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Supporting Information

Aconitine Synthesis Studies. A modeling construction of the functionalized BCDE tetracyclic ring system

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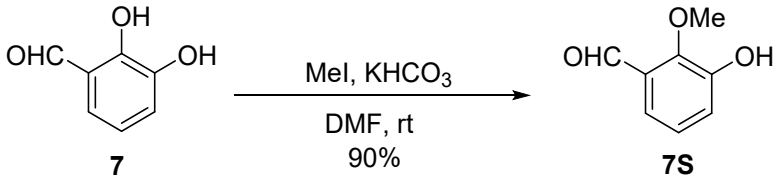
1. General Procedures

Unless the reaction procedure states otherwise, all reactions were carried out under an atmosphere of argon or nitrogen in oven or flame-dried glassware, which was under positive pressure using balloon of argon or nitrogen. Air- or moisture-sensitive liquids and solutions were transferred via syringe. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates GF254 plates. TLC plates were visualized by exposure to ultraviolet light (UV), were stained by submersion in aqueous potassium permanganate solution ($KMnO_4$) or ceric ammonium molybdenate solution (CAM), iodine staining. Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao Marine Chemical Factory, China). All chemicals were purchased from commercial vendors, unless otherwise referenced. Reagents obtained from Acros, Aldrich, J&K, TCI, and Aladdin were used without further purification. Anhydrous THF was dried by distillation over sodium and benzophenone. DCE and DCM were dried by distillation over CaH_2. MeOH was dried by distillation over iodine and magnesium. Unless otherwise noted, all reactions were carried out under an atmosphere of argon. IR spectra were recorded on a Nicolet 200 SXV spectrometer; HRMS were obtained with a Bruker BioTOFQ mass spectrometer; Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) spectra were recorded on a Varian INOVA-400/54 spectrometer and Agilent Technologies 600/54 Premium Compact instrument and calibrated by using residual signals ($CDCl_3$: δ 7.26 for ^{1}H NMR, δ 77.00 for ^{13}C NMR, DMSO-*d*6: δ 2.50 for ^{1}H NMR, δ 39.52 for ^{13}C NMR). Data are presented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, dt = doublet of triplets, m = multiplet and/or multiple resonances).

2. Experimental Procedures and Compound Characterization

Preparation of Compound 7S

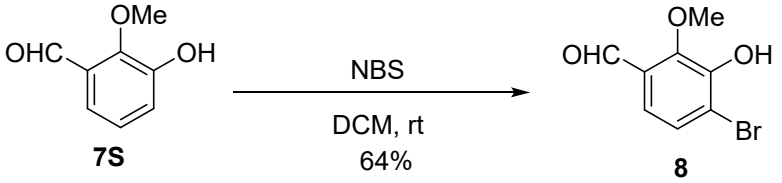


7 **7S**

2,3-Dihydroxy-benzaldehyde **7** (30.00 g, 217.20 mmol) and $KHCO_3$ (86.97 g, 868.80 mmol) were combined in DMF (434 mL) and stirred for 30 min after which the MeI (27.00 mL, 434.40 mmol, 2.0 eq) was added in one portion. After being stirred at rt for 36 h, excess MeI was removed by evaporation under reduced pressure and the residual mixture was quenched by the addition of water (400 mL) and 1 N HCl (100 mL) to reach pH =5. After extraction with EtOAc (4 x 400 mL, 1 x 200 mL), the organic layers were combined, washed with brine (2 x 500 mL), dried over $MgSO_4$ and evaporation under reduced pressure to an amorphous orange solid. The crude product was dissolved in PE/EtOAc = 8/1 (20 mL) and stirred for 24 h. The resulting suspension was filtered on a Buchner filter, the solid is washed with PE (3 x 10 mL), dried in vacuo at rt to yield 3-hydroxy-2-methoxy-benzaldehyde **7S** (29.8g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (d, J = 0.6 Hz, 1H), 7.37 (dd, J = 7.7, 1.7 Hz, 1H), 7.23 (dd, J = 8.0, 1.7 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 5.79 (s, 1H), 3.98 (s, 3H); **HRMS**(ESI) m/z calcd for $C_8H_9O_3$ $[M+H]^+$ 153.0547, found 153.0552.

Preparation of Compound 8



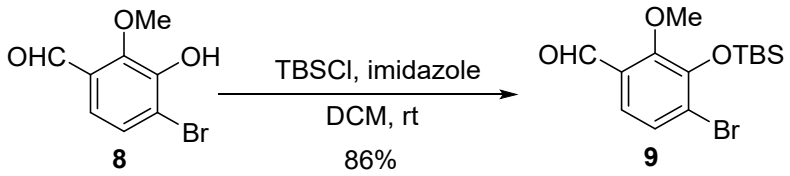
7S **8**

To a solution of 3-hydroxy-2-methoxy-benzaldehyde **7S** (10 g, 65.72 mmol) in 820 ml dry DCM was added N-bromosuccinimide (14.04g, 78.87 mmol). After being stirred at rt for 24 h, the reaction mixture was then quenched by addition of a saturated solution of $NaHSO_3$ (400 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 400 mL). The combined organic layers were washed with

brine (400 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 4/1) to give compound **8** (9.7 g, 64%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (d, *J* = 0.7 Hz, 1H), 7.37 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 5.95 (s, 1H), 4.03 (s, 3H); **HRMS(ESI)** m/z calcd for $C_8H_8BrO_3$ $[M+H]^+$ 230.9652, found 230.9659.

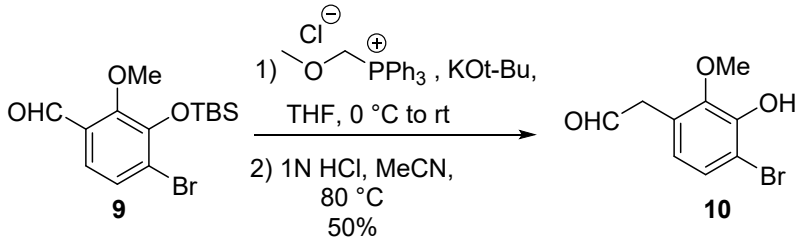
Preparation of Compound 9



To a solution of 4-bromo-3-hydroxy-2-methoxybenzaldehyde **8** (20 g, 86.56 mmol) in DCM (288 mL) were added imidazole (15.65 g, 103.87 mmol) and TBSCl (8.84 g, 129.84 mmol). After being stirred at rt for 30 min, the reaction mixture was then quenched by addition of a saturated solution of NH_4Cl (200 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 200 mL). The combined organic layers were washed with brine (200 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 6/1) to give **9** (26 g, 86%) as a yellow oil.

IR (film, KBr) ν_{max}: 3066, 2825, 2726, 1653, 1583, 1224, 823 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 3.87 (s, *3*H), 1.07 (s, 9H), 0.26 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.4, 155.2, 147.5, 129.7, 129.1, 124.2, 121.3, 62.8, 26.1, 18.8, -3.8; **HRMS(ESI)** m/z calcd for $C_{14}H_{22}BrO_3Si$ $[M+H]^+$ 345.0517, found 345.0505.

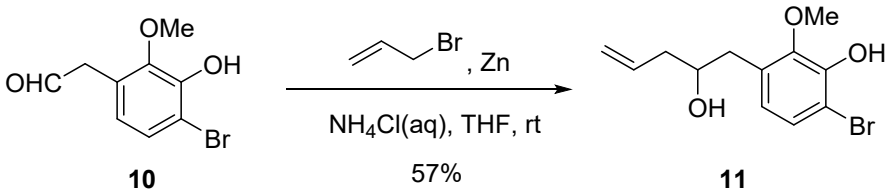
Preparation of Compound 10



To a stirred solution of (methoxymethyl)triphenyl phosphonium chloride (47.60 g, 139.00 mmol) in dry THF (85 mL) at 0 °C was added KOt-Bu (17.15 g, 152.90 mmol). The resulting mixture was stirred at the same temperature for 30 min. A solution of the aldehyde **9** (24g, 69.49 mmol) in THF (30 mL) was added to the reaction, and then the resulting mixture was stirred at room temperature. After 10 min, the reaction was quenched with a saturated solution of NH_4Cl (100 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (200 mL) and dried over Na_2SO_4, and then evaporated in vacuo. The obtained crude methyl vinyl ether derivative was used for the next step without purification. To a stirred solution of the crude product in MeCN (120 mL) at room temperature was added 1N HCl (60 mL), and the resulting solution was refluxed for 12 h. The reaction was quenched with a saturated solution of $NaHCO_3$ (100 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 6/1) to give **10** (8.5 g, 50%) as a yellow oil.

IR (film, KBr) ν_{max}: 3050, 2926, 2836, 2715, 1648, 1576, 1212, 817 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, J = 2..0 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 6.64 (d, J = 8.3 Hz, 1H), 5.71 (s, 1H), 3.83 (s, 3H), 3.67 (d, J = 2.0 Hz, 2H); **HRMS(ESI)** calcd for $C_9H_{10}BrO_3$ $[M+H]^+$ 244.9808, found 244.9815.

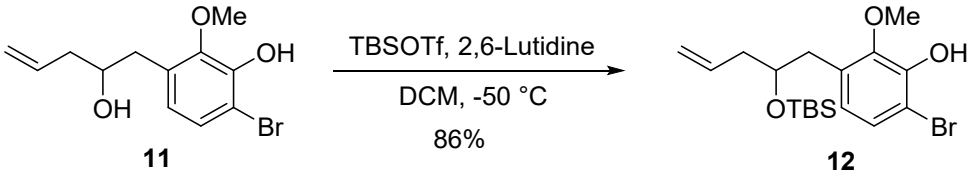
Preparation of Compound 11



To a solution of aldehyde **10** (8.5 g, 34.68 mmol) in THF (70 mL) were added a saturated solution of NH_4Cl (70 mL), Zn-dust (3.38 g, 52.02 mmol) and allyl bromide (4.50 mL, 52.02 mmol). After being stirred at rt for 30 min, the mixture was then filtered and the precipitate was washed thoroughly with EtOAc (5 x 20 mL). The combined filtrate was separated and the aqueous layer extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 4/1) to give **11** (5.6 g, 57%) as a yellow oil.

IR (film, KBr) ν_{max}: 3325, 2936, 1670, 1553, 1250, 833 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.3 Hz, 1H), 6.67 (d, J = 8.3 Hz, 1H), 5.92 (s, 1H), 5.91 – 5.77 (m, 1H), 5.19 – 5.15 (m, 1H), 5.14 (s, 1H), 3.99 – 3.87 (m, 1H), 2.77 (qd, J = 13.8, 6.3 Hz, 2H), 2.51 – 2.19 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 146.3, 134.6, 131.8, 127.6, 123.1, 118.3, 108.3, 71.1, 61.0, 41.6, 37.3; **HRMS(ESI)** calcd for $C_{12}H_{16}BrO_3$ $[M+H]^+$ 287.0278, found 287.0271.

Preparation of Compound 12

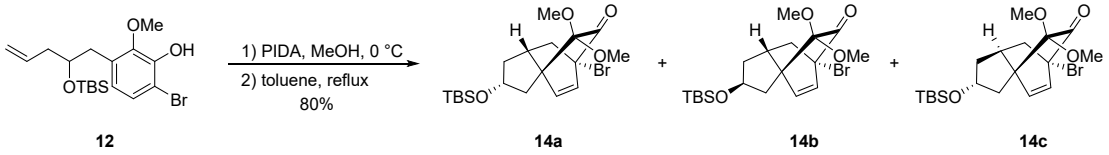


2,6-Lutidine (9.20 mL, 79.4 mmol) and TBSOTf (10.94 mL, 47.46 mmol) was added dropwise to a solution of alcohol **11** (11.4 g, 39.70 mmol) in dry DCM (100 mL) at -50 °C in turn. The reaction mixture was stirred for 30 min at this temperature, and then the mixture was diluted with a saturated solution NH_4Cl (100 mL). The organic

layers were separated and the aqueous layer was extracted with DCM (3 x 100 mL). The combined organic phases was washed with brine (100 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc= 20/1) to give compound **12**(13.8 g, 86%) as a yellow oil.

IR (film, KBr) ν_{max}: 3435, 2910, 1688, 1539, 1238, 812 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 5.86 (ddt, *J* = 17.5, 10.6, 7.1 Hz, 1H), 5.70 (s, 1H), 5.08 (s, 1H), 5.07 – 5.02 (m, 1H), 4.03 – 3.90 (m, 1H), 3.83 (s, 3H), 2.70 (qd, *J* = 13.3, 6.5 Hz, 2H), 2.31 – 2.12 (m, 2H), 0.83 (s, 9H), -0.04 (s, 3H), -0.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 146.3, 135.0, 132.5, 127.0, 123.8, 117.2, 107.6, 72.0, 61.0, 41.9, 37.7, 25.9, 18.1, -4.7; **HRMS(ESI)** m/z calcd for $C_{18}H_{30}BrO_3Si$ $[M+H]^+$ 401.1143, found 401.1151.

Preparation of Compound 14a, 14b and 14c



12 14a 14b 14c

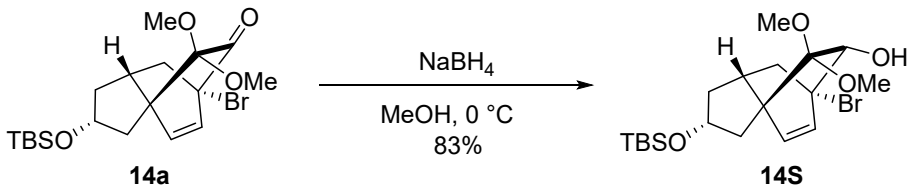
To a solution of phenol **12** (13 g, 32.38 mmol) in MeOH (160 mL) was added PIDA (12.51 g, 38.85 mmol). After being stirred at 0 °C for 30 min, the reaction mixture was then quenched by addition of saturated solution of $Na_2S_2O_3$ (80 mL) and saturated solution of $NaHCO_3$ (80 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 20/1) to give **13** as a yellow oil, which was used immediately for next step. A solution of **13** in toluene (140 mL) was allowed to stir at reflux for 12 h and the solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography (eluting with PE/EtOAc = 150/1) to give **14a** (7.6 g, 55%),**14b** (3.4 g, 25%) and **14c** (2.1 g, 10%) as a colourless oil.

For **14a**: **IR** (film, KBr) ν_{max}: 3045, 2866, 1725, 1647, 1418 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.32 (d, *J* = 8.5 Hz, 1H), 6.18 (d, *J* = 8.5 Hz, 1H), 4.38 (qd, *J* = 6.5, 3.2 Hz, 1H), 3.51 (s, 3H), 3.23 (s, 3H), 2.65 – 2.28 (m, 3H), 2.19 (dt, *J* = 12.9, 6.5 Hz, 1H), 1.99 (dd, *J* = 10.9, 5.9 Hz, 1H), 1.81 (dd, *J* = 12.9, 3.2 Hz, 1H), 1.24 – 1.12 (m, 1H), 0.88 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 138.7, 133.0, 94.2, 73.3, 66.3, 55.2, 51.5, 51.0, 42.4, 41.4, 41.0, 40.5, 25.9, 18.0, -4.8; **HRMS(ESI)** m/z calcd for $C_{19}H_{32}BrO_4Si$ $[M+H]^+$ 431.1248, found 431.1241.

For **14b**: **IR** (film, KBr) ν_{max}: 3041, 2844, 1711, 1636, 1421 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.44 (d, *J* = 8.3 Hz, 1H), 5.95 (d, *J* = 8.3 Hz, 1H), 4.61 – 4.52 (m, 1H), 3.37 (s, 3H), 3.25 (s, 3H), 2.64 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.47 – 2.31 (m, 2H), 2.25 – 2.12 (m, 1H), 2.09 – 1.99 (m, 1H), 1.65 – 1.59 (m, 1H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.4, 143.0, 128.6, 96.3, 75.7, 65.5, 57.0, 54.7, 51.24, 46.1, 40.0, 39.6, 36.3, 26.0, 18.2, -4.7; **HRMS(ESI)** m/z calcd for $C_{19}H_{32}BrO_4Si$ $[M+H]^+$ 431.1248, found 431.1251.

For **14c**: **IR** (film, KBr) ν_{max}: 3031, 2824, 1735, 1655, 1413 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.32 (d, *J* = 8.4 Hz, 1H), 5.88 (d, *J* = 8.5 Hz, 1H), 4.65 – 4.39 (m, 1H), 3.53 (s, 3H), 3.25 (s, 3H), 2.91 (tt, *J* = 12.9, 7.3 Hz, 1H), 2.53 (dd, *J* = 12.5, 9.8 Hz, 1H), 2.25 (dd, *J* = 13.3, 6.9 Hz, 1H), 2.15 (dd, *J* = 13.3, 4.9 Hz, 1H), 1.89 (dd, *J* = 12.4, 6.3 Hz, 1H), 1.76 (ddd, *J* = 13.2, 7.8, 1.7 Hz, 1H), 1.40 (td, *J* = 12.6, 7.3 Hz, 1H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 137.7, 134.3, 94.2, 73.6, 66.2, 56.0, 51.5, 51.1, 42.0, 41.6, 41.4, 39.0, 25.9, 18.1, -4.7; **HRMS(ESI)** m/z calcd for $C_{19}H_{32}BrO_4Si$ $[M+H]^+$ 431.1248, found 431.1255.

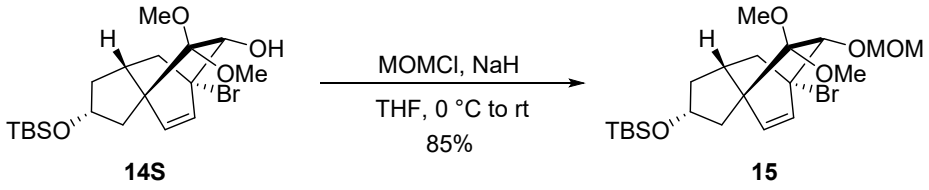
<u>Preparation of Compound 14S</u>



To a solution of phenol **14a** (2 g, 4.64 mmol) in MeOH (46 mL) was added $NaBH_4$ (210.71 mg, 5.57 mmol) at 0 °C. After being stirred at 0 °C for 10 min, the reaction mixture was then quenched by addition of saturated solution of NH_4Cl (40 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 40 mL). The combined organic layers were washed with brine (40 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 10/1) to give **14S** (1.67 g, 83%) as a colourless oil.

IR (film, KBr) ν_{max}: 3432, 2824, 1655, 1413 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.30 (d, *J* = 8.5 Hz, 1H), 5.88 (d, *J* = 8.5 Hz, 1H), 4.29 (dtd, *J* = 9.5, 6.8, 2.7 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.26 (s, 3H), 3.25 (s, 3H),, 2.56 (dd, *J* = 13.5, 8.8 Hz, 1H), 2.31 (dd, *J* = 11.7, 9.6 Hz, 1H), 2.29 – 2.17 (m, 1H), 2.06 (dt, *J* = 13.0, 6.8 Hz, 1H), 1.75 (dd, *J* = 11.7, 5.4 Hz, 1H), 1.67 (dd, *J* = 13.5, 2.8 Hz, 1H), 1.01 (td, *J* = 12.4, 6.8 Hz, 1H), 0.86 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.8, 134.9, 102.1, 78.0, 73.2, 66.1, 52.4, 51.0, 50.6, 42.5, 42.4, 41.1, 39.5, 25.9, 18.1, -4.8; **HRMS(ESI)** m/z calcd for $C_{19}H_{34}BrO_4Si$ $[M+H]^+$ 433.1405, found 433.1413.

Preparation of Compound 15



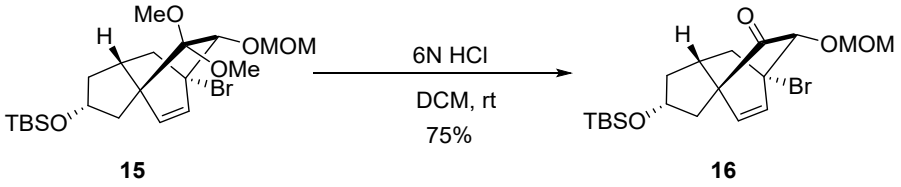
14S **15**

To a solution of alcohol **14S** (1.3 g, 3.00 mmol) in dry THF (15 mL) was added 60 % NaH (216 mg, 9.00 mmol) at 0 °C. After being stirred at 0 °C for 30 min, the MOMCl (483,06 mg, 6.00 mmol) was added dropwise. Following addition, the reaction mixture was allowed to warm to rt and stirred at that temperature for 2 h before being cooled to 0 °C and quenched by addition of saturated solution of $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (15 mL) and dried over

Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 15/1) to give **15** (1.22 g, 85%) as a colourless oil.

IR (film, KBr) ν_{max}: 3055, 2824, 1655, 1413, 930 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.4 (d, *J* = 8.5 Hz, 1H), 6.0 (d, *J* = 8.5 Hz, 1H), 4.9 – 4.9 (m, 2H), 4.3 (dt, *J* = 6.9, 2.3 Hz, 1H), 3.8 (s, 1H), 3.5 (s, 3H), 3.3 (s, 3H), 3.2 (s, 3H), 2.5 (dd, *J* = 13.4, 8.8 Hz, 1H), 2.4 – 2.2 (m, 2H), 2.1 – 2.0 (m, 1H), 1.9 – 1.8 (m, 1H), 1.7 (dd, *J* = 13.4, 2.4 Hz, 1H), 1.0 (td, *J* = 12.5, 6.5 Hz, 1H), 0.9 (s, 9H), δ 0.01 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.7, 135.2, 104.1, 97.9, 83.1, 73.1, 65.4, 56.5, 53.3, 51.2, 49.8, 42.2, 42.0, 41.6, 39.9, 25.9, 18.1, -4.8; **HRMS(ESI)** m/z calcd for $C_{21}H_{38}BrO_5Si$ $[M+H]^+$ 477.1667, found 477.1671.

Preparation of Compound 16



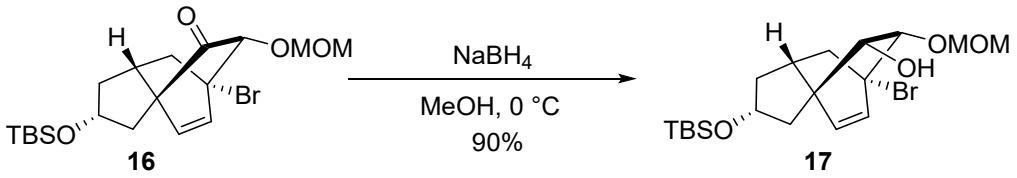
15 **16**

To a solution of compound **15** (1.1 g, 2.31 mmol) in DCM (12 mL) was added 6N HCl (1.16 mL, 6.93 mmol). After being stirred at rt for 2 h, the reaction mixture was then quenched by addition of saturated solution of $NaHCO_3$ (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 15/1) to give **16** (750 mg, 75%) as a colourless oil.

IR (film, KBr) ν_{max}: 3055, 2830, 1722, 1641, 1420, 945 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 8.4 Hz, 1H), 5.87 (d, *J* = 8.4 Hz, 1H), 5.03 (d, *J* = 6.8 Hz, 1H), 4.86 (d, *J* = 6.8 Hz, 1H), 4.45 – 4.20 (m, 1H), 3.80 (s, 1H), 3.53 (s, 3H), 2.50 (td, *J* = 11.8, 3.6 Hz, 1H), 2.43 (dd, *J* = 14.3, 8.4 Hz, 1H), 2.41 (d, *J* = 8.4 Hz, 1H), 2.29 (dt, *J* = 12.8, 6.6 Hz, 1H), 1.98 (q, *J* = 6.2 Hz, 2H), 1.67 (dd, *J* = 14.3, 2.6 Hz, 1H), 1.28 (dq,

J = 12.8, 6.2 Hz, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 138.5, 130.0, 97.7, 76.4, 72.7, 60.3, 59.3, 56.7, 42.4, 41.0, 40.7, 37.2, 25.8, 18.0, -4.8; **HRMS(ESI)** m/z calcd for $C_{19}H_{32}BrO_4Si$ $[M+H]^+$ 431.1248, found 431.1241.

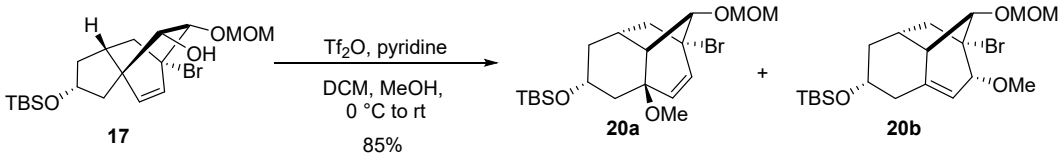
Preparation of Compound 17



To a solution of phenol **16** (750 mg, 1.74 mmol) in MeOH (9 mL) was added $NaBH_4$ (131.65 mg, 3.48 mmol, 2.0 eq.) at 0 °C. After being stirred at 0 °C for 10 min, the reaction mixture was then quenched by addition of saturated solution of NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/E_tOAc = 10/1) to give **17** (680 mg, 90%) as a colourless oil.

IR (film, KBr) ν_{max}: 3660, 2825, 1637, 1418, 926 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 8.5 Hz, 1H), 5.97 (dt, *J* = 8.5, 1.4 Hz, 1H), 4.84 (d, *J* = 6.7 Hz, 1H), 4.78 (d, *J* = 6.7 Hz, 1H), 4.42 – 4.32 (m, 1H), 3.97 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.64 (td, *J* = 7.2, 1.2 Hz, 1H), 3.49 (s, 3H), 2.86 (d, *J* = 6.9 Hz, 1H), 2.30 – 2.14 (m, 2H), 2.04 (dd, *J* = 13.9, 2.1 Hz, 1H), 1.92 (dd, *J* = 13.9, 8.0 Hz, 1H), 1.76 (dd, *J* = 12.6, 6.2 Hz, 1H), 1.68 – 1.56 (m, 1H), 1.13 (dt, *J* = 12.5, 6.3 Hz, 1H), 0.86 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.3, 135.3, 98.3, 81.0, 76.6, 73.4, 63.9, 56.9, 50.3, 43.9, 43.1, 42.5, 40.7, 25.9, 18.0, -4.8; **HRMS(ESI)** m/z calcd for $C_{19}H_{34}BrO_4Si$ $[M+H]^+$ 433.1405, found 433.1408.

Preparation of Compound 20a and 20b



To a solution of alcohol **17** (500 mg, 1.15 mmol) in dry DCM (6 mL) was added pyridine (0.59 mL, 6.90 mmol) and Tf_2O (0.58 mL, 3.45 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 1 min, at which point TLC analysis indicated full consumption of starting material. Then the dry MeOH (3 mL) was added immediately and the reaction mixture was allowed to warm to rt. After being stirred at rt for 1 h, the reaction mixture was then quenched by addition of saturated solution of $NaHCO_3$ (10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 20/1) to give **20a** (340 mg, 66 %) as a colourless oil and **20b** (100 mg, 19 %) as a colourless oil.

For **20a**: **IR** (film, KBr) ν_{max}: 2903, 1649, 1439, 940 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.06 (dd, J = 9.9, 1.7 Hz, 1H), 5.65 (dd, J = 9.9, 2.1 Hz, 1H), 4.89 (d, J = 6.9 Hz, 1H), 4.71 (d, J = 6.9 Hz, 1H), 4.19 – 4.08 (m, 2H), 3.48 (s, 3H), 3.23 (s, 3H), 2.57 – 2.44 (m, 2H), 2.42 – 2.30 (m, 1H), 2.30 – 2.18 (m, 1H), 2.15 – 2.06 (m, 1H), 1.65 (t, J = 2.9 Hz, 2H), 1.53 (dd, J = 13.6, 3.3 Hz, 1H), 0.87 (s, 9H), 0.02 (d, J = 3.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.6, 129.5, 95.1, 82.5, 70.8, 67.7, 63.7, 55.6, 49.4, 45.4, 42.9, 41.5, 33.7, 30.6, 25.9, 18.1, -4.9; **HRMS(ESI)** m/z calcd for $C_{20}H_{36}BrO_4Si$ $[M+H]^+$ 447.1561, found 447.1557.

For **20b**: **IR** (film, KBr) ν_{max}: 2898, 1635, 1444, 927 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.72 (d, J = 5.7 Hz, 1H), 4.93 (d, J = 6.7 Hz, 1H), 4.70 (d, J = 6.7 Hz, 1H), 4.14 – 4.10 (m, 2H), 3.51 (s, 3H), 3.43 (d, J = 6.0 Hz, 1H), 3.39 (s, 3H), 2.65 – 2.50 (m, 2H), 2.41 (d, J = 3.9 Hz, 2H), 2.08 (dd, J = 12.4, 4.8 Hz, 1H), 1.93 (dd, J = 14.2, 5.5 Hz, 1H), 1.81 (ddd, J = 14.2, 6.7, 4.1 Hz, 1H), 1.35 – 1.23 (m, 2H), 0.87 (s, 9H), 0.03 (d, J = 4.4 Hz,6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.0, 118.9, 96.1, 84.3, 82.9, 70.0, 68.0,

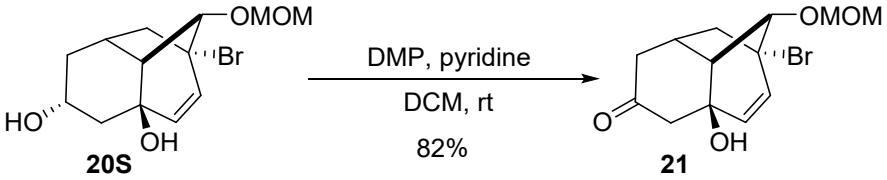
59.0, 55.6, 46.3, 46.3, 43.5, 36.4, 35.1, 25.8, 18.0, -4.8; **HRMS(ESI)** m/z calcd for $C_{20}H_{36}BrO_4Si$ $[M+H]^+$ 447.1561, found 447.1569.

Preparation of Compound 20S

A suspension of compound **20a** and **20b** (400 mg, 0.89 mmol) in MeCN (4.5 ml) containing a drop of 46% HF was stirred for 10 min at rt. The reaction mixture was then quenched by addition of saturated solution of $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 1/1) to give **20S** (215 mg, 75%) as a colourless oil.

IR (film, KBr) ν_{max}: 3642, 2788, 1623, 1414, 945 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.09 (dd, *J* = 9.8, 1.7 Hz, 1H), 5.67 (dd, *J* = 9.8, 2.1 Hz, 1H), 4.94 (d, *J* = 6.6 Hz, 1H), 4.80 (d, *J* = 6.6 Hz, 1H), 4.28 (dd, *J* = 5.0, 1.7 Hz, 1H), 4.12 (t, *J* = 4.1 Hz, 1H), 3.47 (s, 3H), 2.60 – 2.51 (m, 1H), 2.47 (t, *J* = 12.2 Hz, 1H), 2.32 – 2.20 (m, 2H), 2.06 (dd, *J* = 14.1, 4.1 Hz, 1H), 1.84 – 1.73 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.3, 133.7, 96.9, 85.0, 68.0, 67.5, 62.2, 56.2, 46.3, 46.1, 43.1, 33.7, 29.6; **HRMS(ESI)** m/z calcd for $C_{13}H_{20}BrO_4$ $[M+H]^+$ 319.0540, found 319.0544.

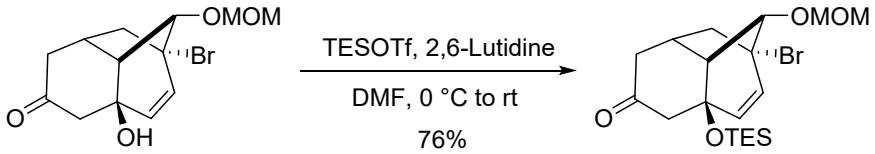
Preparation of Compound 21



Diol **20S** (50 mg, 0.16 mmol,) was dissolved in DCM (0.8 mL), and to this stirred solution was added Dess-Martin periodinane (100.10 mg, 0.24 mmol) and pyridine (37.90 µL, 0.471 mmol) at rt. The reaction mixture was stirred at rt for 30 min and then quenched with a saturated aqueous solution of $Na_2S_2O_3$ (1 mL). The mixture was extracted with DCM (3 x 1 mL), and the organic layers were washed with brine (3 mL), dried over $MgSO_4$. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 1/1) to give **21** (41 mg, 82%) as a colourless oil.

IR (film, KBr) ν_{max}: 3542, 2854, 1718, 1659, 1427, 938 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.08 (dd, *J* = 9.8, 1.7 Hz, 1H), 5.47 (dd, *J* = 9.8, 2.2 Hz, 1H), 4.97 (d, *J* = 6.6 Hz, 1H), 4.82 (d, *J* = 6.6 Hz, 1H), 4.39 (dd, *J* = 5.1, 1.8 Hz, 1H), 3.72 (s, 1H), 3.49 (s, 3H), 2.92 – 2.80 (m, 1H), 2.68 – 2.47 (m, 5H), 2.21 (dt, *J* = 15.4, 2.0 Hz, 1H), 1.86 (dd, *J* = 13.4, 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.8, 135.9, 130.0, 97.1, 84.3, 72.3, 60.6, 56.4, 51.8, 47.6, 46.2, 43.7, 30.8; **HRMS(ESI)** m/z calcd for $C_{13}H_{18}BrO_4$ $[M+H]^+$ 317.0383, found 317.0388.

Preparation of Compound 22



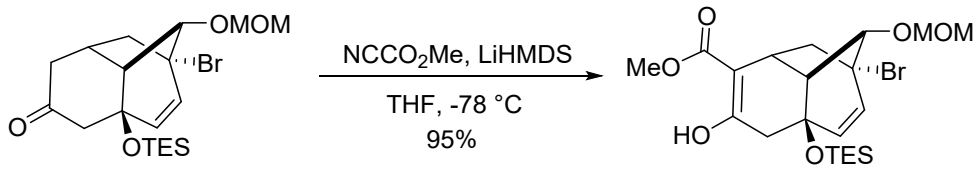
21 **22**

To a solution of compound **21** (200 mg, 0.63 mmol) in DMF (1.6 mL) was added 2,6-Lutidine (0.18 mL, 1.575 mmol) and TESOTf (0.21 mL, 0.945 mmol) at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was then quenched by addition of H_2O (2 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (2 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 6/1) to give **22** (206 mg, 76%) as a colourless oil.

IR (film, KBr) ν_{max}: 2953, 2854, 1728, 1642, 1417, 1380, 932 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 6.06 (dd, *J* = 9.9, 1.7 Hz, 1H), 5.43 (dd, *J* = 9.9, 2.2 Hz, 1H), 4.91 (d,

J = 6.8 Hz, 1H), 4.66 (d, *J* = 6.8 Hz, 1H), 4.29 (dd, *J* = 4.7, 1.7 Hz, 1H), 3.48 (s, 3H), 2.81 (dt, *J* = 12.5, 6.3 Hz, 1H), 2.73 – 2.63 (m, 2H), 2.61 – 2.45 (m, 3H), 2.20 – 2.09 (m, 1H), 1.77 (dd, *J* = 13.3, 5.9 Hz, 1H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.9, 136.0, 129.4, 94.7, 80.6, 74.5, 60.8, 55.6, 55.2, 47.1, 44.7, 43.6, 31.7, 7.1, 6.7; **HRMS(ESI)** m/z calcd for $C_{19}H_{32}BrO_4Si$ $[M+H]^+$ 431.1248, found 431.1241.

Preparation of Compound 23

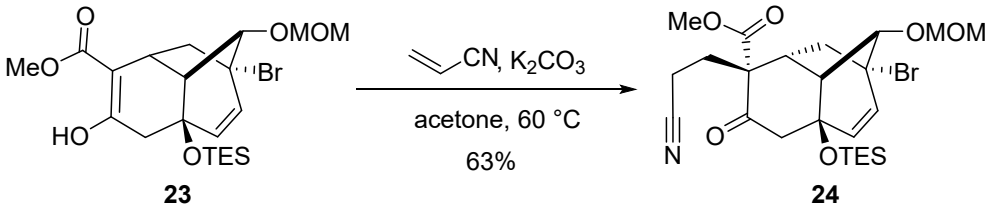


22 **23**

To a solution of compound **22** (130 mg, 0.30 mmol) in THF (1.3 mL) was added LiHMDS (0.6 mL, 0.6 mmol, 1M in THF) and methyl cyanoformate (47 μL, 0.6 mmol) at -78 °C. After being stirred at -78 °C for 10 min, the reaction mixture was then quenched by addition of H_2O (2 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (2 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 10/1) to give **23** (140 mg, 95%) as a white solid.

IR (film, KBr) ν_{max}: 2943, 2838, 1737, 1629, 1425, 1360, 918 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 11.93 (s, 1H), 6.02 (dd, *J* = 9.9, 1.7 Hz, 1H), 5.41 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.91 (d, *J* = 6.7 Hz, 1H), 4.65 (d, *J* = 6.7 Hz, 1H), 4.22 (dd, *J* = 5.2, 1.7 Hz, 1H), 3.75 (s, 3H), 3.48 (s, 3H), 3.19 – 3.01 (m, 1H), 2.66 – 2.35 (m, 4H), 1.82 (dd, *J* = 12.8, 3.8 Hz, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.63 (t, *J* = 7.9 Hz, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 167.7, 136.1, 129.3, 100.1, 94.7, 80.0, 70.1, 61.4, 55.6, 51.7, 47.2, 43.5, 42.3, 31.2, 7.1, 6.8; **HRMS(ESI)** m/z calcd for $C_{21}H_{34}BrO_6Si$ $[M+H]^+$ 489.1303, found 489.1307.

Preparation of Compound 24

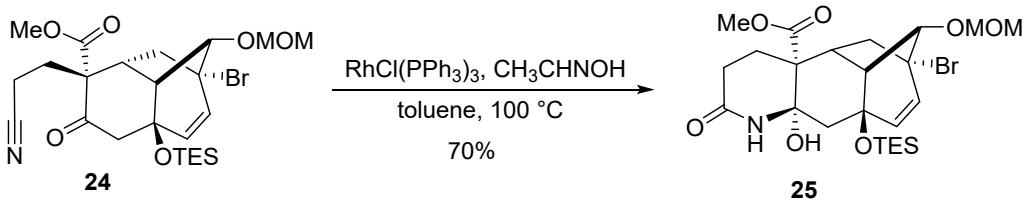


23 **24**

To a solution of compound **23**(20 mg, 0.04 mmol) in acetone (0.8 mL) was added K_2CO_3 (27.64 mg, 0.2 mmol) and acrylonitrile (10 μL, 0.16 mmol) at rt. After being stirred at 60 °C for 8 h, the reaction mixture was then quenched by addition of addition of saturated solution of NH_4Cl (2 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (2 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 6/1) to give **24** (24 mg, 63%) as a colourless oil.

IR (film, KBr) ν_{max}: 2954, 2831, 2245, 1729, 1641, 1417, 1359, 937 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 6.11 (dd, *J* = 9.9, 1.6 Hz, 1H), 5.41 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.89 (d, *J* = 6.8 Hz, 1H), 4.68 (d, *J* = 6.8 Hz, 1H), 4.27 (dd, *J* = 4.4, 1.6 Hz, 1H), 3.76 (s, 3H), 3.48 (s, 3H), 2.89 (d, *J* = 13.1 Hz, 1H), 2.84 – 2.70 (m, 2H), 2.57 (d, *J* = 13.1 Hz, 1H), 2.54 – 2.37 (m, 4H), 2.21 – 1.99 (m, 2H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.8, 169.3, 136.9, 129.3, 118.1, 94.8, 79.7, 74.2, 61.6, 59.6, 55.7, 52.6, 52.1, 44.5, 43.6, 40.4, 32.4, 13.5, 7.1, 6.7; **HRMS(ESI)** m/z calcd for $C_{24}H_{37}BrNO_6Si$ $[M+H]^+$ 542.1569, found 542.1562.

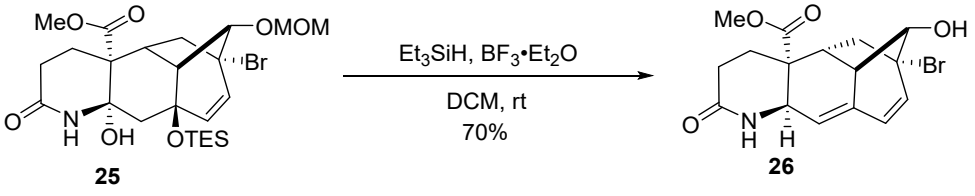
Preparation of Compound 25



To a solution of compound **24** (14 mg, 0.026 mmol) in toluene (0.5 mL) was added $RhCl(PPh_3)_3$ (2.40 mg, 0.0026 mmol) and acetaldoxime (7.67 mg, 0.13 mmol) at rt. The vessel was sealed and heated at 100 °C for 10 h. The reaction mixture was then quenched by addition of H_2O (2 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (2 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 1/4) to give **25** (10 mg, 70%) as a colourless oil.

IR (film, KBr) ν_{max}: 3555, 2938, 2828, 1737, 1628, 1418, 1339, 924 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 5.96 (dd, *J* = 9.9, 1.7 Hz, 1H), 5.74 (s, 1H), 5.56 (d, J = 2.9 Hz, 1H), 5.51 (dd, *J* = 9.9, 2.1 Hz, 1H), 4.88 (d, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 6.8 Hz, 1H), 4.18 (dd, *J* = 4.5, 1.7 Hz, 1H), 3.78 (s, 3H), 3.46 (s, 3H), 2.72 – 2.58 (m, 1H), 2.49 (ddd, *J* = 6.5, 4.4, 2.1 Hz, 1H), 2.42 (dd, *J* = 16.7, 5.1 Hz, 1H), 2.34 – 2.23 (m, 3H), 2.22 – 2.15 (m, 1H), 2.14 – 2.06 (m, 2H), 1.99 (dd, *J* = 14.0, 2.7 Hz, 1H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.59 (q, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 168.7, 133.0, 131.8, 94.7, 84.8, 80.4, 70.4, 60.7, 55.6, 53.1, 50.7, 49.0, 43.1, 42.5, 40.9, 29.4, 28.6, 7.2, 6.9; **HRMS(ESI)** m/z calcd for $C_{24}H_{39}BrNO_7Si$ $[M+H]^+$ 560.1674, found 560.1682.

<u>Preparation of Compound 26</u>

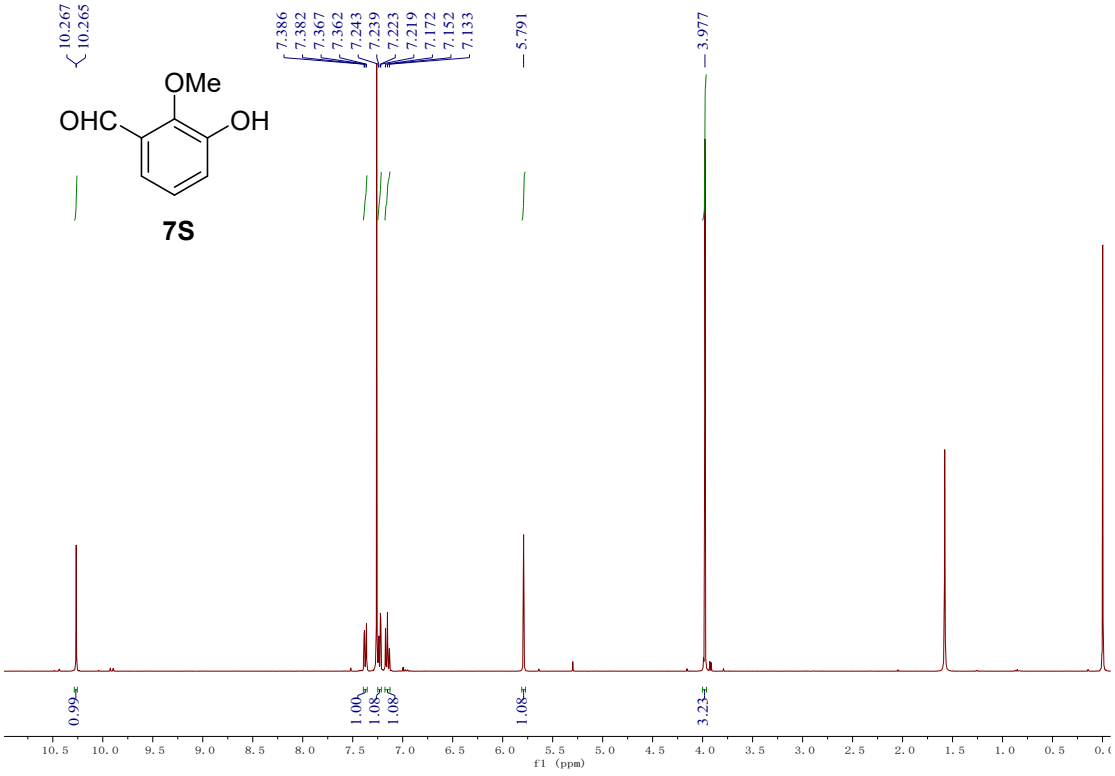


To a solution of compound **25** (10 mg, 0.018 mmol) in dry DCM (0.5 mL) was added BF_3•Et_2O (5.5 μL, 0.0045 mmol) and Et_3SiH (8.6 μL, 0.053 mmol) at rt. After being stirred at rt for 2 h, the reaction mixture was then quenched by addition of H_2O (1 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (2 mL) and dried over Na_2SO_4. The crude product was purified by silica gel chromatography (eluting with PE/EtOAc = 1/1) to give **26** (4.5 mg, 70%) and as a white solid.

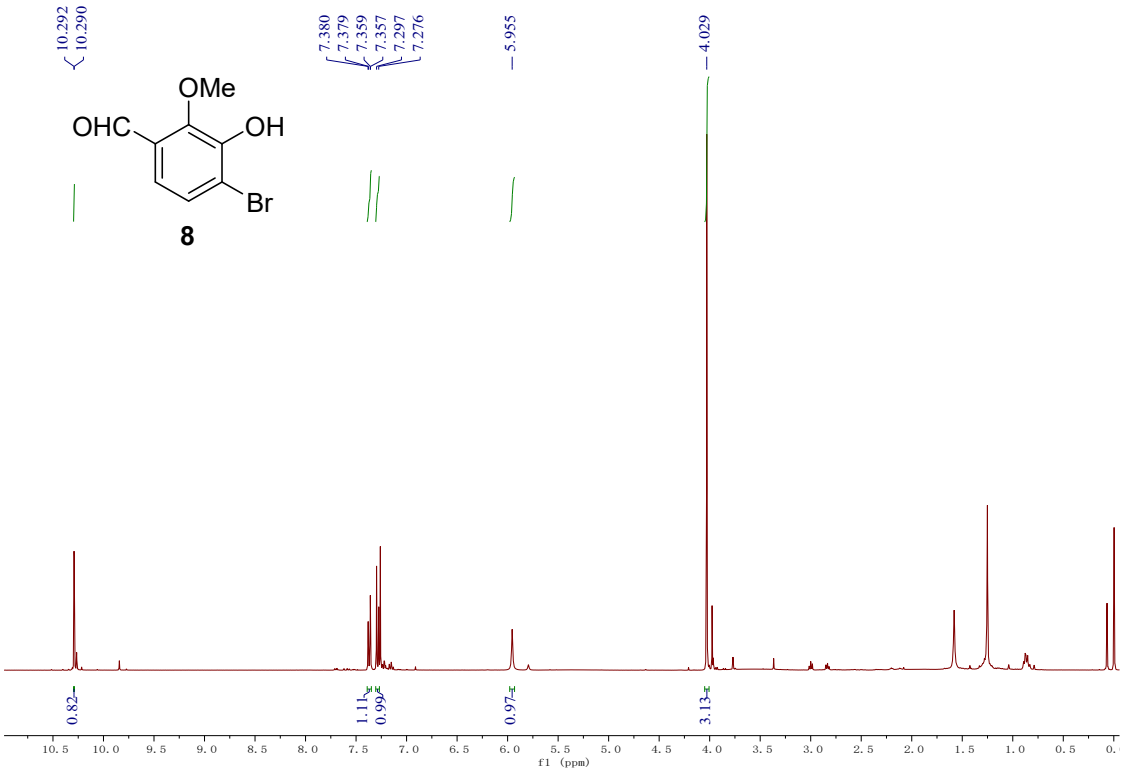
IR (film, KBr) ν_{max}: 3542, 2828, 1745, 1598, 1426, 1344 cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-*d*6) δ 9.63 (s, 1H), 5.69 (dt, *J* = 9.7, 1.9 Hz, 1H), 5.53 (d, *J* = 5.1 Hz, 1H), 5.36 (d, *J* = 7.7 Hz, 1H), 5.32 (ddd, *J* = 9.7, 3.1, 1.5 Hz, 1H), 4.25 (dt, *J* = 6.1, 3.0 Hz, 1H), 3.63 (s, 3H), 2.99 (s, 1H), 2.75 – 2.56 (m, 1H), 2.45 (t, *J* = 12.7 Hz, 1H), 2.32 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.21 – 2.01 (m, 3H), 1.93 – 1.82 (m, 1H), 1.76 (dd, *J* = 13.1, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-*d*6) δ 172.1, 167.6, 136.1, 131.5, 128.0, 107.5, 78.6, 65.8, 51.9, 47.9, 47.1, 39.9, 39.2, 32.7, 31.5, 29.8; **HRMS(ESI)** m/z calcd for $C_{16}H_{19}BrNO_4$ $[M+H]^+$ 368.0492, found 368.0488.

3. ^{1}H NMR and ^{13}C NMR spectra

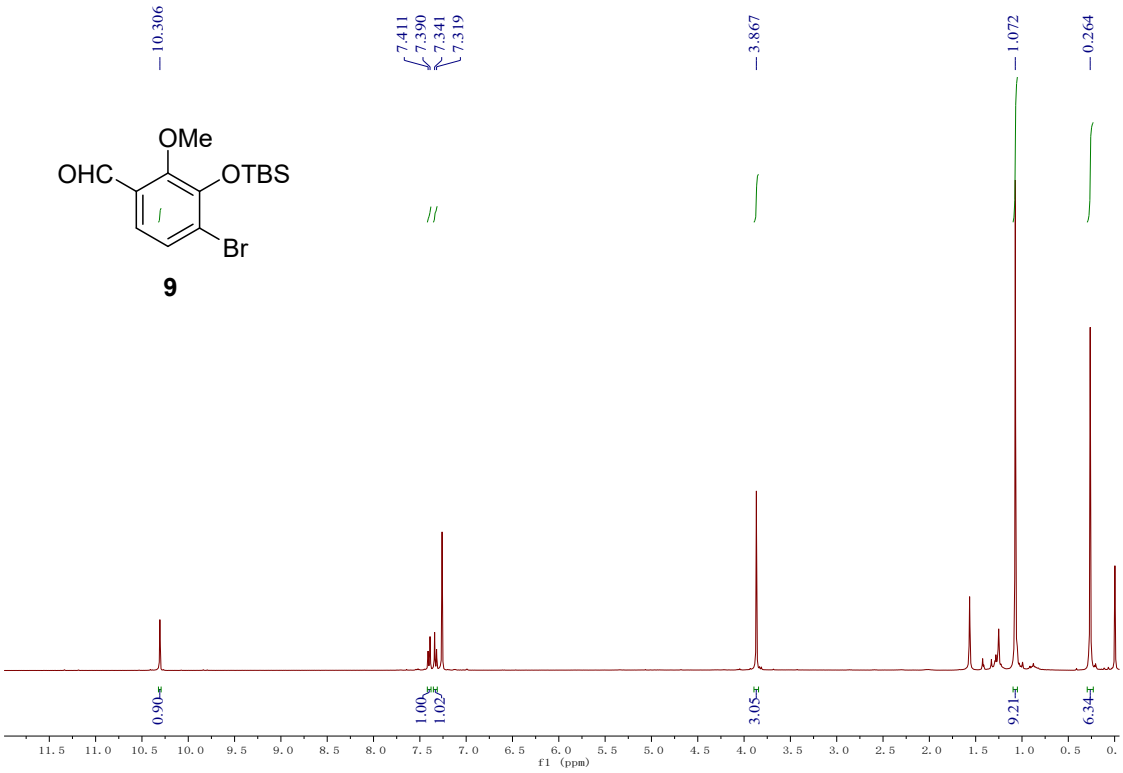
^{1}H NMR Spectrum of 7S (400 MHz, $CDCl_3$)



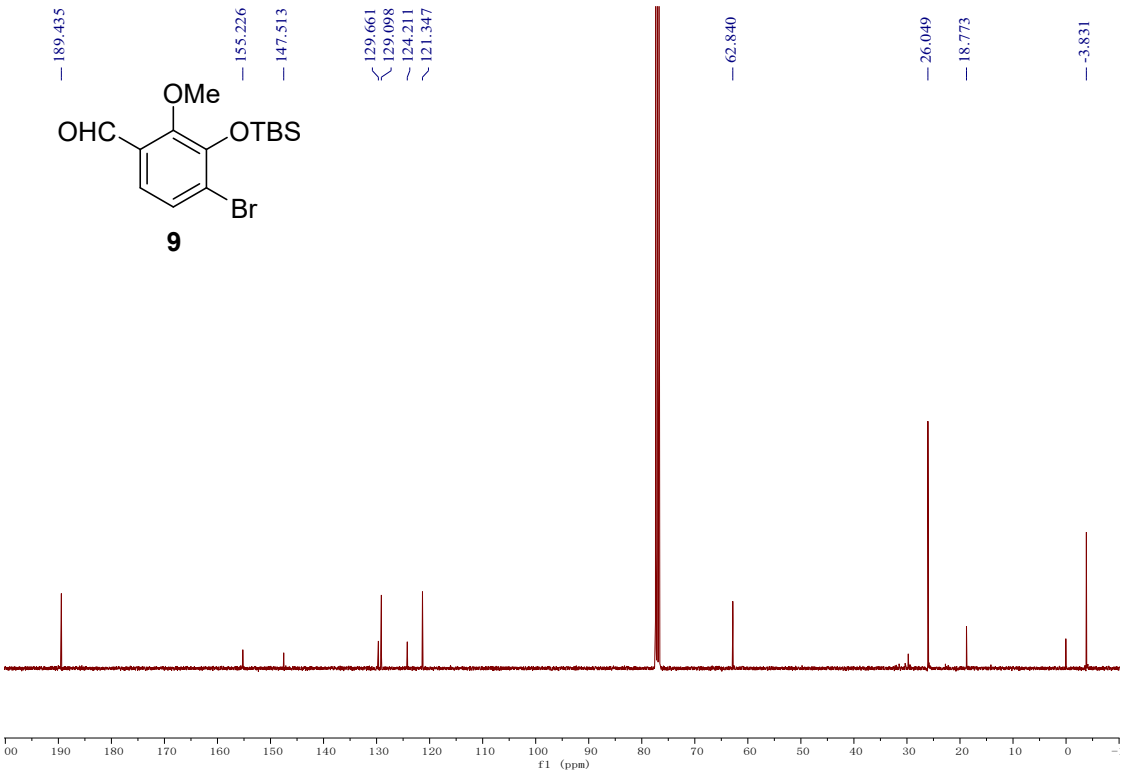
^{1}H NMR Spectrum of 8 (400 MHz, $CDCl_3$)



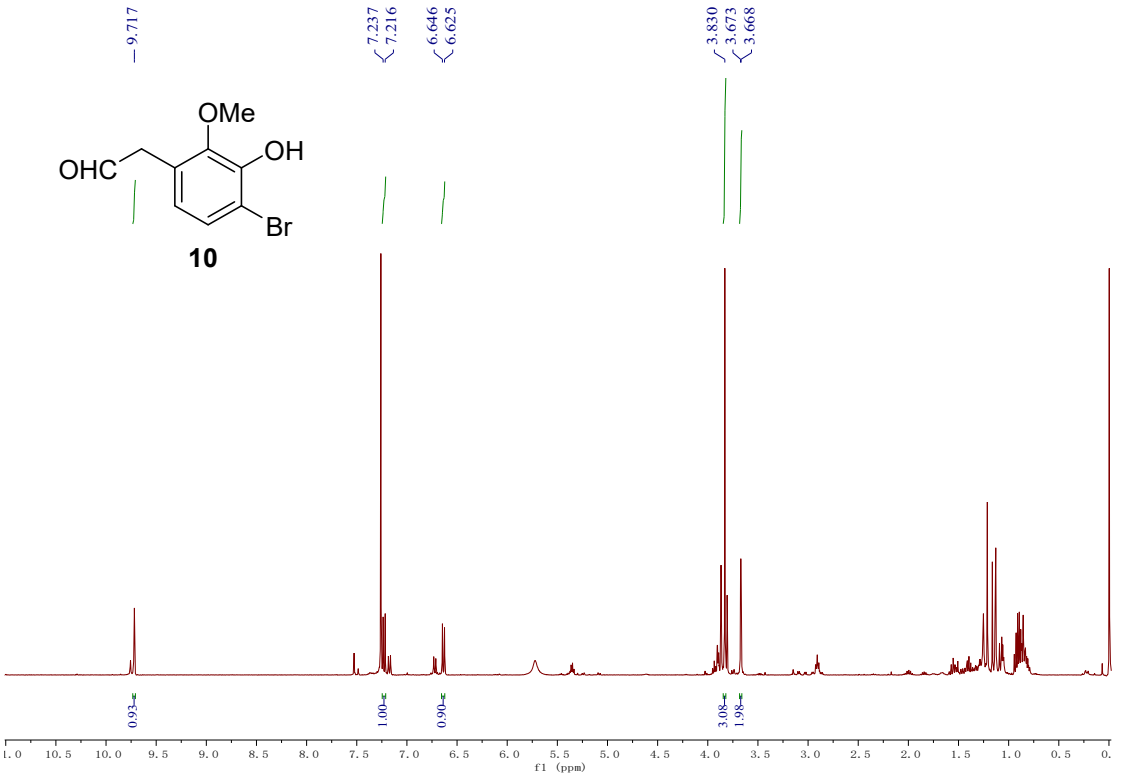
^{1}H NMR Spectrum of 9 (400 MHz, $CDCl_3$)



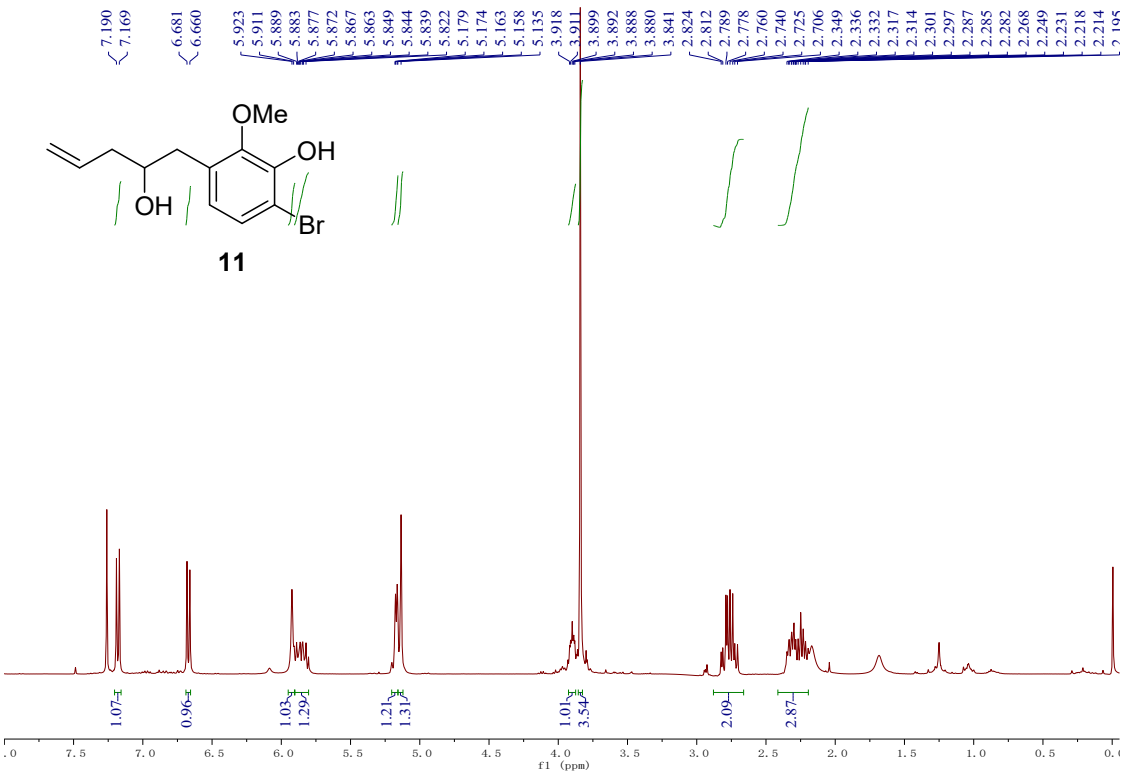
^{13}C NMR Spectrum of 9 (100 MHz, $CDCl_3$)



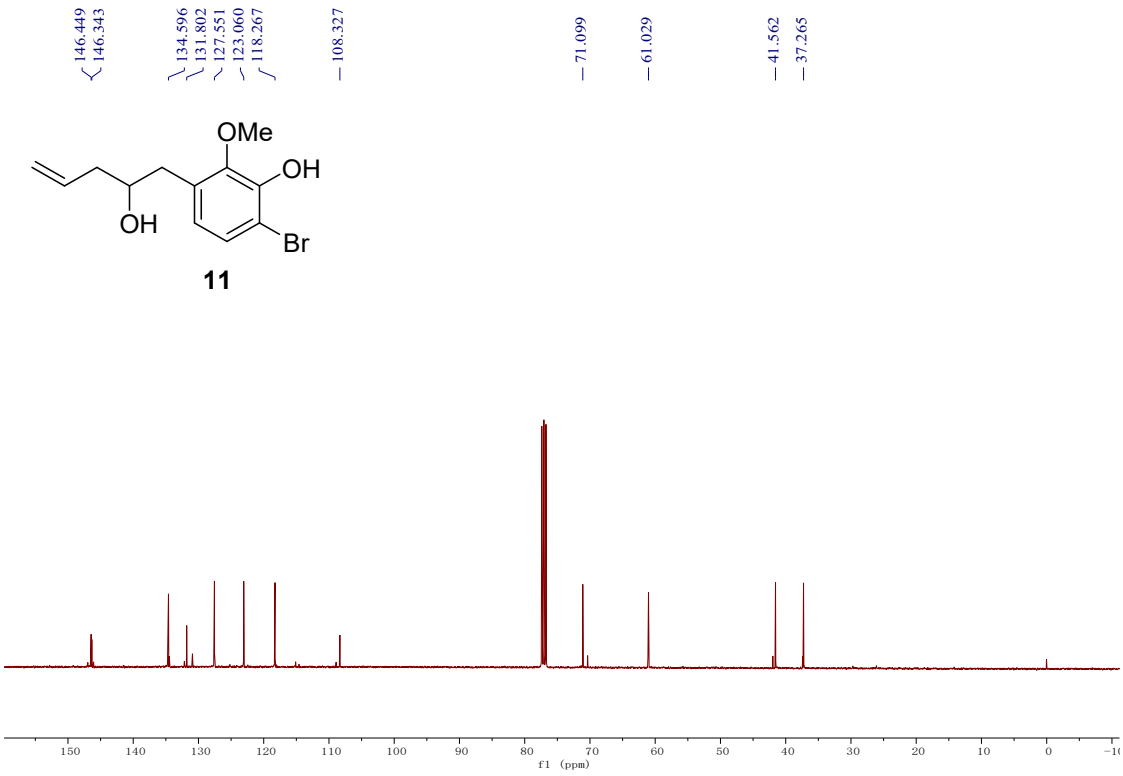
^{1}H NMR Spectrum of 10 (400 MHz, $CDCl_3$)



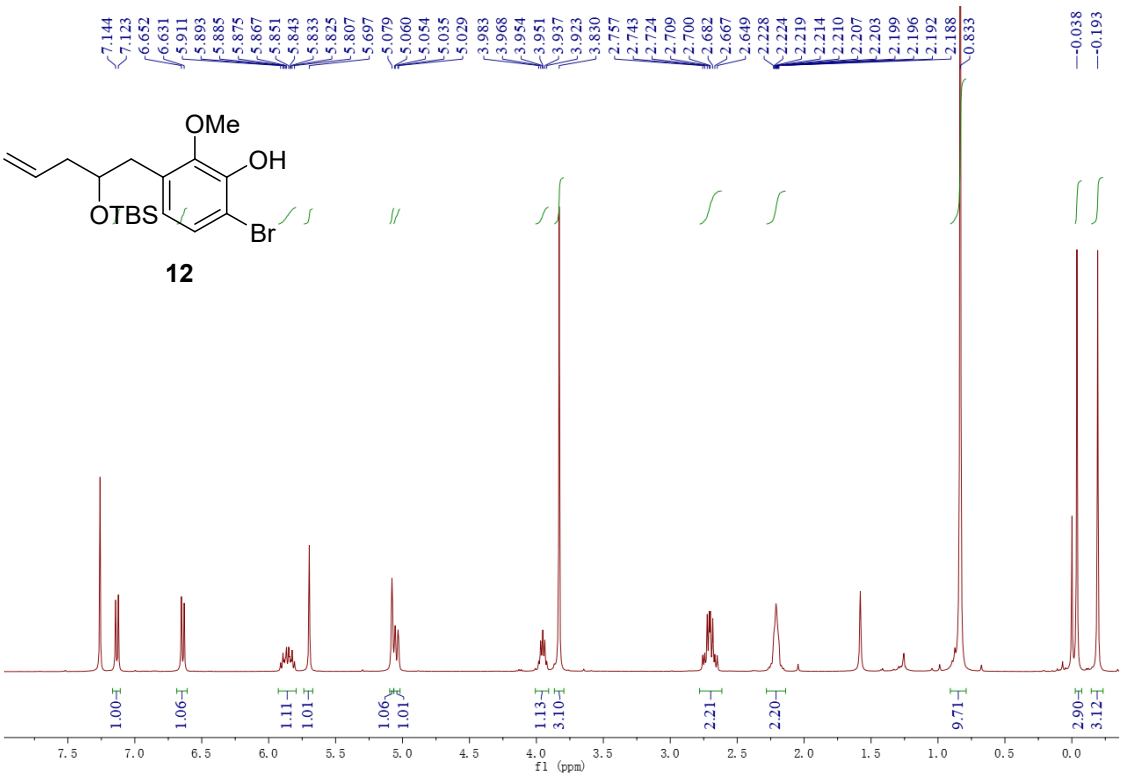
^{1}H NMR Spectrum of 11 (400 MHz, $CDCl_3$)



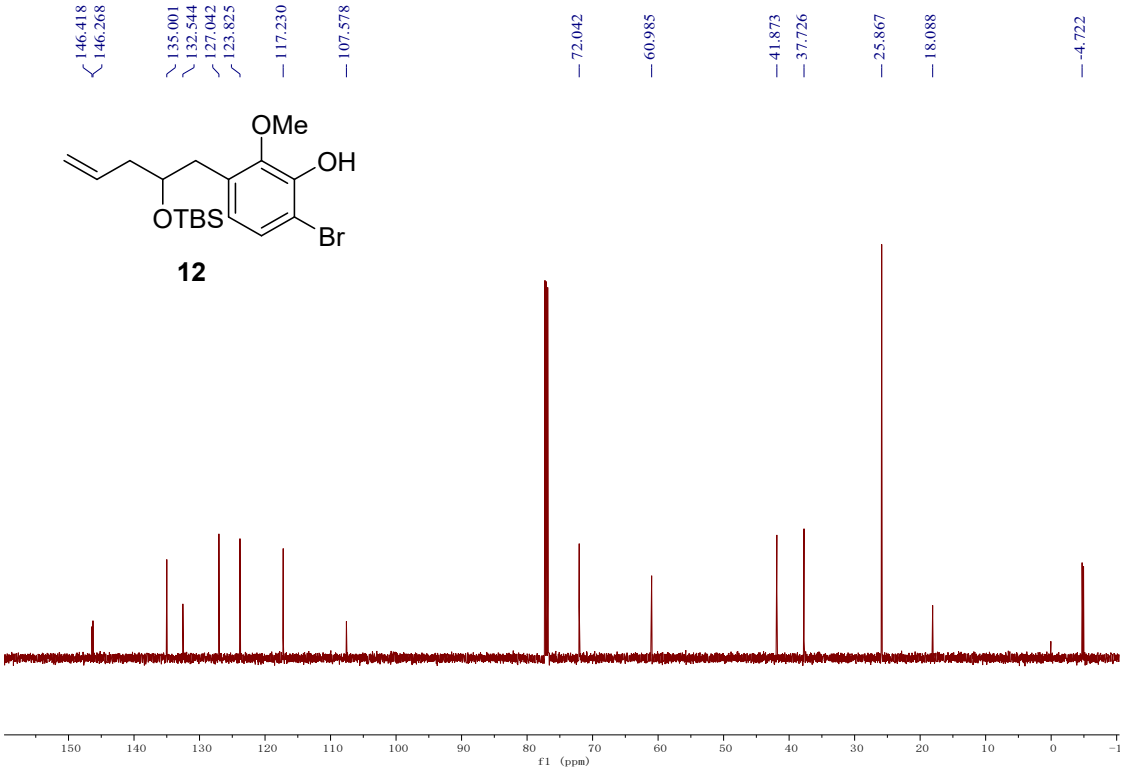
^{13}C NMR Spectrum of 11 (100 MHz, $CDCl_3$)



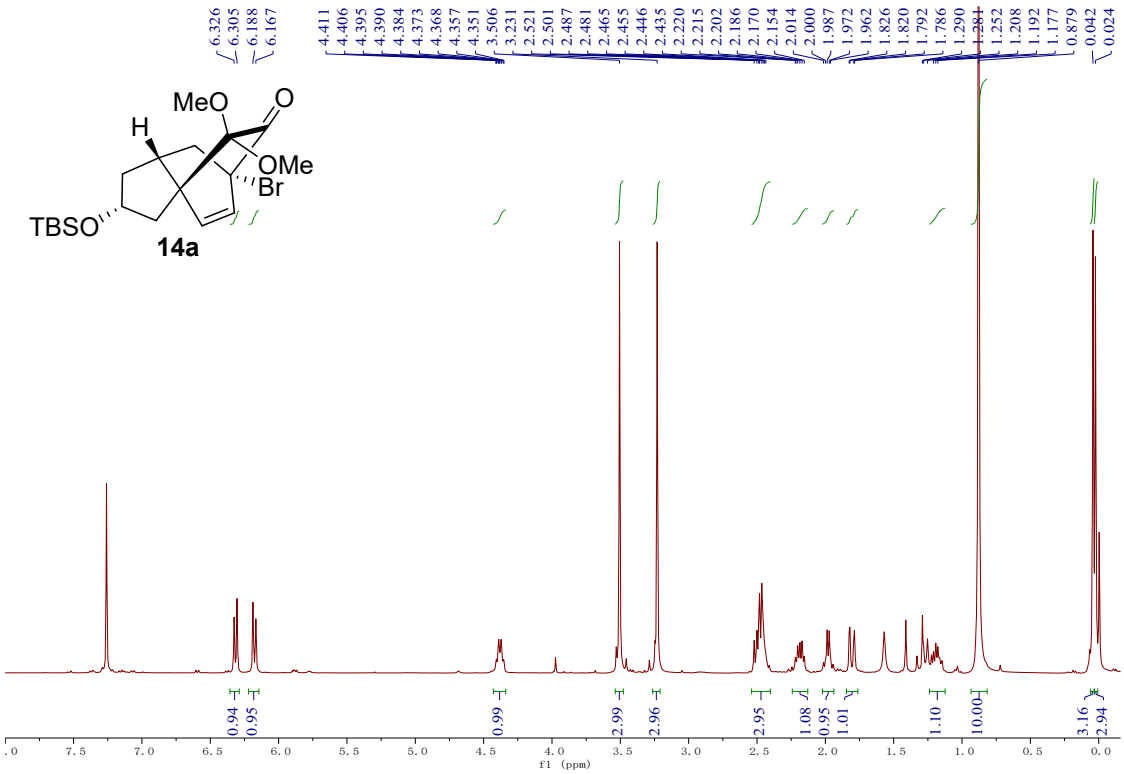
^{1}H NMR Spectrum of 12 (400 MHz, $CDCl_3$)



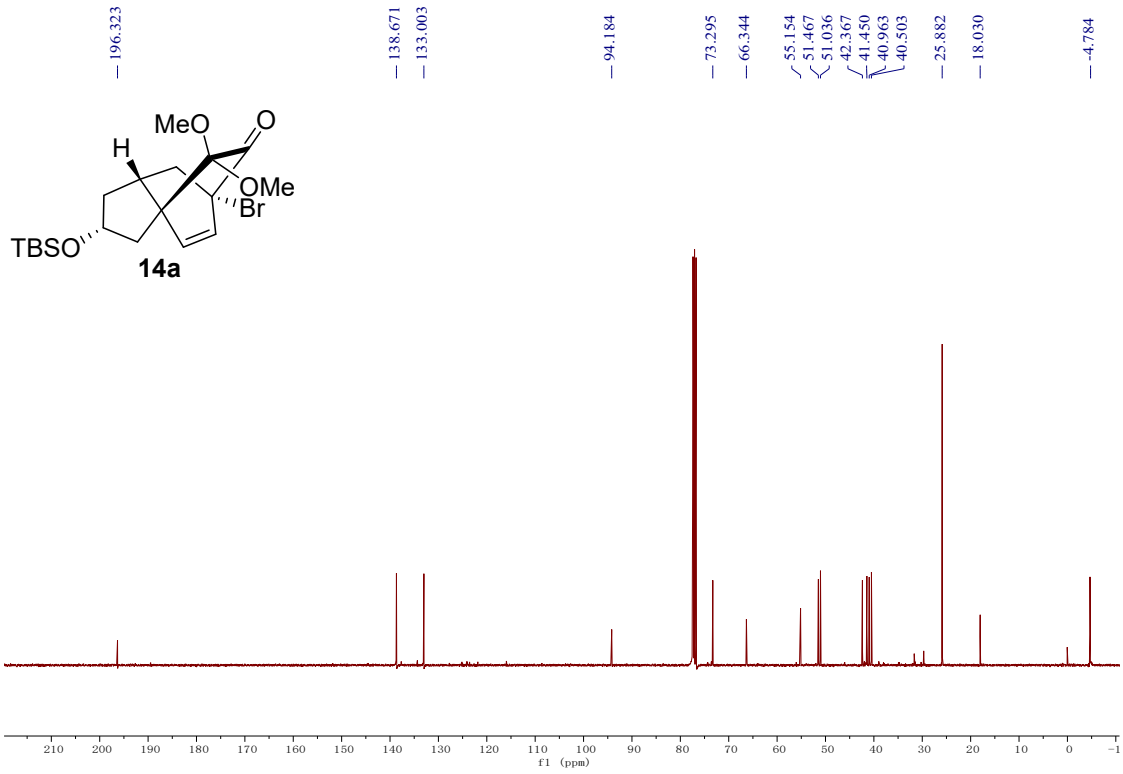
^{13}C NMR Spectrum of 12 (100 MHz, $CDCl_3$)



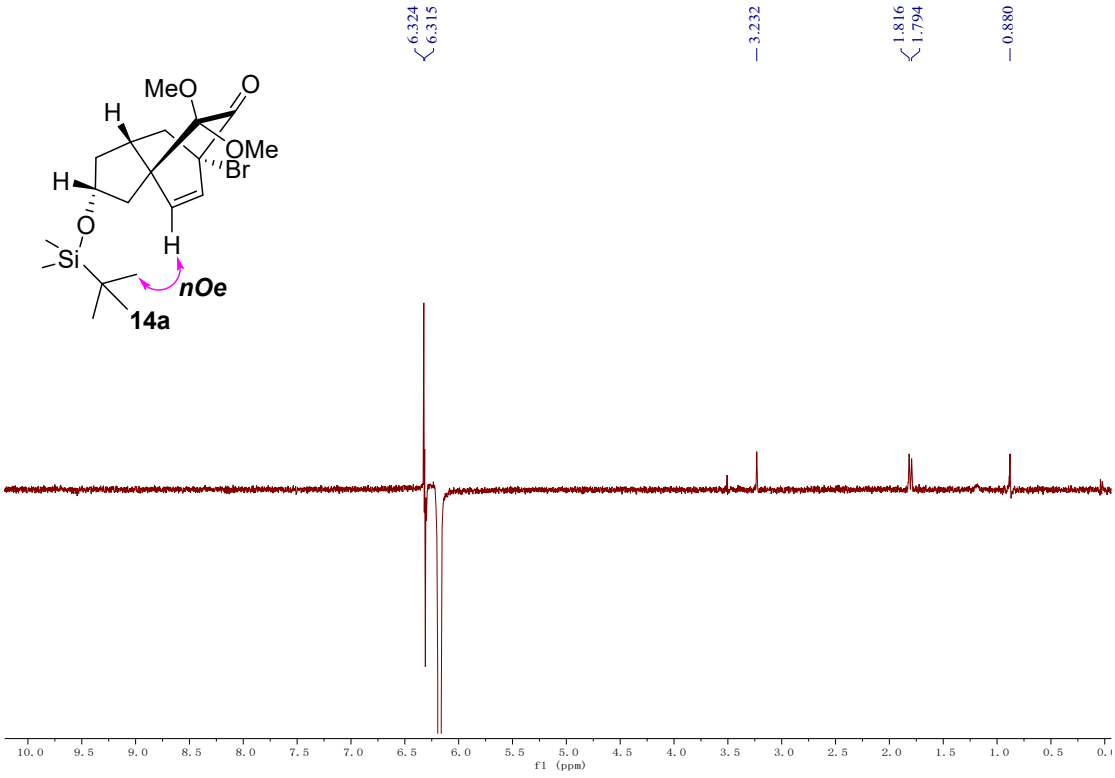
^{1}H NMR Spectrum of 14a (400 MHz, $CDCl_3$)



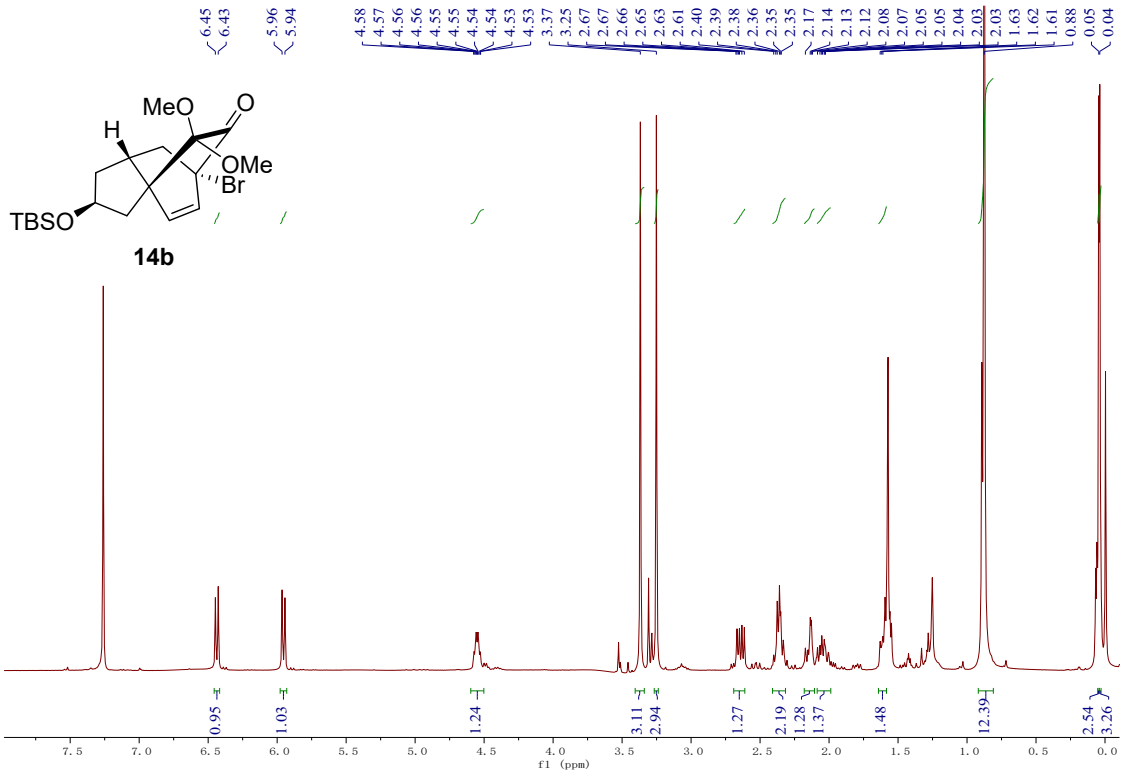
^{13}C NMR Spectrum of 14a (100 MHz, $CDCl_3$)



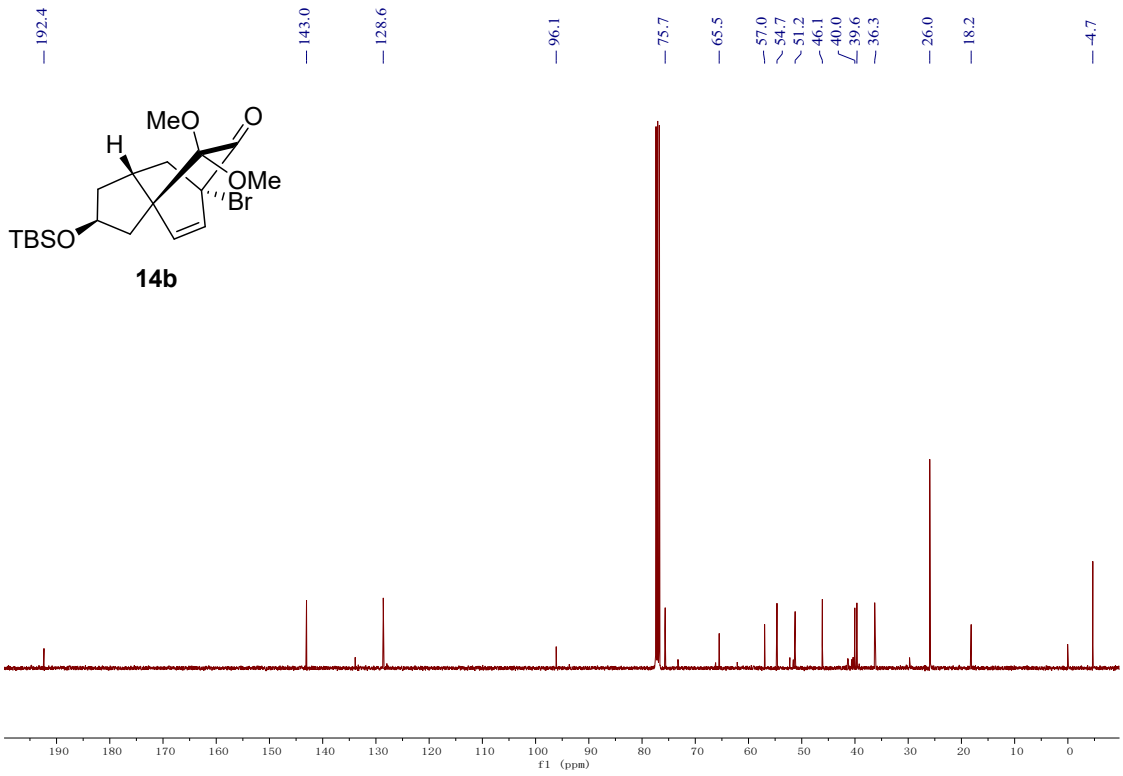
NOEDS Spectrum of 14a (600 MHz, $CDCl_3$)



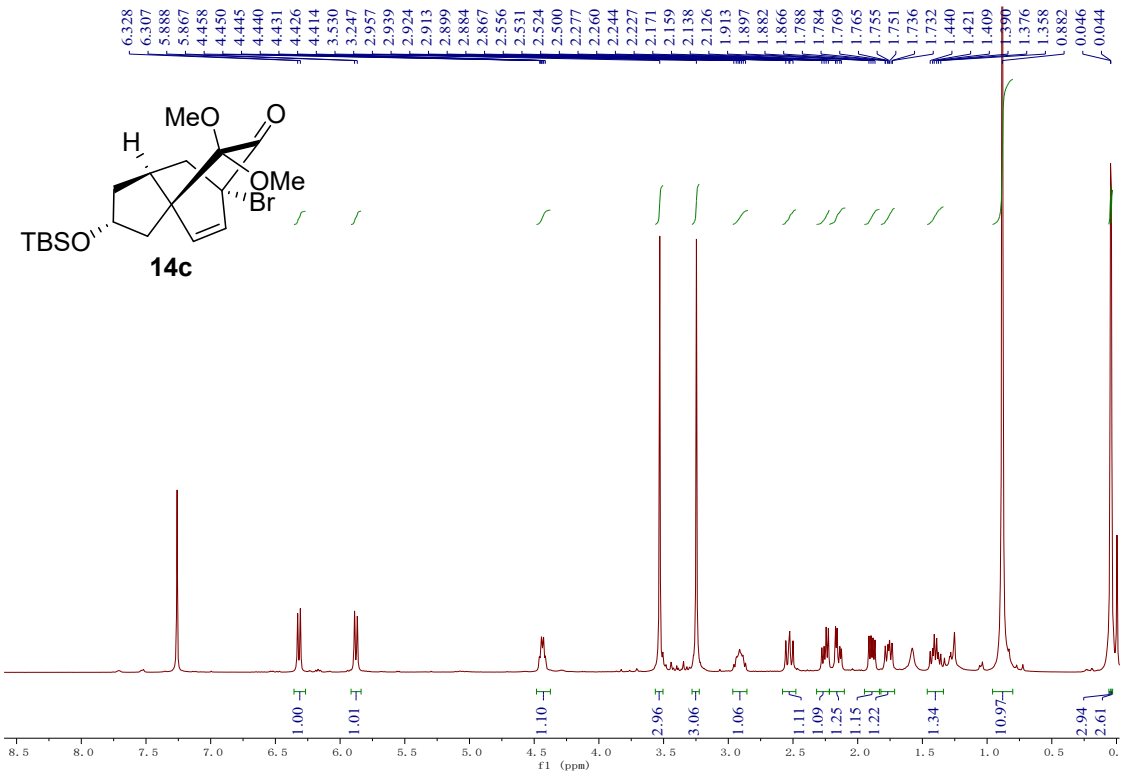
^{1}H NMR Spectrum of 14b (400 MHz, $CDCl_3$)



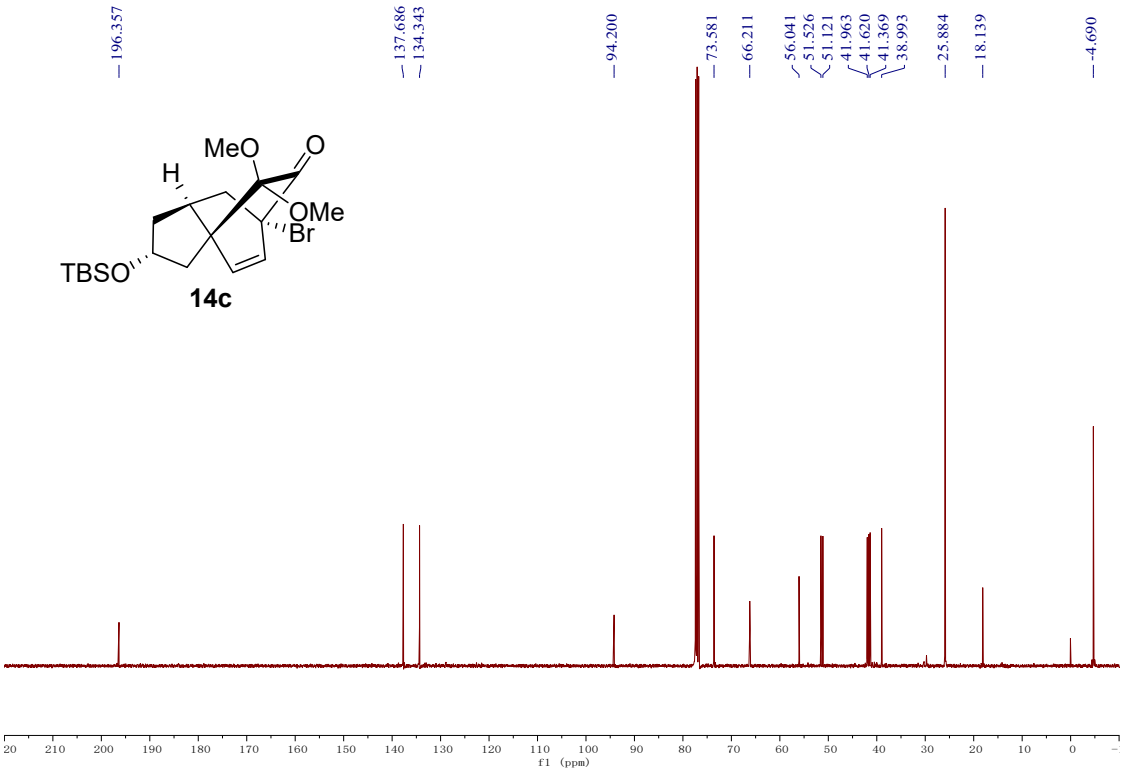
^{13}C NMR Spectrum of 14b (100 MHz, $CDCl_3$)



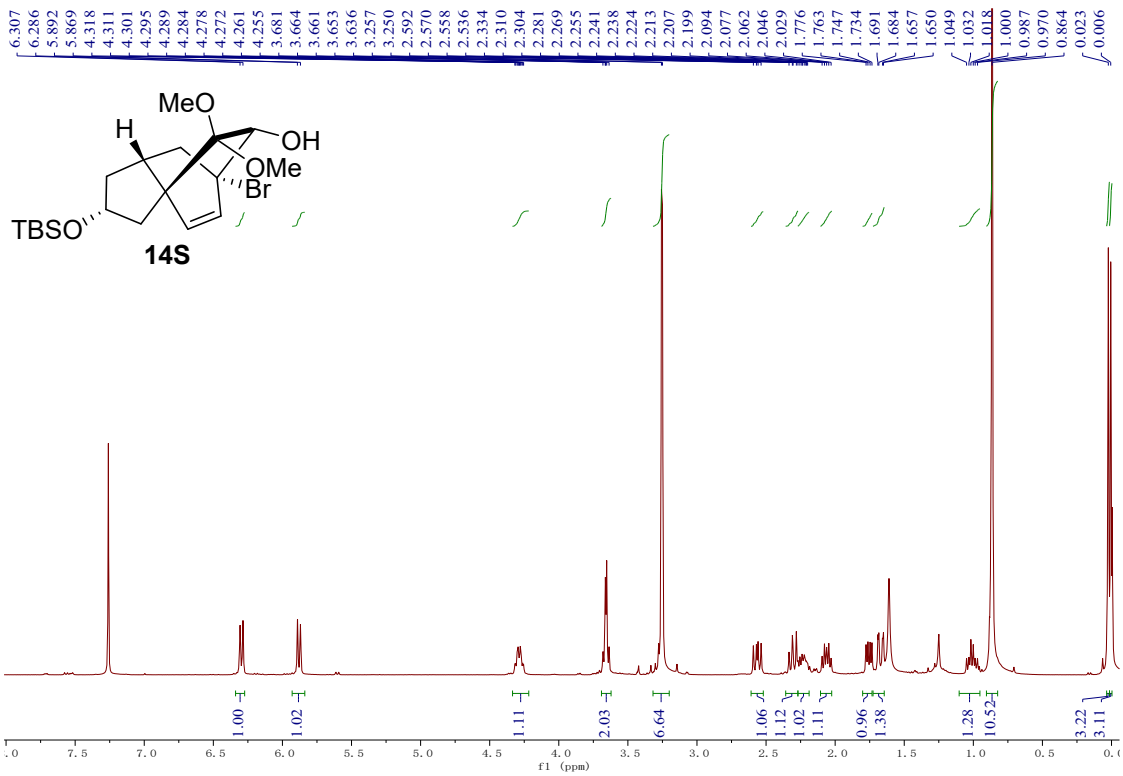
^{1}H NMR Spectrum of 14c (400 MHz, $CDCl_3$)



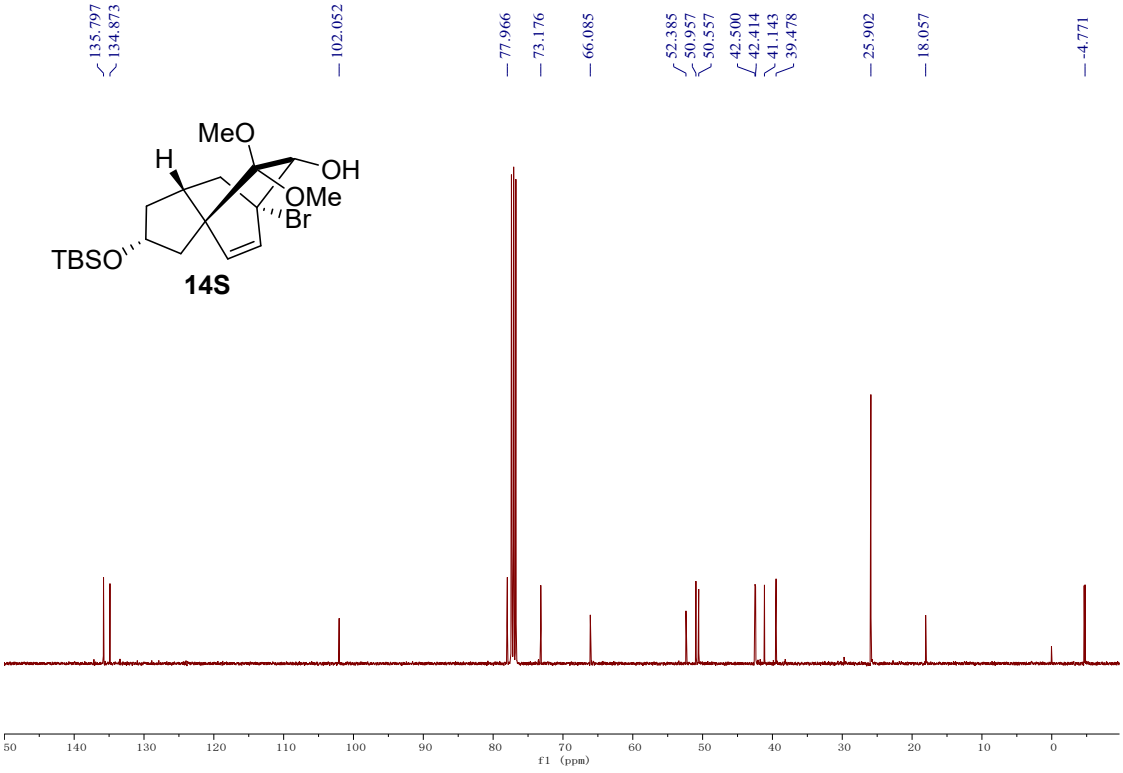
^{13}C NMR Spectrum of 14c (100 MHz, $CDCl_3$)



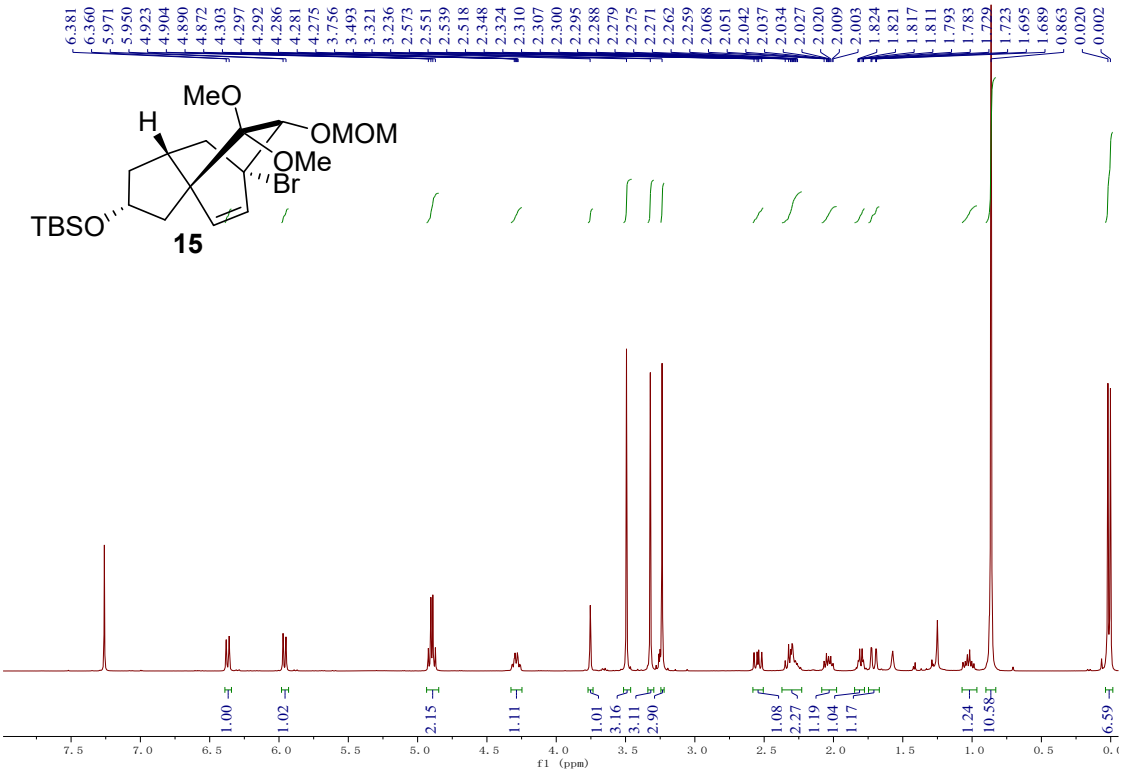
^{1}H NMR Spectrum of 14S (400 MHz, $CDCl_3$)



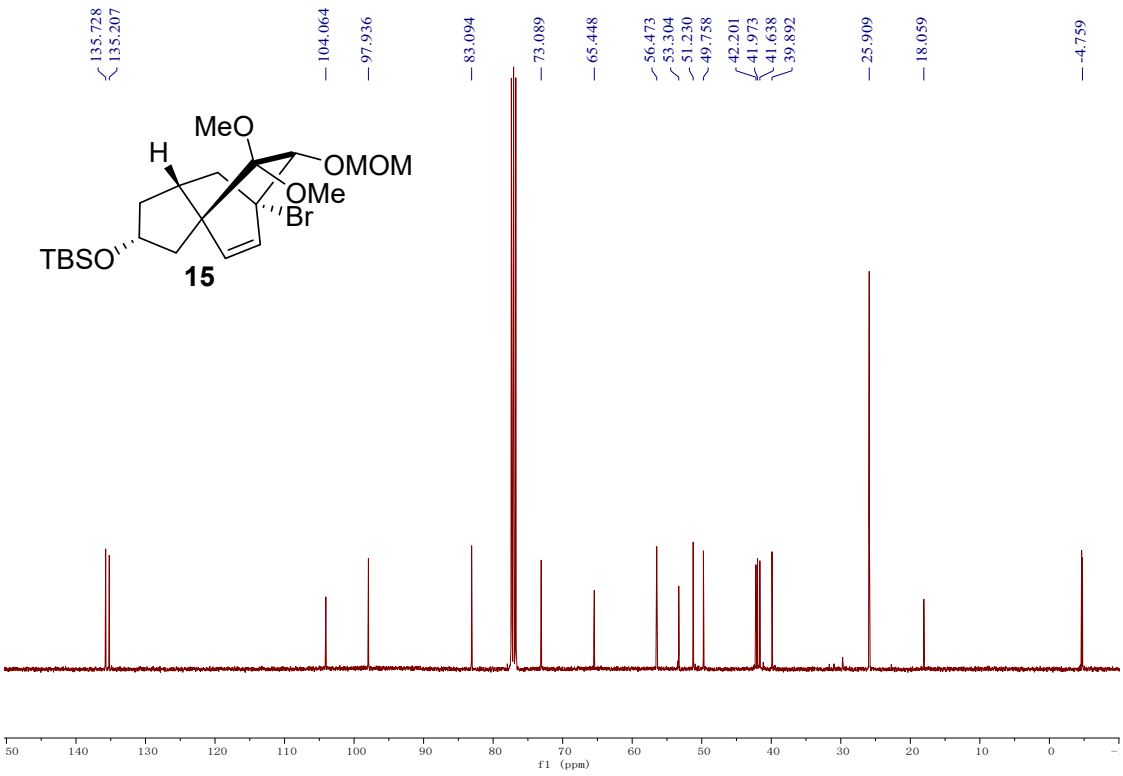
^{13}C NMR Spectrum of 14S (100 MHz, $CDCl_3$)



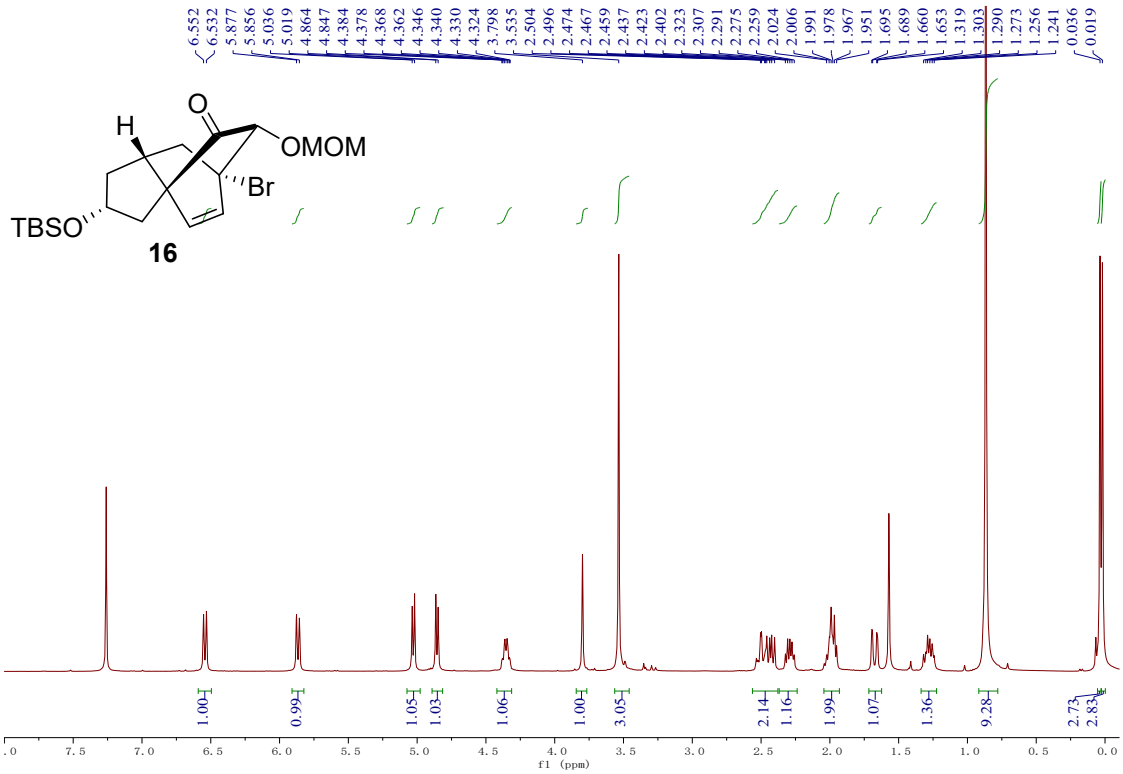
^{1}H NMR Spectrum of 15 (400 MHz, $CDCl_3$)



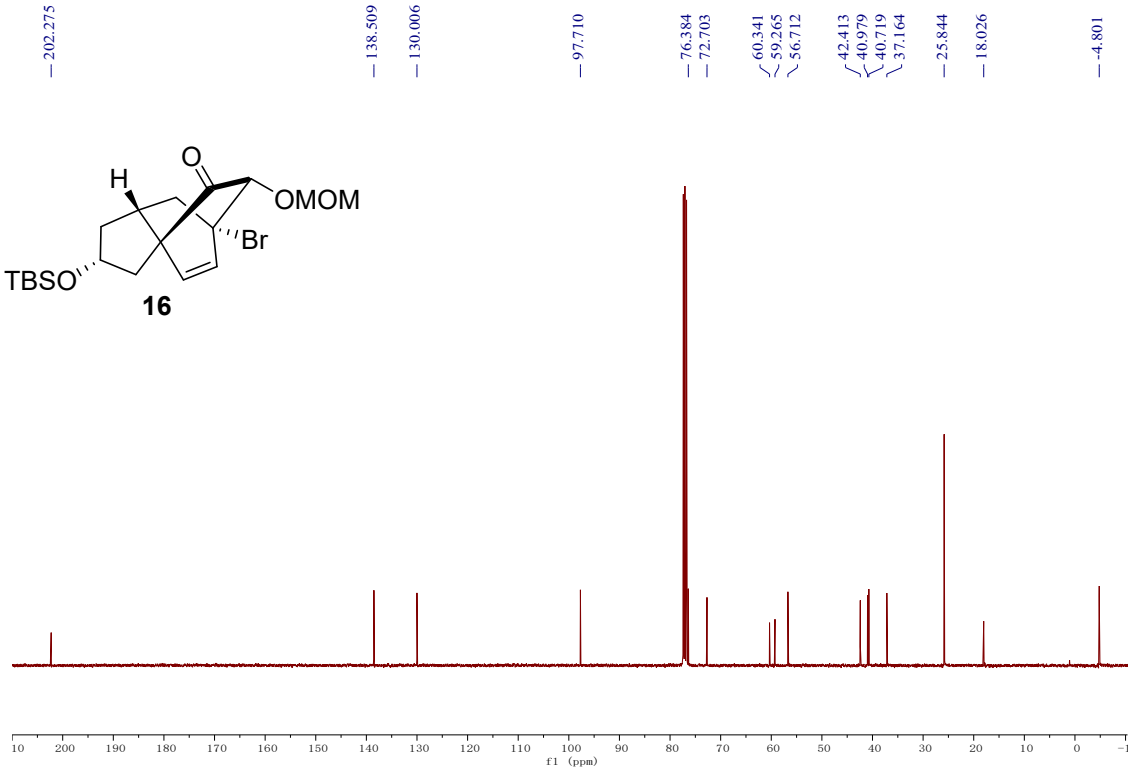
^{13}C NMR Spectrum of 15 (100 MHz, $CDCl_3$)



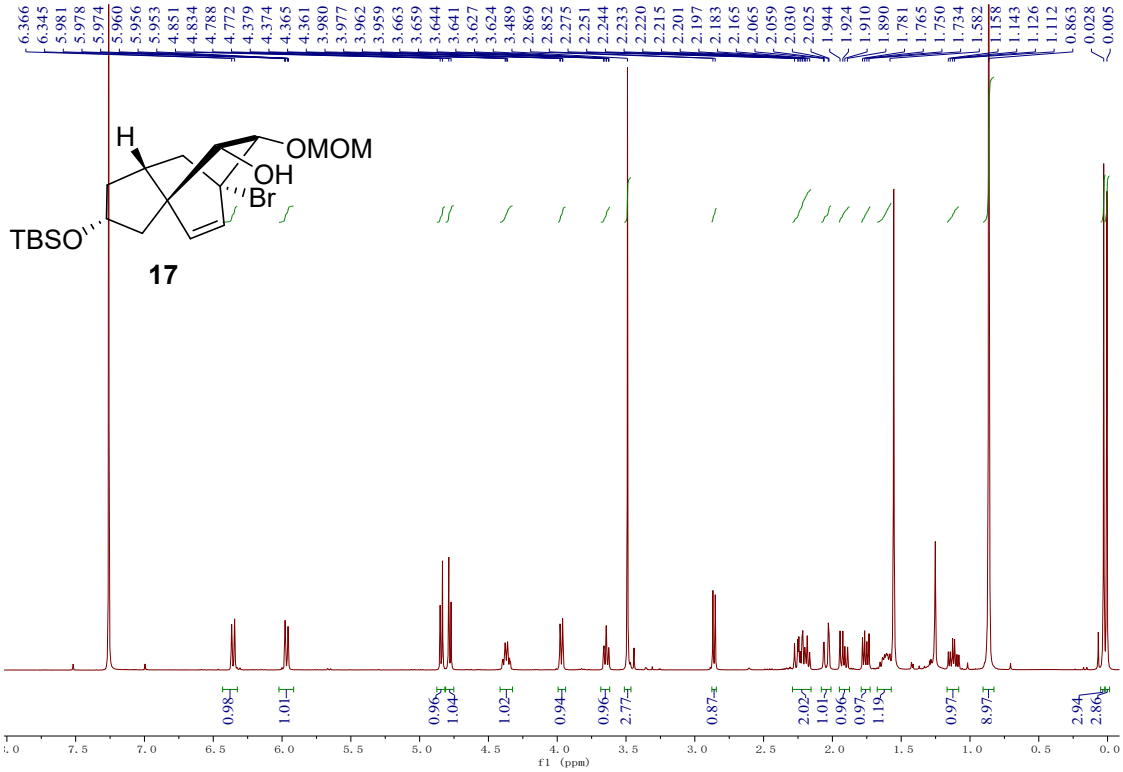
^{1}H NMR Spectrum of 16 (400 MHz, $CDCl_3$)



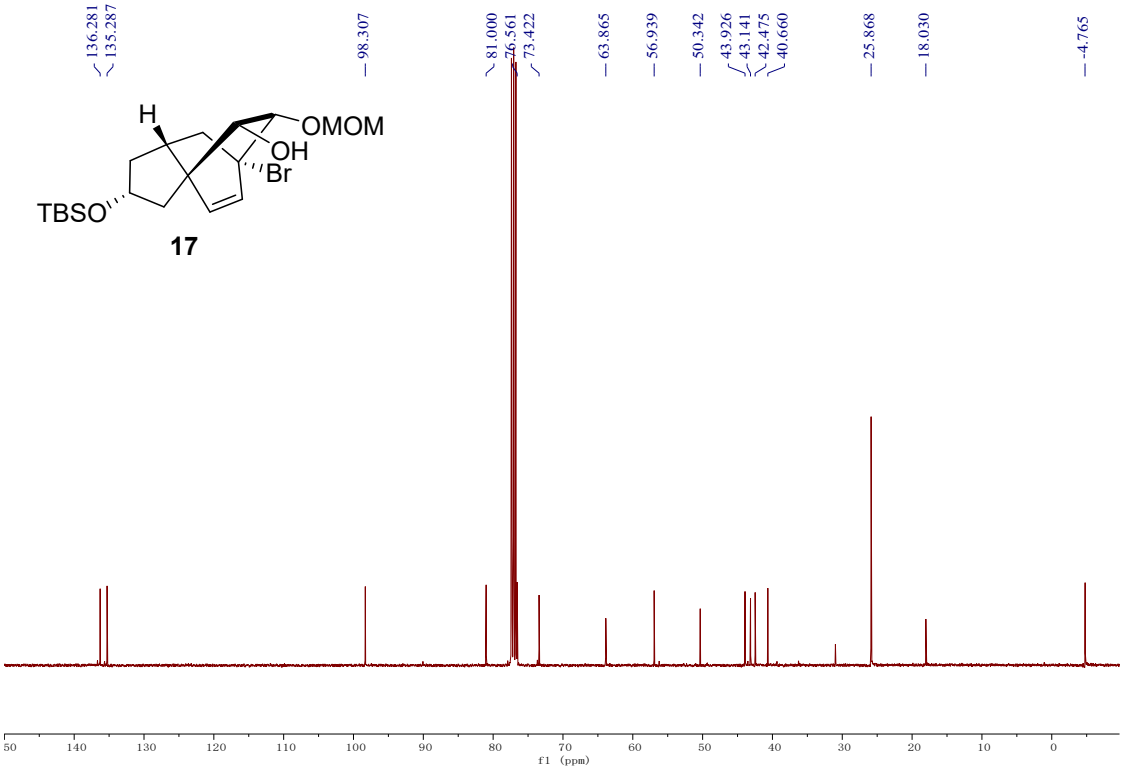
^{13}C NMR Spectrum of 16 (100 MHz, $CDCl_3$)



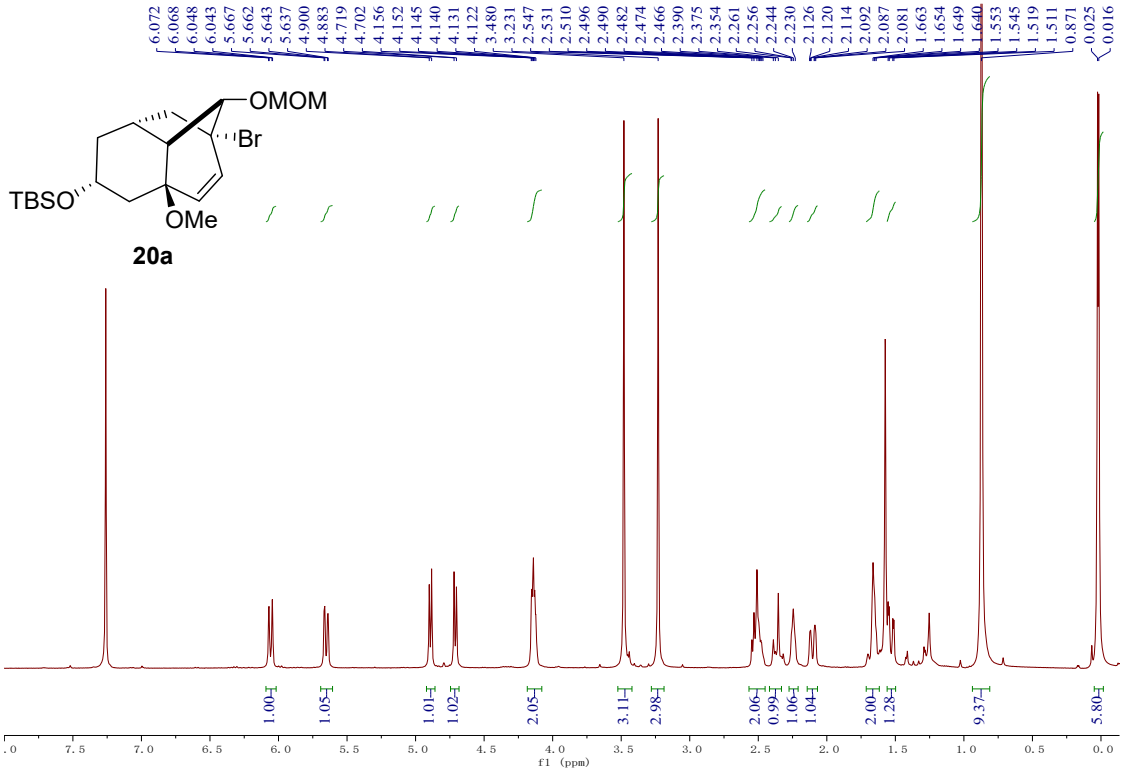
^{1}H NMR Spectrum of 17 (400 MHz, $CDCl_3$)



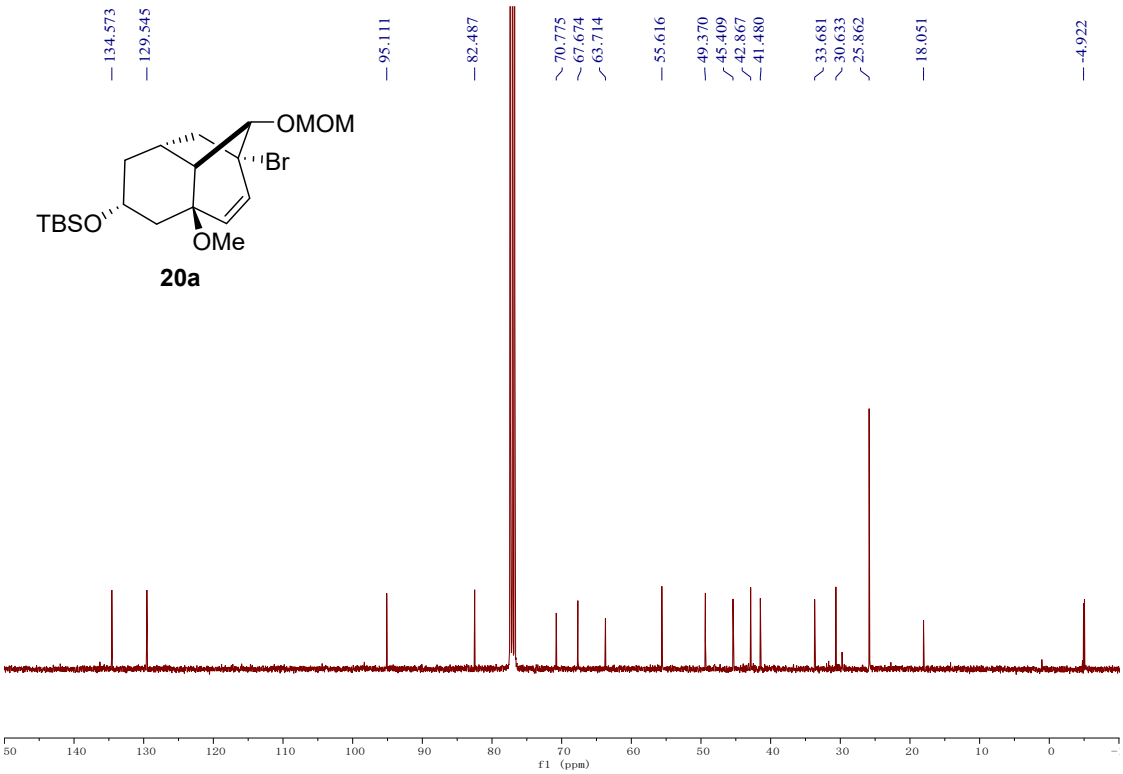
^{13}C NMR Spectrum of 17 (100 MHz, $CDCl_3$)



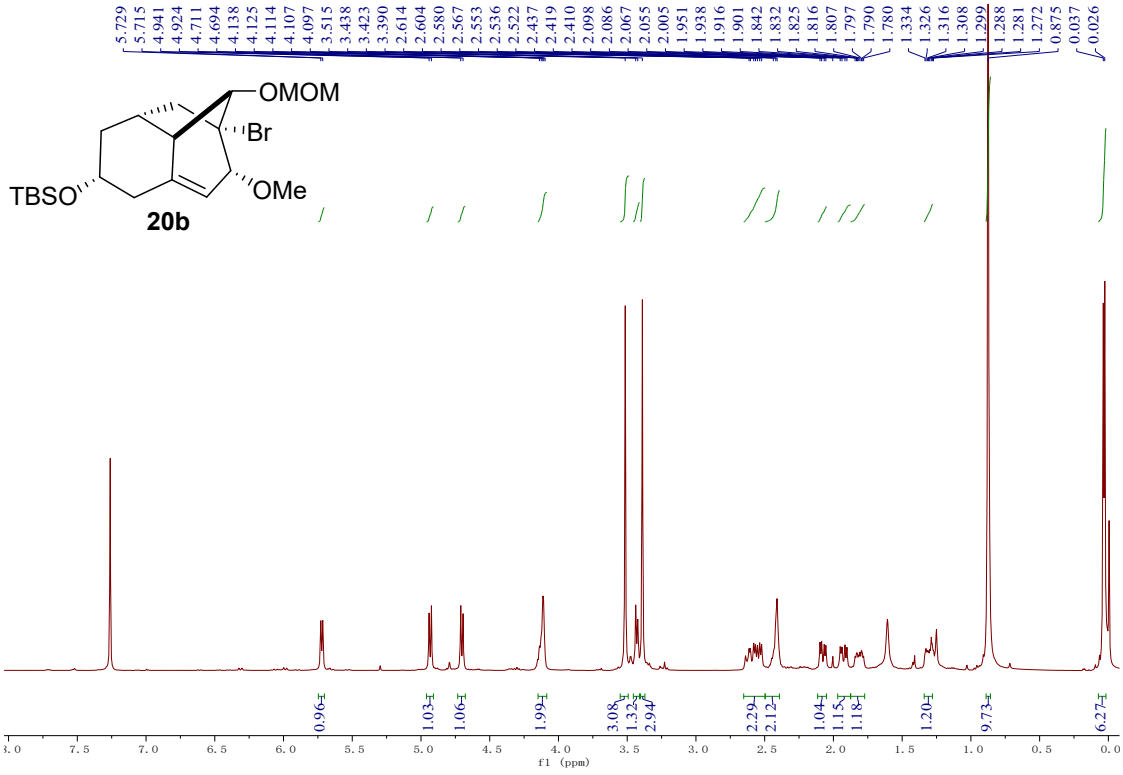
^{1}H NMR Spectrum of 20a (400 MHz, $CDCl_3$)



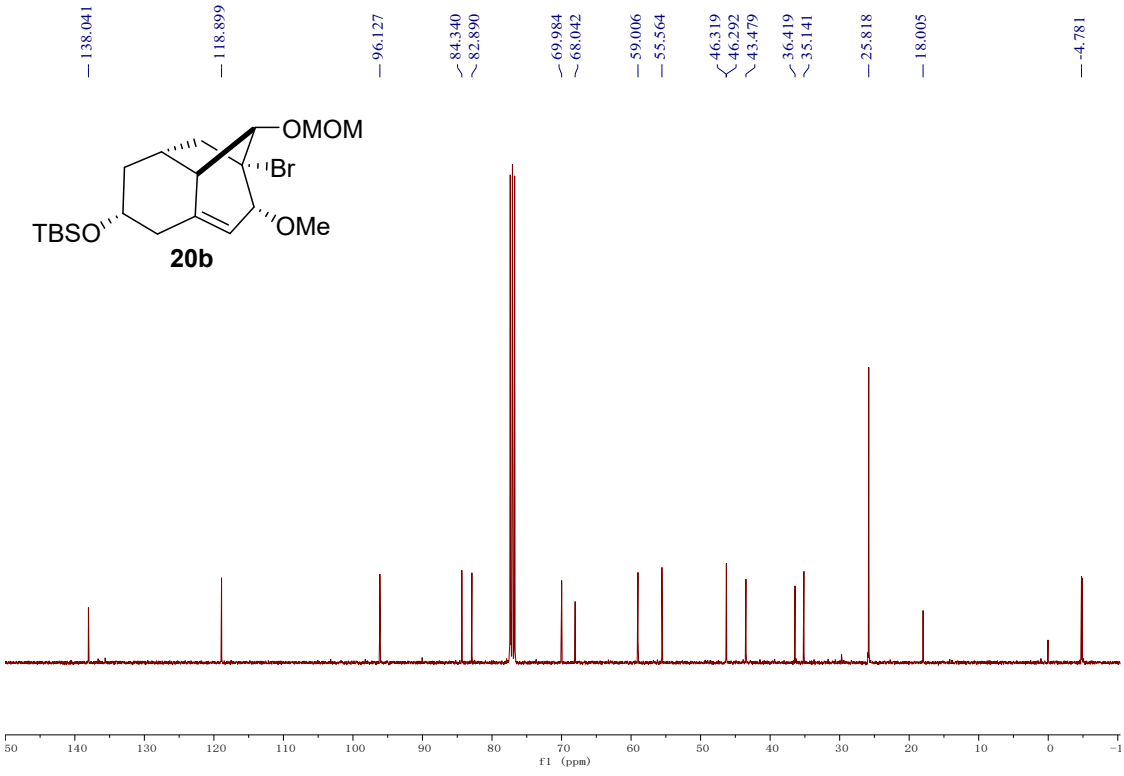
^{13}C NMR Spectrum of 20a (100 MHz, $CDCl_3$)



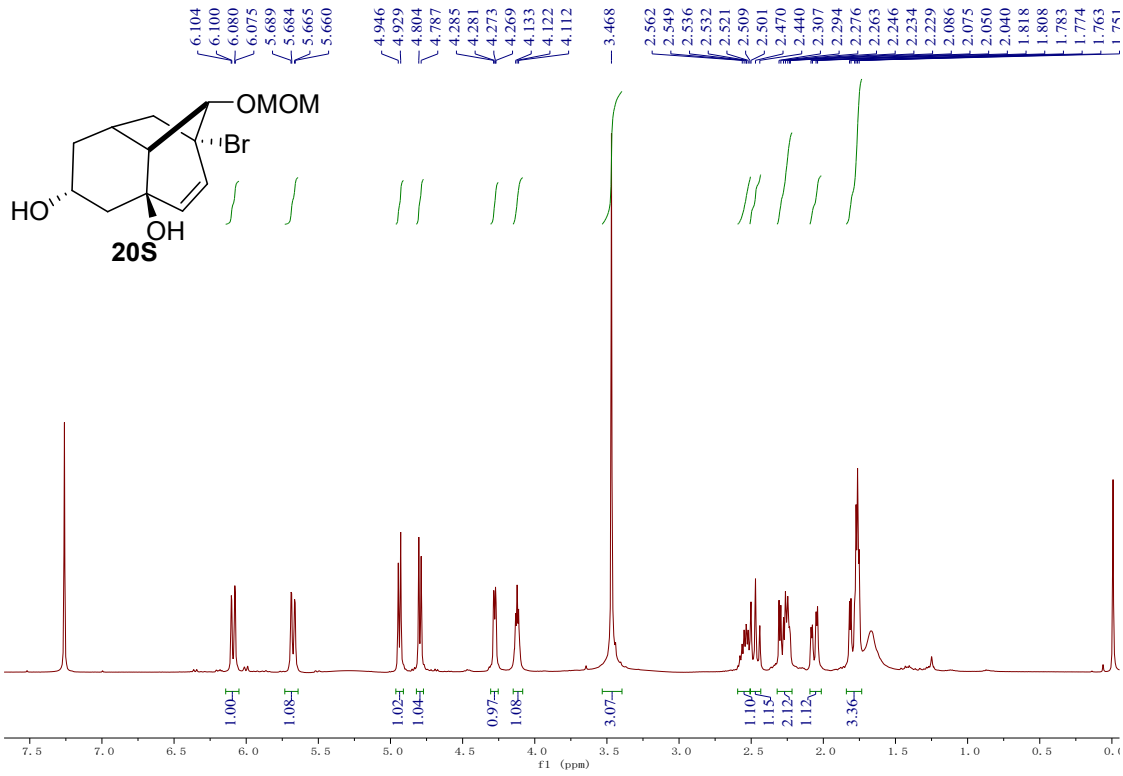
^{1}H NMR Spectrum of 20b (400 MHz, $CDCl_3$)



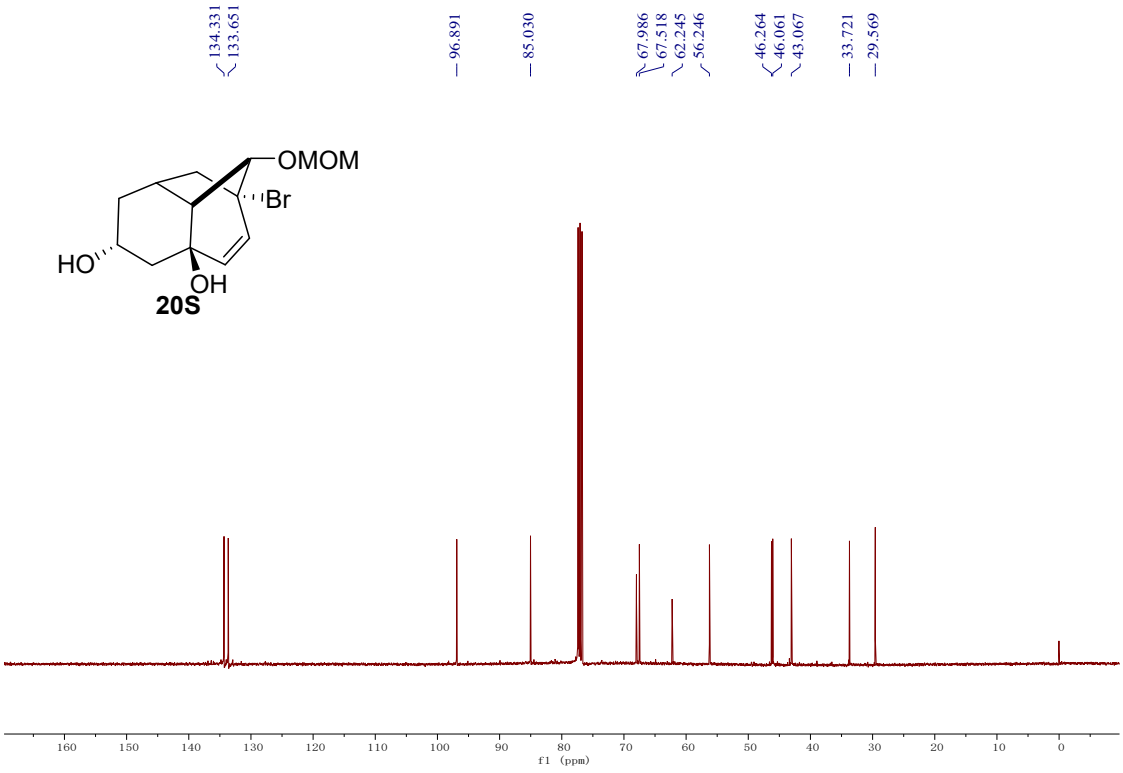
^{13}C NMR Spectrum of 20b (100 MHz, $CDCl_3$)



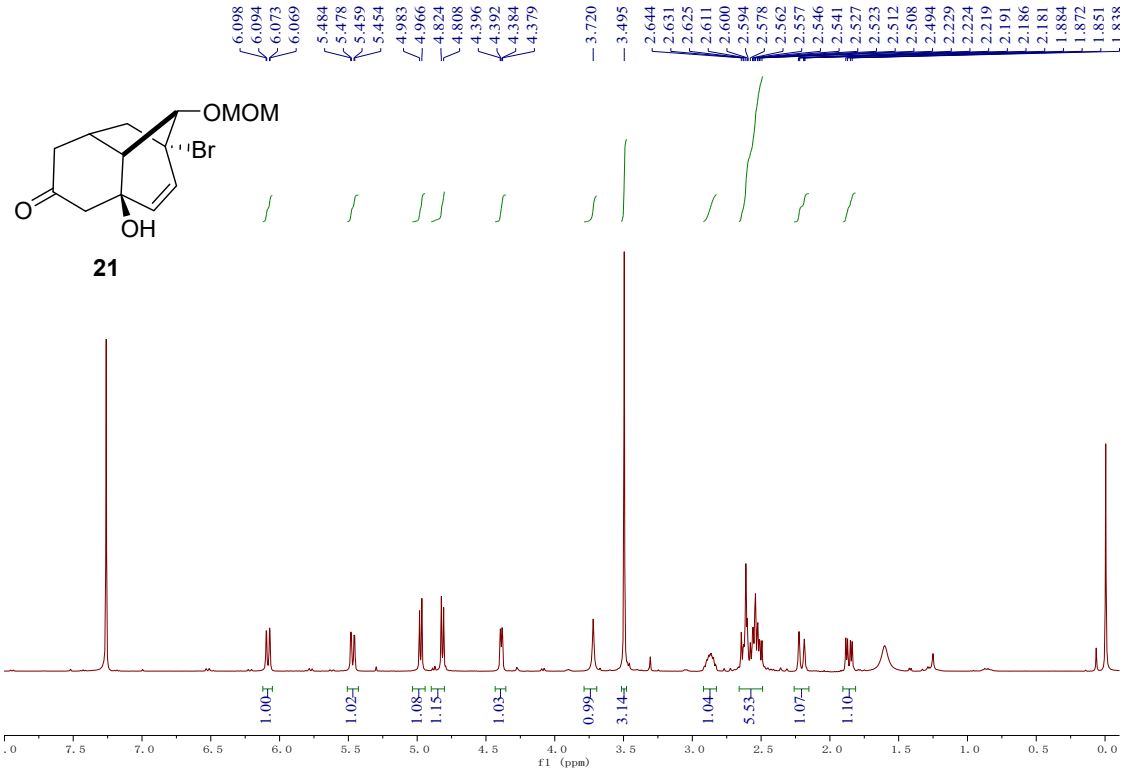
^{1}H NMR Spectrum of 20S (400 MHz, $CDCl_3$)



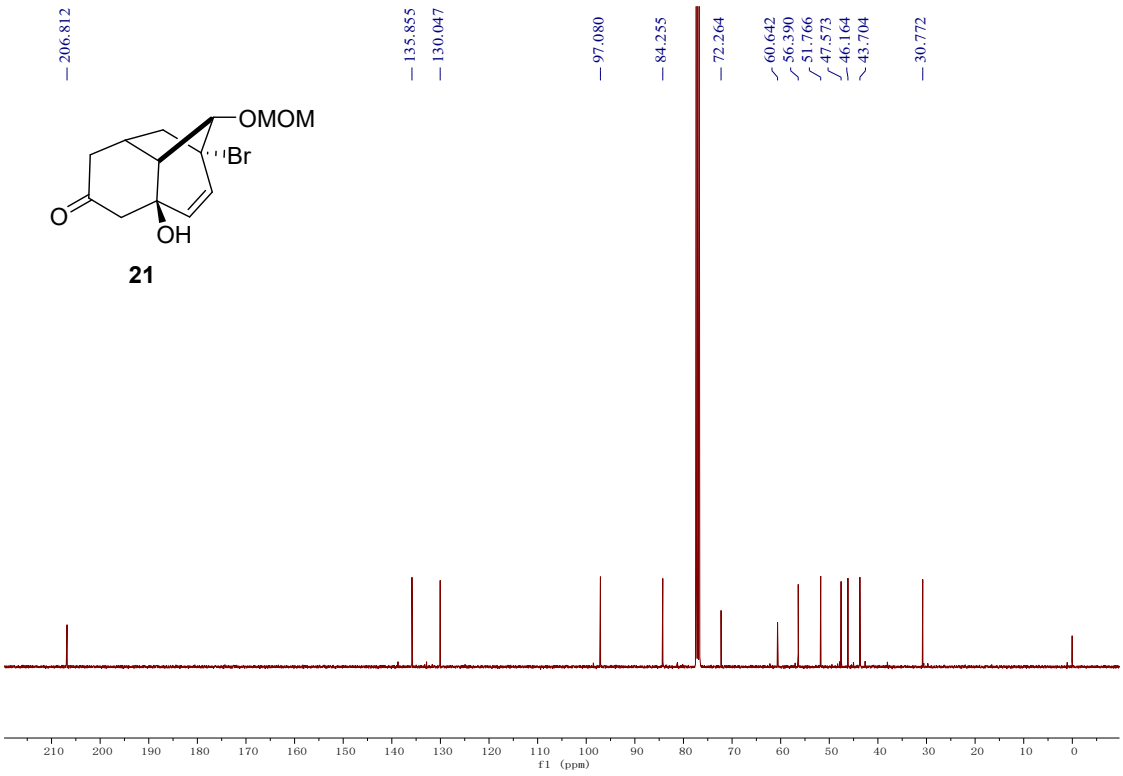
^{13}C NMR Spectrum of 20S (100 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 21 (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 21 (100 MHz, $CDCl_3$)



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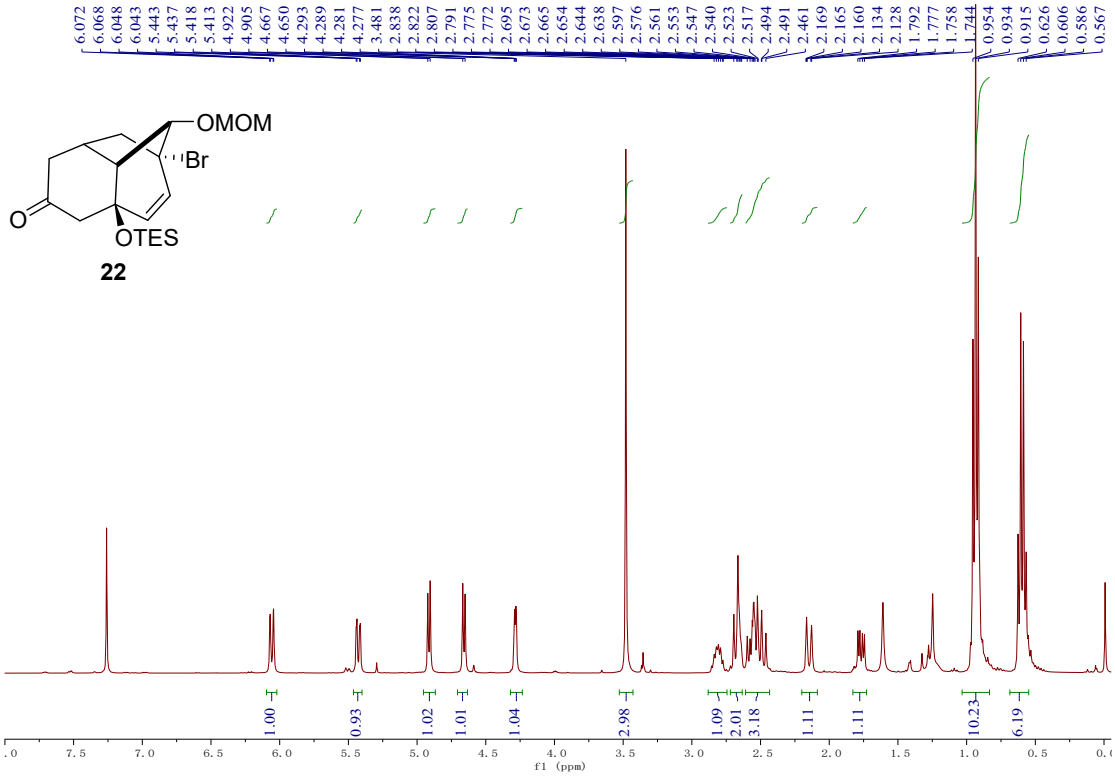
^{1}H NMR Spectrum of 22 (400 MHz, $CDCl_3$)



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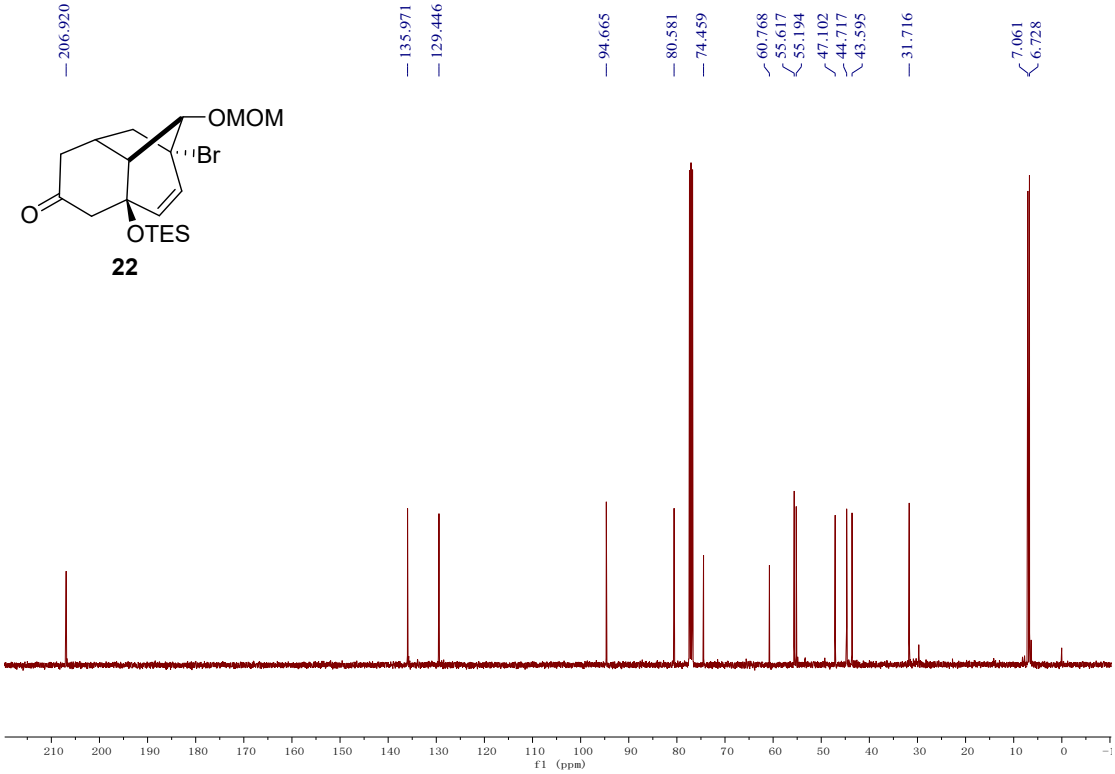
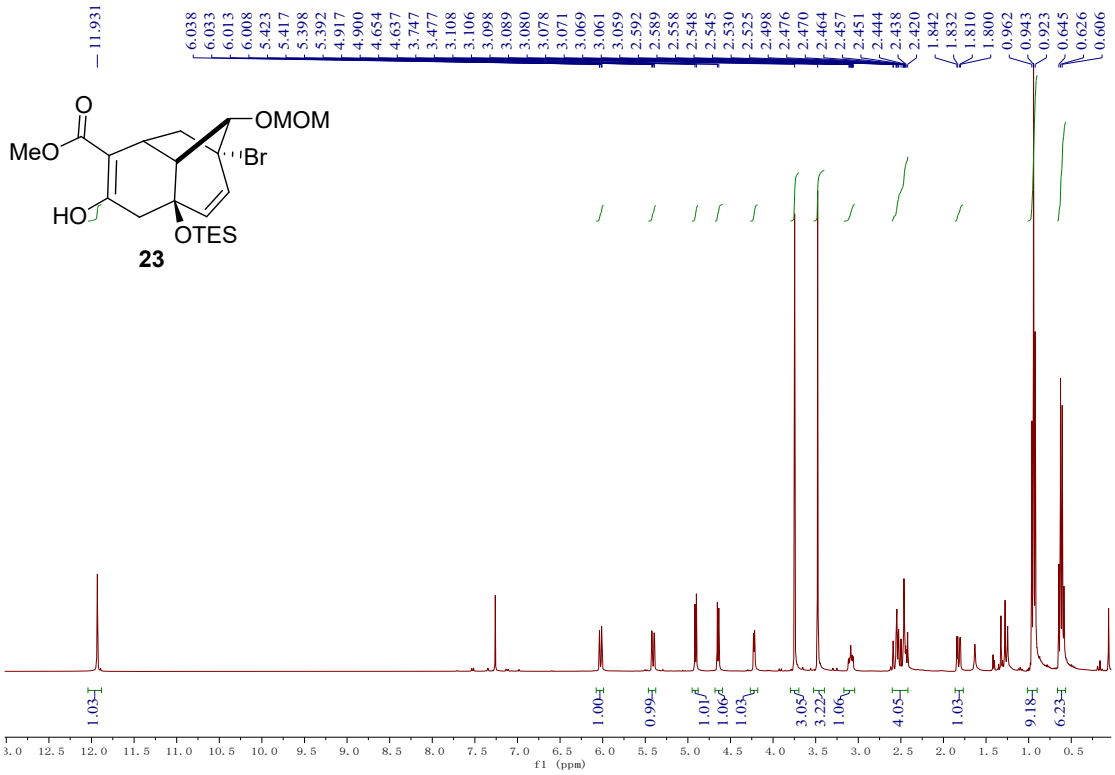
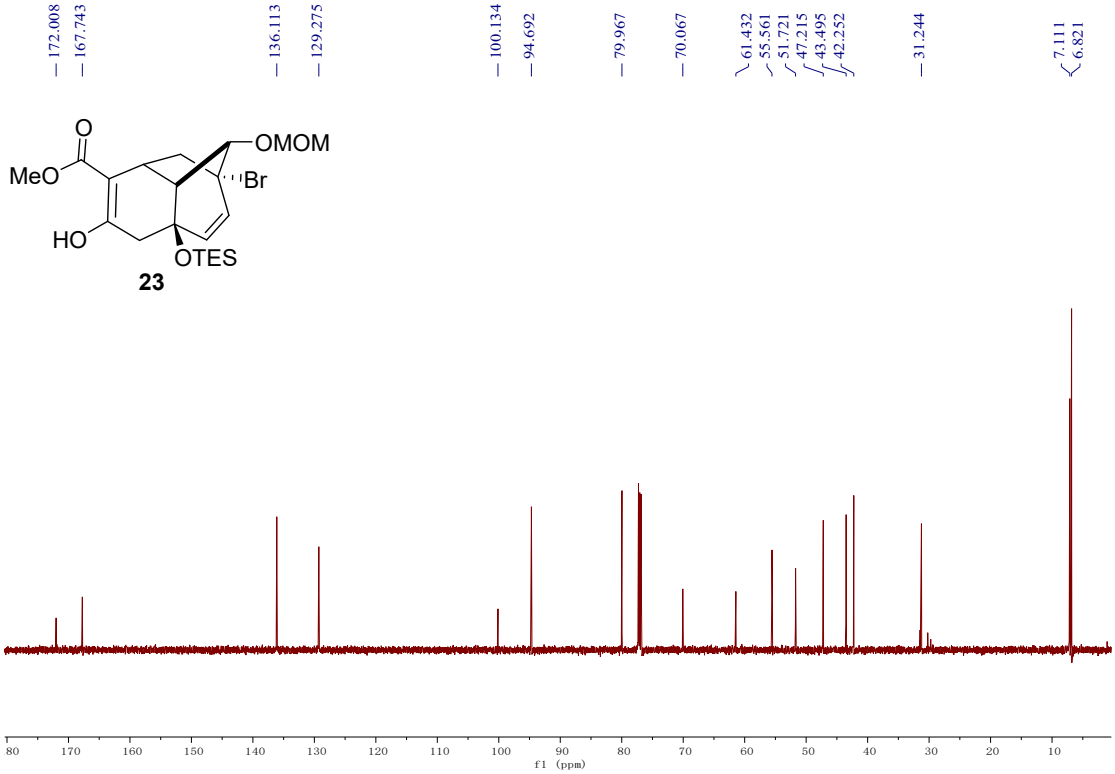
^{13}C NMR Spectrum of 22 (100 MHz, $CDCl_3$)



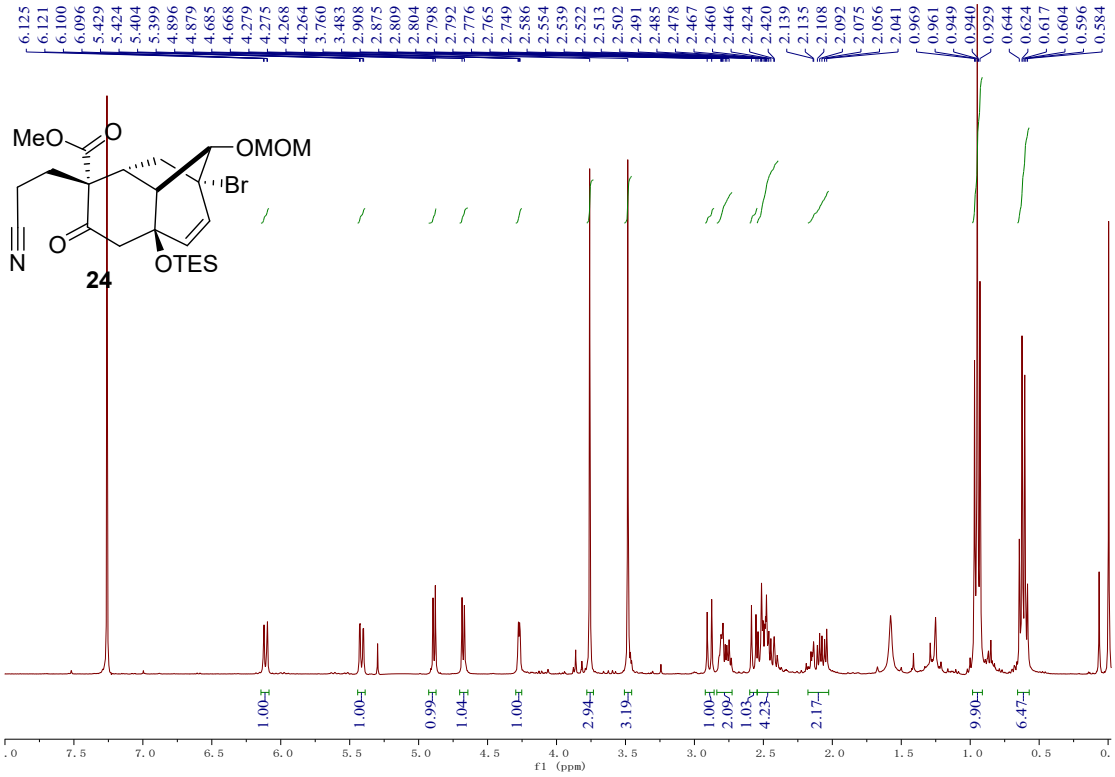
^{1}H NMR Spectrum of 23 (400 MHz, $CDCl_3$)



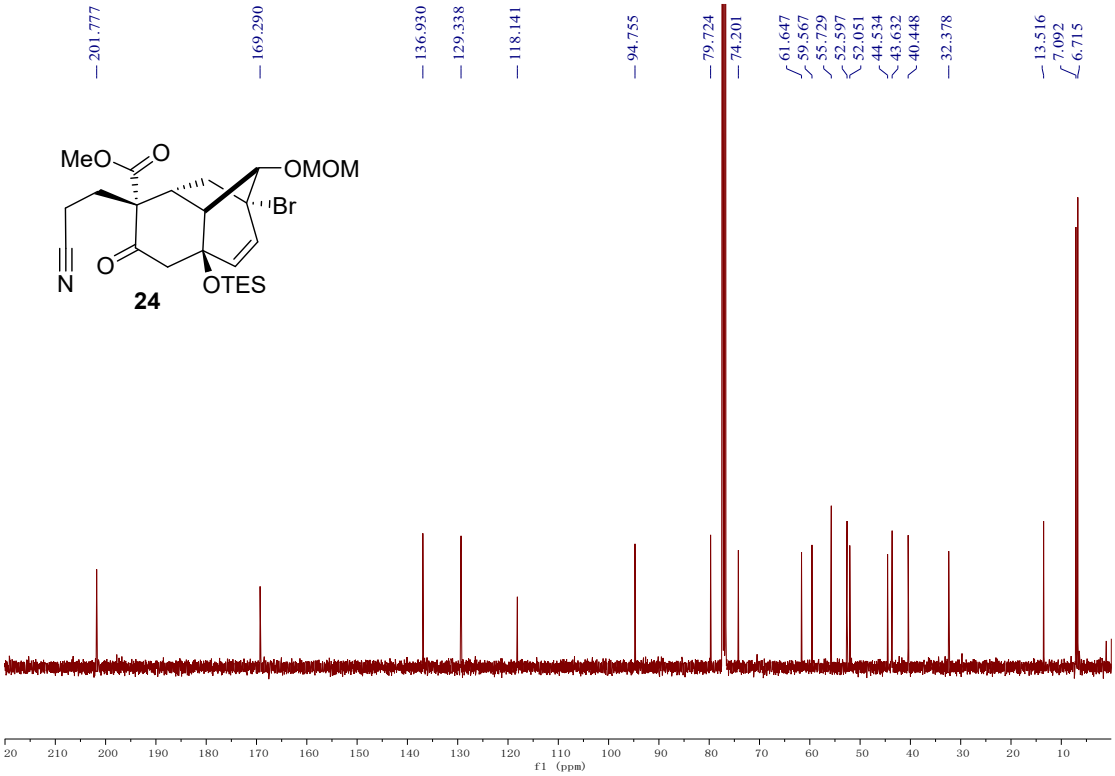
^{13}C NMR Spectrum of 23(100 MHz, $CDCl_3$)



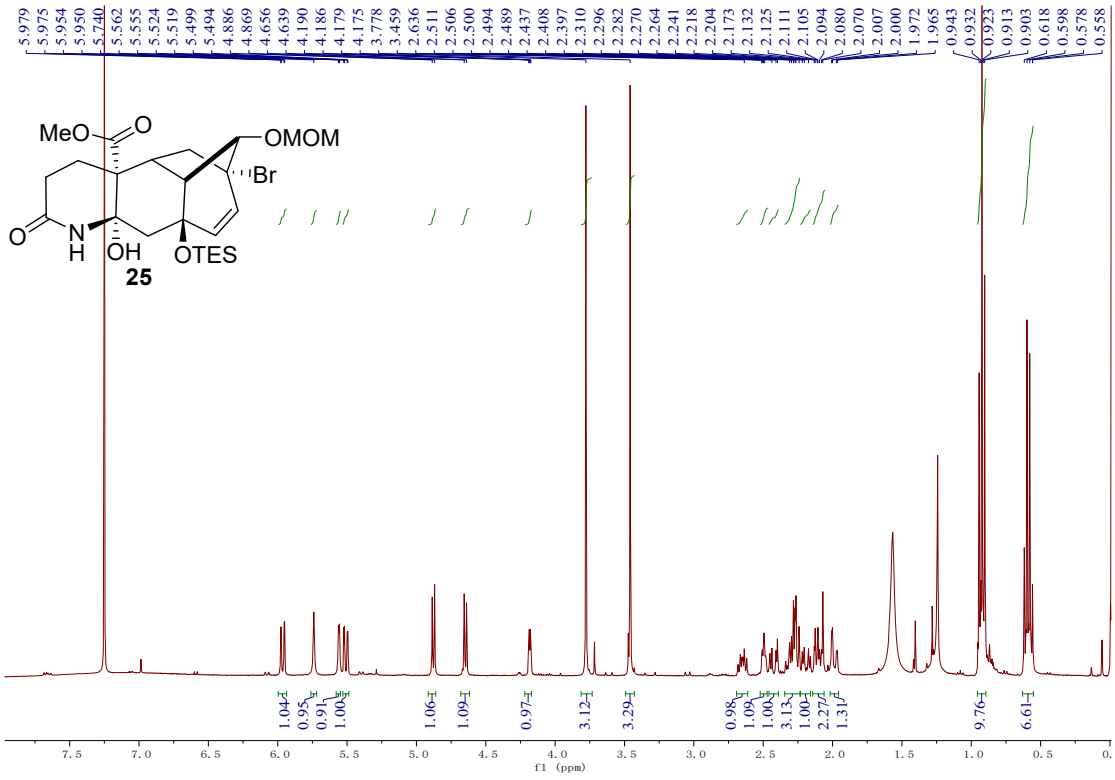
^{1}H NMR Spectrum of 24 (400 MHz, $CDCl_3$)



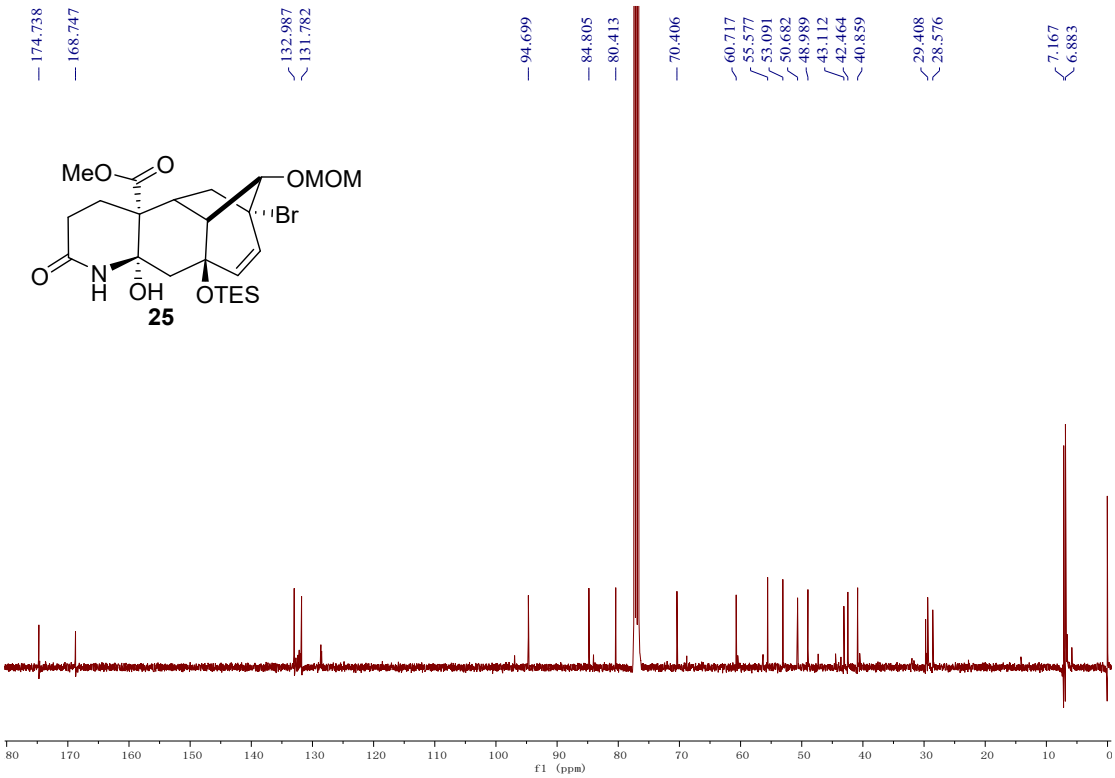
^{13}C NMR Spectrum of 24 (100 MHz, $CDCl_3$)



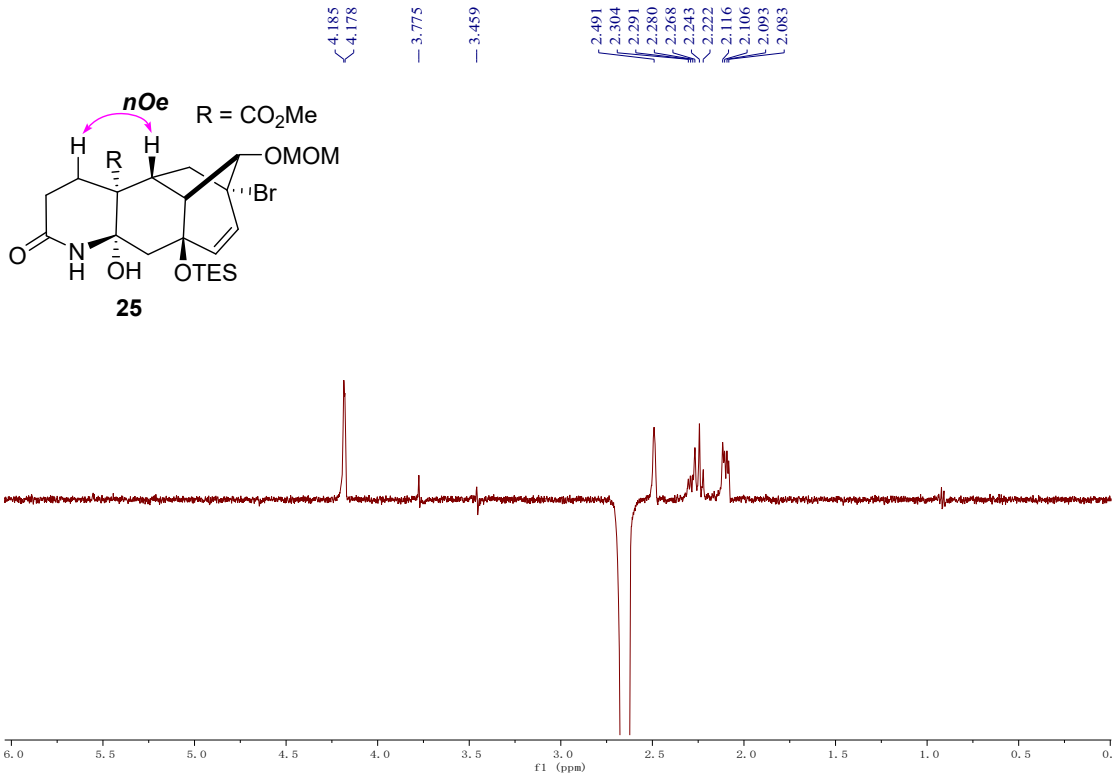
^{1}H NMR Spectrum of 25 (400 MHz, $CDCl_3$)



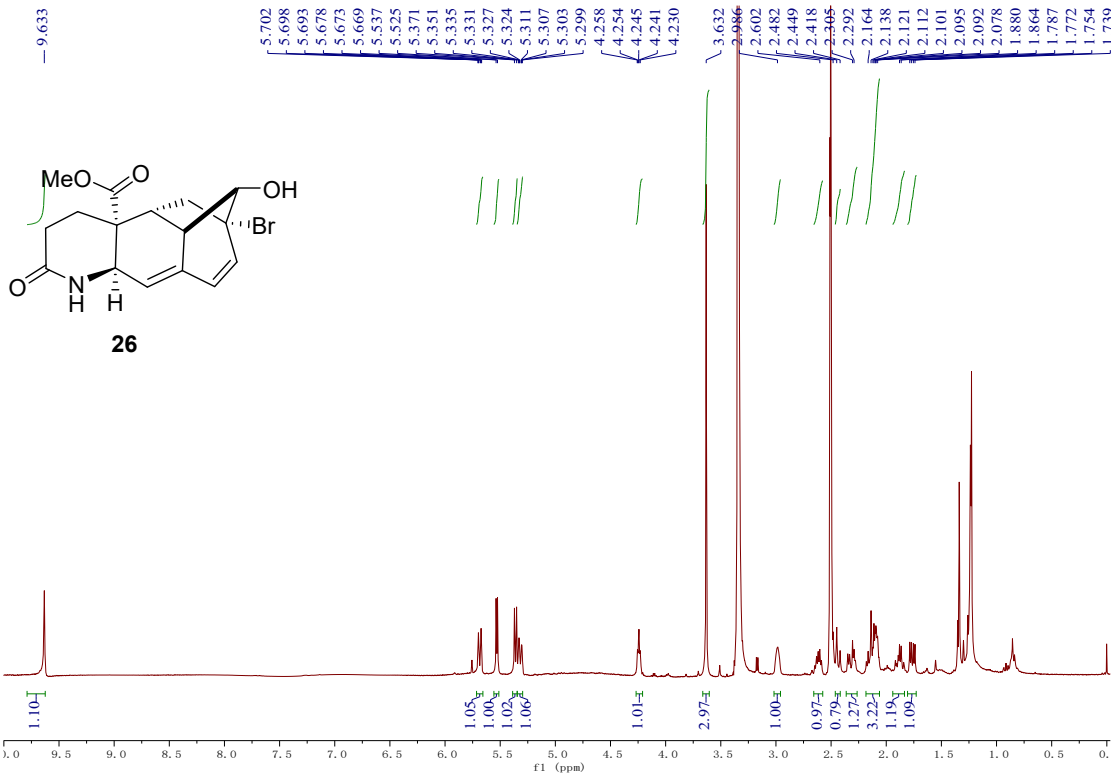
^{13}C NMR Spectrum of 25 (100 MHz, $CDCl_3$)



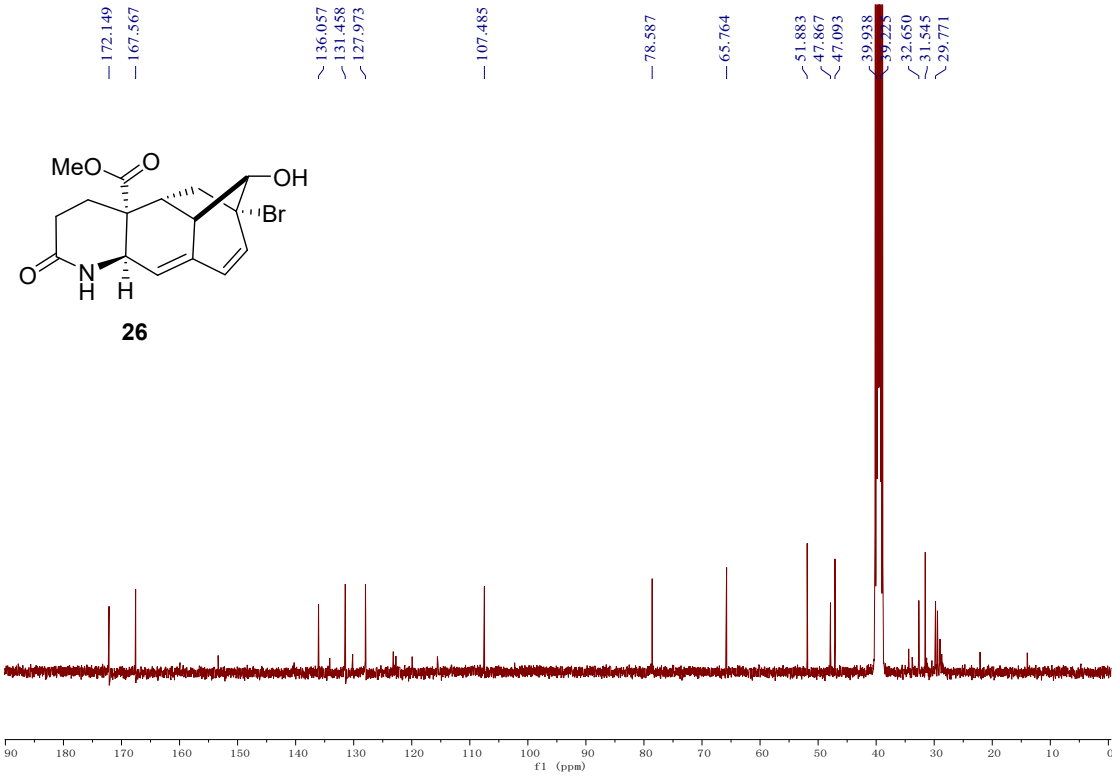
NOEDS Spectrum of 25 (600 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 26 (400 MHz, DMSO-*d*6)



^{13}C NMR Spectrum of 26 (100 MHz, DMSO-*d*6)



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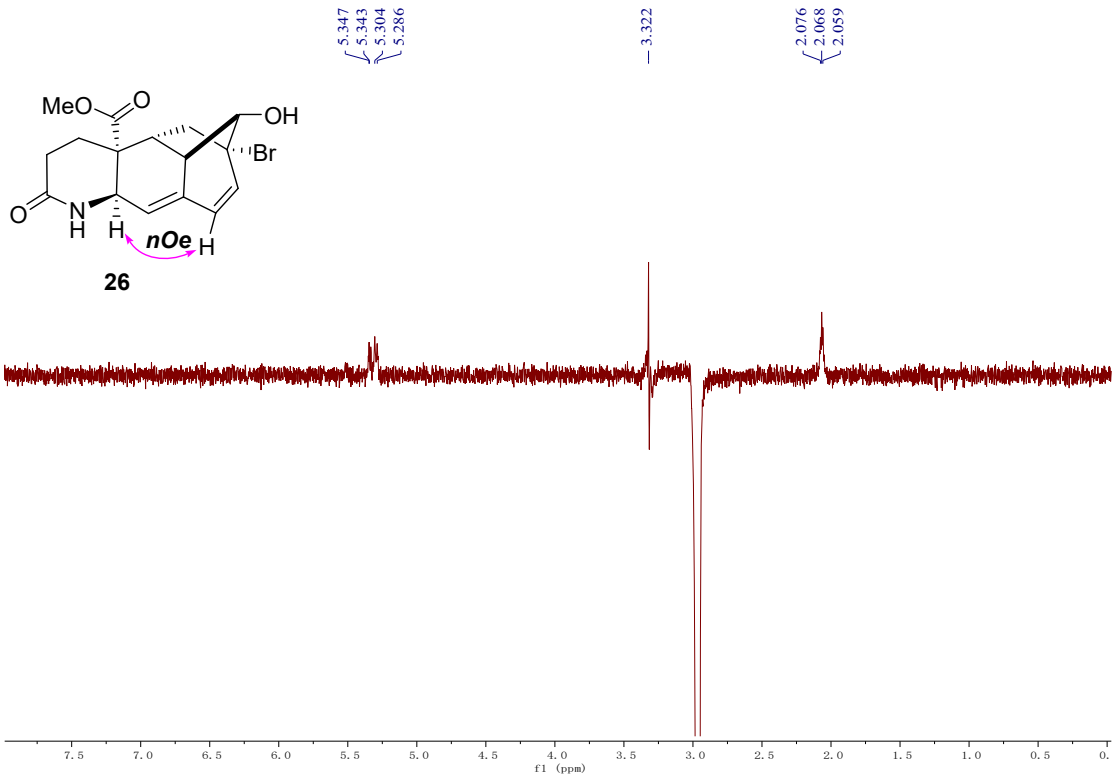
NOEDS Spectrum of 26 (600 MHz, DMSO-*d*6)



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