Electronic Supplementary Information

Co-catalyzed C(sp^3)−C(sp^2) bond cleavage via hydrogen atom transfer

Bingqing Zhou†, Di Tian†, Jinglin An, Yalan Zhou, Rui Yan, Hao Song, Xiao-Yu Liu* and Yong Qin*

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1. General Information

All reactions that require anhydrous conditions were performed in flame-dried glassware under argon atmosphere and all reagents were purchased from commercial suppliers. Solvent purification was conducted according to Purification of Laboratory Chemicals 2nd edn (Perrin, D. D., Armarego, W. L. F. and Perrin, D. R., Pergamon Press: Oxford, 1980). The products were purified by flash column chromatography on silica gel (200 – 300 meshes) from the Anhui Liangchen Silicon Material Company (China). Reactions were monitored by thin layer chromatography (TLC, 0.2 mm, HSGF254) supplied by Yantai Chemicals (China). Visualization was accomplished with UV light, exposure to iodine, stained with ethanolic solution of phosphomolybdic acid or basic solution of $KMnO_4$. ^1H NMR and ^{13}C NMR spectra were recorded on Varian INOVA-400/54 and Agilent DD2-600/54 spectrometer, in the following solvents (reference peaks include ^1H and ^{13}C NMR): $CDCl_3$ (^1H NMR: 7.26 ppm; ^{13}C NMR: 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (*J*) were reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two FTIR spectrometer. The specific optical rotation was obtained from Rudolph Research Analytical Autopol VI automatic polarimeter. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS or Thermo Scientific LTQ Orbitrap XL ESI mass spectrometers.

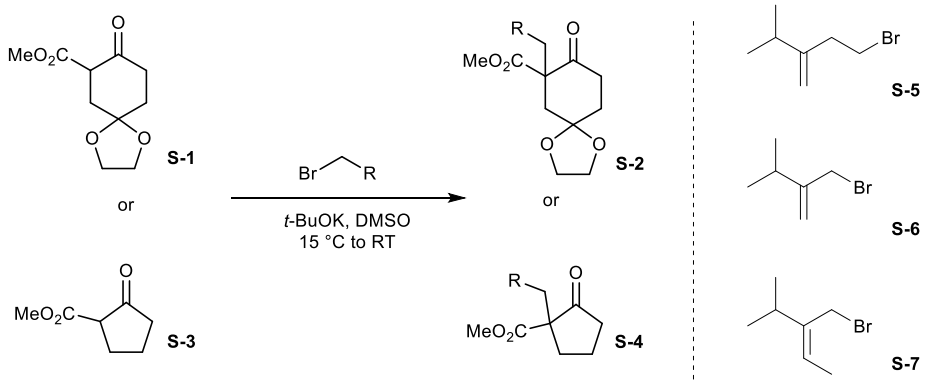
2. Experimental Procedures and Characterization Data

2.1 Ligands and Catalysts

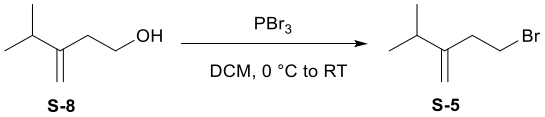
$Co(acac)_3$, $Co(OAc)_2$, $Mn(dpm)_3$, $Mn(OAc)_2$, $Fe(dpm)_3$, $Fe(acac)_3$ and Fe(PC) are commercially available and were used as received. The title compounds **C1** was synthesized according the reported procedure[1] and its analytical data were identical to those reported in literature.

2.2 Substrate Preparation

2.2.1 General Procedure I: Synthesis of Alkenes 3, 8, 29 and 10

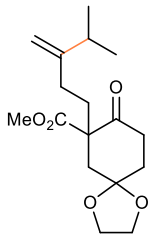


A solution of keto ester[2] (1.00 equiv.) in DMSO (1.6 M) was added to a stirred solution of *t*-BuOK (1.04 equiv.) in DMSO (0.4 M) at 15 ºC. After stirring for 1.5 h, alkyl bromide (1.20 equiv.) was added and the reaction mixture was stirred at room temperature overnight. The mixture was quenched with a saturated solution of NH_4Cl and extracted with CH_2Cl_2 (3×). The organic phase was washed successively with water and brine, dried (anhydrous $MgSO_4$), and concentrated under reduced pressure. Purification of the residue through flash column chromatography provided the corresponding alkene.[3]



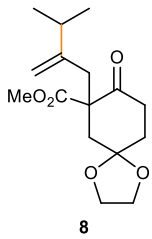
To a solution of alcohol **S-8**[4] (5.06 g, 44.3 mmol) in dry Et_2O (88 mL) at 0 °C was added PBr_3 (6.00 g, 22.2 mmol). The solution was warmed to room temperature and

stirred for 16 hours before it was cooled to 0 °C and quenched by adding water (44 mL) and 5% aq. K_2CO_3 (44 mL). The organic phase was isolated, washed with brine (44 mL), dried (anhydrous $MgSO_4$) and concentrated in *vacuo* to afford the corresponding bromide **S-5**, which was used in the next stage without further purification.



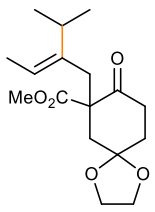
3

The title compound was prepared according to General Procedure I using keto ester **S-1** (1.00 g, 4.67 mmol), alkyl bromide **S-5** (987 mg, 0.850 mL, 5.61 mmol) and *t*-BuOK (545 mg, 4.86 mmol) in DMSO. Purification by chromatography (petroleum ether/EtOAc = 25:1, v/v) gave **3** (596 mg, 41%) as a yellowish oil. **TLC**: (petroleum ether/EtOAc = 10:1, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.67 (s, 1H), 4.04 – 3.97 (m, 4H), 3.73 (s, 3H), 3.06 – 2.95 (m, 1H), 2.60 (d, *J* = 14.0 Hz, 1H), 2.47 (dt, *J* = 14.4, 4.4 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.17 – 2.10 (m, 1H), 2.01 – 1.97 (m, 2H), 1.87 – 1.82 (m, 1H), 1.78 – 1.69 (m, 2H), 1.64 – 1.60 (m, 1H), 1.00 (dd, *J* = 6.8, 2.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.07, 172.97, 155.56, 106.96, 106.87, 65.02, 64.41, 58.16, 52.35, 42.11, 37.96, 35.42, 34.63, 33.93, 29.30, 21.92, 21.88; **IR** (neat): ν_{max} = 2959, 2889, 1715, 1642, 1435, 1363, 1294, 1261, 1217, 1198, 1165, 1107, 1055, 1032, 985, 932, 945, 889, 737, 499 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{27}O_5$ $[M + H]^+$ *m*/*z* 311.1853, found *m*/*z* 311.1854.



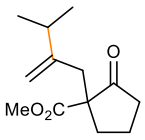
8

The title compound was prepared according to General Procedure I using keto ester **S-1** (300 mg, 1.40 mmol), alkyl bromide **S-6**[5] (273 mg, 138 µL, 1.68 mmol) and *t*-BuOK (164 mg, 1.46 mmol) in DMSO. Purification by chromatography (petroleum ether/EtOAc = 25:1, v/v) gave **8** (182 mg, 44%) as a yellowish oil. **TLC**: (petroleum ether/ EtOAc = 4:1, v/v), R_f = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.87 (s, 1H), 4.63 (s, 1H), 4.03 – 3.94 (m, 4H), 3.69 (s, 3H), 3.04 – 2.95 (m, 1H), 2.67 – 2.46 (m, 4H), 2.10 – 1.95 (m, 3H), 1.87 (d, *J* = 14.0 Hz, 1H), 0.99 (dd, *J* = 6.8, 2.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.61, 172.77, 151.17, 111.25, 106.98, 64.94, 64.42, 59.00, 52.41, 41.62, 39.30, 37.87, 35.15, 34.27, 22.17, 21.69; **IR** (neat): ν_{max} = 2960, 2887, 1719, 1660, 1440, 1363, 1292, 1263, 1230, 1123, 1046, 945, 898, 748 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{16}H_{24}O_5Na$ $[M + Na]^+$ *m*/*z* 319.1516, found *m*/*z* 319.1517.



29

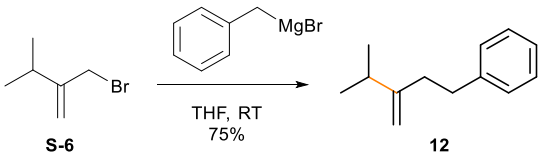
The title compound was prepared according to General Procedure I using keto ester **S-1** (200 mg, 0.935 mmol), alkyl bromide **S-7**[6] (197 mg, 115 µL, 1.12 mmol) and *t*-BuOK (109 mg, 0.970 mmol) in DMSO. Purification by chromatography (petroleum ether/EtOAc = 15:1, v/v) gave **29** (139 mg, 48%) as a yellowish oil. **TLC**: (petroleum ether/ EtOAc = 3:1, v/v), R_f = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.94 – 4.87 (m, 1H), 4.11 – 3.91 (m, 4H), 3.68 (s, 3H), 3.11 – 3.00 (m, 1H), 2.79 – 2.72 (m, 1H), 2.60 – 2.32 (m, 4H), 2.08 – 1.91 (m, 3H), 1.57 (t, *J* = 3.4 Hz, 3H), 0.96 – 0.93 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.31, 173.34, 139.60, 120.50, 107.09, 64.94, 64.47, 58.99, 52.42, 41.88, 35.46, 35.02, 20.64, 20.39; **IR** (neat): ν_{max} = 2959, 1718, 1436, 1363, 1305, 1262, 1220, 1163, 1122, 1053, 945, 730 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{27}O_5$ $[M + H]^+$ *m*/*z* 311.1853, found *m*/*z* 311.1853.



10

The title compound was prepared according to General Procedure I using keto ester **S-3** (300 mg, 2.11 mmol), alkyl bromide **S-6** (410 mg, 207 µL, 2.53 mmol) and *t*-BuOK (246 mg, 2.19 mmol) in DMSO. Purification by chromatography (petroleum ether/EtOAc = 8:1, v/v) gave **10** (223 mg, 47%) as a yellowish oil. **TLC**: (petroleum ether/EtOAc = 8:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.86 (s, 1H), 4.64 (s, 1H), 3.70 (s, 3H), 2.86 (d, *J* = 15.2 Hz, 1H), 2.66 – 2.59 (m, 1H), 2.44 – 2.36 (m, 1H), 2.30 – 2.22 (m, 2H), 2.07 – 1.87 (m, 4H), 1.06 – 0.97 (dd, *J* = 6.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.63, 171.13, 151.58, 110.07, 60.66, 52.76, 38.76, 37.86, 34.14, 32.32, 21.88, 21.80; **IR** (neat): ν_{max} = 2961, 1753, 1724, 1640, 1435, 1406, 1317, 1213, 1142, 1113, 1007, 900, 494 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{21}O_3$ $[M + H]^+$ *m*/*z* 225.1485, found *m*/*z* 225.1487.

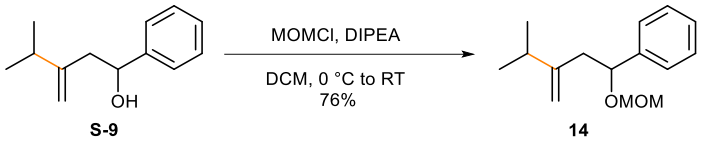
2.2.2 Preparation of Additional Alkene Substrates



S-6 12

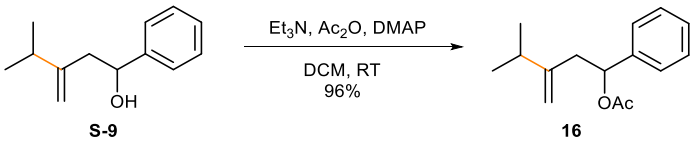
Under argon, to a stirred solution of alkyl bromide **S-6** (162 mg, 82.0 µL, 1.00 mmol) in dry THF (1 mL) was slowly added benzylbromomagnesium (1M in THF, 1.00 mL, 1.00 mmol) at room temperature. After being stirred for 8 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3×). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated to afford a residue, which was purified by column chromatography on silica gel (petroleum ether) to yield compound **12** (130 mg, 75%) as a colorless oil. **TLC**: R_f = 0.80 (petroleum ether); **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 4.80 (s, 1H), 4.74 (s, 1H), 2.77 – 2.73 (m, 2H), 2.34 – 2.24 (m, 3H), 1.05 (d, J = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.61, 142.63, 128.49, 128.44, 125.89, 106.77, 36.32, 34.87, 34.23, 21.97; **IR** (neat): ν_{max} = 3085, 3028, 2962, 2871, 1642, 1604, 1496, 1455, 1380, 1363, 1097, 1074, 1031, 889, 746, 698, 567 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{19}$ $[M + H]^+$ *m*/*z* 175.1481, found *m*/*z* 175.1477.



S-9 **14**

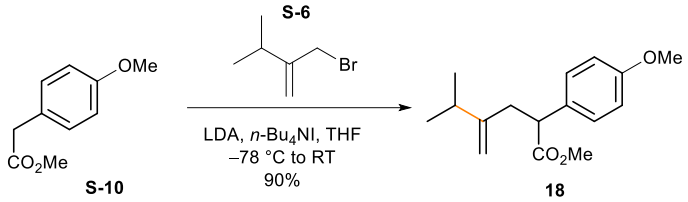
Under an argon atmosphere, DIPEA (204 mg, 275 µL, 1.58 mmol) and MOMCl (85.0 mg, 80.0 µL, 1.05 mmol) were sequentially added to a stirred solution of alcohol **S-9**[8] (100 mg, 0.526 mmol) in CH_2Cl_2 (5 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 6 h. After disappearance of the starting material as monitored by TLC analysis, the reaction was quenched by saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3×). The combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (petroleum ether /EtOAc = 50:1, v/v) gave compound **14** (94.0 mg, 76%) as a colourless oil. **TLC**: R_f = 0.55 (petroleum ether/EtOAc = 20:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 5H), 4.81 (d, J = 18.8 Hz, 2H), 4.70 – 4.67 (m, 1H), 4.45 (s, 2H), 3.27 (s, 3H), 2.52 (dd, J = 14.8, 8.4 Hz, 1H), 2.33 (dd, J = 14.4, 5.2 Hz, 1H), 2.22 – 2.17 (m, 1H), 0.96 (dd, J = 9.6, 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.05, 142.25, 128.45, 127.73, 127.10, 109.57, 94.31, 77.30, 55.77, 43.48, 33.64, 21.83, 21.65; **IR** (neat): ν_{max} = 2950, 1985, 1765, 1219, 1055, 1033, 772, 667, 529, 515, 506, 446 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{15}H_{22}O_2Na$ $[M + Na]^+$ *m*/*z* 257.1512, found *m*/*z* 257.1512.



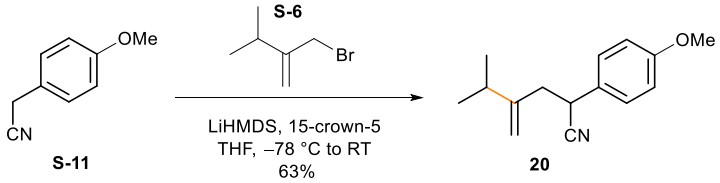
S-9 **16**

Triethylamine (266 mg, 366 µL, 2.63 mmol), acetic anhydride (107 mg, 98.0 µL, 1.05 mmol) and 4-*N*,*N*-dimethylaminopyridine (3.2 mg, 0.026 mmol) were added to a solution of alcohol **S-9** (100 mg, 0.526 mmol) in CH_2Cl_2 (3 mL). The resulting solution was stirred at room temperature for 15 h before CH_2Cl_2 (20 mL) and water (20 mL) were added. The organic phase was separated and washed with aqueous HCl (3.5 M, 15 mL) and brine (15 mL), then dried (anhydrous $MgSO_4$) and concentrated under reduced pressure. Flash column chromatography of the resulting residue on silica gel

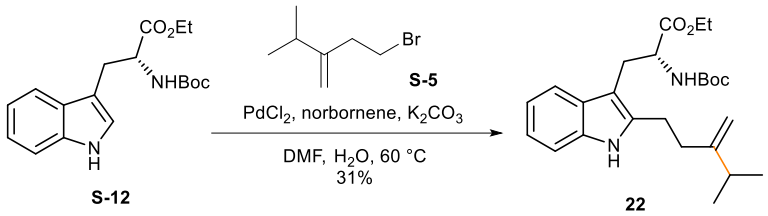
(petroleum ether /EtOAc = 20:1, v/v) afforded compound **16** (117 mg, 96%) as a colorless oil. **TLC**: R_f = 0.57 (petroleum ether/EtOAc = 7:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 5.92 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.83 (s, 1H), 4.72 (s, 1H), 2.63 (dd, *J* = 14.8, 8.4 Hz, 1H), 2.47 (dd, *J* = 14.6, 5.4 Hz, 1H), 2.23 – 2.18 (m, 1H), 2.04 (s, 3H), 1.01 (t, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.37, 151.16, 140.82, 128.52, 128.04, 126.73, 110.10, 74.78, 41.78, 21.88, 21.69, 21.36; **IR** (neat): ν_{max} = 2963, 1740, 1644, 1455, 1372, 1235, 1022, 895, 699 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ *m*/*z* 255.1356, found *m*/*z* 255.1356.



Under argon, to a stirred solution of **S-10** (300 mg, 260 µL, 1.66 mmol) in anhydrous THF (4 mL) at –78 °C was added LDA (2M in THF/hexane, 0.91 mL, 1.83 mmol) dropwise. After stirring for 30 min, alkyl bromide **S-6** (403 mg, 204 µL, 2.49 mmol) and *n*-Bu_4NI (123 mg, 0.330 mmol) were added. The mixture was warmed to room temperature and stirred for 18 h before it was quenched with saturated aqueous NH_4Cl at 0 °C and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated in *vacuo*. Subsequently, the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 30:1, v/v) to give compound **18** (391 mg, 90%) as a pale-yellow oil. **TLC**: R_f = 0.43 (petroleum ether/EtOAc = 15/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.79 (s, 1H), 4.68 (s, 1H), 3.79 – 3.63 (m, 4H), 3.64 (s, 3H), 2.83 (dd, *J* = 15.2, 9.2 Hz, 1H), 2.40 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.27 – 2.15 (m, 1H), 1.01 (dd, *J* = 8.7, 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.55, 158.93, 153.04, 131.28, 129.02, 114.12, 108.19, 55.38, 52.04, 49.46, 38.25, 34.15, 21.86, 21.84; **IR** (neat): ν_{max} = 2959, 1734, 1612, 1512, 1463, 1438, 1250, 1179, 1160, 1036, 894, 831 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{16}H_{23}O_3$ $[M + H]^+$ m/z 263.1642, found m/z 263.1642.

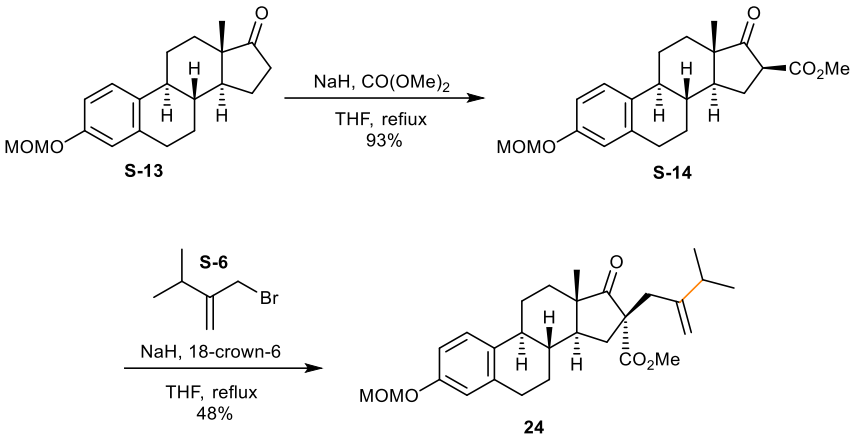


To an oven-dried flask were successively added **S-11** (300 mg, 276 μL, 2.04 mmol), 15-crown-5 (540 mg, 485 μL, 2.45 mmol) and dry THF (12 mL). Then LiHMDS (1 M in THF, 2.45 mL, 2.45 mmol) was added under an argon atmosphere at –30 °C, followed by addition of **S-6** (496 mg, 251 μL, 3.06 mmol) after 15 min later. The resulting mixture was stirred at –30 °C for 16 h. After the reaction was completed (identified by TLC analysis), it was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc (3×) and washed with brine. The combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (petroleum ether/EtOAc = 30:1, v/v) afforded compound **20** (295 mg, 63%) as a yellow oil. **TLC**: R_f = 0.43 (petroleum ether/EtOAc = 15/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.99 (s, 1H), 4.88 (s, 1H), 3.93 – 3.85 (m, 1H), 3.81 (s, 3H), 2.65 – 2.59 (m, 1H), 2.54 – 2.47 (m, 1H), 2.25 – 2.18 (m, 1H), 1.04 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.48, 150.63, 128.56, 128.07, 121.10, 114.55, 110.85, 55.48, 41.15, 36.18, 33.70, 21.79, 21.73; **IR** (neat): ν_{max} = 2962, 2240, 1644, 1612, 1586, 1512, 1463, 1301, 1251, 1180, 1034, 900, 830, 565 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{15}H_{20}NO$ $[M + H]^+$ m/z 230.1539, found m/z 230.1539.



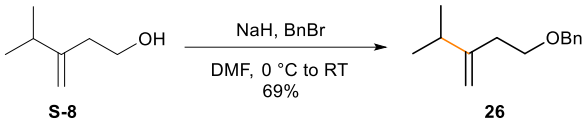
To a mixture of *N*-Boc-(*R*)-tryptophan ethyl ester[9] (**S-12**, 415 mg, 1.25 mmol), norbornene (235 mg, 2.50 mmol), K_2CO_3 (691 mg, 5.00 mmol), and $PdCl_2$ (22.0 mg, 0.125 mmol) was added 6.5 mL of DMF (containing 0.5 M H_2O) and a primary alkyl bromide **S-5** (880 mg, 0.760 mL, 5.00 mmol). The resulting suspension was stirred at 60 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and washed with water. The aqueous layer was then extracted with EtOAc (3 ×), and the combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 8:1, v/v) to give compound **22** (166 mg, 31%) as a white solid. **TLC**: R_f = 0.39 (petroleum ether/EtOAc = 40/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.15 (dt, *J* = 30.0, 7.2 Hz, 2H), 7.00 (d, *J* = 2.0 Hz, 1H), 5.07 (d, *J* = 7.6 Hz, 1H), 4.82 (s, 1H), 4.70 – 4.59 (m, 2H), 4.21 – 4.11 (m, 2H), 3.28 (t, *J* = 5.2 Hz, 2H), 2.28 – 2.15 (m, 3H), 1.43 (s, 9H), 1.36 – 1.19 (m, 3H), 1.01 (d, *J* = 6.8 Hz, 6H), 0.92 – 0.82 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.43, 155.38, 151.36, 136.23, 127.88, 122.82, 122.32, 119.72, 118.94,

111.26, 110.51, 108.96, 79.90, 64.45, 54.39, 34.17, 32.93, 31.77, 28.47, 28.18, 21.72, 14.26; **IR** (neat): ν_{max} = 3350, 2964, 2931, 1694, 1500, 1458, 1366, 1278, 1250, 1165, 1061, 1011, 896, 742, 614, 557 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{25}H_{37}N_2O_4$ $[M + H]^+$ *m*/*z* 429.2478, found *m*/*z* 429.2481.



1) Dimethyl carbonate (215 mg, 201 µL, 2.39 mmol) and a solution of 3-*O*-methoxymethylestrone **S-13**[10] (300 mg, 0.955 mmol) in anhydrous THF (5 mL) were added successively to a suspension of NaH (115 mg, 2.86 mmol, 60% powder in oil) in anhydrous THF (5 mL) under argon. After the mixture was refluxed for 8 h, the reaction was cooled to 0 °C and quenched by adding acetic acid (3 M, 2 mL). The organic layer was separated and the aqueous phase was extracted three times with EtOAc. The combined organic layers were washed with aqueous saturated sodium hydrogen carbonate solution and brine, dried (anhydrous $MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by column chromatography (petroleum ether/EtOAc = 10:1, v/v) to afford keto ester **S-14** (331 mg, 93%) as a white solid. **TLC**: R_f = 0.35 (petroleum ether/EtOAc = 5/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.88 – 6.77 (m, 2H), 5.15 (s, 2H), 3.76 (s, 3H), 3.47 (s, 3H), 3.25 – 3.17 (m, 1H), 2.90 – 2.88 (m, 2H), 2.44 – 2.24 (m, 3H), 2.15 – 1.93 (m, 3H), 1.69 – 1.57 (m, 1H), 1.57 – 1.40 (m, 4H), 0.98 (s, 2H), 0.96 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.53, 212.12, 170.48, 169.95, 155.38, 155.35, 137.90, 137.83, 133.20, 133.09, 126.47, 126.45, 116.39, 114.04, 114.01, 94.54, 56.02, 54.16, 52.69, 52.67, 51.64, 49.02, 48.77, 48.76, 48.02, 44.11, 43.88, 38.42, 37.97, 32.02, 29.65, 29.63, 26.62, 26.48, 25.87, 25.85, 14.46, 13.38; **IR** (neat): ν_{max} = 2925, 2855, 1753, 1724, 1609, 1498, 1453, 1436, 1327, 1280, 1229, 1205, 1149, 1077, 1002, 907, 726, 648, 442 cm^{-1}; **$[\alpha]_D^{25}$** = +308.1 (*c* 0.16, $CHCl_3$); **HRMS (ESI)**: calcd. for $C_{22}H_{28}O_5Na$ $[M + Na]^+$ *m*/*z* 395.1829, found *m*/*z* 395.1826.

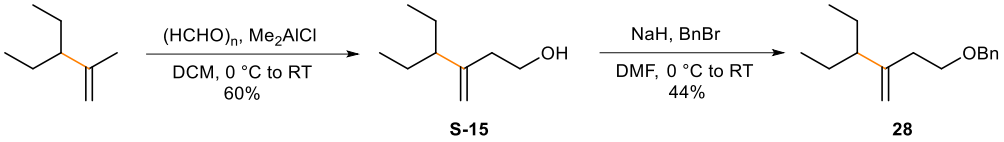
2) Keto ester **S-14** (331 mg, 0.889 mmol), NaH (107 mg, 2.67 mmol, 60% powder in oil), and 18-crown-6 (47.0 mg, 47.0 µL, 0.178 mmol) were mixed in THF (19 mL) and refluxed for 1 h. The mixture was cooled to room temperature, to which was added allyl bromide **S-6** (721 mg, 364 µL, 4.45 mmol). The resulting mixture was then refluxed for 18 h. After being cooled to room temperature, the reaction was quenched by carefully adding water. This mixture was extracted with EtOAc for three times and the combined organic layers were washed with brine. The organic layers were dried with anhydrous $MgSO_4$, filtered, and evaporated. Purification of the residue via flash column chromatography (petroleum ether/EtOAc = 10:1, v/v) afforded compound **24** (194 mg, 48%) as a yellow oil. **TLC**: R_f = 0.55 (petroleum ether/EtOAc = 5/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.8 Hz, 1H), 6.87 – 6.78 (m, 2H), 5.15 (s, 2H), 4.86 (s, 1H), 4.62 (s, 1H), 3.70 (s, 3H), 3.47 (s, 3H), 2.94 – 2.88 (m, 2H), 2.52 (t, J = 13.2 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.29 – 2.17 (m, 3H), 2.16 – 1.95 (m, 3H), 1.64 – 1.34 (m, 6H), 1.03 (d, J = 6.8 Hz, 6H), 0.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.13, 171.86, 155.40, 151.94, 137.97, 133.29, 126.44, 116.45, 114.04, 109.41, 94.61, 59.88, 56.08, 52.84, 49.60, 46.11, 44.27, 39.11, 37.93, 34.39, 32.43, 30.10, 29.65, 26.60, 25.81, 21.94, 21.90, 14.30; **IR** (neat): ν_{max} = 2957, 2930, 2871, 1750, 1722, 1610, 1499, 1453, 1282, 1208, 1153, 1078, 1011, 922 cm^{-1}; **$[\alpha]_D^{25}$** = +203.6 (*c* 0.14, $CHCl_3$); **HRMS (ESI)**: calcd. for $C_{28}H_{39}O_5$ $[M + H]^+$ *m*/*z* 455.2792, found *m*/*z* 455.2791.



S-8 **26**

NaH (52.0 mg, 1.31 mmol) was added to a stirred solution of alcohol **S-8** (100 mg, 0.876 mmol) in dry DMF (8 mL) at 0 °C. After stirring for 30 min, to the resulting mixture was added BnBr (188 mg, 131 µL, 1.10 mmol). The reaction was then stirred overnight. After disappearance of the starting material as monitored by TLC analysis, the reaction was quenched by saturated aqueous NH_4Cl and extracted four times with EtOAc. Then the combined organic layers were sequentially washed with water and brine, and dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude product, which was purified by flash column chromatography (petroleum ether /EtOAc = 20:1, v/v) to give compound **26** (122 mg, 69%) as a colorless oil. **TLC**: R_f = 0.39 (petroleum ether/EtOAc = 40/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, J = 4.4 Hz, 4H), 7.31 – 7.26 (m, 1H), 4.81 (s, 1H), 4.72 (s, 1H), 4.54 – 4.51 (m, 2H), 3.59 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 2.29 – 2.21 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.77, 138.65, 128.50, 127.80, 127.67, 107.96, 73.09,

69.69, 34.37, 34.29, 21.83; **IR** (neat): ν_{max} = 3066, 3031, 2961, 2928, 2861, 1642, 1496, 1454, 1362, 1204, 1098, 1029, 891, 735, 697, 610 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{14}H_{21}O$ $[M + H]^+$ *m*/*z* 205.1587, found *m*/*z* 205.1587.

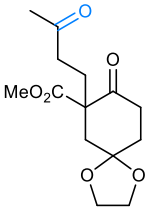


1) To a stirred solution of 3-3-ethyl-2-methyl-1-pentene (720 mg, 1.00 mL, 6.41 mmol,) and paraformaldehyde (580 mg, 6.41 mmol) in dry CH_2Cl_2 (15 mL) was slowly added Me_2AlCl (1 M in hexane, 6.41 mL, 6.41 mmol) at 0 °C. The reaction was stirred overnight at room temperature. After disappearance of the starting material as monitored by TLC analysis, the reaction was quenched by saturated aqueous NaH_2PO_4, leading to the formation of white precipitate, which was removed by treating with 10% HCl aq. solution. The mixture was extracted three times with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 10:1, v/v) to yield compound **S-15** (547 mg, 60%) as a colorless oil. **TLC**: R_f = 0.44 (petroleum ether /EtOAc = 5:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 6.8 Hz, 2H), 3.74 (t, *J* = 6.5 Hz, 2H), 2.20 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.75 (m, 1H), 1.60 (s, 1H), 1.46 – 1.31 (m, 4H), 0.82 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.30, 110.81, 60.66, 49.83, 36.13, 26.06, 11.66; **IR** (neat): ν_{max} = 3330, 2960, 2928, 2873, 1640, 1456, 1378, 1044, 1019, 891, 749, 637 cm^{-1}; **HRMS (ESI)**: calcd. for $C_9H_{19}O$ $[M + H]^+$ *m*/*z* 143.1430, found *m*/*z* 143.1430.
2) NaH (312 mg, 7.80 mmol) was added to a stirred solution of alcohol **S-15** (738 mg, 5.20 mmol) in dry DMF (15 mL) at 0 °C and the mixture was stirred at the same temperature for 30 min before BnBr (1.10 g, 0.77 mL, 6.50 mmol) was added. The resulting mixture was stirred at room temperature overnight. After the reaction was completed (identified by TLC analysis), the reaction was quenched by saturated aqueous NH_4Cl and extracted with EtOAc (4×). Then the combined organic layers were sequentially washed with water and brine, and dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (petroleum ether/EtOAc = 40:1, v/v) afforded compound **28** (528 mg, 44%) as a colorless oil. **TLC**: R_f = 0.45 (petroleum ether/EtOAc = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 3H), 7.31 – 7.24 (m, 1H), 4.80 (s, 1H), 4.77 (s, 1H), 4.53 (s, 2H), 3.61 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.76 (m, 1H), 1.48 – 1.23 (m, 5H), 0.81 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100

MHz, $CDCl_3$) δ 148.59, 138.66, 128.50, 127.81, 127.66, 110.72, 73.13, 69.65, 50.58, 26.29, 12.08; **IR** (neat): ν_{max} = 3067, 3031, 2959, 2928, 2871, 1974, 1640, 1496, 1454, 1362, 1308, 1202, 1100, 1028, 1012, 890, 733, 696, 607, 546, 538 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{16}H_{25}O$ $[M + H]^+$ *m/z* 233.1900, found *m/z* 233.1900.

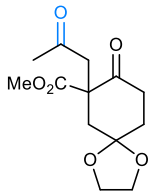
2.3 General Procedure II: Synthesis of Ketones via HAT C(sp^3)−C(sp^2) Bond Cleavage from Alkenes

Under O_2 (balloon), to a solution of alkene (1.0 equiv.) and **C1** (0.1 equiv.) in dry EtOH (0.07 M) was added $PhSiH_3$ (2.5 equiv.). The resulting mixture was heated to 60 °C with stirring for 24 h. The reaction was then cooled to room temperature and concentrated under reduced pressure. The residue was then purified by column chromatography (petroleum ether /EtOAc) to furnish the corresponding ketone.



7

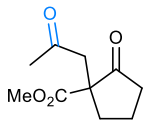
The title compound was prepared according to General Procedure II using alkene **3** (30.0 mg, 0.100 mmol), $PhSiH_3$ (26.0 mg, 30.0 µL, 0.242 mmol) and **C1** (5.5 mg, 0.010 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 3/1, v/v) gave **7** (20.3 mg, 74%) as a yellow oil. **TLC**: R_f = 0.42 (petroleum ether/EtOAc = 1:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.07 – 3.92 (m, 4H), 3.73 (s, 3H), 3.08 – 2.97 (m, 1H), 2.76 – 2.66 (m, 1H), 2.61 – 2.54 (m, 1H), 2.46 (dt, *J* = 13.6, 4.2 Hz, 1H), 2.27 – 2.19 (m, 1H), 2.12 (s, 3H), 2.08 – 1.96 (m, 3H), 1.83 – 1.74 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.68, 207.21, 172.83, 106.70, 65.07, 64.47, 57.38, 52.50, 42.69, 39.09, 37.90, 35.42, 30.07, 29.09; **IR** (neat): ν_{max} = 2957, 2031, 1716, 1432, 1359, 1225, 1164, 1133, 1038, 990, 946, 734, 506, 492, 460, 421, 414 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{14}H_{21}O_6$ $[M + H]^+$ *m/z* 285.1333, found *m/z* 285.1333.



9

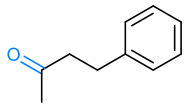
The title compound was prepared according to General Procedure II using alkene **8** (30.0 mg, 0.101 mmol), $PhSiH_3$ (27.0 mg, 31.0 µL, 0.253 mmol) and **C1** (5.5 mg, 0.010 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 3/1, v/v) gave **9** (15.0 mg, 55%) as a yellow oil. **TLC**: R_f = 0.47 (petroleum ether/EtOAc = 1:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.04 – 3.88 (m, 4H), 3.75 (s, 3H), 3.11 – 3.03 (m, 1H), 2.94 (d, *J* = 17.2 Hz, 1H), 2.71 (d, *J* = 17.2 Hz, 1H), 2.58 – 2.47 (m, 2H), 2.19 – 2.14 (m, 4H), 2.10 (dd, *J* = 13.4, 5.6 Hz, 1H), 2.04 – 1.96 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.23, 205.07, 172.87, 106.81, 64.98, 64.57, 57.27, 52.90, 47.76, 41.54, 37.55, 34.62, 30.54; **IR** (neat): ν_{max} = 2956, 1714, 1433, 1361, 1301, 1271, 1229, 1167,

1114, 1058, 1032, 940, 721, 501 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{19}O_6$ $[M + H]^+$ *m*/*z* 271.1176, found *m*/*z* 271.1176.



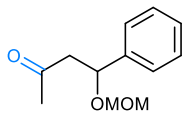
11

The title compound was prepared according to General Procedure II using alkene **10** (30.0 mg, 0.134 mmol), $PhSiH_3$ (36.0 mg, 41.0 µL, 0.335 mmol) and **C1** (7.1 mg, 0.013 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 8/1, v/v) gave **11** (21.2 mg, 80%) as a yellow oil. **TLC**: R_f = 0.41 (petroleum ether/EtOAc = 3:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.21 (d, *J* = 18.6 Hz, 1H), 2.96 (d, *J* = 18.6 Hz, 1H), 2.63 – 2.52 (m, 1H), 2.53 – 2.44 (m, 2H), 2.14 (s, 3H), 2.12 – 1.96 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.85, 205.40, 171.16, 57.50, 52.89, 47.74, 37.80, 33.33, 30.11, 19.91; **IR** (neat): ν_{max} = 2955, 2922, 2852, 1752, 1720, 1434, 1402, 1363, 1260, 1229, 1208, 1167, 1148, 1115, 1053, 747, 730 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{10}H_{15}O_4$ $[M + H]^+$ *m*/*z* 199.0965, found *m*/*z* 199.0966.



13

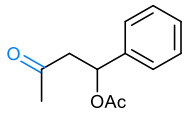
The title compound was prepared according to General Procedure II using alkene **12** (30.0 mg, 0.172 mmol), $PhSiH_3$ (47.0 mg, 54.0 µL, 0.430 mmol) and **C1** (9.3 mg, 0.017 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 50/1, v/v) gave **13** (16.4 mg, 64%) as a colorless oil. **TLC**: R_f = 0.51 (petroleum ether/EtOAc = 6:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.15 (m, 5H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.10, 141.13, 128.43, 126.26, 45.33, 30.23, 29.88; **IR** (neat): ν_{max} = 3028, 2925, 1716, 1496, 1453, 1359, 1276, 1161, 750, 700 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{10}H_{12}ONa$ $[M + Na]^+$ *m*/*z* 171.0780, found *m*/*z* 171.0775.



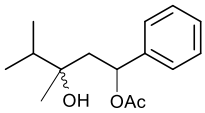
15

The title compound was prepared according to General Procedure II using alkene **14** (30.0 mg, 0.128 mmol), $PhSiH_3$ (35.0 mg, 40.0 µL, 0.320 mmol) and **C1** (7.1 mg, 0.013 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 20/1, v/v) gave **15** (18.0 mg, 67%) as a colorless oil. **TLC**: R_f = 0.37 (petroleum ether/EtOAc = 4:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.11 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.56 – 4.45 (m, 2H), 3.32 (s, 3H), 3.05 (dd, *J* = 16.0, 9.2 Hz, 1H), 2.64 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.39, 140.95, 128.74, 128.14, 126.94, 94.39, 74.12, 55.92, 51.72, 31.18; **IR** (neat): ν_{max} = 3515, 2924, 1716, 1453, 1361, 1310, 1207, 1149, 1094, 1024, 918, 755, 701, 545, 501,

428 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{17}O_3$ $[M + H]^+$ *m/z* 209.1172, found *m/z* 209.1171.

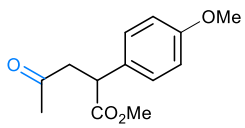


17



17b

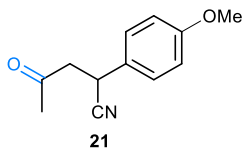
The title compound was prepared according to General Procedure II using alkene **16** (30.0 mg, 0.129 mmol), $PhSiH_3$ (35.0 mg, 40.0 µL, 0.323 mmol) and **C1** (7.1 mg, 0.013 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 8/1, v/v) gave **17** (13.3 mg, 50%, yellow oil), together with the hydration byproduct **17b** as a pair of inseparable diastereomers (7.0 mg, 22%, dr = 1:1) as a yellow oil. Data for **17**: **TLC**: R_f = 0.55 (petroleum ether/EtOAc = 3:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38– 7.27 (m, 5H), 6.19 (dd, *J* = 8.6, 4.8 Hz, 1H), 3.11 (dd, *J* = 16.6, 8.4 Hz, 1H), 2.83 (dd, *J* = 16.6, 4.8 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.77, 169.96, 139.82, 128.78, 128.40, 126.59, 71.76, 50.02, 30.58, 21.22; **IR** (neat): ν_{max} = 2924, 1736, 1720, 1495, 1371, 1237, 1162, 1044, 1024, 949, 757, 700, 539 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{15}O_3$ $[M + H]^+$ *m/z* 207.1016; found *m/z* 207.1017. Data for **17b**: **TLC**: R_f = 0.48 (petroleum ether/EtOAc = 5:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 5H), 6.03 (td, *J* = 8.8, 3.2 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.07 (s, 3H), 1.98 – 1.84 (m, 1H), 1.80 – 1.70 (m, 1H), 1.58 (s, 1H), 1.15 (d, *J* = 6.2 Hz, 3H), 0.98 – 0.85 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.37, 170.23, 141.91, 141.70, 128.77, 128.76, 128.16, 128.08, 126.58, 126.49, 74.38, 74.29, 73.97, 73.54, 45.80, 45.19, 38.25, 37.86, 23.37, 23.14, 21.63, 21.59, 17.87, 17.64, 17.10, 17.06; **IR** (neat): ν_{max} = 3485, 2961, 2925, 1730, 1458, 1372, 1242, 1127, 1074, 1028, 947, 699, 548, 442 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{15}H_{22}O_3Na$ $[M + Na]^+$ *m/z* 273.1461, found *m/z* 273.1458.



19

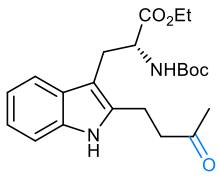
The title compound was prepared according to General Procedure II using alkene **18** (30.0 mg, 0.115 mmol), $PhSiH_3$ (31.0 mg, 35.0 µL, 0.286 mmol) and **C1** (6.6 mg, 0.012 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 9/1, v/v) gave **19** (17.8 mg, 66%) as a yellow oil. **TLC**: R_f = 0.40 (petroleum ether/EtOAc = 3:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 6.88 – 6.81 (m, 2H), 4.05 (dd, *J* = 10.2, 4.4 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.36 (dd, *J* = 18.0, 10.0 Hz, 1H), 2.69 (dd, *J* = 18.0, 4.4 Hz, 1H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.48, 174.13, 159.08, 130.24, 128.88, 114.38, 55.39, 52.38, 47.29, 45.38, 30.11; **IR** (neat): ν_{max} = 2954, 1717, 1610, 1512, 1436, 1356, 1254, 1159, 1032, 750,

555 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{17}O_4$ $[M + H]^+$ *m/z* 237.1121, found *m/z* 237.1121.



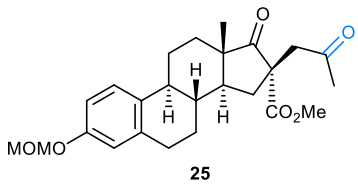
21

The title compound was prepared according to General Procedure II using alkene **20** (30.0 mg, 0.131 mmol), $PhSiH_3$ (35.0 mg, 40.0 µL, 0.327 mmol) and **C1** (7.1 mg, 0.013 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 6/1, v/v) gave **21** (8.7 mg, 33%, 58% brsm) as a yellow oil. **TLC**: R_f = 0.40 (petroleum ether/EtOAc = 2:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 6.92 – 6.86 (m, 2H), 4.33 – 4.24 (m, 1H), 3.80 (s, 3H), 3.15 (dd, *J* = 17.8, 7.6 Hz, 1H), 2.94 (dd, *J* = 18.0, 6.4 Hz, 1H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.33, 159.67, 128.71, 127.05, 120.79, 114.73, 55.50, 48.97, 30.95, 30.16; **IR** (neat): ν_{max} = 2919, 2849, 2242, 1717, 1623, 1535, 1463, 1363, 1302 1253, 1178, 1031, 833, 735, 701, 560, 501 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{14}NO_2$ $[M + H]^+$ *m/z* 204.1019, found *m/z* 204.1017.



23

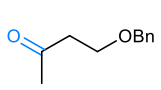
The title compound was prepared according to General Procedure II using alkene **22** (30.0 mg, 0.070 mmol), $PhSiH_3$ (19.0 mg, 22.0 µL, 0.175 mmol) and **C1** (3.8 mg, 0.007 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 4/1, v/v) gave **23** (14.5 mg, 52%, 70% brsm). **TLC**: R_f = 0.54 (petroleum ether/EtOAc = 1:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 4.63 – 4.58 (m, 1H), 4.35 – 4.25 (m, 2H), 3.25 (d, *J* = 5.4 Hz, 2H), 2.68 – 2.5 (m, 2H), 2.08 (s, 3H), 1.42 (s, 9H), 1.25 (s, 3H), 0.90 – 0.84 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.59, 172.34, 155.35, 136.23, 127.89, 123.03, 122.36, 119.79, 118.96, 111.28, 110.34, 79.99, 60.15, 54.43, 41.96, 30.36, 29.85, 29.80, 28.47, 28.15, 22.84, 14.27; **IR** (neat): ν_{max} = 3358, 2980, 2924, 2855, 1710, 1500, 1366, 1274, 1259, 1164, 1057, 749 cm^{-1}; **$[\alpha]_D^{25}$** = −18.4 (*c* 0.13, $CHCl_3$); **HRMS (ESI)**: calcd. for $C_{22}H_{31}N_2O_5$ $[M + H]^+$ *m/z* 403.2227, found *m/z* 403.2229.



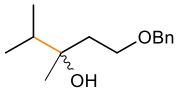
25

The title compound was prepared according to General Procedure II using alkene **24** (30.0 mg, 0.066 mmol), $PhSiH_3$ (18.0 mg, 21.0 µL, 0.165 mmol) and **C1** (3.8 mg, 0.007 mmol) in EtOH (0.07 M). Purification by column

chromatography (petroleum ether/EtOAc = 7/1, v/v) gave **25** (17.8 mg, 63%) as a white solid. **TLC**: R_f = 0.40 (petroleum ether/EtOAc = 3:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 1H), 6.88 – 6.77 (m, 2H), 5.15 (s, 2H), 3.69 (s, 3H), 3.47 (s, 3H), 2.95 – 2.83 (m, 2H), 2.72 (t, J = 13.2 Hz, 1H), 2.57 (d, J = 18.4 Hz, 1H), 2.44 – 2.21 (m, 2H), 2.16 (s, 3H), 2.09 – 1.93 (m, 3H), 1.72 – 1.41 (m, 6H), 1.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.01, 205.31, 170.56, 155.42, 137.95, 133.11, 126.45, 116.47, 114.05, 94.59, 58.24, 56.07, 53.02, 49.90, 48.15, 46.41, 44.31, 37.90, 32.49, 31.71, 30.09, 29.68, 25.83, 14.00; **IR** (neat): ν_{max} = 2926, 1724, 1611, 1499, 1454, 1238, 1205, 1155, 1077, 1009, 922 cm^{-1}; **[α]$_D^{25}$** = +191.2 (*c* 0.20, $CHCl_3$); **HRMS (ESI)**: calcd. for $C_{25}H_{32}O_6Na$ $[M + Na]^+$ *m/z* 451.2091, found *m/z* 451.2090.

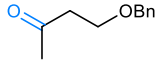


27

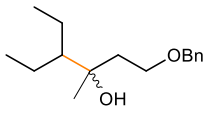


27b

The title compound was prepared according to General Procedure II using alkene **26** (30.0 mg, 0.147 mmol), $PhSiH_3$ (40.0 mg, 46.0 μL, 0.368 mmol) and **C1** (8.2 mg, 0.015 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 20/1, v/v) gave **27** (16.2 mg, 62%, yellow oil), together with the hydration byproduct **27b** as a pair of inseparable diastereomers (5.8 mg, 18%, dr = 1:1) as a yellow oil. Data for **27**: **TLC**: R_f = 0.34 (petroleum ether/EtOAc = 5:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.17 (m, 5H), 4.51 (s, 2H), 3.74 (t, J = 6.4 Hz, 2H), 2.72 (t, J = 6.4 Hz, 2H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.38, 138.20, 128.55, 127.86, 73.39, 65.40, 43.91, 30.62; **IR** (neat): ν_{max} = 3030, 2919, 2859, 1714, 1495, 1453, 1363, 1316, 1275, 1170, 1103, 1086, 1028, 745, 698 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{11}H_{14}O_2$ $[M + H]^+$ *m/z* 179.1067; found *m/z* 179.1069. Data for **27b**: **TLC**: R_f = 0.34 (petroleum ether/EtOAc = 5:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 4.52 (s, 2H), 3.78 – 3.68 (m, 2H), 3.11 (s, 1H), 1.93 – 1.83 (m, 1H), 1.77 – 1.66 (m, 2H), 1.10 (s, 3H), 0.91 (dd, J = 20.8, 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.94, 128.60, 127.92, 127.88, 74.71, 73.61, 67.71, 37.69, 22.72, 17.89, 17.09; **IR** (neat): ν_{max} = 3502, 2960, 2926, 2837, 1457, 1368, 1094, 1027, 909, 735, 697, 438 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{14}H_{22}O_2Na$ $[M + Na]^+$ *m/z* 245.1512, found *m/z* 245.1507.



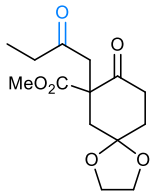
27



28b

The title compound was prepared according to General Procedure II using alkene **28** (30.0 mg, 0.129 mmol), $PhSiH_3$ (35.0 mg, 40.0 μL, 0.323 mmol) and **C1** (7.1 mg, 0.013 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 16/1, v/v) gave **27** (11.5 mg, 50%, yellow oil), together with the hydration byproduct **28b** as a pair of inseparable diastereomers (5.0 mg, 15%, dr = 1:1) as a yellow oil. Data for **28b**: **TLC**: R_f = 0.44 (petroleum ether/EtOAc = 5:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 –

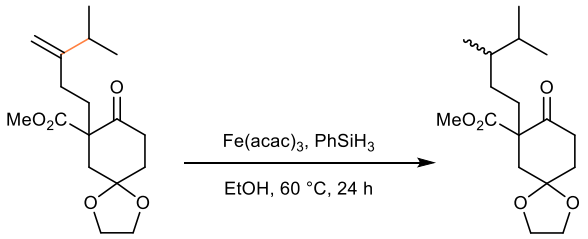
7.19 (m, 5H), 4.52 (d, J = 1.6 Hz, 2H), 3.77 – 3.66 (m, 2H), 3.15 (s, 1H), 1.95 – 1.85 (m, 1H), 1.77 – 1.62 (m, 2H), 1.56 – 1.41 (m, 1H), 1.21 – 1.08 (m, 6H), 0.99 – 0.91 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.90, 128.60, 127.96, 127.94, 75.68, 73.61, 67.71, 52.22, 37.95, 23.99, 23.68, 22.74, 14.59, 14.06; **IR** (neat): ν_{max} = 3511, 2961, 2930, 2872, 1458, 1372, 1097, 1028, 907, 737, 698 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{16}H_{26}O_2Na$ $[M + Na]^+$ m/z 273.1825, found m/z 273.1814.



30

The title compound was prepared according to General Procedure II using alkene **29** (30.0 mg, 0.097 mmol), $PhSiH_3$ (26.0 mg, 30.0 µL, 0.243 mmol) and **C1** (5.5 mg, 0.010 mmol) in EtOH (0.07 M). Purification by column chromatography (petroleum ether/EtOAc = 5/1, v/v) gave **30** (20.0 mg, 73%) as a yellow oil. **TLC**: R_f = 0.39 (petroleum ether/EtOAc = 1:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.04 – 3.90 (m, 4H), 3.76 (s, 3H), 3.15 – 3.03 (m, 1H), 2.90 (d, J = 17.0 Hz, 1H), 2.68 (d, J = 17.0 Hz, 1H), 2.60 – 2.38 (m, 4H), 2.20 – 2.06 (m, 2H), 2.02 – 1.98 (m, 1H), 1.04 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.93, 206.33, 173.00, 106.82, 64.99, 64.58, 52.91, 46.82, 41.73, 37.58, 36.36, 34.64, 7.70; **IR** (neat): ν_{max} = 2957, 2923, 2853, 1740, 1715, 1439, 1362, 1274, 1230, 1141, 1110, 1047, 944, 750 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{14}H_{21}O_6$ $[M + H]^+$ m/z 285.1333, found m/z 285.1332.

2.4 Preparation of 6 in the Initial Condition Screening



3 **6**

Under an argon atmosphere, to a solution of alkene **3** (80.0 mg, 0.258 mmol) and $Fe(acac)_3$ (9.1 mg, 0.026 mmol)) in dry EtOH (0.07 M) was added $PhSiH_3$ (69.8 mg, 79.6 µL, 0.645 mmol). The resulting mixture was heated to 60 °C with stirring for 24 h. The reaction was then cooled to room temperature and concentrated under reduced pressure. The residue was then purified by column chromatography (petroleum ether/EtOAc = 20/1, v/v) gave **6** (54.0 mg, 67%) as a yellow oil. **TLC**: R_f = 0.50 (petroleum ether/EtOAc = 4:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.10 – 3.90 (m, 4H), 3.76 – 3.69 (m, 3H), 3.07 – 2.93 (m, 1H), 2.59 (d, J = 15.6 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.03 – 1.95 (m, 2H), 1.89 – 1.68 (m, 2H), 1.68 – 1.50 (m, 4H), 1.01 (dd, J = 6.8, 2.4 Hz, 1H), 0.86 – 0.74 (m, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.20, 207.18,

173.19, 173.16, 106.96, 106.89, 65.04, 65.01, 64.40, 58.46, 58.41, 52.38, 52.32, 41.90, 41.84, 39.19, 39.12, 37.99, 35.41, 35.39, 33.55, 33.52, 31.76, 31.71, 29.85, 28.91, 20.48, 17.92, 17.89, 15.29, 15.26; **IR** (neat): ν_{max} = 2957, 2927, 1733, 1716, 1660, 1442, 1363, 1291, 1261, 1231, 1197, 1165, 1109, 1058, 1035, 946, 889, 845, 772, 739, 701, 496, 401 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{28}O_5Na$ $[M + Na]^+$ *m*/*z* 335.1829; found *m*/*z* 335.1829.

3. References

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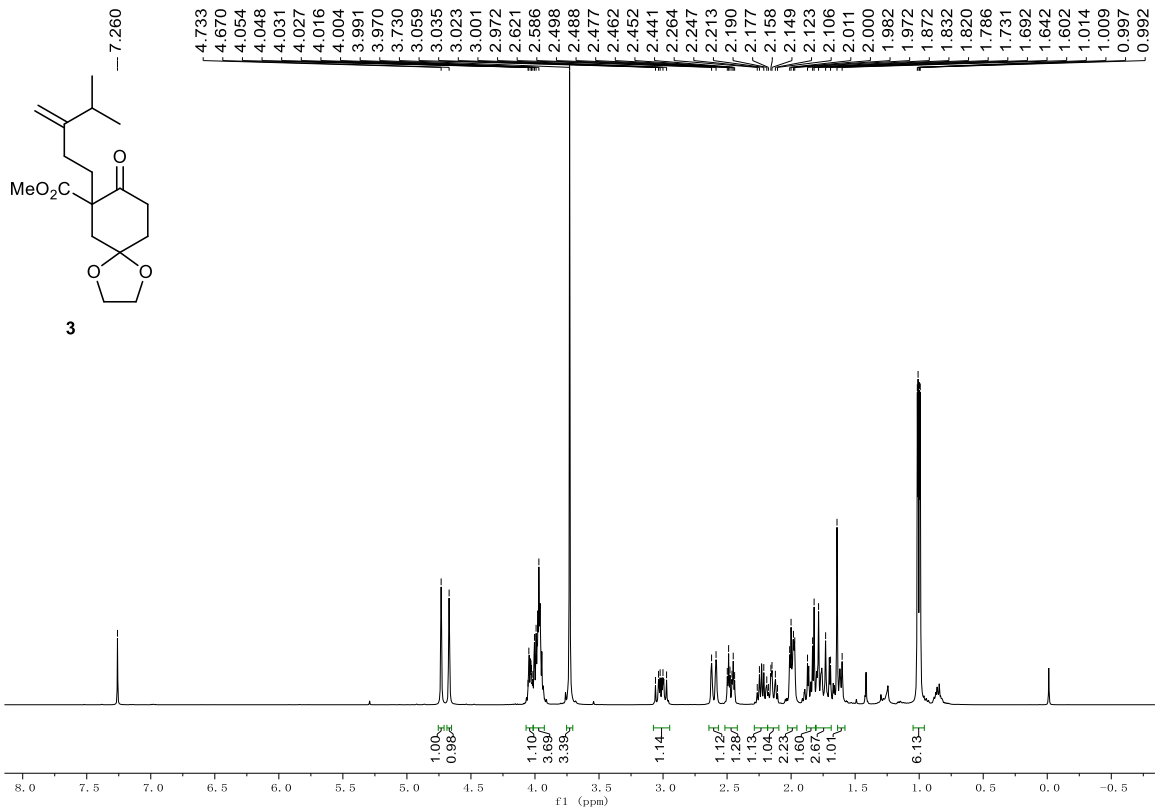
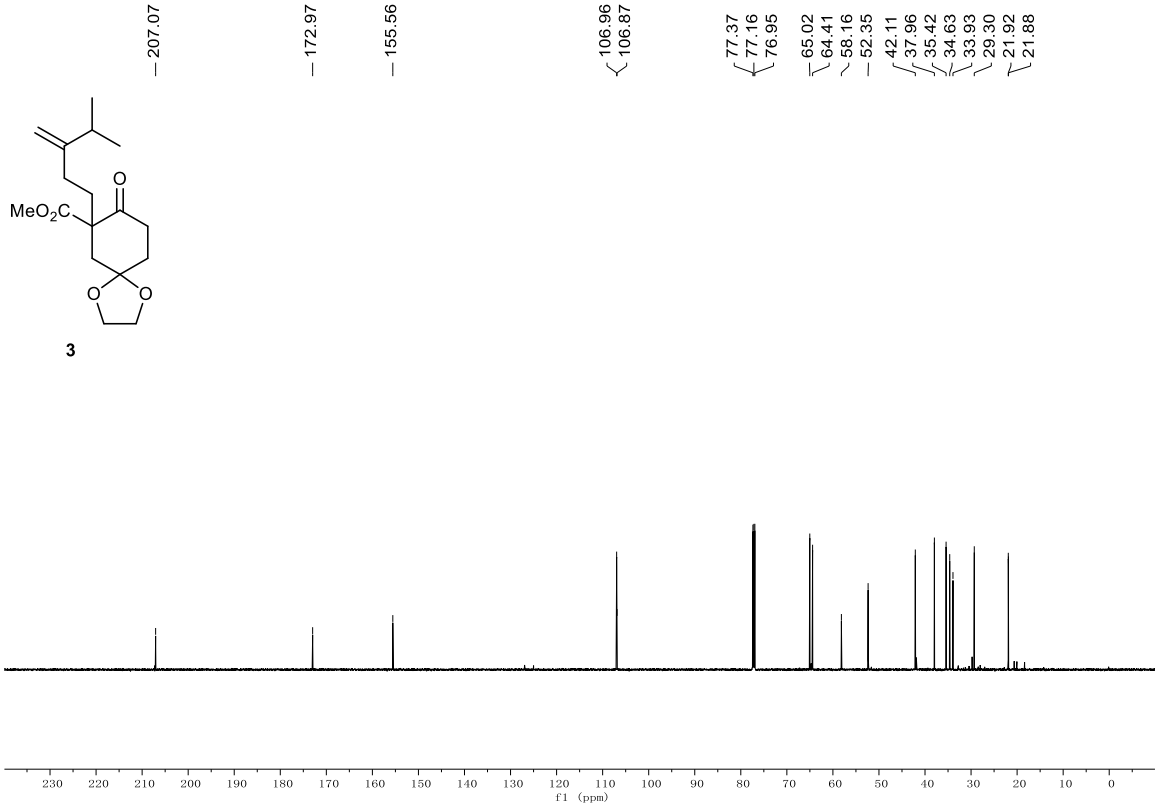
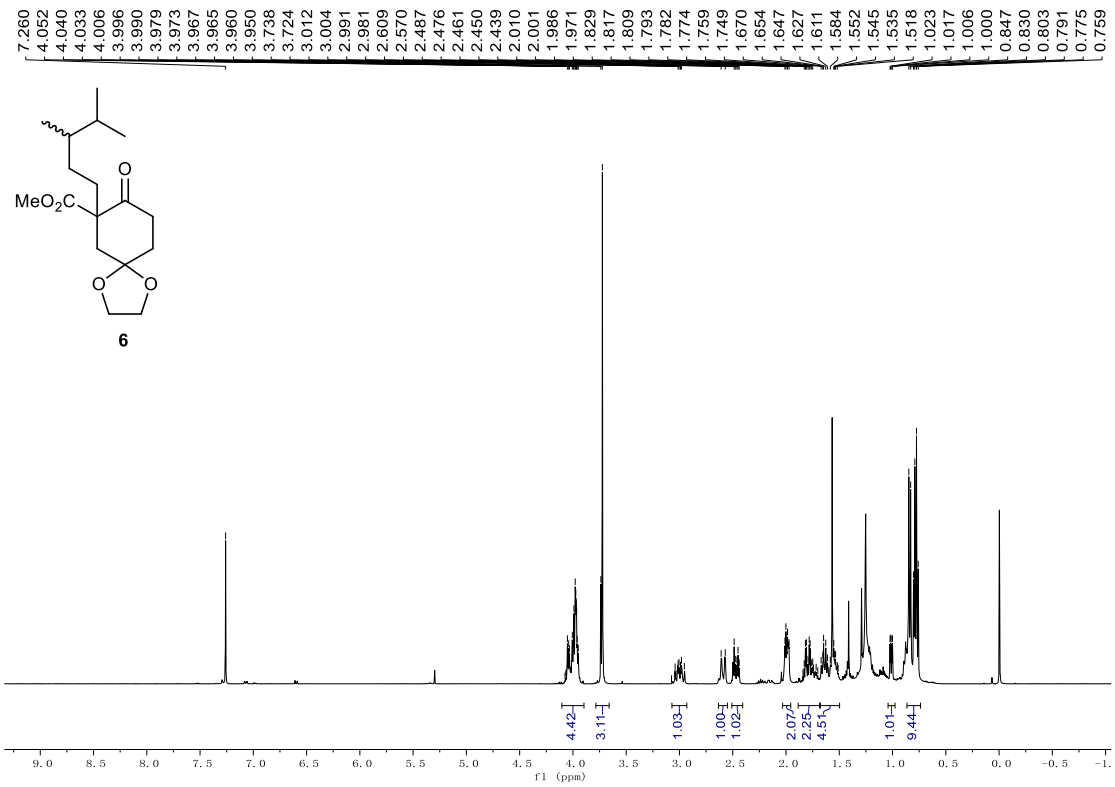
4. NMR Spectra



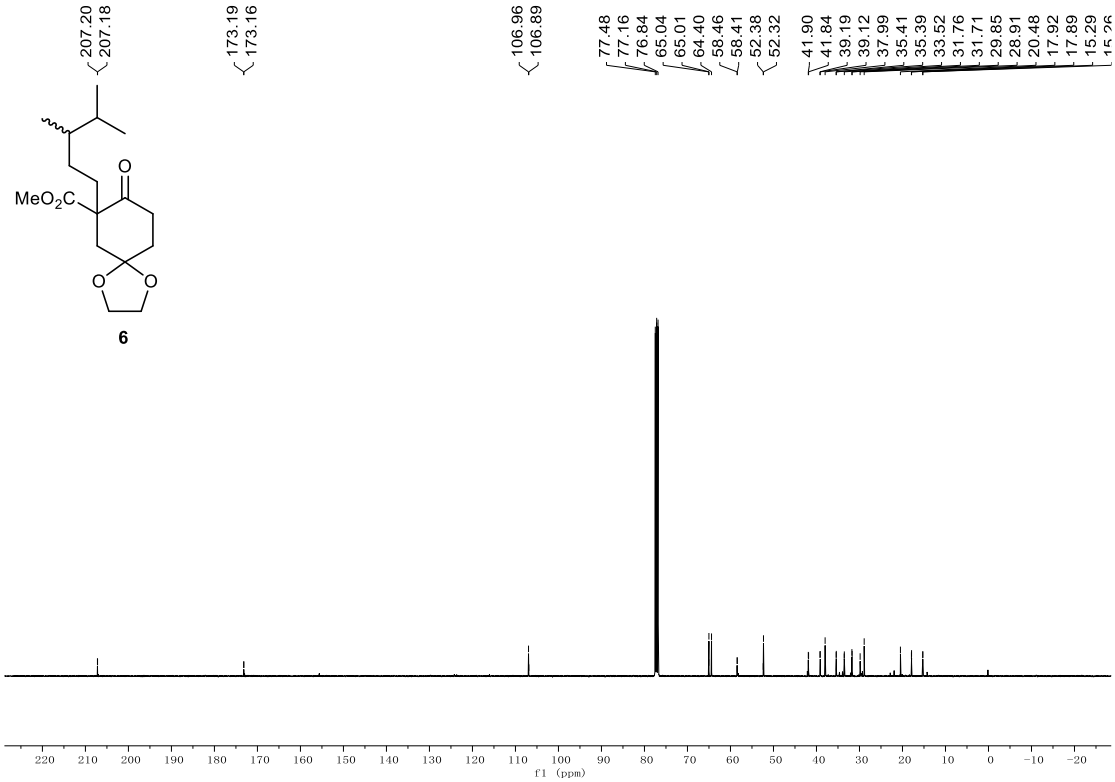
^{1}H NMR spectrum of compound **3**



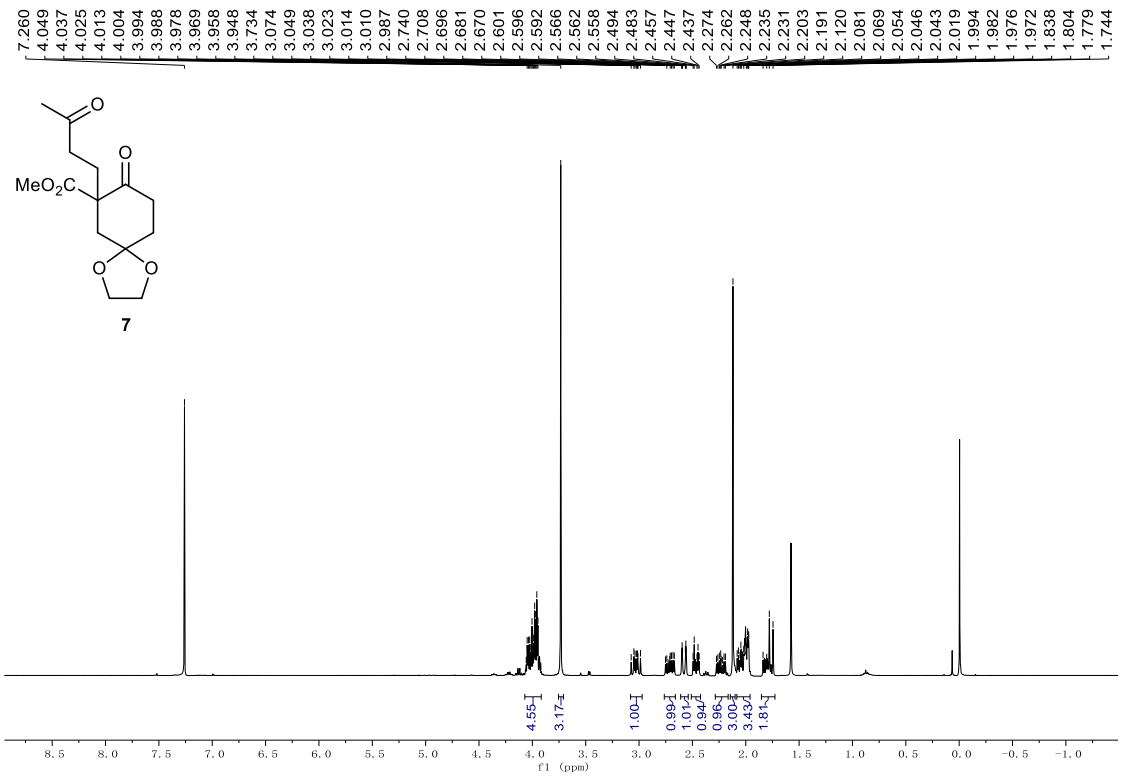
^{13}C NMR spectrum of compound **3**



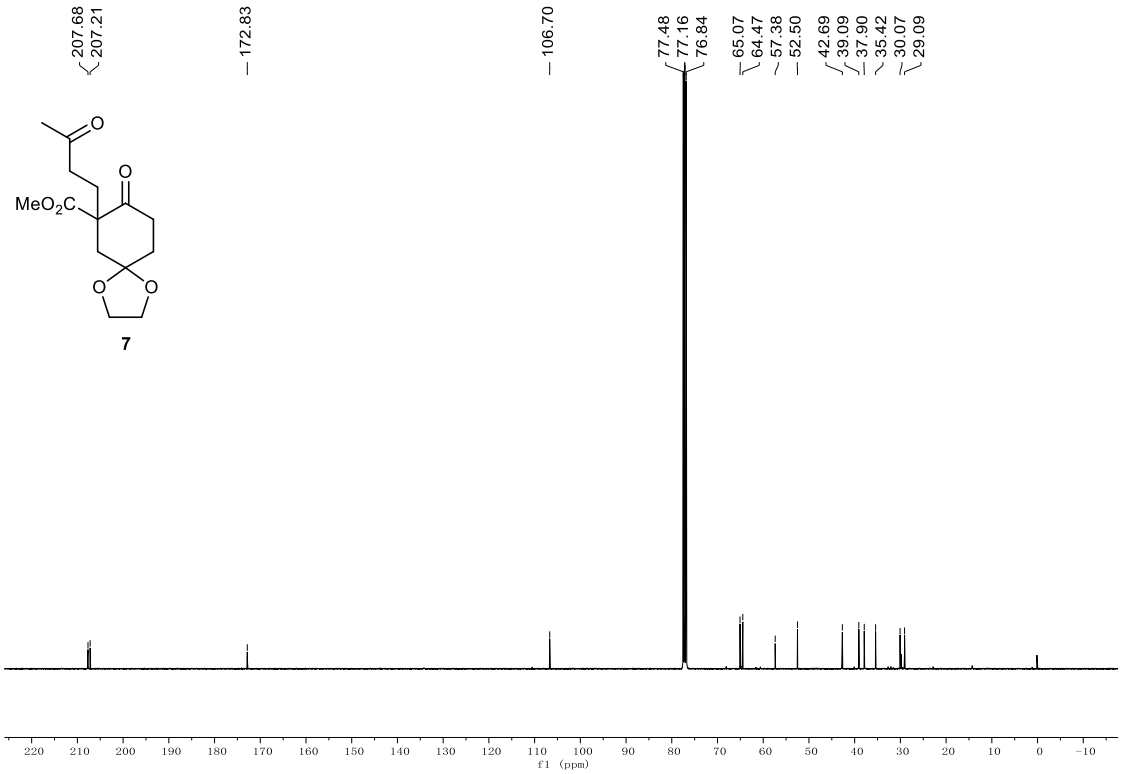
^{1}H NMR spectrum of compound **6**



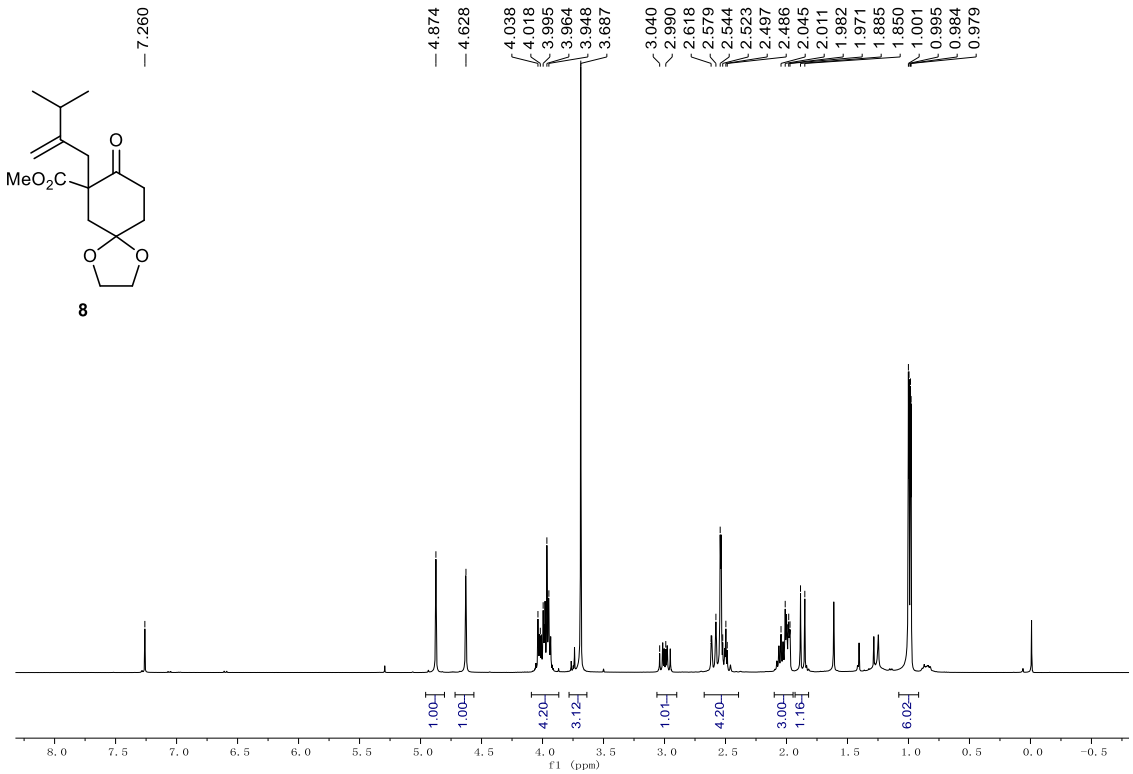
^{13}C NMR spectrum of compound **6**



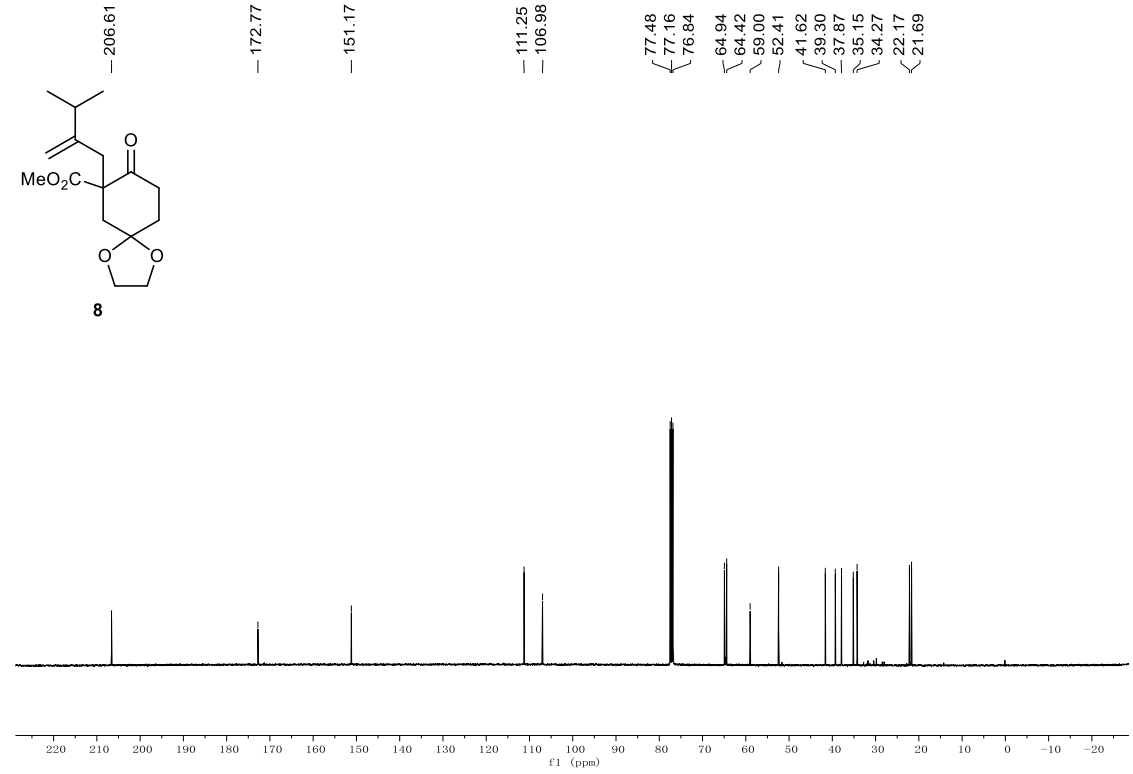
^{1}H NMR spectrum of compound **7**



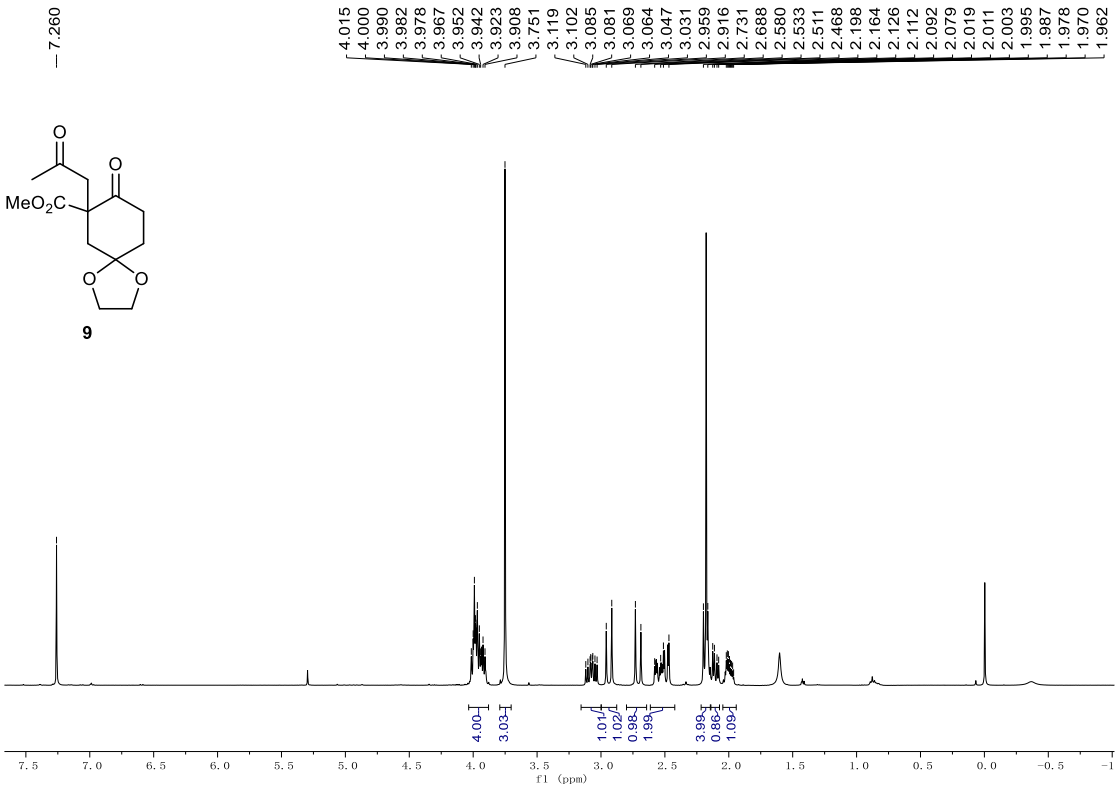
^{13}C NMR spectrum of compound **7**



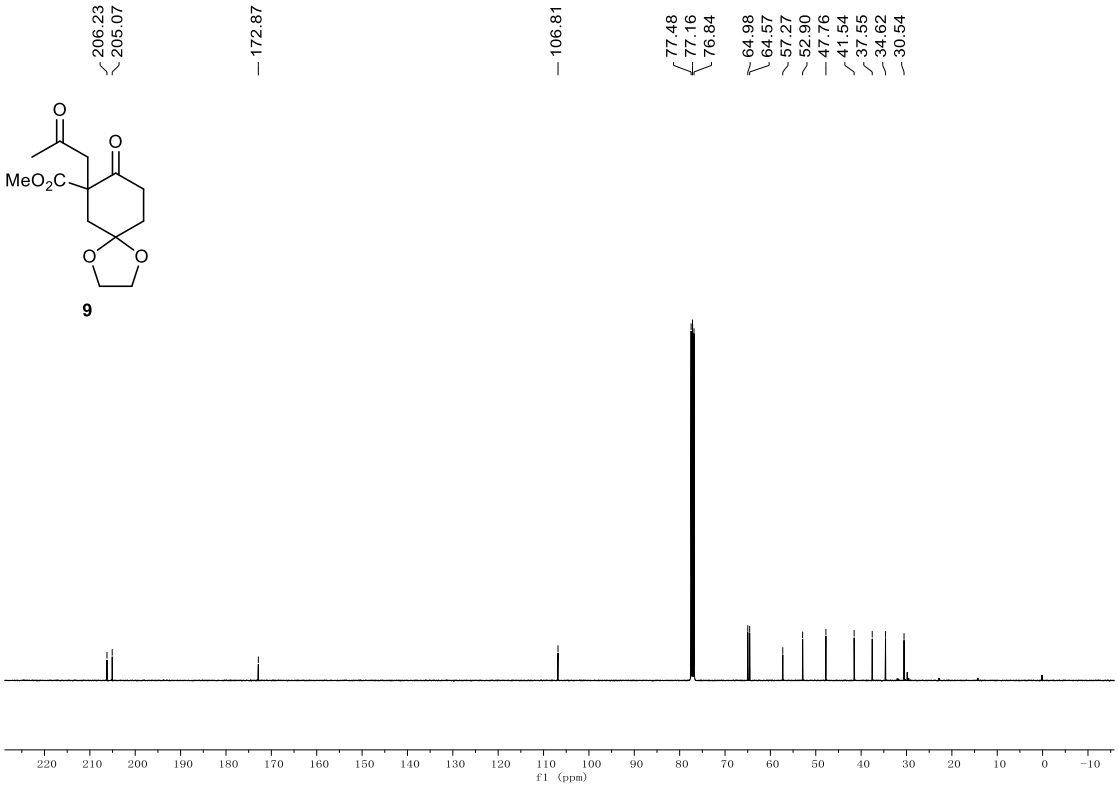
^{1}H NMR spectrum of compound **8**



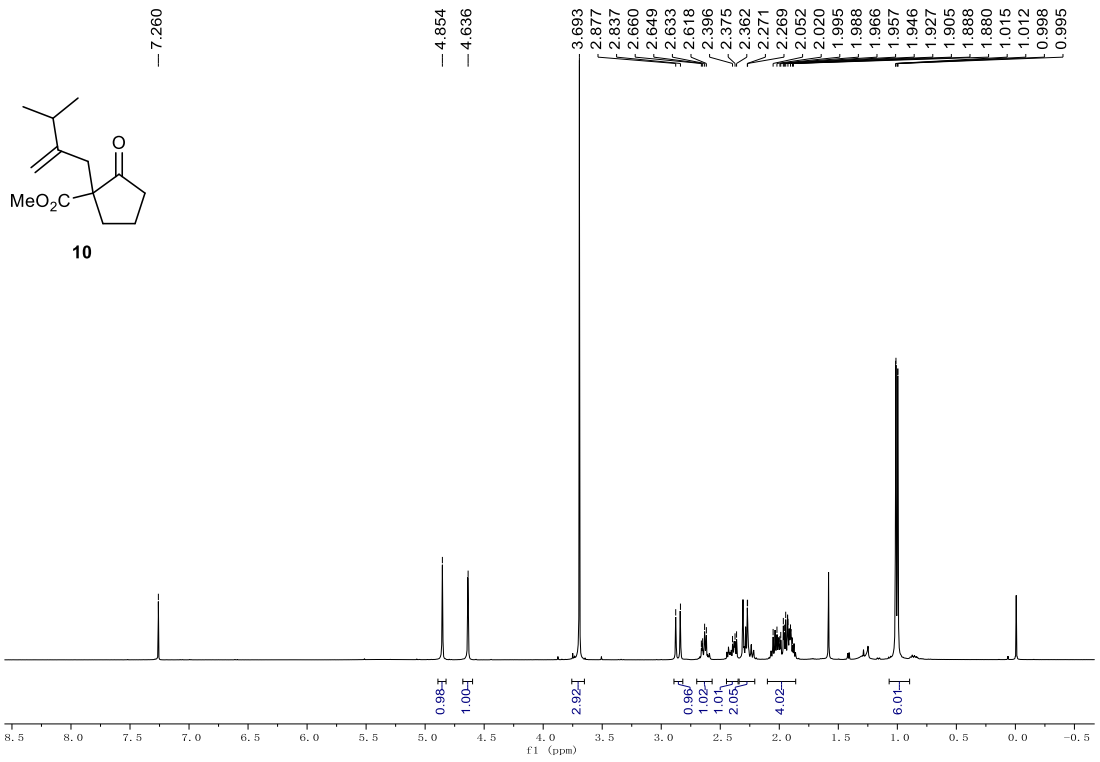
^{13}C NMR spectrum of compound **8**



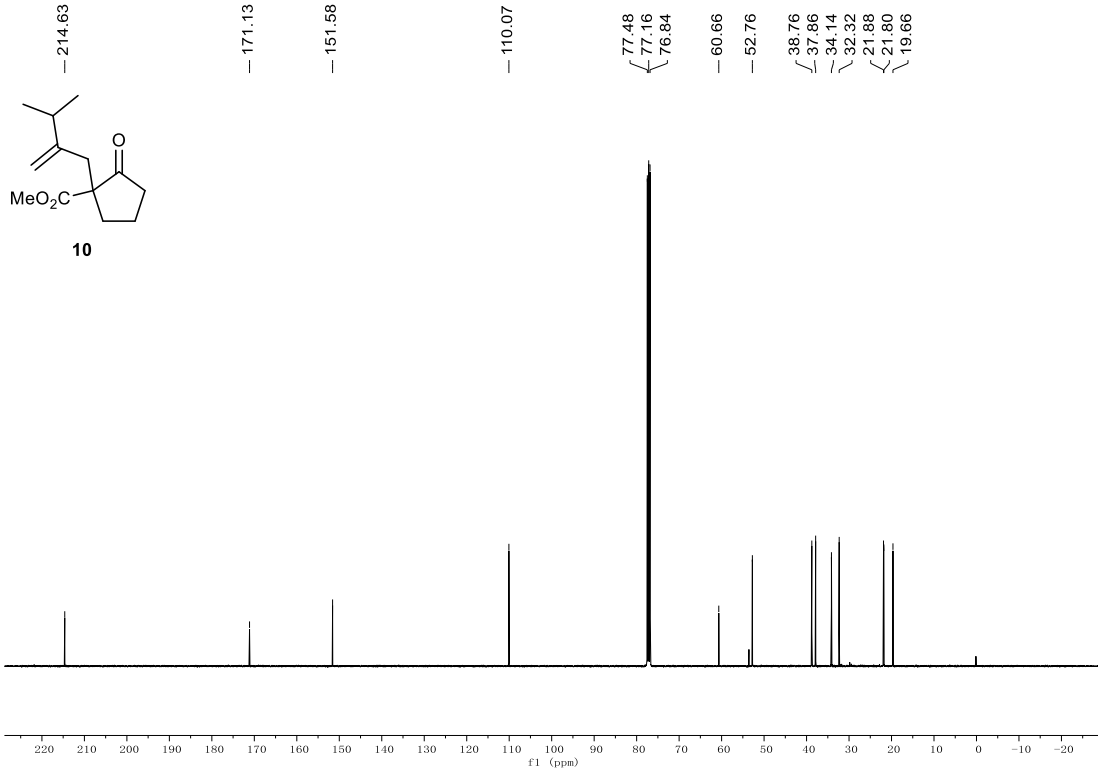
^{1}H NMR spectrum of compound **9**



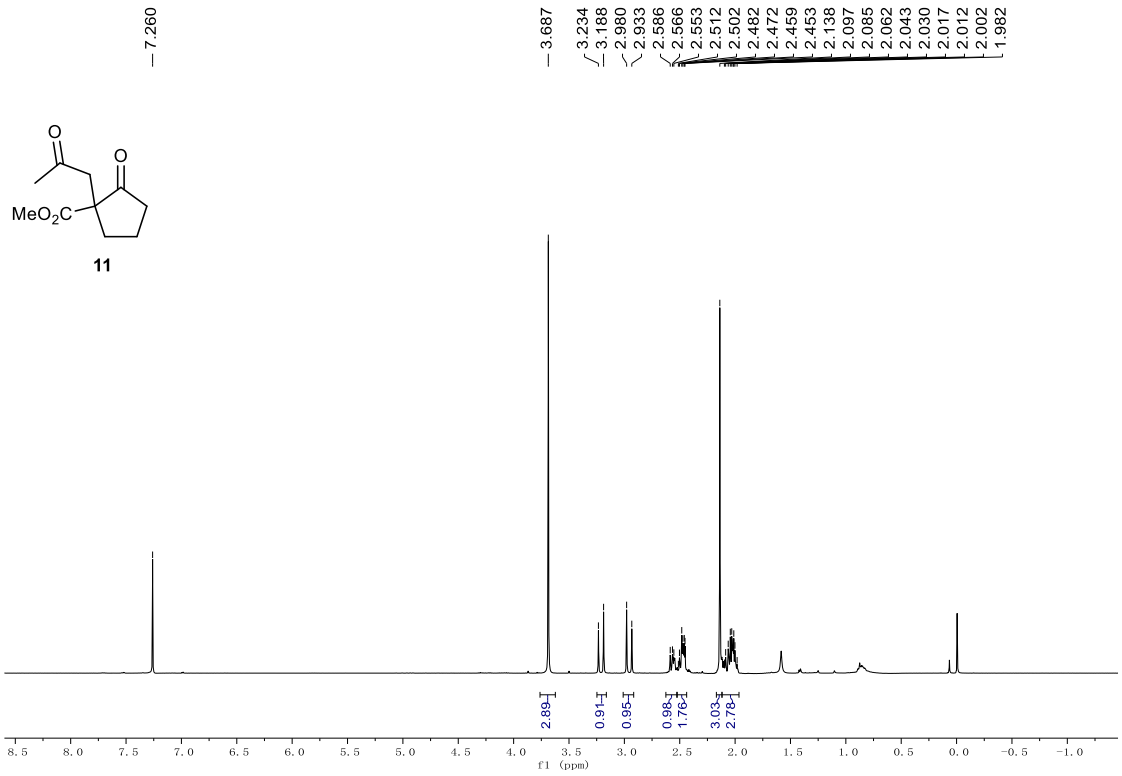
^{13}C NMR spectrum of compound **9**



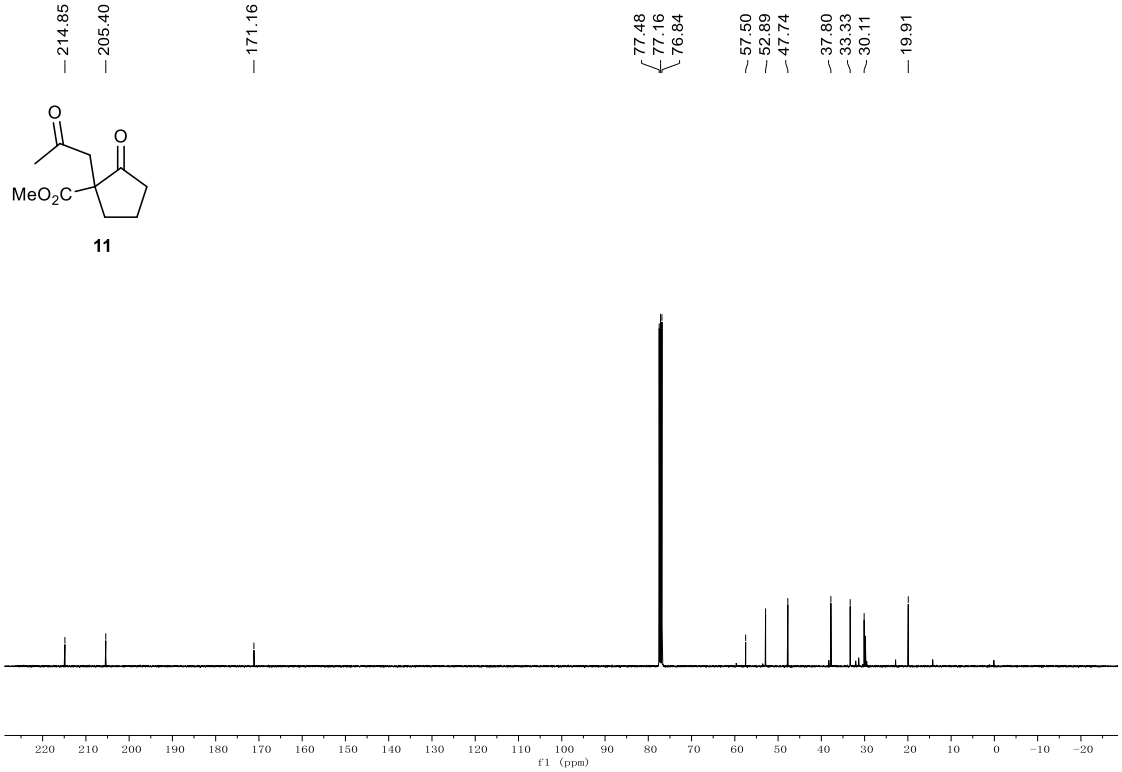
^{1}H NMR spectrum of compound **10**



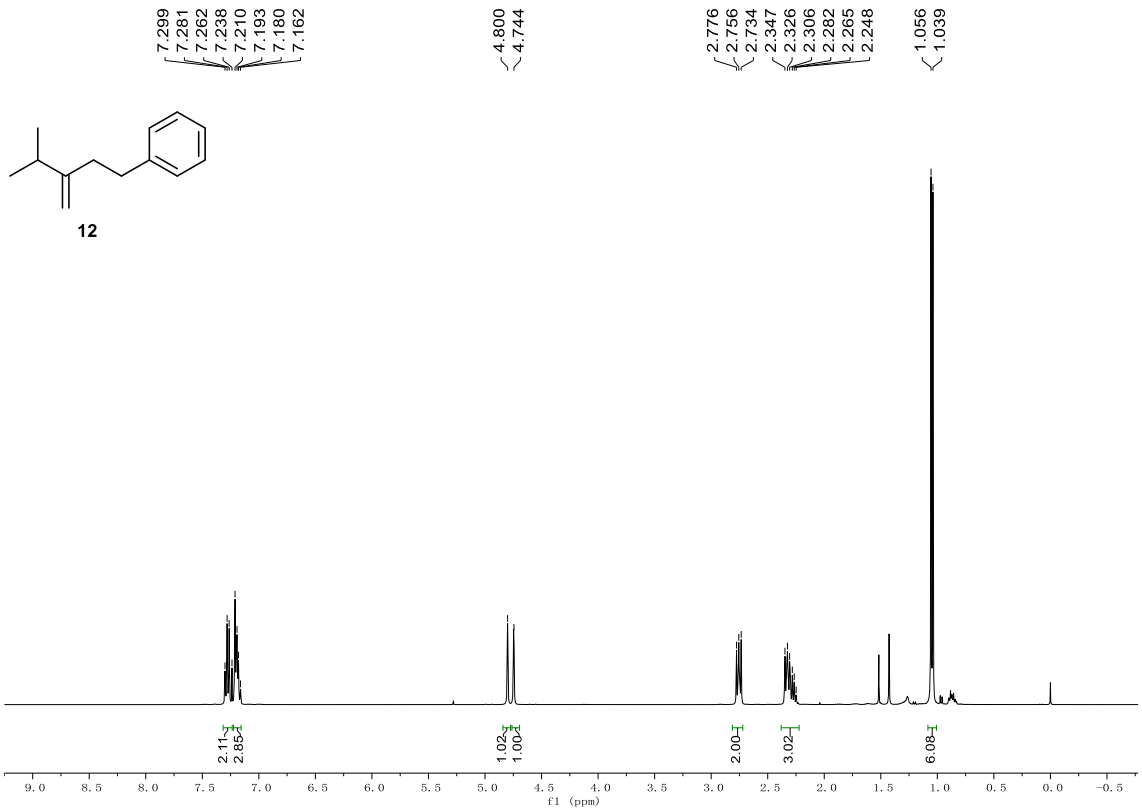
^{13}C NMR spectrum of compound **10**



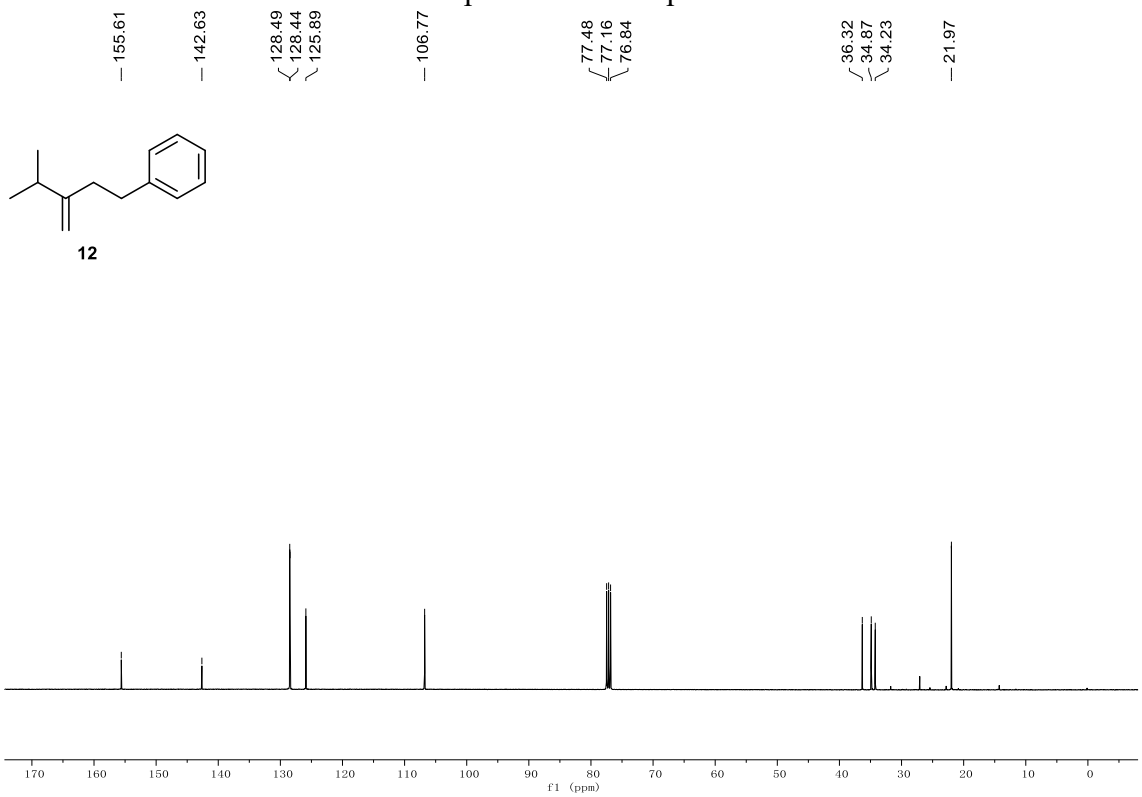
^{1}H NMR spectrum of compound **11**



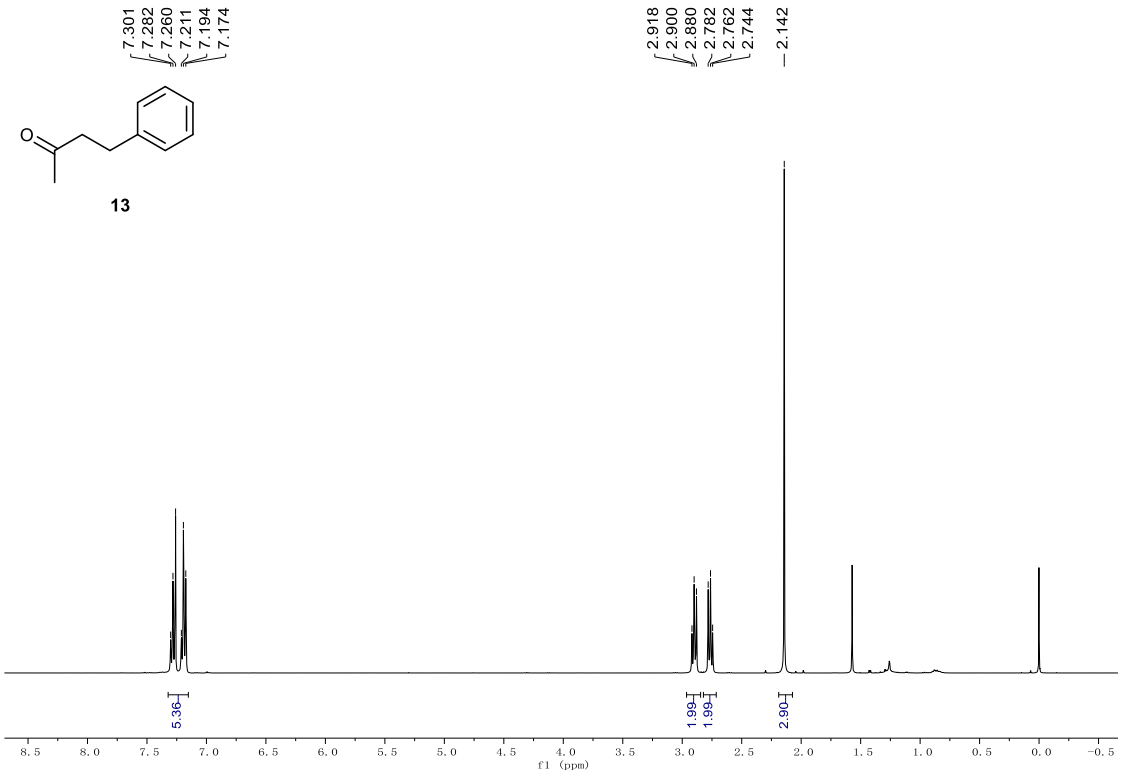
^{13}C NMR spectrum of compound **11**



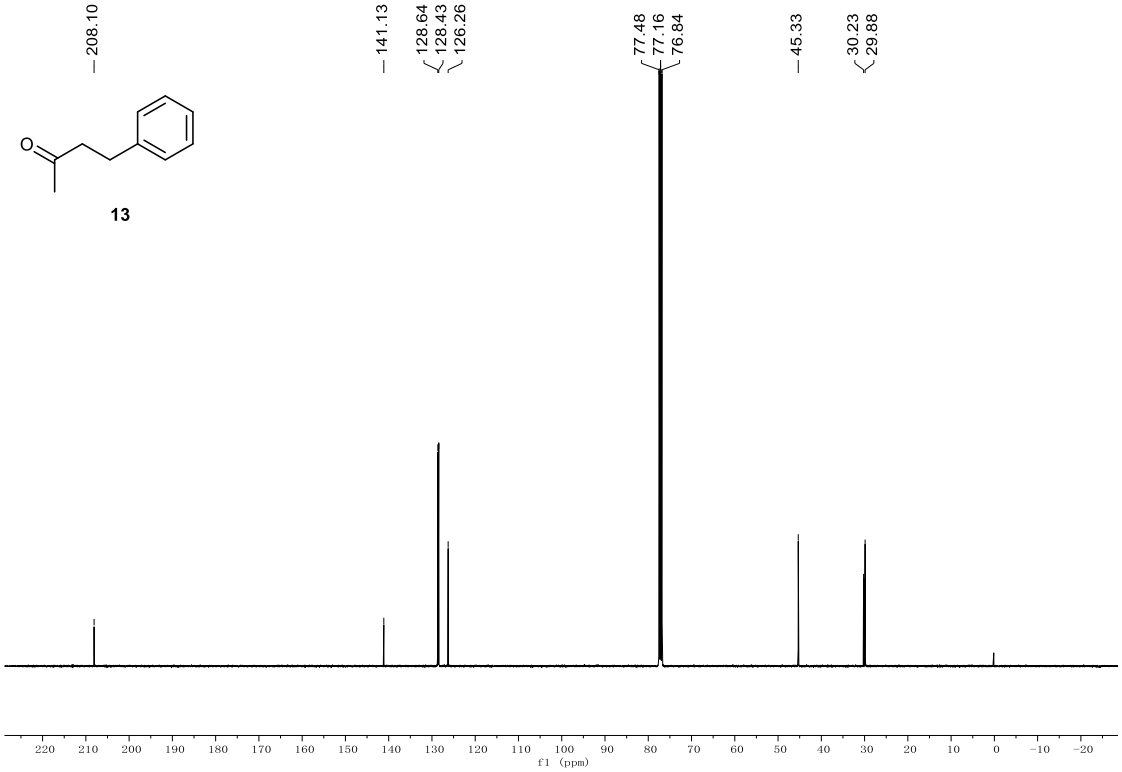
^{1}H NMR spectrum of compound **12**



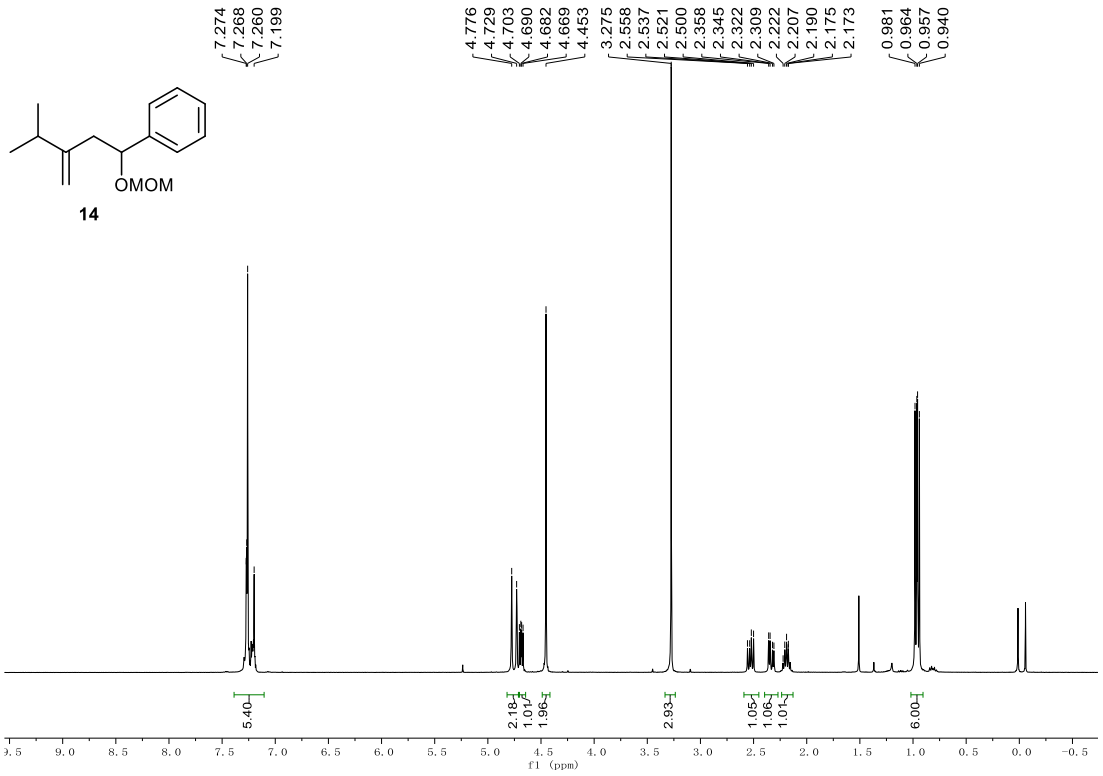
^{13}C NMR spectrum of compound **12**



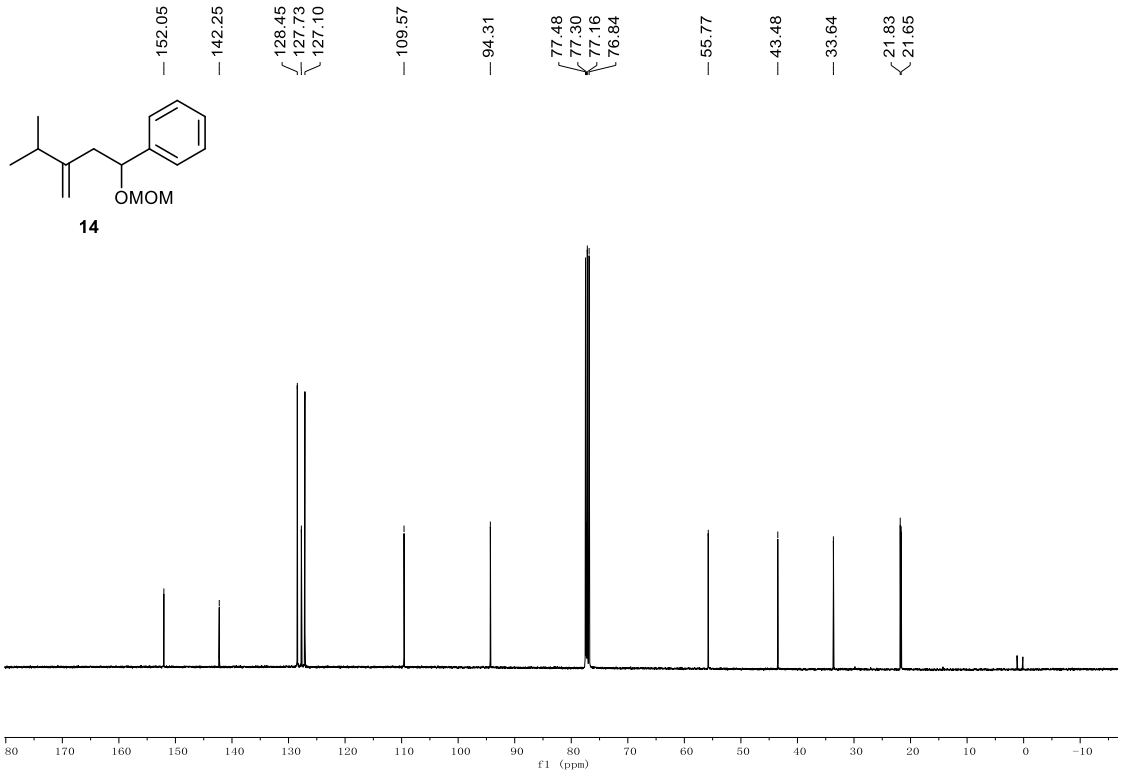
^{1}H NMR spectrum of compound **13**



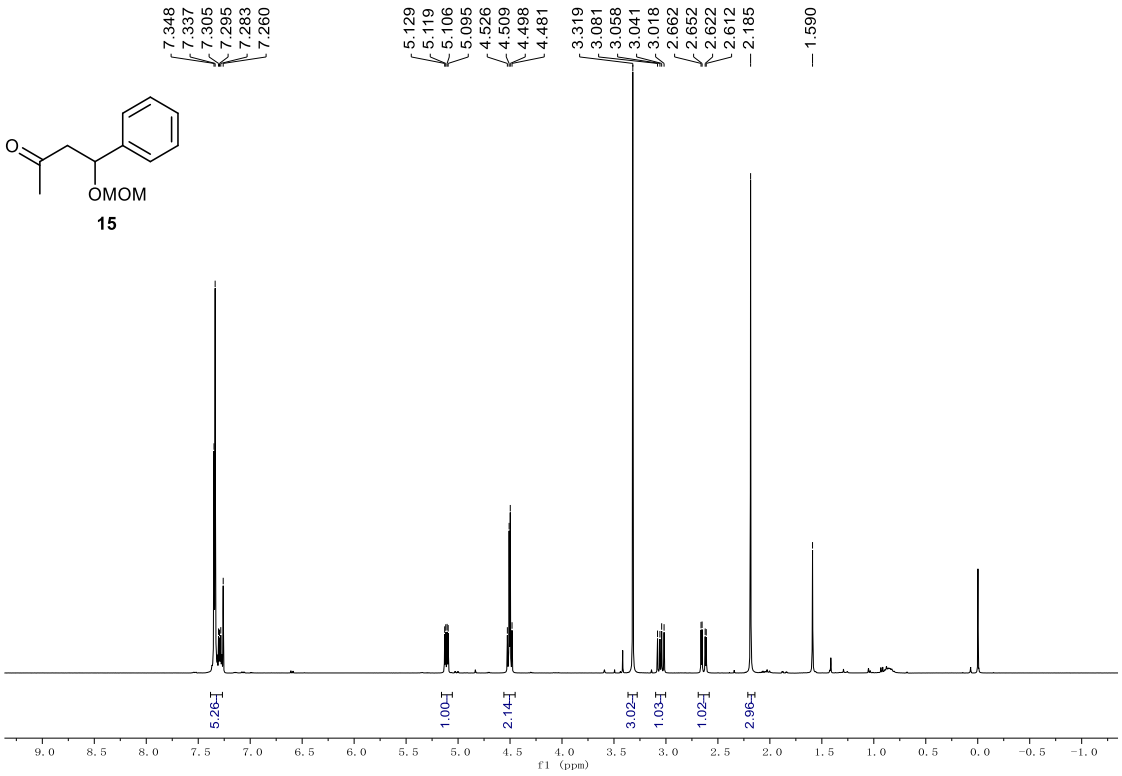
^{13}C NMR spectrum of compound **13**



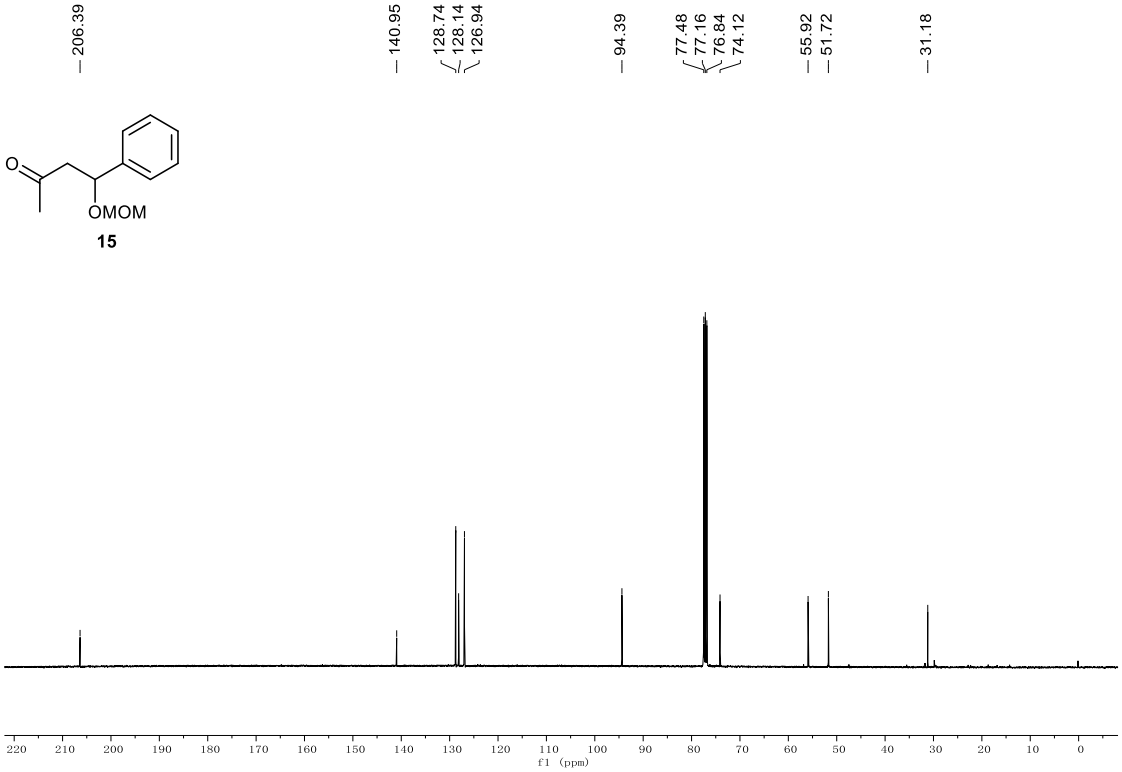
^{1}H NMR spectrum of compound **14**



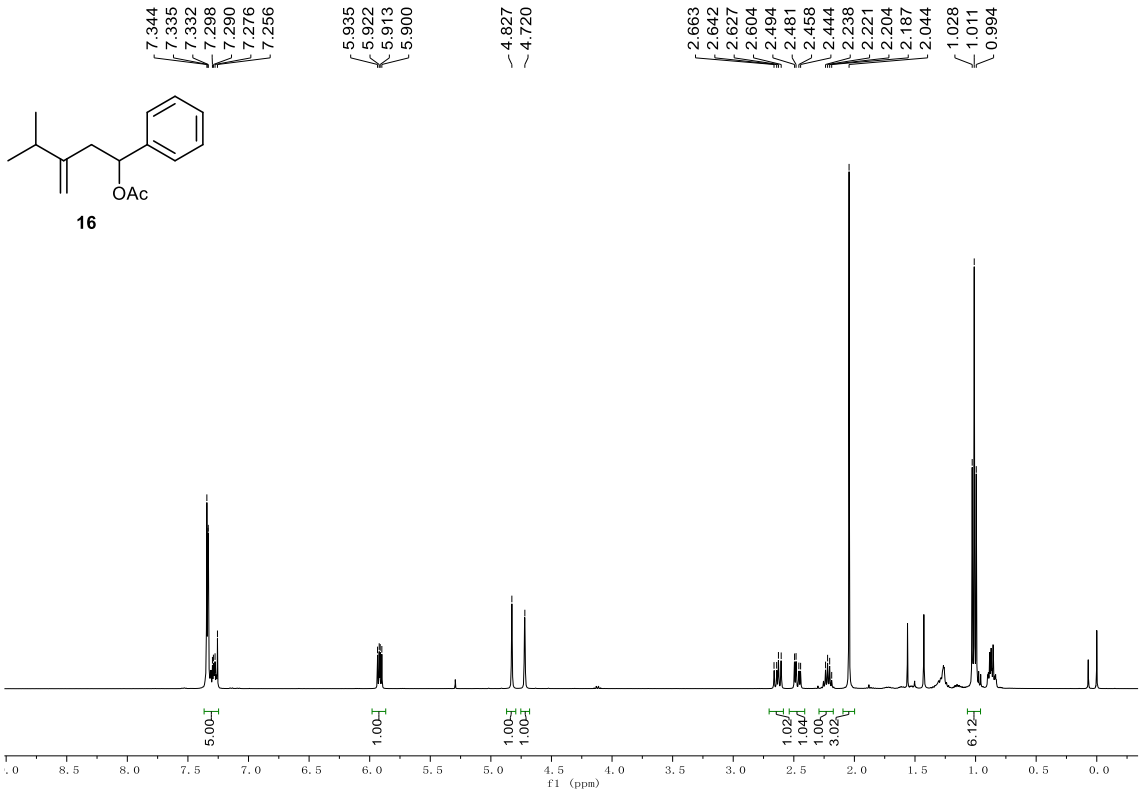
^{13}C NMR spectrum of compound **14**



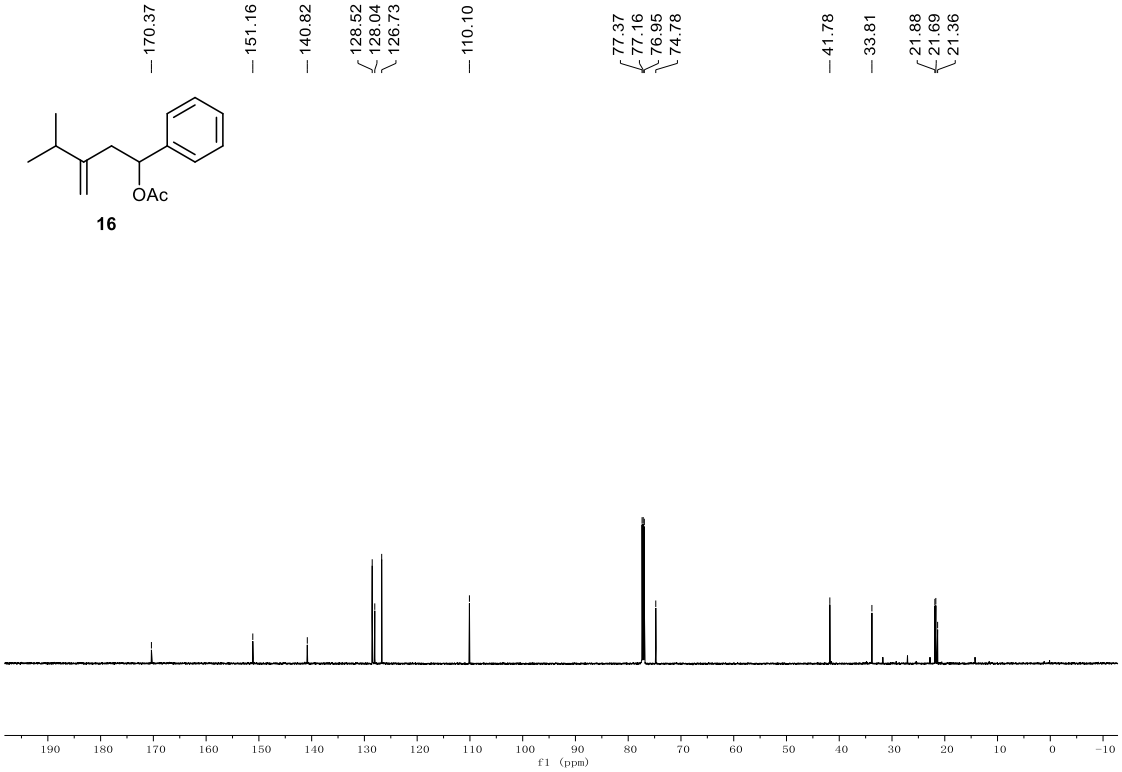
^{1}H NMR spectrum of compound **15**



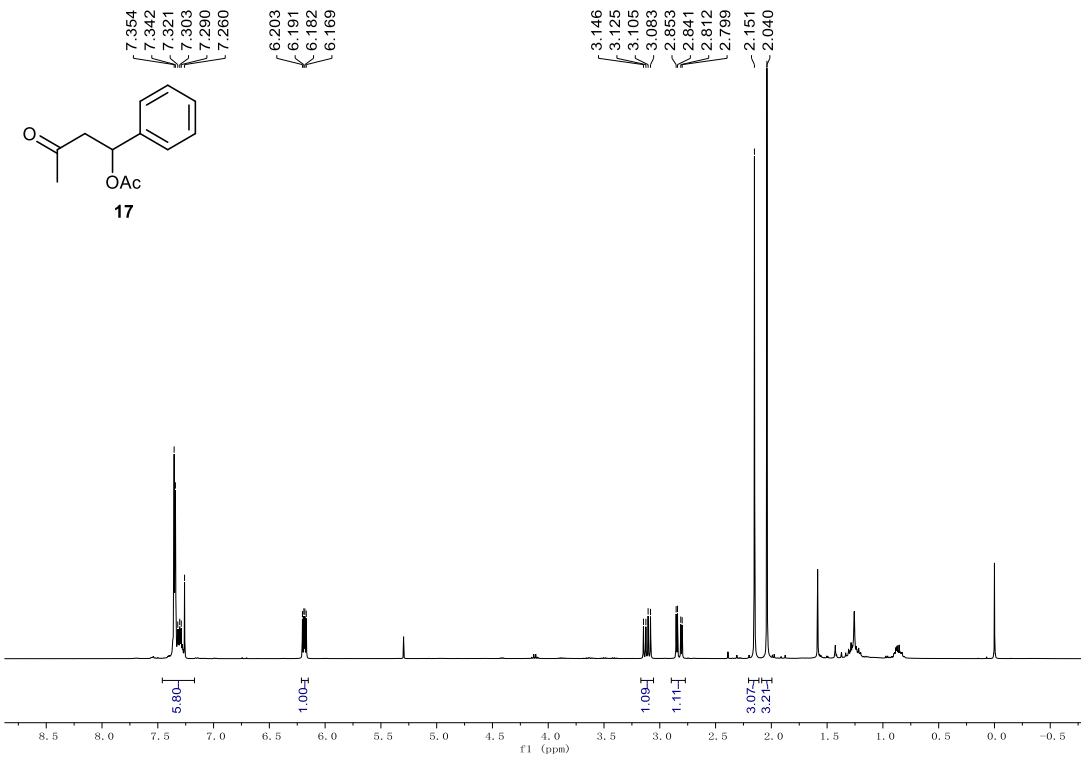
^{13}C NMR spectrum of compound **15**



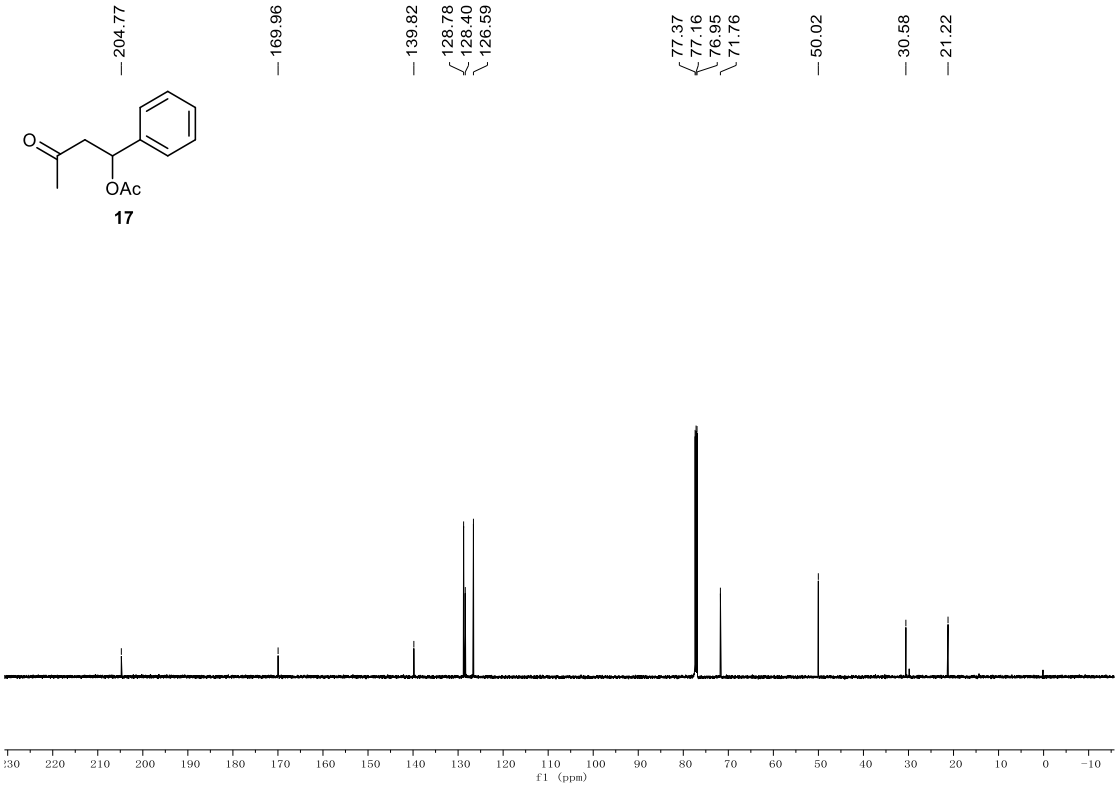
^{1}H NMR spectrum of compound **16**



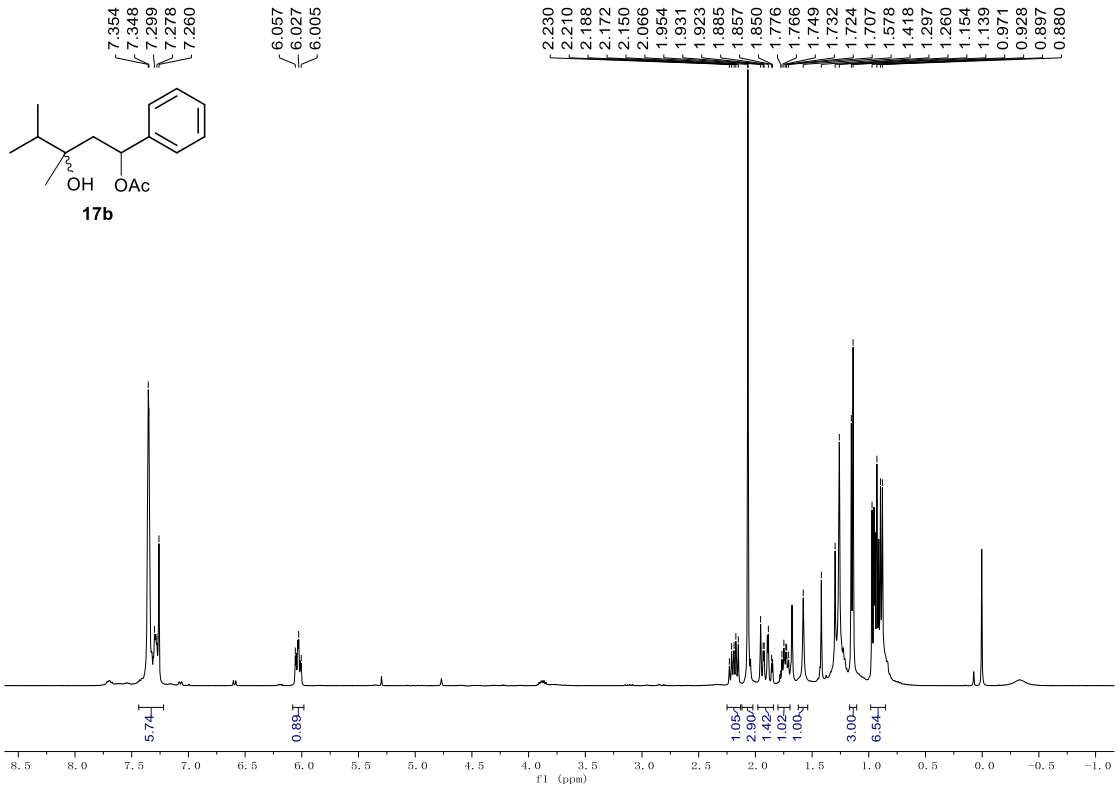
^{13}C NMR spectrum of compound **16**



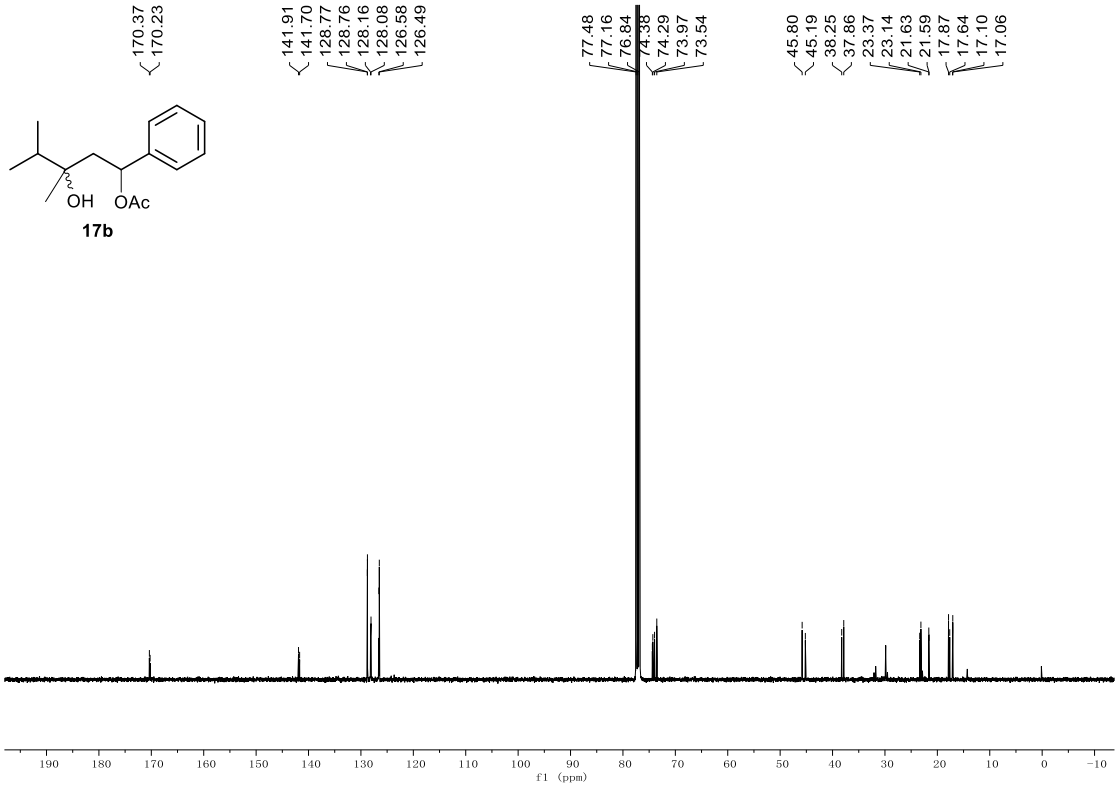
^{1}H NMR spectrum of compound **17**



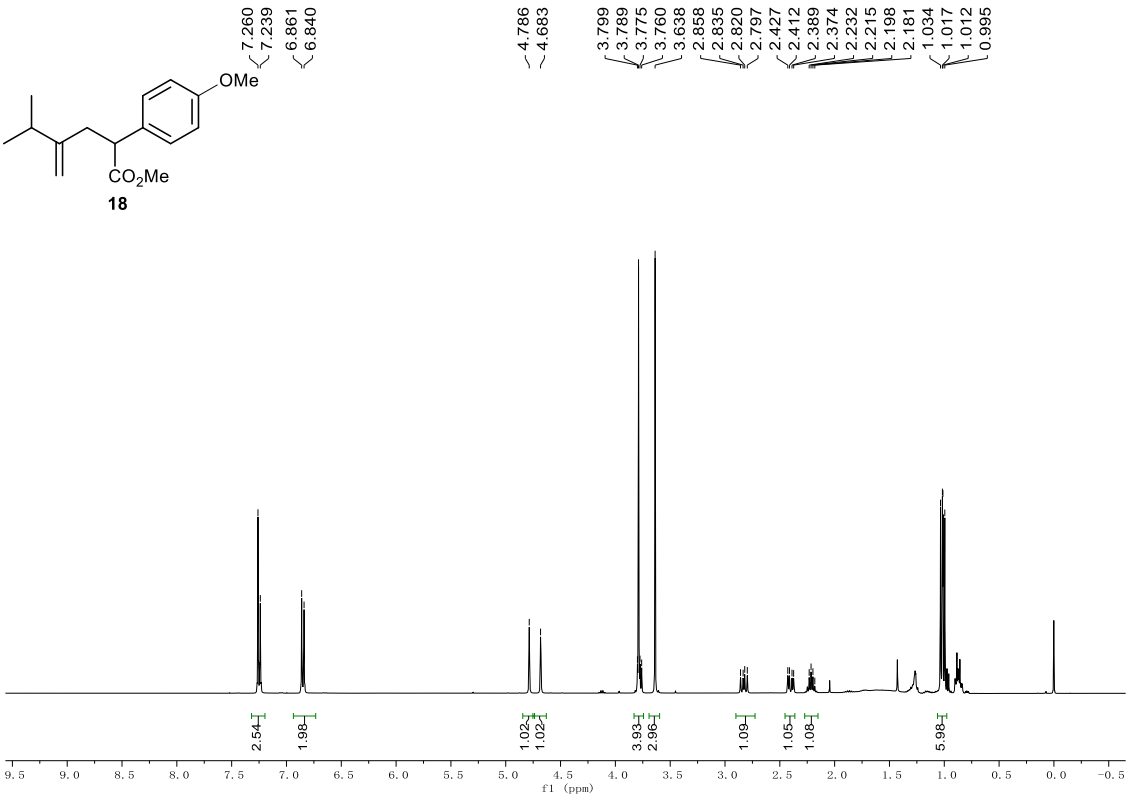
^{13}C NMR spectrum of compound **17**



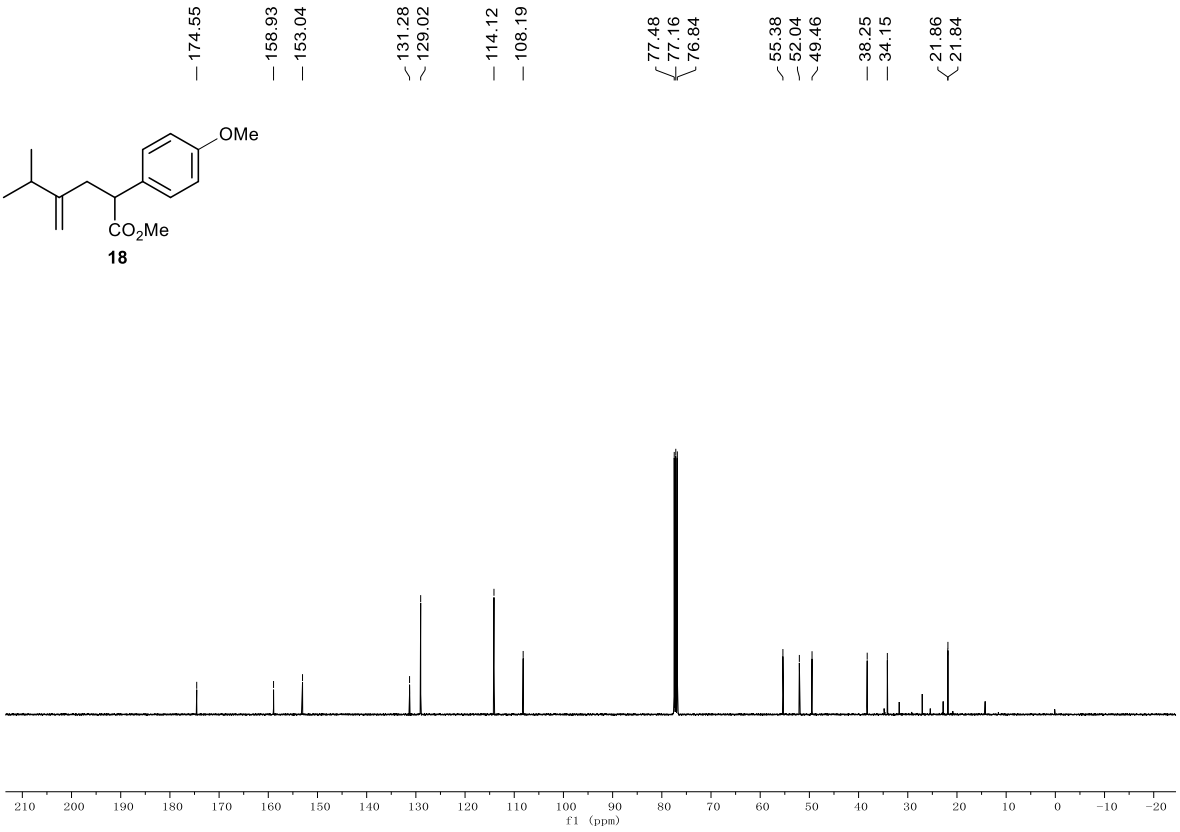
^{1}H NMR spectrum of compound **17b**



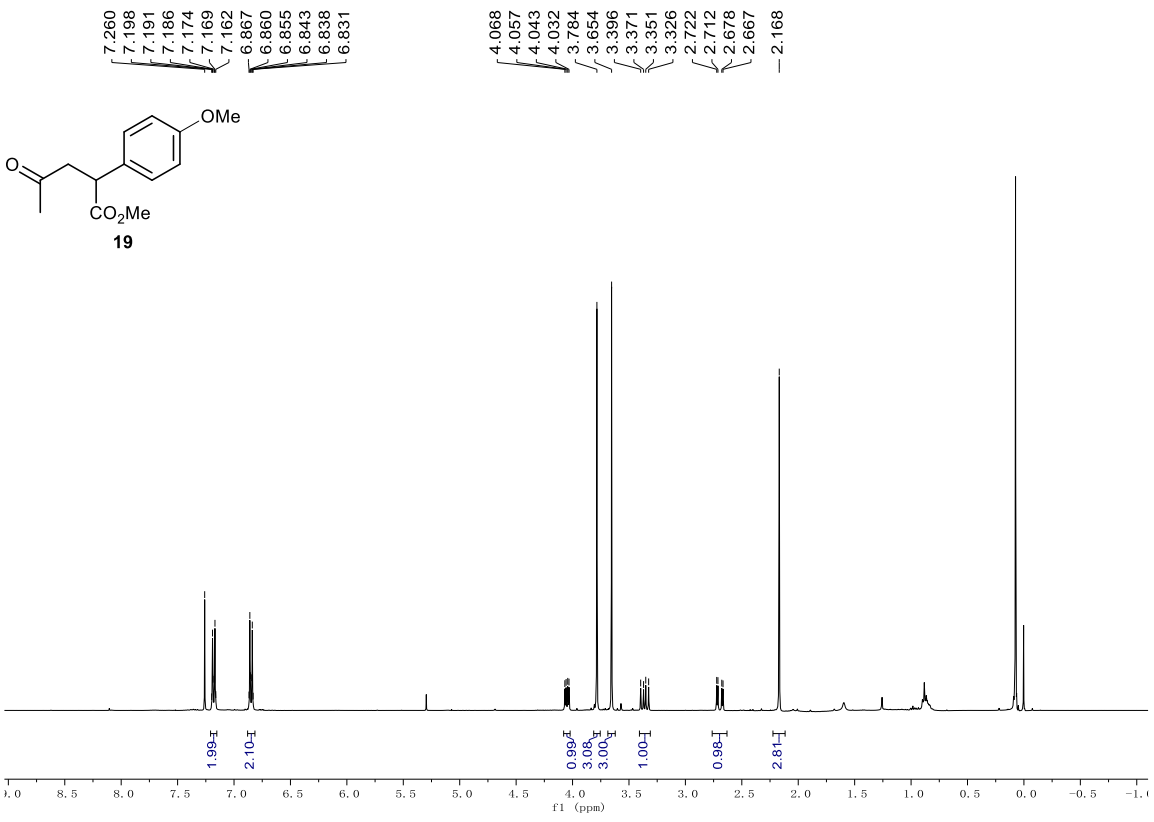
^{13}C NMR spectrum of compound **17b**



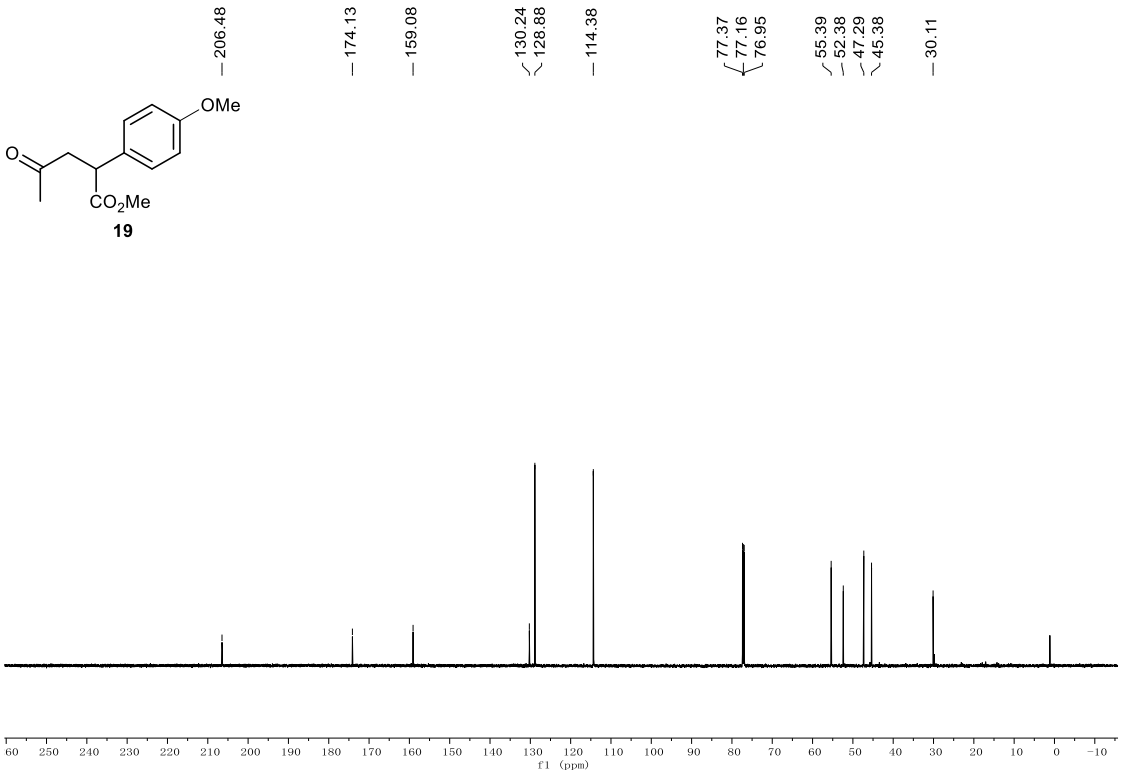
^{1}H NMR spectrum of compound **18**



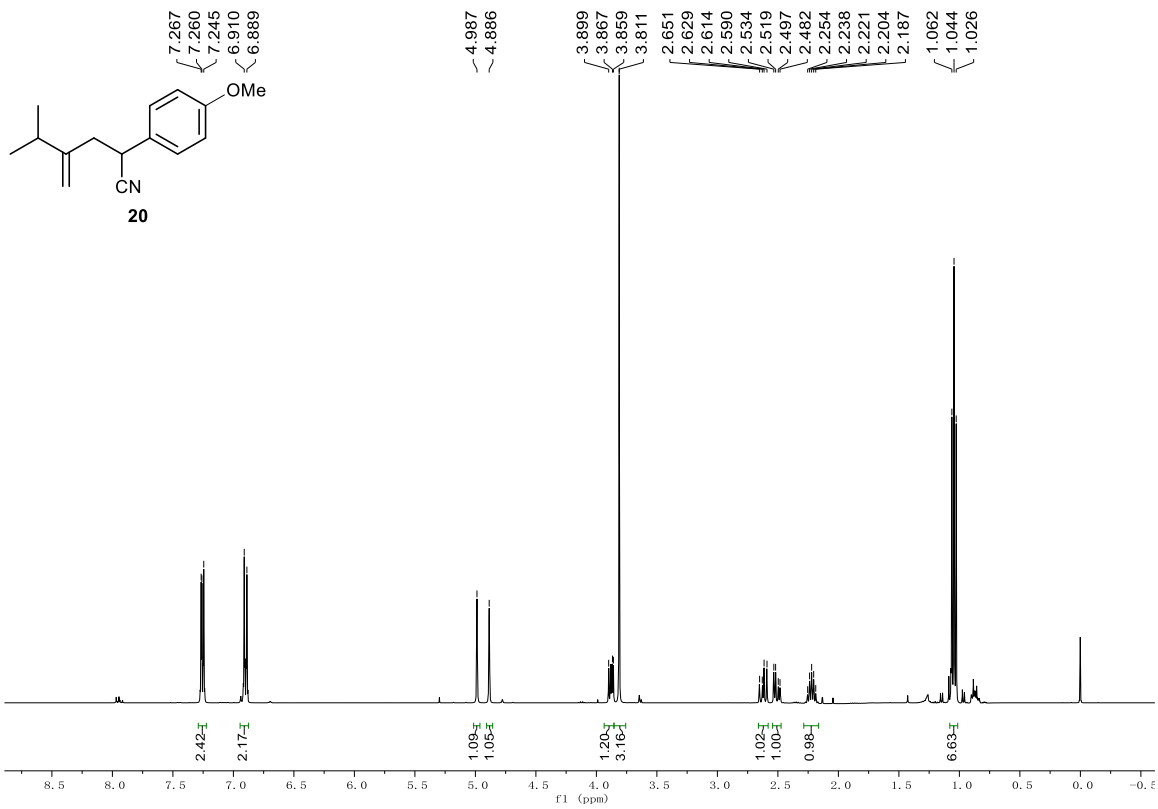
^{13}C NMR spectrum of compound **18**



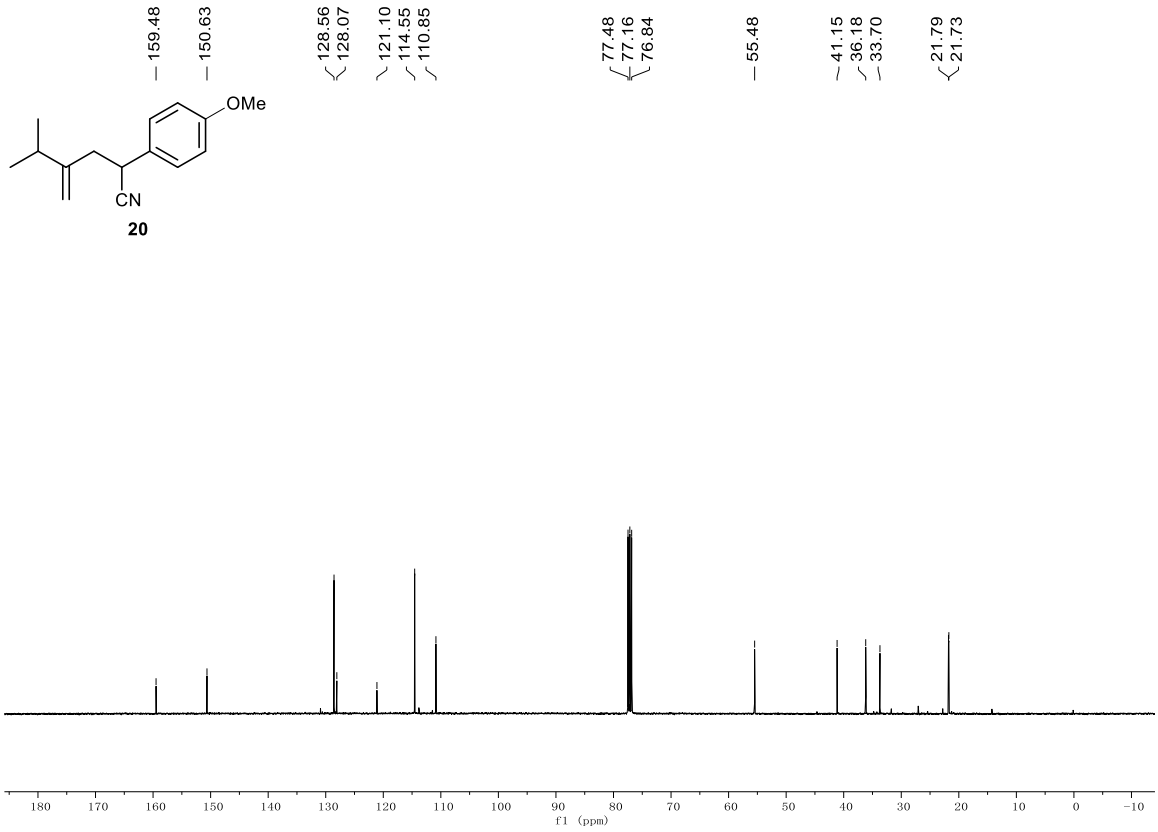
^{1}H NMR spectrum of compound **19**



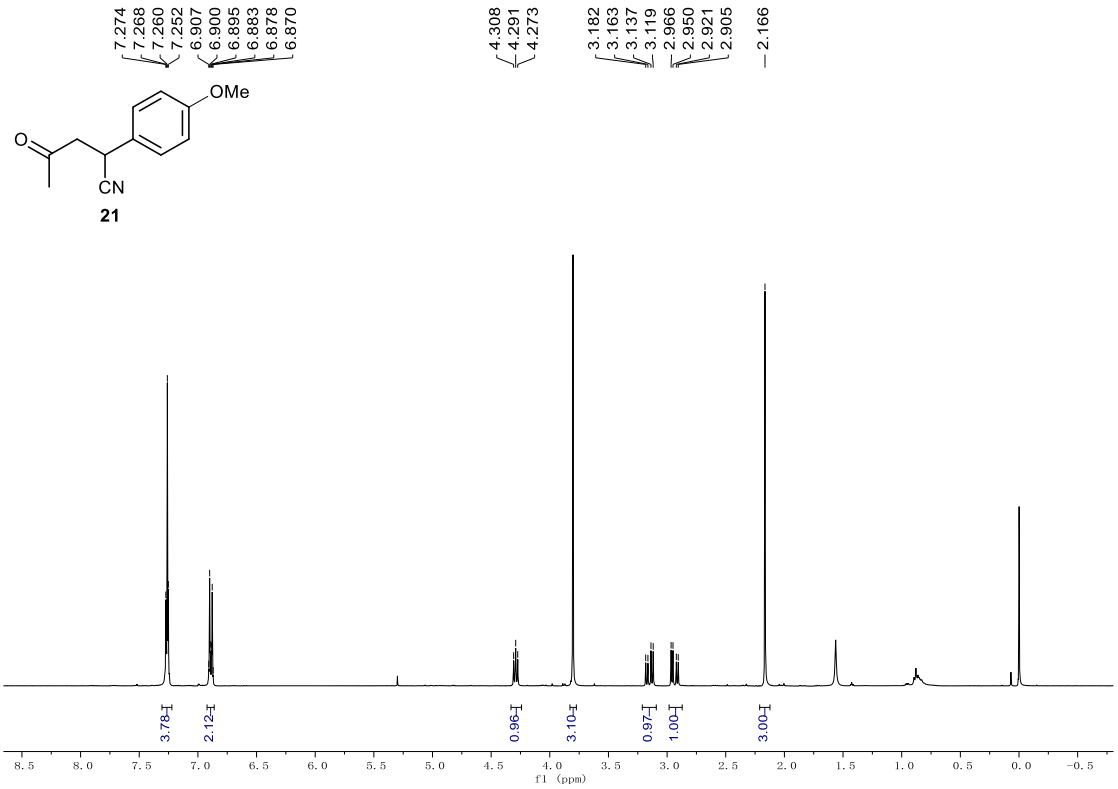
^{13}C NMR spectrum of compound **19**



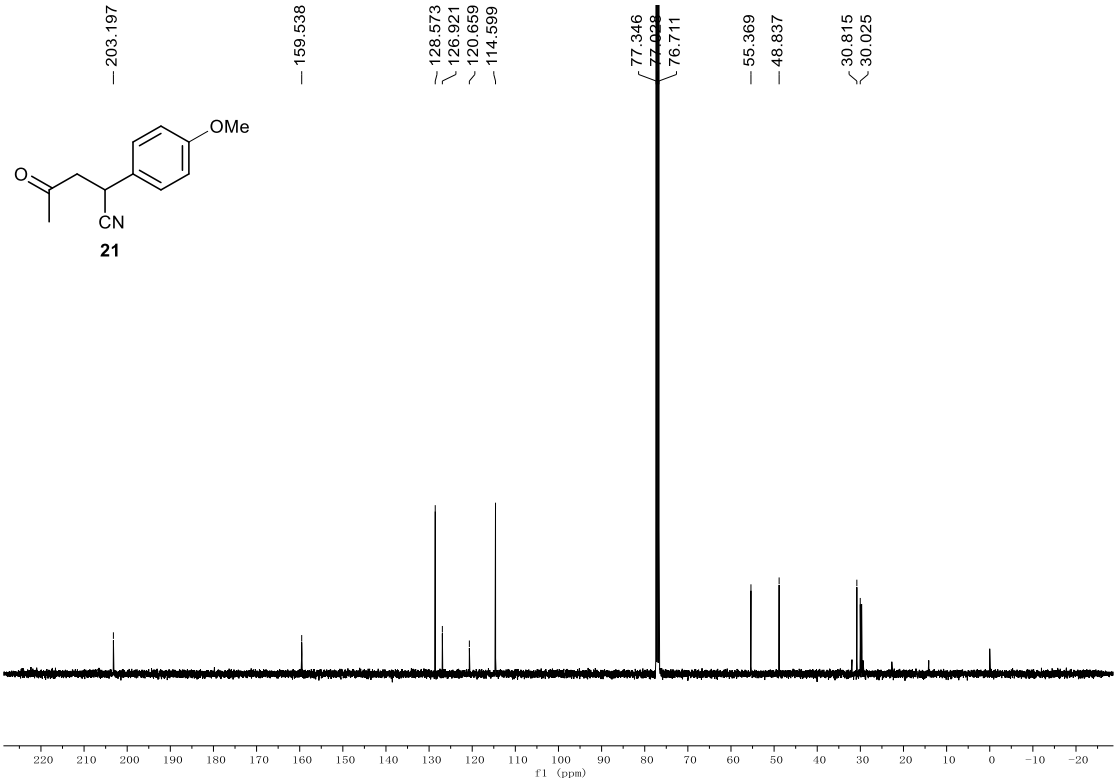
^{1}H NMR spectrum of compound **20**



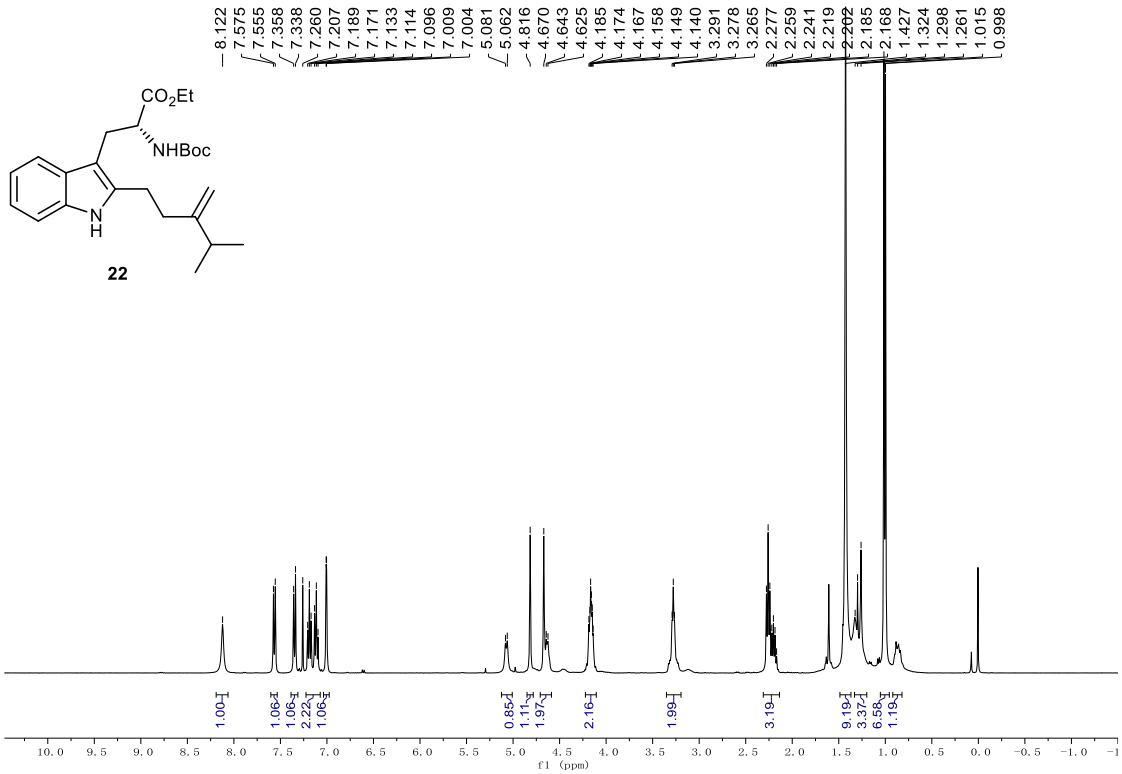
^{13}C NMR spectrum of compound **20**



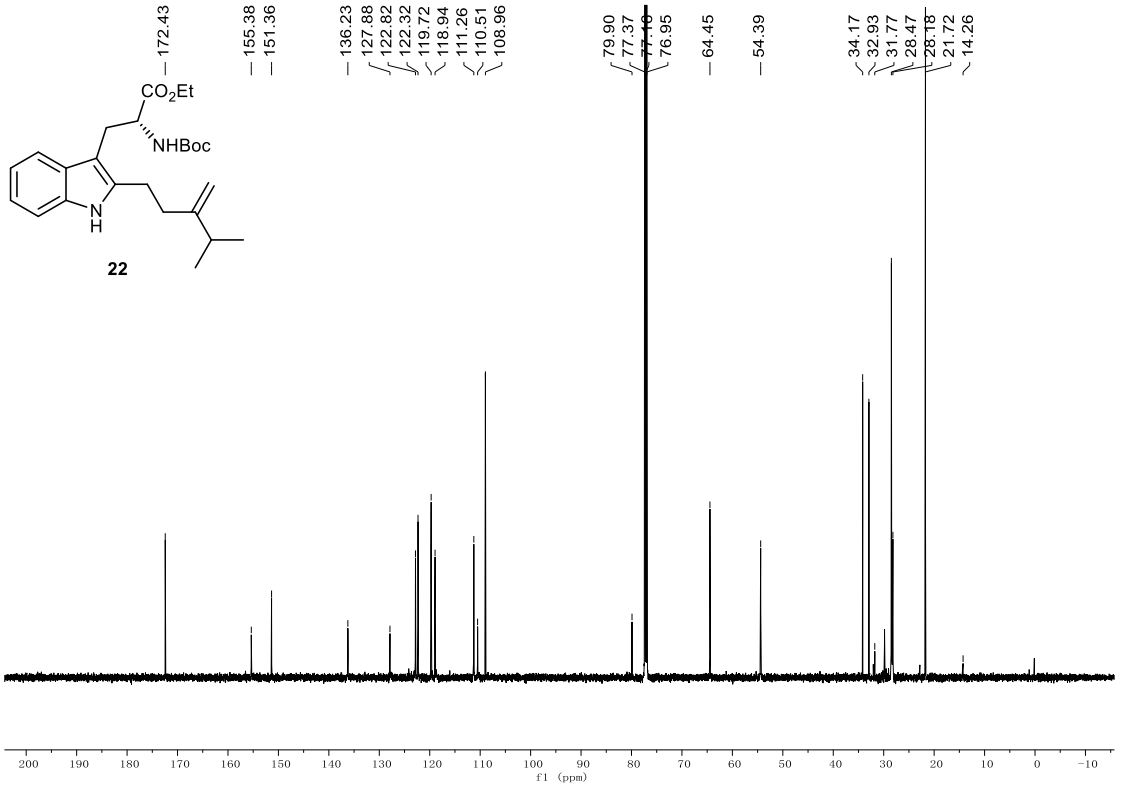
^{1}H NMR spectrum of compound **21**



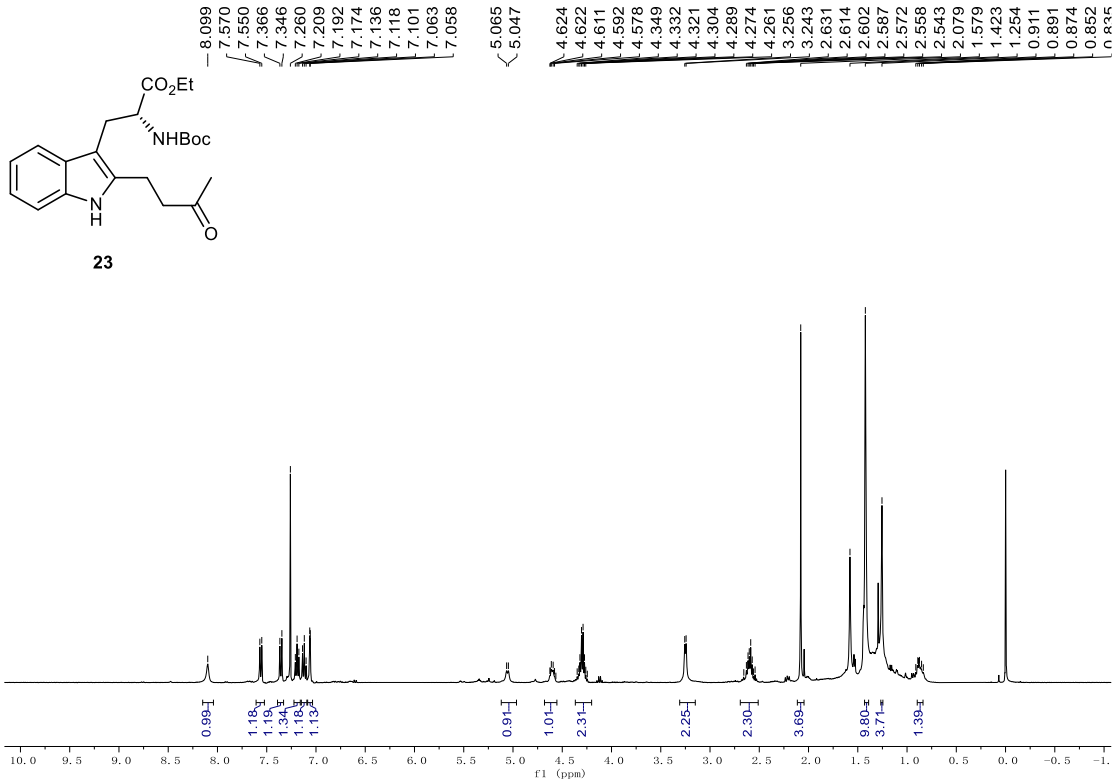
^{13}C NMR spectrum of compound **21**



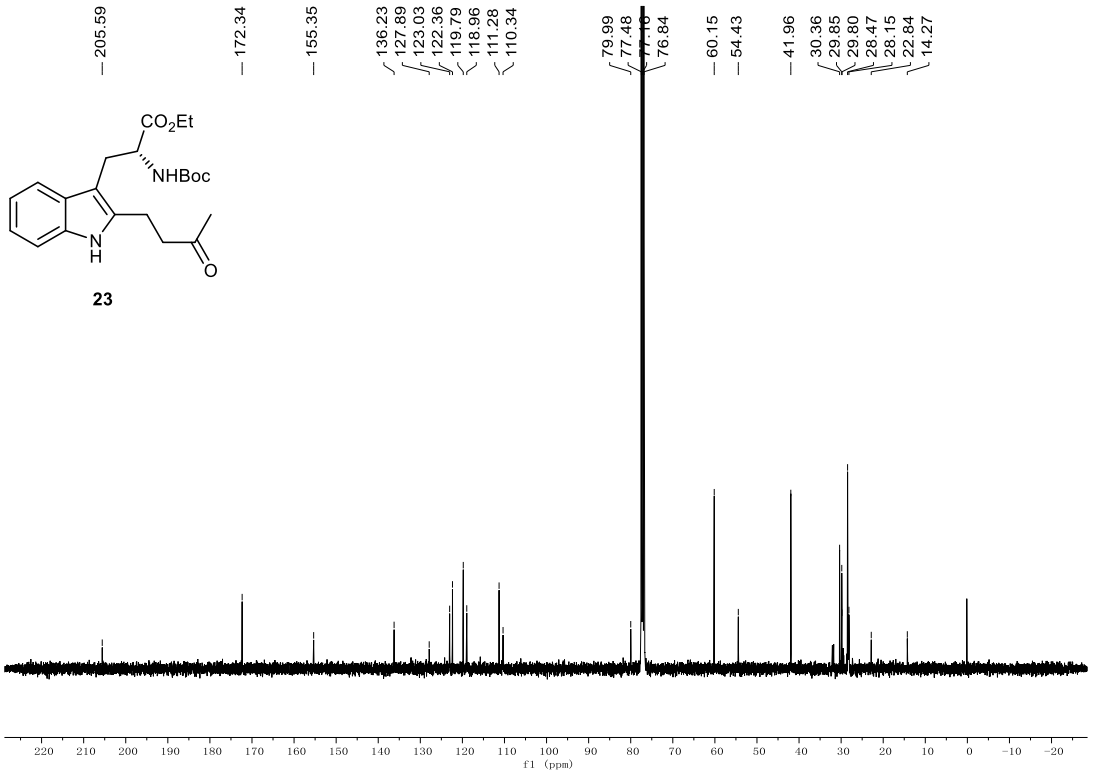
^{1}H NMR spectrum of compound **22**



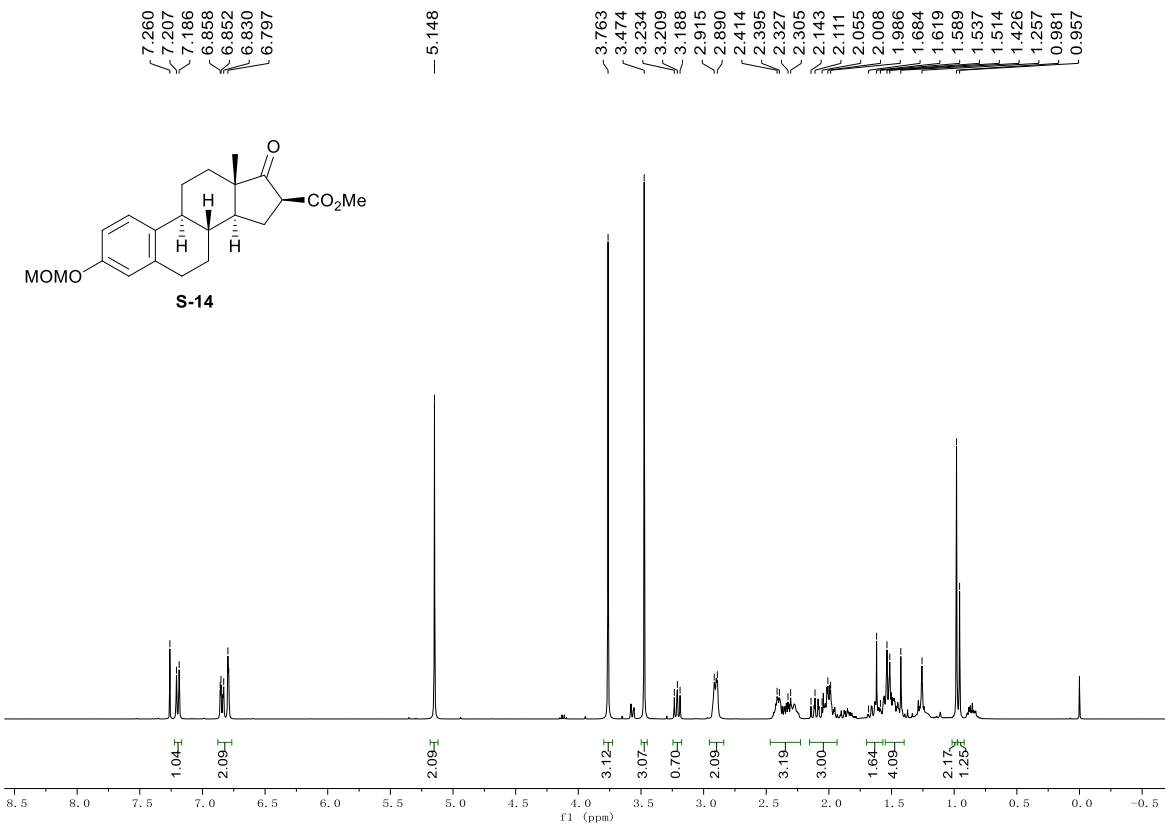
^{13}C NMR spectrum of compound **22**



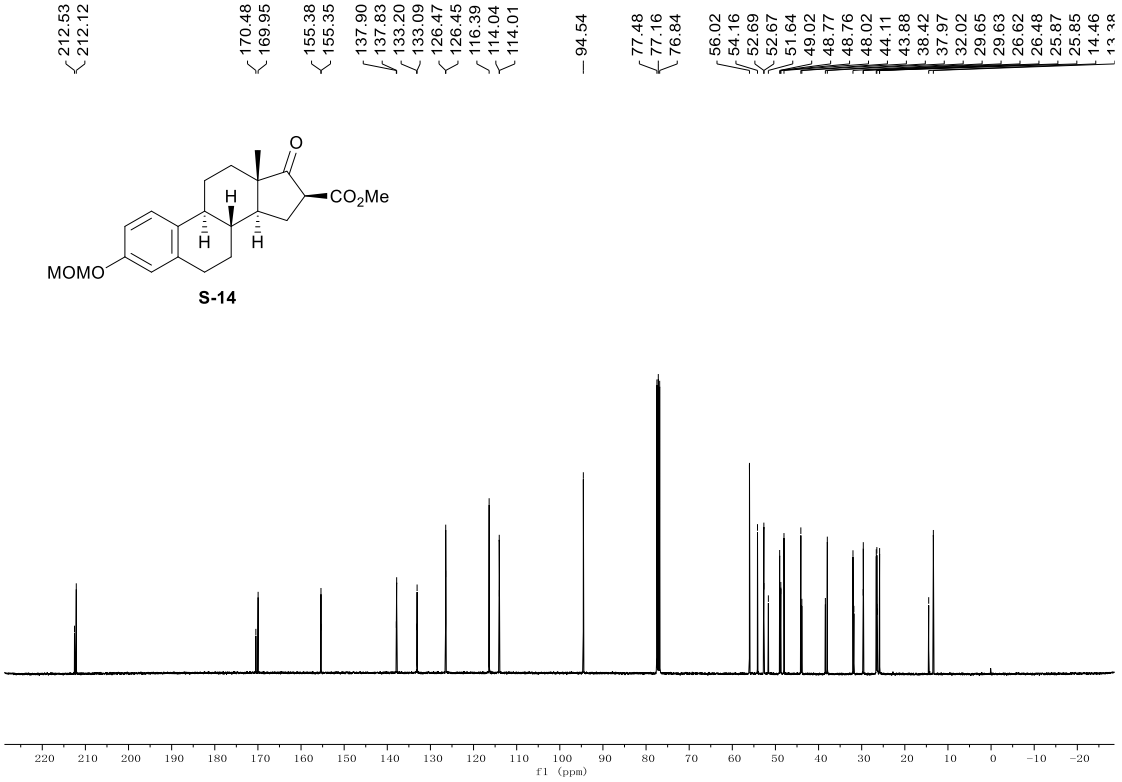
^{1}H NMR spectrum of compound **23**



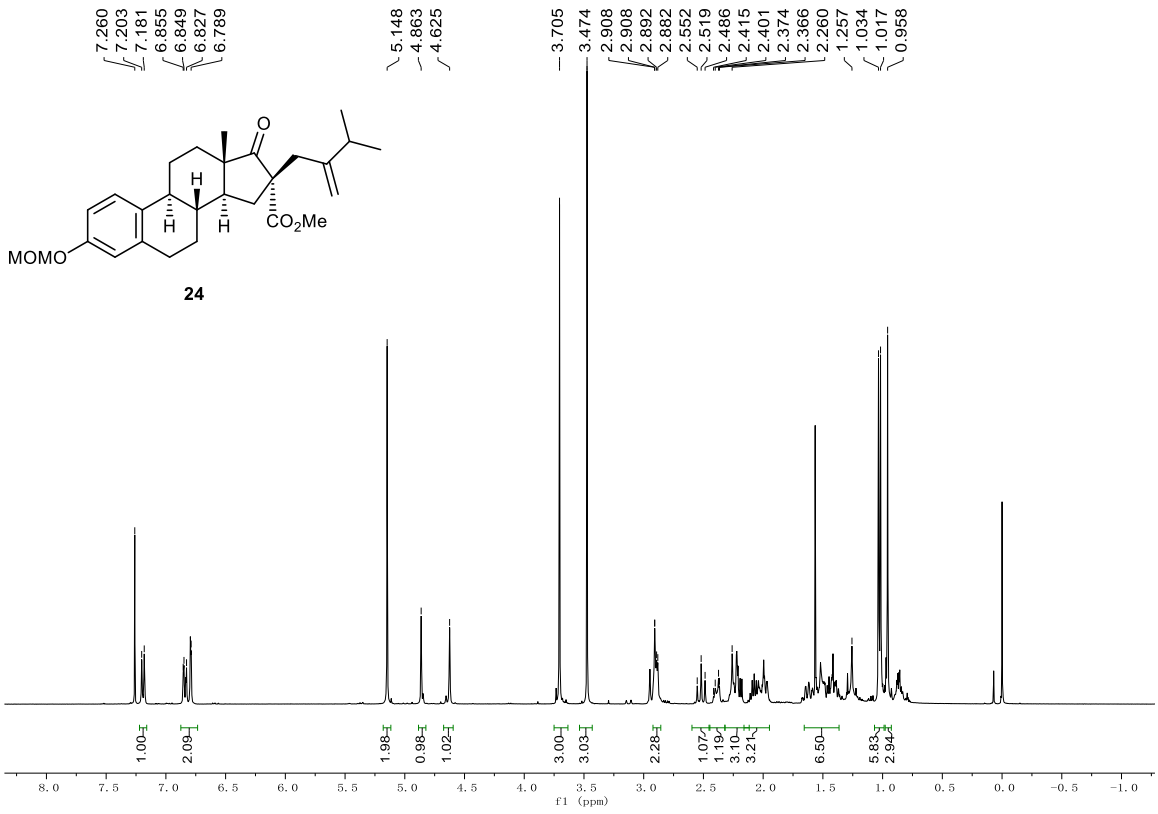
^{13}C NMR spectrum of compound **23**



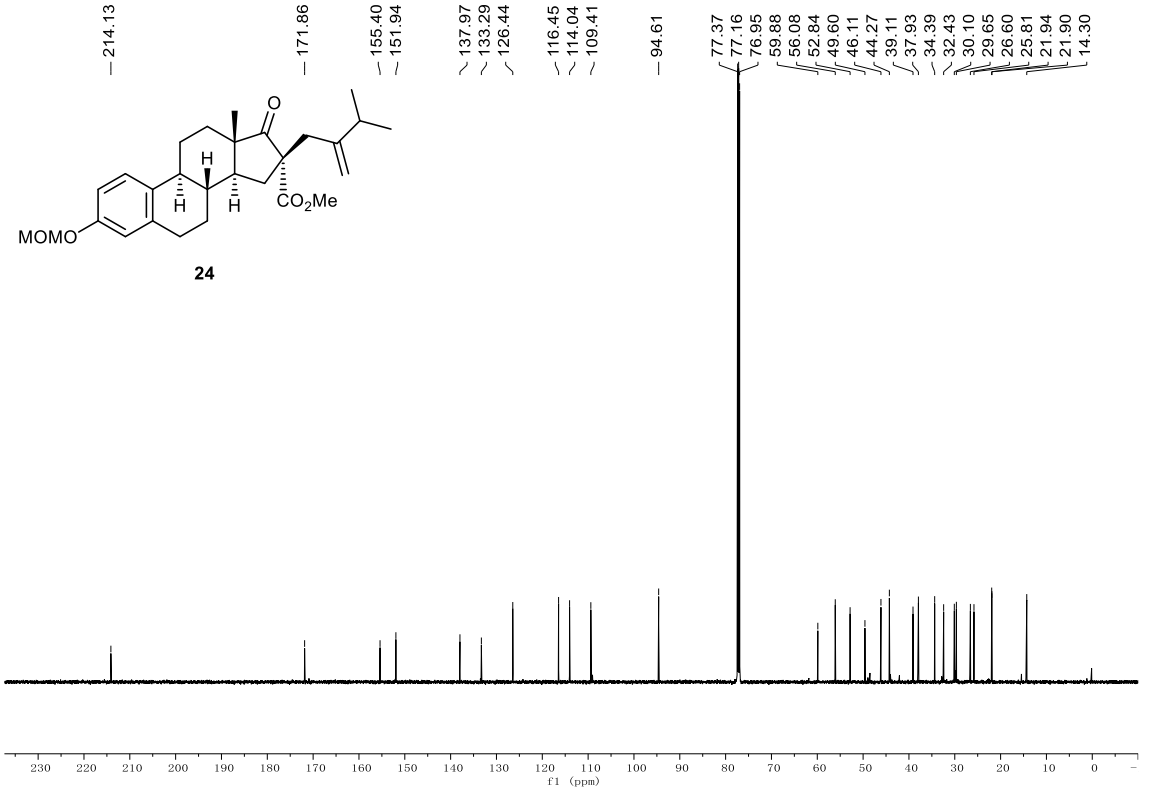
^{1}H NMR spectrum of compound **S-14**



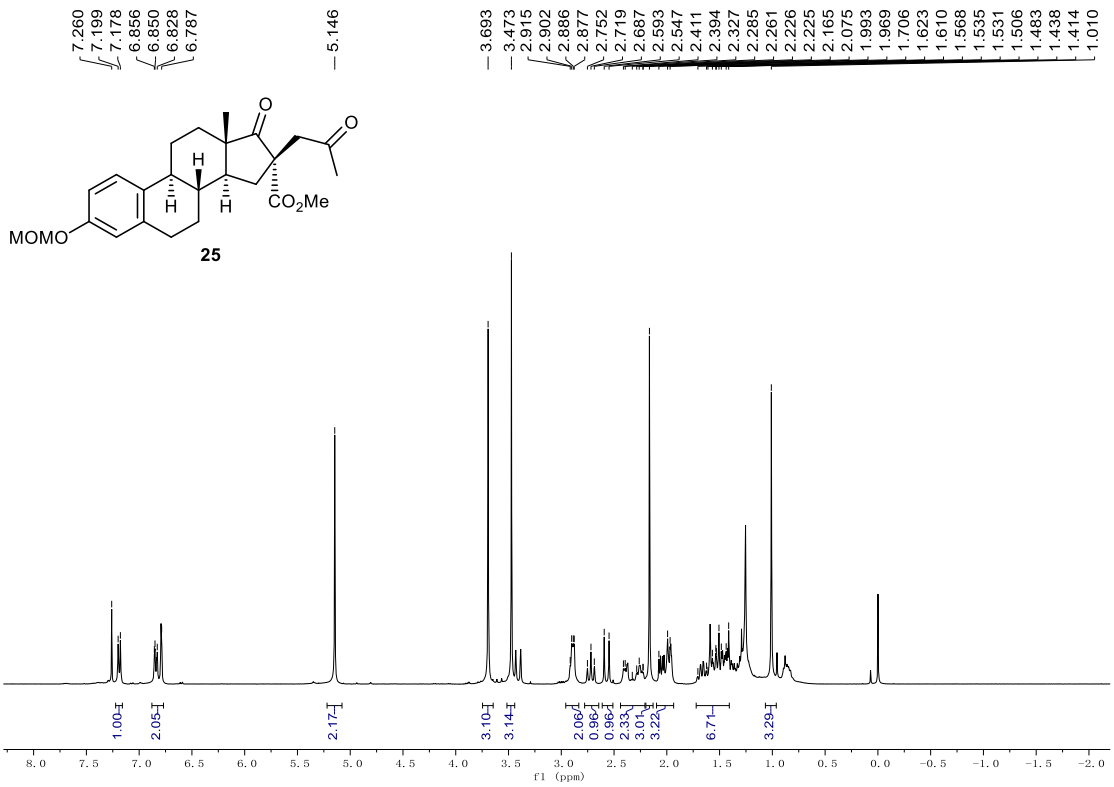
^{13}C NMR spectrum of compound **S-14**



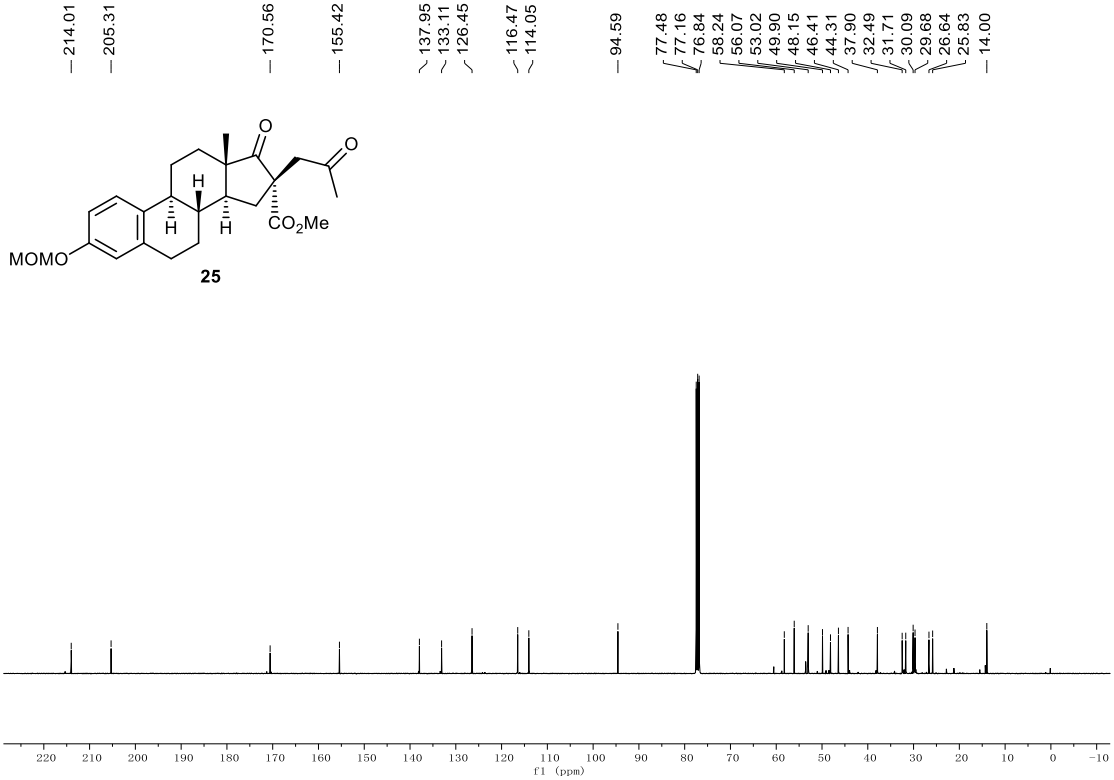
^{1}H NMR spectrum of compound **24**



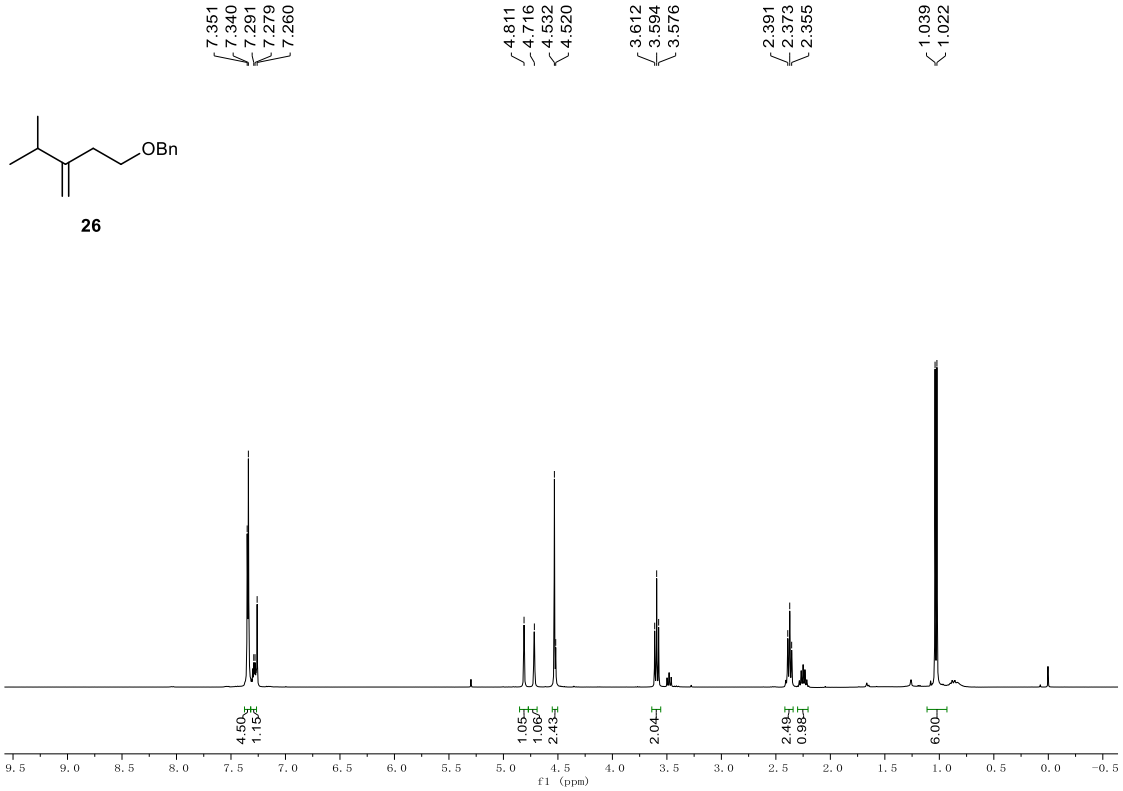
^{13}C NMR spectrum of compound **24**



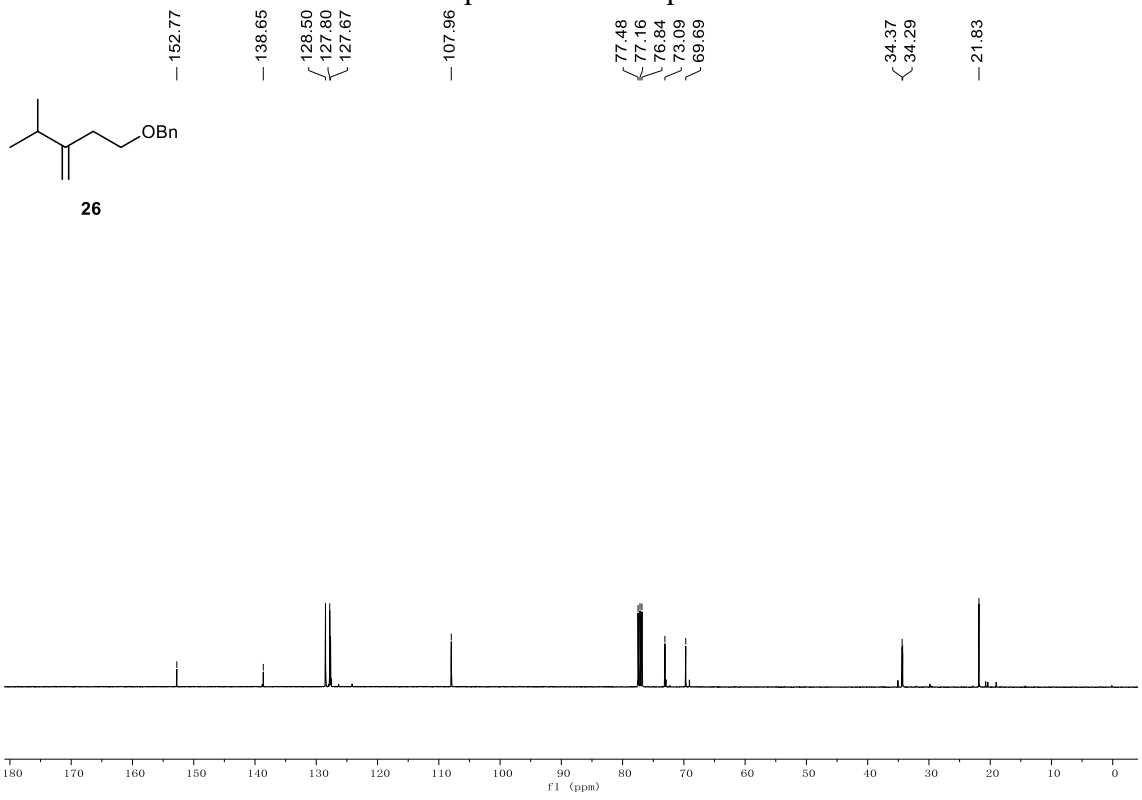
^{1}H NMR spectrum of compound **25**



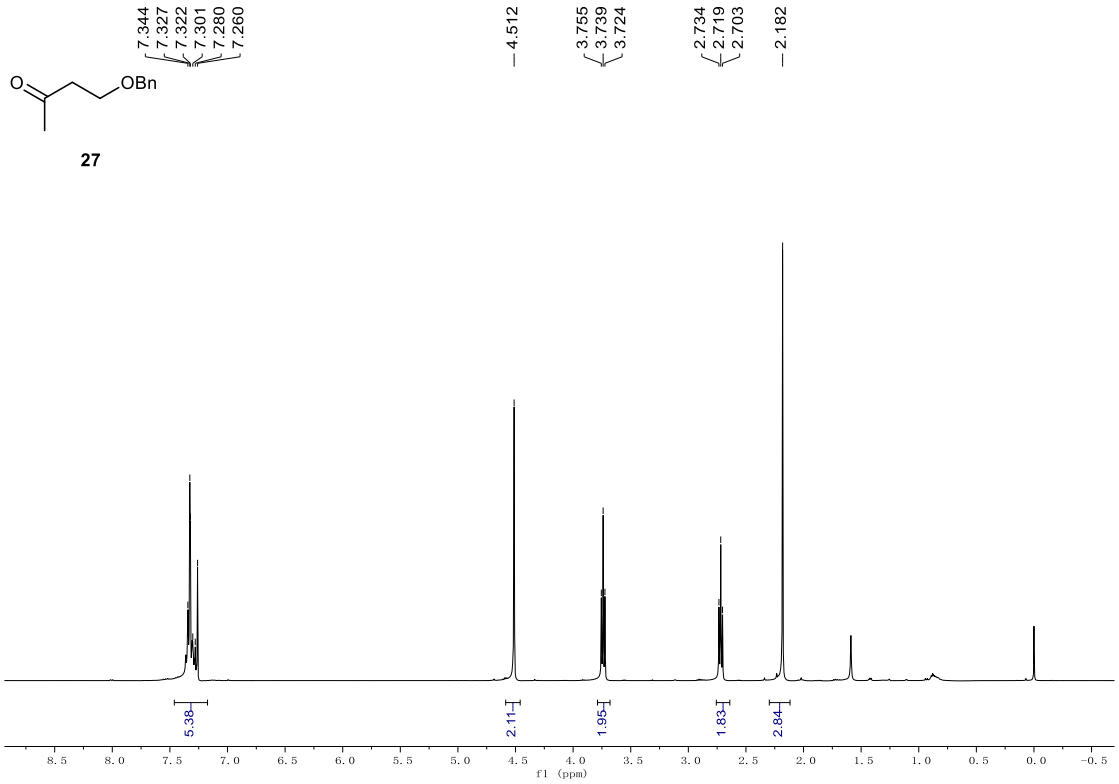
^{13}C NMR spectrum of compound **25**



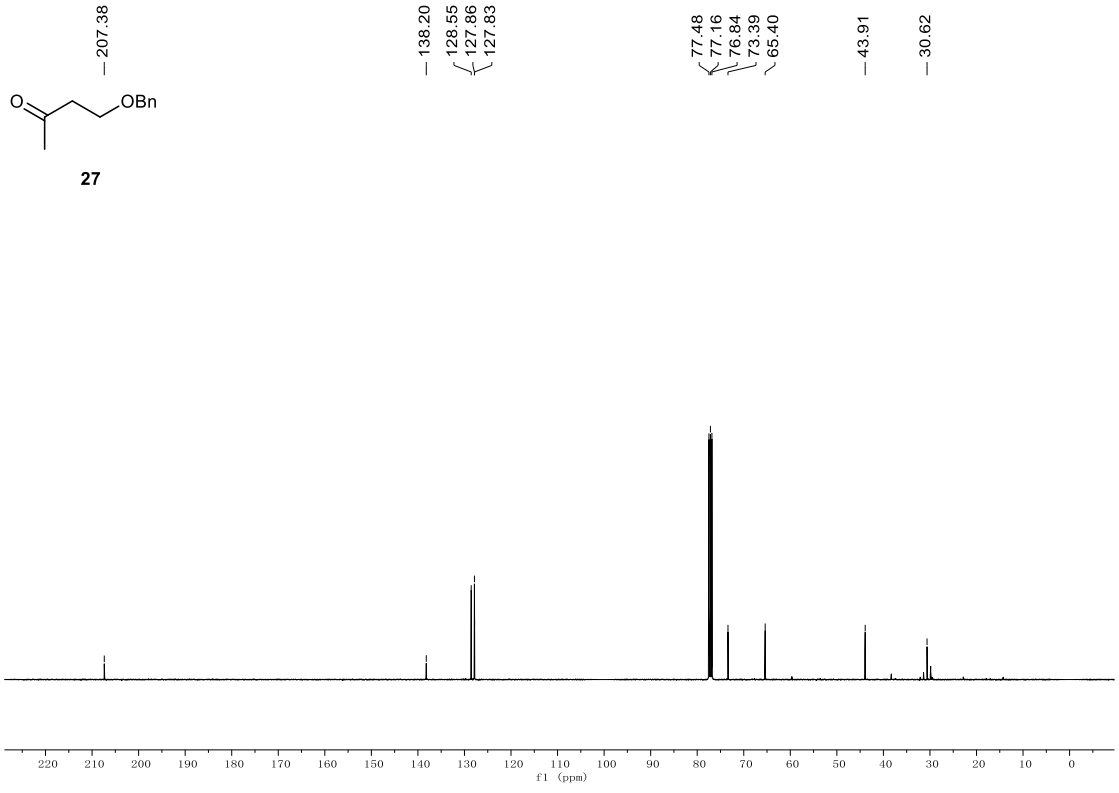
^{1}H NMR spectrum of compound **26**



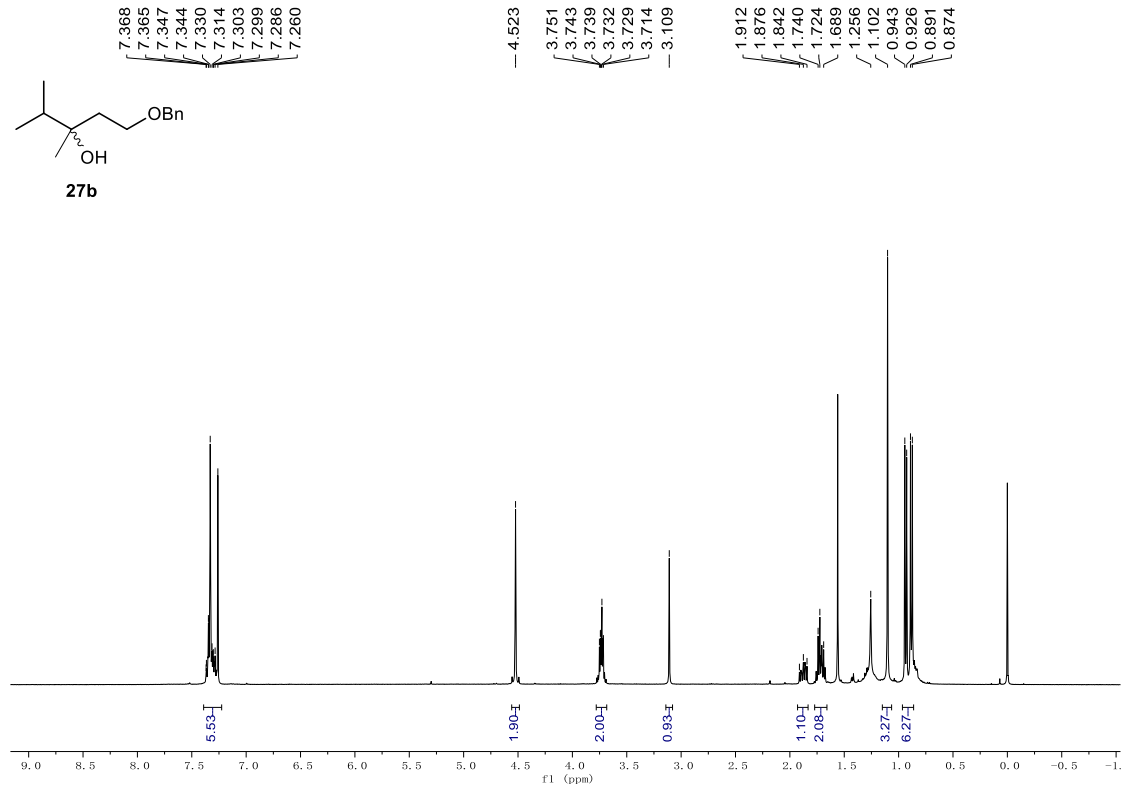
^{13}C NMR spectrum of compound **26**



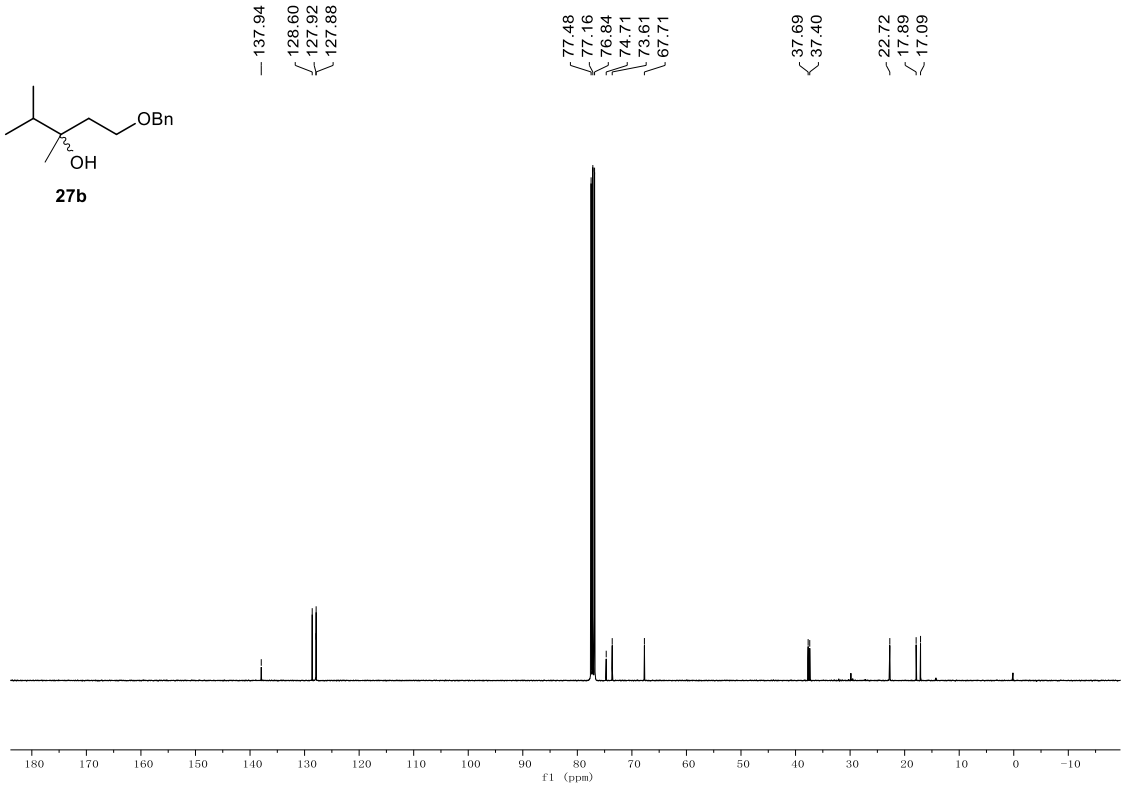
^{1}H NMR spectrum of compound **27**



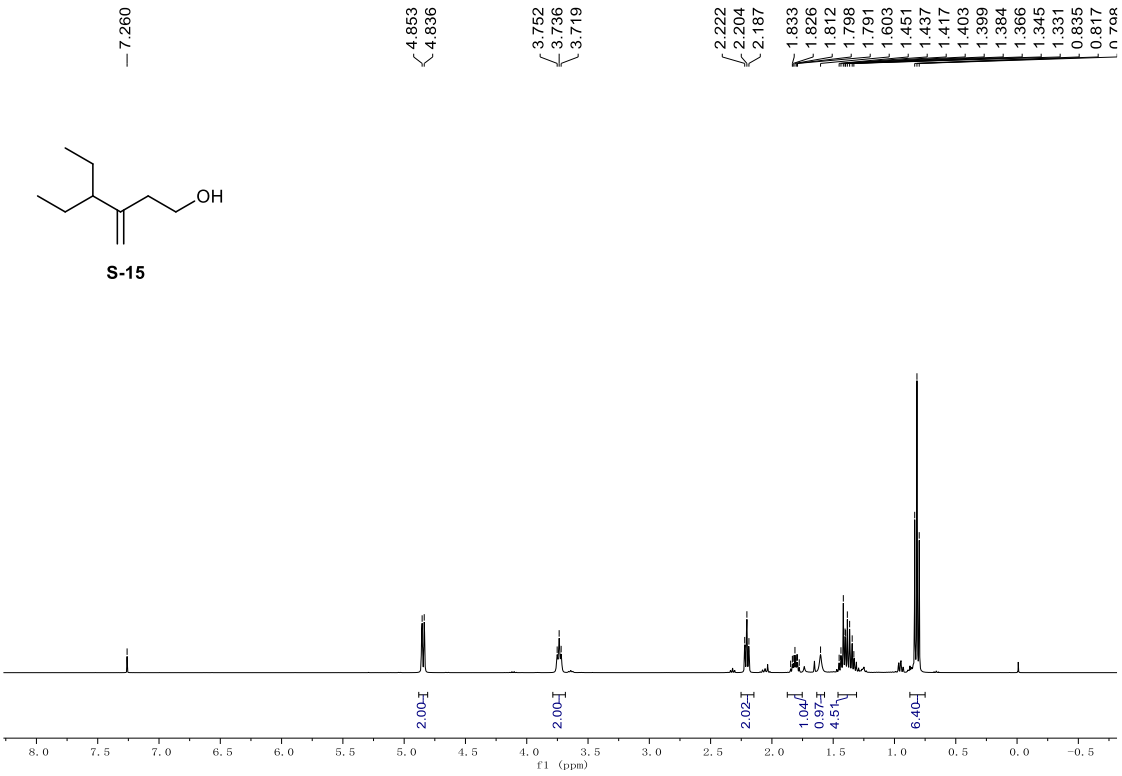
^{13}C NMR spectrum of compound **27**



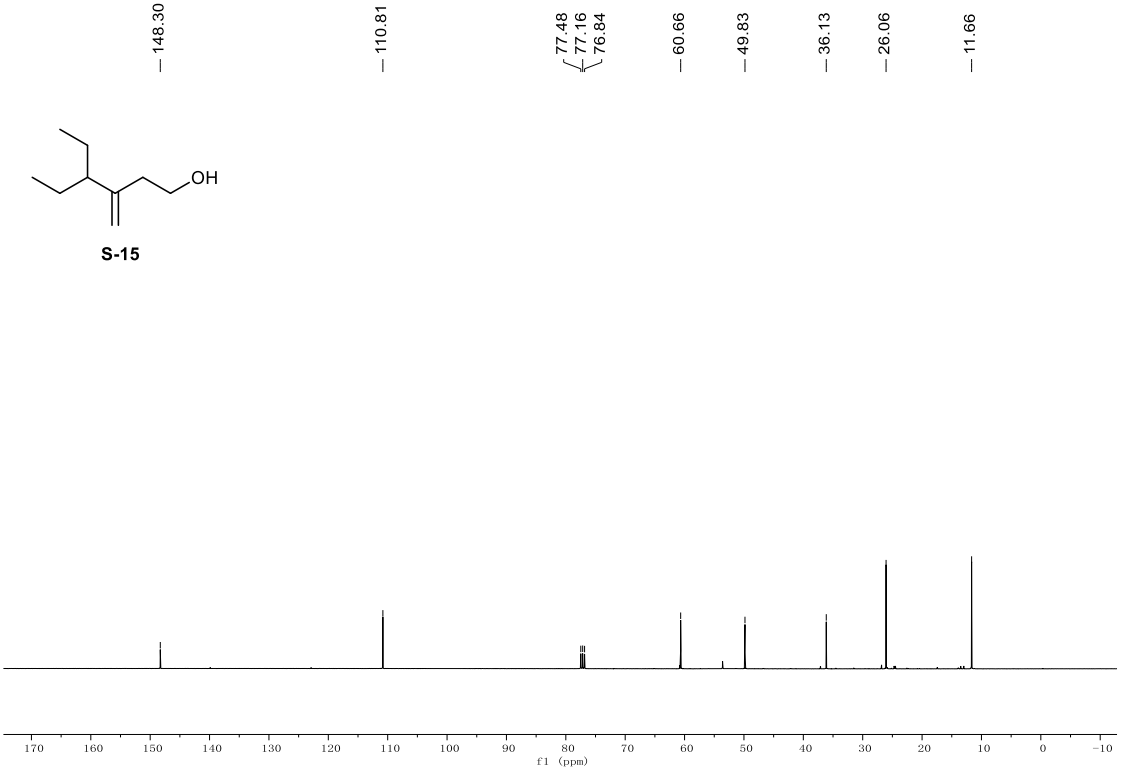
^{1}H NMR spectrum of compound **27b**



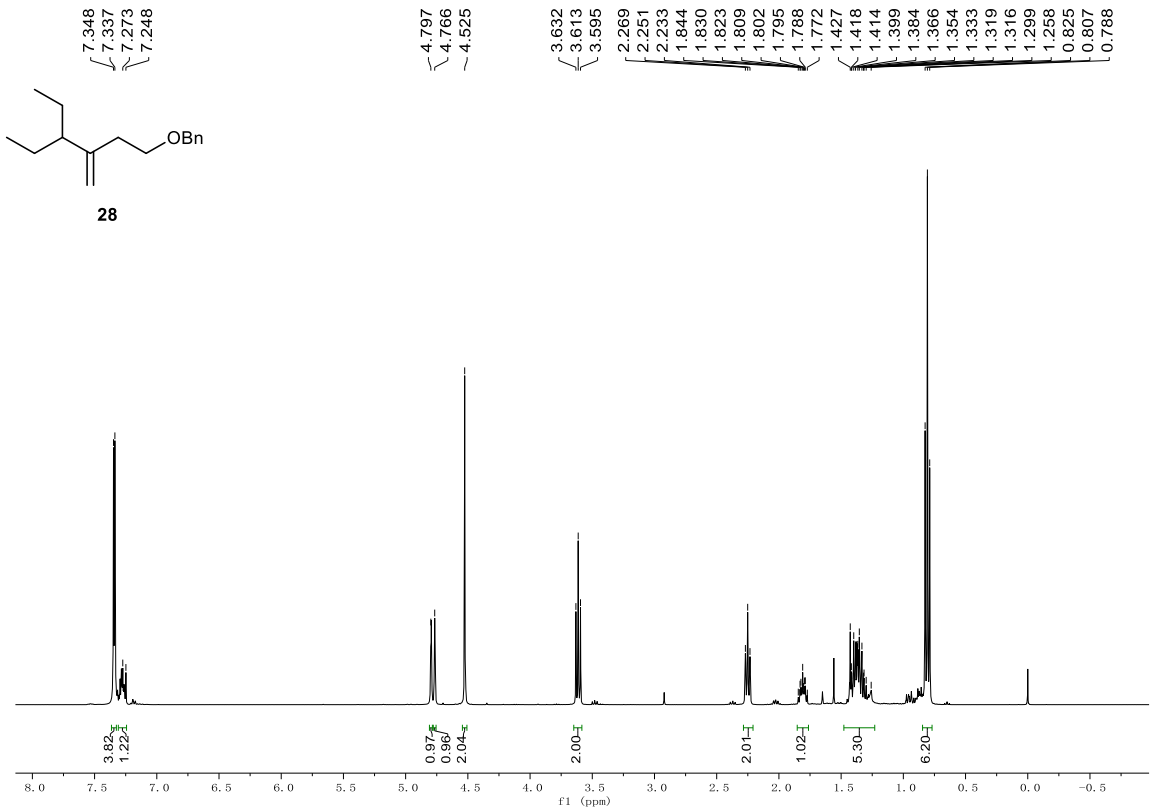
^{13}C NMR spectrum of compound **27b**



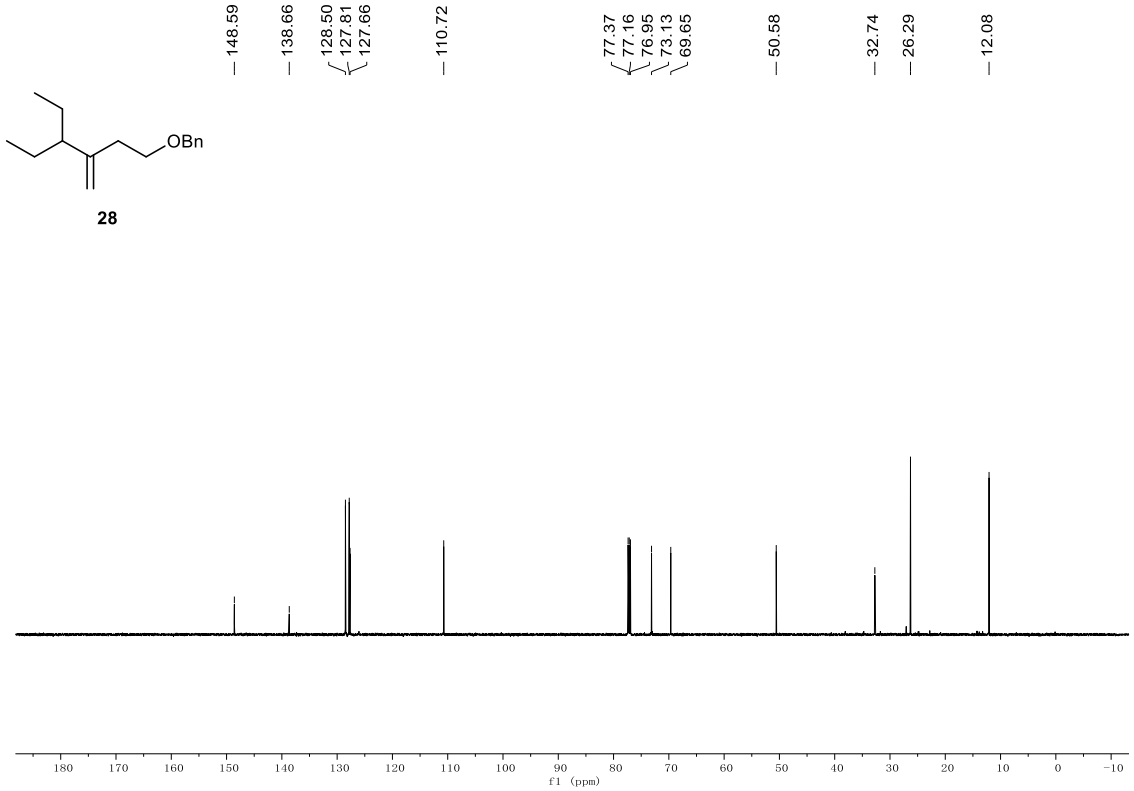
^{1}H NMR spectrum of compound **S-15**



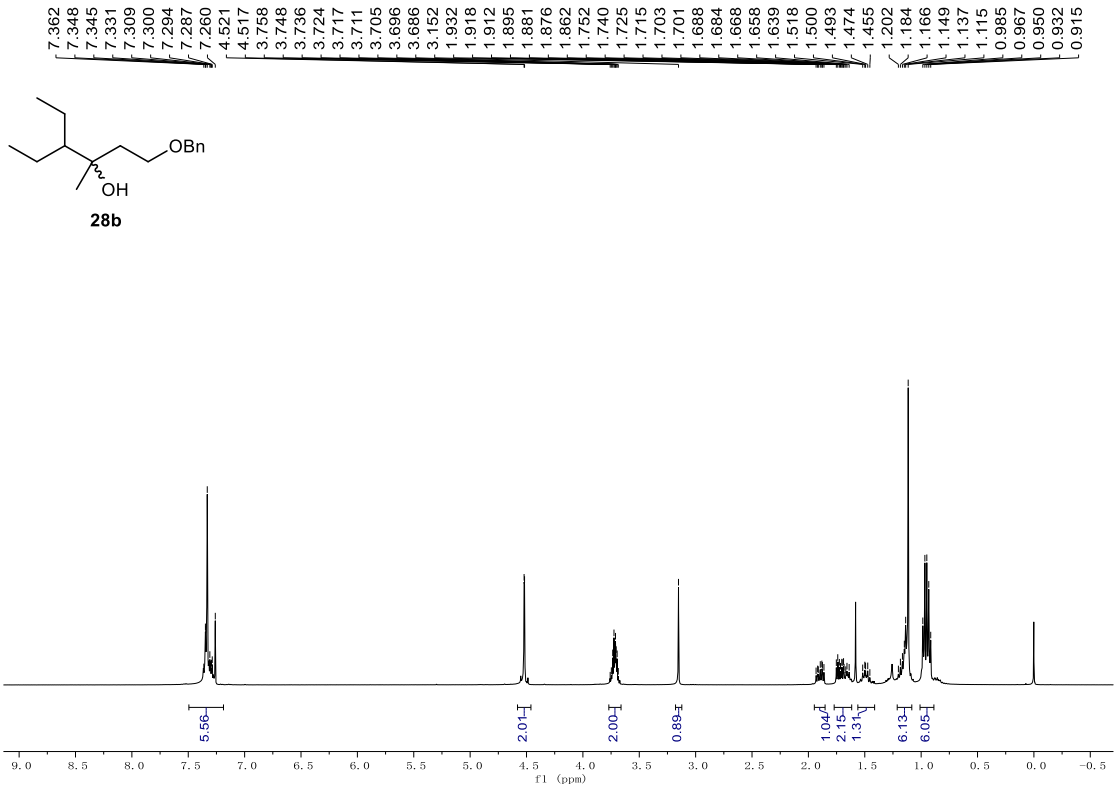
^{13}C NMR spectrum of compound **S-15**



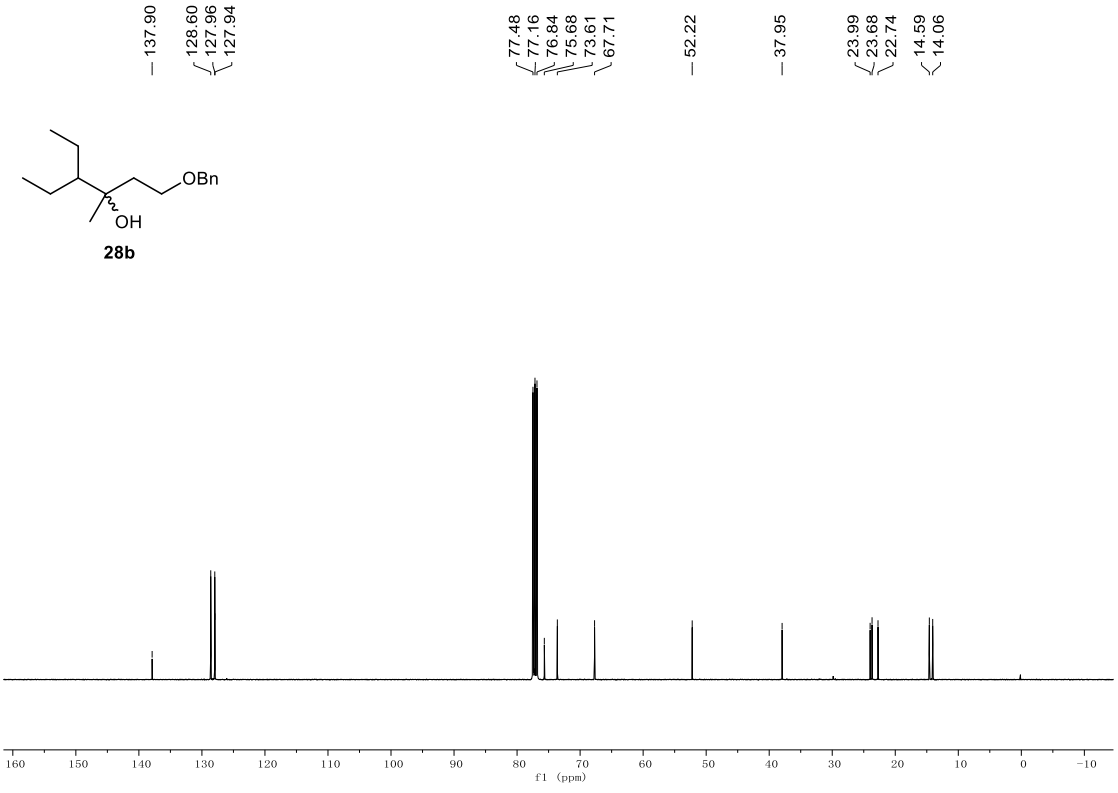
^{1}H NMR spectrum of compound **28**



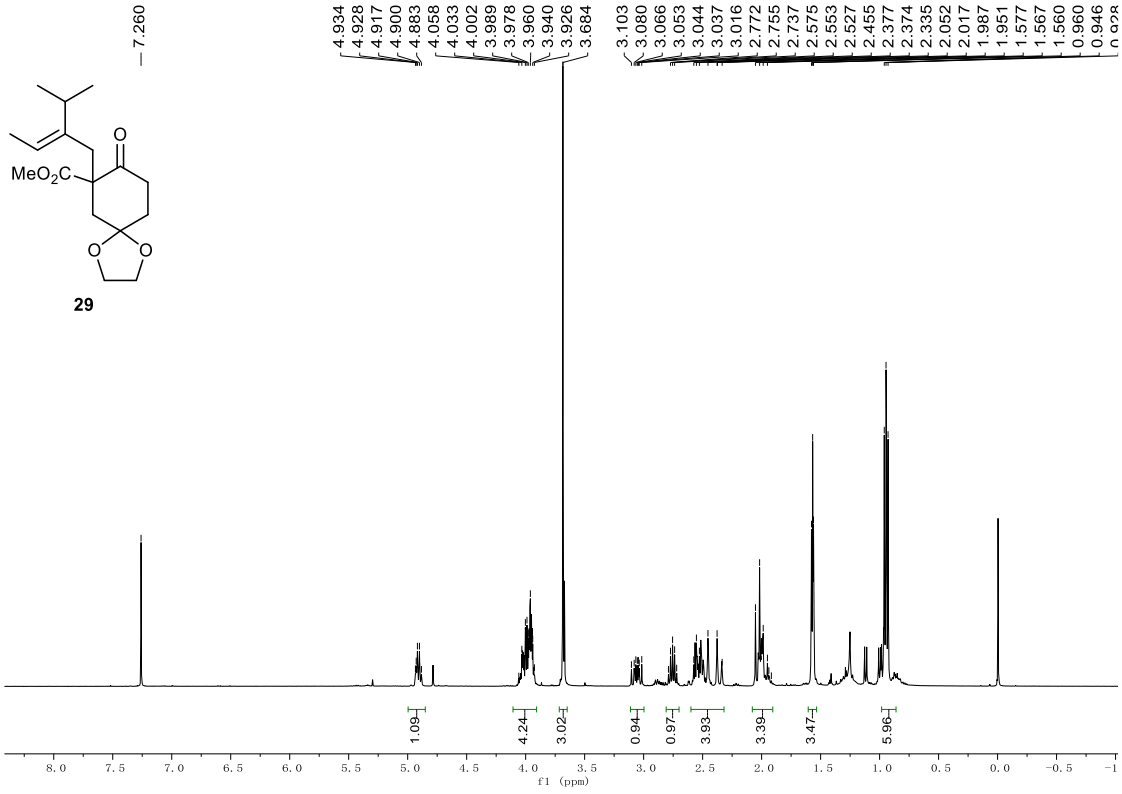
^{13}C NMR spectrum of compound **28**



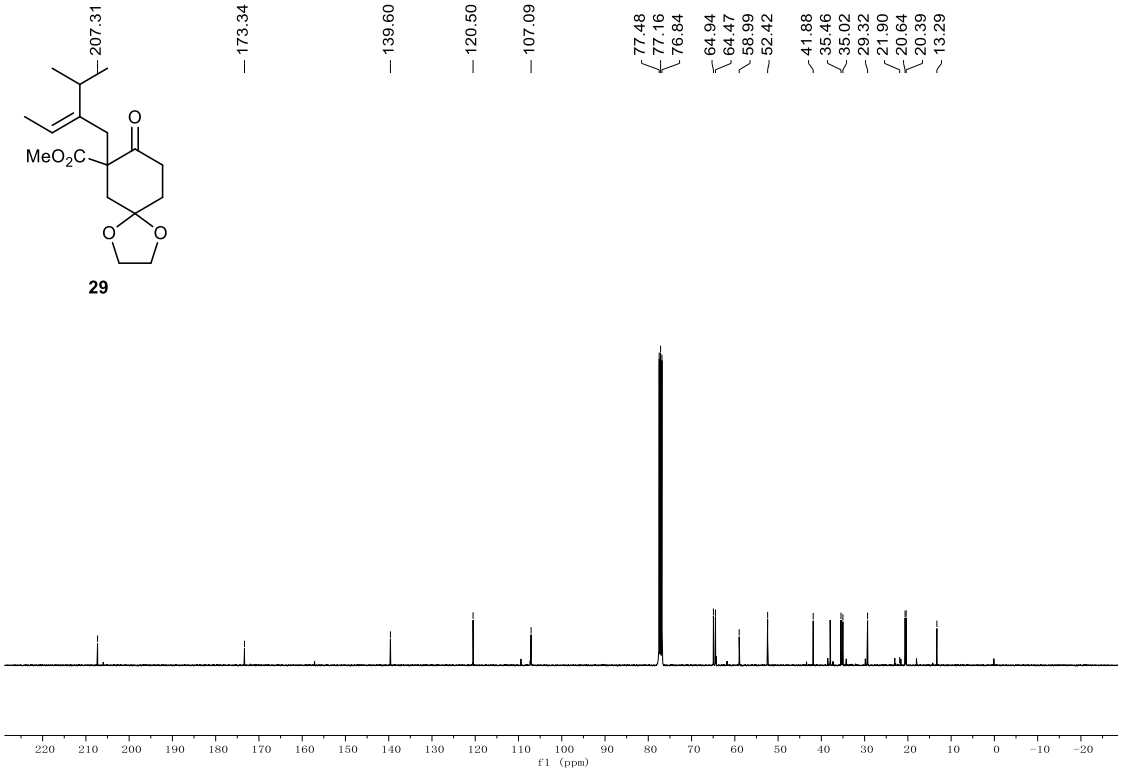
^{1}H NMR spectrum of compound **28b**



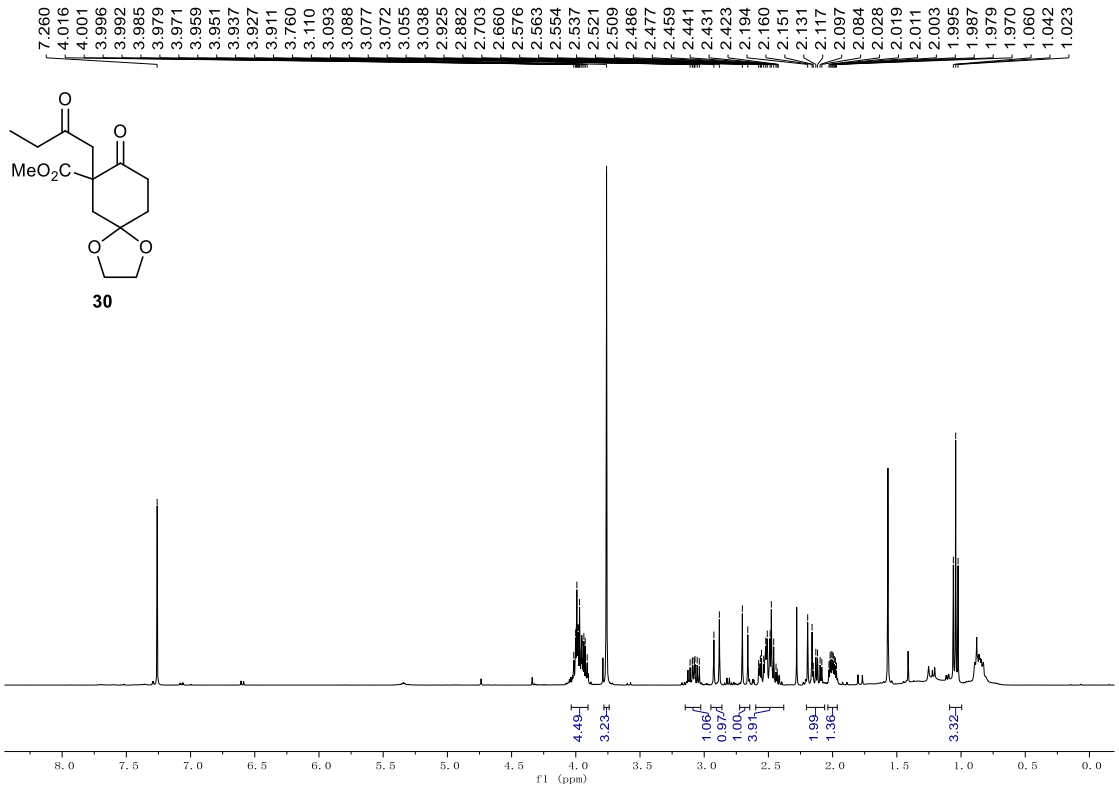
^{13}C NMR spectrum of compound **28b**



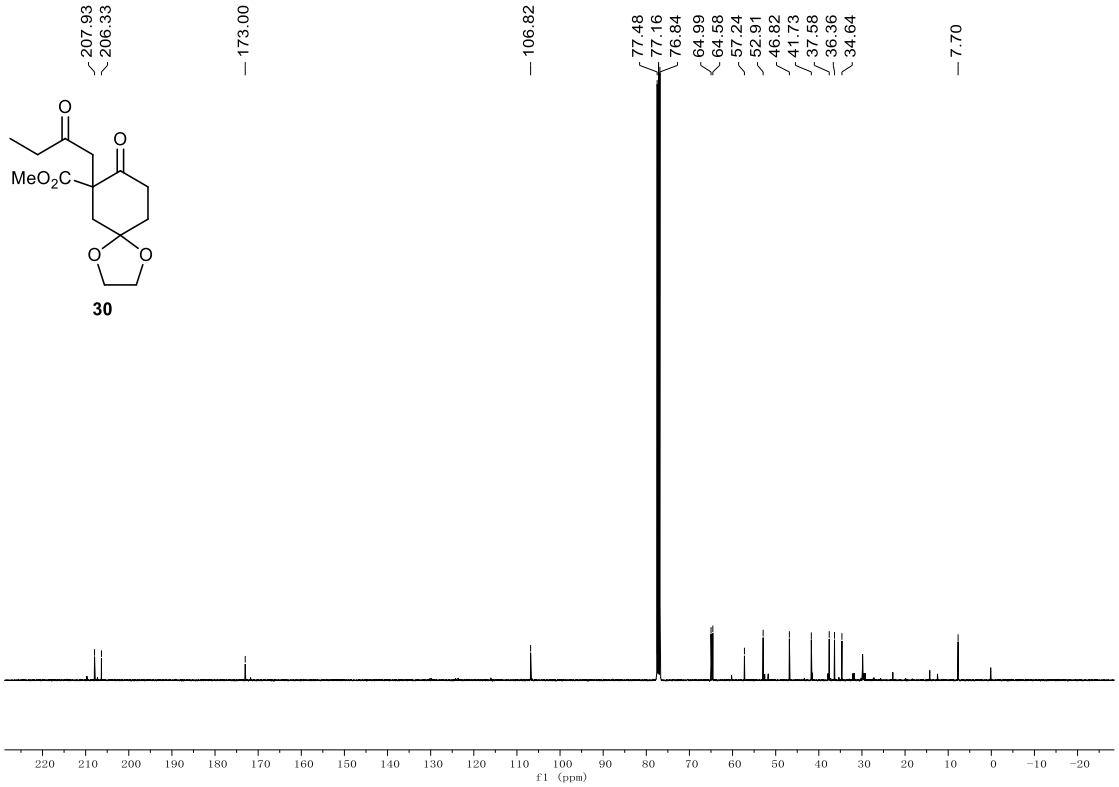
^{1}H NMR spectrum of compound **29**



^{13}C NMR spectrum of compound **29**



^{1}H NMR spectrum of compound **30**



^{13}C NMR spectrum of compound **30**