

Supporting Information

A concise and stereoselective synthesis of the BCDF tetracyclic ring system of C₁₉-diterpenoid alkaloids

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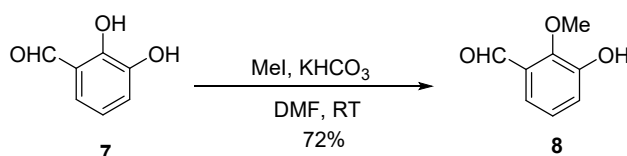
1. General Procedures

Unless otherwise noted, all reactions were performed under an inert atmosphere of argon or nitrogen using oven-dried or flame-dried glassware fitted with rubber septa. Air- and moisture-sensitive liquids were transferred via syringe. Reaction progress was monitored by analytical thin layer chromatography (TLC) using commercial glass plates pre-coated with silica gel GF254. TLC plates were visualized under ultraviolet light (254 nm) or by staining with aqueous potassium permanganate (KMnO₄) or ceric ammonium molybdate (CAM) solutions. Flash column chromatography was carried out using silica gel (200-300 mesh) purchased from Qingdao Marine Chemical Factory, China. Commercially available reagents were used as received without further purification unless referenced otherwise. Anhydrous tetrahydrofuran (THF) was purified by distillation over sodium benzophenone prior to use. Dichloroethane (DCE) and dichloromethane (DCM) were dried by distillation from calcium hydride. Anhydrous methanol was obtained by distillation from magnesium turnings and iodine. Infrared spectra (IR) were recorded on a Nicolet 200 SXV spectrometer and high resolution mass spectra (HRMS) were measured with a Bruker BioTOFQ mass spectrometer. Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were obtained on Varian INOVA-400 and Agilent 600 MHz instruments and calibrated using the residual solvent peaks (CDCl₃: δ 7.26 for ¹H NMR, δ 77.00 for ¹³C NMR; DMSO-*d*₆: δ 2.50 for ¹H NMR, δ 39.52 for ¹³C 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

Synthesis of compound 8



2,3- Dihydroxy-benzaldehyde **7** (30.60 g, 221.42 mmol, 1.0 equiv.) was dissolved in DMF (520 mL), KHCO_3 (88.65 g, 885.67 mmol, 4.0 equiv.) was added and stirred for 30 min at room temperature. MeI (27.57 mL, 442.84 mmol, 2.0 equiv.) was then added to the reaction solution and stirred at room temperature for 30 h. The reaction was complete as detected by TLC and the mixture was filtered to remove KHCO_3 solids, followed by distillation under reduced pressure to remove excess MeI, and then water (400 mL) and 1 N HCl (100 mL) were added to the mixture at 0 °C to reach pH=5. The organic layer was separated, the aqueous layer was extracted with EtOAc (4 × 400 mL), the organic layers were combined, washed with saturated saline (2 × 500 mL), dried with MgSO_4 , filtered and distilled under reduced pressure to give the crude product as an orange solid. The crude product was dissolved in PE / EtOAc = 8/1 (20 mL) and stirred for 12 hours. The resulting suspension was filtered through a suction funnel, the solids were washed with PE (3 × 10 mL) and dried under vacuum at room temperature to give 2-methoxy-3-hydroxy-benzaldehyde **8** (24.2 g, 72%) as a white powdery solid.

TLC: Rf = 0.5 (Petroleum ether/Ethyl acetate = 6/1).

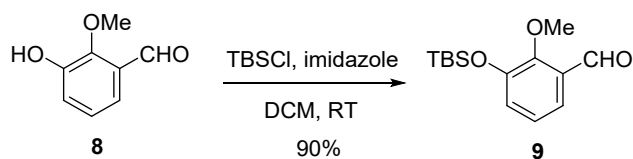
IR (film, KBr) ν_{max} : 3021, 2964, 1729, 1603 cm^{-1} .

^1H NMR (400 MHz, Chloroform-d) δ 10.27 (s, 1H), 7.37 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.23 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.15 (t, $J = 7.8$ Hz, 1H), 5.82 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 189.55, 149.45, 149.15, 129.01, 125.09, 121.86, 121.73, 63.89.

HRMS (ESI⁺) m/z calcd for $\text{C}_8\text{H}_9\text{O}_3$ $[\text{M}+\text{H}]^+$ 152.0473, found 152.0478.

Synthesis of compound 9



Compound **8** (23.70 g, 155.72 mmol, 1.0 equiv.) was dissolved in DCM (480 mL), imidazole (15.91 g, 233.57 mmol, 1.5 equiv.) and TBSCl (28.15 g, 186.86 mmol, 1.2 equiv.) were added sequentially and stirred for 60 min at room temperature. After the reaction was complete as detected by TLC, saturated NH_4Cl (300 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with DCM (3×100 mL), the organic layers were combined, washed with saturated saline (300 mL), dried with Na_2SO_4 , then filtered, and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 16/1) to afford the light yellow oily compound **9** (37.00 g, 90%).

TLC: Rf = 0.4 (Petroleum ether/Ethyl acetate = 16/1).

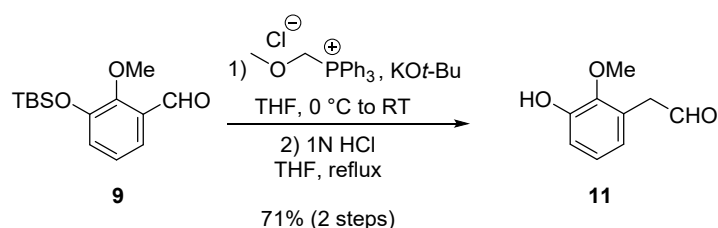
IR (film, KBr) ν_{max} : 3021, 1726, 1601 cm^{-1} .

^1H NMR (400 MHz, Chloroform- d) δ 10.39 (s, 1H), 7.44 (dd, $J = 7.6, 1.9$ Hz, 1H), 7.11 (dd, $J = 8.0, 1.9$ Hz, 1H), 7.06 (td, $J = 7.8, 0.8$ Hz, 1H), 3.93 (s, 3H), 1.03 (s, 9H), 0.22 (s, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 190.3, 154.7, 149.4, 130.4, 127.4, 124.3, 120.7, 62.1, 25.6, 18.3, -4.6.

HRMS (ESI $^+$) m/z calcd for $\text{C}_{14}\text{H}_{24}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 266.1138, found 266.1131.

Synthesis of compound 11



(Methoxymethyl) triphenylphosphonium chloride (67.69 g, 189.71 mmol, 1.4 equiv.) and $\text{KO}t\text{-Bu}$ (22.81 g, 203.26 mmol, 1.5 equiv.) were added sequentially to anhydrous THF (150 mL) at 0 °C and stirred at 0 °C for 30 min. Subsequently, compound **9** (31.10 g, 135.51 mmol, 1.0 equiv.) was dissolved in anhydrous THF (54 mL) and added to the mixture at 0 °C. The reaction solution was brought to room

temperature and stirred for 30 min at 0 °C. The reaction solution was brought to room temperature and stirred for 20 min and the reaction was complete by TLC. The reaction was quenched by the addition of saturated NH₄Cl (200 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 100 mL), the organic layers were combined, washed with saturated saline (200 mL), dried over Na₂SO₄, then filtered and distilled under reduced pressure to obtain the crude product of the methyl vinyl ether. The crude methyl vinyl ether product was dissolved in THF (50 mL) and 1N HCl (50 mL) was added at room temperature. The reaction solution was raised to 100 °C and stirred at reflux for 12 hours. After the reaction was completely detected by TLC, the reaction was quenched by addition of saturated NaHCO₃ (100 mL) at room temperature. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 100 mL), the organic layers were combined, washed with saturated saline (200 mL), dried with Na₂SO₄, filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford the light yellow oily compound **11** (15.98 g, 71%).

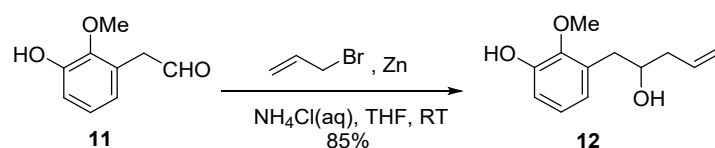
TLC: R_f = 0.4 (Petroleum ether/Ethyl acetate = 1/1).

IR (film, KBr) ν_{max} : 3023, 2974, 1730, 1602 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 9.73 (t, *J* = 2.2 Hz, 1H), 7.06 – 6.98 (m, 1H), 6.93 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.73 (dd, *J* = 7.5, 1.6 Hz, 1H), 5.49 (s, 1H), 3.76 (s, 3H), 3.70 (d, *J* = 2.3 Hz, 2H).

HRMS (ESI⁺) *m/z* calcd for C₉H₁₃O₃ [M+H]⁺ 166.0630, found 166.0627.

Synthesis of compound 12



Compound **11** (26.00 g, 156.5 mmol, 1.0 equiv.) was dissolved in THF (313 mL), and saturated NH₄Cl (313 mL), zinc powder (15.30 g, 234.75 mmol, 1.5 equiv.), and allyl bromide (20.30 mL, 234.75 mmol, 1.5 equiv.) were added sequentially at room temperature. The reaction solution was stirred at room temperature for 30 min before the reaction was detected as complete by TLC, the zinc powder was removed by diatomaceous earth filtration and the filter cake was washed by DCM (3 × 100 m

L). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 100 mL), the organic layers were combined, washed with saturated saline (200 mL), dried with Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 3/2) to give yellow oily compound **12** (23.98 g, 85%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 1/1).

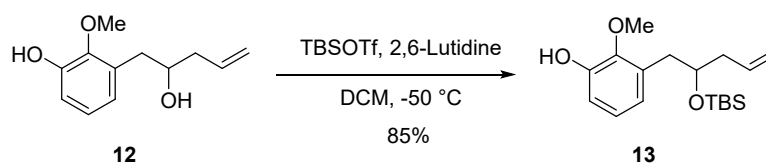
IR (film, KBr) ν_{max} : 3018, 2964, 1604 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 6.98 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.93 – 5.82 (m, 1H), 5.19 – 5.14 (m, 2H), 3.99 – 3.90 (m, 1H), 3.81 (s, 3H), 2.80 (h, *J* = 8.5, 7.9 Hz, 2H), 2.40 – 2.20 (m, 2H).

¹³C NMR (101 MHz, Chloroform-d) δ 149.1, 145.6, 134.7, 131.7, 125.1, 122.4, 118.1, 114.5, 71.2, 61.2, 41.5, 37.3.

HRMS (ESI⁺) *m/z* calcd for C₁₆H₁₇O₃ [M+H]⁺ 208.1099, found 208.1087.

Synthesis of compound 13



Compound **12** (15.3 g, 73.52 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (153 mL) and 2,6-Lutidine (17.09 mL, 147.04 mmol, 2.0 equiv.) and TBSOTf (18.57 mL, 80.87 mmol, 1.1 equiv.) were added sequentially at -50 °C. The reaction solution was stirred for 30 minutes at room temperature. The reaction solution was allowed to stir at -50 °C for 30 min and after the reaction was complete as detected by TLC, the reaction was quenched by the addition of saturated NH₄Cl (100 mL) at room temperature. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 100 mL), the organic layers were combined, washed with saturated saline (100 mL), dried with Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 16/1) to give yellow oily compound **13** (19.76 g, 85%).

TLC: R_f = 0.6 (Petroleum ether/Ethyl acetate = 8/1).

IR (film, KBr) ν_{max} : 3027, 2986, 1649, 1604 cm⁻¹.

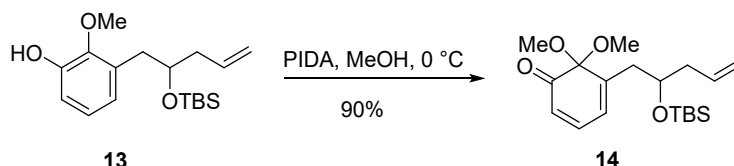
¹H NMR (400 MHz, Chloroform-d) δ 6.92 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 5.87 (ddt, *J* = 15.4, 11.1, 7.2 Hz, 1H), 5.53 (s, 1H), 5.09 – 5.04

(m, 2H), 3.99 (dt, $J = 11.8, 5.9$ Hz, 1H), 3.79 (s, 3H), 2.74 (h, $J = 7.5$ Hz, 2H), 2.23 (t, $J = 5.8$ Hz, 2H), 0.83 (s, 9H), -0.05 (s, 3H), -0.21 (s, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 148.9, 145.7, 135.1, 132.5, 124.6, 123.1, 117.1, 113.8, 72.3, 61.1, 41.9, 37.6, 25.8, 18.0, -4.8, -5.1.

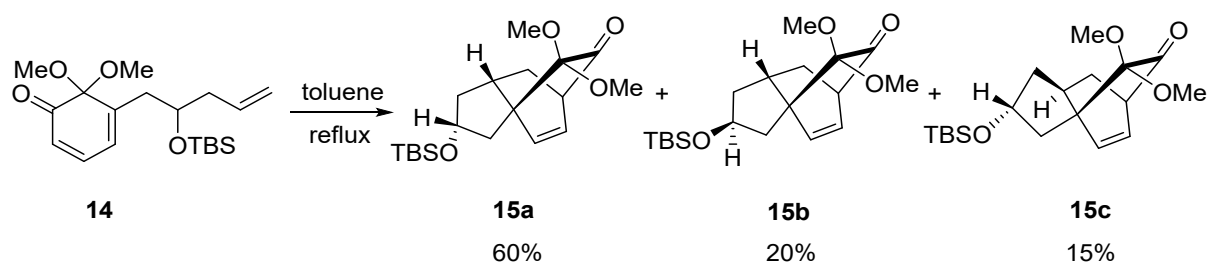
HRMS (ESI $^+$) m/z calcd for $\text{C}_{18}\text{H}_{31}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 322.1964, found 322.1959.

Synthesis of compound 14



Compound **13** (38.00 g, 117.80 mmol, 1.0 equiv.) was dissolved in MeOH (589 mL), PIDA (417.00 g, 129.6 mmol, 1.1 equiv.) was added and stirred at 0 °C for 10 min. After the reaction was complete as detected by TLC, the reaction was quenched by adding saturated $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL) and saturated NaHCO_3 (100 mL) at room temperature to quench the reaction. The organic layer was separated and the aqueous layer was extracted with DCM (5×100 mL), the organic layers were combined, washed with saturated saline (100 mL), dried with anhydrous Na_2SO_4 , then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 16/1) to afford the yellow oily compound **14** (37.32 g, 90%), which was immediately used in the next step of the reaction.

Synthesis of compound 15a, 15b and 15c



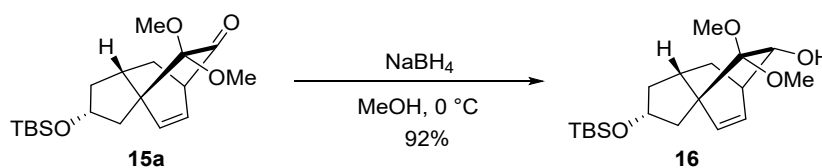
Compound **14** (37.32 g, 106.02 mmol, 1.0 equiv.) was dissolved in toluene (150 mL), heated to reflux and stirred for 12 h. After the reaction was complete by TLC, the crude product was obtained by distillation under reduced pressure. The crude product

was purified by silica gel column chromatography (PE/EtOAc =,70/1) to afford the yellow oily compounds **15a** (22.39 g, 60%), **15b** (7.46 g, 20%) and **15c** (5.60 g, 15%). For **15a**: $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 6.28 – 6.17 (m, 2H), 4.38 (qd, J = 6.9, 2.5 Hz, 1H), 3.48 (s, 3H), 3.21 (s, 3H), 3.01 (dd, J = 4.6, 2.6 Hz, 1H), 2.54 (dd, J = 13.5, 8.7 Hz, 1H), 2.36 (ddt, J = 13.3, 9.4, 6.7 Hz, 1H), 2.18 – 2.01 (m, 1H), 1.78 (dd, J = 13.5, 2.4 Hz, 1H), 1.32 (ddd, J = 12.6, 6.4, 2.3 Hz, 1H), 1.09 (td, J = 12.8, 6.6 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 205.7, 138.9, 127.6, 94.8, 73.5, 55.4, 51.3, 50.8, 48.7, 42.5, 41.1, 38.2, 29.4, 25.9, 18.0, -4.7, -4.8; **HRMS** (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{33}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 352.2070, found 352.2059. **TLC**: R_f = 0.5 (Petroleum ether/Ethyl acetate = 16/1); **IR** (film, KBr) ν_{max} : 3027, 1726, 1664 cm^{-1} .

For **15b**: $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 6.27 – 6.21 (m, 1H), 5.95 (d, J = 8.1 Hz, 1H), 4.48 – 4.36 (m, 1H), 3.50 (s, 3H), 3.24 (s, 3H), 3.03 – 2.97 (m, 1H), 2.83 (ddd, J = 14.2, 10.5, 7.5 Hz, 1H), 2.20 (ddt, J = 28.6, 13.0, 6.2 Hz, 3H), 1.72 (dd, J = 12.6, 8.5 Hz, 1H), 1.45 – 1.28 (m, 2H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 205.7, 137.7, 128.9, 94.8, 73.9, 56.4, 51.3, 50.9, 48.5, 42.1, 41.6, 29.5, 25.9, 18.1, -4.7; **HRMS** (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{33}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 352.2070, found 352.2079. **TLC**: R_f = 0.45 (Petroleum ether/Ethyl acetate = 16/1); **IR** (film, KBr) ν_{max} : 3023, 1729, 1661 cm^{-1} .

For **15c**: $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 6.53 (d, J = 7.8 Hz, 1H), 5.91 – 5.83 (m, 1H), 4.57 (q, J = 5.8 Hz, 1H), 3.35 (s, 3H), 3.24 (s, 3H), 3.21 – 3.17 (m, 1H), 2.65 (dd, J = 14.0, 7.2 Hz, 1H), 2.18 – 2.10 (m, 1H), 2.05 (tt, J = 12.3, 6.1 Hz, 1H), 1.85 (td, J = 11.6, 10.3, 4.8 Hz, 1H), 1.60 (dd, J = 12.8, 9.1 Hz, 2H), 1.54 (d, J = 4.7 Hz, 1H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 200.9, 144.1, 122.5, 96.5, 75.8, 57.3, 54.1, 51.0, 48.7, 44.5, 40.3, 39.9, 25.9, 23.5, 18.1, -4.7, -4.7; **HRMS** (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{33}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 352.2070, found 352.2063. **TLC**: R_f = 0.55 (Petroleum ether/Ethyl acetate = 16/1); **IR** (film, KBr) ν_{max} : 3028, 1733, 1659 cm^{-1} .

Synthesis of compound 16



Compound **15a** (10.50 g, 29.78 mmol, 1.0 equiv.) was dissolved in MeOH (200 mL), NaBH₄ (1.35 g, 35.74 mmol, 1.2 equiv.) was added and stirred at 0 °C for 10 min, and after the reaction was complete as detected by TLC, the reaction was quenched by adding H₂O (60 mL) and saturated NH₄Cl (10 mL) at 0 °C.) to quench the reaction. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 60 mL), the organic layers were combined, washed with saturated saline (40 mL), dried with anhydrous Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 16/1) to afford colorless oily compound **16** (9.70 g, 92%).

TLC: R_f = 0.3 (Petroleum ether/Ethyl acetate = 16/1).

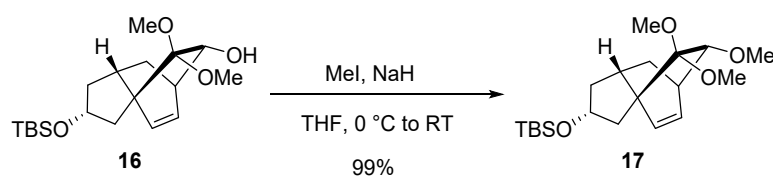
IR (film, KBr) ν_{max} : 3317, 3041, 1629 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 6.29 – 6.16 (m, 1H), 5.97 (d, *J* = 8.1 Hz, 1H), 4.33 – 4.19 (m, 1H), 3.67 (d, *J* = 5.6 Hz, 1H), 3.33 (d, *J* = 6.9 Hz, 1H), 3.24 (s, 3H), 3.23 (s, 3H), 2.63 (dd, *J* = 13.5, 9.1 Hz, 1H), 2.58 (d, *J* = 3.7 Hz, 1H), 2.13 – 2.02 (m, 1H), 2.02 – 1.94 (m, 1H), 1.83 (ddd, *J* = 12.5, 9.3, 3.4 Hz, 1H), 1.63 (dd, *J* = 13.5, 3.3 Hz, 1H), 1.01 – 0.94 (m, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 135.3, 132.1, 102.8, 74.6, 73.6, 53.1, 50.8, 50.2, 42.6, 41.3, 41.1, 37.3, 30.1, 25.9, 18.1, -4.7, -4.8.

HRMS (ESI⁺) *m/z* calcd for C₁₉H₃₅O₄Si [M+H]⁺ 354.2226, found 354.2232.

Synthesis of compound 17



Compound **16** (9.70 g, 27.36 mmol, 1.0 equiv.) was dissolved in anhydrous THF (200 mL), 60% NaH (2.19 g, 54.72 mmol, 2.0 equiv.) was added at 0 °C and stirred for 30 min before MeI (2.56 mL, 41.04 mmol, 1.5 equiv.) was added dropwise to the reaction solution. The reaction solution was brought to room temperature and stirred for 2 h. After complete reaction was detected by TLC, the reaction was quenched by the addition of H₂O (60 mL) saturated with NH₄Cl (10 mL) at 0 °C. The reaction was carried out at 0 °C with the addition of H₂O (60 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 60 mL), the organic layers were

combined, washed with saturated saline (60 mL), dried with anhydrous Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 15/1) to afford colorless oily compound **17** (10.0 g, 99%).

TLC: R_f = 0.4 (Petroleum ether/Ethyl acetate = 15/1).

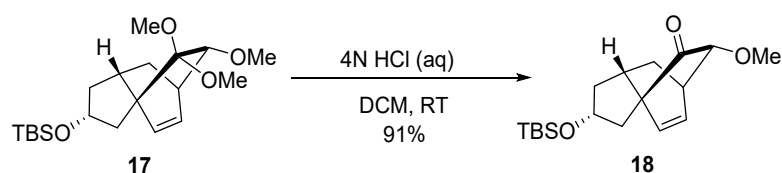
IR (film, KBr) ν_{max} : 3015, 1639 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 6.29 – 6.21 (m, 1H), 6.01 (d, *J* = 8.0 Hz, 1H), 4.27 (ddt, *J* = 10.2, 7.3, 3.2 Hz, 1H), 3.37 (s, 3H), 3.25 (s, 3H), 3.20 (s, 1H), 3.18 (s, 3H), 2.73 (s, 1H), 2.65 (dd, *J* = 13.6, 9.1 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.97 (dt, *J* = 13.2, 6.7 Hz, 1H), 1.78 (ddd, *J* = 12.4, 9.3, 3.3 Hz, 1H), 1.65 (dd, *J* = 13.6, 3.2 Hz, 1H), 1.02 (ddd, *J* = 12.1, 6.3, 2.3 Hz, 1H), 0.94 (dt, *J* = 12.5, 6.2 Hz, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 135.5, 131.7, 104.6, 85.0, 73.6, 57.0, 53.8, 50.9, 49.9, 42.6, 42.0, 36.9, 35.6, 30.8, 25.9, 18.1, -4.7, -4.8.

HRMS (ESI⁺) *m/z* calcd for C₂₀H₃₇O₄Si [M+H]⁺ 368.2383, found 368.2272.

Synthesis of compound 18



Compound **17** (10.0 g, 27.14 mmol, 1.0 equiv.) was dissolved in DCM (135 mL), 4N HCl (1.36 mL 5.42 mmol, 0.2 equiv.) was added and stirred at room temperature for 15 min. after the reaction was complete as detected by TLC, the reaction was diluted by addition of H₂O (60 ml) at 0 °C and saturated NaHCO₃ (20 mL) was added. The reaction was quenched. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 60 mL), the organic layers were combined, washed with saturated saline (60 mL), dried with anhydrous Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 15/1) to afford colorless oily compound **18** (8.0 g, 91%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 15/1).

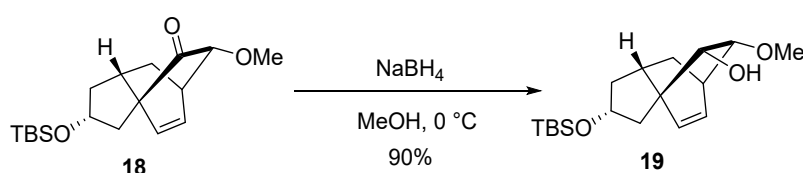
IR (film, KBr) ν_{max} : 3025, 1733, 1647 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 6.50 – 6.36 (m, 1H), 5.91 (d, J = 7.9 Hz, 1H), 4.41 – 4.23 (m, 1H), 3.52 (s, 3H), 3.39 (d, J = 2.0 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.51 (dd, J = 14.3, 8.7 Hz, 1H), 2.21 (dt, J = 12.4, 6.5 Hz, 1H), 2.02 (dd, J = 9.4, 3.3 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.64 (dd, J = 14.3, 3.1 Hz, 1H), 1.35 – 1.27 (m, 1H), 1.20 (dt, J = 12.2, 6.2 Hz, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 206.7, 134.8, 130.9, 78.7, 72.9, 59.5, 58.9, 42.5, 38.7, 37.7, 37.3, 28.7, 25.8, 18.0, -4.8, -4.8.

HRMS (ESI⁺) m/z calcd for C₁₈H₃₁O₃Si [M+H]⁺ 322.1964, found 322.1974.

Synthesis of compound 19



Compound **18** (8.0 g, 24.8 mmol, 1.0 equiv.) was dissolved in MeOH (150 mL), NaBH₄ (1.4 g, 37.2 mmol, 1.5 equiv.) was added and stirred at 0 °C for 10 min, and after the reaction was complete as detected by TLC, the reaction was diluted by adding H₂O (60 mL) at 0 °C, and the reaction was quenched by adding saturated NH₄Cl (10 mL). The reaction was quenched. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 40 mL), the organic layers were combined, washed with saturated saline (40 mL), dried with anhydrous Na₂SO₄, then filtered, and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 12/1) to afford colorless oily compound **19** (7.2 g, 90%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 6/1).

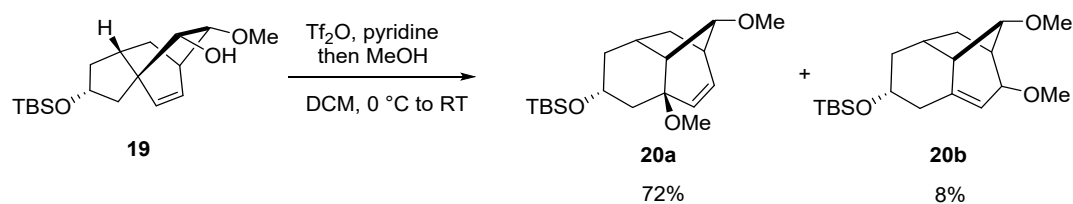
IR (film, KBr) ν_{max} : 3435, 3006, 1641 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 6.29 – 6.21 (m, 1H), 6.03 (d, J = 8.1 Hz, 1H), 4.36 (ddt, J = 10.4, 6.8, 3.7 Hz, 1H), 3.59 (t, J = 6.8 Hz, 1H), 3.48 (d, J = 7.3 Hz, 1H), 3.40 (s, 3H), 2.76 – 2.72 (m, 1H), 2.11 (dt, J = 13.9, 7.0 Hz, 1H), 2.01 – 1.99 (m, 1H), 1.69 (ddd, J = 12.6, 9.4, 3.2 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.04 (dd, J = 12.5, 6.2 Hz, 1H), 1.02 – 0.97 (m, 1H), 0.86 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 136.0, 131.4, 81.1, 75.8, 73.7, 58.6, 51.1, 44.1, 43.2, 38.6, 36.2, 29.7, 25.8, 18.0, -4.8.

HRMS (ESI⁺) m/z calcd for C₁₈H₃₃O₃Si [M+H]⁺ 324.2121, found 324.2135.

Synthesis of compound 20a and 20b



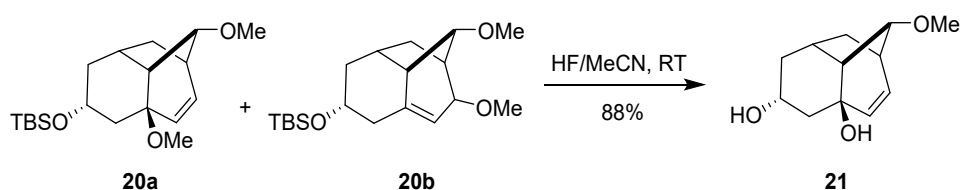
Compound **19** (640 mg, 2.00 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (20 mL), pyridine (0.6 mL, 7.50 mmol, 3.75 equiv.) and trifluoromethanesulfonic anhydride (0.5 mL, 3.00 mmol, 1.5 equiv.) were added sequentially and stirred at 0 °C for 1 min, and after the reaction of the raw material was complete as detected by TLC. After the reaction was complete, anhydrous MeOH (6 mL) was added at 0 °C. The reaction was brought to room temperature and stirred. The reaction was moved to room temperature and stirred for 3 h. After the reaction was complete by TLC, the reaction was quenched with saturated NaHCO_3 (20 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3×10 mL), the organic layers were combined, washed with saturated aqueous saline (20 mL), dried with anhydrous Na_2SO_4 , then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 8/1) to afford the colorless oily compounds **20a** (480 mg, 72%) and **20b** (53 mg, 8%).

For **20a**: $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 5.89 (ddd, $J = 9.7, 6.6, 1.2$ Hz, 1H), 5.74 (dd, $J = 9.7, 1.8$ Hz, 1H), 4.14 (p, $J = 3.5$ Hz, 1H), 3.56 (td, $J = 4.2, 1.1$ Hz, 1H), 3.38 (s, 3H), 3.27 (s, 3H), 2.54 (td, $J = 6.5, 4.1$ Hz, 1H), 2.32 (tdd, $J = 10.8, 6.3, 4.3$ Hz, 1H), 2.27 – 2.22 (m, 1H), 2.12 – 2.02 (m, 1H), 1.86 (ddd, $J = 12.3, 11.0, 6.5$ Hz, 1H), 1.76 (dd, $J = 12.3, 6.6$ Hz, 1H), 1.68 – 1.64 (m, 2H), 1.60 (d, $J = 3.5$ Hz, 1H), 0.86 (s, 9H), 0.04 – -0.11 (m, 6H); $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 130.3, 129.8, 84.6, 72.3, 68.1, 57.3, 49.1, 43.3, 41.8, 37.7, 34.1, 33.6, 31.1, 25.8, 17.9, -5.0, -5.1; **HRMS** (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{35}\text{O}_3\text{Si}$ [$\text{M}+\text{H}$] $^+$ 338.2277, found 338.2265. **TLC**: $R_f = 0.5$ (Petroleum ether/Ethyl acetate = 4/1); **IR** (film, KBr) ν_{max} : 3012, 1621 cm^{-1} .

For **20b**: $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 5.68 (d, $J = 5.4$ Hz, 1H), 4.10 (d, $J = 7.0$ Hz, 1H), 3.54 (t, $J = 4.3$ Hz, 1H), 3.41 (s, 3H), 3.37 (s, 3H), 3.34 (d, $J = 6.8$ Hz, 1H), 2.62 (dd, $J = 12.6, 6.5$ Hz, 1H), 2.53 (d, $J = 6.9$ Hz, 1H), 2.37 (t, $J = 4.6$ Hz, 1H), 2.12 (t, $J = 6.5$ Hz, 1H), 2.04 (d, $J = 4.8$ Hz, 1H), 2.01 (d, $J = 5.7$ Hz, 1H),

1.84 (ddd, $J = 12.6, 7.6, 4.1$ Hz, 1H), 1.42 (d, $J = 4.9$ Hz, 1H), 1.03 (dd, $J = 13.3, 5.2$ Hz, 1H), 0.87 (s, 1H), 0.04 (s, 3H), 0.03 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-d) δ 138.9, 118.9, 81.4, 81.0, 69.8, 57.8, 56.9, 44.0, 43.8, 37.5, 36.4, 34.0, 33.5, 25.8, 18.0, -4.8, -4.9; **HRMS** (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{35}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 338.2277, found 338.2274. **TLC**: $R_f = 0.6$ (Petroleum ether/Ethyl acetate = 4/1); **IR** (film, KBr) ν_{max} : 3014, 1627 cm^{-1} .

Synthesis of compound 21



A mixture of compounds **20a** and **20b** (725 mg, 2.14 mmol, 1.0 equiv.) was dissolved in 40% HF: MeCN (18 mL, 1: 19) and stirred at room temperature for 10 min. After the complete reaction of the raw material was detected by TLC, the reaction was quenched by the addition of saturated NaHCO_3 (18 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with DCM (3×18 mL), the organic layers were combined, washed with saturated saline (18 mL), dried with anhydrous Na_2SO_4 , then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 1/2) to give colorless solid compound **21** (396 mg, 88%).

TLC: $R_f = 0.4$ (Petroleum ether/Ethyl acetate = 1/2).

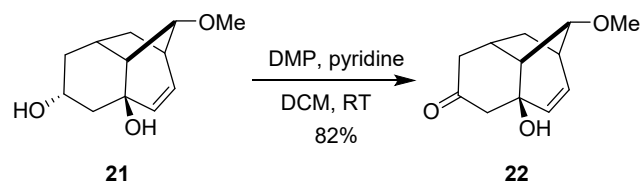
IR (film, KBr) ν_{max} : 3504, 3477, 3018, 1637 cm^{-1} .

$^1\text{H NMR}$ (400 MHz, Chloroform-d) δ 5.87 (ddd, $J = 9.4, 6.8, 1.2$ Hz, 1H), 5.60 (dd, $J = 9.4, 1.8$ Hz, 1H), 3.73 (t, $J = 4.5$ Hz, 1H), 3.54 (tt, $J = 11.5, 4.1$ Hz, 1H), 3.29 (s, 3H), 2.59 (td, $J = 6.7, 4.2$ Hz, 1H), 2.45 (dtd, $J = 12.5, 6.1, 1.8$ Hz, 1H), 2.12 – 2.07 (m, 1H), 2.06 – 2.01 (m, 1H), 2.01 – 1.95 (m, 1H), 1.84 – 1.76 (m, 1H), 1.46 – 1.42 (m, 1H), 1.11 (dd, $J = 13.2, 6.1$ Hz, 1H), 0.94 – 0.81 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-d) δ 132.6, 129.1, 84.0, 72.0, 65.3, 57.0, 46.8, 45.6, 36.7, 35.6, 34.9, 30.8.

HRMS (ESI⁺) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$ 210.1256, found 210.1269.

Synthesis of compound 22



Compound **21** (440 mg, 2.09 mmol, 1.0 equiv.) was dissolved in DCM (20.9 mL), pyridine (540.50 μ L, 6.70 mmol, 3.2 equiv.) and Days-Martin oxidizing agent (1.06 g, 2.51 mmol, 1.2 equiv.) were added sequentially at 0 °C, and the reaction was shifted to room temperature and stirred for 30 min. After the reaction was complete by TLC, saturated NaHCO₃ aqueous solution (8 mL) and saturated Na₂S₂O₃ aqueous solution (2 mL) were added and the reaction was quenched by stirring for 10 min. The organic layer was separated and the aqueous layer was extracted with DCM (3 \times 18 mL), the organic layers were combined, washed with saturated saline (20 mL), dried with anhydrous Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 1/1) to give colorless solid compound **22** (358 mg, 82%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 2/1).

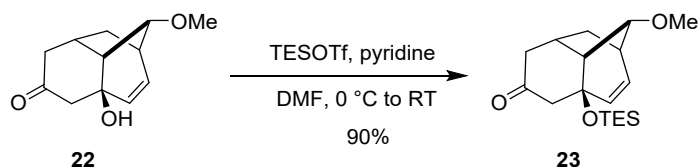
IR (film, KBr) ν_{max} : 3464, 3018, 1722, 1645 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 5.89 (ddd, *J* = 9.5, 6.7, 1.3 Hz, 1H), 5.55 (dd, *J* = 9.5, 1.9 Hz, 1H), 3.90 – 3.87 (m, 1H), 3.87 (s, 1H), 3.34 (s, 3H), 2.79 – 2.67 (m, 1H), 2.65 (d, *J* = 6.6 Hz, 1H), 2.59 – 2.53 (m, 2H), 2.49 (dd, *J* = 12.9, 2.0 Hz, 1H), 2.19 (dt, *J* = 15.1, 1.9 Hz, 1H), 2.14 – 2.05 (m, 1H), 1.30 – 1.23 (m, 1H), 1.17 (dd, *J* = 13.3, 5.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-d) δ 208.5, 131.0, 130.5, 83.9, 73.8, 57.3, 52.2, 46.9, 44.2, 36.5, 35.5, 31.1.

HRMS (ESI⁺) *m/z* calcd for C₁₂H₁₇O₃ [M+H]⁺ 208.1099, found 208.1108.

Synthesis of compound 23



Compound **22** (455 mg, 2.18 mmol, 1.0 equiv.) was dissolved in DMF (5.5 mL) and 2,6-dimethylpyridine (0.63 mL, 5.46 mmol, 2.5 equiv.) and TESOTf (0.74 mL,

3.28 mmol, 1.5 equiv.) were sequentially added at 0 °C for 30 min and the reaction was detected by TLC. After complete reaction detected by TLC, the reaction was quenched by addition of H₂O (5 mL) saturated NaHCO₃ aqueous solution (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 5 mL), the organic layers were combined, washed with saturated saline (5 mL), dried with anhydrous Na₂SO₄, then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 6/1) to afford colorless oily compound **23** (634 mg, 90%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 12/1).

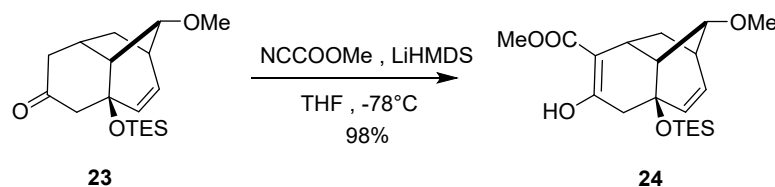
IR (film, KBr) ν_{max} : 3026, 1727, 1648 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 5.93 (ddd, *J* = 9.7, 6.8, 1.1 Hz, 1H), 5.56 (dd, *J* = 9.6, 1.5 Hz, 1H), 3.69 (d, *J* = 4.0 Hz, 1H), 3.39 (s, 3H), 2.84 – 2.45 (m, 7H), 2.13 (dd, *J* = 13.6, 2.2 Hz, 1H), 2.10 – 1.96 (m, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.7 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d) δ 208.5, 132.2, 130.0, 83.5, 76.1, 57.3, 55.9, 45.5, 44.2, 37.3, 35.6, 32.4, 7.1, 6.8.

HRMS (ESI⁺) *m/z* calcd for C₁₈H₃₁O₃Si [M+H]⁺ 322.1964, found 322.1956.

Synthesis of compound 24



Compound **23** (613 mg, 1.9 mmol, 1.0 equiv.) was dissolved in anhydrous THF (7.7 mL), LiHMDS (3.8 mL, 3.8 mmol, 2.0 equiv., 1M in THF) and methyl cyanocarbonate (226 μ L, 2.9 mmol, 1.5 equiv.) were added sequentially and stirred for 10 min at -78 °C. The reaction was fully detected by TLC and diluted with EtOAc (5 mL), H₂O (5 mL), saturated NH₄Cl aqueous solution (2.5 mL). The reaction was stirred at -78 °C for 10 min. After the reaction was complete by TLC, the reaction was diluted with EtOAc (5 mL) and quenched by the addition of H₂O (5 mL) and saturated NH₄Cl aqueous solution (2.5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 5 mL), the organic layers were combined, washed with saturated saline (10 mL), dried with anhydrous Na₂SO₄, then filtered, and the crude

product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 8/1) to afford colorless oily compound **24** (712 mg, 98%).

TLC: Rf = 0.5 (Petroleum ether/Ethyl acetate = 8/1).

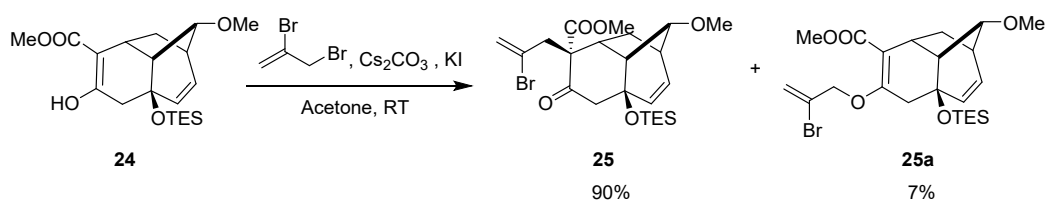
IR (film, KBr) ν_{max} : 3521, 3013, 1737, 1645 cm^{-1} .

^1H NMR (400 MHz, Chloroform- d) δ 11.91 (s, 1H), 5.88 (ddd, J = 9.7, 6.5, 1.2 Hz, 1H), 5.53 (dd, J = 9.7, 2.1 Hz, 1H), 3.74 (s, 3H), 3.65 (t, J = 4.0 Hz, 1H), 3.39 (s, 3H), 3.07 – 2.85 (m, 1H), 2.60 (dd, J = 17.4, 1.1 Hz, 1H), 2.53 (dd, J = 6.2, 3.7 Hz, 1H), 2.48 (ddt, J = 6.2, 4.9, 1.8 Hz, 1H), 2.43 (d, J = 17.5 Hz, 1H), 2.07 (ddd, J = 12.7, 10.5, 6.0 Hz, 1H), 1.11 (dd, J = 12.8, 4.0 Hz, 1H), 0.96 (t, J = 7.9 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 172.4, 167.8, 132.3, 129.7, 101.4, 83.5, 71.6, 57.4, 51.5, 44.1, 43.0, 37.8, 36.2, 31.8, 7.1, 6.8.

HRMS (ESI $^+$) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{O}_5\text{Si}$ [$\text{M}+\text{H}$] $^+$ 380.2019, found 380.2035.

Synthesis of compound **25** and **25a**



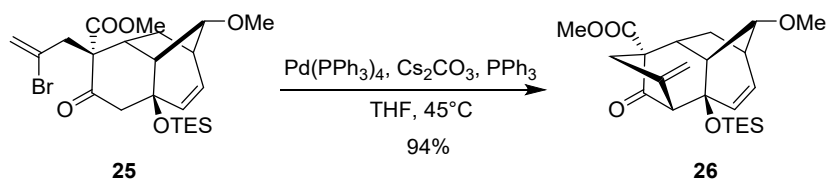
Compound **24** (712 mg, 1.87 mmol, 1.0 equiv.) was dissolved in anhydrous acetone (13 mL), and Cs_2CO_3 (1.22 g, 3.74 mmol, 2.0 equiv.) was added sequentially with KI (621 mg, 3.74 mmol, 2.0 equiv.) and 2,3-dibromo-1-propene (305 μL , 2.80 mmol, 1.5 equiv., 90%) at room temperature and stirred for 4 h. After the reaction was complete by TLC, the reaction was diluted with the addition of EtOAc (10 mL) and quenched by the addition of H_2O (10 mL) and saturated NaHCO_3 aqueous solution (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×5 mL), the organic layers were combined, washed with saturated saline (10 mL), dried with anhydrous Na_2SO_4 , then filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 8/1) to afford colorless oily compounds **25** (841 mg, 90%) and **25a** (50 mg, 7%).

For **25**: **^1H NMR** (400 MHz, Chloroform- d) δ 5.95 (dd, J = 8.8, 6.6 Hz, 1H), 5.67 (d, J = 2.1 Hz, 1H), 5.60 (d, J = 2.1 Hz, 1H), 5.54 (dd, J = 9.6, 1.8 Hz, 1H), 3.71 (s,

3H), 3.68 (t, $J = 4.2$ Hz, 1H), 3.38 (s, 2H), 3.37 (s, 3H), 3.09 (d, $J = 12.5$ Hz, 1H), 2.90 (dt, $J = 10.7, 6.5$ Hz, 1H), 2.86 – 2.82 (m, 1H), 2.55 (d, $J = 6.8$ Hz, 1H), 2.51 (d, $J = 12.5$ Hz, 1H), 2.11 (ddd, $J = 14.0, 10.8, 7.0$ Hz, 1H), 1.13 (dd, $J = 13.9, 7.0$ Hz, 1H), 0.96 (t, $J = 7.9$ Hz, 9H), 0.63 (q, $J = 8.2$ Hz, 6H); ^{13}C NMR (101 MHz, Chloroform- d) δ 202.3, 169.9, 132.3, 130.4, 126.5, 121.6, 82.2, 76.4, 63.1, 57.2, 52.9, 51.8, 47.4, 44.2, 40.9, 36.0, 32.9, 7.1, 6.7; HRMS (ESI $^{+}$) m/z calcd for $\text{C}_{23}\text{H}_{37}\text{BrO}_5\text{Si}$ $[\text{M}+\text{H}]^{+}$ 498.1437, found 498.1450. TLC: $R_f = 0.5$ (Petroleum ether/Ethyl acetate = 12/1); IR (film, KBr) ν_{max} : 3026, 1737, 1721, 1642, 1608 cm^{-1} .

For **25a**: ^1H NMR (400 MHz, Chloroform- d) δ 6.05 (q, $J = 1.8$ Hz, 1H), 5.89 (ddd, $J = 9.6, 6.5, 1.2$ Hz, 1H), 5.65 (q, $J = 1.4$ Hz, 1H), 5.47 (dd, $J = 9.6, 2.1$ Hz, 1H), 4.44 (d, $J = 1.4$ Hz, 1H), 3.71 (s, 3H), 3.65 (t, $J = 4.3$ Hz, 1H), 3.38 (s, 3H), 3.14 (t, $J = 10.6$ Hz, 1H), 2.60 – 2.41 (m, 5H), 2.04 (ddd, $J = 12.7, 10.7, 5.9$ Hz, 1H), 1.30 (dd, $J = 6.4, 3.8$ Hz, 1H), 1.13 (dd, $J = 12.7, 4.0$ Hz, 1H), 0.97 (t, $J = 7.9$ Hz, 9H), 0.64 (q, $J = 7.6$ Hz, 6H); HRMS (ESI $^{+}$) m/z calcd for $\text{C}_{23}\text{H}_{37}\text{BrO}_5\text{Si}$ $[\text{M}+\text{H}]^{+}$ 498.1437, found 498.1462. TLC: $R_f = 0.45$ (Petroleum ether/Ethyl acetate = 12/1); IR (film, KBr) ν_{max} : 3023, 1737, 1645, 1621 cm^{-1} .

Synthesis of compound 26



Compound **25** (350 mg, 0.70 mmol, 1.0 equiv.) was dissolved in anhydrous THF (17.5 mL), and Cs_2CO_3 (1.23 g, 3.50 mmol, 5.0 equiv.) and PPh_3 (184 mg, 0.70 mmol, 1.0 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (81 mg, 0.07 mmol, 0.1 equiv.) were added in turn at room temperature. (162 mg, 0.14 mmol, 0.2 equiv.), the reaction system was protected by substitution of argon at 0 °C and then warmed up to 45 °C for 32 h. After the reaction was complete as detected by TLC, the reaction was diluted by addition of EtOAc (10 mL) and quenched by the addition of H_2O (10 mL) saturated with an aqueous solution of NaHCO_3 (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×5 mL), the organic layers were combined, washed with saturated saline (10 mL), dried with anhydrous Na_2SO_4 , filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by

silica gel column chromatography (PE/EtOAc = 10/1) to afford colorless oily compound **26** (275 mg, 94%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 8/1).

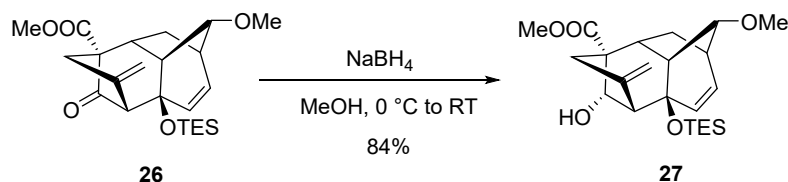
IR (film, KBr) ν_{max} : 3027, 1740, 1713, 1634, 1611 cm⁻¹.

¹H NMR (400 MHz, Chloroform-d) δ 5.93 (ddd, *J* = 9.7, 6.9, 1.1 Hz, 1H), 5.71 (dd, *J* = 9.7, 1.8 Hz, 1H), 5.23 – 5.18 (m, 1H), 5.13 (d, *J* = 2.6 Hz, 1H), 3.72 (s, 3H), 3.64 (td, *J* = 4.2, 1.1 Hz, 1H), 3.31 (s, 3H), 3.13 (dt, *J* = 16.8, 2.7 Hz, 1H), 2.80 (s, 1H), 2.69 – 2.65 (m, 1H), 2.63 – 2.49 (m, 1H), 2.10 (ddd, *J* = 14.1, 10.7, 6.7 Hz, 1H), 1.26 (td, *J* = 10.5, 9.8, 5.5 Hz, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.67 (td, *J* = 8.0, 6.8 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d) δ 205.4, 171.1, 136.3, 132.0, 129.6, 112.4, 81.9, 80.5, 65.5, 61.2, 57.1, 52.2, 43.7, 43.2, 40.1, 36.8, 33.1, 7.3, 6.8.

HRMS (ESI⁺) *m/z* calcd for C₂₃H₃₅O₅Si [M+H]⁺ 418.2176, found 418.2188.

Synthesis of compound 27



Compound **26** (57 mg, 0.14 mmol, 1.0 equiv.) was dissolved in MeOH (1 mL), NaBH₄ (7.7 mg, 0.2 mmol, 1.5 equiv.) was added at 0 °C and stirred at room temperature for 10 min. The reaction was completely detected by TLC, then quenched with H₂O (1 mL) and saturated NH₄Cl (1 mL) at 0 °C. The organic layer was extracted with DCM (3 × 1 mL), washed with saturated saline (3 mL), dried, filtered, and the product was obtained by subtraction. The reaction was extracted with DCM (3 × 1 mL), the organic layers were combined, washed with saturated saline (3 mL), dried with anhydrous Na₂SO₄, filtered and the crude product was obtained by distillation under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford the colorless oily compound **27** (48 mg, 84%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 2/1).

IR (film, KBr) ν_{max} : 3362, 3029, 1741, 1641, 1619 cm⁻¹.

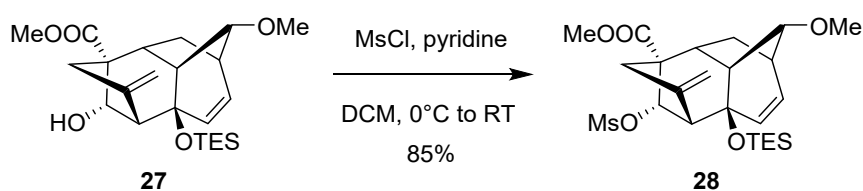
¹H NMR (400 MHz, Chloroform-d) δ 6.15 – 6.06 (m, 2H), 5.14 (s, 1H), 4.97 (s, 1H), 4.31 (ddd, *J* = 10.1, 5.0, 1.7 Hz, 1H), 3.72 (s, 3H), 3.55 (t, *J* = 4.2 Hz, 1H), 3.32 (s, 3H), 2.72 (d, *J* = 5.0 Hz, 1H), 2.66 (dd, *J* = 6.3, 4.3 Hz, 1H), 2.63 – 2.58 (m, 1H),

2.56 (t, $J = 2.7$ Hz, 1H), 2.45 – 2.40 (m, 1H), 2.30 (dt, $J = 16.6, 2.2$ Hz, 1H), 2.07 (ddd, $J = 14.1, 11.3, 6.5$ Hz, 1H), 1.89 (dd, $J = 14.0, 5.8$ Hz, 1H), 0.97 (t, $J = 7.9$ Hz, 9H), 0.72 – 0.62 (m, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 175.1, 141.2, 134.5, 132.8, 111.5, 82.4, 78.0, 73.0, 57.1, 55.6, 52.0, 51.5, 42.5, 41.8, 39.4, 37.7, 32.5, 7.4, 7.1.

HRMS (ESI $^{+}$) m/z calcd for $\text{C}_{23}\text{H}_{37}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^{+}$ 420.2332, found 420.2327.

Synthesis of compound 28



Compound **27** (142 mg, 0.34 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (1.7 mL), and at 0 °C, MsCl (523 μL , 6.77 mmol, 20 equiv.) and pyridine (1.36 mL, 16.92 mmol, 50 equiv.) were added sequentially. The mixture was stirred at room temperature for 50 minutes. After the reaction was confirmed complete by TLC, EtOAc (2 mL) was added to dilute the mixture. Then, H_2O (2 mL) and saturated NH_4Cl aqueous solution (2 mL) were added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×1 mL). The combined organic layers were washed with saturated brine (2 mL), dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure to obtain the crude product. The crude product was purified by silica gel column chromatography (PE/EtOAc = 6/1) to afford compound **28** as a colorless oil (146 mg, 85%).

TLC: $R_f = 0.5$ (Petroleum ether/Ethyl acetate = 4/1).

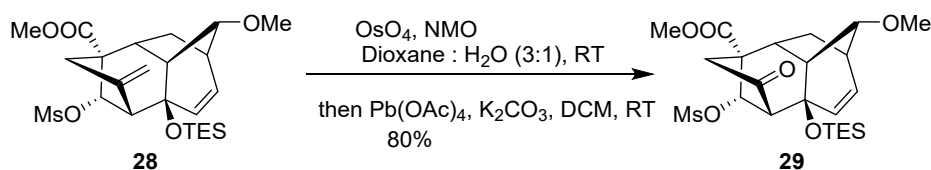
IR (film, KBr) ν_{max} : 3022, 1736, 1642, 1613 cm^{-1} .

^1H NMR (600 MHz, Chloroform- d) δ 6.00 – 5.75 (m, 1H), 5.21 (s, 1H), 5.05 (s, 1H), 4.89 (d, $J = 5.1$ Hz, 1H), 3.73 (s, 1H), 3.52 (t, $J = 4.1$ Hz, 1H), 3.32 (s, 3H), 3.02 (d, $J = 5.1$ Hz, 1H), 3.00 (s, 3H), 2.61 (dt, $J = 15.5, 5.2$ Hz, 2H), 2.54 (d, $J = 16.4$ Hz, 1H), 2.43 (d, $J = 16.6$ Hz, 1H), 2.41 – 2.38 (m, 1H), 1.89 (ddd, $J = 13.4, 11.2, 6.4$ Hz, 1H), 1.74 (dd, $J = 13.3, 5.8$ Hz, 1H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.71 – 0.65 (m, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 173.5, 138.9, 132.4, 129.2, 113.3, 82.3, 81.7, 73.0, 57.1, 54.7, 52.2, 50.8, 42.3, 41.1, 39.8, 37.5, 37.5, 31.4, 7.4, 7.0.

HRMS (ESI $^{+}$) m/z calcd for $\text{C}_{24}\text{H}_{38}\text{O}_7\text{SSi}$ $[\text{M}+\text{H}]^{+}$ 499.2108, found 499.2103.

Synthesis of compound 29



Compound **28** (20 mg, 0.04 mmol, 1.0 equiv.) was dissolved in a mixed solvent of dioxane and water (1 mL, dioxane: water = 3:1). NMO (23.5 mg, 0.2 mmol, 5 equiv.) and OsO₄ (5.1 mg, 0.02 mmol, 0.5 equiv.) were added sequentially at room temperature and stirred for 1 hour. After TLC indicated complete reaction, the mixture was diluted with EtOAc (1 mL), followed by the addition of water (1 mL) and saturated NH₄Cl solution (1 mL) to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with saturated brine (3 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give a crude product.

The crude product was dissolved in DCM (1 mL), and Pb(OAc)₄ (88 mg, 0.2 mmol, 5 equiv.) and K₂CO₃ (65 mg, 0.4 mmol, 10 equiv.) were sequentially added at room temperature and stirred for 30 minutes. After TLC indicated complete reaction, the mixture was diluted with EtOAc (1 mL), followed by the addition of water (1 mL) and saturated NH₄Cl solution (1 mL) to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with saturated brine (2 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give a crude product. The crude product was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain the colorless oily compound **29** (16 mg, 80%).

TLC: R_f = 0.5 (Petroleum ether/Ethyl acetate = 1/1).

IR (film, KBr) ν_{max} : 3025, 1741, 1714, 1642, 1615 cm⁻¹.

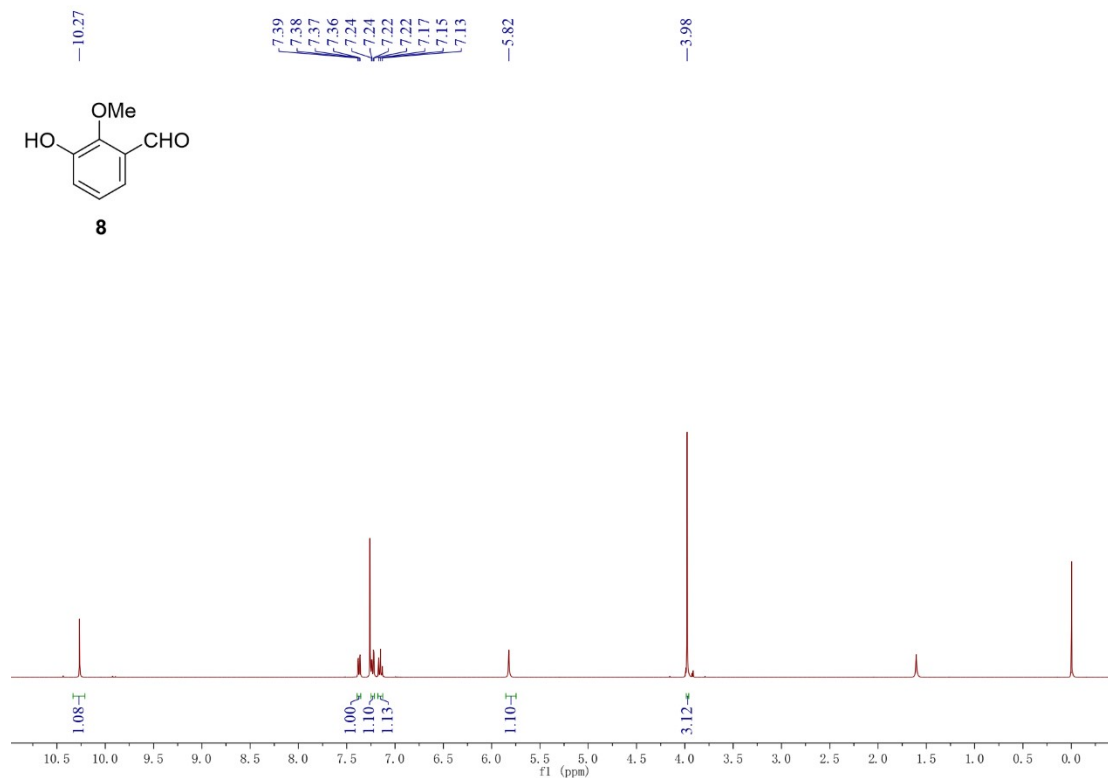
¹H NMR (600 MHz, Chloroform-*d*) δ 6.04 – 5.90 (m, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 5.11 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.59 (t, *J* = 4.1 Hz, 1H), 3.33 (s, 3H), 3.04 (s, 3H), 2.97 (d, *J* = 5.2 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.64 (q, *J* = 5.9 Hz, 1H), 2.57 – 2.33 (m, 3H), 1.97 (ddd, *J* = 13.5, 11.1, 6.2 Hz, 1H), 1.91 (dd, *J* = 13.5, 6.0 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.78 – 0.60 (m, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 204.1, 172.2, 131.2, 130.0, 81.7, 79.5, 73.6, 59.1, 57.2, 52.7, 50.3, 49.8, 43.2, 39.6, 37.7, 37.6, 30.5, 7.0, 6.7.

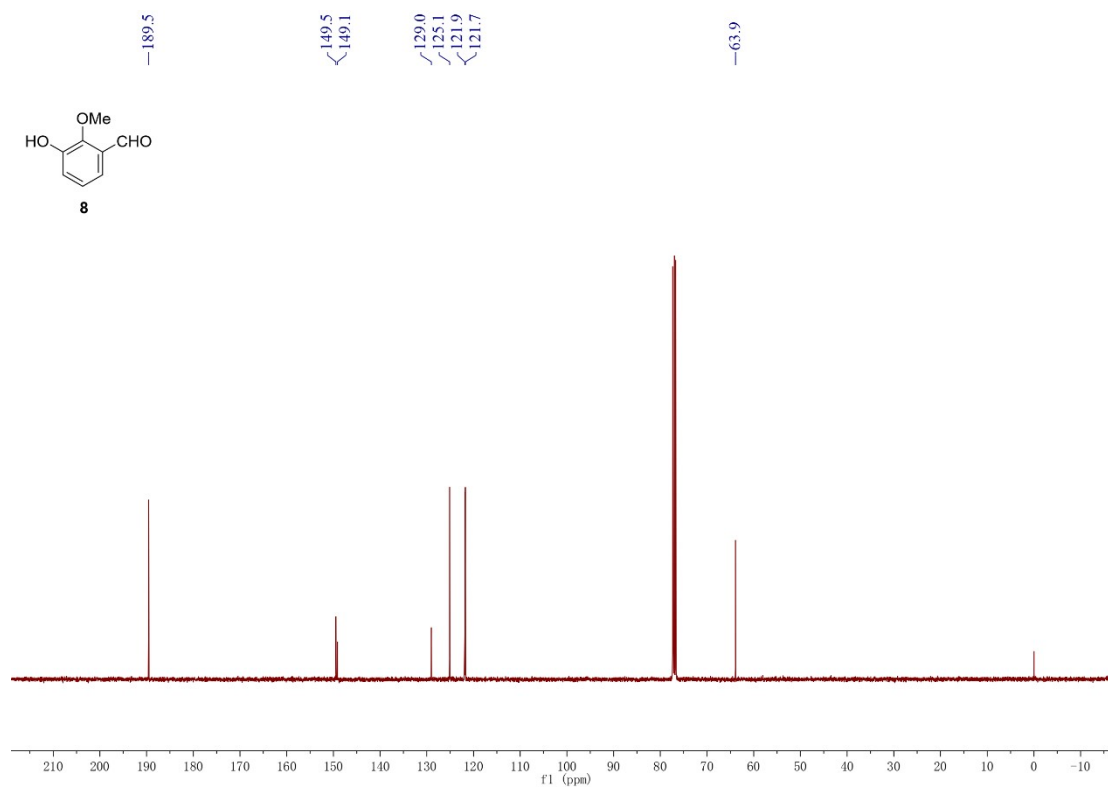
HRMS (ESI⁺) m/z calcd for C₂₃H₃₆O₈SSi [M+H]⁺ 501.1900, found 501.1890.

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

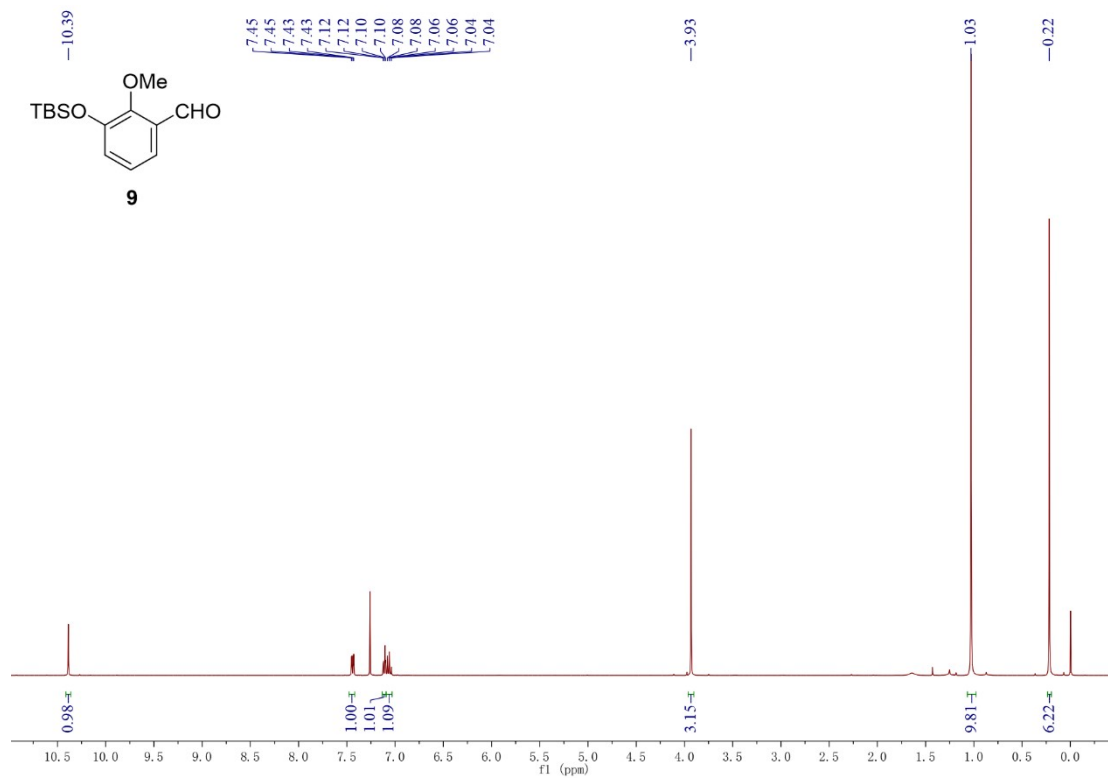
^1H NMR Spectrum of 8 (400 MHz, CDCl_3)



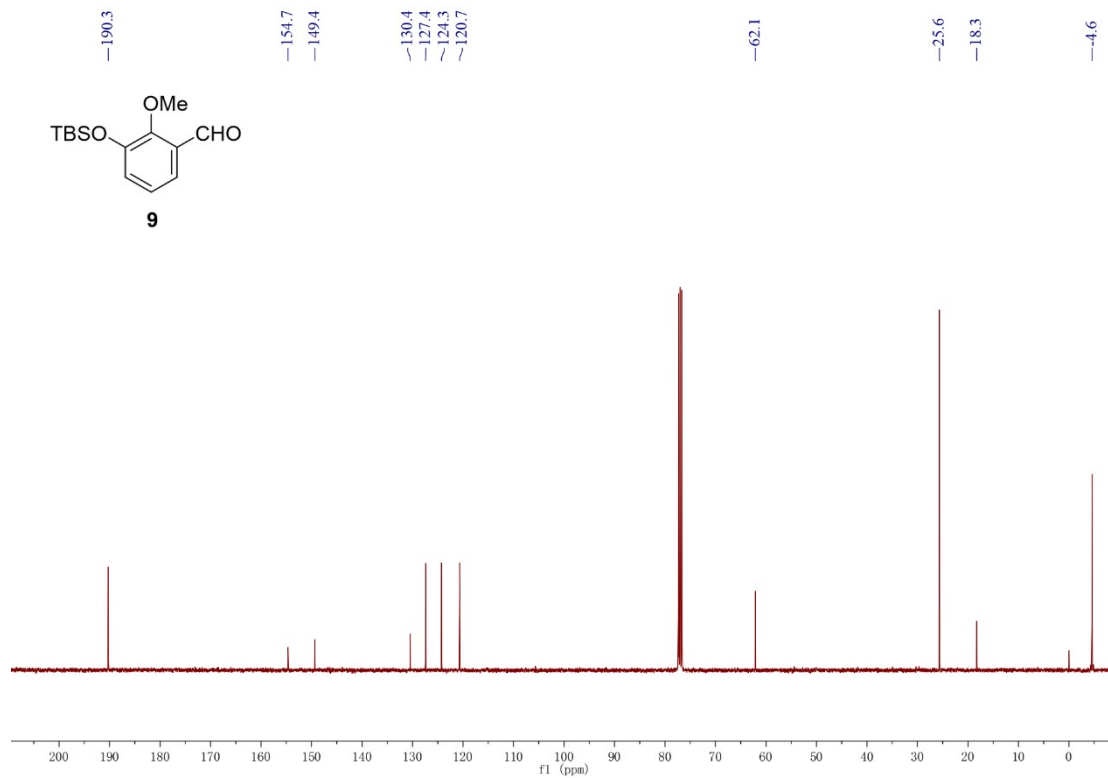
^{13}C NMR Spectrum of 8 (100 MHz, CDCl_3)



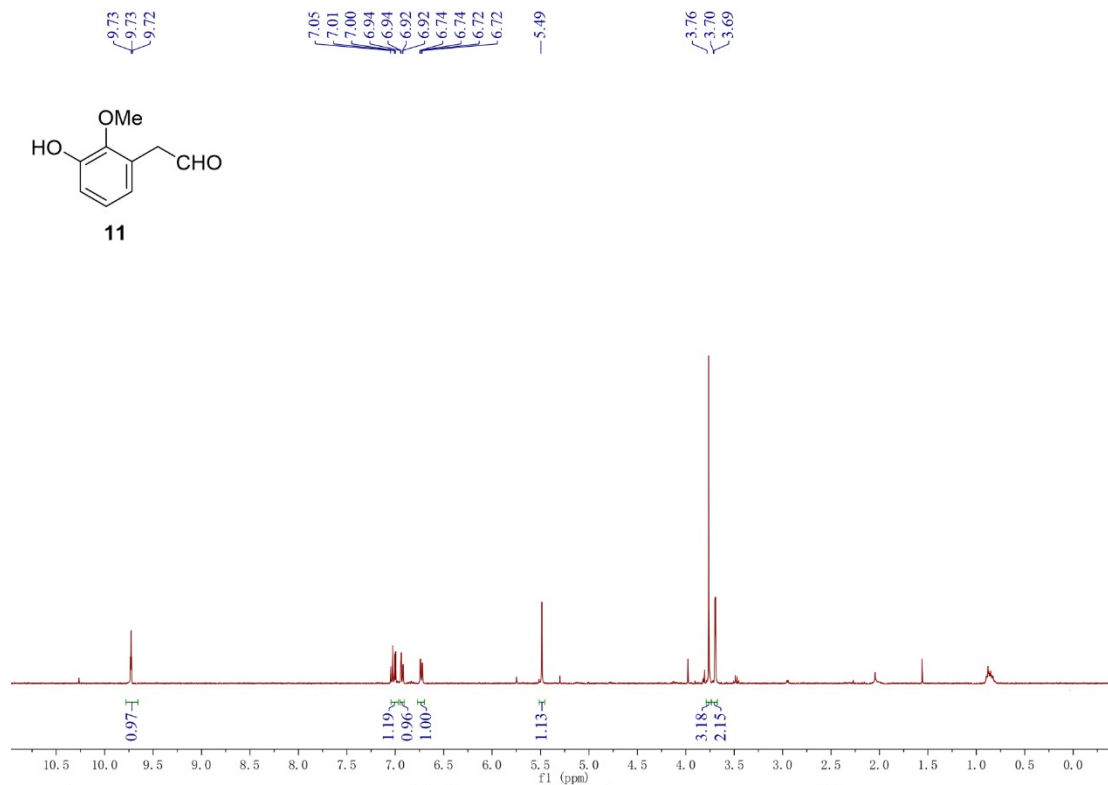
¹H NMR Spectrum of 9 (400 MHz, CDCl₃)



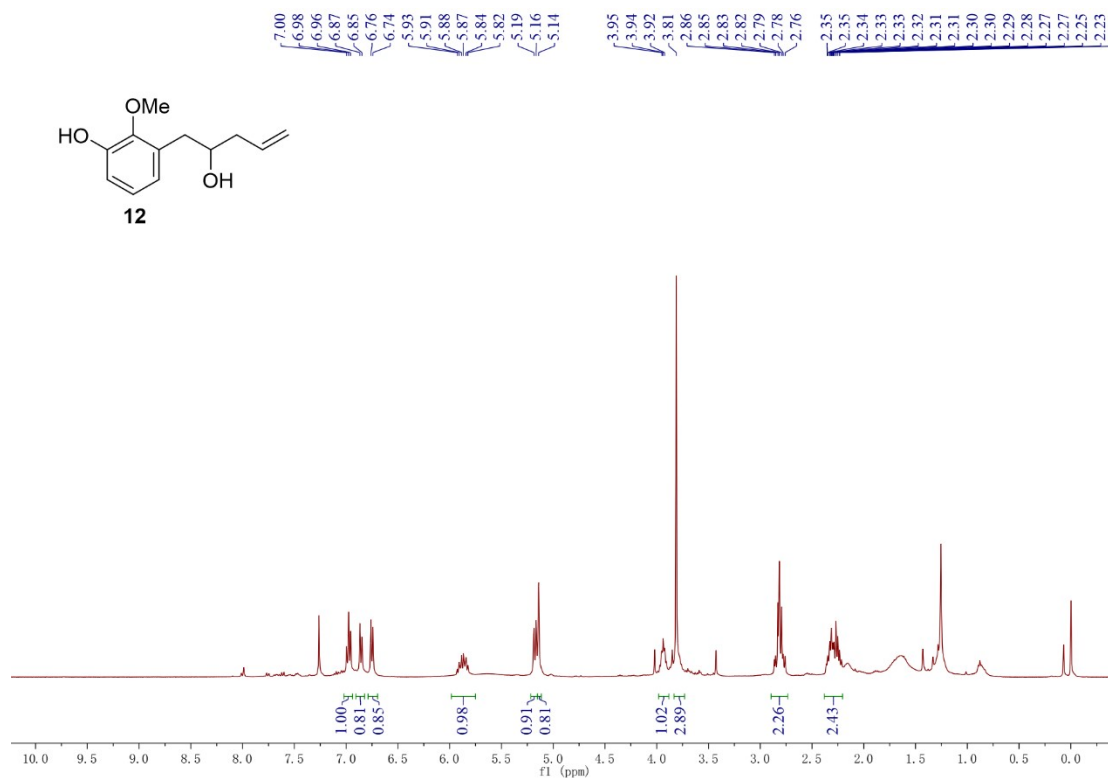
¹³C NMR Spectrum of 9 (100 MHz, CDCl₃)



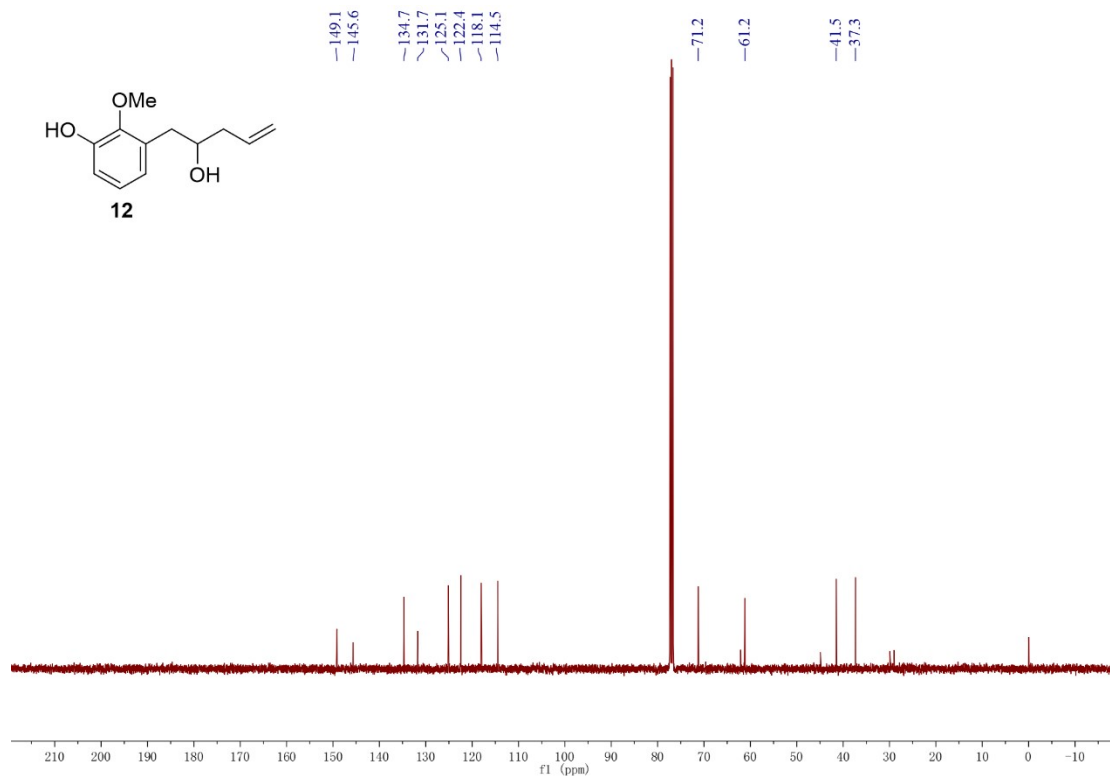
¹H NMR Spectrum of 11 (400 MHz, CDCl₃)



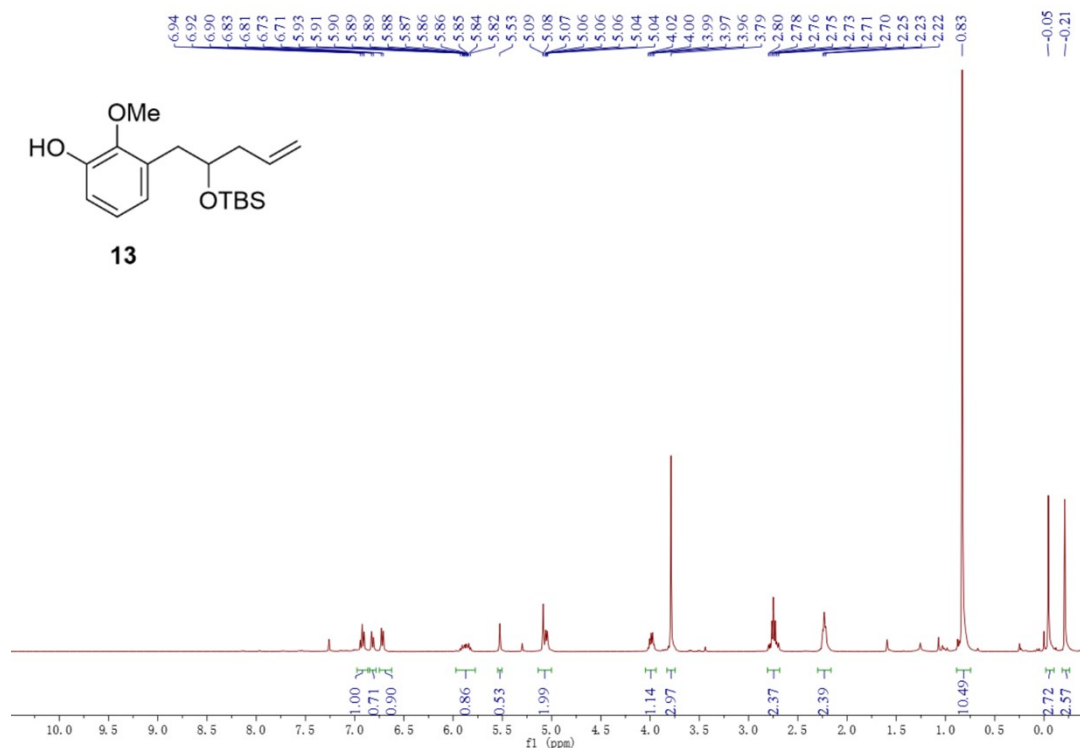
¹H NMR Spectrum of 12 (400 MHz, CDCl₃)



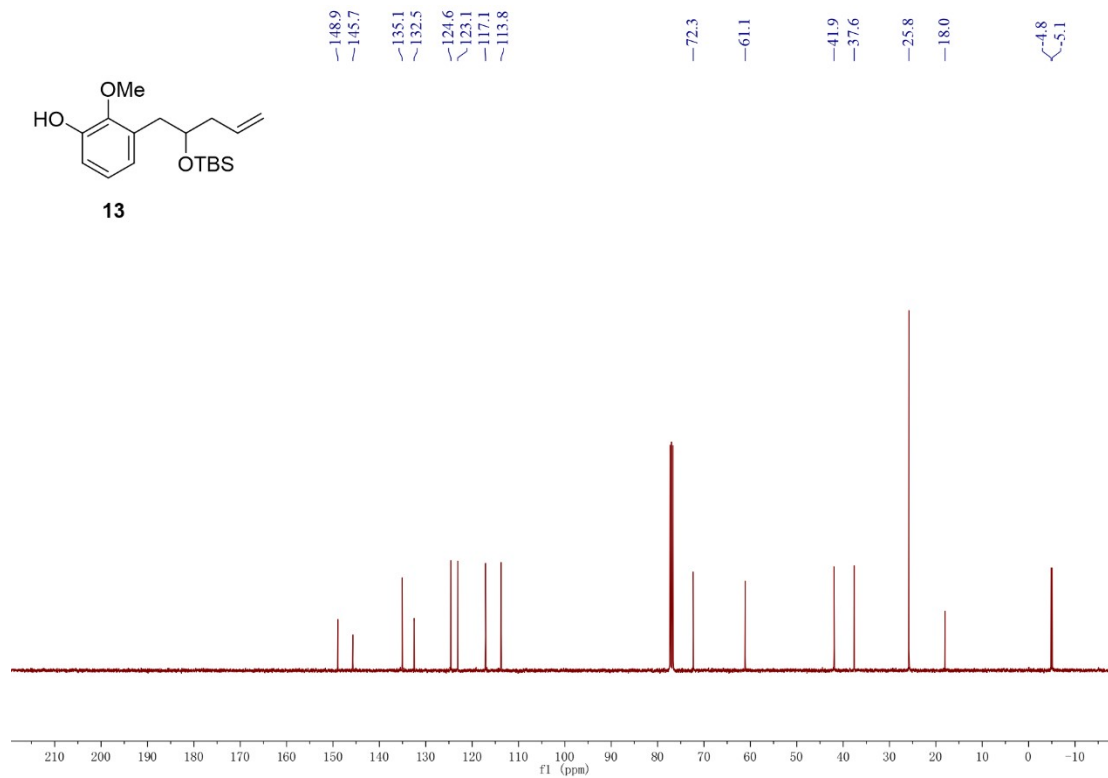
¹³C NMR Spectrum of 12 (100 MHz, CDCl₃)



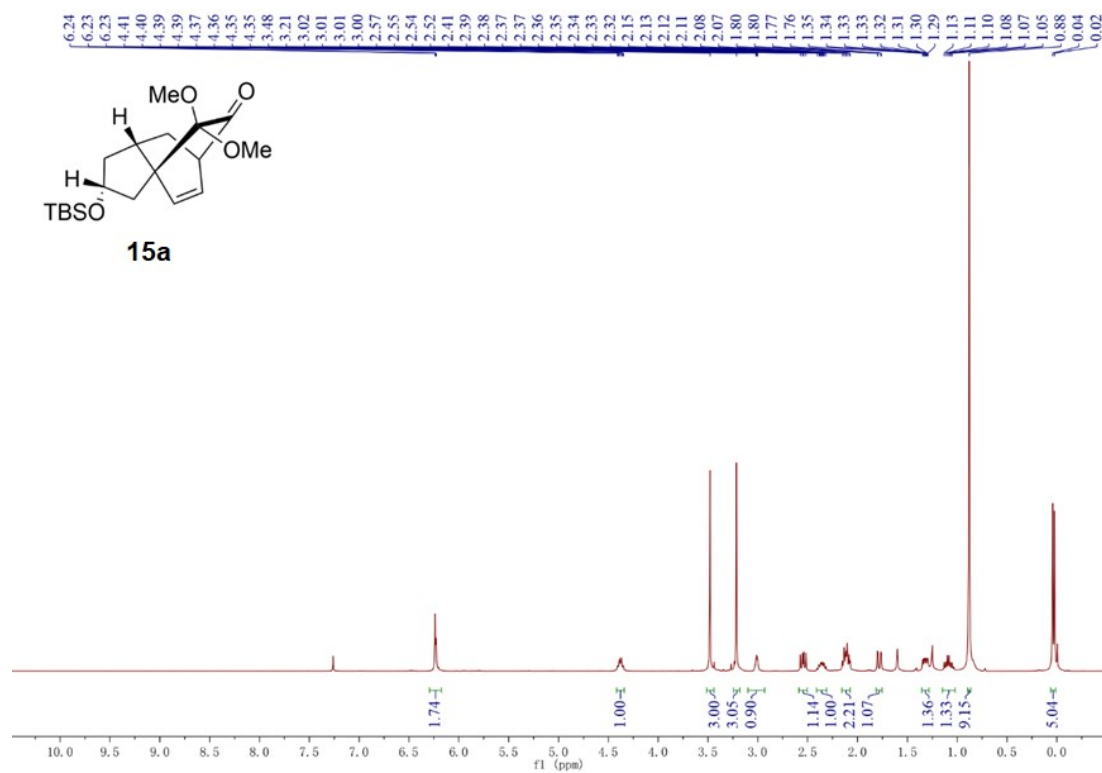
¹H NMR Spectrum of 13 (400 MHz, CDCl₃)



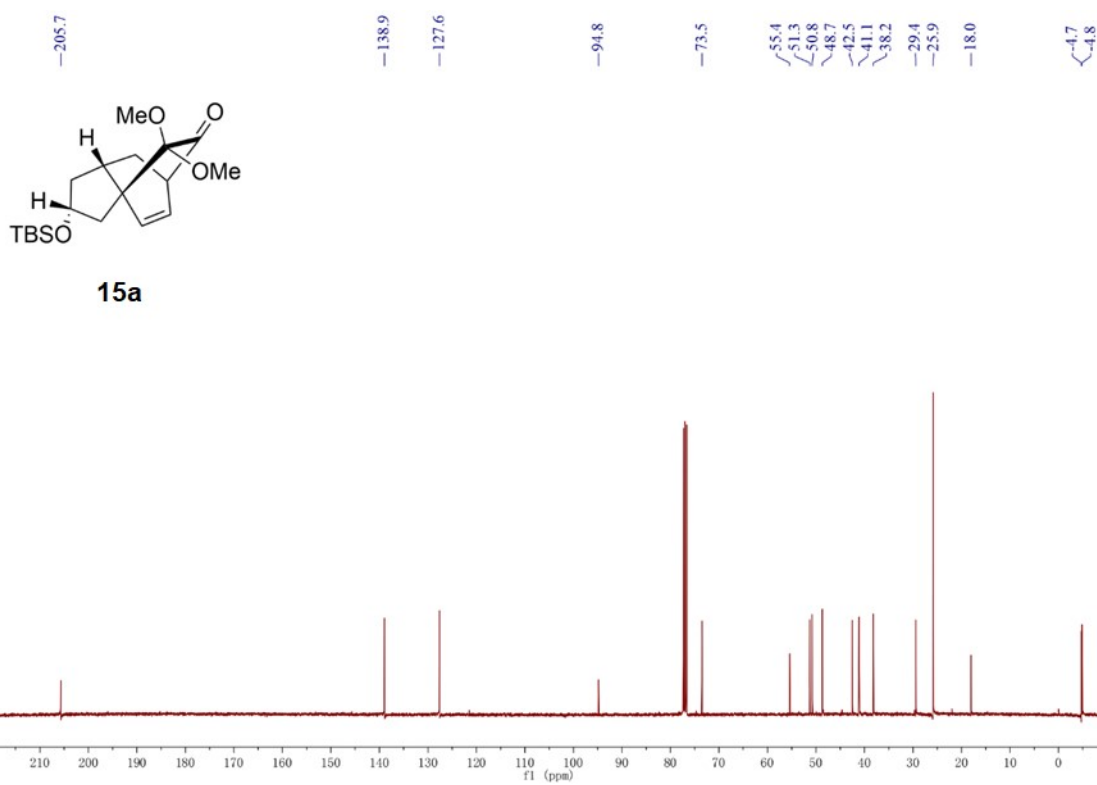
¹³C NMR Spectrum of 13 (100 MHz, CDCl₃)



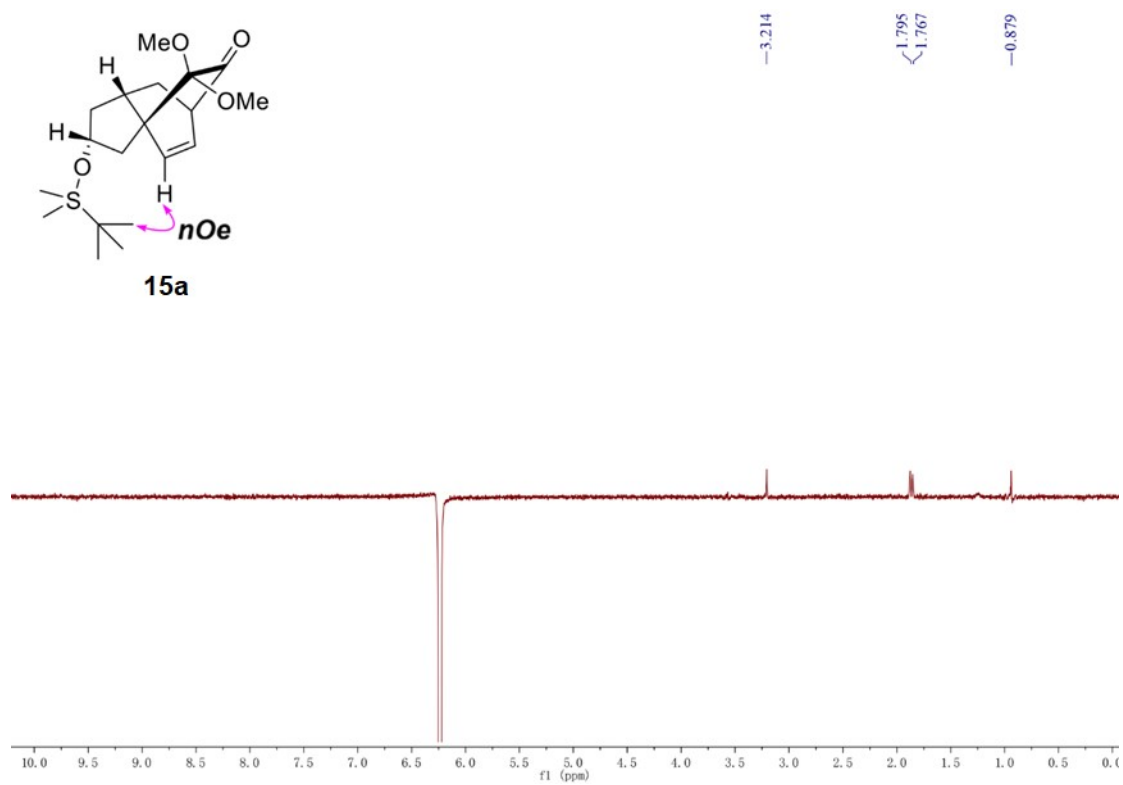
¹H NMR Spectrum of 15a (400 MHz, CDCl₃)



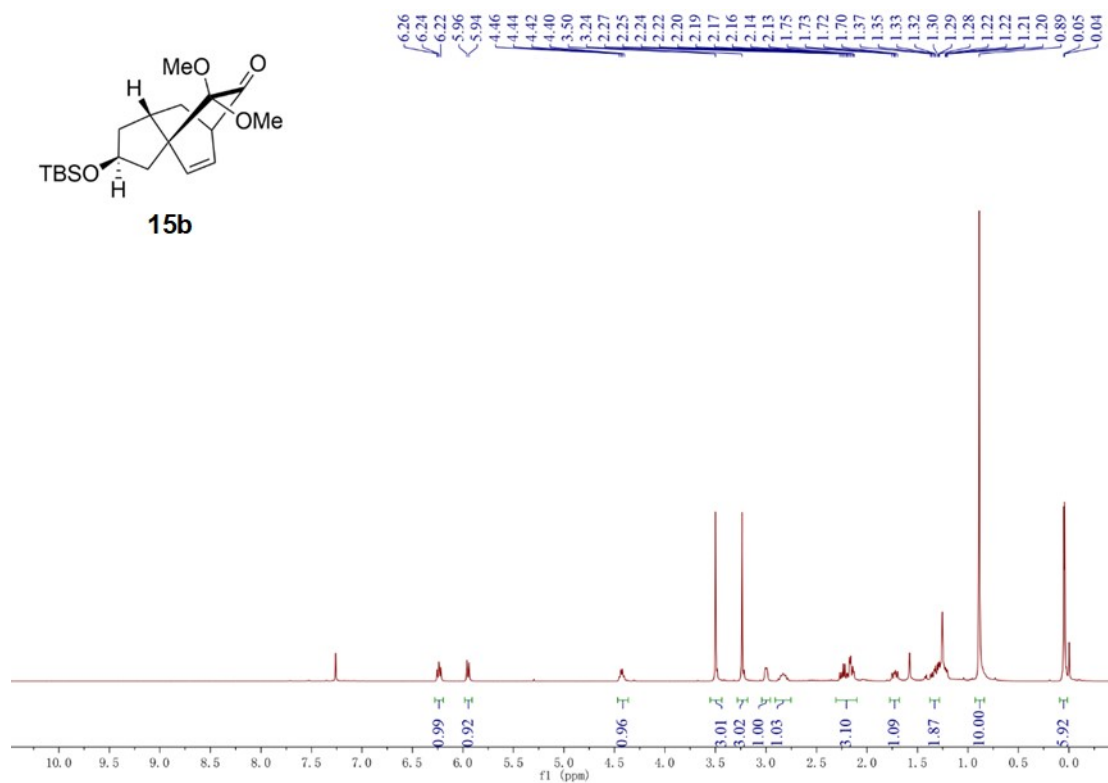
^{13}C NMR Spectrum of 15a (100 MHz, CDCl_3)



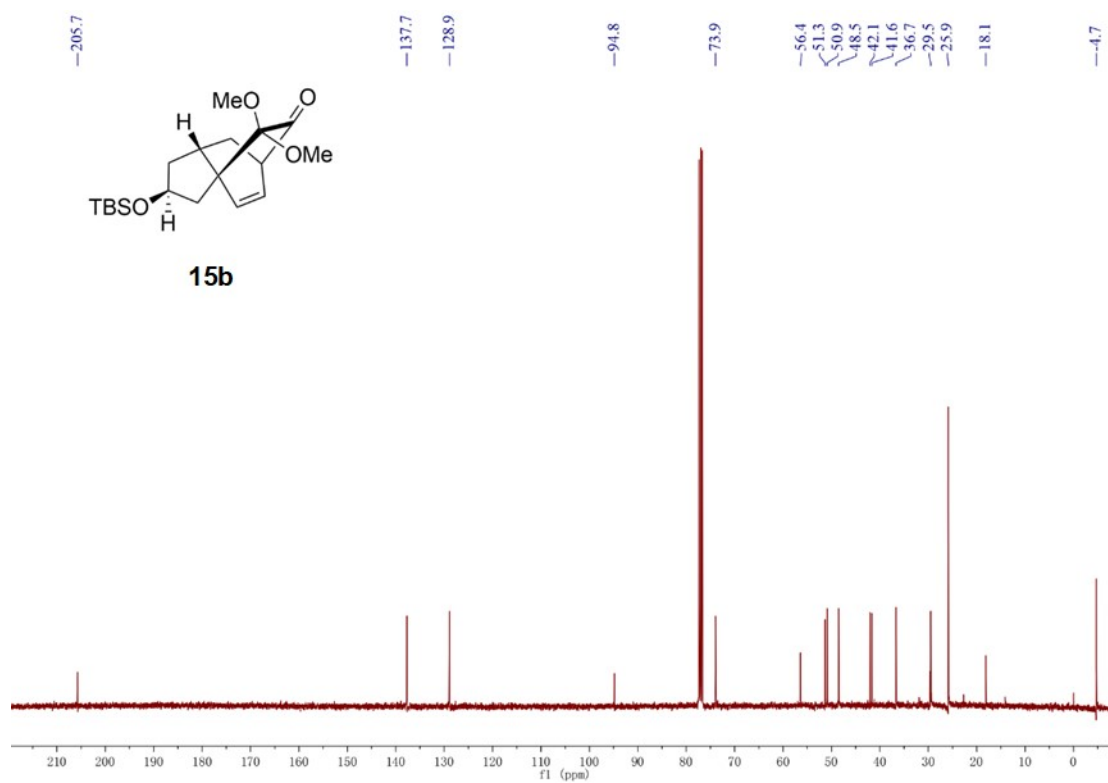
NOEDS Spectrum of 15a (400 MHz, CDCl_3)



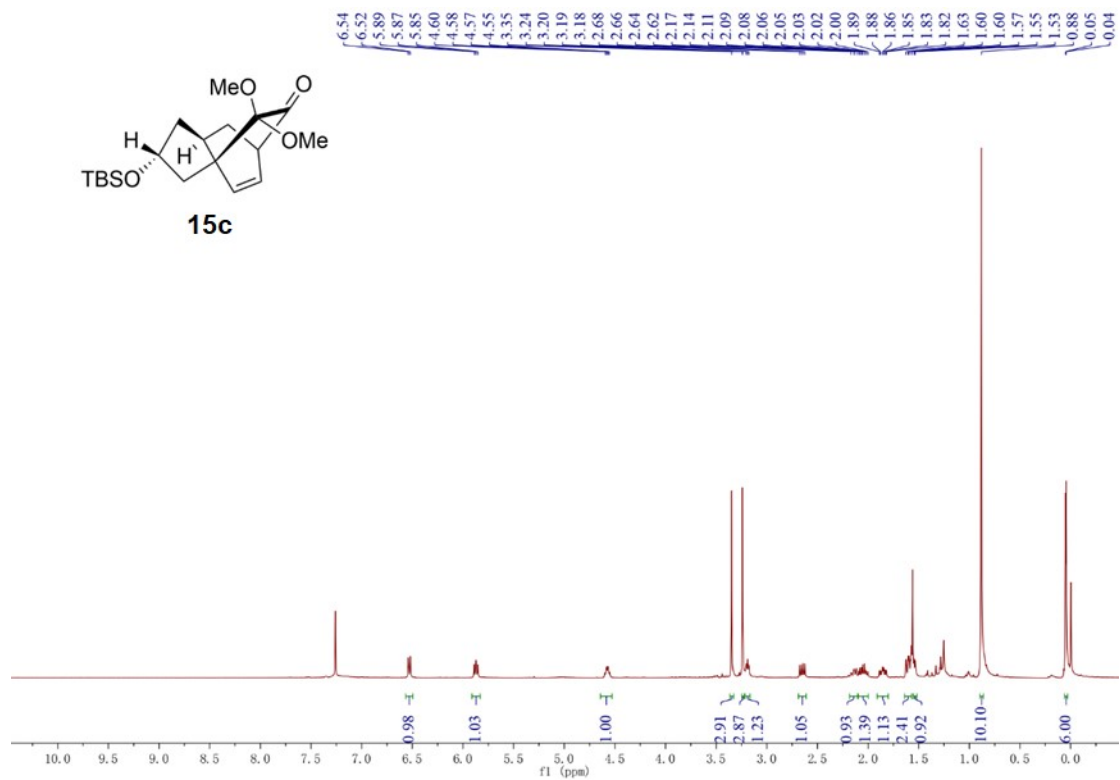
¹H NMR Spectrum of 15b (400 MHz, CDCl₃)



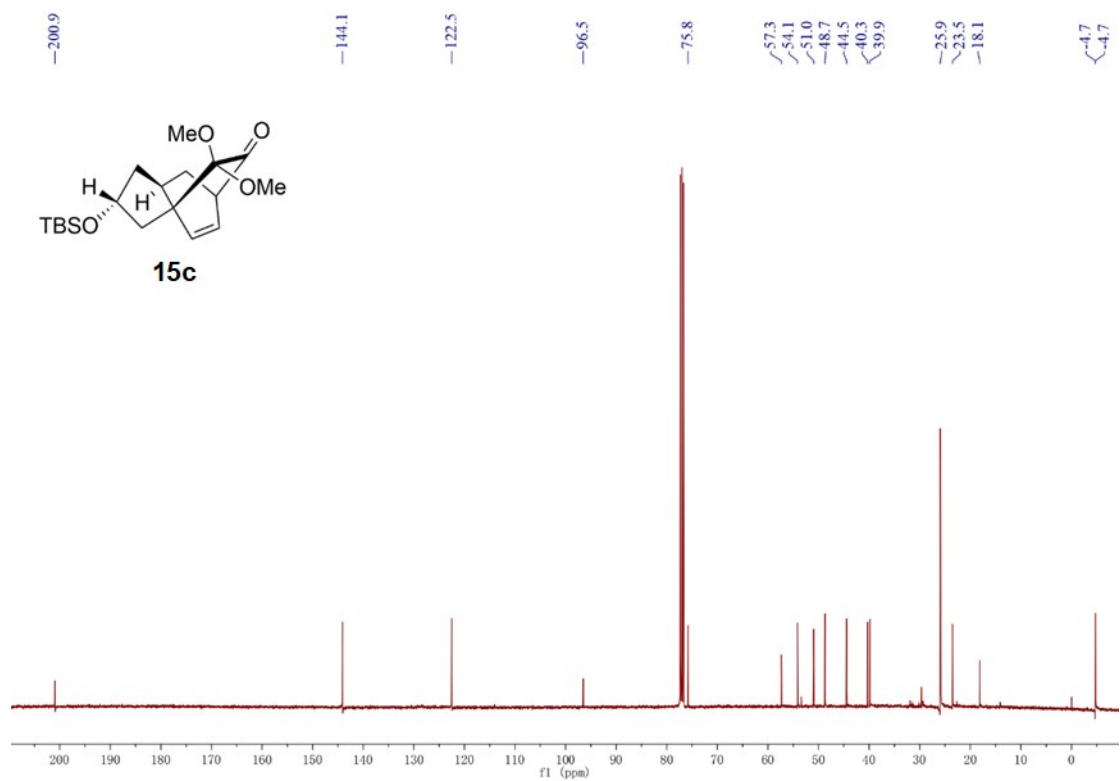
¹³C NMR Spectrum of 15b (100 MHz, CDCl₃)



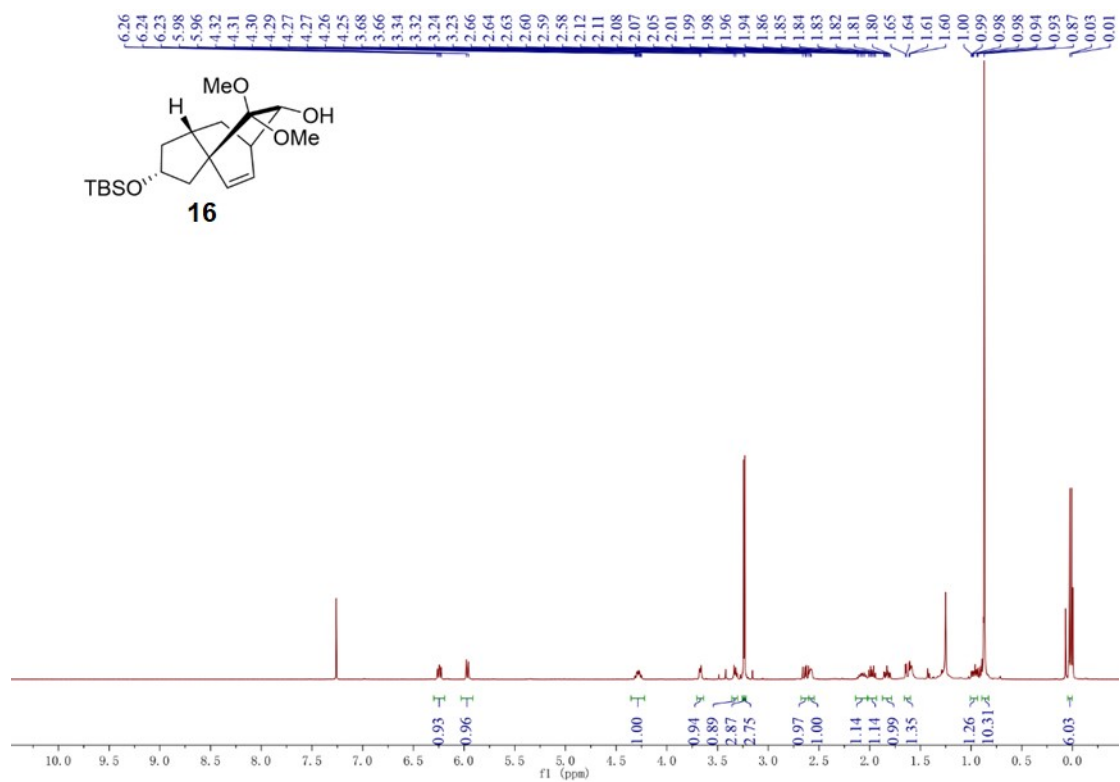
¹H NMR Spectrum of 15c (400 MHz, CDCl₃)



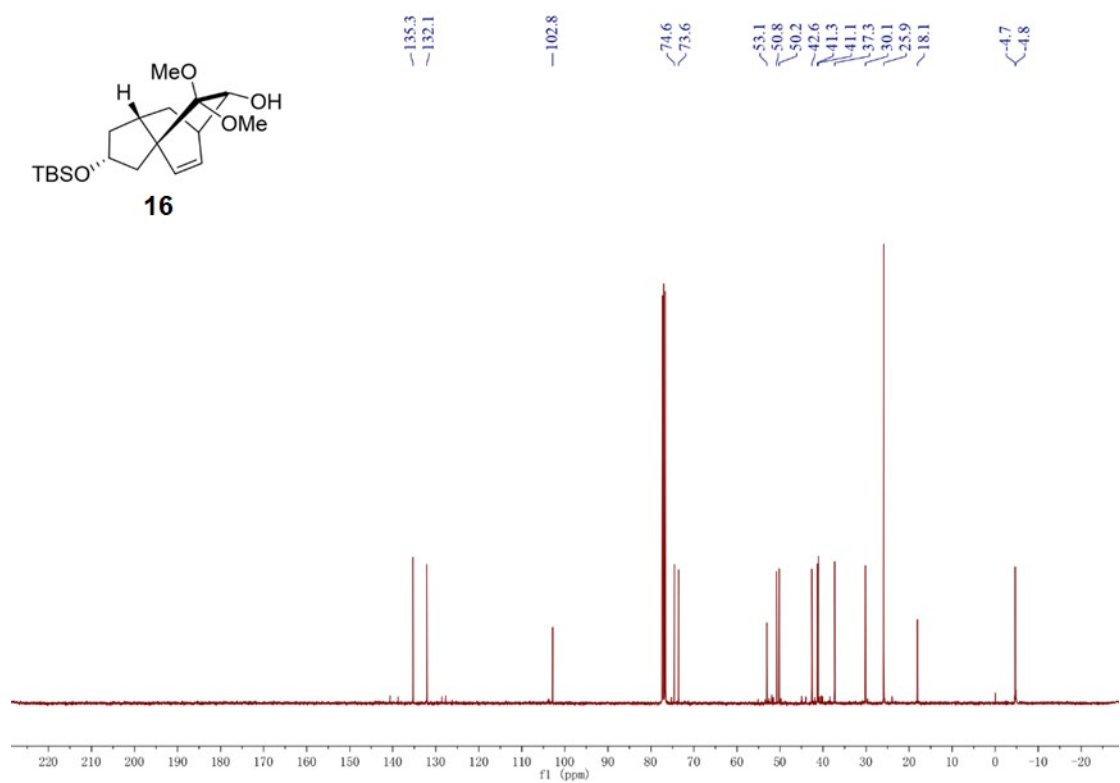
¹³C NMR Spectrum of 15c (100 MHz, CDCl₃)



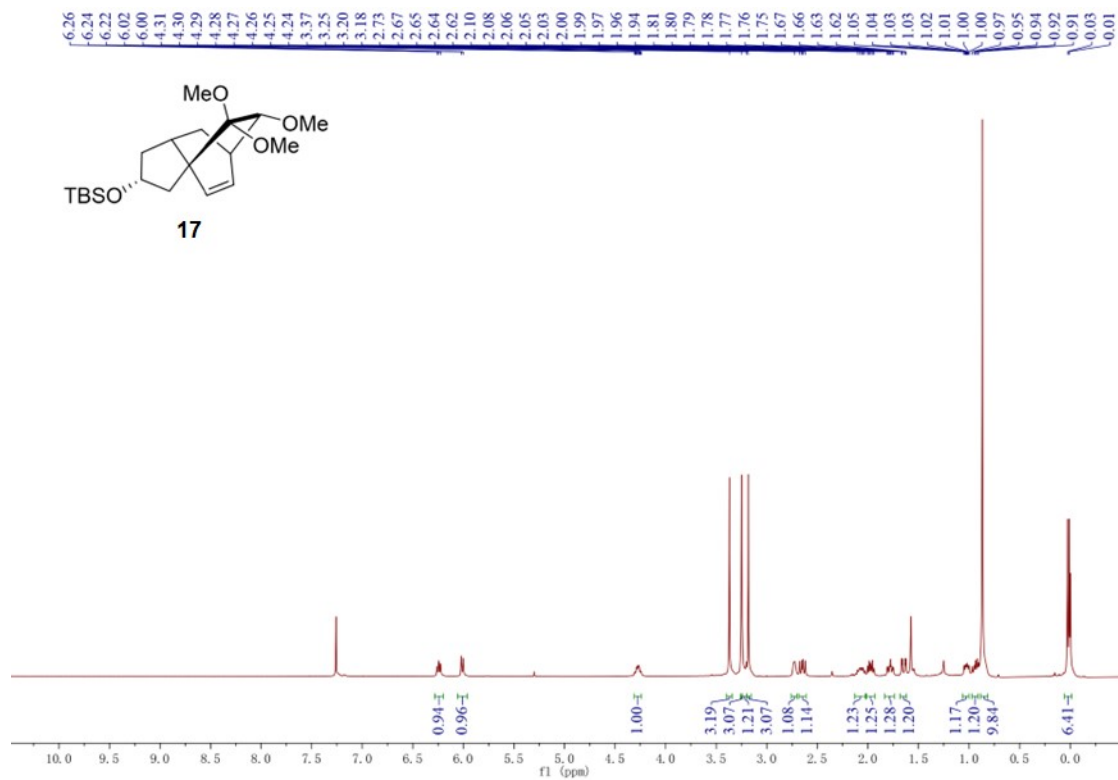
¹H NMR Spectrum of 16 (400 MHz, CDCl₃)



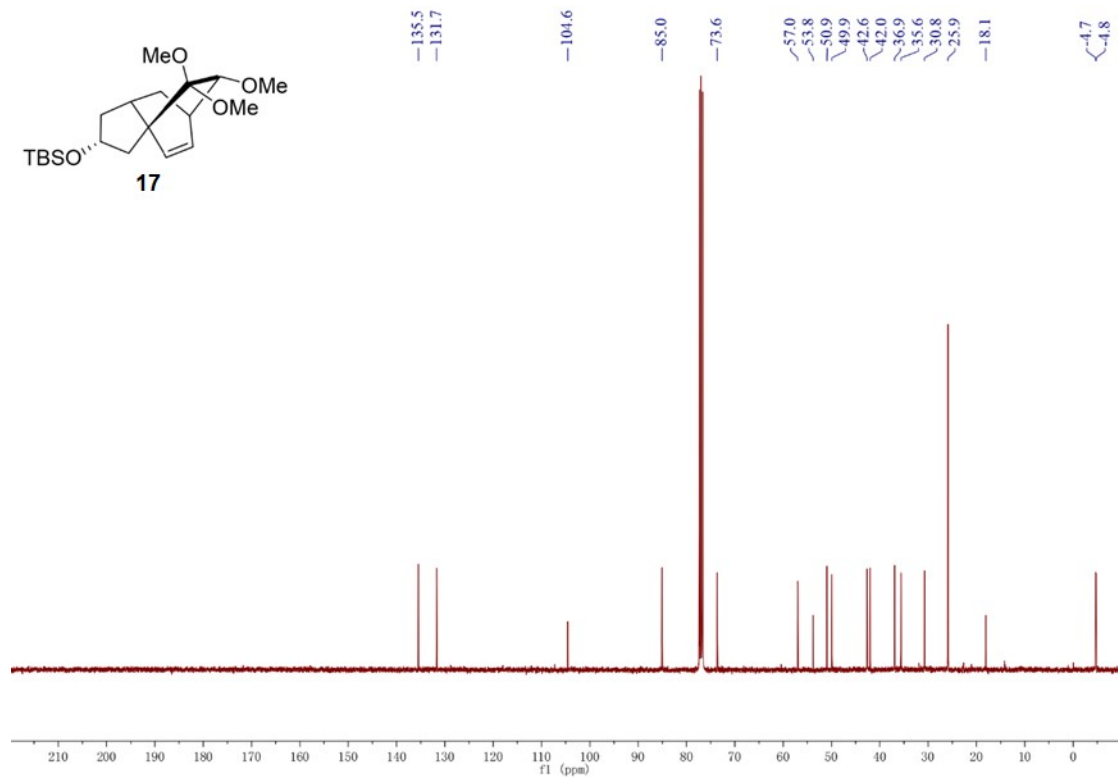
¹³C NMR Spectrum of 16 (100 MHz, CDCl₃)



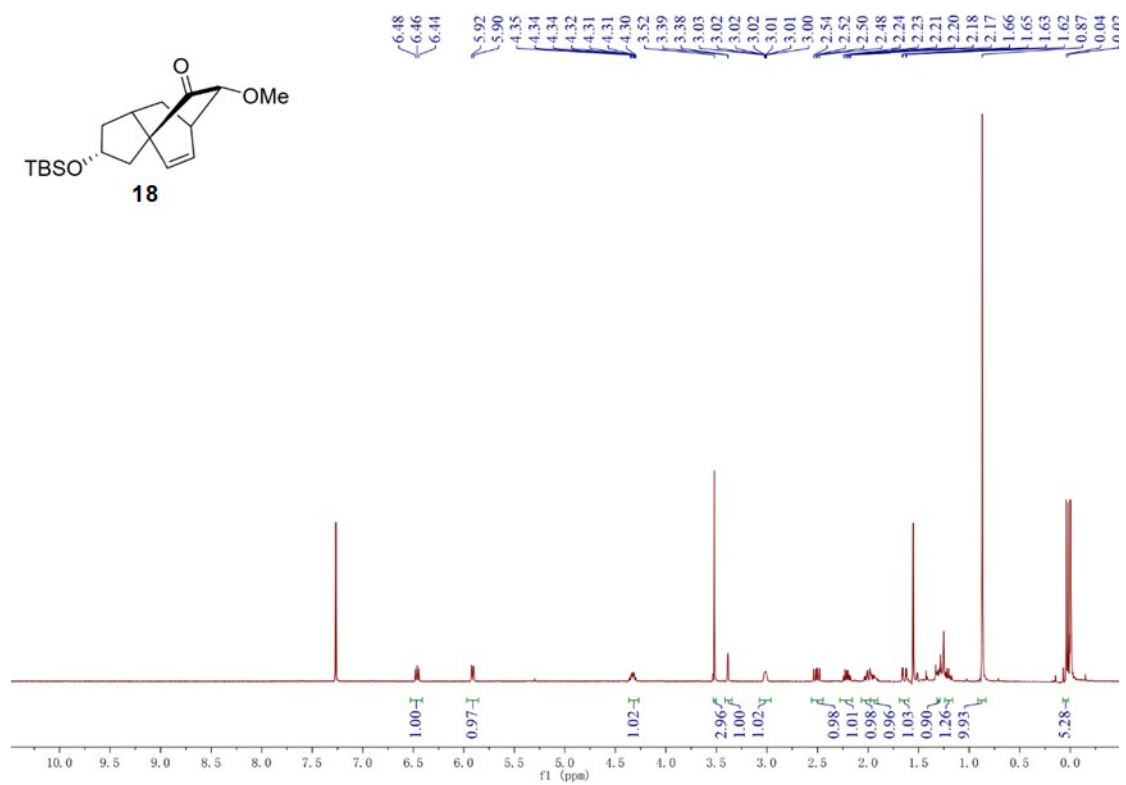
¹H NMR Spectrum of 17 (400 MHz, CDCl₃)



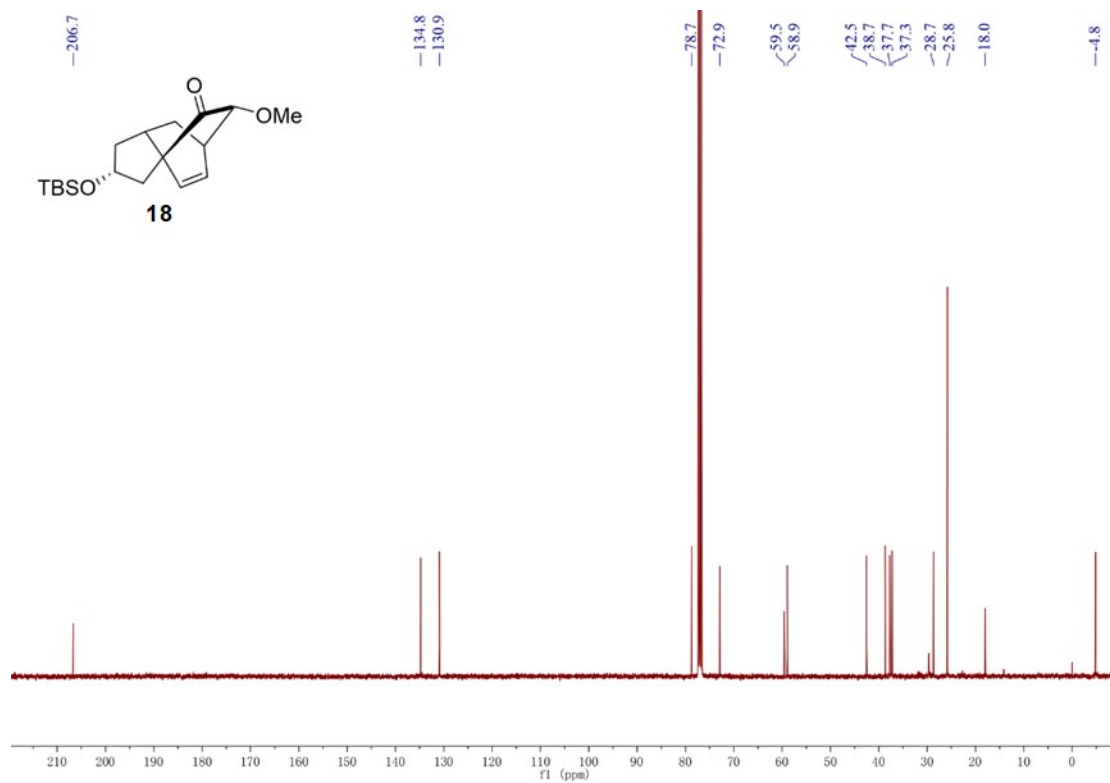
¹³C NMR Spectrum of 17 (100 MHz, CDCl₃)



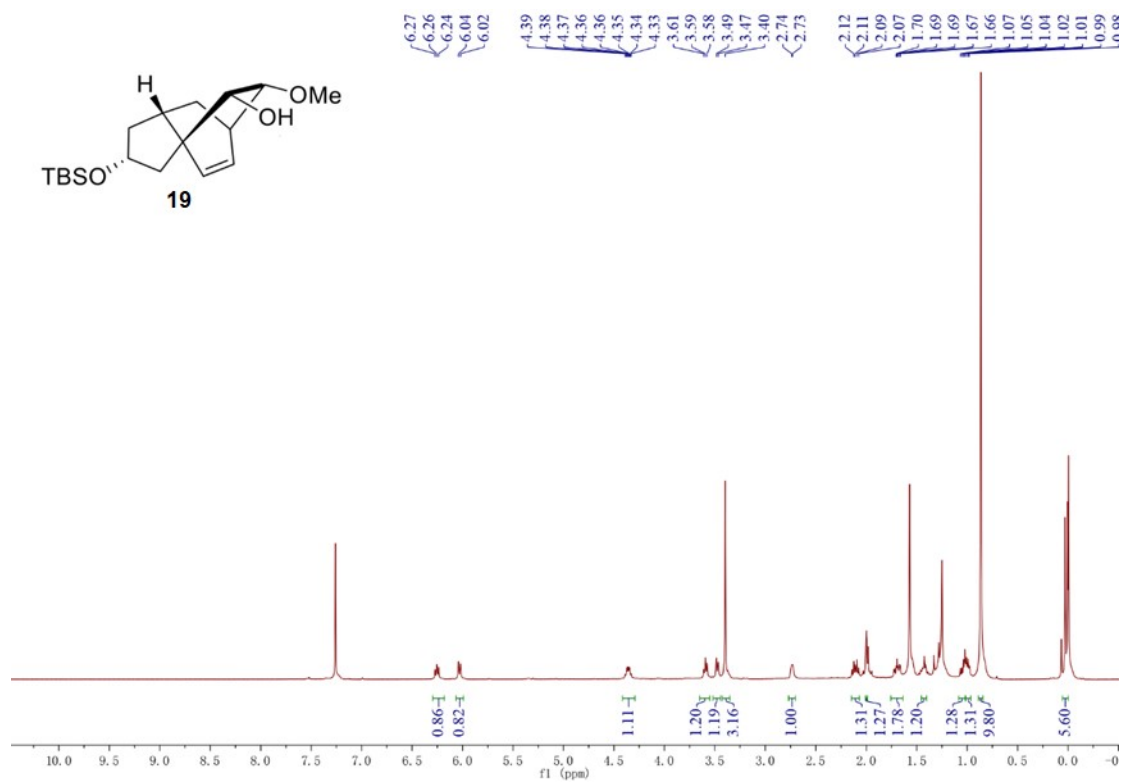
¹H NMR Spectrum of 18 (400 MHz, CDCl₃)



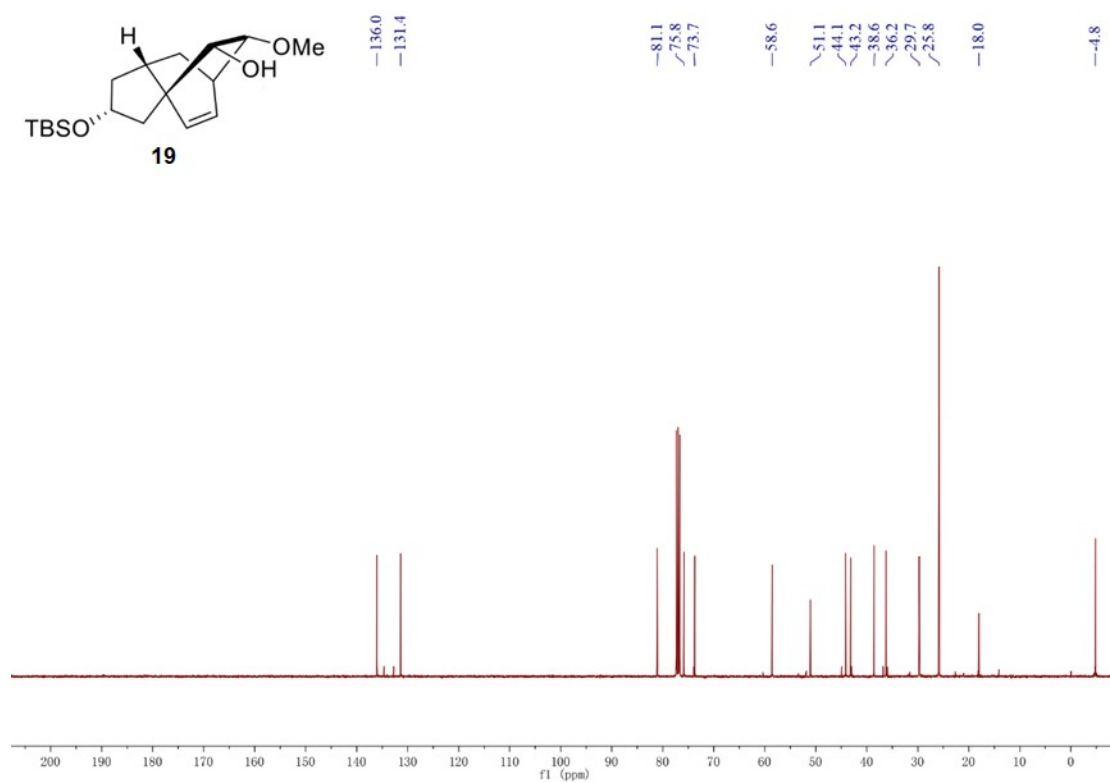
¹³C NMR Spectrum of 18 (100 MHz, CDCl₃)



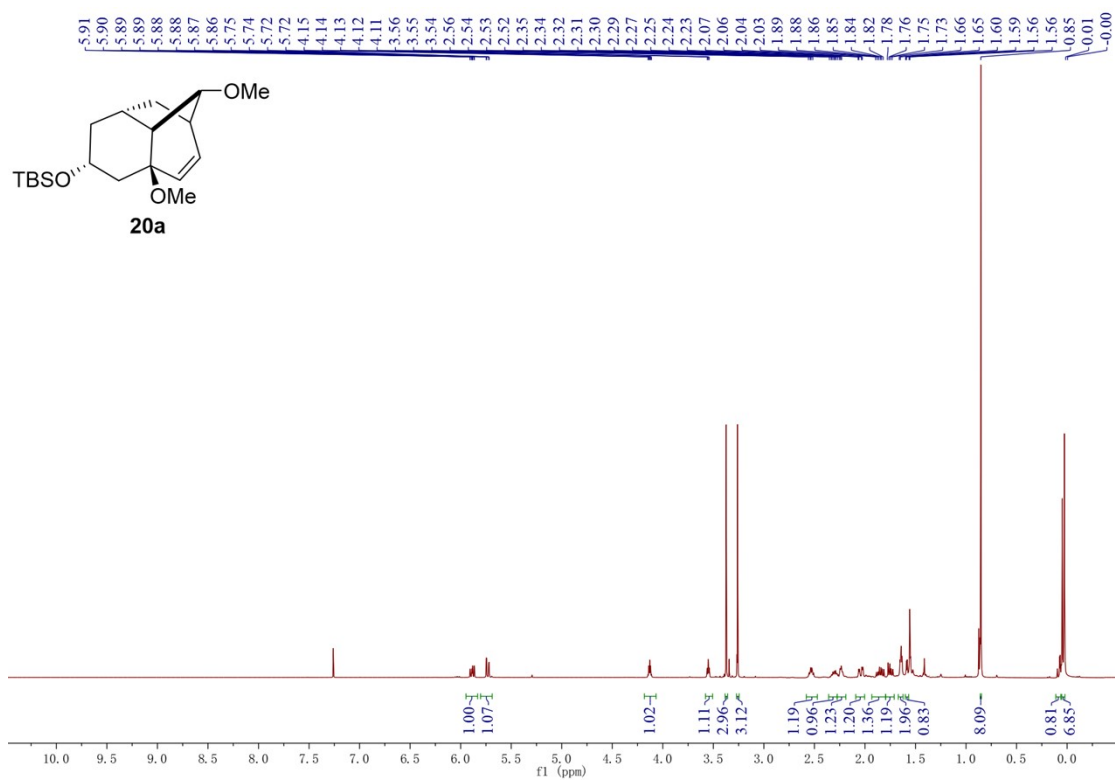
¹H NMR Spectrum of 19 (400 MHz, CDCl₃)



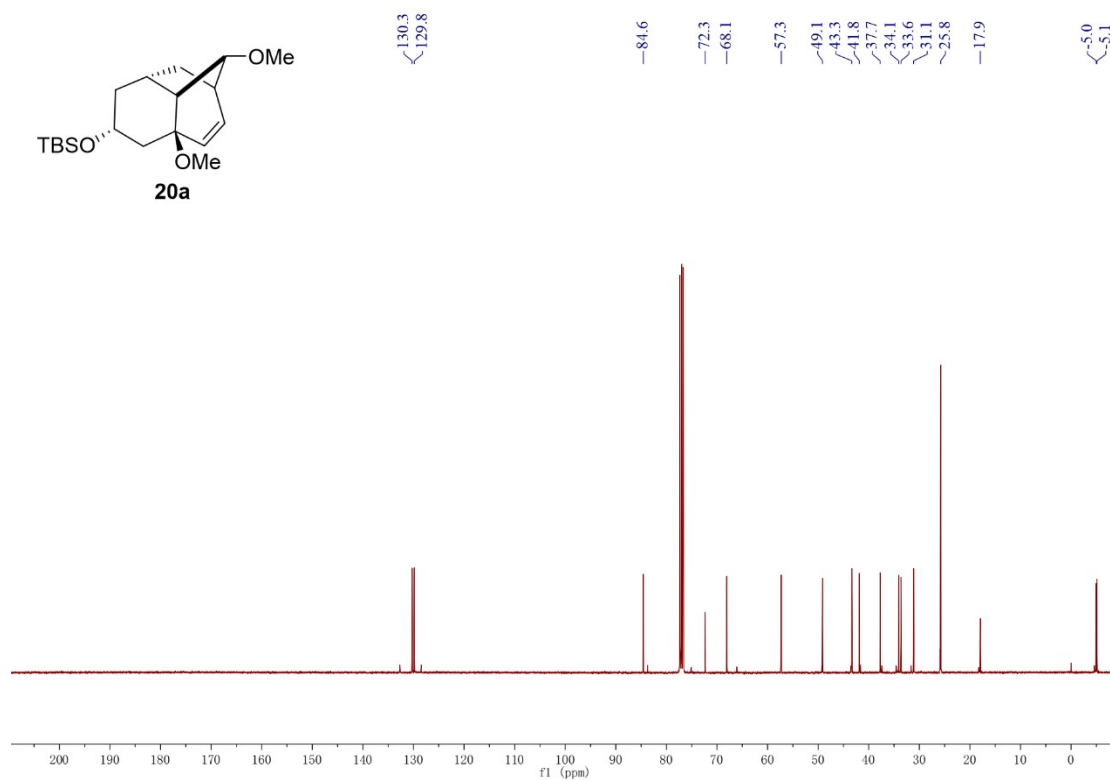
¹³C NMR Spectrum of 19 (100 MHz, CDCl₃)



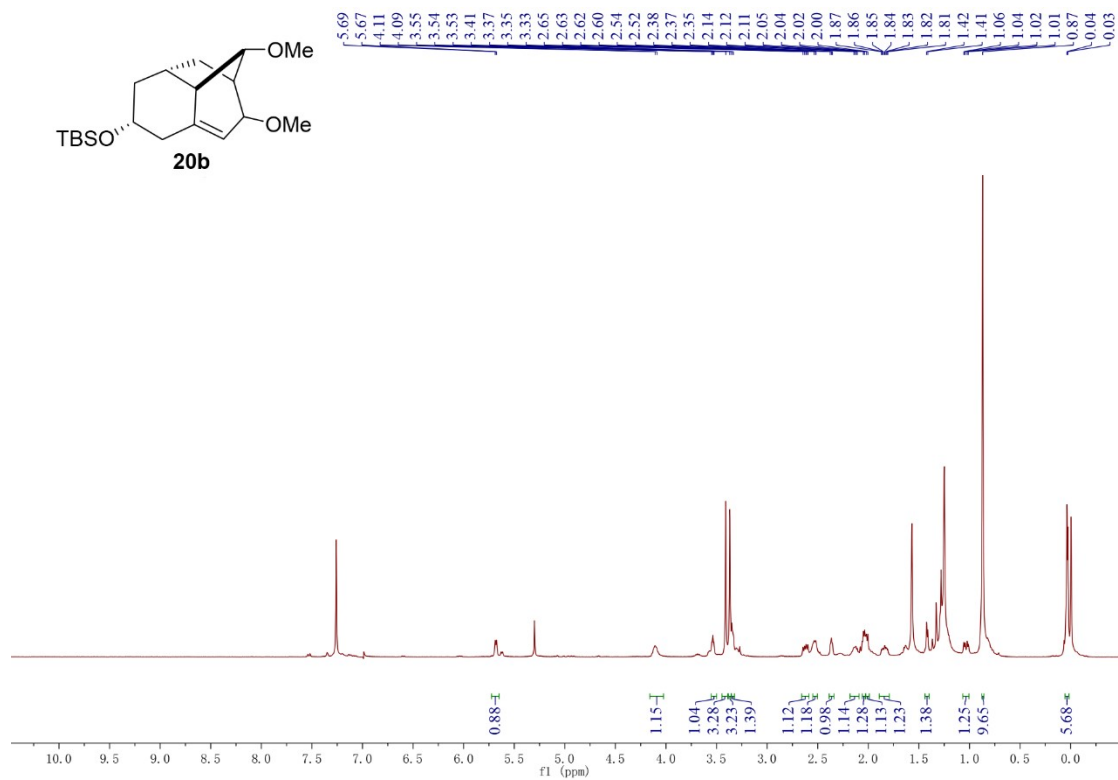
¹H NMR Spectrum of 20a (400 MHz, CDCl₃)



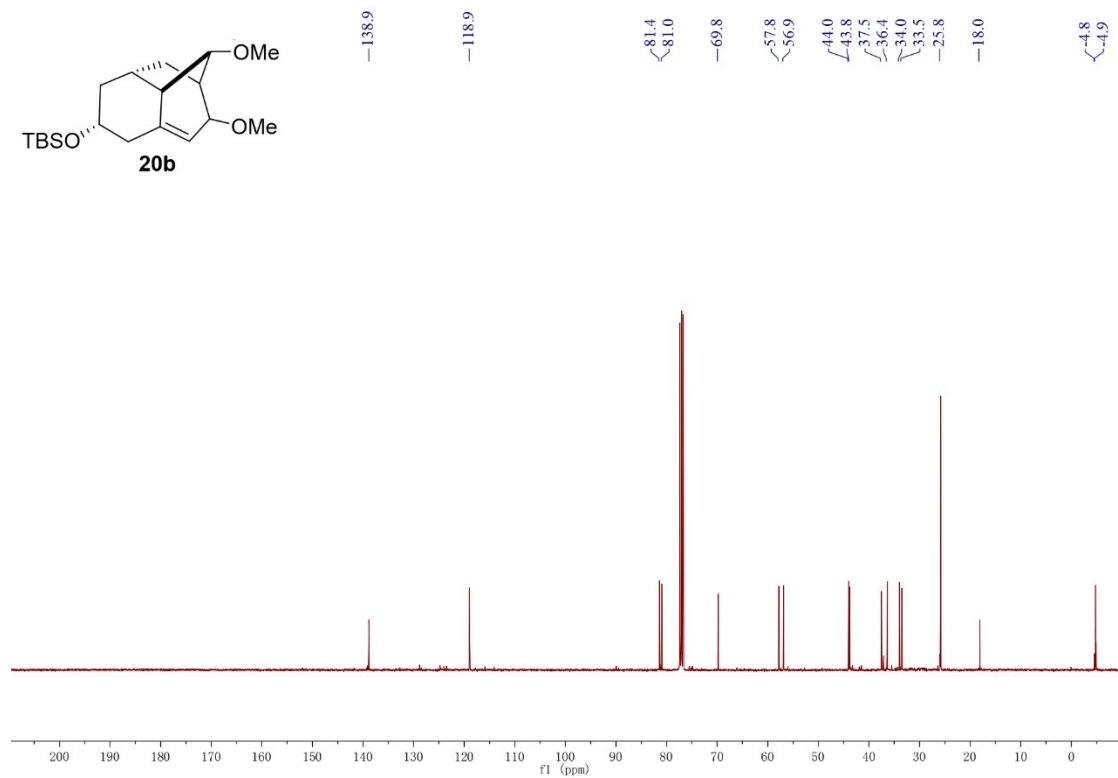
¹³C NMR Spectrum of 20a (100 MHz, CDCl₃)



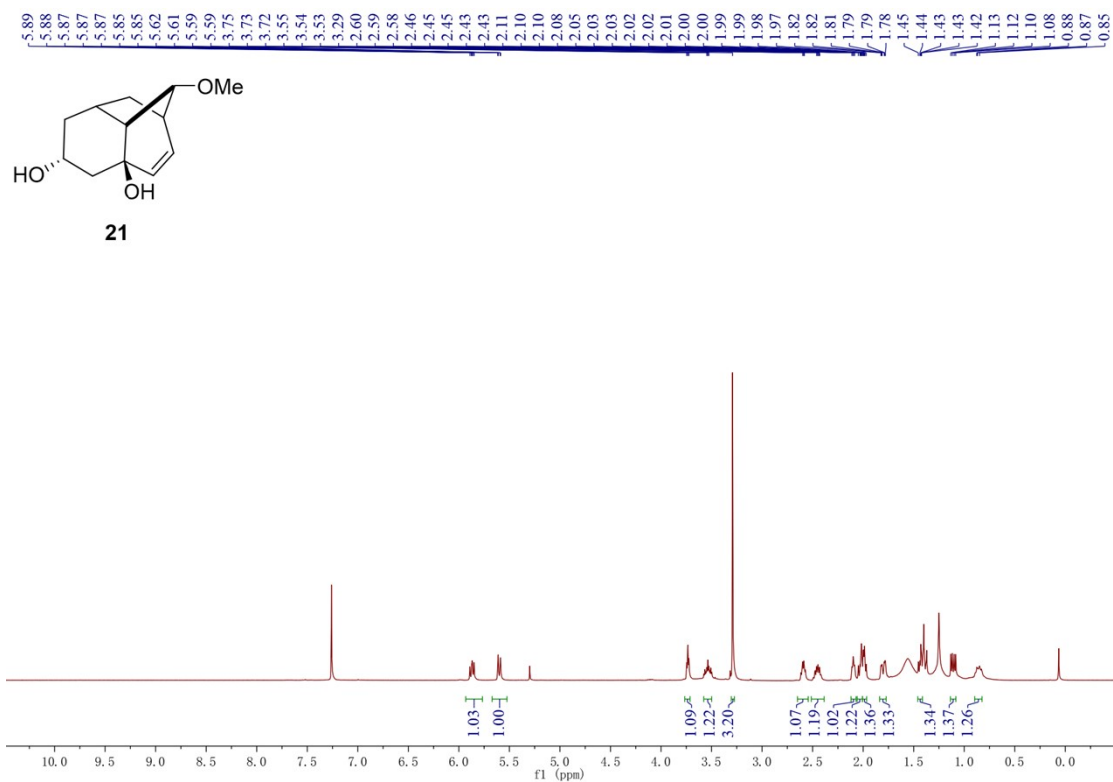
¹H NMR Spectrum of 20b (400 MHz, CDCl₃)



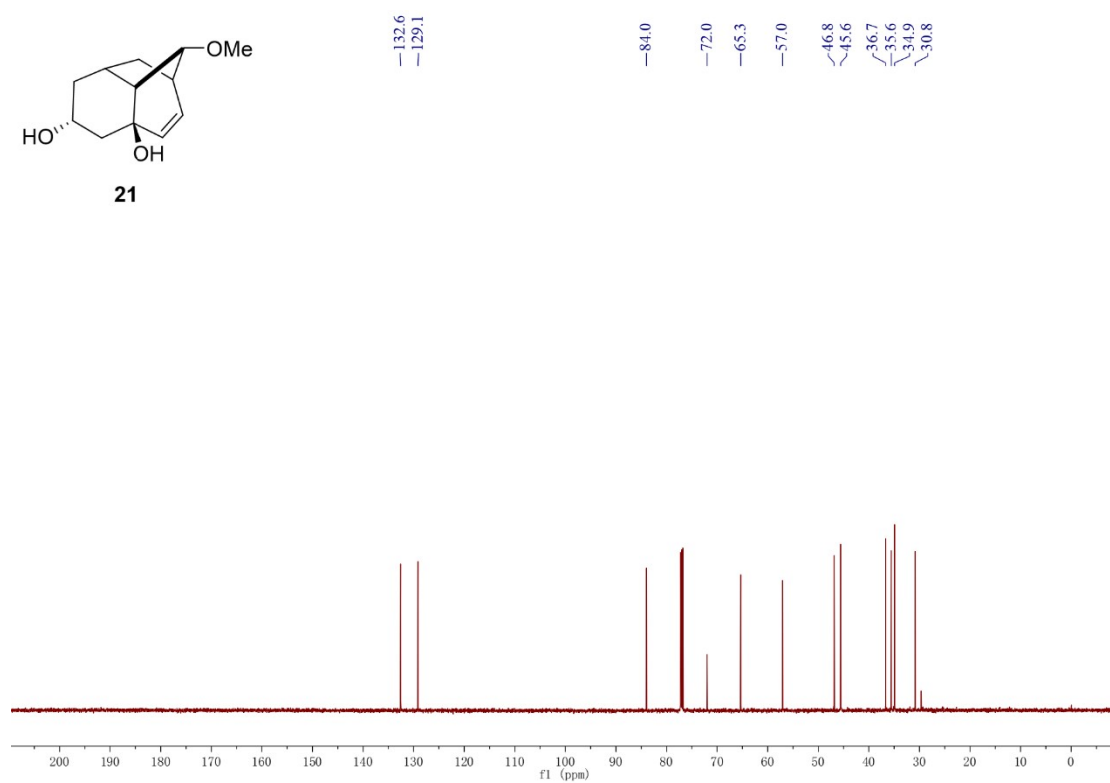
¹³C NMR Spectrum of 20b (100 MHz, CDCl₃)



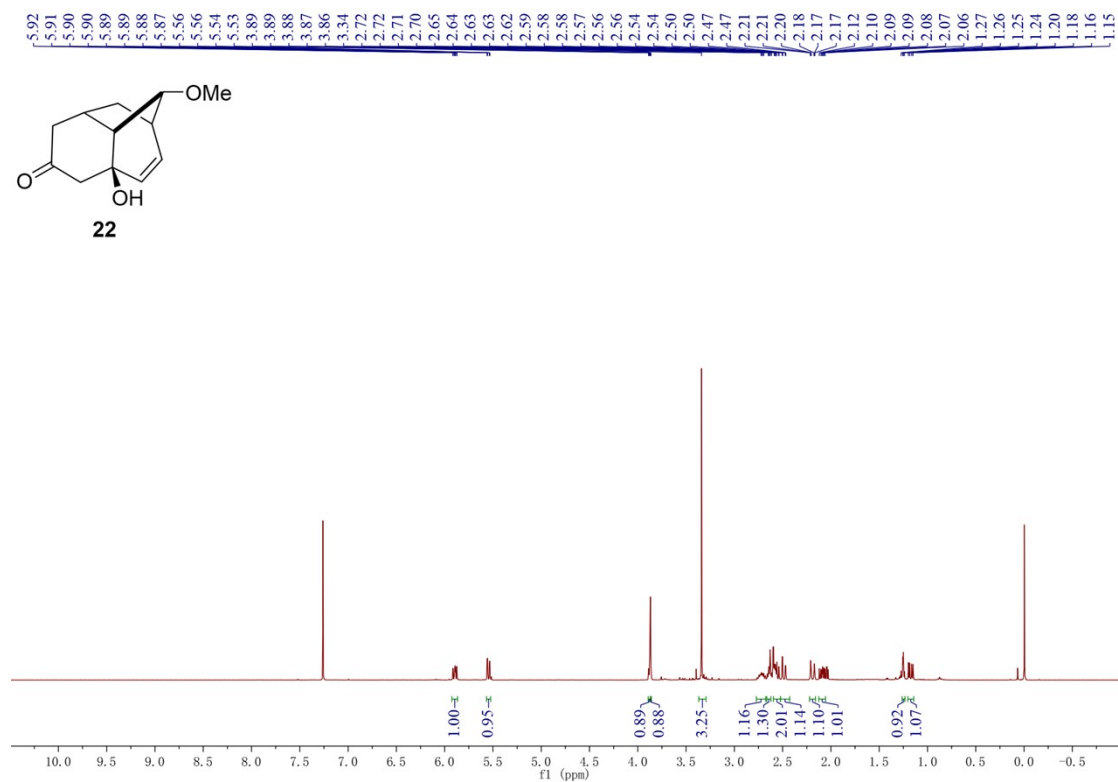
¹H NMR Spectrum of 21 (400 MHz, CDCl₃)



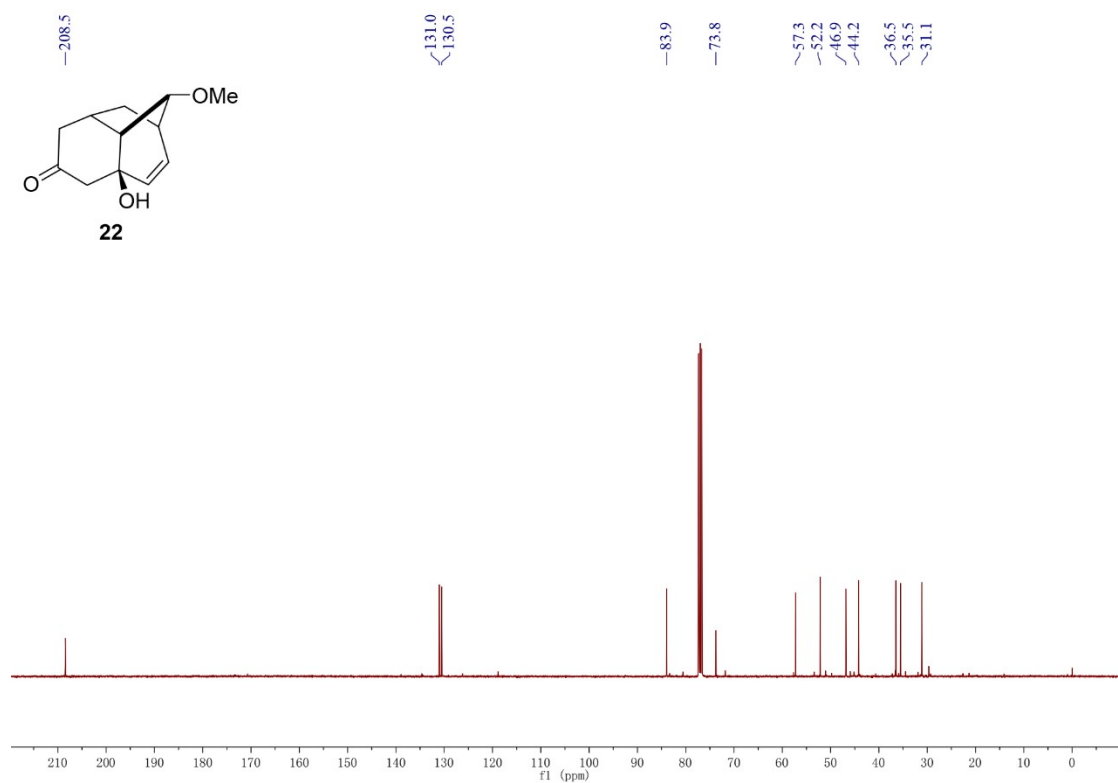
¹³C NMR Spectrum of 21 (100 MHz, CDCl₃)



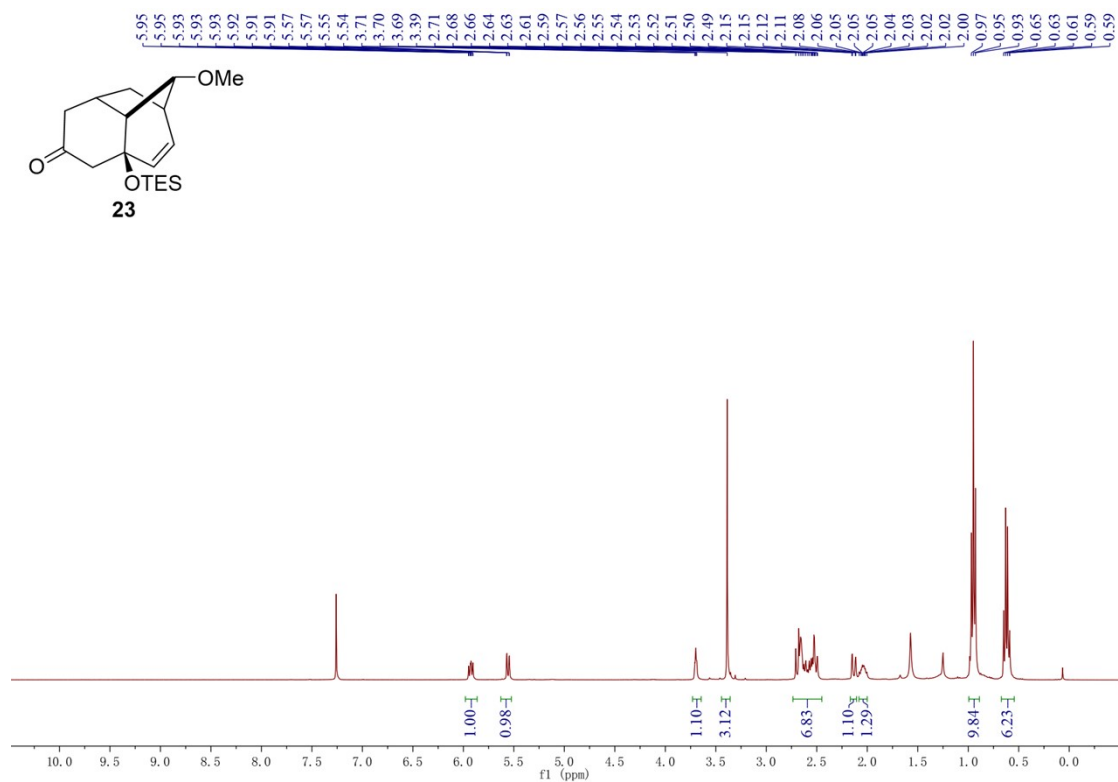
¹H NMR Spectrum of 22 (400 MHz, CDCl₃)



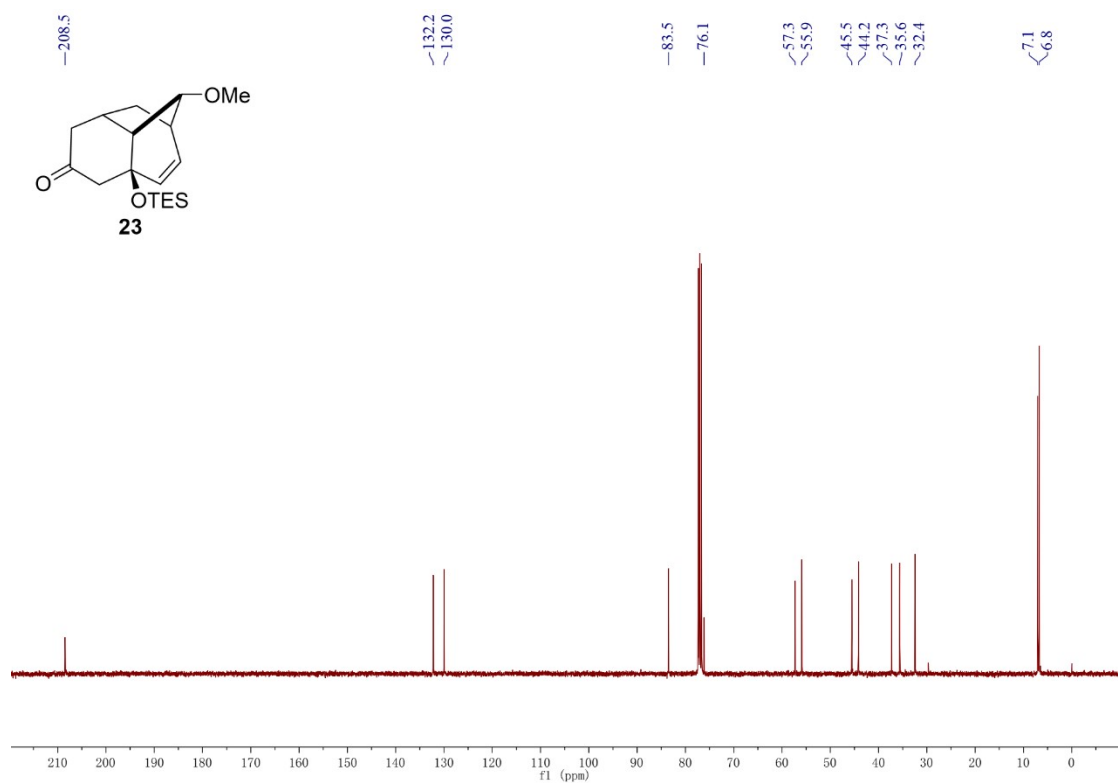
¹³C NMR Spectrum of 22 (100 MHz, CDCl₃)



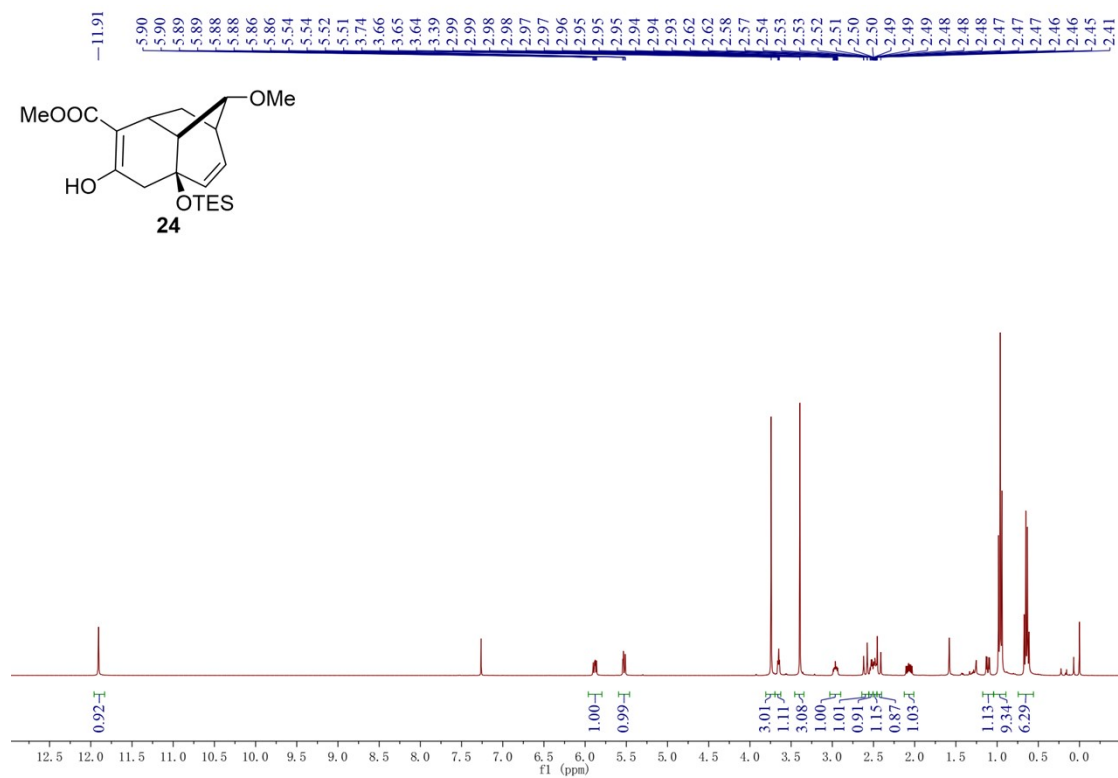
¹H NMR Spectrum of 23 (400 MHz, CDCl₃)



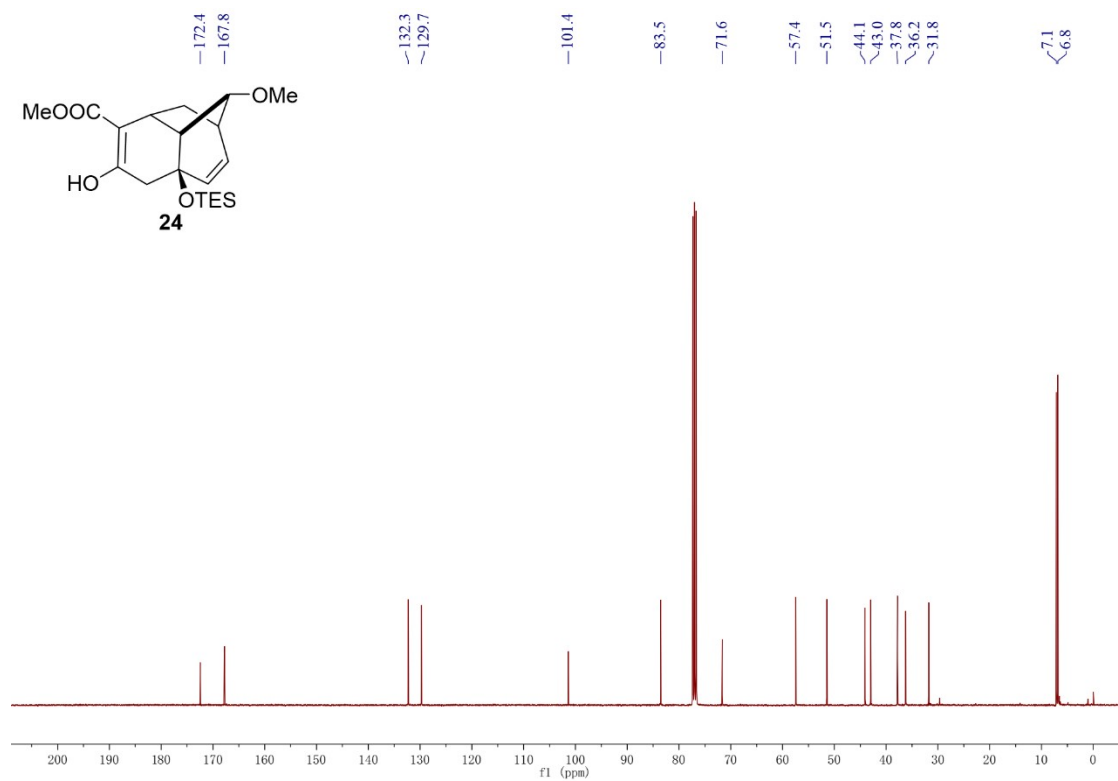
¹³C NMR Spectrum of 23 (100 MHz, CDCl₃)



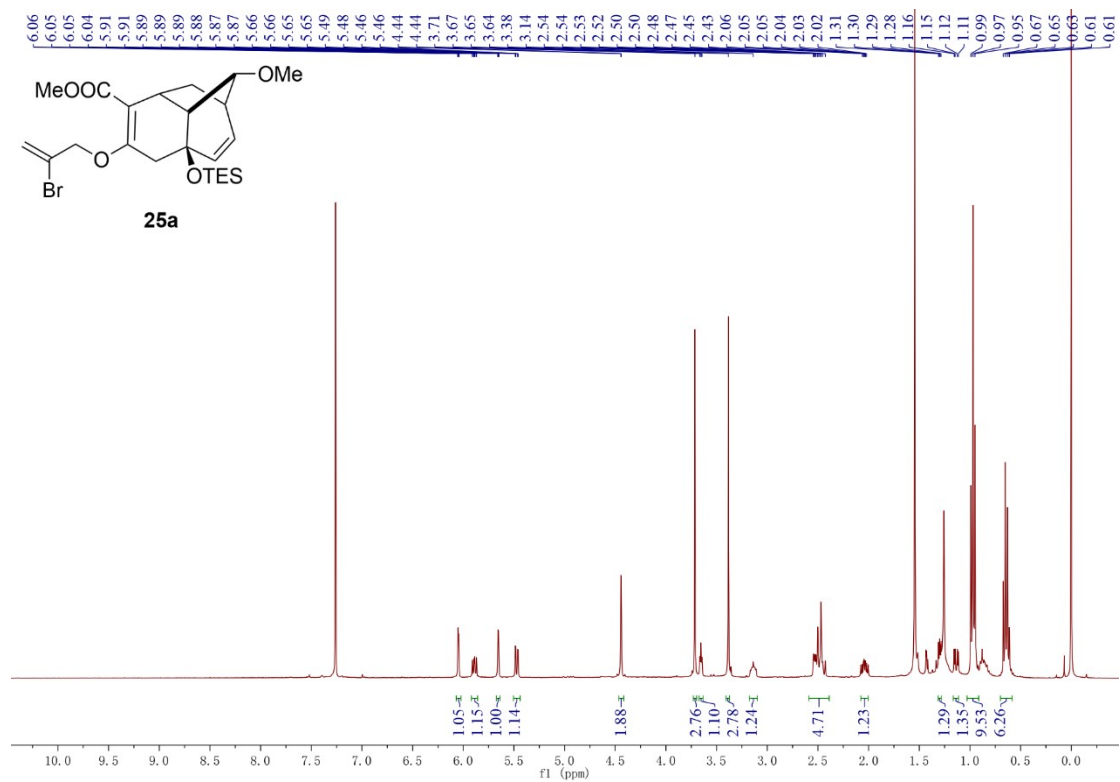
¹H NMR Spectrum of 24 (400 MHz, CDCl₃)



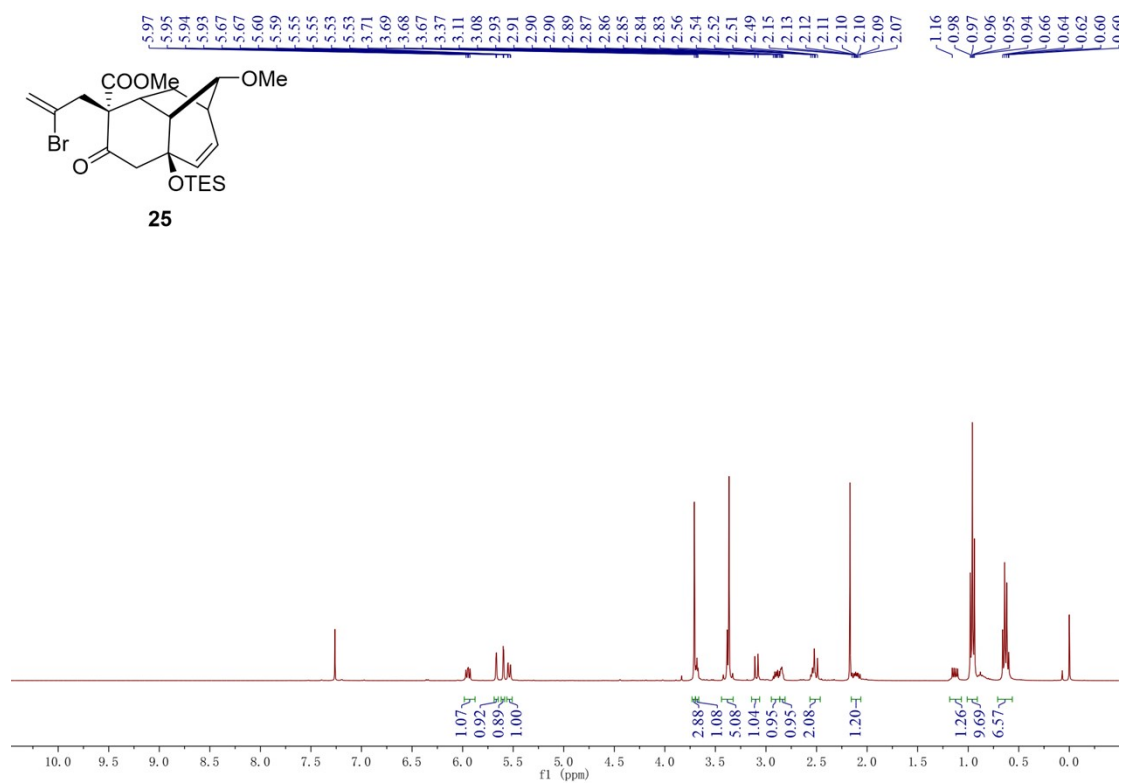
¹³C NMR Spectrum of 24 (100 MHz, CDCl₃)



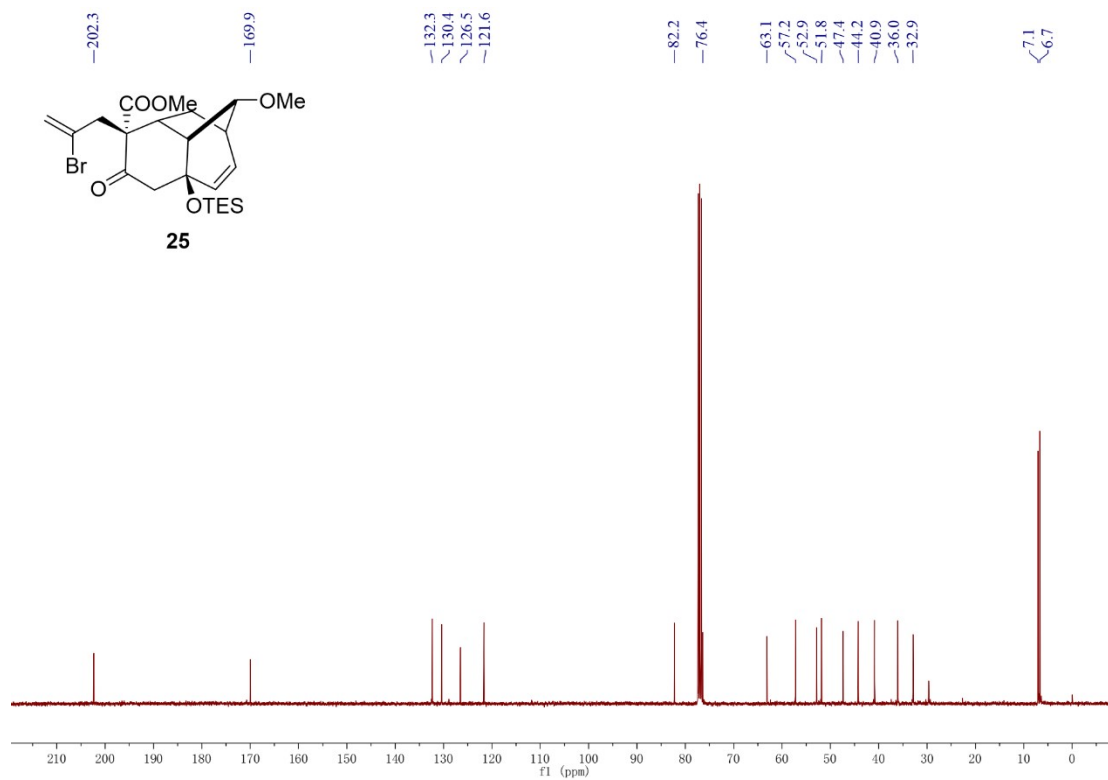
¹H NMR Spectrum of 25a (400 MHz, CDCl₃)



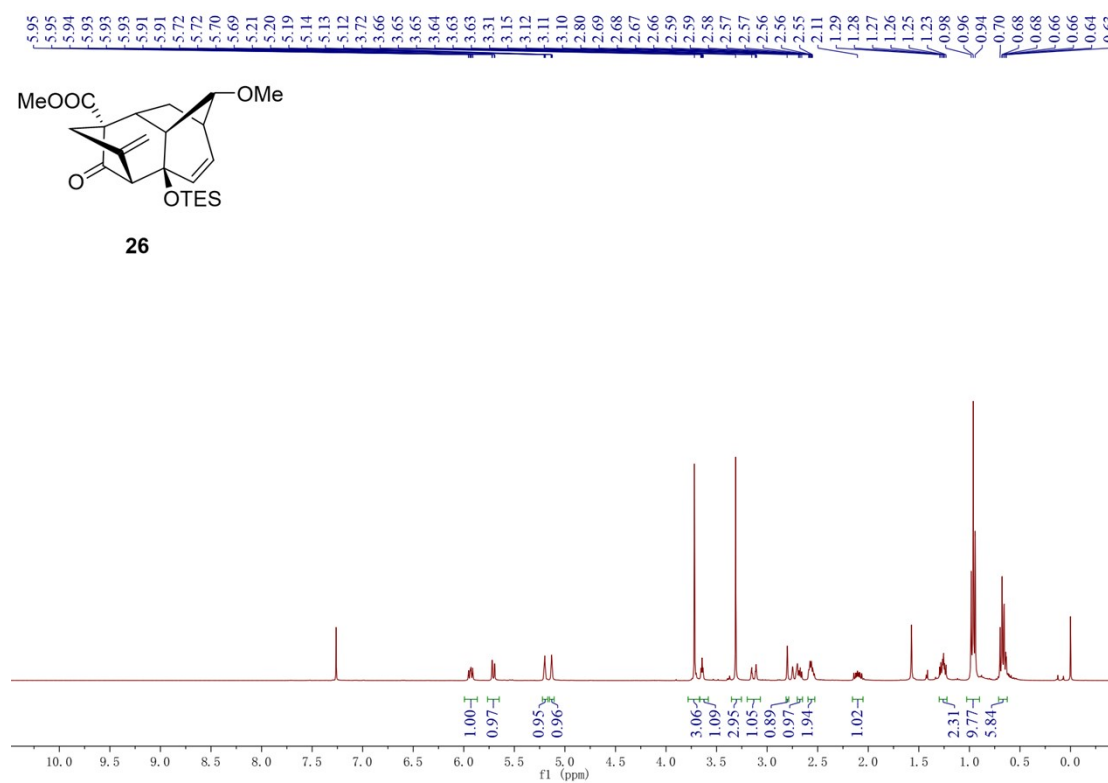
¹H NMR Spectrum of 25 (400 MHz, CDCl₃)



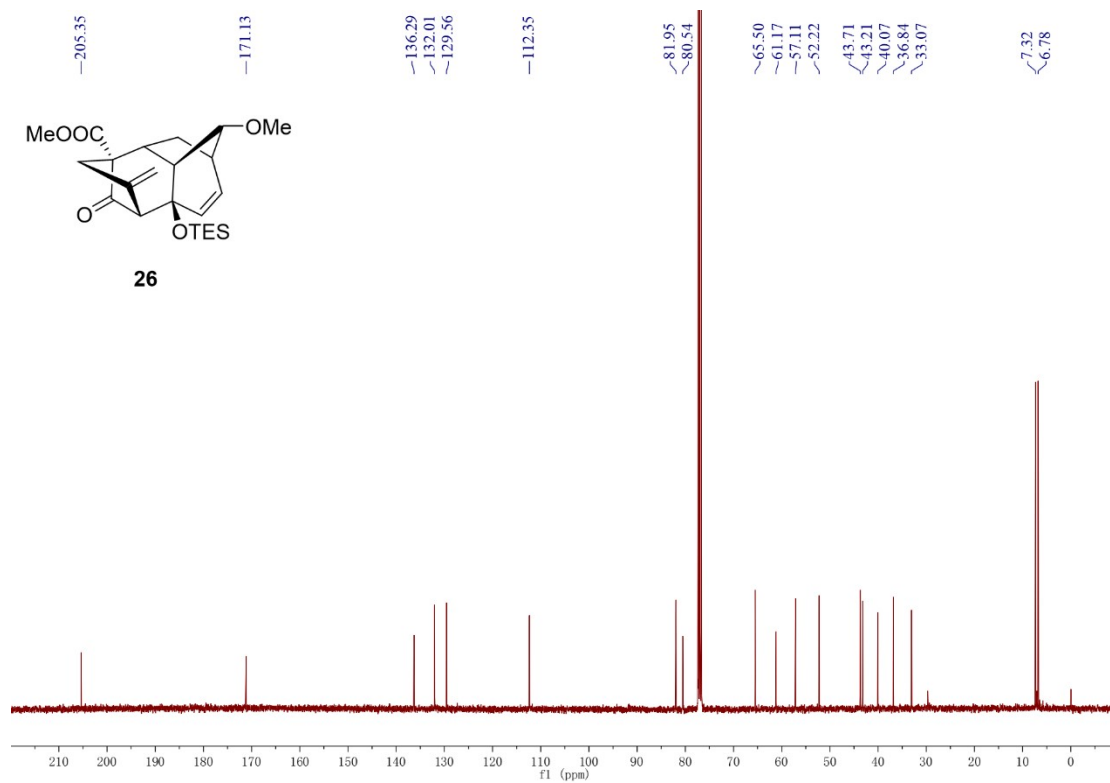
¹³C NMR Spectrum of 25 (100 MHz, CDCl₃)



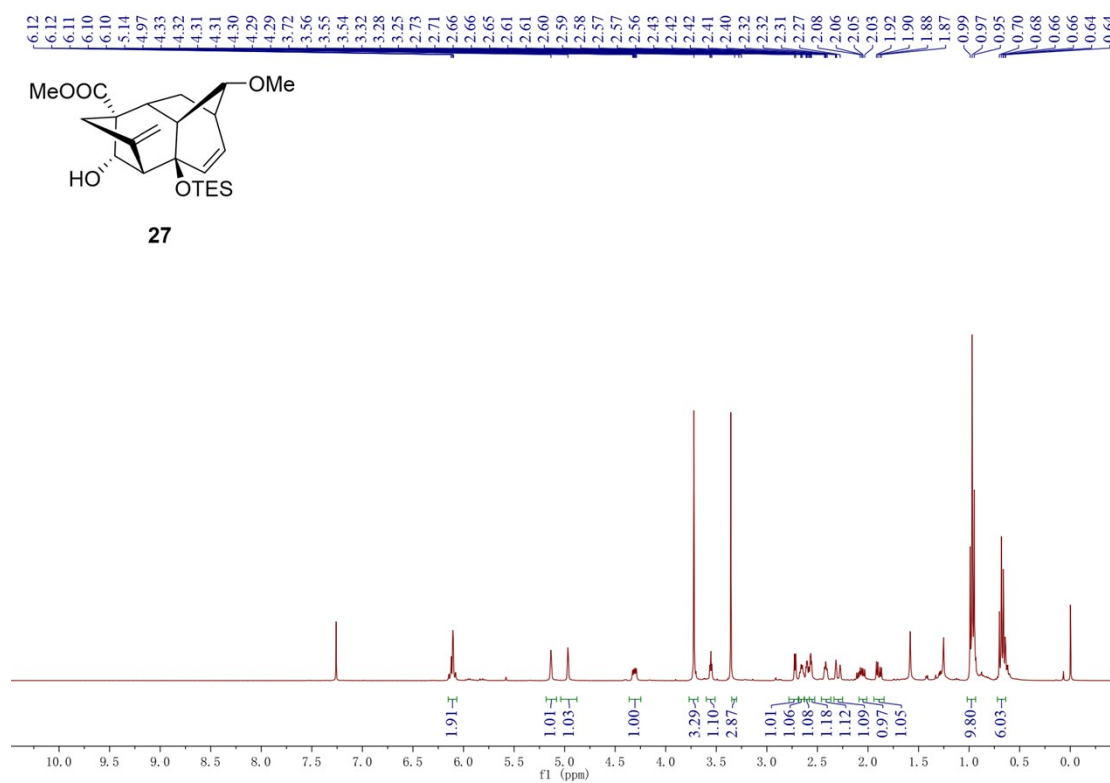
¹H NMR Spectrum of 26 (400 MHz, CDCl₃)



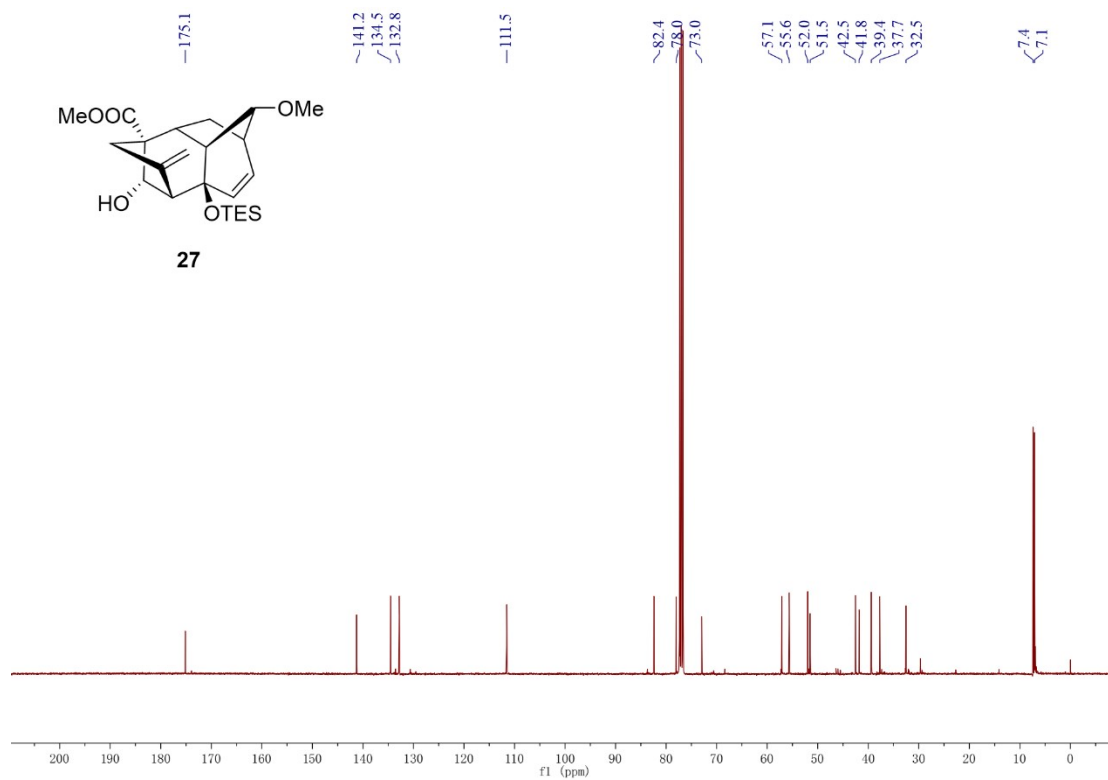
¹³C NMR Spectrum of 26 (100 MHz, CDCl₃)



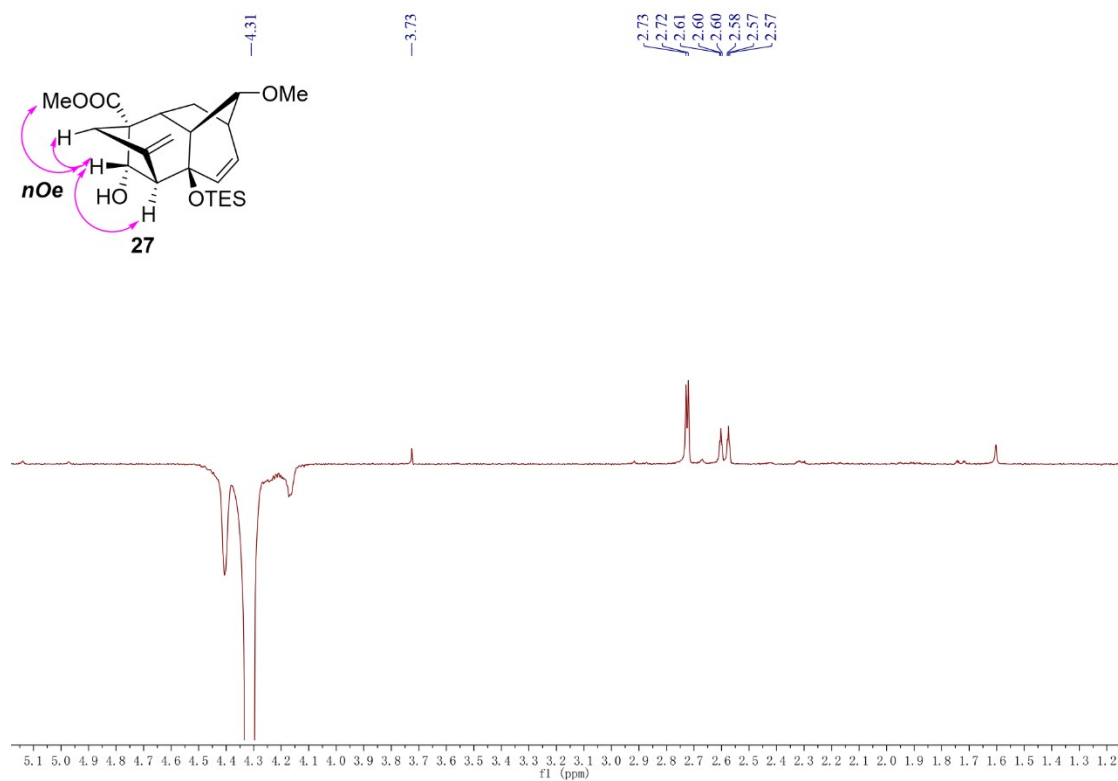
¹H NMR Spectrum of 27 (400 MHz, CDCl₃)



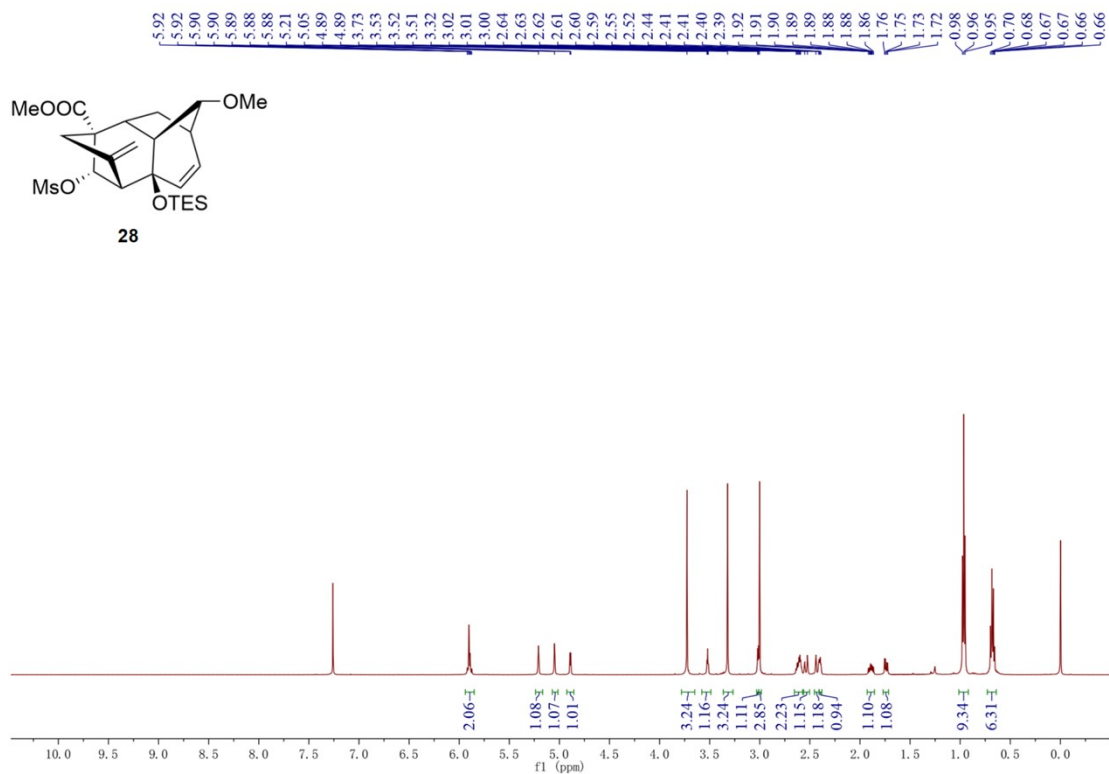
¹³C NMR Spectrum of 27 (100 MHz, CDCl₃)



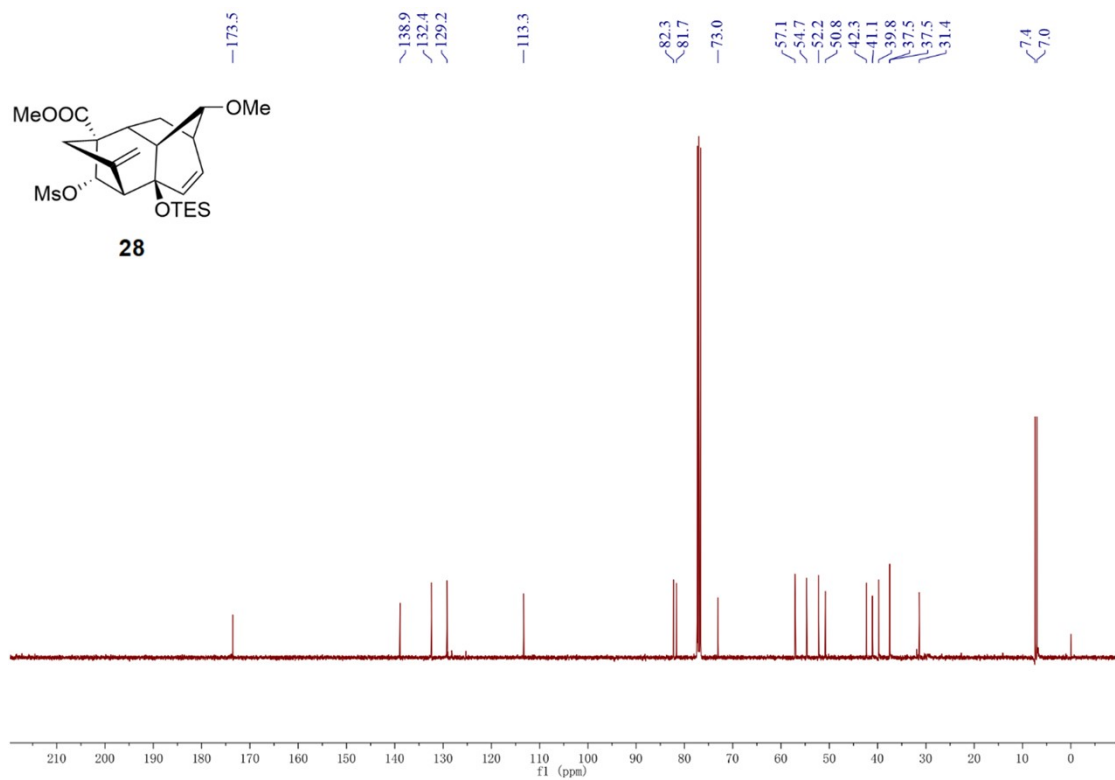
NOESY Spectrum of 27 (400 MHz, CDCl₃)



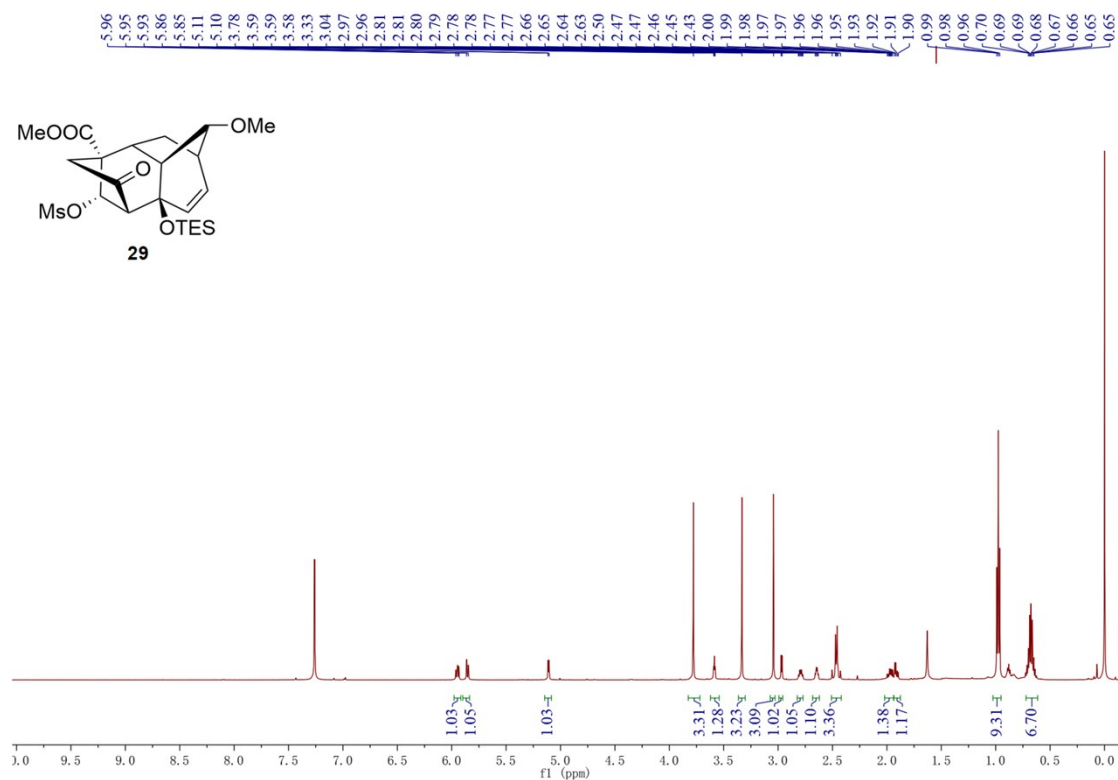
¹H NMR Spectrum of 28 (600 MHz, CDCl₃)



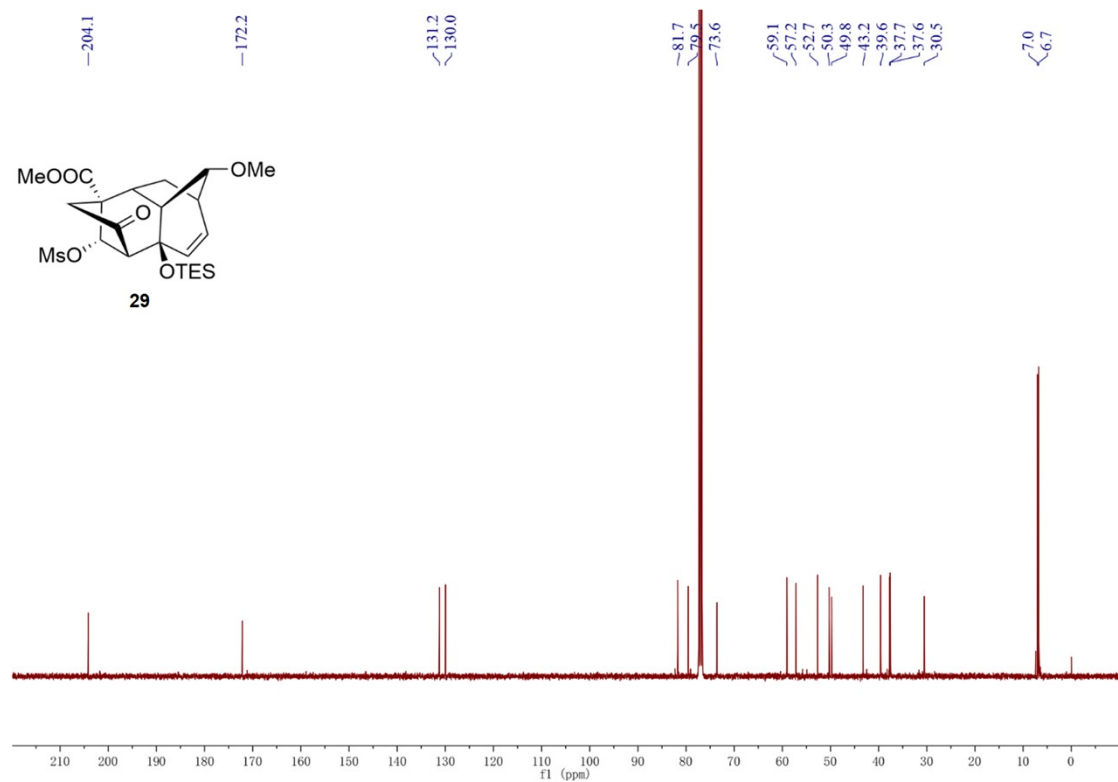
¹³C NMR Spectrum of 28 (100 MHz, CDCl₃)



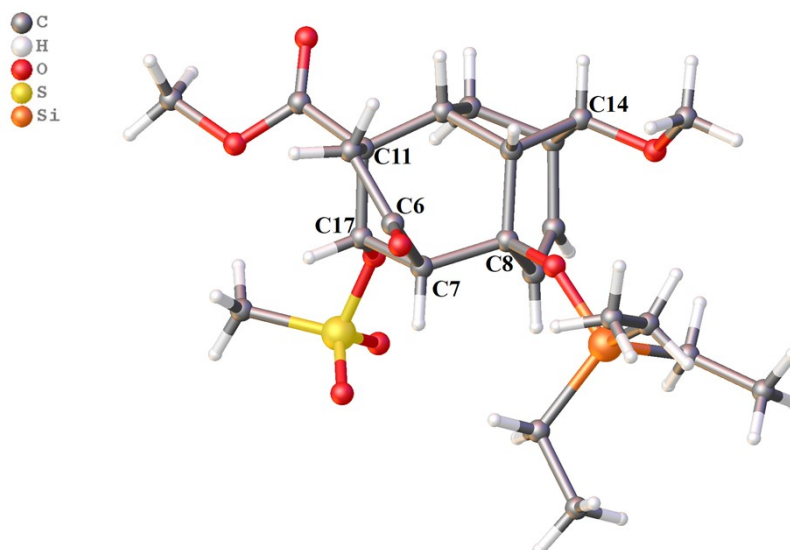
¹H NMR Spectrum of 29 (600 MHz, CDCl₃)



¹³C NMR Spectrum of 29 (100 MHz, CDCl₃)



4. X-ray single crystal structure data of compound 29.



Crystal structure determination of 29

Crystal Data for C₂₃H₃₆O₈SSi ($M = 500.67$ g/mol): triclinic, space group P-1 (no. 2), $a = 9.1191(3)$ Å, $b = 12.1448(7)$ Å, $c = 12.1551(6)$ Å, $\alpha = 76.174(4)^\circ$, $\beta = 80.698(3)^\circ$, $\gamma = 87.947(3)^\circ$, $V = 1289.98(10)$ Å³, $Z = 2$, $T = 293.15$ K, μ (MoK α) = 0.215 mm⁻¹, $D_{calc} = 1.289$ g/cm³, 10610 reflections measured ($5.834^\circ \leq 2\theta \leq 52.746^\circ$), 5268 unique ($R_{int} = 0.0210$, $R_{\sigma} = 0.0437$) which were used in all calculations. The final R_1 was 0.0922 ($I > 2 \sigma(I)$) and wR_2 was 0.3068 (all data).

Crystal data and structure refinement for 29

Identification code	29
Empirical formula	C ₂₃ H ₃₆ O ₈ SSi
Formula weight	500.67
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
$a/\text{Å}$	9.1191(3)
$b/\text{Å}$	12.1448(7)
$c/\text{Å}$	12.1551(6)

$\alpha / ^\circ$	76.174(4)
$\beta / ^\circ$	80.698(3)
$\gamma / ^\circ$	87.947(3)
Volume/ \AA^3	1289.98(10)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.289
μ / mm^{-1}	0.215
F(000)	536.0
Crystal size/ mm^3	$0.35 \times 0.3 \times 0.25$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	5.834 to 52.746
Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 15, -14 \leq l \leq 15$
Reflections collected	10610
Independent reflections	5268 [$R_{\text{int}} = 0.0210, R_{\text{sigma}} = 0.0437$]
Data/restraints/parameters	5268/2/280
Goodness-of-fit on F^2	1.058
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0922, wR_2 = 0.2675$
Final R indexes [all data]	$R_1 = 0.1343, wR_2 = 0.3068$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.93/-0.52