Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Amidyl Radical-mediated aminodifluoroallylation of alkenes via photoredox catalysis

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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, and 377 MHz or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with $CDCl_3$ as the 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 the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR); ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.00 ppm. 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 glassware with 15 cm diameter (Figure S1). The LED strips were wrapped in aluminum foil to maintain a specific reaction temperature. In this case, the reaction temperature is approximately 35 °C. Optimum yields were then observed.

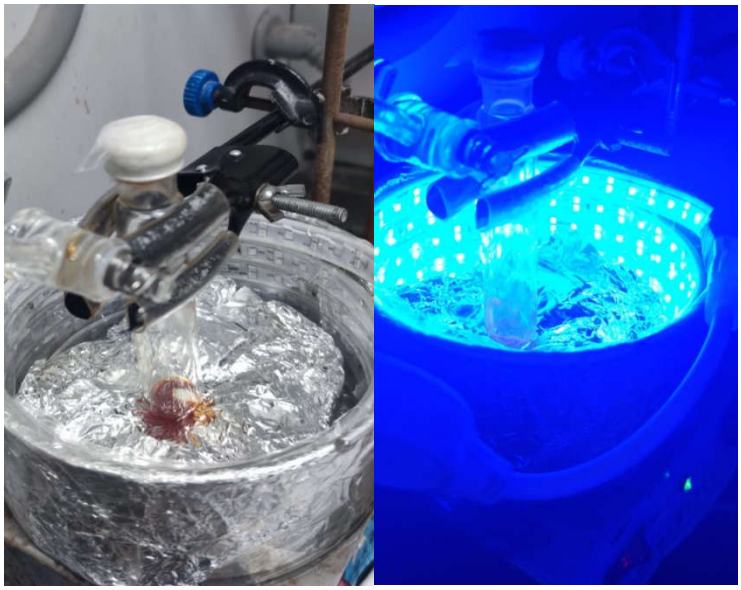
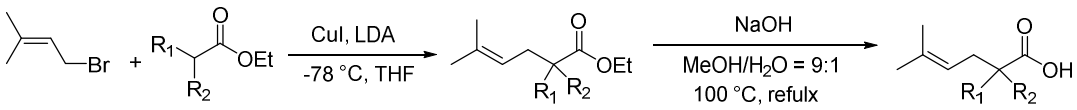


Figure S1. Reaction setup

3. General procedures for synthesis of substrates

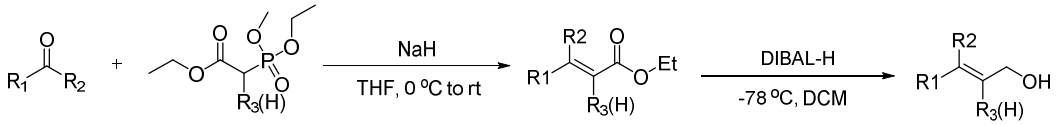
3.1 Synthesis of *γ, δ*-unsaturated carboxylic acids [1]



1) To a flame-dried flask was 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 ºC. The mixture was stirred for 30 min and the propargylic bromide (1.0 equiv.) was then added dropwise. After the resulting mixture was stirred at -78 ºC 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 ºC for 1 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 allylic alcohols [2]

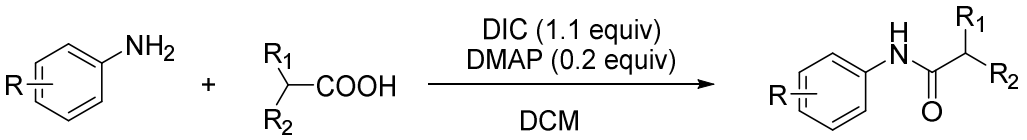


1) To a suspension of NaH (480 mg, 60% in mineral oil, 12 mmol) in THF (10 mL) was slowly added a solution of triethyl phosphonoacetate (2.5 mL, 12 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 30 min. Ketone (10

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.

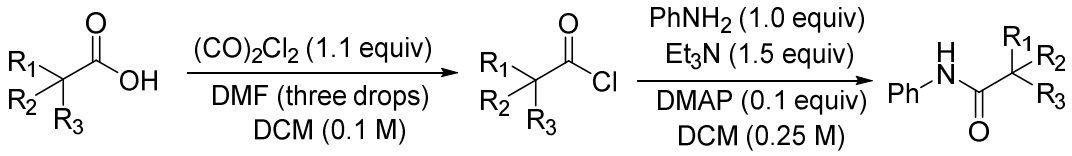
2) To a solution of the ester (1.0 equiv.) obtained in the previous step (dry DCM, 0.1 M) was slowly added DIBAL-H (2.2 equiv.) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and the solution was then warmed to 0 °C. The solution was quenched with a saturated aqueous solution of ammonium 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 General procedure A for synthesis of *N*-arylamides



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 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.

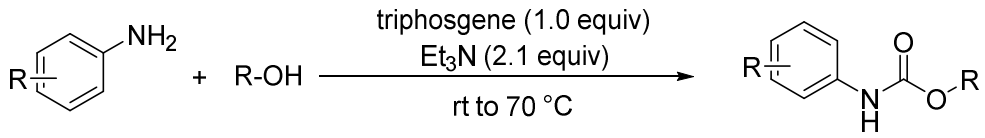
3.4 General procedure B for synthesis of *N*-phenylamides [3]



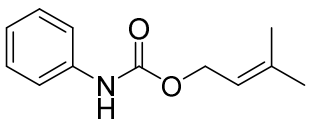
The acid (1.0 equiv) was dissolve in DCM under an inert atmosphere. A few drops of

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 ℃. 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.

3.5 General procedure C for synthesis of *N*-arylcarbamates [4]

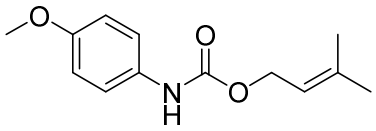


To a solution of substituted aniline (5.0 mmol) dissolved in THF (40 mL) was slowly added triphosgene (1.49 g, 5.0 mmol) solution in THF (10 mL). NEt_3 (1.5 mL, 10.5 mmol) was then added slowly to the reaction mixture. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture 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.

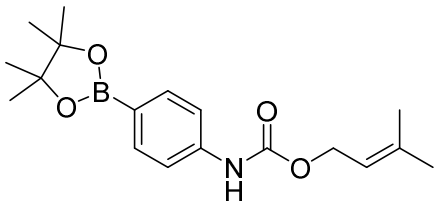


3-Methylbut-2-en-1-yl phenylcarbamate (1a): Prepared using general procedure C from prenol and aniline. White solid, m.p. 64-65 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 5.48 – 5.34 (m, 1H), 4.67 (d, *J* = 7.2 Hz, 2H), 1.78 (s, 3H), 1.75 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.6, 139.4, 137.9, 129.0, 123.3, 118.7, 118.6, 62.0, 25.8, 18.0;

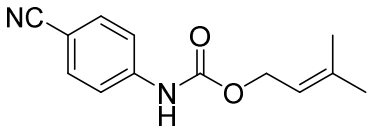
FT-IR (thin film, KBr): ν (cm^{-1}) 3305, 2973, 1698, 1598, 1538, 1444, 1302, 1231, 1050, 1028, 859, 743, 696; **HRMS (ESI)** Calcd $C_{12}H_{15}NO_2Na$ $[M + Na]^+$: 228.0995, found 228.0994.



3-Methylbut-2-en-1-yl(4-methoxyphenyl)carbamate (1b): Prepared using general procedure C from prenol and *p*-anisidine. White solid, m.p. 84-85 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.47 (s, 1H), 5.39 (t, *J* = 7.2 Hz, 1H), 4.65 (d, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.77 (s, 3H), 1.74 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.9, 139.2, 131.0, 126.1, 120.6, 118.8, 114.2, 61.9, 55.5, 25.8, 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.

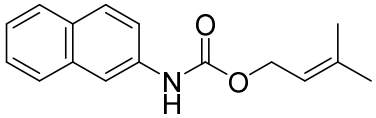


3-Methylbut-2-en-1-yl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (1c): Prepared using general procedure C from prenol and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline. White solid, m.p. 69-70 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 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, $CDCl_3$)** 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.

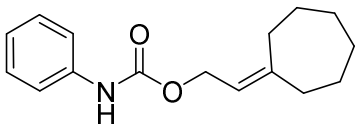


3-Methylbut-2-en-1-yl (4-cyanophenyl)carbamate (1d): Prepared using general

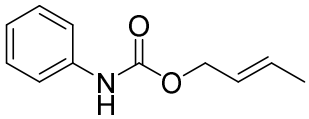
procedure C from prenol and 4-aminobenzonitrile. White solid, m.p. 86-87 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 6.94 (s, 1H), 5.38 (t, 1H), 4.68 (d, *J* = 7.3 Hz, 2H), 1.77 (s, 3H), 1.74 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.0, 142.2, 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.



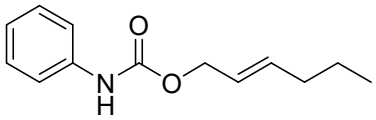
3-Methylbut-2-en-1-yl naphthalen-2-ylcarbamate (1e): Prepared using general procedure C from prenol and naphthalen-2-amine. White solid, m.p. 78-79 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 3H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.34 (m, 2H), 6.77 (s, 1H), 5.44 (t, *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.



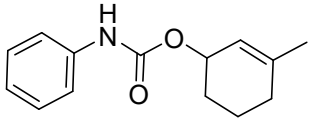
2-Cycloheptylideneethyl phenylcarbamate (1f): Prepared using general procedure C from 2-cycloheptylideneethan-1-ol and aniline. White solid, m.p. 102-103 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 5.39 (t, *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.



(*E*)-But-2-en-1-yl phenylcarbamate (1g): Prepared using general procedure C from (*E*)-but-2-en-1-ol and aniline. White solid, m.p. 79-80 ℃; **^{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 153.35, 137.85, 131.60, 129.02, 125.24, 123.38, 118.60, 65.90, 17.80; **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.

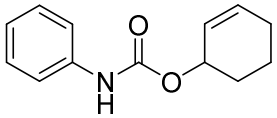


(*E*)-Hex-2-en-1-yl phenylcarbamate (1h): Prepared using general procedure C from (*E*)-hex-2-en-1-ol and aniline. White solid, m.p. 59-60 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 5.89 – 5.76 (m, 1H), 5.70 – 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.

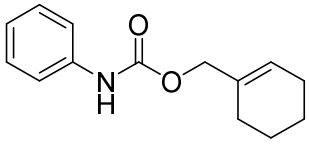


3-Methylcyclohex-2-en-1-yl phenylcarbamate (1i): Prepared using general procedure C from 3-methylcyclohex-2-en-1-ol and aniline, White solid, m.p. 74-75 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.29 (t, 2H), 7.04 (t, 1H), 6.65 (s, 1H), 5.60 – 5.54 (m, 1H), 5.27 (d, *J* = 3.0 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**

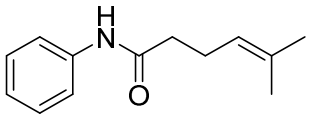
(thin film, KBr): ν (cm^{-1}) 3279, 2932, 1687, 1596, 1537, 1500, 1442, 1299, 1232, 1026, 930, 746, 693; **HRMS (ESI)** Calcd $C_{14}H_{17}NO_2Na$ $[M + Na]^+$: 254.1151, found 254.1142.



Cyclohex-2-en-1-yl phenylcarbamate (1j): Prepared using general procedure C from cyclohex-2-en-1-ol and aniline. White solid, m.p. 100-101 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 6.04 – 5.93 (m, 1H), 5.88 – 5.75 (m, 1H), 5.29 (s, 1H), 2.15 – 2.07 (m, 1H), 2.06 – 1.99 (m, 1H), 1.94 – 1.91 (m, 1H), 1.85 – 1.80 (m, 1H), 1.78-1.74 (m, 1H), 1.69-1.65 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.2, 138.0, 132.8, 129. 0, 125.8, 123.3, 118.6, 68.8, 28.5, 24.9, 18.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3308, 2932, 1690, 1599, 1540, 1441, 1310, 1226, 1050, 929, 749, 692; **HRMS (ESI)** Calcd $C_{13}H_{15}NO_2Na$ $[M + Na]^+$: 240.0995, found 240.0994.

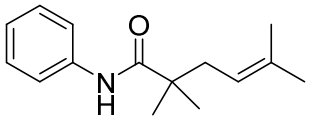


Cyclohex-1-en-1-ylmethyl phenylcarbamate (1k): Prepared using general procedure C from cyclohex-1-en-1-ylmethanol and aniline. White solid, m.p. 95-96 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.11 – 6.98 (m, 1H), 6.78 (s, 1H), 5.77 (s, 1H), 4.53 (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.

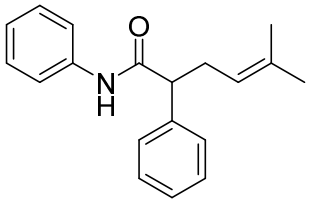


5-Methyl-*N*-phenylhex-4-enamide (1l): Prepared using general procedure A from 5-methylhex-4-enoic acid and aniline. White solid, m.p. 87-88 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.38 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.09 (t,

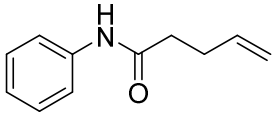
J = 7.4 Hz, 1H), 5.16 (t, *J* = 6.2 Hz, 1H), 2.46 – 2.33 (m, 4H), 1.71 (s, 3H), 1.65 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 138.0, 133.8, 129.0, 124.2, 122.6, 119.8, 37.7, 25.8, 24.2, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3296, 2929, 1665, 1600, 1537, 1496, 1439, 1309, 1240, 1182, 954, 853, 749, 690; **HRMS (ESI)** Calcd $C_{13}H_{17}NONa$ $[M + Na]^+$: 226.1202, found 226.1201.



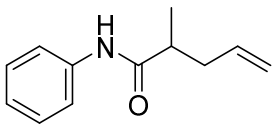
2,2,5-Trimethyl-*N*-phenylhex-4-enamide (1m): Prepared using general procedure B from 2,2,5-trimethylhex-4-enoic acid and aniline. White solid, m.p. 77-78 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.41 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.22 (t, *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.



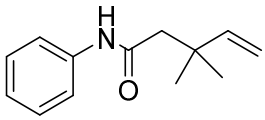
5-Methyl-*N*,2-diphenylhex-4-enamide (1n): Prepared using general procedure B from 5-methyl-2-phenylhex-4-enoic acid and aniline. White solid, m.p. 86-87 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.27 – 7.19 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 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, 128.90, 128.87, 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.



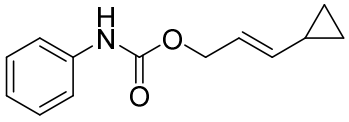
***N*-Phenylpent-4-enamide (1o)**: Prepared using general procedure A from pent-4-enoic acid and aniline. White solid, m.p. 89-90 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.35 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.98 – 5.76 (m, 1H), 5.12 (d, *J* = 17.3 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 2.57 – 2.41 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** 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.



2-Methyl-*N*-phenylpent-4-enamide (1p): Prepared using general procedure A from 2-methylpent-4-enoic acid and aniline. White solid, m.p. 101-102 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.88 – 5.71 (m, 1H), 5.11 (d, *J* = 17.1 Hz, 1H), 5.05 (d, *J* = 10.3 Hz, 1H), 2.54 – 2.38 (m, 2H), 2.27 – 2.18 (m, 1H), 1.23 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 174.4, 138.0, 135.6, 128.9, 124.2, 120.1, 117.1, 42.1, 38.4, 17.5; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3311, 2940, 1694, 1600, 1544, 1503, 1445, 1316, 1230, 1054, 1029, 749, 696; **HRMS (ESI)** Calcd $C_{12}H_{16}NO$ $[M + H]^+$: 190.1226, found 190.1223.

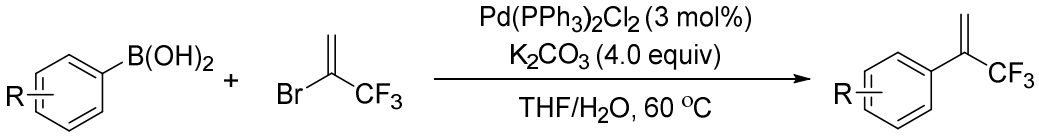


3,3-Dimethyl-*N*-phenylpent-4-enamide (1q): Prepared using general procedure A from 3,3-dimethylpent-4-enoic acid and aniline. White solid, m.p. 101-102 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.22 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.99 (dd, *J* = 17.7, 10.5 Hz, 1H), 5.12 – 5.04 (m, 2H), 2.34 (s, 2H), 1.18 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.7, 147.3, 137.9, 128.9, 124.2, 120.1, 112.1, 50.3, 36.7, 27.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3345, 2962, 1650, 1596, 1493, 1439, 1251, 996, 756, 689; **HRMS (ESI)** Calcd $C_{13}H_{17}NONa$ $[M + Na]^+$: 226.1202, found 226.1207.

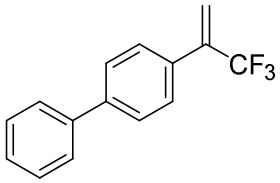


(*E*)-3-Cyclopropylallyl phenylcarbamate (1r): Prepared using general procedure C from cyclohex-1-en-1-ylmethanol and aniline. White solid, m.p. 81-82 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.13 – 7.00 (m, 1H), 6.67 (s, 1H), 5.79 – 5.63 (m, 1H), 5.43 – 5.27 (m, 1H), 4.64 – 4.55 (m, 2H), 1.50 – 1.40 (m, 1H), 0.80 – 0.69 (m, 2H), 0.46 – 0.38 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.4, 140.9, 137.9, 129.0, 123.4, 121.3, 118.6, 65.9, 13.5, 6.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3355, 2998, 1699, 1597, 1525, 1437, 1308, 1211, 1098, 925, 745, 647; **HRMS (ESI)** Calcd $C_{13}H_{15}NO_2Na$ $[M + Na]^+$: 240.0995, found 240.1001.

3.6 General procedures for trifluoromethyl alkenes [5]

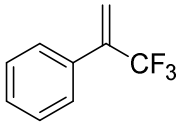


To a Schlenk tube equipped a magnetic stir bar, boronic acid (5 mmol, 1.0 equiv.) and $Pd(PPh_3)_2Cl_2$ (63.2 mg, 3 mol%) were added. The vessel was evacuated and filled with argon (three times), and then THF (15 mL, pre-degased) and aqueous K_2CO_3 (2.0 M, 10 mL, pre-degased) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (1.04 mL, 10 mmol, 2.0 equiv.), the reaction mixture was stirred at 60 °C overnight under an argon atmosphere. The resultant mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired corresponding trifluoromethyl alkene.



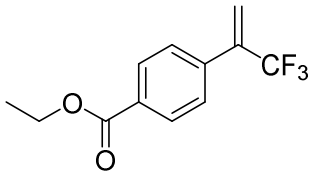
4-(3,3,3-Trifluoroprop-1-en-2-yl)-1,1'-biphenyl (2a): White solid. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.66 – 7.60 (m, 4H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.34 (m, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 5.85 (d, *J* = 1.6 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 141.8, 140.2, 138.5 (q, *J* = 30.1 Hz), 132.4, 128.9, 127.71, 127. 67, 127.2, 127.1, 124.3 (q, *J* = 274.0 Hz), 120.2 (q, *J* = 5.7 Hz); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.64 (s, 3F).

The spectral data were consistent with the literature data.[5]



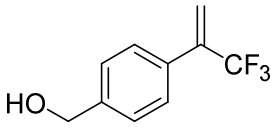
(3,3,3-Trifluoroprop-1-en-2-yl)benzene (2b): Colorless oil. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.50 – 7.45 (m, 2H), 7.42 – 7.38 (m, 3H), 5.97 (d, *J* = 1.3 Hz, 1H), 5.77 (d, *J* = 1.6 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ139.0 (q, *J* = 30.0 Hz), 133.6, 128.9, 128.5, 127.4, 123.3 (q, *J* = 273.9 Hz), 120.4 (q, *J* = 5.7 Hz); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -64.82 (s, 3F).

The spectral data were consistent with the literature data.[6]



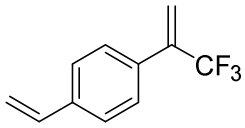
Ethyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (2c): Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 6.04 (s, 1H), 5.86 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 166.0, 138.3 (q, *J* = 30.4 Hz), 137.7, 130.9, 129.7, 127.3, 121.8 (q, *J* = 5.7 Hz), 123.0 (q, *J* = 274.1 Hz), 61.1, 14.3; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.69 (s, 3F).

The spectral data were consistent with the literature data.[7]



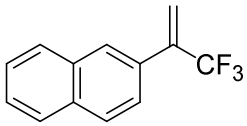
(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)methanol (2d): Colorless oil. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.96 (d, *J* = 1.2 Hz, 1H), 5.77 (d, *J* = 1.5 Hz, 1H), 4.69 (s, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 141.7, 138.6 (q, *J* = 30.1 Hz), 132.9, 127.5, 127.0, 123.3 (q, *J* = 274.0 Hz), 120.3 (q, *J* = 5.7 Hz), 64.7; **^{19}F NMR (564 MHz, CDCl$_3$)** δ -64.84 (s, 3F).

The spectral data were consistent with the literature data.[8]



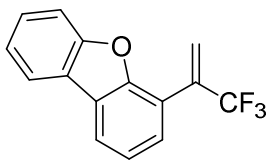
1-(3,3,3-Trifluoroprop-1-en-2-yl)-4-vinylbenzene (2e): Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 (s, 4H), 6.70 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.92 (s, 1H), 5.84 – 5.72 (m, 2H), 5.28 (d, *J* = 10.9 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 138.6 (q, *J* = 30.0 Hz), 138.3, 136.0, 132.9, 127.5, 126.4, 123.4 (q, *J* = 273.9 Hz), 120.1 (q, *J* = 5.8 Hz), 114.9; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.66 (s, 3F).

The spectral data were consistent with the literature data.[9]



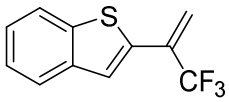
2-(3,3,3-Trifluoroprop-1-en-2-yl)naphthalene (2f): White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 (s, 1H), 7.88 – 7.79 (m, 3H), 7.61 – 7.40 (m, 3H), 6.02 (s, 1H), 5.87 (s, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 138.9 (q, *J* = 30.1 Hz), 133.2, 133.0, 130.9, 128.4, 128.3, 127.6, 126.9, 126.8, 126.6, 124.7, 123.4 (q, *J* = 274.7 Hz), 120.7 (q, *J* = 5.8 Hz); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -64.43 (s, 3F).

The spectral data were consistent with the literature data.[5]



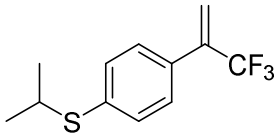
4-(3,3,3-Trifluoroprop-1-en-2-yl)dibenzo[b,d]furan (2g): Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.39 (s, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.0, 153.8, 133.3 (q, *J* = 31.0 Hz), 127.5, 126.5, 125.0, 124.1 (q, *J* = 5.6 Hz), 123.8, 123.0, 122.7, 121.2, 120.7, 118.0, 111.8; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.73 (s, 3F).

The spectral data were consistent with the literature data.[5]



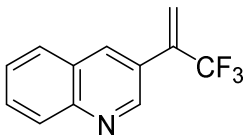
2-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[b]thiophene (2h): Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82 – 7.72 (m, 2H), 7.44 (s, 1H), 7.39 – 7.32 (m, 2H); ^{13}C NMR (**150 MHz, $CDCl_3$**) δ 140.0, 138.7, 135.4, 133.0 (q, *J* = 31.5 Hz), 125.6, 124.8, 124.3, 123.8, 122.5 (q, *J* = 274.5 Hz), 121.9, 119.6 (q, *J* = 5.5 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -65.37 (s, 3F).

The spectral data were consistent with the literature data.[10]



Isopropyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane (2j): Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (s, 4H), 5.94 (s, 1H), 5.78 (s, 1H), 3.62 – 3.28 (m, 1H), 1.33 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.3 (q, *J* = 29.9 Hz) 137.3, 131.4, 130.7, 127.6, 123.2 (q, *J* = 274.0 Hz), 120.0 (q, *J* = 5.7 Hz), 37.7, 23.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -64.69 (s, 3F).

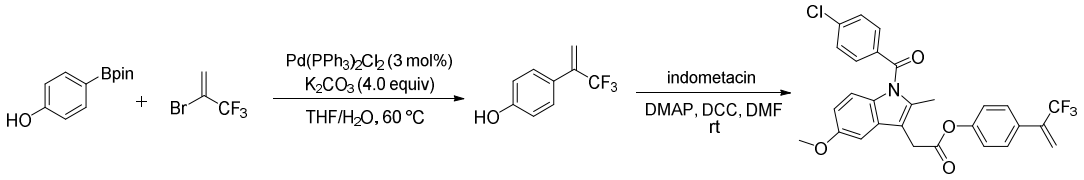
The spectral data were consistent with the literature data.[8]



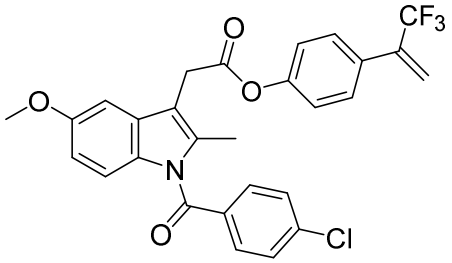
3-(3,3,3-Trifluoroprop-1-en-2-yl)quinolone (2k): White solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.97 (d, *J* = 2.2 Hz, 1H), 8.23 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.68 (m, 1H), 7.63 – 7.55 (m, 1H), 6.15 (d, *J* = 0.7 Hz, 1H), 5.97

(d, J = 1.4 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 148.9, 147.9, 136.2 (q, J = 30.9 Hz), 134.4, 130.3, 129.2, 128.3, 127.4, 127.1, 126.4, 124.9 (d, J = 274.1 Hz), 122.1 (q, J = 5.7 Hz); **^{19}F NMR (282 MHz, $CDCl_3$)** δ -64.97 (s, 3F).

The spectral data were consistent with the literature data.[11]



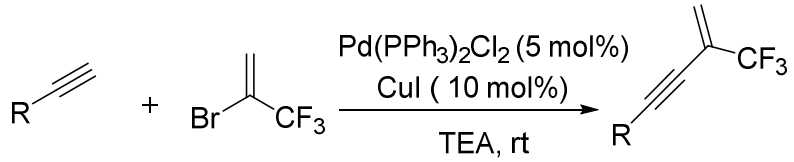
According to the above procedure, gram-scale preparation of the desired 4-(3,3,3-trifluoroprop-1-en-2-yl)phenol was accomplished. To a stirred solution of indometacin (1.07 g, 3.0 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP) (37.0 mg, 10 mol%), and 4-(3,3,3-trifluoroprop-1-en-2-yl)phenol (0.62 g, 3.3 mmol, 1.1 equiv.) in DMF (8 mL) was added *N*,*N*'-dicyclohexylcarbodiimide (DCC) (0.68 g, 3.3 mmol, 1.1 equiv.). The reaction mixture was stirred at room temperature for 5 h (TLC tracking detection) before it was quenched with water. The resultant mixture was extracted with CH_2Cl_2 (40 mL× 3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with EtOAc/petroleum ether (6:1) to give the trifluoromethyl alkene **2k** (1.14 g, 72%) as a white solid.



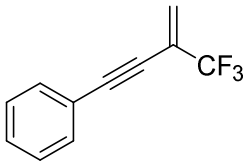
4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (2l): White solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 – 7.62 (m, 2H), 7.52 – 7.40 (m, 4H), 7.14 – 7.08 (m, 2H), 7.06 (d, J = 2.5 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 6.71 (dd, J = 9.0, 2.5 Hz, 1H), 5.96 (d, J = 1.1 Hz, 1H), 5.75 (d, J = 1.5 Hz, 1H), 3.92 (s, 2H), 3.84 (s, 3H), 2.46 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.1, 168.3, 156.1, 151.1, 139.4, 138.0 (q, J = 30.3 Hz), 136.3, 133.7, 131.3, 131.2, 130.8, 130.4, 129.1, 128.6, 123.1 (q, J =

274.0 Hz), 121.6, 120.7 (q, *J* = 5.6 Hz), 115.0, 111.78, 111.76, 101.2, 55.7, 30.5, 13.4; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -64.97 (s, 3F).

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

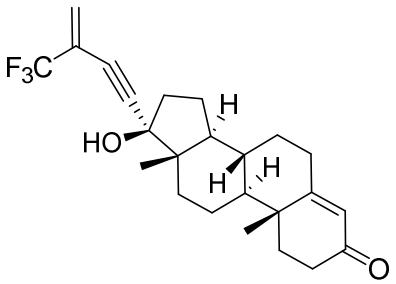


To a mixture of CuI (57.2 mg, 10 mol%), $Pd(PPh_3)_2Cl_2$ (105.3 mg, 5 mol%) and Et_3N (30 mL) were added 2-bromo-3,3,3-trifluoroprop-1-ene (0.498 mL, 4.8 mmol, 1.6 equiv.) and alkyne (3.0 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 16 h. The resultant mixture was diluted with saturated aqueous NH_4Cl (20 mL) followed by extraction with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100 : 1) to give the title compound.



(3-(Trifluoromethyl)but-3-en-1-yn-1-yl)benzene (2i): Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.46 (m, 2H), 7.41 – 7.29 (m, 3H), 6.11 (s, 1H), 5.95 (s, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 131.8, 129.2, 128.4, 126.7 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 35.2 Hz), 121.6, 121.4 (q, *J* = 273,7 Hz), 93.2, 81.4; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -67.93 (s, 3F).

The spectral data were consistent with the literature data.[13]

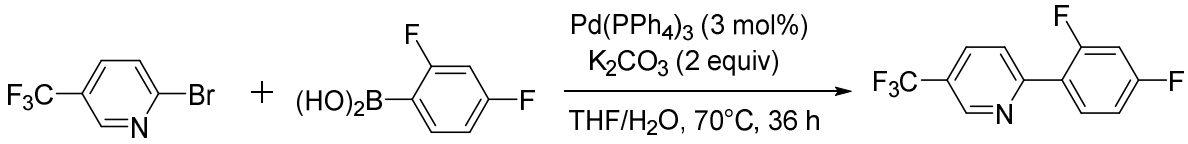


17-Hydroxy-10,13-dimethyl-17-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*3H*-cyclopenta[*a*]phenanthren-3-one

(2m): White solid, m.p. 79-80 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.04 (s, 1H), 5.85 (s, 1H), 5.74 (s, 1H), 2.50 – 2.23 (m, 6H), 2.09 – 2.00 (m, 2H), 1.90 – 1.81 (m, 1H), 1.79 – 1.71 (m, 2H), 1.71 – 1.55 (m, 4H), 1.51 – 1.33 (m, 3H), 1.20 (s, 3H), 1.11 – 0.98 (m, 1H), 0.92 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 199.6, 171.1, 126.8 (q, J = 4.1 Hz), 123.9, 122.2 (q, J = 35.1 Hz), 121.2 (q, J = 273.4 Hz), 97.0, 79.9, 78.3, 77.2, 77.0, 76.8, 53.4, 50.2, 47.3, 38.7, 38.6, 36.2, 35.6, 33.9, 32.7, 32.5, 31.4, 23.1, 20.7, 17.4, 12.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -68.03 (s, 3F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2850, 1731, 1701, 1608, 1578, 1421, 1380, 1268, 1226, 1115, 753, 682; **HRMS (ESI)** Calcd $C_{24}H_{29}F_3NaO_2$ $[M + Na]^+$: 429.2012, found 429.2006.

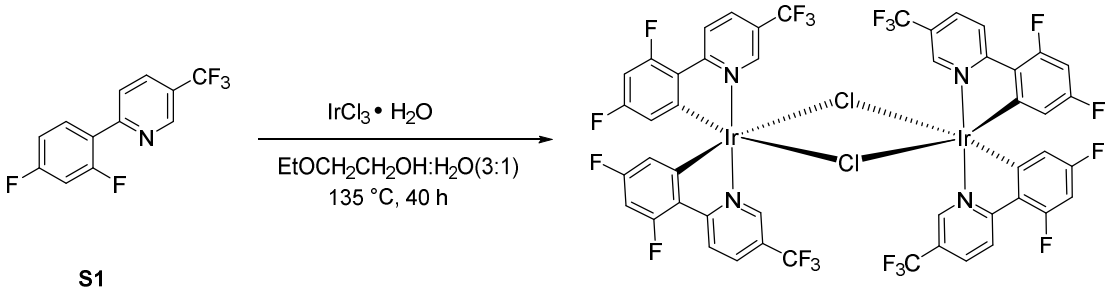
4. Typical procedures for synthesis of Ir-photocatalysts

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.) in THF/H_2O (1.5:1) was stirred at reflux 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 residue was purified by column chromatography to offer the title compound as a white solid.

4.2 Synthesis of [Ir(dF(CF_3)ppy)$_2$Cl]$_2$-dimer [15]

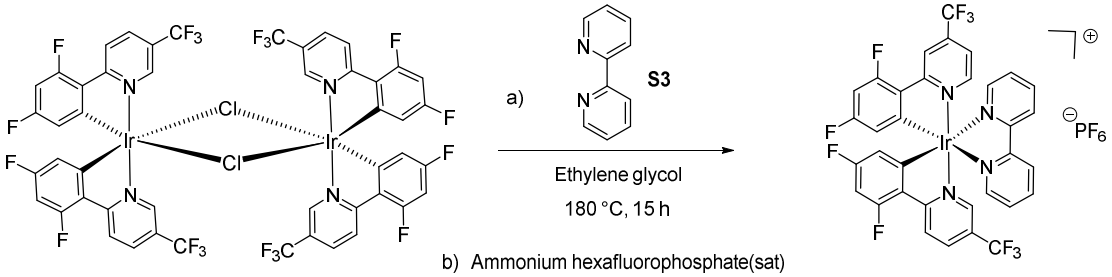


S1 **S2**

To a 25 mL tube containing a stir bar was added **S1** (430 mg, 2.05 equiv.) and $IrCl_3 \cdot H_2O$ (256 mg, 1.0 equiv.). The flask was evacuated and backfilled with argon,

and 2-ethoxyethanol (7.5 mL) and water (2.5 mL) were added. The reaction mixture was heated at 135 ℃ for 40 h. 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 used in the next step without further purification.

4.3 Synthesis of [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ [16]



To a 25 mL tube were added the **S2** (400 mg, 0.27 mmol, 1.0 equiv.), **S3** (92 mg, 0.59 mmol, 2.2 equiv), and ethylene glycol (8 mL) under argon. The resulting yellow suspension was heated at 180 °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.

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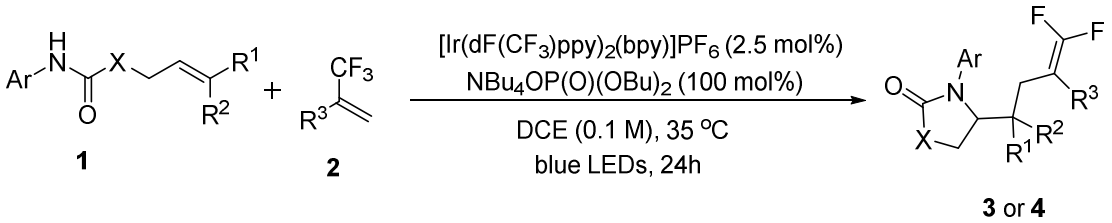
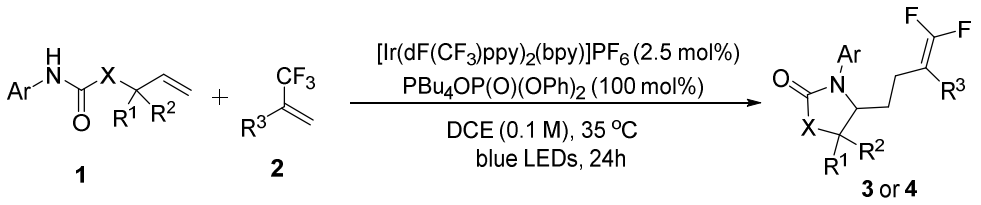
5. General procedures for radical aminodifluoroallylation of alkenes



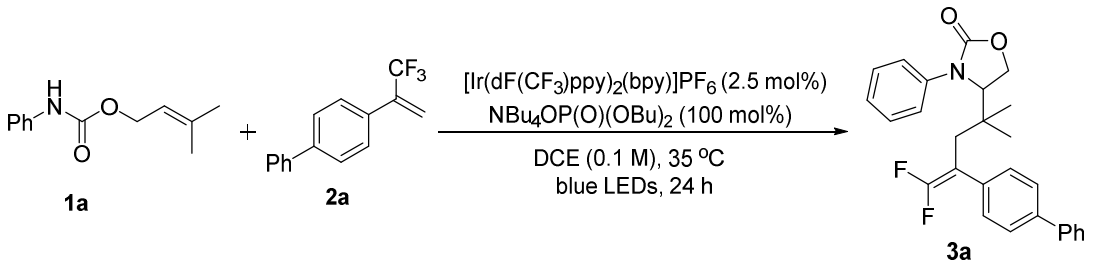
General procedure 1: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar were added amide **1** (0.2 mmol, 1.0 equiv.), trifluoromethyl alkene **2** (0.24 mmol, 1.2 equiv. if solid), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (4.5 mg, 0.005 mmol, 2.5 mol%), and $NBu_4OP(O)(OBu)_2$ (90 mg, 0.2 mmol, 1.0 equiv.). The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. Trifluoromethyl-substituted alkene (0.24 mmol, 1.2 equiv, if liquid) and DCE (2 mL)

were then added under argon atmosphere. The mixture was placed under a 22W blue LEDs and irradiated at 35 °C for 24 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 the corresponding product.



General procedure 2: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar were added amide **1** (0.2 mmol, 1.0 equiv.), trifluoromethyl alkene **2** (0.24 mmol, 1.2 equiv. if solid), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (4.5 mg, 0.005 mmol, 2.5 mol%), and $PBu_4OP(O)(OPh)_2$ (110 mg, 0.2 mmol, 1.0 equiv.). The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. Trifluoromethyl-substituted alkene (0.24 mmol, 1.2 equiv, if liquid) and DCE (2 mL) were then added under argon atmosphere. The mixture was placed under a 22W blue LEDs and irradiated at 35 °C for 24 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 the corresponding product.

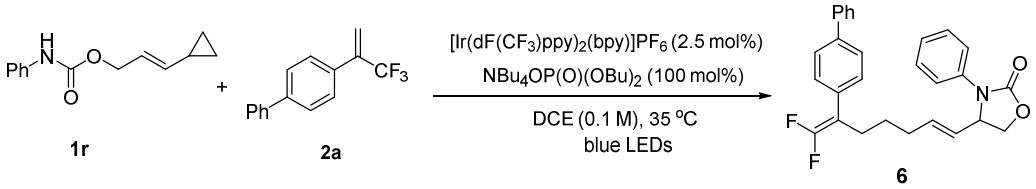
Scale-up synthesis of compound 3a



To a 50 mL oven-dried Schlenk tube equipped with a magnetic stir bar were amide **1a** (780 mg, 3.8 mmol, 1.0 equiv.), trifluoromethyl alkene **2a** (1.5 g, 4.6 mmol, 1.2 equiv.), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (80 mg, 0.095 mmol, 2.5 mol%), and $NBu_4OP(O)(OBu)_2$ (1.7 g, 3.8 mmol, 1.0 equiv.). The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCE (20 mL) were then added under

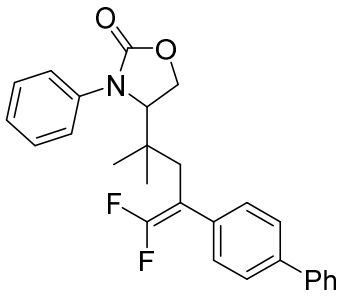
argon atmosphere. The mixture was placed under a 22W blue LEDs and irradiated at 35 °C for 24 h. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **3a** (1.38 g, 84% yield) as a yellow oil.

6. Radical clock experiment

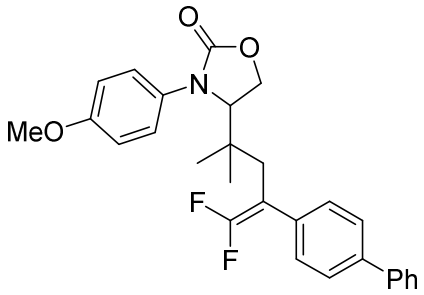


To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar were added amide **1r** (44 mg, 0.2 mmol, 1.0 equiv.), trifluoromethyl alkene **2a** (60 mg, 0.24 mmol, 1.2 equiv.), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (4.5 mg, 0.005 mmol, 2.5 mol%), and $NBu_4OP(O)(OBu)_2$ (90 mg, 0.2 mmol, 1.0 equiv.). The resulting mixture was sealed and then subjected to freeze-pump-thaw for three times. DCE (2 mL) were then added under argon atmosphere. The mixture was placed under a 22W blue LEDs and irradiated at 35 °C. 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 the title compound **6** (76 mg, 85%) as white solid.

7. Characterization of the products

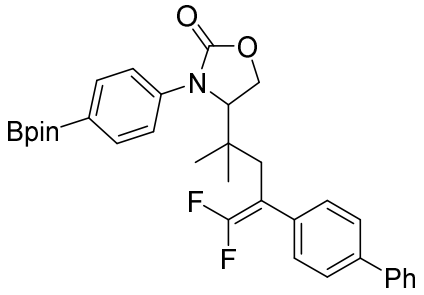


4-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-3-phenyloxazolidin-2-one (3a): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 80 mg of the title compound (yellow oil, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.56 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.35 (m, 5H), 7.32 – 7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 4.32 (dd, *J* = 7.7, 1.9 Hz, 1H), 4.28 – 4.19 (m, 2H), 2.49 – 2.29 (m, 2H), 0.81 (s, 3H), 0.65 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.8, 154.4 (t, *J* = 289.0 Hz), 140.4, 140.1, 138.9, 133.5, 129.2, 128.8, 128.6, 127.6, 127.3, 127.0, 126.2, 124.3, 89.1 (dd, *J* = 21.2, 14.5 Hz), 64.3, 64.1, 40.6, 35.9, 23.9, 22.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.14 (d, *J* = 38.0 Hz, 1F), -90.00 (d, *J* = 37.9 Hz, 1F); **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 $C_{27}H_{25}F_2NO_2Na$ $[M + Na]^+$: 456.1746, found 456.1743.

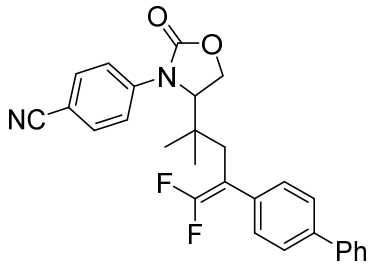


4-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-3-(4-methoxyphenyl)oxazolidin-2-one (3b): Followed the general procedure with 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (47 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 78 mg of the title compound (yellow oil, 84% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 (t, *J* = 7.9 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.31 – 7.25 (m, 4H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.29 (dd, *J* = 9.2, 3.9 Hz, 1H), 4.23 (t, *J* = 9.0 Hz, 1H), 4.15 (dd, *J* = 8.7, 3.8 Hz, 1H), 3.81 (s, 3H), 2.45 – 2.30 (m, 2H), 0.79 (s, 3H), 0.65 (s, 3H); **^{13}C NMR**

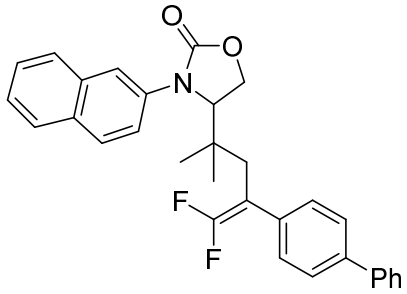
(150 MHz, $CDCl_3$) δ 157.9, 157.2, 154.4 (dd, *J* = 291.1, 289.0 Hz), 140.3, 140.1, 133.6, 131.7, 128.8, 128.6, 127.6, 127.2, 126.9, 126.1, 114.5, 89.1 (dd, *J* = 21.2, 14.5 Hz), 65.0, 64.0, 55.4, 40.3, 35.8, 23.7, 22.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.18 (d, *J* = 38.0 Hz, 1F), -90.06 (d, *J* = 38.0 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2965, 2924, 1733, 1409, 1239, 1181, 1037, 830, 762, 637; **HRMS** (ESI) Calcd $C_{28}H_{27}F_2NO_3Na$ $[M + Na]^+$: 486.1851, found 486.1856.



4-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)oxazolidin-2-one (3c): Followed the general procedure 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 4-(3,3,3-trifluoro prop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 83 mg of the title compound (yellow oil, 74% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.56 (m, 4H), 7.48 – 7.39 (m, 4H), 7.38 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 4.35 – 4.27 (m, 2H), 4.26 – 4.19 (m, 1H), 2.51 – 2.28 (m, 2H), 1.35 (s, 12H), 0.81 (s, 3H), 0.64 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.4, 154.5 (dd, *J* = 291.6, 288.6 Hz), 141.5, 140.4, 140.2, 135.7, 133.6 (dd, *J* = 4.1, 2.9 Hz), 128.9, 128.6 (t, *J* = 2.6 Hz), 127.6, 127.3, 127.0, 123.0, 89.1 (dd, *J* = 21.2, 14.5 Hz), 84.0, 64.1, 63.8, 40.9, 36.0, 24.93, 24.87, 24.0, 22.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.10 (d, *J* = 38.0 Hz, 1F), -90.02 (d, *J* = 37.9 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 3280, 2931, 1747, 1593, 1489, 1447, 1399, 1325, 1226, 1158, 1087, 903, 745, 663; **HRMS (ESI)** calcd $C_{33}H_{37}BF_2NO_4$ $[M + H]^+$: 560.2778, found: 560.2782.

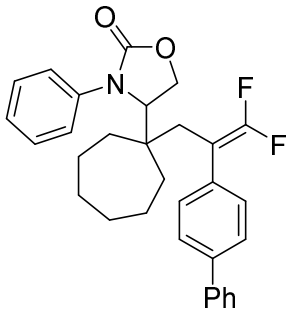


4-(4-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-2-oxooxazolidin-3-yl)benzonitrile (3d): Followed the general procedure with 3-methylbut-2-en-1-yl (4-cyanophenyl)carbamate (46 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 68 mg of the title compound (yellow oil; 74% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.64 (m, 2H), 7.64 – 7.58 (m, 4H), 7.58 – 7.53 (m, 2H), 7.49 – 7.41 (m, 2H), 7.40 – 7.30 (m, 3H), 4.40 – 4.27 (m, 2H), 4.22 – 4.13 (m, 1H), 2.51 – 2.34 (m, 2H), 0.85 (s, 3H), 0.65 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.7, 154.5 (dd, *J* = 292.1, 288.8 Hz), 143.0, 140.6, 139.9, 133.2, 133.1, 128.9, 128.5, 127.7, 127.4, 126.9, 123.2, 118.3, 108.8, 88.8 (dd, *J* = 21.2, 14.9 Hz), 64.1, 62.9, 41.1, 36.1, 24.7, 22.7; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -87.8 (d, *J* = 37.0 Hz, 1F), -89.5 (d, *J* = 37.2 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2968, 2928, 2226, 1751, 1601, 1506, 1479, 1400, 1319, 1284, 1203, 1061, 912, 839, 729; **HRMS (ESI)** calcd $C_{28}H_{24}F_2N_2O_2Na$ $[M + Na]^+$: 481.1698, found: 481.1697.



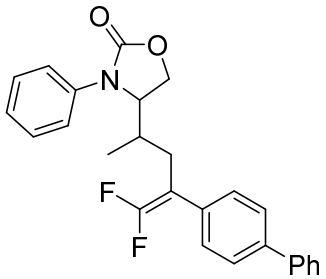
4-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-3-(naphthalen-2-yl)oxazolidin-2-one (3e): Followed the general procedure with 3-methylbut-2-en-1-yl naphthalen-2-ylcarbamate (51 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop -1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 53 mg of the title compound (yellow oil; 55% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.77 (m, 4H), 7.61 – 7.53 (m, 4H), 7.54

– 7.41 (m, 5H), 7.38 – 7.31 (m, 1H), 7.28 – 7.24 (m, 2H), 4.40 – 4.33 (m, 2H), 4.27 (t, *J* = 9.6 Hz, 1H), 2.53 – 2.28 (m, 2H), 0.81 (s, 3H), 0.64 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.9, 154.4 (dd, *J* = 291.2, 288.9 Hz), 140.4, 140.1, 136.3, 133.5, 131.5, 129.2, 128.8, 128.5, 127.74, 127.66, 127.6, 127.3, 127.0, 126.7, 126.1, 122.59, 122.58, 89.0 (dd, *J* = 21.2, 14.6 Hz), 64.4, 64.1, 40.7, 35.9, 23.9, 23.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.43 (d, *J* = 38.8 Hz, 1F), -90.52 (d, *J* = 38.7 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 3280, 2931, 1747, 1593, 1489, 1447, 1399, 1325, 1226, 1158, 1087, 903, 745, 663; **HRMS** (ESI) Calcd $C_{31}H_{27}F_2NO_2Na$ $[M + Na]^+$: 506.1902, found 506.1903.

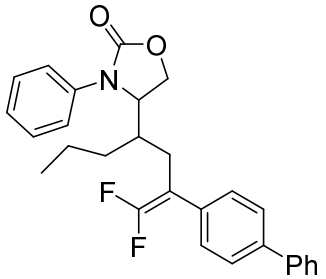


4-(1-(2-([1,1'-Biphenyl]-4-yl)-3,3-difluoroallyl)cycloheptyl)-3-phenyloxazolidin-2-on (3f): Followed the general procedure with 2-cycloheptylideneethyl phenylcarbamate (52 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl) -1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 73 mg of the title compound (yellow oil; 75% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 – 7.59 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.34 (m, 7H), 7.22 – 7.17 (m, 1H), 4.45 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.33 (dd, *J* = 9.4, 2.8 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 2.70 – 2.60 (m, 1H), 2.54 – 2.47 (m, 1H), 1.59 – 1.51 (m, 2H), 1.50 – 1.38 (m, 2H), 1.36 – 1.22 (m, 4H), 1.22 – 1.12 (m, 2H), 1.11 – 1.03 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 157.0, 154.5 (dd, *J* = 291.5, 289.0 Hz), 140.3, 140.1, 139.0, 133.6, 129.0, 128.8, 128.6, 127.6, 127.2, 126.9, 125.9, 123.7, 89.0 (dd, *J* = 21.0, 14.2 Hz), 64.1, 62.2, 45.5, 34.8, 34.0, 33.8, 31.2, 30.8, 23.0, 22.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -87.80 (d, *J* = 37.8 Hz, 1F), -89.24 (d, *J* = 37.6 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2971, 2921, 1751, 1720, 1597, 1499, 1404, 1236, 1106, 1075, 841, 761, 672; **HRMS (ESI)** Calcd $C_{31}H_{32}F_2NO_2$ $[M + H]^+$: 488.2396, found

488.2390.

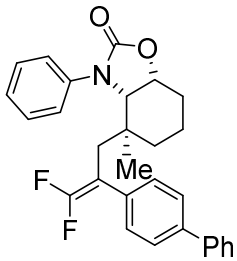


4-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoropent-4-en-2-yl)-3-phenyloxazolidin-2-one (3g): Followed the general procedure with (*E*)-but-2-en-1-yl phenylcarbamate (38 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 75 mg of the title compound (yellow oil, 90% yield, d.r. = 2.5:1); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 – 7.58 (m, 2.76H), 7.54 – 7.34 (m, 6H), 7.29 (d, *J* = 8.2 Hz, 0.63H), 7.22 (t, *J* = 7.3 Hz, 0.40H), 7.19 – 7.11 (m, 2.69H), 7.05 – 6.99 (m, 0.74H), 6.92 (d, *J* = 7.5 Hz, 0.60H), 4.54 – 4.45 (m, 1.32H)/4.39 (t, *J* = 9.0 Hz, 0.75H), 4.34 – 4.27 (m, 1H), 2.51 – 2.45 (m, 1H), 2.42 – 2.36 (m, 0.77H)/2.30 – 2.21 (m, 0.38H), 2.19 – 2.11 (m, 0.74H)/2.05 – 1.99 (m, 0.35H), 0.88 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.9/155.6, 153.8 (dd, *J* = 292.7, 287.2 Hz)/154.1 (dd, *J* = 291.5, 287.0 Hz), 140.8/140.4, 140.2/140.0, 136.4/136.2, 131.1/130.9, 129.3, 129.0, 128.9, 128.8, 128.5, 128.1, 127.7, 127.5, 127.4, 127.0, 126.9, 125.3, 124.8, 122.1, 121.0, 89.8 (dd, *J* = 21.3, 13.8 Hz)/89.5 (dd, *J* = 21.3, 13.8 Hz), 62.8/61.8, 59.6/57.2, 30.3/30.1, 29.8/26.3, 14.1/12.30; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.35 – -89.48 (m, 1F), -89.93 (d, *J* = 40.7 Hz, 0.72F)/-90.18 (d, *J* = 41.3 Hz, 0.29F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 2928, 1751, 1725, 1600, 1502, 1487, 1460, 1403, 1235, 1209, 1106, 840, 760, 695; **HRMS (ESI)** calcd $C_{26}H_{24}F_2NO_2$ $[M + H]^+$: 420.1770, found 420.1773.



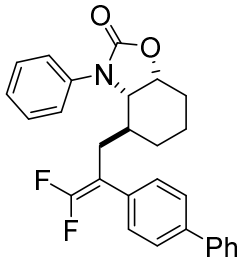
4-(-2-([1,1'-Biphenyl]-4-yl)-1,1-difluorohept-1-en-4-yl)-3-phenyloxazolidin-2-one

(3h): Followed the general procedure with (*E*)-hex-2-en-1-yl phenylcarbamate (42 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 82 mg of the title compound (yellow oil, 92% yield, d.r. = 2:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.53 (m, 2.79H), 7.50 – 7.25 (m, 6.55H), 7.22 – 7.18 (m, 0.87H), 7.15 – 7.09 (m, 0.38H), 7.07 – 6.98 (m, 2.73H), 6.96 – 6.90 (m, 0.66H), 6.85 – 6.77 (m, 0.62H), 4.63 – 4.56 (m, 0.32H)/4.50 – 4.44 (m, 0.73H), 4.40 (t, *J* = 9.1 Hz, 0.35H)/4.32 (t, *J* = 9.0 Hz, 0.7H), 4.26 (dd, *J* = 9.0, 5.9 Hz, 0.36H)/4.21 (dd, *J* = 8.9, 5.2 Hz, 0.67H), 2.73 – 2.58 (m, 0.69H)/2.50 – 2.38 (m, 0.33H), 2.32 – 2.14 (m, 1H), 1.94 – 1.79 (m, 1H), 1.39 – 0.90 (m, 4H), 0.76 (t, *J* = 6.9 Hz, 1H)/0.63 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.8/155.7, 154.0 (dd, *J* = 291.1, 287.1 Hz)/153.7 (dd, *J* = 293.3, 287.2 Hz), 140.8/140.4, 140.1/139.8, 136.3/136.1, 131.0 (t, *J* = 3.4 Hz)/130.9 (t, *J* = 3.3 Hz), 129.2, 129.0, 128.9, 128.8, 128.5 (t, *J* = 2.7 Hz)/128.1 (t, *J* = 2.6 Hz), 127.7/127.4, 127.5/126.9, 127.0/126.9, 125.0/124.7, 121.5/121.0, 89.9 (dd, *J* = 21.4, 13.3 Hz) /89.7 (dd, *J* = 21.2, 14.2 Hz), 62.6/62.3, 56.9/56.6, 34.0/31.2, 28.8, 27.5/25.3, 20.1/20.0, 14.2/13.9; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.16 (dd, *J* = 41.2, 4.6 Hz, 0.69F)/-89.34 (dd, *J* = 41.7, 4.7 Hz, 0.31F), -90.20 (d, *J* = 41.2 Hz, 0.68F)/-90.36 (d, *J* = 41.6 Hz, 0.31F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2926, 2867, 1737, 1594, 1493, 1457, 1402, 1296, 1221, 1117, 1040, 843, 758, 693; **HRMS (ESI)** calcd $C_{28}H_{27}F_2NO_2Na$ $[M + Na]^+$: 470.1902, found: 470.1903.

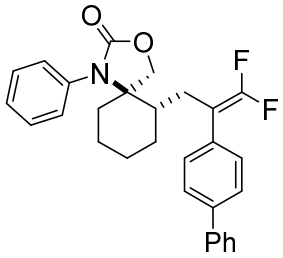


4-(2-([1,1'-Bphenyl]-4-yl)-3,3-difluoroallyl)-4-methyl-3-phenylhexahydrobenzo[d]oxazol-2(3H)-one (3i): Followed the general procedure with 3-methylcyclohex-2-en-1-yl phenylcarbamate (46 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 60 mg of the title

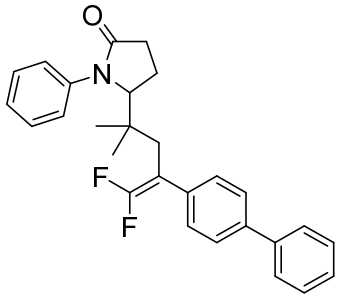
compound (yellow oil, 65% yield, d.r.>20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.55 (m, 2H), 7.51 – 7.41 (m, 8H), 7.38 – 7.32 (m, 1H), 7.31 – 7.26 (m, 1H), 7.01 – 6.94 (m, 2H), 4.74 – 4.66 (m, 1H), 4.06 (d, *J* = 6.3 Hz, 1H), 2.38 – 2.22 (m, 2H), 2.13– 2.05 (m, 1H), 1.71 – 1.56 (m, 2H), 1.53 – 1.41 (m, 2H), 1.13 – 0.99 (m, 1H), 0.86 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.3, 153.4 (dd, *J* = 291.2, 288.8 Hz), 140.3, 140.0, 138.5, 133.6, 129.2, 128.8, 128.4, 127.5, 127.0, 126.9, 125.7, 124.1, 88.7 (dd, *J* = 21.4, 13.8 Hz), 75.0, 64.5, 41.0, 40.6, 34.7, 26.6, 19.7, 15.4; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -87.70 (d, *J* = 37.2 Hz, 1F), -90.36 (d, *J* = 37.2 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2979, 2903, 1724, 1399, 1232, 1065, 894, 761, 687; **HRMS (ESI)** Calcd $C_{29}H_{27}F_2NO_2Na$ $[M + Na]^+$: 482.1902, found 482.1893.



4-(2-([1,1'-Biphenyl]-4-yl)-3,3-difluoroallyl)-3-phenylhexahydrobenzo[d]oxazol-2 (3H)-one (3j)： Followed the general procedure with cyclohex-2-en-1-yl phenylcarbamate (44 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop -1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 49 mg of the title compound (yellow oil, 55% yield, d.r.>20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.32 (m, 5H), 7.23 – 7.18 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.74 – 4.65 (m, 1H), 4.05 (t, *J* = 6.6 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.20 – 2.09 (m, 2H), 1.82 – 1.69 (m, 3H), 1.64 – 1.56 (m, 1H), 1.51 – 1.42 (m, 1H), 1.04 – 0.93 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.0, 154.5 (dd, *J* = 289.3 Hz, 289.5 Hz), 140.5, 140.3, 137.6, 131.0, 129.2, 128.8, 128.4, 127.5, 127.3, 127.0, 125.9, 123.6, 89.7 (dd, *J* = 18.4, 16.9 Hz), 73.9, 61.1, 37.1, 31.7, 27.1, 26.0, 18.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.0 (d, *J* = 2.7 Hz, 2F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2988, 2940, 1757, 1728, 1597, 1488, 1399, 1239, 1067, 853, 761, 693; **HRMS (ESI)** calcd $C_{28}H_{25}F_2NO_2Na$ $[M + Na]^+$: 468.1746, found 468.1749.

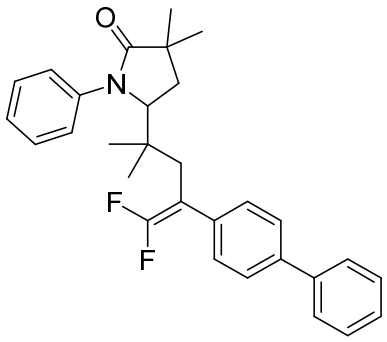


6-(2-([1,1'-Biphenyl]-4-yl)-3,3-difluoroallyl)-1-phenyl-3-oxa-1-azaspiro[4.5]decan -2-one (3k): Followed the general procedure with cyclohex-1-en-1-ylmethyl phenylcarbamate (46 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl) -1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 54 mg of the title compound (yellow oil, 59% yield, d.r. > 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.58 (m, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.20 – 7.14 (m, 2H), 6.97 – 6.91 (m, 2H), 4.53 (d, *J* = 9.0 Hz, 1H), 4.14 (d, *J* = 9.0 Hz, 1H), 2.92 – 2.79 (m, 1H), 2.53 – 2.38 (m, 1H), 2.05 – 1.92 (m, 1H), 1.83 – 1.74 (m, 1H), 1.73 – 1.65 (m, 2H), 1.64 – 1.55 (m, 1H), 1.43 – 1.35 (m, 1H), 1.27 – 1.15 (m, 1H), 1.09 – 0.97 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.4, 154.3 (dd, *J* = 288.7, 288.0 Hz), 140.8, 140.4, 134.7, 132.2 (dd, *J* =4.5, 2.0 Hz), 129.4 (t, *J* = 2.5 Hz), 129.2, 129.0, 128.7, 128.0, 127.6, 127.4, 127.1, 89.7 (dd, *J* =21.8, 16.5 Hz), 69.2, 65.7, 40.8, 37.6, 28.4, 27.4, 24.7, 22.7; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.6 (dd, *J* = 42.9, 4.9 Hz, 1F), -91.5 (d, *J* = 42.7 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 2927, 1722, 1601, 1493, 1455, 1398, 1234, 1052, 836, 761, 692; **HRMS** (ESI) calcd $C_{29}H_{27}F_2NO_2Na$ [M + Na]$^+$: 482.1902, found 482.1901.



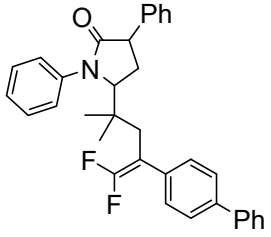
5-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-1-phenylpyrrolid in-2-one (3l): Followed the general procedure with 5-methyl-*N*-phenylhex-4-enamide (41 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24

mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 78 mg of the title compound (yellow oil, 91% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 – 7.55 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.13 (dd, *J* = 8.9, 2.4 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.51 – 2.31 (m, 3H), 2.17 – 2.04 (m, 2H), 0.74 (s, 3H), 0.59 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 175.2, 155.3 (dd, *J* = 290.3, 289.1 Hz), 140.3, 140.14, 140.11, 133.9, 128.9, 128.8, 128.6, 127.5, 127.1, 126.9, 126.2, 125.4, 89.5 (dd, *J* = 21.3, 14.1 Hz), 68.3, 41.8, 36.5, 31.3, 24.8, 23.6, 20.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.4 (d, *J* = 38.8 Hz, 1F), -90.5 (d, *J* = 38.7 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2908, 2799, 1750, 1712, 1605, 1497, 1406, 1269, 1230, 1105, 1055, 860, 743, 700; **HRMS (ESI)** Calcd $C_{28}H_{27}F_2NONa$ $[M + Na]^+$: 454.1953, found 454.1951.

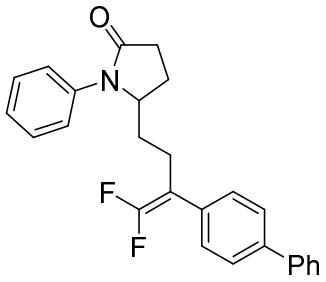


5-(3-([1,1'-Biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)-4,4-dimethyl-1-phenylpyrrolidin-2-one (3m): Followed the general procedure with 2,2,5-trimethyl-*N*-phenylhex-4-enamide (46 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 62 mg of the title compound (yellow oil, 67%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.27 – 7.18 (m, 4H), 4.08 – 3.99 (m, 1H), 2.30 (s, 2H), 1.96 (dd, *J* = 13.1, 7.5 Hz, 1H), 1.80 (dd, *J* = 13.1, 8.6 Hz, 1H), 1.30 (s, 3H), 1.18 (s, 3H), 0.64 (s, 3H), 0.58 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 181.1, 154.3 (dd, *J* = 290.7, 288.4 Hz), 140.6, 140.4, 140.0, 134.0, 129.0, 128.8, 128.6, 127.5, 127.1, 127.0, 126.9, 89.6 (dd, *J* = 21.3, 14.0 Hz), 65.6, 39.8, 39.7, 36.6, 35.8, 26.0, 25.2, 24.3, 23.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.52 (d, *J* = 39.0 Hz, 1F), -90.58 (d, *J* = 38.8 Hz, 1F); **FT-IR** (thin film, KBr): ν

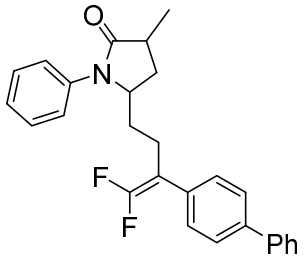
(cm^{-1}) 2971, 1690, 1596, 1492, 1396, 1230, 1107, 1051, 841, 695, 659; **HRMS (ESI)** Calcd $C_{30}H_{31}F_2NONa$ $[M + Na]^+$: 482.2266, found 482.2268.



5-(4-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-1,3-diphenylpyrrolidin-2-one (3n): Followed the general procedure with 5-methyl-*N*,2-diphenylhex-4-enamide (56 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 69 mg of the title separable isomers (yellow oil, 68% yield, d.r. = 3:1); **isomer-1: ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 4H), 7.40 – 7.32 (m, 5H), 7.32 – 7.25 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.13 (t, *J* = 7.9 Hz, 1H), 3.80 (t, *J* = 10.3 Hz, 1H), 2.70 – 2.57 (m, 1H), 2.31 (s, 2H), 2.10 – 1.94 (m, 1H), 0.65 (s, 3H), 0.59 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 176.0, 155.2 (d, *J* = 290.8 Hz), 140.3, 140.0, 139.7, 129.1, 128.77, 128.76, 128.6, 128.1, 127.4, 127.3, 127.03, 126.96, 126.91, 89.5 (dd, *J* = 21.2, 13.9 Hz), 67.0, 47.2, 39.9, 35.7, 30.9, 24.4, 23.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.36 (d, *J* = 38.6 Hz), -90.50 (d, *J* = 38.8 Hz). **Isomer-2: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.55 (m, 4H), 7.49 – 7.42 (m, 2H), 7.42 – 7.34 (m, 5H), 7.33 – 7.29 (m, 4H), 7.26 – 7.20 (m, 4H), 4.23 (dd, *J* = 9.1, 2.1 Hz, 1H), 3.95 (t, *J* = 9.7 Hz, 1H), 2.66 – 2.54 (m, 1H), 2.52 – 2.37 (m, 2H), 2.34 – 2.21 (m, 1H), 0.84 (s, 3H), 0.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 174.9, 154.4 (dd, *J* = 290.9, 288.8 Hz), 140.3, 140.21, 140.17, 139.9, 128.9, 128.8, 128.6, 128.1, 127.5, 127.1, 127.0, 126.9, 126.2, 125.3, 89.5 (dd, *J* = 21.2, 14.1 Hz), 66.2, 48.2, 41.9, 36.8, 31.3, 25.0, 23.9; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -88.33 (d, *J* = 38.4 Hz, 1F), -90.43 (d, *J* = 38.4 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2988, 2901, 1697, 1596, 1492, 1394, 1230, 1107, 1051, 797, 695, 694; **HRMS (ESI)** calcd $C_{34}H_{31}F_2NONa$ $[M + Na]^+$: 530.2266, found: 530.2268.

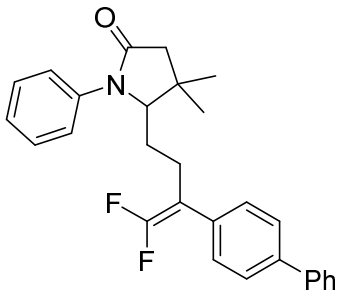


5-(3-([1,1'-Biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)-1-phenylpyrrolidin-2-one (3o): Followed the general procedure with *N*-phenylpent-4-enamide (35 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 61 mg of the title compound (yellow oil, 76 % yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.38 – 7.30 (m, 1H), 7.28 – 7.17 (m, 6H), 7.15 – 7.07 (m, 1H), 4.29 – 4.09 (m, 1H), 2.67 – 2.48 (m, 2H), 2.44 – 2.26 (m, 3H), 1.92 – 1.67 (m, 2H), 1.58 – 1.39 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.1, 153.6 (dd, *J* = 291.5, 287.7 Hz), 140.4, 140.3, 137.4, 131.7 (t, *J* = 3.2 Hz), 129.0, 128.9, 128.4 (t, *J* = 3.3 Hz), 127.6, 127.3, 127.0, 125.7, 123.7, 91.1 (dd, *J* = 20.9, 13.9 Hz), 58.5, 31.3, 31.0, 23.6, 22.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.04 (d, *J* = 41.6 Hz, 1F), -90.24 (d, *J* = 41.6 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2977, 2908, 1752, 1732, 1598, 1492, 1452, 1312, 1233, 1068, 855, 763, 695; **HRMS** (ESI) calcd $C_{26}H_{23}F_2NONa$ $[M + Na]^+$: 426.1640, found 426.1643.



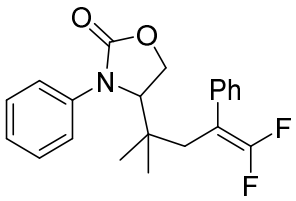
5-(3-([1,1'-Biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)-3-methyl-1-phenylpyrrolidin-2-one (3p): Followed the general procedure with 2-methyl-*N*-phenylpent-4-enamide (38 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 57 mg of the title compound (yellow oil, 68 % yield, d.r. = 2.5:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.55 (m, 2H), 7.55 – 7.49

(m, 2H), 7.48 – 7.41 (m, 2H), 7.40 – 7.29 (m, 2.83H), 7.29 – 7.23 (m, 3.27H), 7.22 – 7.17 (m, 0.71H), 7.16 – 7.05 (m, 1.59H), 4.21 – 4.13 (m, 0.70H)/4.12 – 4.04 (m, 0.28H), 2.78 – 2.38 (m, 3H), 2.20 – 2.11 (m, 0.72H), 1.98 – 1.88 (m, 0.82H), 1.84 – 1.72 (m, 1H), 1.59 – 1.50 (m, 0.70H), 1.48 – 1.37 (m, 0.7H)/1.21 – 1.17 (m, 0.3H), 1.32 (d, *J* = 6.7 Hz, 0.85H)/1.26 (d, *J* = 7.1 Hz, 2.15H); ^{13}C NMR (150 MHz, **$CDCl_3$**) δ 176.6/176.4, 153.6(dd, *J* = 291.5, 287.8 Hz)/153.5 (dd, *J* = 291.8, 287.2 Hz), 140.4, 140.3/140.2, 137.7/137.3, 131.6, 128.9, 128.9/128. 8, 128.4/128.3, 127.5, 127.2, 127.0, 125.7, 125.23, 124.13, 122.9/122.7, 91.1 (dd, *J* = 20.7, 14.0 Hz), 56.5/55.9, 37.0/36.5, 33.5/32.0, 31.2/30.4, 23.1/22.1, 16.6/16.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.96 – -90.34 (m, 2F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2969, 1693, 1597, 1496, 1456, 1392, 1232, 1104, 841, 759, 693; **HRMS (ESI)** calcd $C_{27}H_{25}F_2NONa$ [M + Na]$^+$: 440.1796, found: 440.1801.

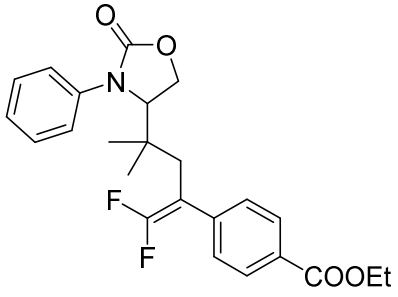


5-(3-([1,1'-Biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)-4,4-dimethyl-1-phenylpyrrolidin-2-one (3q): Followed the general procedure with 3,3-dimethyl-*N*-phenyl pent-4-enamide (41 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 46 mg of the title compound (yellow oil, 53 % yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.29 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 3.76 (t, *J* = 5.7 Hz, 1H), 2.48 (d, *J* = 16.5 Hz, 1H), 2.36 – 2.31 (m, 2H), 2.28 (d, *J* = 16.5 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.66 – 1.60 (m, 1H), 1.26 (s, 3H), 1.16 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.2, 153.5 (dd, *J* = 292.0, 287.3 Hz), 140.4, 140.2, 138.2, 131.6 (t, *J* = 3.7 Hz), 129.1, 128.8, 128.3, 127.5, 127.2, 127.0, 126.1, 124.4, 91.4 (dd, *J* = 21.7, 13.0 Hz), 69.0, 46.5, 36.3, 29.1, 28.4, 24.6, 22.9; **^{19}F NMR (377**

MHz, $CDCl_3$) δ -90.02 (d, *J* = 41.6 Hz, 1F), -90.44 (d, *J* = 41.6 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2972, 2902, 1694, 1597, 1488, 1453, 1396, 1222, 1076, 855, 761, 695; **HRMS (ESI)** calcd $C_{28}H_{27}F_2NONa$ $[M + Na]^+$: 454.1953, found: 454.1956.

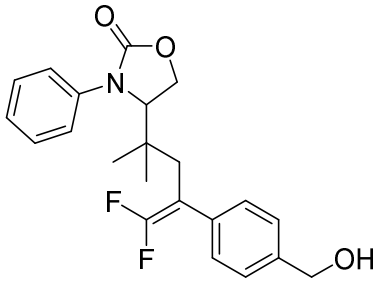


4-(5,5-Difluoro-2-methyl-4-phenylpent-4-en-2-yl)-3-phenyloxazolidin-2-one (4a): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (41 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 66 mg of the title compound (yellow oil, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.31 (m, 6H), 7.30 – 7.26 (m, 1H), 7.25 – 7.19 (m, 3H), 4.27 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.21 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.14 (t, *J* = 8.7 Hz, 1H), 2.44 – 2.23 (m, 2H), 0.78 (s, 3H), 0.61 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.8, 154.4 (dd, *J* = 290.9, 288.7 Hz), 138.9, 134.6, 129.2, 128. 7, 128.2, 127.6, 126.2, 124.3, 89.3 (dd, *J* = 21.1, 14.8 Hz), 64.1, 64.0, 40.6, 36.1, 23.9, 22.7; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -88.8 (d, *J* = 38.5 Hz, 1F), -90.6 (d, *J* = 38.4 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2969, 2931, 1750, 1726, 1599, 1502, 1407, 1236, 1210, 1125, 1087, 964, 753, 696; **HRMS (ESI)** calcd $C_{21}H_{22}F_2NO_2$ $[M + H]^+$: 358.1613, found 358.1603.

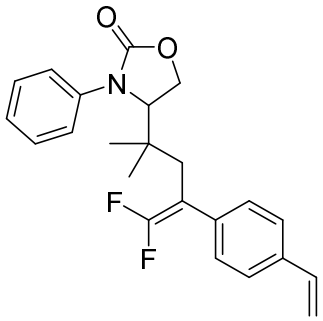


Ethyl 4-(1,1-difluoro-4-methyl-4-(2-oxo-3-phenyloxazolidin-4-yl)pent-1-en-2-yl) benzoate (4b): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and ethyl 4-(3,3,3-trifluoroprop-1-en-2-yl) benzoate (59 mg, 0.24 mmol) and purified by flash chromatography (petroleum

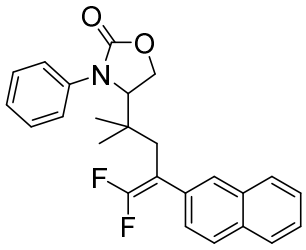
ether/EtOAc = 10:1) to give 74 mg of the title compound (yellow oil, 86% yeild); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.18 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.30 – 4.18 (m, 3H), 2.43 – 2.24 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.71 (s, 3H), 0.57 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.9, 156.7, 154.5 (dd, *J* = 293.0, 289.9 Hz), 139.4, 138.8, 129.8, 129.6, 129.2, 128.1, 126.3, 124.4, 89.1 (dd, *J* = 21.8, 14.0 Hz), 64.5, 64.0, 61.1, 40.6, 35.6, 23.4, 23.0, 14.3; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -86.73 (d, *J* = 34.2 Hz, 1F), -88.65 (d, *J* = 34.2 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2961, 2925, 1739, 1596, 1494, 1404, 1361, 1220, 1121, 1043, 841, 758, 691; **HRMS (ESI)** Calculated $C_{24}H_{25}F_2NO_2Na$ $[M + Na]^+$: 452.1644, found 452.1642.



4-(5,5-Difluoro-4-(4-(hydroxymethyl)phenyl)-2-methylpent-4-en-2-yl)-3-phenyloxazolidin-2-one (4c): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and (4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl) methanol (48 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 60mg of the title compound (yellow oil, 78% yeild); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 4H), 7.24 – 7.18 (m, 3H), 4.68 (s, 2H), 4.27 (dd, *J* = 8.9, 3.0 Hz, 1H), 4.21 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.16 (t, *J* = 8.8 Hz, 1H), 2.44 – 2.17 (m, 2H), 0.77 (s, 3H), 0.60 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156. 8, 154.4 (d, *J* = 290.9 Hz, 289.0 Hz), 140.4, 138.8, 133.8, 129.2, 128.3, 127.1, 126.2, 124.3, 89.1 (dd, *J* = 21.2, 14.9 Hz), 64.7, 64. 2, 64.0, 40.6, 36.1, 23.8, 22.8; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -88.51 (d, *J* = 38.2 Hz, 1F), -90.37 (d, *J* = 38.2 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2958, 2925, 1736, 1595, 1493, 1403, 1352, 1218, 1116, 1076, 843, 758, 692; **HRMS (ESI)** Calcd $C_{22}H_{24}F_2NO_3$ $[M + H]^+$: 388.1719, found 388.1717.

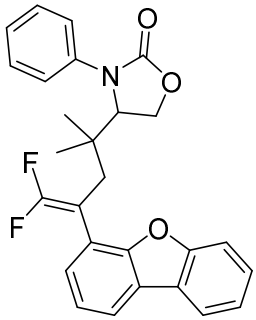


4-(5,5-Difluoro-2-methyl-4-(4-vinylphenyl)pent-4-en-2-yl)-3-phenyloxazolidin-2-one (4d): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and 1-(3,3,3-trifluoroprop-1-en-2-yl)-4-vinylbenzene (48 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 73 mg of the title compound (yellow oil, 95% yeild); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41– 7.34 (m, 6H), 7.25 – 7.20 (m, 1H), 7.19 – 7.16 (m, 2H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 4.29 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.25 – 4.15 (m, 2H), 2.44 – 2.22 (m, 2H), 0.78 (s, 3H), 0.61 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.7, 154.4 (dd, *J* = 291.4, 288.9 Hz), 138.8, 136.9, 136.0, 134.0, 129.2, 128.3, 126.4, 126.2, 124.3, 114.5, 89.1 (dd, *J* = 21.2, 14.5 Hz), 64.2, 64.0, 40.6, 35.9, 23.9, 22.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.10 (d, *J* = 37.4 Hz, 1F), -90.05 (d, *J* = 37.5 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 2926, 1750, 1597, 1497, 1403, 1358, 1273, 1123, 1060, 843, 762, 695; **HRMS (ESI)** Calcd $C_{23}H_{24}F_2NO_2$ $[M + H]^+$: 384.1770, found 384.1766.

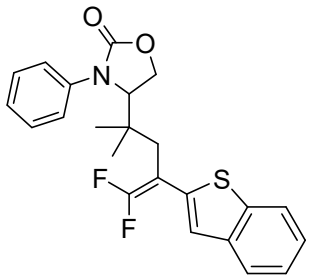


4-(5,5-Difluoro-2-methyl-4-(naphthalen-2-yl)pent-4-en-2-yl)-3-phenyloxazolidin-2-one (4e): Followed the general procedure with 3-methylbut-2-en-1-yl phenyl carbamate (41 mg, 0.2 mmol) and 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (53 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 65 mg of the title compound (yellow oil, 80% yeild); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.77 (m, 3H), 7.67 (s, 1H), 7.55 – 7.47 (m, 2H), 7.42 – 7.30 (m, 5H),

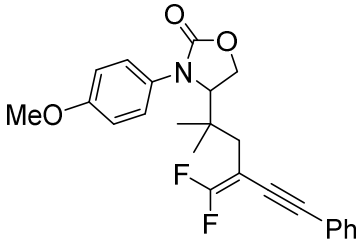
7.25 – 7.18 (m, 1H), 4.31 (dd, *J* = 8.8, 2.9 Hz, 1H), 4.23 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.16 (t, *J* = 8.7 Hz, 1H), 2.56 – 2.35 (m, 2H), 0.79 (s, 3H), 0.63 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.8 154.6 (t, *J* = 290.2 Hz), 138.8, 133.2, 132.5, 132.0, 129.2, 128.4, 127.8, 127.7, 127.3, 126.6, 126.4, 126.2, 125.8, 124.4, 89.4 (dd, *J* = 21.0, 14.8 Hz), 64.3, 64.0, 40.6, 36.1, 23.8, 22.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.43 (d, *J* = 38.8 Hz, 1F), -90.52 (d, *J* = 38.7 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2963, 2927, 1745, 1596, 1495, 1403, 1359, 1214, 1123, 1054, 851, 758, 693; **HRMS (ESI)** Calcd $C_{25}H_{23}F_2NO_2Na$ $[M + Na]^+$: 430.1589, found 430.1586.



4-(4-(Dibenzo[*b,d*]furan-4-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-3-phenyloxazolidin-2-one (4f): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)dibenzo [b,d]furan (63 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 78 mg of the title compound (yellow oil, 87% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.91 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 4H), 7.15 – 7.09 (m, 1H), 4.28 – 4.16 (m, 2H), 3.93 (t, *J* = 8.8 Hz, 1H), 2.70 – 2.46 (m, 2H), 0.83 (s, 3H), 0.60 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.7, 156.0, 154.3 (dd, *J* = 270.6, 269.0 Hz), 153.2, 138.8, 129.0, 127.7, 127.1, 125.9, 124.8, 123.9, 123.9, 123.2, 123.1, 121.0, 120.5, 119.2 (d, *J* = 3.1 Hz), 111.7, 84.5 (dd, *J* = 23.9, 16.8 Hz), 63.9, 63.3, 40.5, 36.5, 24.3, 22.4; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -85.1 (d, *J* = 32.1 Hz, 1F), -88.1 (d, *J* = 32.5 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2973, 2916, 1736, 1594, 1495, 1452, 1405, 1357, 1256, 1059, 845, 753, 694; **HRMS (ESI)** Calcd $C_{27}H_{23}F_2NO_3Na$ $[M + Na]^+$: 470.1538, found 470.1542.

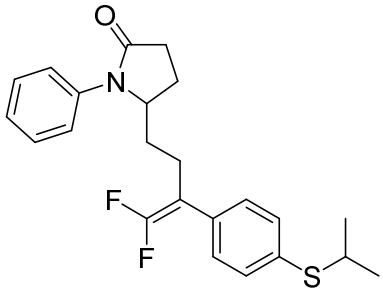


4-(4-(Benzo[b]thiophen-2-yl)-5,5-difluoro-2-methylpent-4-en-2-yl)-3-phenyloxazolidin-2-one (4g)： Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and 2-(3,3,3-trifluoroprop-1-en-2-yl)benzo [b]thiophene (55 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 73 mg of the title compound (yellow oil, 88% yeild); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.39 (m, 1H), 7.38 – 7.29 (m, 2H), 7.26 – 7.19 (m, 1H), 7.16 (s, 1H), 4.44 – 4.37 (m, 2H), 4.36 – 4.30 (m, 1H), 2.49 – 2.28 (m, 2H), 0.83 (s, 3H), 0.76 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.8, 154.7 (dd, *J* = 297.0, 290.8 Hz), 139.4, 139.1, 138.8, 137.1 (t, *J* = 5.1 Hz), 129.3, 126.3, 124.7, 124.6, 124.4, 123.4, 122.6 (t, *J* = 4.2 Hz), 122.0, 85.3 (dd, *J* = 26.0, 13.4 Hz), 64.6, 64.2, 40.9, 36.0, 23.3, 23.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -82.95 (d, *J* = 26.4 Hz, 1F), -84.34 (d, *J* = 26.4 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1747, 1708, 1597, 1500, 1458, 1436, 1371, 1268, 1213, 1125, 1062, 910, 727, 675; **HRMS (ESI)** calcd $C_{23}H_{21}F_2NO_2SNa$ [M + Na]$^+$: 436.1153, found: 436.1157.

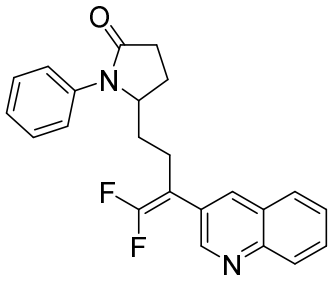


4-(4-(Difluoromethylene)-2-methyl-6-phenylhex-5-yn-2-yl)-3-(4-methoxyphenyl)oxazolidin-2-one (4h): Followed the general procedure with 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (47 mg, 0.2 mmol) and (3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (47 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 66 mg of the title compound (yellow oil, 80% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.25 (m, 7H), 6.91 (d, *J* = 8.2 Hz, 2H),

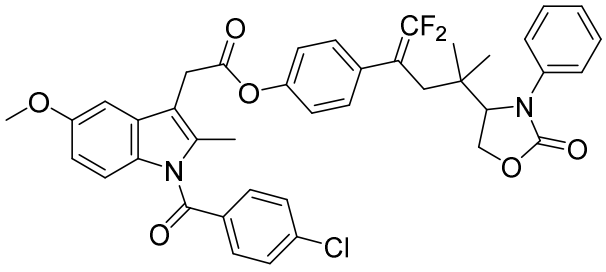
4.50 (t, *J* = 9.8 Hz, 1H), 4.44 – 4.35 (m, 2H), 3.80 (s, 3H), 2.19 – 1.90 (m, 2H), 0.98 (s, 3H), 0.88 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.8 (dd, *J* = 297.9, 294.9 Hz), 158.0, 157.3, 131.6, 131.2, 128.7, 128.5, 126.2, 122.5, 114.5, 94.1 (t, *J* = 5.8 Hz), 82.0 (dd, *J* = 7.8, 4.3 Hz), 74.8 (dd, *J* = 33.9, 16.4 Hz), 64.6, 64.2, 55.5, 39.8 (t, *J* = 2.2 Hz), 36.2, 23.7, 22.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -77.21 (d, *J* = 10.9 Hz, 1F), -81.90 (d, *J* = 11.2 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2969, 2933, 1747, 1709, 1598, 1512, 1413, 1247, 1132, 1030, 831, 757, 684; **HRMS (ESI)** Calcd $C_{24}H_{23}F_2NO_3Na$ $[M + Na]^+$: 434.1538, found 434.1539.



5-(4,4-difluoro-3-(4-(isopropylthio)phenyl)but-3-en-1-yl)-1-phenylpyrrolidin-2-one (4i): Followed the general procedure with *N*-phenylpent-4-enamide (35 mg, 0.2 mmol) and isopropyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane (59 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 45 mg of the title compound (yellow oil, 56% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.21 (m, 4H), 7.19 – 7.09 (m, 3H), 7.01 (d, *J* = 7.7 Hz, 2H), 4.22 – 4.08 (m, 1H), 3.41 – 3.27 (m, 1H), 2.62 – 2.47 (m, 2H), 2.40 – 2.27 (m, 3H), 1.88 – 1.75 (m, 1H), 1.72 – 1.64 (m, 1H), 1.50 – 1.34 (m, 1H), 1.26 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.1, 153.5 (dd, *J* = 291.8, 287.4 Hz), 137.3, 135.2, 131.4, 130.8 (dd, *J* = 2.8 Hz), 129.0, 128.3 (t, *J* =3.4 Hz), 125.8, 123.8, 90.9 (dd, *J* = 21.5, 13.6 Hz), 58.5, 38.0, 31.3, 31.0, 23.6, 23.14, 23.12, 22.4; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.96 (d, *J* = 41.6 Hz, 1F), -90.20 (d, *J* = 41.8 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2969, 2924, 1722, 1694, 1596, 1496, 1457, 1393, 1293, 1233, 1091, 824, 757, 694; **HRMS (ESI)** calcd $C_{23}H_{25}F_2NONaS$ $[M + Na]^+$: 424.1517, found 424.1518.

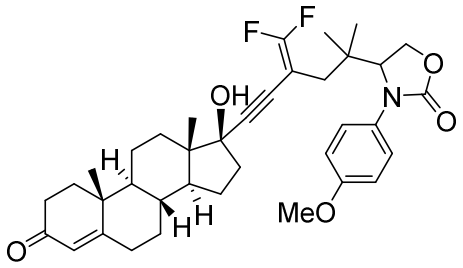


5-(4,4-Difluoro-3-(quinolin-3-yl)but-3-en-1-yl)-1-phenylpyrrolidin-2-one (4j): Followed the general procedure with *N*-phenylpent-4-enamide (35 mg, 0.2 mmol) and 3-(3,3,3-trifluoroprop-1-en-2-yl)quinolone (54 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 37 mg of the title compound (yellow oil, 49% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 1.8 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.26 (s, 1H), 7.23 – 7.19 (m, 3H), 7.15 – 7.07 (m, 1H), 4.31 – 4.20 (m, 1H), 2.67 – 2.57 (m, 2H), 2.55 – 2.47 (m, 2H), 2.42 – 2.36 (m, 1H), 1.94 – 1.84 (m, 1H), 1.80 – 1.70 (m, 1H), 1.65 – 1.51 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 174.0, 154.0 (dd, *J* = 292.9, 289.3 Hz), 149.8, 147.1, 137.1, 134.6, 129.8, 129.2, 129.0, 127.7, 127.5, 127.1, 126.1, 125.9, 123.8, 89.1 (dd, *J* = 23.3, 13.8 Hz), 58.5, 31.2, 31.1, 23.6, 22.5; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -88.41 (d, *J* = 38.1 Hz, 1F), -88.98 (d, *J* = 38.1 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2968, 2926, 1723, 1689, 1597, 1495, 1458, 1394, 1295, 1258, 1148, 1070, 845, 755, 694; **HRMS (ESI)** calcd $C_{23}H_{20}F_2N_2ONa$ $[M + Na]^+$: 401.1436, found 401.1439.



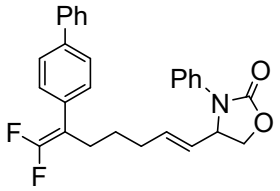
4-(1,1-Difluoro-4-methyl-4-(2-oxo-3-phenyloxazolidin-4-yl)pent-1-en-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (4k): Followed the general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (41 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-

methyl-1H-indol-3-yl)acetate (126 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 107 mg of the title compound (white soild, 75%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.32 (m, 4H), 7.23 – 7.16 (m, 3H), 7.11 – 7.02 (m, 3H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.77 – 6.61 (m, 1H), 4.38 – 4.06 (m, 3H), 3.90 (s, 2H), 3.84 (s, 3H), 2.46 (s, 3H), 2.40 – 2.19 (m, 2H), 0.75 (s, 3H), 0.59 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.0, 168.3, 156.8, 156.1, 154.4 (dd, *J* = 291.3, 289.0 Hz), 149.8, 139.4, 138.8, 136.3, 133.7, 132.3, 131.2, 130.8, 130.4, 129.2, 129.1, 126.3, 124.4, 121.7, 115.0, 111.8, 111.7, 101.3, 88.6 (dd, *J* = 21.7, 14.6 Hz), 64.4, 64.0, 55.7, 40.6, 35.9, 30.5, 23.7, 22.9, 13.4; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.05 (d, *J* = 37.7 Hz, 1F), -89.89 (d, *J* = 37.4 Hz, 1F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2971, 2919, 1741, 1631, 1598, 1469, 1405, 1236, 1214, 1108, 1064, 854, 752, 696; **HRMS (ESI)** calcd $C_{40}H_{35}{}^{35}ClF_2N_2O_6$ $[M + H]^+$: 713.2224, found 713.2222.



4-(4-(Difluoromethylene)-6-((8R,9S,10R,13S,14S,17R)-F17-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)-2-methylhex-5-yn-2-yl)-3-(4-methoxyphenyl)oxazolidin-2-one (4l) : Followed the general procedure with 3-methylbut-2-en-1-yl (4-methoxyphenyl)carbamate (47 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl) phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl -1H-indol-3-yl)acetate (97 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 107 mg of the title compound (white solid, 85%, d.r. = 1:1); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 (d, *J* = 7.1 Hz, 2H), 6.88 (d, *J* = 7.0 Hz, 2H), 5.73 (s, 1H), 4.56 – 4.43 (m, 1H), 4.41 – 4.29 (m, 2H), 3.80 (s, 3H), 2.49 – 2.17 (m, 7H), 2.10 – 1.92 (m, 4H), 1.85 (d, *J* = 11.2 Hz, 1H), 1.75 – 1.52 (m, 6H), 1.49 – 1.34 (m, 3H), 1.20 (s, 3H), 1.03 – 0.94 (m, 1H), 0.90 (s, 6H), 0.83 (d, *J* = 4.8 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)**

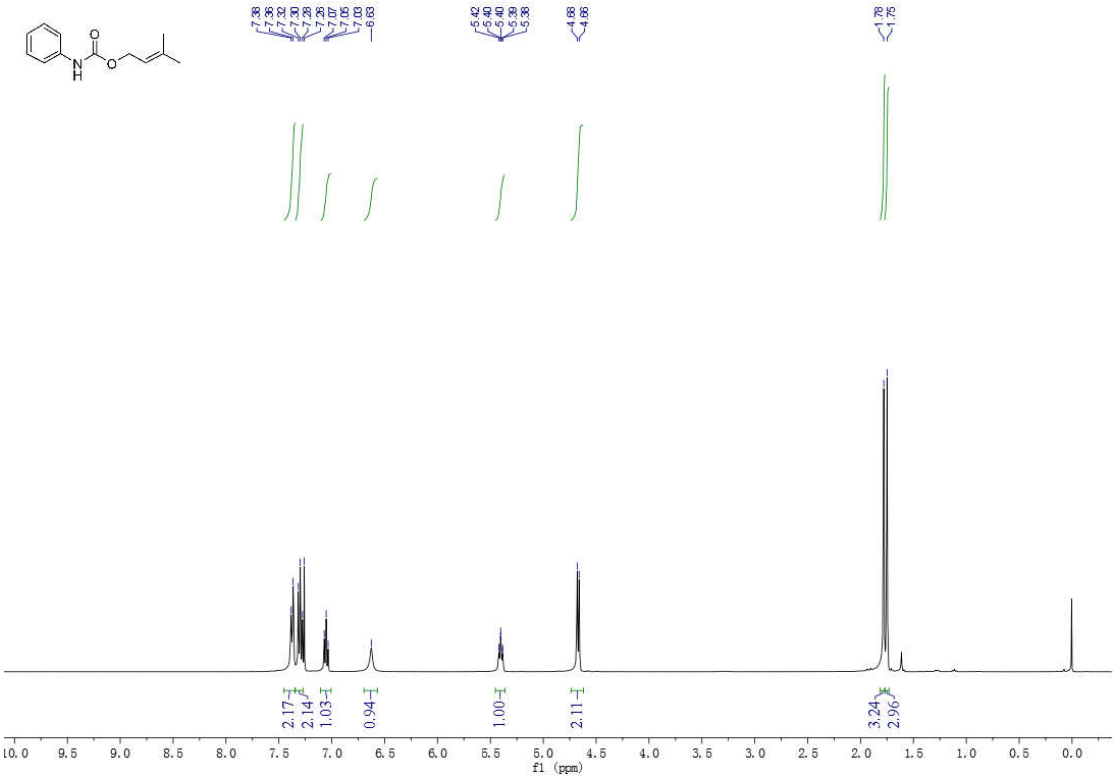
δ 199.6, 171.3, 159.9 (dd, *J* = 299.0, 292.1 Hz)/159.9 (dd, *J* = 299.1, 292.1 Hz) , 157.82/157.78, 157.42/157.40, 131.5, 126.13/126.09, 123.8, 114.4/114.3, 97.6 (dd, *J* = 11.1, 5.5 Hz), 79.8, 78.3 (dd, *J* = 10.8, 7.1 Hz), 74.32 (dd, *J* = 33.6, 16.2 Hz)/74.28 (dd, *J* = 33.6, 16.3 Hz), 64.5/64.4, 64.2, 55.4, 53.6, 50.2/50.1, 47.03/47.01, 39.6, 38.89/38.87 38.6, 36.1, 35.8, 35.7, 35.6, 33.9, 32.7, 32.57/32.56, 31.53/31.51, 23.7/23.6, 23.0, 22.8, 20.70/20.66, 17.3, 12.8; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -77.53 (d, *J* = 12.6 Hz, 1F), -81.65 (d, *J* = 12.3 Hz, 0.5F)/-81.82 (d, *J* = 12.5 Hz, 0.5F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2976, 2930, 1752, 1724, 1605, 1487, 1398, 1360, 1142, 1089, 858, 731, 655; **HRMS (ESI)** calcd $C_{37}H_{45}F_2NO_5Na$ [M + Na]$^+$: 644.3158, found 644.3156.



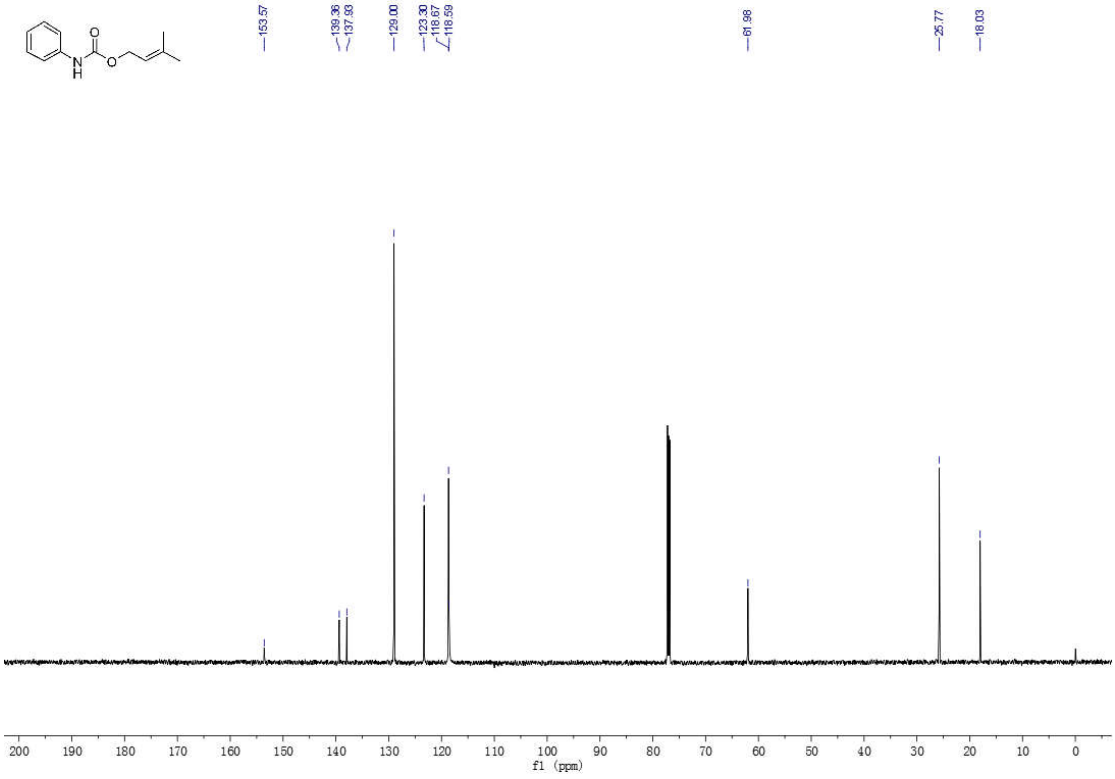
(*E*)-4-(6-([1,1'-Biphenyl]-4-yl)-7,7-difluorohepta-1,6-dien-1-yl)-3-phenyloxazolidin-2-one (5): Followed the general procedure with (*E*)-3-cyclopropylallyl phenylcarbamate (44 mg, 0.2 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (60 mg, 0.24 mmol) and purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give 76 mg of the title compound (yellow oil, 85%, *E/Z*>20:1); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.61 – 7.54 (m, 4H), 7.47 – 7.43 (m, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.29 (m, 5H), 7.15– 7.10 (m, 1H), 5.72 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.36 (dd, *J* = 15.4, 8.2 Hz, 1H), 4.79 (dd, *J* = 15.0, 8.2 Hz, 1H), 4.53 (t, *J* = 8.6 Hz, 1H), 4.05 (dd, *J* = 8.6, 6.6 Hz, 1H), 2.35 – 2.26 (m, 2H), 2.06 – 1.98 (m, 2H), 1.47 – 1.38 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.7, 153.6 (t, *J* = 289.1 Hz), 140.4, 140.1, 136.9, 136.5, 132.3, 128.8, 128.5 (t, *J* = 3.0 Hz), 127.5, 127.1, 127.0, 124.9, 121.6, 91.6 (dd, *J* = 18.4, 16.2 Hz), 67.4, 59.2, 31.2, 26.8, 26.6; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -90.83 (s, 2F); **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 2902, 1749, 1598, 1501, 1451, 1353, 1295, 1044, 842, 758, 692; **HRMS (ESI)** calcd $C_{28}H_{25}F_2NO_2Na$ [M + Na]$^+$: 468.1746, found 468.1752.

28. NMR Spectra for the substrates and product

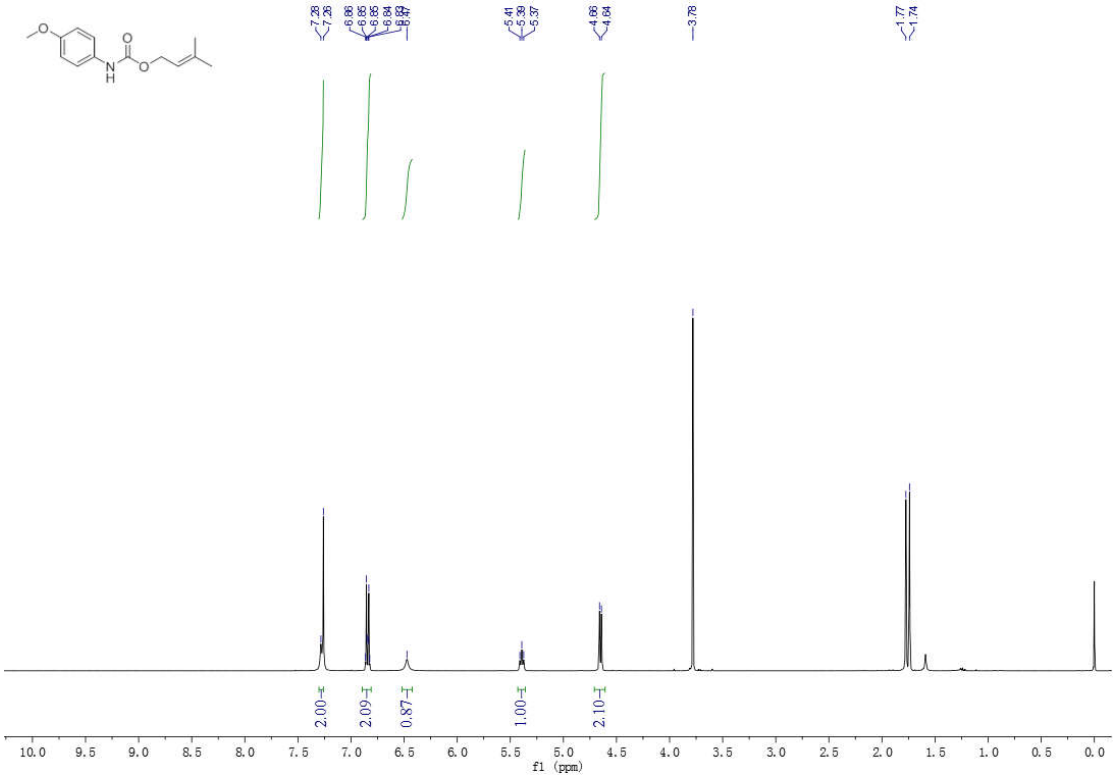
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 1a



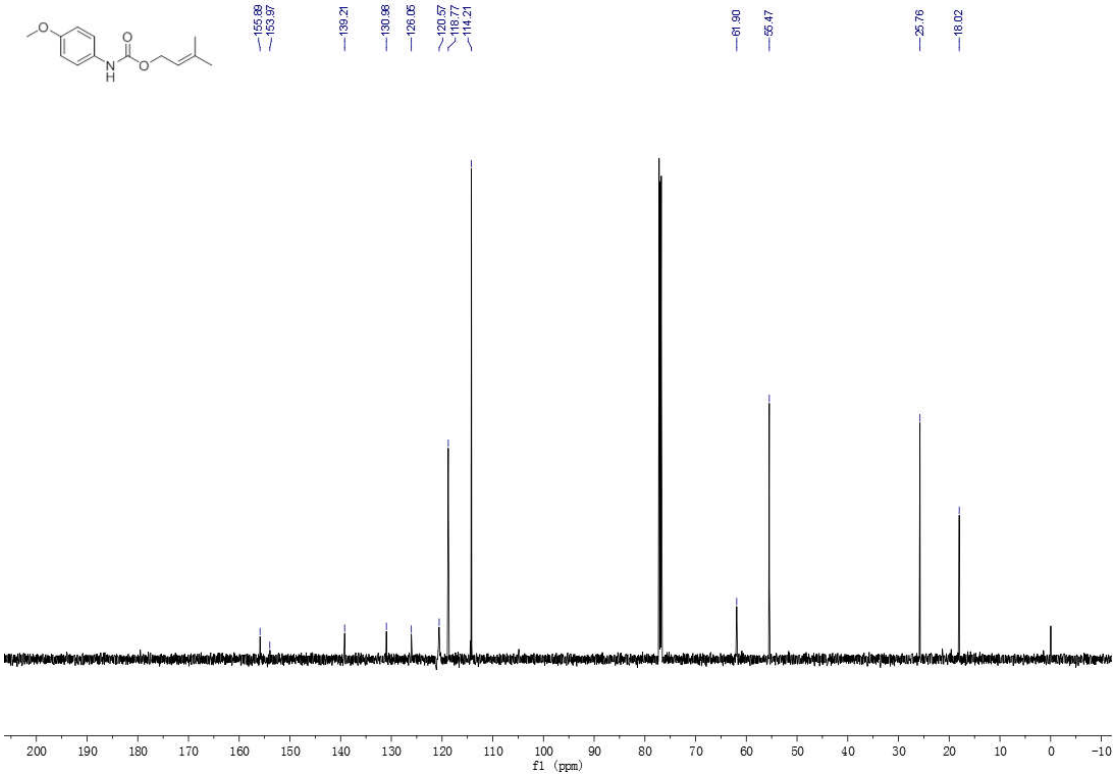
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 1a



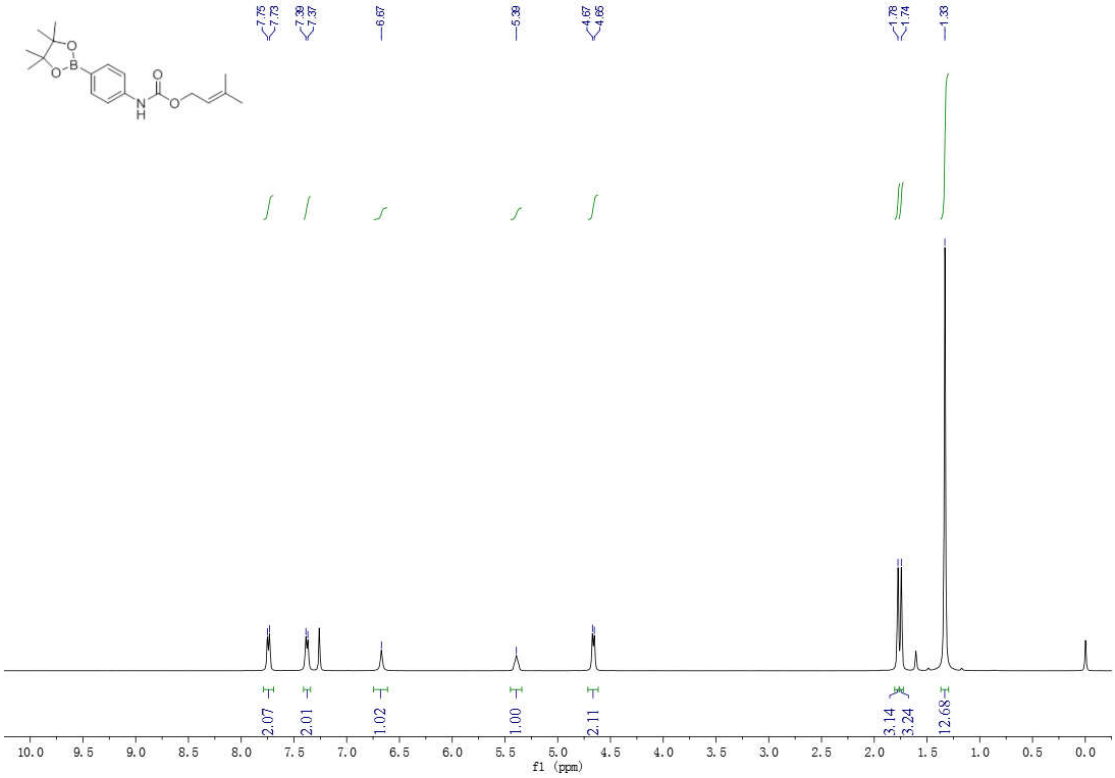
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1b



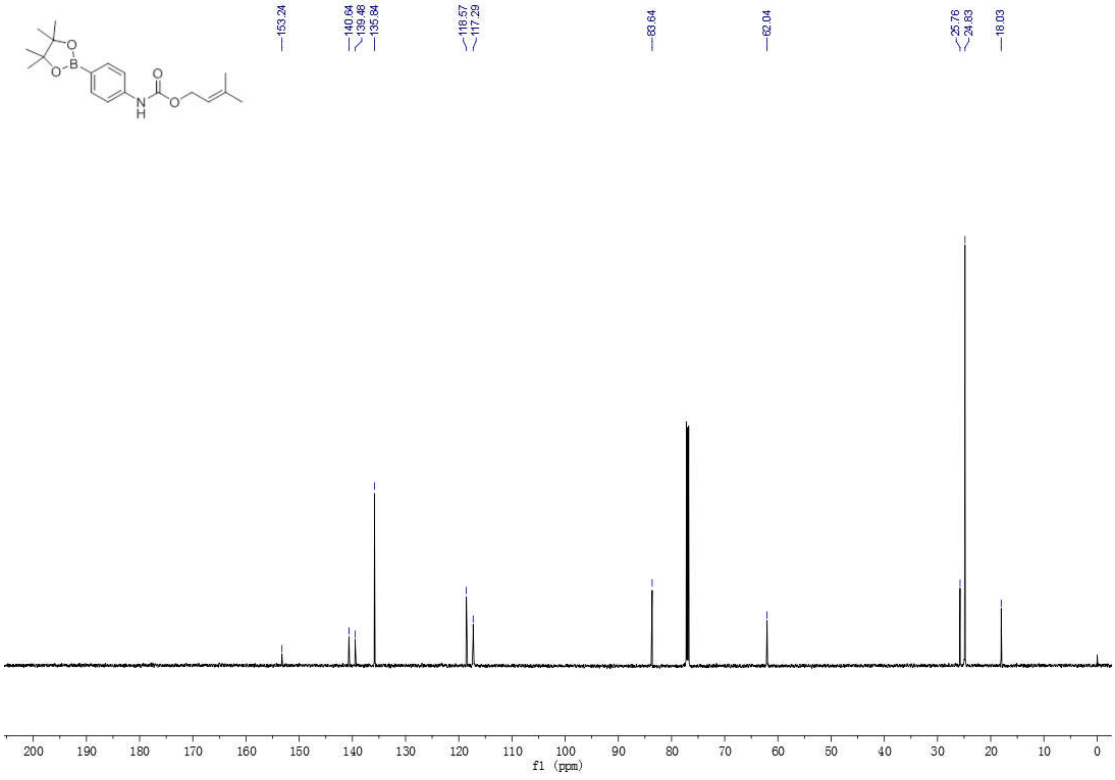
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1b



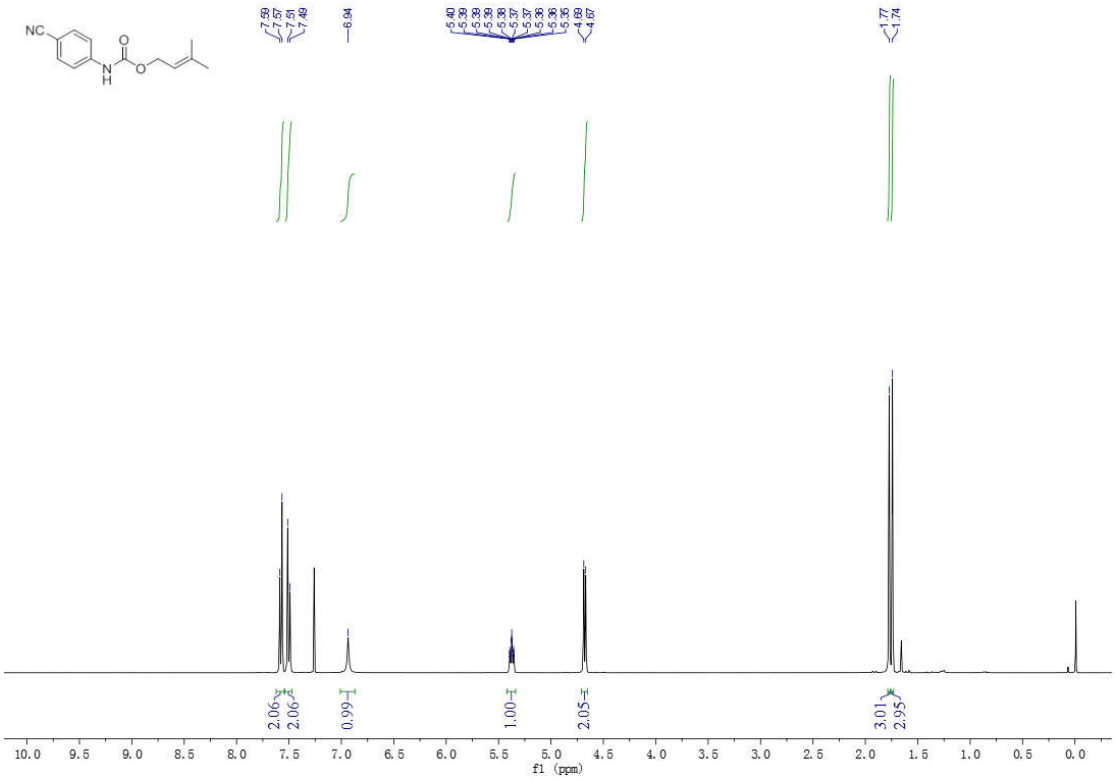
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1c



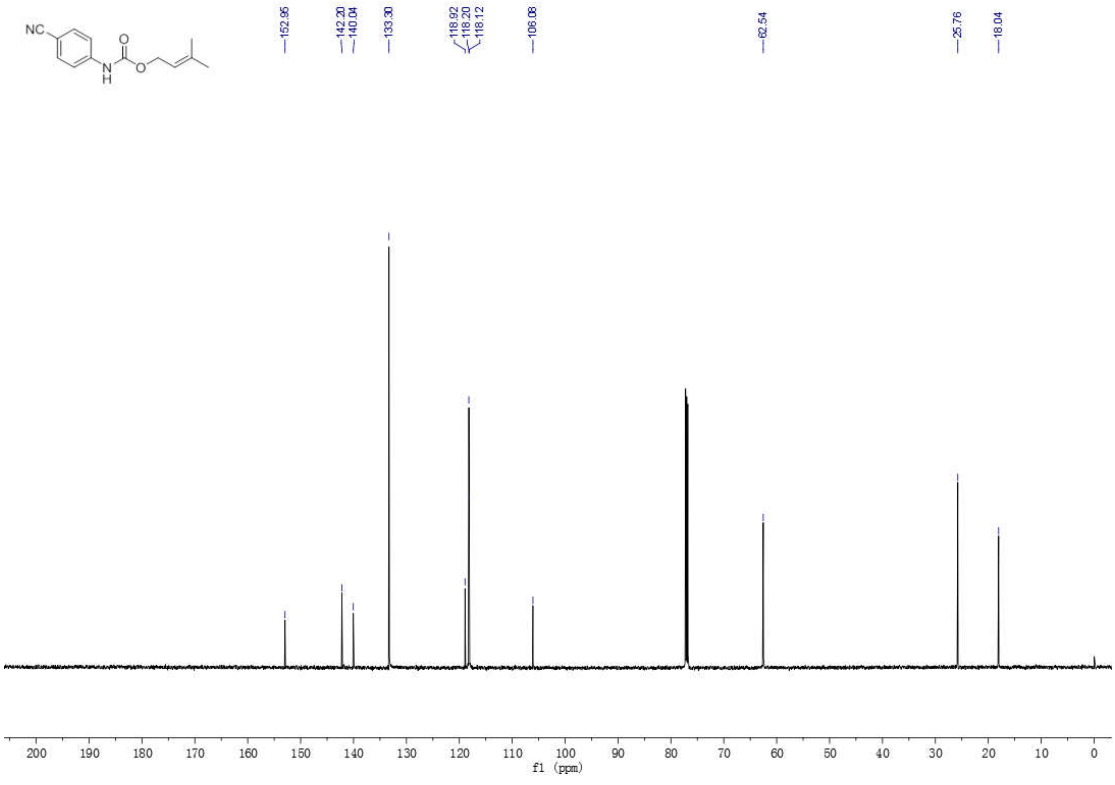
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1c



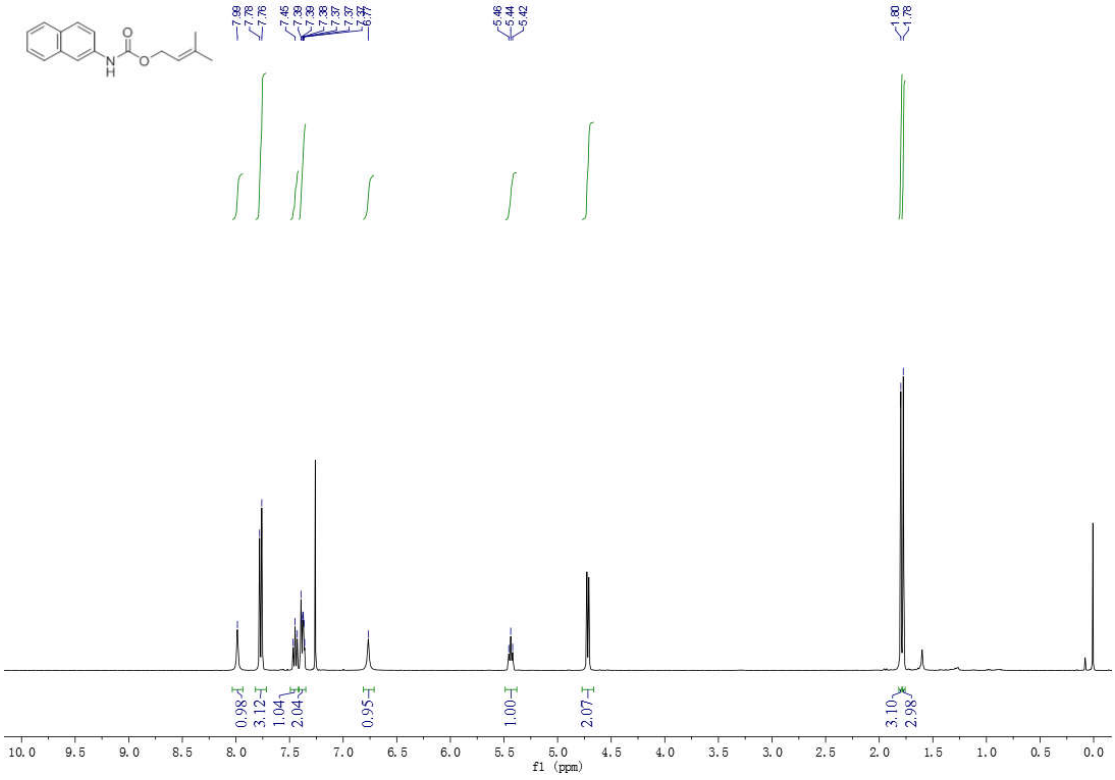
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1d



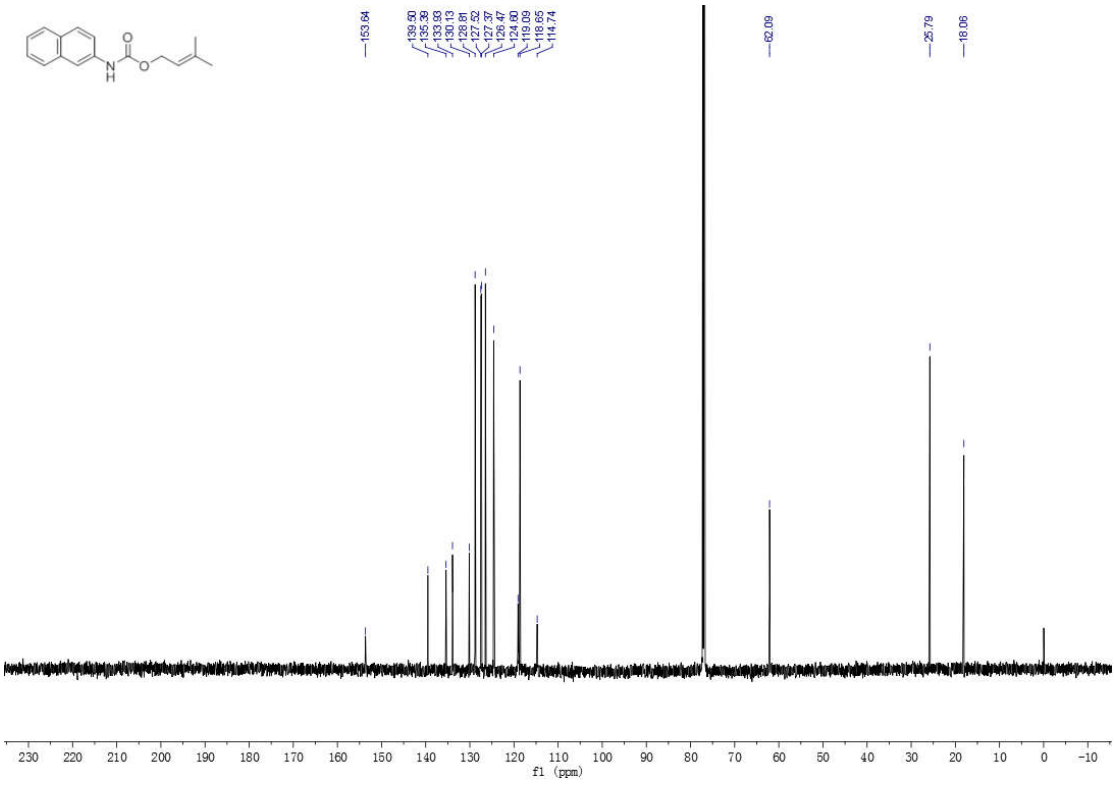
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1d



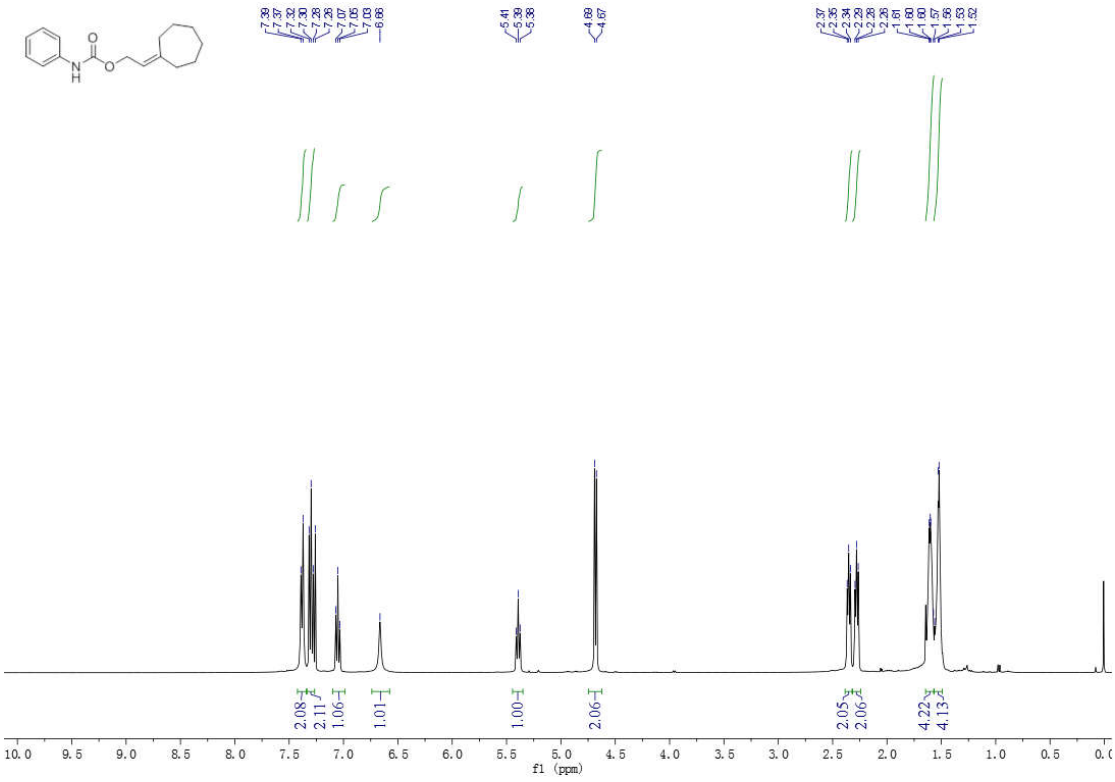
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1e



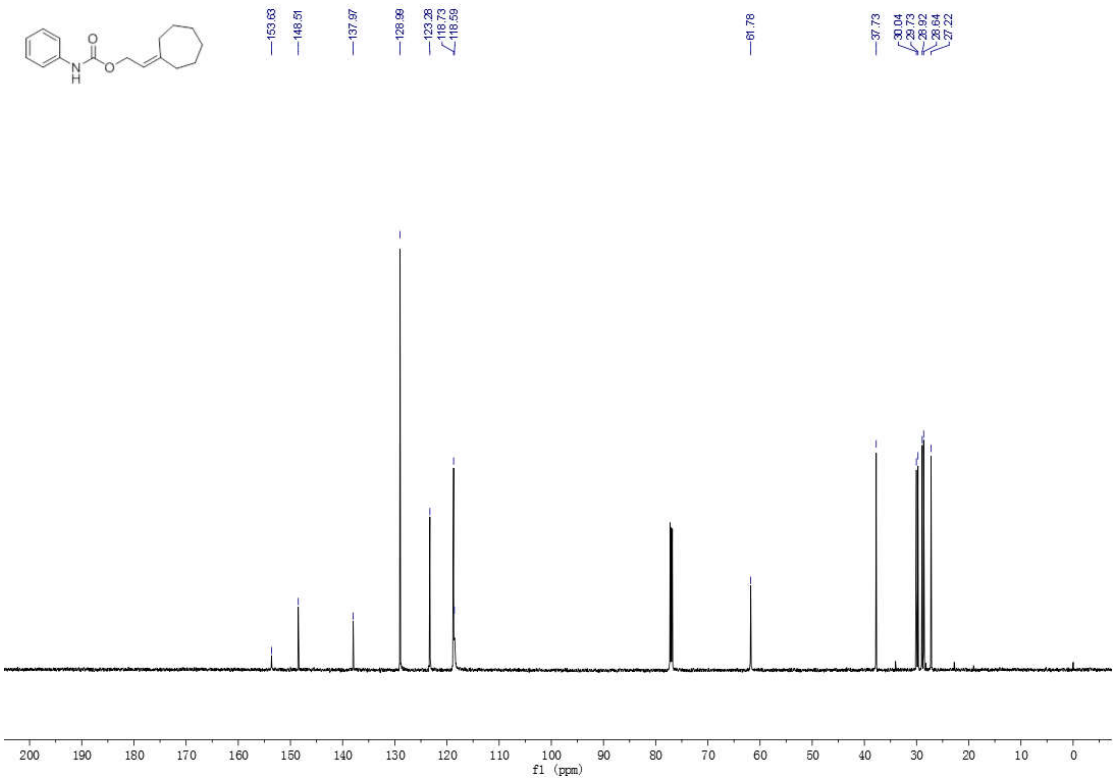
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1e



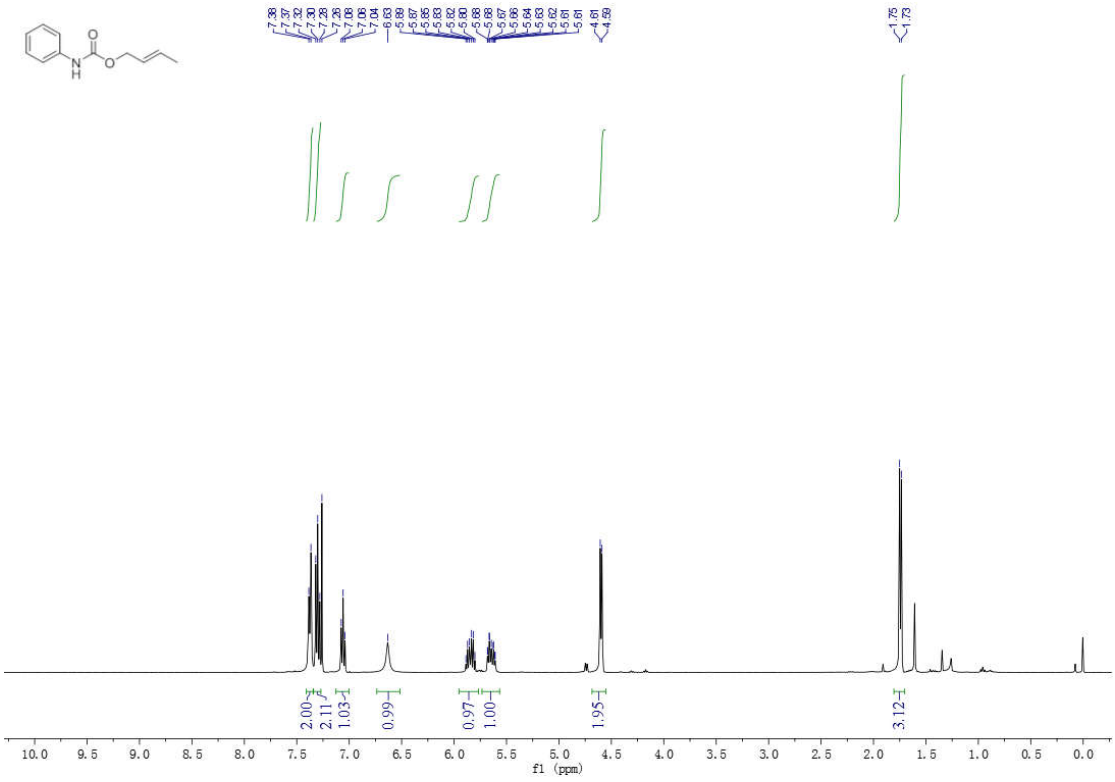
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1f



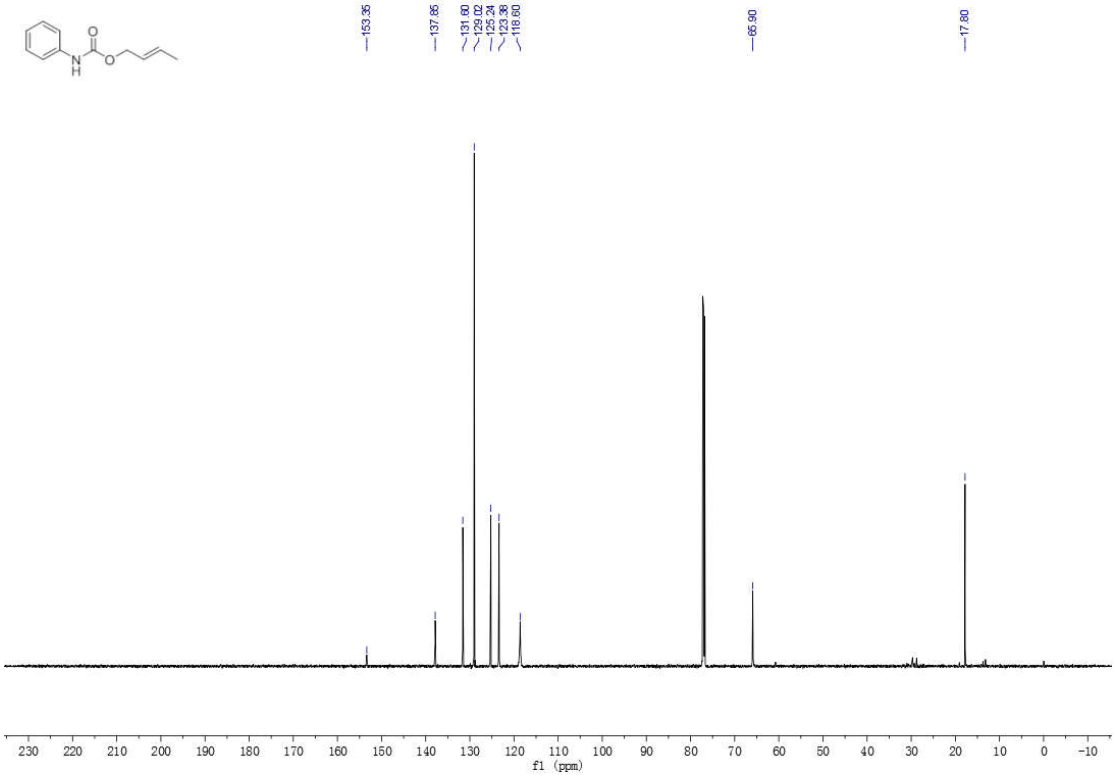
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1f



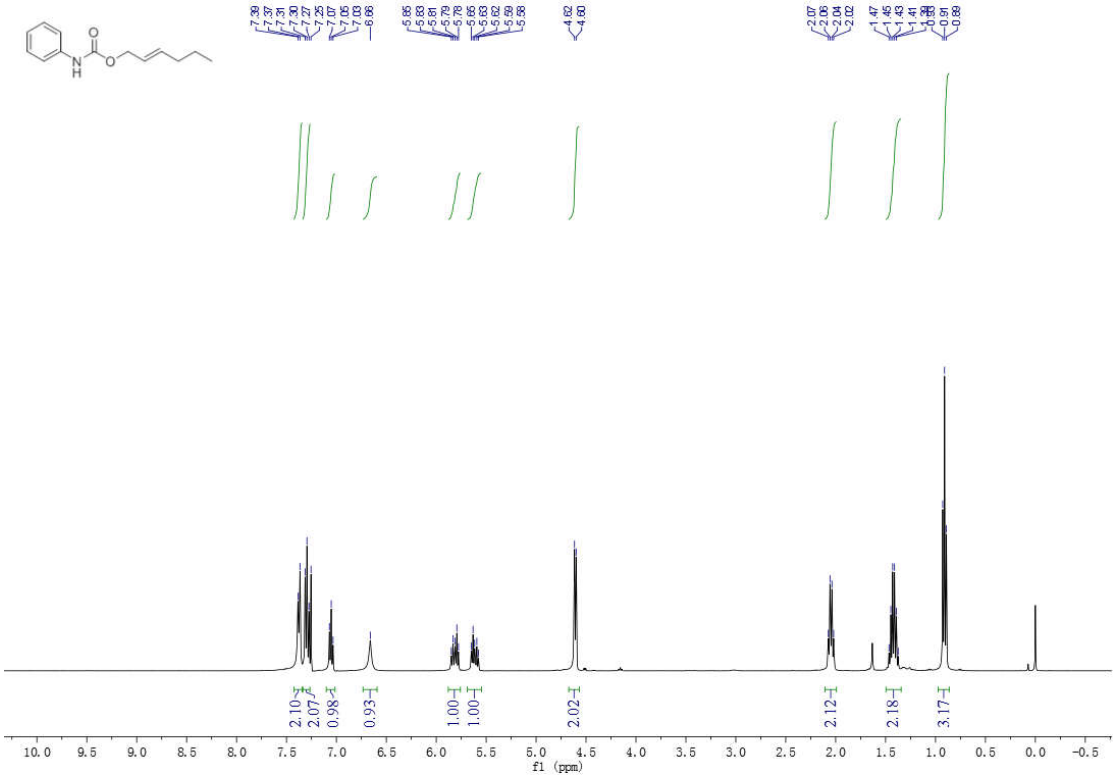
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1g



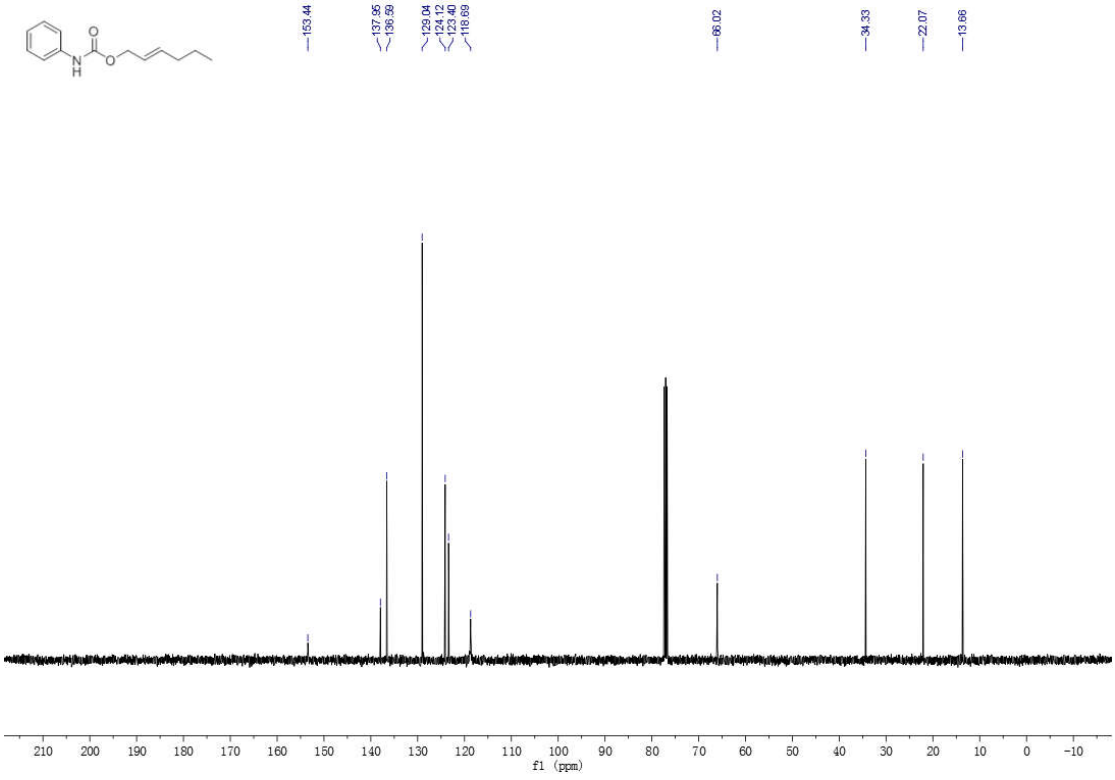
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1g



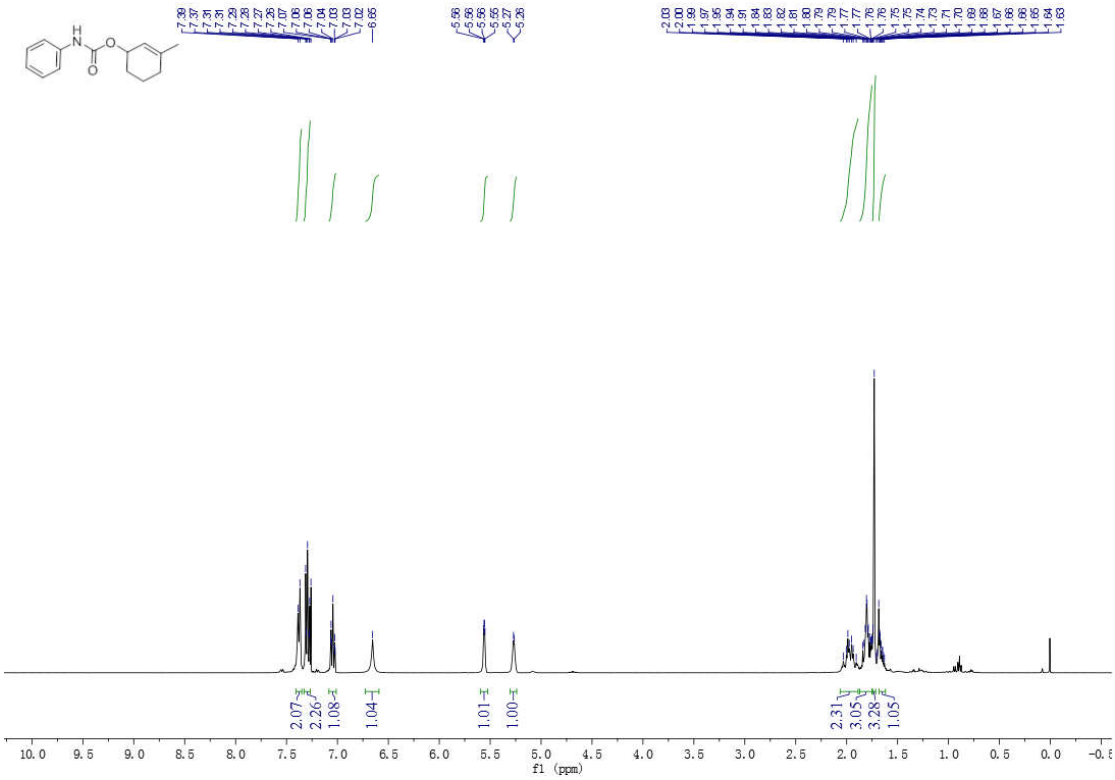
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1h



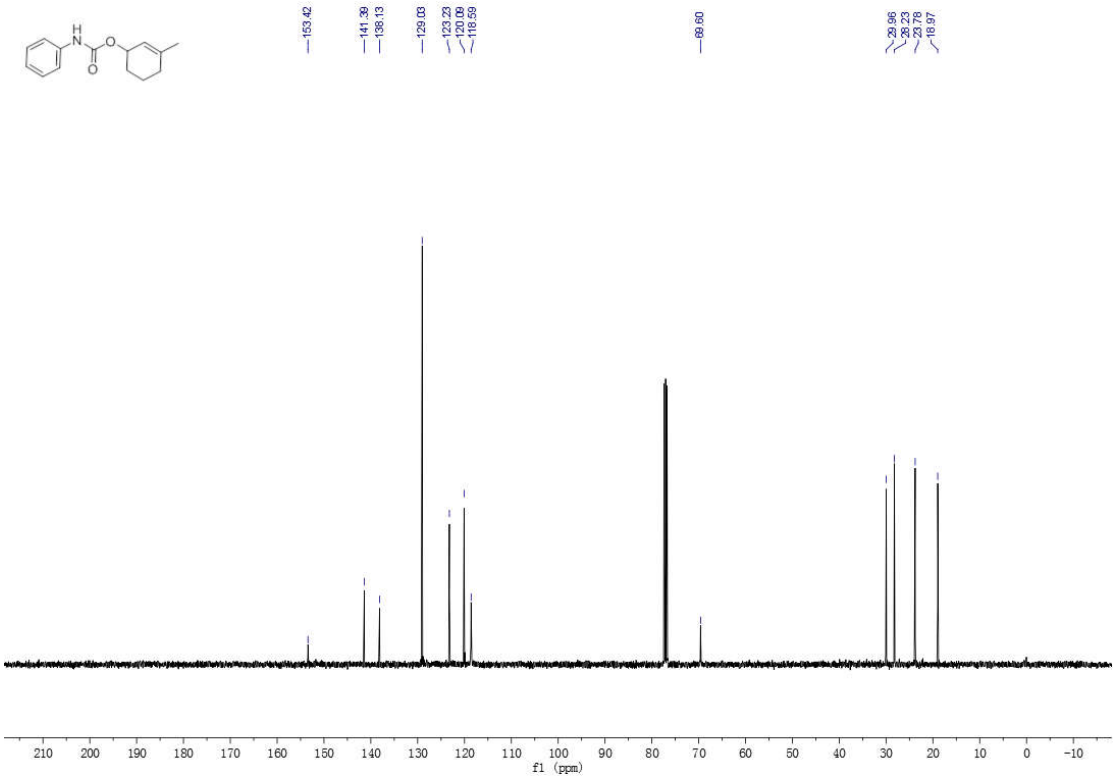
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1h



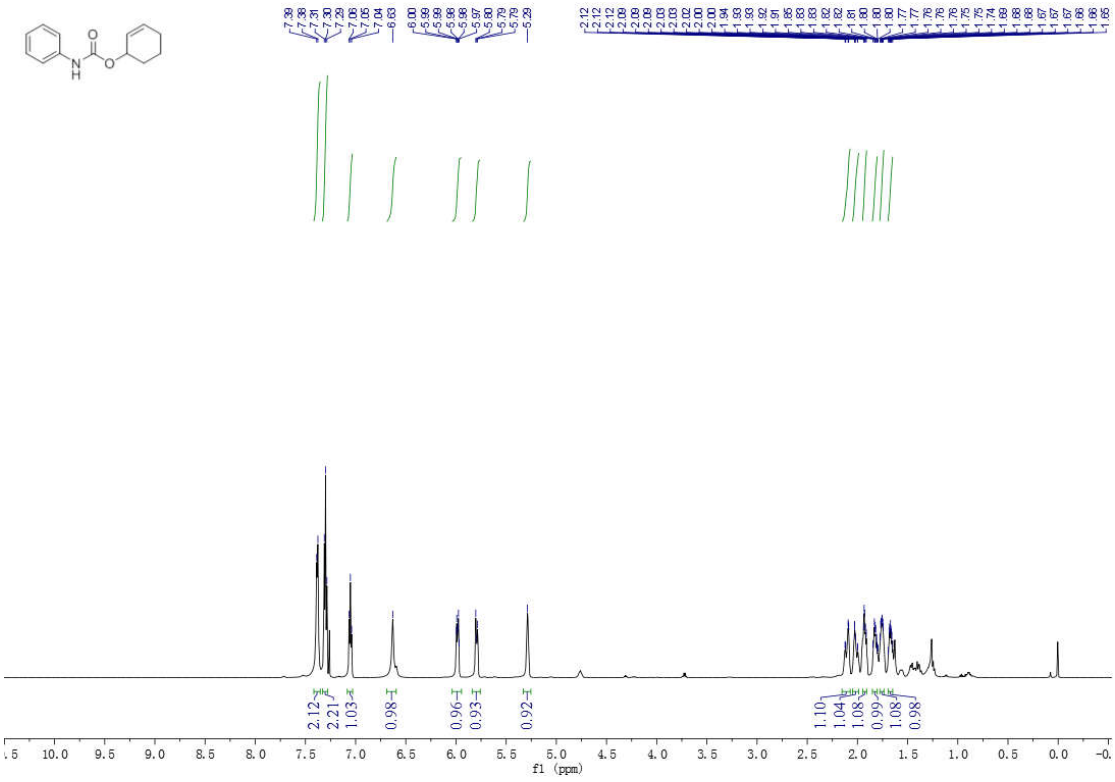
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1i



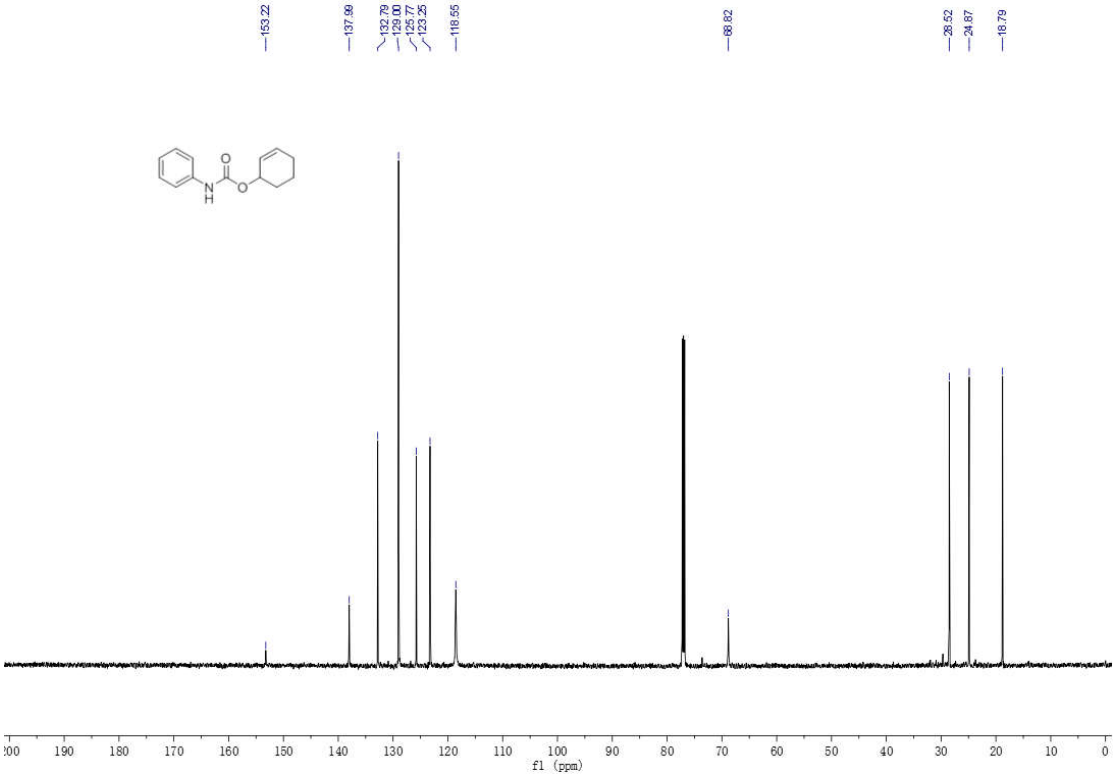
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1i



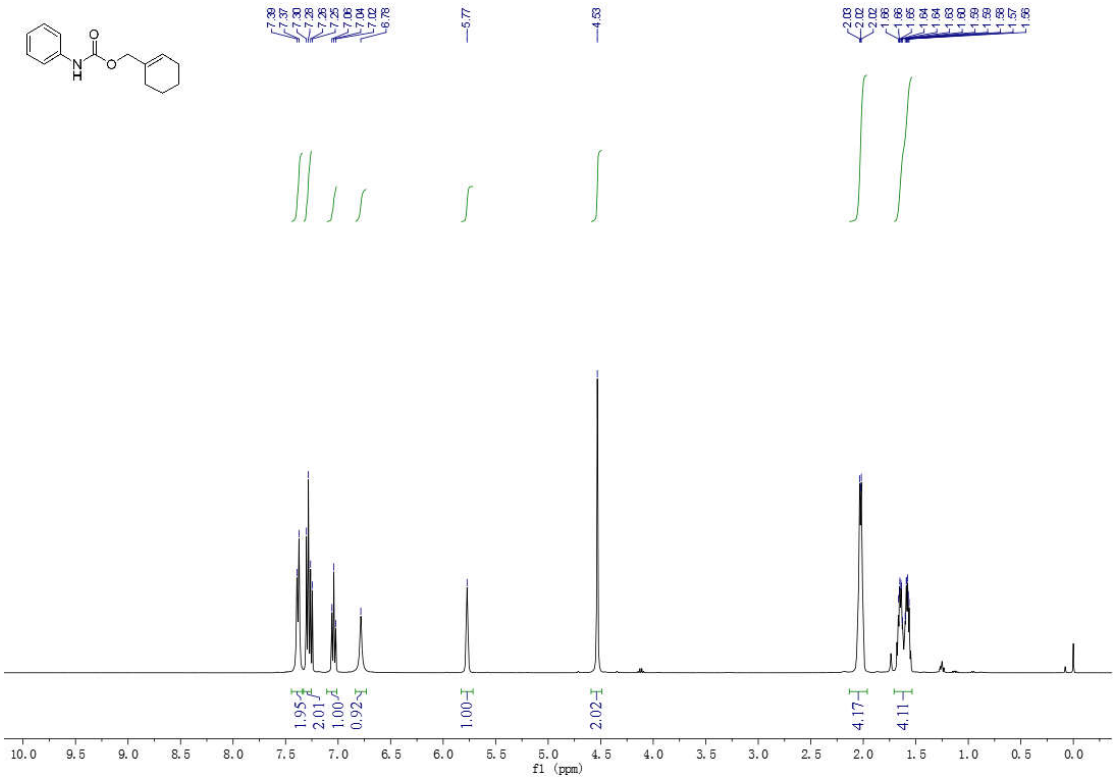
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1j



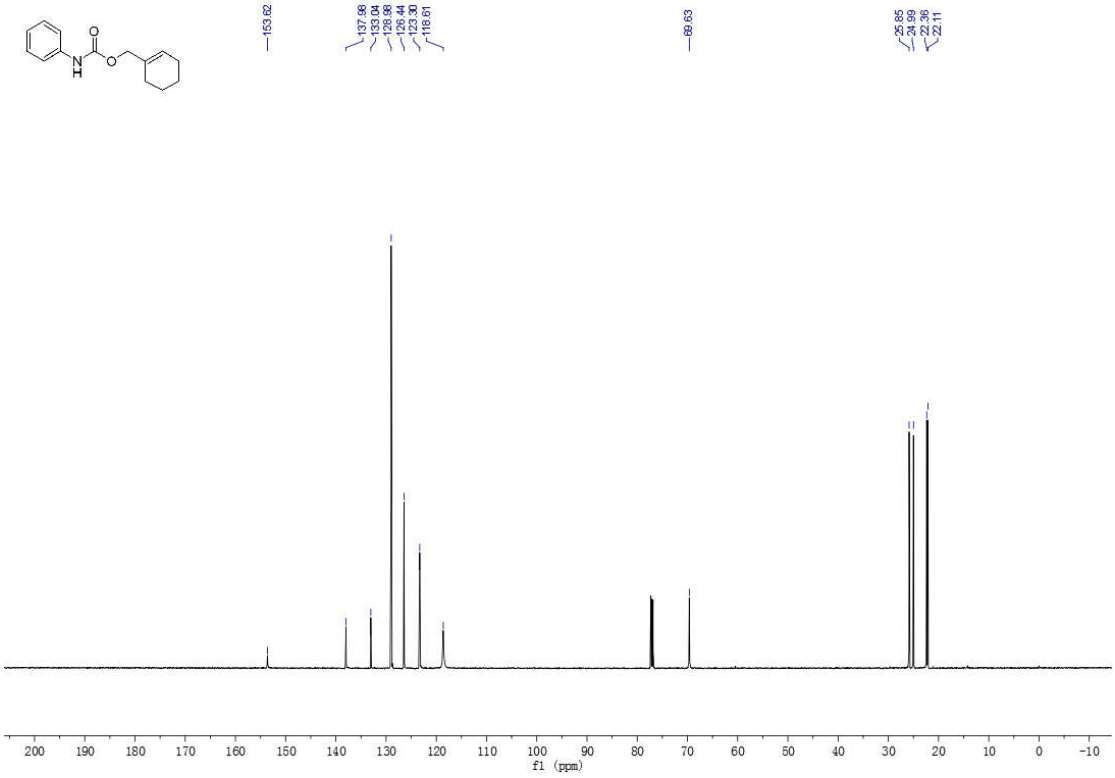
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1j



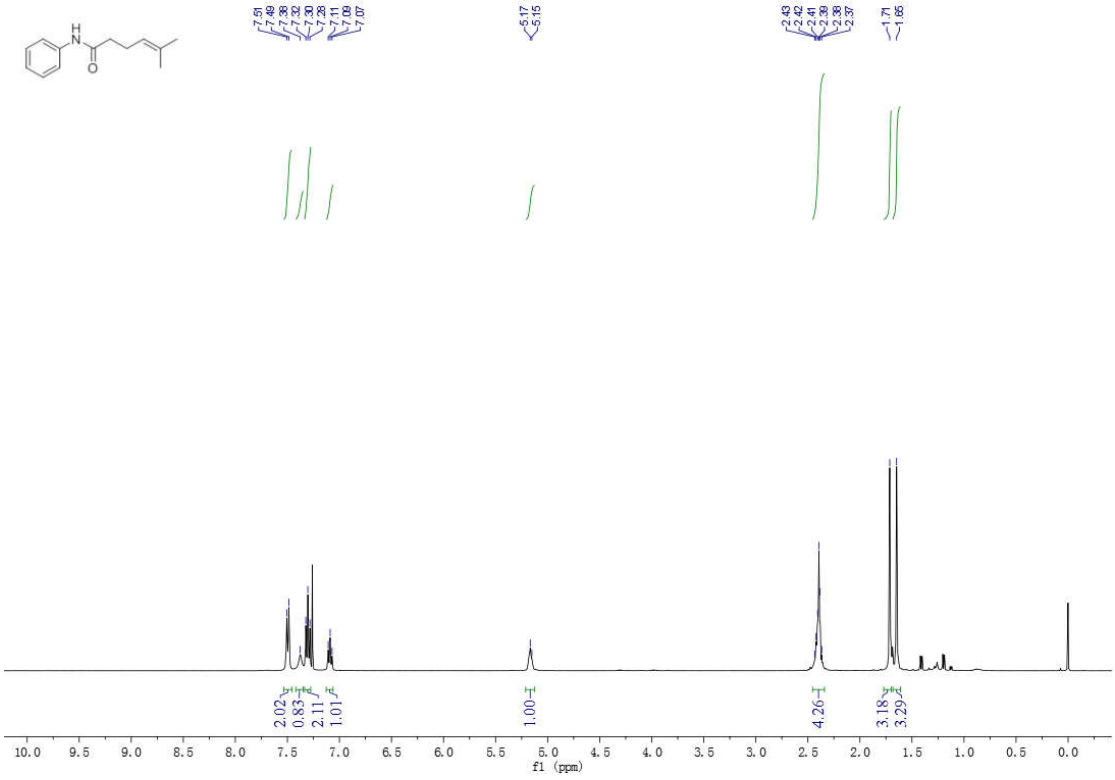
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1k



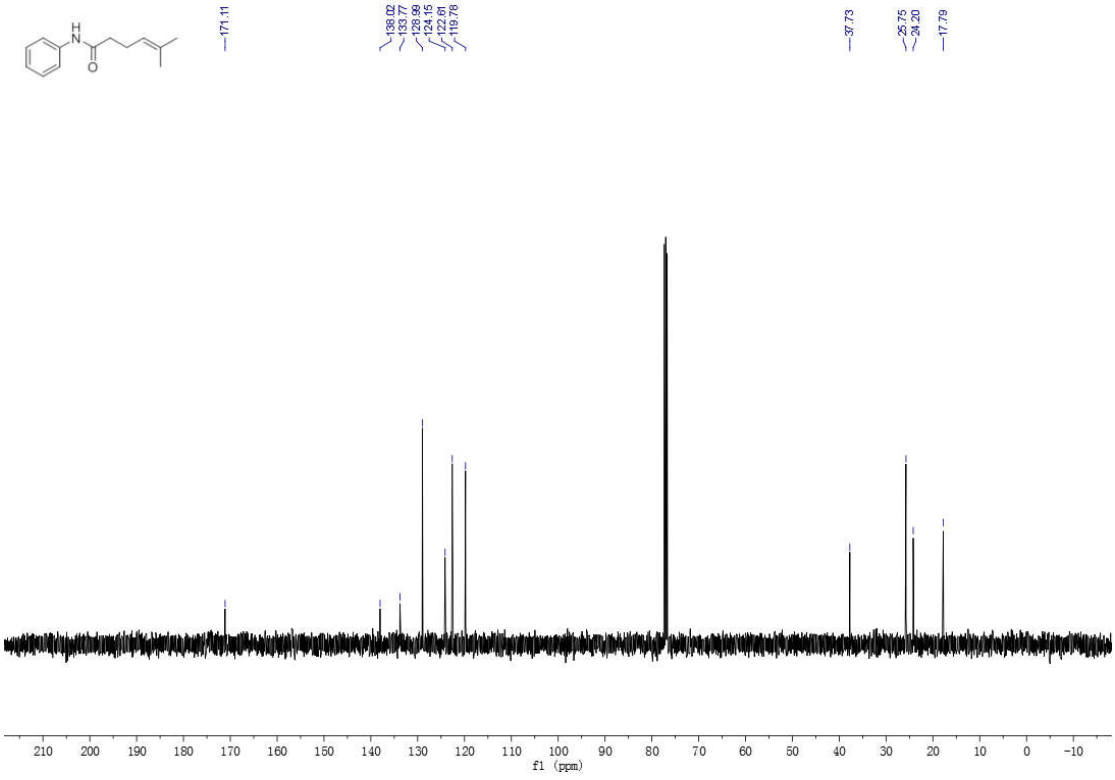
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1k



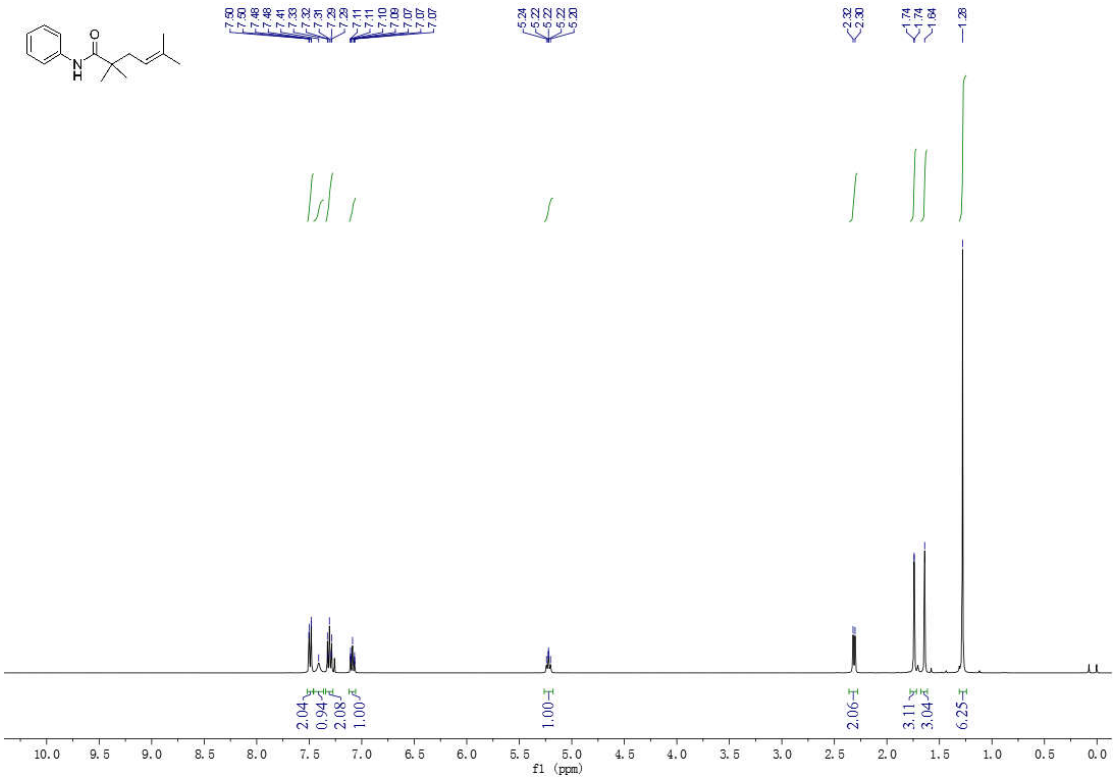
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1l



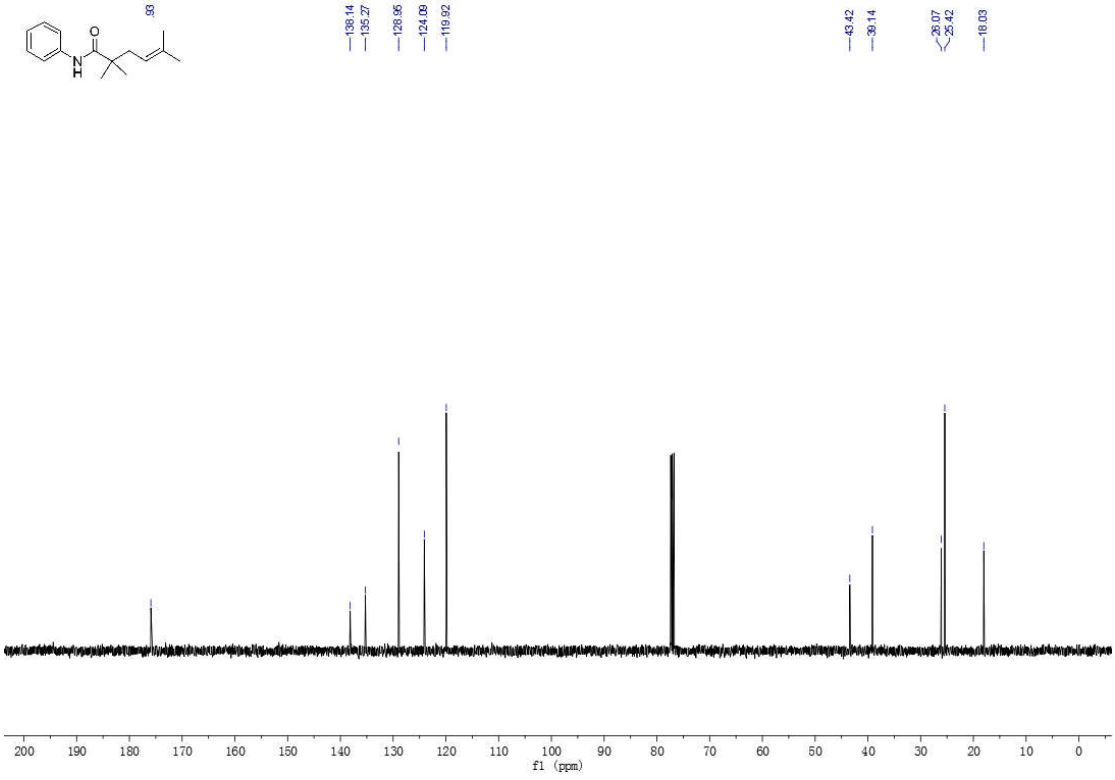
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1l



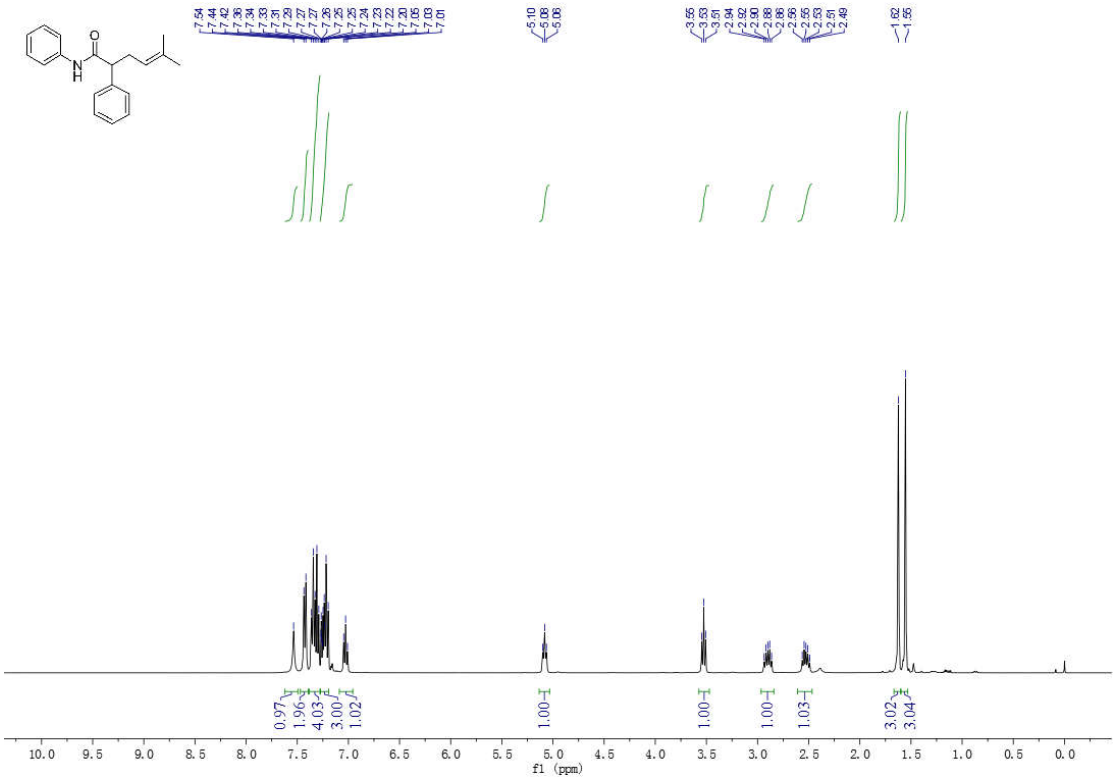
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1m



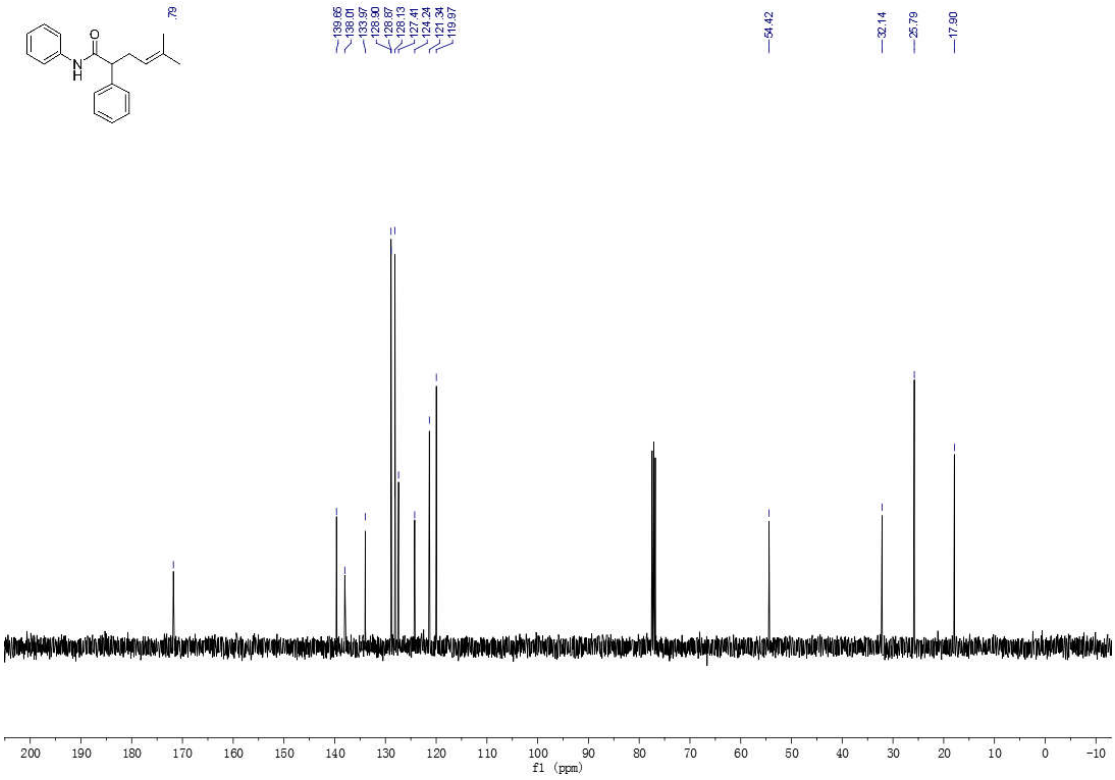
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1m



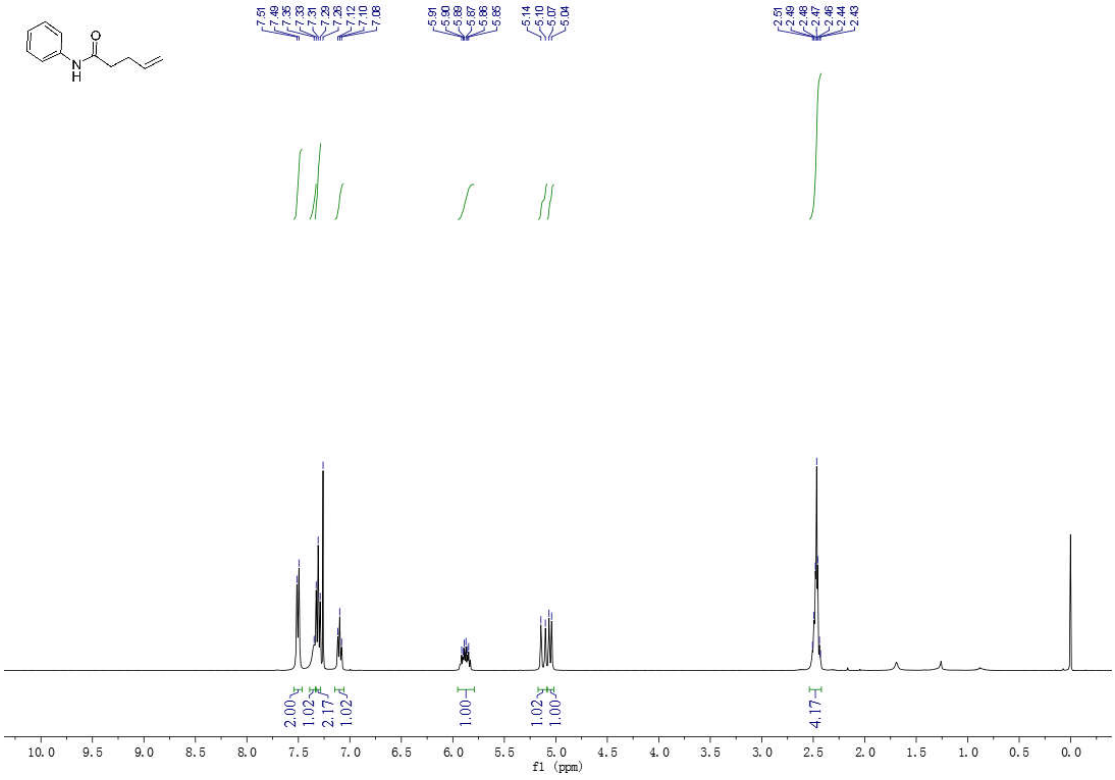
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1n



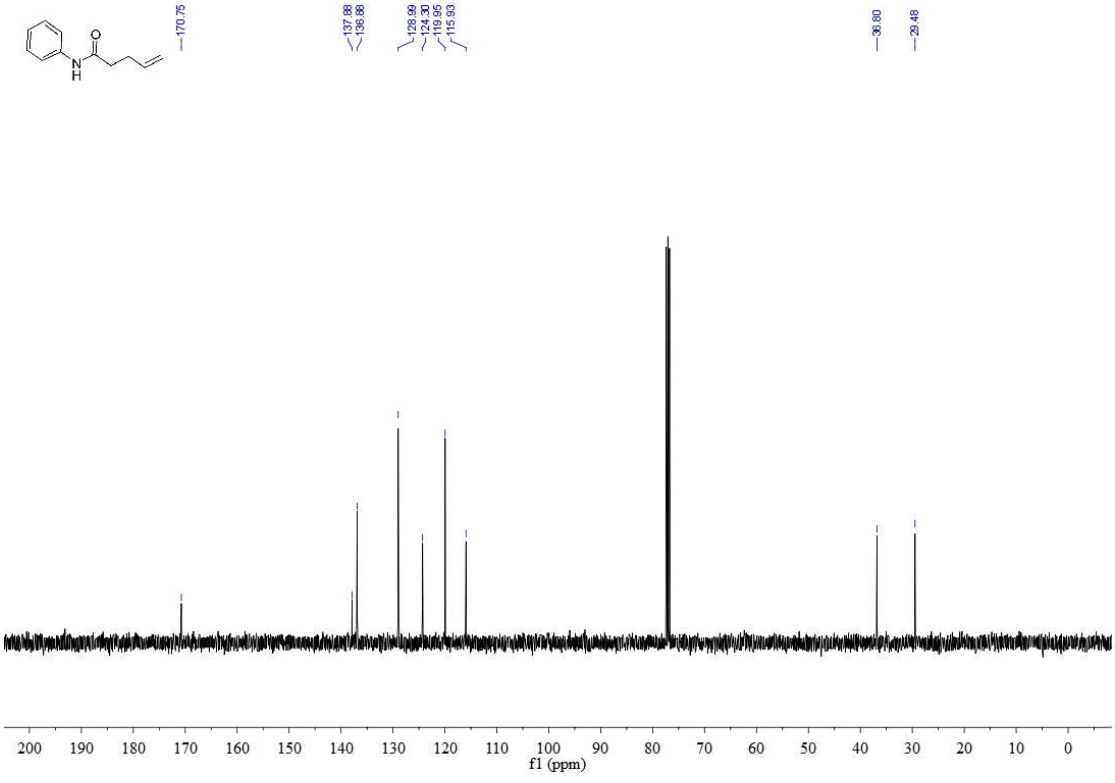
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1n



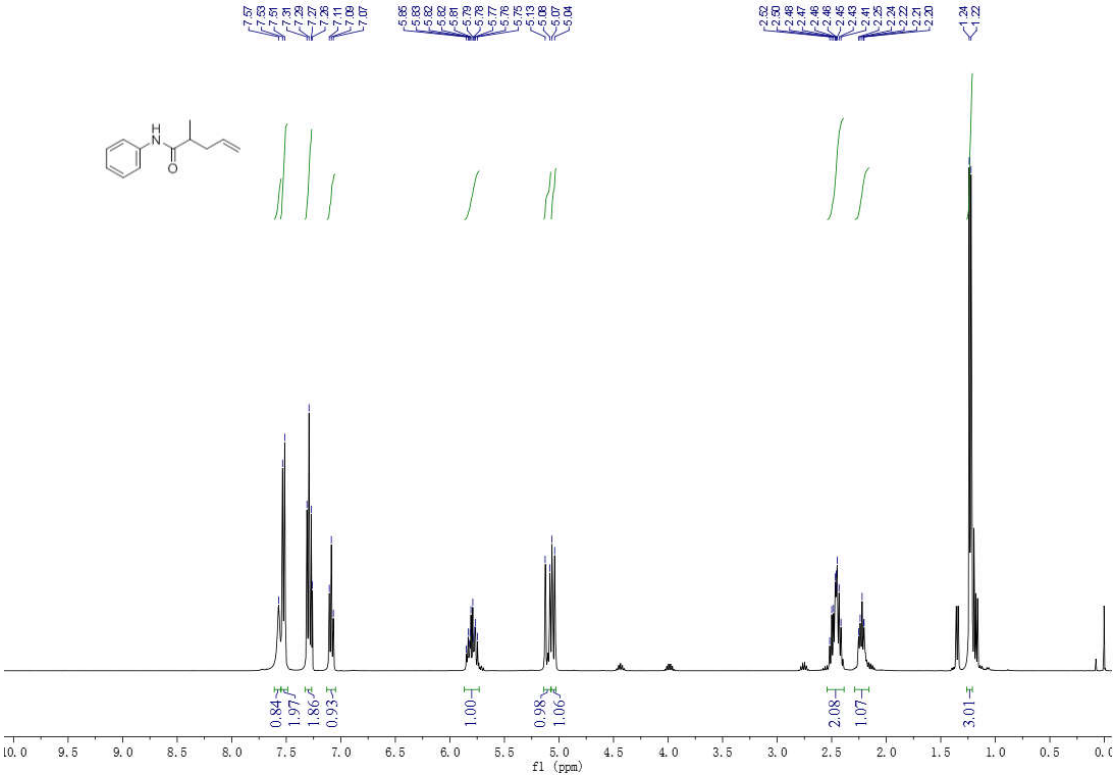
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1o



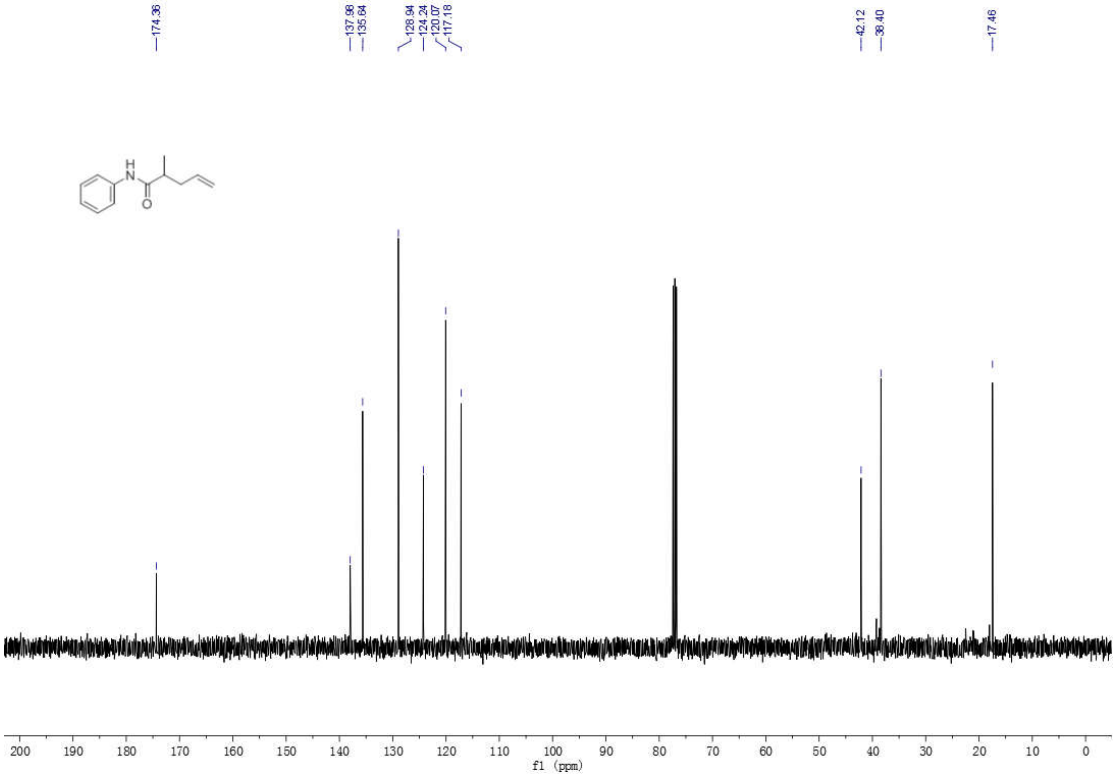
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1o



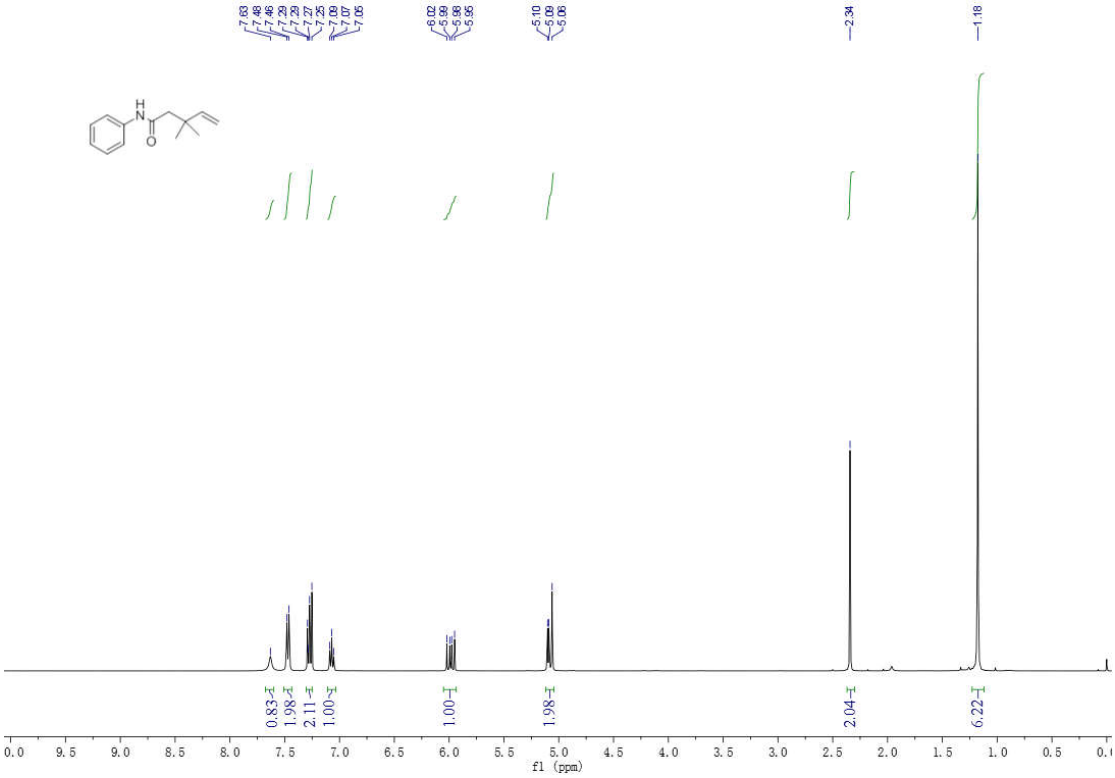
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 1p



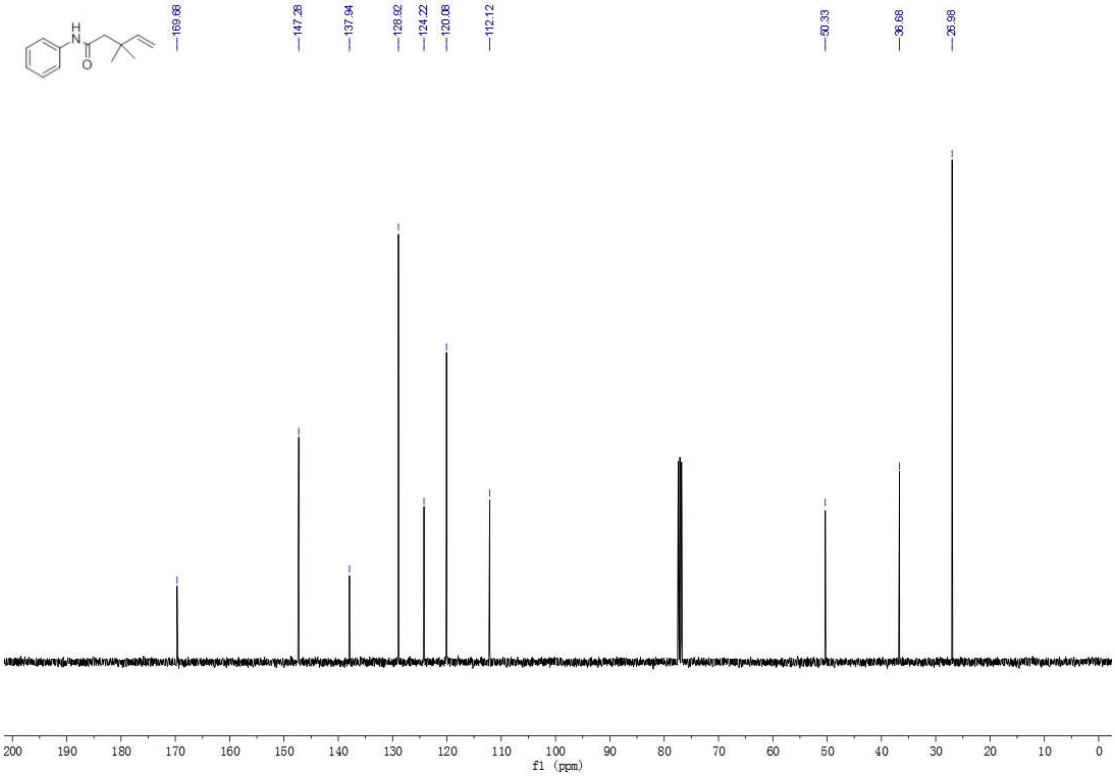
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1p



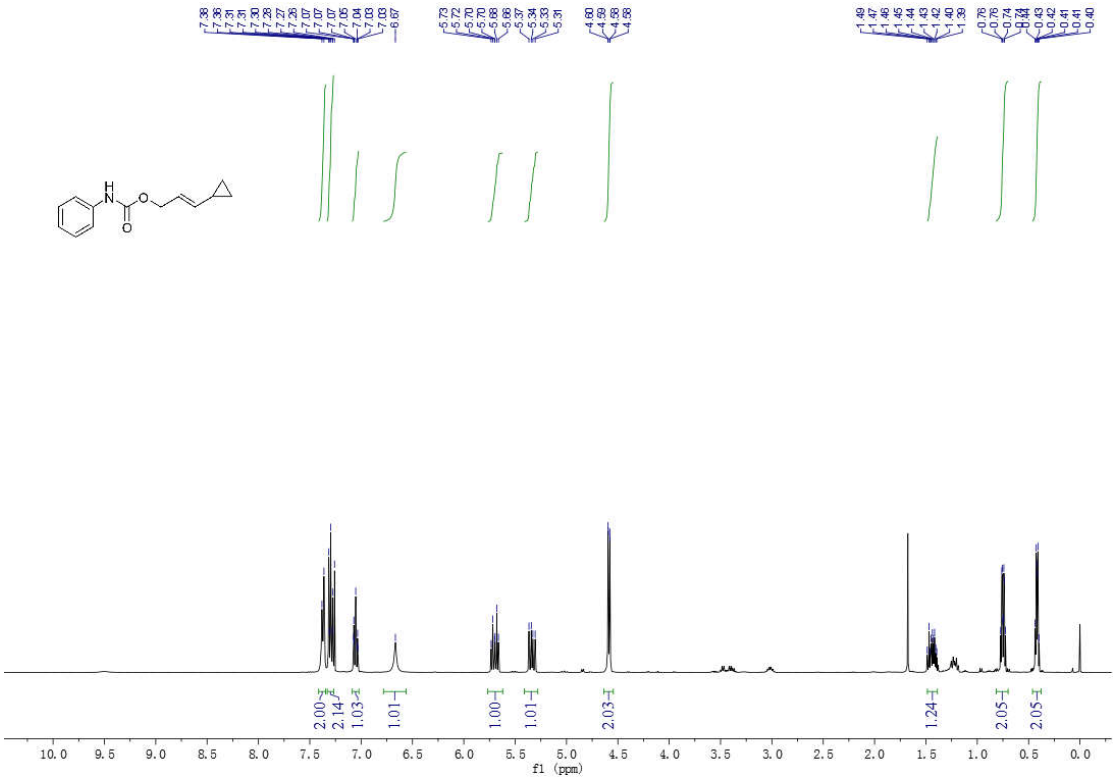
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1q



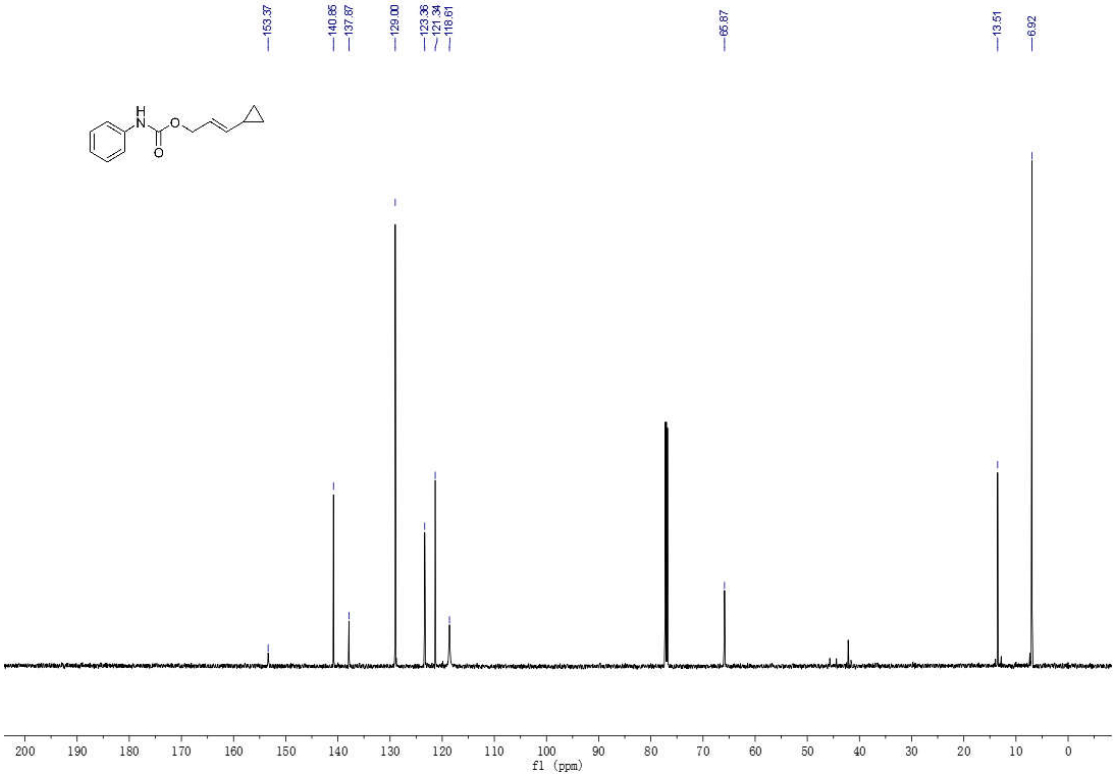
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 1q



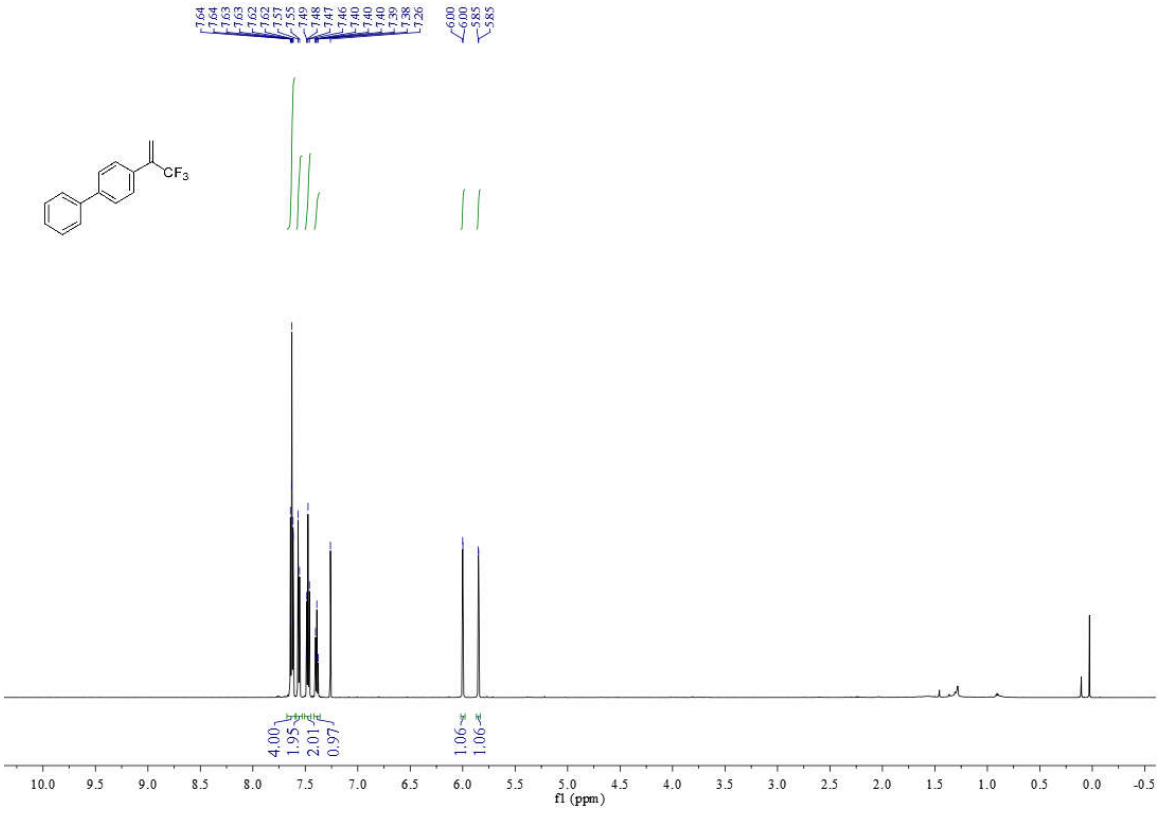
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 1r



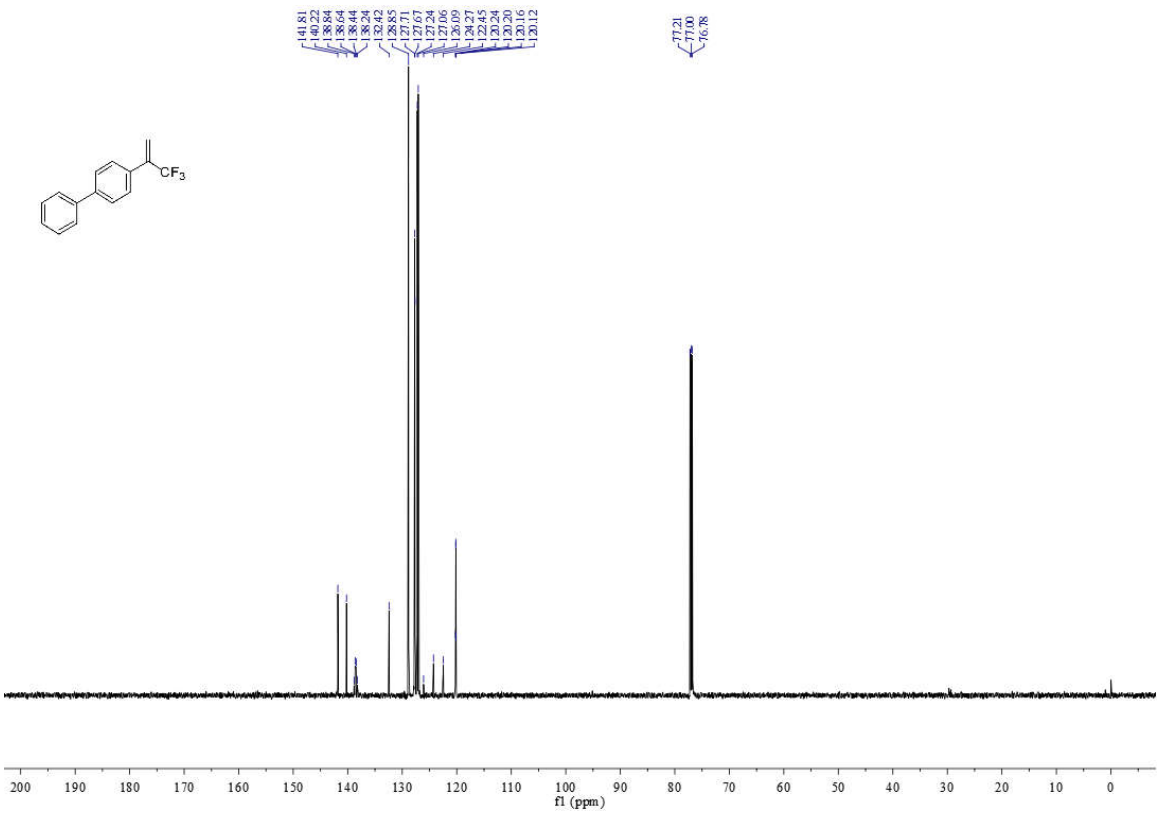
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 1r



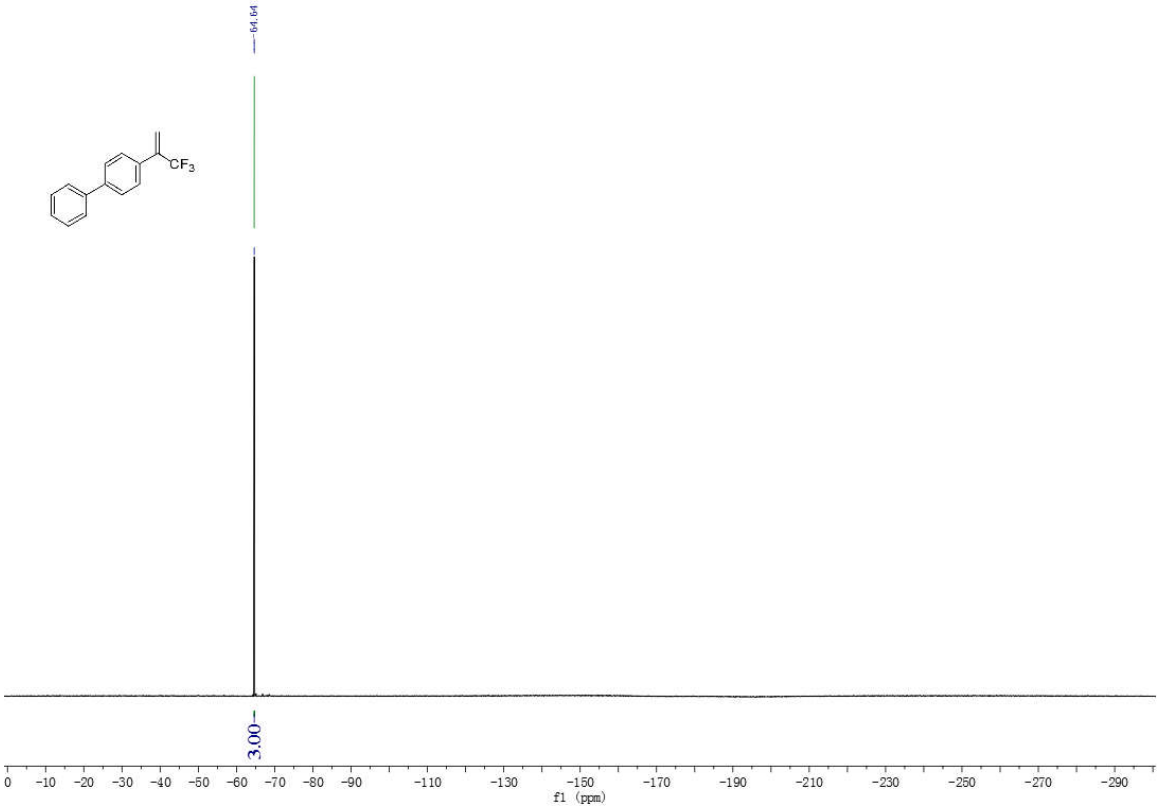
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 2a



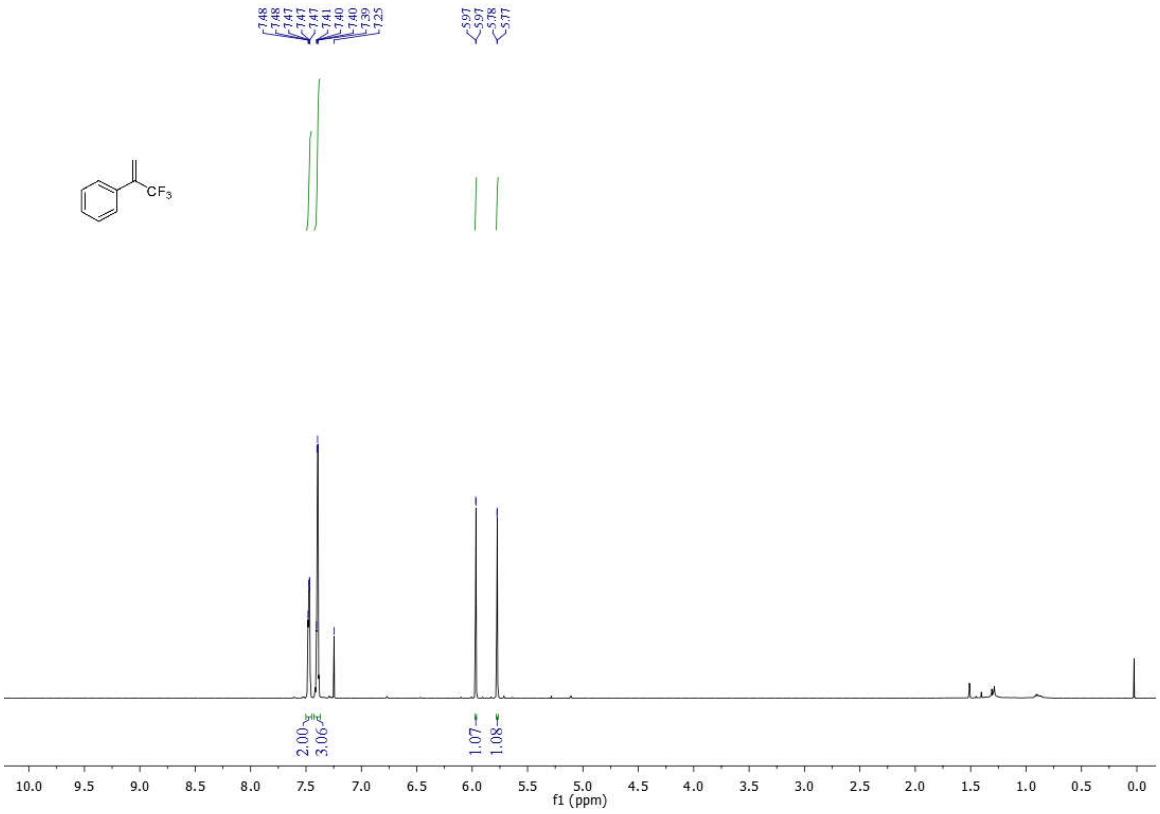
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 2a



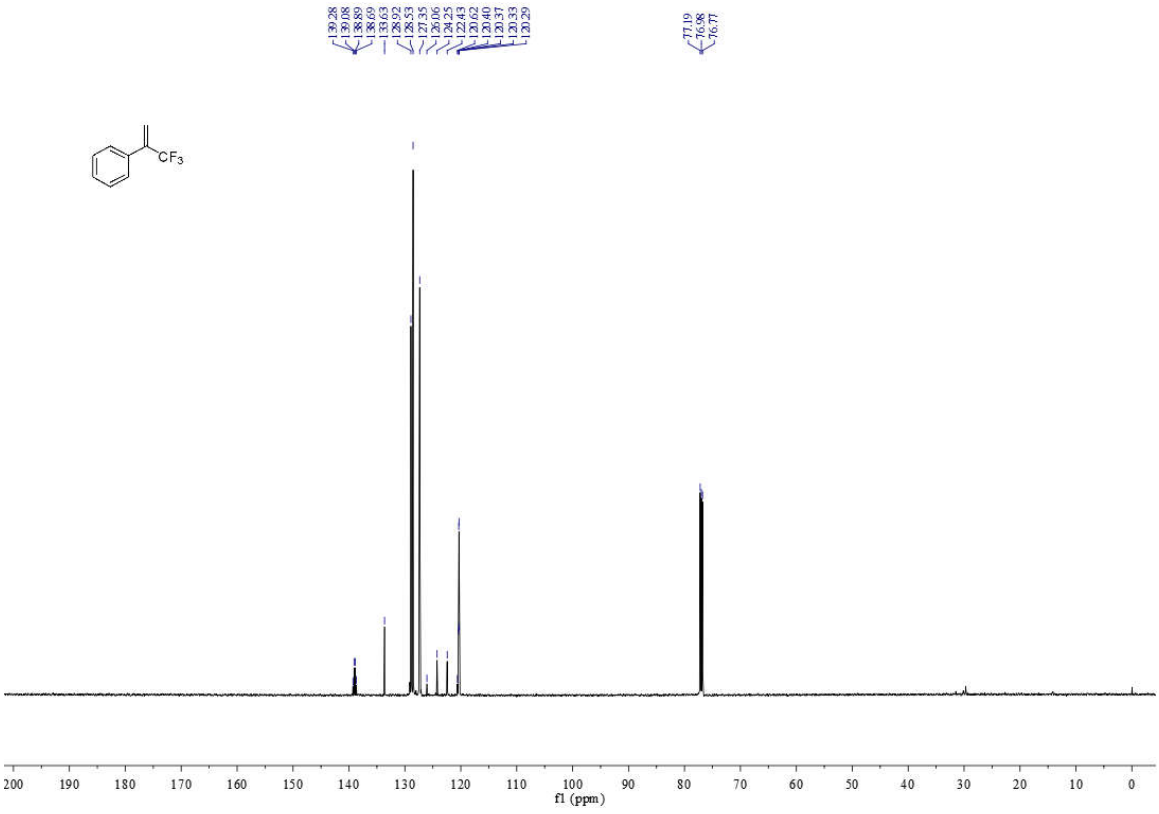
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 °C) of 2a



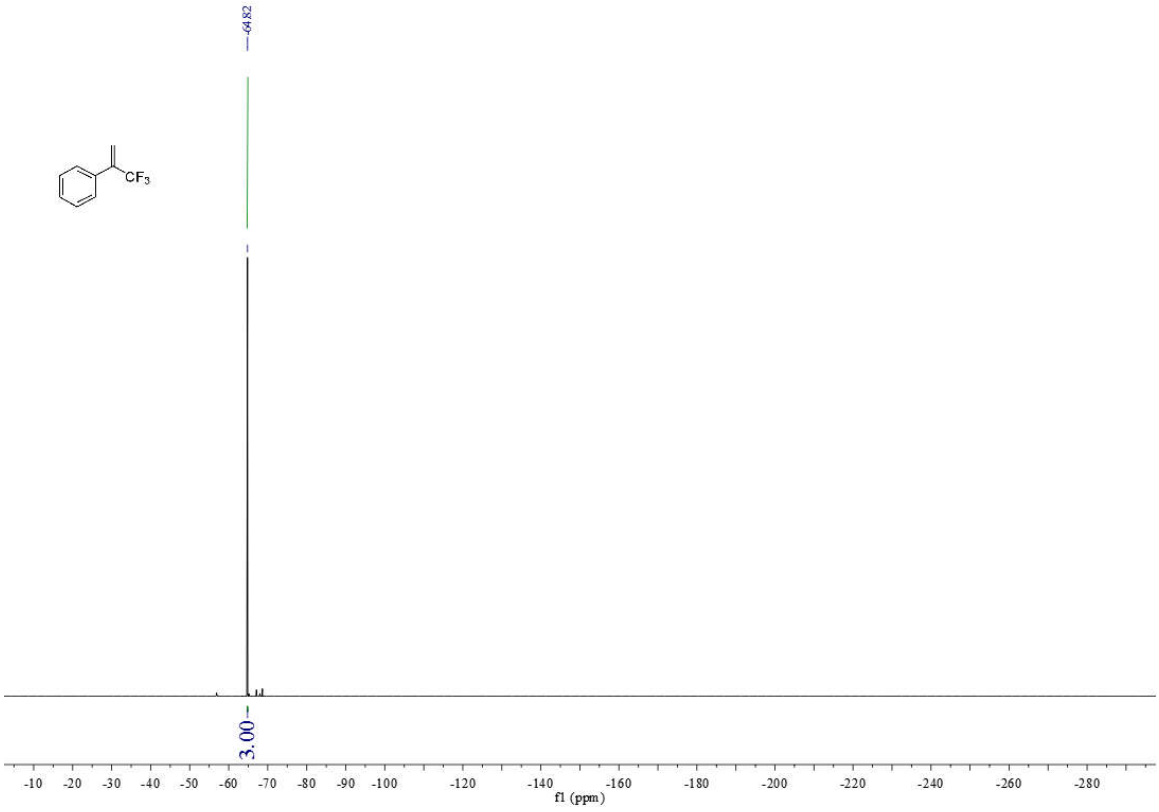
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 2b



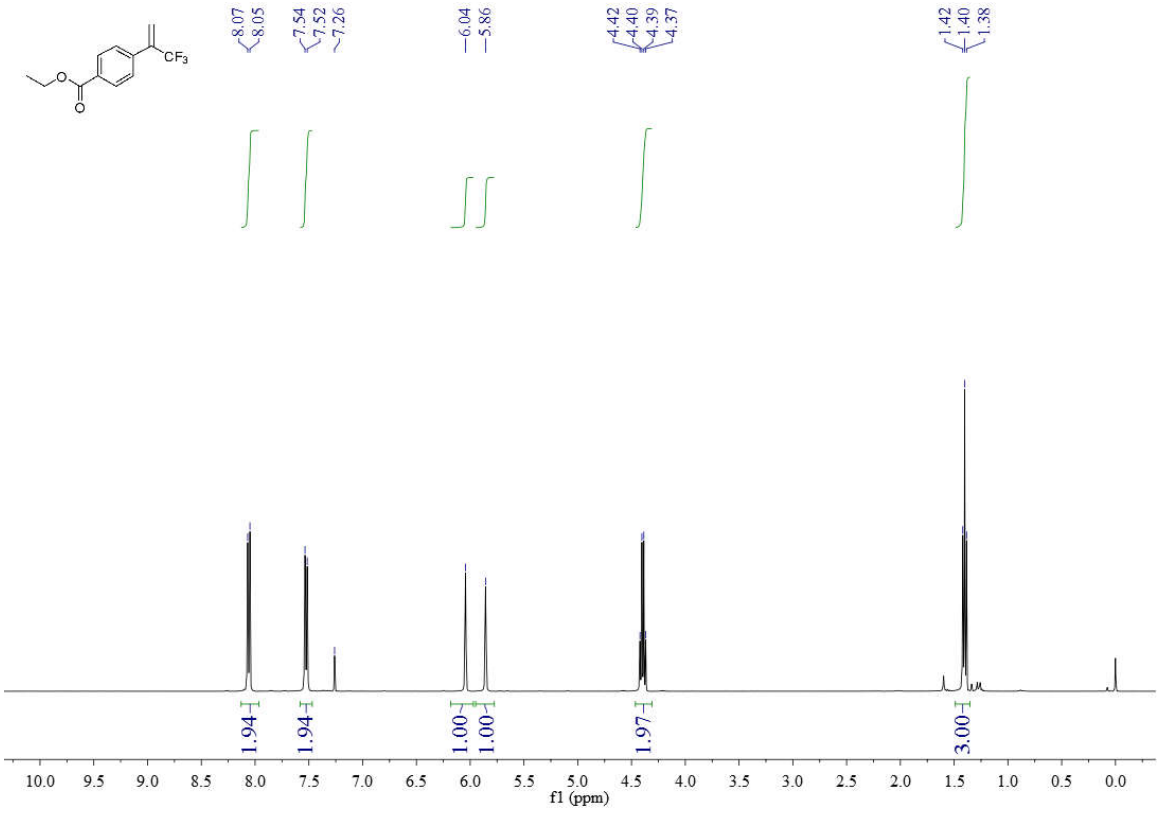
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 2b



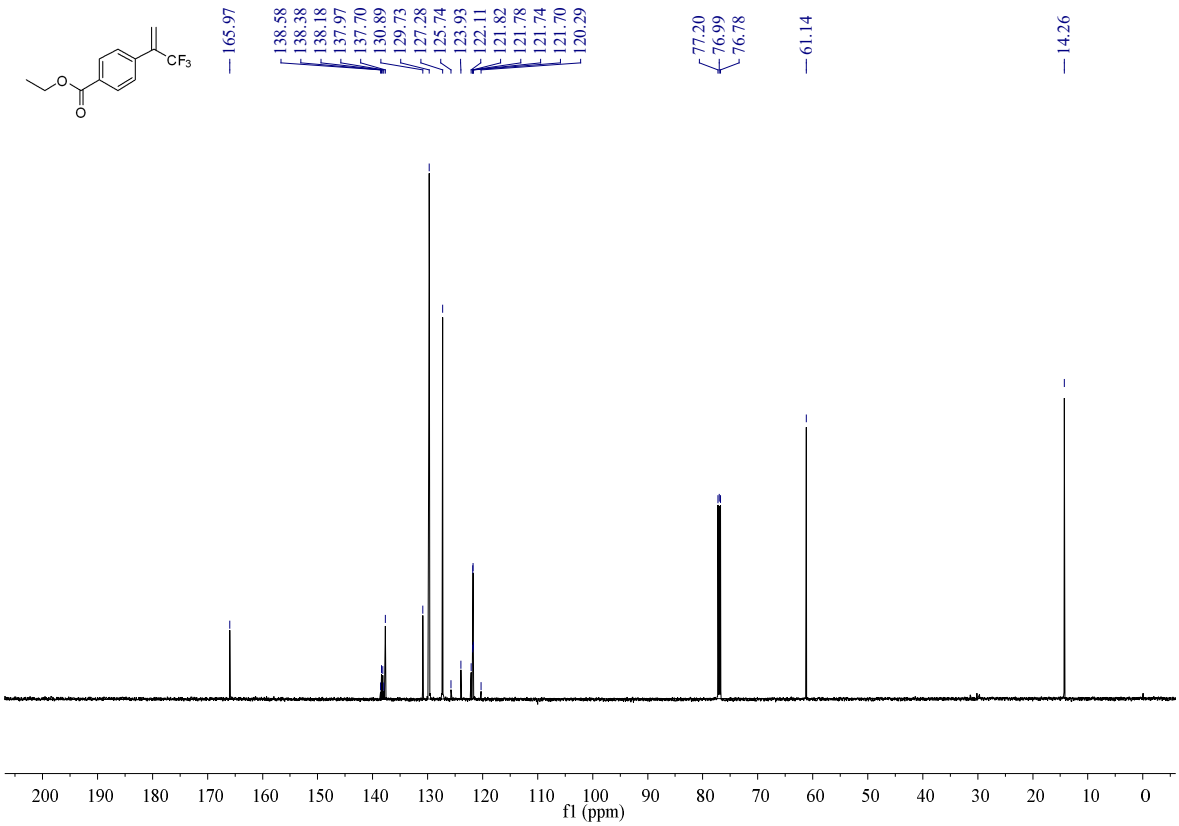
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 23 ºC) of 2b



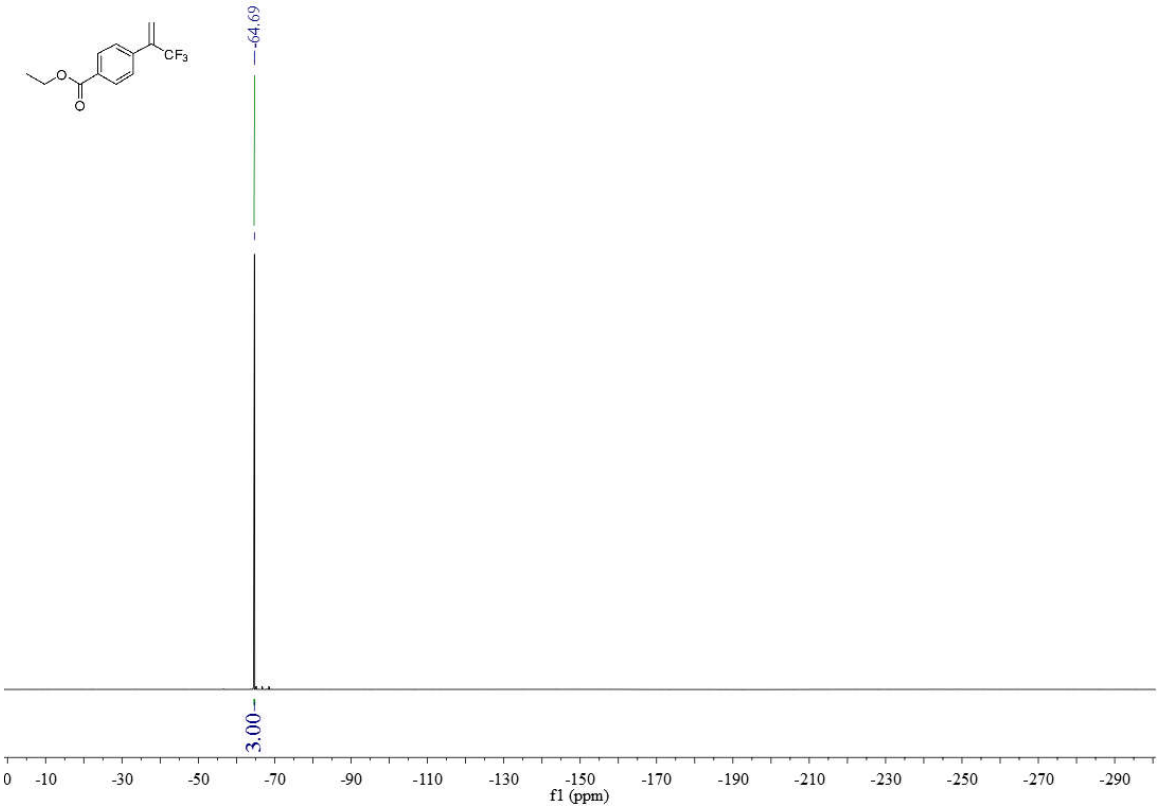
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2c



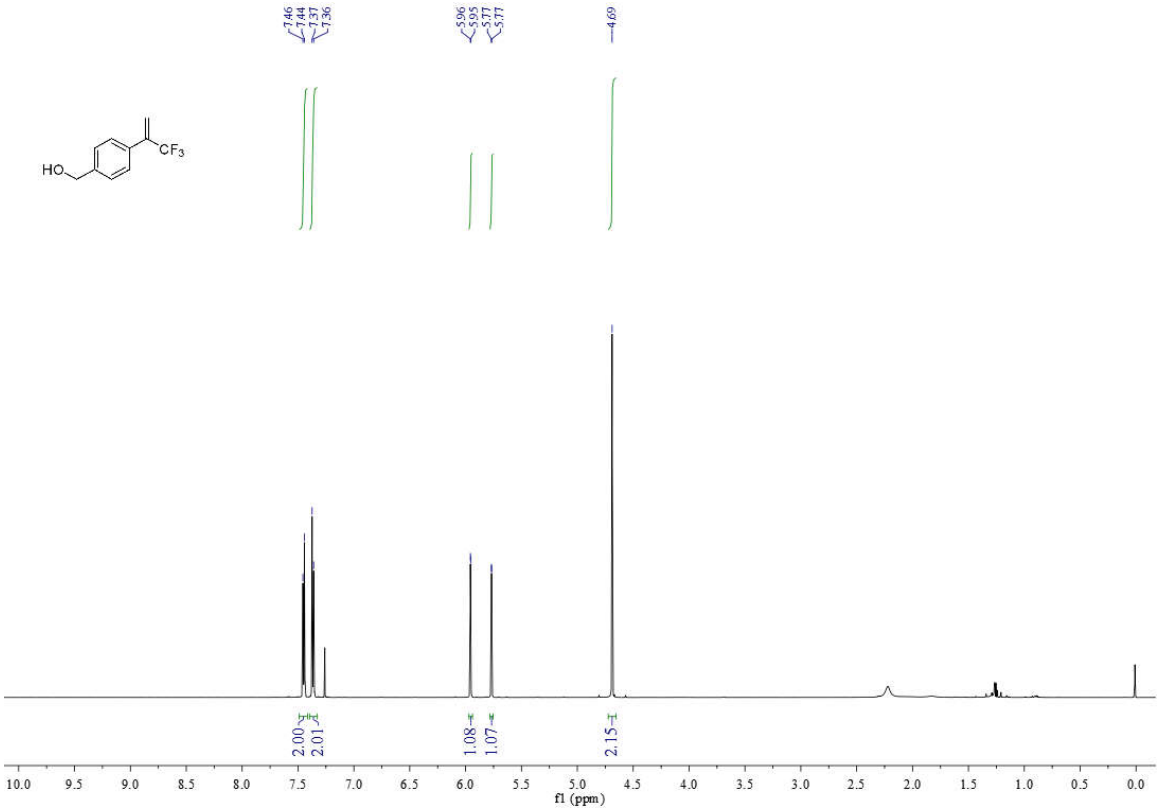
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 2c



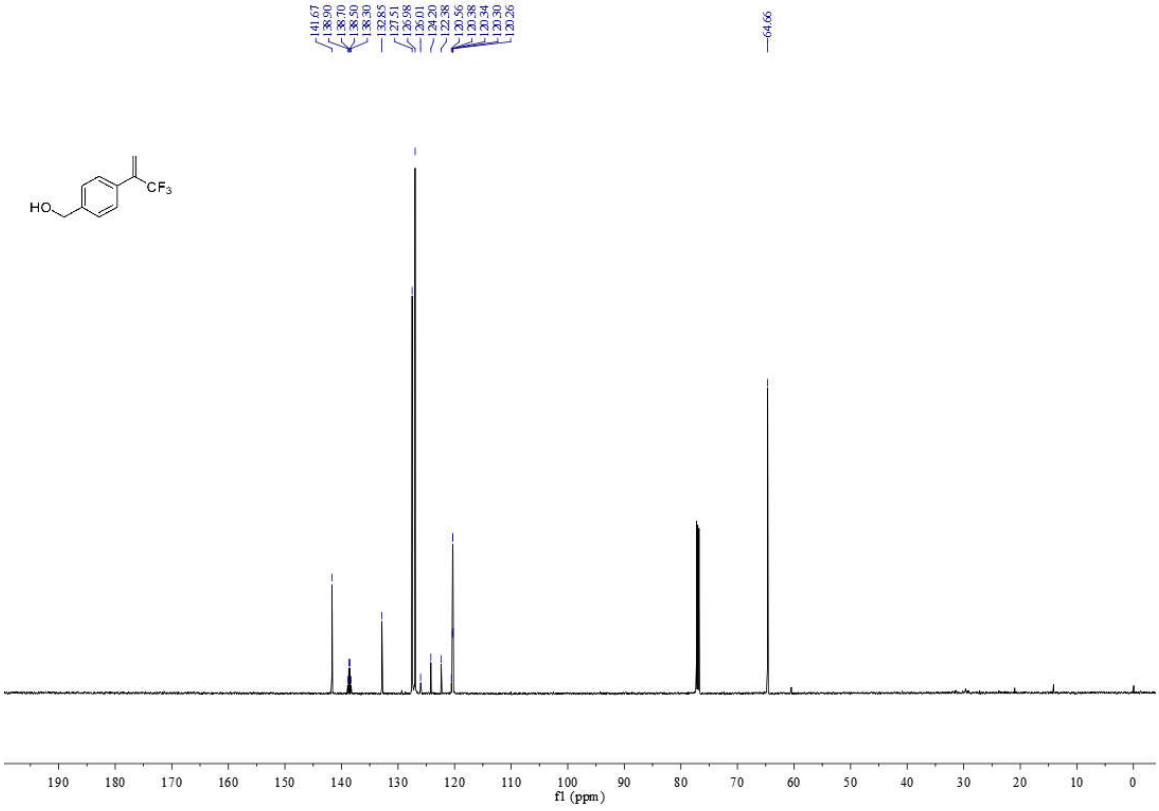
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 23 ºC) of 2c



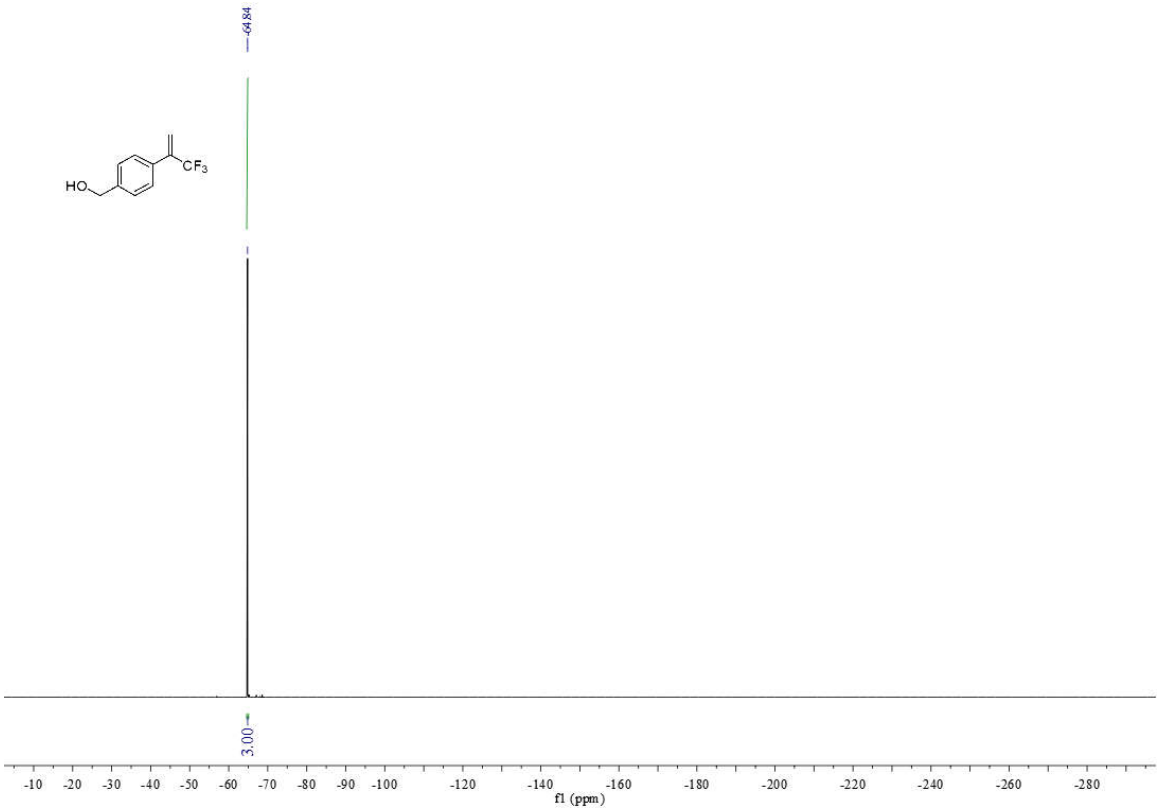
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 2d



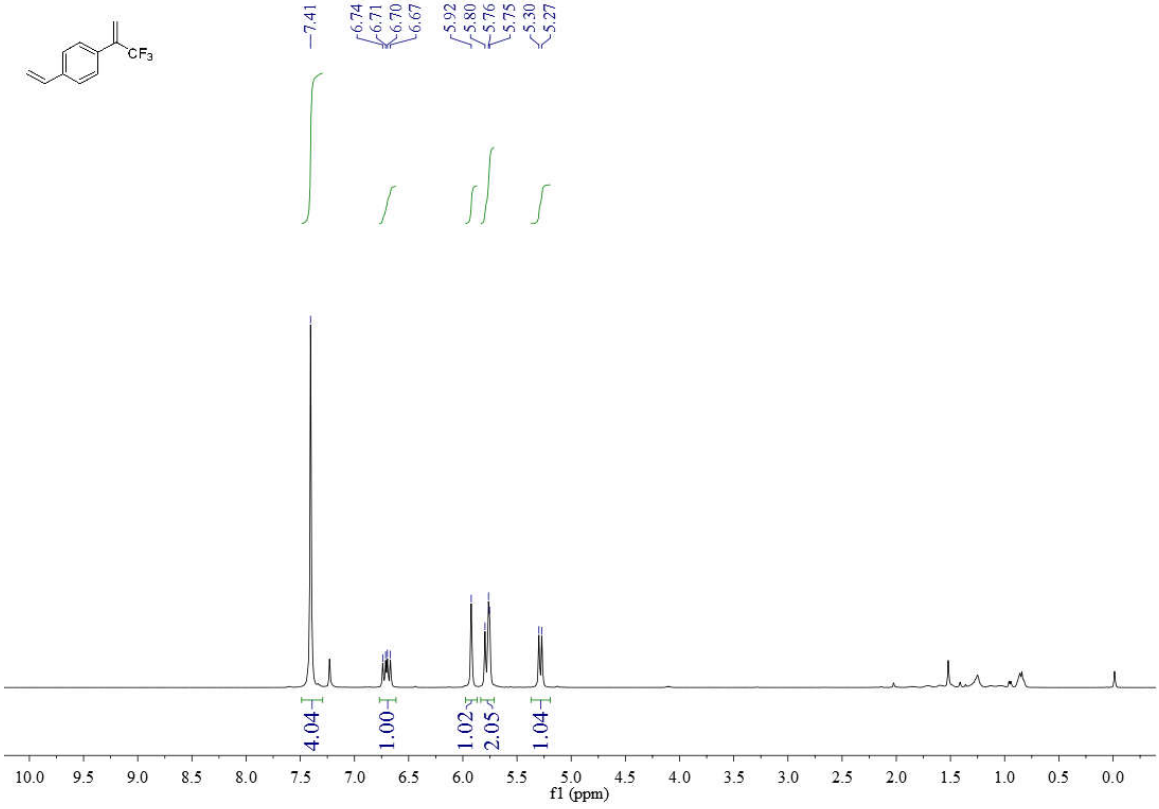
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 2d



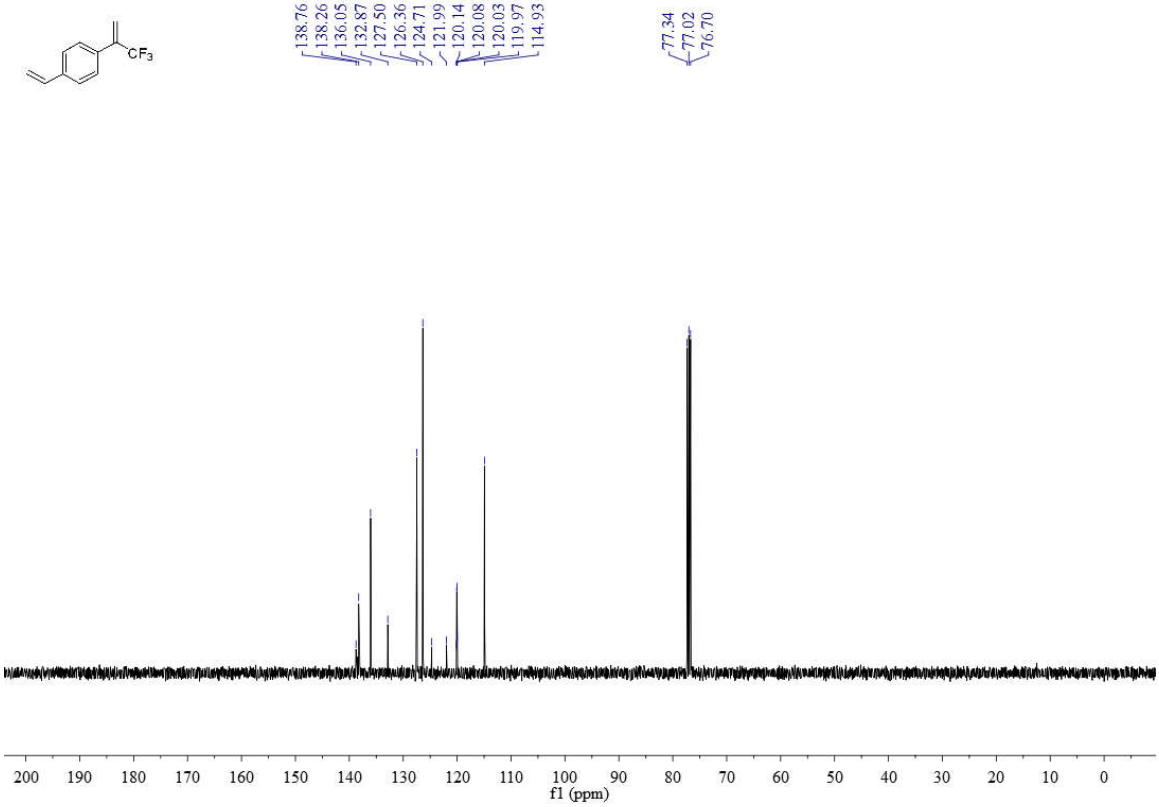
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 23 ºC) of 2d



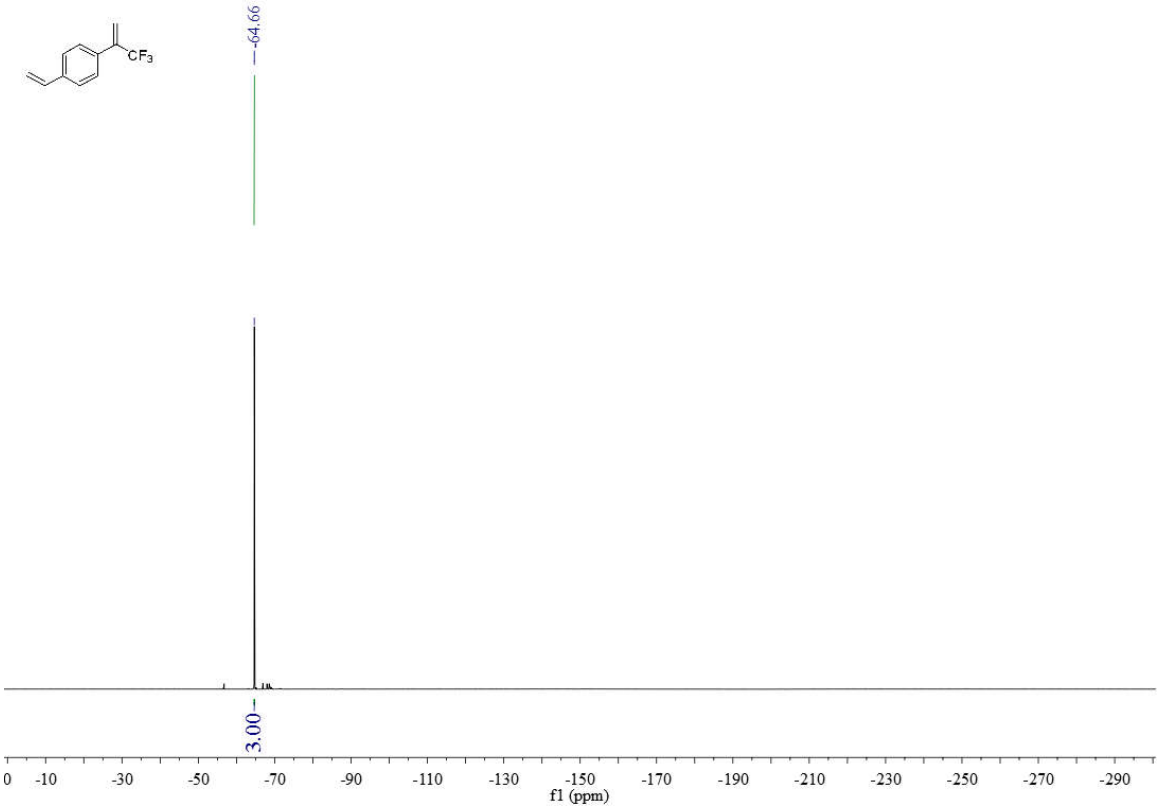
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2e



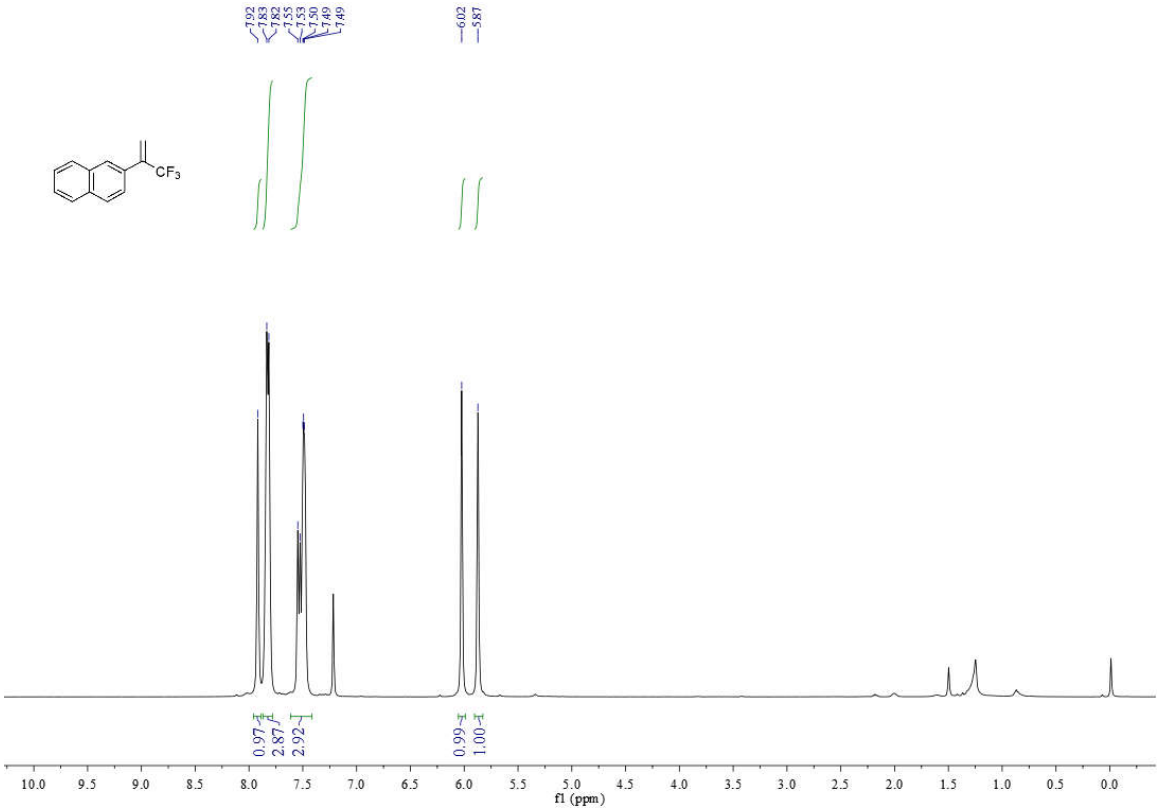
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 2e



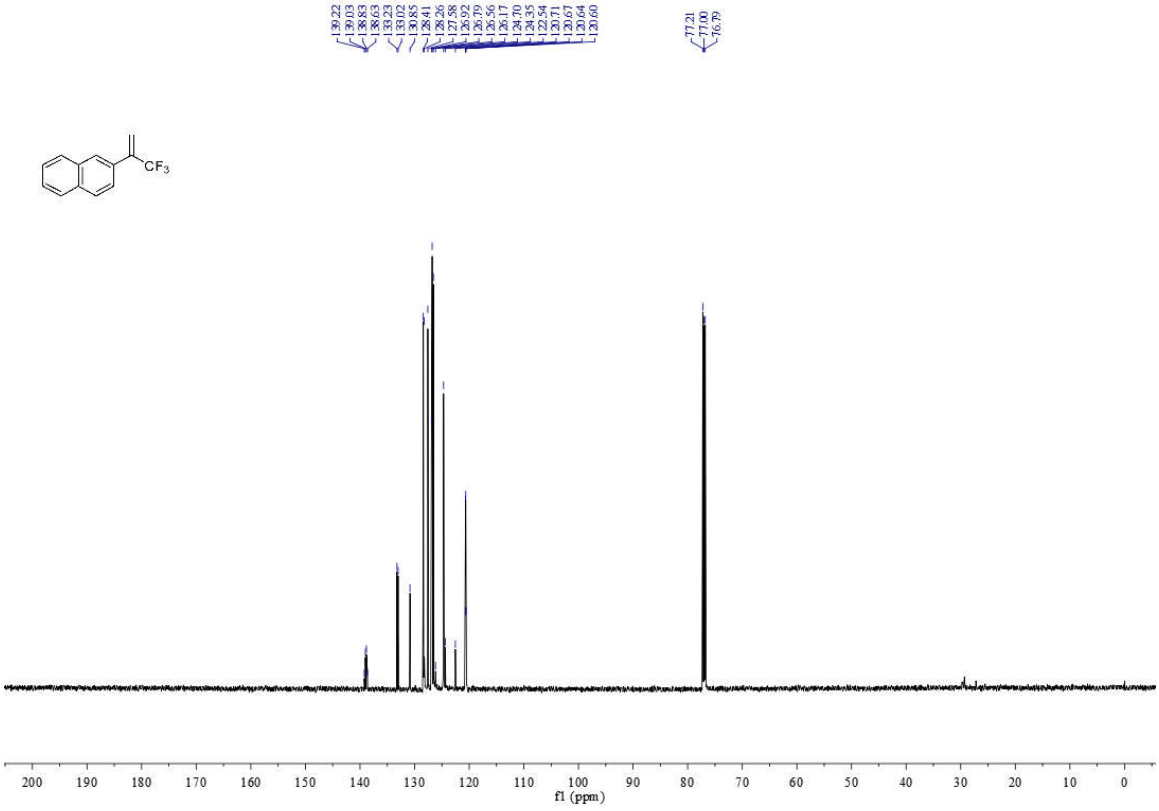
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 °C) of 2e



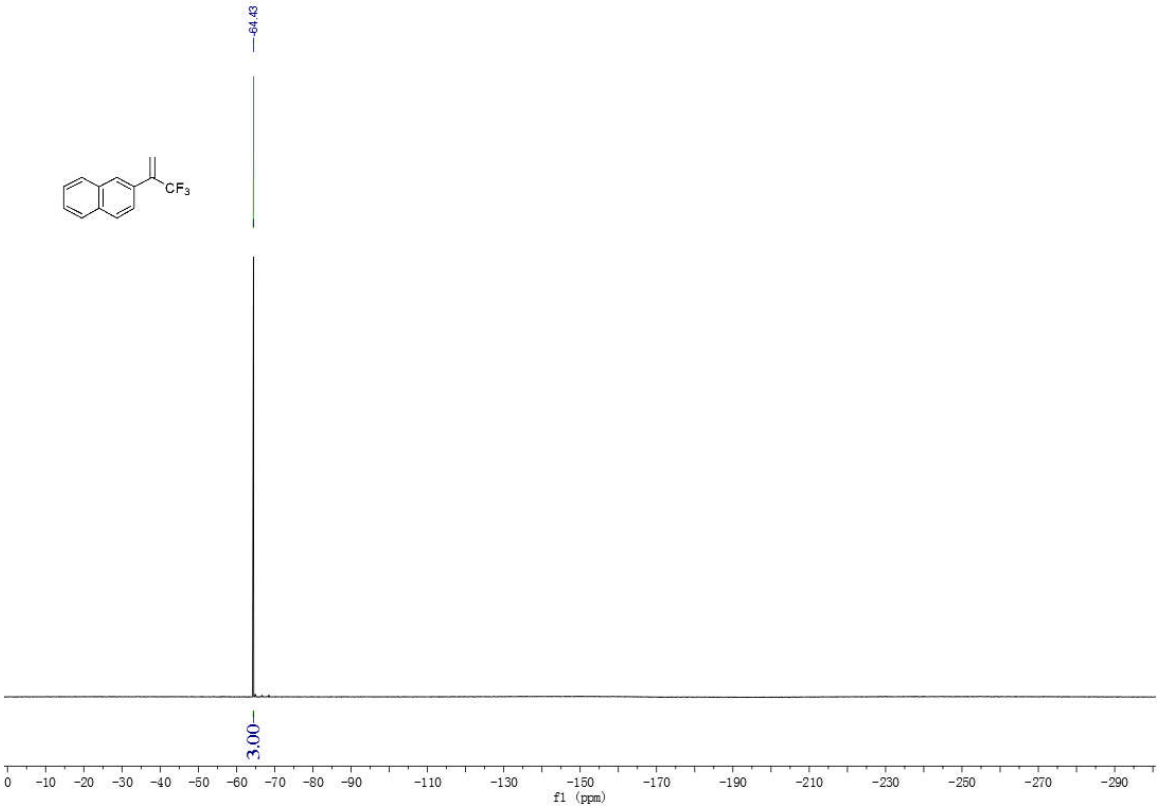
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2f



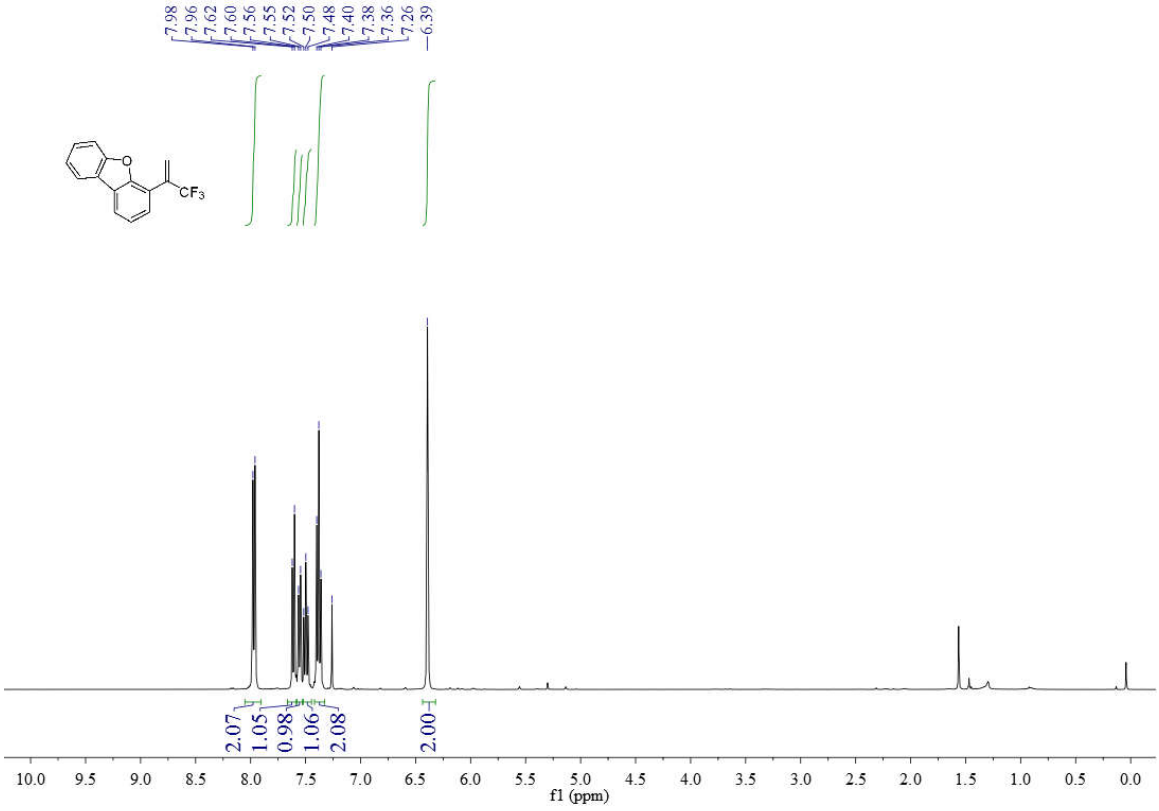
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 2f



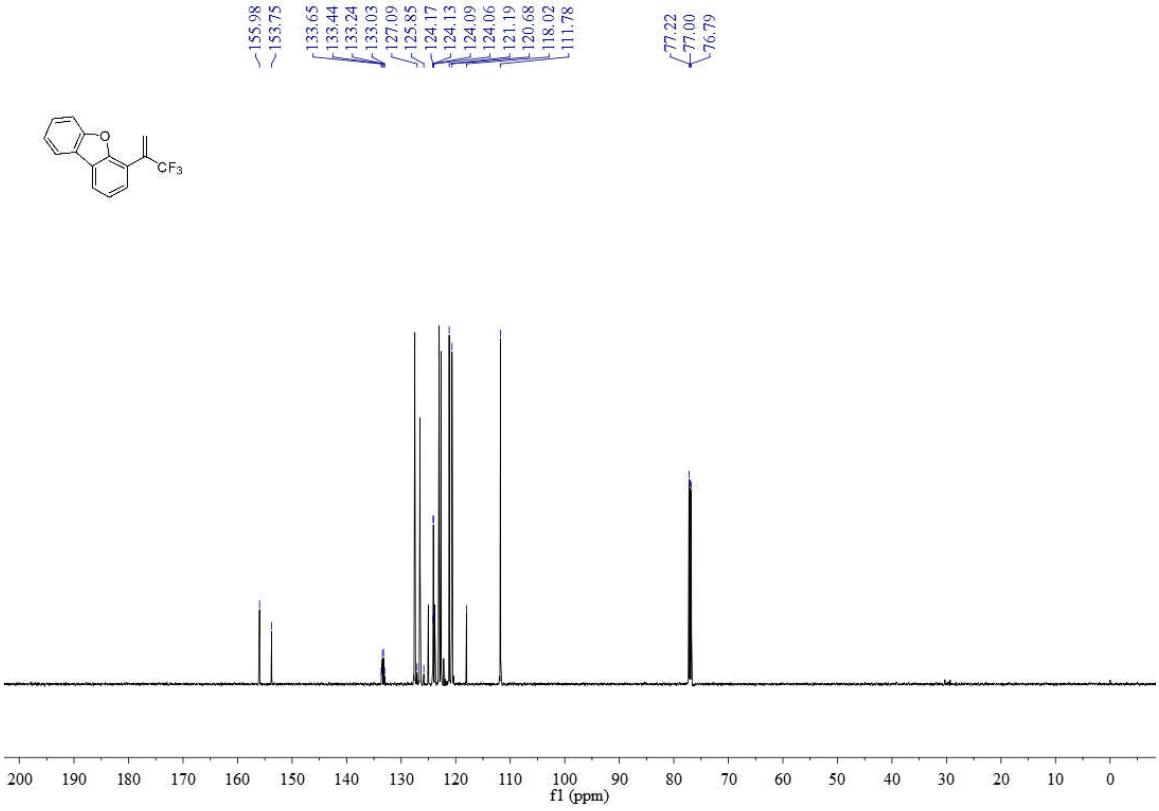
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 ºC) of 2f



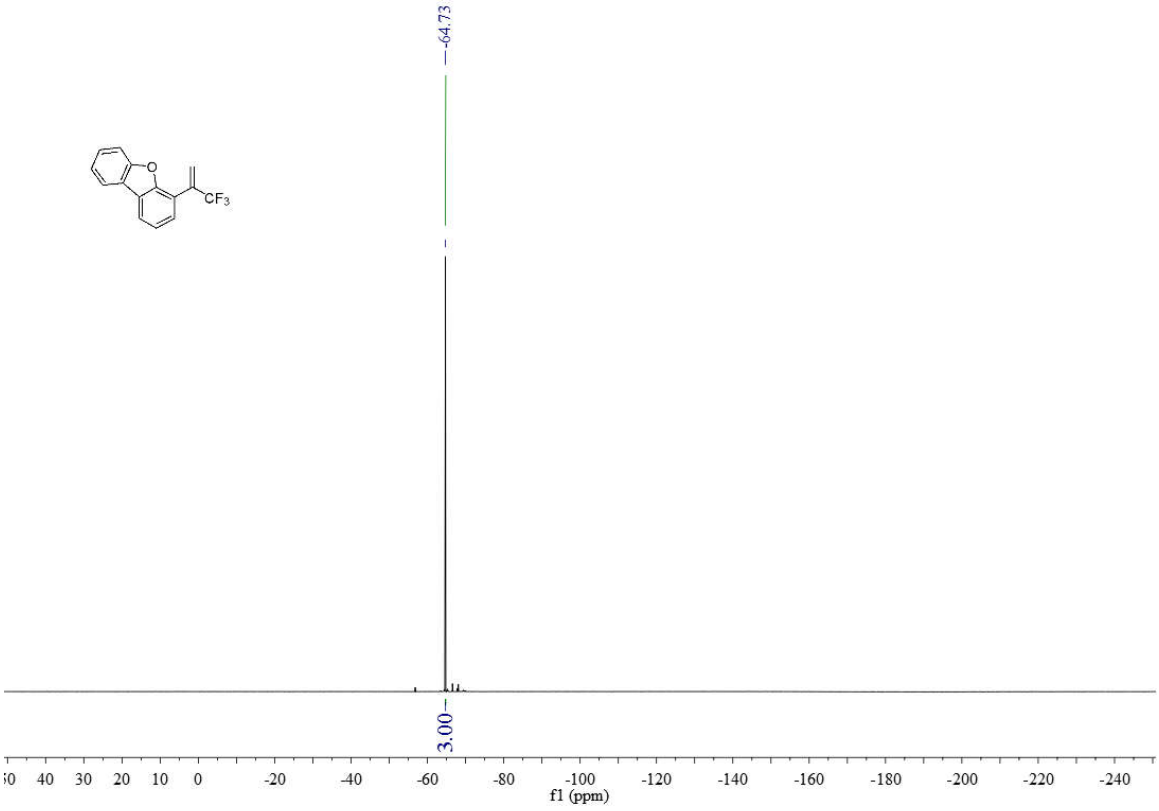
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2g



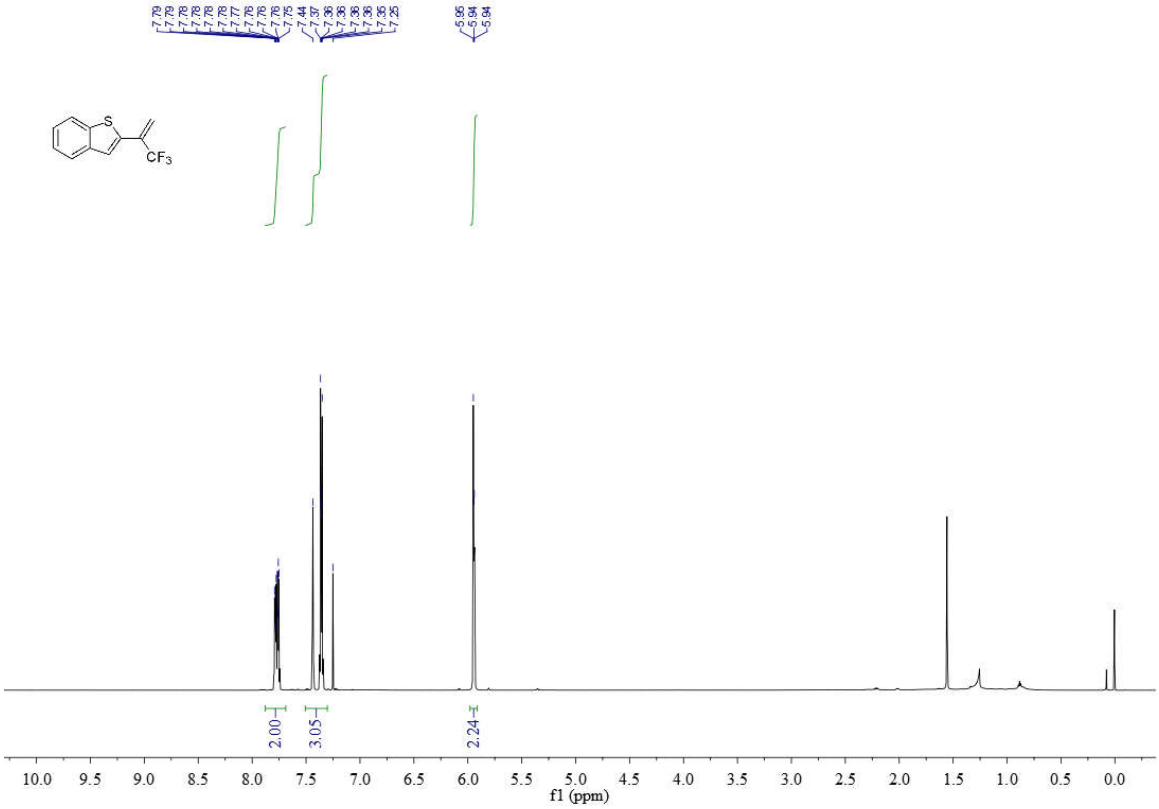
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 2g



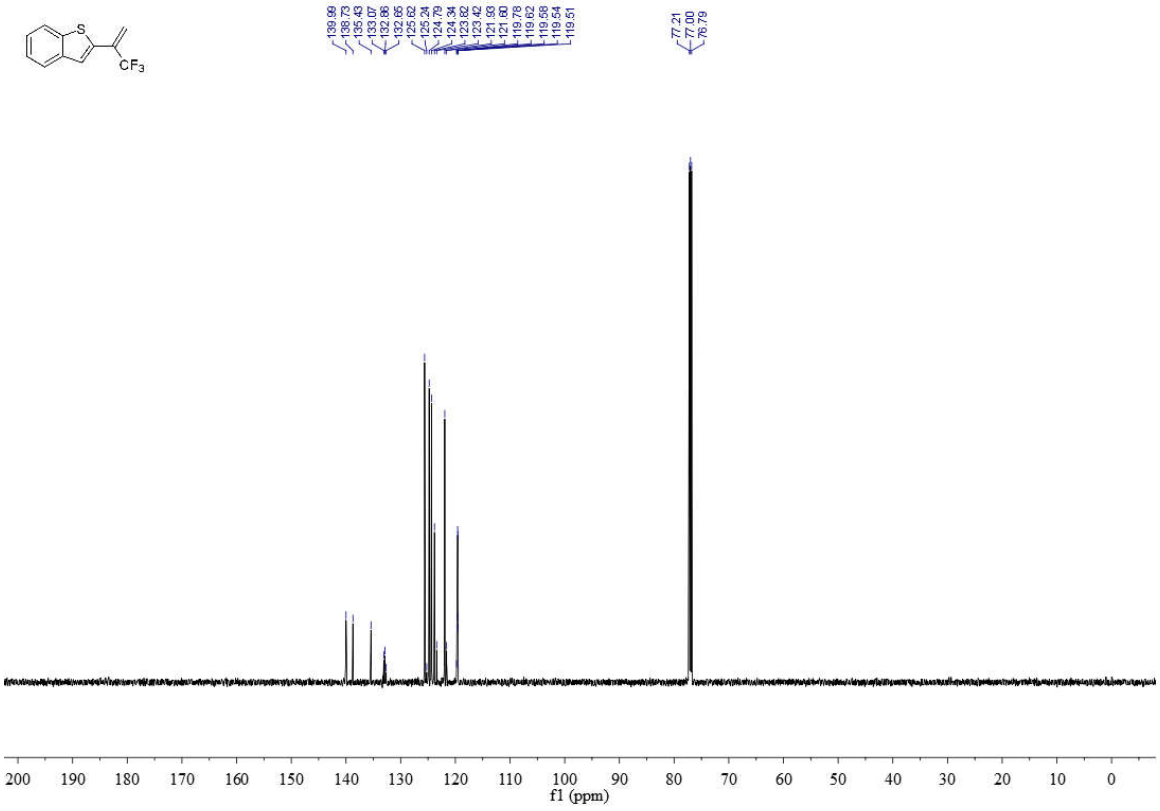
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 °C) of 2g



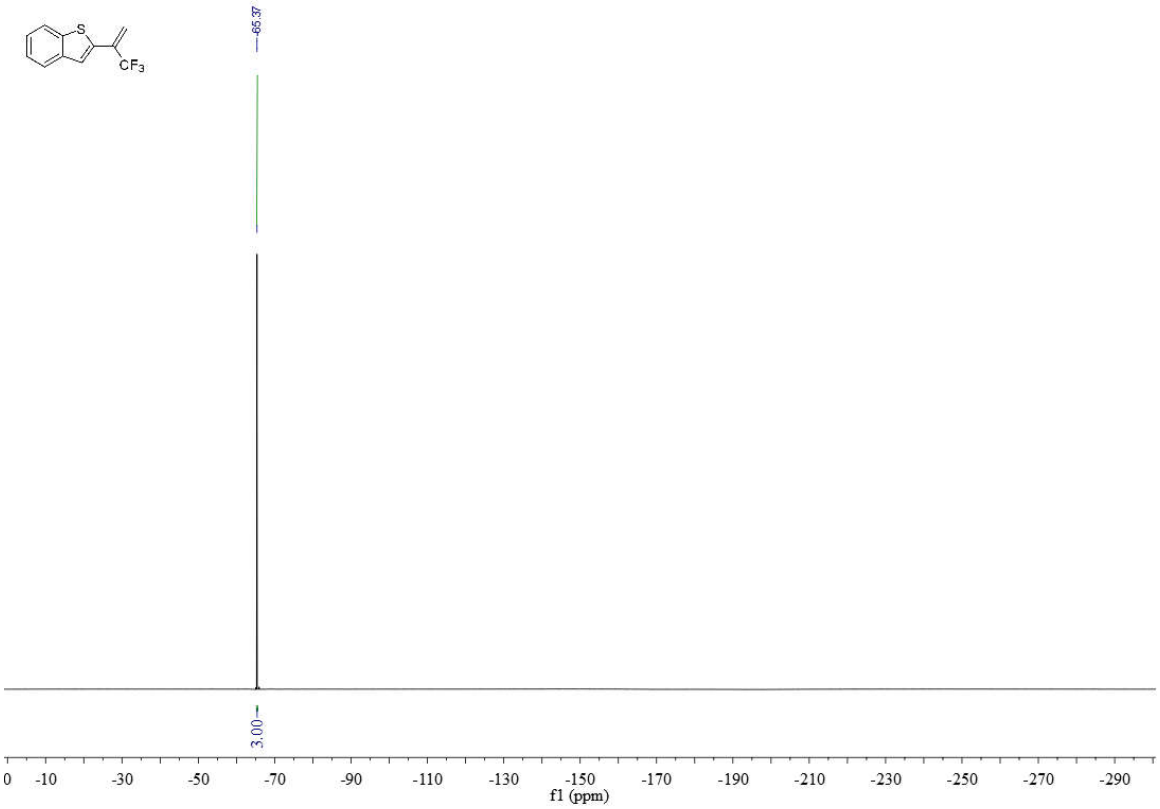
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2h



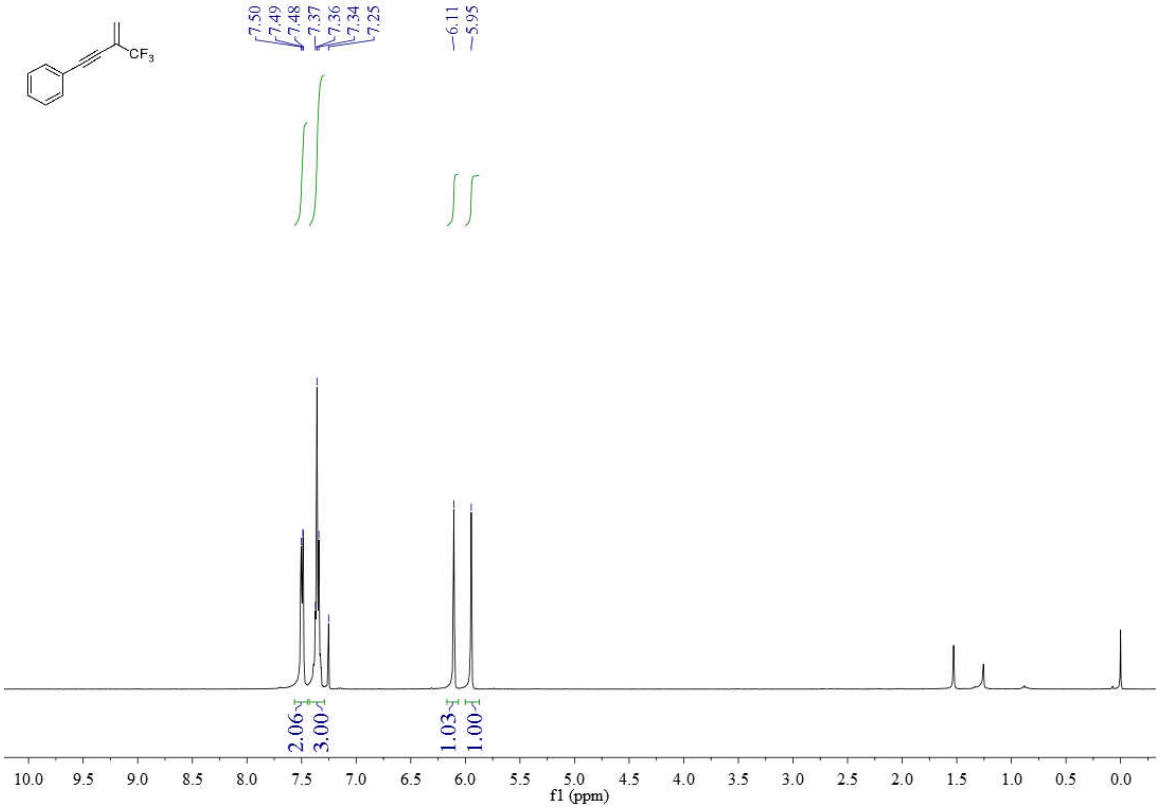
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 2h



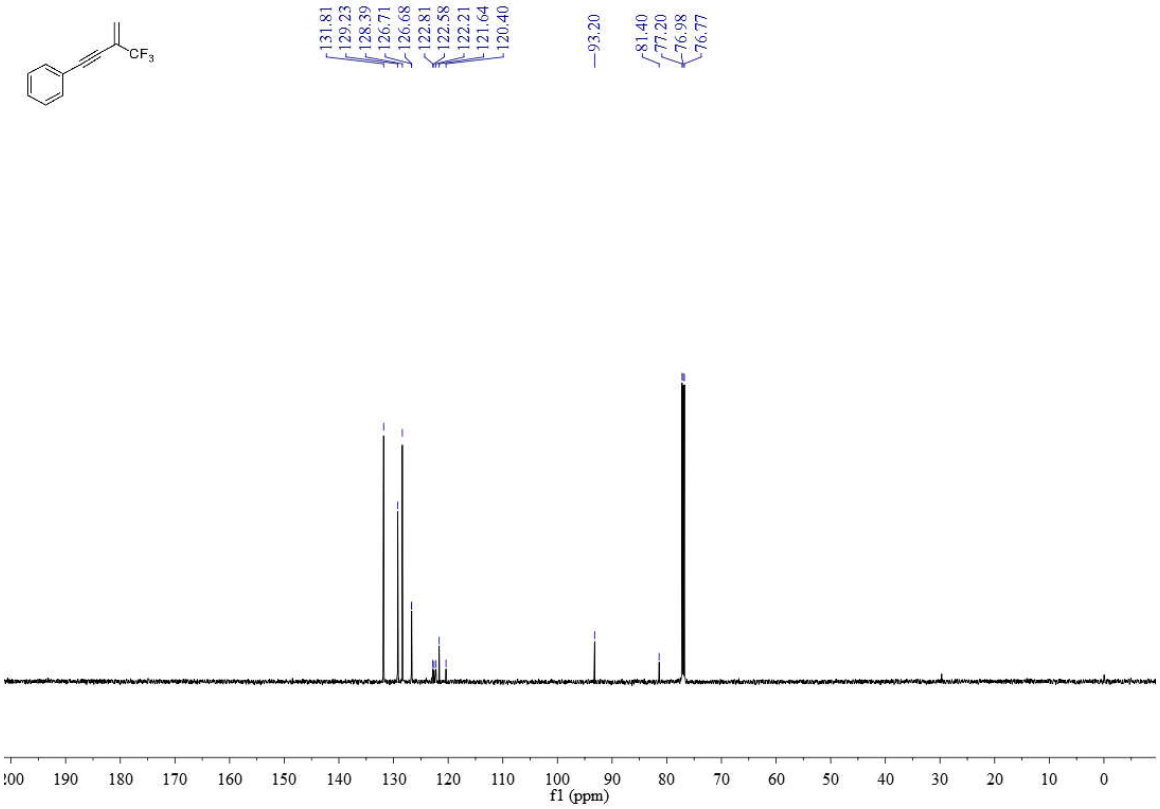
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 23 ºC) of 2h



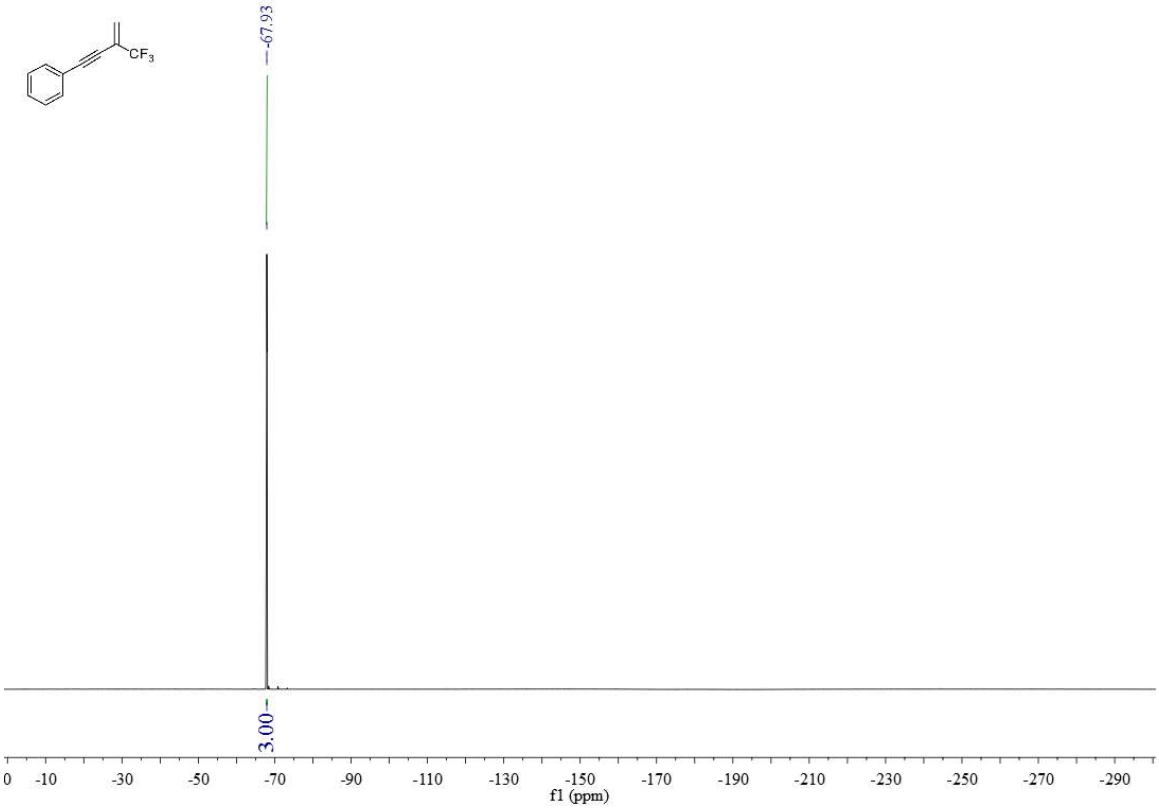
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2i



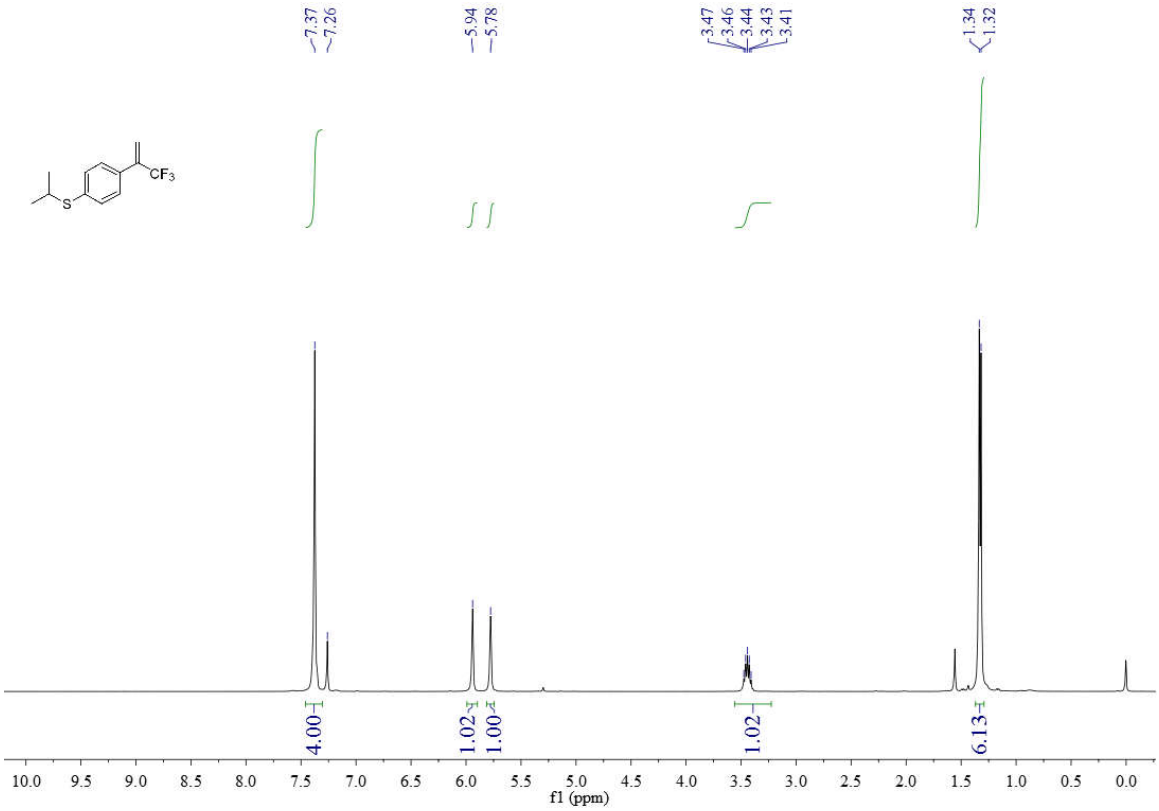
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 2i



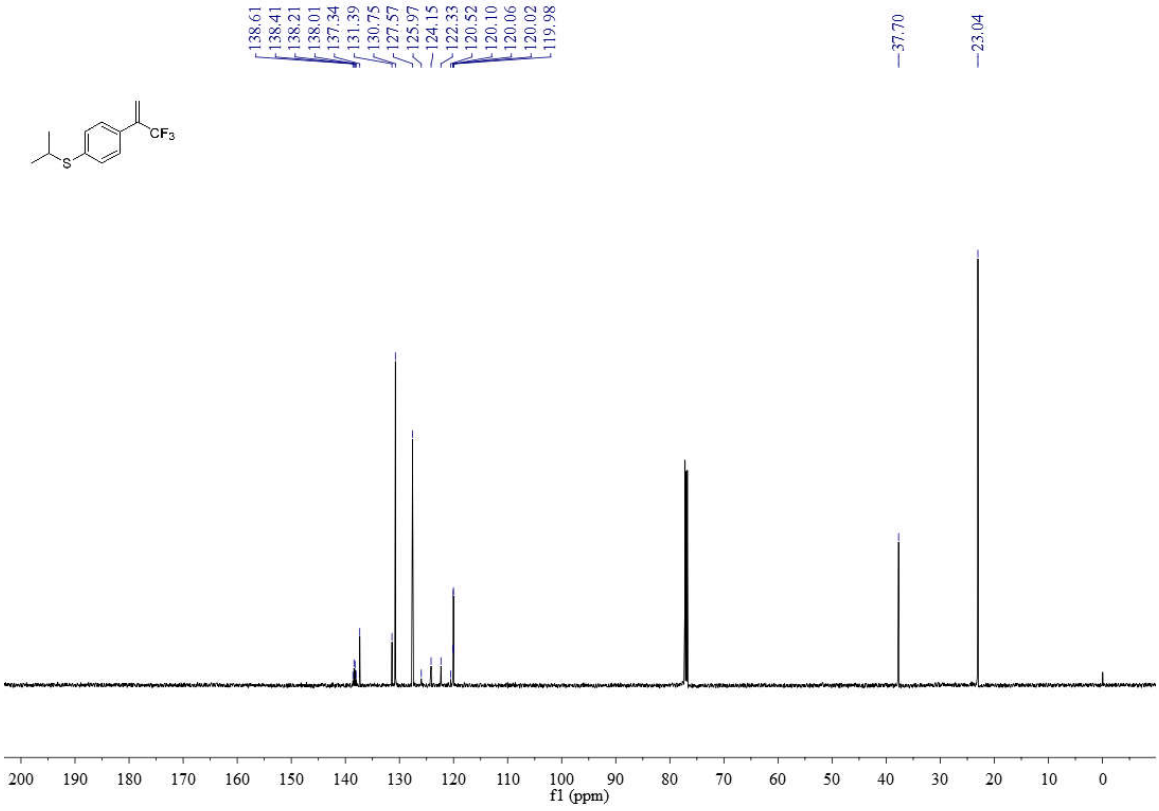
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 °C) of 2i



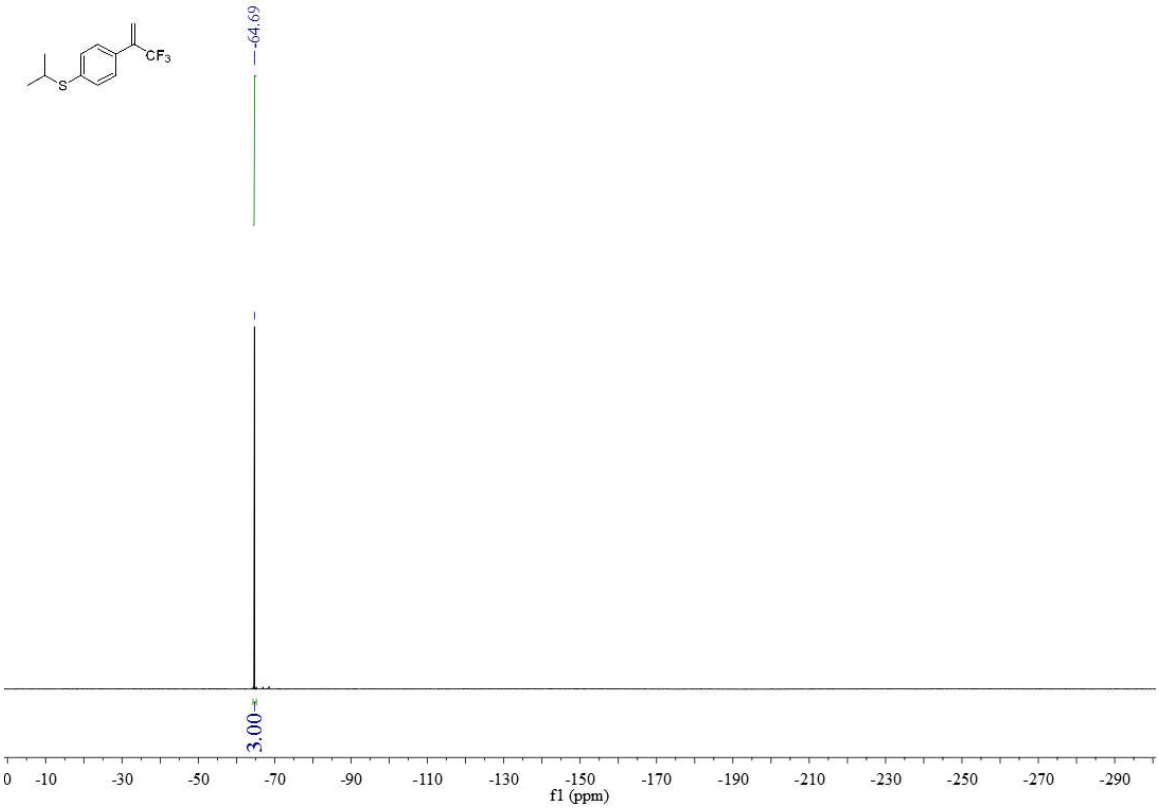
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2j



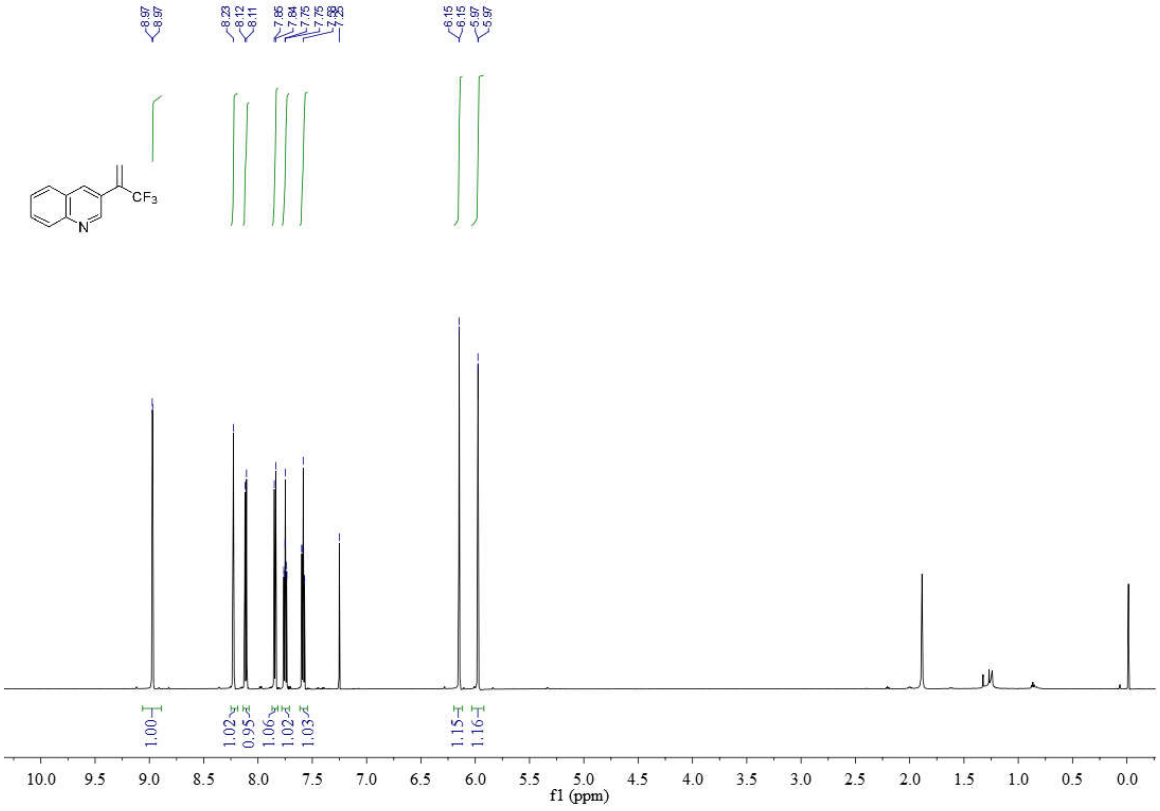
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 2j



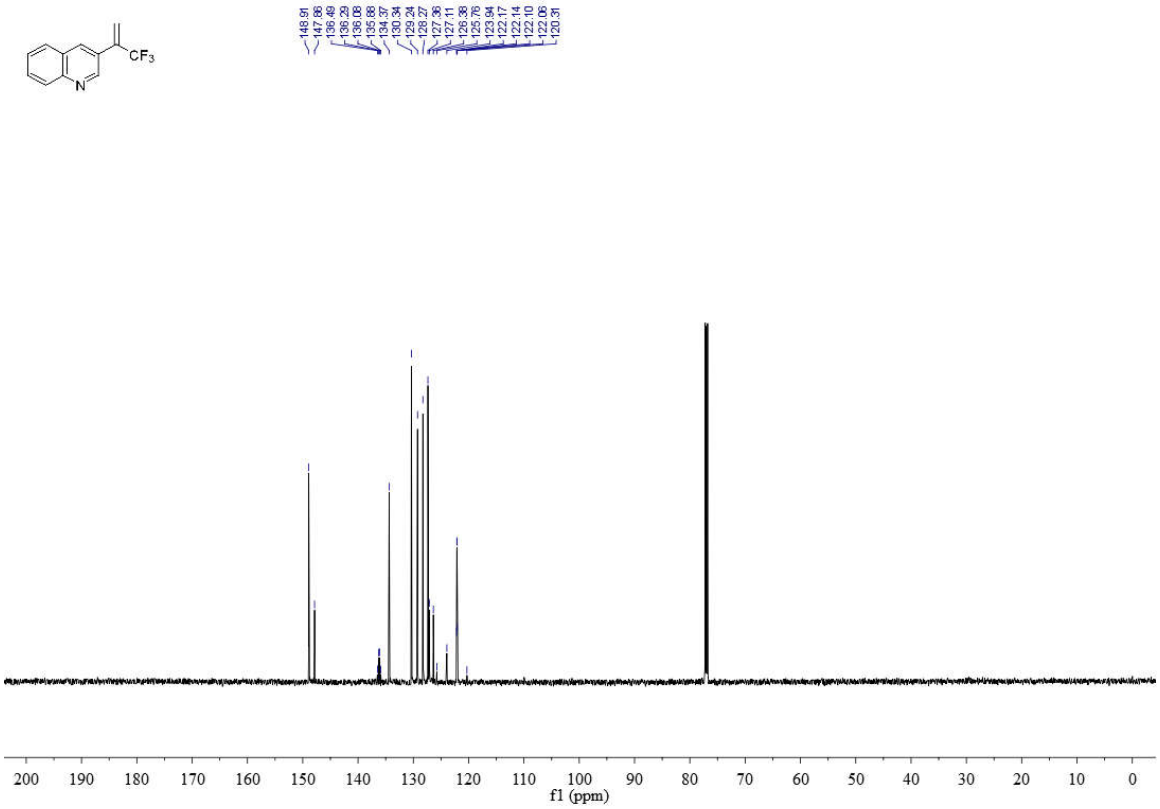
^{19}F NMR spectrum (377 MHz, $CDCl_3$, 23 °C) of 2j



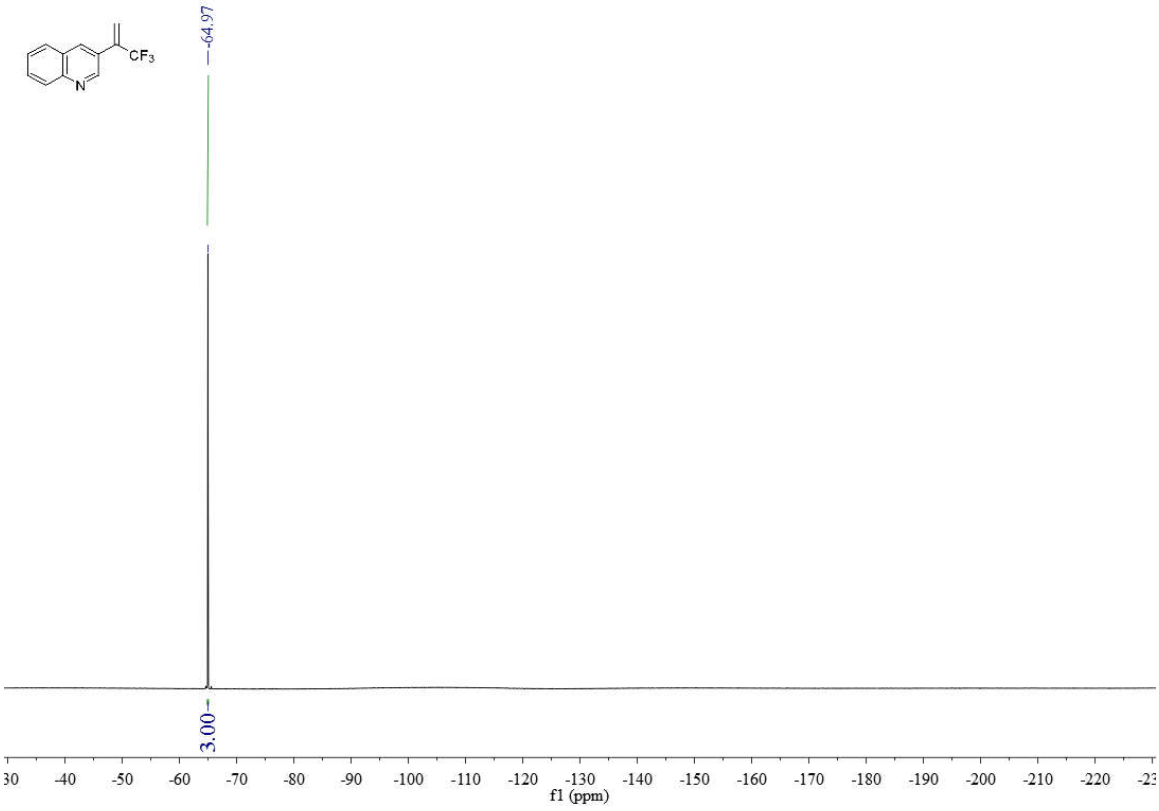
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2k



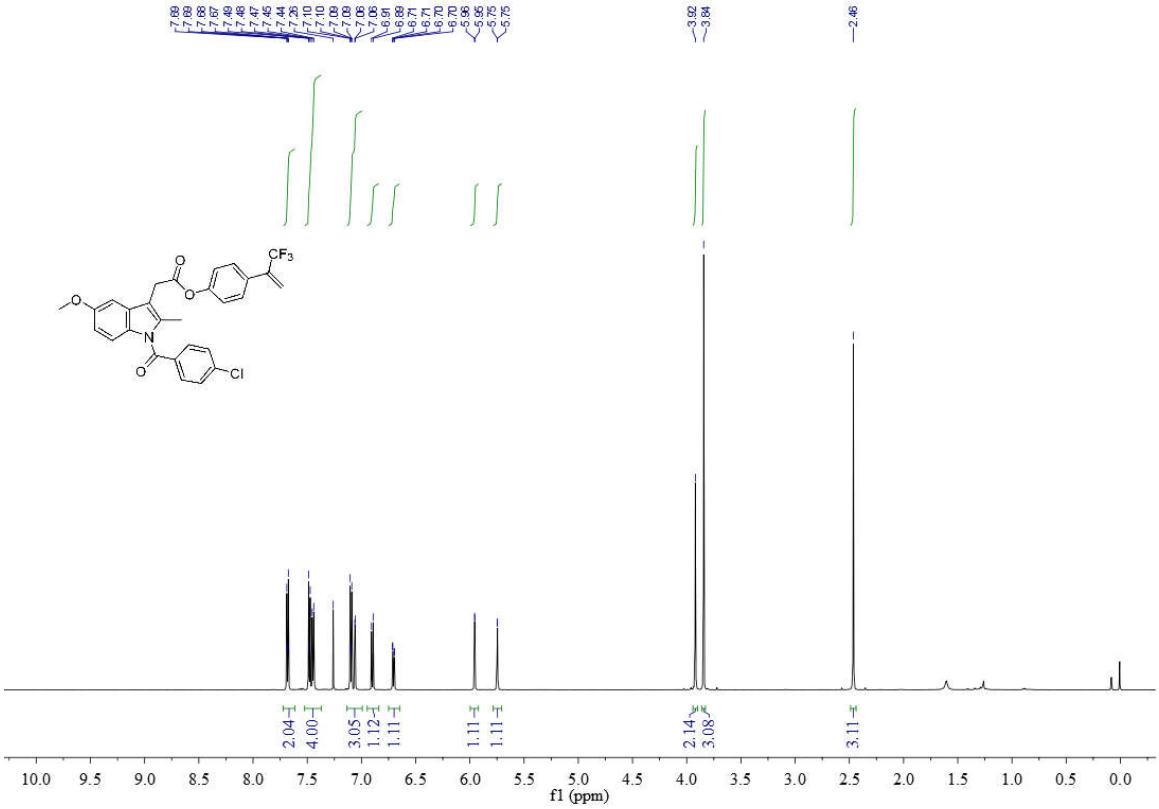
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 2k



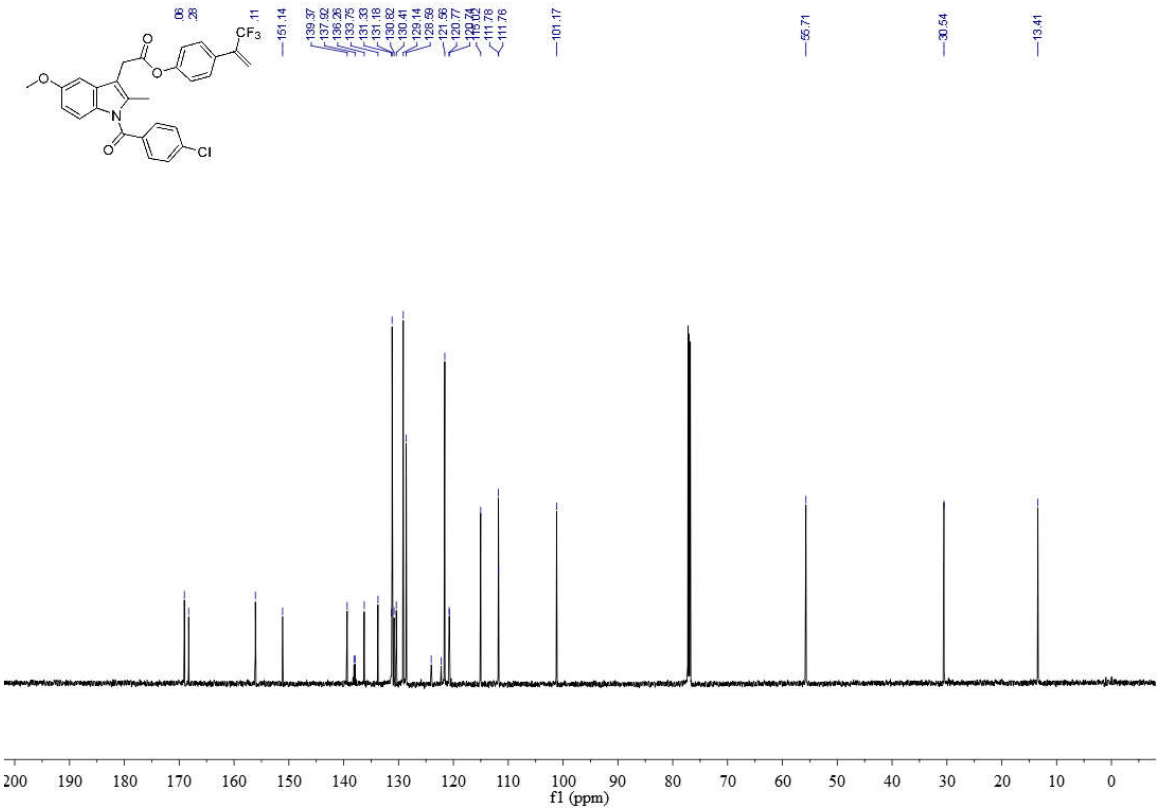
^{19}F NMR spectrum (282 MHz, $CDCl_3$, 23 °C) of 2k



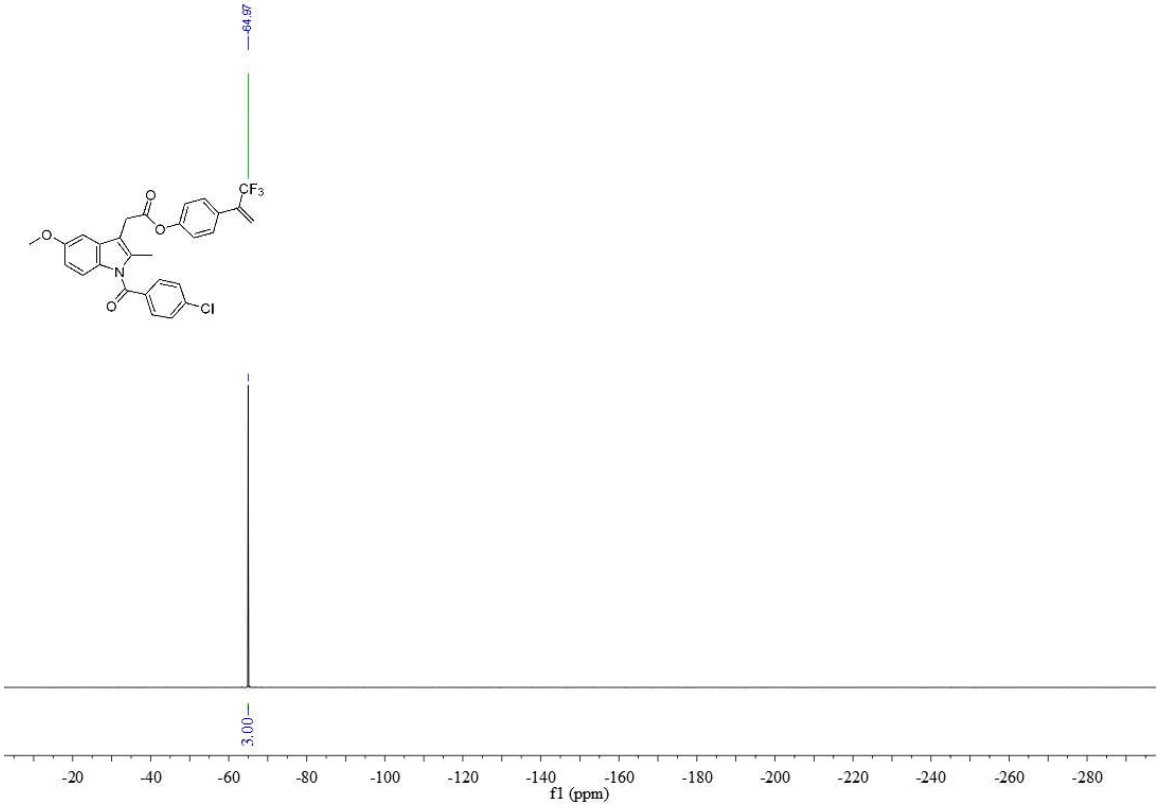
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2l



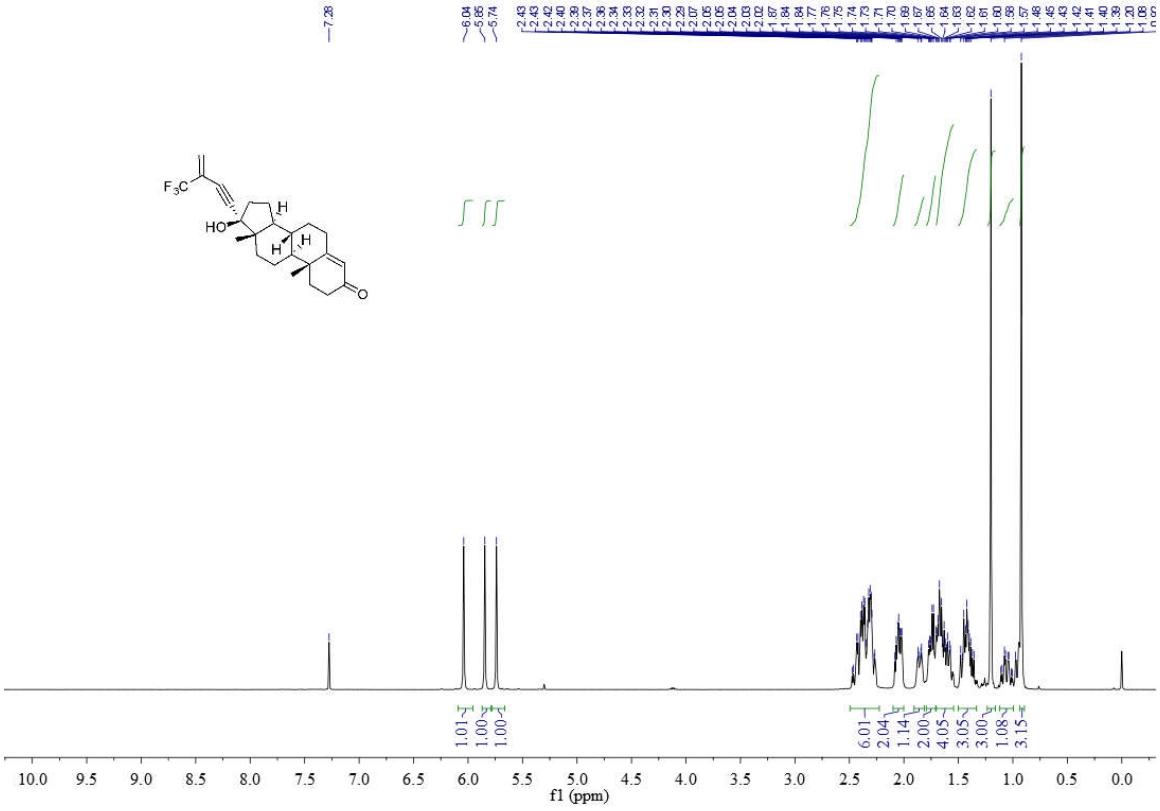
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 2l



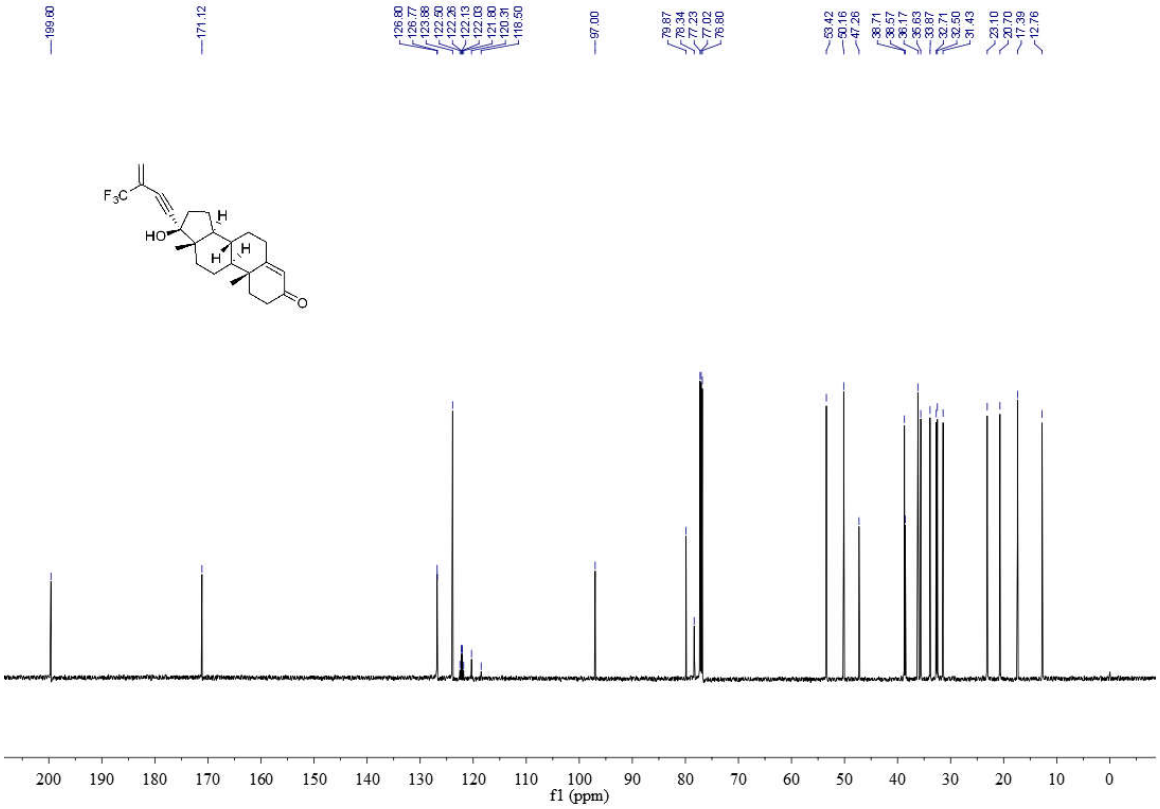
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 23 ºC) of 2l



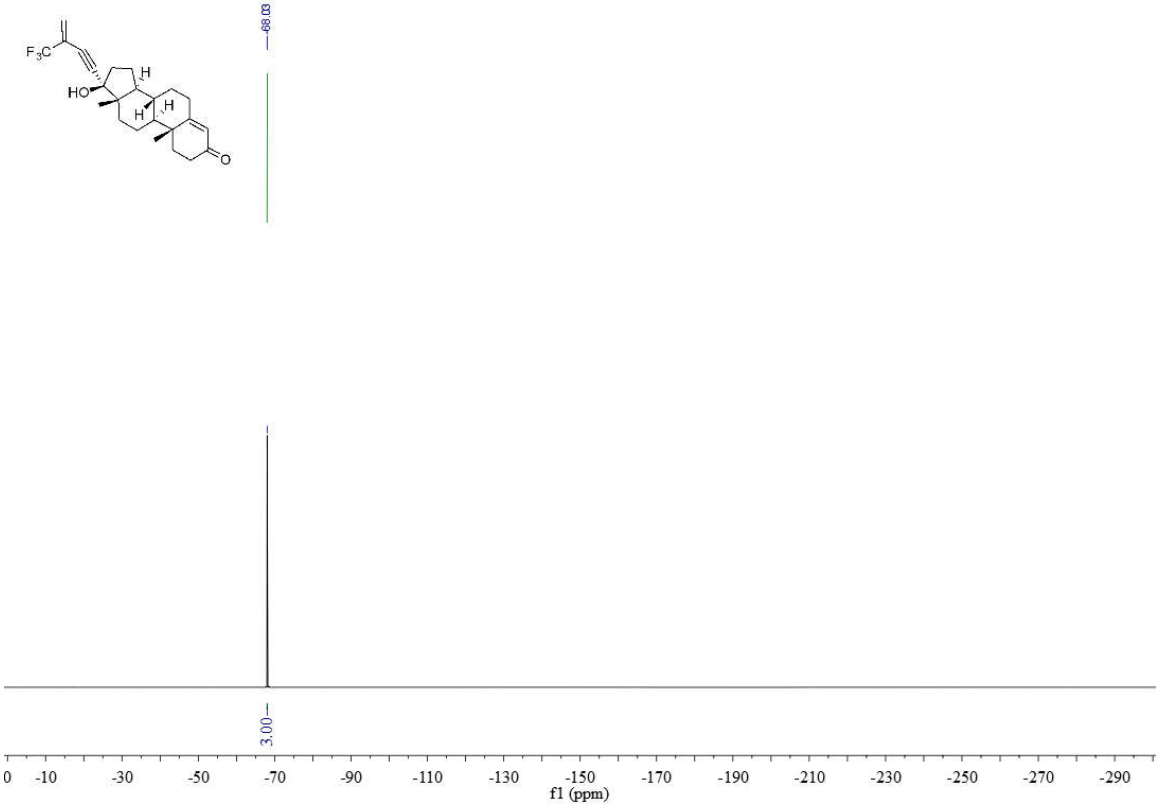
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 2m



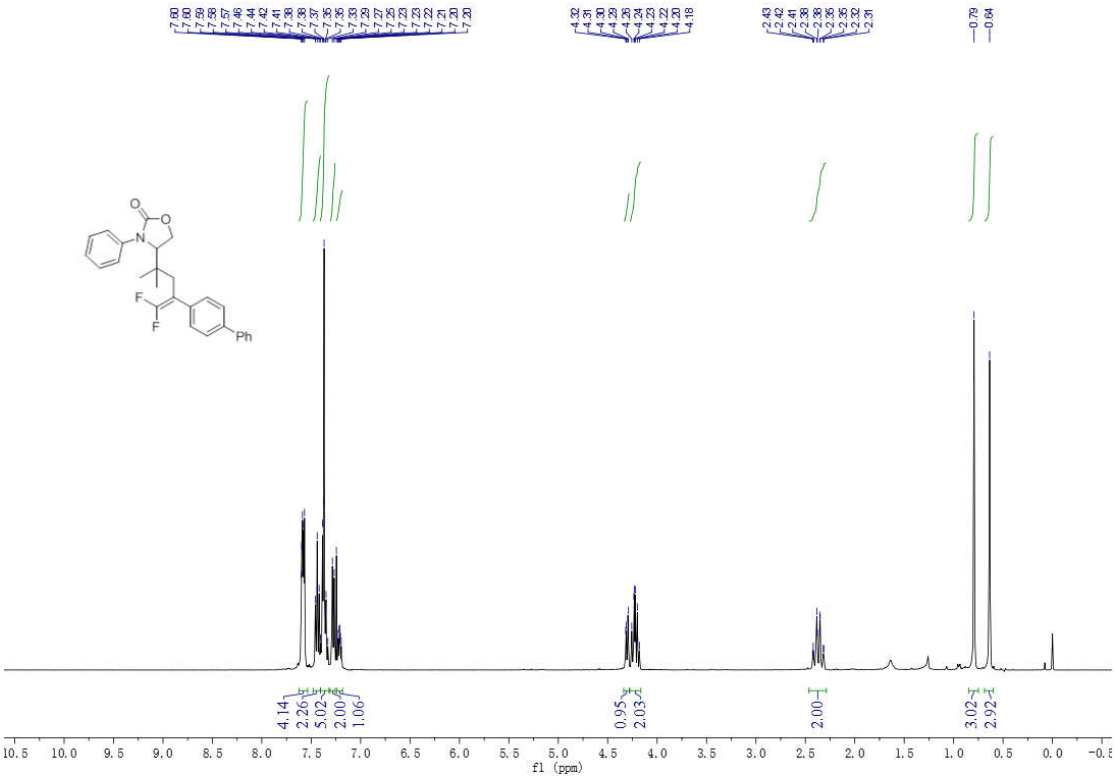
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 2m



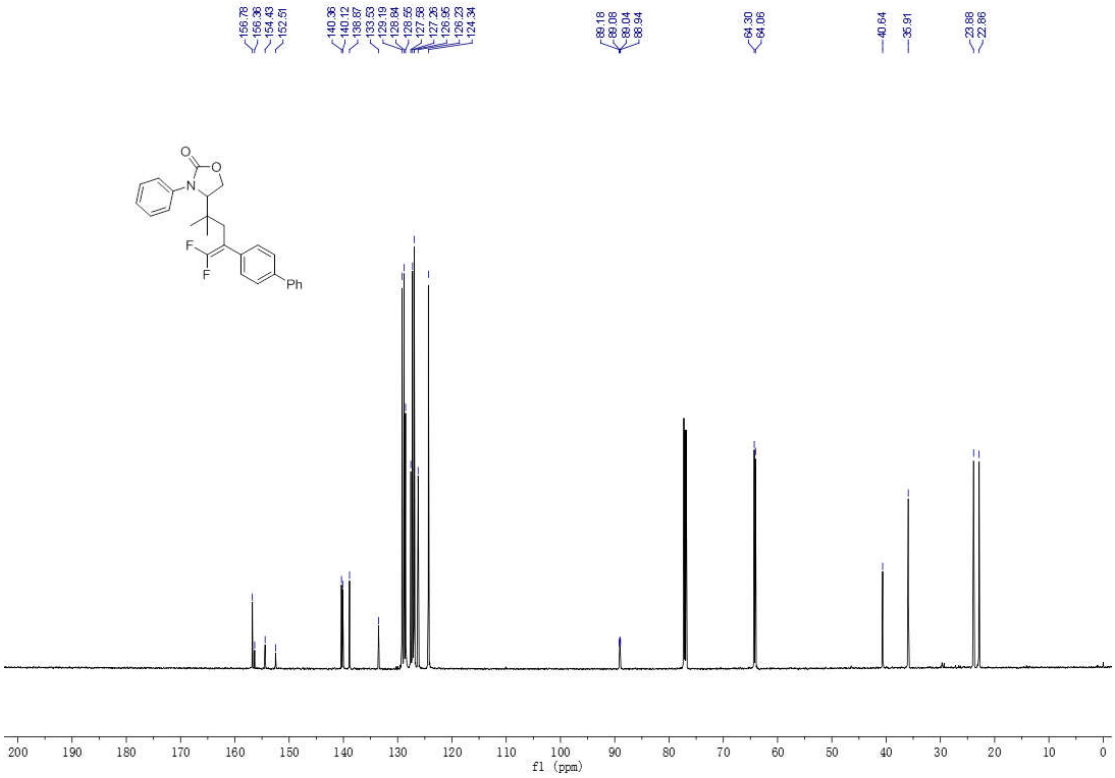
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 2m



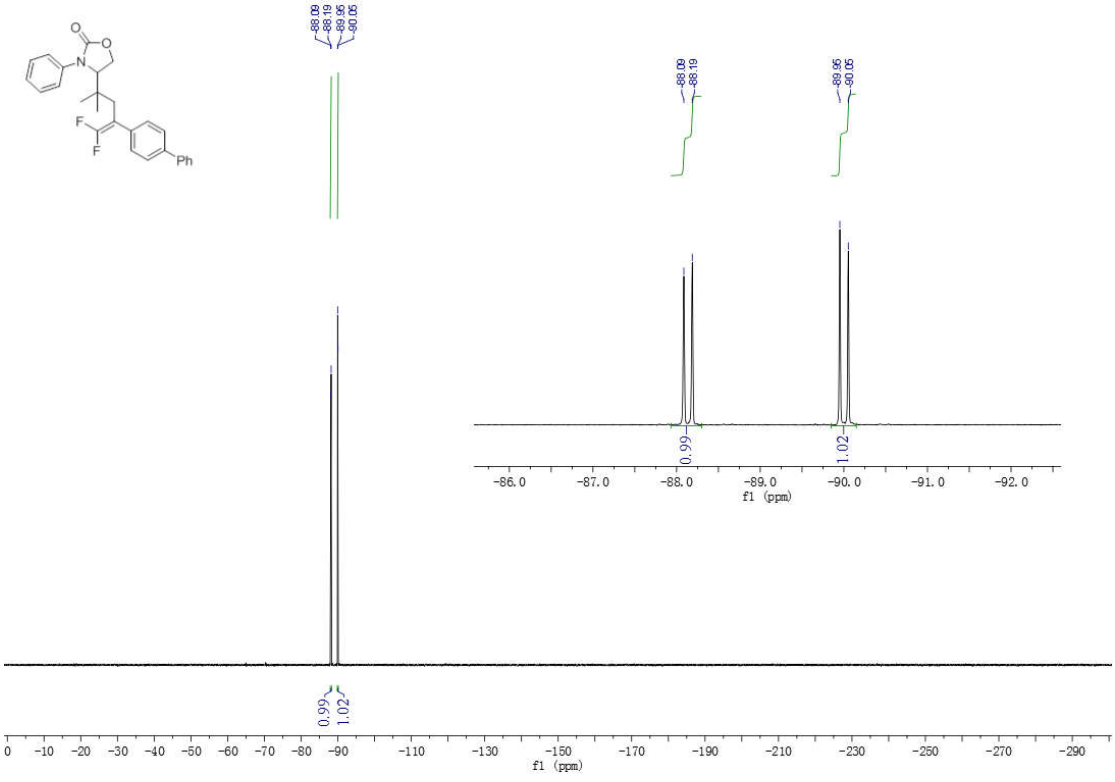
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3a



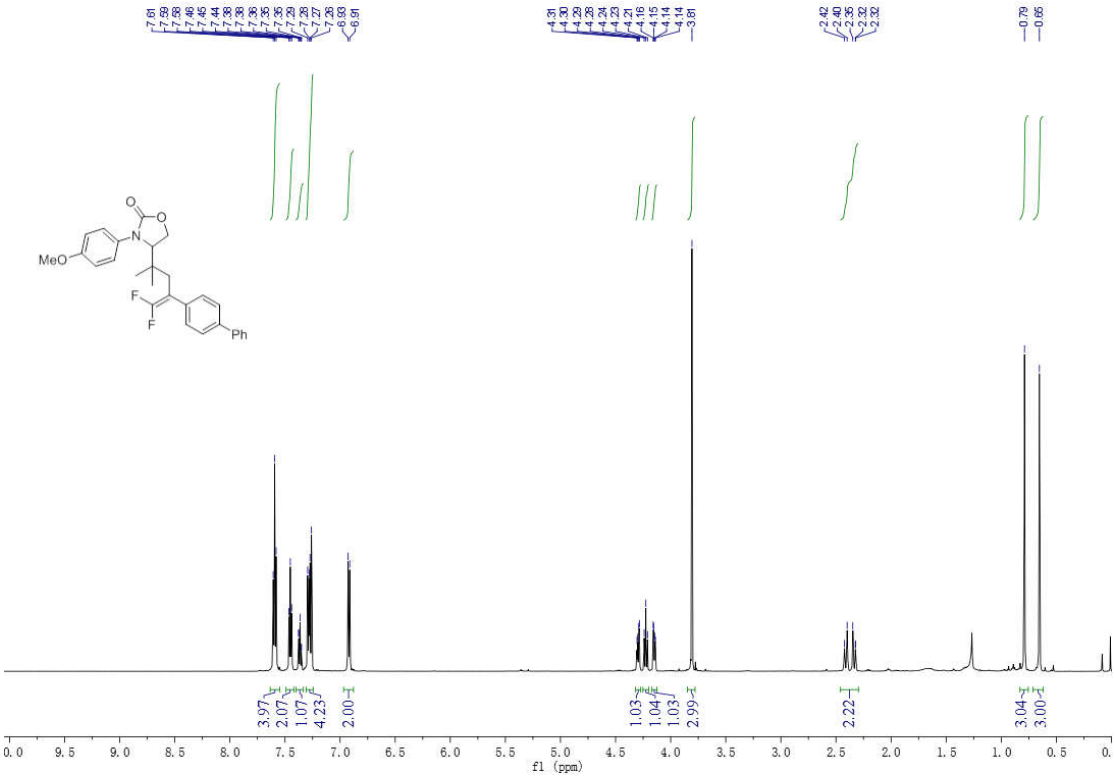
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3a



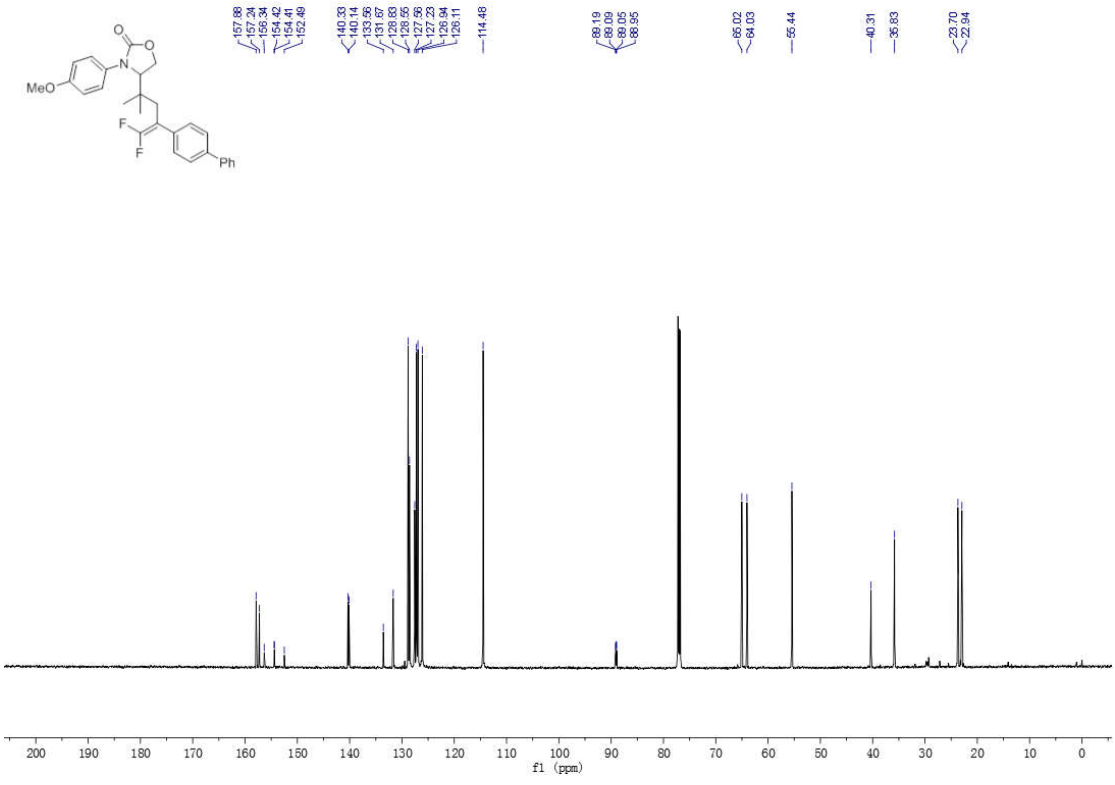
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3a



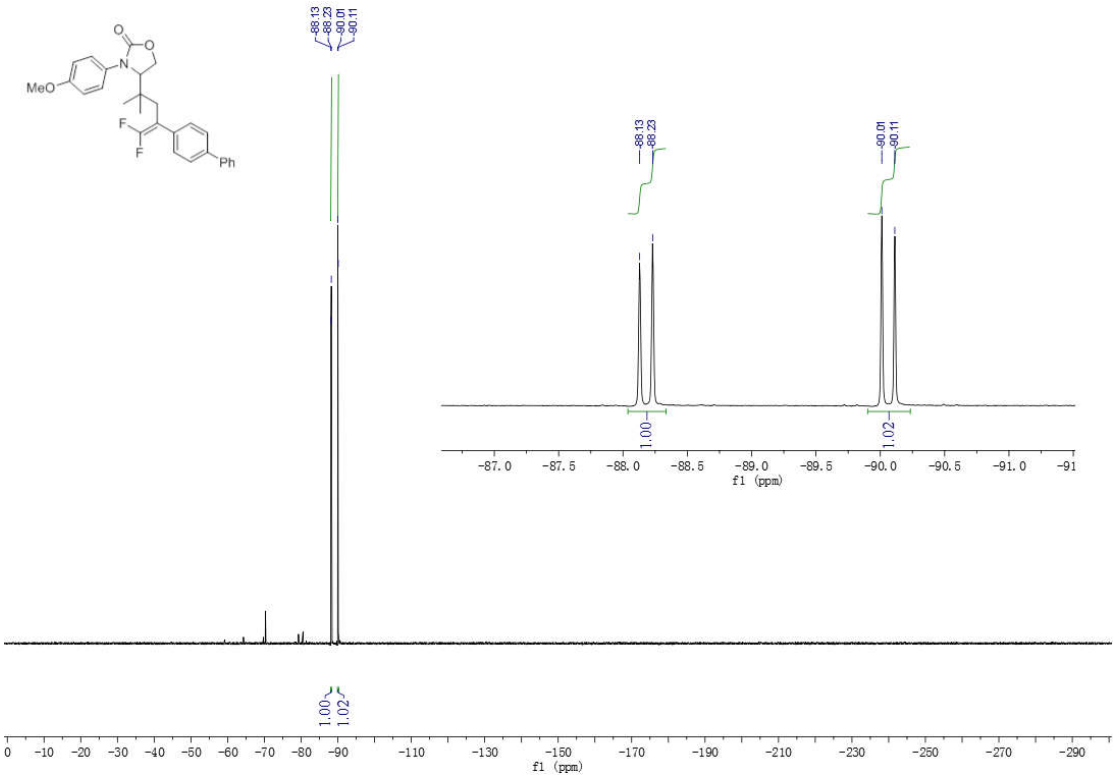
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 3b



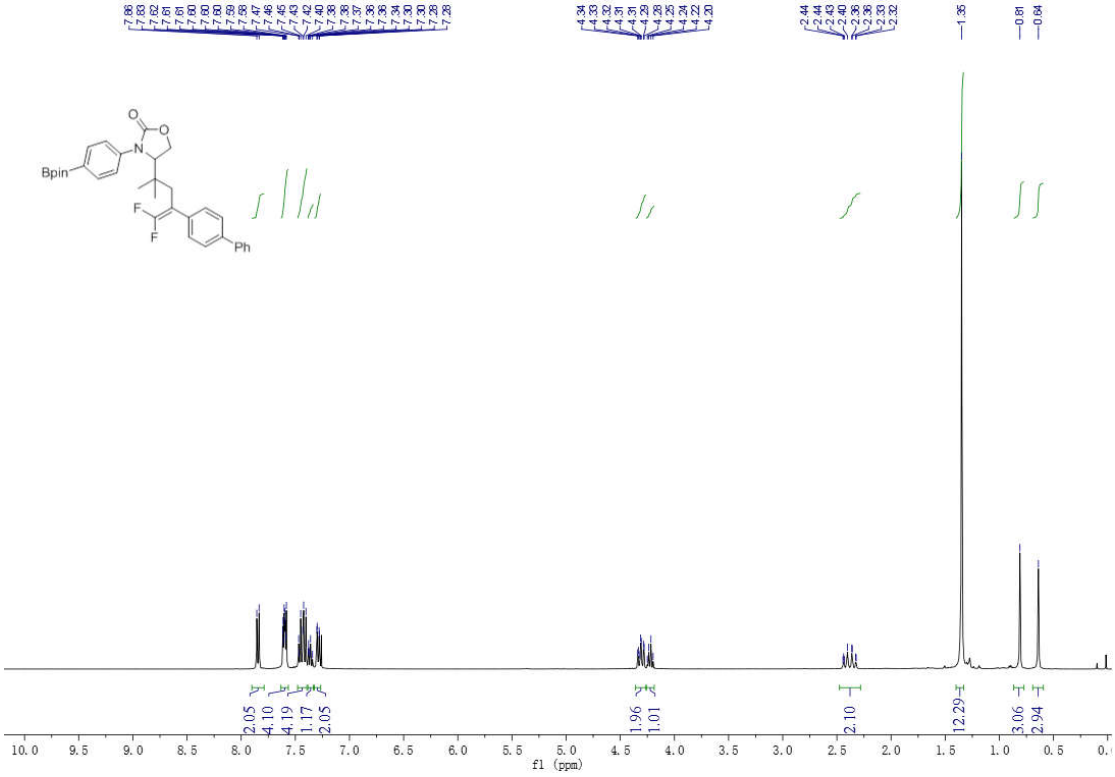
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3b



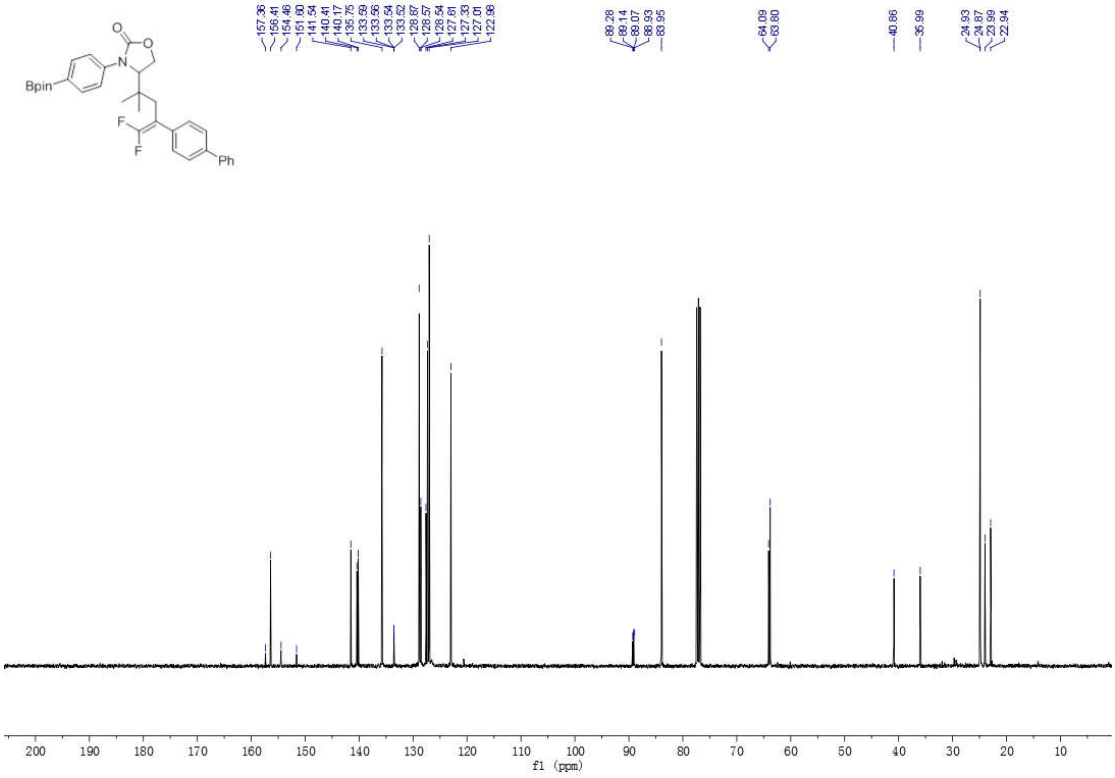
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3b



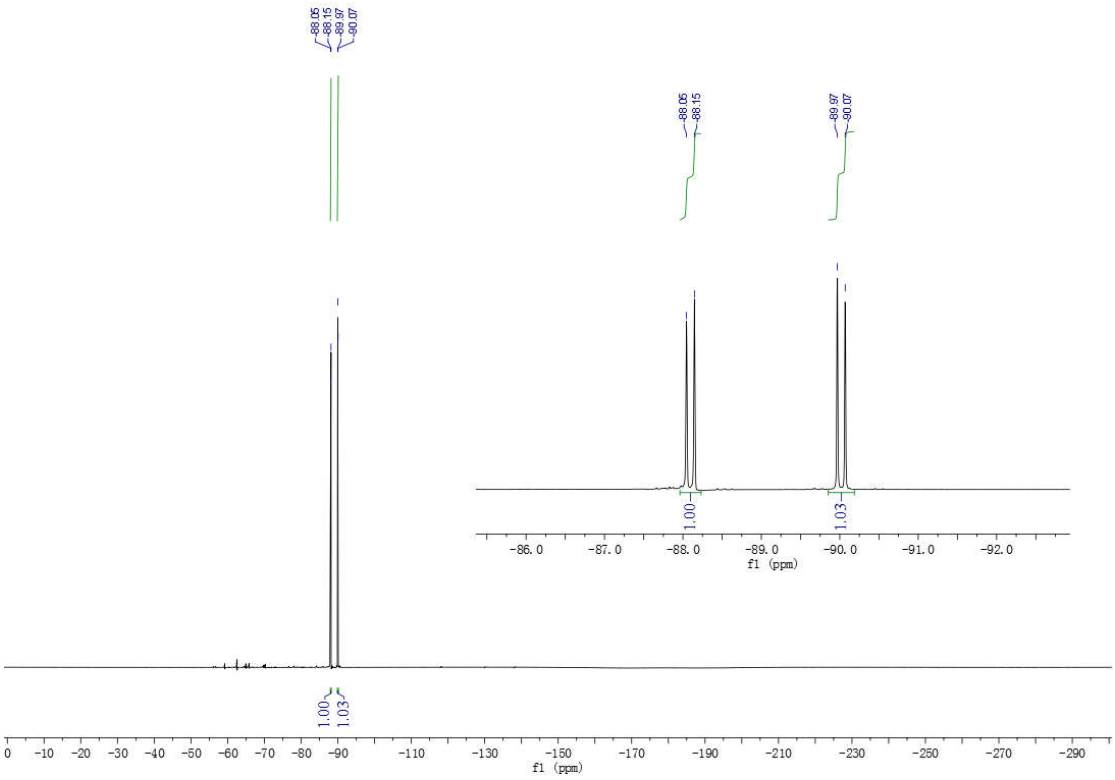
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3c



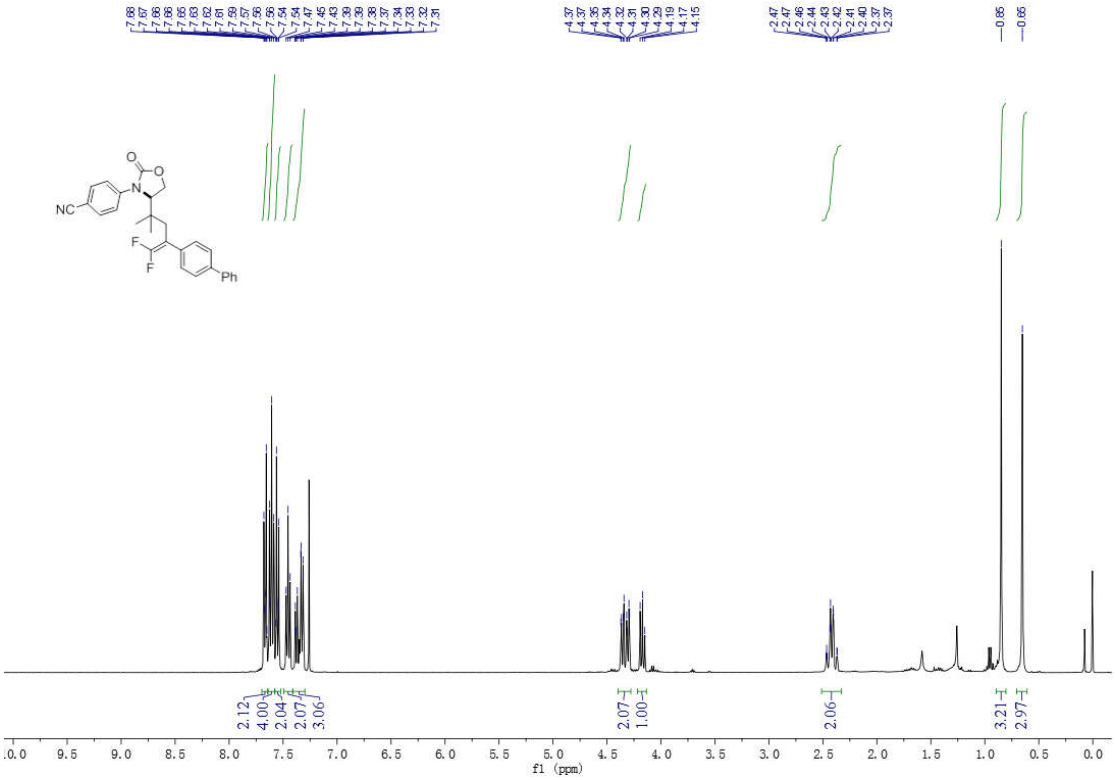
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of 3c



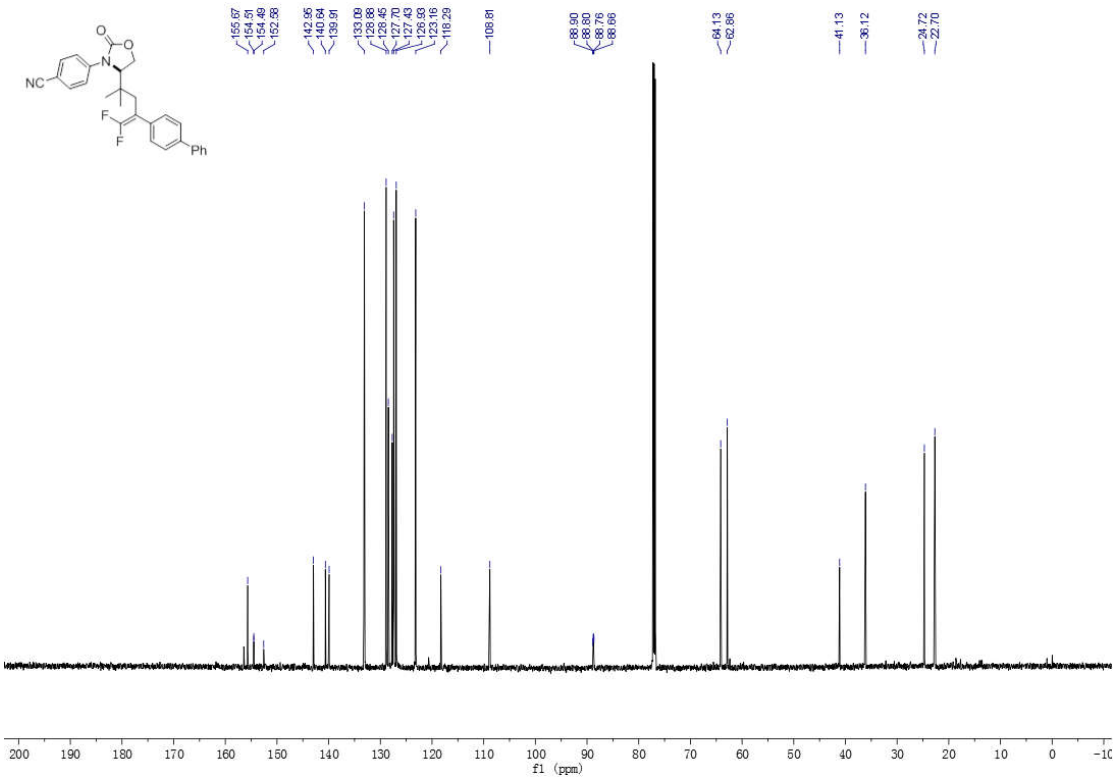
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 °C) of 3c



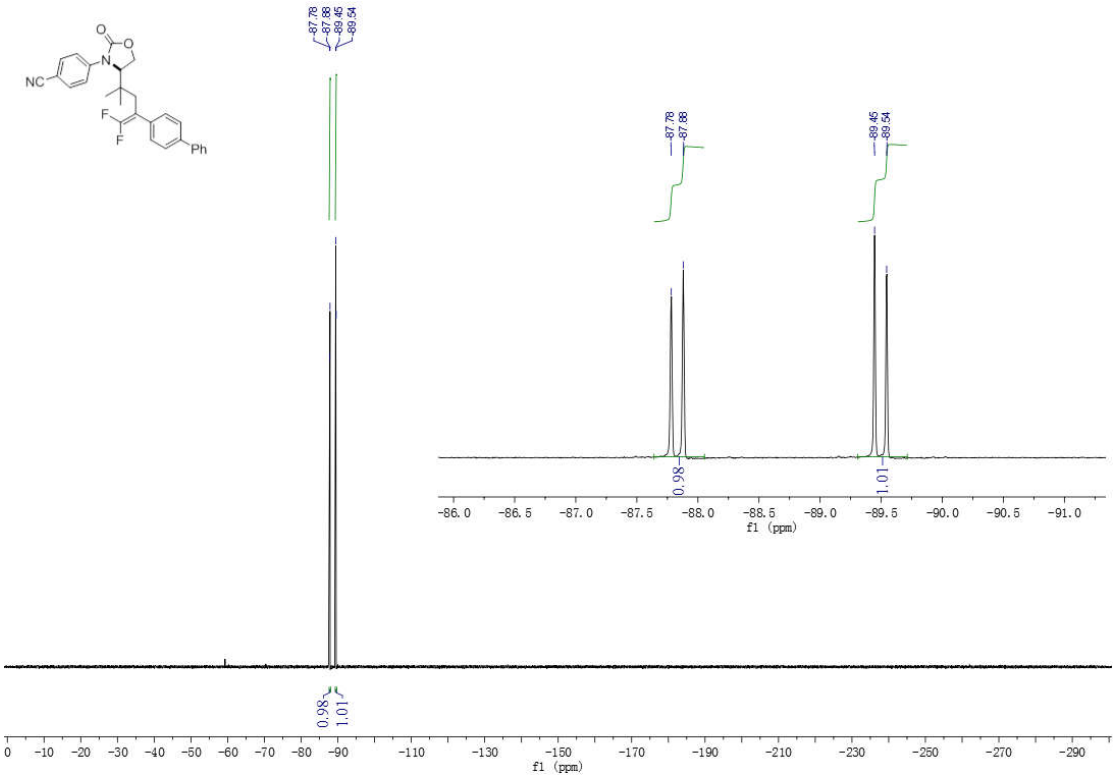
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 3d



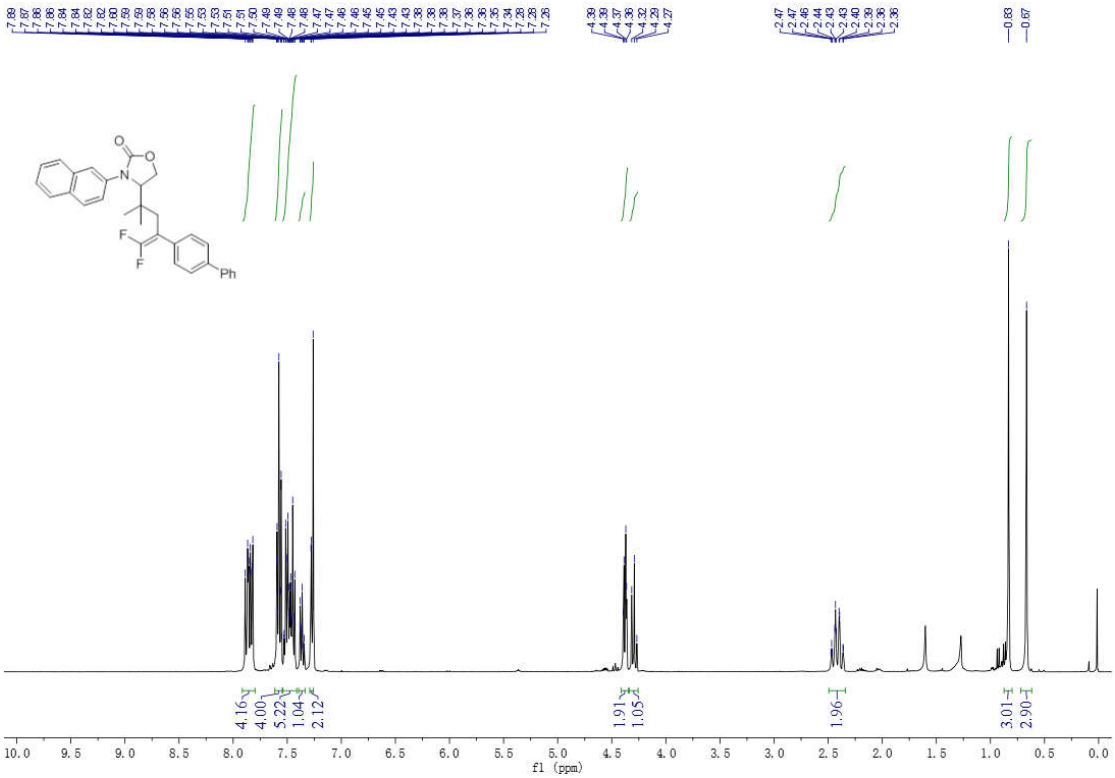
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3d



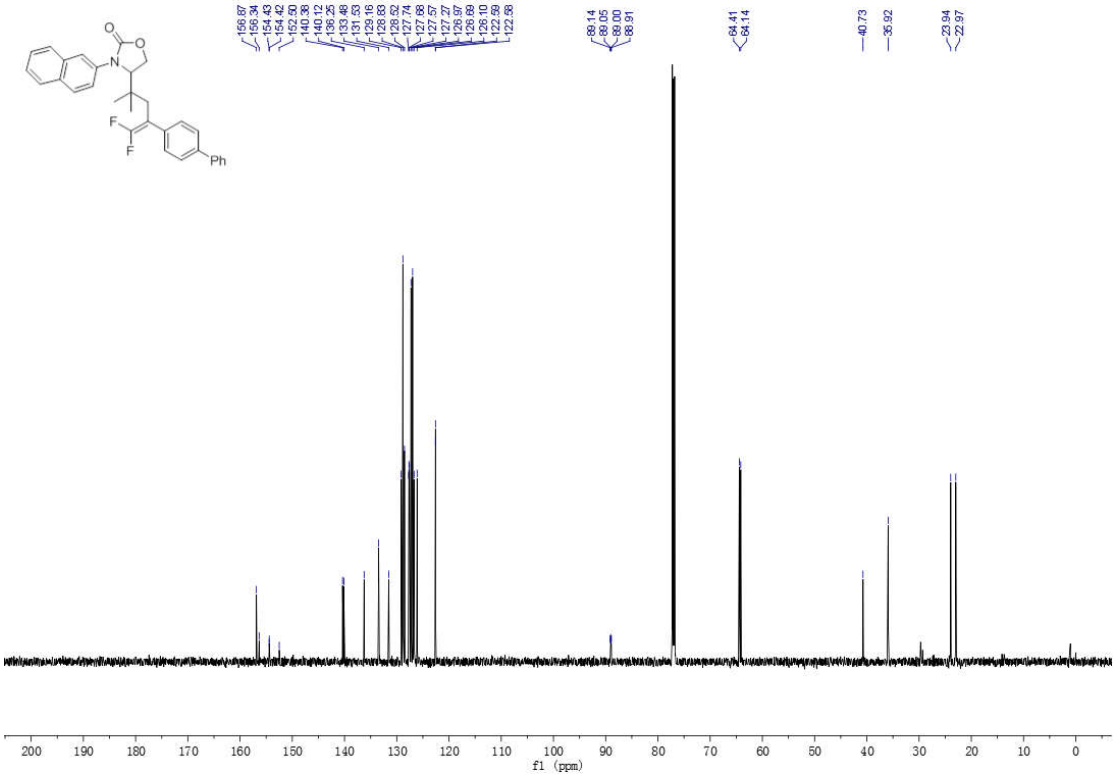
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3d



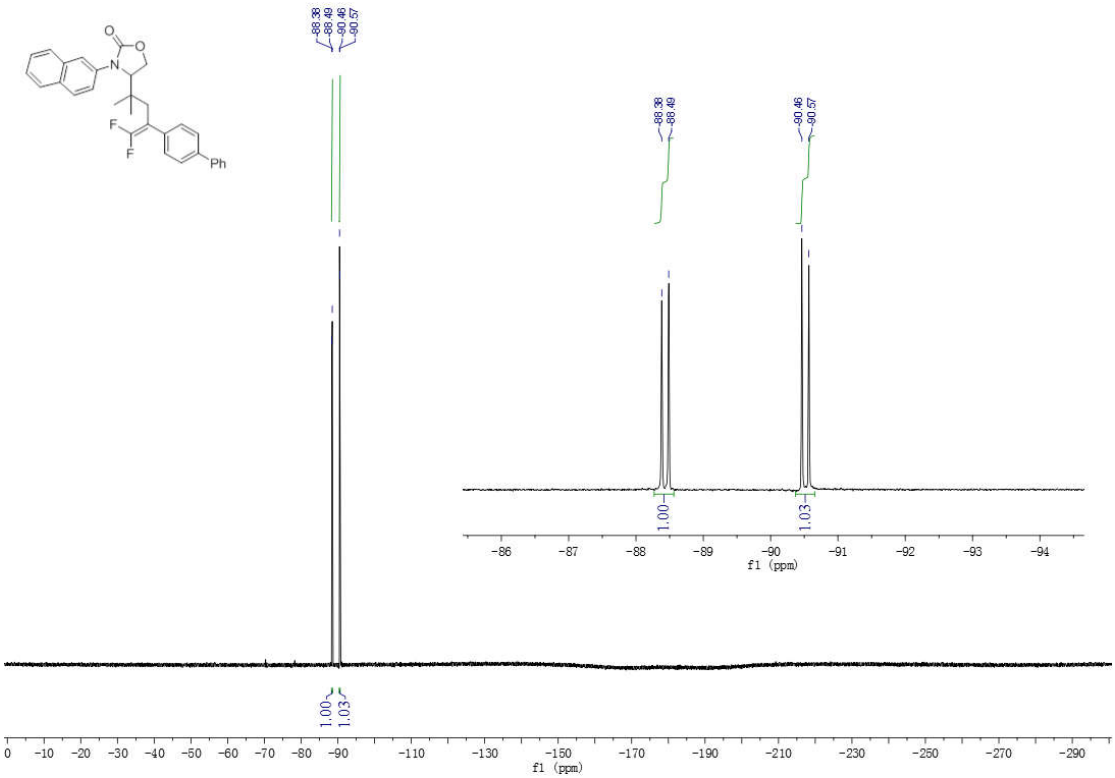
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3e



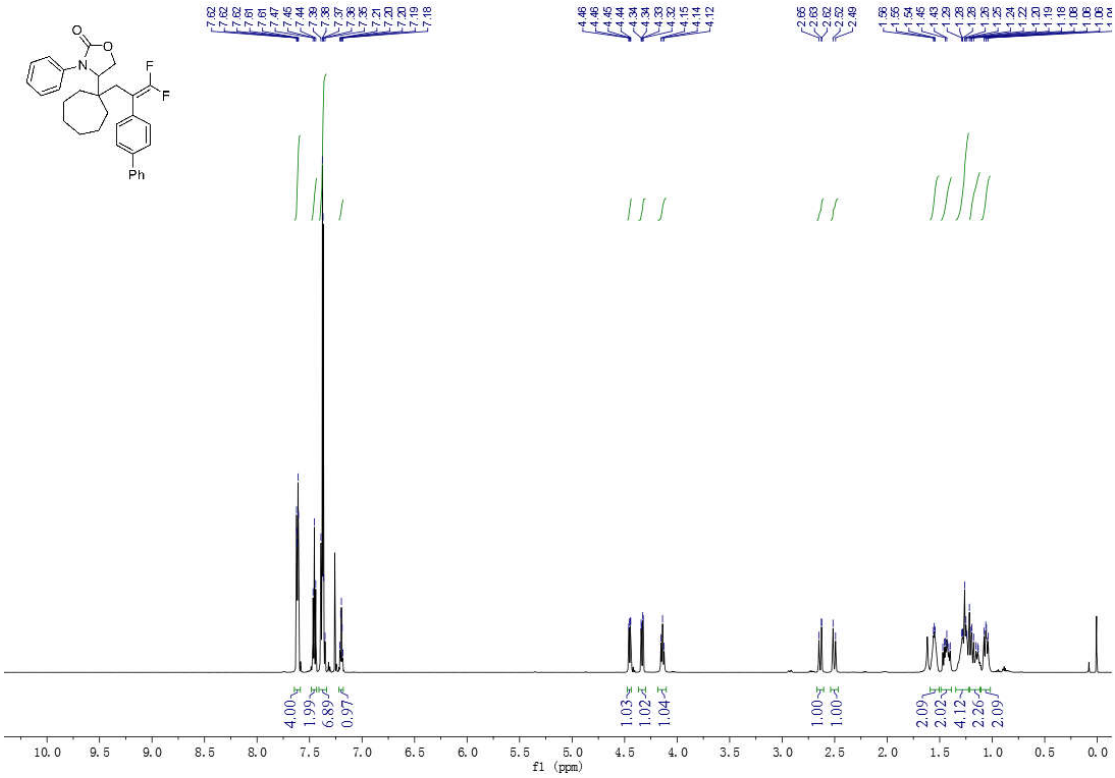
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3e



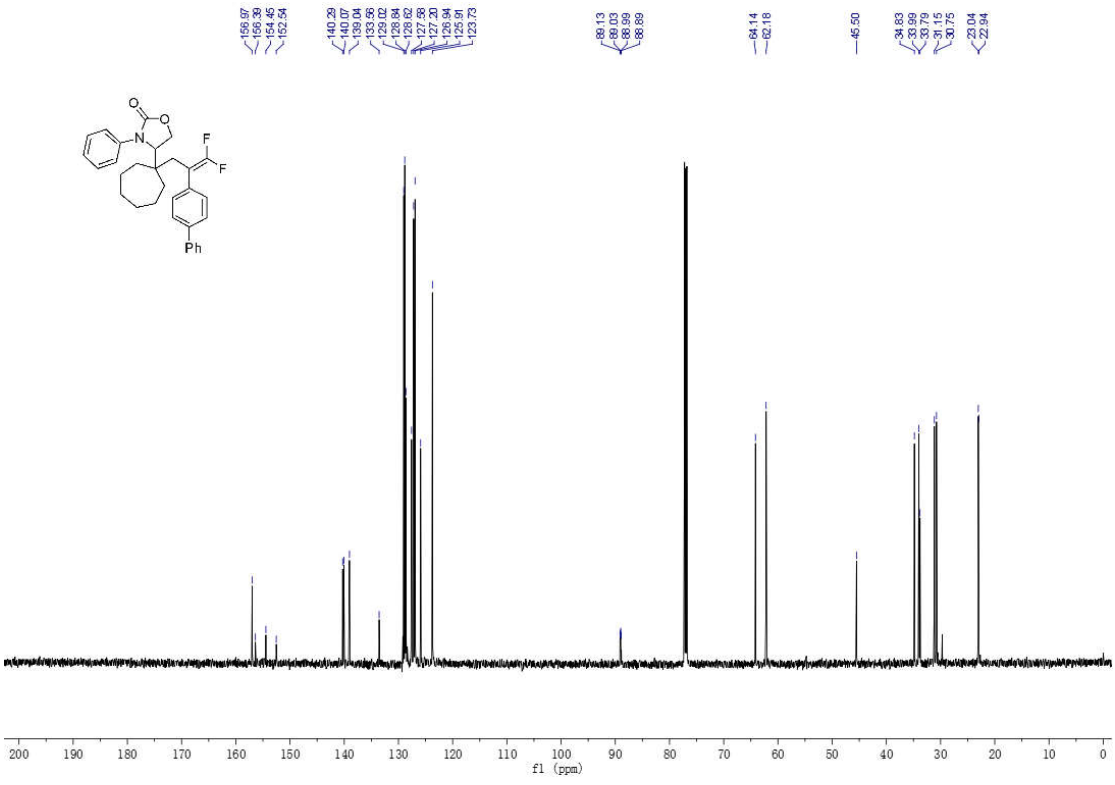
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3e



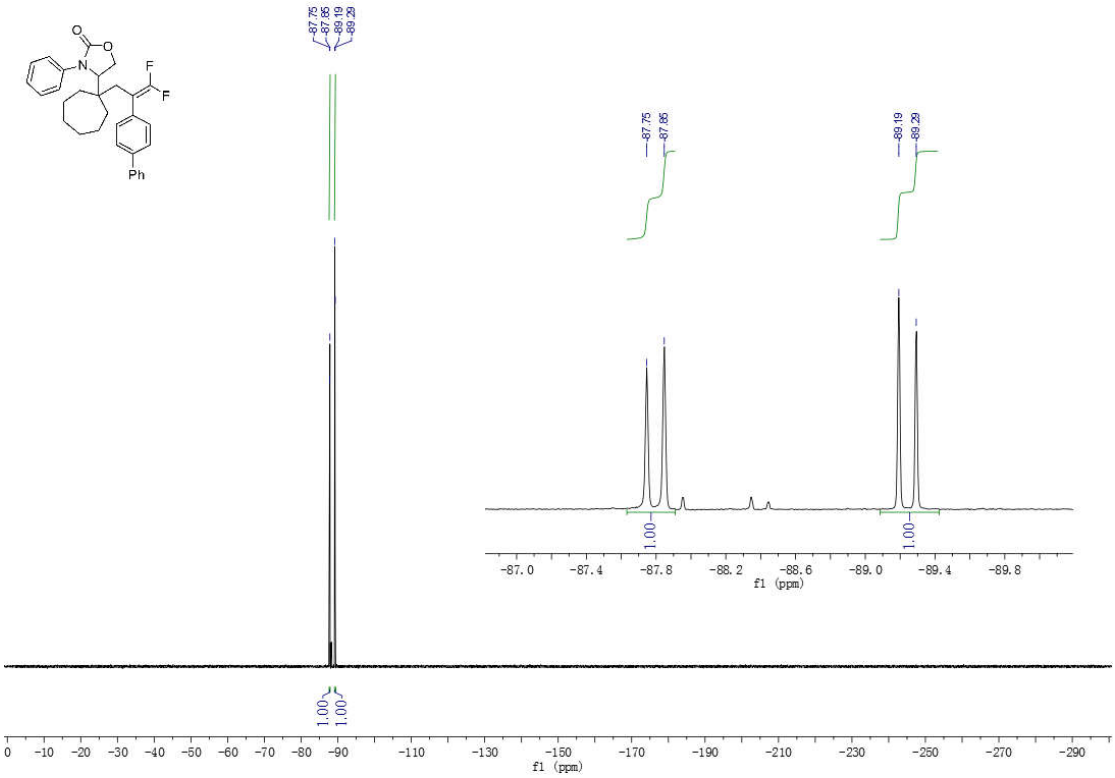
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 3f



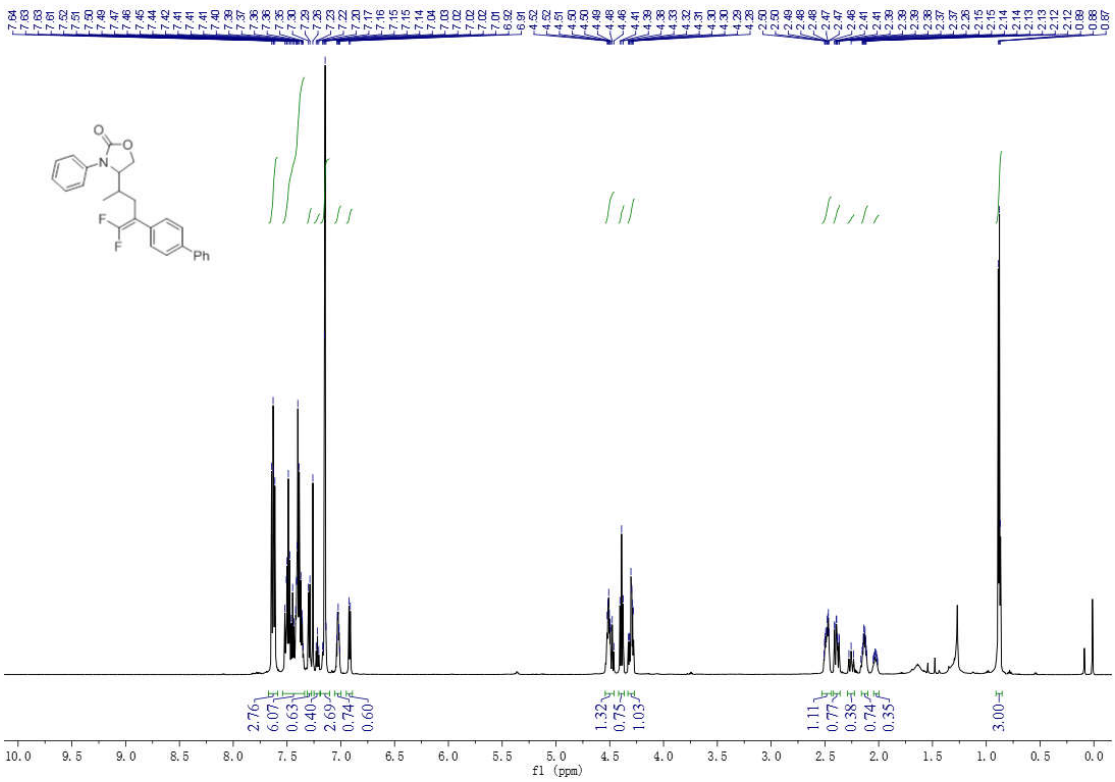
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3f



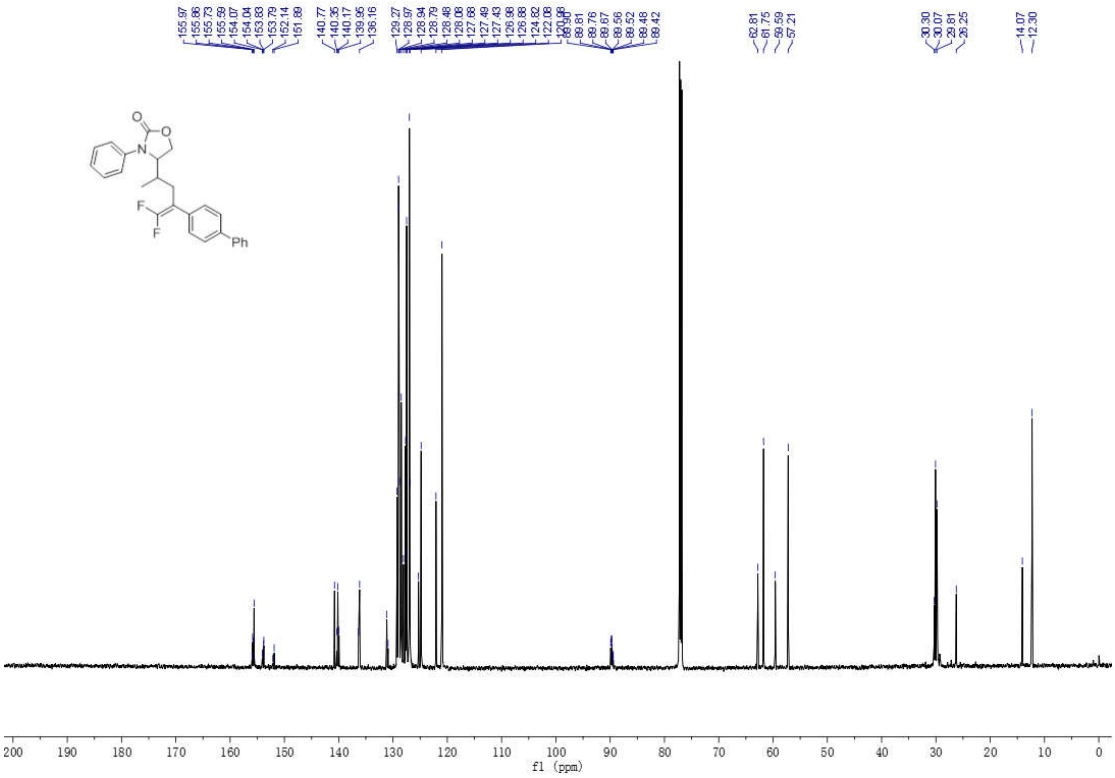
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3f



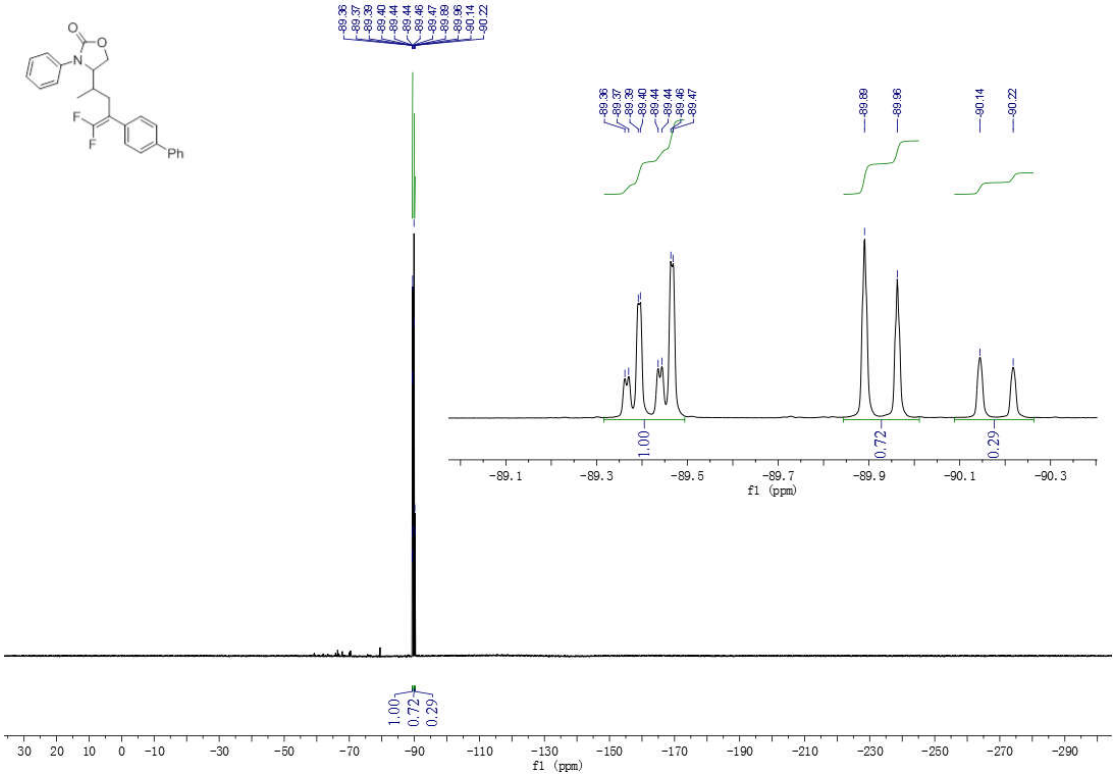
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of 3g



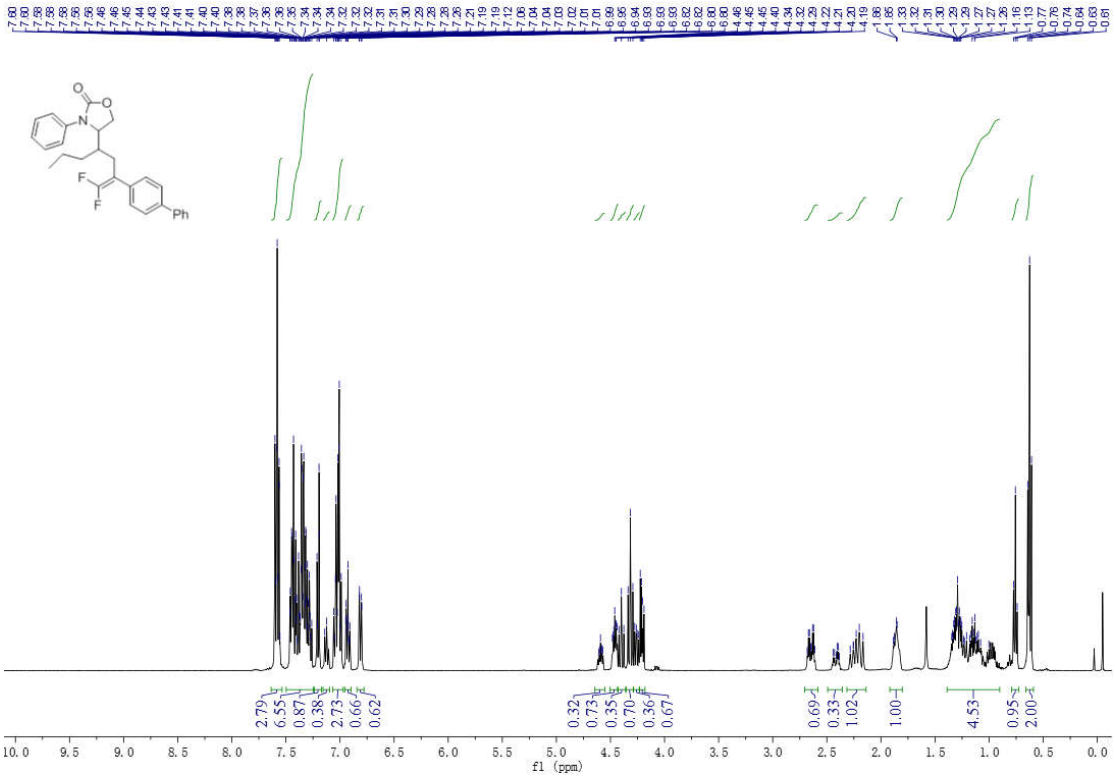
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3g



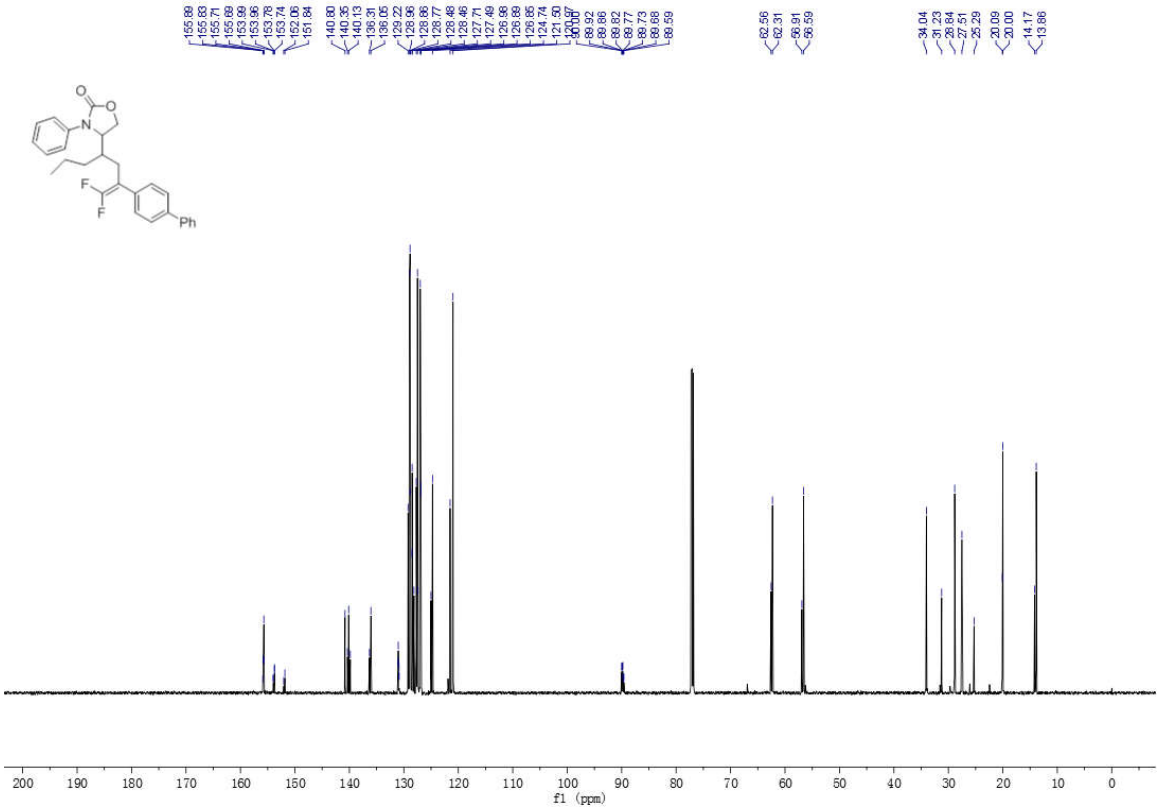
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3g



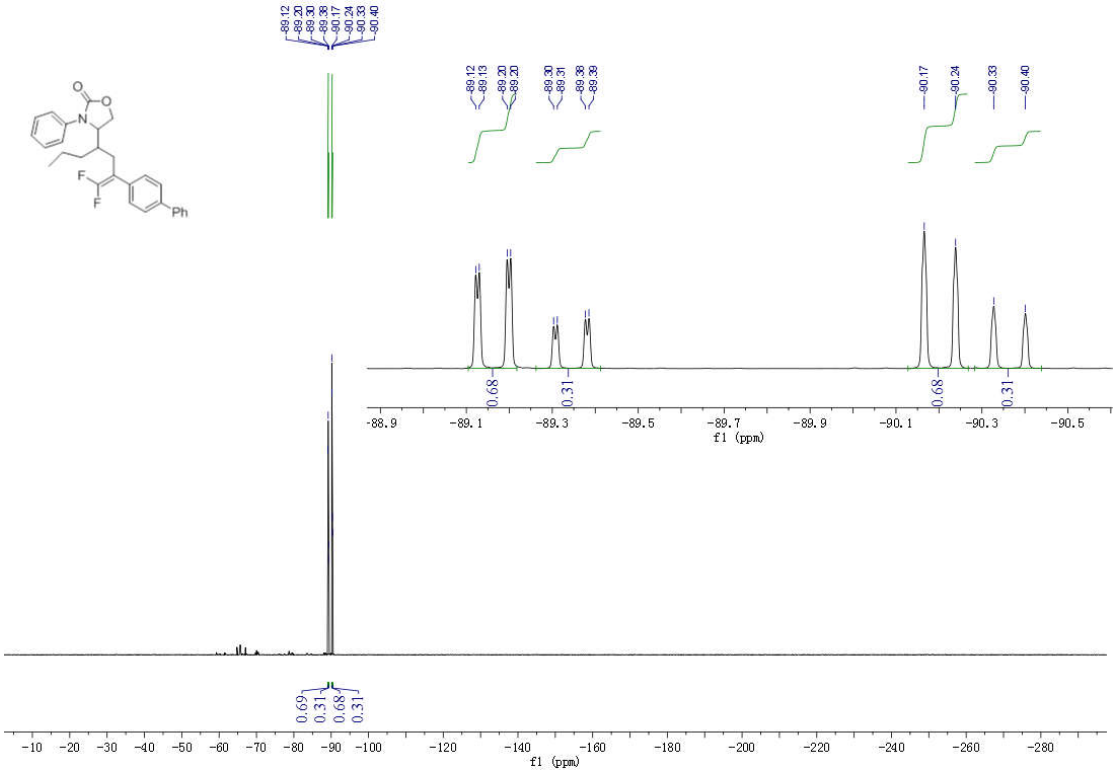
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3h



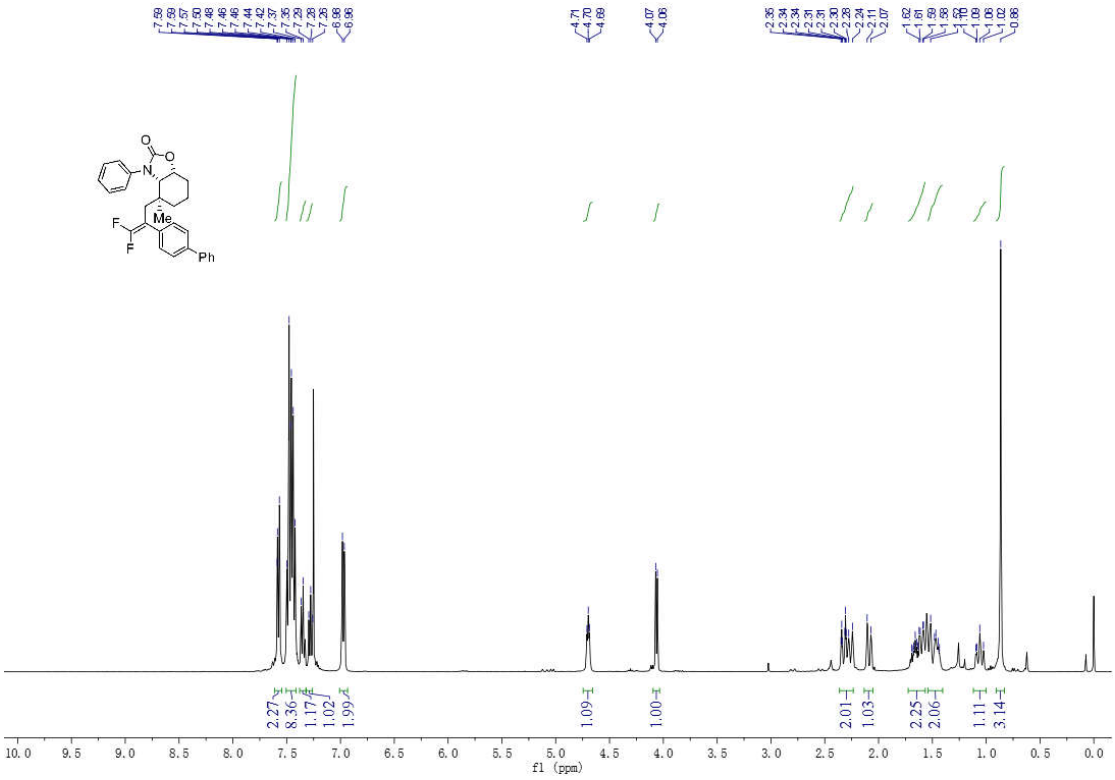
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3h



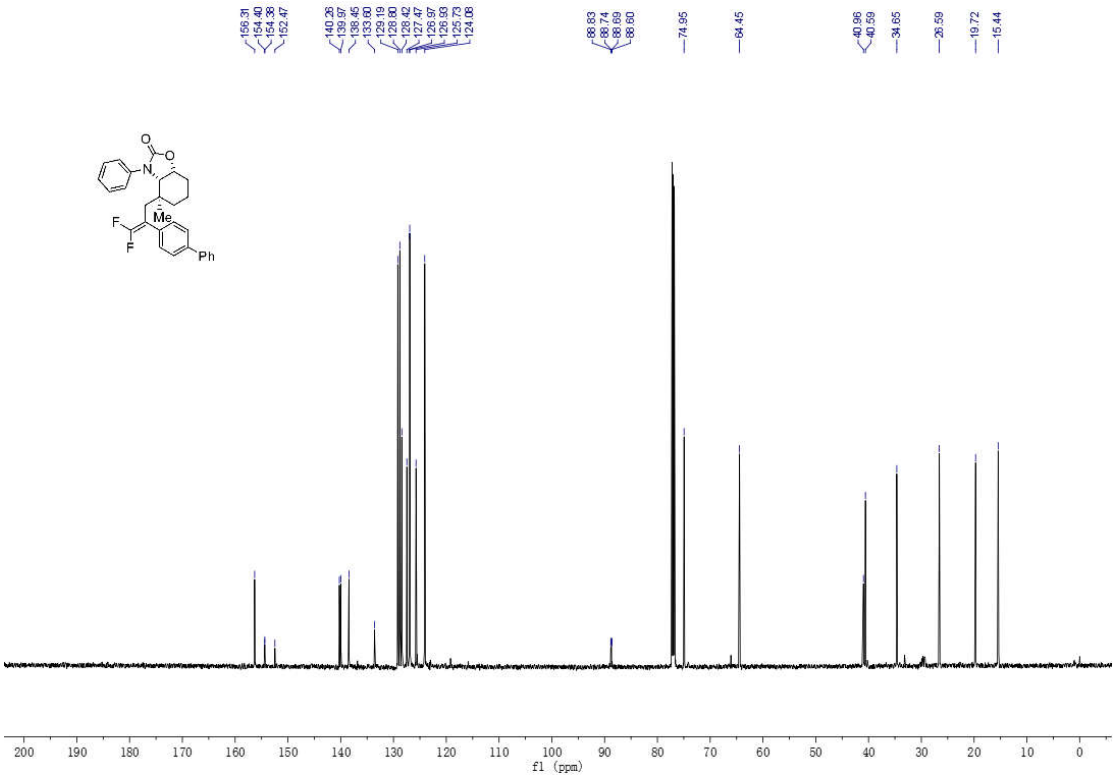
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3h



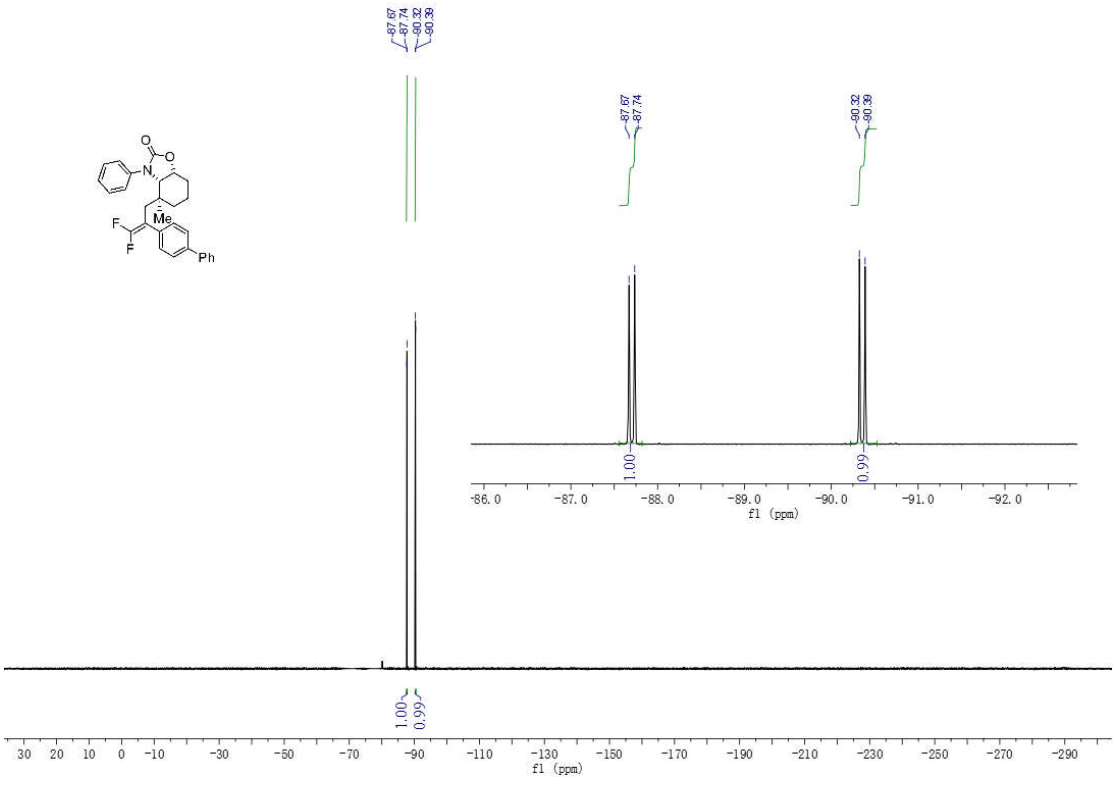
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3i



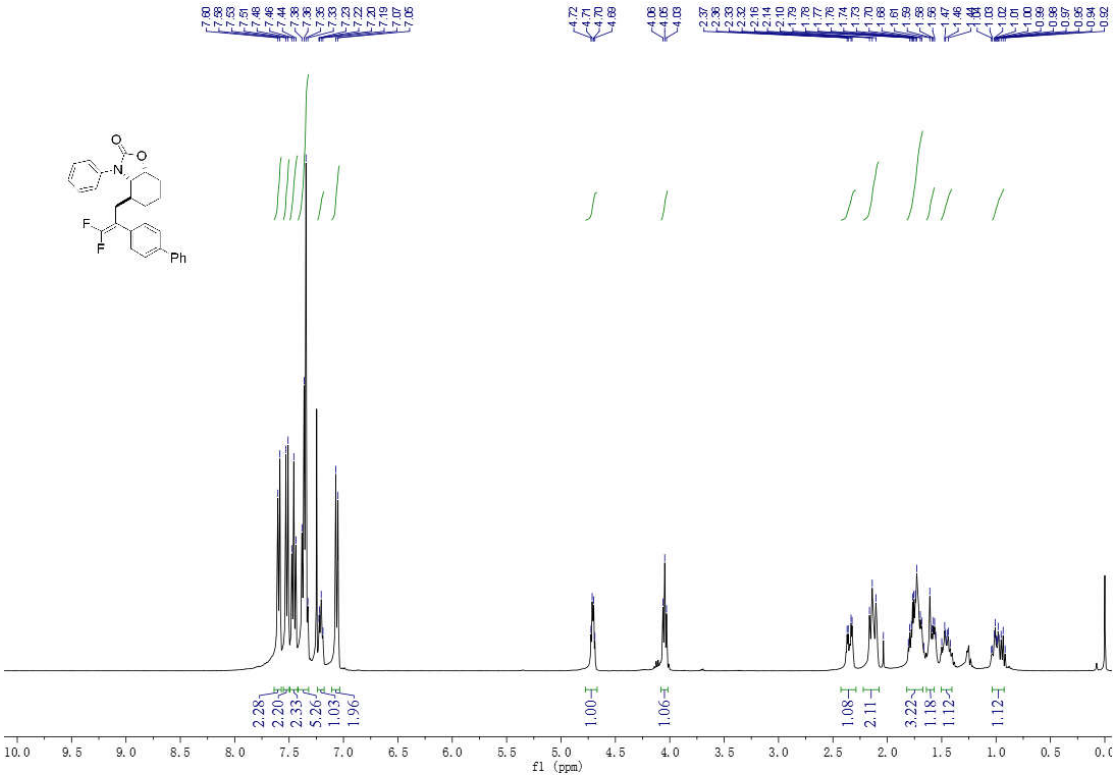
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3i



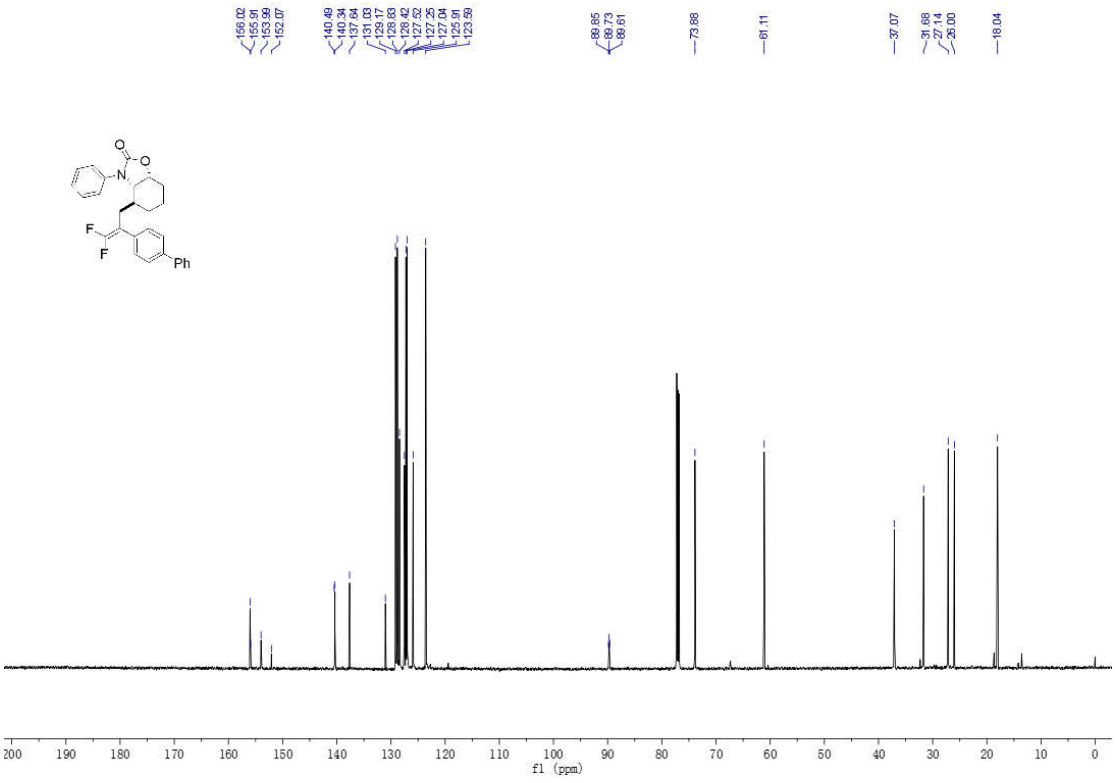
^{19}F NMR spectrum (564MHz, $CDCl_3$, 23 ºC) of 3i



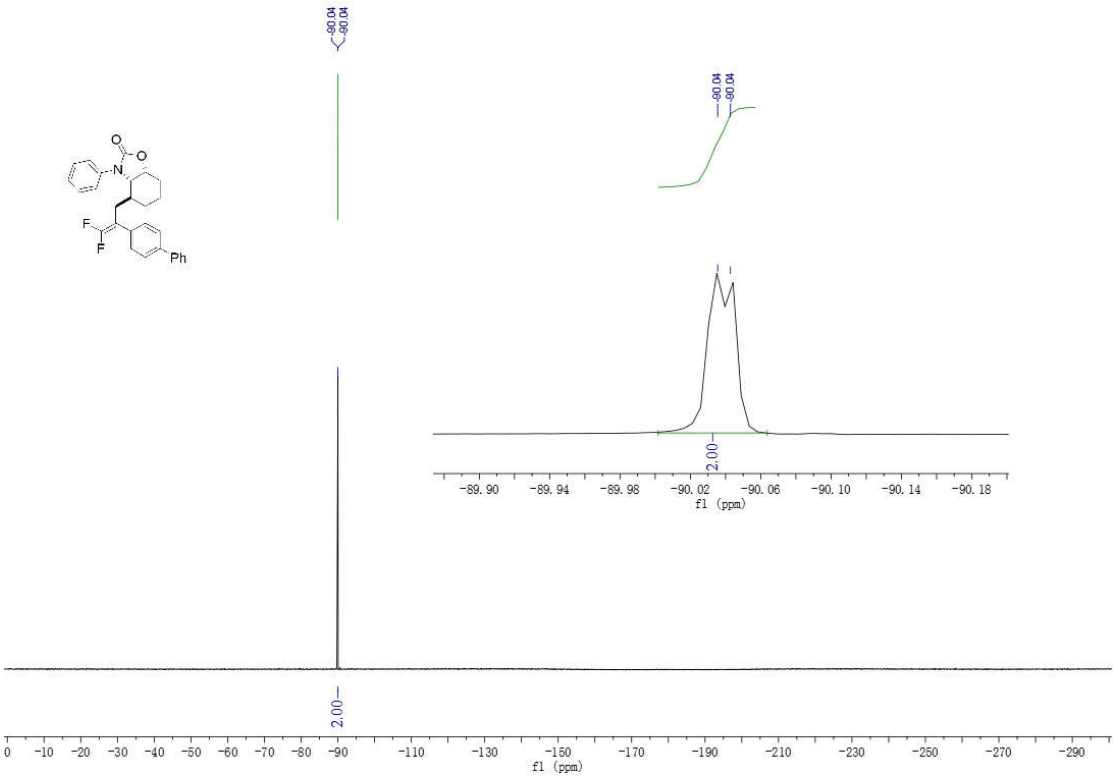
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 3j



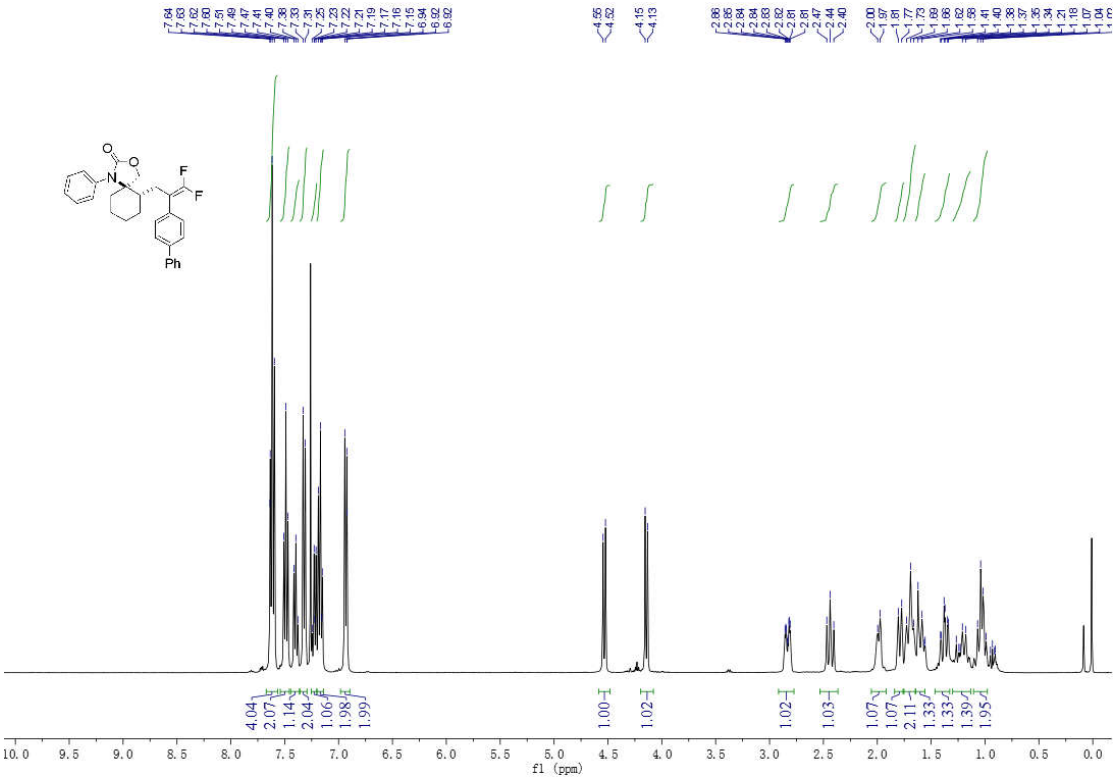
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3j



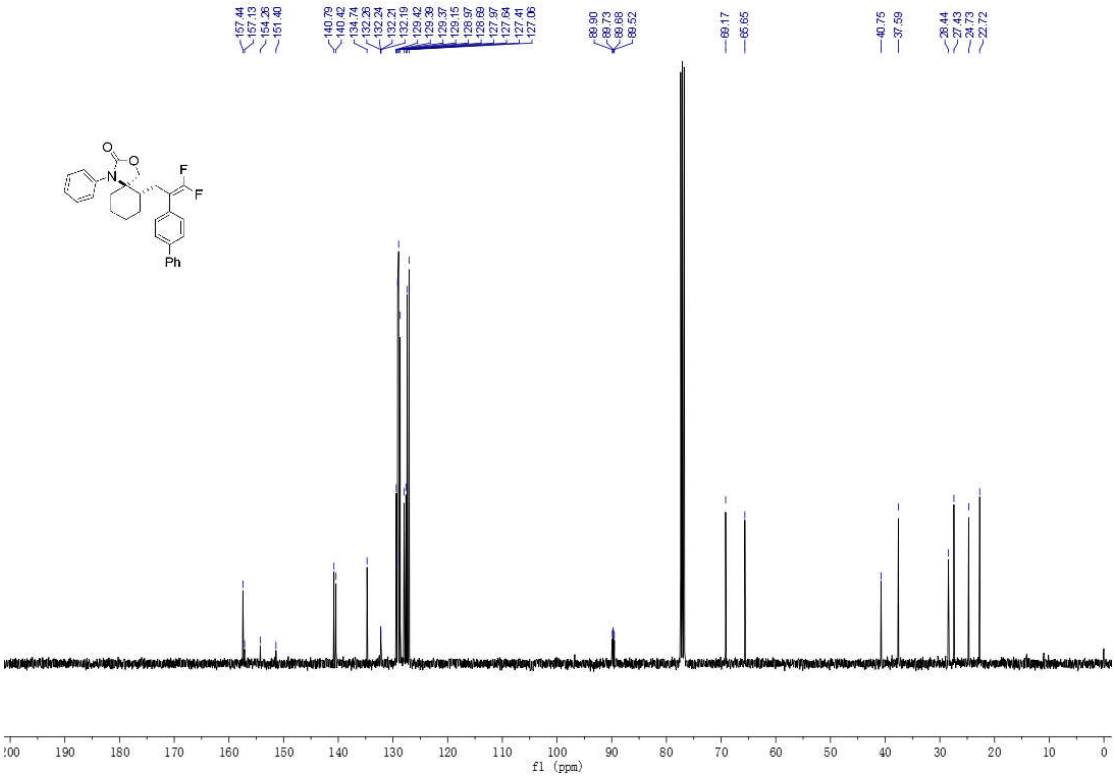
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3j



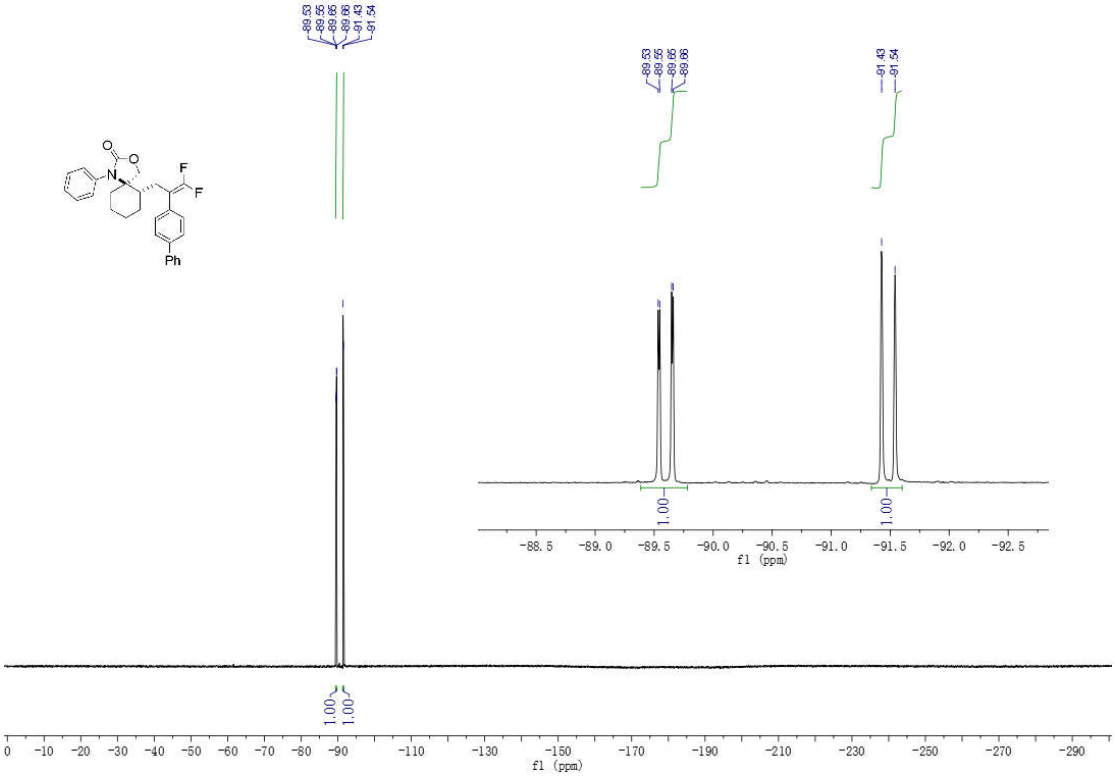
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3k



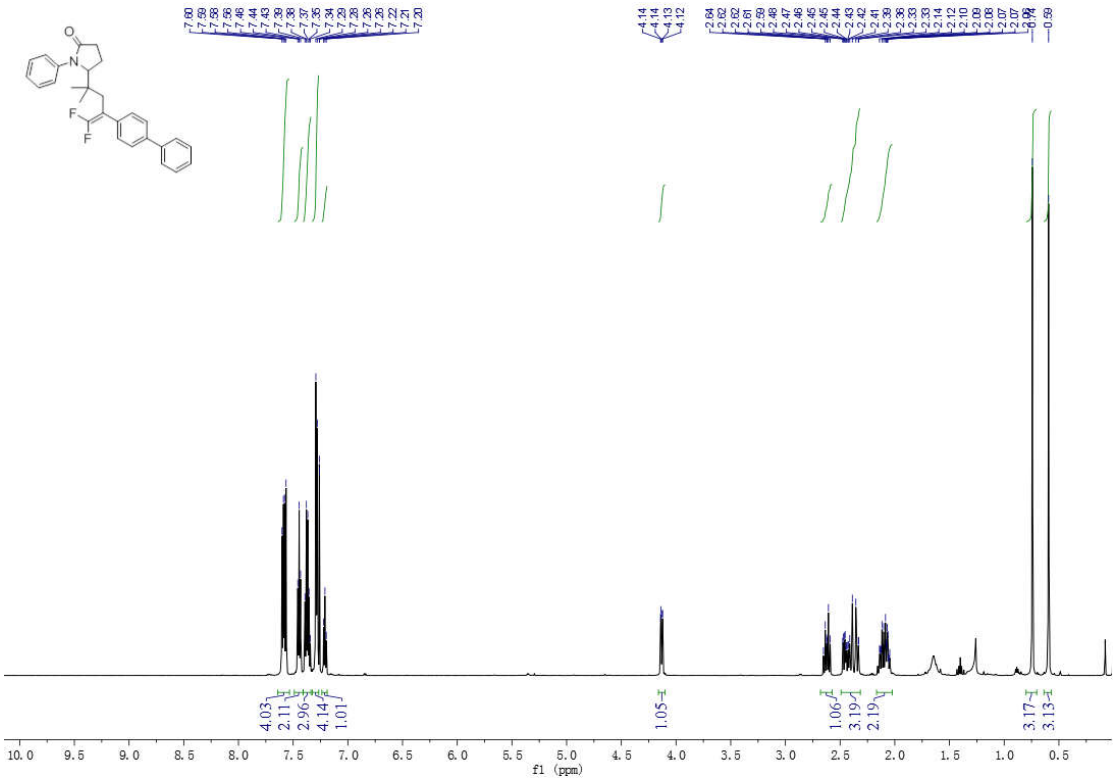
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3k



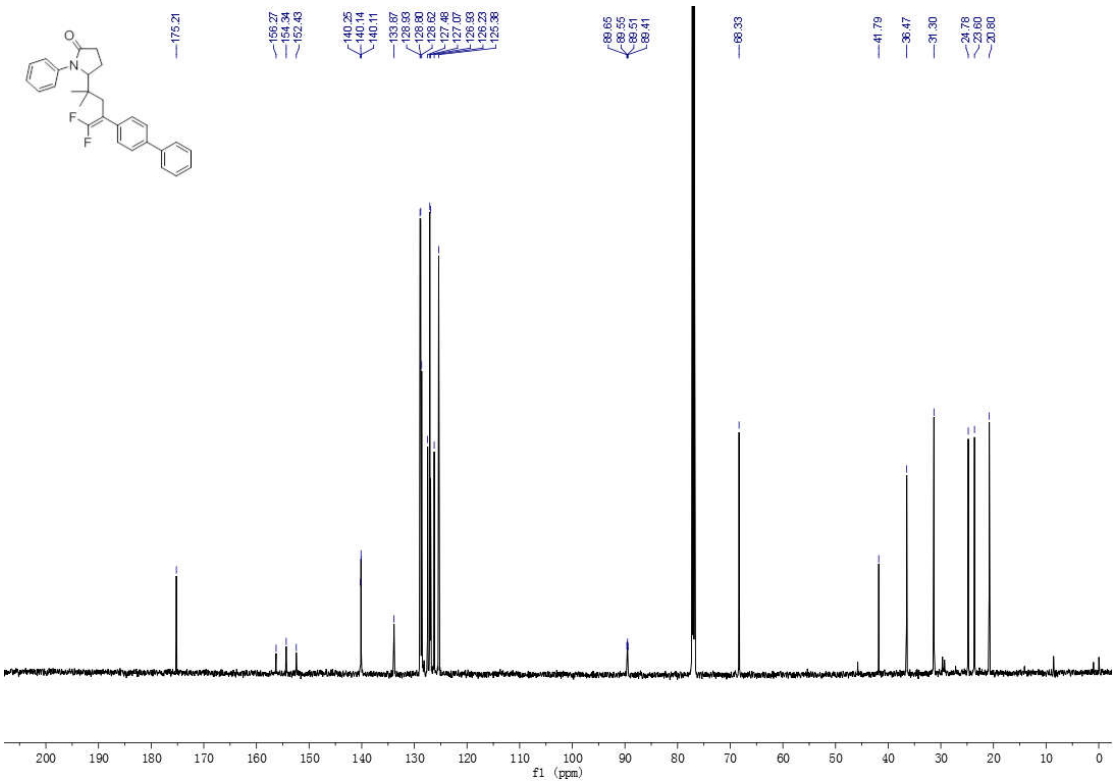
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3k



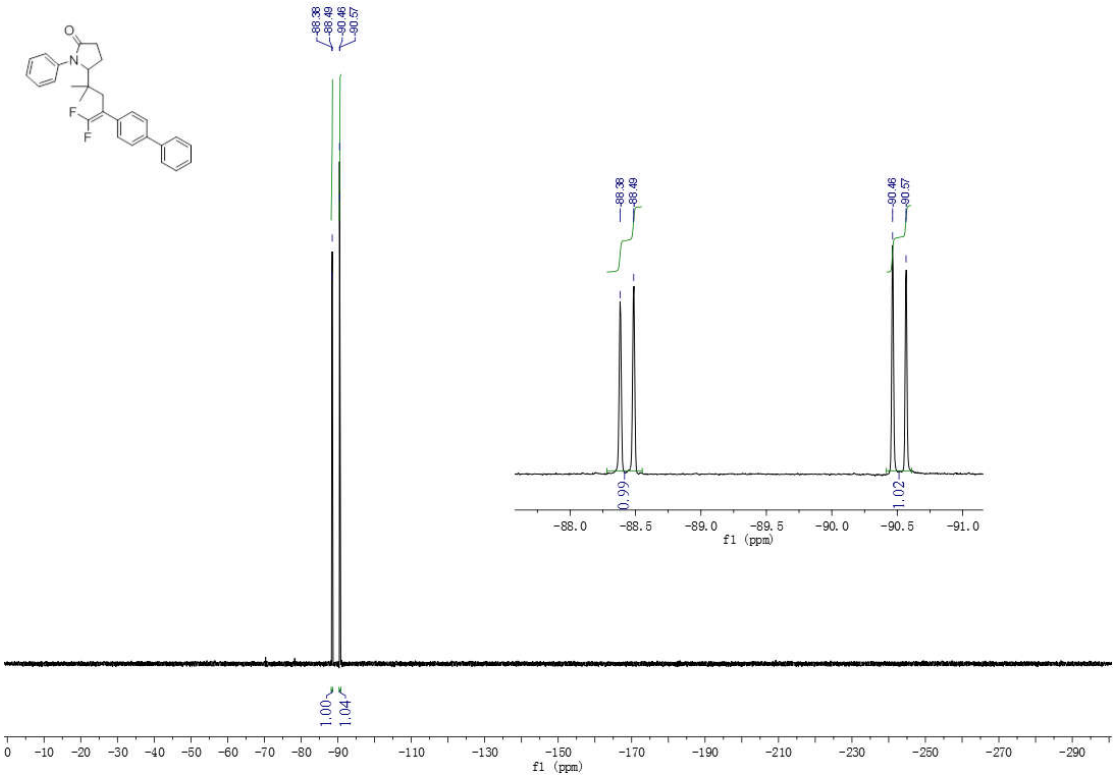
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 3l



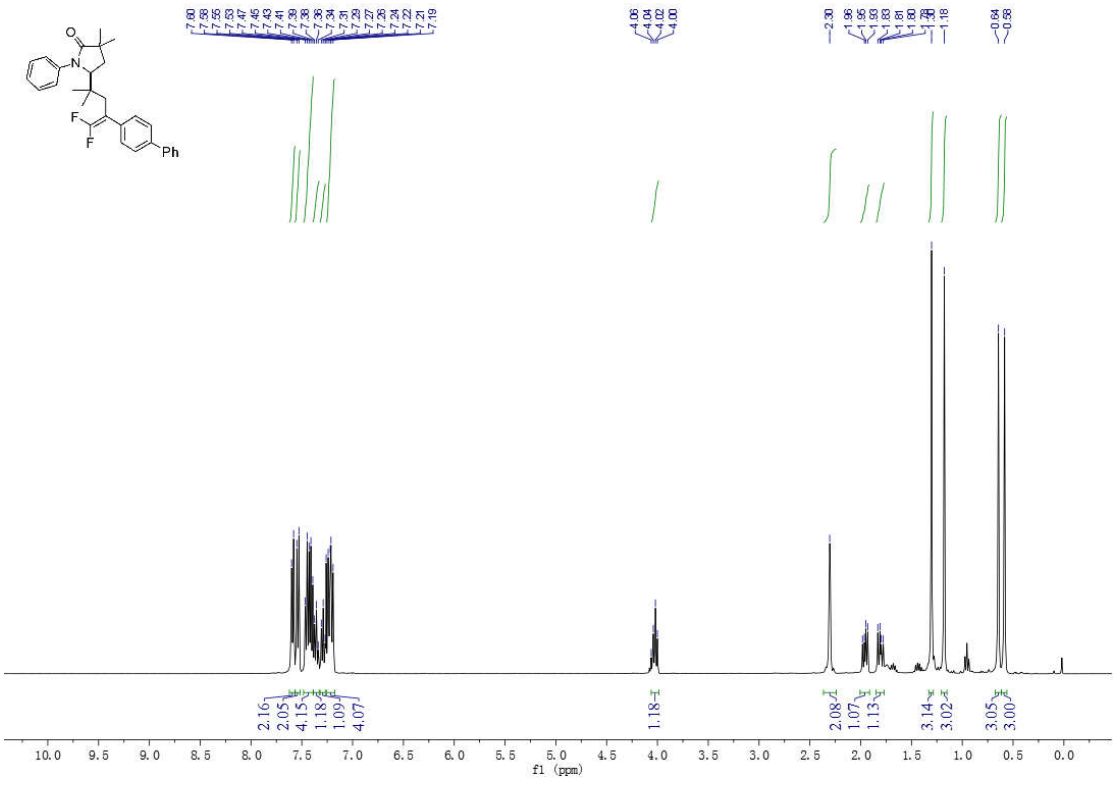
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3l



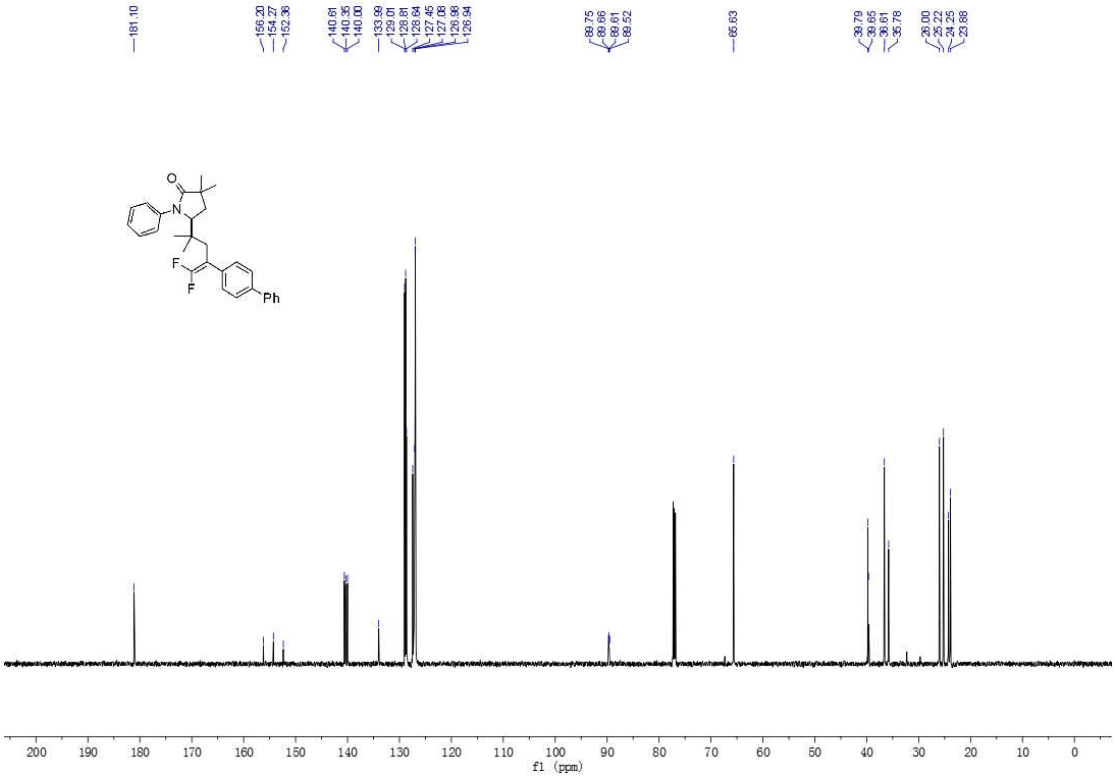
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3l



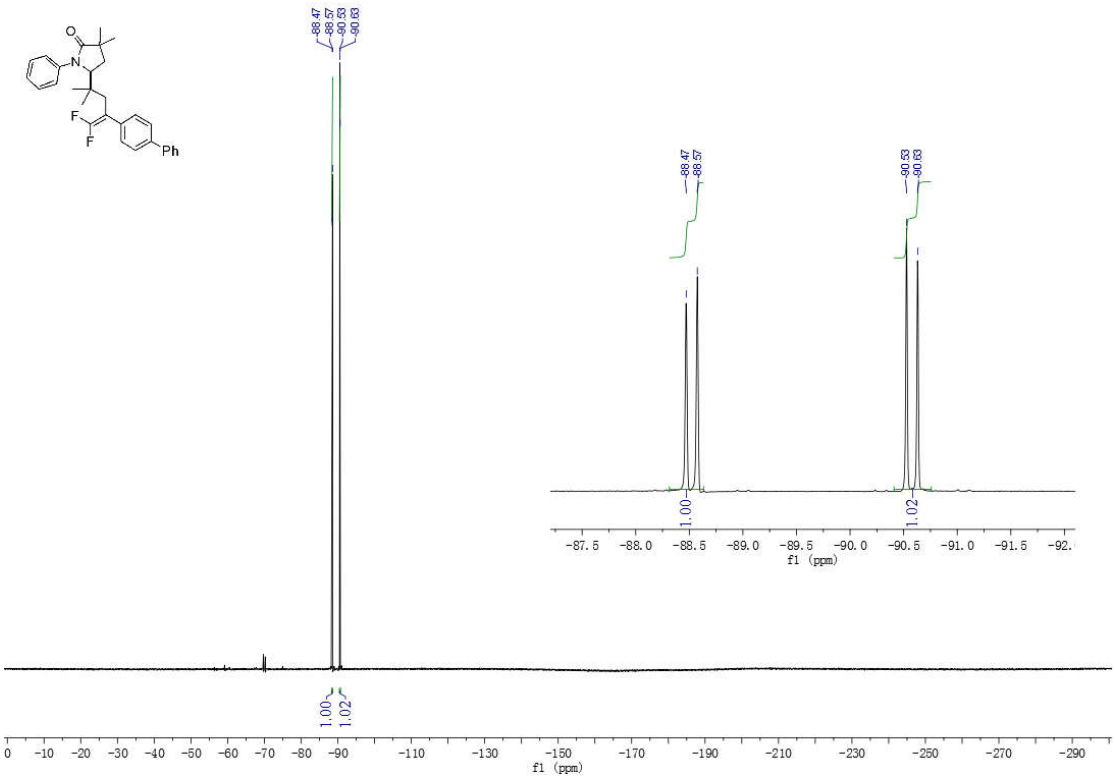
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3m



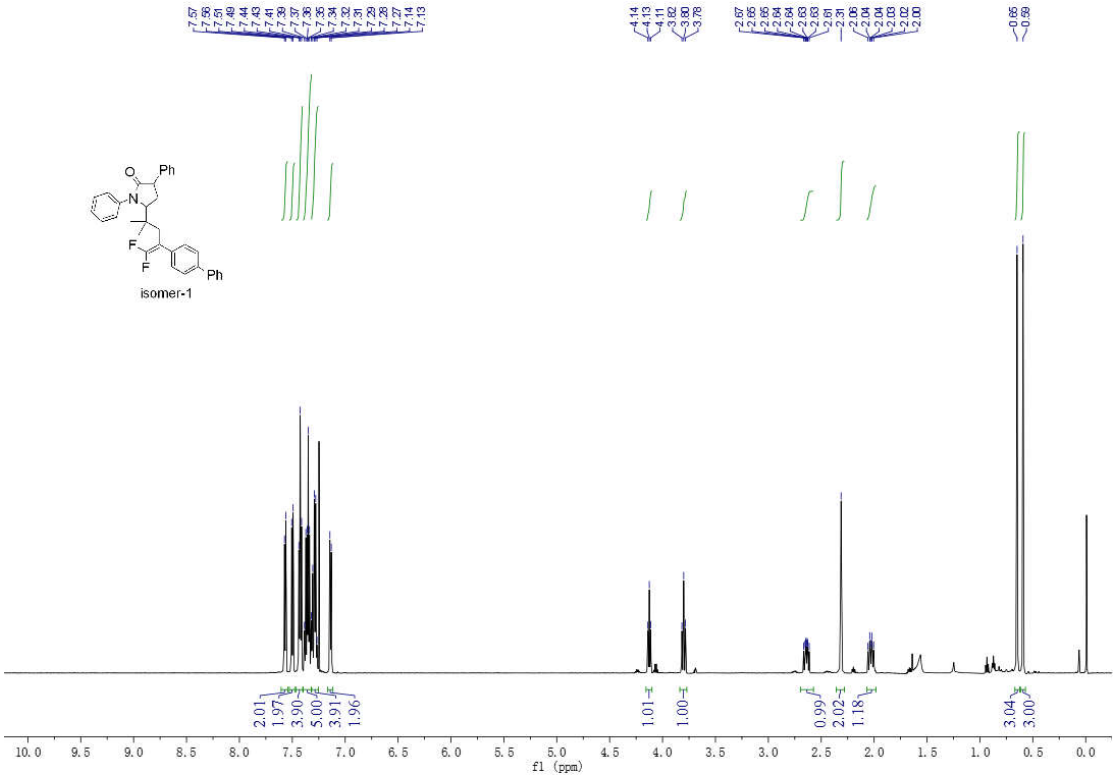
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3m



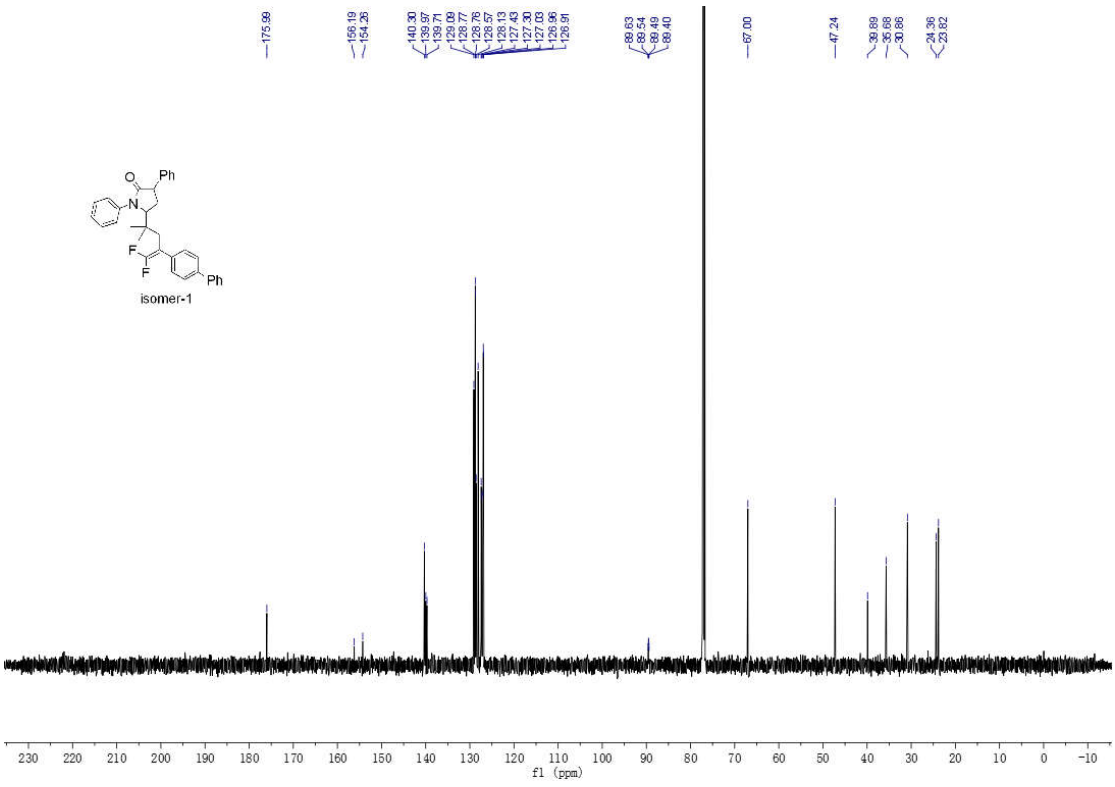
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 °C) of 3m



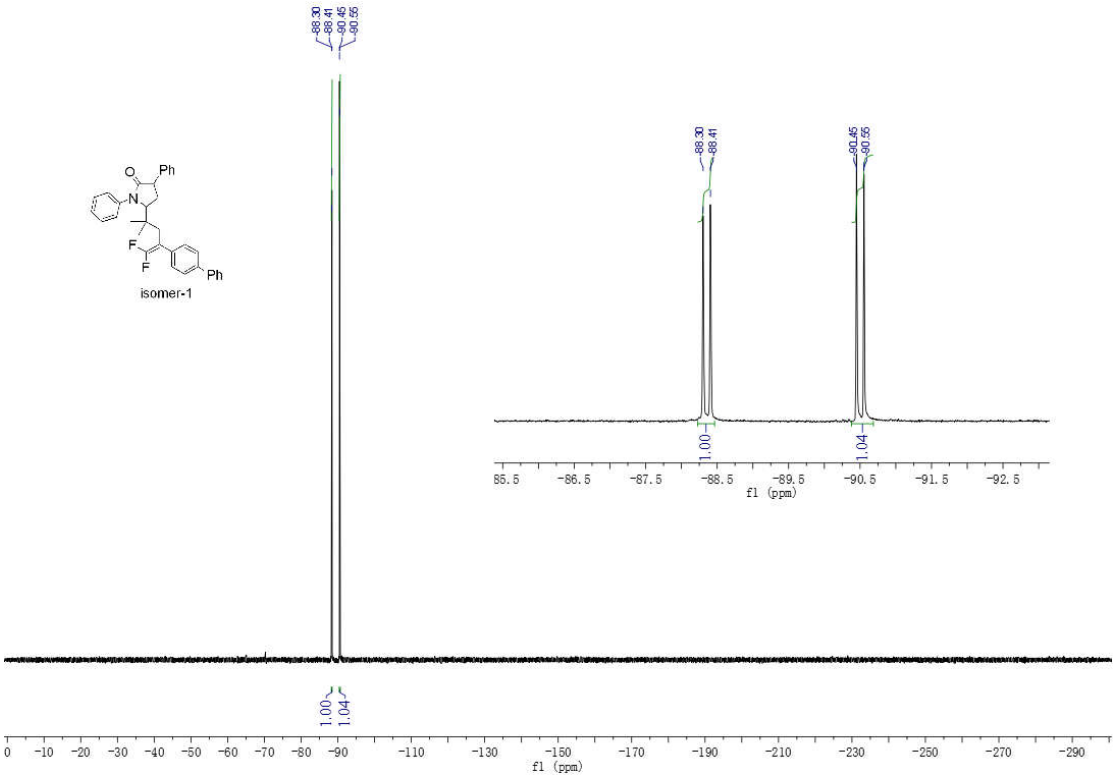
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 3n-1



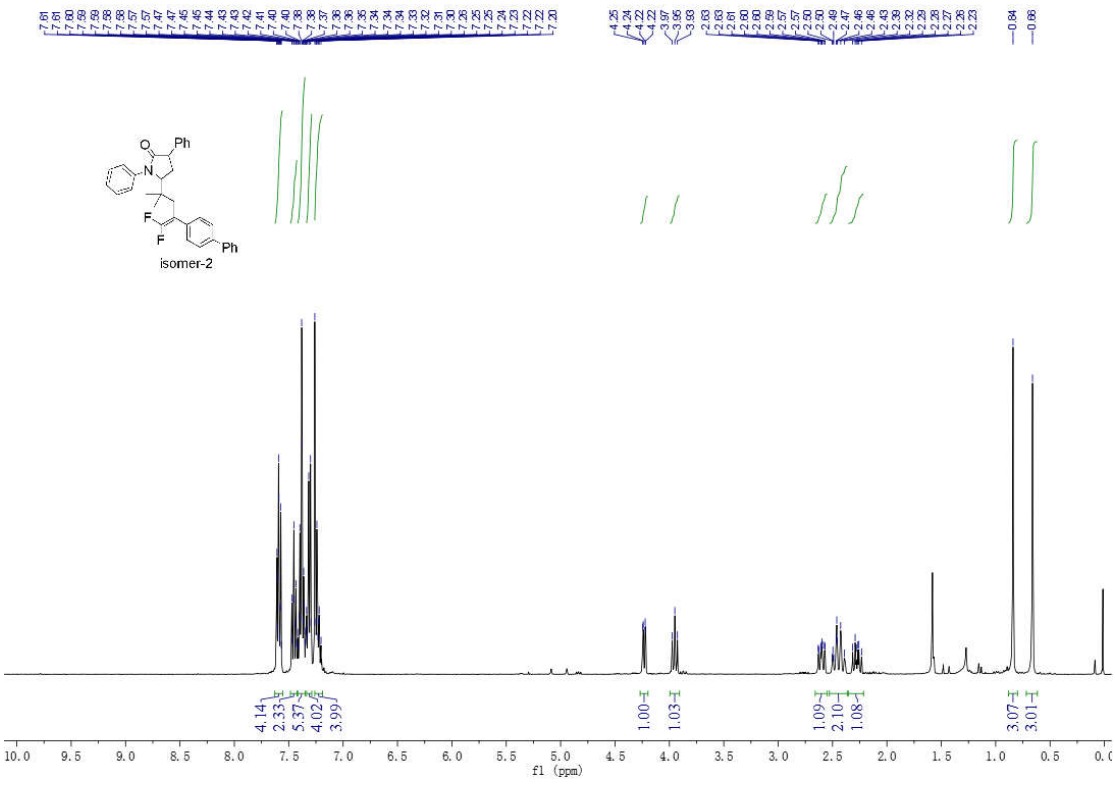
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3n-1



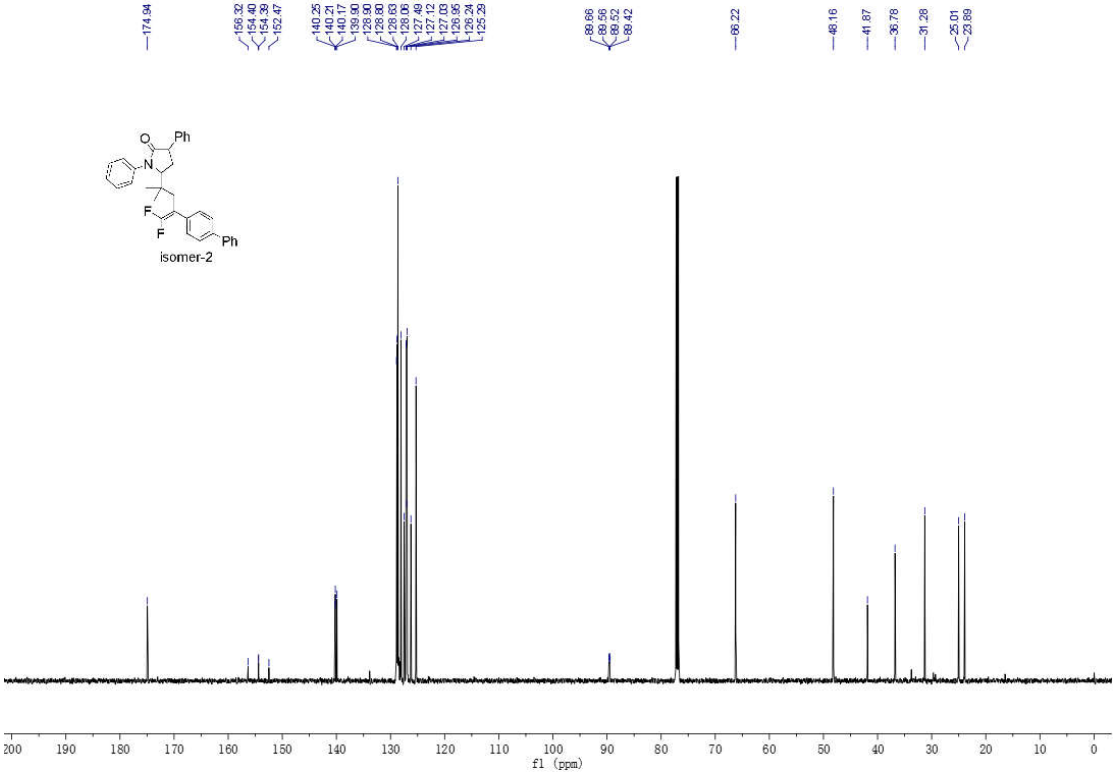
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3n-1



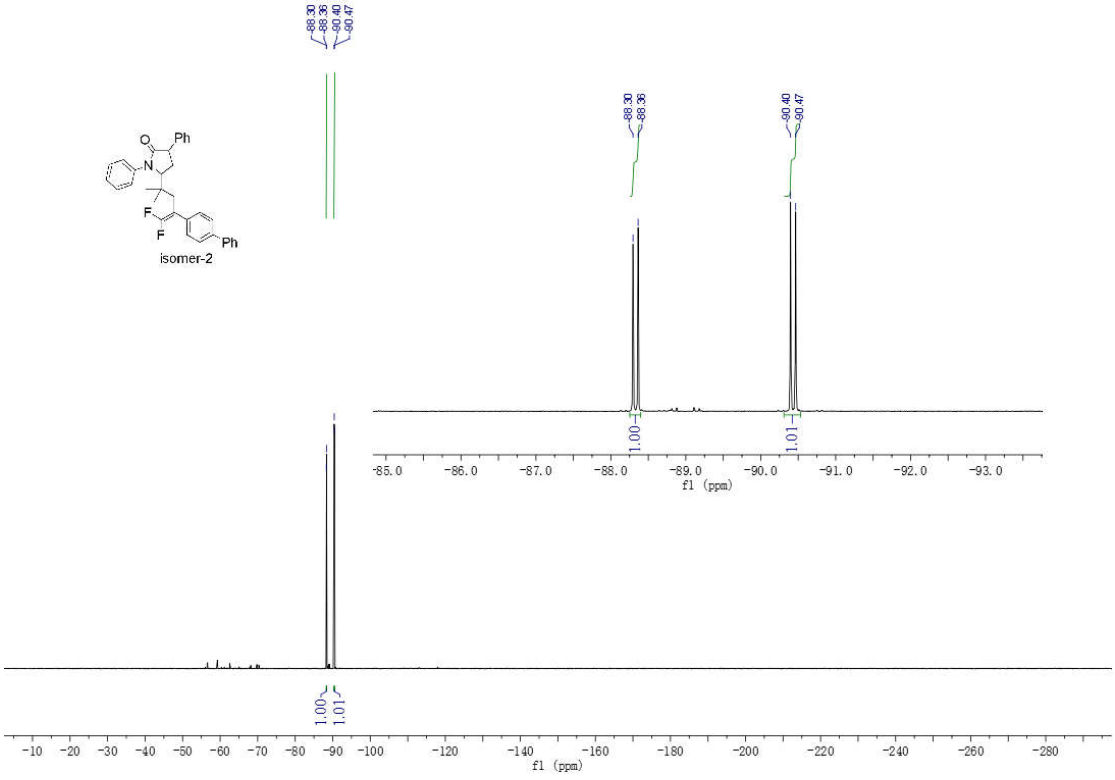
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3n-2



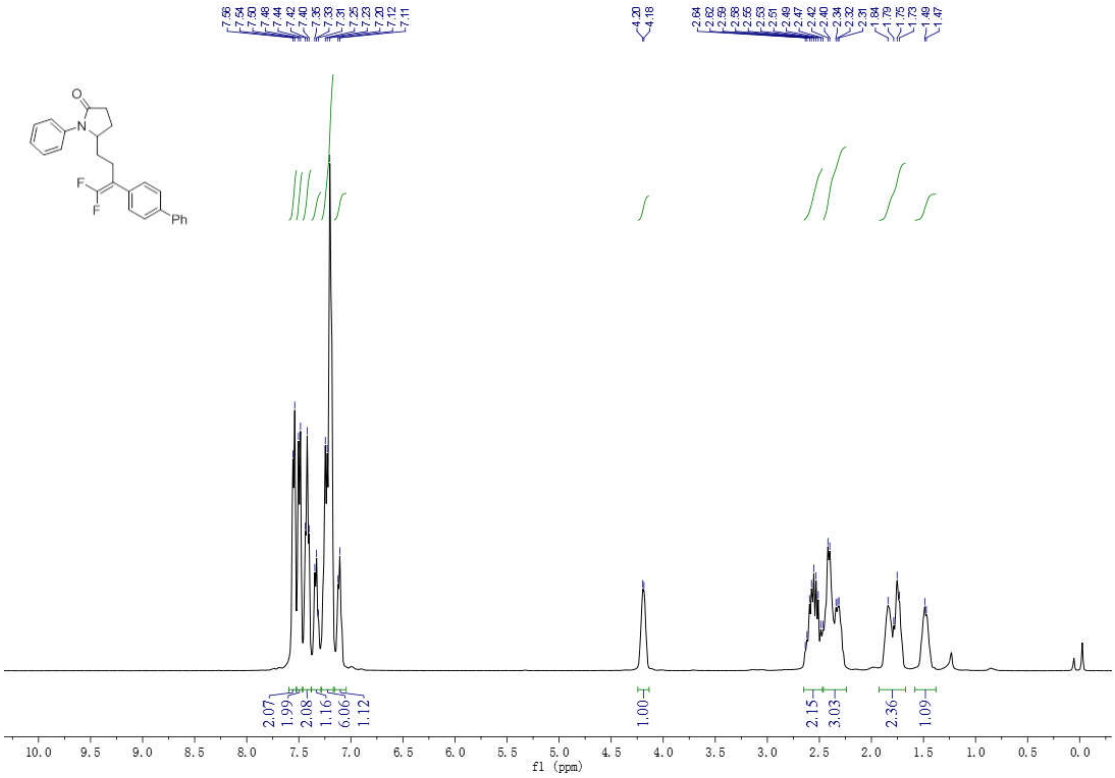
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 3n-2



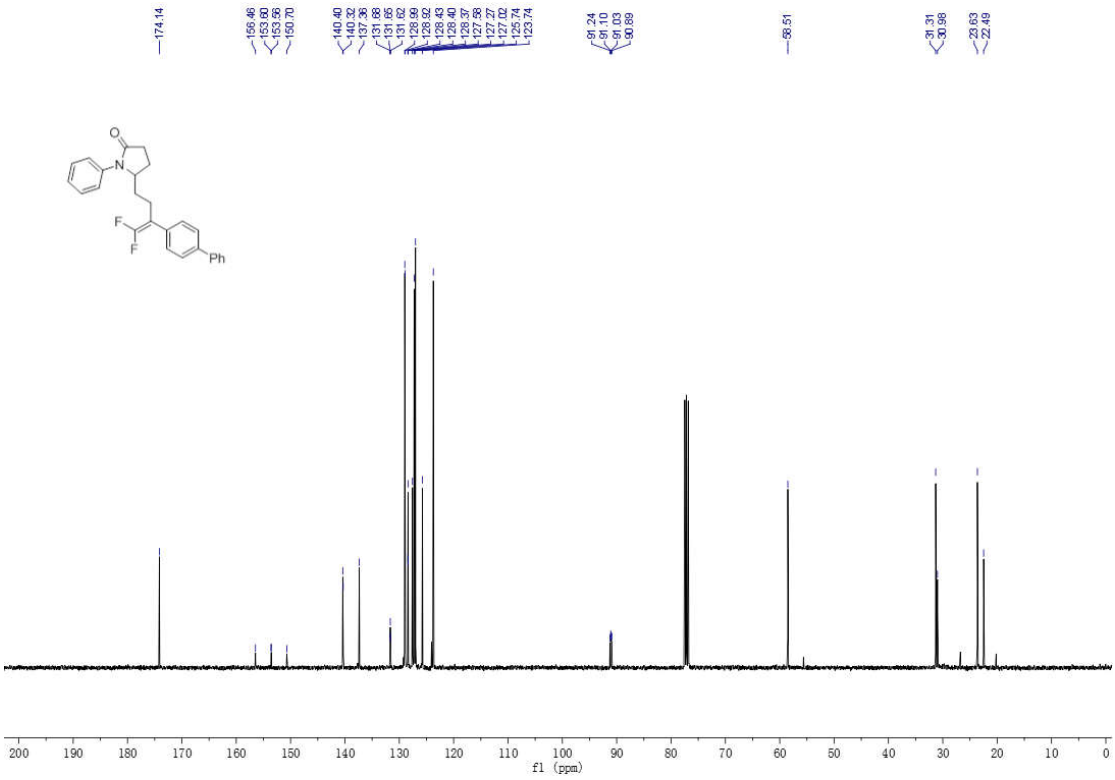
^{19}F NMR spectrum (564MHz, $CDCl_3$, 23 ºC) of 3n-2



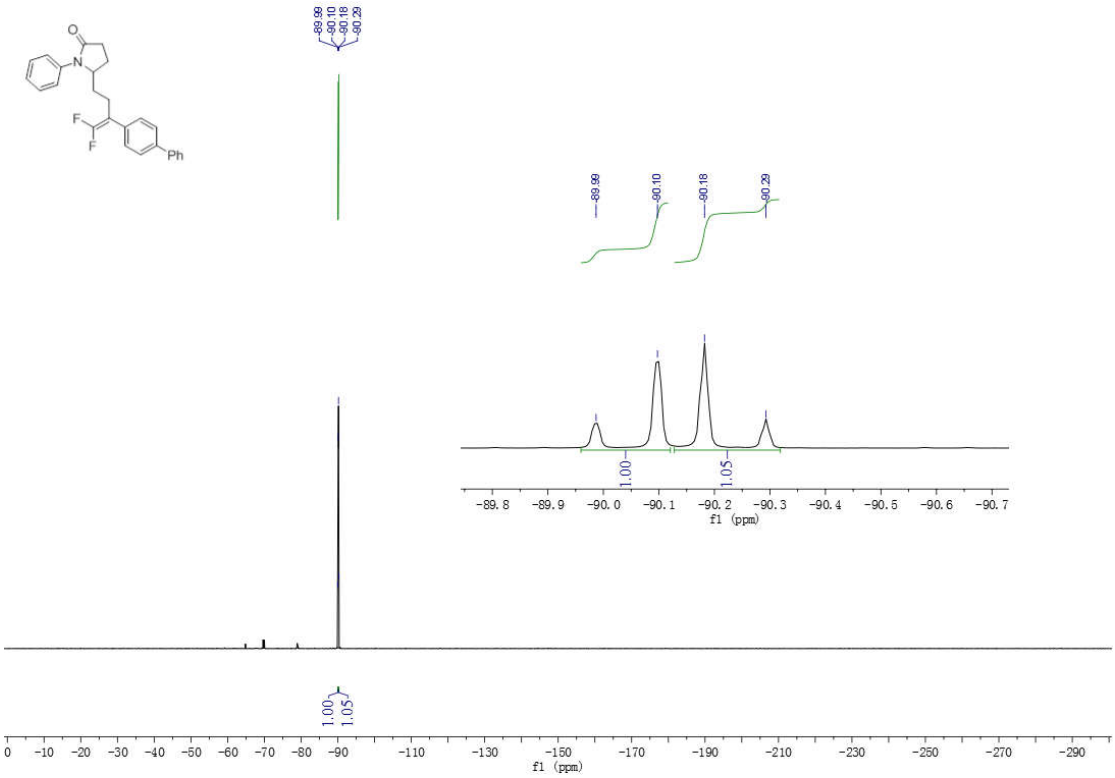
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 3o



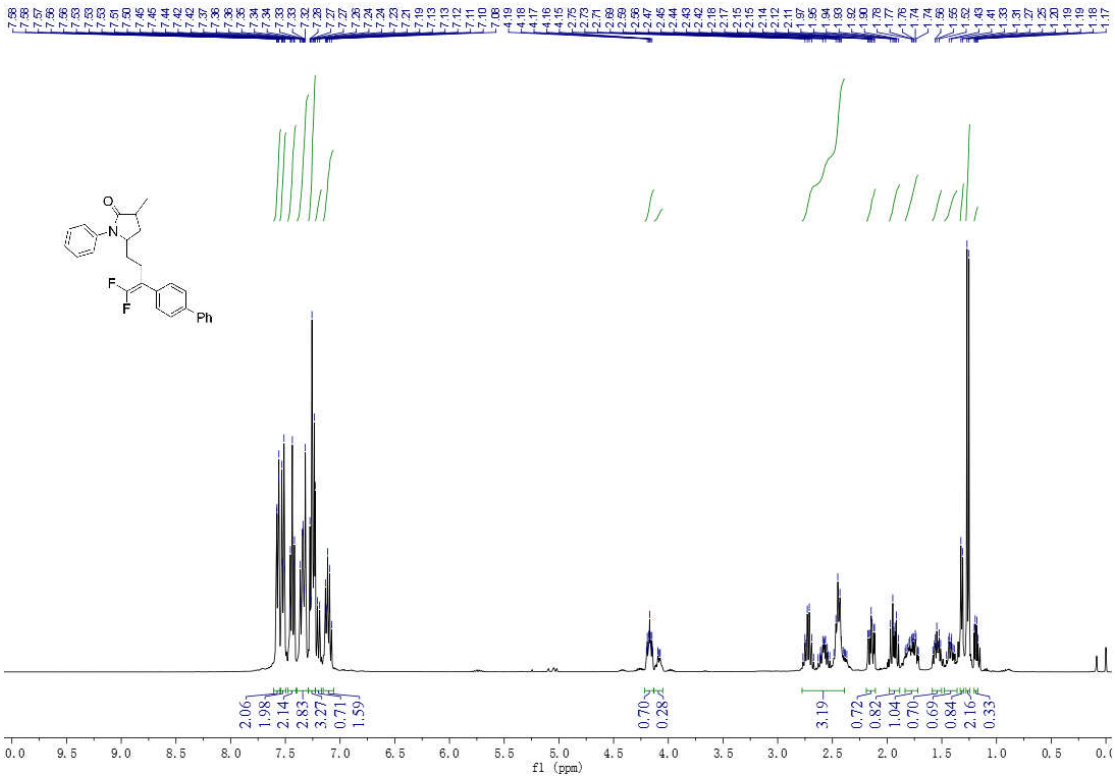
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3o



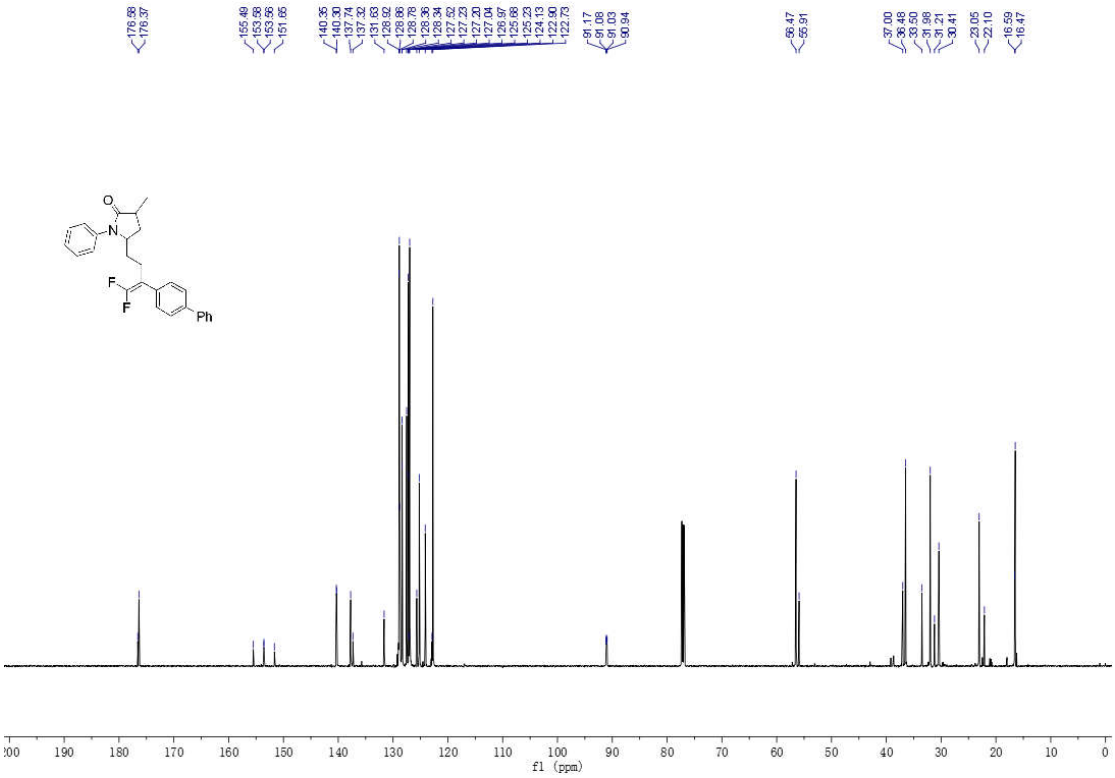
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3o



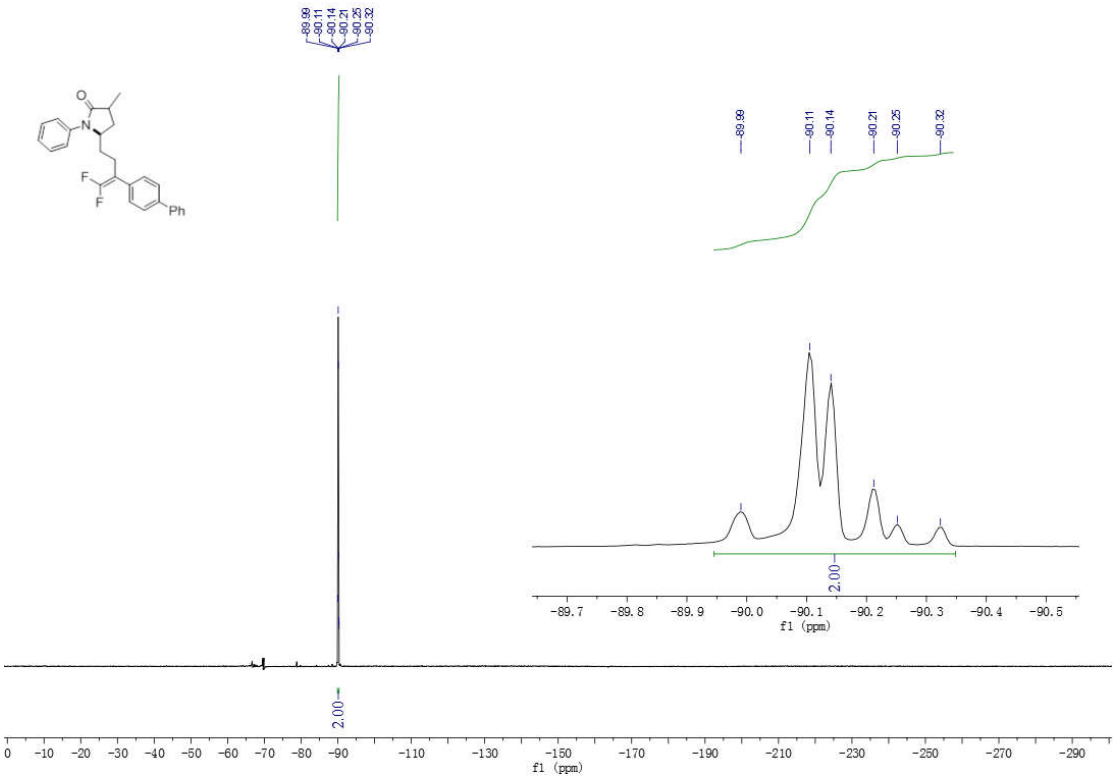
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 3p



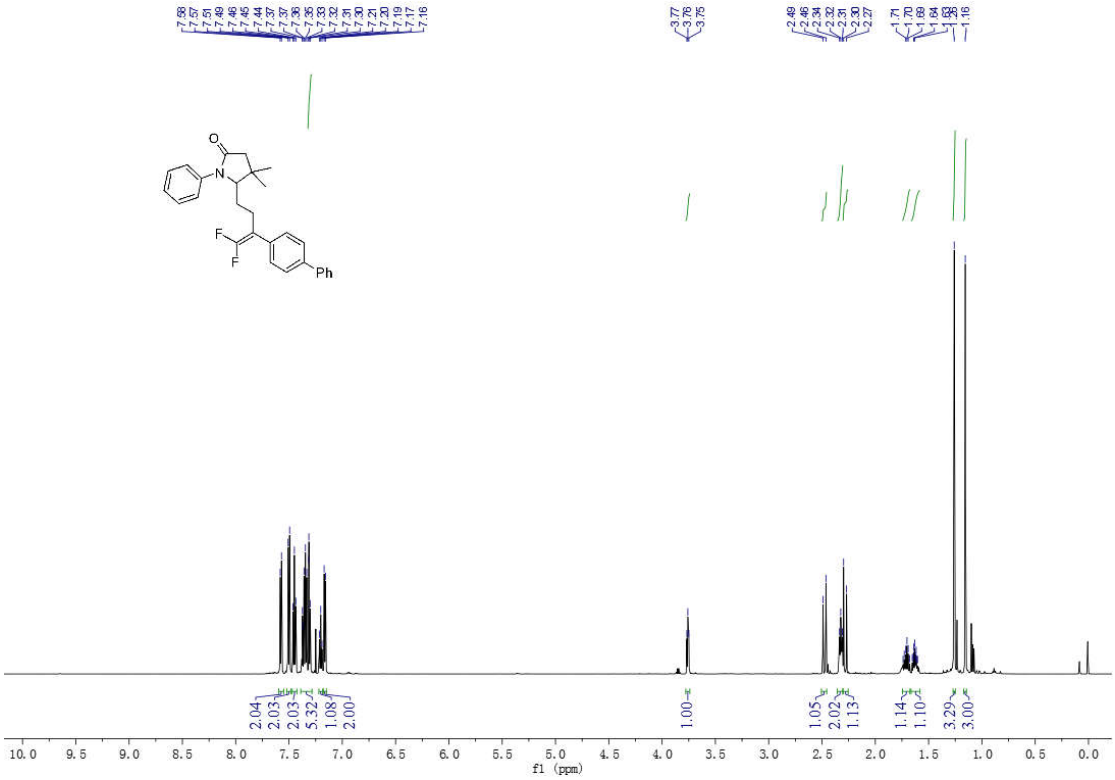
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3p



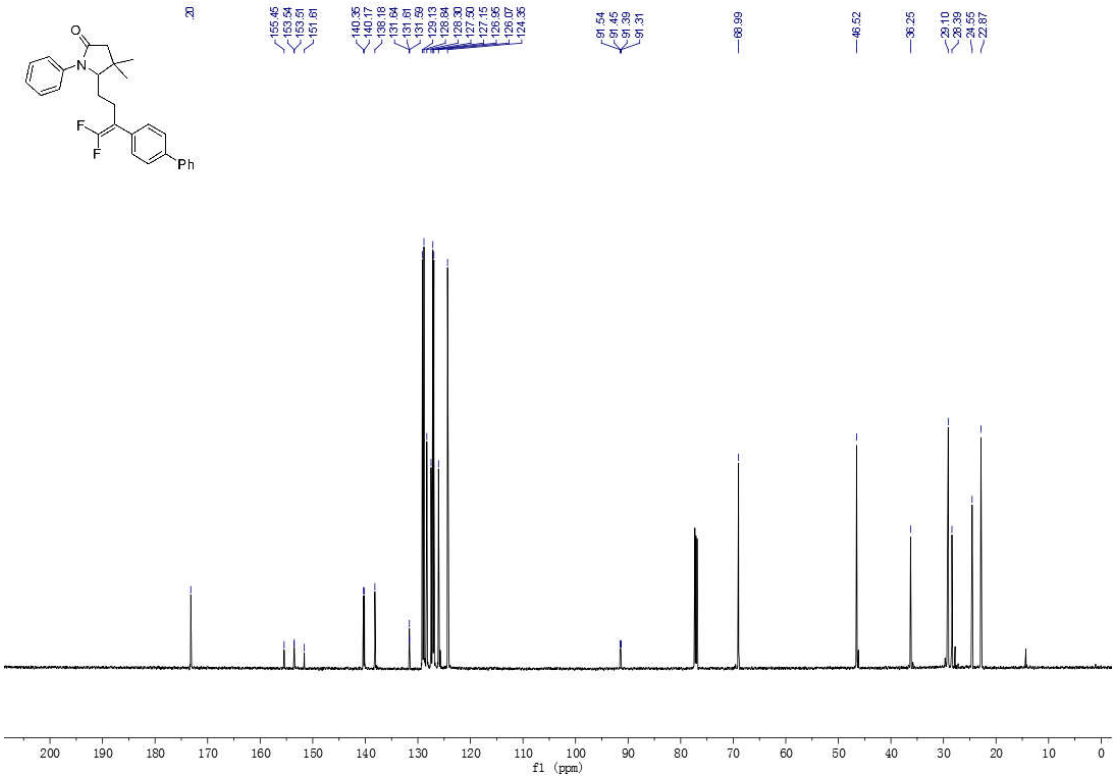
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 °C) of 3p



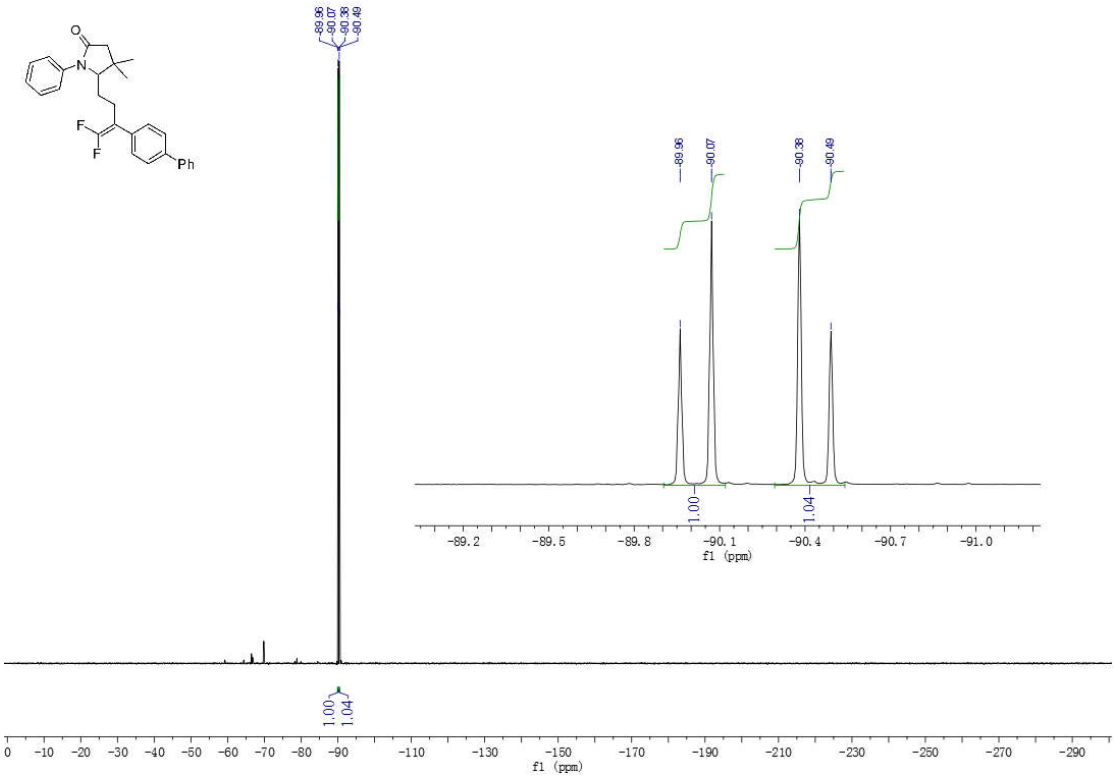
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 3q



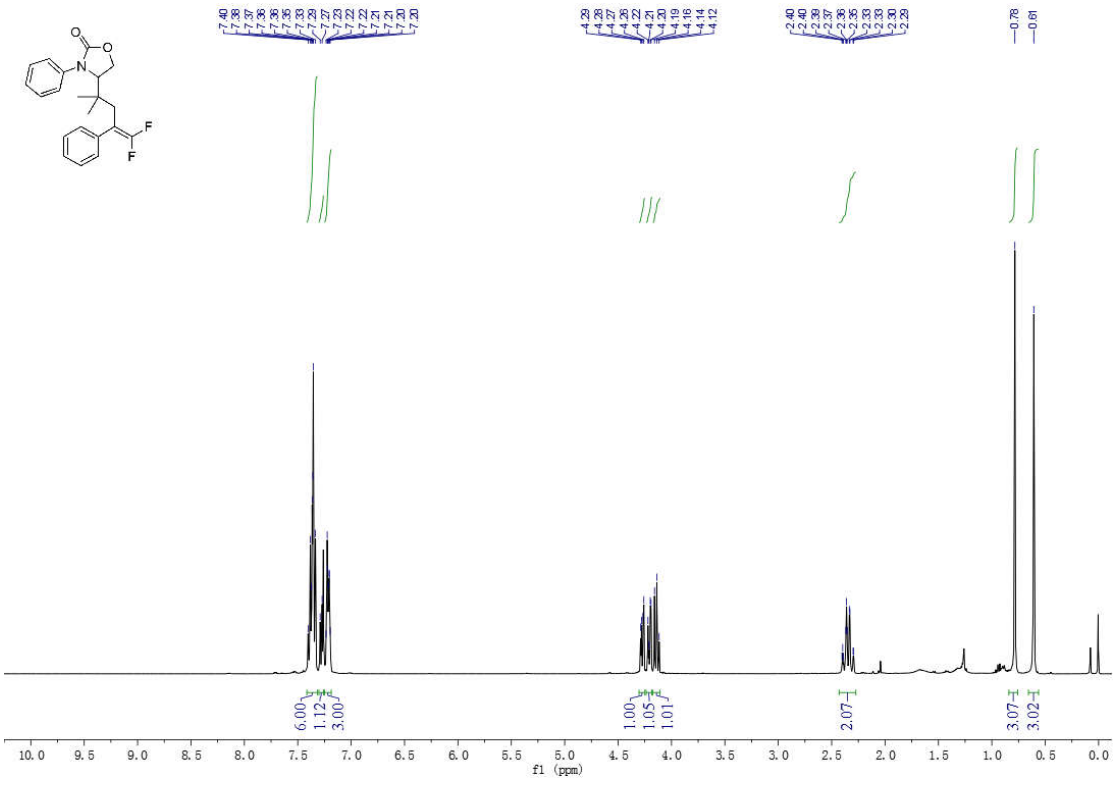
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 3q



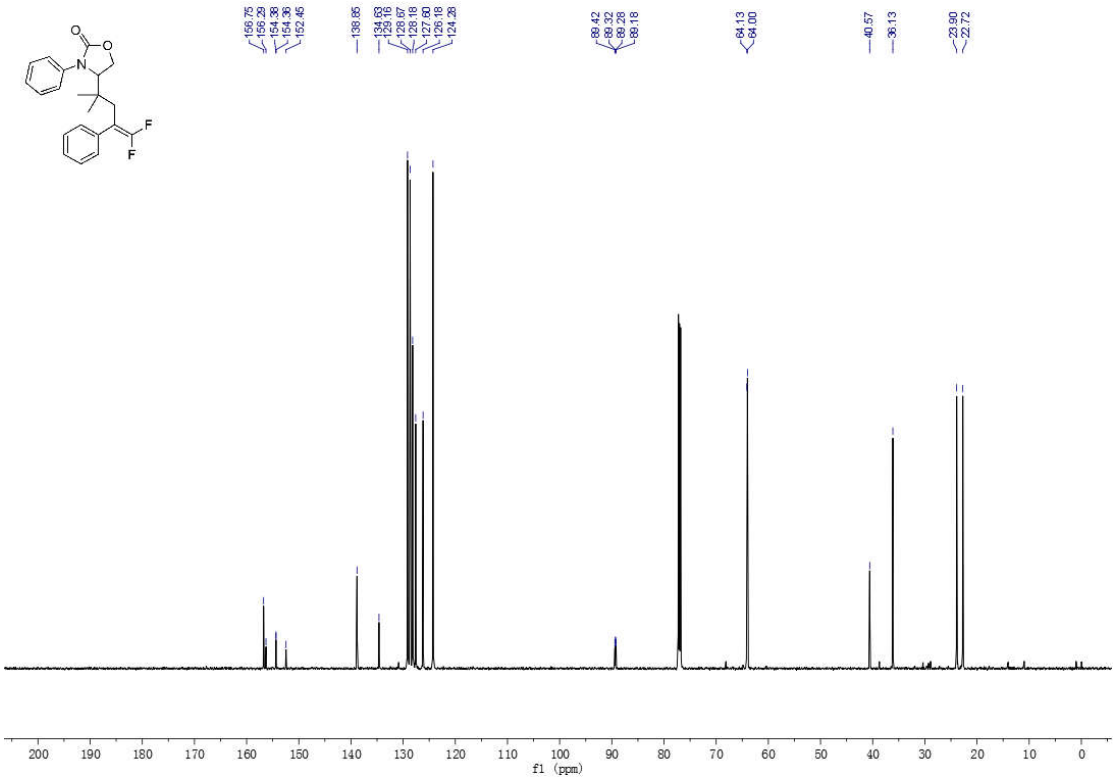
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 3q



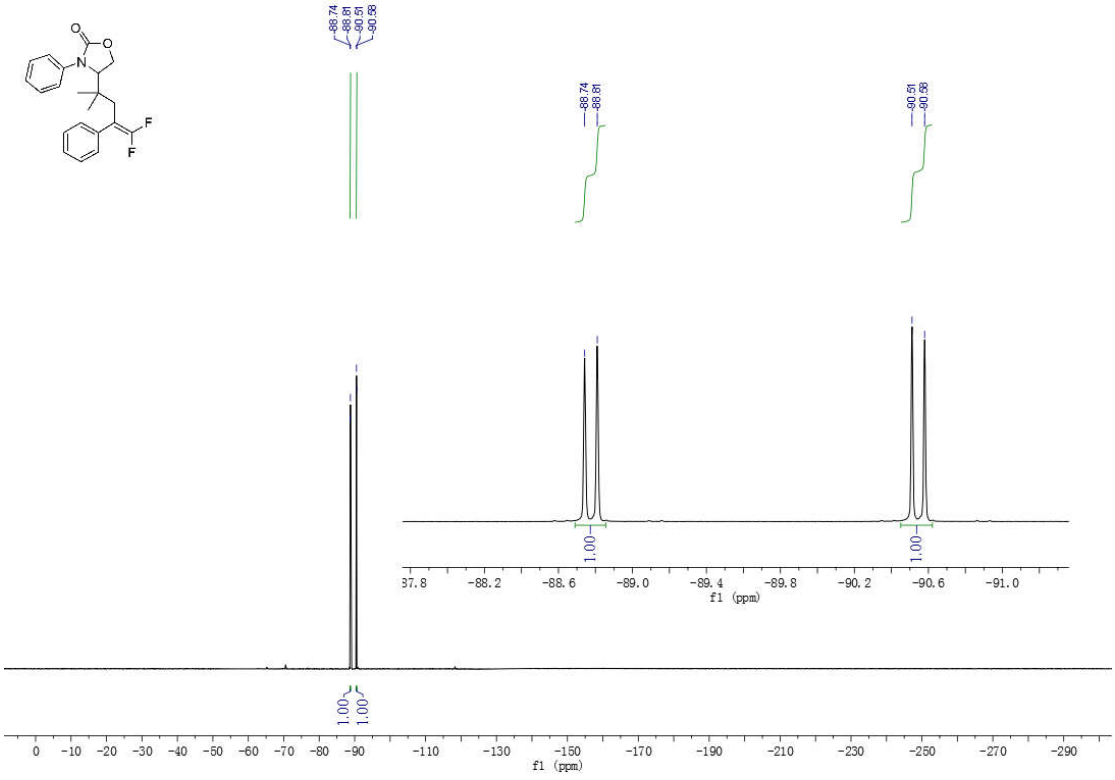
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4a



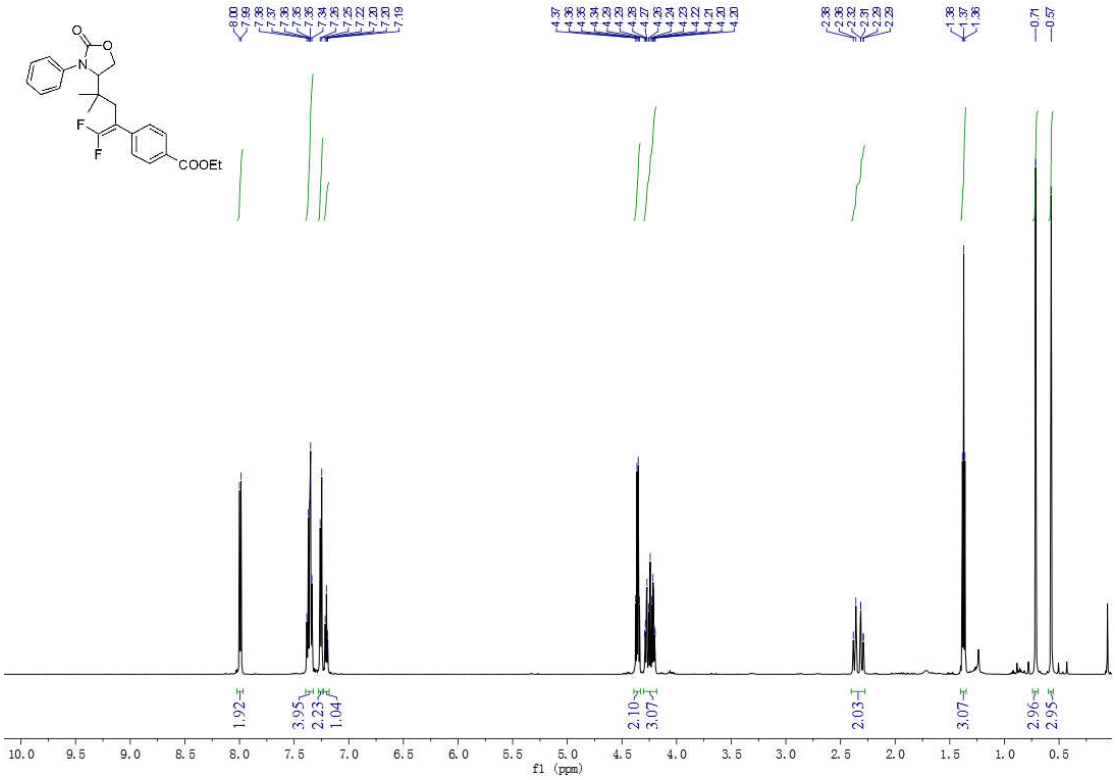
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 4a



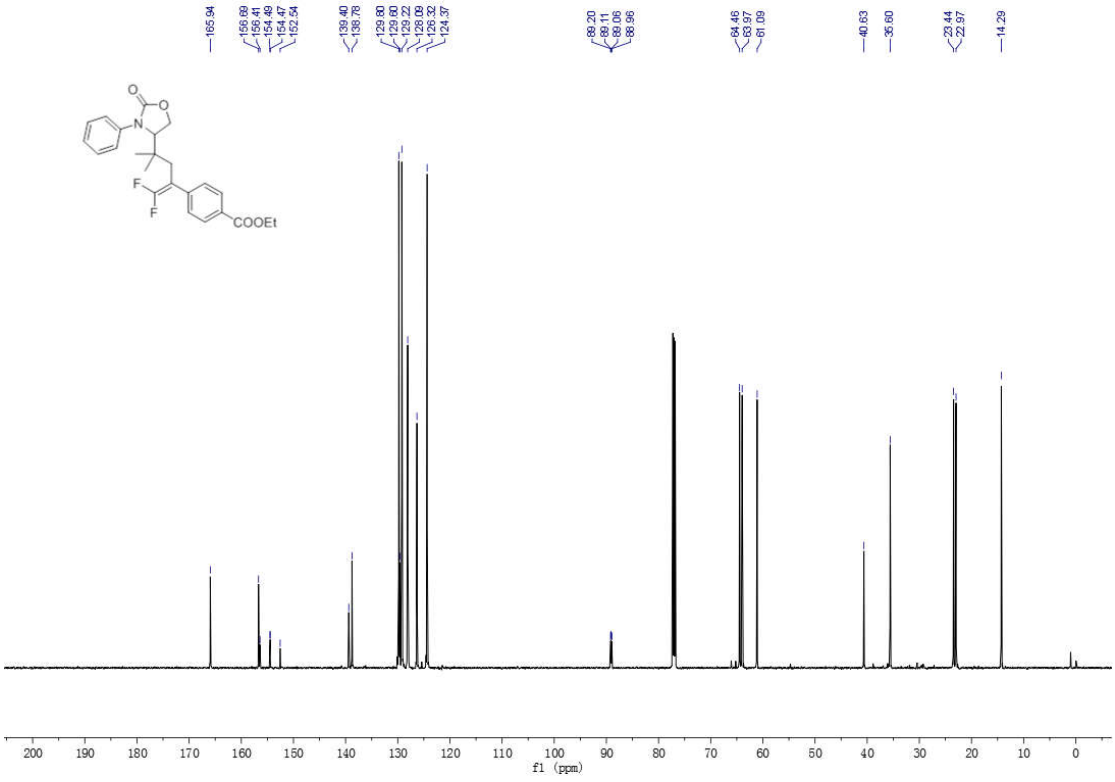
^{19}F NMR spectrum (564MHz, $CDCl_3$, 23 ºC) of 4a



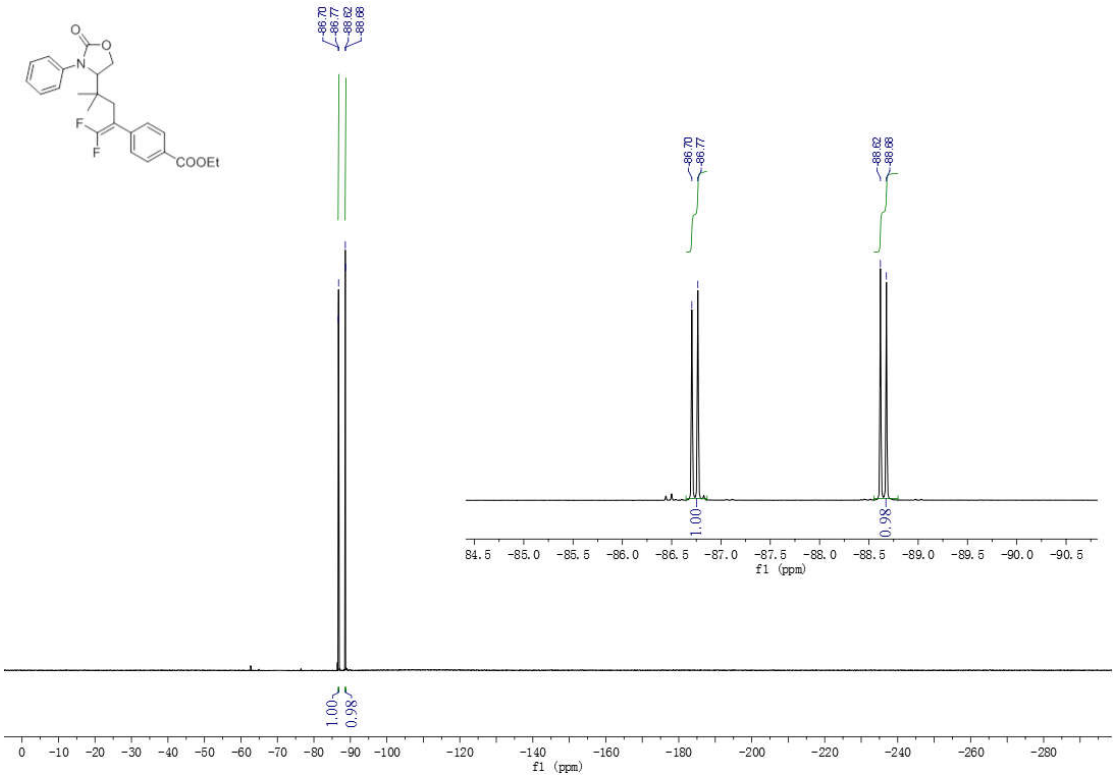
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 4b



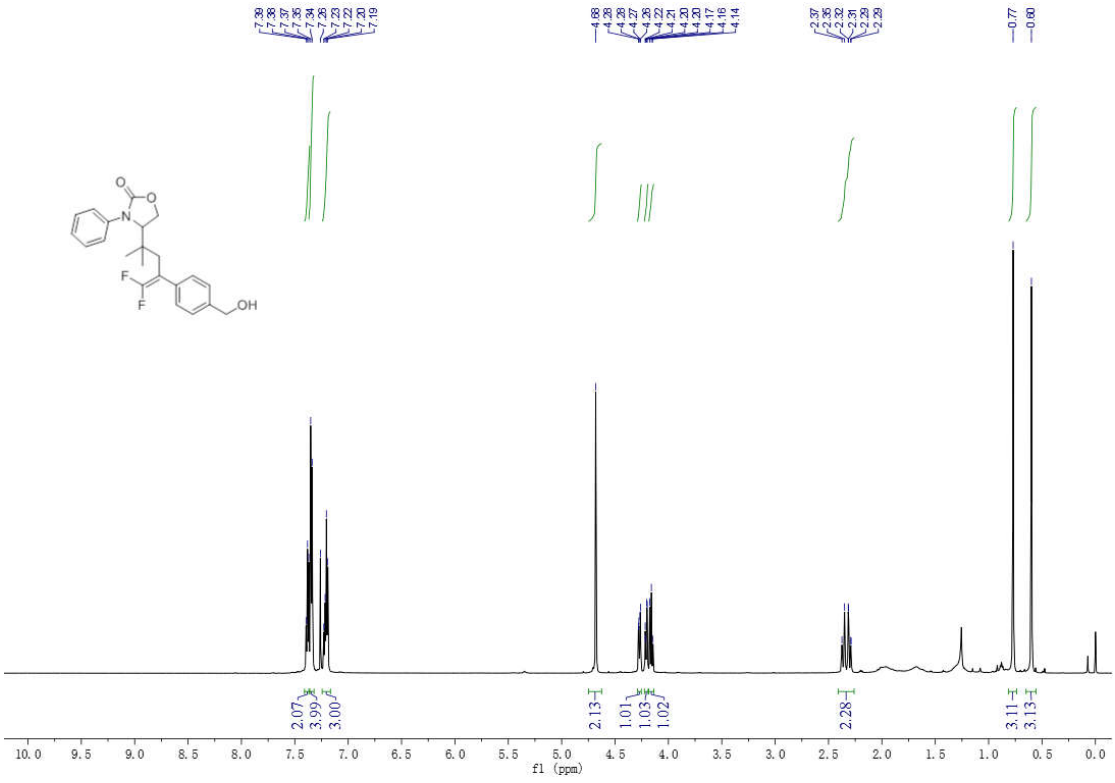
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4b



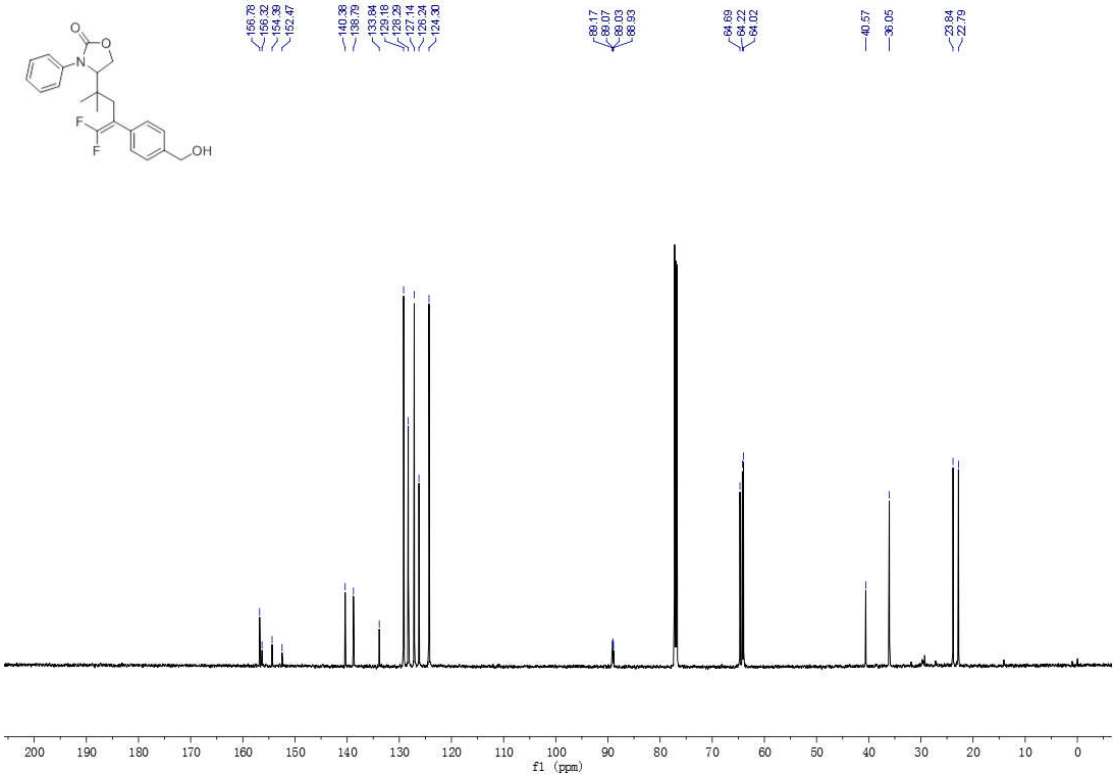
^{19}F NMR spectrum (564MHz, $CDCl_3$, 23 ºC) of 4b



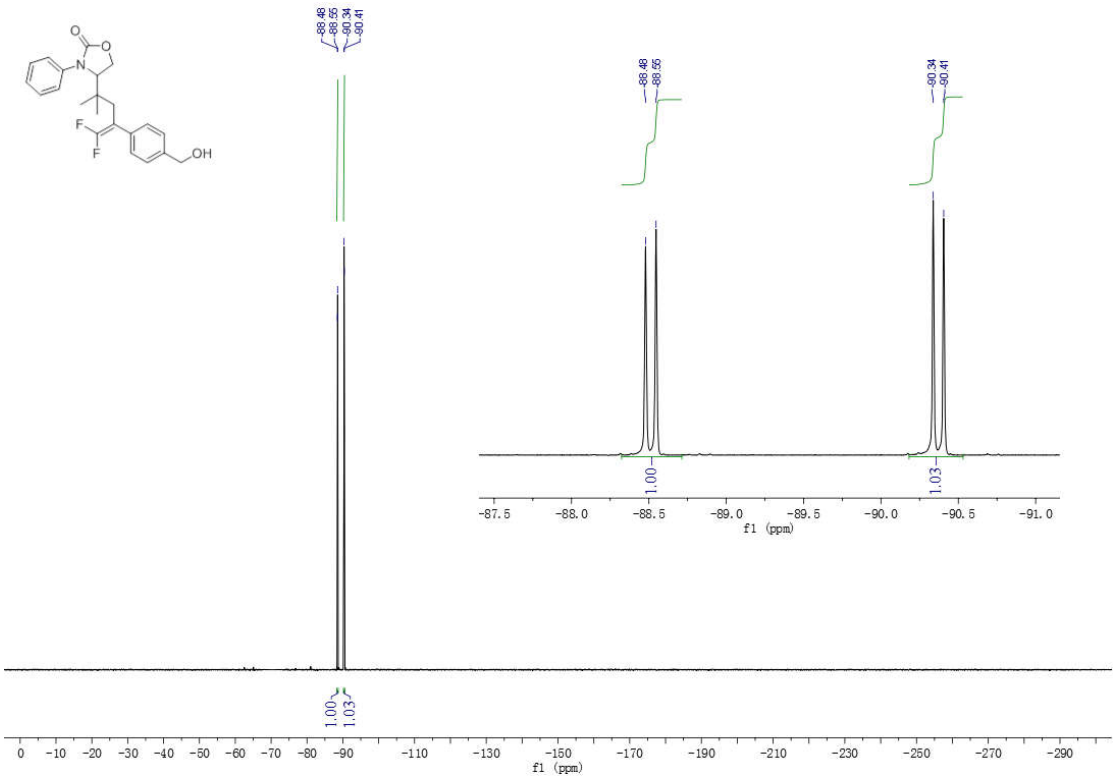
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4c



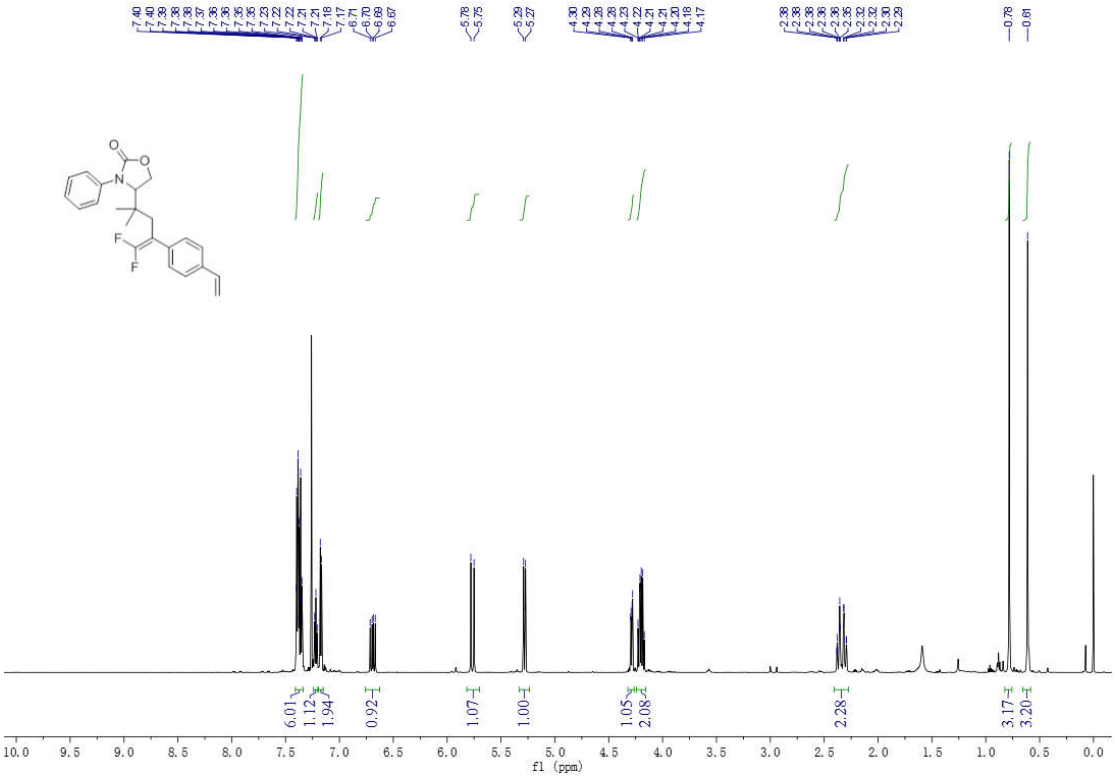
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 4c



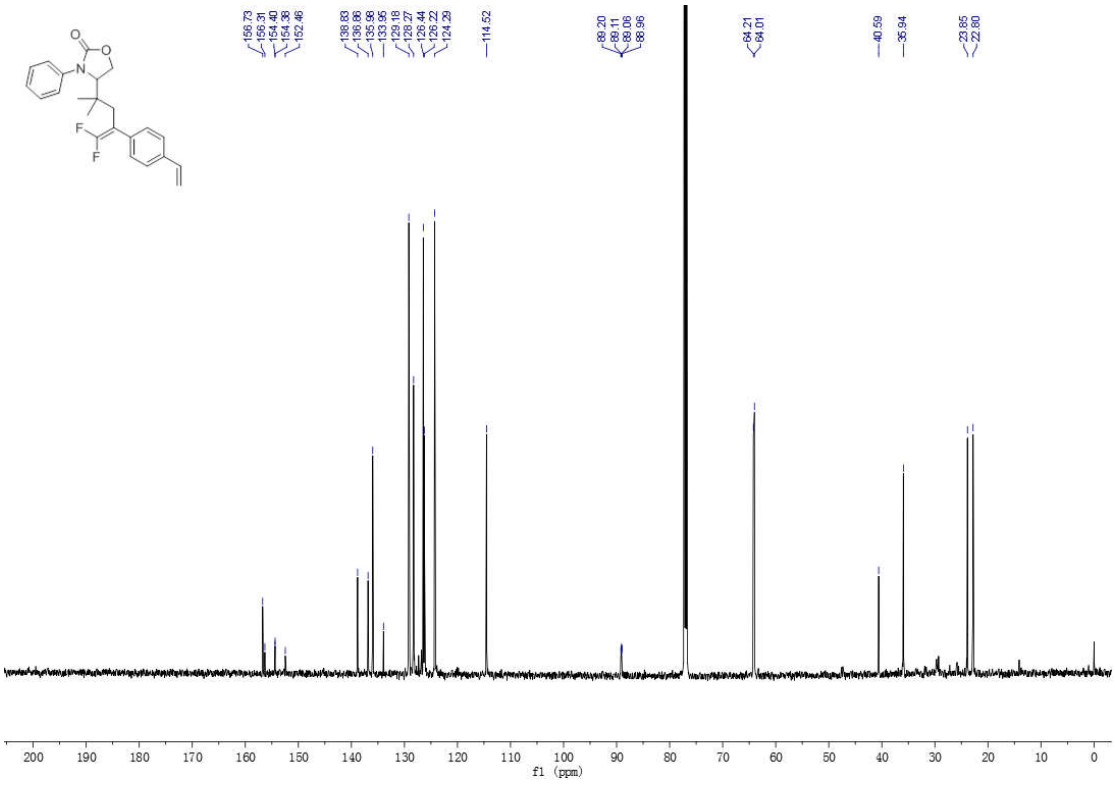
^{19}F NMR spectrum (564MHz, $CDCl_3$, 23 ºC) of 4c



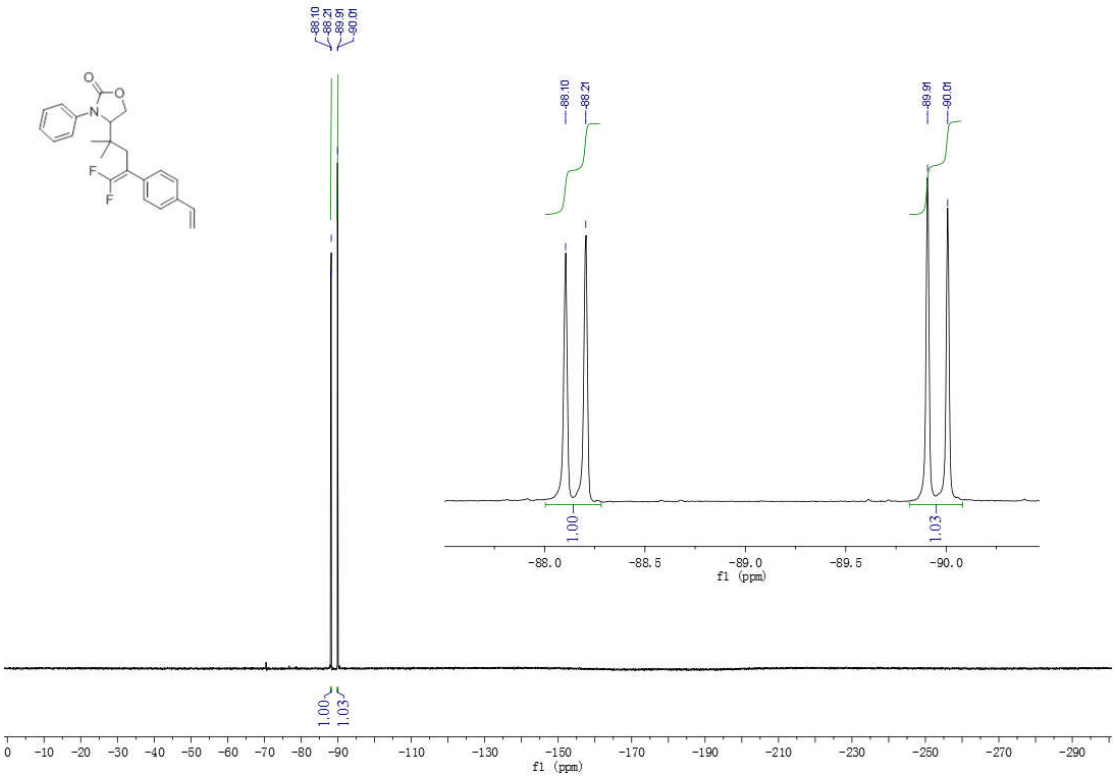
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 4d



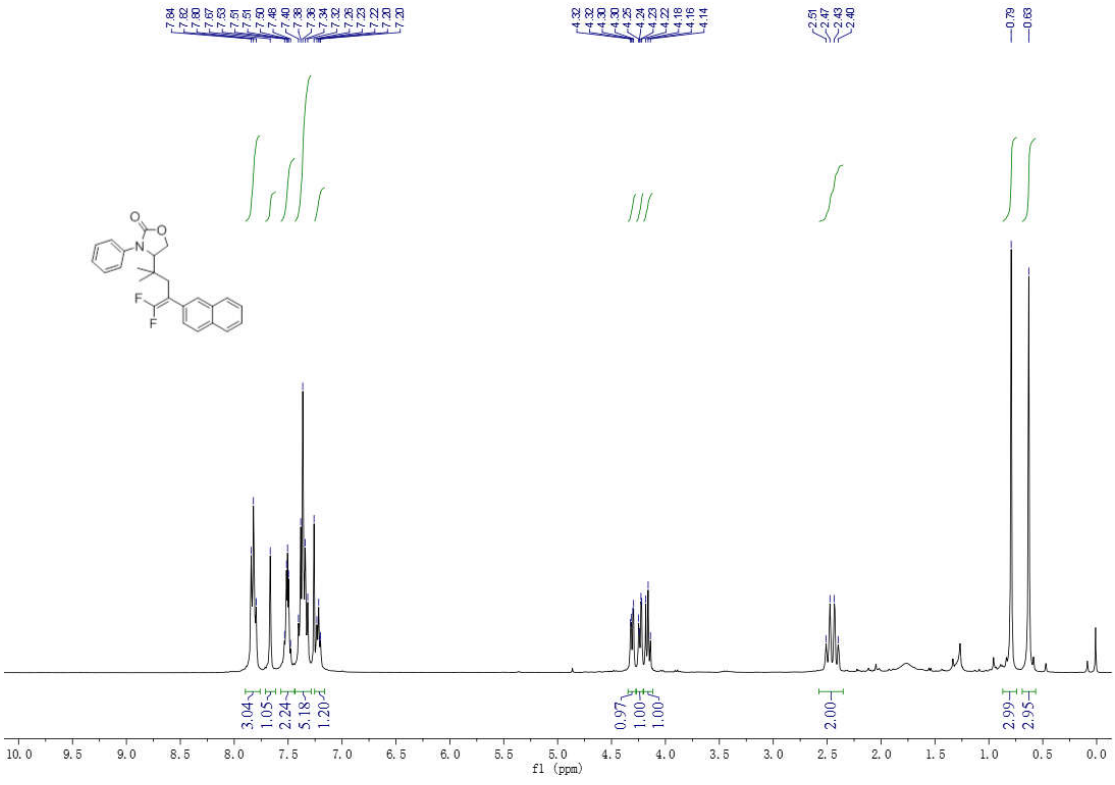
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4d



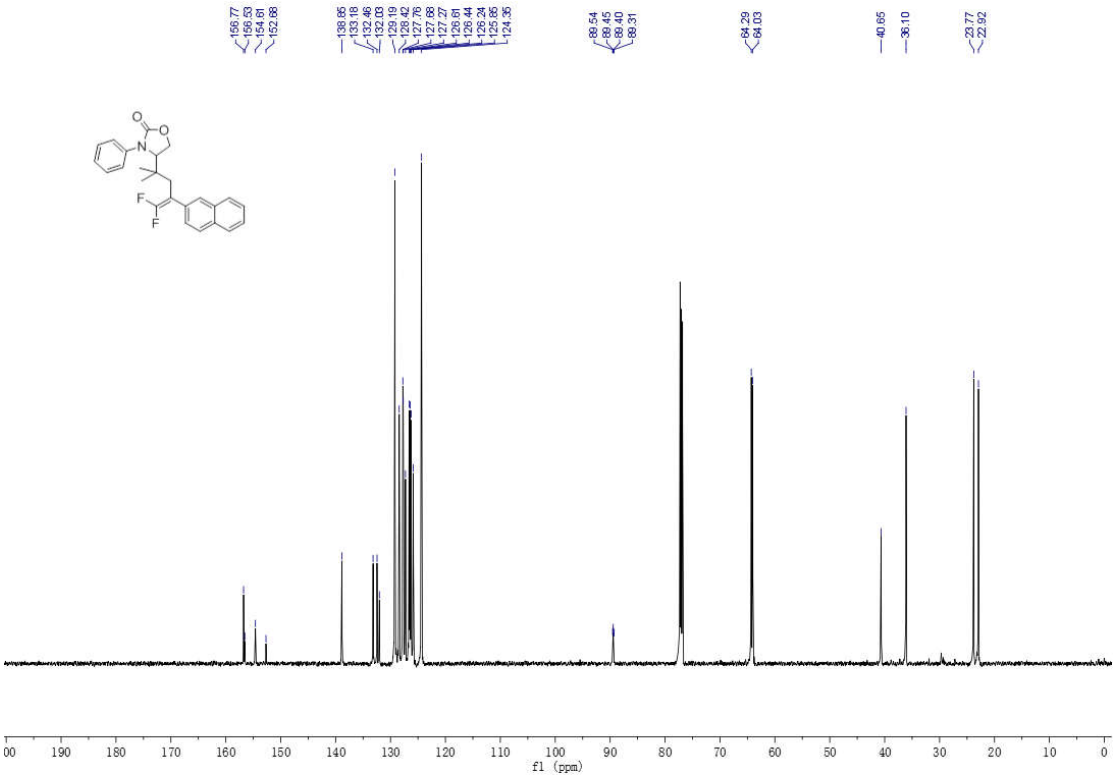
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 4d



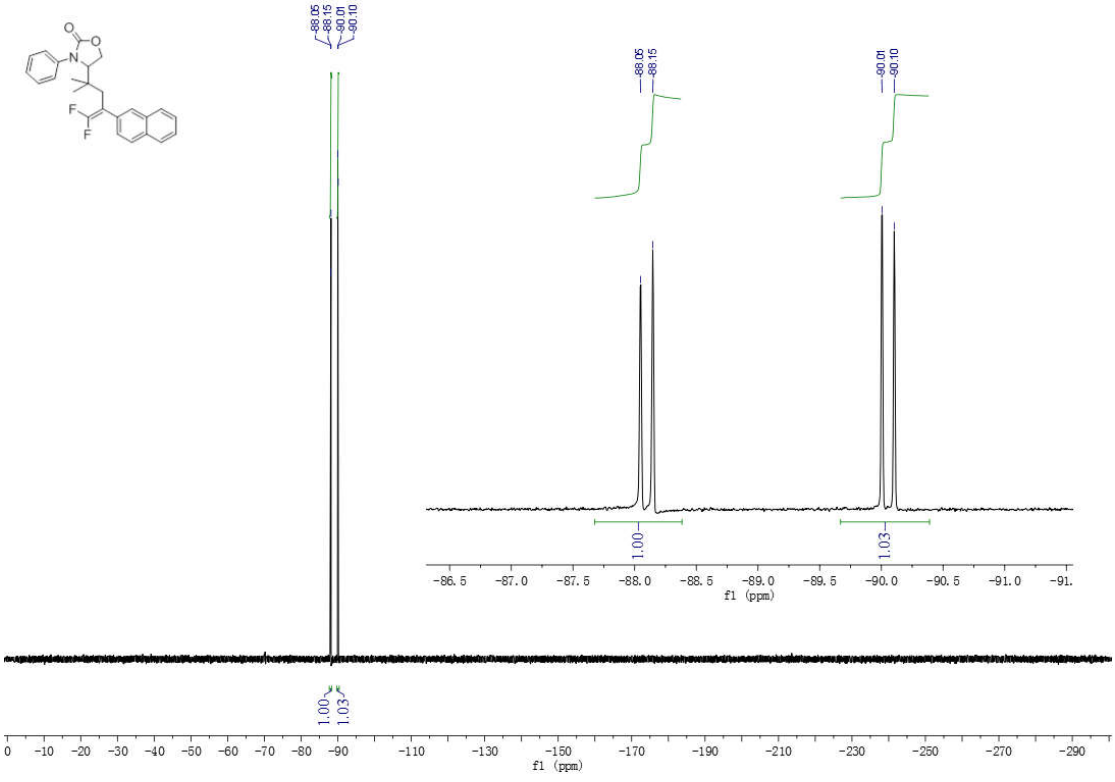
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4e



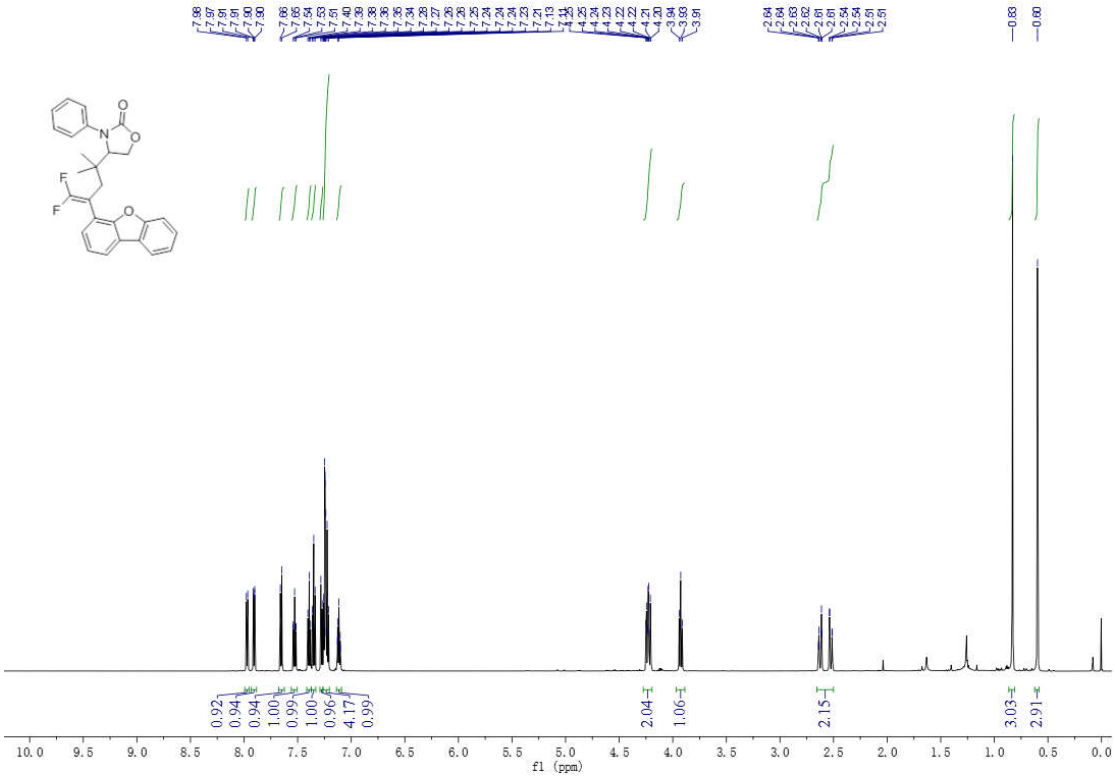
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of 4e



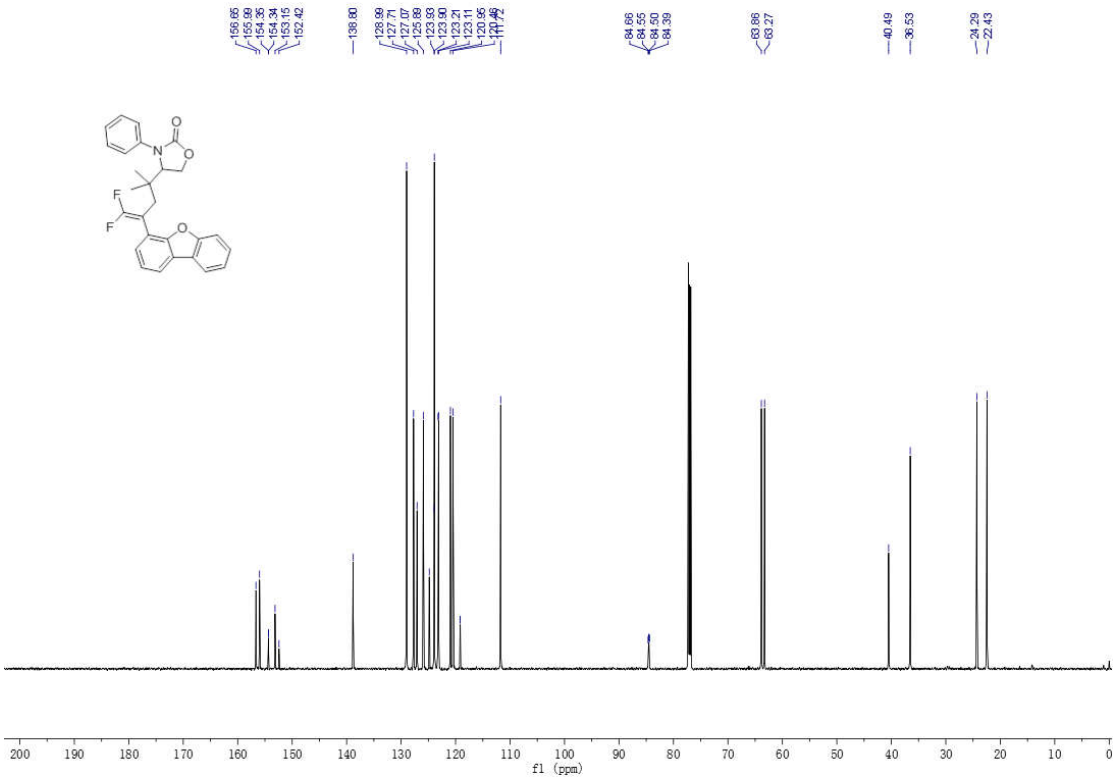
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 4e



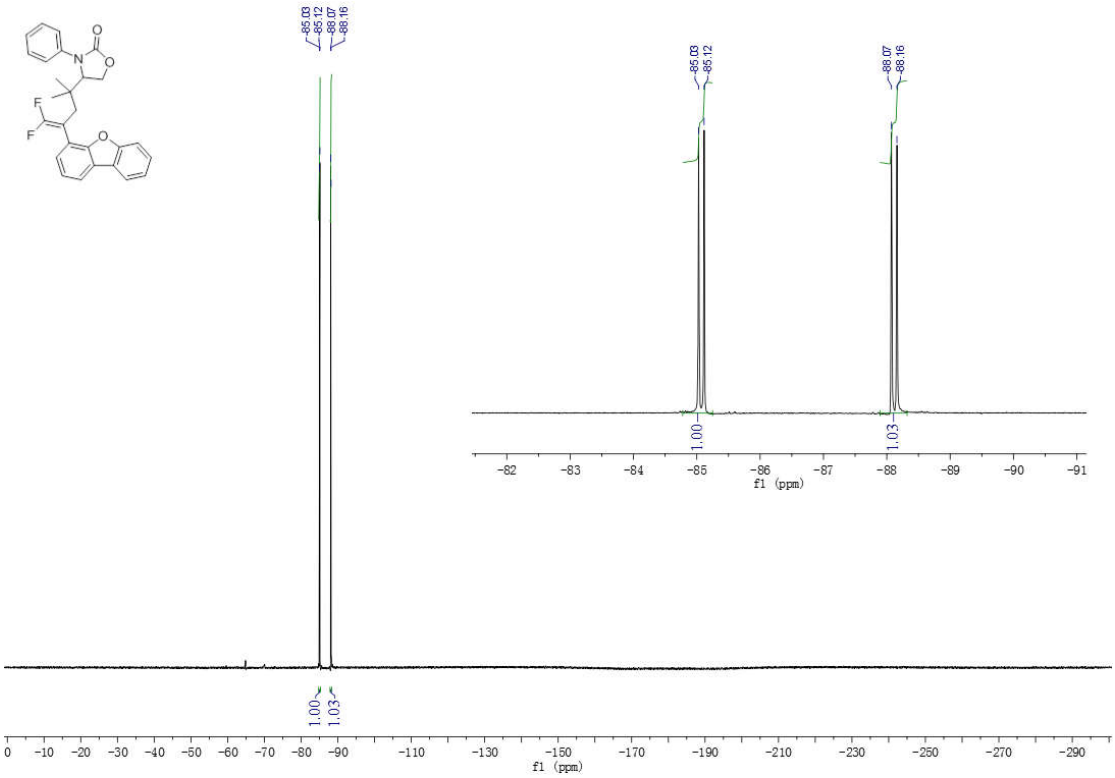
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 4f



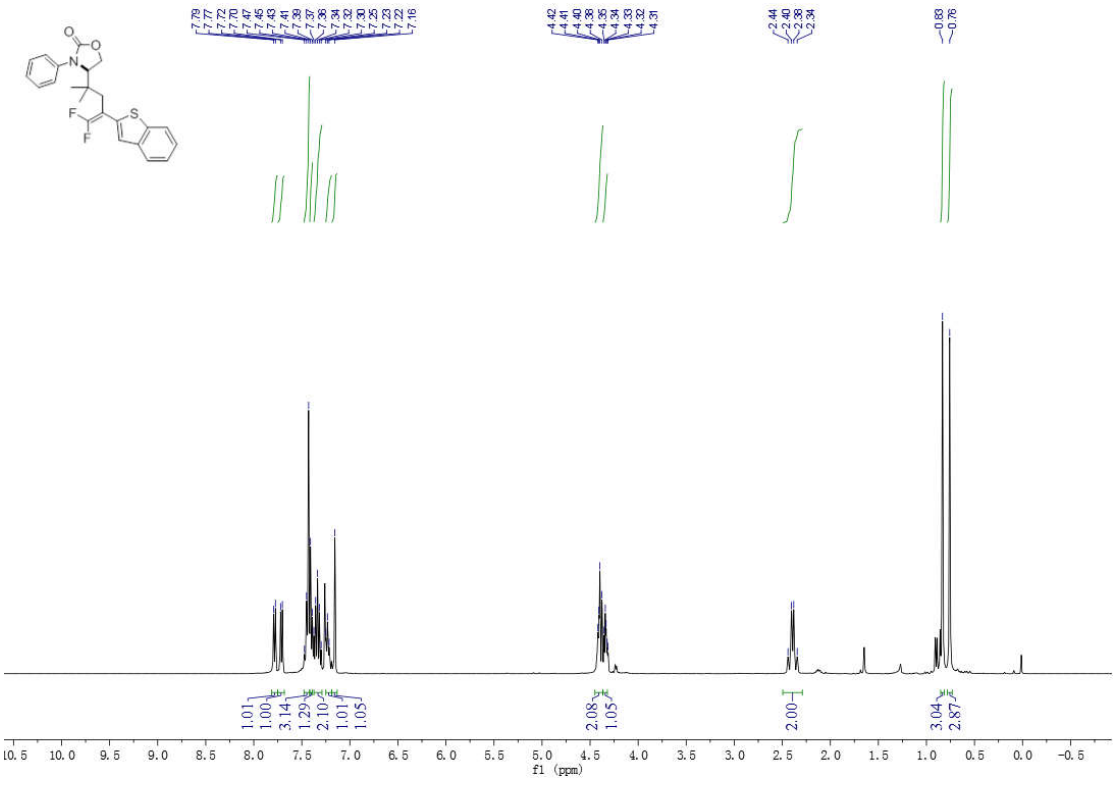
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4f



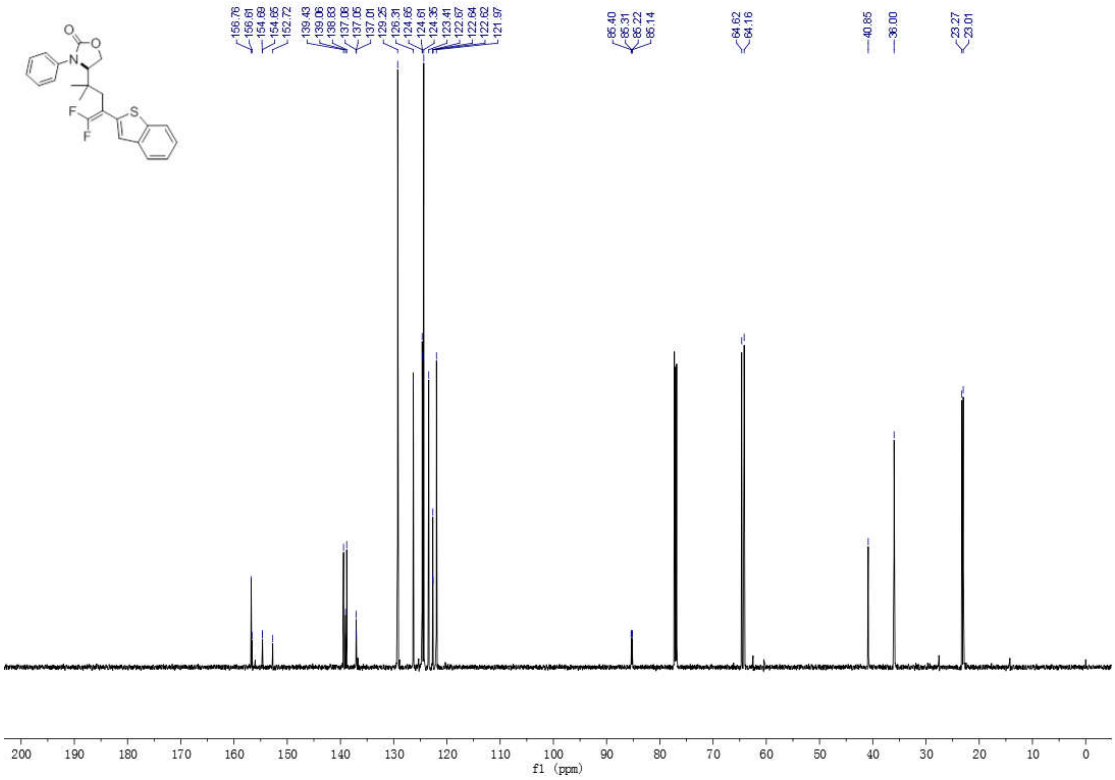
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 4f



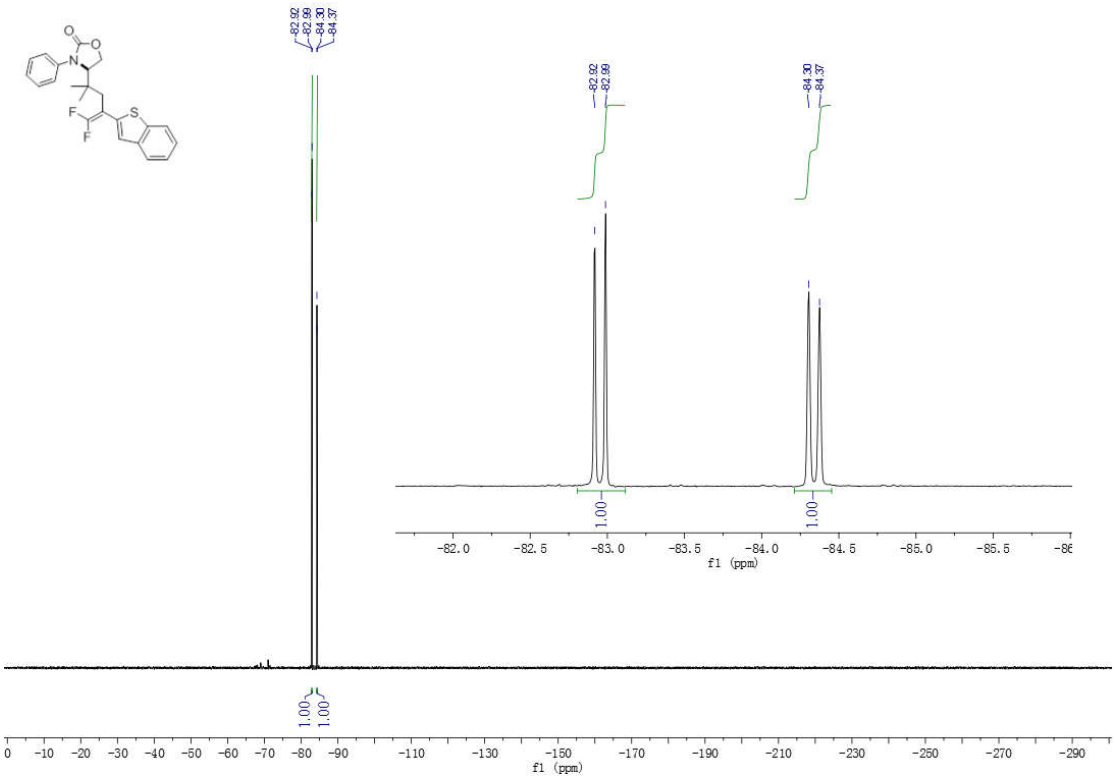
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of 4g



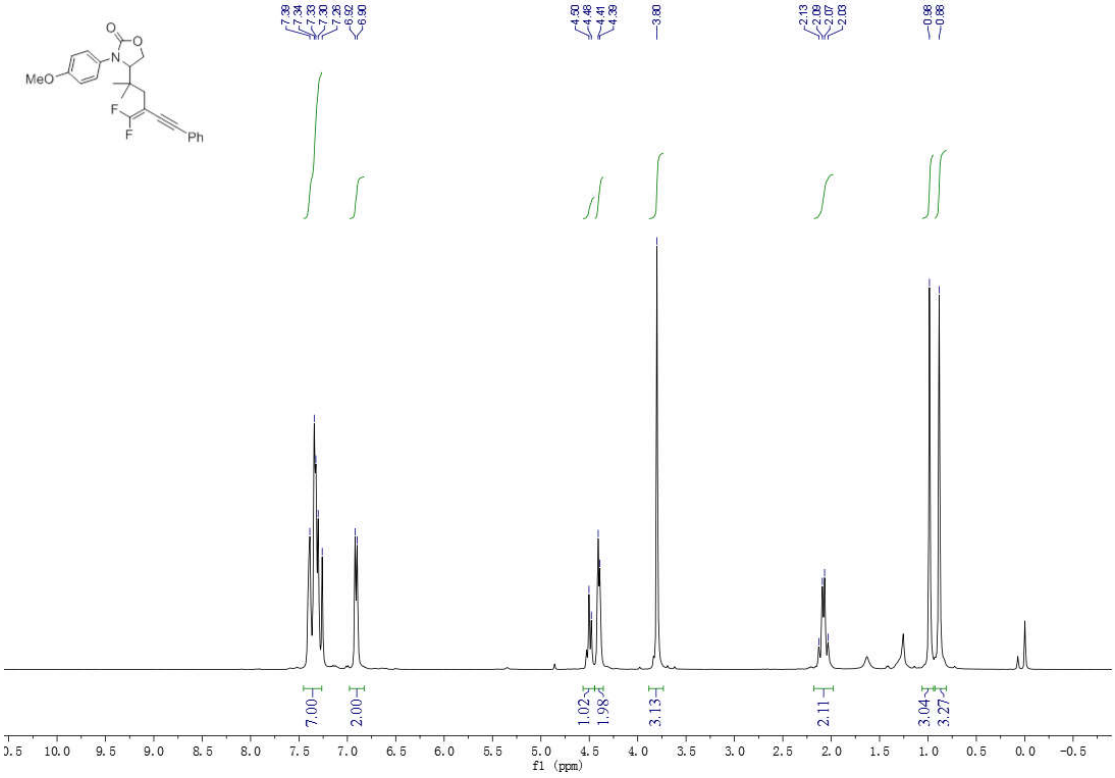
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4g



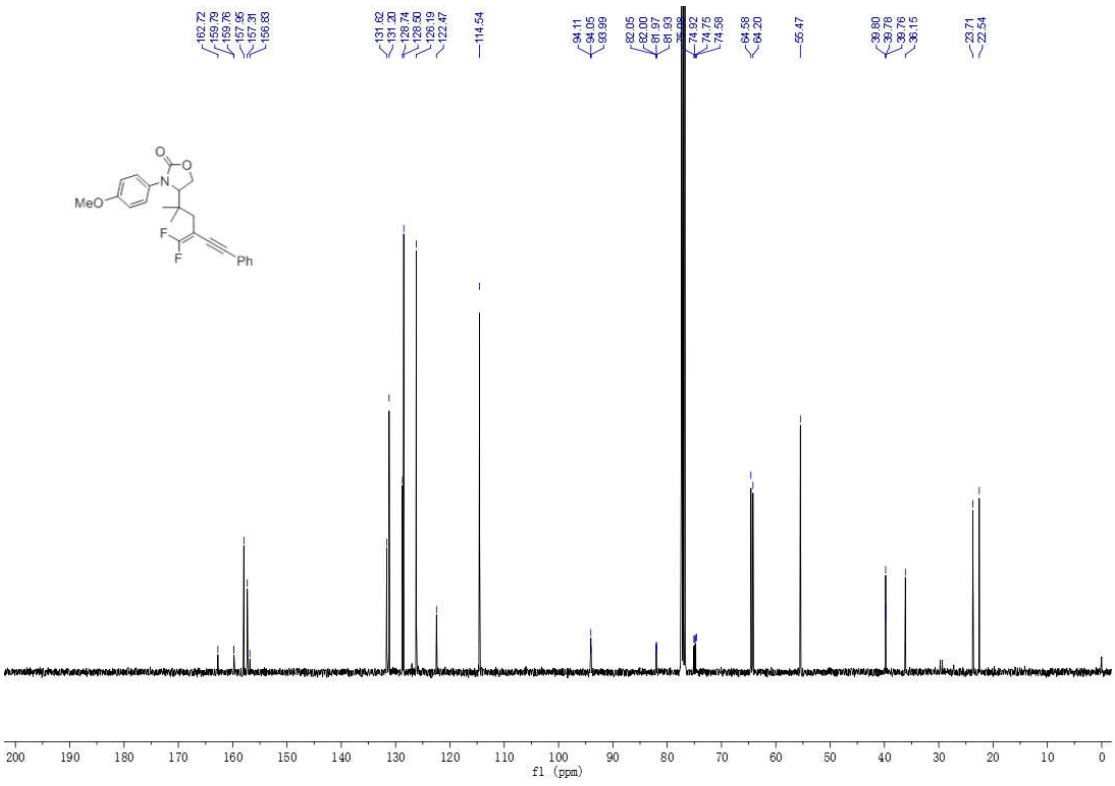
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 °C) of 4g



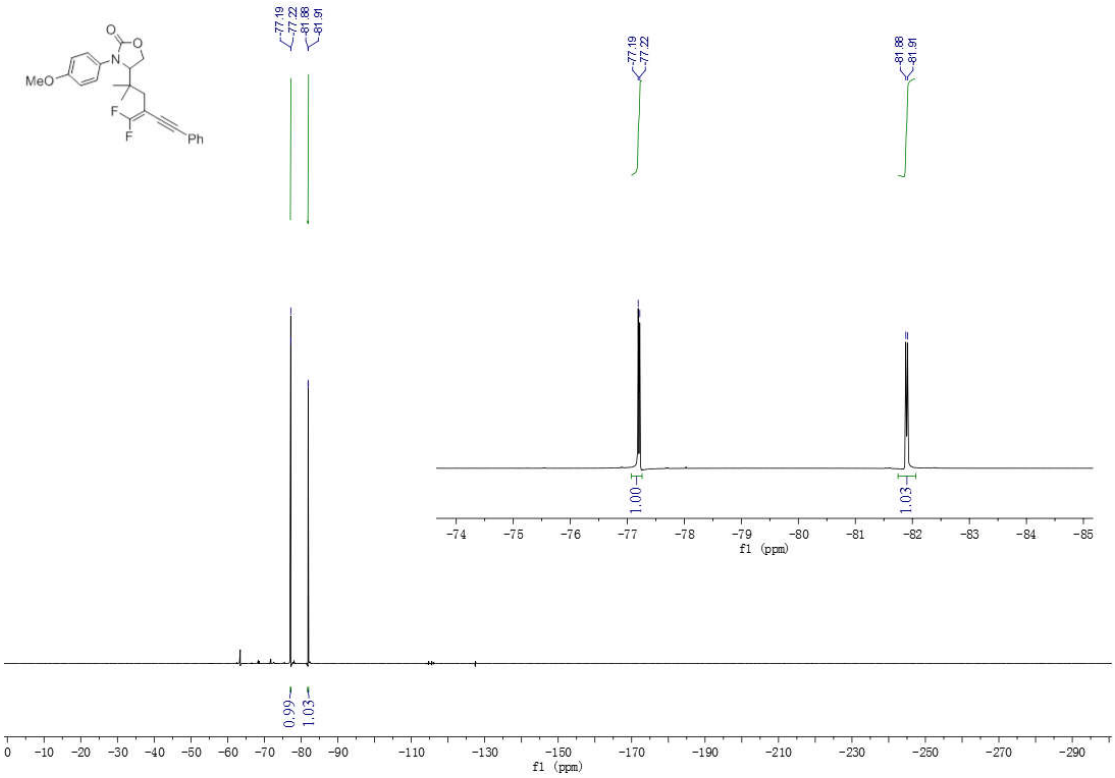
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4h



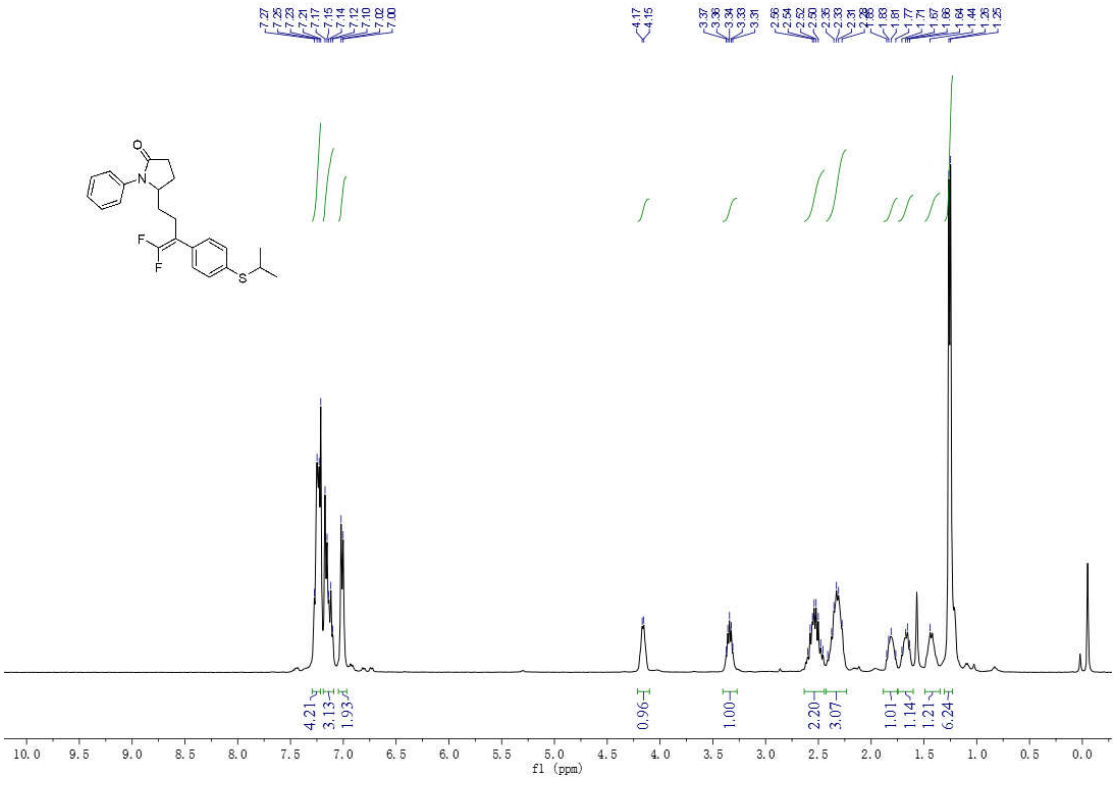
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of 4h



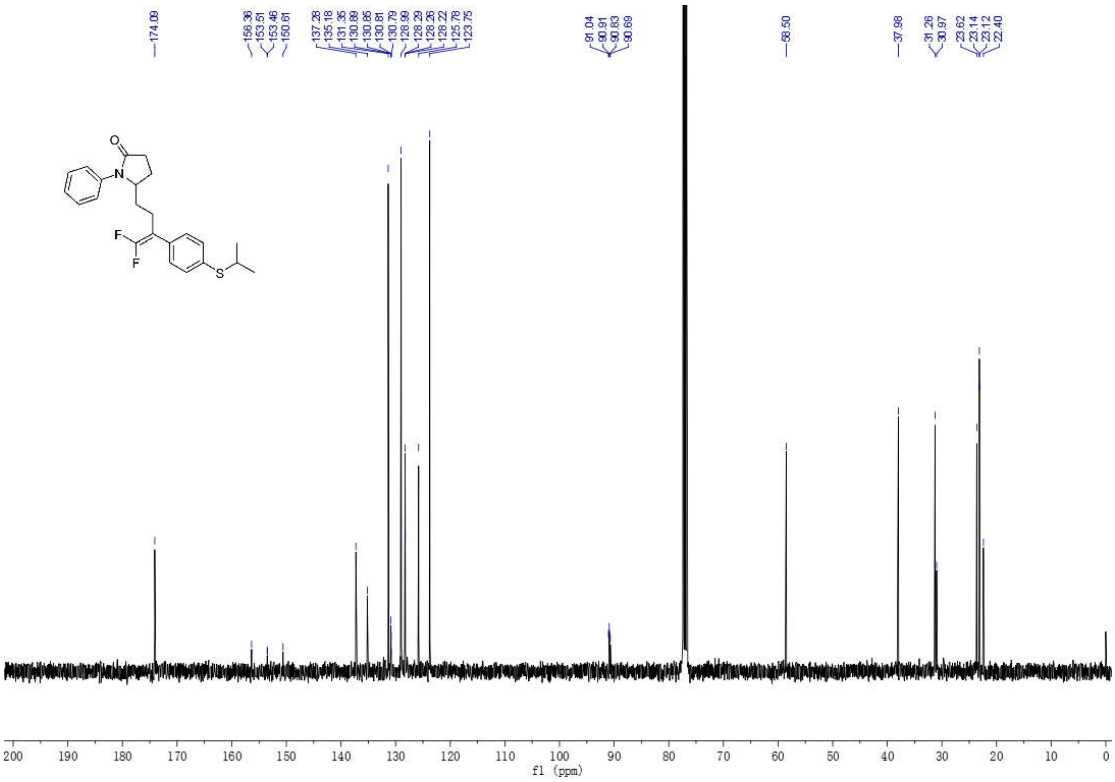
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 4h



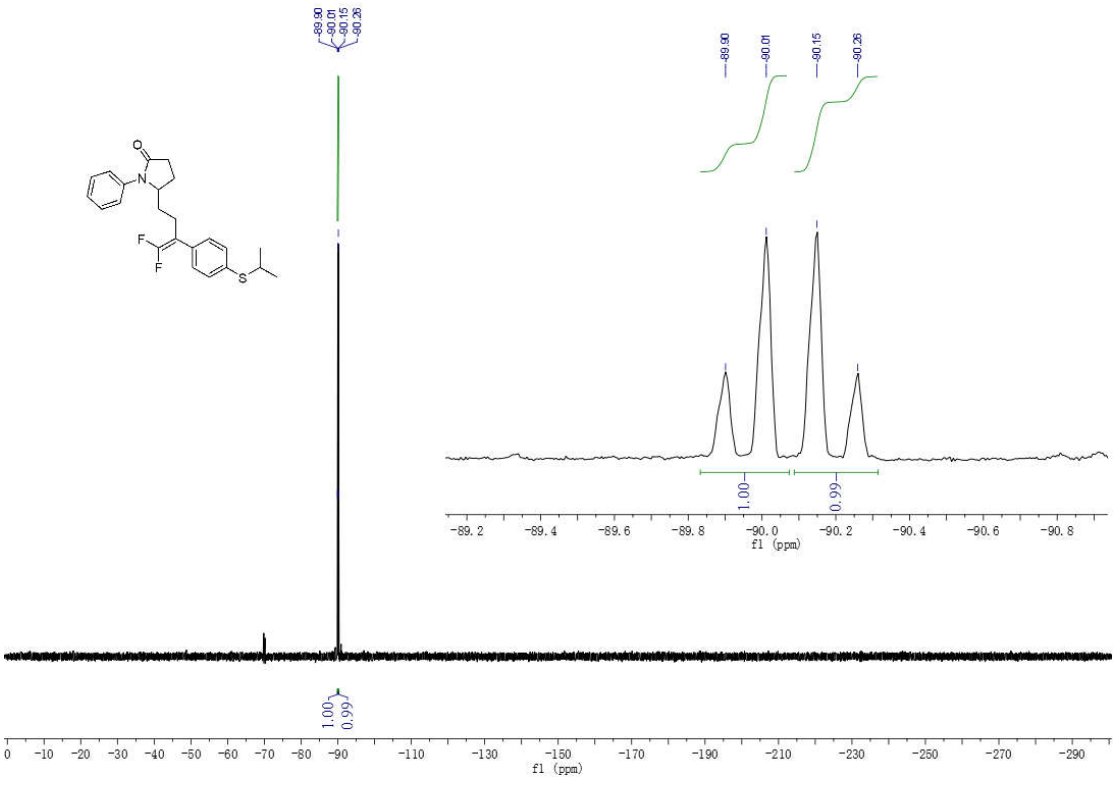
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4i



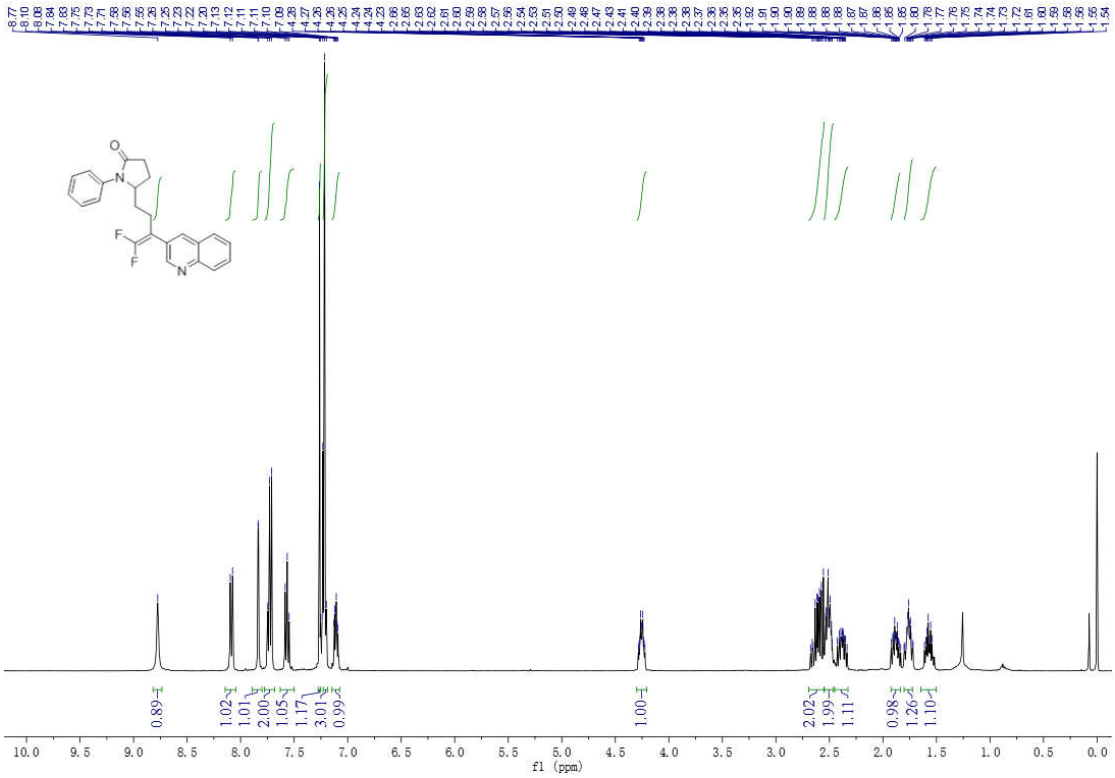
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of 4i



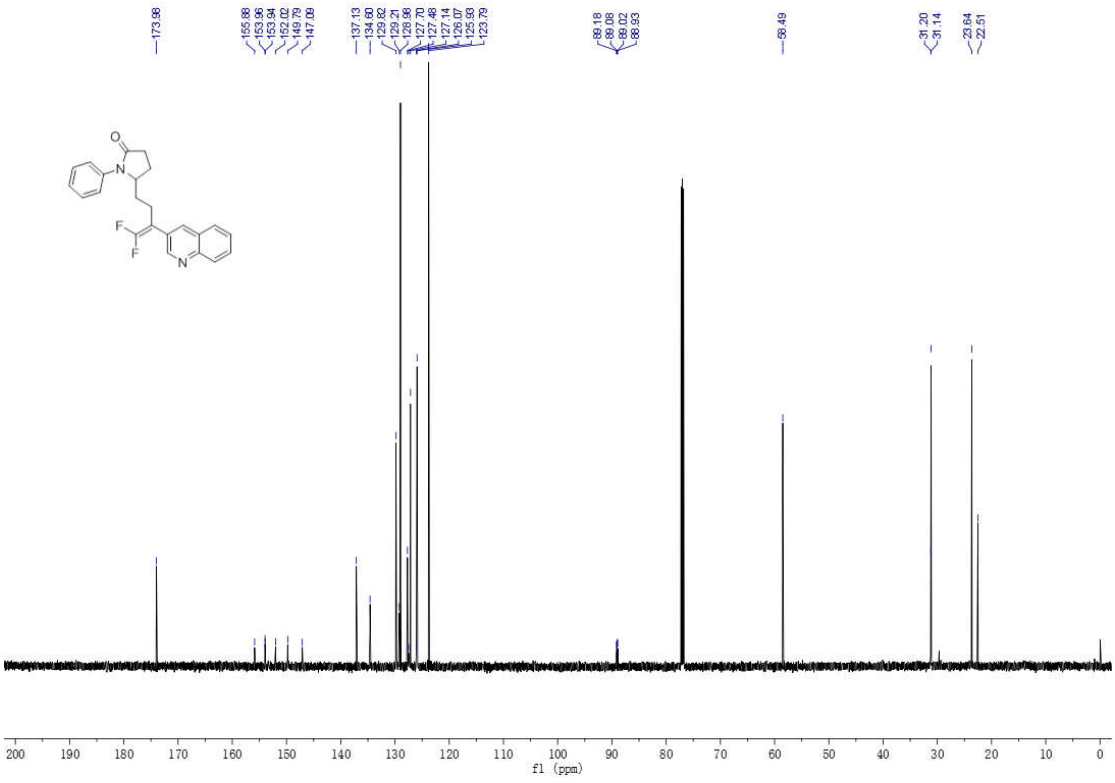
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 4i



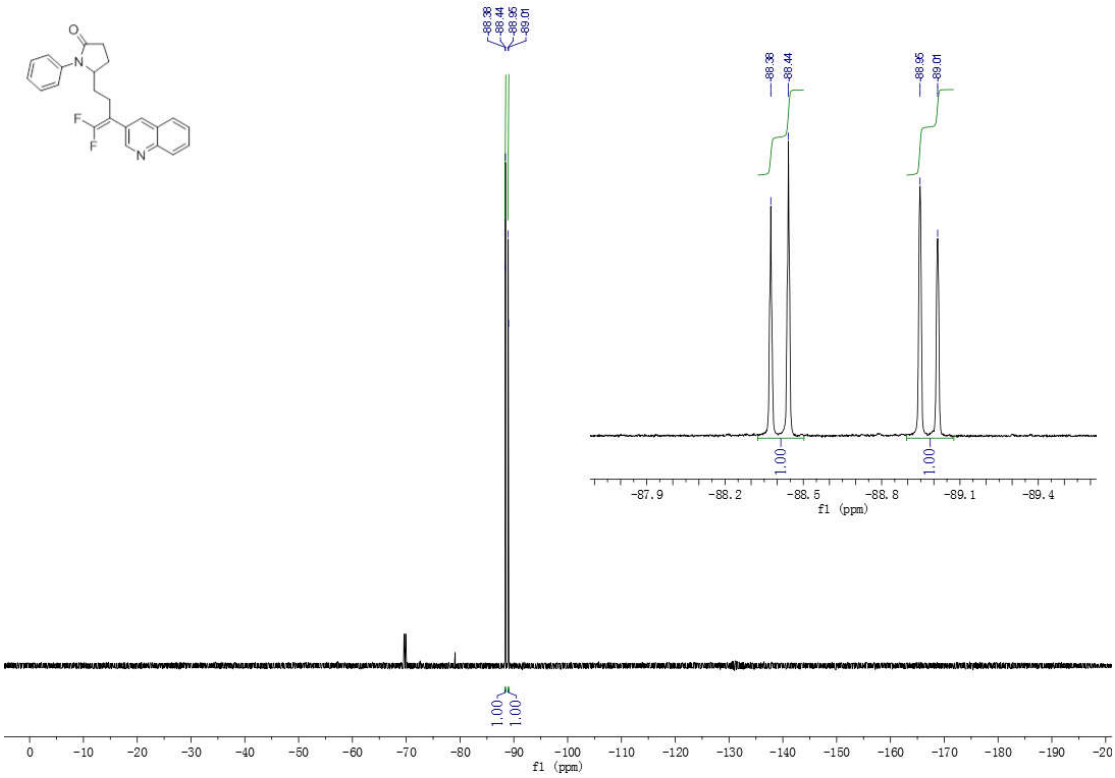
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of 4j



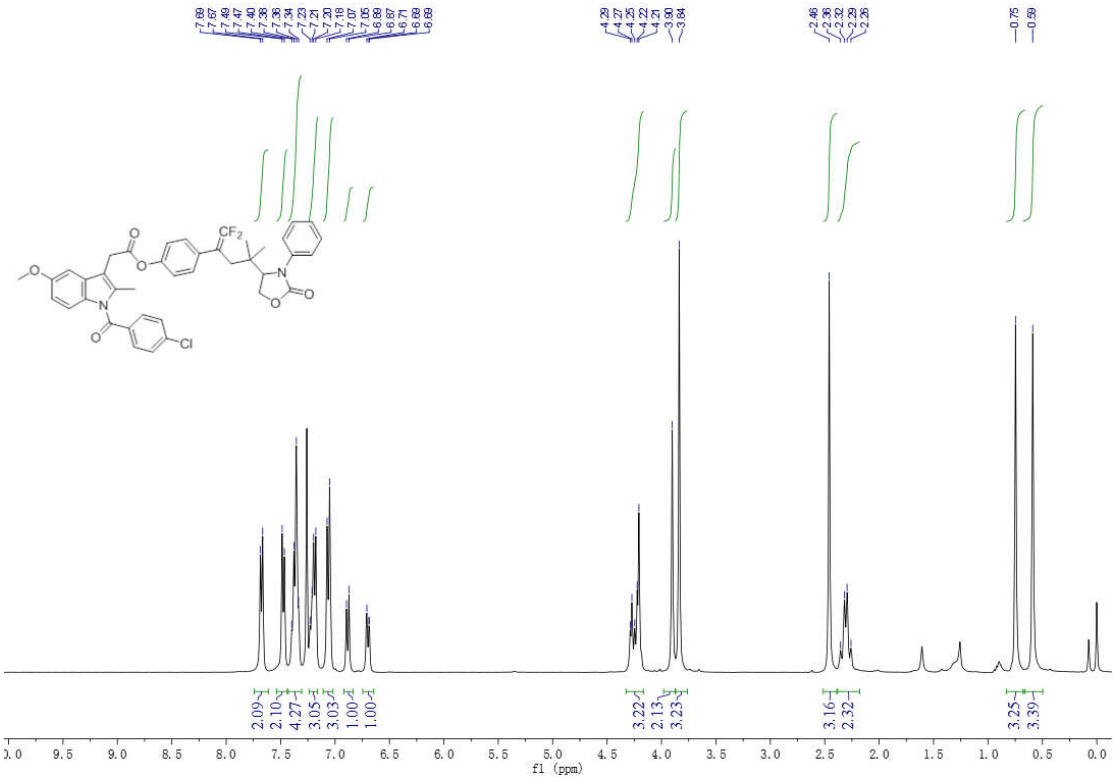
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4j



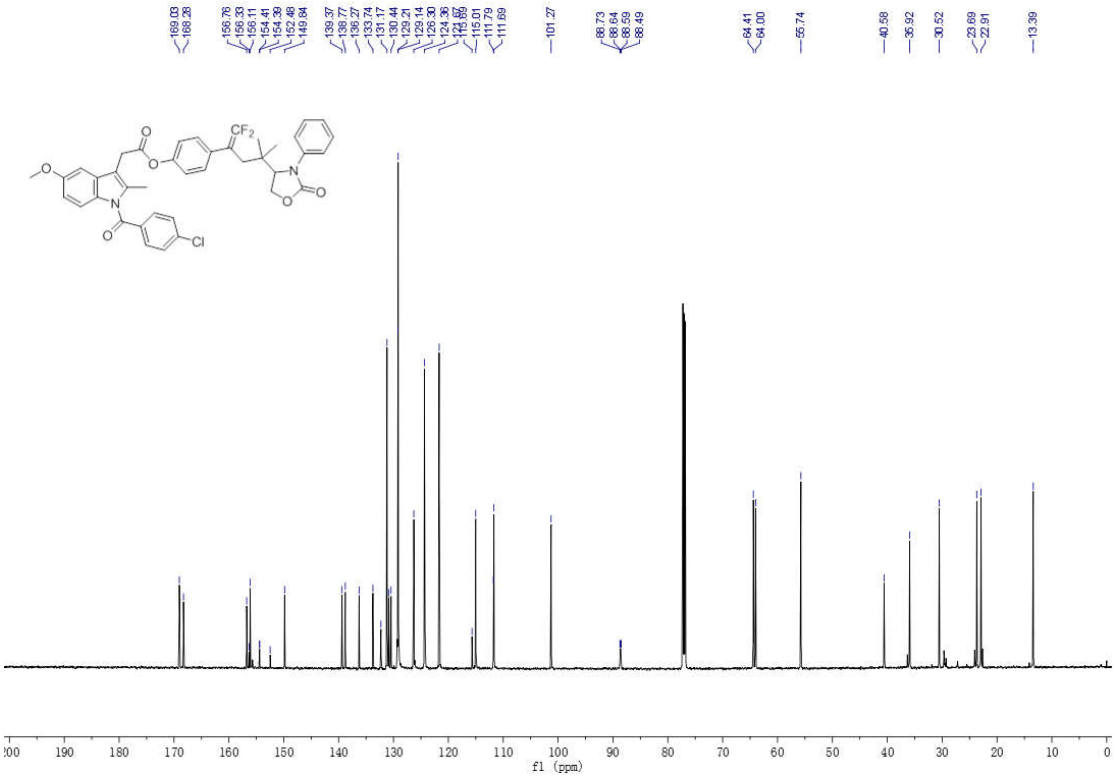
^{19}F NMR spectrum (564MHz, $CDCl_3$, 23 ºC) of 4j



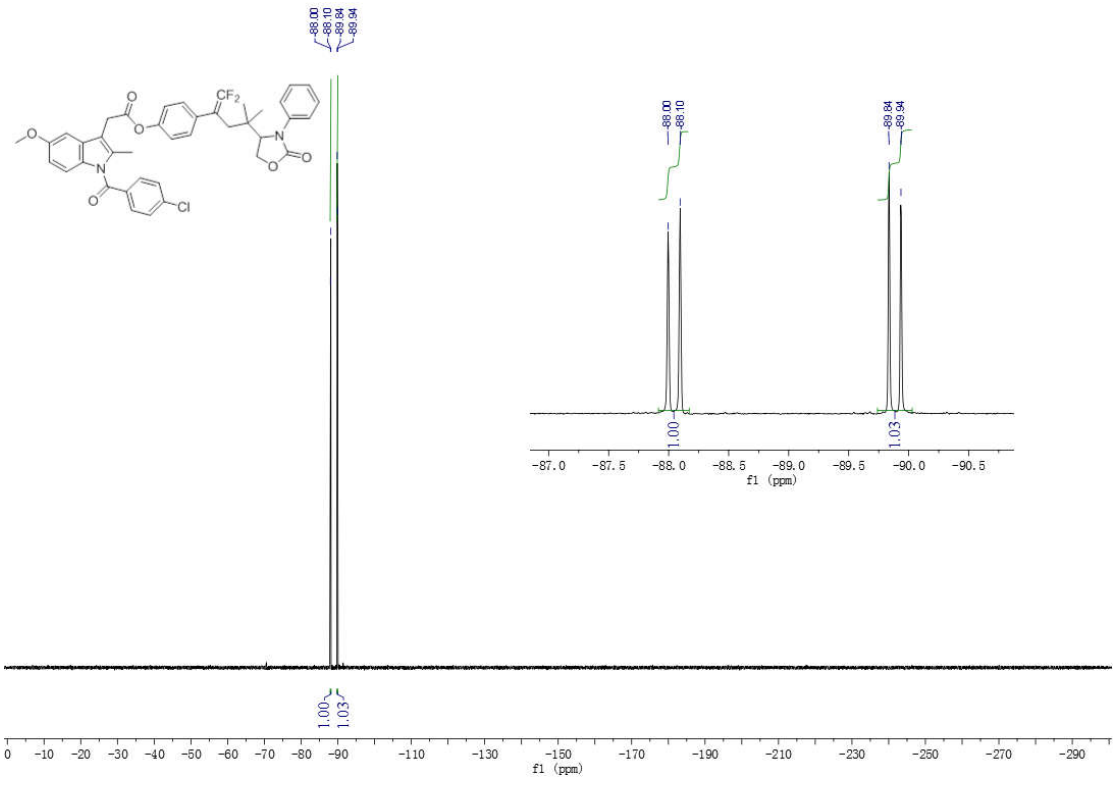
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4k



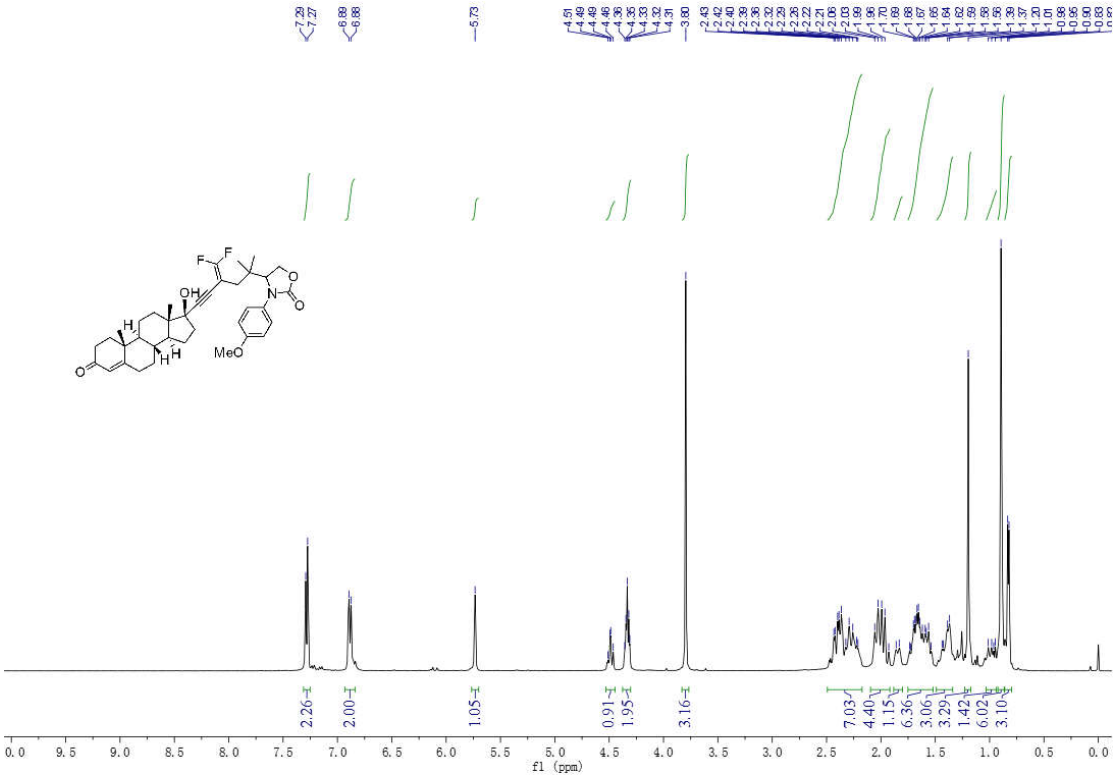
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4k



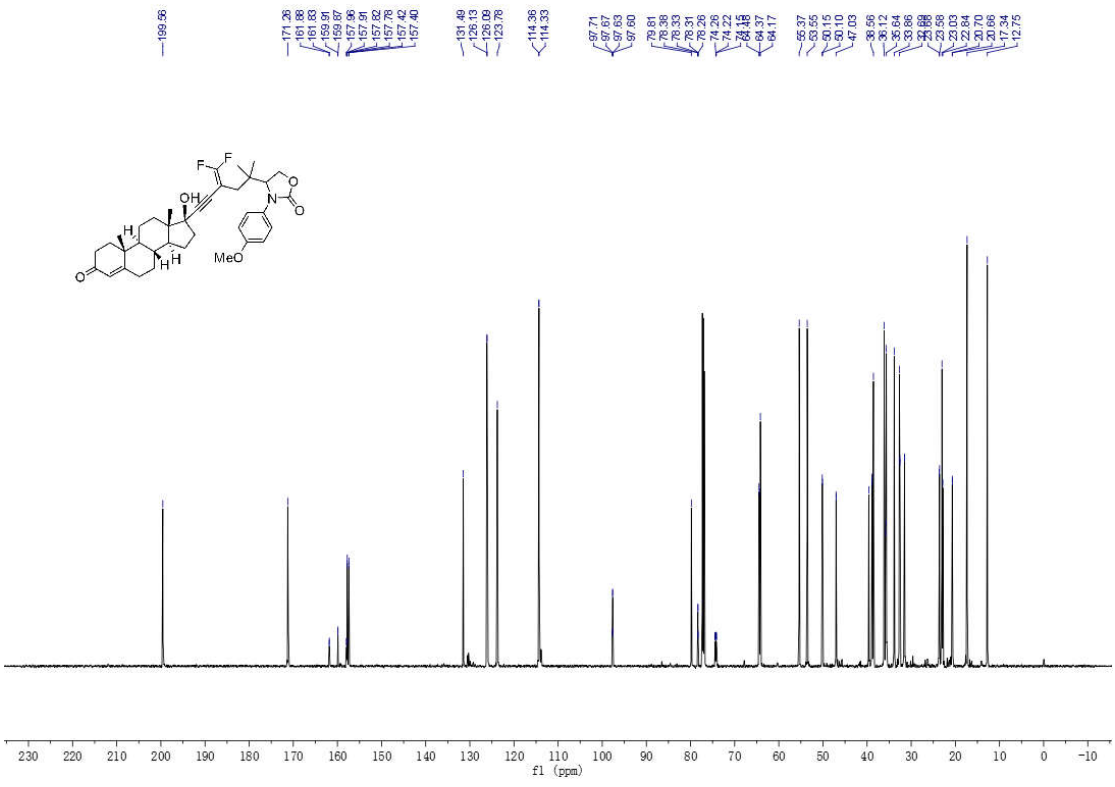
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 °C) of 4k



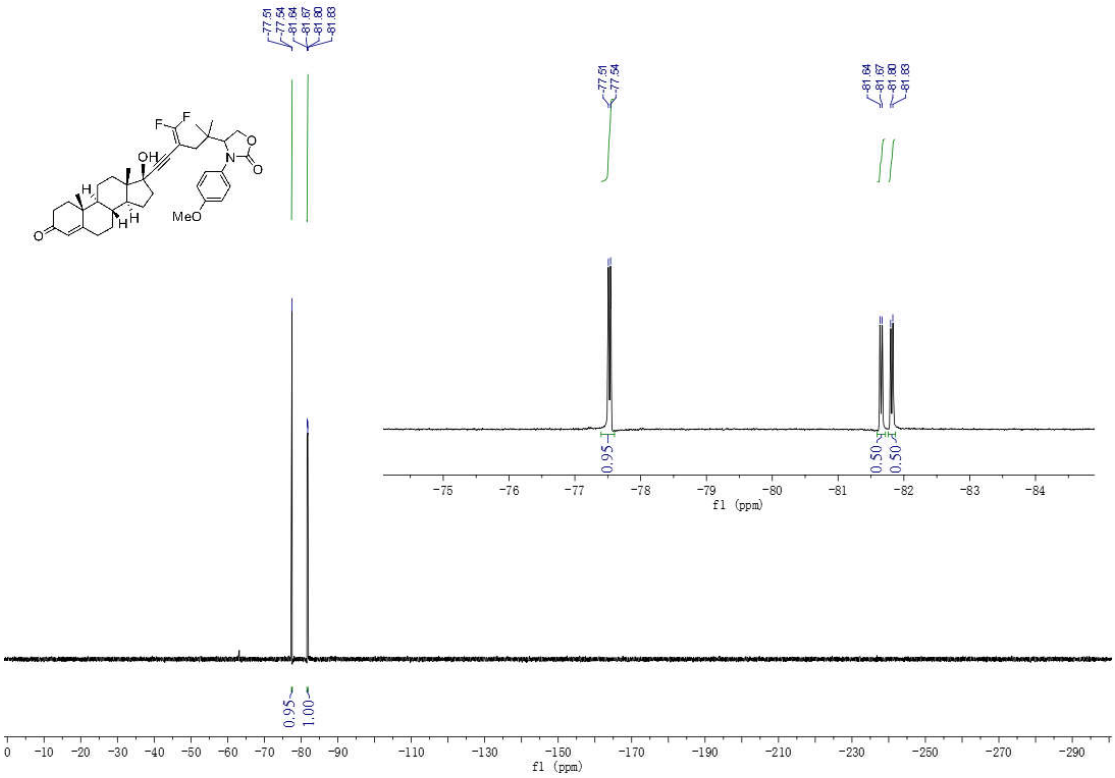
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 °C) of 4l



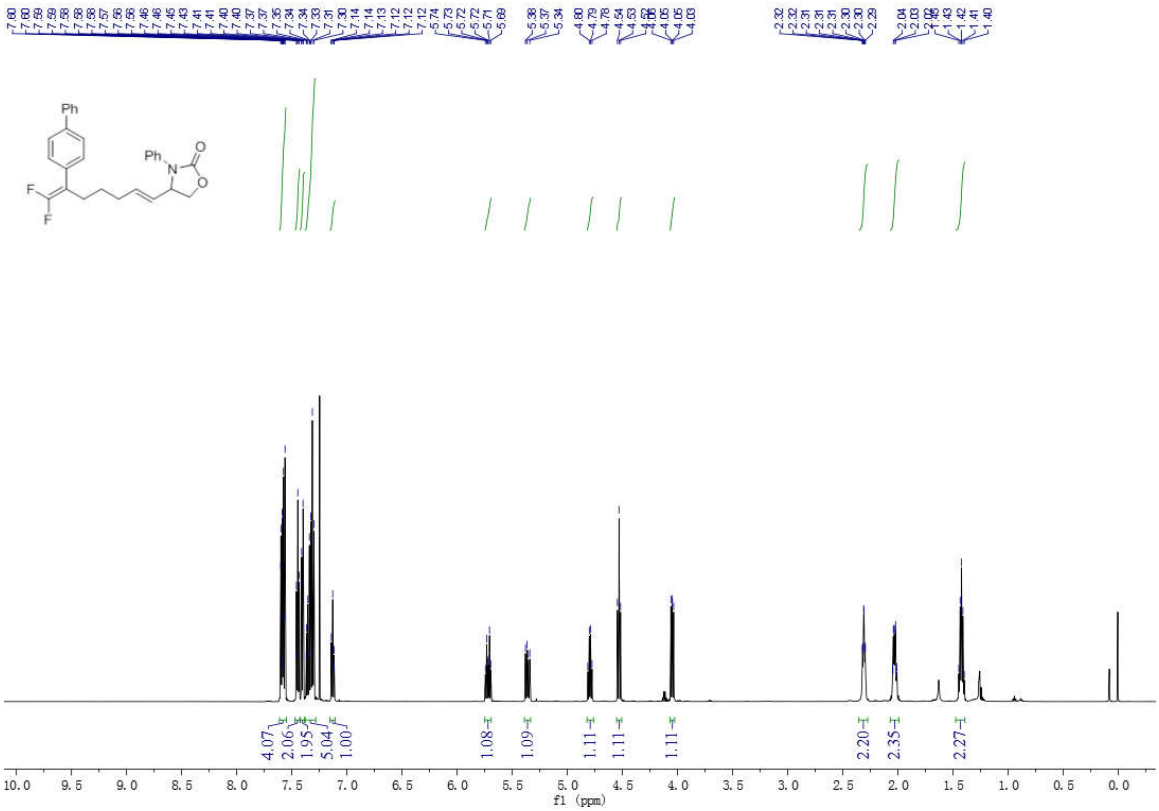
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 4l



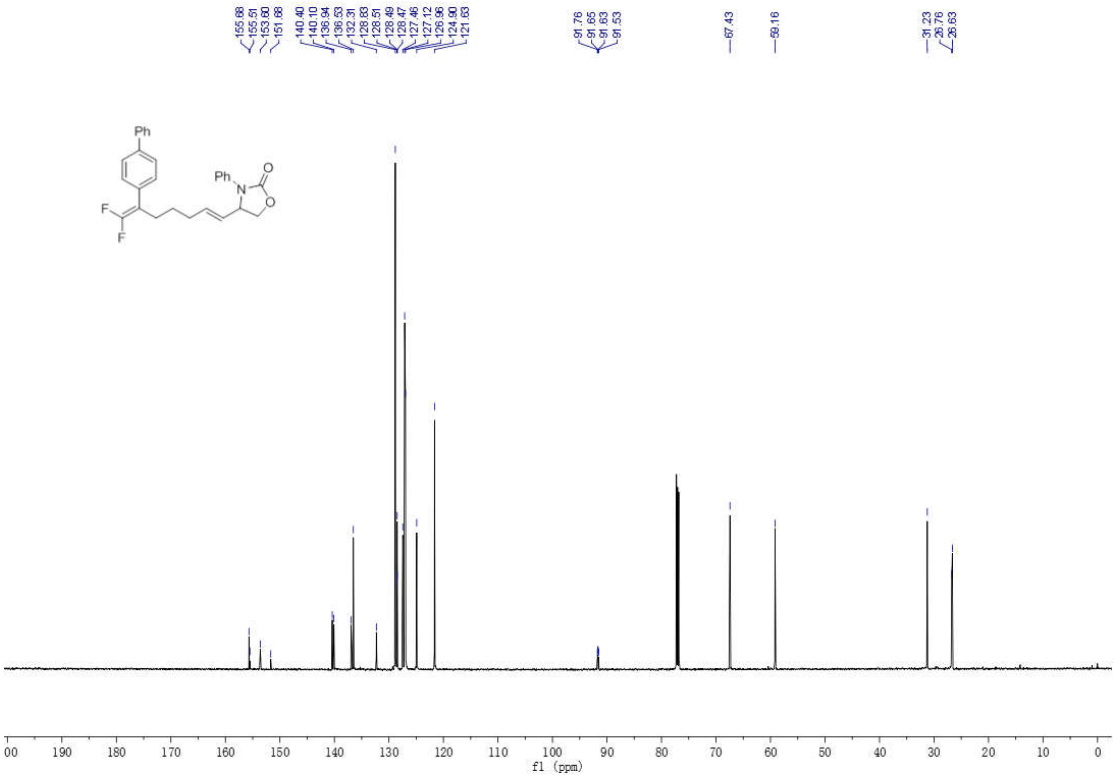
^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 ºC) of 4l



^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of 5



^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 °C) of 5



^{19}F NMR spectrum (377MHz, $CDCl_3$, 23 °C) of 5