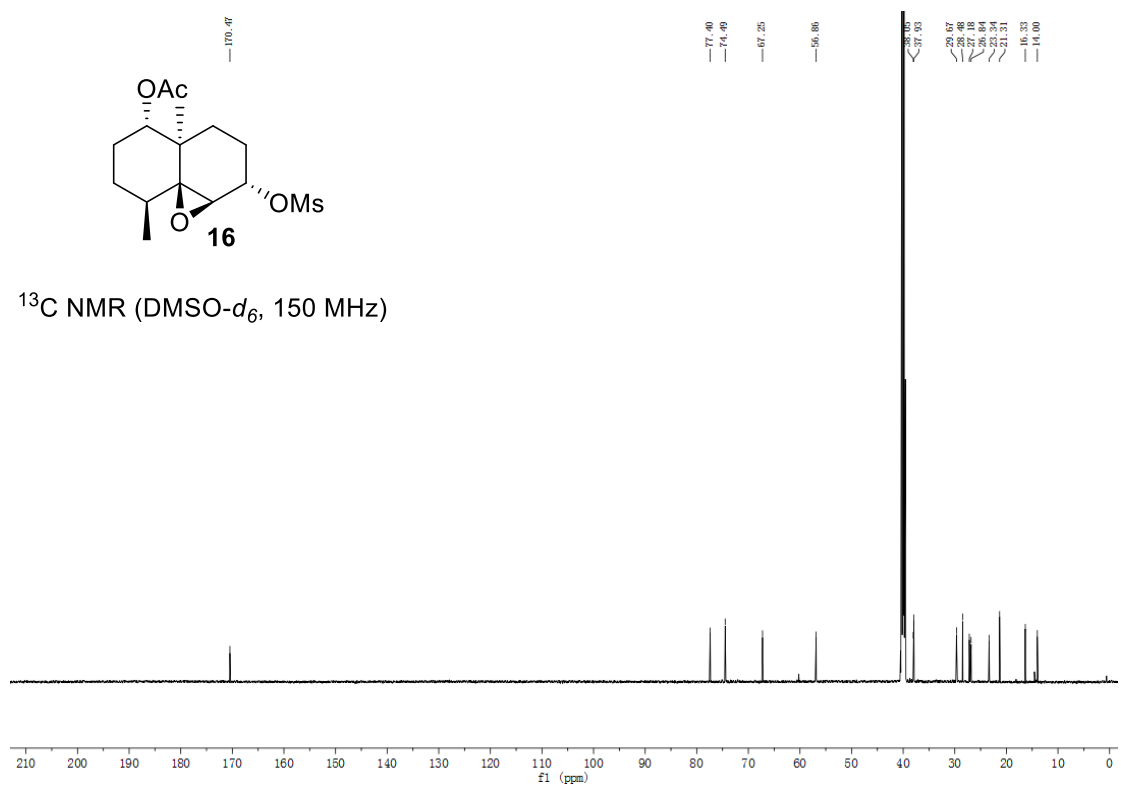
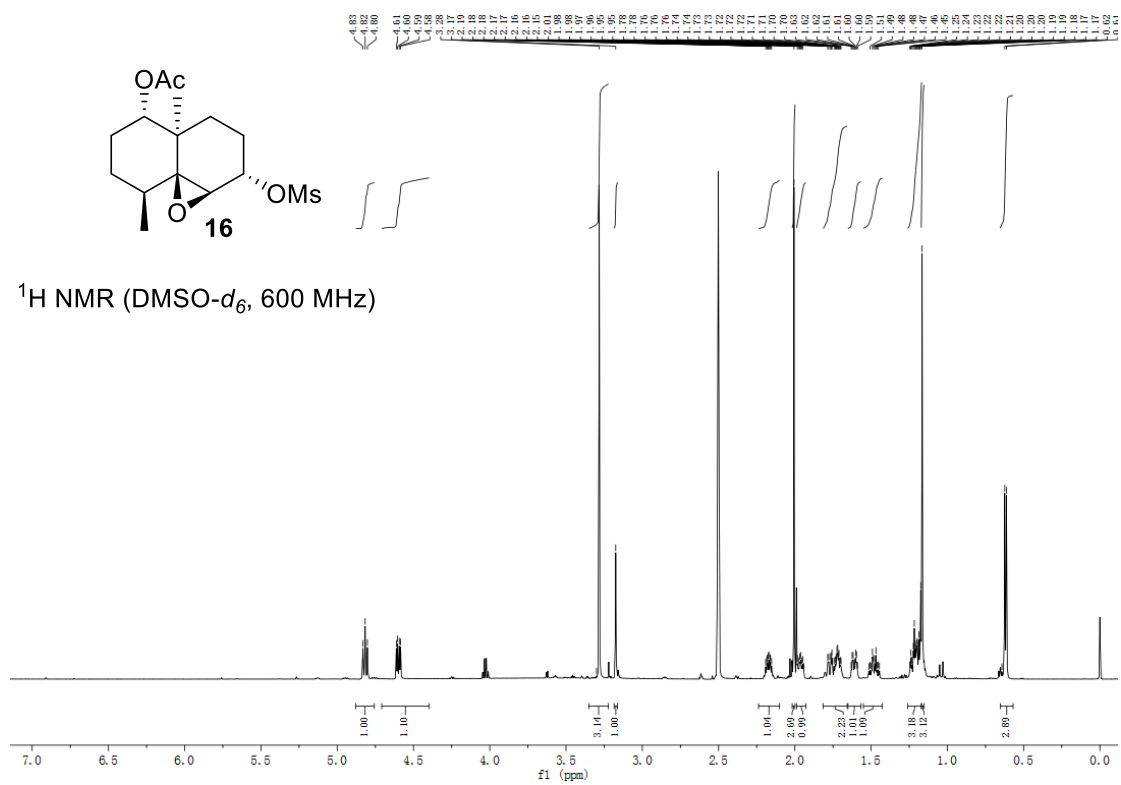


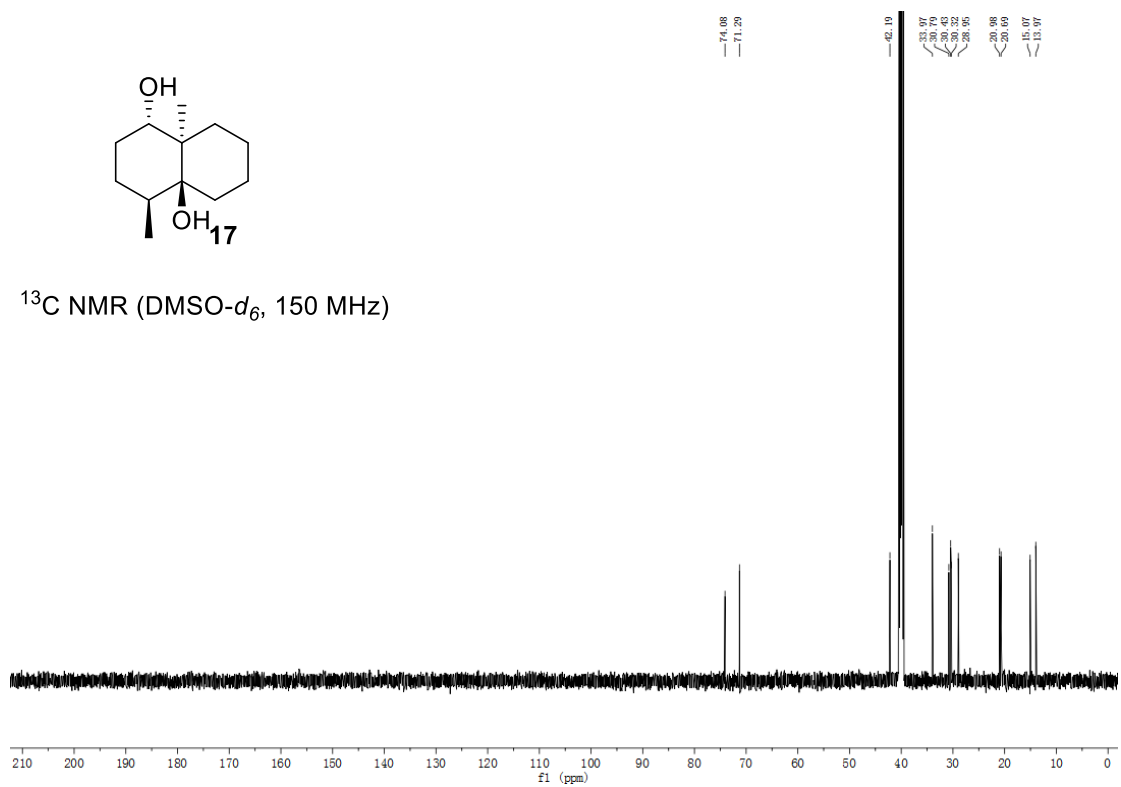
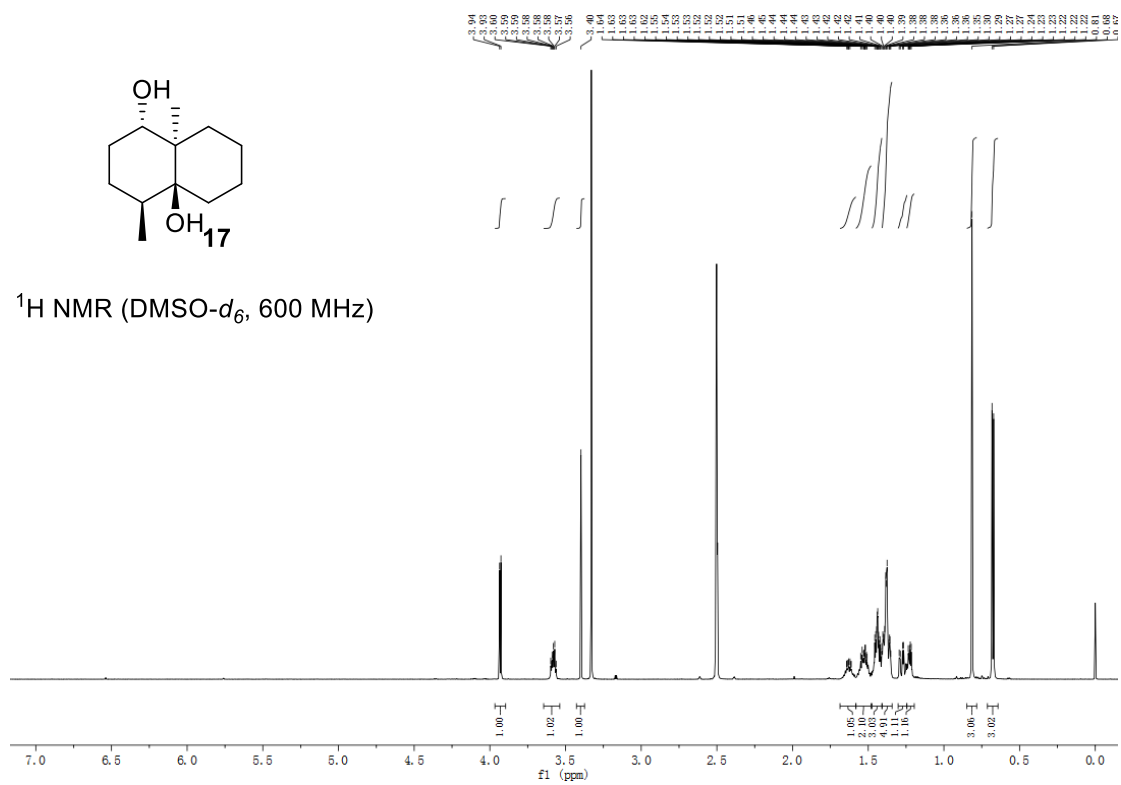


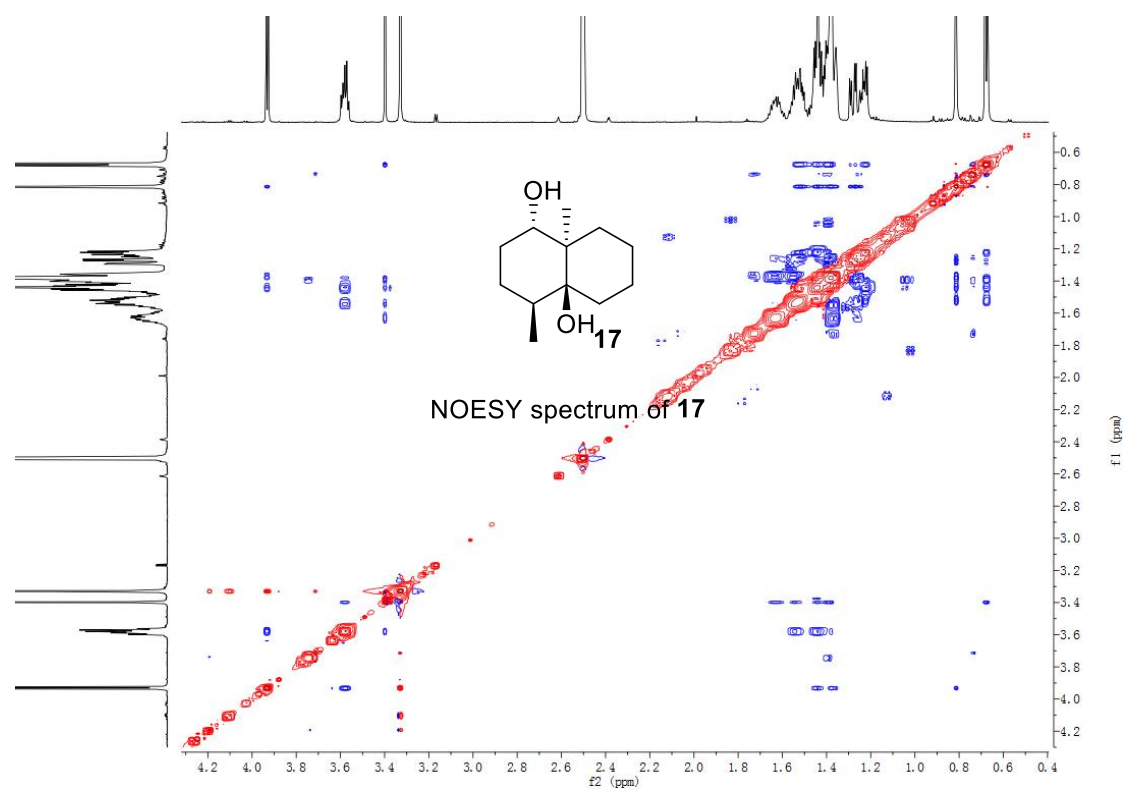


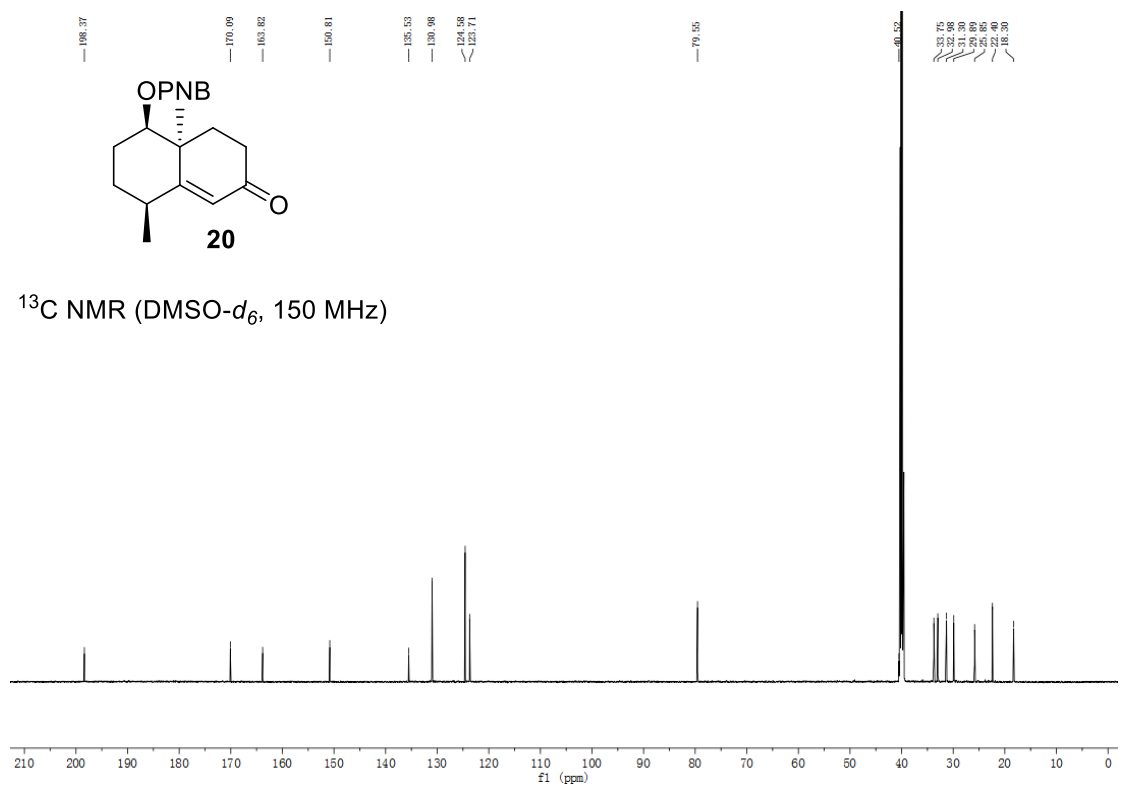
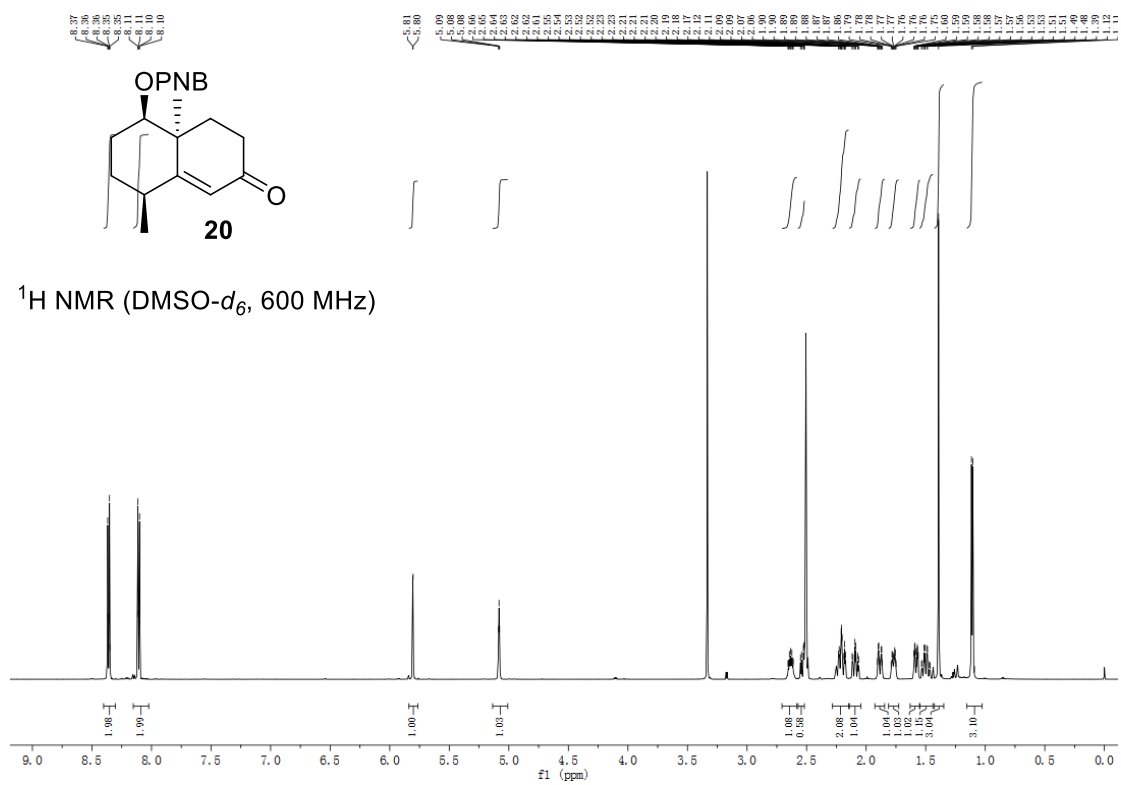














Chemical Structure of 21: C[C@H]1C=CC(=O)C2=CC=CC=C2C1

¹H NMR (DMSO-*d*₆, 600 MHz) Data:

Chemical Shift (ppm)	Integration
0.0	3.09
1.0	3.11
1.5	3.10
2.0-2.5	1.04, 1.11, 1.10, 1.07
2.6	1.02
5.5-6.0	1.10, 1.00

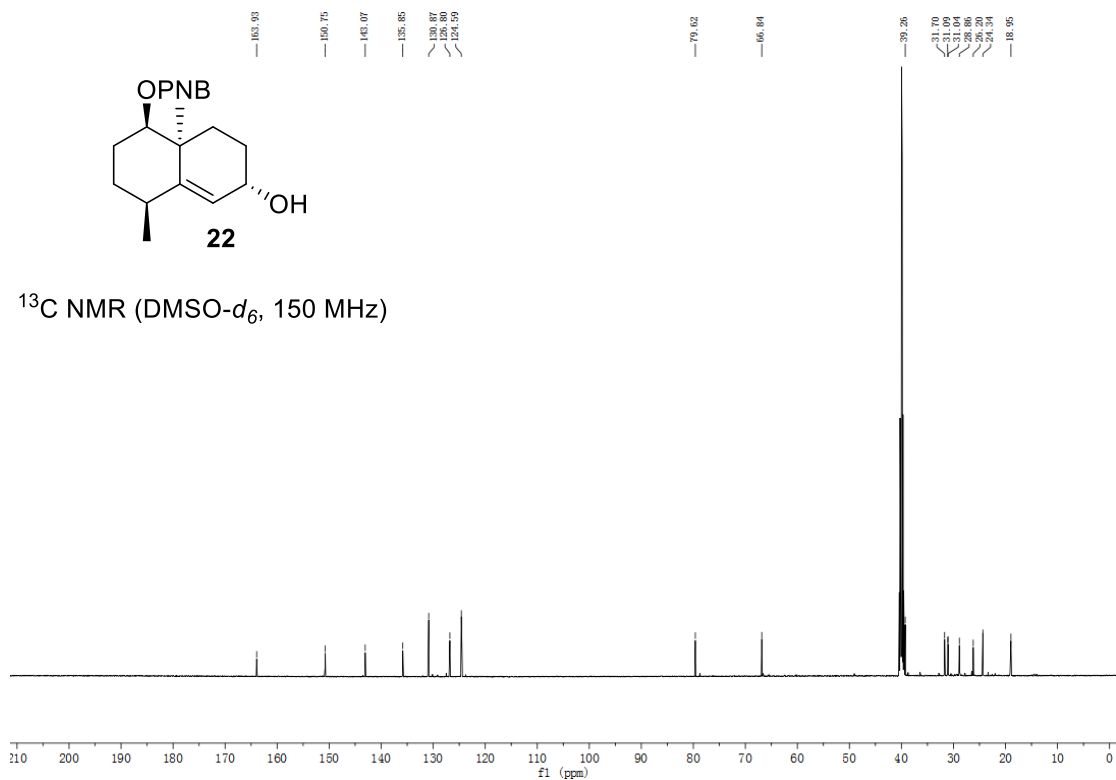
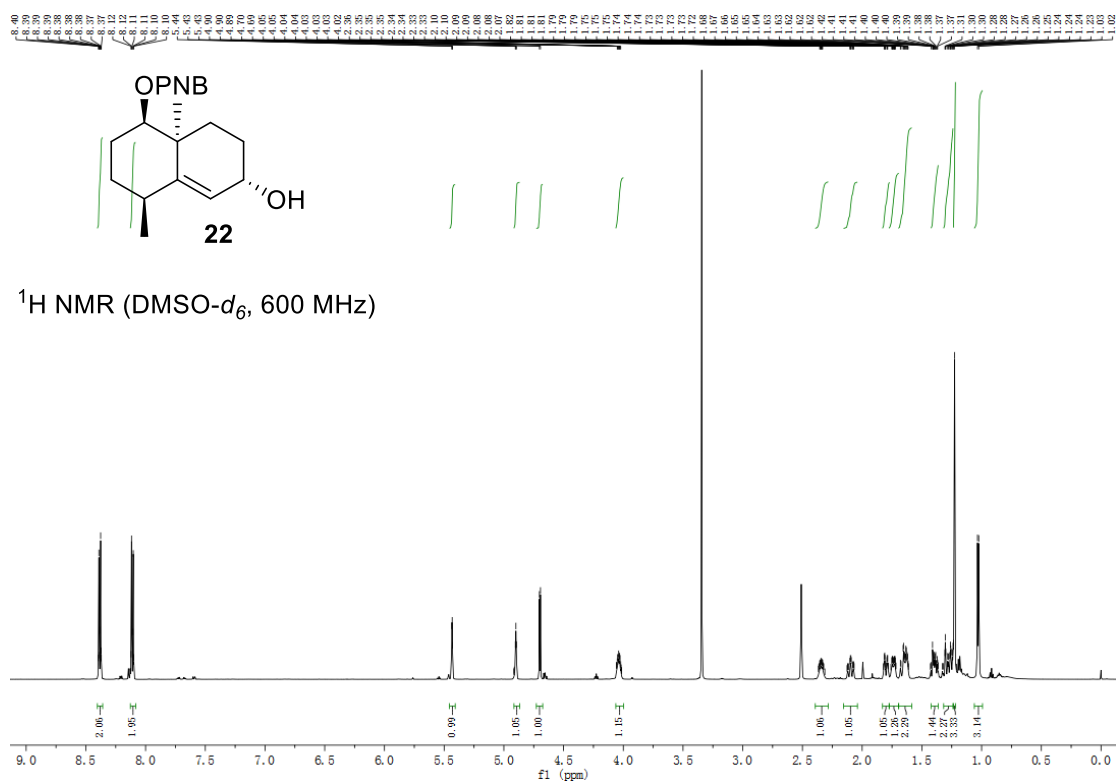


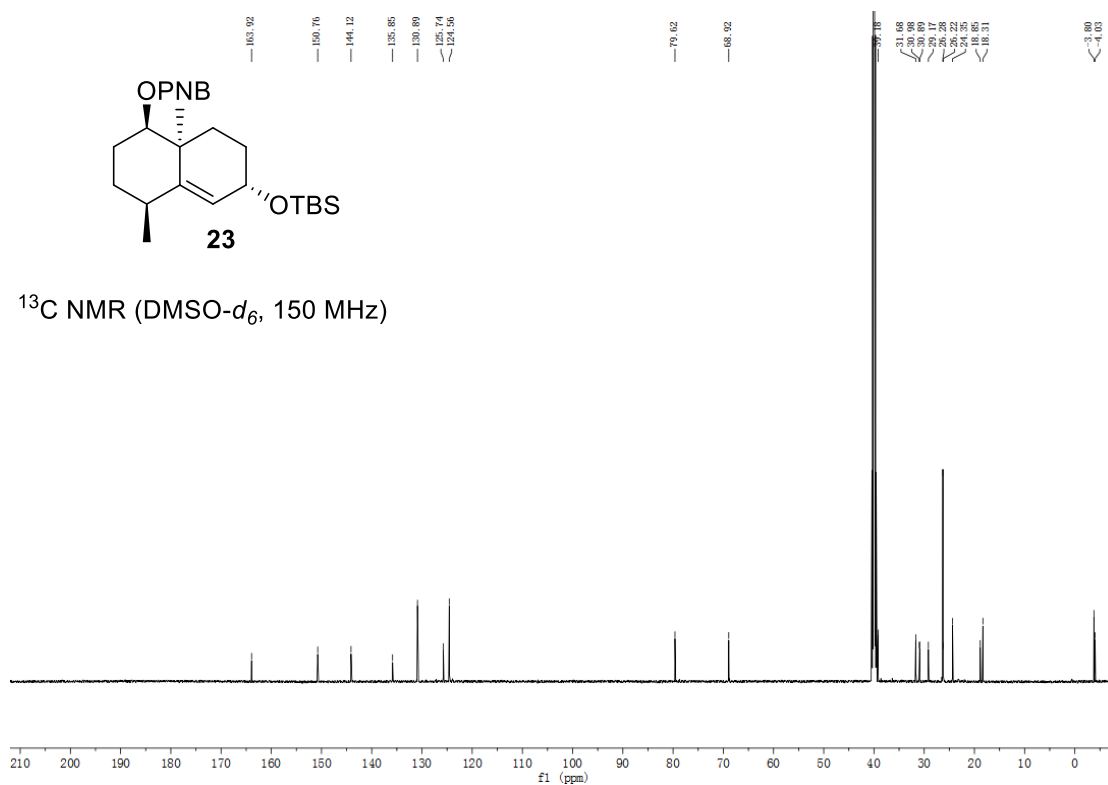
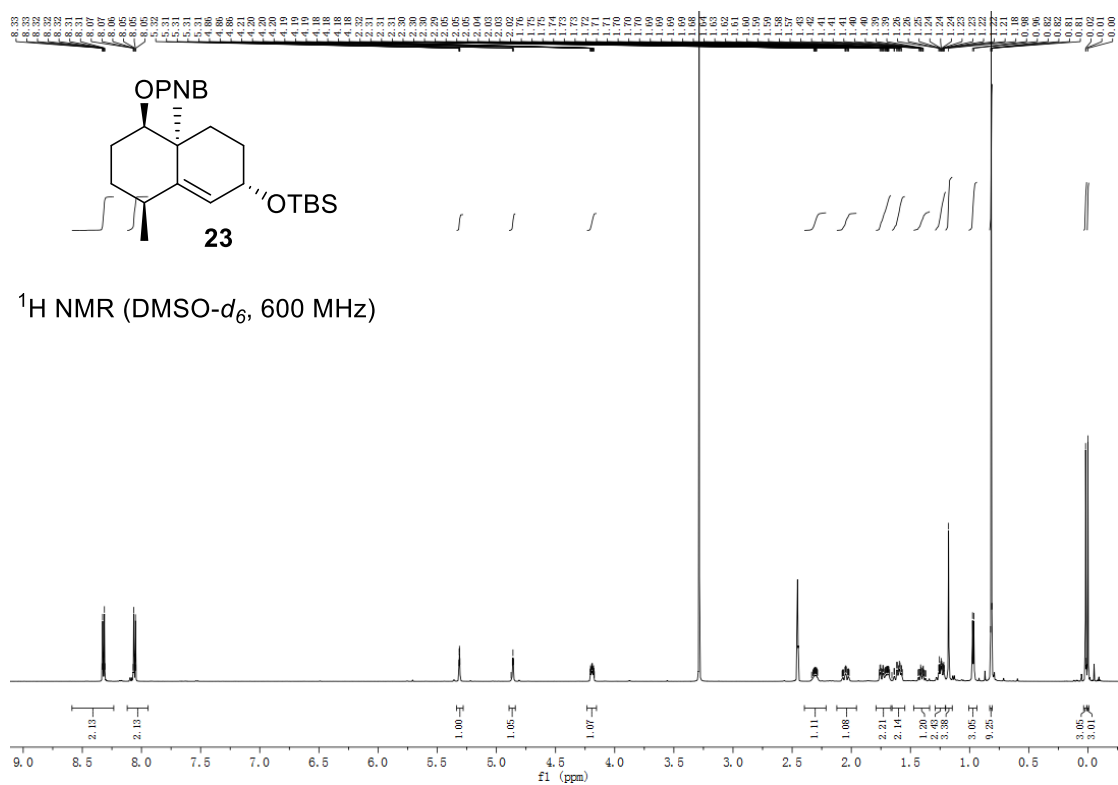
21

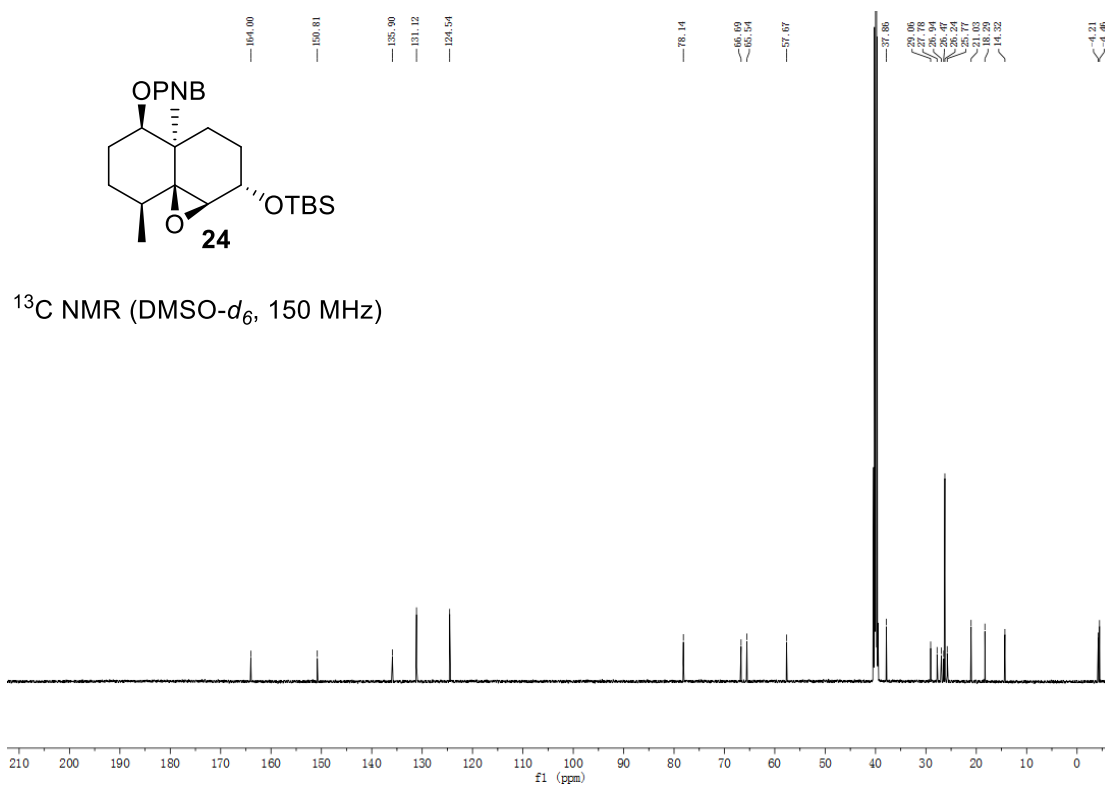
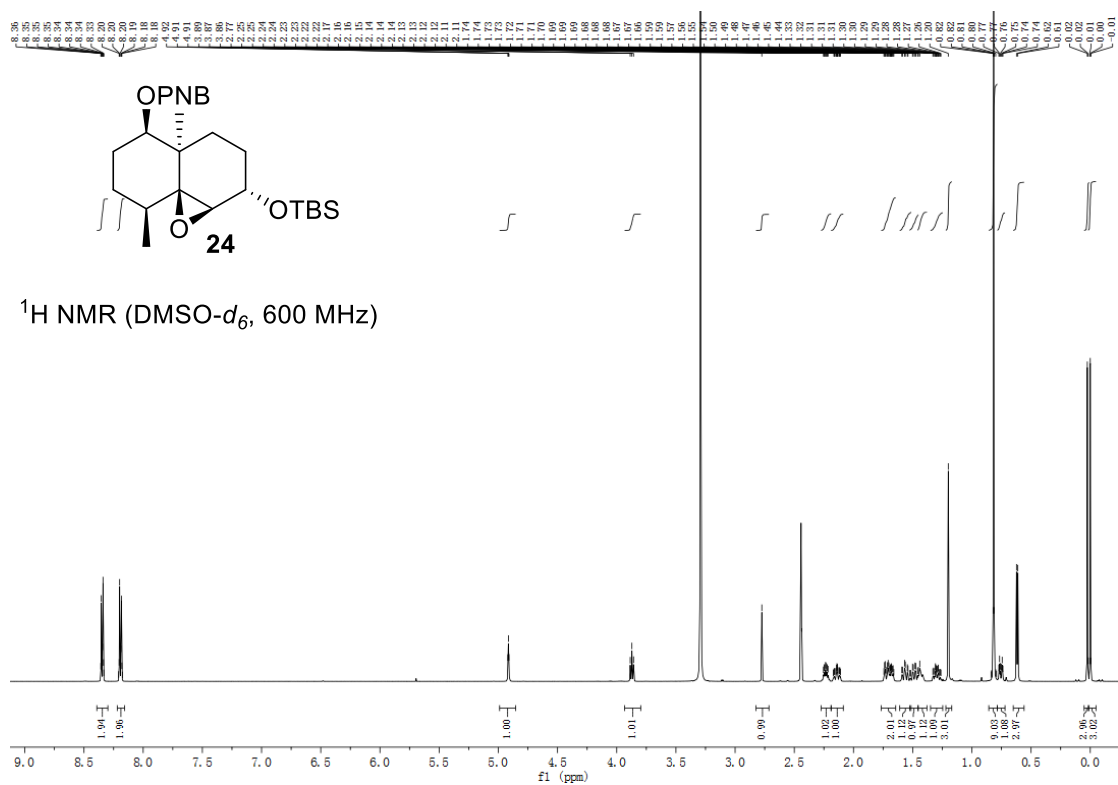
^{13}C NMR (DMSO- d_6 , 150 MHz)

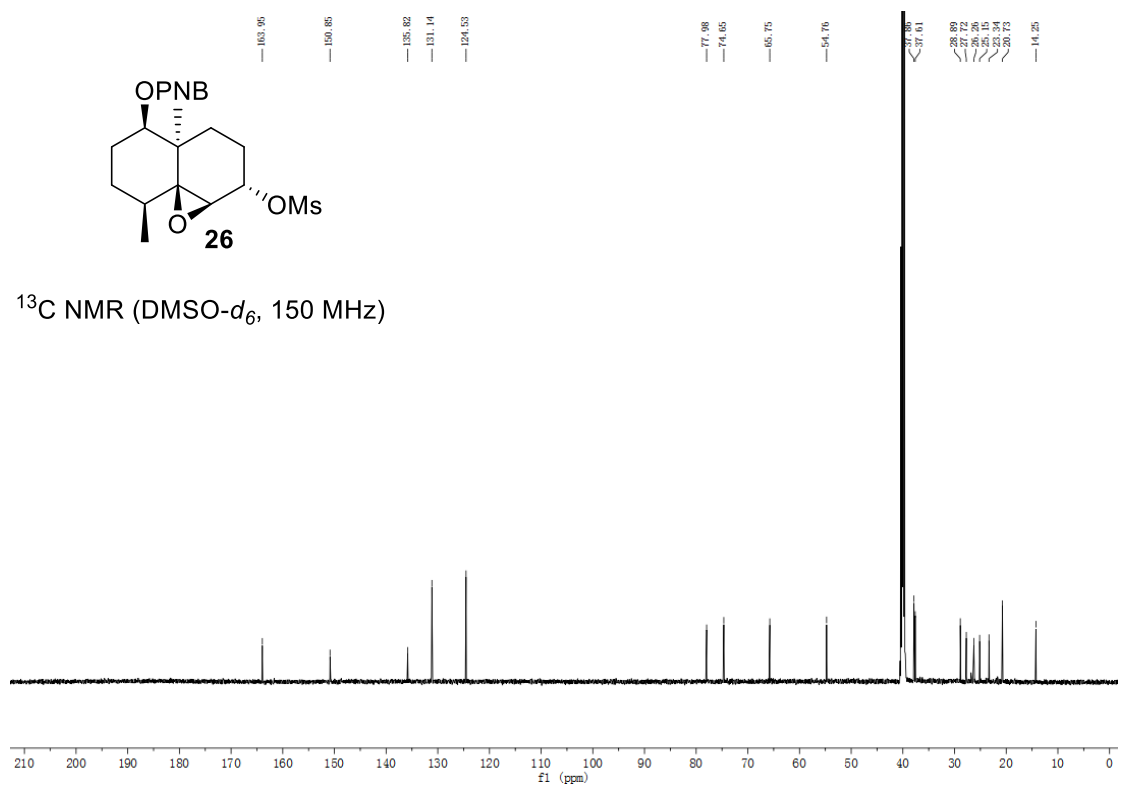
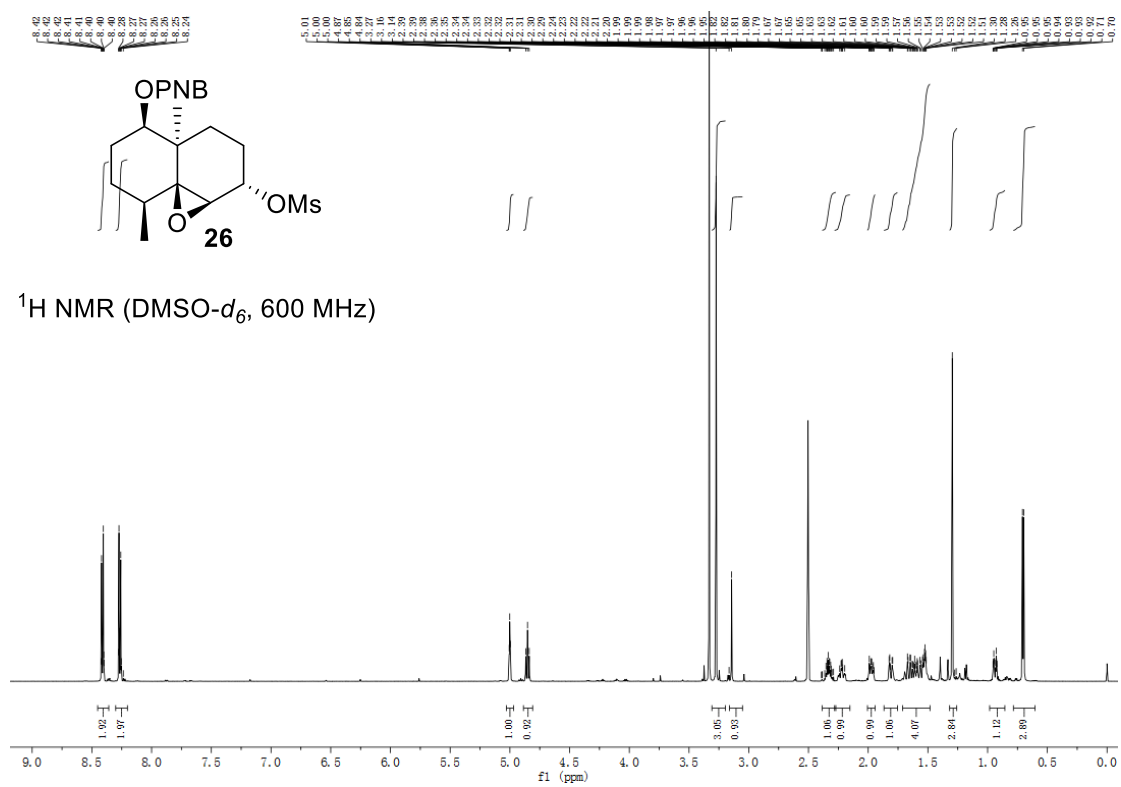
Chemical structure of **21** is shown above the spectrum. The structure is a bicyclic compound with a cyclohexene ring fused to a cyclohexanone ring. The cyclohexene ring has a methyl group at the 2-position (wedge) and a methyl group at the 3-position (dash). The cyclohexanone ring has a methyl group at the 2-position (wedge).

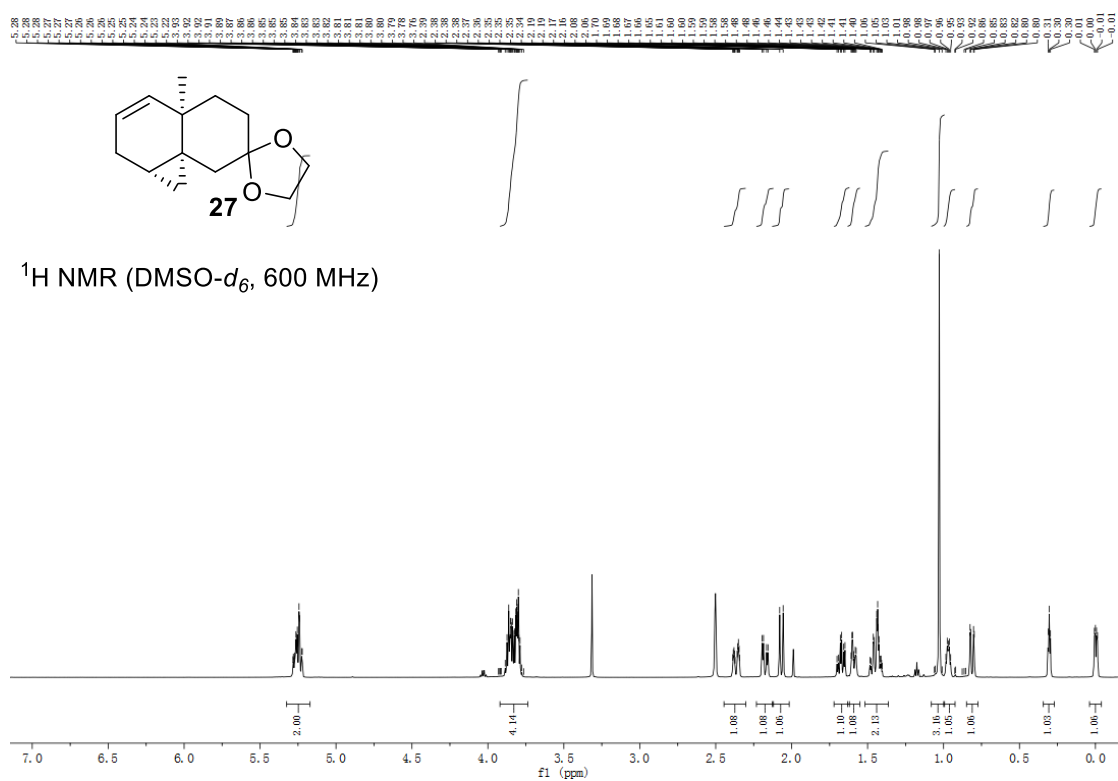
Peak list (ppm): 198.60, 172.97, 136.23, 124.08, 120.71, 39.82, 35.86, 33.84, 33.83, 31.86, 25.17, 17.15.

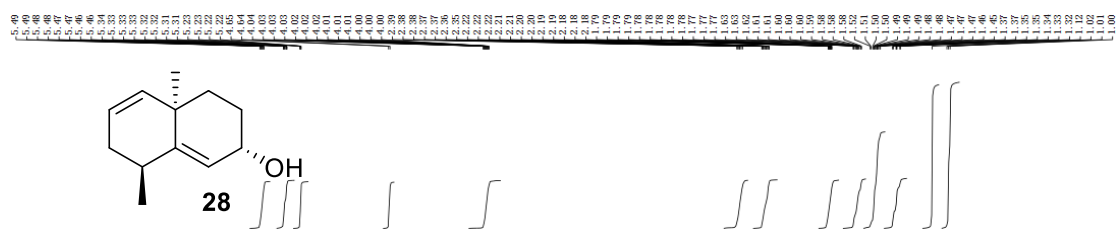




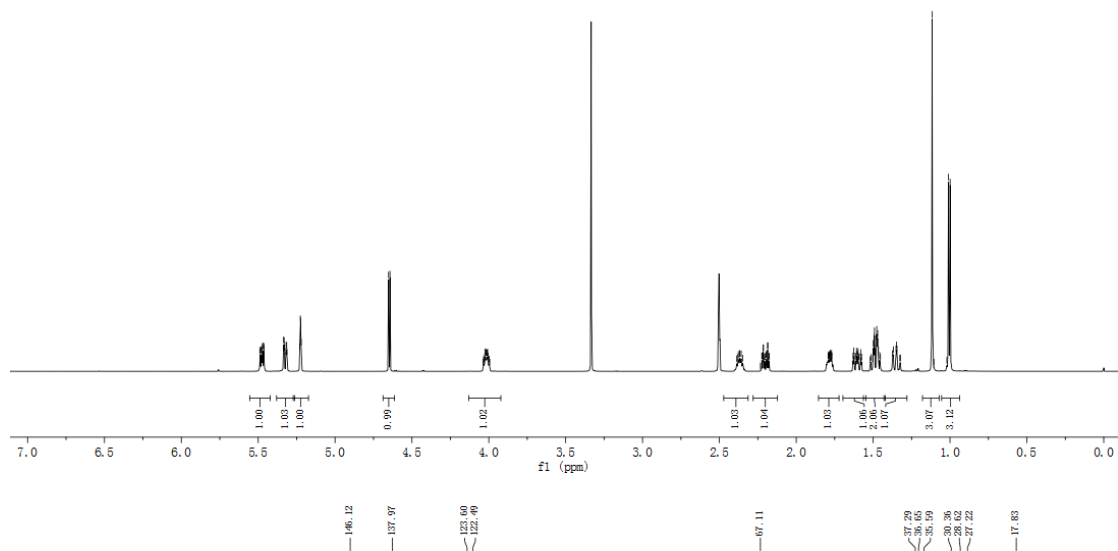




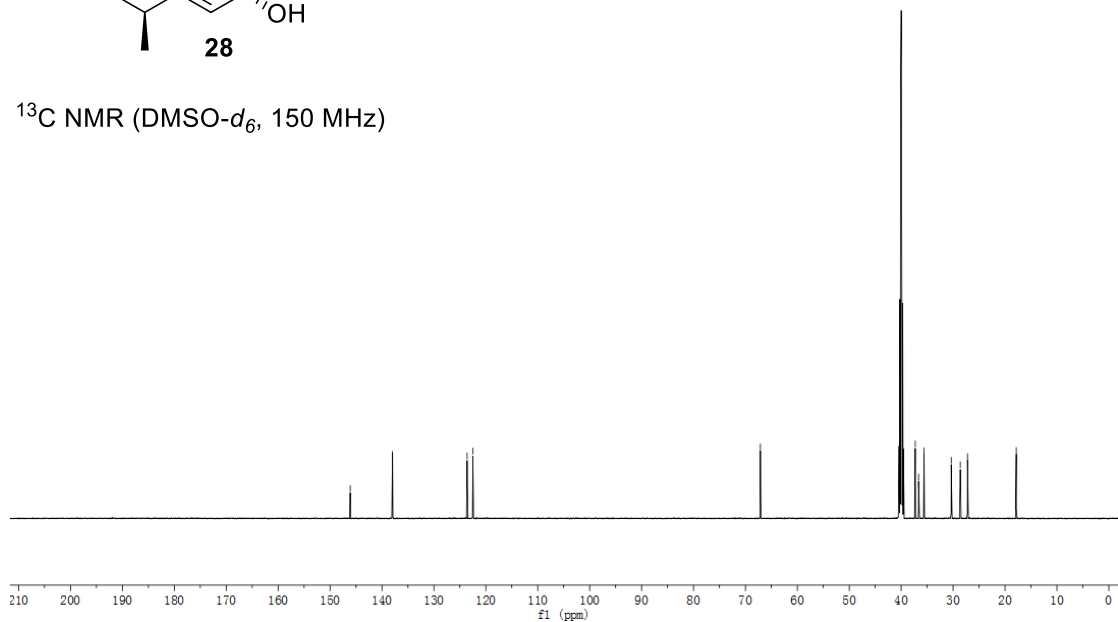


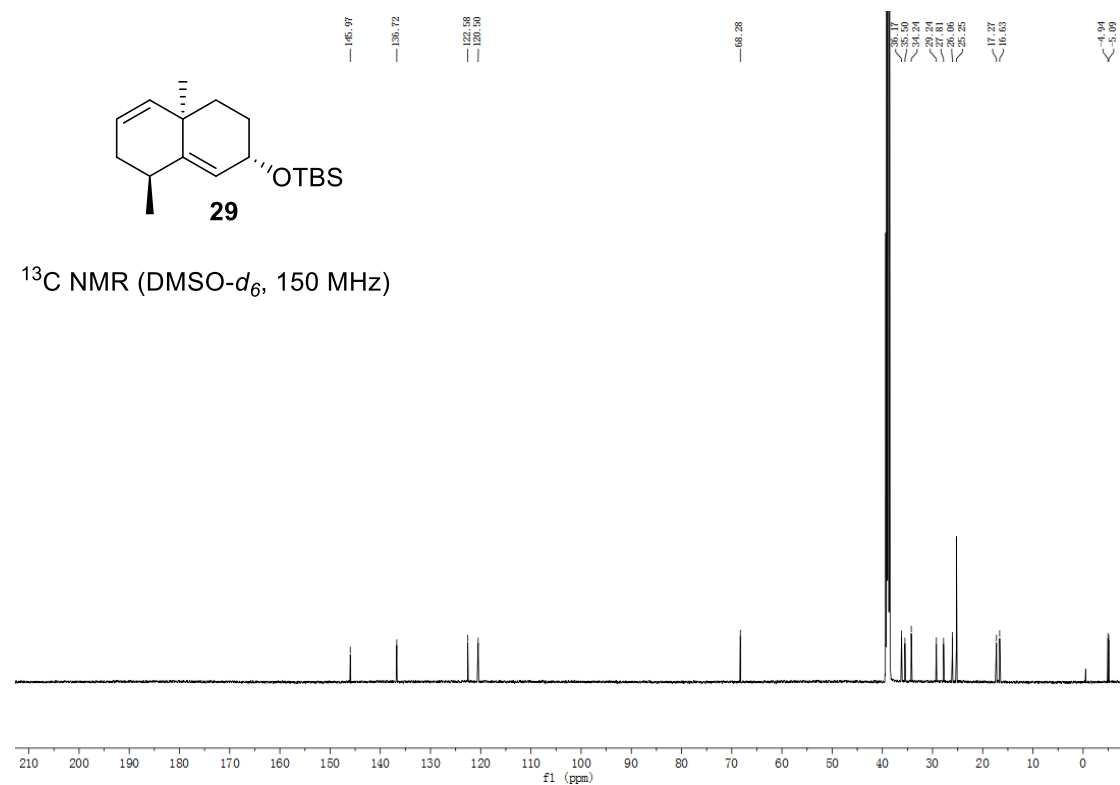
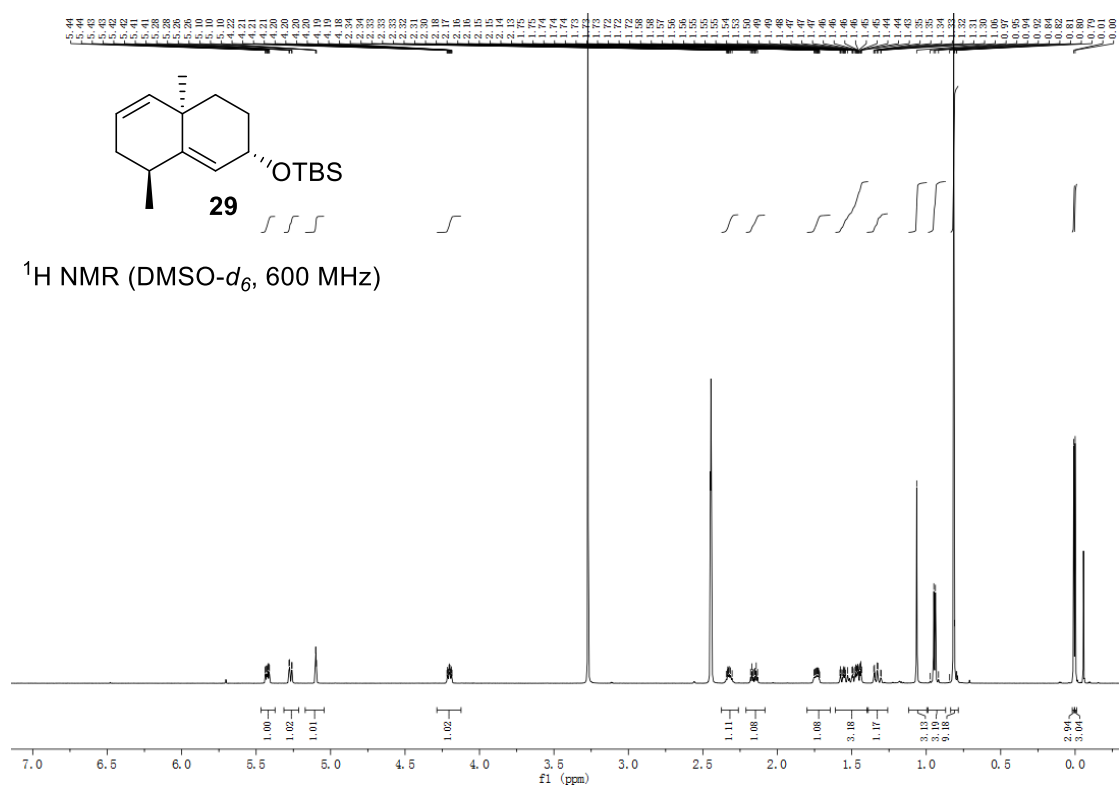


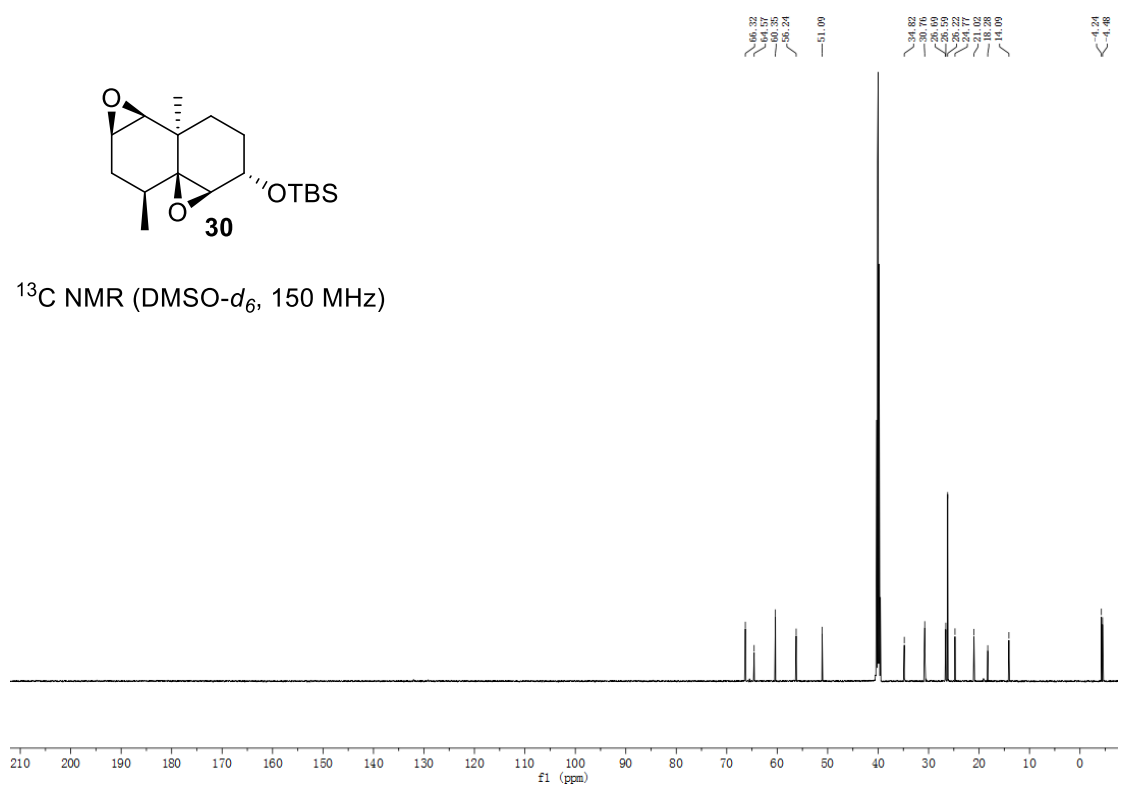
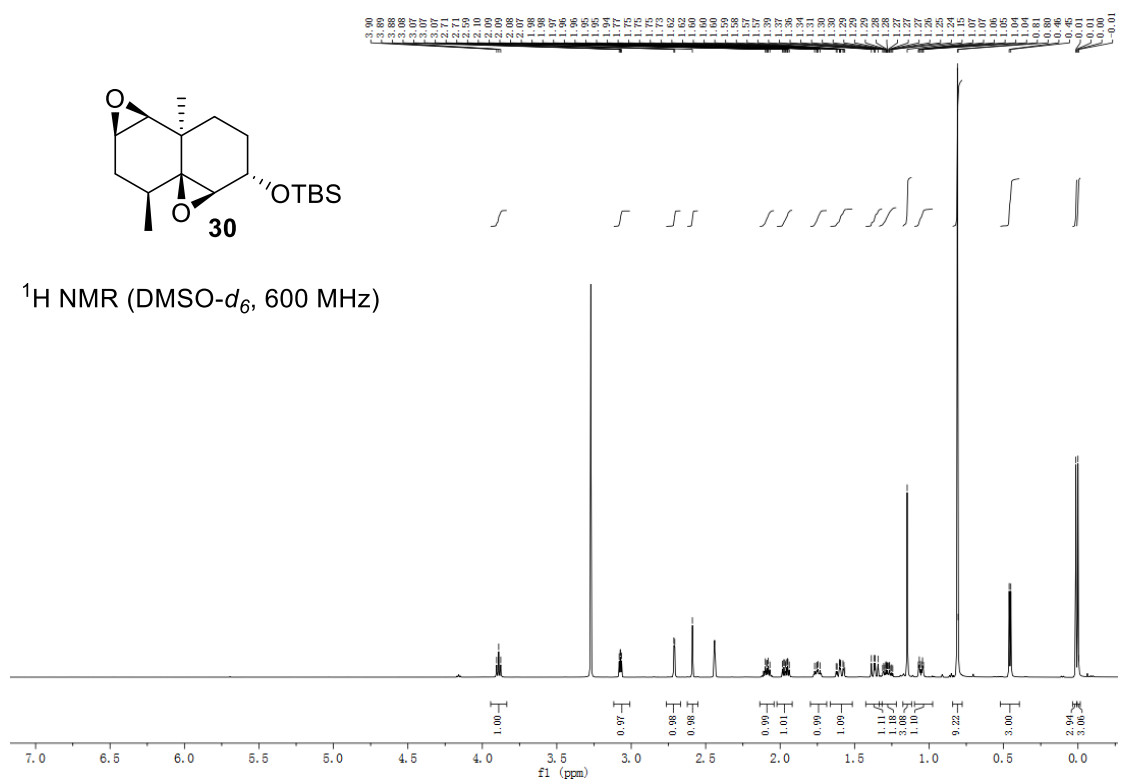
¹H NMR (DMSO-*d*₆, 600 MHz)

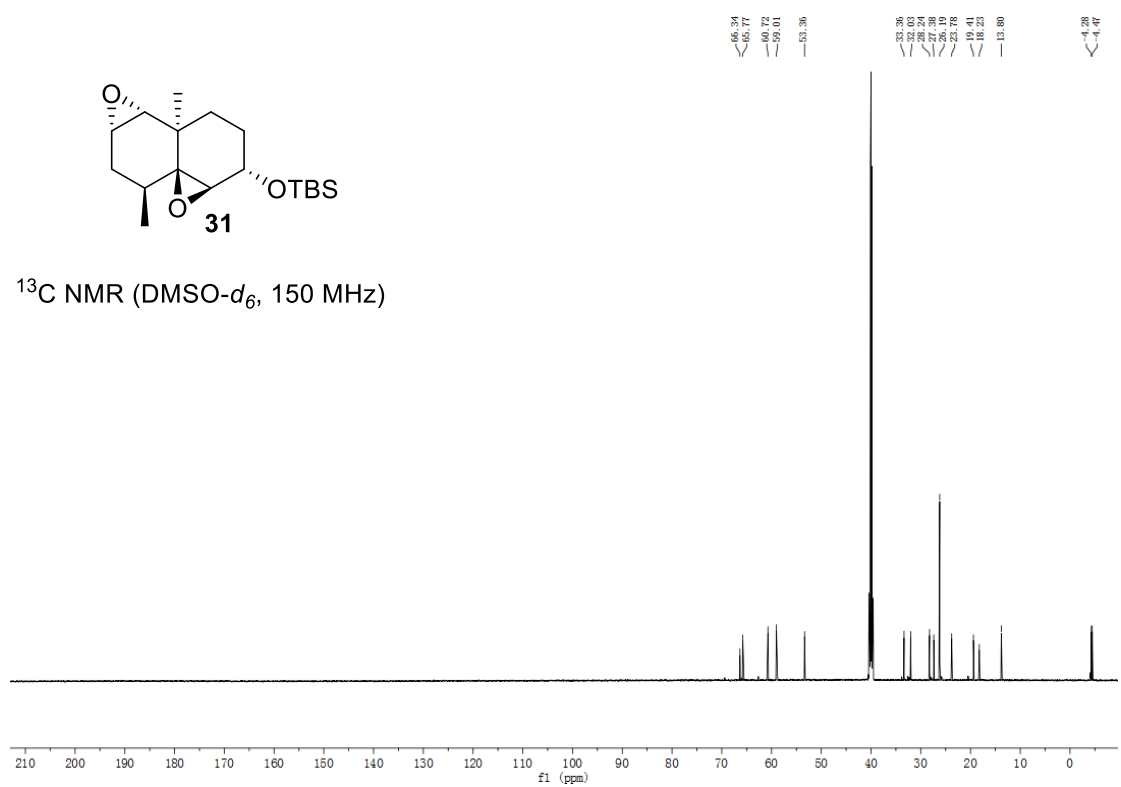
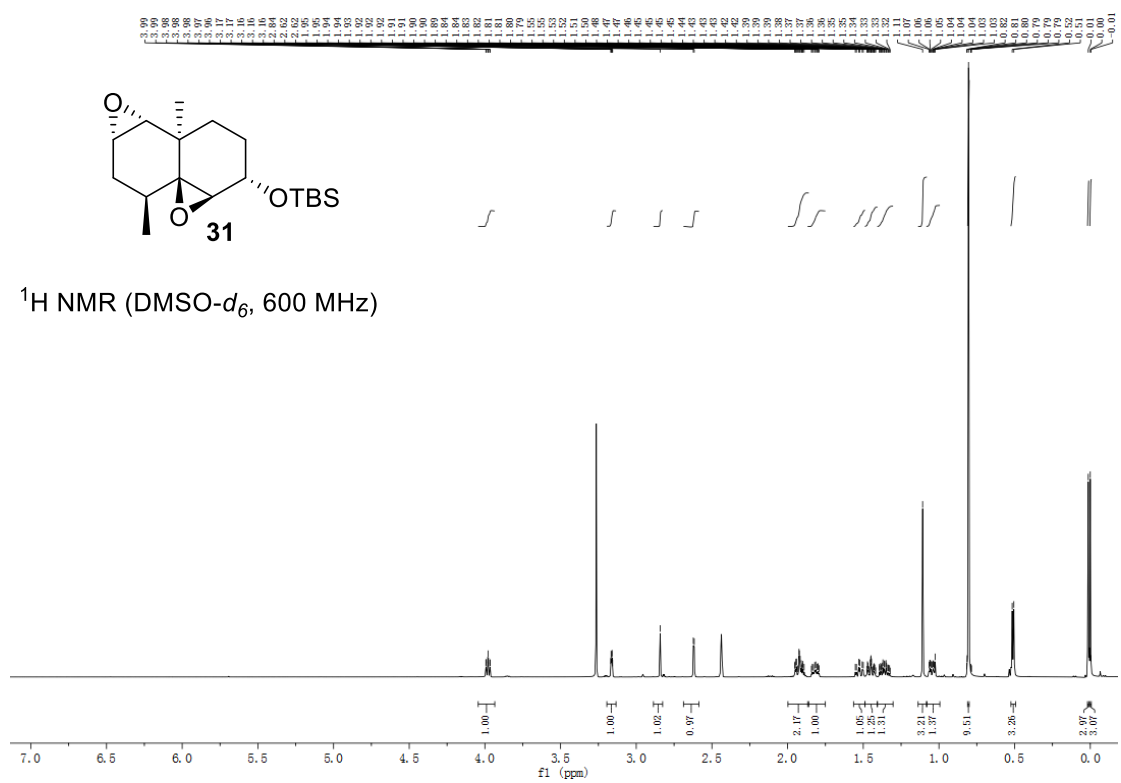


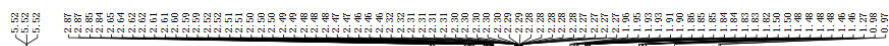
¹³C NMR (DMSO-*d*₆, 150 MHz)











32

¹H NMR (DMSO-*d*₆, 600 MHz)

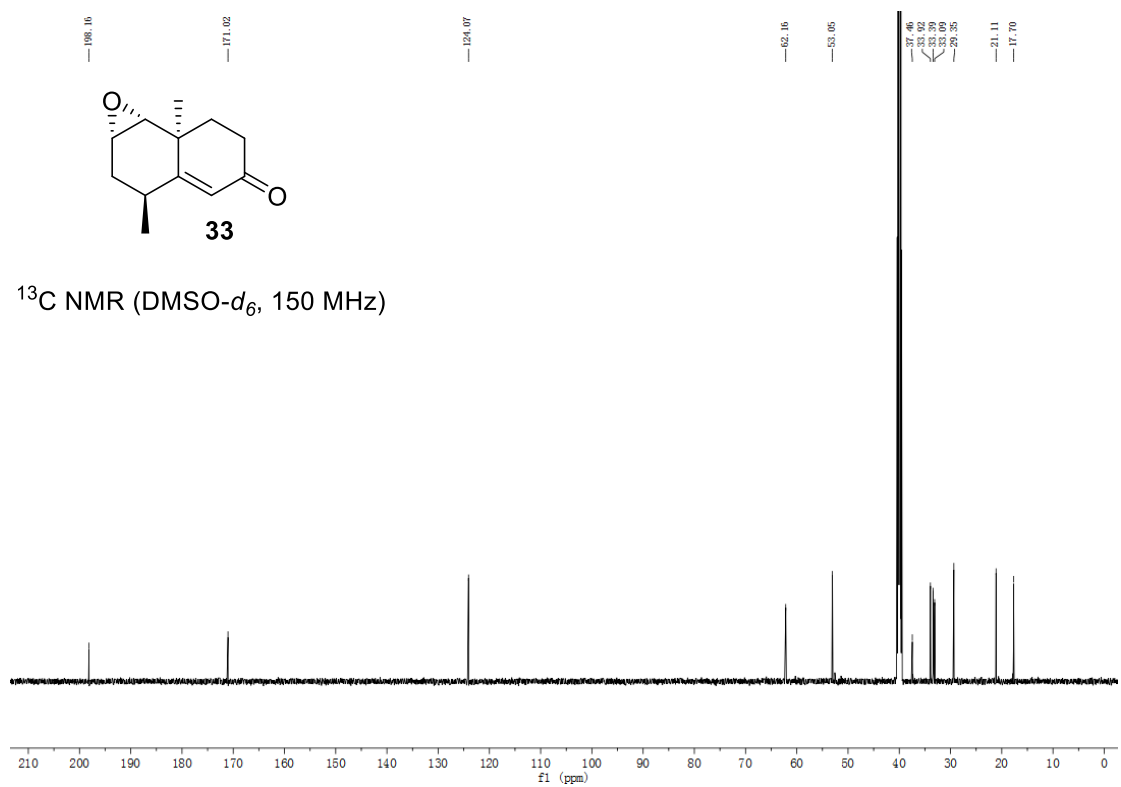
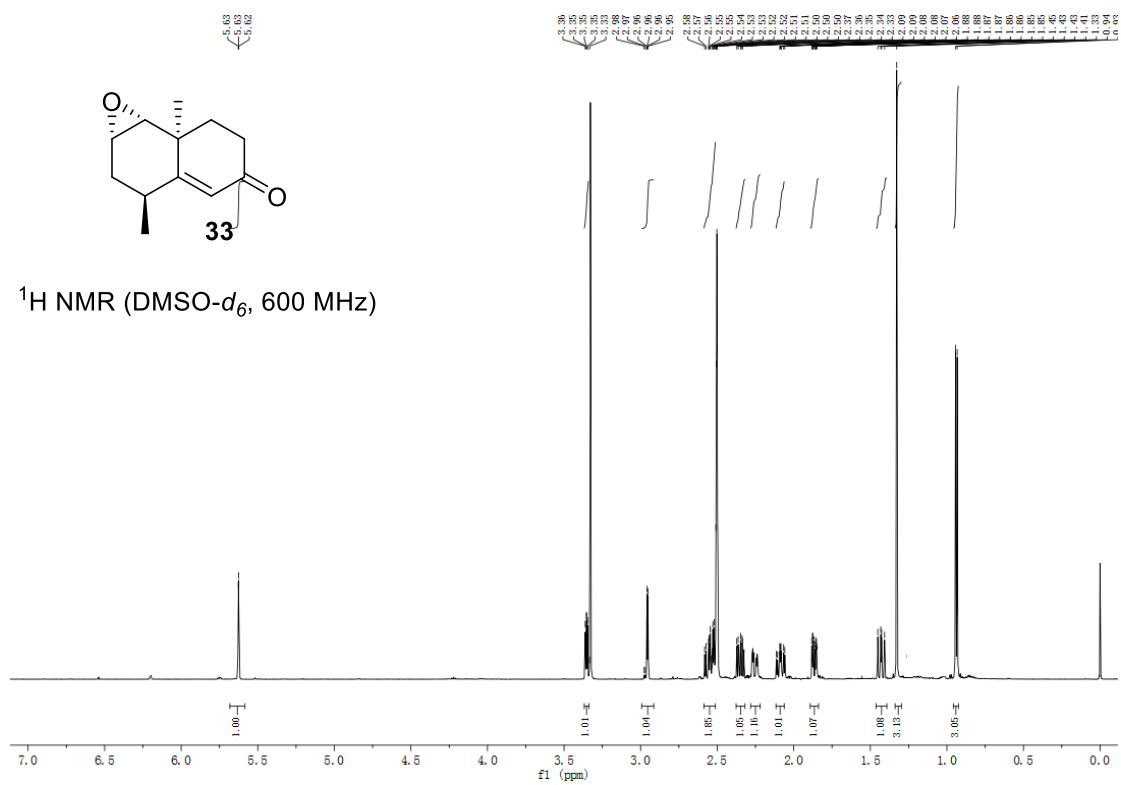
Chemical structure of compound **32** is shown above the spectrum. The structure is a bicyclic molecule with a ketone group, a double bond, and a cyclopropane ring fused to a six-membered ring. The spectrum displays the following integration values (from left to right): 1.00, 1.01, 1.11, 2.27, 2.13, 1.09, 1.07, 1.11, 3.22, and 3.20.

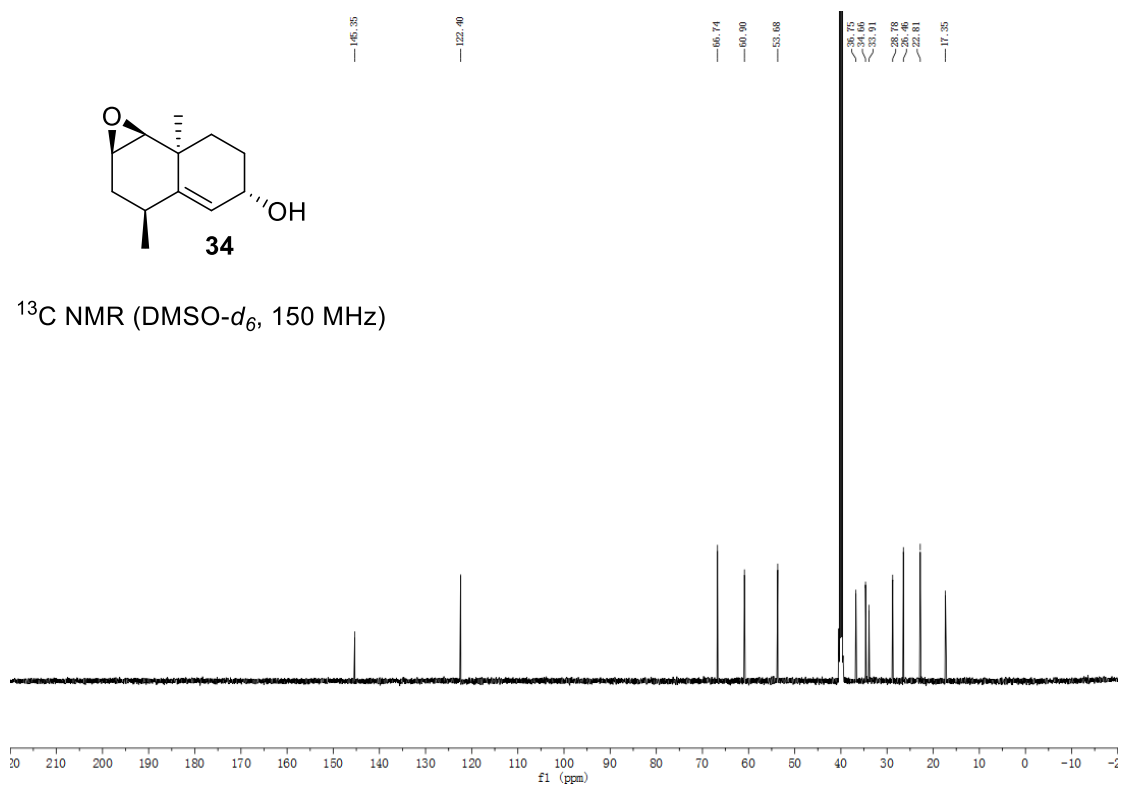
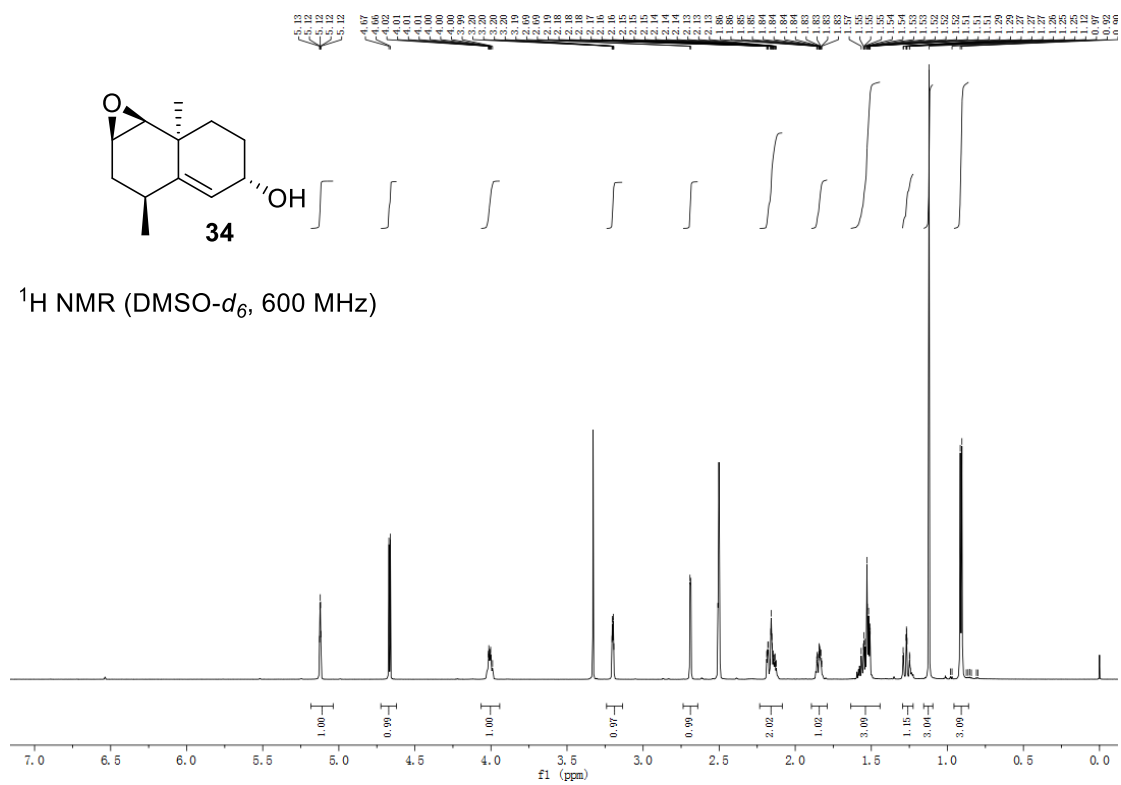


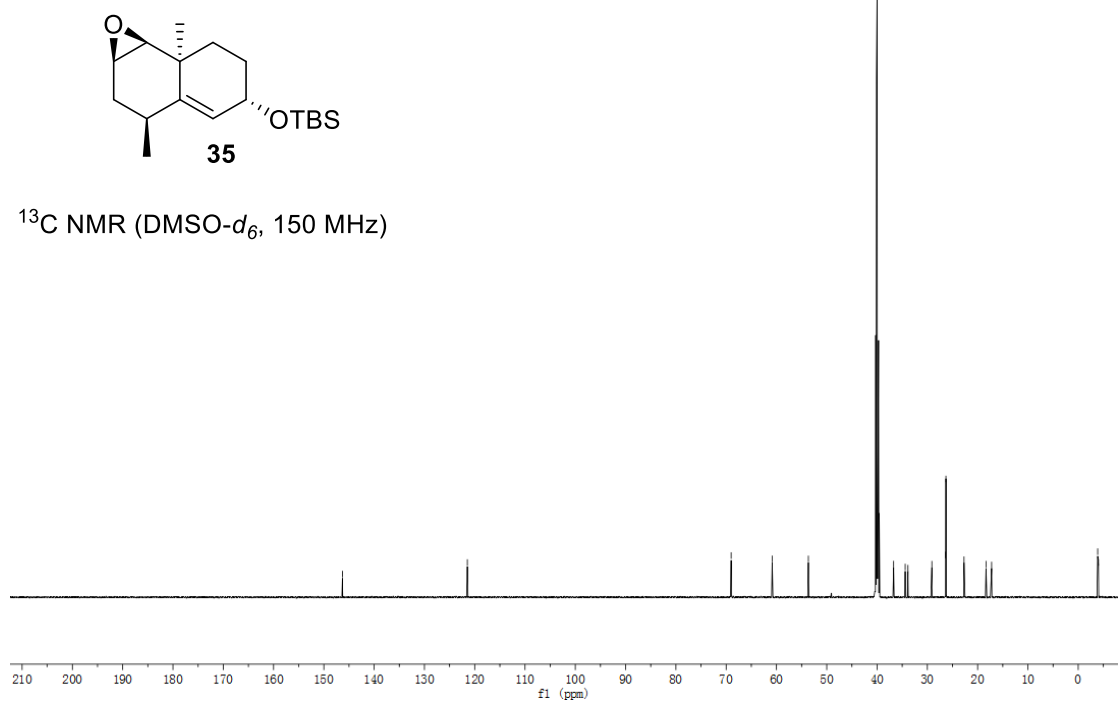
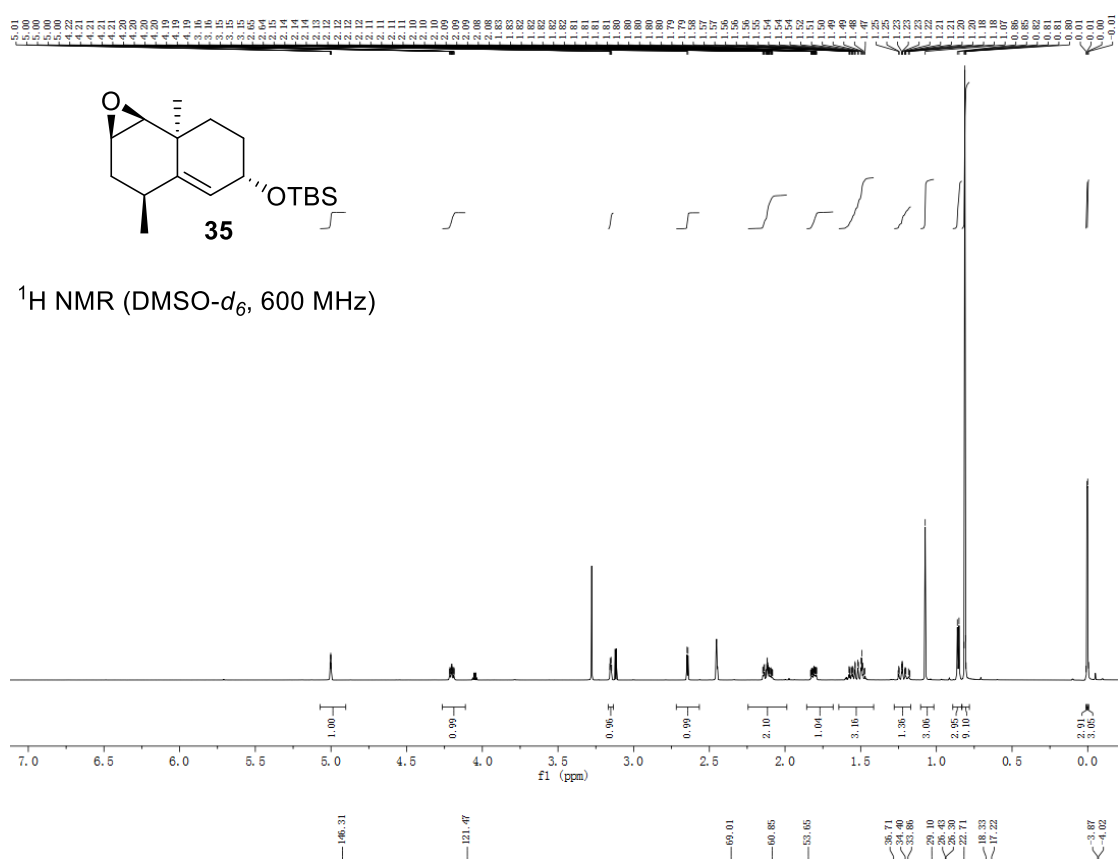
32

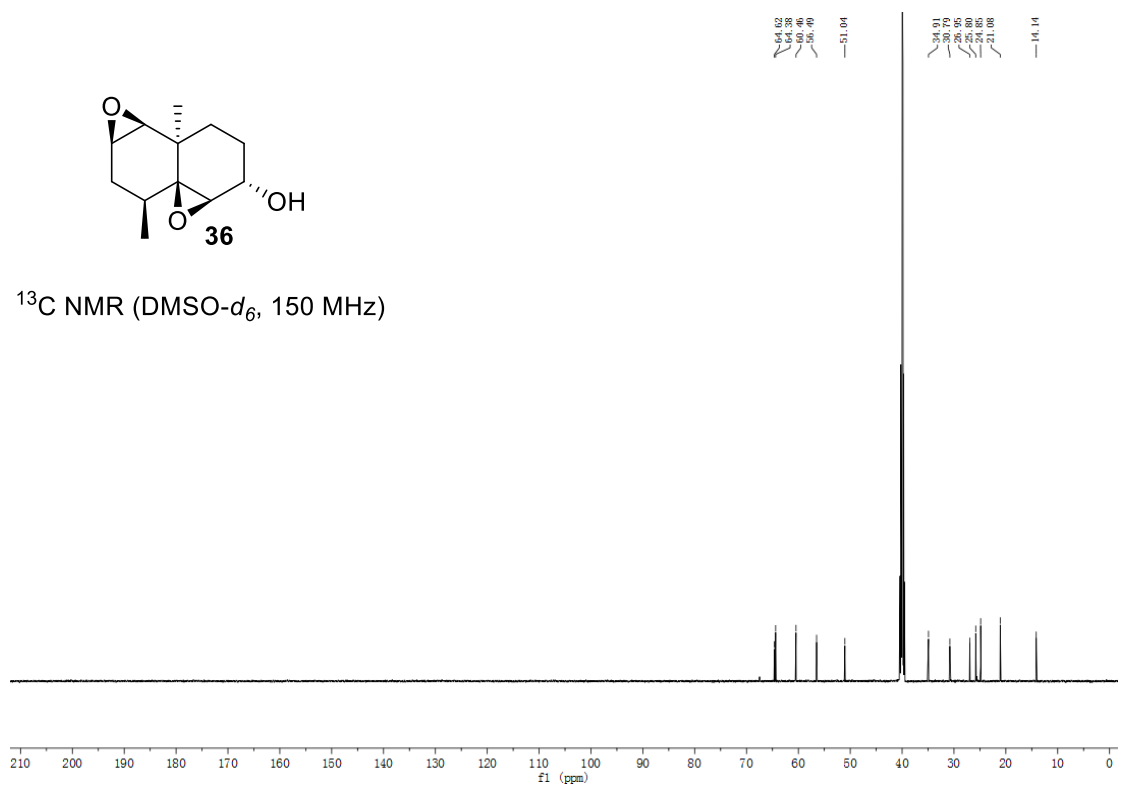
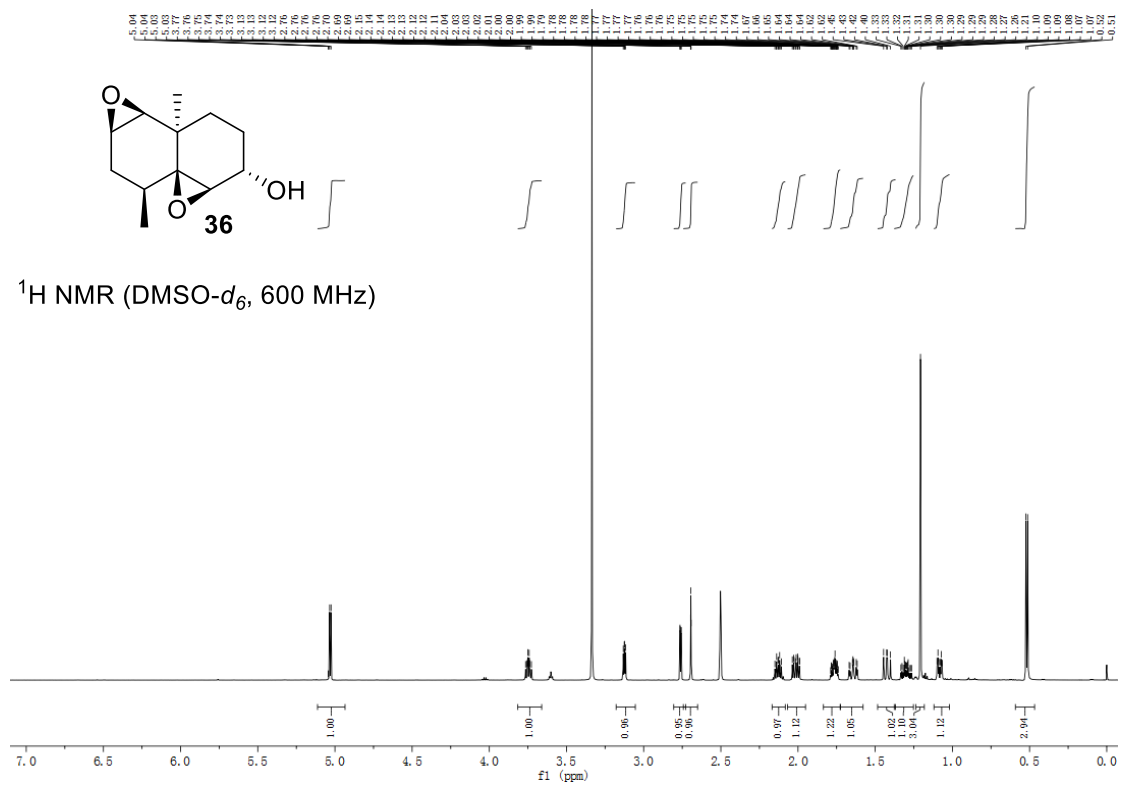
^{13}C NMR (DMSO- d_6 , 150 MHz)

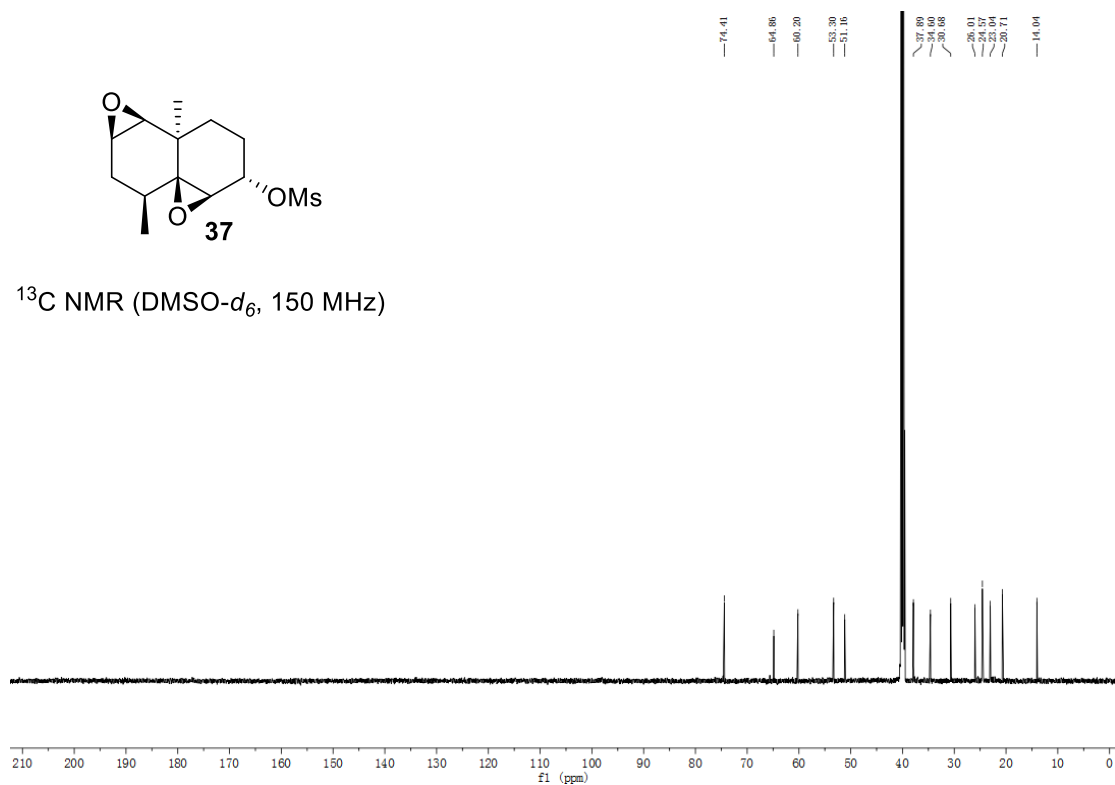
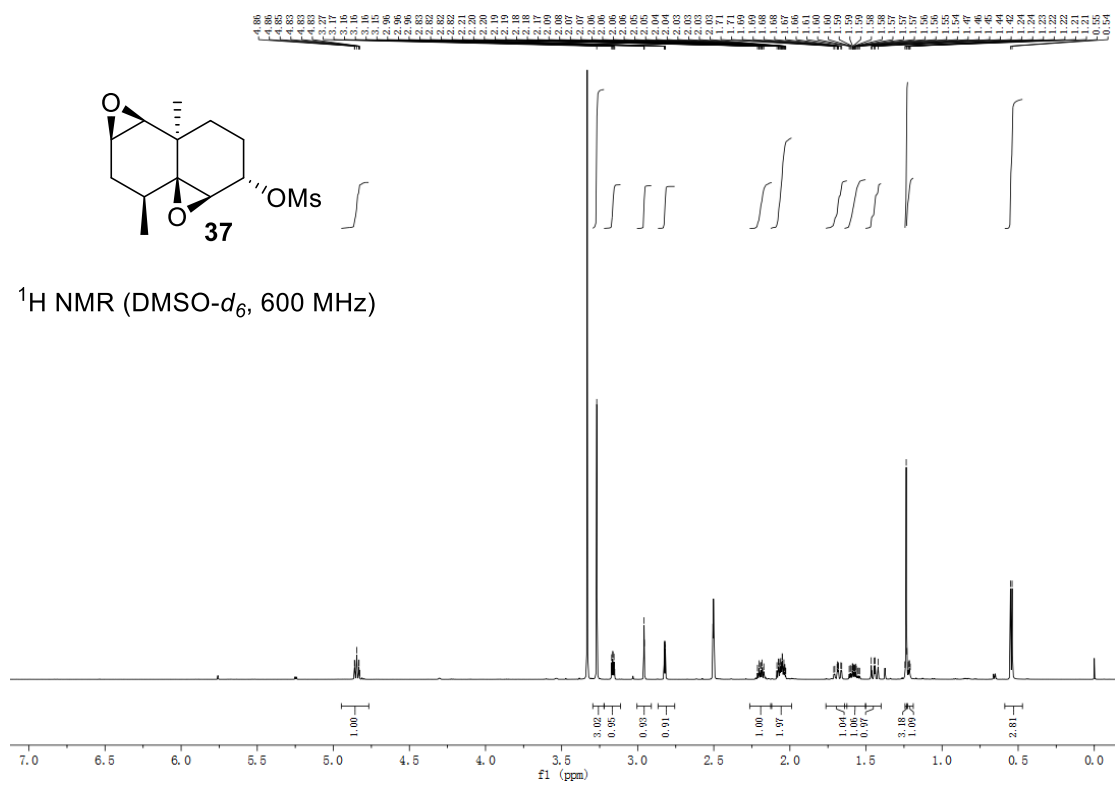
Chemical structure of **32** is shown above the spectrum. The structure is a bicyclic compound with a cyclohexanone ring fused to a cyclohexane ring. The cyclohexane ring has a methyl group and an epoxide ring. The cyclohexanone ring has a methyl group. The spectrum shows peaks at 198.27, 171.84, 120.56, 60.05, 53.36, 35.23, 34.60, 33.61, 27.63, 21.10, and 16.72 ppm.

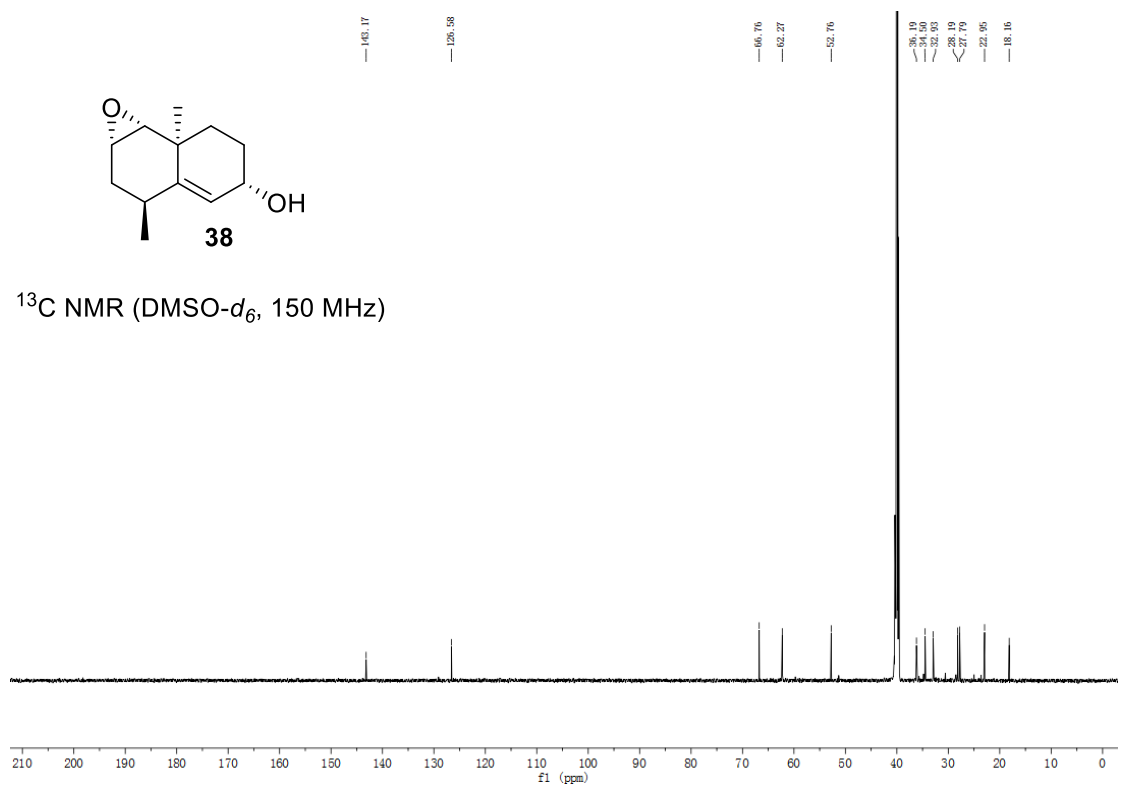
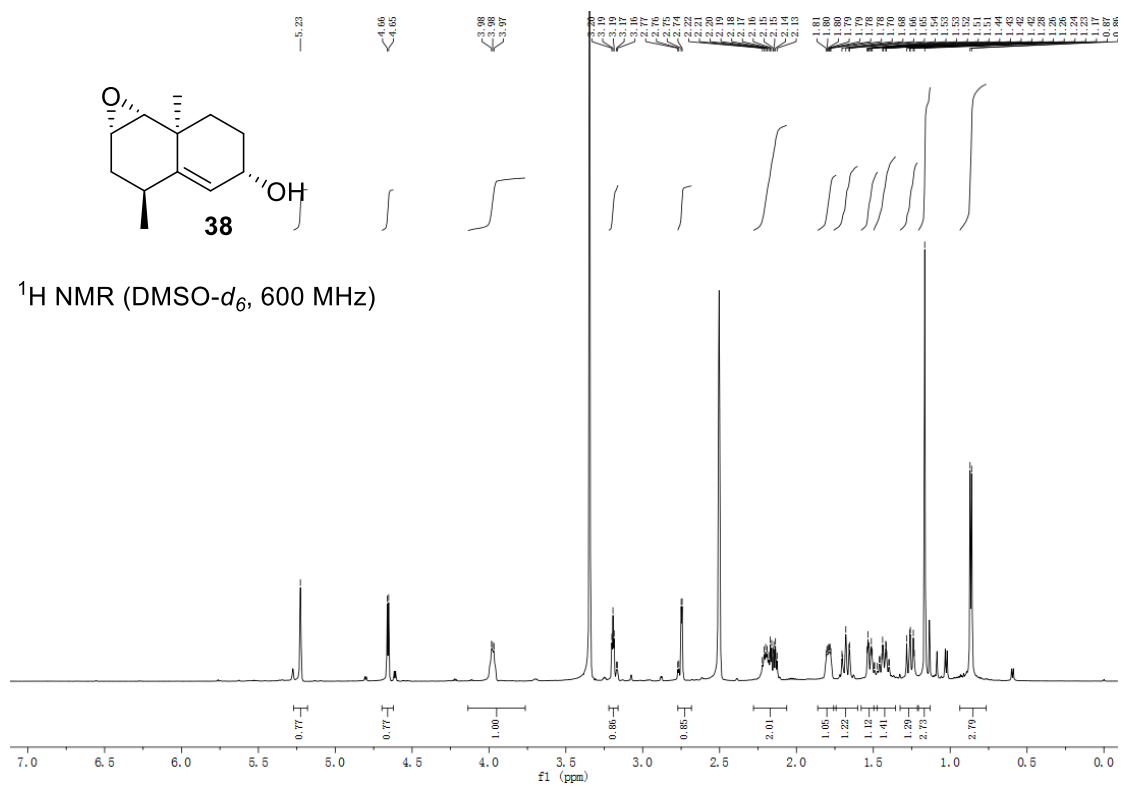


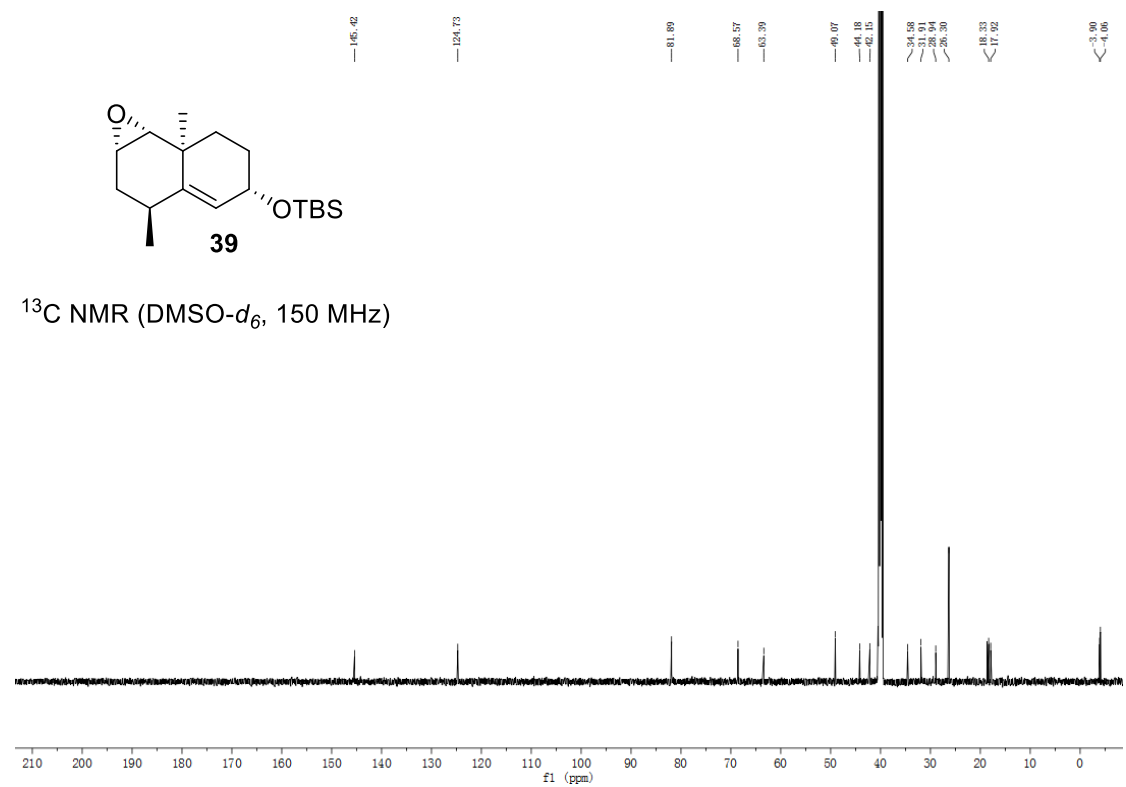
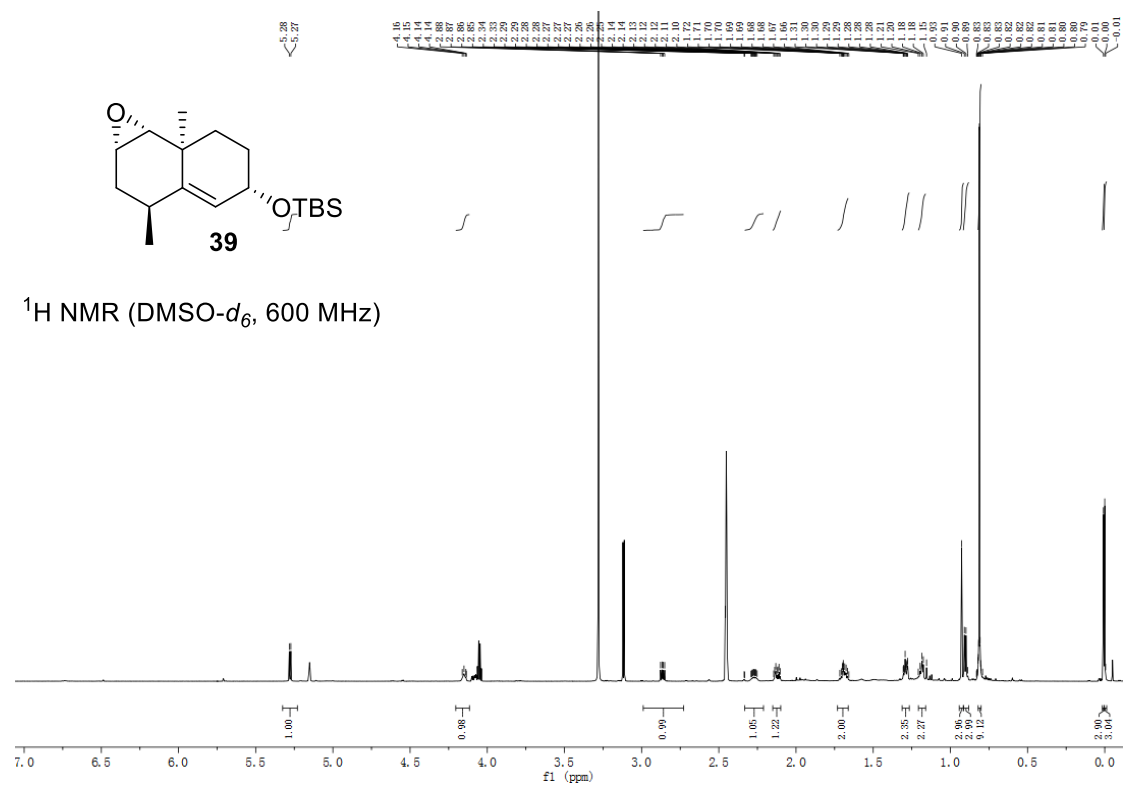


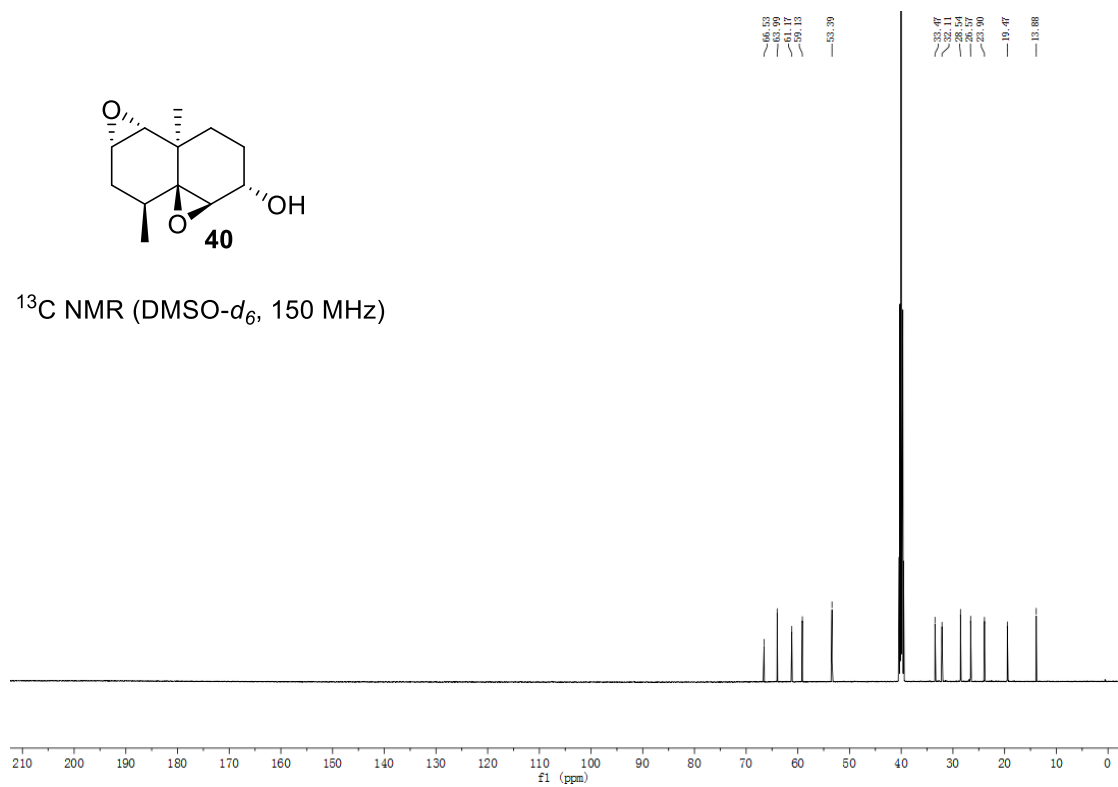
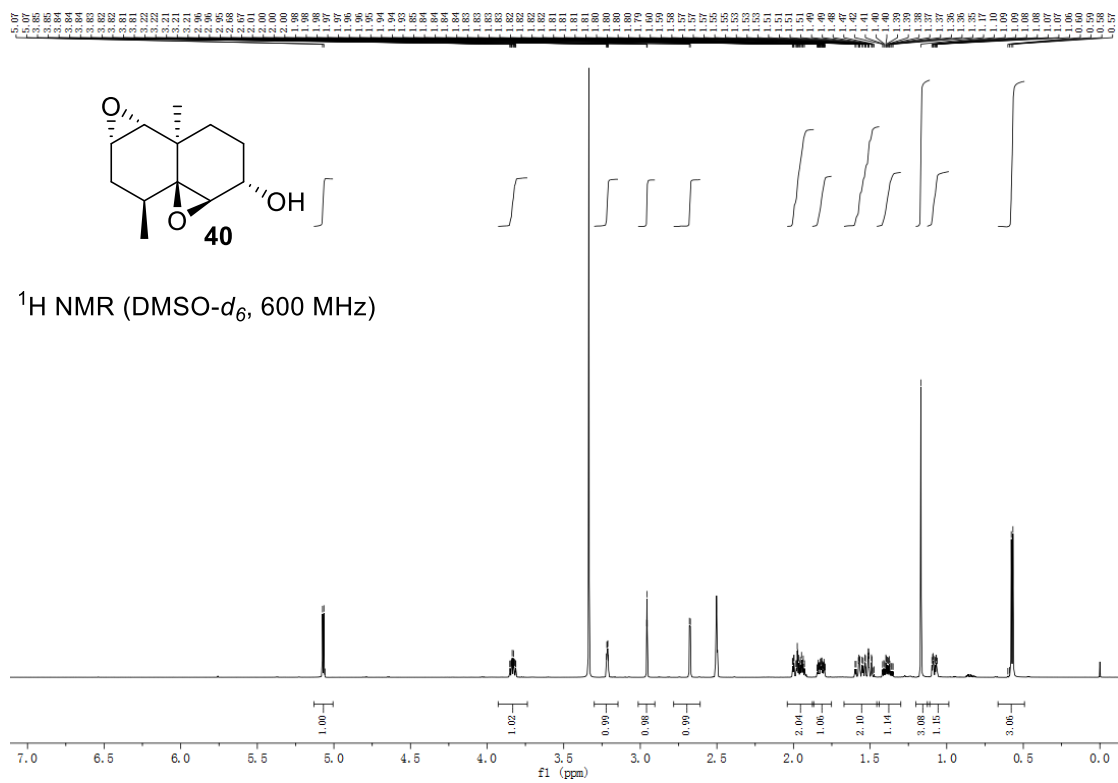


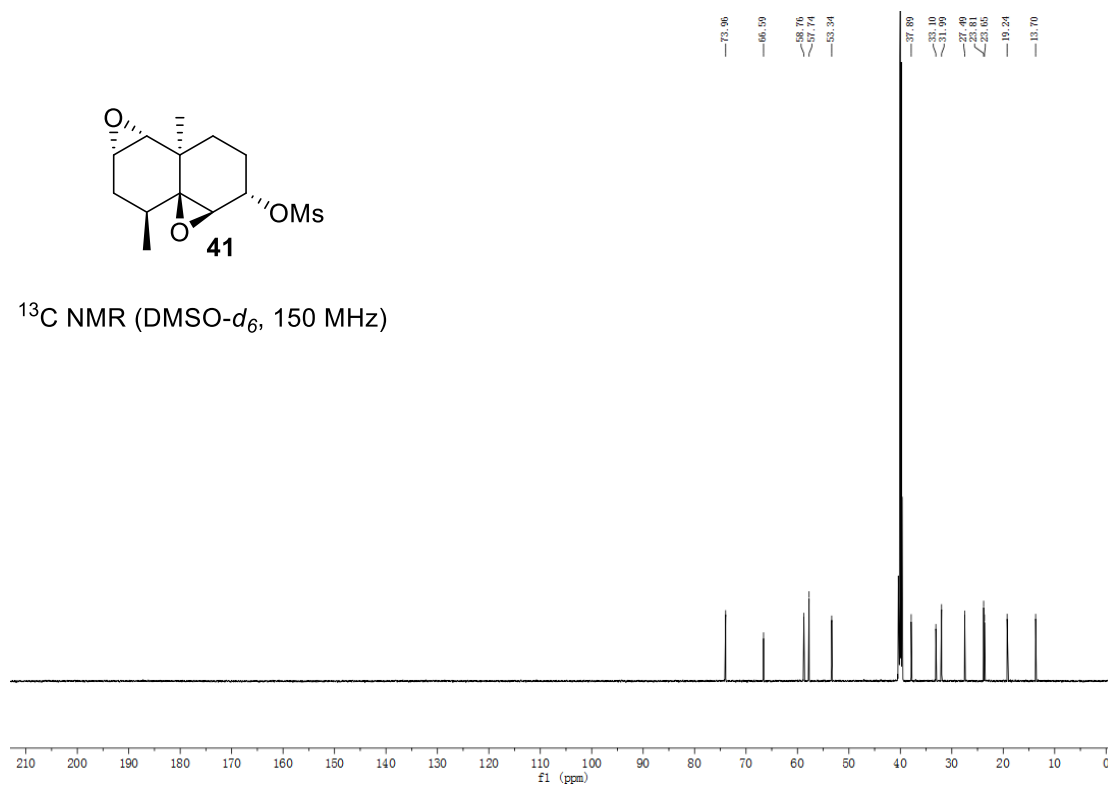
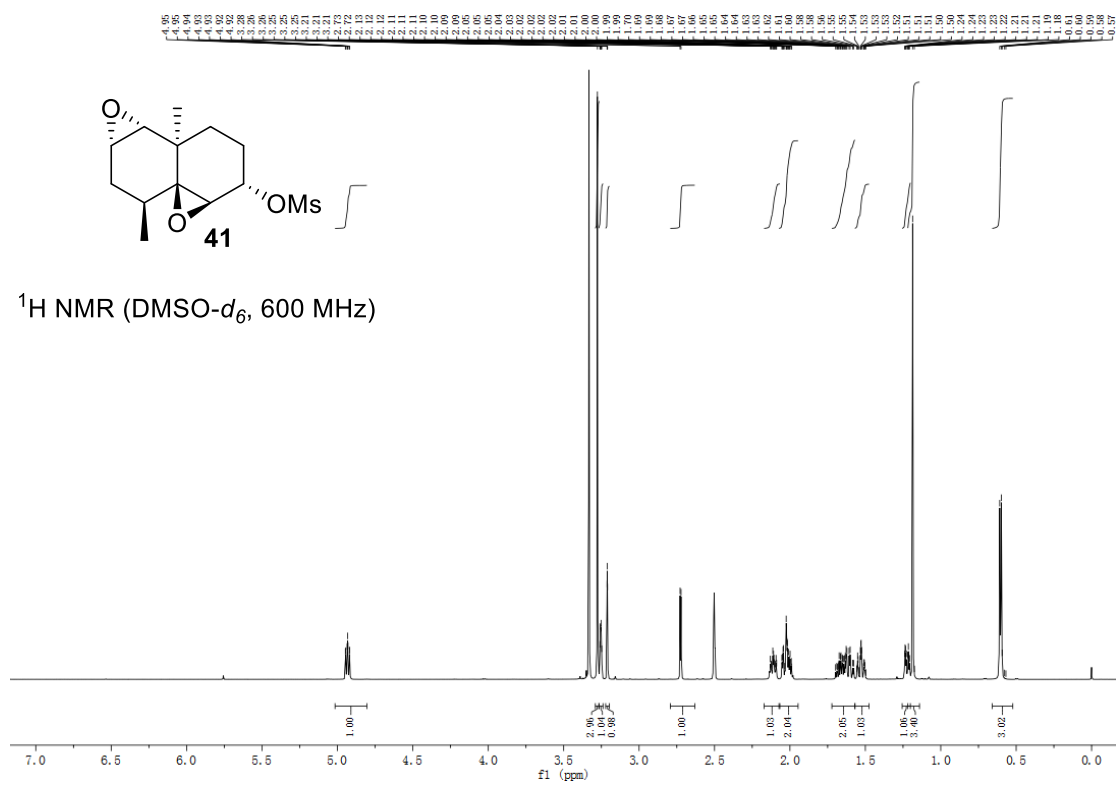


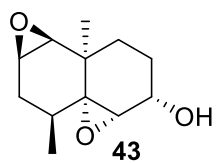




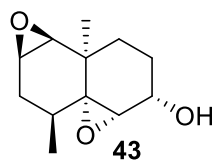
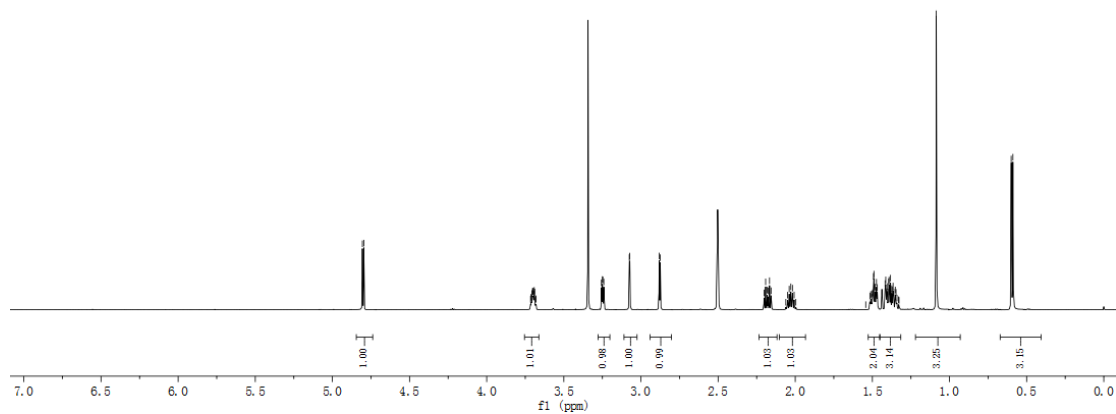




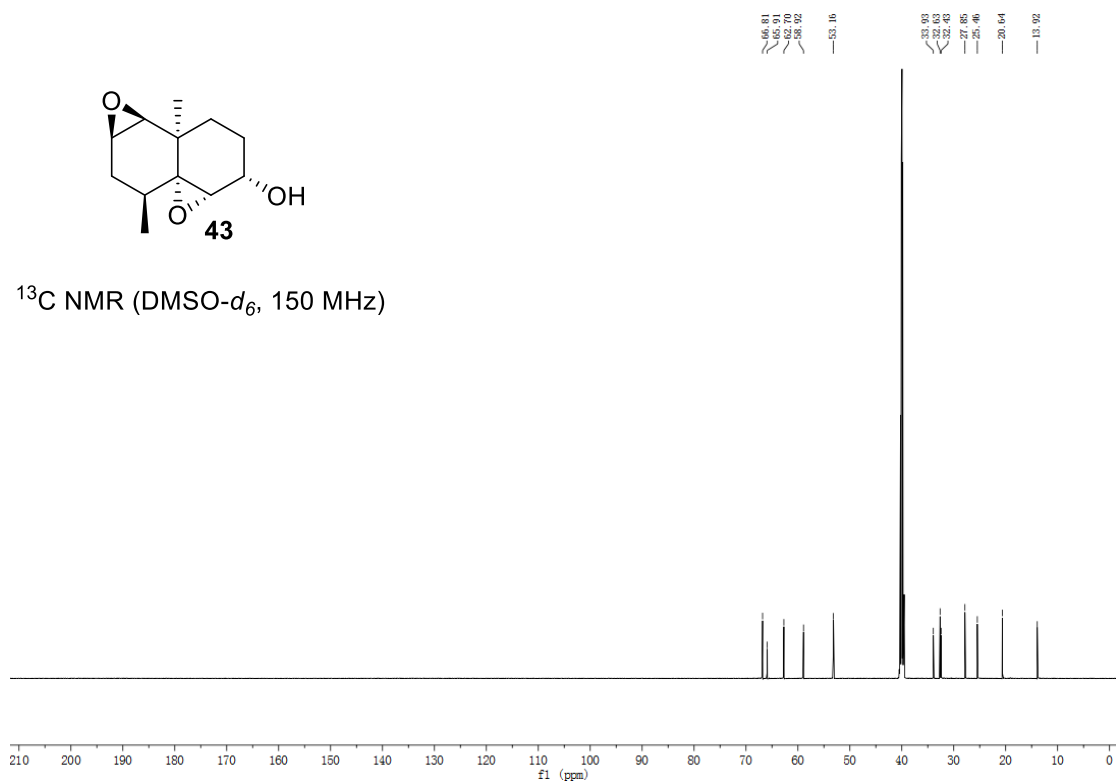


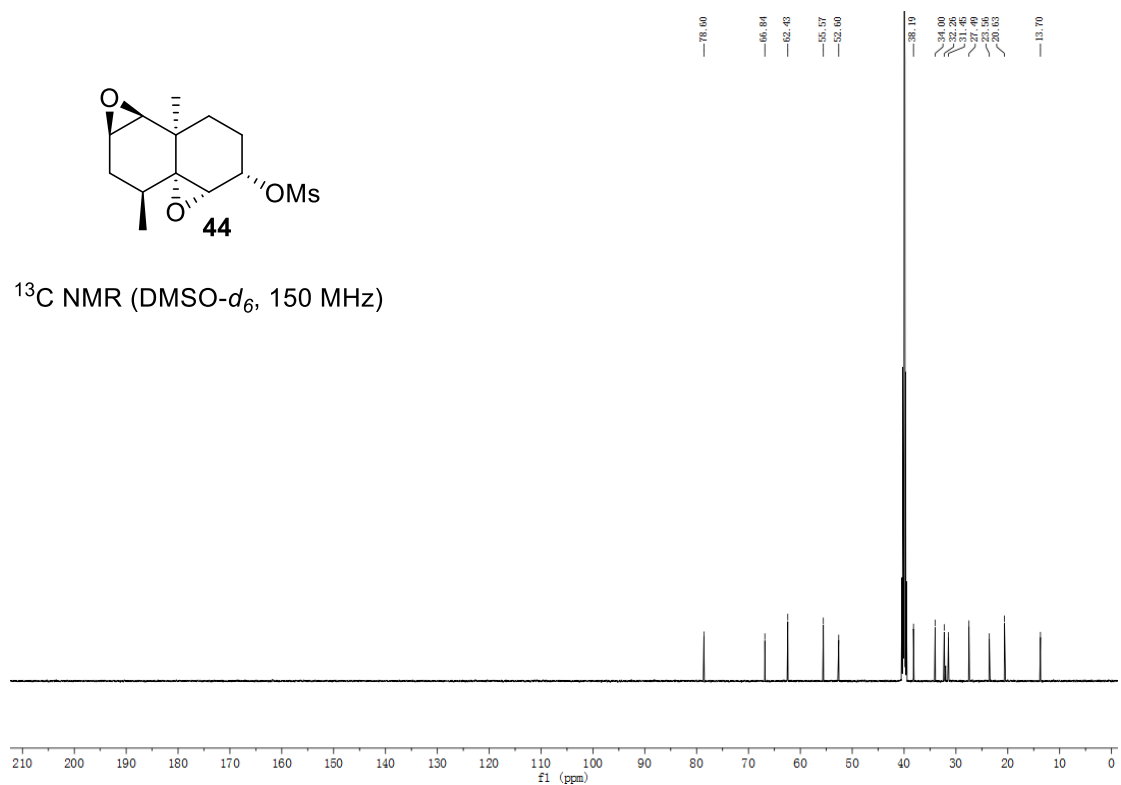
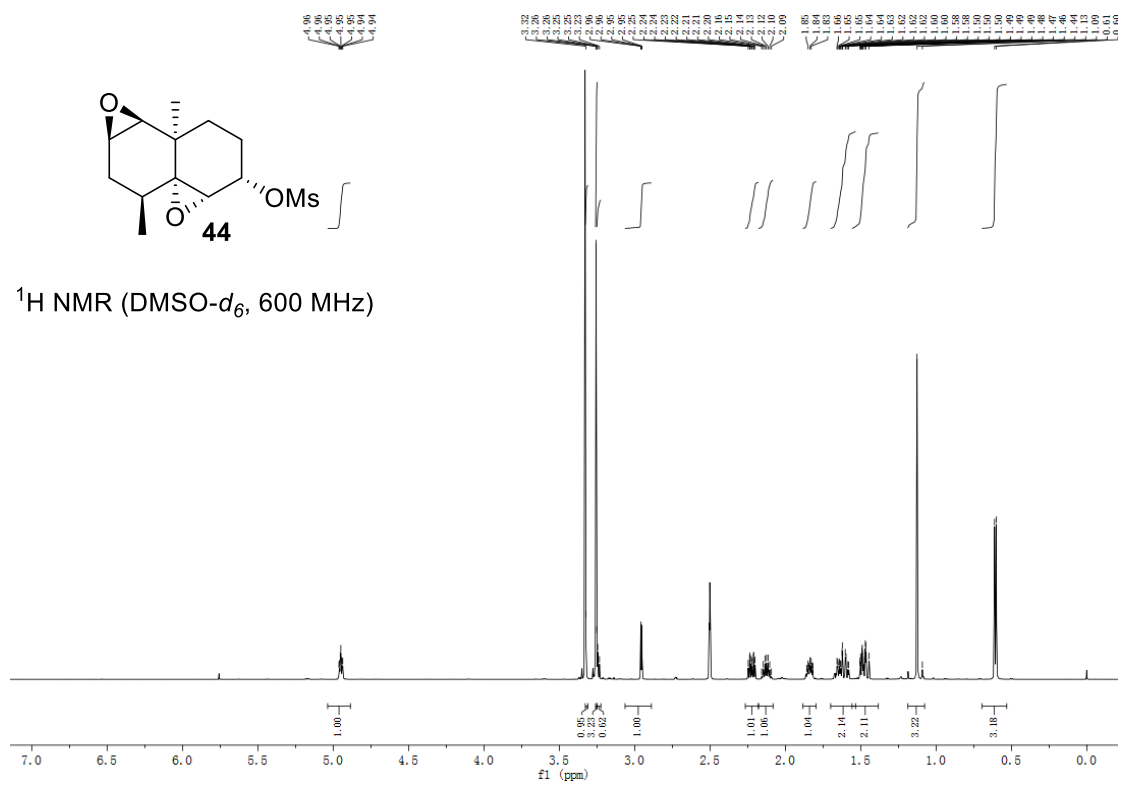


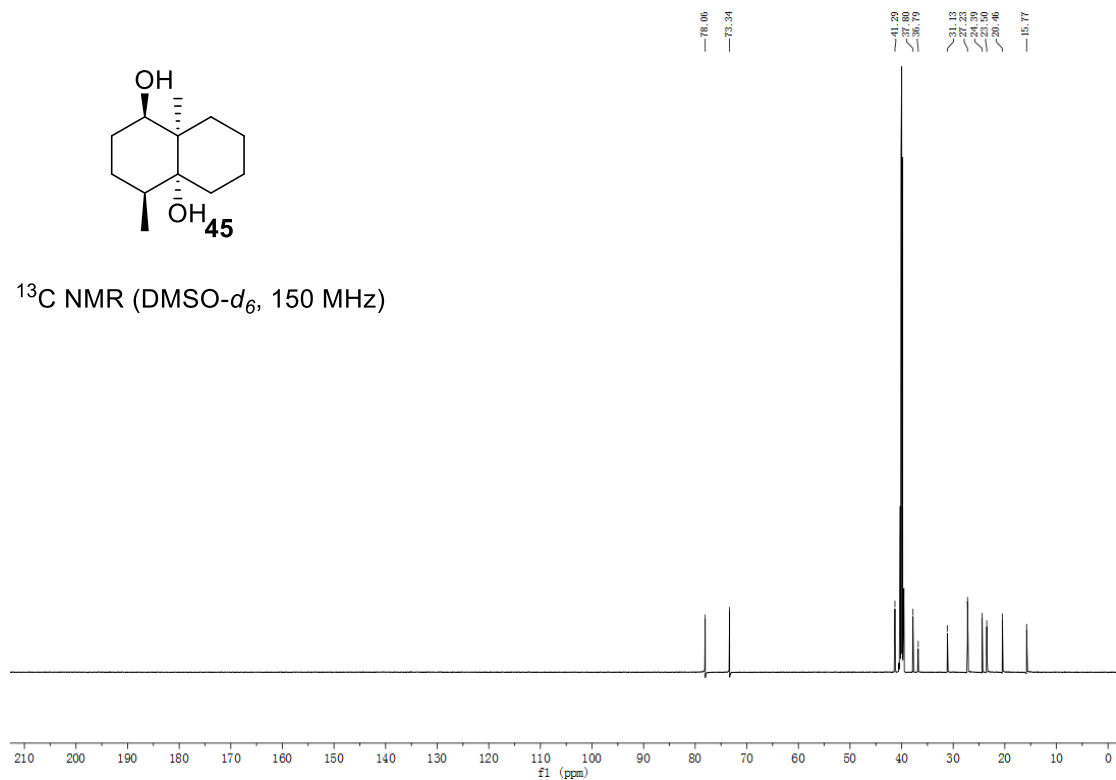
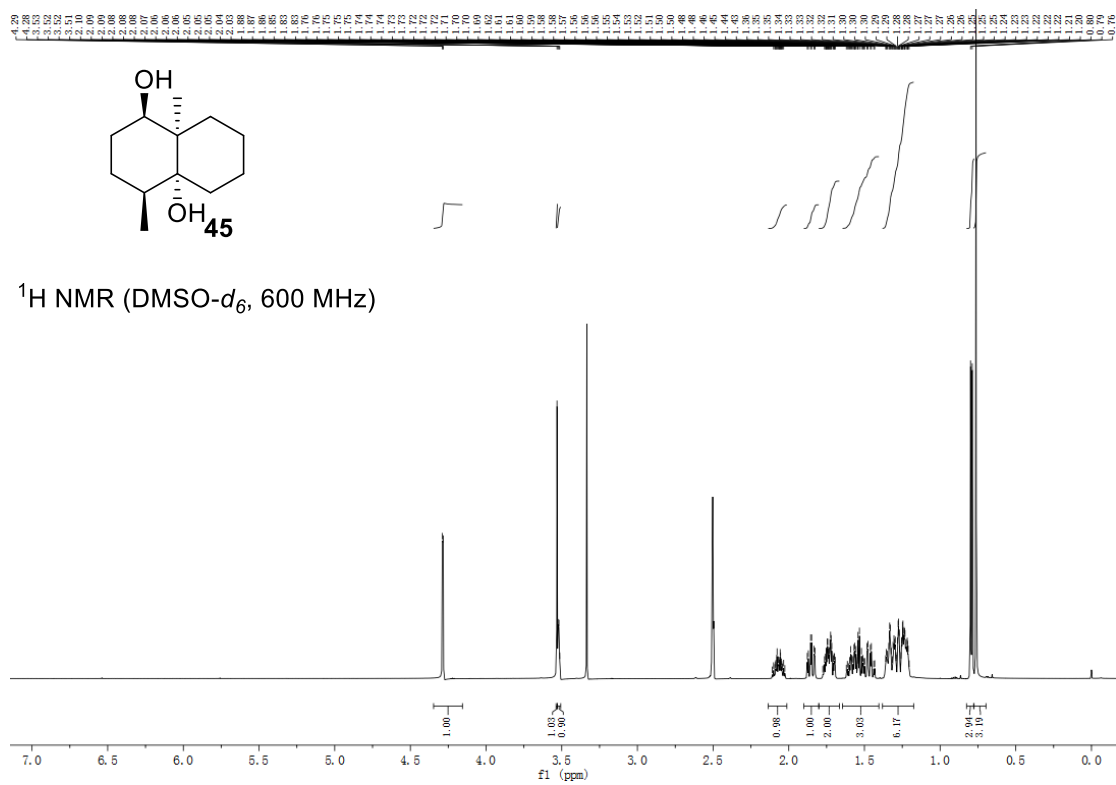
^1H NMR (DMSO- d_6 , 600 MHz)

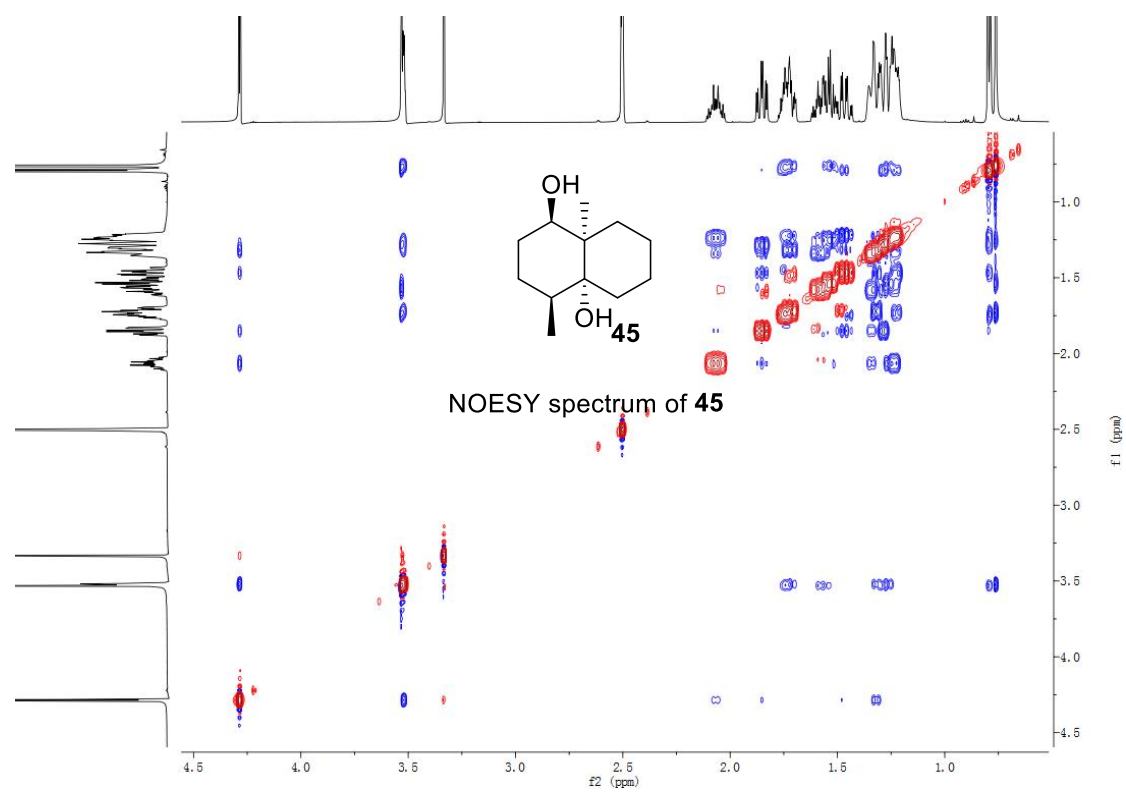


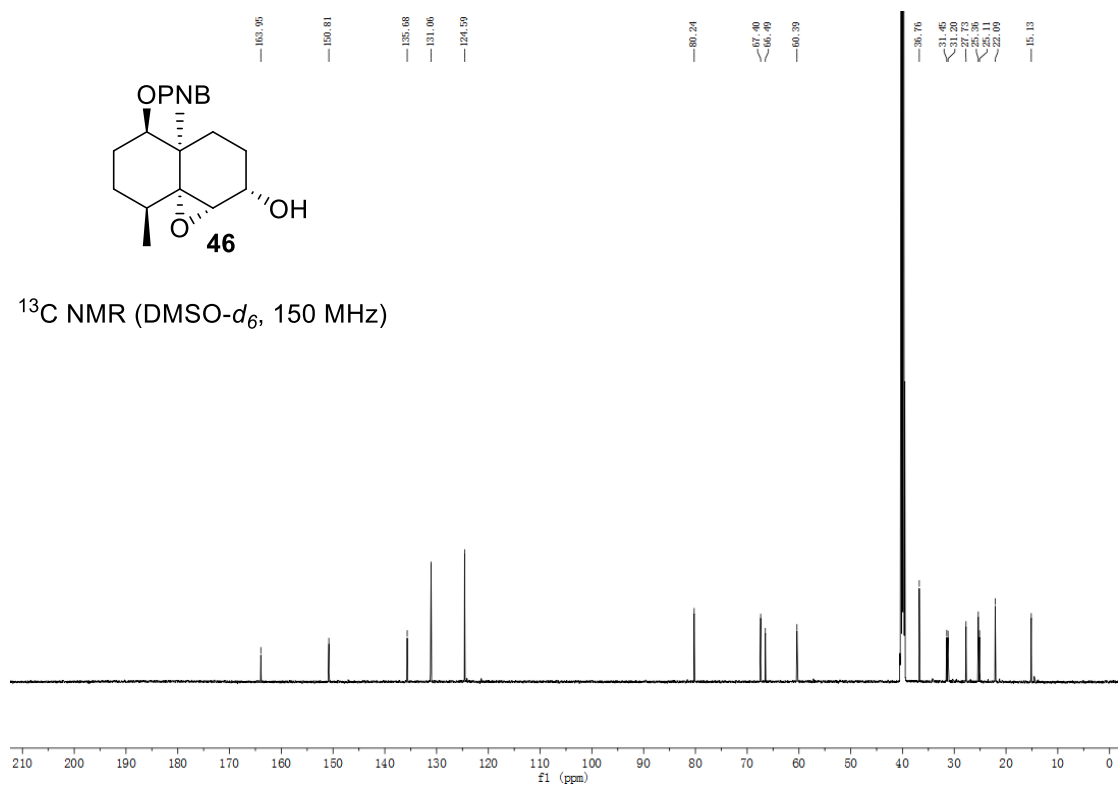
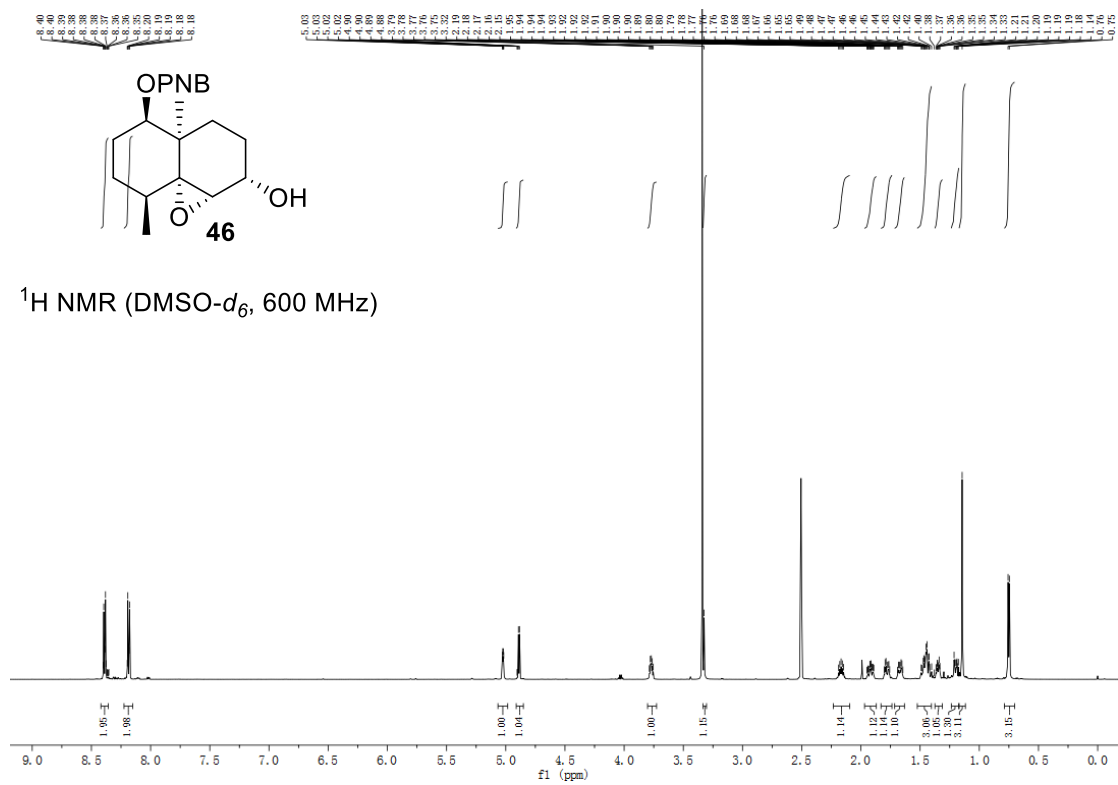
^{13}C NMR (DMSO- d_6 , 150 MHz)

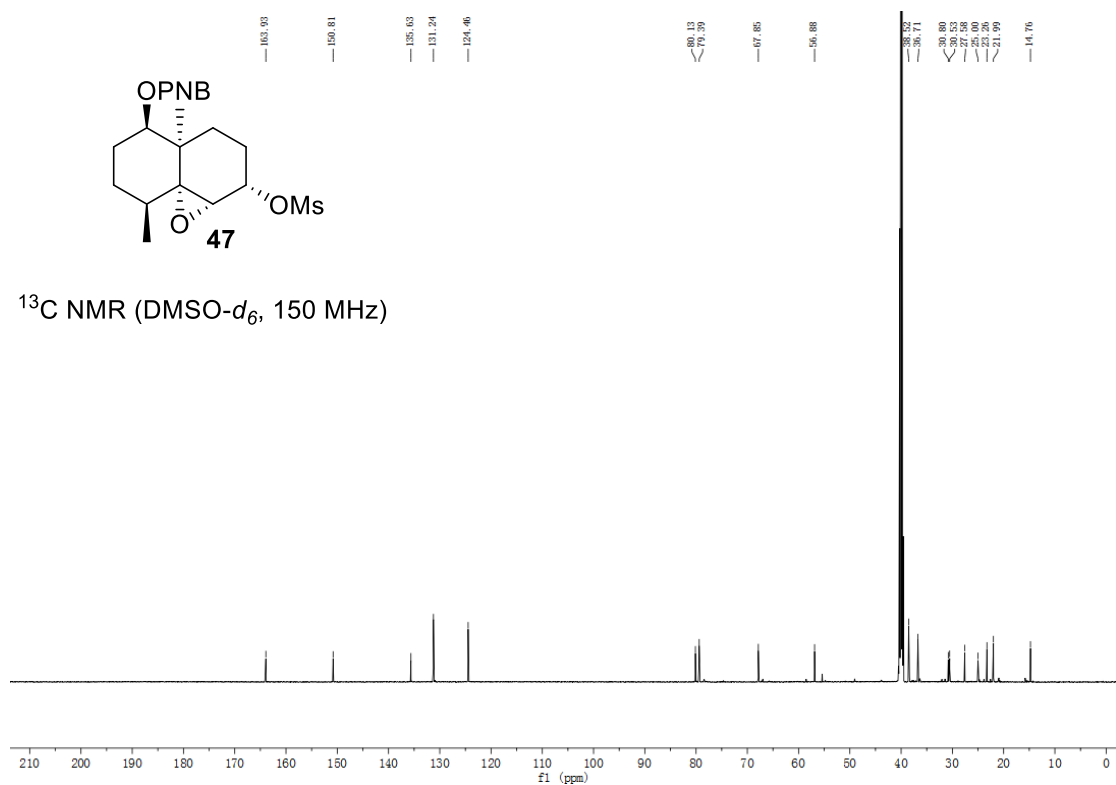
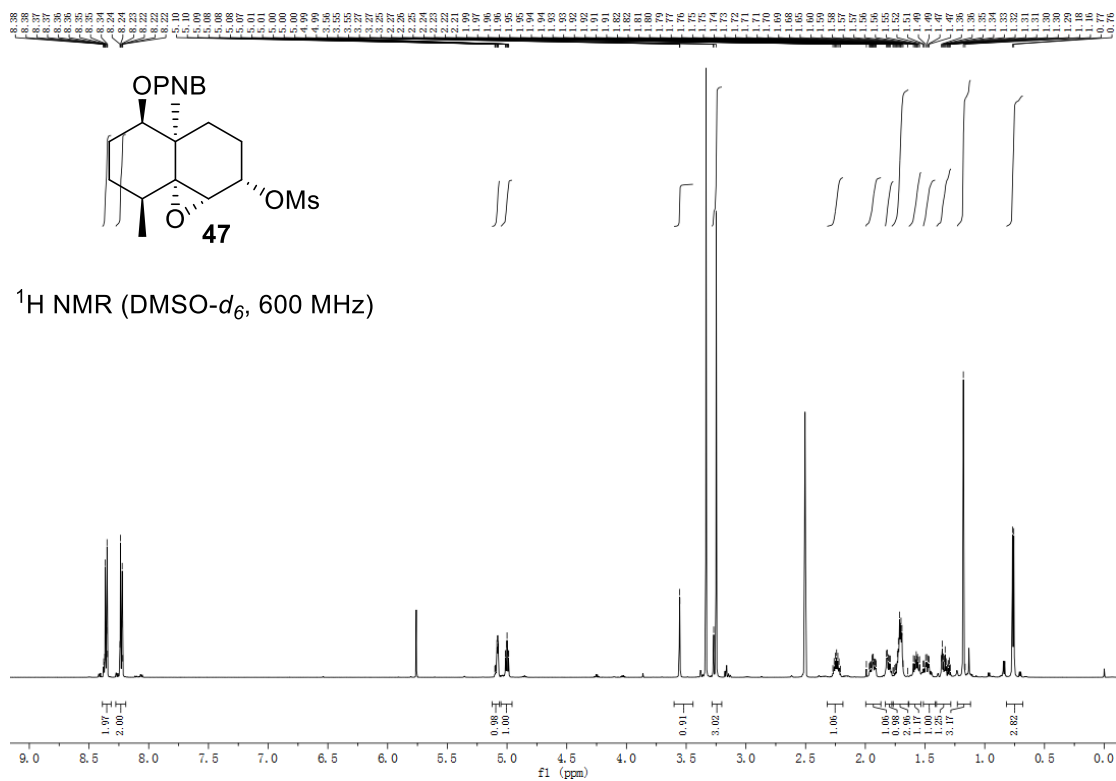


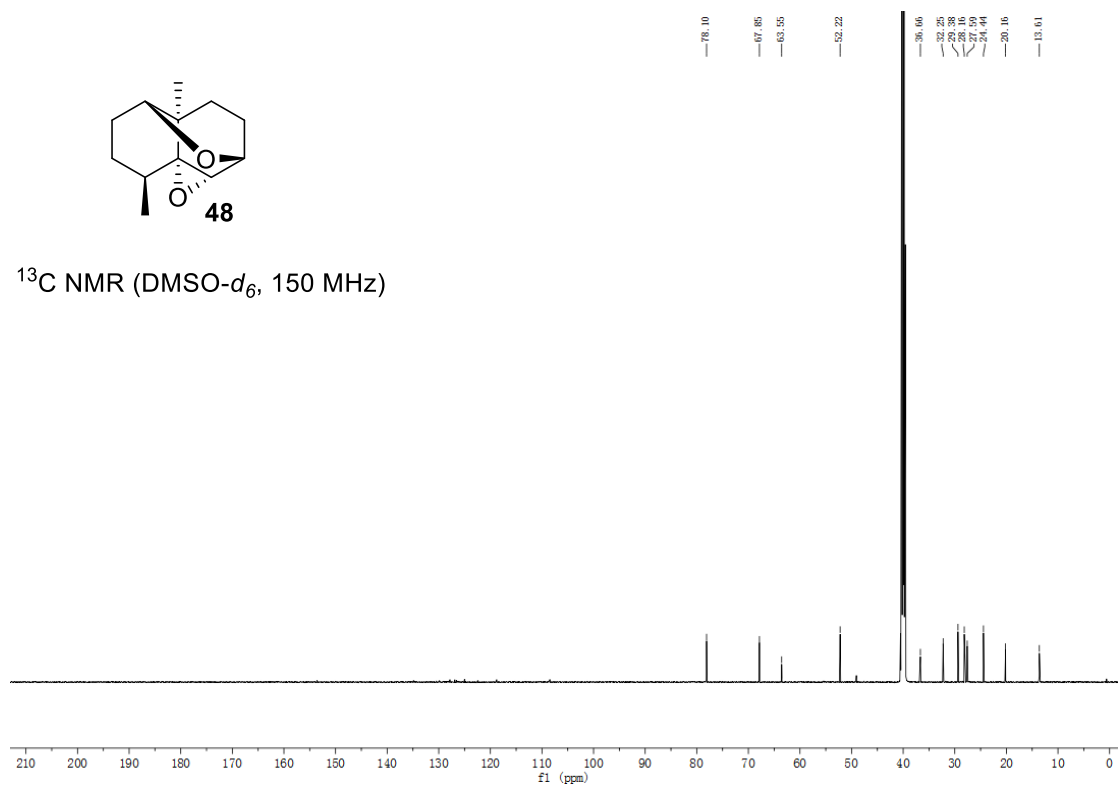
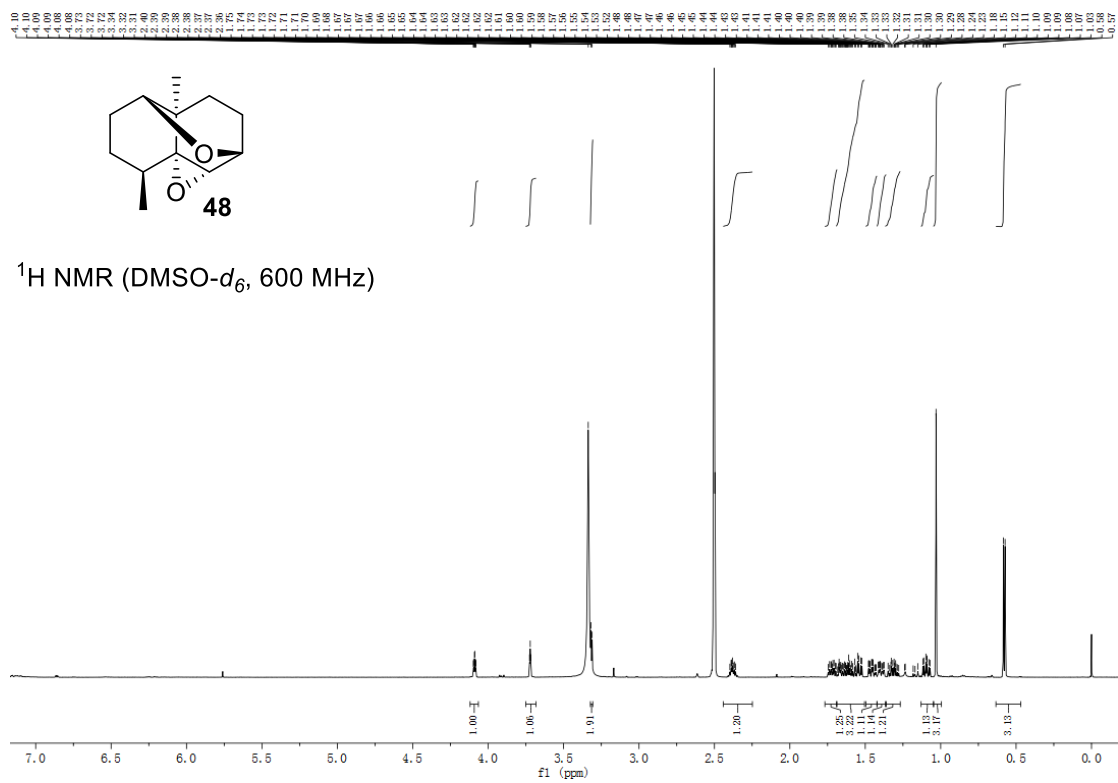


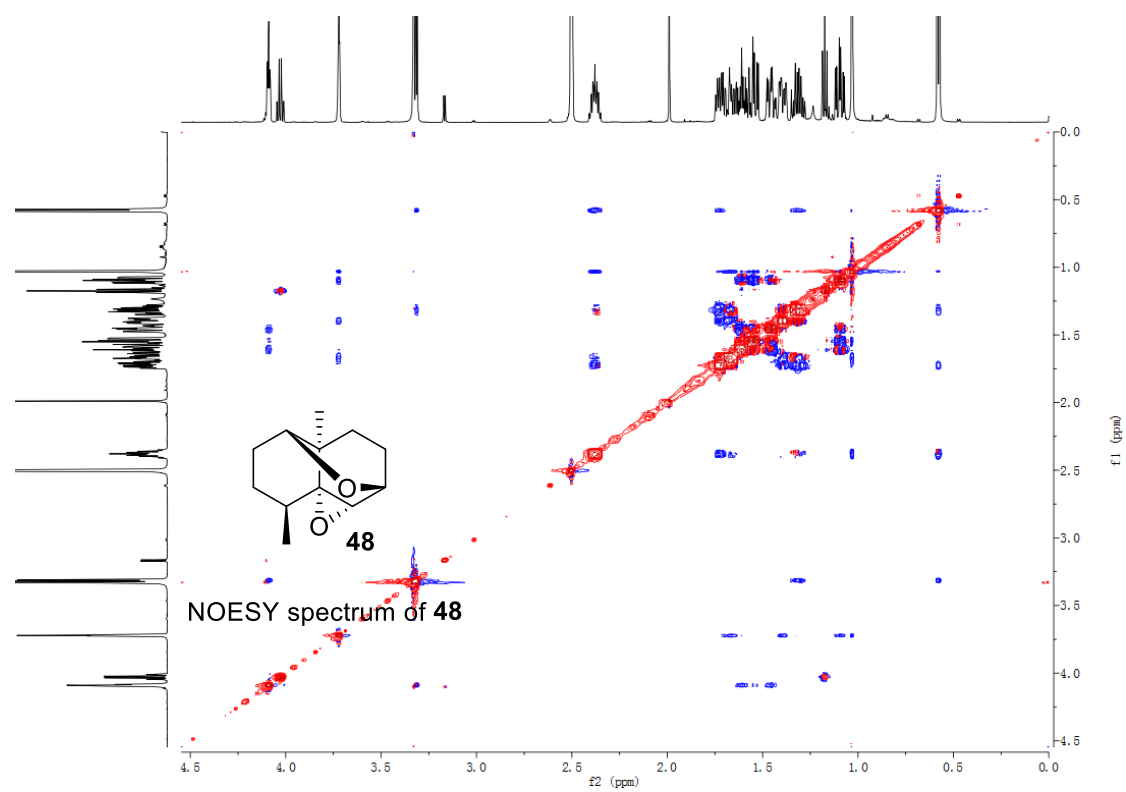


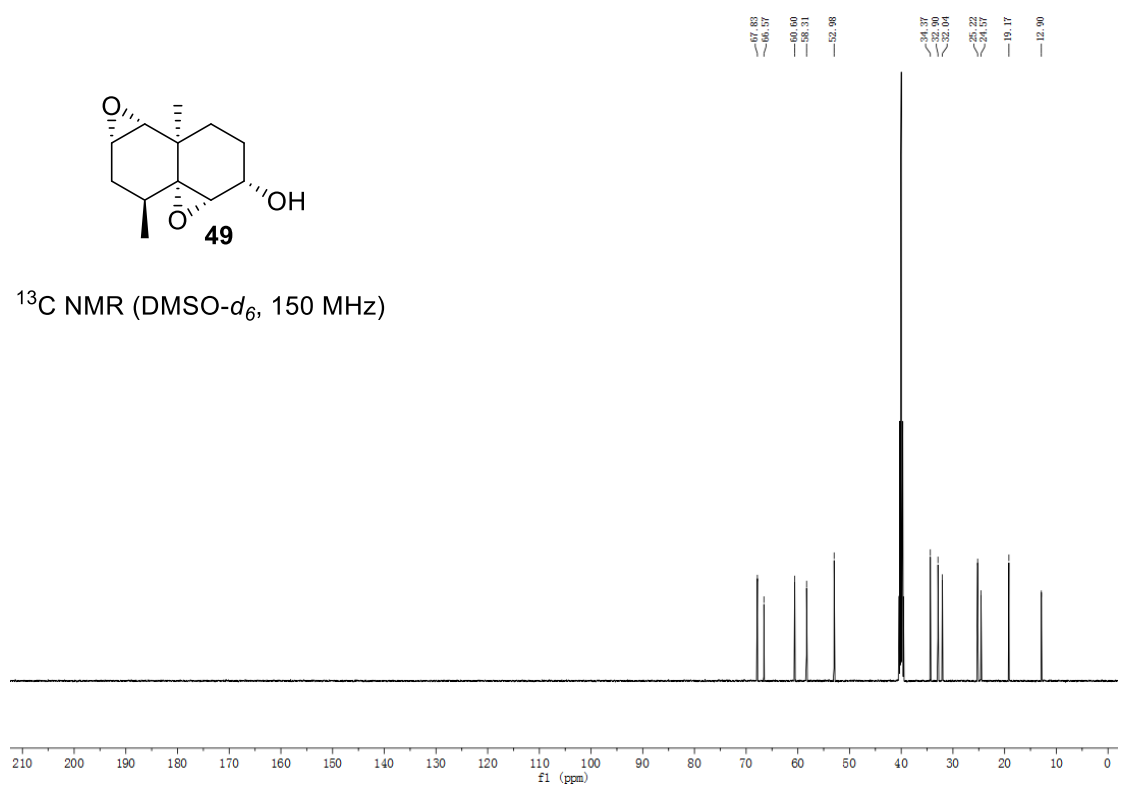
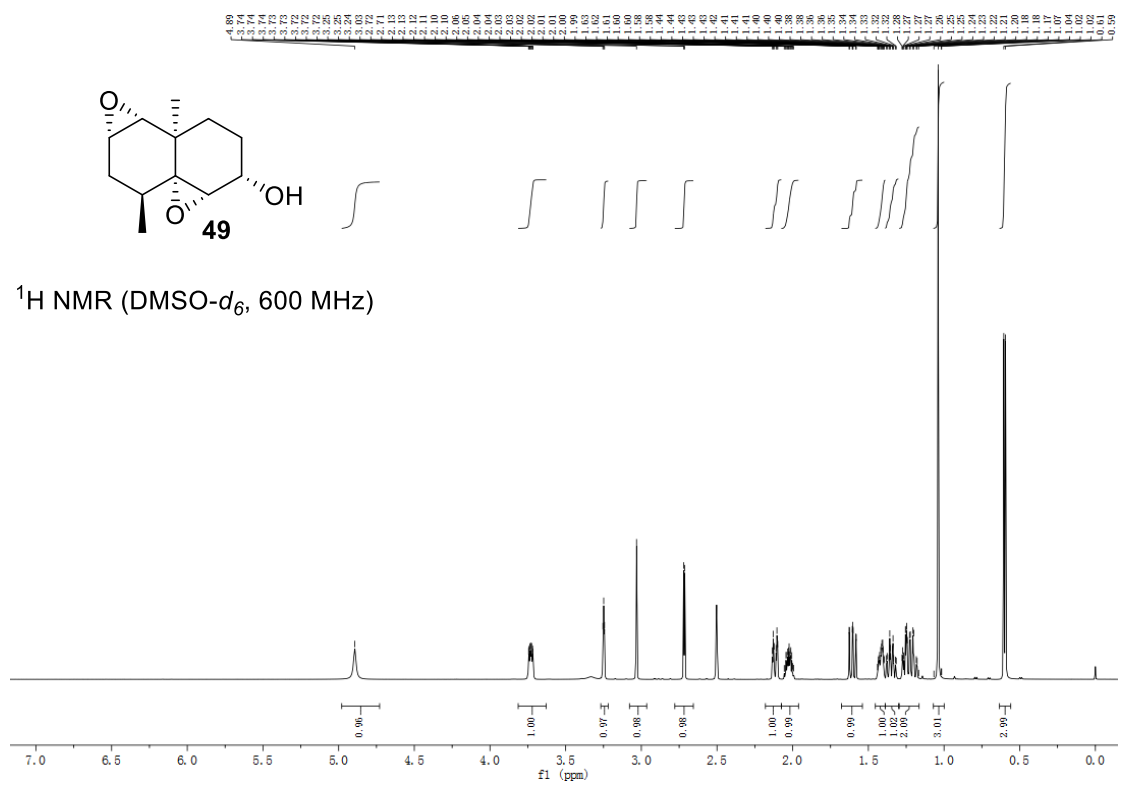


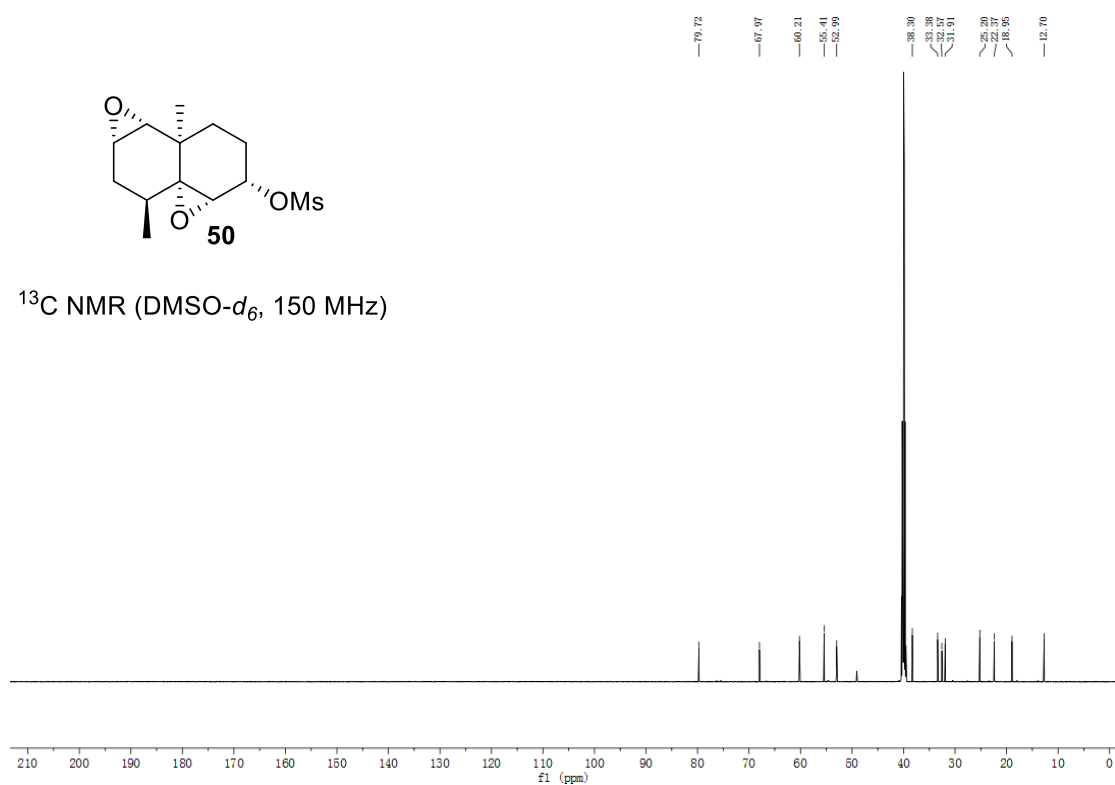
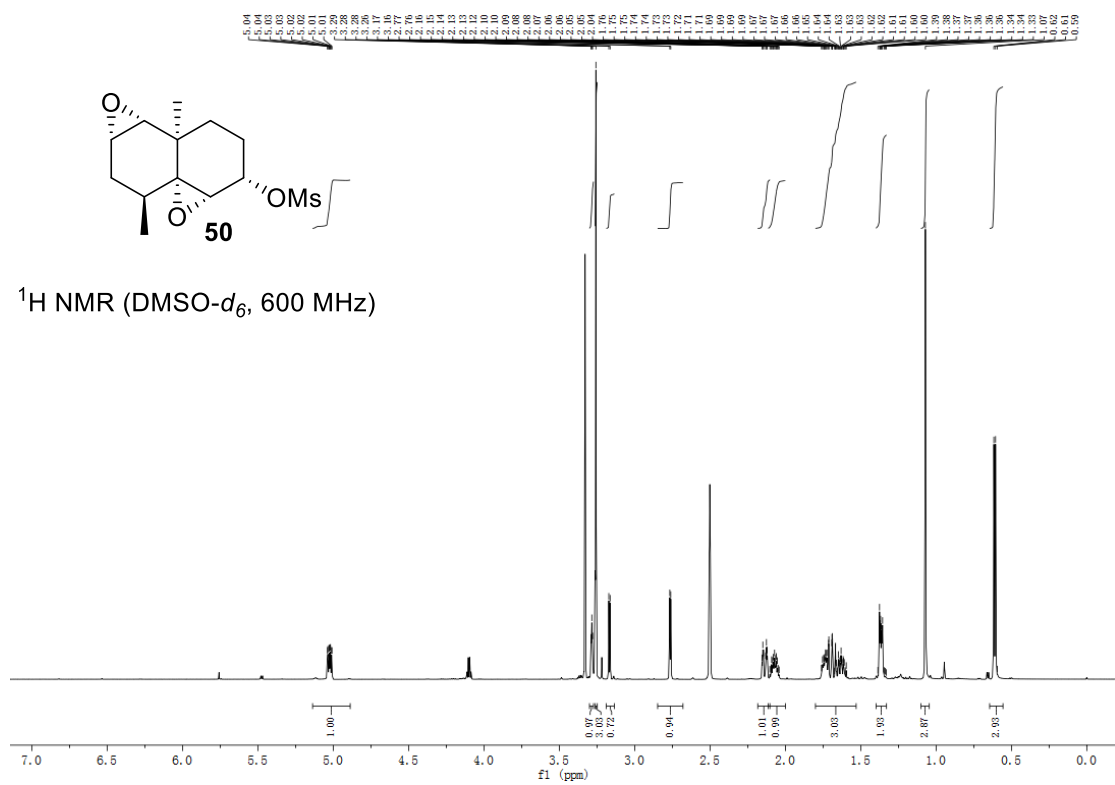


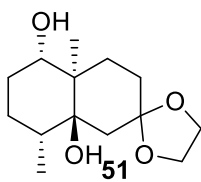
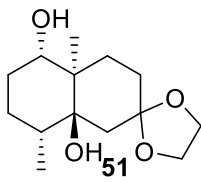


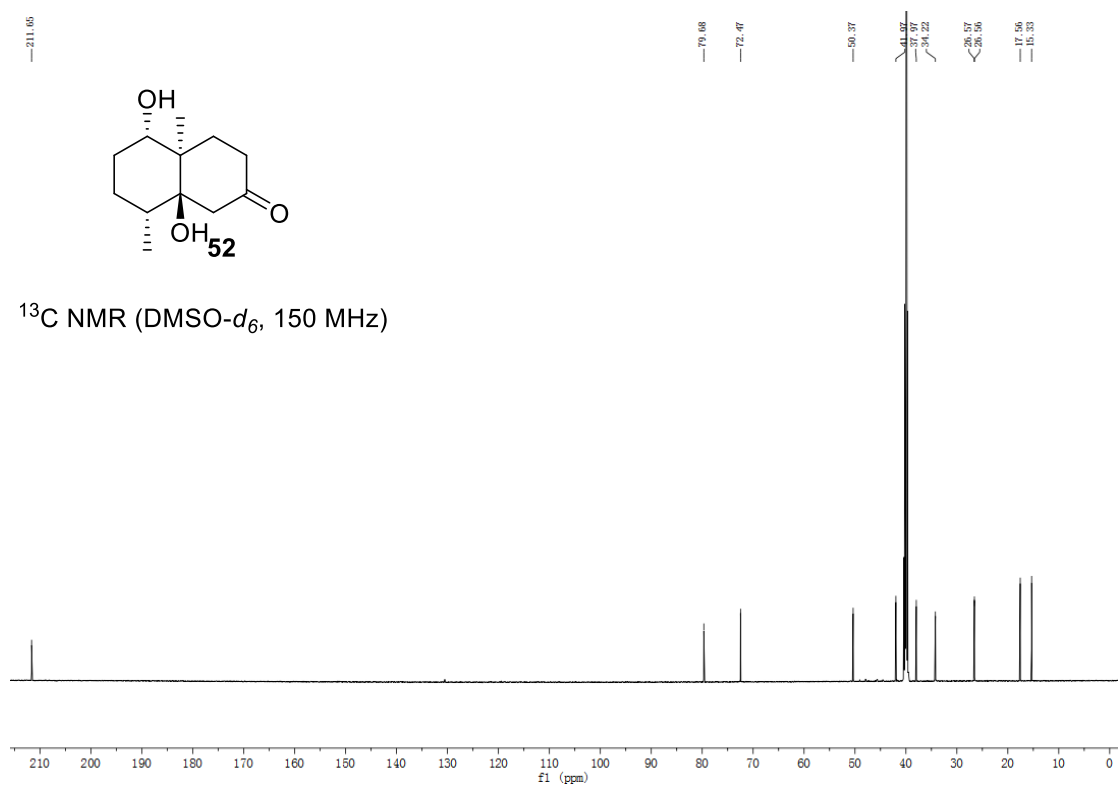
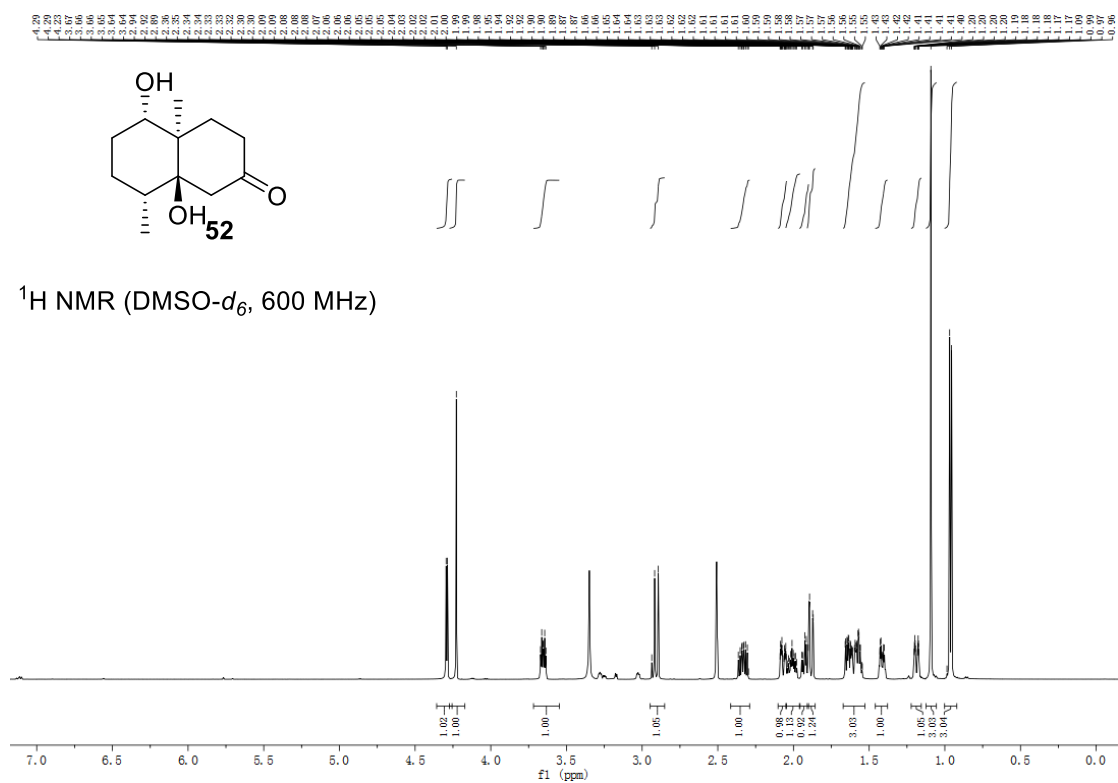


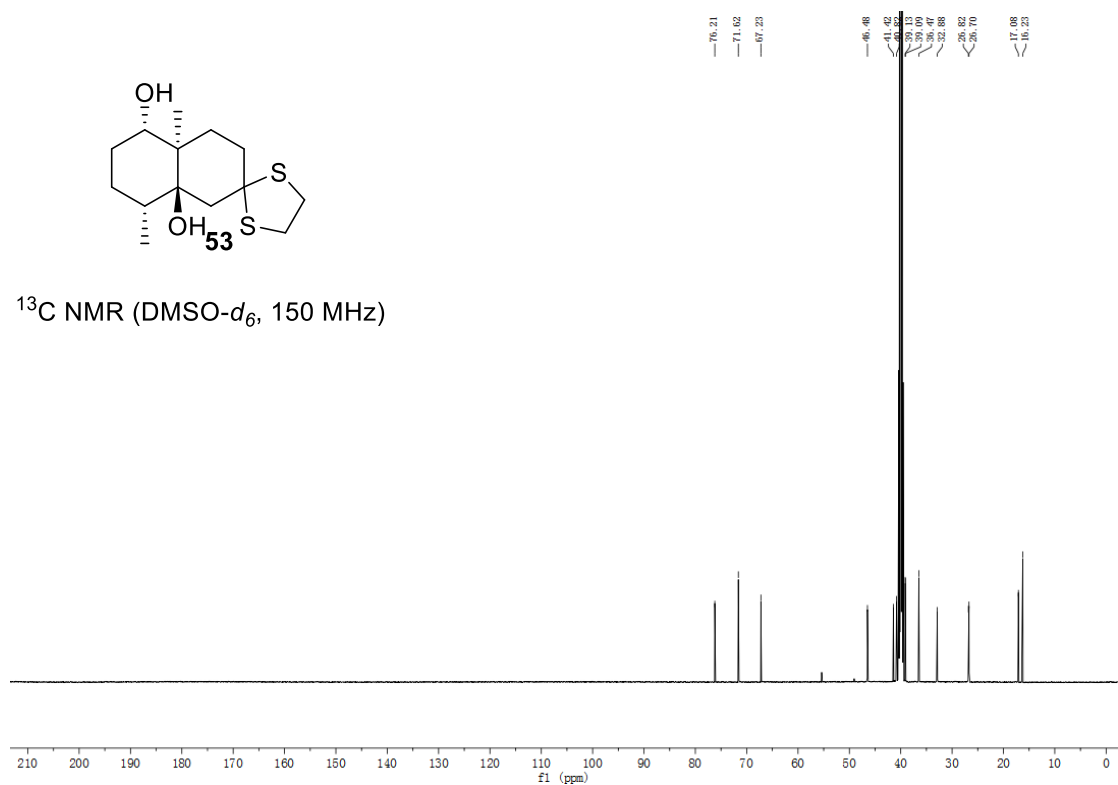
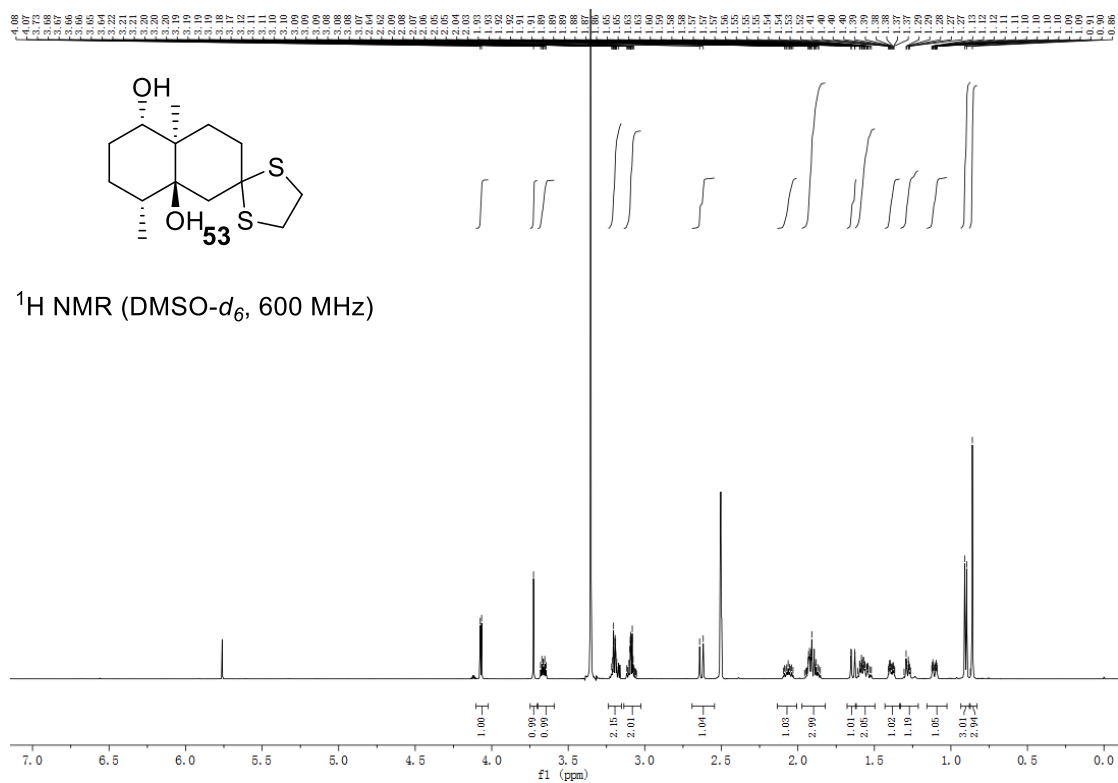


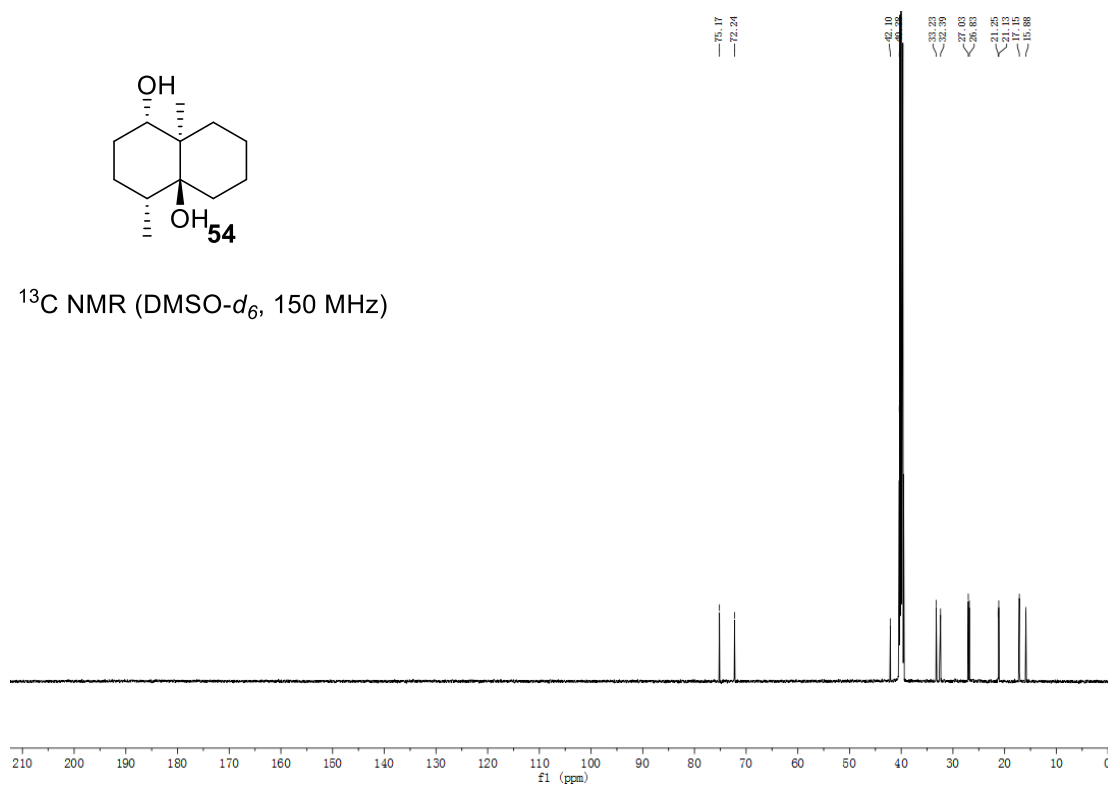
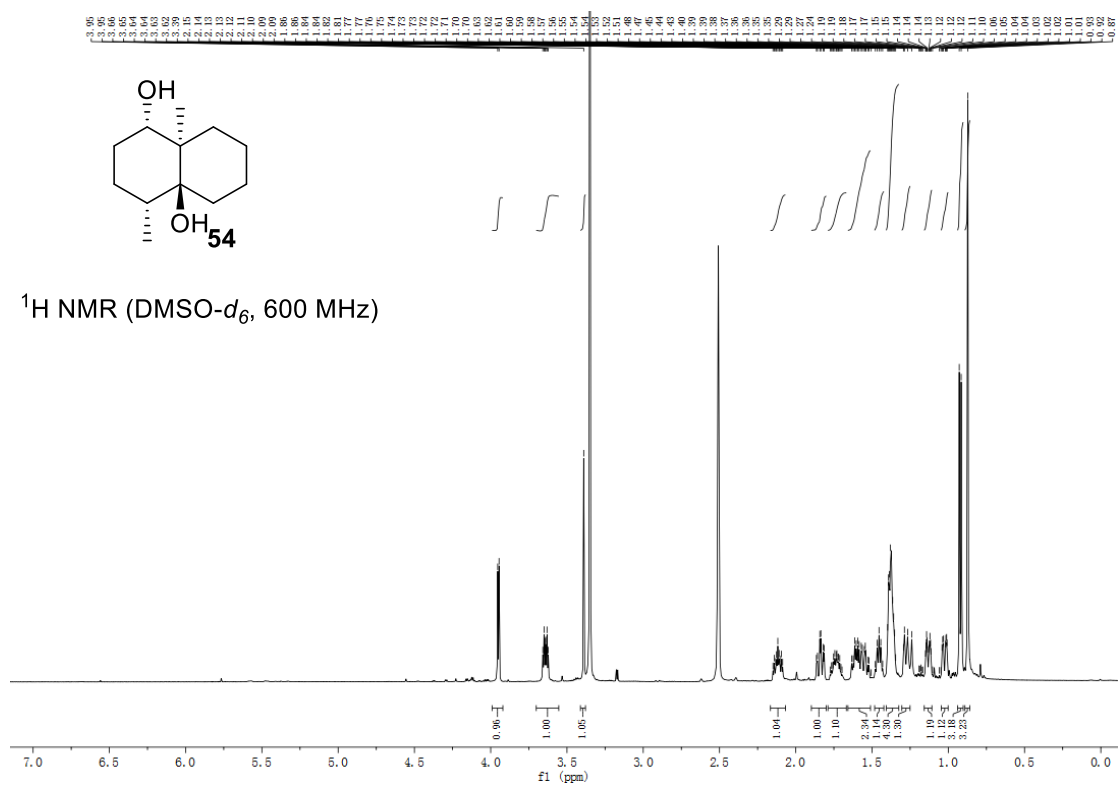


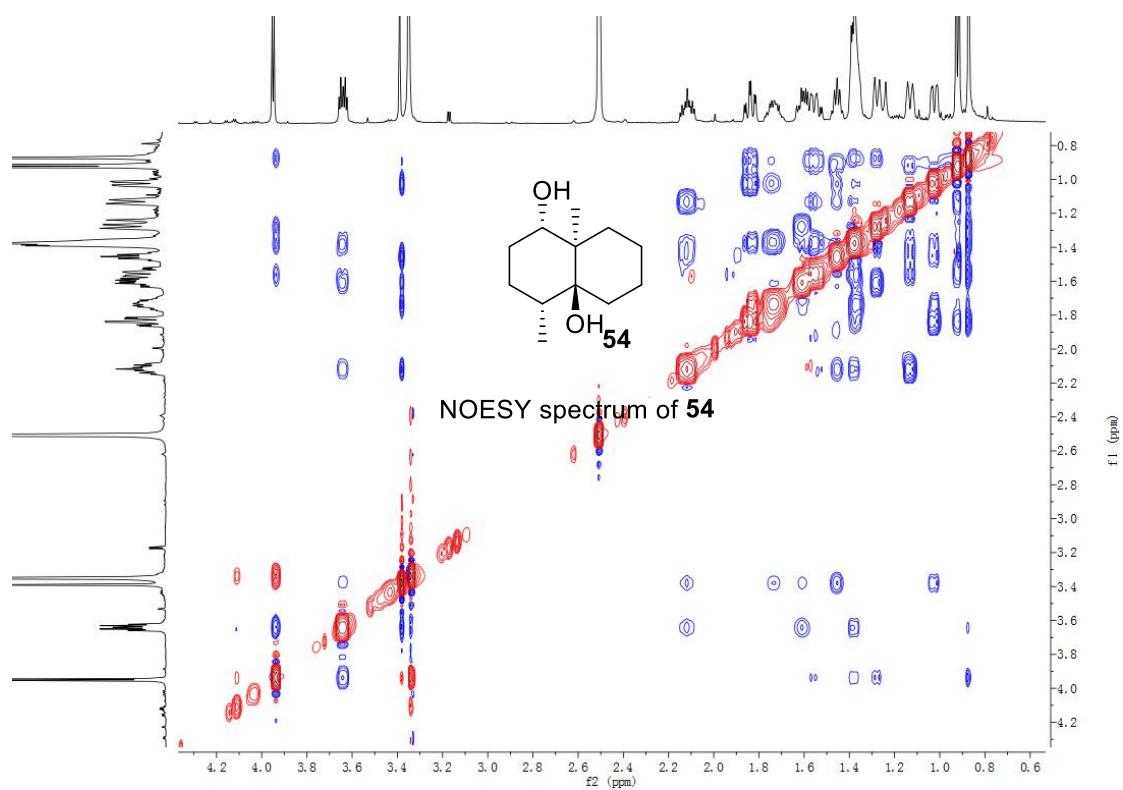


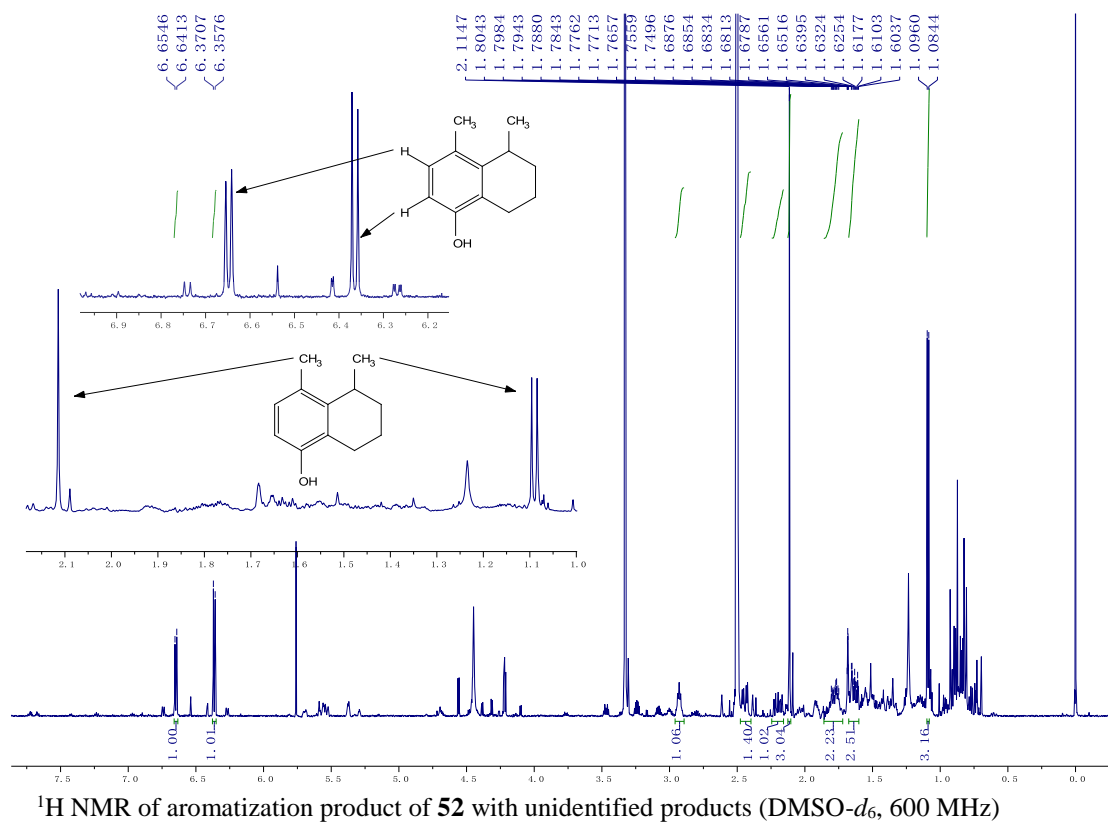
¹H NMR (DMSO-*d*₆, 600 MHz) ^{13}C NMR (DMSO- d_6 , 150 MHz)



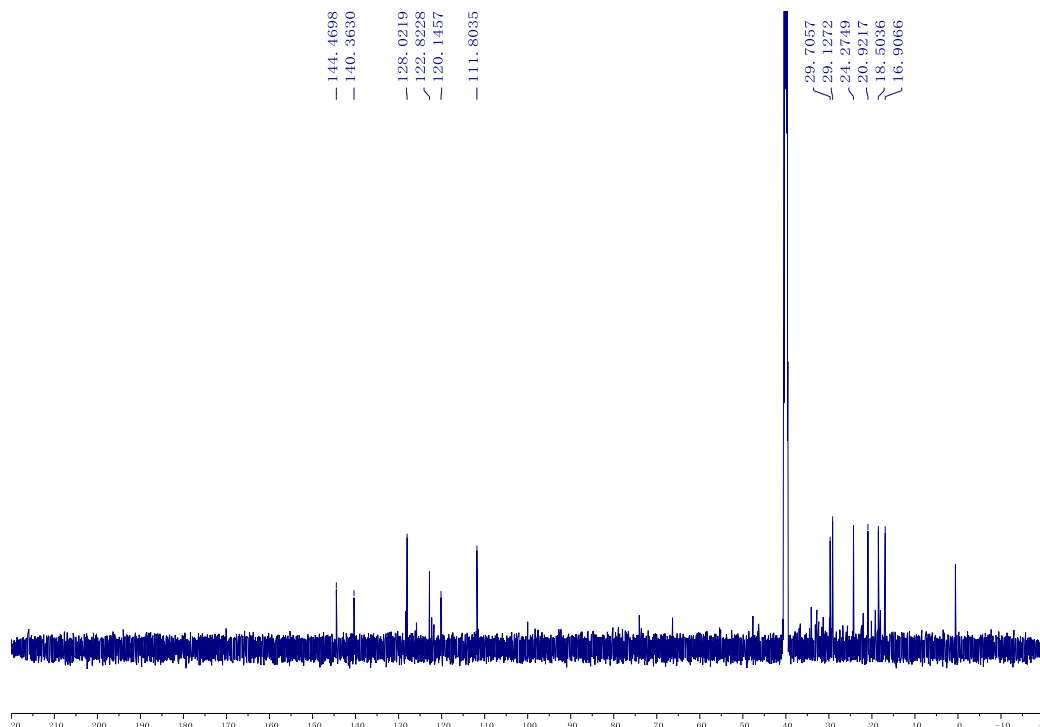




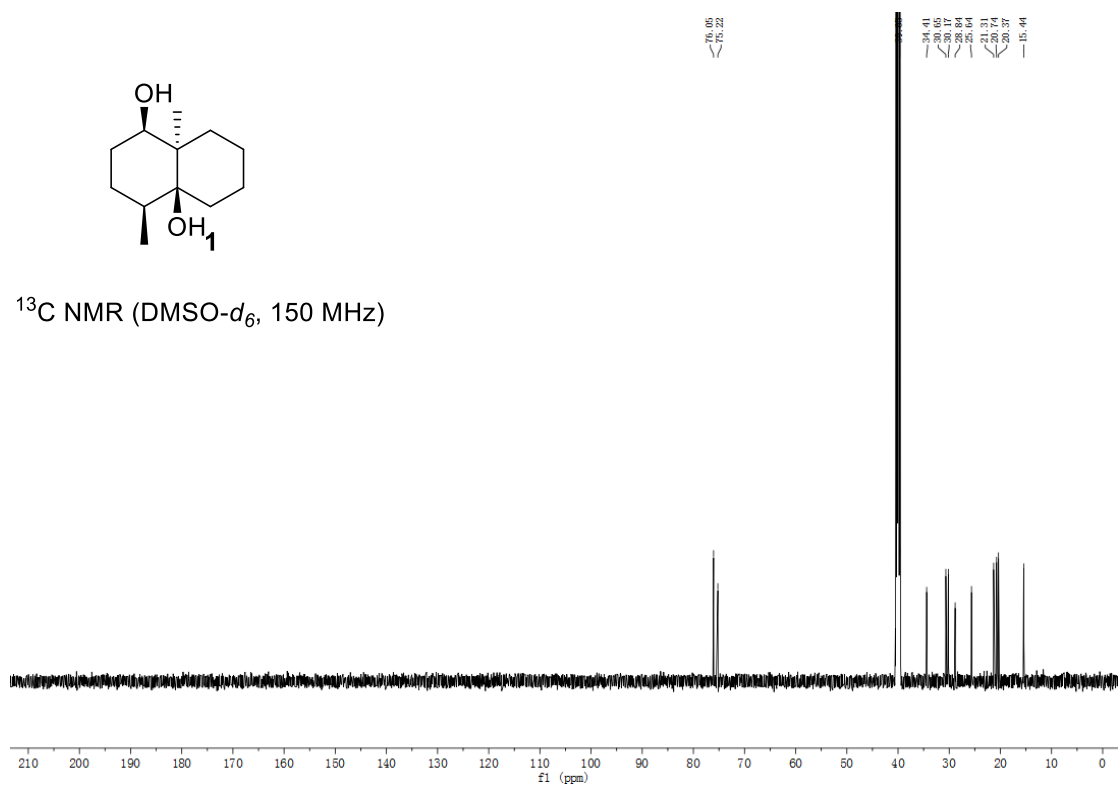
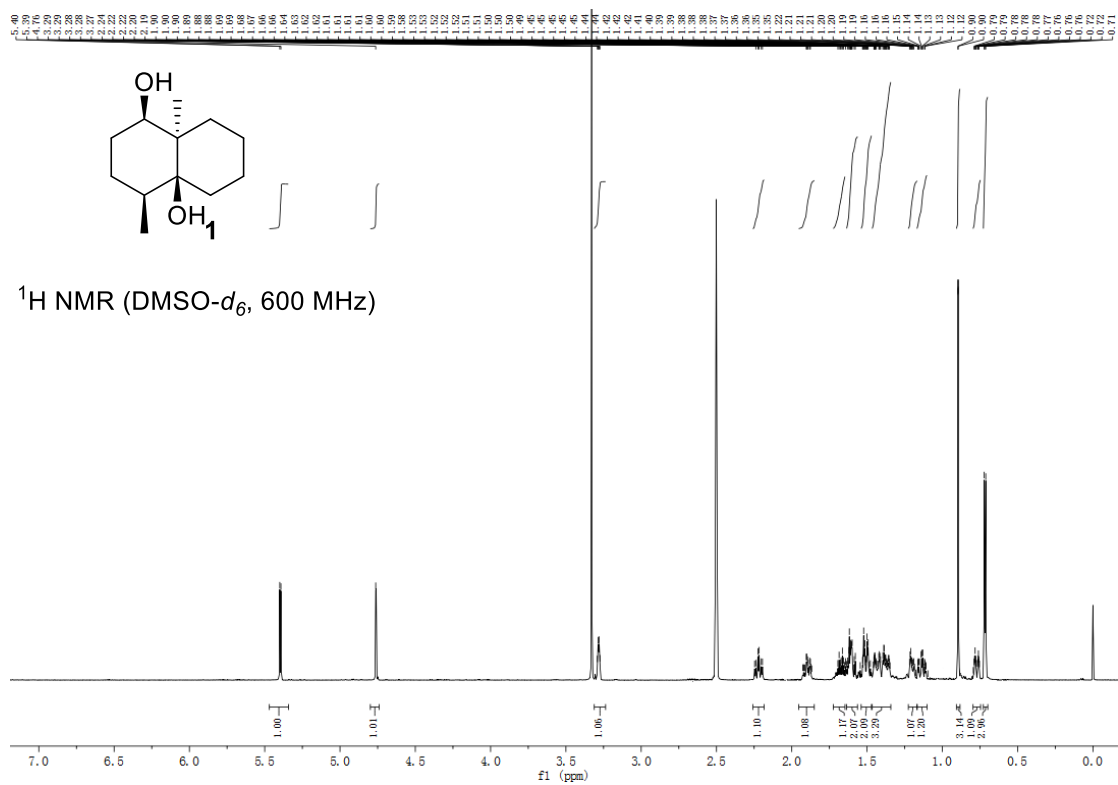


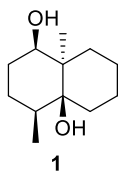


¹H NMR of aromatization product of **52** with unidentified products (DMSO-*d*₆, 600 MHz)

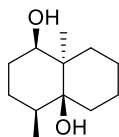
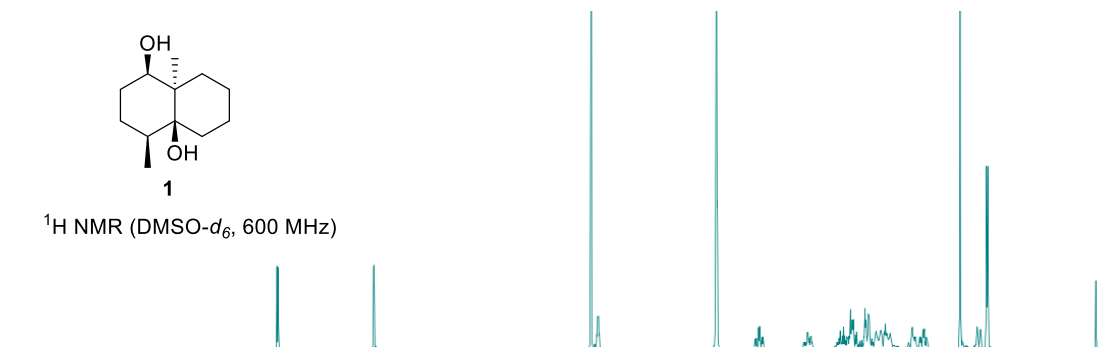


¹³C NMR of aromatization product of **52** with unidentified products (DMSO-*d*₆, 150 MHz)



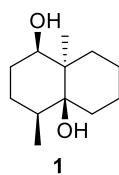
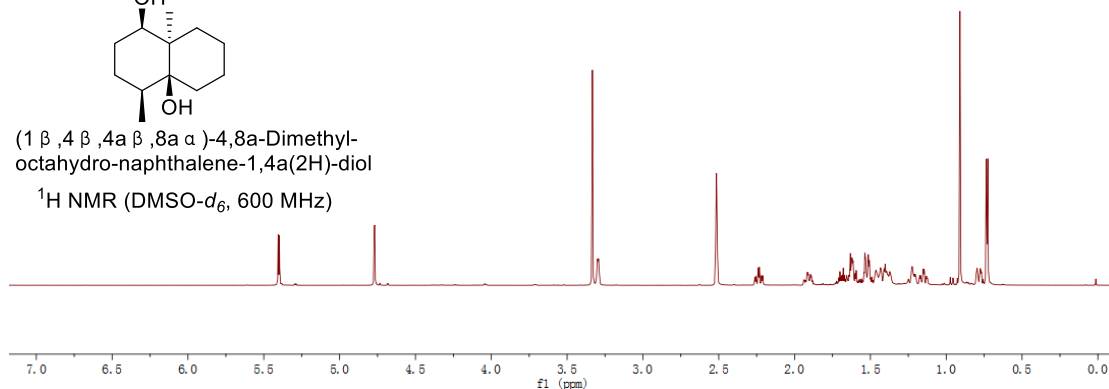


^1H NMR (DMSO- d_6 , 600 MHz)

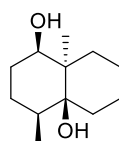
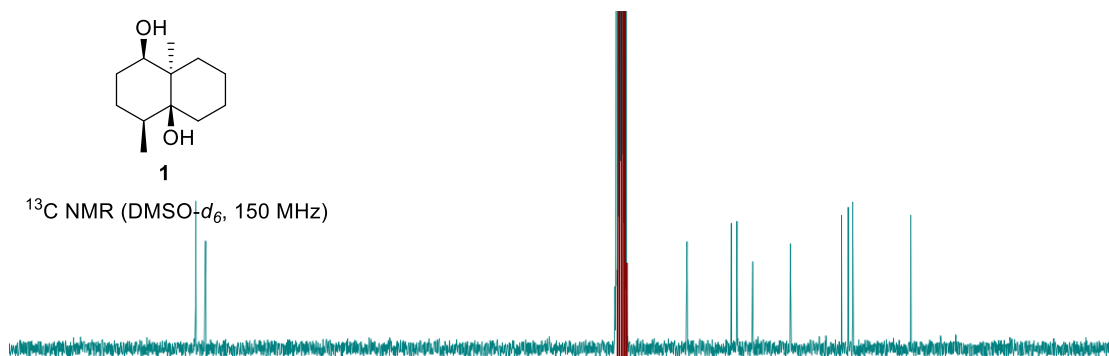


(1 β , 4 β , 4a β , 8a α)-4,8a-Dimethyl-octahydro-naphthalene-1,4a(2H)-diol

^1H NMR (DMSO- d_6 , 600 MHz)



^{13}C NMR (DMSO- d_6 , 150 MHz)



(1 β , 4 β , 4a β , 8a α)-4,8a-Dimethyl-octahydro-naphthalene-1,4a(2H)-diol

^{13}C NMR (DMSO- d_6 , 150 MHz)

