Supporting Information

For

Acceptorless dehydrogenative amination of alkenes for the synthesis of *N*-heterocycles

Jia-Lin Tu,[1] Wan Tang,[1] Shi-Hui He,[1] Ma Su[1] and Feng Liu[1,2]*

[1] Jiangsu Key Laboratory of Neuropsychiatric Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

[2] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

E-mail: fliu2@suda.edu.cn

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1. General remarks

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR) agilent NMR spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) and 77.16 ppm (for ^{13}C NMR). HRMS was recorded on an Agilent 6540 Q-TOF (ESI) or GCT Premier^{TM} (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified.

2. Photochemical reaction setup

Household blue LED strips (22 W) were coiled around the inside of a 15 cm diameter glassware (Figure S1a) or an 8 cm diameter glassware (Figure S1b). The LED strips were wrapped in aluminum foil to maintain a specific reaction temperature. In this case, the reaction temperature is approximately 35 °C (Figure 1a) and 55 °C (Figure 1b). Optimum yields were then observed.

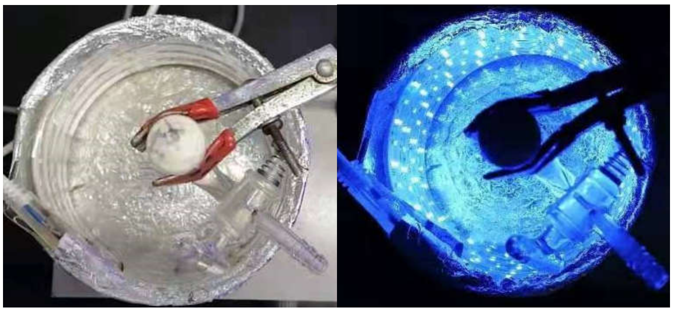


Figure S1a: Reaction setup for 35 °C

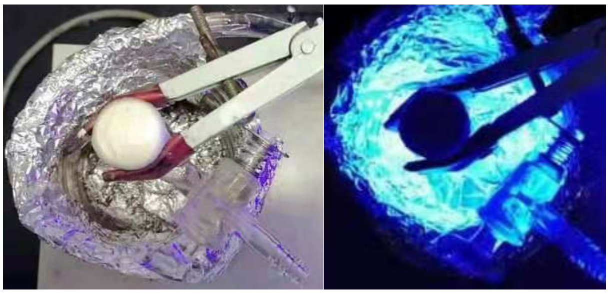
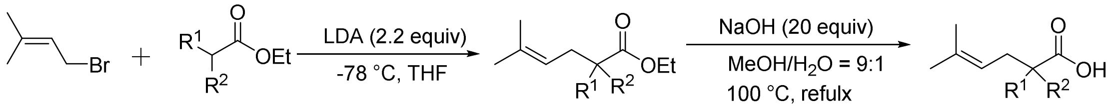


Figure S1b: Reaction setup for 55 °C

3. General procedures for synthesis of substrates

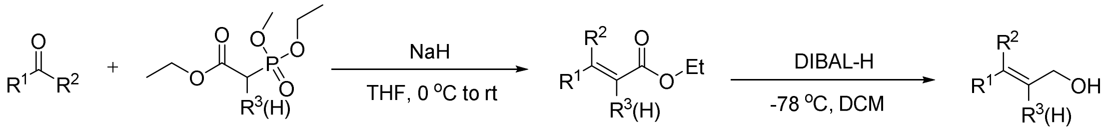
3.1 Synthesis of unsaturated carboxylic acid[1]



1) To a flame-dried flask were added ester (1.0 equiv., if ethyl acetate, 2.0 equiv.) and CuI (4.0 equiv.), followed by THF (0.2 M). the resulting mixture was stirred under nitrogen for 1 h. LDA (1 equiv., if ethyl acetate, 2.0 equiv.) was added in -78 °C. The mixture was stirred for 30 min and the allylic bromide (1.0 equiv.) was then added dropwise. After the resulting mixture was stirred at -78 °C for 6 h, the reaction was quenched with saturated aqueous ammonium chloride, and then extracted with EtOAc (30 mL × 2). The phases were separated and the organic phase washed three times with H_2O, and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by silica-gel chromatography (petroleum ether/EtOAc as eluent) to afford the desired compound.

2) A mixture of the ester (1.0 equiv.) obtained in the previous step, NaOH (20 equiv.) and MeOH/H_2O = 9:1 (0.1M) was stirred at 100 °C for 6 h. After cooling to room temperature, MeOH in the mixture was removed *in vacuo*, the residue was extracted with EtOAc (25 mL × 3). The aqueous phase was acidified to pH = 6 with 2 M HCl, extracted with EtOAc (25 mL × 3), washed with brine (15 mL), and dried over Na_2SO_4. After concentration of the organic phase, the residue was directly used in next step without further purification.

3.2 Synthesis of unsaturated alcohol[2]

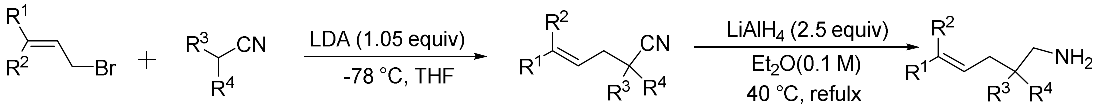


1) To a suspension of NaH (480 mg, 60% in mineral oil, 12 mmol) in THF (10 mL) was slowly added a solution of triethyl phosphonoacetate (2.5 mL, 12 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 30 min. Ketone (10

mmol) in THF (5 mL) was added at 0 °C, and the mixture was stirred at room temperature. After totally consumption of the ketone (determined by TLC), a solution of saturated aqueous sodium bicarbonate (15 mL) was added. The mixture was extracted with EtOAc (25 mL × 3), washed with brine (15 mL), and dried over Na_2SO_4. After concentration of the organic phase, the residue was purified by silica gel column chromatography (petroleum ether/EtOAc as eluent) to give the title ester.

2) To a solution of the ester (1.0 equiv.) obtained in the previous step (dry DCM, 0.1 M) was slowly added DIBAL-H (2.2 equiv.) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and the solution was then warmed to 0 °C. The solution was quenched with a saturated aqueous solution of ammonium chloride and stirred at room temperature until white precipitate was appeared. The white jelly was removed by filtration, and the resulting solution was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc as eluent) to give the title allylic alcohol.

3.3 Synthesis of unsaturated amines[3]

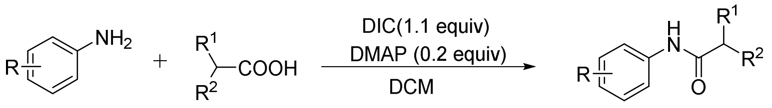


1) To a suspension of LDA (1.1 equiv.) in THF at -78°C was added to the nitrile (1 equiv.) or acetonitrile (2.0 equiv.). The reaction as stirred for 30 min and brominated substance (1.0 equiv.) was added via syringe and the reaction mixture was stirred at -78 °C overnight. The reaction was cooled in an ice-water bath and quenched with H_2O. Extraction was performed with ether (100 mL × 3), then drying over $MgSO_4$ and removal of the solvent gave the crude nitrile as colorless or light-yellow oil.

2) To a suspension of $LiAlH_4$ (2.5 equiv.) in diethyl ether under inert atmosphere was added the nitrile (1.0 equiv.). The mixture was stirred for 30 min at room temperature, then refluxed for 3 h and cooled to room temperature and stirred overnight. The reaction was quenched by THF: H_2O = 95: 5 at -20 °C. The solid was filtered, then

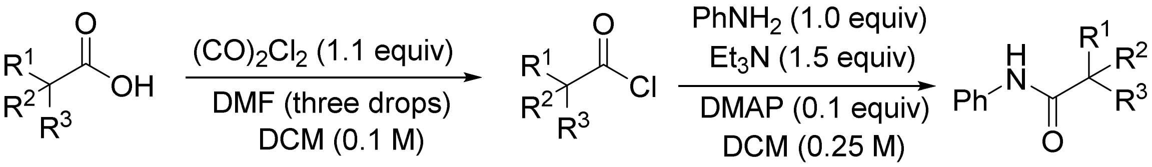
washed with diethyl ether (50 mL × 3). The combined filtrates were washed with H_2O, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the crude amino alkene.

3.4 General procedures A for amide synthesis



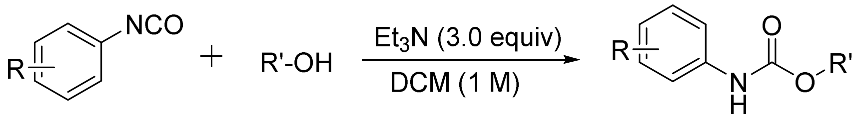
To a solution of acid (20 mmol) and DMAP (20 mmol) in CH_2Cl_2 (0.2 M) was added an aniline derivative (20 mmol) at room temperature. *N,N'*-Diisopropylcarbodiimide (DIC, 22 mmol) was then added to the mixture and stirred overnight. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5: 1) to afford the title amides.

3.5 General procedures B for amide synthesis[4]



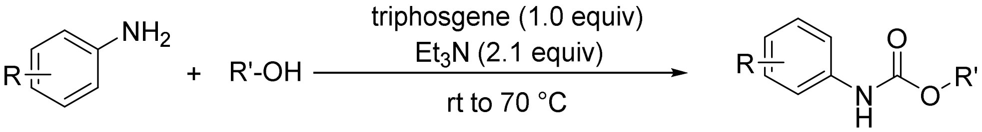
The acid (1.0 equiv.) was dissolve in DCM under an inert atmosphere. A few drops of DMF were then added slowly to the reaction mixture after the oxalyl chloride (1.1 equiv) was added. The solvent was removed *in vacuo* after 3 hours of reaction and the resulting acyl chloride was dissolved in dry DCM directly used for the next step. To a solution of aniline (1.0 equiv), DMAP (0.1 equiv) and Et_3N (1.5 equiv) in dry DCM (20 mL) was slowly added acyl chloride (0.7 mL, 6.0 mmol, 1.2 equiv) at 0 °C. The resulting mixture was warmed to room temperature and stirred overnight. The reaction mixture was washed with a saturated aqueous solution of ammonium chloride. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography to afford the title amide.

3.6 General procedures C for amide synthesis[5]



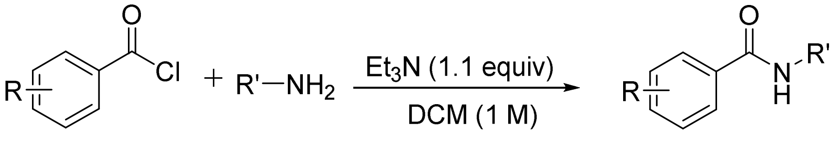
A flame-dried round-bottomed flask was degassed, flushed with argon, and charged with phenyl isocyanate (10 mmol, 1 equiv), DCM (10 mL, 1.0 M), Et_3N (30 mmol, 3.0 equiv) and alcohol (10 mmol, 1 equiv). The reaction mixture was stirred at room temperature until the alcohol/amine was fully consumed by TLC. The reaction mixture was then diluted with DCM (20 mL), washed with 1M HCl (3 x 20 mL), water (20 mL), and brine (20 mL), and then dried Na_2SO_4 and concentrated. The crude product was purified by either silica gel column chromatography or recrystallization to afford the desired product.

3.7 General procedures D for carbamate synthesis[6]



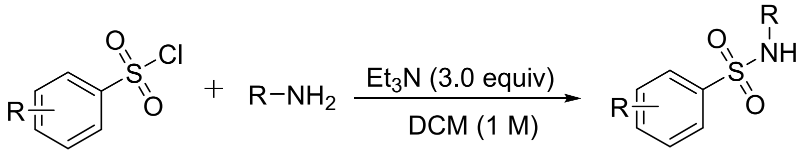
To a solution of substituted aniline (5.0 mmol) dissolved in THF (40 mL) was slowly added triphosgene (1.49 g, 5.0 mmol) solution in THF (10 mL). Et_3N (1.5 mL, 10.5 mmol) was then added slowly to the reaction mixture. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was then concentrated and was degassed, followed by the addition of acetonitrile (80 mL), NEt_3 (1.5 mL, 10.5 mmol), and alcohol. The resulting mixture was then stirred at 70 ºC for 8 h. The reaction mixture was concentrated, and the crude residue was purified by flash chromatography to afford the title carbamates.

3.8 General procedures E for amide Synthesis[6]

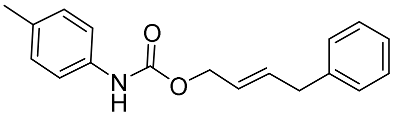


To an oven-dried round bottom flask charged with amine (1.0 mmol, 1.0 equiv.), DCM (5 mL), and Et_3N (1.1 equiv.), benzoyl chloride was added dropwise with ice bath. The reaction was then stirred at room temperature for two hours. The reaction mixture was then diluted with DCM, washed with saturated potassium carbonate solution and brine, and then dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography (PE/EA = 4:1 to 2:1) to afford the desired product.

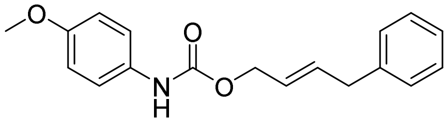
3.9 General procedures F for sulfonamide synthesis[7]



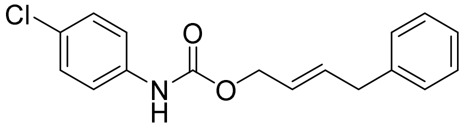
To a flame-dried round bottom flask was charged with magnetic stir bar, amine (10.0 mmol, 1.0 equiv.), dichloromethane (40 mL, 0.25 M) and triethylamine (4.18 mL, 30.0 mmol, 3.0 equiv.). The flask was cooled to 0 °C. Corresponding sulfonyl chloride (1.1 equiv., 11.0 mmol) was added dropwise or in small portions. After addition, reaction was warmed up to room temperature gradually and stirred at room temperature for two hours. Reaction was quenched by adding 100 mL brine, then extracted by 3 × 30 mL dichloromethane. Combined organic phase was washed by brine for three times. Collect the organic phase and dried over Na_2SO_4. Crude product was purified by silica gel flash chromatography to obtain the sulfonamide products.



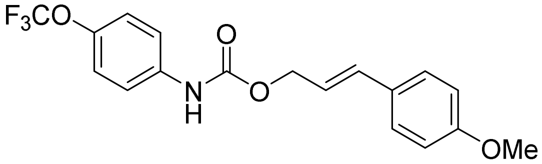
(*E*)-4-Phenylbut-2-en-1-yl p-tolylcarbamate (1a): Synthesized using general procedure C starting from 4-phenylbut-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 79 – 80°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.68 (s, 1H), 6.09 – 5.93 (m, 1H), 5.83 – 5.63 (m, 1H), 4.69 (d, *J* = 6.2 Hz, 2H), 3.46 (d, *J* = 6.7 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5, 139.6, 135.3, 134.6, 133.1, 129.6, 128.7, 128.6, 126.3, 125.6, 118.8, 65.6, 38.7, 20.8; **T-IR** (thin film, KBr): ν (cm^{-1}) 3334, 3027, 1698, 1597, 1532, 1449, 1314, 1296, 1223, 1051, 854, 722; **HRMS (ESI)** Calcd $C_{18}H_{19}NO_2Na$ [M + Na]$^+$: 304.1308, found 304.1313.



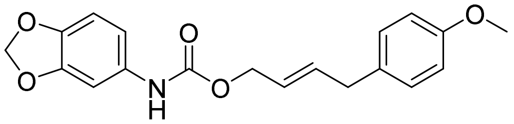
(*E*)-4-Phenylbut-2-en-1-yl (4-methoxyphenyl)carbamate (1b): Synthesized using general procedure C starting from 4-phenylbut-2-en-1-ol and 1-isocyanato-4-methoxybenzene as a white solid; m.p. 75 – 76 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.29 (m, 4H), 7.29 – 7.21 (m, 3H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.57 (s, 1H), 6.00 (dt, *J* = 13.9, 6.7 Hz, 1H), 5.78 – 5.66 (m, 1H), 4.67 (d, *J* = 6.2 Hz, 2H), 3.82 (s, 3H), 3.45 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 156.0, 153.7, 139.6, 134.6, 128.7, 128.6, 128.3, 126.3, 125.6, 120.7, 114.3, 65.5, 55.6, 38.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3302, 2955, 1697, 1601, 1530, 1512, 1414, 1231, 1181, 1028, 825, 739; **HRMS (ESI)** Calcd $C_{18}H_{20}NO_3$ [M + H]$^+$: 298.1438, found 298.1434.



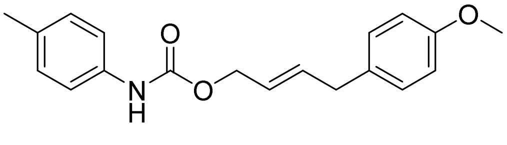
(*E*)-4-Phenylbut-2-en-1-yl (4-chlorophenyl)carbamate (1c): Synthesized using general procedure C starting from 4-phenylbut-2-en-1-ol and 1-chloro-4-isocyanatobenzene as a white solid; m.p. 77 – 78 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.34 – 7.27 (m, 5H), 7.26 – 7.21 (m, 2H), 7.21 – 7.15 (m, 2H), 6.63 (s, 1H), 6.08 – 5.82 (m, 1H), 5.79 – 5.58 (m, 1H), 4.63 (dd, *J* = 6.3, 0.7 Hz, 2H), 3.40 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.1, 139.4, 136.4, 134.9, 129.0, 128.6, 128.5, 126.3, 125.2, 119.8, 65.7, 38.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3329, 2971, 1700, 1592, 1518, 1494, 1306, 1285, 1231, 1091, 1077, 824, 693; **HRMS (ESI)** Calcd $C_{17}H_{17}{}^{35}ClNO_2$ [M + H]$^+$: 302.0942, found 302.0945.



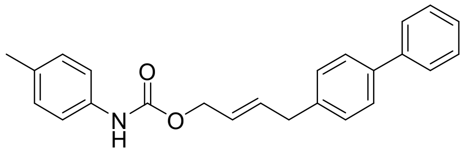
(*E*)-4-(4-Methoxyphenyl)but-3-en-1-yl (4-(trifluoromethoxy)phenyl)carbamate (1d): Synthesized using general procedure C starting from (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol and 4-(trifluoromethoxy)aniline as a white solid; m.p. 91 – 92 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.89 – 6.80 (m, 2H), 6.71 (s, 1H), 6.01 – 5.88 (m, 1H), 5.71 – 5.58 (m, 1H), 4.64 (d, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 3.35 (d, *J* = 6.6 Hz, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 158.1, 153.2, 144.7, 136.5, 135.4, 131.5, 129.5, 124.8, 121.8, 120.5 (q, *J* = 256.5 Hz), 119.6, 113.9, 65.8, 55.2, 37.7; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -58.20 (s, 3F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 3326, 3023, 1692, 1593, 1520, 1405, 1310, 1290, 1227, 1107, 1016, 814, 736; **HRMS (ESI)** Calcd $C_{19}H_{19}F_3NO_4$ [M + H]$^+$: 382.1261, found 382.1261.



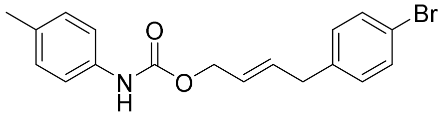
(*E*)-4-(4-Methoxyphenyl)but-2-en-1-yl benzo[d][1,3]dioxol-5-ylcarbamate (1e): Synthesized using general procedure C starting from (*E*)-4-(4-methoxyphenyl)but-2-en-1-ol and 5-isocyanatobenzo[d][1,3]dioxole as a white solid; m.p. 103 – 104 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.29 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.79 – 6.66 (m, 2H), 6.54 (s, 1H), 6.04 – 5.88 (m, 3H), 5.67 (dt, *J* = 13.7, 5.6 Hz, 1H), 4.65 (d, *J* = 6.1 Hz, 2H), 3.82 (s, 3H), 3.38 (d, *J* = 6.5 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 158.1, 153.5, 148.0, 143.8, 135.2, 132.1, 131.6, 129.6, 125.1, 113.9, 108.1, 101.3, 65.7, 55.3, 37.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3334, 2963, 1698, 1598, 1532, 1458, 1315, 1223, 1051, 817, 675; **HRMS (ESI)** Calcd $C_{19}H_{20}NO_5$ [M + H]$^+$: 342.1336, found 342.1330.



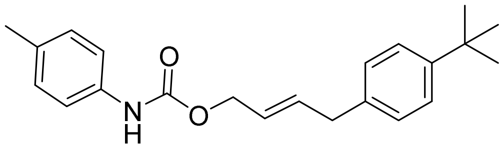
(*E*)-4-(4-Methoxyphenyl)but-2-en-1-yl p-tolylcarbamate (1f): Synthesized using general procedure C starting from (*E*)-4-(4-methoxyphenyl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 78 – 79°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 (d, *J* = 7.0 Hz, 2H), 7.13 – 7.07 (m, 4H), 6.90 – 6.76 (m, 2H), 6.55 (s, 1H), 6.00 – 5.87 (m, 1H), 5.71 – 5.59 (m, 1H), 4.62 (dd, *J* = 6.3, 0.8 Hz, 2H), 3.78 (s, 3H), 3.34 (d, *J* = 6.7 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.0, 153.4, 135.2, 135.01, 133.0, 131. 6, 129.5, 129.4, 125.1, 118.7, 113. 9, 65.5, 55.3, 37.7, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3320, 2928, 1725, 1591, 1512, 1312, 1233, 1039, 820, 765; **HRMS (ESI)** Calcd $C_{19}H_{22}NO_3$ $[M + H]^+$: 312.1594, found 312.1589.



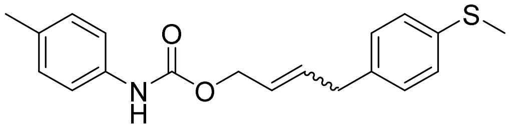
(*E*)-4-([1,1'-Biphenyl]-4-yl)but-2-en-1-yl p-tolylcarbamate (1g): Synthesized using general procedure C starting from (*E*)-4-([1,1'-biphenyl]-4-yl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 98 – 99 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 1H), 6.14 – 5.97 (m, 1H), 5.83 – 5.72 (m, 1H), 4.71 (d, *J* = 6.2 Hz, 2H), 3.50 (d, *J* = 6.7 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.5, 141.0, 139.3, 138.7, 135.3, 134.4, 133.1, 129.6, 129.1, 128.8, 127.3, 127.2, 127.1, 125.7, 118.8, 65.5, 38.3, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3327, 2947, 1700, 1596, 1539, 1485, 1410, 1315, 1294, 1123, 846, 763; **HRMS (ESI)** Calcd $C_{24}H_{24}NO_2$ $[M + H]^+$: 358.1802, found 358.1804.



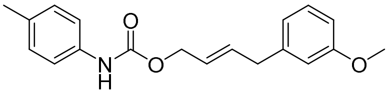
(*E*)-4-(4-Bromophenyl)but-2-en-1-yl p-tolylcarbamate (1h): Synthesized using general procedure C starting from 4-(4-bromophenyl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 112 – 113 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.35 (m, 2H), 7.28 – 7.20 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.56 (s, 1H), 6.47 – 6.33 (m, 0.05H)/6.00 – 5.82 (m, 0.95H), 6.25 – 6.11 (m, 0.05H)/5.73 – 5.56 (m, 0.95H), 4.62 (d, *J* = 5.6 Hz, 2H), 3.34 (d, *J* = 6.6 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.4, 138.5, 135.2, 133. 7, 133.1, 131.5, 130.3, 129.5, 126.0, 120.0, 118.8, 65.3, 38.0, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3314, 2902, 1724, 1698, 1600, 1540, 1515, 1380, 1233, 1071, 818, 683; **HRMS (ESI)** Calcd $C_{18}H_{19}{}^{79}BrNO_2$ [M + H]$^+$: 360.0594, found 360.0587.



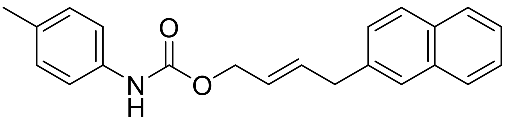
(*E*)-4-(4-(*tert*-Butyl)phenyl)but-2-en-1-yl p-tolylcarbamate (1i): Synthesized using general procedure C starting from (*E*)-4-(4-(tert-butyl)phenyl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 98 – 99 °C; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.40 – 7.33 (m, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.09 (m, 4H), 6.65 (s, 1H), 6.12 – 5.89 (m, 1H), 5.79 – 5.58 (m, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.32 (s, 3H), 1.33 (s, 9H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.5, 149.1, 136.5, 135.3, 134.8, 133.0, 129.5, 128.2, 125.4, 125.3, 118.8, 65.5, 38.2, 34.4, 31.4, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3336, 2975, 1650, 1599, 1524, 1493, 1441, 1319, 1214, 1182, 757, 700; **HRMS (ESI)** Calcd $C_{22}H_{28}NO_2$ [M + H]$^+$: 338.2115, found 338.2108.



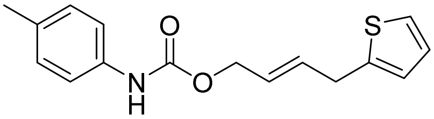
4-(4-(Methylthio)phenyl)but-2-en-1-yl p-tolylcarbamate (1j): Synthesized using general procedure C starting from 4-(4-(methylthio)phenyl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 85 – 86 °C, *E/Z* = 5:1; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.59 (d, *J* = 8.1 Hz, 0.32H), 7.35 (d, *J* = 8.1 Hz, 0.32H), 7.25 (d, *J* = 6.5 Hz, 1.87H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 3.84H), 6.59 (s, 1H), 6.00 – 5.86 (m, 1H), 5.77 – 5.59 (m, 1H), 4.68 – 4.58 (m, 2H), 3.47 (d, *J* = 6.6 Hz, 0.33H)/3.36 (d, *J* = 6.6 Hz, 1.74H), 2.72 (s, 0.57H)/2.47 (s, 2.69H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.4, 143.1, 136.6, 136.0, 135.2/134.3, 133.4/133.1, 129.7/129.6, 129.2, 127.2/126.5, 125.7/123.9, 118.8, 65.5/65.3, 44.0/38.1, 38.4/20.8, 16.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3317, 2894, 1694, 1616, 1514, 1494, 1437, 1365, 1244, 1033, 819, 655; **HRMS (ESI)** Calcd $C_{19}H_{22}NO_2S$ [M + H]$^+$: 328.1366, found 328.1368.



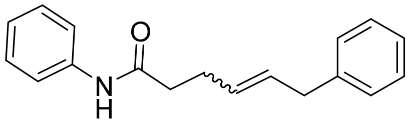
(*E*)-4-(3-Methoxyphenyl)but-2-en-1-yl p-tolylcarbamate (1k): Synthesized using general procedure C starting from (*E*)-4-(3-methoxyphenyl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 103 – 104 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 – 7.27 (m, 3H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.87 – 6.78 (m, 3H), 6.71 (s, 1H), 6.09 – 5.92 (m, 1H), 5.81 – 5.67 (m, 1H), 4.69 (d, *J* = 6.2 Hz, 2H), 3.85 (s, 3H), 3.44 (d, *J* = 6.7 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.8, 153.5, 141.3, 135.3, 134.4, 133.1, 129.6, 129.5, 125.7, 121.0, 118.8, 114.4, 111.6, 65.5, 55.2, 38.7, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3317, 2964, 1736, 1712, 1608, 1590, 1399, 1358, 1214, 1109, 830, 654; **HRMS (ESI)** Calcd $C_{19}H_{22}NO3$ [M + H]$^+$: 312.1594, found 312.1601.



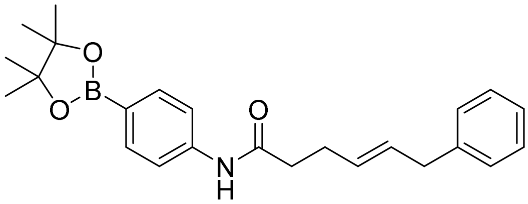
(*E*)-4-(Naphthalen-2-yl)but-2-en-1-yl *p*-tolylcarbamate (1l): Synthesized using general procedure C starting from (*E*)-4-(naphthalen-2-yl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 101 – 102 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 – 7.71 (m, 3H), 7.61 (s, 1H), 7.51 – 7.37 (m, 2H), 7.31 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.27 – 7.17 (m, 2H), 7.13 – 7.05 (m, 2H), 6.55 (s, 1H), 6.13 – 5.92 (m, 1H), 5.80 – 5.59 (m, 1H), 4.65 (dd, *J* = 6.3, 0.8 Hz, 2H), 3.56 (d, *J* = 6.7 Hz, 2H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.4, 137.0, 135.2, 134.4, 133.6, 133.0, 132.1, 129.5, 128.1, 127.6, 127.5, 127.3, 126.7, 126.0, 125.8, 125.4, 118.8, 65.5, 38.8, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3317, 2964, 1712, 1509, 1466, 1399, 1358, 1315, 1143, 858, 654; **HRMS (ESI)** Calcd $C_{22}H_{22}NO_2$ [M + H]$^+$: 332.1645, found 332.1644.



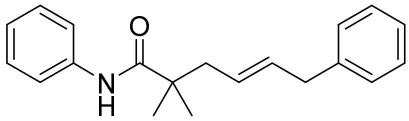
(*E*)-6-(Thiophen-2-yl)-N-(p-tolyl)hex-4-enamide (1m): Synthesized using general procedure C starting from (*E*)-4-(thiophen-2-yl)but-2-en-1-ol and 4-tolyl isocyanate as a white solid; m.p. 86 – 87 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.27 – 7.22 (m, 2H), 7.15 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.94 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.85 – 6.77 (m, 1H), 6.54 (s, 1H), 6.06 – 5.91 (m, 1H), 5.79 – 5.66 (m, 1H), 4.64 (d, *J* = 5.7 Hz, 2H), 3.60 (d, *J* = 6.6 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.3, 142.3, 135.2, 133.4, 133.0, 129.5, 126.9, 125.9, 124.8, 123.8, 118.8, 65.2, 32.6, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3328, 2922, 1698, 1598, 1531, 1328, 1225, 1050, 820, 691; **HRMS (ESI)** Calcd $C_{16}H_{18}NOS$ [M + H]$^+$: 288.1053, found 288.1053.



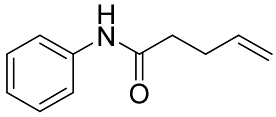
***N*,6-Diphenylhex-4-enamide (1n)**: Synthesized using general procedure A starting from 6-phenylhex-4-enoic acid and aniline as a white solid; m.p. 59 – 60 °C; *E/Z* = 3:1. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.88 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 0.55H)/7.50 (d, *J* = 8.1 Hz, 1.42H), 7.33 – 7.24 (m, 4H), 7.22 – 7.15 (m, 3H), 7.13 – 7.06 (m, 1H), 5.72 – 5.63 (m, 1H), 5.58 – 5.51 (m, 1H), 3.43 (d, *J* = 7.4 Hz, 0.54H)/3.33 (d, *J* = 6.8 Hz, 1.55H), 2.60 – 2.54 (m, 0.55H)/2.48 – 2.44 (m, 1.56H), 2.43 – 2.39 (m, 2H); **^{13}C NMR (150 MHz,** CDCl$_3$**)** δ 171.2/171.1, 140.7/140.5, 138.04/138.01, 130.7, 129.9/129.7, 128.9, 128.6/128.5, 128.4/128.4, 126.0/125.9, 124.2, 120.1, 39.0/33.5, 37.4/37.3, 28.5/23.5; FT-IR (thin film, KBr): ν (cm-1) 3300, 2973, 1697, 1654, 1597, 1530, 1490, 1437, 1390, 1257, 1079, 753, 694; **HRMS (ESI)** Calcd $C_{18}H_{20}NO$ [M + H]$^+$: 266.1539, found 266.1534.



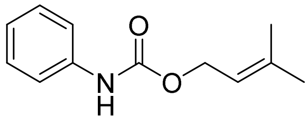
(*E*)-6-Phenyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hex-4-enamide (1o): Synthesized using general procedure A starting from 6-phenylhex-4-enoic acid and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline as a white solid; m.p. 89 – 90 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.21 – 7.12 (m, 3H), 5.76 – 5.65 (m, 1H), 5.61 – 5.51 (m, 1H), 3.34 (d, *J* = 6.6 Hz, 2H), 2.53 – 2.29 (m, 4H), 1.34 (s, 12H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 170.6, 140.5, 140.4, 135.8, 130.9, 129.6, 128.41, 128.39, 126.0, 118.5, 83.7, 38.9, 37.5, 28.2, 24.8; FT-IR (thin film, KBr): ν (cm-1) 3311, 2940, 1694, 1600, 1544, 1503, 1445, 1316, 1230, 1054, 1029, 749, 696; **HRMS (ESI)** Calcd $C_{24}H_{31}BNO_3$ [M + H]$^+$: 392.2392, found 392.2395.



(*E*)-2,2-Dimethyl-N,6-diphenylhex-4-enamide (1p): Synthesized using general procedure A starting from (*E*)-2,2-dimethyl-6-phenylhex-4-enoic acid and aniline as a white solid; m.p. 106 – 107 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.48 – 7.41 (m, 2H), 7.34 – 7.27 (m, 3H), 7.26 – 7.20 (m, 2H), 7.19 – 7.12 (m, 3H), 7.12 – 7.07 (m, 1H), 5.78 – 5.65 (m, 1H), 5.61 – 5.50 (m, 1H), 3.35 (d, *J* = 6.7 Hz, 2H), 2.35 (d, *J* = 7.3 Hz, 2H), 1.29 (s, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.5, 140.4, 137.9, 133.2, 129.0, 128.4, 127.0, 126.0, 124.2, 120.0, 44.0, 43.2, 39.1, 25.4; FT-IR (thin film, KBr): ν (cm-1) 3345, 2962, 1650, 1596, 1493, 1439, 1251, 996, 756, 689; **HRMS (ESI)** Calcd $C_{20}H_{24}NO$ [M + H]$^+$: 294.1852, found 294.1855.

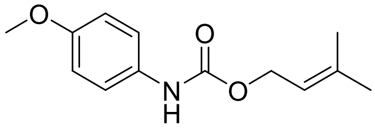


***N*-Phenylpent-4-enamide (1q)**: Synthesized using general procedure A starting from pent-4-enoic acid and aniline as a white solid; m.p. 89 – 90 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.35 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.98 – 5.76 (m, 1H), 5.12 (d, *J* = 17.3 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 2.57 – 2.41 (m, 4H); **^{13}C NMR (150 MHz, CDCl3)** δ 170.8, 137.9, 136.9, 129.0, 124.3, 119.95, 115.9, 36.8, 29.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 2928, 1750, 1722, 1597, 1521, 1500, 1404, 1234, 1209, 1127, 1065, 843, 761, 693; **HRMS (ESI)** Calcd $C_{11}H_{13}NO_2Na$ [M + Na]$^+$: 198.0889, found 198.0893.

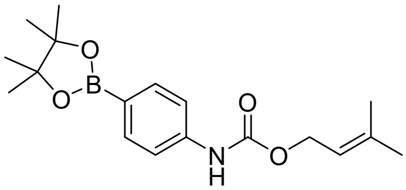


3-Methylbut-2-en-1-yl phenylcarbamate (7a): Prepared using general procedure C from prenol and aniline. White solid, m.p. 64 – 65 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 5.48 – 5.34 (m, 1H), 4.67 (d, *J* = 7.2 Hz, 2H), 1.78 (s, 3H), 1.75 (s, 3H); **^{13}C NMR**

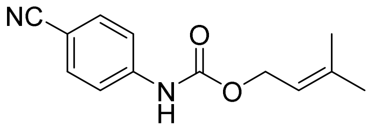
(150 MHz, CDCl3) δ 153.6, 139.4, 137.9, 129.0, 123.3, 118.7, 118.6, 62.0, 25.8, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3305, 2973, 1698, 1598, 1538, 1444, 1302, 1231, 1050, 1028, 859, 743, 696; **HRMS (ESI)** Calcd $C_{12}H_{15}NO_2Na$ [M + Na]$^+$: 228.0995, found 228.0994.



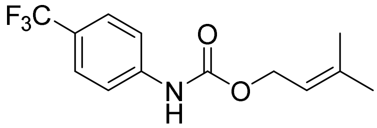
3-Methylbut-2-en-1-yl(4-methoxyphenyl) carbamate (7b): Prepared using general procedure C from prenol and *p*-anisidine. White solid, m.p. 84 – 85 °C; **^{1}H NMR (400 MHz, CDCl3)** δ 7.27 (d, *J* = 9.3 Hz, 2H), 6.90 (s, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.37 (t, 1H), 4.64 (d, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H); **^{13}C NMR (101 MHz, CDCl3)** δ 155.9, 154.3, 120.8, 119.0, 114.2, 61.9, 55.5, 25.7, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3325, 2916, 1691, 1604, 1540, 1513, 1446, 1320, 1176, 1057, 987, 829, 770; **HRMS (ESI)** Calcd $C_{13}H_{17}NO_3Na$ [M + Na]$^+$: 258.1101, found 258.1098.



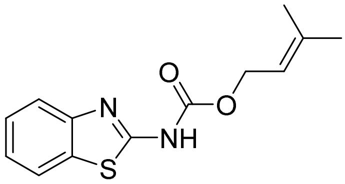
3-Methylbut-2-en-1-yl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (7c): Prepared using general procedure C from prenol and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline. White solid, m.p. 69 – 70 °C; **^{1}H NMR (400 MHz, CDCl3)** δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 6.67 (s, 1H), 5.39 (t, 1H), 4.66 (d, *J* = 6.9 Hz, 2H), 1.78 (s, 3H), 1.74 (s, 3H), 1.33 (s, 12H); **^{13}C NMR (150 MHz, CDCl3)** δ 153.2, 140.6, 139.5, 135.8, 118.6, 117.3, 83.6, 62.0, 25.8, 24.8, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3273, 2976, 1697, 1592, 1533, 1360, 1313, 1282, 1184, 1091, 963, 830, 654; **HRMS (ESI)** Calcd $C_{18}H_{26}BNO_4Na$ [M + Na]$^+$: 354.1847, found 354.1845.



3-Methylbut-2-en-1-yl (4-cyanophenyl) carbamate (7d): Prepared using general procedure C from prenol and 4-aminobenzonitrile. White solid, m.p. 86 – 87 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 6.94 (s, 1H), 5.38 (t, 1H), 4.68 (d, *J* = 7.3 Hz, 2H), 1.77 (s, 3H), 1.74 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.0, 142.2, 140.0, 133.3, 118.9, 118.2, 118.1, 106.1, 62.5, 25.8, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3351, 2931, 2219, 1728, 1690, 1595, 1523, 1313, 1293, 1224, 1055, 868, 834, 756; **HRMS (ESI)** Calcd $C_{13}H_{14}N_2O_2Na$ [M + Na]$^+$: 253.0947, found 253.0945.

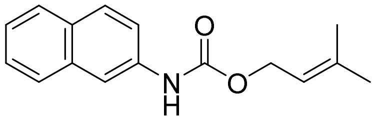


3-Methylbut-2-en-1-yl (4-(trifluoromethyl)phenyl)carbamate (7e): Synthesized using General Procedure C starting from prenol and *p*-trifluoromethylaniline as a white solid, m.p. 86 – 87 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 5.39 (t, *J* = 7.3 Hz, 1H), 4.69 (d, *J* = 7.3 Hz, 2H), 1.77 (s, 3H), 1.75 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.2, 141.1, 139.9,, 126.3 (q, *J* = 3.5 Hz), 125.1 (q, *J* = 32.6 Hz), 125.0 (q, *J* = 271.4 Hz), 118.3, 118.0, 62.3, 25.8, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3316, 2922, 1692, 1618,1600, 1542, 1506, 1466, 1325, 1233, 1111, 1069, 836, 769, 650; **HRMS (ESI)** Calcd $C_{13}H_{14}F_3NO_2Na$ [M + Na]$^+$: 296.0869, found 296.0861.

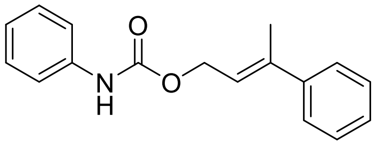


3-Methylbut-2-en-1-yl benzo[d]thiazol-2-ylcarbamate (7f): Synthesized using General Procedure C starting from prenol and benzo[d]thiazol-2-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.88 (s, 1H), 8.31 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.35–7.26 (m, 1H), 7.18 (s, 1H), 5.40 (t, *J* = 7.2 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 2H), 1.77 (s, 3H), 1.75 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.8, 152.9, 149.4, 139.6, 136.0, 135.0, 123.6, 118.6, 118.2, 111.0, 62.3, 25.8, 18.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3294, 2983, 1699, 1601, 1538, 1440, 1315, 1225, 736, 695; **HRMS (ESI)**

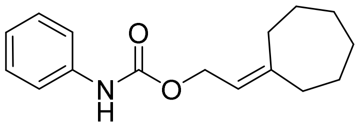
Calcd $C_{13}H_{14}N_2O_2NaS$ [M + Na]$^+$: 285.0668, found 285.0662.



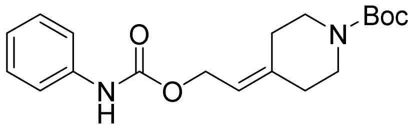
3-Methylbut-2-en-1-yl naphthalen-2-ylcarbamate (7g): Prepared using general procedure C from prenol and naphthalen-2-amine. White solid, m.p. 78 – 79 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 3H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.34 (m, 2H), 6.77 (s, 1H), 5.44 (t, *J* = 7.3 Hz, 1H), 4.72 (d, *J* = 7.3 Hz, 2H), 1.80 (s, 3H), 1.78 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.6, 139.5, 135.4, 133.9, 130.1, 128.8, 127.5, 127.4, 126.5, 124.6, 119.1, 118.7, 114.7, 62.1, 25.8, 18.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3315, 2971, 1699, 1633, 1585, 1538, 1504, 1433, 1358, 1212, 1054, 952, 884, 744; **HRMS (ESI)** Calcd $C_{16}H_{17}NO_2Na$ [M + Na]$^+$: 278.1151, found 278.1150.



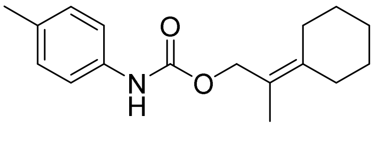
(*E*)-3-Phenylbut-2-en-1-yl phenylcarbamate (7h): Synthesized using General Procedure C starting from (*E*)-3-phenylbut-2-en-1-ol and 4-aminobenzonitrile as a white solid, m.p. 81 – 82 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.38 (m, 4H), 7.38 – 7.27 (m, 5H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 5.96 (t, *J* = 6.9, 1.0 Hz, 1H), 4.90 (d, *J* = 6.9 Hz, 2H), 2.16 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.6, 140.4, 137.9, 129.1, 128.3, 127.6, 125.9, 123.5, 121.5, 118.8, 62.3, 16.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3335, 2928, 1702, 1598, 1539, 1445, 1312, 1213, 1050, 754 695; **HRMS (ESI)** Calcd $C_{17}H_{17}NO_2Na$ [M + Na]$^+$: 290.1151, found 290.1148.



2-Cycloheptylideneethyl phenylcarbamate (7i): Prepared using general procedure C from 2-cycloheptylideneethan-1-ol and aniline. White solid, m.p. 102 – 103 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 5.39 (t, *J* = 7.1 Hz, 1H), 4.68 (d, *J* = 7.1 Hz, 2H), 2.39 – 2.32 (m, 2H), 2.32 – 2.25 (m, 2H), 1.64 – 1.57 (m, 4H), 1.57 – 1.49 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.6, 148.5, 138.0, 129.0, 123.3, 118.7, 118.6, 61.8, 37.7, 30.0, 29.7, 28.9, 28.6, 27.2; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3317, 2922, 2852, 1702, 1600, 1536, 1501, 1443, 1312, 1213, 1052, 1027, 751, 691; **HRMS (ESI)** Calcd $C_{16}H_{21}NO_2Na$ [M + Na]$^+$: 282.1465, found 282.1464.



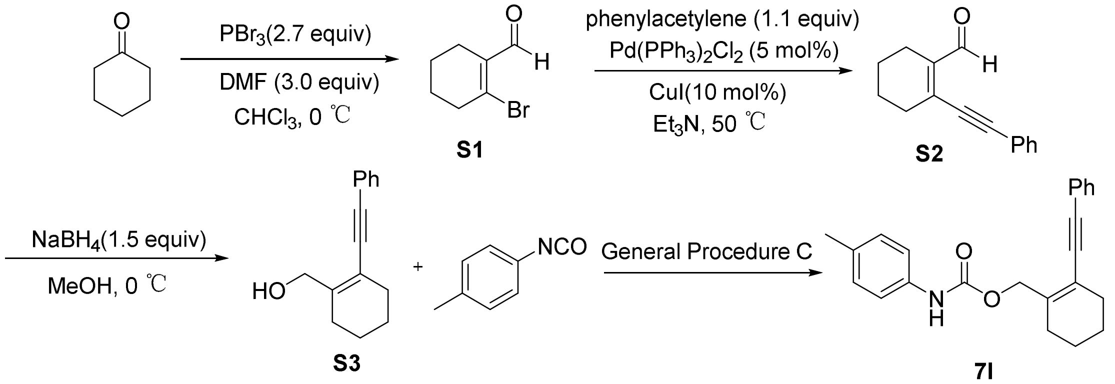
***tert*-Butyl 4-(2-((phenylcarbamoyl)oxy)ethylidene)piperidine-1-carboxylate (7j)**: Synthesized using General Procedure C starting from tert-butyl 4-(2-hydroxyethylidene)piperidine-1-carboxylate and aniline as a white solid, m.p. 125 – 126 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.65 (s, 1H), 5.47 (t, *J* = 7.2 Hz, 1H), 4.69 (d, *J* = 7.2 Hz, 2H), 3.52 – 3.35 (m, 4H), 2.36 – 2.30 (m, 2H), 2.25 – 2.17 (m, 2H), 1.47 (s, 9H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 154.7, 153.4, 142.3, 137.8, 129.1, 129.0, 123.4, 118.6, 118.0, 79.7, 60.7, 35.7, 28.7, 28.4; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3304, 2976, 1726, 1653, 1601, 1533, 1433, 1312, 1220, 1163, 1054, 1032, 862, 756, 670; **HRMS (ESI)** Calcd $C_{19}H_{26}N_2O_4Na$ [M + Na]$^+$: 369.1785, found 369.1784.



2-Cyclohexylidenepropyl p-tolylcarbamate (7k): Synthesized using General Procedure C starting from 2-cyclohexylidenepropan-1-ol and 1-isocyanato-4-methylbenzene as a white solid, m.p. 76 – 77 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.29 – 7.21 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.56 (s, 1H), 4.69 (s, 2H), 2.29 (s, 3H), 2.29 – 2.24 (m, 2H), 2.23 – 2.17 (m, 2H), 1.76 (s, 3H), 1.59 – 1.46 (m, 6H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.9, 140.6, 135.4, 132.8, 129.5, 119.6, 118.7, 65.8, 30.8, 30.5, 28.3, 27.8, 26.7, 20.7, 16.4; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3322, 2980, 2921, 1692, 1601, 1541, 1405, 1314, 1231, 1052, 961, 818, 686; **HRMS**

(ESI) Calcd $C_{17}H_{23}NO_2Na$ $[M + Na]^+$: 296.1621, found 296.1622.

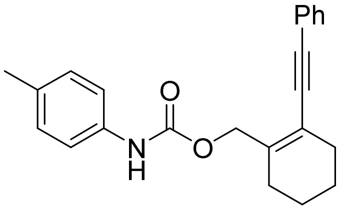
3.10 Preparation of compound 7l



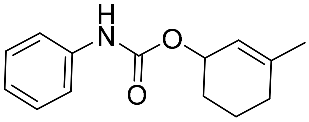
1) To a mixture of DMF (3.0 equiv.) and chloroform (1 M) was added PBr_3 (2.7 equiv.) dropwise at 0 °C, and the mixture was stirred for 60 min before the addition of cyclohexanone (1.0 equiv.). The resulting solution was stirred for 8 h at room temperature, before it was poured into 50 ml water, neutralized with solid $NaHCO_3$, and extracted with DCM. The extract was washed with NaCl (aq), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column to afford **S1** as a yellow oil.[8]

2) To a solution of **S1** (1.0 equiv.) in Et_3N (0.08 M), was added $(PPh_3)_2PdCl_2$ (0.05 equiv.) and phenylacetylene (1.1 equiv.). The solution was stirred at room temperature for 15 min before addition of CuI (0.1 equiv.). The resulting mixture was stirred at 50 °C for 12 h. The reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was concentrated under reduced pressure. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S2** as a yellow oil.[9]

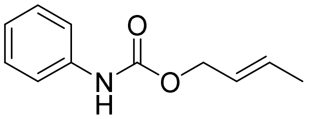
3) To a mixture of MeOH (0.1M) and **S2** was added $NaBH_4$ (1.5 equiv.) at 0 °C. The resulting solution was stirred for 8 h at room temperature. Quench the remaining $NaBH_4$ with ice water (10 ml). The solvent was removed *in vacuo*， the residue was extracted with EtOAc (25 mL × 3). After concentration of the organic phase, the residue was directly used in next step without further purification.



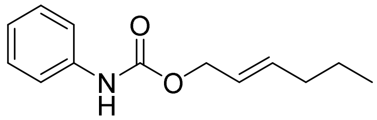
(2-(Phenylethynyl)cyclohex-1-en-1-yl)methyl p-tolylcarbamate (7l): Synthesized using general procedure C starting from **S3** and 1-isocyanato-4-methylbenzene as a white solid, m.p. 96 – 97 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.47 – 7.41 (m, 2H), 7.32 – 7.25 (m, 5H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.58 (s, 1H), 4.99 (s, 2H), 2.34 – 2.30 (m, 2H), 2.30 (s, 3H), 2.25 – 2.18 (m, 2H), 1.74 – 1.63 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.7, 139.3, 135.3, 132.9, 131.4, 129.5, 128.2, 128.0, 123.4, 119.9, 118.7, 93.2, 88.1, 67.0, 30.2, 27.0, 22.1, 22.0, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3297, 2971, 1697, 1601, 1539, 1449, 1321, 1225, 1053, 739, 698; **HRMS (ESI)** Calcd $C_{23}H_{24}NO_2$ [M + H]$^+$: 346.1802, found 346.1802.



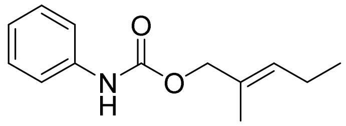
3-Methylcyclohex-2-en-1-yl phenylcarbamate (7m) : Prepared using general procedure C from 3-methylcyclohex-2-en-1-ol and aniline, White solid, m.p. 74 – 75 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.29 (t, 2H), 7.04 (t, 1H), 6.65 (s, 1H), 5.60 – 5.54 (m, 1H), 5.27 (d, *J* = 3.0 Hz, 1H), 2.07 – 1.89 (m, 2H), 1.87 – 1.76 (m, 3H), 1.73 (s, 3H), 1.68 – 1.62 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.4, 141.4, 138.1, 129.0, 123.2, 120.1, 118.6, 69.6, 30.0, 28.2, 23.8, 19.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3279, 2932, 1687, 1596, 1537, 1500, 1442, 1299, 1232, 1026, 930, 746, 693; **HRMS (ESI)** Calcd $C_{14}H_{17}NO_2Na$ [M + Na]$^+$: 254.1151, found 254.1142.



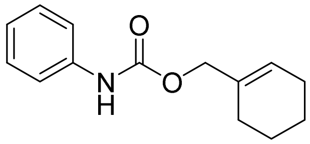
(*E*)-But-2-en-1-yl phenylcarbamate (7n): Prepared using general procedure C from (*E*)-but-2-en-1-ol and aniline. White solid, m.p. 79 – 80 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 5.96 – 5.74 (m, 1H), 5.72 – 5.58 (m, 1H), 4.60 (d, *J* = 6.5 Hz, 2H), 1.74 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.4, 137.9, 131.6, 129.0, 125.2, 123.4, 118.6, 65.9, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3296, 2970, 1697, 1597, 1538, 1492, 1440, 1307, 1226, 1051, 966, 744, 694; **HRMS (ESI)** Calcd $C_{11}H_{13}NO_2Na$ [M + Na]$^+$: 214.0838, found 214.0838.



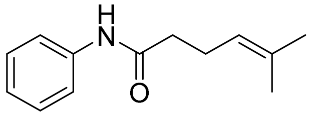
(*E*)-Hex-2-en-1-yl phenylcarbamate (7o): Prepared using general procedure C from (*E*)-hex-2-en-1-ol and aniline. White solid, m.p. 59 – 60 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 5.89 – 5.76 (m, 1H), 5.70 – 5.55 (m, 1H), 4.61 (d, *J* = 6.4 Hz, 2H), 2.05 (q, *J* = 6.8 Hz, 2H), 1.49 – 1.35 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.4, 138.0, 136.6, 129.0, 124.1, 123.4, 118.7, 66.0, 34.3, 22.1, 13.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3308, 2955, 1695, 1603, 1540, 1494, 1440, 1313, 1222, 1052, 975, 750, 691; **HRMS (ESI)** Calcd $C_{13}H_{17}NO_2Na$ [M + Na]$^+$: 242.1151, found 242.1148.



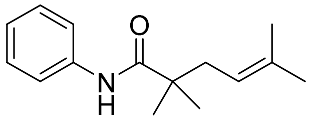
(*E*)-2-Methylpent-2-en-1-yl phenylcarbamate (7p): Prepared using general procedure C from (*E*)-2-methylpent-2-en-1-yl phenylcarbamate and aniline. White solid, m.p. 62 – 63 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.73 (s, 1H), 5.52 (t, *J* = 7.1, 0.9 Hz, 1H), 4.56 (s, 2H), 2.18 – 1.98 (m, 2H), 1.69 (s, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.6, 138.0, 131.8, 129.5, 129.1, 123.4, 118.7, 71.1, 21.0, 13.8, 13.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3277, 2936, 1737, 1685, 1598, 1539, 1435, 1298, 1228, 1045, 751, 695; **HRMS (ESI)** Calcd $C_{13}H_{17}NO_2Na$ [M + Na]$^+$: 242.1151, found 242.1150.



Cyclohex-1-en-1-ylmethyl phenylcarbamate (7q): Prepared using general procedure C from cyclohex-1-en-1-ylmethanol and aniline. White solid, m.p. 95 – 96 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.11 – 6.98 (m, 1H), 6.78 (s, 1H), 5.77 (s, 1H), 4.53 (s, 2H), 2.11 – 1.93 (m, 4H), 1.69 – 1.54 (m, 4H); **^{13}C NMR (150MHz, CDCl$_3$)** δ 153.6, 138.0, 133.0, 129.0, 126.4, 123.3, 118.6, 69.6, 25.9, 25.0, 22.4, 22.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3292, 2929, 1694, 1599, 1543, 1440, 1309, 1230, 1052, 752, 703; **HRMS (ESI)** Calcd $C_{14}H_{17}NO_2Na$ [M + Na]$^+$: 254.1151, found 254.1154.

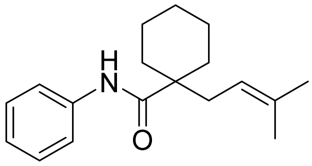


5-Methyl-*N*-phenylhex-4-enamide (7r): Prepared using general procedure A from 5-methylhex-4-enoic acid and aniline. White solid, m.p. 87 – 88 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.38 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.16 (t, *J* = 6.2 Hz, 1H), 2.46 – 2.33 (m, 4H), 1.71 (s, 3H), 1.65 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.1, 138.0, 133.8, 129.0, 124.2, 122.6, 119.8, 37.7, 25.8, 24.2, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3296, 2929, 1665, 1600, 1537, 1496, 1439, 1309, 1240, 1182, 954, 853, 749, 690; **HRMS (ESI)** Calcd $C_{13}H_{17}NONa$ [M + Na]$^+$: 226.1202, found 226.1201.

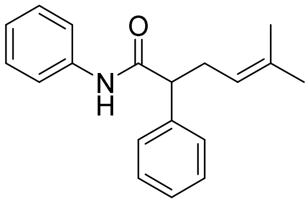


2,2,5-Trimethyl-*N*-phenylhex-4-enamide (7s): Prepared using general procedure B from 2,2,5-trimethylhex-4-enoic acid and aniline. White solid, m.p. 77 – 78 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.41 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.22 (t, *J* = 7.6 Hz, 1H), 2.31 (d, *J* = 7.6 Hz, 2H), 1.74 (s, 3H), 1.64 (s, 3H), 1.28 (s, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 175.9, 138.1, 135.3, 129.0, 124.1, 119.9, 43.4, 39.1, 26.1, 25.4, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3300, 2973, 1697, 1654, 1597, 1530, 1490, 1437, 1390, 1257, 1079, 753, 694; **HRMS**

(ESI) Calcd $C_{15}H_{21}NONa$ [M + Na]$^+$: 254.1515, found 254.1514.

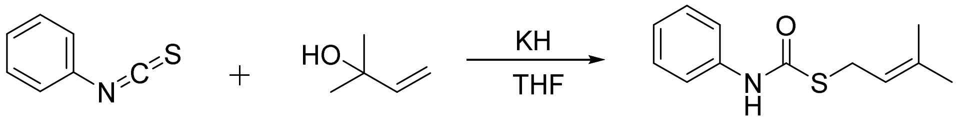


1-(3-Methylbut-2-en-1-yl)-*N*-phenylcyclohexane-1-carboxamide (7t): Synthesized using general procedure B starting from 1-(3-methylbut-2-en-1-yl)cyclohexane -1-carboxylic acid and aniline as a white solid, m.p. 82 – 83 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52 – 7.45 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.19 (t, *J* = 7.8 Hz, 1H), 2.26 (d, *J* = 7.8 Hz, 2H), 2.10 – 1.99 (m, 2H), 1.71 (s, 3H), 1.67 – 1.59 (m, 3H), 1.58 (s, 3H), 1.46 (m, 5H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 174.6, 138.2, 135.4, 129.0, 124.0, 120.0, 119.1, 47.8, 38.5, 34.2, 26.1, 26.0, 23.0, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3353, 2916, 2855, 1732, 1657, 1599, 1530, 1490, 1435, 1379, 1300, 1238, 1074, 755, 694; **HRMS (ESI)** Calcd $C_{18}H_{25}NONa$ [M + Na]$^+$: 294.1828, found 294.1826.

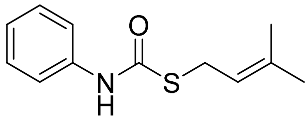


5-Methyl-*N*,2-diphenylhex-4-enamide (7u): Prepared using general procedure B from 5-methyl-2-phenylhex-4-enoic acid and aniline. White solid, m.p. 86 – 87 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.27 – 7.19 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.08 (t, *J* = 7.1 Hz, 1H), 3.53 (t, *J* = 7.5 Hz, 1H), 2.97 – 2.78 (m, 1H), 2.62 – 2.47 (m, 1H), 1.62 (s, 3H), 1.55 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.8, 139.7, 138.0, 134.0, 128.9, 128.9, 128.1, 127.4, 124.2, 121.3, 120.0, 54.4, 32.1, 25.8, 17.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3353, 2916, 2855, 1732, 1657, 1599, 1530, 1490, 1435, 1379, 1300, 1238, 1074, 755, 694; **HRMS (ESI)** Calcd $C_{19}H_{21}NONa$ [M + Na]$^+$: 302.1515, found 302.1514.

3.11 Preparation of compound 7v[5]

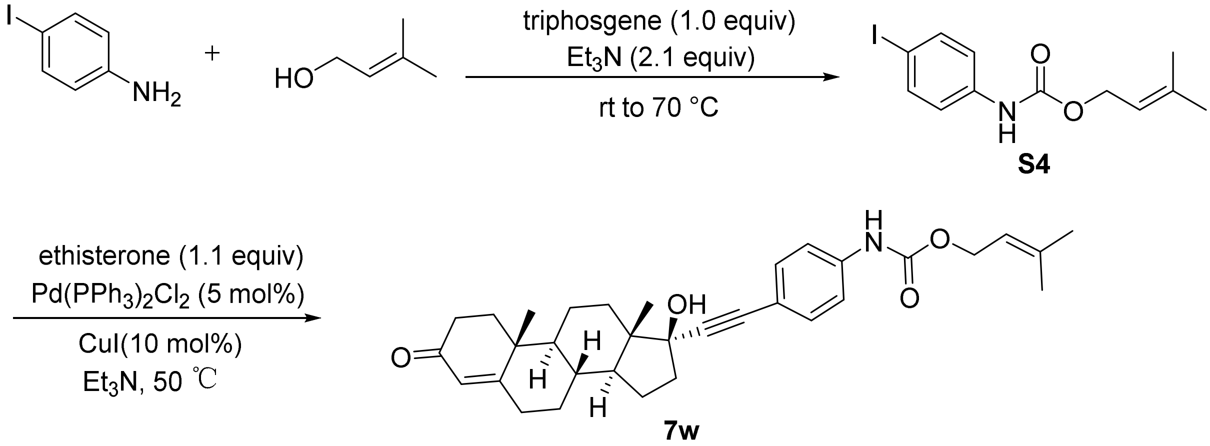


A flame dried round-bottomed flask was charged with dry, oil-free KH (672 mg, 16.75 mmol), THF (20 mL) was added, and the suspension was cooled to 0 ºC. 2-methyl-3-buten-2-ol (1.75 mL, 16.75 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. Phenyl isothiocyanate (2 mL, 16.75 mmol) was then added and the reaction was stirred for 6 hours or until complete consumption of alcohol was seen by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with Et_2O three times. The combined organic layers were then washed with brine, dried with Na_2SO_4, and concentrated to yield the crude product, which was then purified by recrystallization from petroleum ether and ethyl acetate to give 1.2 g (44% yield).



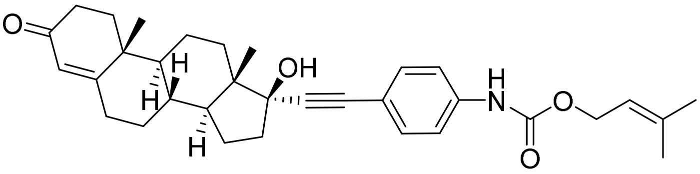
***S*-(3-Methylbut-2-en-1-yl) phenylcarbamothioate (7v)**: yellow solid, m.p. 46 – 47 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 2H), 5.31 (t, *J* = 7.8 Hz, 1H), 3.64 (d, *J* = 7.8 Hz, 2H), 1.73 (s, 3H), 1.71 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.9, 137.7, 136.7, 129.2, 129.1, 124.4, 119.8, 119.1, 28. 5, 25.7, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3296, 2973, 2855, 1702, 1609, 1575, 1531, 1479, 1477, 1405, 1321, 1214, 1064, 862, 833, 769; **HRMS (ESI)** Calcd $C_{12}H_{15}NONaS$ $[M + Na]^+$: 244.0767, found 244.0765.

3.12 Preparation of compound 7w[9]

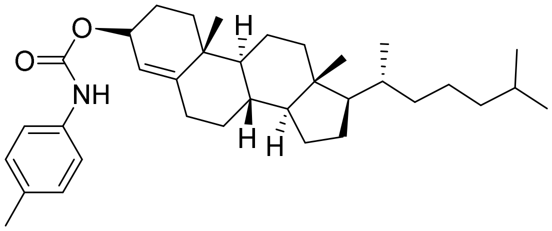


1) A flame dried round-bottomed flask was degassed, flushed with argon, and charged with triphosgene (1.49 g, 5.0 mmol) in THF (10 mL). Then, a solution of 4-iodoaniline (5.0 mmol) dissolved in THF (40 mL) was slowly dripped into the triphosgene solution. NEt_3 (1.5 mL, 10.5 mmol) was then added slowly to the reaction mixture after the aniline was added. The reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was then concentrated and the flask containing the resulting residue was degassed and acetonitrile (80 mL), Et_3N (1.5 mL, 10.5 mmol), and 3-methylbut-2-en-1-ol (6.0 mmol) were added. The reaction mixture was then stirred at 70 ºC for 8 hours. The reaction mixture was concentrated and the crude residue was purified by alumina column chromatography (PE/EA = 10 : 1) to give **S4** (80%, 4.0 mmol).

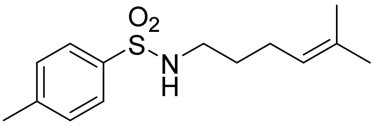
2) To a solution of **S4** (4.0 mmol, 1.0 equiv.) in Et_3N (50 ml), was added $(PPh_3)_2PdCl_2$ (140 mg, 0.05 equiv.) and phenylacetylene (1.37 g, 1.1 equiv.). The solution was stirred at room temperature for 15 min before addition of CuI (76 mg, 0.1 equiv.). The resulting mixture was stirred at 50 °C for 12 h. The reaction mixture was cooled to rt and filtered through Celite. The filtrate was concentrated under reduced pressure. The reaction mixture was concentrated and the crude residue was purified by alumina column chromatography to give **1w** (68% yield).



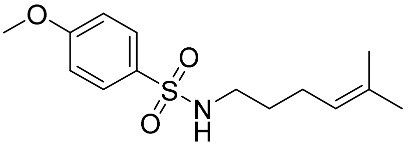
3-Methylbut-2-en-1-yl (4-(((*8R,9S,10R,13S,14S,17S*)-17-hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*1H*-cyclopenta[a]phenanthren-17-yl)ethynyl)phenyl)carbamate (7w): white solid; m.p. 255 – 256 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.33 (s, 4H), 6.84 (s, 1H), 5.72 (s, 1H), 5.41 – 5.33 (m, 1H), 4.65 (d, *J* = 7.3 Hz, 2H), 2.50 – 2.18 (m, 6H), 2.14 – 2.00 (m, 2H), 1.89 – 1.82 (m, 1H), 1.76 (s, 3H), 1.73 (s, 3H), 1.72 – 1.69 (m, 2H), 1.69 – 1.54 (m, 3H), 1.55 – 1.32 (m, 3H), 1.19 (s, 3H), 1.13 – 0.94 (m, 2H), 0.94 (d, *J* = 9.4 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 199.8, 171.5, 153.4, 139.5, 138.2, 132.5, 123.9, 118.6, 118.1, 117.3, 91.8, 85.8, 80.1, 62.2, 60.5, 53.5, 50.1, 47.2, 39.0, 38.7, 36.3, 35.7, 33.9, 32.8, 31.5, 25.8, 23.2, 21.1, 20.8, 18.1, 17.4, 14.2, 12.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2960, 1650, 1592, 1519, 1406, 1309, 1213, 1053, 833; **HRMS (ESI)** Calcd $C_{33}H_{42}NO_4$ [M + H]$^+$: 516.3108, found 516.3109.



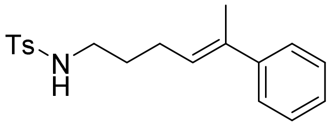
(*3R,8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*1H*-cyclopenta[a]phenanthren-3-yl p-tolylcarbamate (7x): Synthesized using general procedure C starting from allocholesterol and 4-tolyl isocyanate as a white solid; m.p. 159 – 160 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.49 (s, 1H), 5.31 (s, 1H), 5.27 – 5.18 (m, 1H), 2.30 (s, 3H), 2.26 – 2.15 (m, 1H), 2.09 – 1.96 (m, 3H), 1.89 – 1.78 (m, 1H), 1.78 – 1.69 (m, 2H), 1.66 – 1.53 (m, 3H), 1.54 – 1.41 (m, 3H), 1.41 – 1.30 (m, 5H), 1.30 – 1.20 (m, 2H), 1.19 – 1.08 (m, 4H), 1.07 (s, 3H), 1.00 – 0.93 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.7 Hz, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.81 – 0.73 (m, 1H), 0.68 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.5, 149.7, 135.4, 132.8, 129.5, 119.1, 118.7, 71.6, 56.1, 56.1, 54.1, 42.5, 39.8, 39.5, 37.3, 36.1, 35.9, 35.8, 34.9, 33.0, 32.3, 28.2, 28.0, 25.4, 24.2, 23.8, 22.8, 22.5, 21.0, 20.7, 18.9, 18.6, 12.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3388, 2928, 1720, 1522, 1400, 1208, 1045, 815, 765; **HRMS (ESI)** Calcd $C_{35}H_{54}NO_2$ [M + H]$^+$: 520.4149, found 520.4153.



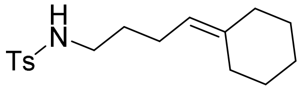
4-Methyl-N-(5-methylhex-4-en-1-yl)benzenesulfonamide (9a): Synthesized using general procedure F starting from 4-methylbenzenesulfonyl chloride and 5-methylhex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.68 (t, *J* = 6.0 Hz, 1H), 3.03 – 2.77 (m, 2H), 2.42 (s, 3H), 2.00 – 1.89 (m, 2H), 1.64 (s, 3H), 1.53 (s, 3H), 1.52 – 1.42 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.3, 137.0, 132.7, 129.7, 127.1, 123.0, 42.9, 29.6, 25.7, 25.1, 21.5, 17. 7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3280, 2925, 1599, 1436, 1322, 1155, 1093, 814, 661; **HRMS (ESI)** Calcd $C_{14}H_{21}NO_2SNa$ [M + Na]$^+$: 290.1185, found 290.1183.



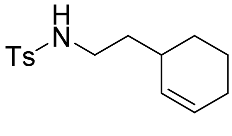
4-Methoxy-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (9b): Synthesized using general procedure F starting from 4-methoxybenzenesulfonyl chloride and 5-methylhex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.97 (t, *J* = 7.1 Hz, 1H), 4.75 (t, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 2.96 – 2.83 (m, 2H), 1.99 – 1.88 (m, 2H), 1.63 (s, 3H), 1.52 (s, 3H), 1.51 – 1.39 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 162.8, 132.7, 131.6, 129.2, 123.0, 114.2, 55.6, 42.9, 29.6, 25.7, 25.1, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3273, 2931, 1596, 1497, 1439, 1301, 1259, 1149, 1095, 1019, 903, 670; **HRMS (ESI)** Calcd $C_{14}H_{21}NO_3SNa$ [M + Na]$^+$: 306.1134, found 306.1132.



(*E*)-4-Methyl-*N*-(5-phenylhex-4-en-1-yl)benzenesulfonamide (9c): Synthesized using General Procedure F starting from 4-methylbenzenesulfonyl chloride and (*E*)-5-phenylhex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ7.76 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.28 (m, 6H), 7.25 – 7.19 (m, 1H), 5.62 (t, *J* = 7.2 Hz, 1H), 4.69 (t, *J* = 6.1 Hz, 1H), 3.07 – 2.92 (m, 2H), 2.41 (s, 3H), 2.25 – 2.13 (m, 2H), 1.97 (s, 3H), 1.71 – 1.57 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.6, 143.4, 136.9, 136.0, 129.7, 128.2, 127.1, 126.7, 126.6, 125.6, 42.9, 29. 5, 25.8, 21.5, 15.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3236, 2922, 1598, 1499, 1373, 1271, 1155, 1094, 972, 628; **HRMS (ESI)** Calcd $C_{19}H_{23}NO_2SNa$ [M + Na]$^+$: 352.1342, found 352.1340.

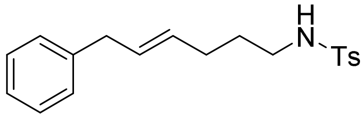


***N*-(4-Cyclohexylidenebutyl)-4-methylbenzenesulfonamide (9d)**: Synthesized using general procedure F starting from 4-methylbenzenesulfonyl chloride and 4-cyclohexylidenebutan-1-amine as a yellow oil. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.94 (t, *J* = 7.3 Hz, 1H), 4.43 (t, *J* = 6.0 Hz, 1H), 2.99 – 2.84 (m, 2H), 2.43 (s, 3H), 2.06 – 1.99 (m, 4H), 1.99 – 1.93 (m, 2H), 1.52 – 1.47 (m, 6H), 1.45 – 1.41 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 143.3, 141.0, 137.0, 129.6, 127.1, 119.5, 42.9, 37.1, 29.8, 28.6, 28.6, 27.7, 26.8, 24.1, 21.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3278, 2925, 1598, 1446, 1322, 1217, 1156, 1093, 813, 661; **HRMS (ESI)** Calcd $C_{17}H_{25}NO_2SNa$ [M + Na]$^+$: 330.1498, found 330.1499.

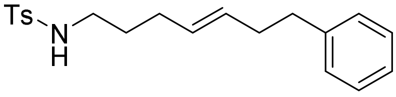


***N*-(2-(Cyclohex-2-en-1-yl)ethyl)-4-methylbenzenesulfonamide (9e)**: Synthesized using general procedure F starting from 4-methylbenzenesulfonyl chloride and 2-(cyclohex-2-en-1-yl)ethan-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.69 – 5.58 (m, 1H), 5.48 – 5.37 (m, 1H), 4.56 (t, *J* = 5.9 Hz, 1H), 3.10 – 2.89 (m, 2H), 2.42 (s, 3H), 2.16 – 2.02 (m, 1H), 1.98 – 1.86 (m, 2H), 1.76 – 1.58 (m, 2H), 1.55 – 1.37 (m, 3H), 1.19 – 1.05 (m, 1H);

^{13}C NMR (150 MHz, CDCl$_3$) δ 143.3, 136.9, 130.5, 129.7, 127.8, 127.1, 41.0, 35.8, 32.4, 28.5, 25.1, 21.5, 21.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3278, 2926, 1598, 1446, 1322, 1217, 1156, 1093, 813, 661; **HRMS (ESI)** Calcd $C_{15}H_{21}NO_2SNa$ [M + Na]$^+$: 302.1185, found 302.1189.



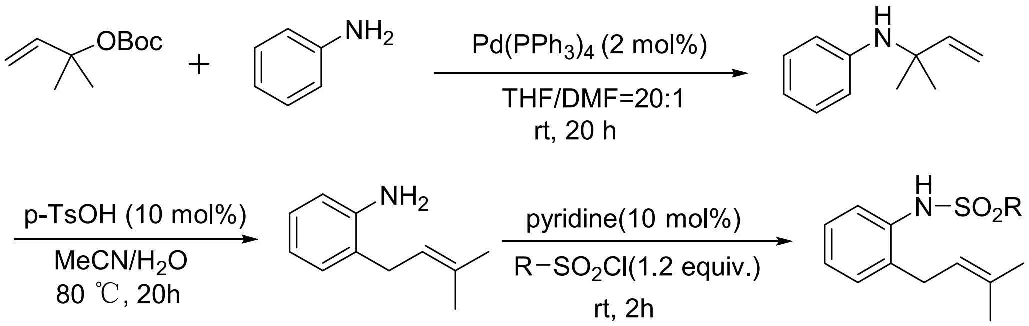
(*E*)-4-Methyl-*N*-(6-phenylhex-4-en-1-yl)benzenesulfonamide (9f): Synthesized using general procedure F starting from 4-methylbenzenesulfonyl chloride and (*E*)-6-phenylhex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.23 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 5.57 – 5.44 (m, 1H), 5.43 – 5.29 (m, 1H), 4.66 (t, *J* = 6.1 Hz, 1H), 3.28 (d, *J* = 6.6 Hz, 2H), 2.93 (dd, *J* = 13.5, 6.8 Hz, 2H), 2.40 (s, 3H), 2.00 (q, *J* = 7.0 Hz, 2H), 1.60 – 1.48 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.3, 140.7, 137.1, 130.2, 130.2, 129.7, 128.5, 128.4, 127.1, 126.0, 42.7, 39.0, 29.4, 29.2, 21.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3278, 2925, 1598, 1494, 1324, 1154, 1192, 960, 814, 661; **HRMS (ESI)** Calcd $C_{19}H_{23}NO_2SNa$ [M + Na]$^+$: 352.1342, found 352.1345.



(*E*)-4-Methyl-*N*-(7-phenylhept-4-en-1-yl)benzenesulfonamide (9g): Synthesized using general procedure F starting from 4-methylbenzenesulfonyl chloride and (*E*)-7-phenylhept-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.23 (m, 4H), 7.20 – 7.10 (m, 3H), 5.45 – 5.33 (m, 1H), 5.33 – 5.20 (m, 1H), 4.76 (t, *J* = 6.1 Hz, 1H), 2.88 (dd, *J* = 13.4, 6.8 Hz, 2H), 2.69 – 2.54 (m, 2H), 2.41(s, 3H), 2.25 (dd, *J* = 14.8, 7.1 Hz, 2H), 1.95 (q, *J* = 6.9 Hz, 2H), 1.57 – 1.42 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.3, 142.0, 137.1, 130.8, 129.7, 129.3, 128.5, 128.3, 127.1, 125.8, 42.6, 36.0, 34.3, 29.4, 29.2, 21.5; **HRMS (ESI)** Calcd $C_{20}H_{25}NO_2SNa$ [M + Na]$^+$: 366.1498, found 366.1499.

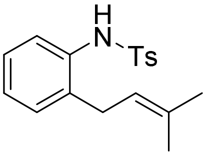
(*E*)-4-Methyl-*N*-(oct-4-en-1-yl)benzenesulfonamide (9h): Synthesized using general procedure F starting from 4-methylbenzenesulfonyl chloride and (*E*)-oct-5-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.39 – 5.17 (m, 2H), 4.97 (t, *J* = 6.1 Hz, 1H), 3.01 – 2.85 (m, 2H), 2.42 (s, 3H), 2.05 – 1.80 (m, 4H), 1.62 – 1.45 (m, 2H), 1.41 – 1.26 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.3, 137.0, 131.6, 129.7, 128.6, 127.1, 42.6, 34.6, 29.5, 29.3, 22.5, 21.5, 13.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3279, 2927, 1599, 1435, 1323, 1156, 1093, 968, 814, 660; **HRMS (ESI)** Calcd $C_{15}H_{23}NO_2SNa$ [M + Na]$^+$: 304.1342, found 304.1346.

3.13 Preparation of compound 9i and 9j

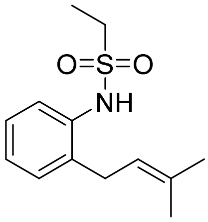


1) A solution of aniline (1.0 equiv.) and *tert*-butyl-(2-methylbut-3-en-2-yl) carbonate (1.4 equiv.) in THF/DMF = 20:1 (0.5 M) was treated with Pd(PPh$_3$)$_4$ (2 mol%) and stirred at room temperature for 20 h. The mixture was diluted with ethyl acetate (0.5 M) and washed with brine (15 mL), dried over Na$_2$SO$_4$, filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography to give aniline as a light-yellow oil (73%).[10]
2) To a solution of aniline (574 mg, 3.56 mmol) in MeCN: H$_2$O = 10:1 (0.3 M) under inert atmosphere was added *p*TsOH-H$_2$O (0.1 equiv), and it was heated at 80 °C overnight. After cooling to room temperature, washed with water (20 mL) and the aqueous layer was extracted with EtOAc (20 mL × 2). The combined organic layer was washed with brine (30 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The crude product was directly used in next step without further purification.[11]

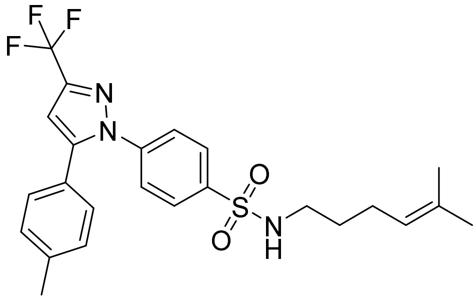
3) To a solution of the above crude material in pyridine (10 mol%) at room temperature under inert atmosphere was added sulfonyl chloride (1.2 equiv.). After one hour, EtOAc (20 mL) was added, and it was washed with 10% aq HCl (100 mL). The aqueous layer was extracted with EtOAc (20 mL × 2). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by flash chromatography to give target product.[11]



4-Methyl-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (9i): white solid; m.p. 69-70 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.11 – 7.02 (m, 2H), 6.61 (s, 1H), 5.09 – 4.85 (m, 1H), 2.96 (d, *J* = 7.0 Hz, 2H), 2.37 (s, 3H), 1.73 (s, 3H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 136.8, 135.0, 134.7, 133.6, 129.9, 129.6, 127.3, 127.1, 125.9, 123.7, 121.3, 31.0, 25.7, 21.5, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3279, 2922, 1619, 1554, 1486, 1345, 1170, 1137, 958, 833, 658; **HRMS (ESI)** Calcd $C_{18}H_{21}NO_2SNa$ $[M + Na]^+$: 339.1185, found 338.1193.



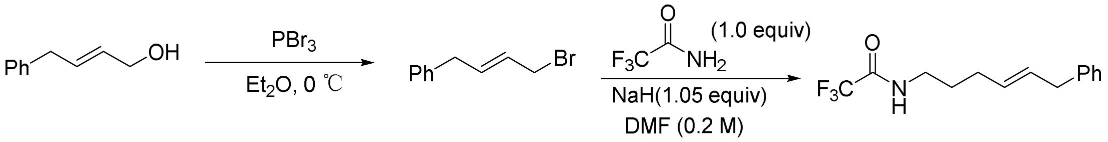
***N*-(2-(3-Methylbut-2-en-1-yl)phenyl)ethanesulfonamide (9j)**: white solid; m.p. 52-53 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.13 – 7.05 (m, 1H), 6.48 (s, 1H), 5.18 (t, *J* = 7.1 Hz, 1H), 3.37 (d, *J* = 7.1 Hz, 2H), 3.15 (q, *J* = 7.4 Hz, 2H), 1.81 (s, 3H), 1.77 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.6, 135.1, 131.8, 130.4, 127.6, 125.2, 121.3, 120.7, 46.4, 31.5, 25.7, 17.9, 8.2; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3279, 2932, 1618, 1552, 1490, 1451, 1328, 1159, 1045, 904, 811, 658; **HRMS (ESI)** Calcd $C_{13}H_{19}NO_2S$ Na $[M + Na]^+$: 276.1029, found 276.1034.



***N*-(5-Methylhex-4-en-1-yl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-*1H*-pyrazol-1-yl)benzenesulfonamide (9k)**: Synthesized using general procedure F starting from 5-methylhex-4-en-1-amine and Celecoxib as a white solid; m.p. 129-130 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 4.74 (t, *J* = 6.0 Hz, 1H), 2.94 (dd, *J* = 13.4, 6.8 Hz, 2H), 2.37 (s, 3H), 1.95 (q, *J* = 7.2 Hz, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 1.53 – 1.44 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 145.2, 144.0 (q, *J* = 38.5 Hz), 142.4, 139.8, 139.5, 132.9, 129.7, 128. 7, 128.0, 125.7, 125.5, 122.7, 121.0 (q, *J* = 269.2 Hz), 43.0, 29.6, 25.6, 25.0, 21.3, 17.7; **HRMS (ESI)** Calcd $C_{24}H_{27}F_3N_3O_2S$ [M + H]$^+$: 478.1768, found 478.1768.

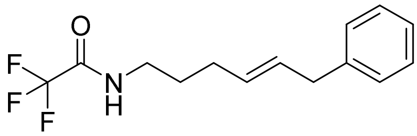
The spectral data were consistent with the literature data.[12]

3.14 Preparation of compound 9l[13]

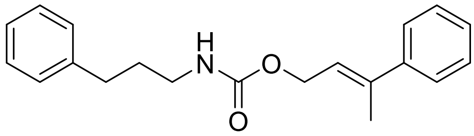


1) The allylic alcohol (10 mmol) was dissolved in ether (12 ml) and the mixture was cooled to 0ºC. PBr$_3$ (0.6 eq) was added dropwise and the mixture was kept stirring at 0ºC for 1 hour. Saturate NaHCO$_3$ solution (20 ml) was added to quench the reaction and the water layer was washed by ether for three times. The combined ether layers are further washed with brine and dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure by means of rotary evaporation. The crude product was direct use for next step.

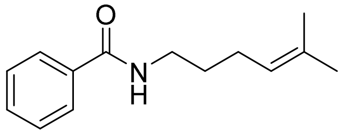
2) 2,2,2-trifluoroacetamide (1.0 eq.) was dissolved in DMF (10 ml) and added to a suspension of 1.05 eq. sodium hydride in DMF (10 ml) at 0 °C. After all gas evolution ceased, 1.05 eq. of the appropriate bromide was added and the reaction mixture was heated to 50 °C for 3 h. After the reaction showed full conversion (by TLC), 50 mL EtOAc was added and the reaction mixture was washed with water (30 ml). After drying over Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography (PE/EA = 4:1 to 2:1) to afford **9l**.



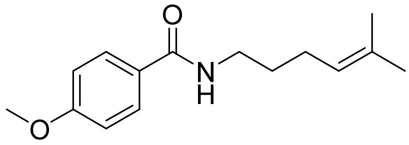
(*E*)-2,2,2-Trifluoro-*N*-(6-phenylhex-4-en-1-yl)acetamide (9l): yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.35 – 7.26 (m, 2H), 7.23 – 7.13 (m, 3H), 6.39 (s, 1H), 5.71 – 5.54 (m, 1H), 5.57 – 5.37 (m, 1H), 3.47 – 3.22 (m, 4H), 2.16 – 2.02 (m, 2H), 1.72 – 1.59 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 157.3 (q, *J* = 36.7 Hz), 140.6, 130.6, 130.0, 128.5, 128.5, 126.1, 116.0 (q, *J* = 287.8 Hz)., 39.6, 39.0, 29.7, 28.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3305, 2937, 2928, 1702, 1722, 1557, 1494, 1453, 1156, 968, 843, 722, 697; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -75.96 (3F); **HRMS (ESI)** Calcd $C_{14}H_{16}F_3NONa$ $[M + Na]^+$: 294.1076, found 294.1078.



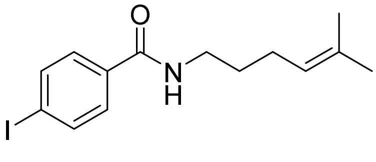
(*E*)-3-Phenylbut-2-en-1-yl (3-phenylpropyl)carbamate (9m): Synthesized using general procedure A starting from 3-phenylpropan-1-amine and (*E*)-3-phenylbut-2-en-1-ol as a white solid; m.p. 79 – 80 °C. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.22 – 7.16 (m, 3H), 5.90 (t, *J* = 6.7 Hz, 1H), 4.78 (d, *J* = 6.7 Hz, 2H), 3.29 – 3.19 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.12 (s, 3H), 1.90 – 1.80 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.6, 142.6, 141.4, 139.7, 128.4, 128.4, 128.3, 127.4, 126.0, 125.8, 122.1, 62.0, 40.6, 33.0, 31.6, 16.2; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2932, 1690, 1599, 1540, 1441, 1310, 1226, 1050, 929, 749, 692; **HRMS (ESI)** Calcd $C_{20}H_{24}NO_2Na$ [M + H]$^+$: 310.1802, found 310.1797.



***N*-(5-Methylhex-4-en-1-yl)benzamide (11a)**: Synthesized using general procedure A starting from benzoyl chloride and 5-methylhex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 – 7.68 (m, 2H), 7.48 – 7.39 (m, 1H), 7.39 – 7.30 (m, 2H), 6.75 (s, 1H), 5.10 (t, *J* = 7.2 Hz, 1H), 3.52 – 3.21 (m, 2H), 2.14 – 1.94 (m, 2H), 1.66 (s, 3H), 1.65 – 1.59 (m, 2H), 1.57 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.7, 134.8, 132.3, 131.2, 128.4, 126.9, 123.7, 40.0, 29.6, 25.7, 25.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3264, 2929, 1619, 1552, 1449, 1305, 1147, 953, 837, 663; **HRMS (ESI)** Calcd $C_{14}H_{19}NONa$ [M + Na]$^+$: 240.1359, found 240.1358.

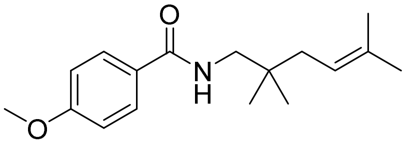


4-Methoxy-*N*-(5-methylhex-4-en-1-yl)benzamide (11b): Synthesized using general procedure A starting from 4-methoxybenzoyl chloride and 5-methylhex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.87 – 7.53 (m, 2H), 7.01 – 6.75 (m, 2H), 6.20 (s, 1H), 5.15 (t, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 3.47 – 3.32 (m, 2H), 2.17 – 2.04 (m, 2H), 1.70 (s, 3H), 1.68 – 1.63 (m, 2H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.0, 162.0, 132.5, 128.6, 127.1, 123.7, 113.7, 55.4, 39.9, 29.7, 25.8, 25.7, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3317, 2927, 1625, 1607, 1539, 1129, 1209, 1251 1026, 841, 771, 667; **HRMS (ESI)** Calcd $C_{15}H_{22}NO_2$ [M + H]$^+$: 248.1645, found 248.1646.

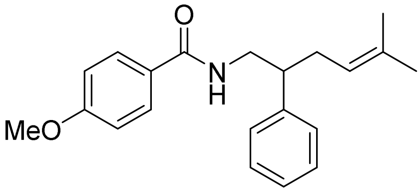


4-Iodo-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzamide (11c): Synthesized using general procedure A starting from 4-iodobenzoyl chloride and 5-methylhex-4-en-1-amine as a yellow solid; m.p. 99-100 °C. **^{1}H NMR (400 MHz,**

$CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 6.45 (s, 1H), 5.13 (t, *J* = 7.2 Hz, 1H), 3.59 – 3.17 (m, 2H), 2.35 – 1.97 (m, 2H), 1.69 (s, 3H), 1.67 – 1.62 (m, 2H), 1.60 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.7, 137.7, 134.2, 132.6, 128.5, 123.6, 98.2, 40.0, 29.5, 25.8, 25.6, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3294, 2926, 1624, 1586, 1538, 1470, 1302, 1152, 1006, 838, 665; **HRMS (ESI)** Calcd $C_{14}H_{18}INONa$ $[M + Na]^+$: 366.0325, found 366.0320.

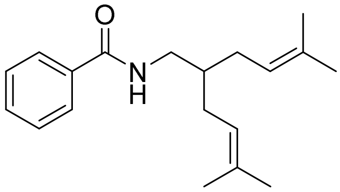


4-Methoxy-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzamide (11d): Synthesized using general procedure A starting from 4-methoxybenzoyl chloride and 2,2,5-trimethylhex-4-en-1-amine as a yellow oil. **^1H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.17 (s, 1H), 5.26 (t, *J* = 7.7 Hz, 1H), 3.85 (s, 3H), 3.29 (d, *J* = 6.2 Hz, 2H), 1.99 (d, *J* = 7.7 Hz, 2H), 1.75 (s, 3H), 1.63 (s, 3H), 0.95 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.0, 162.1, 133.8, 128.5, 127.3, 120.6, 113.8, 55.4, 49.6, 38.7, 35.6, 26.1, 25.2, 17.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3323, 2962, 1636, 1607, 1545, 1504, 1465, 1311, 1253, 1177, 1032, 844, 767; **HRMS (ESI)** Calcd $C_{17}H_{25}NO_2Na$ $[M + Na]^+$: 298.1778, found 298.1775.

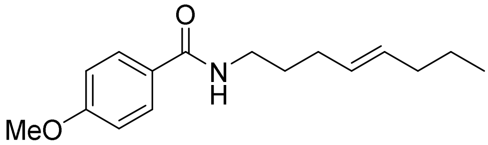


4-**Methoxy-*N*-(5-methyl-2-phenylhex-4-en-1-yl)benzamide (11e)**: Synthesized using general procedure A starting from 4-methoxybenzoyl chloride and 5-methyl-2-phenylhex-4-en-1-amine as a white solid; m.p. 72 – 73 °C. **^1H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.42 (m, 2H), 7.28 – 7.18 (m, 2H), 7.18 – 7.08 (m, 3H), 6.80 – 6.67 (m, 2H), 6.00 (s, 1H), 5.00 (t, *J* = 6.9 Hz, 1H), 3.88 – 3.77 (m, 1H), 3.69 (s, 3H), 3.38 – 3.24 (m, 1H), 2.94 – 2.77 (m, 1H), 2.38 – 2.17 (m, 2H), 1.55 (s, 3H), 1.45 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.9, 162.0, 142.9, 133.3, 128.7, 128.6, 127.8, 127.0, 126.8, 121.8, 113.7, 55.3, 46.0, 44.9, 32.8, 25.8, 17.9; **FT-IR** (thin film, KBr):

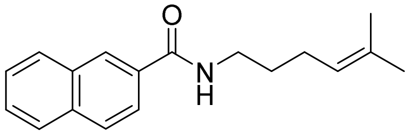
ν (cm^{-1}) 3295, 2929, 1663, 1600, 1537, 1496, 1438, 1370, 1309, 1240, 1182, 954, 749, 689; **HRMS (ESI)** Calcd $C_{21}H_{25}NO_2Na$ [M + Na]$^+$: 346.1778, found 346.1776.



***N*-(5-Methyl-2-(3-methylbut-2-en-1-yl)hex-4-en-1-yl)benzamide (11f)**: Synthesized using general procedure A starting from benzoyl chloride and 5-methyl-2-(3-methylbut-2-en-1-yl)hex-4-en-1-amine as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 – 7.68 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 6.39 (s, 1H), 5.19 (t, *J* = 7.3 Hz, 2H), 3.39 (t, *J* = 6.1 Hz, 2H), 2.14 – 1.98 (m, 4H), 1.78 – 1.72 (m, 1H), 1.71 (s, 6H), 1.61 (s, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.3, 134.9, 133.2, 131.3, 128.5, 126.8, 122.6, 44.3, 39.7, 31.3, 25.9, 17.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3262, 2868, 1618, 1554, 1450, 1304, 1146, 953, 778; **HRMS (ESI)** Calcd $C_{20}H_{28}NO$ [M + H]$^+$: 286.2165, found 286.2160.



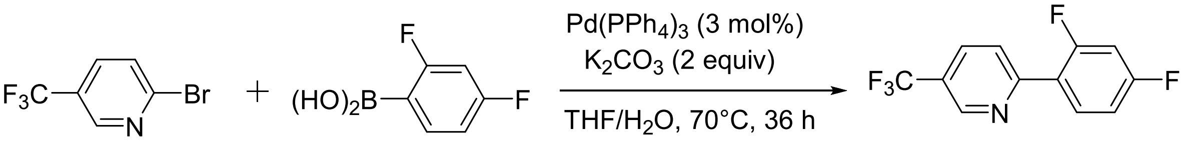
(*E*)-4-Methoxy-*N*-(oct-4-en-1-yl)benzamide (11g): Synthesized using general procedure A starting from 4-methoxybenzoyl chloride and (*E*)-oct-4-en-1-amine as a yellow oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.72 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.09 (s, 1H), 5.54 – 5.36 (m, 2H), 3.84 (s, 3H), 3.58 – 3.41 (m, 2H), 2.19 – 2.05 (m, 2H), 2.04 – 1.91 (m, 2H), 1.74 – 1.61 (m, 3H), 1.44 – 1.32 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.0, 162.1, 131.4, 129.3, 128.6, 127.2, 113.7, 55.4, 39.7, 34.7, 30.2, 29.5, 22.6, 13.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3311, 2953, 1697, 1601, 1543, 1500, 1442, 1314, 1225, 1099, 1050, 977, 846, 691; **HRMS (ESI)** Calcd : $C_{16}H_{23}NO_2Na$ [M + Na]$^+$: 284.1621, found 284.1620.



***N*-(5-Methylhex-4-en-1-yl)-2-naphthamide (11h)**: Synthesized using general procedure A starting from 2-naphthoyl chloride and 5-methylhex-4-en-1-amine as a yellow solid; m.p. 75-76 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.26 (s, 1H), 7.94 – 7.85 (m, 3H), 7.84 – 7.78 (m, 1H), 7.59 – 7.50 (m, 2H), 6.36 (s, 1H), 5.19 (t, *J* = 7.2 Hz, 1H), 3.60 – 3.44 (m, 2H), 2.21 – 2.03 (m, 2H), 1.78 – 1.68 (m, 5H), 1.63 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 167.5, 134.6, 132.6, 132.6, 132.0, 128.8, 128.4, 127.7, 127.5, 127.2, 126.7, 123.7, 123.51, 40.1, 29.6, 25.8, 25.7, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3263, 2941, 1618, 1554, 1449, 1337, 1304, 1146, 953, 778, 658; **HRMS (ESI)** Calcd $C_{18}H_{21}NONa$ [M + Na]$^+$: 290.1515, found 290.1512.

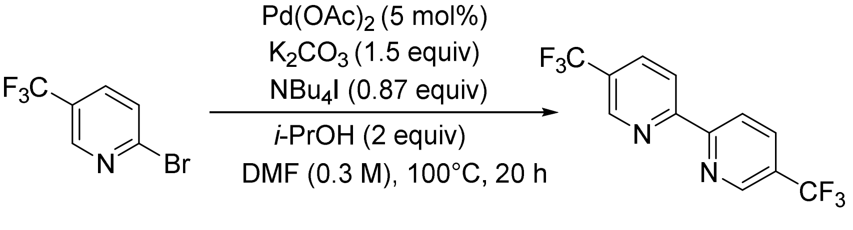
4. General procedures for synthesis of ligands and catalysts

4.1 Synthesis of dF(CF$_3$)ppy[14]



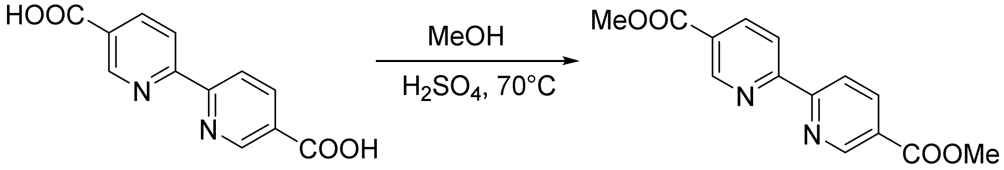
A mixture of 2,4-difluorophenylboronic acid (1.3 equiv.), 2-Bromo-5-(trifluoromethyl) pyridine (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol%) and K_2CO_3 (2.0 equiv.) was combined with THF (0.2 M) and distilled water (0.33 M) in a flask. After freeze-pump-thaw degassing for three cycles, the mixture was refluxed for 36 h under nitrogen. The mixture was then cooled to ambient temperature and poured into brine, extracted with ethyl acetate, and dried over anhydrous $MgSO_4$. The organic solvent was removed under vacuum, and the product was purified by column chromatography to yield the product as a white solid.

4.2 Synthesis of 5,5’-bis(trifluoromethyl)-2,2’-bipyridine[15]



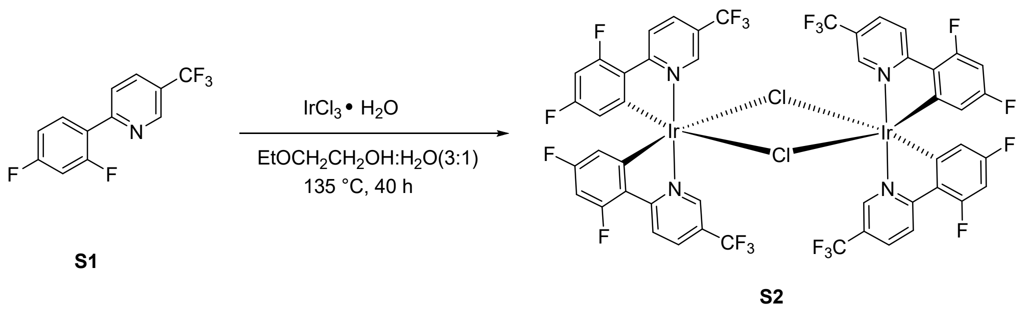
To a 100 mL round-bottom flask charged with a stir bar was added 2-bromo-5-(trifluoromethyl) pyridine, $Pd(OAc)_2$ (112 mg, 0.50 mmol, 5 mol%), K_2CO_3 (2.07 g, 15 mmol, 1.5 equiv.), and NBu_4I (3.2 g, 8.7 mmol, 0.87 equiv.). The flask was evacuated and backfilled with N_2 three times. To this flask was added *i*-PrOH (1.54 mL, 20 mmol, 2.0 equiv.) and dry DMF (33 mL, 0.30 M). The reaction was heated to 100 ºC with vigorous stirring for 20 h. The reaction mixture was then cooled to room temperature and filtered, washing copiously with EtOAc. The aqueous layer was backwashed once with EtOAc (50 mL) and the combined organic layer waswashed with water (40 mL) and sat. brine (40 mL) before drying over Na2SO4. Following removal of the solvent *in vacuo*, the crude residue was purified by silica gel chromatography to afford 5,5'-bis(trifluoromethyl)-2,2'-bipyridine (1.36 g) as a white solid. Characterization data was consistent with reported literature values.

4.3 Synthesis of (2,2′-bipyridine)-5,5′-dicarboxylic acid dimethyl ester[16]



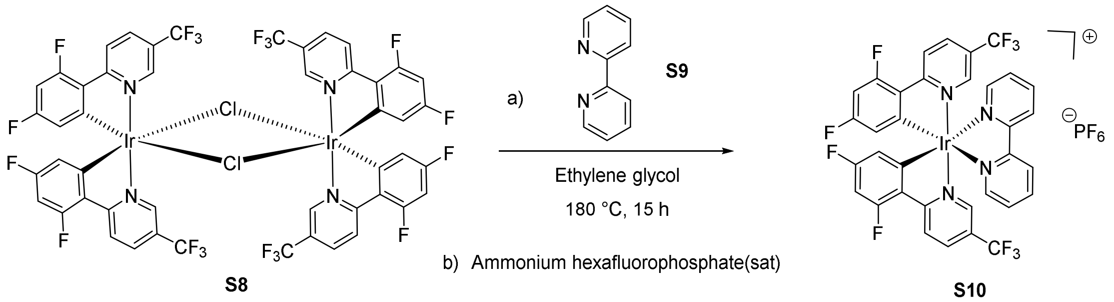
An appropriate amount of (2,2′-bipyridine)-5,5′-dicarboxylic acid (500 mg, 2 mmol) in methanol (30 mL) was added to concentrated sulfuric acid (2 mL), which had been placed in an ice bath. After refluxing overnight, the solution was poured into water (40 mL), forming a white slurry. The pH of the slurry was adjusted to 7 with powdered Na_2CO_3. The product was then extracted with chloroform, dried over magnesium sulfate and evaporated to dryness. Characterization data was consistent with reported literature values.

4.4 Synthesis of $[Ir(dF(CF_3)ppy)_2Cl]_2$-dimer[17]



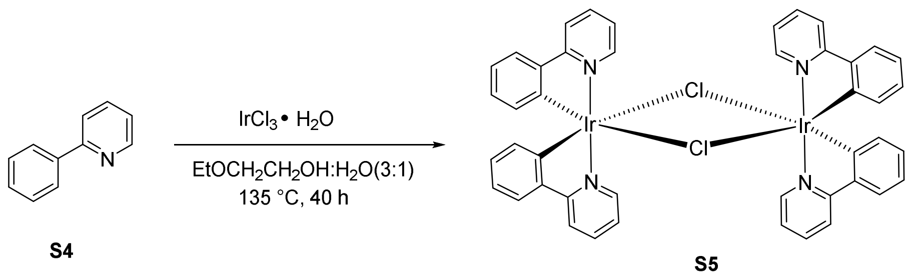
To a 25 mL tube containing a stir ◦ bar was added **S1** (430 mg, 2.05 equiv) and $IrCl_3·H_2O$ (256 mg, 1.0 equiv). The flask was evacuated and backfilled with argon, and 7.5 mL 2-ethoxyethanol and 2.5 mL water (3:1 ratio) were added. The mixture was degassed with Ar and heated at 135 °C for 40 hours. The mixture was cooled to room temperature, which resulted in the formation of a large amount of yellow precipitate. The solid was filtered and washed with water three times. The solid was dried in an oven at 75 ℃ for 1h. The crude dimer was carried onto the next step without further purification.

4.5 Synthesis of Ir[dFCF$_3$ppy]$_2$(bpy))PF$_6$[18]



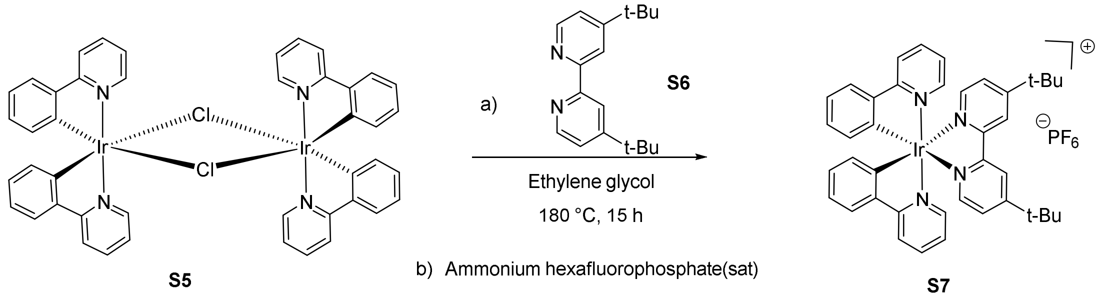
In a 25 mL tube were added the **S2** (400 mg, 0.268mmol, 1.0 equiv.) and S3 (92 mg, 0,590 mmol, 2.2 equiv.) in ethylene glycol (8 mL) to give a yellow suspension. The flask was evacuated and backfilled with argon and heated at 150 °C overnight. The mixture was cooled and washed with hexane (20 mL × 3) and the ethylene glycol layer was heated to 85 °C for 5 min to remove residual hexane. An aqueous saturated ammonium hexafluorophosphate solution was added, causing the iridium-PF6 salt to precipitate, which was filtered, dried and recrystallized (acetone/ether), affording **S4** as a yellow solid.

4.6 Synthesis of [Ir(d(*t*-Bu)ppy)$_2$Cl]$_2$-dimer



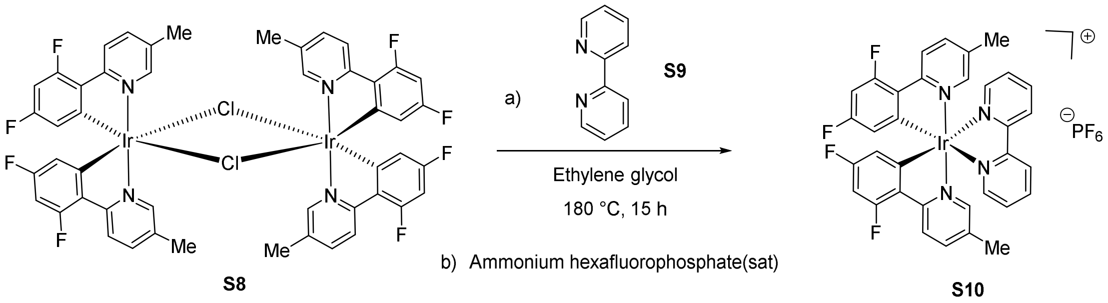
To a 25 mL tube containing a stir bar was added **S4** (430mg, 2.05 equiv.) and $IrCl_3 \cdot H_2O$ (256 mg, 1.0 equiv.). The flask was evacuated and backfilled with argon, and 7.5 mL 2-ethoxyethanol and 2.5 mL water (3:1 ratio) were added. The mixture was degassed with Ar and heated at 135 °C for 40 hours. The mixture was cooled to room temperature, which resulted in the formation of a large amount of yellow precipitate. The solid was filtered and washed with water three times. The solid was dried in an oven at 75°C for 1h. The crude dimer was carried onto the next step without further purification.

4.7 Synthesis of Ir[ppy]$_2$(dtbbpy))PF$_6$

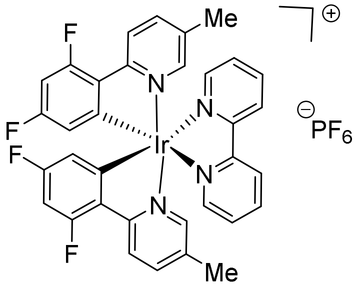


In a 25 mL tube were added the **S5** (400 mg, 0.268mmol, 1.0 equiv.) and **S6** (92 mg, 0,590 mmol, 2.2 equiv.) in ethylene glycol (8 mL) to give a yellow suspension. The flask was evacuated and backfilled with argon and heated at 150 °C overnight. The mixture was cooled and washed with hexane (20 mL× 3) and the ethylene glycol layer was heated to 85 °C for 5 min to remove residual hexane. An aqueous saturated ammonium hexafluorophosphate solution was added, causing the iridium-PF_6 salt to precipitate, which was filtered, dried and recrystallized (acetone/ether), affording **S7** as a yellow solid.

4.8 Synthesis of [Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$

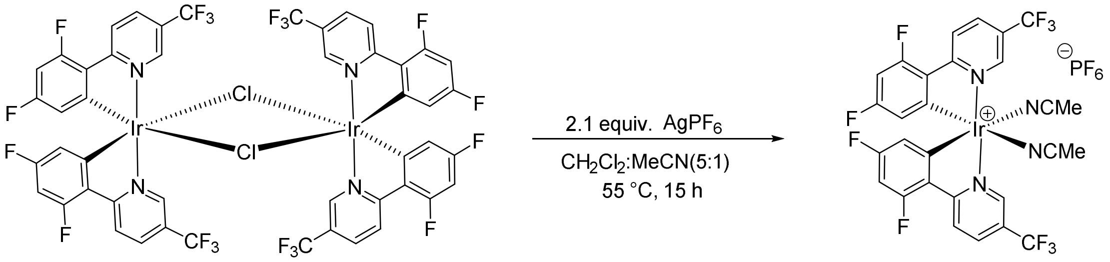


In a 25 mL tube were added the **S8** (400 mg, 0.314 mmol, 1.0 equiv.) and **S9** (92 mg, 0.590 mmol, 2.2 equiv.) in ethylene glycol (8 mL) to give a yellow suspension. The flask was evacuated and backfilled with argon and heated at 150 °C overnight. The mixture was cooled and washed with hexane (20 mL × 3) and the ethylene glycol layer was heated to 85 °C for 5 min to remove residual hexane. An aqueous saturated ammonium hexafluorophosphate solution was added, causing the iridium-PF6 salt to precipitate, which was filtered, dried and recrystallized (acetone/ether), affording **S10** as a yellow solid.



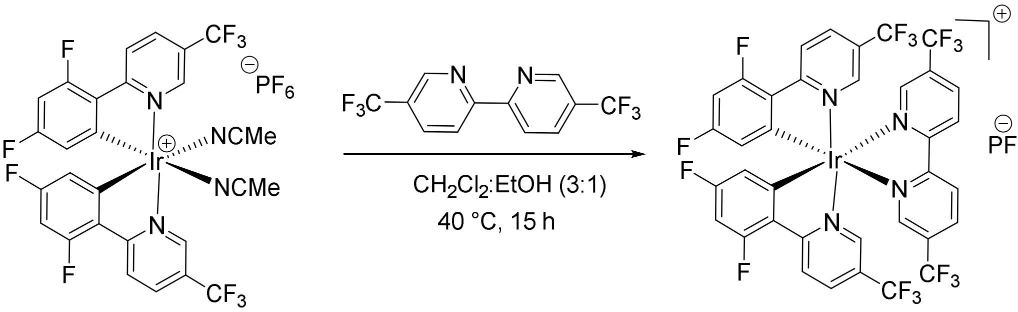
[Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$: ^{1}H NMR (600 MHz, acetone-d6) δ 8.84 (d, *J* = 8.2 Hz, 2H), 8.38 – 8.30 (m, 2H), 8.29 – 8.24 (m, 2H), 8.22 – 8.17 (m, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.76 – 7.71 (m, 2H), 6.77 – 6.69 (m, 2H), 5.86 – 5.73 (m, 2H), 2.12 (s, 6H); **^{13}C NMR (150 MHz, acetone-d6)** δ 164.0 (d, *J* = 12.7 Hz), 162.3 (d, *J* = 12.6 Hz), 161.8 (d, *J* = 12.8 Hz), 161.2 (d, *J* = 6.7 Hz), 160.1 (d, *J* = 13.0 Hz), 155.9, 154.0, 153.9, 150.9, 149.1, 140.4, 140.0, 134.5, 128.8, 127.9, 125.1, 123.3 (d, *J* = 19.5 Hz), 113.7 (dd, *J* = 17.7, 2.7 Hz), 110.0, 98.5 (t, *J* = 27.0 Hz).

4.9 Synthesis of [Ir(dF(CF$_3$)ppy)$_2$(MeCN)$_2$]PF$_6$[17]



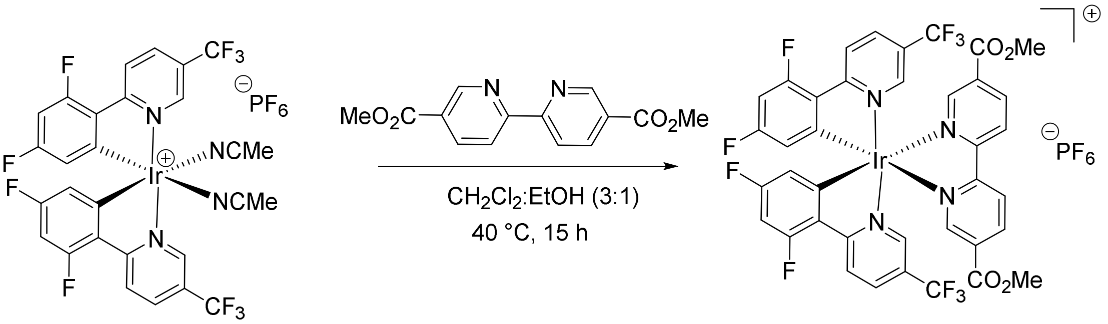
To a flame-dried 50-mL round bottom flask equipped with a reflux condenser and stir bar was added $[Ir(dF(CF_3)ppy)_2Cl]_2$-dimer (1.01 mmol, 1.0 equiv., 530 mg) and, in the glove box, was added $AgPF_6$ (2.12 mmol, 2.1 equiv., 186 mg). The flask and reflux condenser were evacuated backfilled with argon three times. Next, 7.5 mL anhydrous CH_2Cl_2 and 1.5 mL anhydrous MeCN (5:1 ratio) were added, and the reaction mixture was heated to 55 °C overnight. The reaction was cooled to room temperature, and the precipitated AgCl was filtered out of the product. The filtrate was concentrated *in vacuo*, leaving behind a yellow solid, which was redissolved in hot CH_2Cl_2. The mixture was allowed to cool to room temperature, and pentane was added to afford pale yellow crystals of the cationic iridium complex. The crystals were filtered and washed with pentane to give the crude product, which was carried onto the next step without further purification.

4.10 Synthesis of $[Ir(dF(CF_3)ppy)_2(5,5\text{-}CF_3bpy)]PF_6$[17]

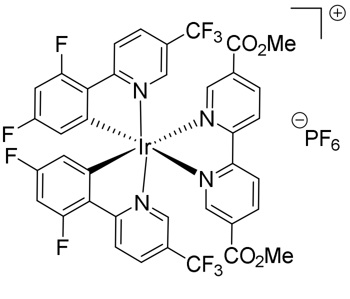


To a flame-dried 100-mL round bottom flask equipped with a reflux condenser and stir bar was added $[Ir(dF(CF_3)ppy)_2(MeCN)_2]PF_6$ (2.67 mmol, 1.0 equiv., 460 mg) and 5,5′- bis(trifluoromethyl)-2,2′-bipyridine (2.94 mmol, 1.2 equiv., 859 mg). The flask was evacuated and backfilled with argon three times, and 10 mL CH_2Cl_2 and 0.4 mL EtOH (3:1 ratio) were added. The reaction was heated to 40 °C and allowed to stir under argon overnight. The reaction mixture was cooled to room temperature and filtered. Copious amounts of CH_2Cl_2 were used to wash the filter to ensure dissolution of the crude iridium complex. The filtrate was concentrated *in vacuo*. The crude product was purified using silica gel chromatography (gradient from 100% CH_2Cl_2 to 25% acetone/CH_2Cl_2) to afford a yellow-red solid. The solid was dissolved in a minimal amount of acetone and recrystallized using pentane to give a fine, bright yellow powder.

4.11 Synthesis of [Ir(dF(CF$_3$)ppy)$_2$(5,5-CO$_2$Mebpy)]PF$_6$



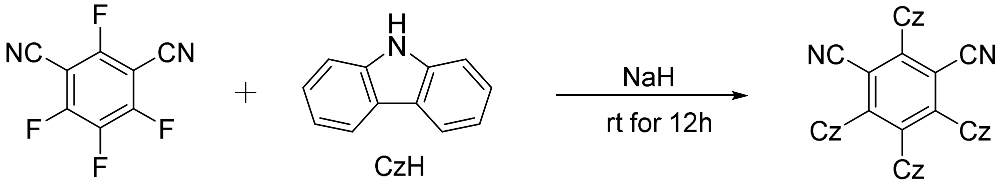
To a flame-dried 100-mL round bottom flask equipped with a reflux condenser and stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(MeCN)$_2$]PF$_6$ (2.67 mmol, 1.0 equiv., 460 mg) and dimethyl [2,2'-bipyridine]-5,5'-dicarboxylate (2.94 mmol, 1.2 equiv., 800 mg). The flask was evacuated and backfilled with argon three times, and 10 mL CH_2Cl_2 and 0.4 mL EtOH (3:1 ratio) were added. The reaction was heated to 40 °C and allowed to stir under argon overnight. The reaction mixture was cooled to room temperature and filtered. Copious amounts of CH_2Cl_2 were used to wash the filter to ensure dissolution of the crude iridium complex. The filtrate was concentrated *in vacuo*. The crude product was purified using silica gel chromatography (gradient from 100% CH_2Cl_2 to 25% acetone/CH_2Cl_2) to afford a yellow-red solid. The solid was dissolved in a minimal amount of acetone and recrystallized using pentane to give a fine, bright yellow powder.



[Ir(dF(CF$_3$)ppy)$_2$(5,5-COOMebpy)]PF$_6$: **^{1}H NMR (600 MHz, acetone-d6)** δ 9.12

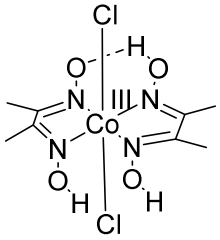
(d, *J* = 8.5 Hz, 2H), 8.84 – 8.78 (m, 2H), 8.65 (d, *J* = 1.4 Hz, 2H), 8.63 – 8.60 (m, 2H), 8.39 (d, *J* = 8.9 Hz, 2H), 8.15 (s, 2H), 6.02 – 5.98 (m, 2H), 3.85 (s, 6H); **^{13}C NMR (150 MHz, acetone-d6)** δ 173.4, 167.3 (d, *J* = 6.4 Hz), 163.5 (d, *J* = 12.6 Hz), 162.8, 157.9, 153.8 (d, *J* = 6.6 Hz), 152.4, 147.0 (dd, *J* = 8.7, 4.6 Hz), 140.7, 137.5, 130.9, 126.9 (t, *J* = 2.9 Hz), 126.3, 125.3 (q, *J* = 34.3 Hz), 124.0 (d, *J* = 21.0 Hz), 122.0 (q, *J* = 272.0 Hz) 114.9 (d, *J* = 15.9 Hz), 99.6 (t, *J* = 27.1 Hz), 52.7.

4.12 Synthesis of 4CzIPN[18]

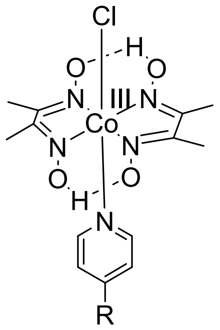


NaH (60% in oil, 0.60 g, 15.0 mmol) was added slowly to a stirred solution of carbazole (1.67 g, 10.0 mmol) or diphenylamine (1.69 g, 10.0 mmol) in dry THF (40 mL) under a nitrogen atmosphere at room temperature. After 30 min, tetrafluoroisophthalonitrile (0.40 g, 2.00 mmol) was added. After stirring at room temperature for 12 h, 2 mL of water was added to the mixture to quench the excess NaH. The resulting mixture was then concentrated under reduced pressure and washed with water and EtOH to yield the crude product, which was purified by recrystallization from hexane/CH_2Cl_2, column chromatography on silica gel (CH_2Cl_2: Petroleum = 4:1) were used for further purification) to give 1.51g (96%, 4-CzIPN).

4.13 Synthesis of Cobalt catalyst

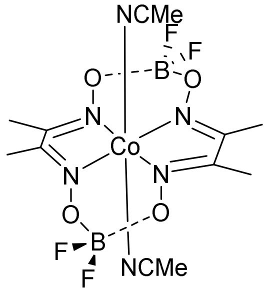


Co(dmgH)(dmgH$_2$)Cl$_2$[19]: Cobaltous chloride hexahydrate (5.0 g, 0.021 mol) was dissolved in acetone (150 mL) and dimethylglyoxime (4.9 g, 0.042 mol) was added. The mixture was stirred for 10 min and filtered to remove undissolved material. Then the solution was allowed to stand overnight and green crystal was formed, which was further collected and washed with acetone to obtained Co(dmgH)(dmgH$_2$)Cl$_2$.



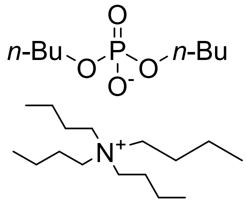
R = H ,Co(dmgH)$_2$PyCl
R=OMe,Co(dmgH)$_2$(4-OMe-Py)Cl
R=CF$_3$,Co(dmgH)$_2$(4-CF$_3$-Py)Cl
R=CN,Co(dmgH)$_2$(4-CN-Py)Cl
R= N(CH$_3$)$_2$,Co(dmgH)$_2$(DMAP)Cl

Co(dmgH)$_2$(4-R-Py)Cl[20]: Co(dmgH)(dmgH$_2$)Cl$_2$ (1.0 equiv.) was suspended in 0.03 M methanol. Then pyridine derivative (1.0 equiv.) was added and the suspension was dissolved. After 1 hour, a brown precipitate was formed, which was filtered and washed with water (10 mL), ethanol (10 mL), and diethyl ether (10 mL) to give a series of cobalt catalysts as shown.



Co(dmgBF$_2$)$_2$(MeCN)$_2$[21,22]: Diethyl ether (150 mL, O$_2$-free) was added to a flask containing Co(OAc)$_2$•4H$_2$O (2.0 g, 8 mmol) and dmgH$_2$ (1.9 g, 16 mmol), followed by freshly distilled BF$_3$•Et$_2$O (10 mL, an excess). The mixture was stirred for 6 hours under argon. The resulting solid was filtered under argon, washed with ice-cold water (10 mL × 3, O$_2$-free) and air-dried to produce a brownish-red solid product [Co(dmgBF$_2$)$_2$(H$_2$O)$_2$]. Then this product was stirred in CH$_3$CN for 1 hour, filtrated, washed with CH$_3$CN and dried under vacuum to afford Co(dmgBF$_2$)$_2$(CH$_3$CN)$_2$.

4.14 **Synthesis of Brønsted base**

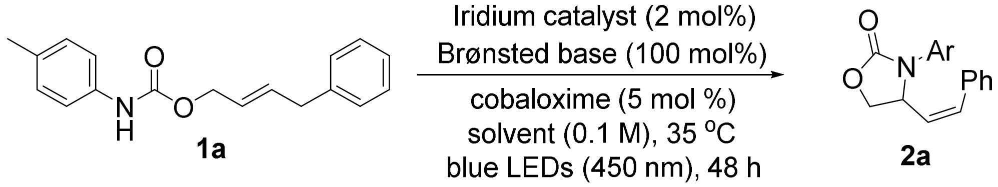


$NBu_4OP(O)(OBu)_2$

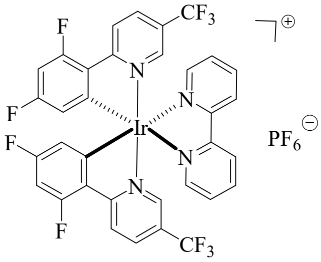
Tetrabutylammonium dibutyl phosphate[23]: In a 100 mL flame-dried round bottom flask charged with a stir bar, dibutyl phosphoric acid (1.0 eq, 20 mmol, 4.20 g) was added, followed by the addition of 10 mL MeOH. The reaction was cooled to 0°C in an ice bath and 20 mL 1M tetrabutylammonium hydroxide methanol solution was added slowly. After addition, the reaction was warmed to room temperature and was stirred for an hour. After the reaction was completed, solvent was removed under vacuum. The reaction mixture was kept under vacuum and heated in a 60 °C (oil bath) under stirring to remove the remaining water. Other Brønsted base such as $PBu_4OP(O)(OBu)_2$, $NBu_4OP(O)(OPh)_2$, $PBu_4OP(O)(OPh)_2$ synthesis methods are the same. Notably, it does not need to be heated in vacuum for 3 days, but only needs half a day under the condition of stirring and vacuumizing, following by freeze overnight in the refrigerator at -20 °C. But it must be noted that the equivalence of acid and base must be consistent, otherwise the ideal white solid cannot be obtained.

5. Optimization of the reaction conditions

Table S1. Optimization of cyclization of *N*-arylamides with *Z*-selectivity

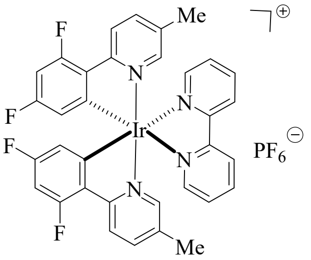


Iridium photocatalyst



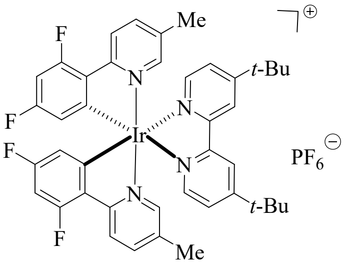
PC1 = [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$

Ir(II)/Ir*(III)= +1.32 V vs SCE
Ir(III*)/Ir(IV)= -1.00 V vs SCE



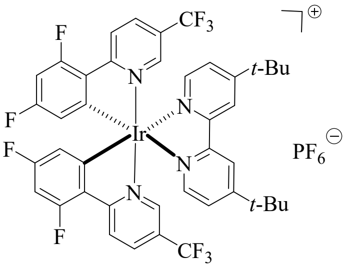
PC2 = [Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$[a]

Ir(II)/Ir*(III)= +1.29 V vs SCE
Ir(III*)/Ir(IV)= -0.93 V vs SCE



PC3 = [Ir(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$[24c]

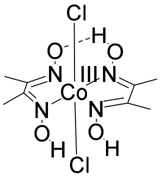
Ir(II)/Ir*(III)= +0.97 V vs SCE
Ir(III*)/Ir(IV)= -0.92 Vvs SCE



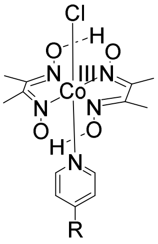
PC4 = [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$[24c]

Ir(II)/Ir*(III)= +0.89 V vs SCE
Ir(III*)/Ir(IV)= -1.21 V vs SCE

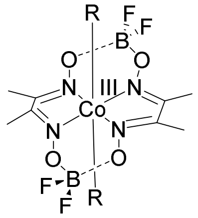
Cobaloxime



Co-1: Co(dmgH)(dmgH$_2$)Cl$_2$

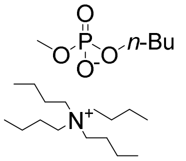


Co-2: R = H ,Co(dmgH)$_2$PyCl
Co-3: R=OMe,Co(dmgH)$_2$(4-OMe-Py)Cl
Co-4: R=CF$_3$,Co(dmgH)$_2$(4-CF$_3$-Py)Cl
Co-5: R=CN,Co(dmgH)$_2$(4-CN-Py)Cl
Co-6: R= N(CH$_3$)$_2$,Co(dmgH)$_2$(DMAP)Cl



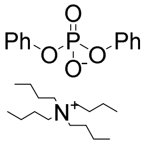
Co-7: R=H$_2$O, Co(dmgBF$_2$)$_2$(H$_2$O)$_2$
Co-8: R=CH$_3$CN, Co(dmgBF$_2$)$_2$(CH$_3$CN)$_2$

Brønsted base



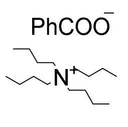
NBu$_4$OP(O)(OBu)$_2$

base 1



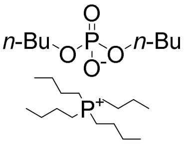
NBu$_4$OP(O)(OPh)$_2$

base 2



NBu$_4$OBz

base 3



PBu$_4$OP(O)(OBu)$_2$

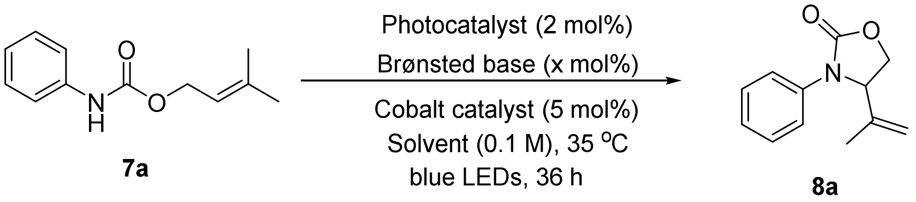
base 4

Entry[b]	Ir catalyst	Cobaloxime	Brønsted base	Solvent	Yield (%)	*Z*/*E*
1[c]	PC1	Co-1	base 1	DCM	25	>20:1

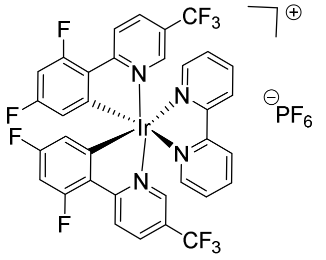
2[d]	PC1	Co-1	base 1	DCM	38	>20:1
3	PC1	Co-1	base 1	DCM	48	>20:1
4	PC1	Co-1	base 1	DCE	44	>20:1
5	PC1	Co-1	base 1	1,4-Dioxane	< 5	-
6	PC1	Co-1	base 1	NMP	< 5	-
7	PC1	Co-1	base 1	$PhCF_3$	< 5	-
8	PC1	Co-2	base 1	DCM	37	>20:1
9	PC1	Co-3	base 1	DCM	33	10:1
10	PC1	Co-4	base 1	DCM	46	>20:1
11	PC1	Co-5	base 1	DCM	52	>20:1
12	PC1	Co-6	base 1	DCM	62	>20:1
13	PC1	Co-7	base 1	DCM	12	>20:1
14	PC1	Co-8	base 1	DCM	27	3:1
15	PC1	Co-6	base 2	DCM	50	>20:1
16	PC1	Co-6	base 3	DCM	18	>20:1
17	**PC1**	**Co-6**	**base 4**	**DCM**	**65**	**>20:1**
18	PC2	Co-6	base 2	DCM	54	>20:1
19	PC3	Co-6	base 2	DCM	14	>20:1
20	PC4	Co-6	base 2	DCM	39	10:1
21	–	Co-6	base 2	DCM	NR	–
22	PC1	–	base 2	DCM	NR	–
23	PC1	Co-6	–	DCM	NR	–
24[e]	PC1	Co-6	base 2	DCM	NR	–

[a]The excited-state electrochemical potentials (*E*, V vs. SCE) are roughly calculated by cyclic voltammetry (Calculation process is shown in Mechanistic studies). [b]Reaction conditions: **1a** (0.20 mmol), photocatalyst (2 mol%), cobaloxime (5 mol%), and Brønsted base (100 mol%) in solvent (2 mL, 0.1 M), 35 °C, household blue LEDs (22 W), 36 h; Isolated yield; *E*/Z ratios determined by the crude ^{1}H NMR spectra. [c]Brønsted base (40 mol%). [d]Brønsted base (80 mol%). [e]In the dark.

Table S2. Optimization of cyclization of *N*-arylamides



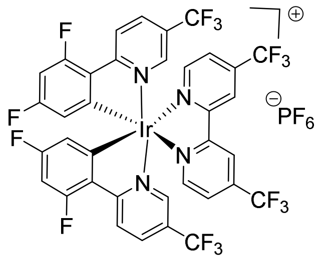
Photocatalyst



PC1 = [Ir(dF(CF3)ppy)$_2$(bpy)]PF$_6$[24a]

Ir(II)/Ir*(III)= +1.32 V vs SCE

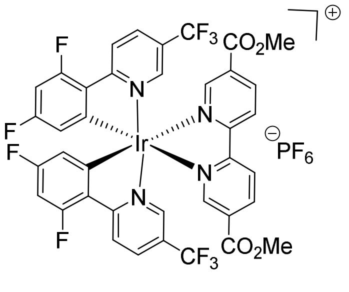
Ir(III*)/Ir(IV)= -1.00 V vs SCE



PC2 = [Ir(dF(CF$_3$)ppy)$_2$(4,4'-dCF$_3$bpy)]PF$_6$[24b]

Ir(II)/Ir*(III)= +1.65 V vs SCE

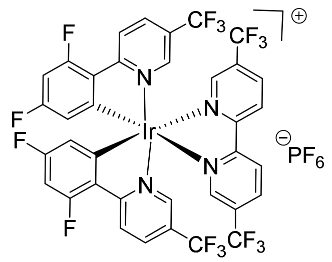
Ir(III*)/Ir(IV)= -0.51 V vs SCE



PC3 = [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCO$_2$Mebpy)]PF$_6$[a]

Ir(II)/Ir*(III)= +1.64 V vs SCE

Ir(III*)/Ir(IV)= -0.59 V vs SCE

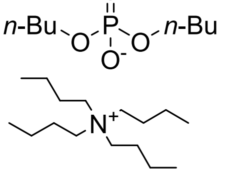


PC4 = [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpy)]PF$_6$[24b]

Ir(II)/Ir*(III)= +1.68 V vs SCE

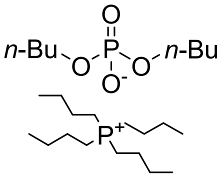
Ir(III*)/Ir(IV)= -0.43 V vs SCE

Brønsted base



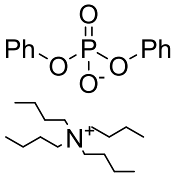
NBu$_4$OP(O)(OBu)$_2$

base 1



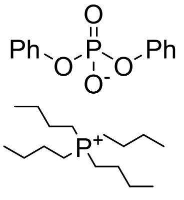
PBu$_4$OP(O)(OBu)$_2$

base 2



NBu$_4$OP(O)(OPh)$_2$

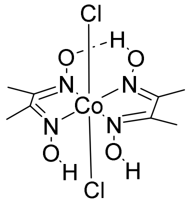
base 3



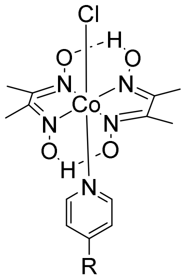
PBu$_4$OP(O)(OPh)$_2$

base 4

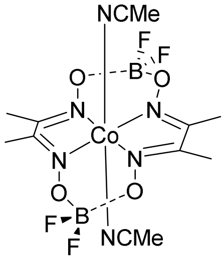
Cobaloxime



Co-1: Co(dmgH)(dmgH$_2$)Cl$_2$



Co-2: R = H, Co(dmgH)$_2$PyCl
Co-3: R = OMe, Co(dmgH)$_2$(4-OMe-Py)Cl
Co-4: R = CF$_3$, Co(dmgH)$_2$(4-CF$_3$-Py)Cl
Co-5: R = CN, Co(dmgH)$_2$(4-CN-Py)Cl
Co-6: R = N(CH$_3$)$_2$, Co(dmgH)$_2$(DMAP)Cl



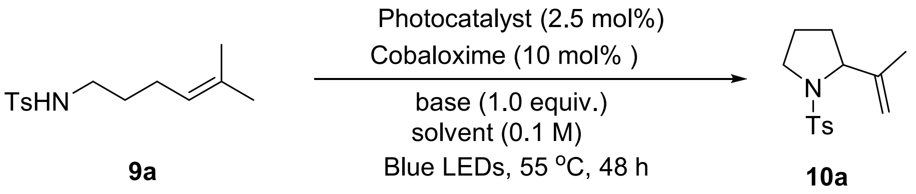
Co-7: Co(dmgBF$_2$)$_2$(MeCN)$_2$

Entry ^{b}	Solvent	Photocatalyst	Cobaloxime	Brønsted base	Yield (%)
1	DCM	PC1	Co-1	base 1 (100 mol%)	35
2	DCM	PC1	Co-1	base 1 (50 mol%)	70
3	DCM	PC1	Co-1	base 1 (40 mol%)	85
4	DCM	PC1	Co-1	base 1 (20 mol%)	82
5	DCM	PC1	Co-1	base 1 (10 mol%)	65
6	DCM	PC1	Co-2	base 1 (40 mol%)	70
7	DCM	PC1	Co-3	base 1 (40 mol%)	65
8	DCM	PC1	Co-4	base 1 (40 mol%)	82
9	DCM	PC1	Co-5	base 1 (40 mol%)	95
10	**DCM**	**PC1**	**Co-6**	**base 1 (40 mol%)**	**99**
11	DCM	PC1	Co-7	base 1 (40 mol%)	92
12^{c}	DCM	PC1	Co-1	base 1 (40 mol%)	95
13	DCE	PC1	Co-6	base 1 (40 mol%)	90
14	PhCF$_3$	PC1	Co-6	base 1 (40 mol%)	32
15	DMSO	PC1	Co-6	base 1 (40 mol%)	< 5
16	DMF	PC1	Co-6	base 1 (40 mol%)	< 5
17	DCM	PC2~4	Co-6	base 1 (40 mol%)	< 5
18	DCM	PC1	Co-6	base 2 (40 mol%)	90
19	DCM	PC1	Co-6	base 3 (40 mol%)	82
20	DCM	PC1	Co-6	base 4 (40 mol%)	52
21	DCM	PC1	–	base 1 (40 mol%)	NR

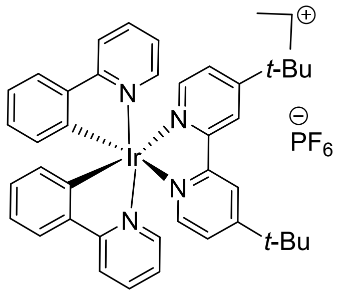
Entry [b]	Solvent	Photocatalyst	Cobaloxime	Brønsted base	Yield (%)
22	DCM	PC1	Co-6	–	NR
23	DCM	–	Co-6	base 1 (40 mol%)	NR
24 [d]	DCM	PC1	Co-6	base 1 (40 mol%)	NR

[a] The excited-state electrochemical potentials (*E*, V vs SCE) are roughly calculated by cyclic voltammetry (Calculation process is shown in Mechanistic studies). [b] Reaction conditions: **7a** (0.20 mmol) photocatalyst (2 mol%), cobaloxime (5 mol%), and Brønsted base (x mol%) in solvent (2 mL, 0.1 M), 35 °C, household blue LEDs (22 W), 36 h. Isolated yield. [c] dry DCM. [d] In the dark.

Table S3. Optimization of cyclization of sulfonamides



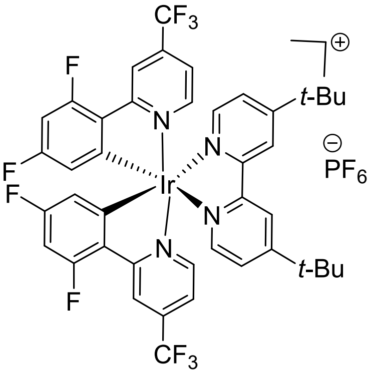
Photocatalyst



PC1 = [Ir(ppy)$_2$(dtbbpy)]PF$_6$[24c]

Ir(II)/Ir*(III)= +0.66 V vs SCE

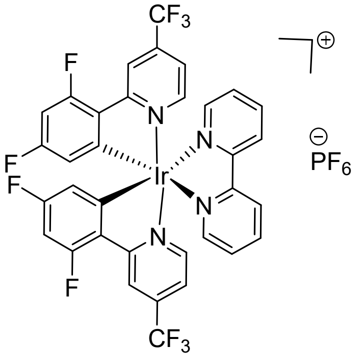
Ir(III*)/Ir(IV)= -0.96 V vs SCE



PC2 = [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$

Ir(II)/Ir*(III)= +0.89 V vs SCE

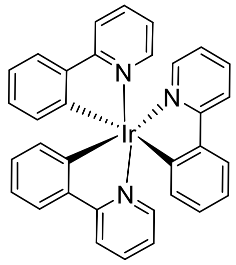
Ir(III*)/Ir(IV)= -1.21 V vs SCE



PC3 = [Ir(dF(CF3)ppy)$_2$(bpy)]PF$_6$

Ir(II)/Ir*(III)= +1.32 V vs SCE

Ir(III*)/Ir(IV)= -1.00 V vs SCE

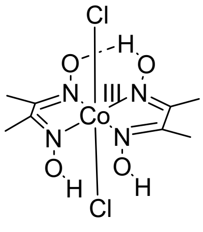


PC4 = *fac*-Ir(ppy)$_3$^{24d}

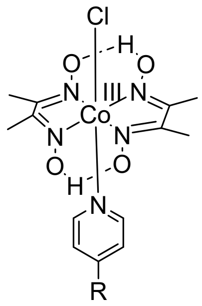
Ir(II)/Ir*(III)= +0.31 V vs SCE

Ir(III*)/Ir(IV)= -1.73 V vs SCE

Cobaloxime



Co-1: Co(dmgH)(dmgH$_2$)Cl$_2$



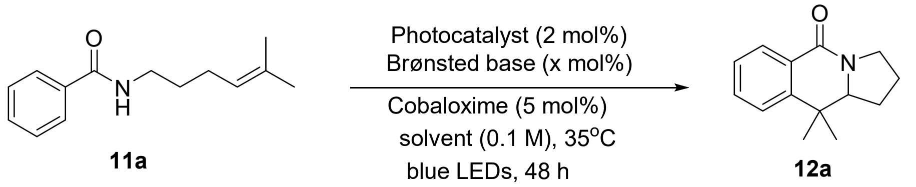
Co-2: R=OMe,Co(dmgH)$_2$(4-OMe-Py)Cl
Co-3: R=CF$_3$,Co(dmgH)$_2$(4-CF$_3$-Py)Cl
Co-4: R=CN,Co(dmgH)$_2$(4-CN-Py)Cl
Co-5: R= N(CH$_3$)$_2$,Co(dmgH)$_2$(DMAP)Cl

Entry	Solvent	Photocatalyst	Cobaloxime	Brønsted base	Yield (%)^a
1	CH_3CN	PC1	Co-1 (5 mol%)	K_3PO_4	16
2	CH_3CN	PC1	Co-2 (5 mol%)	K_3PO_4	20
3	CH_3CN	PC1	Co-3 (5 mol%)	K_3PO_4	33
4	CH_3CN	PC1	Co-4 (5 mol%)	K_3PO_4	42
5	CH_3CN	PC1	Co-5 (5 mol%)	K_3PO_4	40
6	**CH_3CN**	**PC1**	**Co-4 (10 mol%)**	**K_3PO_4**	**58**
7^b	CH_3CN	PC1	Co-4 (10 mol%)	K_3PO_4	50
8^c	CH_3CN	PC1	Co-4 (10 mol%)	K_3PO_4	28
9	CH_3CN	PC1	Co-4 (10 mol%)	K_2HPO_4	NR
10	CH_3CN	PC1	Co-4 (10 mol%)	Na_3PO4	12
11	CH_3CN	PC1	Co-4 (10 mol%)	K_2CO_3	NR
12	CH_3CN	PC1	Co-4 (10 mol%)	KOH	<5%
13	CH_3CN	PC2~4	Co-4 (10 mol%)	K_3PO_4	NR

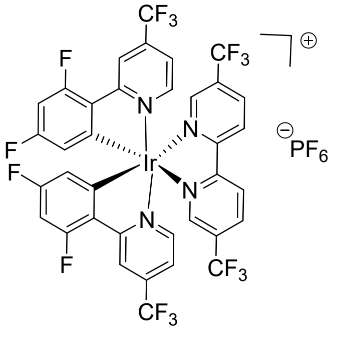
14	$PhCF_3$	PC1	Co-4 (10 mol%)	K_3PO_4	52
15	DCM	PC1	Co-4 (10 mol%)	K_3PO_4	< 5
16	DMF	PC1	Co-4 (10 mol%)	K_3PO_4	< 5
17	–	PC1	Co-4 (10 mol%)	K_3PO_4	NR
18	CH_3CN	–	Co-4 (10 mol%)	K_3PO_4	NR
19	CH_3CN	PC1	–	K_3PO_4	NR
20[d]	CH_3CN	PC1	Co-4 (10 mol%)	K_3PO_4	< 5
21[e]	CH_3CN	PC1	Co-4 (10 mol%)	K_3PO_4	20

[a]Reaction conditions: **9a** (0.10 mmol), photocatalyst (2 mol%), cobaloxime (5 mol%), and Brønsted base (x mol%) in solvent (2 mL, 0.1 M), 55 °C, household blue LEDs (22 W), 36 h. Isolated yield. [b]50 mol% K_3PO_4. [c]10 mol% K_3PO_4. [d]25 °C. [e]35 °C.

Table S4. Optimization for synthesis of benzoindolizidinones



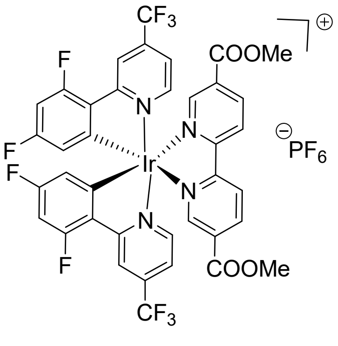
Photocatalyst



PC1=[Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpy)]PF$_6$

Ir(II)/Ir*(III)= +1.68 V vs SCE

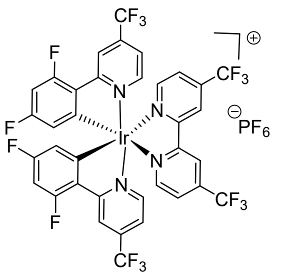
Ir(III*)/Ir(IV)= -0.43 V vs SCE



PC2=[Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCOOMebpy)]PF$_6$

Ir(II)/Ir*(III)= +1.64 V vs SCE

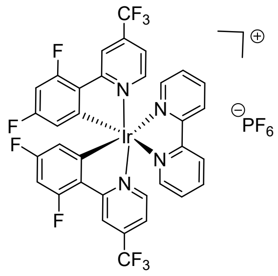
Ir(III*)/Ir(IV)= -0.59 V vs SCE



PC3=[Ir(dF(CF_3)ppy)$_2$(4,4'-dCF_3bpy)]PF_6

Ir(II)/Ir*(III)= +1.65 V vs SCE

Ir(III*)/Ir(IV)= -0.51 V vs SCE

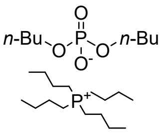


PC4=[Ir(dF(CF_3)ppy)$_2$(bpy)]PF_6

Ir(II)/Ir*(III)= +1.32 V vs SCE

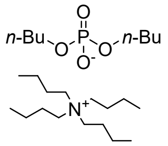
Ir(III*)/Ir(IV)= -1.00 V vs SCE

Bronsted base



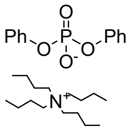
$PBu_4OP(O)(OBu)_2$

base 1



$NBu_4OP(O)(OBu)_2$

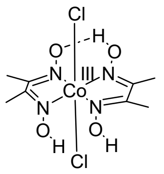
base 2



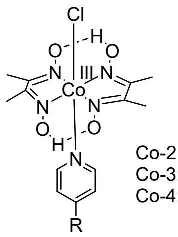
$NBu_4OP(O)(OPh)_2$

base 3

Cobaloxime



Co-1: Co(dmgH)($dmgH_2$)Cl_2



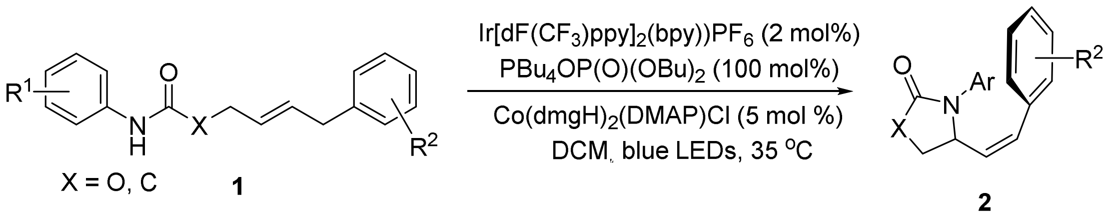
Co-2: R = OMe, Co(dmgH)$_2$(4-OMe-Py)Cl
Co-3: R = CF_3, Co(dmgH)$_2$(4-CF_3-Py)Cl
Co-4: R = $N(CH_3)_2$, Co(dmgH)$_2$(DMAP)Cl

Entry[a]	Solvent	Photocatalyst	Cobaloxime	Brønsted base	Yield (%)[b]
1	DCE	PC1	Co-4	base 1 (100 mol%)	< 5
2	DMF	PC1	Co-4	base 1 (100 mol%)	< 5
3	CH_3CN	PC1	Co-4	base 1 (100 mol%)	< 5
4	DMSO	PC1	Co-4	base 1 (100 mol%)	< 5
5	PhMe	PC1	Co-4	base 1 (100 mol%)	6
6	$PhCF_3$	PC1	Co-4	base 1 (100 mol%)	8
7	$PhCF_3$	PC1	Co-4	base 1 (20 mol%)	15
8	$PhCF_3$	PC1	Co-4	base 1 (5 mol%)	30
9	$PhCF_3$	PC1	Co-4	base 2 (5 mol%)	12
10	$PhCF_3$	PC1	Co-4	base 3 (5 mol%)	24
11	$PhCF_3$	PC2	Co-4	base 1 (5 mol%)	35
12	$PhCF_3$	PC3	Co-4	base 1 (5 mol%)	28
13	$PhCF_3$	PC4	Co-4	base 1 (5 mol%)	NR

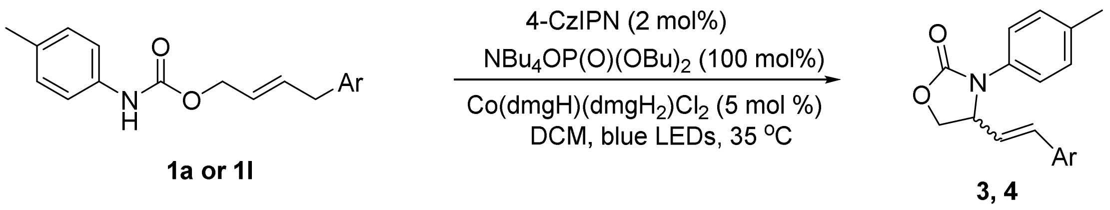
14[c]	**$PhCF_3$**	**PC2**	**Co-4**	**base 1 (5 mol%)**	**43**
15[c]	$PhCF_3$	PC2	Co-1	base 1 (5 mol%)	26
16[c]	$PhCF_3$	PC2	Co-2	base 1 (5 mol%)	28
17[c]	$PhCF_3$	PC2	Co-3	base 1 (5 mol%)	21
18[c]	$PhCF_3$	–	Co-4	base 1 (5 mol%)	NR
19[c]	$PhCF_3$	PC2	–	base 1 (5 mol%)	NR
20[c]	$PhCF_3$	PC2	Co-4	–	NR

[a]Reaction conditions: **11a** (0.20 mmol), photocatalyst (2 mol%), cobaloxime (5 mol%), and Brønsted base (x mol%) in solvent (2 mL, 0.1 M), 35 °C, household blue LEDs (22 W), 36 h. [b]Isolated yield. [c]10 μL H_2O in $PhCF_3$.

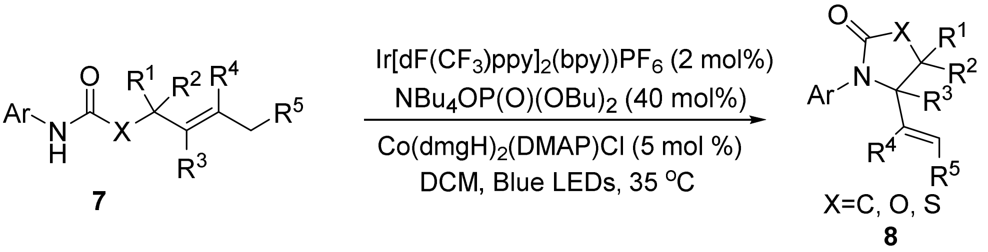
6. General procedures for cyclization



General procedure 1: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, the corresponding *N*-arylamide (0.2 mmol, 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (4.2 mg, 2 mol%), $Co(dmgH)_2(DMAP)Cl$ (4.3 mg, 0.01 mmol, 5 mol%), and $PBu_4OP(O)(OBu)_2$ (94 mg, 0.2 mmol, 1.0 equiv.) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCM (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 48 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

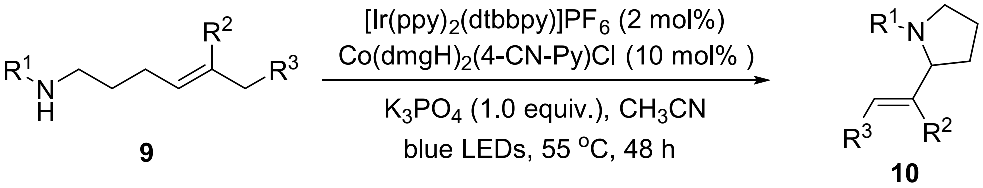


General procedure 2: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, **1a** or **1l** (0.2 mmol, 1.0 equiv.), 4-CzIPN (3.2 mg, 2 mol%), Co(dmgH)(dmgH$_2$)Cl$_2$ (3.6 mg, 0.01 mmol, 5 mol%), and NBu$_4$OP(O)(OBu)$_2$ (90 mg, 0.2 mmol, 1.0 equiv.) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCM (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 16 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

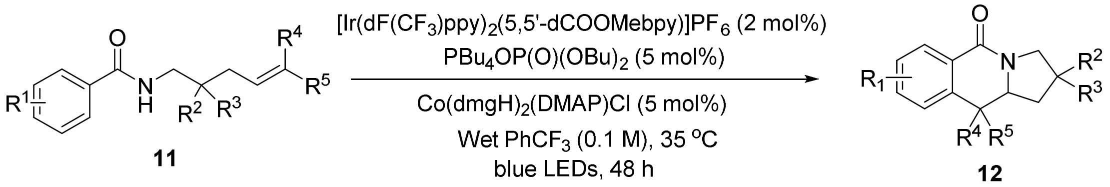


General procedure 3: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, the corresponding *N*-arylamide (0.2 mmol, 1.0 equiv.), [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (4.2 mg, 2 mol%), Co(dmgH)$_2$ (DMAP)Cl (4.3 mg, 0.01 mmol, 5 mol%), and NBu$_4$OP(O)(OBu)$_2$ (36 mg, 0.08 mmol, 40 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCM (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 36 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

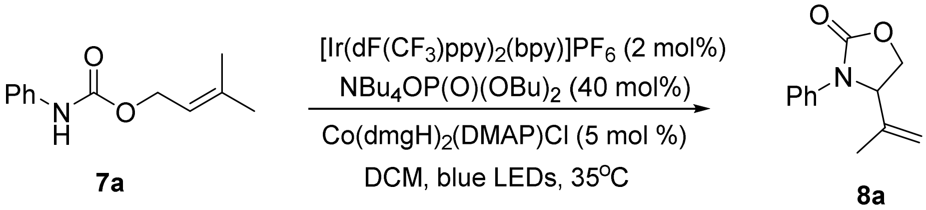
General procedure 4: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, the corresponding *N*-arylamide (0.2 mmol, 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (4.2 mg, 2 mol%), $Co(dmgH)_2(DMAP)Cl$ (4.3 mg, 0.01 mmol, 5 mol%), and $NBu_4OP(O)(OBu)_2$ (90 mg, 0.2 mmol, 100 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCM (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 36 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



General procedure 5: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, the corresponding sulfanilamide (0.2 mmol, 1.0 equiv.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (4.3 mg, 2 mol%), $Co(dmgH)_2(4\text{-}CN\text{-}Py)Cl$ (8.8 mg, 0.02 mmol, 10 mol%), and potassium phosphate (42 mg, 0.2 mmol, 1.0 equiv.) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. CH_3CN (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 48 hours. The temperature was maintained at 55 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



General procedure 6: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, the corresponding *N*-alkyl amide (0.2 mmol, 1.0 equiv., if solid), $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}dCO_2Mebpy)]PF_6$ (4.8 mg, 2 mol%), $Co(dmgH)_2(DMAP)Cl$ (4.3 mg, 0.01 mmol, 5 mol%), and $PBu_4OP(O)(OBu)_2$ (4.6 mg, 0.01 mmol, 5 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. *N*-alkyl amide (0.2 mmol, 1.0 equiv., if oil), $PhCF_3$ (2 mL) and 10 µL H_2O were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 48 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



Scale-up synthesis of compound 8a: To a 100 mL oven-dried Schlenk tube equipped with a magnetic stir bar were amide **7a** (1.03 g, 5 mmol, 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (100 mg, 0.1 mmol, 2 mol%), $Co(dmgH)_2(DMAP)Cl$ (108 mg, 0.25 mmol, 5 mol%), and $NBu_4OP(O)(OBu)_2$ (900 mg, 2 mmol, 40 mol%). The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCM (30 mL) were then added under argon atmosphere. The mixture was placed under a 22W blue LEDs and irradiated at 35 °C for 36 h. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **8a** (873 mg, 86% yield) as a yellow oil.

7. Mechanistic Studies

7.1 Control experiments

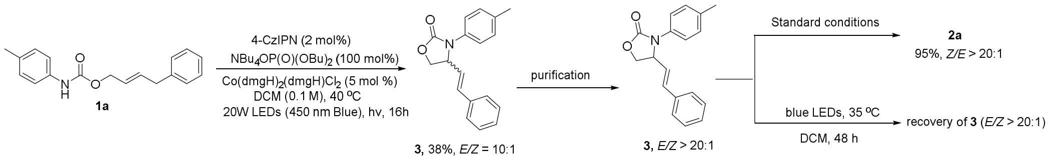


Figure S2. The reaction of **1a**. *E*/Z ratios were determined by ^{1}H NMR spectra. Under standard reaction conditions, *Z*-products can be obtained from *E*-products. On the other hand, the *E*-configuration is not affected by 450 nm blue-light irradiation.

7.2 Stern-Volmer fluorescence quenching experiments

Emission intensities were recorded using F-320 Luminescence Spectrometer for all experiments. Acetonitrile was degassed with argon for at least 30 minutes by ultrasonic treatment. All Ir[dF(CF$_3$)ppy]$_2$(bpy))PF$_6$ solutions were excited at 412 nm and the emission intensity was collected at 450-600 nm. In a typical experiment, the CH$_3$CN solution of Ir[dFCF$_3$ppy]$_2$(bpy))PF$_6$ (0.04 μM) was added the appropriate amount of NBu$_4$OP(O)(OBu)$_2$ and **7a** in a screw-top 1.0 cm quartz cuvette. After degassing with argon for 10 min, the emission spectra of the samples were collected. In order to further verify the mechanism, we also carried out fluorescence quenching with the absence of Brønsted base.

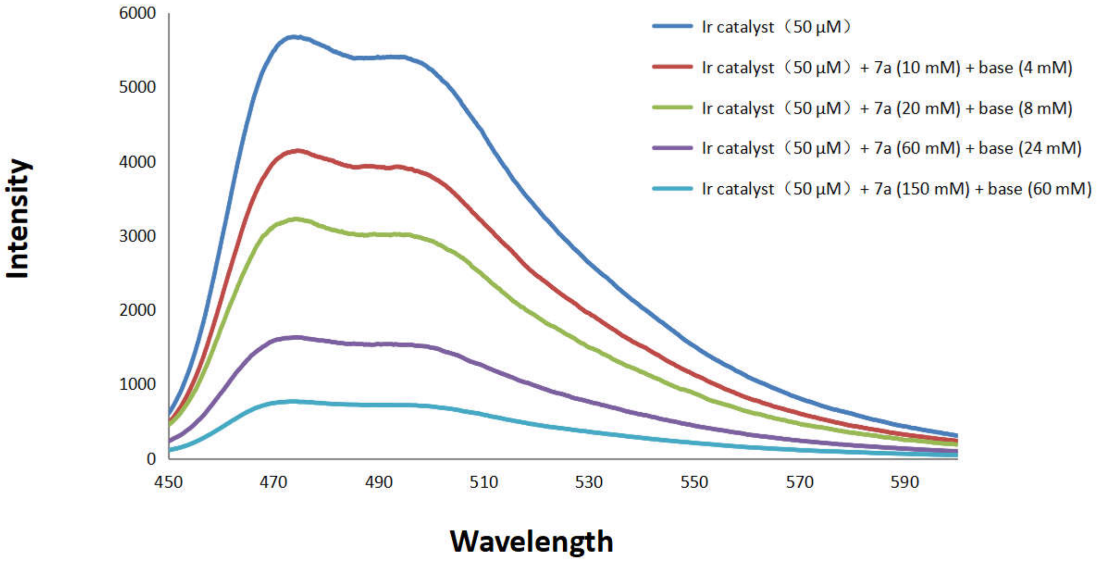


Figure S3. PL quenching by amide **7a** in the presence of Brønsted base.

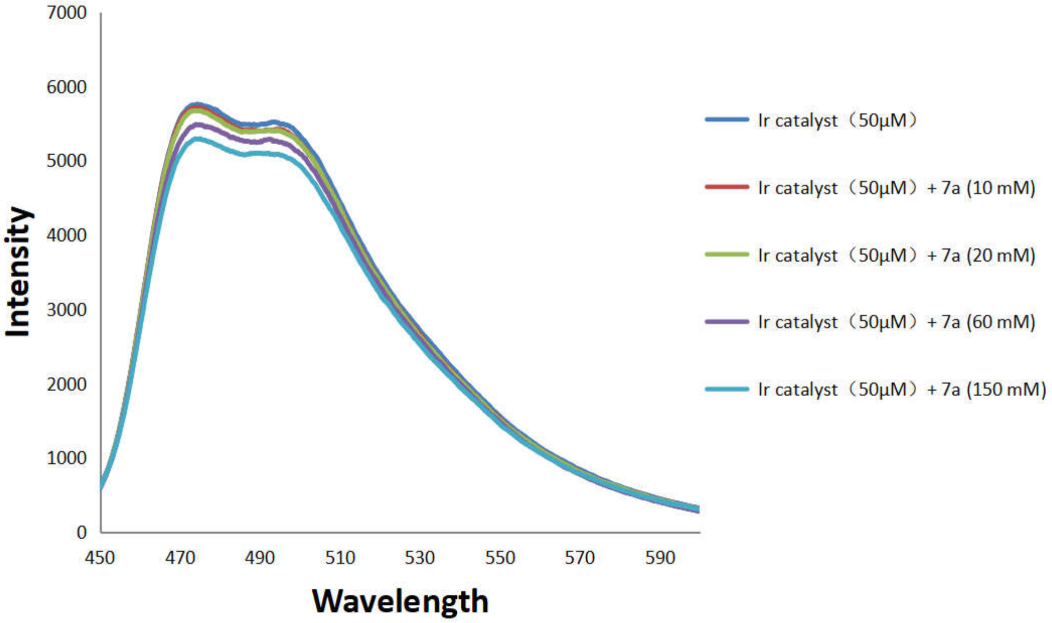


Figure S4. PL quenching by amide **7a** in the absence of Brønsted base.

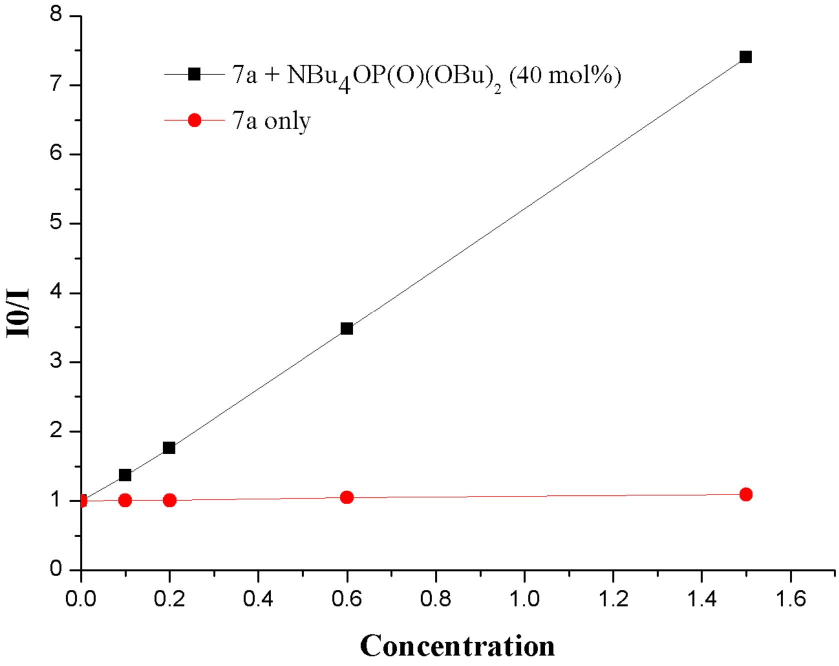
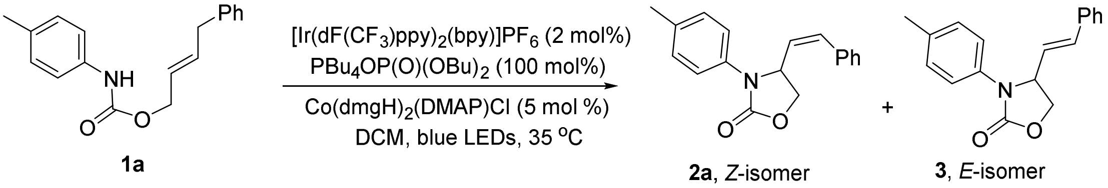


Figure S5. Stern–Volmer emission quenching data.

7.3 *E*- and *Z*- isomer products monitoring experiment



Entry	Time	Overall yield [a]	Yield of **2a**[b]	Yield of **3**[b]	*Z/E*[c]
1	6 h	12%	1.1%	10.9%	1:10
2	12 h	20%	16.4%	3.6%	4.5:1
3	24 h	42%	39.2%	2.8%	14:1
4	48 h	65%	65%	0%	> 20:1

[a] Reaction conditions: **1a** (0.20 mmol), [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (2 mol%), Co(dmgH)$_2$ (DMAP)Cl (5 mol%), and PBu$_4$OP(O)(OBu)$_2$ (100 mol%) in solvent (2

mL, 0.1 M), 35 °C, household blue LEDs (22 W, 450 nm). Isolated overall yields. [b] Calculated through *E*/Z ratios. [c] *E*/Z ratios determined by the crude ^{1}H NMR spectra.

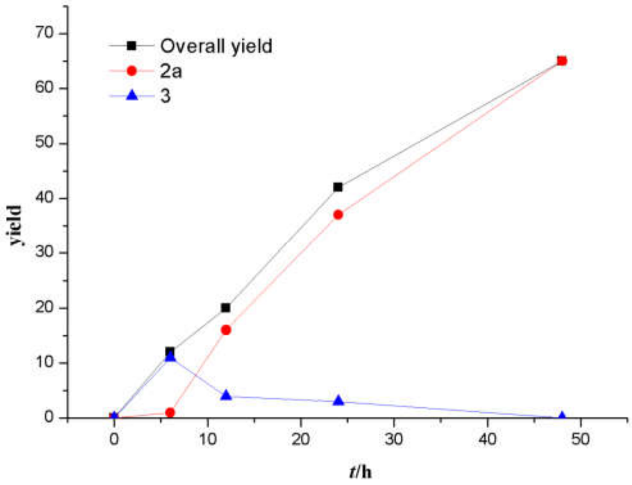


Figure S6. Real-time monitoring experiment.

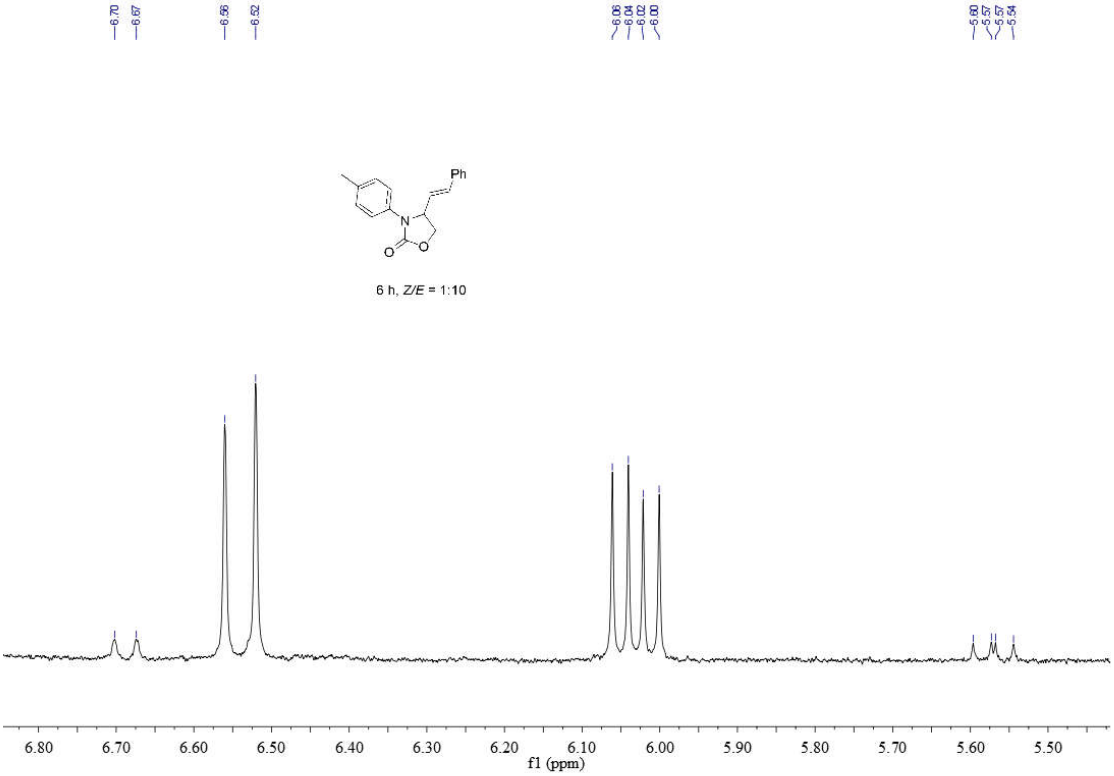


Figure S7. ^{1}H NMR spectrum of reaction mixture (6 h).

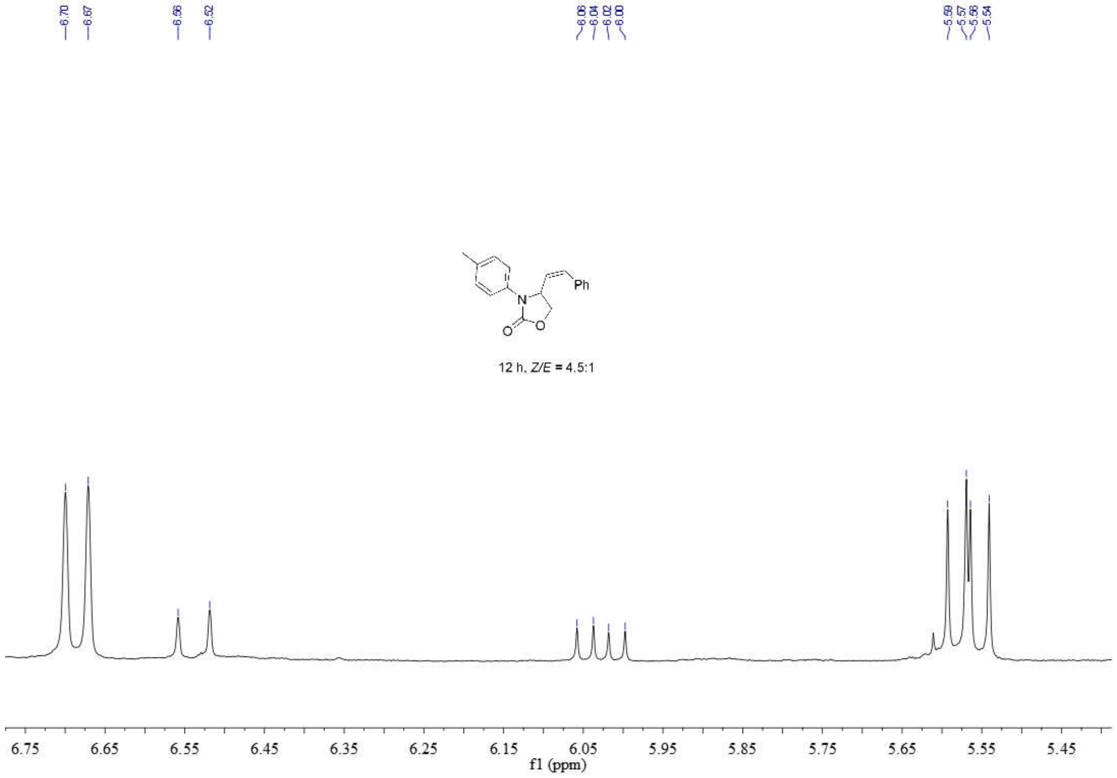


Figure S8. ^{1}H NMR spectrum of reaction mixture (12 h).

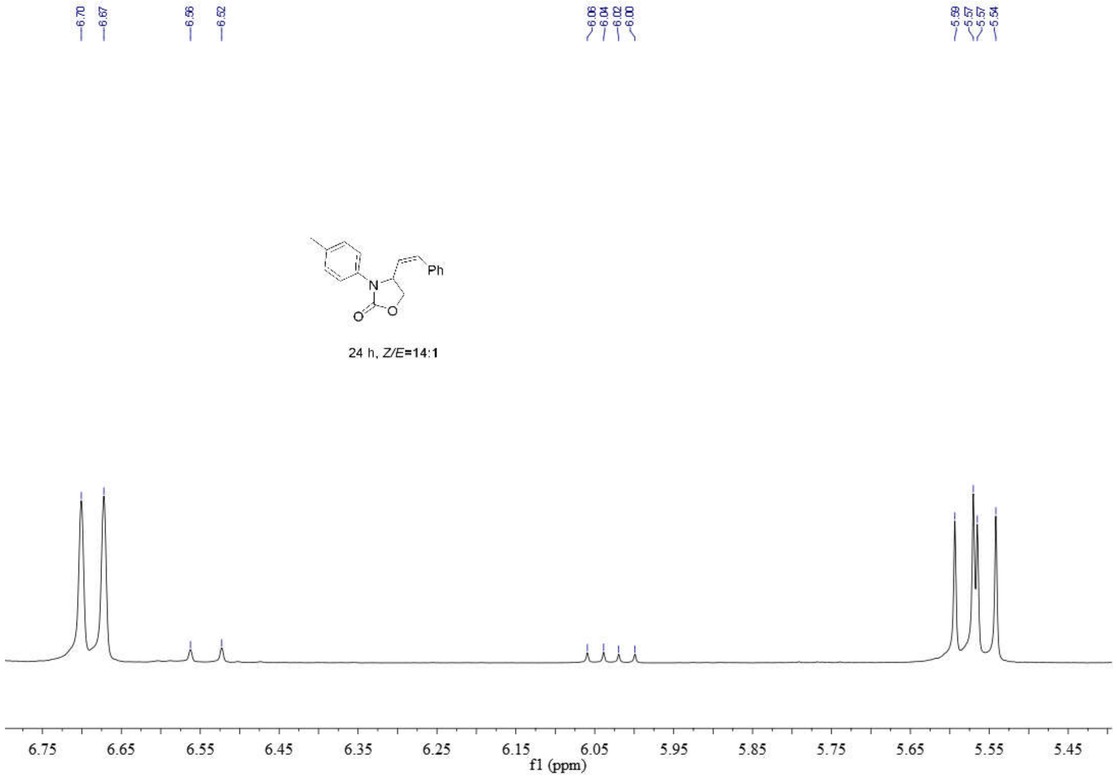


Figure S9. ^{1}H NMR spectrum of reaction mixture (24 h).

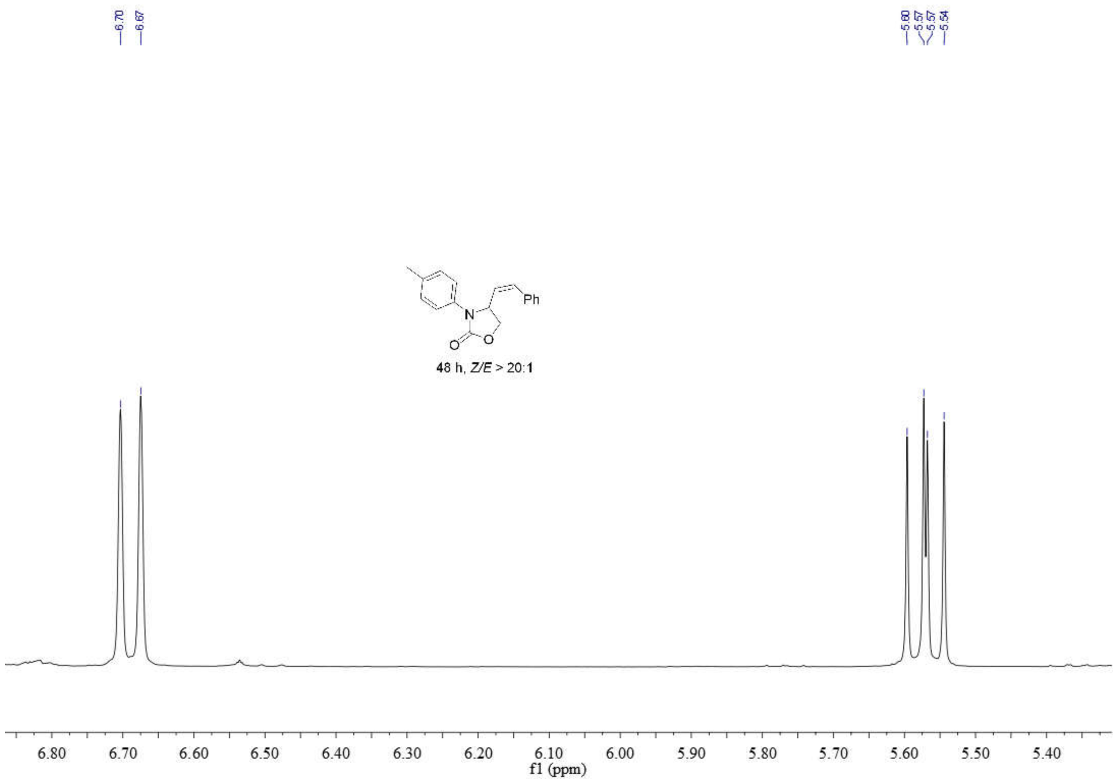


Figure S10. ^{1}H NMR spectrum of reaction mixture (48 h).

7.4 Cyclic Voltammetry and Determination of Excited State Potentials

The redox potentials were determined through cyclic voltammetry employing a 0.2 mM solution of the iridium complex in a 0.1 M solution of *tetra*-*n*-butylammonium hexafluorophosphate at a Pt working electrode with a Pt counter electrode and Ag wire quasireference. Ferrocene was used as an internal standard; potential sweep rate was 100 mV/s.[25] The Fc/Fc+ couple is 380 mV less positive than SCE. Excited state potentials are estimated using the Rehm-Weller equations as given.[26]

$$E^{0*}_{OX} = E^{0'}_{OX} - E^{0-0}$$

$$E^{0*}_{Red} = E^{0'}_{Red} + E^{0-0}$$

Where E^{o*} represents the excited state potential, $E^{o'}$ represents the ground state potential, and E^{0-0} refers to the energy gap between the zeroth level vibrational levels of the ground and excited state. E_{ox} refers to the Ir(III)/Ir(IV) couples and E_{red} to the

Ir(II)/(III) couple. Because of poor overlap between the absorption and emission spectra, $E^{0\text{-}0}$ is approximated as the high-energy onset of phosphorescence where the emission intensity is 10% of that obtained at the maximum emission wavelength, using the "10% rule".[27]

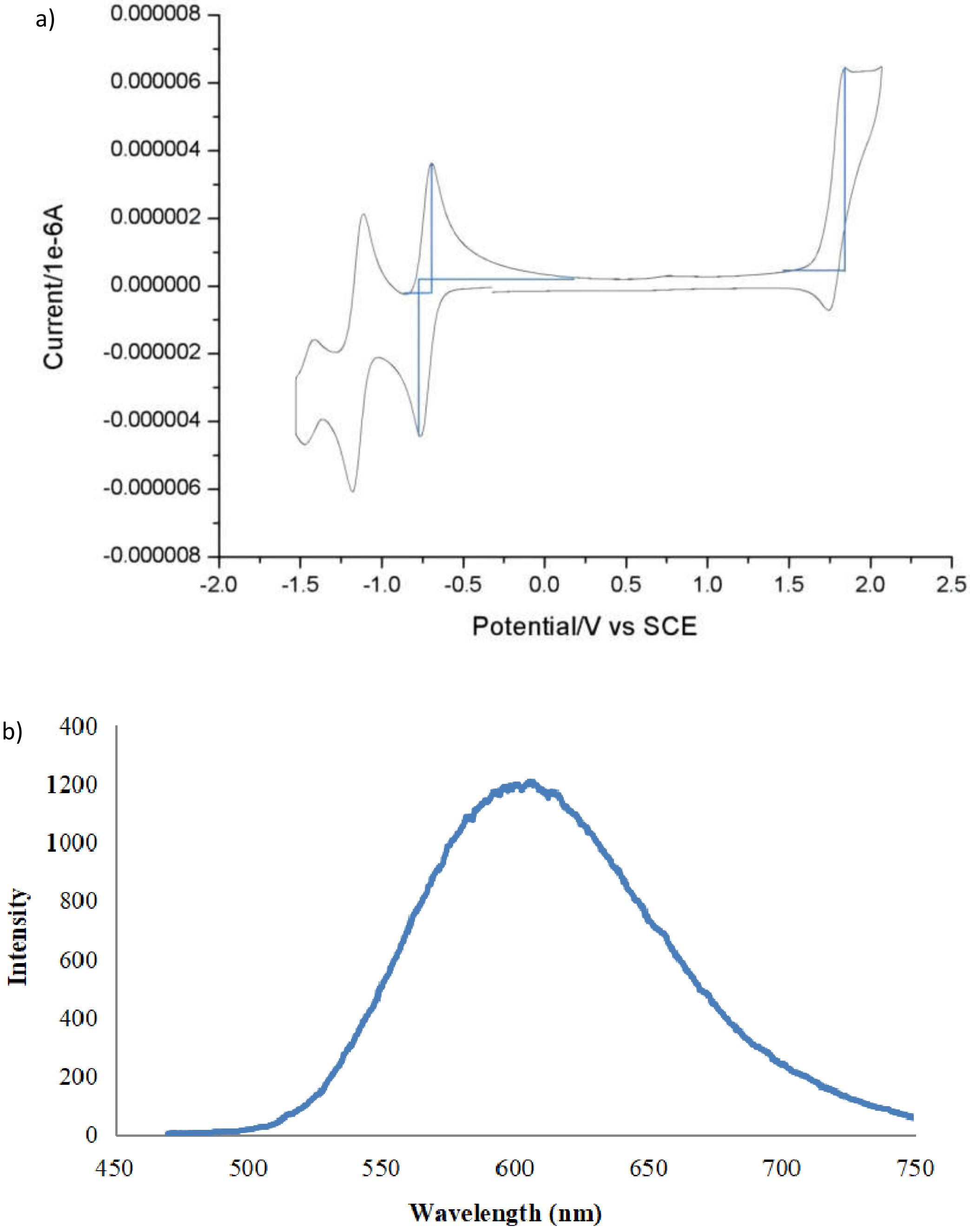


Figure S11: a) Cyclic voltammogram of $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}dCO_2Mebpy)]PF_6$ with data tabulated. In cases where peaks are reversible, $E_{1/2}$ is provided. b) Emission spectra for of [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCO$_2$Mebpy)]PF$_6$. The maxima were obtained at 606 nm; the intensity is 10% of the emission maxima at 521 nm, $E_{0\text{-}0} = 2.38$.

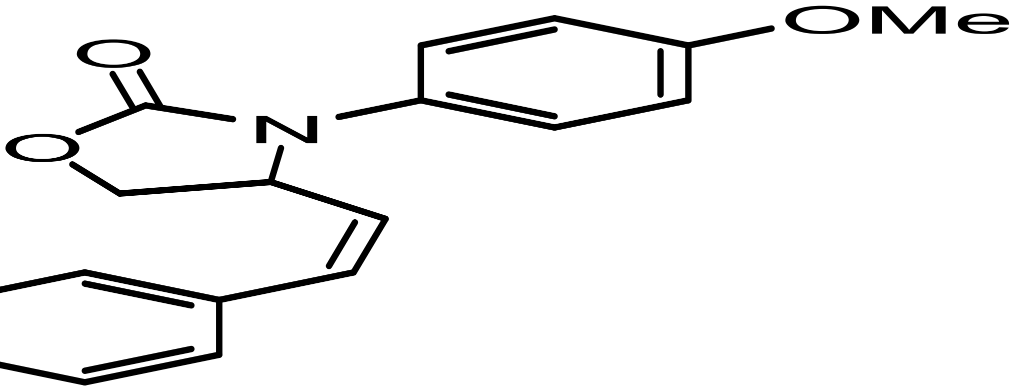
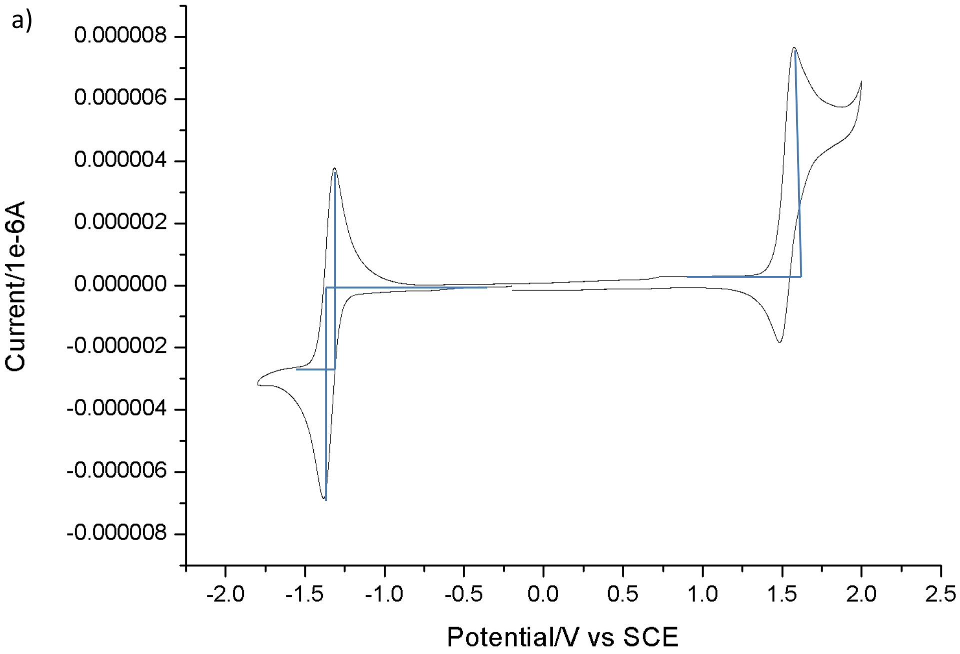


Figure S12: Redox potential data of [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCO$_2$Mebpy)]PF$_6$.

a)



b)

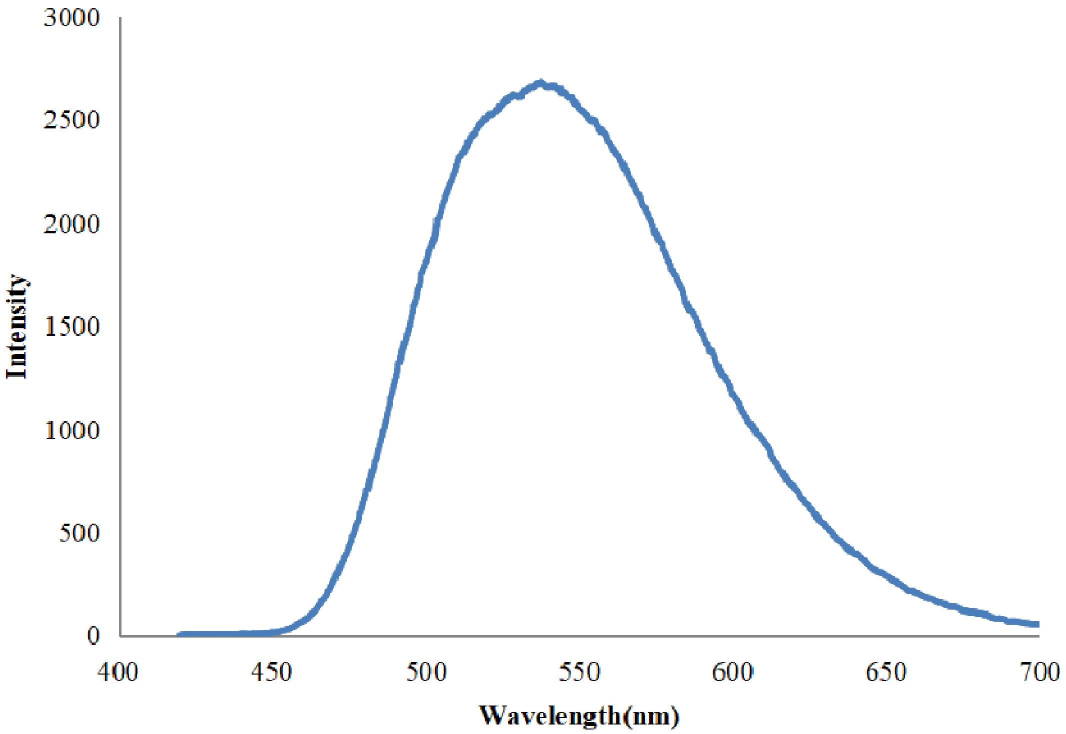
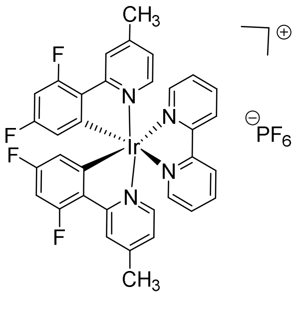


Figure S13: a) Cyclic voltammogram of [Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$ with data tabulated. In cases where peaks are reversible, $E_{1/2}$ is provided. b) Emission spectra for of [Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$. The maxima were obtained at 540 nm; the intensity is 10% of the emission maxima at 468 nm, $E_{0\text{-}0}$ = 2.65.



[Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$

Ir(II)/Ir(III)

$E_{1/2}$= -1.36 V vs SCE

$E_{1/2}$= -1.74 V vs Fc/Fc$^+$

Ir(III)/Ir(IV)

E_P=1.72 V vs SCE

E_P=1.34 V vs Fc/Fc$^+$

Ir(II)/Ir*(III)

E*= 1.29 V vs SCE

E*= 0.91 V vs Fc/Fc$^+$

Ir(III*)/Ir(IV)

E*= -0.93 V vs SCE

E*= -1.31 V vs Fc/Fc$^+$

Figure S14: Redox potential data of [Ir(dF(Me)ppy)$_2$(bpy)]PF$_6$.

7.5 UV-vis absorption study

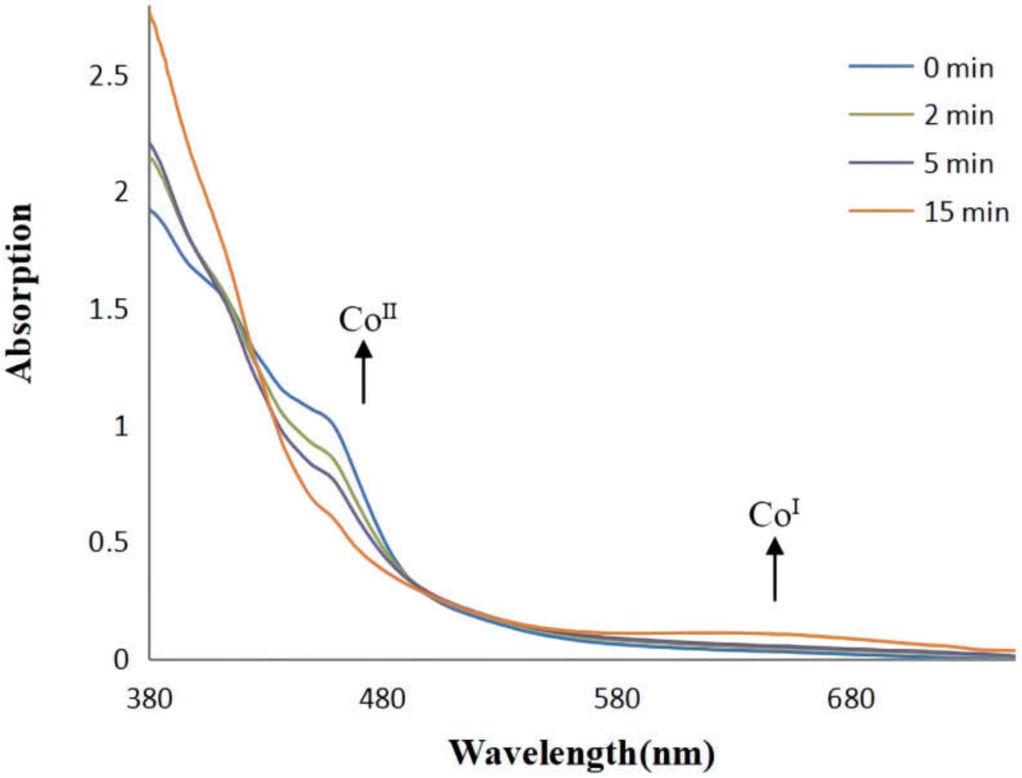


Figure S15: UV-vis absorption of a solution of 3-methylbut-2-en-1-yl phenylcarbamate **7a** (0.1 mmol), Ir[dF(CF_3)ppy]$_2$(bpy))PF_6 (0.002 mmol, 2 mol%), Co($dmgBF_2$)$_2$(MeCN)$_2$ (0.005 mmol, 5 mol%), $NBu_4OP(O)(OBu)_2$ (0.04 mmol, 40 mol%) in 20 mL DCM was irradiation with blue LEDs for 0 min, 2 min, 5 min, 15 min under argon atmosphere.

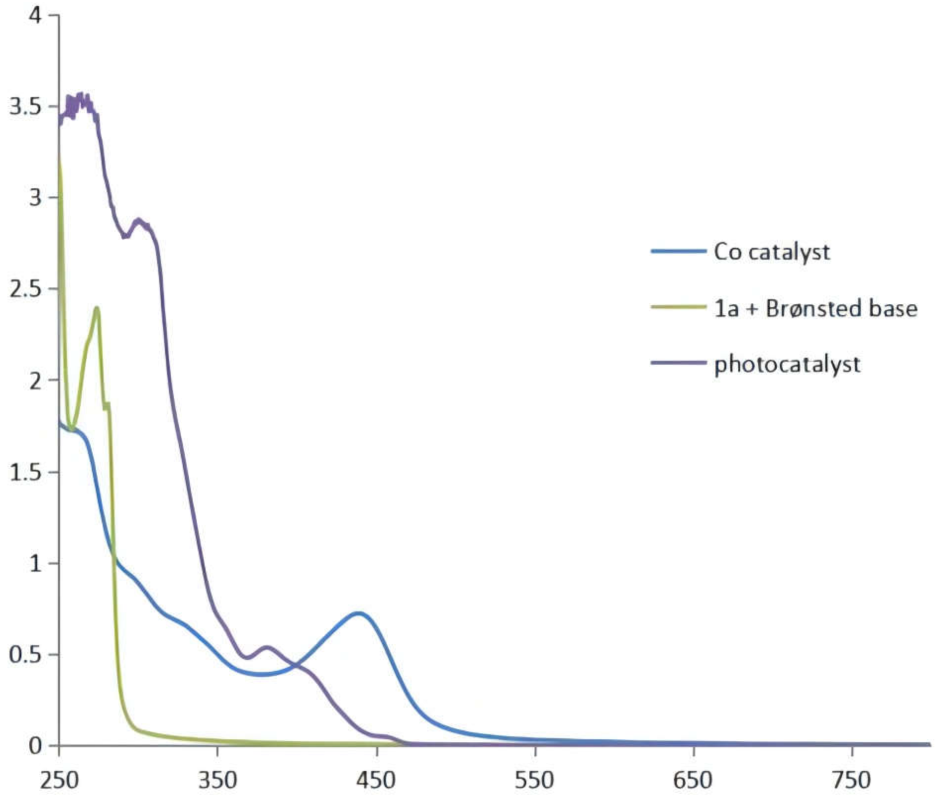


Figure S16. UV-vis absorption of Ir[dF(CF$_3$)ppy]$_2$(bpy))PF$_6$ (0.1 mM), Co^{II}(dmgBF$_2$)$_2$(MeCN)$_2$ (0.25 mM) and **7a** (5 mM) + NBu$_4$OP(O)(OBu)$_2$ (2 mM) in DCM.

7.6 Determination of gas produced in reaction with GC

Qualitative detection of hydrogen was obtained by Agilent 7890b gas chromatography (GC). Considering that DCM with low boiling point cannot be frozen by liquid nitrogen, which will affect the detection of gas chromatograph, we changed the solvent to dichloroethane. To a 50 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, 3-methylbut-2-en-1-yl phenylcarbamate (**7a**, 1 mmol, 1.0 equiv.), [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (24 mg, 2 mol%), Co(dmgH)$_2$ (DMAP)Cl (22 mg, 0.01 mmol, 5 mol%), and NBu$_4$OP(O)(OBu)$_2$ (72 mg, 0.8 mmol, 40 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCE (10 mL) were then added under argon atmosphere. After the reaction finished, the sealed tube was cooled in liquid nitrogen. Gas produced in the sealed tube was injected into gas chromatography with syringe.

By comparing with the retention time of standard gas, it is determined that the produced gas is hydrogen.

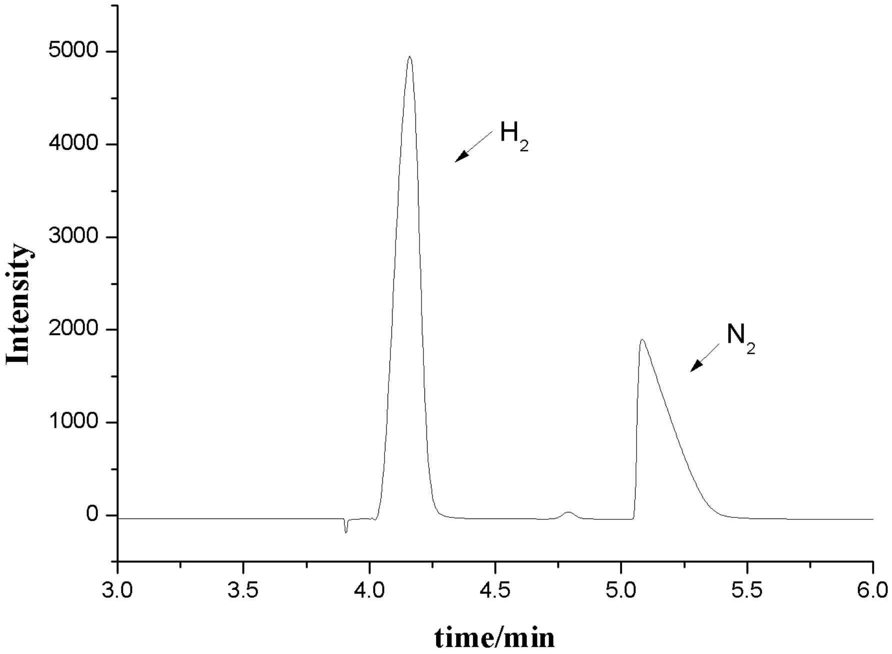


Figure S17: Determination of gas produced in reaction with GC

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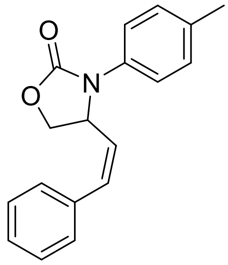
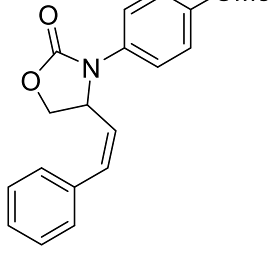
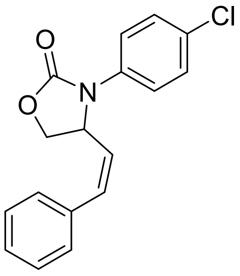
8. Characterization of the products



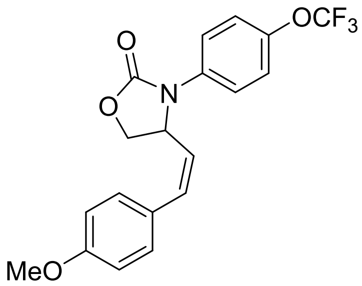
(*Z*)-4-Styryl-3-(p-tolyl)oxazolidin-2-one (2a): Followed the general procedure 1 with *E*-4-phenylbut-2-en-1-yl p-tolylcarbamate (56 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 36 mg of the title compound (yellow oil; 65% yield; *Z/E* > 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.24 (m, 3H), 7.06 – 6.97 (m, 6H), 6.69 (d, *J* = 11.4 Hz, 1H), 5.57 (dd, *J* = 11.4, 9.4 Hz, 1H), 5.25 – 5.06 (m, 1H), 4.59 (t, *J* = 8.6 Hz, 1H), 4.13 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.21 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.7, 135.4, 135.2, 134.8, 134.2, 129.5, 129.1, 128.7, 128.3, 128.1, 121.5, 67.1, 54.5, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2971, 1750, 1610, 1503, 1408 1237, 1104, 1049, 869, 746; **HRMS (ESI)** calcd $C_{18}H_{18}NO_2$ $[M + H]^+$: 280.1332, found: 280.1342.



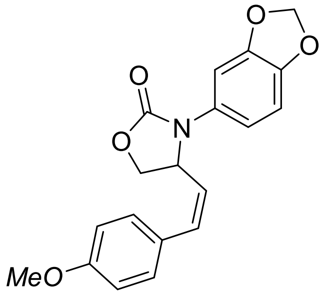
(*Z*)-3-(4-Methoxyphenyl)-4-styryloxazolidin-2-one (2b): Followed the general procedure 1 with *E*-4-phenylbut-2-en-1-yl (4-methoxyphenyl)carbamate (60 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 33 mg of the title compound (yellow oil; 55% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38 (t, *J* = 7.3 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.15 – 7.10 (m, 2H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.86 – 6.79 (m, 2H), 6.78 (d, *J* = 11.5 Hz, 1H), 5.66 (dd, *J* = 11.4, 9.4 Hz, 1H), 5.27 – 5.14 (m, 1H), 4.67 (t, *J* = 8.6 Hz, 1H), 4.21 (dd, *J* = 8.5, 7.4 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 157.2, 155.9, 135.3, 135.3, 129.5, 128.9, 128.6, 128.2, 128.0, 123.4, 114.1, 67.1, 55.4, 54.9. **FT-IR** (thin film, KBr): ν (cm^{-1}) 2918, 1748, 1512, 1395, 1296, 1247, 1208, 1032, 967, 827, 699; **HRMS (ESI)** calcd $C_{18}H_{18}NO_3$ [M + H]$^+$: 296.1281, found: 296.1280.



(*Z*)-3-(4-Chlorophenyl)-4-styryloxazolidin-2-one (2c): Followed the general procedure 1 with (*E*)-4-phenylbut-2-en-1-yl (4-chlorophenyl)carbamate (60 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 32 mg of the title compound (yellow oil; 54% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.46 – 7.40 (m, 2H), 7.39 – 7.35 (m, 1H), 7.27 – 7.20 (m, 2H), 7.15 – 7.09 (m, 4H), 6.81 (d, *J* = 11.3 Hz, 1H), 5.67 – 5.55 (m, 1H), 5.33 – 5.19 (m, 1H), 4.73 – 4.63 (m, 1H), 4.31 – 4.19 (m, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.2, 135.6, 135.3, 135.1, 130.1, 128.84, 128.81, 128.4, 128.3, 128.2, 122.1, 67.0, 54.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2923, 1751, 1598, 1494, 1392, 1296, 1204, 1125, 1042, 965, 824, 699; **HRMS (ESI)** calcd $C_{17}H_{14}{}^{35}ClNO_2$ [M + H]$^+$: 300.0786, found: 300.0789.

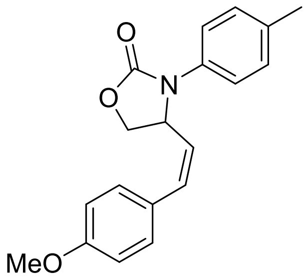


(*Z*)-4-(4-Methoxystyryl)-3-(4-(trifluoromethoxy)phenyl)oxazolidin-2-one (2d): Followed the general procedure 1 with (*E*)-4-(4-methoxyphenyl)but-3-en-1-yl (4-(trifluoromethoxy)phenyl)carbamate (76 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 37 mg of the title compound (yellow oil; 49% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.24 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 11.4 Hz, 1H), 5.60 – 5.48 (m, 1H), 5.29 (dd, *J* = 16.4, 8.6 Hz, 1H), 4.71 (t, *J* = 8.6 Hz, 1H), 4.31 – 4.16 (m, 1H), 3.84 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 159.6, 155.2, 145.6, 135.5, 135.1, 129.6, 127.5, 126.9, 122.1, 121.2, 120.4 (q, *J* = 257.1 Hz), 114.2, 67.1, 55.3, 54.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1744, 1512, 1394, 1355, 1317, 1209, 1124, 1087, 811, 722; **HRMS (ESI)** calcd $C_{19}H_{17}F_3NO_4$ [M + H]$^+$: 380.1104, found: 380.1107.

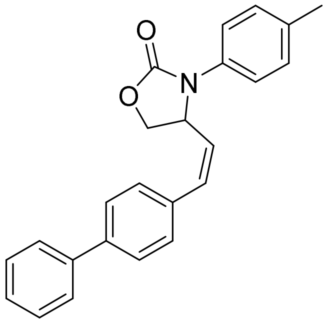


(*Z*)-3-(Benzo[d][1,3]dioxol-5-yl)-4-(4-methoxystyryl)oxazolidin-2-one (2e): Followed the general procedure 1 with *E*-4-(4-methoxyphenyl)but-3-en-1-yl benzo[d][1,3]dioxol-5-ylcarbamate (68 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 30 mg of the title compound (yellow oil; 44% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.72 – 6.65 (m, 2H), 6.53 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.94 – 5.91 (m, 2H), 5.54 (dd, *J* = 11.3, 9.4 Hz, 1H), 5.19 (dd, *J* = 16.8, 8.5 Hz, 1H), 4.65 (t, *J* = 8.6 Hz, 1H), 4.26 – 4.14 (m, 1H), 3.83 (s, 3H);

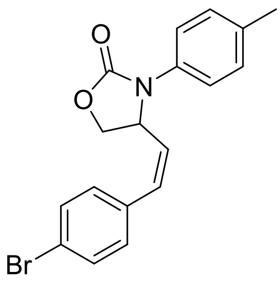
^{13}C NMR (150 MHz, CDCl$_3$) δ 159.4, 155.9, 147.9, 145.2, 134.9, 130.7, 129.6, 127.7, 127.3, 115.5, 114.1, 107.9, 104.6, 101.4, 67.2, 55.3, 55.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2922, 1751, 1597, 1494, 1392, 1203, 1125, 1042, 823, 699; **HRMS (ESI)** calcd $C_{19}H_{17}NO_5$ [M + H]$^+$: 340.1179, found: 340.1175.



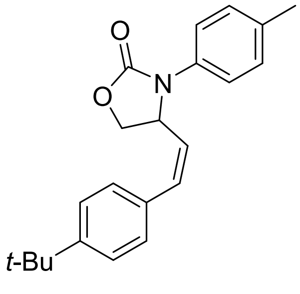
(*Z*)-4-(4-Methoxystyryl)-3-(p-tolyl)oxazolidin-2-one (2f): Followed the general procedure 1 with (*E*)-4-(4-methoxyphenyl)but-2-en-1-yl p-tolylcarbamate (62 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 33 mg of the title compound (yellow oil; 54% yield; *Z/E* > 20:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.17 – 7.03 (m, 6H), 6.97 – 6.88 (m, 2H), 6.69 (d, *J* = 11.4 Hz, 1H), 5.55 (dd, *J* = 11.4, 9.3 Hz, 1H), 5.37 – 5.22 (m, 1H), 4.68 (t, *J* = 8.6 Hz, 1H), 4.20 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.84 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 159.5, 155.7, 134.7, 134.6, 134.2, 129.7, 129.4, 127.9, 127.6, 121.4, 114.2, 67.2, 55.4, 54.5, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1745, 1514, 1396, 1354, 1294, 1205, 1127, 1038, 811, 747; **HRMS (ESI)** calcd $C_{19}H_{20}NO_3$ [M + H]$^+$: 310.1438, found: 310.1440.



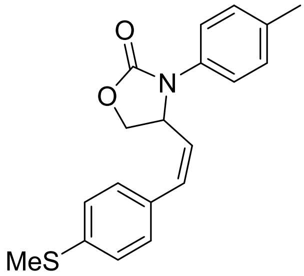
(*Z*)-4-(2-([1,1'-Biphenyl]-4-yl)vinyl)-3-(p-tolyl)oxazolidin-2-one (2g): Followed the general procedure 1 with *E*-4-([1,1'-biphenyl]-4-yl)but-2-en-1-yl p-tolylcarbamate (71 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 40 mg of the title compound (yellow oil; 57% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.62 (t, *J* = 7.5 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.07 (m, 4H), 6.79 (d, *J* = 11.5 Hz, 1H), 5.68 (dd, *J* = 11.4, 9.4 Hz, 1H), 5.33 (dd, *J* = 16.5, 8.6 Hz, 1H), 4.72 (t, *J* = 8.6 Hz, 1H), 4.24 (dd, *J* = 8.4, 7.3 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.6, 140.9, 140.2, 134.8, 134.7, 134.3, 134.1, 129.5, 129.1, 128.9, 128.7, 127.7, 127.4, 127.0, 121.5, 67.1, 54.6, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1748, 1514, 1486, 1393, 1354, 1206, 1118, 1041, 812, 730; **HRMS (ESI)** calcd $C_{24}H_{22}NO_2$ [M + H]$^+$: 356.1645, found: 356.1639.



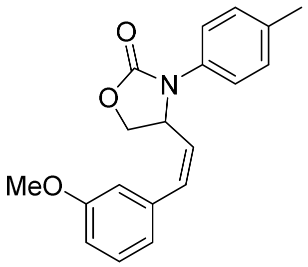
(*Z*)-4-(4-Bromostyryl)-3-(p-tolyl)oxazolidin-2-one (2h): Followed the general procedure 1 with *E*-4-(4-bromophenyl)but-2-en-1-yl p-tolylcarbamate (72 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 44 mg of the title compound (yellow oil; 62% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.15 – 7.05 (m, 4H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 11.5 Hz, 1H), 5.69 (dd, *J* = 11.4, 9.5 Hz, 1H), 5.19 (dd, *J* = 16.5, 8.7 Hz, 1H), 4.66 (t, *J* = 8.6 Hz, 1H), 4.20 (dd, *J* = 8.4, 7.3 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.6, 151.2, 135.0, 134.2, 133.9, 131.9, 129.8, 129.7, 129.5, 122.2, 121.7, 66.9, 54.5, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1745, 1512, 1394, 1356, 1293, 1210, 1064, 812, 774; **HRMS (ESI)** calcd $C_{18}H_{17}{}^{79}BrNO_2$ [M + H]$^+$: 358.0437, found: 358.0445.



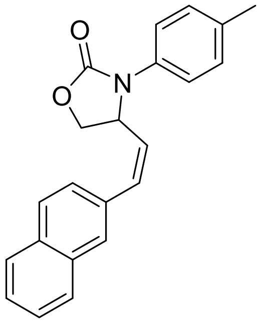
(*Z*)-4-(4-(*tert*-Butyl)styryl)-3-(p-tolyl)oxazolidin-2-one (2i): Followed the general procedure 1 with (*E*)-4-(4-(tert-butyl)phenyl)but-2-en-1-yl p-tolylcarbamate (67 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 34 mg of the title compound (yellow oil; 51% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 11.4 Hz, 1H), 5.61 (dd, *J* = 11.4, 9.3 Hz, 1H), 5.30 (dd, *J* = 16.7, 8.5 Hz, 1H), 4.69 (t, *J* = 8.6 Hz, 1H), 4.21 (dd, *J* = 8.4, 7.4 Hz, 1H), 2.29 (s, 3H), 1.35 (s, 9H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.7, 151.2, 134.9, 134.7, 134.2, 132.5, 129.4, 128.5, 128.0, 125.6, 121.4, 67.2, 54.6, 34.7, 31.3, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1745, 1512, 1394, 1356, 1293, 1210, 1064, 812, 774; **HRMS (ESI)** calcd $C_{22}H_{26}NO_2$ [M + H]$^+$: 336.1958, found: 336.1952.



(*Z*)-4-(4-(Methylthio)styryl)-3-(p-tolyl)oxazolidin-2-one **(2j):** Followed the general procedure 1 with 4-(4-(methylthio)phenyl)but-2-en-1-yl p-tolylcarbamate (65 mg, 0.2 mmol, *E/Z* = 5:1) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 34 mg of the title compound (yellow oil; 52% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.27 – 7.23 (m, 2H), 7.09 (s, 4H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 11.5 Hz, 1H), 5.61 (dd, *J* = 11.4, 9.4 Hz, 1H), 5.26 (dd, *J* = 16.4, 8.8 Hz, 1H), 4.67 (t, *J* = 8.6 Hz, 1H), 4.21 (dd, *J* = 8.5, 7.3 Hz, 1H), 2.51 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.6, 139.0, 134.8, 134.5, 134.1, 131.9, 129.4, 128.7, 128.6, 126.3, 121.5, 67.0, 54.5, 20.8, 15.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2920, 1749, 1594, 1514, 1393, 1120, 1040, 814, 753; **HRMS (ESI)** calcd $C_{16}H_{16}NO_2S$ [M + H]$^+$: 326.1209, found: 326.1203.

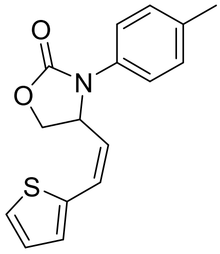


(*Z*)-4-(3-Methoxystyryl)-3-(p-tolyl)oxazolidin-2-one (2k): Followed the general procedure 1 with *E*-4-(3-methoxyphenyl)but-2-en-1-yl p-tolylcarbamate (62 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 36 mg of the title compound (yellow oil; 58% yield; *Z/E* > 20:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.32 (t, *J* = 7.9 Hz, 1H), 7.15 – 7.06 (m, 4H), 6.89 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.74 (d, *J* = 11.4 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.63 (s, 1H), 5.65 (dd, *J* = 11.4, 9.4 Hz, 1H), 5.27 (dd, *J* = 16.3, 8.9 Hz, 1H), 4.67 (t, *J* = 8.6 Hz, 1H), 4.21 (dd, *J* = 8.5, 7.1 Hz, 1H), 3.82 (s, 3H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 159.7, 155.6, 136.7, 135.0, 134.8, 134.1, 129.7, 129.4, 129.2, 121.5, 120.5, 114.2, 113.2, 67.1, 55.3, 54.6, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2920, 1745, 1513, 1395, 1204, 11127, 1038, 811, 746; **HRMS (ESI)** calcd $C_{19}H_{20}NO_3$ [M + H]$^+$: 310.1438 found: 310.1439.

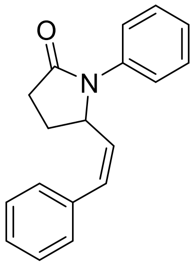


4-(2-(Naphthalen-2-yl)vinyl)-3-(p-tolyl)oxazolidin-2-one (2l): Followed the general procedure 1 with (*E*)-4-(naphthalen-2-yl)but-2-en-1-yl *p*-tolylcarbamate (66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 29 mg of the title compound (yellow oil; 44% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.84 – 7.79 (m, 1H), 7.55 – 7.51 (m, 2H), 7.49 (s, 1H), 7.28 – 7.19 (m, 1H), 7.15 – 7.04 (m, 4H), 6.91 (d, *J* = 11.4 Hz, 0.95H)/6.77 (d, *J* = 15.7 Hz, 0.04H), 6.22 (dd, *J* = 15.8, 8.2 Hz, 0.03H)/5.72 (dd, *J* = 11.2, 9.6 Hz, 0.94H), 5.33 (dd, *J* = 16.6, 8.6 Hz, 1H), 4.73 (t, *J* = 8.6 Hz, 1H), 4.31 –

4.24 (m, 1H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.7, 135.2, 134.9, 134.1, 133.1, 132.8, 132.7, 129.5, 129.3, 128.4, 128.0, 127.7, 127.3, 126.7, 126.6, 126.0, 121.8, 67.2, 54.7, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1745, 1514, 1396, 1205, 1127, 1038, 811, 747; **HRMS (ESI)** calcd $C_{22}H_{20}NO_2$ [M + H]$^+$: 330.1489, found: 330.1481.

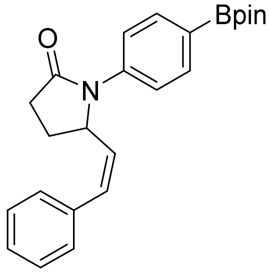


(*Z*)-4-(2-(Thiophen-2-yl)vinyl)-3-(p-tolyl)oxazolidin-2-one (2m): Followed the general procedure 3 with (*E*)-6-(thiophen-2-yl)-*N*-(p-tolyl)hex-4-enamide (57 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 28 mg of the title compound (yellow oil; 49% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38 (d, *J* = 5.1 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.05 (m, 1H), 6.99 (d, *J* = 3.5 Hz, 1H), 6.74 (d, *J* = 11.4 Hz, 1H), 5.62 (dd, *J* = 15.9, 8.4 Hz, 1H), 5.55 (dd, *J* = 11.4, 9.1 Hz, 1H), 4.77 (t, *J* = 8.6 Hz, 1H), 4.14 (dd, *J* = 8.5, 6.8 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.5, 137.6, 134.7, 134.3, 129.5, 129.4, 127.6, 127.2, 126.9, 126.5, 120.9, 66.9, 55.1, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2923, 1749, 1514, 1395, 1356, 1295, 1211, 1126, 1042, 817, 776; **HRMS (ESI)** calcd $C_{16}H_{16}NO_2S$ [M + H]$^+$: 286.0896, found: 286.0889.

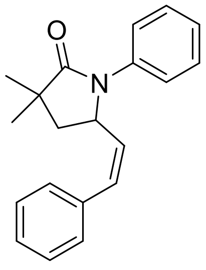


(Z)-1-Phenyl-5-styrylpyrrolidin-2-one (2n): Followed the general procedure 1 with *N*,6-diphenylhex-4-enamide (53 mg, 0.2 mmol, *E/Z*=3:1) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 33 mg of the title compound (yellow oil; 62% yield; *Z/E* > 20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38 (t, *J* = 7.5

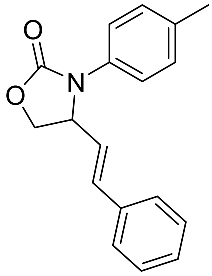
Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 11.5 Hz, 1H), 5.57 (dd, *J* = 11.5, 9.6 Hz, 1H), 5.10 (dd, *J* = 16.4, 6.9 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.64 – 2.56 (m, 1H), 2.56 – 2.48 (m, 1H), 2.14 – 1.97 (m, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 174.0, 137.7, 136.1, 132.4, 132.3, 128.6, 128.5, 128.4, 127.6, 125.3, 122.9, 57.3, 31.5, 26.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1745, 1512, 1394, 1356, 1293, 1210, 1064, 812, 774; **HRMS (ESI)** calcd $C_{18}H_{17}NONa$ [M + Na]$^+$: 286.1202 found: 286.1204.



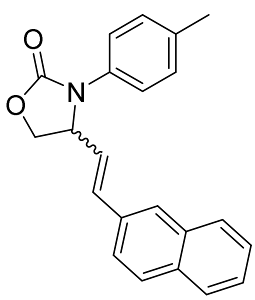
5-Styryl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolidin-2-one (2o): Followed the general procedure 1 with (*E*)-6-phenyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hex-4-enamide (78 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 44 mg of the title compound (yellow oil; 56% yield; *Z/E* = 18:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.78 – 7.74 (m, 0.10H)/7.72 – 7.66 (m, 1.84H), 7.54 – 7.49 (m, 0.11H)/7.42 – 7.36 (m, 1.89H), 7.34 – 7.29 (m, 1H), 7.27 – 7.22 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 11.5 Hz, 0.91H)/6.48 (d, *J* = 16.0 Hz, 0.05H), 6.09 (dd, *J* = 15.9, 7.2 Hz, 0.05H)/5.54 (dd, *J* = 11.2, 9.8 Hz, 0.92H), 5.18 – 5.07 (m, 0.95H)/4.91 – 4.80 (m, 0.05H), 2.75 – 2.64 (m, 1H), 2.63 – 2.55 (m, 1H), 2.53 – 2.46 (m, 1H), 2.10 – 1.99 (m, 1H), 1.31 (d, *J* = 2.2 Hz, 12H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 173.9, 140.4, 136.1, 135.1, 132.4, 132.3, 128.5, 128.4, 127.6, 121.3, 83.7, 56.9, 31.7, 26.1, 24.83, 24.81; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1741, 1606, 1414, 1362, 1326, 1267, 1067, 1025, 861, 756; **HRMS (ESI)** calcd $C_{24}H_{28}BNO_3Na$ [M + Na]$^+$: 412.2054 found: 412.2061.



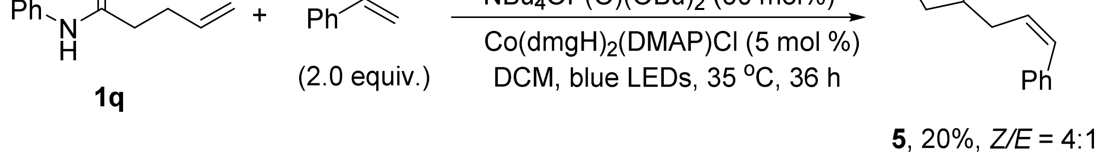
(*Z*)-3,3-Dimethyl-1-phenyl-5-styrylpyrrolidin-2-one (2p): Followed the general procedure 1 with (*E*)-2,2-dimethyl-N,6-diphenylhex-4-enamide (59 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 35 mg of the title compound (yellow oil; 60% yield; *Z/E* > 20:1);**^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.23 – 7.17 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 11.5 Hz, 1H), 5.48 (t, *J* = 10.4 Hz, 1H), 5.06 (dd, *J* = 16.1, 8.0 Hz, 1H), 2.37 (dd, *J* = 12.7, 7.4 Hz, 1H), 1.94 (dd, *J* = 12.6, 7.6 Hz, 1H), 1.35 (s, 3H), 1.23 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 178.7, 137.9, 136.2, 133.0, 132.3, 128.5, 128.43, 128.38, 127.6, 125.0, 122.9, 53.5, 41.9, 41.2, 25.9, 25.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1745, 1512, 1394, 1356, 1293, 1210, 1025, 756, 655; **HRMS (ESI)** calcd $C_{20}H_{22}NO$ [M + H]$^+$: 292.1696 found: 292.1696.



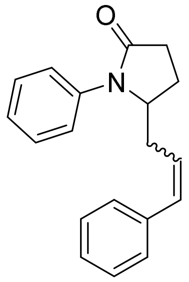
4-Styryl-3-(p-tolyl)oxazolidin-2-one (3): Followed the general procedure 2 with *E*-4-phenylbut-2-en-1-yl p-tolylcarbamate (56 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 21 mg of the title compound (yellow oil; 38% yield; the *E*-isomer); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.34 – 7.29 (m, 5H), 7.29 – 7.24 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 8.3 Hz, 1H), 4.97 (dd, *J* = 15.1, 8.3 Hz, 1H), 4.63 (t, *J* = 8.7 Hz, 1H), 4.17 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.8, 135.2, 135.1, 134.9, 134.3, 129.6, 128.7, 128.6, 126.7, 125.7, 121.9, 67.3, 59.8, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2925, 1690, 1596, 1496, 1388, 1293, 1220, 1113, 1070, 967, 754, 692; **HRMS (ESI)** calcd $C_{18}H_{17}NO_2Na$ [M + Na]$^+$: 302.1151, found: 302.1142.



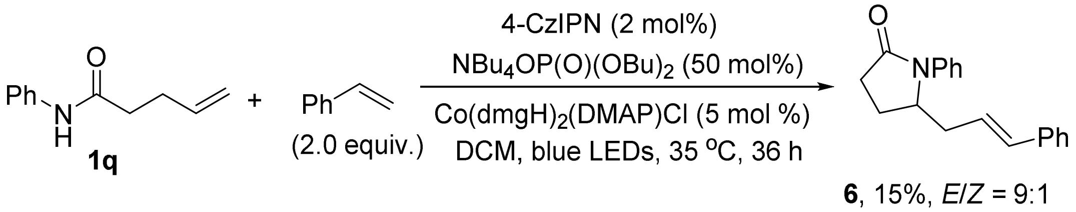
4-(2-(Naphthalen-2-yl)vinyl)-3-(p-tolyl)oxazolidin-2-one (4): Followed the general procedure 2 with (*E*)-4-(naphthalen-2-yl)but-2-en-1-yl *p*-tolylcarbamate (66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 23 mg of the title compound (yellow oil; 35% yield; *E/Z* = 5:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.87 – 7.85 (m, 0.36H)/7.83 – 7.77 (m, 1.69H), 7.77 – 7.74 (m, 1H), 7.68 (s, 1H), 7.53 – 7.44 (m, 3H), 7.37 – 7.33 (m, 1.68H)/7.23 – 7.19 (m, 0.36H), 7.16 – 7.11 (m, 1.65H)/7.10 – 7.08 (m, 0.43H), 6.91 (d, *J* = 11.4 Hz, 0.17H)/6.77 (d, *J* = 15.8 Hz, 0.84H), 6.22 (dd, *J* = 15.8, 8.3 Hz, 0.86H)/5.72 (dd, *J* = 11.0, 9.7 Hz, 0.17H), 5.33 (dd, *J* = 16.6, 8.5 Hz, 0.18H)/5.02 (dd, *J* = 15.2, 8.2 Hz, 0.87H), 4.73 (t, *J* = 8.6 Hz, 0.19H)/4.65 (t, *J* = 8.7 Hz, 0.89H), 4.31 – 4.25 (m, 0.18H)/4.25 – 4.15 (m, 0.91H), 2.29 (s, 0.46H), 2.27 (s, 2.46H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.9, 135.2, 134.9, 134.3, 133.3, 132.7, 129.6,/129.5, 129.3/128.4, 128.0, 127.7, 127.3/127.2, 126.7/126.5, 126.6/126.4, 125.9, 123.2, 121.9/121.8, 67.4/67.2, 59.9/54.7, 29.7/20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1731, 1513, 1395, 1357, 1293, 1210, 1126, 1035, 965, 811; **HRMS (ESI)** calcd $C_{22}H_{20}NO_2$ [M + H]$^+$: 330.1489, found: 330.1491.



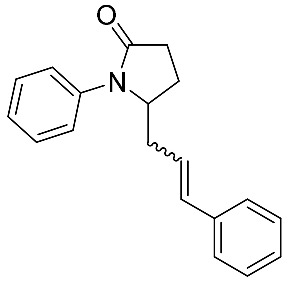
To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, *N*-phenylpent-4-enamide (35 mg, 0.2 mmol, 1.0 equiv.), [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (4.2 mg, 2 mol%), Co(dmgH)$_2$ (DMAP)Cl (4.3 mg, 0.01 mmol, 5 mol%), and NBu$_4$OP(O)(OBu)$_2$ (45 mg, 0.1 mmol, 50 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. Styrene (46 μL, 0.4 mmol, 2.0 equiv.) and DCM (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 36 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. The crude product was purified by silica gel column chromatography (PE/EA = 20:1 to 10:1) to afford **7** (11 mg, colorless oil, 20% yield; *Z/E* = 4:1).



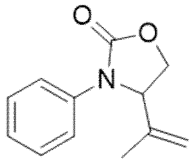
***N*-Phenyl-5-(3-phenylallyl)pyrrolidin-2-one (5)**: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.45 – 7.41 (m, 1H), 7.38 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 2H), 7.19 – 7.08 (m, 2H), 6.58 (d, *J* = 11.7 Hz, 0.77H)/6.39 (d, *J* = 15.8 Hz, 0.19H), 6.12 – 5.97 (m, 0.20H)/5.64 – 5.50 (m, 0.79H), 4.41 – 4.35 (m, 0.21H)/4.35 – 4.28 (m, 0.79H), 2.75 – 2.62 (m, 1H), 2.60 – 2.49 (m, 2H), 2.49 – 2.41 (m, 1H), 2.35 – 2.22 (m, 1H), 2.03 – 1.95 (m, 0.23H)/1.90 – 1.80 (m, 0.81H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 174.3, 137.4, 136.9, 133.8/132.5, 129.1/129.04, 128.6/128.52, 128.4/128.2, 127.5/126.9, 126.1/125.9, 125.9, 124.2/124.1, 123.9, 59.5/59.4, 36.8/31.8, 31.22/31.16, 23.3/23.2; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2923, 1758, 1691, 1597, 1496, 1392, 1298, 1210, 1043, 808, 754, 604; **HRMS (ESI)** calcd C$_{19}$H$_{19}$NONa [M + Na]$^+$: 300.1359, found: 300.1363



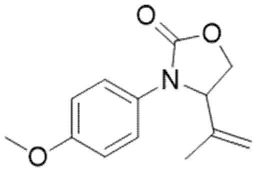
To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, *N*-phenylpent-4-enamide (35 mg, 0.2 mmol, 1.0 equiv.), 4-CzIPN (4.2 mg, 2 mol%), Co(dmgH)$_2$ (DMAP)Cl (4.3 mg, 0.01 mmol, 5 mol%), and NBu$_4$OP(O)(OBu)$_2$ (45 mg, 0.1 mmol, 50 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. Styrene (46 μL, 0.4 mmol, 2.0 equiv.) and DCM (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 36 hours. The temperature was maintained at 35 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. The crude product was purified by silica gel column chromatography (PE/EA = 20:1 to 10:1) to afford **8** (8 mg, colorless oil, 20% yield; *E/Z* = 9:1).



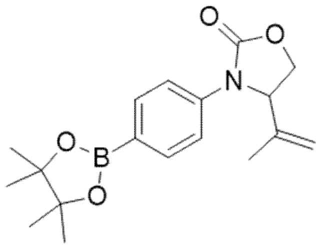
1-Phenyl-5-(3-phenylallyl)pyrrolidin-2-one (6): **(400 MHz, CDCl$_3$)** δ 7.44 – 7.40 (m, 3H), 7.39 – 7.34 (m, 1H), 7.32 – 7.26 (m, 4H), 7.25 – 7.20 (m, 2H), 6.57 (d, *J* = 11.7 Hz, 0.11H)/6.38 (d, *J* = 15.8 Hz, 0.90H), 6.04 (dt, *J* = 15.7, 7.3 Hz, 0.91H)/5.56 (dt, *J* = 11.7, 7.3 Hz, 0.11H), 4.41 – 4.34 (m, 0.91H)/4.32 – 4.27 (m, 0.13H), 2.70 – 2.47 (m, 3H), 2.43 – 2.27 (m, 2H), 2.05 – 1.90 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 174.3, 137.6, 137.0, 133.9, 129.2, 128.6, 127.5, 126.1, 126.0, 124.2, 124.0, 59.5, 36.8, 31.3, 23.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2925, 1691, 1596, 1497, 1388, 1294, 1070, 967, 754; **HRMS (ESI)** calcd C$_{19}$H$_{19}$NONa [M + Na]$^+$: 300.1359, found: 300.1365.



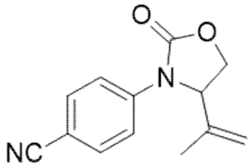
3-Phenyl-4-(prop-1-en-2-yl)oxazolidin-2-one (8a): Followed the general procedure 3 with 3-mthylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 40 mg of the title compound (yellow oil; 99% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52 – 7.44 (m, 2H), 7.38 – 7.30 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.09 (s, 1H), 5.03 (s, 1H), 4.89 (dd, *J* = 9.1, 5.5 Hz, 1H), 4.56 (t, *J* = 8.9 Hz, 1H), 4.12 (dd, *J* = 8.8, 5.5 Hz, 1H), 1.68 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 155.7, 141.4, 137.3, 128.9, 124.7, 120.4, 116.2, 66.2, 62.1, 16.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1730, 1597, 1498, 1398, 1260, 1122, 1014, 963, 768, 672; **HRMS (ESI)** calcd $C_{12}H_{13}NO_2Na$ [M + Na]$^+$: 226.0838, found: 226.0832.



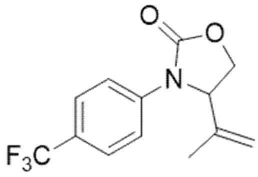
3-(4-Methoxyphenyl)-4-(prop-1-en-2-yl)oxazolidin-2-one (8b): Followed the general procedure 3 with 3-methylbut-2-en-1-yl(4-methoxyphenyl)carbamate (47 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 42 mg of the title compound (yellow oil; 90% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.44 – 7.31 (m, 2H), 6.93 – 6.83 (m, 2H), 5.05 (s, 1H), 5.00 (s, 1H), 4.83 (dd, *J* = 9.1, 5.8 Hz, 1H), 4.54 (t, *J* = 9.0 Hz, 1H), 4.11 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.78 (s, 3H), 1.68 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 156.8, 156.1, 141.3, 130.1, 122.6, 116.6, 114.2, 66.0, 62.7, 55.5, 16.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2926, 1743, 1511, 1397, 1296, 1246,, 1125, 1029, 966, 828, 646; **HRMS (ESI)** calcd $C_{13}H_{15}NO_3Na$ [M + Na]$^+$: 256.0944, found: 256.0945.



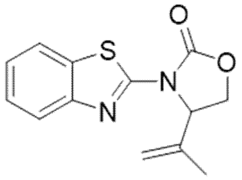
4-(Prop-1-en-2-yl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)oxazolidin-2-one (8c): Followed the general procedure 3 with 3-methylbut-2-en-1-yl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 59 mg of the title compound (yellow oil; 90% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.77 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 5.06 (s, 1H), 5.00 (s, 1H), 4.89 (dd, *J* = 9.1, 5.3 Hz, 1H), 4.54 (t, *J* = 8.9 Hz, 1H), 4.09 (dd, *J* = 8.7, 5.3 Hz, 1H), 1.64 (s, 3H), 1.32 (s, 12H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.3, 141.2, 139.8, 135.7, 135.5, 118.9, 116.1, 83.8, 66.2, 61.7, 24.9, 24.8, 16.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2929, 1722, 1335, 1156, 1090, 971, 814, 652; **HRMS (ESI)** calcd $C_{18}H_{24}BNO_4Na$ [M + Na]$^+$: 352.1691, found: 352.1690.



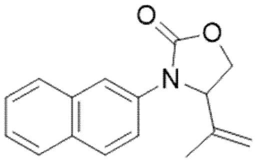
4-(2-Oxo-4-(prop-1-en-2-yl)oxazolidin-3-yl)benzonitrile (8d): Followed the general procedure 3 with 3-methylbut-2-en-1-yl (4-cyanophenyl)carbamate (46 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 36 mg of the title compound (yellow oil; 78% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.69 – 7.64 (m, 2H), 7.64 – 7.59 (m, 2H), 5.12 (s, 1H), 5.10 (s, 1H), 4.89 (dd, *J* = 9.0, 4.9 Hz, 1H), 4.60 (t, *J* = 9.0 Hz, 1H), 4.15 (dd, *J* = 8.8, 5.0 Hz, 1H), 1.68 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 154.9, 141.4, 140.6, 133.1, 119.4, 118.7, 116.6, 107.4, 66.4, 61.5, 16.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2920, 2227, 1746, 1605, 1512, 1476, 1422, 1397, 1202, 1138, 1060, 835, 731; **HRMS (ESI)** calcd $C_{14}H_{15}NO_2Na$ [M + Na]$^+$: 251.0791, found: 251.0786.



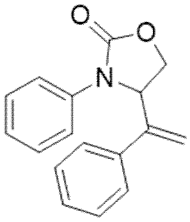
4-(Prop-1-en-2-yl)-3-(4-(trifluoromethyl)phenyl)oxazolidin-2-one (8e): Followed the general procedure 3 with 3-methylbut-2-en-1-yl (4-(trifluoromethyl)phenyl) carbamate (55 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 41 mg of the title compound (yellow oil; 76% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 5.12 (d, *J* = 0.6 Hz, 1H), 5.08 (s, 1H), 4.91 (dd, *J* = 9.1, 5.2 Hz, 1H), 4.60 (t, *J* = 9.0 Hz, 1H), 4.14 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.68 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 155.2, 140.8, 140.5, 126.5 (q, *J* = 32.6 Hz), 126.1 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.5 Hz), 119.4, 116.5, 66.3, 61.7, 16.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2925, 1738, 1616, 1523, 1396, 1324, 1201, 1118, 1070, 908, 845, 743; **HRMS (ESI)** calcd $C_{13}H_{12}F_3NO_2Na$ [M + Na]$^+$: 294.0712, found: 294.0711.



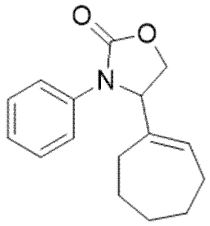
3-(Benzo[d]thiazol-2-yl)-4-(prop-1-en-2-yl)oxazolidin-2-one (8f): Followed the general procedure 3 with 3-methylbut-2-en-1-yl benzo[d]thiazol-2-ylcarbamate (52 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 48 mg of the title compound (yellow oil; 92% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.93 (s, 1H), 8.23 (d, *J* = 2.2 Hz, 1H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.55 (dd, *J* = 8.9, 2.3 Hz, 1H), 5.13 (s, 1H), 5.05 (s, 1H), 4.96 (dd, *J* = 9.1, 5.5 Hz, 1H), 4.61 (t, *J* = 8.9 Hz, 1H), 4.16 (dd, *J* = 8.8, 5.5 Hz, 1H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 155.7, 153.9, 150.2, 141.0, 135.1, 134.7, 123.6, 119.1, 116.7, 113.5, 66.2, 62.4, 16.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1744, 1605, 1473, 1391, 1203, 1130, 1054, 850, 755, 631; **HRMS (ESI)** calcd $C_{13}H_{12}N_2O_2NaS$ [M + Na]$^+$: 283.0512, found: 283.0508.



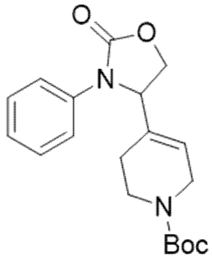
3-(Naphthalen-2-yl)-4-(prop-1-en-2-yl)oxazolidin-2-one (8g): Followed the general procedure 3 with 3-methylbut-2-en-1-yl naphthalen-2-ylcarbamate (51 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 39 mg of the title compound (yellow oil; 77% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.84 – 7.72 (m, 5H), 7.51 – 7.40 (m, 2H), 5.15 (s, 1H), 5.04 (s, 1H), 5.01 (dd, *J* = 9.0, 5.6 Hz, 1H), 4.60 (t, *J* = 8.9 Hz, 1H), 4.16 (dd, *J* = 8.5, 5.7 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.8, 141.3, 134.8, 133.4, 130.6, 128.8, 127.6, 127.5, 126.5, 125.4, 119.8, 117.6, 116.4, 66.2, 62.2, 16.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2915, 1735, 1628, 1628, 1510, 1399, 1279, 1058, 806, 814, 748; **HRMS (ESI)** calcd $C_{16}H_{15}NO_2Na$ [M + Na]$^+$: 276.0995, found: 276.0992.



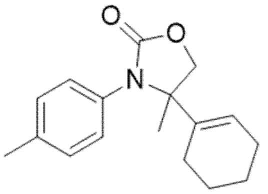
3-Phenyl-4-(1-phenylvinyl)oxazolidin-2-one (8h): Followed the general procedure 3 with (*E*)-3-phenylbut-2-en-1-yl phenylcarbamate (53 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 44 mg of the title compound (yellow oil; 83% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.60 – 7.49 (m, 2H), 7.46 – 7.30 (m, 7H), 7.19 – 7.09 (m, 1H), 5.52 (s, 1H), 5.35 – 5.29 (m, 1H), 5.29 (s, 1H), 4.63 (t, *J* = 8.6 Hz, 1H), 4.16 (dd, *J* = 8.4, 4.4 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 155.5, 144.1, 137.5, 137.4, 129.03, 128.97, 128.7, 126.5, 124.4, 119.8, 115.7, 67.7, 59.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2915, 1742, 1597, 1502, 1397, 1353, 1208, 1127, 1053, 962, 840, 751; **HRMS (ESI)** calcd $C_{17}H_{15}NO_2Na$ [M + Na]$^+$: 288.0995, found: 288.0993.



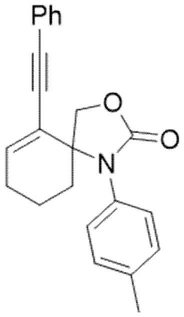
4-(Cyclohept-1-en-1-yl)-3-phenyloxazolidin-2-one (8i): Followed the general procedure 3 with 2-cycloheptylideneethyl phenylcarbamate (52 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 42 mg of the title compound (yellow oil; 82% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.94 (t, *J* = 6.4 Hz, 1H), 4.83 (dd, *J* = 8.9, 7.1 Hz, 1H), 4.49 (t, *J* = 8.9 Hz, 1H), 4.04 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.16 – 2.06 (m, 3H), 2.01 – 1.95 (m, 1H), 1.66 – 1.60 (m, 2H), 1.47 – 1.41 (m, 1H), 1.39 – 1.29 (m, 2H), 1.14 – 1.07 (m, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.0, 139.0, 137.1, 134.0, 128.7, 124.6, 121.3, 65.9, 64.1, 32.1, 28.3, 26.8, 26.5, 26.4; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2915, 1735, 1599, 1495, 1401, 1352, 1271, 1130, 1046, 978, 752, 687; **HRMS (ESI)** calcd $C_{16}H_{19}NO_2Na$ [M + Na]$^+$: 280.1308, found: 280.1306.



***tert*-Butyl 4-(2-oxo-3-phenyloxazolidin-4-yl)-3,6-dihydropyridine-1(2H)-carboxylate (8j)**: Followed the general procedure 3 with *tert*-butyl 4-(2-((phenylcarbamoyl)oxy)ethylidene)piperidine-1-carboxylate (69 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 50 mg of the title compound (yellow oil; 72% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.77 (br, 1H), 4.88 (dd, *J* = 8.7, 5.9 Hz, 1H), 4.55 (t, *J* = 8.9 Hz, 1H), 4.11 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.97 – 3.77 (m, 2H), 3.55 (br, 1H), 3.29 – 3.20 (m, 1H), 2.19 – 2.08 (m, 1H), 1.92 (br, 1H), 1.43 (s, 9H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.6, 154.7, 137.0, 133.1, 129.0, 124.9, 120.6, 80.0, 66.0, 61.6, 42.8, 40.5/39.2, 28.4, 23.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2922, 1737, 1686, 1599, 1497, 1399, 1365, 1244, 1123, 1044, 979, 756, 691; **HRMS (ESI)** calcd $C_{16}H_{19}NO_2Na$ [M + Na]$^+$: 367.1628, found: 367.1619.

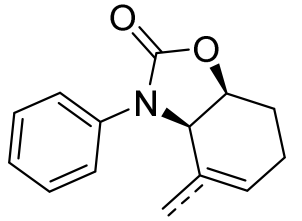


4-(Cyclohex-1-en-1-yl)-4-methyl-3-(p-tolyl)oxazolidin-2-one (8k): Followed the general procedure 3 with 2-cyclohexylidenepropyl p-tolylcarbamate (55 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 51 mg of the title compound (yellow oil; 94% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.17 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.74 (s, 1H), 4.25 (d, *J* = 8.5 Hz, 1H), 4.04 (d, *J* = 8.4 Hz, 1H), 2.31 (s, 3H), 2.18 – 2.02 (m, 4H), 1.78 – 1.71 (m, 1H), 1.71 – 1.54 (m, 3H), 1.45 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.7, 138.2, 135.9, 133.3, 129.5, 125.2, 124.7, 73.9, 65.3, 25.3, 23.8, 22.6, 22.5, 21.9, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2975, 2918, 1742, 1394, 1363, 1327, 1294, 1267, 1029, 962, 758, 656; **HRMS (ESI)** calcd $C_{17}H_{21}NO_2Na$ [M + Na]$^+$: 294.1465, found: 294.1463.



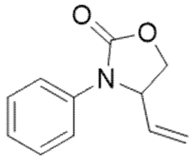
6-(Phenylethynyl)-1-(p-tolyl)-3-oxa-1-azaspiro[4.5]dec-6-en-2-one (8l): Followed the general procedure 3 with (2-(phenylethynyl)cyclohex-1-en-1-yl)methyl p-tolylcarbamate (69 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 51 mg of the title compound (yellow oil; 75% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52 – 7.43 (m, 2H), 7.37 – 7.28 (m, 5H), 7.17

(d, J = 8.0 Hz, 2H), 6.42 (t, J = 3.8 Hz, 1H), 4.56 (d, J = 8.5 Hz, 1H), 4.26 (d, J = 8.5 Hz, 1H), 2.33 (s, 3H), 2.12 – 1.85 (m, 4H), 1.68 – 1.51 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 157.3, 139.6, 137.5, 133.0, 131.7, 129.8, 128.4, 128.3, 128.0, 124.5, 122.6, 91.5, 86.5, 74.2, 64.0, 33.2, 25.2, 21.1, 18.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2920, 1742, 1515, 1391, 1342, 1229, 1185, 1053, 977, 812, 755; **HRMS (ESI)** calcd $C_{23}H_{21}NO_2Na$ [M + Na]$^+$: 366.1465, found: 366.1460.

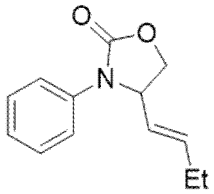


T:*I* = 2:1

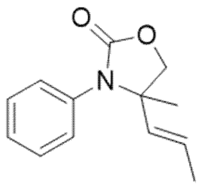
4-Methyl-3-phenyl-3a,6,7,7a-tetrahydrobenzo[d]oxazol-2(3H)-one *T*-2m and 4-methylene-3-phenylhexahydrobenzo[d]oxazol-2(3H)-one *I*-2m (8m): Followed the general procedure 3 with 3-methylcyclohex-2-en-1-yl phenylcarbamate (46 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 33 mg of the title compound (yellow oil; 73% yield; *T*:*I* = 2:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.48 (d, J = 7.6 Hz, 0.86H, I), 7.41 – 7.38 (m, 2H, T), 7.37 – 7.32 (m, 2.5H, T+I), 7.19 (t, J = 7.4 Hz, 0.47H, I), 7.15 (t, J = 7.3 Hz, 0.97H, T), 5.72 (d, J = 5.9 Hz, 0.43H, I), 5.05 (s, 1H, T), 5.03 (s, 1H, T), 4.98 – 4.95 (m, 0.45H, I), 4.83 – 4.80 (m, 1H, T), 4.78 (d, J = 7.9 Hz, 1H, T), 4.69 (d, J = 7.1 Hz, 1H, 0.45H, I), 2.36 – 2.27 (m, 0.48H, I), 2.28 – 2.23 (m, 0.48H, I), 2.23 – 2.18 (m, 2H, T), 2.03 – 1.98 (m, 0.45H, I), 1.98 – 1.91 (m, 1H, T), 1.89 – 1.83 (m, 2H, T), 1.77 – 1.72 (m, 0.46H, I), 1.62 – 1.56 (m, 1H, T), 1.33 (s, 1.36H, I); **^{13}C NMR (150 MHz, CDCl$_3$, T+I)** δ 156.1, 141.1, 138.3, 137.3, 130.9, 129.1, 128.8, 127.6, 125.7, 125.1, 123.5, 121.9, 117.4, 74.5, 73.6, 62.1, 58.4, 28.6, 27.0, 24.8, 22.3, 19.2, 18.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2922, 1740, 1597, 1501, 1392, 1206, 1135, 1072, 1016, 922, 749, 694; **HRMS (ESI)** calcd $C_{14}H_{15}NO_2Na$ [M + Na]$^+$: 252.0995, found: 252.0996.



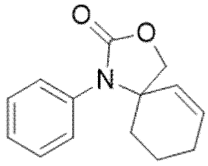
3-Phenyl-4-vinyloxazolidin-2-onen (8n): Followed the general procedure 4 with (*E*)-but-2-en-1-yl phenylcarbamate (38 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 27 mg of the title compound (yellow oil; 72% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.84 – 5.73 (m, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 4.85 (dd, *J* = 14.8, 8.0 Hz, 1H), 4.58 (t, *J* = 8.6 Hz, 1H), 4.10 (dd, *J* = 8.6, 6.4 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.6, 136.9, 134.7, 128.9, 124.9, 121.4, 120.5, 67.1, 59.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2975, 1742, 1606, 1482, 1393, 1363, 1294, 1092, 961, 757, 656; **HRMS (ESI)** calcd $C_{11}H_{11}NO_2Na$ [M + Na]$^+$: 212.0682, found: 212.0681.



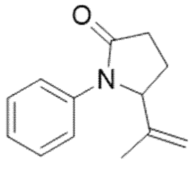
4-(But-1-en-1-yl)-3-phenyloxazolidin-2-one (8o): Followed the general procedure 4 with (*E*)-hex-2-en-1-yl phenylcarbamate (44 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 29 mg of the title compound (yellow oil; 67% yield; *E/Z* = 10:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.44 – 7.39 (m, 2H), 7.39 – 7.37 (m, 0.22H)/7.36 – 7.32 (m, 1.81H), 7.21 – 7.17 (m, 0.11H)/7.16 – 7.12 (m, 0.88H), 5.87 – 5.76 (m, 0.93H)/5.70 – 5.58 (m, 0.1H), 5.36 (dd, *J* = 15.4, 8.2 Hz, 0.90H)/5.18 (dd, *J* = 16.6, 8.5 Hz, 0.11H), 4.81 (dd, *J* = 15.2, 8.2 Hz, 0.93H), 4.61 – 4.50 (m, 1.16H), 4.44 – 4.38 (m, 0.13H), 4.13 (dd, *J* = 8.5, 5.4 Hz, 0.14H)/4.07 (dd, *J* = 8.4, 6.9 Hz, 0.90H), 2.17 – 2.09 (m, 0.18H)/2.06 – 1.99 (m, 1.90H), 0.98 (t, *J* = 7.5 Hz, 0.25H)/0.93 (t, *J* = 7.4 Hz, 2.69H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.8, 139.1, 137.0, 128.8, 125.4, 124.8, 121.7, 67.6, 59.3, 25.1, 13.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2962, 1740, 1596, 1497, 1396, 1365, 1297, 1208, 1126, 970, 761, 670; **HRMS (ESI)** calcd $C_{13}H_{15}NO_2Na$ [M + Na]$^+$: 240.0995, found: 240.1004.



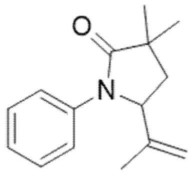
4-Methyl-3-phenyl-4-(prop-1-en-1-yl)oxazolidin-2-one (8p): Followed the general procedure 4 with (*E*)-2-methylpent-2-en-1-yl phenylcarbamate (44 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 30 mg of the title compound (yellow oil; 70% yield; *E/Z* = 5:1); The major isomer: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 – 7.33 (m, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 5.77 – 5.59 (m, 2H), 4.23 (d, *J* = 8.4 Hz, 1H), 4.13 (d, *J* = 8.4 Hz, 1H), 1.74 (d, *J* = 5.1 Hz, 3H), 1.44 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.6, 135.4, 132.6, 128.9, 128.3, 127.0, 127.0, 74.7, 63.3, 22.1, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2928, 1729, 1461, 1379, 1273, 1123, 1072, 697; **HRMS (ESI)** calcd $C_{13}H_{15}NO_2Na$ [M + Na]$^+$: 240.0995, found: 240.0994.



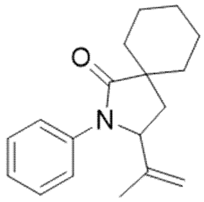
Phenyl-3-oxa-1-azaspiro[4.5]dec-6-en-2-one (8q): Followed the general procedure 4 with cyclohex-1-en-1-ylmethyl phenylcarbamate (46 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 33 mg of the title compound (yellow oil; 73% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 – 7.34 (m, 2H), 7.34 – 7.26 (m, 3H), 6.07 – 5.94 (m, 1H), 5.88 – 5.78 (m, 1H), 4.24 (d, *J* = 8.6 Hz, 1H), 4.16 (d, *J* = 8.6 Hz, 1H), 2.04 – 1.81 (m, 4H), 1.74 – 1.61 (m, 1H), 1.61 – 1.47 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 156.9, 135.8, 133.3, 129.2, 129.1, 127.5, 127.3, 73.5, 63.0, 31.5, 24.0, 19.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1749, 1495, 1394, 1341, 1224, 1186, 1126, 1056, 777, 758; **HRMS (ESI)** calcd $C_{14}H_{15}NO_2Na$ [M + Na]$^+$: 252.0995, found: 252.0994.



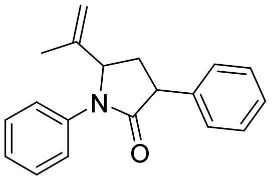
1-Phenyl-5-(prop-1-en-2-yl)pyrrolidin-2-one (8r): Followed the general procedure 3 with 5-methyl-*N*-phenylhex-4-enamide (41 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 37 mg of the title compound (yellow oil; 91% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.91 (s, 1H), 4.86 (s, 1H), 4.66 (dd, *J* = 8.4, 4.6 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.58 – 2.47 (m, 1H), 2.38 – 2.28 (m, 1H), 1.97 – 1.86 (m, 1H), 1.64 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 174.6, 143.2, 138.1, 128.6, 125.0, 122.1, 113.6, 65.2, 31.3, 24.1, 17.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2961, 2922, 1673, 1597, 1487, 1459, 1286, 1026, 905, 797, 696; **HRMS (ESI)** calcd $C_{13}H_{15}NONa$ [M + Na]$^+$: 224.1046, found: 224.1047.



3,3-Dimethyl-1-phenyl-5-(prop-1-en-2-yl)pyrrolidin-2-one (8s): Followed the general procedure 3 with 2,2,5-trimethyl-*N*-phenylhex-4-enamide (46 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 44 mg of the title compound (yellow oil; 95% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.99 (s, 1H), 4.90 – 4.87 (m, 1H), 4.69 (t, *J* = 7.9 Hz, 1H), 2.14 (dd, *J* = 12.9, 7.6 Hz, 1H), 1.82 (dd, *J* = 12.9, 8.1 Hz, 1H), 1.52 (s, 3H), 1.32 (s, 3H), 1.22 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 179.3, 143.3, 138.3 128.4, 124.9, 122.4, 114.5, 61.4, 41.0, 39.6, 25.7, 25.3, 16.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2958, 2929, 1722, 1598, 1494, 1335, 1156, 1090, 971, 719, 652; **HRMS (ESI)** calcd $C_{15}H_{19}NONa$ [M + Na]$^+$: 252.1359, found: 252.1362.

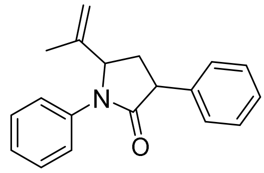


2-Phenyl-3-(prop-1-en-2-yl)-2-azaspiro[4.5]decan-1-one (8t): Followed the general procedure 3 with 1-(3-methylbut-2-en-1-yl)-*N*-phenylcyclohexane-1-carboxamide (54 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 42 mg of the title compound (yellow oil; 78% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 4.98 (s, 1H), 4.87 (s, 1H), 4.68 (t, *J* = 7.9 Hz, 1H), 2.34 (dd, *J* = 13.1, 8.0 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.80 – 1.71 (m, 3H), 1.71 – 1.60 (m, 2H), 1.60 – 1.55 (m, 1H), 1.53 (s, 3H), 1.49 – 1.24 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 179.1, 143.6, 138.2, 128.4, 124.8, 122.4, 114.4, 61.7, 45.5, 35.4, 34.5, 32.3, 25.4, 22.24, 22.19, 16.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2927, 1736, 1694, 1599, 1497, 1378, 1217, 1173, 957, 757, 693; **HRMS (ESI)** calcd $C_{18}H_{23}NONa$ [M + Na]$^+$: 292.1672, found: 292.1673.



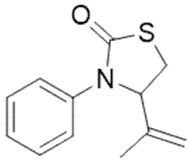
First eluting diasteromer

1,3-Diphenyl-5-(prop-1-en-2-yl)pyrrolidin-2-one (8u-1): Followed the general procedure 3 with 5-methyl-*N*,2-diphenylhex-4-enamide (56 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 21 mg of the title compound (yellow oil; 38% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.97 (s, 2H), 4.71 (dd, *J* = 8.0, 3.4 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 2.52 – 2.39 (m, 2H), 1.80 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 174.4, 142.6, 139.2, 138.5, 128.74, 128.68, 128.1, 127.2, 124.8, 121.3, 113.2, 62.9, 48.0, 33.9, 18.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2917, 1681, 1599, 1497, 1455, 1382, 1213, 1013, 921, 722, 689; **HRMS (ESI)** calcd $C_{19}H_{29}NONa$ [M + Na]$^+$: 300.1359, found: 300.1369.

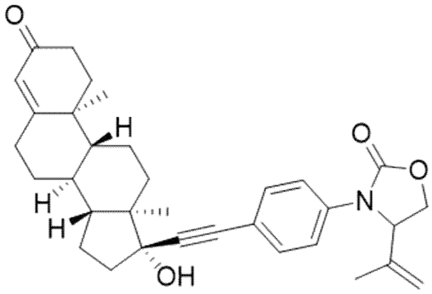


Second eluting diasteromer

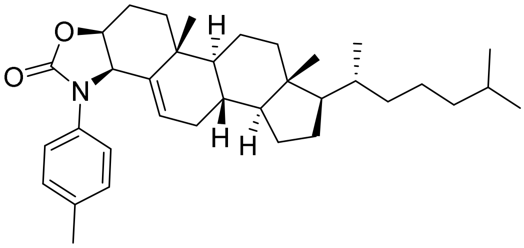
1,3-Diphenyl-5-(prop-1-en-2-yl)pyrrolidin-2-one (8u-2): Followed the general procedure 3 with 5-Methyl-*N*,2-diphenylhex-4-enamide (56 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 32 mg of the title compound (yellow oil; 58% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.45 – 7.42 (m, 2H), 7.42 – 7.33 (m, 6H), 7.33 – 7.28 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.09 (s, 1H), 4.95 – 4.93 (m, 1H), 4.84 (dd, *J* = 9.0, 7.1 Hz, 1H), 3.87 (dd, *J* = 11.3, 9.3 Hz, 1H), 2.84 – 2.69 (m, 1H), 2.17 – 2.05 (m, 1H), 1.57 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 174.3, 143.0, 139.2, 137.9, 128.7, 128.5, 128.2, 127.2, 125.3, 122.9, 115.4, 62.9, 48.3, 33.8, 16.5.



3-Phenyl-4-(prop-1-en-2-yl)thiazolidin-2-one (8v): Followed the general procedure 3 with *S*-(3-methylbut-2-en-1-yl) phenylcarbamothioate (44 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 27 mg of the title compound (yellow oil; 62% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.1 Hz, 1H), 5.05 (s, 1H), 4.97 (s, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 3.62 – 3.47 (m, 1H), 3.27 – 3.16 (m, 1H), 1.72 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 171.6, 141.6, 138.1, 128.8, 126.0, 124.0, 116.1, 66.7, 30.1, 17.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2921, 1655, 1592, 1496, 1446, 1348, 1296, 1203, 908, 722, 620; **HRMS (ESI)** calcd $C_{12}H_{13}NONaS$ [M + Na]$^+$: 242.0610, found: 242.0609.

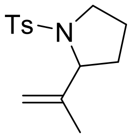


3-(4-(((*8S,9R,10S,13R,14R,17R*)-17-Hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*1H*-cyclopenta[a]phenanthren-17-yl)ethynyl)phenyl)-4-(prop-1-en-2-yl)oxazolidin-2-one (8w): Followed the general procedure 3 with 3-methylbut-2-en-1-yl (4-(((*8R,9S,10R,13S,14S,17S*)-17-hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethynyl)phenyl)carbamate (103 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 69 mg of the title compound (yellow solid; m.p. 169-170 °C; 67% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 5.71 (s, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.85 (dd, *J* = 8.9, 5.4 Hz, 1H), 4.54 (t, *J* = 8.9 Hz, 1H), 4.09 (dd, *J* = 8.6, 5.5 Hz, 1H), 2.44 – 2.30 (m, 5H), 2.28 – 2.22 (m, 1H), 2.11 – 1.98 (m, 3H), 1.86 – 1.81 (m, 1H), 1.75 – 1.69 (m, 3H), 1.63 (s, 3H), 1.60 – 1.55 (m, 1H), 1.53 – 1.48 (m, 1H), 1.47 – 1.41 (m, 1H), 1.39 – 1.32 (m, 1H), 1.18 (s, 3H), 1.08 – 1.01 (m, 1H), 1.00 – 0.95 (m, 1H), 0.92 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 199.6, 171.2, 155.2, 141.0, 137.2, 132.2, 123.8, 119.6, 118.8, 116.3, 92.5, 85.4, 80.0, 66.2, 61.7, 53.5, 50.2, 47.1, 39.0, 38.6, 36.3, 35.6, 33.9, 32.8, 31.5, 23.2, 20.8, 17.41, 16.4, 12.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2924, 1751, 1657, 1512, 1392, 1349, 1203, 1055, 911, 835, 728; **HRMS (ESI)** calcd $C_{33}H_{39}NO_4Na$ [M + Na]$^+$: 536.2771, found: 536.2767.

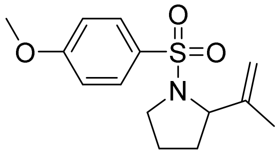


(*5aR,7aR,8R,10aS,10bS*)-5a,7a-Dimethyl-8-((*R*)-6-methylheptan-2-yl)-1-(*p*-tolyl)-1,3a,4,5,5a,5b,6,7,7a,8,9,10,10a,10b,11,12b-hexadecahydro-*2H*-cyclopenta[7,8]ph

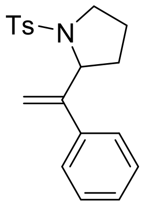
enanthro[1,2-d]oxazol-2-one (8x): Followed the general procedure 3 with (8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl p-tolylcarbamate (104 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 77 mg of the title compound (yellow solid; m.p. 127-128 °C; 74% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 5.76 (s, 1H), 4.82 – 4.75 (m, 2H), 2.31 (s, 3H), 2.10 – 2.03 (m, 1H), 2.03 – 1.97 (m, 1H), 1.90 – 1.78 (m, 2H), 1.72 – 1.65 (m, 2H), 1.63 – 1.56 (m, 1H), 1.53 – 1.49 (m, 3H), 1.46 – 1.37 (m, 2H), 1.37 – 1.29 (m, 5H), 1.24 – 1.20 (m, 1H), 1.16 – 1.10 (m, 3H), 1.09 – 1.02 (m, 2H), 1.01 – 0.94 (m, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 2.6 Hz, 1H), 0.85 (d, *J* = 2.6 Hz, 1H), 0.84 (s, 3H), 0.61 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.6, 135.6, 134.9, 134.6, 133.0, 129.2, 122.5, 74.1, 63.8, 57.0, 56.0, 47.1, 42.4, 39.6, 39.5, 36.3, 36.1, 35.7, 31.8, 31.4, 29.1, 28.2, 28.0, 25.3, 24.0, 23.8, 22.8, 22.5, 21.9, 20.9, 20.6, 18.6, 11.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2932, 1751, 1515, 1374, 1203, 1065, 814, 752; **HRMS (ESI)** calcd $C_{35}H_{51}NO_2Na$ [M + Na]$^+$: 540.3812, found: 540.3806.



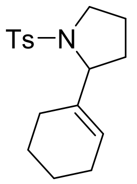
2-(Prop-1-en-2-yl)-1-tosylpyrrolidine (10a): Followed the general procedure 5 with 4-methyl-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (53 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 31 mg of the title compound (yellow oil; 58% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 1H), 4.86 (s, 1H), 4.04 (t, *J* = 6.3 Hz, 1H), 3.50 – 3.39 (m, 1H), 3.35 – 3.39 (m, 1H), 2.43 (s, 3H), 1.85 – 1.76 (m, 1H), 1.74 (s, 3H), 1.72 – 1.66 (m, 2H), 1.58 – 1.51 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 145.1, 143.2, 135.0, 129.6, 127.6, 111.8, 64.9, 49.3, 31.4, 24.0, 21.5, 18.6; **HRMS (ESI)** calcd $C_{14}H_{19}NO_2Na$ [M + Na]$^+$: 288.1029, found: 288.1032.



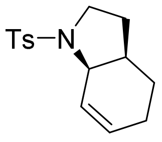
1-((4-Methoxyphenyl)sulfonyl)-2-(prop-1-en-2-yl)pyrrolidine (10b): Followed the general procedure 5 with 4-methoxy-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (57 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 38 mg of the title compound (yellow oil; 67% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.99 (s, 1H), 4.85 (s, 1H), 4.02 (t, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 3.50 – 3.37 (m, 1H), 3.33 – 3.22 (m, 1H), 1.86 – 1.76 (m, 1H), 1.73 (s, 3H), 1.72 – 1.67 (m, 2H), 1.62 – 1.54 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 162.8, 145.1, 129.8, 129.6, 114.1, 111.7, 64.9, 55.6, 49.3, 31.5, 24.0, 18.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3677, 2976, 1596, 1576, 1500, 1464, 1335, 1261, 1156, 1092, 1014, 901, 671; **HRMS (ESI)** calcd $C_{14}H_{19}NO_3NaS$ [M + Na]$^+$: 304.0978, found: 304.0981.



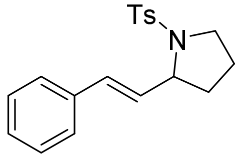
2-(1-Phenylvinyl)-1-tosylpyrrolidine (10c): Followed the general procedure 5 with (*E*)-4-methyl-*N*-(5-phenylhex-4-en-1-yl)benzenesulfonamide (66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 42 mg of the title compound (yellow oil; 64% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.27 (m, 7H), 5.39 (s, 1H), 5.34 (s, 1H), 4.75 (dd, *J* = 7.0, 2.9 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.33 – 3.23 (m, 1H), 2.43 (s, 3H), 1.90 – 1.72 (m, 1H), 1.68 – 1.55 (m, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 148.9, 143.4, 139.9, 135.2, 129.7, 128.4, 127.6, 127.5, 126.9, 113.8, 63.0, 49.0, 31.8, 23.5, 21.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3676, 2972, 1595, 1494, 1441, 1250, 1192, 1154, 1065, 1012, 908, 665; **HRMS (ESI)** calcd $C_{19}H_{21}NO_2Na$ [M + Na]$^+$: 350.1185, found: 350.1194.



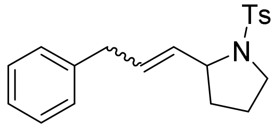
2-(Cyclohex-1-en-1-yl)-1-tosylpyrrolidine (10d): Followed the general procedure 5 with *N*-(4-cyclohexylidenebutyl)-4-methylbenzenesulfonamide (61 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 35 mg of the title compound (yellow oil; 57% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.61 (s, 1H), 3.99 (t, *J* = 6.3 Hz, 1H), 3.48 – 3.29 (m, 2H), 2.41 (s, 3H), 1.98 (s, 2H), 1.94 – 1.81 (m, 2H), 1.78 (ddd, *J* = 11.4, 7.9, 5.3 Hz, 1H), 1.73 – 1.65 (m, 2H), 1.64 – 1.46 (m, 5H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.0, 137.2, 129.4, 127.5, 123.3, 65.5, 49.2, 31.4, 25.0, 24.4, 24.2, 22.5, 22.4, 21.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2943, 1597, 1445, 1330, 1307, 1198, 1154, 1092, 1057, 851, 658; **HRMS (ESI)** calcd $C_{17}H_{23}NO_2NaS$ [M + Na]$^+$: 328.1342, found: 328.1345.



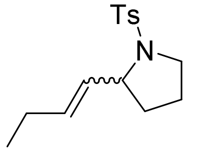
1-Tosyl-2,3,3a,4,5,7a-hexahydro-1H-indole (10e): Followed the general procedure 5 with *N*-(2-(cyclohex-2-en-1-yl)ethyl)-4-methylbenzenesulfonamide (60 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 29 mg of the title compound (yellow oil; 52% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.88 – 5.81 (m, 1H), 5.81 – 5.74 (m, 1H), 4.00 (d, *J* = 7.1 Hz, 1H), 3.54 – 3.41 (m, 1H), 3.25 – 3.10 (m, 1H), 2.43 (s, 3H), 2.09 – 1.86 (m, 3H), 1.84 – 1.72 (m, 1H), 1.74 – 1.60 (m, 2H), 1.57 – 1.50 (m, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 143.1, 135.0, 129.6, 128.2, 127.6, 127.5, 57.4, 47.3, 36.5, 27.7, 22.8, 21.5, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2923, 1597, 1450, 1338, 1210, 1156, 1090, 1047, 847, 656; **HRMS (ESI)** calcd $C_{15}H_{19}NO_2NaS$ [M + Na]$^+$: 300.1029, found: 300.1031.



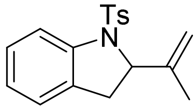
(*E*)-2-Styryl-1-tosylpyrrolidine (10f): Followed the general procedure 5 with (*E*)-4-methyl-*N*-(6-phenylhex-4-en-1-yl)benzenesulfonamide (66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 39 mg of the title compound (yellow oil; 60% yield; *E/Z* > 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25-7.18 (m, 3H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 6.7 Hz, 1H), 4.42 – 4.26 (m, 1H), 3.53 – 3.43 (m, 1H), 3.42 – 3.30 (m, 1H), 2.38 (s, 3H), 1.93 – 1.80 (m, 2H), 1.77 – 1.64 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.3, 136.7, 135.6, 130.6, 130.0, 129.6, 128.5, 127.6 127.5, 126.5, 61.7, 48.7, 32.8, 24.0, 21.5; **HRMS (ESI)** calcd $C_{19}H_{21}NO_2NaS$ [M + Na]$^+$: 350.1185, found: 350.1187.



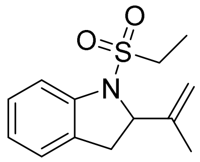
2-(3-Phenylprop-1-en-1-yl)-1-tosylpyrrolidine (10g): Followed the general procedure 5 with (*E*)-4-methyl-*N*-(7-phenylhept-4-en-1-yl)benzenesulfonamide (68 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 29 mg of the title compound (yellow oil; 43% yield; *E/Z* = 7:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 – 7.66 (m, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.14 (m, 3H), 5.87 – 5.74 (m, 0.89H)/5.59 (m, 0.11H), 5.58 – 5.53 (m, 0.13H)/ 5.47 (dd, *J* = 15.2, 6.6 Hz, 0.90H), 4.53 – 4.41 (m, 0.12H)/ 4.19 – 4.08 (m, 0.89H), 3.58 – 3.49 (m, 0.26H)/ 3.47 – 3.35 (m, 2.8H), 3.34 – 3.22 (m, 1H), 2.42 (s, 3H), 1.91 – 1.60 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.1, 140.2, 135.5, 132.0, 130.3, 129.5, 128.6, 128.4, 127.5, 126.1, 61.4, 48.7, 38.5, 32.8, 23.9, 21.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2924, 1600, 1496, 1445, 1345, 1197, 1158, 1094, 972, 817, 665; **HRMS (ESI)** calcd $C_{20}H_{23}NO_2NaS$ [M + Na]$^+$: 364.1342, found: 364.1344.



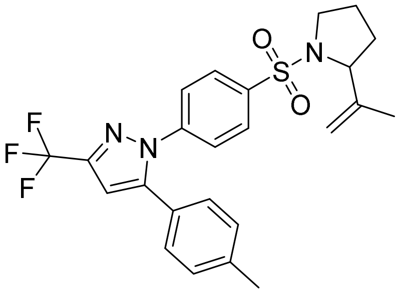
2-(But-1-en-1-yl)-1-tosylpyrrolidine (10h): Followed the general procedure 5 with **(*E*)-4-methyl-*N*-(oct-5-en-1-yl)benzenesulfonamide** (56 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 25 mg of the title compound (yellow oil; 45% yield; *E/Z* = 5:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 11.5, 3.6 Hz, 2H), 5.73 – 5.64 (m, 0.87H)/5.42 – 5.37 (m, 0.14H), 5.36 – 5.28 (m, 1H), 4.38 – 4.30 (m, 0.14H)/4.16 – 4.10 (m, 0.85H), 3.44 – 3.37 (m, 1H), 3.30 – 3.22 (m, 1H), 2.42 (s, 0.5H)/2.41(s, 2.5H), 2.18 – 2.06 (m, 0.27H)/ 2.04 – 1.97 (m, 1.79H), 1.85 – 1.78 (m, 1H), 1.75 – 1.66 (m, 1H), 1.65 – 1.57 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 0.42H)/ 0.95 (t, *J* = 7.5 Hz, 2.57H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.1, 135.8, 133.5, 129.5, 129.2, 127.6, 61.6, 48.6, 32.8, 25.1, 23.9, 21.5, 13.3; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2963, 1598, 1457, 1344, 1157, 1092, 966, 815, 663; **HRMS (ESI)** calcd $C_{15}H_{21}NO_2NaS$ [M + Na]$^+$: 302.1185, found: 302.1189.



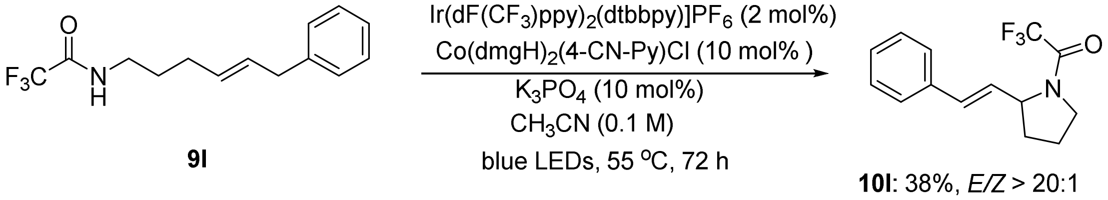
2-(Prop-1-en-2-yl)-1-tosylindoline (10i): Followed the general procedure 5 with 4-methyl-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (63 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 35 mg of the title compound (yellow oil; 56% yield); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.16 (m, 3H), 7.08 – 6.95 (m, 2H), 5.07 (s, 1H), 4.86 (s, 1H), 4.66 (dd, *J* = 10.1, 3.7 Hz, 1H), 2.98 (dd, *J* = 16.2, 10.2 Hz, 1H), 2.69 (dd, *J* = 16.2, 3.8 Hz, 1H), 2.36 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 144.3, 143.8, 142.0, 135.1, 131.4, 129.5, 127.7, 127.1, 124.8, 124.3, 116.4, 112.2, 66.7, 34.3, 21.5, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2963, 1603, 1460, 1344, 1157, 1092, 977, 815, 665; **HRMS (ESI)** calcd $C_{18}H_{19}NO_2Na$ [M + Na]$^+$: 336.1029, found: 336.1030.



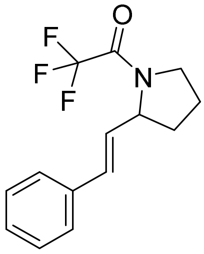
1-(Ethylsulfonyl)-2-(prop-1-en-2-yl)indoline (10j): Followed the general procedure 5 with *N*-(2-(3-methylbut-2-en-1-yl)phenyl)ethanesulfonamide (51 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 16 mg of the title compound (yellow oil; 32% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.13 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.06 (s, 1H), 4.89 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.85 (s, 1H), 3.51 (dd, *J* = 16.3, 10.4 Hz, 1H), 3.16 – 3.03 (m, 2H), 2.88 (dd, *J* = 16.4, 3.3 Hz, 1H), 1.71 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.5, 142.1, 130.3, 128.0, 125.2, 123.7, 114.3, 112.4, 67.0, 45.4, 34.6, 17.4, 7.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2958, 1597, 1444, 1342, 1200, 1087, 972, 820, 673; **HRMS (ESI)** calcd $C_{13}H_{17}NO_2Na$ [M + Na]$^+$: 274.0872, found: 274.0877.



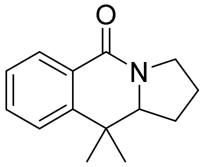
1-(4-((2-(Prop-1-en-2-yl)pyrrolidin-1-yl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (10k): Followed the general procedure 5 with *N*-(5-methylhex-4-en-1-yl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (95 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 53 mg of the title compound (yellow oil; 56% yield); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 – 7.79 (m, 2H), 7.51 – 7.44 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.74 (s, 1H), 4.94 (s, 1H), 4.84 (s, 1H), 4.04 (t, *J* = 6.2 Hz, 1H), 3.50 – 3.42 (m, 1H), 3.37 – 3.24 (m, 1H), 2.37 (s, 3H), 1.88 – 1.79 (m, 1H), 1.78 – 1.72 (m, 2H), 1.70 (s, 3H), 1.66 – 1.54 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 145.3, 144.6, 144.1 (q, *J* = 38.5 Hz), 142.4, 139.8, 137.7, 129.7, 128.7, 128.4, 125.7, 125.5, 121.1 (q, *J* = 269.1 Hz), 112.1, 106.2, 65.1, 49.3, 31.4, 24.0, 21.3, 18.5; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -62.4 (s, 3F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2925, 1596, 1471, 1344, 1235, 1157, 1127, 1009, 974, 839, 638; **HRMS (ESI)** calcd $C_{24}H_{25}F_3N_3O_2S$ [M + H]$^+$: 476.1614, found: 476.1621.



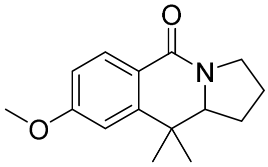
To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, (*E*)-2,2,2-trifluoro-*N*-(6-phenylhex-4-en-1-yl)acetamide (54 mg, 0.2 mmol, 1.0 equiv.), Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.3 mg, 2 mol%), Co(dmgH)$_2$(4-CN-Py)Cl (8.8 mg, 0.02 mmol, 10 mol%), and Potassium phosphate (4.2 mg, 0.02 mmol, 10 mol%) was added. The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. CH$_3$CN (2 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 72 hours. The temperature was maintained at 55 °C when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. The crude product was purified by silica gel column chromatography (PE/EA = 20:1 to 10:1) to afford **10l** (20 mg, 38% yield, *E/Z* > 20:1) as a yellow oil as a mixture of two conformers in 3:1 ratio (determined by ^{1}H NMR at 23 °C).



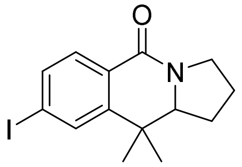
(*E*)-2,2,2-Trifluoro-1-(2-styrylpyrrolidin-1-yl)ethan-1-one (10l): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.18 (m, 5H), 6.49 (d, *J* = 15.9 Hz, 0.72H)/6.34 (d, *J* = 15.9 Hz, 0.28H), 6.15 – 6.04 (m, 1H), 4.95 – 4.80 (m, 1H), 3.88 – 3.62 (m, 2H), 2.21 – 1.87 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ156.2 (q, *J* = 35.6 Hz)/155.5(q, *J* = 36.7 Hz), 136.3/136.0, 131.3/130.4, 128.6/128.5, 128.2/127.7, 127.9/126.8, 126.5/126.4, 116.3 (q, J = 288.0 Hz)/116.3 (q, J = 287.4 Hz), 60.3/47.5, 59.6 (q, J = 2.6 Hz)/46.7 (q, J = 3.4 Hz), 33.0/30.3, 24.2/20.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -70.65 (s, 0.81F)/-72.49 (s, 2.31F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 3676, 2987, 1673, 1598, 1493, 1450, 1349, 1236, 1179, 1075, 968, 750, 696; **HRMS (ESI)** calcd $C_{14}H_{14}F_3NONa$ [M + Na]$^+$: 292.0920, found: 292.0923.



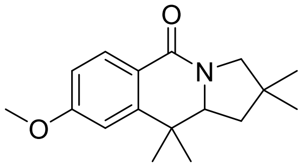
10,10-Dimethyl-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12a): Followed the general procedure 6 with *N*-(5-methylhex-4-en-1-yl)benzamide (43 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 18 mg of the title compound (yellow oil; 43% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 – 8.01 (m, 1H), 7.50 – 7.42 (m, 1H), 7.36 – 7.28 (m, 2H), 3.94 – 3.83 (m, 1H), 3.73 – 3.63 (m, 1H), 3.62 – 3.49 (m, 1H), 2.14 – 2.00 (m, 2H), 1.96 – 1.78 (m, 2H), 1.40 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.2, 147.9, 132.0, 129.2, 127.9, 126.6, 123.1, 64.7, 45.7, 37.2, 27.4, 23.5, 23.1, 23.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2968, 2864, 1644, 1599, 1467, 1429, 1349, 1326, 1175, 1033, 766, 701; **HRMS (ESI)** calcd $C_{14}H_{17}NONa$ [M + Na]$^+$: 238.1202, found: 238.1201.



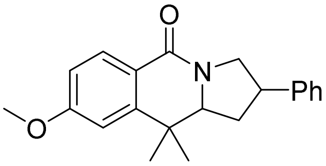
8-Methoxy-10,10-dimethyl-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12b): Followed the general procedure 6 with 4-methoxy-*N*-(5-methylhex-4-en-1-yl)benzamide (49 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 35 mg of the title compound (yellow oil; 72% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.02 (d, J = 9.2 Hz, 1H), 6.89 – 6.76 (m, 2H), 3.89 – 3.85 (m, 1H), 3.84 (s, 3H), 3.65 (dd, J = 10.1, 6.0 Hz, 1H), 3.54 (ddd, J = 11.7, 9.9, 7.2 Hz, 1H), 2.09 – 2.04 (m, 2H), 1.91 – 1.81 (m, 2H), 1.36 (s, 3H), 1.02 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.1, 162.5, 150.1, 129.9, 122.1, 110.9, 109.4, 64.7, 55.3, 45.5, 37.3, 27.3, 23.4, 23.1, 22.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2968, 1633, 1601, 1443, 1414, 1313, 1279, 1172, 1037, 779, 704; **HRMS (ESI)** calcd $C_{15}H_{19}NO_2$ Na $[M + Na]^+$: 268.1308, found: 268.1307.



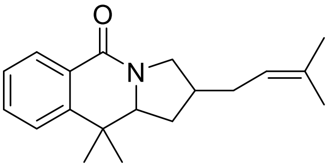
8-Iodo-10,10-dimethyl-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12c): Followed the general procedure 6 with 4-iodo-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzamide (69 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 34 mg of the title compound (yellow solid; m.p. 78 – 79 °C; 49% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.60 (m, 2H), 3.89 – 3.80 (m, 1H), 3.64 (dd, *J* = 9.8, 6.2 Hz, 1H), 3.57 – 3.49 (m, 1H), 2.13 – 1.99 (m, 2H), 1.94 – 1.80 (m, 2H), 1.35 (s, 3H), 1.02 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 162.5, 149.7, 135.9, 132.5, 129.6, 128.7, 99.4, 64.6, 45.7, 37.3, 27.3, 23.3, 23.0, 22.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 1642, 1581, 1551, 1464, 1389, 1068, 778, 691; **HRMS (ESI)** calcd $C_{14}H_{16}NO_2NaI$ $[M + Na]^+$: 364.0169, found: 364.0163.



8-Methoxy-2,2,10,10-tetramethyl-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12d): Followed the general procedure 6 with 4-methoxy-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzamide (55 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 34 mg of the title compound (yellow oil; 62% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 9.2 Hz, 1H), 6.86 – 6.74 (m, 2H), 3.89 – 3.78 (m, 4H), 3.66 (d, *J* = 11.7 Hz, 1H), 3.23 (d, *J* = 11.8 Hz, 1H), 1.74 (d, *J* = 9.1 Hz, 2H), 1.31 (s, 3H), 1.20 (s, 3H), 1.09 (s, 3H), 1.01 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.2, 162.5, 150.3, 129.9, 122.2, 110.9, 109.3, 63.8, 58.2, 55.3, 41.1, 37.2, 36.1, 27.1, 23.2, 22.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2962, 2863, 1640, 1602, 1436, 1415, 1387, 1278, 1116, 1032, 778, 703; **HRMS (ESI)** calcd $C_{17}H_{23}NO_2Na$ [M + Na]$^+$: 296.1621, found: 296.1617.

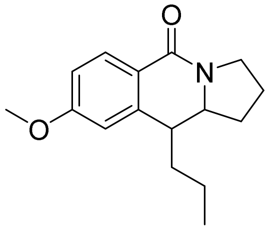


8-Methoxy-10,10-dimethyl-2-phenyl-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12e): Followed the general procedure 6 with 4-methoxy-N-(5-methyl-2-phenylhex-4-en-1-yl)benzamide (65 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 36 mg of the title compound (yellow oil; 56% yield; d.r = 4:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.04 – 7.94 (m, 1H), 7.33 – 7.24 (m, 2H), 7.24 – 7.11 (m, 3H), 6.82 – 6.71 (m, 2H), 4.29 (dd, *J* = 11.7, 8.2 Hz, 0.87H)/4.06 (dd, *J* = 12.3, 7.1 Hz, 0.22H), 3.88 (dd, *J* = 12.3, 4.8 Hz, 1H)/3.84 – 3.80 (m, 0.84H), 3.78 (s, 2.39H)/3.77 (s, 0.66H), 3.49 (t, *J* = 11.3 Hz, 1H), 3.41-3.28 (m, 1H), 2.41-2.29 (m, 1H), 2.07-1.92 (m, 1H), 1.33 (s, 2.37H)/1.24 (s, 0.64H), 1.04 (s, 2.35H)/ 1.03 (s, 0.62H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.1/162.9, 162.7/162.7, 150.14/150.06, 142.9/140.7, 130.2/130.1, 128.73/128.71, 127.1/126.9, 127.0/126.7, 122.0, 111.1, 109.6/109.5, 65.2/62.9, 55.4, 51.7/51.0, 41.6/41.1, 37.5/37.4, 35.3/35.1, 23.42, 23.1/22.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2962, 1644, 1600 1438, 1313, 1277, 1069, 1032, 783, 704; **HRMS (ESI)** calcd $C_{21}H_{23}NO_2Na$ [M + Na]$^+$: 344.1621, found: 344.1615.



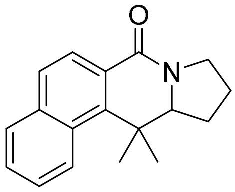
10,10-Dimethyl-2-(3-methylbut-2-en-1-yl)-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12f): Followed the general procedure 6 with *N*-(5-methyl-2-(3-methylbut-2-en-1-yl)hex-4-en-1-yl)benzamide (57 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 22 mg of the title compound (yellow oil; 39% yield; d.r. = 10:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.08 – 8.01 (m, 1H), 7.48 – 7.42 (m, 1H), 7.34 – 7.28 (m, 2H), 5.19 – 5.13

(m, 0.85H)/5.13 – 5.10 (m, 0.1H), 4.03 (dd, *J* = 11.9, 7.0 Hz, 0.93H), 3.86 – 3.78 (m, 0.19H), 3.72 (dd, *J* = 11.4, 5.5 Hz, 0.90H), 3.46 (dd, *J* = 12.1, 4.0 Hz, 0.09H)/3.10 (dd, *J* = 11.9, 9.7 Hz, 0.92H), 2.23 – 2.13 (m, 3H), 2.13 – 1.98 (m, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.60 – 1.53 (m, 1H), 1.37 (s, 2.75H)/1.36 (s, 0.32H), 1.04 (s, 2.76H)/1.02 (s, 0.29H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.1, 148.0, 133.3, 131.9, 129.1, 127.9, 126.6, 123.0, 121.7, 65.1, 51.0, 37.2, 37.1, 33.6, 31.4, 25.8, 23.4, 23.1, 17.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2968, 2924, 1635, 1601, 1572, 1471, 1322, 1066, 1032, 798, 702; **HRMS (ESI)** calcd $C_{19}H_{25}NONa$ [M + Na]$^+$: 306.1828, found: 306.1827.

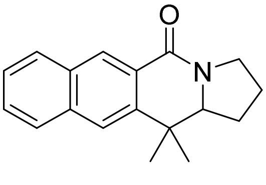


the major isomer

8-Methoxy-10-propyl-2,3,10,10a-tetrahydropyrrolo[1,2-b]isoquinolin-5(1H)-one (12g): Followed the general procedure 6 with (*E*)-4-methoxy-*N*-(oct-4-en-1-yl)benzamide (52 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 25 mg of the title compound (yellow oil; 48% yield; the major isomer); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.03 (d, *J* = 8.5 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.78 (s, 1H), 3.84 (s, 3H), 3.82 – 3.77 (m, 1H), 3.63 – 3.57 (m, 2H), 2.85 – 2.74 (m, 1H), 2.36 – 2.26 (m, 1H), 2.12 – 2.04 (m, 1H), 1.93 – 1.78 (m, 3H), 1.76 – 1.67 m, 1H), 1.49 – 1.41 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 163.1, 162.3, 142.7, 129.8, 123.9, 110.8, 110.5, 60.1, 55.3, 45.0, 43.1, 32.9, 30.2, 22.9, 18.7, 14.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2966, 2929, 1643, 1598, 1466, 1427, 1326, 1033, 766, 701; **HRMS (ESI)** calcd $C_{16}H_{21}NO_2Na$ [M + Na]$^+$: 282.1465, found: 282.1462.



12h-a

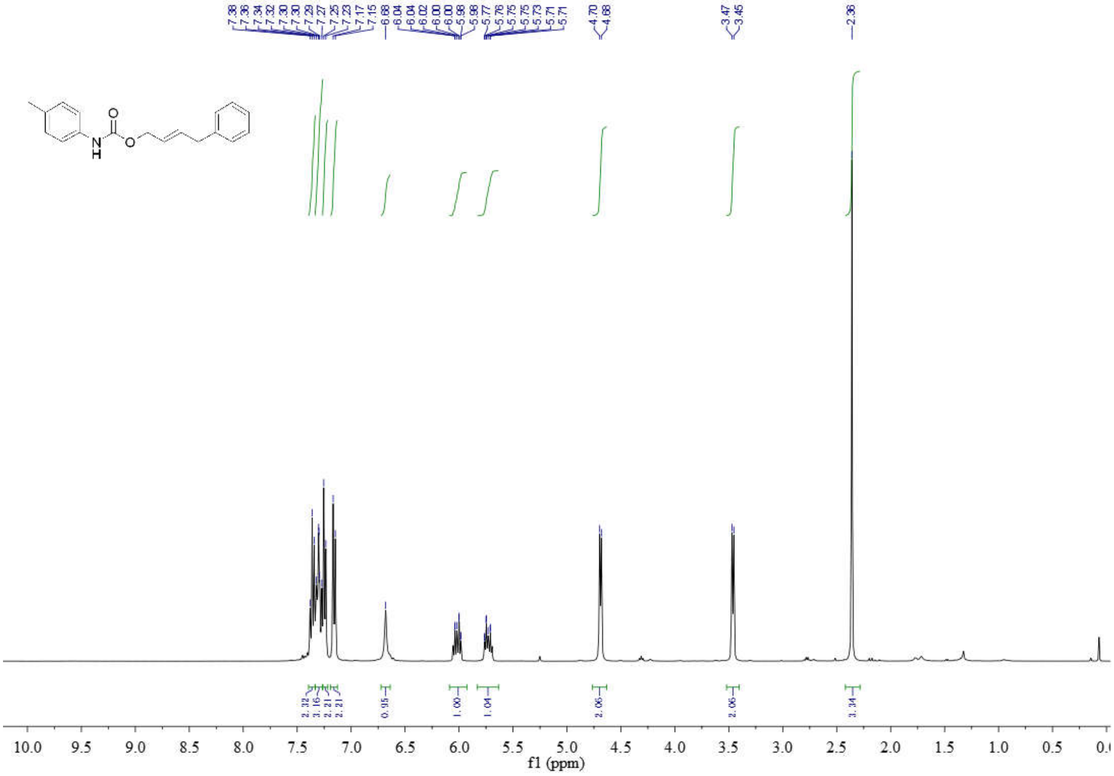


12h-b

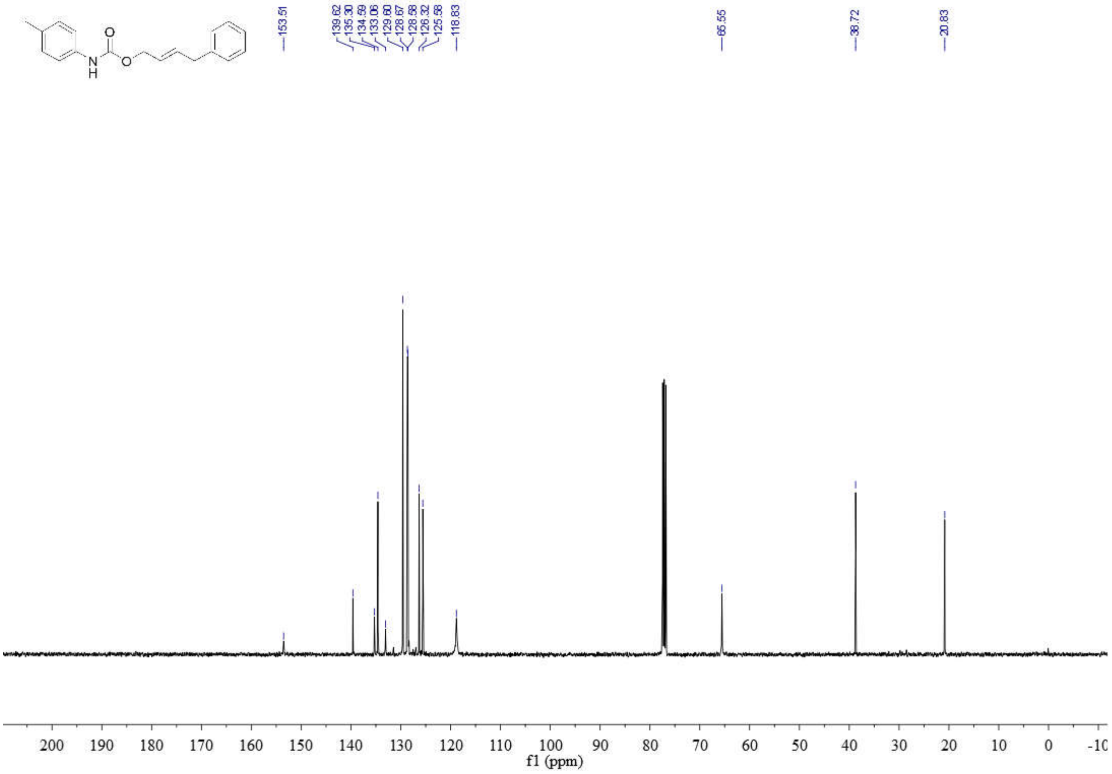
12,12-Dimethyl-2,3,12,12a-tetrahydrobenzo[g]pyrrolo[1,2-b]isoquinolin-5(1H)-one (12h-a) and 12,12-dimethyl-10,11,11a,12-tetrahydrobenzo[f]pyrrolo[1,2-b] isoquinolin-7(9H)-one (12h-b) : Followed the general procedure 6 with *N*-(2,2,5-trimethylhex-4-en-1-yl)-2-naphthamide (53 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 28 mg of the title compound (yellow oil**;** 52% yield; **12h-a/12h-b** = 12:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.63 (s, 0.06H, 12h-b), 8.40 – 8.34 (m, 1H, 12h-a), 8.17 (d, *J* = 8.5 Hz, 1H, 12h-a), 7.95 (d, *J* = 8.0 Hz, 0.08H, 12h-b), 7.91 – 7.85 (m, 1H, 12h-a), 7.83 (d, *J* = 8.5 Hz, 0.09H, 12h-b), 7.78 (d, *J* = 8.5 Hz, 1H, 12h-a), 7.73 (s, 0.08H, 12h-b), 7.56 – 7.44 (m, 2H, 12h-a + 12h-b), 4.17 – 4.07 (m, 0.08H, 12h-b), 4.04 – 3.94 (m, 1H, 12h-a + 12h-b), 3.82 – 3.72 (m, 1H, 12h-a + 12h-b), 3.69 – 3.60 (m, 1H, 12h-a + 12h-b), 2.29 – 2.18 (m, 1H, 12h-a + 12h-b), 2.16 – 2.04 (m, 2H, 12h-a + 12h-b), 1.97 – 1.88 (m, 1H, 12h-a + 12h-b), 1.74 (s, 3H, 12h-a), 1.53 (s, 0.23H, 12h-b), 1.47 (s, 3H, 12h-a), 1.12 (s, 0.23H, 12h-b); **^{13}C NMR (150 MHz, CDCl$_3$, 12h-a + 12h-b)** δ 163.7, 145.4, 136.5, 130.0, 129.4, 129.1 (12h-b), 128.8 (12h-b), 127.8, 127.6 (12h-b), 127.5 (12h-b), 126.5, 126.5, 126.0 (12h-b), 125.3, 124.3, 121.7 (12h-b), 65.9, 64.8 (12h-b), 45.9 (12h-b), 45.8, 39.2, 27.7, 27.5, 23.5 (12h-b), 23.2 (12h-b), 23.0, 20.2; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2969, 2874, 1643, 1557, 1466, 1442, 1391, 1196, 1035, 869, 762, 644; **HRMS (ESI)** calcd $C_{18}H_{19}NONa$ [M + Na]$^+$: 288.1359, found: 288.1357.

9. NMR Spectra for the substrates and products

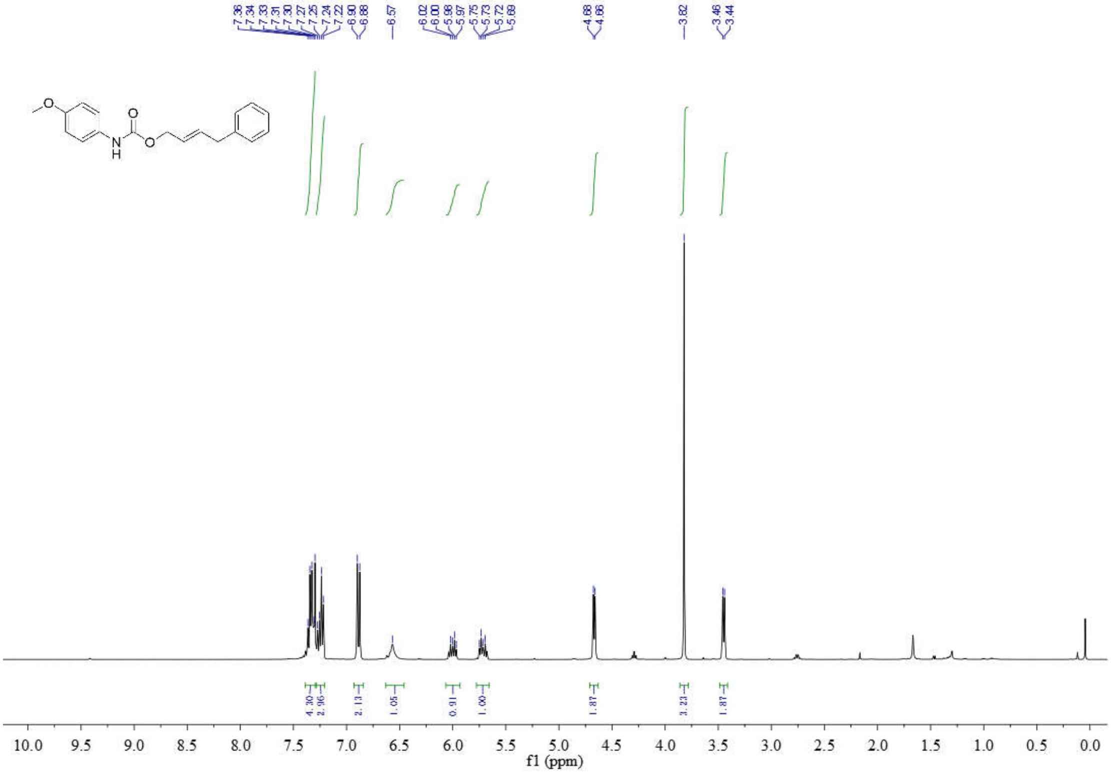
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1a**



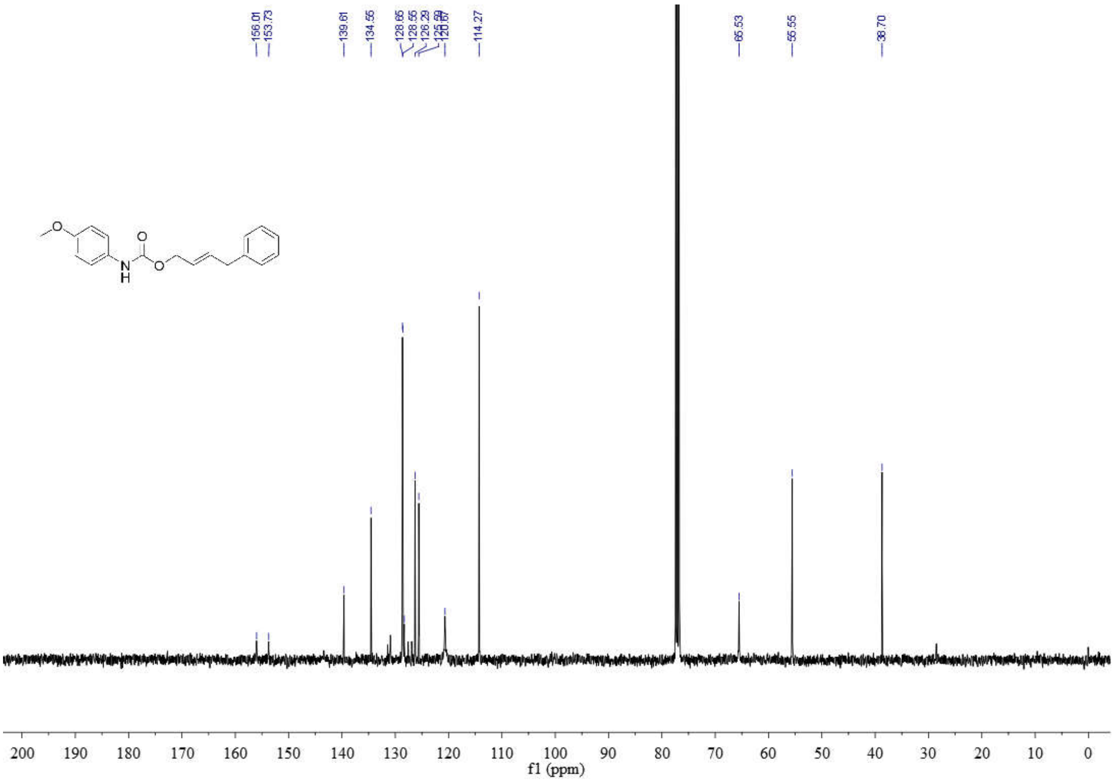
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **1a**



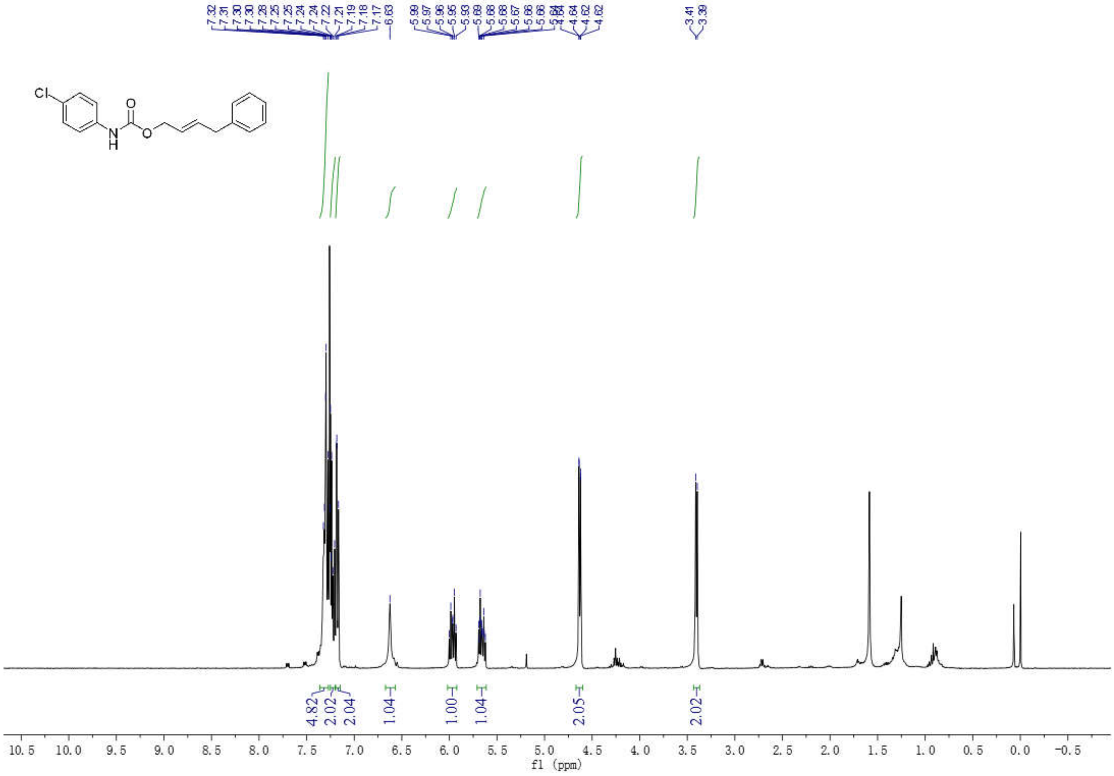
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1b**



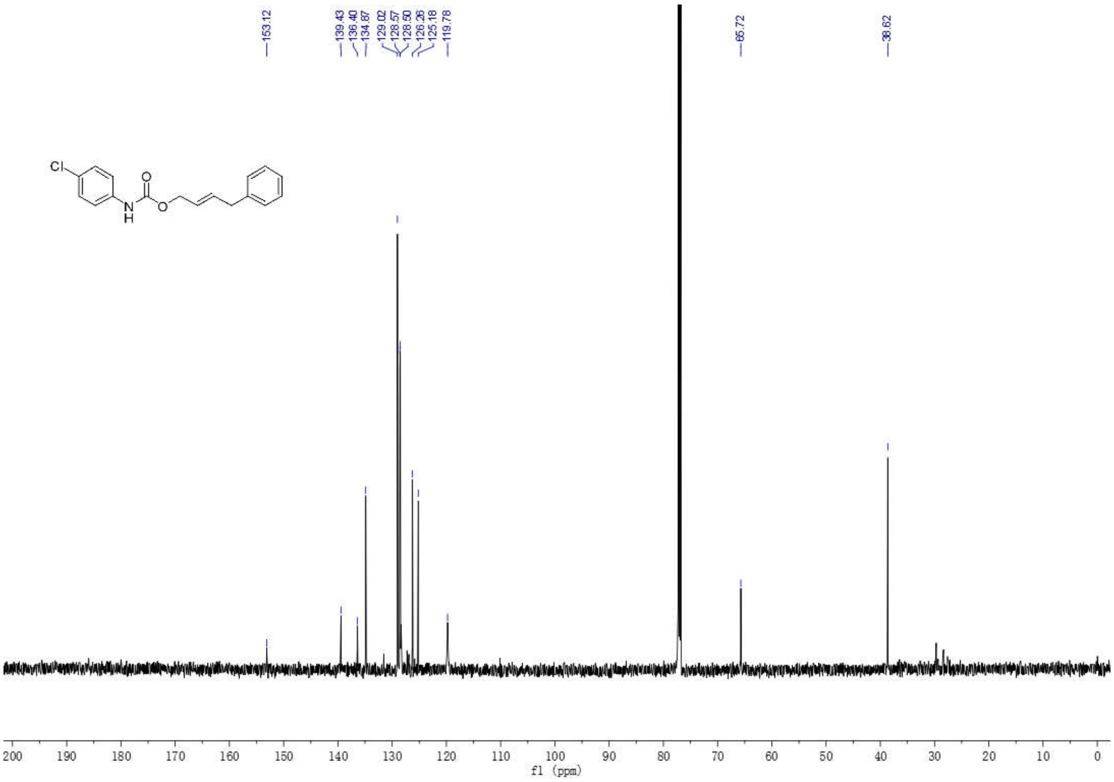
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1b**



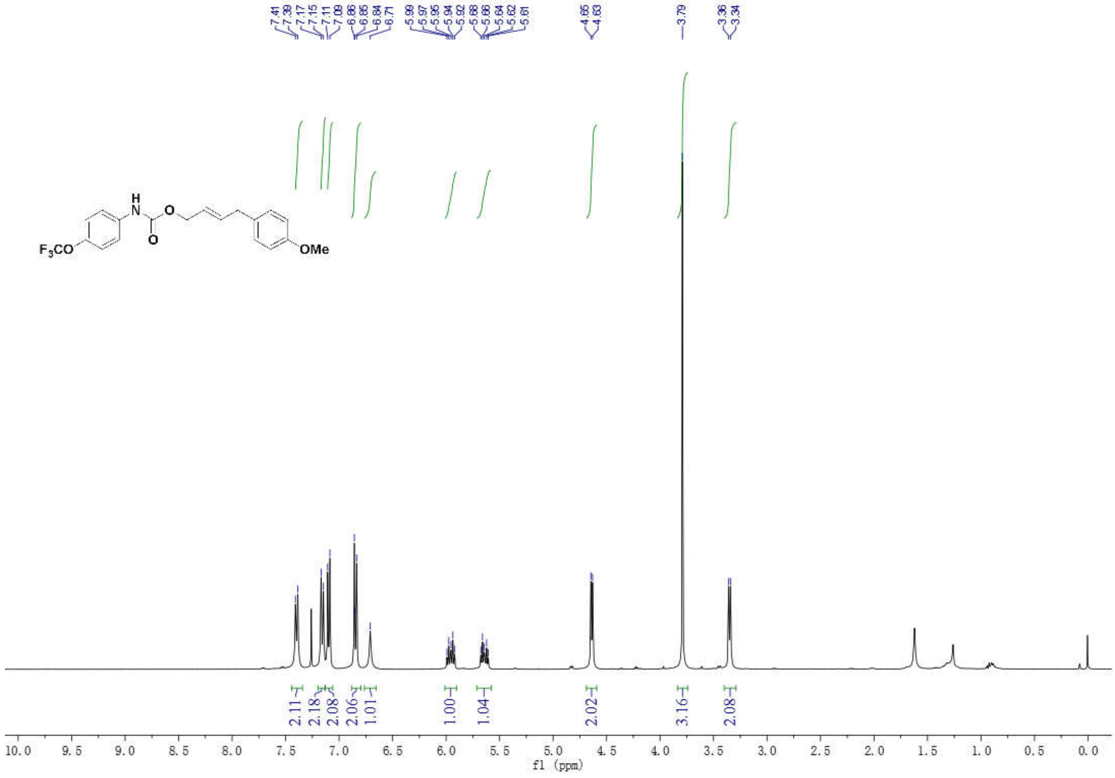
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1c**



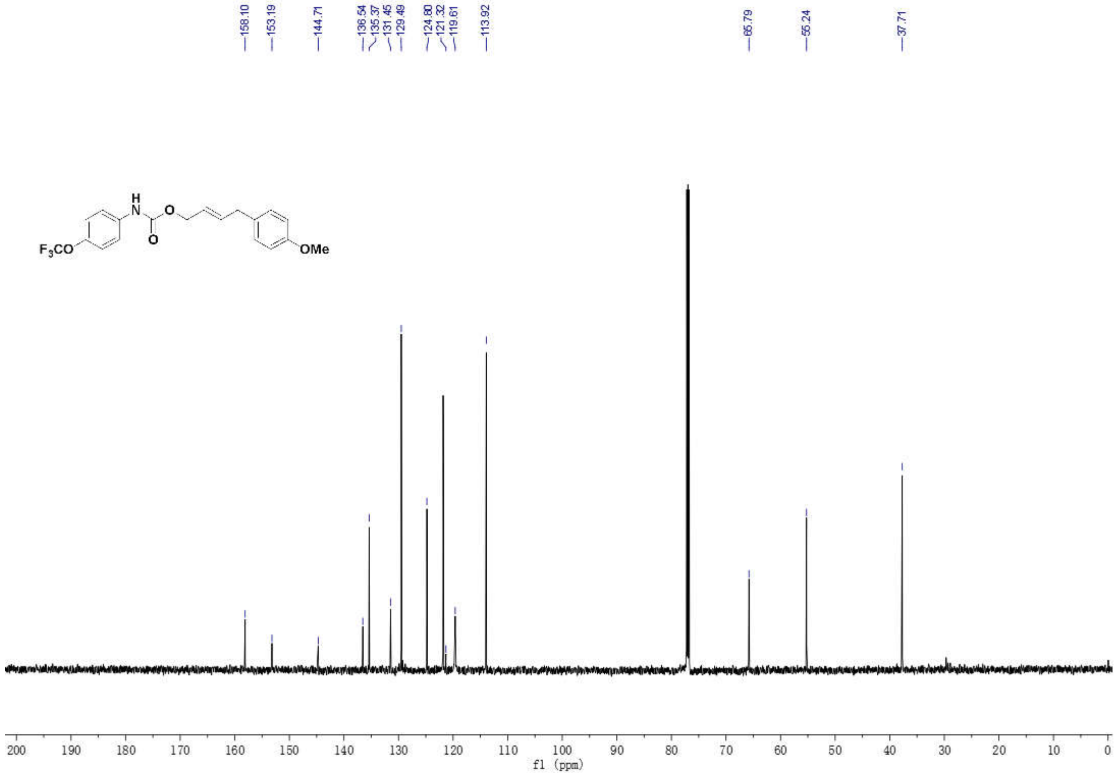
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1c**



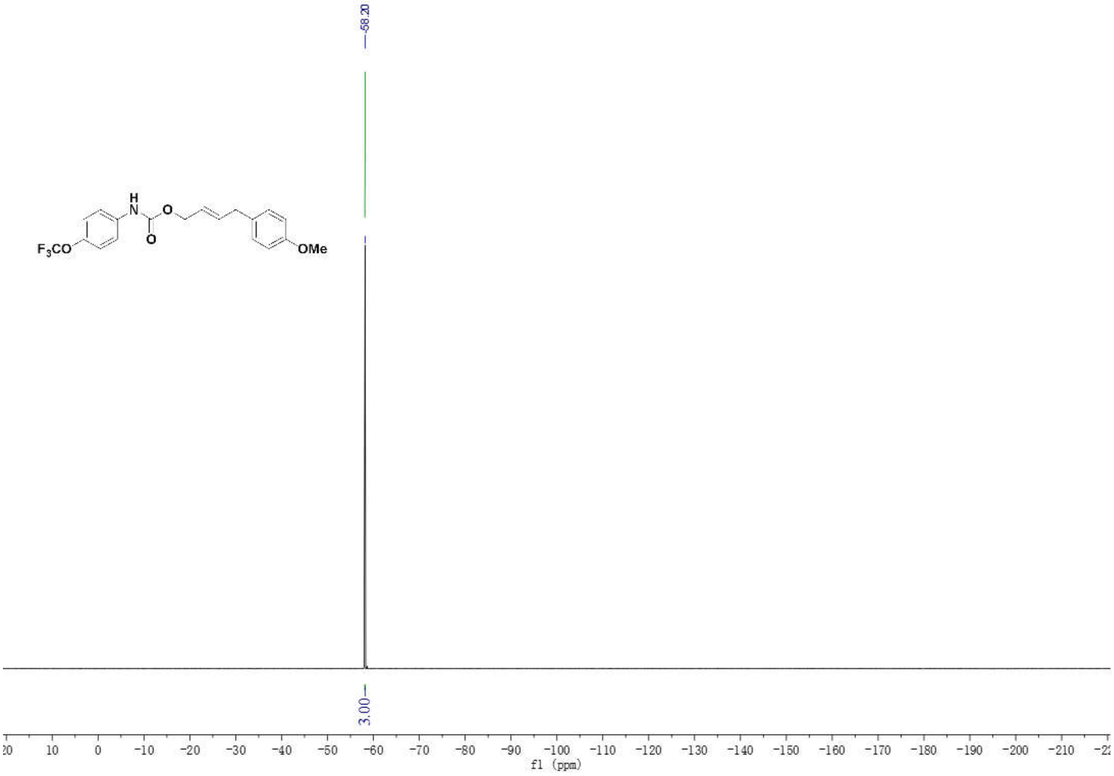
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1d**



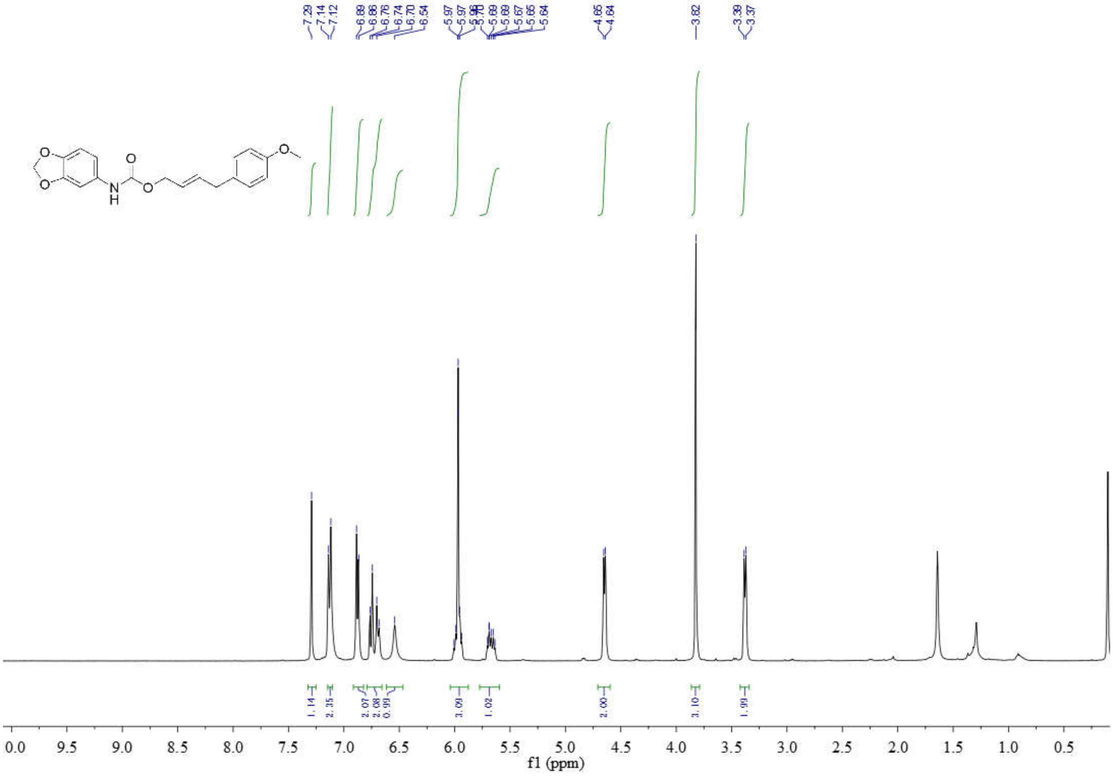
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **1d**



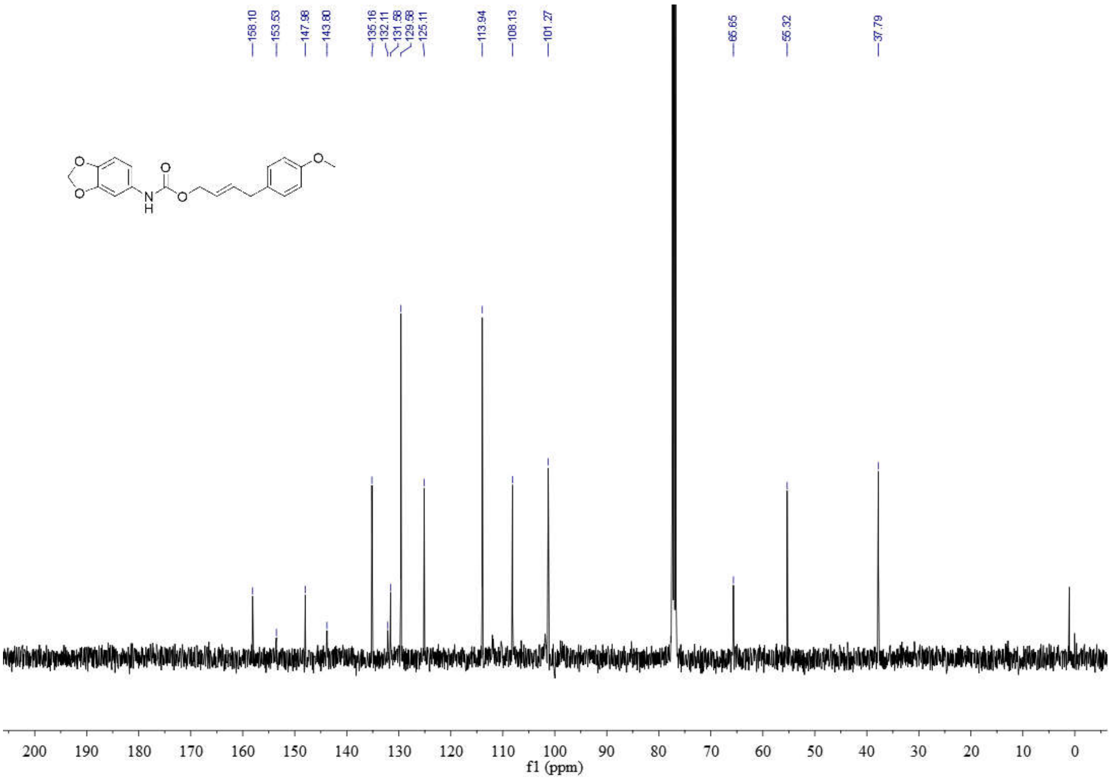
^{19}F NMR spectrum (377 MHz, CDCl$_3$, 23 ºC) of **1d**



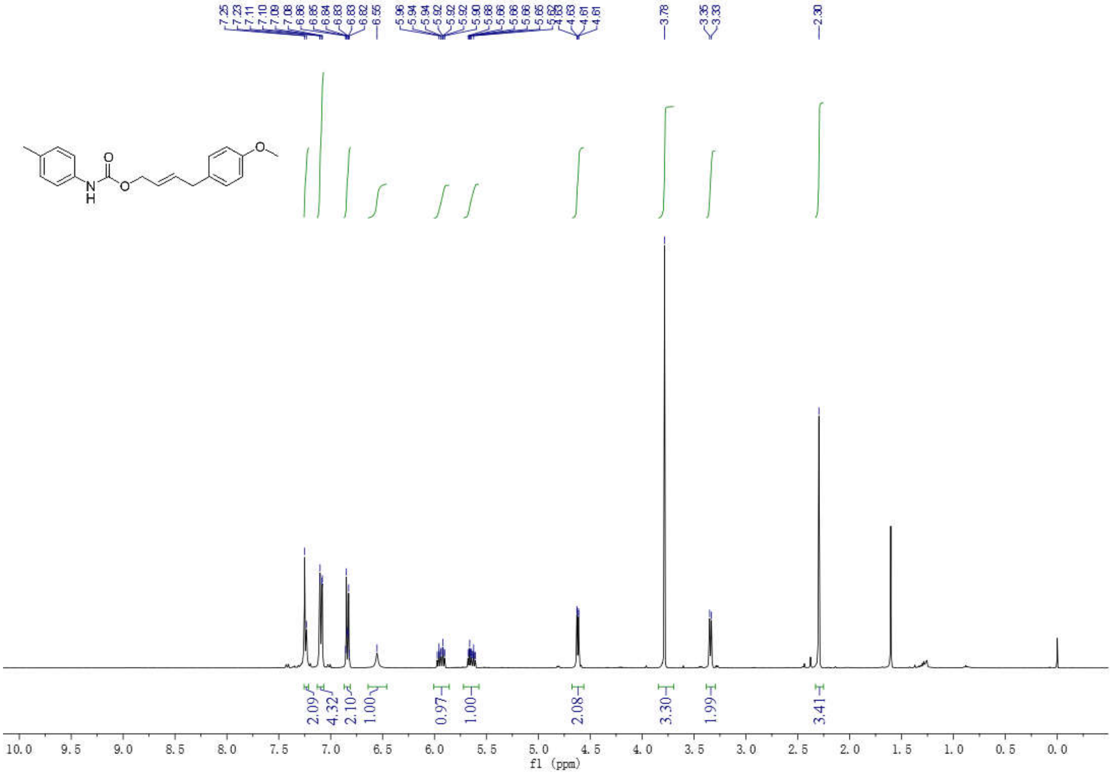
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1e**



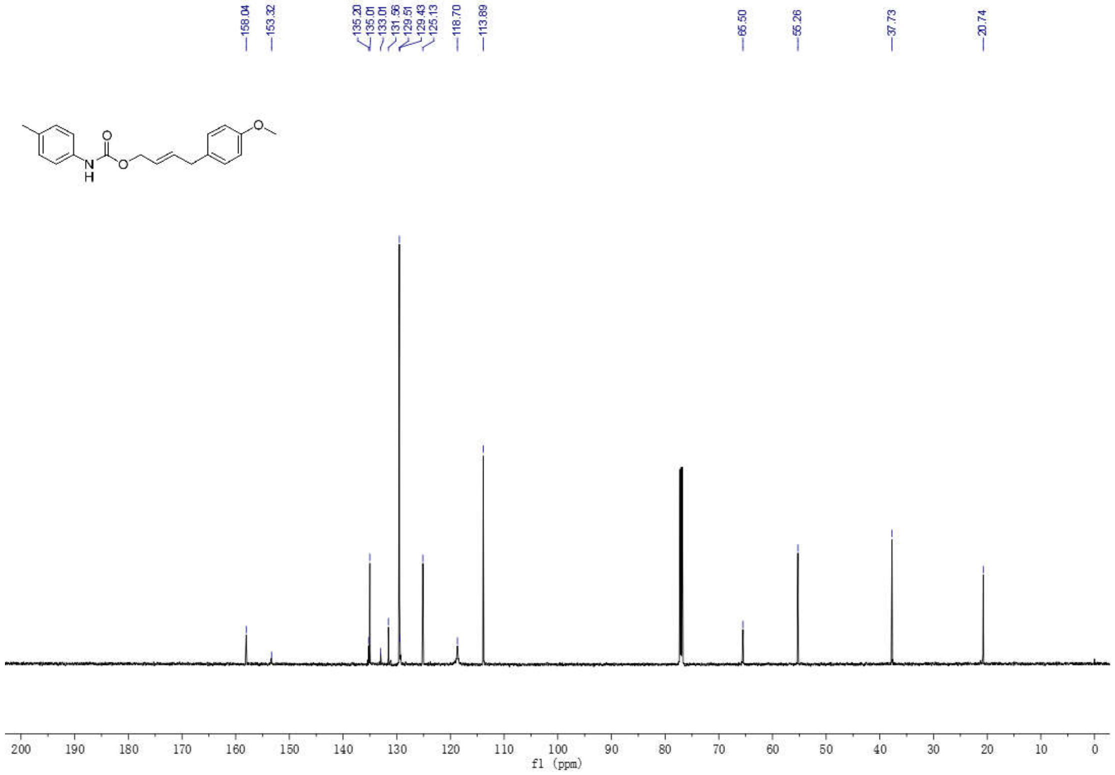
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **1e**



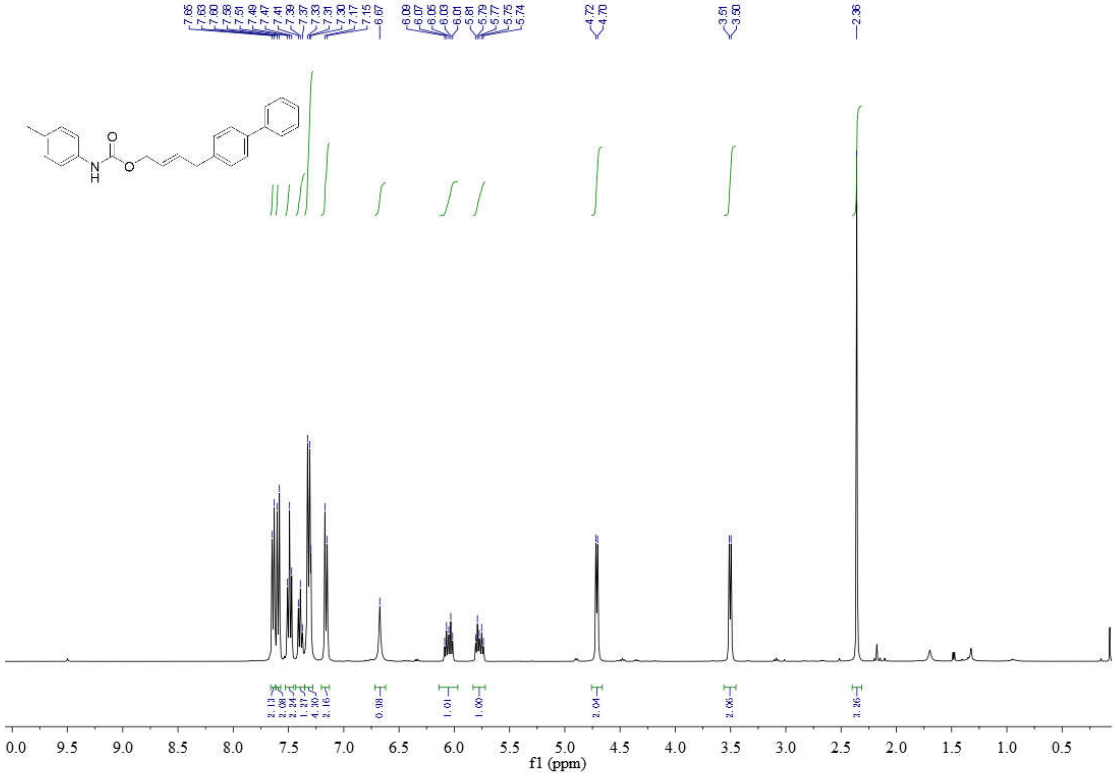
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1f**



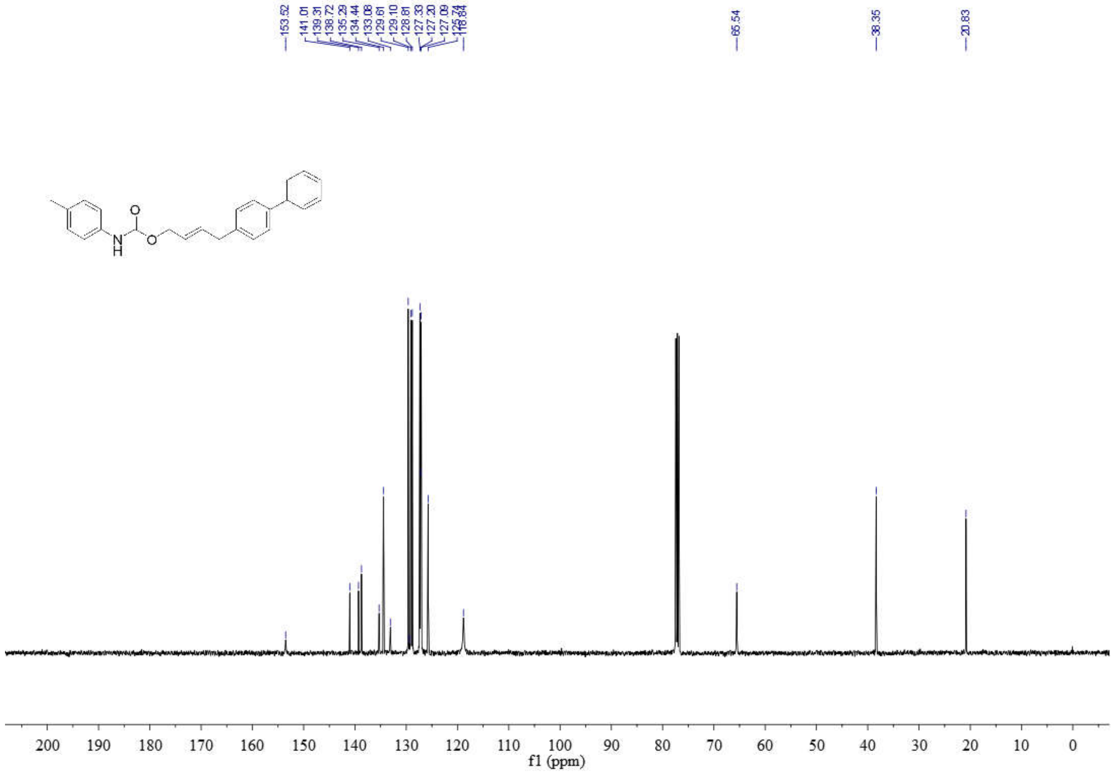
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **1f**



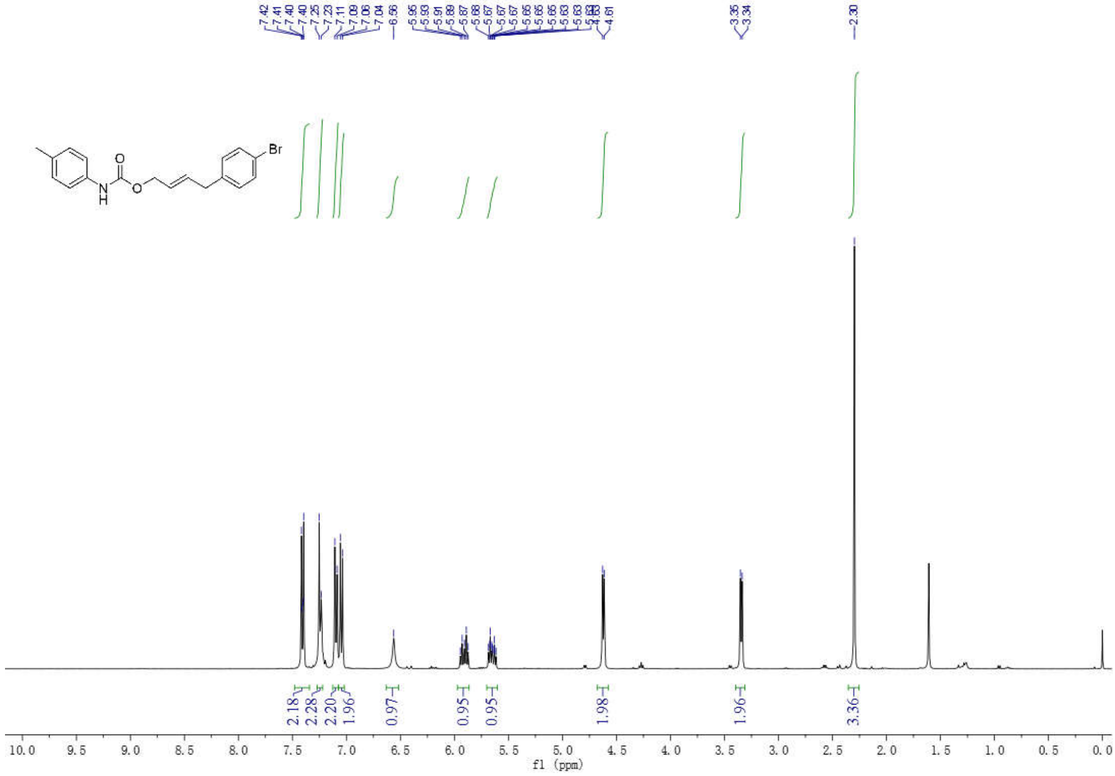
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1g**



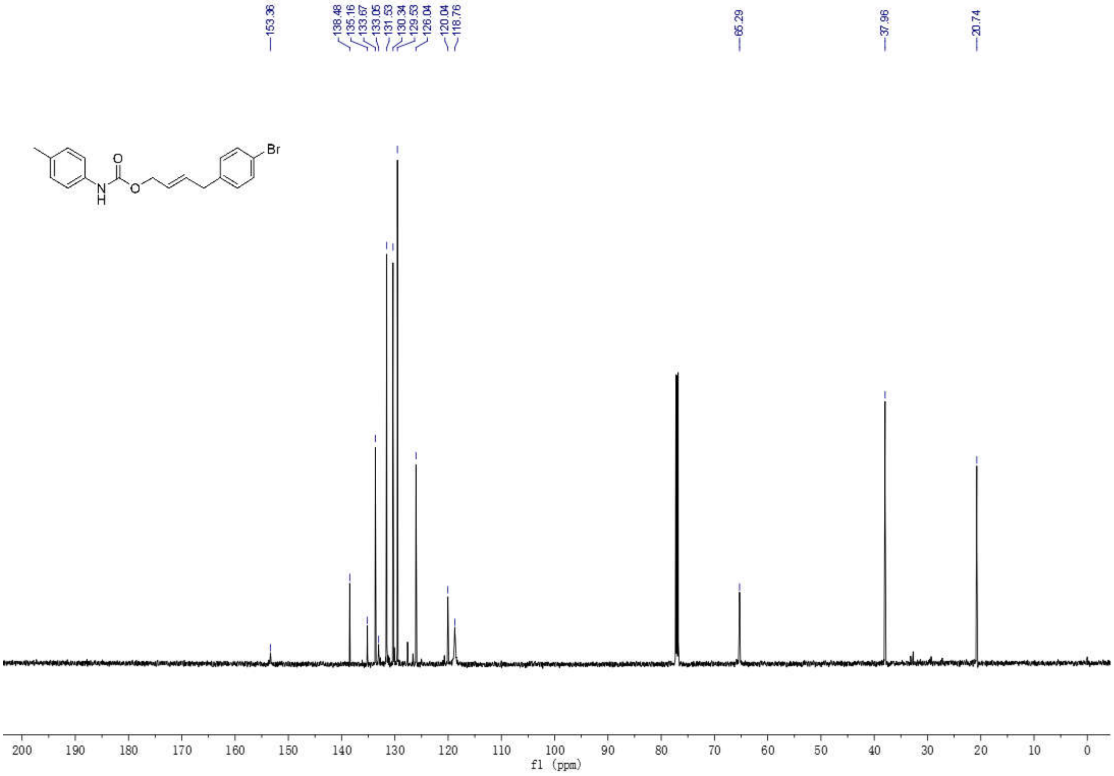
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1g**



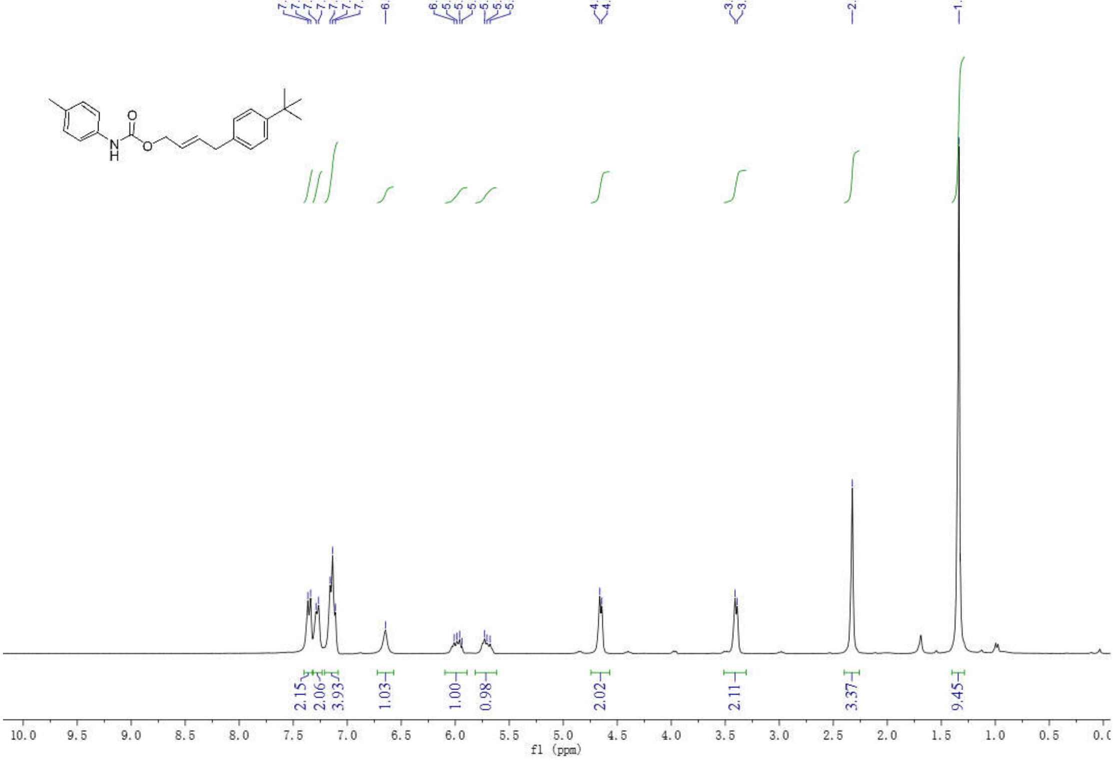
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1h**



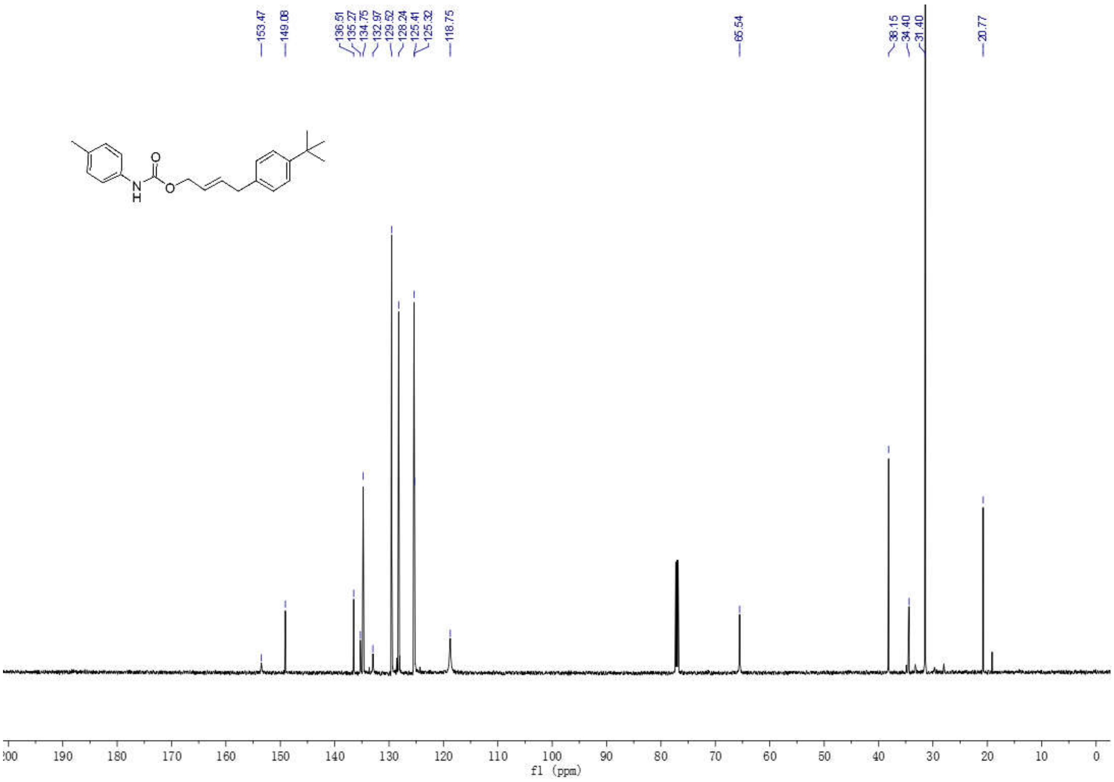
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **1h**



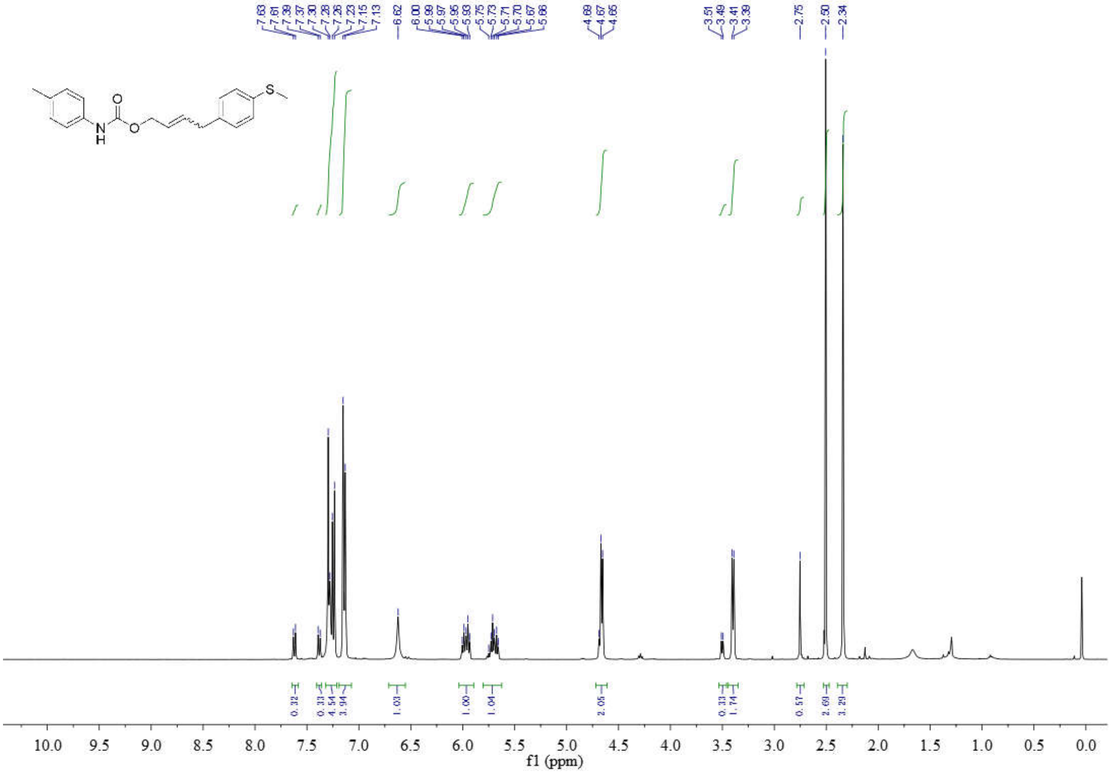
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1i**



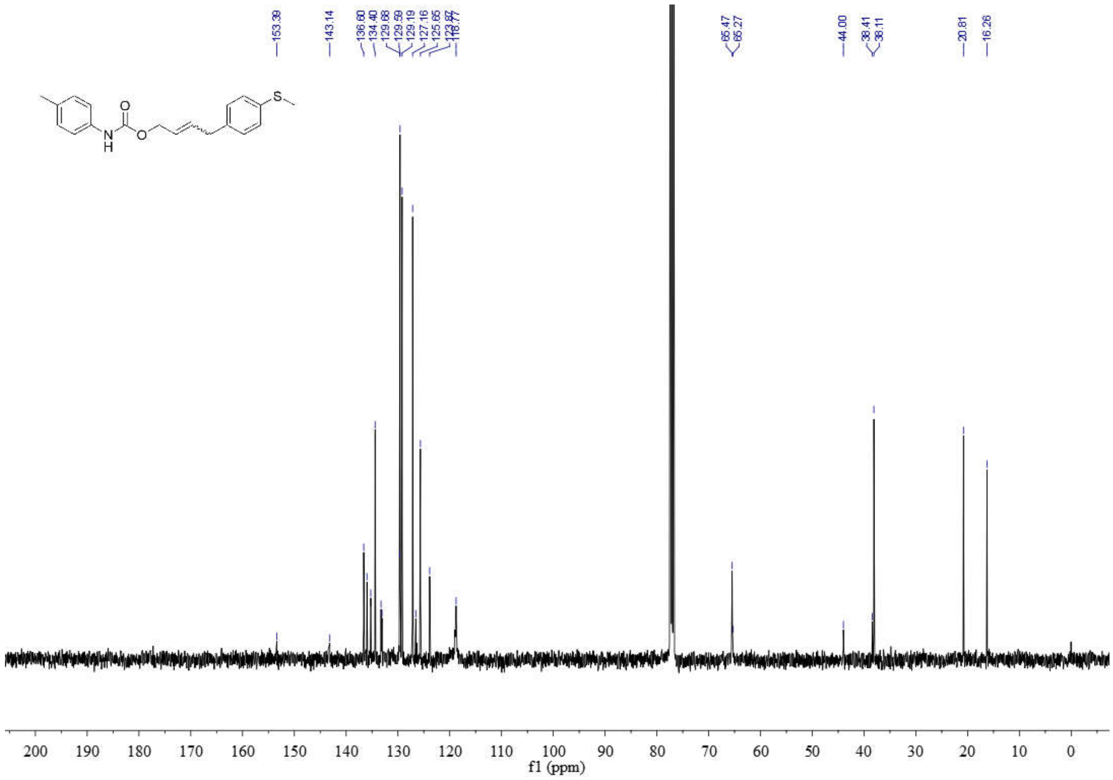
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1i**



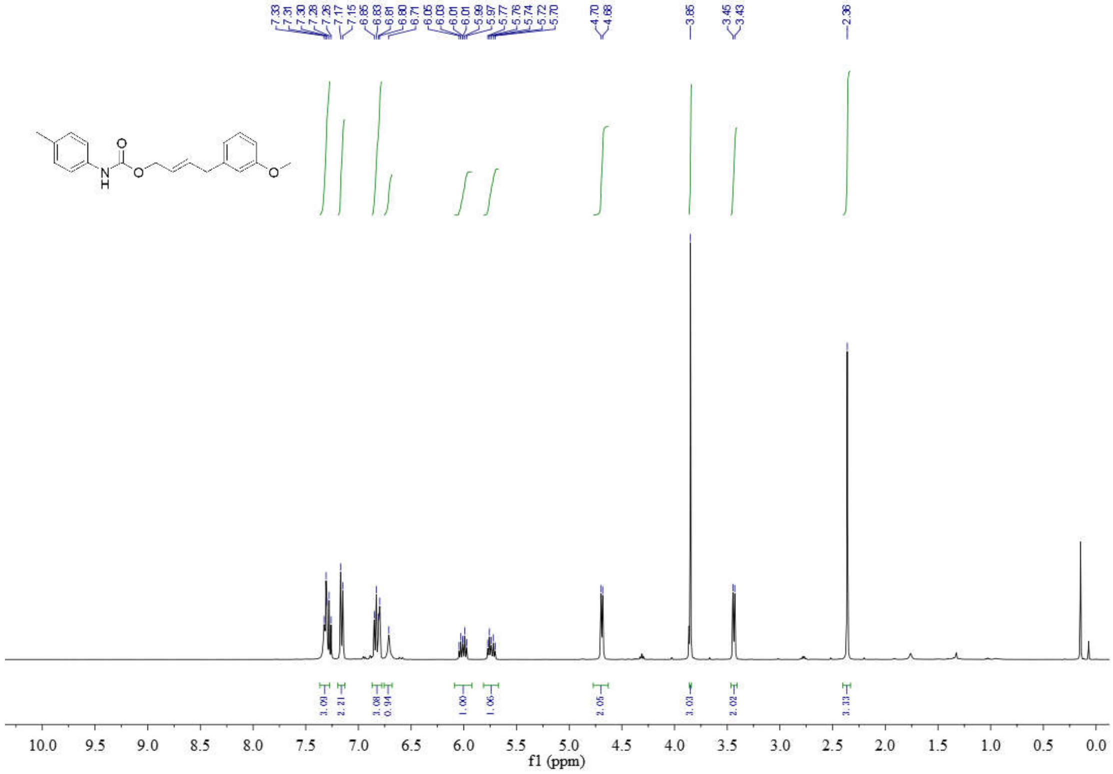
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1j**



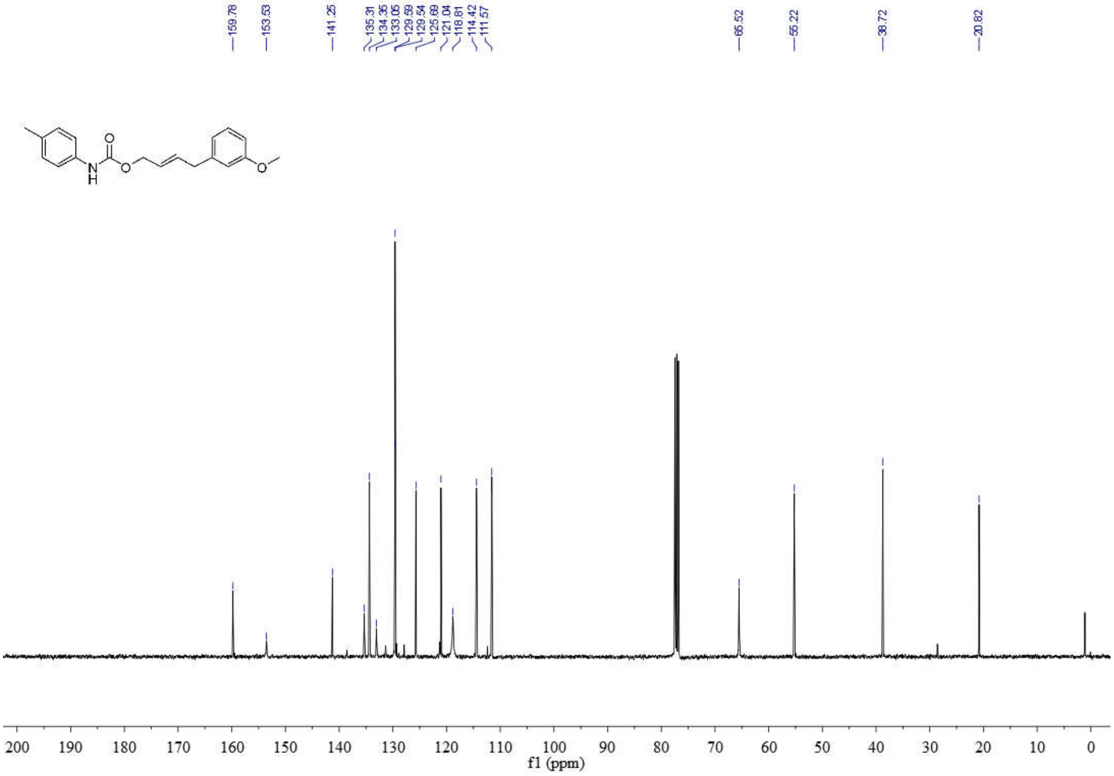
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1j**



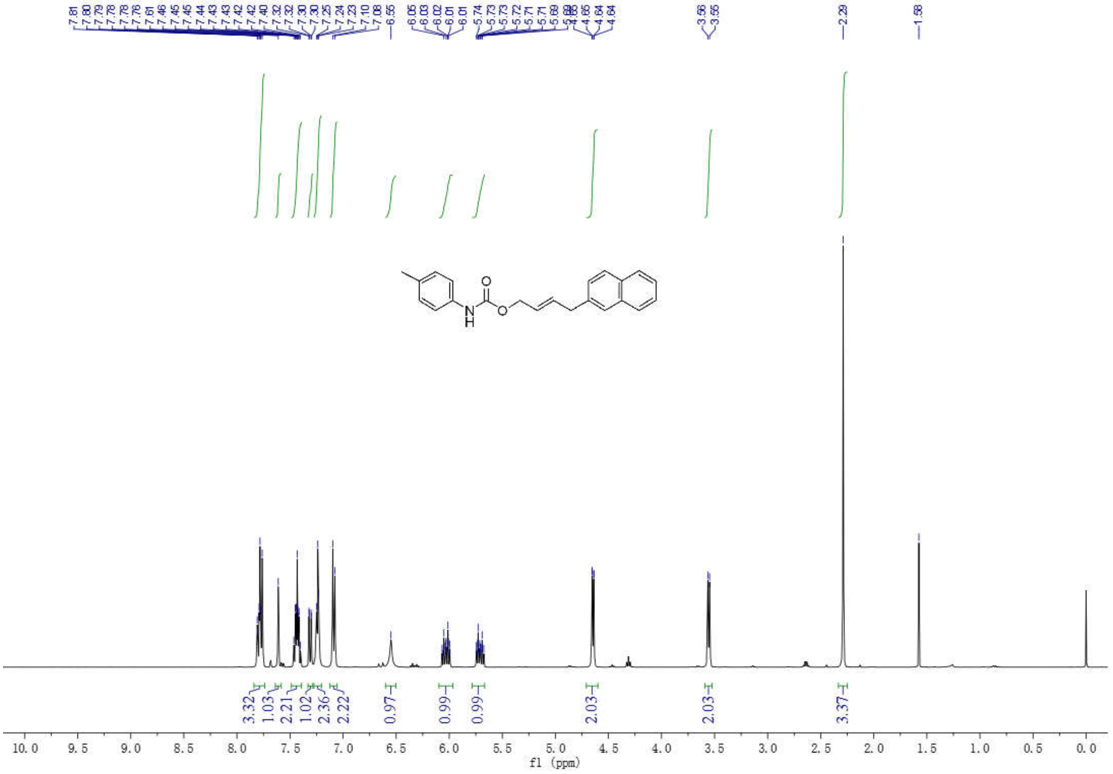
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1k**



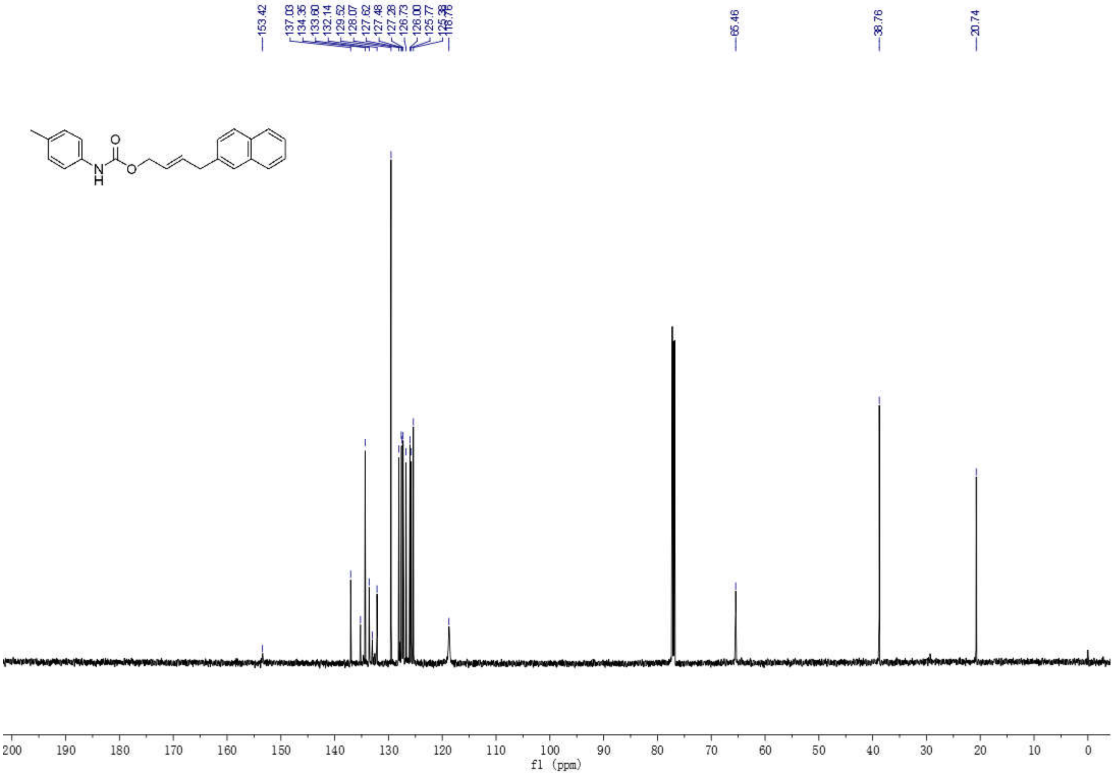
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1k**



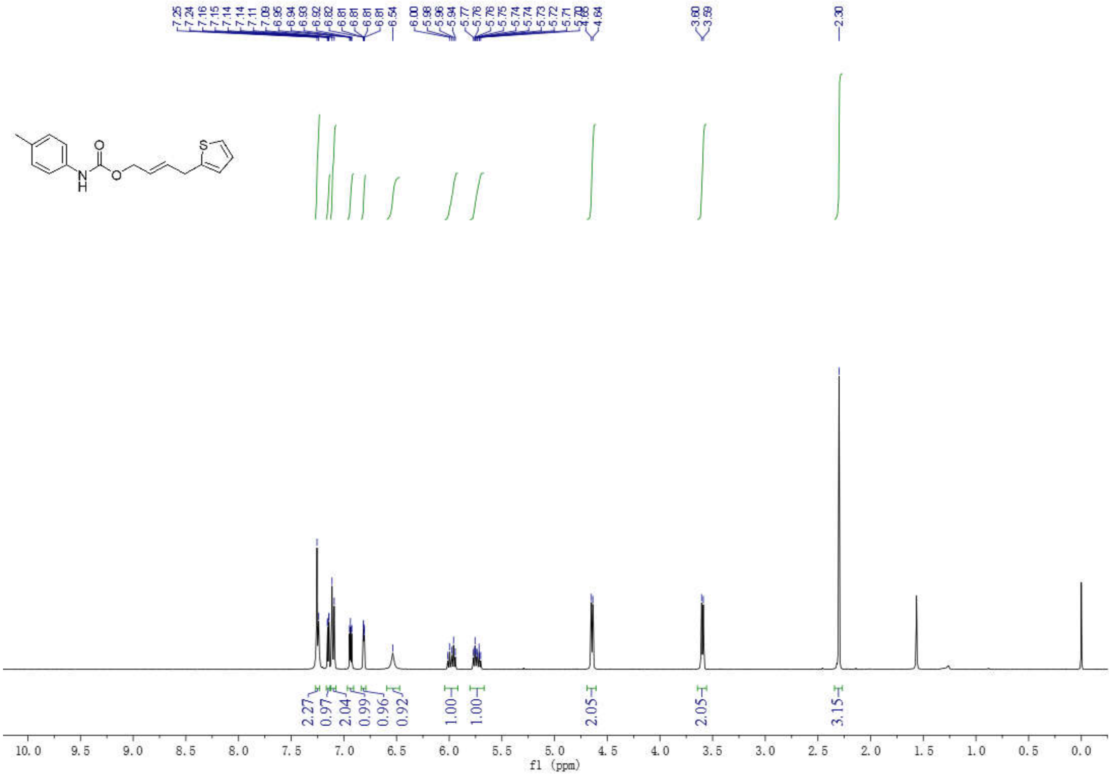
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1l**



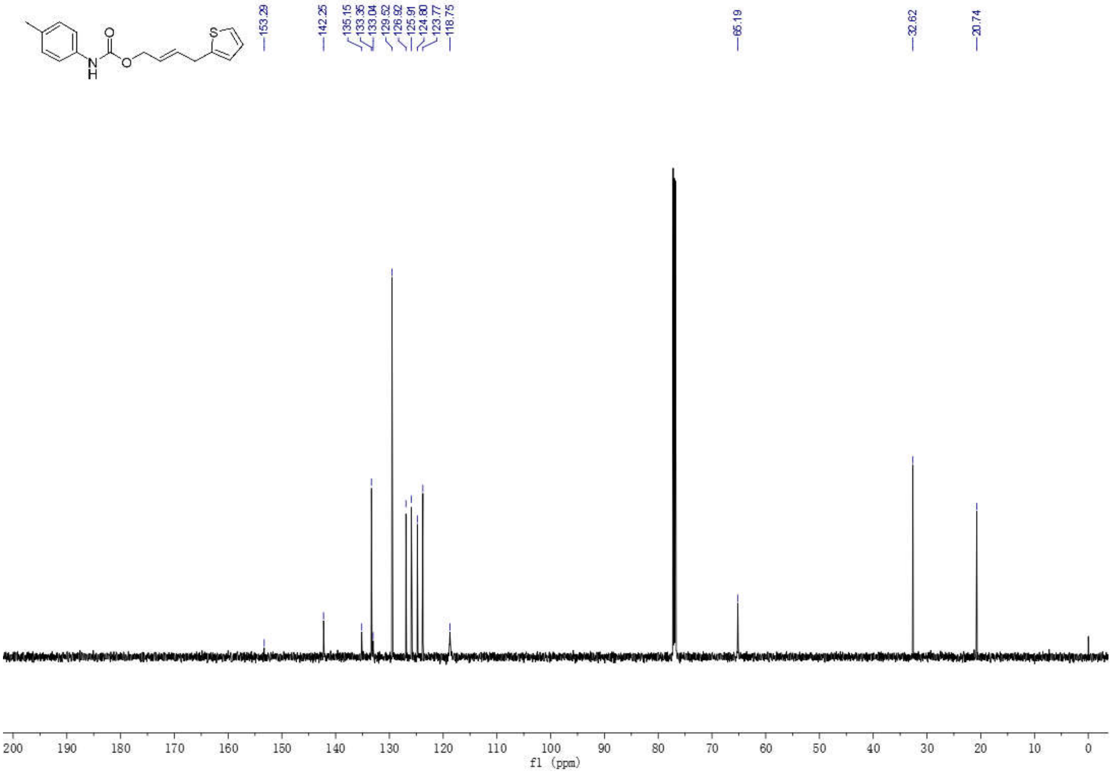
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1l**



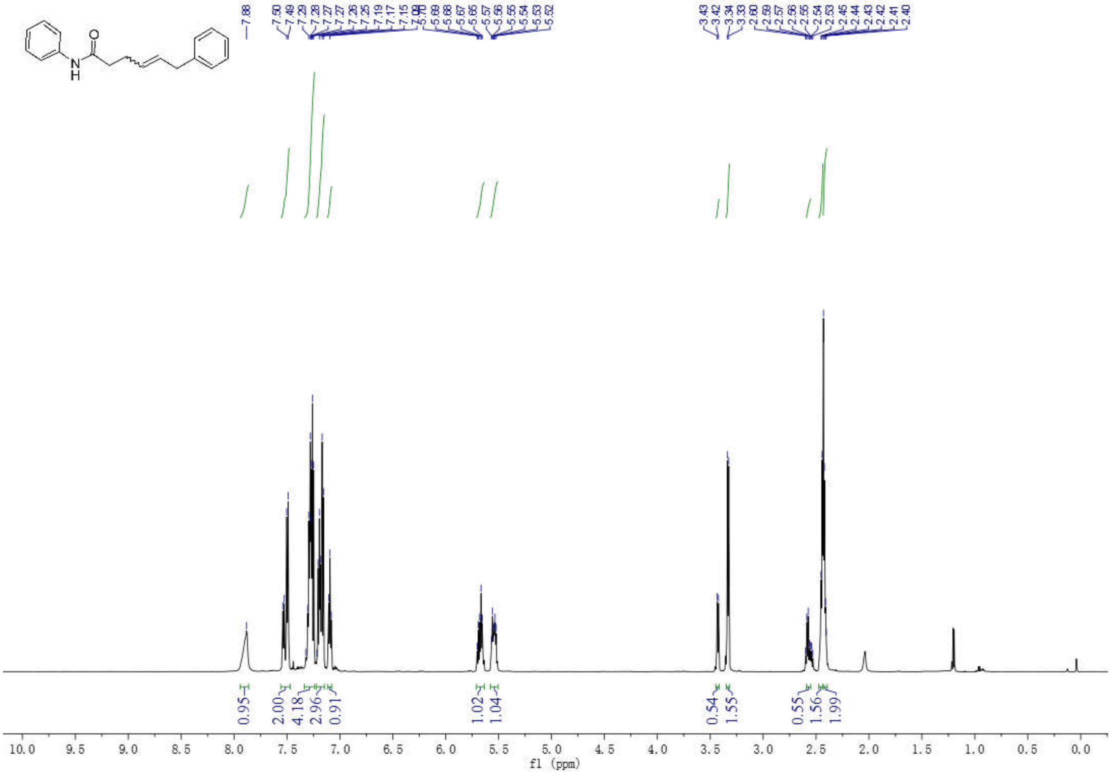
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1m**



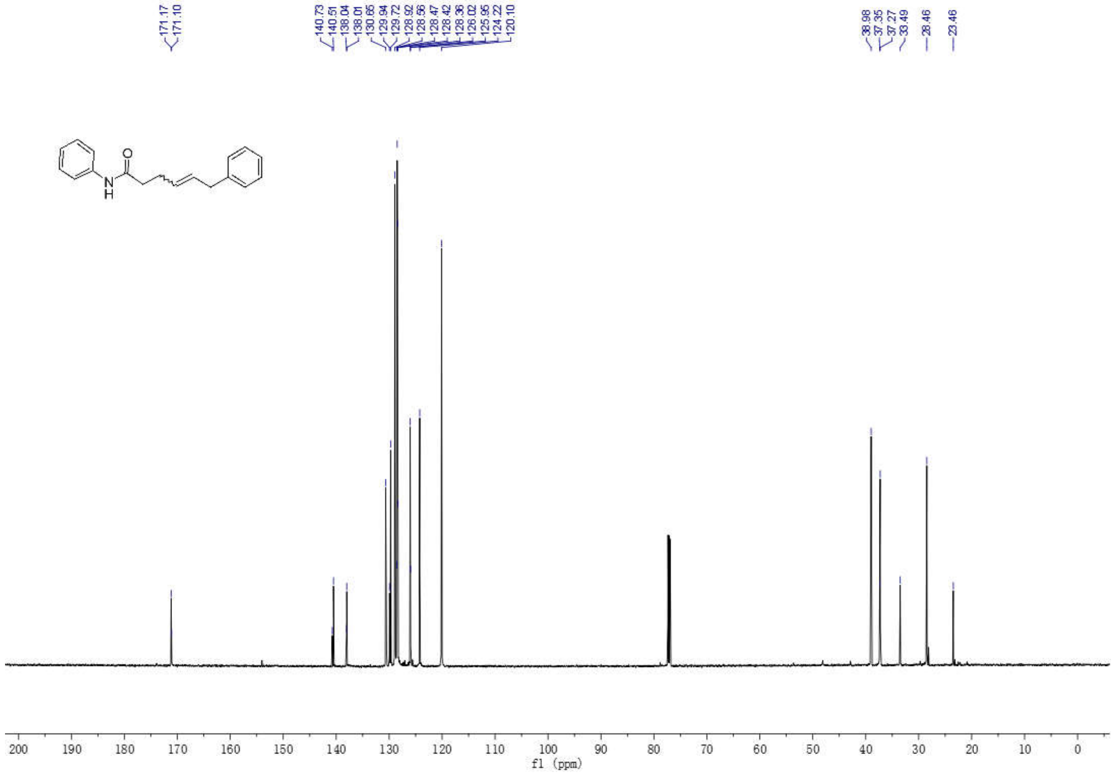
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1m**



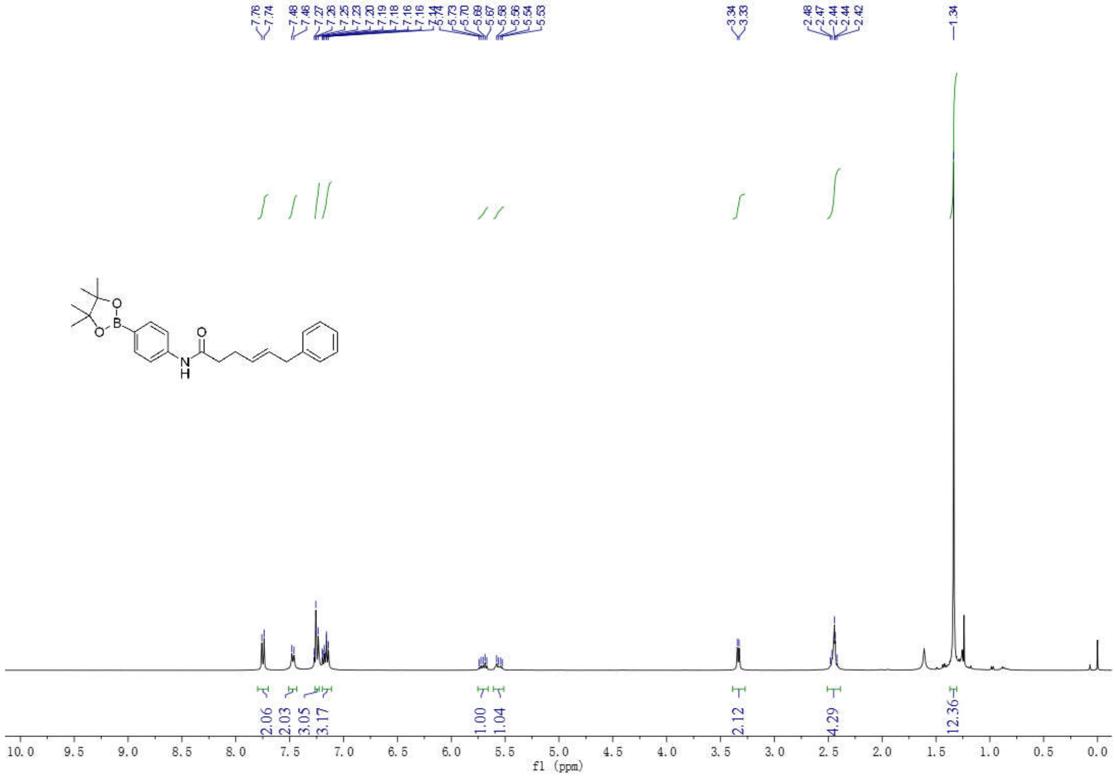
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1n**



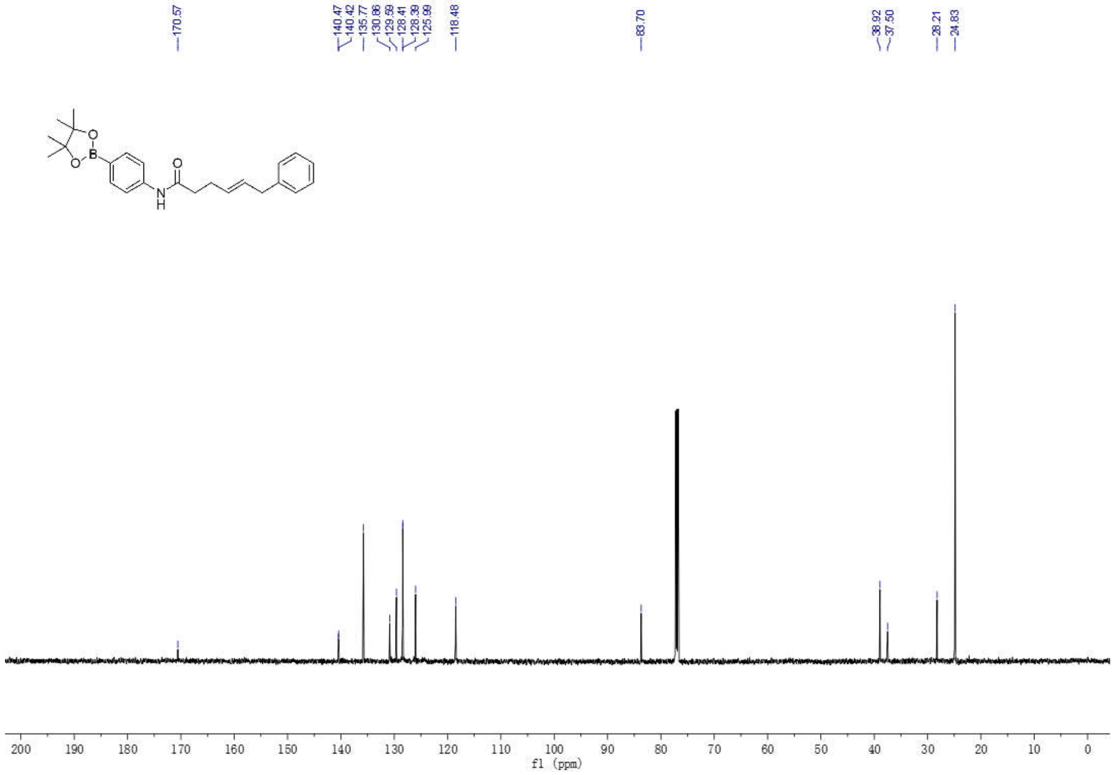
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1n**



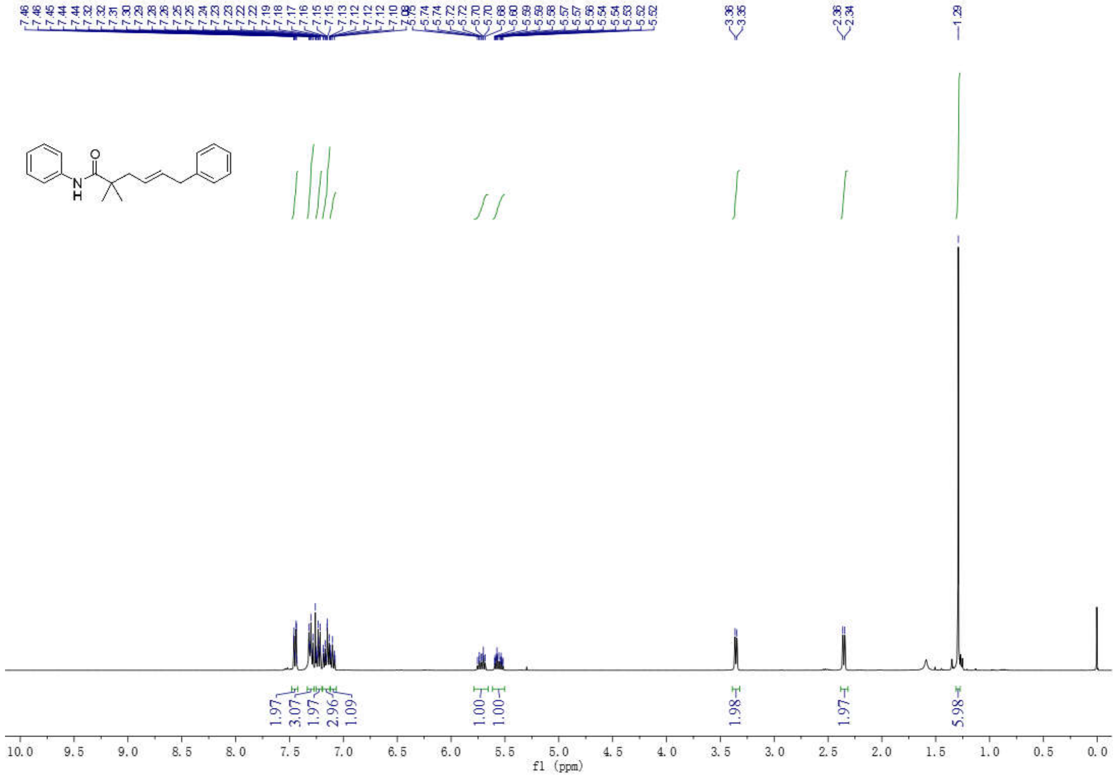
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1o**



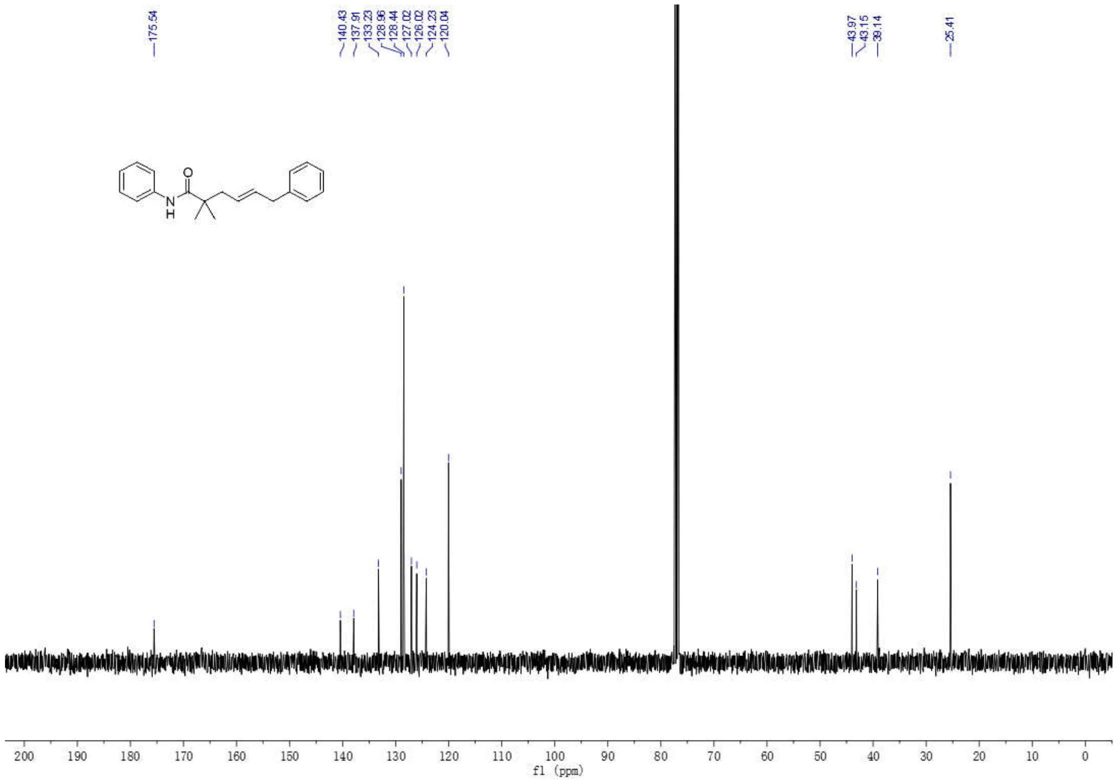
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **1o**



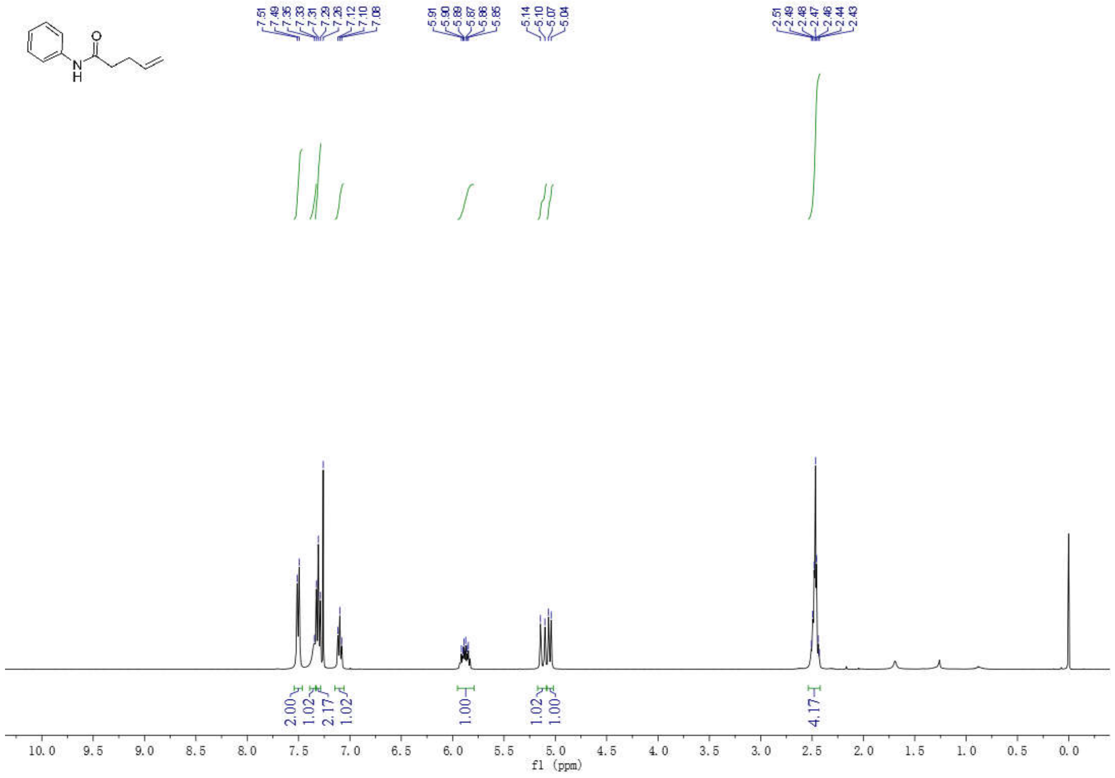
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1p**



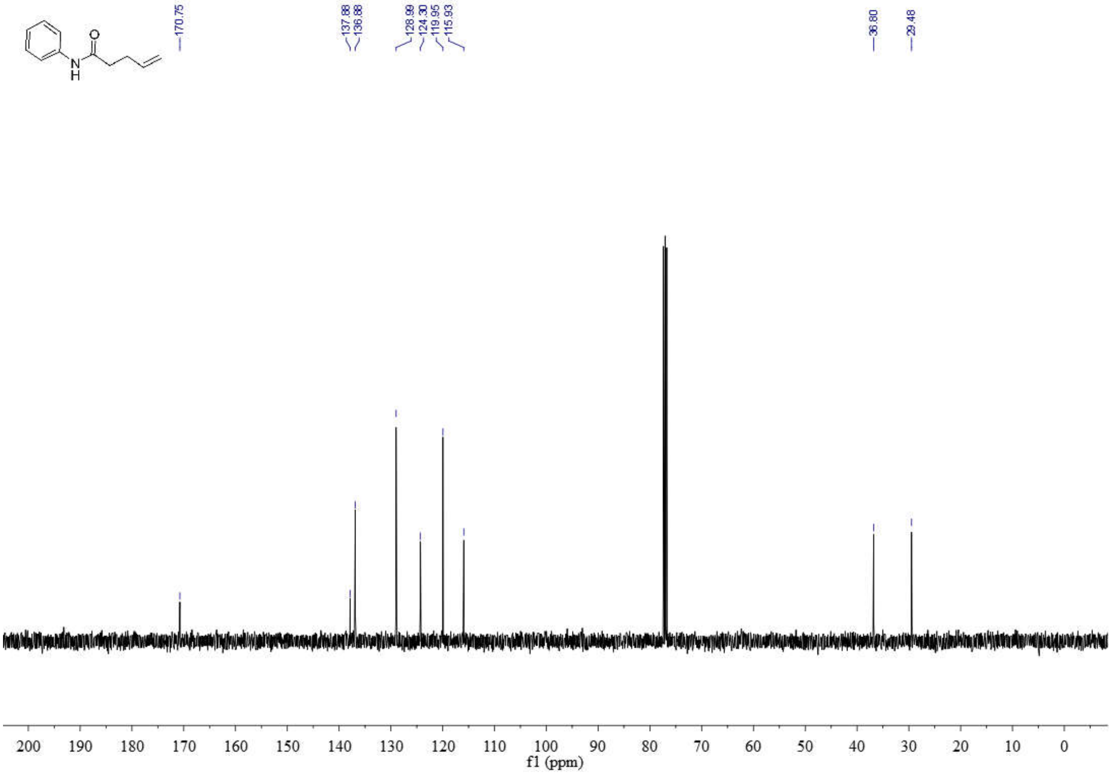
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1p**



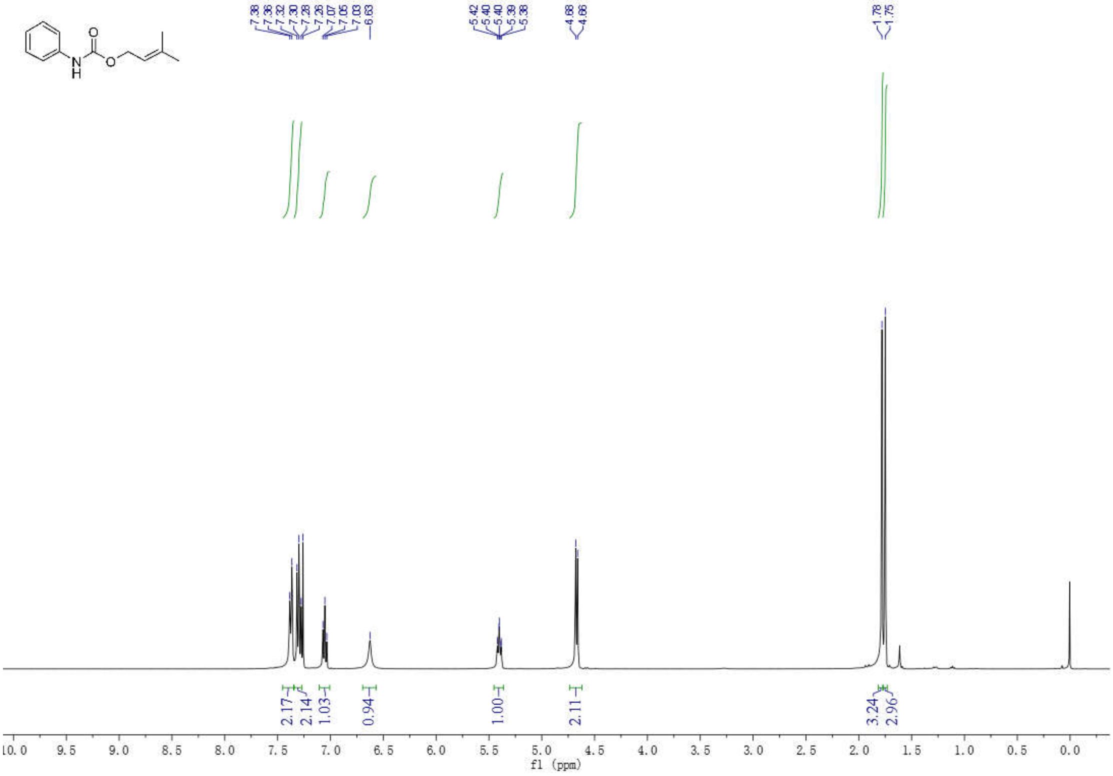
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **1q**



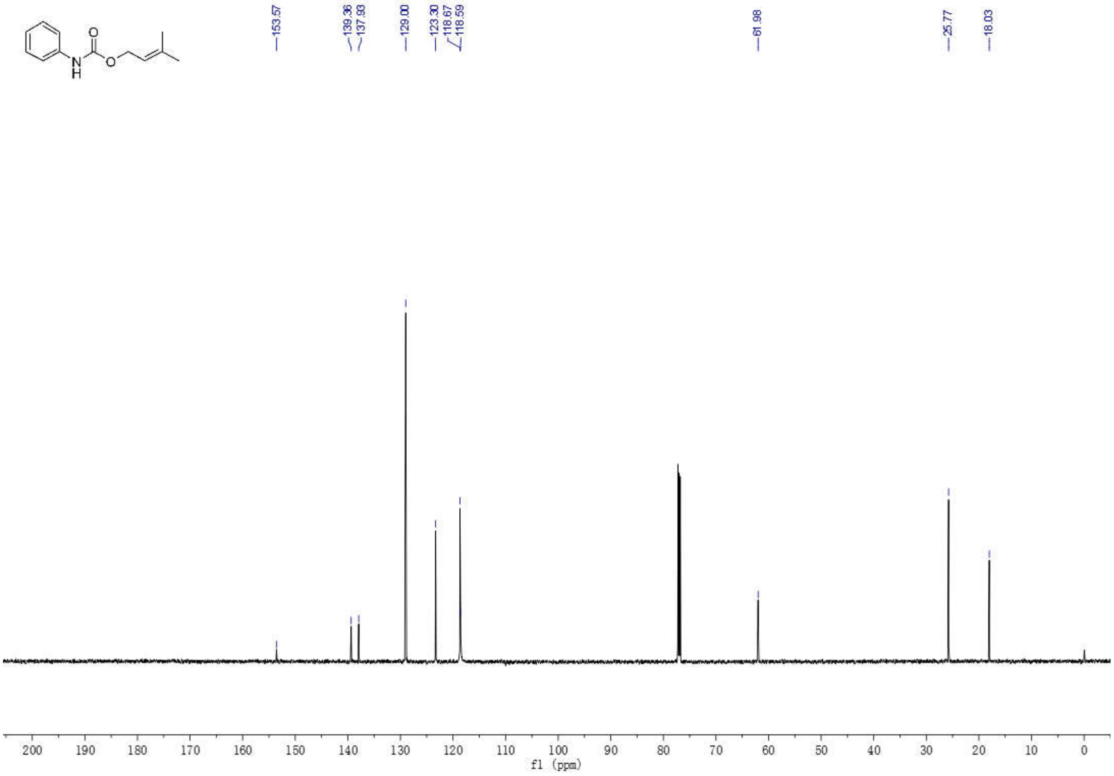
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **1q**



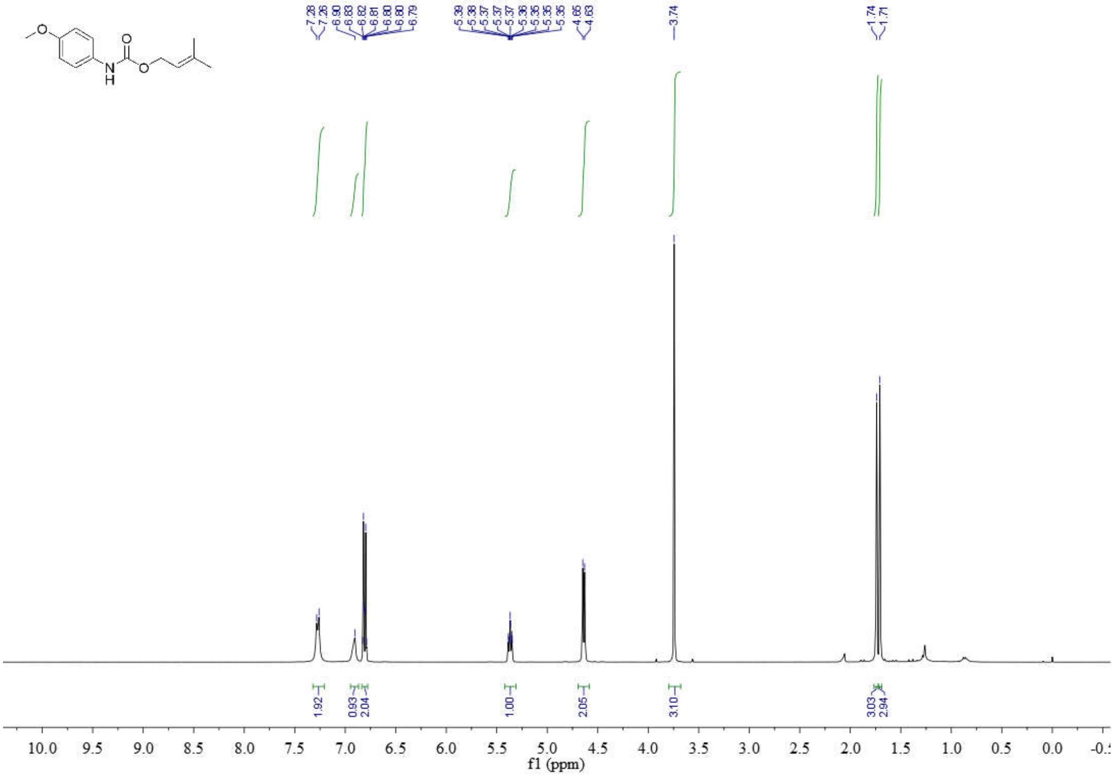
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7a**



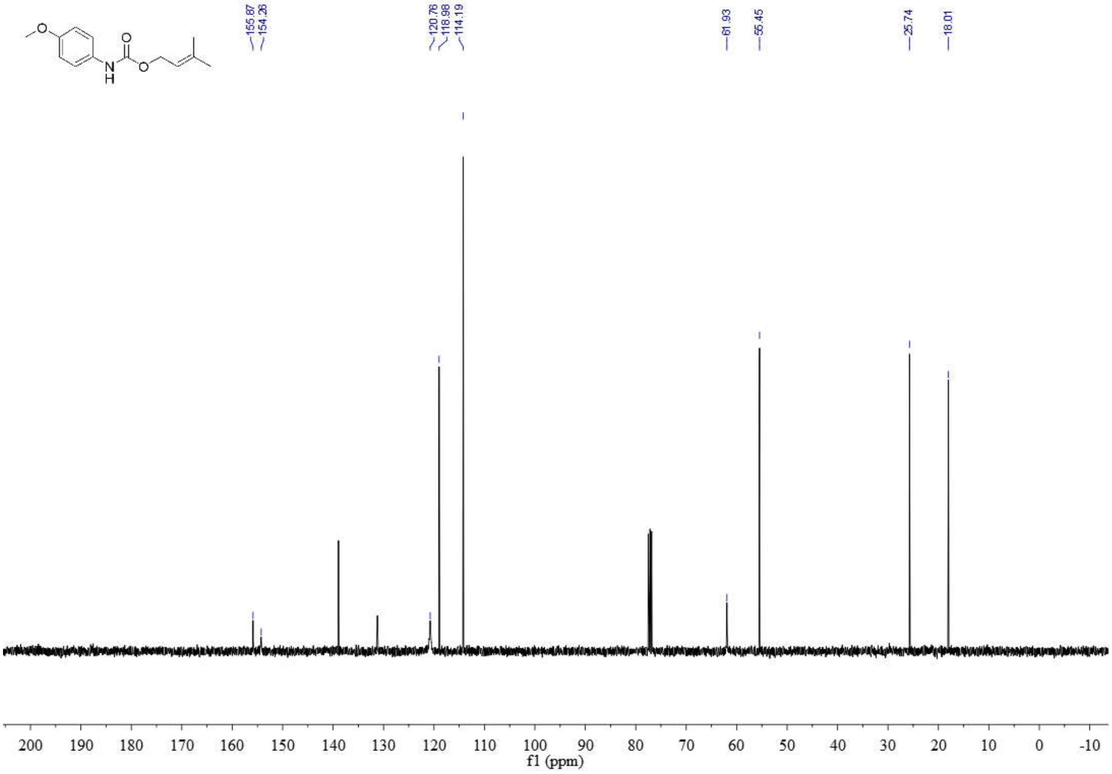
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7a**



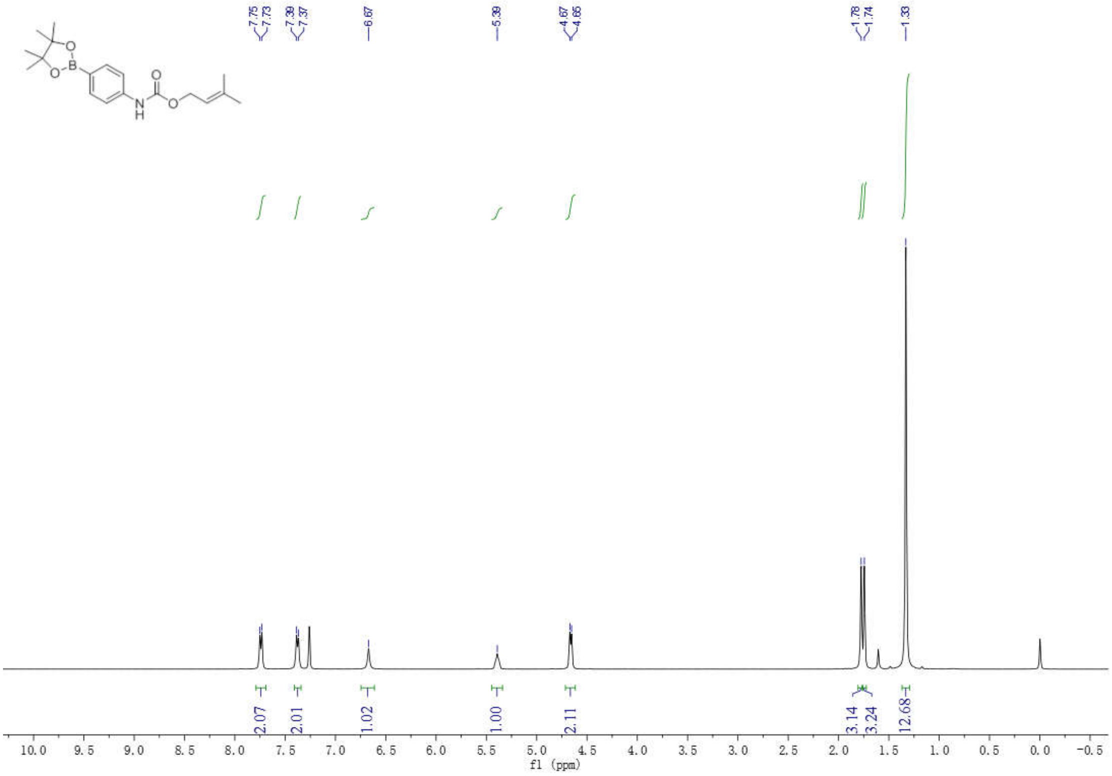
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7b**



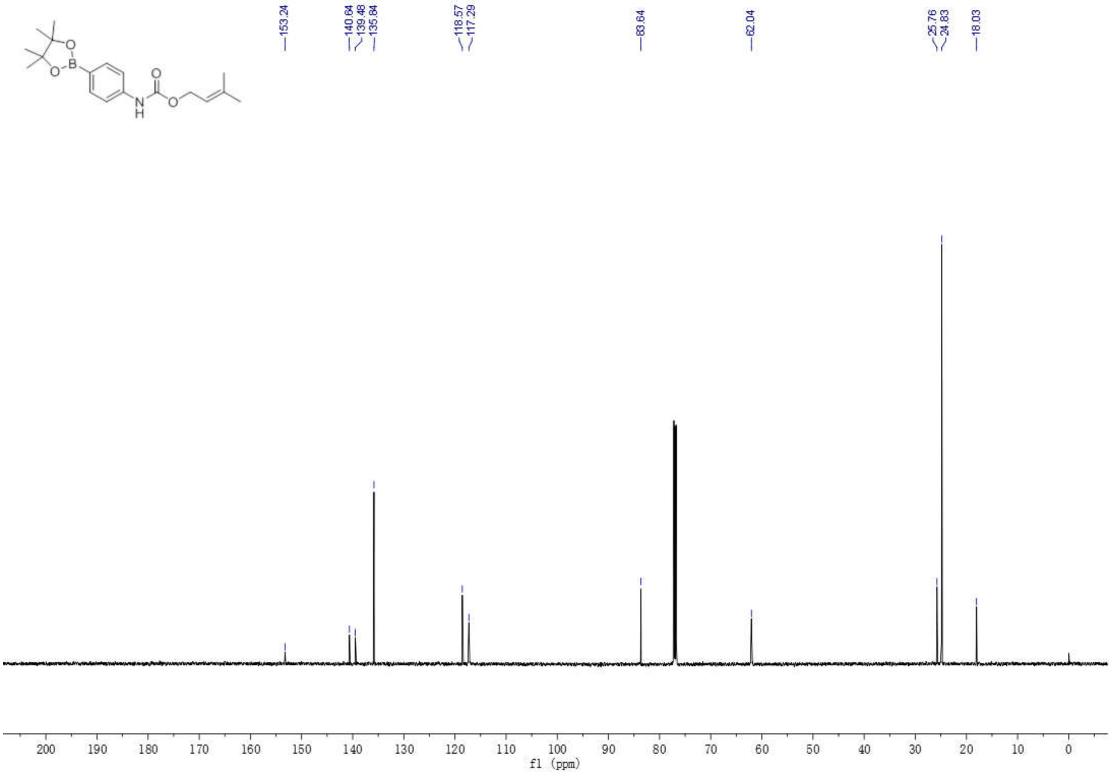
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7b**



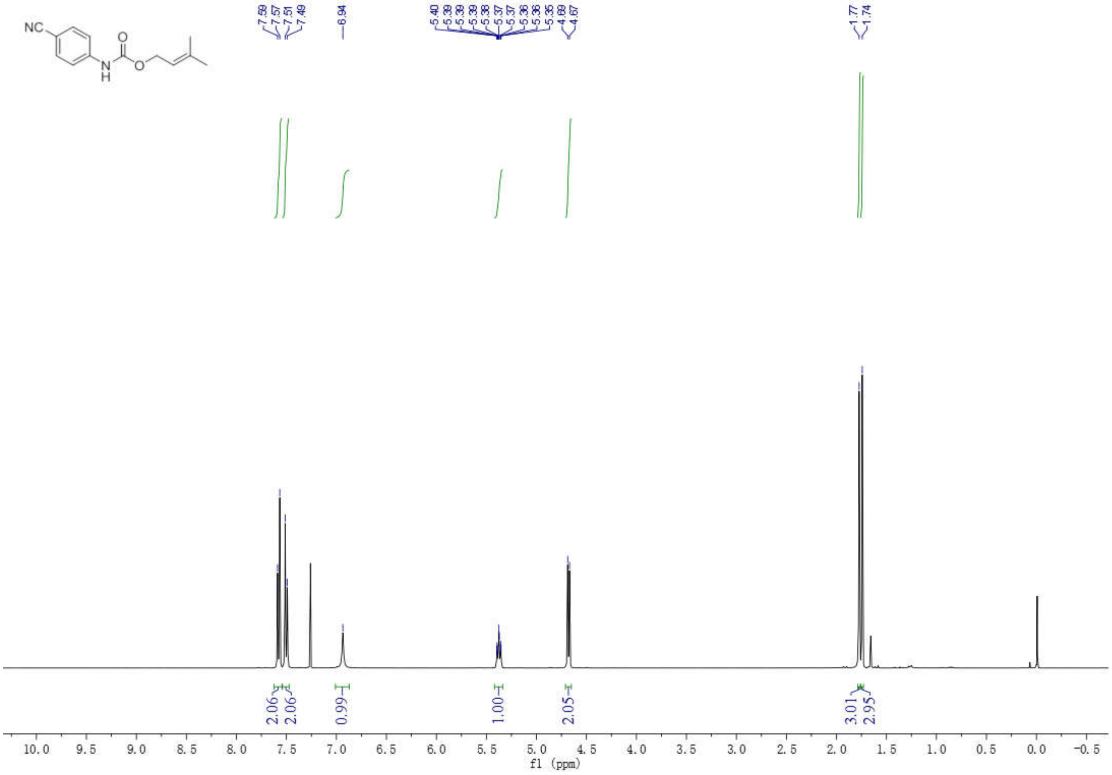
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7c**



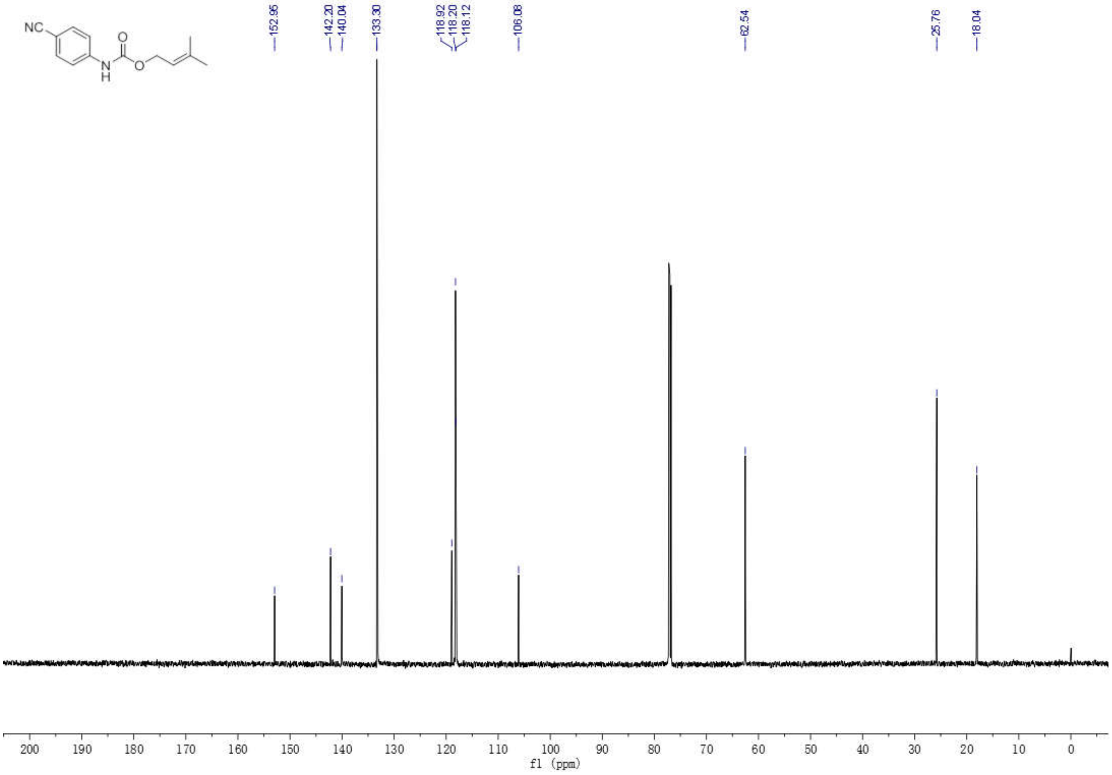
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **7c**



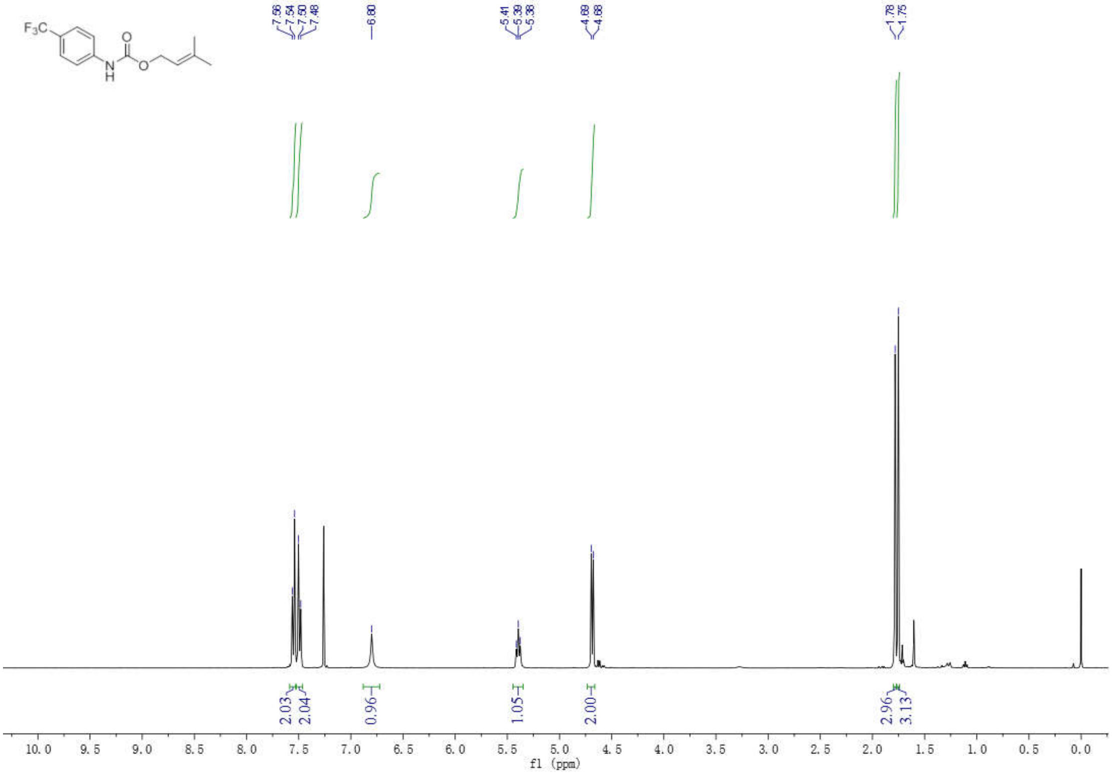
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **7d**



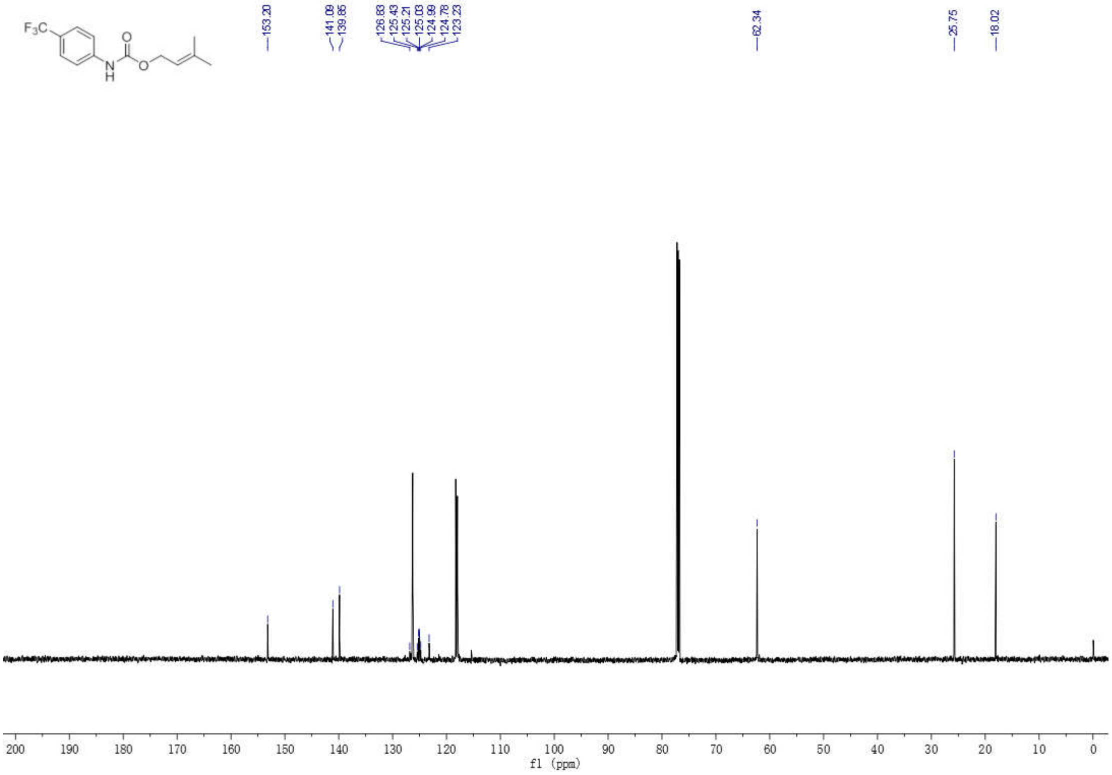
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7d**



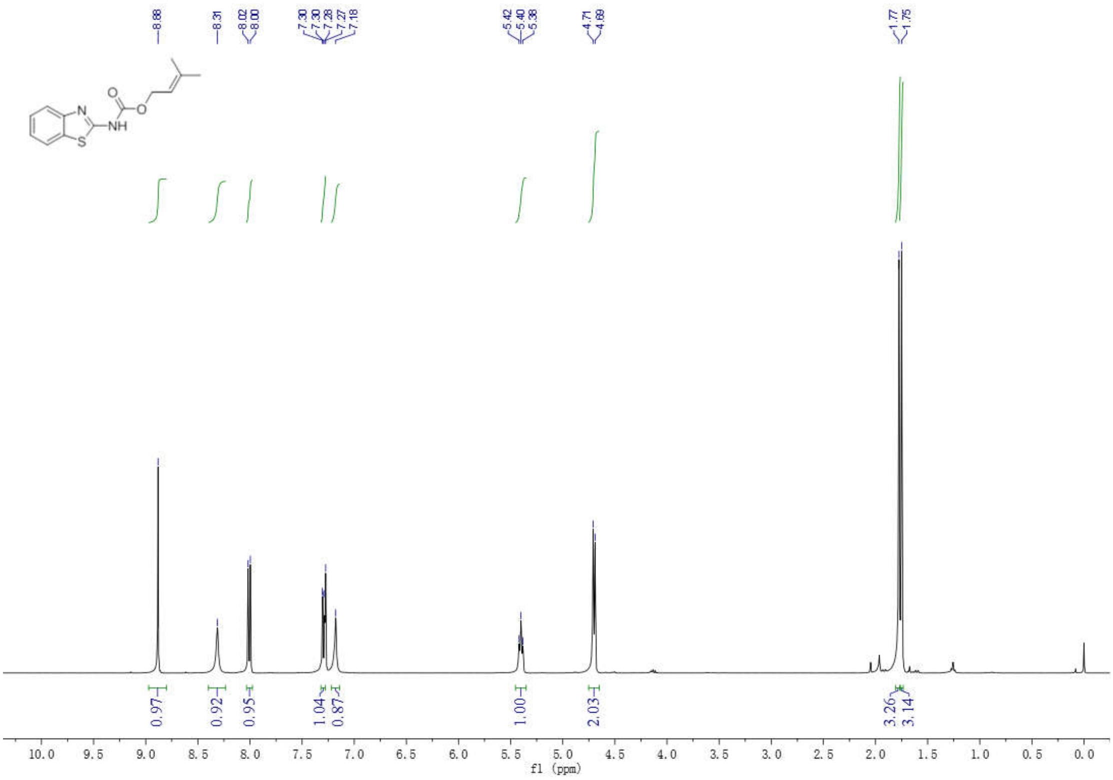
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7e**



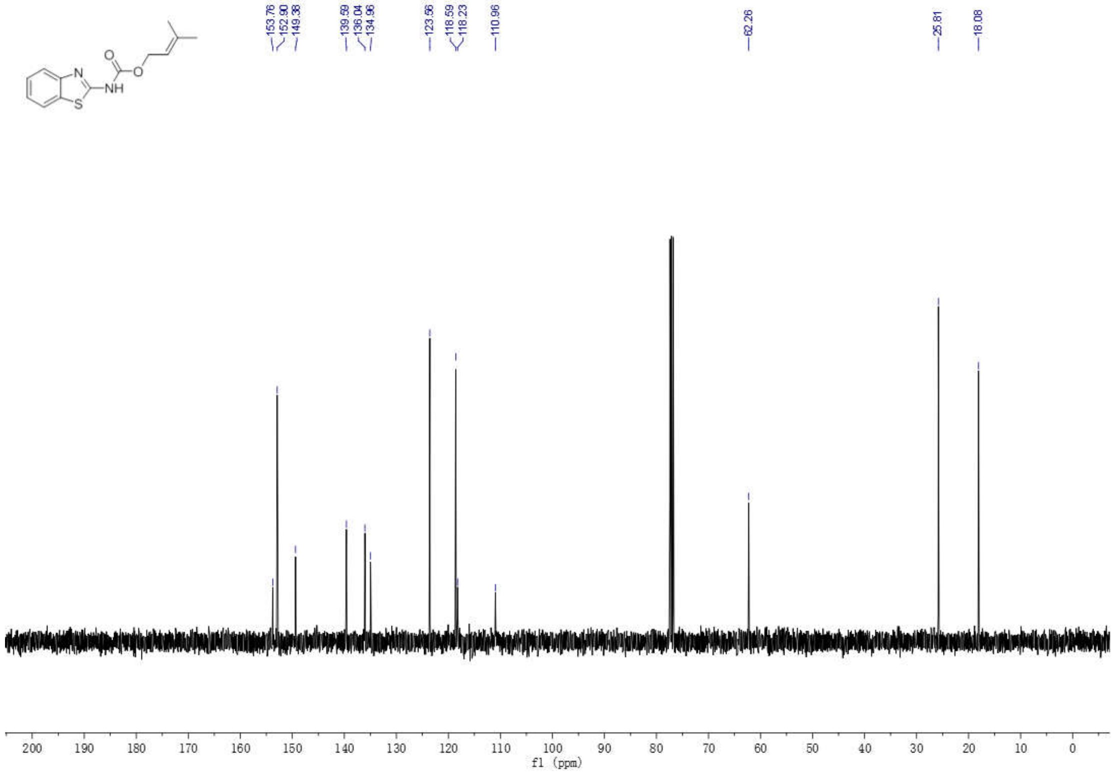
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7e**



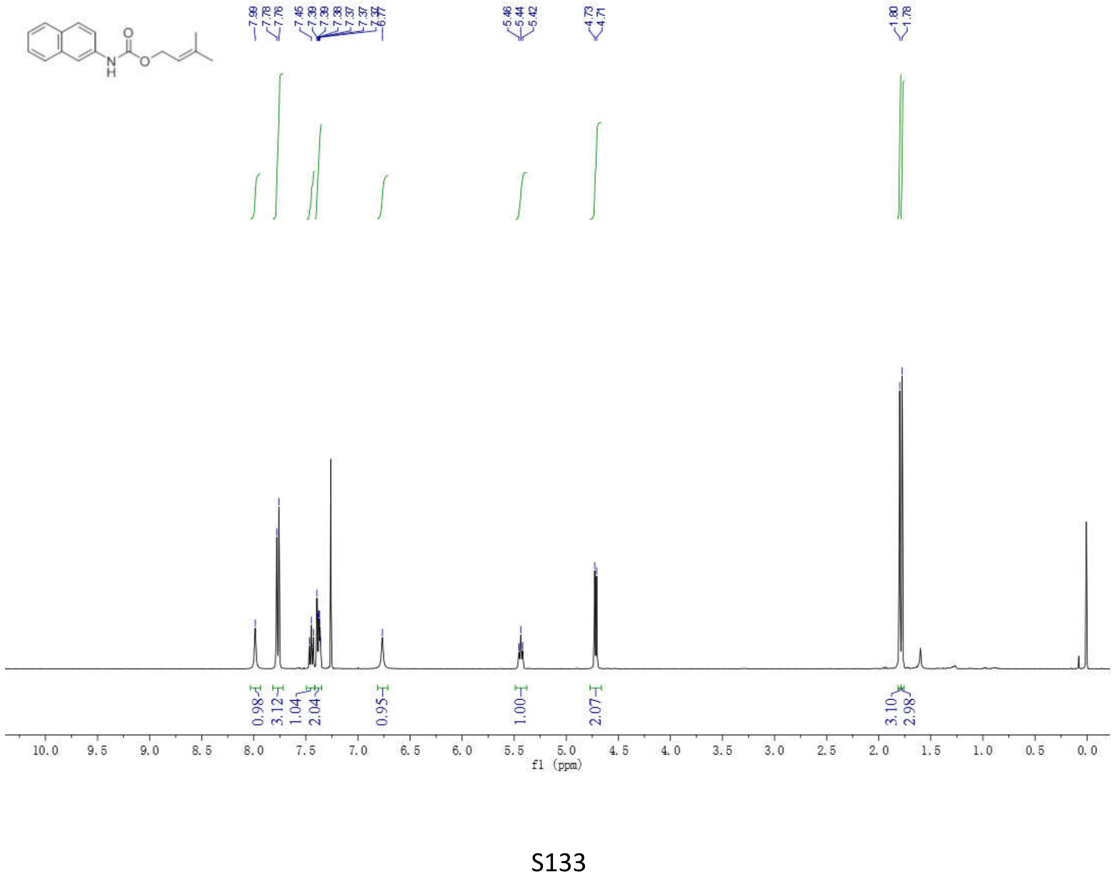
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7f**



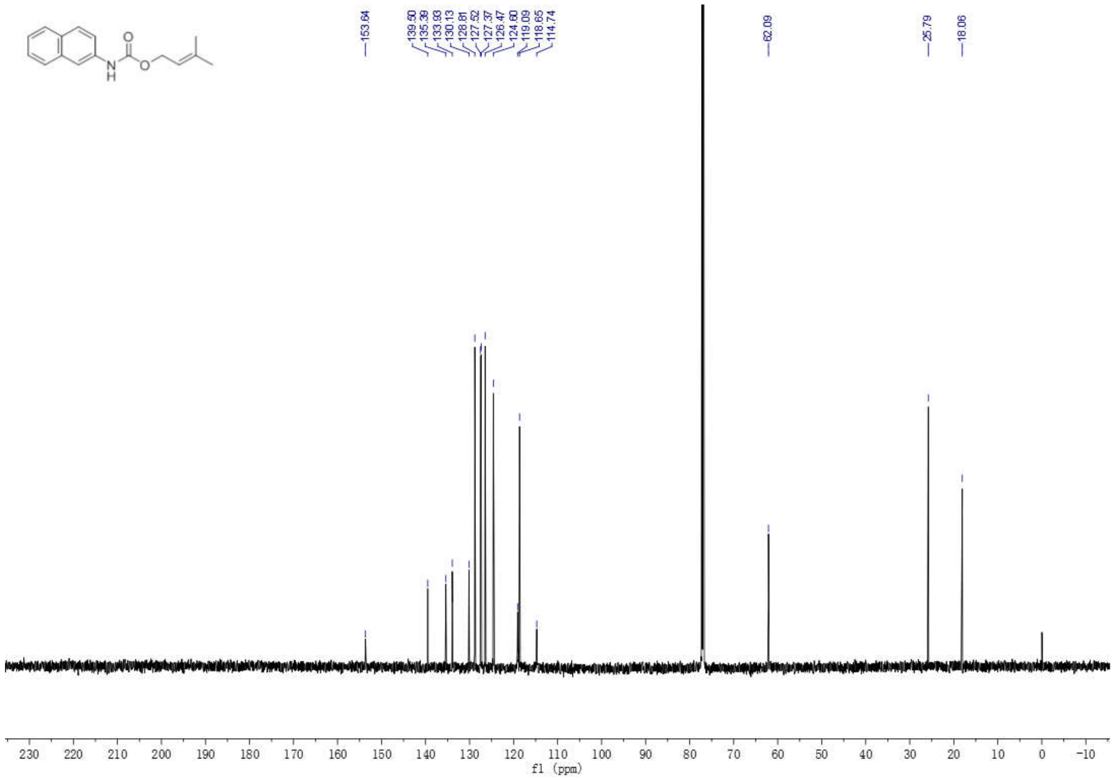
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7f**



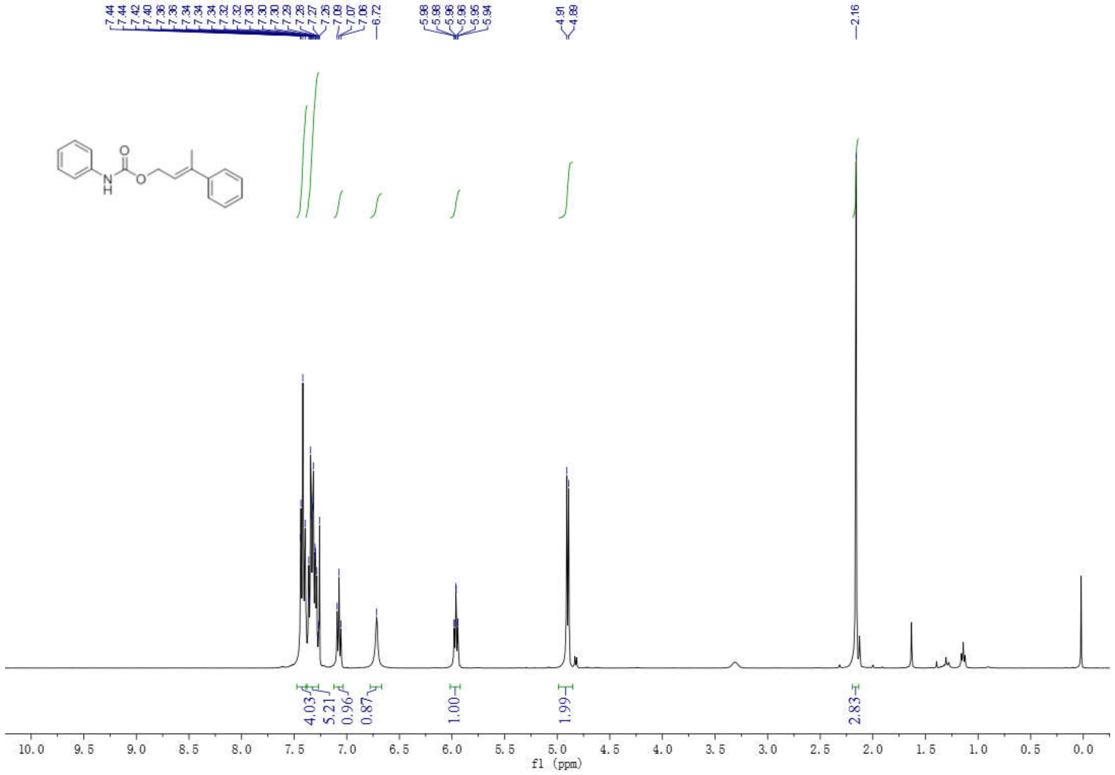
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7g**



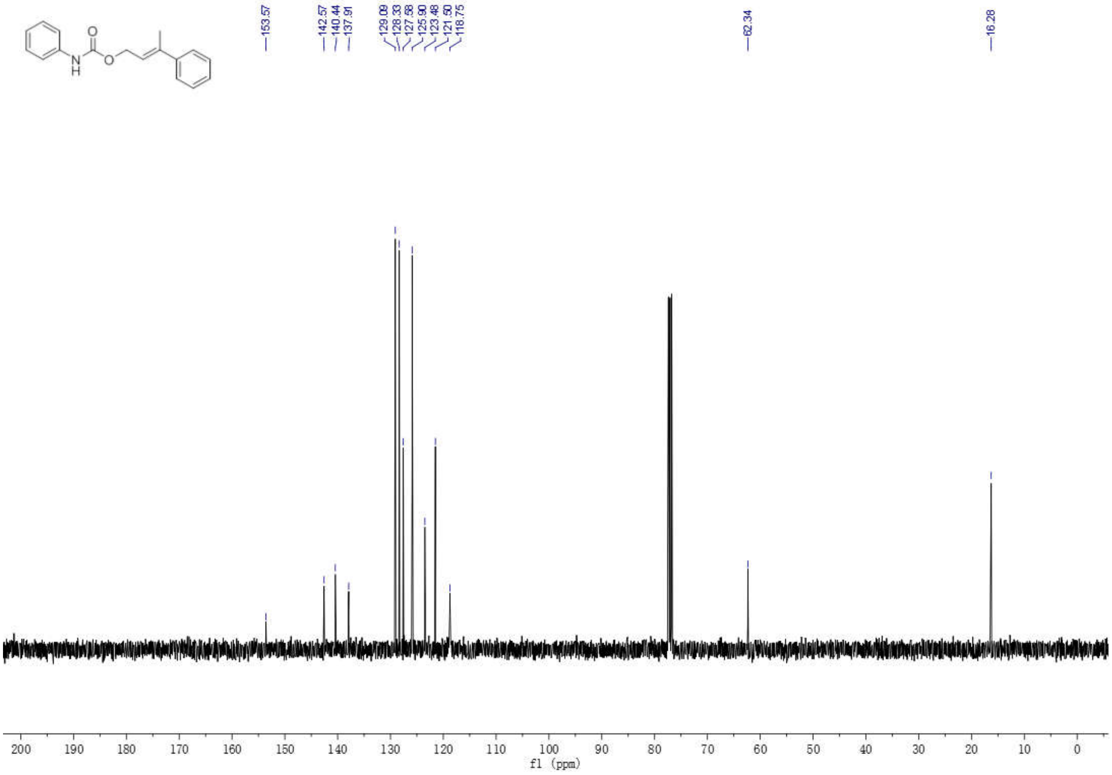
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **7g**



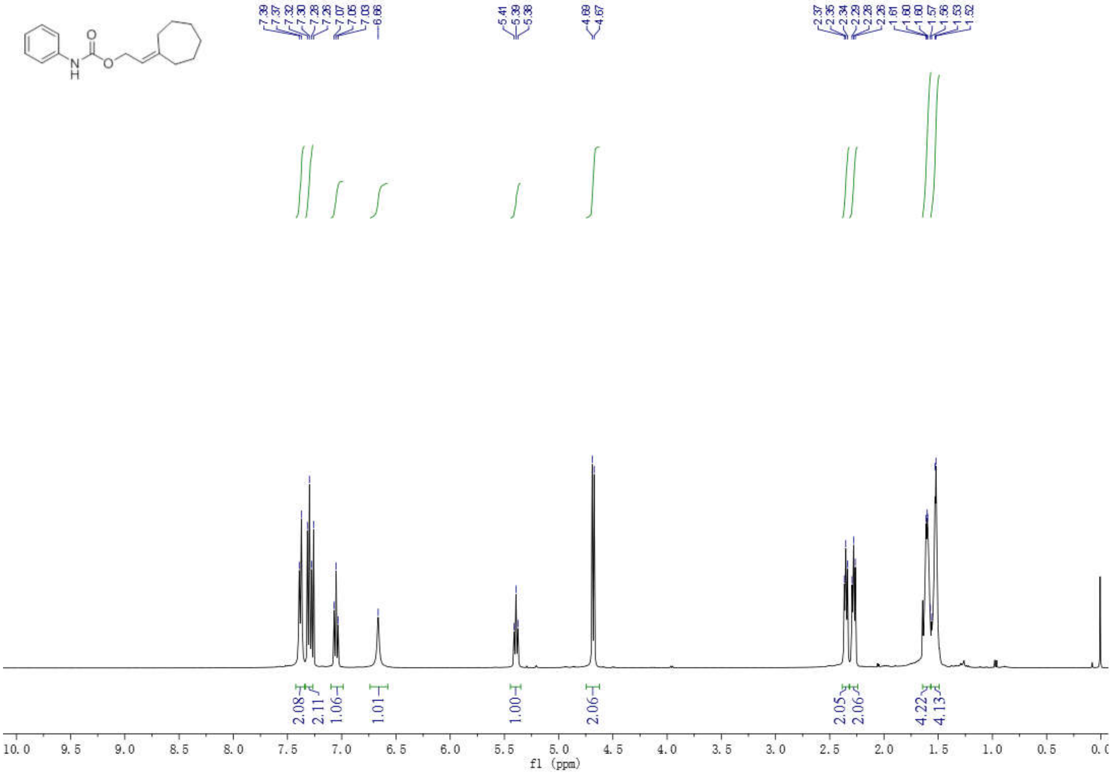
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **7h**



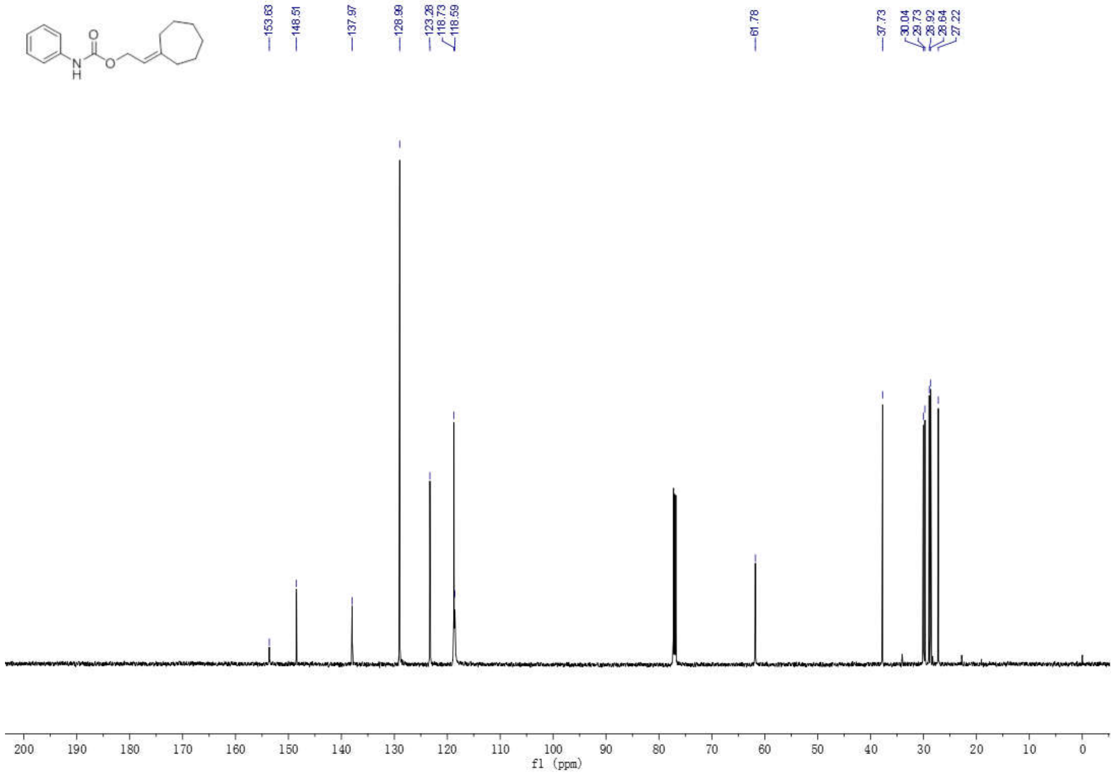
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7h**



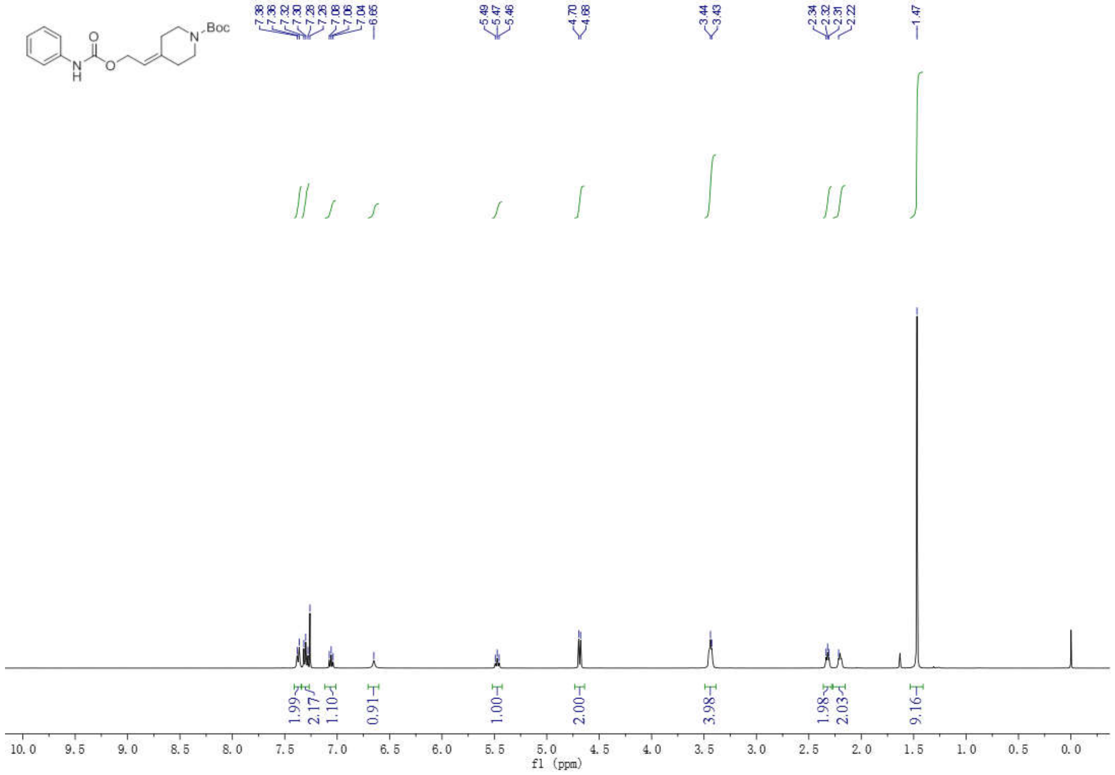
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7i**



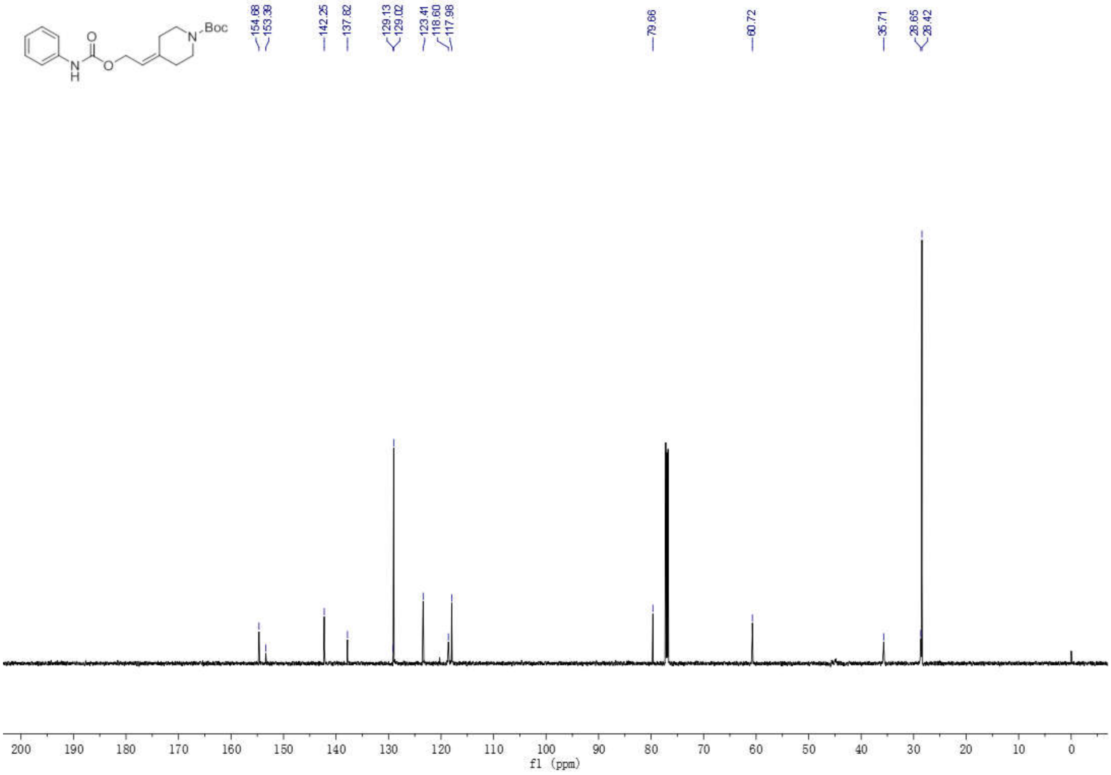
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of 7**i**



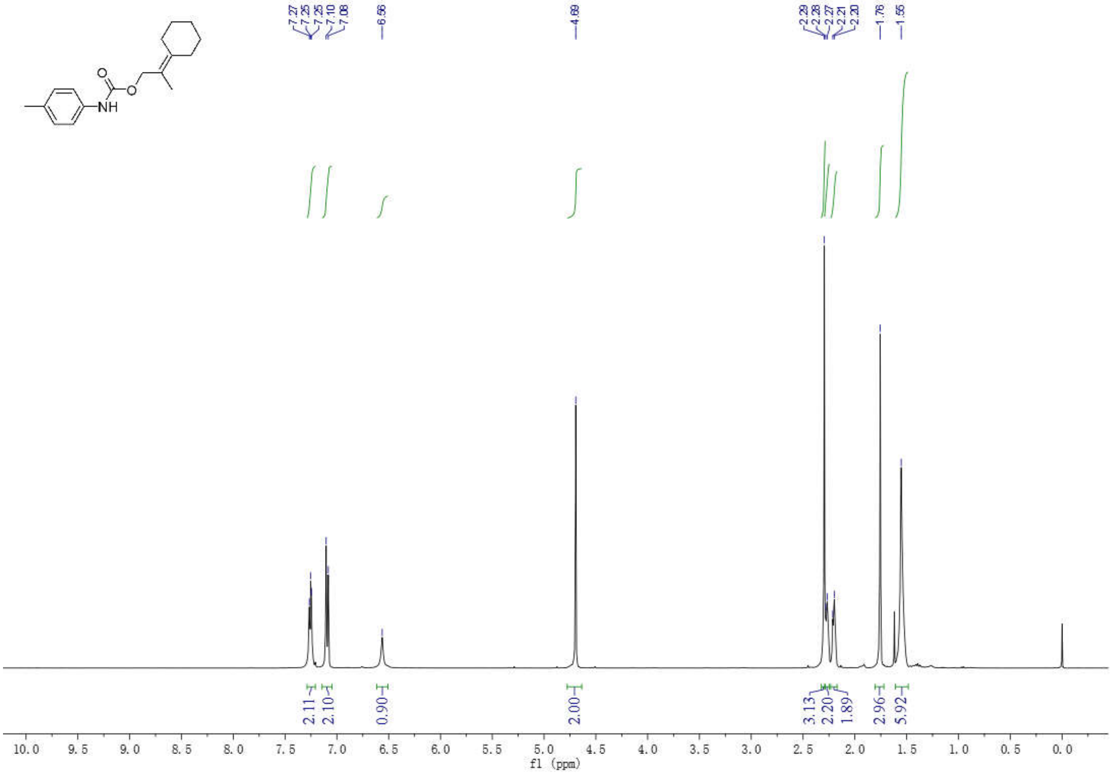
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7j**



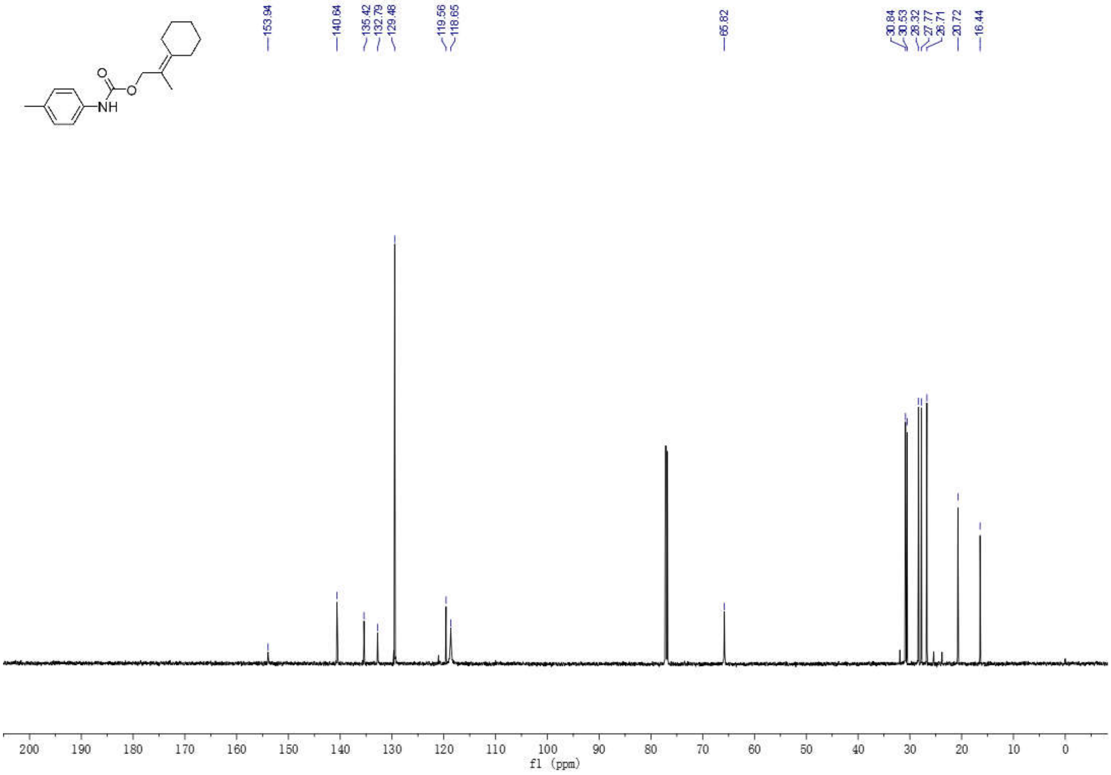
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7j**



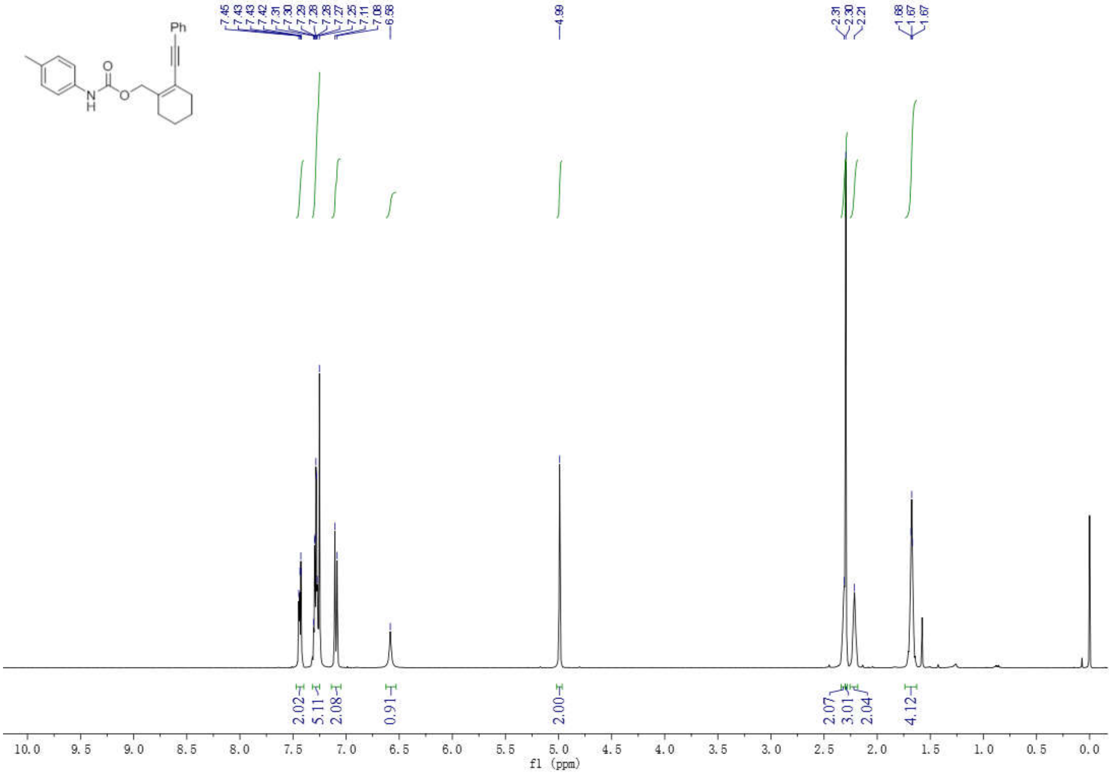
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7k**



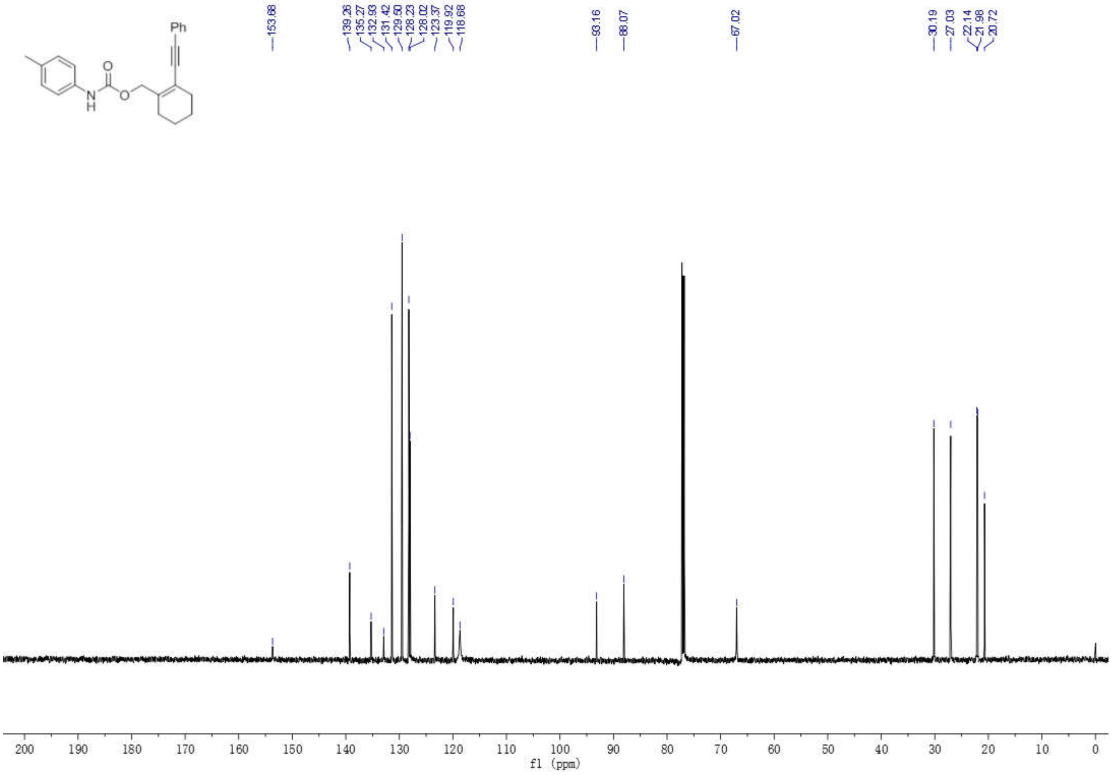
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **7k**



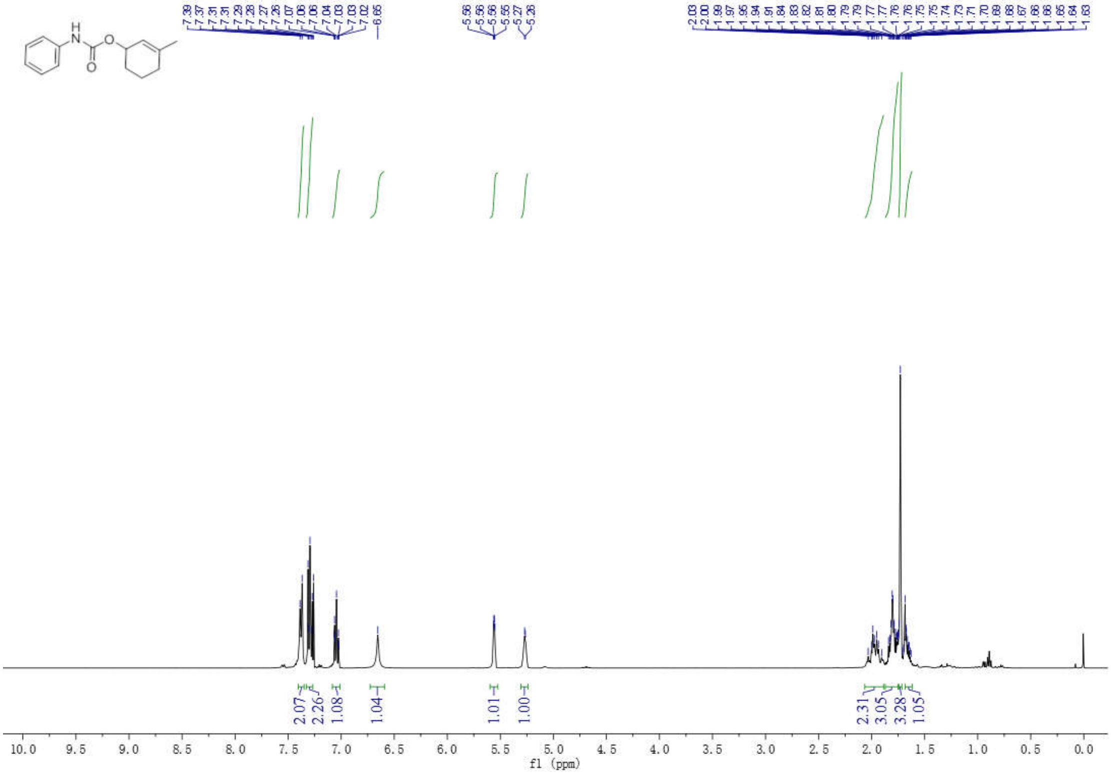
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **7l**



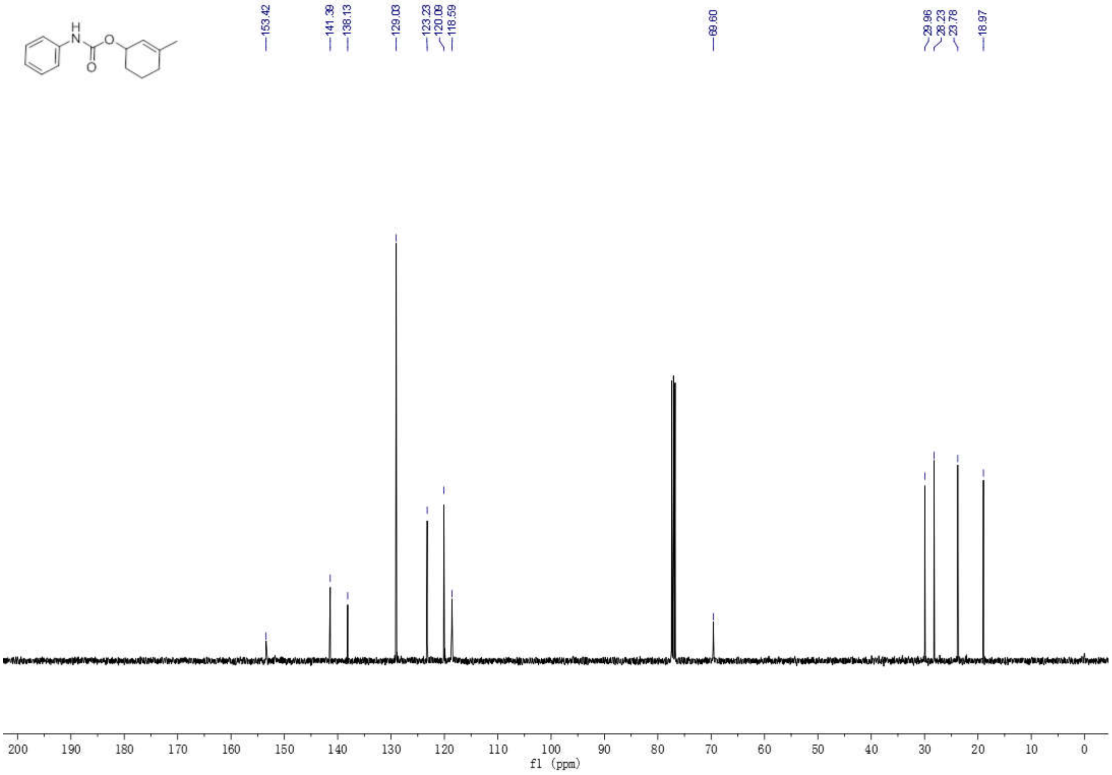
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7l**



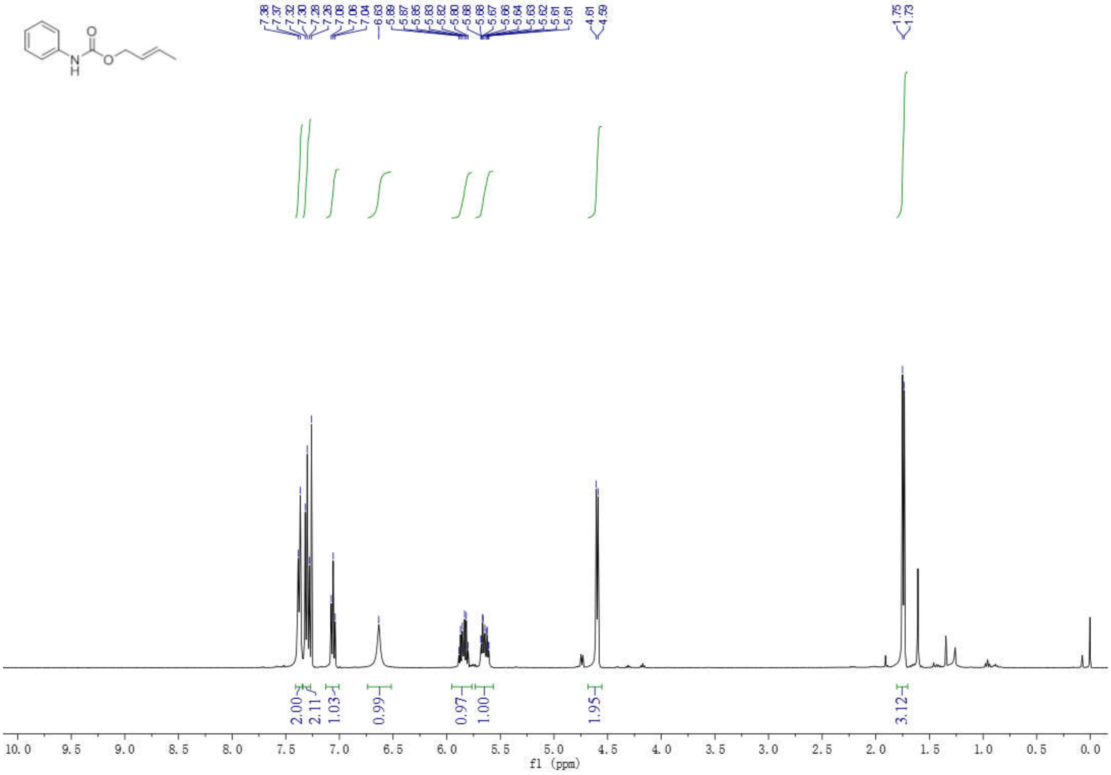
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7m**



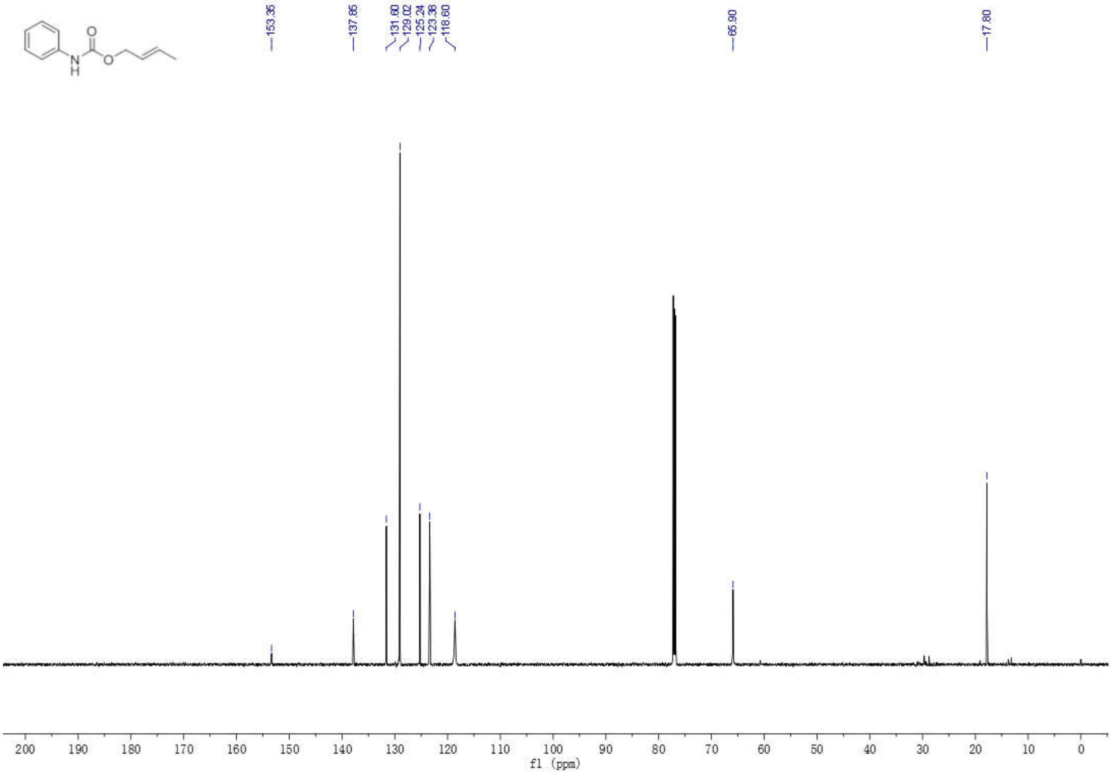
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7m**



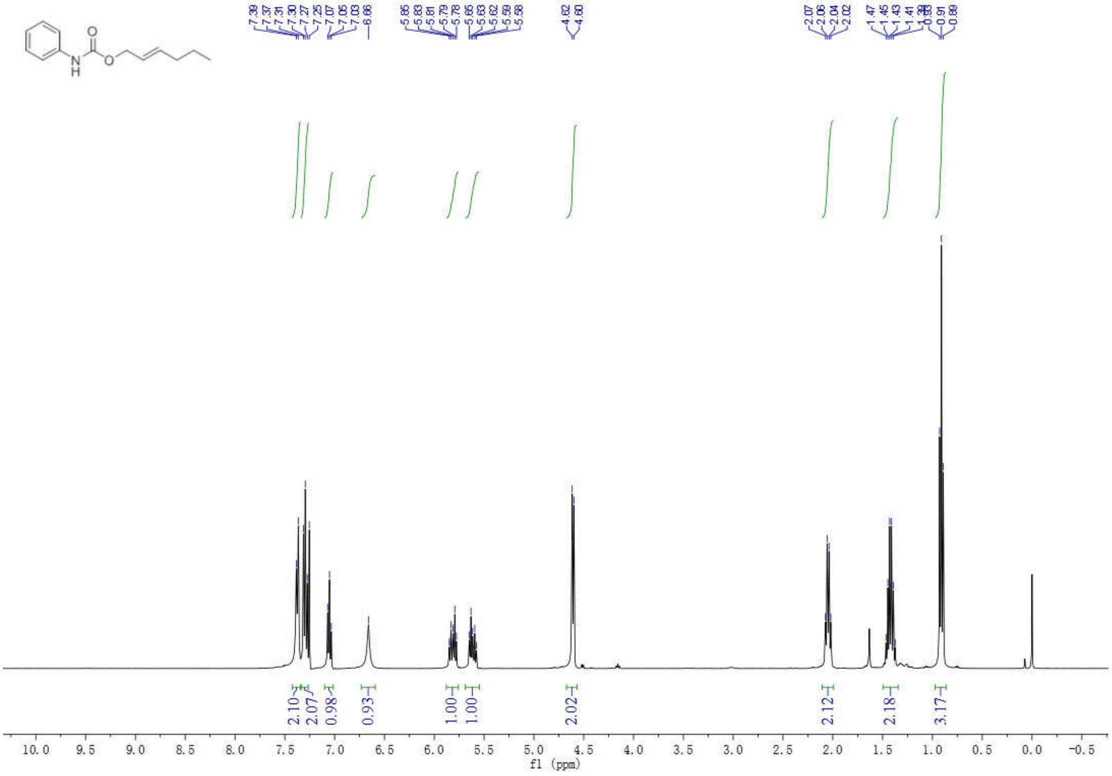
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7n**



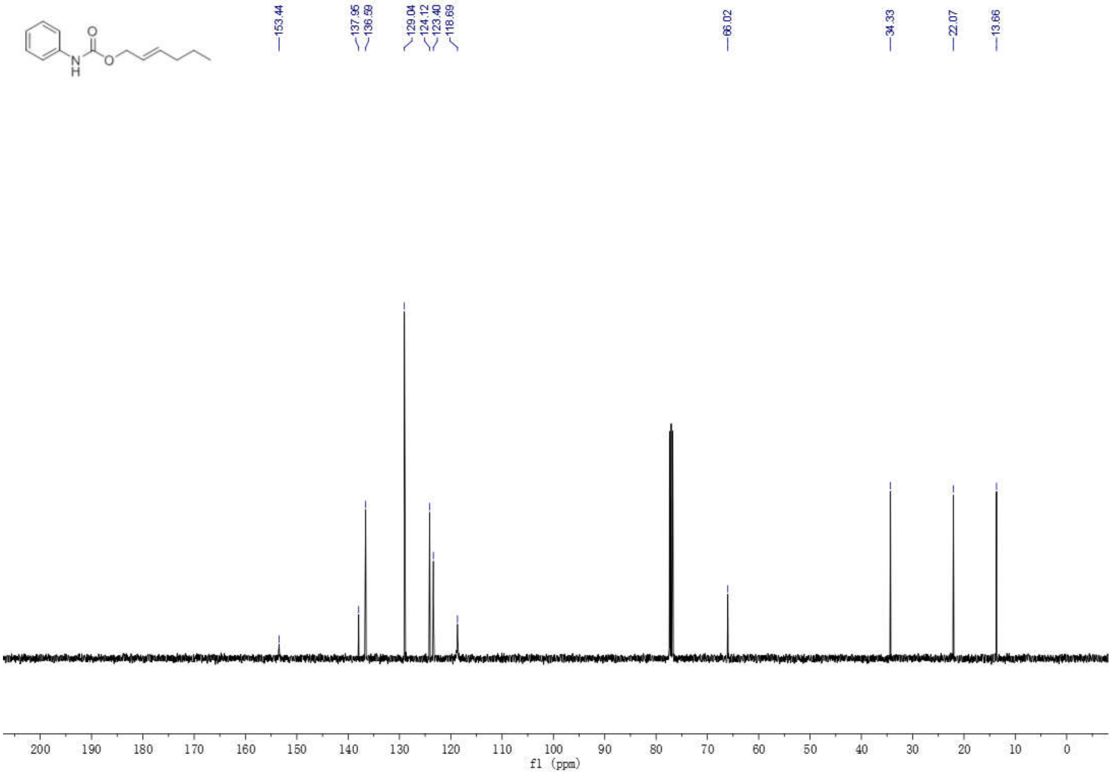
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **7n**



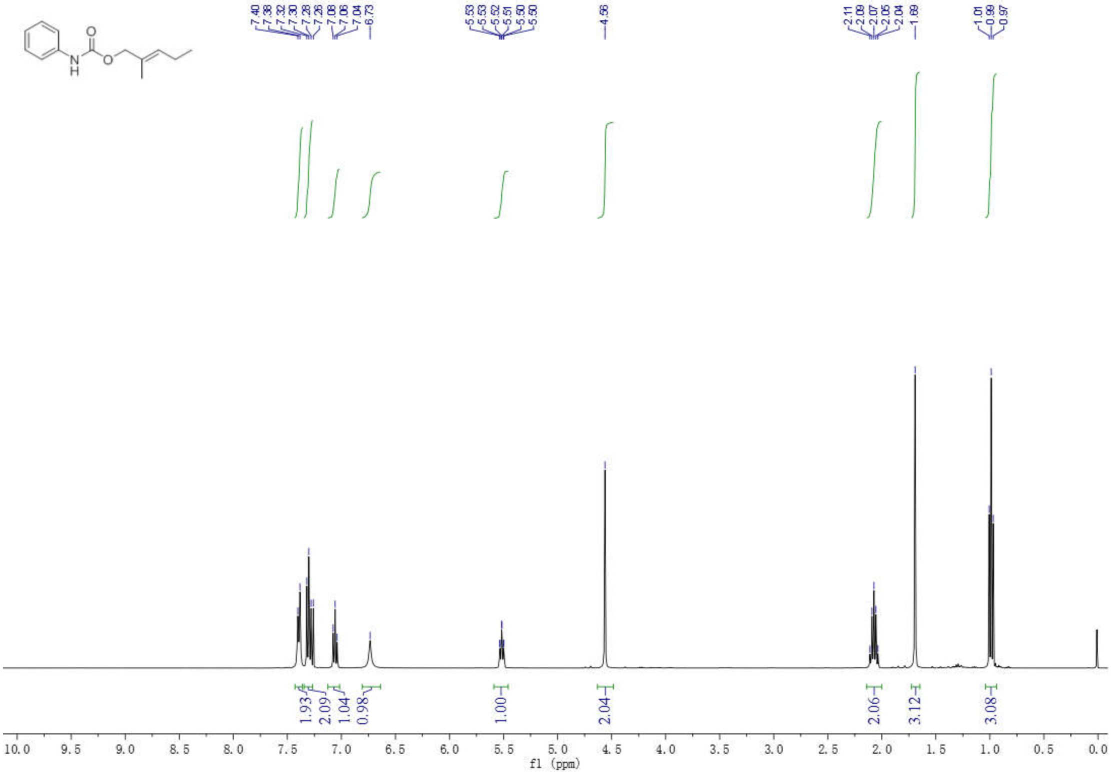
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **7o**



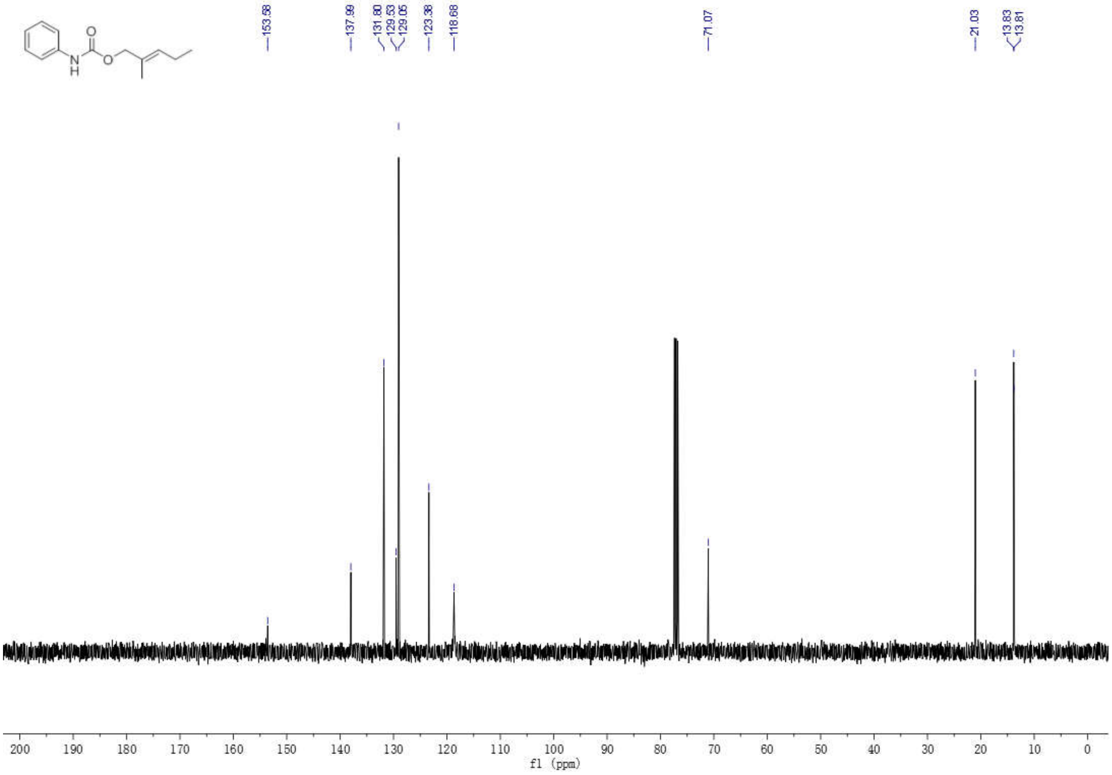
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7o**



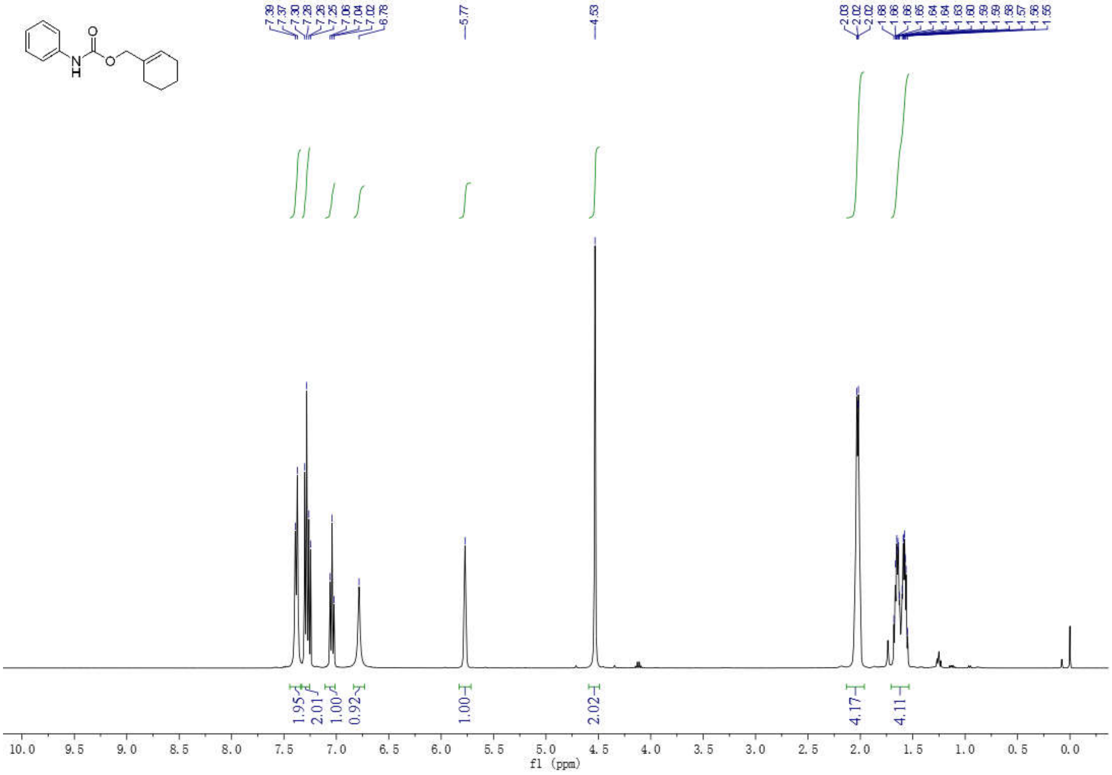
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7p**



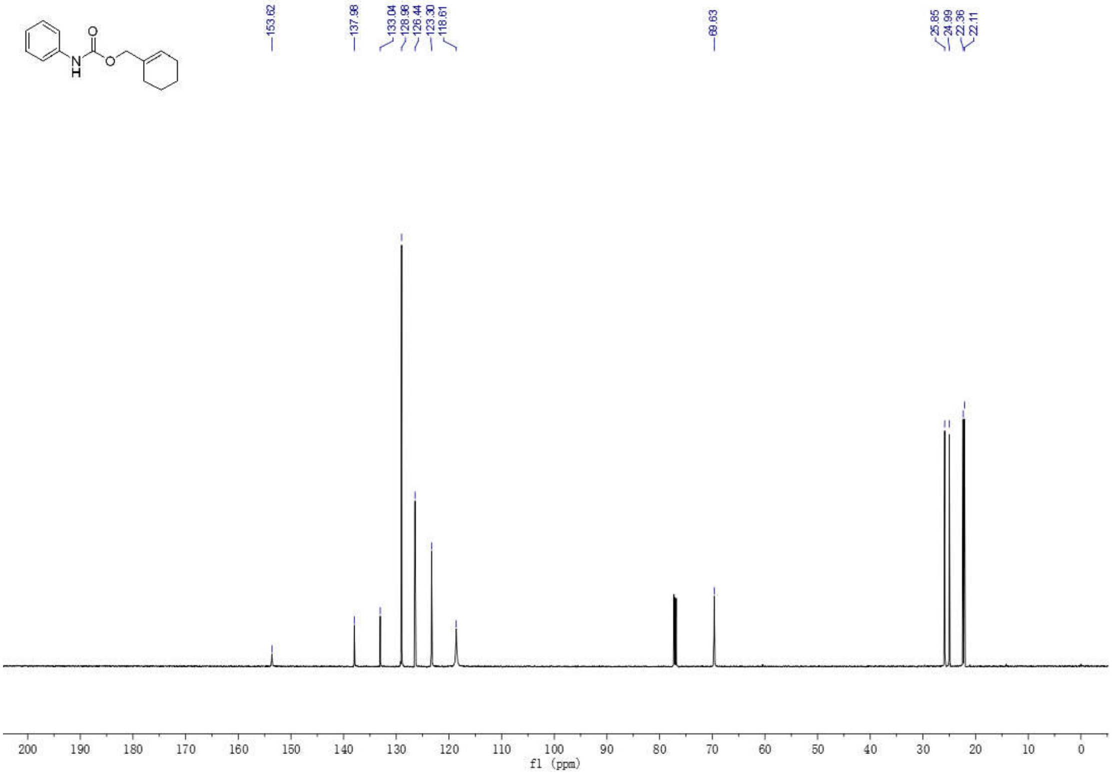
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7p**



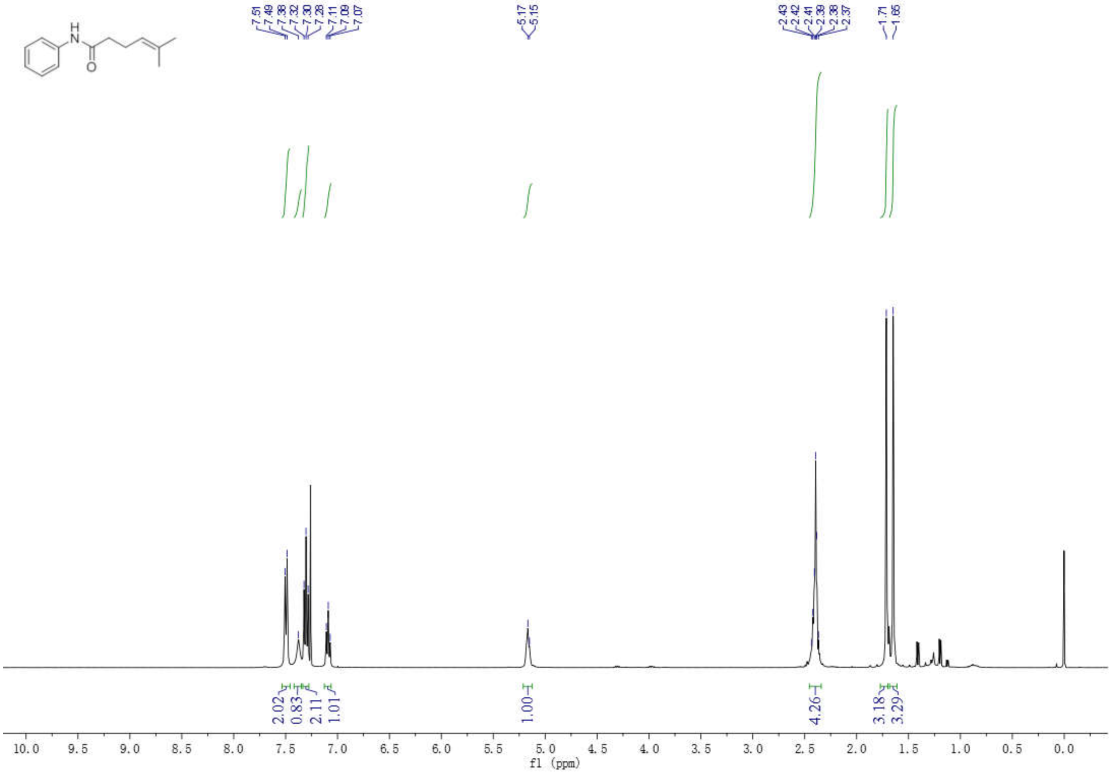
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7q**



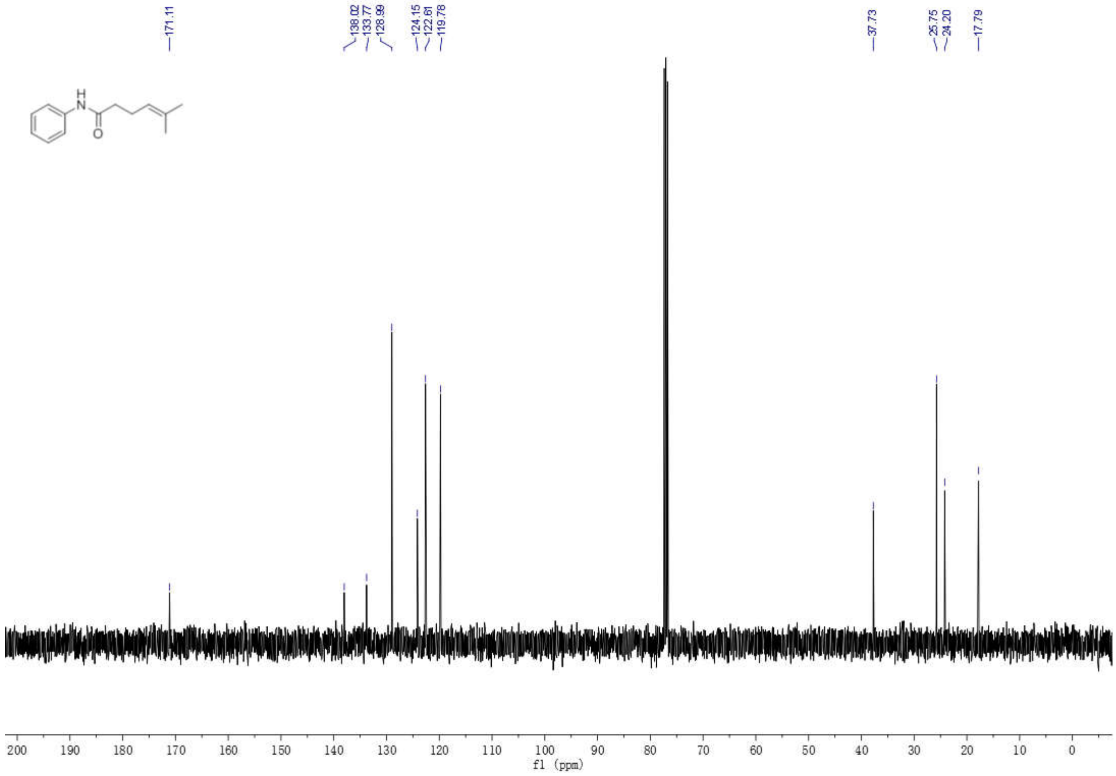
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7q**



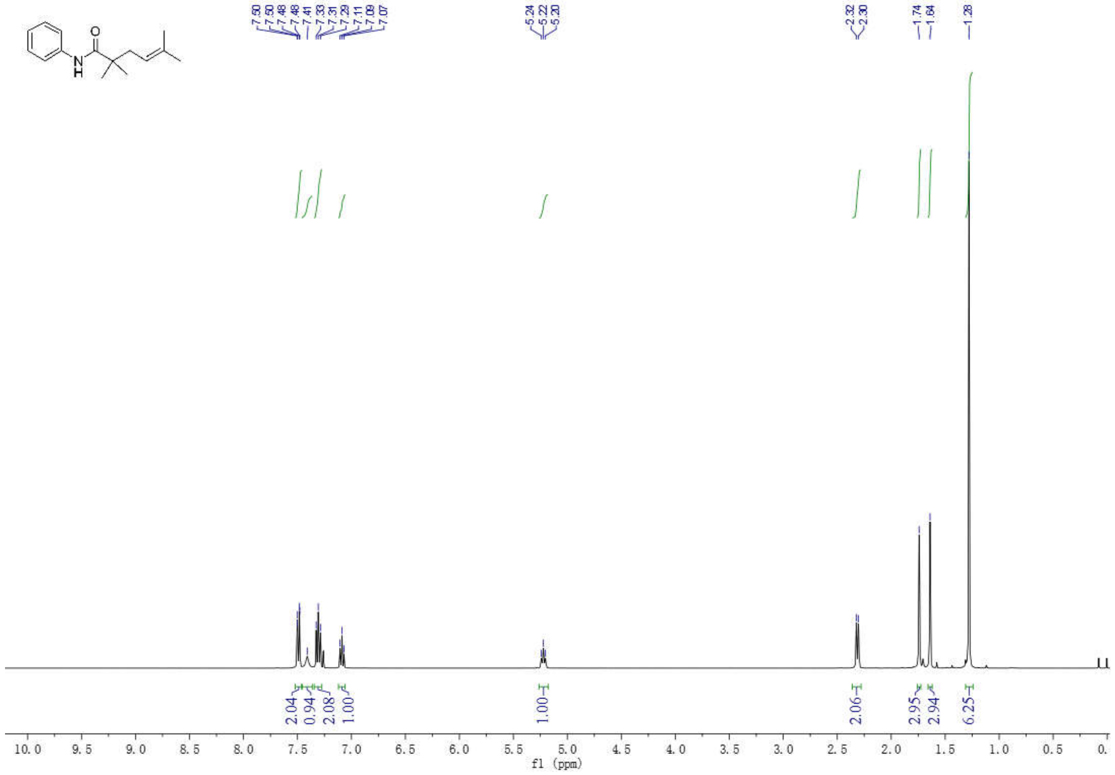
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7r**



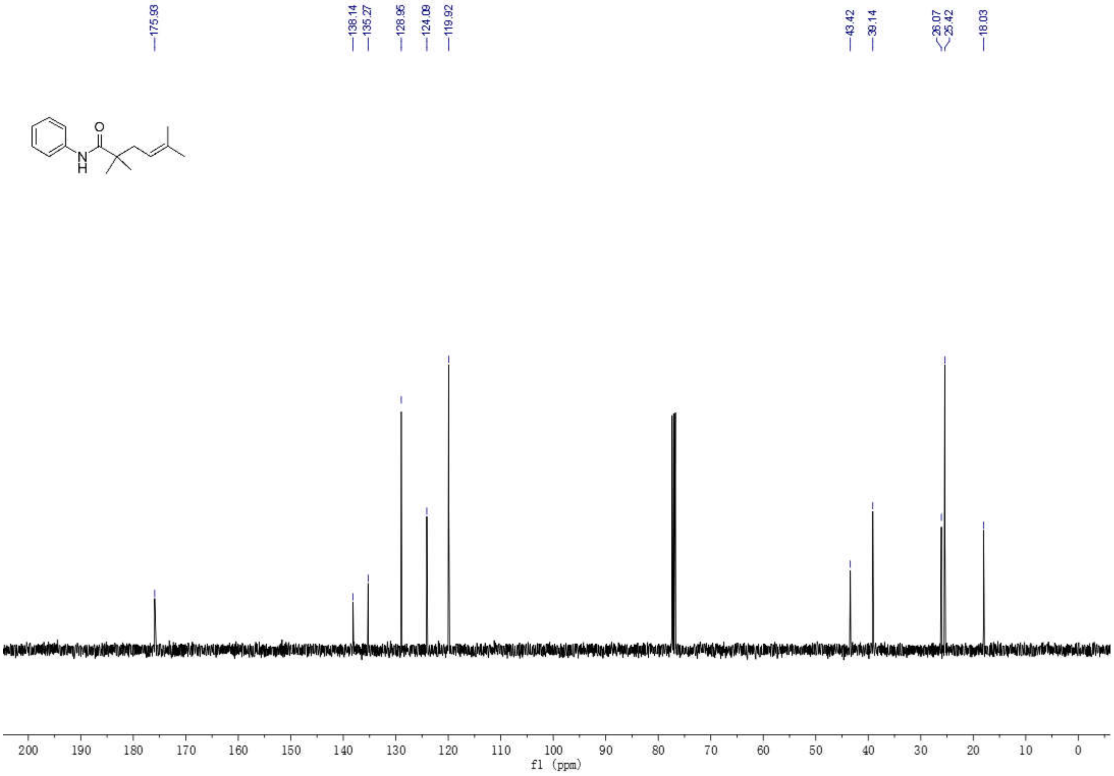
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **7r**



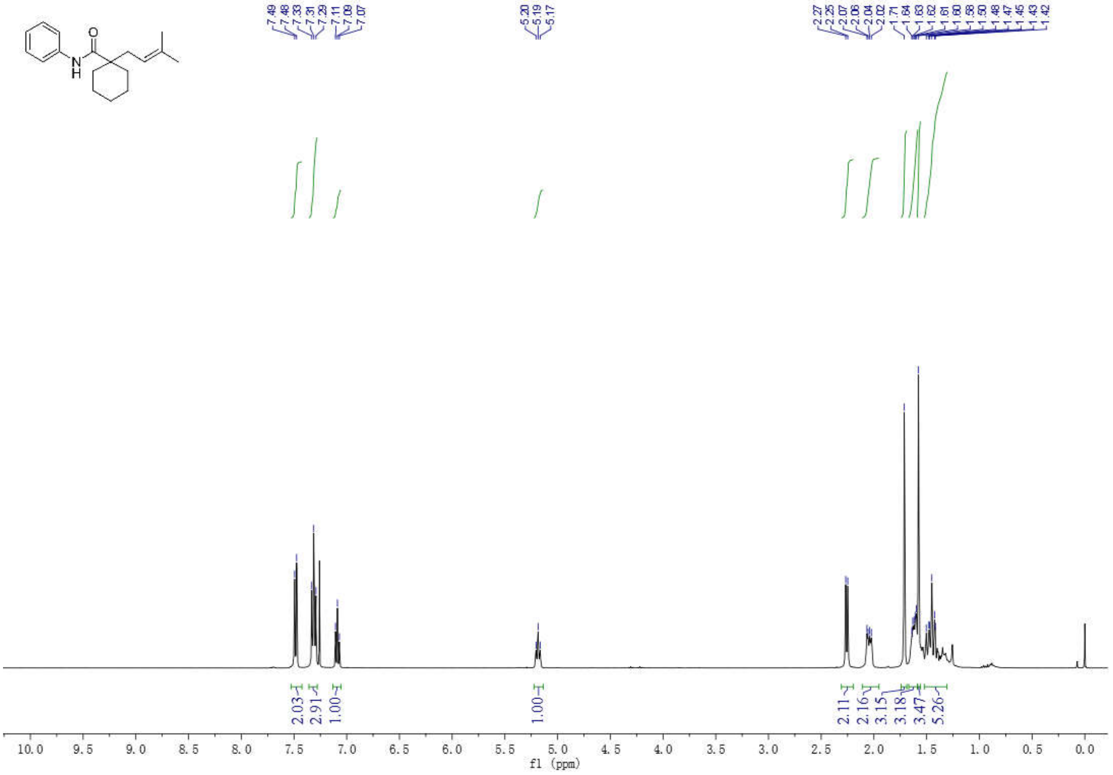
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **7s**



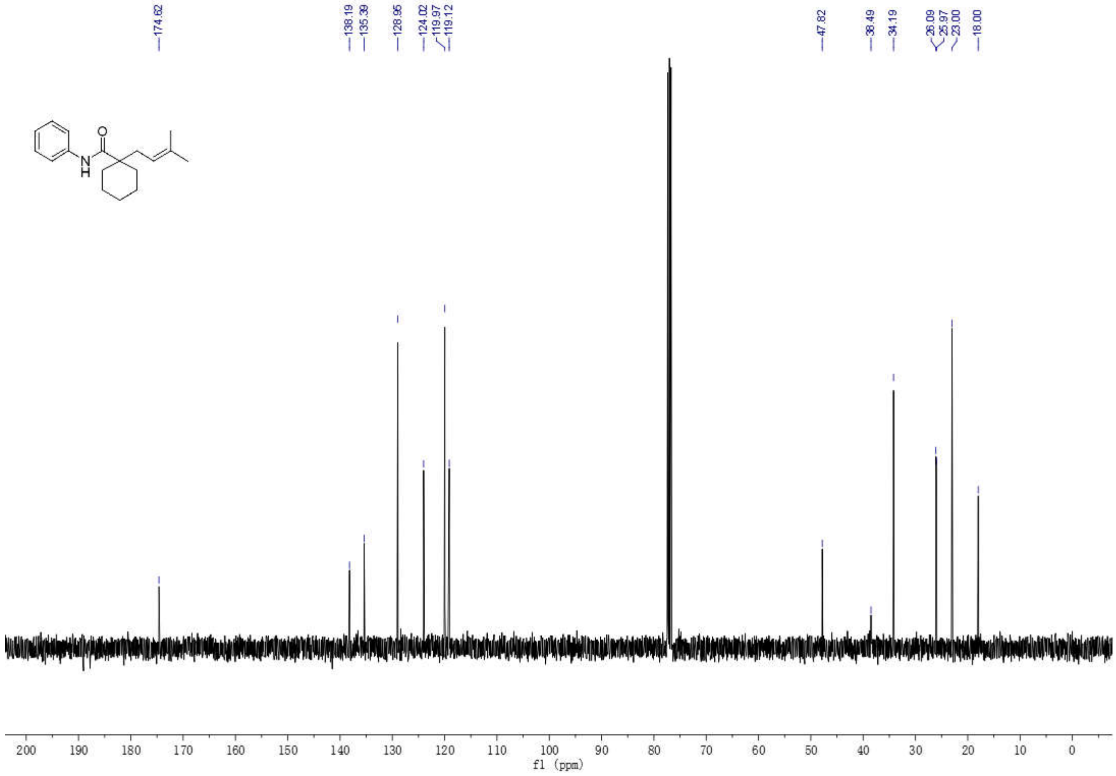
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7s**



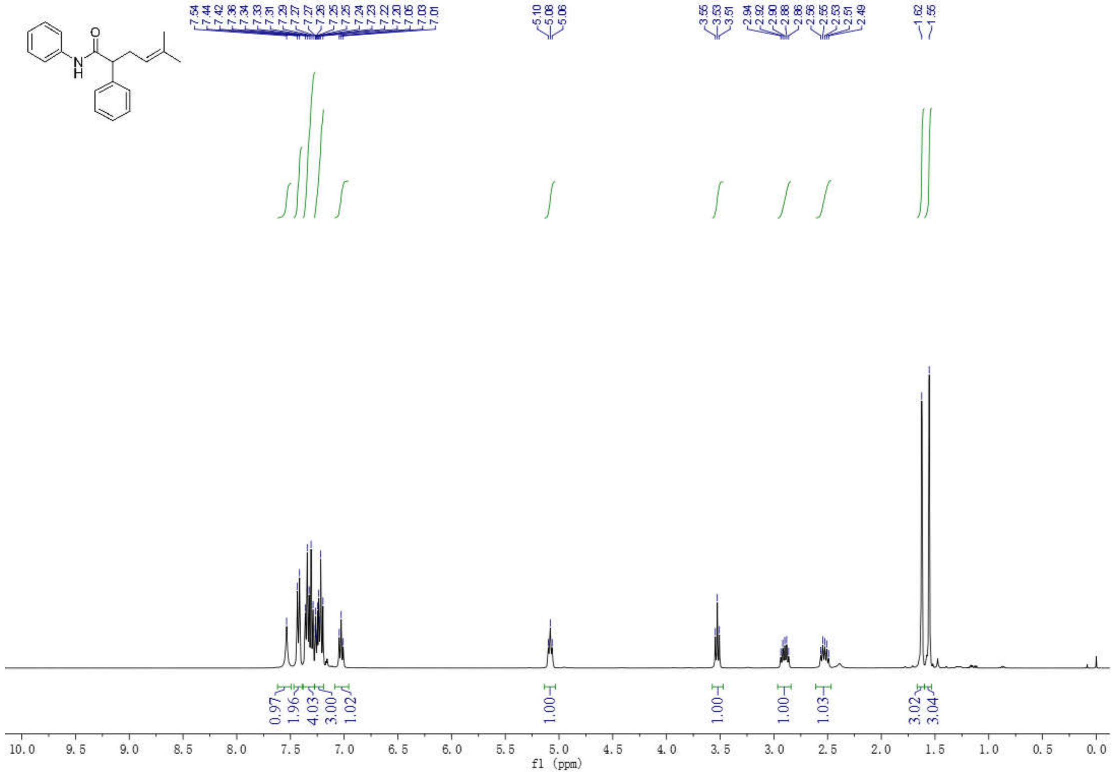
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7t**



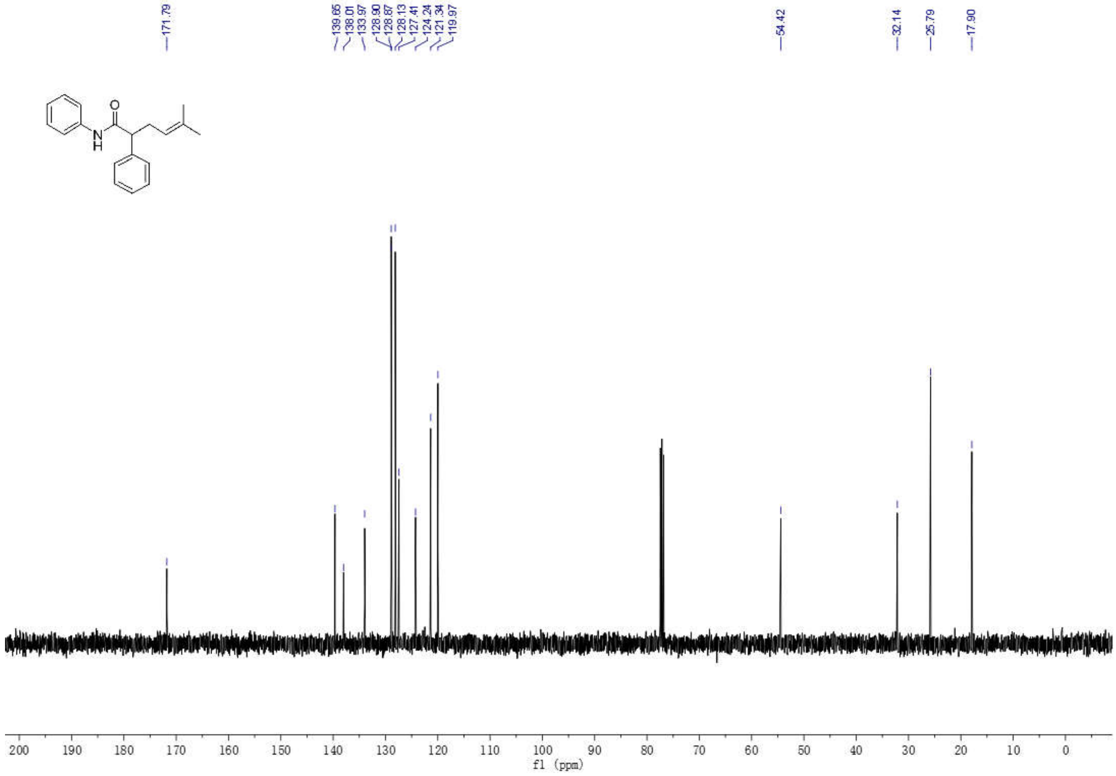
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **7t**



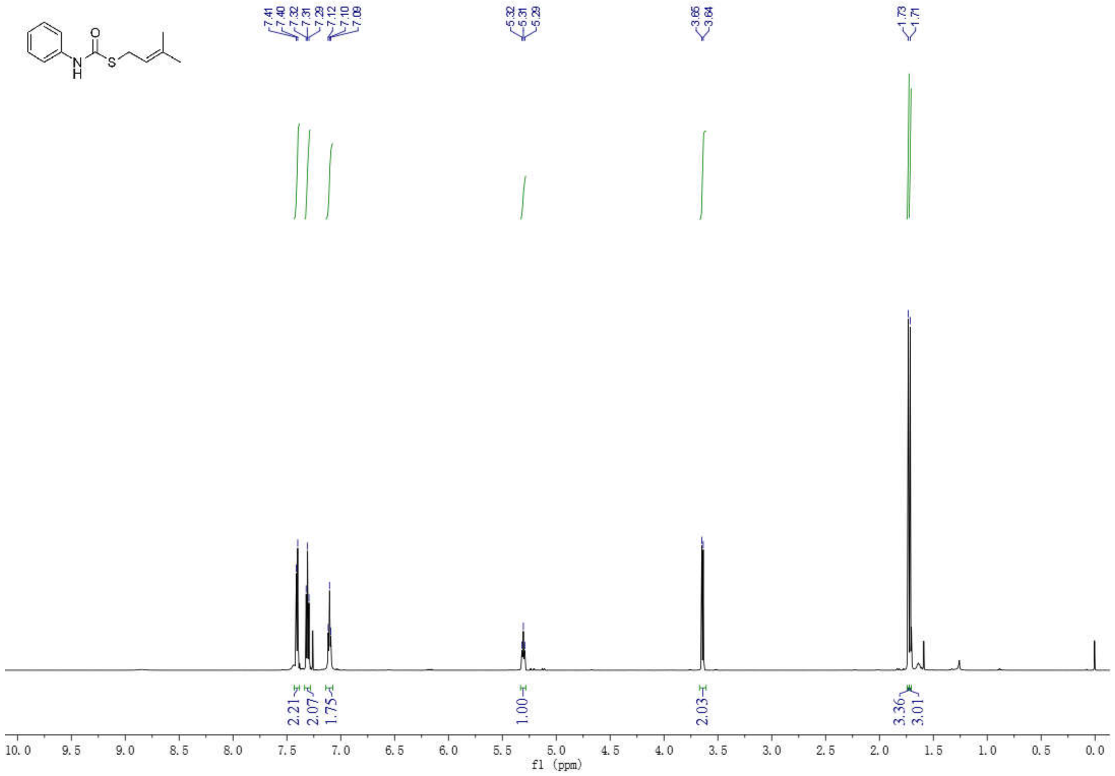
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **7u**



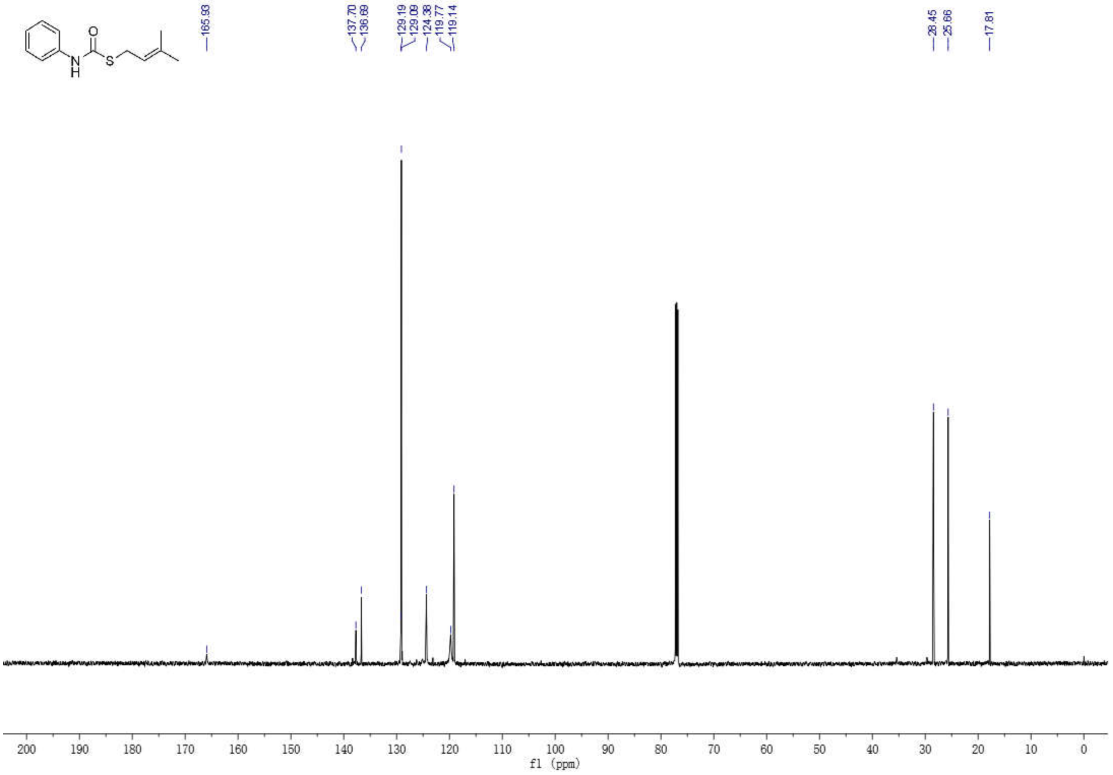
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7u**



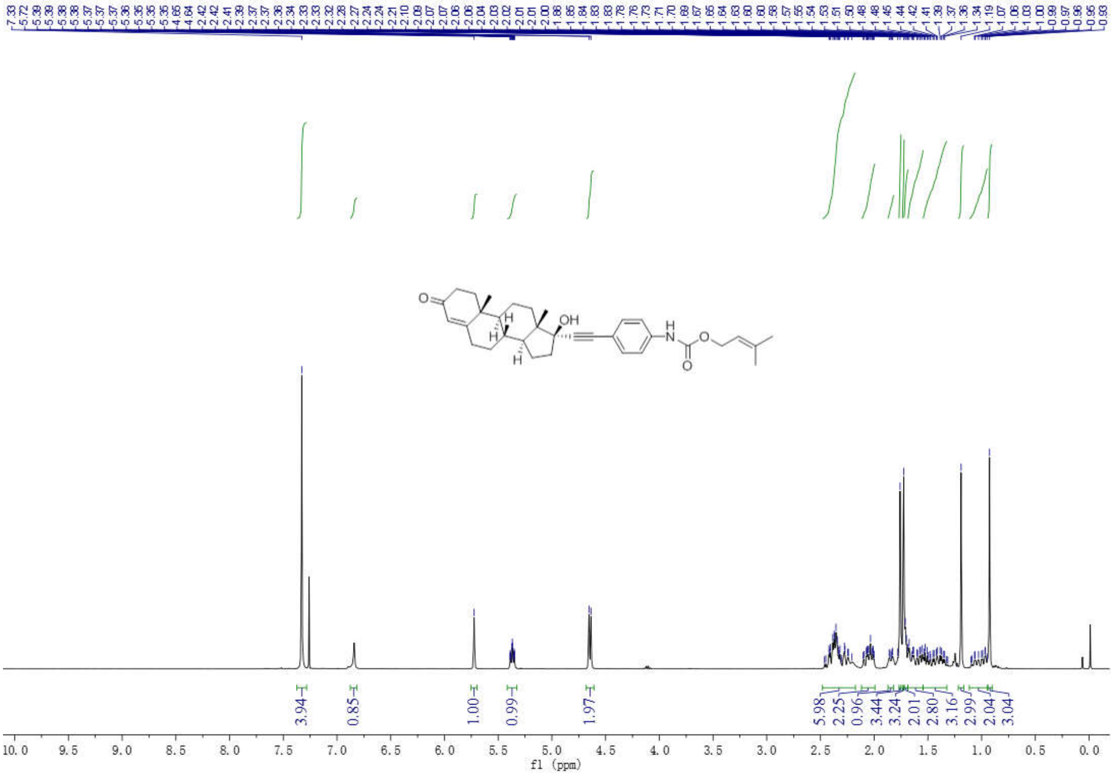
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **7v**



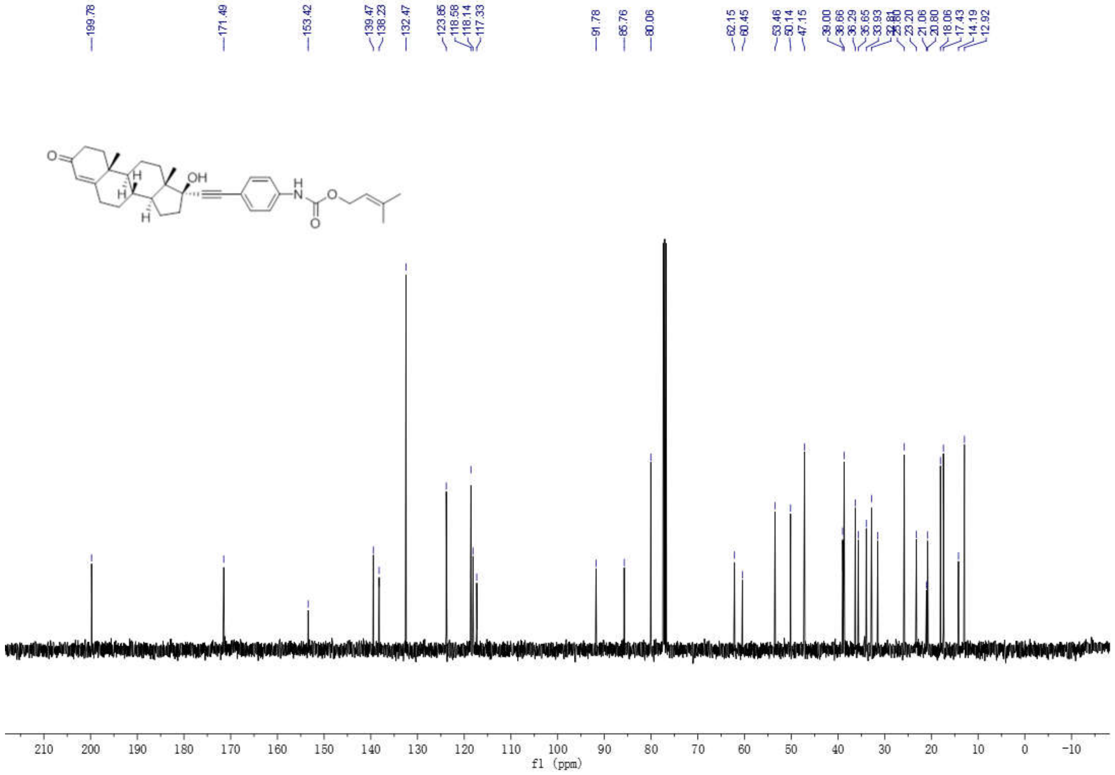
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **7v**



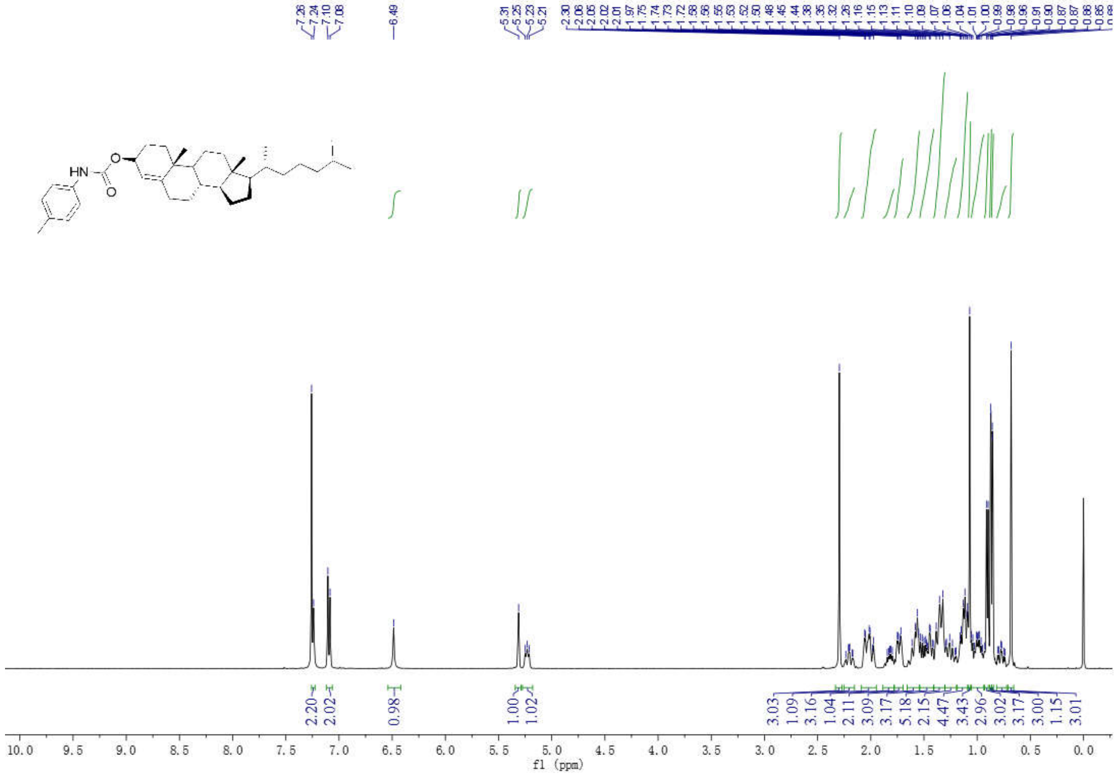
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7w**



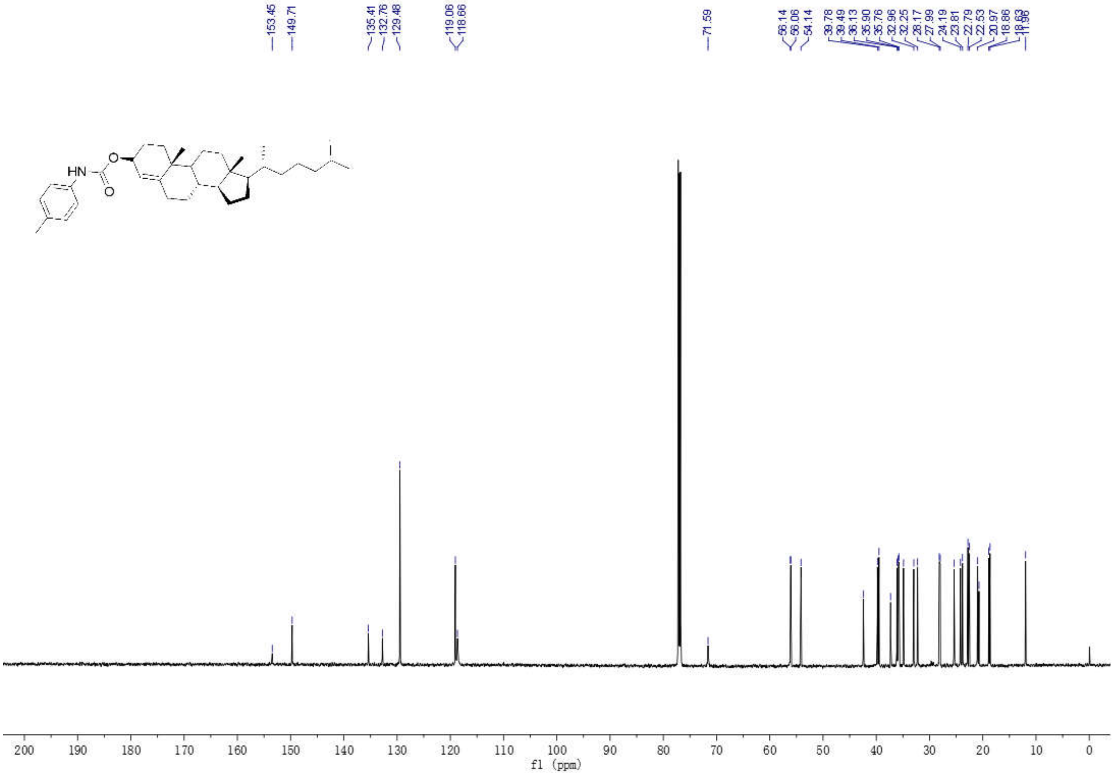
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7w**



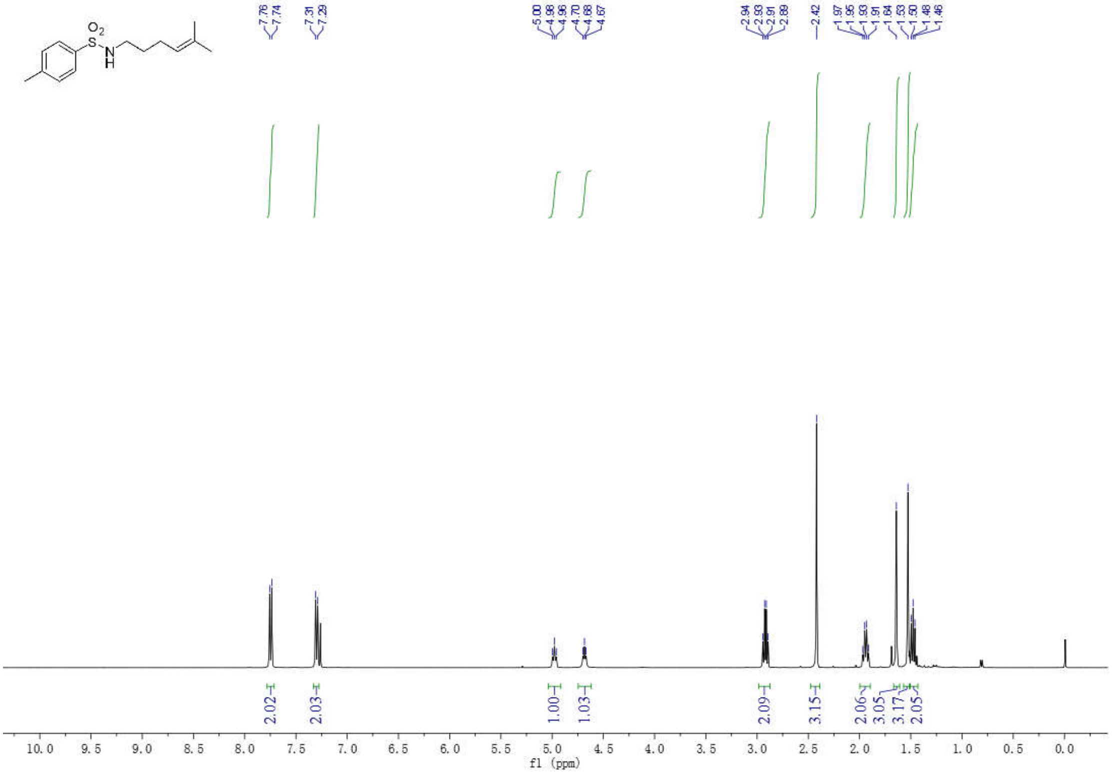
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **7x**



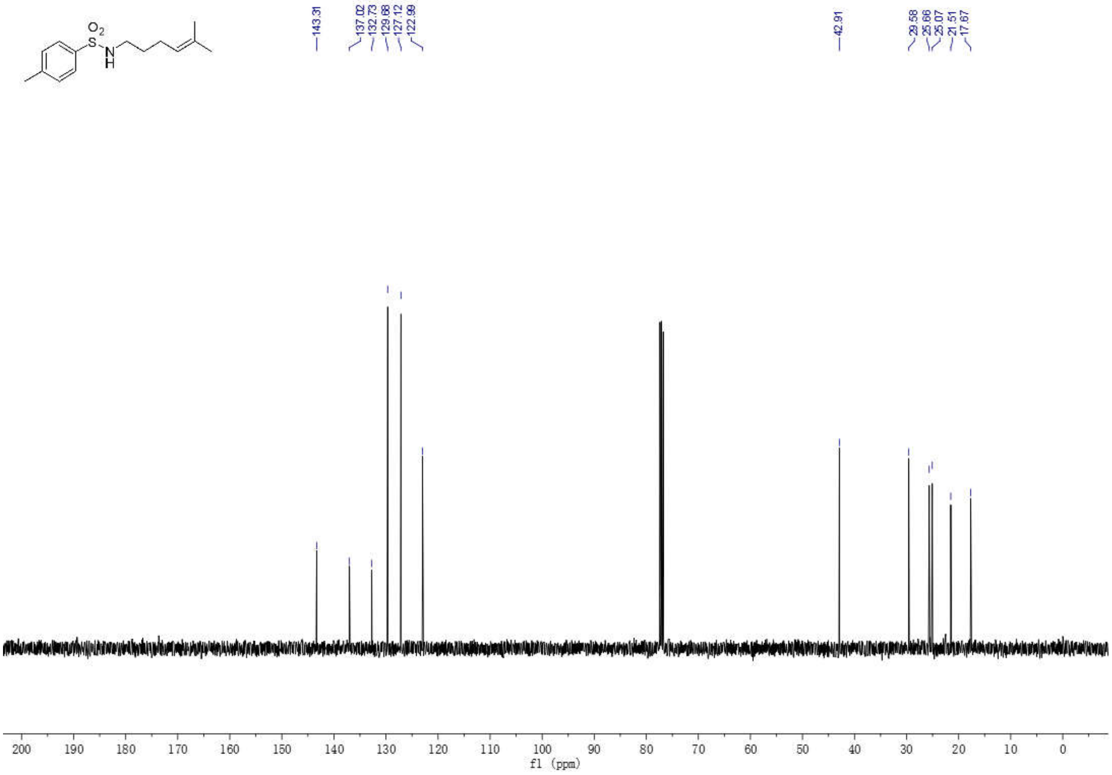
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **7x**



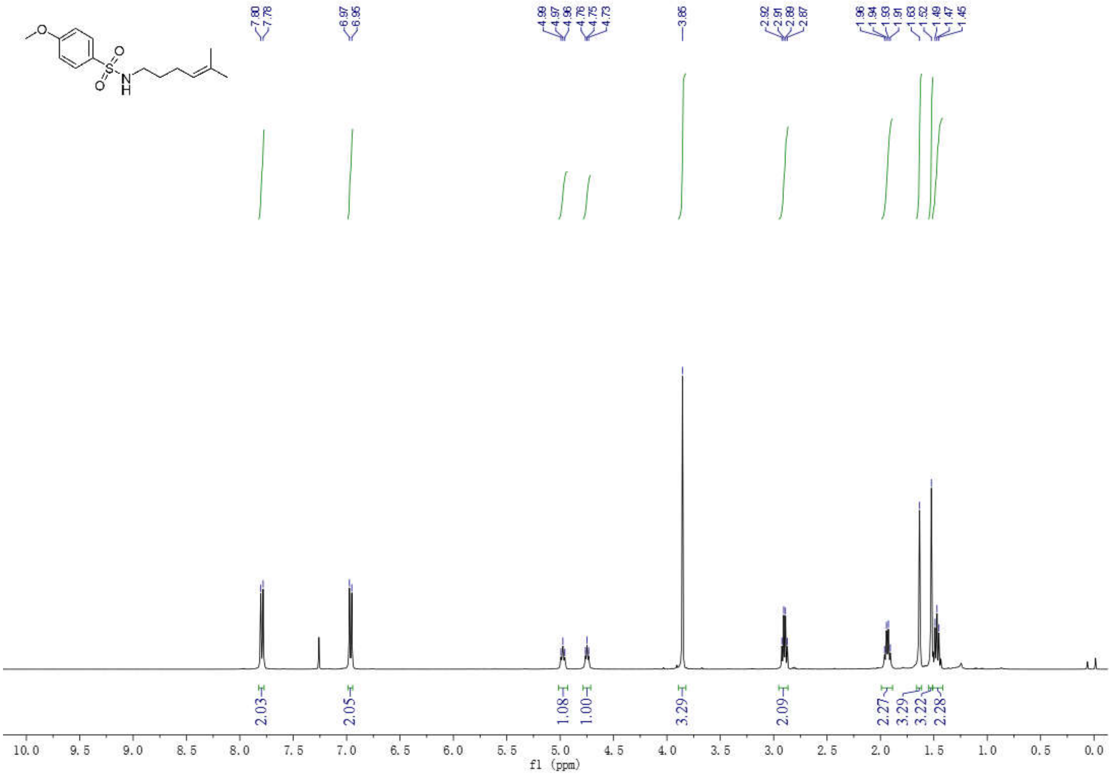
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9a**



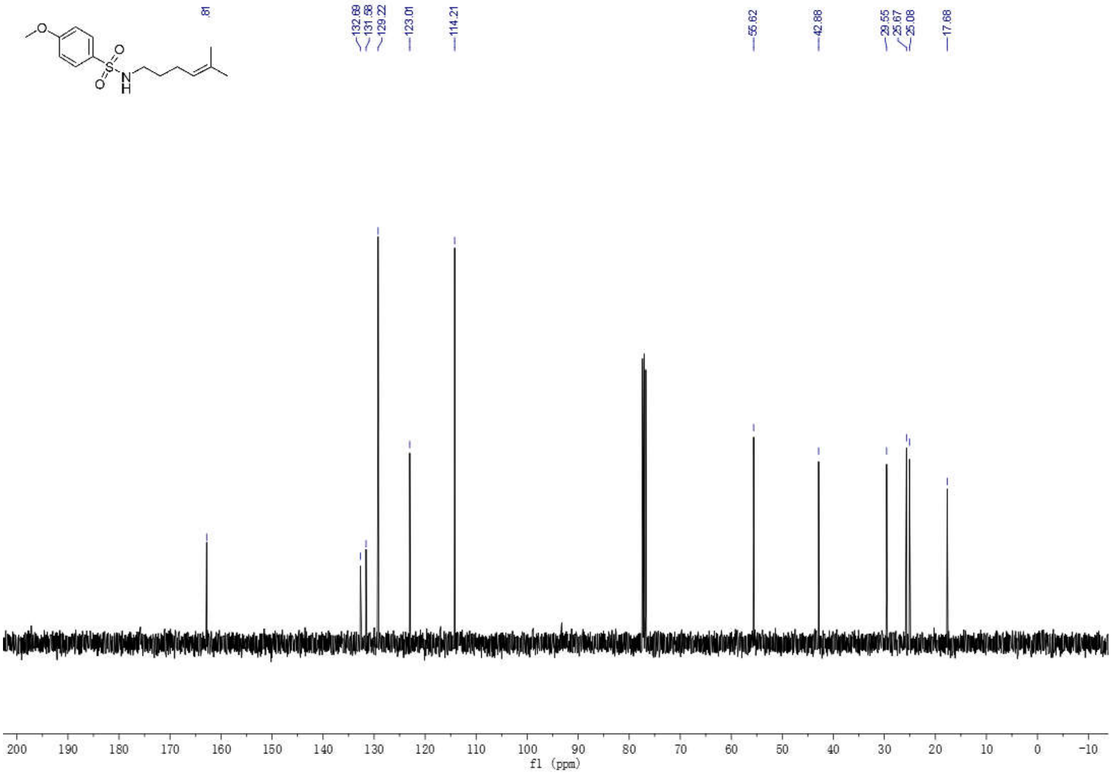
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **9a**



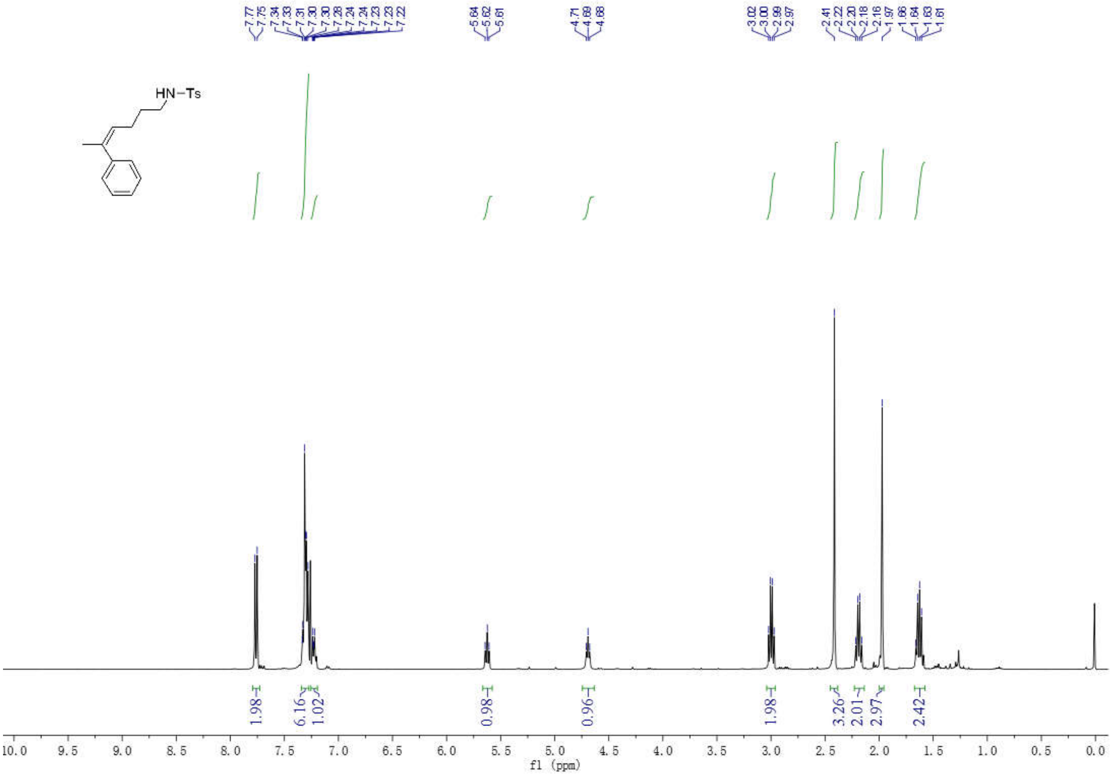
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9b**



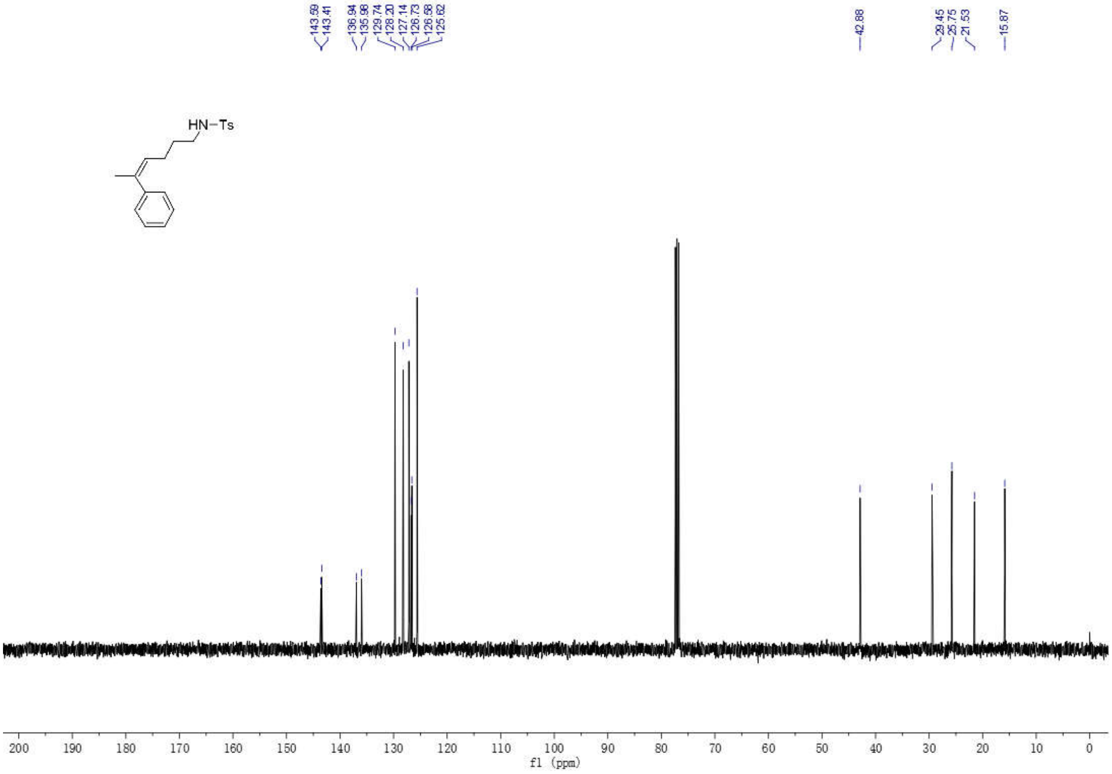
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **9b**



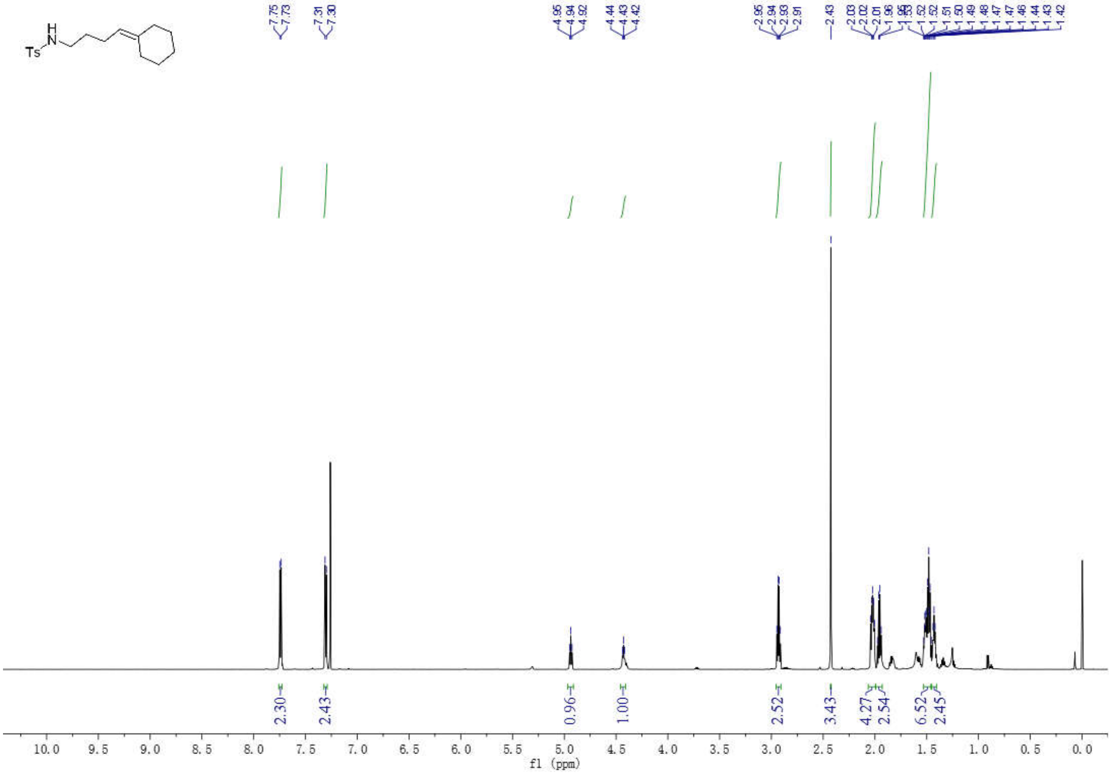
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9c**



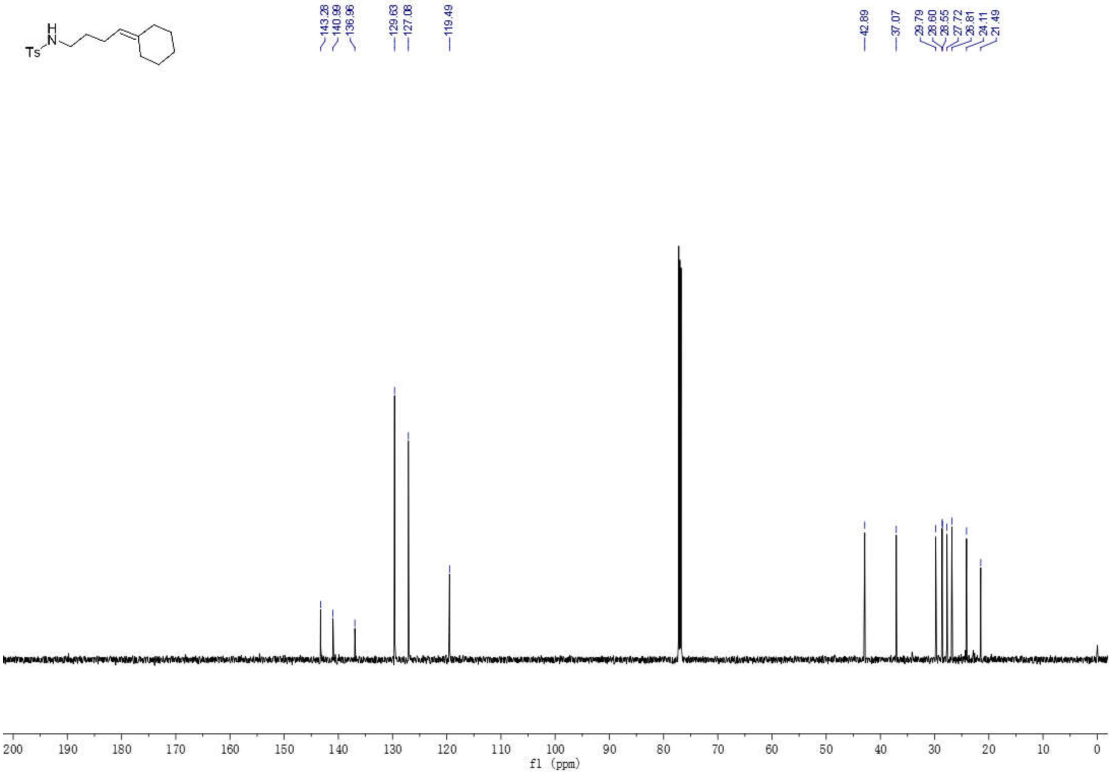
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **9c**



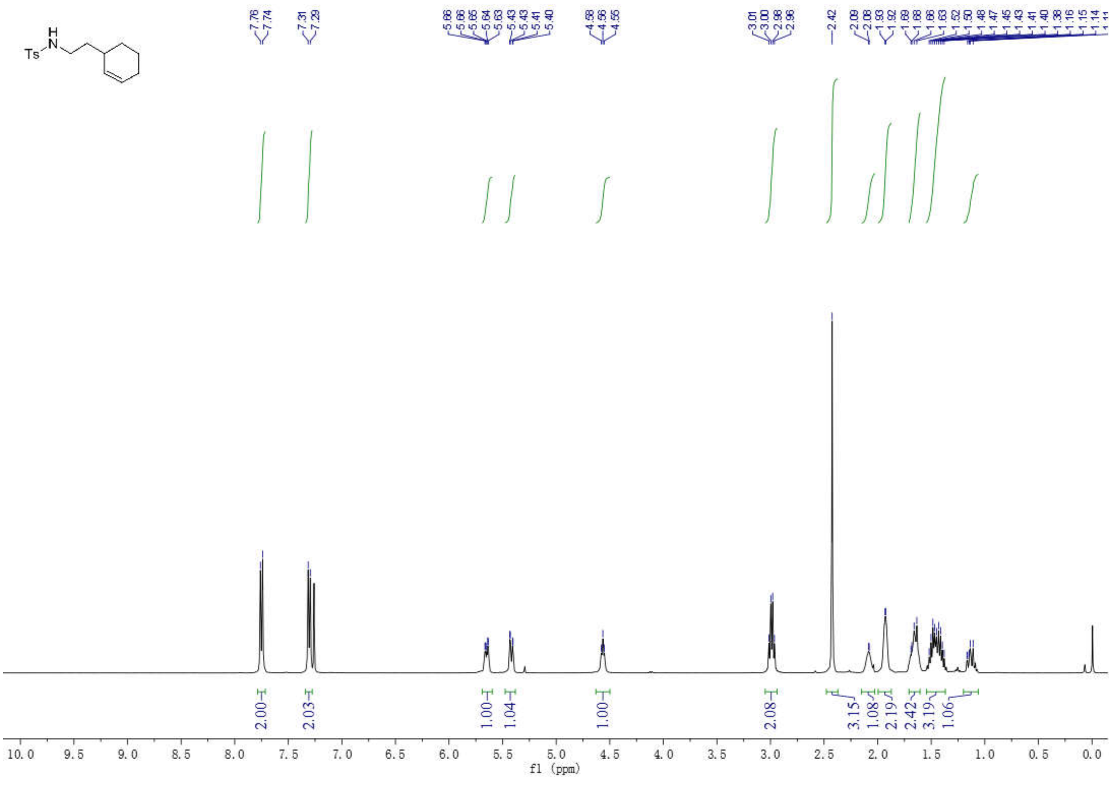
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **9d**



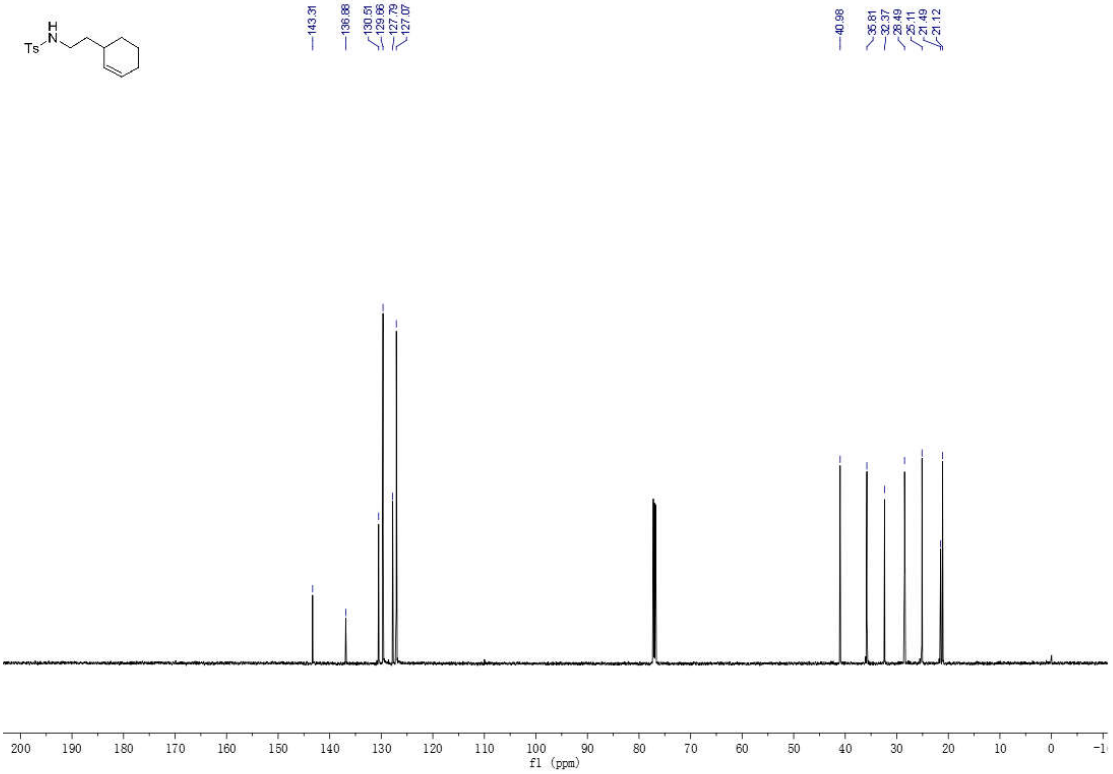
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **9d**



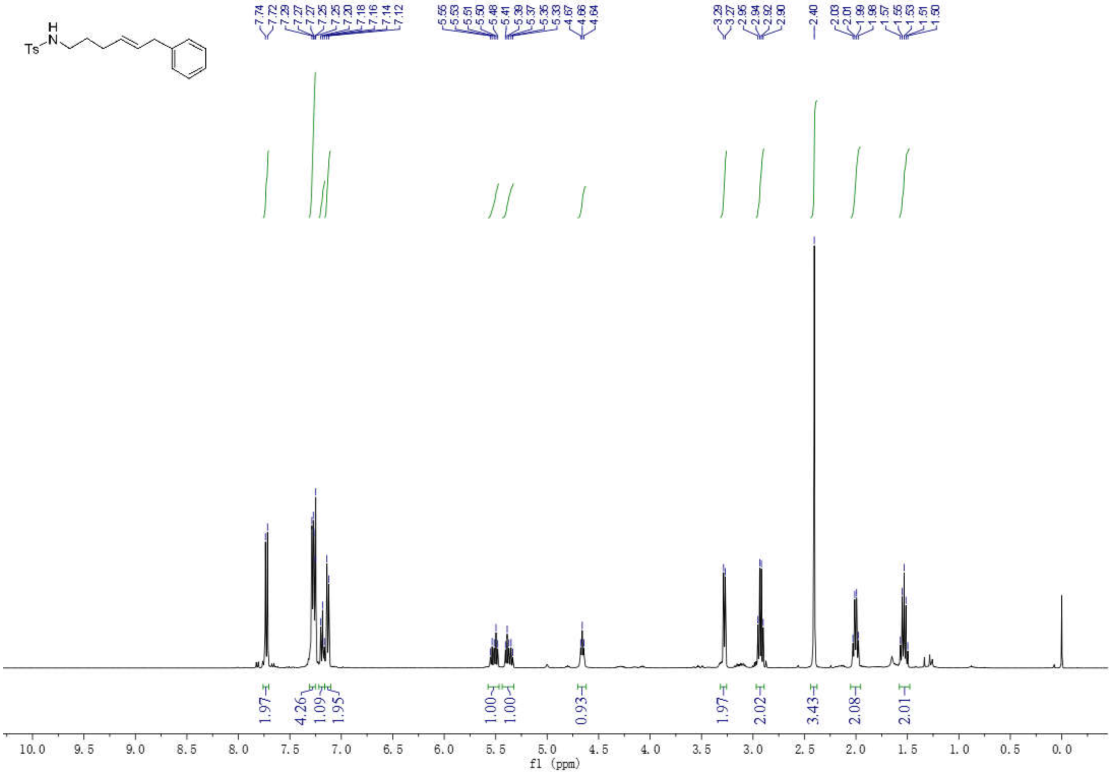
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **9e**



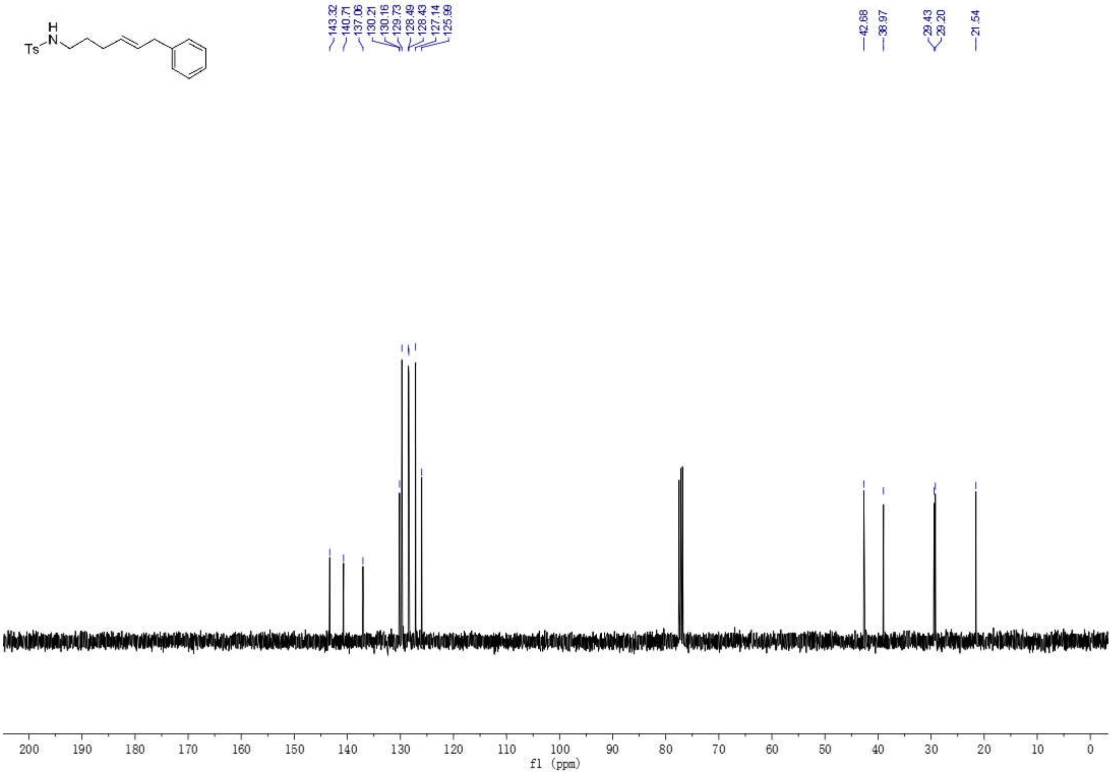
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **9e**



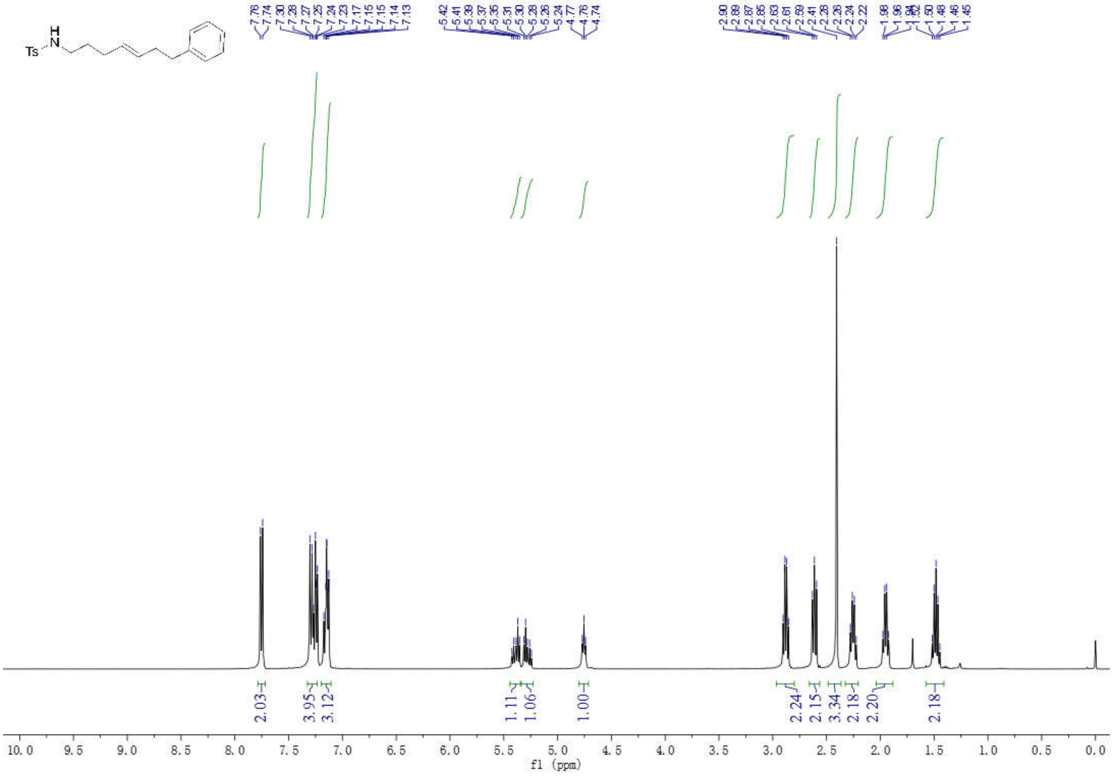
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9f**



^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **9f**



^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9g**



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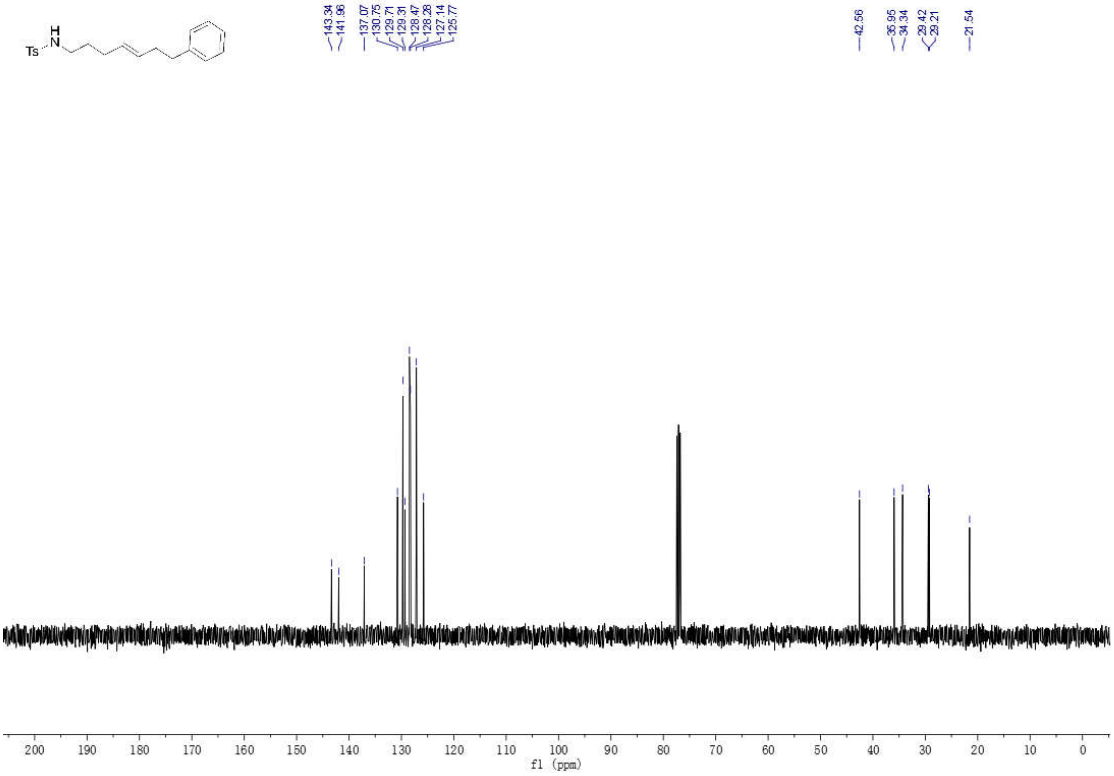
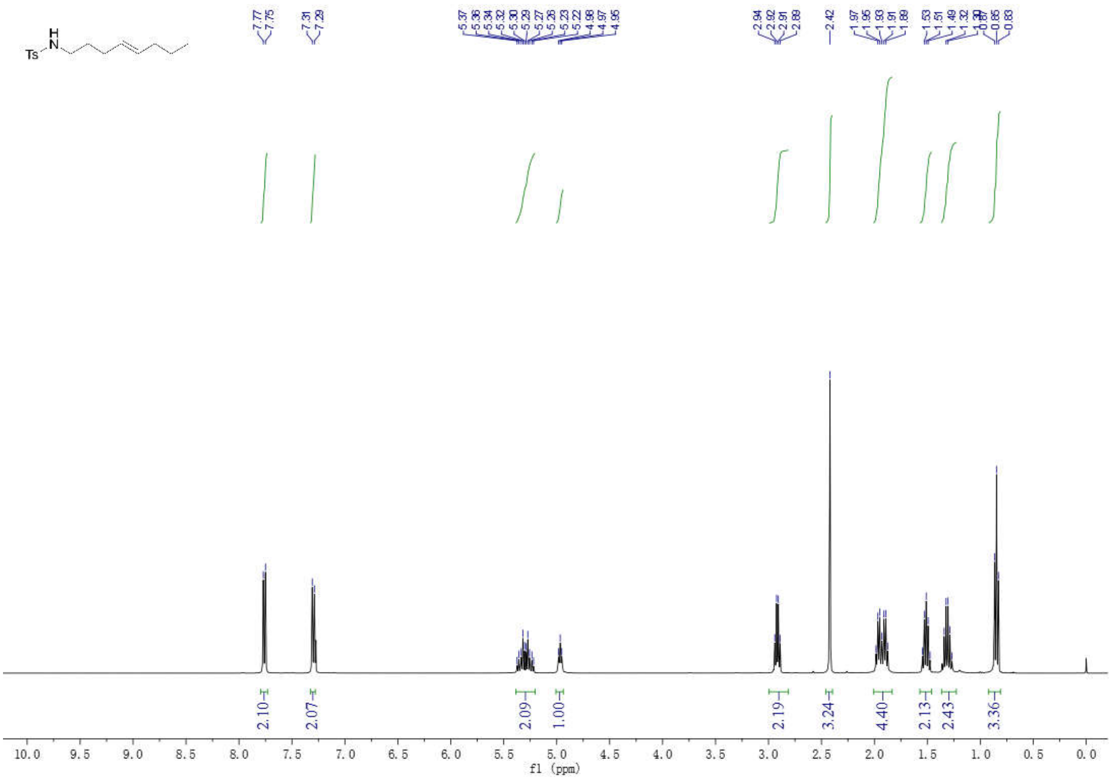


^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9h**



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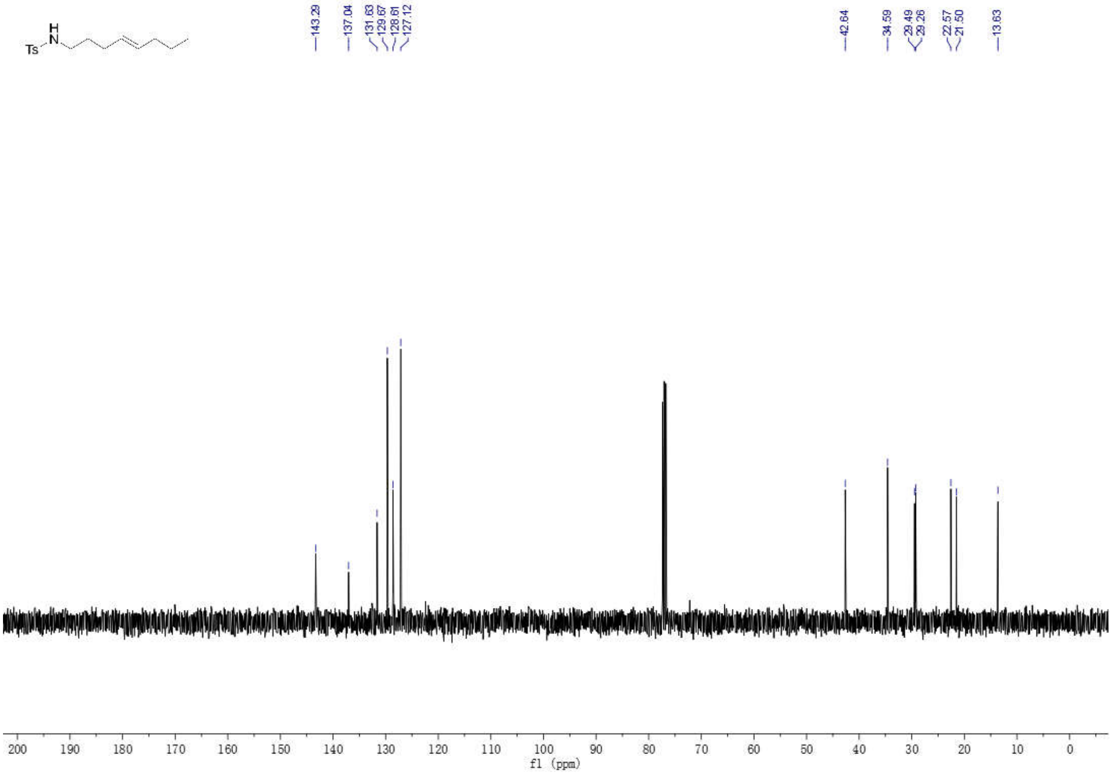
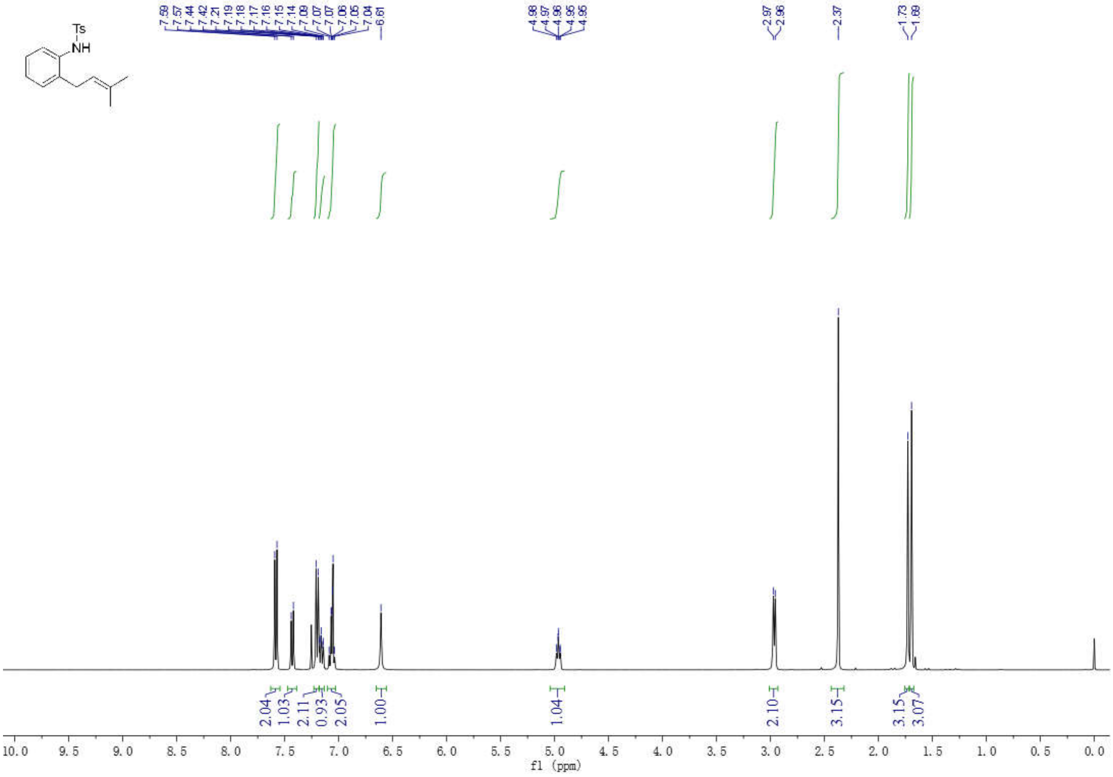
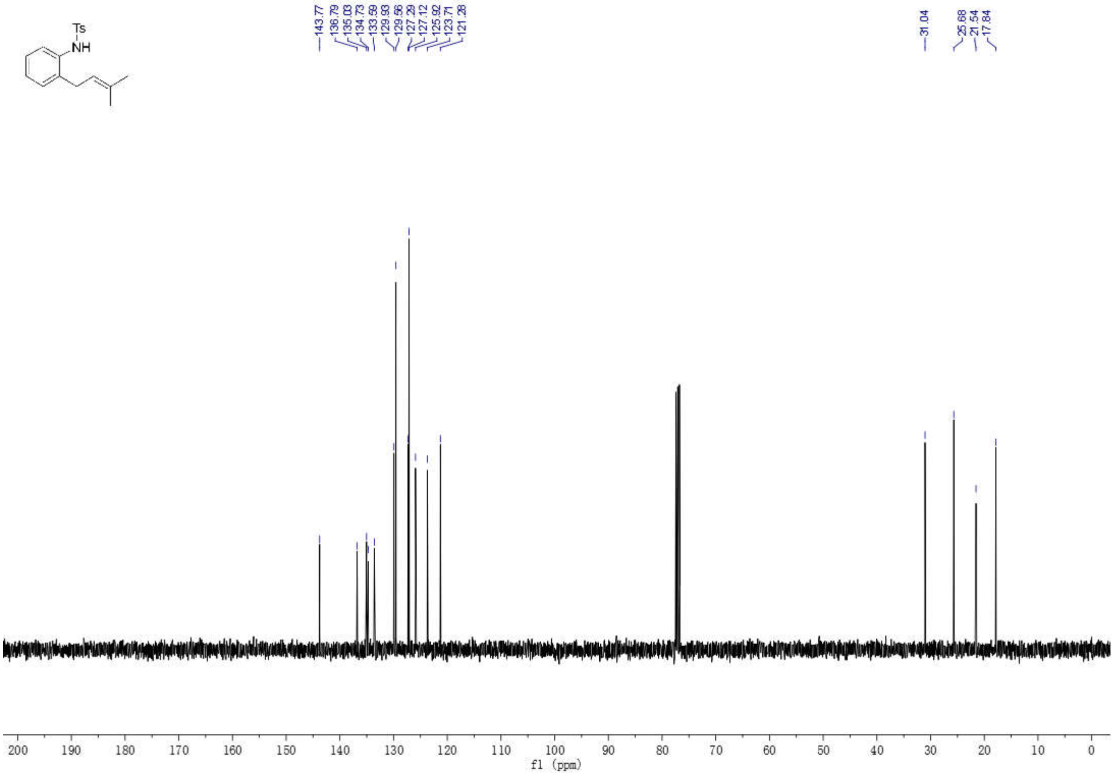


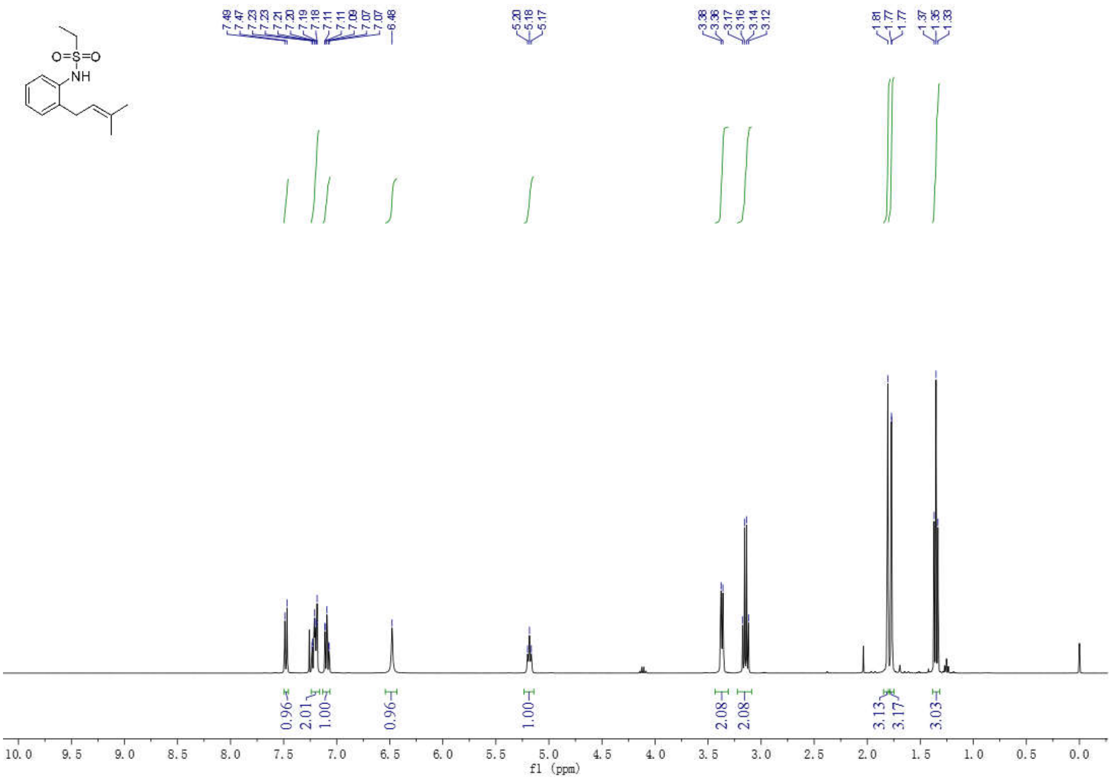
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9i**



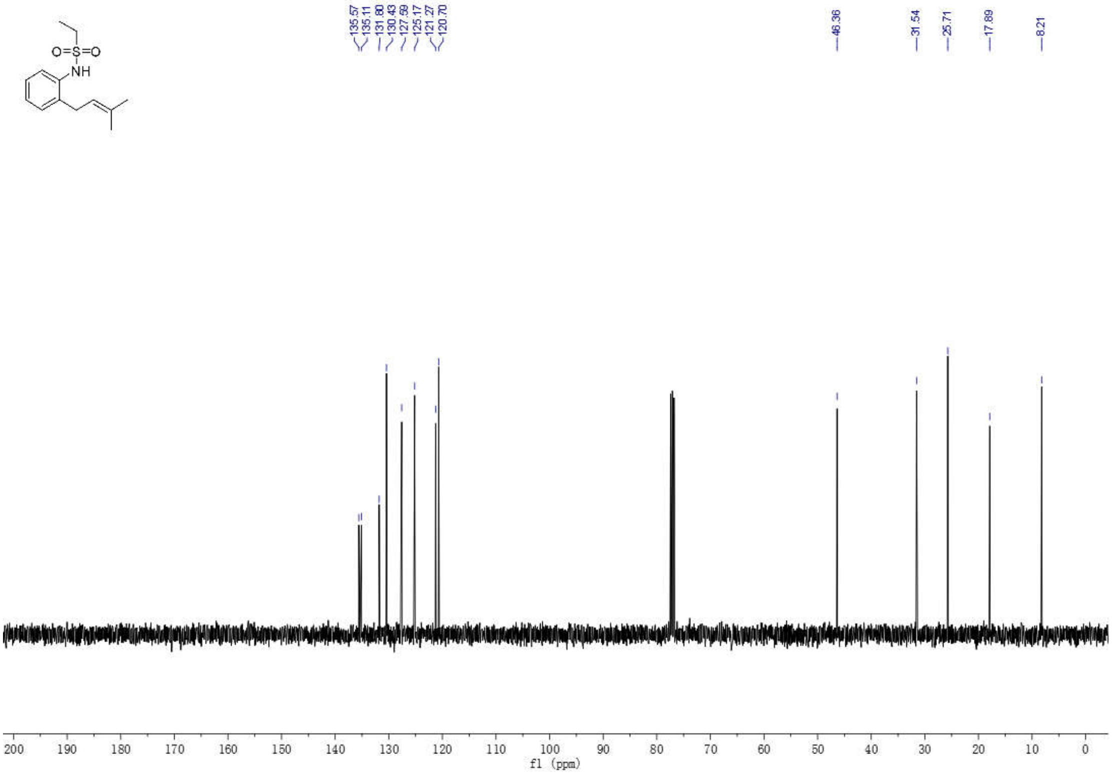
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **9i**



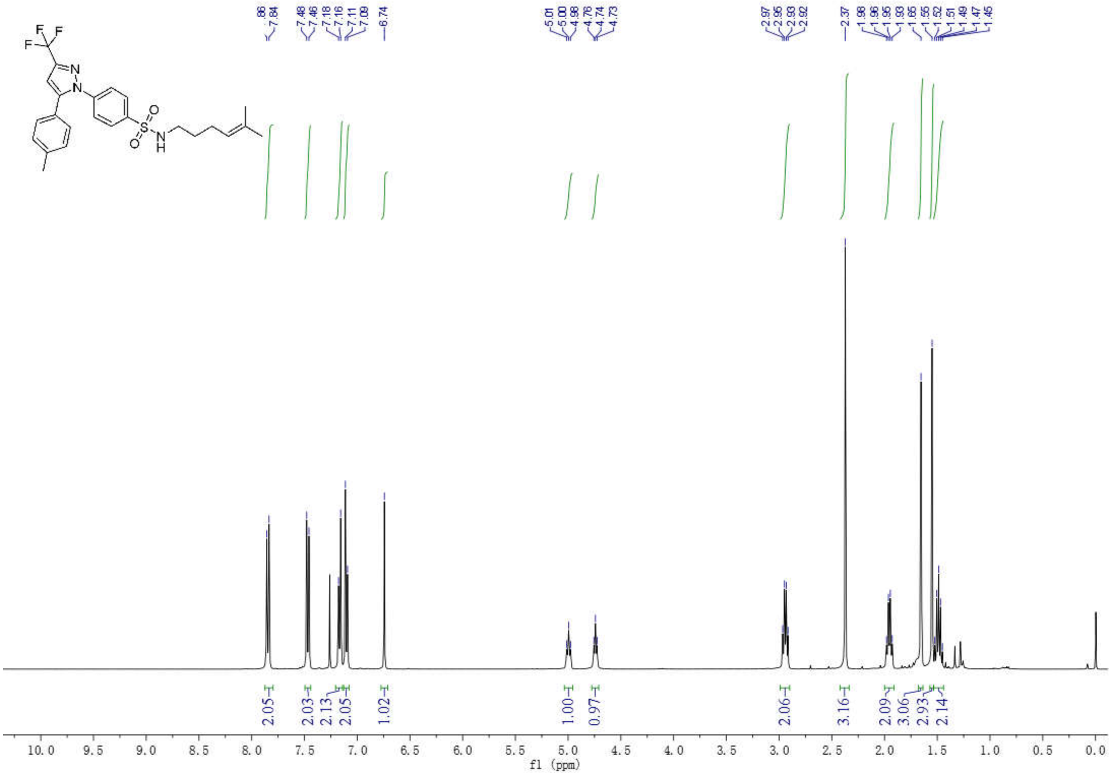
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **9j**



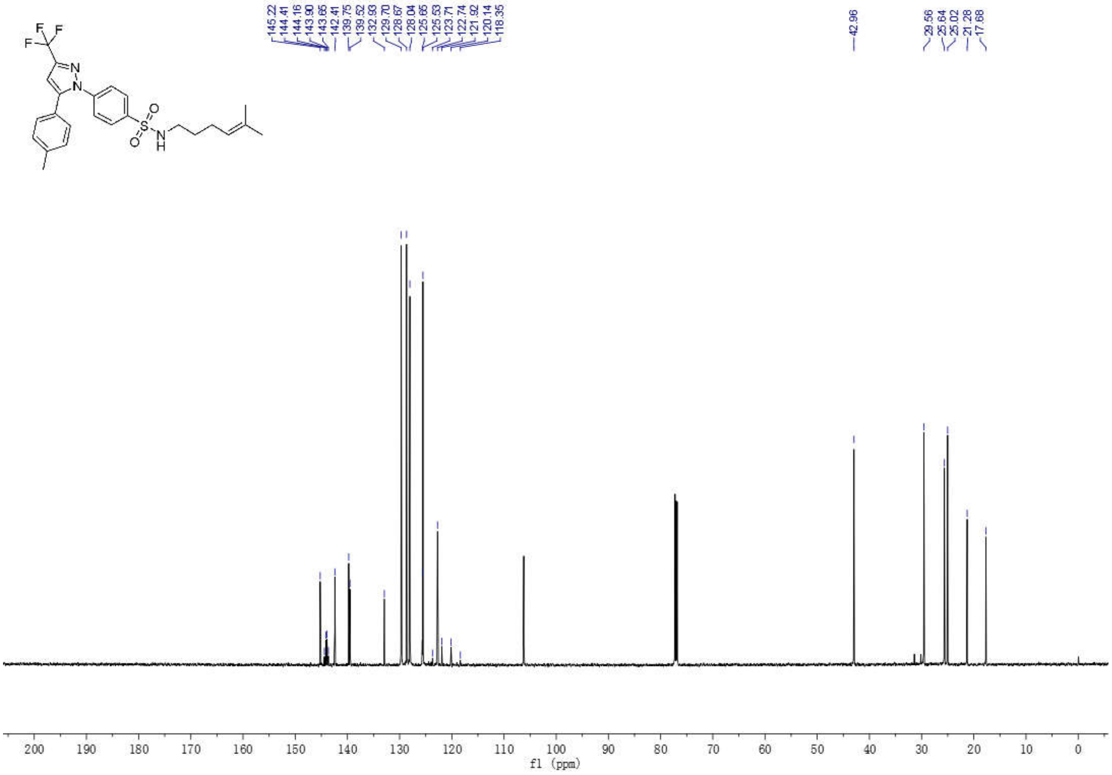
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **9j**



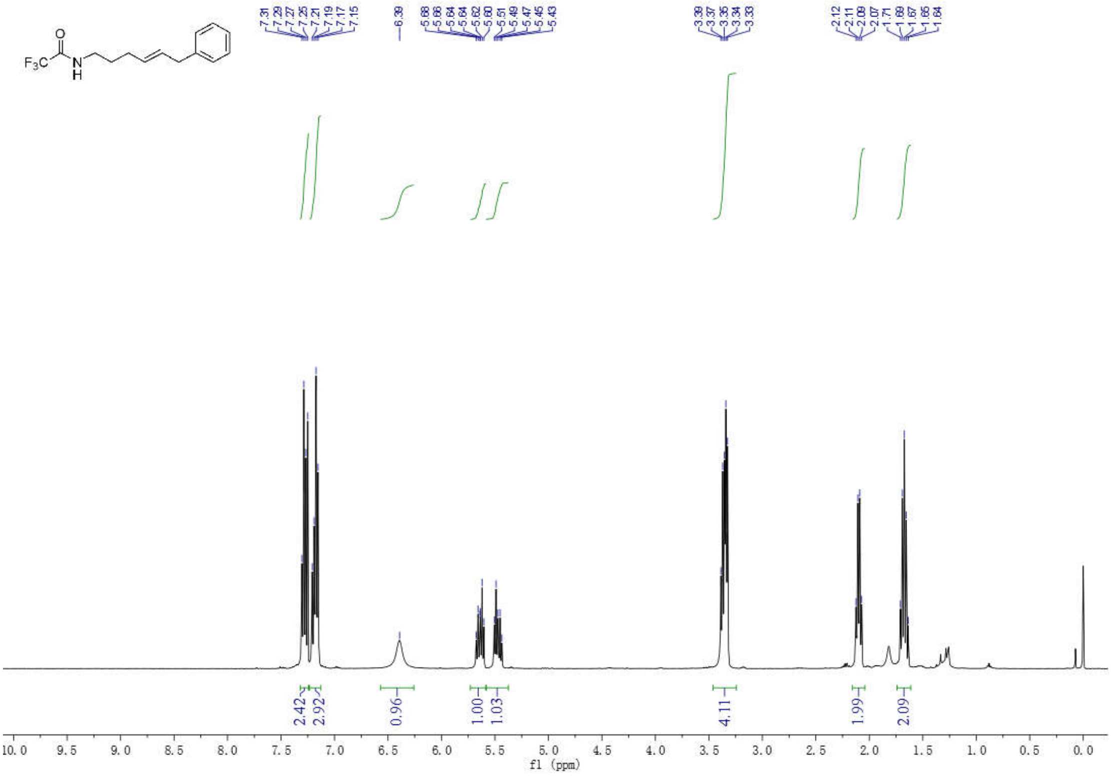
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9k**



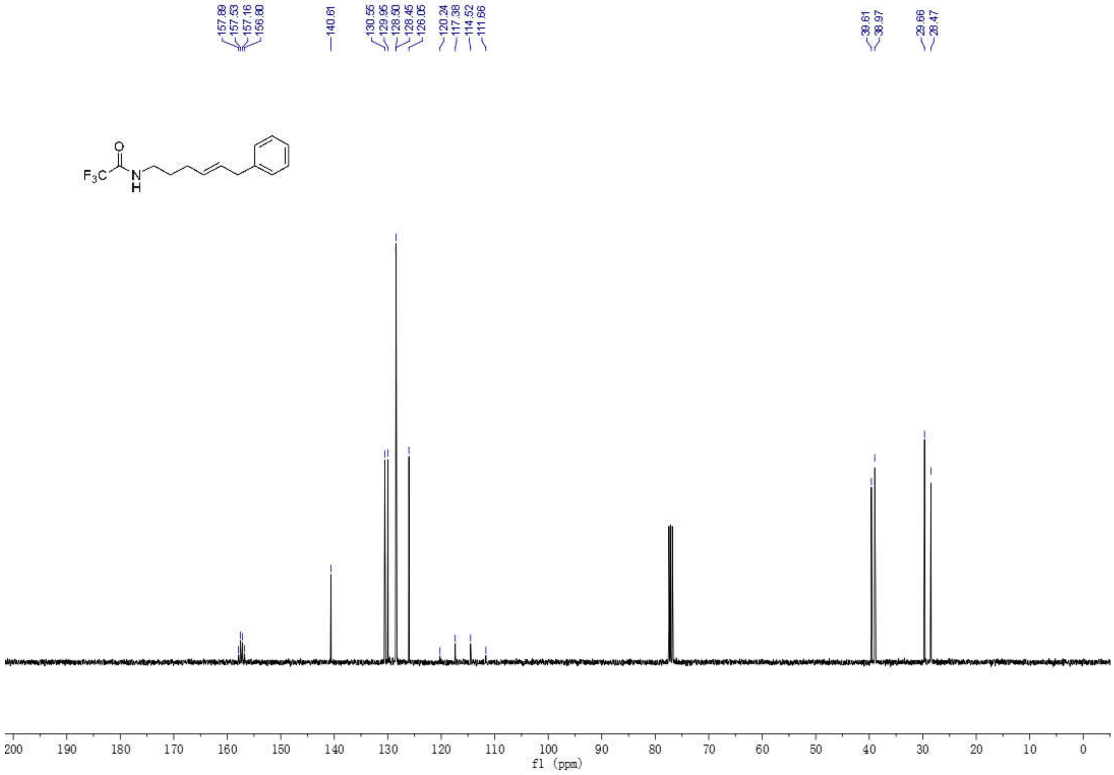
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **9k**



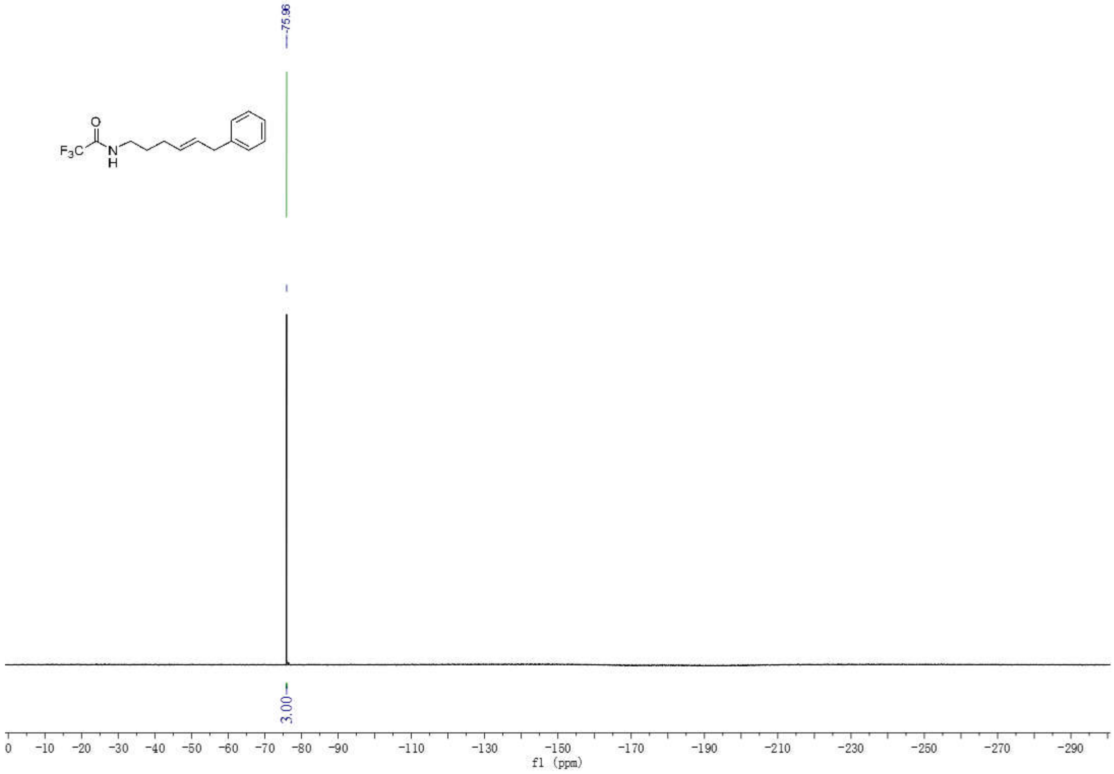
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **9l**



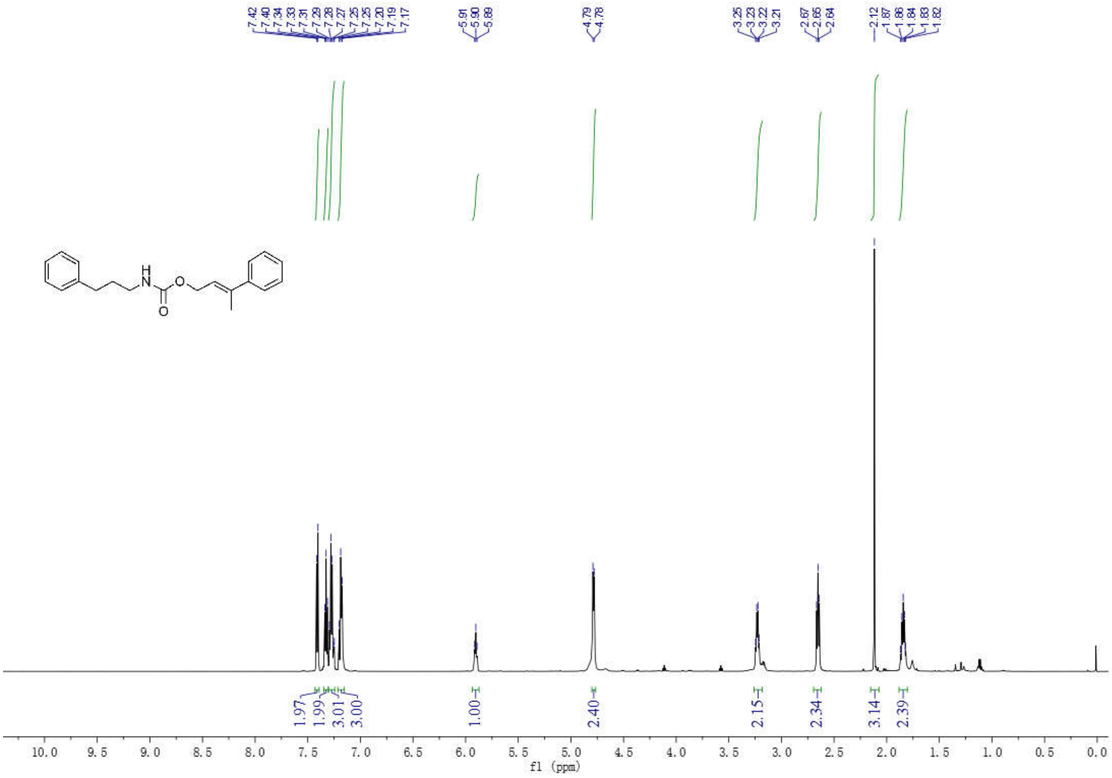
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **9l**



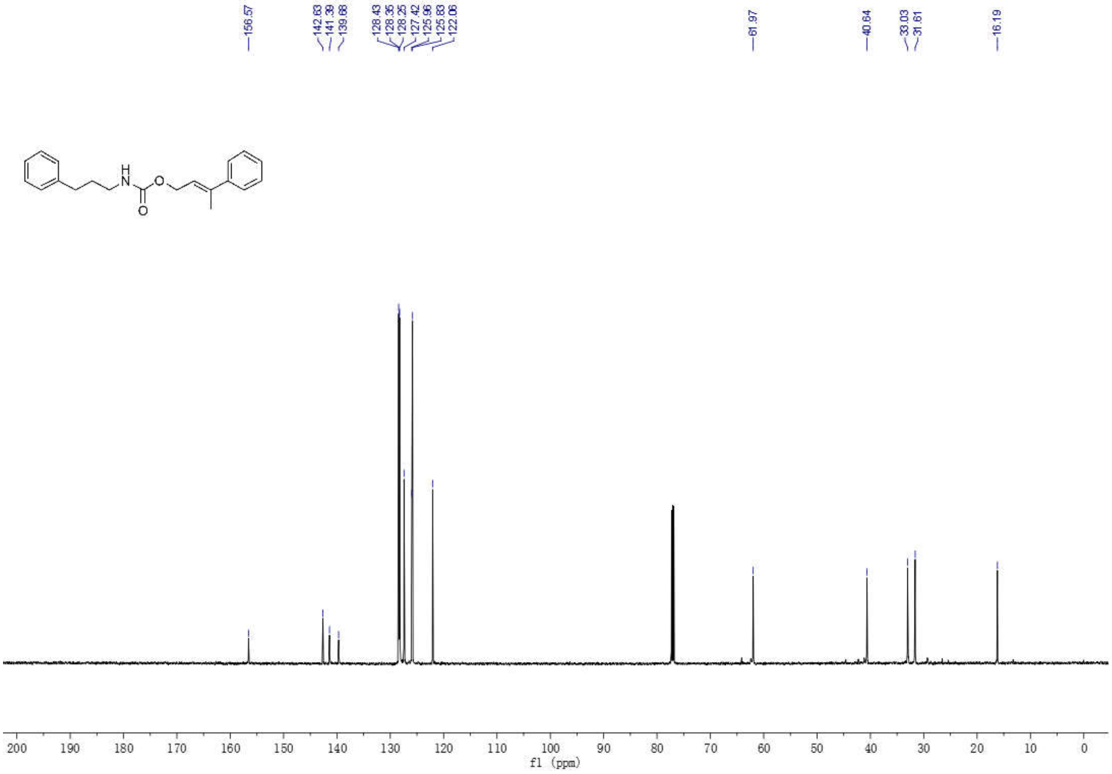
^{19}F NMR spectrum (377 MHz, CDCl$_3$, 23 ºC) of **9l**



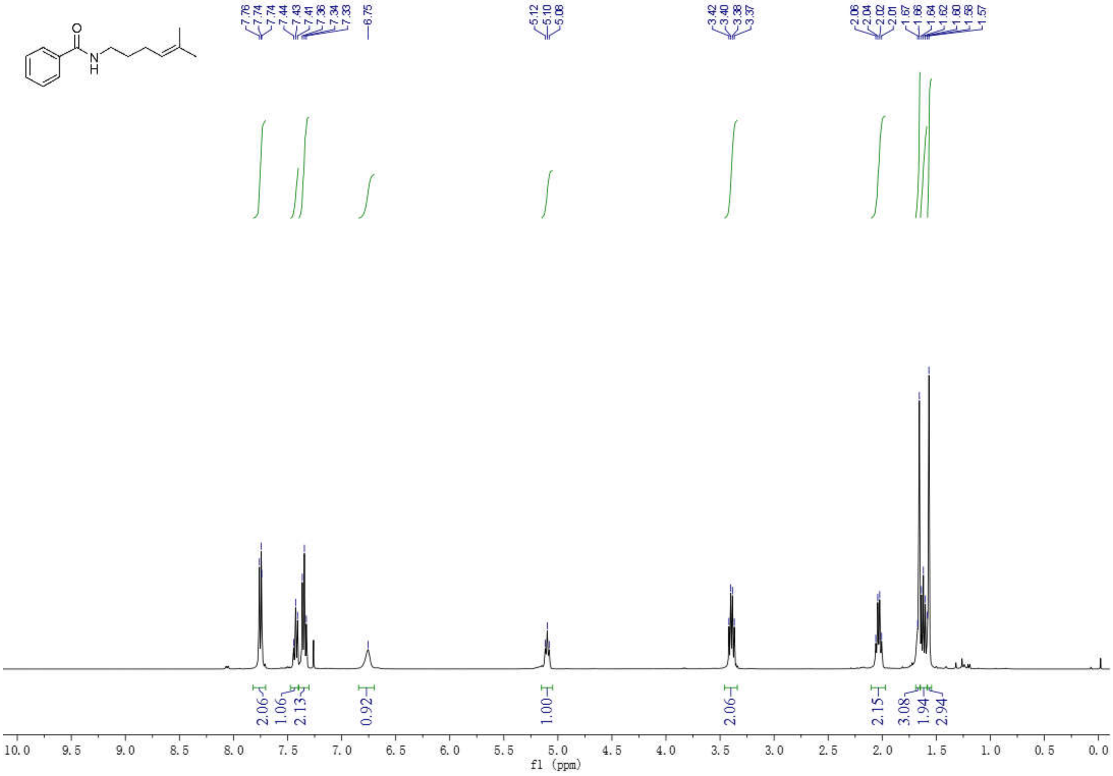
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **9m**



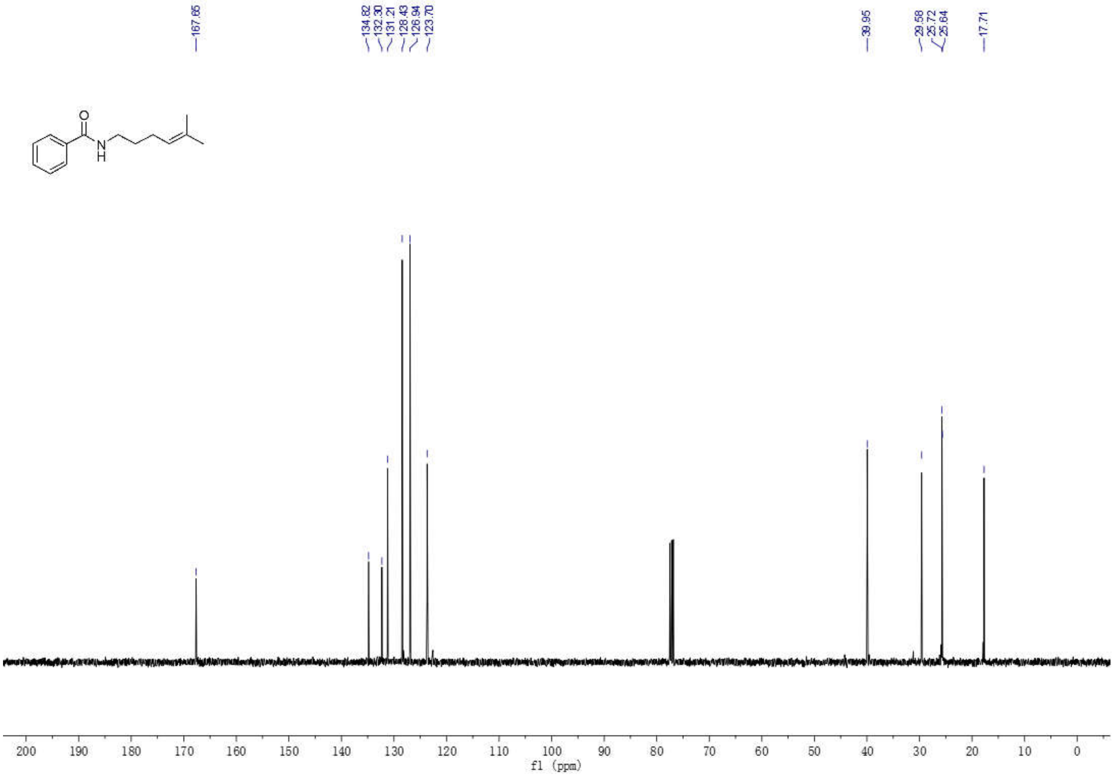
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **9m**



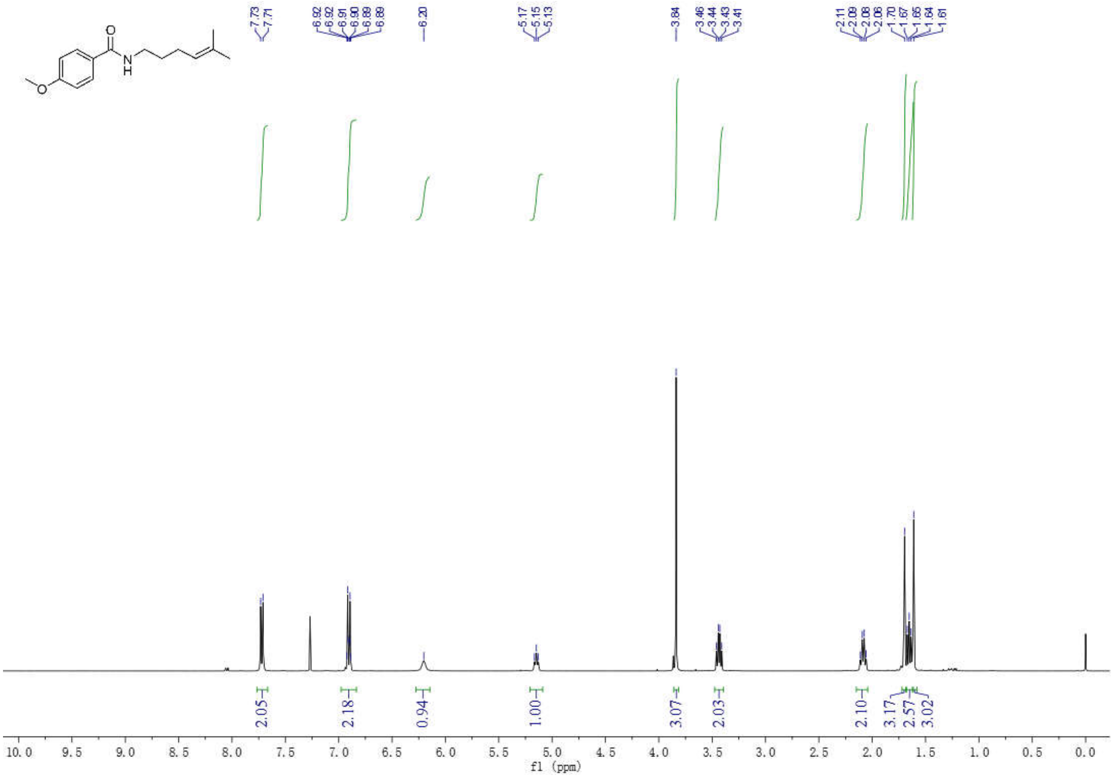
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **11a**



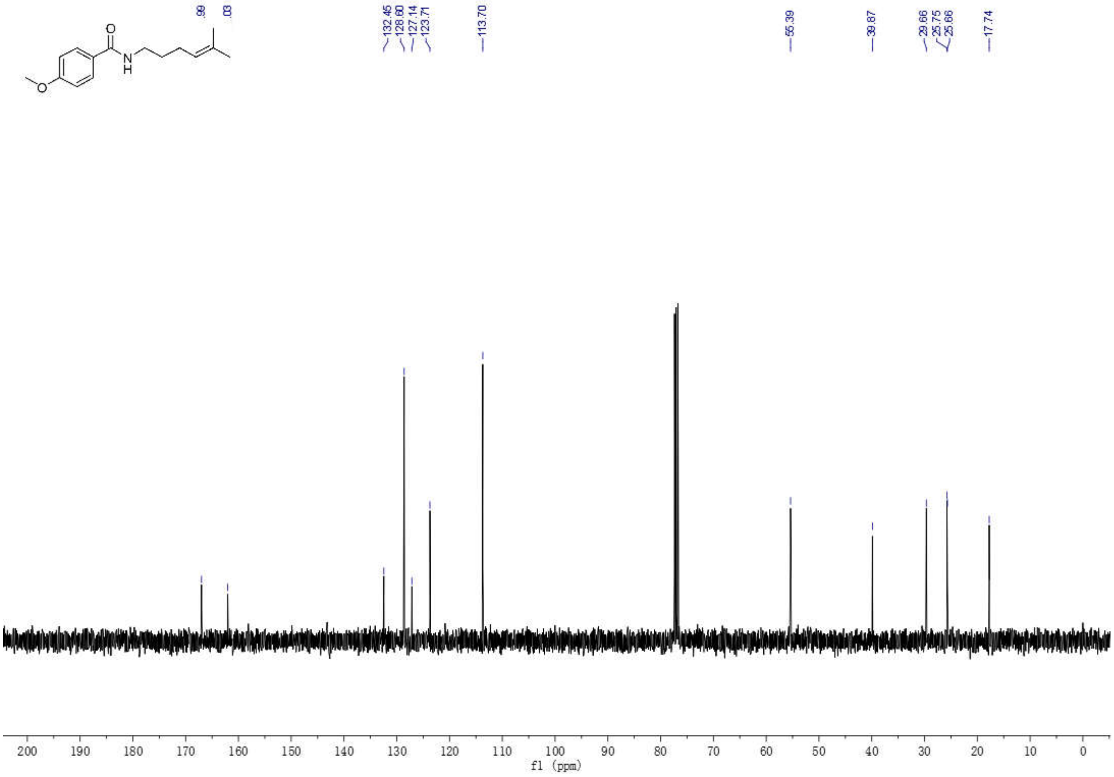
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **11a**



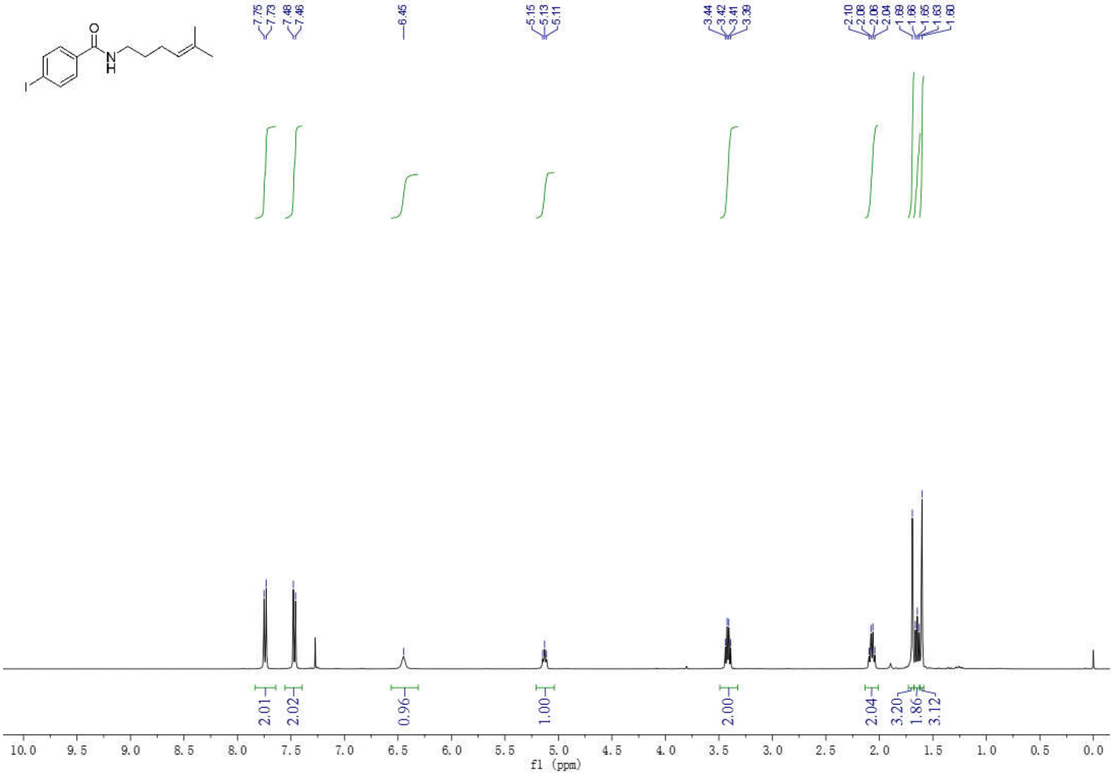
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **11b**



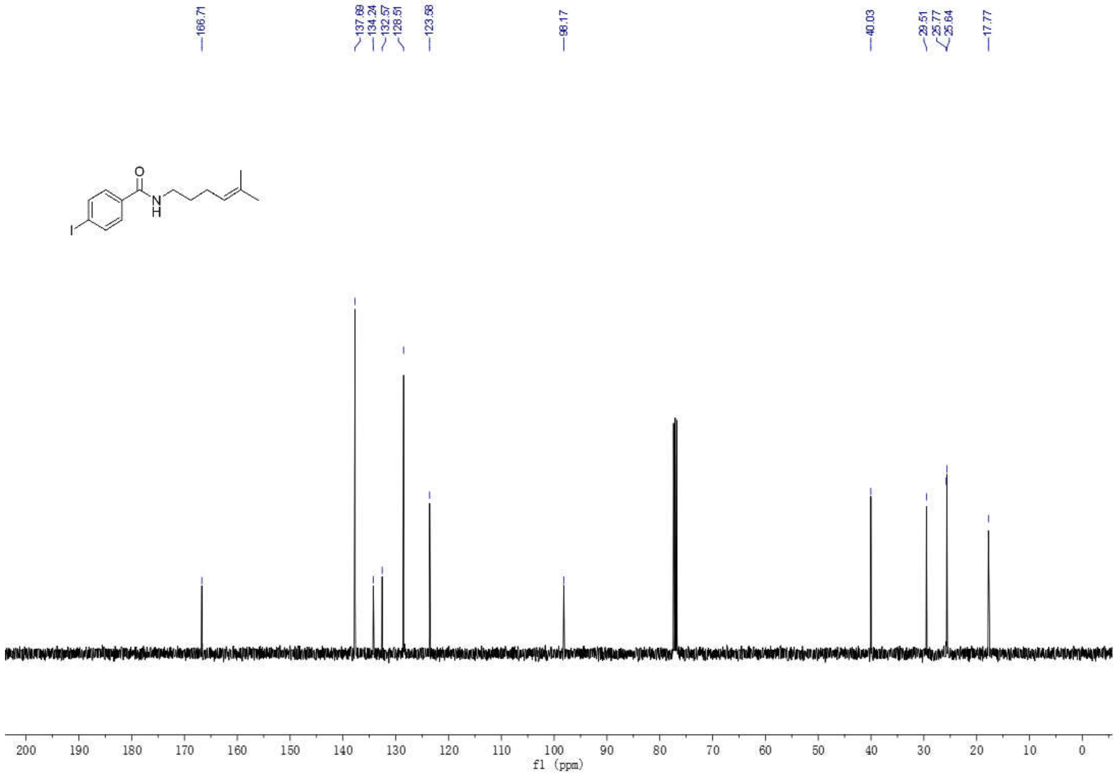
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **11b**



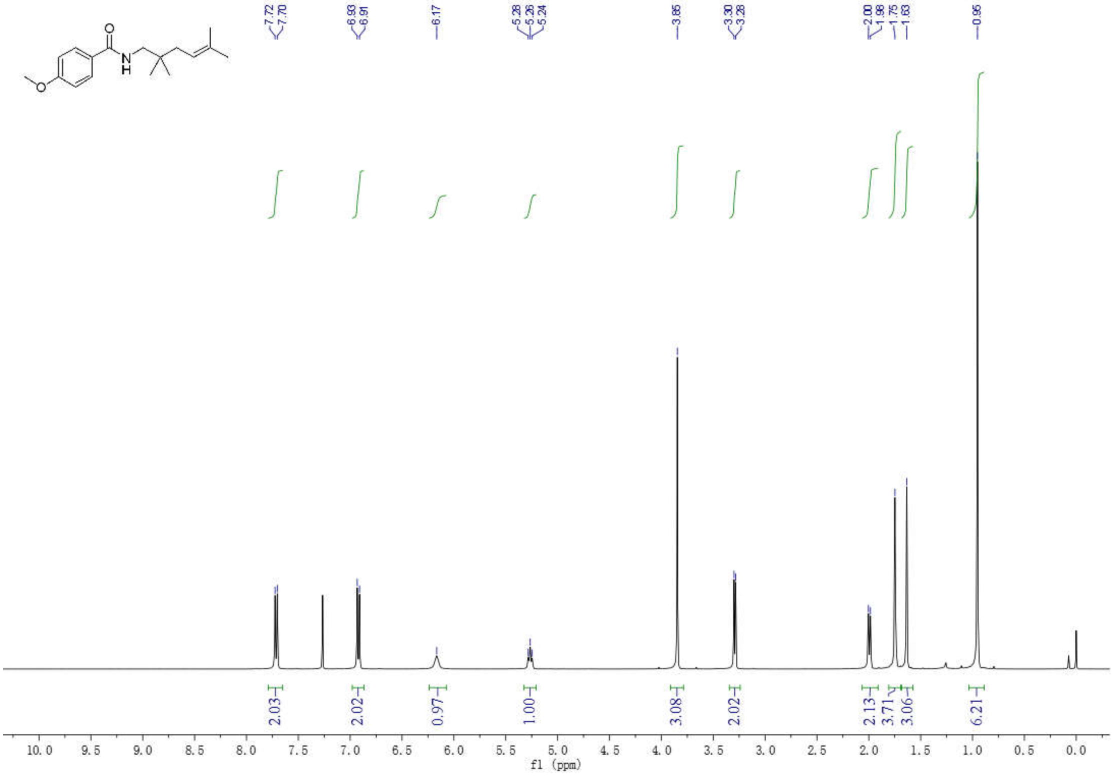
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **11c**



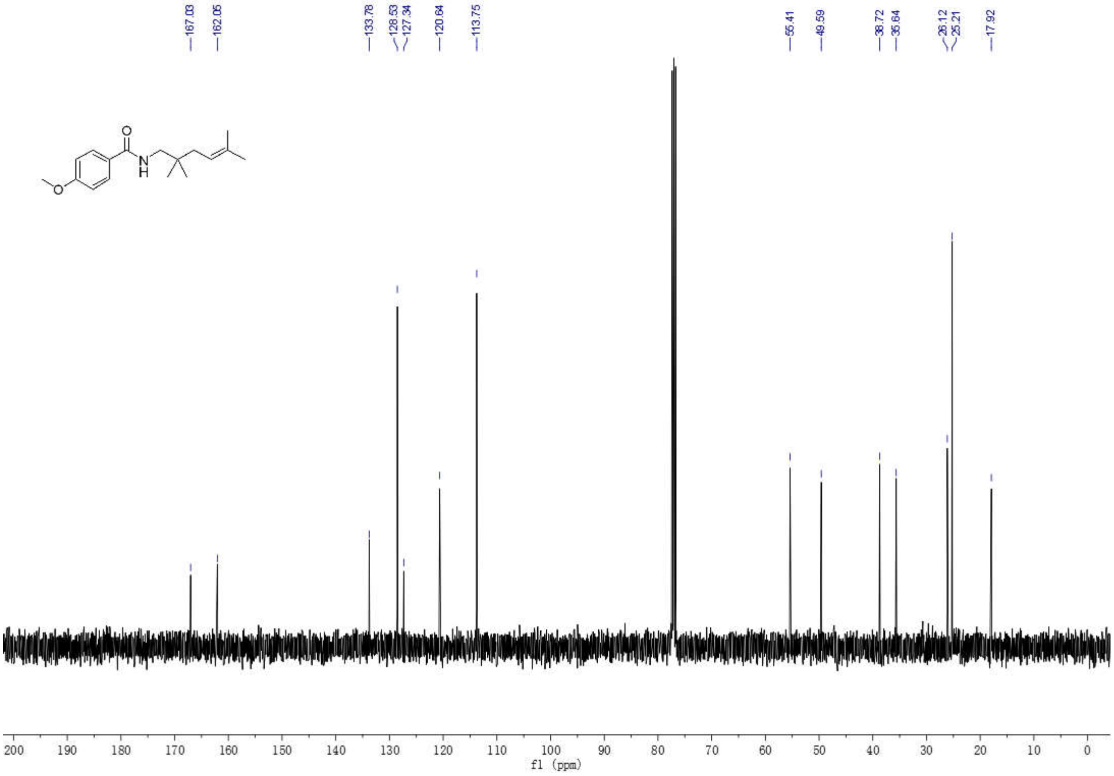
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **11c**



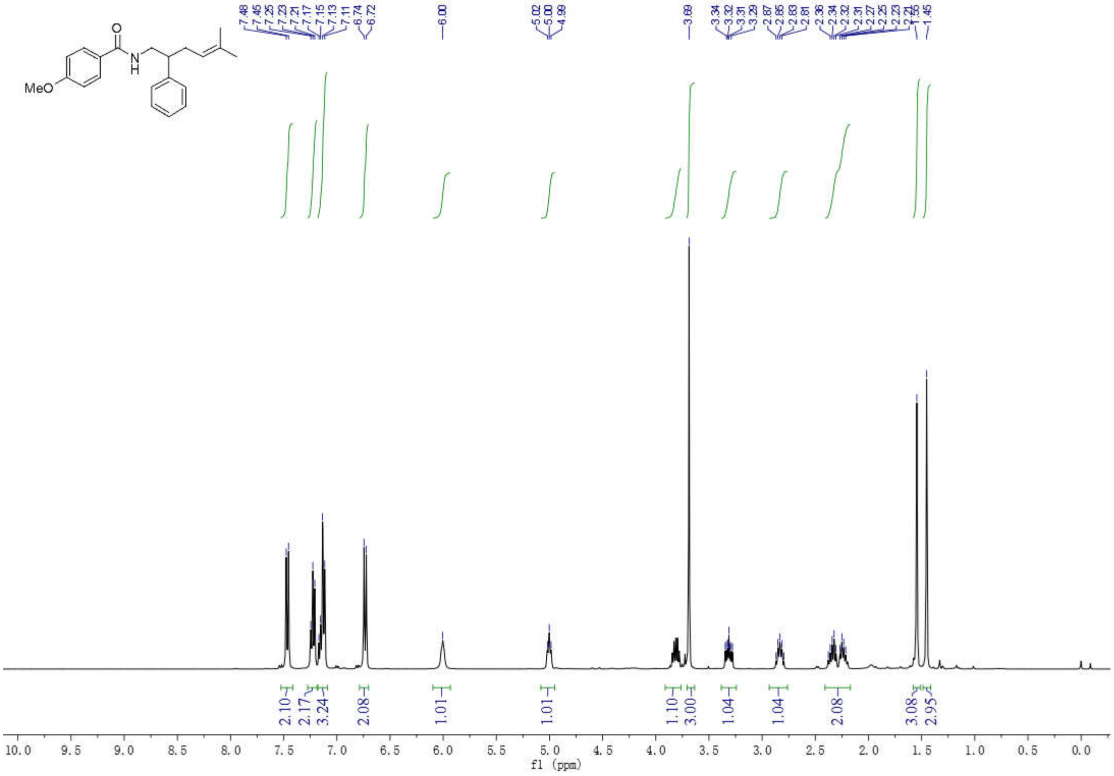
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **11d**



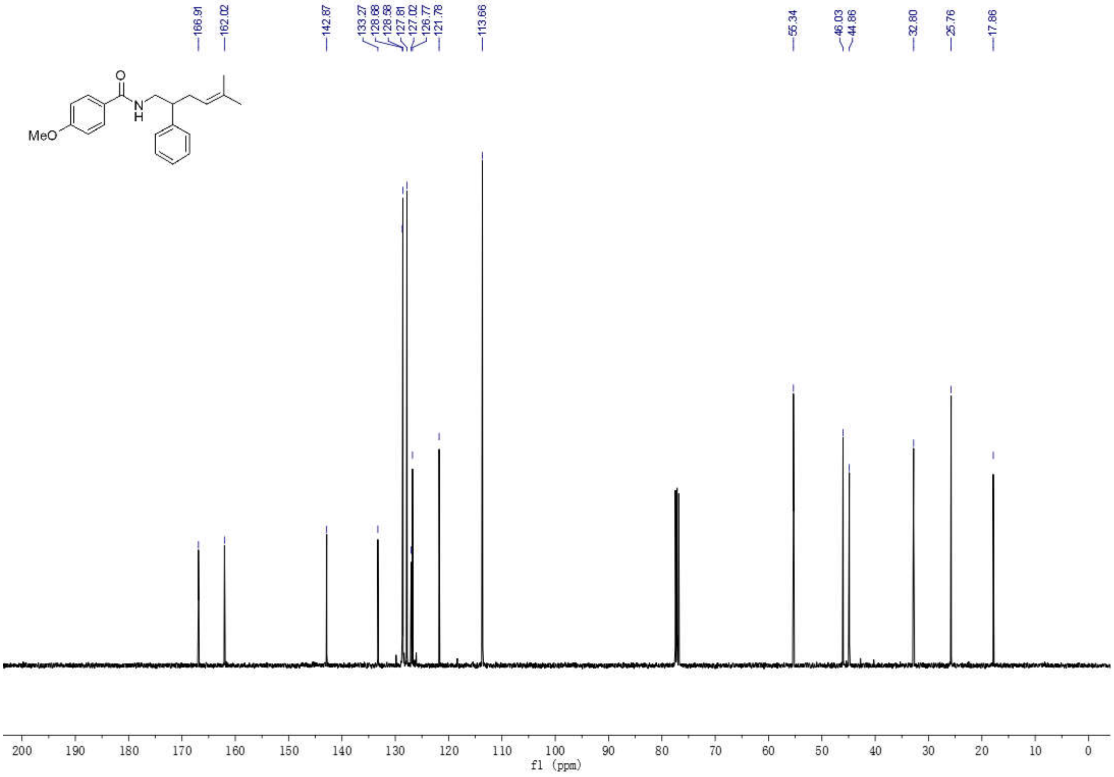
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **11d**



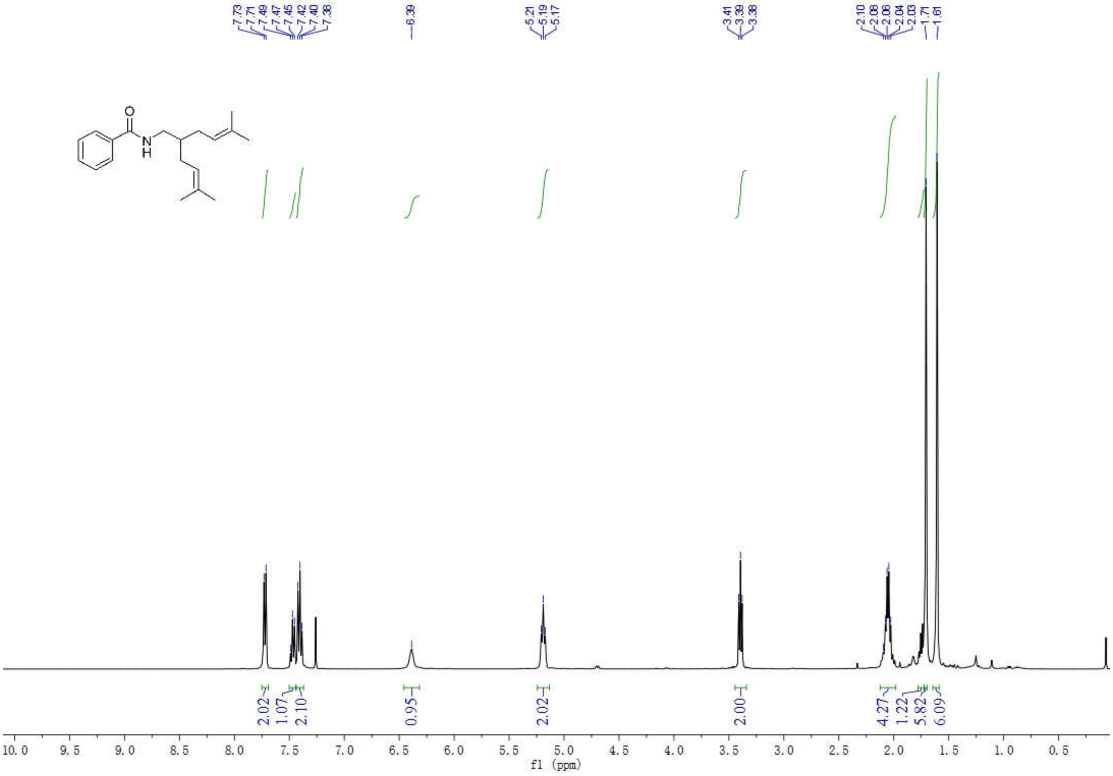
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **11e**



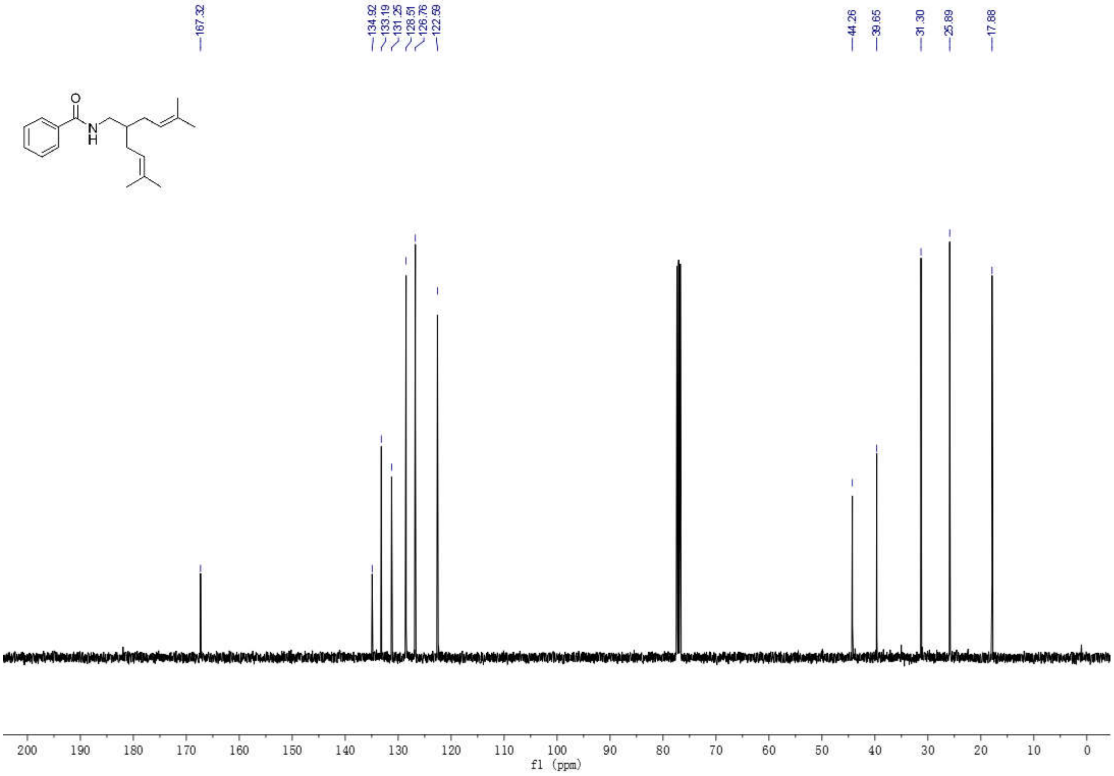
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **11e**



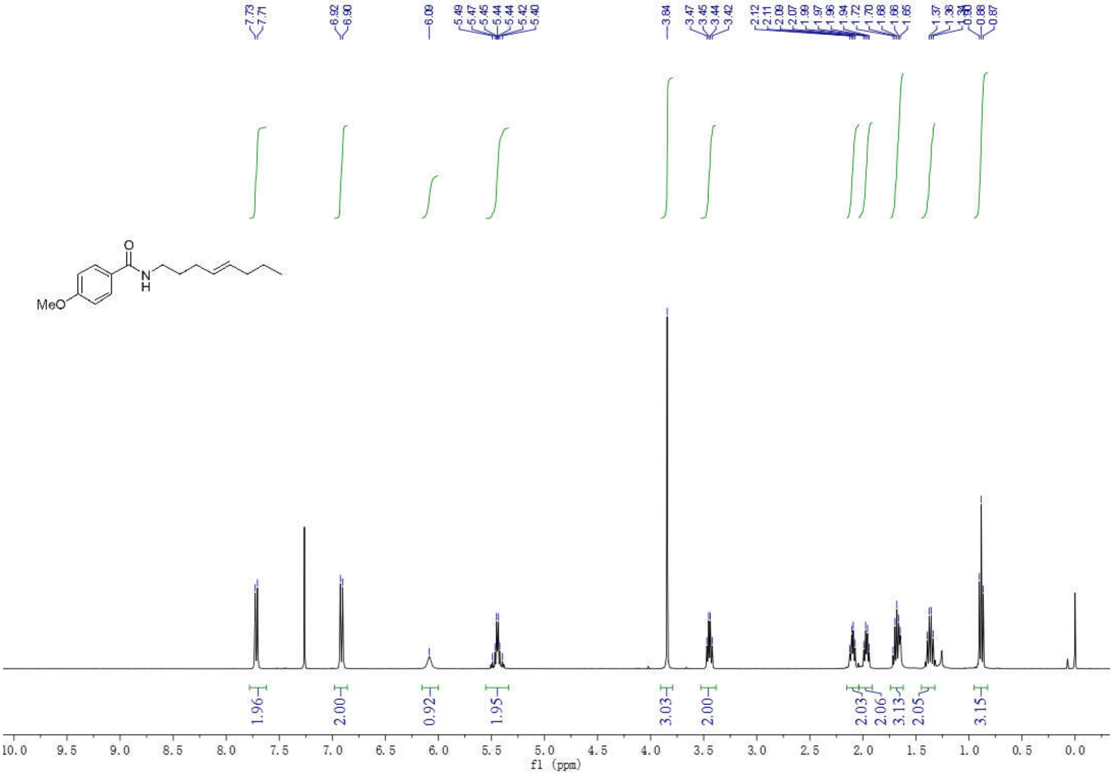
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **11f**



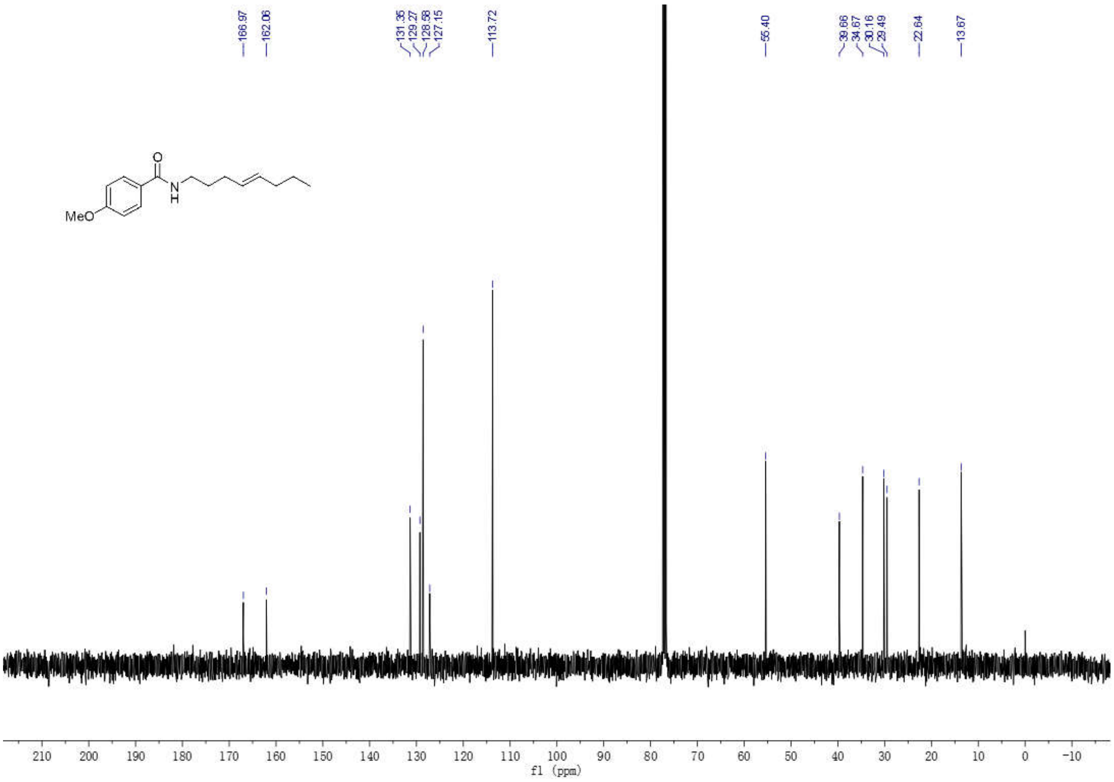
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **11f**



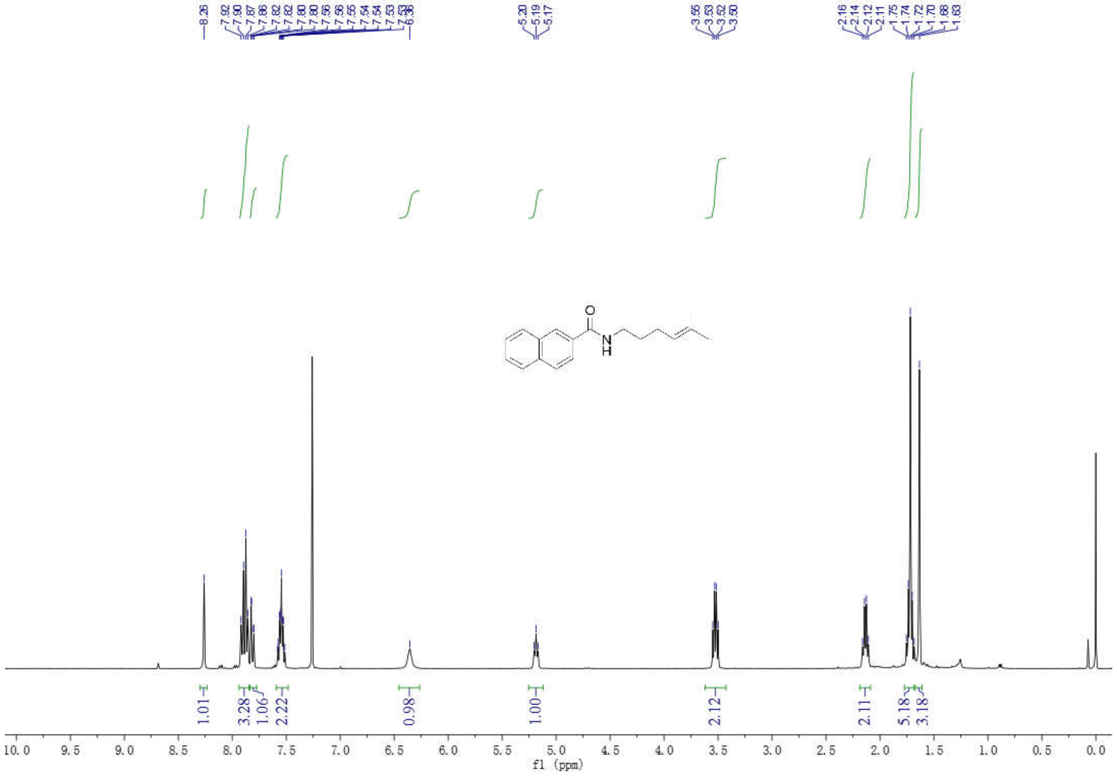
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **11g**



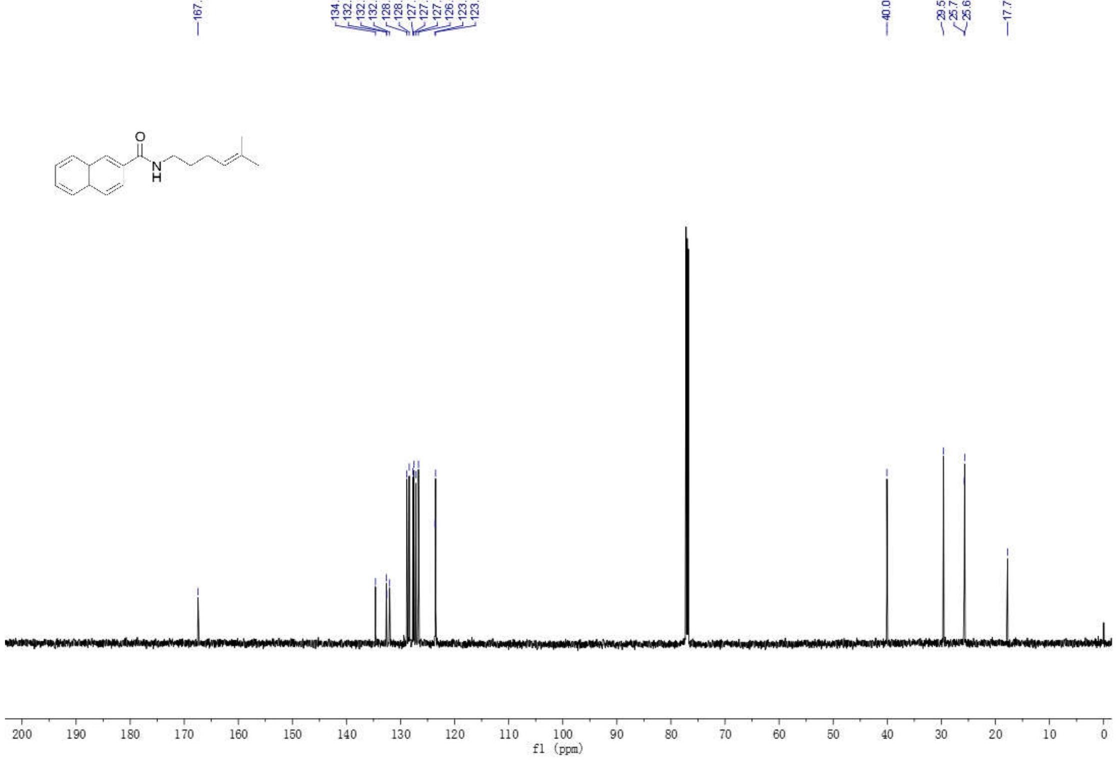
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **11g**



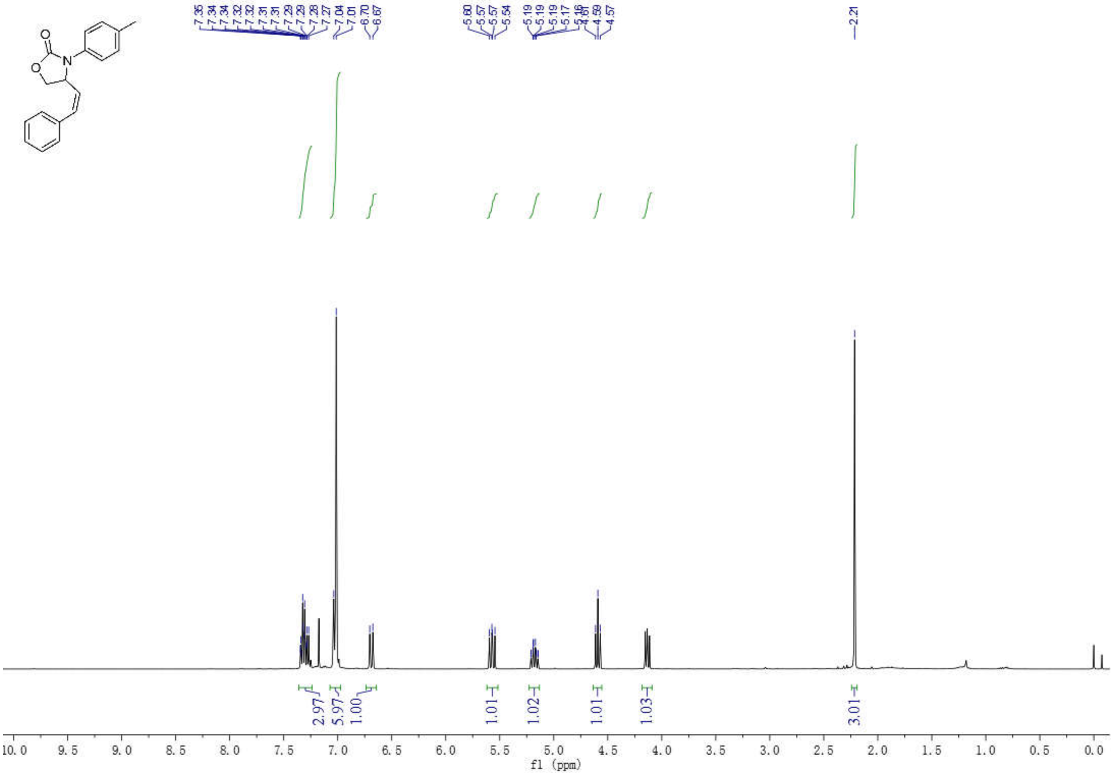
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **11h**



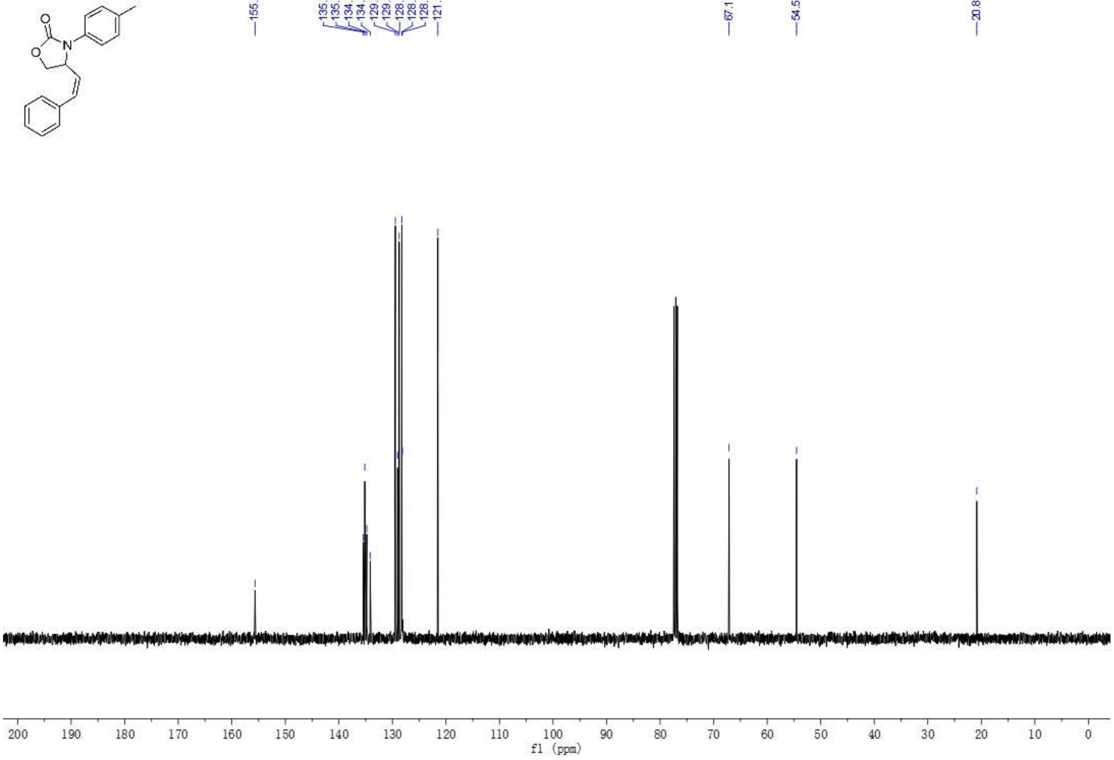
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **11h**



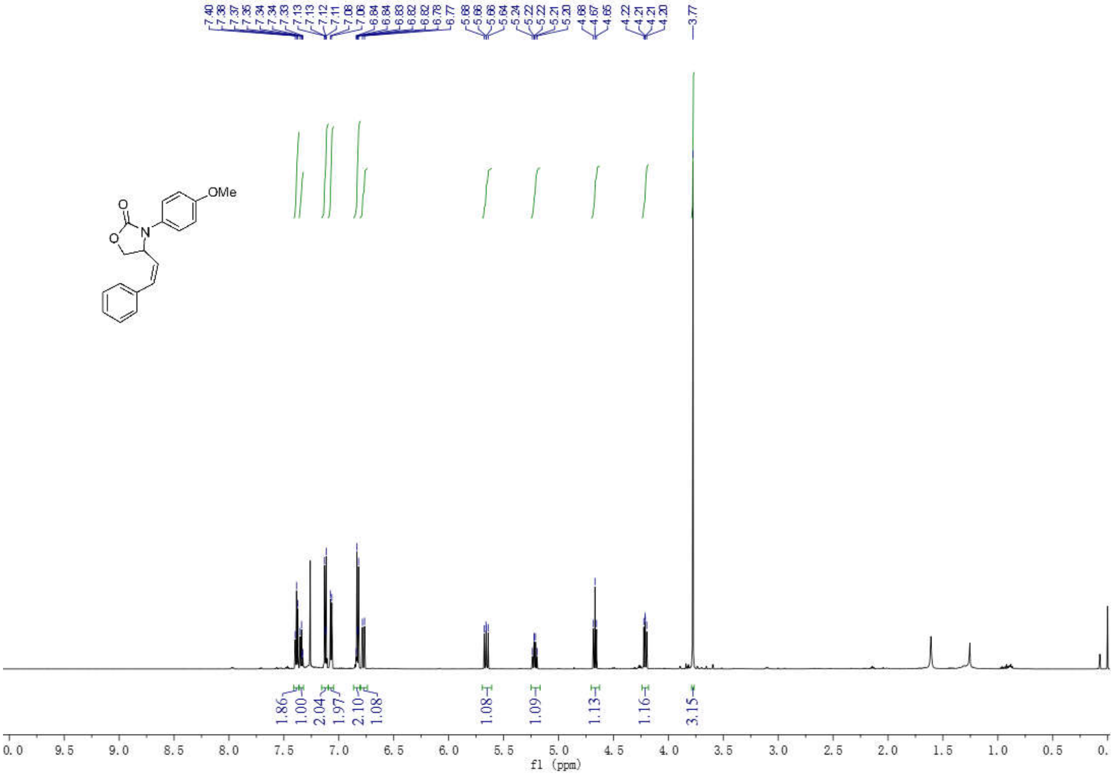
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **2a**



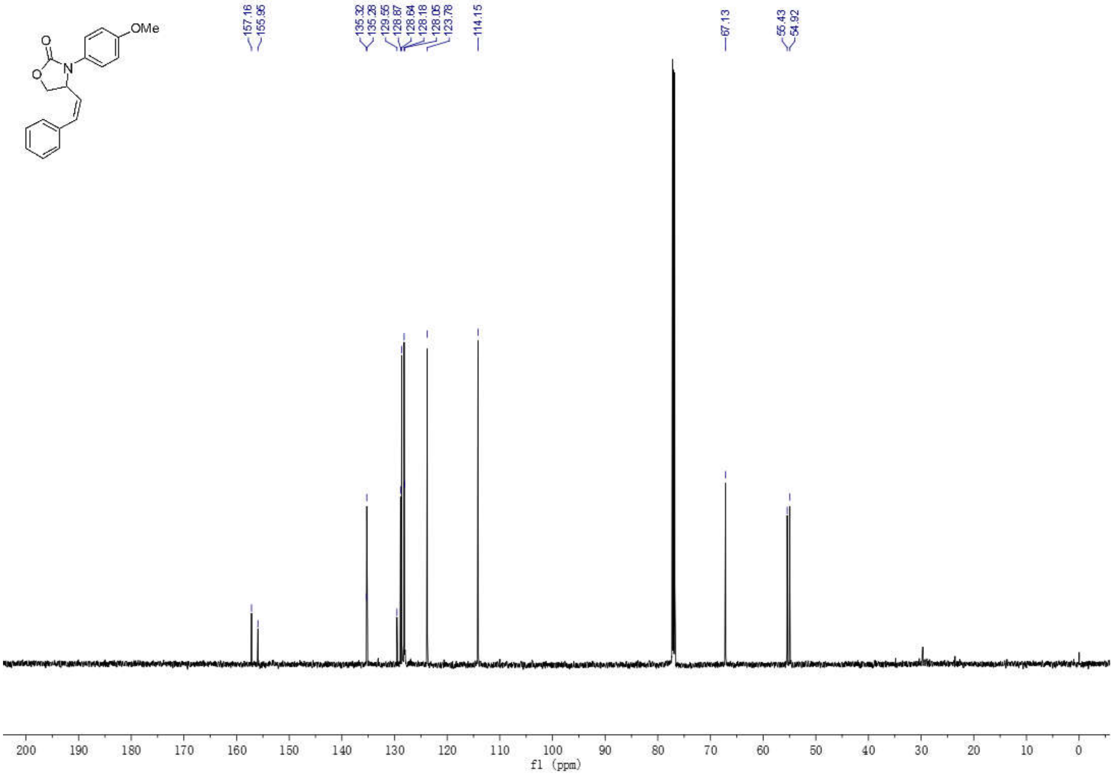
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **2a**



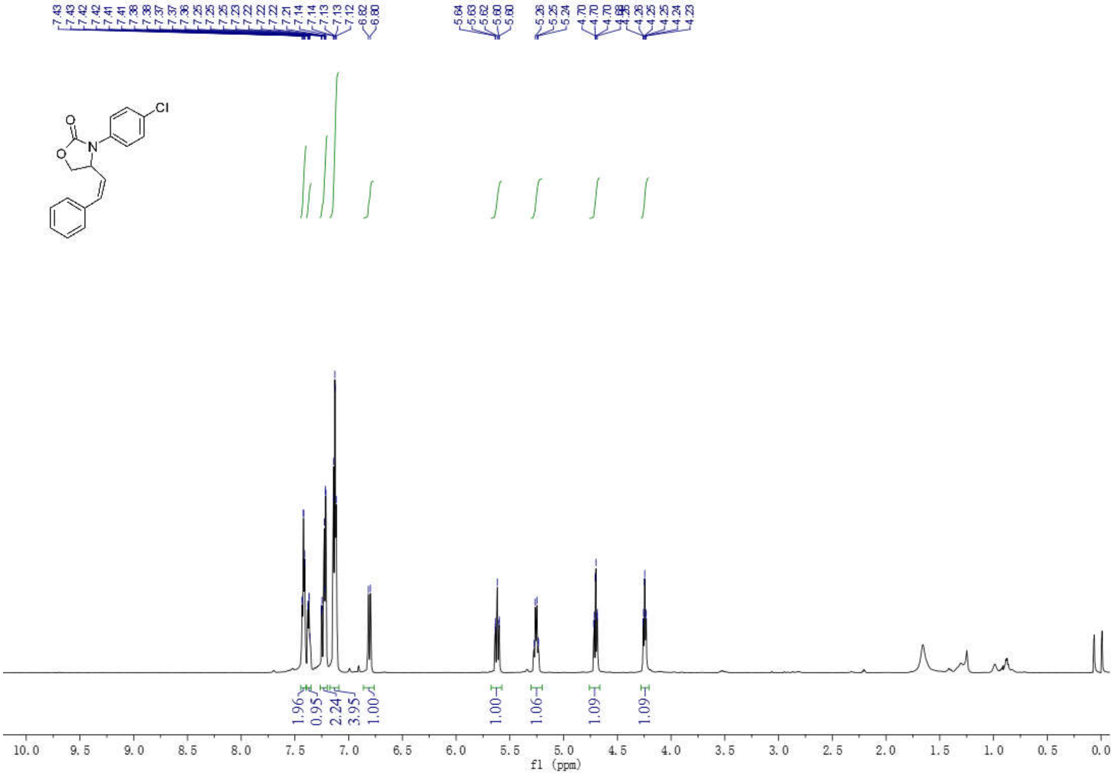
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2b**



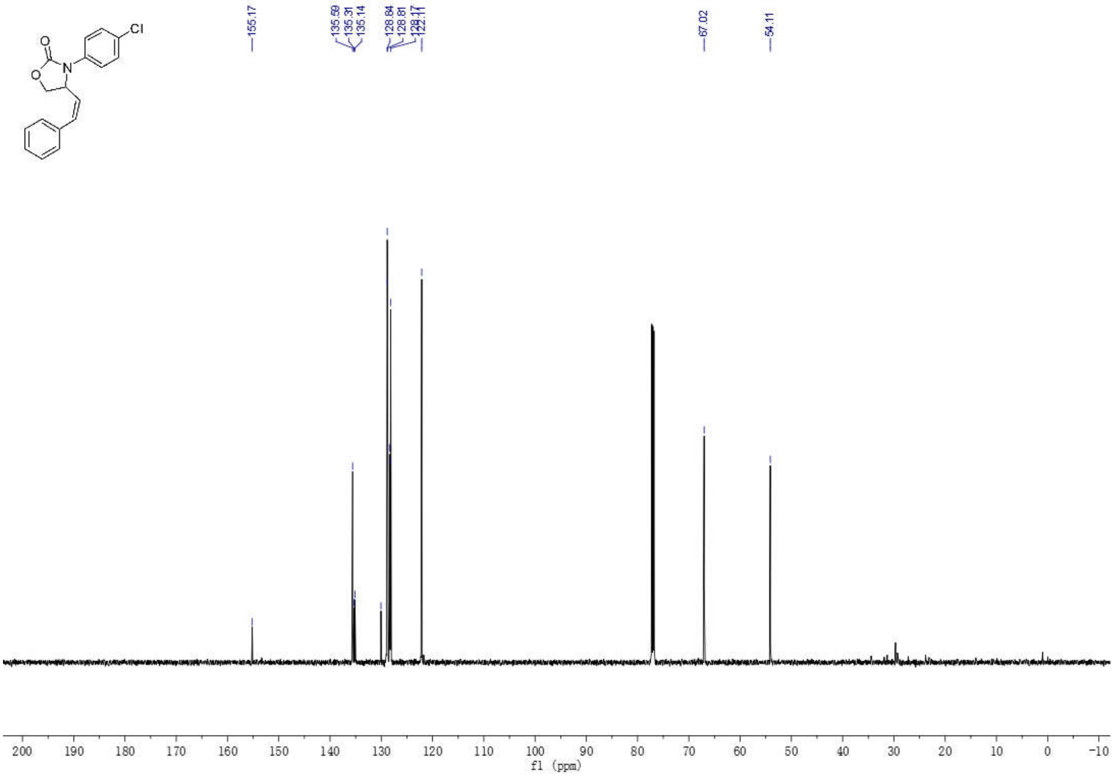
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2b**



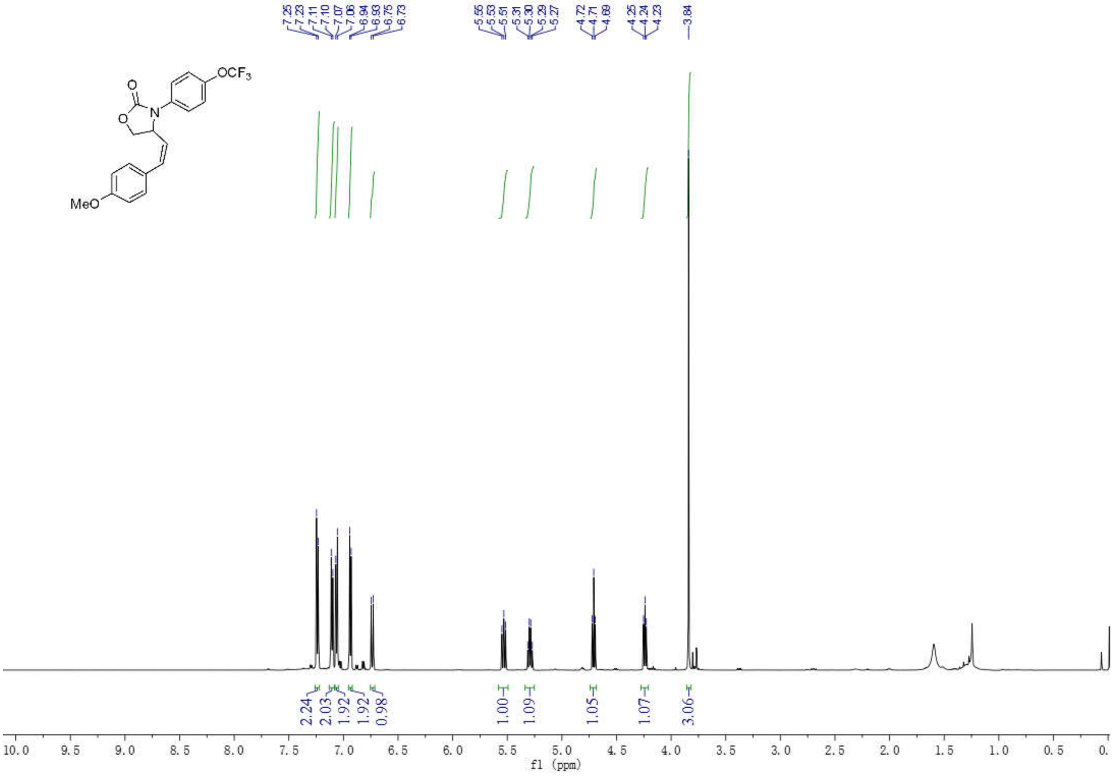
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2c**



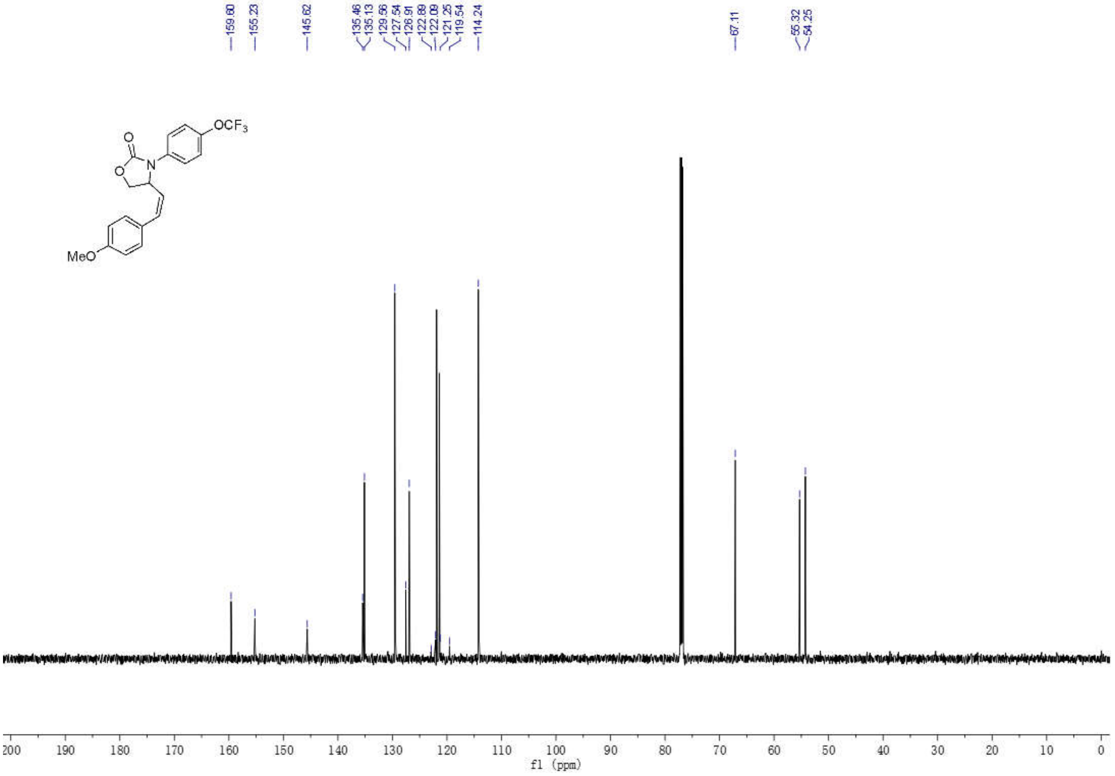
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2c**



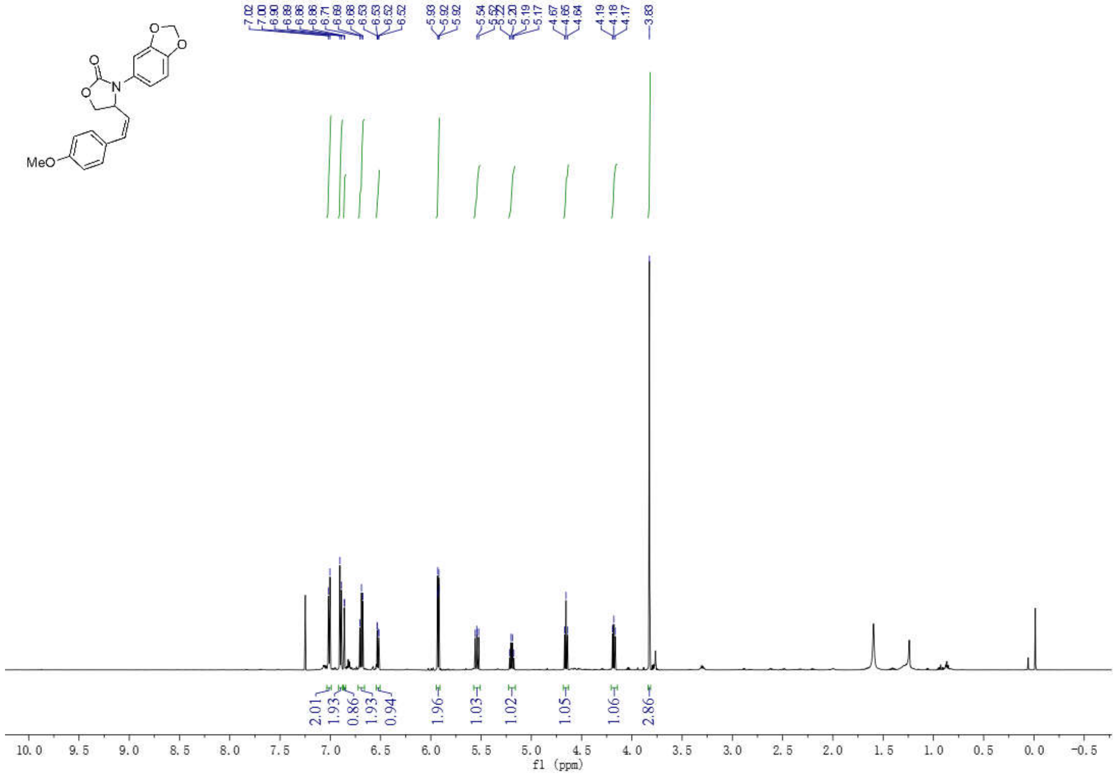
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2d**



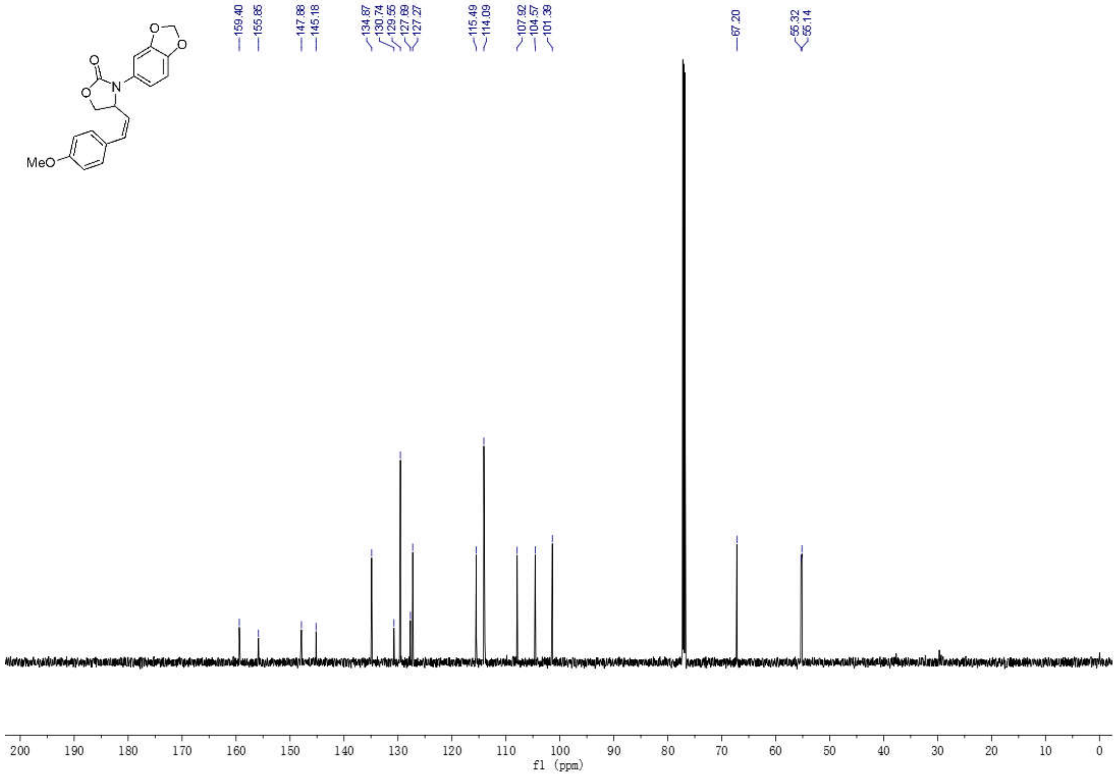
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2d**



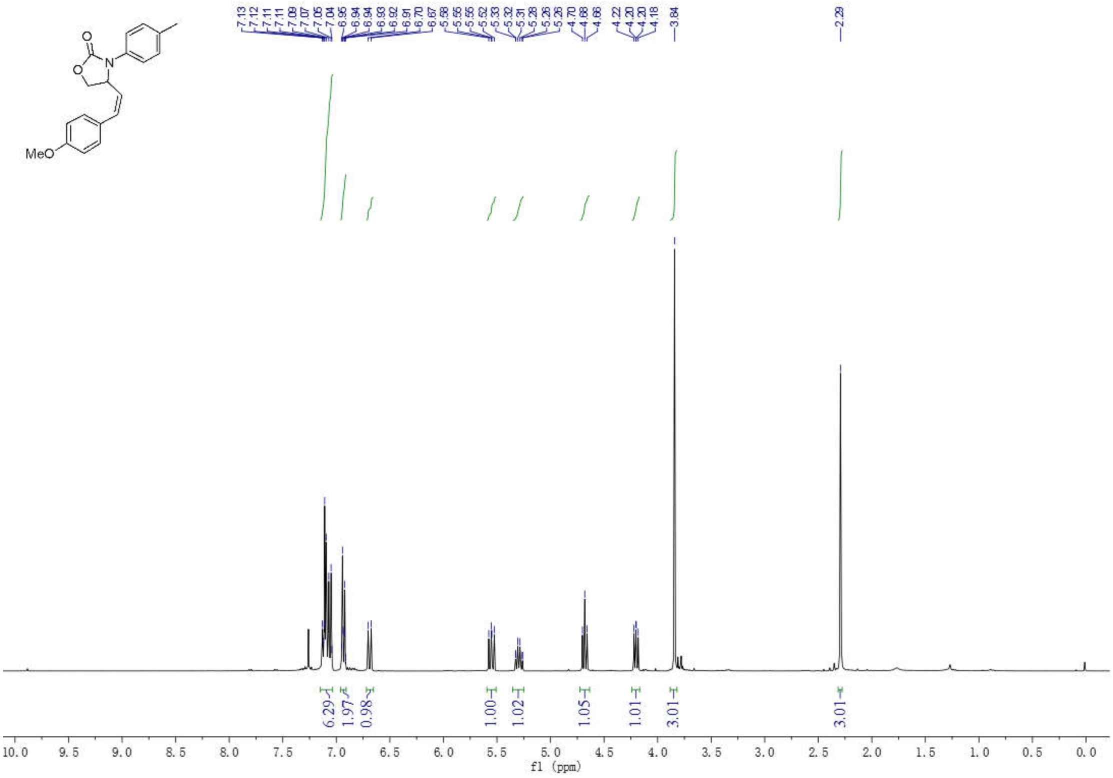
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **2e**



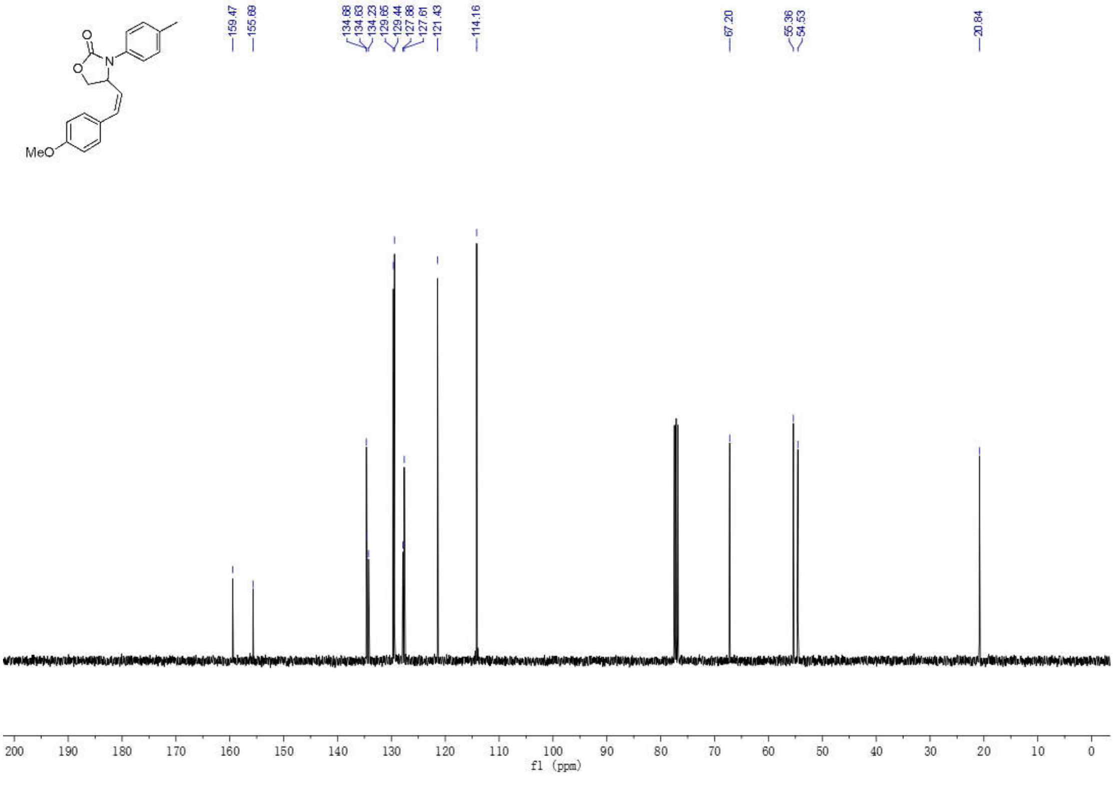
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **2e**



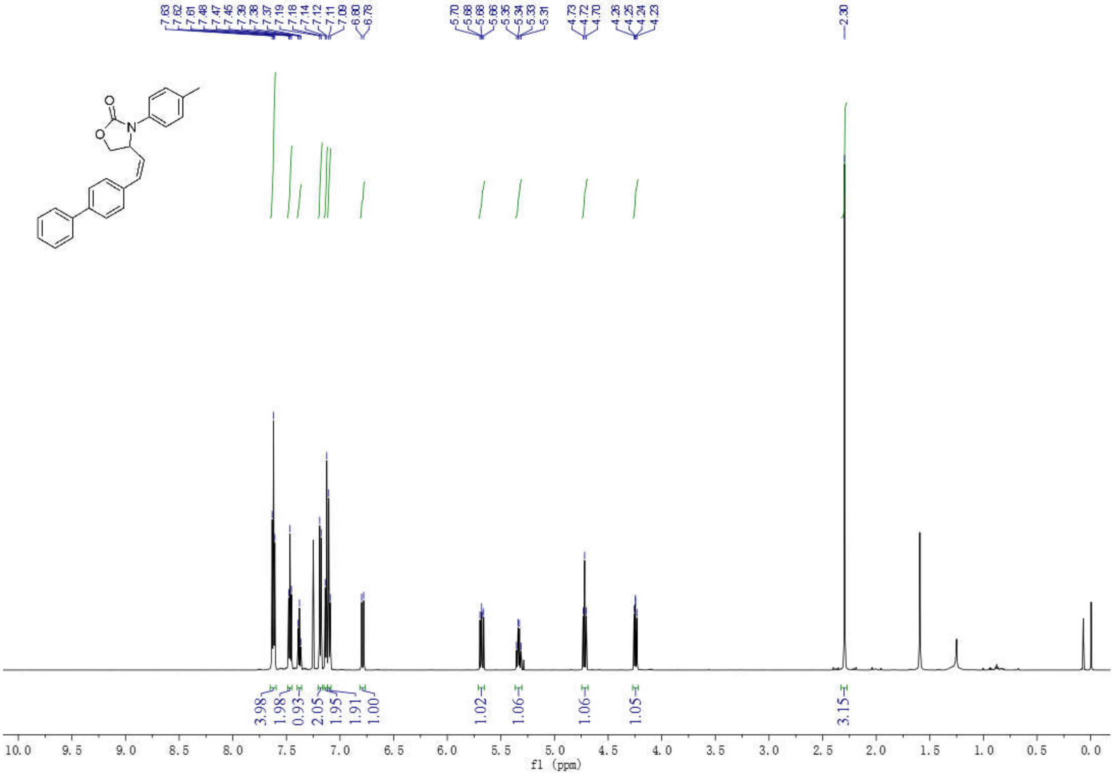
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **2f**



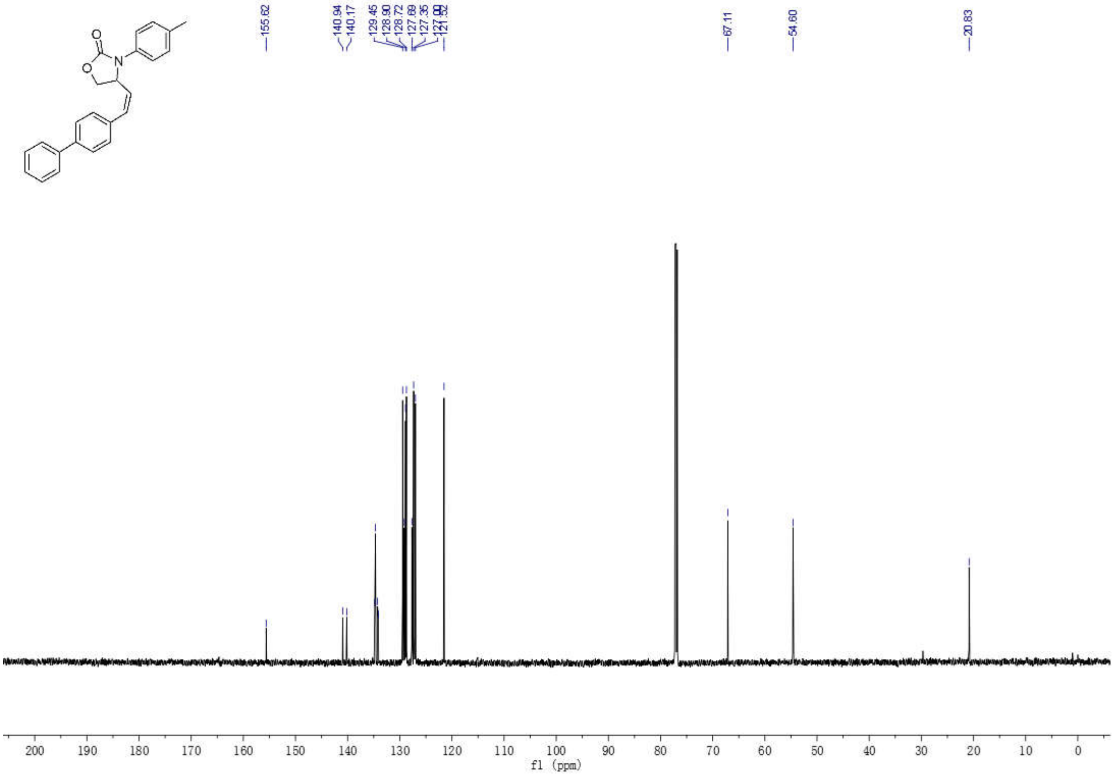
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **2f**



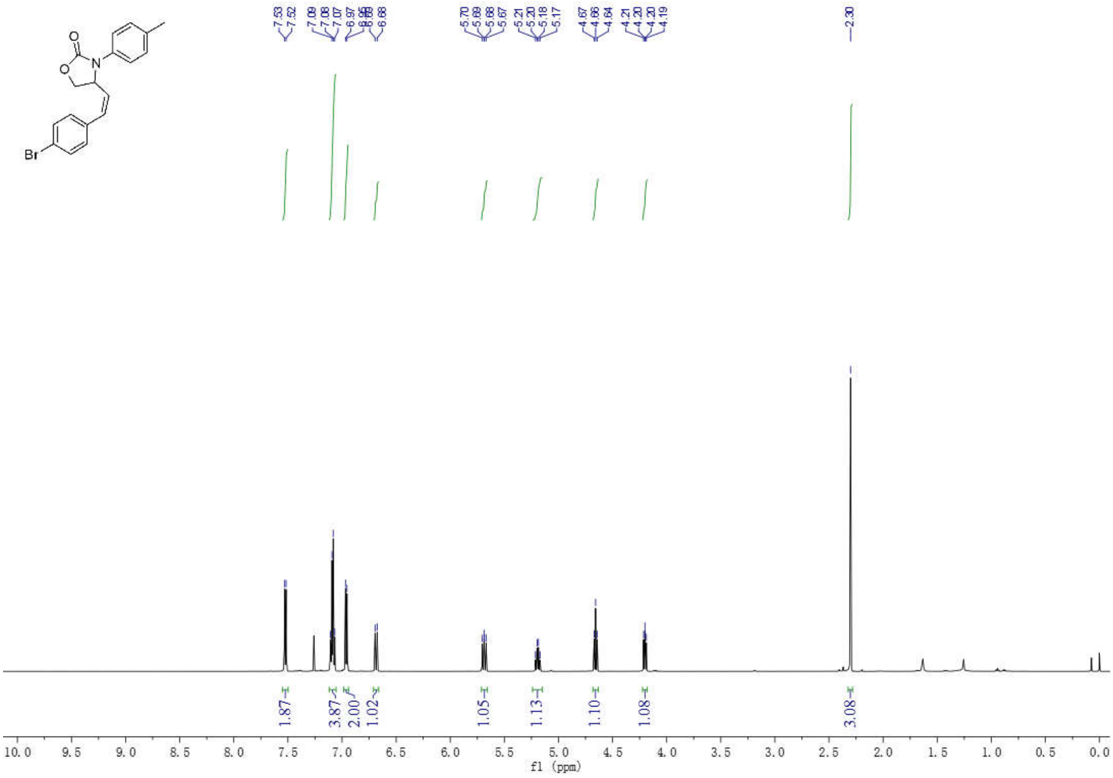
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **2g**



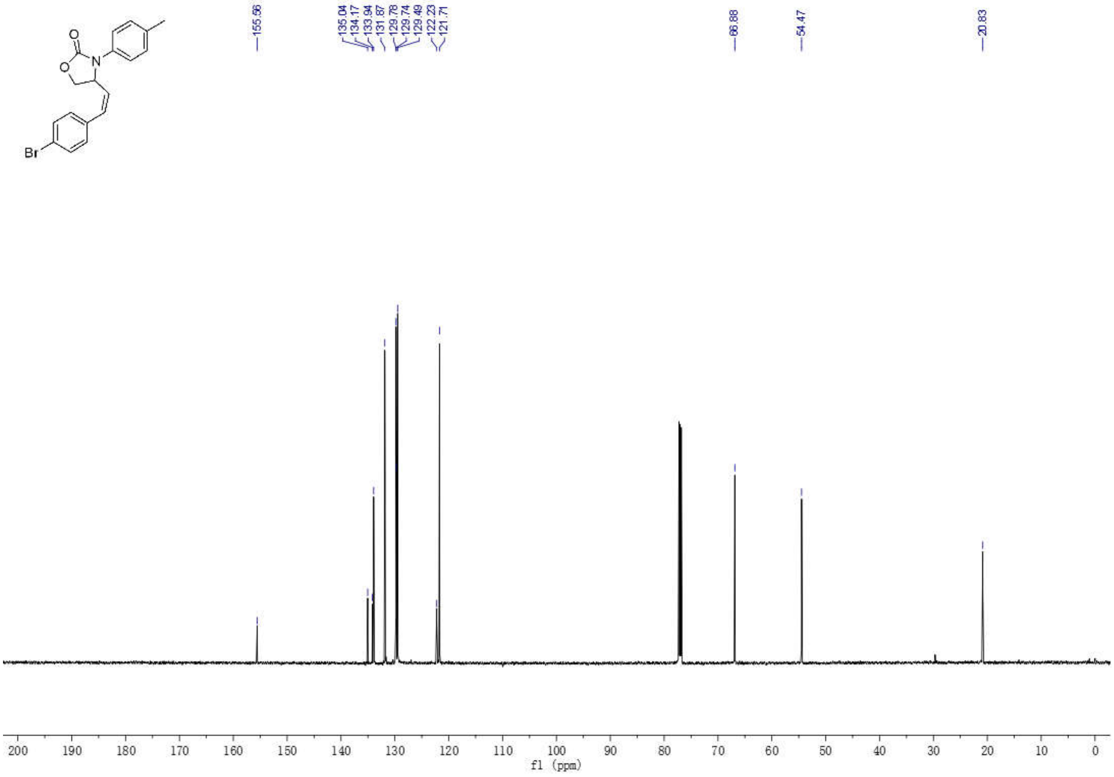
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **2g**



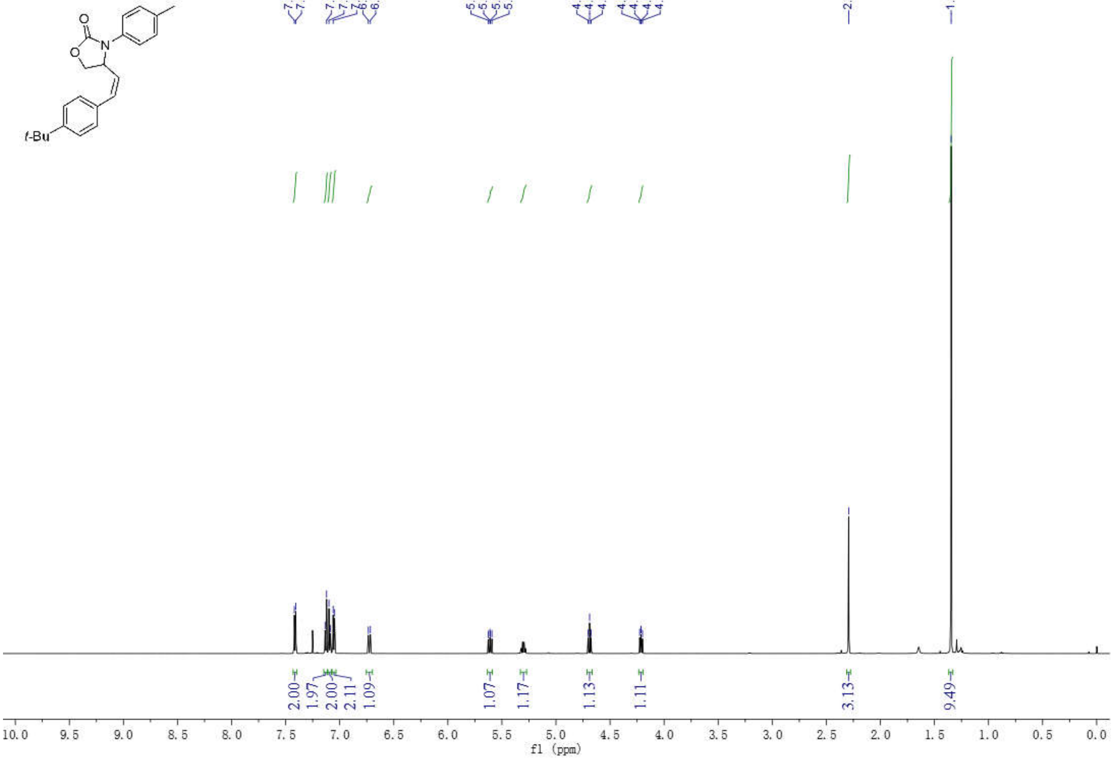
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2h**



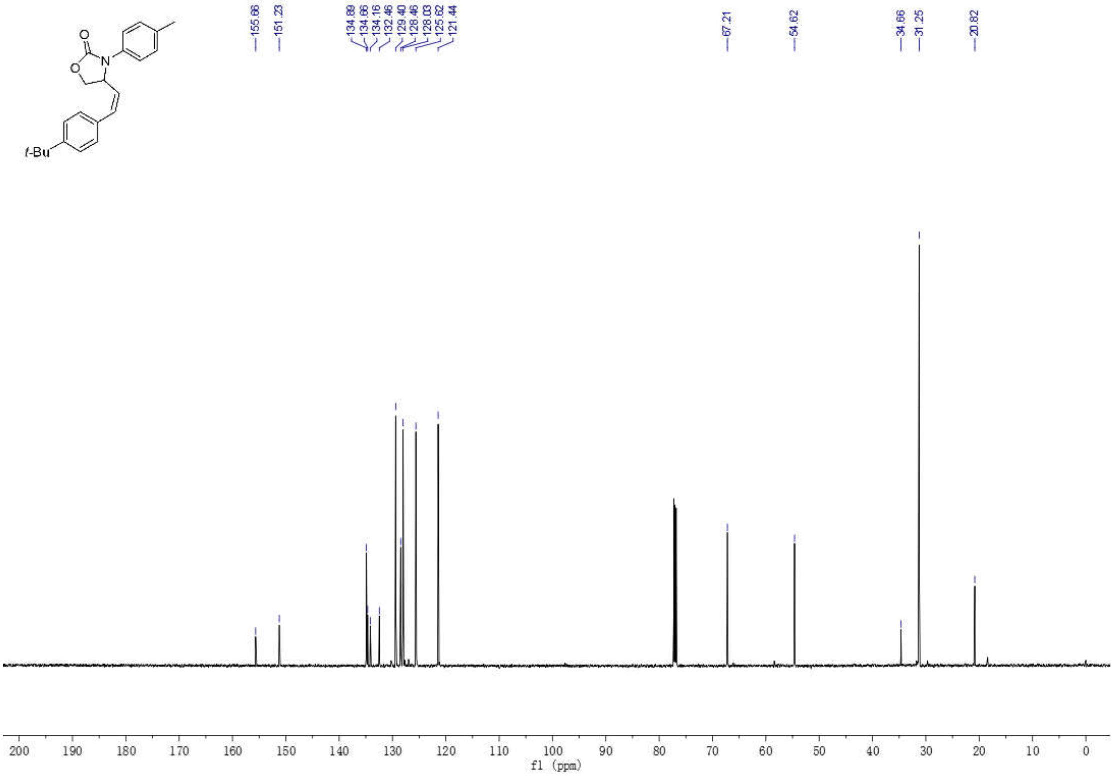
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2h**



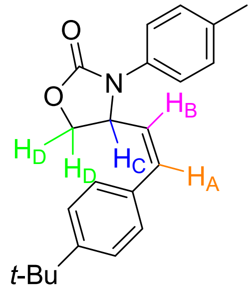
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **2i**

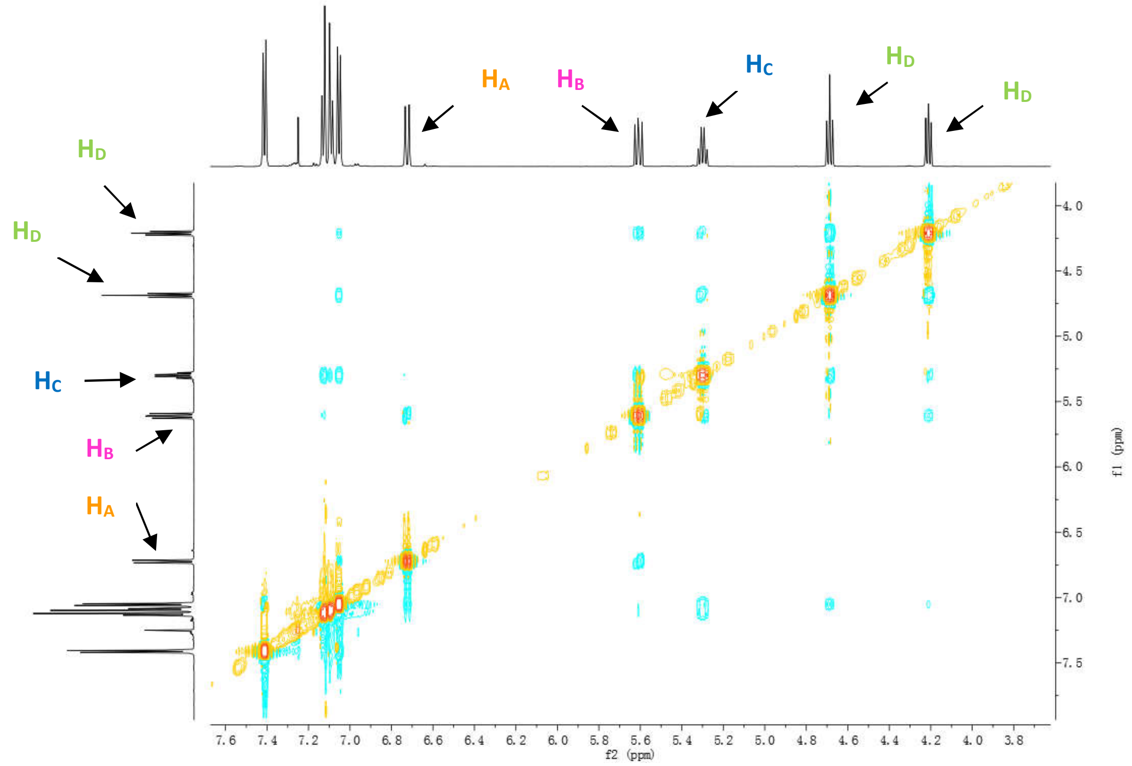


^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **2i**

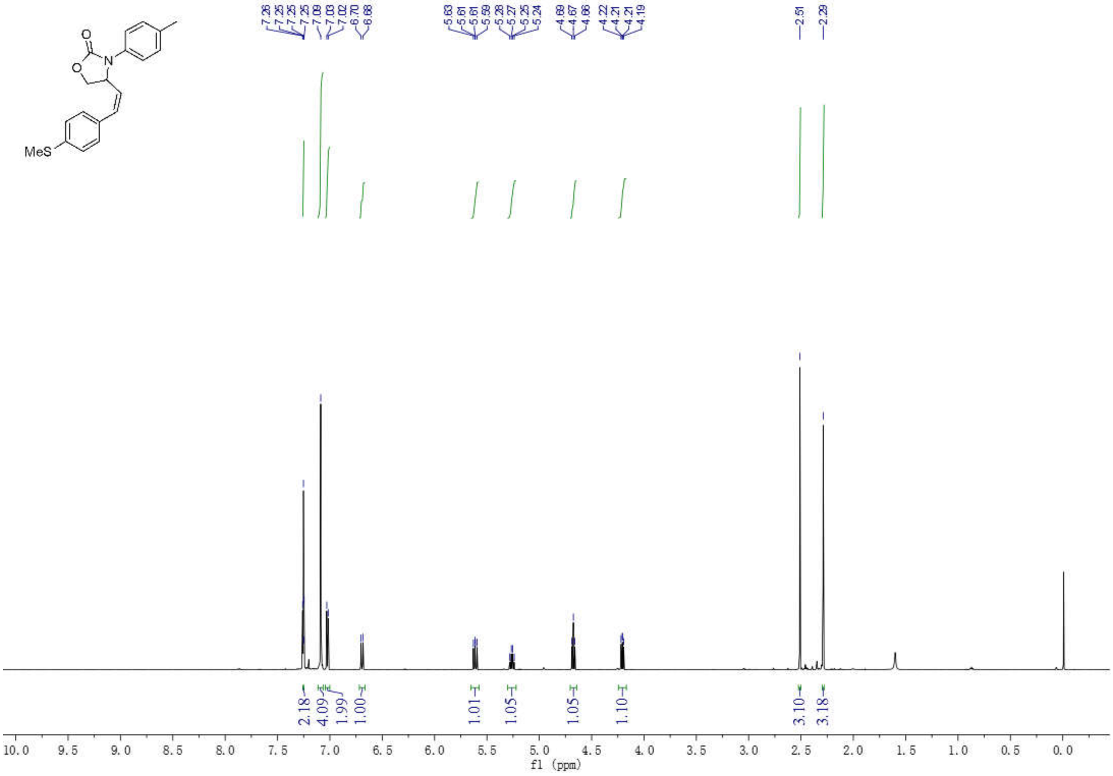


2D-NOE spectrum of **2i**

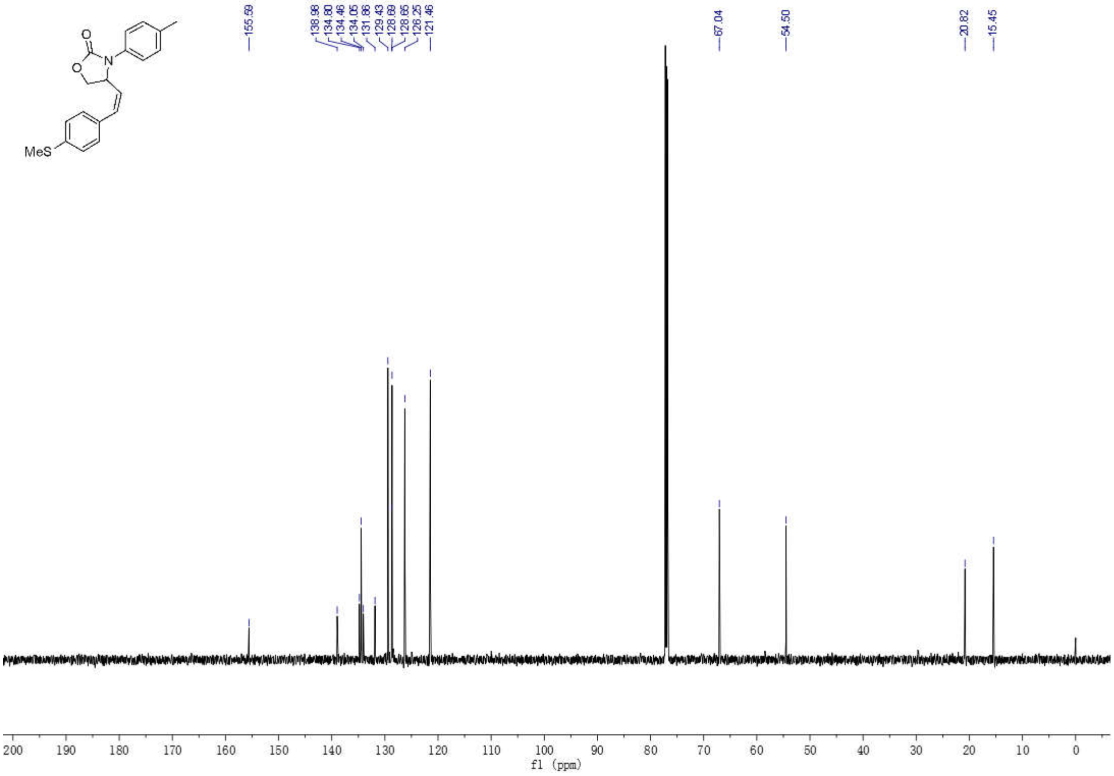




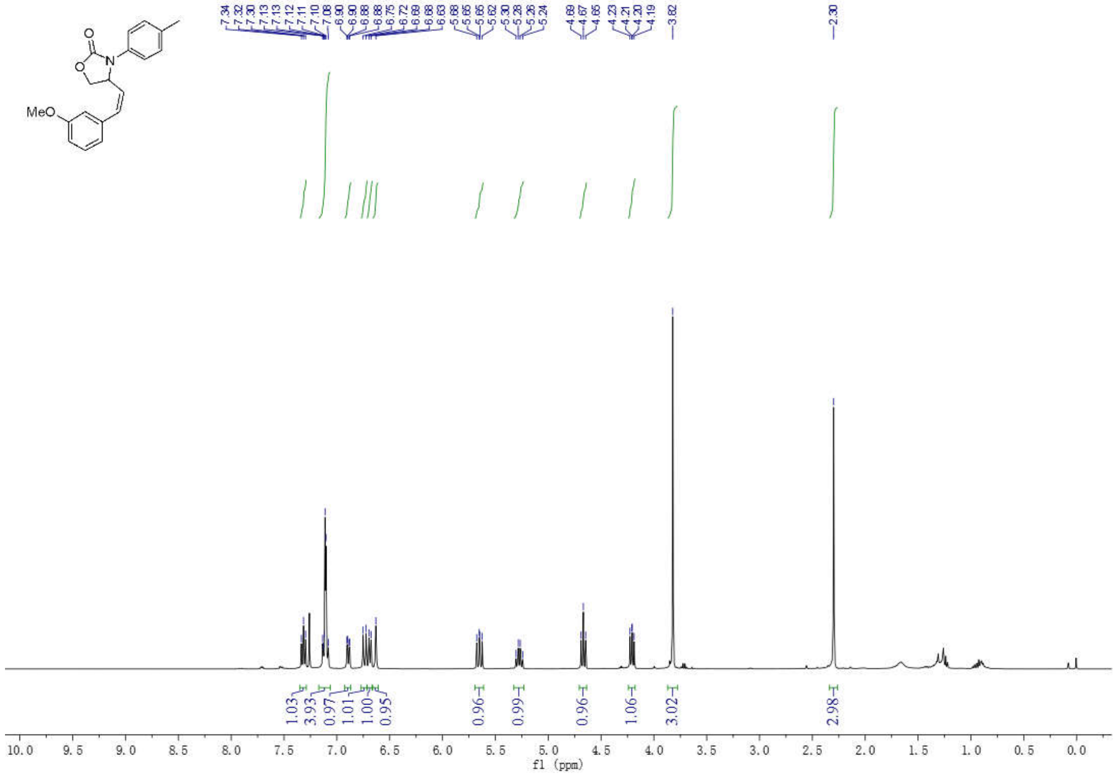
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **2j**



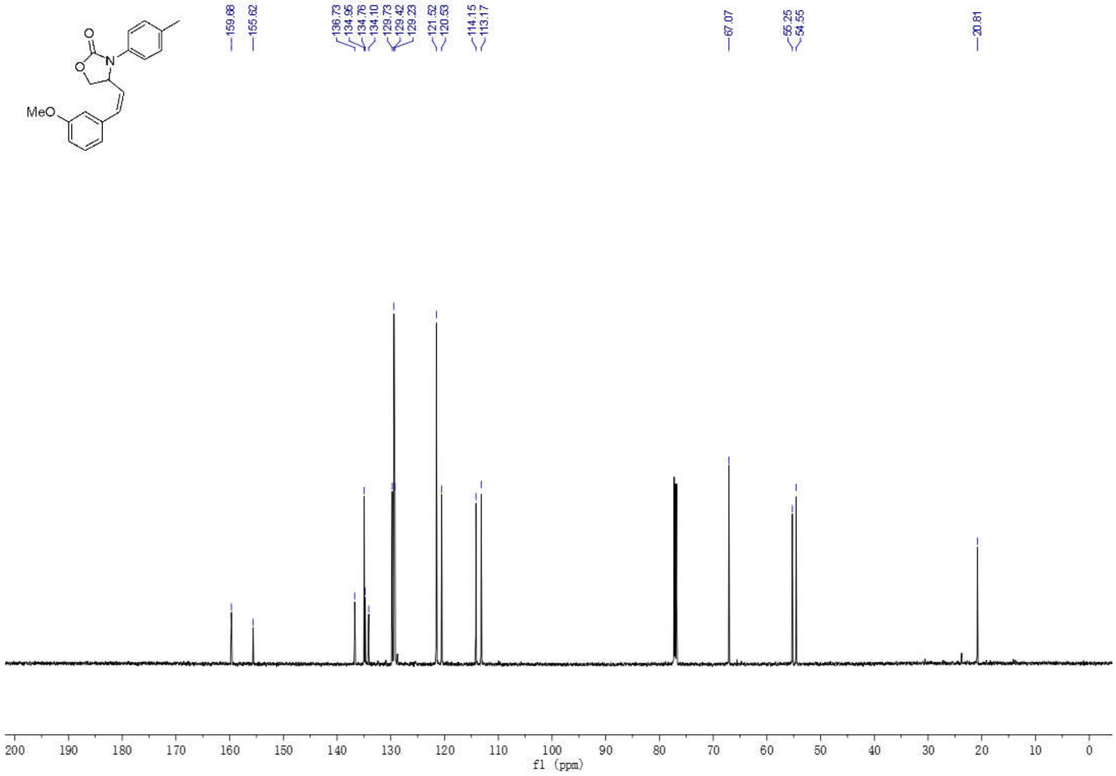
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **2j**



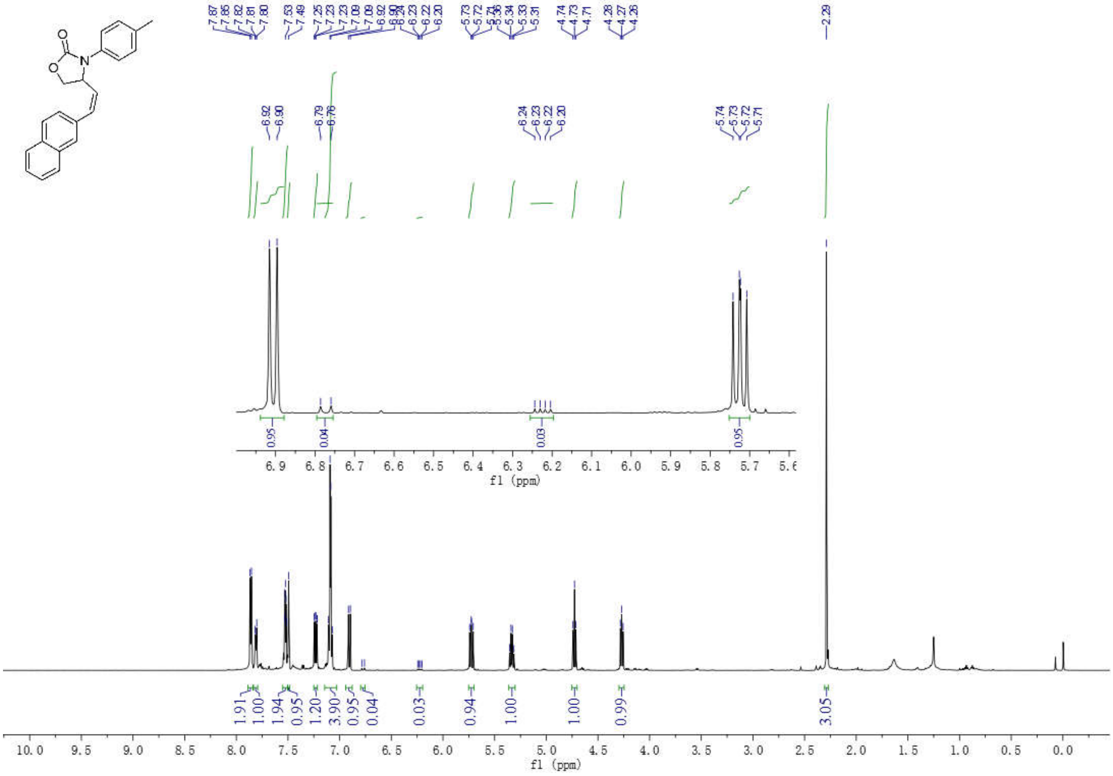
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **2k**



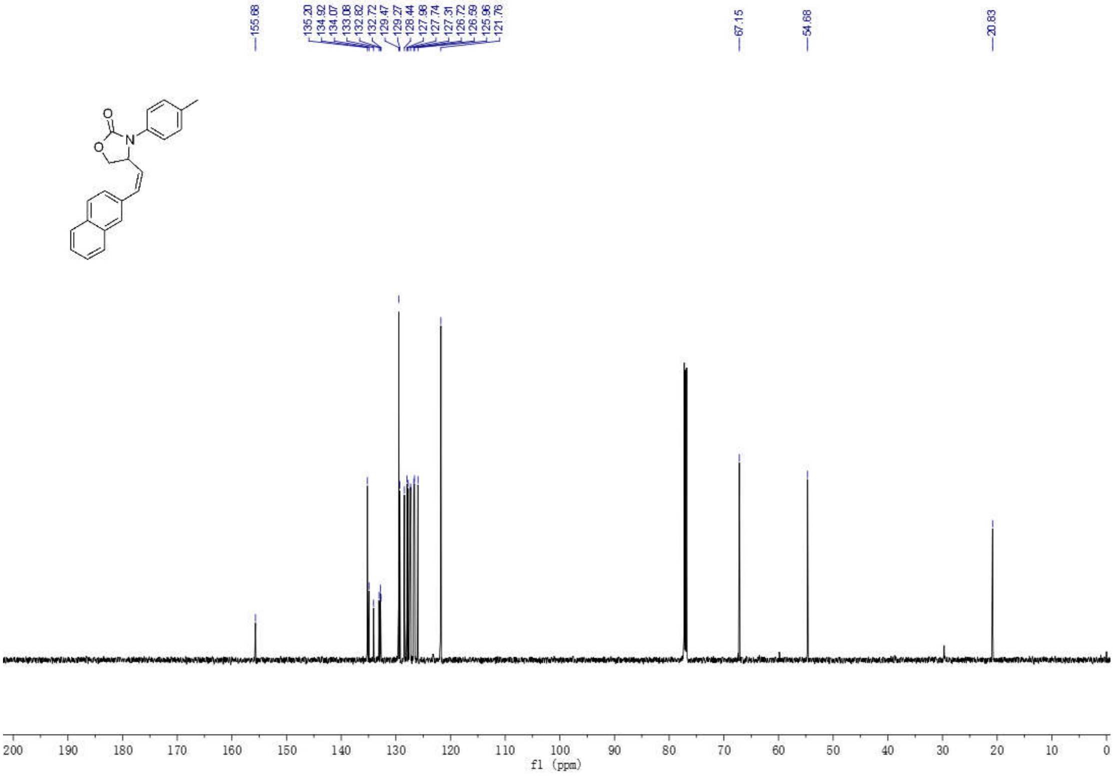
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **2k**



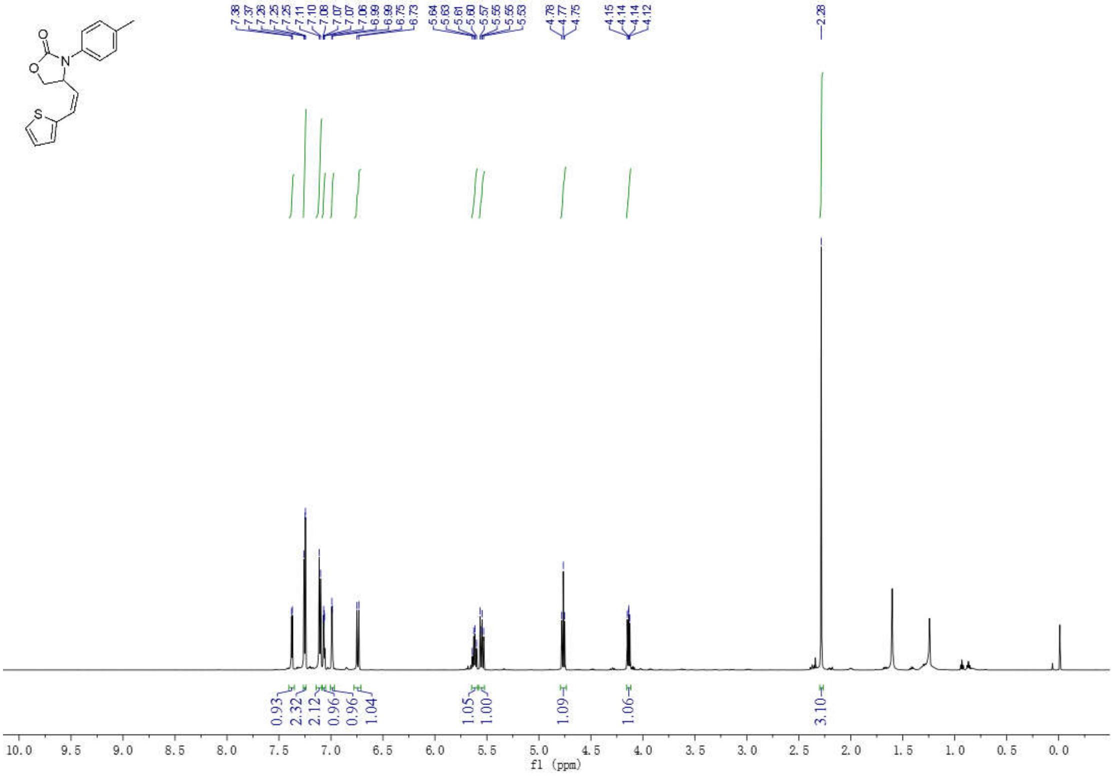
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2l**



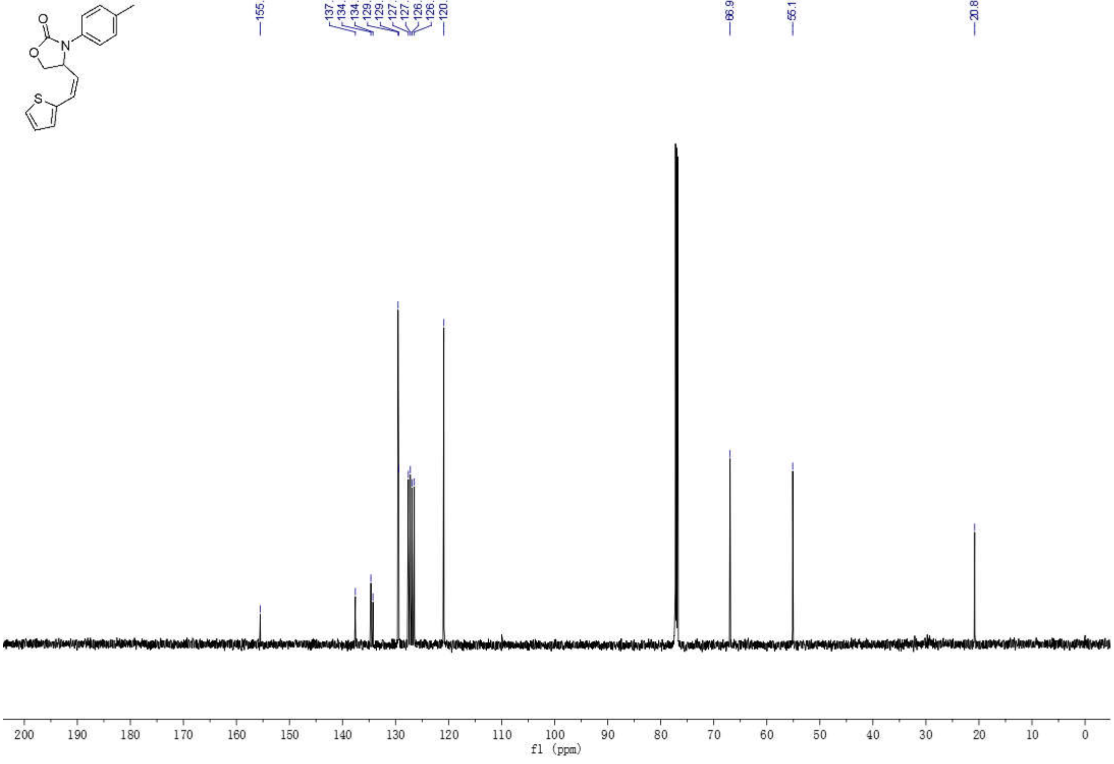
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2l**



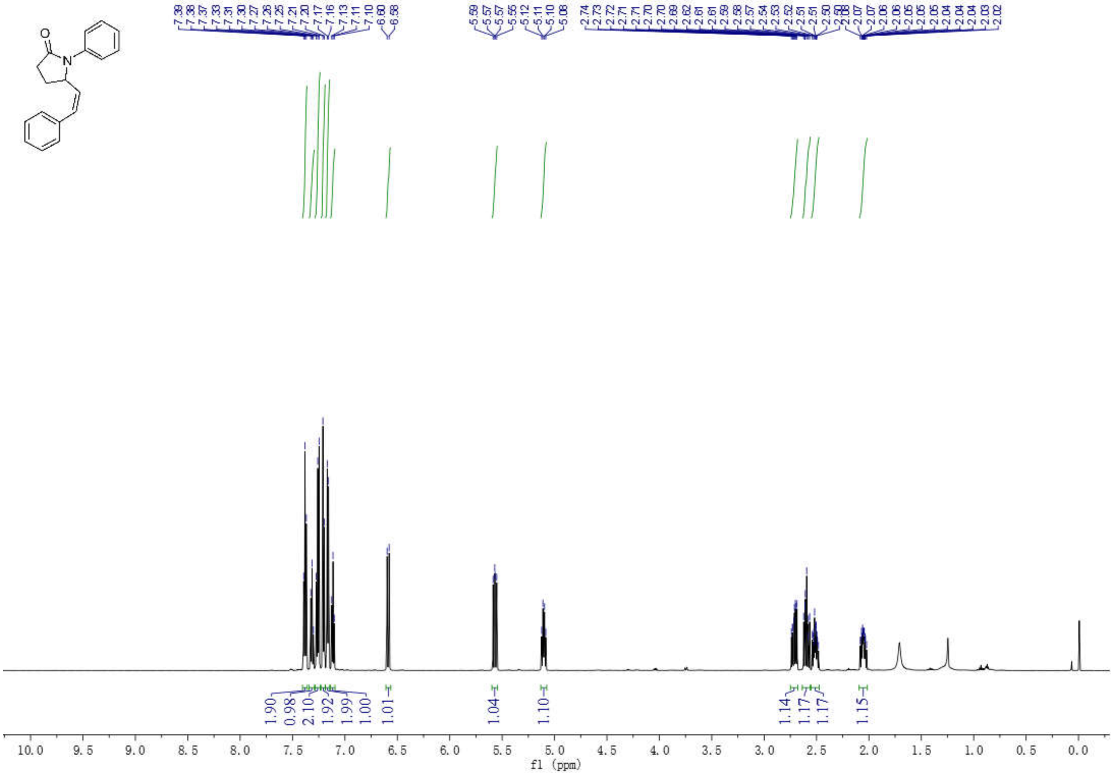
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **2m**



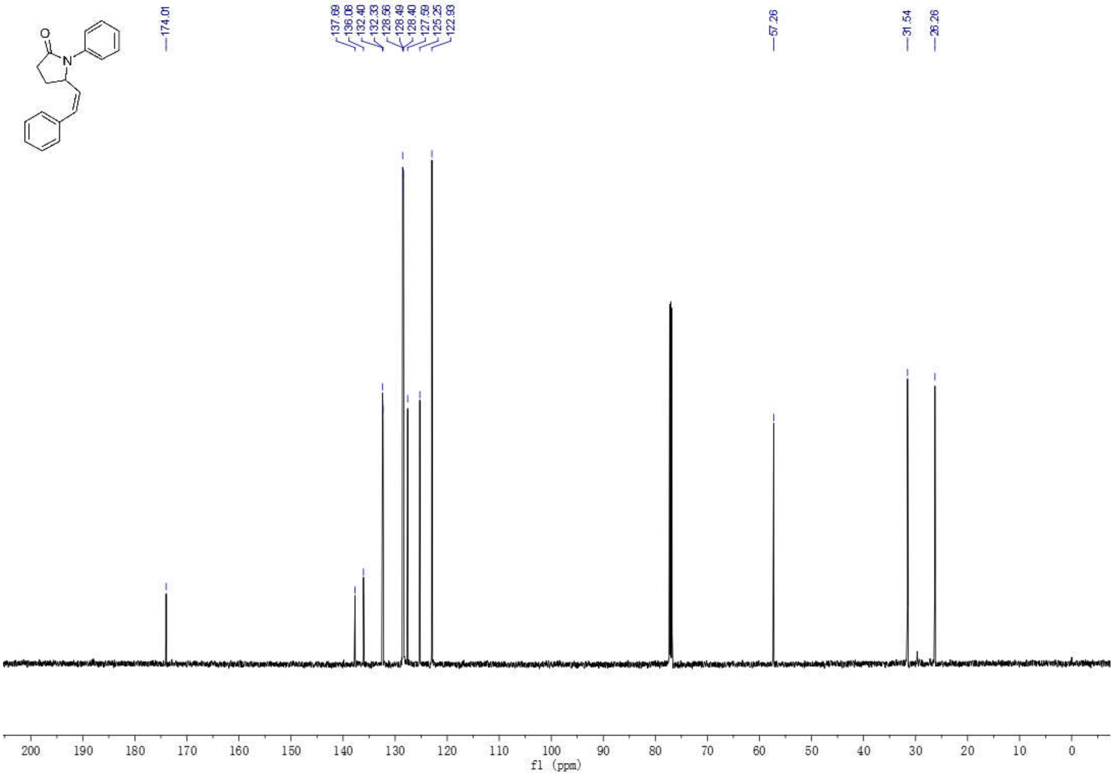
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2m**



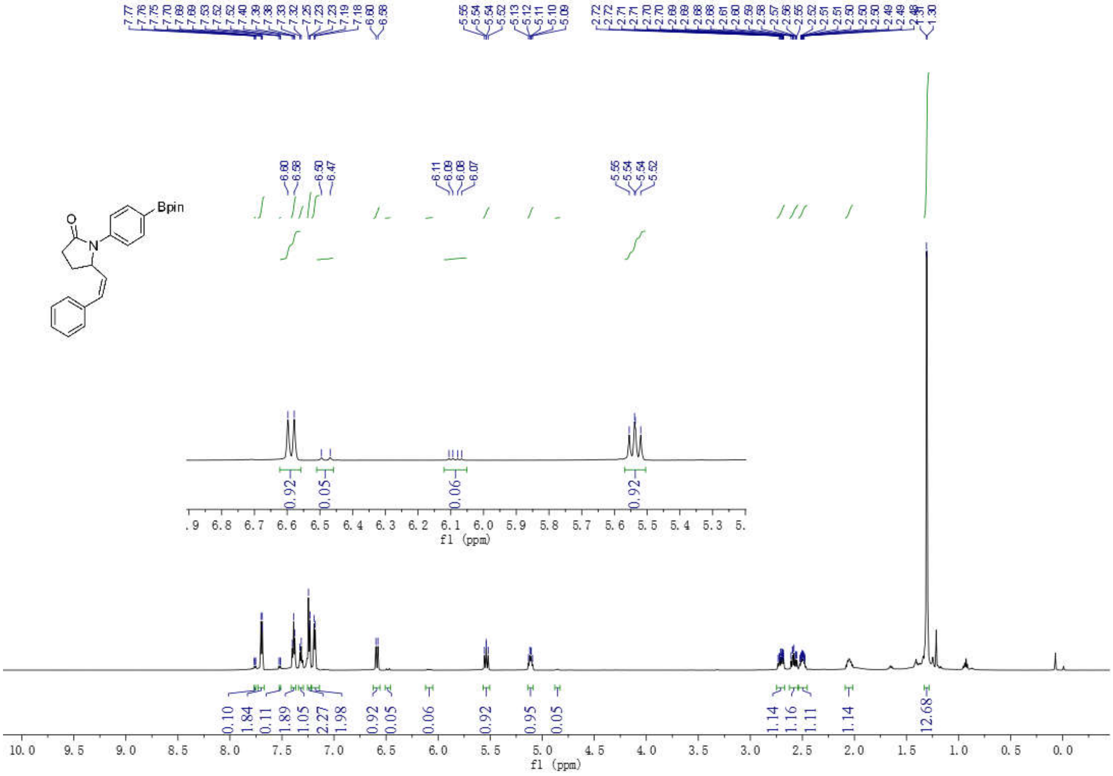
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2n**



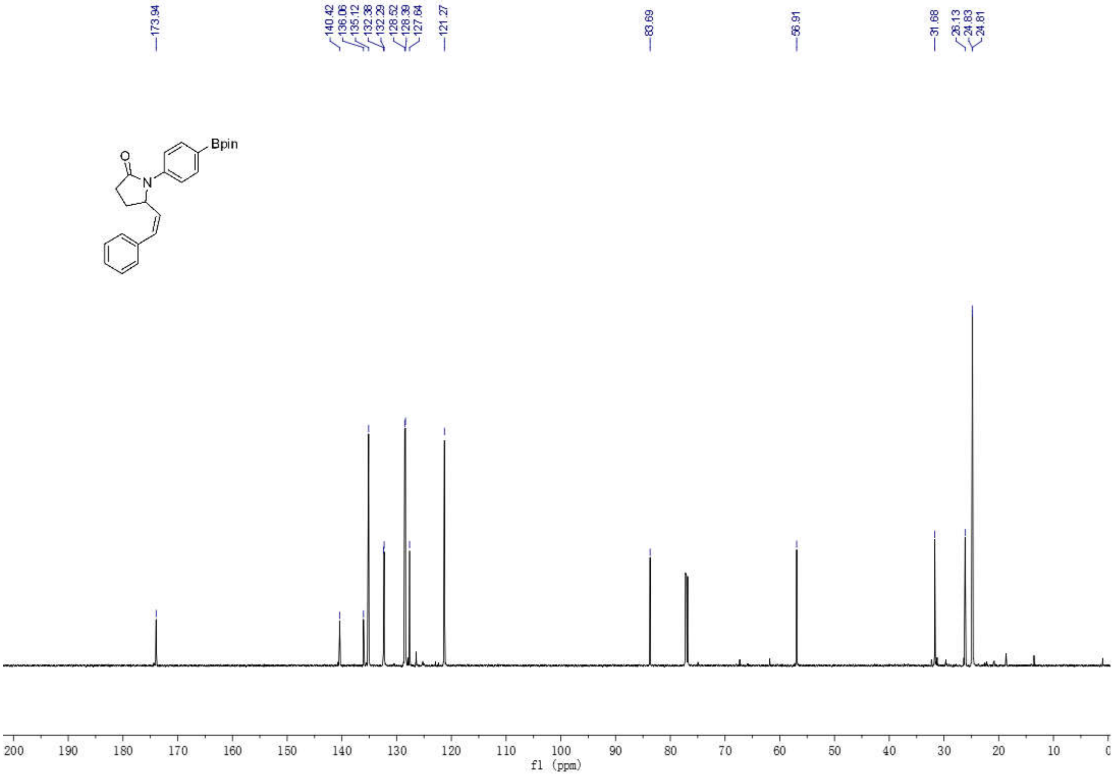
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2n**



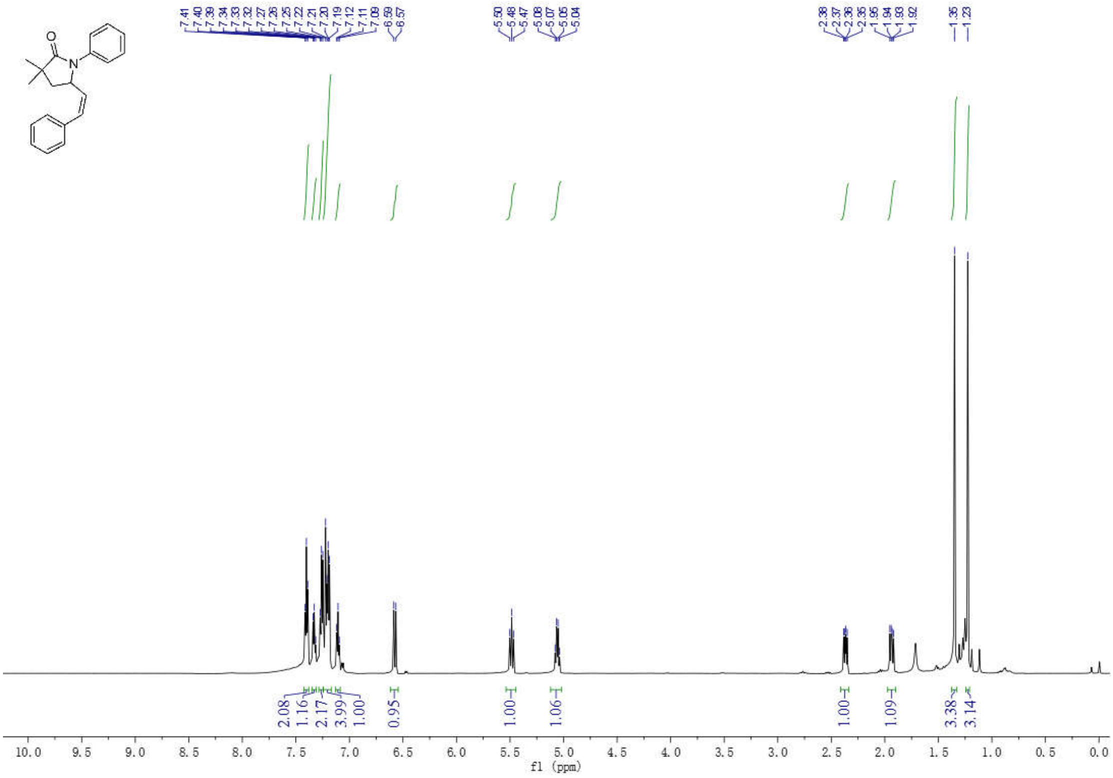
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **2o**



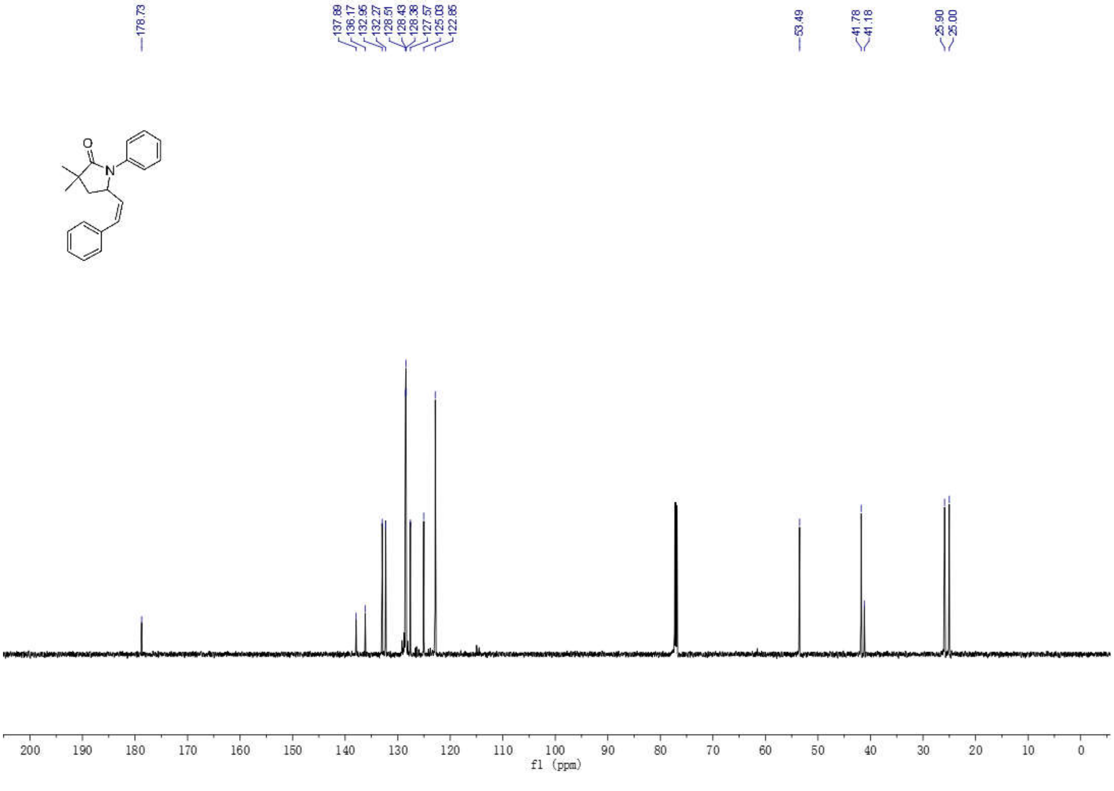
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **2o**



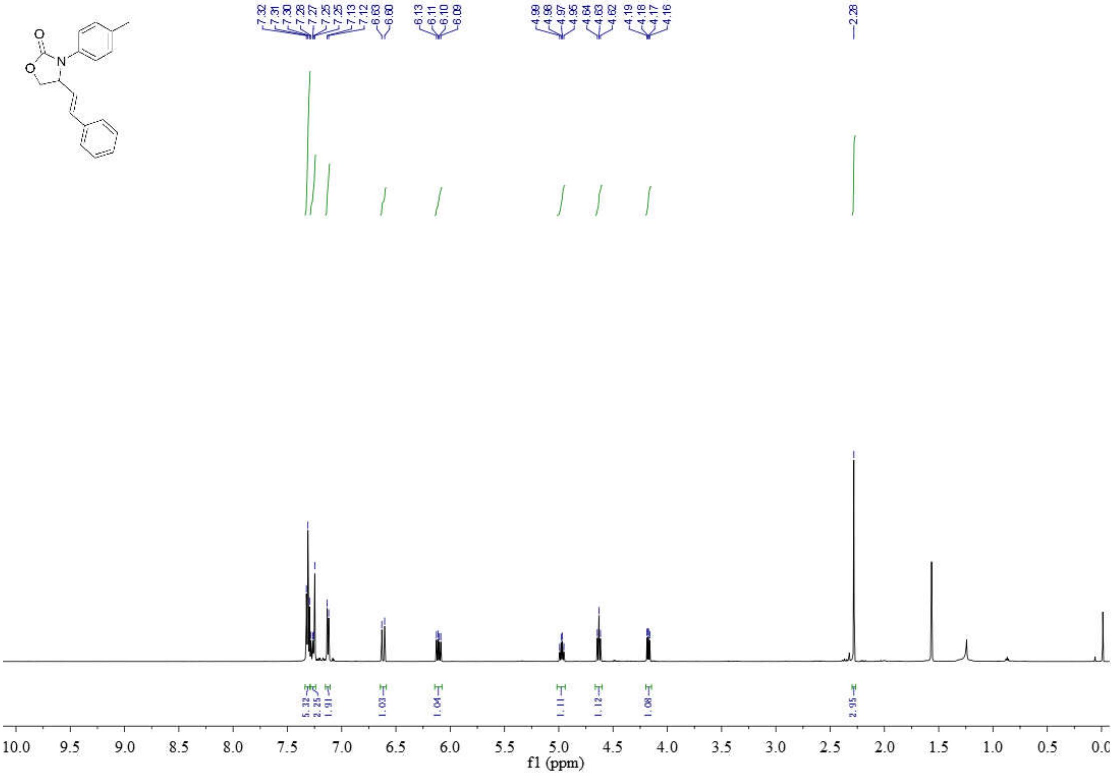
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **2p**



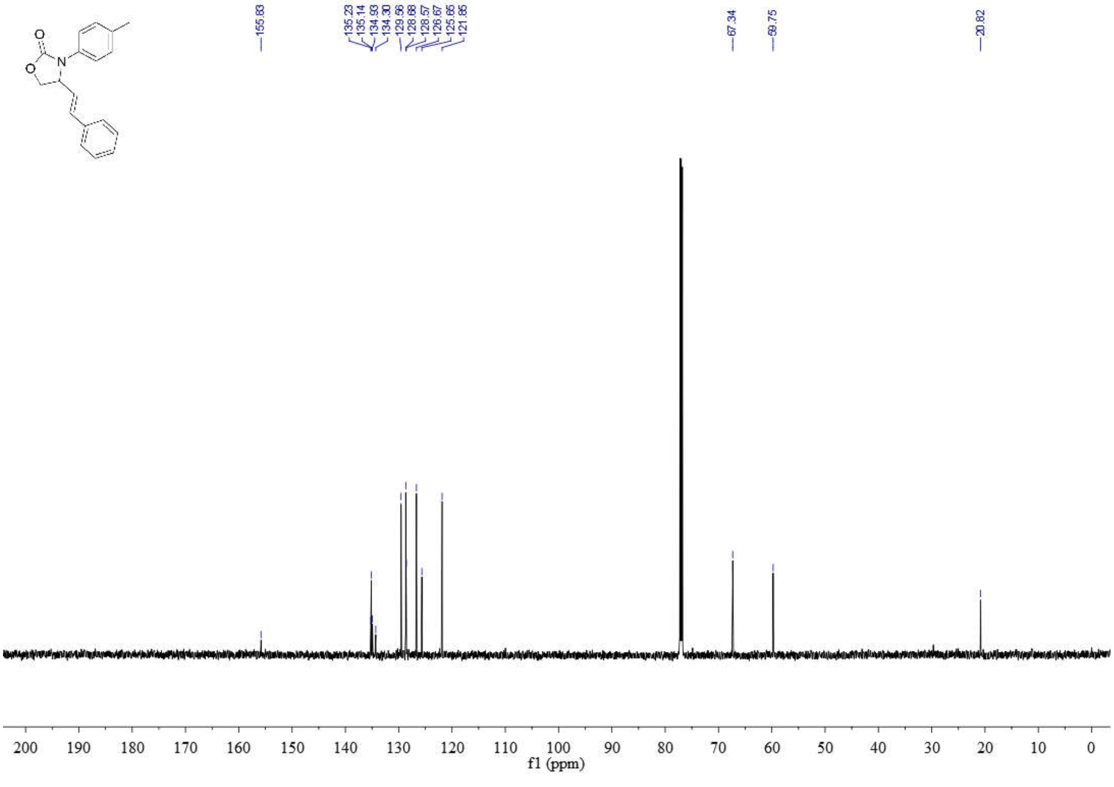
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **2p**



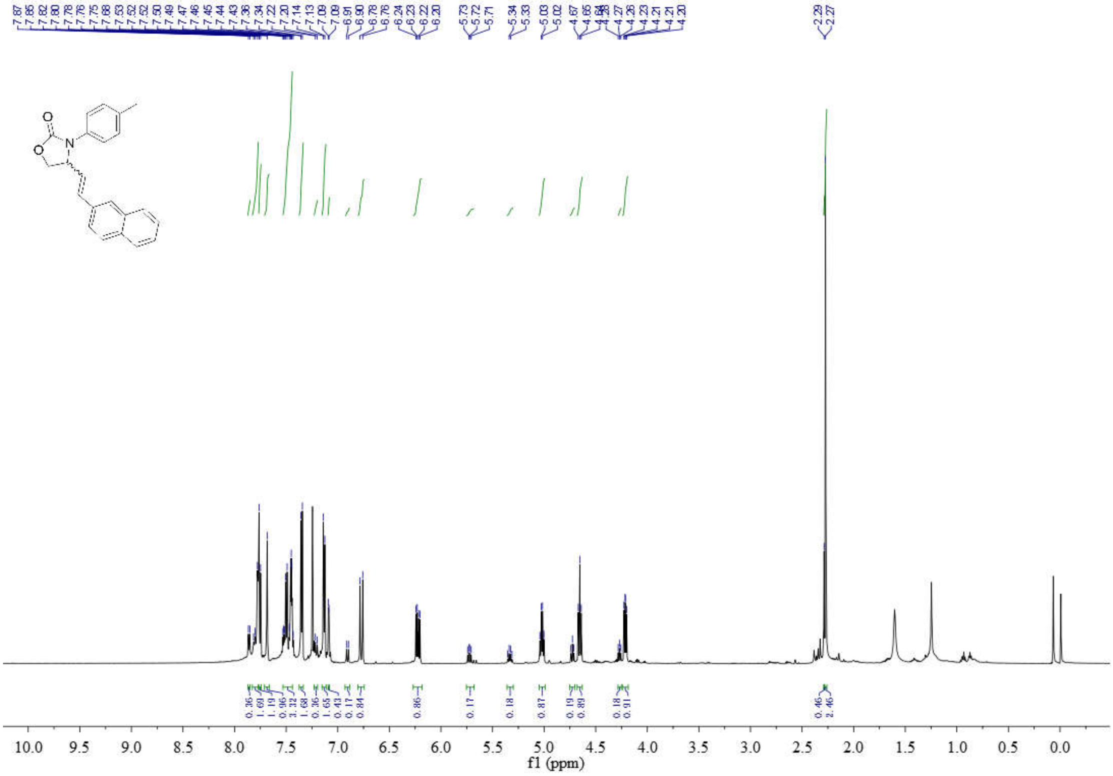
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **3**



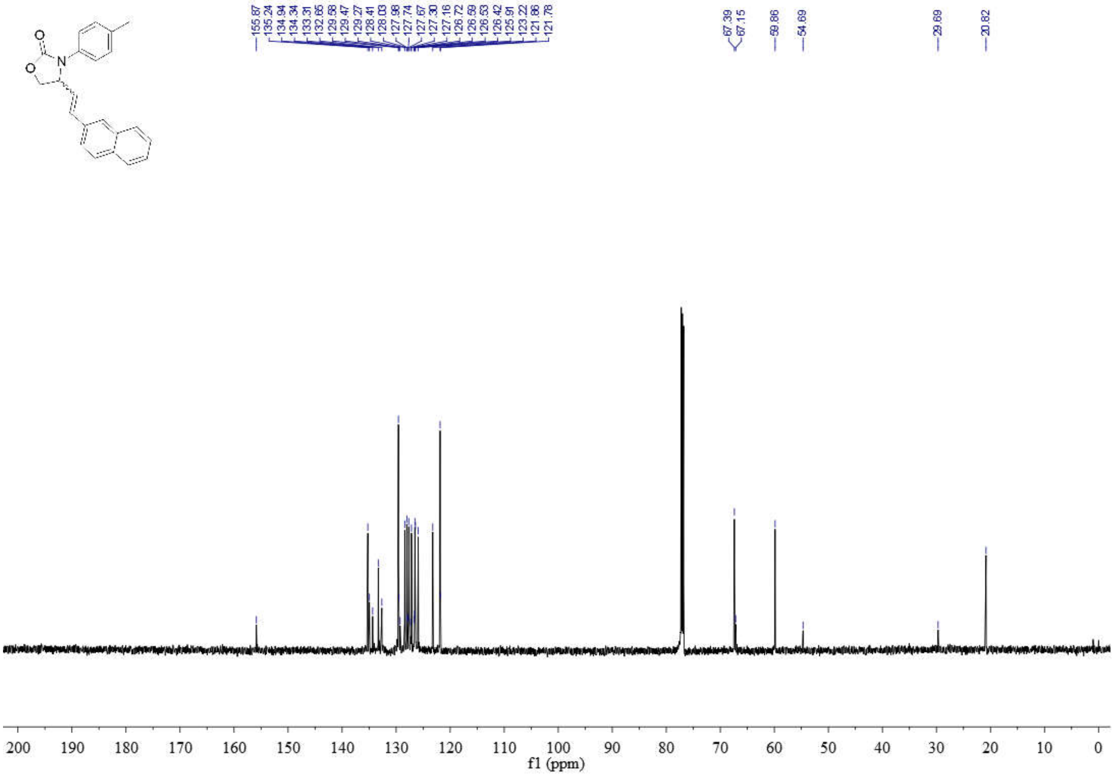
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **3**



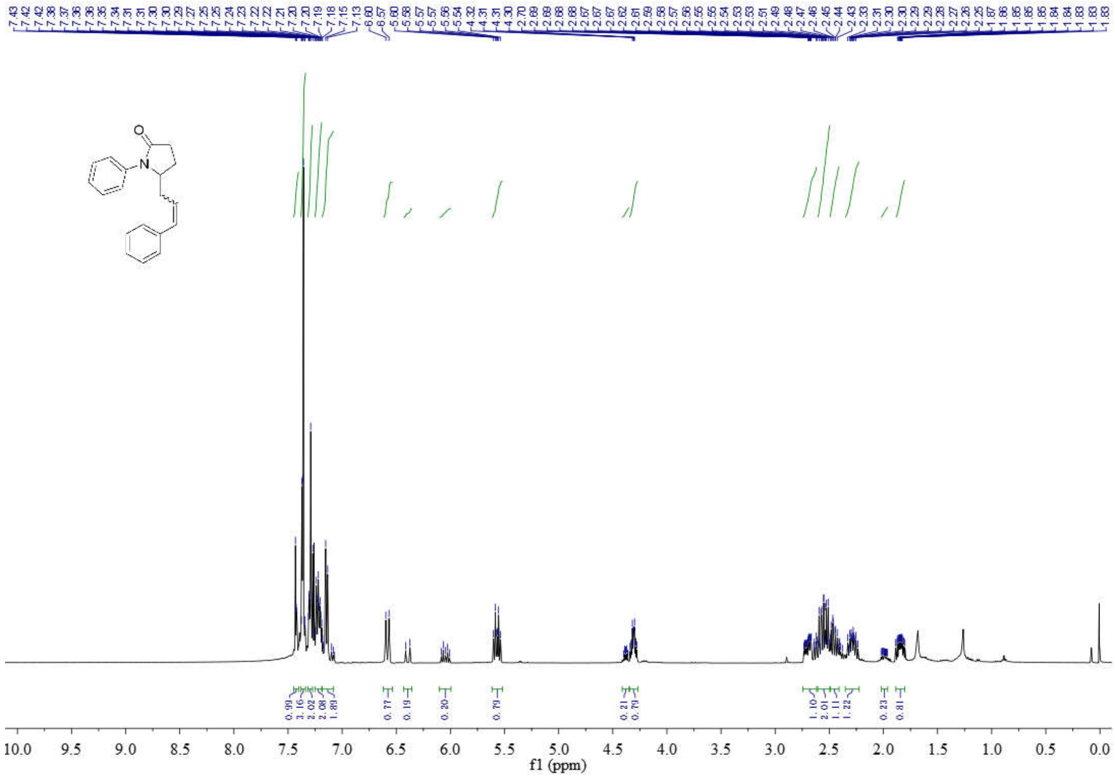
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4**



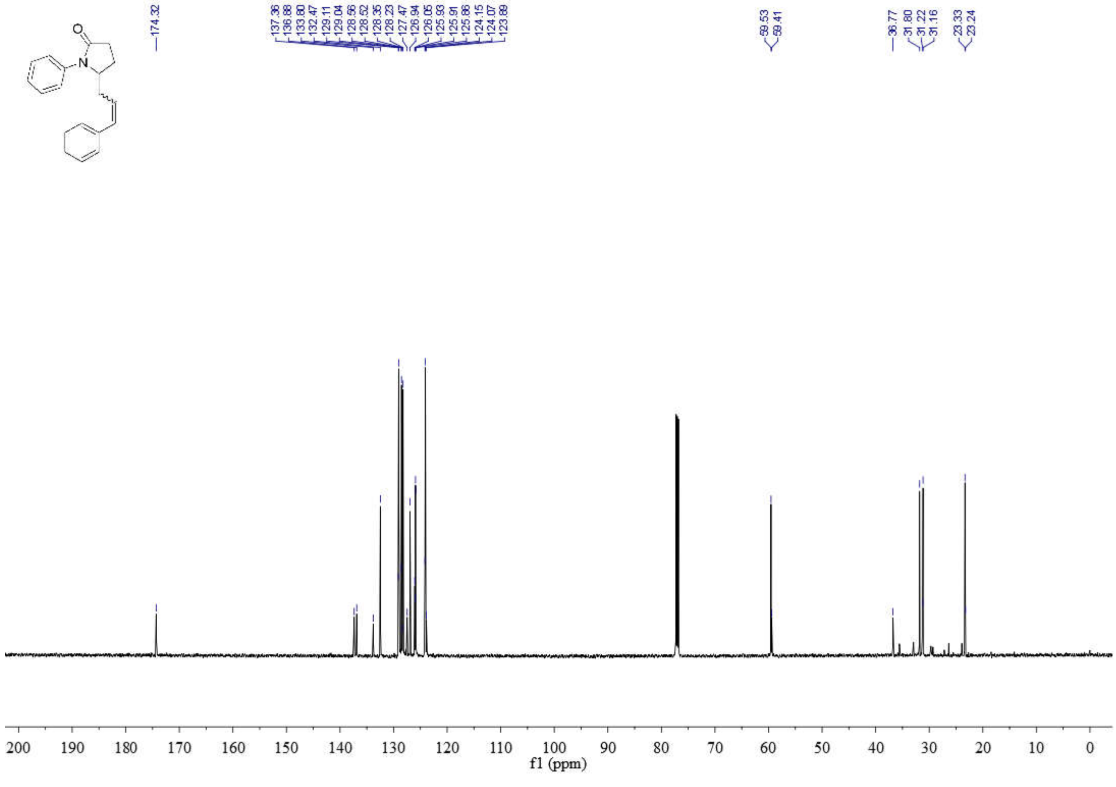
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **4**



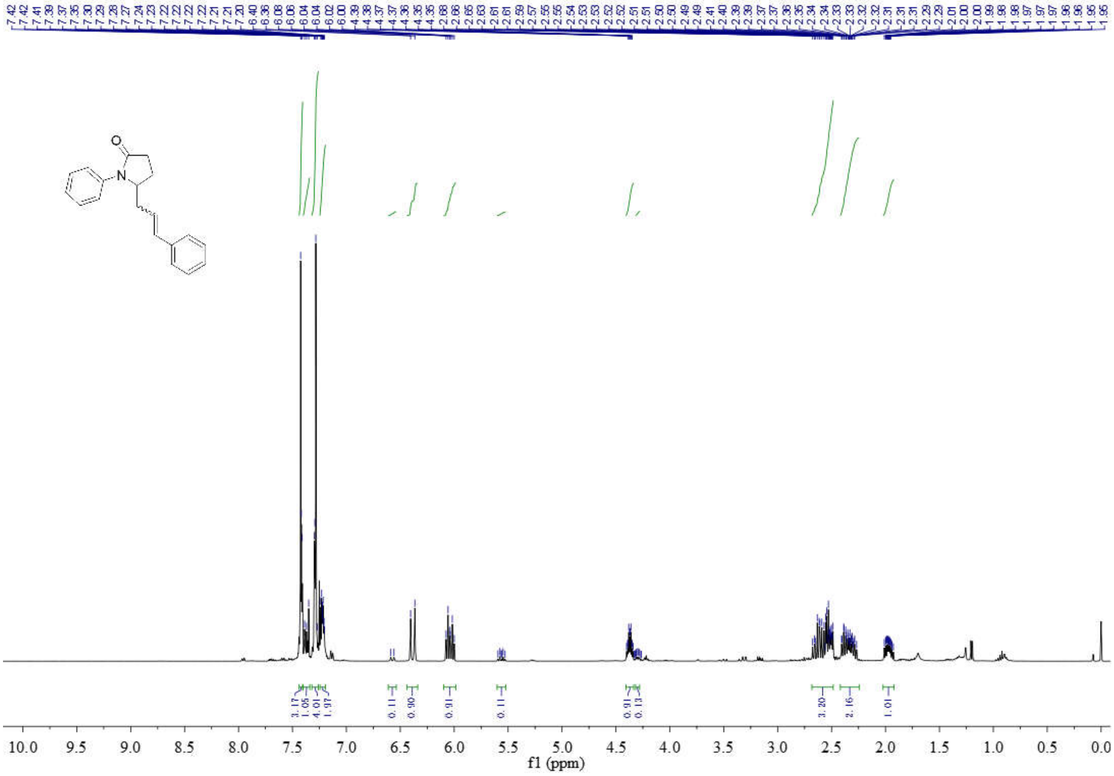
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **5**



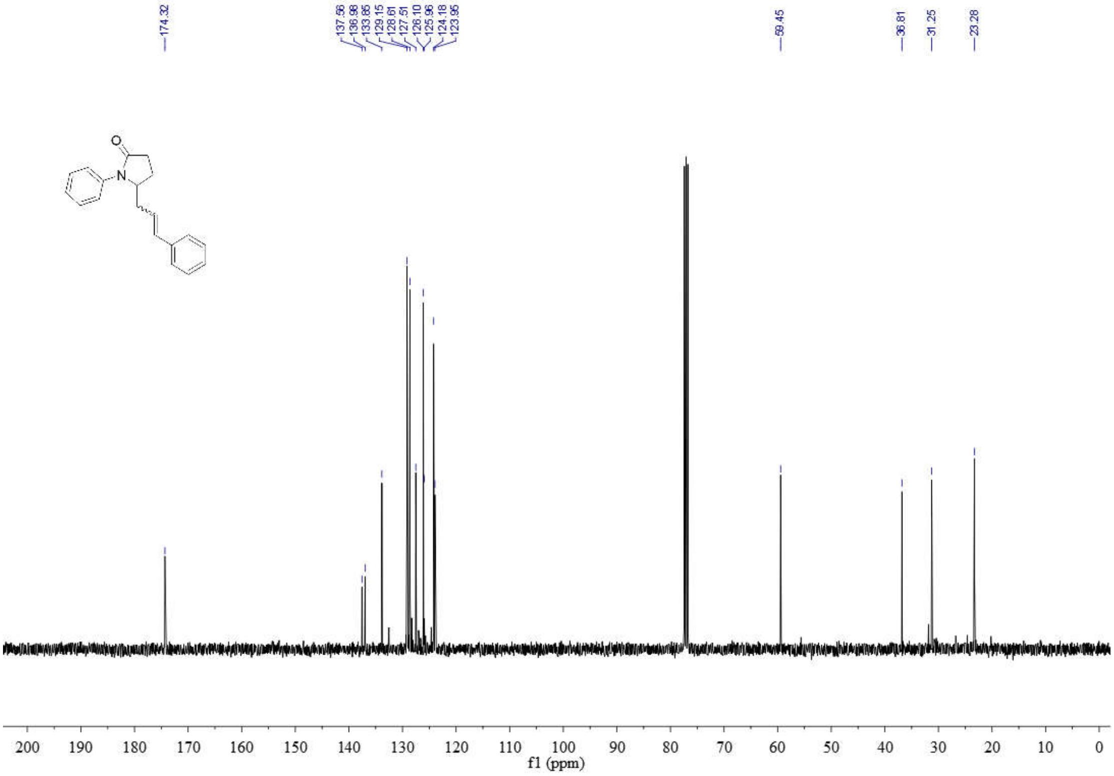
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **5**



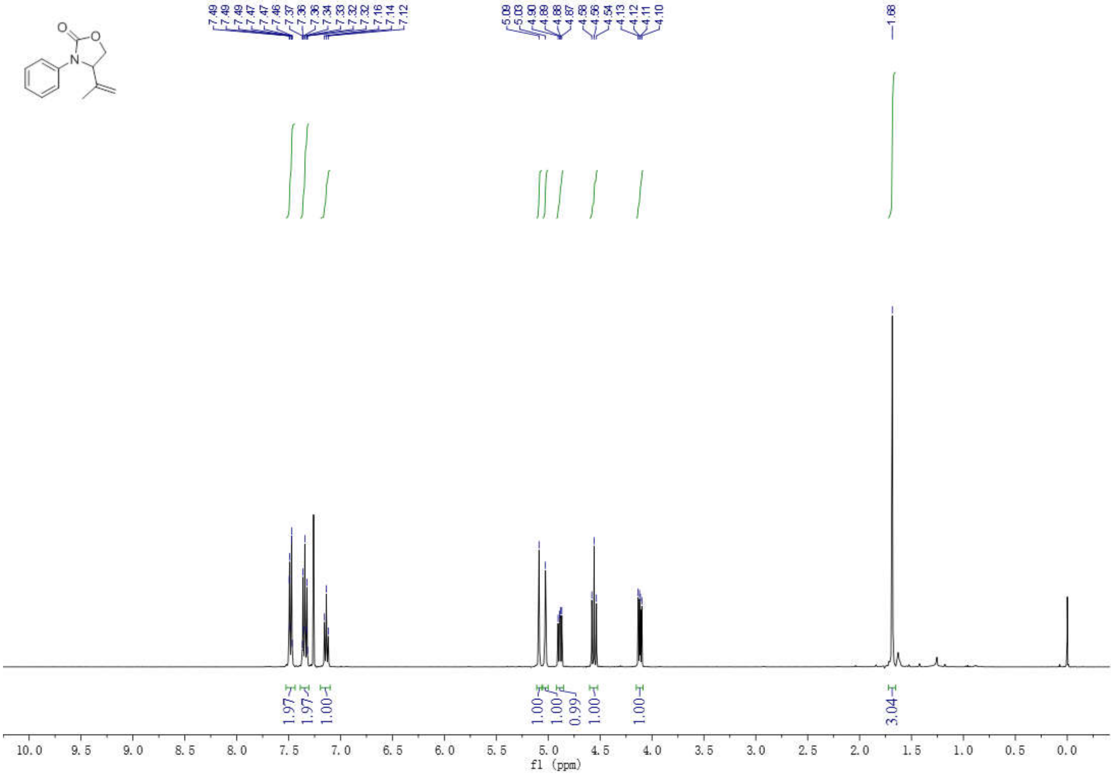
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **6**



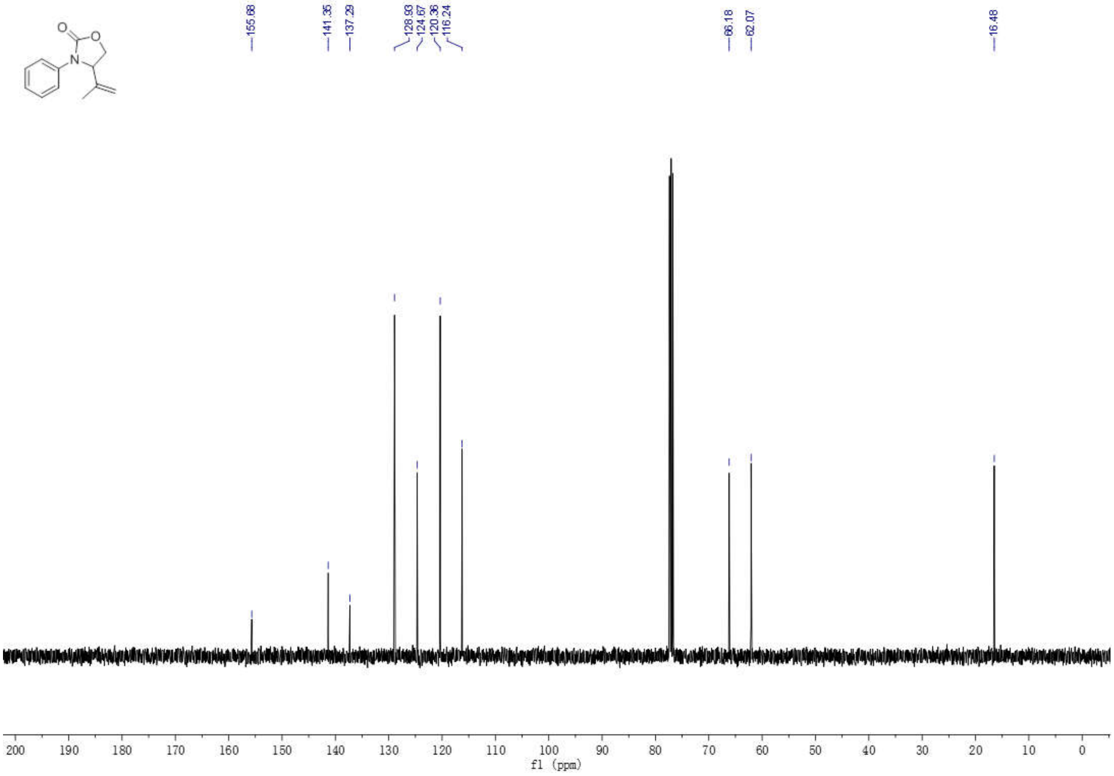
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **6**



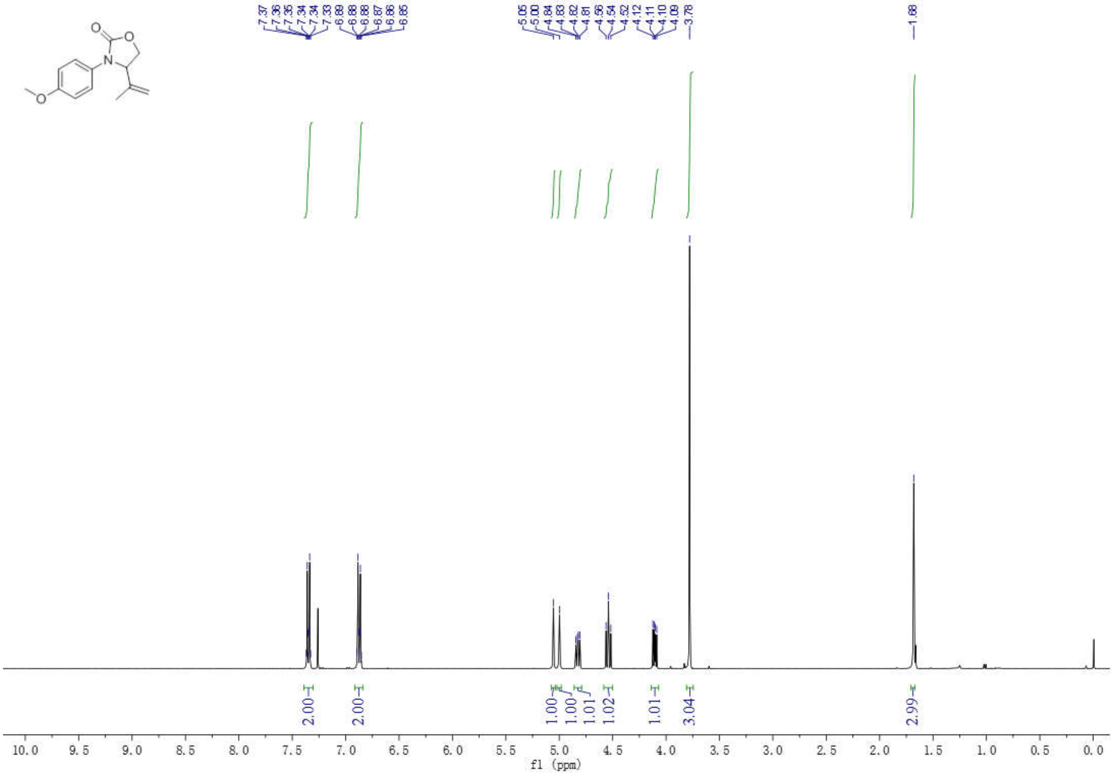
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8a**



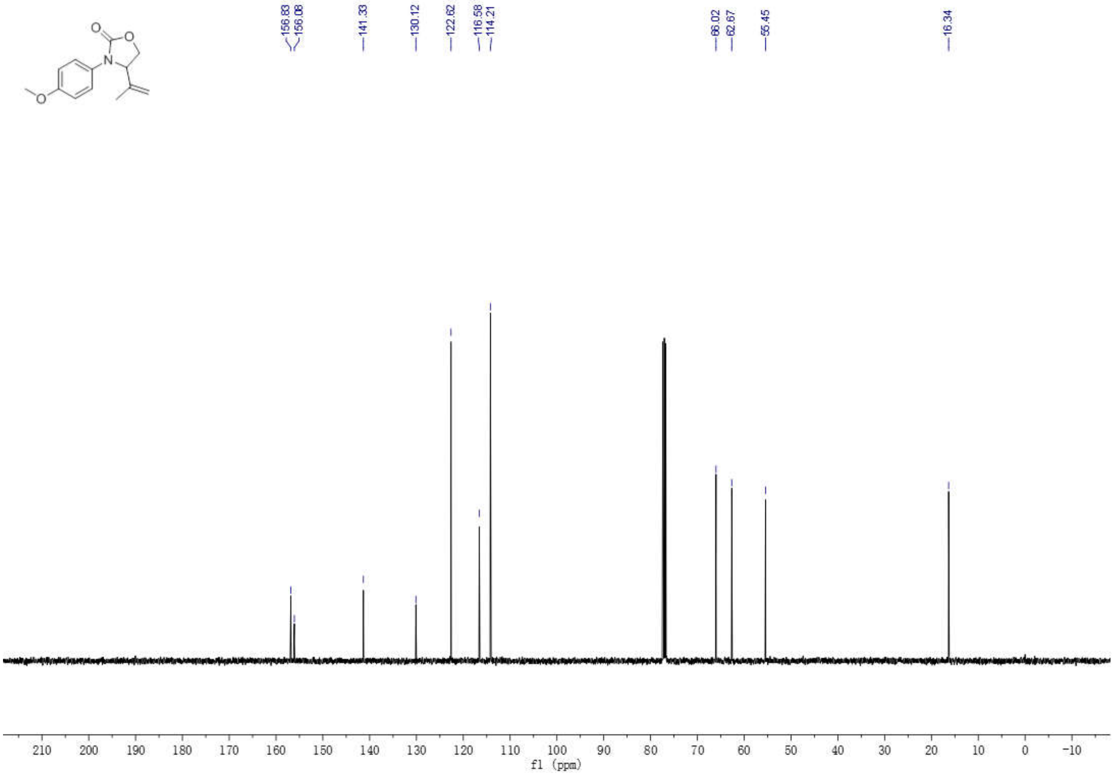
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8a**



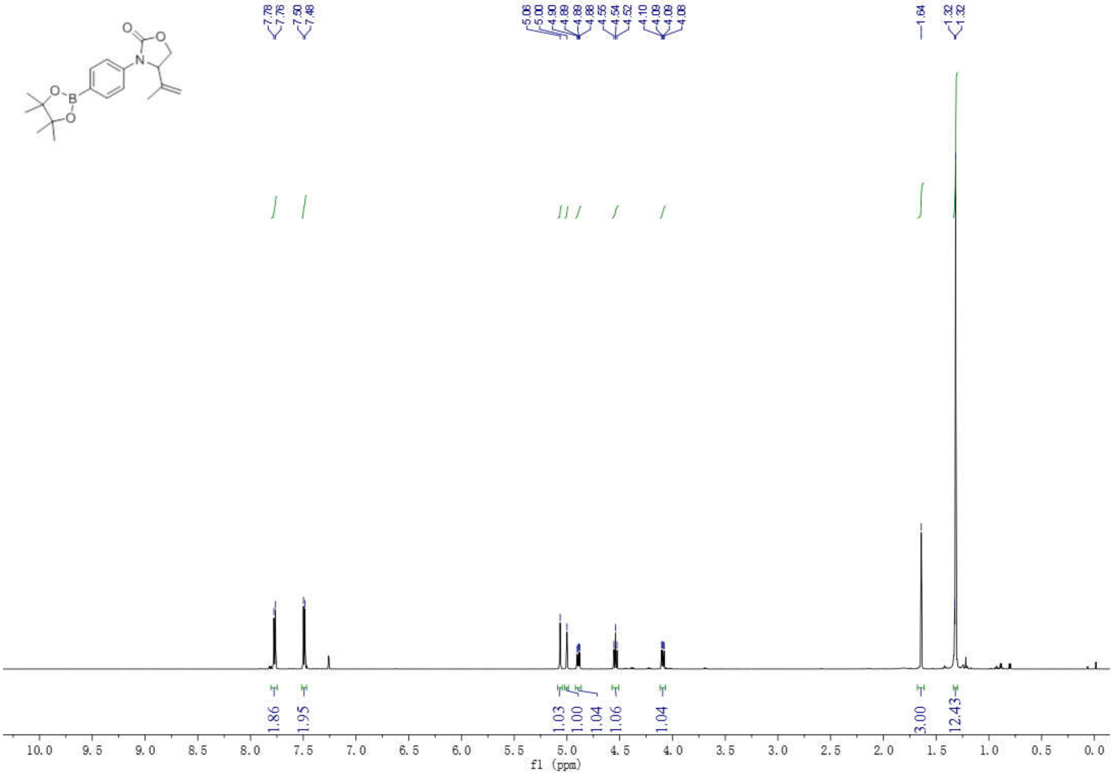
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8b**



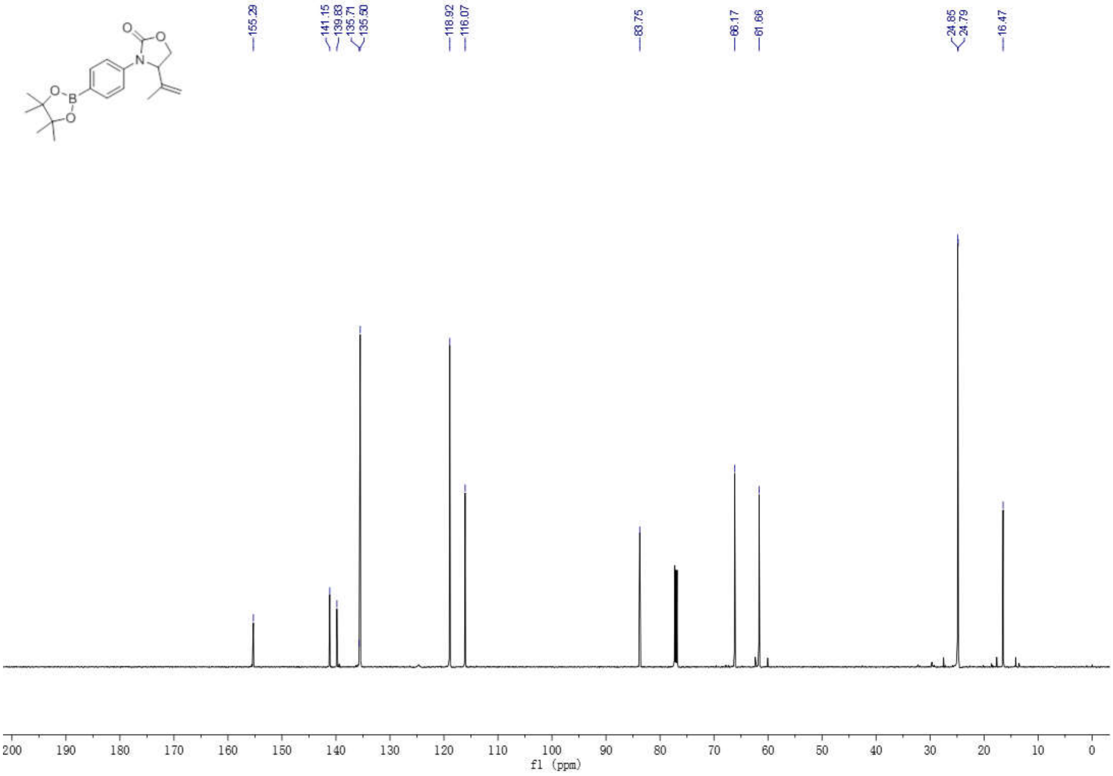
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8b**



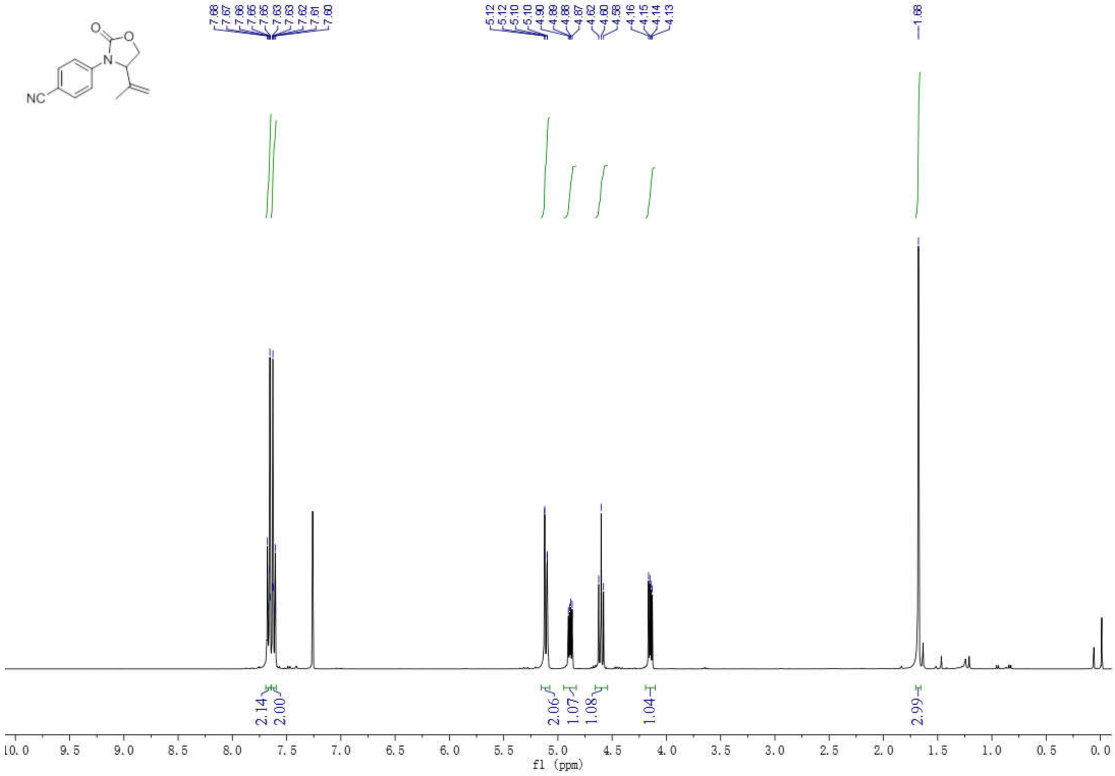
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8c**



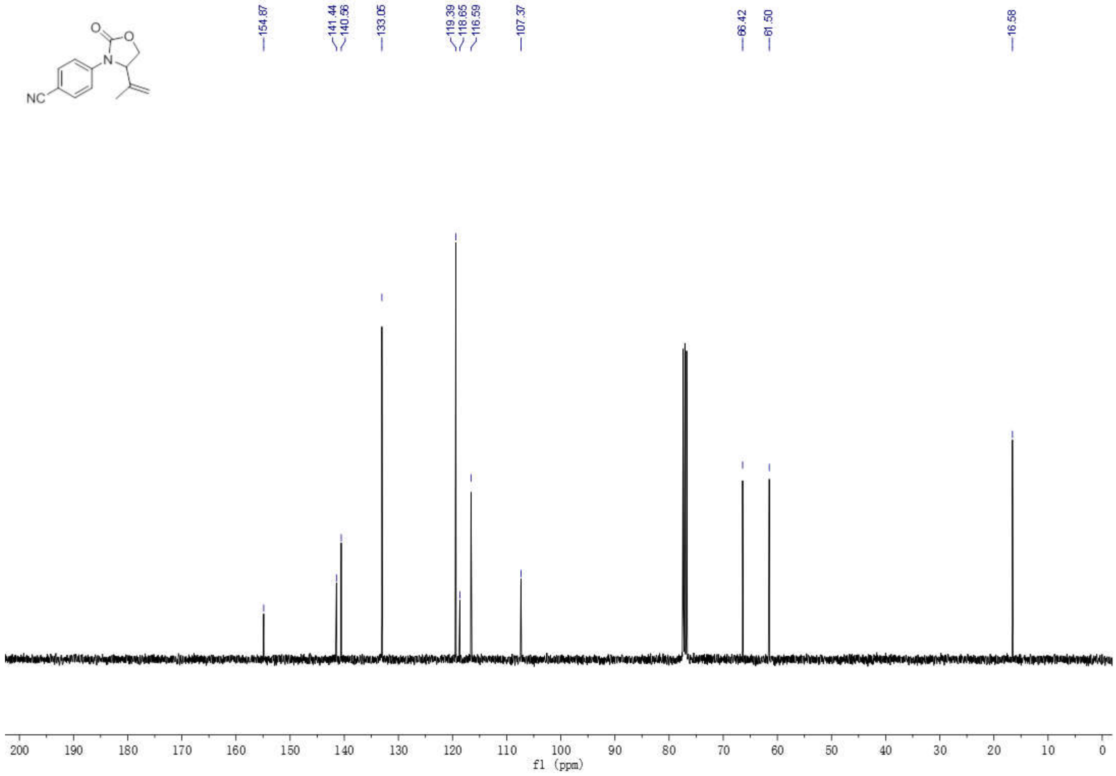
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8c**



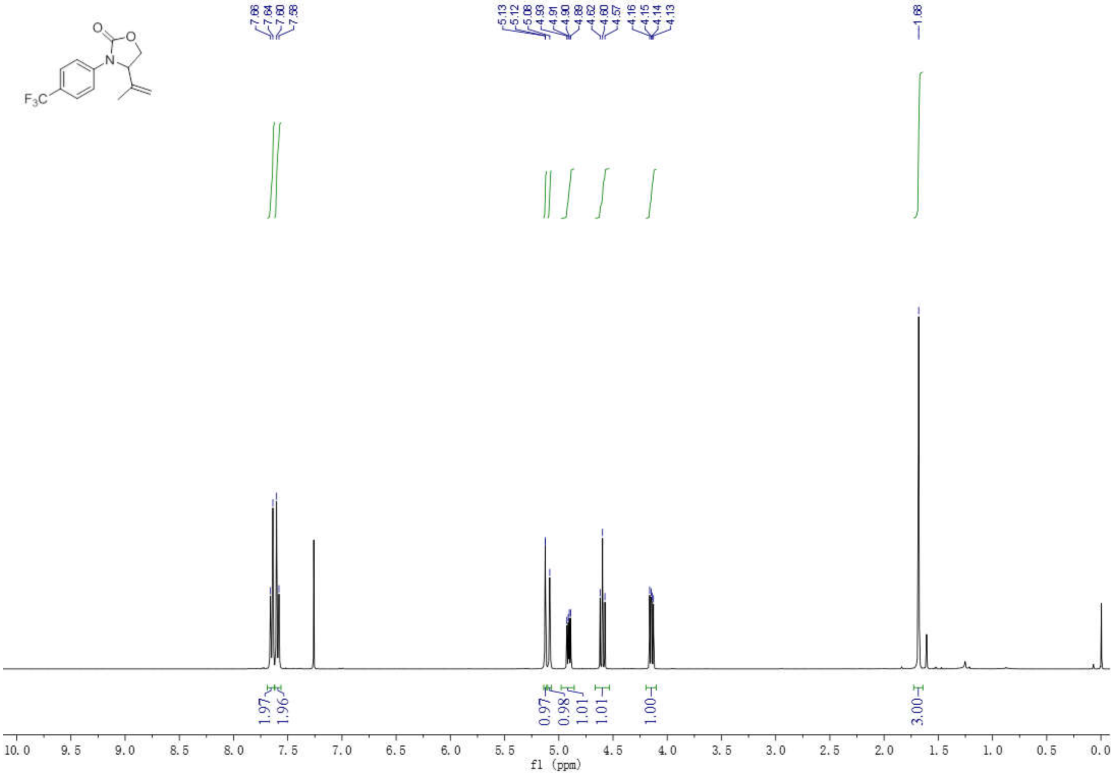
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8d**



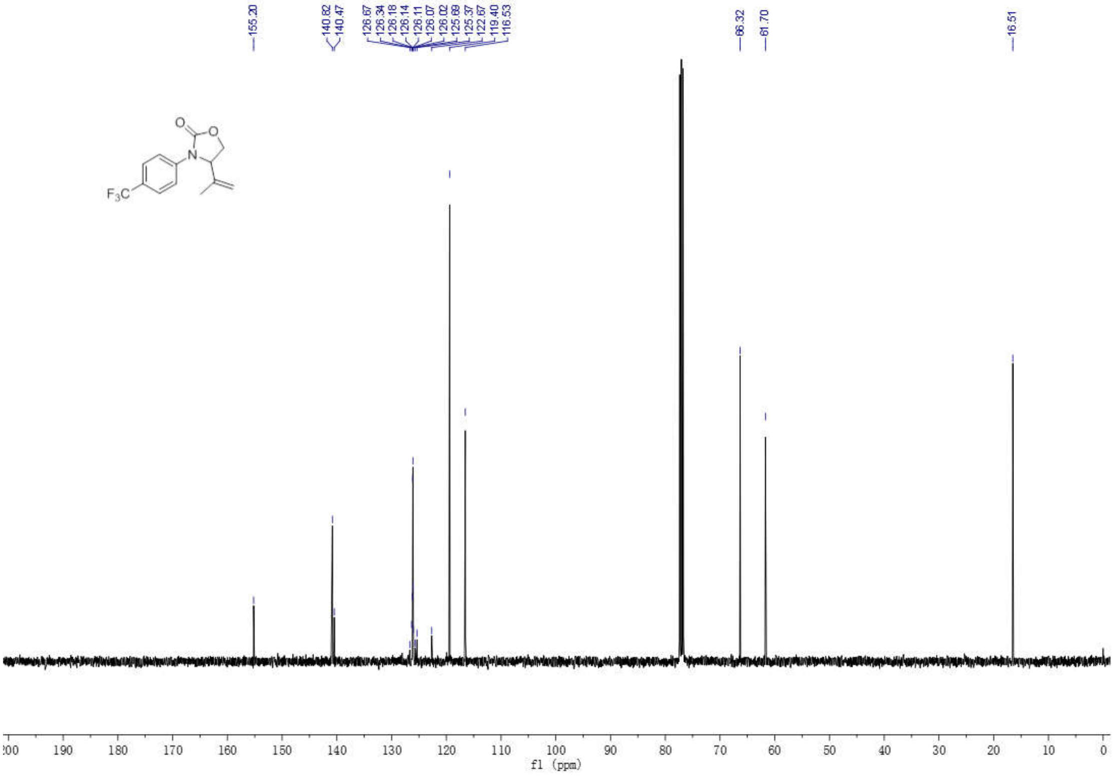
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8d**



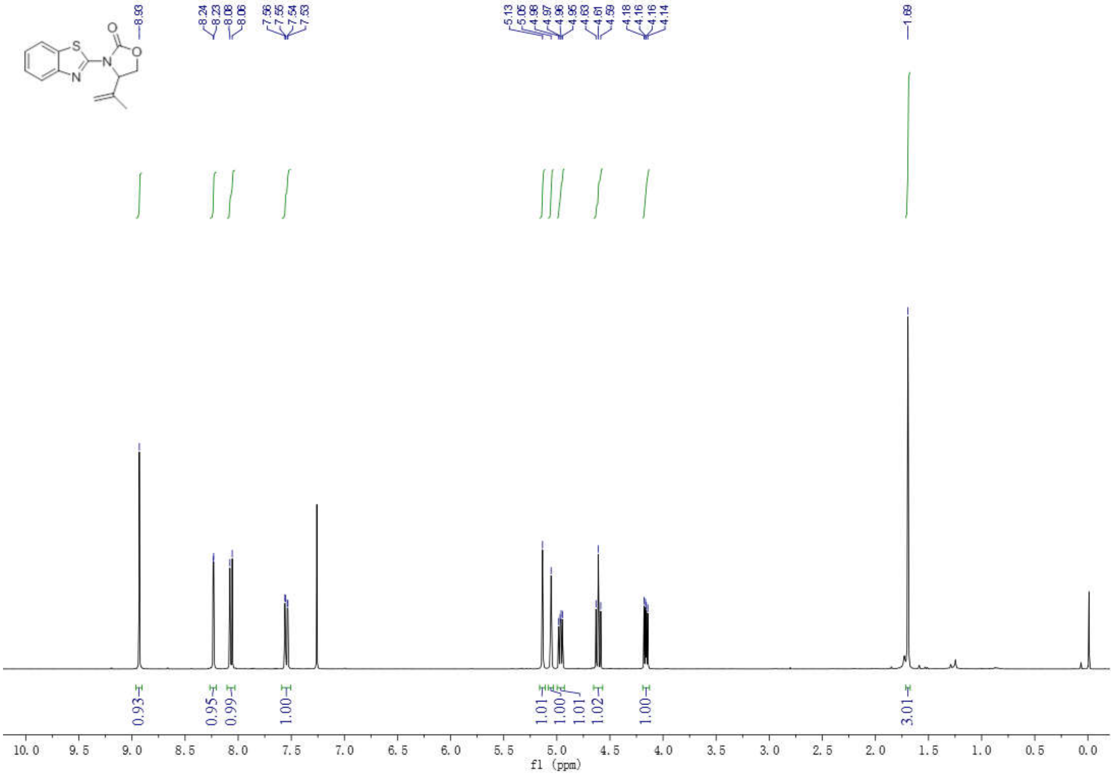
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **8e**



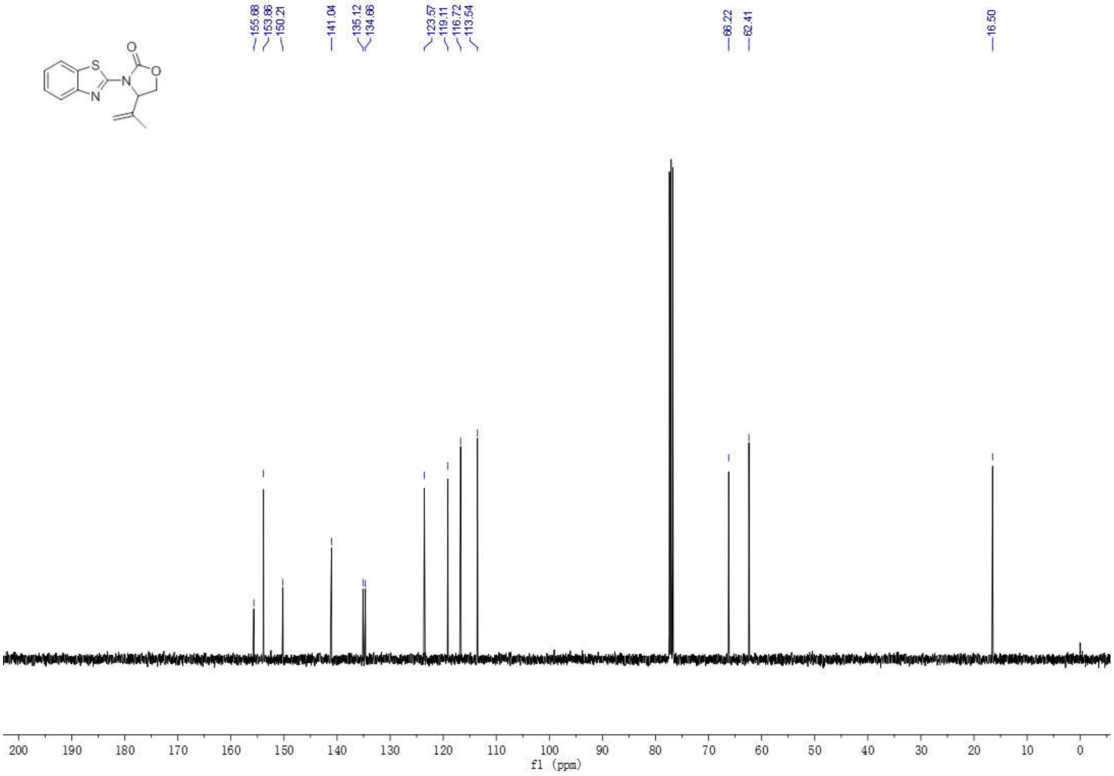
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **8e**



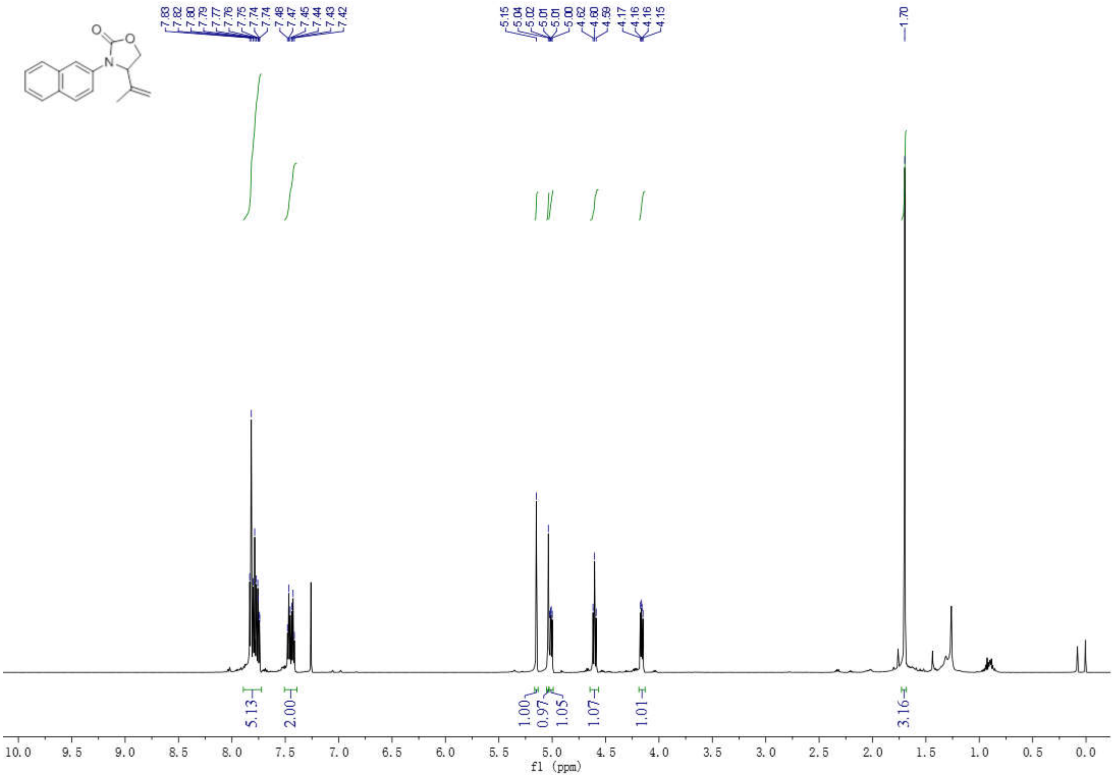
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8f**



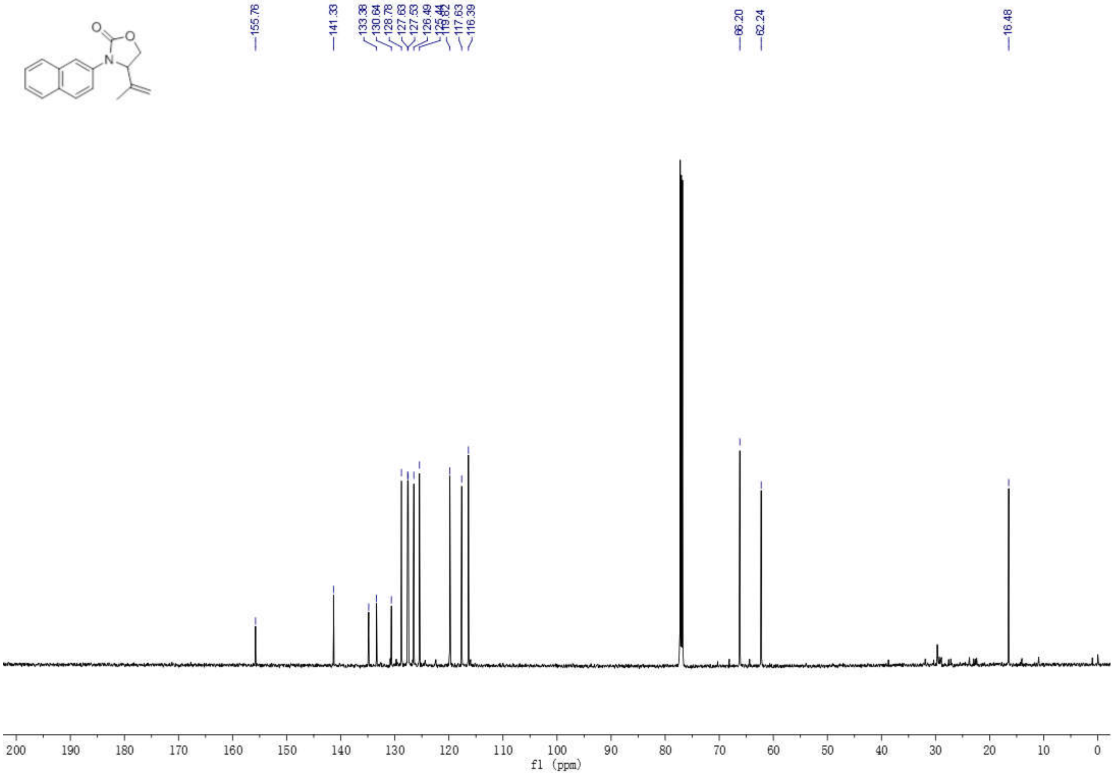
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8f**



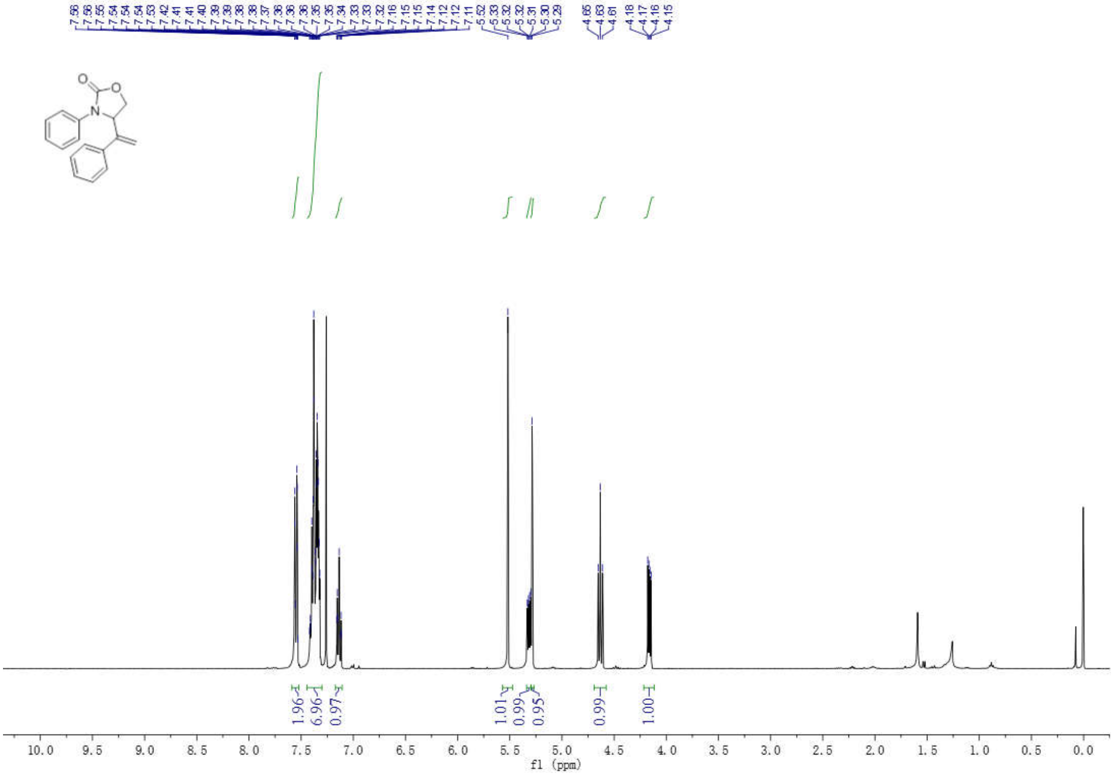
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8g**



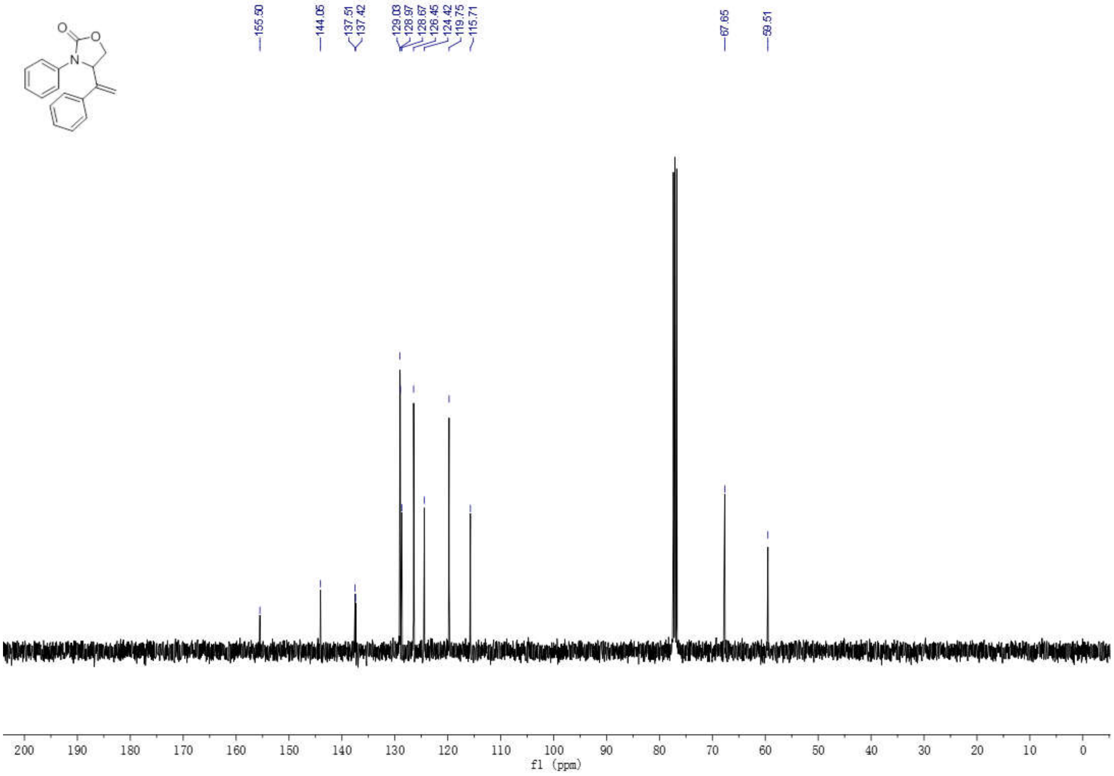
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8g**



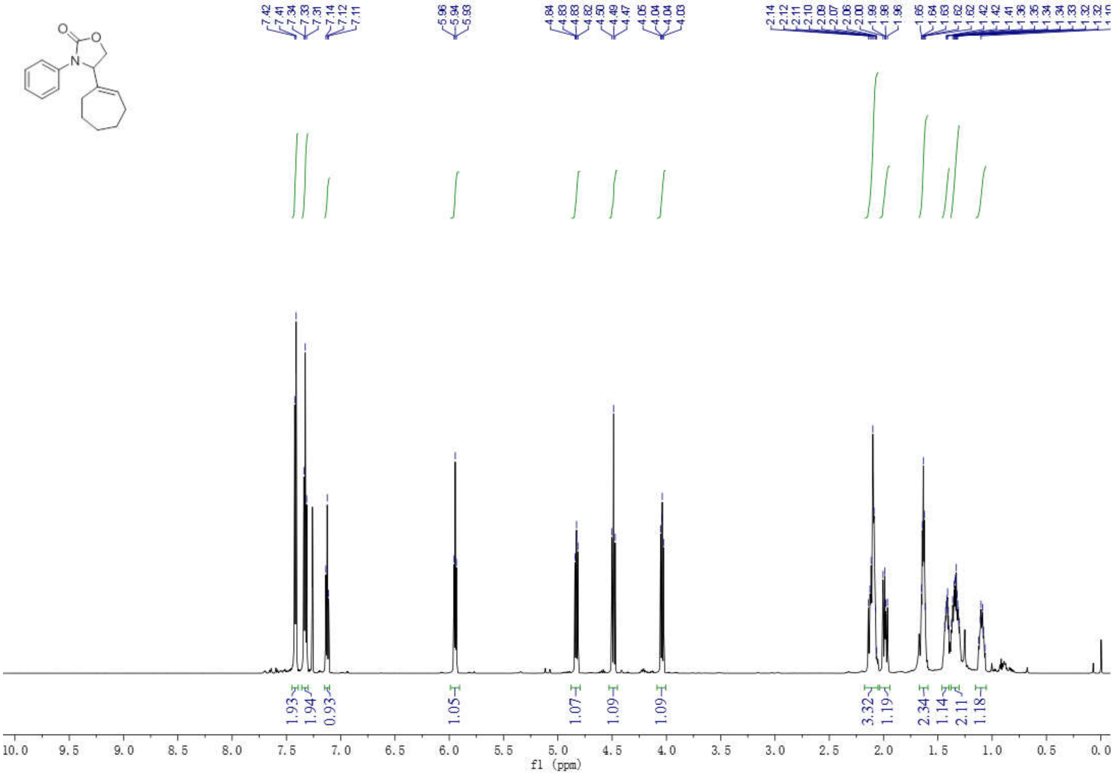
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8h**



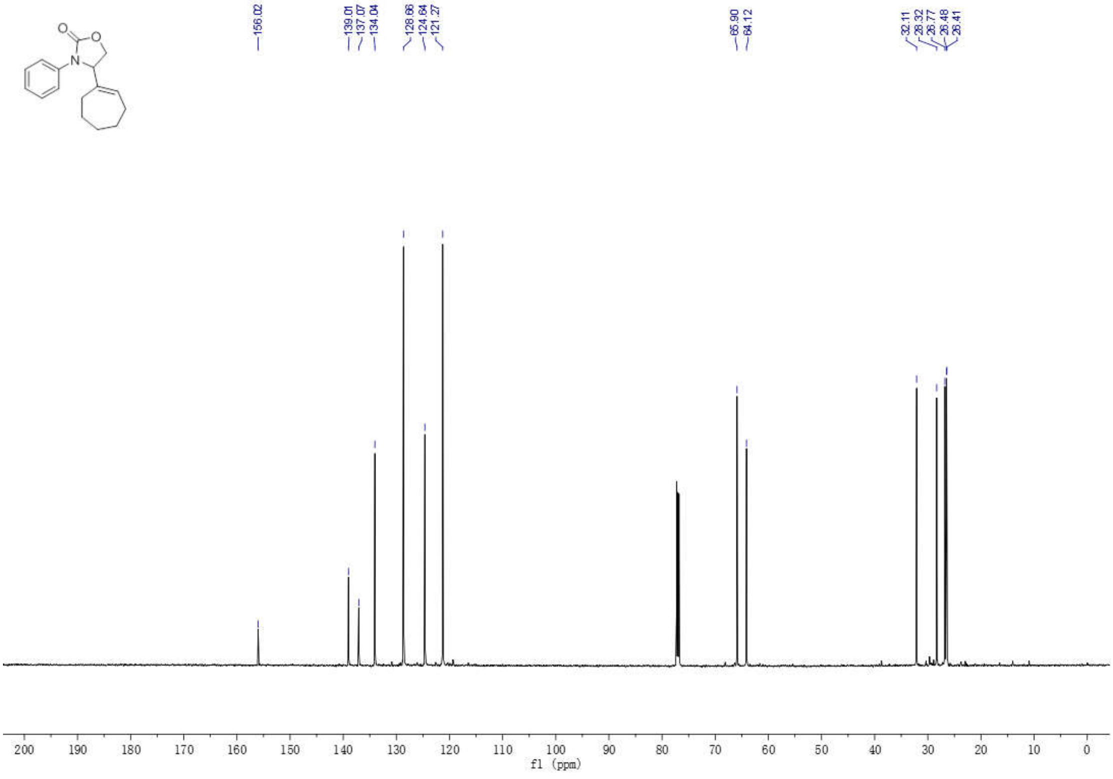
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8h**



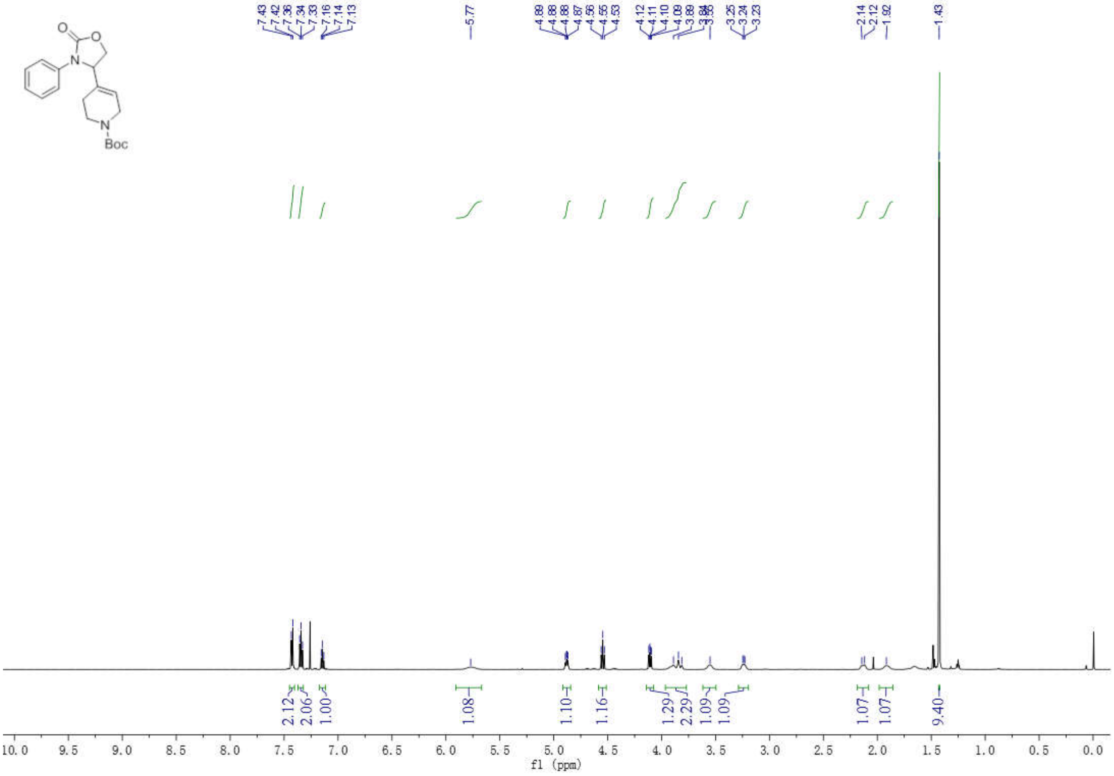
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8i**



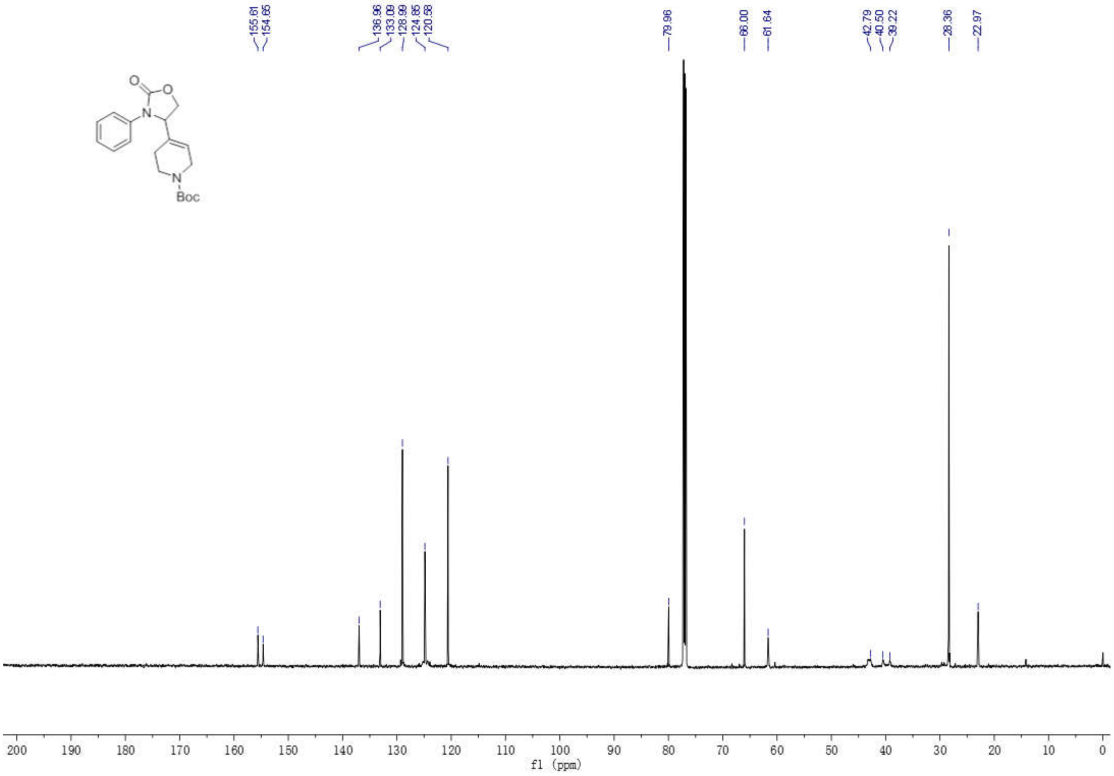
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8i**



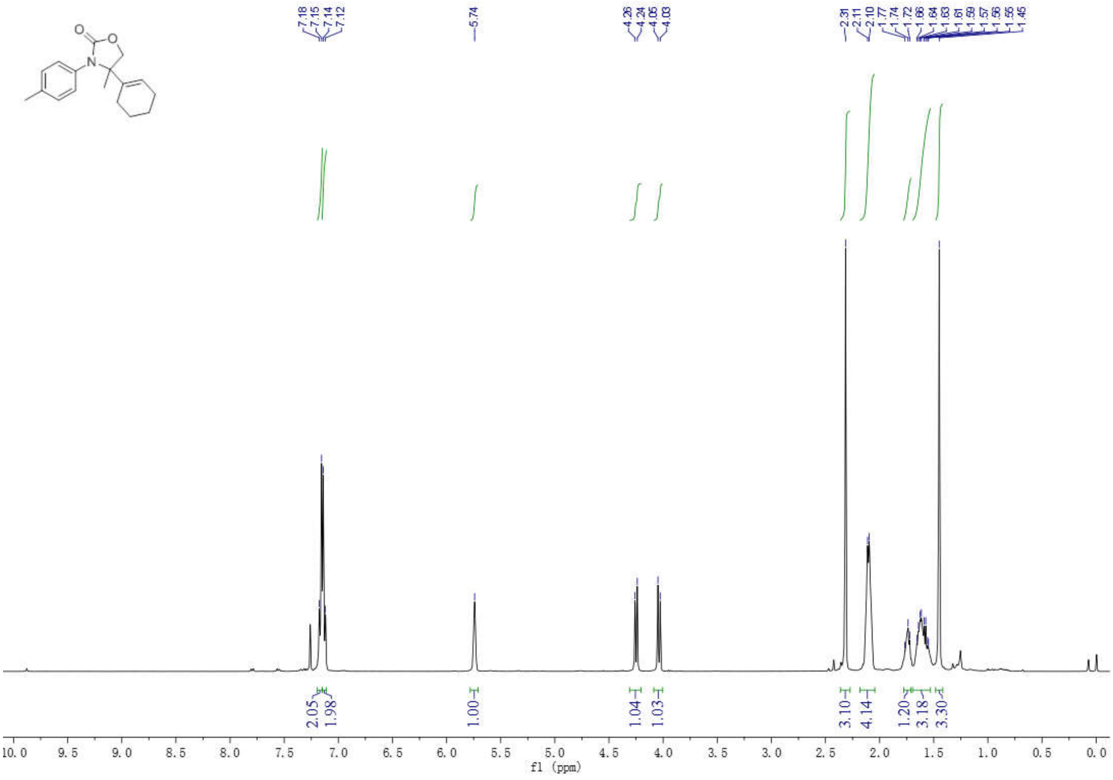
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8j**



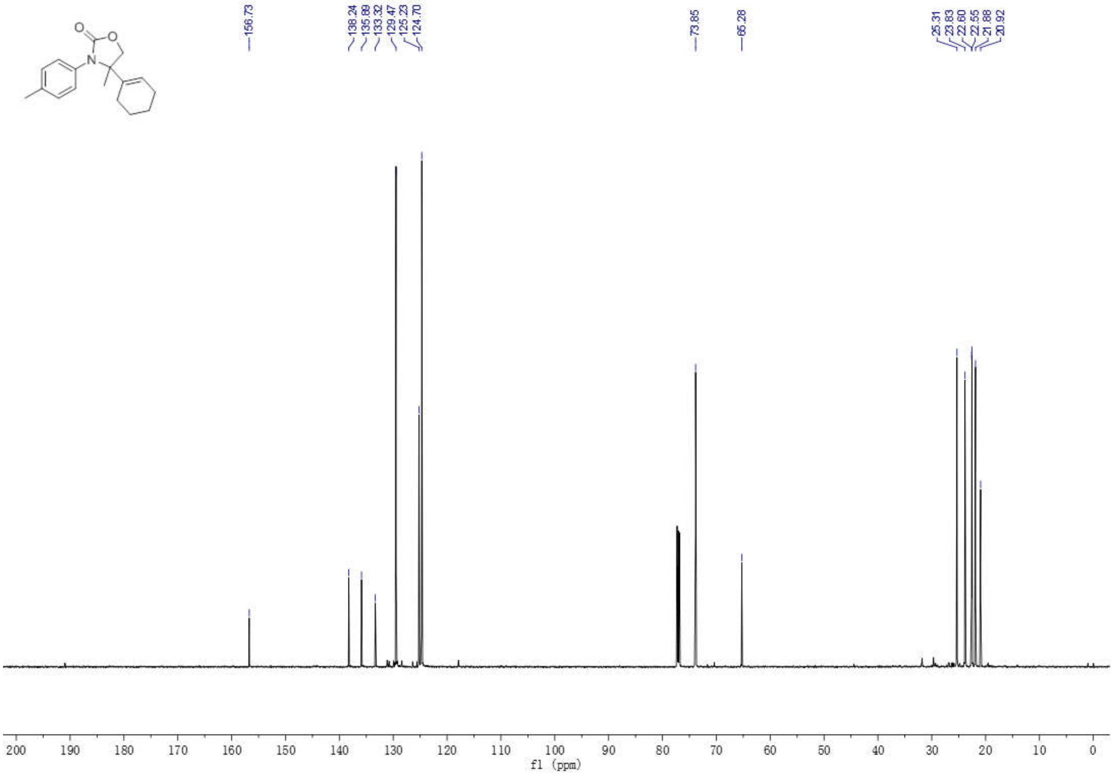
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8j**



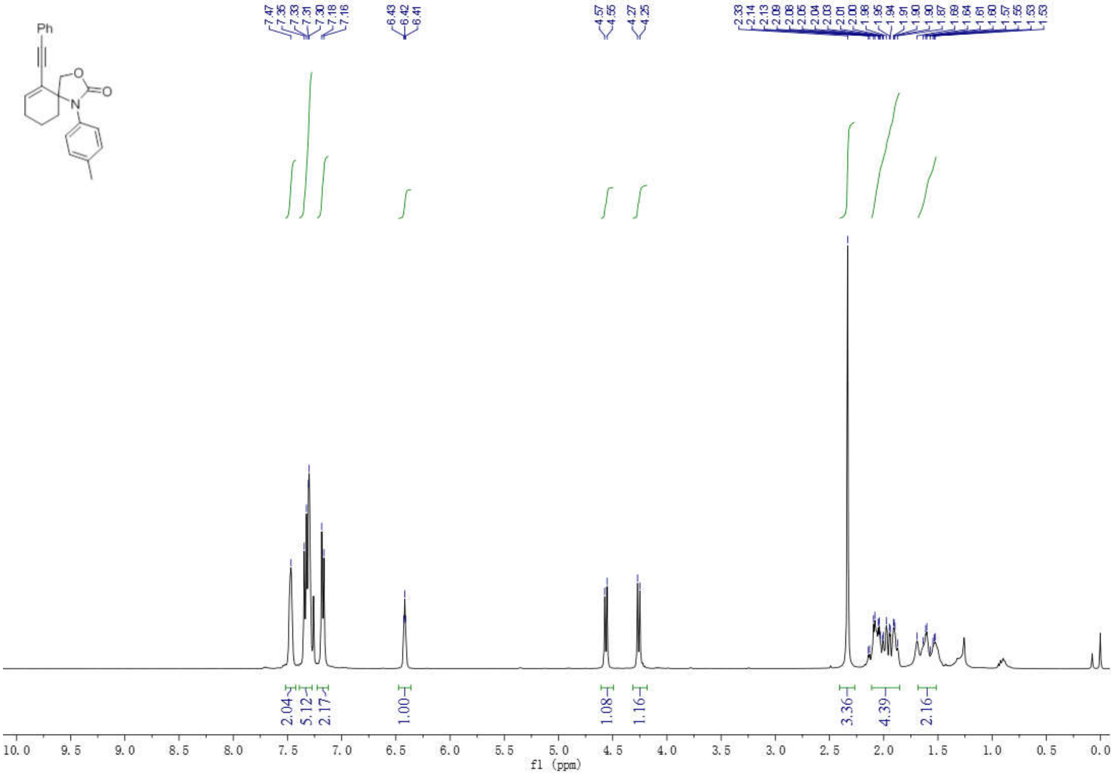
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8k**



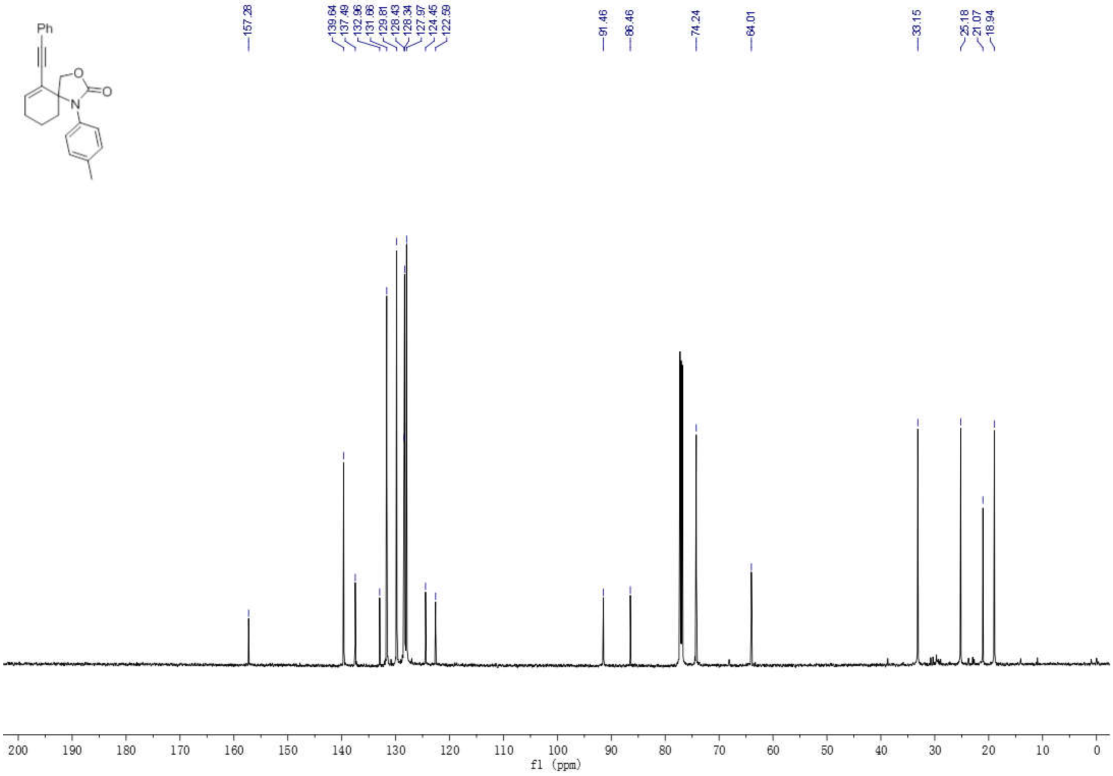
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8k**



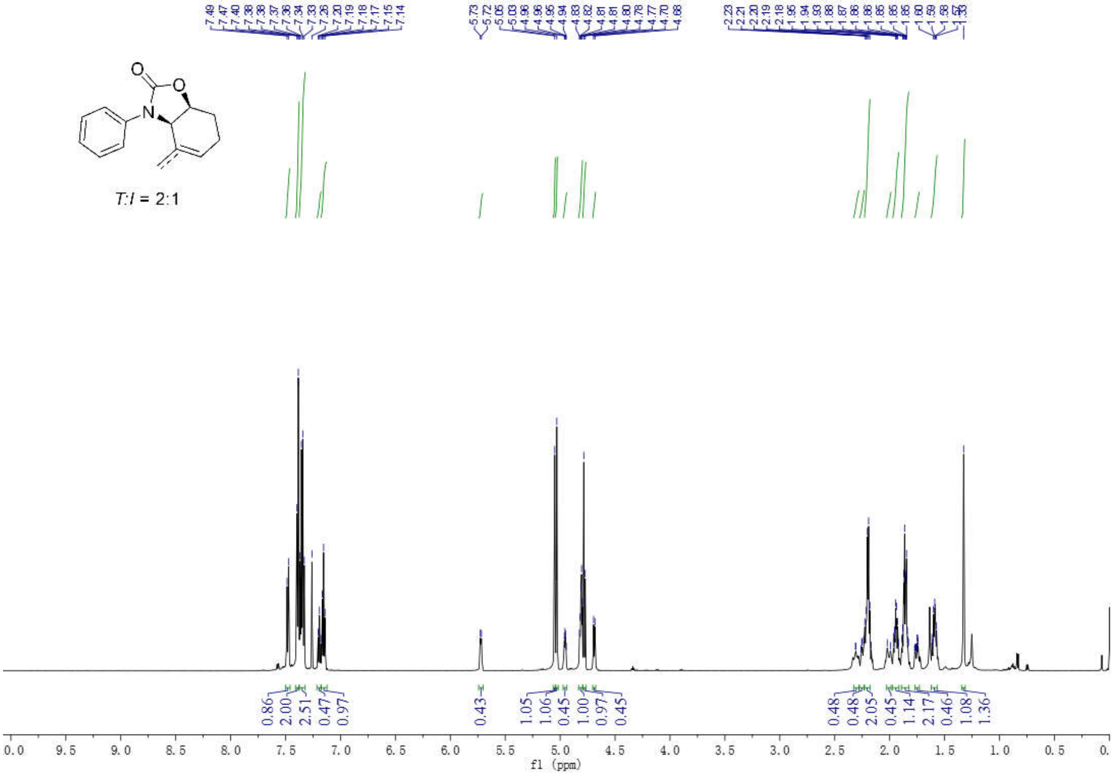
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8l**



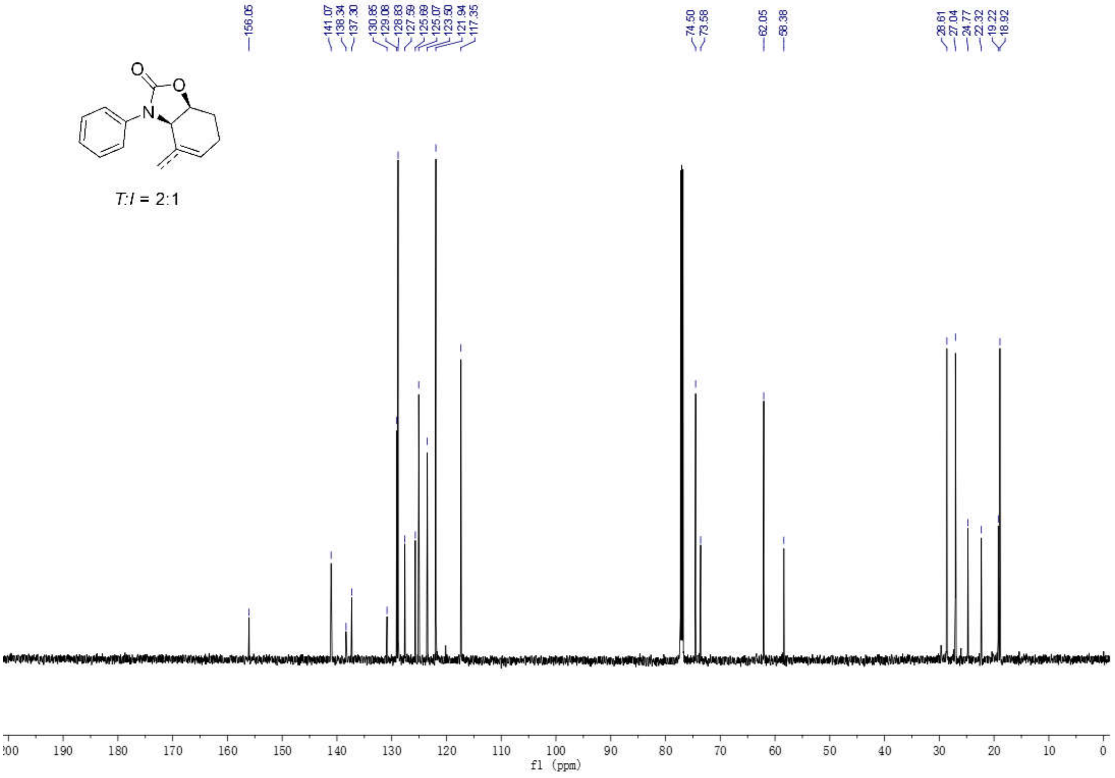
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8l**



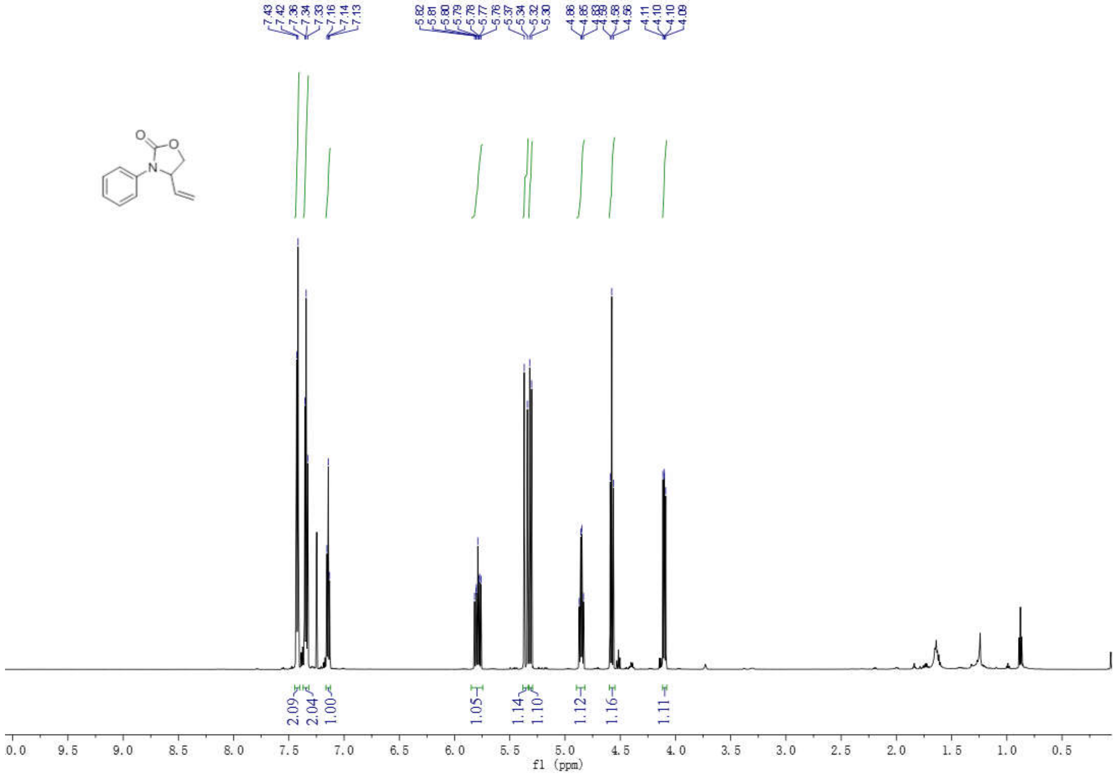
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8m**



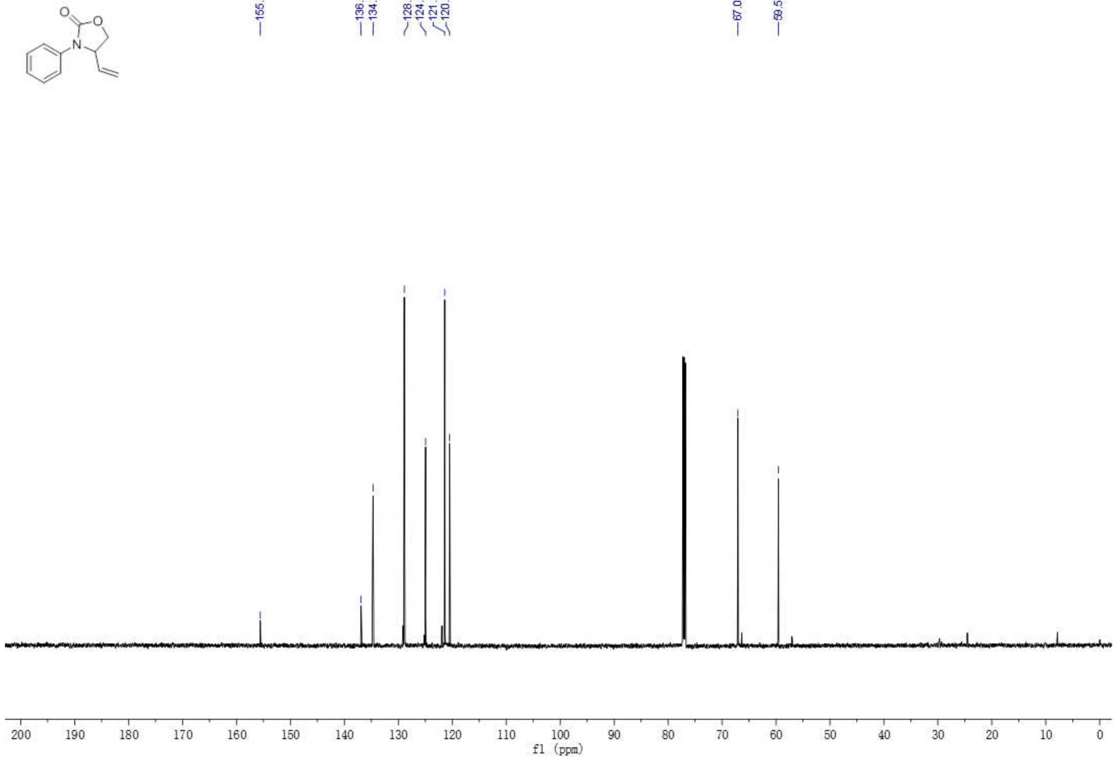
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8m**



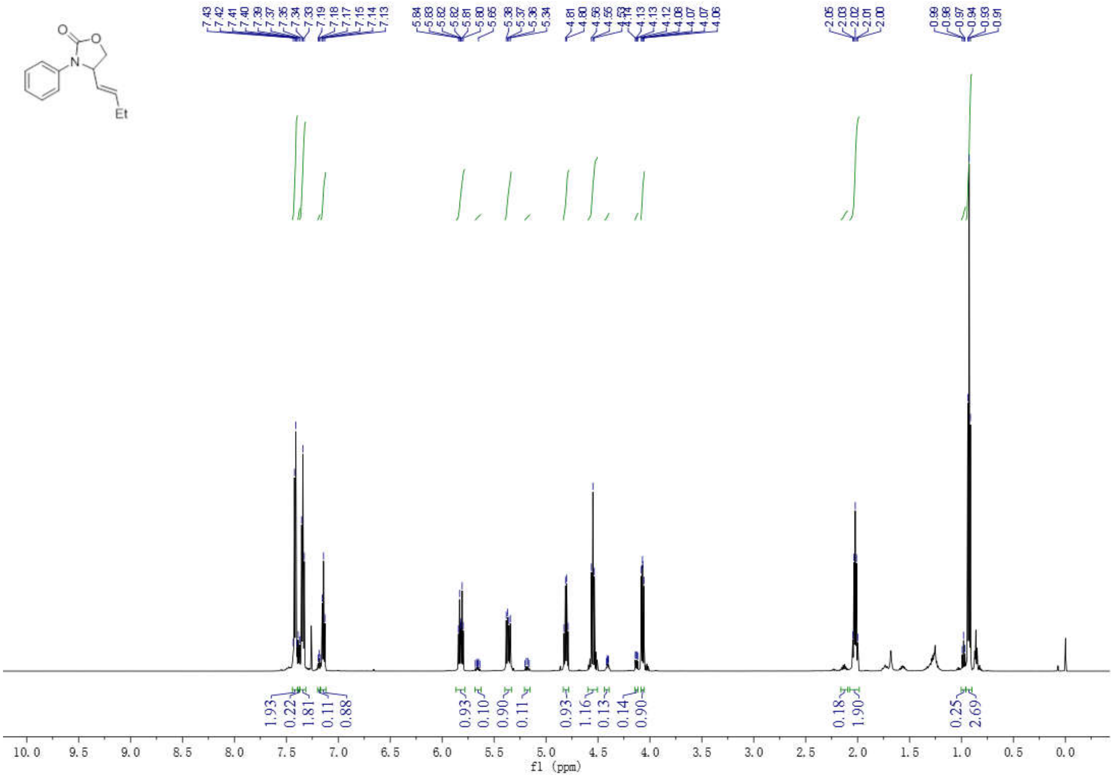
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8n**



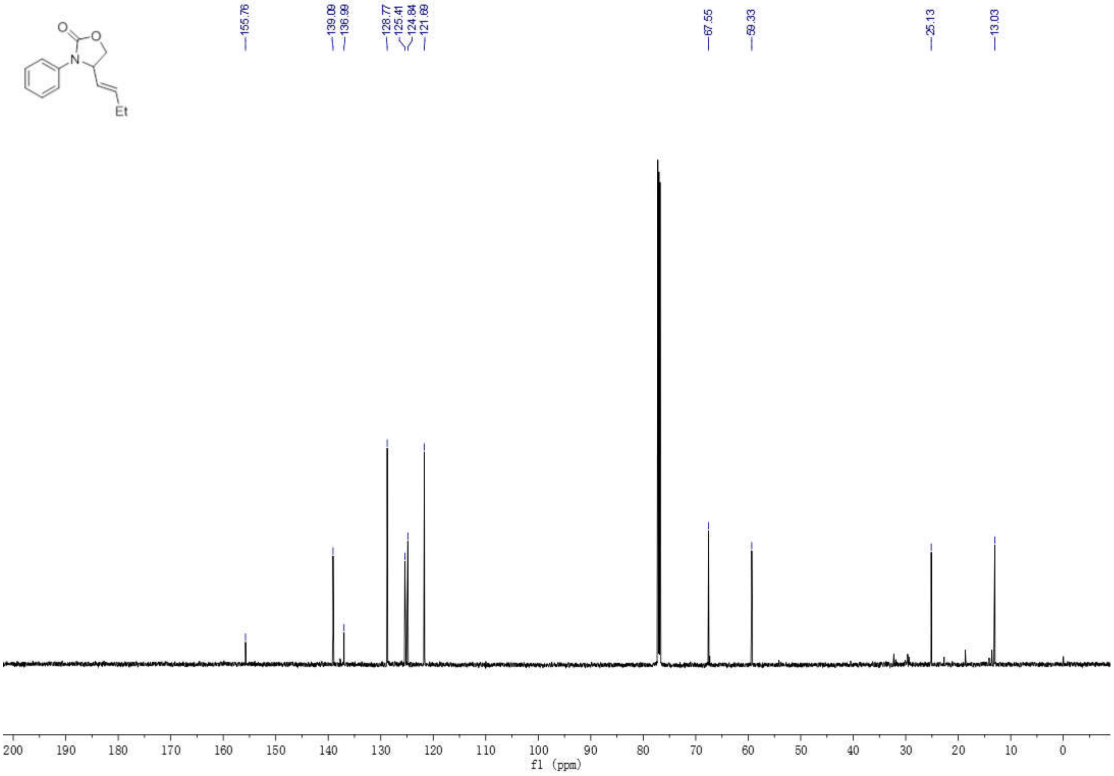
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8n**



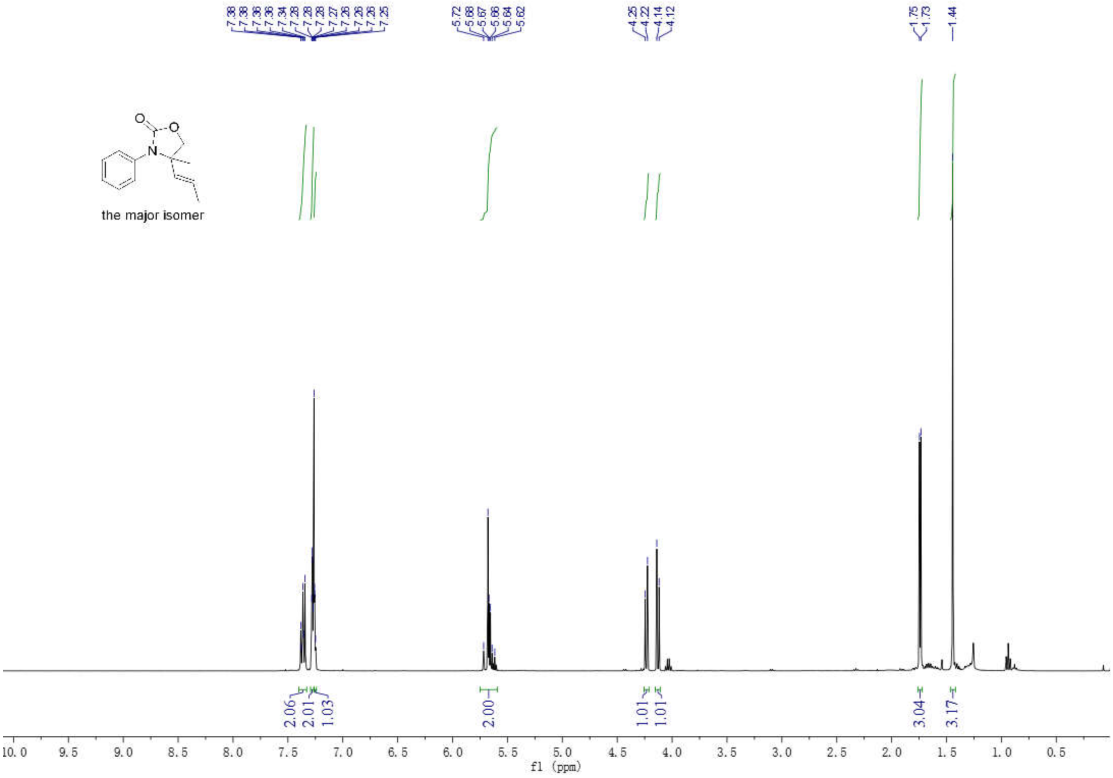
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8o**



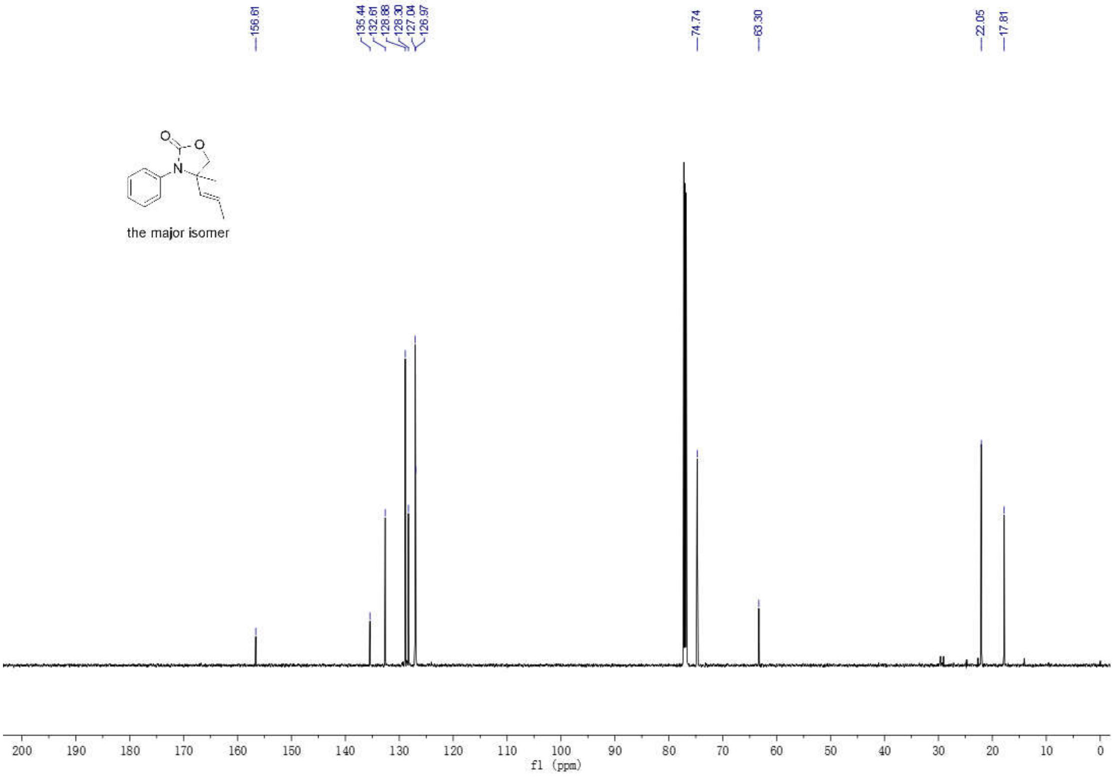
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8o**



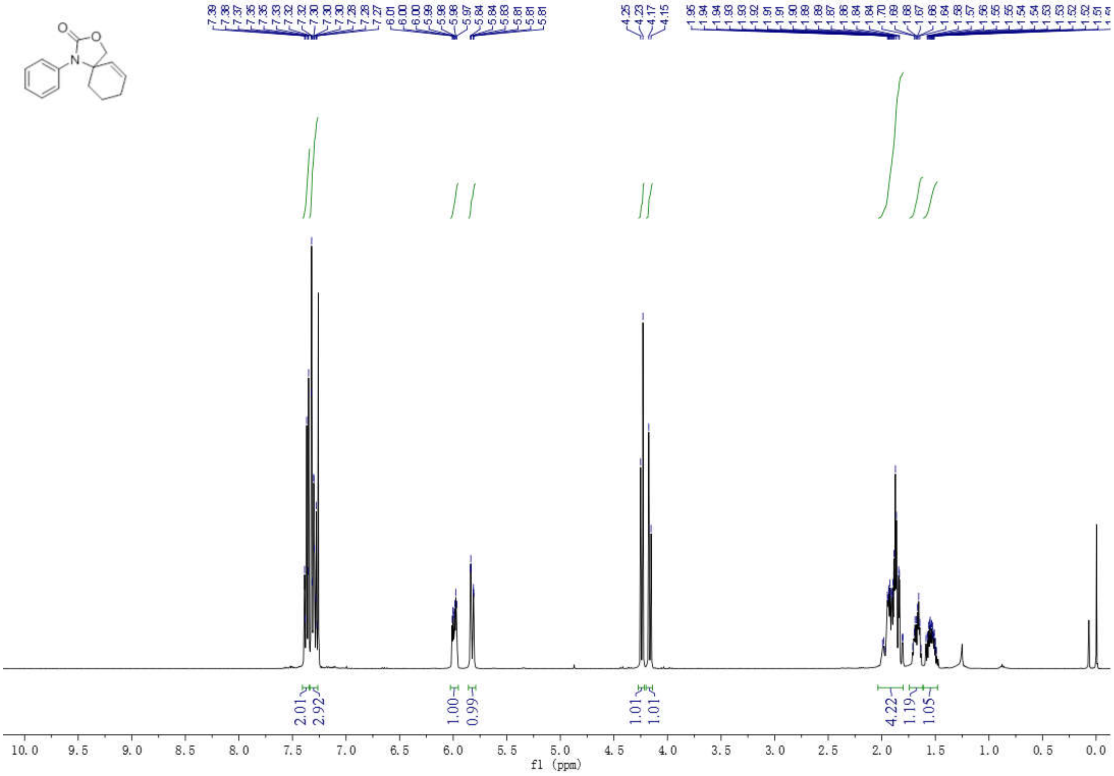
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8p**



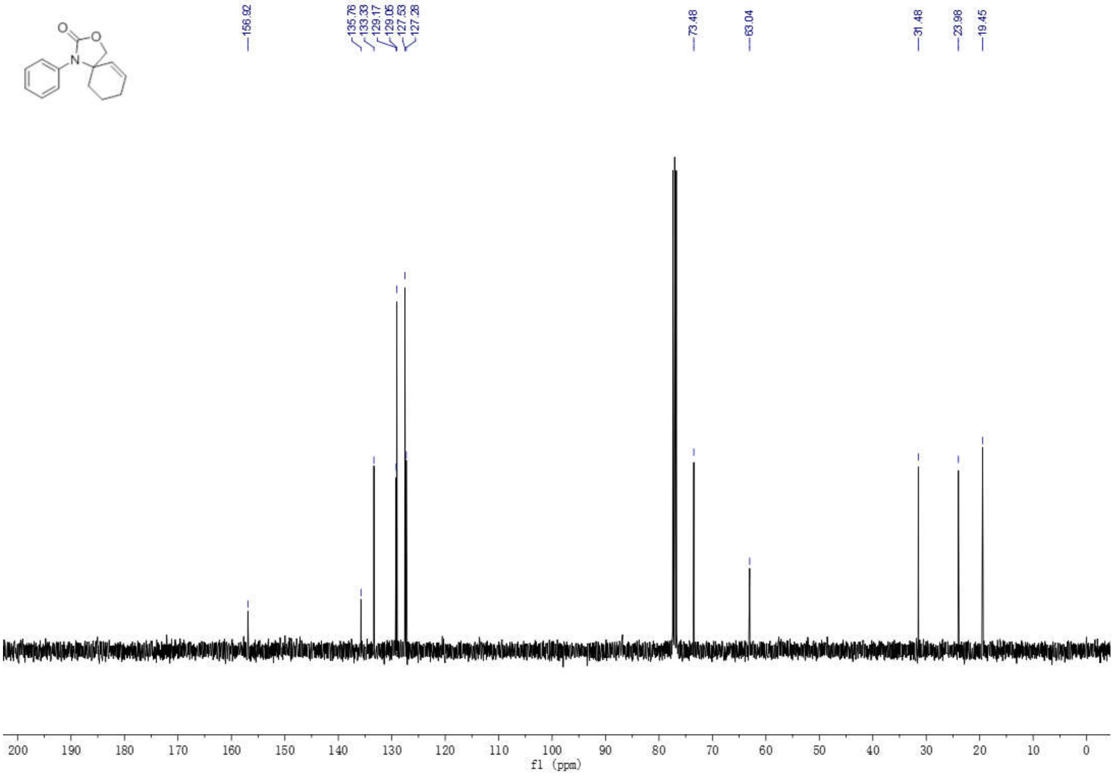
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8p**



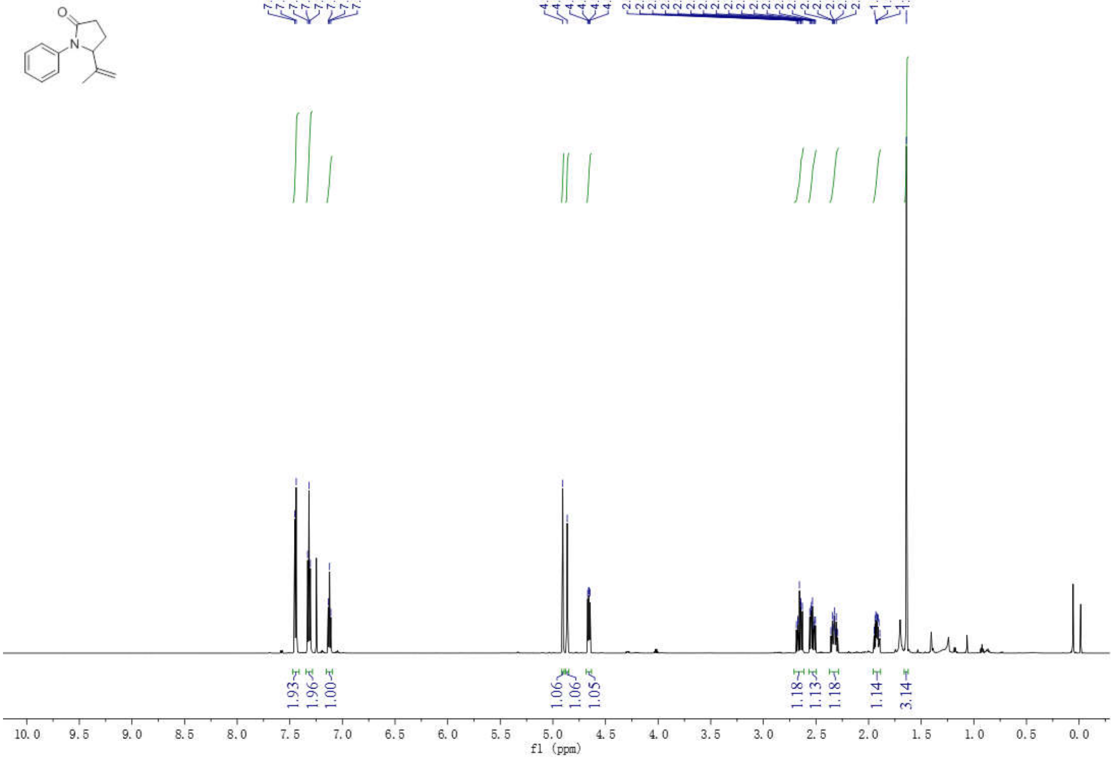
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8q**



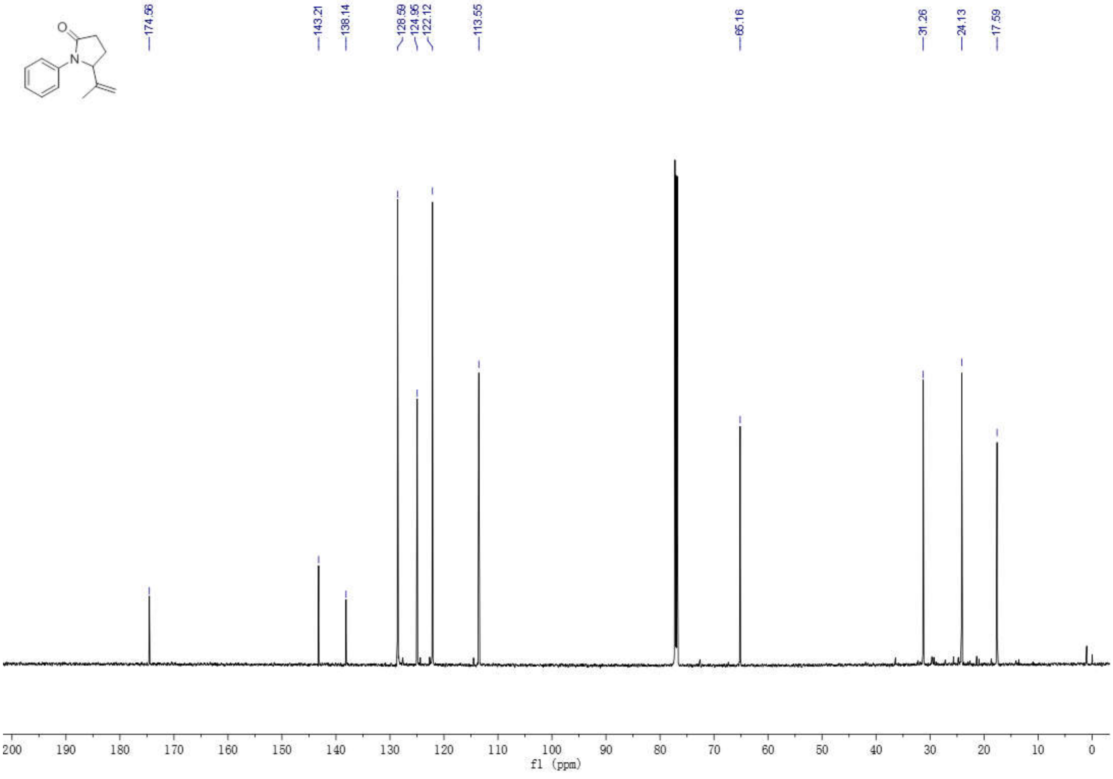
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8q**



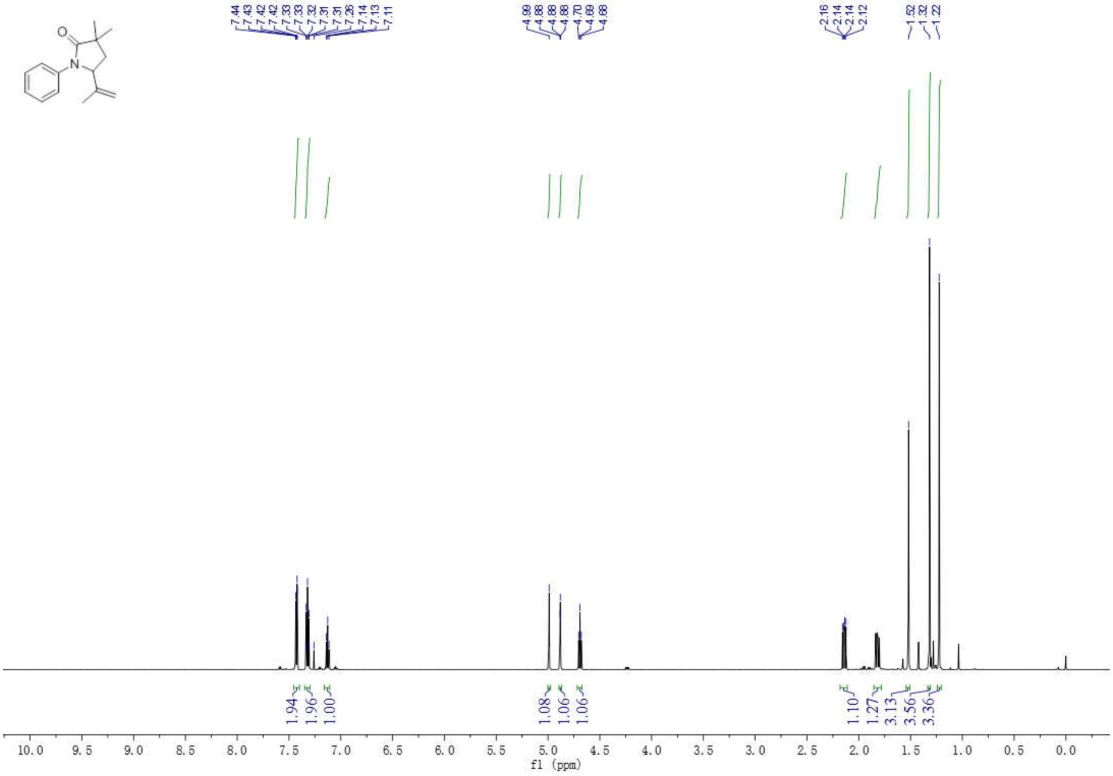
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8r**



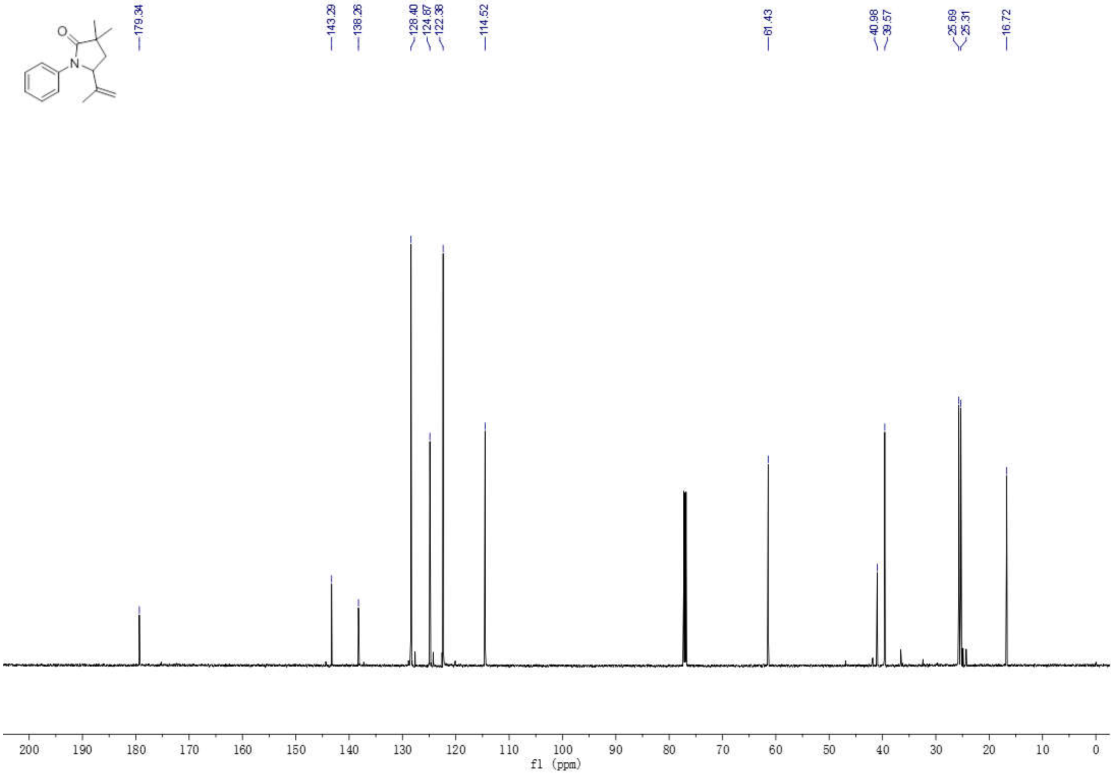
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8r**



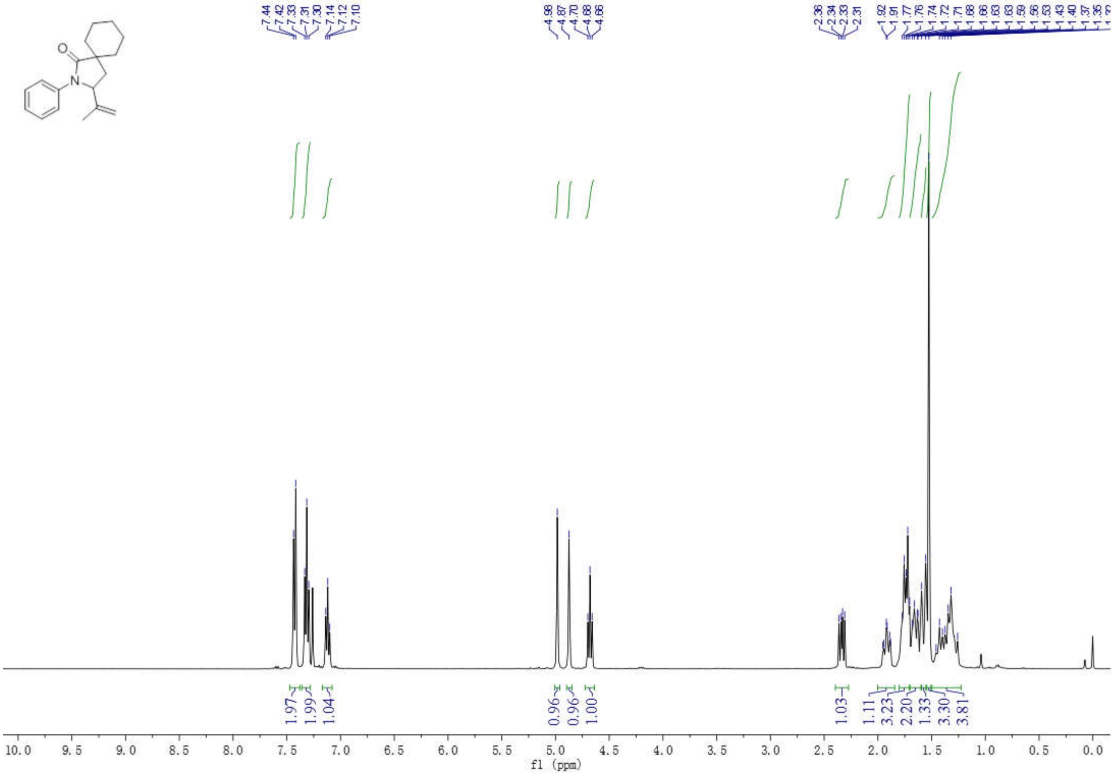
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8s**



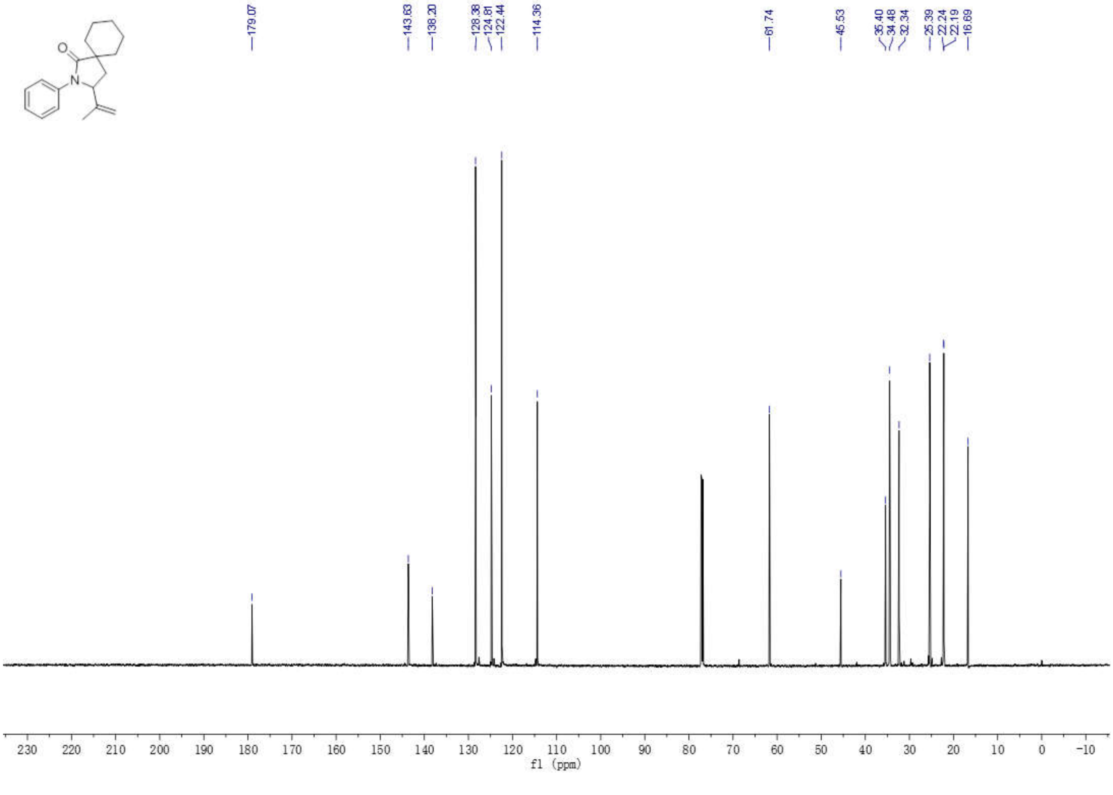
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8s**



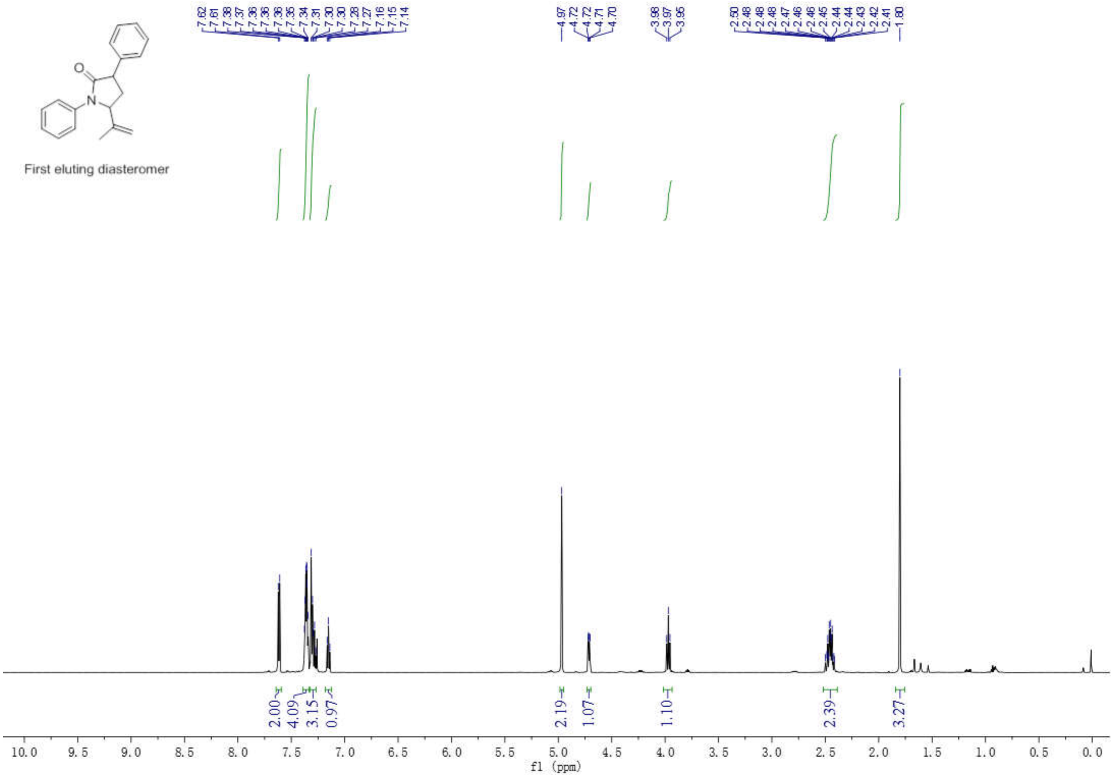
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **8t**



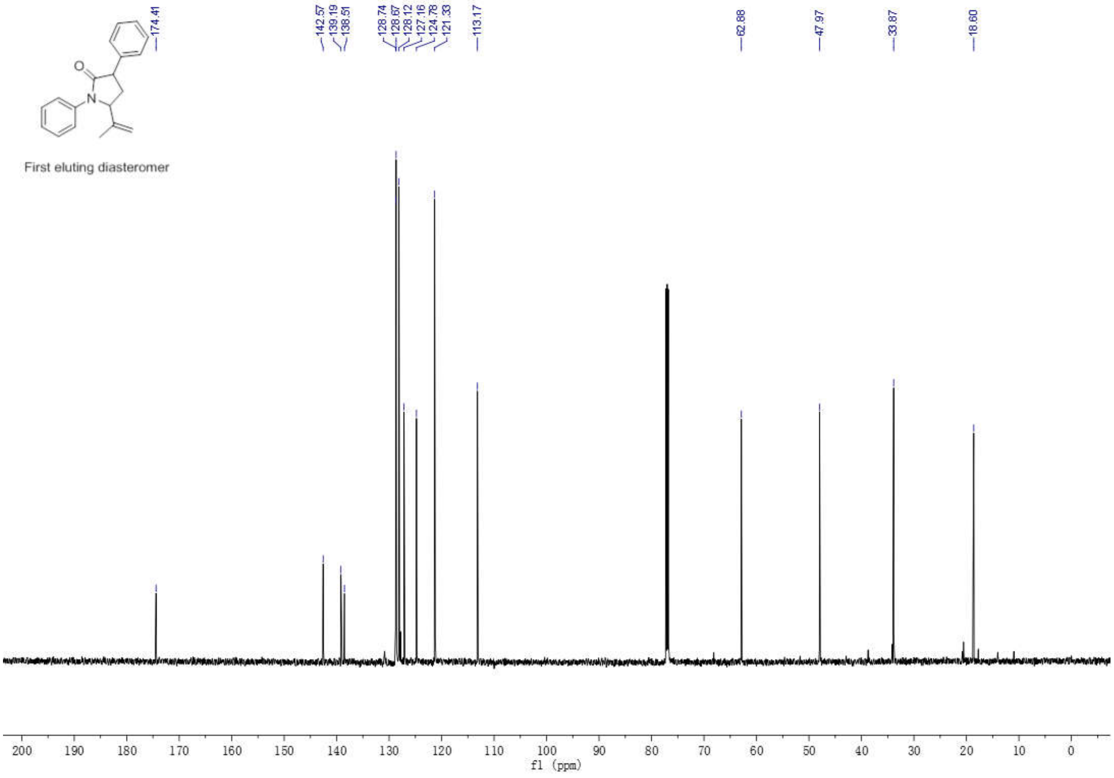
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **8t**



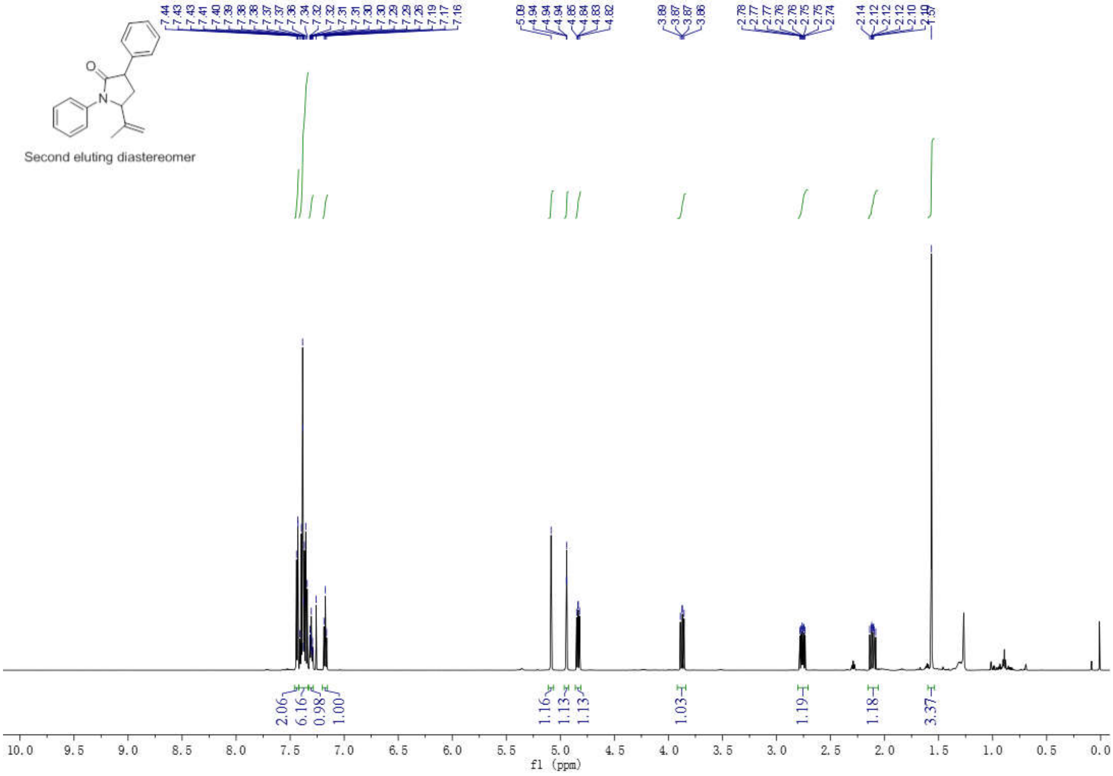
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **8u-1**



^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **8u-1**



^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8u-2**



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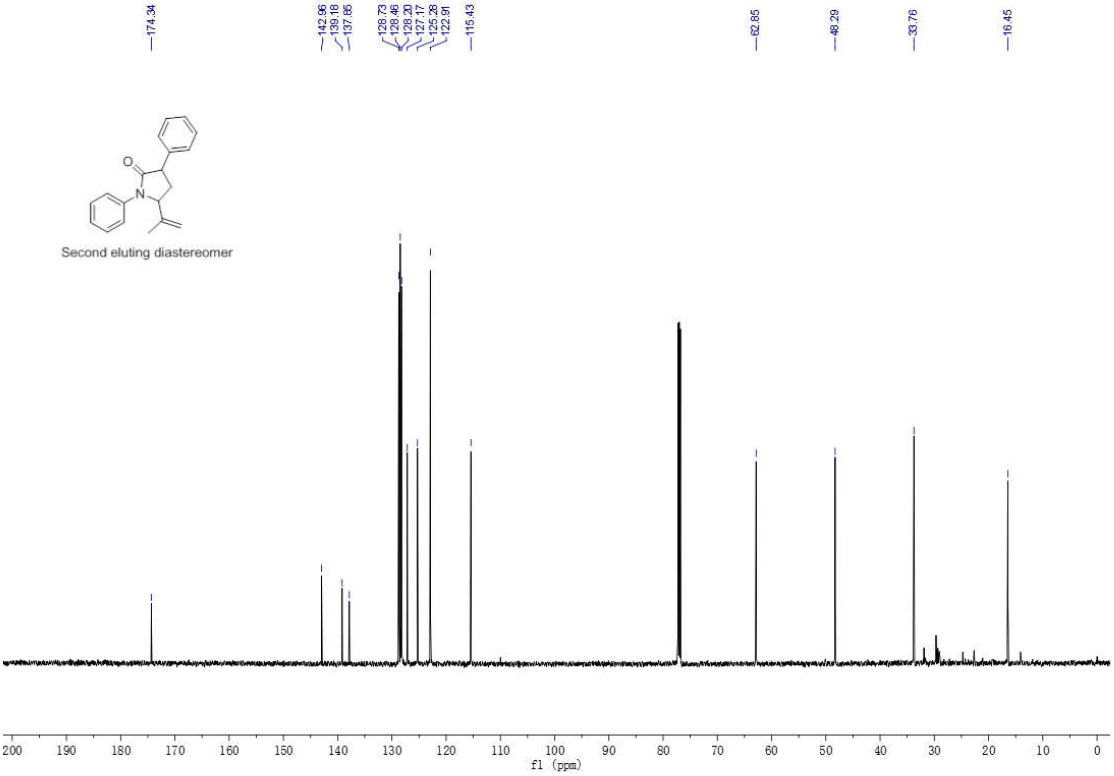
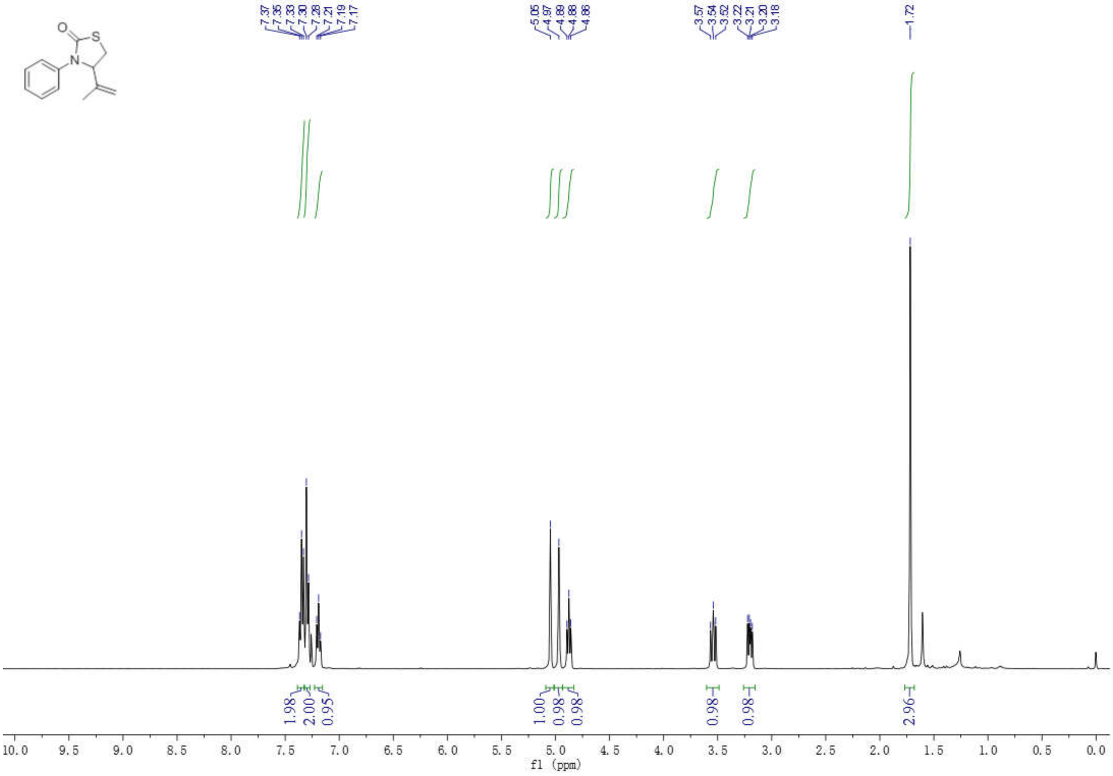
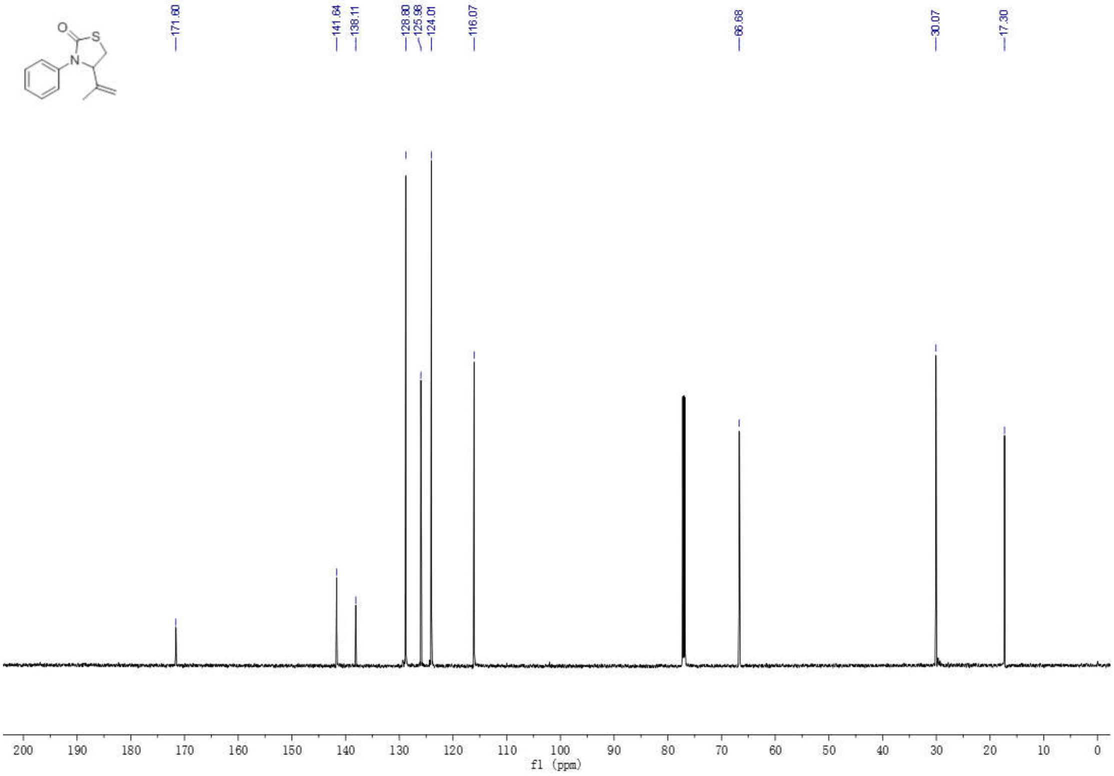


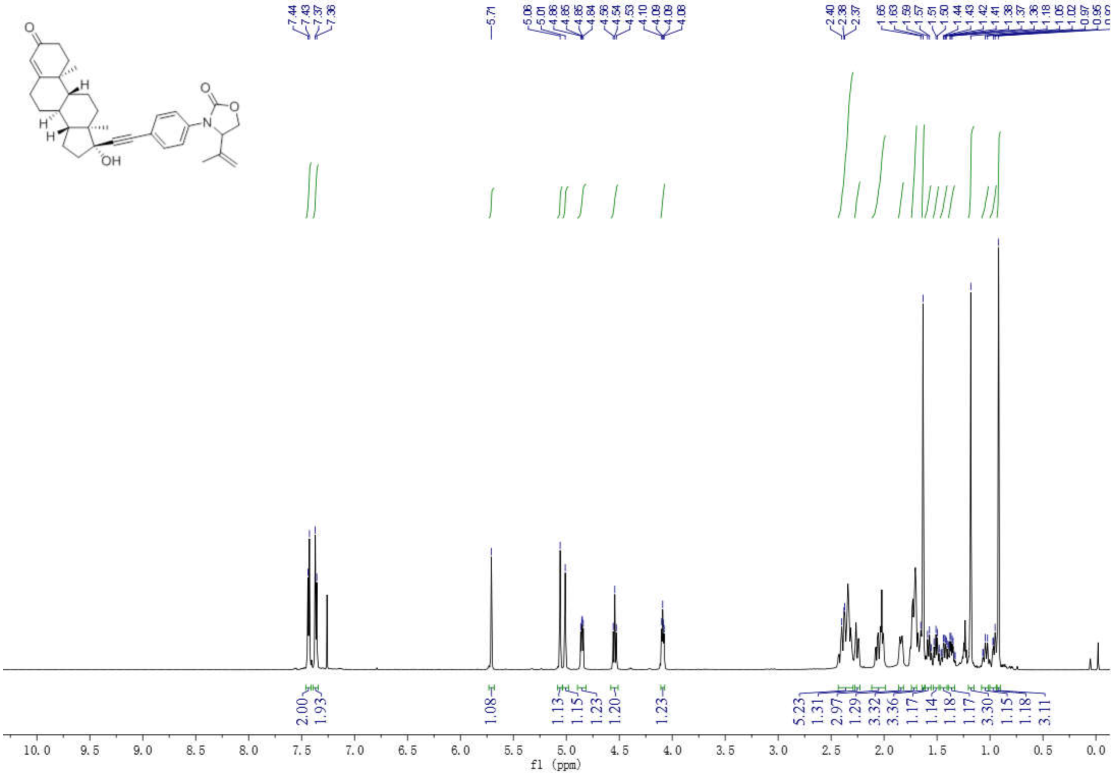
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **8v**



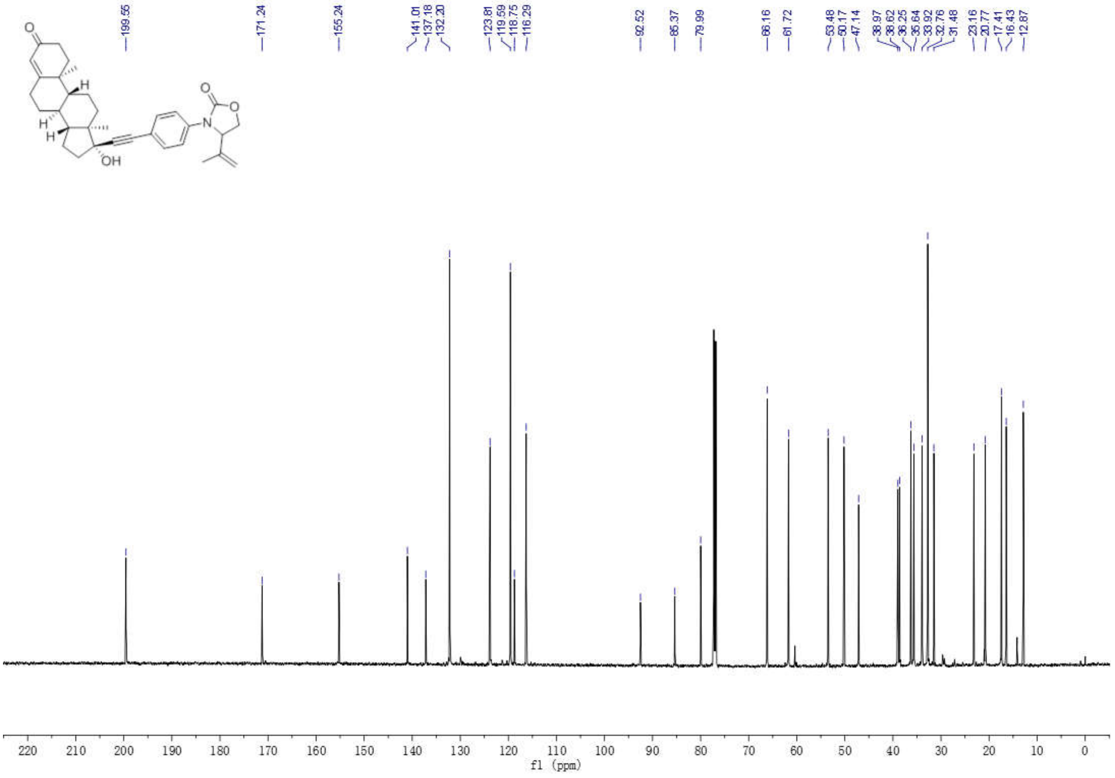
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **8v**



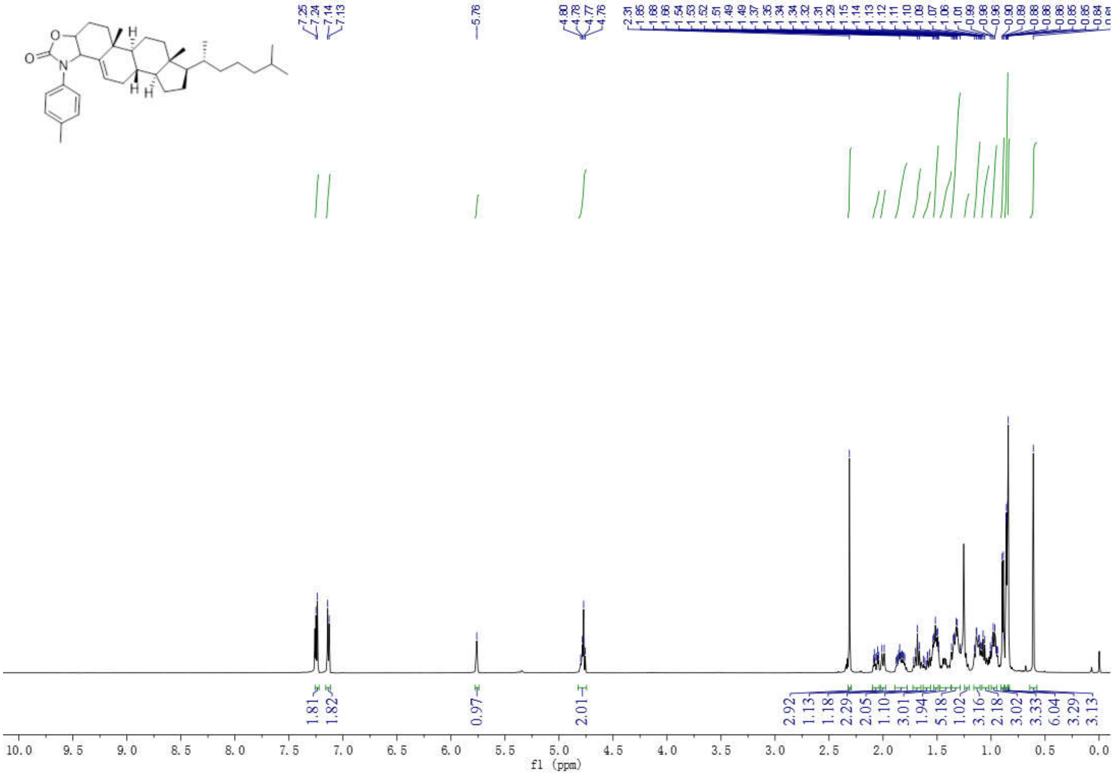
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **8w**



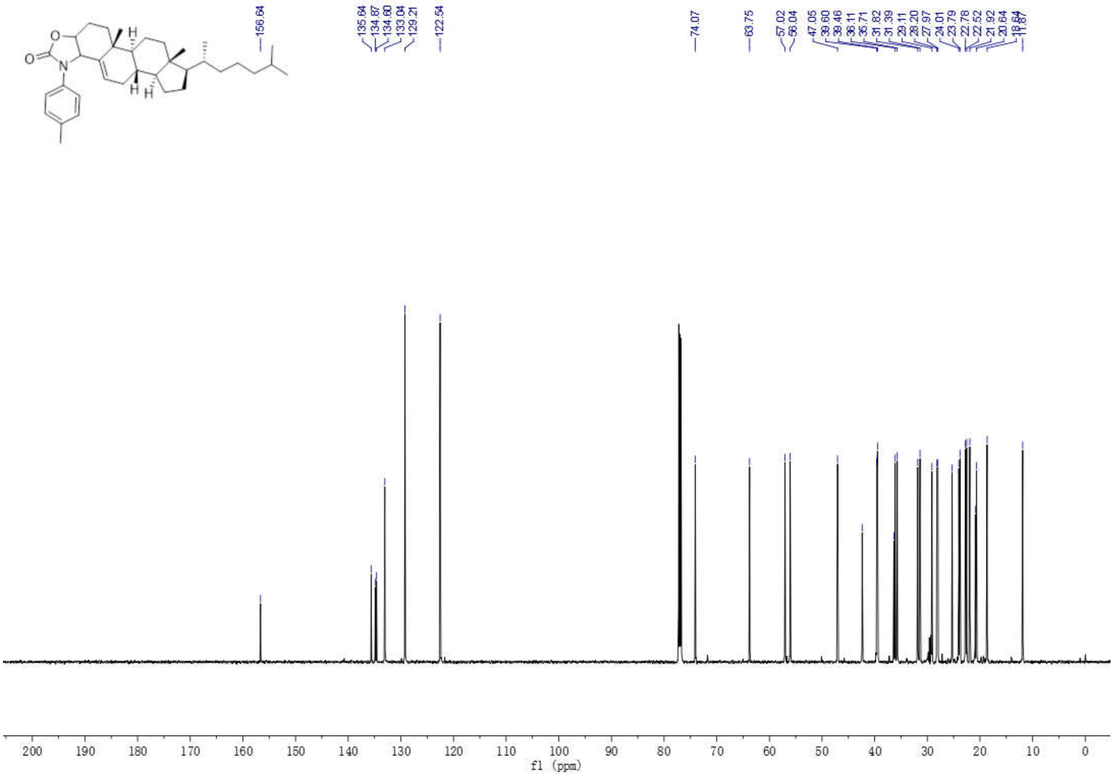
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **8w**



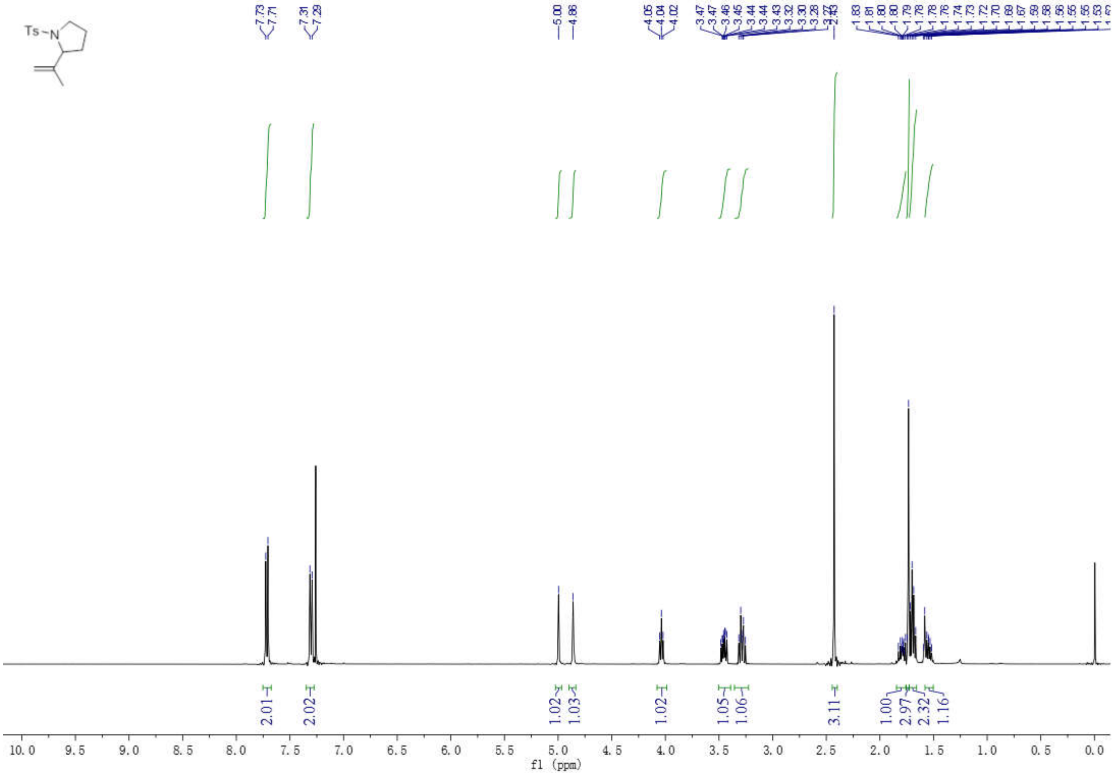
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **8x**



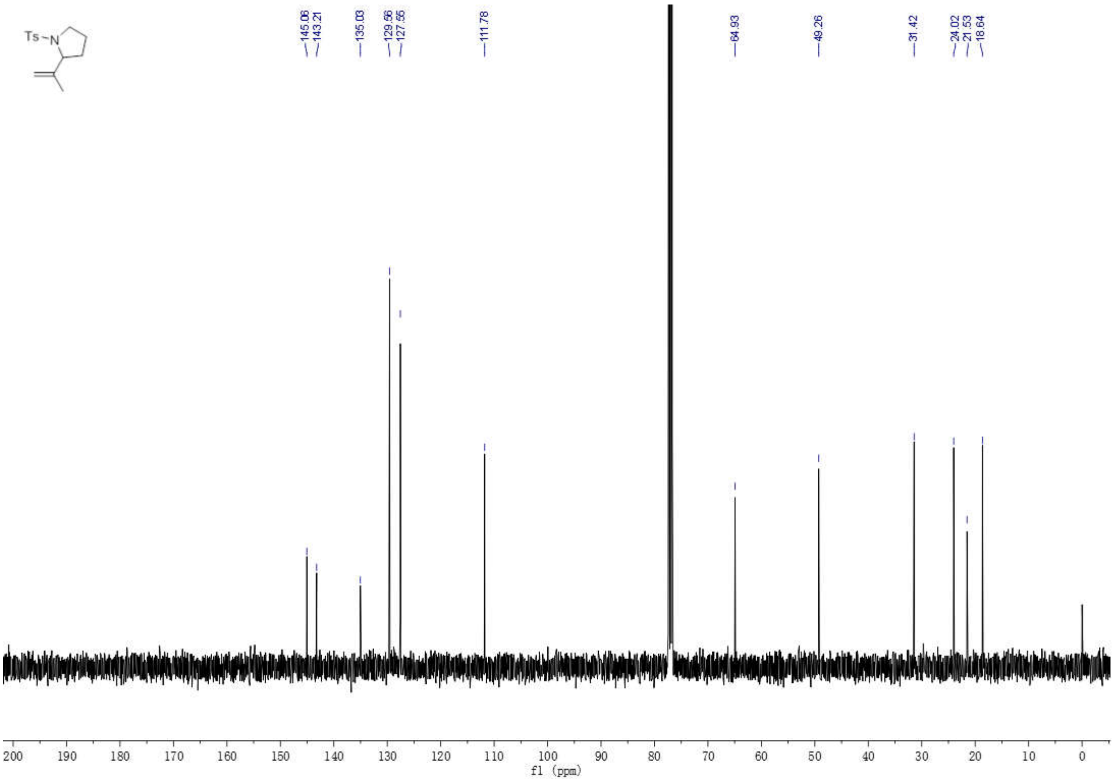
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **8x**



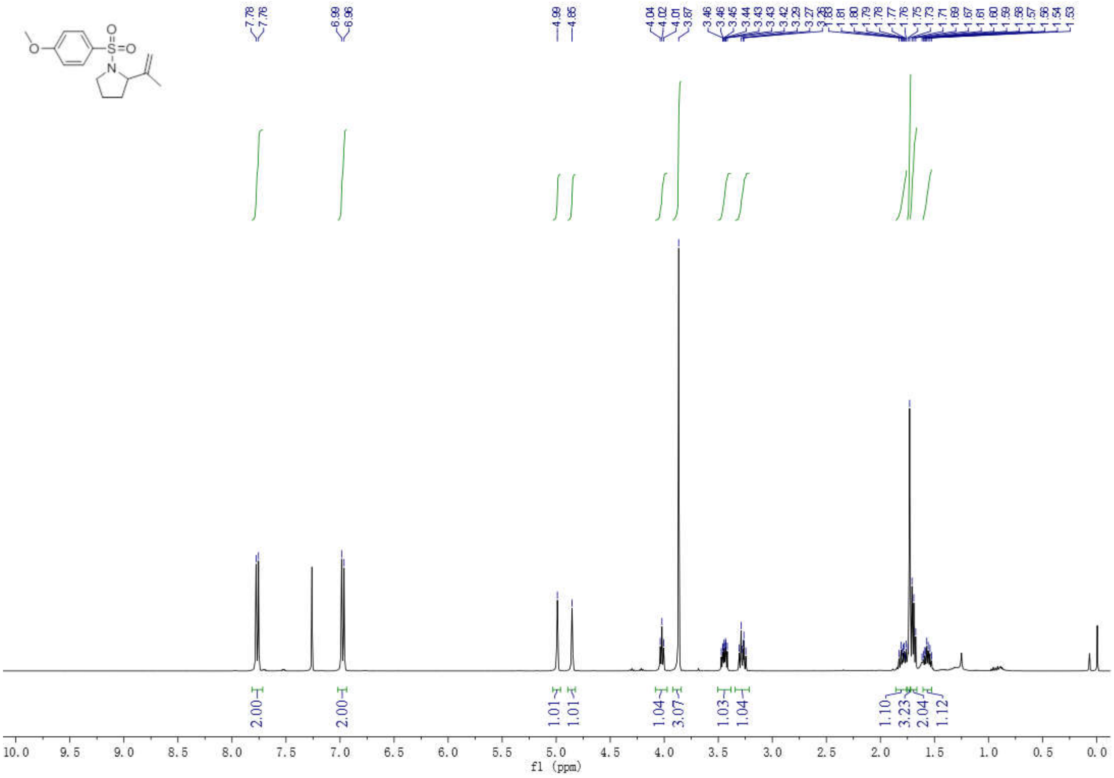
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **10a**



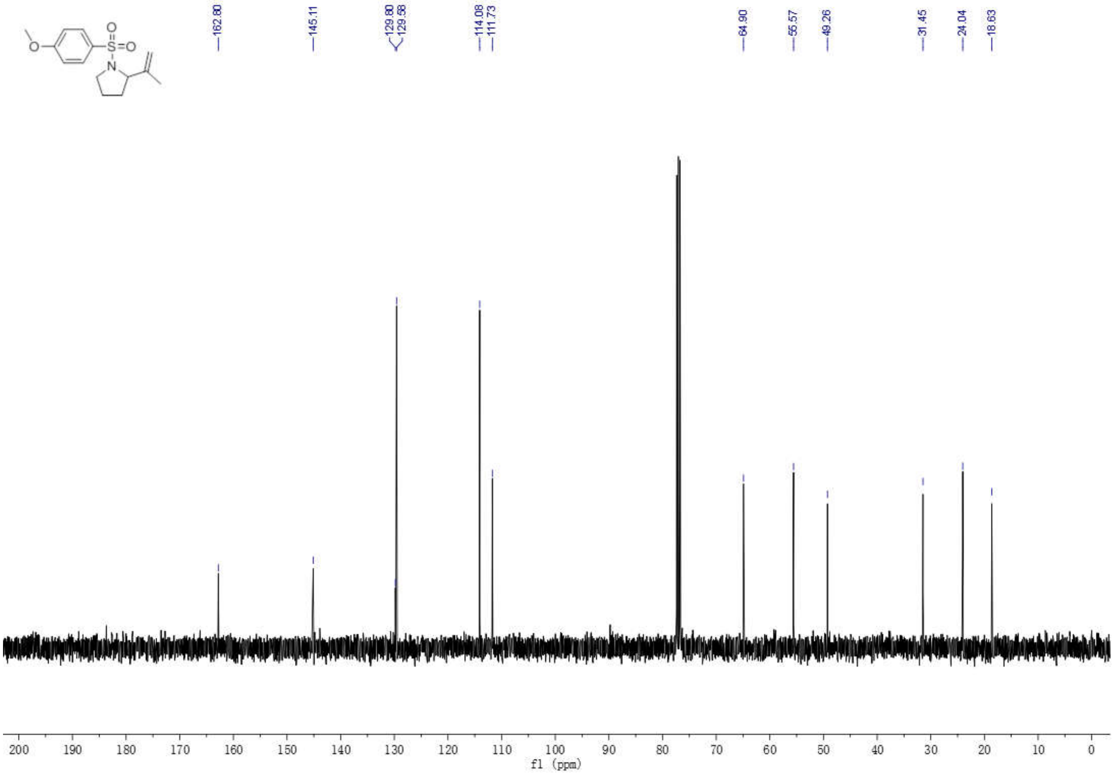
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **10a**



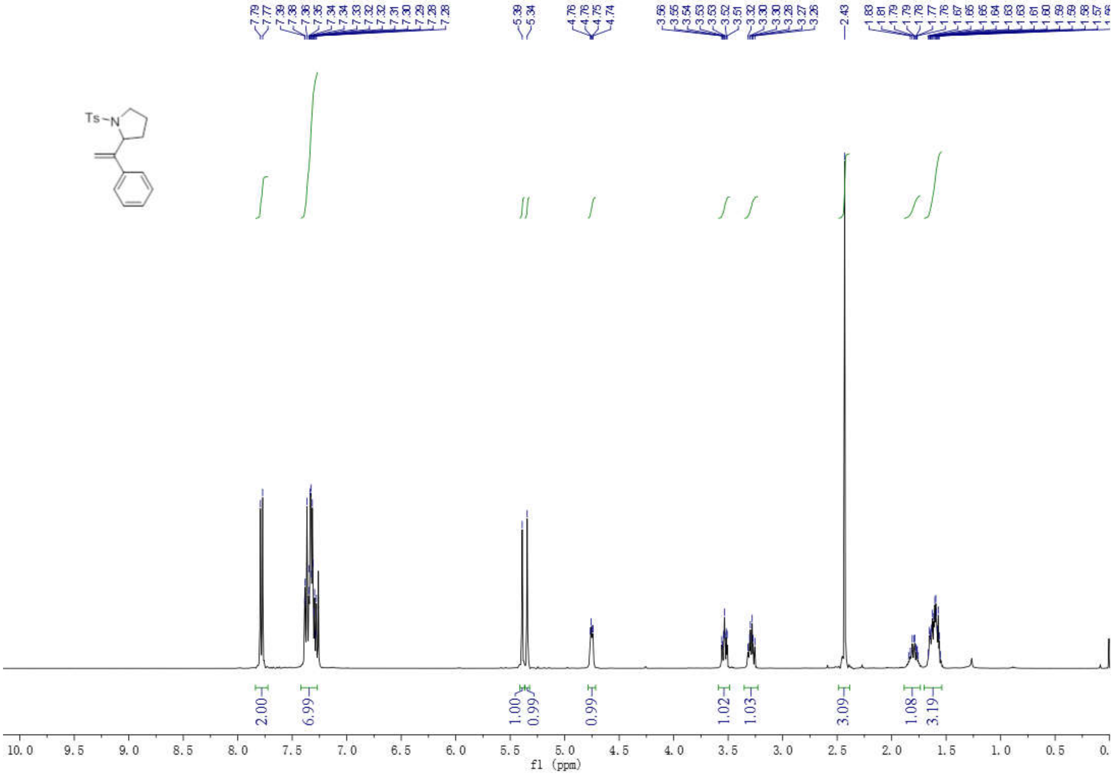
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10b**



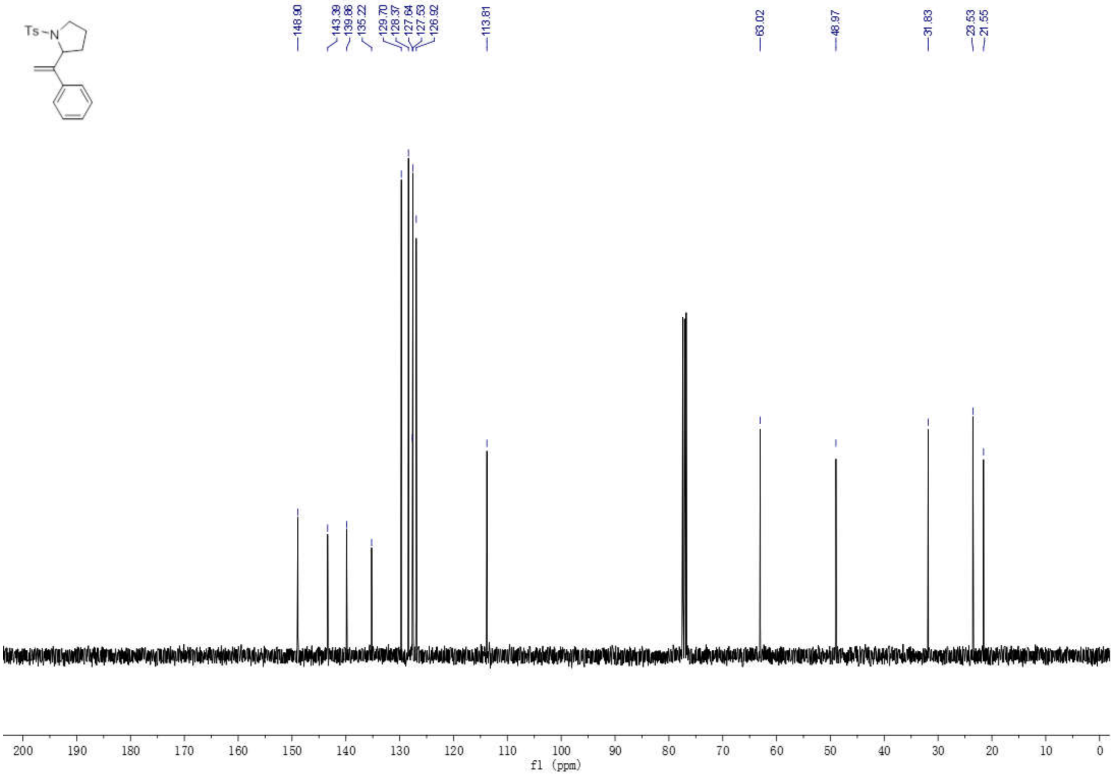
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10b**



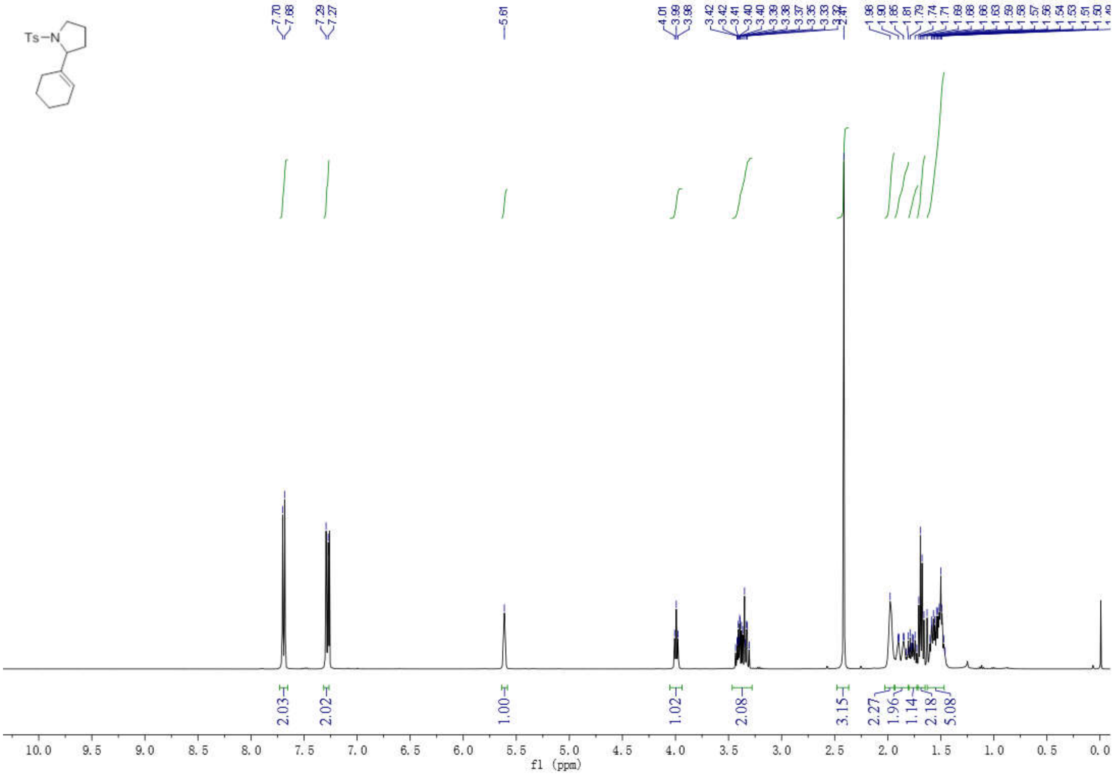
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10c**



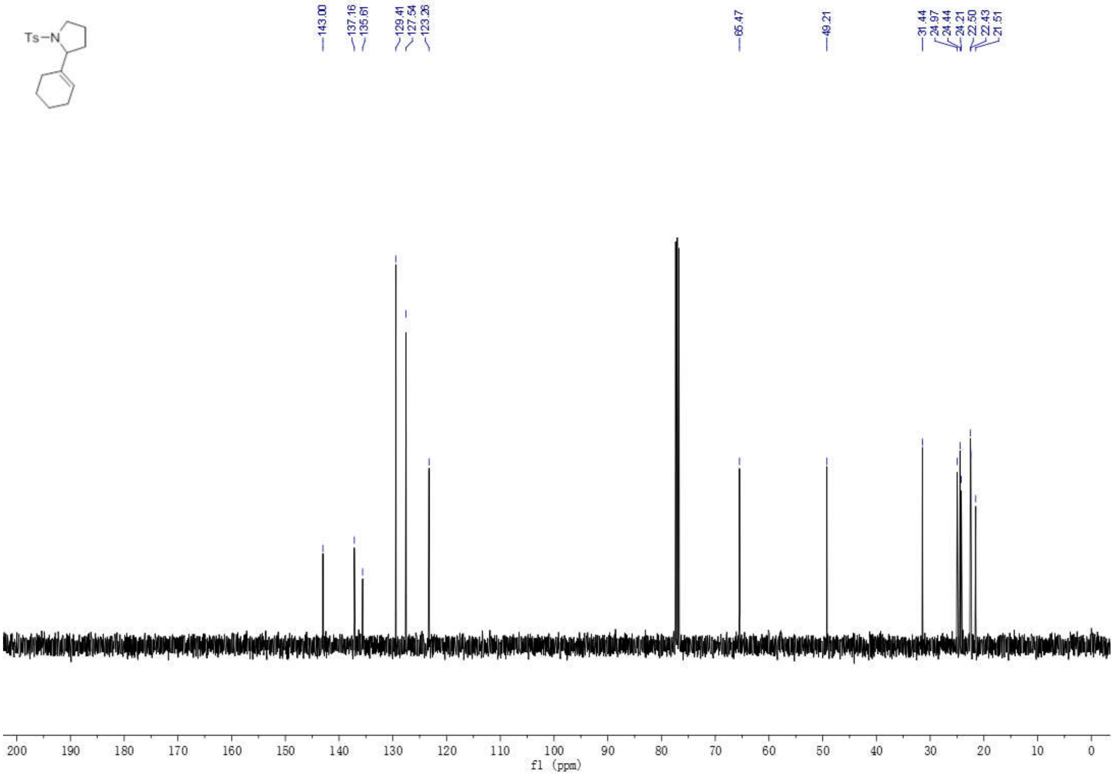
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10c**



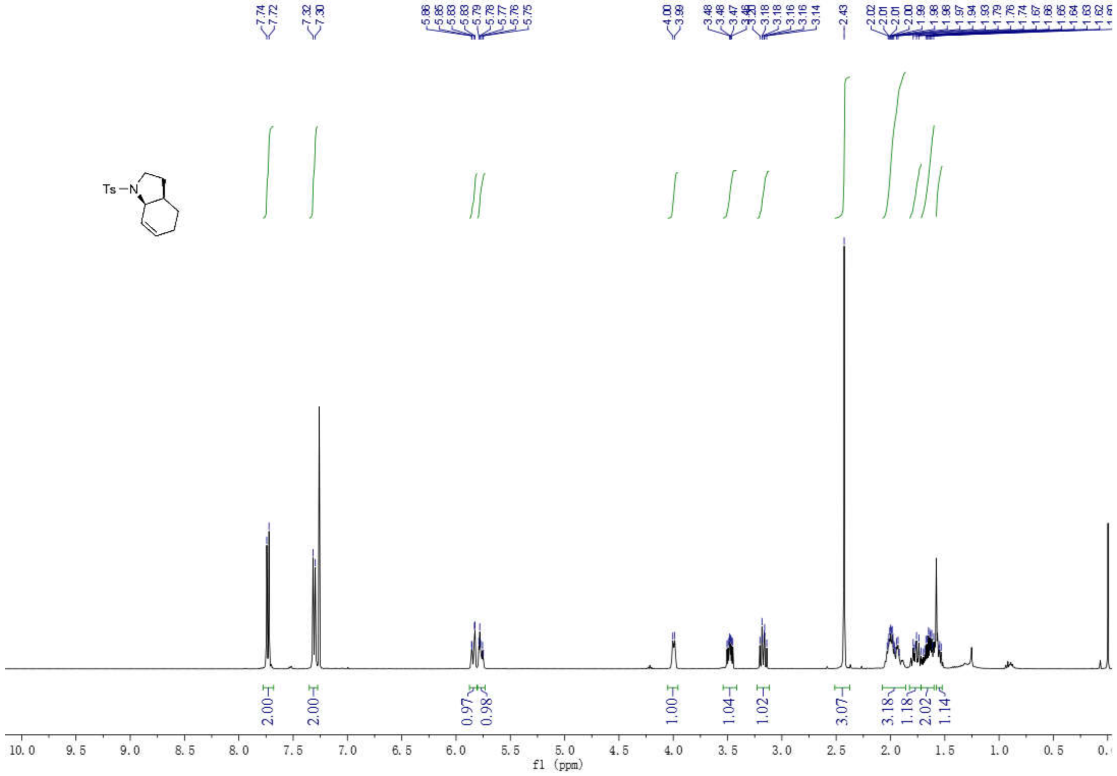
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10d**



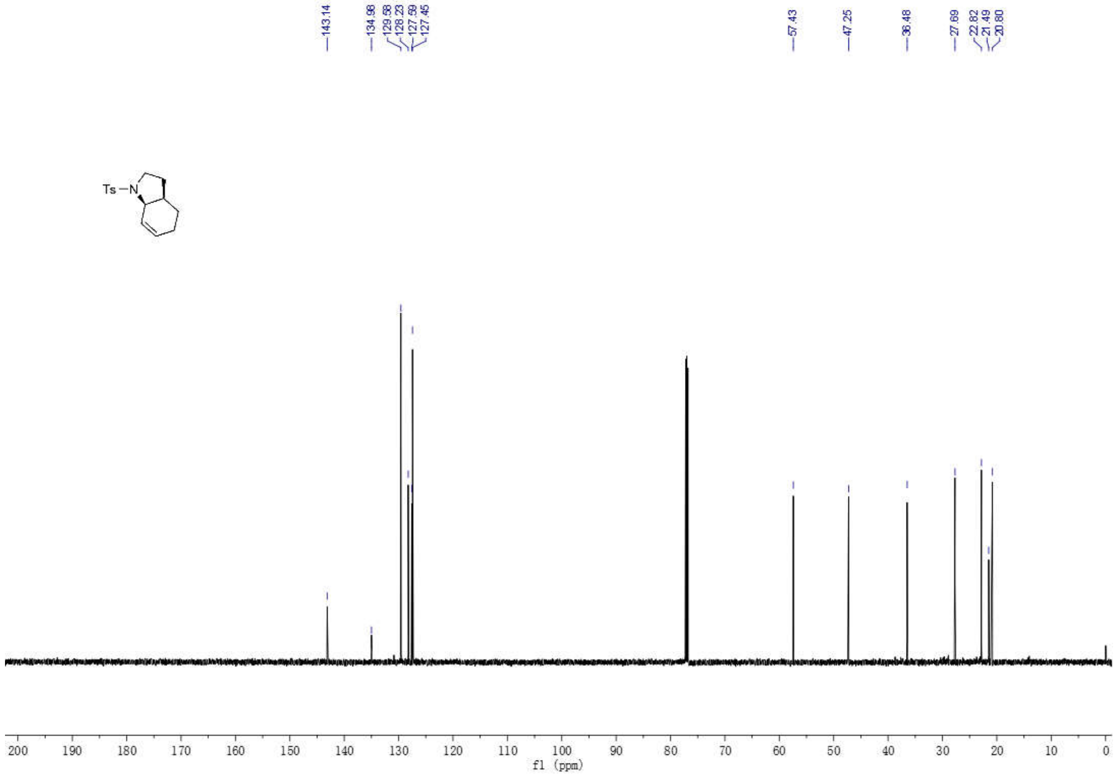
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10d**



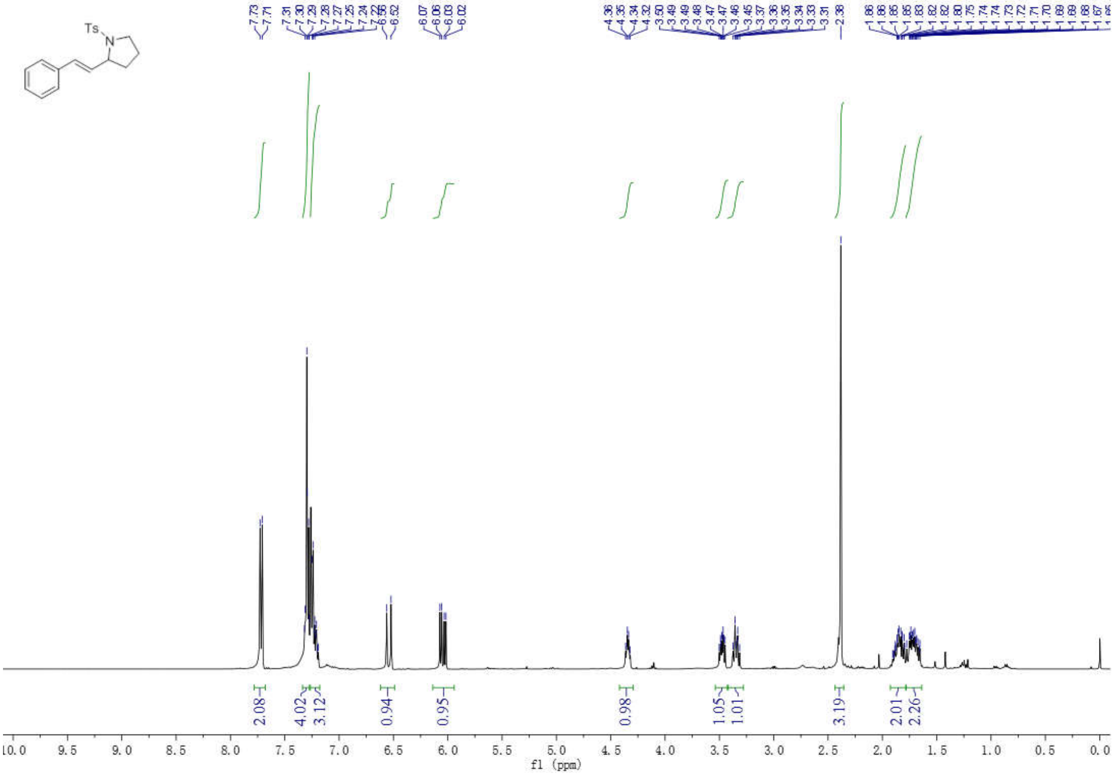
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **10e**



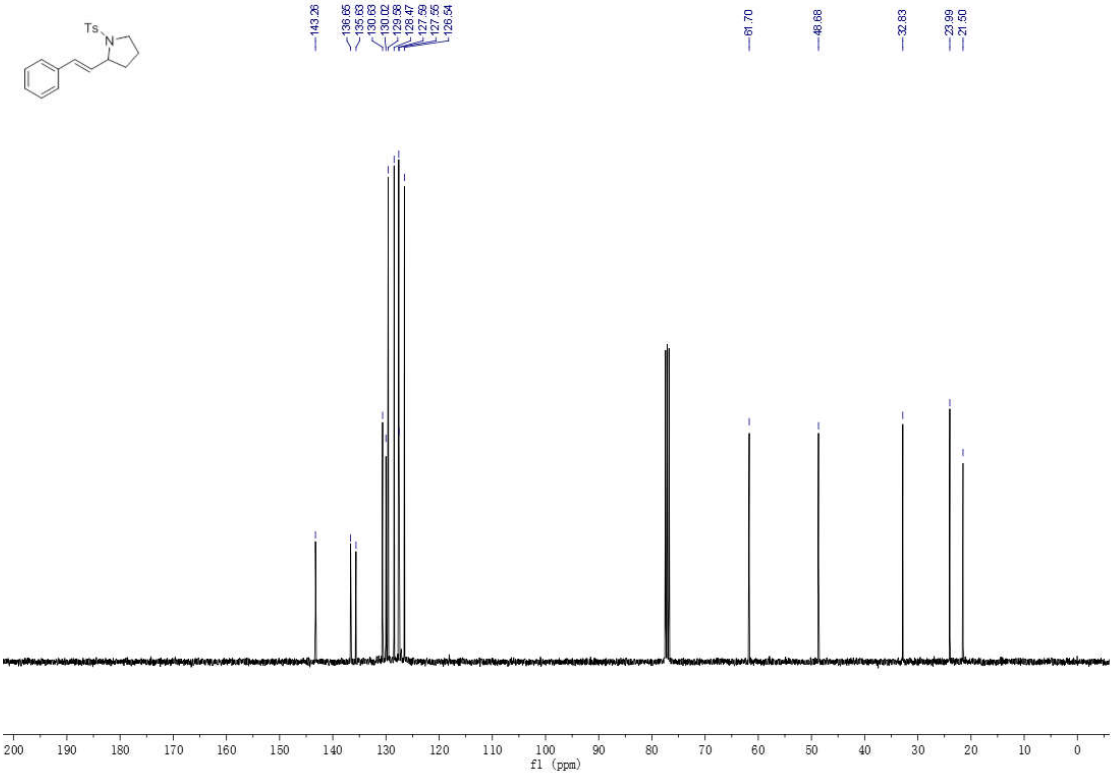
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **10e**



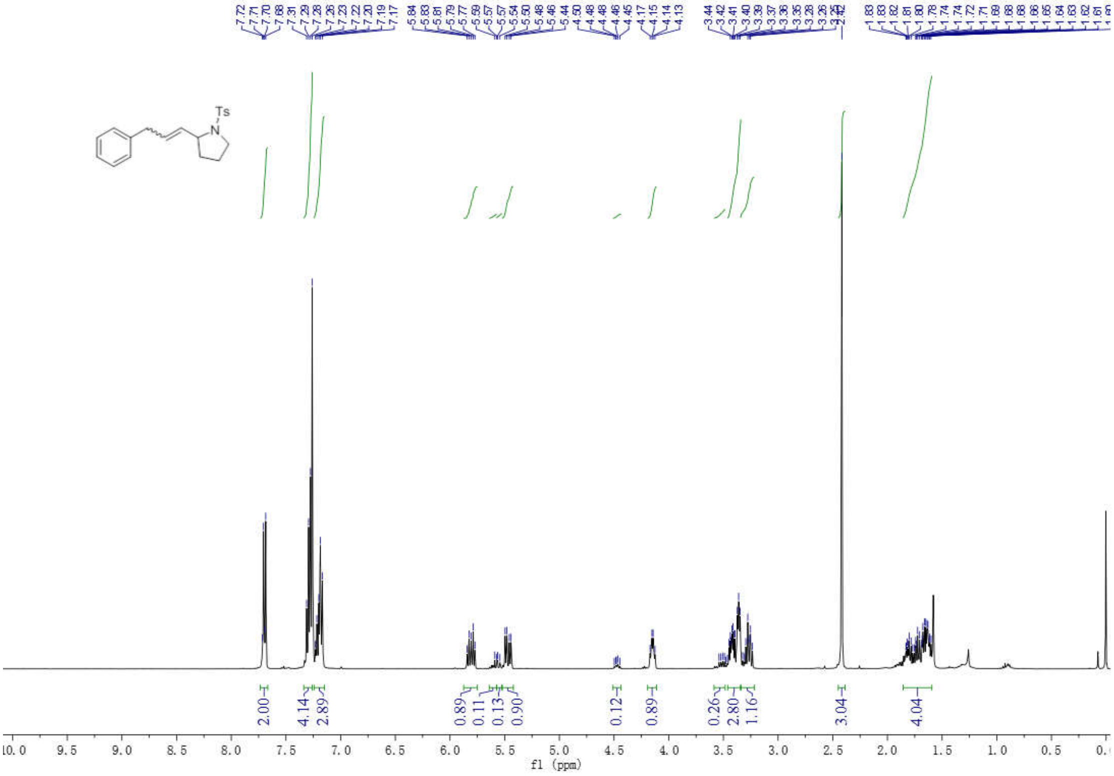
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **10f**



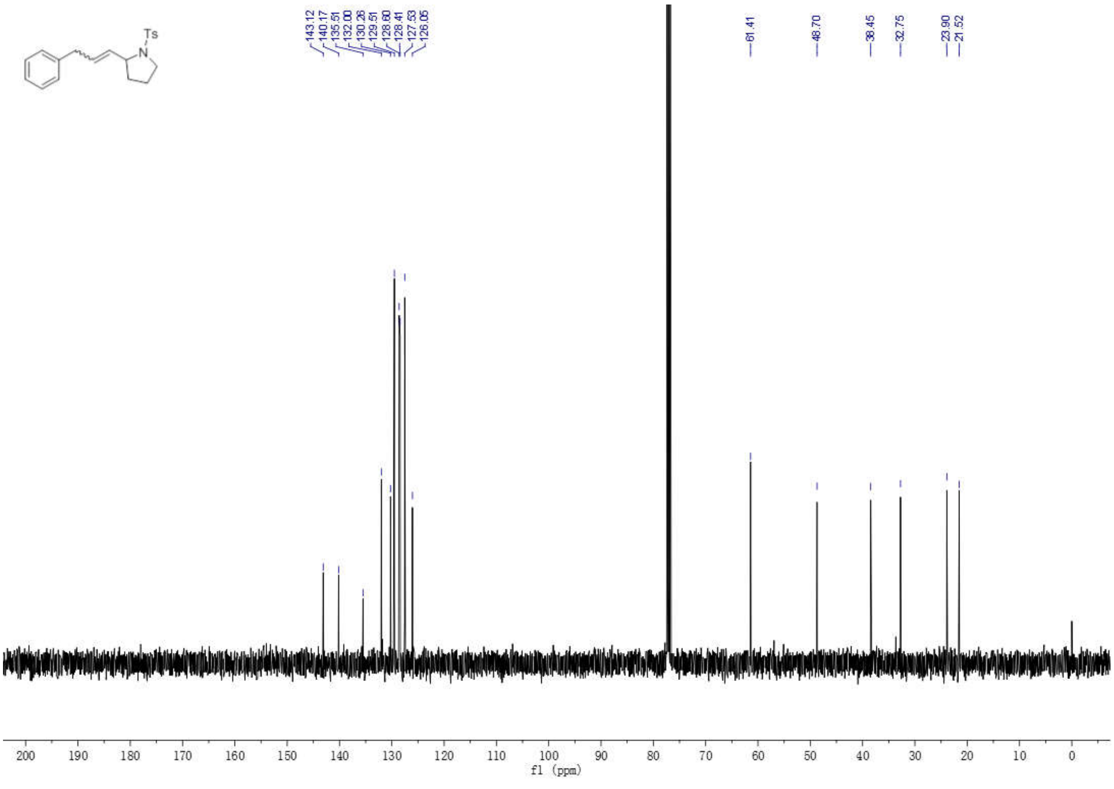
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **10f**



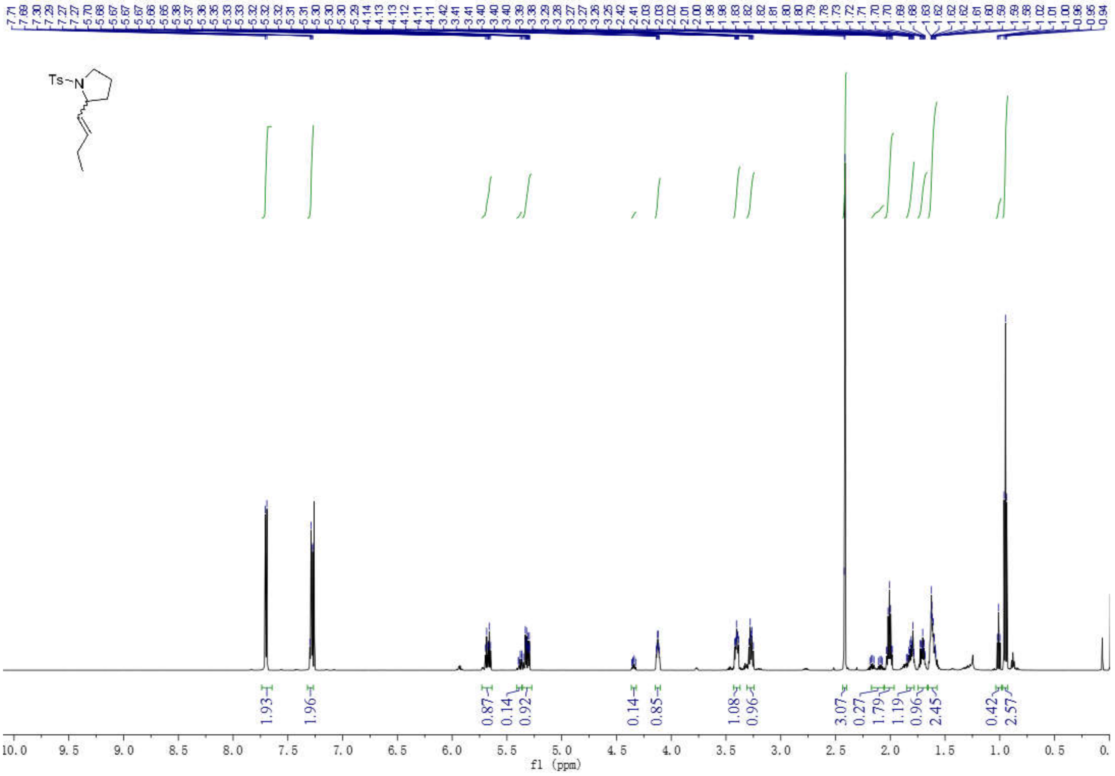
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10g**



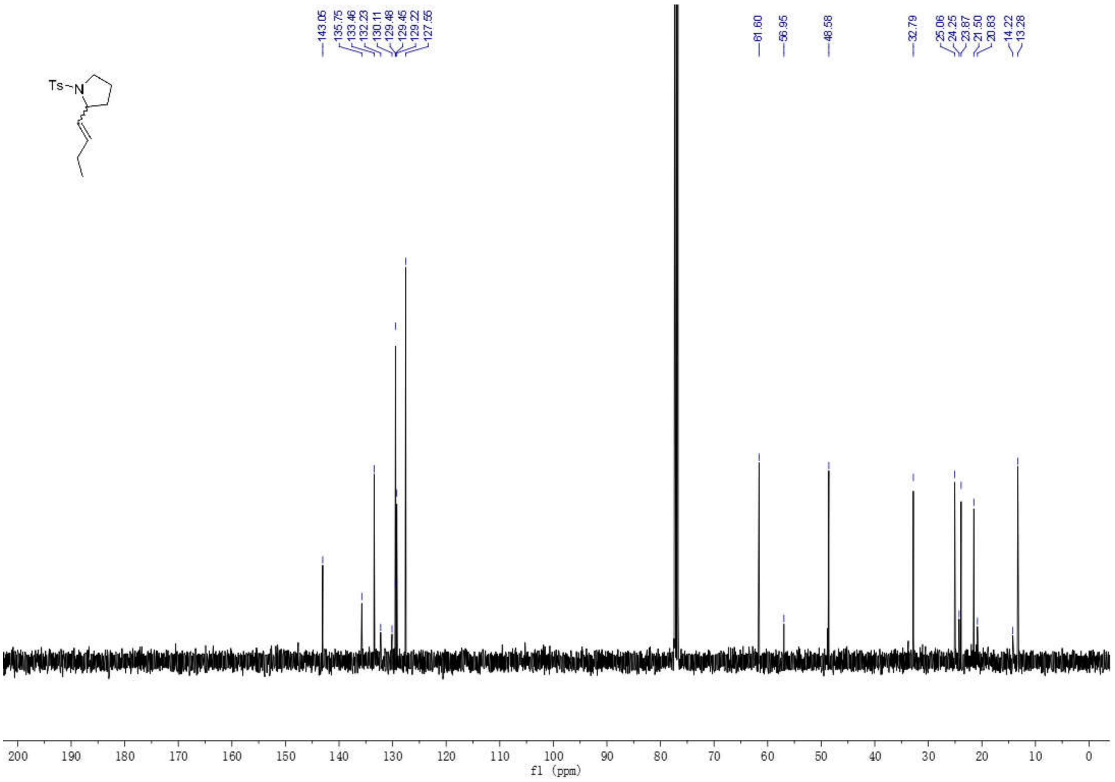
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10g**



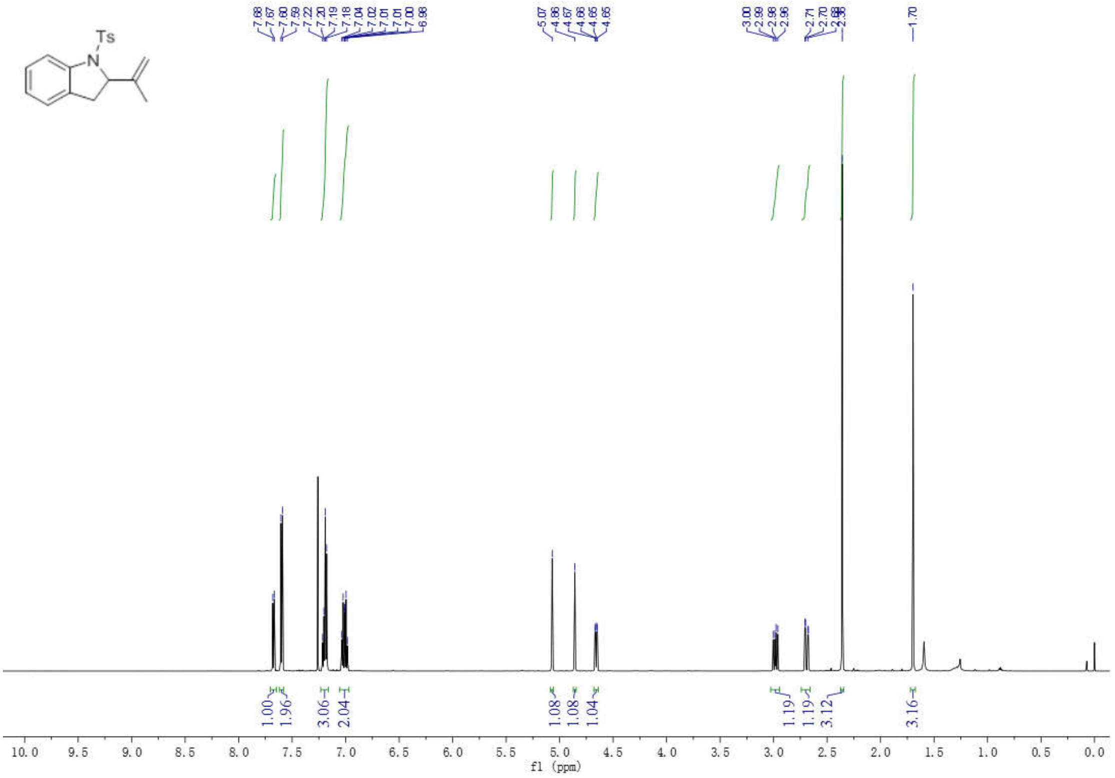
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **10h**



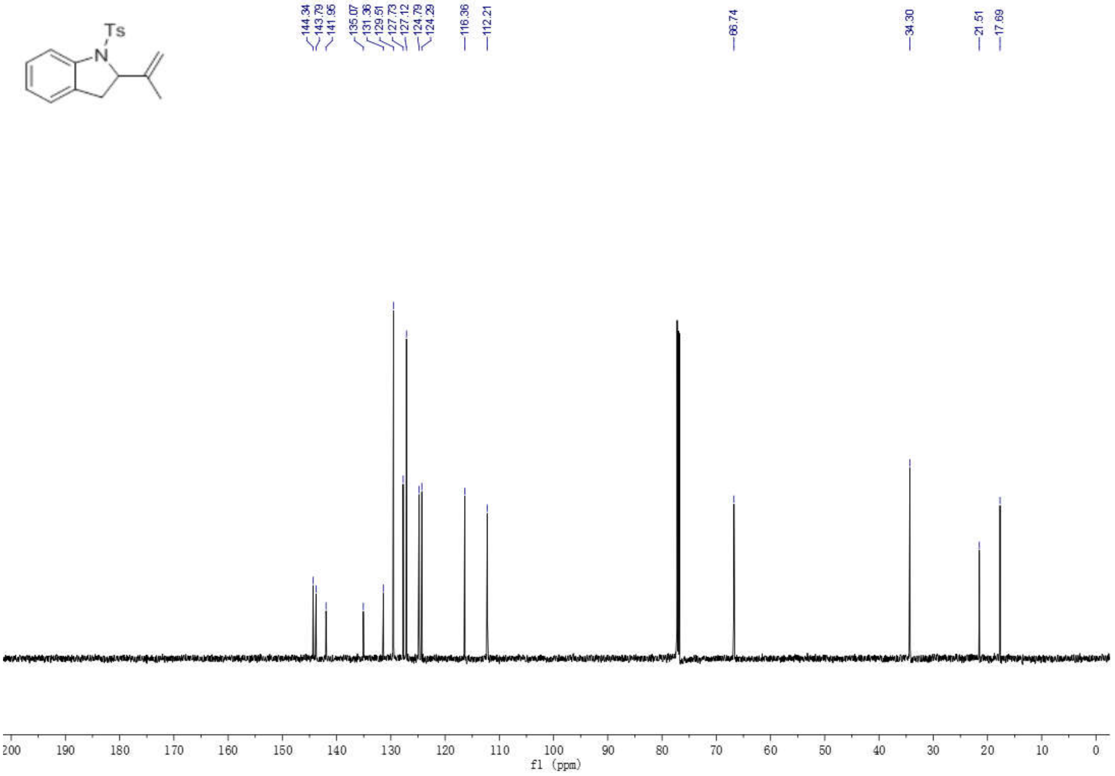
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10h**



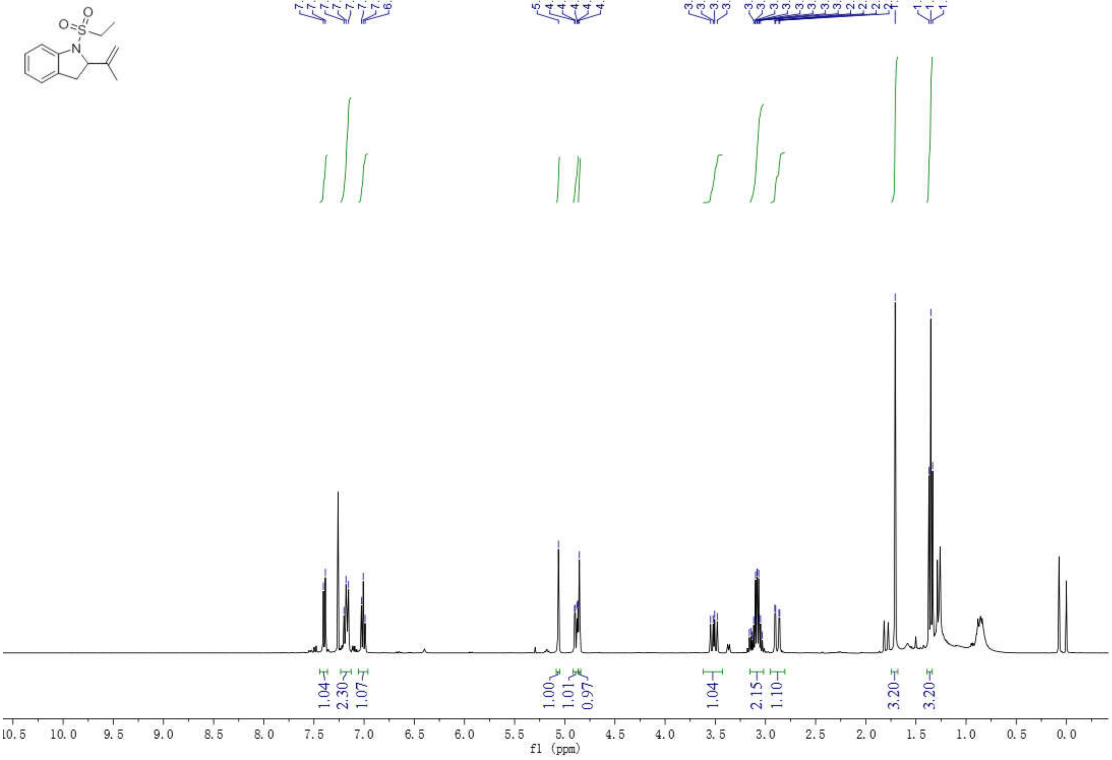
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10i**



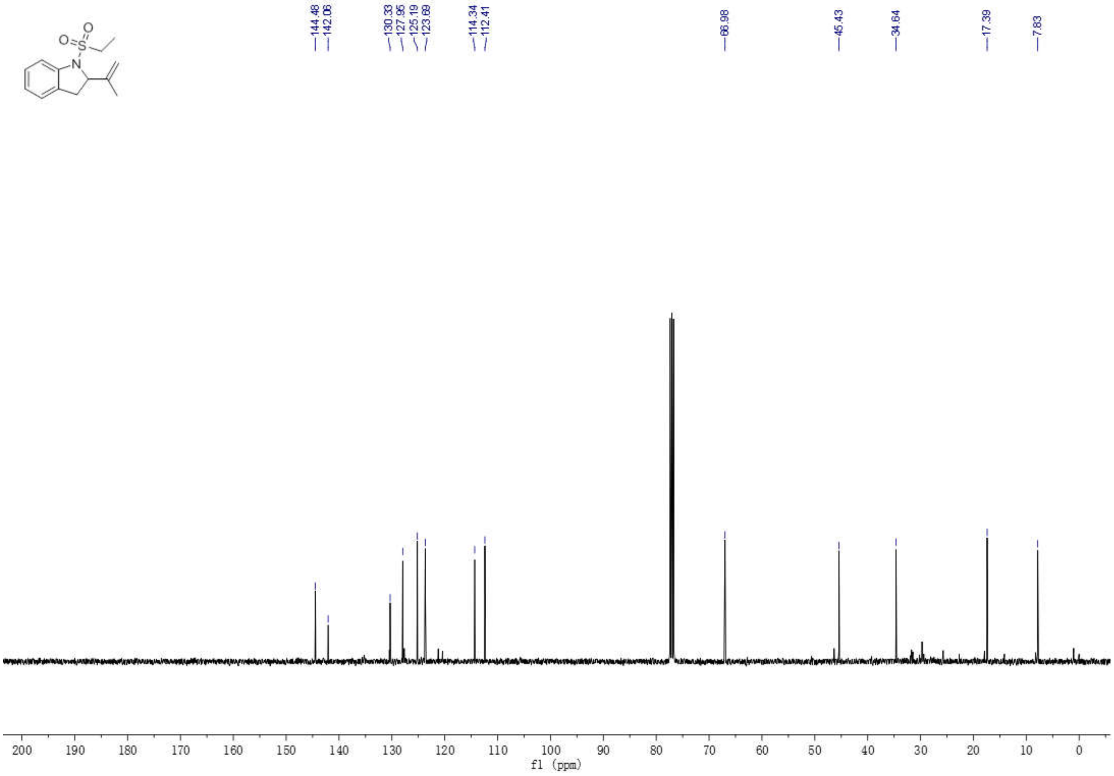
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10i**



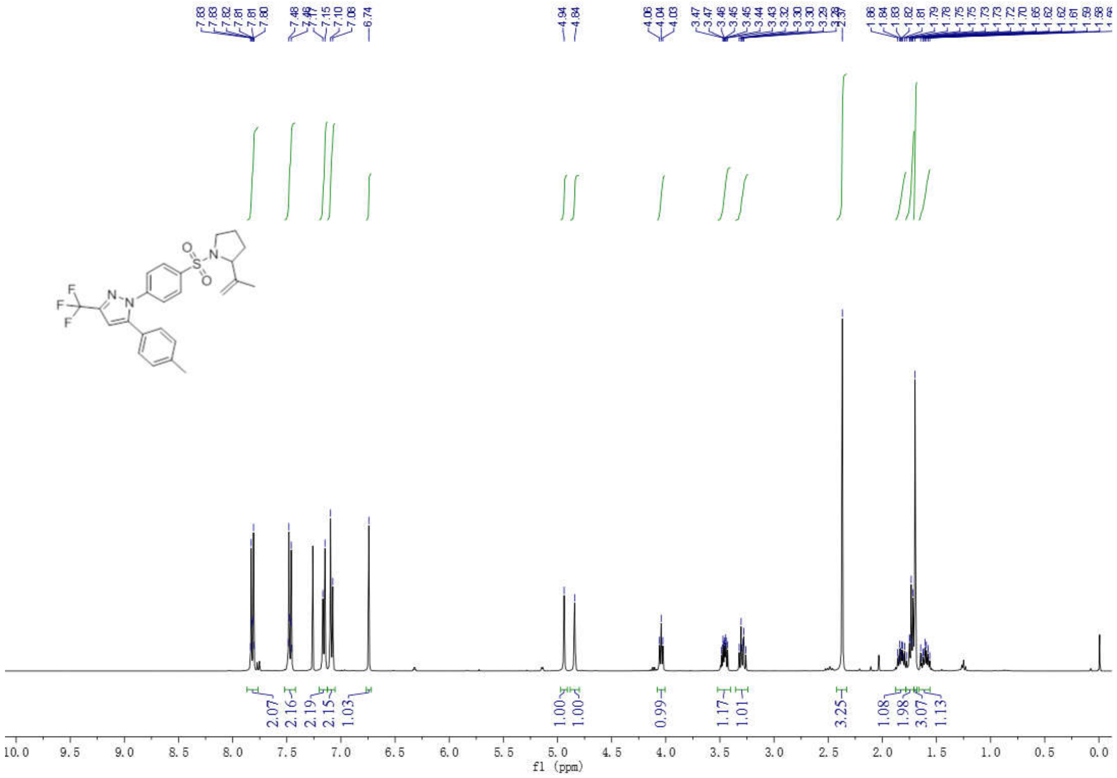
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10j**



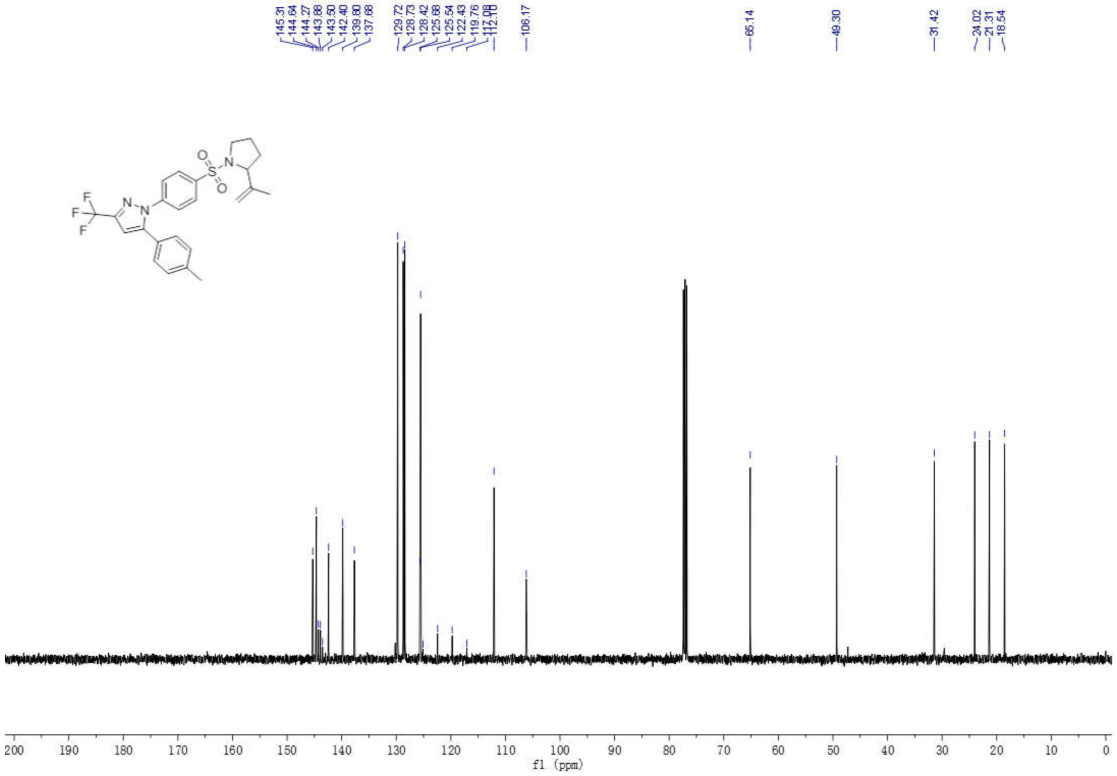
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10j**



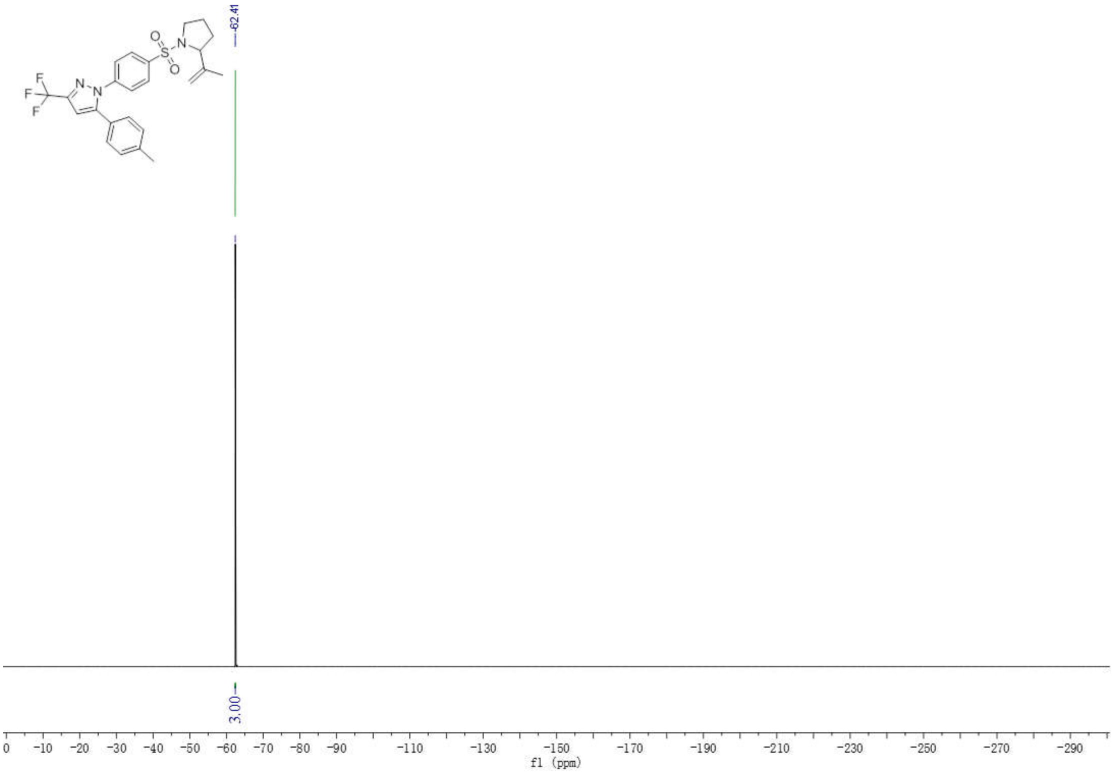
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **10k**



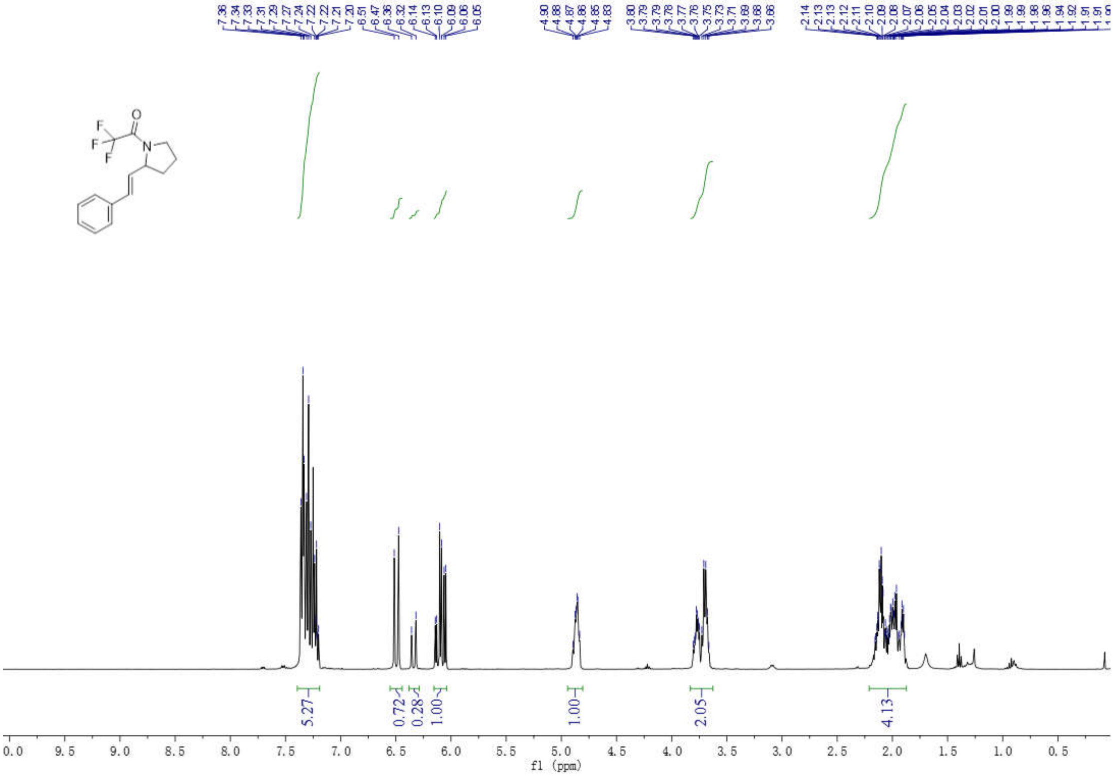
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **10k**



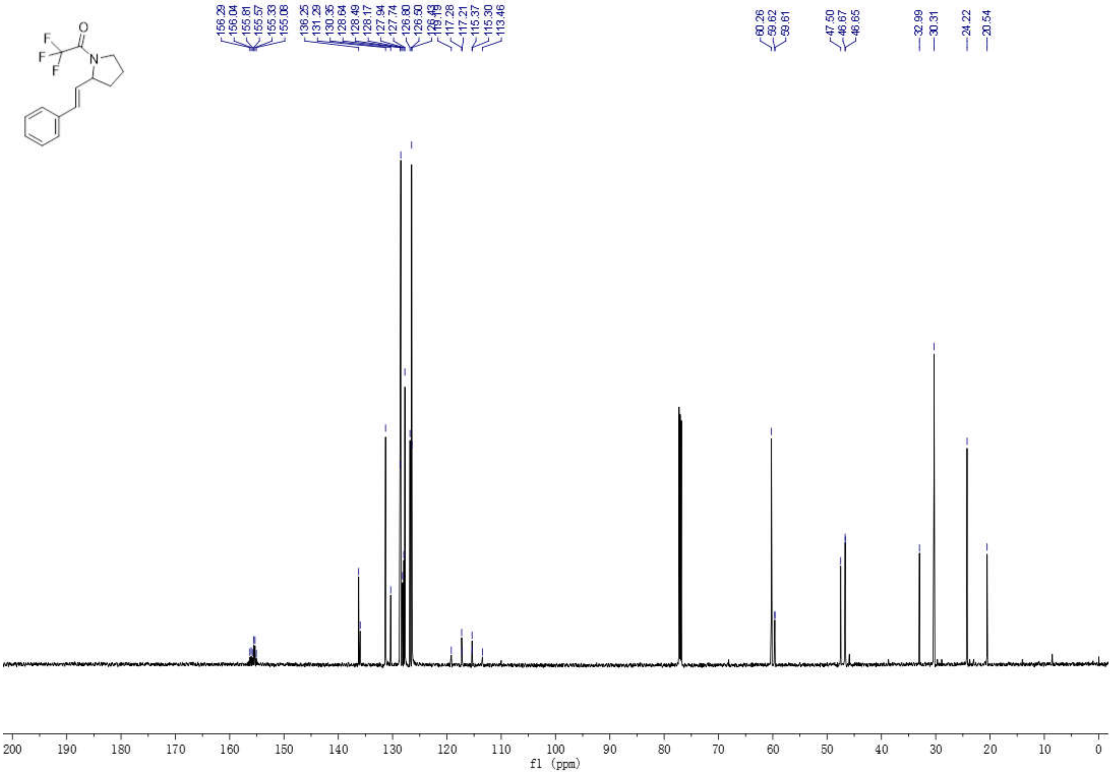
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 ºC) of **10k**



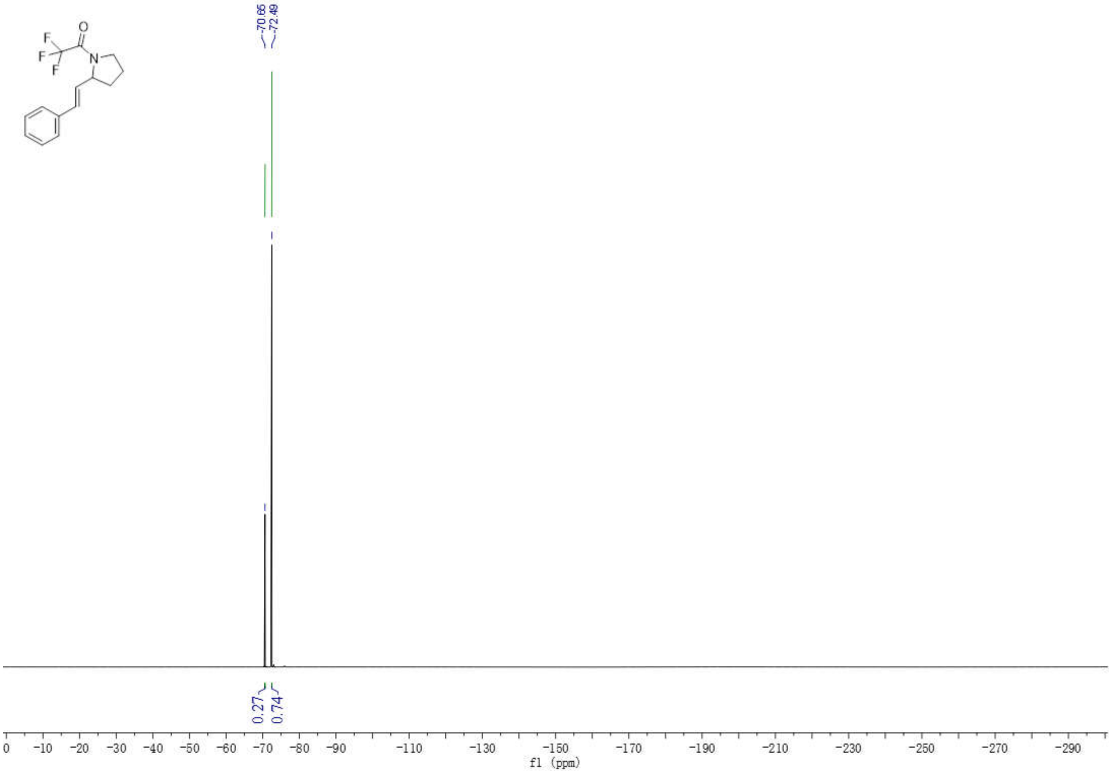
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **10l**



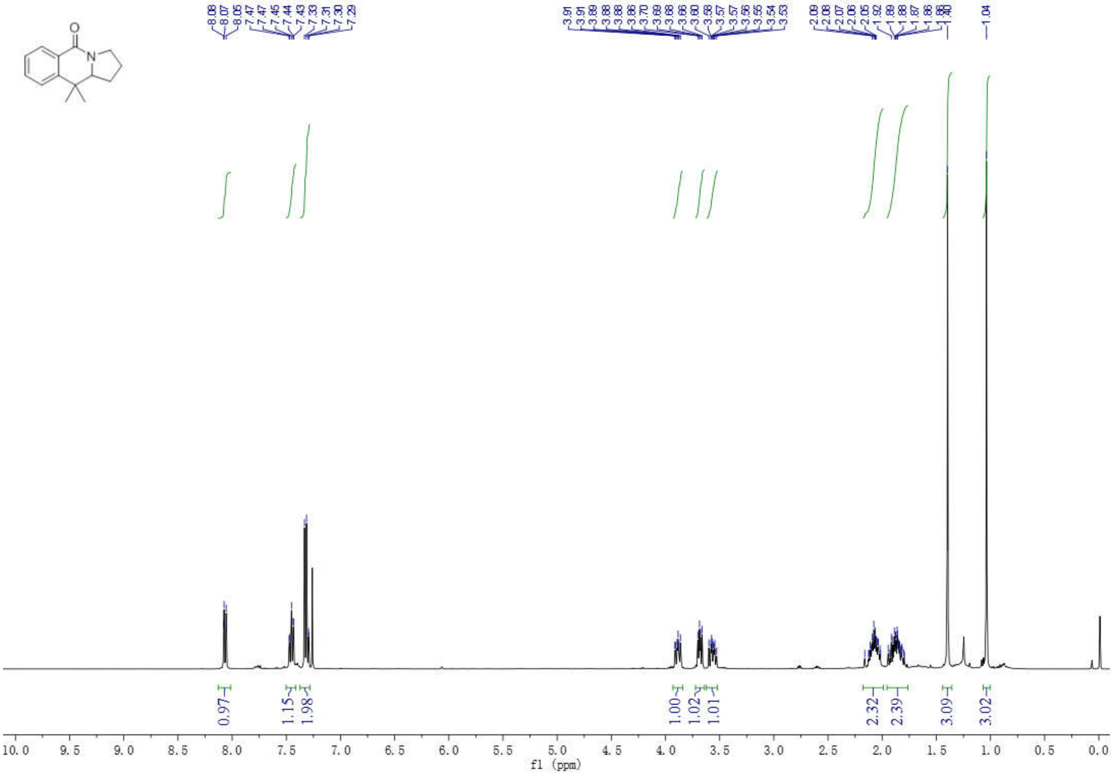
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **10l**



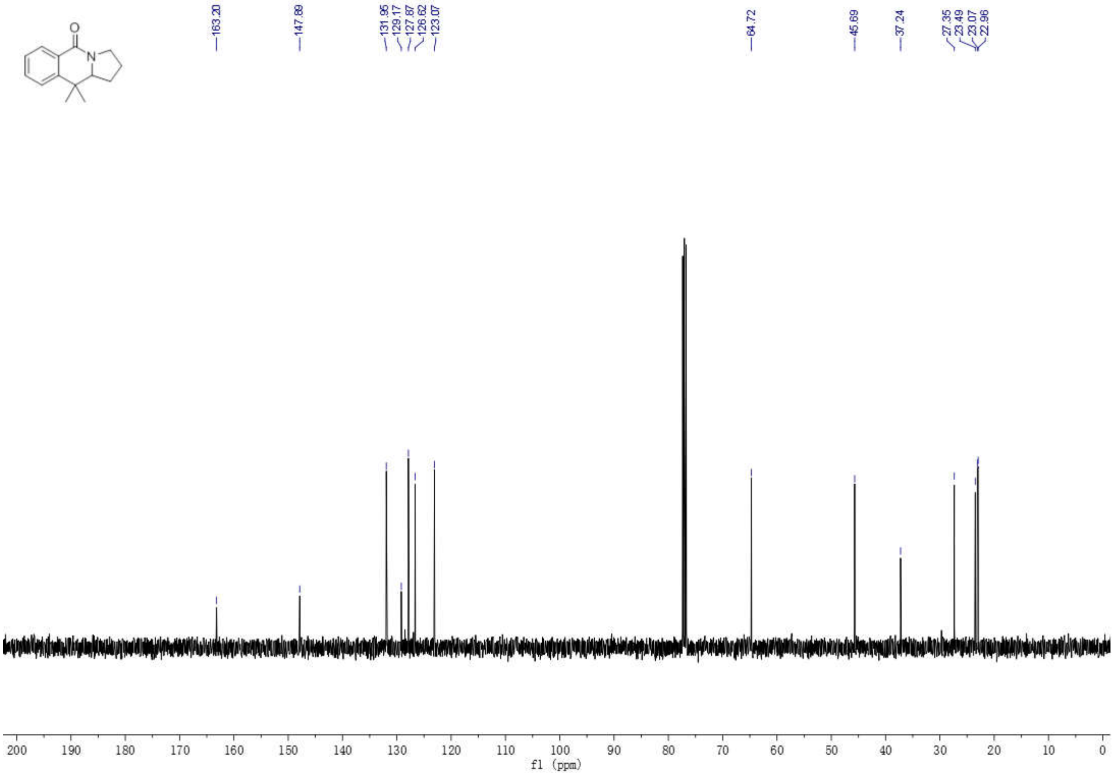
^{19}F NMR spectrum (377 MHz, CDCl$_3$, 23 ºC) of **10l**



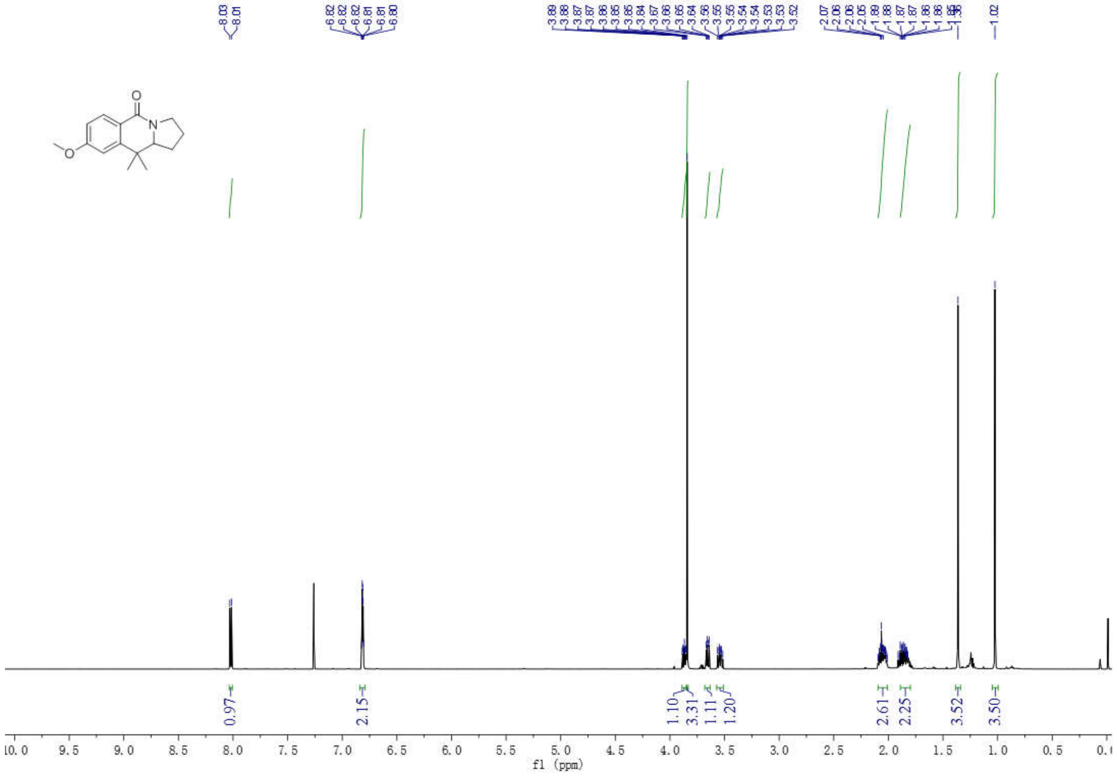
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **12a**



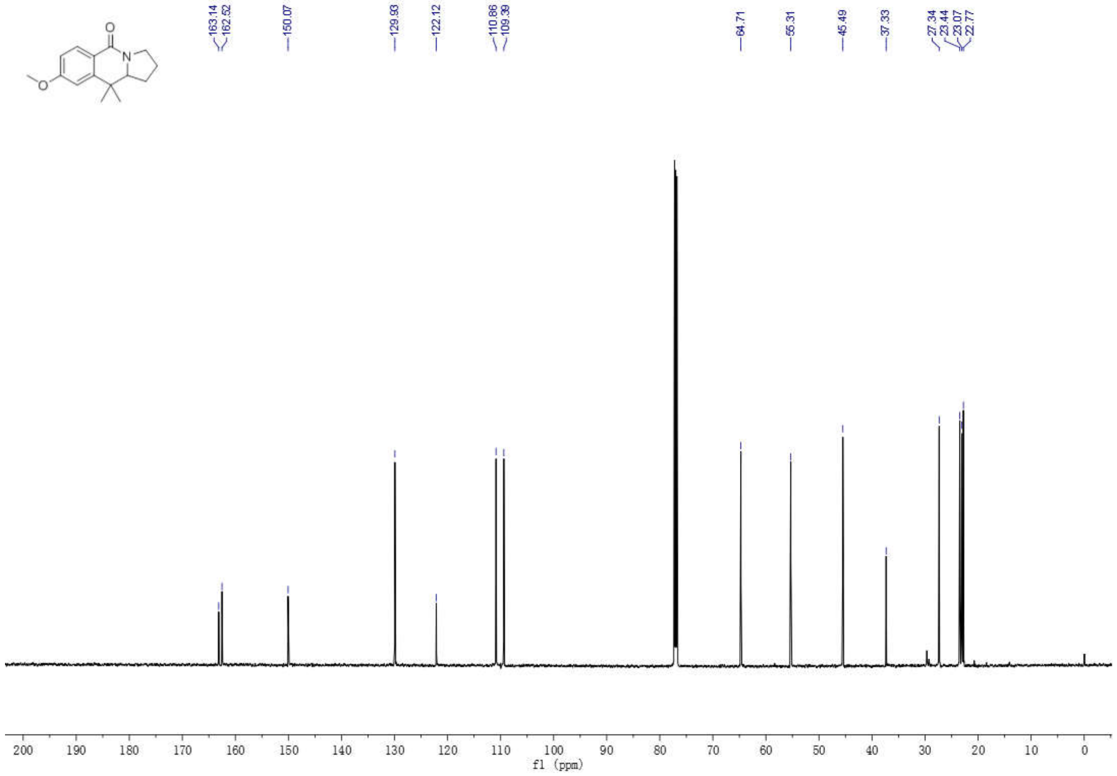
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **12a**



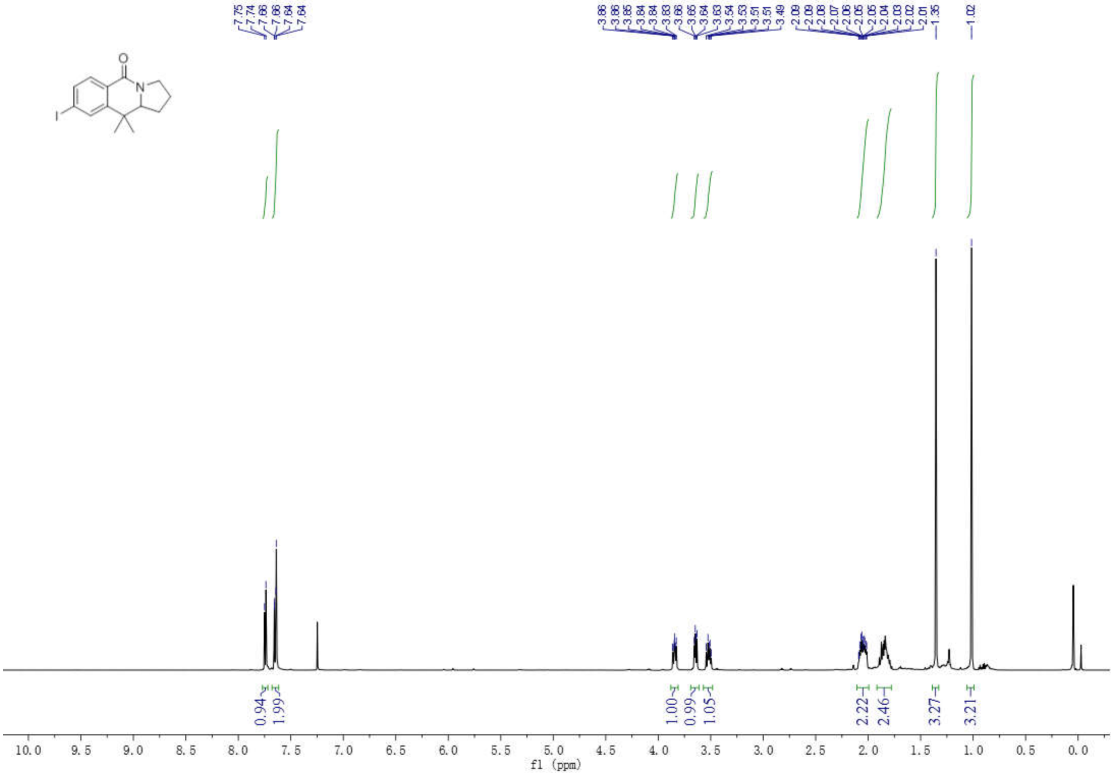
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **12b**



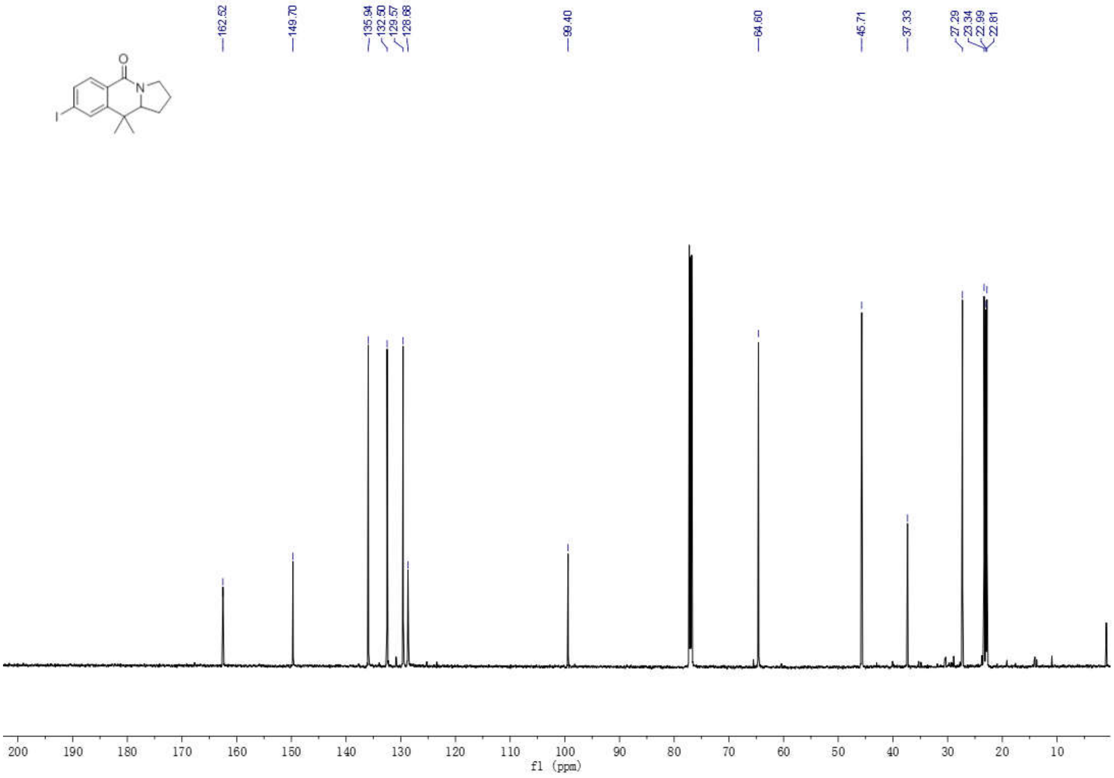
^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **12b**



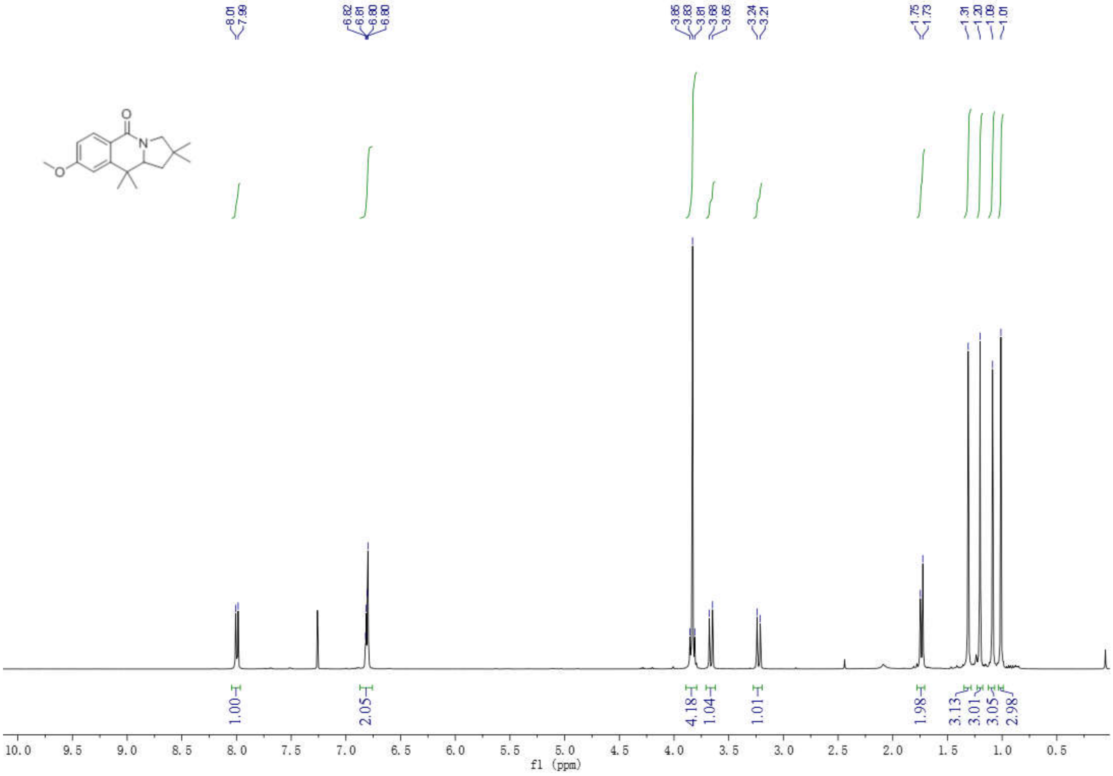
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **12c**



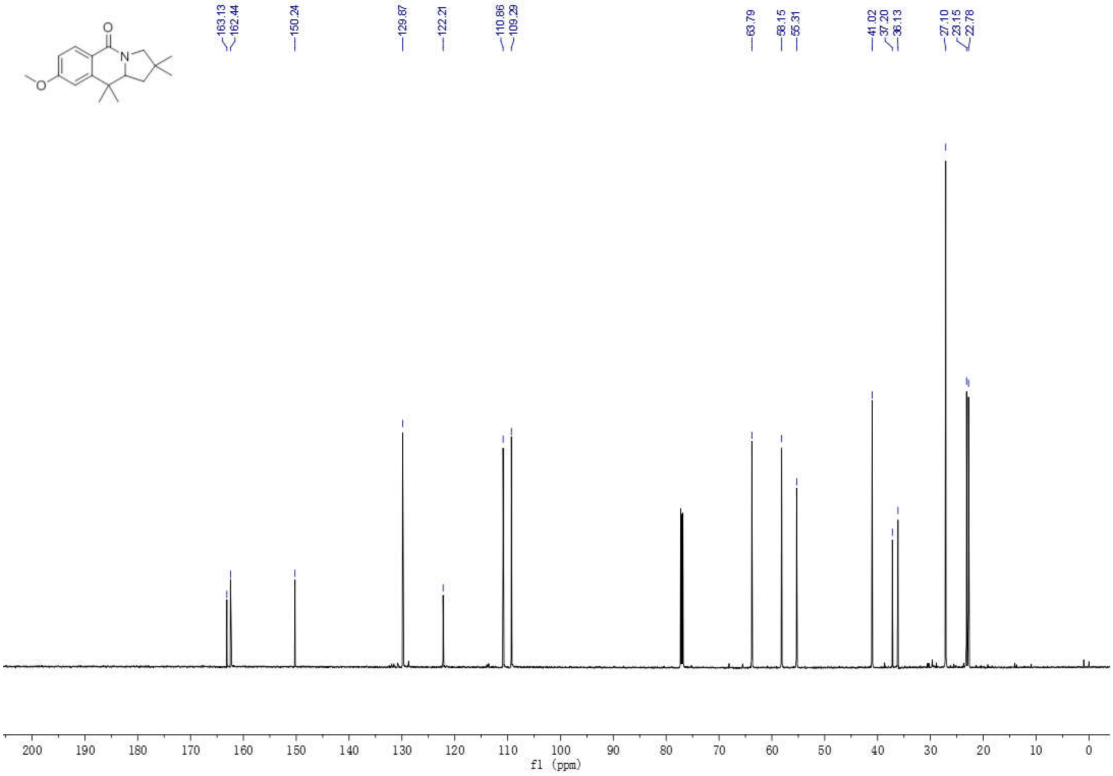
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **12c**



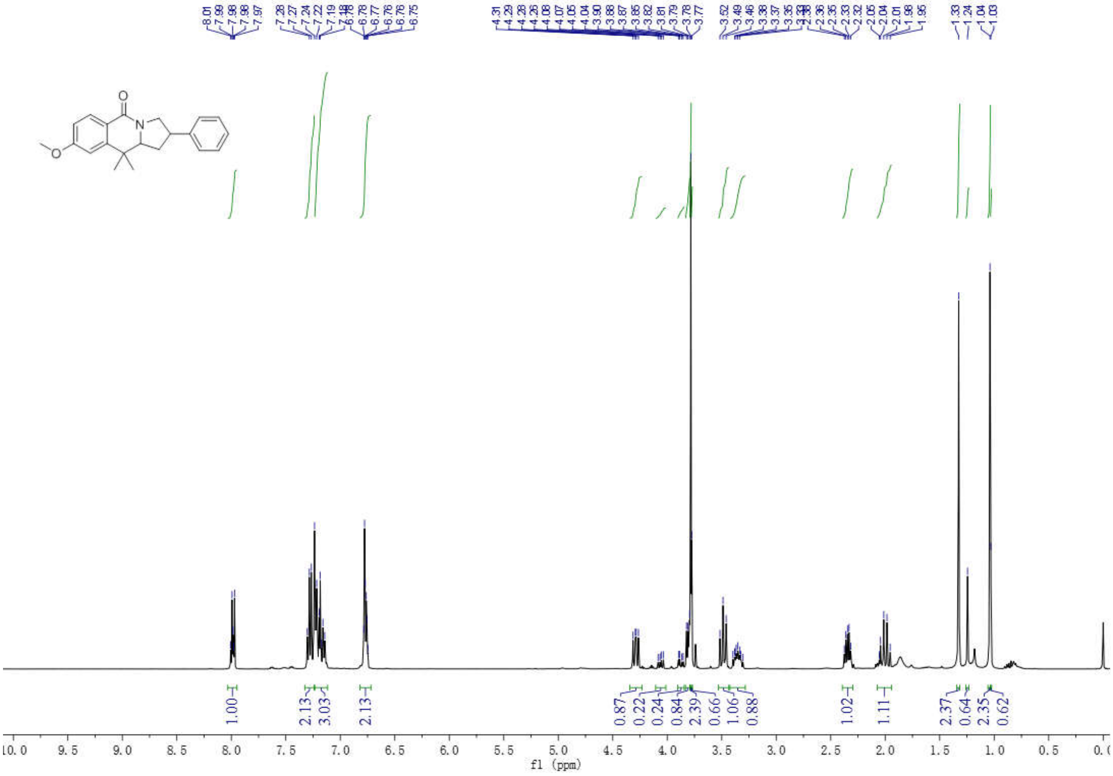
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **12d**



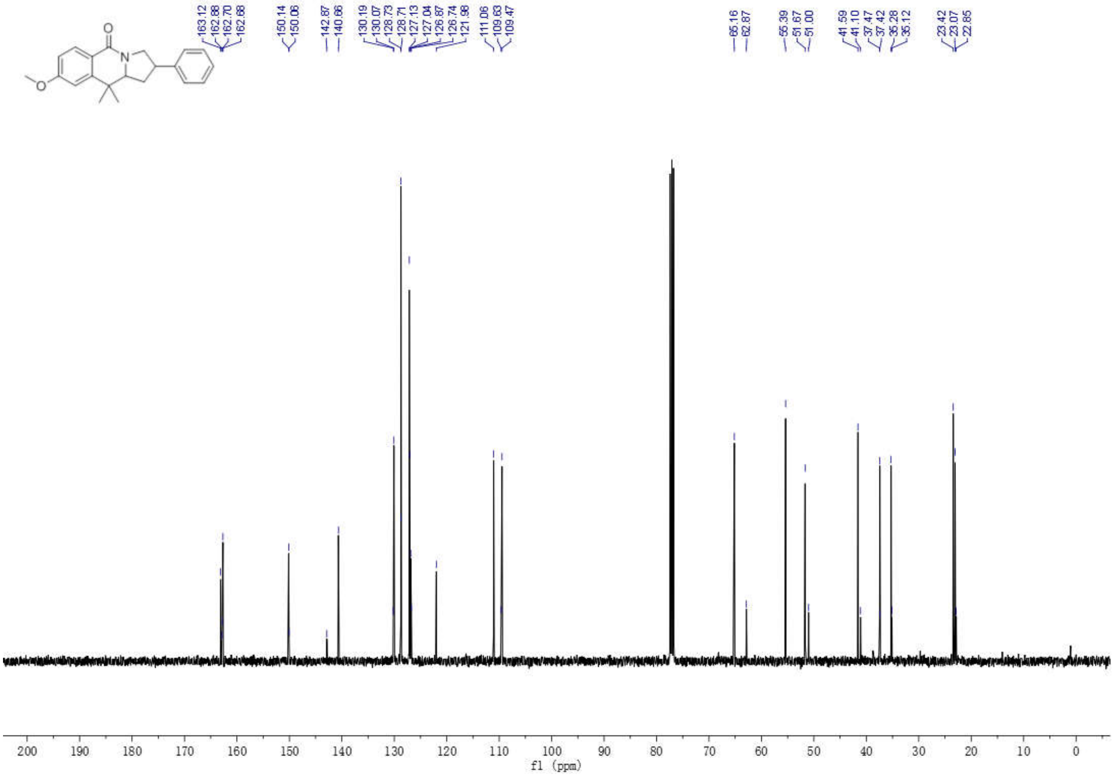
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **12d**



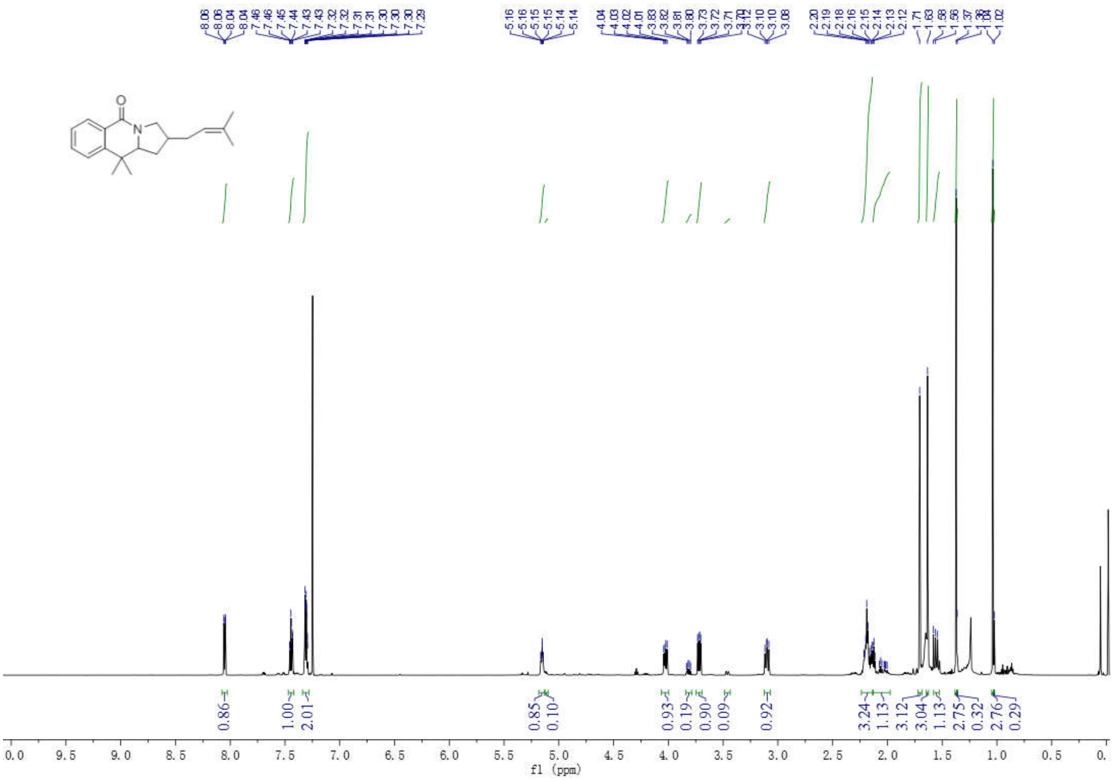
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **12e**



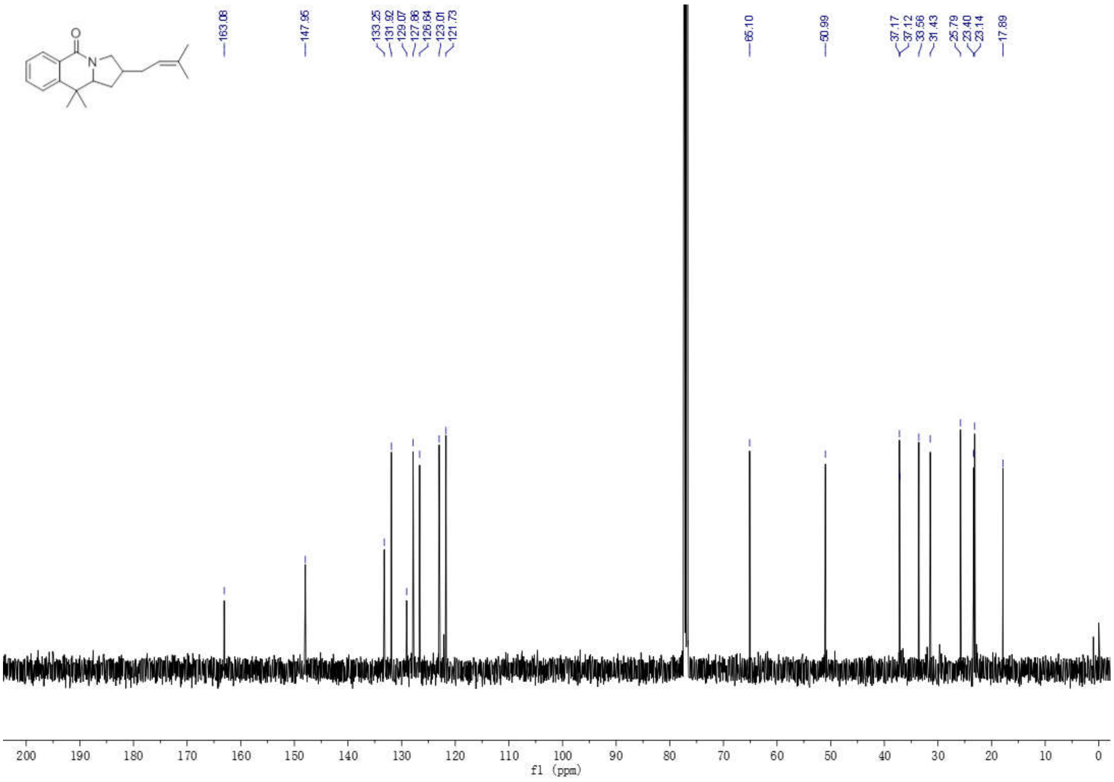
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **12e**



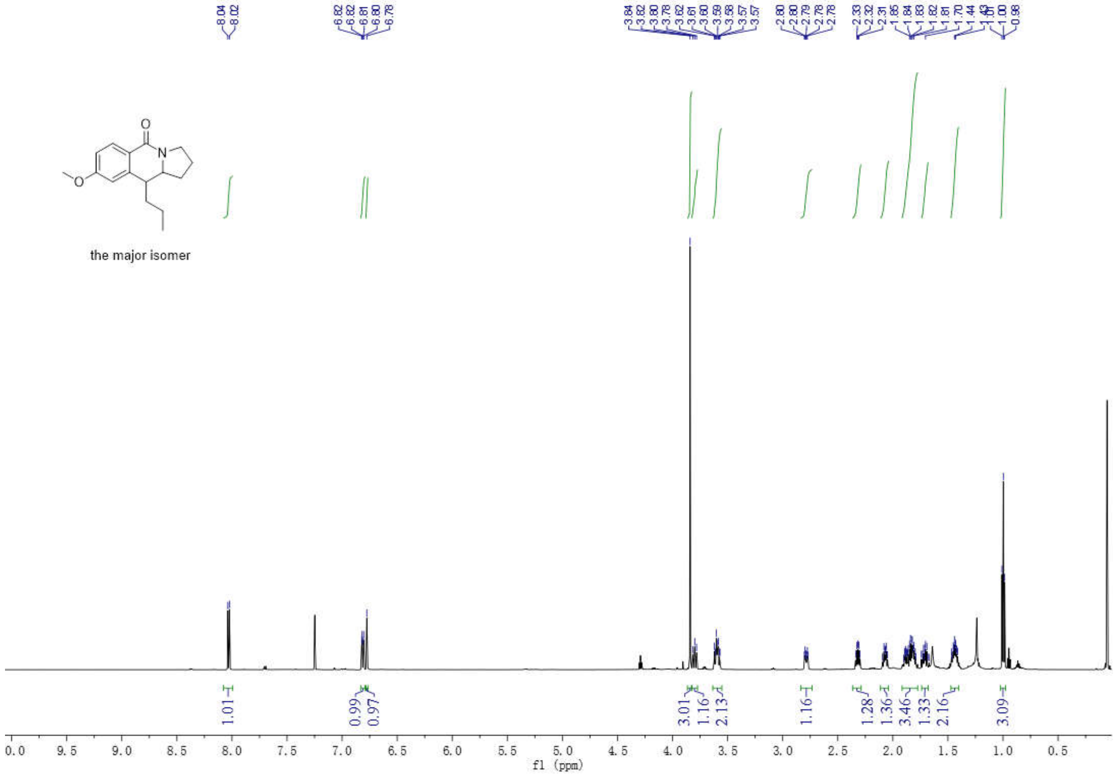
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **12f**



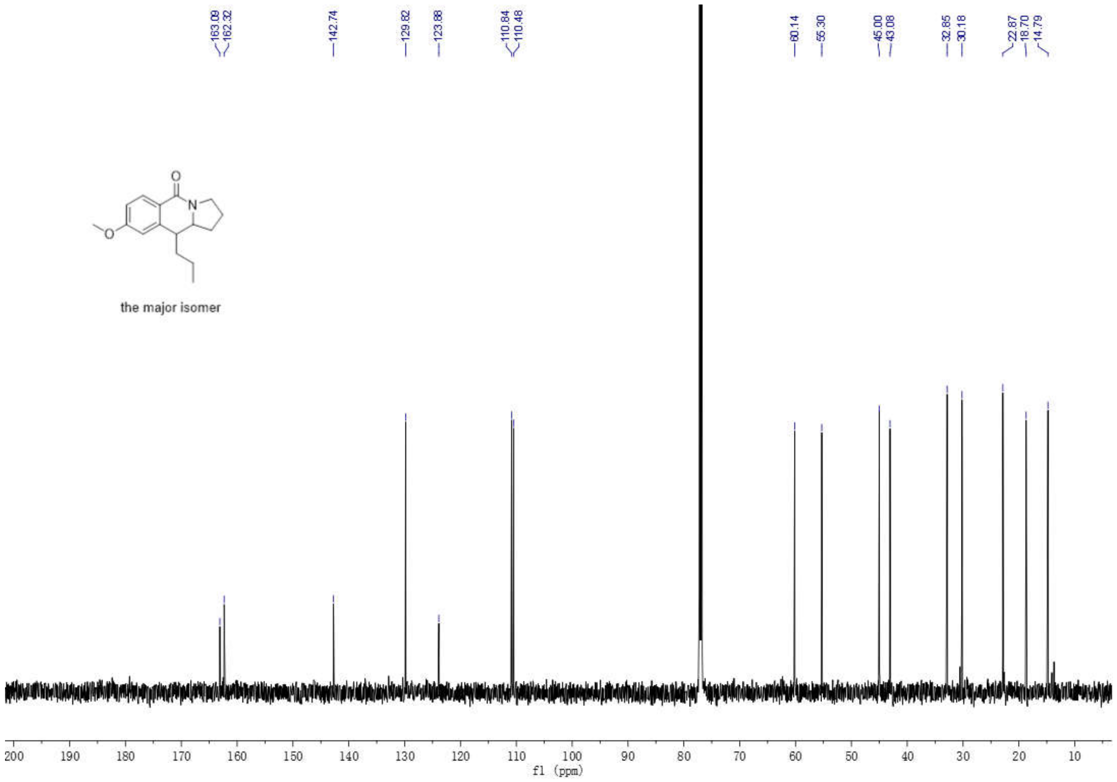
^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **12f**



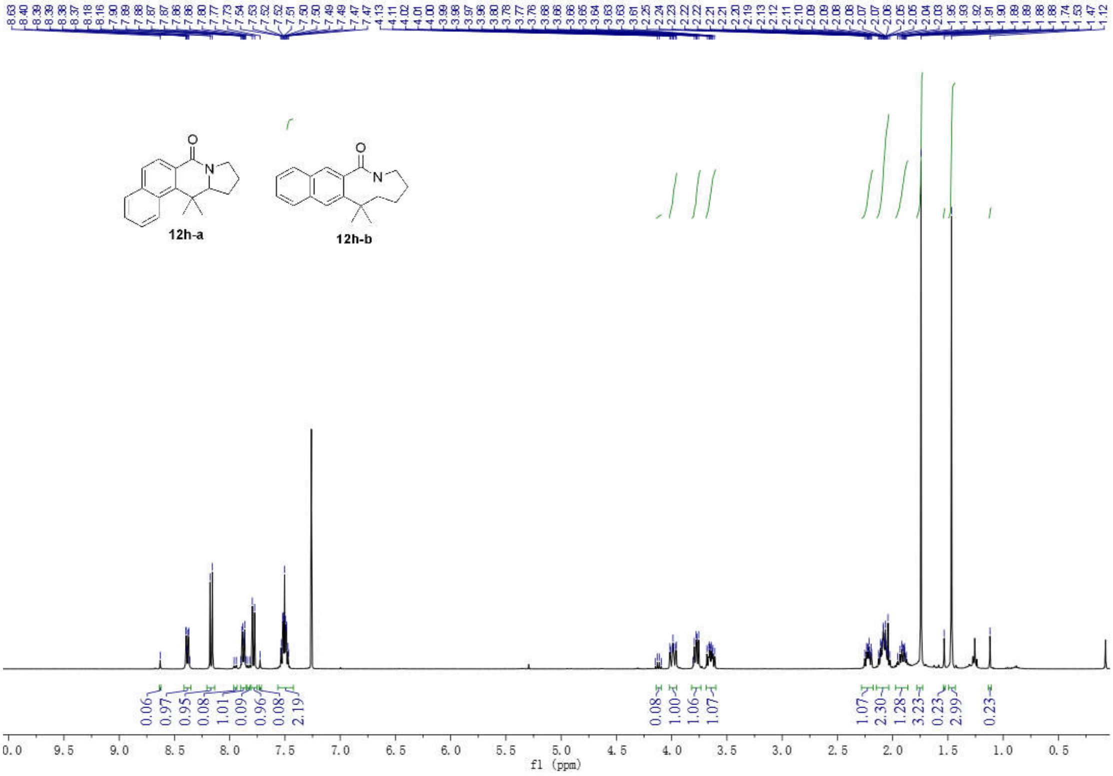
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23 ºC) of **12g**



^{13}C NMR spectrum (150 MHz, CDCl$_3$, 23 ºC) of **12g**



^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ºC) of **12h**



^{13}C NMR spectrum (100 MHz, CDCl$_3$, 23 ºC) of **12h**