Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Development of an Expedient Intramolecular Pauson-Khand Reaction Approach to Stereoselectively Construct the *trans*-Decalin with C1 Quaternary Chiral Center

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Contents

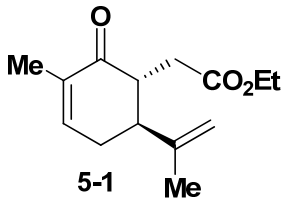
General Information

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF and dioxane were distilled from sodium-benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. Tsingdao silica gel (60, particle size 0.040 – 0.063 mm) was used for flash column chromatography.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Brüker Advance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C 125 MHz). Mass spectrometric data were obtained using Bruker Apex IV RTMS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

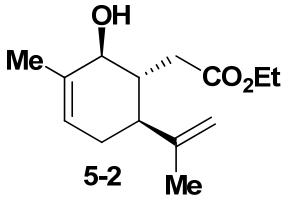
Synthesis of ethyl 2-((1R,6S)-3-methyl-2-oxo-6-(prop-1-en-2-yl)cyclohex-3-en-1-yl)acetate (5-1):



5-1

To a solution of LDA (2 N in THF, 48 mL, 95.8 mmol) in dry distilled THF (150 mL) was added *S*- (-)-carvone (12 g, 12.5 mL, 80 mmol) dropwise at -78 ^{o}C, and the mixture was stirred at the same temperature for 1 h. To this solution was slowly added ethyl bromoacetate (15.5 g, 10.3 mL, 88 mmol) at -78 ^{o}C, and the mixture was first stirred at the same temperature for 10 min, and then gradually warmed up to room temperature, and stirred overnight. The reaction was quenched by addition of a saturated solution of NH_4Cl (80 mL), and then extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were dried with Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to a column chromatography on silica gel (hexane/ethyl acetate = 40/1) to give ester **5-1** as yellow oil in 75% yield; R_f = 0.50 (silica gel, EtOAc/hexanes = 1/16); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (d, J = 5.8 Hz, 1H), 4.81 (d, J = 9.4 Hz, 2H), 4.11 (dd, J = 14.1, 7.0, 2H), 2.85 (ddd, J = 13.0, 6.6, 4.8 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.51 – 2.36 (m, 3H), 2.28 (ddd, J = 18.4, 7.7, 2.8 Hz, 1H), 1.79 – 1.71 (m, 3H), 1.69 (s, 3H), 1.23 (dd, J = 8.6, 5.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.58, 172.64, 144.91, 143.44, 134.72, 114.10, 60.22, 48.16, 46.32, 32.22, 31.17, 18.08, 15.83, 14.07; IR (KBr, thin film): 3074.53, 2978.09, 2924.29, 1732.08, 1645.28, 1435.04, 1350.17, 1155.36, 898.83 cm $^{-1}$; HRMS-ESI Calcd. For $C_{14}H_{20}O_3Na^+$ [M + Na^+]: 259.1305; Found: 259.1303.

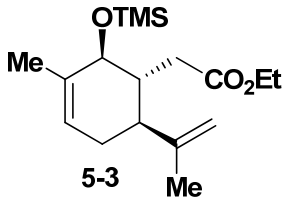
Synthesis of ethyl 2-((1R,2S,6S)-2-hydroxy-3-methyl-6-(prop-1-en-2-yl)cyclohex-3-en-1-yl) acetate (5-2):



5-2

To a solution of compound **5-1** (3.9 g, 16.5 mmol) in methanol (60 mL) was added $CeCl_3$ $7H_2O$ (6.1 g, 16.5 mmol) at -78 ^{o}C, followed by $NaBH_4$ (690 mg, 18.1 mmol) in several portions, and the mixture was gradually warmed up to -30 ^{o}C, and stirred for 30 min. The reaction was quenched by addition of a saturated solution of NH_4Cl (10 mL). After removal of the solvent under vacuum, the residue was extracted with ethyl acetate (3 x 20 mL), and the combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate =25/1) to give alcohol **5-2** as colorless oil in 79% yield; R_f = 0.5 (silica gel, EtOAc/hexanes = 1/8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 – 5.38 (m, 1H), 4.74 (d, J = 7.2 Hz, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.88 (t, J = 7.1 Hz, 1H), 2.64 (d, J = 7.7 Hz, 1H), 2.49 (dd, J = 15.8, 3.6 Hz, 1H), 2.23 (ddd, J = 23.5, 13.5, 6.5 Hz, 2H), 2.16 – 1.99 (m, 2H), 1.90 (dt, 1H), 1.69 (s, 3H), 1.63 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.42, 146.62, 135.78, 122.86, 113.29, 75.61, 60.42, 46.32, 41.87, 36.83, 30.56, 19.21, 18.28, 14.13; IR (KBr, thin film): 3309.85, 2976.16, 2341.58, 1732.08, 1373.32, 1190.08, 1155.36, 893.04, 748.38 cm $^{-1}$; HRMS-ESI Calcd. For $C_{14}H_{22}O_3Na^+$ [M + Na^+]: 261.1461; Found: 261.1457.

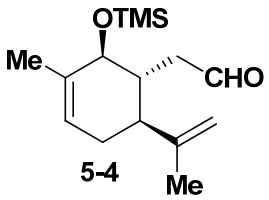
Synthesis of ethyl 2-((1R,2S,6S)-3-methyl-6-(prop-1-en-2-yl)-2-((trimethylsilyl)oxy) cyclohex-3-en-1-yl) acetate (5-3):



5-3

To a solution of the alcohol **5-2** (1.96 g, 8.22 mmol) and Et_3N (2.49 g, 24.6 mmol) in dry CH_2Cl_2 (50 mL) was added TMSOTf (3.64 g, 16.4 mmol) at 0 ^oC in a dropwise manner, and the reaction mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (20 mL), and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 50/1) to give compound **5-3** in 98% yield; R_f = 0.85 (silica gel, EtOAc/hexanes = 1/4). ^1H NMR (500 MHz, $CDCl_3$) δ 5.51 – 5.45 (m, 1H), 4.76 (s, 2H), 4.36 (d, J = 8.8 Hz, 1H), 4.09 (qd, J = 7.2, 3.3 Hz, 2H), 2.61 – 2.47 (m, 2H), 2.37 (dd, J = 17.0, 4.2 Hz, 1H), 2.19 – 2.07 (m, 1H), 2.00 (ddd, J = 16.4, 8.9, 4.4 Hz, 1H), 1.96 – 1.87 (m, 1H), 1.70 (d, J = 1.1 Hz, 3H), 1.65 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.54, 146.59, 135.83, 123.50, 113.20, 74.93, 59.93, 45.36, 41.78, 33.69, 30.72, 20.78, 18.29, 14.25, 0.88; IR (KBr, thin film): 2954.95, 2922.16, 2357.01, 1737.86, 1633.71, 1377.17, 1251.80, 1159.22, 894.97, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{17}H_{30}O_3SiNa^+$ [M + Na^+]: 333.1856; Found: 333.1857.

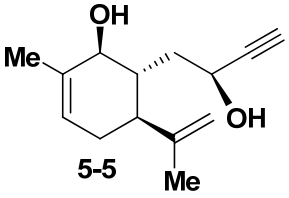
Synthesis of 2-((1R,2S,6S)-3-methyl-6-(prop-1-en-2-yl)-2-((trimethylsilyl)oxy)cyclohex-3-en-1 -yl) acetaldehyde (5-4):

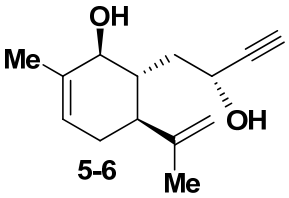


5-4

To a solution of ester **5-3** (2.51 g, 8.0 mmol) in dry distilled toluene (50 mL) was added DIBAL (1.0 M in toluene, 4.8 mL, 4.8 mmol) at -78 ^oC dropwise. Stirred at this temperature for 10 min and then added DIBAL (1.0 M in toluene, 4.0 mL, 4.0 mmol) at -78^oC dropwise. After stirring at the same temperature for 0.5 h, the reaction was quenched with methanol (10 mL), diluted with Et_2O (30 mL) and sat. Na/K tartrate (50 mL). The solution was stirred at room temperature for 2 h. Extracted the solution with ethyl acetate (3 x 50 mL), and the combined extracts were dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane/ethyl acetate (50/1) gave aldehyde **5-4** as colorless oil in 92% yield; R_f = 0.4 (silica gel, EtOAc/hexanes = 1/16). ^1H NMR (500 MHz, $CDCl_3$) δ 9.74 (t, J = 1.7 Hz, 1H), 5.54 – 5.43 (m, 1H), 4.85 – 4.72 (m, 2H), 4.15 (d, J = 8.9 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.41 (ddd, J = 16.6, 8.1, 3.5 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.98 – 1.87 (m, 1H), 1.76 – 1.66 (m, 3H), 1.62 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.10, 146.66, 135.77, 123.60, 113.82, 76.17, 46.35, 44.53, 41.67, 30.69, 20.70, 18.40, 1.05; IR (KBr, thin film): 3072.60, 2954.95, 2843.07, 2719.63, 1724.36, 1643.35, 1438.90, 1251.80, 1087.85, 894.97 cm^{-1}; HRMS-ESI Calcd. For $C_{15}H_{26}O_2SiNa^+$ [M + Na^+]: 289.1594; Found:289.1595.

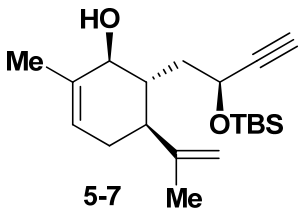
Synthesis of Compound 5-5 and 5-6:





To a solution of **5-4** (2.03 g, 7.6 mmol) in distilled THF (40 mL) was added ethynylmagnesium chloride (0.5 M in THF, 45 mL, 227 mmol) at 0 ^{o}C and then stirred at 0 ^{o}C for 0.5 h. The reaction was quenched with sat. NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 50 mL). The organic layers were dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was directly dissolved in THF (40 mL). Added TBAF (1.0 M in THF, 11.4 mL, 11.4 mmol) into the above solution. The reaction was stirred at 0 ^{o}C for 15 min, and then quenched with sat. NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 50 mL). The organic layers were dried with Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane/ethyl acetate (8/1) gave diol **5-5** as colorless oil in 33% yield for two steps; R_f = 0.35 (silica gel, EtOAc/hexanes = 1/3). Elution with hexane/ethyl acetate (50/1) gave diol **5-6** as colorless oil in 30% yield for two steps; R_f = 0.3 (silica gel, EtOAc/hexanes = 1/4). Compound **5-5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (d, J = 3.8 Hz, 1H), 4.81 (d, J = 16.1 Hz, 2H), 4.56 – 4.47 (m, 1H), 4.28 (s, 1H), 3.90 (d, J = 7.4 Hz, 1H), 3.59 (s, 1H), 2.46 (d, J = 1.9 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.17 – 2.08 (m, 1H), 2.08 – 2.00 (m, 1H), 1.95 (d, J = 17.3 Hz, 1H), 1.74 (d, J = 8.3 Hz, 3H), 1.71 (dd, J = 12.9, 2.6 Hz, 1H), 1.67 (d, J = 5.4 Hz, 3H), 1.64 (d, J = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.90, 134.94, 123.68, 113.41, 85.43, 77.30, 77.04, 76.79, 76.40, 72.48, 62.29, 47.35, 43.18, 41.86, 30.91, 19.30, 18.54; IR (KBr, thin film): 3300.20, 2914.44, 2357.01, 1643.35, 1440.83, 1014.56, 893.04, 657.73 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{20}O_2Na^+$ [M + Na^+]: 243.1356; Found: 243.1355. Compound **5-6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 – 5.50 (m, 1H), 5.22 (s, 1H), 4.82 – 4.74 (m, 2H), 4.67 – 4.60 (m, 1H), 3.87 (d, J = 7.5 Hz, 1H), 3.27 (s, 1H), 2.47 (d, J = 2.2 Hz, 1H), 2.26 – 2.10 (m, 2H), 2.09 – 1.97 (m, 2H), 1.96 – 1.87 (m, 1H), 1.74 (s, 3H), 1.67 (s, 3H), 1.56 (ddd, J = 15.0, 9.7, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.01, 134.62, 124.31, 113.28, 84.95, 76.47, 73.35, 60.81, 47.47, 40.74, 40.42, 30.80, 19.34, 18.05; IR (KBr, thin film): 3302.13, 2912.51, 2358.94, 1643.35, 1436.97, 1078.21, 1014.56, 891.11, 650.01 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{20}O_2Na^+$ [M + Na^+]: 243.1356; Found: 243.1355.

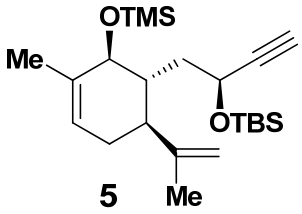
Synthesis of compound 5-7.



To a solution of diol **5-5** (375 mg, 1.7 mmol) in dry CH_2Cl_2 (8 mL) was added imidazole (347 mg, 5.1 mmol) at 0 ^{o}C. After stirring for a while, TBSCl (384 mg, 2.6 mmol) was added into the above solution slowly and then was allowed to warm to rt. The reaction was stirred for 1 h, quenched with sat. $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were dried

over Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane/ethyl acetate (20/1) gave mono-protected alcohol **5-7** as colorless oil in 92% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (d, J = 1.2 Hz, 1H), 4.81 (d, J = 7.8 Hz, 2H), 4.66 (td, J = 7.1, 1.9 Hz, 1H), 3.82 (t, J = 6.5 Hz, 1H), 2.49 (d, J = 6.8 Hz, 1H), 2.44 (d, J = 2.0 Hz, 1H), 2.25 (td, J = 9.8, 5.2 Hz, 1H), 2.19 – 2.10 (m, 1H), 2.03 – 1.90 (m, 2H), 1.85 (ddd, J = 10.4, 6.8, 3.3 Hz, 1H), 1.75 (s, 3H), 1.72 (s, 3H), 1.64 (dt, J = 14.7, 7.5 Hz, 1H), 0.93 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.53, 135.60, 122.72, 112.82, 85.71, 76.17, 73.06, 62.80, 46.31, 42.01, 41.67, 30.30, 25.88, 19.57, 19.12, 18.25, -4.42, -4.79; IR (KBr, thin film): 2954.95, 2926.01, 2856.58, 2358.94, 1259.92, 1083.99, 839.03, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{20}H_{34}O_2SiNa^+$ [M + Na^+]: 357.2220; Found: 357.2215.

Synthesis of compound 5.

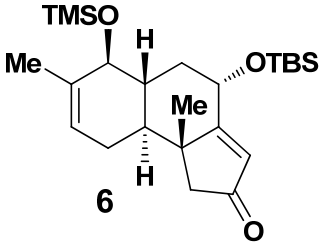


5

To a solution of alcohol **5-7** (696 mg, 2.08 mmol) in dry CH_2Cl_2 (10 mL) was added NEt_3 (631 mg, 6.24 mmol) at 0^{o}C slowly. After stirring for a while, TMSOTf (924 mg, 4.16 mmol) was added into the above solution slowly. The reaction was stirred for 1 h at 0^{o}C, quenched with sat. $NaHCO_3$, and extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were dried with Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane/ethyl acetate (100/1) gave compound **5** as colorless oil in 100% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/16).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (s, 1H), 4.74 (d, J = 13.2 Hz, 2H), 4.53 (td, J = 6.7, 2.0 Hz, 1H), 3.80 (d, 1H), 2.42 (d, J = 2.1 Hz, 1H), 2.29 (dd, J = 10.5, 5.2 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.17 – 2.12 (m, 1H), 2.07 (ddd, J = 17.9, 3.8, 1.9 Hz, 1H), 1.77 (s, 3H), 1.72 (dd, J = 6.6, 1.4 Hz, 2H), 1.69 (d, J = 1.3 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.91, 134.13, 122.83, 111.03, 86.04, 74.01, 72.74, 61.20, 42.32, 41.52, 40.19, 26.91, 25.95, 25.87, 21.81, 21.44, 18.19, 18.15, -3.68, -4.33, -4.87. IR (KBr, thin film): 3309.85, 2954.95, 2929.87, 2856.58, 2357.01, 1251.80, 1091.71, 837.11, 777.31, 651.94 cm^{-1}; HRMS-ESI Calcd. For $C_{23}H_{42}O_2Si_2Na^+$ [M + Na^+]: 429.2616; Found: 429.2616.

Synthesis of Compound 6:

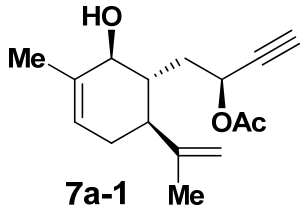


6

To a solution of Pauson-Khand reaction enyene **5** (67 mg, 0.16 mmol) in dry toluene (5 mL, 0.03M) was added $Co_2(CO)_8$ (65 mg, 0.19 mmol) at room temperature. The mixture was stirred at the

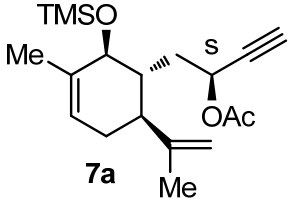
same temperatute for 1.5 h under Ar atmosphere, and TLC indicated that the enyne was converted to its Co-alkyne complex. To this solution was added TMANO (36 mg, 0.48 mmol), and the mixture was stirred 110 ^{o}C for 10 h. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 12/1) to give compound **6** as colorless oil in 80% yield; R_f = 0.2 (silica gel, EtOAc/hexanes = 1/16). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 – 5.45 (m, 1H), 4.86 (td, J = 8.2, 6.2, 2.0 Hz, 1H), 4.81 (d, 2H), 3.84 (t, J = 6.7 Hz, 1H), 2.45 (d, J = 2.0 Hz, 1H), 2.26 (td, J = 9.5, 5.2 Hz, 1H), 2.20 (d, J = 7.8 Hz, 1H), 2.17 – 2.12 (m, 1H), 2.00 (ddd, J = 5.0, 3.5, 1.7 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.75 (d, J = 0.6 Hz, 3H), 1.73 (s, 3H), 1.64 (ddd, J = 15.0, 10.4, 5.8 Hz, 1H), 1.21 – 1.13 (m, 3H), 1.10 (t, J = 6.4 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.69, 135.39, 123.06, 112.69, 85.90, 76.29, 73.07, 62.76, 46.25, 42.25, 41.50, 30.16, 19.65, 19.08, 18.08, 18.05, 17.93, 12.39; IR (KBr, thin film): 2927.94, 2854.65, 1716.65, 1629.85, 1458.18, 1377.17, 1147.65, 837.11, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{24}H_{42}O_3Si_2Na^+$ [M + Na^+]: 457.2565; Found: 457.2563.

Synthesis of Compound 7a-1:



To a solution of diol **5-5** (265 mg, 1.2 mmol) and NEt_3 (364 mg, 3.6 mmol) in dry CH_2Cl_2 (6 mL) was added AcCl (188 mg, 2.4 mmol) at -40 ^{o}C in a dropwise manner, and the reaction mixture was stirred at the same temperature for 1 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (5 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL), and then dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 8/1) to give **7a-1** as colorless oil in 70% yield; R_f = 0.5 (silica gel, EtOAc/hexanes = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.76 (m, 1H), 5.55 – 5.47 (m, 1H), 4.88 – 4.76 (m, 2H), 3.87 (t, 1H), 2.50 (d, J = 2.0 Hz, 1H), 2.22 (dd, J = 9.9, 3.9 Hz, 1H), 2.19 – 2.12 (m, 1H), 2.11 – 2.04 (m, 3H), 2.00 – 1.88 (m, 3H), 1.86 (d, J = 8.3 Hz, 1H), 1.74 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.88, 147.15, 135.12, 123.43, 113.07, 81.80, 76.51, 73.96, 63.89, 46.16, 40.83, 38.15, 30.08, 21.07, 19.39, 18.68; IR (KBr, thin film): 3460.30, 2358.94, 1238.30, 1018.41, 750.31, 669.30 cm^{-1}; HRMS-ESI Calcd. For $C_{16}H_{22}O_3Na^+$ [M + Na^+]: 285.1461; Found: 285.1460.

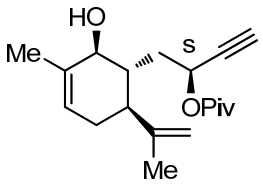
Synthesis of Compound 7a:



To a solution of alcohol **7a-1** (119 mg, 0.45 mmol) and NEt_3 (138 mg, 1.36 mmol) in dry CH_2Cl_2 (4 mL) was added TMSBr (138 mg, 0.9 mmol) at 0 ^{o}C slowly, and the mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by addition of a saturated solution of

$NaHCO_3$ (5 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL), and the combined extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 15/1) to give compound **14a** as colorless oil in 80% yield; R_f = 0.75 (silica gel, EtOAc/hexanes = 1/6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 – 5.47 (m, 1H), 5.43 (td, 1H), 4.86 – 4.79 (m, 2H), 3.98 (d, J = 6.9 Hz, 1H), 2.45 (d, J = 1.9 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.17 – 2.11 (m, 1H), 2.08 (s, 3H), 1.97 – 1.82 (m, 4H), 1.69 (s, 6H), 0.22 (s, 9H); 13C NMR (125 MHz, $CDCl_3$) δ 169.92, 146.68, 135.31, 123.74, 113.04, 82.03, 77.03, 73.46, 62.86, 46.98, 40.73, 37.12, 30.10, 21.01, 20.93, 18.95, 1.09; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.92, 146.68, 135.31, 123.74, 113.04, 82.03, 76.77, 73.46, 62.86, 46.98, 40.73, 37.12, 30.10, 21.01, 20.93, 18.95, 1.09; IR (KBr, thin film): 2954.95, 2920.23, 1743.65, 1645.28, 1373.32, 1251.80, 1091.77, 1020.34 cm^{-1}; HRMS-ESI Calcd. For $C_{19}H_{30}O_3SiNa^+$ [M + Na^+]: 357.1856; Found: 357.1854.

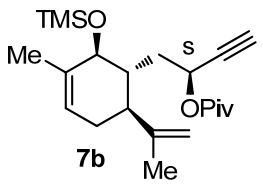
Synthesis of Compound 7b-1:



7b-1

To a solution of the diol **5-5** (111 mg, 0.5 mmol), NEt_3 (153 mg, 1.51 mmol), and DMAP (3 mg, 0.025 mmol) in dry CH_2Cl_2 (5 mL) was added PivCl (72 mg, 0.6 mmol) at room temperature, and the reaction mixture was stirred at the same temperature for 1 h. The reaction was worked up by addition of a saturated NH_4Cl solution (2 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give compound **7b-1** as colorless oil in 85% yield; R_f = 0.7 (silica gel, EtOAc/hexanes = 1/3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 – 5.71 (m, 1H), 5.53 – 5.47 (m, 1H), 4.83 – 4.78 (s, 2H), 3.86 (d, J = 6.4 Hz, 1H), 2.45 (d, J = 2.1 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.19 – 2.12 (m, 1H), 2.01 – 1.86 (m, 3H), 1.73 (s, 6H), 1.69 – 1.62 (m, 1H), 1.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.46, 147.35, 135.11, 123.26, 112.90, 81.97, 76.30, 73.62, 63.58, 45.78, 40.58, 38.67, 37.99, 29.85, 27.05, 19.52, 18.94; IR (KBr, thin film): 3473.80, 2970.38, 2920.23, 1730.15, 1643.35, 1456.26, 1278.81, 1153.43, 894.97, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{19}H_{28}O_3Na^+$ [M + Na^+]: 327.1931; Found: 327.1931.

Synthesis of Compound 7b:

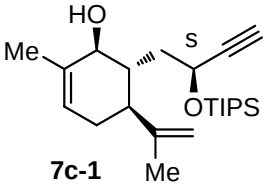


7b

To a solution of alcohol **7b-1** (130 mg, 0.43 mmol) and NEt_3 (130 mg, 1.28 mmol) in dry CH_2Cl_2 (5 mL) was added TMSOTf (189 mg, 0.85 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (2 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over

Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 25/1) to give compound **7b** as colorless oil in 95% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 – 5.46 (m, 1H), 5.40 (td, 1H), 4.81 (s, 2H), 3.97 (d, J = 4.7 Hz, 1H), 2.41 (d, J = 2.0 Hz, 1H), 2.23 (td, J = 9.4, 4.7 Hz, 1H), 2.20 – 2.11 (m, 1H), 1.96 – 1.83 (m, 4H), 1.69 (s, 3H), 1.68 (s, 3H), 1.21 (s, 9H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.29, 146.80, 135.33, 123.57, 112.86, 82.24, 76.79, 73.20, 62.67, 46.69, 40.35, 38.67, 37.14, 29.86, 27.07, 21.00, 18.99, 1.08; IR (KBr, thin film): 3072.60, 2958.80, 1737.86, 1643.36, 1479.40, 1456.26, 1251.80, 1147.65, 1070.49, 883.40 cm^{-1}; HRMS-ESI Calcd. For $C_{22}H_{36}O_3SiNa^+$ [M + Na^+]: 399.2326; Found: 399.2318.

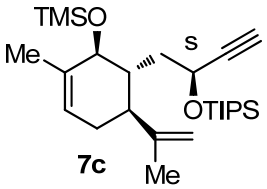
Synthesis of Compound 7c-1:



7c-1

To a solution of diol **5-5** (170 mg, 0.77 mmol) and NEt_3 (195 mg, 1.93 mmol) in dry CH_2Cl_2 (6 mL) was added TIPSOTf (260 mg, 0.85 mmol) at -78 °C in a dropwise manner, and the reaction mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (5 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 12/1) to give compound **7c-1** as colorless oil in 94% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 – 5.45 (m, 1H), 4.86 (td, J = 8.2, 6.2, 2.0 Hz, 1H), 4.81 (d, 2H), 3.84 (t, J = 6.7 Hz, 1H), 2.45 (d, J = 2.0 Hz, 1H), 2.26 (td, J = 9.5, 5.2 Hz, 1H), 2.20 (d, J = 7.8 Hz, 1H), 2.17 – 2.12 (m, 1H), 2.00 (ddd, J = 5.0, 3.5, 1.7 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.75 (d, J = 0.6 Hz, 3H), 1.73 (s, 3H), 1.64 (ddd, J = 15.0, 10.4, 5.8 Hz, 1H), 1.21 – 1.13 (m, 3H), 1.10 (t, J = 6.4 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.69, 135.39, 123.06, 112.69, 85.90, 76.29, 73.07, 62.76, 46.25, 42.25, 41.50, 30.16, 19.65, 19.08, 18.08, 18.05, 17.93, 12.39; IR (KBr, thin film): 3309.85, 2922.16, 1463.97, 1379.10, 1259.52, 1085.92, 1060.85, 883.40, 680.87 cm^{-1}; HRMS-ESI Calcd. For $C_{23}H_{40}O_2SiNa^+$ [M + Na^+]: 399.2690; Found: 399.2690.

Synthesis of Compound 7c:

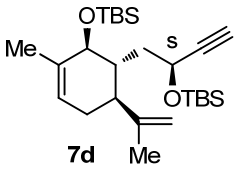


7c

To a solution of **7c-1** (273 mg, 0.72 mmol) and NEt_3 (220 mg, 2.17 mmol) in dry CH_2Cl_2 (6 mL) was added TMSOTf (322 mg, 1.45 mmol) at 0 °C in a dropwise manner, and the reaction mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (5 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and then concentrated under vacuum. The residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 100/1) to give compound **7c** as colorless oil in 85% yield; R_f = 0.7 (silica gel, EtOAc/hexanes = 1/32). ^{1}H NMR

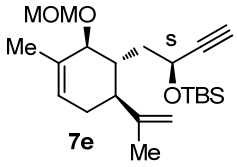
(500 MHz, $CDCl_3$) δ 5.55 – 5.49 (m, 1H), 4.81 – 4.76 (m, 2H), 4.73 (td, 1H), 4.12 (d, J = 5.7 Hz, 1H), 2.43 (d, J = 2.1 Hz, 1H), 2.30 (td, J = 8.3, 5.7 Hz, 1H), 2.23 – 2.12 (m, 1H), 2.10 – 2.03 (m, 1H), 1.99 (dt, J = 17.5, 5.0 Hz, 1H), 1.89 (ddd, J = 13.0, 8.8, 4.0 Hz, 1H), 1.76 (s, 3H), 1.73 (d, J = 6.2 Hz, 1H), 1.69 (s, 3H), 1.18 – 1.12 (m, 3H), 1.11 – 1.07 (m, 18H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.63, 134.78, 123.65, 111.67, 86.44, 75.60, 73.20, 61.51, 44.88, 40.86, 40.58, 29.11, 21.26, 19.87, 18.12, 18.10, 12.41, 1.11; IR (KBr, thin film): 2945.30, 2926.01, 2866.22, 1454.33, 1379.10, 1251.80, 1091.71, 883.40, 750.31, 680.87 cm^{-1}; HRMS-ESI Calcd. For $C_{26}H_{48}O_2Si_2Na^+$ [M + Na^+]: 471.3085; Found: 471.3081.

Synthesis of Compound 7d:



To a solution of diol **5-5** (240 mg, 1.09 mmol) and NEt_3 (1.1 g, 10.9 mmol) in dry CH_2Cl_2 (10 mL) was added TBSOTf (863 mg, 3.27 mmol) at -78 ^oC, and the mixture was then stirred at 0 ^oC for 0.5 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (10 mL), and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 80/1) to give compound **7d** as colorless oil in 92% yield; R_f = 0.9 (silica gel, EtOAc/hexanes = 1/8). ^1H NMR (500 MHz, $CDCl_3$) δ 5.50 (s, 1H), 4.74 (d, J = 13.2 Hz, 2H), 4.53 (td, J = 6.7, 2.0 Hz, 1H), 3.80 (d, J = 1.8 Hz, 1H), 2.42 (d, J = 2.1 Hz, 1H), 2.29 (dd, J = 10.5, 5.2 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.12 – 2.03 (m, 1H), 1.77 (s, 3H), 1.73 – 1.67 (m, 6H), 0.92 (s, 9H), 0.89 (s, 9H), 0.16 (s, 3H), 0.13 (d, J = 3.2 Hz, 6H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.91, 134.13, 122.83, 111.03, 86.04, 77.27, 77.01, 76.76, 74.01, 72.74, 61.20, 42.32, 41.52, 40.19, 26.91, 25.95, 25.87, 21.81, 21.44, 18.19, 18.15, -3.68, -4.33, -4.87; IR (KBr, thin film): 2954.95, 2929.87, 2858.51, 1471.69, 1256.66, 1062.78, 837.11, 773.46, 669.30 cm^{-1}; HRMS-ESI Calcd. For $C_{26}H_{48}O_2Si_2Na^+$ [M + Na^+]: 471.3085; Found: 471.3085.

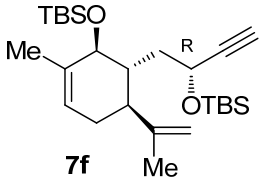
Synthesis of Compound 7e:



To a solution of the alcohol **5-7** (36 mg, 0.11 mmol) and DIPEA (71 mg, 0.55 mmol), and DMAP (1.3 mg, 0.01 mmol) in dry CH_2Cl_2 (1 mL) was added MOMCl (47.6 mg, 0.59 mmol) at 0 ^oC, and the mixture was first stirred at the same temperature for 0.5 h, and then at 40 ^oC overnight. The reaction was quenched by addition of a saturated solution of NaCl (2 mL), and the mixture was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 100/1) to give compound **14e** as colorless oil in 75% yield; R_f = 0.7 (silica gel, EtOAc/hexanes = 1/32). ^1H NMR (500 MHz, $CDCl_3$) δ 5.65 – 5.59 (m,

1H), 4.81 – 4.76 (m, 3H), 4.73 – 4.67 (m, 1H), 4.64 (d, J = 6.4 Hz, 1H), 3.88 (d, J = 6.0 Hz, 1H), 3.44 (s, 3H), 2.42 (d, J = 2.0 Hz, 1H), 2.28 – 2.18 (m, 1H), 2.18 – 2.10 (m, 2H), 2.04 – 1.94 (m, 1H), 1.84 (ddd, J = 12.8, 8.2, 4.4 Hz, 1H), 1.73 (s, 6H), 1.71 – 1.63 (m, 1H), 0.91 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.12, 133.32, 125.47, 112.17, 95.60, 86.07, 81.46, 72.80, 61.65, 56.20, 45.56, 41.59, 37.31, 29.06, 25.85, 20.68, 19.63, 18.20, -4.39, -4.88; IR (KBr, thin film): 2954.95, 2856.58, 1643.35, 1463.97, 1257.59, 1149.57, 1089.78, 891.11, 661.58 cm^{-1}; HRMS-ESI Calcd. For $C_{22}H_{38}O_3SiNa^+$ [M + Na^+]: 401.2482; Found: 401.2467.

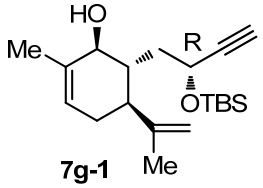
Synthesis of Compound 7f:



7f

To a solution of diol **5-6** (127 mg, 0.58 mmol) and NEt_3 (291 mg, 2.9 mmol) in dry CH_2Cl_2 (5 mL) was added. TBSOTf (459 mg, 1.74 mmol) at -78 °C, and the mixture was then stirred at 0 °C for 0.5 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (2 mL), and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 80/1) to give compound **7f** as colorless oil in 88% yield; R_f = 0.9 (silica gel, EtOAc/hexanes = 1/8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (s, 1H), 4.74 (d, J = 13.7 Hz, 2H), 4.54 (td, J = 6.7, 2.0 Hz, 1H), 3.80 (d, J = 1.9 Hz, 1H), 2.42 (d, J = 2.1 Hz, 1H), 2.29 (dd, J = 10.4, 5.2 Hz, 1H), 2.25 – 2.13 (m, 2H), 2.12 – 2.03 (m, 1H), 1.78 (s, 3H), 1.72 (dd, J = 6.6, 1.8 Hz, 2H), 1.69 (d, J = 1.4 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.17 (s, 3H), 0.13 (d, J = 3.0 Hz, 6H), 0.10 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 147.91, 134.14, 122.84, 111.03, 86.04, 77.27, 77.01, 76.76, 74.02, 72.74, 61.21, 42.33, 41.53, 40.21, 26.91, 25.95, 25.87, 21.81, 21.44, 18.18, 18.15, -3.68, -4.31, -4.33, -4.87; IR (KBr, thin film): 2954.95, 2895.15, 2360.87, 1645.28, 1456.26, 1257.59, 1062.78, 837.11, 765.74, 669.30 cm^{-1}; HRMS-ESI Calcd. For $C_{26}H_{48}O_2Si_2Na^+$ [M + Na^+]: 471.3085; Found: 471.3072.

Synthesis of Compound 7g-1:

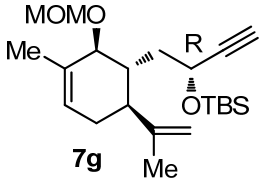


7g-1

To a solution of diol **5-6** (375 mg, 1.7 mmol) and imidazole (347 mg, 5.1 mmol) in dry CH_2Cl_2 (8 mL) was added TBSCl (384 mg, 2.6 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (5 mL), and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give mono-protected alcohol **7g-1** as colorless oil in 87% yield; R_f = 0.85 (silica gel, EtOAc/hexanes = 1/6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 – 5.44 (m, 1H), 4.76 (s, 2H), 4.70 (td, J = 3.9, 2.0 Hz, 1H), 4.01 (s, 1H), 3.81 (d,

J = 5.7 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.17 (t, J = 9.8 Hz, 2H), 2.13 – 2.00 (m, 1H), 1.99 – 1.85 (m, 2H), 1.75 (s, 3H), 1.72 – 1.64 (m, 3H), 1.56 – 1.47 (m, 1H), 0.92 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.85, 135.48, 122.85, 112.75, 84.08, 75.54, 73.90, 62.39, 47.05, 41.46, 40.88, 30.46, 25.71, 19.70, 18.35, 18.16, -4.73, -5.23; IR (KBr, thin film): 3308.95, 2954.95, 2927.94, 2856.58, 1257.59, 1083.99, 837.11, 779.24 cm^{-1}; HRMS-ESI Calcd. For $C_{20}H_{34}O_2SiNa^+$ [M + Na^+]: 357.2220; Found: 357.2213.

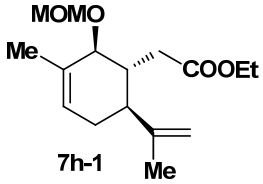
Synthesis of Compound 7g:



7g

To a solution of the alcohol **7g-1** (36 mg, 0.11 mmol), DIPEA (71 mg, 0.55 mmol), and DMAP (1.3 mg, 0.01 mmol) in dry CH_2Cl_2 (1 mL) was added MOMCl (47.6 mg, 0.59 mmol) at 0 °C, and the mixture was first stirred at 0 °C for 0.5 h, and then at 40 °C overnight. The reaction was quenched by addition of a saturated solution of NaCl (1 mL), and the mixture was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 80/1) to give compound **7g** as colorless oil in 75% yield; R_f = 0.9 (silica gel, EtOAc/hexanes = 1/8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (dd, J = 2.9, 1.5 Hz, 1H), 4.81 – 4.77 (m, 3H), 4.69 (d, J = 6.6 Hz, 1H), 4.65 – 4.55 (m, 1H), 3.91 (d, J = 6.8 Hz, 1H), 3.45 (s, 3H), 2.40 (d, J = 2.1 Hz, 1H), 2.27 – 2.19 (m, 1H), 2.19 – 2.12 (m, 1H), 2.12 – 2.06 (m, 1H), 1.99 – 1.91 (m, 1H), 1.87 – 1.76 (m, 2H), 1.73 (s, 6H), 0.91 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.34, 133.93, 124.73, 112.21, 96.89, 86.07, 81.88, 72.42, 61.67, 56.27, 46.01, 40.54, 37.98, 29.46, 25.86, 20.54, 19.23, 18.16, -4.43, -4.85; IR (KBr, thin film): 2954.95, 2924.09, 2854.65, 1261.45, 1043.49, 894.97, 806.25, 750.31, 669.30 cm^{-1}; HRMS-ESI Calcd. For $C_{22}H_{38}O_3SiNa^+$ [M + Na^+]: 401.2482; Found: 401.2488.

Synthesis of Compound 7h-1:

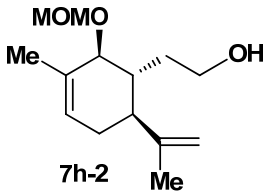


7h-1

To a solution of the alcohol **5-2** (200 mg, 0.84 mmol), DIPEA (217 mg, 1.68 mmol), and DMAP (10 mg, 0.084 mmol) in dry CH_2Cl_2 (5 mL) was added MOMCl (122 mg, 1.5 mmol) at 0 °C, and the mixture was first stirred at 0 °C for 0.5 h, and then at 40 °C overnight. The reaction was quenched by addition of a saturated solution of NaCl (5 mL), and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give compound **7h-1** as colorless oil in 75% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (d, J = 2.5 Hz, 1H), 4.75 (s, 2H), 4.71 (d, J = 6.7 Hz, 1H), 4.64 (d, J = 6.7 Hz, 1H), 4.11 – 4.01 (m, 3H), 3.38 (s, 3H), 2.52 (dd, J = 16.6, 4.5

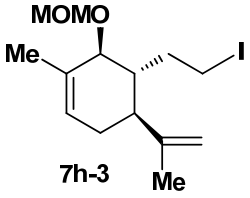
Hz, 1H), 2.44 (td, J = 11.0, 5.1 Hz, 1H), 2.37 (dd, J = 16.6, 5.1 Hz, 1H), 2.21 – 2.07 (m, 2H), 1.91 (d, J = 17.4 Hz, 1H), 1.70 (s, 3H), 1.64 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.76, 146.38, 134.23, 124.96, 113.09, 97.21, 82.02, 59.86, 56.05, 45.76, 39.60, 34.52, 30.32, 19.96, 18.41, 14.15; IR (KBr, thin film): 2970.38, 2920.23, 1734.01, 1643.35, 1244.09, 1028.06, 920.05, 894.97 cm^{-1}; HRMS-ESI Calcd. For $C_{16}H_{26}O_4Na^+$ [M + Na^+]: 305.1723; Found: 305.1723.

Synthesis of Compound 7h-2:



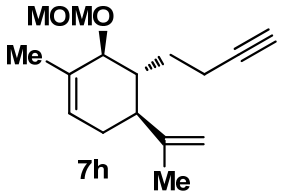
To a solution of $LiAlH_4$ (377 mg, 9,9 mmol) in dry THF (25 mL) was added the solution of ester **7h-1** (1.4 g, 5 mmol) in dry THF (15 mL) at 0 °C in a dropwise manner, and the reaction mixture was allowed to warm up to rt, and the mixture was stirred at rt for 40 min. The reaction was worked up by addition of ethyl acetate (5 mL) at 0 °C in a dropwise manner, followed by addition of a saturated solution of Na/K tartrate (10 mL) and water (10 mL). The resultant mixture was stirred at room temperature until a clear solution was obtained. The mixture was extracted with ethyl acetate (3 x 40 mL), and the combined organic extracts were dried with Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 3/1) to give compound **7h-2** as yellow oil in 90% yield; R_f = 0.1 (silica gel, EtOAc/hexanes = 1/4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 – 5.52 (m, 1H), 4.76 (s, 2H), 4.73 (d, J = 6.7 Hz, 1H), 4.69 – 4.62 (m, 1H), 4.03 (d, J = 7.9 Hz, 1H), 3.76 (dd, J = 11.1, 5.9 Hz, 1H), 3.66 (dt, J = 10.9, 5.4 Hz, 1H), 3.43 (d, J = 1.1 Hz, 3H), 2.77 (t, J = 5.5 Hz, 1H), 2.22 (td, J = 10.5, 4.8 Hz, 1H), 2.18 – 2.07 (m, 1H), 1.96 – 1.86 (m, 2H), 1.86 – 1.77 (m, 1H), 1.66 (d, J = 5.7 Hz, 6H), 1.59 – 1.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.90, 133.62, 126.07, 112.60, 95.81, 82.71, 60.47, 56.15, 46.85, 38.83, 34.09, 30.46, 19.99, 18.32; IR (KBr, thin film): 3412.08, 2918.30, 1641.42, 1274.95, 1091.71, 920.05, 891.11, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{24}O_3Na^+$ [M + Na^+]: 263.1618; Found: 263.1617.

Synthesis of Compound 7h-3:



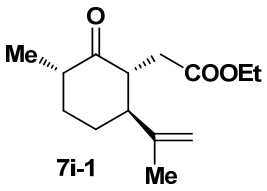
To a solution of the alcohol **7h-2** (50 mg, 0.21 mmol) in dry CH_2Cl_2 (5 mL) was sequentially added PPh_3 (71 mg, 0.27 mmol), iodine (75 mg, 0.29 mmol), and imidazole (21 mg, 0.32 mmol) at 0 °C, and the mixture was then stirred at room temperature for 1 h. The reaction was quenched by addition of water (3 mL), and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed with a saturated solution of $Na_2S_2O_3$ (5 mL), and finally dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was filtered through a Buchner funnel filled with silica gel, and eluted with hexane/ethyl acetate (10/1) gave compound **7h-3** as yellow oil in 86% yield; R_f = 0.9 (silica gel, EtOAc/hexanes = 1/4).

Synthesis of Compound 7h:



To a solution of trimethyl silyl acetylene (45 mg, 0.46 mmol) in dry THF (3 mL) was added ^{n}BuLi (2.5 M in hexane, 0.18 mL, 0.46 mmol) at -78 ^{o}C in a dropwise manner, and the mixture was first stirred at the same temperature for 0.5 h, and then warmed to 0 ^{o}C. To this solution was added a solution of iodide **7h-3** (80 mg, 0.23 mmol) in HMPA (2 mL), and the mixture was stirred at 0 ^{o}C for 15 min. The reaction was quenched by addition of a saturated solution of NH_4Cl (5 mL), and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic extracts were dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was dissolved in MeOH (2 mL), followed by addition of K_2CO_3 (107 mg, 0.78 mmol), and the mixture was then stirred at rt for 1 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (3 mL), and mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by b a flash column chromatography on silica gel (hexane/ethyl acetate = 40/1) to give compound **7h** as yellow oil in 70% yield; R_f = 0.75 (silica gel, EtOAc/hexanes = 1/16). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (dd, J = 2.5, 1.2 Hz, 1H), 4.78 (s, 2H), 4.74 (d, J = 6.8 Hz, 1H), 4.69 (d, J = 6.9 Hz, 1H), 3.87 (d, J = 7.9 Hz, 1H), 3.44 (s, 3H), 2.26 (tt, J = 12.8, 5.1 Hz, 2H), 2.22 – 2.16 (m, 1H), 2.16 – 2.07 (m, 1H), 1.91 (dd, J = 14.4, 3.6 Hz, 3H), 1.79 (ddd, J = 11.3, 8.1, 4.3 Hz, 1H), 1.73 – 1.64 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.63, 133.94, 125.23, 112.50, 96.47, 84.93, 80.42, 67.97, 56.19, 45.53, 40.42, 30.08, 29.21, 20.20, 18.56, 14.91; IR (KBr, thin film): 3309.85, 2918.30, 2848.86, 2322.29, 1265.30, 1026.13, 896.90, 802.39, 740.67 cm^{-1}; HRMS-ESI Calcd. For $C_{16}H_{24}O_2Na^+$ [M + Na^+]: 271.1669; Found: 271.1668.

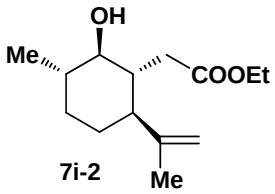
Synthesis of Compound 7i-1:



To a solution of enone **5-1** (340 mg, 1.43 mmol) in dry THF (3 mL) was added L-Selectride (1 M in THF, 1.5 mL, 1.51 mmol) at -78 ^{o}C in a dropwise manner, and the mixture was then stirred at the same temperature for 2 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (10 mL) at 0 ^{o}C, and the resultant mixture was stirred until a colorless solution was obtained. The mixture was extracted with ethyl acetate (3×15mL), and the combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 30/1) to give compound **7i-1** as yellow oil in 60% yield (*dr*>10:1); R_f = 0.5 (silica gel, EtOAc/hexanes = 1/10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 (s, 1H), 4.72 (s, 1H), 4.10 – 4.01 (m, 2H), 2.89 – 2.81 (m, 1H), 2.52 (dd, J = 16.9, 9.7 Hz, 1H), 2.45 (dd, J = 12.8, 6.4 Hz, 1H), 2.19 – 2.10 (m, 2H), 2.11 – 2.02 (m, 1H), 1.89 – 1.79 (m,

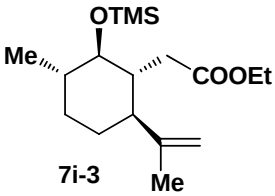
1H), 1.74 (ddd, J = 13.5, 6.8, 3.6 Hz, 1H), 1.67 (s, 3H), 1.33 (qd, J = 13.1, 3.7 Hz, 1H), 1.20 (q, J = 7.0 Hz, 3H), 0.98 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.54, 172.90, 145.54, 112.94, 60.22, 53.27, 49.38, 44.92, 35.25, 32.04, 31.16, 18.14, 14.40, 14.12; IR (KBr, thin film): 2966.52, 2931.80, 1768.72, 1448.54, 1375.25, 1240.23, 1056.99, 891.11, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{22}O_3Na^+$ [M + Na^+]: 261.1461; Found: 261.1460.

Synthesis of Compound 7i-2:



To a solution of ketone **7i-1** (101 mg, 0.42 mmol) in dry MeOH (4 mL) was added $NaBH_4$ (18 mg, 0.46 mmol) at 0 °C, and the mixture was stirred at the same temperature for 0.5 h. the reaction was quenched by addition of water (3 mL), and the mixture was concentrated under vacuum to remove methanol. The remained mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 15/1) to give compound **7i-2** as yellow oil in 40% yield (together with its isomer in 45% yield); R_f = 0.7 (silica gel, EtOAc/hexanes = 1/3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (s, 1H), 4.73 (s, 1H), 4.18 – 4.04 (m, 2H), 2.92 (dd, J = 16.8, 9.6 Hz, 1H), 2.49 (dd, J = 15.9, 2.9 Hz, 1H), 2.24 (dd, J = 15.9, 7.5 Hz, 1H), 2.04 (d, J = 7.1 Hz, 1H), 1.92 (ddd, J = 12.6, 10.4, 3.1 Hz, 1H), 1.86 (ddd, J = 11.4, 6.1, 2.7 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.66 (d, J = 5.8 Hz, 3H), 1.58 (ddd, J = 13.1, 6.6, 3.3 Hz, 1H), 1.46 – 1.34 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.13 – 1.04 (m, 1H), 1.04 – 0.98 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.79, 147.30, 112.39, 81.05, 60.37, 50.29, 43.79, 40.11, 36.32, 32.94, 31.54, 18.71, 18.59, 14.17; IR (KBr, thin film): 3358.09, 2926.01, 2856.58, 1732.08, 1643.35, 1454.33, 1375.25, 1273.02, 1165.00, 891.11 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{25}O_3^+$ [M + H^+]: 241.1798; Found: 241.1804.

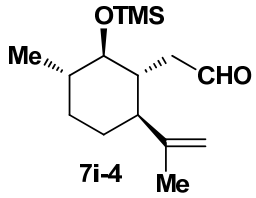
Synthesis of Compound 7i-3:



To a solution of the alcohol **7i-2** (347 mg, 1.44 mmol) and 2,6-lutidine (773 mg, 7.22 mmol) in dry CH_2Cl_2 (10 mL) was added TMSOTf (962 mg, 4.33 mmol) at 0 °C in a dropwise manner, and the reaction mixture was then stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (10 mL), and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 40/1) to give compound **7i-3** as yellow oil in 90% yield; R_f = 0.9 (silica gel, EtOAc/hexanes = 1/6). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68 (d, J = 2.8 Hz, 2H), 4.10 – 4.01 (m, 2H), 3.34 (t, J = 9.7 Hz, 1H), 2.45 (dd, J = 17.0, 4.4 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.22 – 2.12 (m, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 1.63 (m, 1H), 1.61 (s, 3H), 1.54 – 1.48 (m, 1H), 1.39 (dt, J = 7.6, 3.6 Hz,

1H), 1.37 – 1.30 (m, 1H), 1.21 (t, J = 7.1 Hz, 3H), 1.09 (ddd, J = 25.6, 13.1, 3.6 Hz, 1H), 0.95 (d, J = 6.5 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.76, 147.51, 111.99, 80.18, 59.75, 49.23, 43.80, 40.43, 33.65, 33.00, 31.52, 19.98, 18.50, 14.20, 0.95; IR (KBr, thin film): 2926.01, 2854.65, 2360.87, 1734.01, 1458.18, 1375.25, 1261.45, 1176.58, 896.90, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{17}H_{32}O_3SiNa^+$ [M + Na^+]: 335.2013; Found: 335.2007

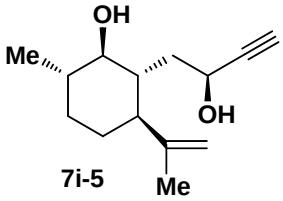
Synthesis of Compound 7i-4:



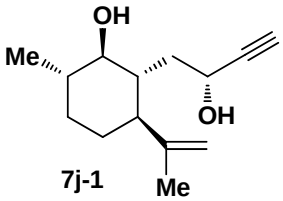
7i-4

To a solution of ester **7i-3** (747 mg, 2.4 mmol) in dry distilled toluene (10 mL) was added DIBAL (1.0 M in toluene, 1.4 mL, 1.4 mmol) at -78 °C in a dropwise manner, and the mixture was stirred at the same temperature for 10 min. To this solution was added second portion of DIBAL solution (1.0 M in toluene, 1.2 mL, 1.2 mmol) at -78 °C in dropwise manner, and the resultant mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by first addition of methanol (2.5 mL) at -78 °C in a dropwise manner, followed by addition of a saturated solution of Na/K tartrate (10 mL), as well as Et_2O (10 mL). The resultant mixture was then stirred at room temperature for 2 h. The mixture was extracted with ethyl acetate (3×20 mL), and the combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by filtration through a Buchner funnel filled with silica gel eluted with hexane/ethyl acetate (10/1) to give compound **7i-4** as yellow oil in 80% yield; R_f = 0.75 (silica gel, EtOAc/hexanes = 1/8).

Synthesis of Compounds 7i-5 and 7j-1:



7i-5



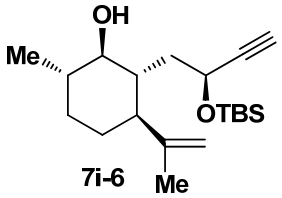
7j-1

To a solution of aldehyde **7i-4** (493 mg, 1.84 mmol) in distilled THF (10 mL) was added ethynylmagnesium chloride (0.5 M in THF, 11 mL, 5.51 mmol) at 0 °C, and the mixture was then stirred at 0 °C for 2 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (10 mL), and the resultant mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was directly dissolved in THF (10 mL). To this solution was added TBAF (1.0 M in THF, 2.76 mL, 2.76 mmol), and the reaction mixture was stirred at 0 °C for 15 min. The reaction was quenched by addition of a saturated solution of NH_4Cl (10 mL), and the mixture was extracted with ethyl acetate (3 x10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 8/1) to give **7i-5** as colorless oil in 35% yield for two steps; R_f = 0.3 (silica gel, EtOAc/hexanes = 1/3), and **7j-1** as colorless oil in 42% yield for two steps; R_f = 0.35 (silica gel, EtOAc/hexanes = 1/3).

Compound **7i-5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (d, J = 1.4 Hz, 1H), 4.75 (s, 1H), 4.37 (ddd, J = 9.9, 3.7, 2.1 Hz, 1H), 2.92 (t, J = 9.7 Hz, 1H), 2.43 (d, J = 2.1 Hz, 1H), 1.99 (ddd, J = 14.9, 3.7, 2.3 Hz, 1H), 1.93 – 1.80 (m, 1H), 1.78 – 1.68 (m, 2H), 1.66 (s, 3H), 1.62 – 1.54 (m, 1H), 1.52 – 1.44 (m, 1H), 1.44 – 1.38 (m, 1H), 1.36 (dd, J = 12.5, 3.5 Hz, 1H), 1.13 – 1.05 (m, 1H), 1.03 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.35, 112.52, 85.77, 81.07, 72.05, 62.30, 51.54, 44.47, 41.01, 39.84, 32.79, 31.76, 19.19, 18.64; IR (KBr, thin film): 3307.92, 2924.09, 1643.35, 1456.26, 1377.17, 1259.52, 1062.78, 891.11, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{22}O_2Na^+$ [M + Na^+]: 245.1512; Found: 245.1506.

Compound **7j-1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 (d, J = 17.4 Hz, 2H), 4.59 (dt, J = 5.5, 2.5 Hz, 1H), 2.93 (t, J = 9.6 Hz, 1H), 2.45 (d, J = 2.1 Hz, 1H), 2.10 – 1.99 (m, 1H), 1.89 (td, J = 11.7, 3.5 Hz, 1H), 1.80 – 1.69 (m, 2H), 1.67 (s, 3H), 1.65 – 1.53 (m, 2H), 1.49 – 1.38 (m, 2H), 1.15 – 1.07 (m, 1H), 1.04 (t, J = 7.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.60, 112.50, 85.39, 81.04, 73.03, 60.76, 51.20, 42.51, 39.95, 39.56, 32.89, 31.61, 18.68; IR (KBr, thin film): 3307.92, 2924.09, 1643.35, 1456.26, 1377.17, 1259.52, 1087.85, 891.11, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{14}H_{22}O_2Na^+$ [M + Na^+]: 245.1512; Found: 245.1506.

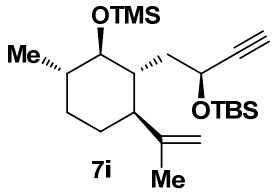
Synthesis of Compounds 7i-6:



7i-6

To a solution of diol **7i-5** (1.24 g, 5.6 mmol) and NEt_3 (1.11 g, 11 mmol) in dry CH_2Cl_2 (15 mL) was added TBSOTf (1.85 g, 7.0 mmol) at -78 °C, the the mixture was stirred at the same temperature for 1 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (10 mL), and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give product **7i-6** as yellow oil in 75% yield (together with double protected product in 15% yield); R_f = 0.65 (silica gel, EtOAc/hexanes = 1/4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (d, J = 18.1 Hz, 2H), 4.53 – 4.43 (m, 1H), 2.90 (d, J = 4.3 Hz, 1H), 2.86 (dd, J = 9.5, 4.3 Hz, 1H), 2.42 (d, J = 2.0 Hz, 1H), 1.96 – 1.86 (m, 2H), 1.83 – 1.72 (m, 1H), 1.69 (d, J = 3.4 Hz, 1H), 1.67 (s, 3H), 1.60 – 1.52 (m, 1H), 1.45 – 1.37 (m, 1H), 1.37 – 1.29 (m, 2H), 1.11 – 1.06 (m, 1H), 1.03 (d, J = 6.4 Hz, 3H), 0.92 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.47, 112.31, 85.73, 80.81, 72.92, 63.13, 51.33, 43.82, 40.87, 40.40, 32.87, 31.91, 25.86, 19.25, 18.76, 18.23, -4.47, -4.87; IR (KBr, thin film): 3311.78, 2926.01, 2858.51, 1724.36, 1653.00, 1456.26, 1259.52, 1068.56, 891.11, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{20}H_{36}O_2SiNa^+$ [M + Na^+]: 359.2377; Found: 359.2374.

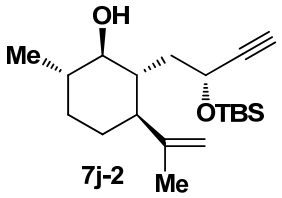
Synthesis of Compounds 7i:



7i

To a solution of alcohol **7i-6** (1.39 g, 4.14 mmol) and 2,6-lutidine (2.22 g, 20.7 mmol) in dry CH_2Cl_2 (15 mL) was added TMSOTf (2.76 g, 12.42 mmol) at 0 ^oC, and the mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (15 mL), and the mixture was extracted with CH_2Cl_2 (3×15 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 80/1) to give compound **7i** as yellow oil in 90% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/10); ^1H NMR (500 MHz, $CDCl_3$) δ 4.77 (s, 2H), 4.55 (td, J = 7.6, 2.0 Hz, 1H), 3.10 (t, J = 9.5 Hz, 1H), 2.37 (d, J = 2.1 Hz, 1H), 1.96 (td, J = 11.9, 3.6 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.76 – 1.72 (m, 1H), 1.70 (d, J = 7.5 Hz, 3H), 1.68 – 1.65 (m, 1H), 1.58 – 1.47 (m, 2H), 1.45 – 1.32 (m, 2H), 1.11 – 1.00 (m, 1H), 0.95 (dd, J = 11.0, 6.1 Hz, 3H), 0.92 – 0.87 (m, 9H), 0.19 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.05, 112.07, 86.71, 82.23, 72.87, 61.89, 51.28, 33.25, 31.95, 25.90, 20.22, 19.16, 18.15, 1.46, -3.81, -4.53; IR (KBr, thin film): 2954.95, 2927.94, 1645.28, 1251.80, 1091.71, 906.54, 837.11, 777.31, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{23}H_{44}O_2Si_2Na^+$ [M + Na^+]: 431.2772; Found: 431.2779

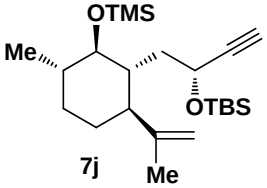
Synthesis of Compounds 7j-2:



7j-2

To a solution of diol **7j-1** (1.24 g, 5.6 mmol) and NEt_3 (1.11 g, 11 mmol) in dry CH_2Cl_2 (15 mL) was added TBSOTf (1.85 g, 7.0 mmol) at -78 ^oC, and reaction mixture was then stirred at this temperature for 1 h. The reaction was quenched by addition of a saturated solution of $NaHCO_3$ (10 mL), and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give product **7j-2** as yellow oil in 75% yield (together with double protected product in 15% yield); R_f = 0.65 (silica gel, EtOAc/hexanes = 1/4); ^1H NMR (400 MHz, $CDCl_3$) δ 4.72 (d, J = 8.7 Hz, 2H), 4.68 – 4.60 (m, 1H), 3.74 (s, 1H), 2.88 (t, J = 9.2 Hz, 1H), 2.44 (d, J = 2.1 Hz, 1H), 2.00 (ddd, J = 8.9, 7.5, 3.2 Hz, 1H), 1.87 (td, J = 11.7, 3.6 Hz, 1H), 1.74 – 1.66 (m, 2H), 1.65 (s, 3H), 1.62 – 1.49 (m, 2H), 1.48 – 1.34 (m, 2H), 1.07 (d, J = 3.4 Hz, 1H), 1.03 (d, J = 6.4 Hz, 3H), 0.91 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.99, 112.08, 84.53, 79.82, 73.48, 62.00, 50.93, 42.75, 40.19, 39.27, 32.91, 31.58, 25.74, 25.66, 18.97, 18.49, 18.06, -4.72, -5.22; IR (KBr, thin film): 3311.78, 2927.94, 2360.87, 1724.36, 1637.56, 1463.97, 1361.74, 1257.59, 1072.42, 891.11 cm^{-1}; HRMS-ESI Calcd. For $C_{20}H_{36}O_2SiNa^+$ [M + Na^+]: 359.2377; Found: 359.2377.

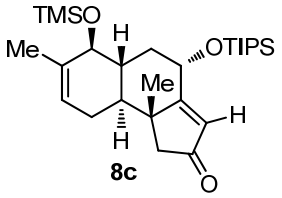
Synthesis of Compounds 7j:



7j

To a solution of alcohol **7j-2** (1.39 g, 4.14 mmol) in dry CH_2Cl_2 (15 mL) was added 2,6-lutidine (2.22 g, 20.7 mmol) at 0 ^oC slowly. After stirring for a while, TMSOTf (2.76 g, 12.42 mmol) was added into the above solution slowly. The reaction was warmed to rt and stirred for 2 h before quenched with sat. $NaHCO_3$ (15 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent gave a residue which was subjected directly to column chromatography on silica gel. Elution with hexane/ethyl acetate (80/1) gave compound **7j** as yellow oil in 85% yield; R_f = 0.8 (silica gel, EtOAc/hexanes = 1/10); ^1H NMR (500 MHz, $CDCl_3$) δ 4.75 – 4.70 (m, 2H), 4.67 – 4.60 (m, 1H), 3.03 (t, J = 9.5 Hz, 1H), 2.36 (d, J = 2.1 Hz, 1H), 1.87 (td, J = 11.7, 3.6 Hz, 1H), 1.79 – 1.70 (m, 1H), 1.69 (d, J = 5.2 Hz, 3H), 1.67 – 1.61 (m, 1H), 1.60 – 1.46 (m, 2H), 1.46 – 1.35 (m, 2H), 1.13 – 1.03 (m, 1H), 0.96 – 0.93 (m, 3H), 0.91 (d, J = 9.0 Hz, 9H), 0.91 – 0.87 (m, 1H), 0.19 (d, J = 3.1 Hz, 9H), 0.15 – 0.12 (m, 3H), 0.11 (d, J = 2.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.46, 111.96, 86.52, 83.77, 72.15, 62.59, 51.88, 42.27, 40.61, 40.19, 33.47, 32.06, 25.97, 20.14, 18.43, 18.29, 1.38, -4.58; IR (KBr, thin film): 2954.95, 2927.94, 2330.01, 1633.71, 1259.52, 1080.14, 906.54, 837.11, 777.31, cm^{-1}; HRMS-ESI Calcd. For $C_{23}H_{44}O_2Si_2Na^+$ [M + Na^+]: 431.2772; Found: 431.2779

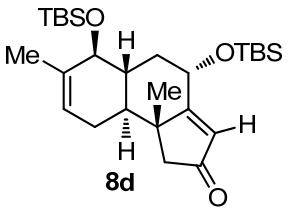
Synthesis of Compounds 8c:



8c

To a solution of enyne **7c** (115 mg, 0.26 mmol) in dry toluene (9 mL, 0.03M) was added $Co_2(CO)_8$ (106 mg, 0.31 mmol), and the mixture was stirred at rt for 1.5 h under Ar atmosphere. To this solution was added TMANO (58 mg, 0.78 mmol), and the mixture was stirred at 110 ^oC for 10 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 16/1) to give product **8c** as colorless oil in 75% yield; R_f = 0.4 (silica gel, EtOAc/hexanes = 1/8). ^1H NMR (500 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.49 (s, 1H), 4.65 (dd, J = 11.2, 5.9 Hz, 1H), 3.85 (d, J = 7.8 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.34 (d, J = 18.6 Hz, 1H), 2.20 (d, J = 18.6 Hz, 1H), 2.04 (dd, J = 14.9, 11.4 Hz, 1H), 1.88 (d, J = 17.1 Hz, 1H), 1.81 – 1.71 (m, 1H), 1.66 (s, 3H), 1.38 (td, J = 11.7, 5.0 Hz, 1H), 1.23 (q, J = 11.9 Hz, 1H), 1.17 – 1.09 (m, 6H), 1.07 (t, J = 6.5 Hz, 18H), 0.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.89, 190.74, 135.54, 123.90, 122.78, 77.73, 68.34, 50.90, 47.35, 46.18, 42.91, 41.16, 26.47, 20.44, 20.20, 18.07, 12.36, 0.98; IR (KBr, thin film): 2960.73, 2854.65, 1716.65, 1627.92, 1456.26, 1261.45, 1114.86, 885.33, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{27}H_{48}O_3Si_2Na^+$ [M + Na^+]: 499.3034; Found: 499.3032.

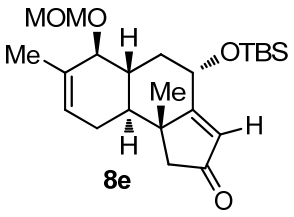
Synthesis of Compounds 8d:



8d

To a solution of enyne **7d** (70 mg, 0.15 mmol) in dry toluene (5 ml, 0.03 M) was added $Co_2(CO)_8$ (62 mg, 0.18 mmol) and stirred at rt for 1.5 h under Ar atmosphere. To this solution was added TMANO (34 mg, 0.45 mmol), and the mixture was stirred at 110 ^oC for 10 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 16/1) to give product **8d** as colorless oil in 65% yield; R_f = 0.4 (silica gel, EtOAc/hexanes = 1/8). ^1H NMR (400 MHz, $CDCl_3$) δ 5.99 (s, 1H), 5.47 (s, 1H), 4.49 (dd, J = 10.8, 6.3 Hz, 1H), 3.83 (d, J = 7.7 Hz, 1H), 2.61 (ddd, J = 12.0, 5.9, 4.2 Hz, 1H), 2.33 (d, J = 18.6 Hz, 1H), 2.20 (d, J = 18.5 Hz, 1H), 2.11 – 1.98 (m, 1H), 1.92 – 1.82 (m, 1H), 1.82 – 1.70 (m, 1H), 1.67 (s, 3H), 1.38 (td, J = 11.7, 5.1 Hz, 1H), 1.19 (d, J = 12.0 Hz, 1H), 1.13 (s, 3H), 0.93 (s, 9H), 0.91 (s, 9H), 0.11 (s, 6H), 0.08 (d, J = 1.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.95, 190.43, 135.88, 123.51, 122.70, 77.17, 67.94, 50.89, 47.01, 46.08, 42.63, 41.01, 26.23, 26.09, 25.61, 20.74, 20.39, 18.33, 18.17, -3.00, -3.54, -5.12, -5.17; IR (KBr, thin film): 2954.95, 2927.94, 1714.72, 1629.85, 1458.18, 1274.95, 1101.35, 1004.91, 860.25, 765.74 cm^{-1}; HRMS-ESI Calcd. For $C_{27}H_{48}O_3Si_2Na^+$ [M + Na^+]: 499.3034; Found: 499.3031.

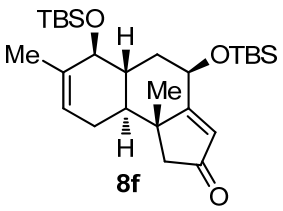
Synthesis of Compounds 7e:



8e

To a solution of enyne **7e** (90 mg, 0.24 mmol) in dry toluene (8 ml, 0.03 M) was added $Co_2(CO)_8$ (96 mg, 0.28 mmol) and stirred at rt for 1.5 h under Ar atmosphere. To this solution was added TMANO (54 mg, 0.72 mmol), and the mixture was stirred at 110 ^oC for 15 h. the reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 16/1) to give product **8e** as colorless oil in 57% yield; R_f = 0.4 (silica gel, EtOAc/hexanes = 1/4). ^1H NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 1H), 5.53 (d, J = 3.3 Hz, 1H), 4.66 (dd, J = 17.5, 7.0 Hz, 2H), 4.49 (dd, J = 11.2, 6.0 Hz, 1H), 3.66 (d, J = 8.0 Hz, 1H), 3.40 (s, 3H), 2.68 – 2.57 (m, 1H), 2.29 (d, J = 18.5 Hz, 1H), 2.16 (d, J = 18.5 Hz, 1H), 2.10 – 1.94 (m, 1H), 1.93 – 1.80 (m, 2H), 1.63 (s, 3H), 1.33 (td, 1H), 1.22 (dd, J = 16.2, 7.5 Hz, 1H), 1.10 (s, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.78, 190.27, 133.82, 124.67, 123.61, 97.04, 84.34, 67.90, 56.15, 50.81, 47.28, 46.02, 41.85, 38.86, 26.20, 25.64, 20.33, 19.60, 18.13, -4.99, -5.15; IR (KBr, thin film): 2954.95, 2927.94, 1712.79, 1627.92, 1462.04, 1257.59, 1114.86, 1031.92, 860.25, 765.74 cm^{-1}; HRMS-ESI Calcd. For $C_{23}H_{38}O_4SiNa^+$ [M + Na^+]: 429.2432; Found: 429.2423

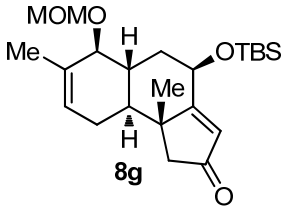
Synthesis of Compounds 8f:



8f

To a solution of enyne **7f** (100 mg, 0.22 mmol) in dry toluene (7 ml, 0.03 M) was added $Co_2(CO)_8$ (90 mg, 0.26 mmol), and the mixture was stirred at rt for 1.5 h under Ar atmosphere. To this solution was added TMANO (50 mg, 0.66 mmol), and the mixture was stirred at 110 ^oC for 10 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 16/1) to give product **8f** as colorless oil in 38% yield; R_f = 0.5 (silica gel, EtOAc/hexanes = 1/8); ^1H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, J = 1.6 Hz, 1H), 5.51 – 5.41 (m, 1H), 4.49 (ddd, J = 11.5, 6.2, 1.4 Hz, 1H), 3.83 (d, J = 7.2 Hz, 1H), 2.61 (ddd, J = 12.3, 6.2, 4.1 Hz, 1H), 2.33 (d, J = 18.6 Hz, 1H), 2.19 (d, J = 18.5 Hz, 1H), 2.10 – 1.95 (m, 1H), 1.93 – 1.81 (m, 1H), 1.81 – 1.70 (m, 1H), 1.65 (s, 3H), 1.37 (td, J = 11.7, 5.2 Hz, 1H), 1.21 (dd, J = 19.5, 7.5 Hz, 1H), 1.14 (d, J = 5.0 Hz, 3H), 0.93 (s, 9H), 0.91 (s, 9H), 0.10 (d, J = 1.3 Hz, 6H), 0.08 (d, J = 1.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.94, 190.44, 135.87, 123.50, 122.69, 77.17, 67.94, 50.88, 47.01, 46.07, 42.62, 41.01, 26.22, 26.08, 25.61, 20.74, 20.39, 18.32, 18.16, -3.00, -3.54, -5.12, -5.17; IR (KBr, thin film): 2954.95, 2929.87, 1712.79, 1629.85, 1471.69, 1255.66, 1062.78, 860.25, 748.38 cm^{-1}; HRMS-ESI Calcd. For $C_{27}H_{49}O_3Si_2^+$ [M + H^+]: 477.3215; Found: 477.3214.

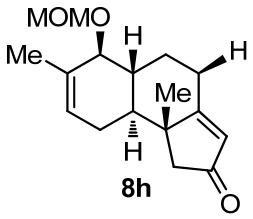
Synthesis of Compounds 8g:



8g

To a solution of enyne **7g** (123 mg, 0.32 mmol) in dry toluene (10 ml, 0.03 M) was added $Co_2(CO)_8$ (131 mg, 0.38 mmol), and the mixture was stirred at rt for 1.5 h under Ar atmosphere. To this solution was added TMANO (72 mg, 0.96 mmol), and the mixture was stirred at 110 ^oC for 20 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 6/1) to give product **8g** as colorless oil in 40% yield; R_f = 0.15 (silica gel, EtOAc/hexanes = 1/8); ^1H NMR (500 MHz, $CDCl_3$) δ 5.80 (s, 1H), 5.60 (d, J = 4.6 Hz, 1H), 4.80 (t, J = 2.8 Hz, 1H), 4.74 (d, J = 6.9 Hz, 1H), 4.70 (d, J = 7.0 Hz, 1H), 3.64 (d, J = 8.1 Hz, 1H), 3.44 (s, 3H), 2.53 (dt, J = 14.0, 3.3 Hz, 1H), 2.29 (d, J = 18.6 Hz, 1H), 2.24 (dt, J = 12.0, 3.5 Hz, 1H), 2.19 (d, J = 18.5 Hz, 1H), 2.17 – 2.09 (m, 1H), 1.94 – 1.80 (m, 1H), 1.69 (s, 3H), 1.41 (td, J = 11.8, 4.7 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.32 (d, J = 9.8 Hz, 3H), 0.89 (s, 9H), 0.07 (d, J = 32.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.29, 184.95, 133.93, 126.04, 124.99, 97.50, 84.87, 67.66, 56.14, 51.86, 48.73, 45.69, 40.98, 35.02, 26.23, 25.71, 22.45, 19.81, 18.12, -4.88, -5.12; IR (KBr, thin film): 2954.95, 2927.94, 1712.79, 1627.92, 1462.04, 1379.10, 1257.59, 1031.92, 860.25, 750.31 cm^{-1}; HRMS-ESI Calcd. For $C_{23}H_{38}O_4SiNa^+$ [M + Na^+]: 429.2432; Found: 429.2423.

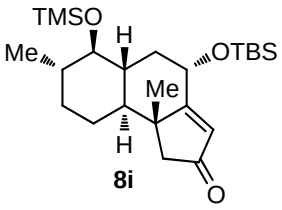
Synthesis of Compounds 8h:



8h

To a solution of enyne **7h** (370 mg, 1.50 mmol) in dry toluene (50 mL, 0.03 M) was added $Co_2(CO)_8$ (615 mg, 1.8 mmol), and the mixture was stirred at rt for 1.5 h under Ar atmosphere. To this solution was added TMANO (337 mg, 4.50 mmol), and the mixture was stirred at 110 ^oC for 11 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 8/1) to give product **8h** as colorless oil in 23% yield; R_f = 0.2 (silica gel, EtOAc/hexanes = 1/8); ^1H NMR (500 MHz, $CDCl_3$) δ 5.75 (s, 1H), 5.56 (s, 1H), 4.71 (dd, J = 6.8, 2.6 Hz, 1H), 4.67 (dd, J = 6.9, 2.6 Hz, 1H), 3.64 (d, J = 8.2 Hz, 1H), 3.42 (d, J = 2.7 Hz, 3H), 2.73 – 2.62 (m, 1H), 2.51 (dd, J = 7.9, 5.1 Hz, 1H), 2.40 (td, J = 13.6, 5.4 Hz, 1H), 2.24 (d, J = 18.5 Hz, 1H), 2.15 (dd, J = 18.5, 2.6 Hz, 1H), 2.06 (ddd, J = 14.2, 8.6, 4.0 Hz, 1H), 1.89 – 1.83 (m, 2H), 1.66 (s, 4H), 1.45 – 1.35 (m, 1H), 1.25 – 1.16 (m, 1H), 1.12 (d, J = 2.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.74, 188.22, 133.97, 125.23, 124.62, 97.49, 84.68, 56.12, 50.22, 47.83, 45.49, 39.56, 32.18, 26.73, 26.36, 19.83, 19.71; IR (KBr, thin film): 2918.90, 2927.94, 1712.49, 1259.52, 1030.14, 896.48, 740.67, 704.02 cm^{-1}; HRMS-ESI Calcd. For $C_{17}H_{25}O_3^+$ [M + H^+]: 277.1798; Found: 277.1798.

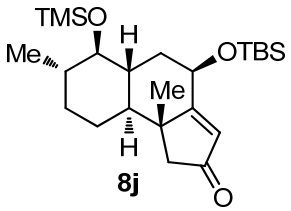
Synthesis of Compounds 8i:



8i

To a solution of enyne **7i** (80 mg, 0.19 mmol) in dry toluene (6.5 mL, 0.03 M) was added $Co_2(CO)_8$ (78 mg, 0.23 mmol) and stirred at rt for 1.5 h under Ar atmosphere. The mixture was stirred at 110 ^oC for 6 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 16/1) to give product **8i** as colorless oil in 85% yield; R_f = 0.35 (silica gel, EtOAc/hexanes = 1/8); ^1H NMR (500 MHz, $CDCl_3$) δ 5.97 (s, 1H), 4.47 (dd, J = 11.0, 6.2 Hz, 1H), 2.85 (t, J = 9.3 Hz, 1H), 2.48 (dd, J = 8.0, 4.0 Hz, 1H), 2.31 (d, J = 18.5 Hz, 1H), 2.20 (d, J = 18.5 Hz, 1H), 1.81 – 1.70 (m, 1H), 1.56 – 1.45 (m, 2H), 1.38 (s, 1H), 1.24 (dd, J = 23.9, 11.3 Hz, 1H), 1.13 – 1.08 (m, 4H), 1.02 (t, J = 12.2 Hz, 2H), 0.94 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 15.3 Hz, 9H), 0.14 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.02, 190.58, 123.75, 82.24, 68.52, 51.35, 50.95, 46.56, 43.22, 41.77, 40.08, 32.76, 27.16, 25.74, 20.46, 19.61, 18.28, 1.06, -5.00; IR (KBr, thin film): 2954.95, 2927.94, 2883.58, 1716.65, 1251.80, 1085.92, 887.26, 775.38, 669.30 cm^{-1}; HRMS-ESI Calcd. For $C_{24}H_{44}O_3Si_2Na^+$ [M + Na^+]: 459.2721; Found: 459.2722.

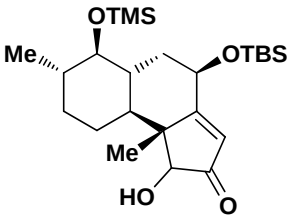
Synthesis of Compounds 8j:



8j

To a solution of enyne **7j** (65 mg, 0.16 mmol) in dry toluene (5 mL, 0.03 M) was added $Co_2(CO)_8$ (65 mg, 0.19 mmol) and stirred at rt for 1.5 h under Ar atmosphere. The mixture was stirred at 110 ^oC for 10.5 h. The reaction was worked up by removal of the solvent under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 8/1) to give product **8j** as colorless oil in 75% yield; R_f = 0.4 (silica gel, EtOAc/hexanes = 1/8); ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H), 4.78 (t, J = 2.7 Hz, 1H), 2.83 (t, J = 9.5 Hz, 1H), 2.37 (dt, J = 13.6, 3.1 Hz, 1H), 2.23 (q, J = 18.6 Hz, 2H), 1.88 (dd, J = 9.2, 2.6 Hz, 1H), 1.81 – 1.71 (m, 1H), 1.54 – 1.41 (m, 2H), 1.34 (dd, J = 12.6, 3.2 Hz, 1H), 1.30 – 1.23 (m, 3H), 1.20 – 1.10 (m, 1H), 1.09 – 0.99 (m, 2H), 0.95 (d, J = 6.5 Hz, 3H), 0.88 (s, 9H), 0.14 (s, 9H), 0.09 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.67, 185.50, 125.86, 82.61, 67.62, 51.97, 51.93, 46.03, 40.26, 39.72, 38.80, 32.74, 27.06, 25.68, 22.14, 19.65, 18.12, 1.06, -5.00, -5.09; IR (KBr, thin film): 2954.95, 2927.94, 1716.65, 1249.87, 1091.71, 835.18, 775.38, 669.30 cm^{-1}; HRMS-ESI Calcd. For $C_{24}H_{45}O_3Si_2^+$ [M + H^+]: 437.2902; Found: 437.2902.

Synthesis of Compound 9:

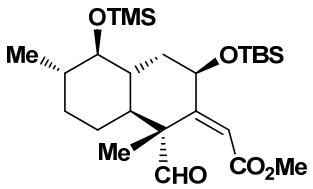


9

To a solution of enone **8i** (31 mg, 0.07 mmol) in a mixed solvent (1.5 mL, CH_2Cl_2 /acetone/H_2O 1:1:1) was added 18-crown-6 (74 mg, 0.28 mmol) and $NaHCO_3$ (411 mg, 4.9 mmol) sequentially, followed by addition of Oxone (387 mg, 063 mmol) in three portions, the resultant mixture was then stirred at room temperature for 1 h. The reaction was worked up by addition of H_2O (2 mL), and the mixture was extracted with ethyl acetate (3×3 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give compound **9** as colorless oil in 88% yield (*dr*=4:1); R_f = 0.5 (silica gel, EtOAc/hexanes = 1/4); ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (d, J = 21.2 Hz, 1H), 4.80 – 4.71 (m, 1H), 3.79 (d, J = 45.0 Hz, 1H), 2.87 (dd, J = 15.8, 6.3 Hz, 1H), 2.42 – 2.20 (m, 2H), 1.95 – 1.87 (m, 1H), 1.80 – 1.63 (m, 1H), 1.46 (td, J = 11.4, 2.7 Hz, 2H), 1.36 (d, J = 6.2 Hz, 2H), 1.30 – 1.23 (m, 3H), 1.15 – 1.01 (m, 2H), 0.96 (t, J = 5.1 Hz, 3H), 0.89 (d, J = 5.4 Hz, 9H), 0.15 (d, J = 5.4 Hz, 9H), 0.11 – 0.06 (m, 3H), 0.03 (d, J = 8.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.69, 207.83, 185.90, 182.86, 123.04, 122.65, 84.21, 82.78, 82.63, 80.79, 68.04, 67.48, 51.60, 49.94, 48.22, 45.00, 40.01, 39.73, 39.65, 39.35, 38.55, 38.47, 32.75, 29.61, 27.73, 26.88, 25.69, 25.62, 22.84, 19.71, 18.12, 18.05, 17.18, 1.24, 1.05, 0.75, -4.96, -5.02; IR (KBr, thin

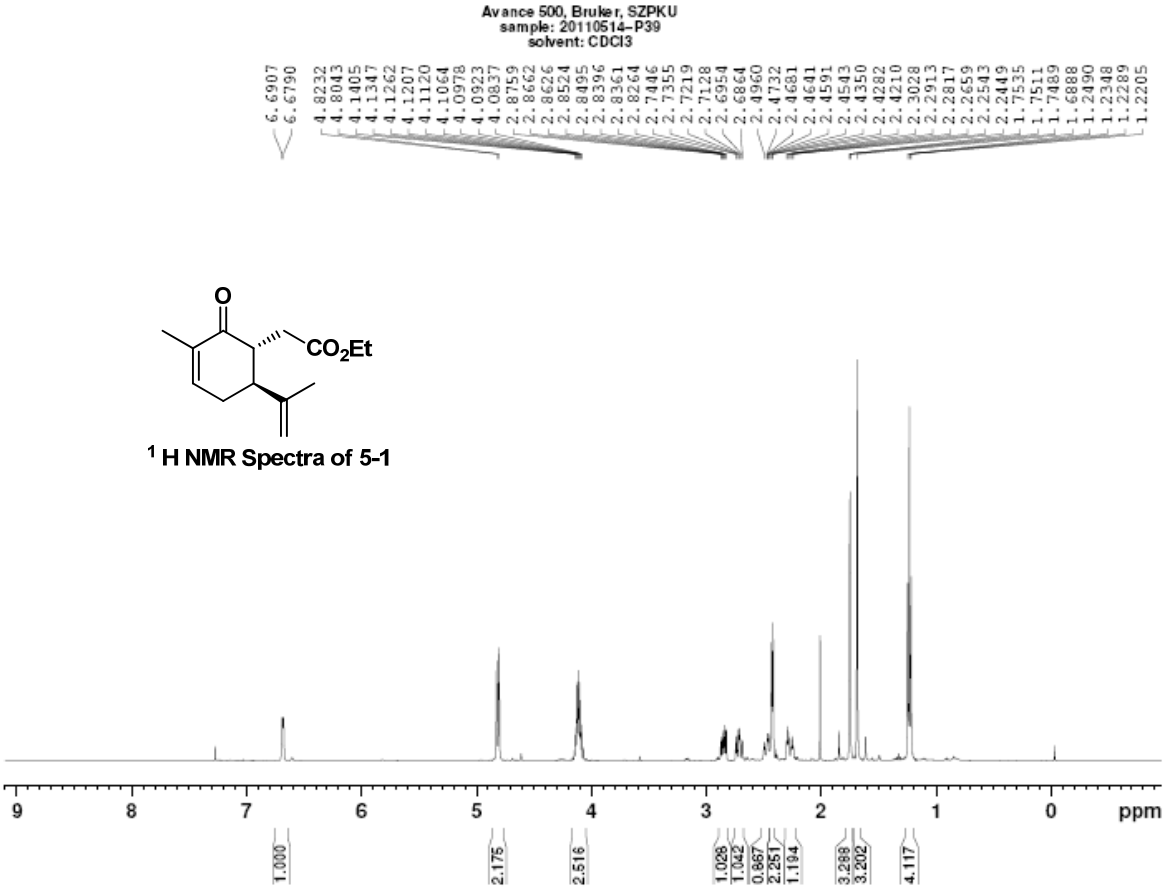
film): 3402.19, 2954.95, 2927.94, 1716.65, 1246.72, 1091.73, 835.18, 775.38, 669.30 cm $^{-1}$; HRMS-ESI Calcd. For $C_{24}H_{44}O_4Si_2Na^+$ [M + Na^+]: 475.2670; Found: 475.2671.

Synthesis of Compound 10:



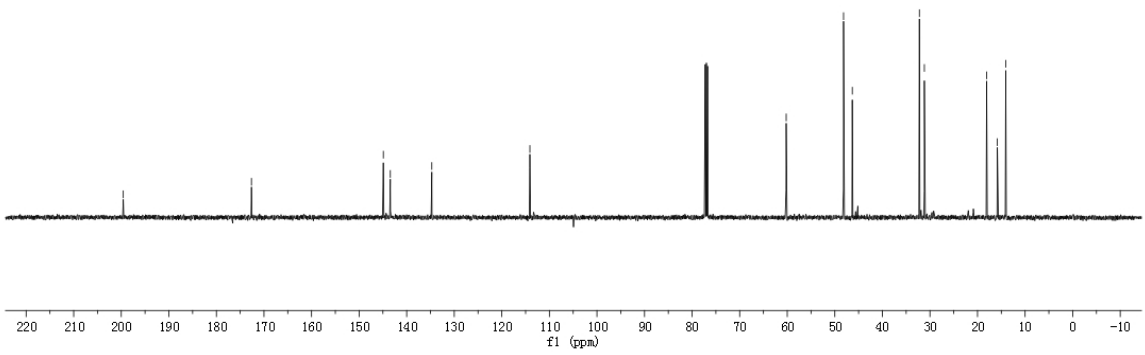
10

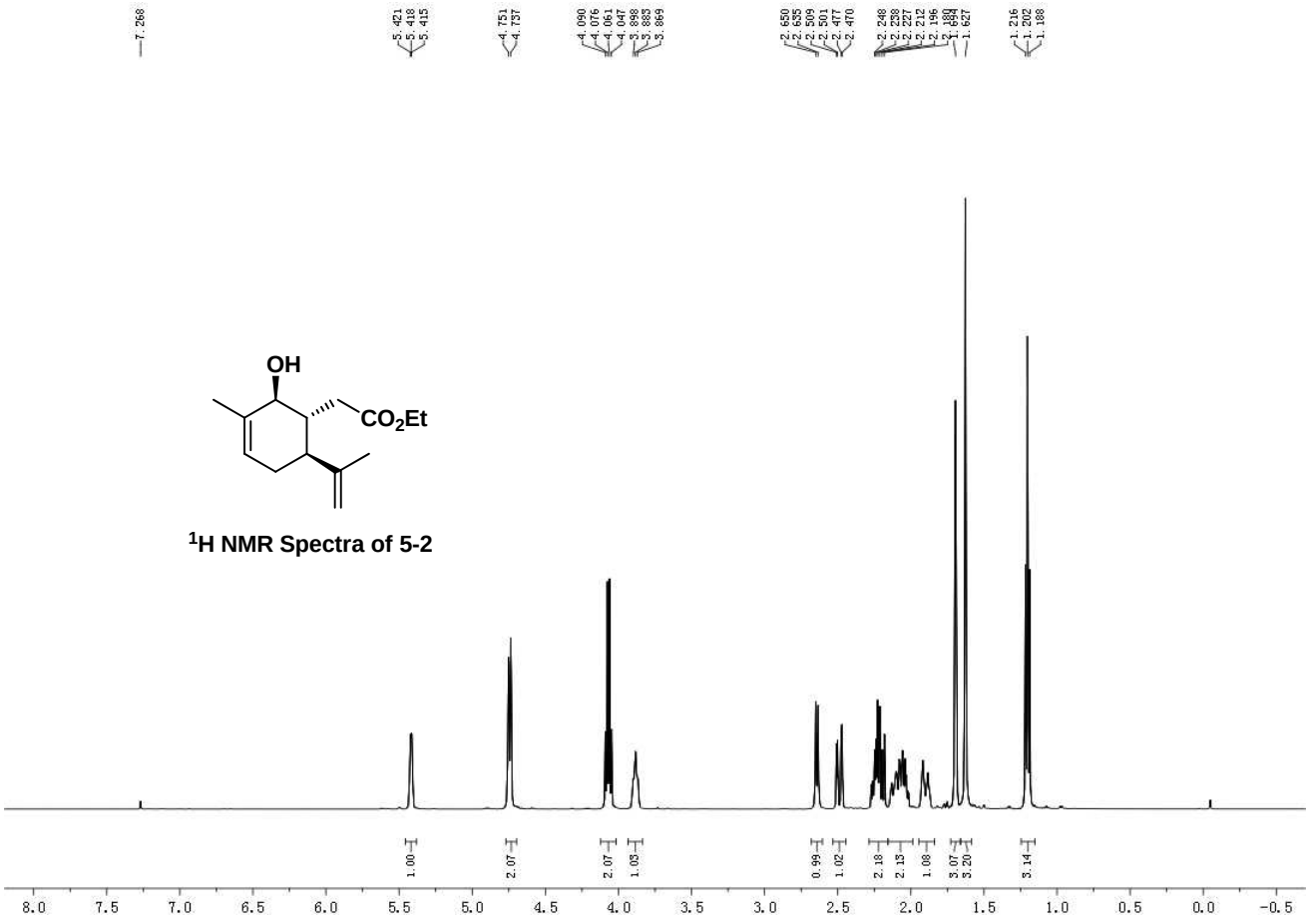
To a solution of **19** (30 mg, 0.066 mmol) in dry MeOH (2 mL) was added $Pb(OAc)_4$ (58 mg, 0.13 mmol) at 0 ^{o}C, and the mixture was the stirred at the same temperature for 15 min. The reaction was quenched by addition of a saturated solution of NH_4Cl (2 mL), and the mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried over Na_2SO_4. The extract was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/ethyl acetate = 16/1) to give compound **10** as yellow oil in 52% yield; R_f = 0.7 (silica gel, EtOAc/hexanes = 1/4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 5.91 (s, 1H), 4.40 – 4.32 (m, 1H), 3.67 (s, 3H), 2.88 (t, J = 9.5 Hz, 1H), 2.13 (dt, J = 13.4, 5.2 Hz, 1H), 1.89 – 1.76 (m, 1H), 1.69 (dd, J = 13.6, 3.3 Hz, 1H), 1.46 (s, 3H), 1.40 (d, J = 11.2 Hz, 2H), 1.36 (d, J = 4.7 Hz, 1H), 1.26 (s, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.90 (s, 9H), 0.15 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.70, 166.70, 159.71, 117.42, 82.87, 73.55, 53.29, 51.41, 42.66, 39.94, 37.74, 36.65, 32.59, 29.69, 25.76, 25.61, 19.64, 18.12, 16.59, 1.15, -4.67, -4.81; IR (KBr, thin film): 2929.87, 2856.58, 2357.01, 2328.08, 1712.13, 1670.35, 1259.52, 1201.65, 1037.70, 748.38 cm $^{-1}$; HRMS-ESI Calcd. For $C_{25}H_{47}O_5Si_2^+$ [M + H^+]: 483.2957; Found: 483.2955.



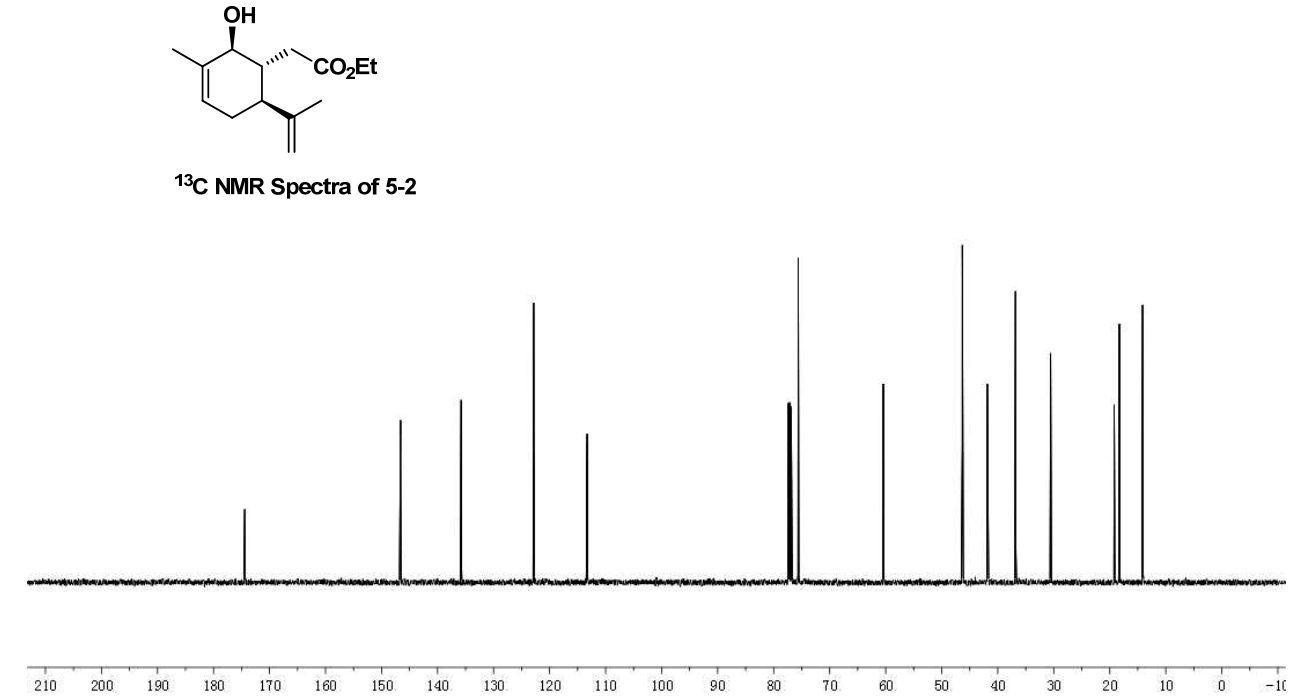
^{1}H NMR Spectra of 5-1

^{13}C NMR Spectra of 5-1

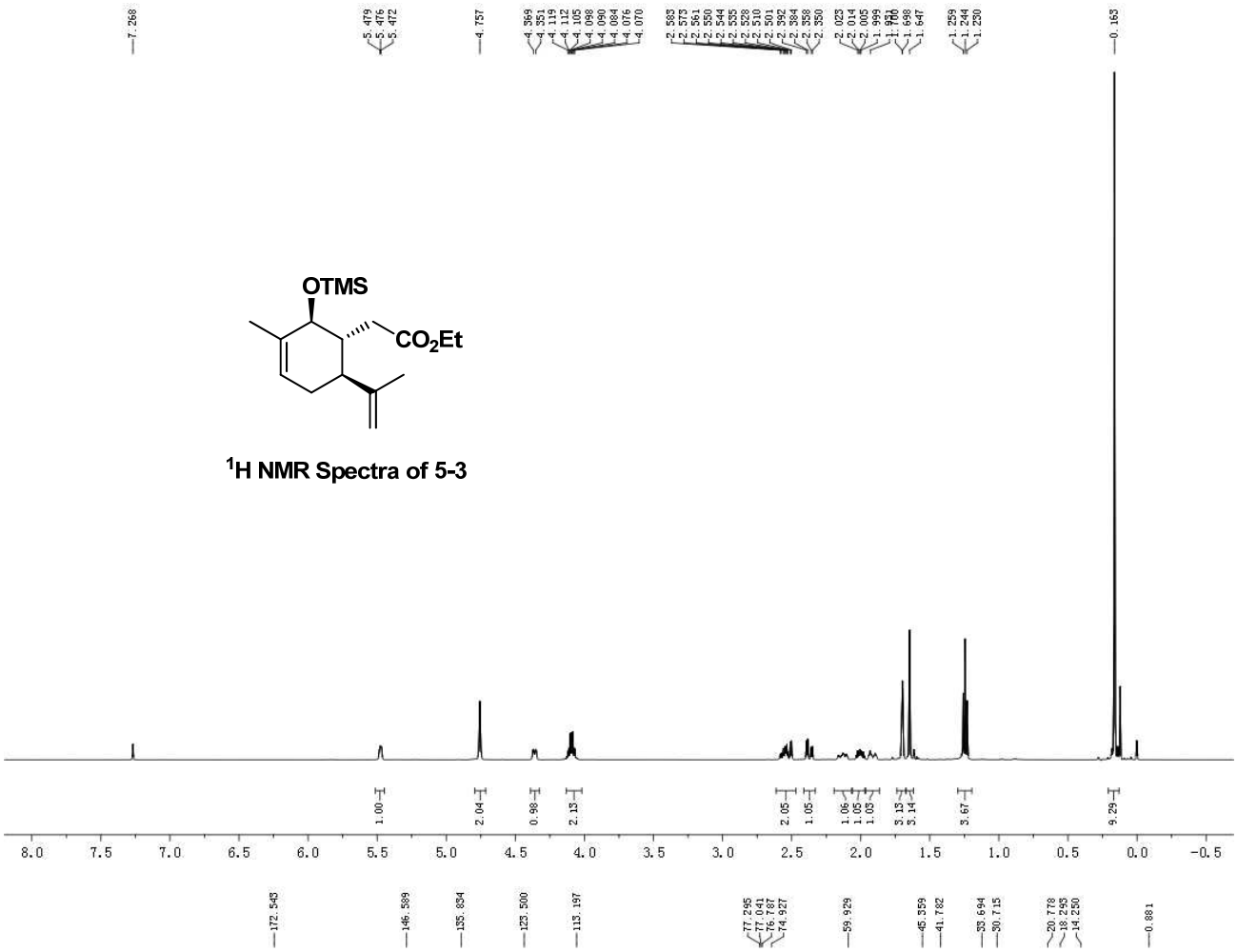




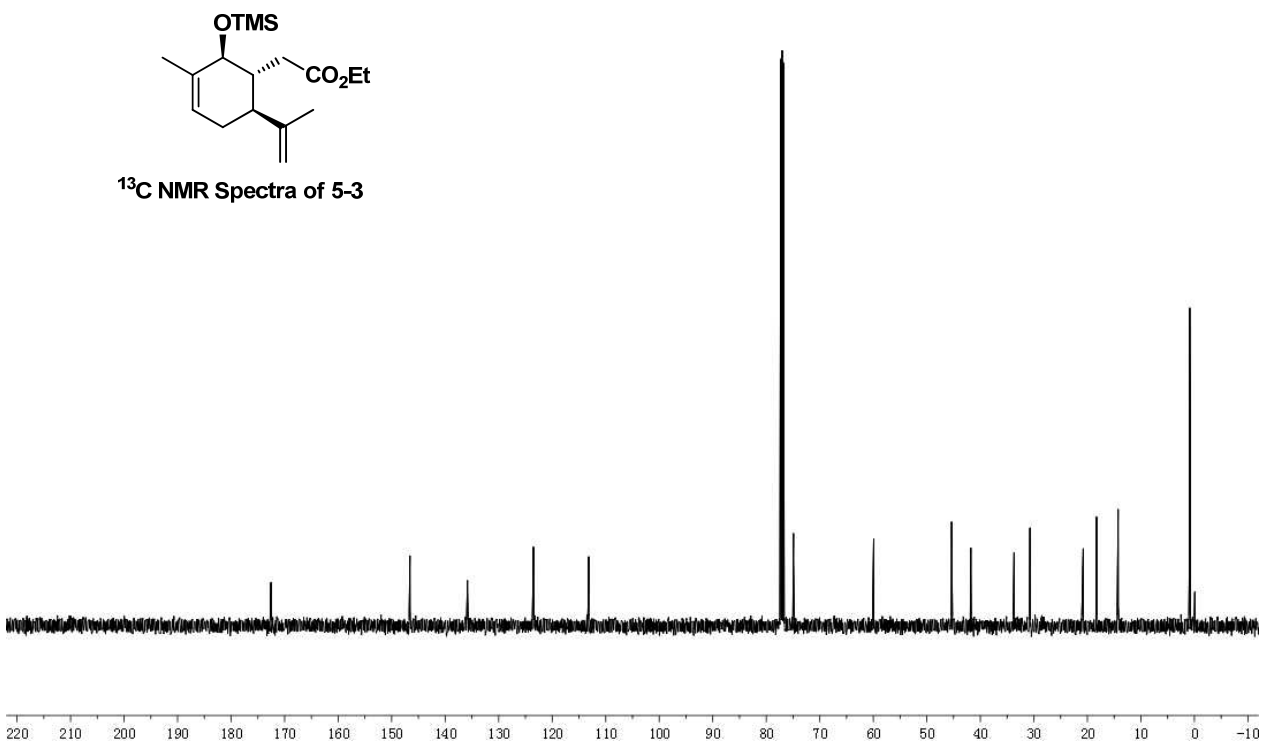
^{1}H NMR Spectra of 5-2



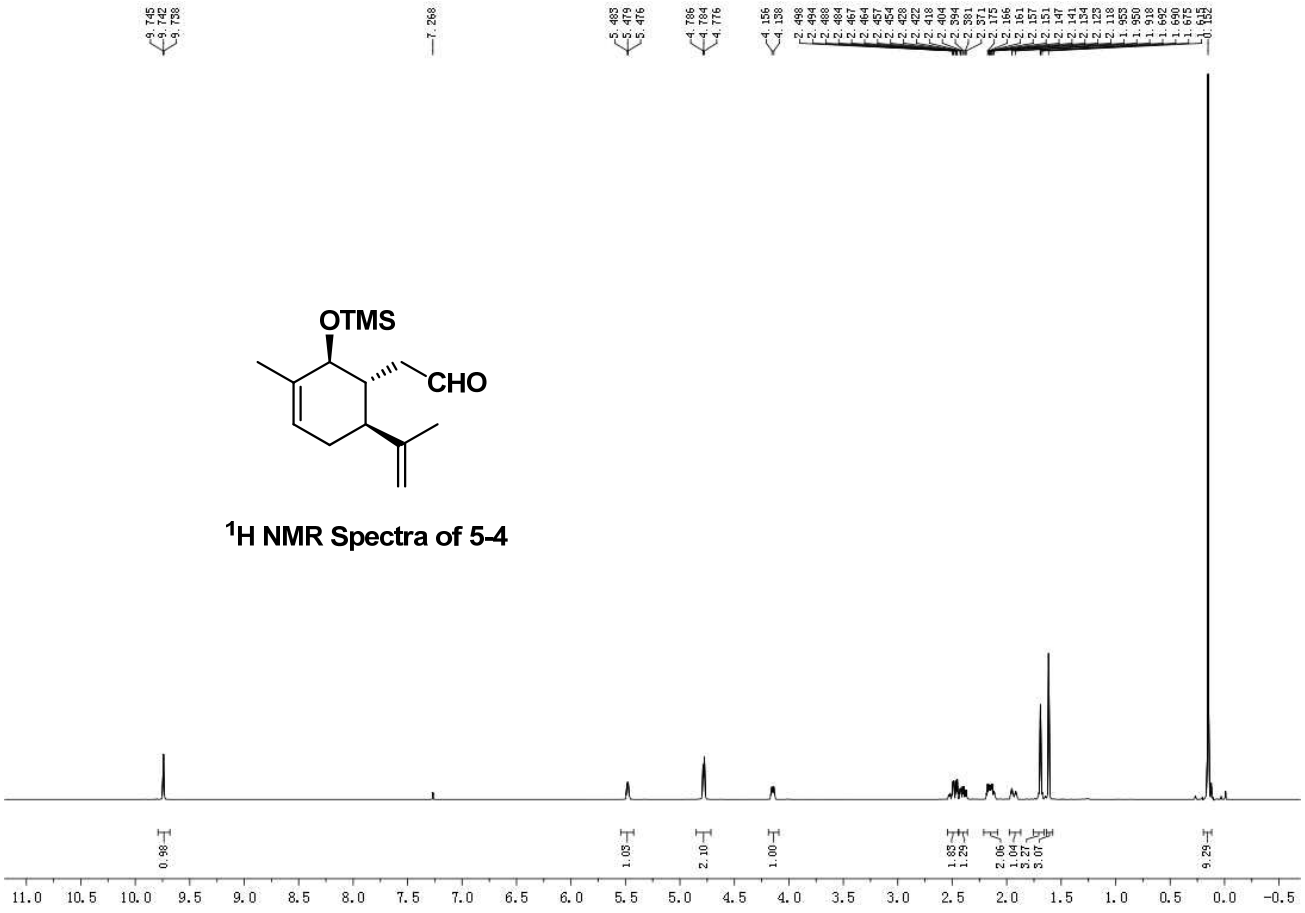
^{13}C NMR Spectra of 5-2



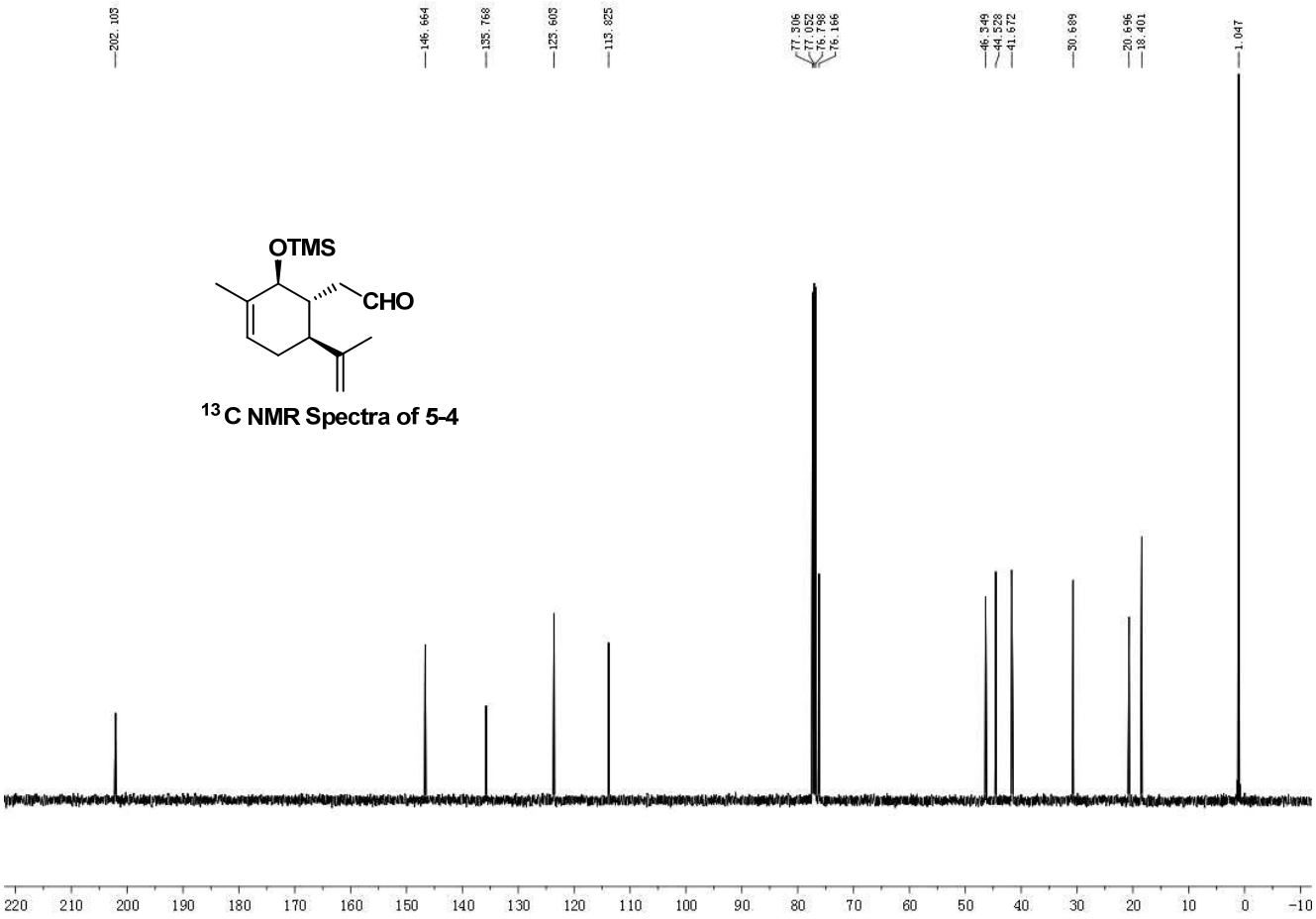
^{1}H NMR Spectra of 5-3



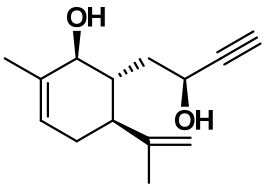
^{13}C NMR Spectra of 5-3



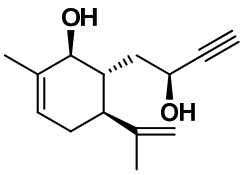
^{1}H NMR Spectra of 5-4



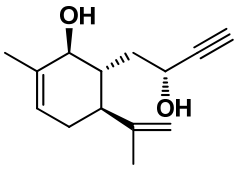
^{13}C NMR Spectra of 5-4



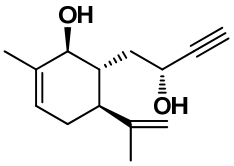
^{1}H NMR Spectra of 5-5



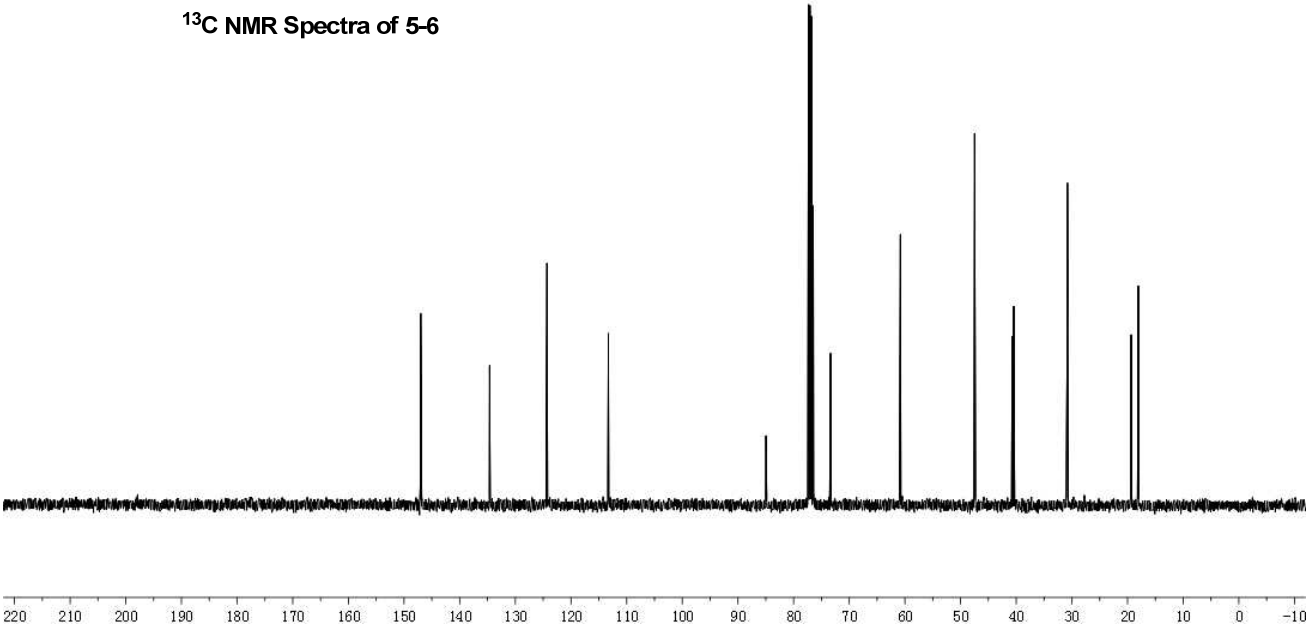
^{13}C NMR Spectra of 5-5

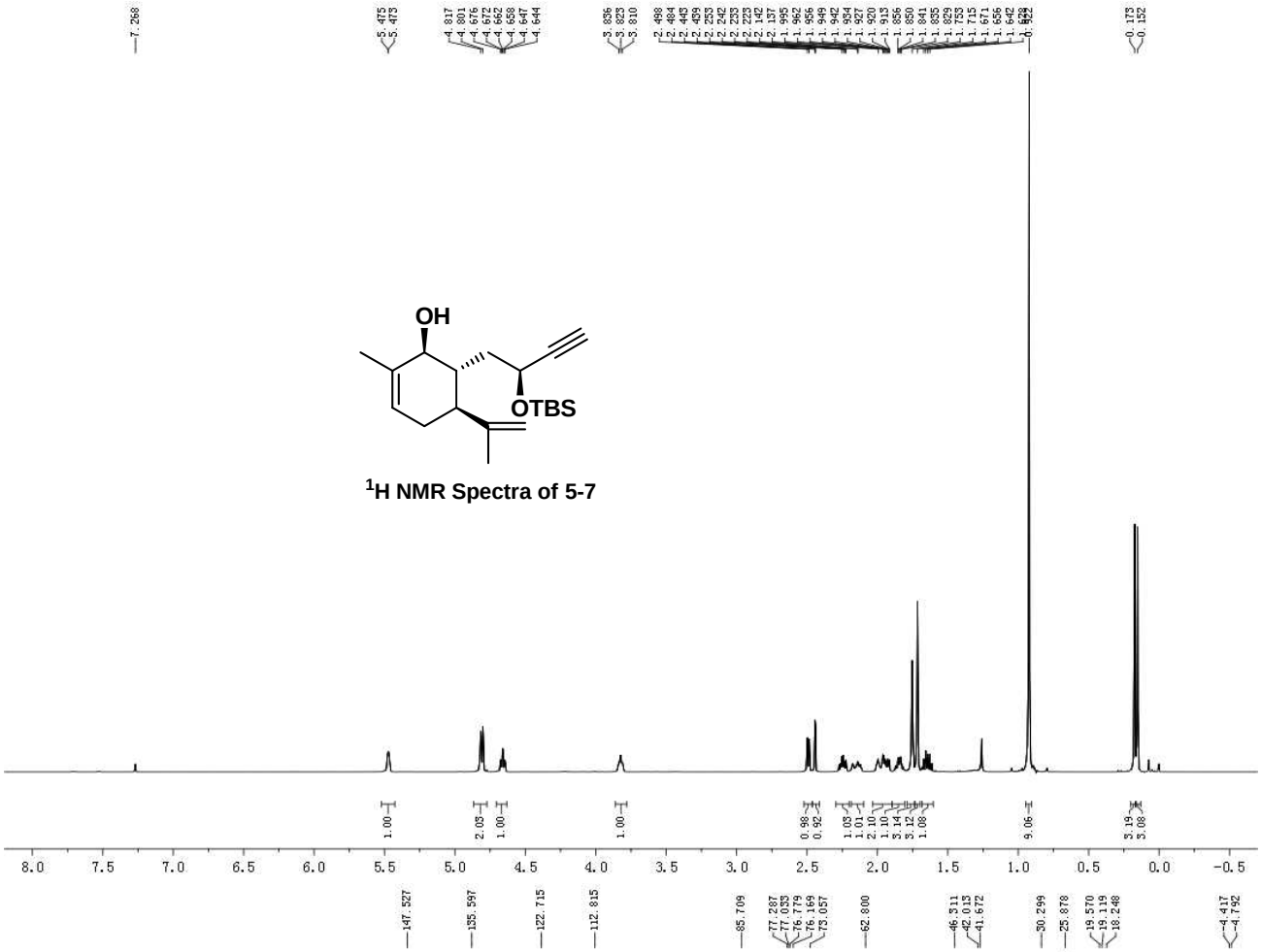


^{1}H NMR Spectra of 5-6

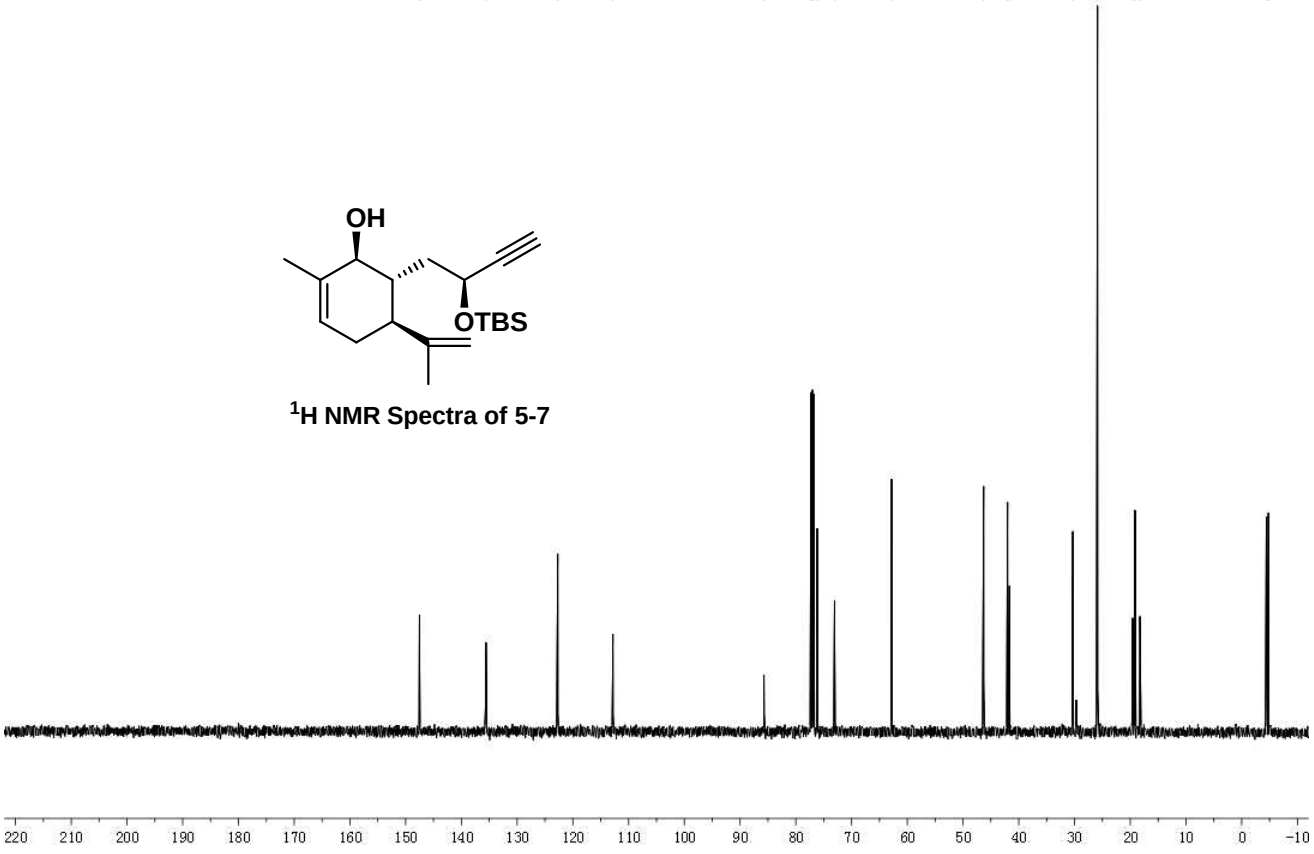


^{13}C NMR Spectra of 5-6

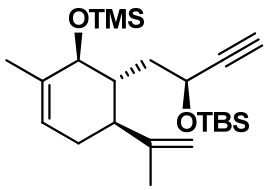




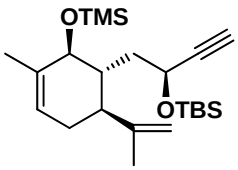
^{1}H NMR Spectra of 5-7



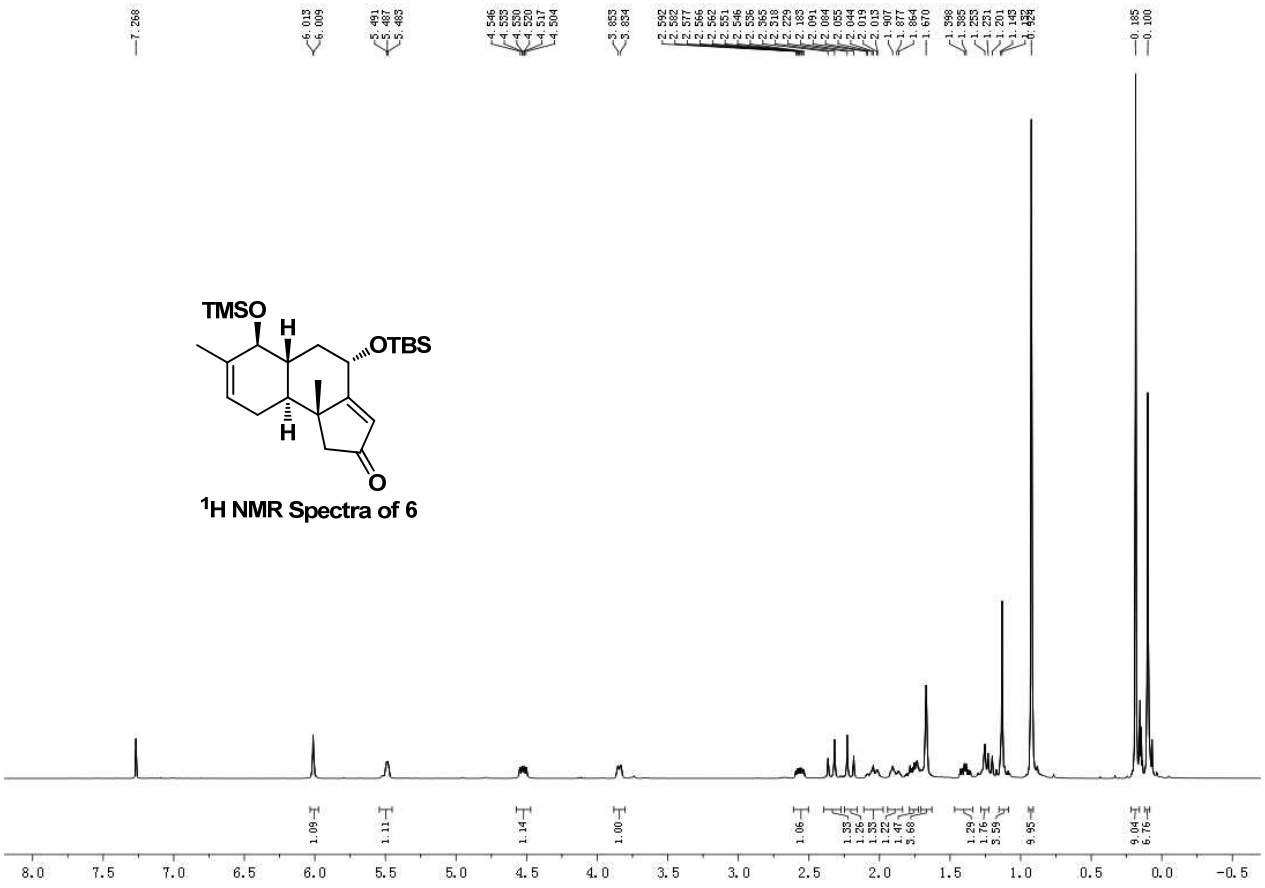
^{1}H NMR Spectra of 5-7



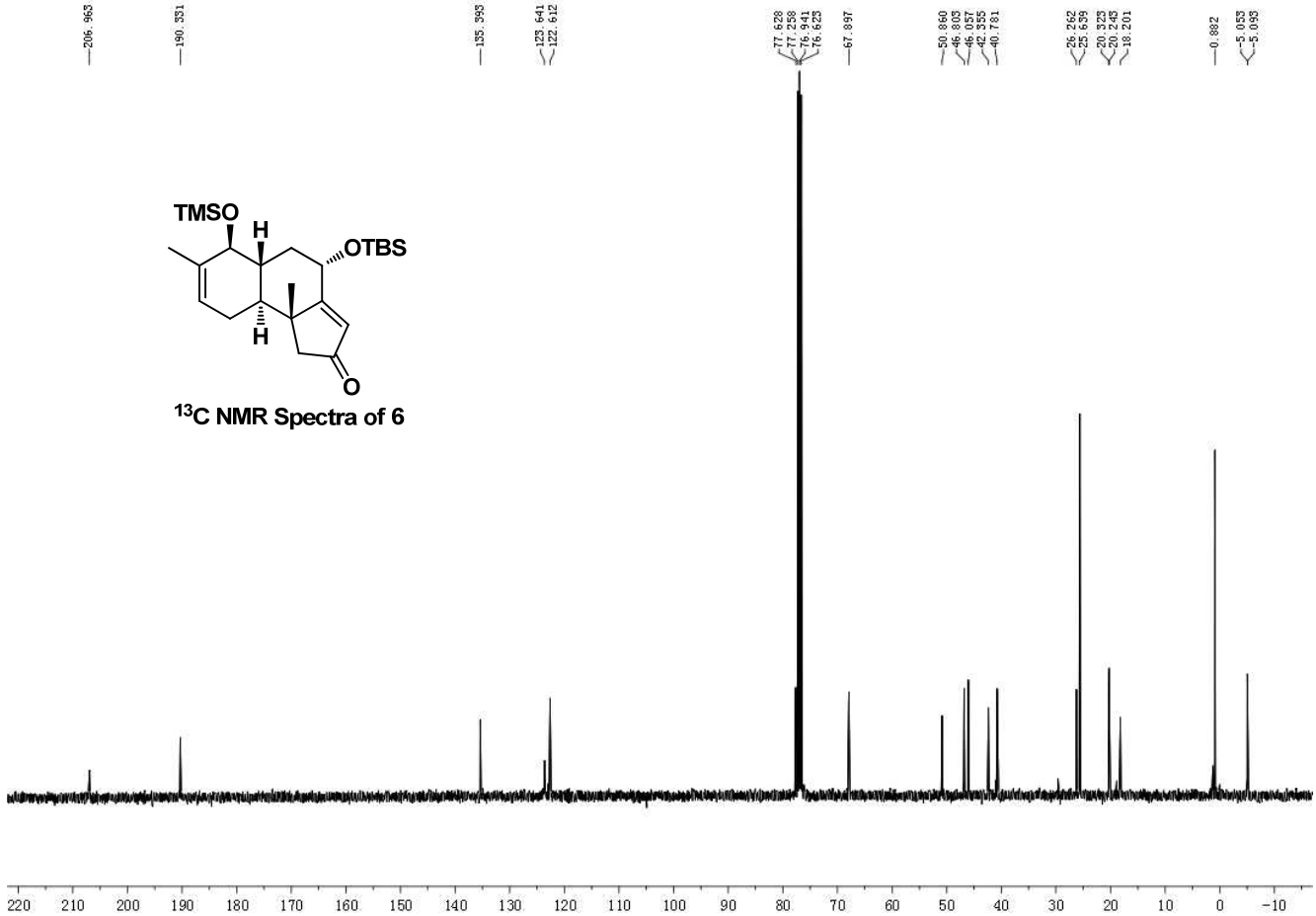
^{1}H NMR Spectra of 5



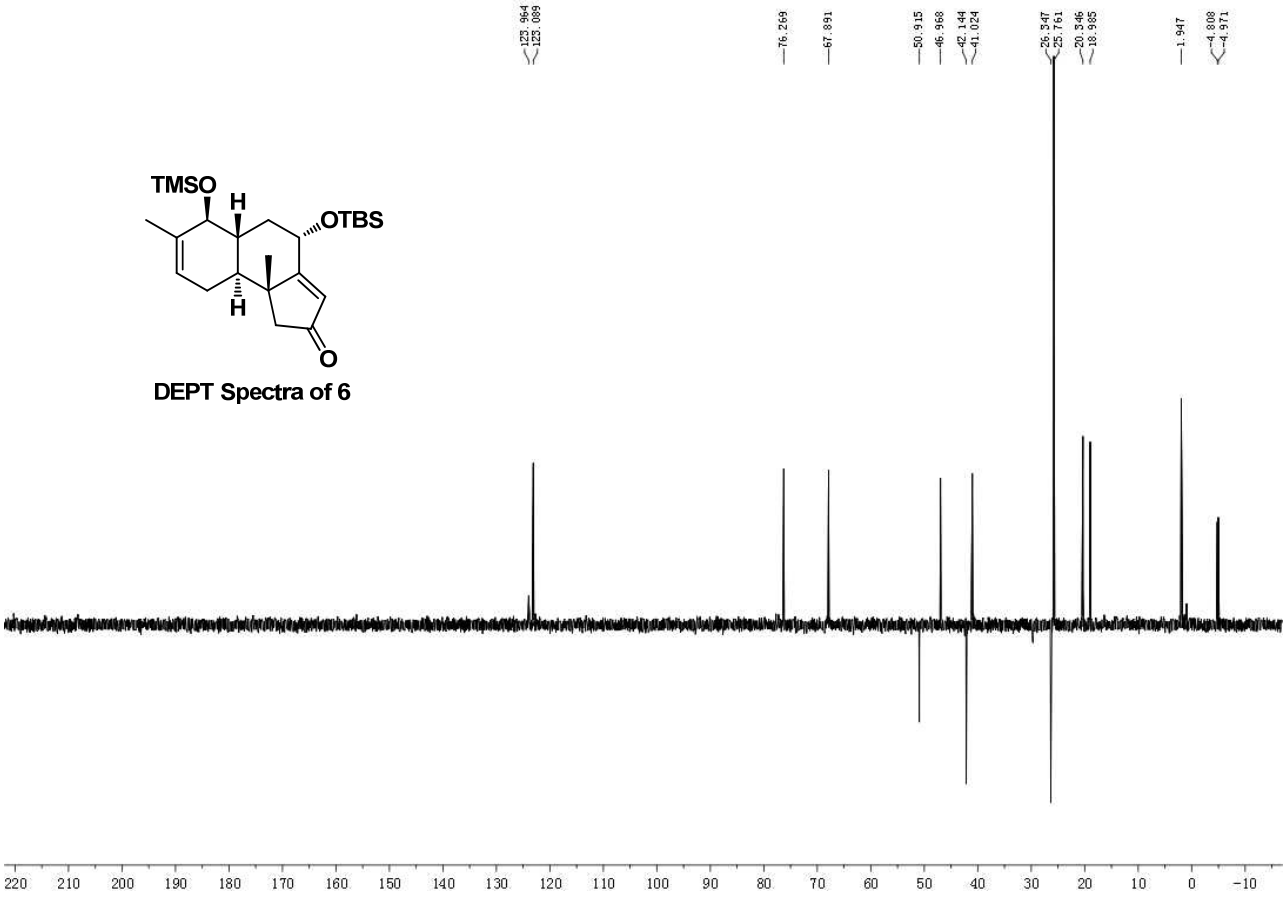
^{13}C NMR Spectra of 5



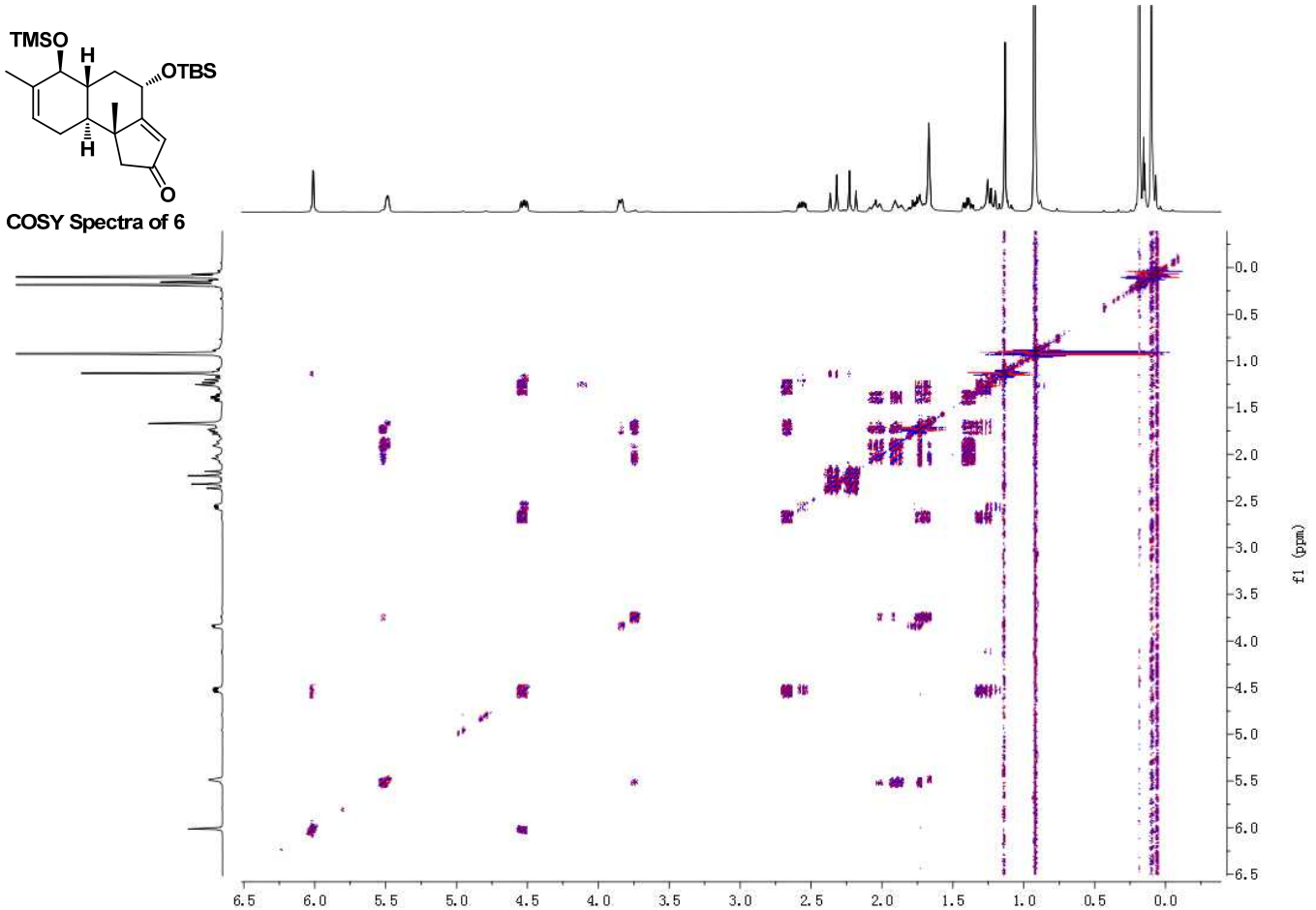
^{1}H NMR Spectra of 6



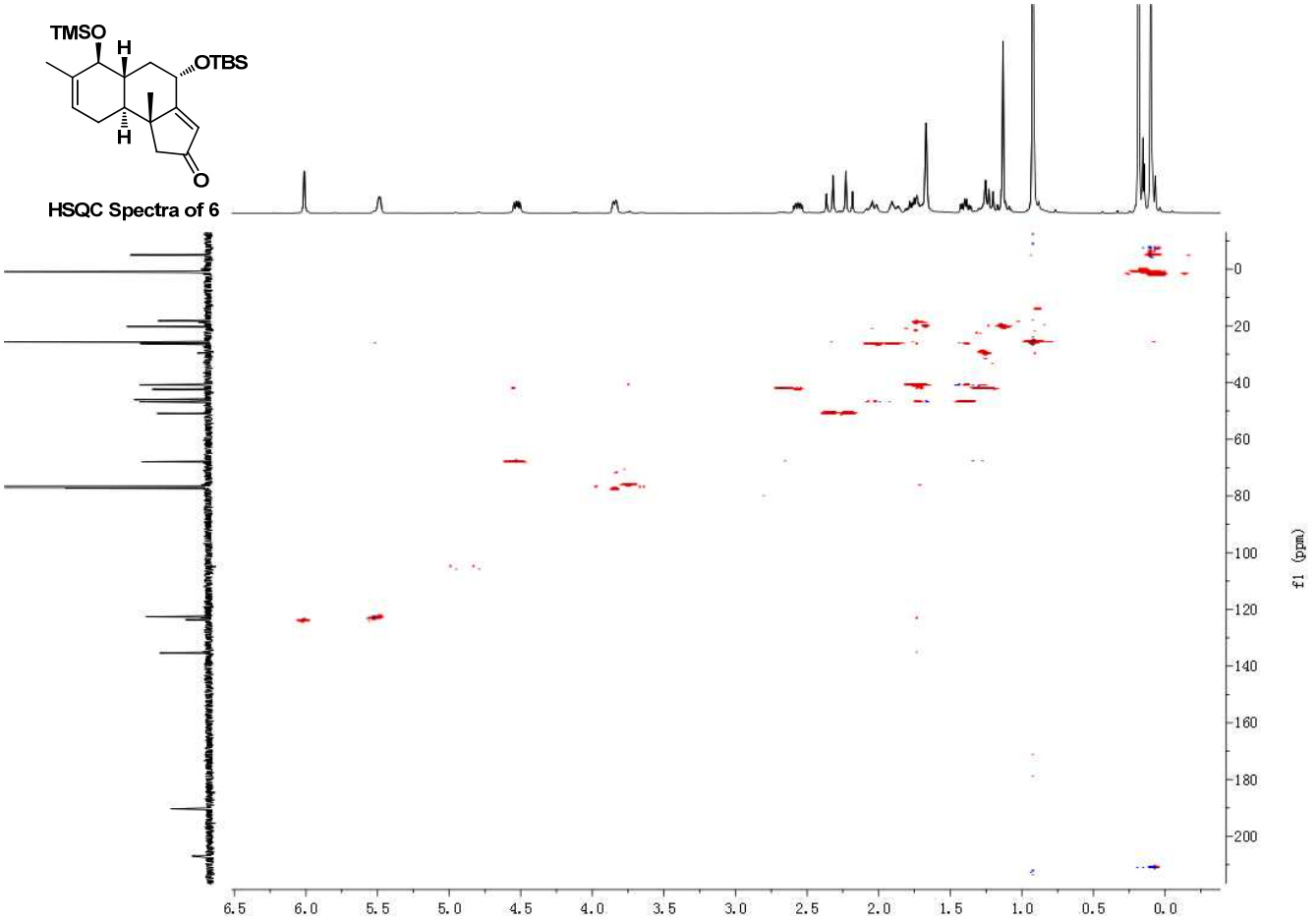
^{13}C NMR Spectra of 6

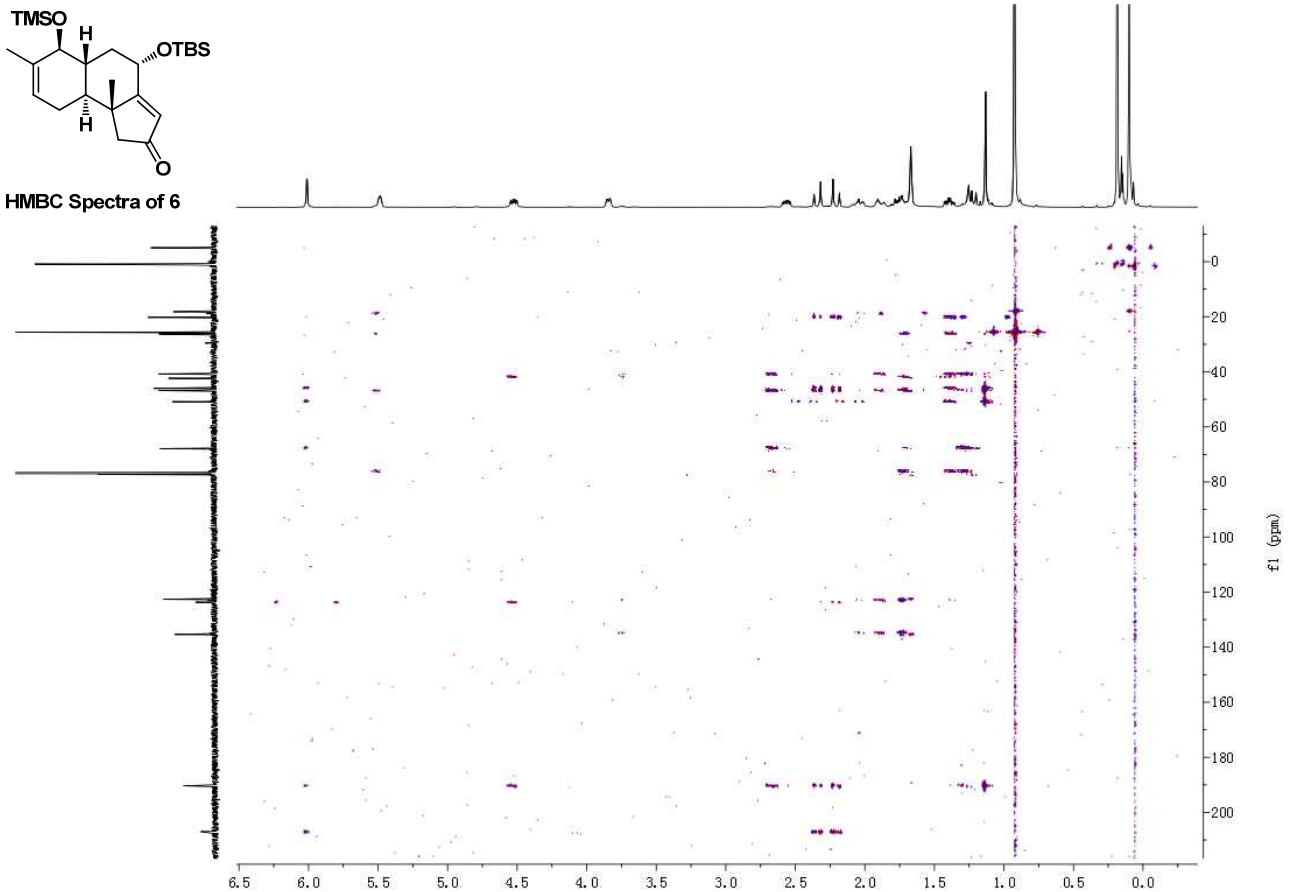


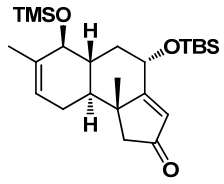
DEPT Spectra of 6



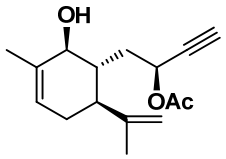
COSY Spectra of 6


TMSO
H
OTBS
H
O
HSQC Spectra of 6
f1 (ppm)

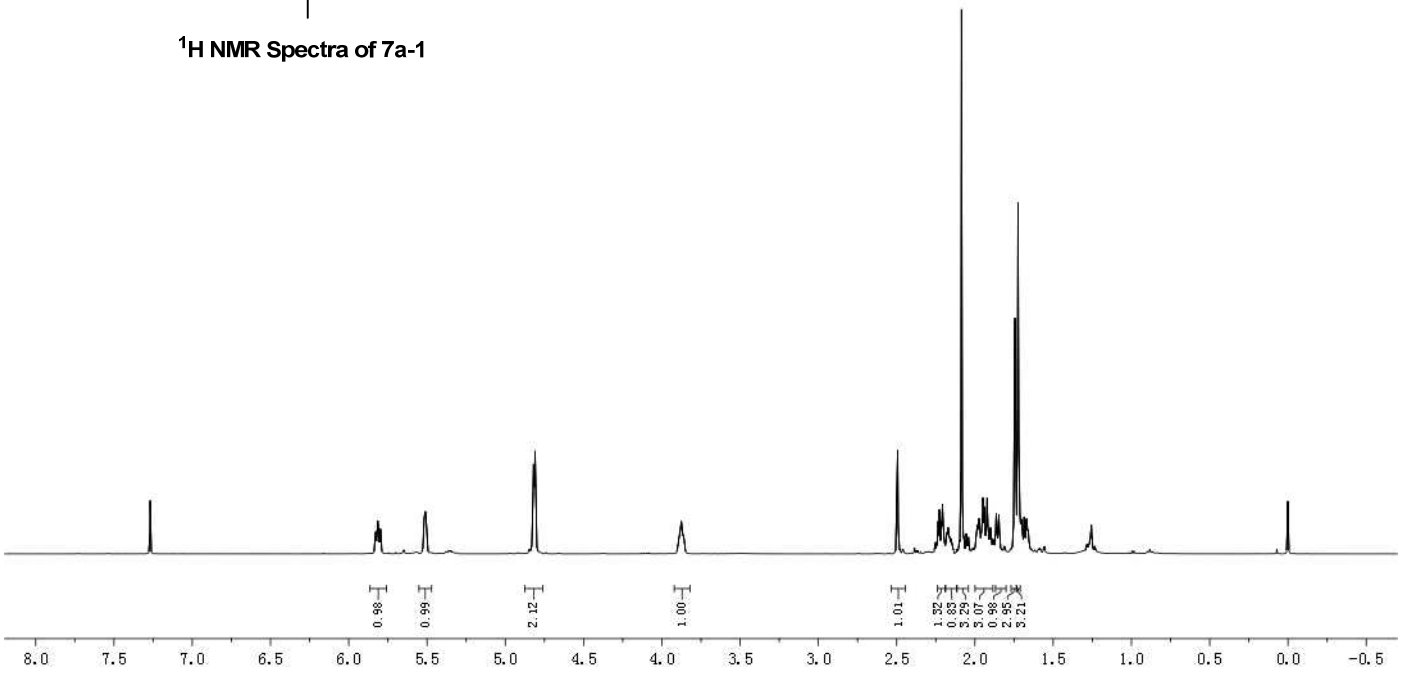

TMSO
H
OTBS
H
O
HMBC Spectra of 6
f1 (ppm)

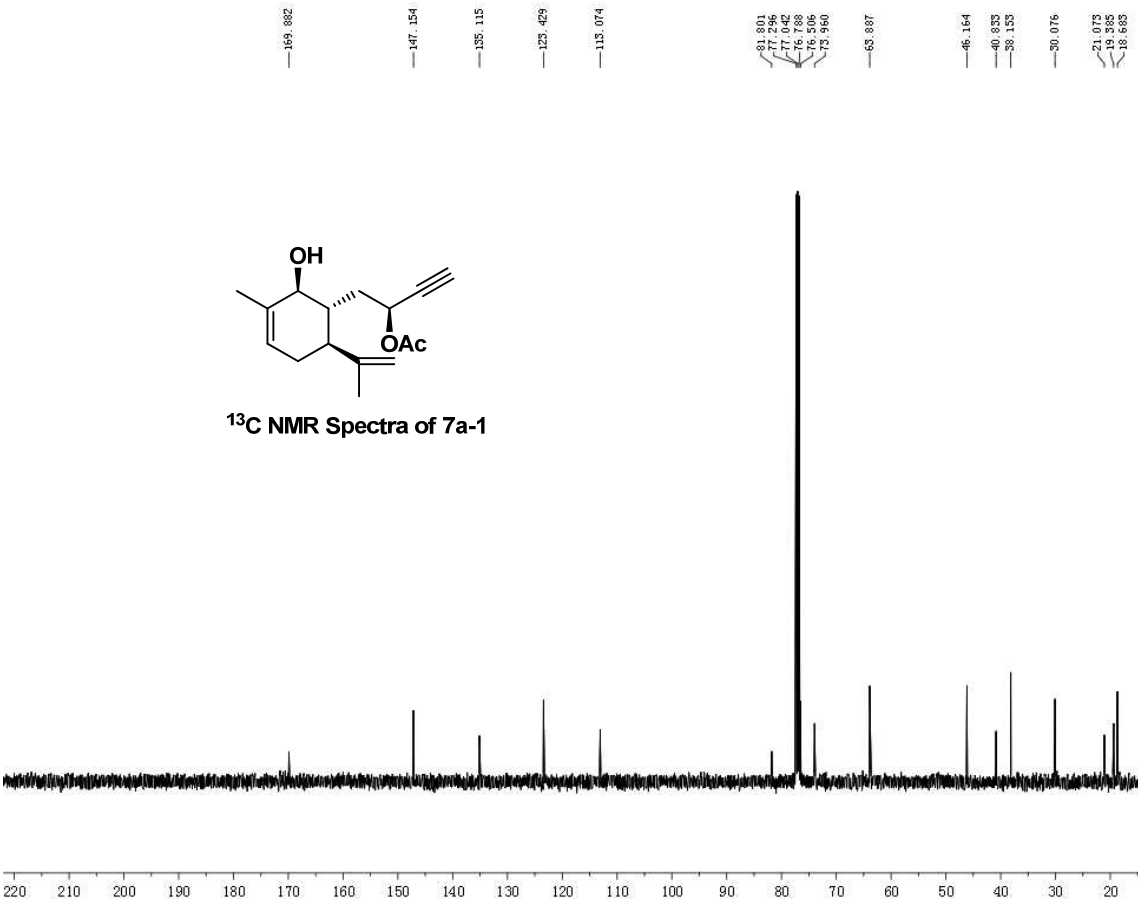


NOESY Spectra of 6

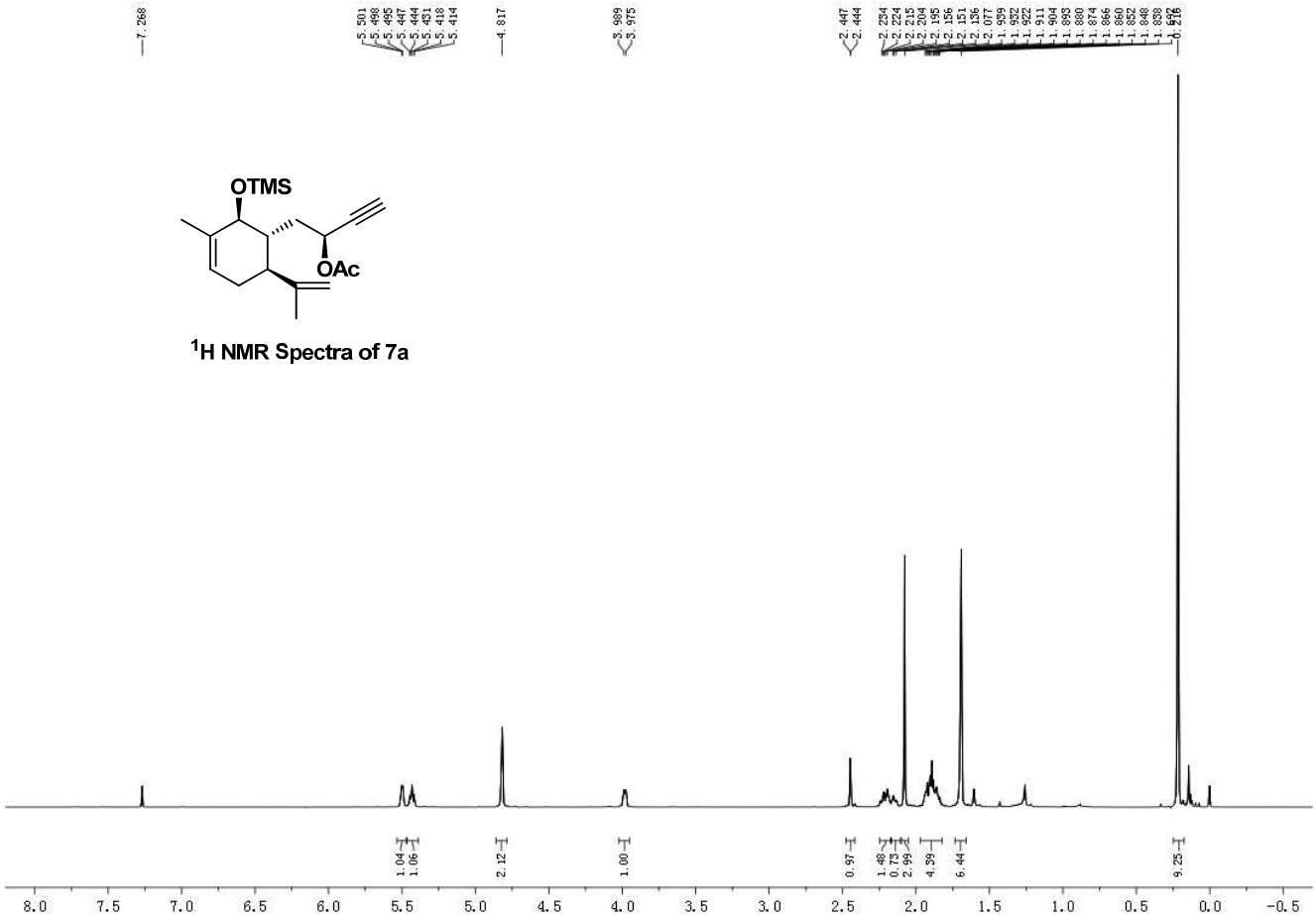


^{1}H NMR Spectra of 7a-1

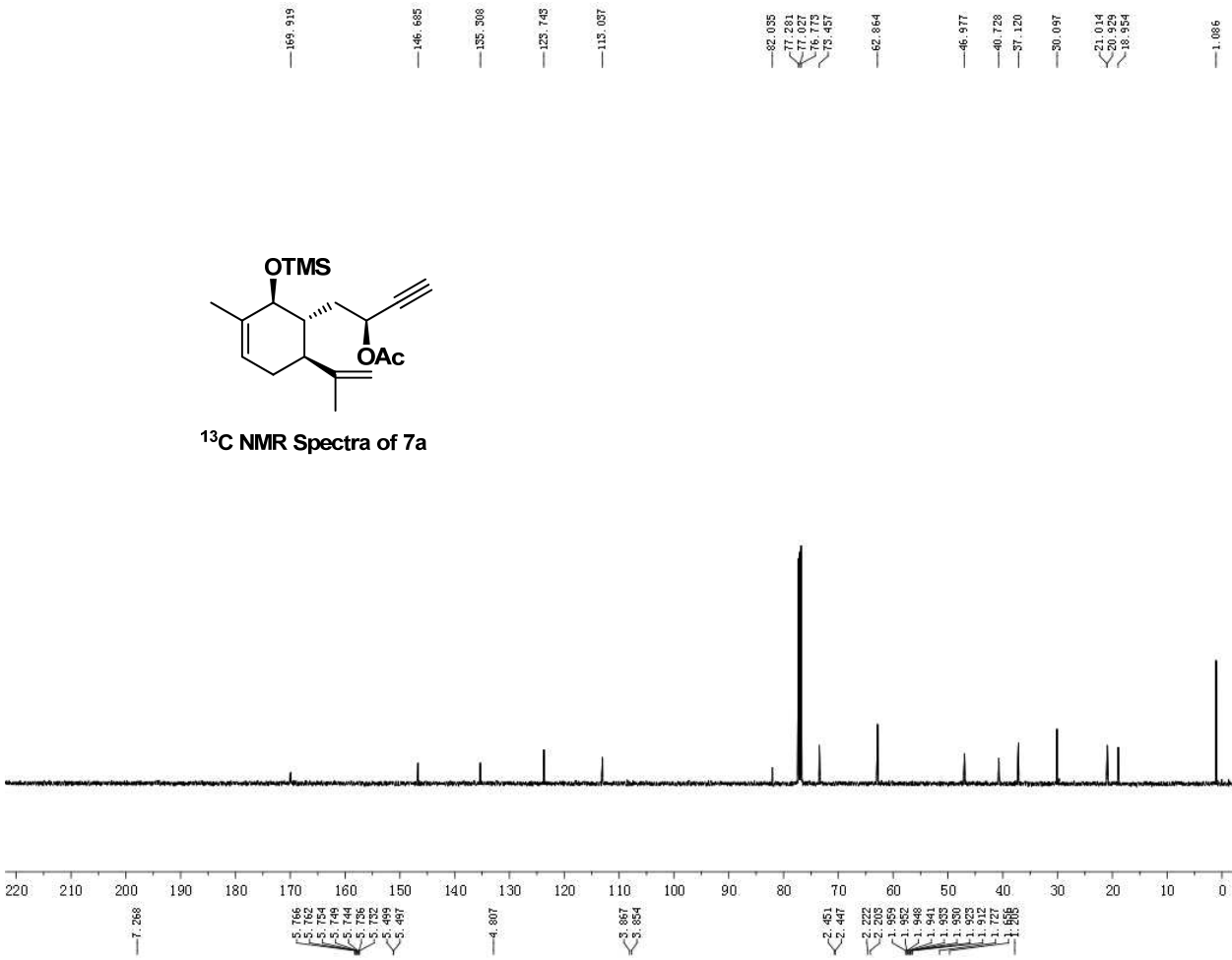




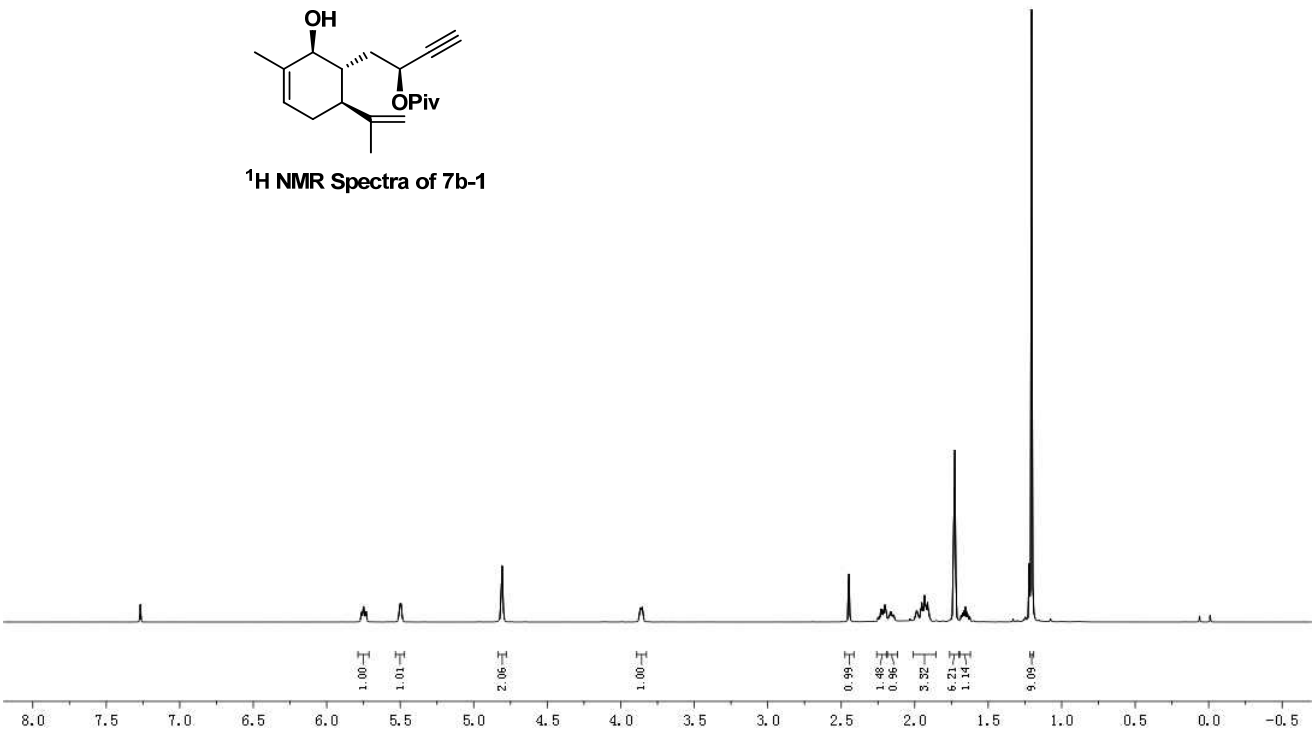
^{13}C NMR Spectra of 7a-1



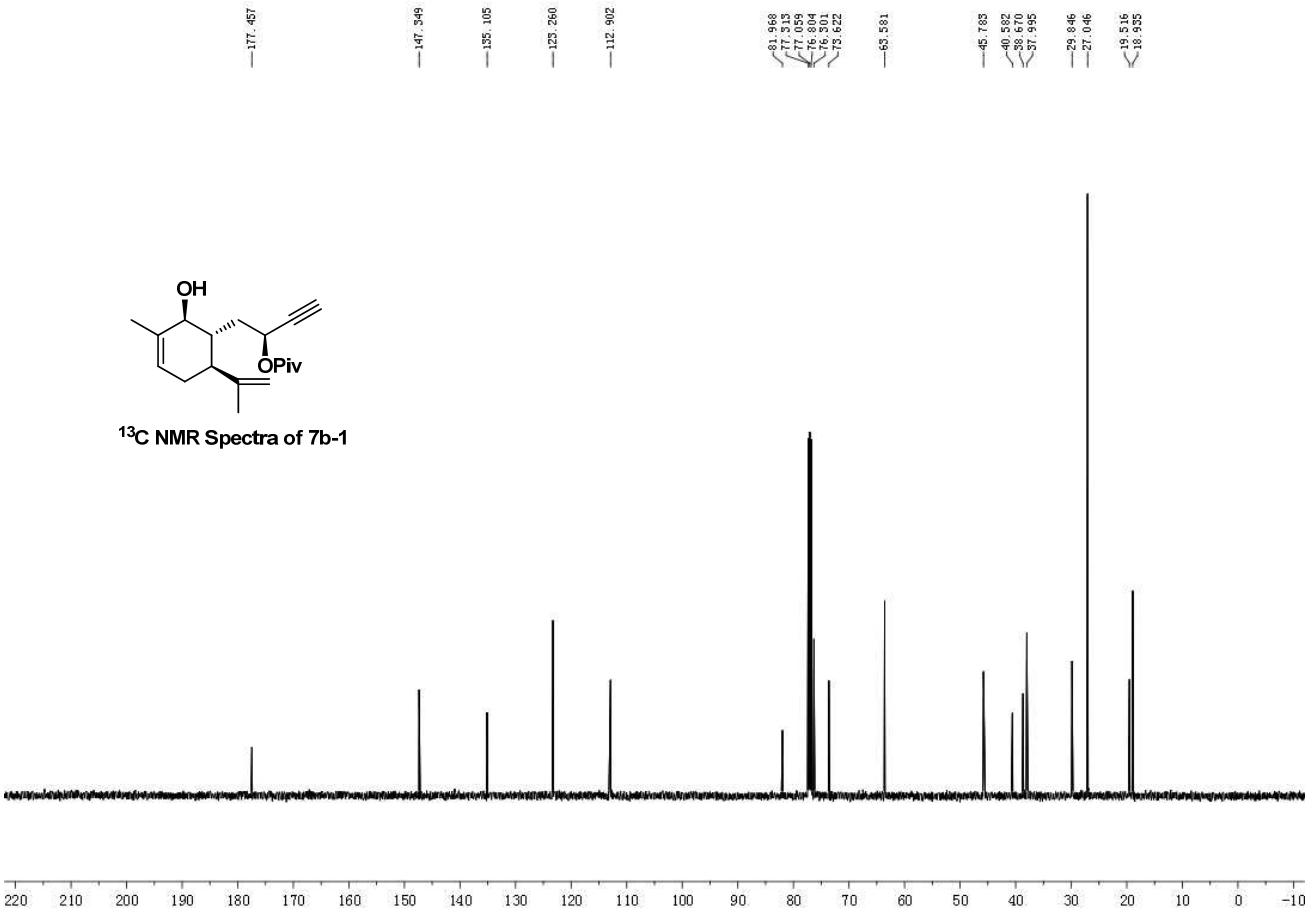
^{1}H NMR Spectra of 7a



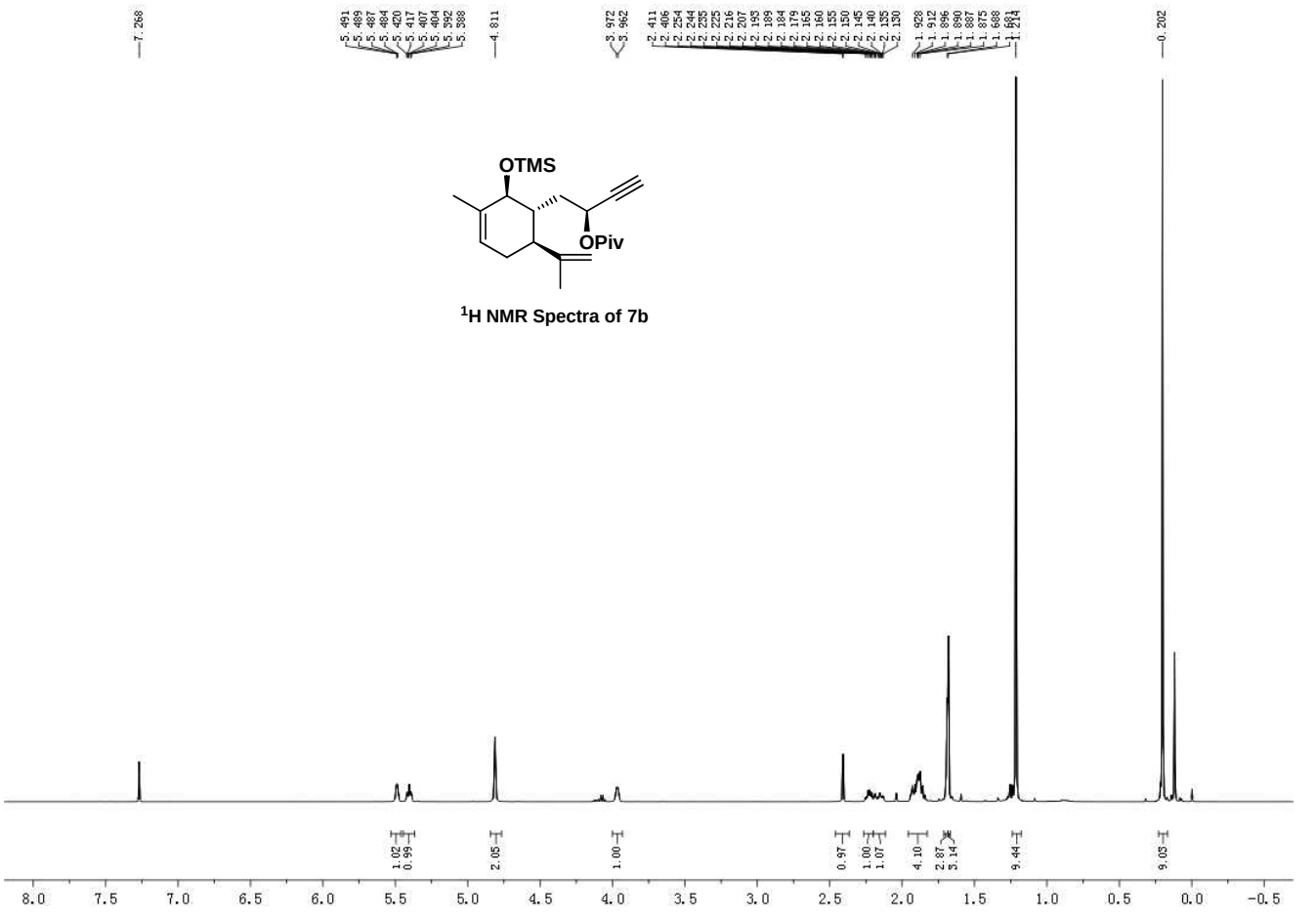
^{13}C NMR Spectra of 7a



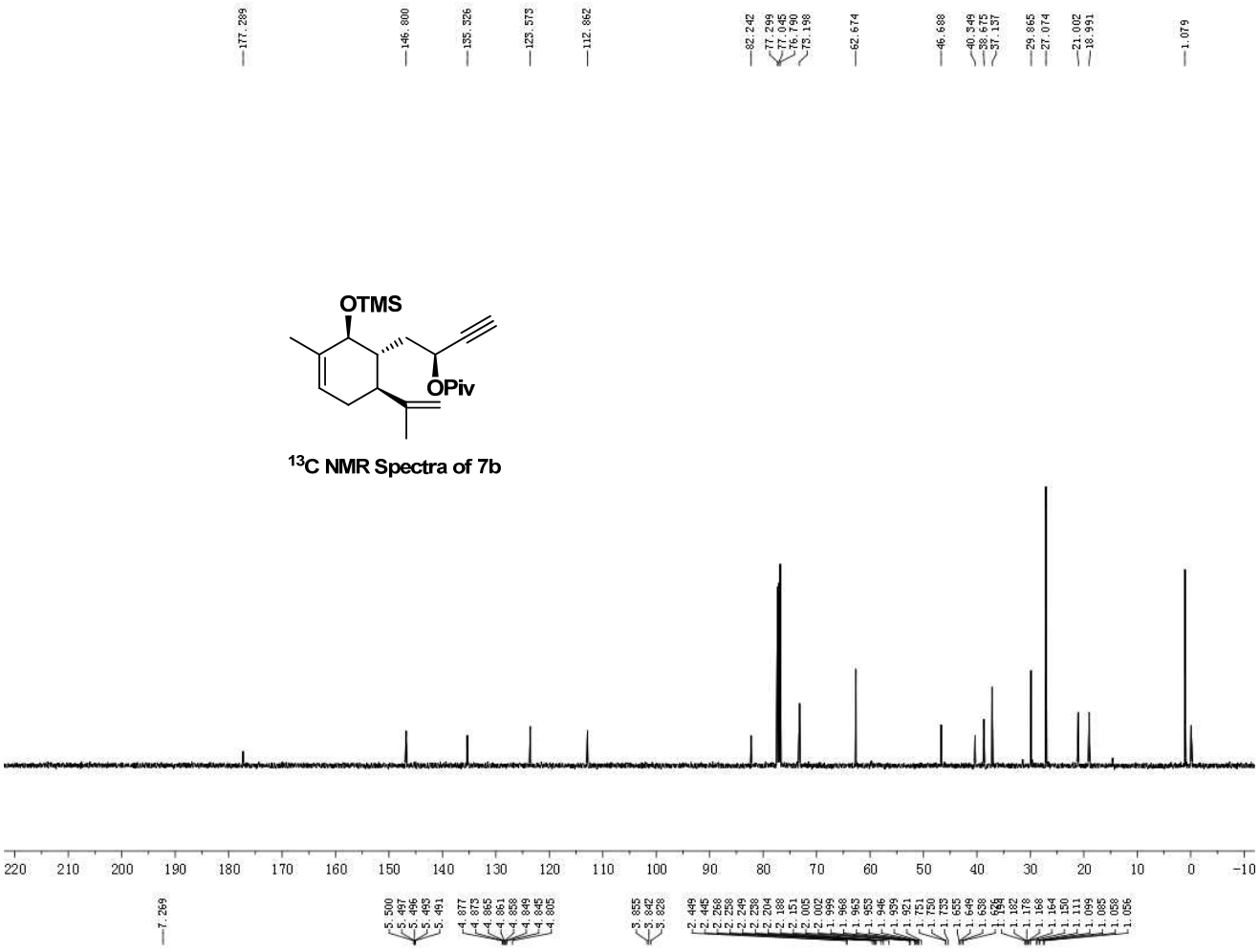
^{1}H NMR Spectra of 7b-1



^{13}C NMR Spectra of 7b-1

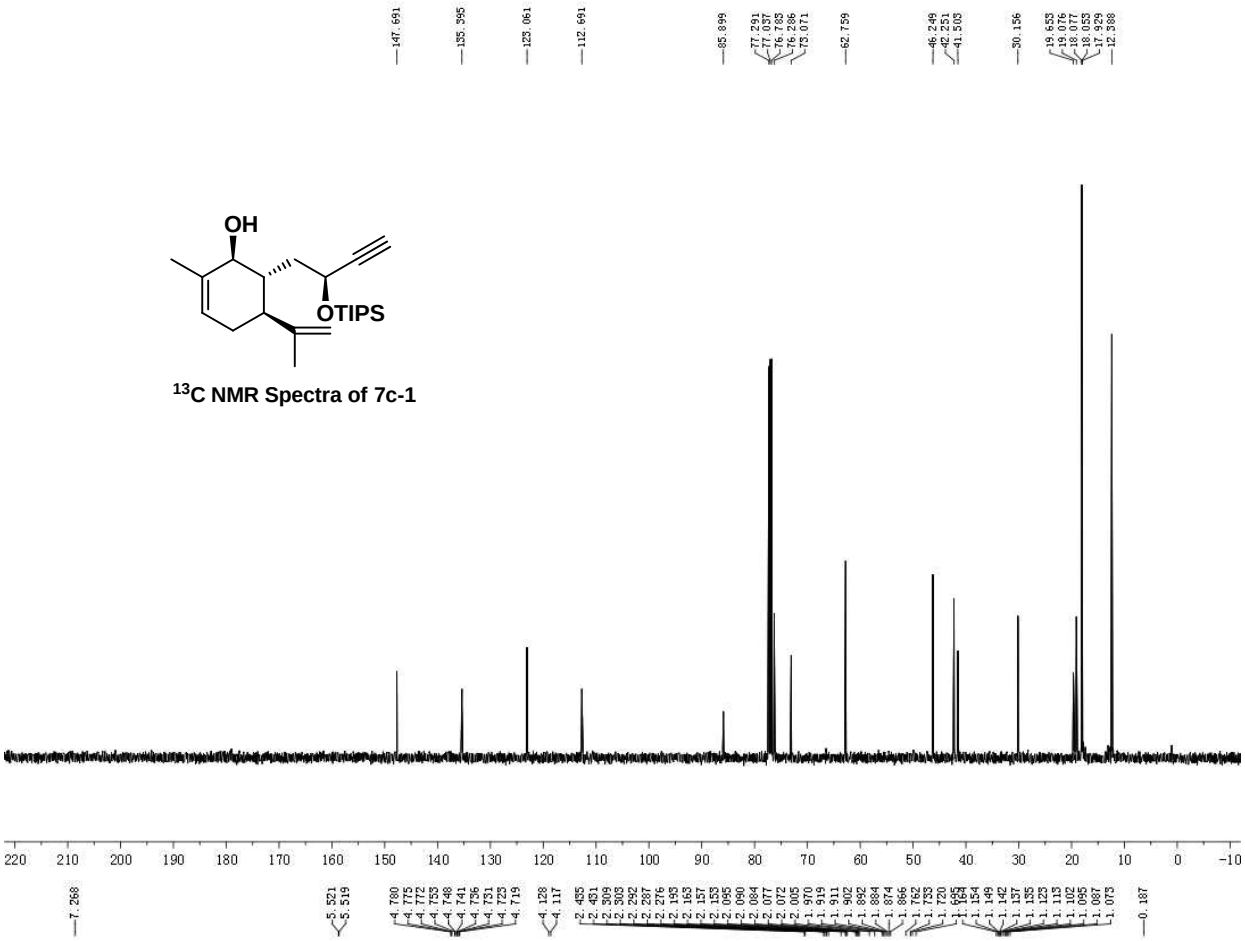


^{1}H NMR Spectra of 7b

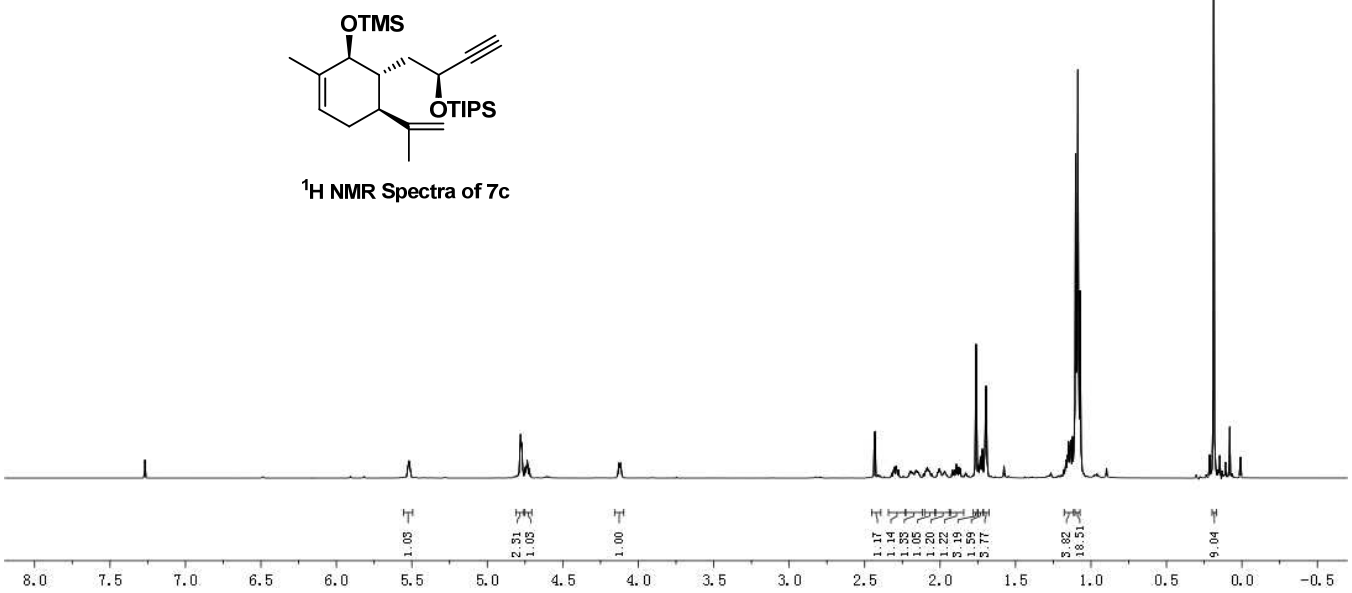


^{13}C NMR Spectra of 7b

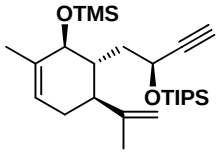
^{1}H NMR Spectra of 7c-1



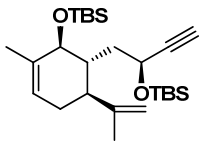
^{13}C NMR Spectra of 7c-1



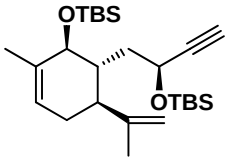
^{1}H NMR Spectra of 7c



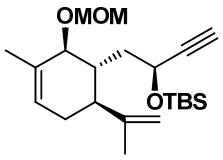
^{13}C NMR Spectra of 7c



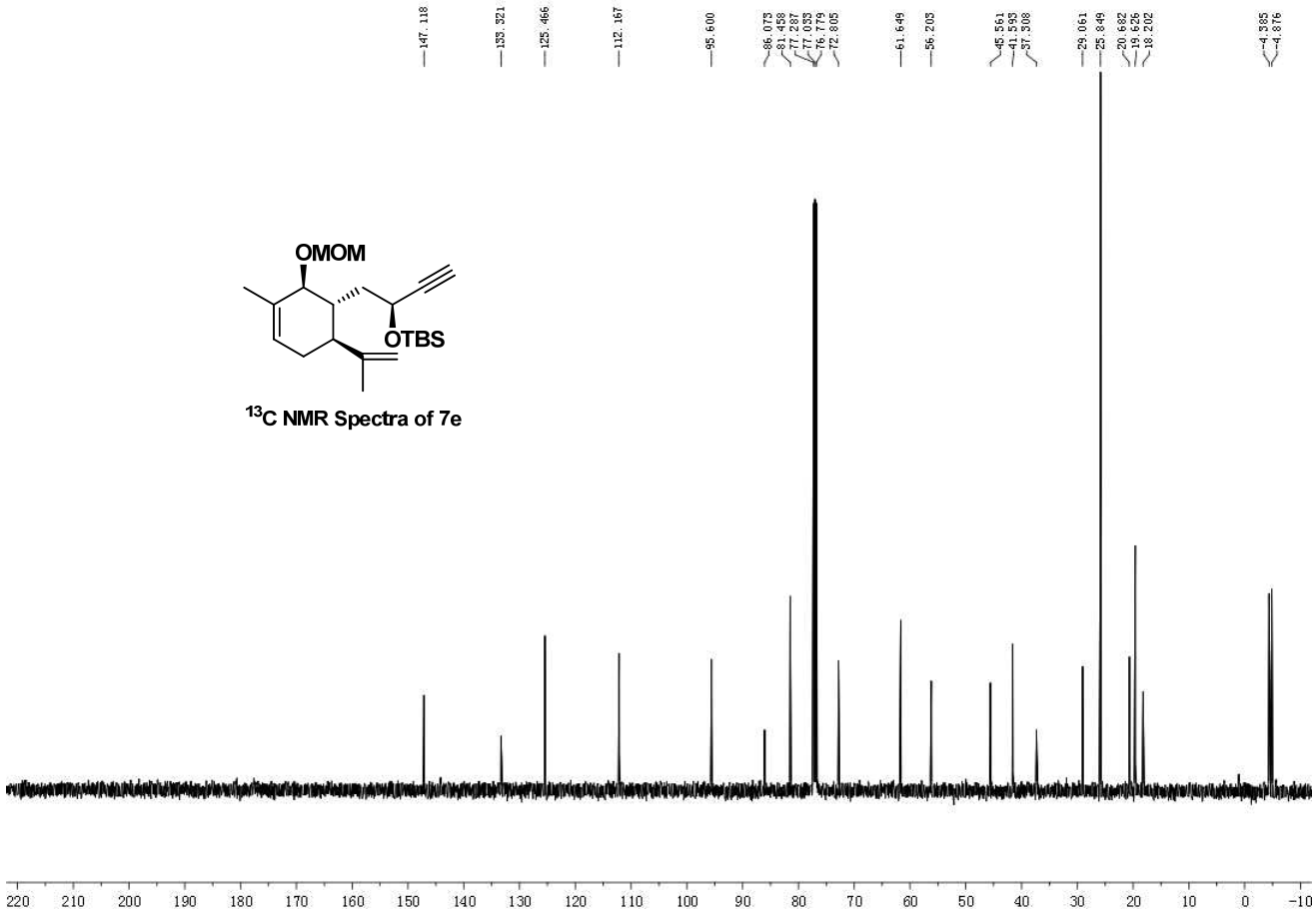
^{1}H NMR Spectra of 7d



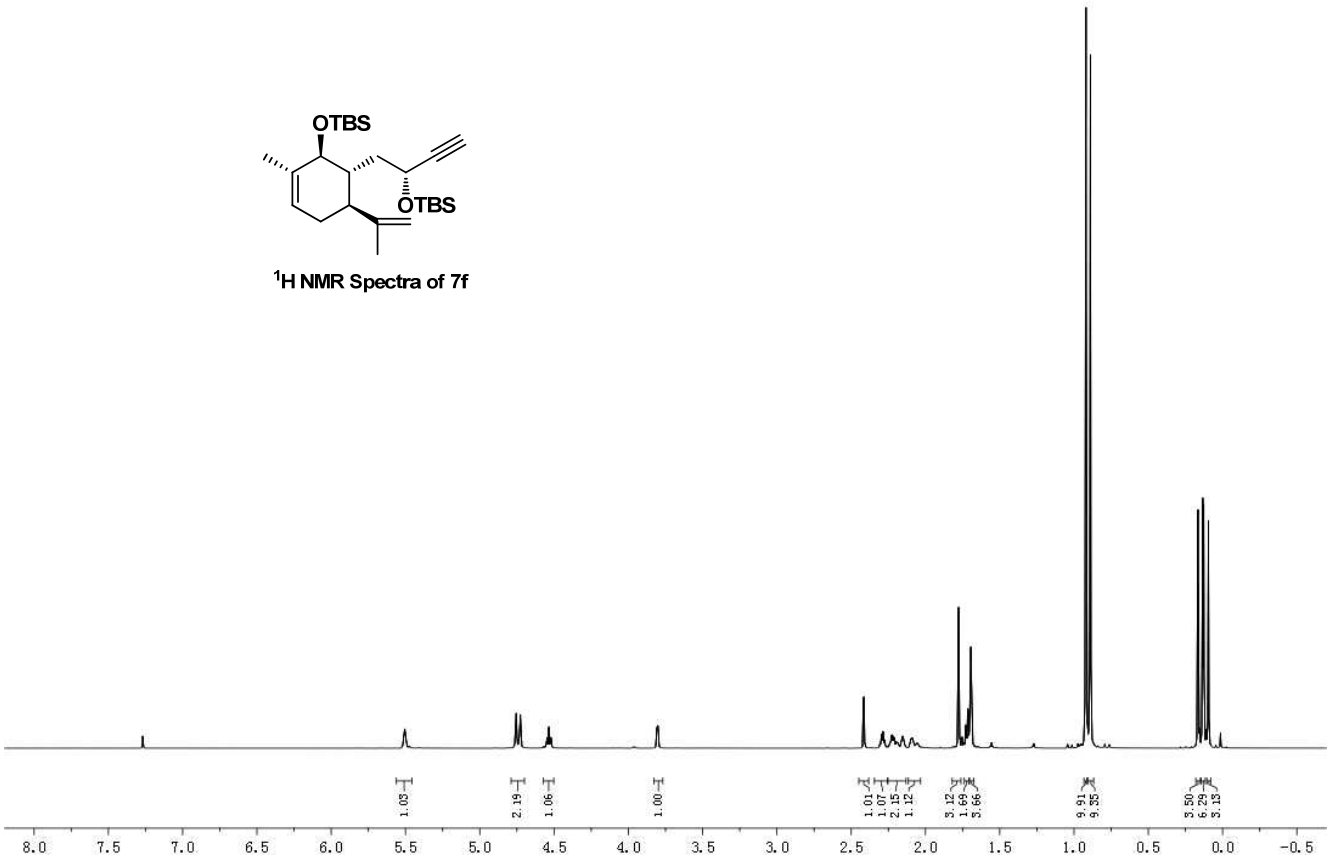
^{1}H NMR Spectra of 7d



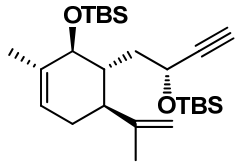
^{1}H NMR Spectra of 7e



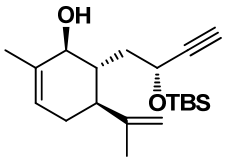
^{13}C NMR Spectra of 7e



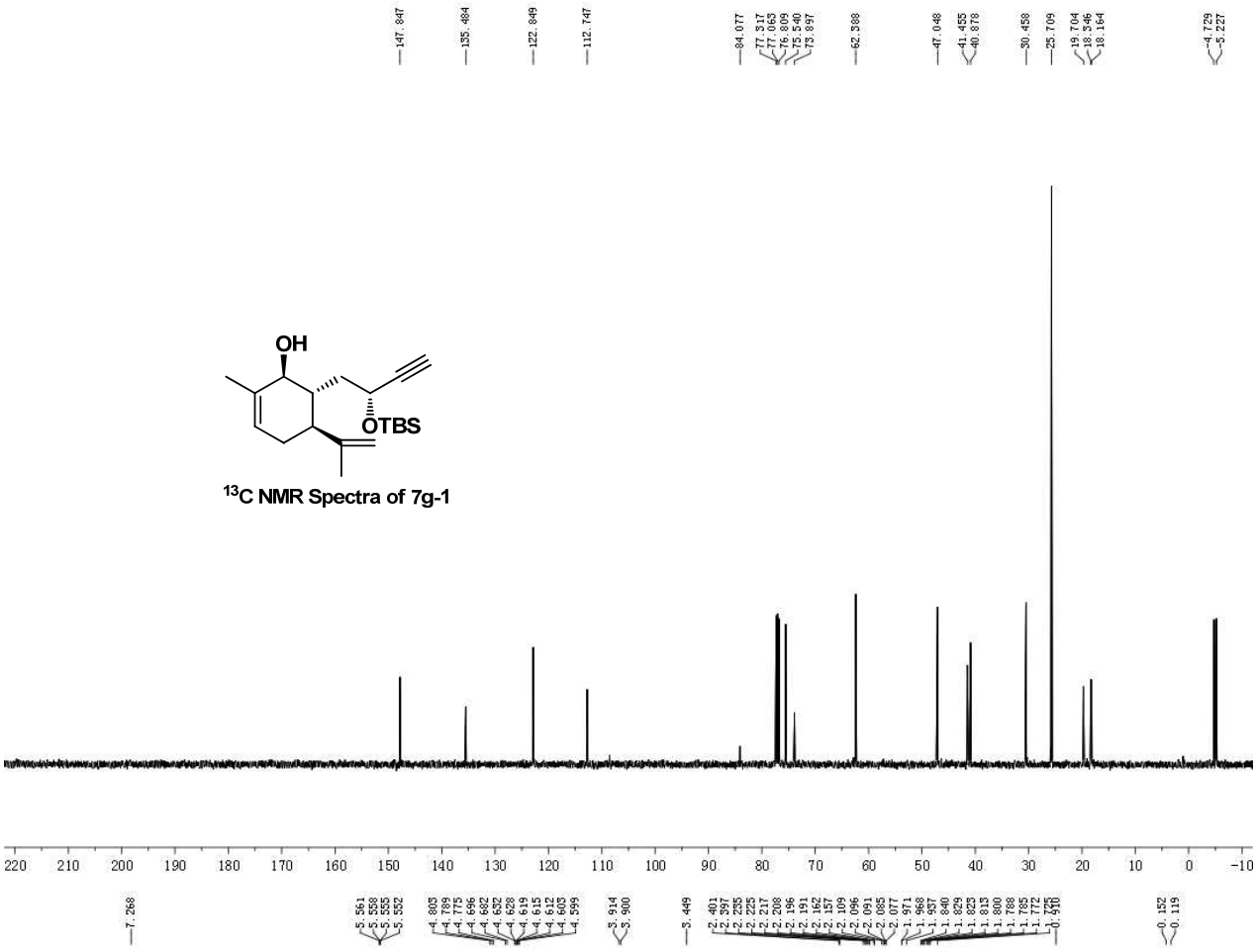
^{1}H NMR Spectra of 7f



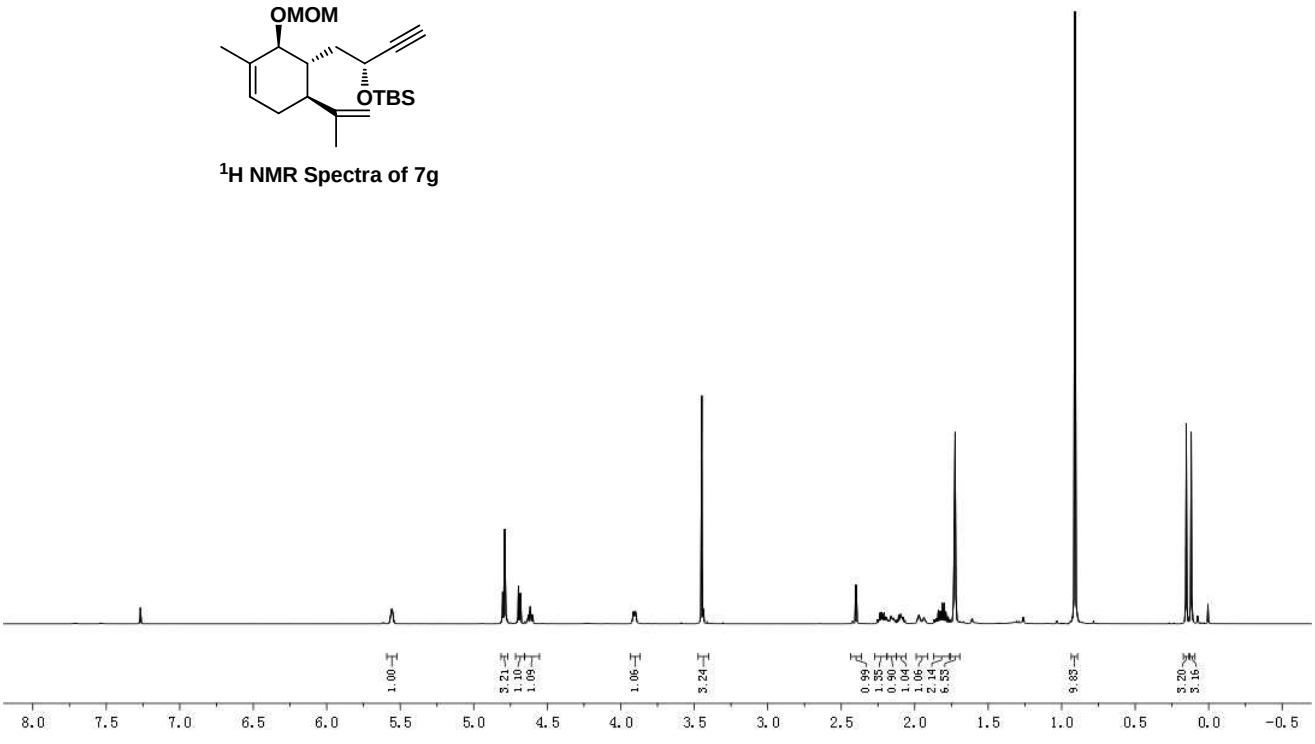
^{13}C NMR Spectra of 7f



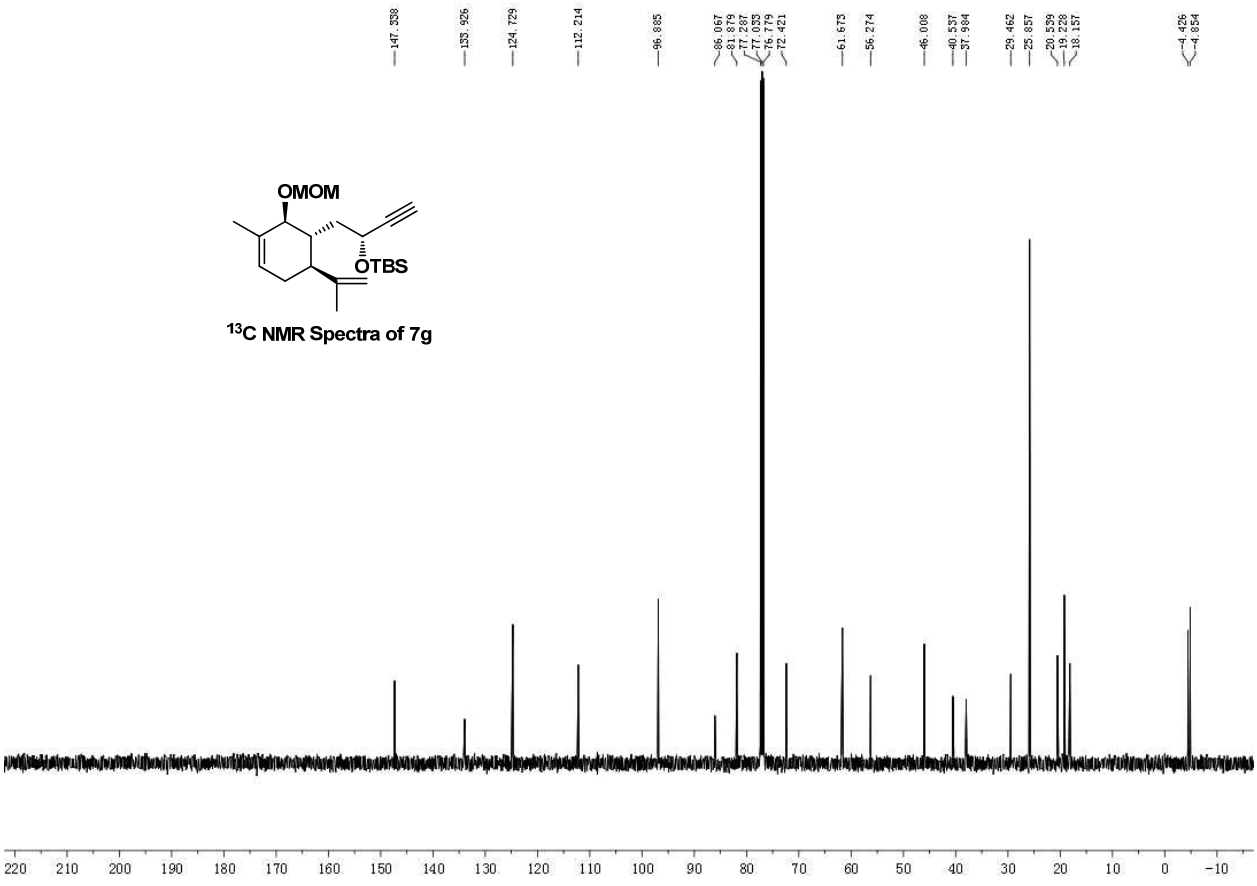
^{1}H-NMR Spectra of 7g-1



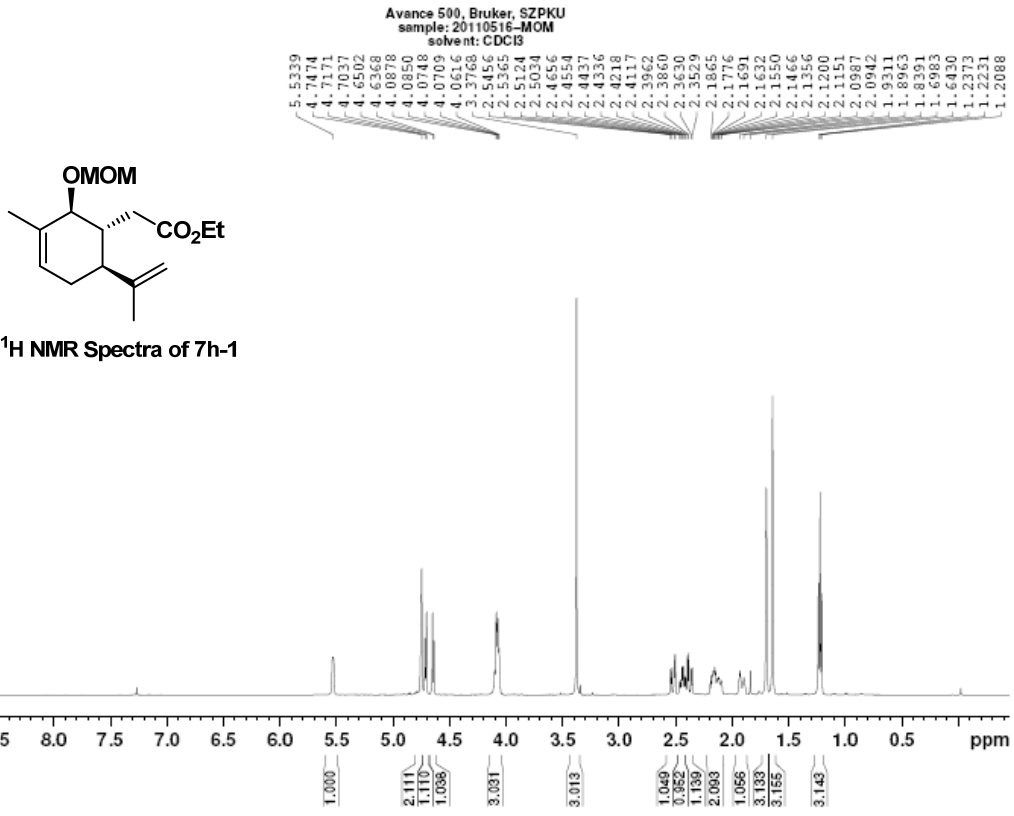
^{13}C NMR Spectra of 7g-1



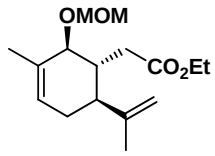
^{1}H NMR Spectra of 7g



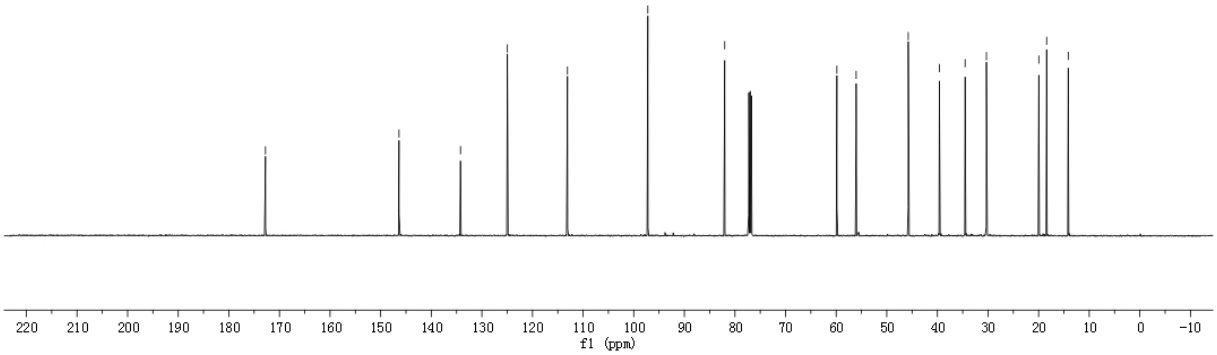
^{13}C NMR Spectra of 7g

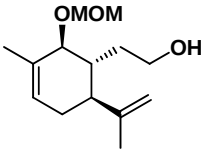


^{1}H NMR Spectra of 7h-1

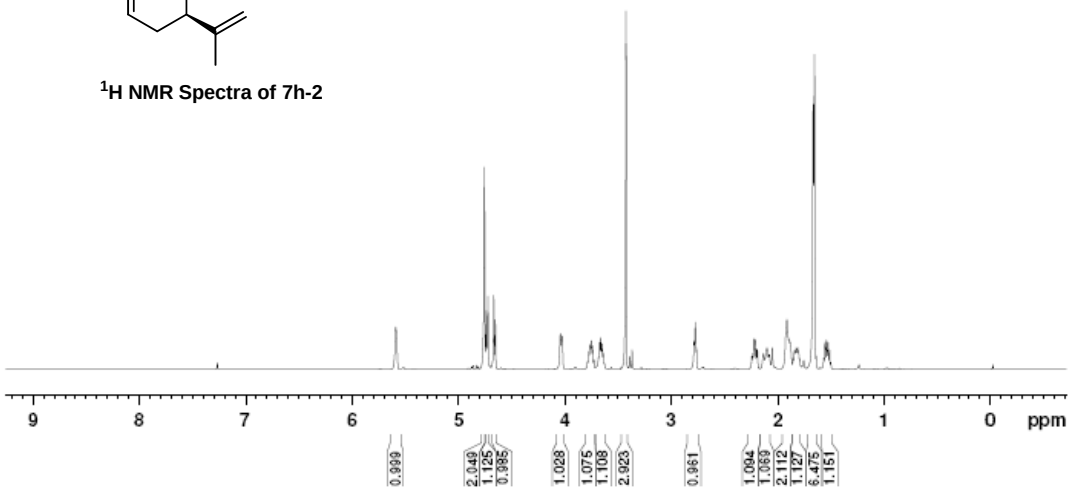


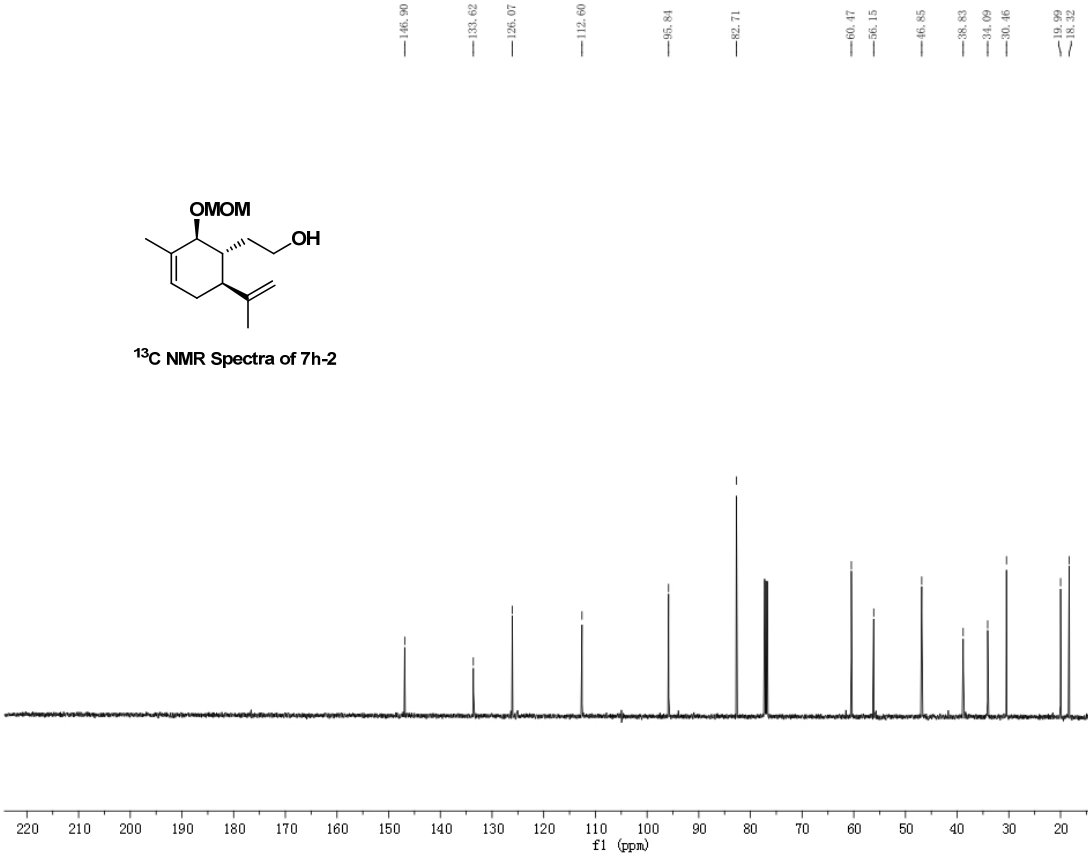
^{13}C NMR Spectra of 7h-1



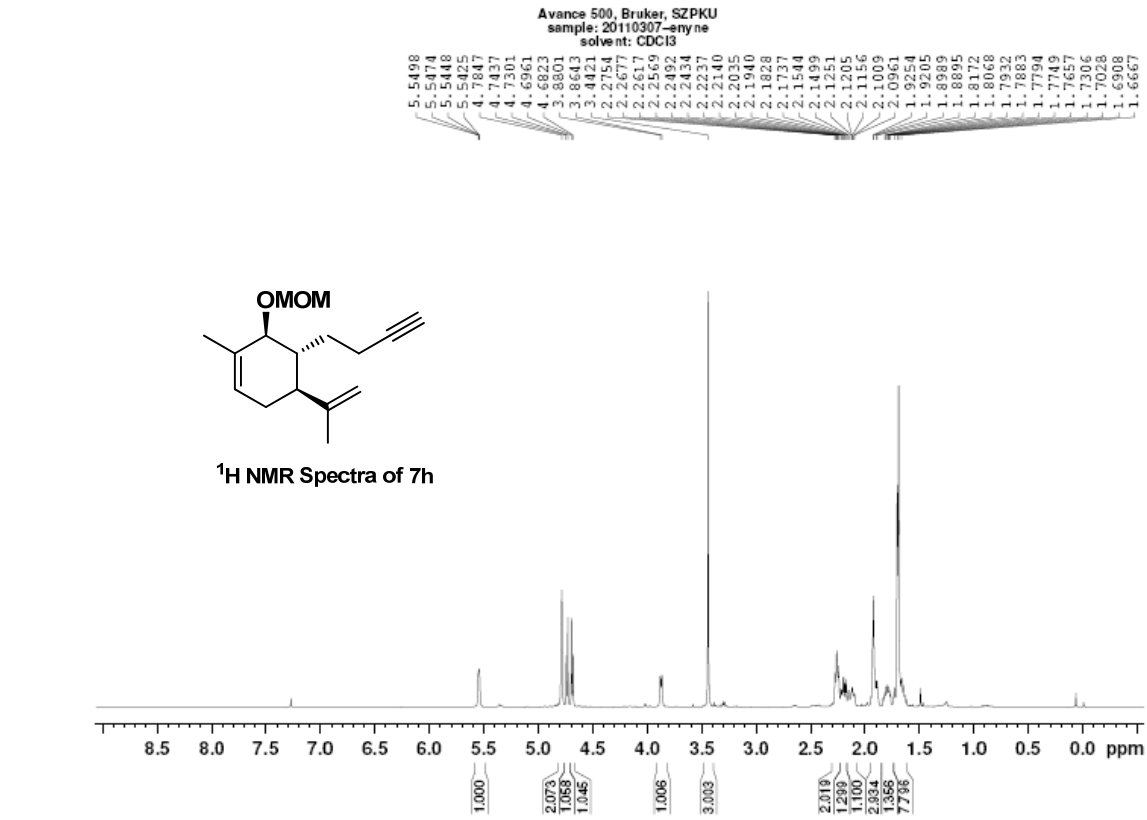


^{1}H NMR Spectra of 7h-2

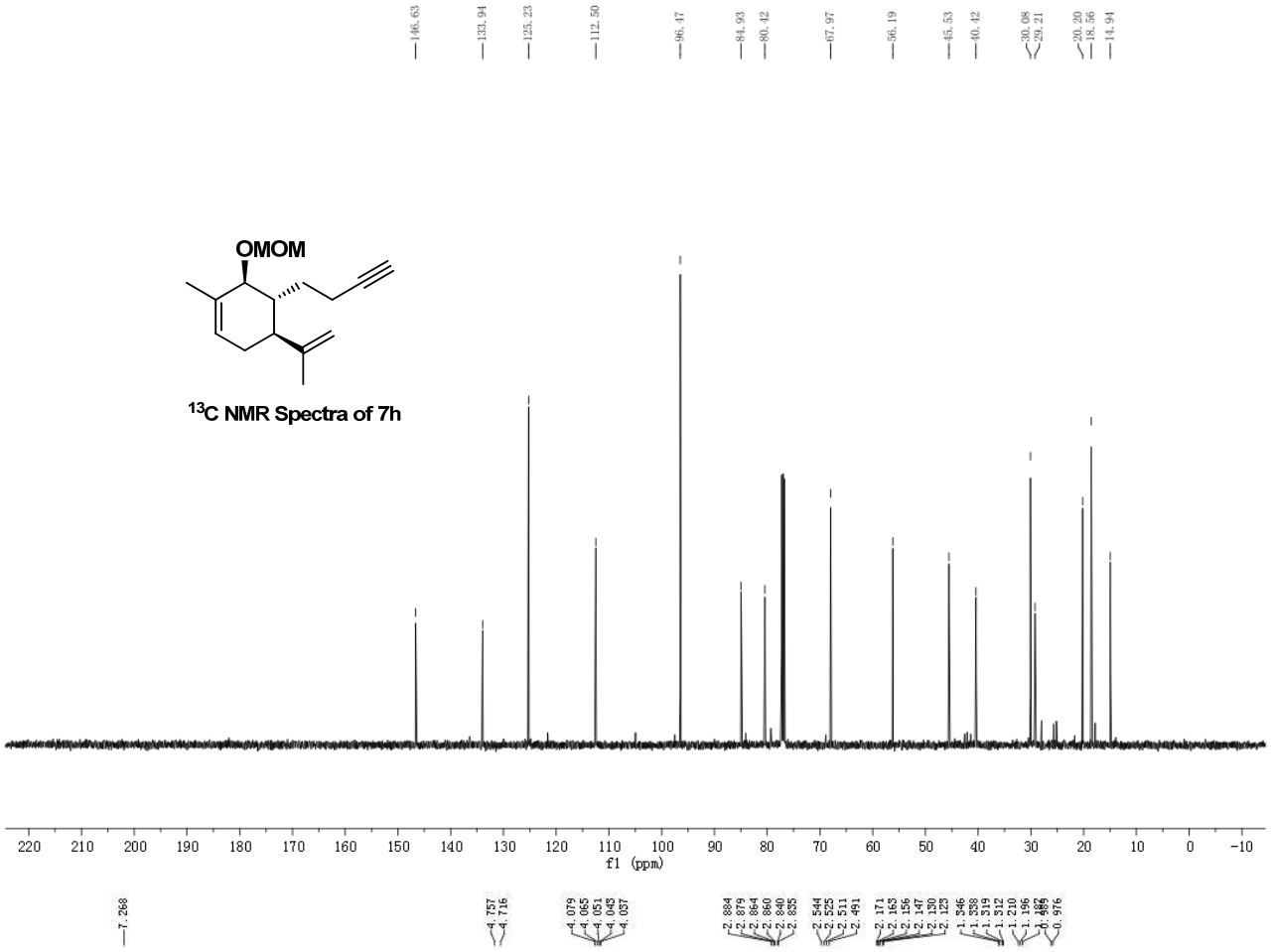




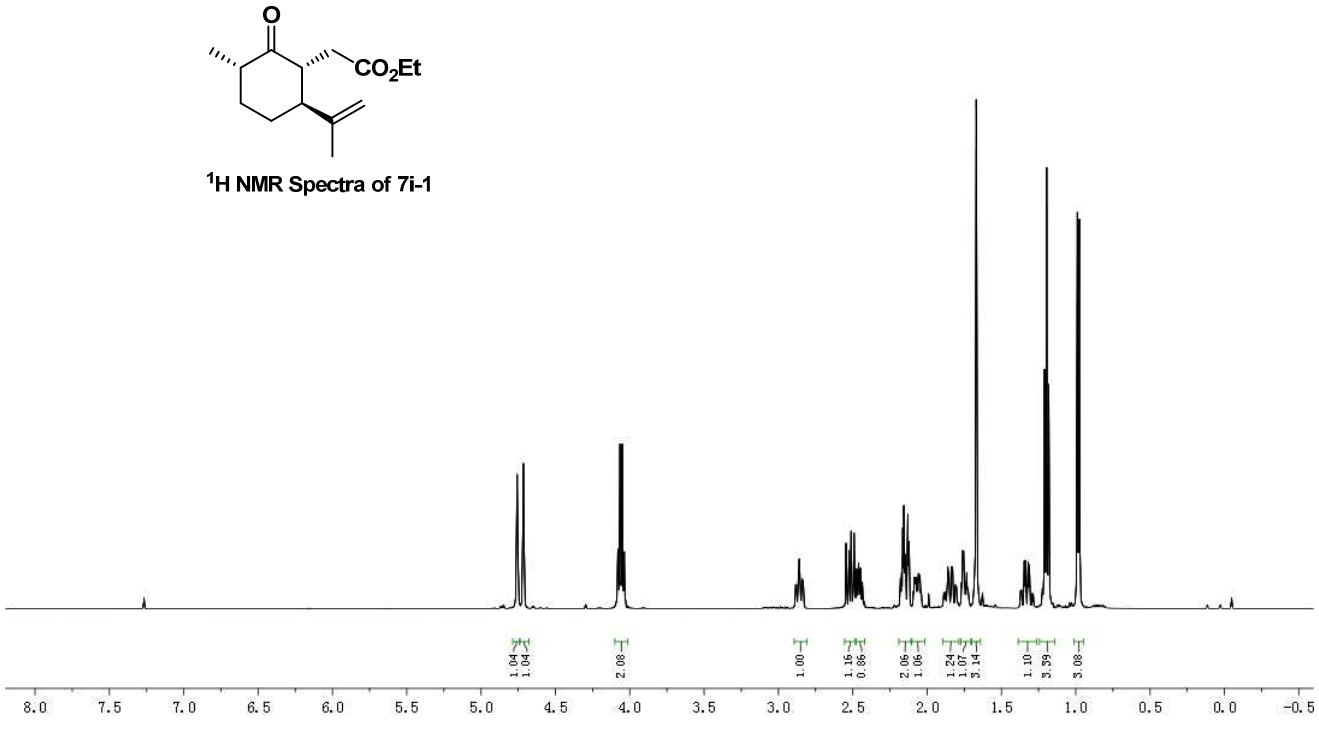
^{13}C NMR Spectra of 7h-2



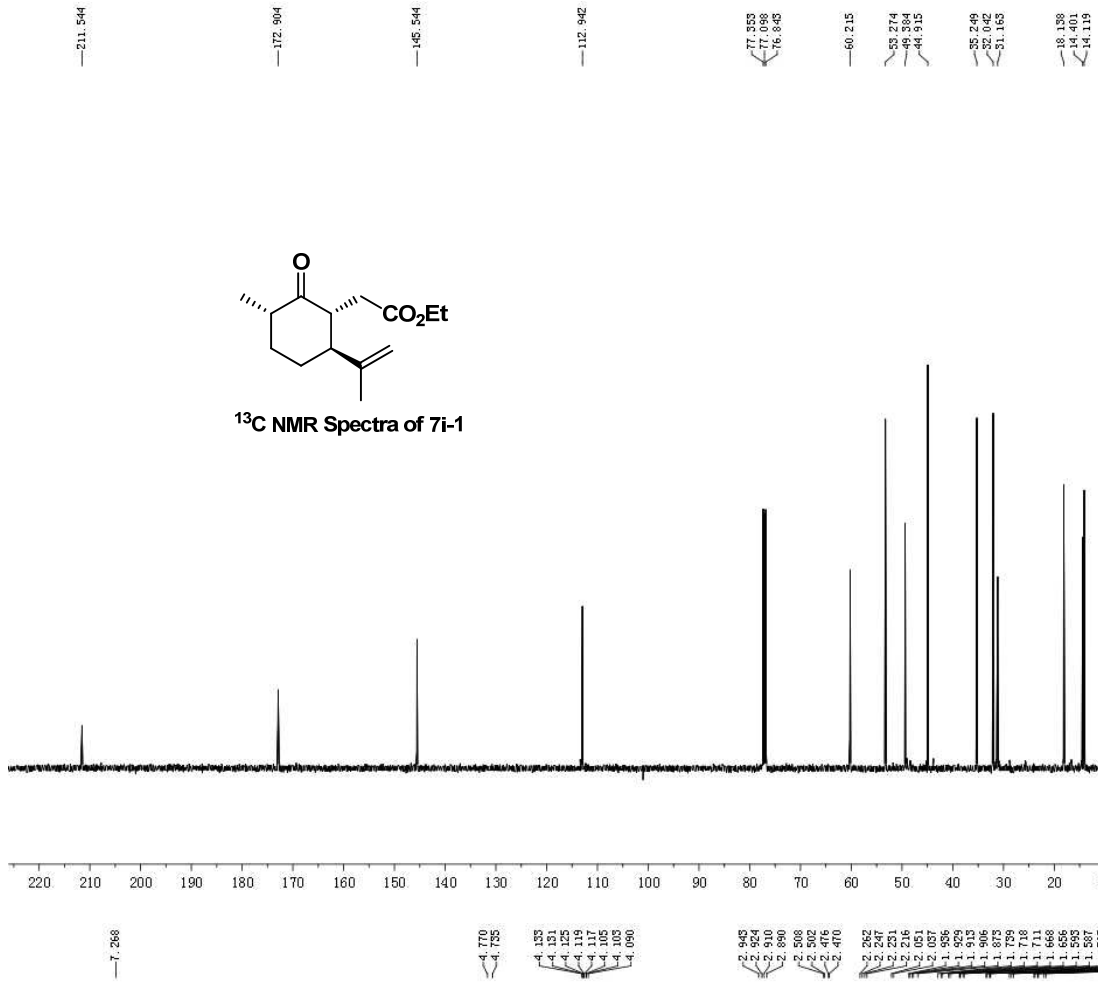
^{1}H NMR Spectra of 7h



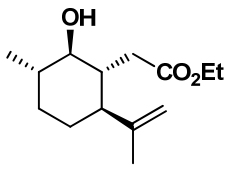
^{13}C NMR Spectra of 7h



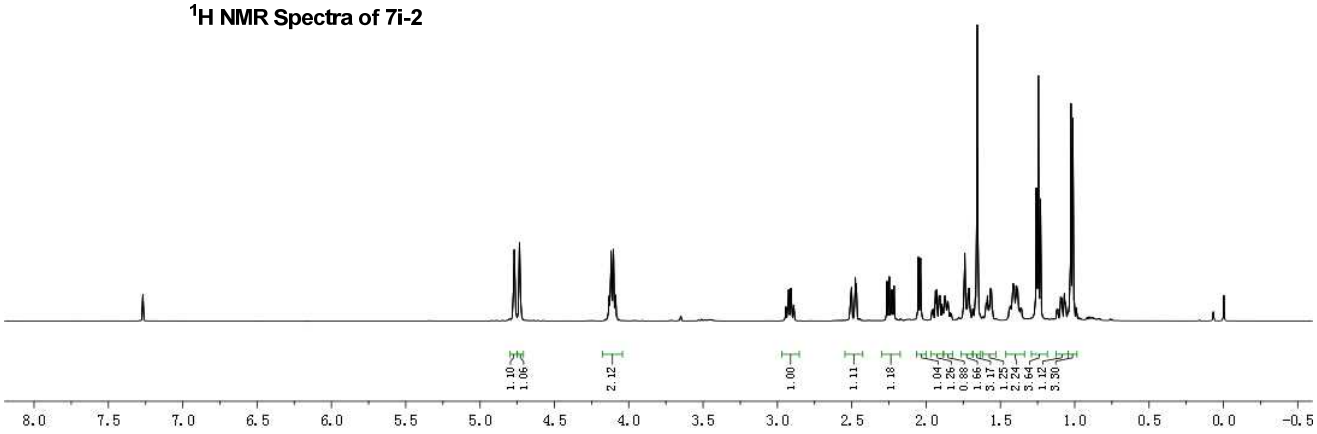
^{1}H NMR Spectra of 7i-1

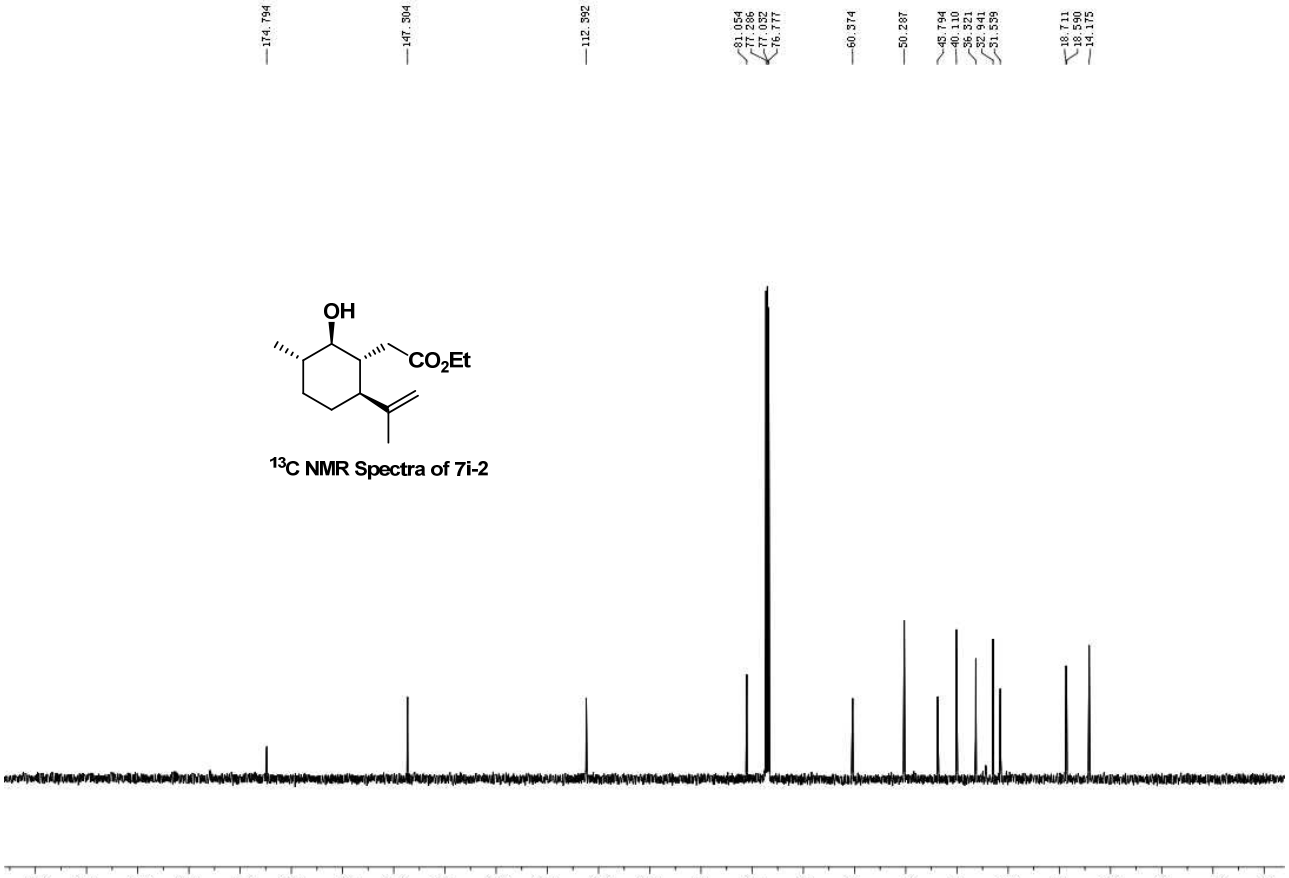


^{13}C NMR Spectra of 7i-1

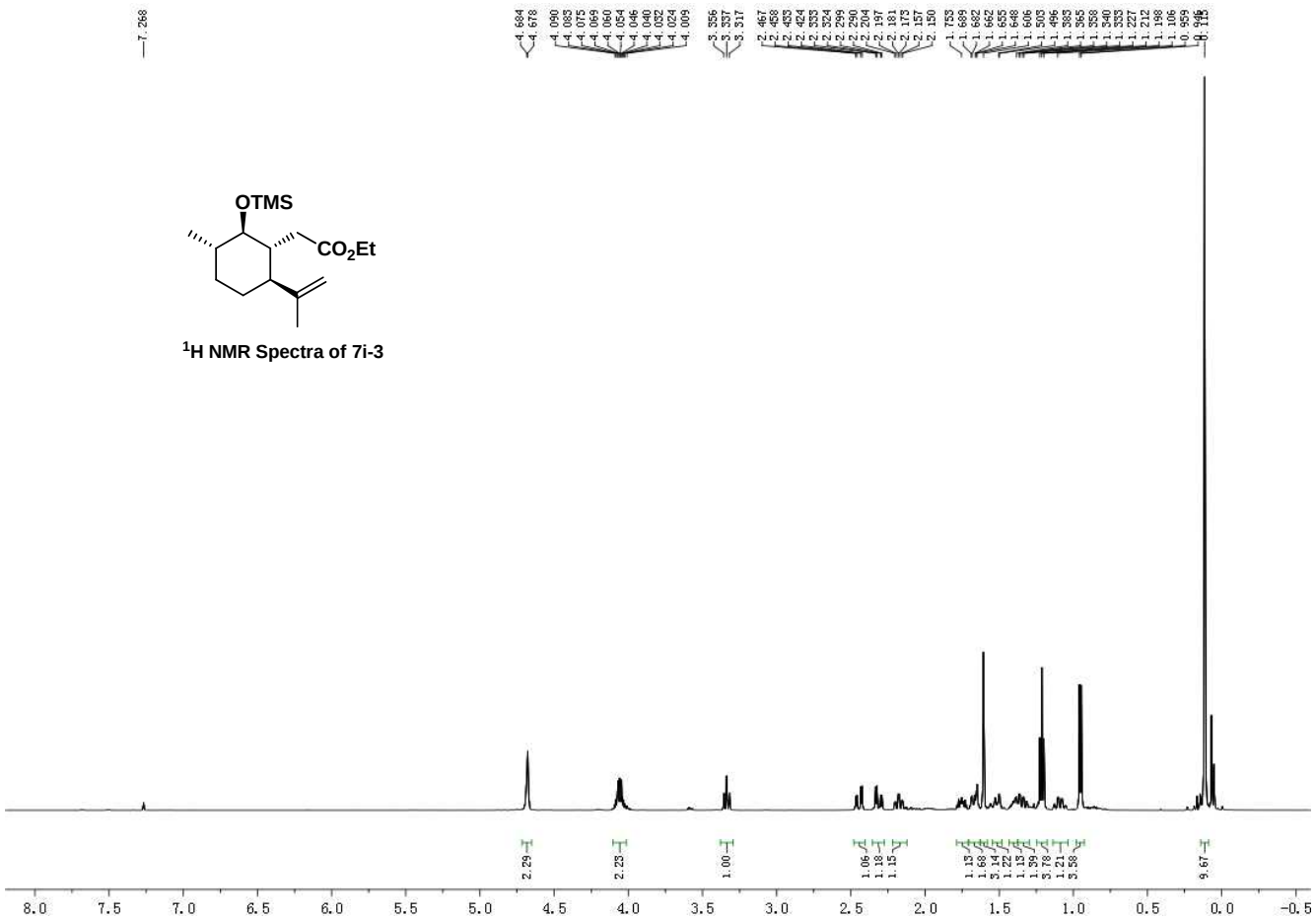


^{1}H NMR Spectra of 7i-2

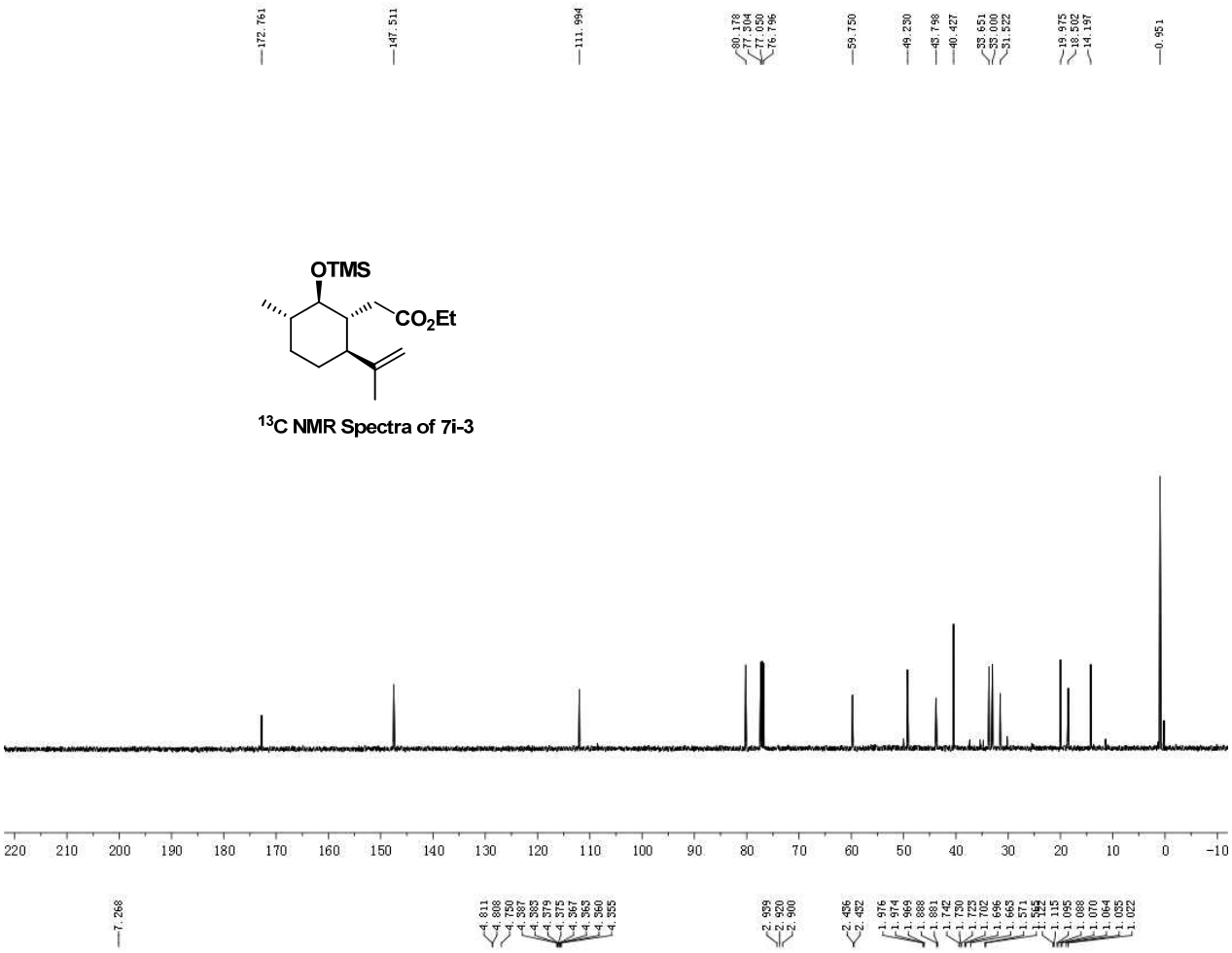




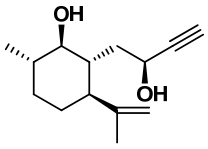
^{13}C NMR Spectra of 7i-2



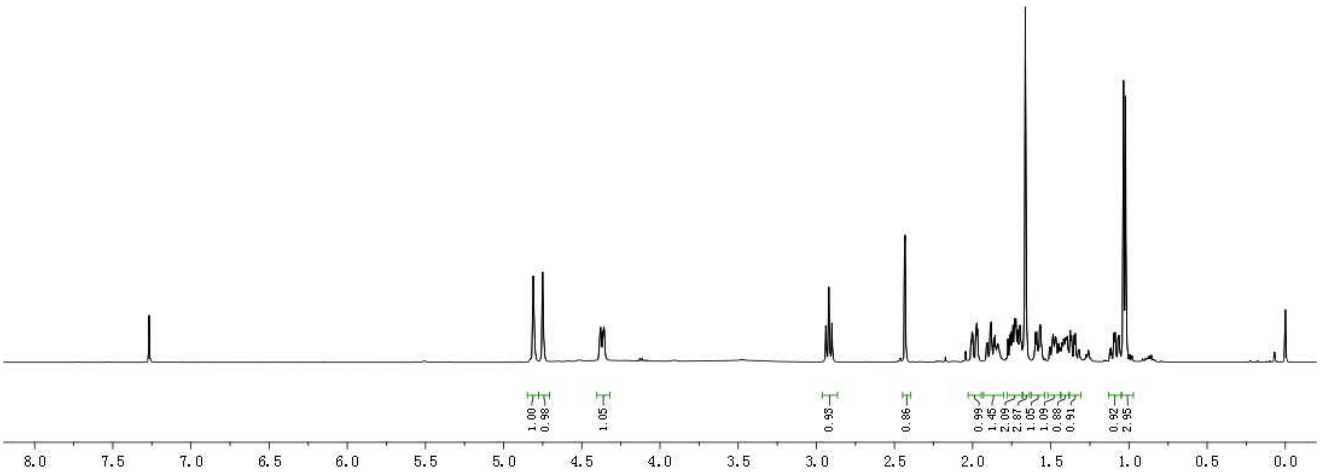
^{1}H NMR Spectra of 7i-3

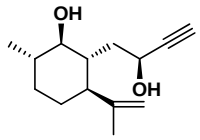


^{13}C NMR Spectra of 7i-3

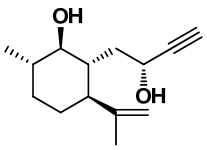


^{1}H NMR Spectra of 7i-5

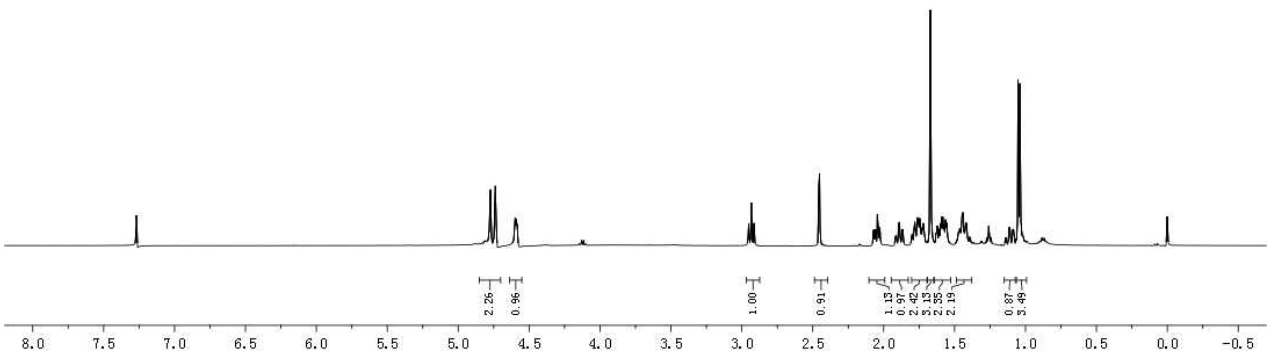


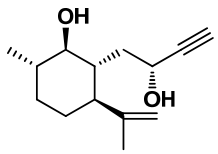


^{13}C NMR Spectra of 7i-5

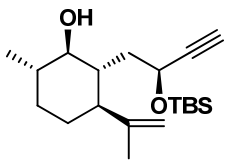


^{1}H NMR Spectra of 7j-1

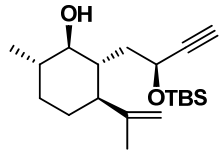




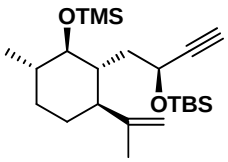
^{13}C NMR Spectra of 7j-1



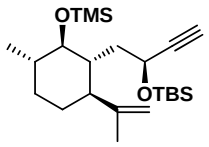
^{1}H NMR Spectra of 7i-6



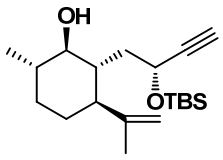
^{13}C NMR Spectra of 7i-6



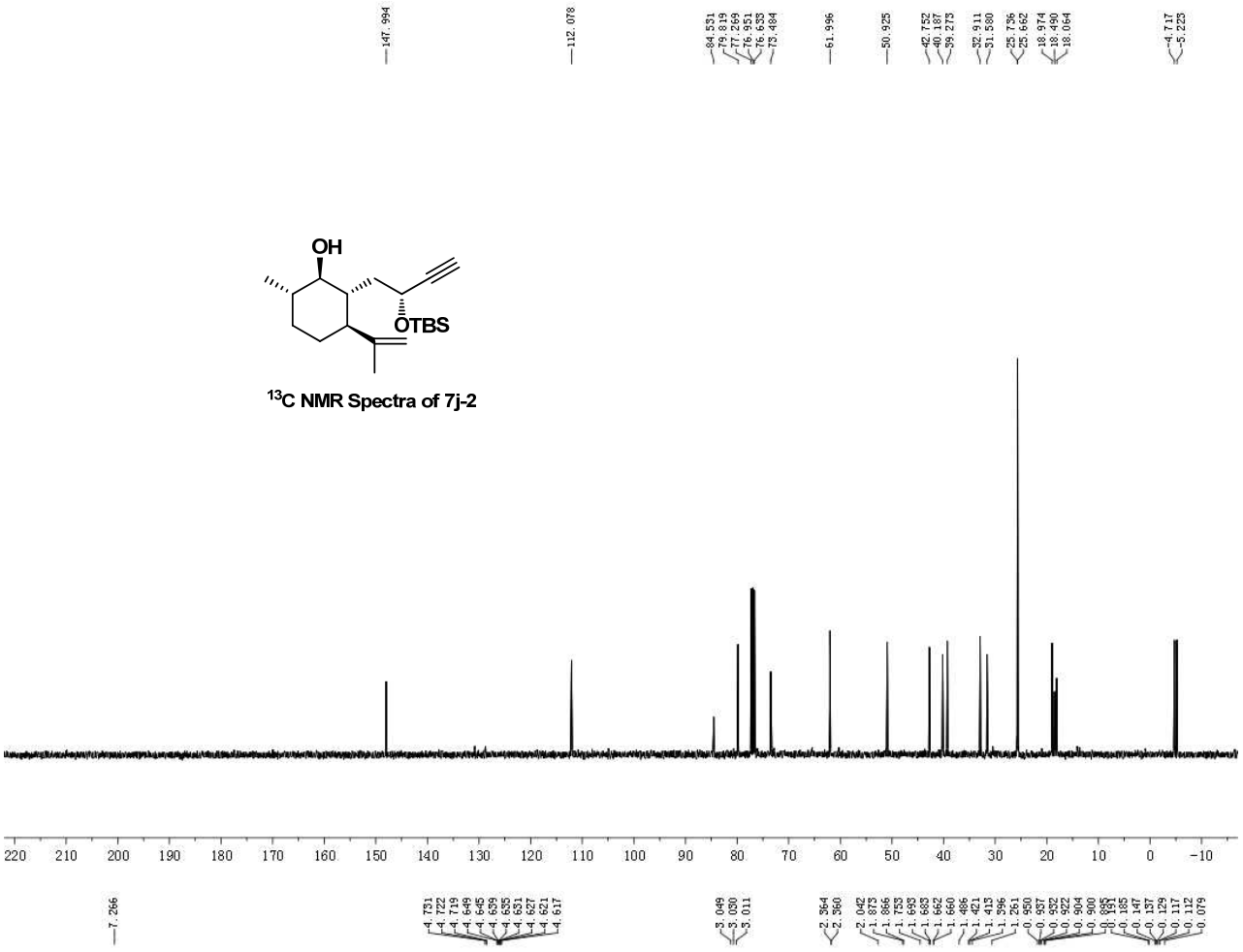
^{1}H NMR Spectra of 7i



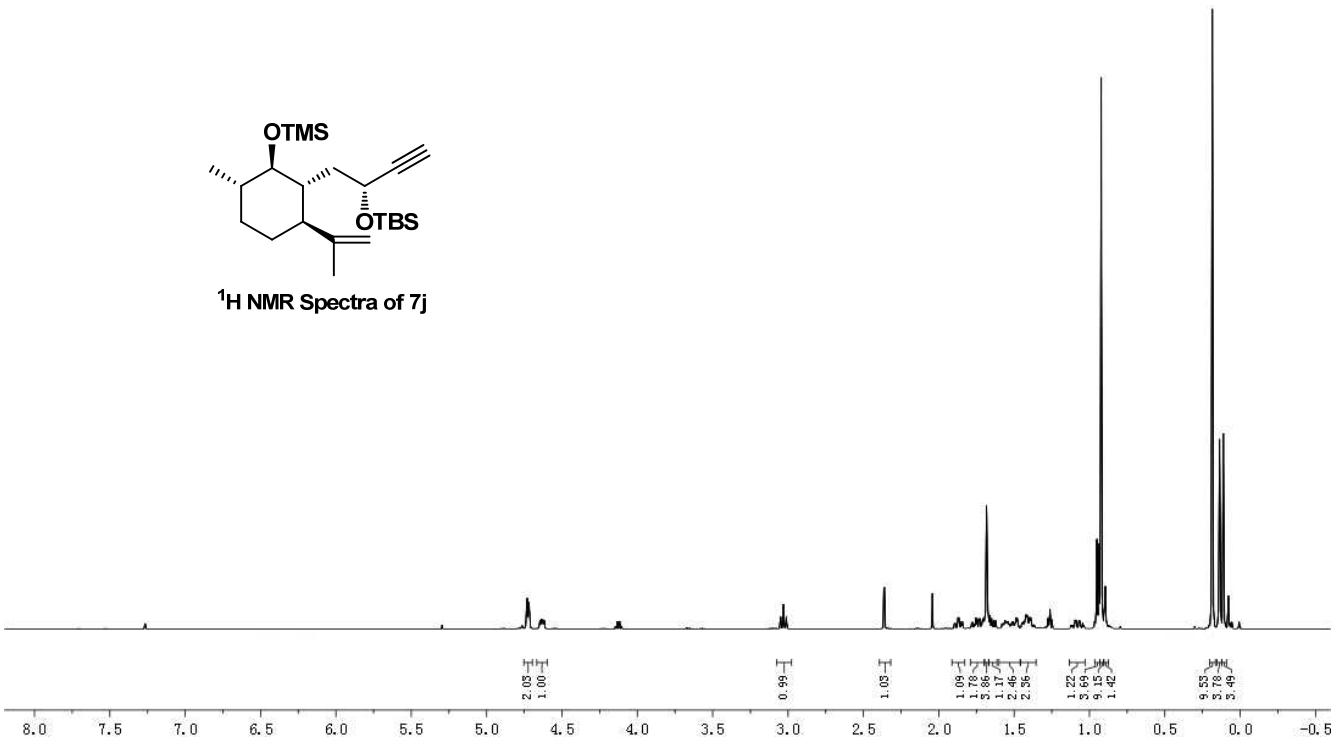
^{13}C NMR Spectra of 7i



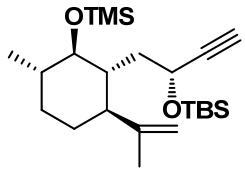
^{1}H NMR Spectra of 7j-2



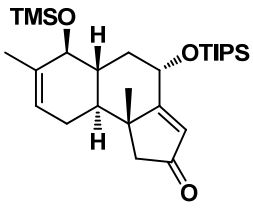
^{13}C NMR Spectra of 7j-2



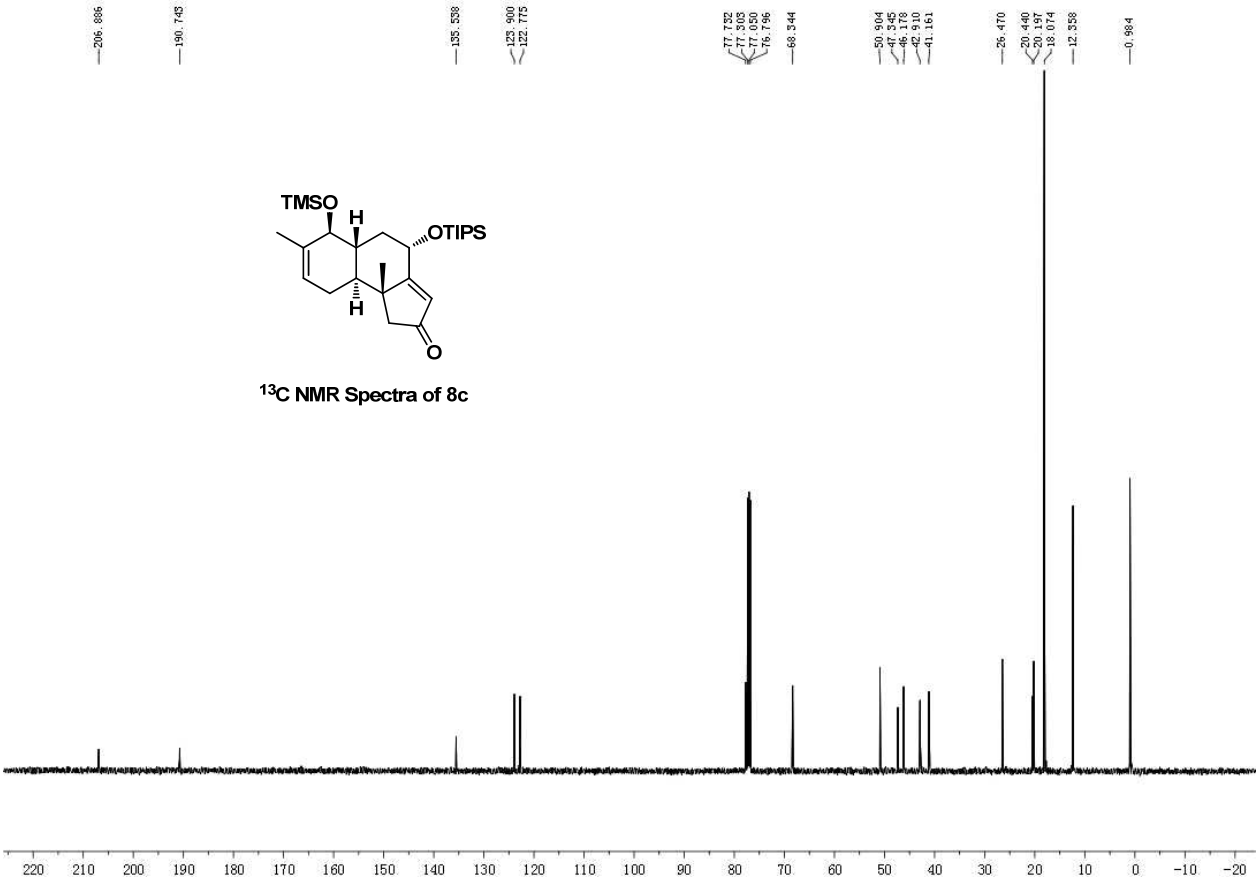
^{1}H NMR Spectra of 7j



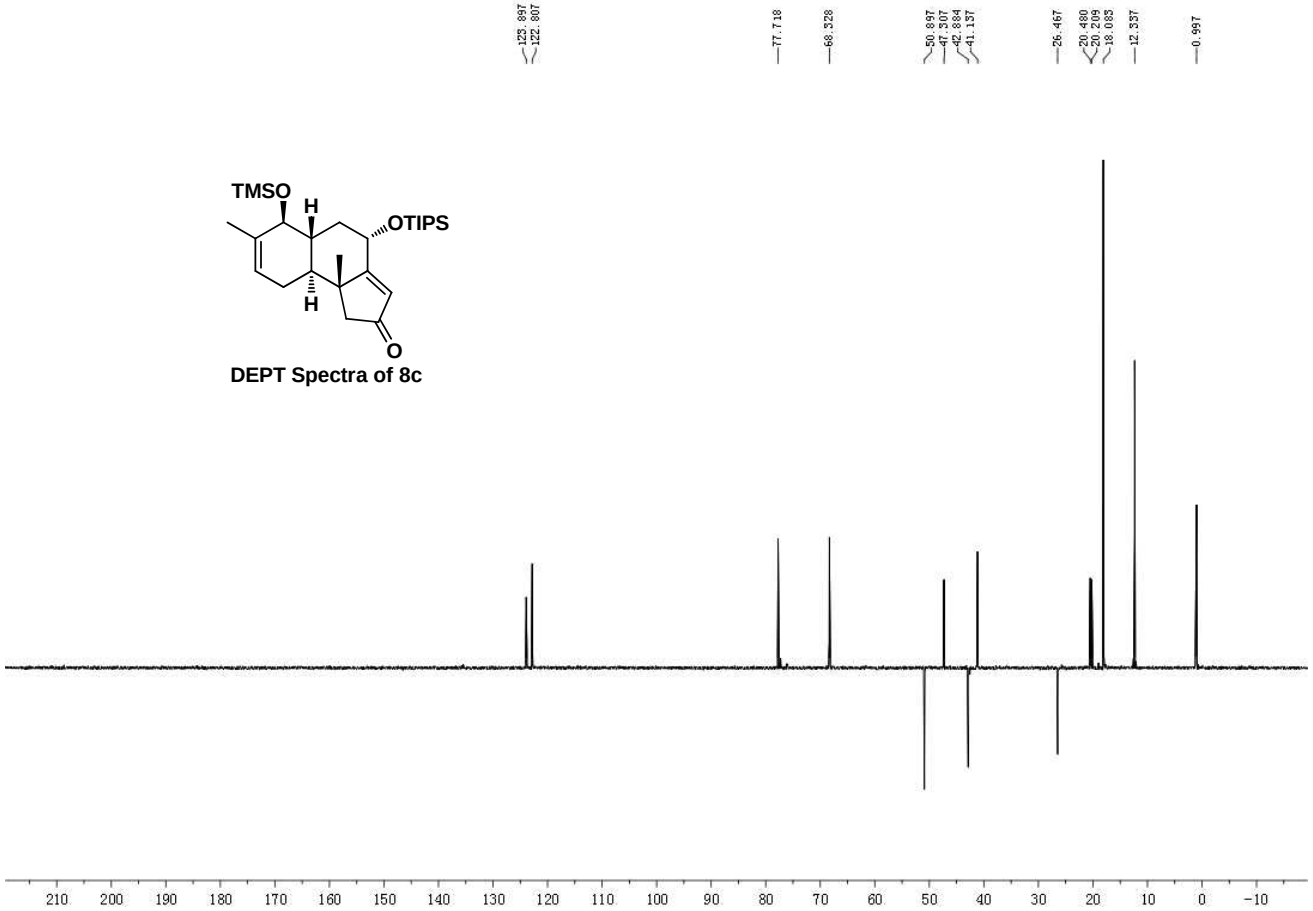
^{13}C NMR Spectra of 7j



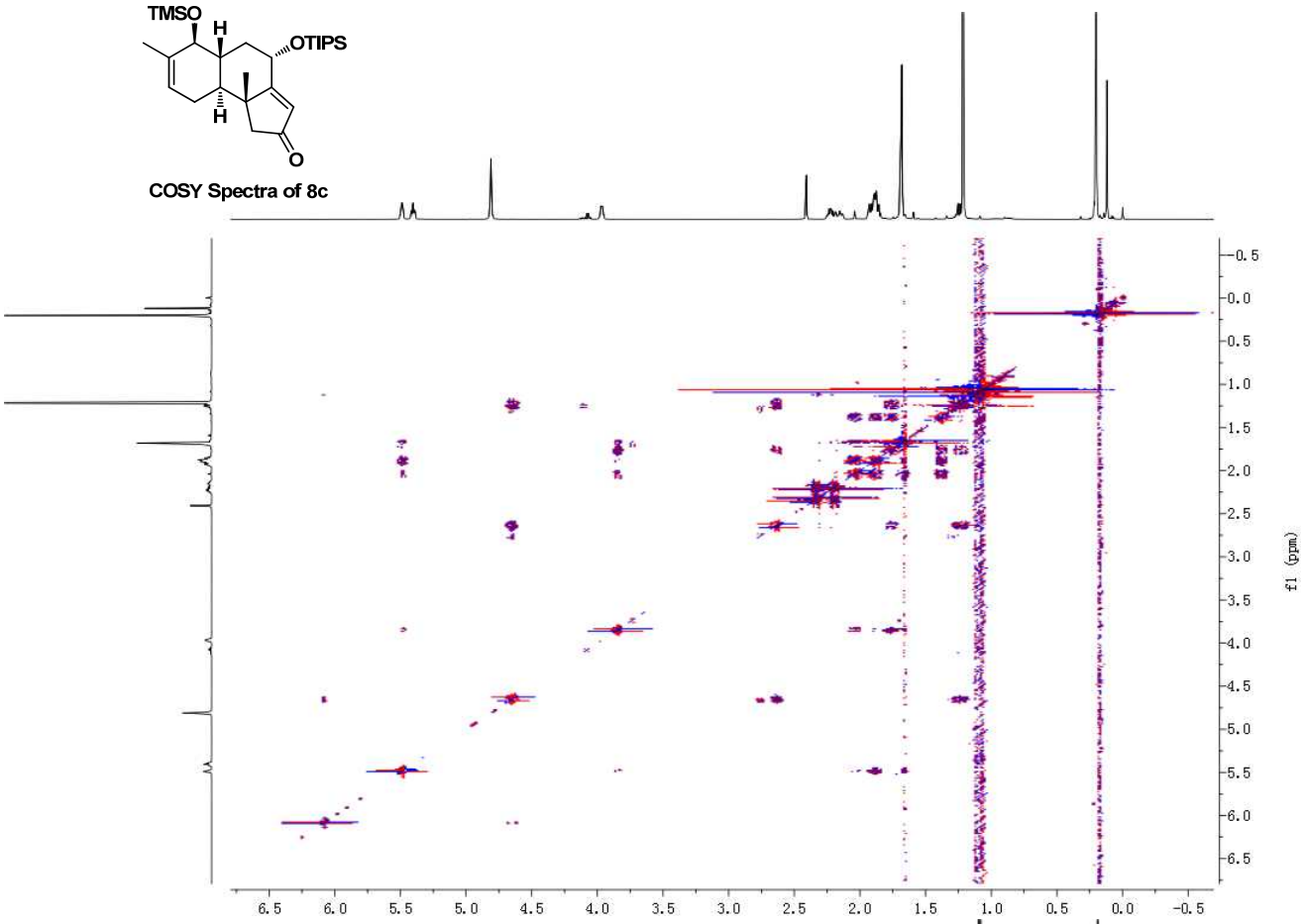
^{1}H NMR Spectra of 8c



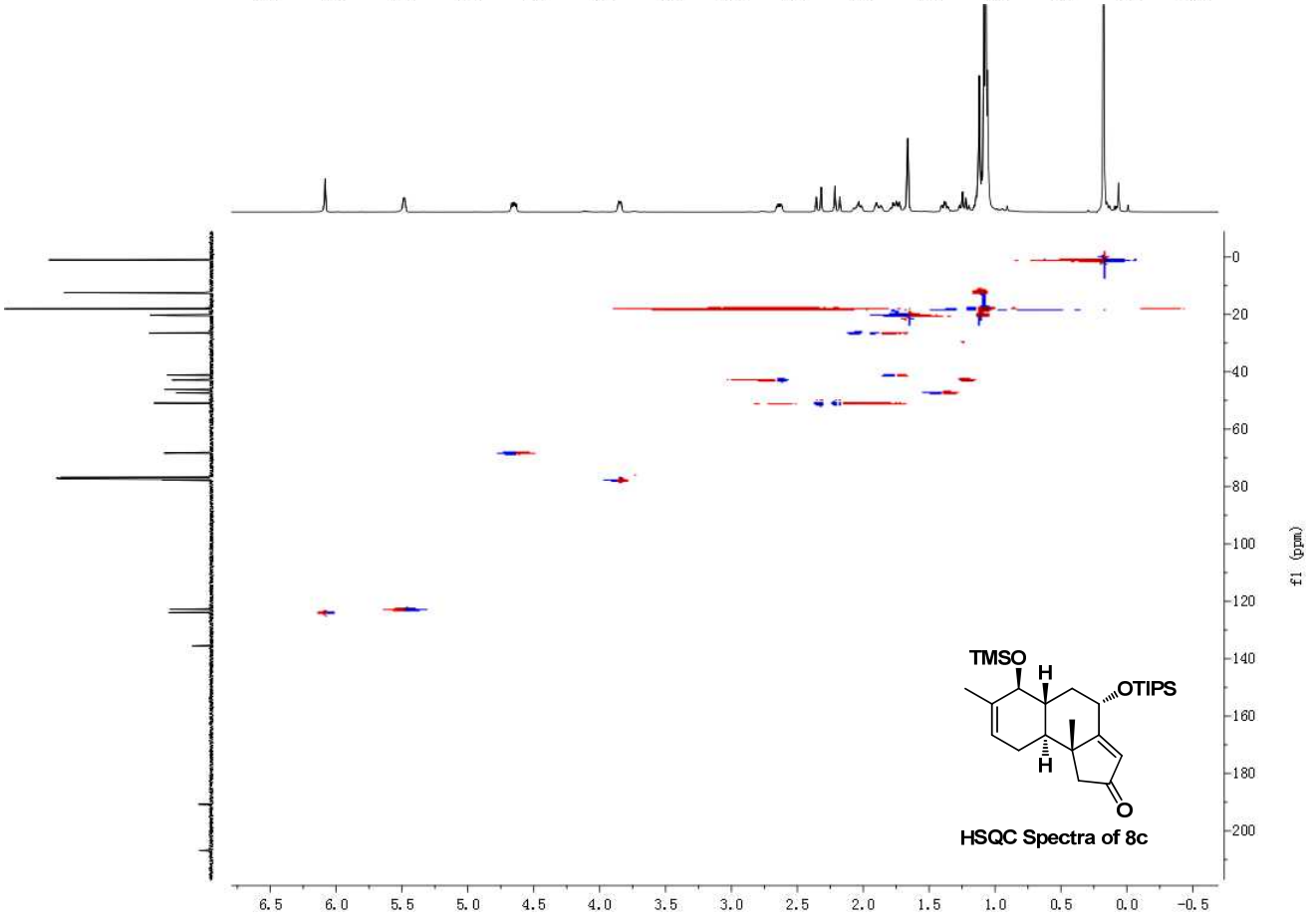
^{13}C NMR Spectra of 8c



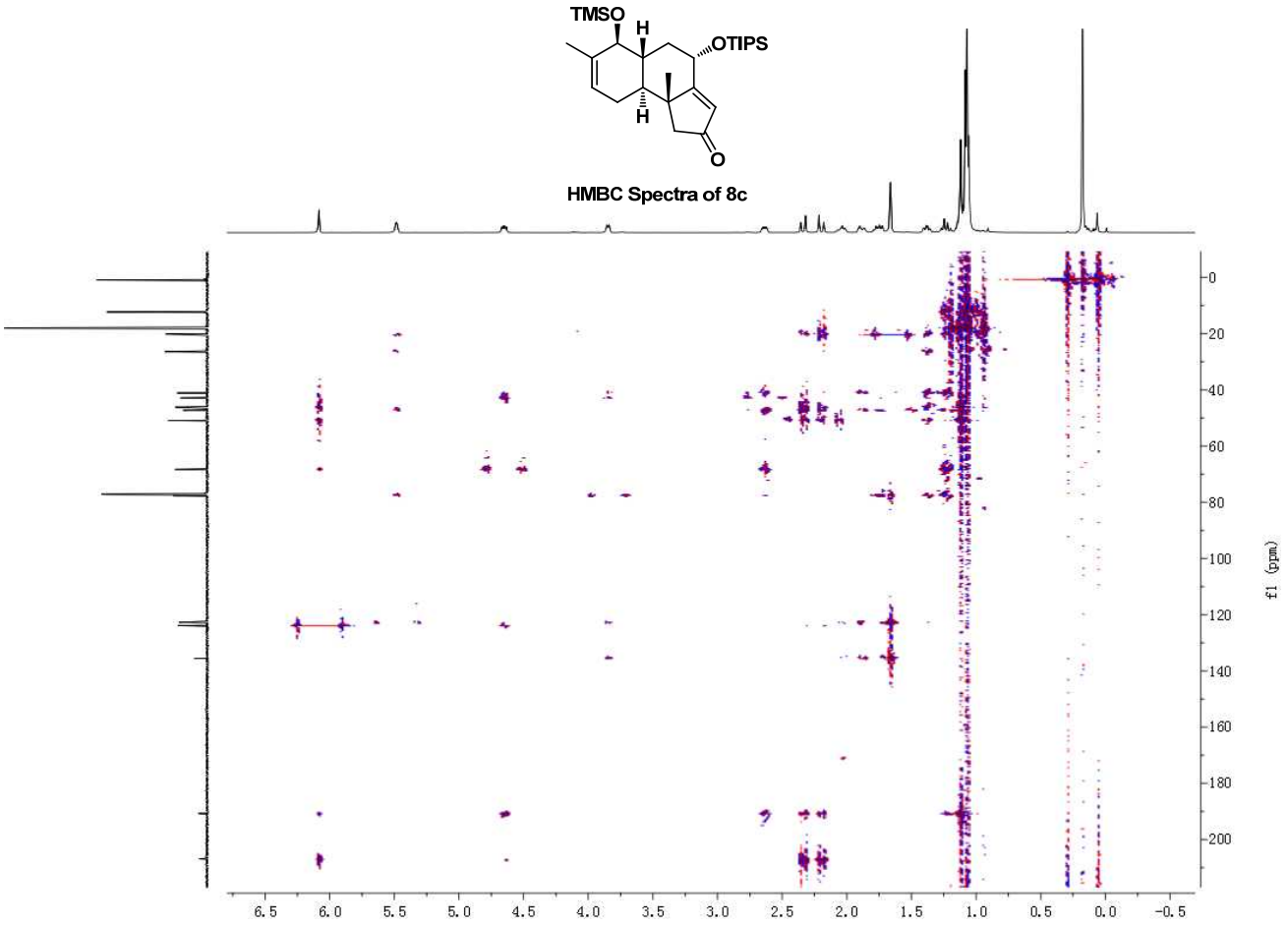
DEPT Spectra of 8c



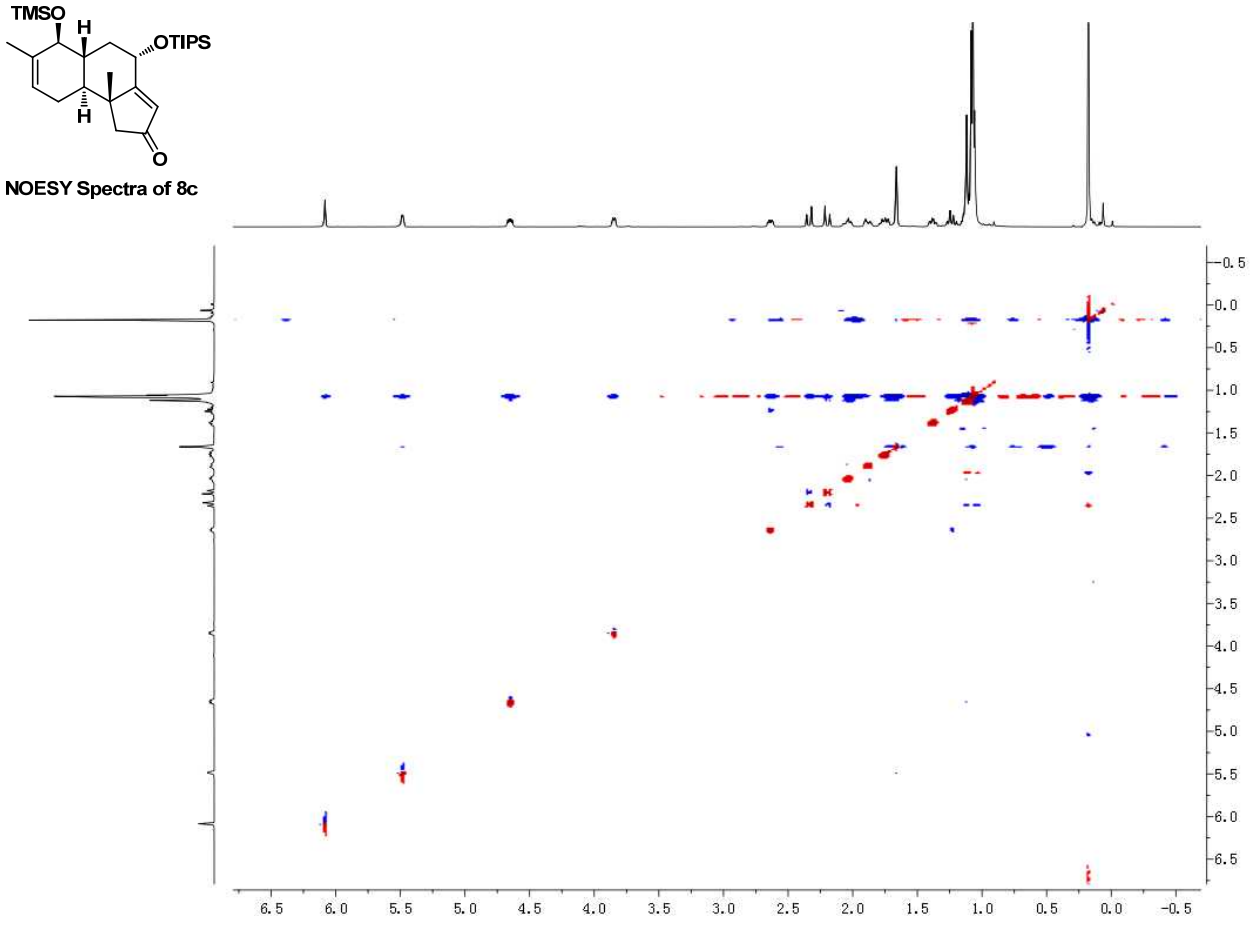
COSY Spectra of 8c



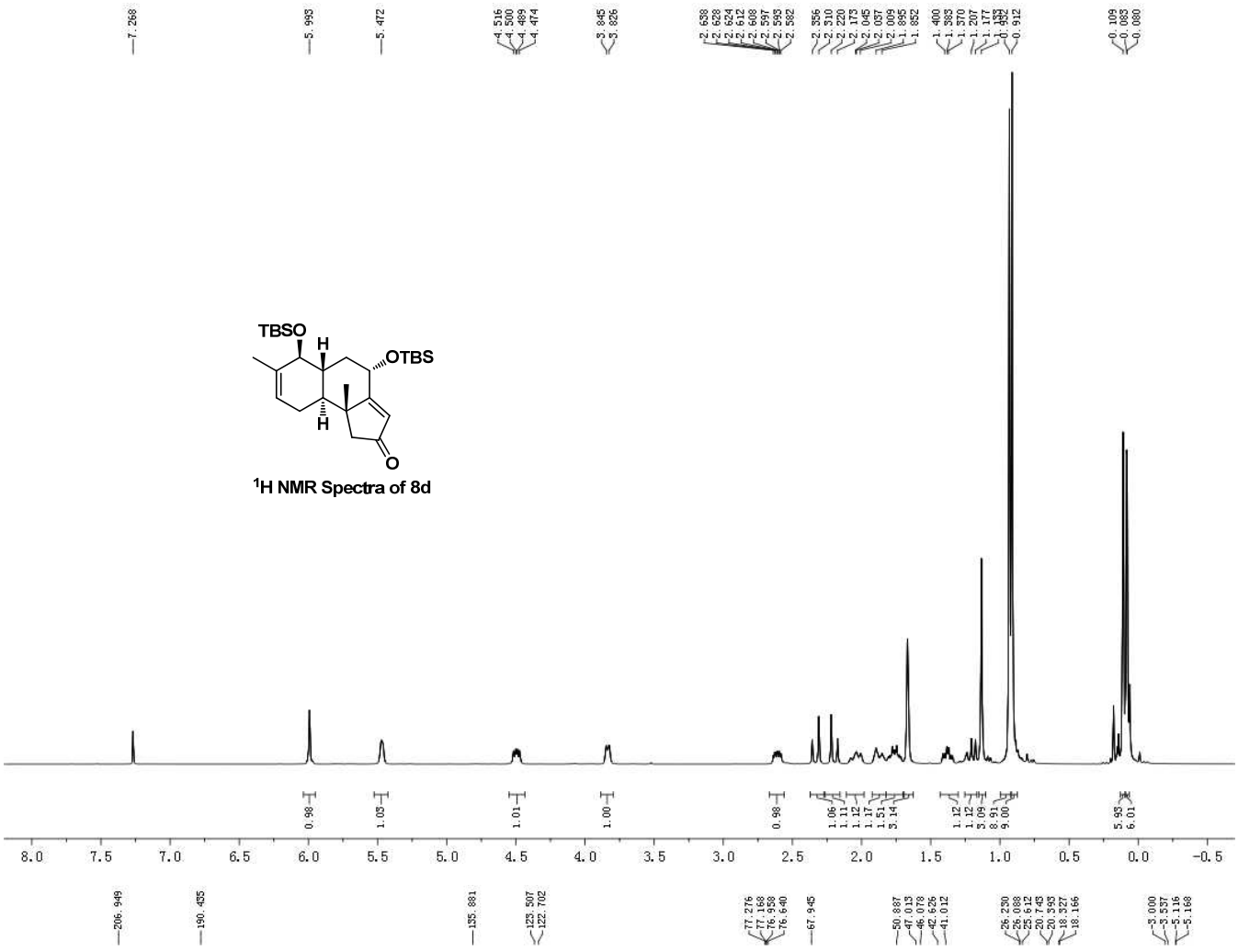
HSQC Spectra of 8c



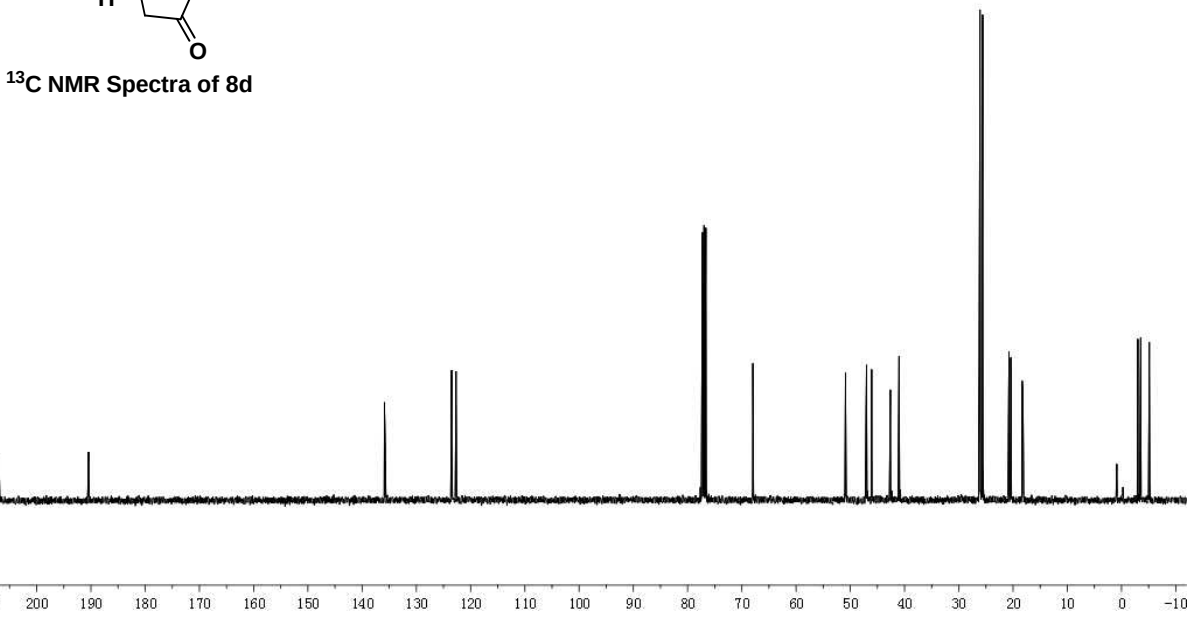
HMBC Spectra of 8c



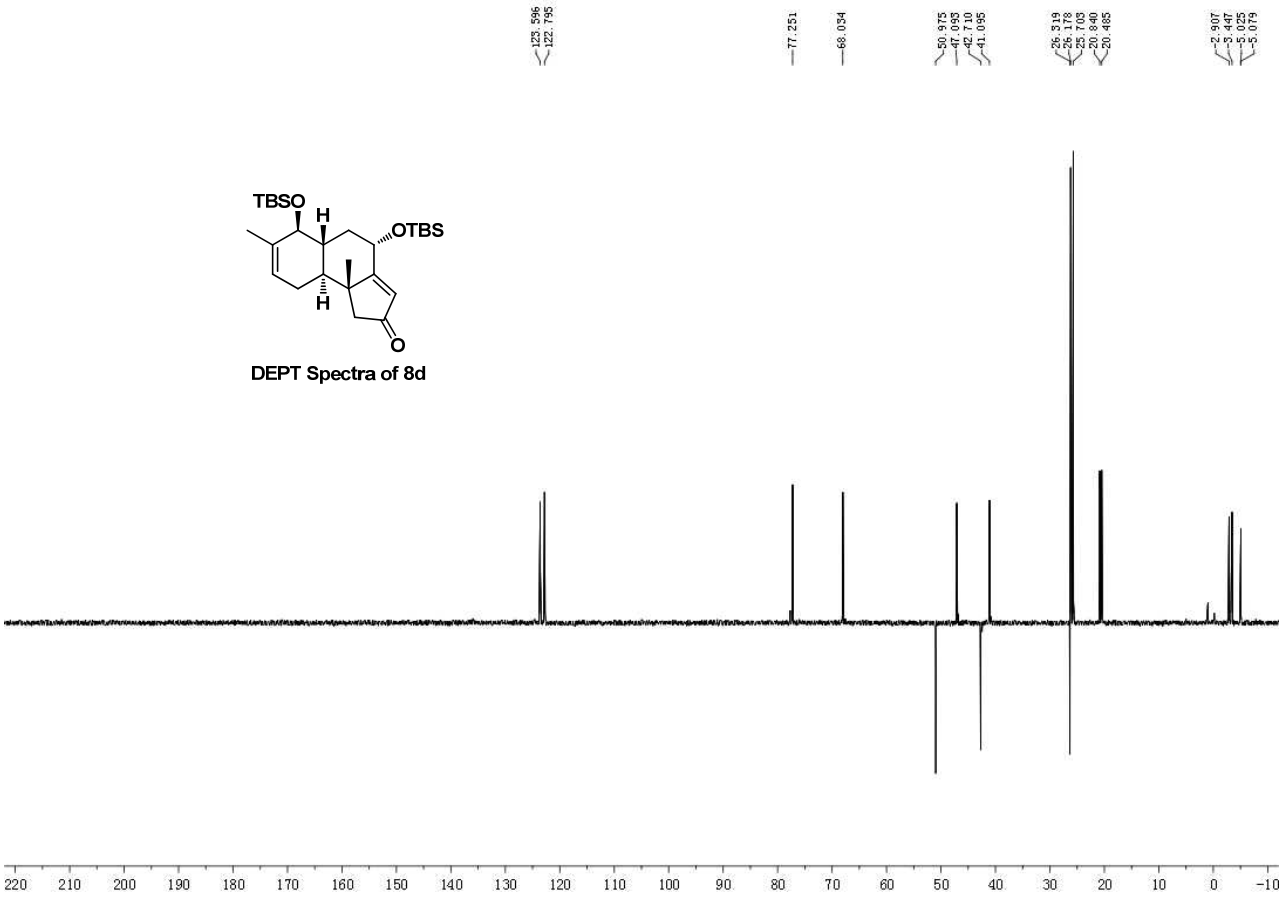
NOESY Spectra of 8c



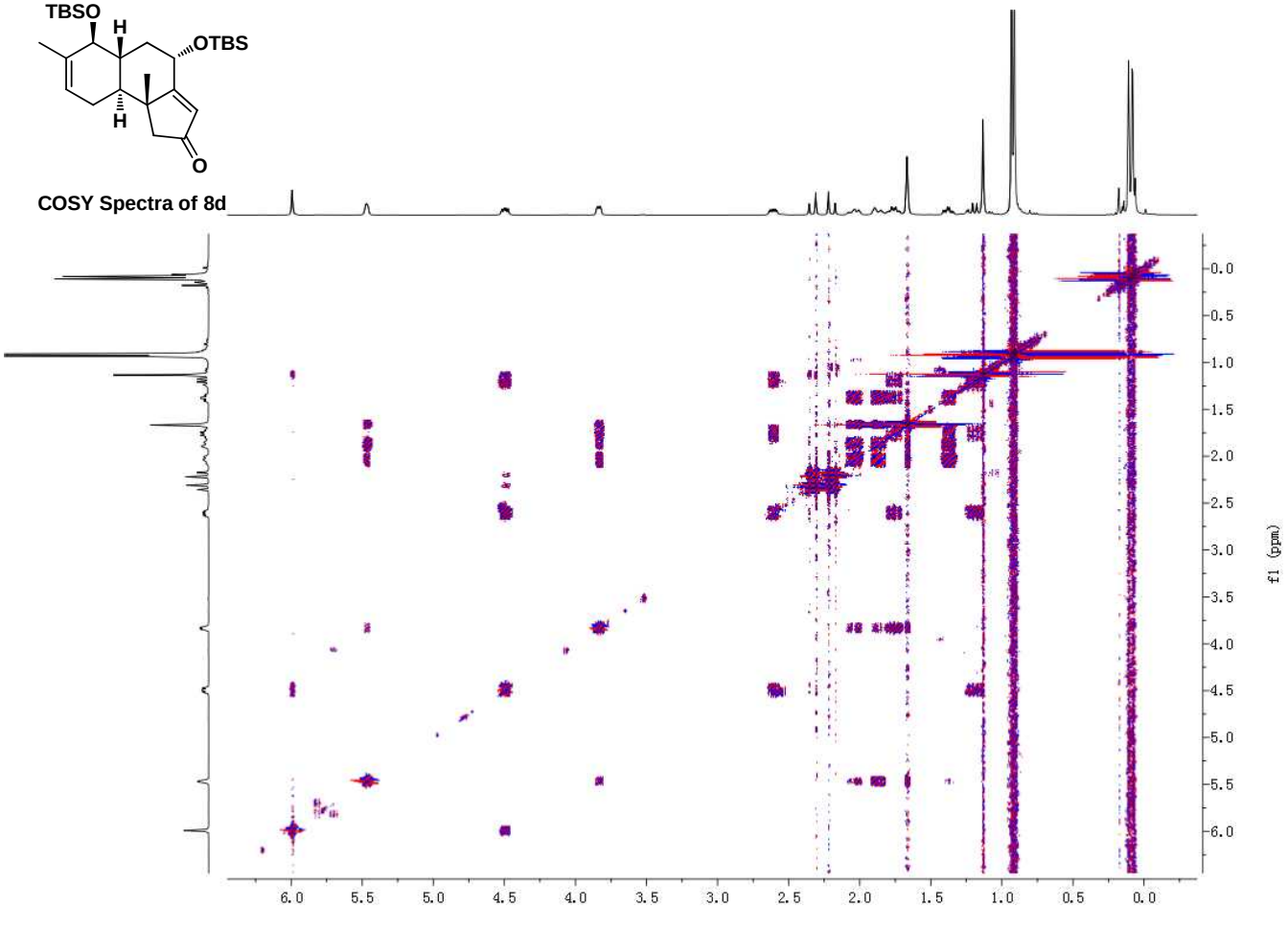
^{1}H NMR Spectra of 8d



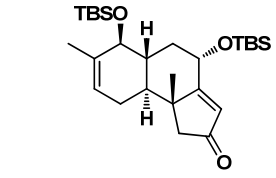
^{13}C NMR Spectra of 8d



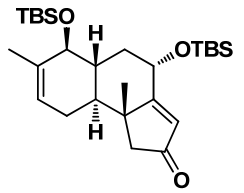
DEPT Spectra of 8d



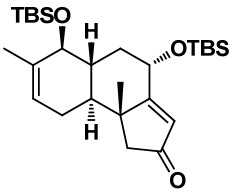
COSY Spectra of 8d



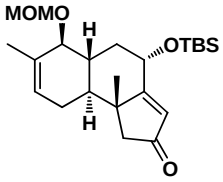
HSQC Spectra of 8d



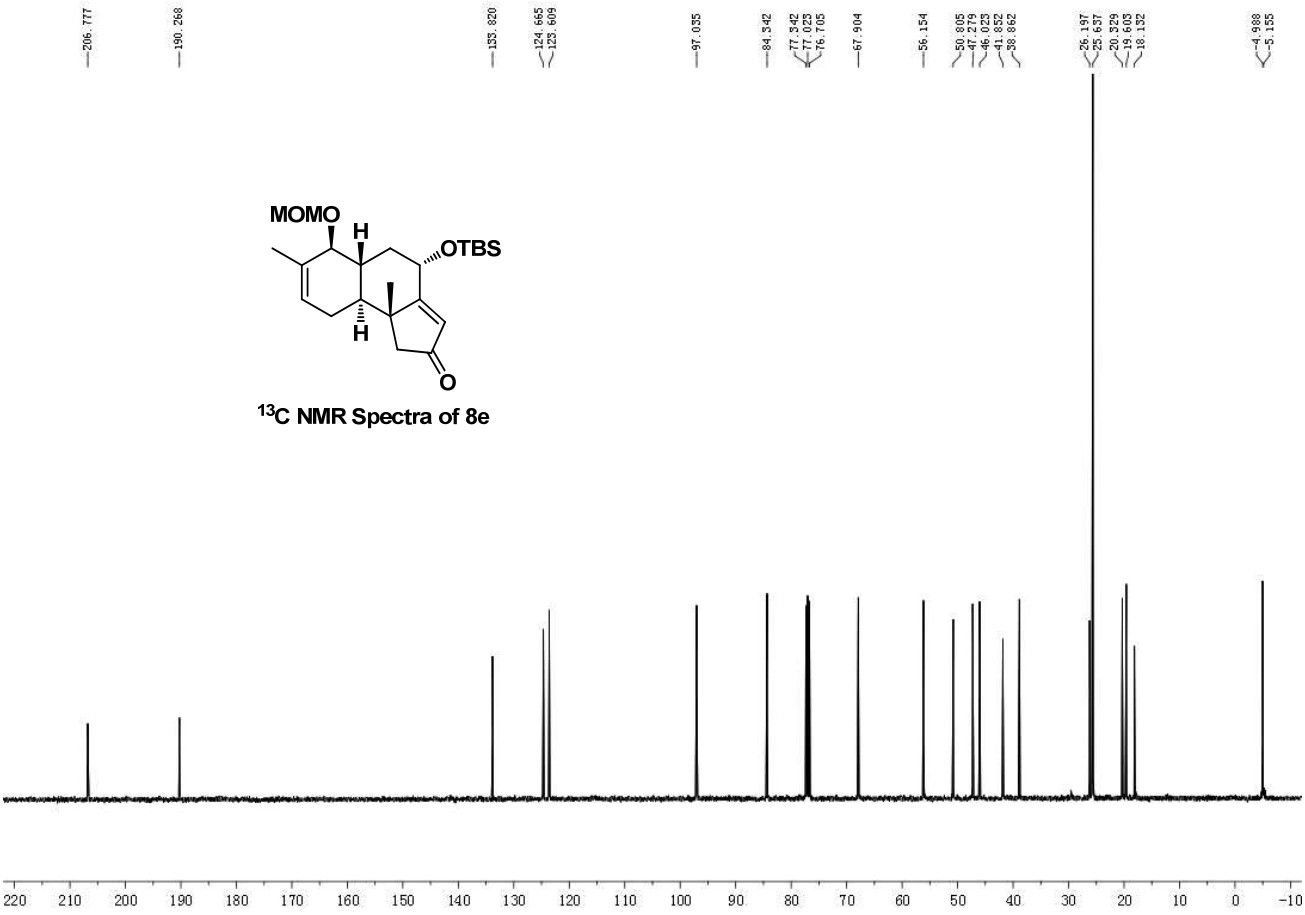
HMBC Spectra of 8d



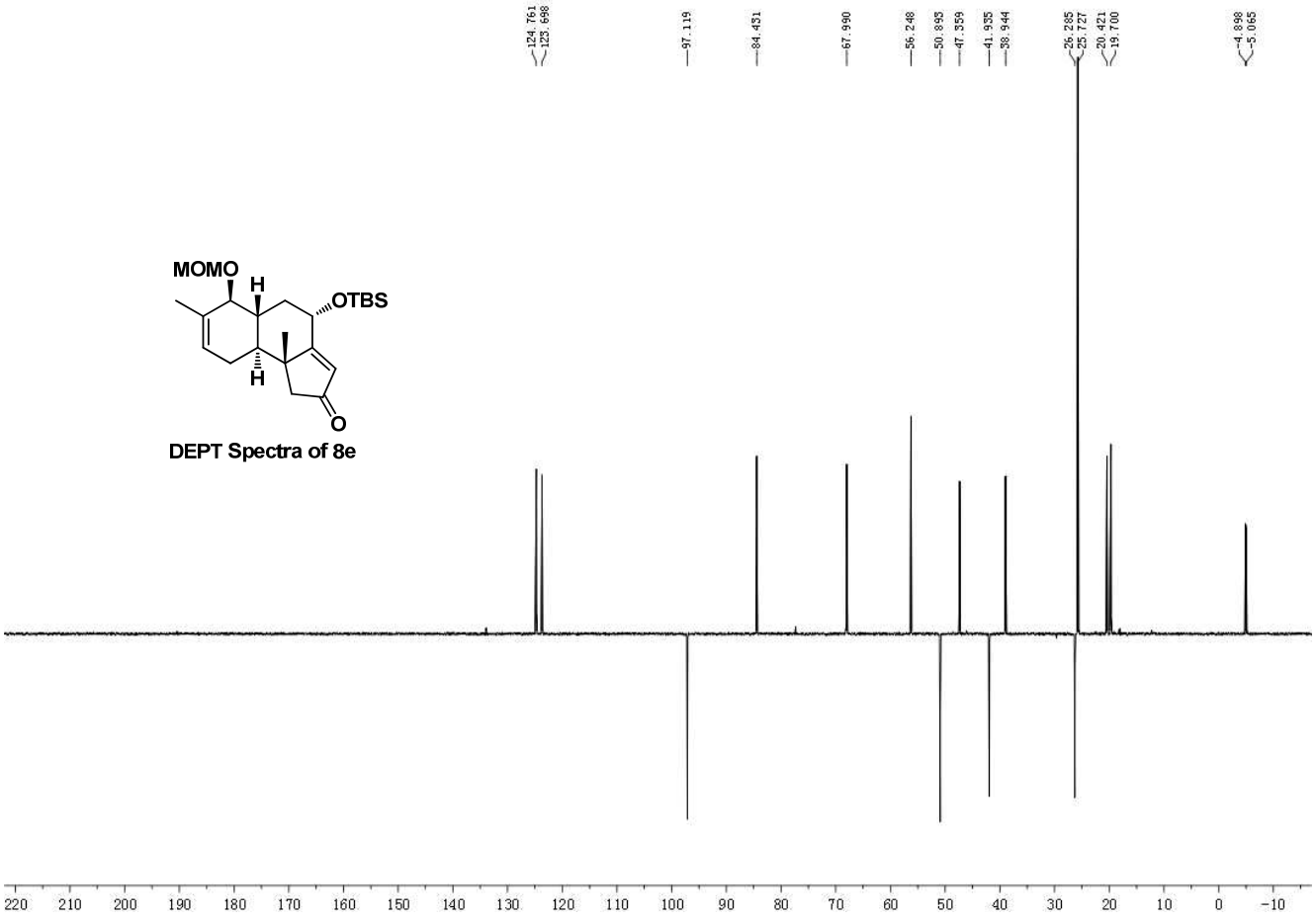
NOESY Spectra of 8d



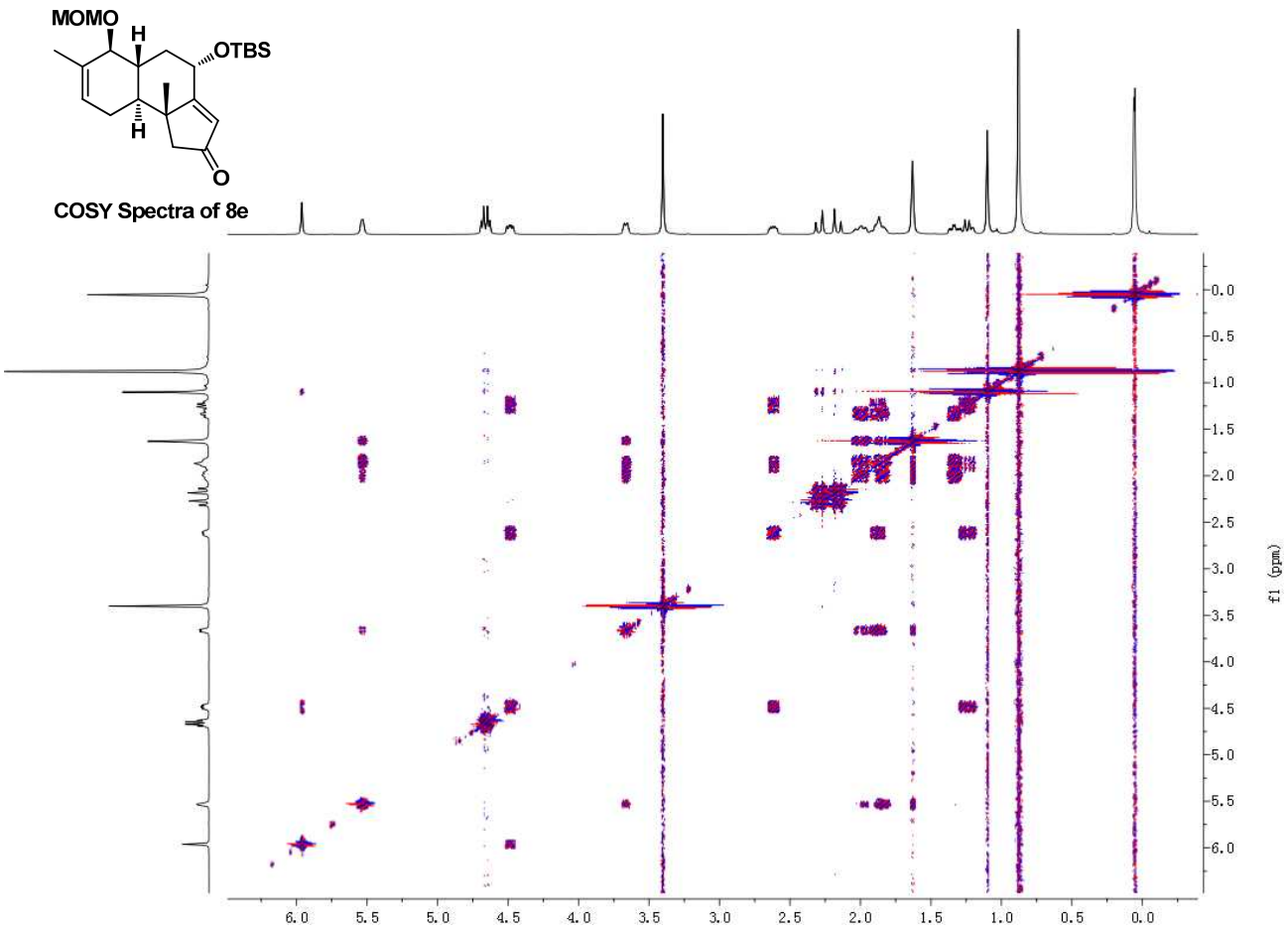
^{1}H NMR Spectra of 8e



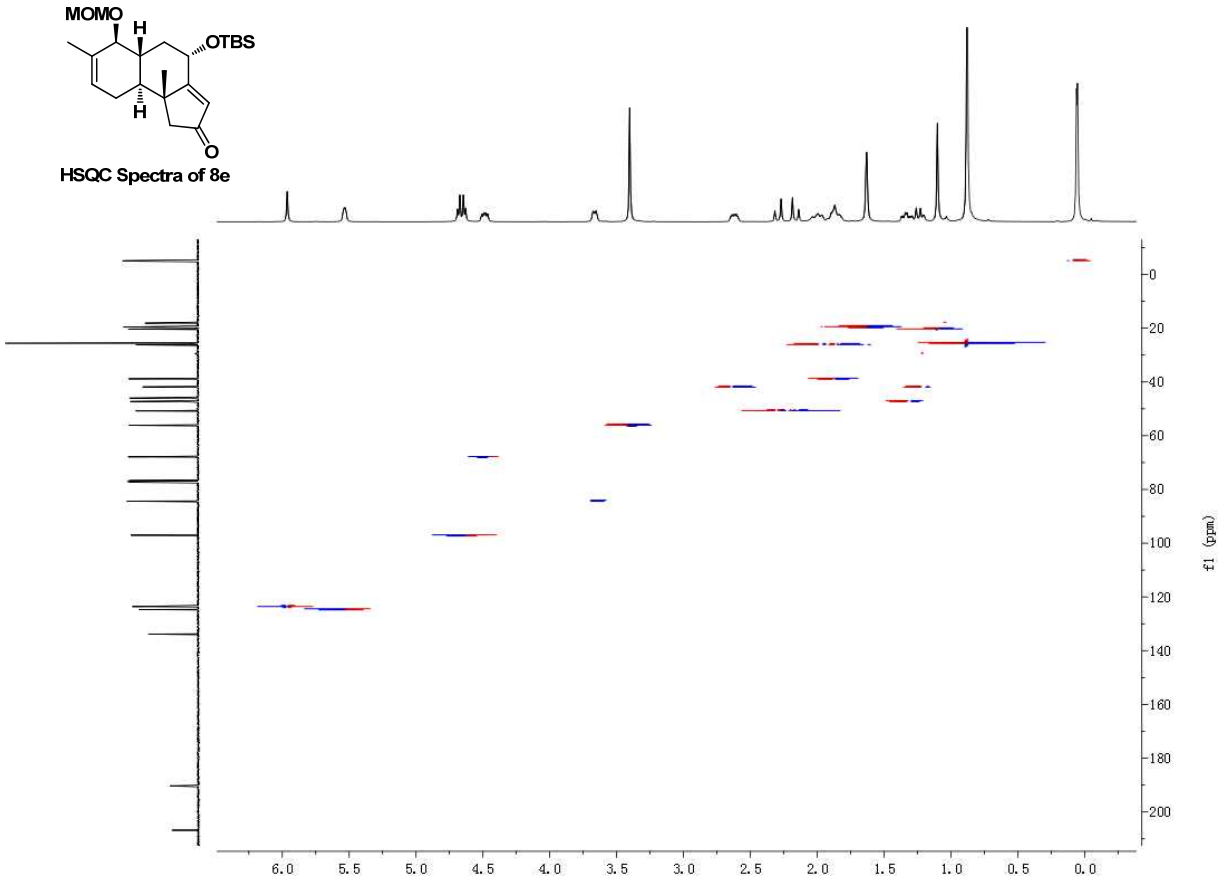
^{13}C NMR Spectra of 8e



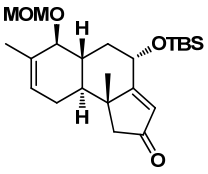
DEPT Spectra of 8e



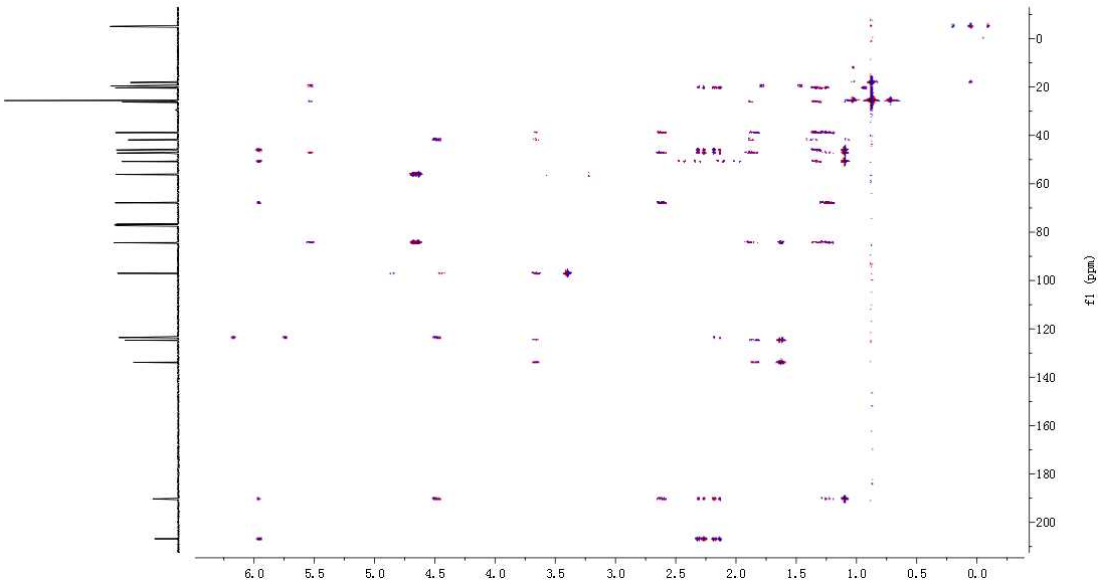
COSY Spectra of 8e

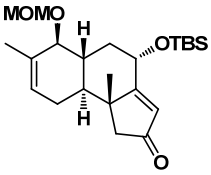


HSQC Spectra of 8e

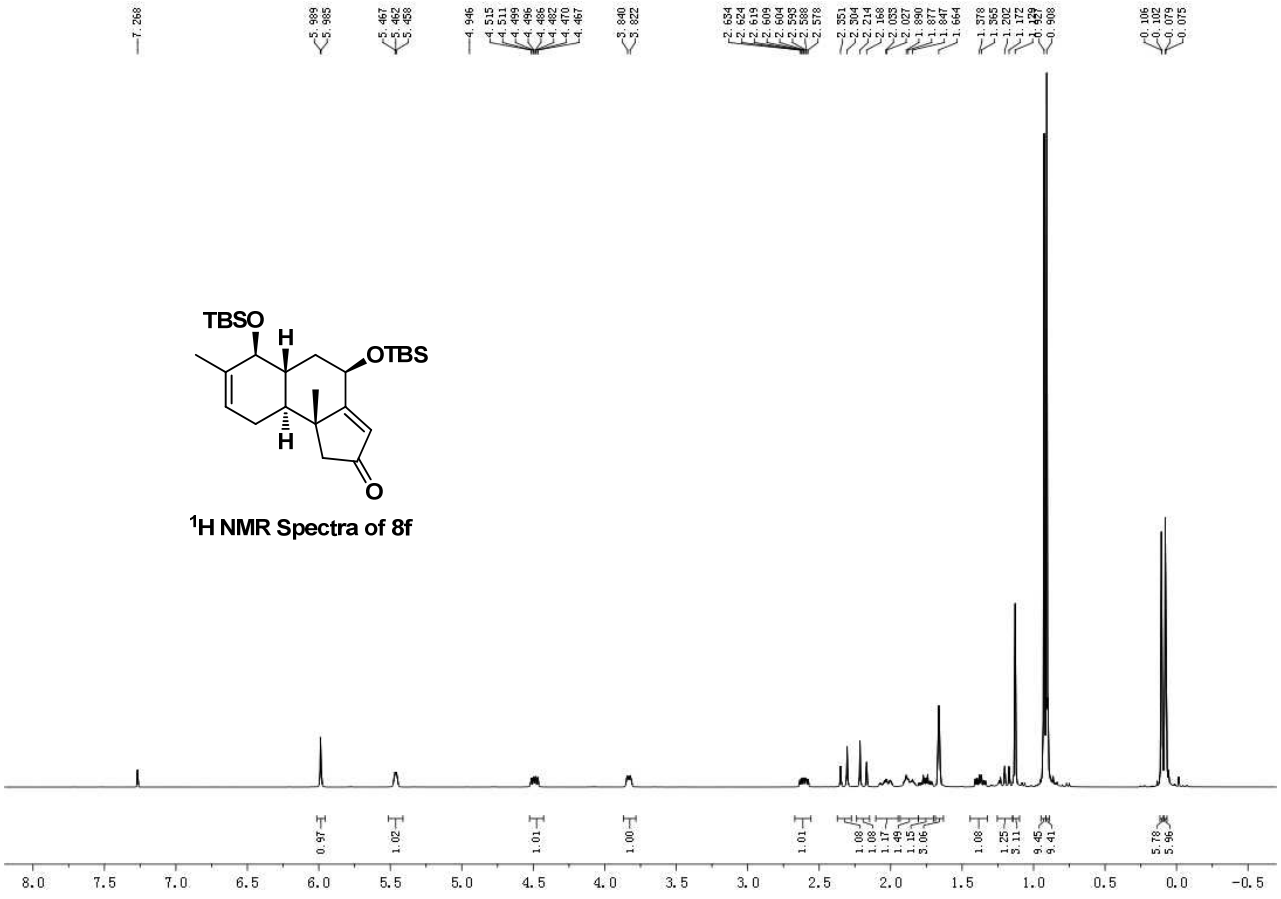


HMBC Spectra of 8e

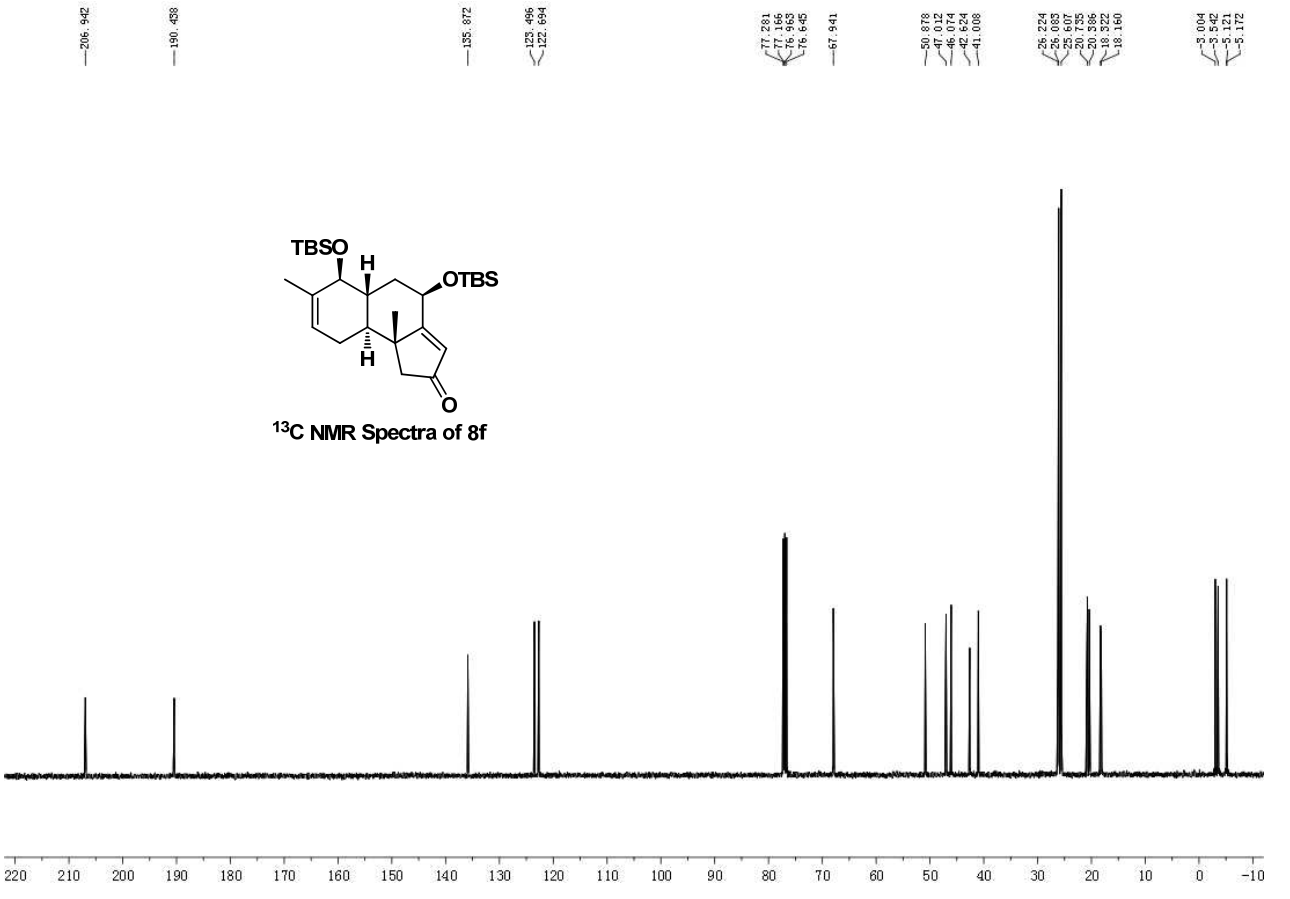




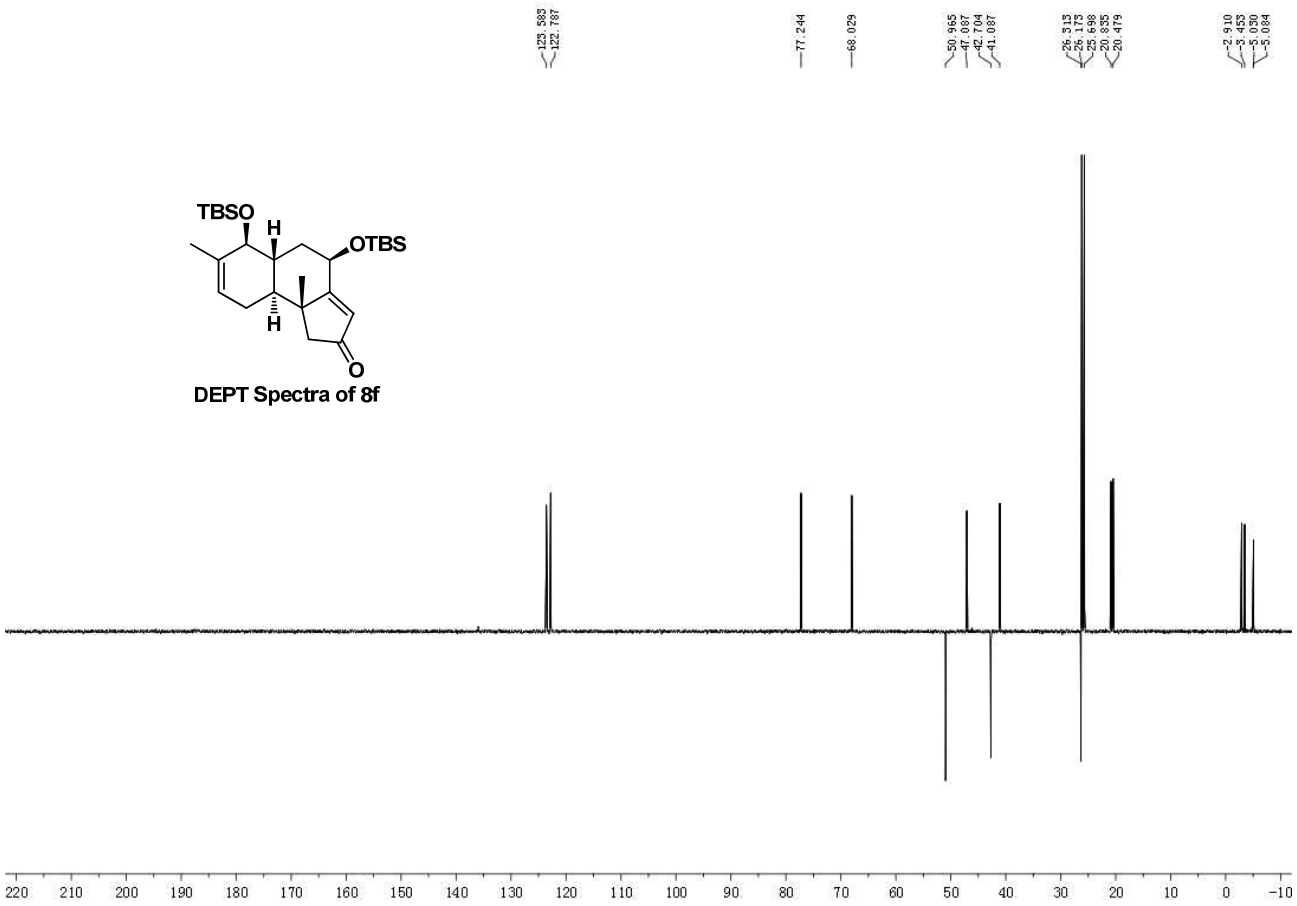
NOESY Spectra of 8e

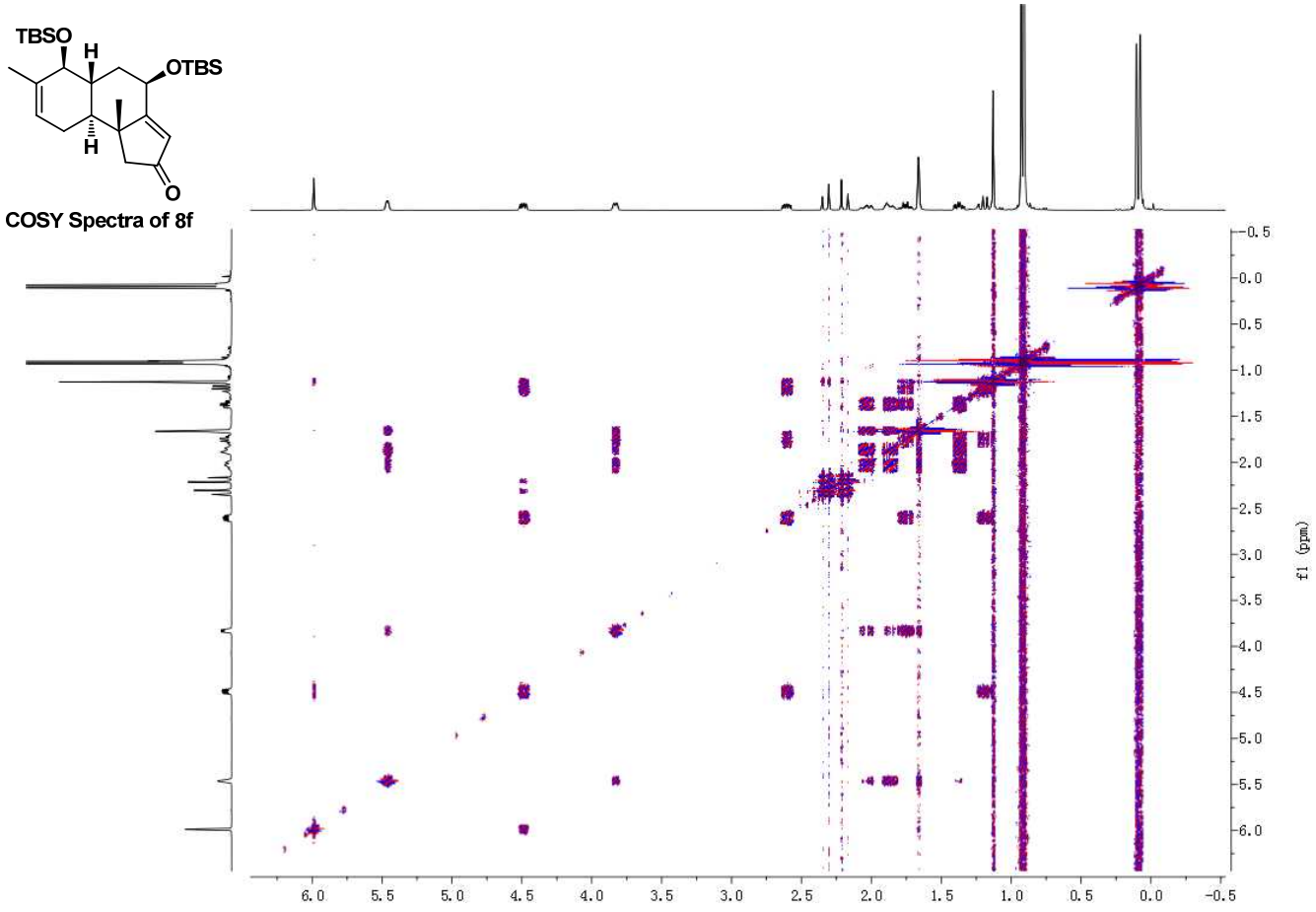


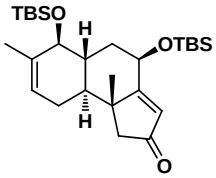
^{1}H NMR Spectra of 8f



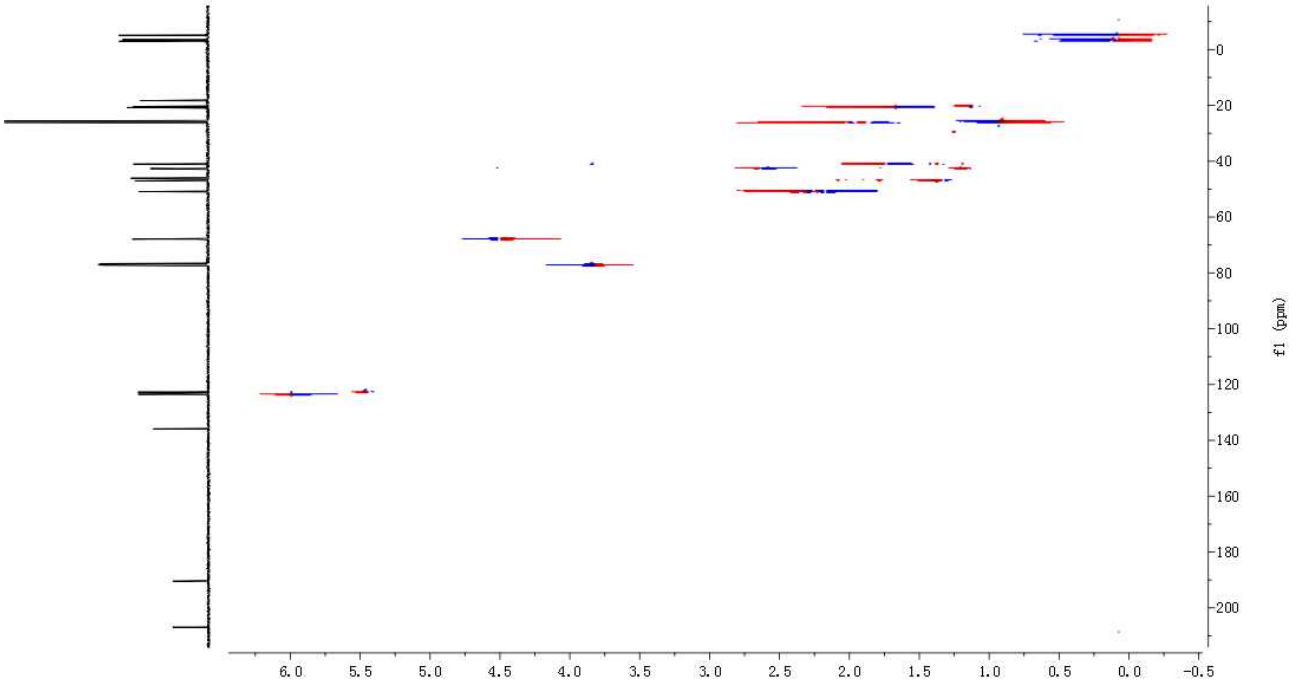
^{13}C NMR Spectra of 8f

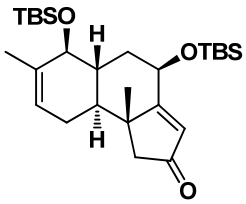

123.583
122.787
77.244
68.029
50.965
47.087
42.704
41.087
26.313
25.173
25.698
20.835
20.479
-2.910
-3.453
-5.030
-5.084
TBSO
H
OTBS
H
O
DEPT Spectra of 8f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


TBSO
H
OTBS
H
O
COSY Spectra of 8f
f1 (ppm)
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

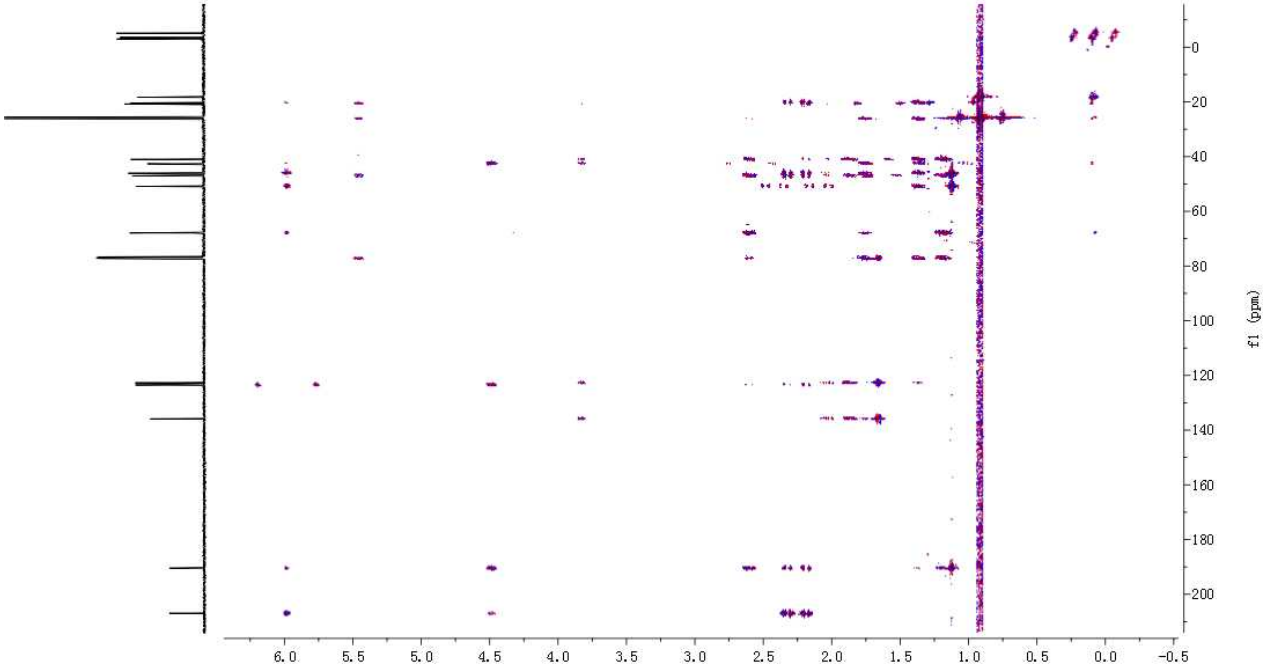


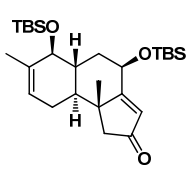
HSQC Spectra of 8f



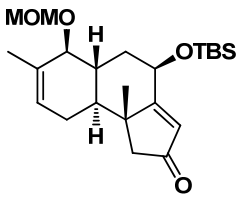


HMBC Spectra of 8f

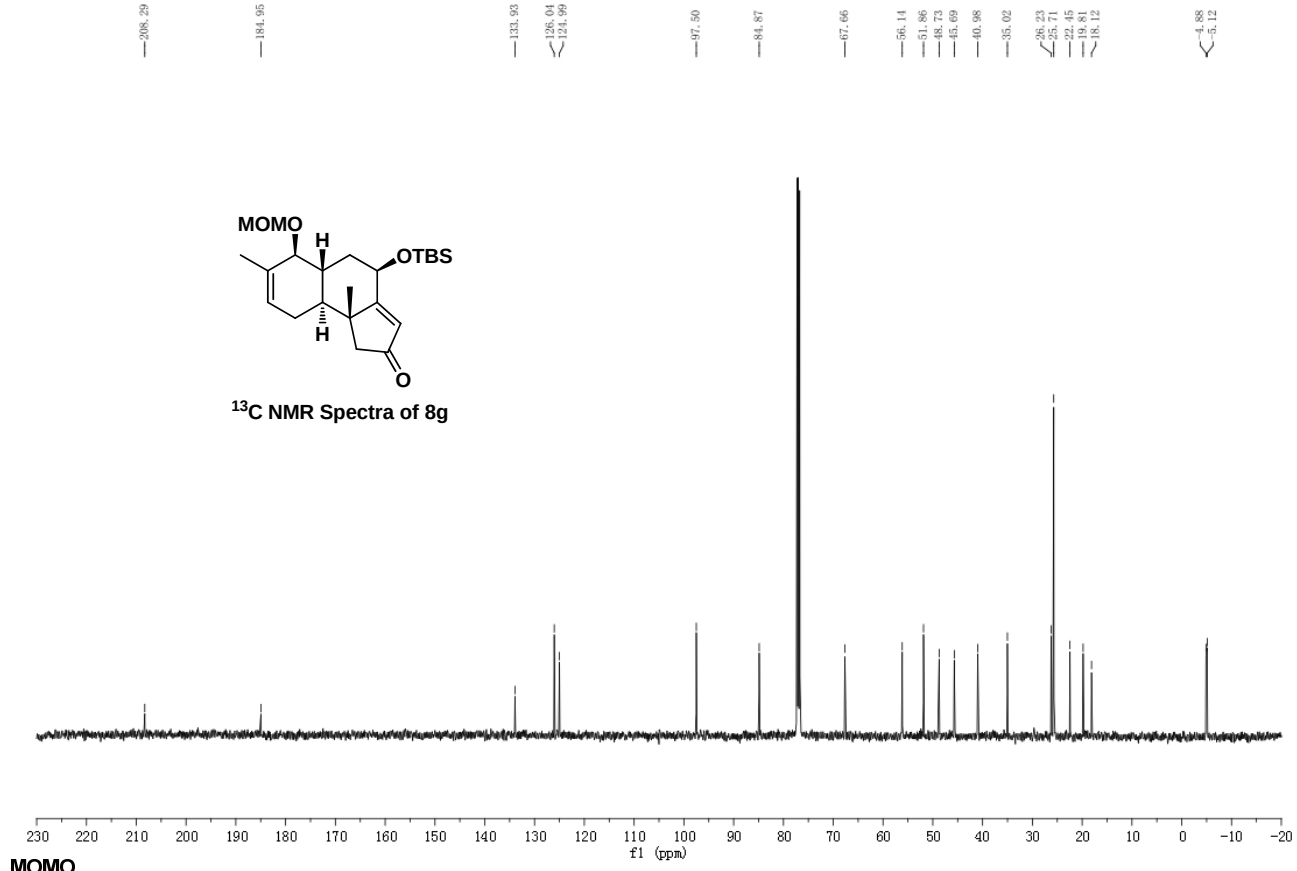




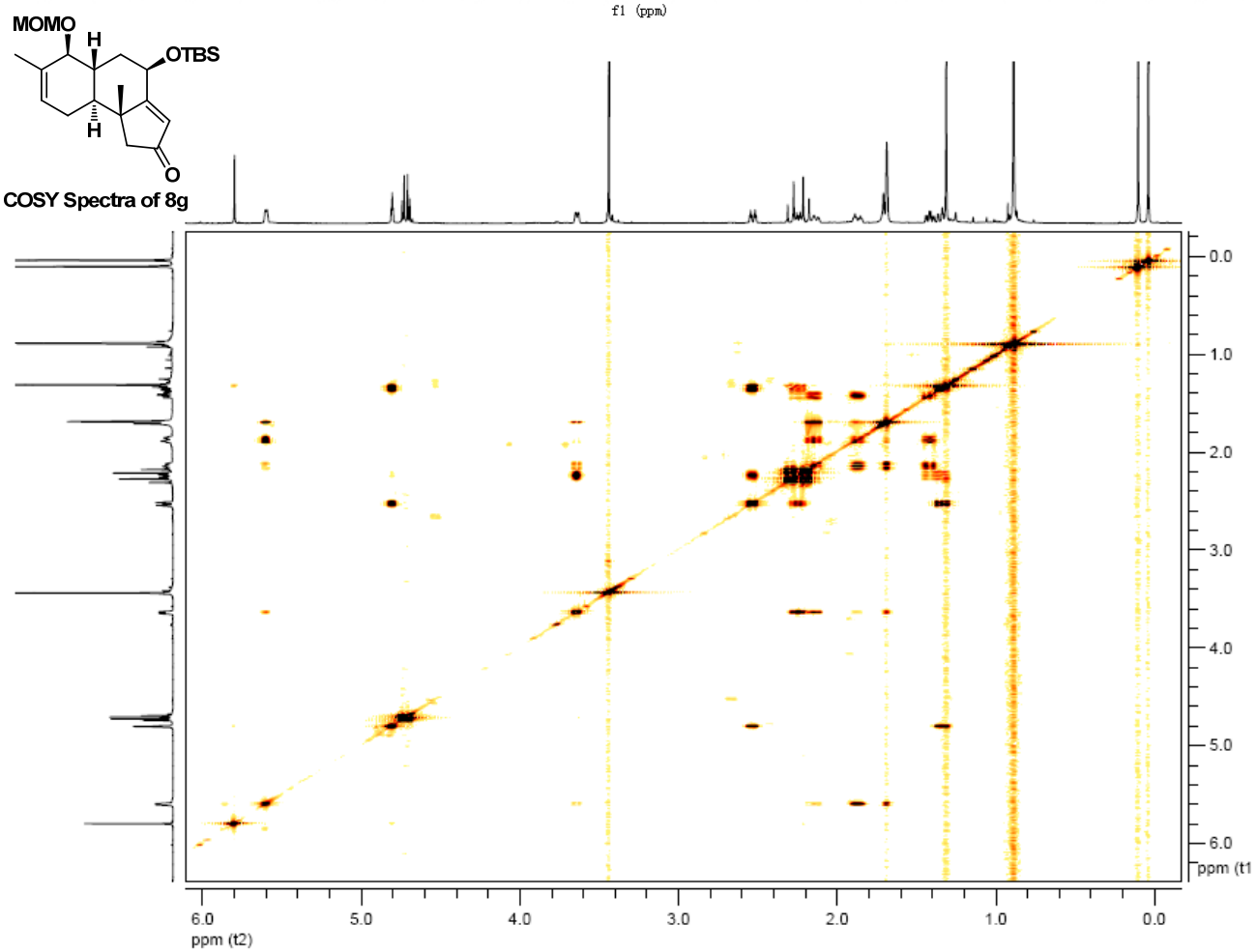
NOESY Spectra of 8f



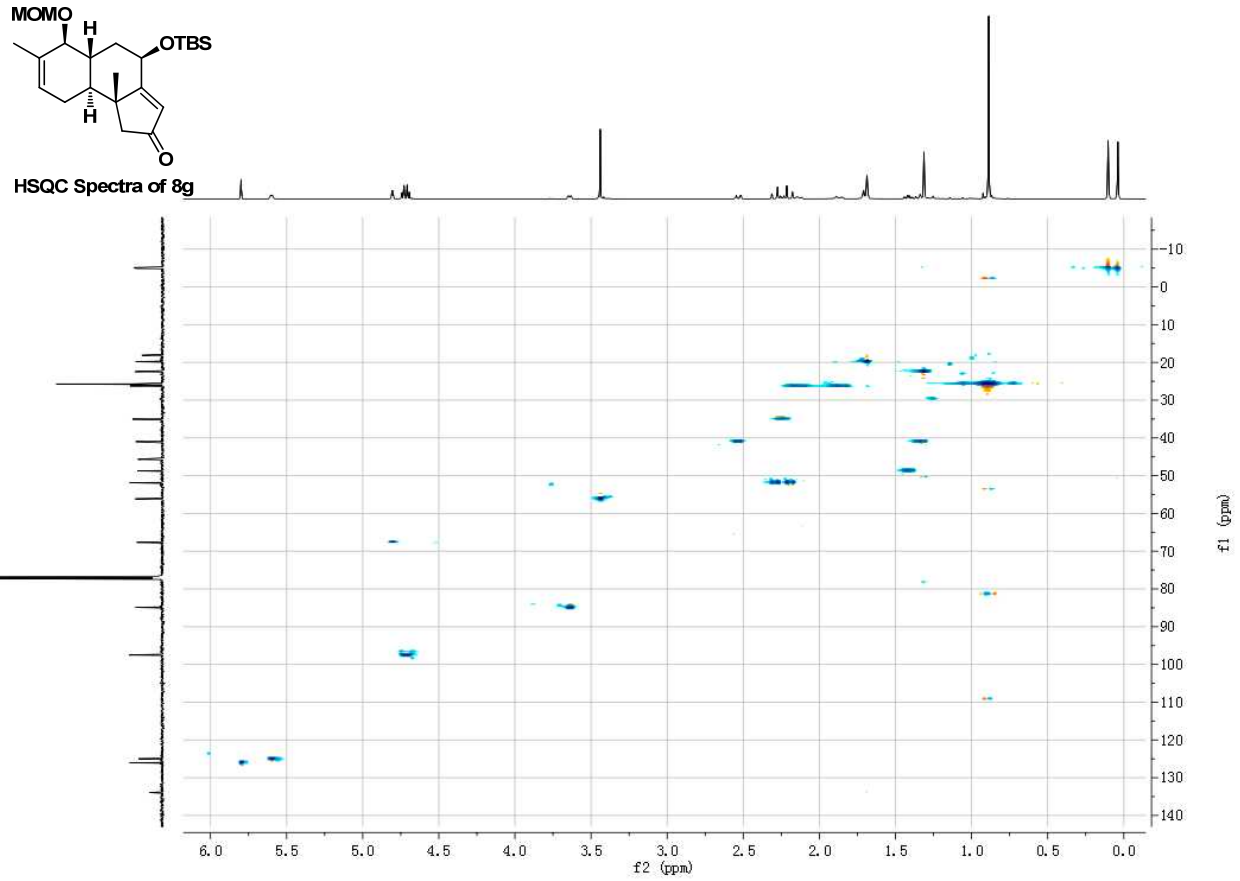
^{1}H NMR Spectra of 8g

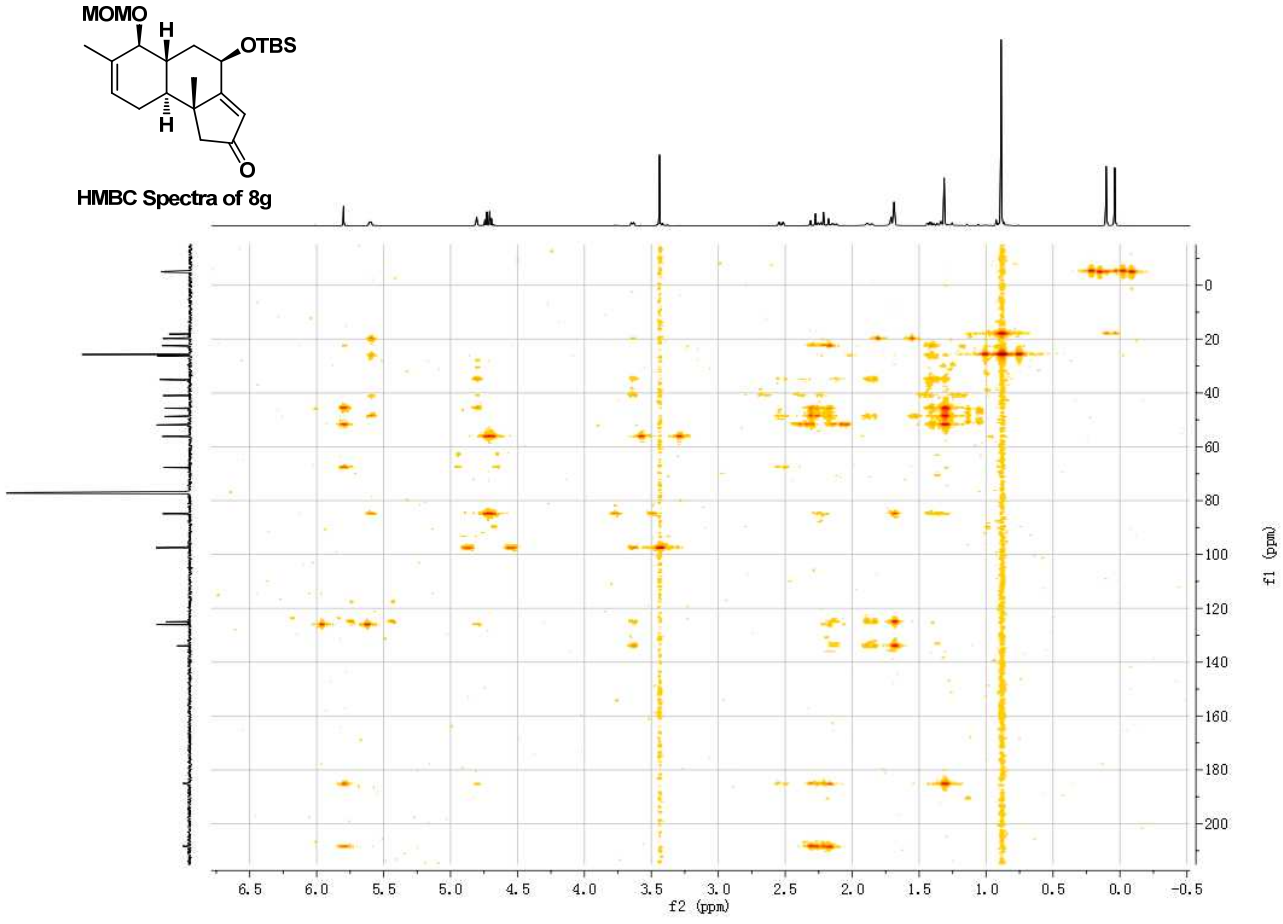


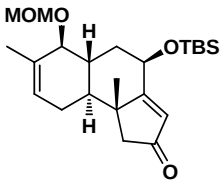
^{13}C NMR Spectra of 8g



COSY Spectra of 8g


MOMO
H
OTBS
H
O
HSQC Spectra of 8g
f2 (ppm)
f1 (ppm)

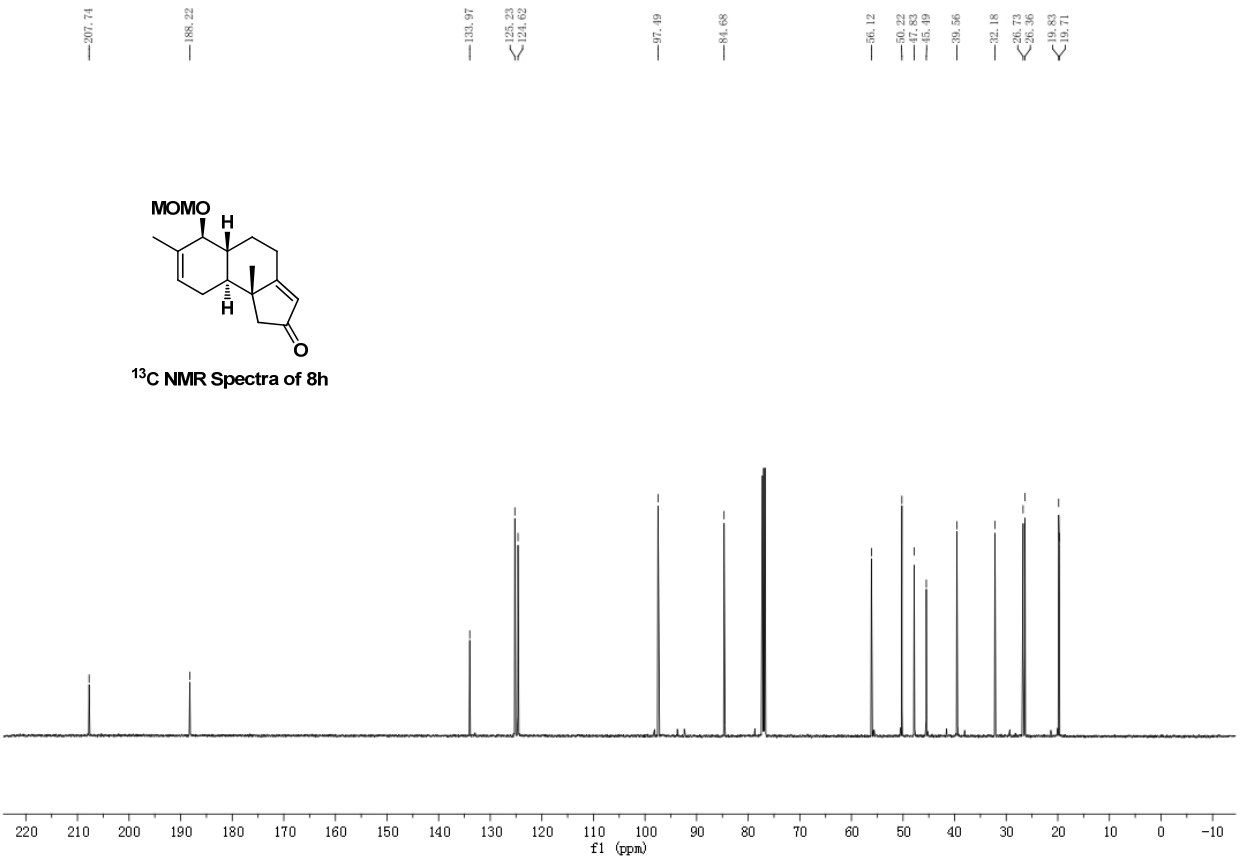

MOMO
H
OTBS
H
O
HMBC Spectra of 8g
f2 (ppm)
f1 (ppm)



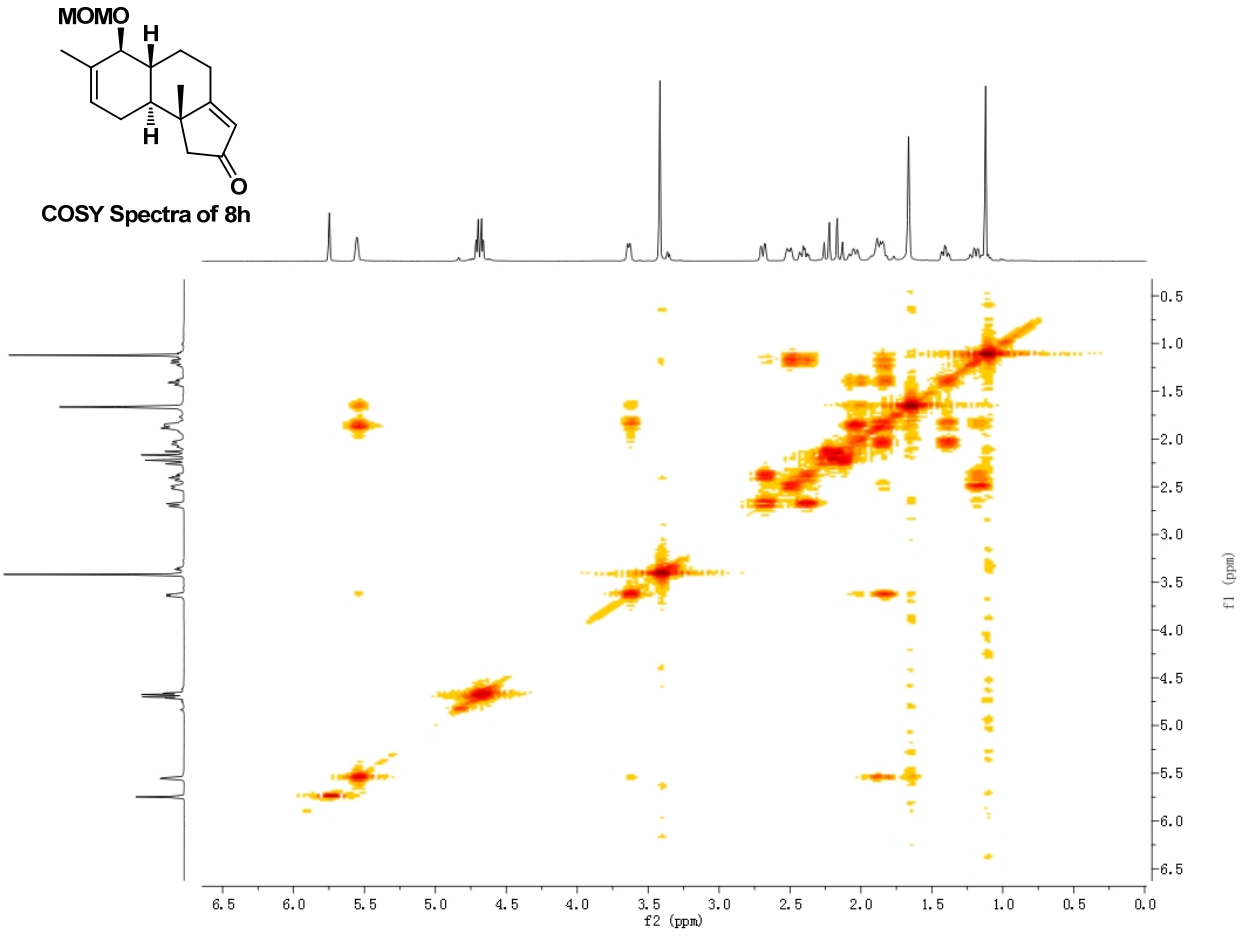
NOESY Spectra of 8g

PK-20110606
Avance 500, Bruker, SZPKU
sample: PK-20110606
solvent: CDCl3

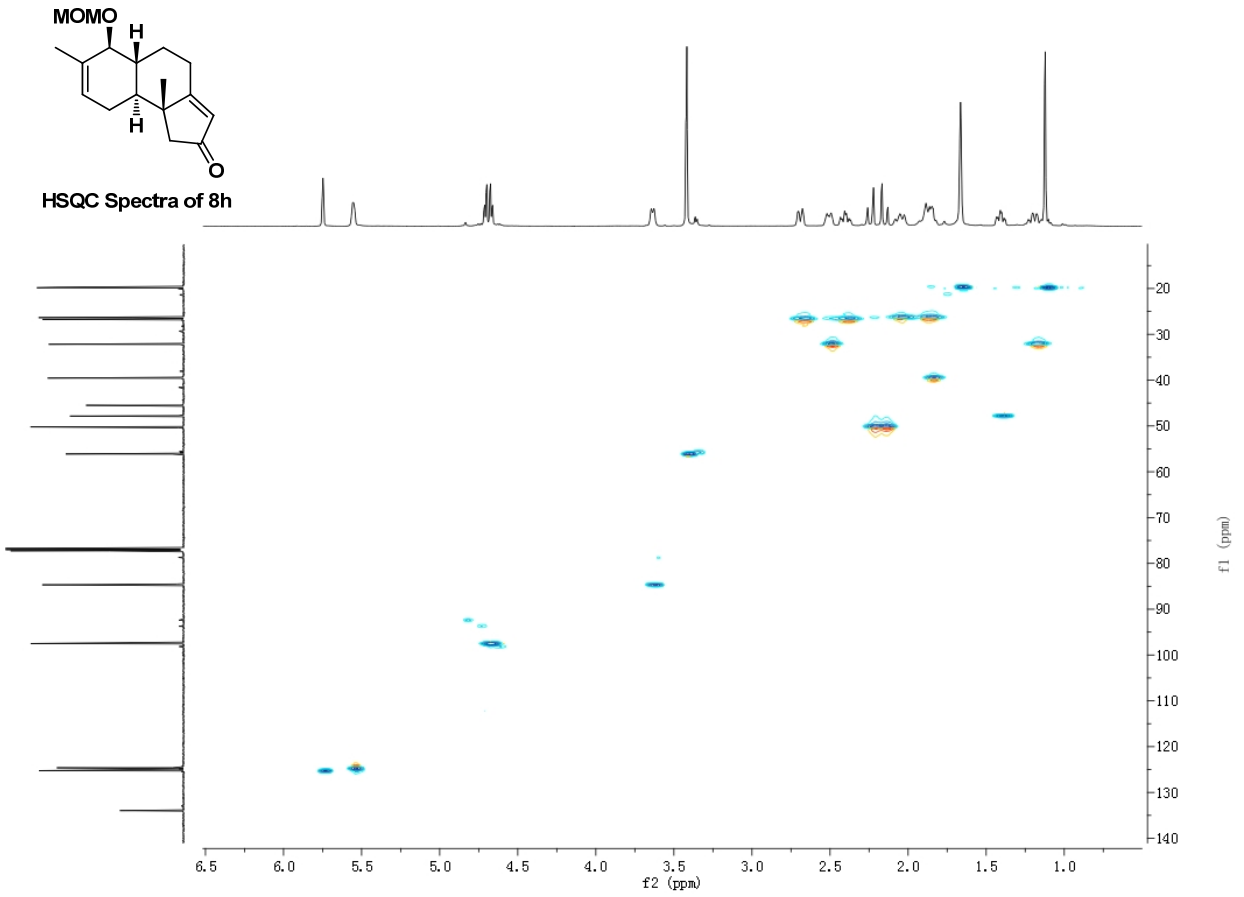
^{1}H NMR Spectra of 8h



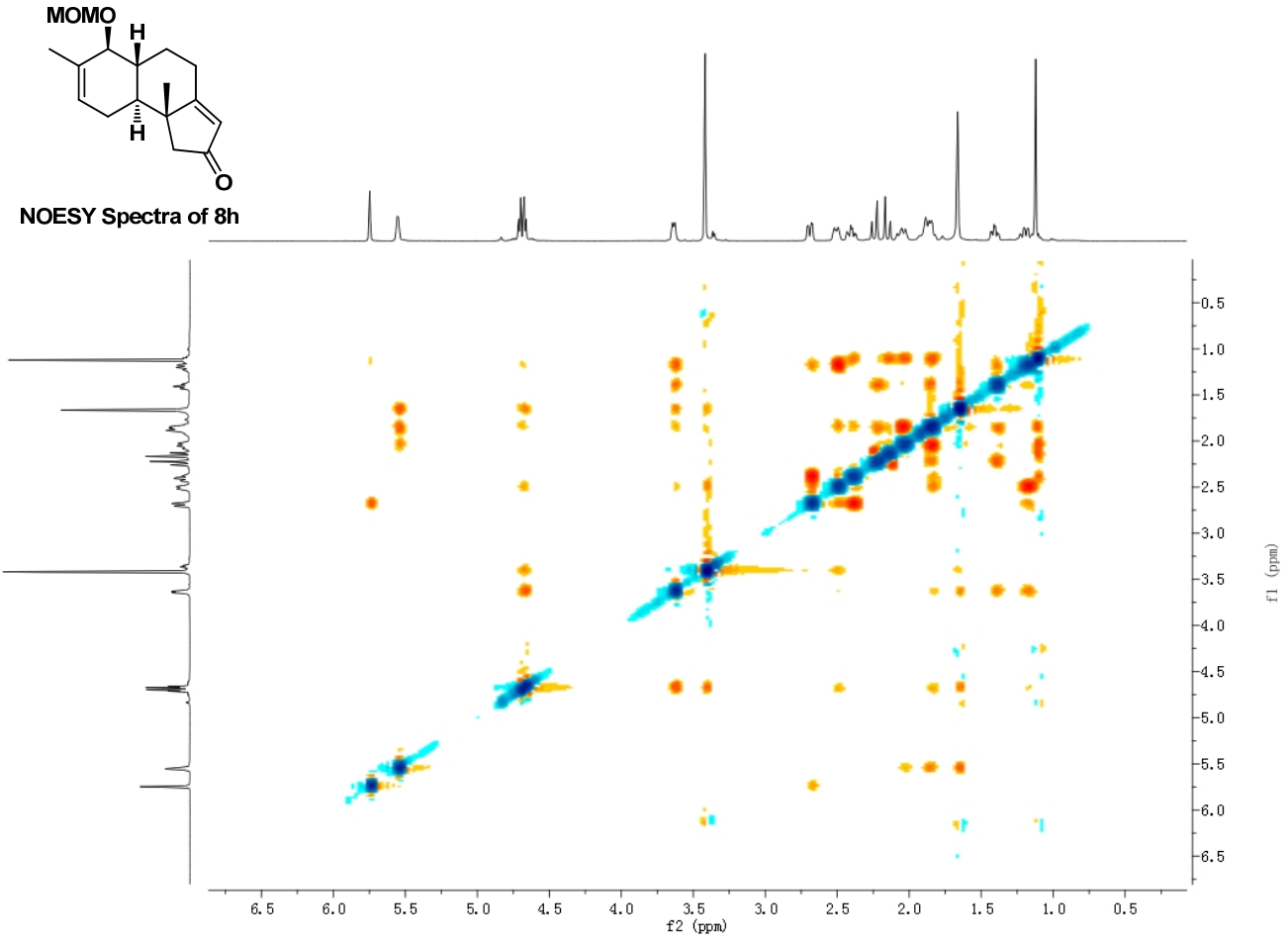
^{13}C NMR Spectra of 8h



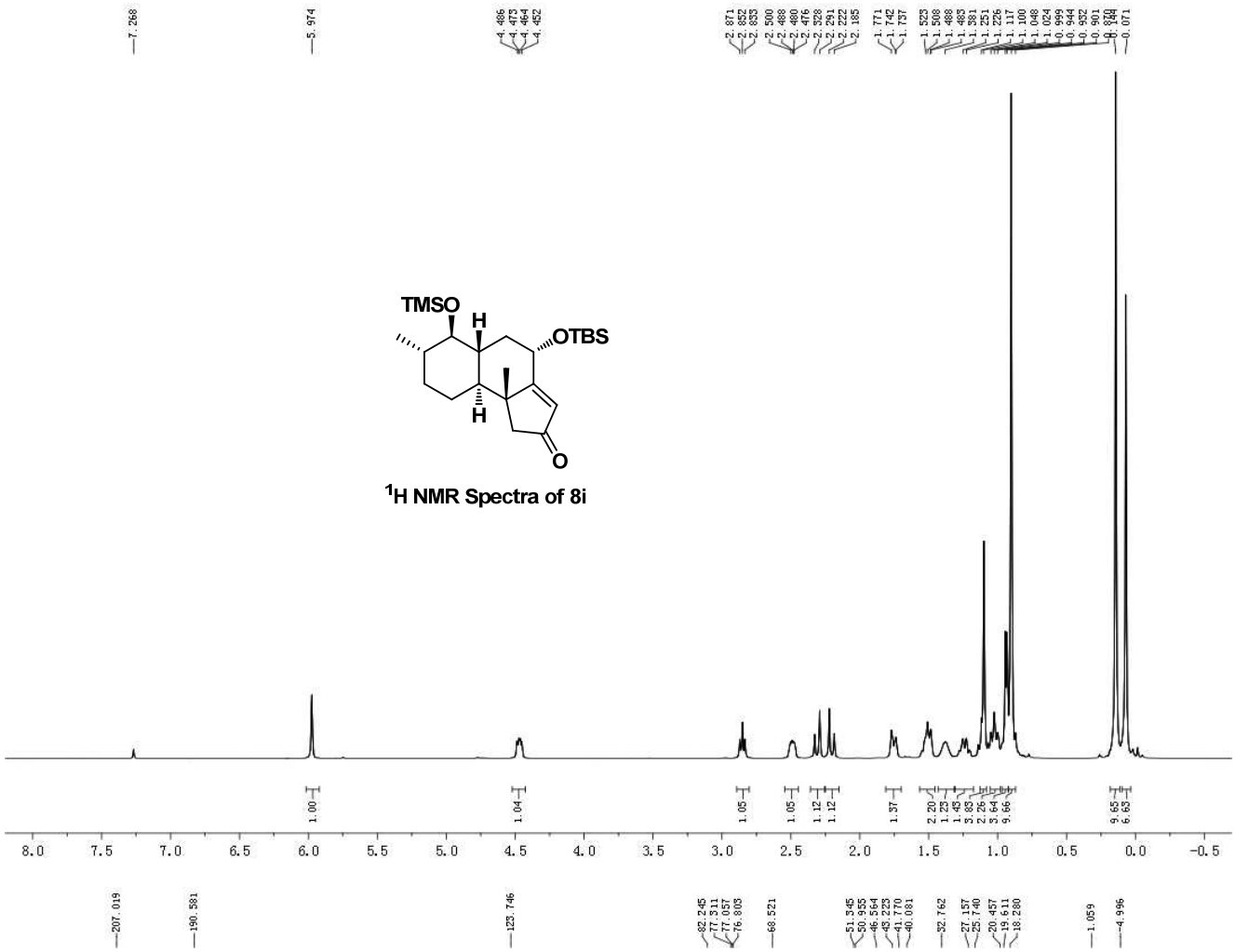
COSY Spectra of 8h



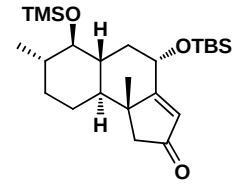
HSQC Spectra of 8h



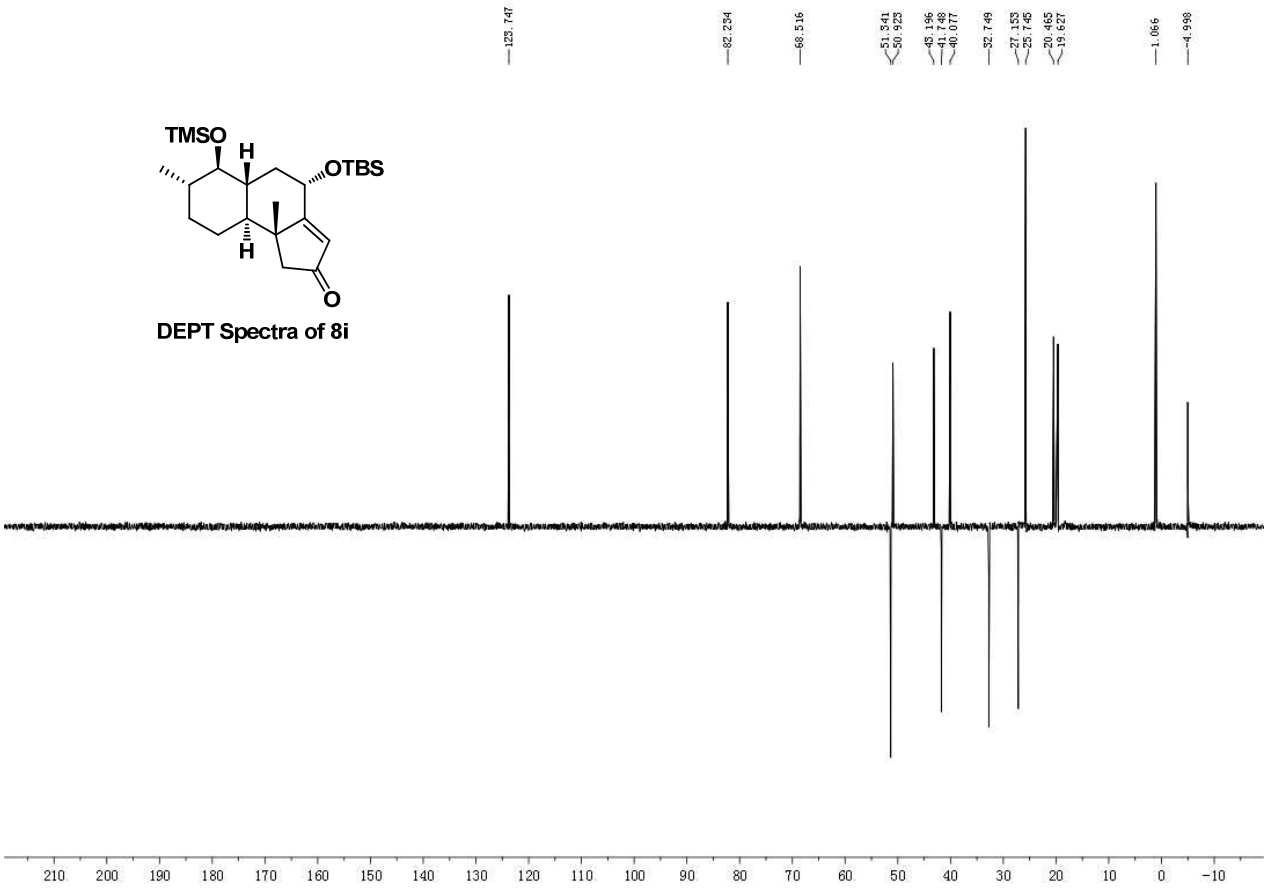
NOESY Spectra of 8h



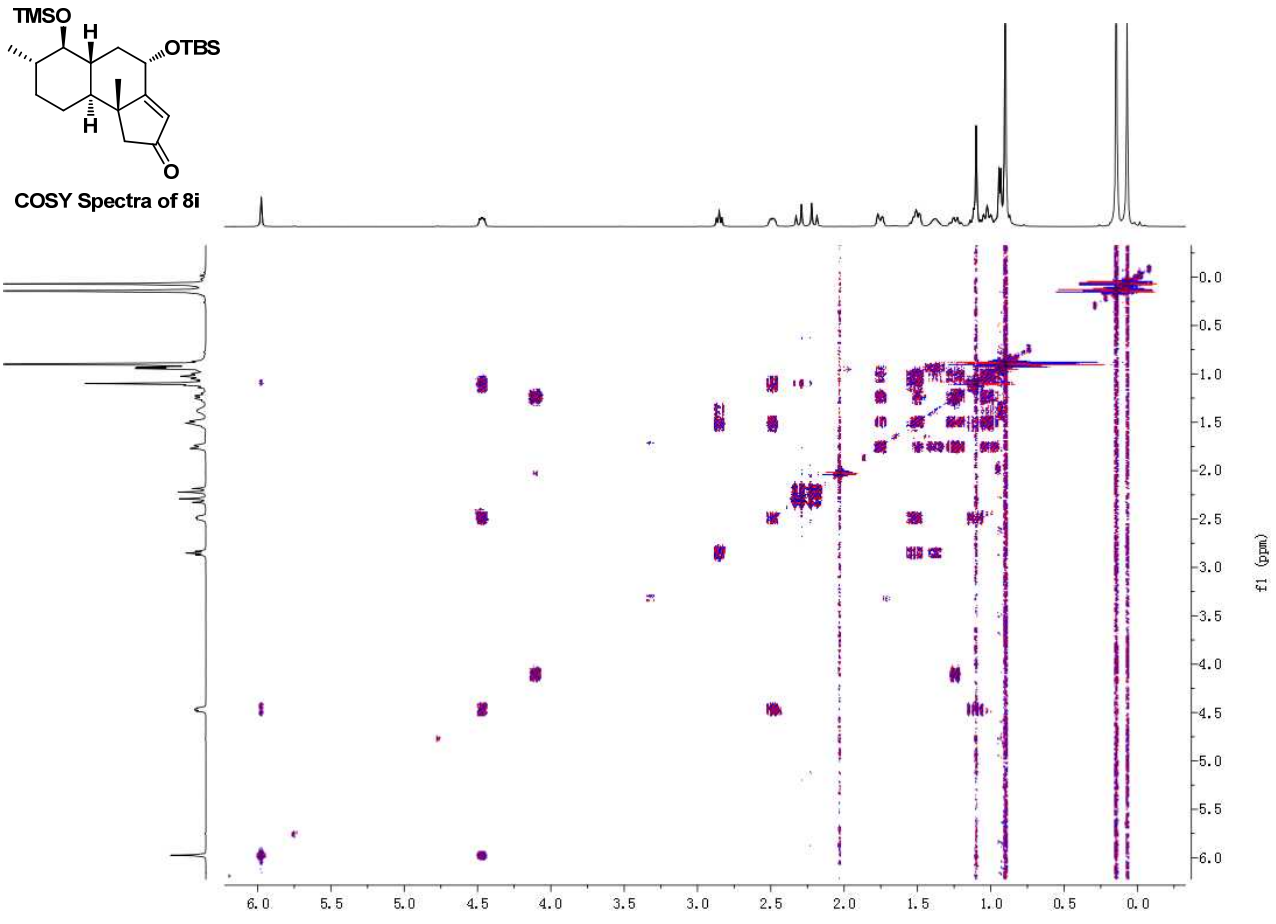
^{1}H NMR Spectra of 8i



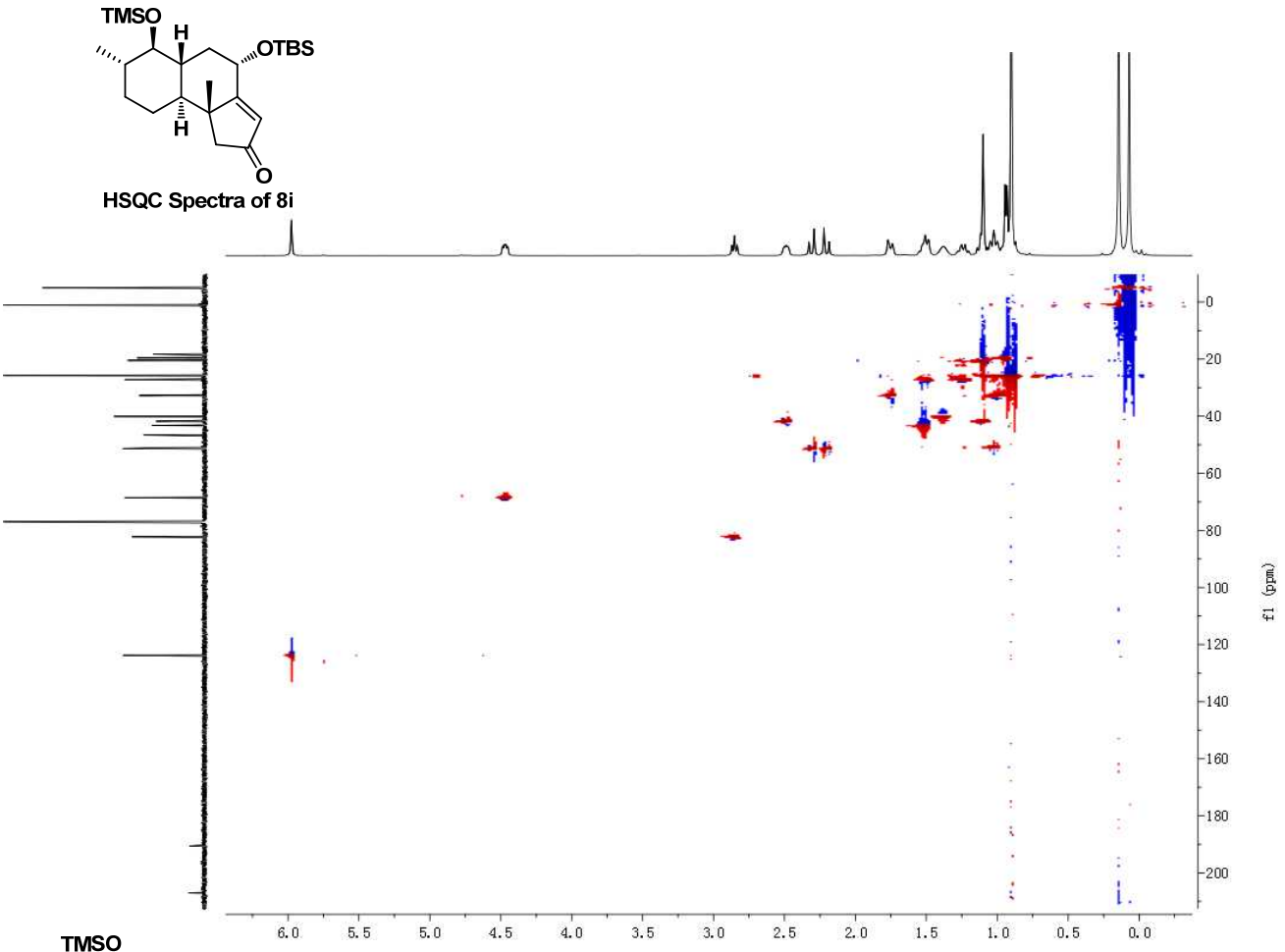
^{13}C NMR Spectra of 8i

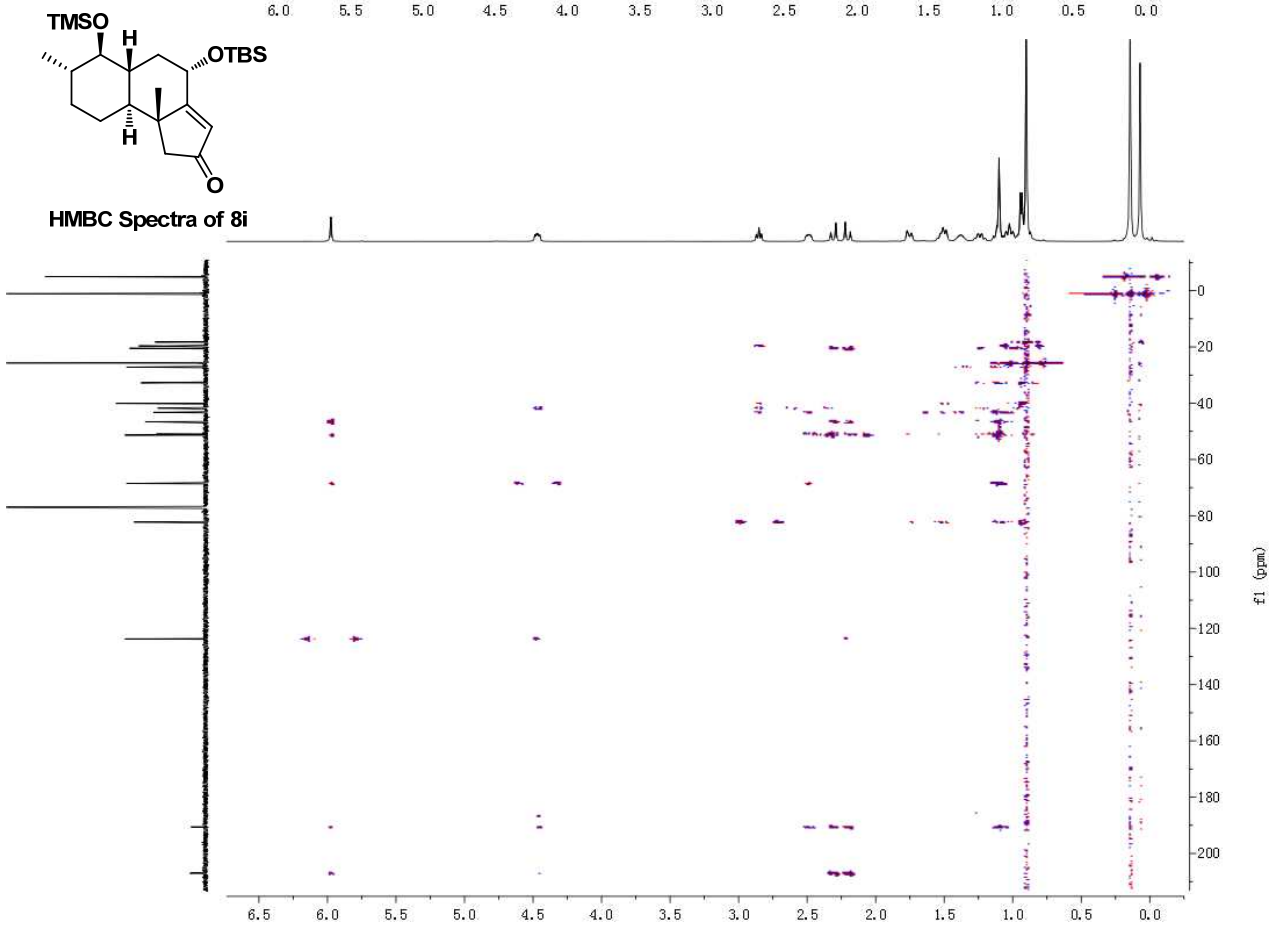


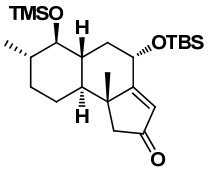
DEPT Spectra of 8i



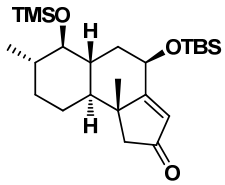
COSY Spectra of 8i


TMSO
H
OTBS
H
O
HSQC Spectra of 8i
f1 (ppm)

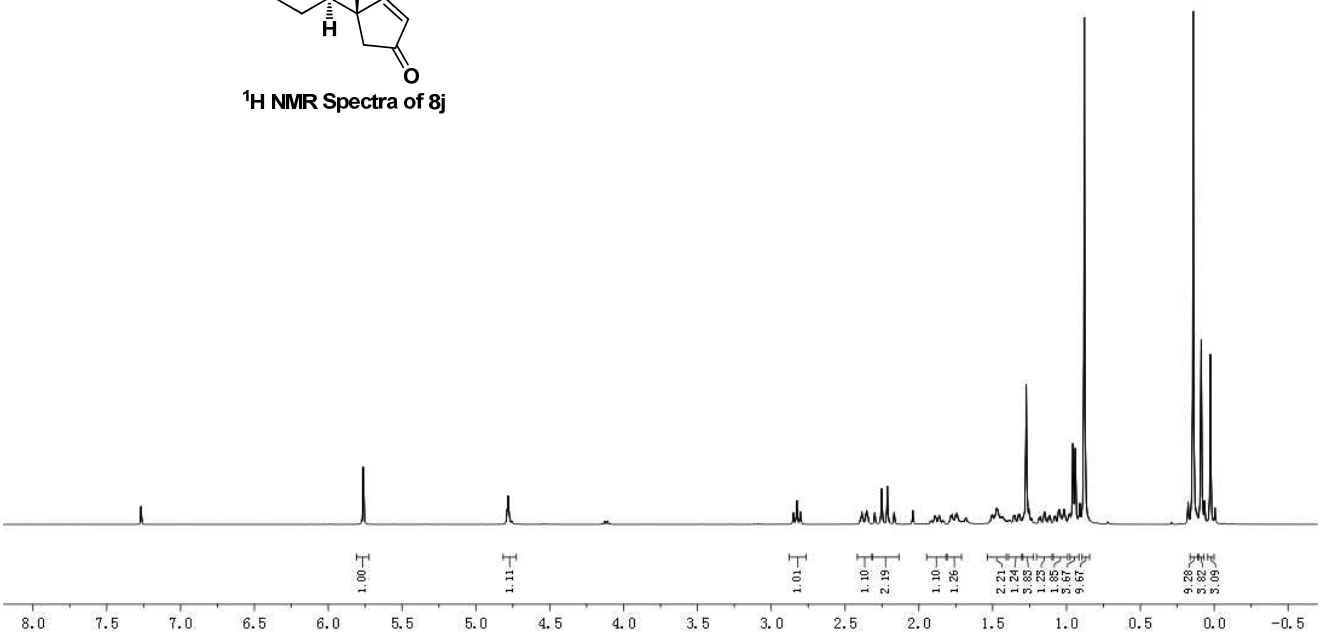

TMSO
H
OTBS
H
O
HMBC Spectra of 8i
f1 (ppm)

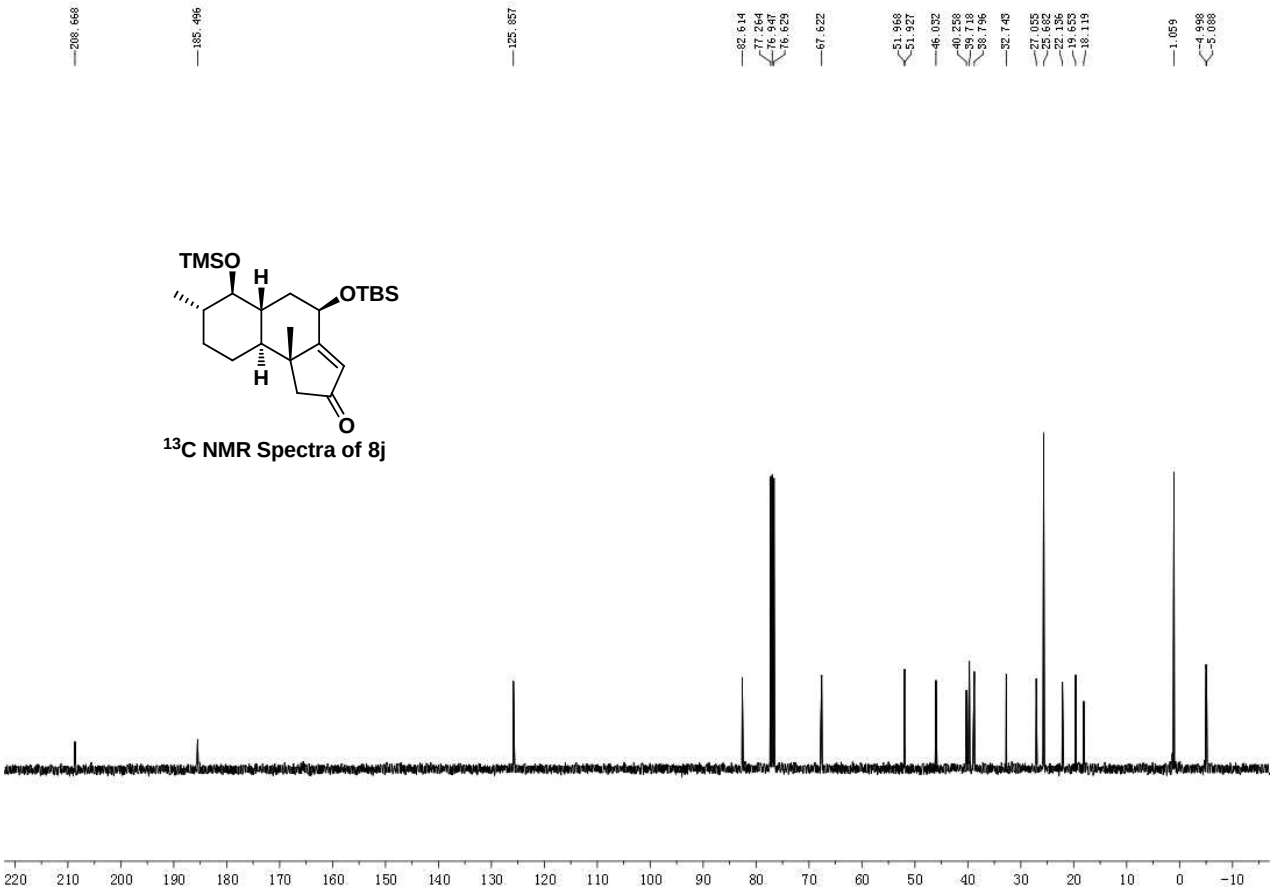


NOESY Spectra of 8i

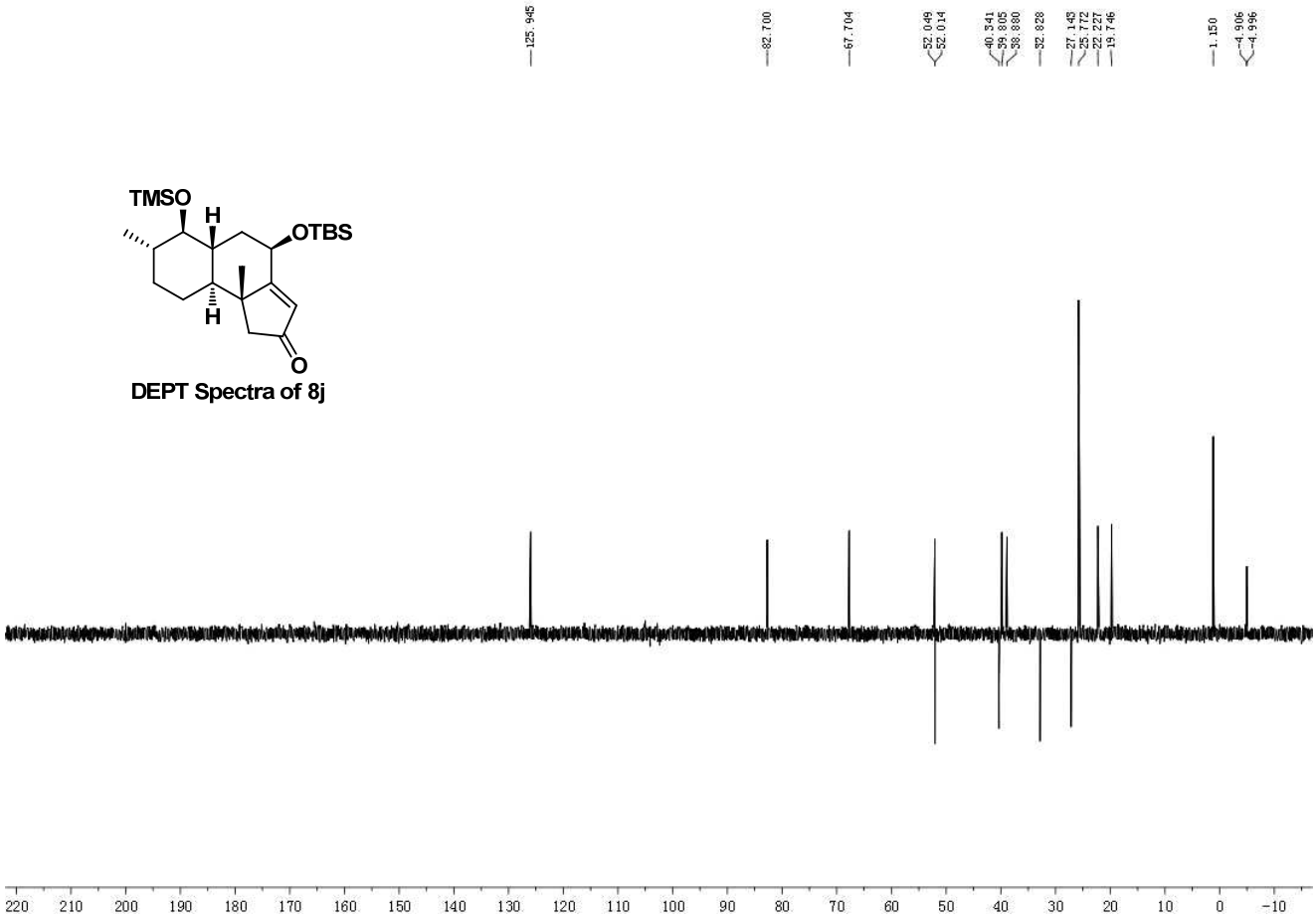


^{1}H NMR Spectra of 8j

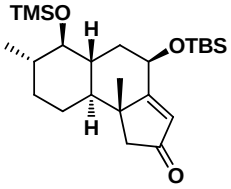




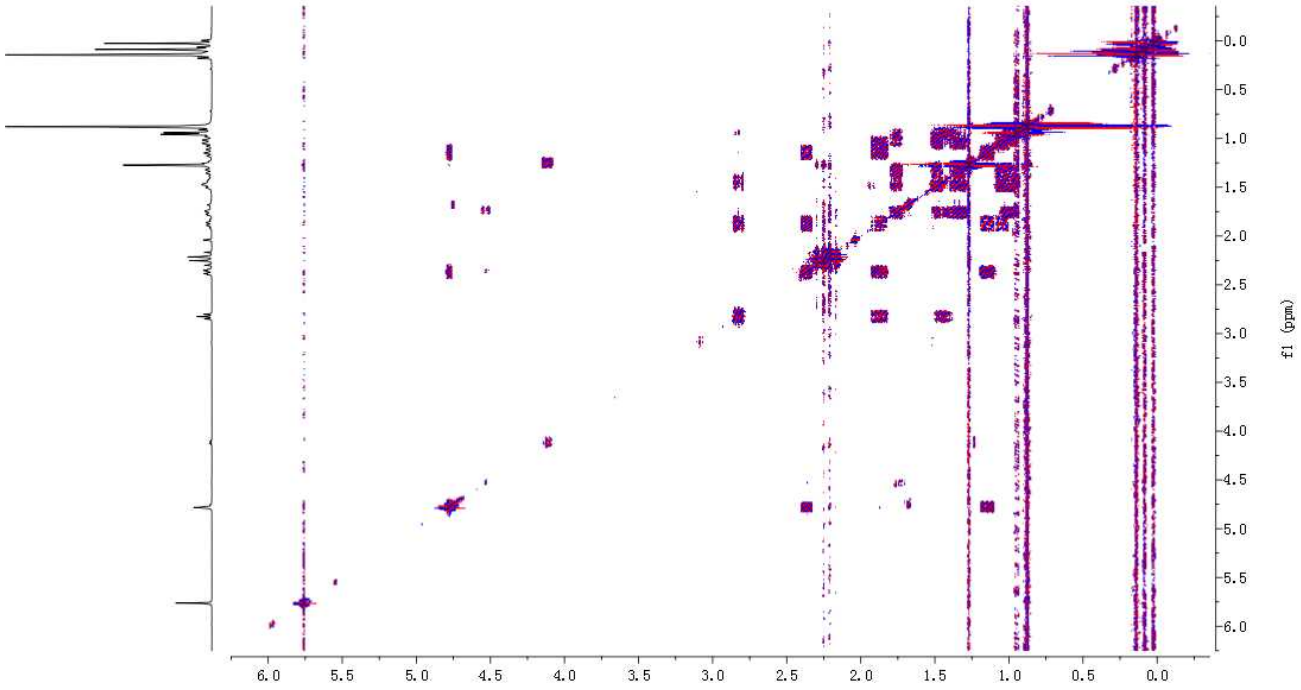
^{13}C NMR Spectra of 8j

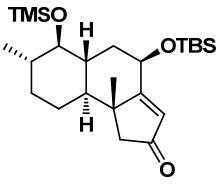


DEPT Spectra of 8j

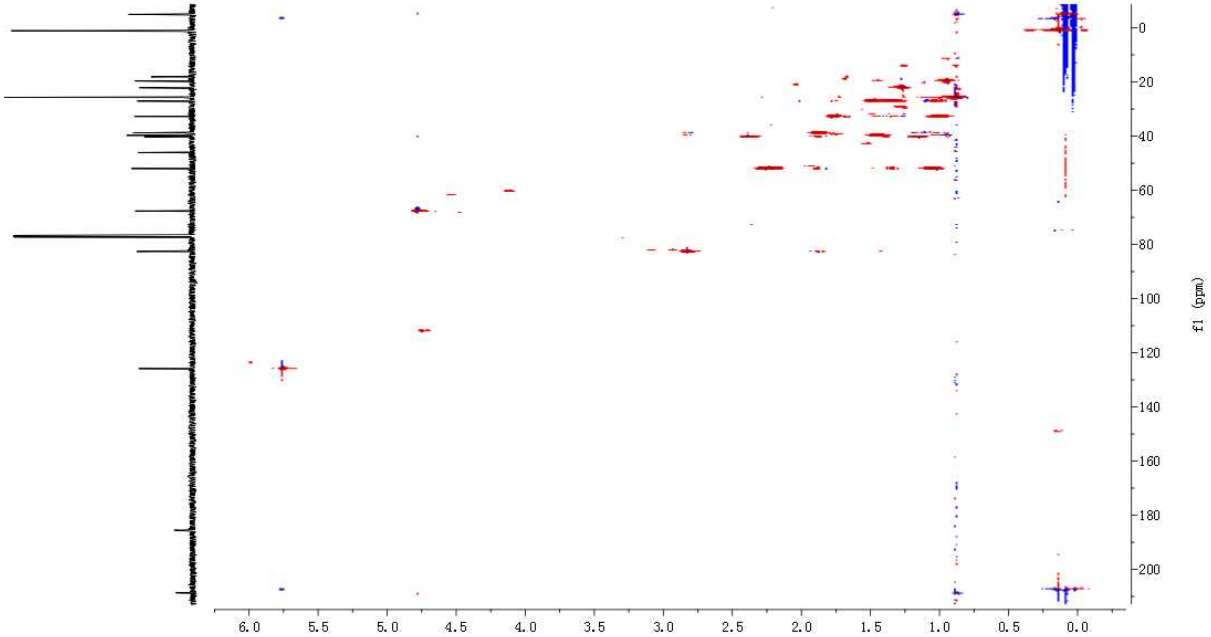


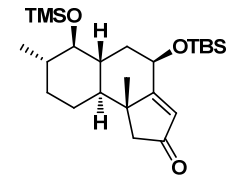
COSY Spectra of 8j



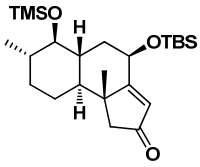


HSQC Spectra of 8j

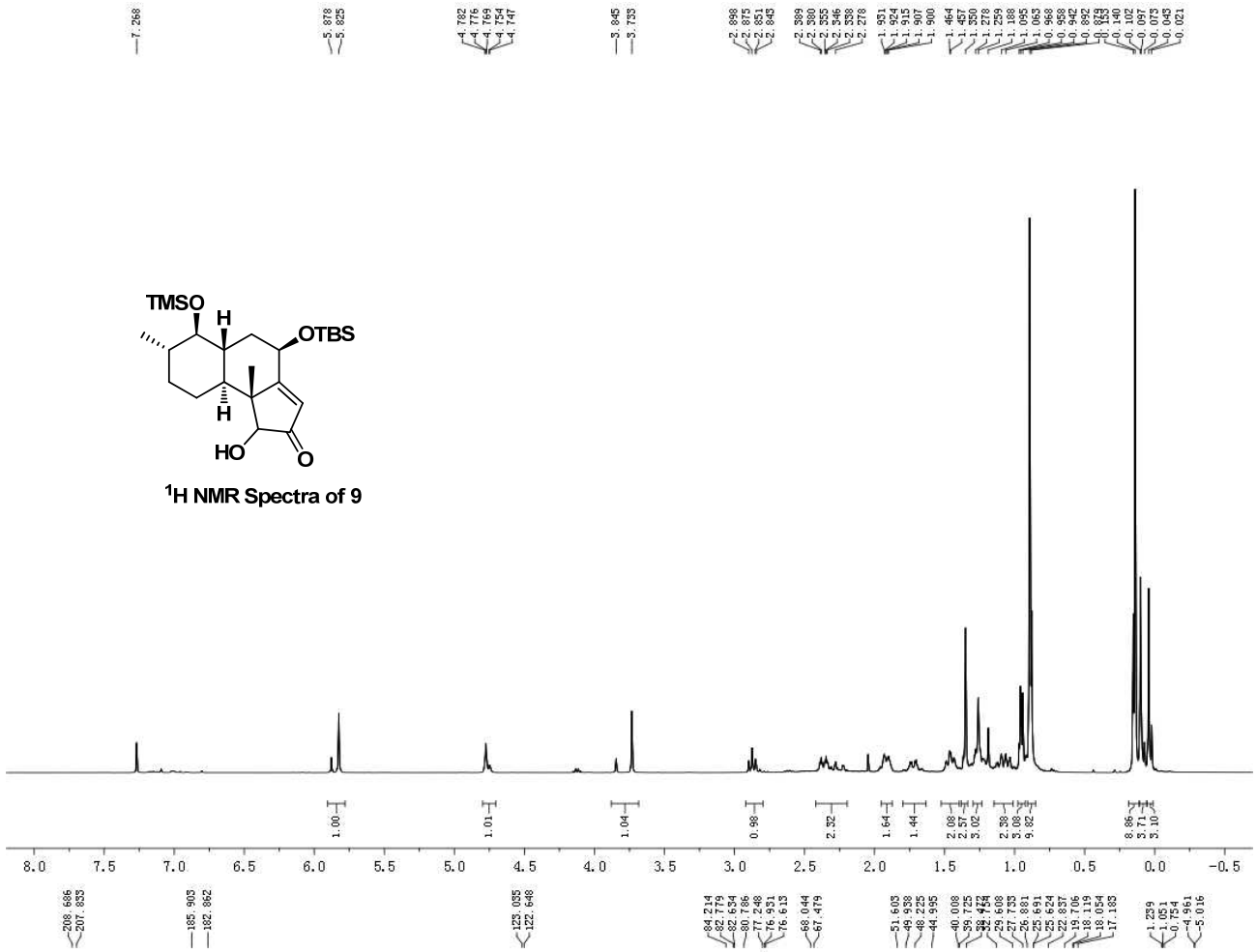




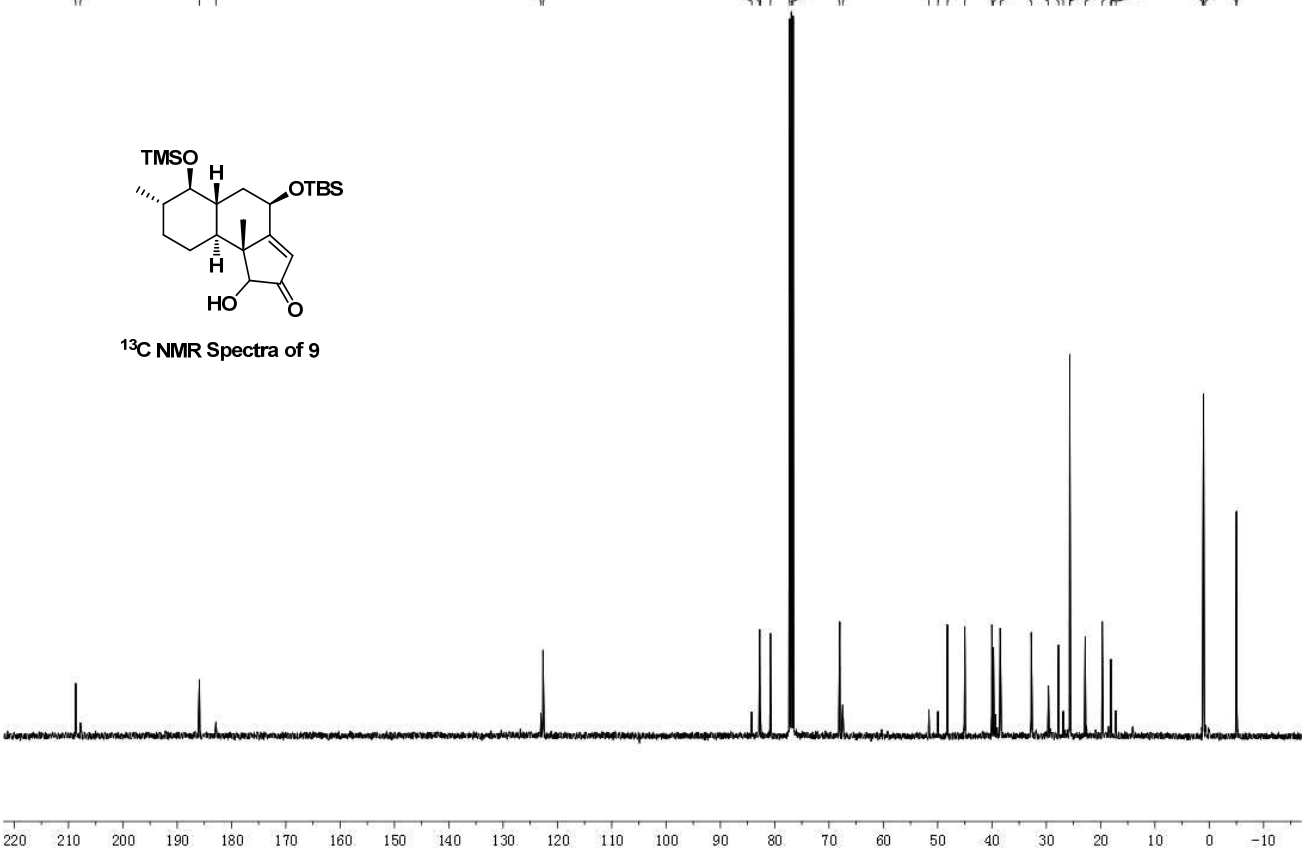
HMBC Spectra of 8j



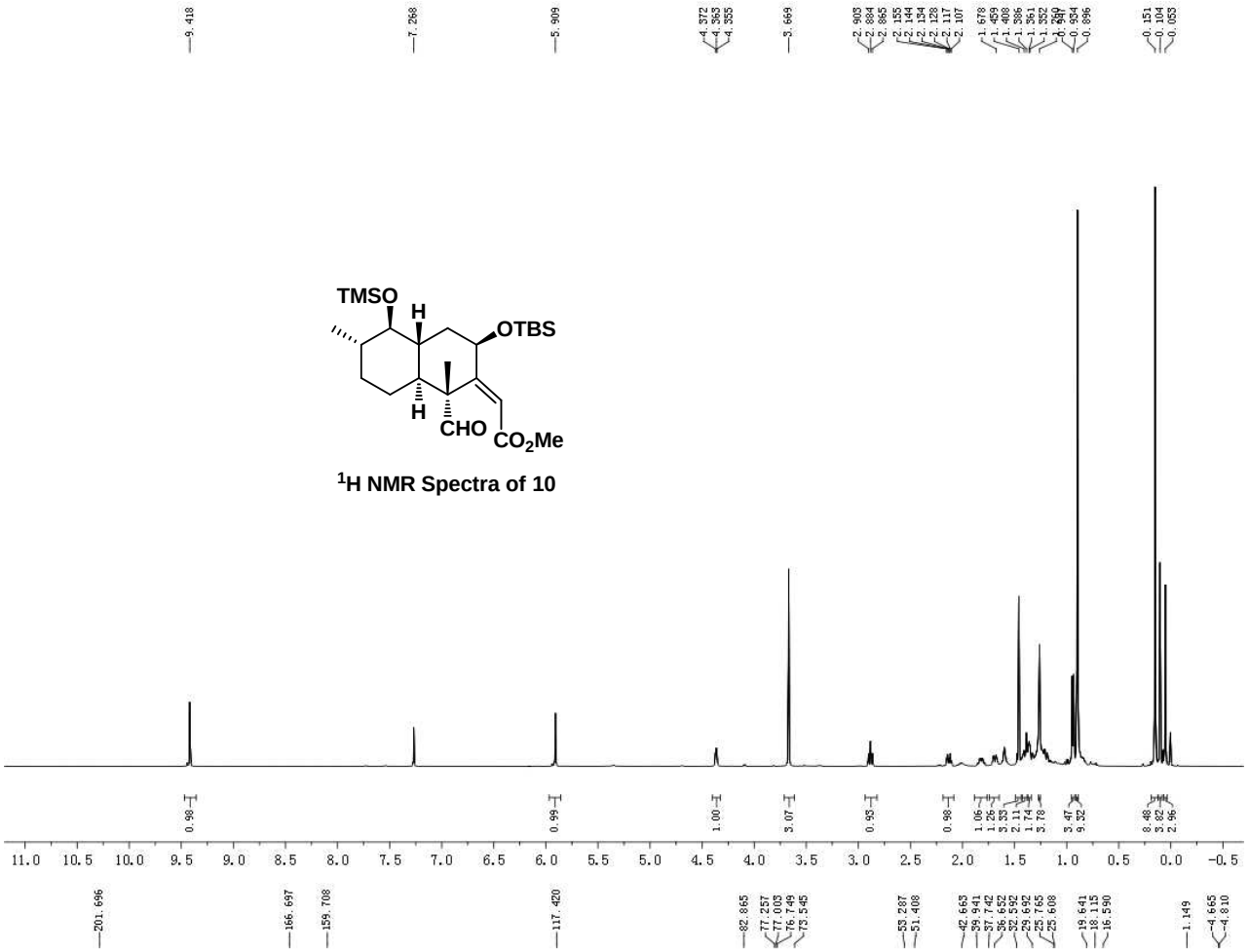
NOESY Spectra of 8j



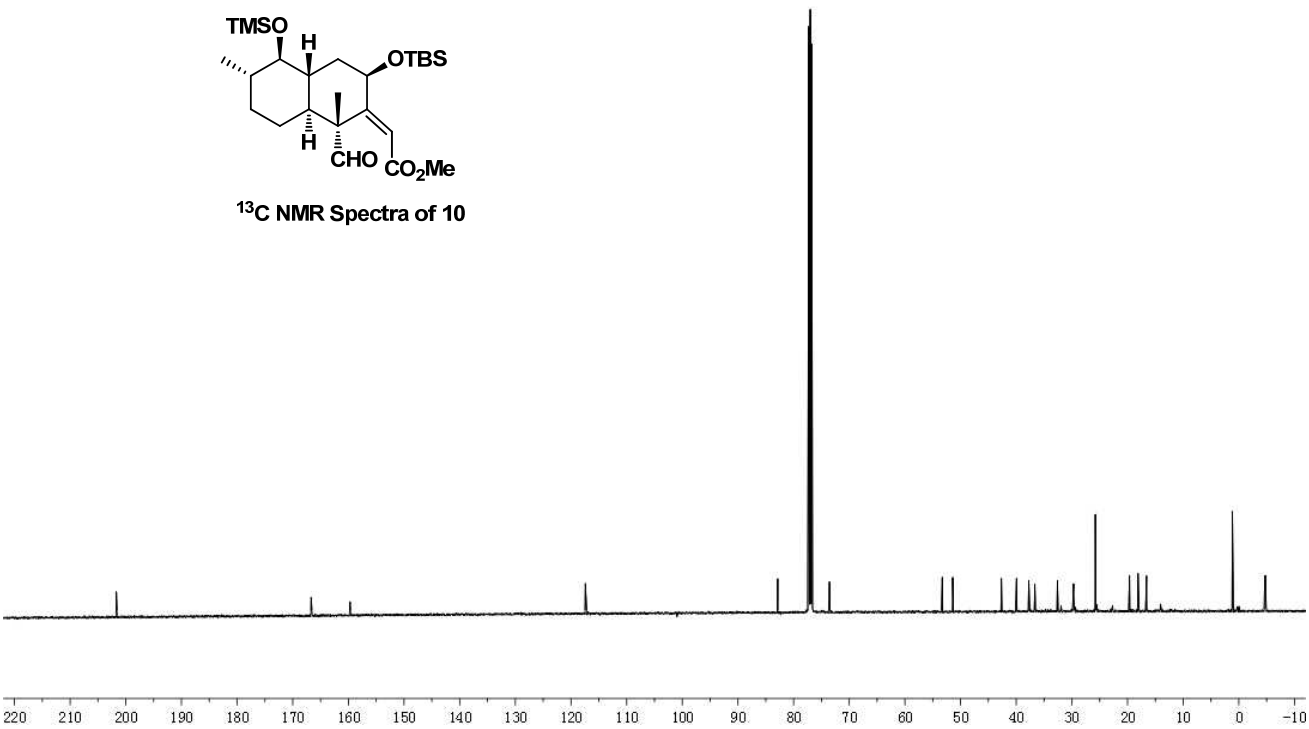
^{1}H NMR Spectra of 9



^{13}C NMR Spectra of 9



^{1}H NMR Spectra of 10



^{13}C NMR Spectra of 10

X-ray structure of the enantimer of compound 8j