Construction of *gem*-difluoroalkenyl indoles via photoinduced Fukuyama-type cyclization of isocyanides

Jingxuan Zhang,[a,#] Haixia Zhao,[a,#] Yue Pu,[a] Kaijie Tang,[a] He Chen, Qihang Huang,[a] Chen Chen,[*,a] and Jian Wang[*a]

[a]Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials (State Key Laboratory Cultivation Base), College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China.

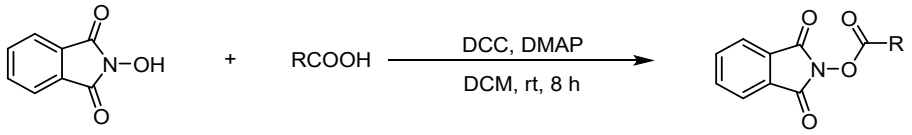
Content

1. General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. NMR data were obtained for ^{1}H at 400 MHz or 500 MHz, and for ^{13}C at 125 MHz or 100 MHz, and for ^{19}F at 376 MHz. Chemical shifts of 1H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.16 ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization *(ESI) as the ion source. Flash column chromatography was carried out using* commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

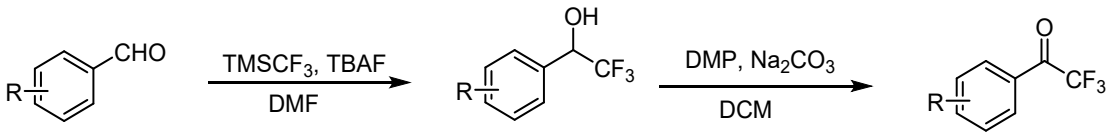
2. Procedures for the synthesis of substrates

2.1 Synthesis of NHPI esters[1]



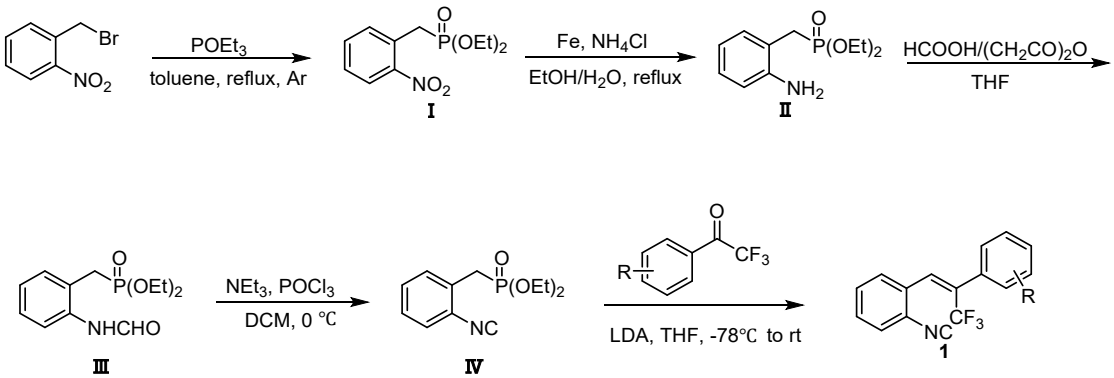
N-hydroxyphthalimide (0.33 g, 2.0 mmol, 1.0 equiv.), Carboxylic acid (1.2 equiv.), and DMAP (10 mol%) were dissolved in DCM in one portion. DCC (0.49 g, 2.4 mmol, 1.2 equiv.) were added. The reaction is allowed to stir overnight. The reaction mixture was quenched with saturated $NaHCO_3$, diluted with DCM (50 mL), subjected to column chromatography with silica gel powder (200-300 mesh), and the eluent is eluted with PE: EA = 30: 1 to obtain the product.

2.2 Synthesis of *o*-alkenyl aryl isocyanide [2]



Step 1: To a solution of aldehyde (5 mmol) in DMF (5 mL) in a 25 mL round-bottom flask equipped, under nitrogen atmosphere, $TMSCF_3$ (6.5 mmol, 1.3 equiv.) was added and the mixture was stirred in an ice bath. After approximately 10 min, TBAF (1 M in THF, 0.05 mmol, 0.05 mL, 0.01 equiv.) was added dropwise via a syringe. After 10 min, the ice bath was removed and the solution was stirred for approximately 6 h at room temperature. To cleave the silyl ether intermediate, the reaction mixture was cooled to 0 °C in an ice bath and after 10 min; water and TBAF (1 M in THF, 0.5 mL, 0.5 mmol, 0.1 equiv.) were added. The ice bath was removed and the reaction mixture was stirred at room temperature. Finally, the mixture was extracted with ethyl acetate (20 mL × 3). The organic phase was washed with brine and then dried over anhydrous Na_2SO_4. After filtration and evaporation under vacuum, the residue was subjected to silica gel column chromatography using hexane/ethyl acetate as eluent to give trifluoromethyl alcohols.

Step 2: To a solution of the α-CF_3 alcohol (5 mmol, 1 equiv.) in DCM (30 mL), was added DMP (17.5 mmol, 3.5 equiv.) and Na_2CO_3 (20 mmol, 4 equiv.). The solution was stirred at room temperature for 3 h. Then water was added and the obtained suspension was stirred for an additional hour, the mixture was extracted with DCM (20 mL × 3). The organic phase was washed with brine and then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo by rotary evaporation in a room-temperature water bath to give α-CF_3 ketones.



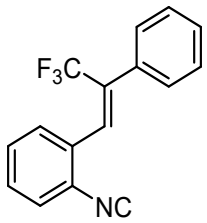
Step 1 A solution of 2-nitrobenzyl bromide (2.16 g, 10 mmol, 1.0 equiv.) and triethylphosphite (3.64 mL, 20 mmol, 2.0 equiv.) was heated to reflux intoluene (0.3 M) for 24 h. After completion of the reaction, the system was cooled to room temperature, quenched with saturated brine, extracted with ethyl acetate, and dried over anhydrous sodium sulfate. After evaporating under reduced pressure, compound **I** was obtained without further purification.

Step 2 In an unprotected round-bottom flask, iron powder (2.8 g, 50 mmol, 5.0 equiv.) and NH_4Cl (0.64 g, 12 mmol, 1.2 equiv.) were added. Then, a solution of product **I** in ethanol (0.5 M) was introduced, followed by the addition of water (2.0 M). The mixture was refluxed at 90 °C for 6 h. Then the reaction was quenched with water (50 mL) filtered through Celite, and extracted with ethyl acetate. The organic layer was washed with brine and dried with anhydrous Na_2SO_4. After evaporating under reduced pressure, compound **II** was obtained without further purification.

Step 3 Under an argon atmosphere, product **II** was dissolved in dry THF (0.5 M), followed by the addition of a pre-mixed solution of formic acid (1.3 mL, 35 mmol, 3.5 equiv.) and acetic anhydride (1.3 mL, 15 mmol, 1.5 equiv.) (prepared by stirring for 30 min). The reaction mixture was stirred at room temperature for 12 h. Upon completion, a saturated aqueous sodium bicarbonate solution was slowly added dropwise with stirring until gas evolution ceased. The mixture was extracted with ethyl acetate, The organic layer was washed with brine and dried with anhydrous Na_2SO_4. After evaporating under reduced pressure, compound **III** was obtained without further purification.

Step 4 Under an argon atmosphere, product **III** was dissolved in dry DCM (0.2 M), followed by the addition of Et_3N (7 mL, 50 mmol, 5.0 equiv.) at 0 °C. Then, $POCl_3$ (1.1 mL, 12 mmol, 1.2 equiv.) was added dropwise slowly, and the reaction was continued at 0 °C for 2 h. After completion, the reaction was quenched by the slow addition of saturated aqueous sodium bicarbonate solution at 0 °C. The mixture was extracted with DCM (20 mL×3), The organic layer was washed with brine and dried with anhydrous Na_2SO_4. After evaporating under reduced pressure, the residue was purified using flash column chromatography with silica gel to give compound **VI**.

Step 5 Under an argon atmosphere, LDA (2 M in THF, 1.2 mL, 2.4 mmol, 1.2 equiv.) was added to 10 mL of anhydrous THF and cooled to -78 °C. A solution of product **IV** (0.56 g, 2.2 mmol, 1.1 equiv.) in THF was added dropwise, followed by the dropwise addition of 2,2,2-trifluoro-1-phenylethan-1-one (0.28 mL, 2.0 mmol, 1.0 equiv.) over 20 minutes. After stirring for an additional 30 minutes at -78 °C, the reaction mixture was warmed to room temperature and stirred for 3 hours. The reaction was then quenched with saturated aqueous ammonium chloride, and the mixture was extracted with ethyl acetate. the residue was purified using flash column chromatography with silica gel to give compound **1**.



(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-phenylprop-1-en-1-yl)benzene (1a)

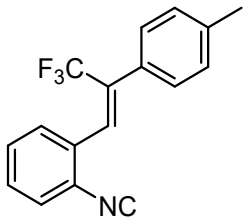
Purple solid (0.42 g, 76% yield, m.p. = 64-65 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.53 (m, 1H), 7.44-7.35 (m, 4H), 7.33-7.24 (m, 3H), 7.11-7.07 (m, 1H), 6.91-6.89 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 134.5 (q, J = 29.9 Hz), 131.6, 130.5, 130.1, 129.7, 129.6, 129.3, 129.0, 128.9, 127.9 (q, J = 6.1 Hz), 127.1, 126.5, 123.4 (q, J = 275.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.88.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}F_3N$: 273.0838, found: 273.0845.



(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(*p*-tolyl)prop-1-en-1-yl)benzene (1b)

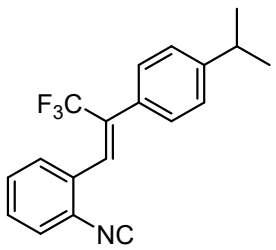
Purple solid (0.34 g, 59% yield, m.p. = 55-56 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 1H), 7.41-7,39 (m, 1H), 7.30-7.26 (m, 1H), 7.20 (s, 4H), 7.14-7.10 (m, 1H), 6.96-6.94 (m, 1H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 139.3, 134.5 (q, J = 30.2 Hz), 130.7, 130.2, 129.7, 129.53, 129.46, 128.9, 128.6, 128.1, 127.5 (q, J = 6.1 Hz), 127.1, 123.2 (q, J = 237.8 Hz), 21.3.

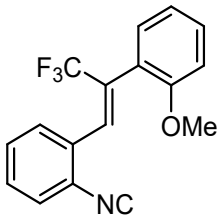
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.92.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}F_3N$: 288.0995, found: 288.0988.

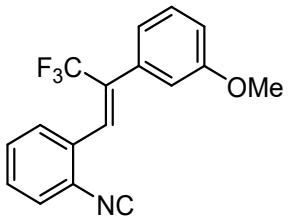


(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(4-isopropylphenyl)prop-1-en-1-yl)benzene (1c)

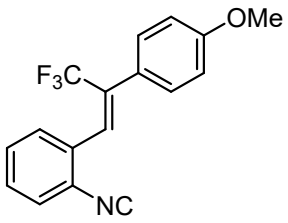
Purple solid (0.28 g, 44% yield, m.p. = 44-45 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 1H), 7.41-7.39 (m, 1H), 7.31-7.17 (m, 5H), 7.11-7.07 (m, 1H), 6.91-6.89 (m, 1H), 3.02-2.85 (m, 1H), 1.29 (d, J = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 150.1, 134.5 (q, J = 30.2 Hz), 130.8, 130.2, 129.6 (2C), 129.4, 128.9, 128.8, 127.4 (q, J = 6.1 Hz), 127.1, 127.0, 123.2 (q, J = 249.1 Hz), 33.9, 23.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.92.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_3N$: 316.1308, found: 316.1302.



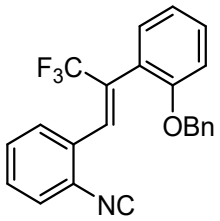
(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(2-methoxyphenyl)prop-1-en-1-yl)benzene (1d)
White solid (0.36 g, 59% yield, m.p. = 96-97 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.41-7.36 (m, 2H), 7.27-7.23 (m, 2H), 7.10-7.06 (m, 1H), 7.04-6.93 (m, 2H), 6.91-6.88 (m, 1H), 3.66 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 157.4, 131.3, 130.93, 130.87, 130.7 (q, J = 31.3 Hz), 129.31, 129.26 (q, J = 6.1 Hz), 128.9, 126.8, 124.7, 123.3 (q, J = 274.7 Hz),122.0, 120.9, 120.5, 111.4, 55.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.02.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}F_3NO$: 304.0944, found: 304.0951.



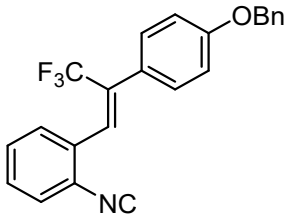
(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(3-methoxyphenyl)prop-1-en-1-yl)benzene (1e)
Purple solid (0.34 g, 56% yield, m.p. = 43-44 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.48 (m, 1H), 7.40-7.38 (m, 1H), 7.30-7.23 (m, 2H), 7.11-7.08 (m, 1H), 6.94-6.90 (m, 2H), 6.88-6.78 (m, 2H), 3.76 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 160.2, 134.6 (q, J = 30.2 Hz), 133.2, 130.9, 130.5 (2C), 129.9, 129.3, 128.1 (q, J = 6.3 Hz), 127.5, 127.0, 123.6 (q, J = 274.7 Hz), 122.4, 115.5, 115.2, 55.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.94.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}F_3NO$: 304.0944, found: 304.0946.



(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)benzene (1f)
Purple solid (0.32 g, 53% yield, m.p. = 59-60 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.45 (m, 1H), 7.40-7.38 (m, 1H), 7.29-7.25 (m, 1H), 7.24-7.17 (m, 2H), 7.14-7.10 (m, 1H), 6.96-6.93 (m, 1H), 6.92-6.87 (m, 2H), 3.82 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 160.2, 134.1 (q, J = 30.3 Hz), 131.0, 130.9, 130.1, 129.4, 128.9, 127.4 (q, J = 6.1 Hz), 127.1, 126.5, 123.4 (q, J = 272.0 Hz), 123.6, 114.4, 55.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.99.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}F_3NO$: 304.0944, found: 304.0941.



(*Z*)-1-(benzyloxy)-2-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)benzene (1g)
Purple solid (0.54 g, 71% yield, m.p. = 72-73 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39-7.27 (m, 6H), 7.27-7.22 (m, 1H), 7.20-7.18 (m, 2H), 7.07-7.00 (m, 2H), 6.97-6.96 (m, 1H), 6.93-6.92 (m, 1H), 5.01-4.89 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 156.7, 137.0, 131.6, 131.5, 131.2, 130.8 (q, J = 31.5 Hz), 129.7, 129.5 (q, J = 6.3 Hz), 129.2, 129.1, 128.9, 128.2, 127.7, 127.4, 127.2, 123.8 (q, J = 233.1 Hz), 121.5, 121.1, 113.0, 70.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.95.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}F_3NO$: 380.1257, found: 380.1255.



(*Z*)-1-(2-(4-(benzyloxy)phenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-isocyanobenzene (1h)

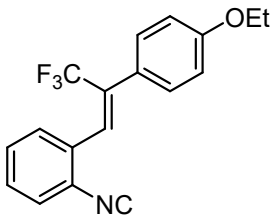
Purple solid (0.58 g, 76% yield, m.p. = 55-56 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 7H), 7.20-7.16 (m, 1H), 7.15-7.09 (m, 2H), 7.07-6.99 (m, 1H), 6.93-6.81 (m, 3H), 4.98 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 159.9, 136.9, 134.5 (q, J = 30.2 Hz), 131.5, 131.3, 130.6, 129.8, 129.3, 129.1, 128.6, 128.0, 127.8 (q, J = 6.3 Hz), 127.6, 127.0, 124.3, 123.8 (q, J = 274.7 Hz), 115.7, 70.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.89.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}F_3NO$: 380.1257, found: 380.1263.



(*Z*)-1-(2-(4-ethoxyphenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-isocyanobenzene (1i)

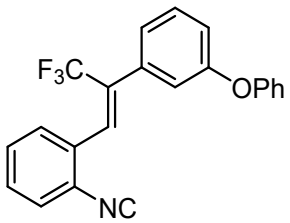
Purple solid (0.49 g, 78% yield, m.p. = 54-55 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.38-7.36 (m, 1H), 7.26-7.22 (m, 1H), 7.16-7.14 (m, 2H), 7.09 (t, J = 7.8 Hz, 1H), 6.90-6.89 (m, 1H), 6.87-6.81 (m, 2H), 4.03 (q, J = 6.9 Hz, 2H), 1.42 (t, J = 14.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 159.7, 134.3 (q, J = 29.4 Hz), 131.1, 130.2, 129.4, 129.0, 127.3 (q, J = 6.3 Hz), 127.2, 126.8, 123.53, 123.45 (q, J = 267.9 Hz), 114.9, 114.3, 63.6, 14.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.04.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_3NO$: 318.1100, found: 318.1102.

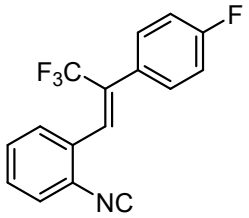


(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(3-phenoxyphenyl)prop-1-en-1-yl)benzene (1j)

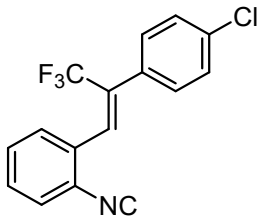
Purple solid (0.37 g, 51% yield, m.p. = 66-67 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 1H), 7.32-7.28 (m, 2H), 7.25-7.17 (m, 3H), 7.10-7.06 (m, 1H), 7.04-7.00 (m, 1H), 7.00-6.92 (m, 2H), 6.86-6.84 (m, 1H), 6.83-6.74 (m, 3H).

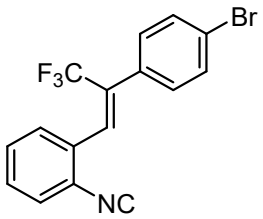
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 157.6, 156.6, 134.0 (q, J = 30.3 Hz), 133.2, 130.5, 130.4, 130.2, 129.8, 129.6, 128.9, 128.3 (q, J = 6.1 Hz). 127.2, 124.3, 123.7, 122.4 (q, J = 139.4 Hz), 120.1, 119.7, 119.1, 118.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.94.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}F_3NO$: 366.1100, found: 366.1095.



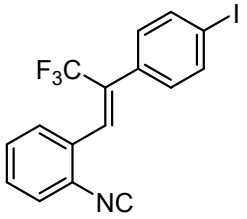
(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(4-fluorophenyl)prop-1-en-1-yl)benzene (1k)
Purple solid (0.45 g, 77% yield, m.p. = 80-81 ℃), purified by flash column chromatography on silica gel using petroleum ether ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H), 7.39-7.38 (m, 1H), 7.30-7.21 (m, 3H), 7.13-7.09 (m, 1H), 7.08-7.01 (m, 2H), 6.87-6.83 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 164.5, 162.5, 134.0 (q, J = 30.2 Hz), 132.1 (d, J = 7.6 Hz), 130.8, 130.4, 130.0, 129.3, 128.7 (q, J = 6.3 Hz), 127.9 (d, J = 3.8 Hz), 127.6, 123.5 (q, J = 274.7 Hz), 116.5 (d, J = 10.1 Hz).
^{19}F NMR (470 MHz, $CDCl_3$) δ -66.10, -111.41.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}F_4N$: 292.0744, found: 292.0739.



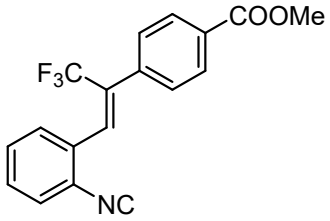
(*Z*)-1-(2-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-isocyanobenzene (1l)
Purple oil (0.42 g, 69% yield, *Z*/*E* = 6/1), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.49 (m, 1H), 7.41-7.37 (m, 1H), 7.36-7.30 (m, 2H), 7.31-7.25 (m, 1H), 7.22-7.18 (m, 2H), 7.14-7.11 (m, 1H), 6.86-6.87 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 135.9, 133.8 (q, J = 27.3 Hz), 131.5, 130.7, 130.4, 130.1, 130.0, 129.7, 129.4, 129.3, 128.9 (q, J = 6.0 Hz), 127.7, 123.4 (q, J = 246.86 Hz).
^{19}F NMR (470 MHz, $CDCl_3$) δ -65.88.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}ClF_3N$: 308.0448, found: 308.0457.



(*Z*)-1-(2-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-isocyanobenzene (1m)
Purple oil (0.53 g, 75% yield, *Z*/*E* = 5/1), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.47 (m, 3H), 7.42-7.39 (m, 1H), 7.30-7.27 (m, 1H), 7.15-7.10 (m, 3H), 6.87-6.85 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 133.8 (q, J = 37.5 Hz), 132.7, 131.8, 130.7, 130.4, 130.2, 130.0, 129.5, 129.0 (q, J = 6.3 Hz), 127.7, 126.9, 124.1, 123.4 (q, J = 274.7 Hz).
^{19}F NMR (470 MHz, $CDCl_3$) δ -65.88.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}BrF_3N$: 351.9943, found: 351.9951.

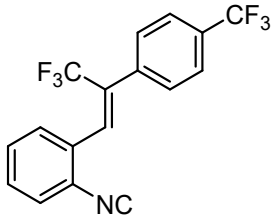


(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(4-iodophenyl)prop-1-en-1-yl)benzene (1n)
Purple solid (0.61 g, 78% yield, *Z*/*E* = 5/1, m.p. = 76-77 ℃), purified by flash column chromatography on silica gel using petroleum ether ethyl acetate = 80: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.67 (m, 2H), 7.53-7.52 (m, 1H), 7.41-7.39 (m, 1H), 7.31-7.27 (m, 1H), 7.16-7.12 (m, 1H), 7.04-7.02 (m, 2H), 6.92-6.90 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 138.2, 133.4 (q, J = 30.2 Hz), 131.5, 130.2, 130.0, 129.8, 129.6, 129.2, 128.5 (q, J = 6.1 Hz), 127.3, 127.1, 122.9 (q, J = 255.2 Hz), 95.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.65.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}F_3IN$: 399.9805, found: 399.9800.

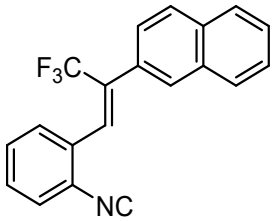


methyl (*Z*)-4-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)benzoate (1o)

Purple oil (0.31 g, 47% yield, *Z*/*E* = 2/1), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.61-7.60 (m, 1H), 7.53-7.52 (m, 1H), 7.35-7.33 (m, 2H), 7.28-7.24 (m, 1H), 7.08-7.05 (m, 1H), 6.82-6.80 (m, 1H), 3.91 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 166.8, 140.0, 136.7, 133.1 (q, J = 30.2 Hz), 132.1, 131.2, 130.5, 130.3, 130.2, 129.4, 129.3 (q, J = 6.3 Hz), 128.6, 127.6, 123.4 (q, J = 274.7 Hz), 52.7.
^{19}F NMR (470 MHz, $CDCl_3$) δ -65.61.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}F_3NO_2$: 332.0893, found: 332.0889.

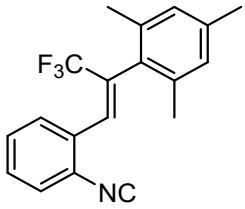


(*Z*)-1-isocyano-2-(3,3,3-trifluoro-2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)benzene (1p)
Purple oil (0.26 g, 38% yield, *Z*/*E* = 3/1), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.68 (m, 1H), 7.62-7.61 (m, 2H), 7.42-7.40 (m, 3H), 7.31-7.28 (m, 1H), 7.14-7.10 (m, 1H), 6.84-6.82 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 135.8, 134.9 (q, J = 4.2 Hz), 133.7 (q, J = 30.2 Hz), 131.9 (q, J = 16.4 Hz), 131.4 (q, J = 16.4 Hz), 130.7, 130.4, 129.5, 129.1, 127.7, 126.9, 126.3 (q, J = 3.8 Hz), 124.2 (q, J = 273.0 Hz), 123.4 (q, J = 274.2 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88, -65.70.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{10}F_6N$: 342.0712, found: 342.0715.

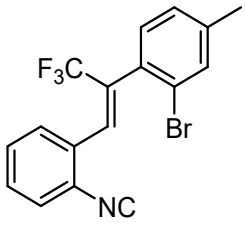


(*Z*)-2-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)naphthalene (1q)
Purple solid (0.34 g, 53% yield, m.p. = 57-58 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.79 (m, 4H), 7.59 (s, 1H), 7.57-7.50 (m, 2H), 7.38-7.39 (m, 1H), 7.31-7.29 (m, 1H), 7.23-7.20 (m, 1H), 6.99-6.95 (m, 1H), 6.88-6.86 (m, 1H).

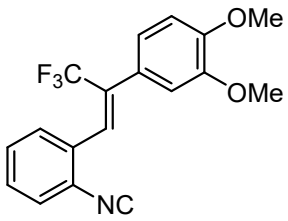
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 134.8 (q, J = 29.8 Hz), 133.7, 133.6, 131.0, 130.6, 129.9, 129.6, 129.4, 129.3, 129.1, 128.7, 128.4 (q, J = 5.9 Hz), 128.2, 127.6, 127.5, 127.4, 127.0, 125.9, 123.8 (q, J = 269.2 Hz).
^{19}F NMR (470 MHz, $CDCl_3$) δ -65.57.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{13}F_3NO$: 324.0995, found: 324.0999.



(*Z*)-1,3,5-trimethyl-2-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)benzene (1r)
White solid (0.33 g, 52% yield, m.p. = 104-105 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (m, 1H), 7.41-7.39 (m, 1H), 7.28-7.25 (m, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.94 (s, 2H), 6.78-6.76 (m, 1H), 2.32 (s, 3H), 2.15 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 139.2, 137.5, 132.9 (q, J = 31.5 Hz), 130.4, 130.2, 129.8, 129.5, 128.9, 128.3 (q, J = 6.3 Hz), 127.9, 127.7, 126.9, 124.1 (q, J = 257.9 Hz), 21.5, 20.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -65.19.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_3N$: 316.1308, found: 316.1307.



(*Z*)-2-bromo-4-methyl-1-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)benzene (1s)
Purple solid (0.34 g, 46% yield, m.p. = 51-52 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 7.8 Hz, 1H), 7.52-7.50 (m, 1H), 7.43-7.39 (m, 2H), 7.37-7.35 (m, 2H), 7.33-7.28 (m, 2H), 2.42 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 138.6, 134.9, 134.1, 133.7, 129.9, 129.8, 128.7, 127.8, 127.8, 126.2, 125.4, 124.5, 122.7, 20.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.60.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}BrF_3N$: 360.0100, found: 360.0105.



(*Z*)-1,2-dimethoxy-4-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)benzene (1t)

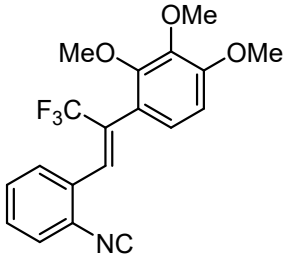
Purple solid (0.31 g, 47% yield, m.p. = 72-73 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 2.0 Hz, 1H), 7.36-7.34 (m, 1H), 7.25-7.21 (m, 1H), 7.11-7.06 (m, 1H), 6.94-6.90 (m, 1H), 6.82-6.81 (m, 2H), 6.69 (s, 1H), 3.86 (s, 3H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 149.7, 149.1, 134.2 (q, J = 29.8 Hz), 130.8, 130.0, 129.4, 128.9, 127.4 (q, J = 6.1 Hz), 127.1, 126.4, 123.7, 122.4, 121.3 (q, J = 240.0 Hz), 112.5, 111.3, 55.9, 55.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.93.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_3NO_2$: 342.1049, found: 308.1052.



(*Z*)-1,2,3-trimethoxy-4-(3,3,3-trifluoro-1-(2-isocyanophenyl)prop-1-en-2-yl)benzene (1u)

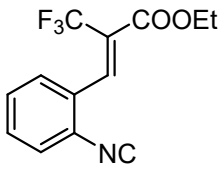
Purple oil (0.56 g, 77% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.36-7.35 (m, 1H), 7.23-7.20 (m, 1H), 7.08-7.05 (m, 1H), 6.96-6.90 (m, 2H), 6.69-6.67 (m, 1H), 3.87 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 155.2, 152.4, 143.0, 131.8, 130.4 (q, J = 30.2 Hz), 129.9 (q, J = 6.3 Hz), 129.7, 129.4, 129.2, 127.3, 125.5, 123.7 (q, J = 273.6 Hz), 122.6, 118.3, 107.7, 61.2, 61.1, 56.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.94.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_3NO_3$: 364.1155, found: 364.1158.

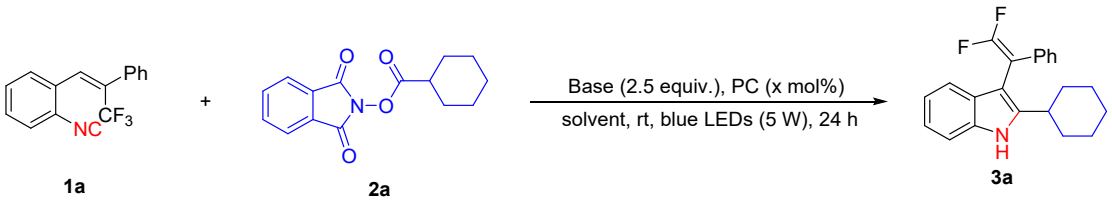


ethyl (*Z*)-3-(2-isocyanophenyl)-2-(trifluoromethyl)acrylate (1v)
Yellow oil (0.23 g, 42% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 80: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.51-7.35 (m, 4H), 4.21 (q, J = 6.9 Hz, 2H), 1.15 (t, J = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 162.1, 136.6, 130.8, 130.6, 130.0, 129.3, 129.2, 127.3, 127.0, 121.6 (q, J = 272.5 Hz), 62.3, 13.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ -64.4.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}F_3NO_2$: 270.0736, found: 270.0735

3. Optimization of the reaction conditions

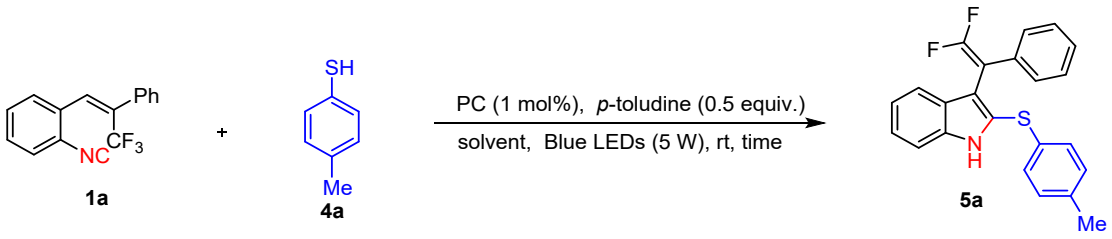
Table S1. Optimization of the reaction conditions



Entry[a]	Solvent	Base	PC	Yield[b] (%)
1	DMSO	DIPEA	4CzIPN (4 mol%)	58
2	DMF	DIPEA	4CzIPN (4 mol%)	62
3	1,4-Dioxane	DIPEA	4CzIPN (4 mol%)	49
4	Toluene	DIPEA	4CzIPN (4 mol%)	66
5	DCM	DIPEA	4CzIPN (4 mol%)	45
6	THF	DIPEA	4CzIPN (4 mol%)	68
7	Acetone	DIPEA	4CzIPN (4 mol%)	90
8	DCE	DIPEA	4CzIPN (4 mol%)	95
9	DME	DIPEA	4CzIPN (4 mol%)	57
10	Et_2O	DIPEA	4CzIPN (4 mol%)	47
11	DMA	DIPEA	4CzIPN (4 mol%)	62
12	MeCN	DIPEA	4CzIPN (4 mol%)	96
13	MeCN	DIPEA	4CzIPN (1 mol%)	63
14	MeCN	DIPEA	4CzIPN (2 mol%)	88
15	MeCN	DIPEA	4CzPN (4 mol%)	86
16	MeCN	DIPEA	4CzIPN-^{t}Bu (4 mol%)	41
17	MeCN	DIPEA	4CzIPN-Br (4 mol%)	89
18	MeCN	DIPEA	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4 mol%)	58

19	MeCN	DIPEA	$Ir(dFppy)_2(dtbbpy)PF_6$ (4 mol%)	63
20	MeCN	DABCO	4CzIPN (4 mol%)	NR
21	MeCN	DBU	4CzIPN (4 mol%)	NR
22	MeCN	NEt_3	4CzIPN (4 mol%)	47

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), PC (x mol%), Base (2.5 equiv.) were dissolved in solvent (4 mL), and the solution was irradiated with 5 W blue LEDs under Ar at room temperature for 24 h. Yield of isolated products.

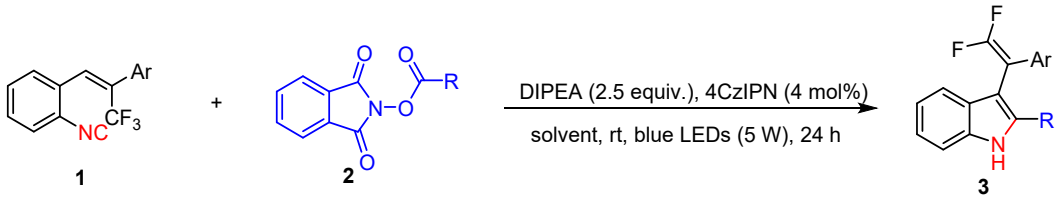


Entry[a]	PC	Solvent	Time	Yield (%)
1	$[Ru(bpy)_3](PF_6)_2$	DMSO (1.0 mL)	12 h	62
2	$[Ru(bpy)_3]Cl_2·6H_2O$	DMSO (1.0 mL)	12 h	trace
3	$[Ru(phen)_3]Cl_2$	DMSO (1.0 mL)	12 h	trace
4	$[Ru(dtbbpy)_3](PF_6)_2$	DMSO (1 mL)	12 h	trace
5	$[Ru(dmbpy)_3](PF_6)_2$	DMSO (1.0 mL)	12 h	trace
6	$[Ru(bpy)_3](PF_6)_2$	DMSO (1.0 mL)	16 h	67
7	$[Ru(bpy)_3](PF_6)_2$	DMSO (1.0 mL)	20 h	71
8	$[Ru(bpy)_3](PF_6)_2$	DMSO (1.0 mL)	24 h	77
9	$[Ru(bpy)_3](PF_6)_2$	DMF (1.0 mL)	24 h	64
10	$[Ru(bpy)_3](PF_6)_2$	THF (1.0 mL)	24 h	37
11	$[Ru(bpy)_3](PF_6)_2$	DCM (1.0 mL)	24 h	61
12	$[Ru(bpy)_3](PF_6)_2$	MeCN (1.0 mL)	24 h	trace
13	$[Ru(bpy)_3](PF_6)_2$	DMSO (0.5 mL)	24 h	65
14	$[Ru(bpy)_3](PF_6)_2$	DMSO (2.0 mL)	24 h	86
15	$[Ru(bpy)_3](PF_6)_2$	DMSO (3.0 mL)	24 h	54

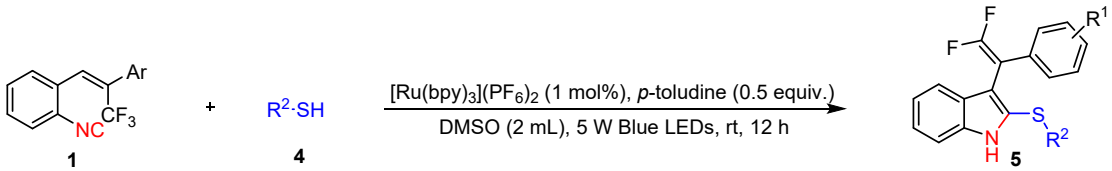
[a]Reaction conditions: **4a** (0.12 mmol), **1a** (0.1 mmol), *p*-toludine (0.5 equiv.), PC (1 mol%) were dissolved in solvent, and the solution was irradiated with 5W blue LEDs under Ar at room temperature for 24 h. Yield of isolated products.

4. General procedures

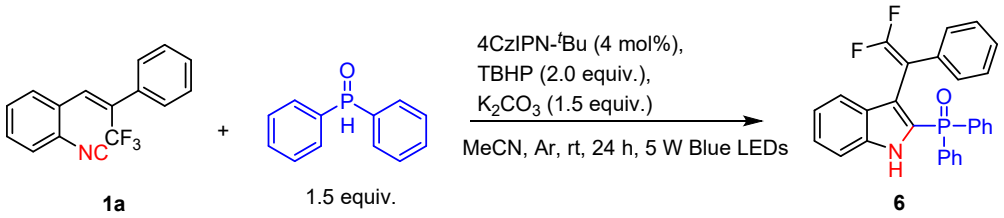
The photoreactor used is an 8-hole blue light reactor purchased from Wuhan Ge'ao Chemical Technology Co., Ltd., with a wavelength of 450-464 nm and a total power of 40 watts. The power of each reaction well is approximately 5 watts. The reaction tube type is P160002 from Synthware. The material of the irradiation vessel is borosilicate glass and no filters.



To a flame-dried Pressure tube were added *o*-alkenyl aryl isocyanide **1** (0.2 mmol, 1.0 equiv.), NHPI esters **2** (0.3 mmol, 1.5 equiv.), and 4CzIPN (6.4 mg, 4 mol%) under an argon atmosphere, then DIPEA (88 μL, 0.5 mmol, 2.5 equiv.) and MeCN (4.0 mL) was added via syringe. The resulting mixture was stirred for 24 h under irradiation with a 5 W blue LEDs at room temperture. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford the corresponding products.

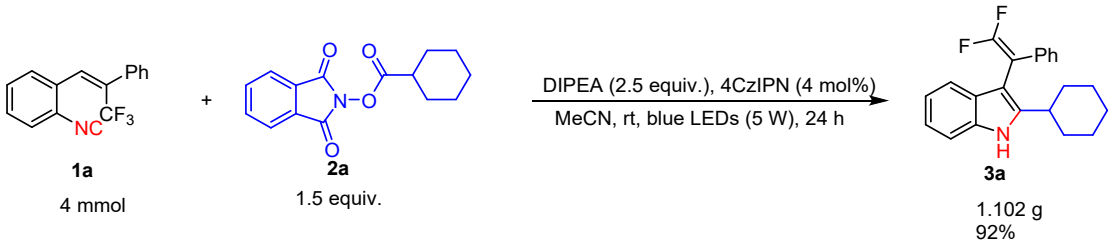


To a flame-dried Pressure tube were added *o*-alkenyl aryl isocyanide **1** (0.12 mmol, 1.2 equiv.), thiophenol or mercaptan (0.1 mmol, 1.0 equiv.), and $[Ru(bpy)_3](PF_6)$ (0.9 mg, 1 mol%), under a argon atmosphere, then *p*-toludine (73 μL, 0.05 mmol, 0.5 equiv.) and DMSO (2.0 mL) was added via syringe. The resulting mixture was stirred for 24 h under irradiation with a 5 W blue LEDs at room temperture. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford the corresponding products.



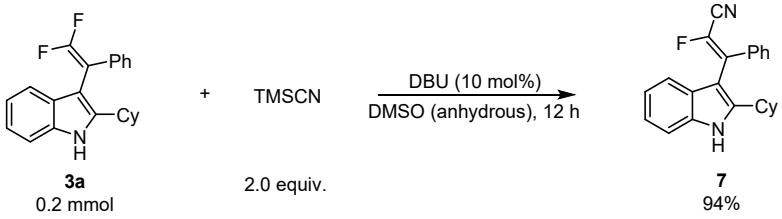
To a flame-dried Pressure tube were added **1a** (0.1 mmol, 1.0 equiv.), diphenylphosphine oxide (0.15 mmol, 1.5 equiv.), TBHP (64 mg, 0.2 mmol, 2.0 equiv.), and 4CzIPN-*t*Bu (5.0 mg, 4 mol%), under an argon atmosphere, then MeCN (2.0 mL) was added via syringe. The resulting mixture was stirred for 24 h under irradiation with a 5 W blue LEDs at room temperture. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford the corresponding products.

5. Gram-scale synthesis and further transformations



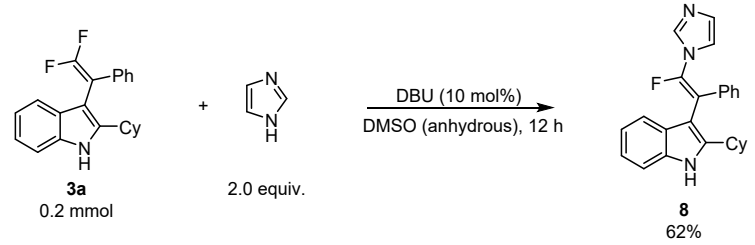
To a flame-dried 100 mL reaction flask were added **1a** (1.09 g, 4 mmol, 1.0 equiv.), **2a** (1.64 g, 6 mmol, 1.5 equiv.), and 4CzIPN (6.4 mg, 4 mol%) under an argon atmosphere, then DIPEA (1.76 mL, 6.0 mmol, 2.5 equiv.) and MeCN (40 mL) was added via syringe. The resulting mixture was stirred for 24 h under irradiation with a 5 W blue LEDs at room temperture. The resulting mixture was quenched with H_2O (100 mL), extracted with ethyl acetate (30 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 50: 1) to afford **3a** (1102 mg, 92% yield): yellow solid.

Synthesis of **7**



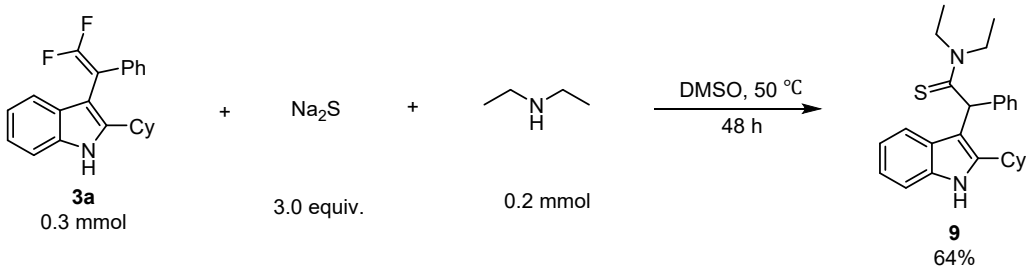
To a flame-dried pressure tube were added **3a** (0.2 mmol, 1.0 equiv.) and TMSCN (0.4 mmol), then DBU (3 μL, 0.02 mmol, 10 mol%) and DMSO (2.0 mL) was added via syringe. The resulting mixture was stirred for 12 h at room temperture. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 50: 1) to afford the corresponding products as a yellow oil (63.5 mg, 94% yield).

Synthesis of **8**



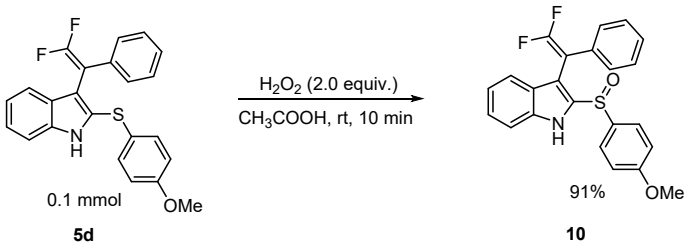
To a flame-dried pressure tube were added **3a** (0.2 mmol, 1.0 equiv.) and imidazole (0.4 mmol), then DBU (3 μL, 0.02 mmol, 10 mol%) and DMSO (2.0 mL) was added via syringe. The resulting mixture was stirred for 12 h at room temperture. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 50: 1) to afford the corresponding products as a yellow oil (47.8 mg, 62% yield).

Synthesis of **9**



To a flame-dried pressure tube were added **3a** (0.3 mmol, 1.5 equiv.), Na_2S (0.6 mmol), $HNEt_2$ (0.2 mmol, 1.0 equiv.) and DMSO (2.0 mL). The resulting mixture was stirred for 48 h at 50 ℃. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 10: 1) to afford the corresponding products as a white solid (52 mg, 64% yield).

Synthesis of **10**

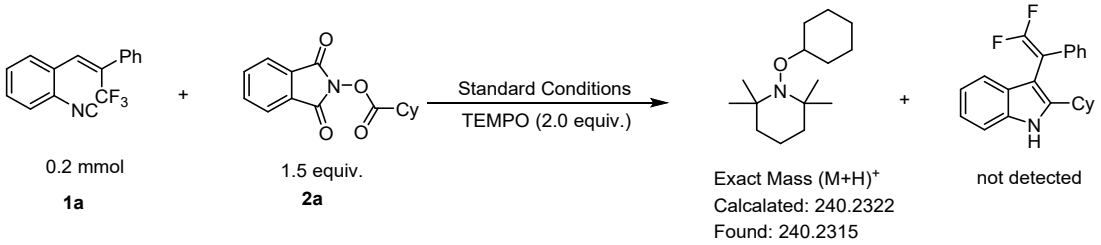


A solution of compound **5d** (0.1 mmol, 1.0 equiv.) in acetic acid (1 mL) was treated with H_2O_2 (0.2 mmol, 2.0 equiv.) at ambient temperature under an air atmosphere. The resulting mixture was stirred for 10 minutes. The resulting mixture was quenched with $NaHCO_3$, extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the

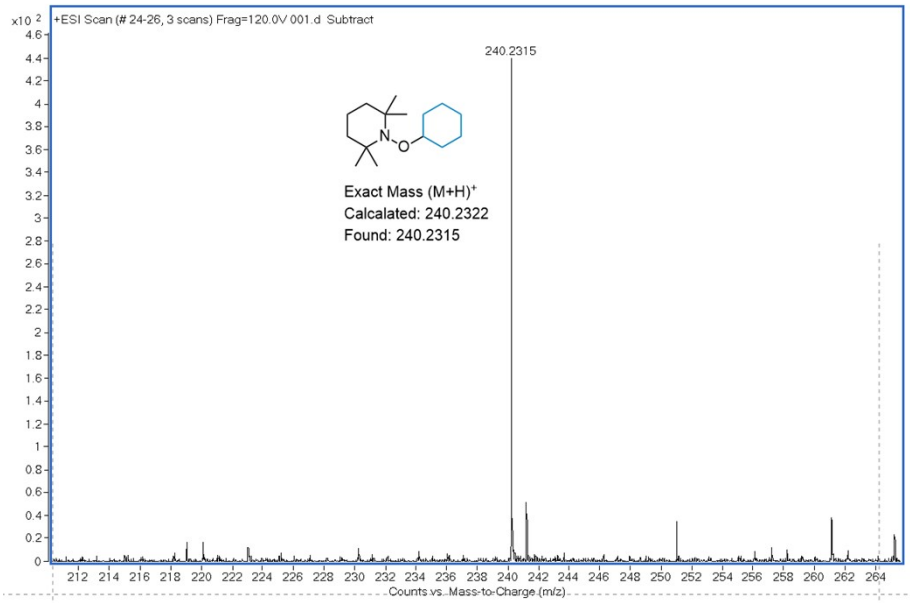
obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 3: 1) to afford the corresponding products as a colorless oil (38 mg, 92% yield).

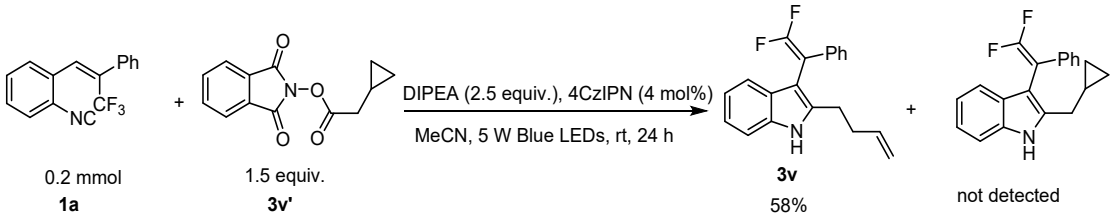
6. Mechanistic experiments

6.1 Radical-trapping and radical clock experiment



To a flame-driedpressure tube were added *o*-alkenyl aryl isocyanide **1a** (0.2 mmol, 1.0 equiv.), NHPI ester **2a** (0.3 mmol, 1.5 equiv.), TEMPO (0.4 mmol, 2.0 equiv.) and 4CzIPN (6.4 mg, 4 mol%) under an argon atmosphere, then DIPEA (88 μL, 0.5 mmol, 2.5 equiv.) and MeCN (4.0 mL) was added via syringe. The resulting mixture was stirred for 24 h under irradiation with a 5 W blue LEDs at room temperture. The reaction was monitored by HRMS analysis.



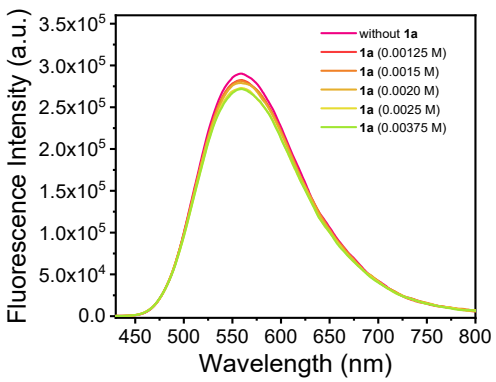


To a flame-dried pressure tube were added *o*-alkenyl aryl isocyanide **1a** (0.2 mmol, 1.0 equiv.), NHPI ester **3v'** (0.3 mmol, 1.5 equiv.), and 4CzIPN (6.4 mg, 4 mol%) under an argon atmosphere, then DIPEA (88 μL, 0.5 mmol, 2.5 equiv.) and MeCN (4.0 mL) was added via syringe. The resulting mixture was stirred for 24 h under irradiation with a 5 W blue LEDs at room temperture. The resulting mixture was quenched with H_2O (10 mL), extracted with ethyl acetate (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 50: 1) to afford as a colorless oil.

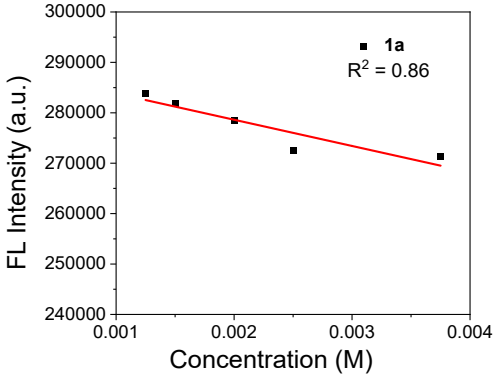
6.2 Fluorescence Quenching Experiment

A 8.0×10^{-5} M solution of 4CzIPN (2.5 mg, 3.2×10^{-3} mmol) in anhydrous and degassed MeCN (40 mL) was prepared in a nitrogen filled glovebox. 4CzIPN solution (2.0 mL) was transferred by pipetting gun (5 mL) to a 3.5 mL quartz cuvette (path length: l = 1.0 cm) and sealed quartz cuvette with Teflon cap under an atmosphere of nitrogen in glove box, then sealed the cap with parafilm and removed the quartz cuvette out of glove box. Emission spectra of the solution were measured (λex = 420 nm), other four 2 mL 4CzIPN (8.0×10^{-5} M) solution containing various concentrations of corresponding quencher (0.00125 M, 0.0015 M, 0.0020 M, 0.0025 M, 0.00375 M) also were prepared in glove box under nitrogen atmosphere, then transferred to 3.5 mL quartz cuvette (path length: l = 1.0 cm) and sealed quartz cuvette with Teflon cap under an atmosphere of nitrogen in glove box, then sealed the cap with parafilm and removed the quartz cuvette out of glove box. Emission spectra of each solution was measured (λex = 420 nm), The Stern-Volmer plots at λmax = 559 nm was shown in Figure **S1**. (Note: the fluorescence of 4CzIPN in MeCN solution is very easy to be quenched by O_2, so all the solution needed to be prepared and transferred in glove box under N_2 atomsphere to obtain accurate results.)

(a)



(b)



(c)

(d)

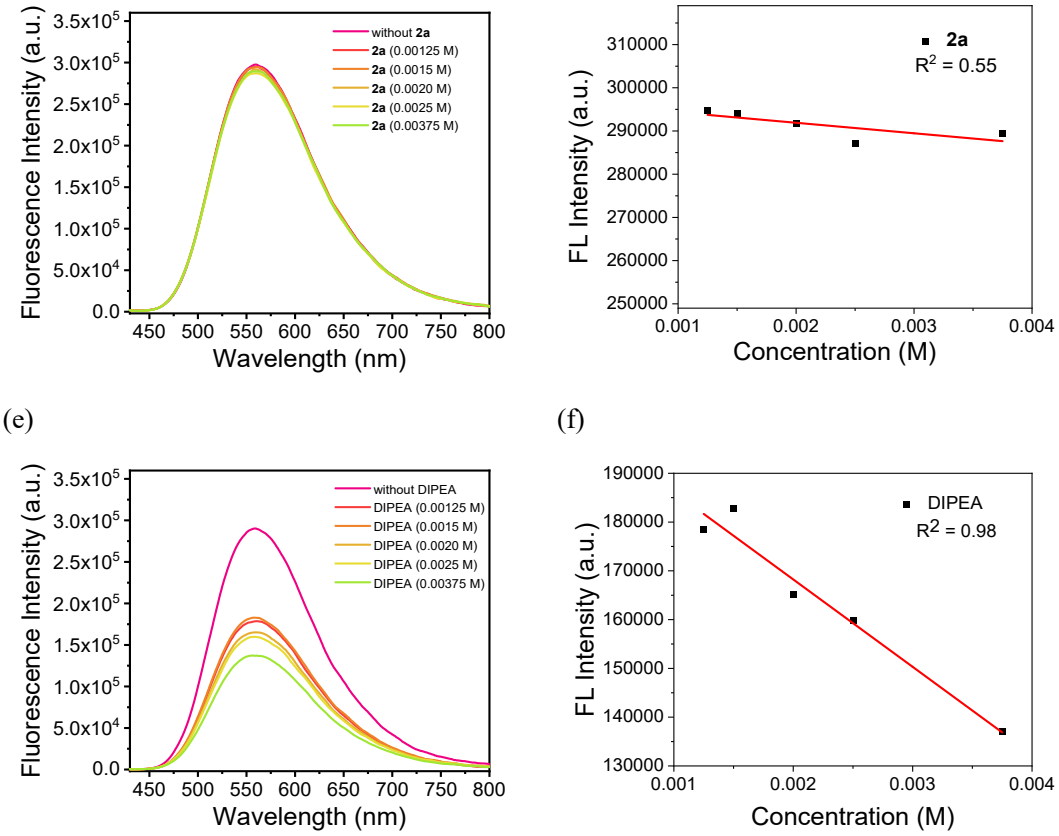


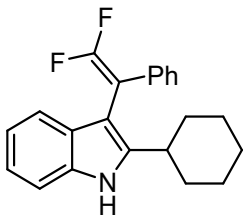
Figure S1: (a) Fluoresence of quenching 4CzIPN by **1a** in anhydrous MeCN. (b) The linear relationship over the increasing concentration of **1a**. (c) Fluoresence of quenching 4CzIPN by **2a** in anhydrous MeCN. (d) The linear relationship over the increasing concentration of **2a**. (e) Fluoresence of quenching 4CzIPN by DIPEA in anhydrous MeCN, (f) The linear relationship over the increasing concentration of DIPEA.

7. References

[1] A. Serafino, H. Pierre, F. L. Vaillant, J. Boutet, G. Guillamot, L. Neuville, G. Masson. Visible-Light-Driven Decarboxylative Borylation: Rapid Access to *α*- and *β*-Amino-boronamides. *Org. Lett.,* **2023***, 25*, 9249-9254.

[2] Z. X. Fang, Y. M. Gong, B. B. Liu, J. Zhang, X. Y. Han, Z. H. Liu, Y. Q. Ning. Rh-Catalyzed Coupling Reactions of Fluoroalkyl *N*-Sulfonylhydrazones with Azides Leading to *α*-Trifluoroethylated Imines. *Org. Lett.,* **2022**, *24*, 8920-8924.

8. Characterization data



2-cyclohexyl-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3a)

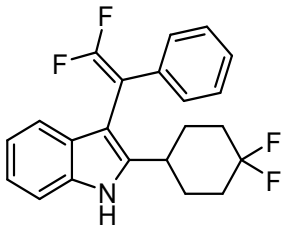
Yellow solid (65 mg, 96% yield, m.p. = 97-98 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 7.39-7.20 (m, 6H), 7.05-7.02 (m, 2H), 6.90-6.87 (m, 1H), 2.64-2.57 (m, 1H), 1.79-1.55 (m, 7H), 1.32-1.13 (m, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 153.6 (dd, J = 296.0, 286.1 Hz), 143.9 (d, J = 3.1 Hz), 136.0, 134.9 (dd, J = 5.7, 4.4 Hz), 128.8, 128.7 (dd, J = 4.0, 4.0 Hz), 127.72, 127.67 (d, J = 3.0 Hz), 121.1, 119.4, 118.4, 111.5, 102.1 (d, J = 4.6 Hz), 89.4 (dd, J = 21.6, 17.7 Hz), 36.7, 32.5, 26.6, 26.0.

^{19}F NMR (376 MHz, DMSO-d_6) δ -85.61 (d, J = 34.0 Hz), -89.96 (d, J = 34.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}F_2N$: 338.1715, found: 338.1707.



3-(2,2-difluoro-1-phenylvinyl)-2-(4,4-difluorocyclohexyl)-1*H*-indole (3b)

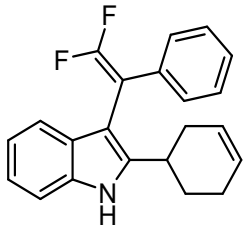
Purple solid (38 mg, 51% yield, m.p. = 141-142 ℃), purified by flash column chromatography on silica gel using petroleum ether ethyl acetate = 50: 1 as eluent

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.41-7.37 (m, 3H), 7.36-7.33 (m, 2H), 7.32-7.28 (m, 1H), 7.27-7.26 (m, 1H), 7.24-7.19 (m, 1H), 7.11-7.08 (m, 1H), 2.83-2.77 (m, 1H), 2.26-2.18 (m, 2H), 1.99-1.92 (m, 2H), 1.89-1.74 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9 (dd, J = 300.0, 288.9 Hz), 140.0, 135.3, 134.4 (dd, J = 5.6, 3.5 Hz), 128.4, 127.8, 127.3, 122.8, 122.1, 120.2, 119.3, 110.8, 104.8 (d, J = 3.0 Hz), 88.3 (dd, J = 21.7, 17.7 Hz), 34.4, 33.8 (dd, J = 25.3, 23.2 Hz), 28.8, 28.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.49 (d, J = 30.1 Hz), -87.86 (d, J = 30.0 Hz), -91.73 (d, J = 237.1 Hz), -102.50 (d, J = 237.1 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}F_4N$: 374.1526, found: 374.1533.



2-(cyclohex-3-en-1-yl)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3c)

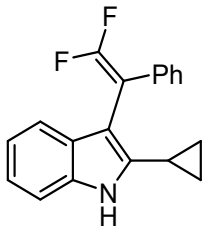
Yellow oil (26 mg, 36% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.37-7.34 (m, 3H), 7.31-7.28 (m, 2H), 7.25-7.21 (m, 2H), 7.17-7.14 (m, 1H), 7.06-7.02 (m, 1H), 5.81 (s, 2H), 3.10-3.05 (m, 1H), 2.27-2.09 (m, 4H), 1.94-1.89 (m, 1H), 1.79-1.70 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (dd, J = 299.9, 289.4 Hz), 142.3 (d, J = 4.0 Hz), 135.2, 134.6 (dd, J = 7.5, 3.8 Hz), 128.5 (dd, J = 5.6, 3.5 Hz), 128.3, 128.0, 127.7, 127.1, 126.3, 121.6, 120.0, 119.1, 110.6, 104.2, 88.4 (dd, J = 21.8, 17.7 Hz), 31.3, 30.9, 28.0, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.41 (d, J = 29.9 Hz), -87.96 (d, J = 30.2 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}F_2N$: 336.1558, found: 336.1552.



2-cyclopropyl-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3d)

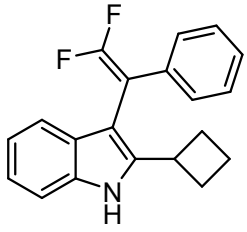
Yellow oil (28 mg, 48% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.38-7.37 (m, 2H), 7.34-7.27 (m, 4H), 7.16-7.12 (m, 2H), 7.04-7.00 (m, 1H), 1.94-1.87 (m, 1H), 0.95-0.88 (m, 2H), 0.78-0.71 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2 (dd, J = 298.6, 289.8 Hz), 139.3, 135.2, 134.9 (dd, J = 5.0, 3.8 Hz), 129.0 (dd, J = 5.0, 3.8 Hz), 128.8, 128.7, 127.4, 122.0, 120.4, 119.3, 110.8, 106.5, 89.0 (dd, J = 20.8, 18.3 Hz), 8.5, 7.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.71 (d, J = 29.3 Hz), -88.96 (d, J = 29.3 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}F_2N$: 296.1245, found: 296.1242.



2-cyclobutyl-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3e)

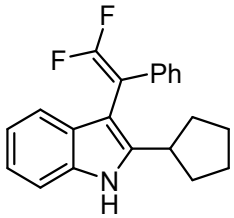
Yellow oil (27 mg, 43% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.38-7.27 (m, 5H), 7.26-7.20 (m, 1H), 7.16-7.12 (m, 2H), 7.04-6.97 (m, 1H), 3.70-3.53 (m, 1H), 2.36-2.15 (m, 4H), 2.09-1.95 (m, 1H), 1.93-1.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (dd, J = 297.5, 288.4 Hz), 141.0, 135.2, 134.6 (dd, J = 7.5, 3.8 Hz), 128.6 (dd, J = 5.6, 3.5 Hz), 128.3, 128.2, 127.2, 121.6, 120.0, 119.2, 110.6, 104.1, 88.3, 32.7, 28.9, 18.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.99 (d, J = 29.8 Hz), -88.77 (d, J = 30.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}F_2N$: 310.1402, found: 310.1407.



2-cyclopentyl-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3f)

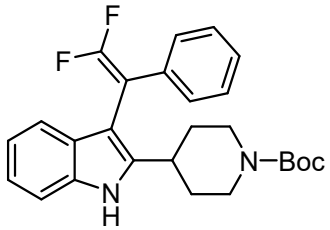
White solid (51 mg, 79% yield, m.p. = 94-95 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 (s, 1H), 7.38-7.30 (m, 3H), 7.29-7.27 (m, 3H), 7.05-7.01 (m, 2H), 6.90-6.86 (m, 1H), 3.07-2.98 (m, 1H), 1.91-1.64 (m, 6H), 1.61-1.55 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 153.6 (dd, J = 298.0, 286.8 Hz), 142.5 (d, J = 3.0 Hz), 136.2, 134.8 (dd, J = 4.5, 3.5 Hz), 128.9, 128.7 (dd, J = 5.0, 5.0 Hz), 127.81 (d, J = 2.0 Hz), 127.75, 121.1, 119.4, 118.3, 111.5, 103.2 (d, J = 4.0 Hz), 89.4 (dd, J = 21.6, 17.5 Hz), 37.8, 33.1, 25.7.

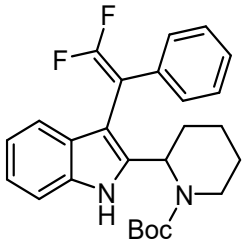
^{19}F NMR (376 MHz, DMSO-d_6) δ -85.32 (d, J = 33.6 Hz), -89.78 (d, J = 33.7 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}F_2N$: 324.1558, found: 324.1553.

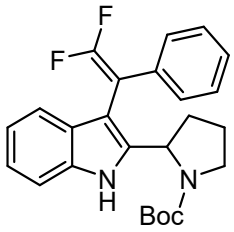


***tert*-butyl 4-(3-(2,2-difluoro-1-phenylvinyl)-1*H*-indol-2-yl)piperidine-1-carboxylate (3g)**

White solid (59 mg, 68% yield, m.p. = 206-207 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.42-7.39 (m, 3H), 7.33 (t, J = 7.5 Hz, 2H), 7.30-7.23 (m, 2H), 7.20-7.17 (m, 1H), 7.08-7.05 (m, 1H), 4.42-4.10 (m, 2H), 2.90-2.84 (m, 1H), 2.75-2.68 (m, 2H), 1.78 (s, 4H), 1.57 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 154.3 (dd, J = 298.6, 288.5 Hz), 141.3, 136.2, 135.1 (dd, J = 5.0, 2.5 Hz), 128.9 (dd, J = 5.0, 3.8 Hz), 128.7, 128.1, 127.5, 122.0, 120.2, 119.5, 111.4, 104.4 (d, J = 3.8 Hz), 88.9 (dd, J = 22.1, 18.3 Hz), 80.3, 45.0, 35.1, 32.1, 29.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.71 (d, J = 30.4 Hz), -88.20 (d, J = 30.2 Hz)
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{28}F_2N_2NaO_2$: 461.2011, found: 461.2005.

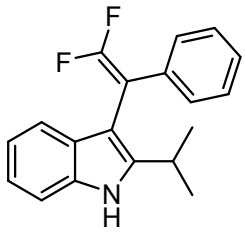


***tert*-butyl 2-(3-(2,2-difluoro-1-phenylvinyl)-1*H*-indol-2-yl)piperidine-1-carboxylate (3h)**
White solid (75 mg, 86% yield, m.p. = 211-212 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.40-7.39 (m, 1H), 7.36-7.35 (m, 2H), 7.32-7.27 (m, 3H), 7.25-7.17 (m, 2H), 7.10-7.07 (m, 1H), 5.50 (s, 1H), 4.17-4.14 (m, 1H), 2.95-2.91 (m, 1H), 2.24-2.21 (m, 1H), 1.87-1.86 (m, 1H), 1.77-1.66 (m, 2H), 1.64-1.61 (m, 2H), 1.46 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 153.7 (dd, J = 298.1, 286.9 Hz), 136.5, 134.7, 134.1, 129.3, 128.5, 128.3 (dd, J = 4.4, 3.1 Hz), 127.2, 122.1, 120.2, 119.1, 110.9, 104.4, 88.7 (dd, J = 17.5, 16.3 Hz), 80.6, 50.3, 41.6, 28.4, 27.8, 25.2, 20.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -81.99 (d, J = 7.2 Hz), -86.95 (d, J = 27.3 Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{28}F_2N_2NaO_2$: 461.2011, found: 461.2018.

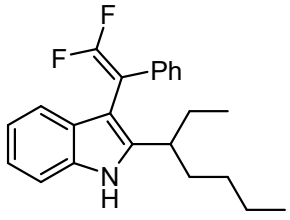


***tert*-butyl 2-(3-(2,2-difluoro-1-phenylvinyl)-1*H*-indol-2-yl)pyrrolidine-1-carboxylate (3i)**
White solid (32 mg, 38% yield, m.p. = 203-204 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.90-7.76 (m, 1H), 7.42-7.33 (m, 3H), 7.32-7.28 (m, 3H), 7.20-7.16 (m, 1H), 7.10-7.06 (m, 1H), 4.86-4.84 (m, 1H), 3.54 (s, 2H), 2.07-1.76 (m, 4H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.4 (dd, J = 181.8, 181.8 Hz), 134.44 (dd, J = 5.6, 4.5 Hz), 134.35, 132.8, 128.7, 128.4, 127.2, 123.6, 121.7, 120.0, 119.0, 111.0, 103.3, 88.2 (dd, J = 24.7, 24.7 Hz), 80.4, 54.9, 47.2, 33.9, 28.3, 23.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -82.46 (d, J = 25.4 Hz), -88.35 (d, J = 25.4 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}F_2N_2O_2$: 425.2035, found: 425.2044.

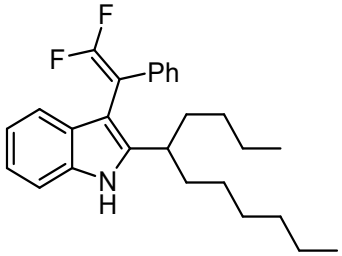


3-(2,2-difluoro-1-phenylvinyl)-2-isopropyl-1*H*-indole (3j)
Yellow oil (49 mg, 82% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.37-7.34 (m, 3H), 7.31-7.27 (m, 2H), 7.26-7.19 (m, 2H), 7.18-7.14 (m, 1H), 7.06-7.02 (m, 1H), 3.19-2.95 (m, 1H), 1.26 (d, J = 7.0 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3 (dd, J = 298.6, 288.5 Hz), 143.9 (d, J =2.5 Hz), 135.6, 135.0 (dd, J = 5.0, 3.8 Hz), 128.9 (dd, J = 5.0, 3.8 Hz), 128.7, 127.4, 126.7, 122.0, 120.3, 119.5, 112.0, 104.0 (d, J = 2.5 Hz), 88.8 (dd, J = 22.1, 18.3 Hz), 26.6, 22.7.
^{19}F NMR (470 MHz, $CDCl_3$) δ -83.44 (d, J = 29.9 Hz), -88.20 (d, J = 30.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}F_2N$: 298.1402, found: 298.1403.

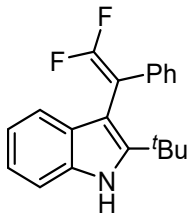


3-(2,2-difluoro-1-phenylvinyl)-2-(heptan-3-yl)-1*H*-indole (3k)
Yellow oil (64 mg, 91% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.45-7.39 (m, 3H), 7.39-7.30 (m, 3H), 7.30-7.21 (m, 2H), 7.18-7.12 (m, 1H), 2.69-2.61 (m, 1H), 1.72-1.62 (m, 2H), 1.60-1.52 (m, 2H), 1.26-1.16 (m, 2H), 1.16-1.06 (m, 2H), 0.84-0.76 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4 (dd, J = 298.0, 290.4 Hz), 142.0 (d, J = 5.0 Hz), 135.7, 135.5 (dd, J = 5.0, 3.8 Hz), 129.1 (dd, J = 5.0, 3.8 Hz), 128.7, 128.6, 127.4, 121.9, 120.3, 119.3, 111.0, 106.7 (d, J = 5.0 Hz), 88.8 (dd, J = 20.8, 18.3 Hz), 39.3, 35.4, 30.2, 28.8, 23.1, 14.4, 12.6.
^{19}F NMR (470 MHz, $CDCl_3$) δ -83.00 (d, J = 29.0 Hz), -88.39 (d, J = 28.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}F_2N$: 354.2028, found: 354.2022.

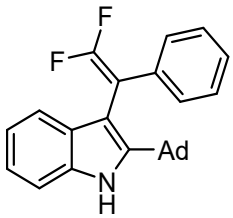


3-(2,2-difluoro-1-phenylvinyl)-2-(undecan-5-yl)-1*H*-indole (3l)
Yellow oil (63 mg,77% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.39-7.35 (m, 4H), 7.31-7.28 (m, 2H), 7.25-7.18 (m, 2H), 7.13-7.10 (m, 1H), 2.70-2.64 (m, 1H), 1.62-1.55 (m, 2H), 1.52-1.45 (m, 2H), 1.32-1.29 (m, 2H), 1.23-1.06 (m, 10H), 0.86 (t, J = 7.1 Hz, 3H), 0.79 (t, J = 7.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4 (dd, J = 298.6, 289.8 Hz), 142.3 (d, J = 2.5 Hz), 135.7, 135.5 (dd, J = 3.8, 3.8 Hz), 129.0 (dd, J = 3.8, 3.8 Hz), 128.7, 128.6, 127.4, 121.9, 120.3, 119.3, 110.9, 106.4 (d, J = 3.8 Hz), 88.7 (dd, J = 21.4, 17.6 Hz), 37.6, 36.0, 35.7, 32.1, 30.0, 29.7, 28.0, 23.1, 23.0, 14.5, 14.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -82.89 (d, J = 28.9 Hz), -88.33 (d, J = 29.0 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{34}F_2N$: 410.2654, found: 410.2646.

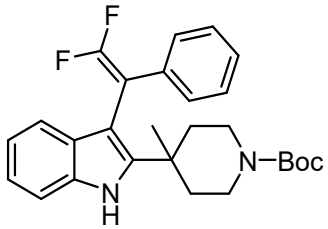


2-(*tert*-butyl)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3m)
Yellow solid (55 mg, 89% yield, m.p. = 96-97 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.02 (s, 1H), 7.39-7.36 (m, 1H), 7.36-7.29 (m, 2H), 7.27-7.24 (m, 3H), 7.18-7.16 (m, 1H), 7.10-7.05 (m, 1H), 6.96-6.92 (m, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 153.5 (dd, J = 299.4, 283.6 Hz), 145.4 (d, J = 3.8), 135.32, 135.26 (d, J = 3.0 Hz), 129.1 (d, J = 3.0 Hz), 128.9, 128.2 (dd, J = 5.7, 3.4 Hz), 127.6, 121.5, 119.6, 118.0, 111.4, 101.5 (d, J = 6.3 Hz), 90.1 (dd, J = 22.2, 15.9 Hz), 33.6, 30.4.
^{19}F NMR (376 MHz, DMSO-d_6) δ -82.15 (d, J = 31.3 Hz), -87.86 (d, J = 31.4 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}F_2N$: 312.1558, found: 312.1553.

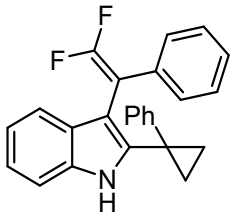


2-((3r,5r,7r)-adamantan-1-yl)-3-(2,2-difluoro-1-phenylethyl)-1*H*-indole (3n)
White solid (61 mg, 78% yield, m.p. = 138-137 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.37-7.35 (m, 4H), 7.30-7.27 (m, 2H), 7.24-7.15 (m, 2H), 7.10-7.07 (m, 1H), 2.06-1.93 (m, 9H), 1.79-1.64 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6 (dd, J = 302.0, 287.9 Hz), 144.6 (d, J = 3.0 Hz), 135.4 (dd, J = 7.5, 3.8 Hz), 134.0, 129.6 (dd, J = 7.5, 5.0 Hz), 128.3, 128.2 (dd, J = 6.1, 4.0 Hz), 126.8, 121.7, 120.0, 118.5, 110.4, 103.1 (d, J = 5.1 Hz), 89.2 (dd, J = 22.2, 16.2 Hz), 41.5, 36.6, 35.4, 28.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -80.14 (d, J = 27.4 Hz), -86.46 (d, J = 27.3 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}F_2N$: 390.2028, found: 390.2026.

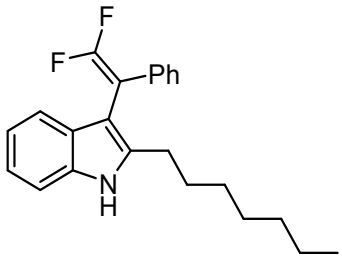


***tert*-butyl 4-(3-(2,2-difluoro-1-phenylvinyl)-1*H*-indol-2-yl)-4-methylpiperidine-1-carboxylate (3o)**
White solid (52 mg, 58% yield, m.p. = 229-230 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.45-7.43 (m, 1H), 7.39-7.37 (m, 1H), 7.31-7.27 (m, 4H), 7.24-7.19 (m, 2H), 7.16-7.13 (m, 1H), 3.64-3.11 (m, 4H), 2.19-2.07 (m, 2H), 1.64-1.56 (m, 2H), 1.45 (s, 9H), 1.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 153.7 (dd, J = 298.8, 286.3 Hz), 141.6, 134.9, 134.6, 129.7, 128.5, 128.3 (dd, J = 5.0, 3.8 Hz), 127.2, 122.2, 120.3, 118.6, 110.7, 104.6, 88.9 (dd, J = 22.5, 16.3 Hz), 79.7, 36.5, 36.2, 35.7, 28.6, 26.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -80.25 (d, J = 108.6 Hz), -86.59 (d, J = 131.2 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{31}F_2N_2O_2$: 453.2348, found: 453.2346.

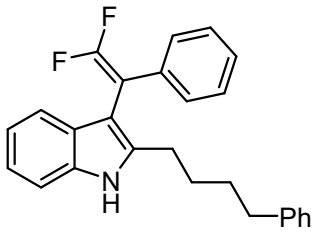


3-(2,2-difluoro-1-phenylvinyl)-2-(1-phenylcyclopropyl)-1*H*-indole (3p)
White solid (30 mg, 40% yield, m.p. = 125-126 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.34-7.28 (m, 2H), 7.27-7.22 (m, 4H), 7.22-7.13 (m, 5H), 7.10-7.05 (m, 1H), 7.00-6.98 (m, 2H), 1.37-1.34 (m, 2H), 1.25-1.19 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9 (dd, J = 299.5, 290.4 Hz), 143.4, 139.1 (d, J = 3.0 Hz), 135.0, 134.5 (dd, J = 5.1, 4.0 Hz), 128.5 (dd, J = 5.1, 3.0 Hz), 128.4, 128.24, 128.15, 127.0, 126.6, 126.0, 122.3, 120.1, 119.3, 110.6, 106.7, 88.2 (dd, J = 21.7, 18.7 Hz), 22.9, 16.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -81.88 (d, J = 27.6 Hz), -87.74 (d, J = 27.3 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}F_2N$: 372.1588, found: 372.1563.

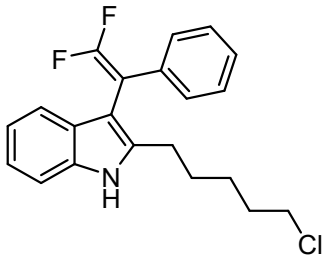


3-(2,2-difluoro-1-phenylvinyl)-2-heptyl-1*H*-indole (3q)
Yellow oil (40 mg, 56% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.36-7.24 (m, 6H), 7.20-7.19 (m, 1H), 7.16-7.13 (m, 1H), 7.05-7.02 (m, 1H), 2.61 (t, J = 7.8 Hz, 2H), 1.64-1.58 (m, 2H), 1.30-1.22 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7 (dd, J = 315.0, 302.4 Hz), 139.0 (d, J = 2.5 Hz), 135.7, 135.0, 129.0 (dd, J = 6.0, 6.0 Hz), 128.8, 128.7, 127.4, 121.9, 120.3, 119.4, 110.8, 105.5 (d, J = 3.8 Hz), 88.9 (dd, J = 22.1, 18.3 Hz), 32.1, 29.7, 29.42, 29.37, 27.1, 23.0, 14.5.

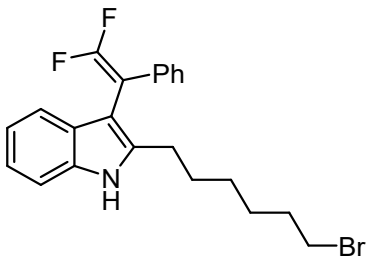
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.88 (d, J = 29.8 Hz), -88.68 (d, J = 30.2 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}F_2N$: 354.2028, found: 354.2026.



3-(2,2-difluoro-1-phenylvinyl)-2-(4-phenylbutyl)-1*H*-indole (3r)
Yellow solid (45 mg, 58% yield, m.p. = 96-97 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.37-7.34 (m, 2H), 7.33-7.28 (m, 5H), 7.28-7.25 (m, 1H), 7.24-7.21 (m, 2H), 7.17-7.14 (m, 3H), 7.08-7.03 (m, 1H), 2.65 (t, J = 7.1 Hz, 2H), 2.60 (t, J = 6.9 Hz, 2H), 1.67-1.59 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (dd, J = 299.0, 288.9 Hz), 142.1, 138.2 (d, J = 3.0 Hz), 135.3, 134.5 (dd, J = 5.6, 3.5 Hz), 128.6 (dd, J = 4.5, 3.5 Hz), 128.5, 128.4, 128.3, 128.2 (d, J = 3.0 Hz), 127.1, 125.8, 121.6, 119.9, 119.0, 110.5, 105.2 (d, J = 6.1 Hz), 88.5 (dd, J = 21.2, 18.2 Hz), 35.5, 30.9, 28.4, 26.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.80 (d, J = 33.1 Hz), -88.59 (d, J = 33.4 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}F_2N$: 388.1871, found: 388.1872.



2-(5-chloropentyl)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3s)
Yellow oil (61 mg, 84% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.41-7.38 (m, 2H), 7.38-7.33 (m, 3H), 7.31-7.27 (m, 2H), 7.23-7.20 (m, 1H), 7.13-7.08 (m, 1H), 3.51 (t, J = 6.5 Hz, 2H), 2.67 (t, J = 7.7 Hz, 2H), 1.79-1.73 (m, 2H), 1.70-1.64 (m, 2H), 1.49-1.43 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3 (dd, J = 299.9, 289.8 Hz), 138.4, 135.7, 135.0 (dd, J = 3.8, 3.8 Hz), 129.0 (dd, J = 5.0, 3.8 Hz), 128.8, 128.6, 127.5, 122.1, 120.4, 119.5, 111.0, 105.7, 88.9 (dd, J = 21.4, 17.6 Hz), 45.3, 32.6, 30.2, 28.7, 26.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.72 (d, J = 29.4 Hz), -88.44 (d, J = 29.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}ClF_2N$: 360.1325, found: 360.1329.



2-(6-bromohexyl)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3t)

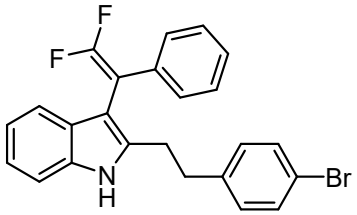
Yellow oil (38 mg, 46% yield), purified by flash column chromatography on silica gel using petroleum ether ethyl acetate = 50: 1 as eluent

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.36-7.28 (m, 6H), 7.26-7.20 (m, 1H), 7.19-7.15 (m, 1H), 7.10-7.03 (m, 1H), 3.46.3.35 (m, 2H), 2.65-2.61 (m, 2H), 1.82-1.76 (m, 2H), 1.67-1.59 (m, 2H), 1.42-1.33 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2 (dd, J = 298.6, 289.8 Hz), 138.6 (d, J = 3.8 Hz), 135.7, 134.9 (d, J = 5.0 Hz), 128.9 (dd, J = 3.8, 3.8 Hz), 128.7, 128.6, 127.5, 122.0, 120.4, 119.4, 110.9, 105.7 (d, J = 5.0 Hz), 88.9 (dd, J = 20.8, 18.3 Hz), 34.3, 33.0, 29.2, 28.7, 28.2, 26.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ -83.71 (d, J = 29.7 Hz), -88.43 (d, J = 29.4 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}BrF_2N$: 418.0976, found: 418.0974.



2-(4-bromophenethyl)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3u)

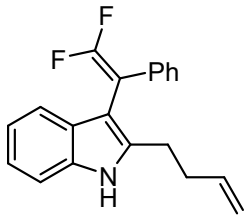
Yellow oil (59 mg, 67% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.38-7.34 (m, 2H), 7.31-7.28 (m, 4H), 7.26-7.18 (m, 3H), 7.17-7.13 (m, 1H), 7.07-7.01 (m, 1H), 6.94-6.88 (m, 2H), 2.91-2.87 (m, 2H), 2.83-2.79 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2 (dd, J = 298.6, 289.8 Hz), 140.1, 137.3 (d, J =2.5 Hz), 135.7, 134.8 (dd, J = 3.8, 3.8 Hz), 132.0, 130.6, 129.0 (dd, J = 3.8, 3.8 Hz), 128.7, 128.4, 127.6, 122.2, 120.6, 120.5, 119.6, 111.0, 106.2 (d, J = 5.0 Hz), 88.8 (dd, J = 22.1, 18.3 Hz), 35.3, 29.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.65 (d, J = 29.3 Hz), -88.58 (d, J = 29.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}BrF_2N$: 438.0663, found: 438.0653.



2-(but-3-en-1-yl)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (3v)

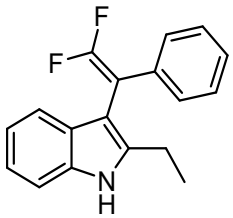
Colorless oil (40 mg, 64% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.36-7.26 (m, 5H), 7.26-7.23 (m, 1H), 7.20-7.12 (m, 2H), 7.04-7.01 (m, 1H), 5.87-5.79 (m, 1H), 5.10-5.01 (m, 2H), 2.75-2.68 (m, 2H), 2.39-2.34 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2 (dd, J = 298.0, 289.2 Hz), 138.2, 138.0, 135.7, 134.9, 129.0 (dd, J = 3.8, 3.8 Hz), 128.7, 127.5, 122.0, 120.4, 119.5, 116.5, 115.5 (d, J =21.4 Hz), 110.9, 105.8, 88.9, 33.4, 26.4.

^{19}F NMR (470 MHz, $CDCl_3$) δ -83.78 (d, J = 29.8 Hz), -88.52 (d, J = 29.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}F_2N$: 310.1402, found: 310.1397.



3-(2,2-difluoro-1-phenylvinyl)-2-ethyl-1*H*-indole (3w)

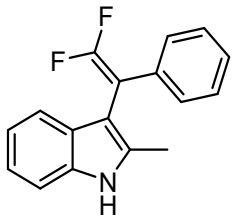
Yellow oil (40 mg, 70% yield,), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.25 (s, 1H), 7.38-7.32 (m, 3H), 7.30-7.28 (m, 3H), 7.06-7.00 (m, 2H), 6.91-6.88 (m, 1H), 2.59 (q, J = 7.7 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 153.9 (dd, J = 294.2, 289.2 Hz), 141.1, 136.4, 135.1 (dd, J = 5.0, 3.8 Hz), 129.3, 129.1 (dd, J = 3.8, 3.8 Hz), 128.9-128.7 (m), 128.2, 121.5, 119.9, 118.8, 111.8, 103.3, 89.8 (dd, J = 20.8, 17.0 Hz), 20.4, 14.4.

^{19}F NMR (470 MHz, $CDCl_3$) δ -83.93 (d, J = 29.9 Hz), -88.66 (d, J = 29.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}F_2N$: 284.1245, found: 284.1249.



3-(2,2-difluoro-1-phenylvinyl)-2-methyl-1*H*-indole (3x)

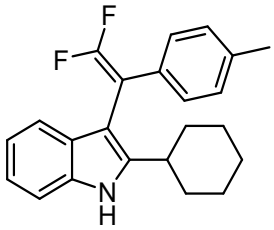
Yellow solid (25 mg, 42% yield, m.p. = 83-84 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.40-7.38 (m, 2H), 7.37-7.31 (m, 3H), 7.30-7.27 (m, 1H), 7.20-7.13 (m, 2H), 7.05-7.02 (m, 1H), 2.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8 (dd, J = 295.6, 286.9 Hz), 135.4, 134.4 (dd, J = 5.0, 5.0 Hz), 134.2 (d, J = 2.5 Hz), 129.8, 128.7 (dd, J = 5.0, 2.5 Hz), 128.4, 127.2, 121.6, 120.0, 119.1, 110.5, 105.5, 88.8 (dd, J = 21.3, 17.5 Hz), 12.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.43 (d, J = 30.0 Hz), -89.03 (d, J = 30.4 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}F_2N$: 270.1089, found: 270.1086.



2-cyclohexyl-3-(2,2-difluoro-1-(*p*-tolyl)vinyl)-1*H*-indole (3y)

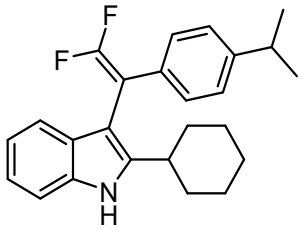
Yellow oil (60 mg, 85% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.38-7.36 (m, 1H), 7.32-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.20-7.14 (m, 3H), 7.09-7.05 (m, 1H), 2.78-2.70 (m, 1H), 2.38 (s, 3H), 1.98-1.91 (m, 2H), 1.88-1.85 (m, 2H), 1.81-1.77 (m, 1H), 1.53-1.44 (m, 2H), 1.41-1.27 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (dd, J = 299.0, 288.9 Hz), 142.9 (d, J = 3.0 Hz), 136.8, 135.2, 131.6 (dd, J = 5.0, 3.0 Hz), 129.0, 128.4 (dd, J = 5.6, 3.5 Hz), 128.2 (d, J = 3.0 Hz), 121.5, 119.9, 119.1, 110.5, 103.8, 88.3 (dd, J = 22.2, 18.2 Hz), 36.3, 32.9, 26.5, 26.1, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.29 (d, J = 31.8 Hz), -88.59 (d, J = 31.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}F_2N$: 352.1871, found: 352.1873.



2-cyclohexyl-3-(2,2-difluoro-1-(4-isopropylphenyl)vinyl)-1*H*-indole (3z)

Yellow solid (67 mg, 88% yield, m.p. = 71-72 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

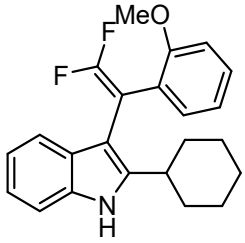
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.35-7.33 (m, 1H), 7.29-7.26 (m, 2H), 7.23-7.21 (m, 1H), 7.18-7.12 (m, 3H), 7.05-7.01 (m, 1H), 2.95-2.83 (m, 1H), 2.72-2.65

(m, 1H), 1.92-1.85 (m, 2H), 1.84-1.80 (m, 2H), 1.78-1.71 (m, 1H), 1.49-1.39 (m, 2H), 1.36-1.26 (m, 3H), 1.24 (d, J = 6.8 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2 (dd, J = 298.6, 288.5 Hz), 148.1, 143.3 (d, J = 2.5 Hz), 135.5, 132.4 (dd, J = 5.0, 3.8 Hz), 128.8 (dd, J = 3.8, 3.8 Hz), 128.5, 126.7, 121.8, 120.2, 119.5, 110.9, 104.3 (d, J = 3.8 Hz), 88.6 (dd, J = 27.7, 23.4 Hz), 36.7, 34.2, 33.3, 26.9, 26.4, 24.3.

^{19}F NMR (470 MHz, $CDCl_3$) δ -84.30 (d, J = 31.3 Hz), -88.62 (d, J = 31.3 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}F_2N$: 380.2184, found: 380.2179.



2-cyclohexyl-3-(2,2-difluoro-1-(2-methoxyphenyl)vinyl)-1*H*-indole (3aa)

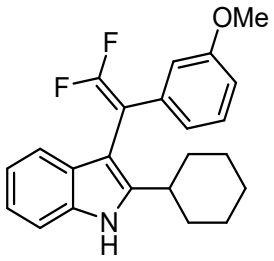
Yellow solid (52 mg, 71% yield, m.p. = 134-135 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.42-7.40 (m, 1H), 7.31-7.30 (m, 2H), 7.22-7.12 (m, 2H), 7.10-7.06 (m, 1H), 6.97-6.95 (m, 1H), 6.92-6.88 (m, 1H), 3.88 (s, 3H), 2.84-2.76 (m, 1H), 1.88-1.80 (m, 4H), 1.49-1.21 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 153.1 (dd, J = 356.5, 356.5 Hz), 142.5, 135.0, 131.4 (dd, J = 4.0, 2.0 Hz), 128.9, 128.0, 124.0 (dd, J = 4.0, 4.0 Hz), 121.2, 120.4, 119.7, 119.1, 111.0, 110.4, 104.9, 83.8, 55.6, 36.2, 32.8, 26.7, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.77 (d, J = 28.1 Hz), -86.97 (d, J = 28.0 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}F_2NO$: 368.1820, found: 368.1822.



2-cyclohexyl-3-(2,2-difluoro-1-(3-methoxyphenyl)vinyl)-1*H*-indole (3ab)

Purple solid (51 mg, 69% yield, m.p. = 146-147 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

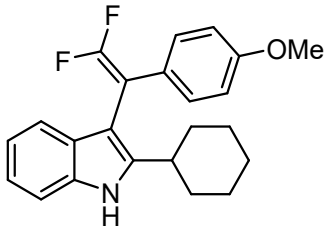
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.38-7.37 (m, 1H), 7.29-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.11-7.08 (m, 1H), 7.02-7.01 (m, 2H), 6.86 (d, J = 8.2 Hz, 1H), 3.81

(s, 3H), 2.78-2.72 (m, 1H), 1.98-1.91 (m, 2H), 1.90-1.84 (m, 2H), 1.81-1.78 (m, 1H), 1.51-1.32 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 154.4 (dd, J = 298.6, 288.5 Hz), 143.4, 136.6 (dd, J = 3.8, 3.8 Hz), 135.6, 129.6, 128.5, 121.9, 121.6 (dd, J = 5.0, 3.8 Hz), 120.3, 119.5, 114.9 (dd, J = 5.0, 3.8 Hz), 112.7, 111.0, 104.0 (d, J =5.0 Hz), 88.9 (dd, J = 21.4, 17.6 Hz), 55.7, 36.7, 33.3, 26.9, 26.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.23 (d, J = 29.3 Hz), -87.41 (d, J = 29.2 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}F_2NO$: 368.1820, found: 368.1815.



2-cyclohexyl-3-(2,2-difluoro-1-(4-methoxyphenyl)vinyl)-1*H*-indole (3ac)

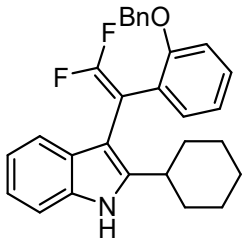
Yellow oil (53 mg, 74% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.35-7.33 (m, 1H), 7.31-7.27 (m, 2H), 7.21-7.19 (m, 1H), 7.17-7.13 (m, 1H), 7.07-7.00 (m, 1H), 6.88-6.82 (m, 2H), 3.81 (s, 3H), 2.75-2.67 (m, 1H), 1.95-1.87 (m, 2H), 1.85-1.81 (m, 2H), 1.79-1.72 (m, 1H), 1.50-1.40 (m, 2H), 1.39-1.26 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.6 (dd, J = 298.0, 287.9 Hz), 142.9 (d, J = 3.0 Hz), 135.2, 129.7 (dd, J = 5.0, 4.0 Hz), 128.2 (d, J = 3.0 Hz), 127.0 (dd, J = 6.0, 3.0 Hz), 121.5, 119.9, 119.1, 113.8, 110.5, 103.9 (d, J = 5.1 Hz), 87.9 (dd, J = 22.7, 16.7 Hz), 55.3, 36.3, 32.9, 26.5, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.23 (d, J = 34.1 Hz), -89.56 (d, J = 33.5 Hz).

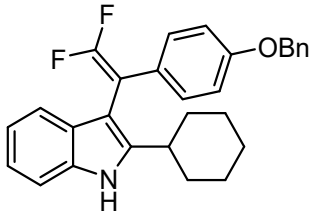
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}F_2NO$: 368.1820, found: 368.1818.



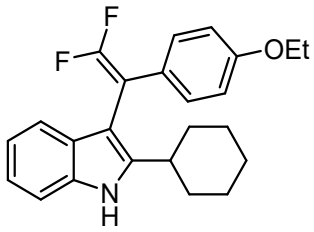
3-(1-(2-(benzyloxy)phenyl)-2,2-difluorovinyl)-2-cyclohexyl-1*H*-indole (3ad)

Yellow solid (67 mg, 76% yield, m.p. = 147-148 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.37-7.35 (m, 1H), 7.31-7.30 (m, 1H), 7.29-7.27 (m, 4H), 7.26-7.23 (m, 1H), 7.22-7.19 (m, 2H), 7.14-7.11 (m, 1H), 7.04-7.02 (m, 1H), 6.96-6.95 (m, 1H), 6.89-6.87 (m, 1H), 5.12 (s, 2H), 2.76-2.69 (m, 1H), 1.76-1.71 (m, 4H), 1.70-1.69 (m, 1H), 1.38-1.25 (m, 4H), 1.24-1.21 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 153.5 (dd, J = 291.7, 291.7 Hz), 142.9 (d, J = 3.8 Hz), 137.6, 135.3, 132.1, 129.3, 128.9, 128.4, 128.0, 127.3, 124.7, 121.7, 121.0, 120.2, 119.6, 112.6, 110.8, 105.3, 84.5 (dd, J = 23.9, 23.9 Hz), 70.3, 36.5, 33.2, 27.0, 26.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.58 (d, J = 27.8 Hz), -86.66 (d, J = 27.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{28}F_2NO$: 444.2133, found: 444.2139.

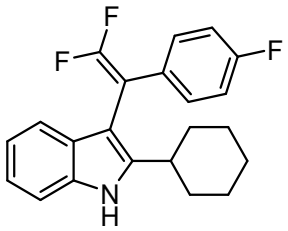


3-(1-(4-(benzyloxy)phenyl)-2,2-difluorovinyl)-2-cyclohexyl-1*H*-indole (3ae)
Yellow solid (39 mg, 44% yield, m.p. = 126-127 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.44-7.42 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.20-7.18 (m, 1H), 7.17-7.12 (m, 1H), 7.04-7.01 m, 1H), 6.93-6.89 (m, 2H), 5.05 (s, 2H), 2.72-2.66 (m, 1H), 1.94-1.85 (m, 2H), 1.82 (m, 2H), 1.48-1.39 (m, 2H), 1.34-1.24 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 153.7 (dd, J = 295.0, 286.2 Hz), 143.0, 137.0, 135.2, 129.8 (dd, J =3.8, 3.8 Hz), 128.7, 128.2, 128.1, 127.6, 127.3 (dd, J = 5.0, 2.5 Hz), 121.5, 119.9, 119.2, 114.7, 110.6, 103.9 (d, J = 5.0 Hz), 88.0 (dd, J = 21.3, 17.5 Hz), 70.1, 36.4, 33.0, 26.6, 26.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -85.11 (d, J = 33.3 Hz), -89.43 (d, J = 33.4 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{28}F_2NO$: 444.2133, found: 444.2137.

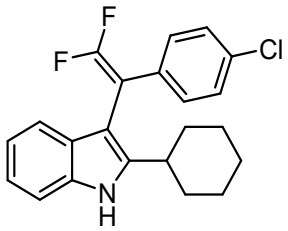


2-cyclohexyl-3-(1-(4-ethoxyphenyl)-2,2-difluorovinyl)-1*H*-indole (3af)
Yellow oil (59 mg, 93% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.35-7.33 (m, 1H), 7.30-7.26 (m, 2H), 7.22-7.20 (m, 1H), 7.17-1.13 (m, 1H), 7.05-7.02 (m, 1H), 6.87-6.81 (m, 2H), 4.03 (q, J

= 7.0 Hz, 2H), 2.77-2.68 (m, 1H), 1.94-1.87 (m, 2H), 1.87-1.72 (m, 3H), 1.50-1.43 (m, 2H), 1.42 (t, *J* = 5.0 Hz, 3H), 1.37-1.21 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 154.0 (dd, *J* = 296.7, 287.9 Hz), 143.2 (d, *J* = 2.5 Hz), 135.5, 130.0 (dd, *J* = 3.8, 3.8 Hz), 128.6, 127.2, 121.8, 120.2, 119.5, 114.7, 110.9, 104.3 (d, *J* = 3.8 Hz), 88.3 (dd, *J* = 22.1, 18.3 Hz), 63.8, 36.7, 33.3, 26.9, 26.4, 15.2.
^{19}F NMR (470 MHz, $CDCl_3$) δ -85.32 (d, *J* = 33.8 Hz), -89.62 (d, *J* = 33.7 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}F_2NO$: 382.1977, found: 382.1976.



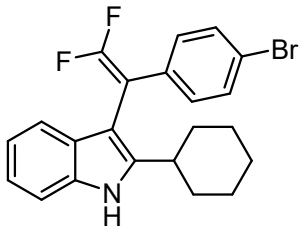
2-cyclohexyl-3-(2,2-difluoro-1-(4-fluorophenyl)vinyl)-1*H*-indole (3ag)
Yellow solid (45 mg, 63% yield, m.p. = 93-94 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.36-7.30 (m, 3H), 7.21-7.13 (m, 2H), 7.05-6.96 (m, 3H), 2.70-2.63 (m, 1H), 1.89-1.81 (m, 4H), 1.77-1.72 (m, 1H), 1.48-1.39 (m, 2H), 1.35-1.20 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (d, *J* = 248.2 Hz), 154.2 (dd, *J* = 297.4, 288.5 Hz), 143.4 (d, *J* = 2.5 Hz), 135.5, 131.0 (dd, *J* = 5.0, 2.5 Hz), 130.6 (dd, *J* = 7.5, 3.8 Hz), 128.4, 122.0, 120.4, 119.3, 115.6 (d, *J* = 21.4 Hz), 111.0, 103.9 (d, *J* = 3.8 Hz), 88.1 (dd, *J* = 22.1, 18.3 Hz), 36.7, 33.3, 26.9, 26.4.
^{19}F NMR (470 MHz, $CDCl_3$) δ -84.02 (d, *J* = 30.9 Hz), -88.68 (d, *J* = 31.0 Hz), -115.00.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}F_3N$: 356.1621, found: 356.1617.



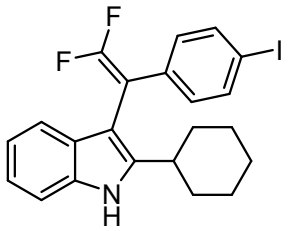
3-(1-(4-chlorophenyl)-2,2-difluorovinyl)-2-cyclohexyl-1*H*-indole (3ah)
Yellow oil (70 mg, 94% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.36-7.35 (m, 1H), 7.32-7.25 (m, 4H), 7.20-7.15 (m, 2H), 7.07-7.04 (m, 1H), 2.71-2.65 (m, 1H), 1.93-1.81 (m, 4H), 1.80-1.75 (m, 1H), 1.51-1.40 (m, 2H), 1.39-1.28 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4 (dd, J = 299.9, 288.5 Hz), 143.5, 135.6, 133.6 (dd, J = 5.0, 3.8 Hz), 133.2, 130.2 (dd, J = 5.0, 5.0 Hz), 128.9, 128.4, 122.1, 120.4, 119.3, 111.0, 103.5 (d, J = 3.8 Hz), 88.2 (dd, J = 22.7, 17.6 Hz), 36.8, 33.3, 26.9, 26.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.75 (d, J = 28.6 Hz), -87.26 (d, J = 28.0 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}ClF_2N$: 372.1325, found: 372.1326.

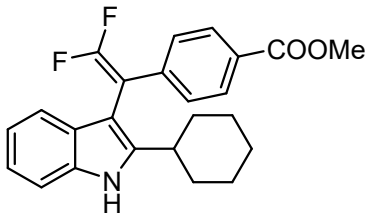


3-(1-(4-bromophenyl)-2,2-difluorovinyl)-2-cyclohexyl-1*H*-indole (3ai)
Yellow oil (77 mg, 92% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.43-7.36 (m, 2H), 7.34-7.31 (m, 1H), 7.22-7.17 (m, 2H), 7.16-7.11 (m, 2H), 7.05 -6.98 (m, 1H), 2.67-2.61 (m, 1H), 1.90-1.77 (m, 4H), 1.77-1.70 (m, 1H), 1.47-1.37 (m, 2H), 1.36-1.23 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3 (dd, J = 299.9, 289.8 Hz), 143.4 (d, J = 3.5 Hz), 135.5, 134.0 (dd, J = 6.3, 5.0 Hz), 131.8, 130.4 (dd, J = 5.0, 3.8 Hz), 128.3 (d, J = 3.8 Hz), 122.0, 121.3, 120.4, 119.3, 111.0, 103.4 (d, J = 3.8 Hz), 88.2 (dd, J = 21.4, 16.4 Hz), 36.7, 33.3, 26.9, 26.4.
^{19}F NMR (470 MHz, $CDCl_3$) δ -82.54 (d, J = 27.9 Hz), -87.05 (d, J = 27.9 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}BrF_2N$: 416.0820, found: 416.0818.

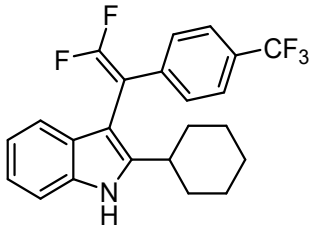


2-cyclohexyl-3-(2,2-difluoro-1-(4-iodophenyl)vinyl)-1*H*-indole (3aj)
Yellow oil (50 mg, 54% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.62-7.57 (m, 2H), 7.36-7.30 (m, 1H), 7.16-7.11 (m, 2H), 7.09-7.05 (m, 2H), 7.04-6.98 (m, 1H), 2.66-2.60 (m, 1H), 1.90-1.77 (m, 4H), 1.77-1.69 (m, 1H), 1.46-1.38 (m, 2H), 1.33-1.22 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9 (dd, J = 301.1, 287.9 Hz), 143.1 (d, J = 2.0 Hz), 137.4, 135.1, 134.3 (d, J = 7.1 Hz), 130.3 (dd, J = 5.6, 3.4 Hz), 128.3, 121.7, 120.0,

118.9, 110.6, 103.0 (d, J = 4.0 Hz), 92.5, 88.9 (dd, J = 22.7, 17.7 Hz), 36.3, 32.9, 26.5, 26.0.
^{19}F NMR (470 MHz, $CDCl_3$) δ -82.24 (d, J = 27.4 Hz), -86.74 (d, J = 27.3 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}F_2IN$: 464.0681, found: 464.0687.

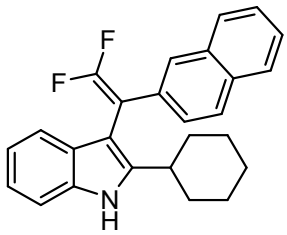


methyl 4-(1-(2-cyclohexyl-1*H*-indol-3-yl)-2,2-difluorovinyl)benzoate (3ak)
Yellow oil (51 mg, 65% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.98-7.92 (m, 2H), 7.46-7.40 (m, 2H), 7.40-7.33 (m, 1H), 7.19-7.11 (m, 2H), 7.05-7.01 (m, 1H), 3.90 (s, 3H), 2.66-2.55 (m, 1H), 1.90-1.68 (m, 5H), 1.48-1.26 (m, 5H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 153.9 (dd, J = 300.0, 288.9 Hz), 144.2, 140.0 (dd, J = 6.1, 4.0 Hz), 136.0, 129.8, 129.0 (dd, J = 4.0, 4.0 Hz), 128.7, 121.2, 119.6, 118.3, 111.6, 101.3 (d, J = 5.1 Hz), 89.1 (dd, J = 23.2, 17.2 Hz), 79.6, 52.6, 36.6, 32.5, 26.6, 26.0.
^{19}F NMR (376 MHz, DMSO-d_6) δ -82.98 (d, J = 27.8 Hz), -87.20 (d, J = 27.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}F_2NO_2$: 396.1770, found: 396.1773.



2-cyclohexyl-3-(2,2-difluoro-1-(4-(trifluoromethyl)phenyl)vinyl)-1*H*-indole (3al)
Yellow oil (67 mg, 83% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.56-7.54 (m, 2H), 7.48-7.45 (m, 2H), 7.37-7.33 (m, 1H), 7.19-7.13 (m, 2H), 7.05-7.01 (m, 1H), 2.68-2.61 (m, 1H), 1.89-1.82 (m, 4H), 1.47-1.40 (m, 2H), 1.35-1.22 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8 (dd, J = 298.6, 289.8 Hz), 143.6, 138.9, 135.6, 129.6 (dd, J = 19.5, 13.2 Hz), 129.1 (dd, J = 5.0, 5.0 Hz), 128.3, 125.6 (q, J = 5.0 Hz), 122.7 (q, J = 198.7 Hz), 122.2, 120.5, 119.2, 111.1, 103.2 (d, J = 5.0 Hz), 88.4 (dd, J = 23.9, 16.4 Hz), 36.8, 33.3, 26.9, 26.4.
^{19}F NMR (470 MHz, $CDCl_3$) δ -62.51, -81.05 (d, J = 24.6 Hz), -85.87 (d, J = 24.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}F_5N$: 406.1589, found: 406.1593.



2-cyclohexyl-3-(2,2-difluoro-1-(naphthalen-2-yl)vinyl)-1*H*-indole (3am)

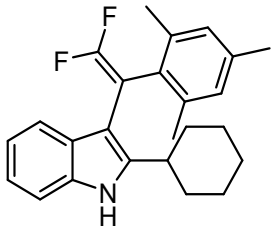
Yellow oil (69 mg, 89% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.81-7.73 (m, 4H), 7.50-7.44 (m, 3H), 7.37-7.36 (m, 1H), 7.16-7.13 (m, 2H), 7.02-6.99 (m, 1H), 2.75-2.70 (m, 1H), 1.92-1.90 (m, 2H), 1.81-1.78 (m, 2H), 1.73-1.72 (m, 1H), 1.50-1.42 (m, 3H), 0.99-0.81 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5 (dd, J = 294.2, 294.2 Hz), 143.5, 135.6, 133.7, 132.8, 132.5, 128.6, 128.5, 128.2, 127.99, 127.95, 126.8, 126.5, 126.4, 121.9, 120.4, 119.5, 110.9, 104.1, 89.0 (dd, J = 22.7, 17.6 Hz), 36.7, 33.3, 26.9, 26.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.03 (d, J = 29.0 Hz), -87.91 (d, J = 28.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}F_2NO$: 388.1871, found: 388.1879.



2-cyclohexyl-3-(2,2-difluoro-1-mesitylvinyl)-1*H*-indole (3an)

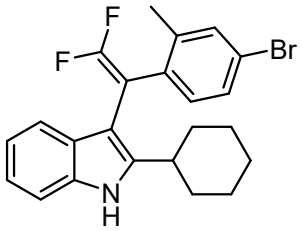
Yellow oil (35 mg, 46% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.32-7.29 (m, 2H), 7.15-7.12 (m, 1H), 7.08-7.05 (m, 1H), 6.89 (s, 2H), 2.59-2.53 (m, 1H), 2.29 (s, 3H), 2.21 (s, 6H), 1.78-1.62 (m, 5H), 1.34-1.25 (m, 5H).

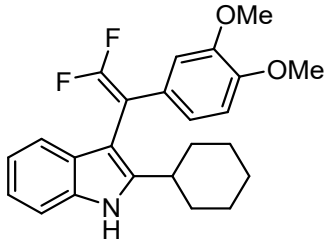
^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5 (dd, J = 295.5, 287.9 Hz), 142.7 (d, J = 4.1 Hz), 138.0, 137.6, 135.4, 130.4, 129.0, 127.4, 121.7, 120.2, 120.0 (d, J = 3.9 Hz), 110.8, 103.8, 86.7 (dd, J = 25.2, 18.9 Hz), 36.6, 33.4, 27.0, 26.5, 21.4, 20.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.56 (d, J = 33.0 Hz), -88.01 (d, J = 32.4 Hz).

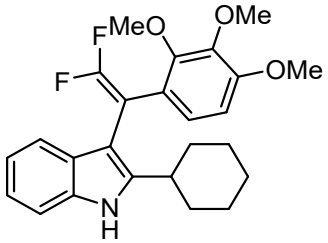
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}F_2N$: 380.2184, found: 380.2189.



3-(1-(4-bromo-2-methylphenyl)-2,2-difluorovinyl)-2-cyclohexyl-1*H*-indole (3ao)
Yellow solid (57 mg, 66% yield, m.p. = 153-154 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, DMSO-d_6) δ 11.17 (s, 1H), 7.48 (s, 1H), 7.41-7.39 (m, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 7.05-7.02 (m, 1H), 6.94-6.91 (m, 1H), 2.58-2.52 (m, 1H), 2.15 (s, 3H), 1.76-1.74 (m, 2H), 1.69-1.67 (m, 2H), 1.59-1.54 (m, 4H), 1.32-1.22 (m, 2H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 152.9 (dd, J = 296.7, 285.4 Hz), 144.2 (d, J = 2.5 Hz), 140.2, 136.3, 134.0, 133.6, 133.2, 129.5, 127.4, 121.7, 121.5, 120.0, 118.9, 112.0, 102.2, 88.5 (dd, J = 23.3, 19.5 Hz), 37.0, 32.8, 27.1, 26.4, 19.9.
^{19}F NMR (376 MHz, DMSO-d_6) δ -88.03 (d, J = 33.5 Hz), -88.43 (d, J = 34.0 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}BrF_2N$: 430.0976, found: 430.0914.



2-cyclohexyl-3-(1-(3,4-dimethoxyphenyl)-2,2-difluorovinyl)-1*H*-indole (3ap)
White solid (74 mg, 93% yield, m.p. = 215-216 ℃), purified by flash column chromatography on silica gel using petroleum ether ethyl acetate = 50: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.34-7.33 (m, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.15-7.12 (m, 1H), 7.04-7.01 (m, 1H), 6.94 (s, 1H), 6.85-6.84 (m, 1H), 6.78-6.77 (m, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.72-2.66 (m, 1H), 1.90-1.87 (m, 2H), 1.85-1.78 (m, 2H), 1.48-1.40 (m, 2H), 1.35-1.21 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2 (dd, J = 483.2, 454.2 Hz), 149.0, 148.5, 143.3, 140.7, 135.5, 128.5, 127.7, 121.8, 120.3, 119.5, 112.0 (d, J = 5.0 Hz), 111.3, 110.9, 100.1, 88.4 (dd, J = 22.7, 18.9 Hz), 56.30, 56.25, 36.7, 33.3, 26.9, 26.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -84.75 (d, J = 33.3 Hz), -89.02 (d, J = 33.2 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}F_2NO_2$: 398.1926, found: 398.1928.



2-cyclohexyl-3-(2,2-difluoro-1-(2,3,4-trimethoxyphenyl)vinyl)-1*H*-indole (3aq)

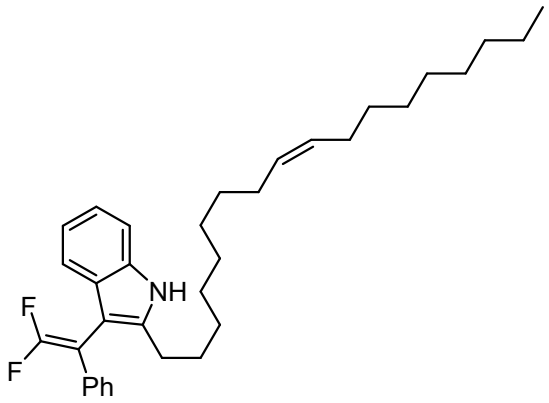
Yellow oil (57 mg, 67% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.13-7.10 (m, 1H), 7.06-7.03 (m, 1H), 6.96 (d, J = 8.7 Hz, 1H), 6.63 (d, J = 8.7 Hz, 1H), 3.85 (m, 6H), 3.61 (s, 3H), 2.78-2.72 (m, 1H), 1.93-1.71 (m, 6H), 1.45-1.30 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5 (dd, J = 247.6, 247.6 Hz), 153.8, 152.5, 142.7, 142.6, 135.3, 128.2, 125.9, 122.0, 121.6, 120.1, 119.6, 110.8, 107.3, 105.1, 85.0 (dd, J = 23.3, 23.3 Hz), 61.1, 60.8, 56.4, 36.5, 33.2, 27.0, 26.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -87.20 (d, J = 31.2 Hz), -87.95 (d, J = 31.6 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}F_2NO_3$: 428.2032, found: 428.2028.



(*Z*)-3-(2,2-difluoro-1-phenylvinyl)-2-(octadec-9-en-1-yl)-1*H*-indole (3ar)

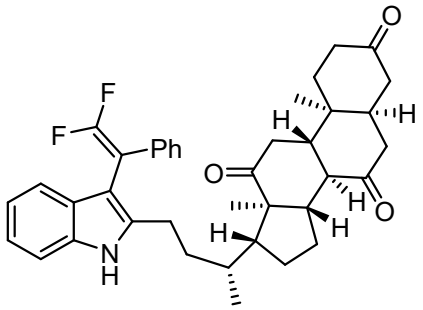
Yellow oil (37 mg, 37% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.35-7.28 (m, 4H), 7.26-7.22 (m, 2H), 7.20-7.17 (m, 1H), 7.16-7.11 (m, 1H), 7.04-7.00 (m, 1H), 5.38-5.30 (m, 2H), 2.62-2.59 (m, 2H), 2.06-1.96 (m, 4H), 1.62-1.58 (m, 2H), 1.35-1.23 (m, 22H), 0.88 (t, J = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2 (dd, J = 296.7, 286.7 Hz), 139.0, 135.7, 135.0, 130.4, 130.2, 129.0, 128.71, 128.67, 127.4, 121.9, 120.3, 119.4, 110.8, 105.5 (d, J = 5.0 Hz), 89.1 (dd, J = 23.3, 19.5 Hz), 32.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.74, 29.70, 29.61, 29.55, 29.4, 27.63, 27.57, 27.0, 23.1, 14.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ -83.86 (d, J = 29.7 Hz), -88.65 (d, J = 29.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{46}F_2N$: 506.3593, found: 506.3597.



(5S,8R,9S,10S,13R,14S,17R)-17-((R)-4-(3-(2,2-difluoro-1-phenylvinyl)-1*H*-indol-2-yl)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (3as)

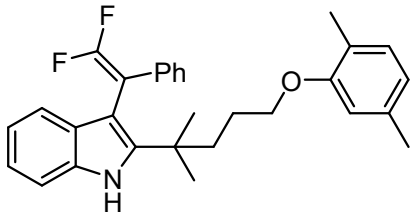
Yellow solid (64 mg, 52% yield, m.p. = 109-110 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.37-7.26 (m, 5H), 7.23-7.20 (m, 2H), 7.15-7.12 (m, 1H), 7.05-7.02 (m, 1H), 2.95-2.78 (m, 3H), 2.72-2.66 (m, 1H), 2.56-2.50 (m, 1H), 2.44-2.09 (m, 8H), 2.05-1.70 (m, 6H), 1.62-1.55 (m, 1H), 1.46-1.39 (m, 1H), 1.37 (s, 3H), 1.31-1.16 (m, 3H), 1.00 (s, 3H), 0.81 (d, J = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.2, 209.4, 209.1, 153.9 (dd, J =296.2, 286.2 Hz), 138.9, 135.4, 134.6 (dd, J =3.8, 3.8 Hz), 128.6 (dd, J =5.0, 5.0 Hz), 128.32, 128.26, 127.1, 121.4, 119.8, 118.9, 110.6, 104.9 (d, J = 3.8 Hz), 88.6 (dd, J =21.2, 18.8 Hz), 56.9, 51.8, 49.0, 46.9, 45.7, 45.5, 45.0, 42.8, 38.7, 36.5, 36.0, 35.9, 35.3, 34.9, 27.8, 25.2, 24.0, 21.9, 18.8, 11.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ -83.65 (d, J = 29.5 Hz), -88.53 (d, J = 29.6 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{44}F_2NO_3$: 612.3284, found: 612.3281.



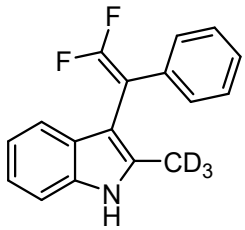
3-(2,2-difluoro-1-phenylvinyl)-2-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)-1*H*-indole (3at)

Colorless oil (86 mg, 94% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

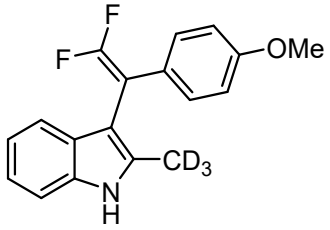
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.39-7.31 (m, 3H), 7.29-7.23 (m, 2H), 7.22-7.17 (m, 2H), 7.16-7.09 (m, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 1.3 Hz, 1H), 6.49 (s, 1H), 3.66-3.58 (m, 2H), 2.29 (s, 3H), 2.18 (s, 3H), 1.82-1.70 (m, 2H), 1.69-1.59 (m, 2H), 1.37-1.34 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 154.2 (dd, J = 301.1, 287.3 Hz), 43.4 (d, J = 3.8 Hz), 137.0, 135.7 (dd, J = 5.7, 3.2 Hz), 134.7, 130.7, 130.3, 128.8, 128.5 (dd, J = 5.7,

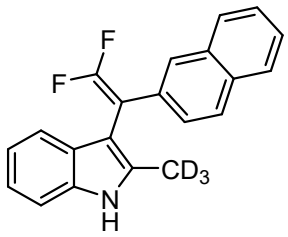
3.2 Hz), 127.3, 123.8, 122.3, 121.2, 120.6, 118.9, 112.5, 110.9, 104.8 (d, J = 5.0 Hz), 89.3 (dd, J = 22.1, 17.0 Hz), 68.2, 40.0, 36.8, 28.7, 28.1, 25.6, 21.9, 16.4.
^{19}F NMR (470 MHz, $CDCl_3$) δ -80.36 (d, J = 26.8 Hz), -86.42 (d, J = 26.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{32}F_2NO$: 460.2446, found: 460.2442.



3-(2,2-difluoro-1-phenylvinyl)-2-(methyl-d$_3$)-1*H*-indole (3au)
Red solid (26 mg, 48% yield, m.p. = 92-93 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 10: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.38-7.33 (m, 2H), 7.32-7.29 (m, 3H), 7.27-7.22 (m, 1H), 7.16-7.10 (m, 2H), 7.03-6.99 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2 (dd, J = 299.3, 289.2 Hz), 135.7, 134.7, 134.5, 129.0 (dd, J = 5.0, 5.0 Hz), 128.7, 128.6, 127.5, 121.9, 120.3, 119.4, 110.8, 105.8, 89.1 (dd, J = 21.4, 18.9 Hz), 30.2-29.3 (m).
^{19}F NMR (470 MHz, $CDCl_3$) δ -84.48 (d, J = 30.4 Hz), -89.06 (d, J = 30.4 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}D_3F_2N$: 273.1277, found: 273.1275.



3-(2,2-difluoro-1-(4-methoxyphenyl)vinyl)-2-(methyl-d$_3$)-1*H*-indole (3av)
Red solid (25 mg, 41% yield, m.p. = 71-72 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 10: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.35-7.21 (m, 3H), 7.14-6.98 (m, 3H), 6.85-6.81 (m, 2H), 3.79 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 153.8 (dd, J = 298.0, 288.5 Hz), 135.7, 134.4, 130.2 (dd, J = 3.8, 3.8 Hz), 128.6 (d, J = 1.3 Hz), 127.0, 121.8, 120.2, 119.5, 114.2, 110.7, 106.0, 88.5 (dd, J = 22.7, 20.2 Hz), 55.7, 31.2-28.9 (m).
^{19}F NMR (376 MHz, DMSO-d_6) δ -87.59 (d, J = 37.7 Hz), -91.87 (d, J = 37.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}D_3F_2NO$: 303.1383, found: 303.1390



3-(2,2-difluoro-1-(naphthalen-2-yl)vinyl)-2-(methyl-d$_3$)-1*H*-indole (3aw)

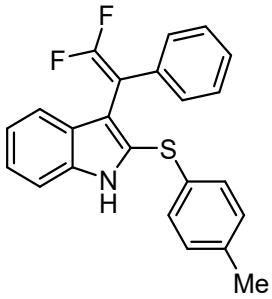
Red solid (34 mg, 52% yield, m.p. = 125-126 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 10: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87-7.71 (m, 4H), 7.54-7.43 (m, 3H), 7.34-7.33 (m, 1H), 7.19-7.12 (m, 2H), 7.04-6.98 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4 (dd, J = 298.6, 289.8 Hz), 135.7, 134.6, 133.7, 132.8, 132.3 (dd, J = 3.8, 3.8 Hz), 128.7, 128.5, 128.3, 128.1 (dd, J = 3.8, 3.8 Hz), 128.0, 126.9 (dd, J = 5.0, 5.0 Hz), 126.5, 126.4, 121.9, 120.3, 119.5, 110.8, 105.9, 89.3 (dd, J = 20.8, 18.3 Hz), 30.4-29.7 (m).

^{19}F NMR (471 MHz, $CDCl_3$) δ -83.89 (d, J = 29.4 Hz), -88.87 (d, J = 29.4 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{13}D_3F_2N$: 323.1434, found: 323.1436.



3-(2,2-difluoro-1-phenylvinyl)-2-(*p*-tolylthio)-1*H*-indole (5a)

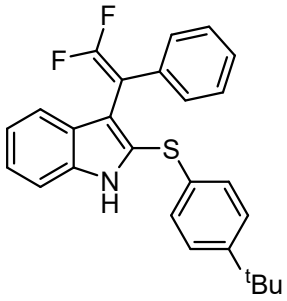
Yellow oil (32 mg, 86% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.42-7.21 (m, 8H), 7.20-7.04 (m, 5H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 297.8, 290.0 Hz), 137.1, 136.8, 134.1 (dd, J = 5.3, 3.3 Hz), 131.3, 130.0, 129.6, 128.6 (dd, J = 5.1, 3.0 Hz), 128.3, 127.9 (d, J = 2.8 Hz), 127.3 (dd, J = 5.1 Hz), 127.1, 123.4, 120.5, 119.8, 114.1 (dd, J = 5.3, 2.4 Hz), 110.9, 88.1 (dd, J = 21.2, 20.2 Hz), 21.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.48 (d, J = 26.6 Hz), -87.32 (d, J = 26.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}F_2NS$: 378.1123, found: 378.1116.



2-((4-(*tert*-butyl)phenyl)thio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5b)

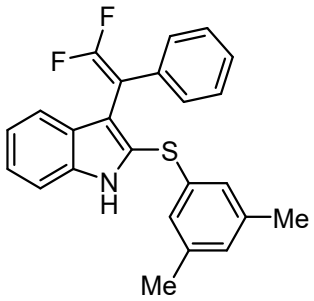
Yellow oil (36 mg, 87% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.41-7.21 (m, 10H), 7.21-7.16 (m, 2H), 7.15-7.07 (m, 1H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 297.8, 289.9 Hz), 150.3, 136.8, 134.1 (dd, J = 5.2, 3.3 Hz), 131.5, 129.2, 128.6 (dd, J = 4.9, 3.3 Hz), 128.3, 127.9 (d, J = 2.9 Hz), 127.2, 127.1, 126.3, 123.4, 120.5, 119.8, 114.3 (dd, J = 5.3, 2.4 Hz), 110.9, 88.2 (dd, J = 21.2, 20.2 Hz), 34.6, 31.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.45 (d, J = 26.6 Hz), -87.30 (d, J = 26.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}F_2NS$: 420.1592, found: 420.1599.



3-(2,2-difluoro-1-phenylvinyl)-2-((3,5-dimethylphenyl)thio)-1*H*-indole (5c)

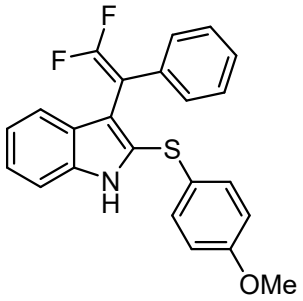
Yellow oil (32 mg, 82% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.40-7.32 (m, 5H), 7.31-7.25 (m, 3H), 7.17-7.09 (m, 1H), 6.86 (m, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 297.8, 290.0 Hz), 139.0, 136.8, 134.4, 134.1 (dd, J = 5.2, 3.3 Hz), 128.8, 128.7 (dd, J = 4.8, 3.2 Hz), 128.3, 128.0 (d, J = 2.9 Hz), 127.1, 127.0 (dd, J = 3.6, 1.3 Hz), 126.9, 123.4, 120.5, 119.8, 114.5 (dd, J = 5.3, 2.2 Hz), 110.9, 88.1 (dd, J = 20.5, 20.5 Hz), 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.38 (d, J = 26.4 Hz), -87.18 (d, J = 26.4 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_2NS$: 392.1279, found: 392.1282.



3-(2,2-difluoro-1-phenylvinyl)-2-((4-methoxyphenyl)thio)-1*H*-indole (5d)

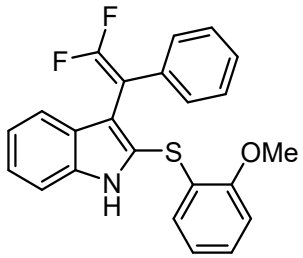
Yellow solid (35 mg, 88% yield, m.p. = 70-71 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.38-7.27 (m, 7H), 7.26-7.19 (m, 3H), 7.10-7.06 (m, 1H), 6.84-6.80 (m, 2H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 154.2 (dd, J = 297.9, 289.9 Hz), 136.7, 134.1 (dd, J = 5.4, 3.3 Hz), 132.6, 128.6 (dd, J = 4.8, 3.2 Hz), 128.3 (2C), 128.0 (d, J = 2.7 Hz), 127.1, 124.6, 123.1, 120.5, 119.6, 115.0, 112.8 (dd, J = 5.3, 2.1 Hz), 110.7, 88.1 (dd, J = 21.2, 19.2 Hz), 55.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.53 (d, J = 26.6 Hz), -87.38 (d, J = 26.6 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}F_2NS$: 394.1072, found: 394.1069.



3-(2,2-difluoro-1-phenylvinyl)-2-((2-methoxyphenyl)thio)-1*H*-indole (5e)

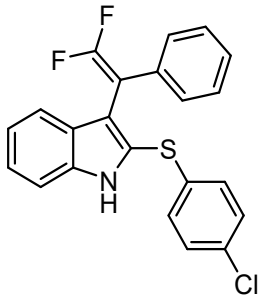
Yellow solid (32 mg, 82% yield, m.p. = 65-66 ℃), purified by flash column chromatography on silica gel using petroleum ether ethyl acetate = 50: 1 as eluent

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.44-7.17 (m, 9H), 7.12-7.08 (m, 1H), 6.96-6.87 (m, 2H), 6.84-6.80 (m, 1H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 154.2 (dd, J = 298.5, 291.4 Hz), 136.9, 134.1 (dd, J = 5.2, 3.0 Hz), 130.3, 128.6 (dd, J = 4.7, 3.4 Hz), 127.8 (d, J = 2.8 Hz), 128.24, 128.20, 127.1, 125.9 (d, J = 2.3 Hz), 123.7, 123.4, 121.5, 120.4, 119.8, 115.1 (dd, J = 5.2, 2.2 Hz), 111.0, 110.9, 88.1 (dd, J = 21.2, 21.2 Hz), 56.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.47 (d, J = 26.6 Hz), -87.28 (d, J = 26.6 Hz)

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}F_2NS$: 394.1072, found: 394.1070.



2-((4-chlorophenyl)thio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5f)

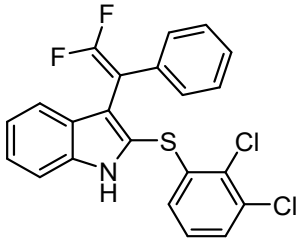
White solid (32 mg, 81% yield, m.p. = 135-136 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.42-7.23 (m, 8H), 7.23-7.17 (m, 2H), 7.16-7.12 (m, 1H), 7.10-7.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 298.0, 290.2 Hz), 136.9, 134.2, 133.9 (dd, J = 5.4, 3.2 Hz), 132.6, 129.5, 129.3, 128.6 (dd, J = 4.0, 4.0 Hz), 128.3, 127.8 (d, J = 3.1 Hz), 127.2, 125.3 (d, J = 4.1 Hz), 123.9, 120.8, 120.1, 115.7 (dd, J = 5.2, 2.4 Hz), 111.1, 88.0 (dd, J = 20.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.29 (d, J = 26.1 Hz), -86.97 (d, J = 26.1 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}ClF_2NS$: 398.0576, found: 398.0569.



2-((2,3-dichlorophenyl)thio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5g)

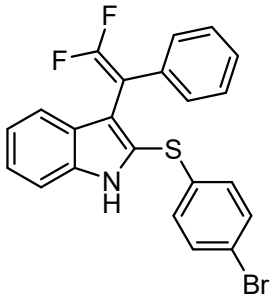
Yellow solid (36 mg, 84% yield, m.p. = 96-97 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.44-7.36 (m, 2H), 7.34-7.26 (m, 4H), 7.26-7.20 (m, 3H), 7.17-7.13 (m, 1H), 6.93 (t, J = 8.0 Hz, 1H), 6.61-6.58 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 297.9, 290.4 Hz), 138.5, 137.2, 133.7 (dd, J = 5.0, 3.3 Hz), 133.5, 129.0, 128.6 (dd, J = 4.1, 4.1 Hz), 128.3, 127.7 (d, J = 2.4 Hz), 127.4 (d, J = 3.8 Hz), 127.3, 126.5, 125.7 (d, J = 1.5 Hz), 124.4, 123.1 (d, J = 3.8 Hz), 121.0, 120.3, 117.7 (dd, J = 5.3, 2.4 Hz), 111.3, 87.9 (dd, J = 20.5, 20.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.14 (d, J = 25.7 Hz), -86.58 (d, J = 25.7 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{14}Cl_2F_2NS$: 432.0187, found: 432.0188.



2-((4-bromophenyl)thio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5h)

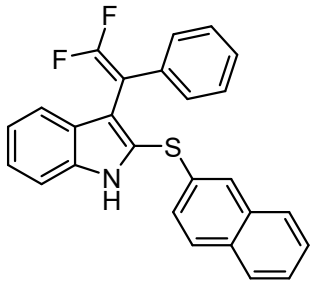
Yellow solid (36 mg, 82% yield, m.p. = 139-140 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.39-7.33 (m, 4H), 7.33-7.24 (m, 6H), 7.16-7.12 (m, 1H), 7.03-6.96 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 297.9, 290.3 Hz), 137.0, 134.9, 133.9 (dd, J = 5.0, 3.4 Hz), 132.2, 129.7, 128.6 (dd, J = 3.9, 3.8 Hz), 128.3, 127.8 (d, J = 2.0 Hz), 127.3, 125.1 (d, J = 3.9 Hz), 124.0, 120.8, 120.4, 120.1, 115.8 (dd, J = 5.3, 2.1 Hz), 111.1, 88.0 (dd, J = 20.7, 20.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.27 (d, J = 26.1 Hz), -86.94 (d, J = 26.1 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}BrF_2NS$: 442.0071, found: 442.0067.



3-(2,2-difluoro-1-phenylvinyl)-2-(naphthalen-2-ylthio)-1*H*-indole (5i)

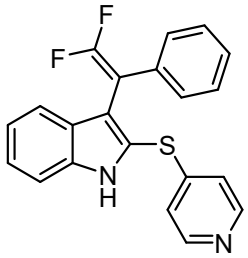
Yellow solid (33 mg, 81% yield, m.p. = 134-135 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.82-7.79 (m, 1H), 7.77-7.63 (m, 3H), 7.52-7.46 (m, 2H), 7.42-7.22 (m, 9H), 7.17-7.13 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (dd, J = 298.0, 290.1 Hz), 137.0, 134.1 (dd, J = 5.1, 3.0 Hz), 133.7, 132.6, 132.1, 129.0, 128.7 (dd, J = 4.0, 4.0 Hz), 128.3, 127.9 (d, J = 2.3 Hz), 127.8, 127.32, 127.29, 127.2, 126.8, 126.5, 126.3 (d, J = 3.8 Hz), 126.2, 123.7, 120.7, 119.9, 115.1 (dd, J = 5.0, 2.0 Hz), 111.0, 88.1 (dd, J = 20.6, 20.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.29 (d, J = 26.3 Hz), -87.09 (d, J = 26.3 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{18}F_2NS$: 414.1123, found: 414.1126.



3-(2,2-difluoro-1-phenylvinyl)-2-(pyridin-4-ylthio)-1*H*-indole (5j)

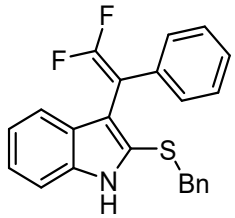
Yellow solid (31 mg, 84% yield, m.p. = 151-152 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.29-8.27 (m, 2H), 7.53-7.51 (m, 1H), 7.44-7.42 (m, 1H), 7.40-7.38 (m, 1H), 7.37-7.27 (m, 5H), 7.22-7.18 (m, 1H), 6.88 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, *J* = 298.0, 290.3 Hz), 149.4, 148.9, 137.6, 133.8 (dd, *J* = 4.9, 3.5 Hz), 128.6 (dd, *J* = 4.7, 3.2 Hz), 128.3, 127.6 (d, *J* = 2.4 Hz), 127.3, 124.4, 121.1 (dd, *J* = 4.0, 1.5 Hz), 120.8, 120.6, 120.3, 117.5, 111.5, 88.0 (dd, *J* = 20.6, 20.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.28 (d, *J* = 26.2 Hz), -86.77 (d, *J* = 26.1 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}F_2N_2S$: 365.0919, found: 365.0913.



2-(benzylthio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5k)

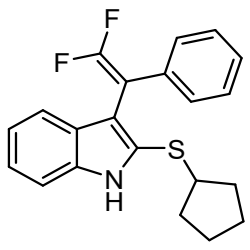
Yellow oil (27 mg, 71% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.34-7.32 (m, 4H), 7.31-7.26 (m, 5H), 7.26-7.20 (m, 2H), 7.17-7.14 (m, 2H), 7.11-7.07 (m, 1H), 3.82 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, *J* = 297.6, 289.5 Hz), 138.2, 136.4, 134.4 (dd, *J* = 5.3, 3.4 Hz), 131.0, 128.9, 128.7, 128.6 (dd, *J* = 4.8, 3.2 Hz), 128.3, 127.7 (dd, *J* = 3.0, 2.0 Hz), 127.5, 127.1, 123.3, 120.4, 119.7, 114.8 (dd, *J* = 5.2, 2.3 Hz), 110.8, 88.3 (dd, *J* = 21.2, 19.6 Hz), 40.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.54 (d, *J* = 27.3 Hz), -87.63 (d, *J* = 27.3 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}F_2N_2S$: 378.1123, found: 378.1122.



2-(cyclopentylthio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5l)

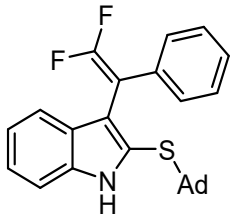
Yellow solid (33 mg, 93% yield, m.p. = 68-69 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.41-7.23 (m, 8H), 7.12-7.08 (m, 1H), 3.42-3.37 (m, 1H), 1.93-1.85 (m, 2H), 1.82-1.69 (m, 2H), 1.61-1.51 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, J = 297.8, 289.6 Hz), 136.4, 134.4 (dd, J = 5.2, 3.5 Hz), 129.2 (d, J = 2.7 Hz), 128.6 (dd, J = 5.0, 3.3 Hz), 128.3, 128.0 (d, J = 2.9 Hz), 127.1, 123.1, 120.4, 119.6, 114.1 (d, J = 5.9 Hz), 110.7, 88.4 (dd, J = 20.2, 20.2 Hz), 48.5, 33.8, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.41 (d, J = 26.7 Hz), -87.47 (d, J = 26.8 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}F_2NS$: 356.1279, found: 356.1273.



2-(((3r)-adamantan-1-yl)thio)-3-(2,2-difluoro-1-phenylvinyl)-1*H*-indole (5m)

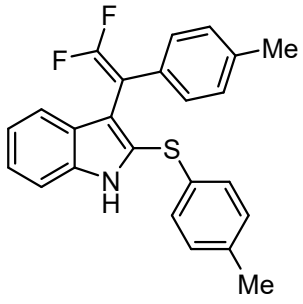
White solid (40 mg, 95% yield, m.p. = 138-139 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.46-7.26 (m, 8H), 7.16-7.12 (m, 1H), 2.03 (s, 3H), 1.88 (m, 6H), 1.69-1.60 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 297.8, 289.9 Hz), 136.4, 134.6 (dd, J = 5.6, 3.4 Hz), 128.7 (dd, J = 5.2, 3.3 Hz), 128.2, 128.0 (d, J = 2.0 Hz), 127.0, 126.0 (d, J = 4.6 Hz), 123.3, 120.3, 119.9, 116.6 (dd, J = 5.4, 2.5 Hz), 110.8, 88.7 (dd, J = 20.6, 19.2 Hz), 51.1, 44.2, 36.0, 30.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.65 (d, J = 26.2 Hz), -87.45 (d, J = 25.9 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}F_2NS$: 422.1749, found: 422.1752.

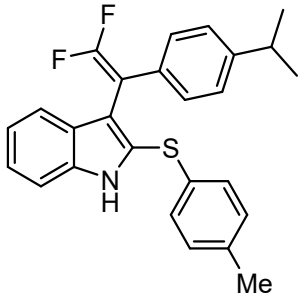


3-(2,2-difluoro-1-(*p*-tolyl)vinyl)-2-(*p*-tolylthio)-1*H*-indole (5n)

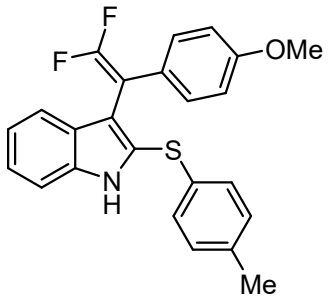
Yellow oil (30 mg, 77% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.31-7.27 (m, 2H), 7.25-7.22 (m, 3H), 7.17-7.06 (m, 7H), 2.35 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, J = 297.2, 289.4 Hz), 137.0, 136.9, 136.8, 131.4, 131.1 (dd, J = 5.2, 3.2 Hz), 130.0, 129.5, 129.0, 128.5 (dd, J = 4.9, 3.4 Hz), 127.9 (d, J = 2.2 Hz), 127.2 (d, J = 3.0 Hz), 123.3, 120.5, 119.8, 114.3 (dd, J = 5.3, 2.4 Hz), 110.8, 87.9 (dd, J = 20.2, 20.2 Hz), 21.2, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.12 (d, J = 28.2 Hz), -87.71 (d, J = 28.1 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_2NS$: 392.1279, found: 392.1271.

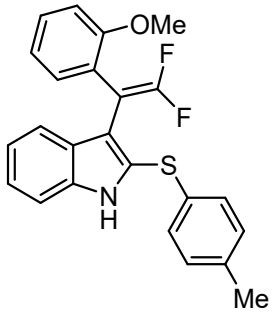


3-(2,2-difluoro-1-(4-isopropylphenyl)vinyl)-2-(*p*-tolylthio)-1*H*-indole (5o)
White solid (31 mg, 75% yield, m.p. = 112-113 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.36-7.21 (m, 5H), 7.21-7.01 (m, 7H), 2.95-2.87 (m, 1H), 2.34 (s, 3H), 1.27 (d, J = 6.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, J = 297.4, 289.4 Hz), 147.8, 137.0, 136.8, 131.44, 131.37, 130.0, 129.5, 128.5 (dd, J = 5.0, 3.3 Hz), 128.0 (d, J = 2.5 Hz), 127.1 (dd, J = 3.8, 1.5 Hz), 126.4, 123.4, 120.5, 119.9, 114.4 (dd, J = 5.3, 2.3 Hz), 110.8, 87.9 (dd, J = 20.7, 20.7 Hz), 33.8, 23.9, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.07 (d, J = 28.2 Hz), -87.51 (d, J = 28.0 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}F_2NS$: 420.1592, found: 420.1585.

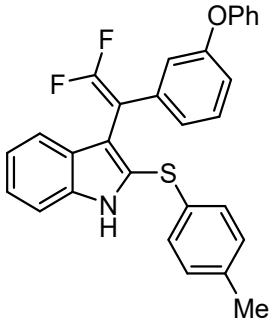


3-(2,2-difluoro-1-(4-methoxyphenyl)vinyl)-2-(*p*-tolylthio)-1*H*-indole (5p)
Yellow solid (30 mg, 74% yield, m.p. = 103-104 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.35-7.20 (m, 5H), 7.18-7.09 (m, 3H), 7.09-7.00 (m, 2H), 6.89-6.79 (m, 2H), 3.82 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 153.9 (dd, J = 296.3, 289.1 Hz), 137.0, 136.8, 131.4, 130.0, 129.8 (dd, J = 4.8, 3.3 Hz), 129.5, 127.9 (d, J = 2.2 Hz), 127.1 (dd, J =

3.5, 1.1 Hz), 126.4 (dd, *J* = 5.2, 3.1 Hz), 123.3, 120.5, 119.8, 114.3 (dd, *J* = 5.1, 3.0 Hz), 113.7, 110.8, 87.6 (dd, *J* = 20.7, 20.7 Hz), 55.2, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.97 (d, *J* = 30.1 Hz), -88.59 (d, *J* = 30.1 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_2NOS$: 408.1228, found: 408.1236.

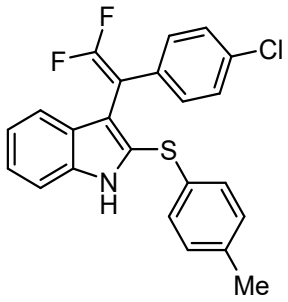


3-(2,2-difluoro-1-(2-methoxyphenyl)vinyl)-2-(*p*-tolylthio)-1*H*-indole (5q)
Yellow oil (39 mg, 96% yield, m.p. = 106-107 ℃), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41-7.19 (m, 4H), 7.19-7.02 (m, 5H), 7.06-6.83 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 153.6 (dd, *J* = 292.9, 292.9 Hz), 136.73, 136.68, 132.0, 131.6 (dd, *J* = 5.3, 2.1 Hz), 130.0, 129.1, 129.0, 127.8 (d, *J* = 2.0 Hz), 126.0 (dd, *J* = 3.8, 1.3 Hz), 123.20, 123.16, 120.4, 120.3, 120.0, 115.4 (d, *J* = 4.1 Hz), 111.2, 110.7, 83.9 (dd, *J* = 25.4, 22.5 Hz), 55.6, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -84.89 (d, *J* = 25.1 Hz), -85.55 (d, *J* = 25.3 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_2NOS$: 408.1228, found: 408.1230.

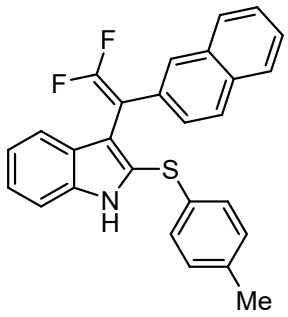


3-(2,2-difluoro-1-(3-phenoxyphenyl)vinyl)-2-(*p*-tolylthio)-1*H*-indole (5r)
Yellow oil (37 mg, 78% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.33-7.25 (m, 6H), 7.17-7.03 (m, 8H), 6.99-6.97 (m, 2H), 6.91-6.89 (m, 1H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 156.9, 154.3 (dd, *J* = 299.5, 291.4 Hz), 137.1, 136.8, 136.0 (dd, *J* = 5.3, 3.5 Hz), 131.2, 130.1, 129.7, 129.5, 129.4, 127.8 (d, *J* = 2.8 Hz), 127.3 (d, *J* = 3.7 Hz), 123.7 (dd, *J* = 4.7, 3.4 Hz), 123.4, 123.1, 120.6, 119.7, 119.6

(dd, J = 4.3, 4.3 Hz), 118.6, 117.7, 113.8 (dd, J = 4.5, 2.5 Hz), 110.9, 87.9 (dd, J = 21.4, 19.5 Hz), 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -81.70 (d, J = 24.7 Hz), -86.18 (d, J = 24.7 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}F_2NOS$: 470.1385, found: 470.1388.

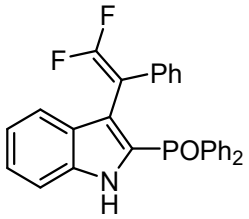


3-(1-(4-chlorophenyl)-2,2-difluorovinyl)-2-(*p*-tolylthio)-1*H*-indole (5s)
Yellow oil (31 mg, 76% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.42-7.21 (m, 7H), 7.14-7.07 (m, 5H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (dd, J = 298.3, 290.9 Hz), 137.2, 136.8, 132.9, 132.6 (dd, J = 5.5, 3.5 Hz), 131.1, 130.1, 129.9 (dd, J = 5.0, 3.5 Hz), 129.5, 128.5, 127.7 (d, J = 2.9 Hz), 127.5 (d, J = 3.7 Hz), 123.5, 120.7, 119.6, 113.5 (dd, J = 5.1, 2.4 Hz), 111.0, 87.5 (dd, J = 21.8, 19.6 Hz), 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -81.63 (d, J = 25.0 Hz), -86.51 (d, J = 25.1 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}ClF_2NS$: 412.0733, found: 412.0731.



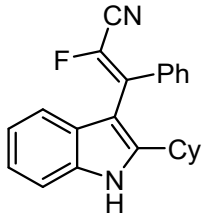
3-(2,2-difluoro-1-(naphthalen-2-yl)vinyl)-2-(*p*-tolylthio)-1*H*-indole (5t)
Yellow oil (35 mg, 82% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 50: 1 as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.86-7.66 (m, 4H), 7.52-7.44 (m, 3H), 7.37-7.35 (m, 2H), 7.31-7.21 (m, 1H), 7.14-7.09 (m, 3H), 7.05-7.03 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4 (dd, J = 299.0, 291.9), 137.1, 136.8, 133.2, 132.4, 131.6 (dd, J = 5.3, 3.3 Hz), 131.3, 130.1, 130.0, 129.5, 128.1, 127.8, 127.6, 126.8 (d, J = 2.8 Hz), 126.5 (dd, J = 5.1, 2.7 Hz), 126.2, 126.1, 126.0, 123.4, 120.6, 119.8, 114.2 (dd, J = 5.0, 2.3 Hz), 110.9, 88.3 (dd, J = 21.0, 19.8 Hz), 21.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ -82.00 (d, J = 25.6 Hz), -87.17 (d, J = 25.8 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{20}F_2NS$: 428.1279, found: 428.1285.



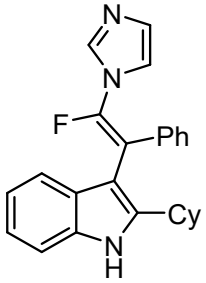
(3-(2,2-difluoro-1-phenylvinyl)-1*H*-indol-2-yl)diphenylphosphine oxide (6)
Yellow oil (30 mg, 65% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 3: 1 as eluent.
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.34 (s, 1H), 7.57-7.46 (m, 9H), 7.32-7.27 (m, 4H), 7.14-7.09 (m, 4H), 6.89-6.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6 (dd, J = 259.6, 259.6 Hz), 138.6, 134.0, 132.7, 132.4, 132.3, 128.9, 128.7, 128.6, 128.4, 128.3 (dd, J = 5.0, 2.5 Hz), 127.2, 125.2, 121.2, 120.5, 116.7, 113.0 (d, J = 4.0 Hz), 91.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -78.03 (d, J = 24.4 Hz), -84.56 (d, J = 24.4 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{21}F_2NOP$: 456.1323, found: 456.1320.

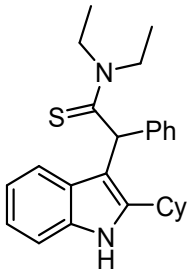


(*Z*)-3-(2-cyclohexyl-1*H*-indol-3-yl)-2-fluoro-3-phenylacrylonitrile (7)
Yellow oil (65 mg, 94% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 10: 1 as eluent.
^{1}H NMR (500 MHz, DMSO-d_6) δ 11.62 (s, 1H), 7.54-7.50 (m, 1H), 7.49-7.48 (m, 4H), 7.38-7.37 (m, 1H), 7.12-7.04 (m, 1H), 6.96-6.93 (m, 2H), 2.34-2.29 (m, 1H), 1.74-1.71 (m, 2H), 1.68-1.51 (m, 5H), 1.27-1.15 (m, 1H), 1.11-1.03 (m, 2H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 147.4, 136.7, 135.6 (d, J = 15.1 Hz), 135.3 (d, J = 2.5 Hz), 131.0, 130.5, 129.6, 128.1, 127.0, 126.2, 122.4 (d, J = 18.2 Hz), 119.9, 115.2 (d, J = 45.4 Hz), 112.2, 104.4, 37.4, 32.8, 26.9, 26.2.

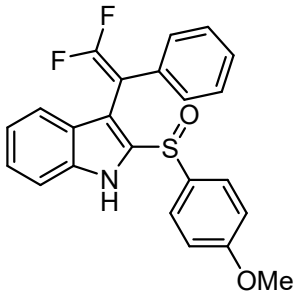
^{19}F NMR (470 MHz, DMSO-d_6) δ -124.16.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}FN_2$: 345.1762, found: 345.1765.



(*Z*)-2-cyclohexyl-3-(2-fluoro-2-(1*H*-imidazol-1-yl)-1-phenylvinyl)-1*H*-indole (8)
Yellow oil (48 mg, 62% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 20: 1 as eluent.
^{1}H NMR (500 MHz, DMSO-d_6) δ 11.26 (s, 1H), 7.84 (s, 1H), 7.50 (s, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.26-7.18 (m, 3H), 7.11 (d, J = 7.9 Hz, 1H), 7.06-7.03 (m, 4H), 6.93-6.90 (m, 1H), 2.62-2.57 (m, 1H), 1.75-1.57 (m, 7H), 1.27-1.15 (m, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 144.6, 143.5, 141.4, 139.3, 137.5, 136.4, 130.2, 129.4, 129.1, 128.4, 127.6, 121.3 (d, J = 48.6 Hz), 119.6 (d, J = 54.7 Hz). 112.5, 112.3, 111.9, 105.1, 37.2, 32.9, 27.0, 26.4.
^{19}F NMR (470 MHz, DMSO-d_6) δ -85.04.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{25}FN_3$: 386.2027, found: 386.2026.



2-(2-cyclohexyl-1*H*-indol-3-yl)-*N*,*N*-diethyl-2-phenylethanethioamide (9)
Yellow oil (52 mg, 64% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 8: 1 as eluent.
^{1}H NMR (500 MHz, DMSO-d_6) δ 10.77 (s, 1H), 7.25-7.09 (m, 7H), 6.91-6.88 (m, 1H), 6.75-6.71 (m, 1H), 5.71 (s, 1H), 4.03-3.85 (m, 2H), 3.60-3.43 (m, 2H), 2.85-2.80 (m, 1H), 1.78-1.40 (m, 7H), 1.15 (t, J = 7.0 Hz, 6H), 1.03 (t, J = 7.0 Hz, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 202.6, 143.5, 142.8, 136.1, 130.0, 128.4, 126.9, 120.7, 119.6, 119.0, 111.5, 109.5, 53.2, 48.4, 46.5, 36.2, 32.9, 32.8, 27.1, 26.4, 14.0, 11.5.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{33}N_2S$: 405.2359, found: 405.2355.



3-(2,2-difluoro-1-phenylvinyl)-2-((4-methoxyphenyl)sulfinyl)-1*H*-indole (10)

Colorless oil (38 mg, 92% yield), purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 3: 1 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.49-7.47 (m, 2H), 7.40-7.39 (m, 1H), 7.26-7.23 (m, 5H), 7.19-7.17 (m, 2H), 7.08-7.05 (m, 1H), 6.86-6.84 (m, 2H), 3.78 (s, 3H).

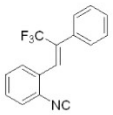
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 153.9 (dd, J = 296.9, 288.8 Hz), 136.8, 135.2, 134.3, 133.5, 129.2, 128.7, 128.6, 127.7, 127.5, 124.8, 121.1, 120.5, 115.0, 112.5, 111.0, 87.3 (dd, J = 20.0, 20.0 Hz), 55.6.

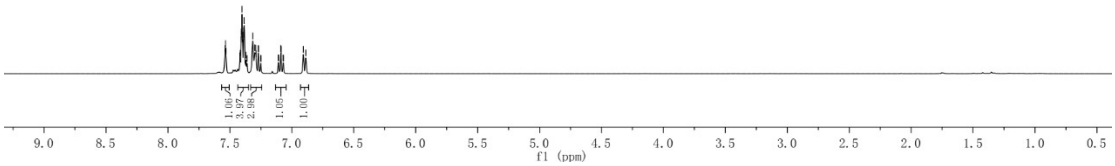
^{19}F NMR (470 MHz, $CDCl_3$) δ -81.4, (d, J = 28.2 Hz), -86.4, (d, J = 23.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}F_2NO_2S$: 410.1021, found: 410.1019.

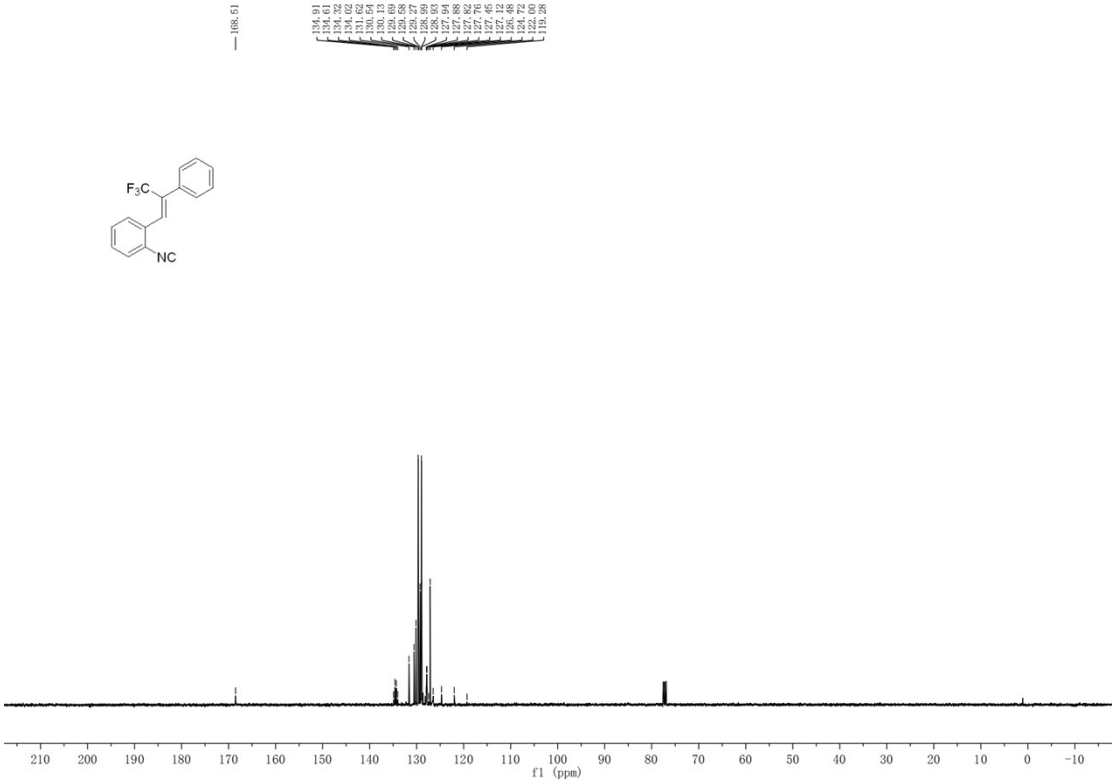
9. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

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

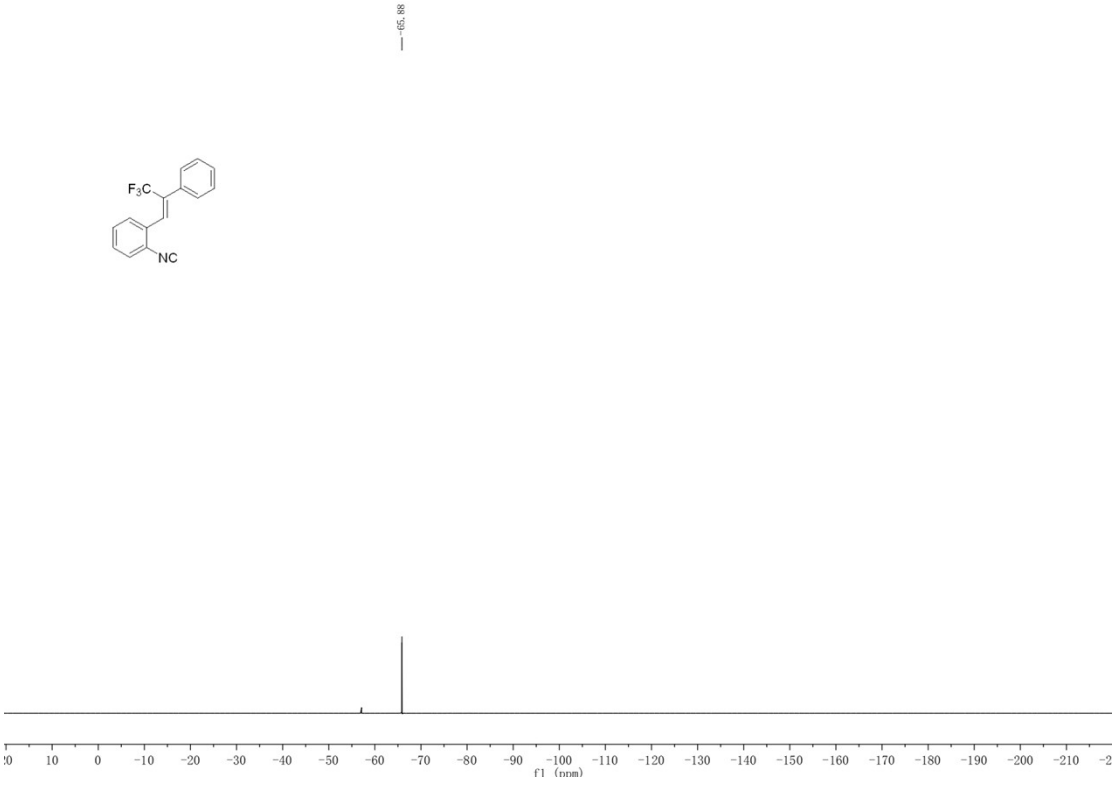




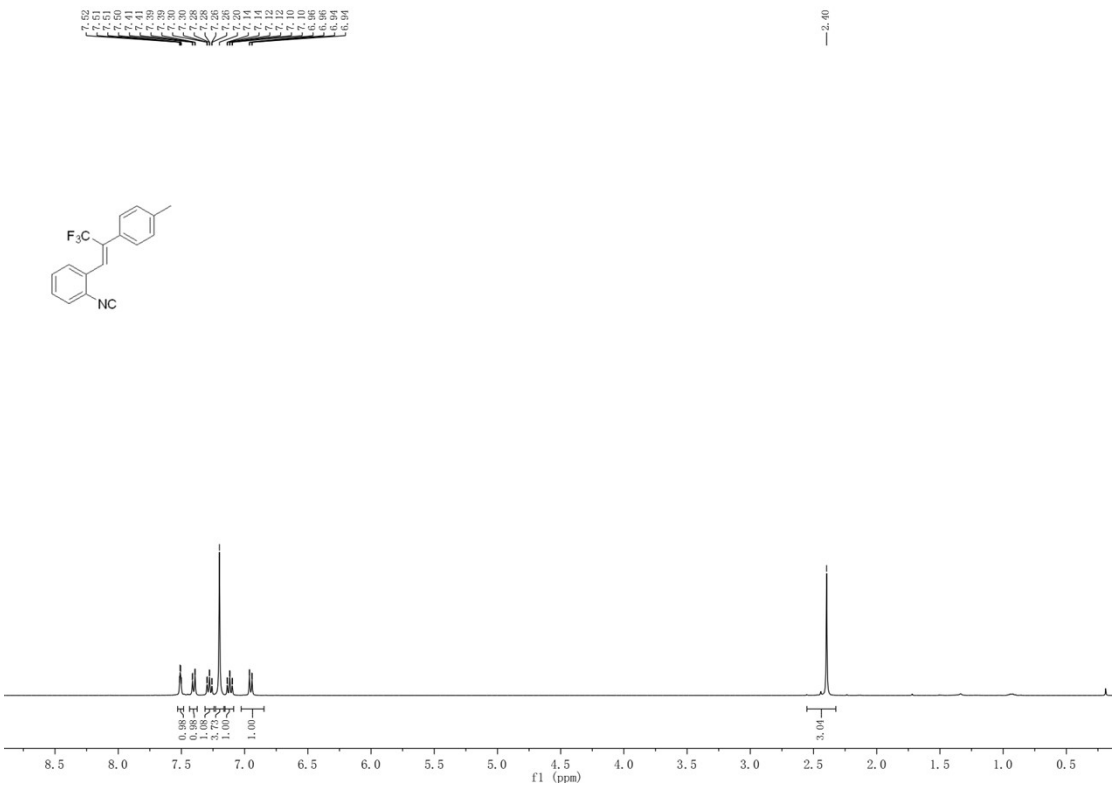
^{13}C NMR spectra of **1a** (100 MHz, $CDCl_3$)



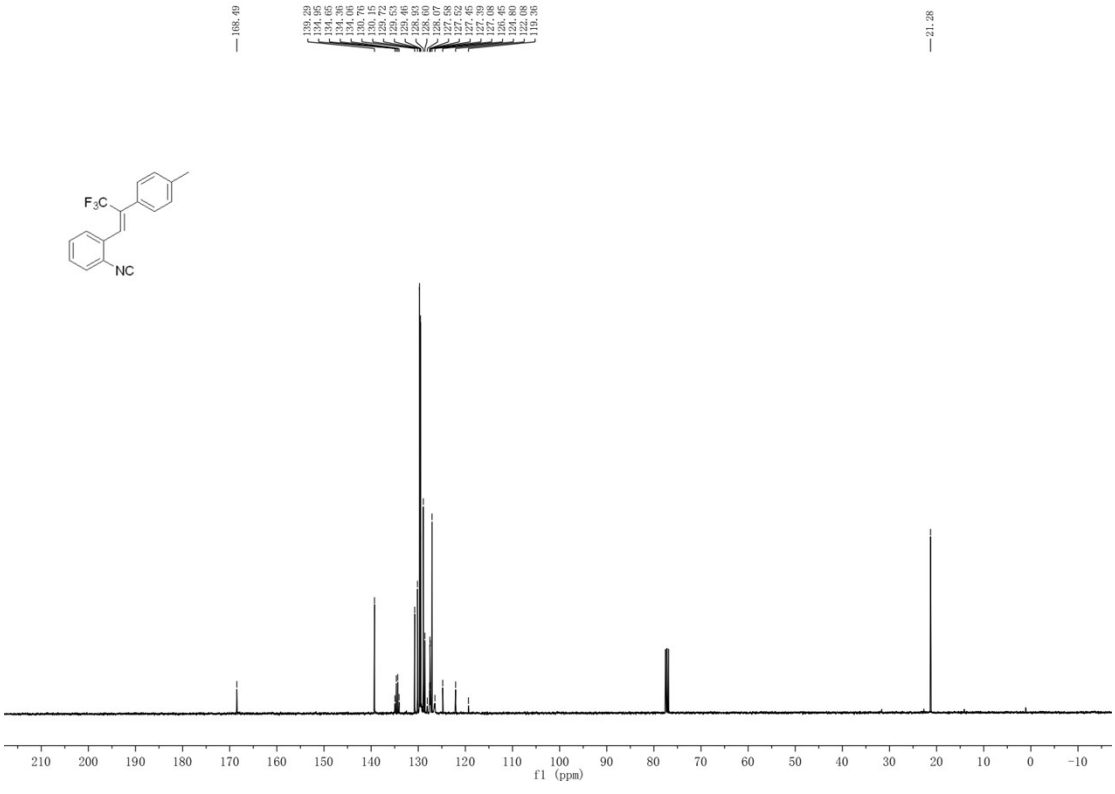
^{19}F NMR spectra of **1a** (376 MHz, $CDCl_3$)



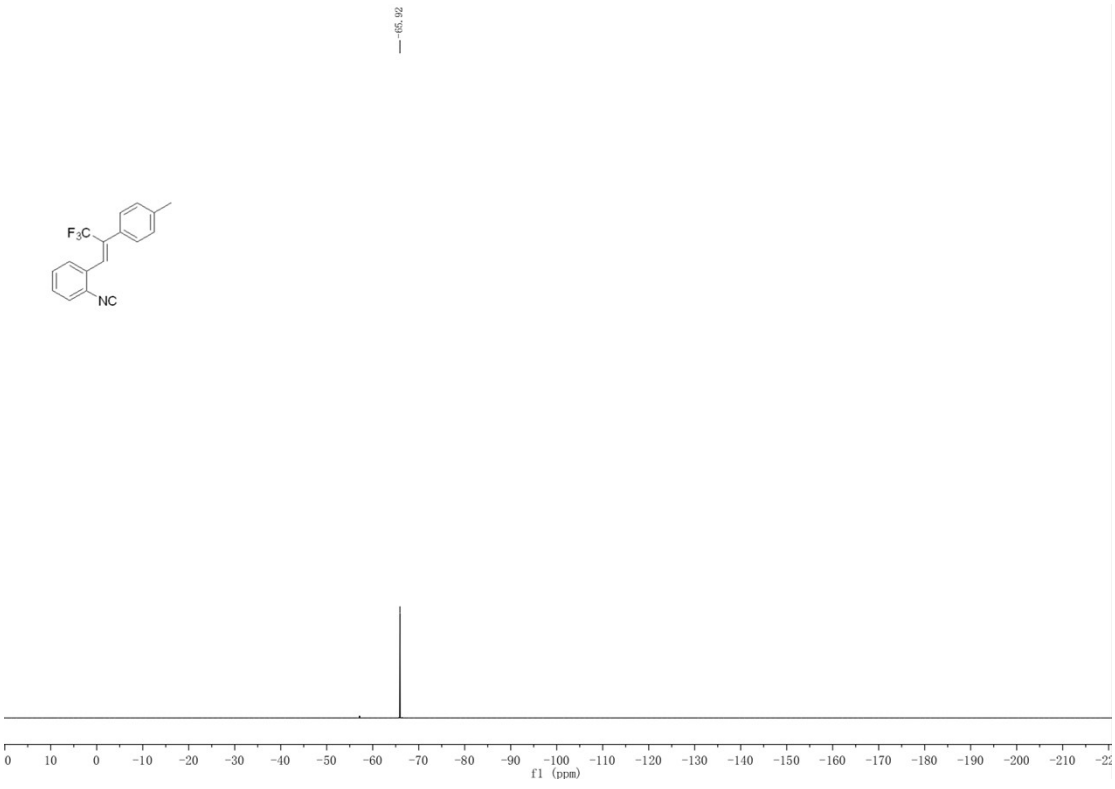
^{1}H NMR spectra of **1b** (400 MHz, $CDCl_3$)



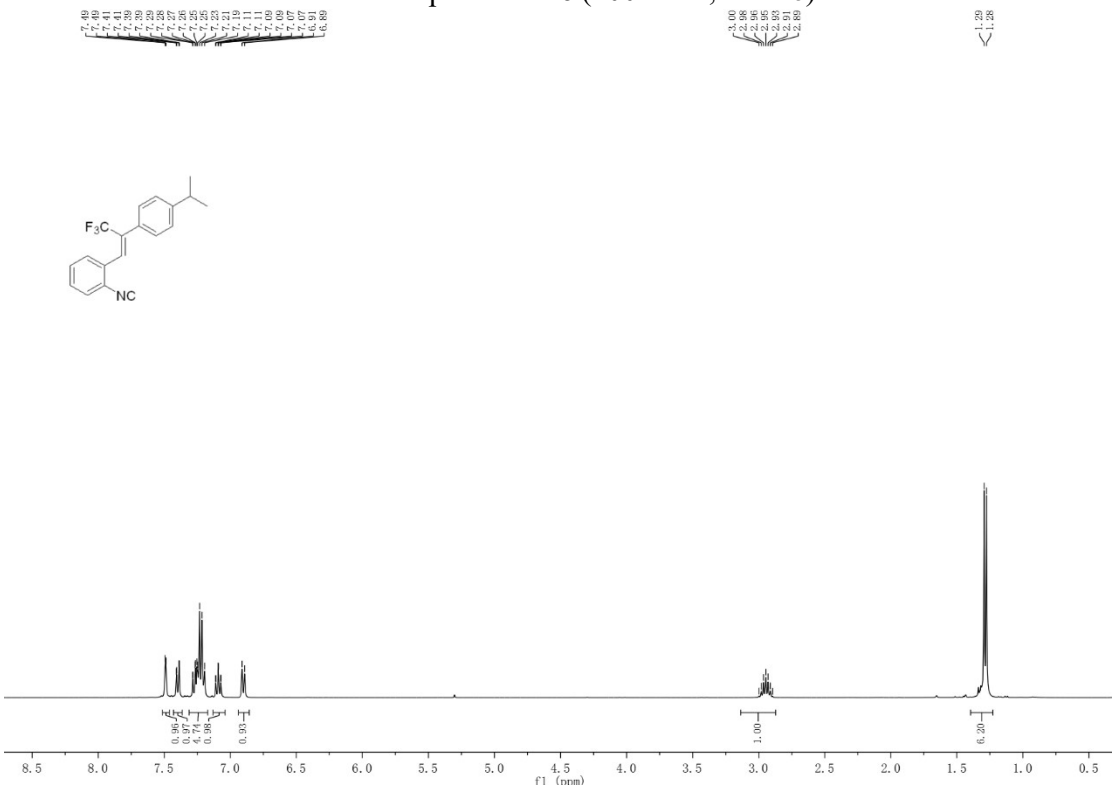
^{13}C NMR spectra of **1b** (100 MHz, $CDCl_3$)



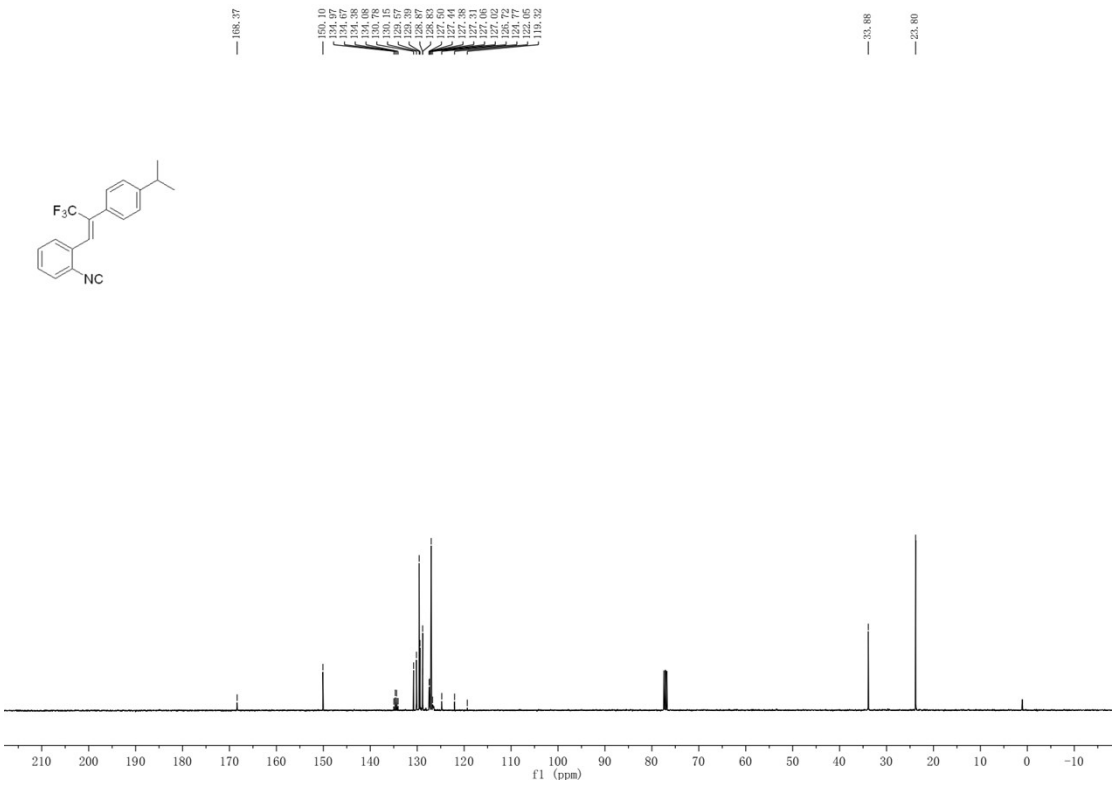
^{19}F NMR spectra of **1b** (376 MHz, $CDCl_3$)



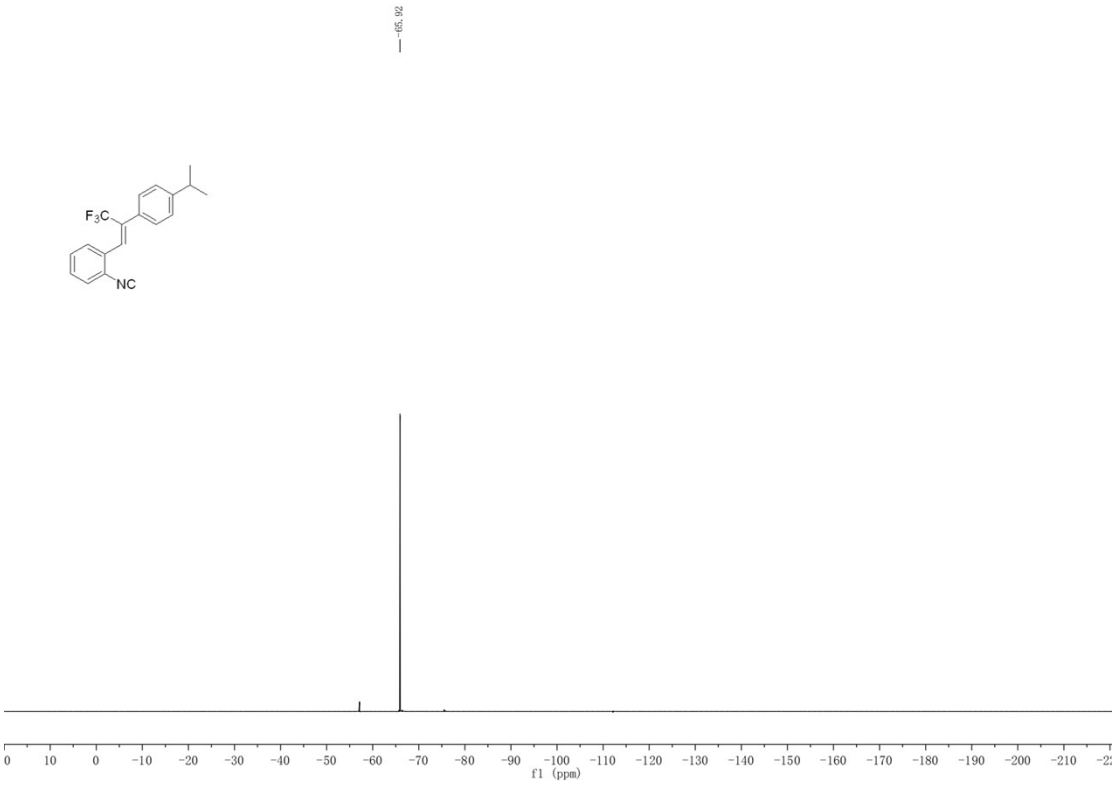
^{1}H NMR spectra of **1c** (400 MHz, $CDCl_3$)



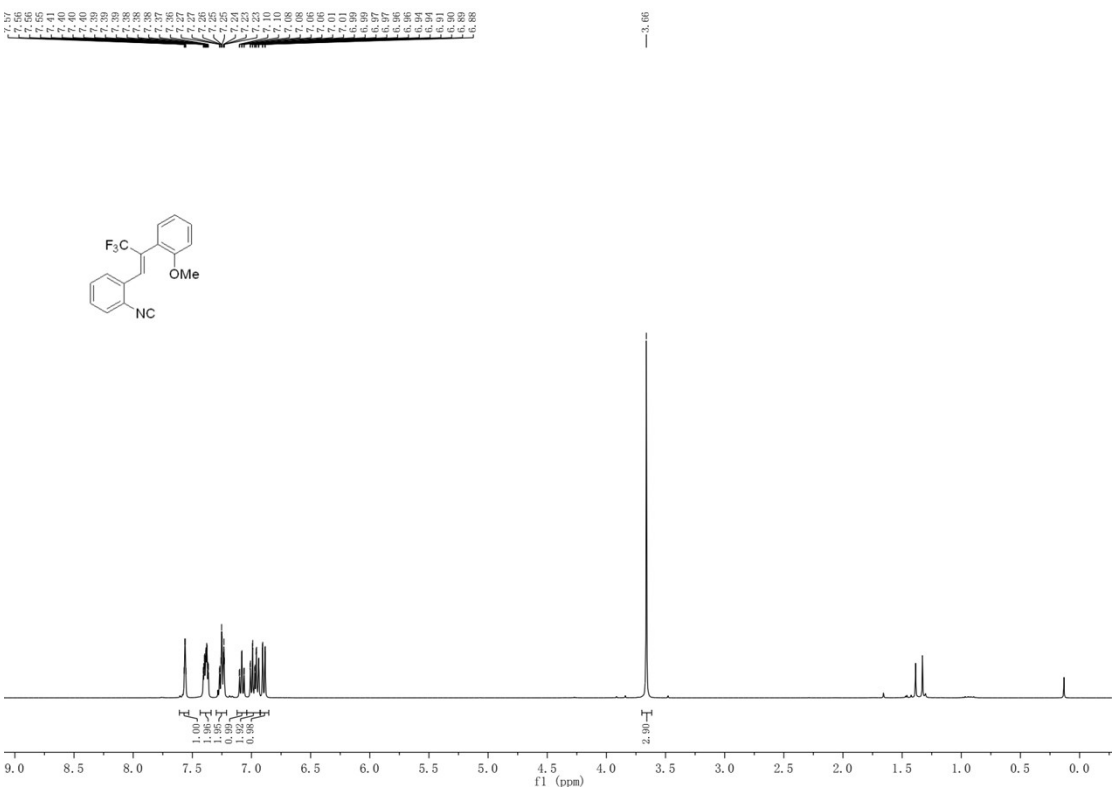
^{13}C NMR spectra of **1c** (100 MHz, $CDCl_3$)



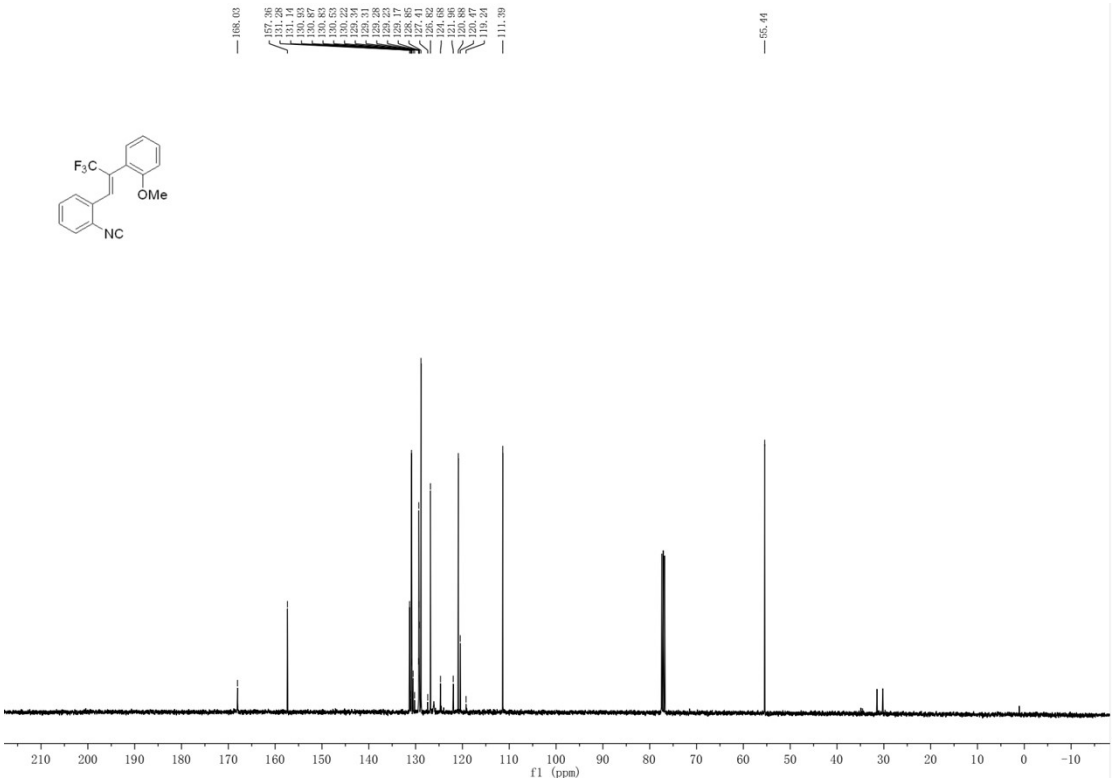
^{19}F NMR spectra of **1c** (376 MHz, $CDCl_3$)



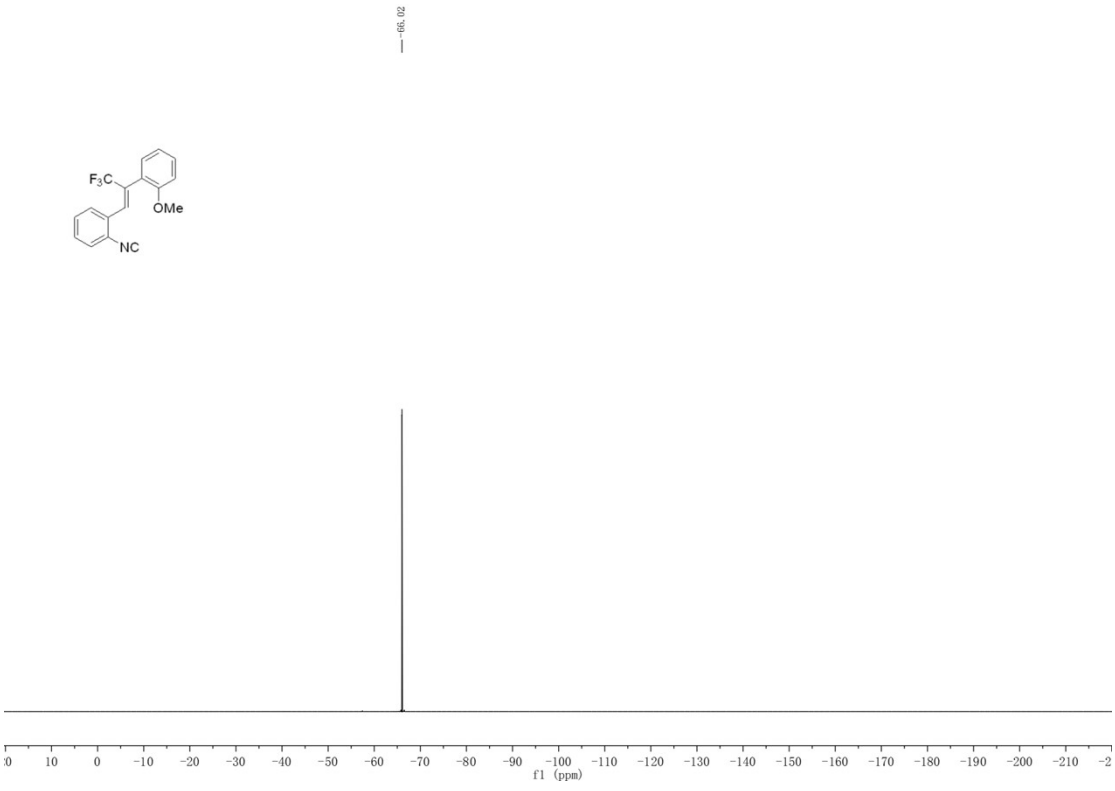
^{1}H NMR spectra of **1d** (400 MHz, $CDCl_3$)



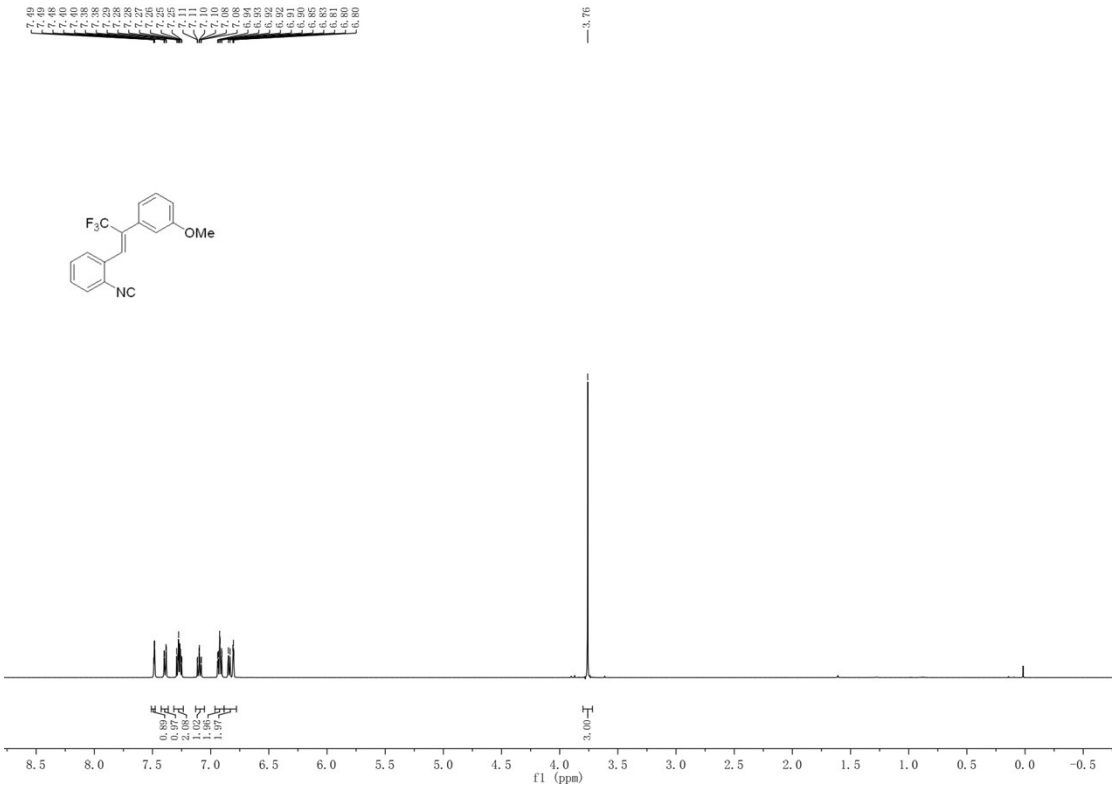
^{13}C NMR spectra of **1d** (100 MHz, $CDCl_3$)



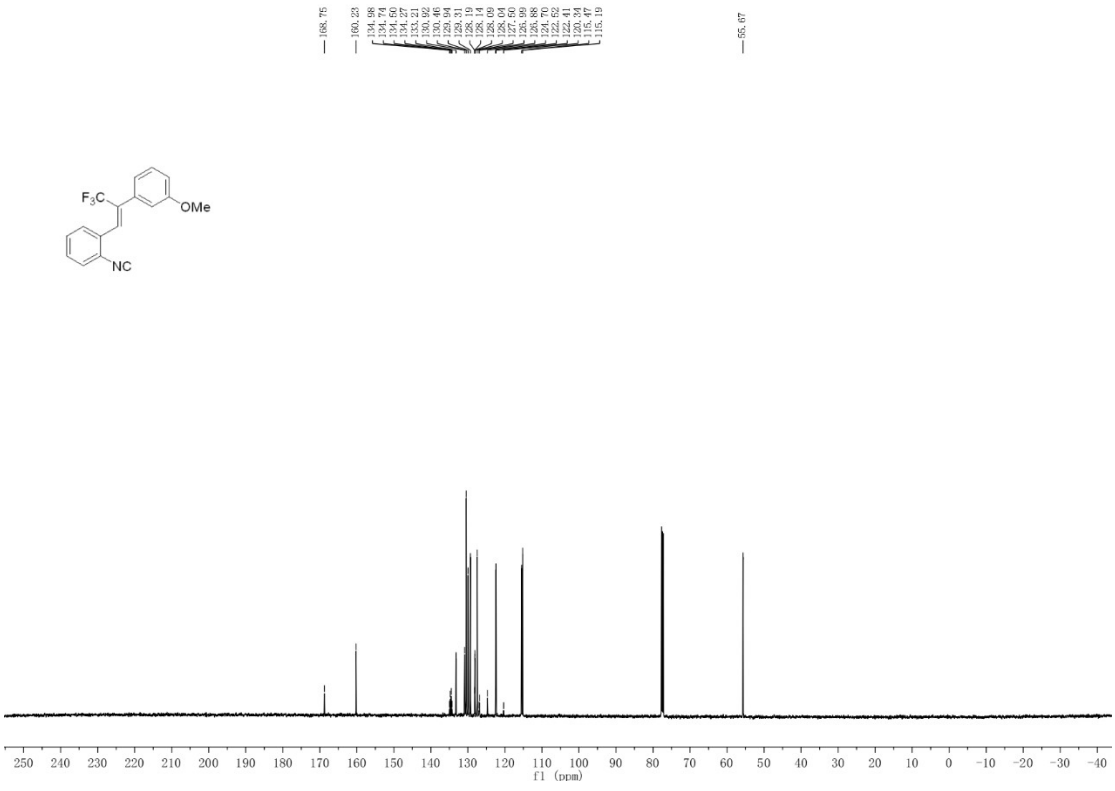
^{19}F NMR spectra of **1d** (376 MHz, $CDCl_3$)



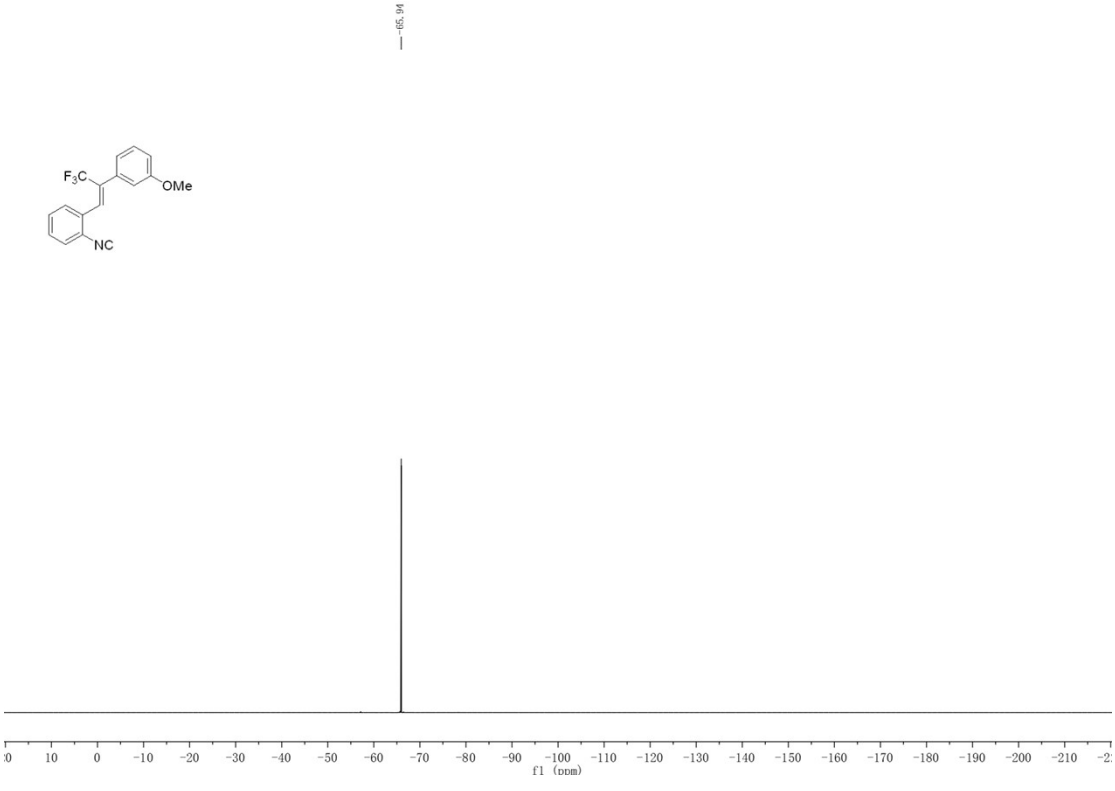
^{1}H NMR spectra of **1e** (500 MHz, $CDCl_3$)



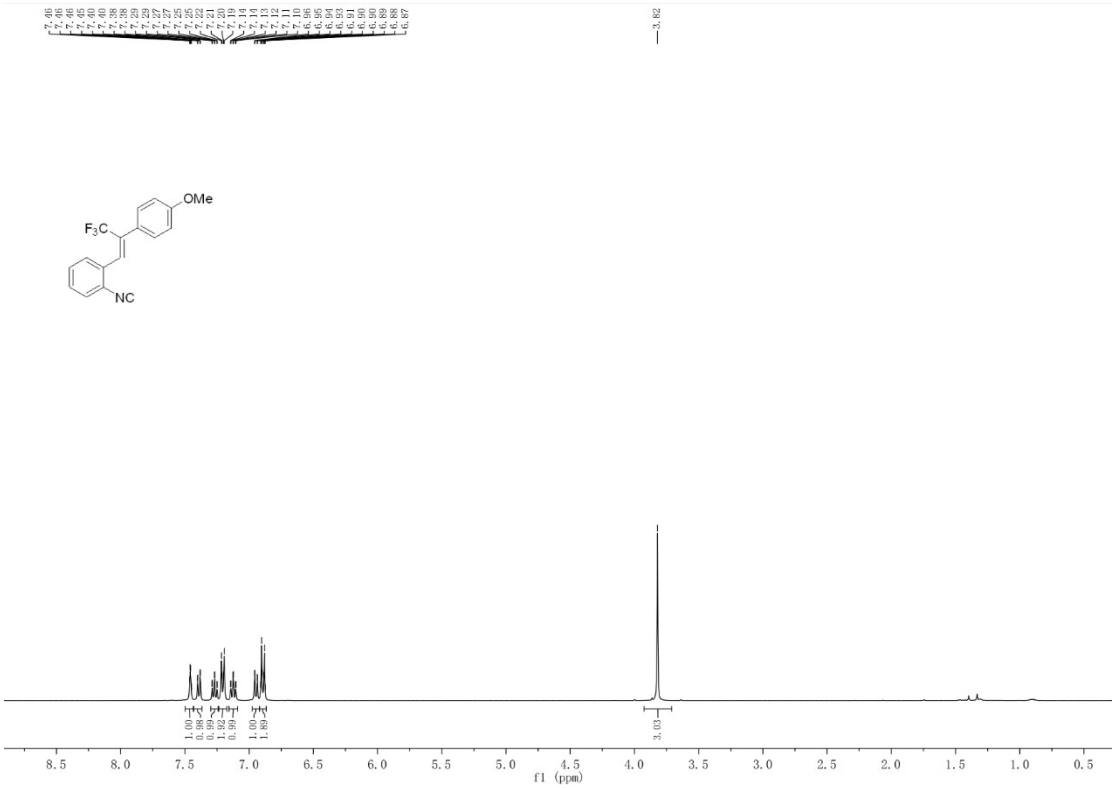
^{13}C NMR spectra of **1e** (125 MHz, $CDCl_3$)



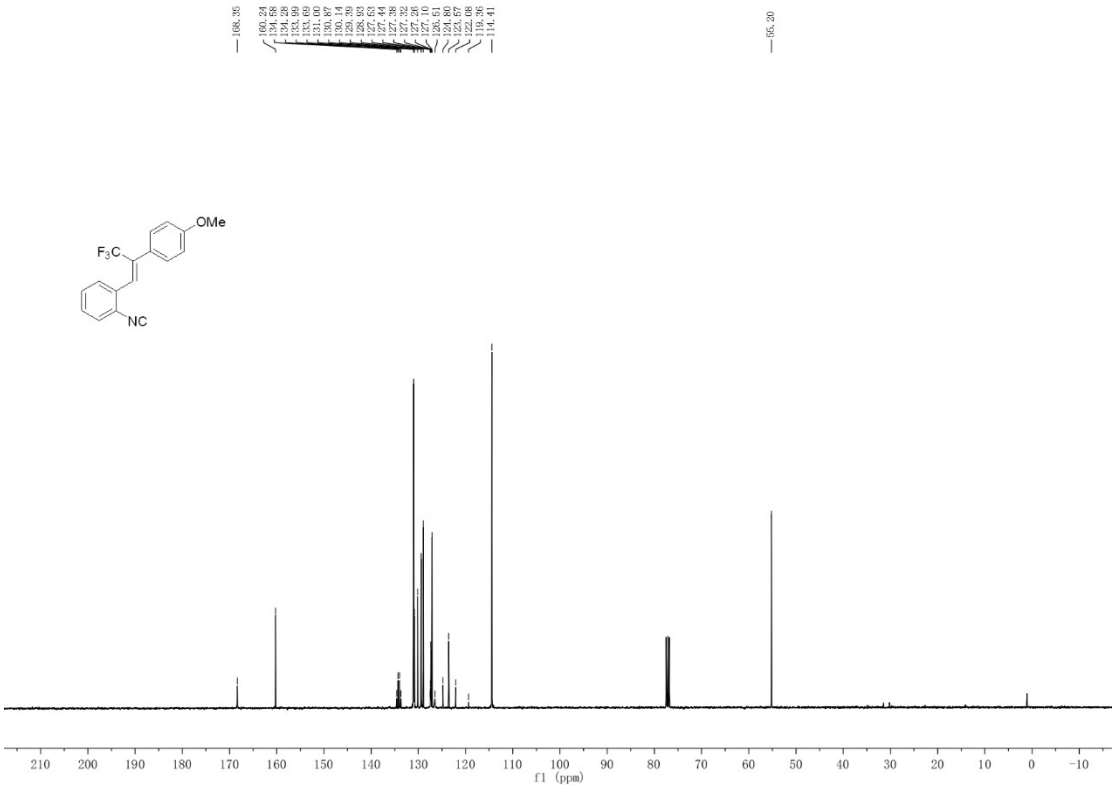
^{19}F NMR spectra of **1e** (376 MHz, $CDCl_3$)



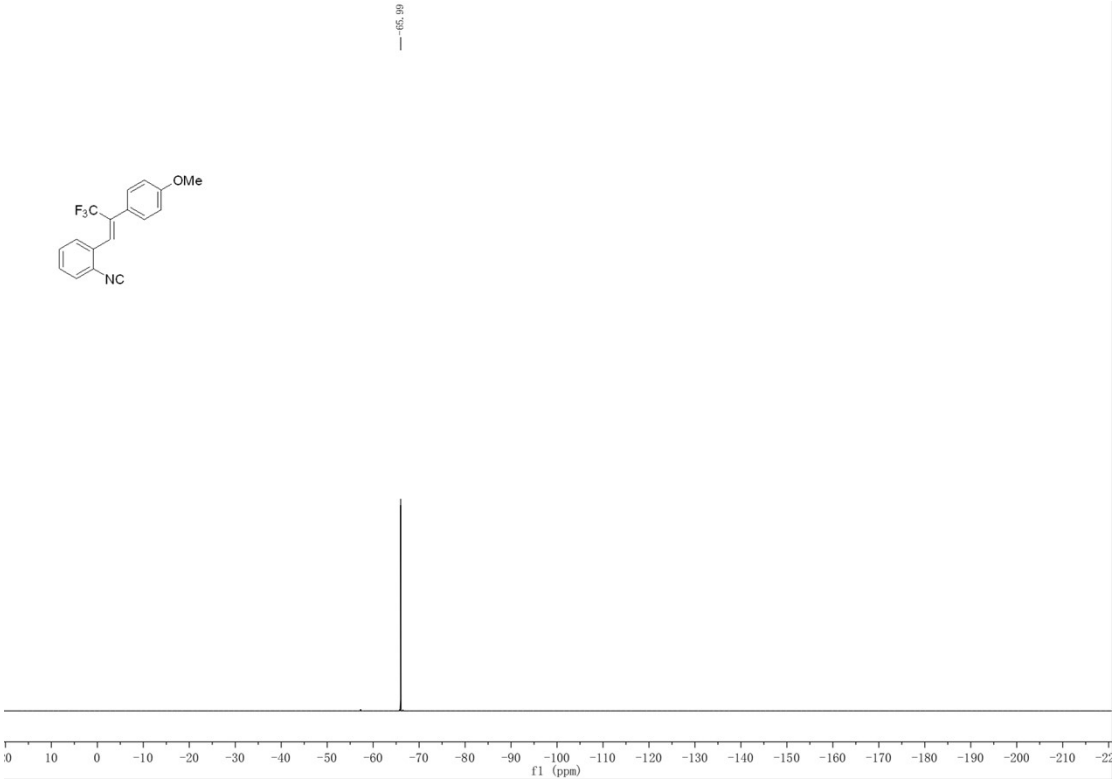
^{1}H NMR spectra of **1f** (400 MHz, $CDCl_3$)



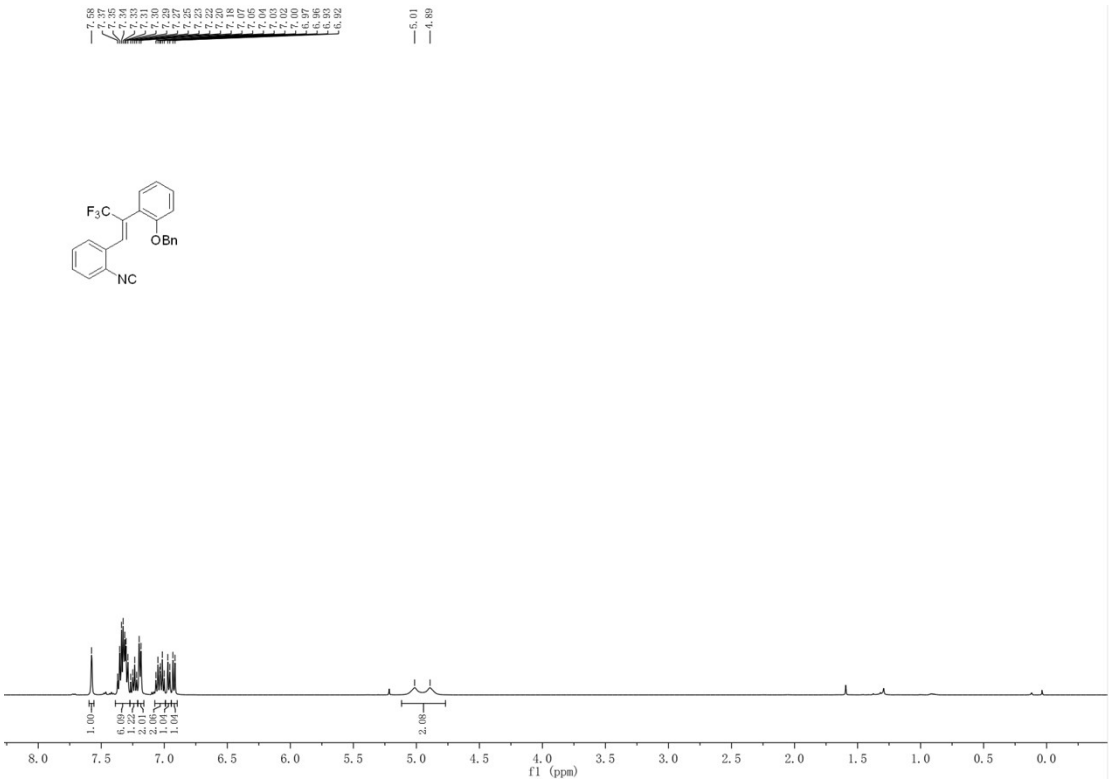
^{13}C NMR spectra of **1f** (100 MHz, $CDCl_3$)



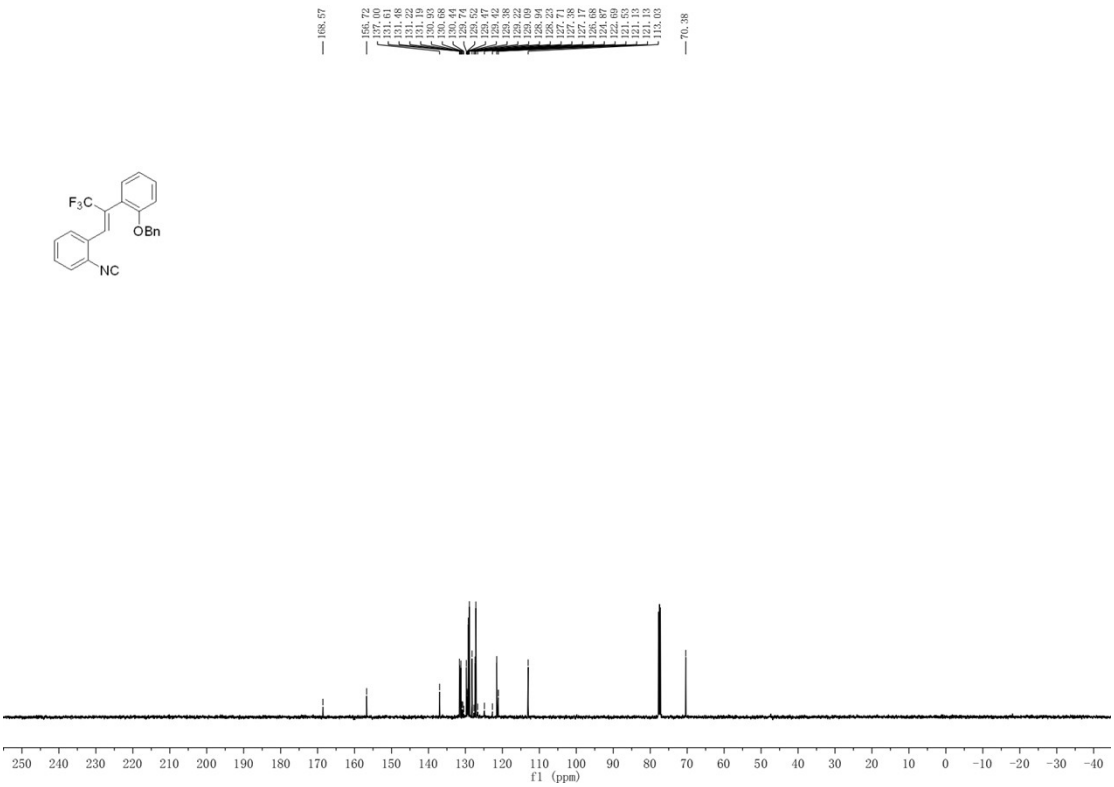
^{19}F NMR spectra of **1f** (376 MHz, $CDCl_3$)



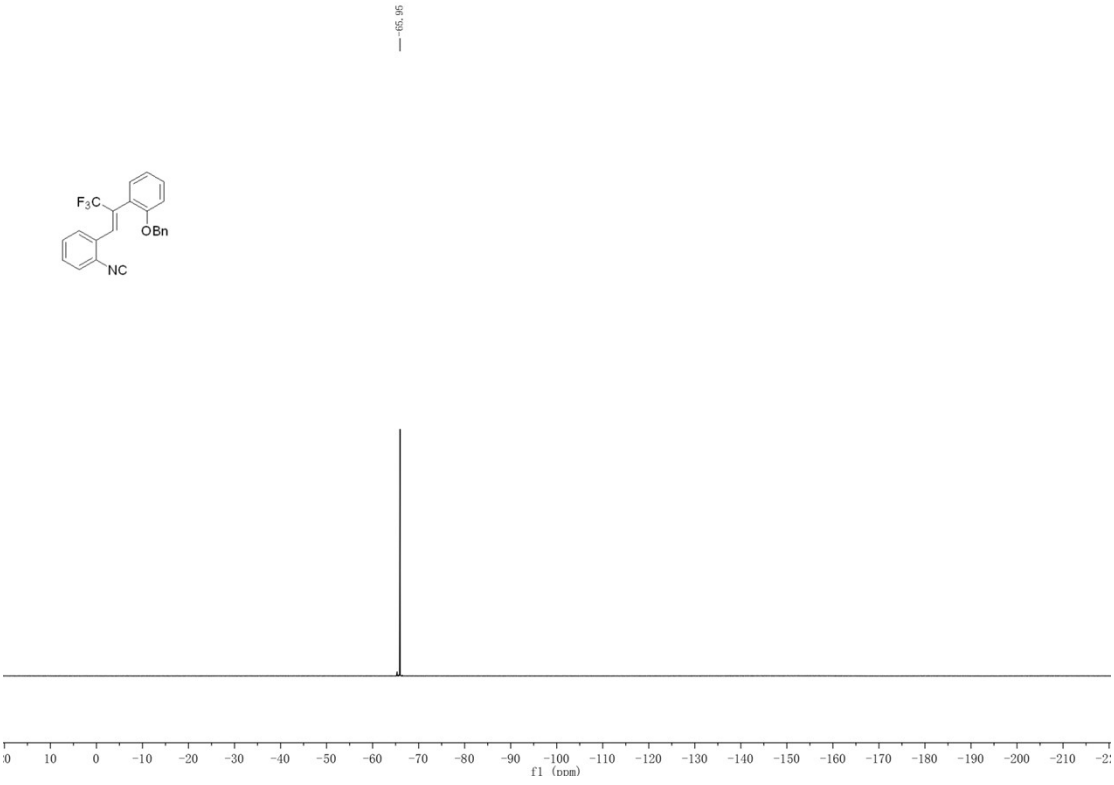
^{1}H NMR spectra of **1g** (500 MHz, $CDCl_3$)



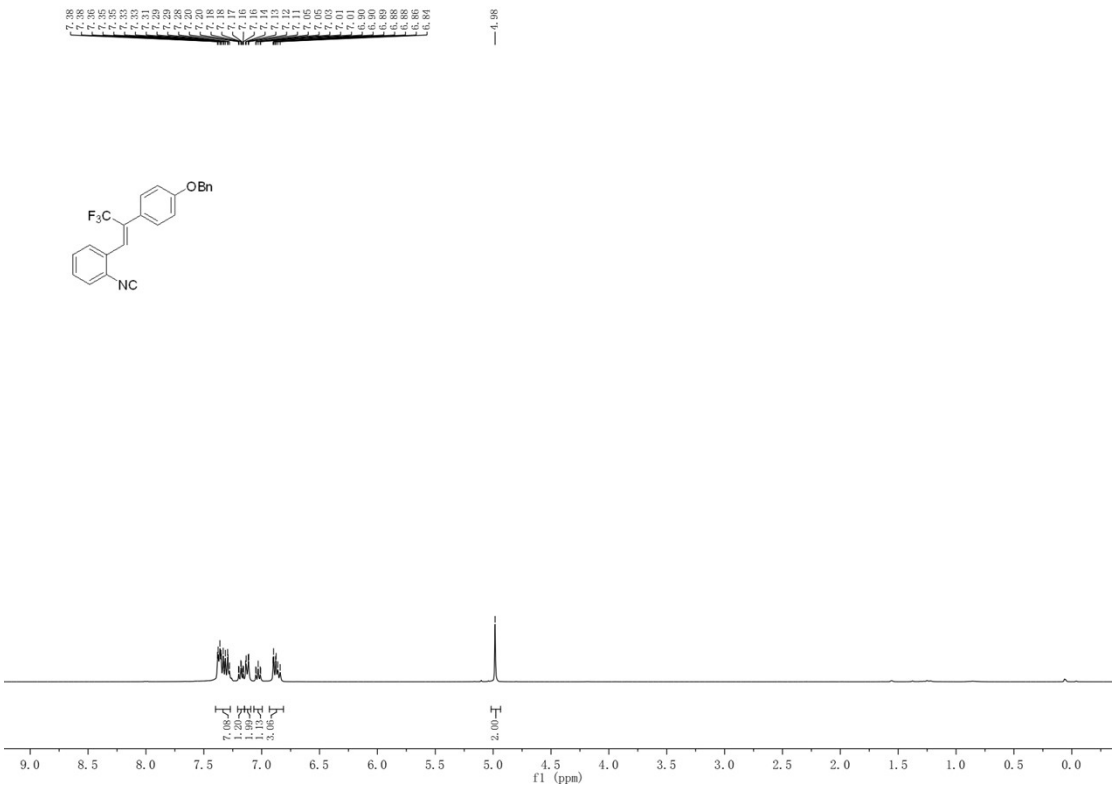
^{13}C NMR spectra of **1g** (125 MHz, $CDCl_3$)



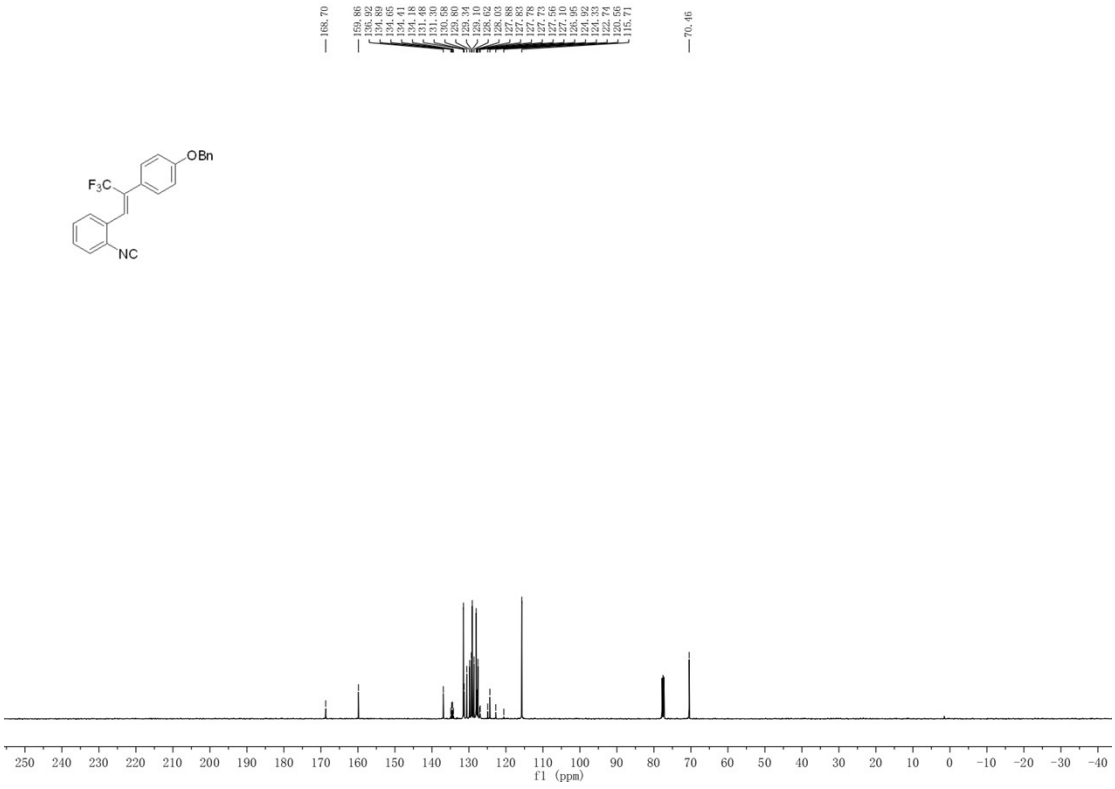
^{19}F NMR spectra of **1g** (376 MHz, $CDCl_3$)



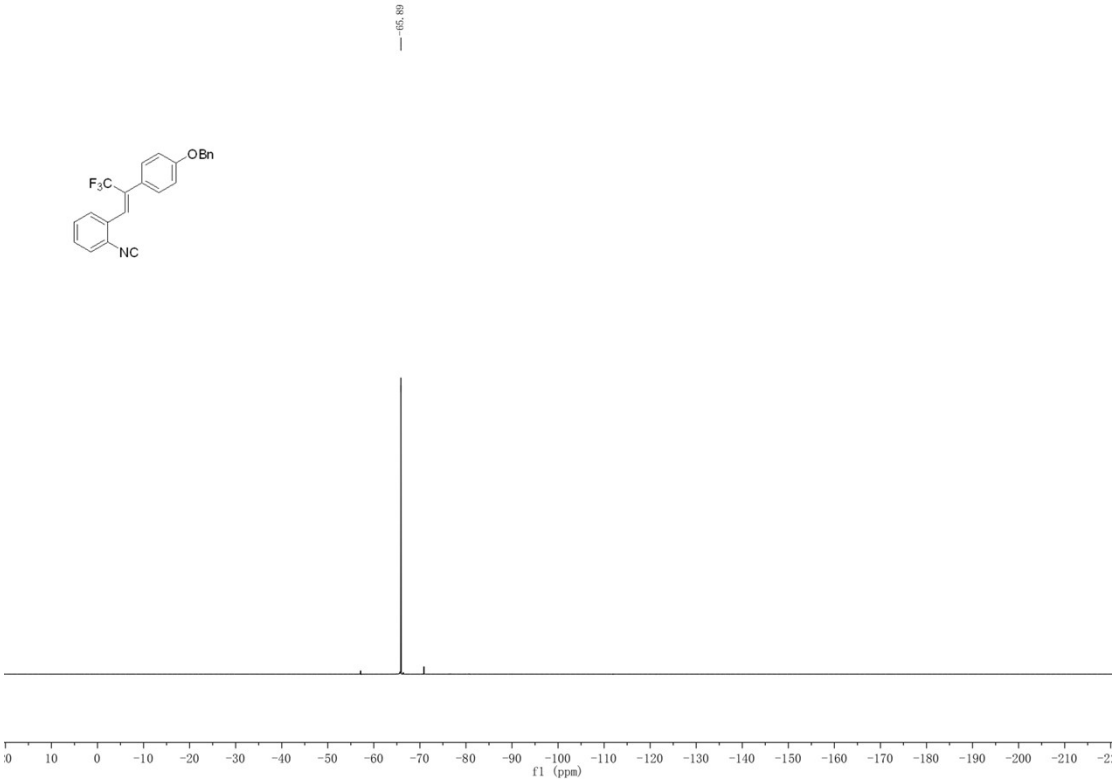
^{1}H NMR spectra of **1h** (400 MHz, $CDCl_3$)



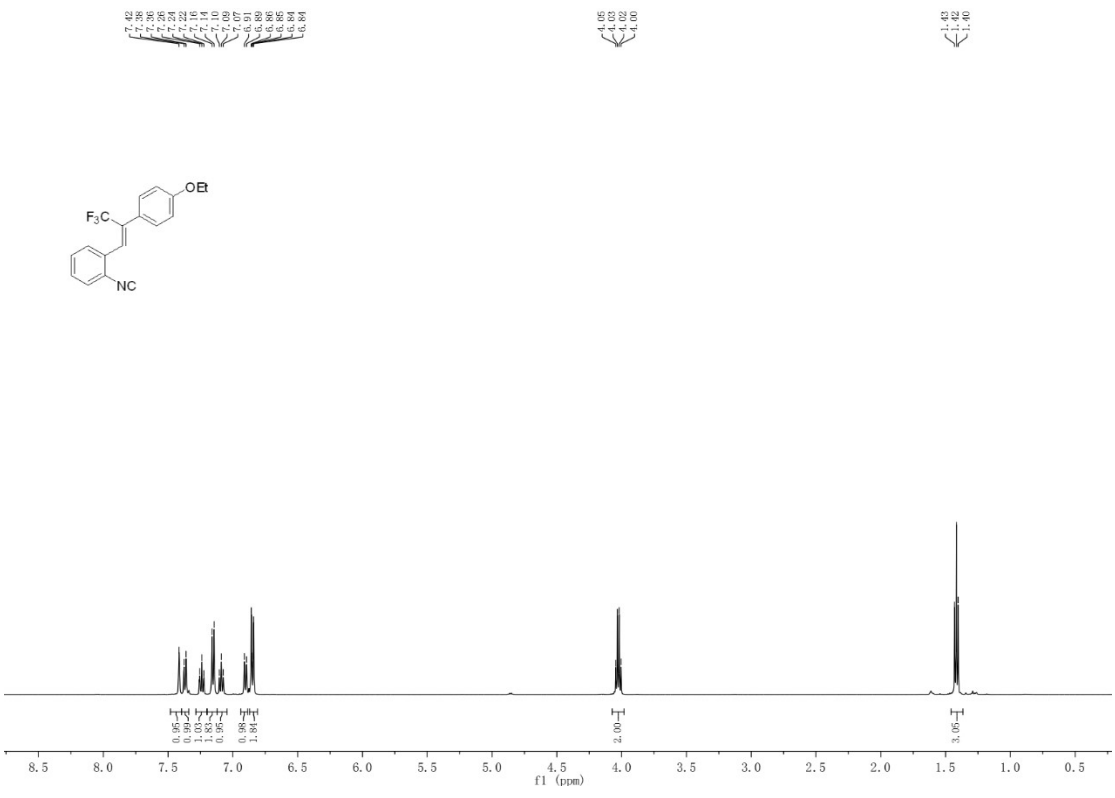
^{13}C NMR spectra of **1h** (125 MHz, $CDCl_3$)



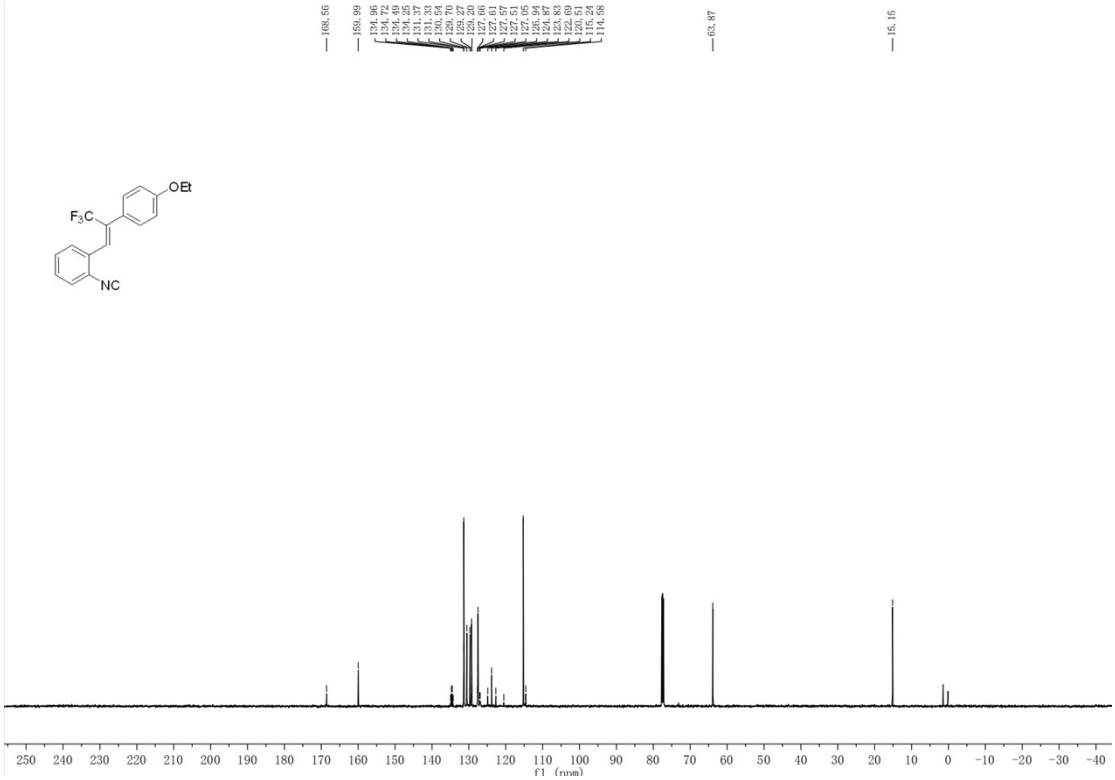
^{19}F NMR spectra of **1h** (376 MHz, $CDCl_3$)



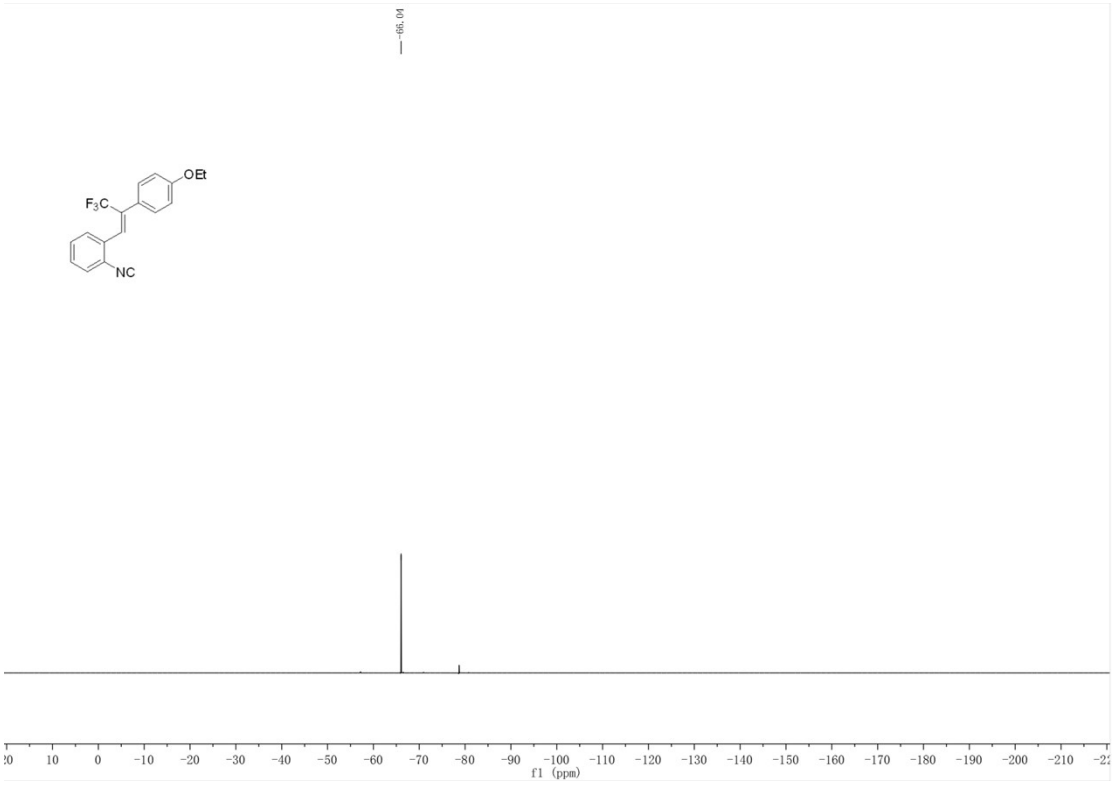
^{1}H NMR spectra of **1i**(500 MHz, $CDCl_3$)



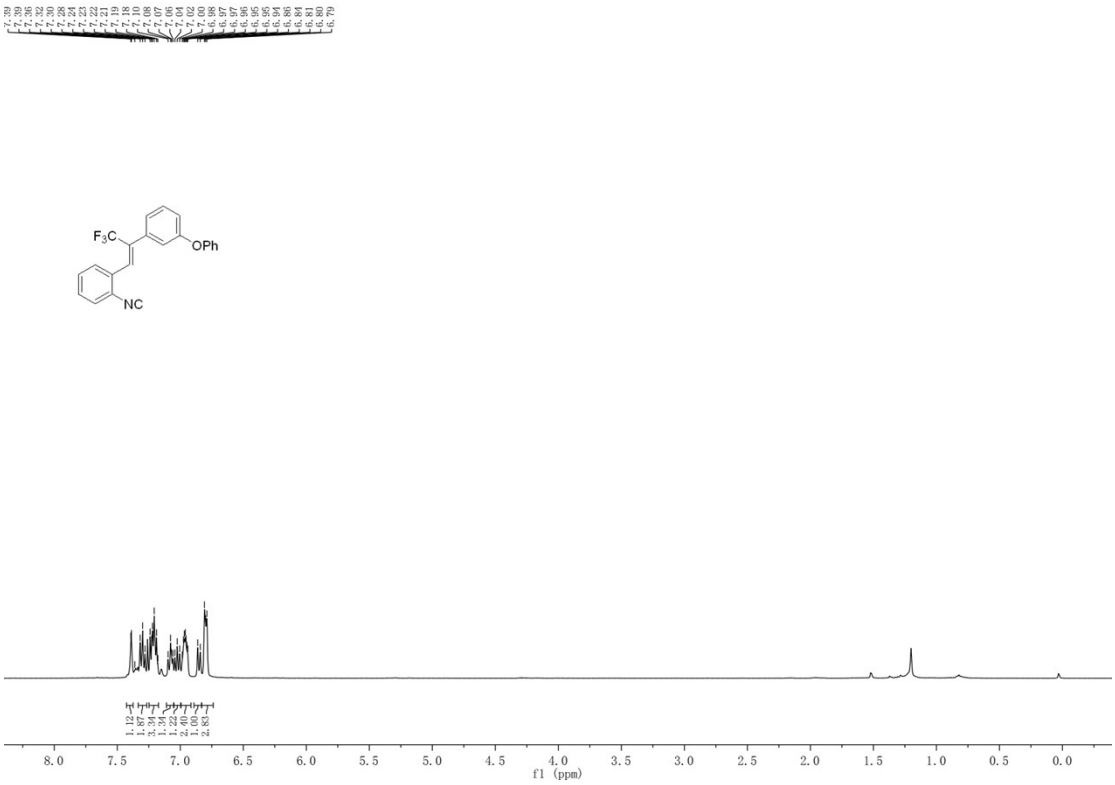
^{13}C NMR spectra of **1i** (125 MHz, $CDCl_3$)



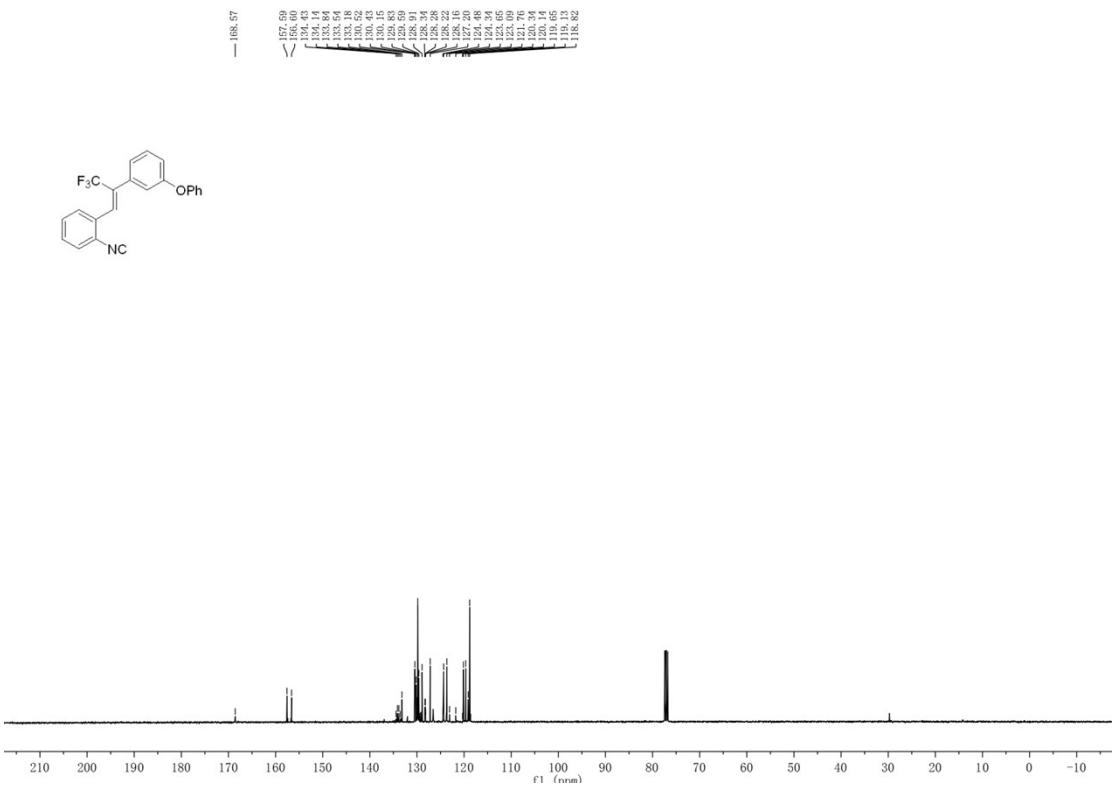
^{19}F NMR spectra of **1i** (376 MHz, $CDCl_3$)



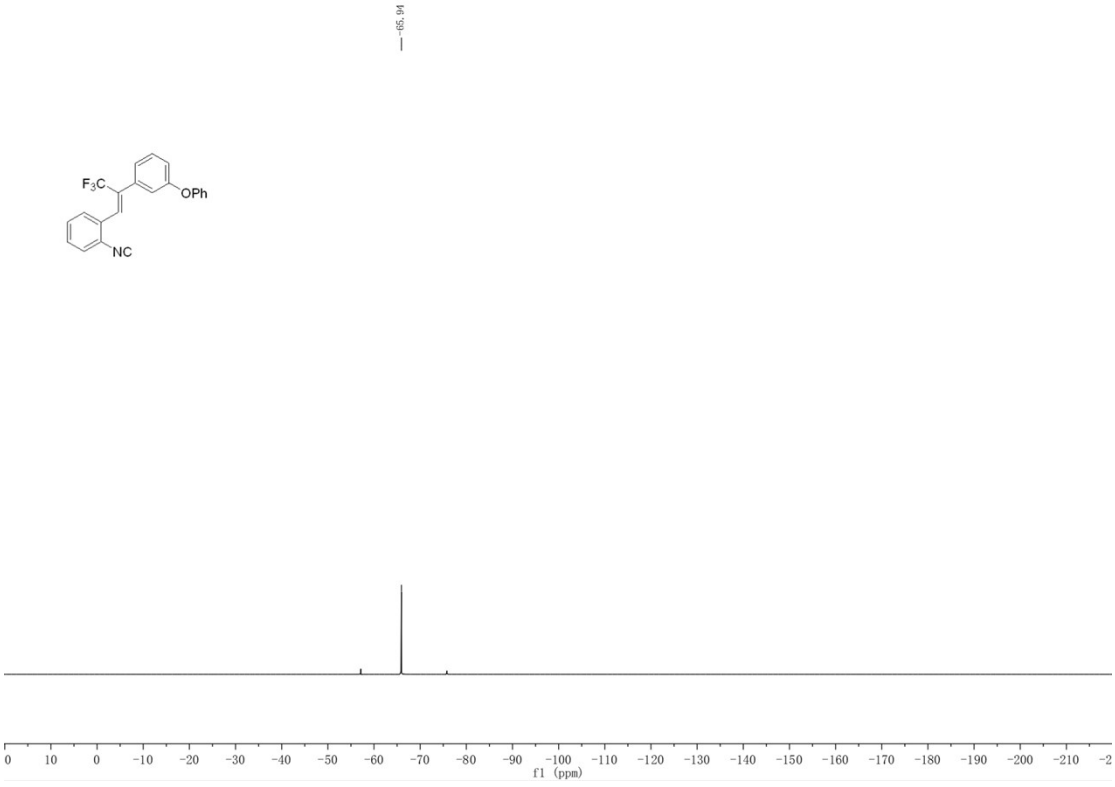
^{1}H NMR spectra of **1j** (400 MHz, $CDCl_3$)



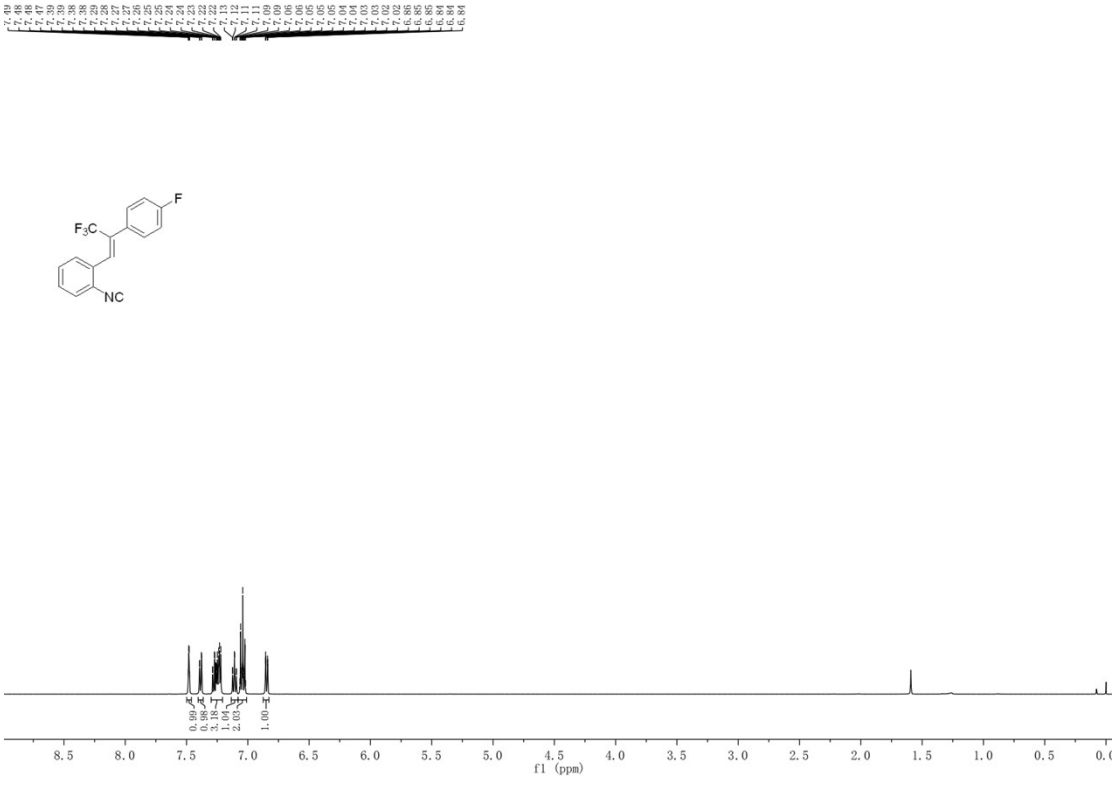
^{13}C NMR spectra of **1j** (100 MHz, $CDCl_3$)



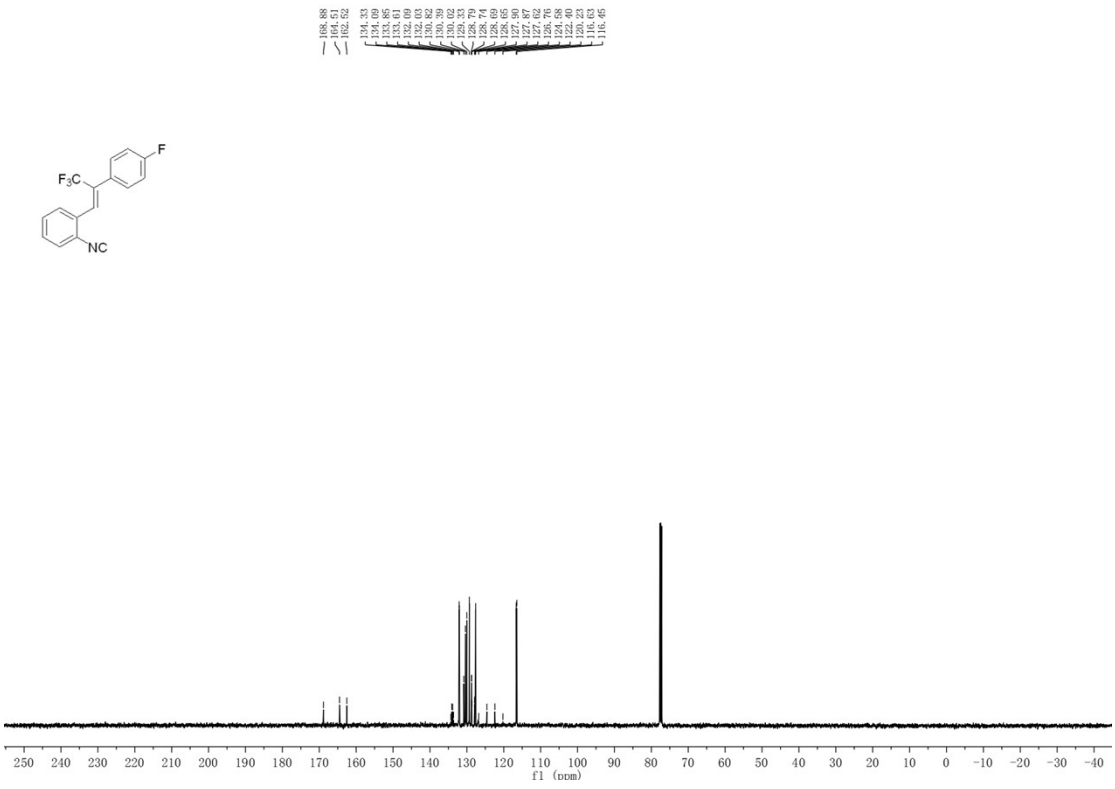
^{19}F NMR spectra of **1j** (376 MHz, $CDCl_3$)



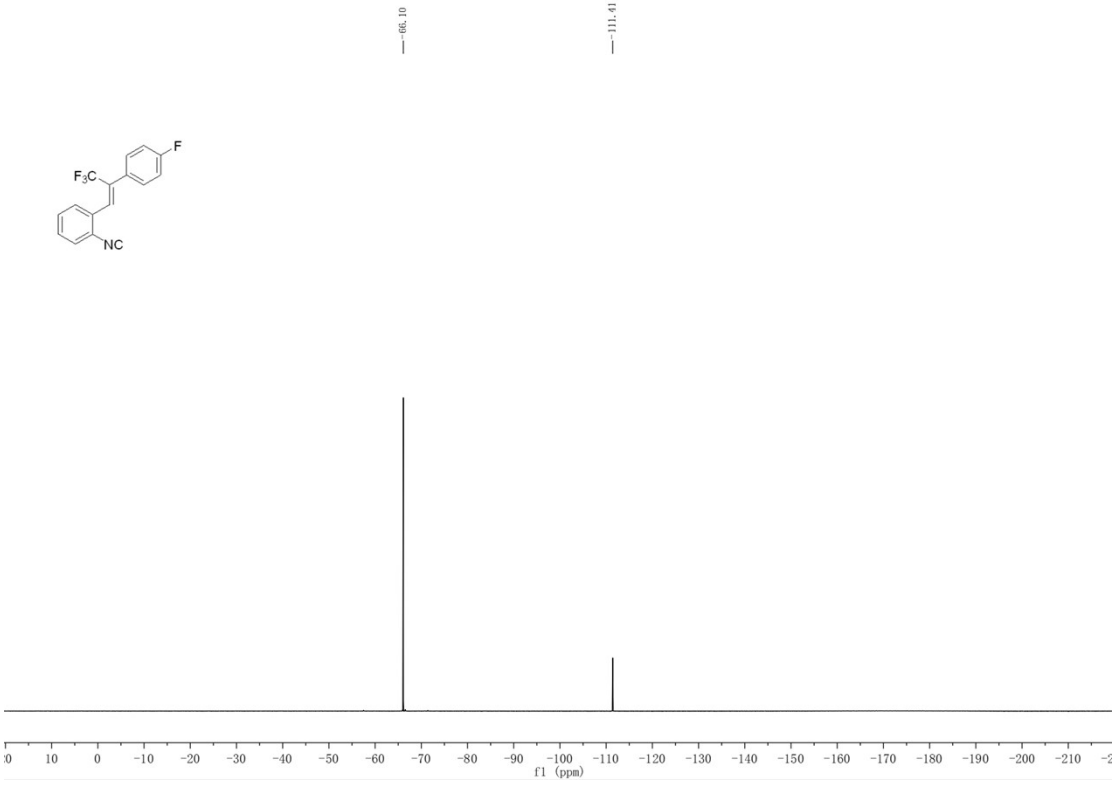
^{1}H NMR spectra of **1k** (500 MHz, $CDCl_3$)



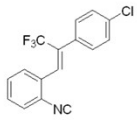
^{13}C NMR spectra of **1k** (125 MHz, $CDCl_3$)

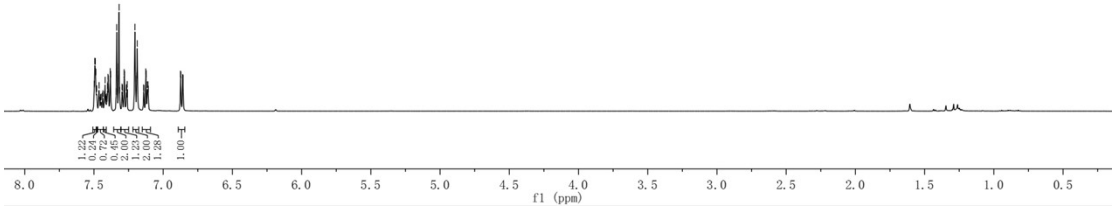


^{19}F NMR spectra of **1k** (470 MHz, $CDCl_3$)

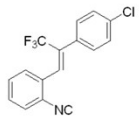


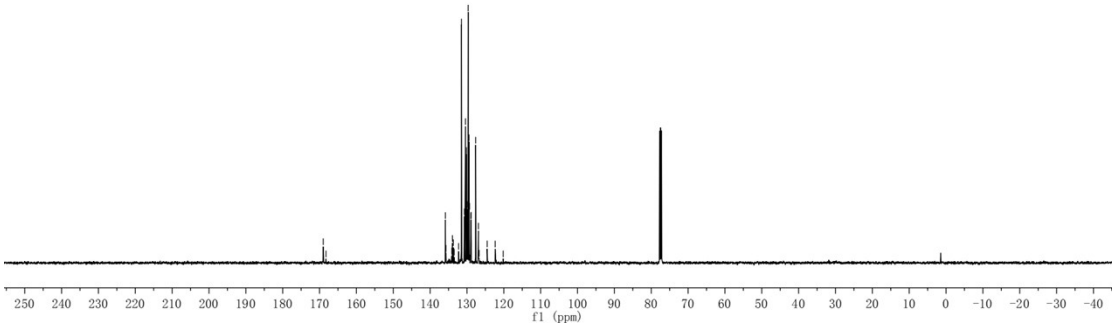
^{1}H NMR spectra of **1l** (500 MHz, $CDCl_3$)



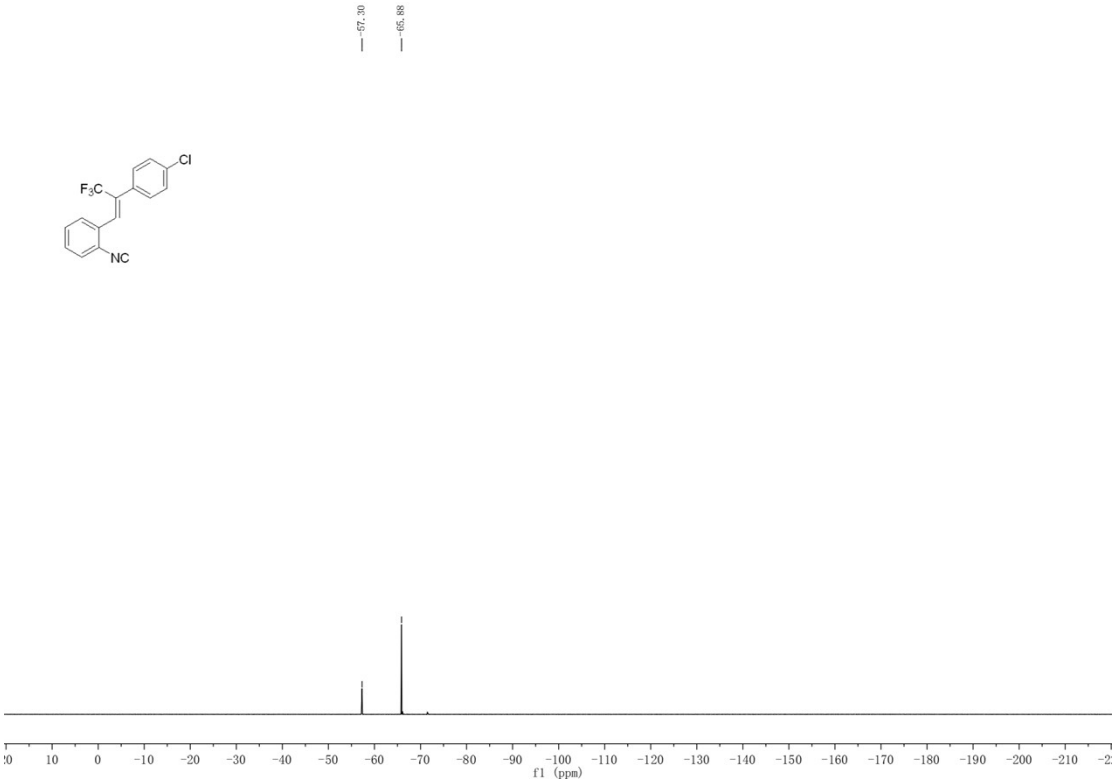


^{13}C NMR spectra of **1l** (125 MHz, $CDCl_3$)

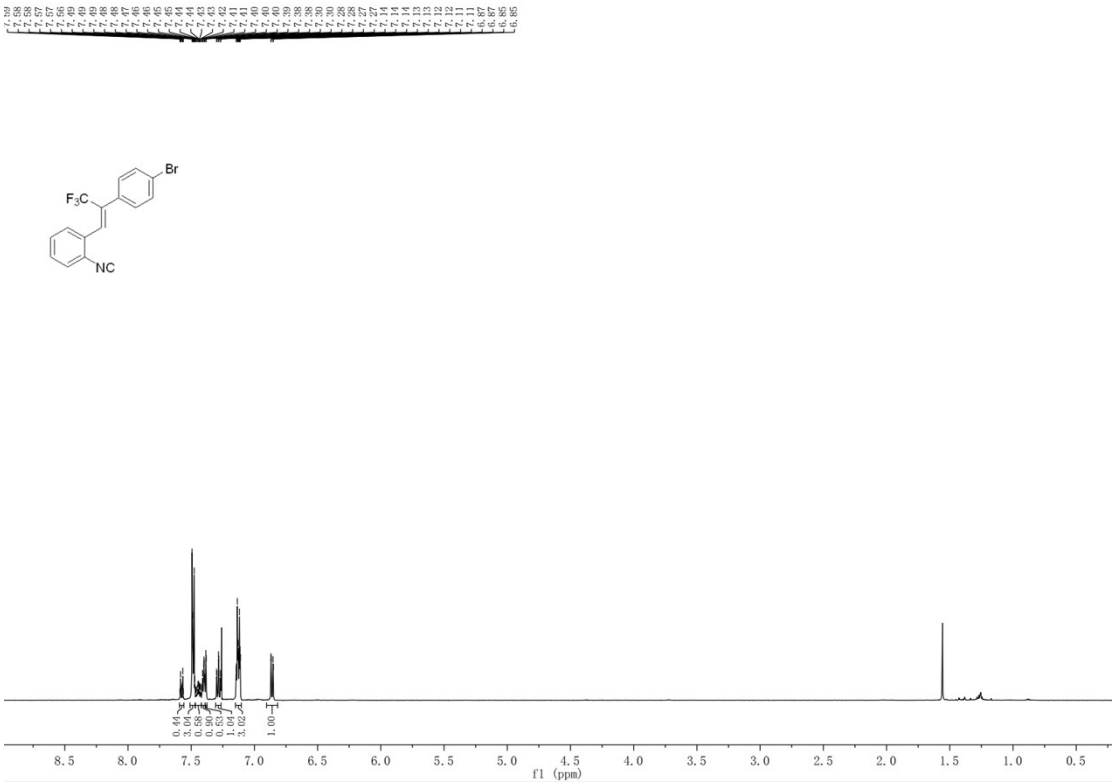




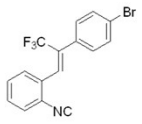
^{19}F NMR spectra of **1l** (470 MHz, $CDCl_3$)

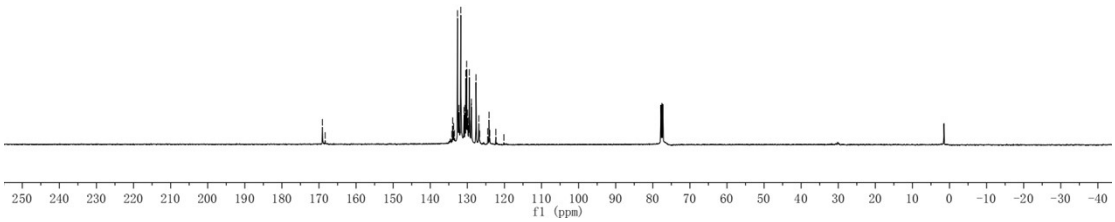


^{1}H NMR spectra of **1m** (500 MHz, $CDCl_3$)

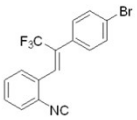


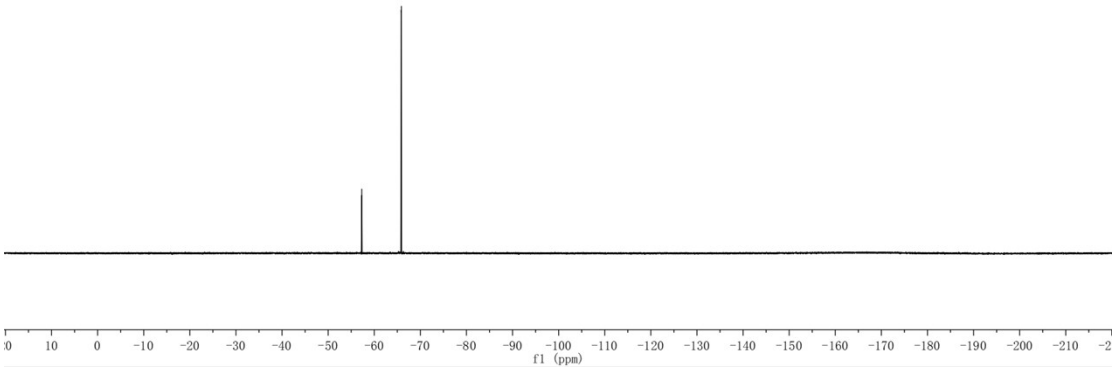
^{13}C NMR spectra of **1m** (125 MHz, $CDCl_3$)



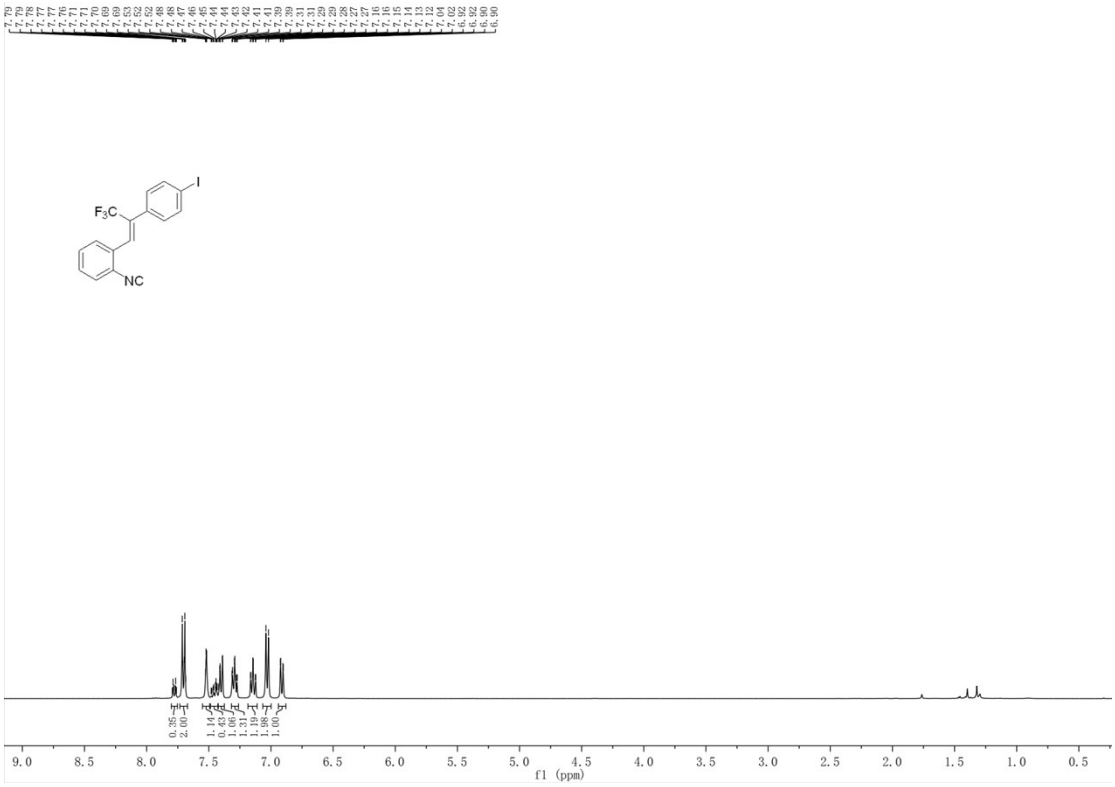


^{19}F NMR spectra of **1m** (470 MHz, $CDCl_3$)

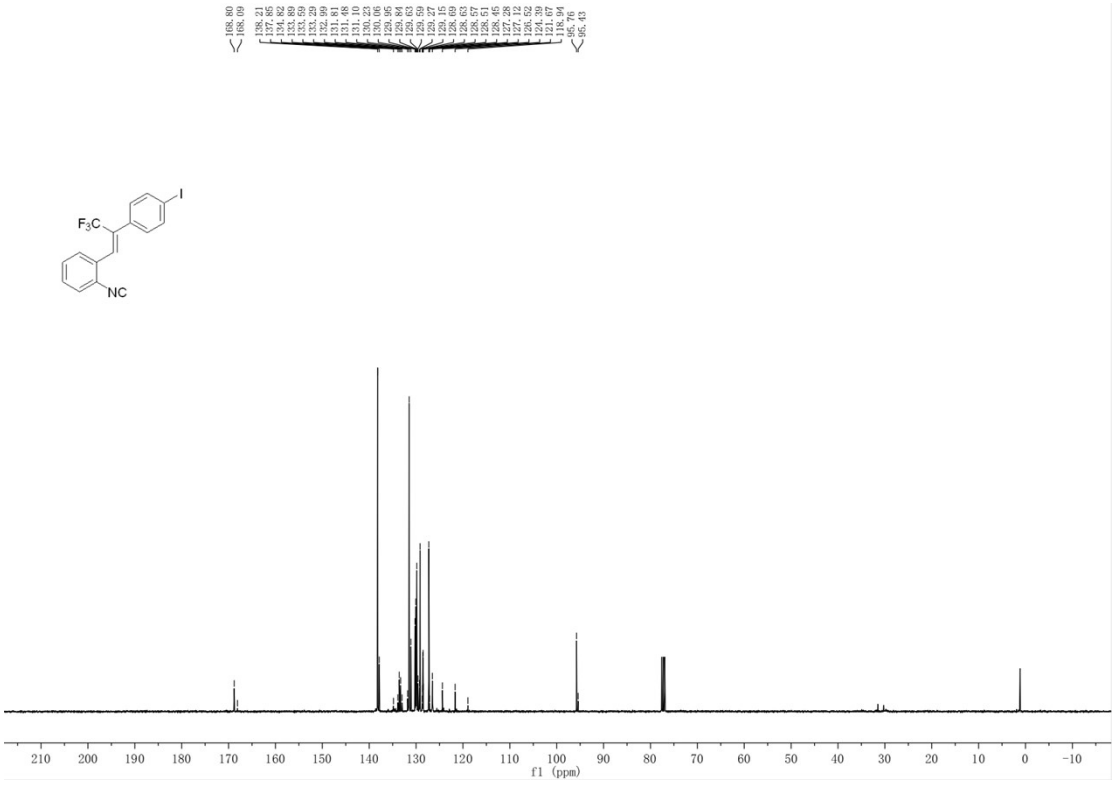




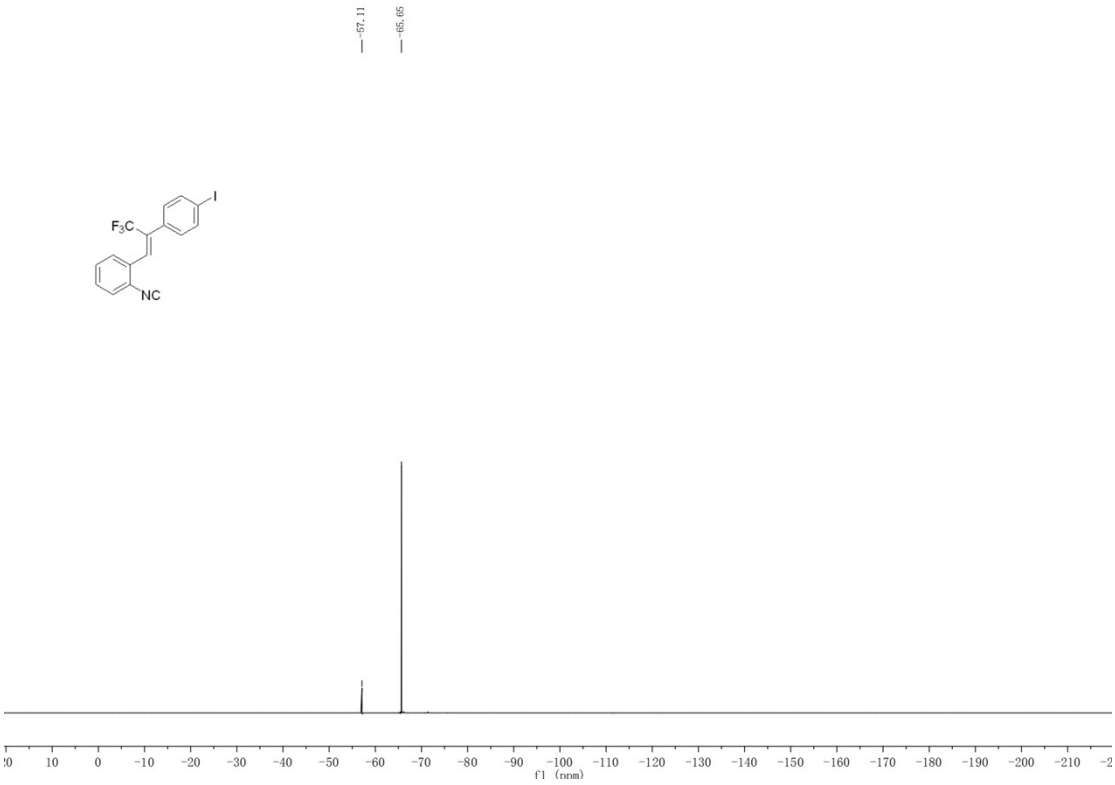
^{1}H NMR spectra of **1n** (400 MHz, $CDCl_3$)



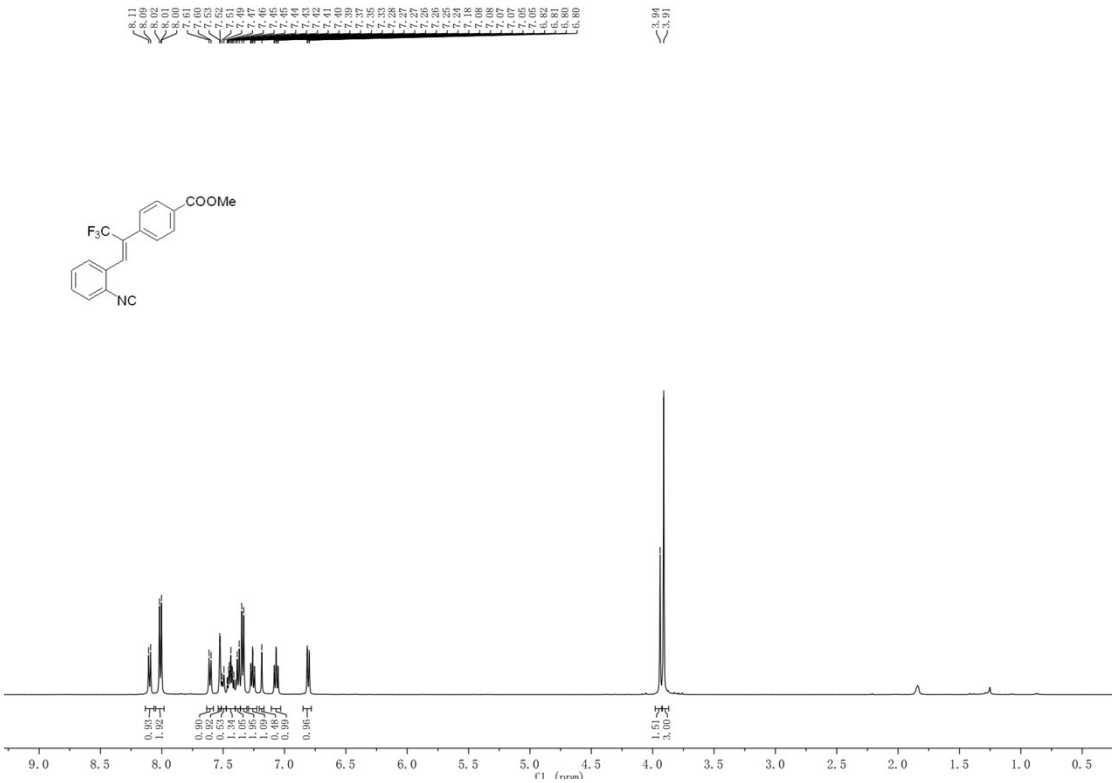
^{13}C NMR spectra of **1n** (100 MHz, $CDCl_3$)



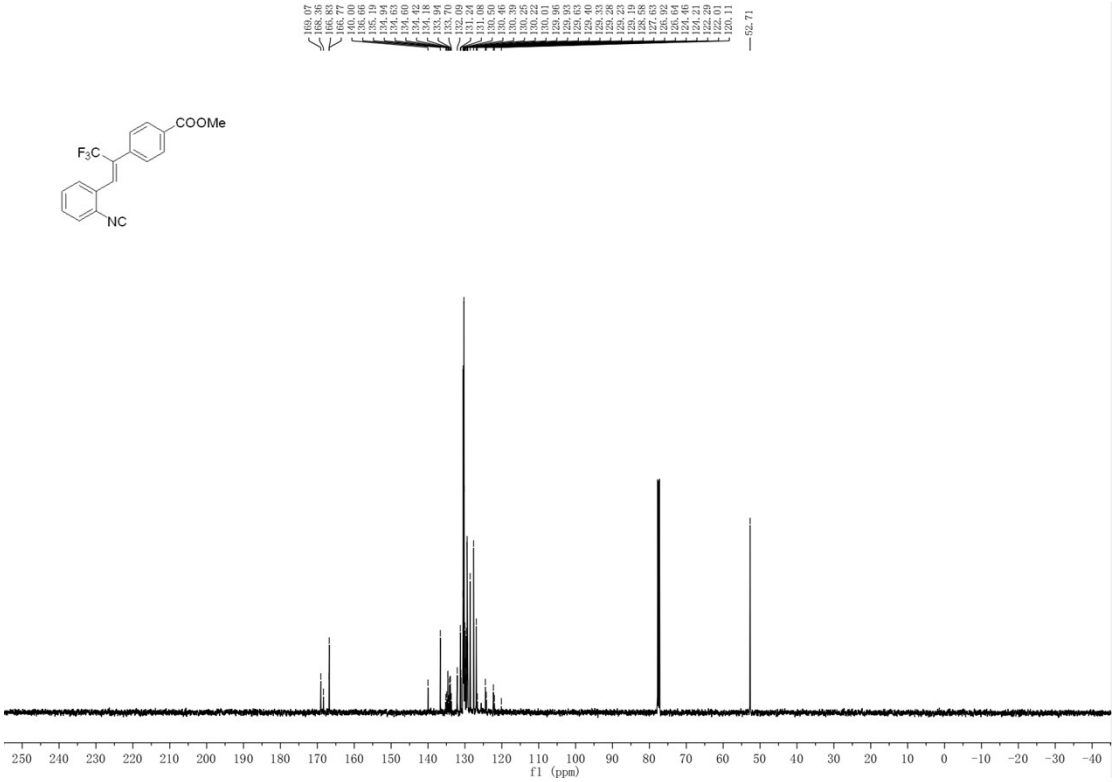
^{19}F NMR spectra of **1n** (376 MHz, $CDCl_3$)



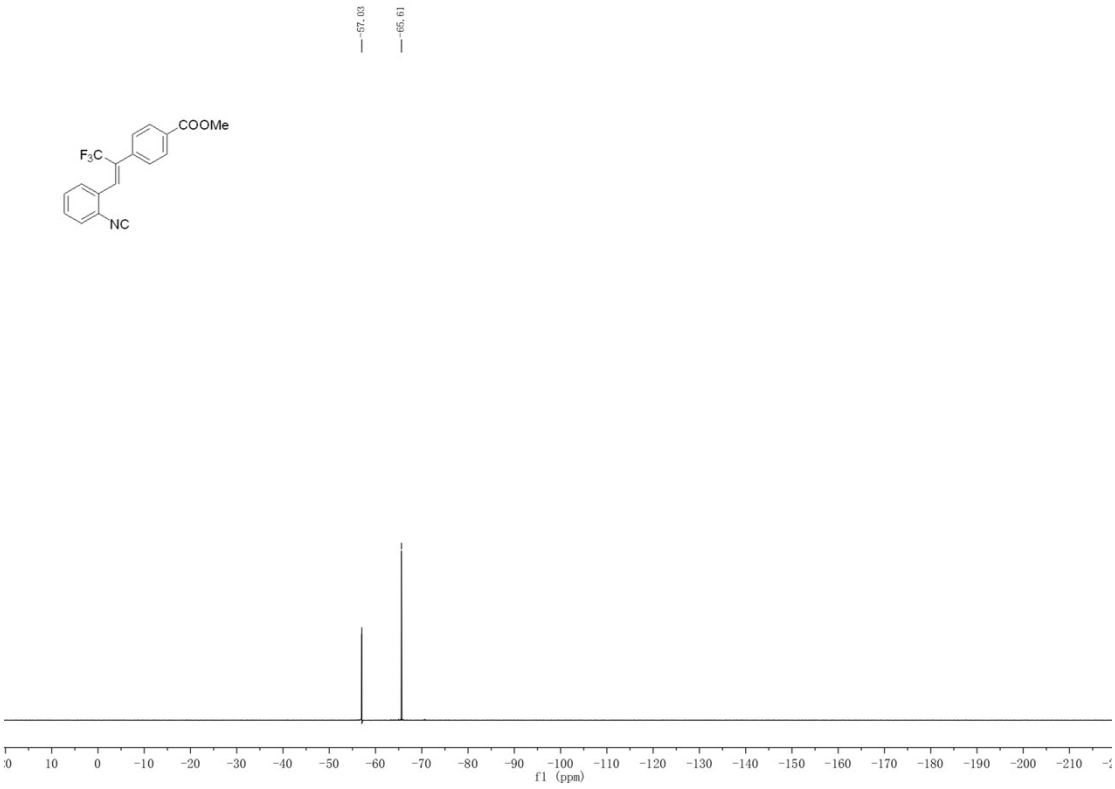
^{1}H NMR spectra of **1o** (500 MHz, $CDCl_3$)



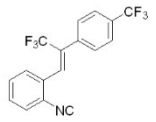
^{13}C NMR spectra of **1o** (125 MHz, $CDCl_3$)

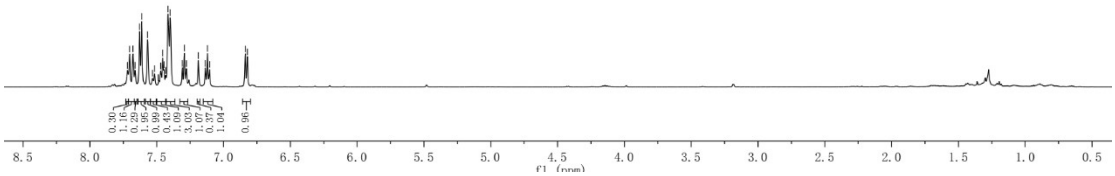


^{19}F NMR spectra of **1o** (470 MHz, $CDCl_3$)

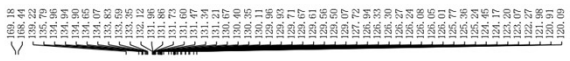


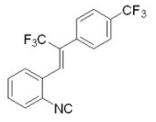
^{1}H NMR spectra of **1p** (500 MHz, $CDCl_3$)

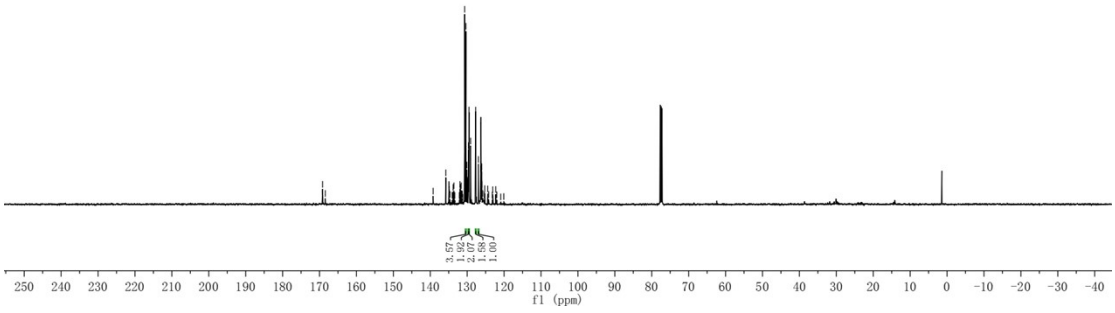




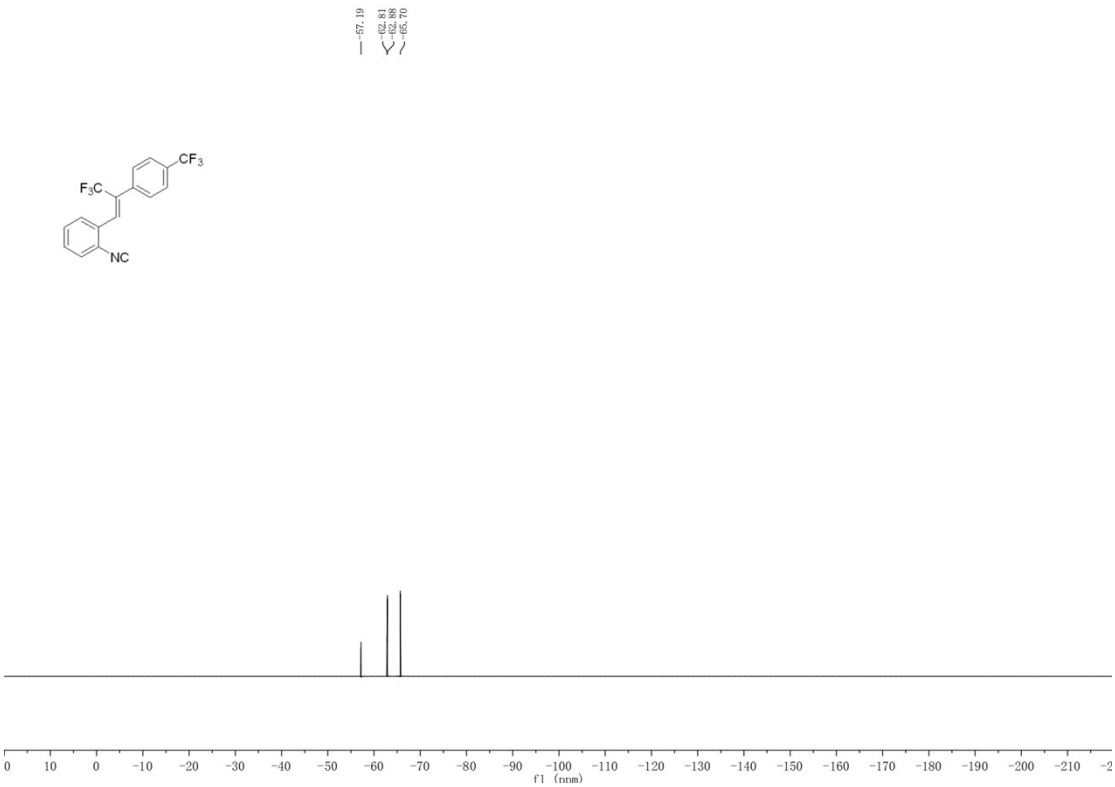
^{13}C NMR spectra of **1p** (125 MHz, $CDCl_3$)



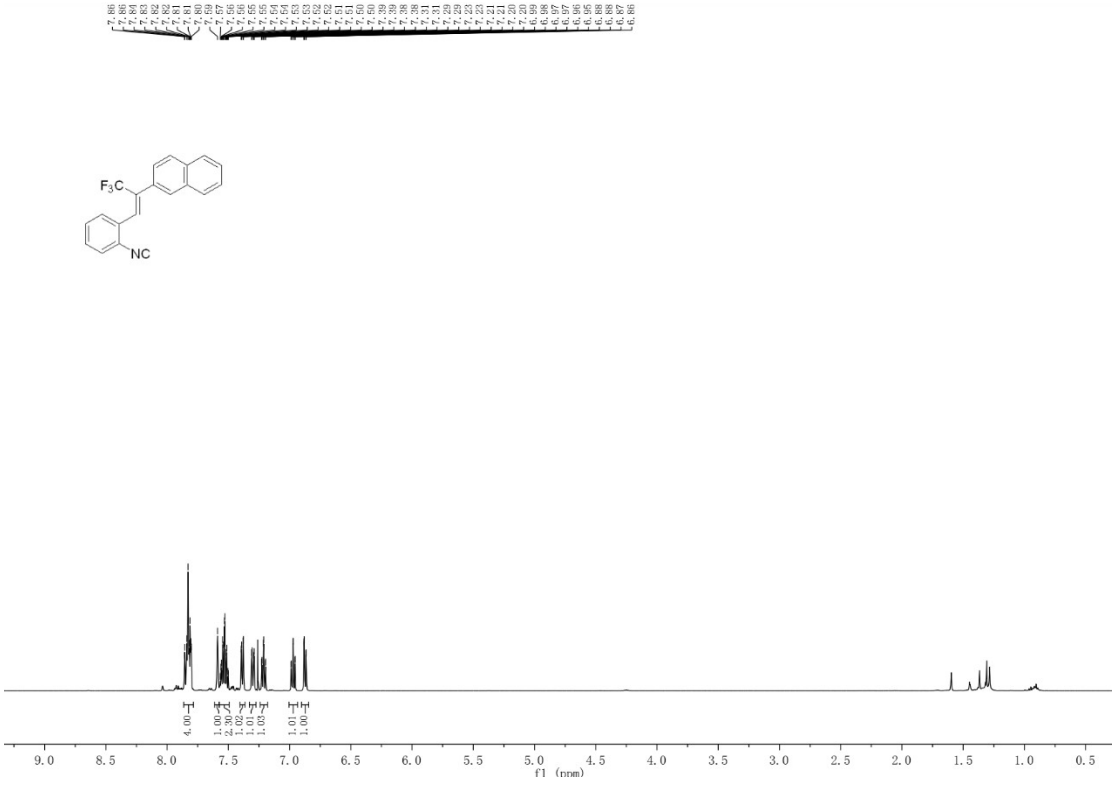




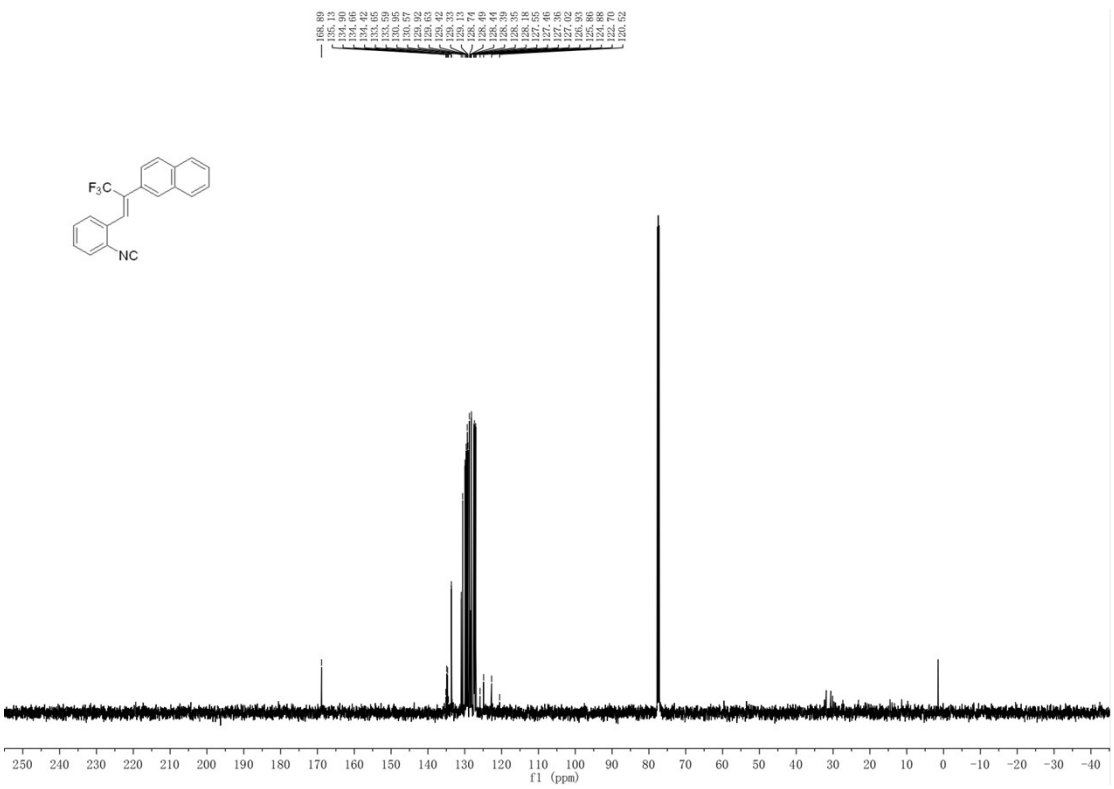
^{19}F NMR spectra of **1p** (376 MHz, $CDCl_3$)



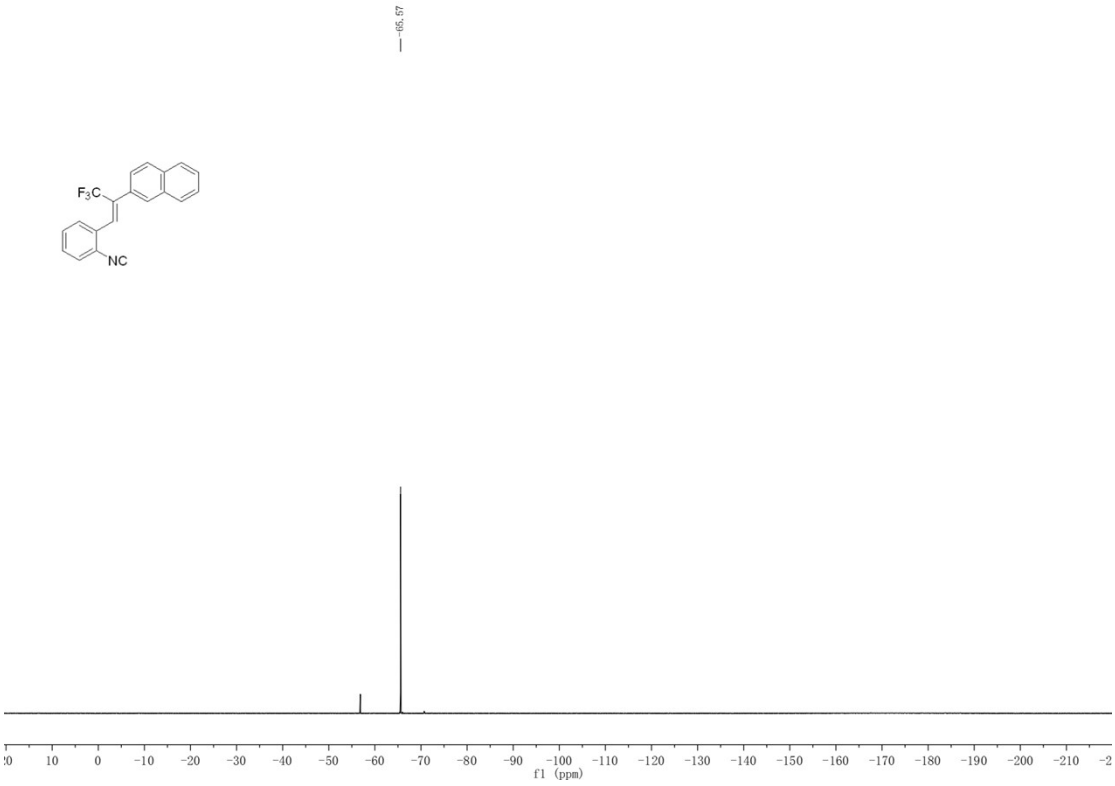
^{1}H NMR spectra of **1q** (500 MHz, $CDCl_3$)



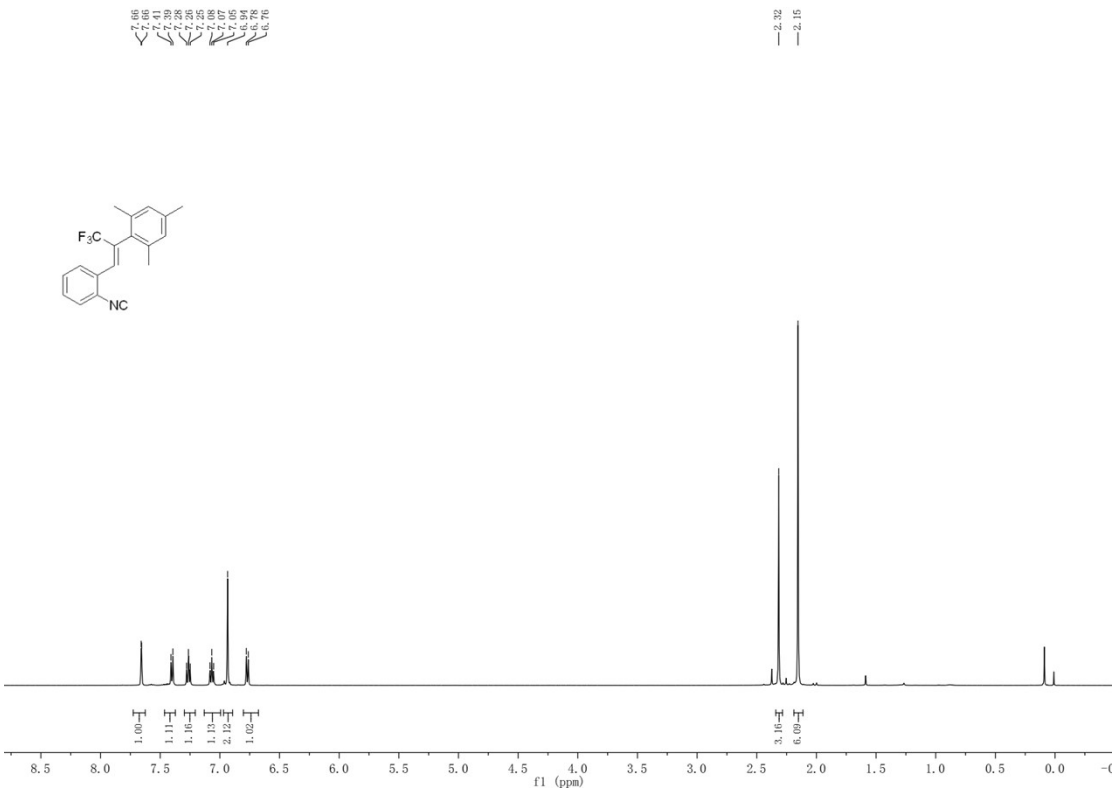
^{13}C NMR spectra of **1q** (125 MHz, $CDCl_3$)



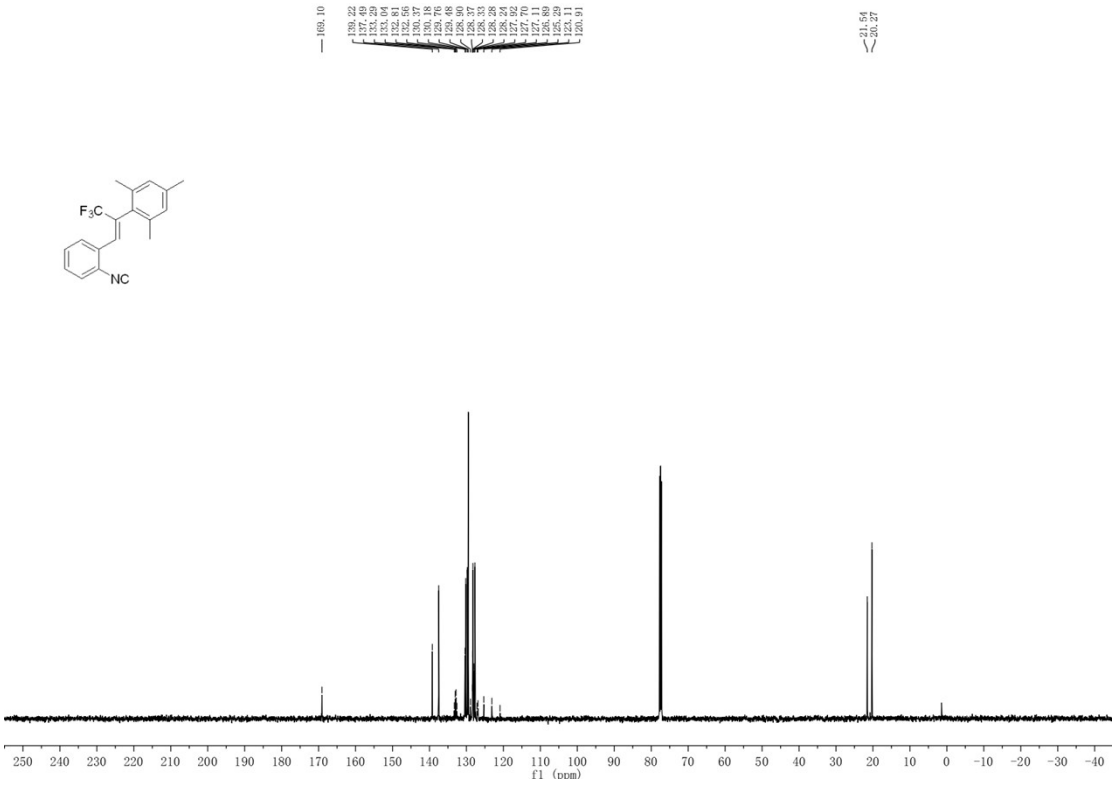
^{19}F NMR spectra of **1q** (470 MHz, $CDCl_3$)



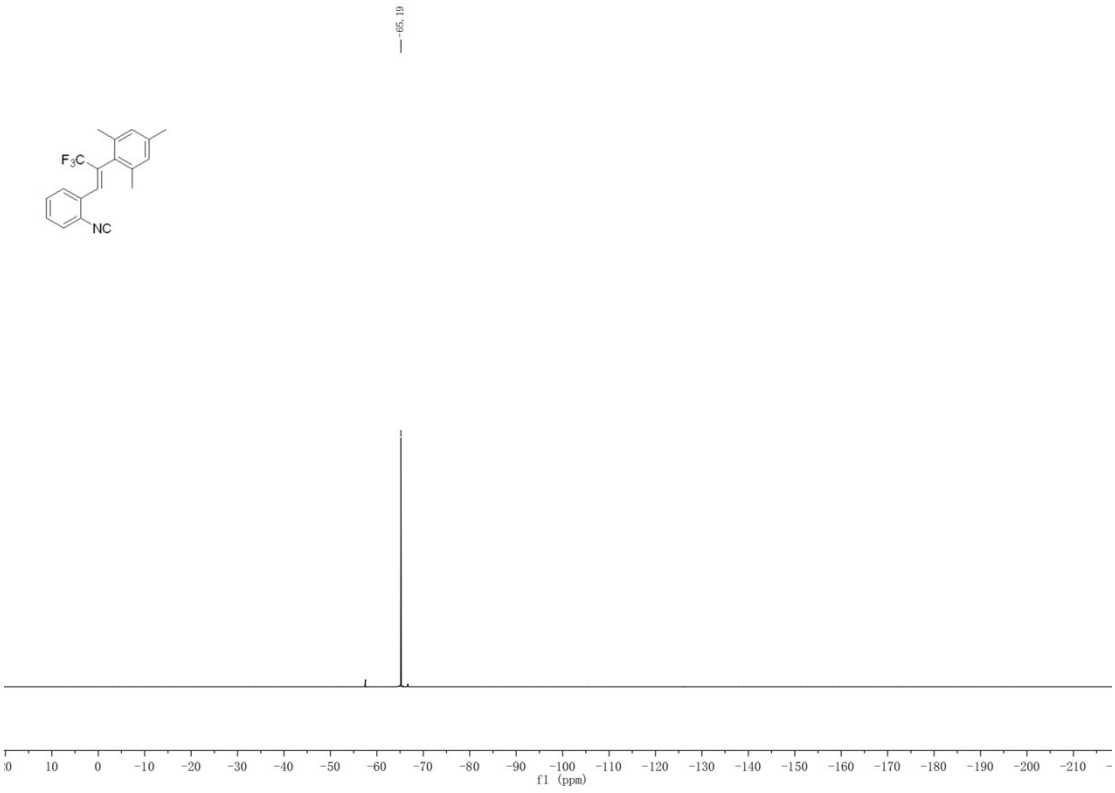
^{1}H NMR spectra of **1r** (500 MHz, $CDCl_3$)



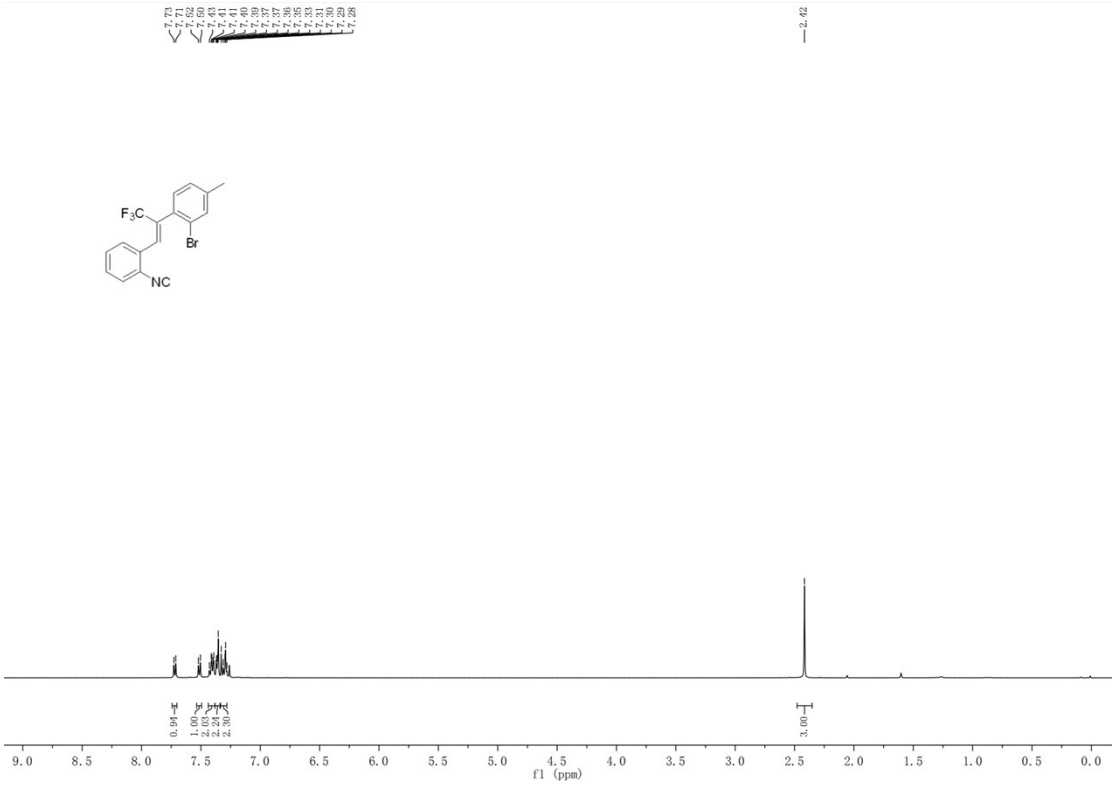
^{13}C NMR spectra of **1r** (125 MHz, $CDCl_3$)



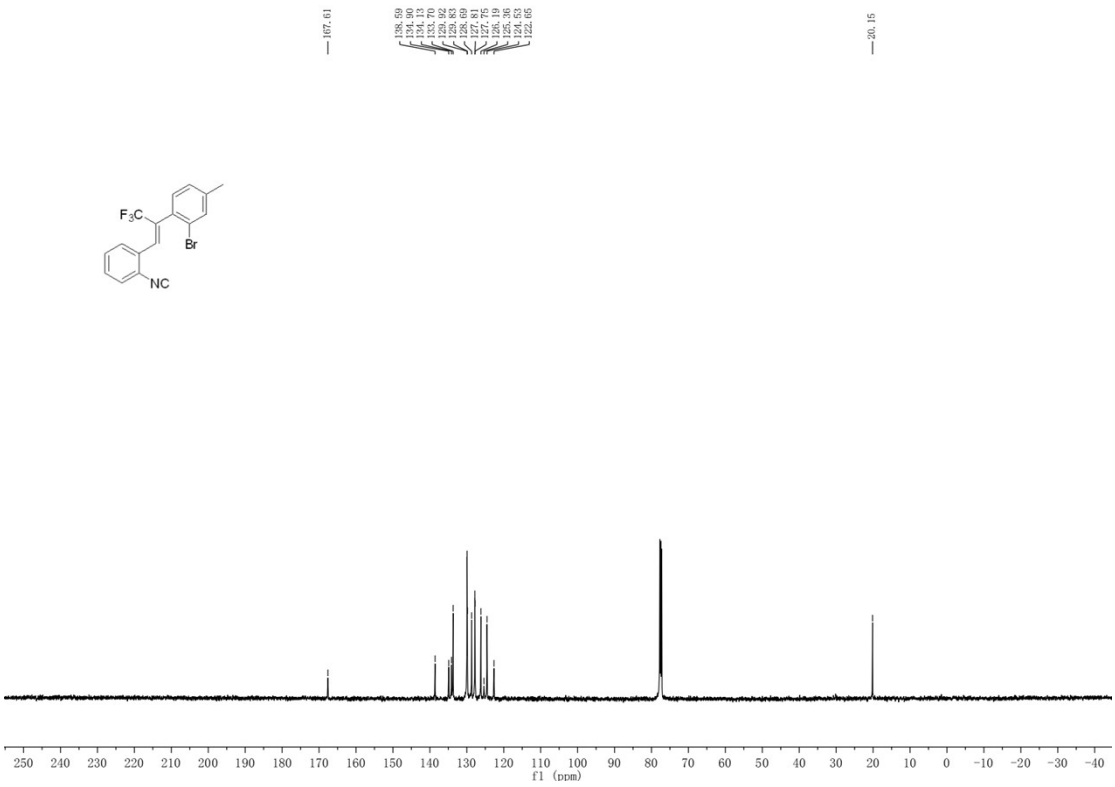
^{19}F NMR spectra of **1r** (376 MHz, $CDCl_3$)



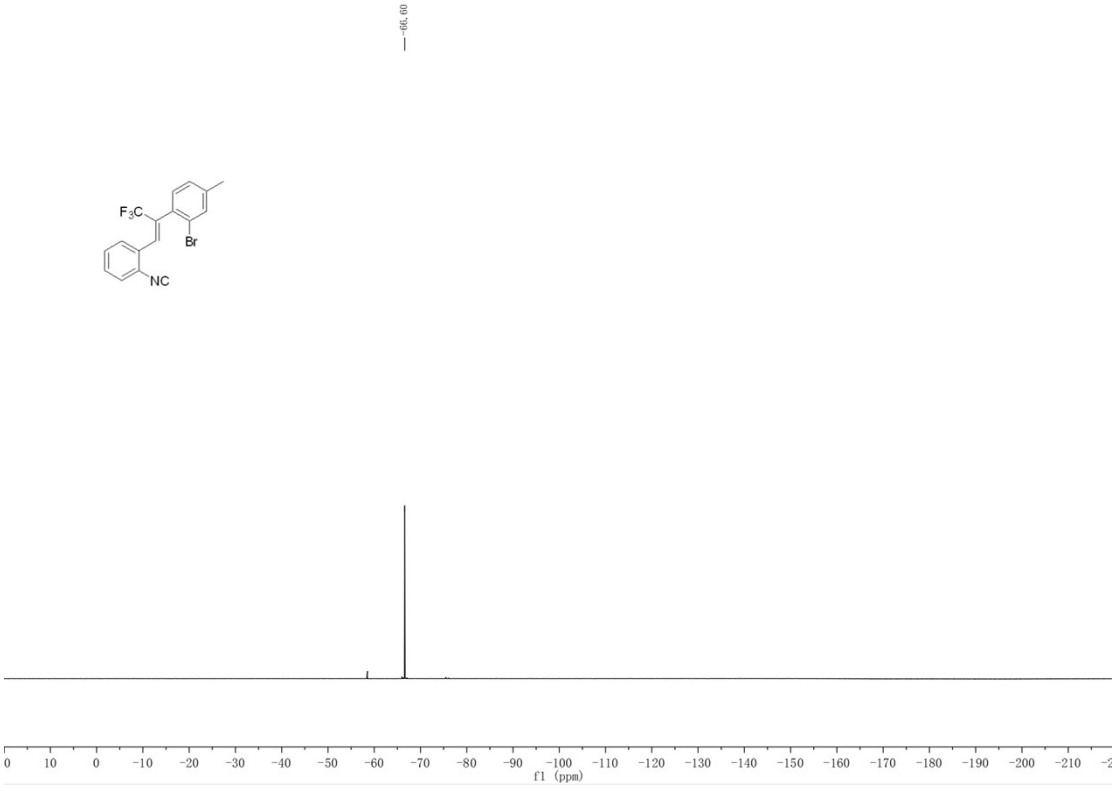
^{1}H NMR spectra of **1s** (500 MHz, $CDCl_3$)



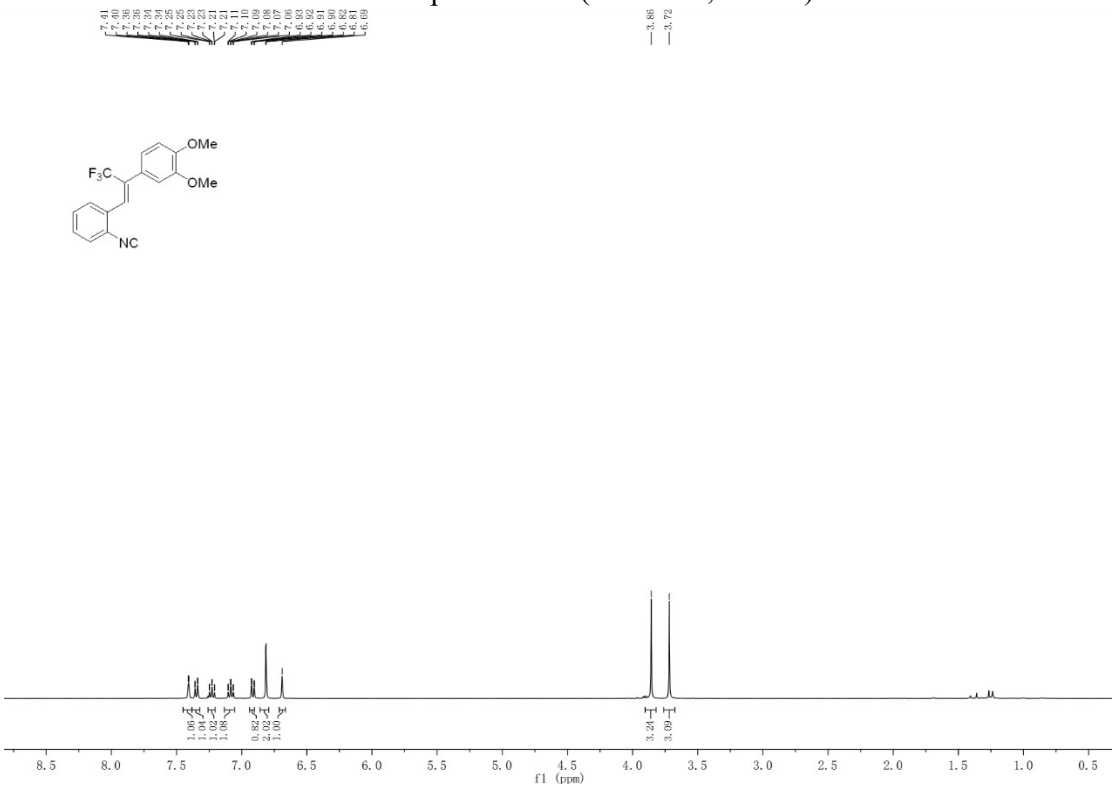
^{13}C NMR spectra of **1s** (125 MHz, $CDCl_3$)



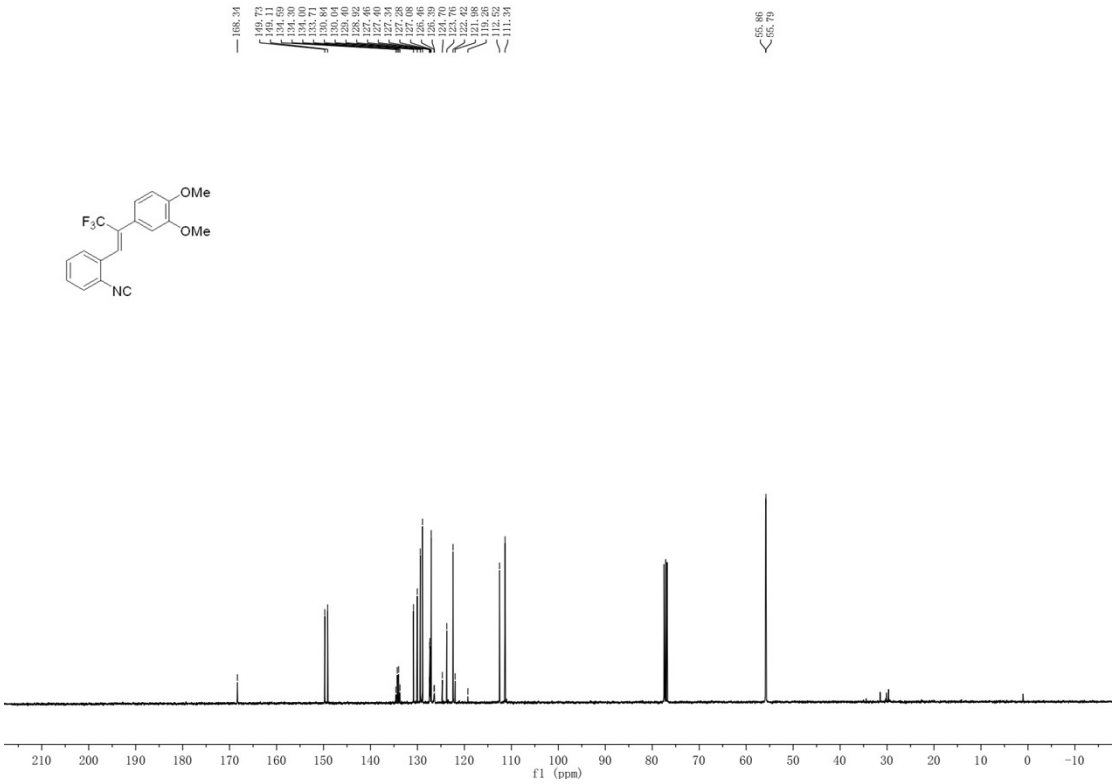
^{19}F NMR spectra of **1s** (376 MHz, $CDCl_3$)



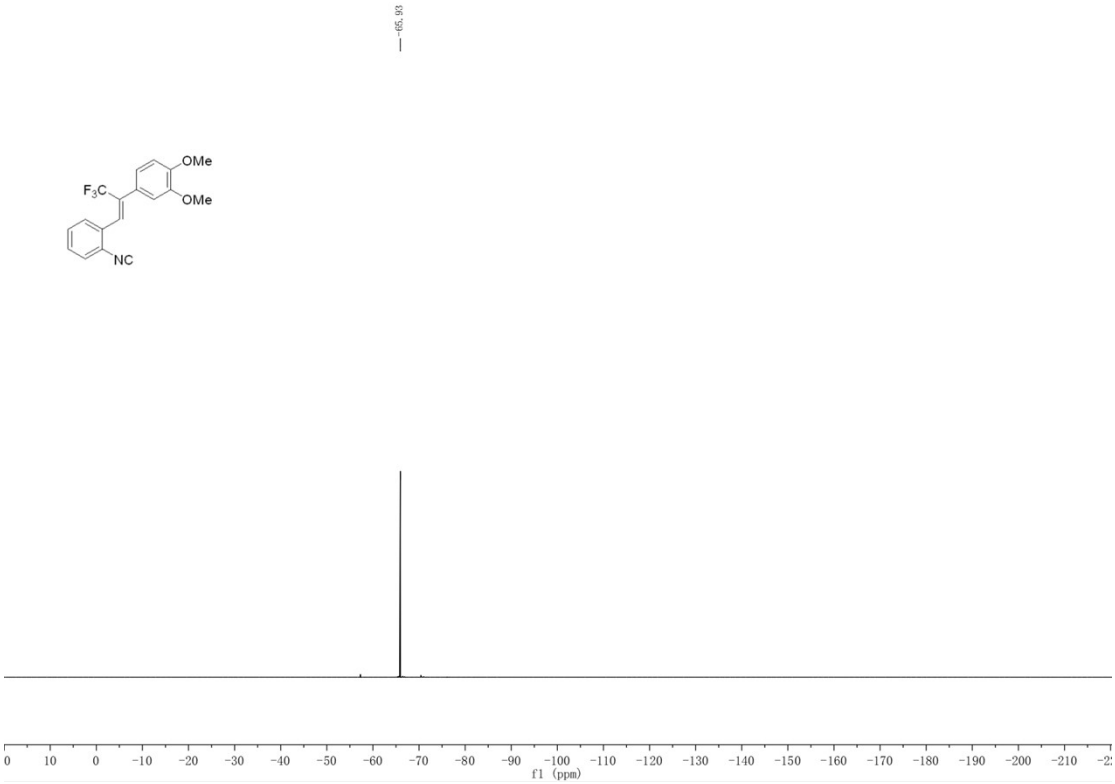
^{1}H NMR spectra of **1t** (400 MHz, $CDCl_3$)



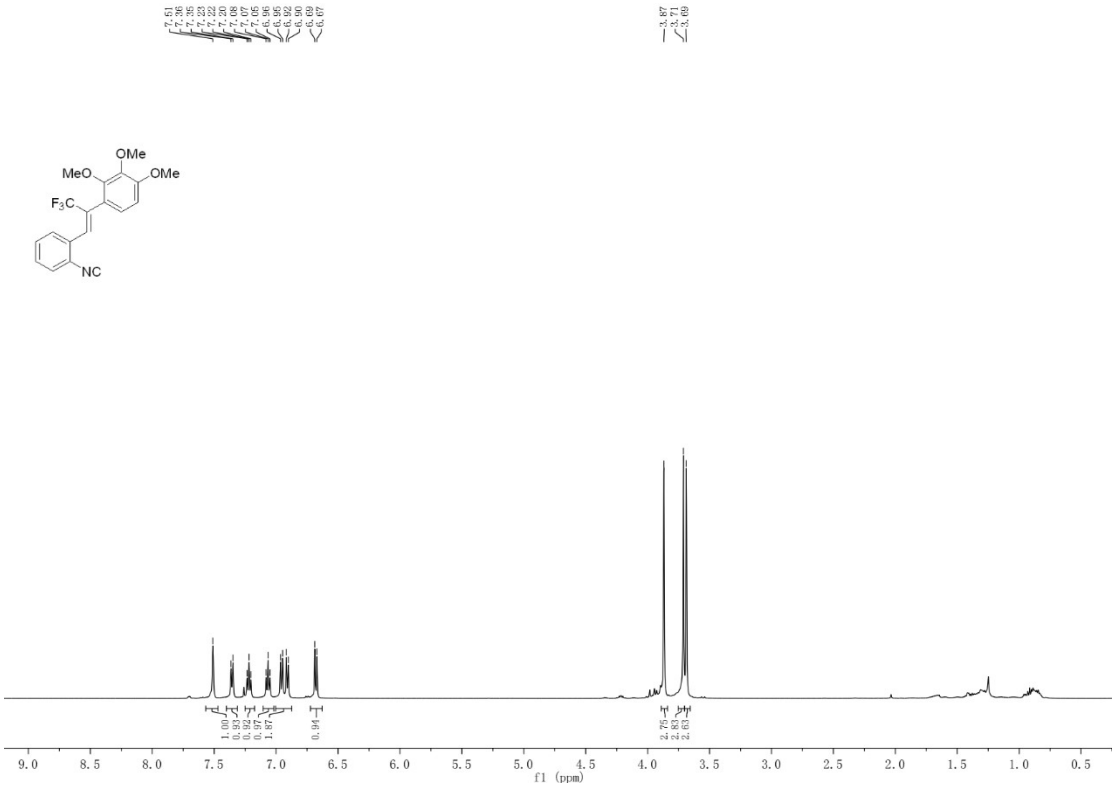
^{13}C NMR spectra of **1t** (100 MHz, $CDCl_3$)



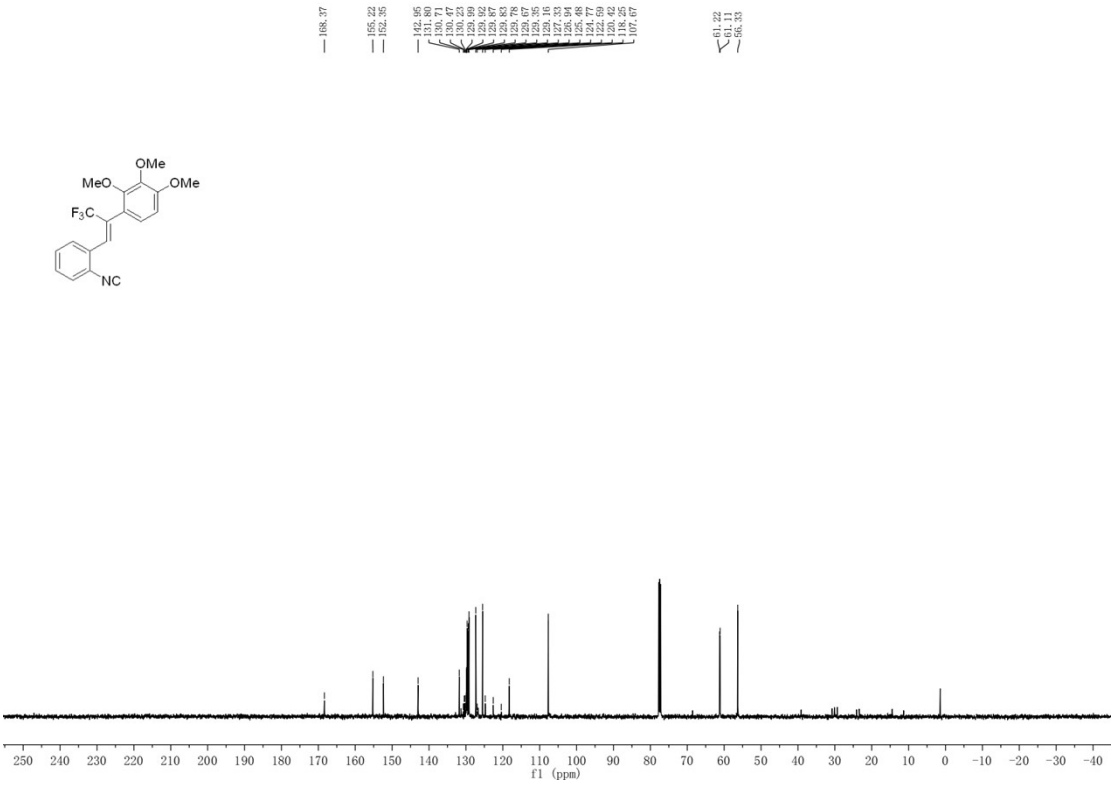
^{19}F NMR spectra of **1t** (376 MHz, $CDCl_3$)



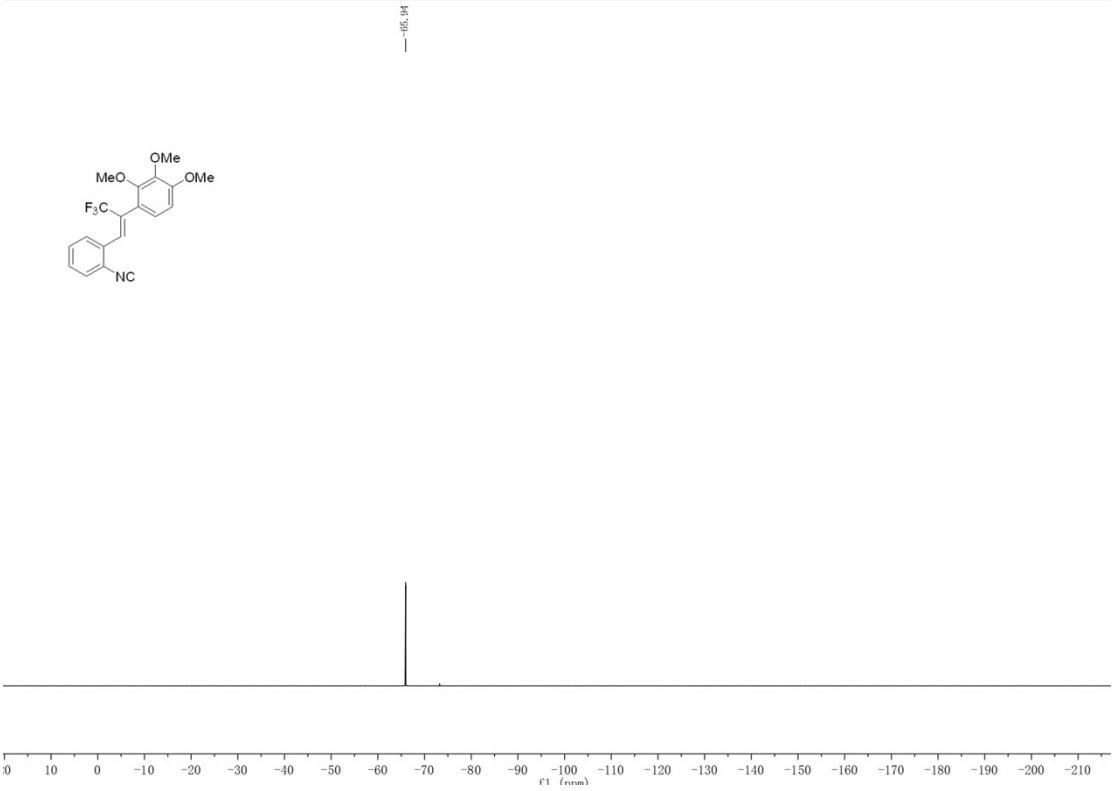
^{1}H NMR spectra of **1u** (500 MHz, $CDCl_3$)



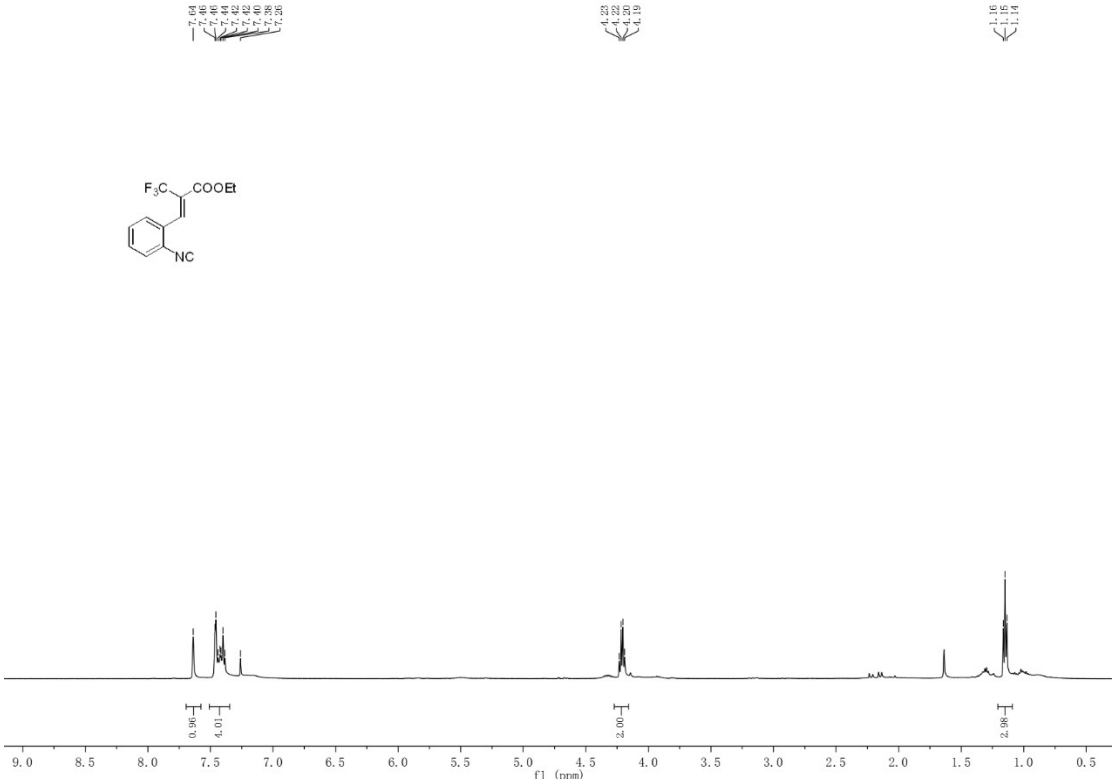
^{13}C NMR spectra of **1u** (125 MHz, $CDCl_3$)



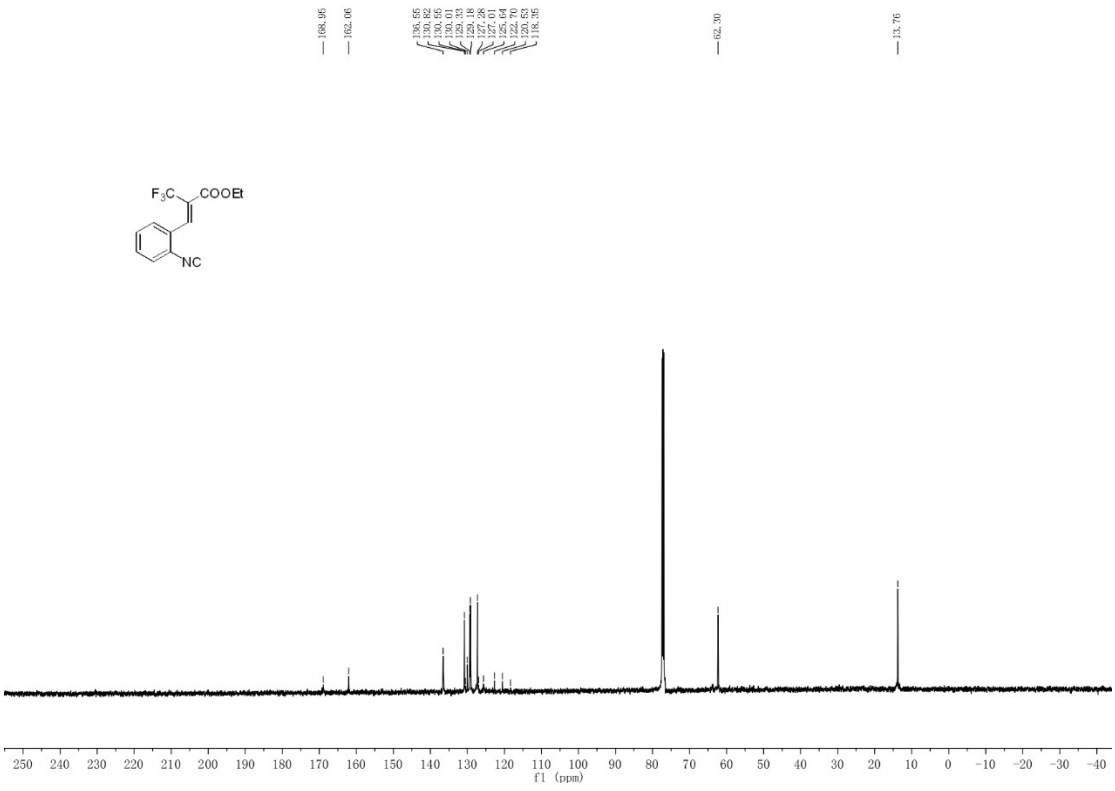
^{19}F NMR spectra of **1u** (376MHz, $CDCl_3$)



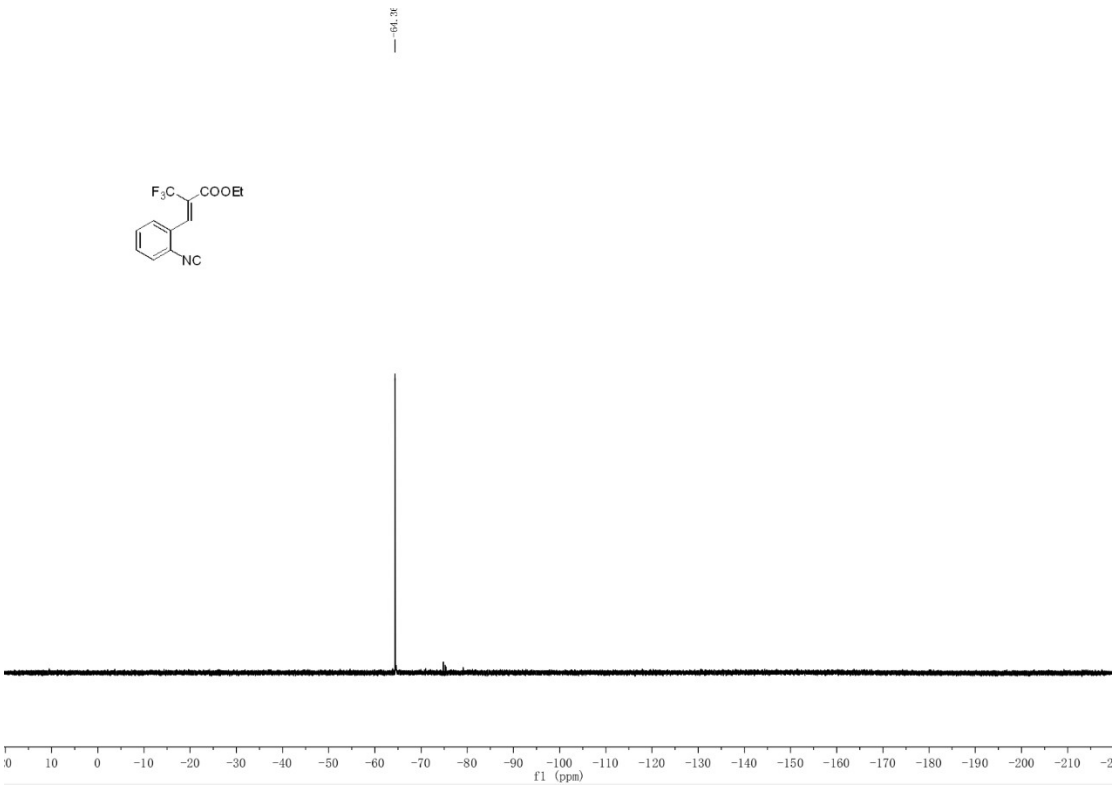
^{1}H NMR spectra of **1v** (500 MHz, $CDCl_3$)



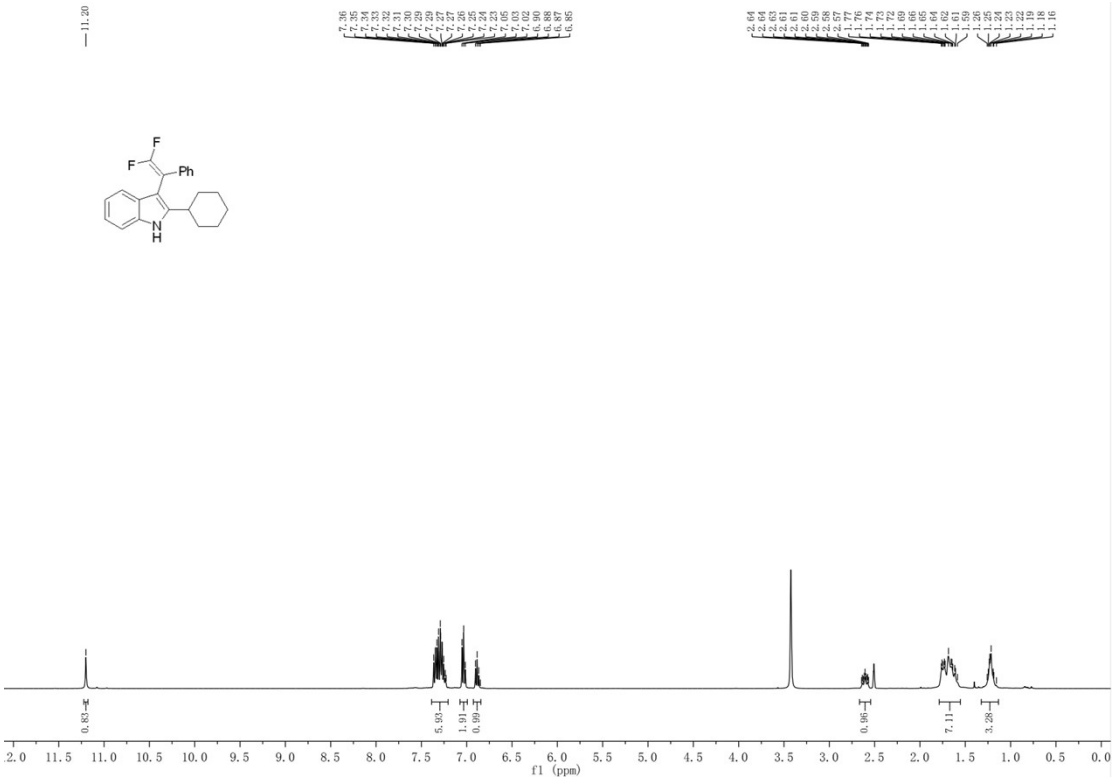
^{13}C NMR spectra of **1v** (125 MHz, $CDCl_3$)



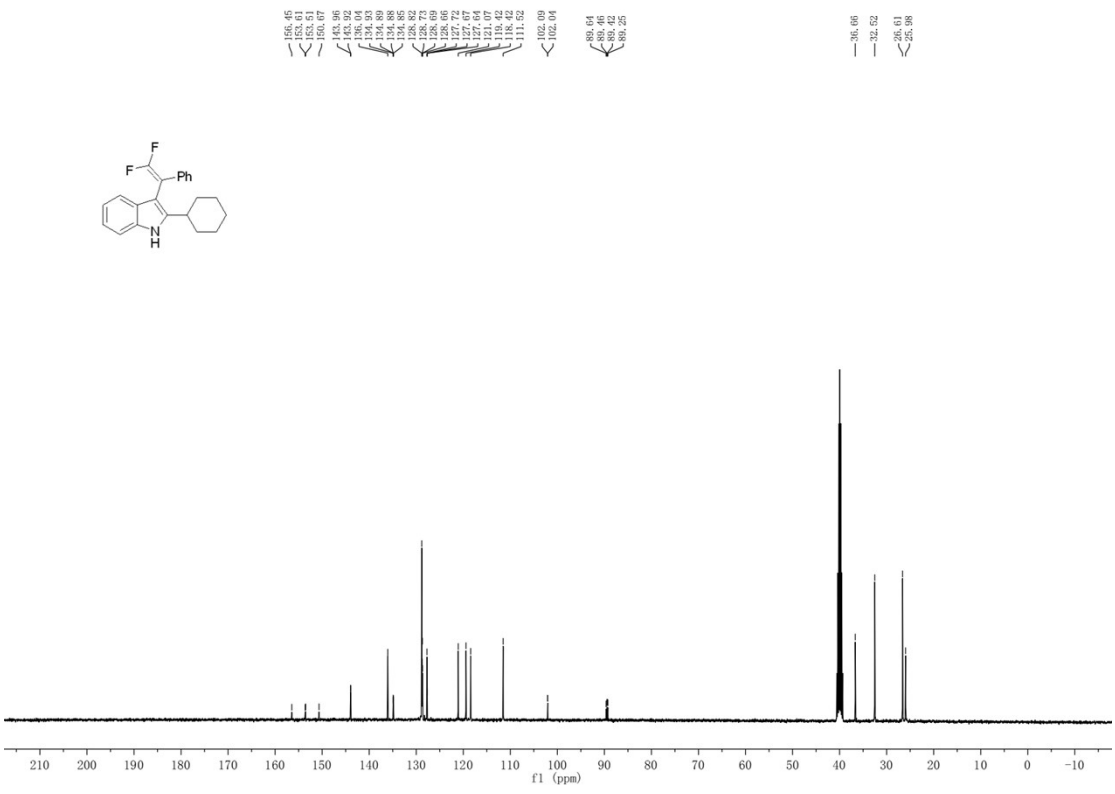
^{19}F NMR spectra of **1v** (470MHz, $CDCl_3$)



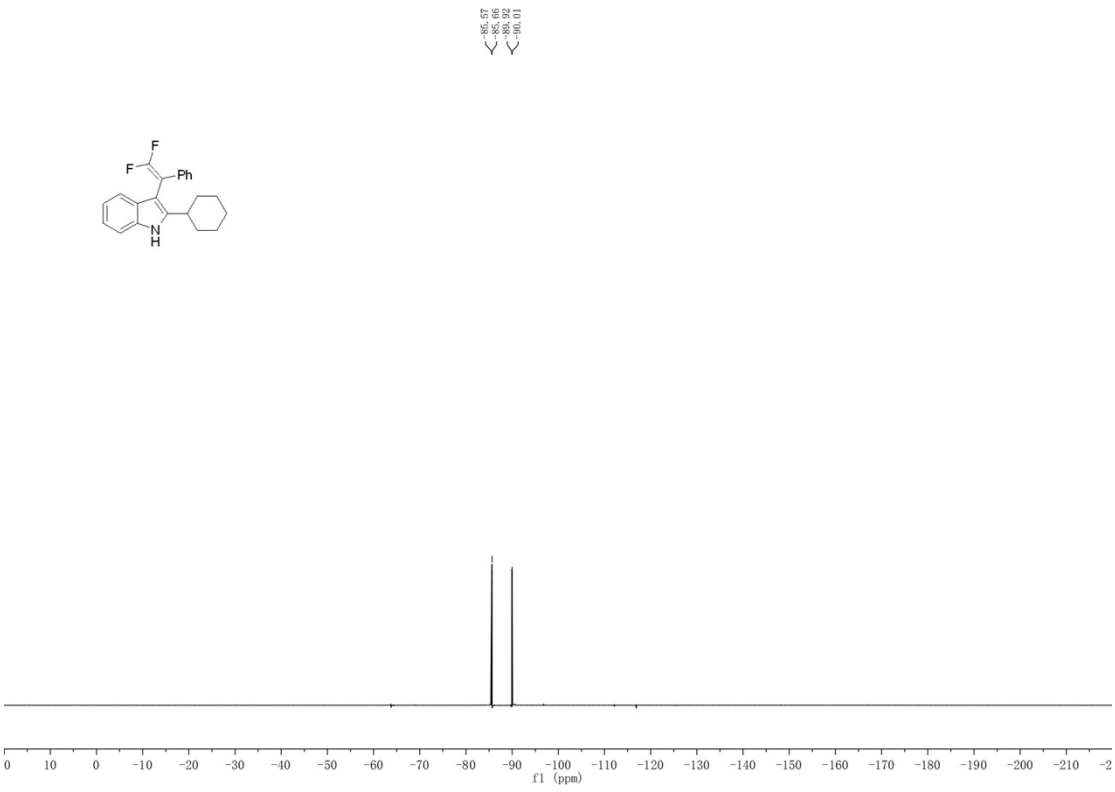
^{1}H NMR spectra of **3a** (400 MHz, DMSO-d_6)



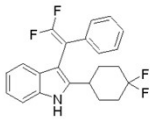
^{13}C NMR spectra of **3a** (100 MHz, DMSO-d_6)

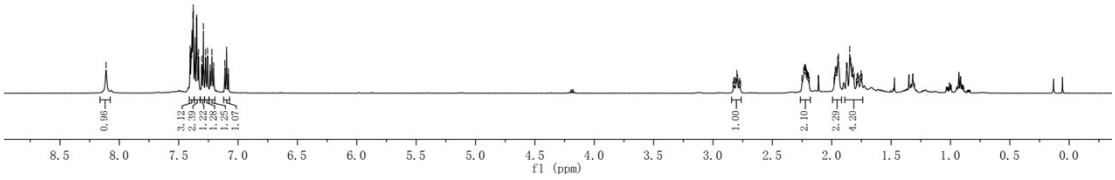


^{19}F NMR spectra of **3a** (376 MHz, DMSO-d_6)

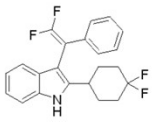


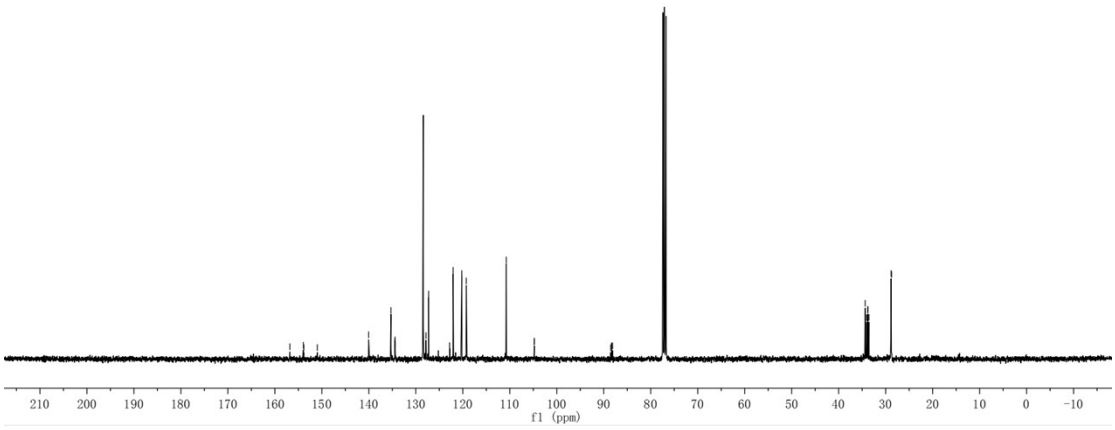
^{1}H NMR spectra of **3b** (500 MHz, $CDCl_3$)



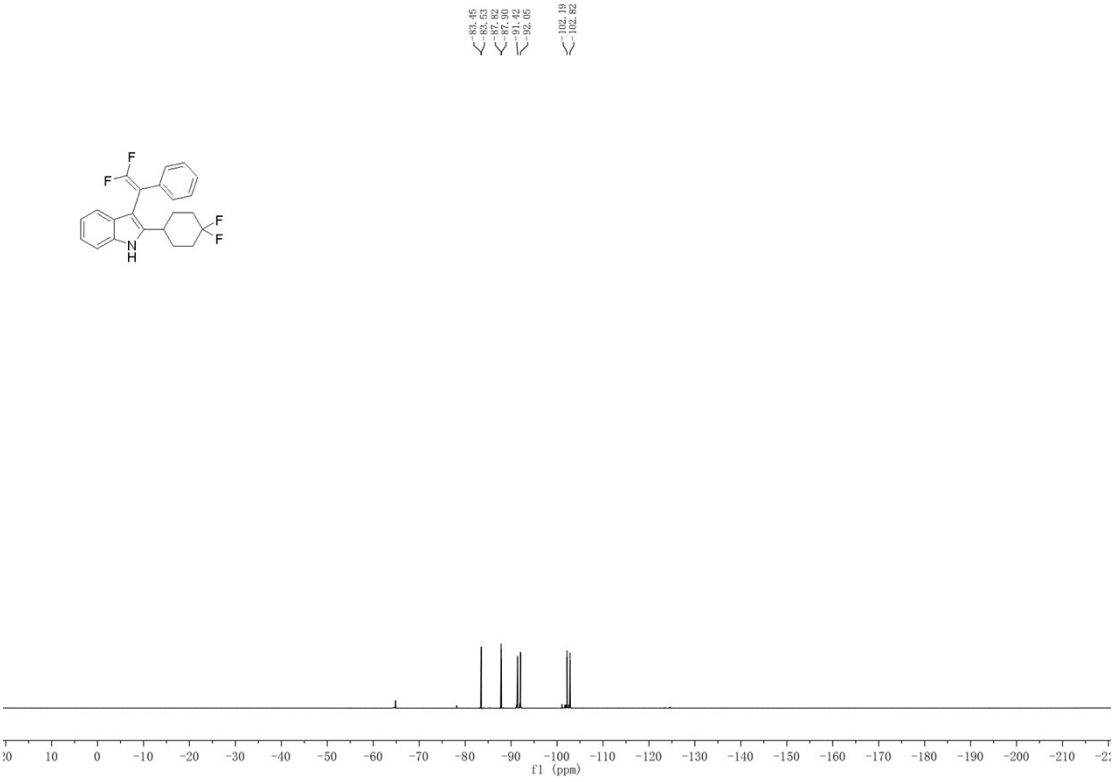


^{13}C NMR spectra of **3b** (100 MHz, $CDCl_3$)

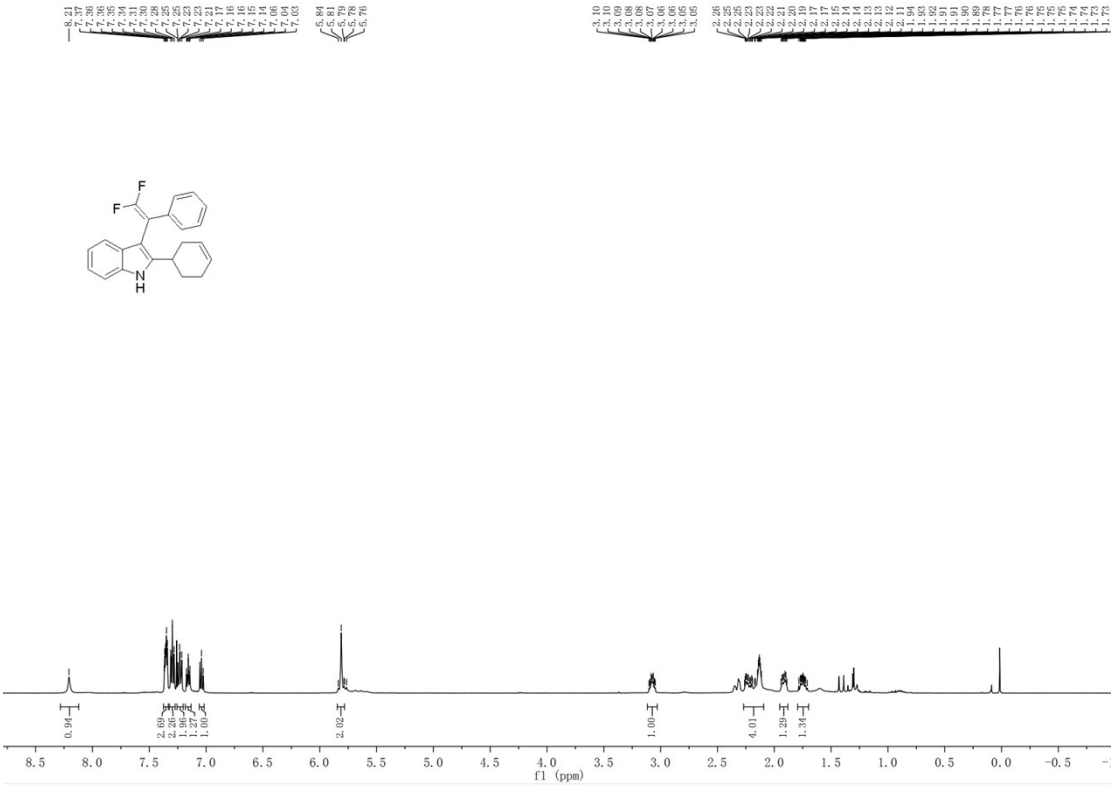




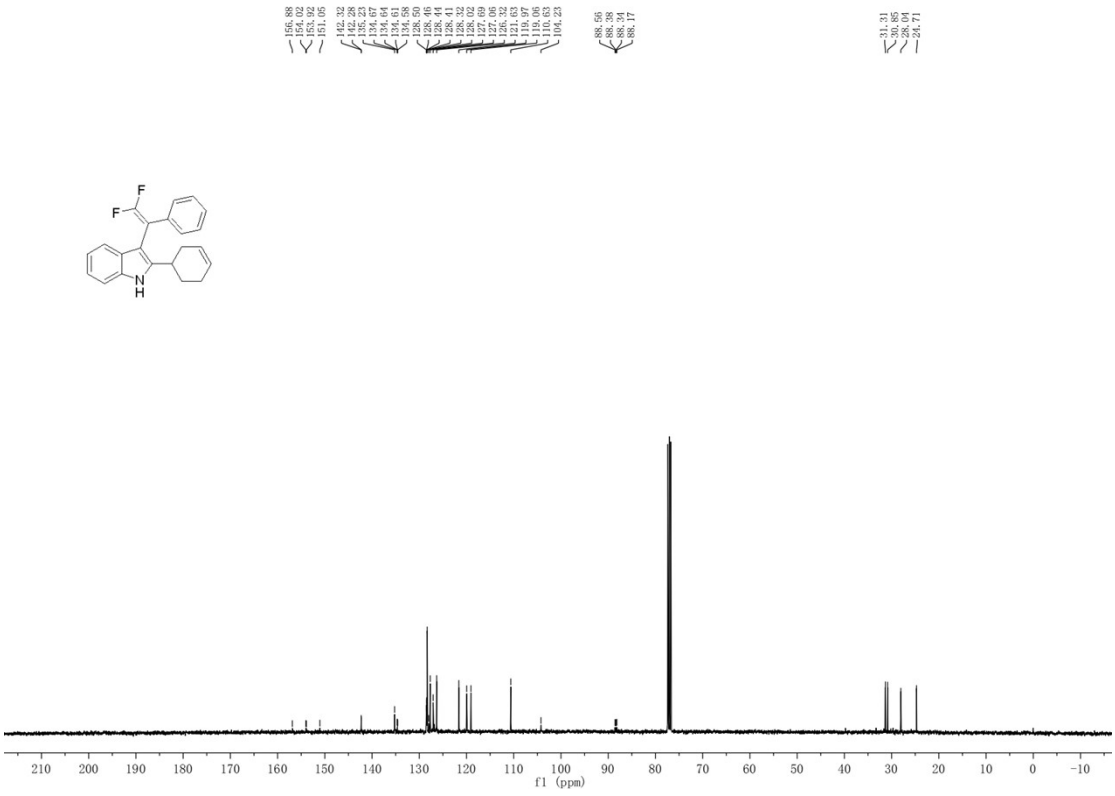
^{19}F NMR spectra of **3b** (376 MHz, $CDCl_3$)



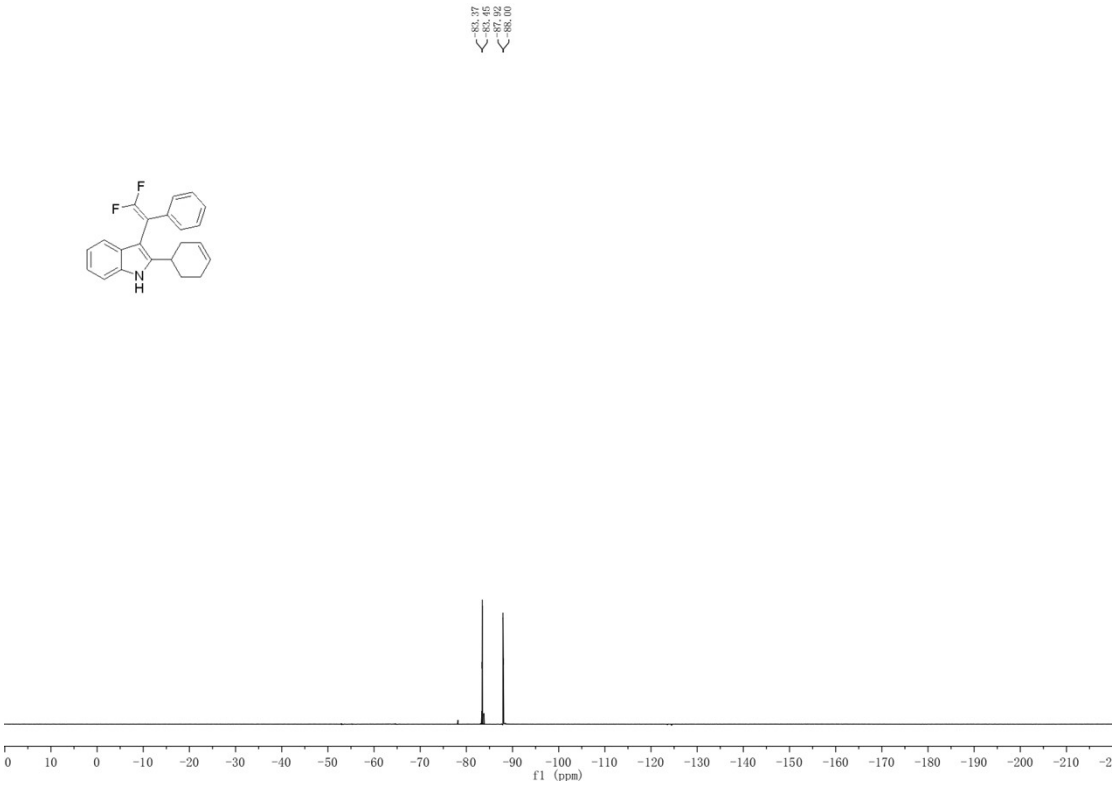
^{1}H NMR spectra of **3c** (500 MHz, $CDCl_3$)



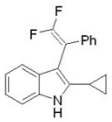
^{13}C NMR spectra of **3c** (100 MHz, $CDCl_3$)

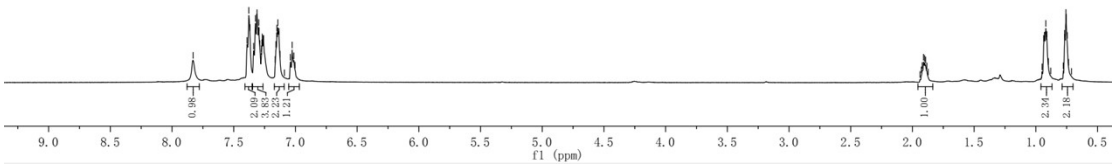


^{19}F NMR spectra of **3c** (376 MHz, $CDCl_3$)

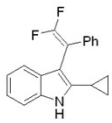


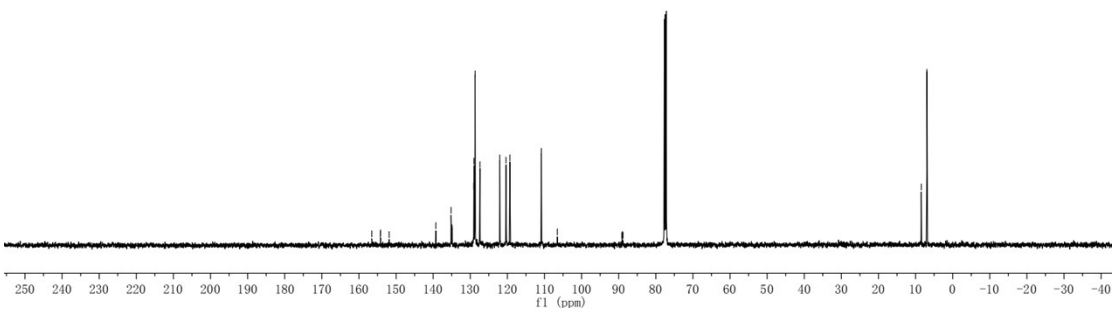
^{1}H NMR spectra of **3d** (500 MHz, $CDCl_3$)



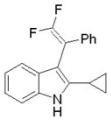


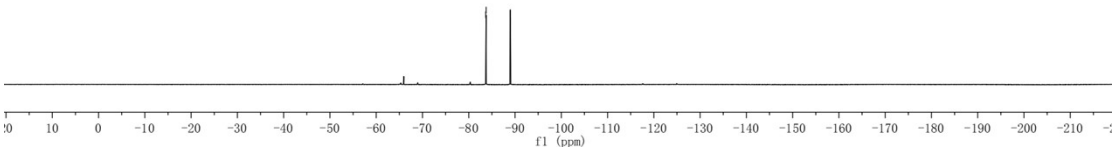
^{13}C NMR spectra of **3d** (125 MHz, $CDCl_3$)



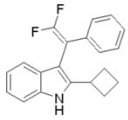


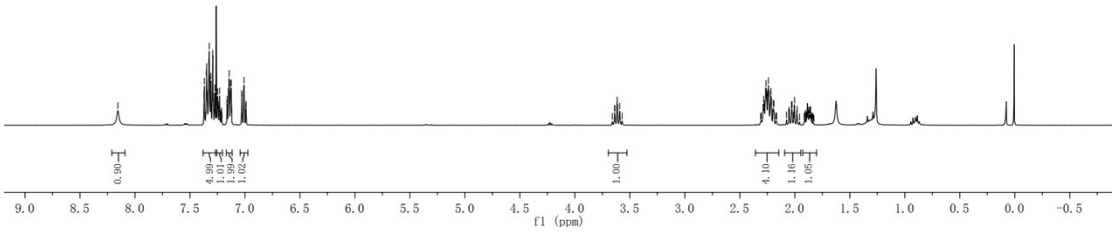
^{19}F NMR spectra of **3d** (376 MHz, $CDCl_3$)



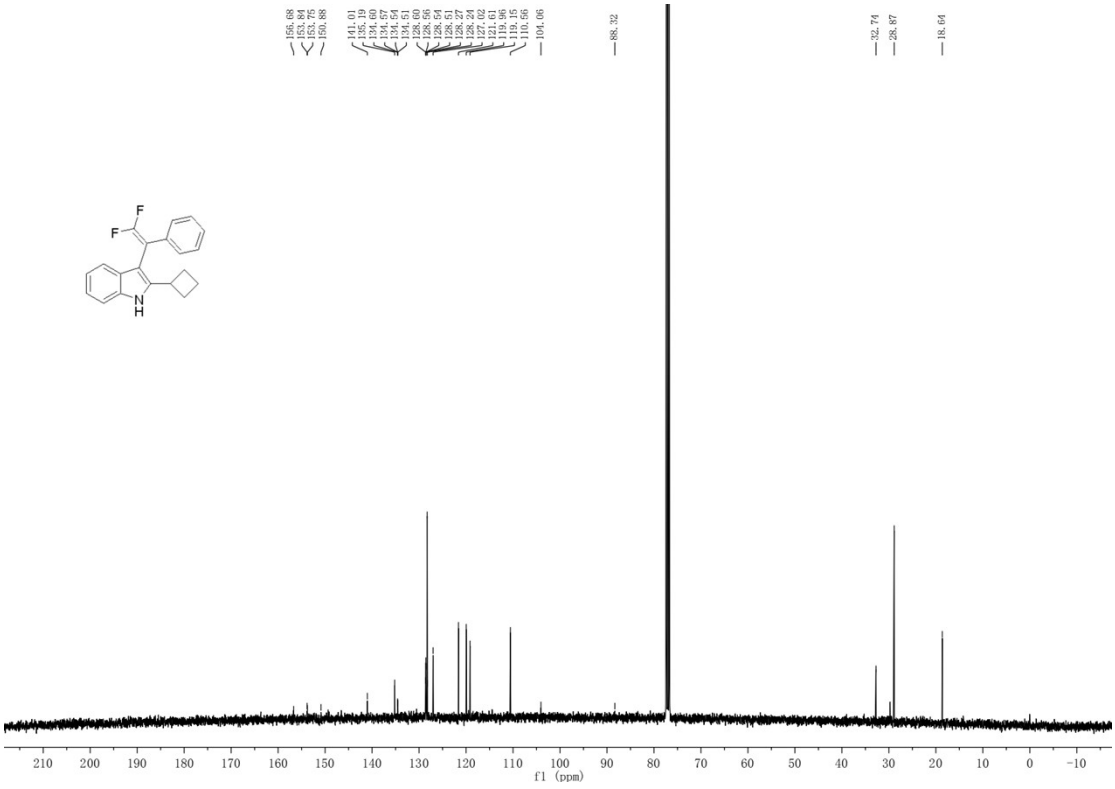


^{1}H NMR spectra of **3e** (400 MHz, $CDCl_3$)

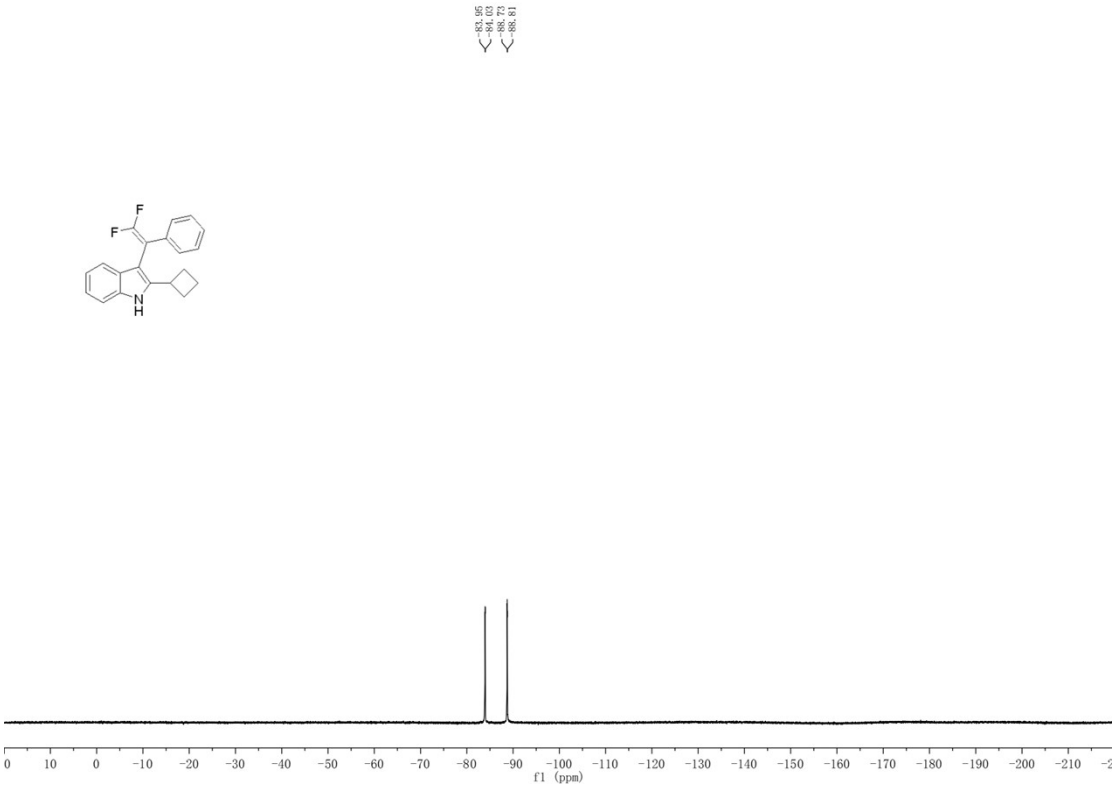




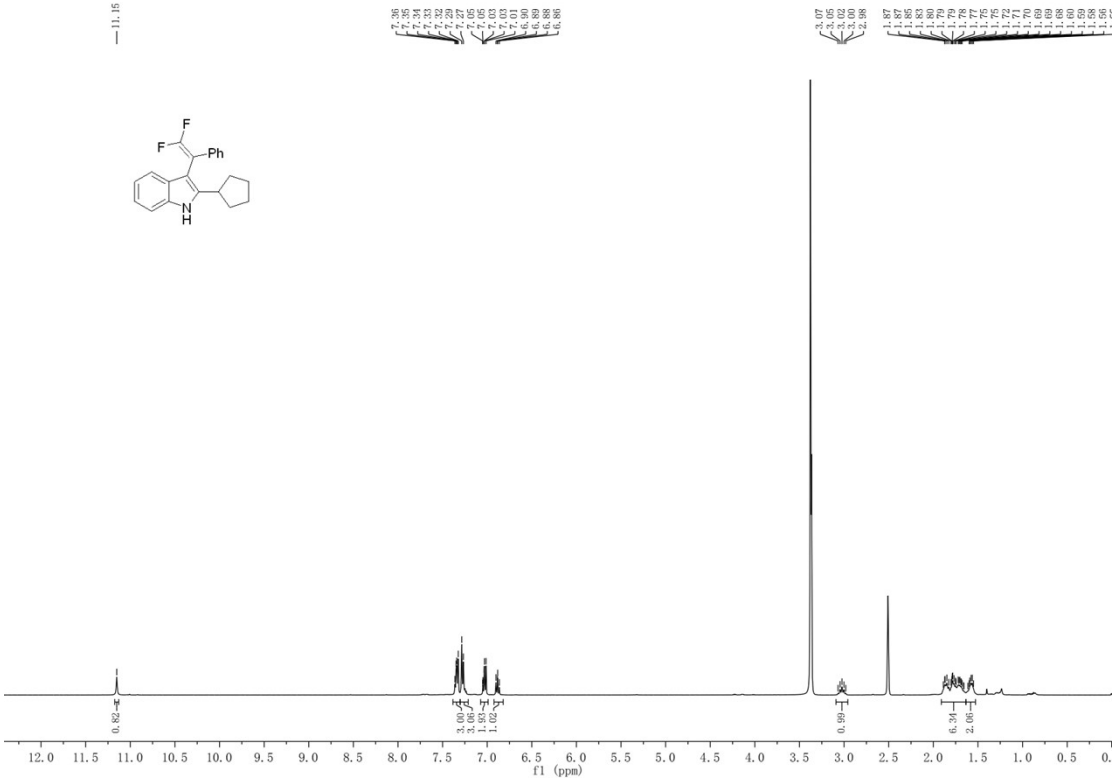
^{13}C NMR spectra of **3e** (100 MHz, $CDCl_3$)



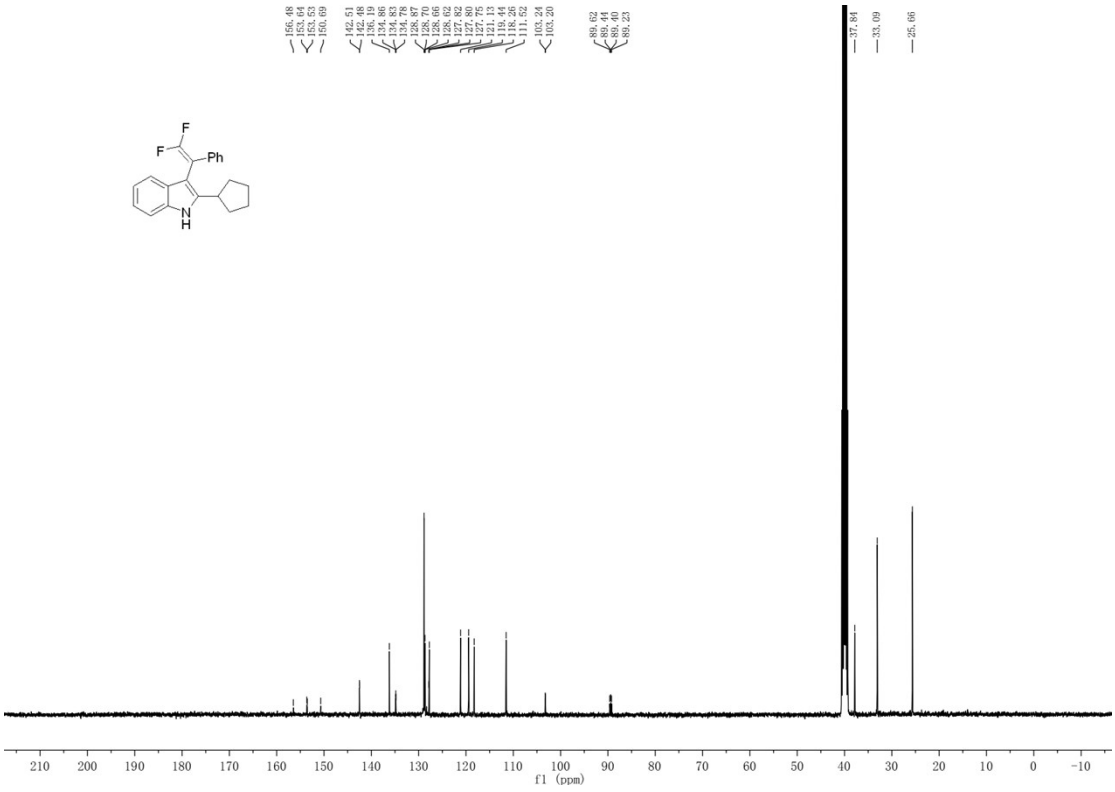
^{19}F NMR spectra of **3e** (376 MHz, $CDCl_3$)



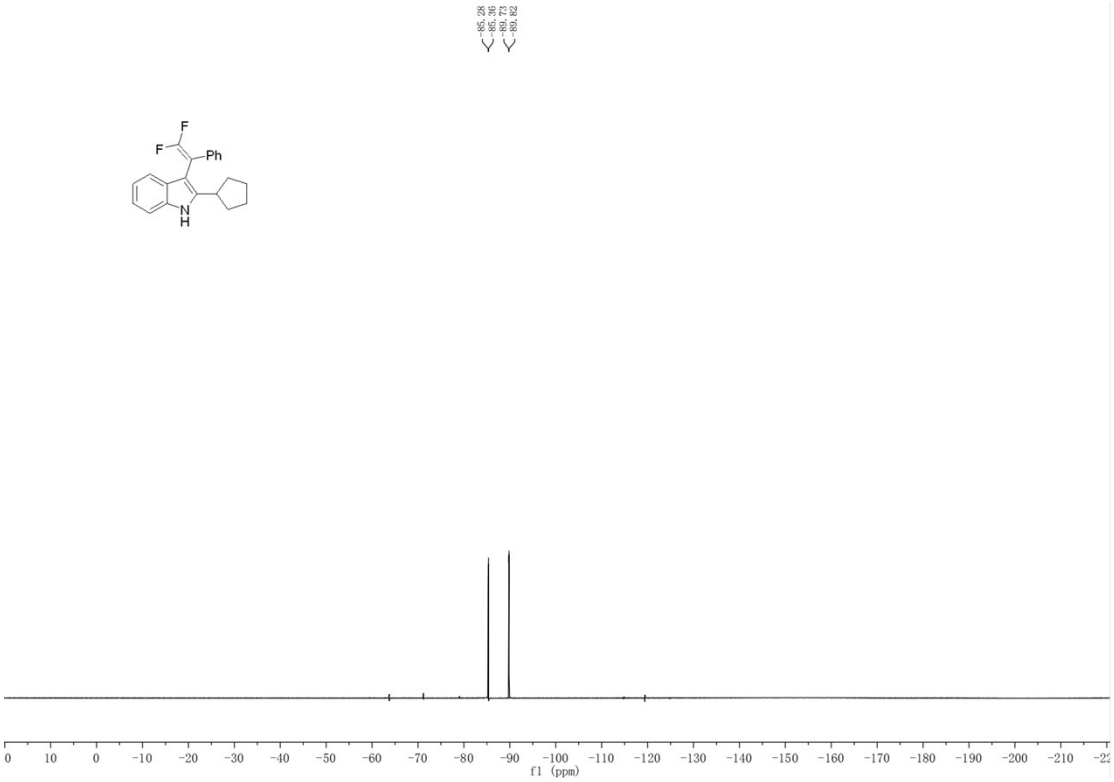
^{1}H NMR spectra of **3f** (400 MHz, DMSO-d_6)



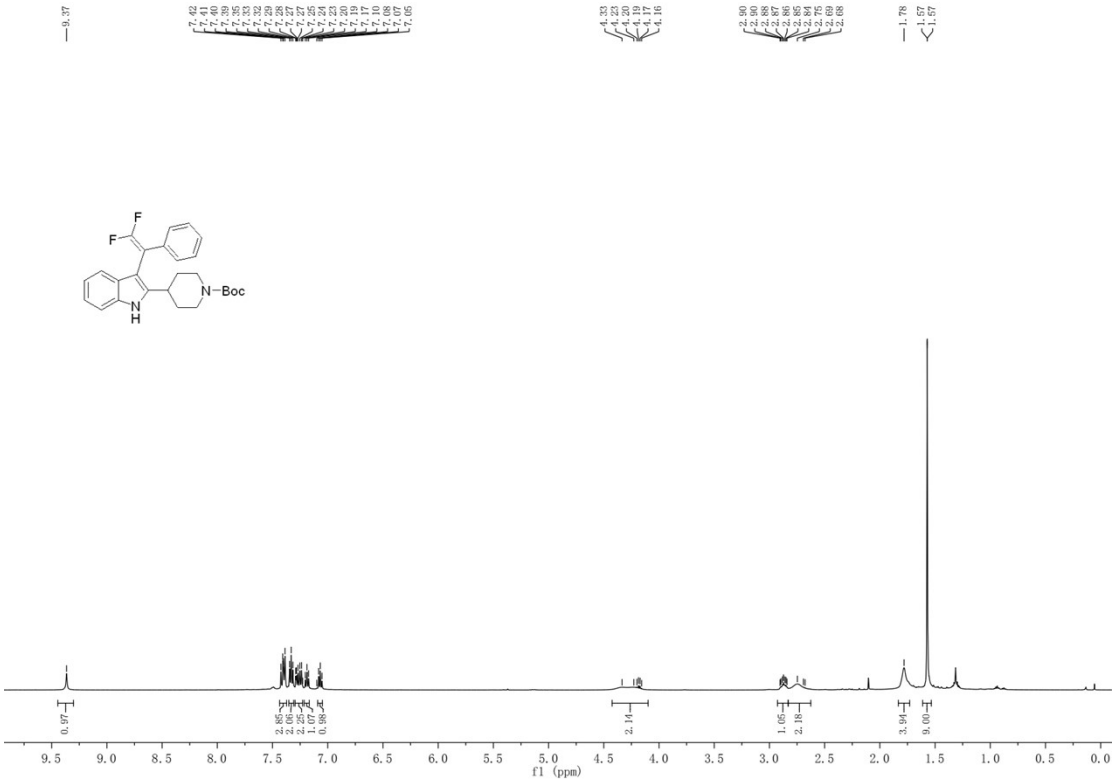
^{13}C NMR spectra of **3f** (100 MHz, DMSO-d_6)



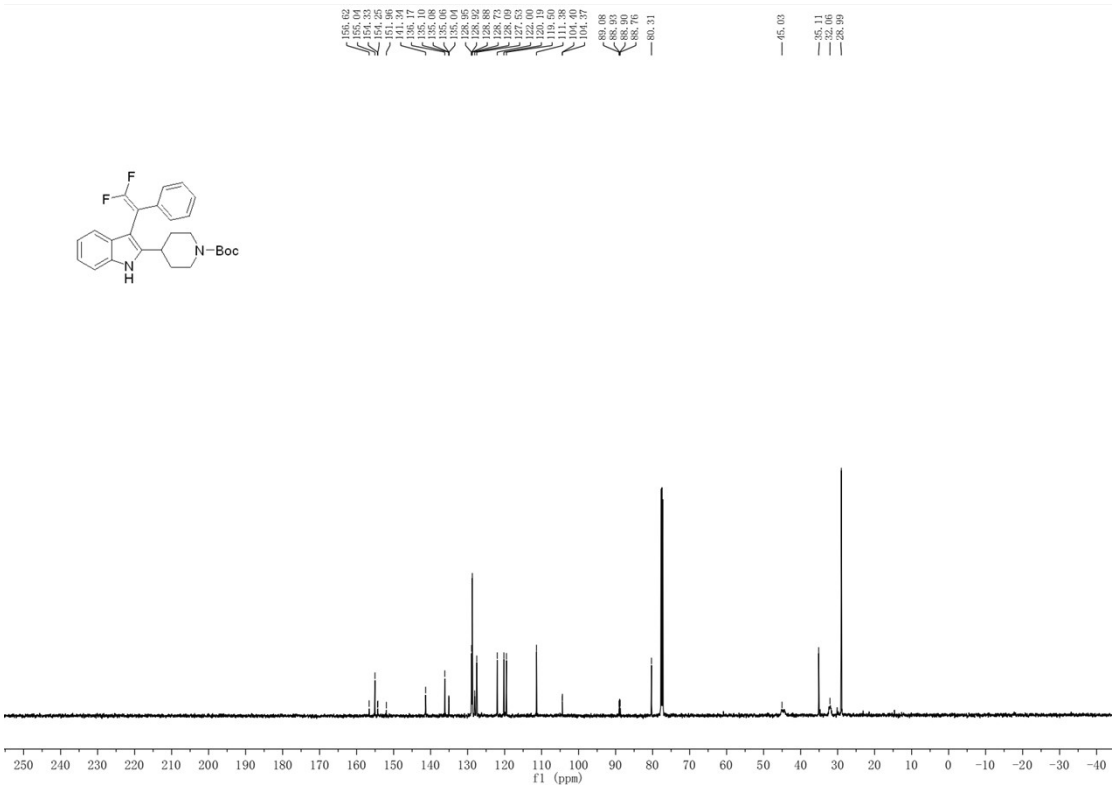
^{19}F NMR spectra of **3f** (376 MHz, DMSO-d_6)



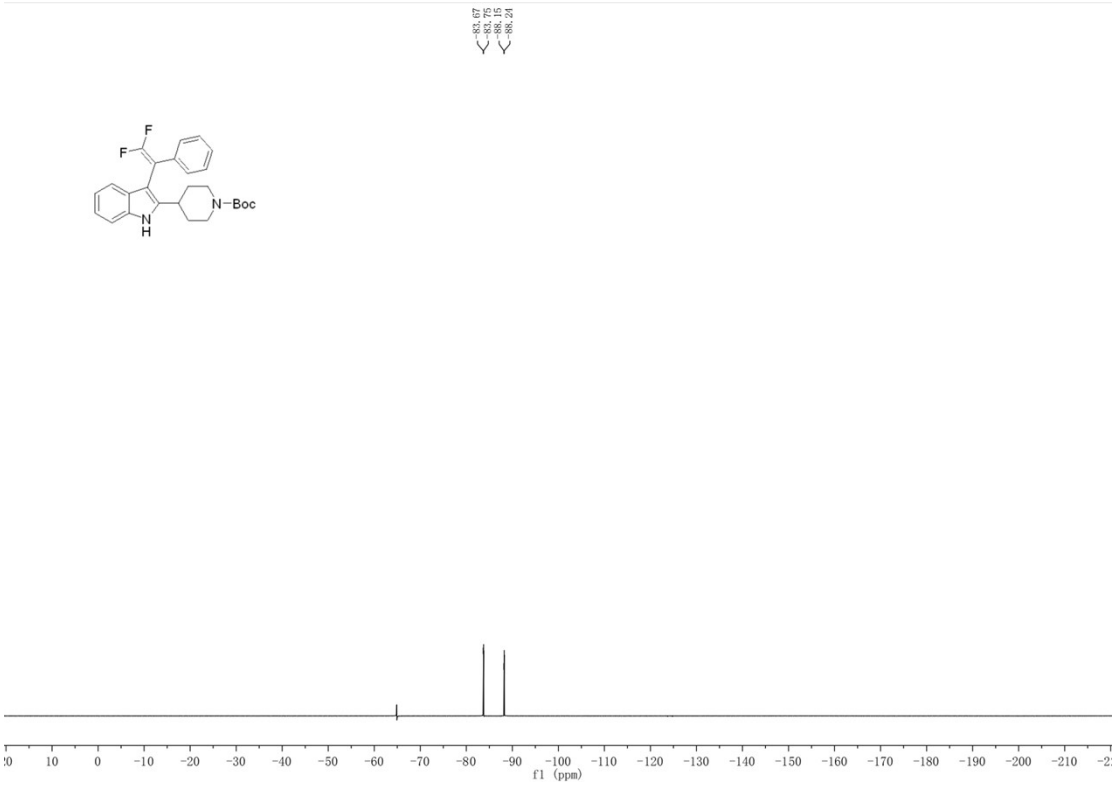
^{1}H NMR spectra of **3g** (500 MHz, $CDCl_3$)



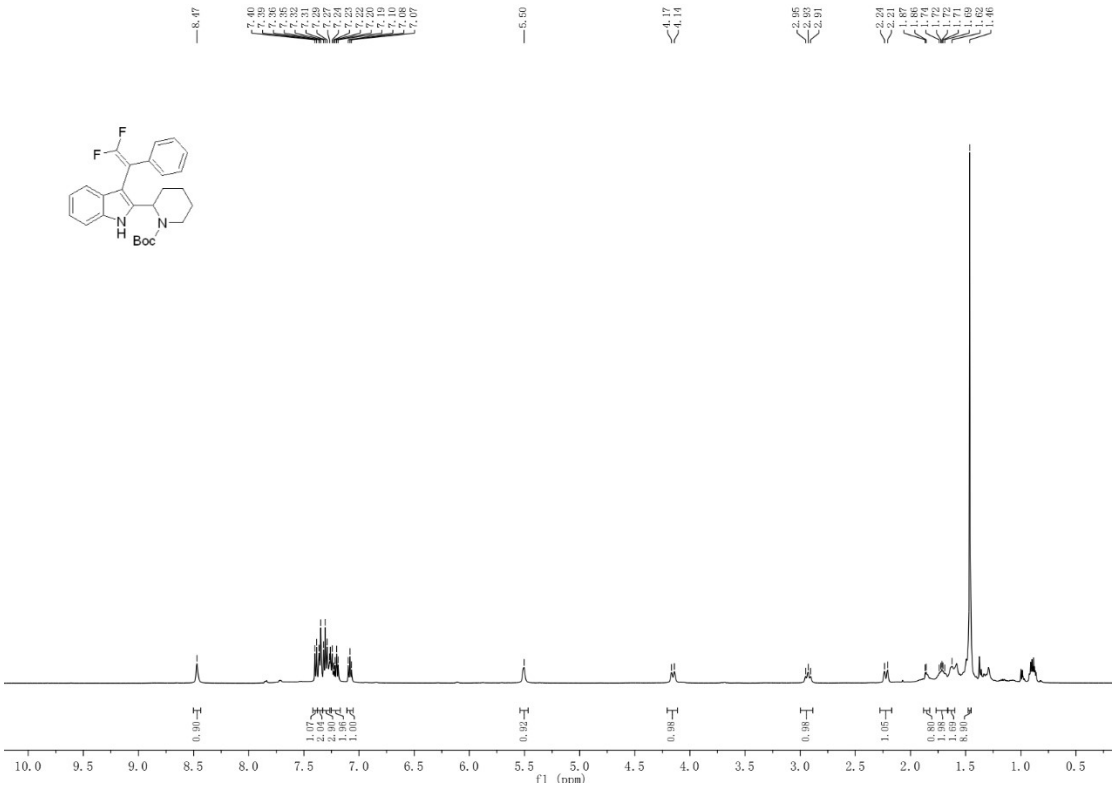
^{13}C NMR spectra of **3g** (125 MHz, $CDCl_3$)



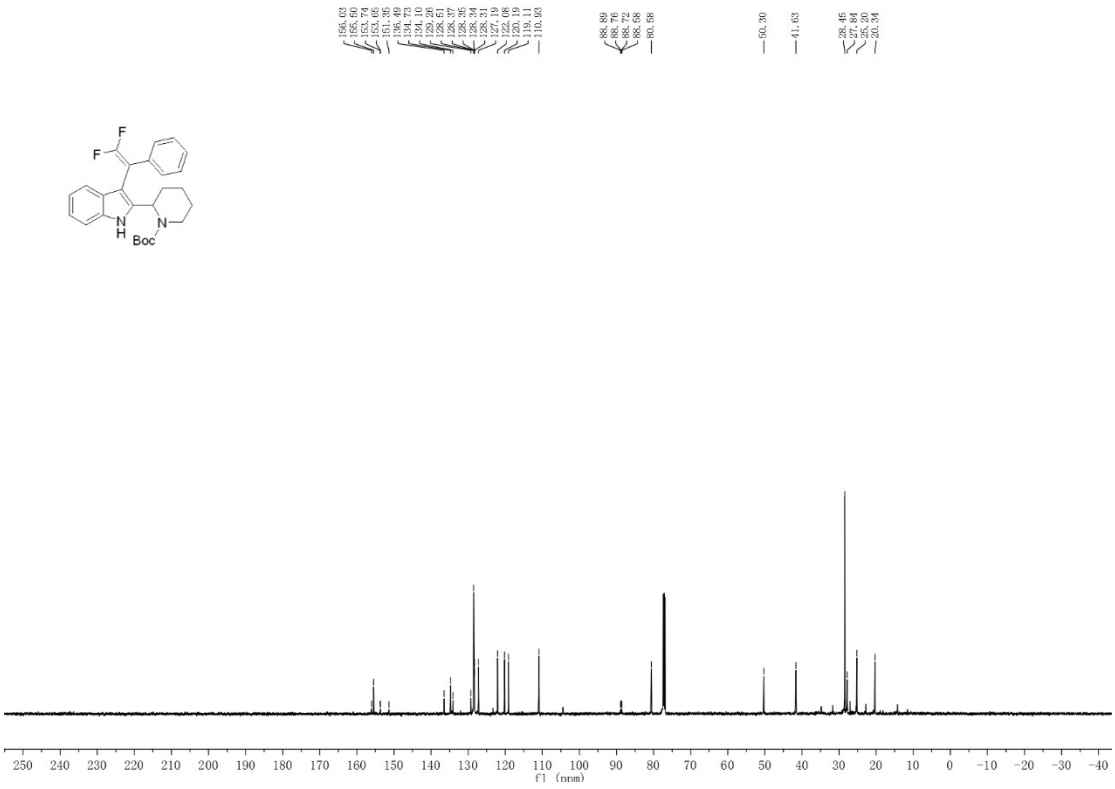
^{19}F NMR spectra of **3g** (376 MHz, $CDCl_3$)



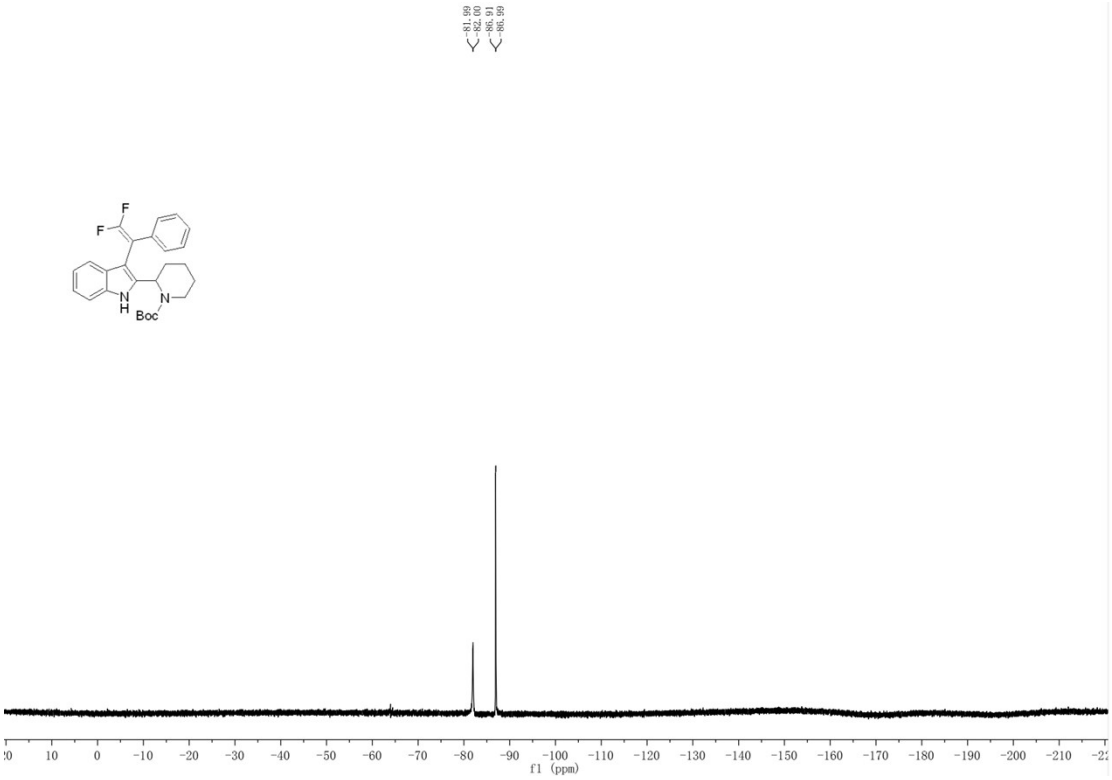
^{1}H NMR spectra of **3h** (500 MHz, $CDCl_3$)



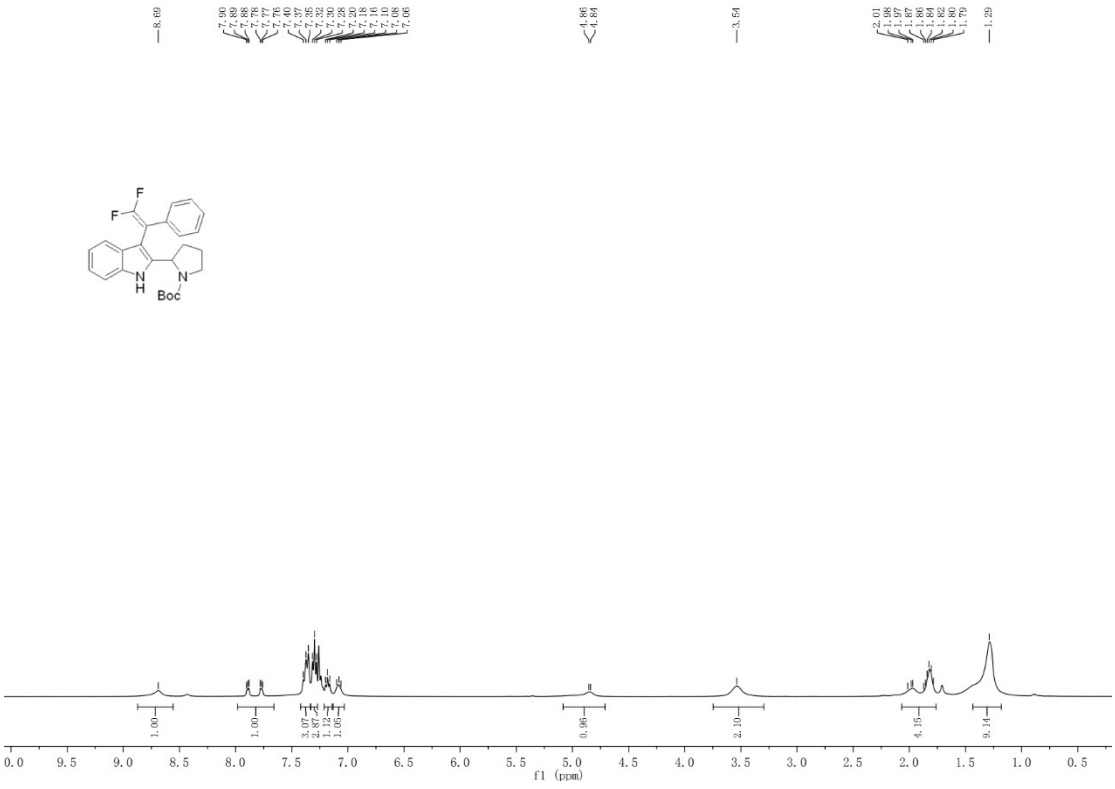
^{13}C NMR spectra of **3h** (125 MHz, $CDCl_3$)



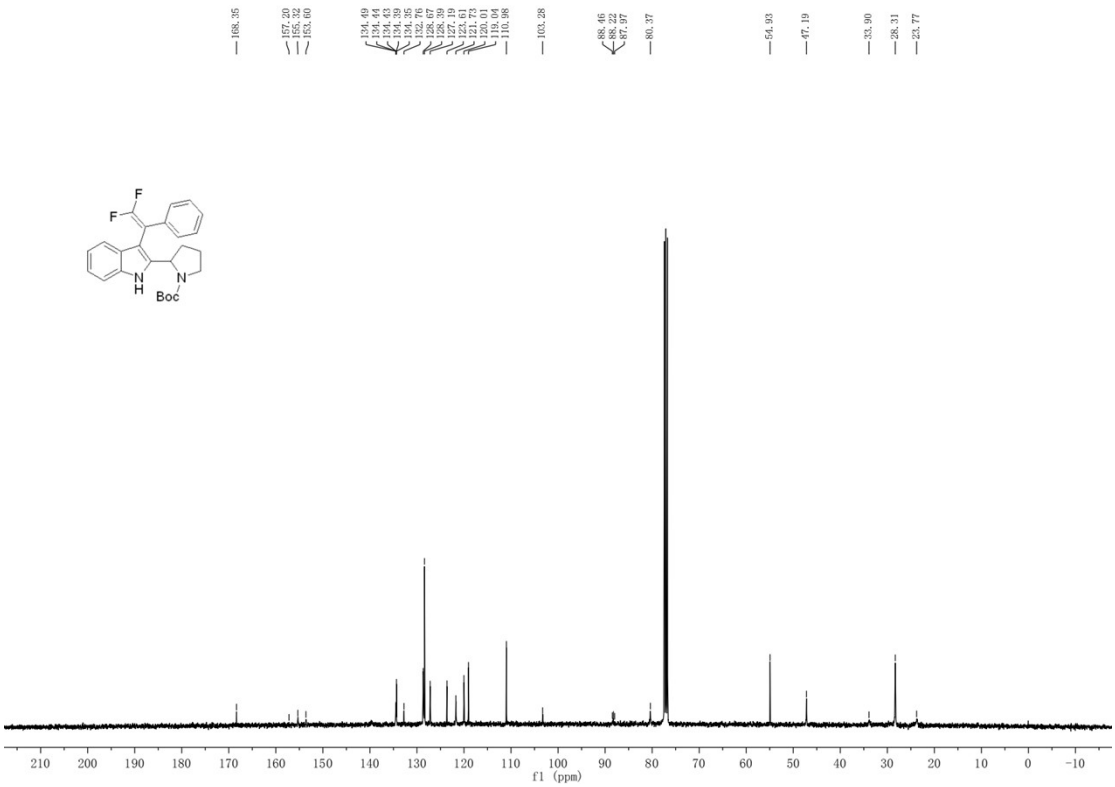
^{19}F NMR spectra of **3h** (376 MHz, $CDCl_3$)



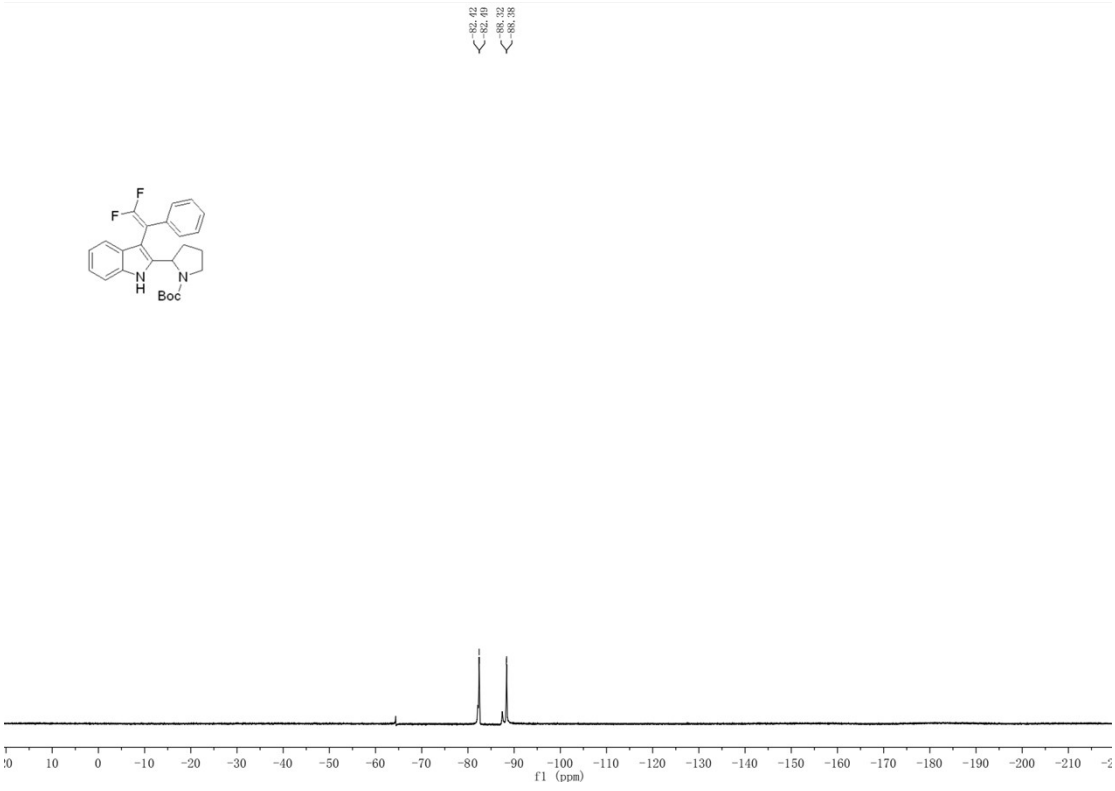
^{1}H NMR spectra of **3i** ($CDCl_3$)



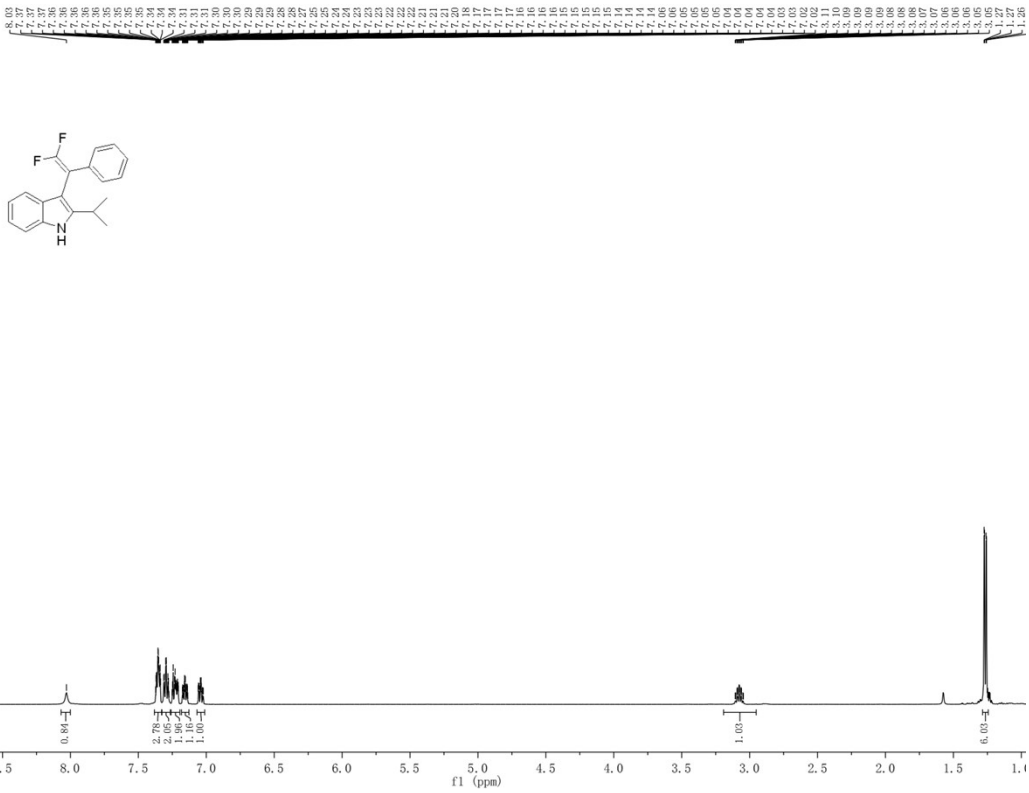
^{13}C NMR spectra of **3i** (100 MHz, $CDCl_3$)



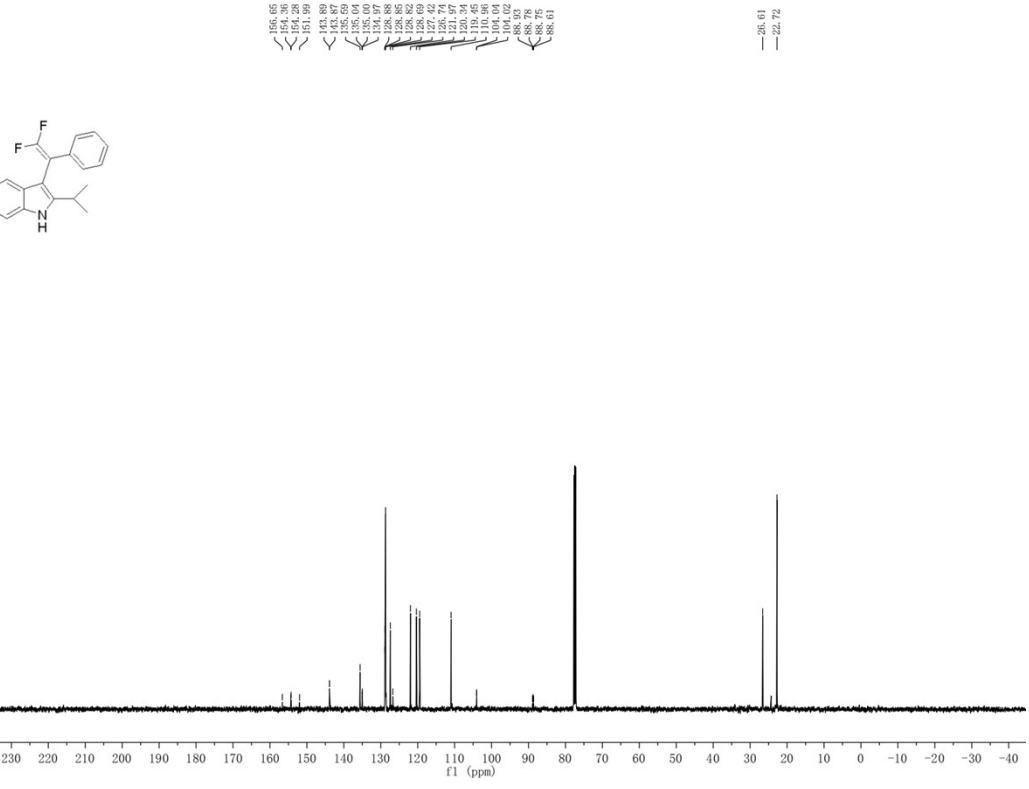
^{19}F NMR spectra of **3i** (376 MHz, $CDCl_3$)



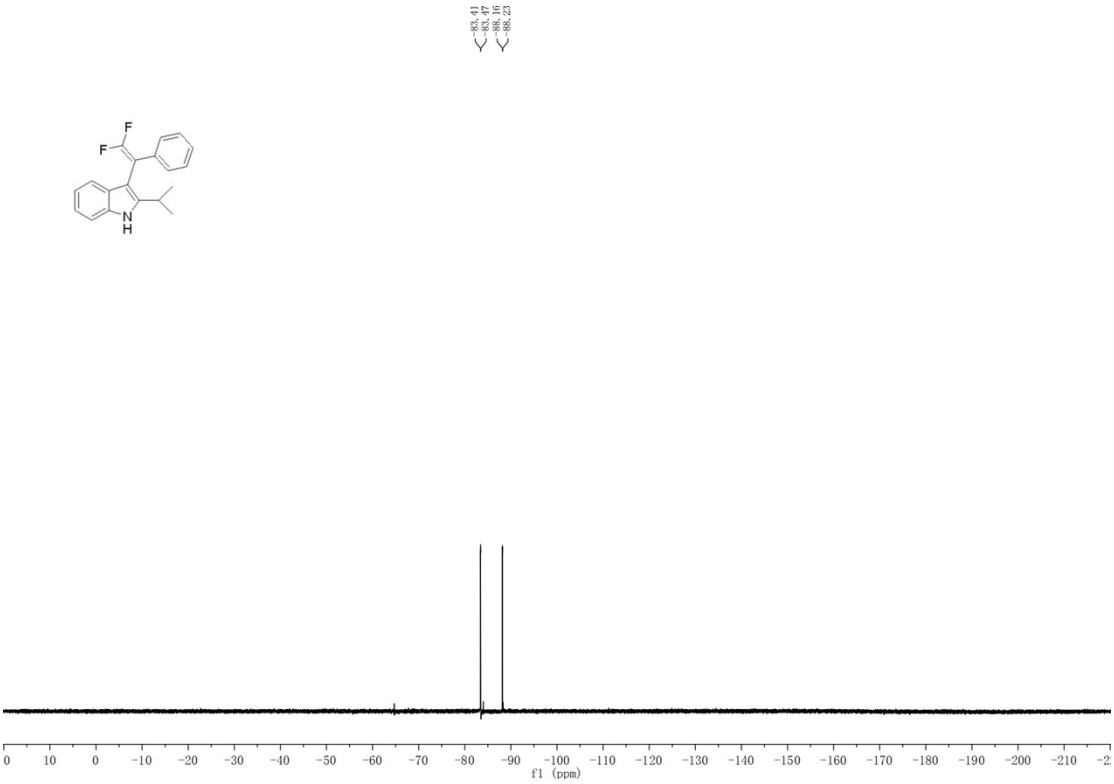
^{1}H NMR spectra of **3j** (500 MHz, $CDCl_3$)



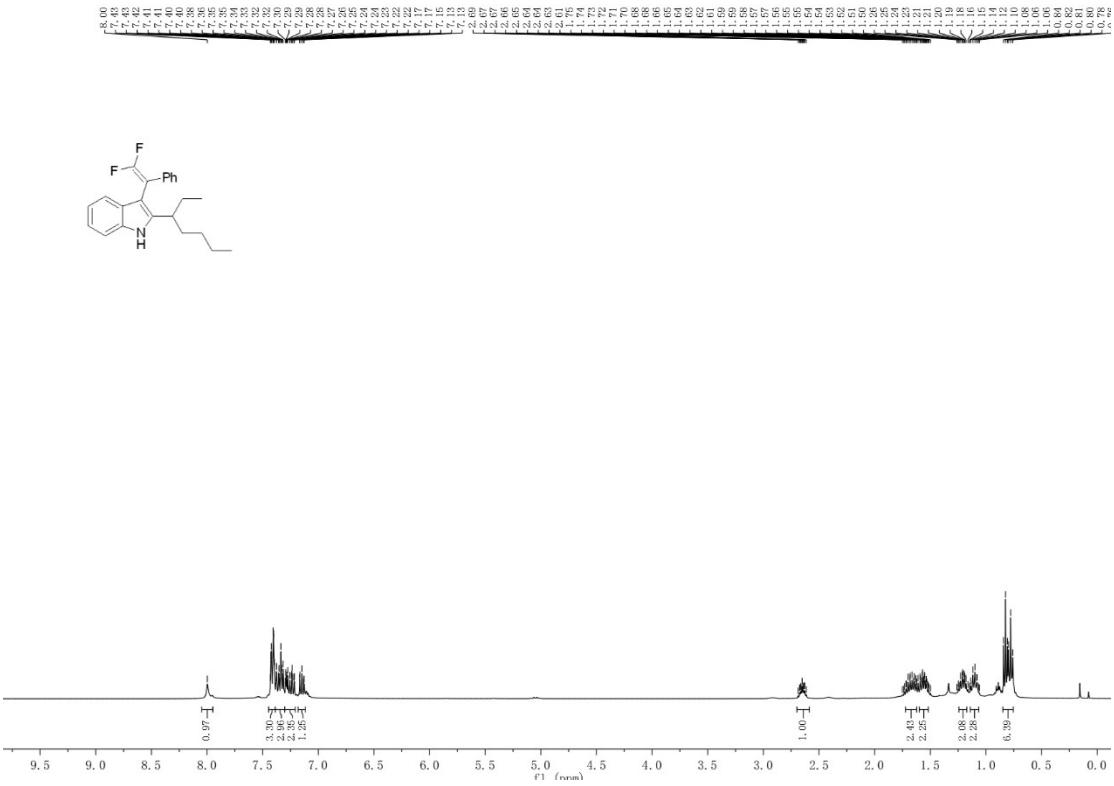
^{13}C NMR spectra of **3j** (125 MHz, $CDCl_3$)



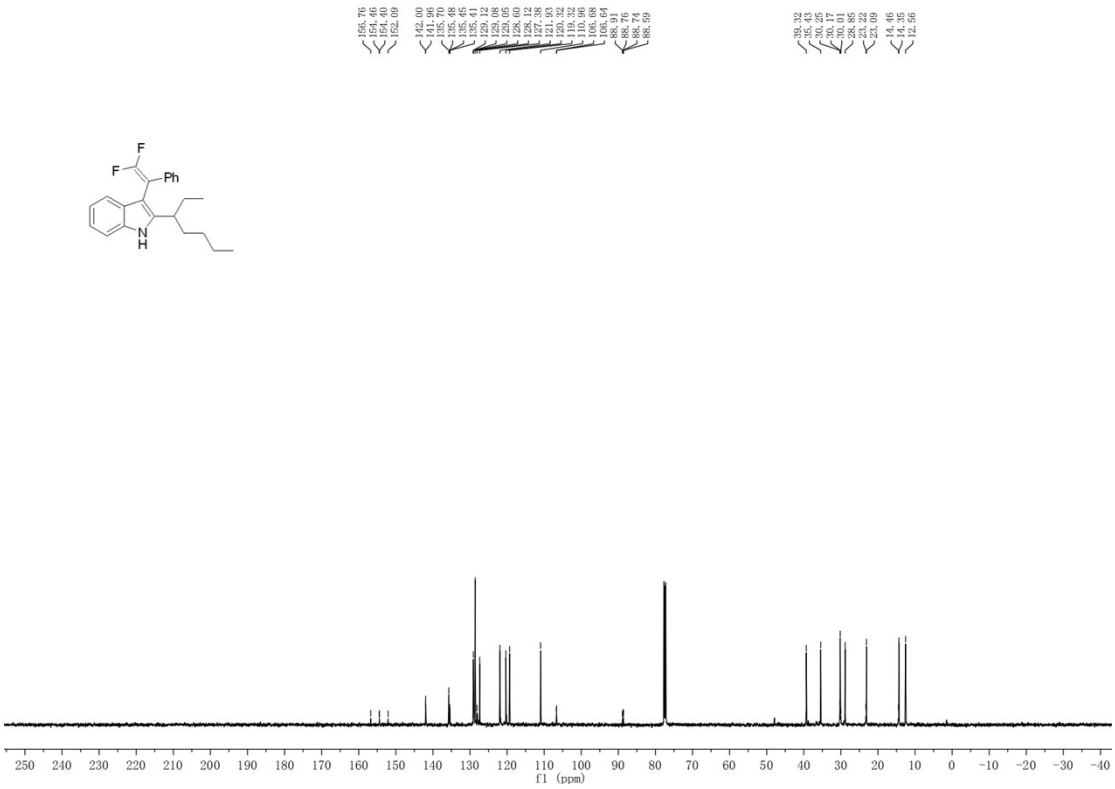
^{19}F NMR spectra of **3j** (470 MHz, $CDCl_3$)



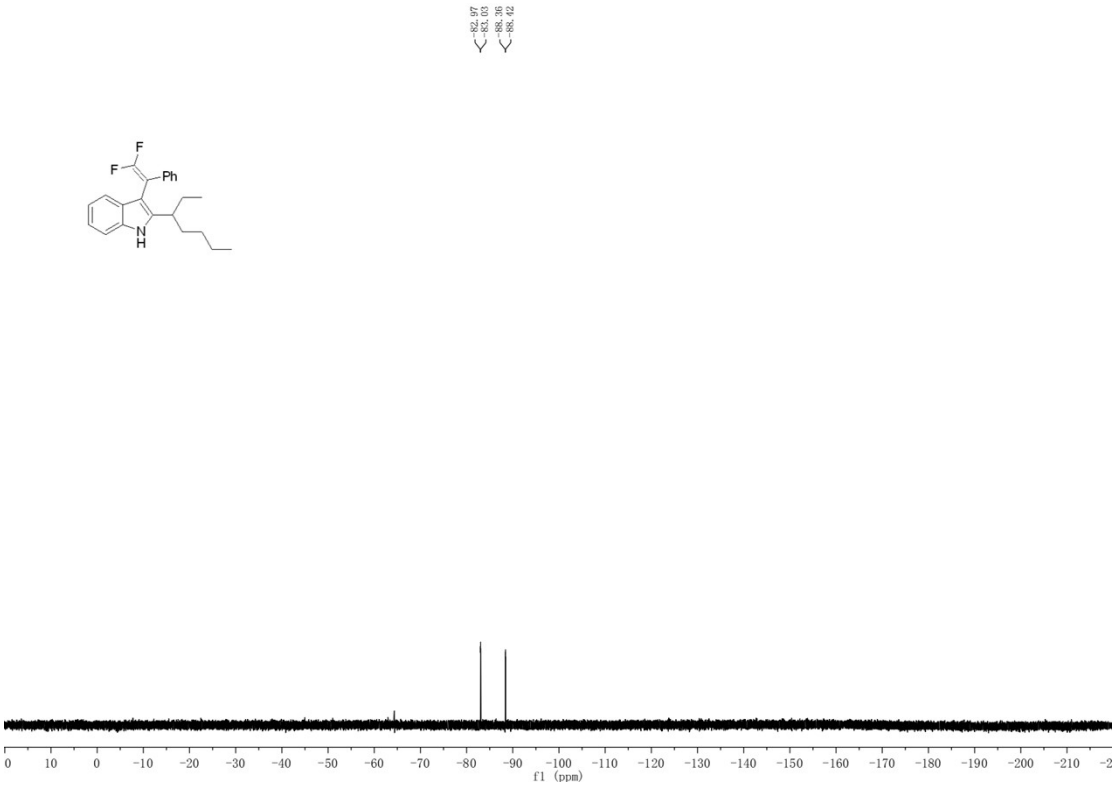
^{1}H NMR spectra of **3k** (400 MHz, $CDCl_3$)



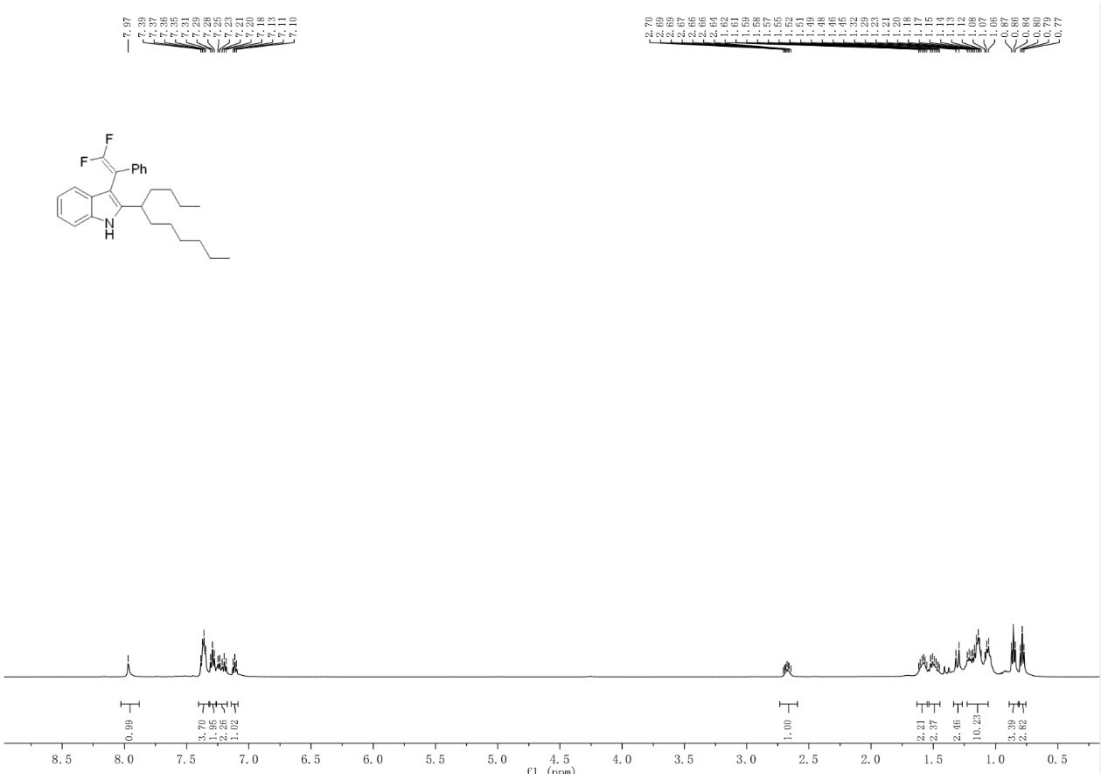
^{13}C NMR spectra of **3k** (125 MHz, $CDCl_3$)



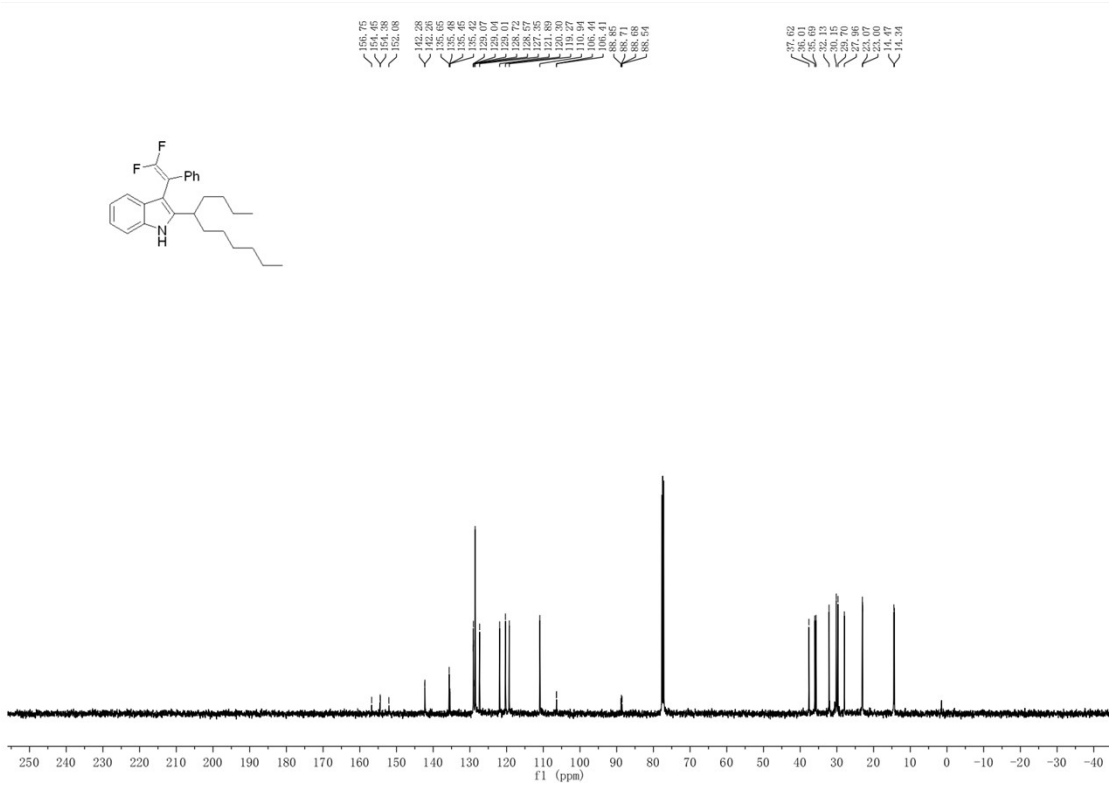
^{19}F NMR spectra of **3k** (470 MHz, $CDCl_3$)



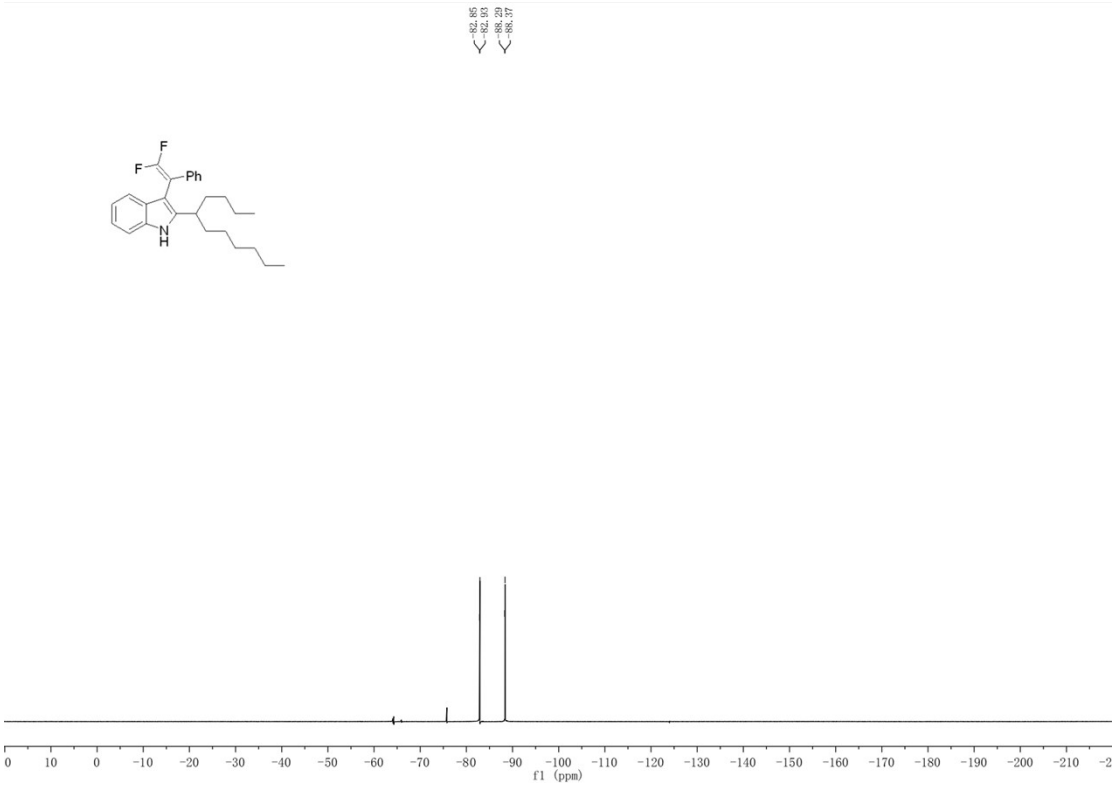
^{1}H NMR spectra of **3l** (500 MHz, $CDCl_3$)



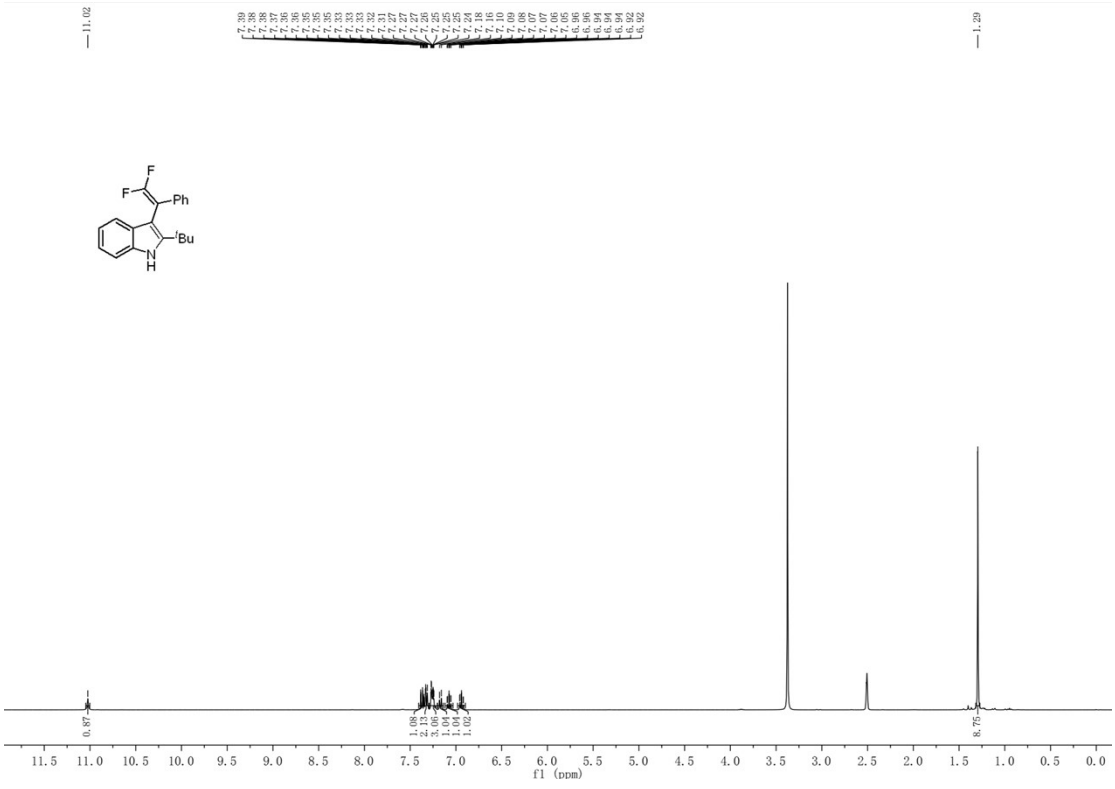
^{13}C NMR spectra of **3l** (125 MHz, $CDCl_3$)



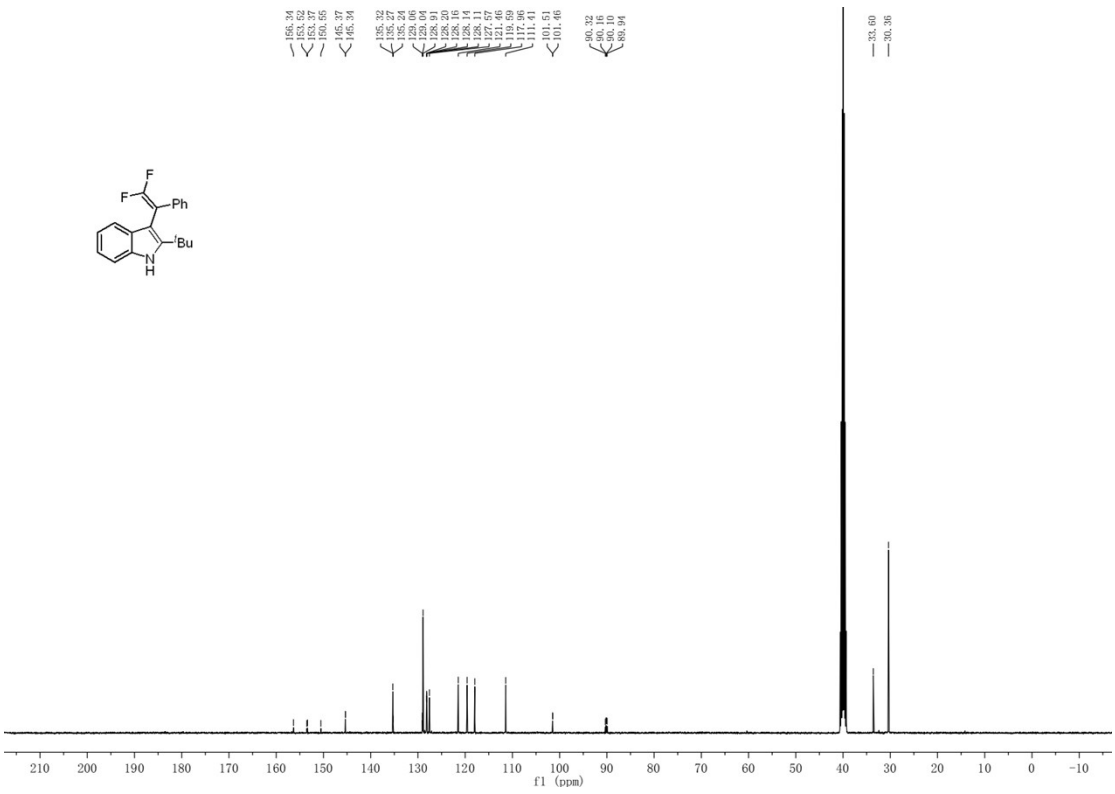
^{19}F NMR spectra of **3l** (376 MHz, $CDCl_3$)



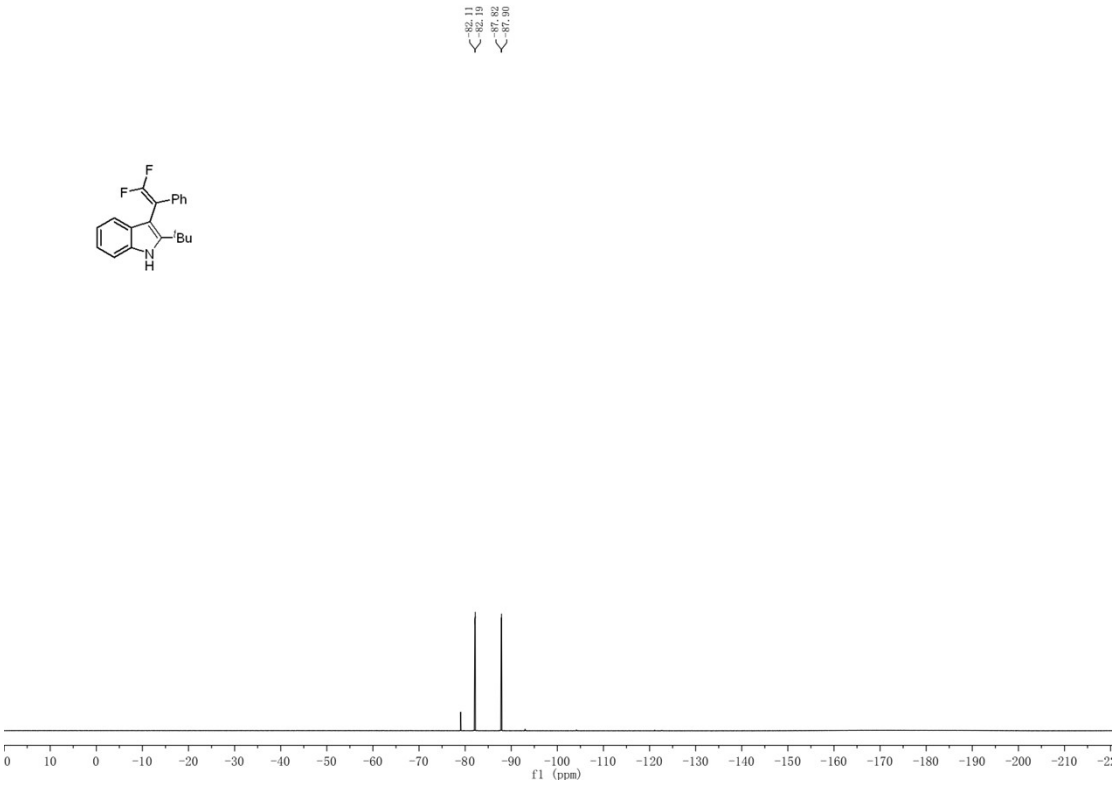
^{1}H NMR spectra of **3m** (400 MHz, DMSO-d_6)



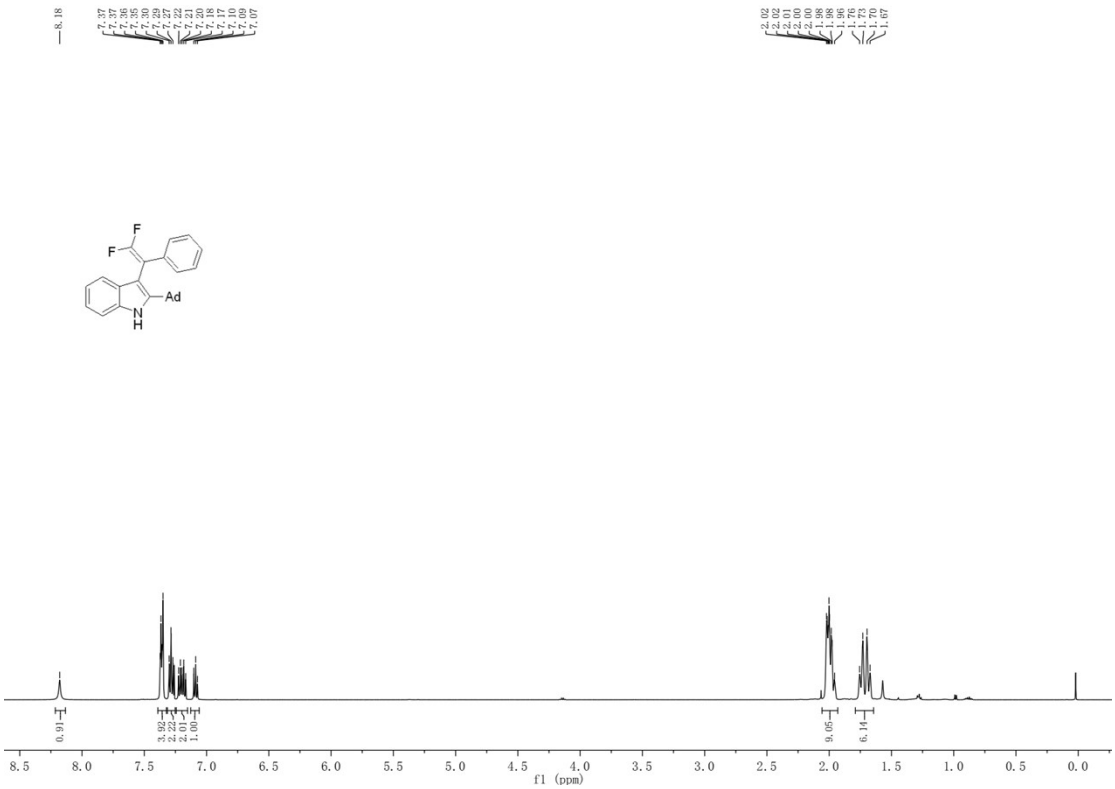
^{13}C NMR spectra of **3m** (100 MHz, DMSO-d_6)



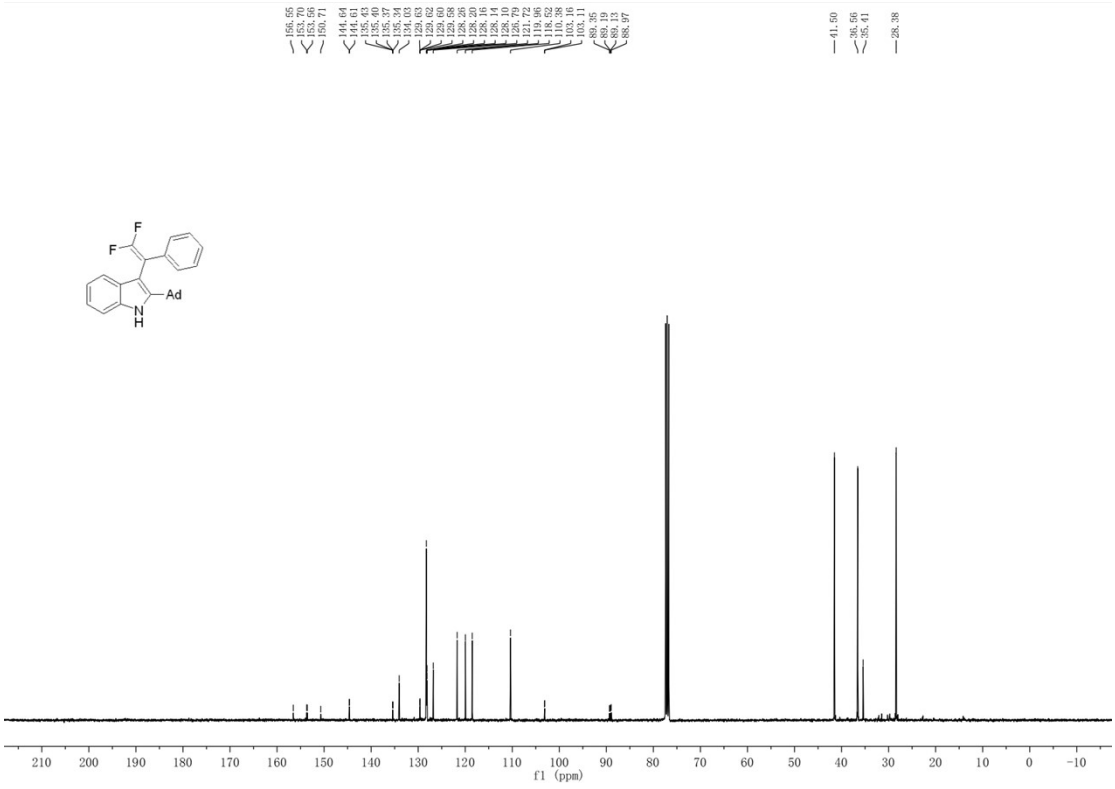
^{19}F NMR spectra of **3m** (376 MHz, DMSO-d_6)



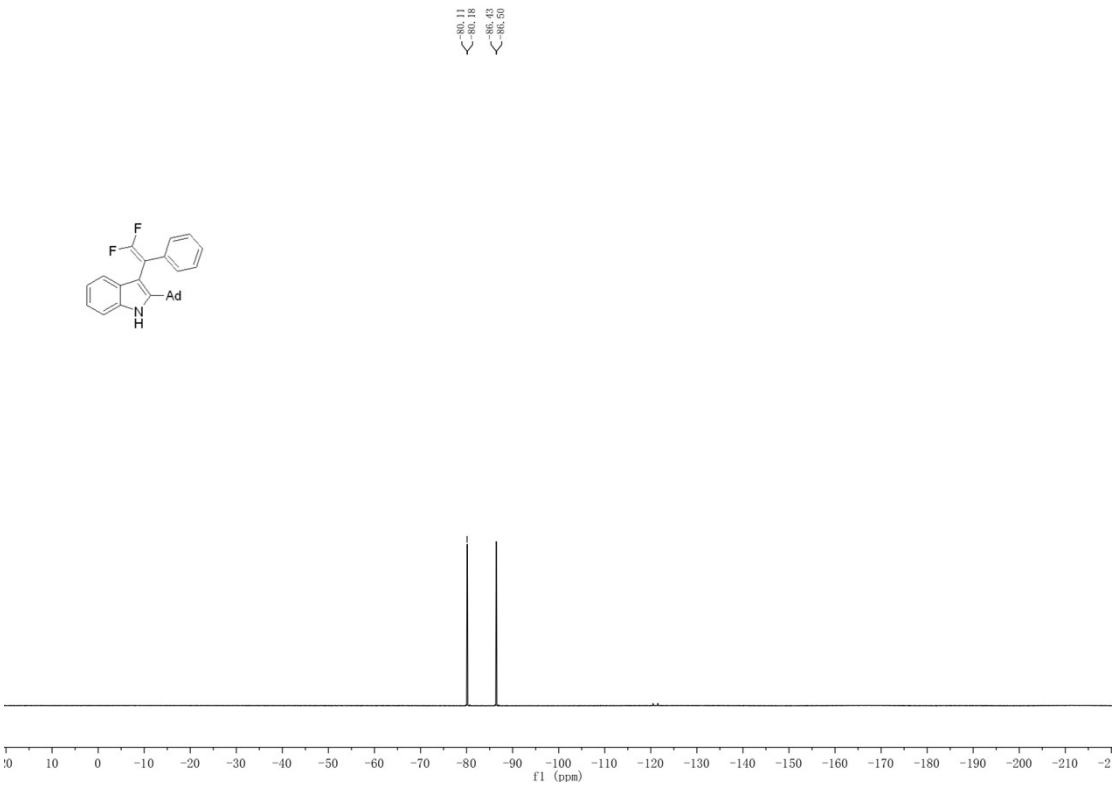
^{1}H NMR spectra of **3n** (500 MHz, $CDCl_3$)



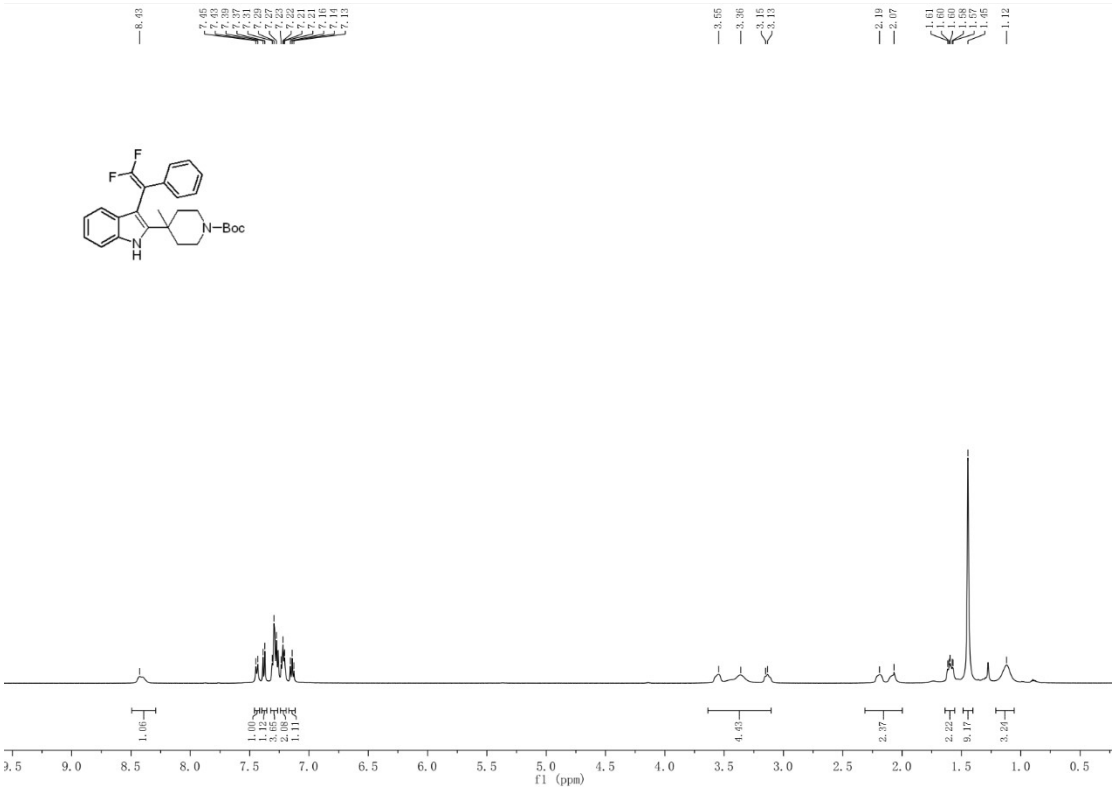
^{13}C NMR spectra of **3n** (100 MHz, $CDCl_3$)



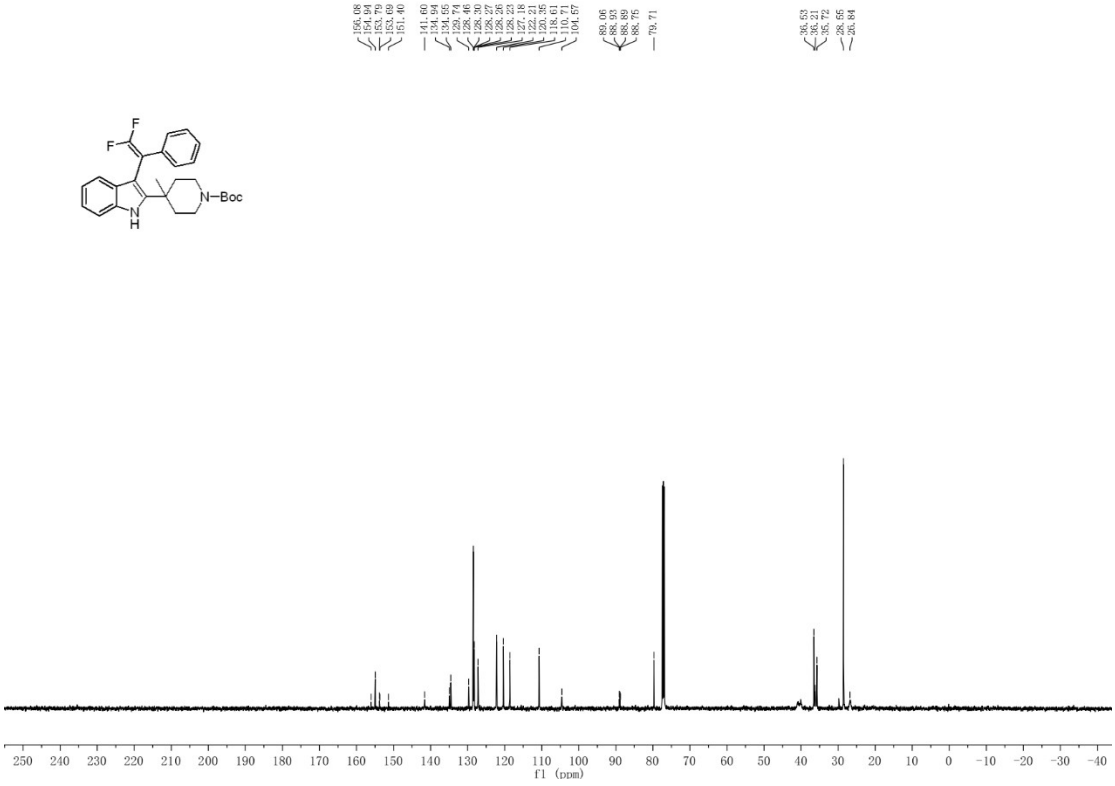
^{19}F NMR spectra of **3n** (376 MHz, $CDCl_3$)



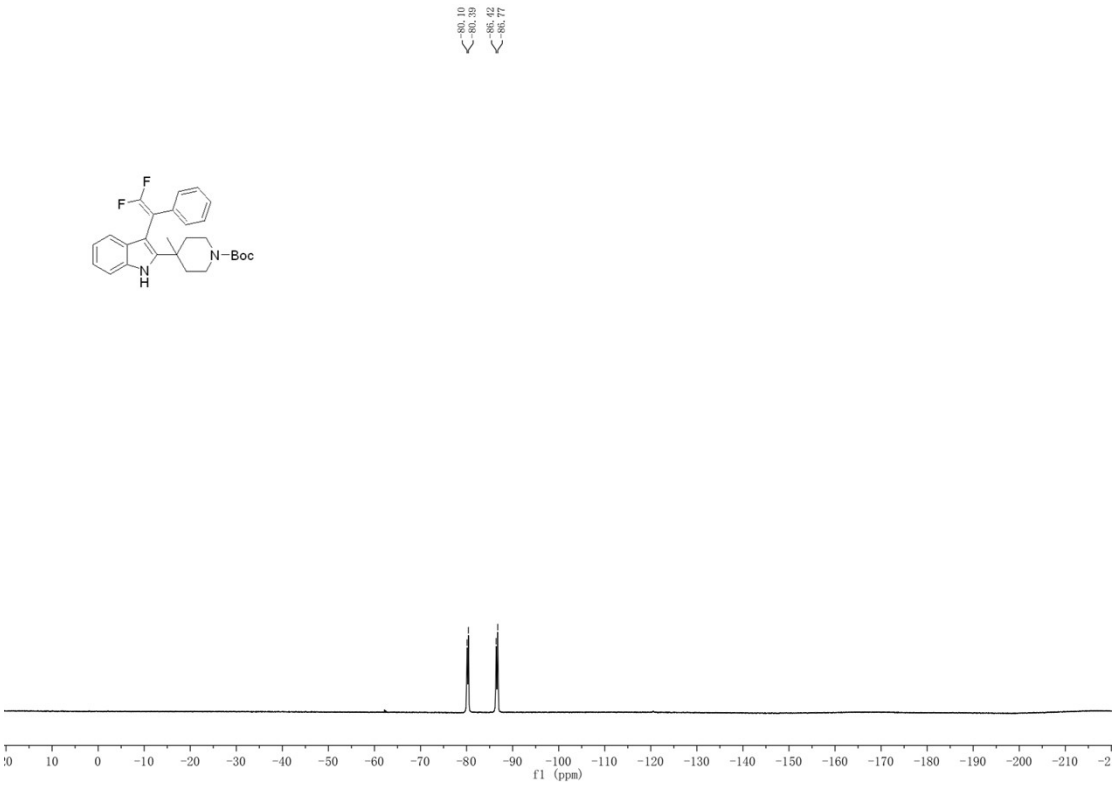
^{1}H NMR spectra of **3o** (500 MHz, $CDCl_3$)



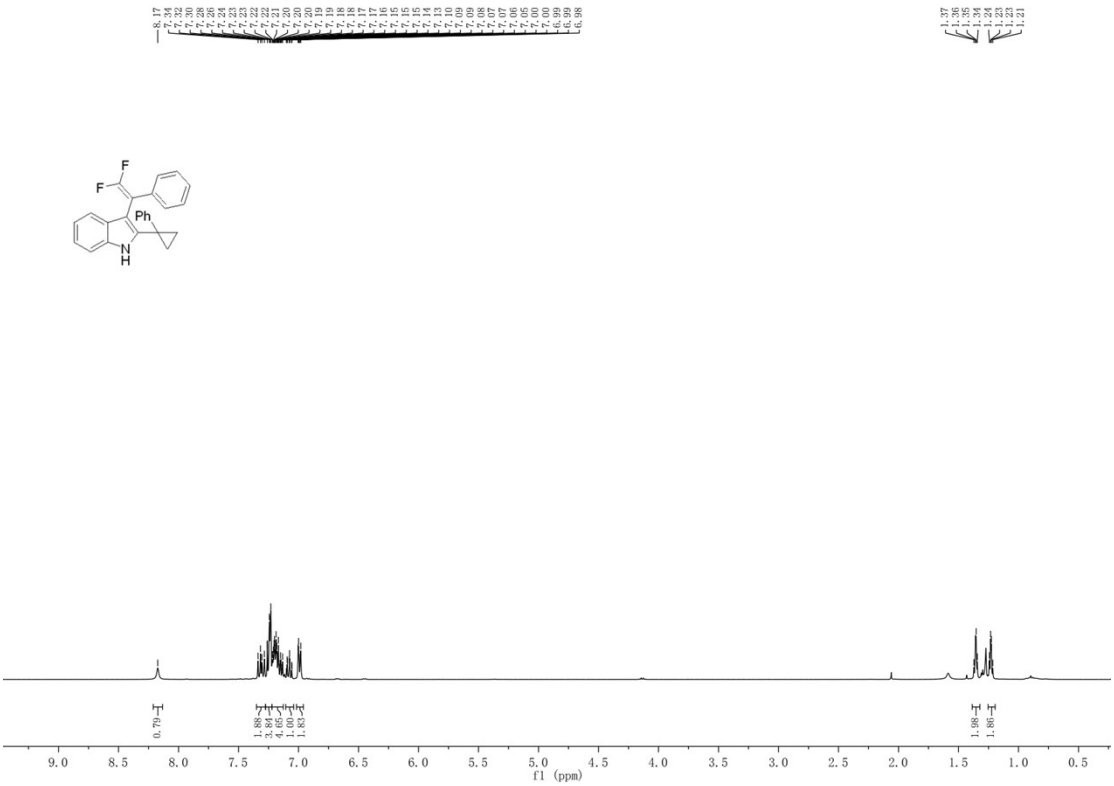
^{13}C NMR spectra of **3o** (125 MHz, $CDCl_3$)



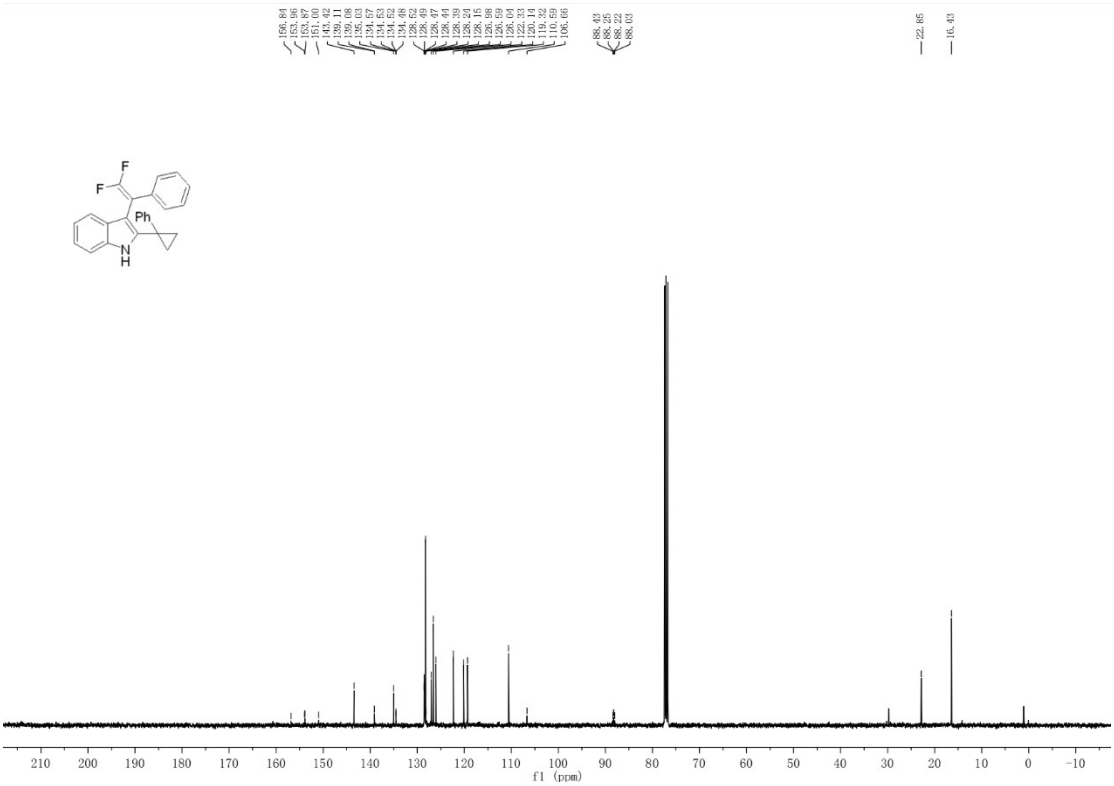
^{19}F NMR spectra of **3o** (376 MHz, $CDCl_3$)



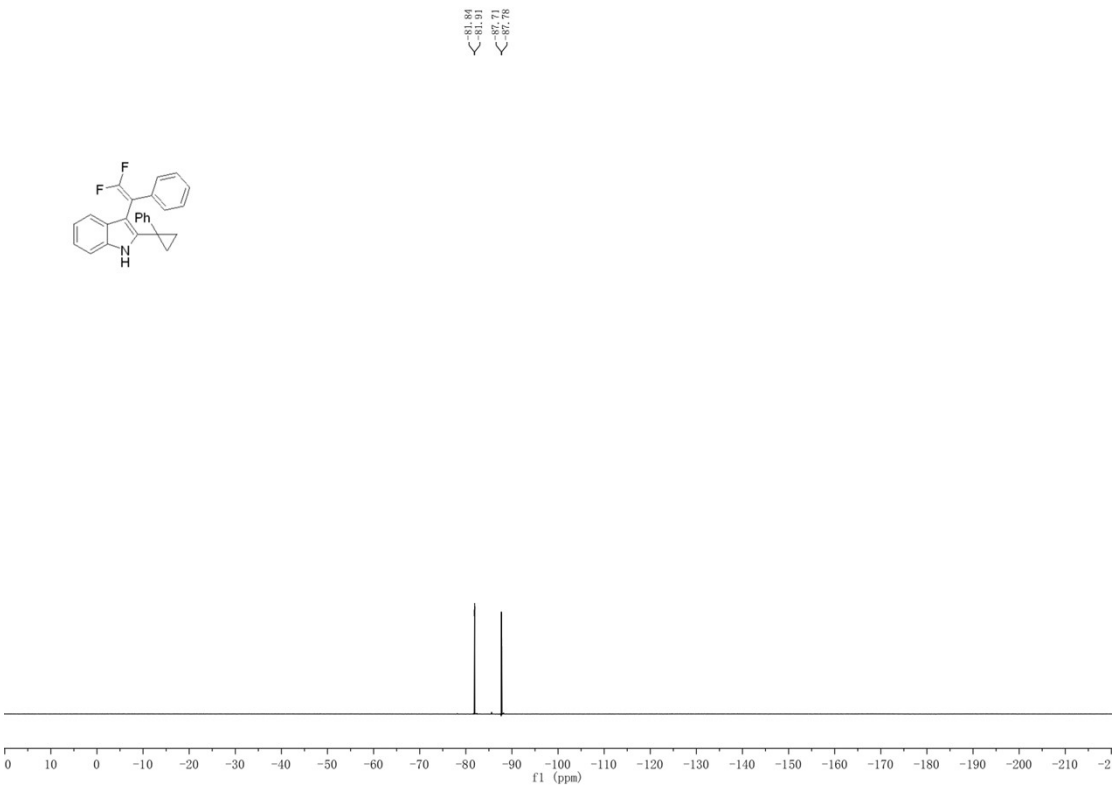
^{1}H NMR spectra of **3p** (400 MHz, $CDCl_3$)



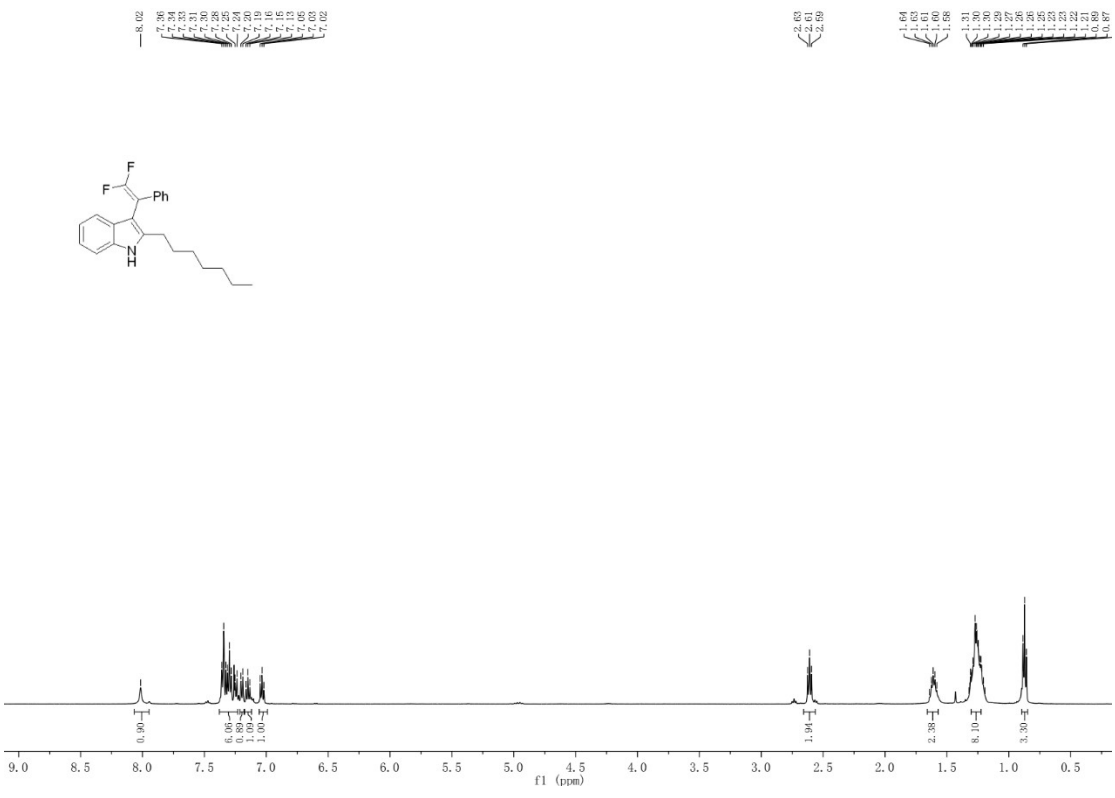
^{13}C NMR spectra of **3p** (100 MHz, $CDCl_3$)



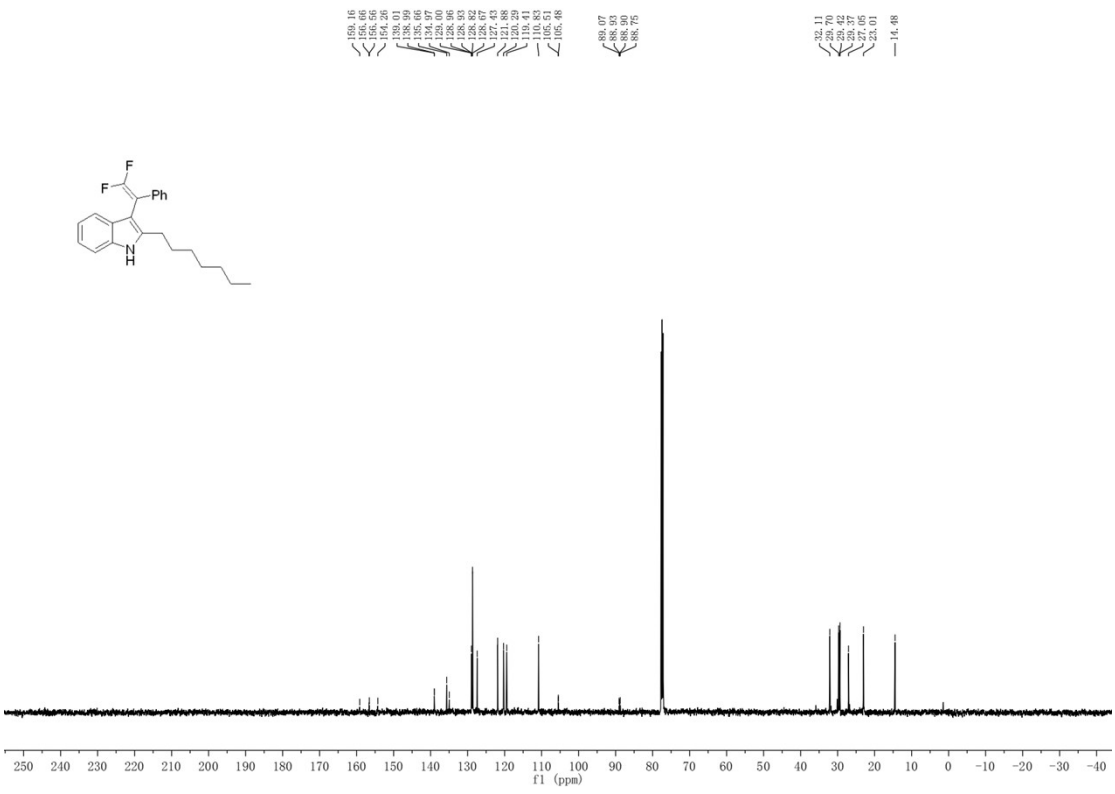
^{19}F NMR spectra of **3p** (376 MHz, $CDCl_3$)



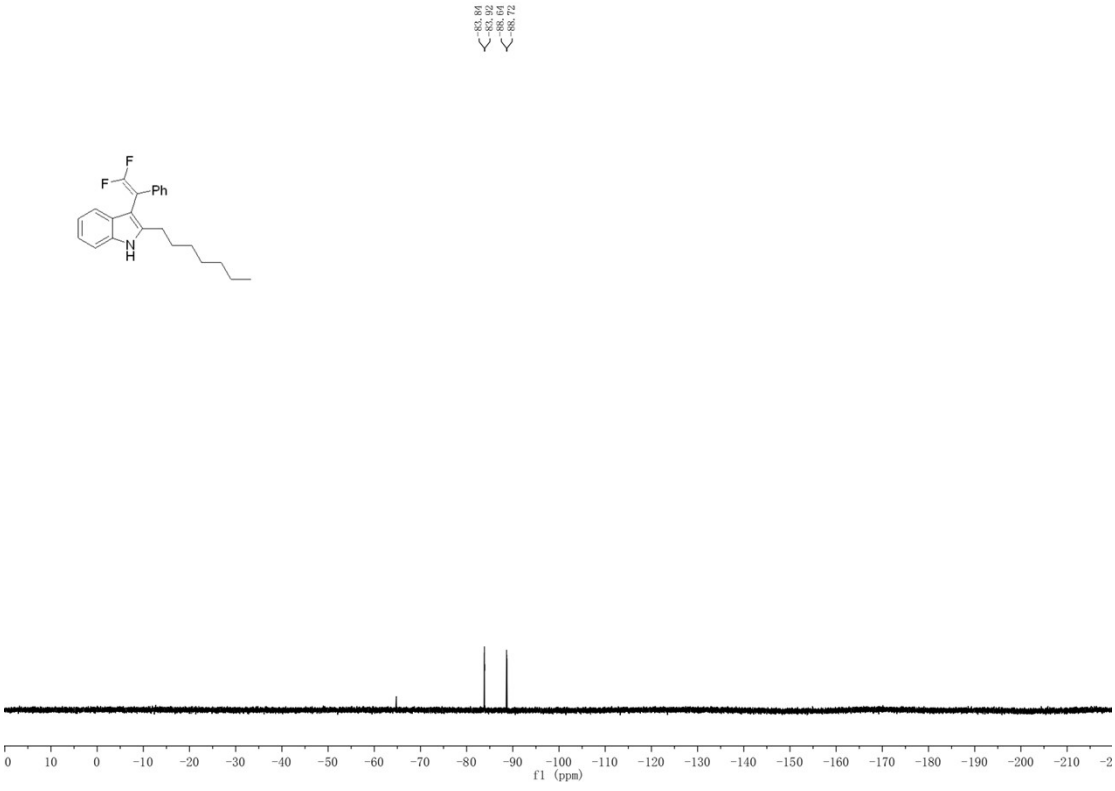
^{1}H NMR spectra of **3q** (500 MHz, $CDCl_3$)



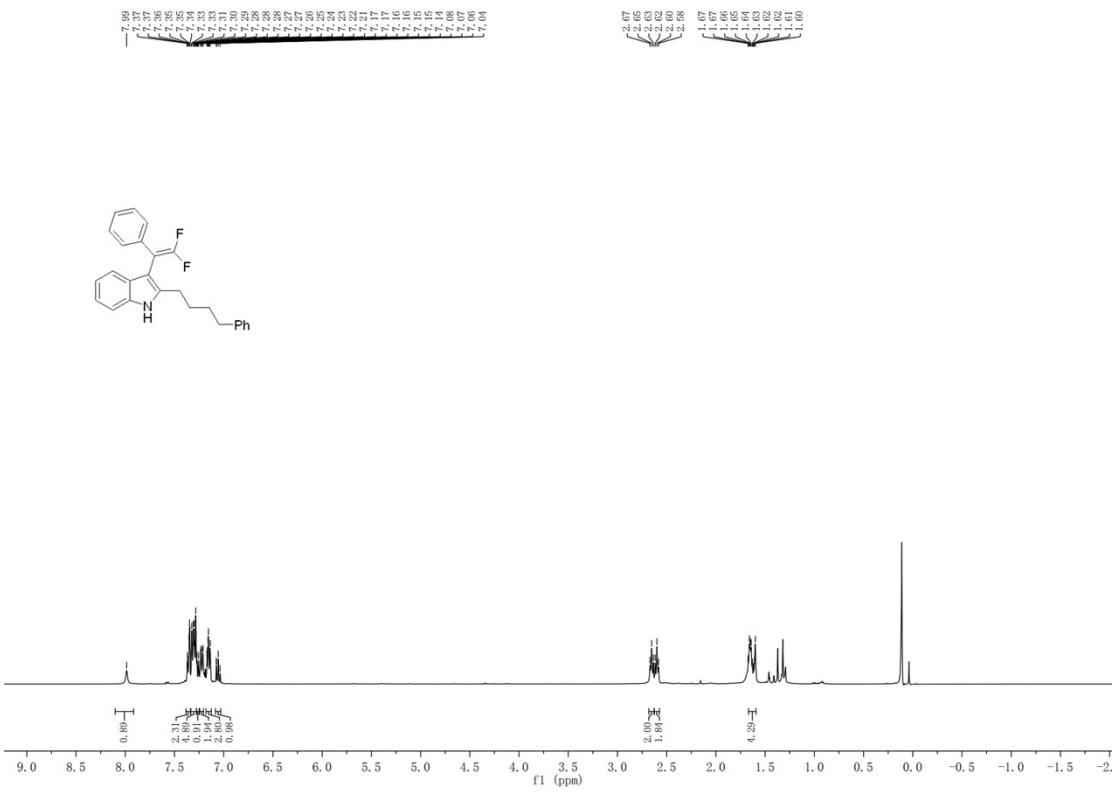
^{13}C NMR spectra of **3q** (125 MHz, $CDCl_3$)



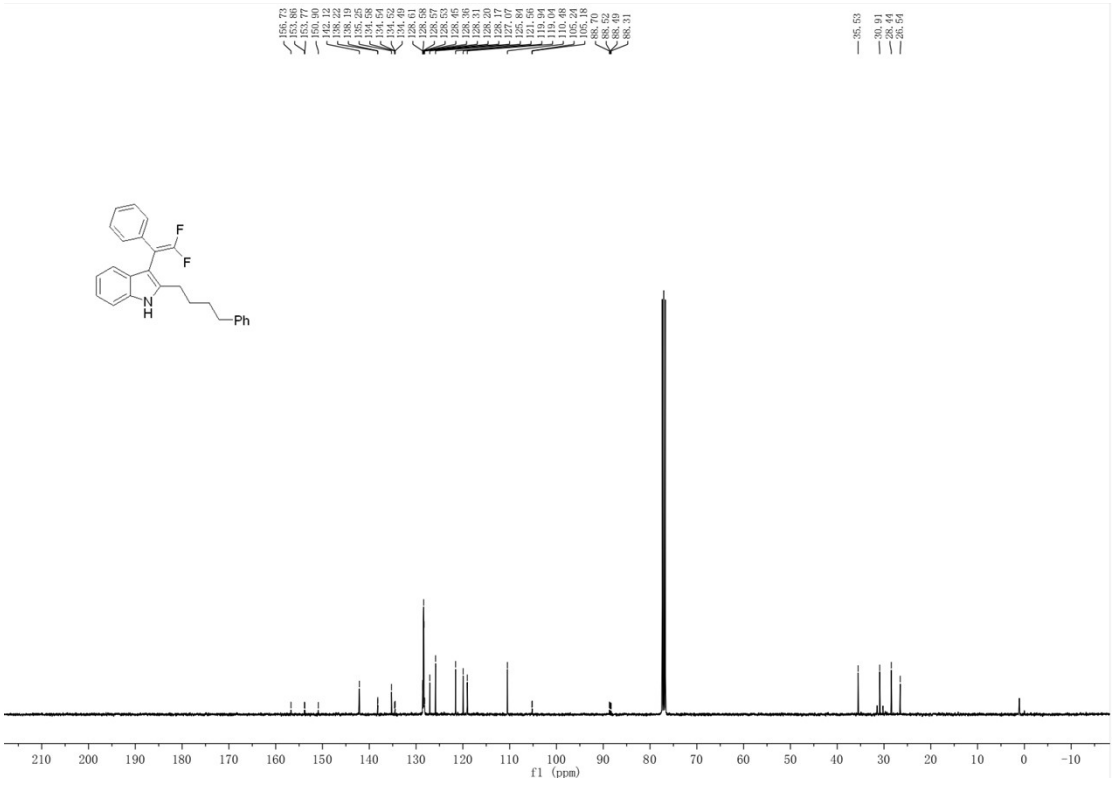
^{19}F NMR spectra of **3q** (376 MHz, $CDCl_3$)



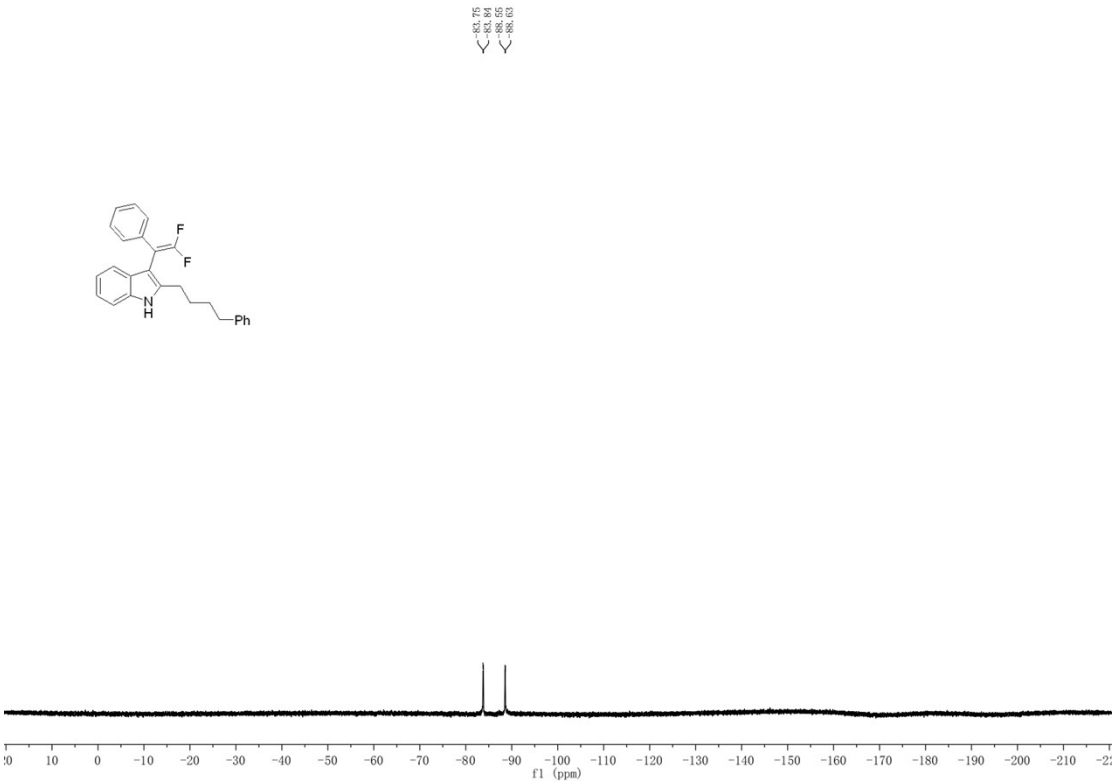
^{1}H NMR spectra of **3r** (400 MHz, $CDCl_3$)



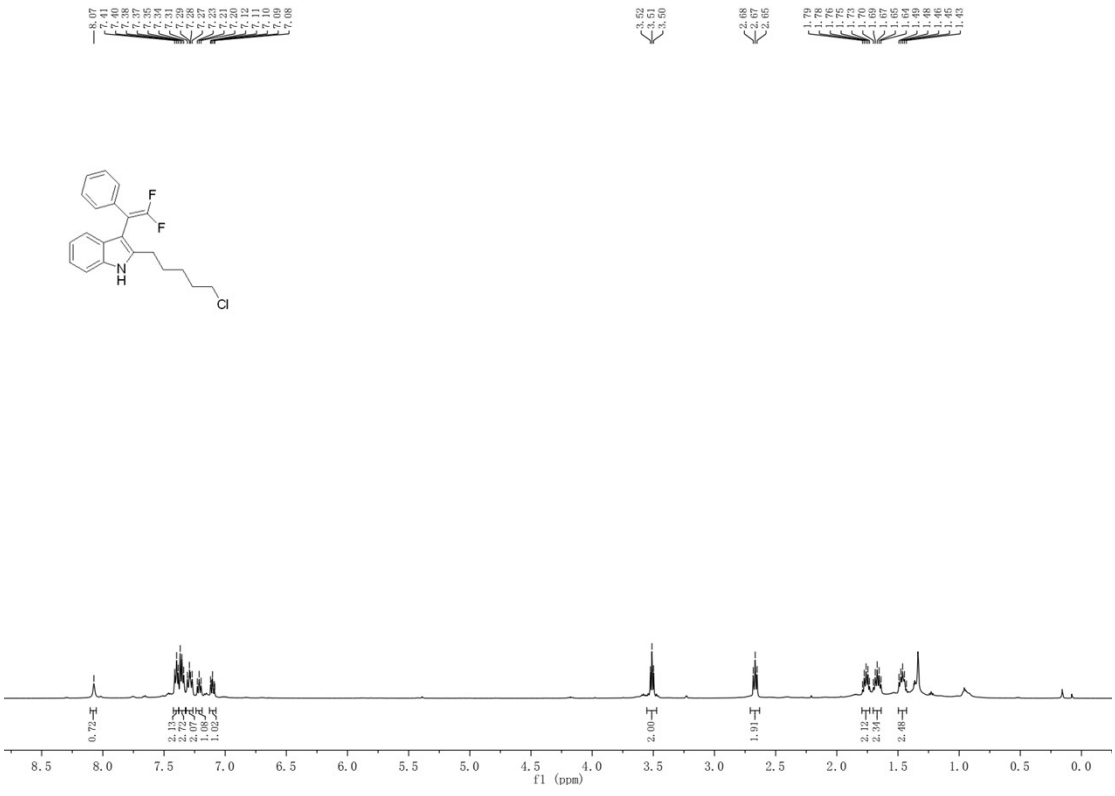
^{13}C NMR spectra of **3r** (100 MHz, $CDCl_3$)



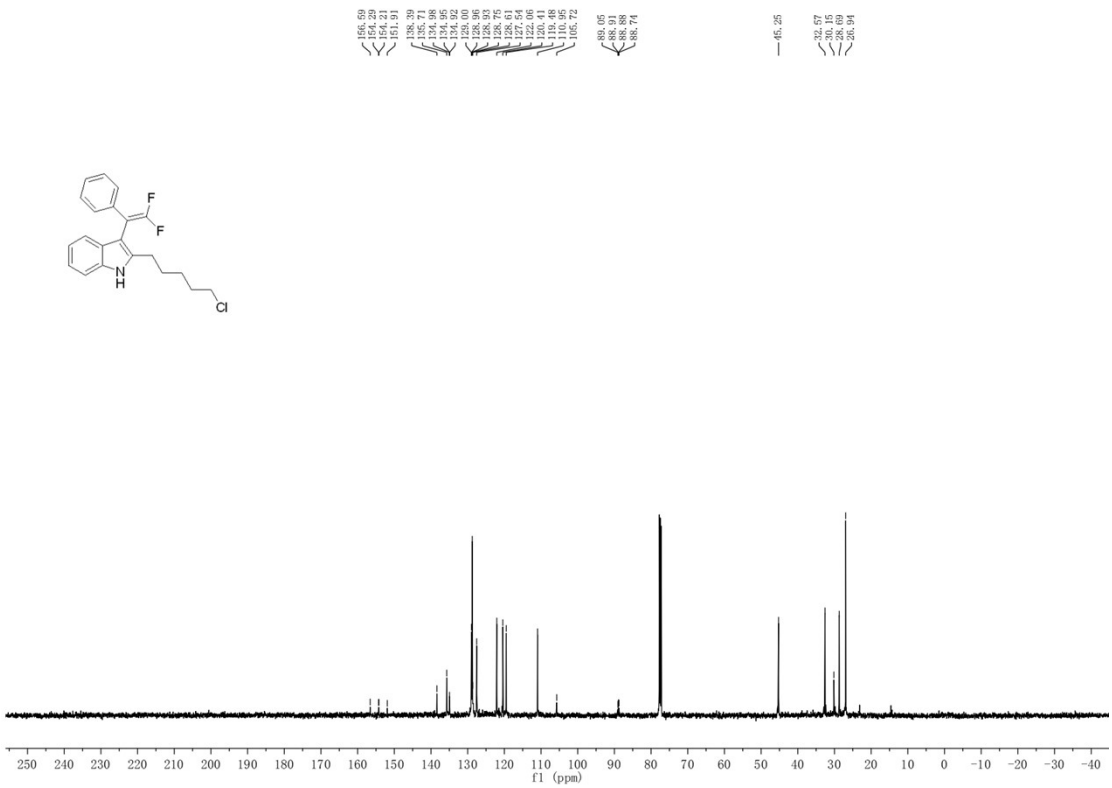
^{19}F NMR spectra of **3r** (376 MHz, $CDCl_3$)



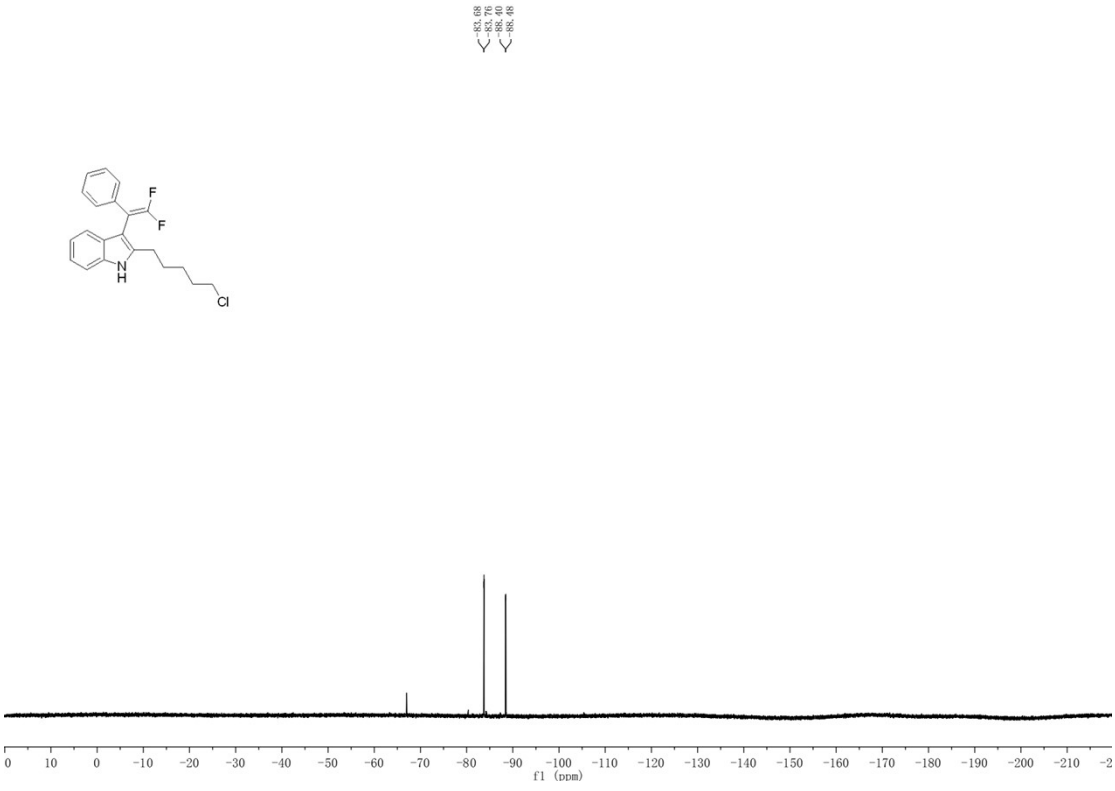
^{1}H NMR spectra of **3s** (500 MHz, $CDCl_3$)



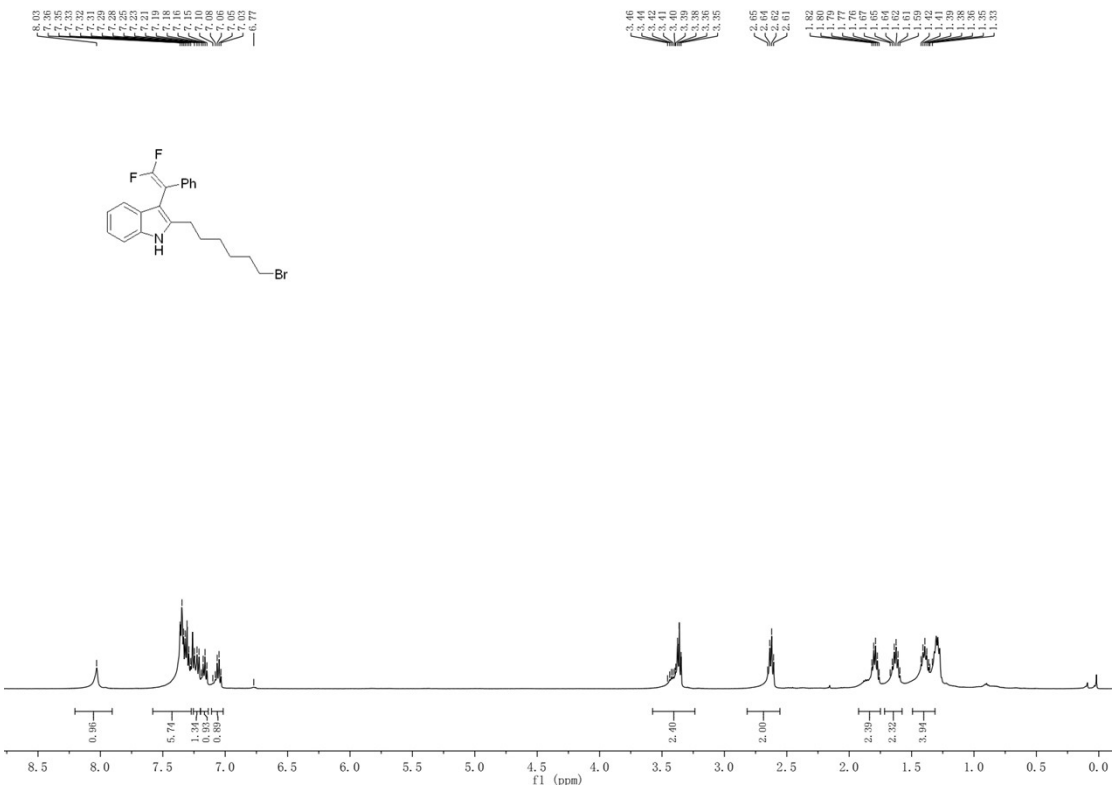
^{13}C NMR spectra of **3s** (125 MHz, $CDCl_3$)



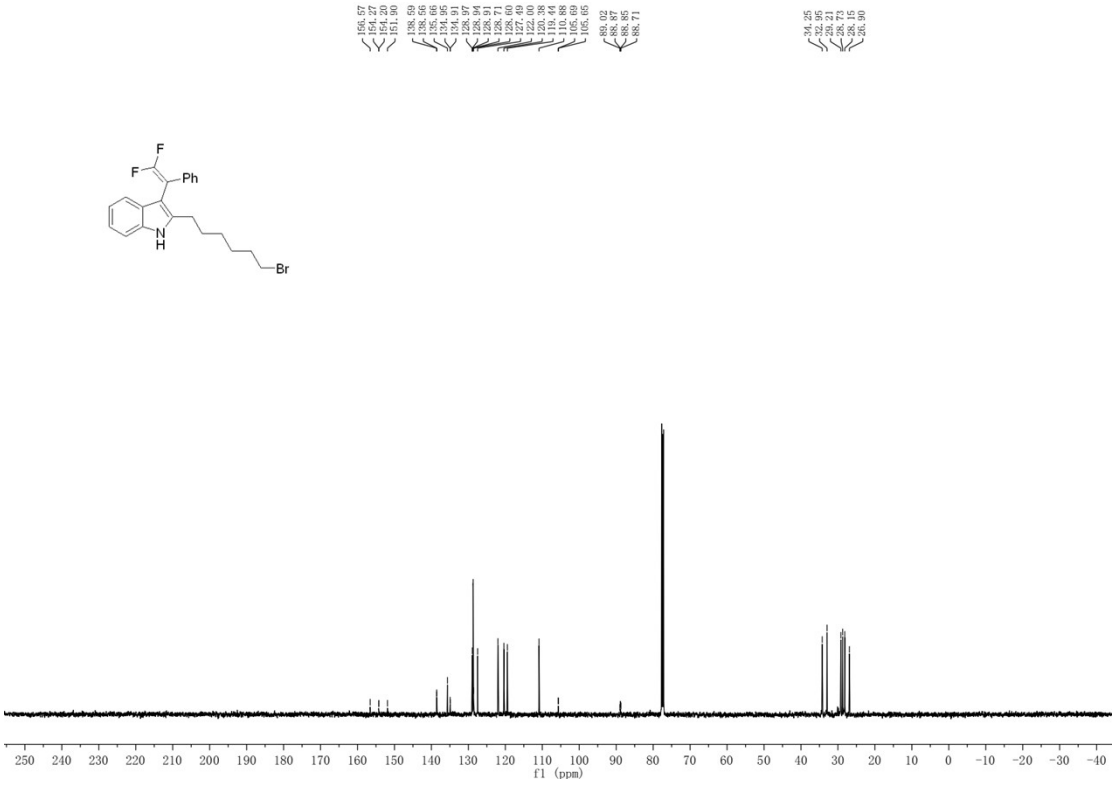
^{19}F NMR spectra of **3s** (376 MHz, $CDCl_3$)



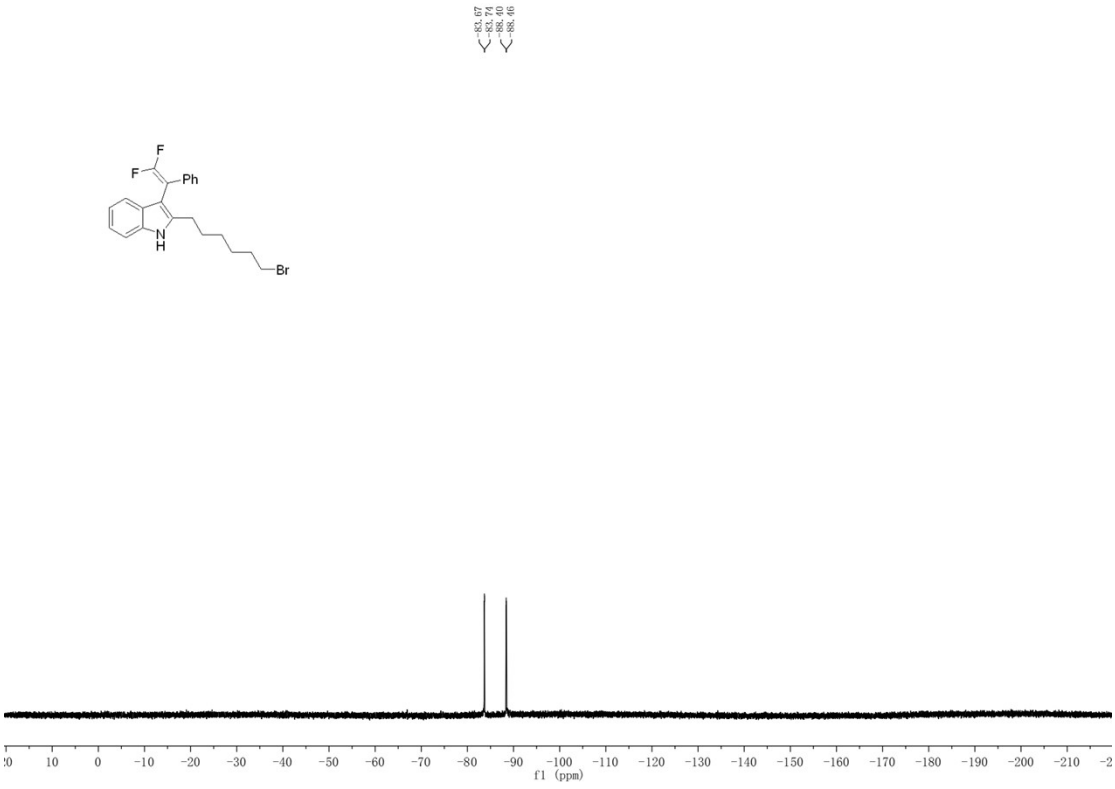
^{1}H NMR spectra of **3t** (500 MHz, $CDCl_3$)



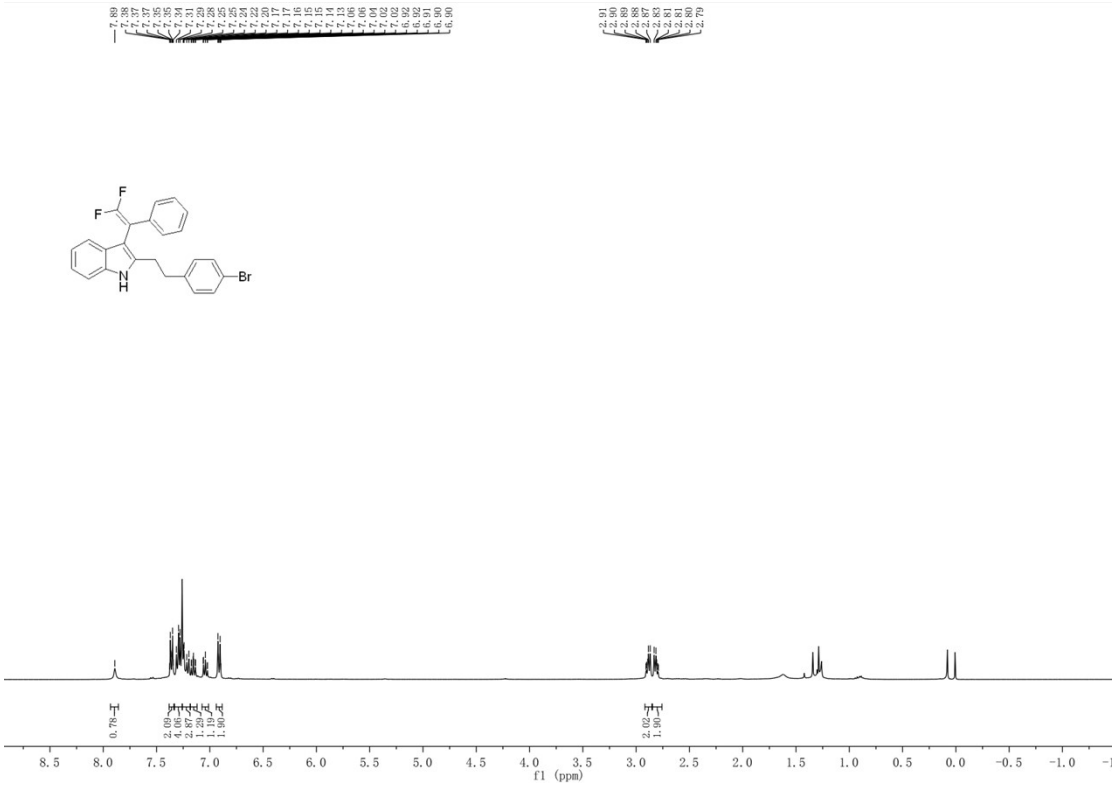
^{13}C NMR spectra of **3t** (125 MHz, $CDCl_3$)



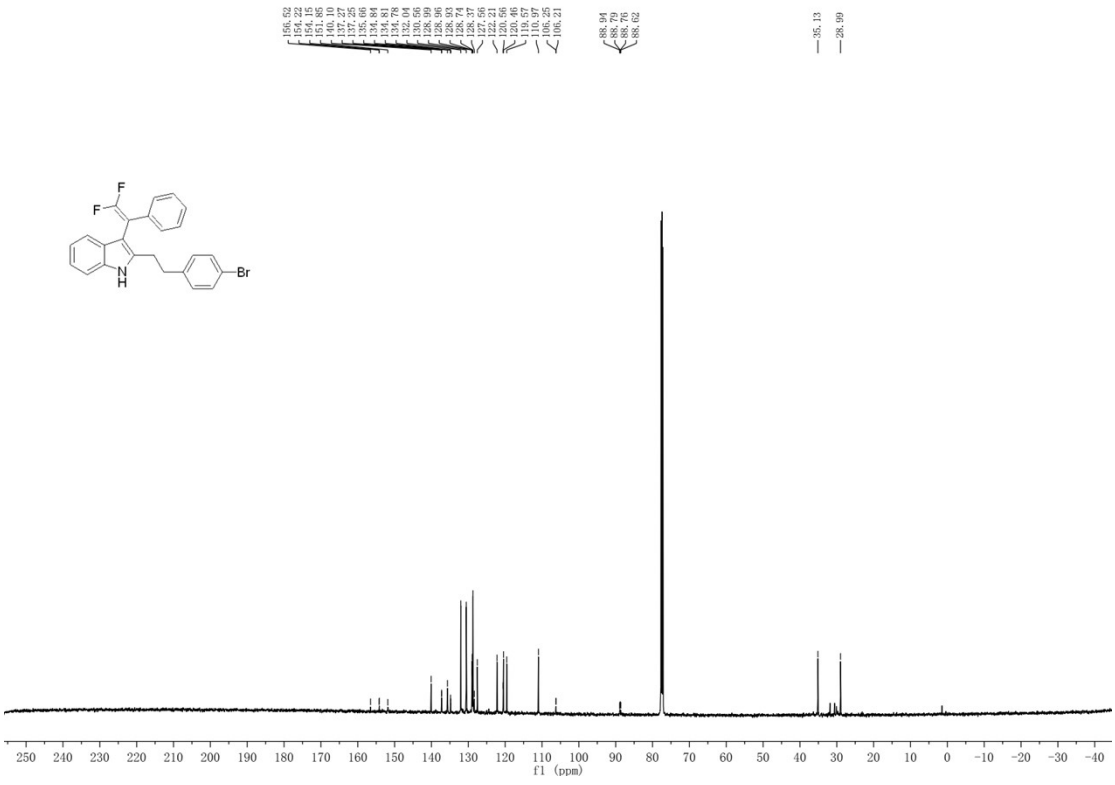
^{19}F NMR spectra of **3t** (470 MHz, $CDCl_3$)



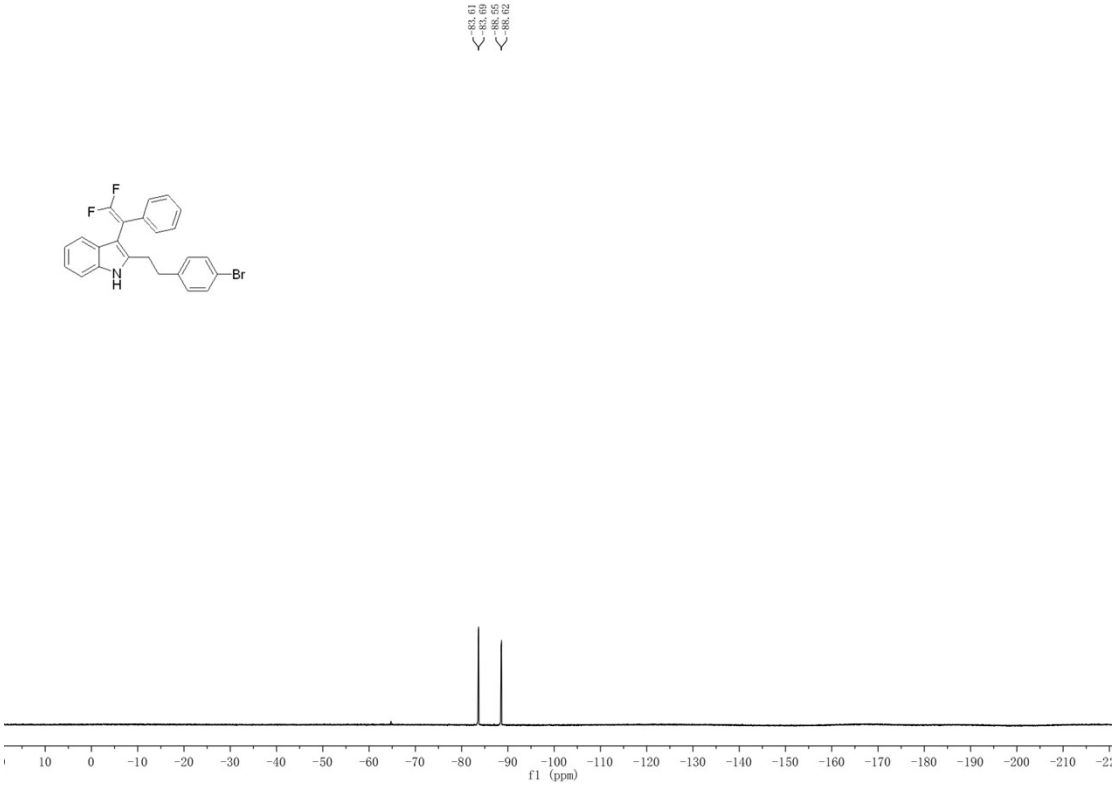
^{1}H NMR spectra of **3u** (400 MHz, $CDCl_3$)



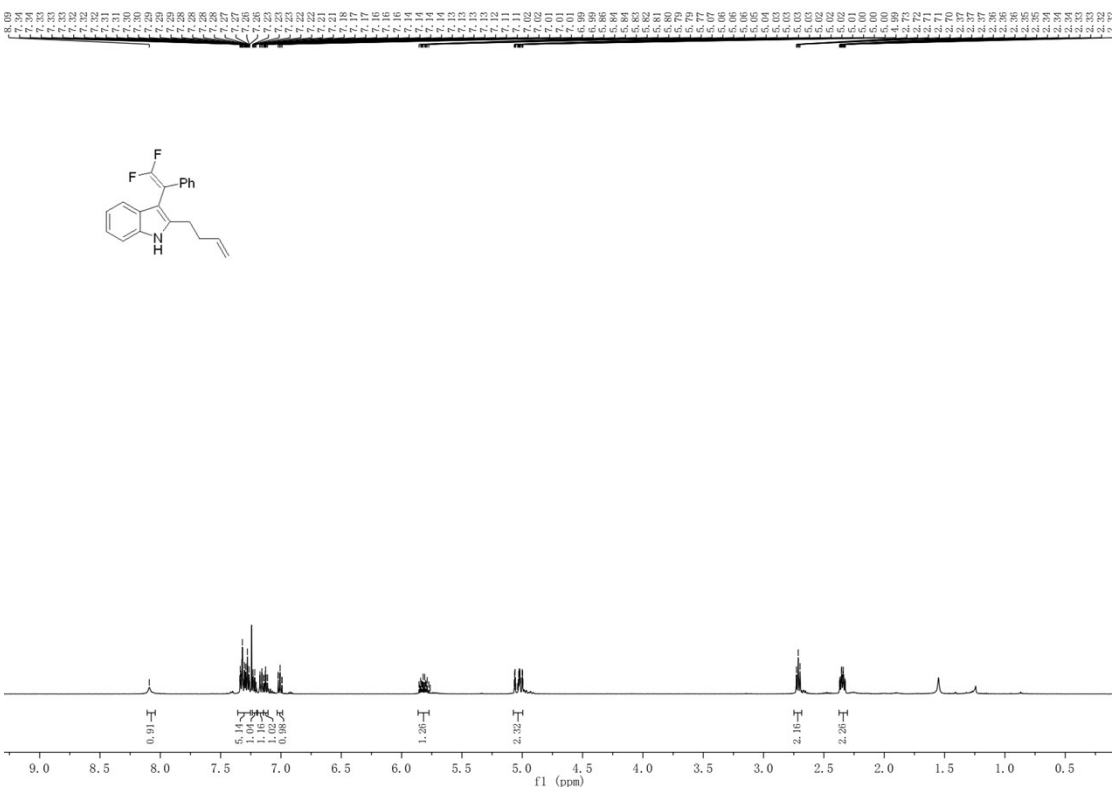
^{13}C NMR spectra of **3u** (125 MHz, $CDCl_3$)



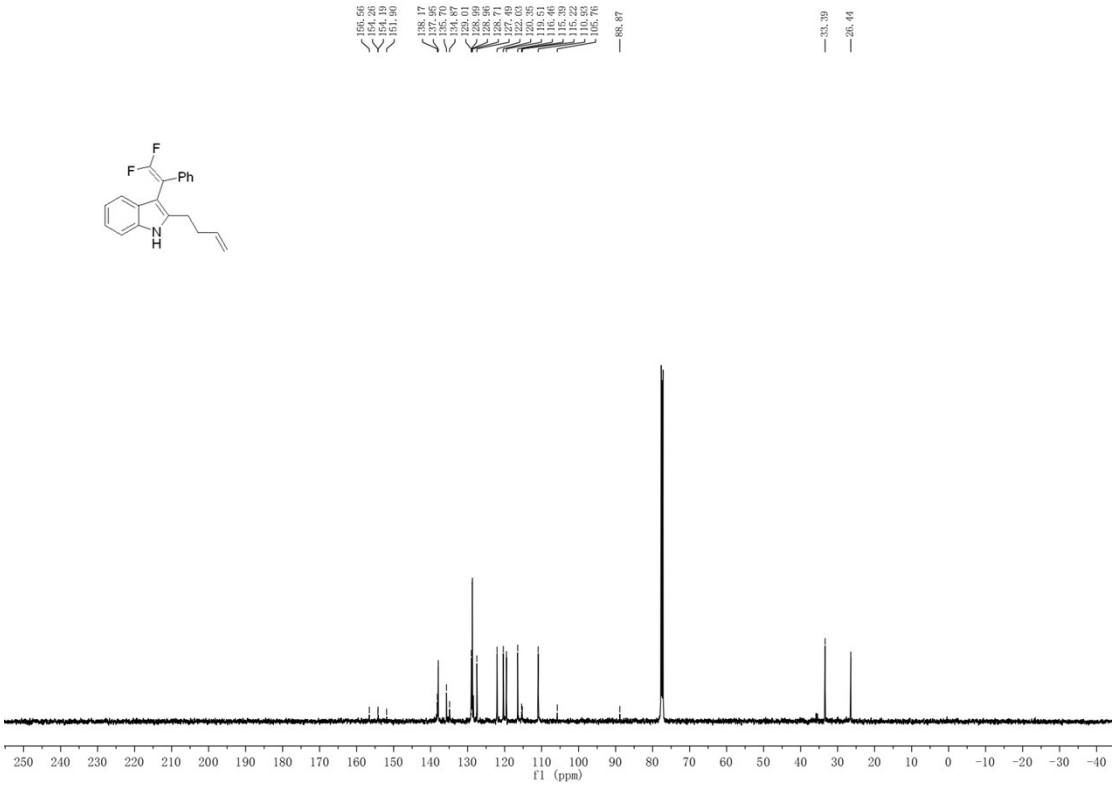
^{19}F NMR spectra of **3u** (376 MHz, $CDCl_3$)



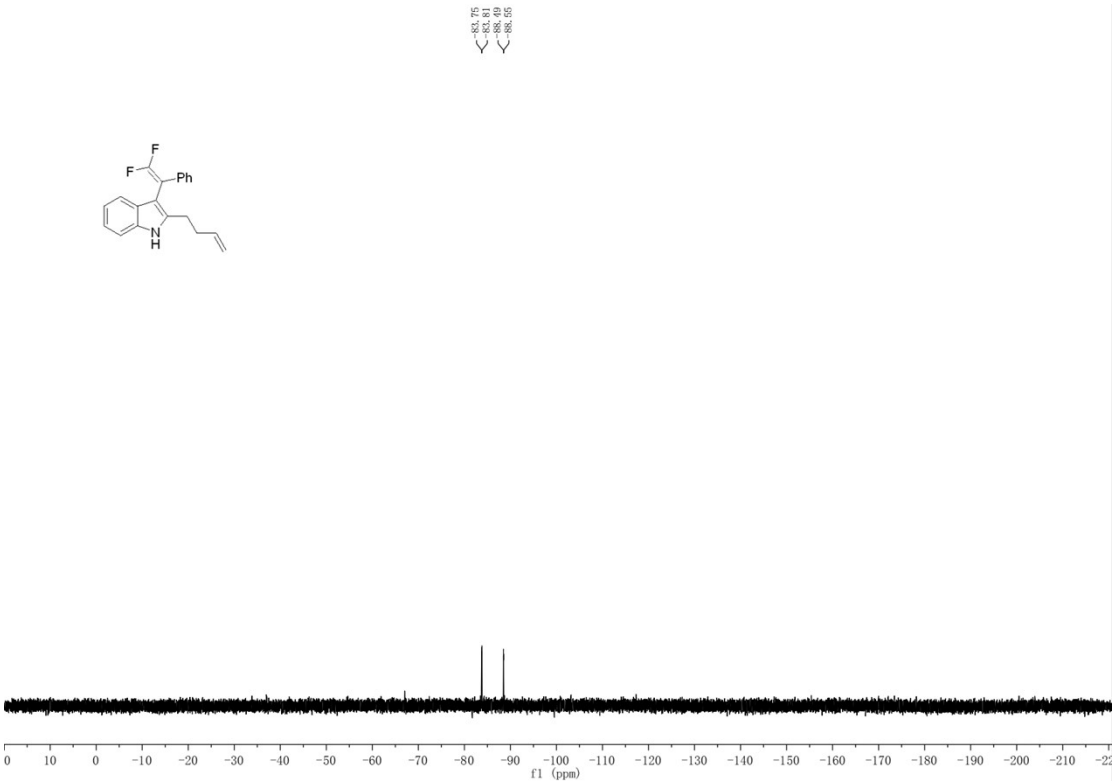
^{1}H NMR spectra of **3v** (500 MHz, $CDCl_3$)



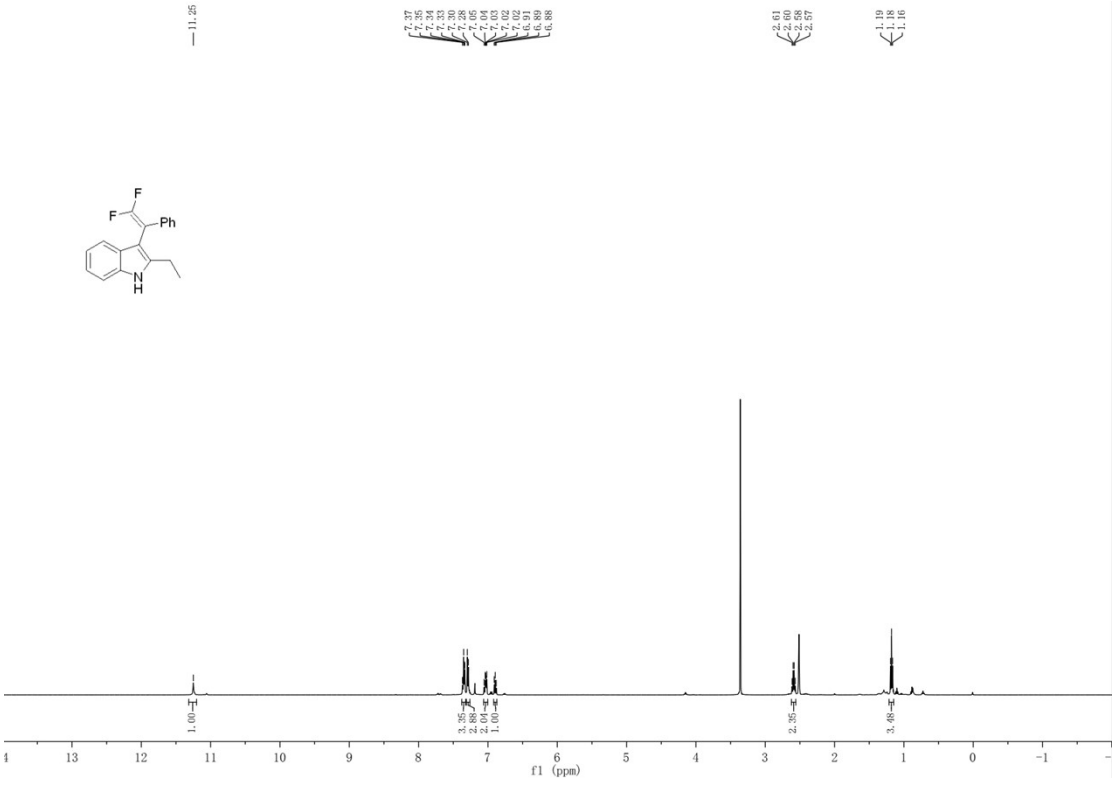
^{13}C NMR spectra of **3v** (125 MHz, $CDCl_3$)



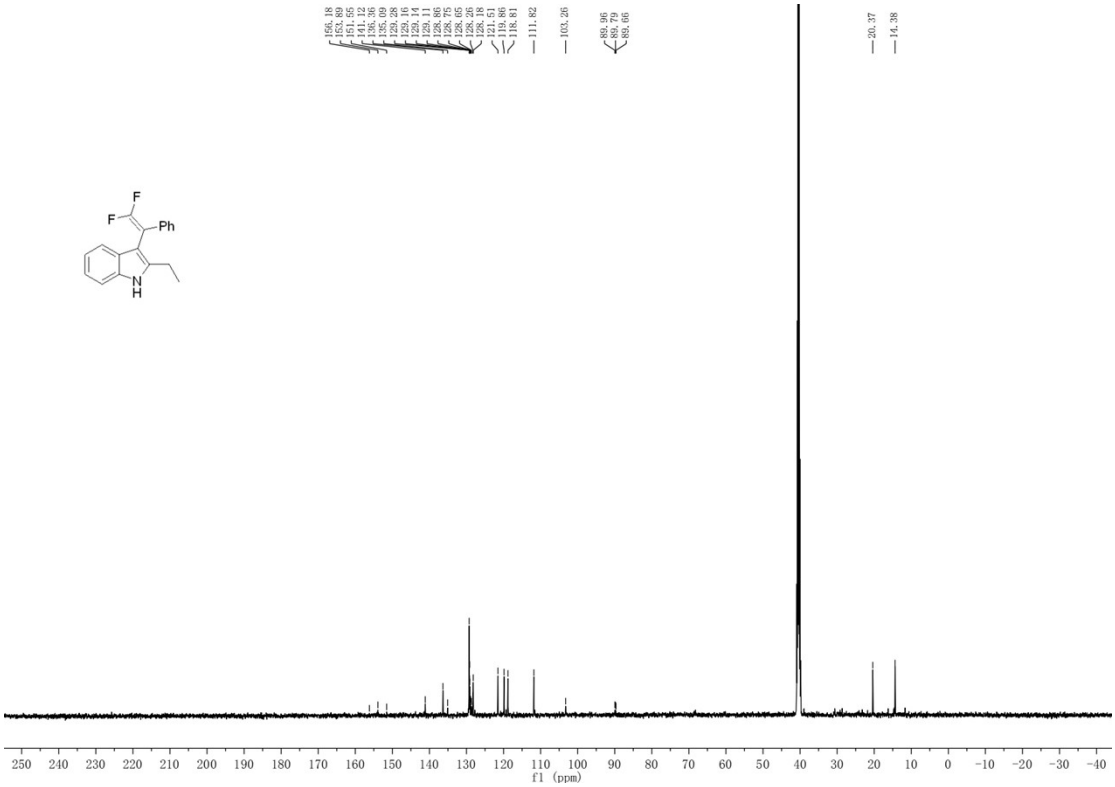
^{19}F NMR spectra of **3v** (470 MHz, $CDCl_3$)



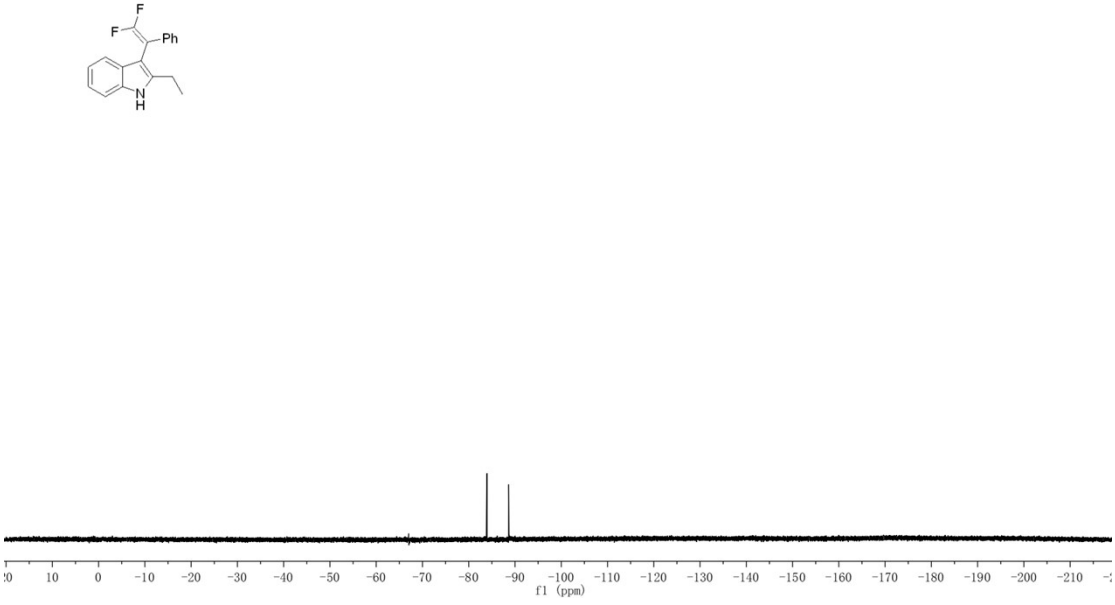
^{1}H NMR spectra of **3w** (500 MHz, DMSO-d_6)



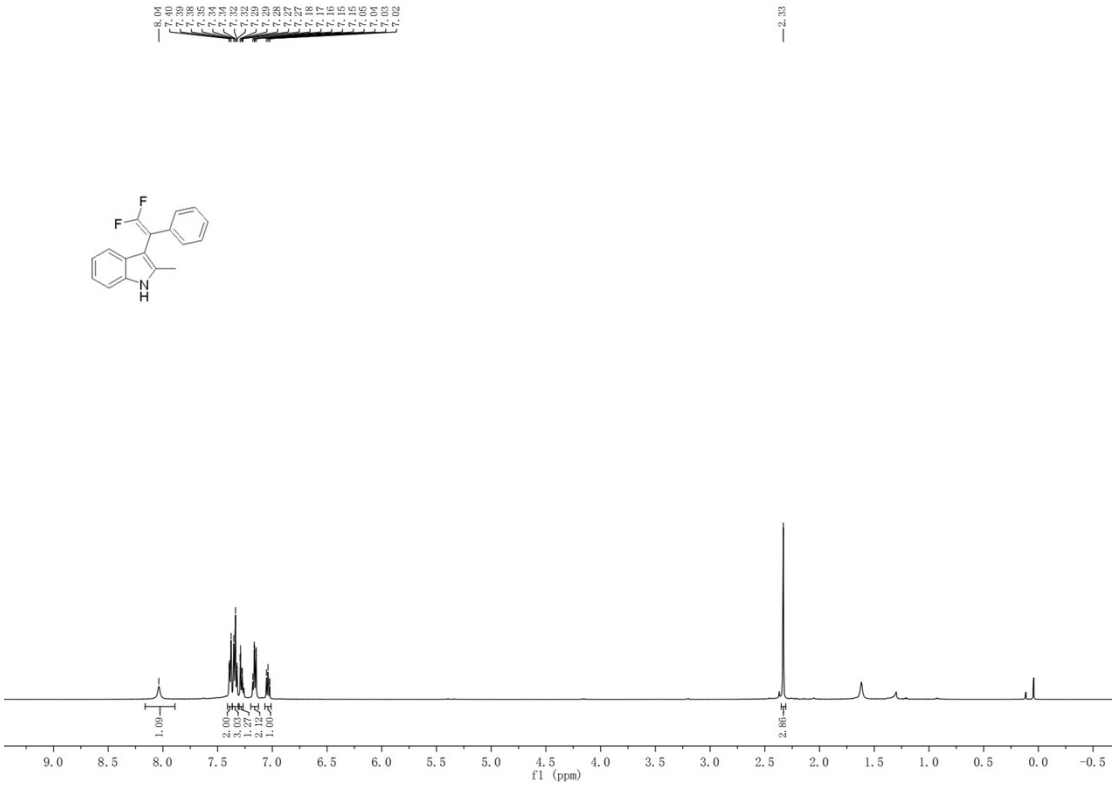
^{13}C NMR spectra of **3w** (125 MHz, DMSO-d_6)



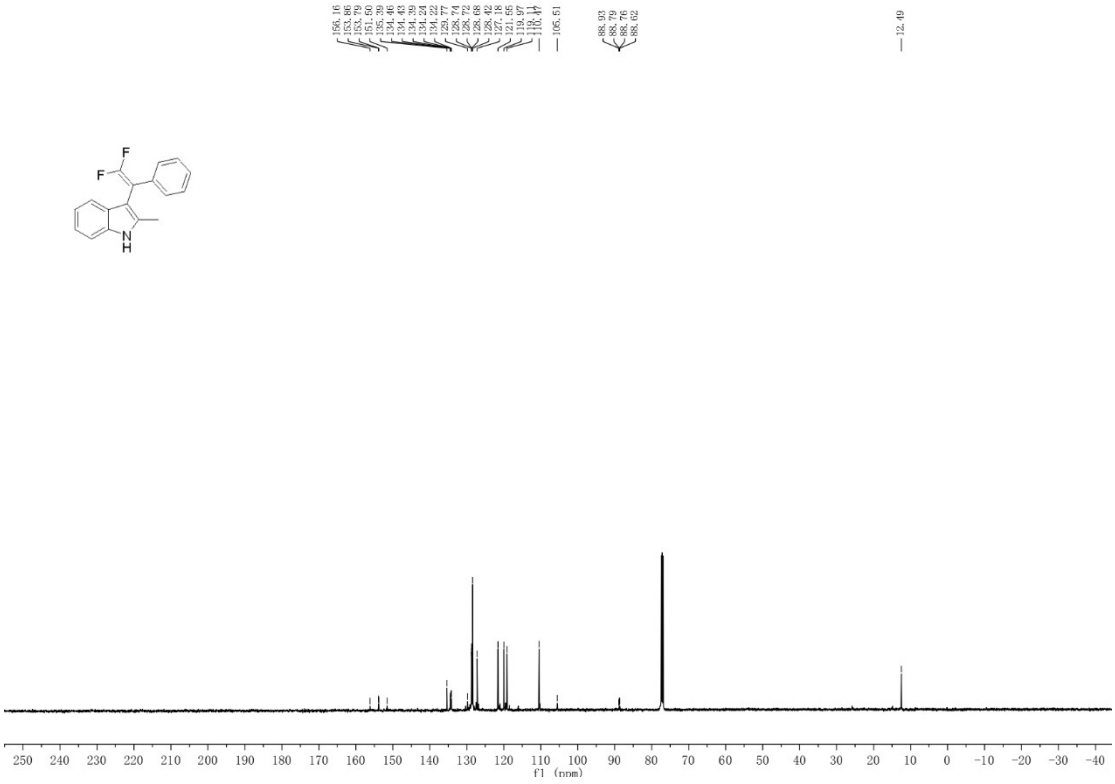
^{19}F NMR spectra of **3w** (470 MHz, $CDCl_3$)



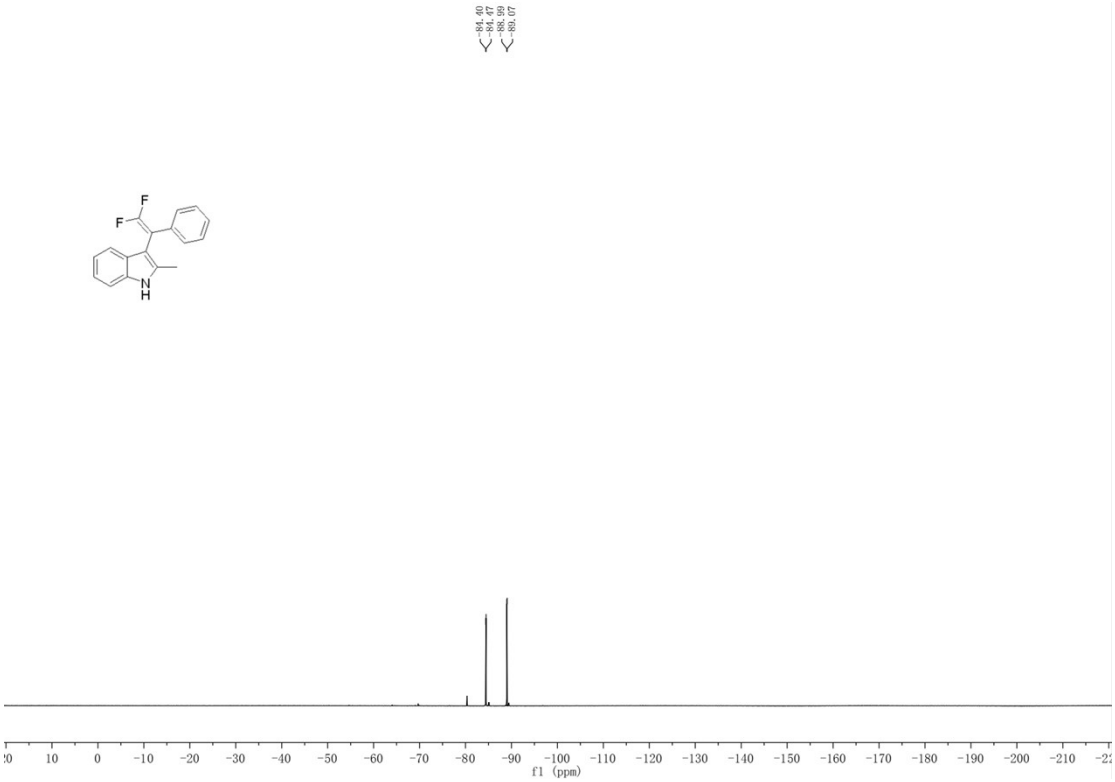
^{1}H NMR spectra of **3x** (500 MHz, $CDCl_3$)



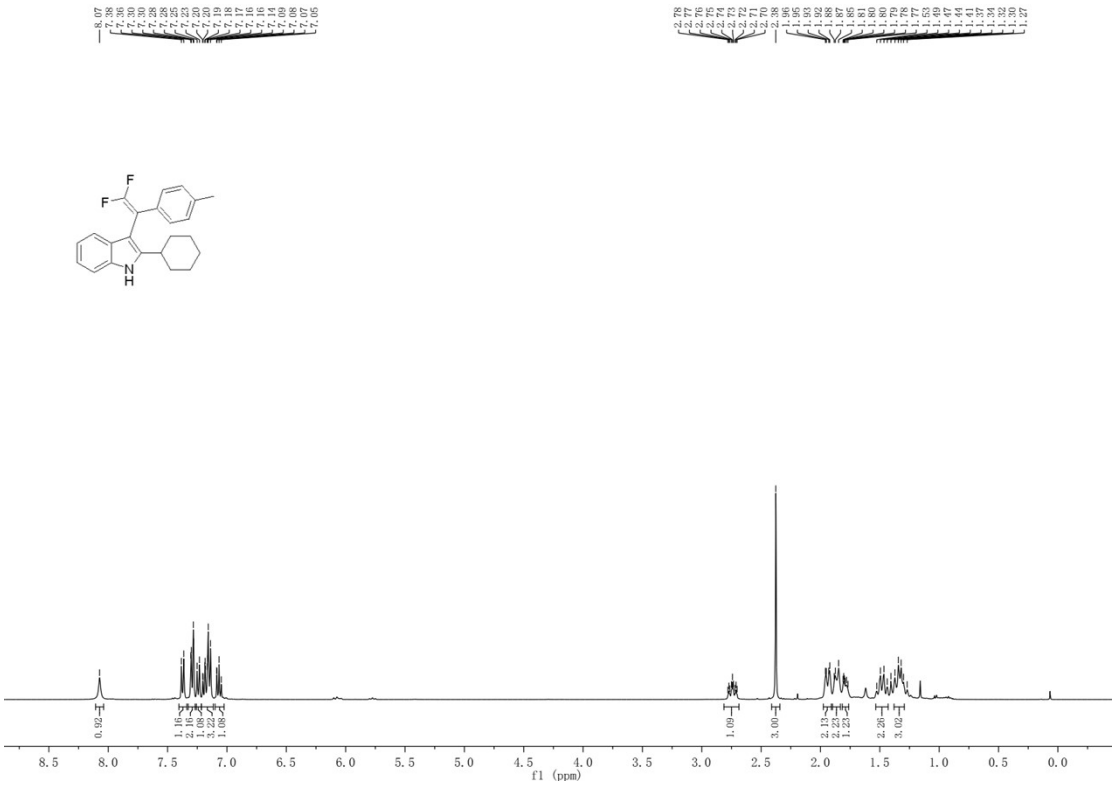
^{13}C NMR spectra of **3x** (125 MHz, $CDCl_3$)



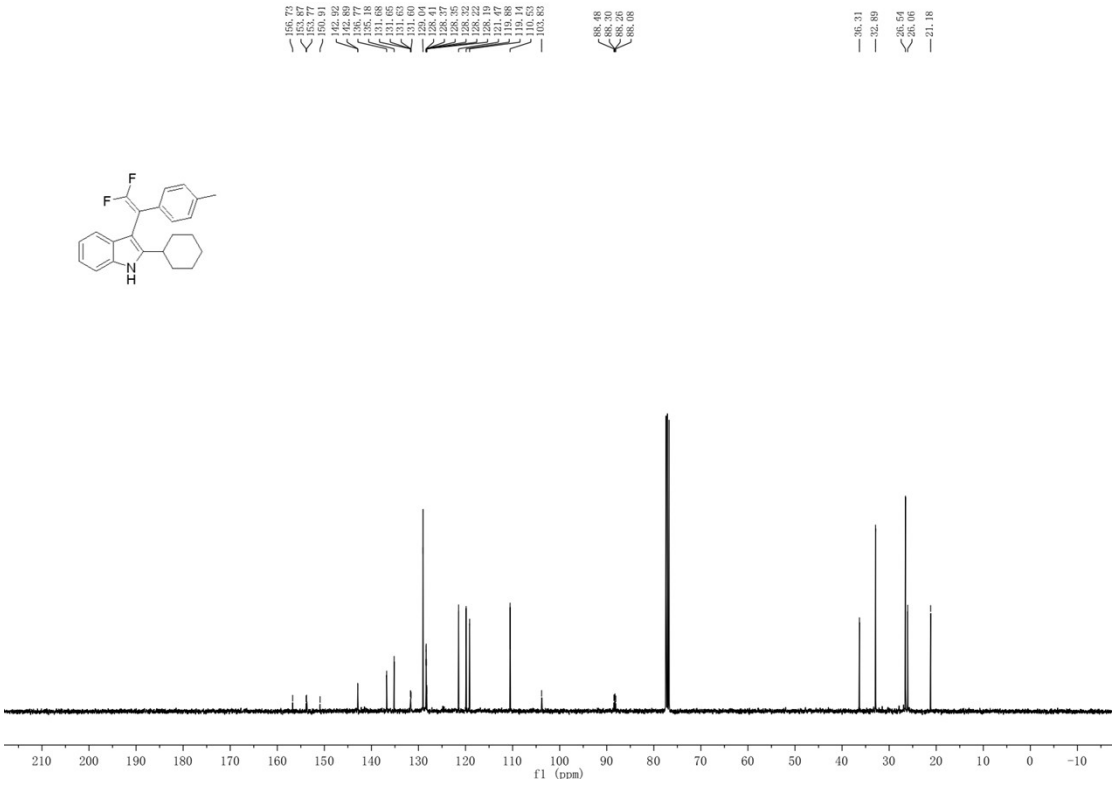
^{19}F NMR spectra of **3x** (376 MHz, $CDCl_3$)



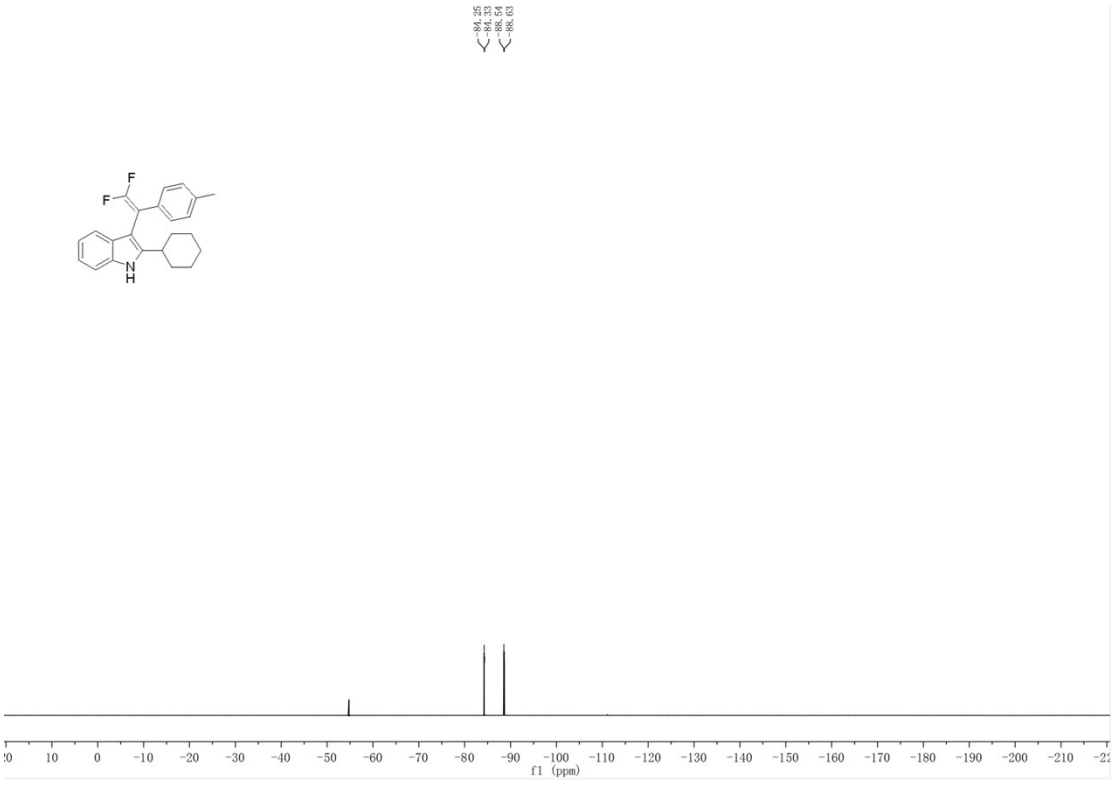
^{1}H NMR spectra of **3y** (400 MHz, $CDCl_3$)



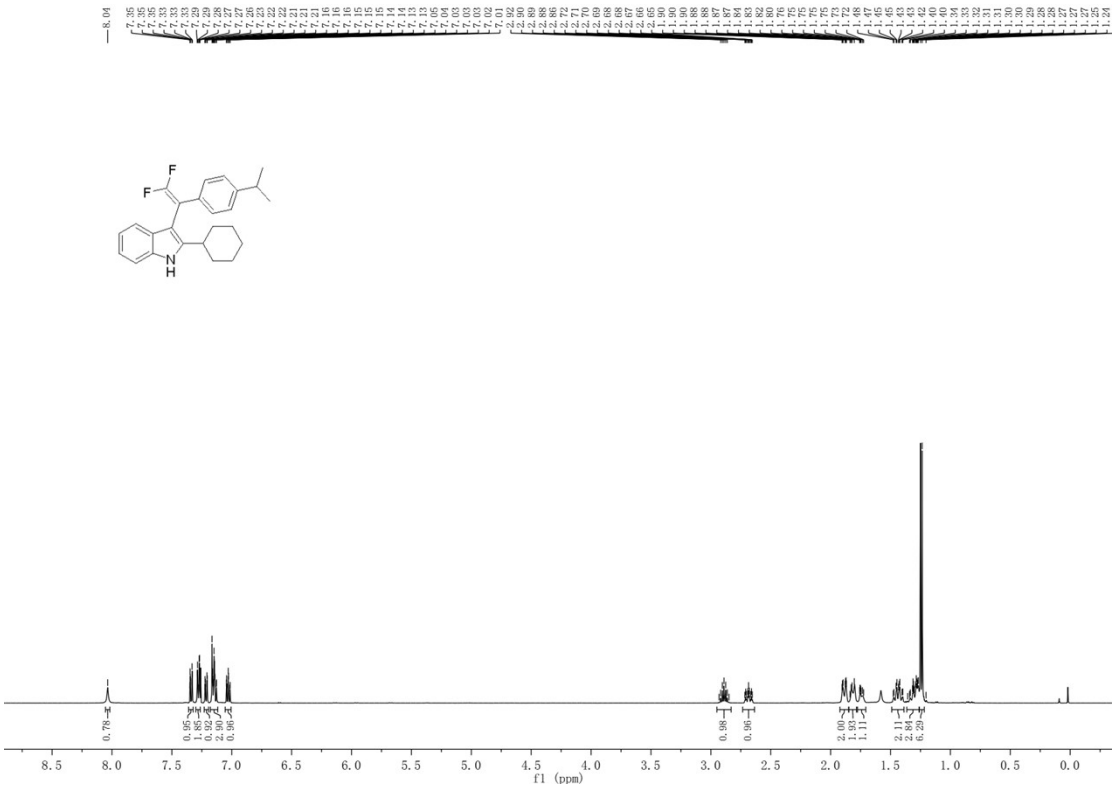
^{13}C NMR spectra of **3y** (100 MHz, $CDCl_3$)



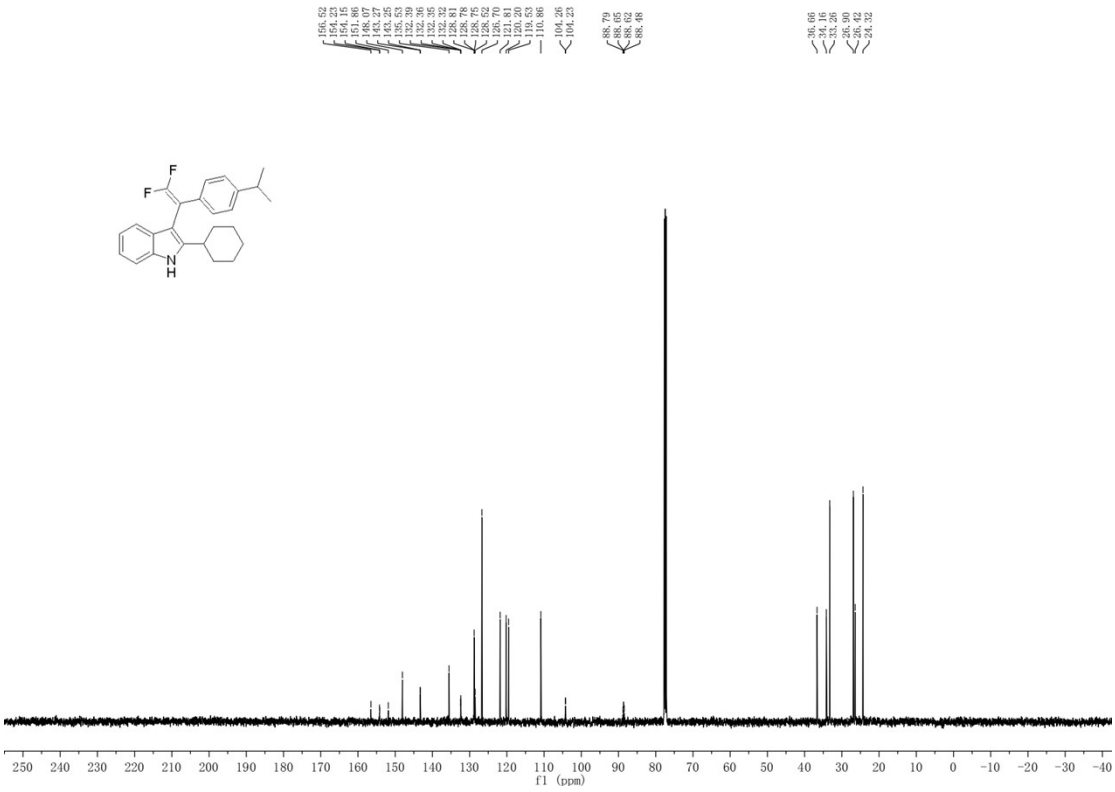
^{19}F NMR spectra of **3y** (376 MHz, $CDCl_3$)



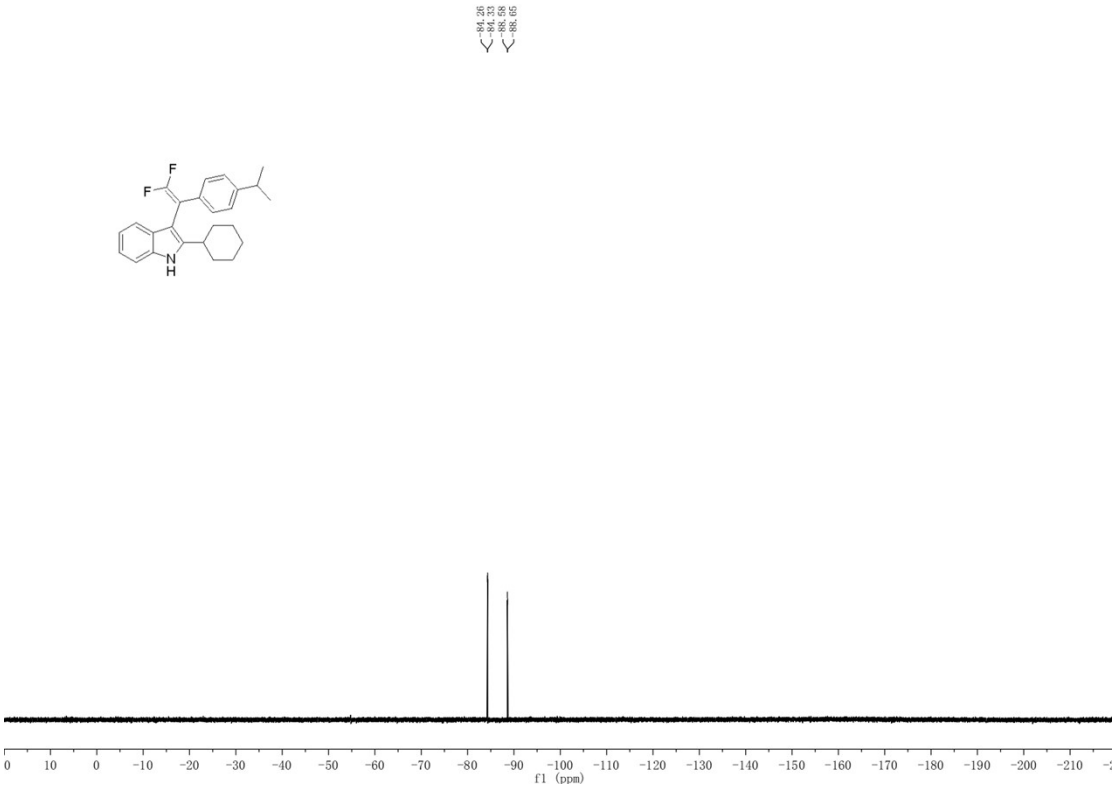
^{1}H NMR spectra of **3z** (500 MHz, $CDCl_3$)



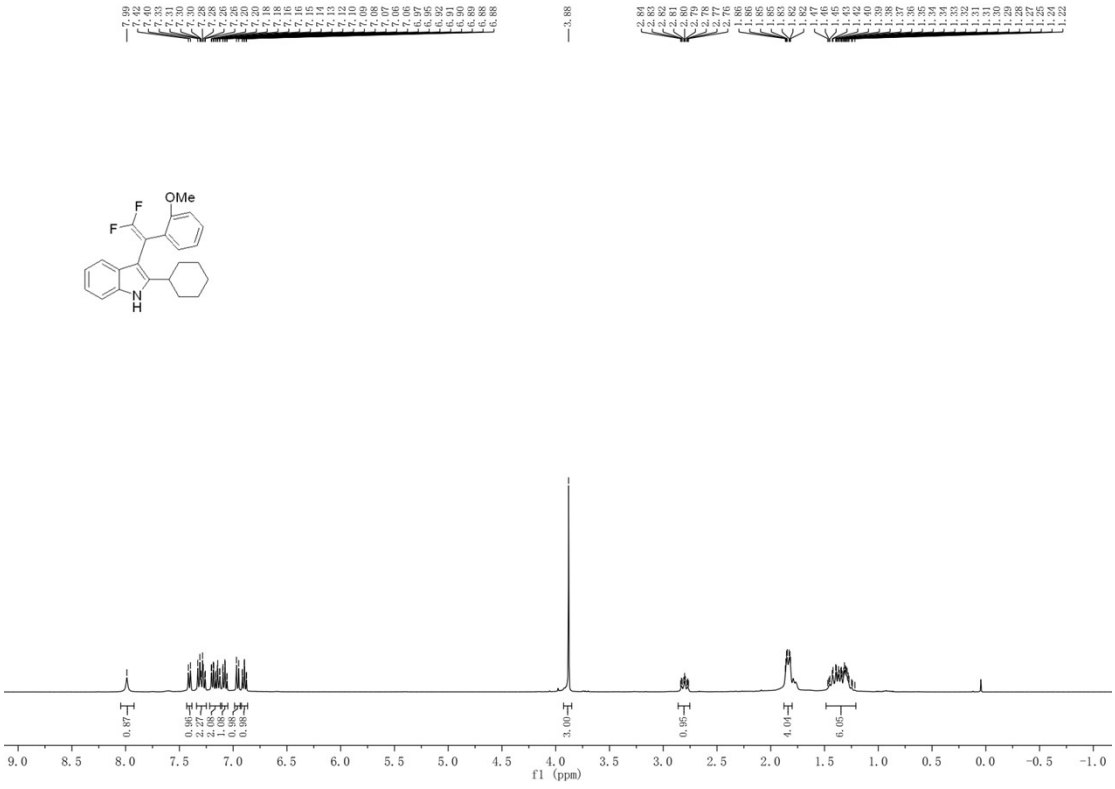
^{13}C NMR spectra of **3z** (125 MHz, $CDCl_3$)



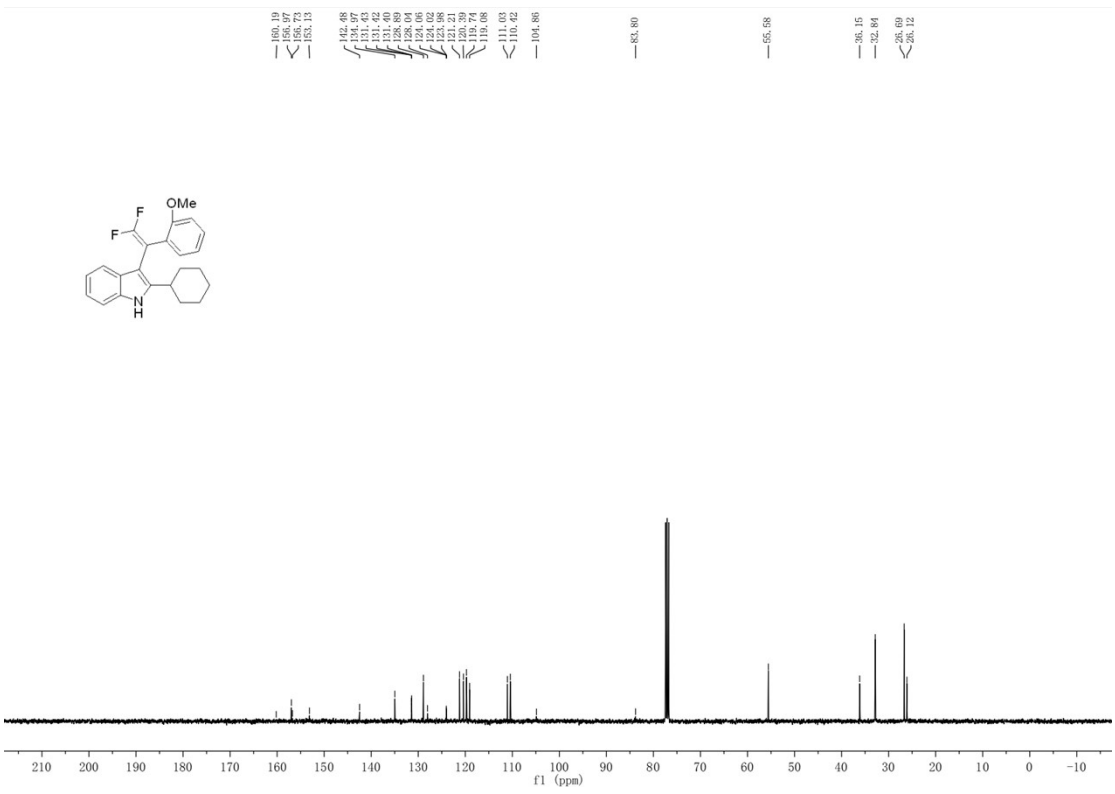
^{19}F NMR spectra of **3z** (470 MHz, $CDCl_3$)



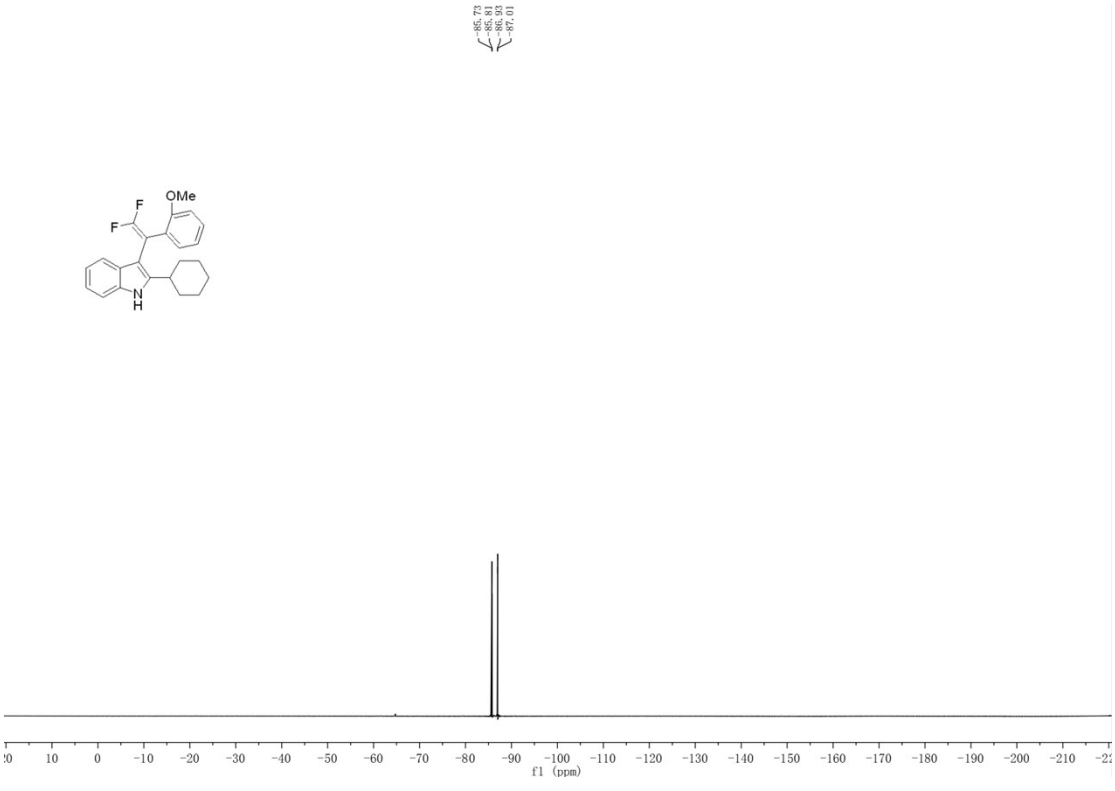
^{1}H NMR spectra of **3aa** (400 MHz, $CDCl_3$)



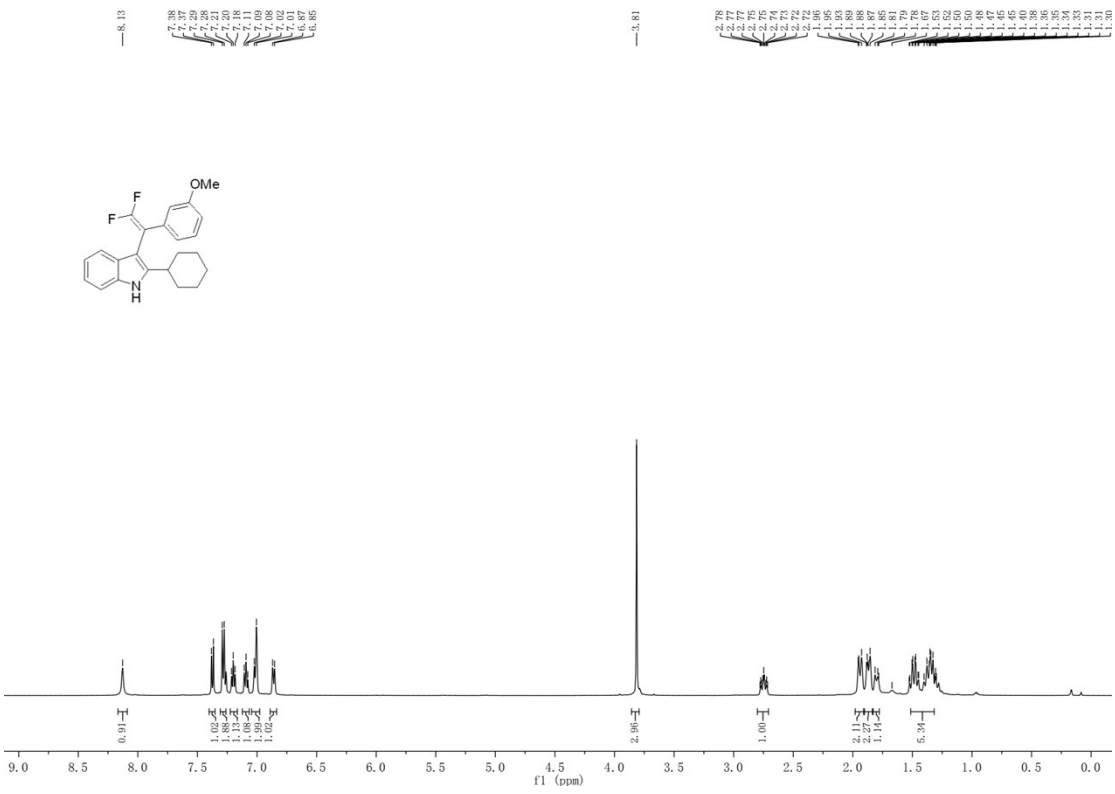
^{13}C NMR spectra of **3aa** (100 MHz, $CDCl_3$)



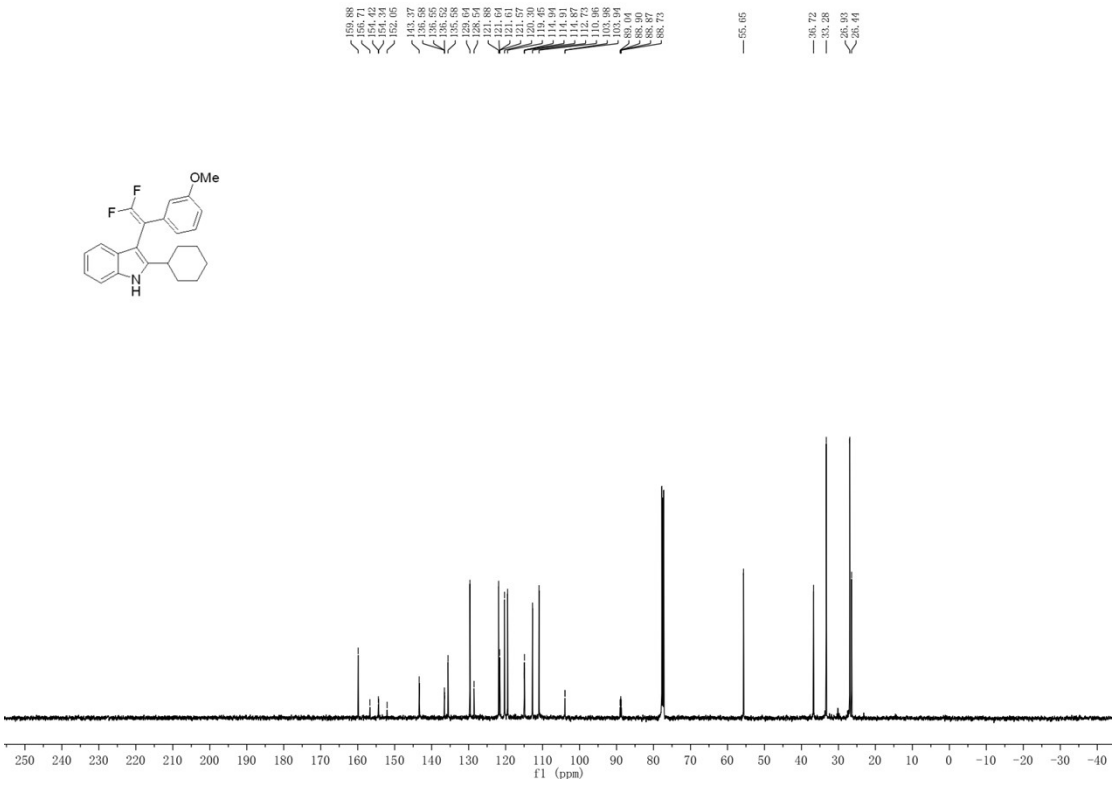
^{19}F NMR spectra of **3aa** (376 MHz, $CDCl_3$)



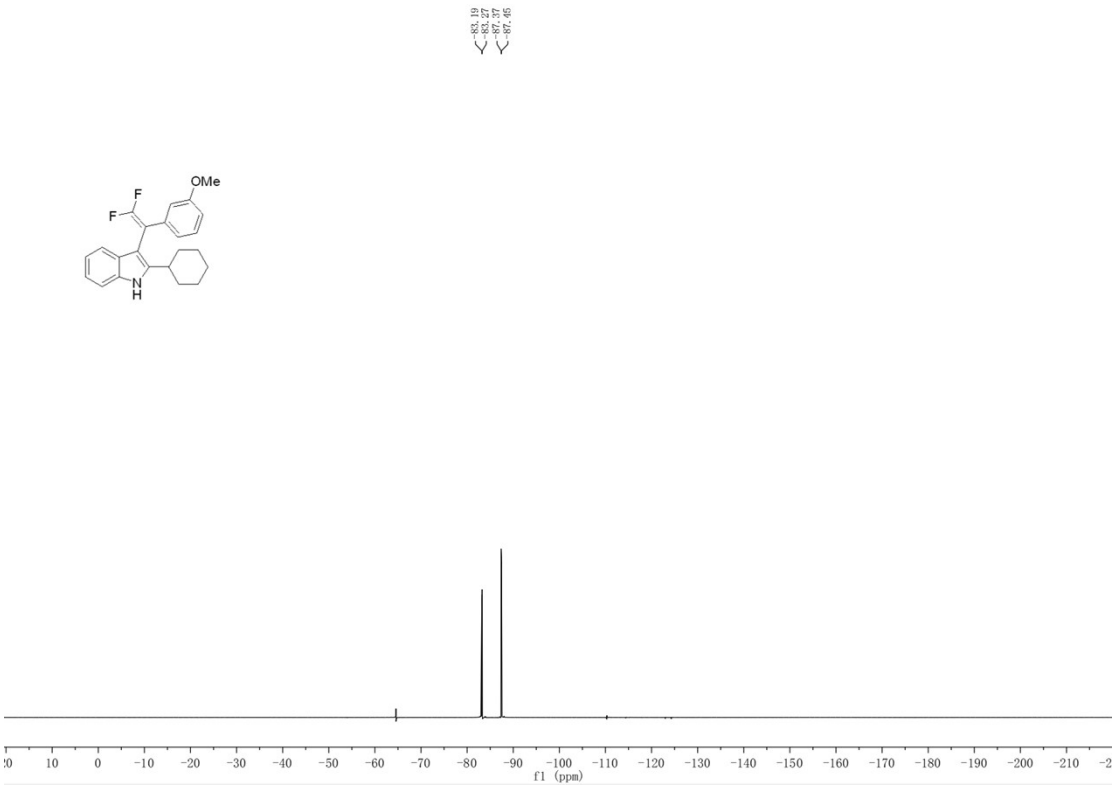
^{1}H NMR spectra of **3ab** (400 MHz, $CDCl_3$)



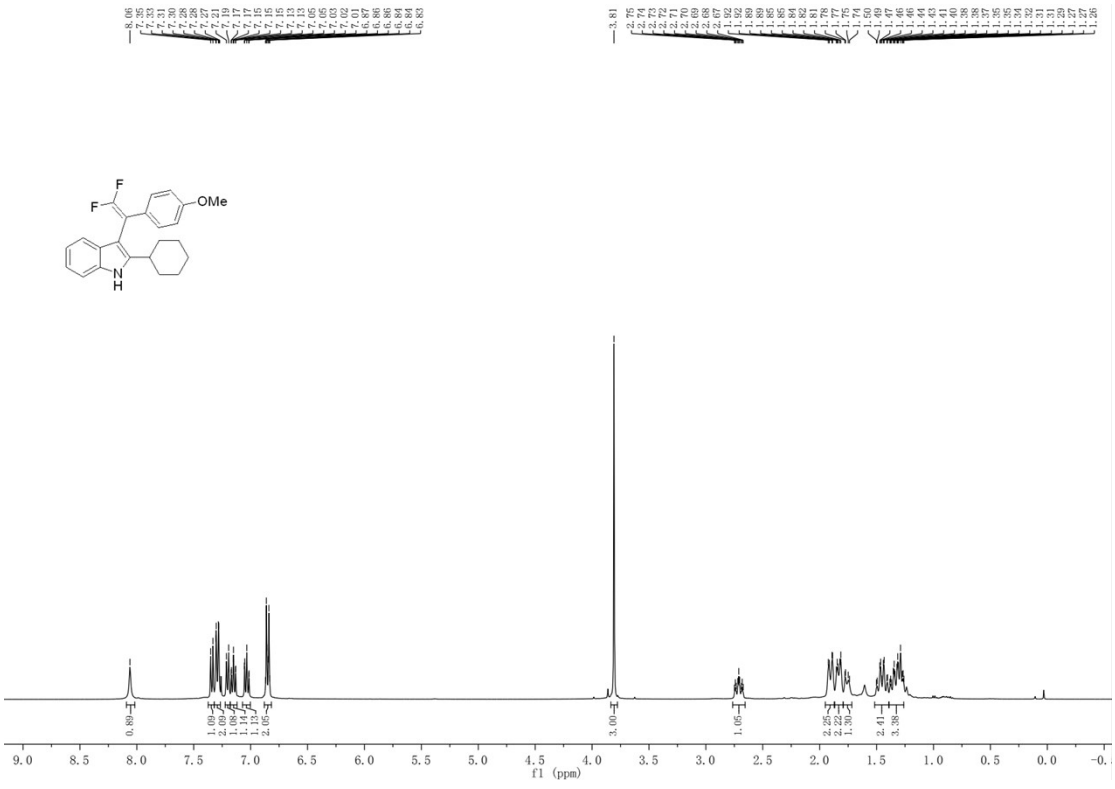
^{13}C NMR spectra of **3ab** (100 MHz, $CDCl_3$)



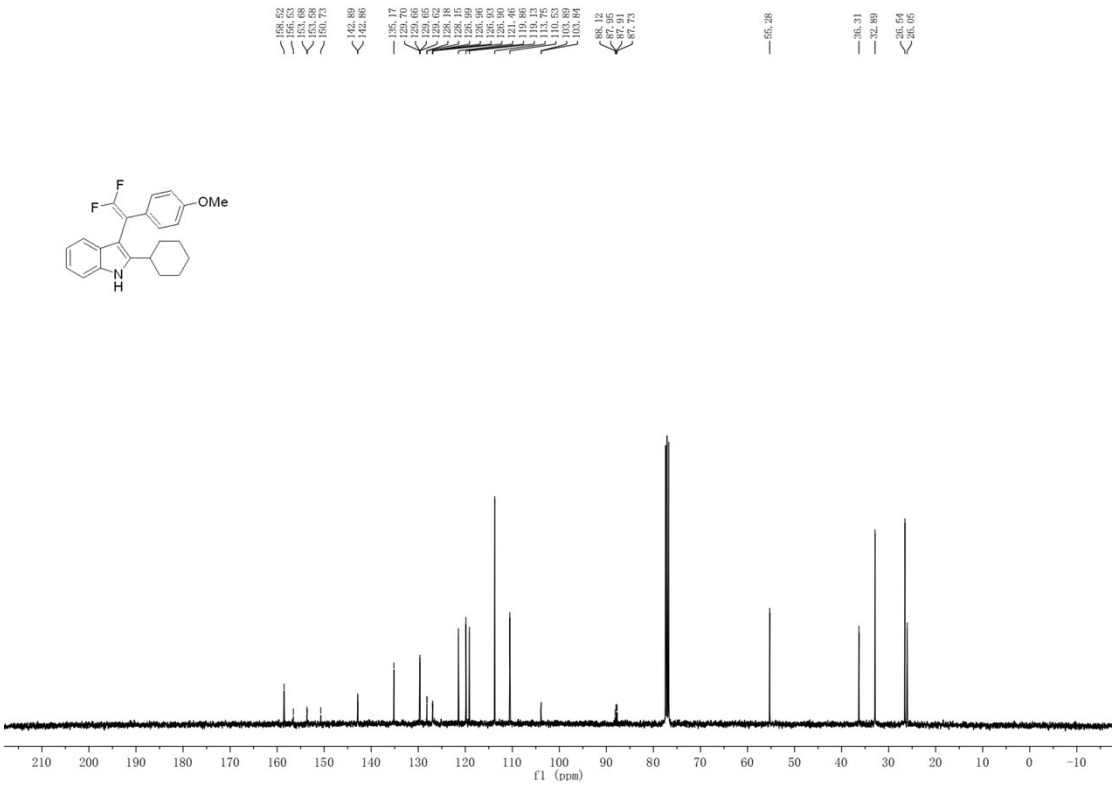
^{19}F NMR spectra of **3ab** (376 MHz, $CDCl_3$)



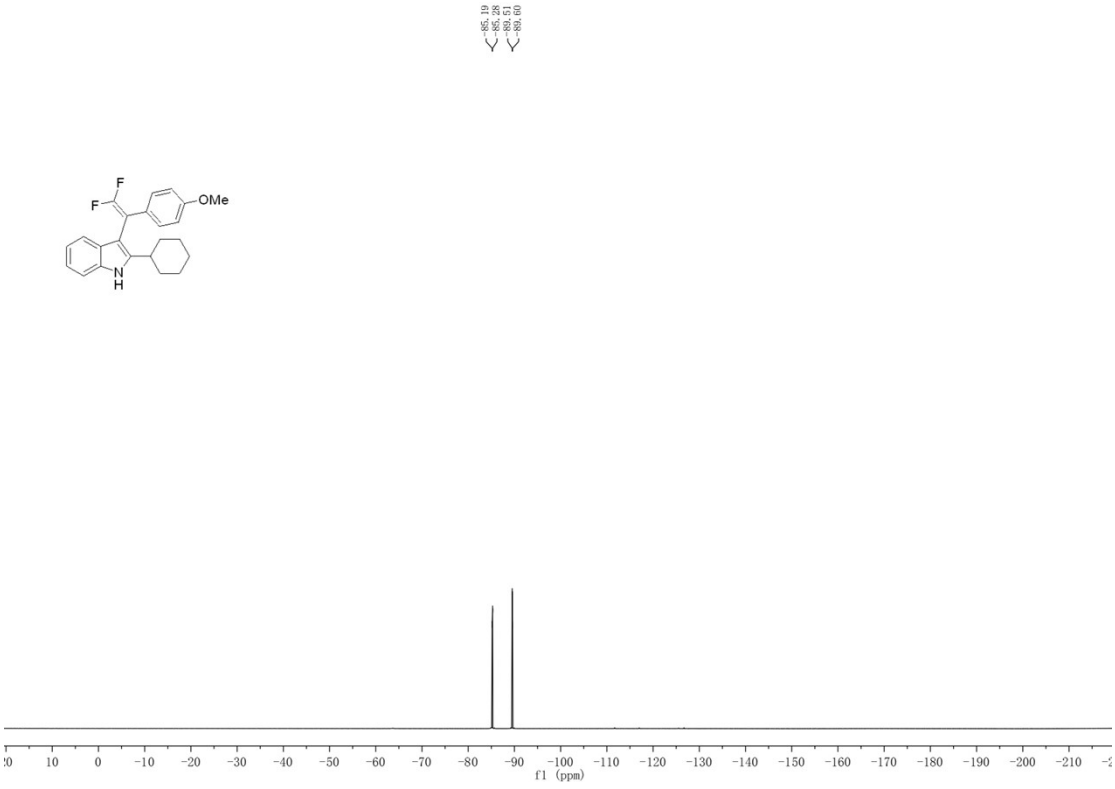
^{1}H NMR spectra of **3ac** (400 MHz, $CDCl_3$)



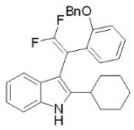
^{13}C NMR spectra of **3ac** (100 MHz, $CDCl_3$)

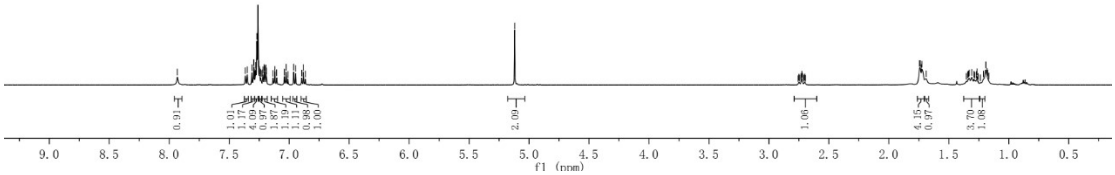


^{19}F NMR spectra of **3ac** (376 MHz, $CDCl_3$)

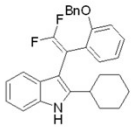


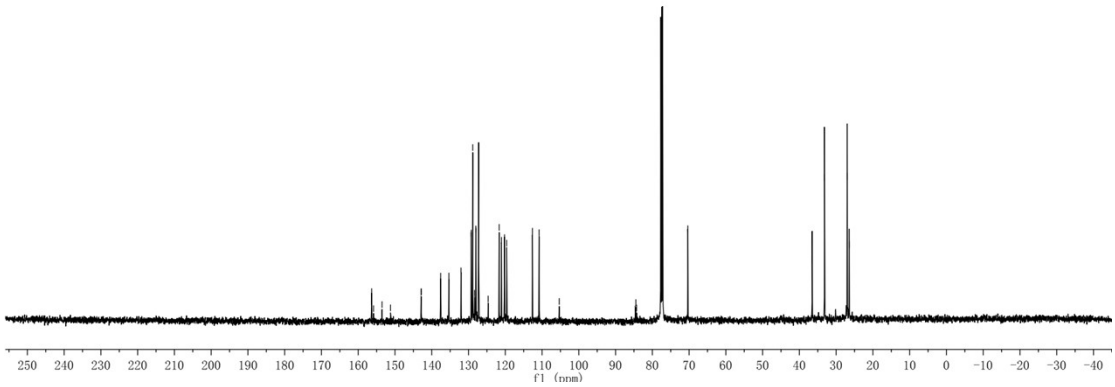
^{1}H NMR spectra of **3ad** (500 MHz, $CDCl_3$)



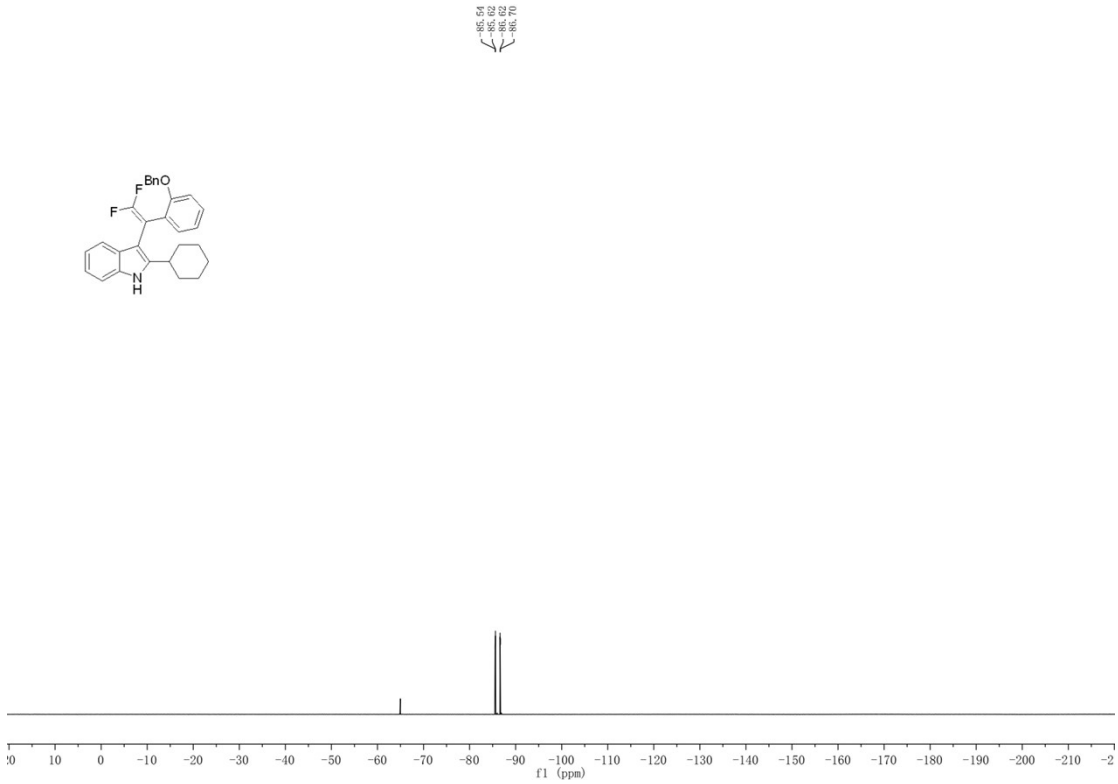


^{13}C NMR spectra of **3ad** (125 MHz, $CDCl_3$)

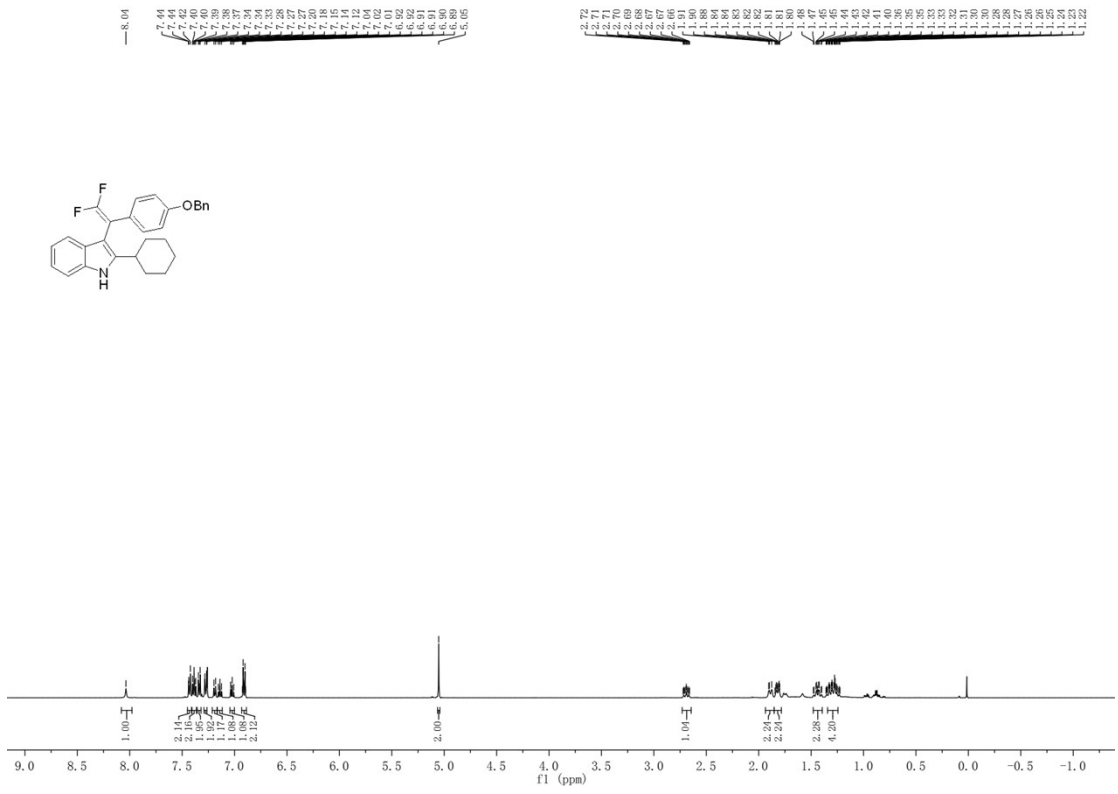




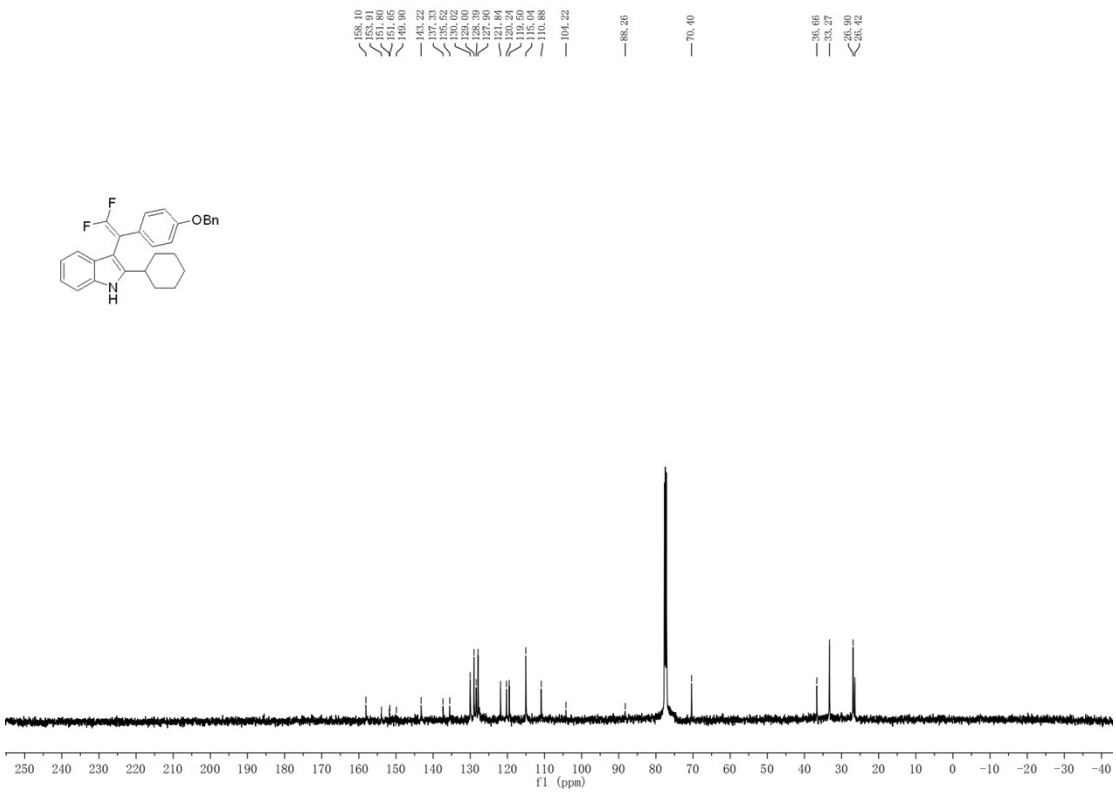
^{19}F NMR spectra of **3ad** (376 MHz, $CDCl_3$)



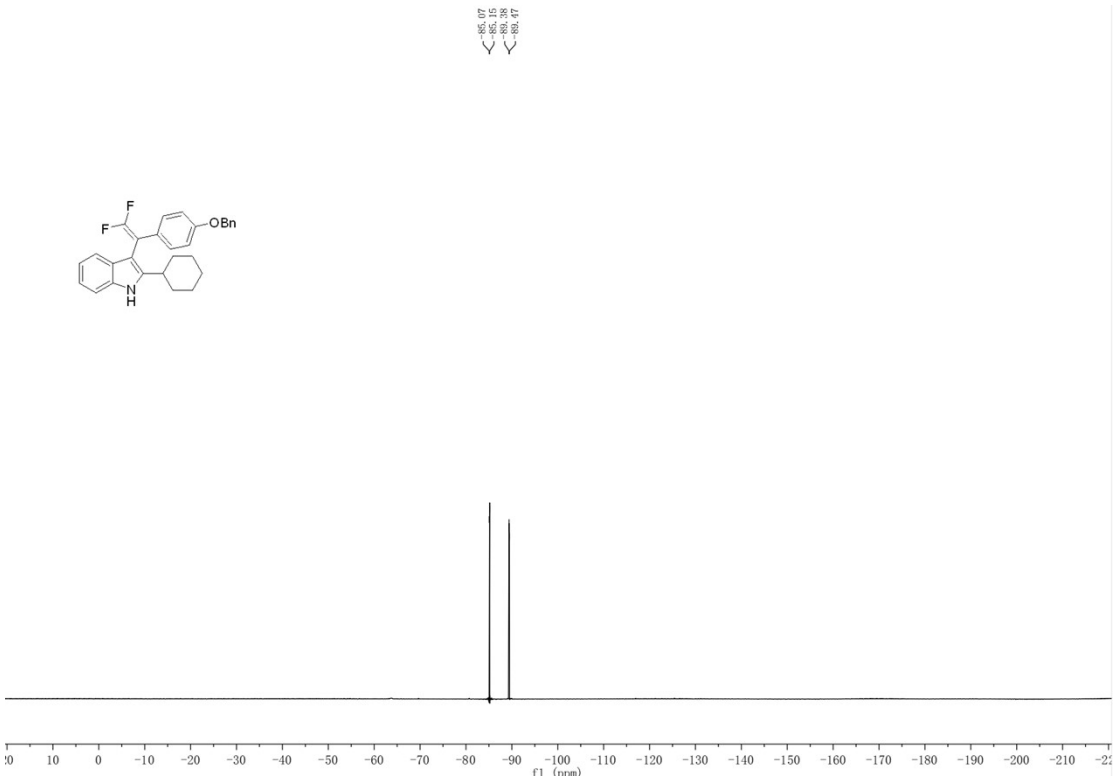
^{1}H NMR spectra of **3ae** (500 MHz, $CDCl_3$)



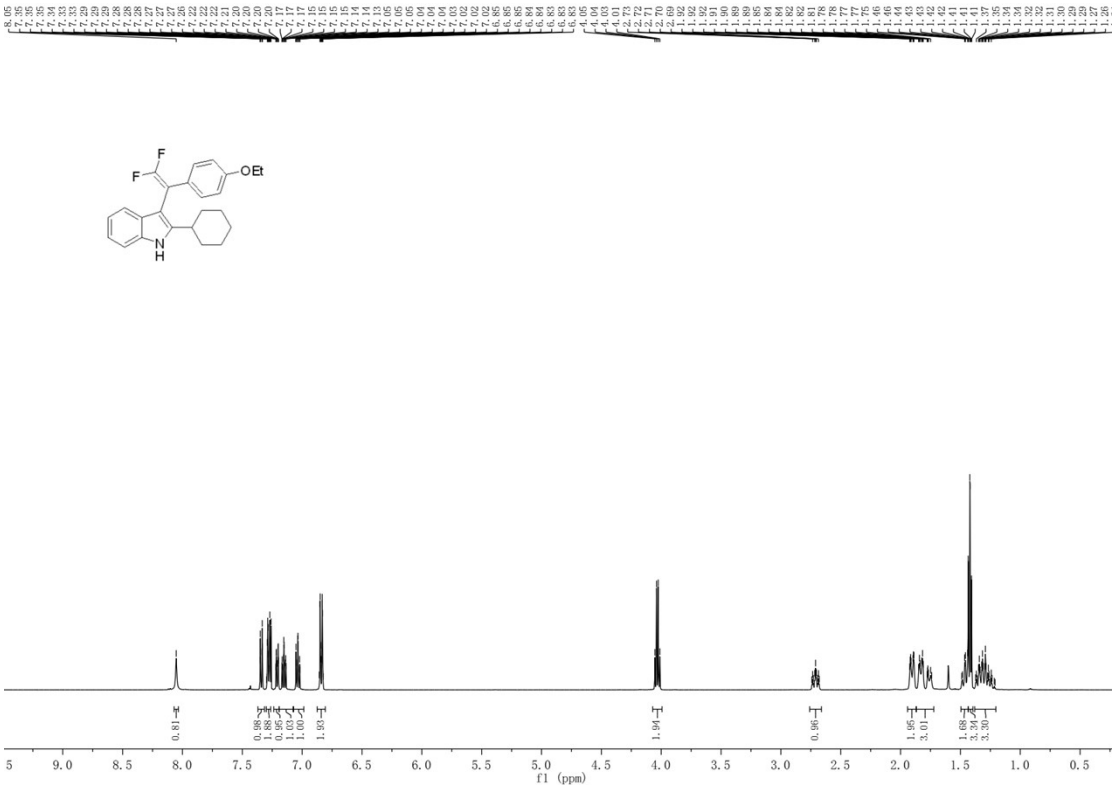
^{13}C NMR spectra of **3ae** (125 MHz, $CDCl_3$)



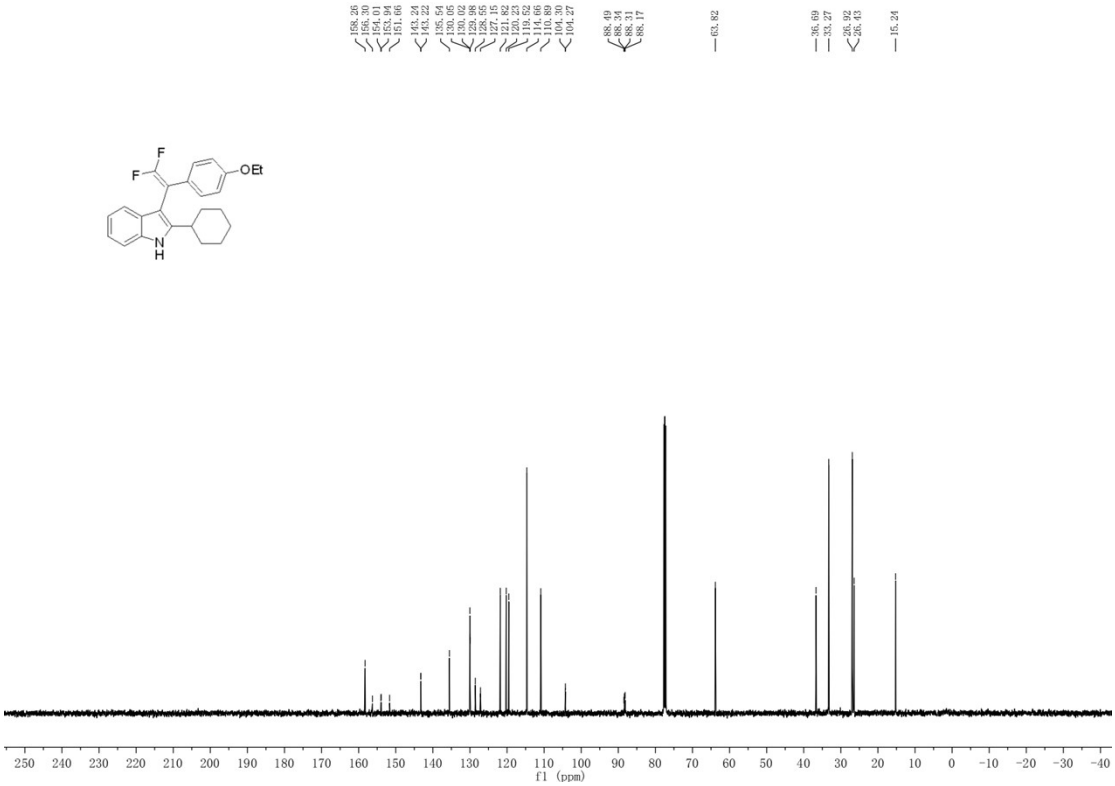
^{19}F NMR spectra of **3ae** (376 MHz, $CDCl_3$)



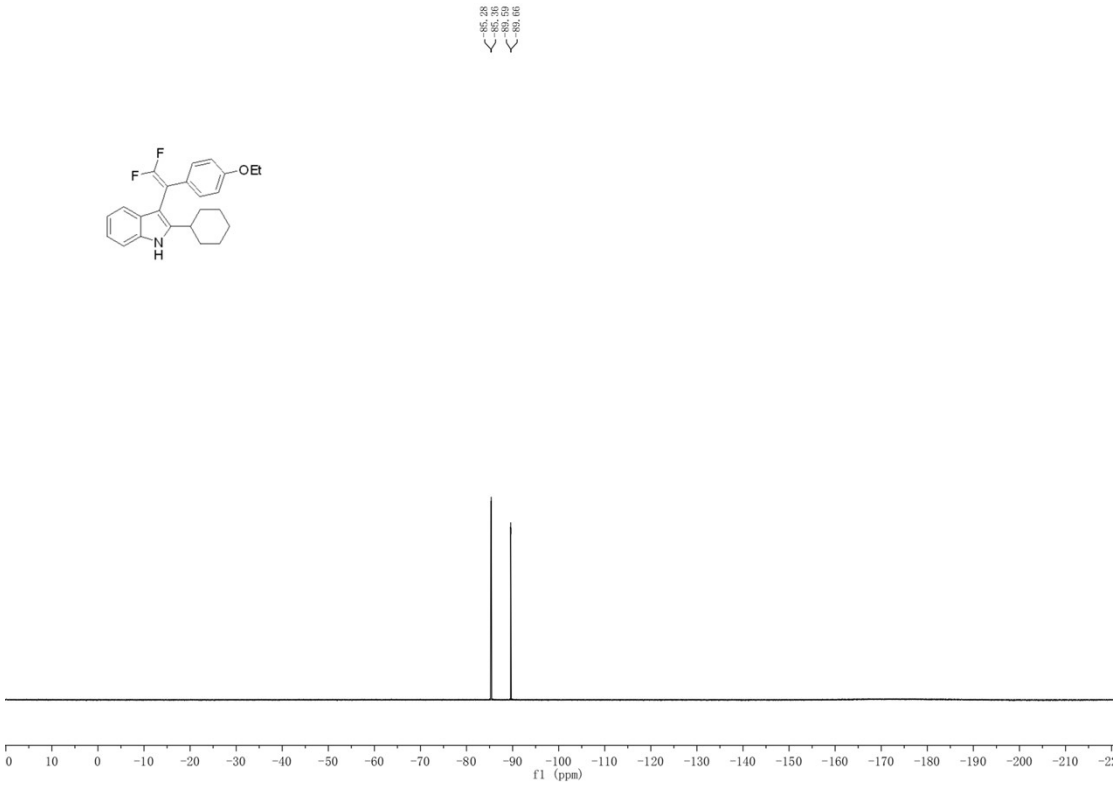
^{1}H NMR spectra of **3af** (500 MHz, $CDCl_3$)



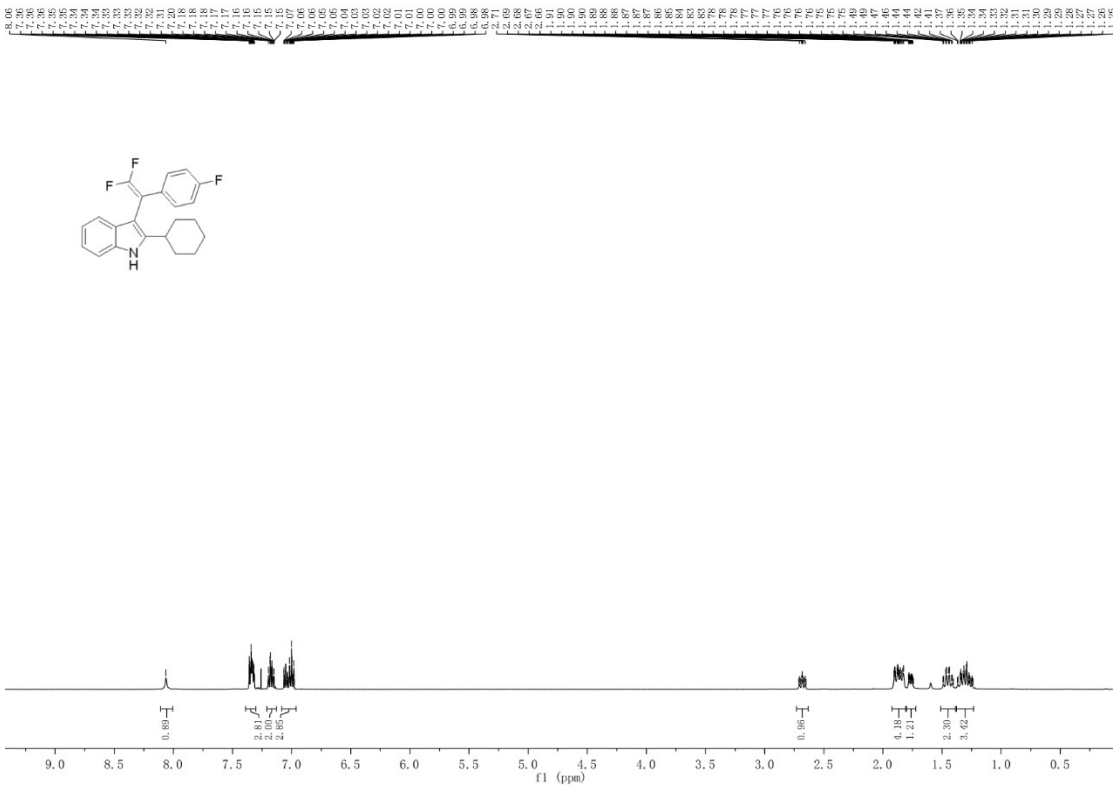
^{13}C NMR spectra of **3af** (125 MHz, $CDCl_3$)



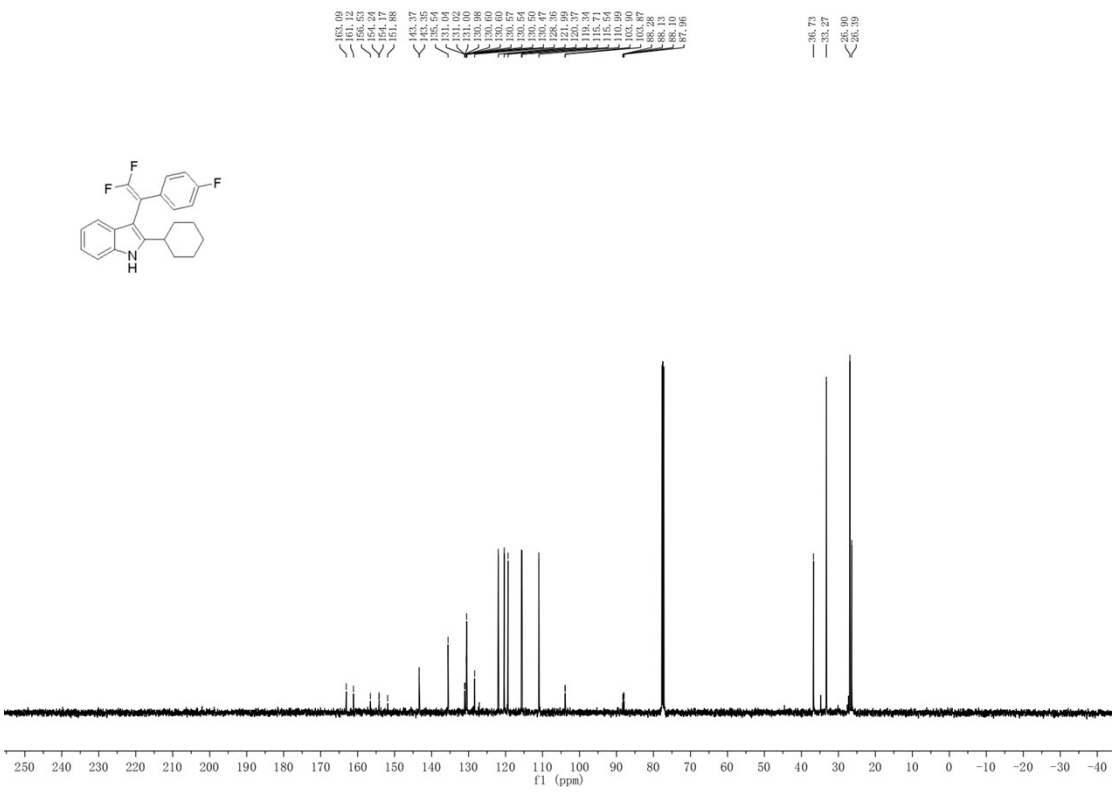
^{19}F NMR spectra of **3af** (470 MHz, $CDCl_3$)



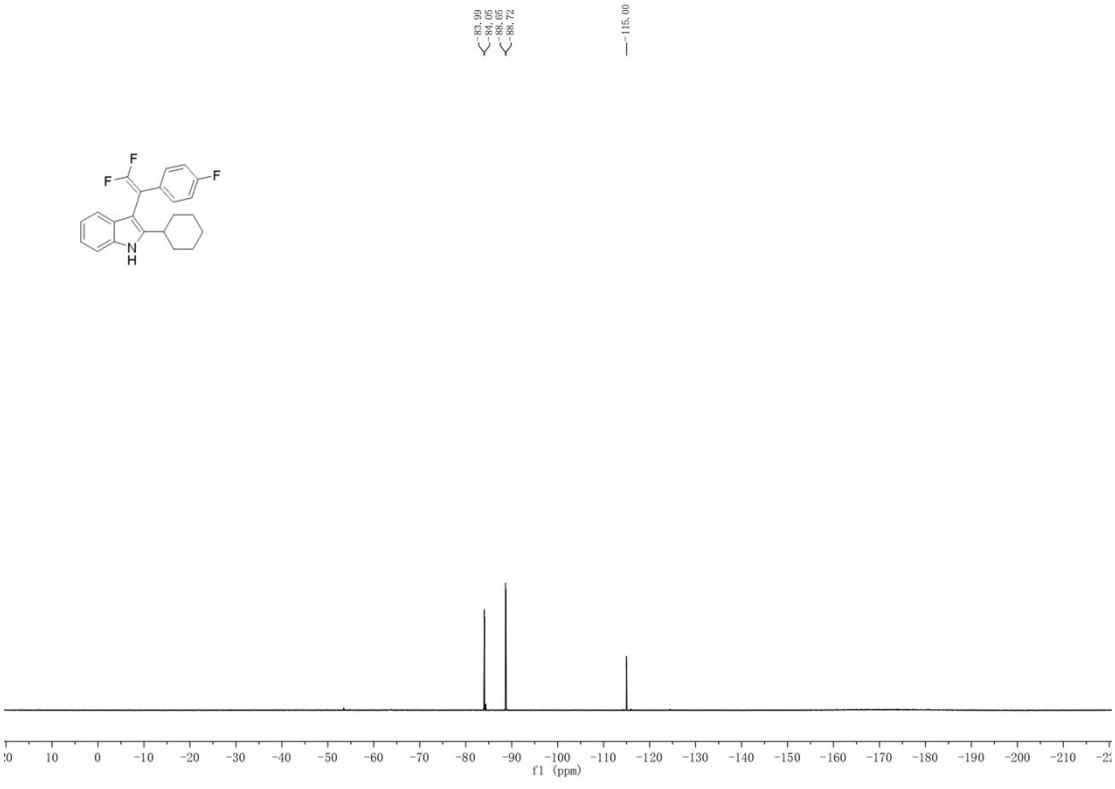
^{1}H NMR spectra of **3ag** (500 MHz, $CDCl_3$)



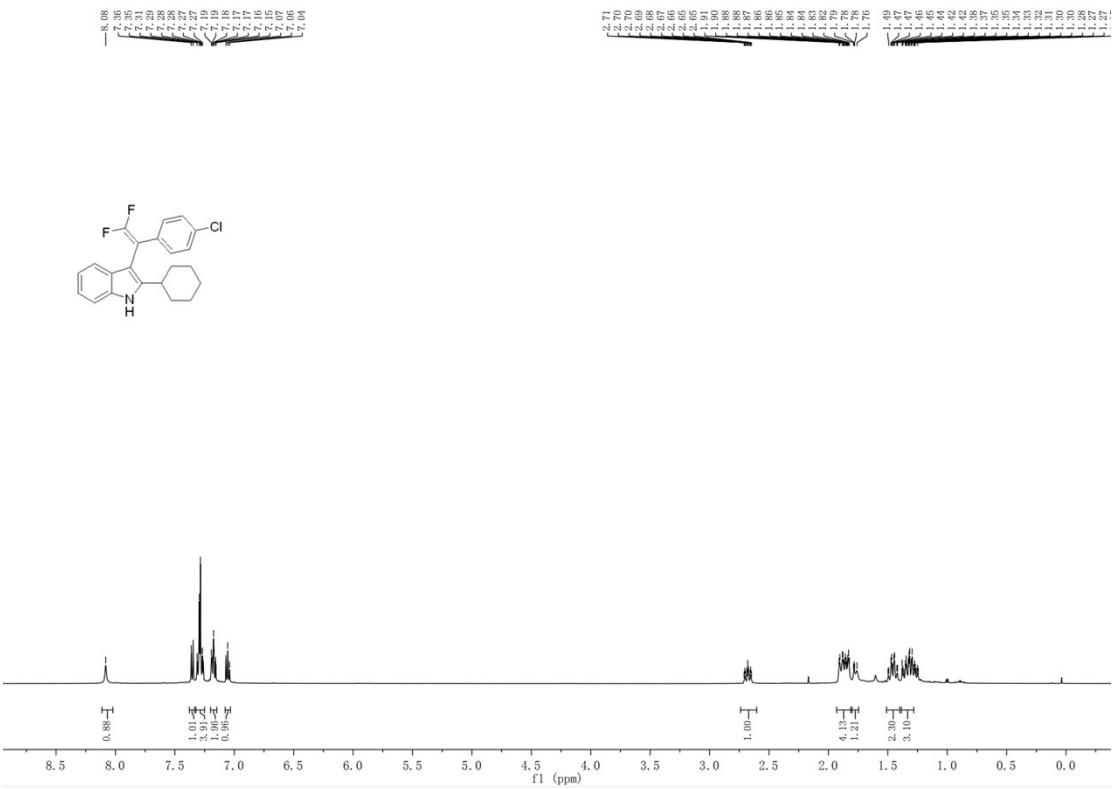
^{13}C NMR spectra of **3ag** (125 MHz, $CDCl_3$)



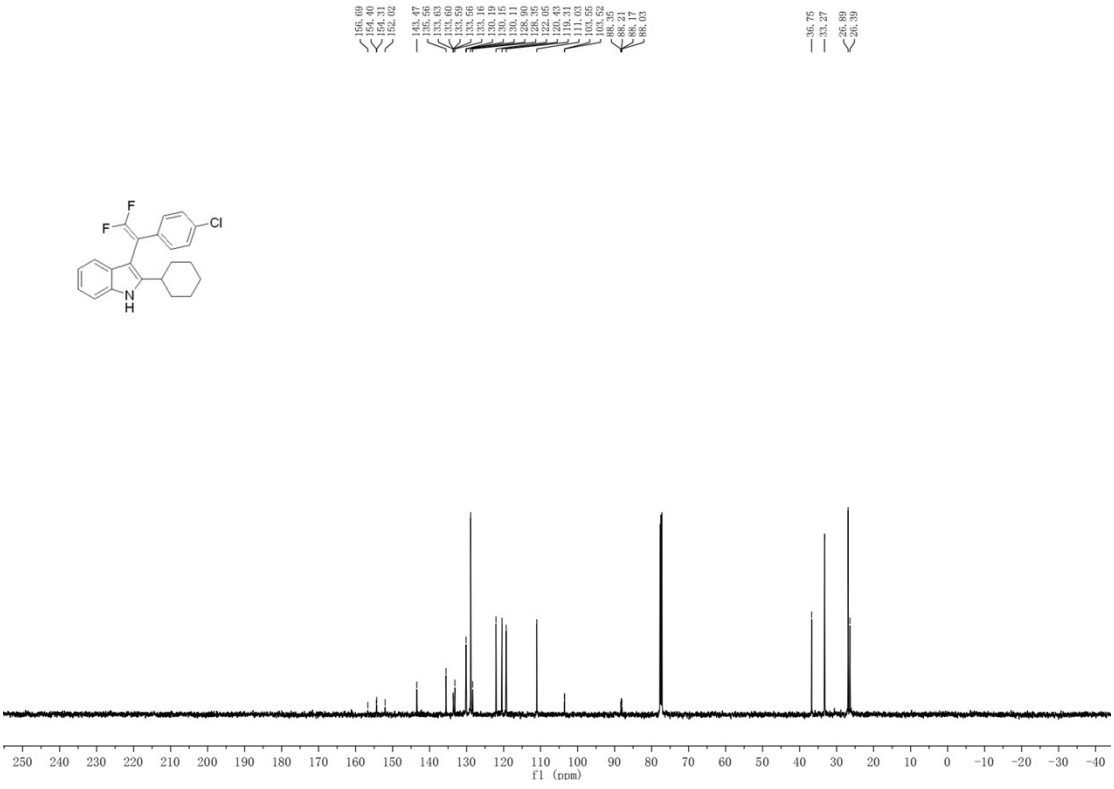
^{19}F NMR spectra of **3ag** (470 MHz, $CDCl_3$)



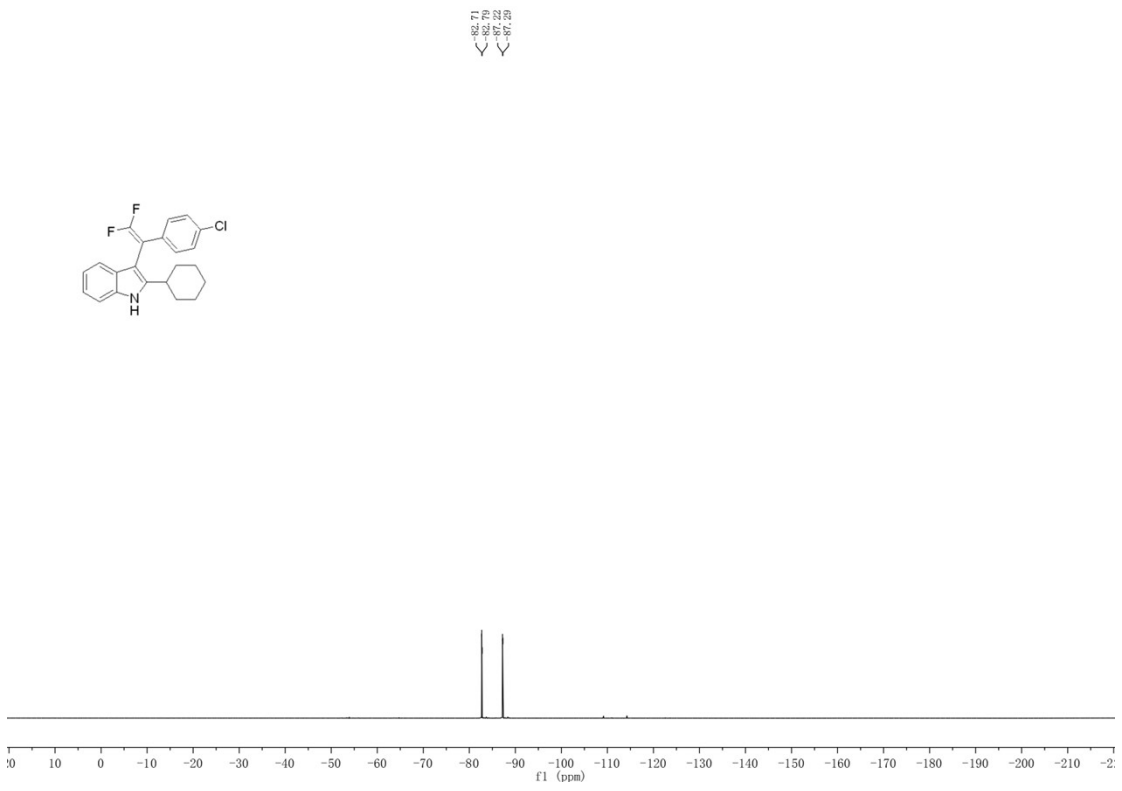
^{1}H NMR spectra of **3ah** (500 MHz, $CDCl_3$)



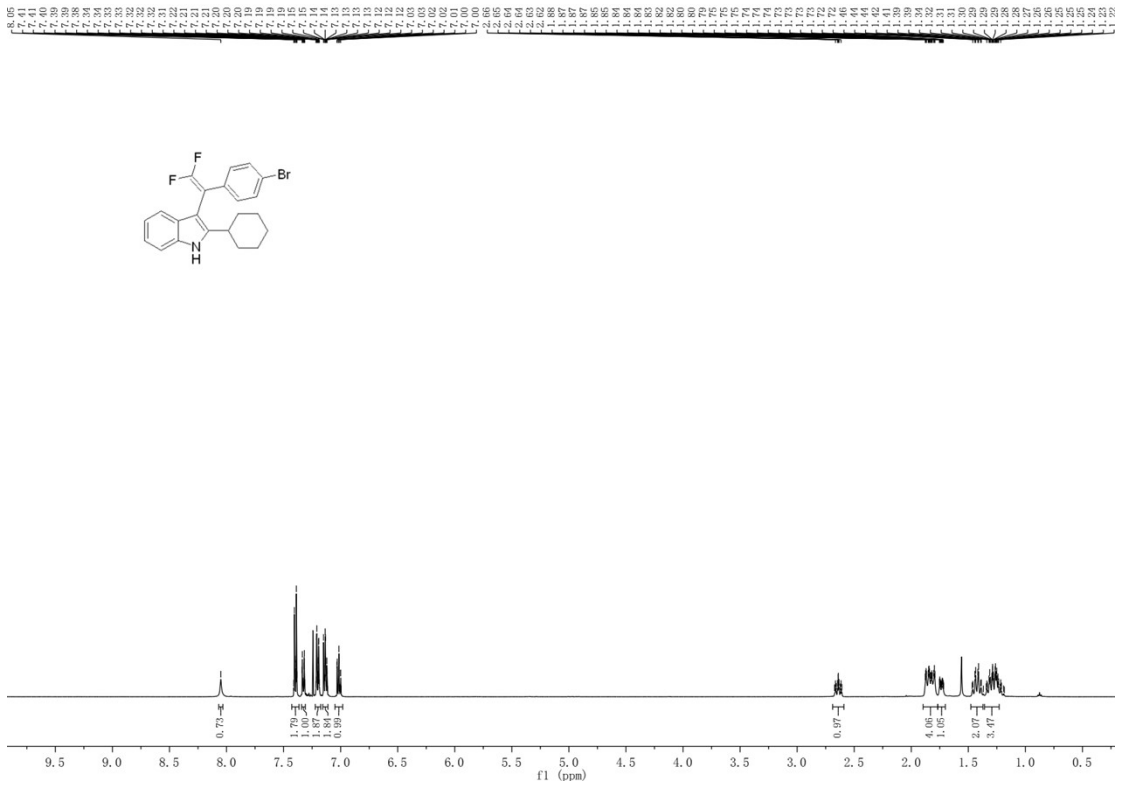
^{13}C NMR spectra of **3ah** (125 MHz, $CDCl_3$)



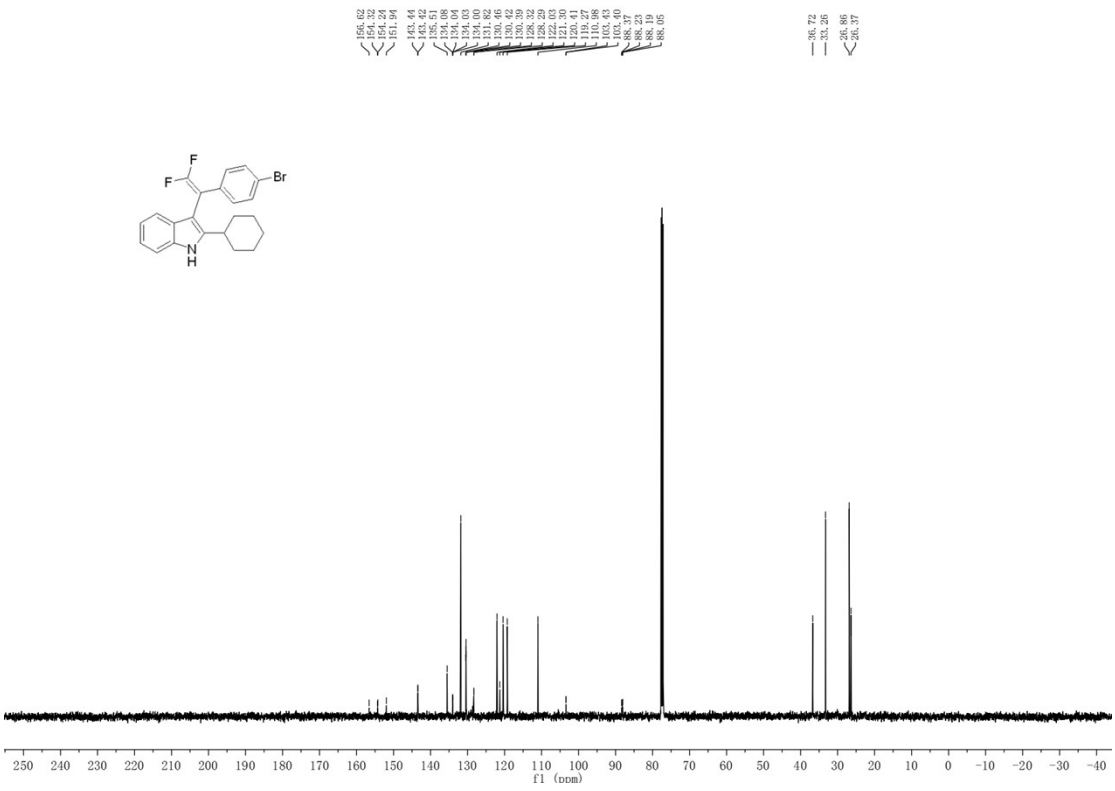
^{19}F NMR spectra of **3ah** (376 MHz, $CDCl_3$)



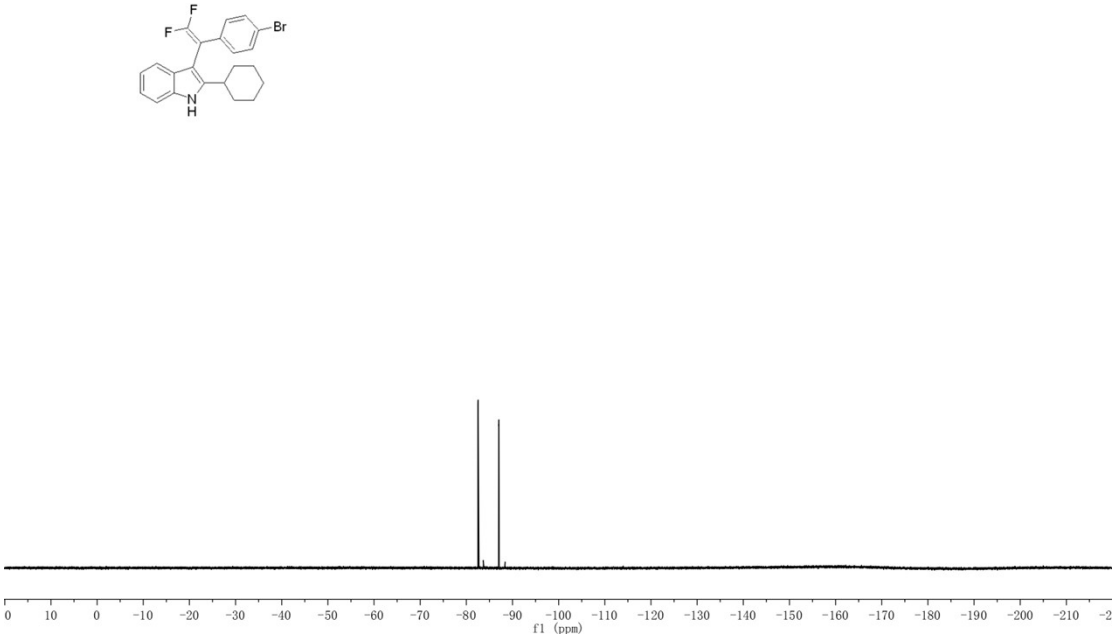
^{1}H NMR spectra of **3ai** (500 MHz, $CDCl_3$)



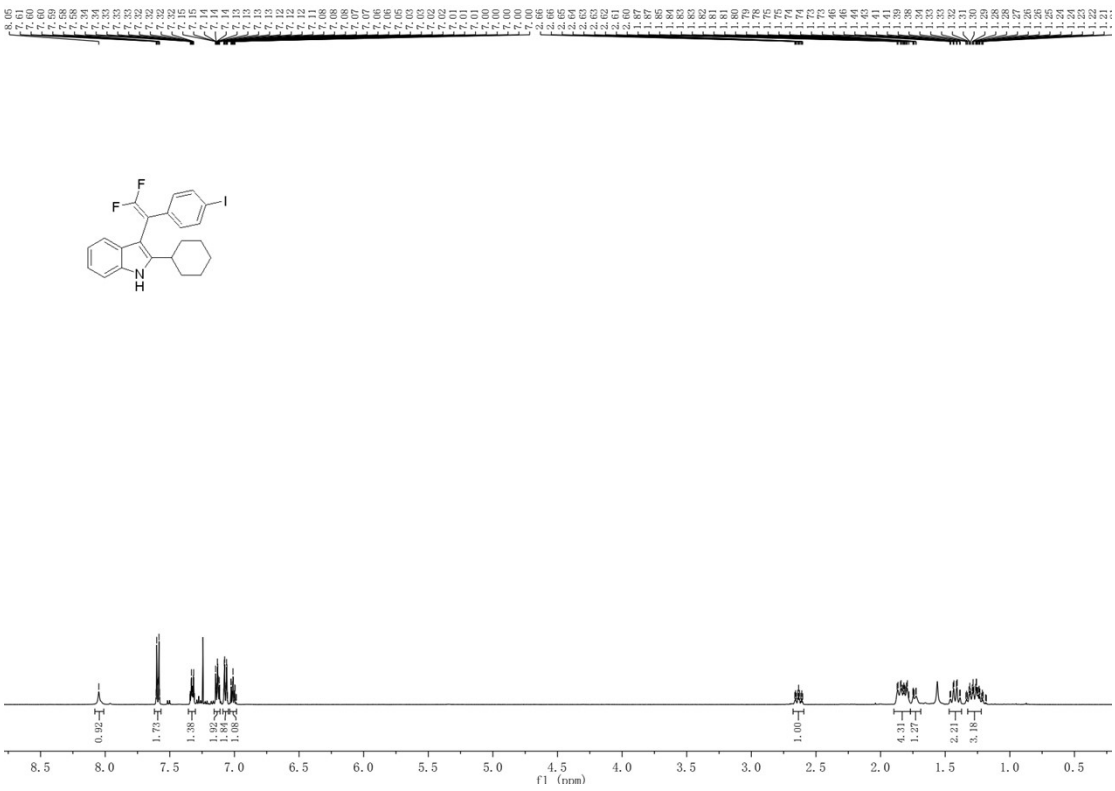
^{13}C NMR spectra of **3ai** (125 MHz, $CDCl_3$)



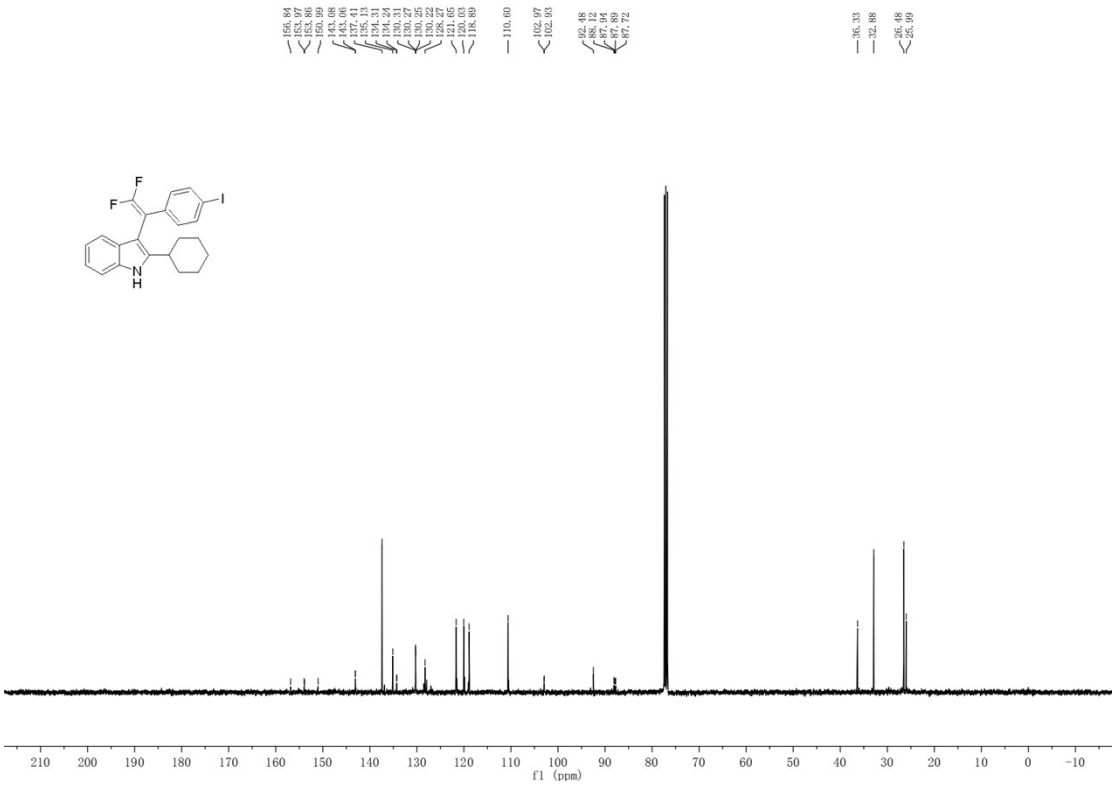
^{19}F NMR spectra of **3ai** (470 MHz, $CDCl_3$)



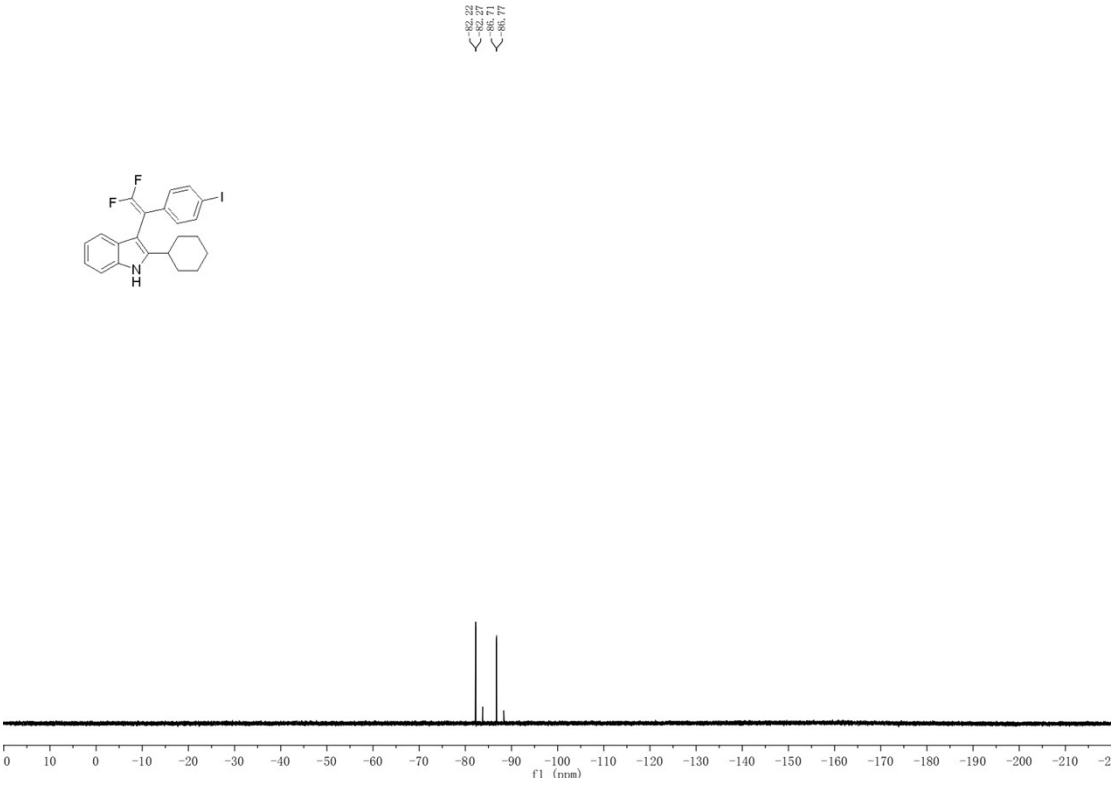
^{1}H NMR spectra of **3aj** (500 MHz, $CDCl_3$)



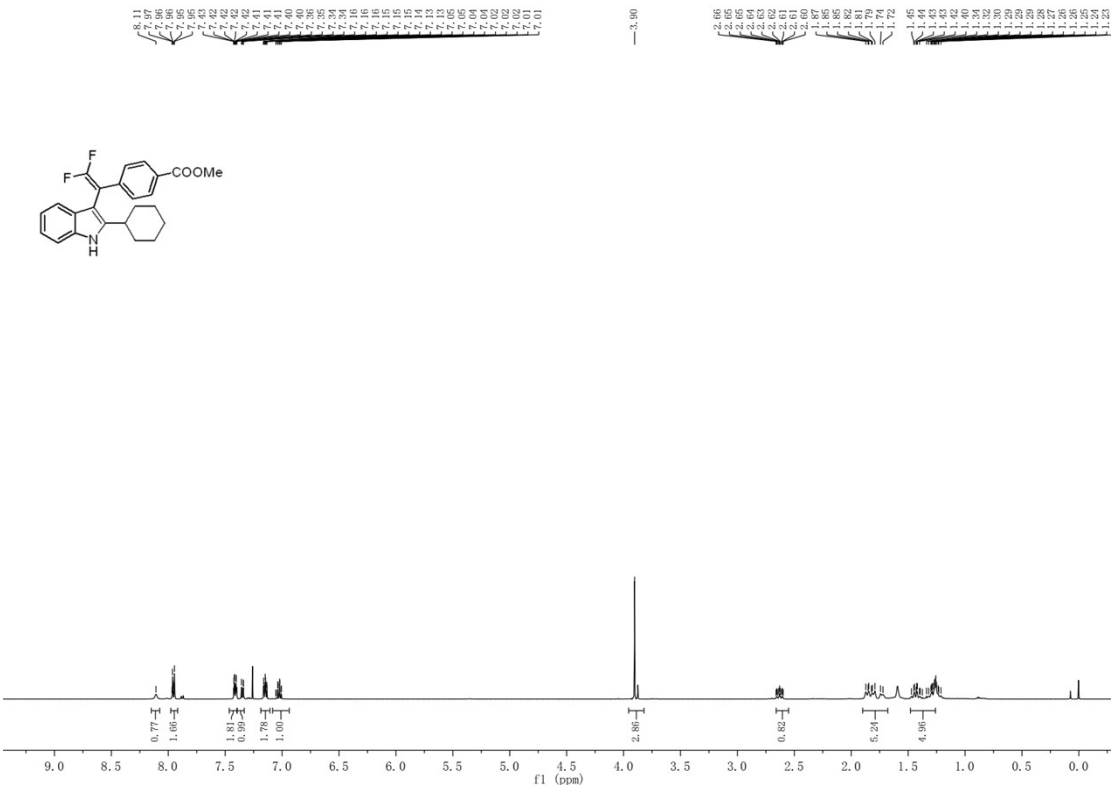
^{13}C NMR spectra of **3aj** (125 MHz, $CDCl_3$)



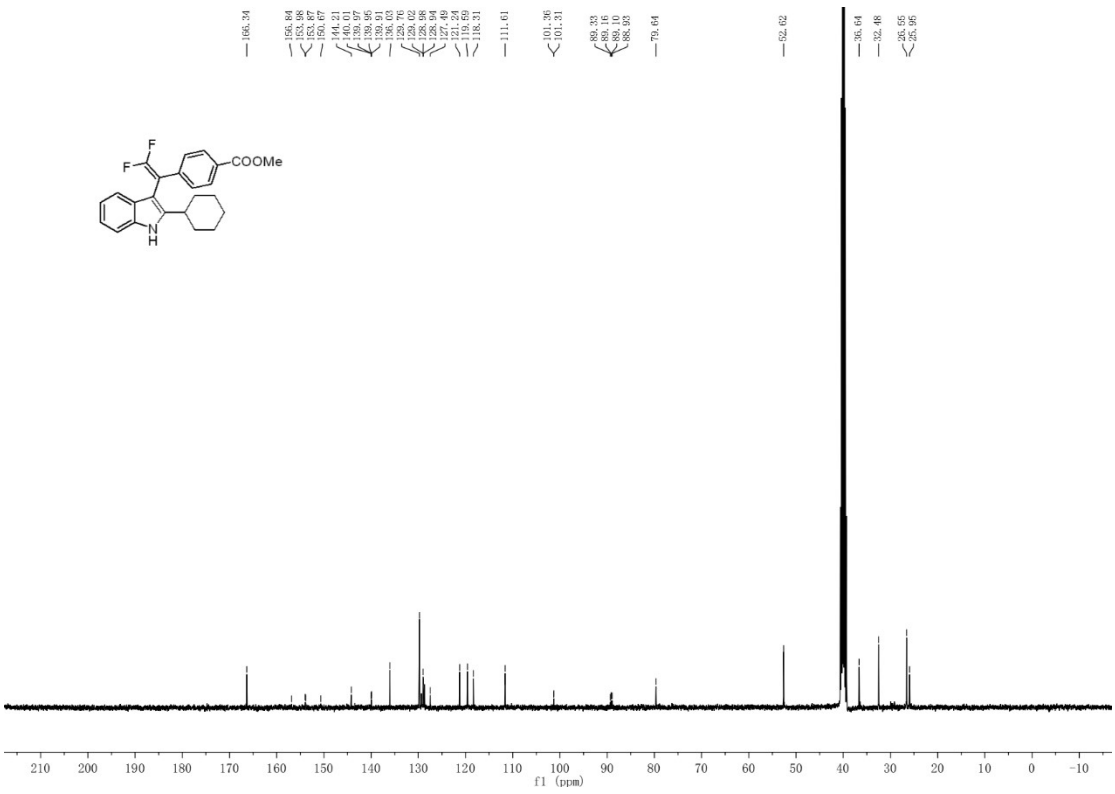
^{19}F NMR spectra of **3aj** (470 MHz, $CDCl_3$)



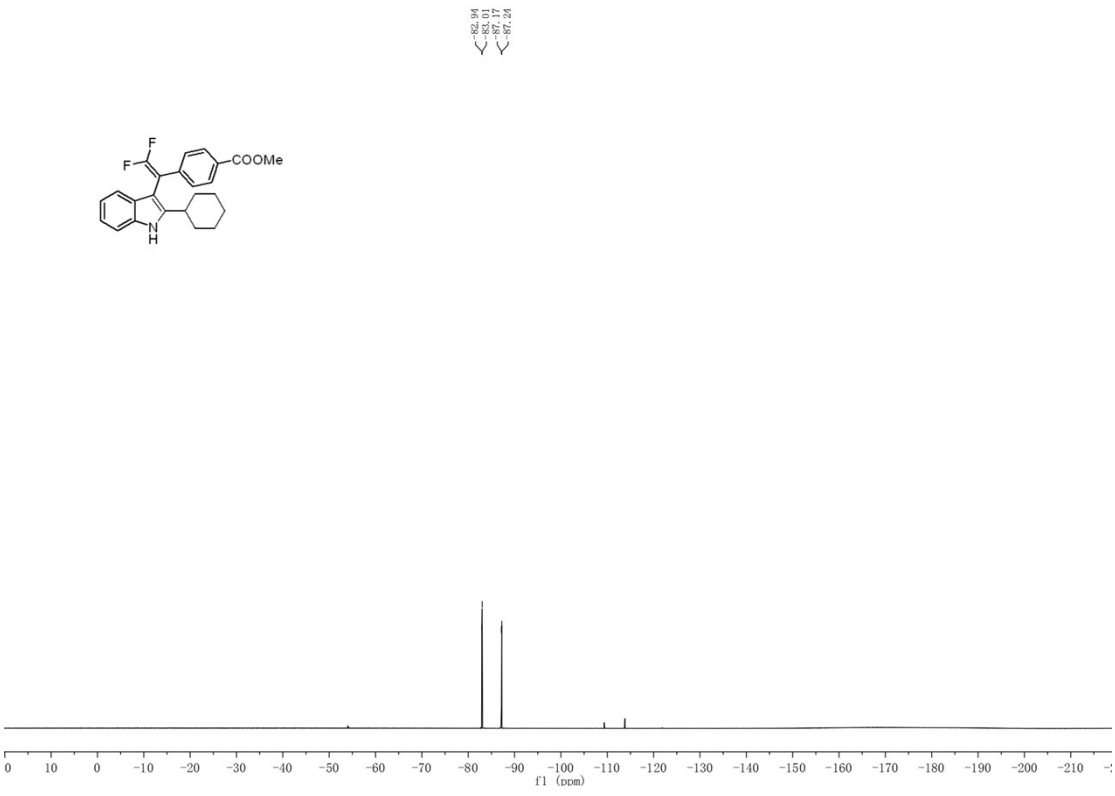
^{1}H NMR spectra of **3ak** (500 MHz, $CDCl_3$)



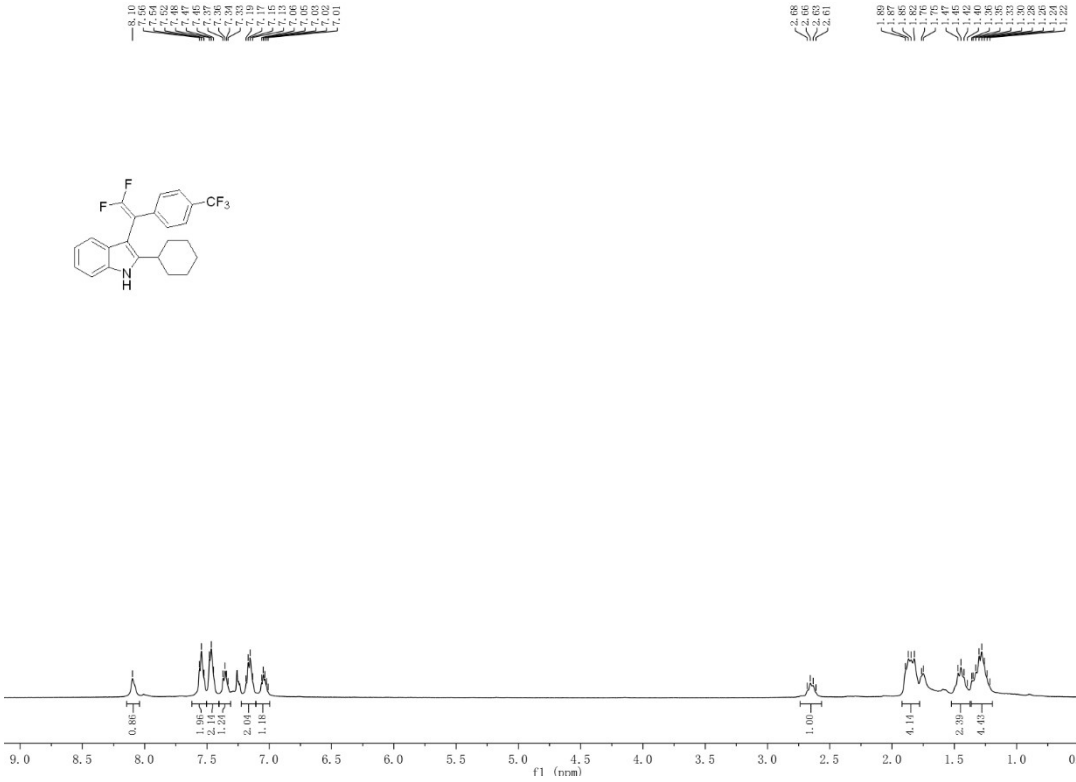
^{13}C NMR spectra of **3ak** (100 MHz, DMSO-d_6)



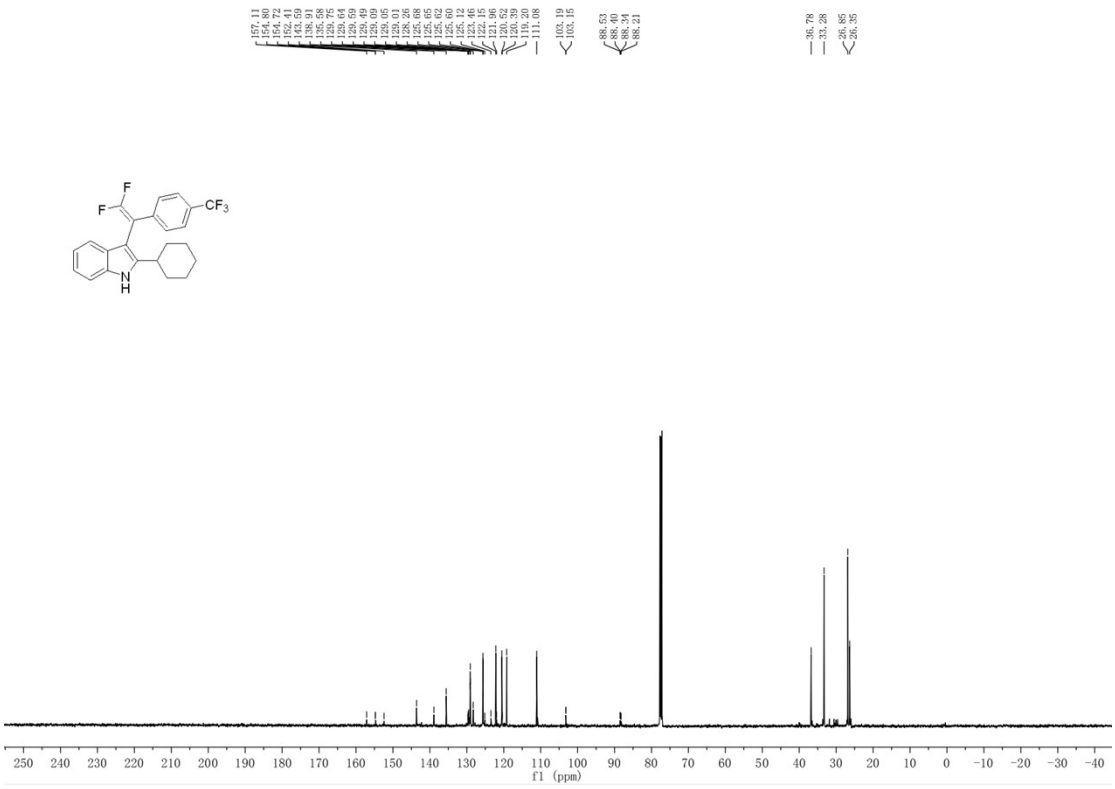
^{19}F NMR spectra of **3ak** (376 MHz, DMSO-d_6)



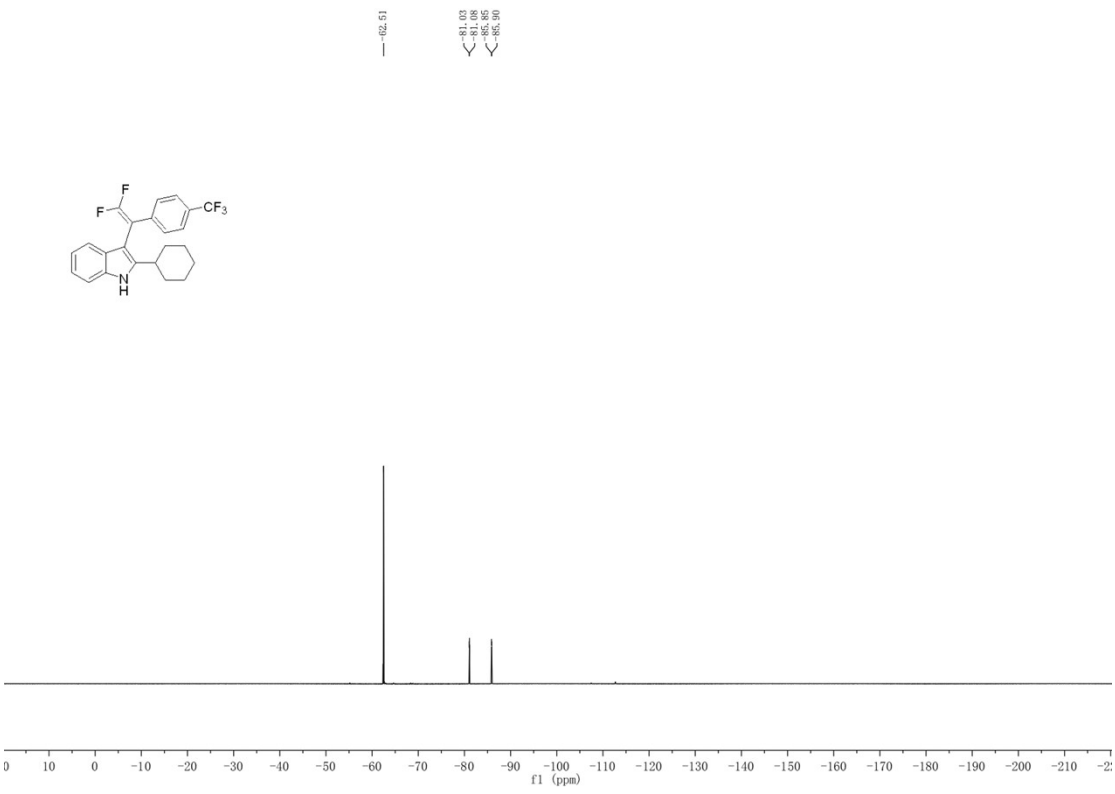
^{1}H NMR spectra of **3al** (500 MHz, $CDCl_3$)



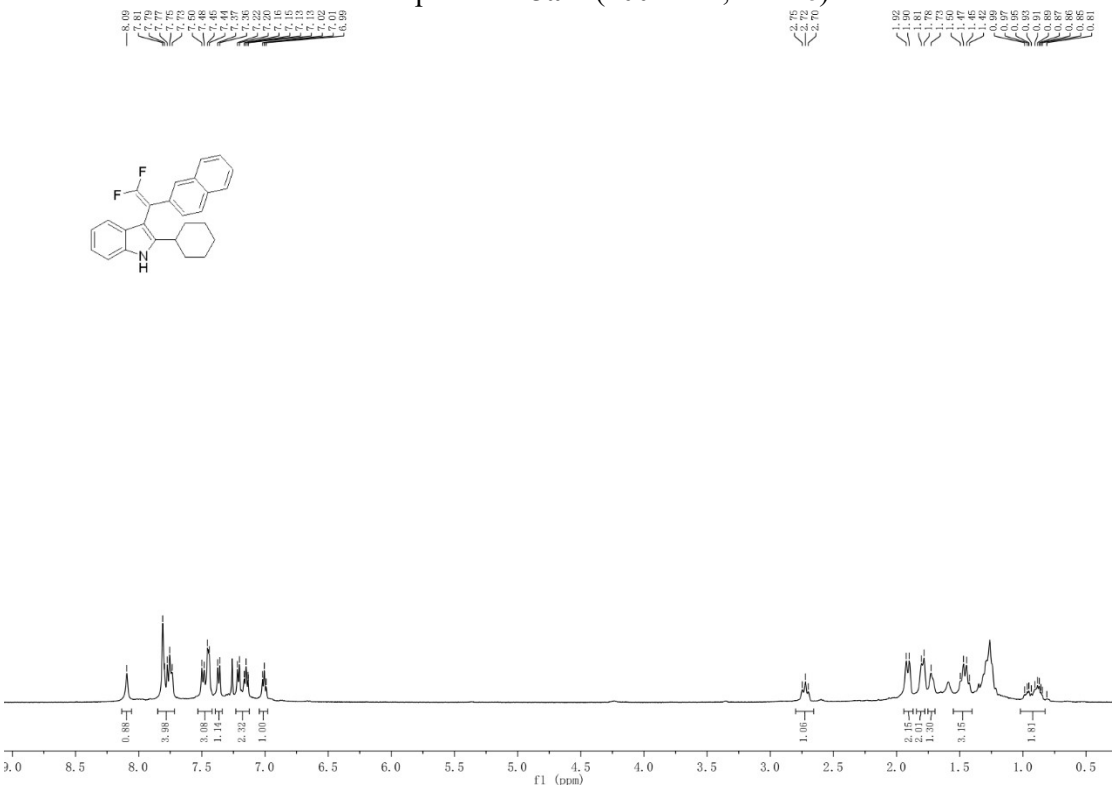
^{13}C NMR spectra of **3al** (125 MHz, $CDCl_3$)



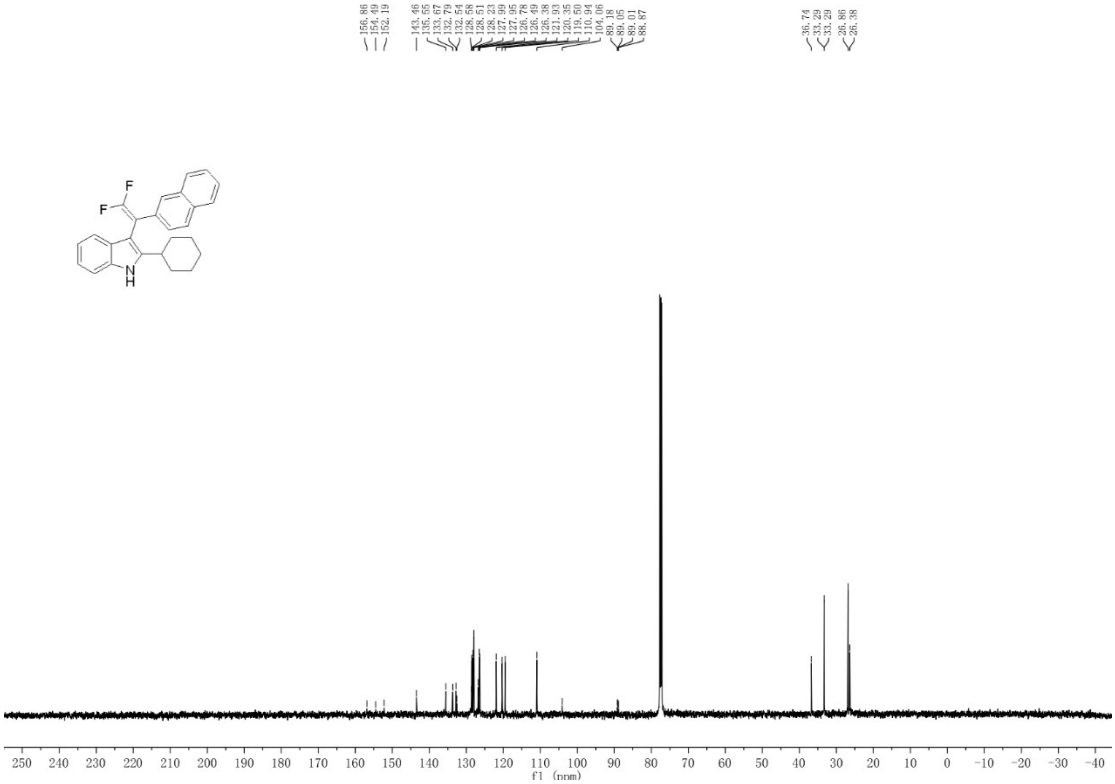
^{19}F NMR spectra of **3al** (470 MHz, $CDCl_3$)



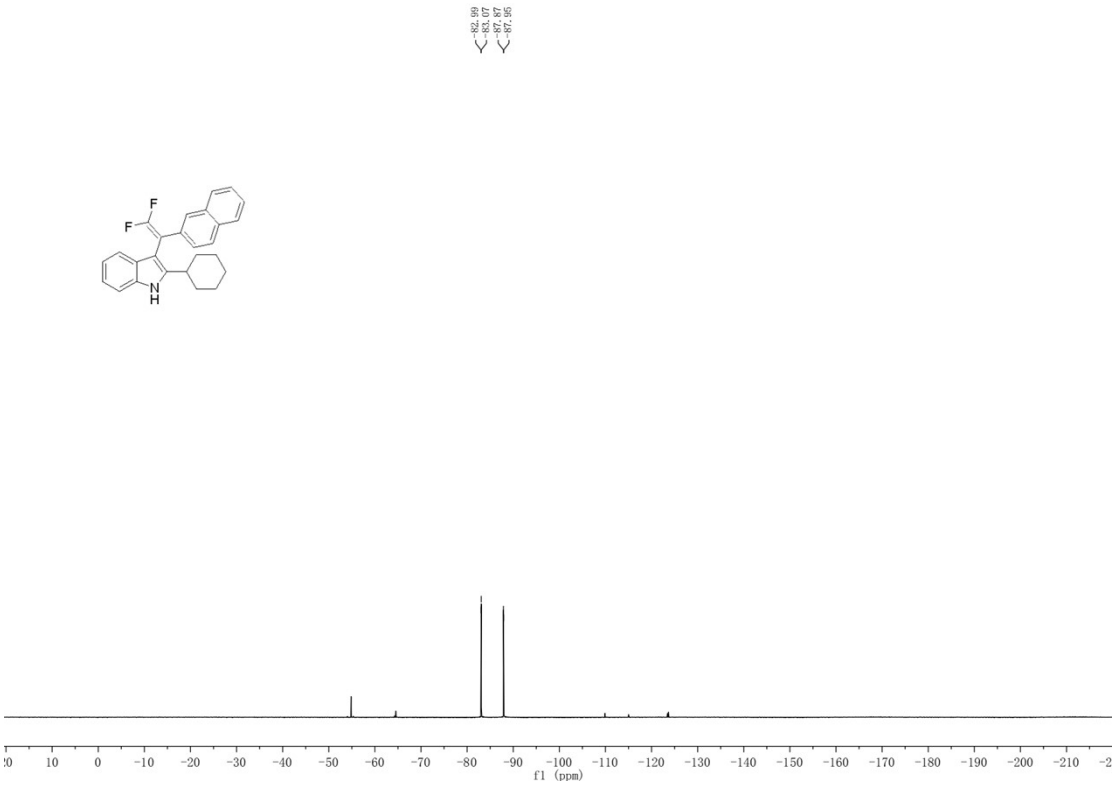
^{1}H NMR spectra of **3am** (400 MHz, $CDCl_3$)



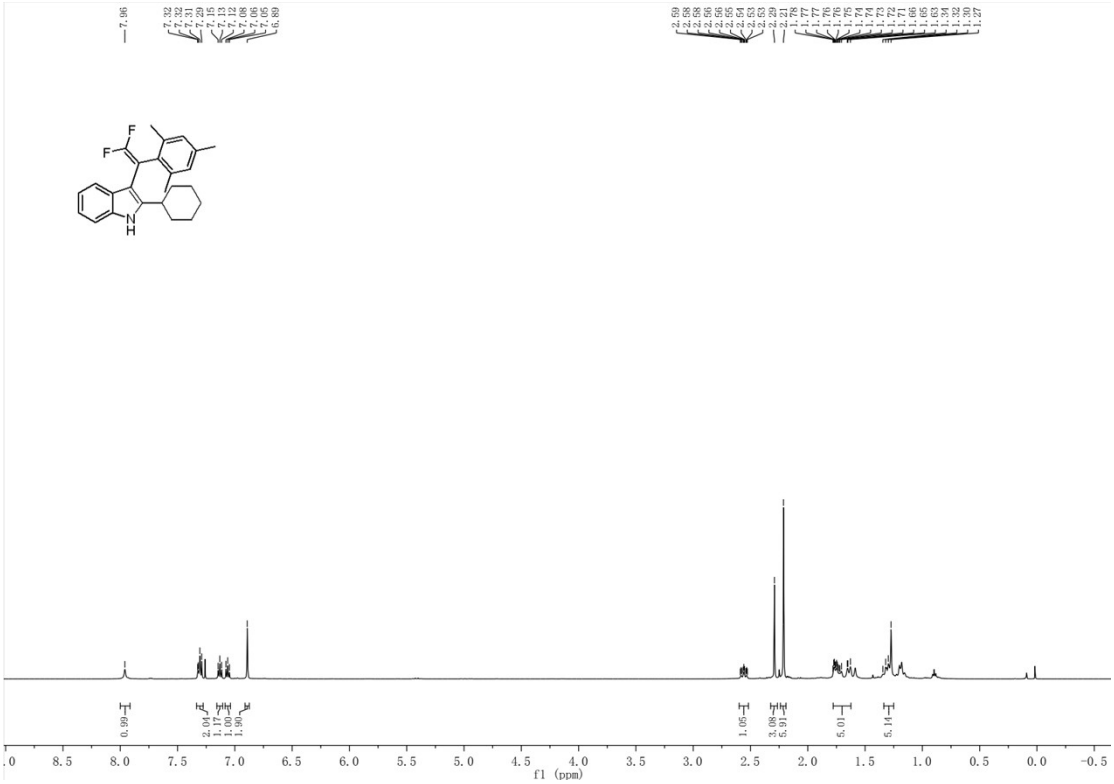
^{13}C NMR spectra of **3am** (100 MHz, $CDCl_3$)



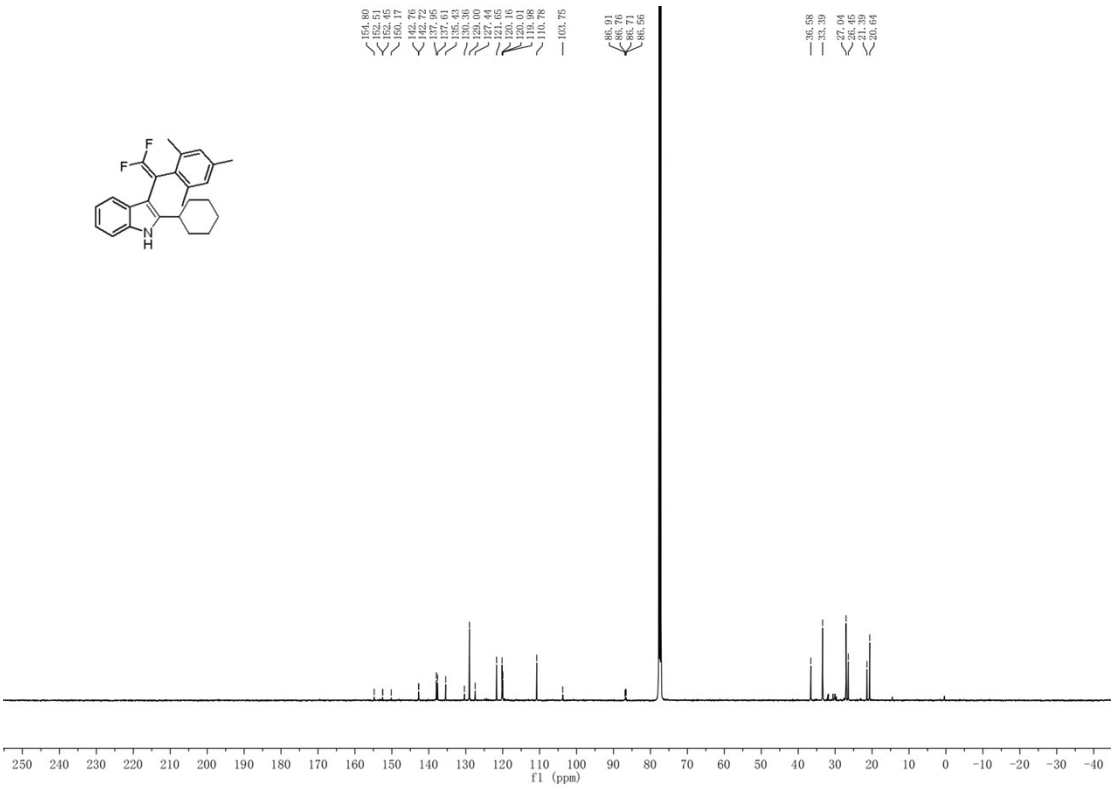
^{19}F NMR spectra of **3am** (376 MHz, $CDCl_3$)



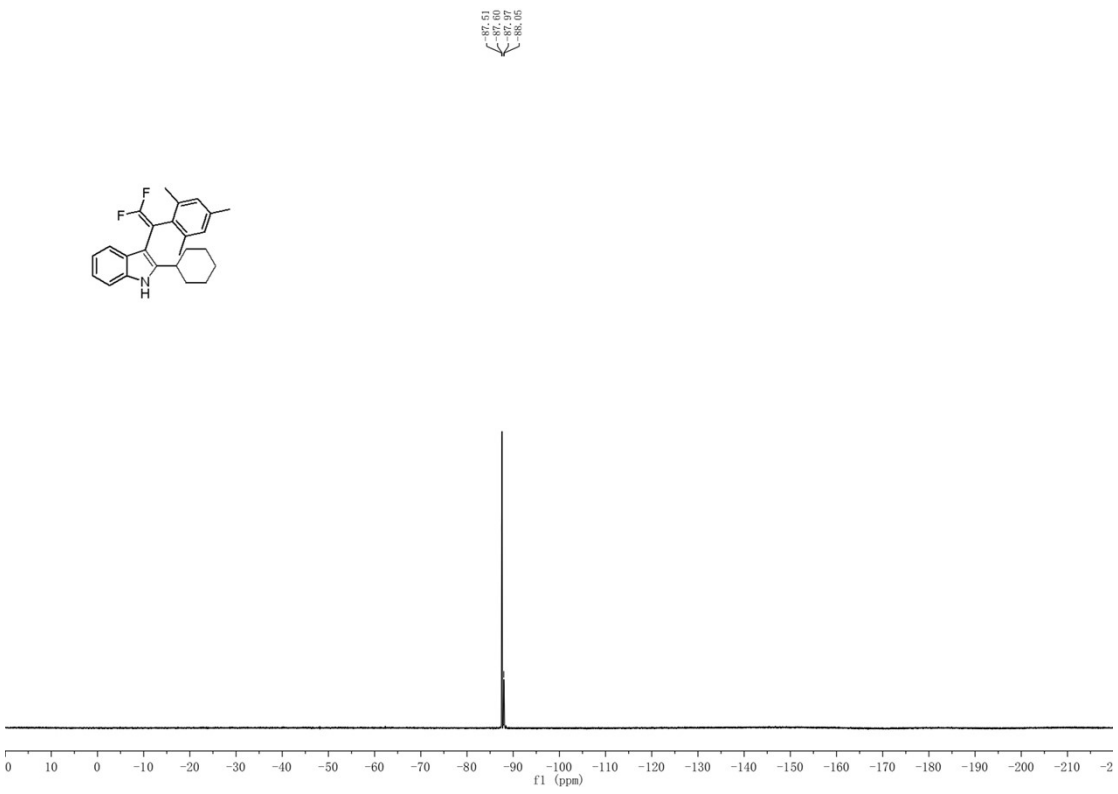
^{1}H NMR spectra of **3an** (500 MHz, $CDCl_3$)



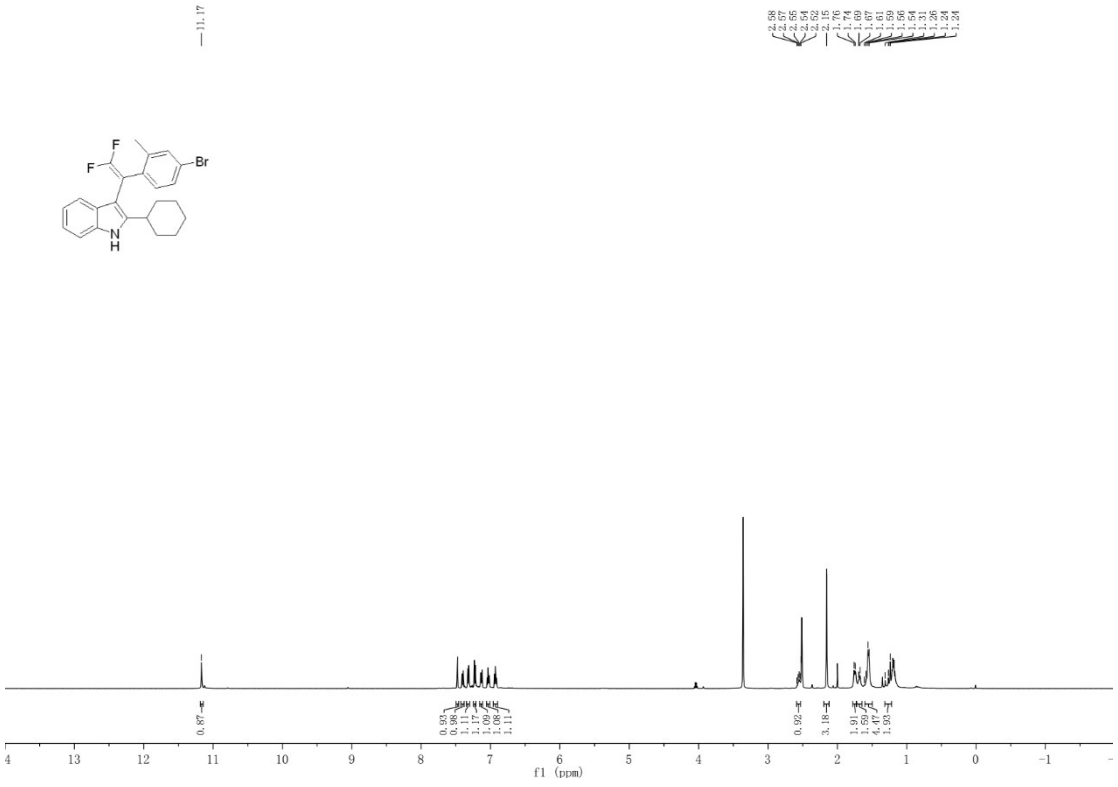
^{13}C NMR spectra of **3an** (125 MHz, $CDCl_3$)



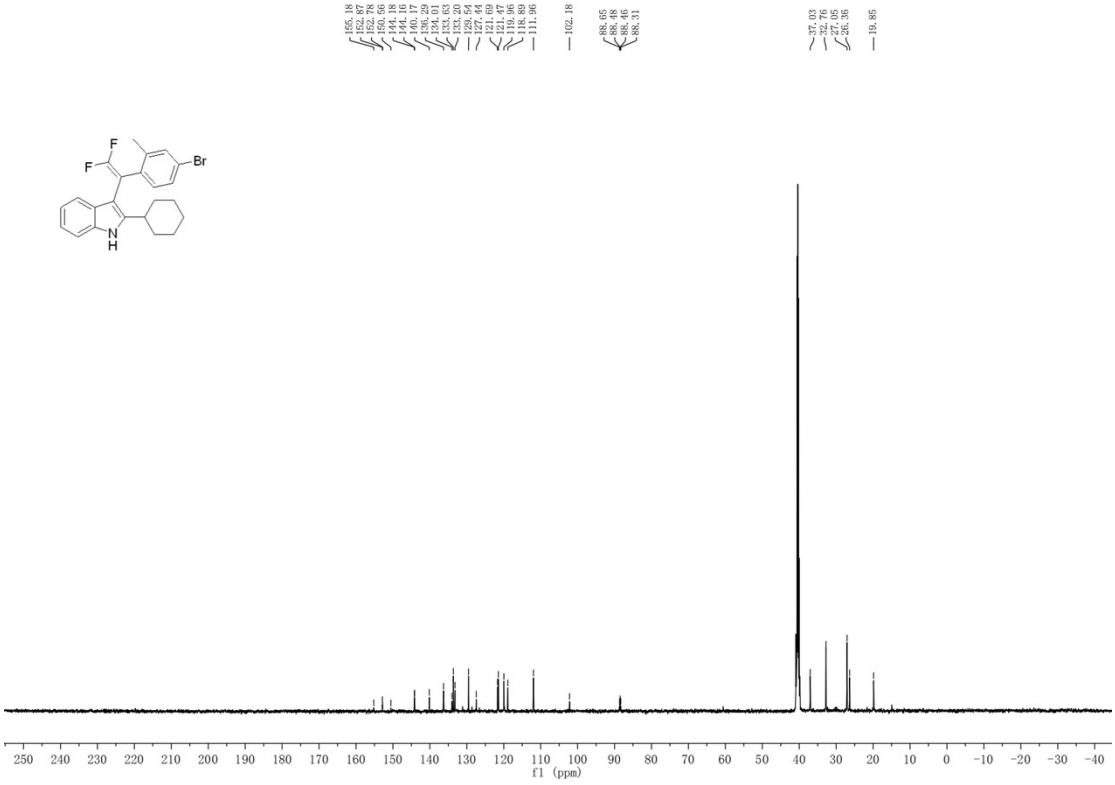
^{19}F NMR spectra of **3an** (376 MHz, $CDCl_3$)



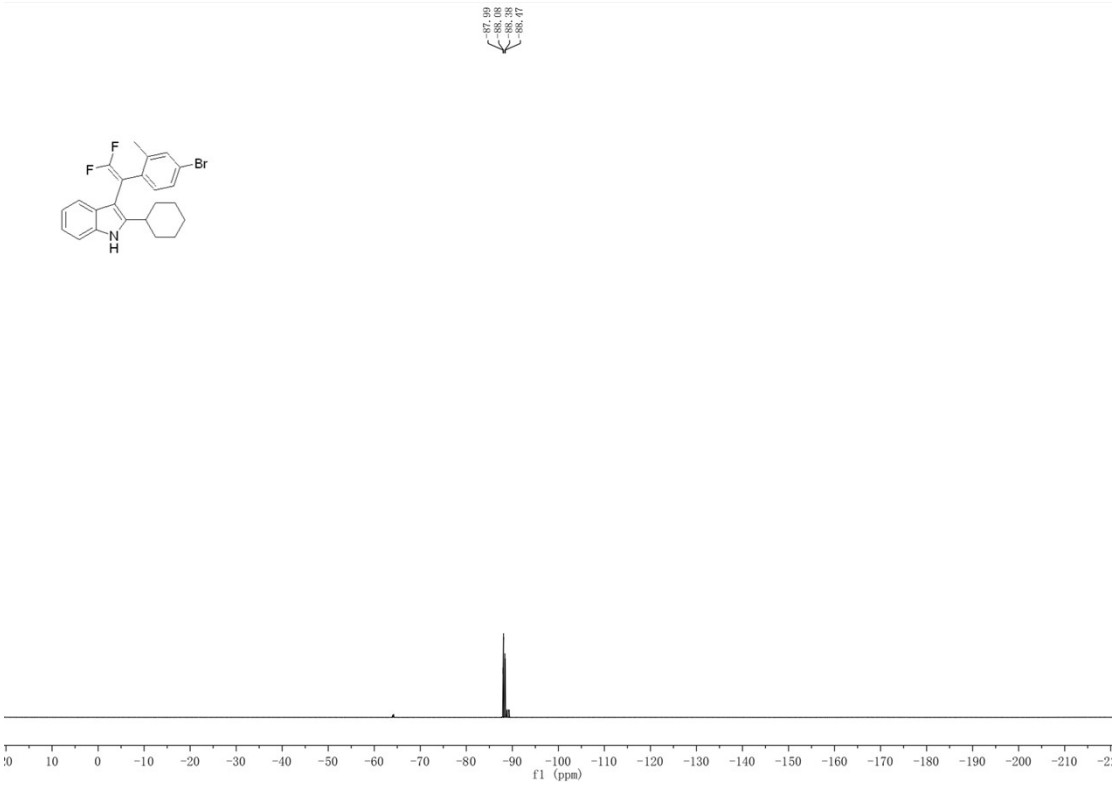
^{1}H NMR spectra of **3ao** (500 MHz, DMSO-d_6)



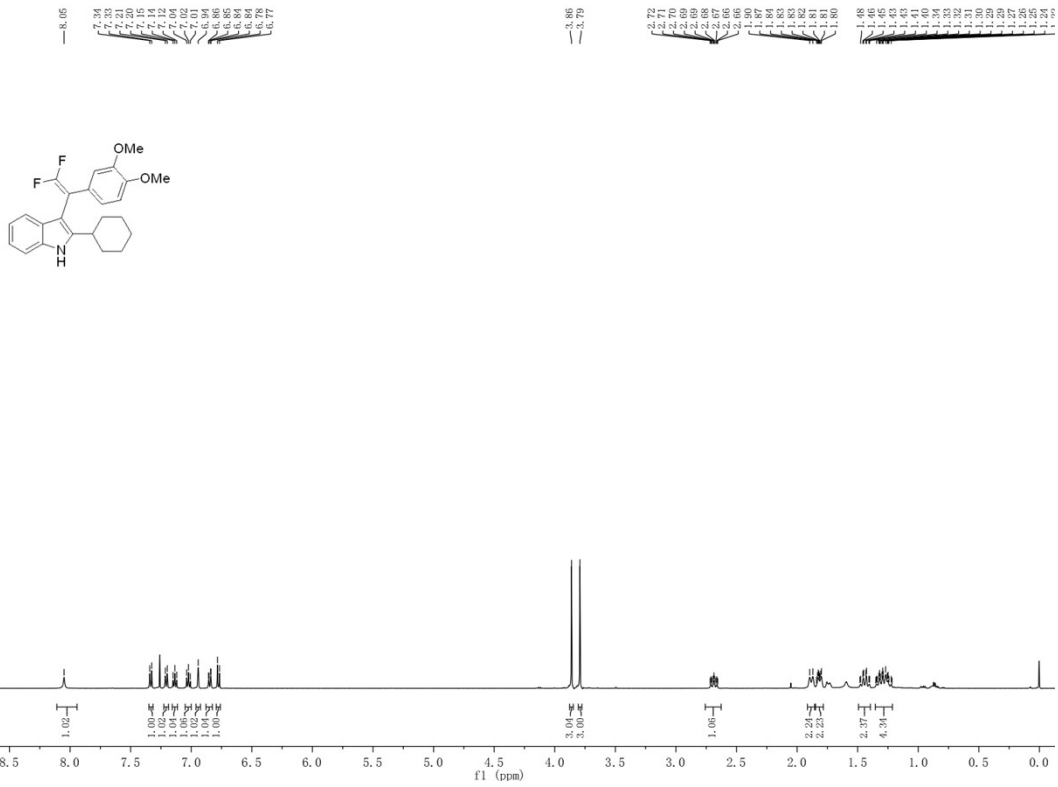
^{13}C NMR spectra of **3ao** (125 MHz, DMSO-d_6)



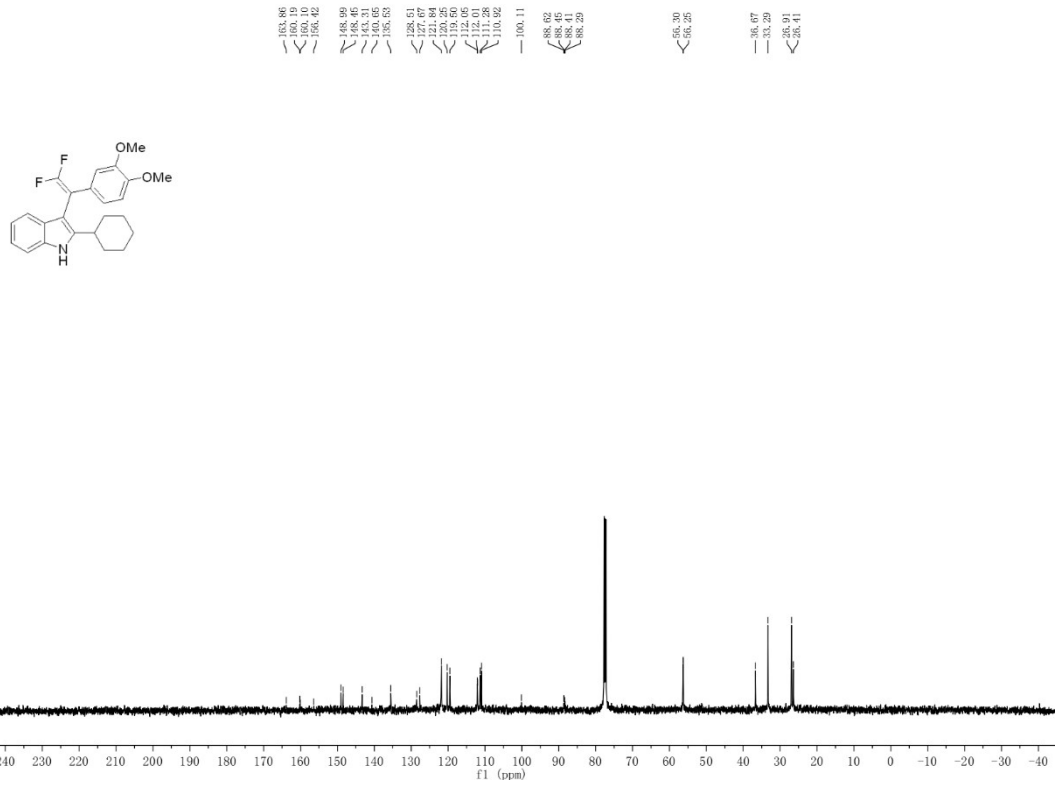
^{19}F NMR spectra of **3ao** (376 MHz, DMSO-d_6)



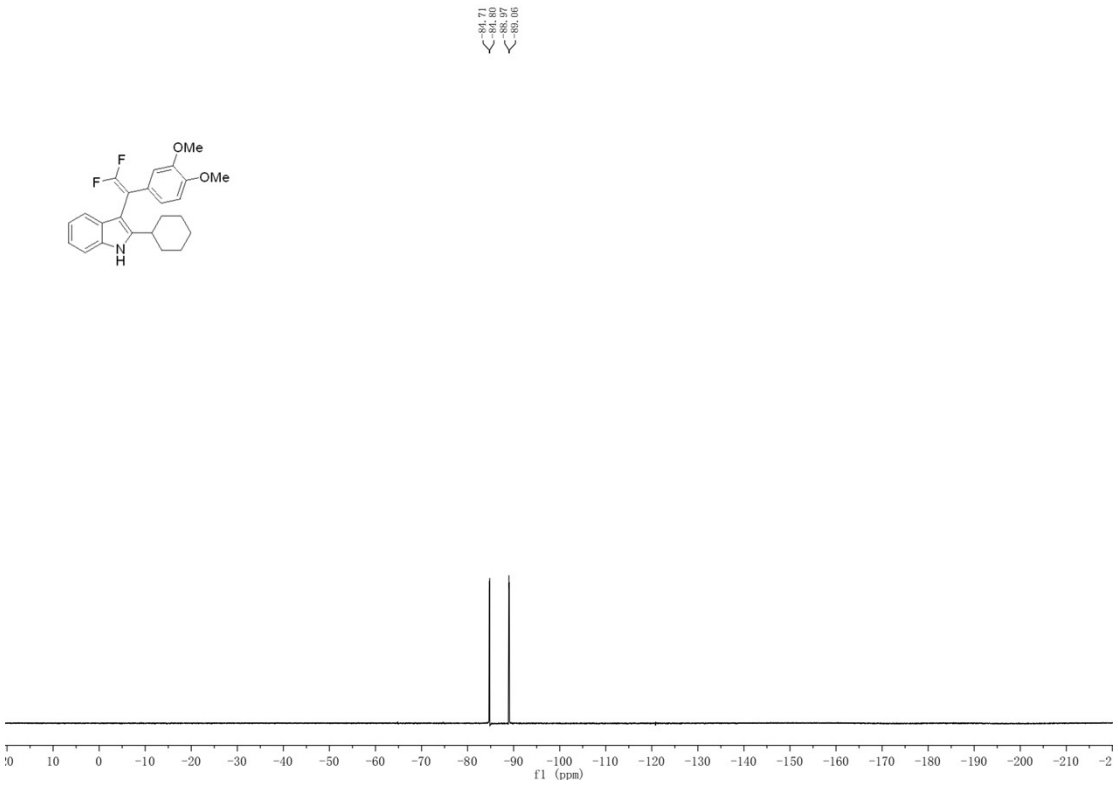
^{1}H NMR spectra of **3ap** (500 MHz, $CDCl_3$)



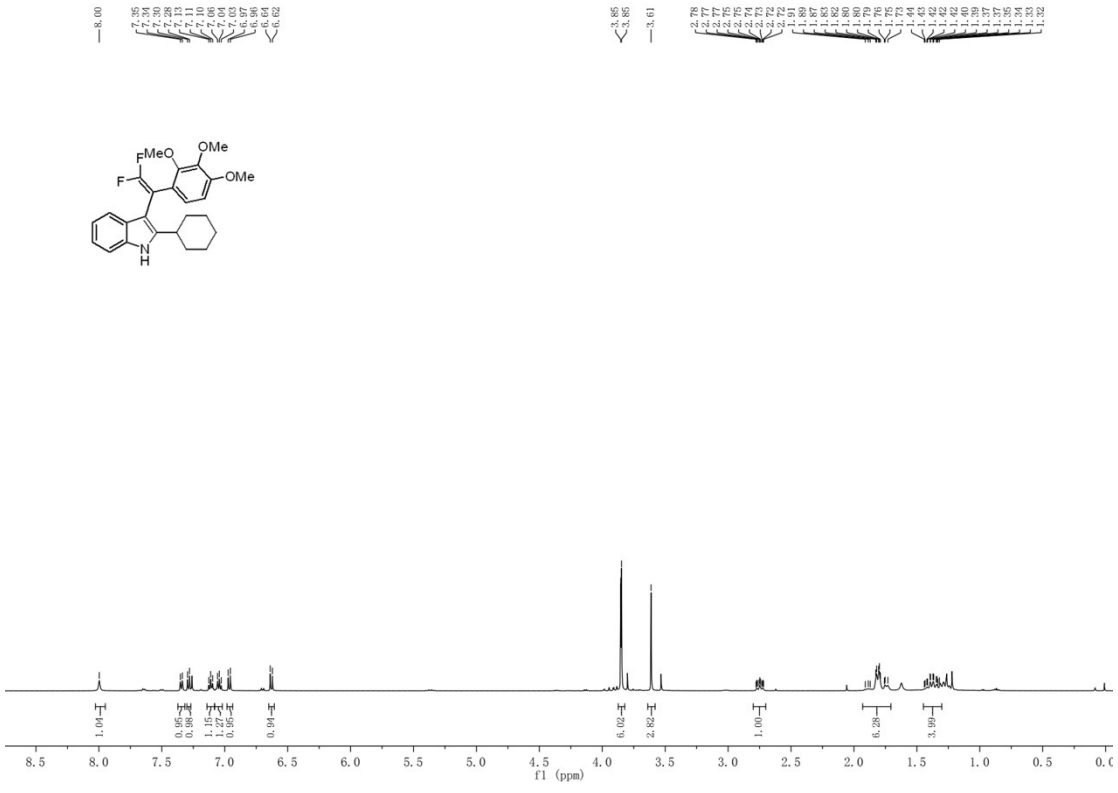
^{13}C NMR spectra of **3ap** (125 MHz, $CDCl_3$)



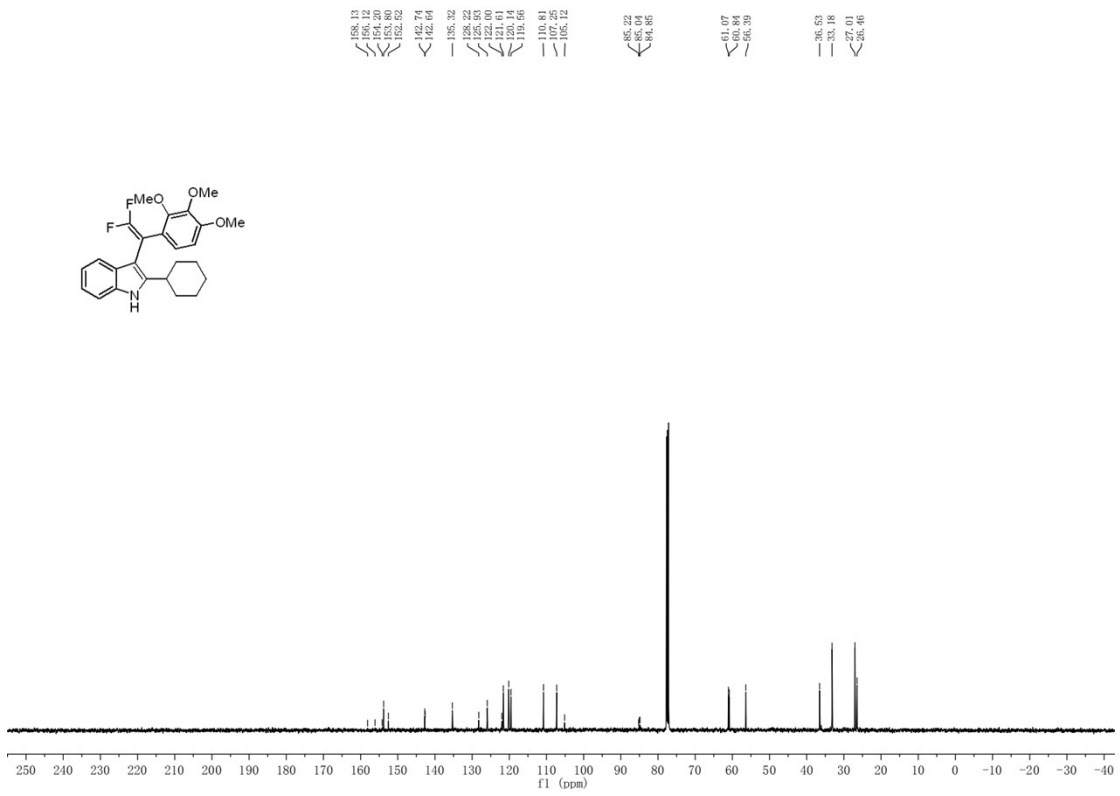
^{19}F NMR spectra of **3ap** (376 MHz, $CDCl_3$)



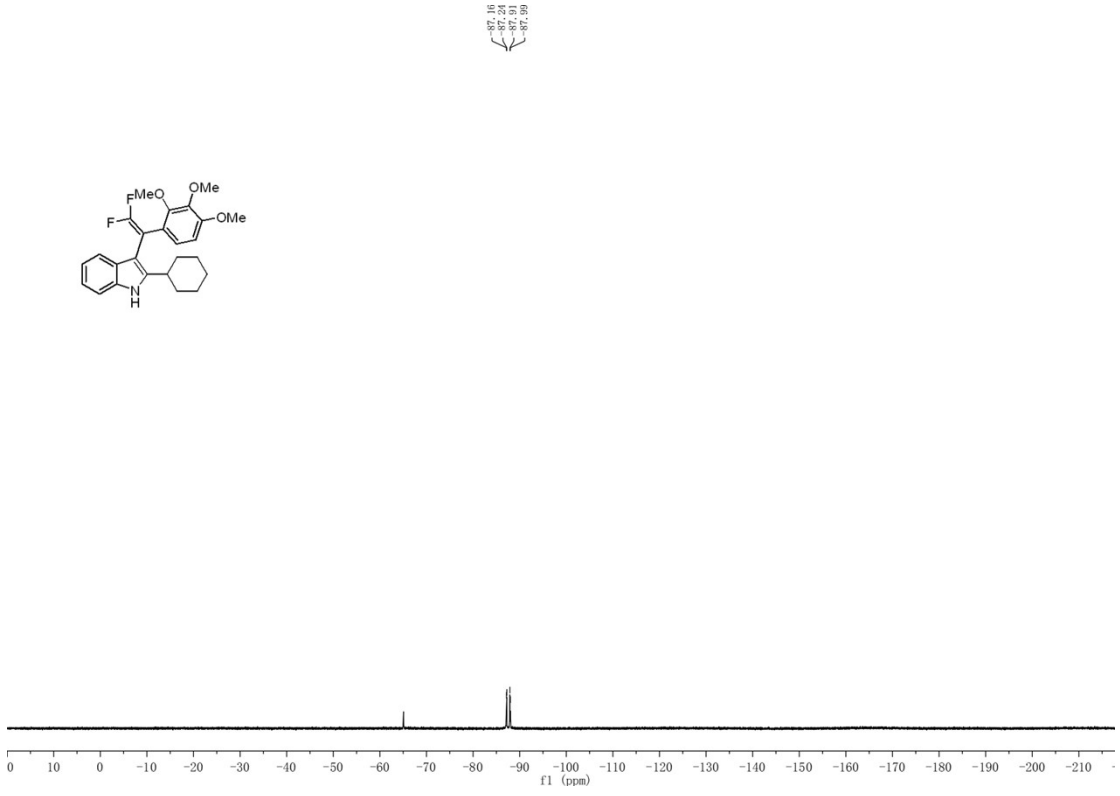
^{1}H NMR spectra of **3aq** (500 MHz, $CDCl_3$)



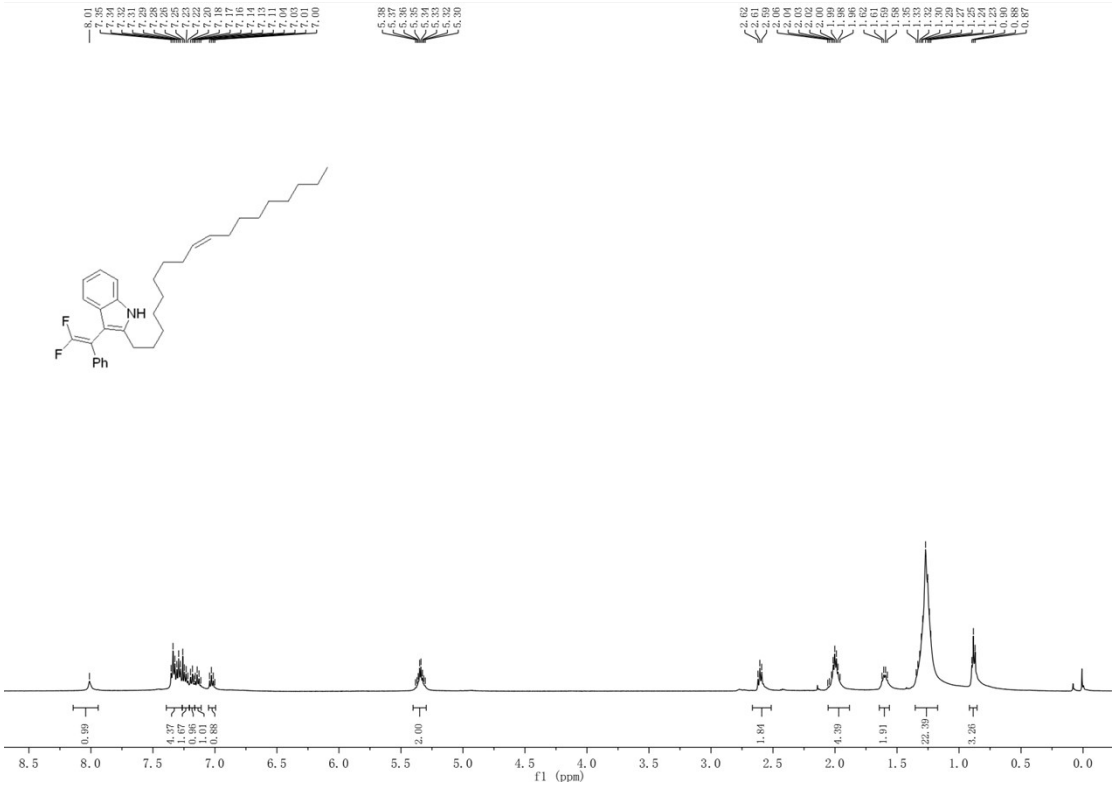
^{13}C NMR spectra of **3aq** (125 MHz, $CDCl_3$)



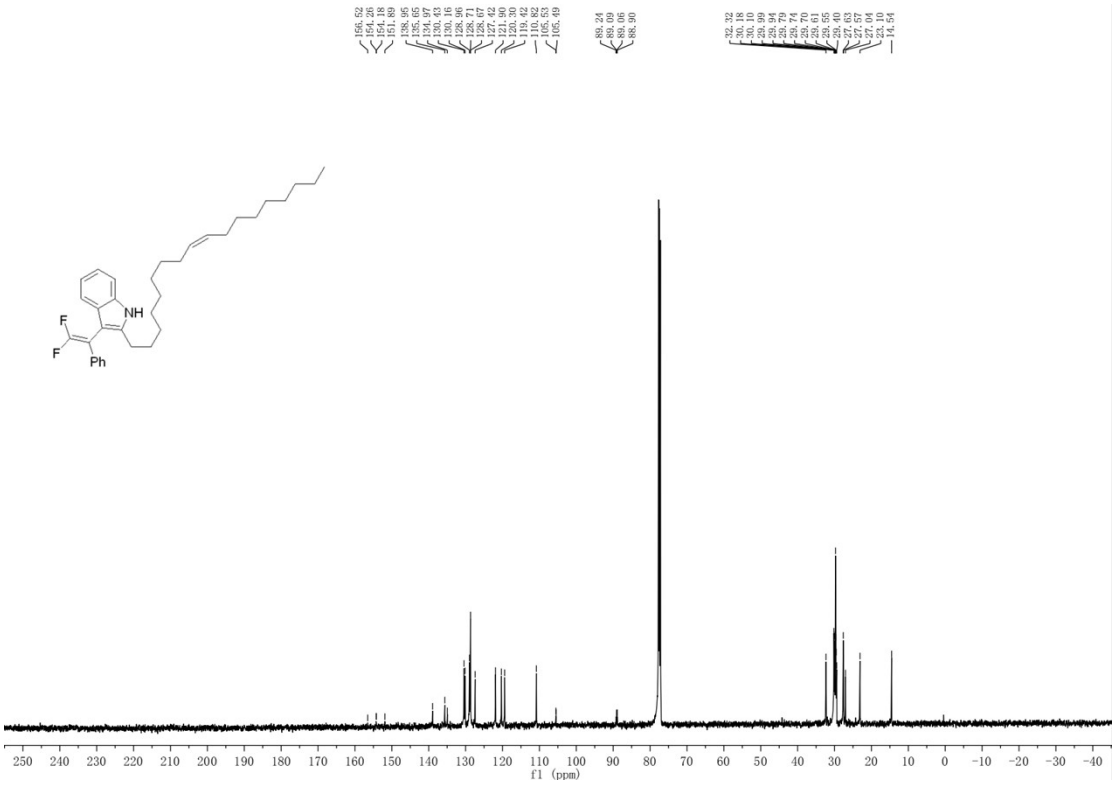
^{19}F NMR spectra of **3aq** (376 MHz, $CDCl_3$)



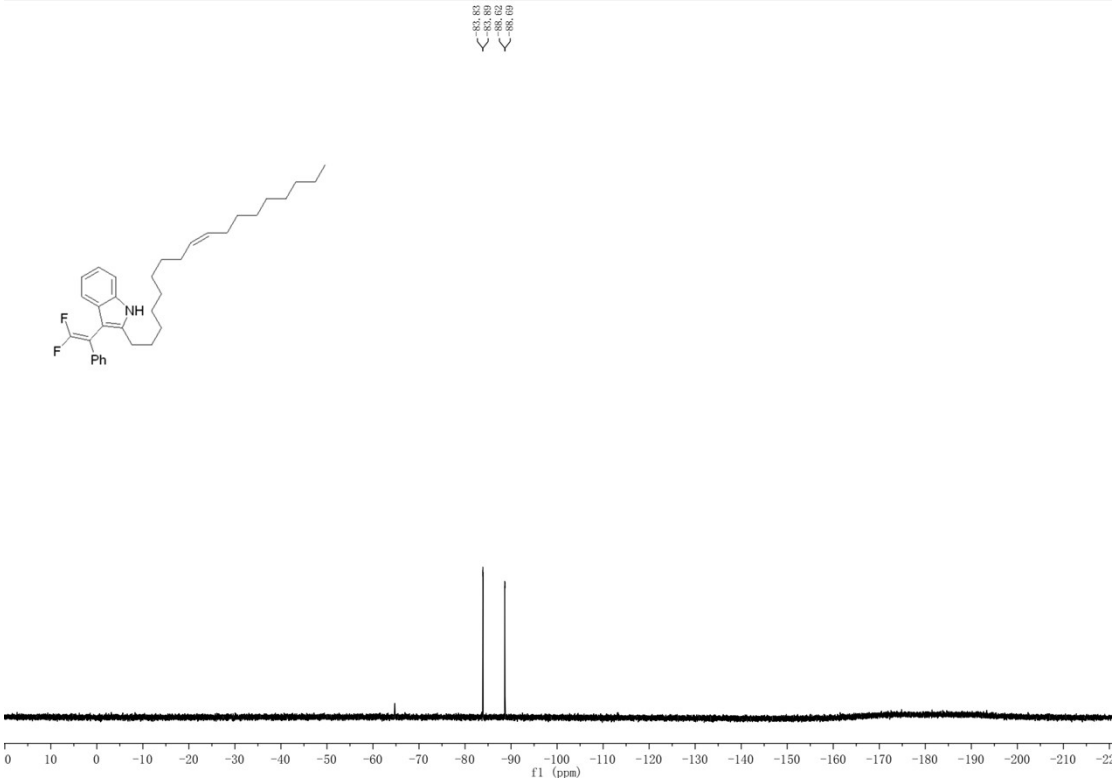
^{1}H NMR spectra of **3ar** (500 MHz, $CDCl_3$)



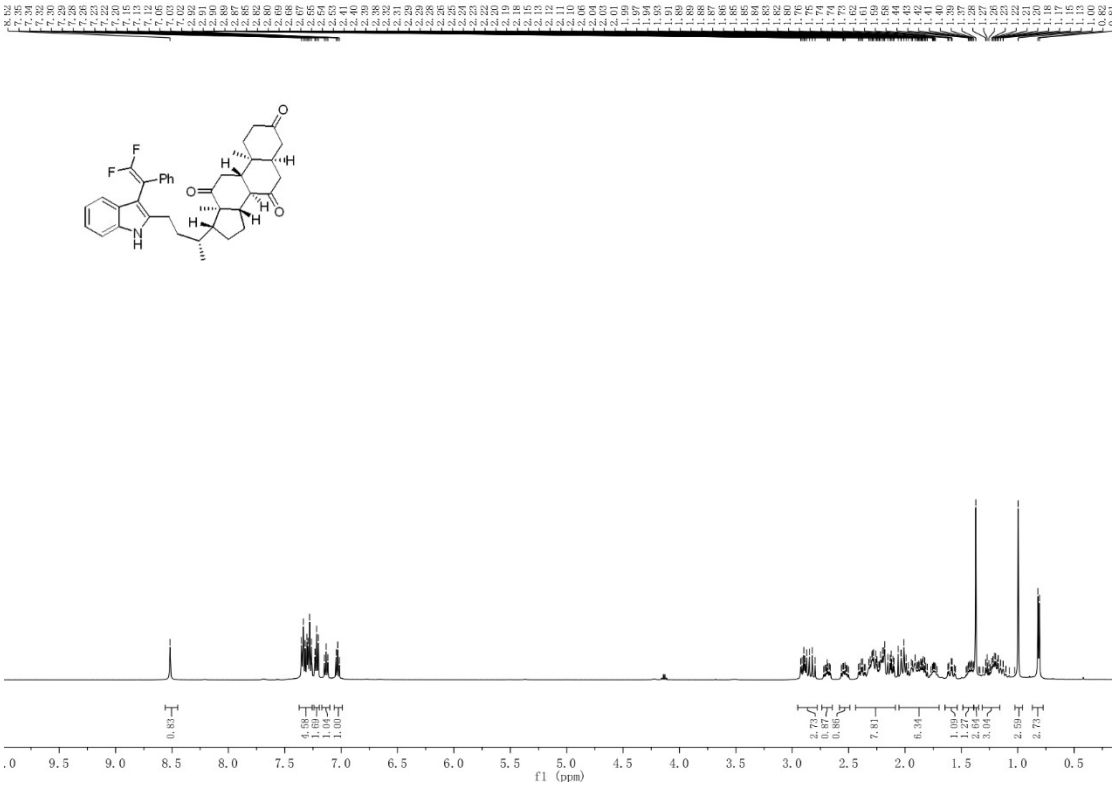
^{13}C NMR spectra of **3ar** (125 MHz, $CDCl_3$)



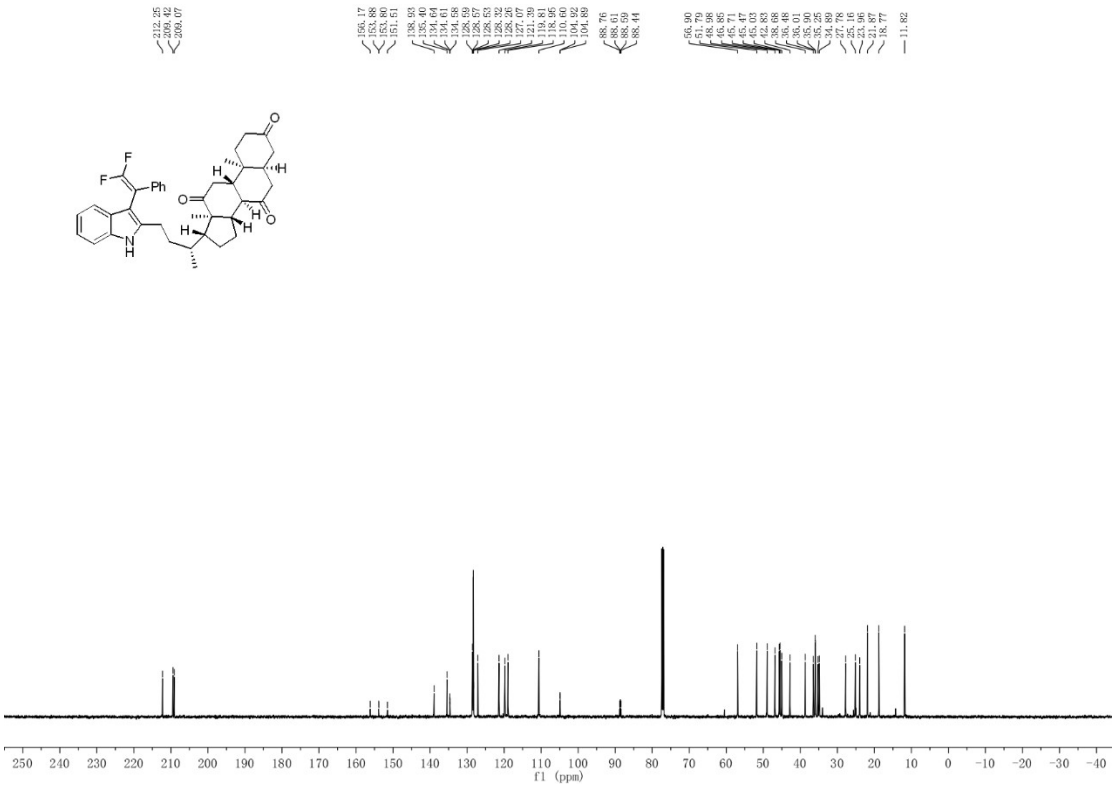
^{19}F NMR spectra of **3ar** (470 MHz, $CDCl_3$)



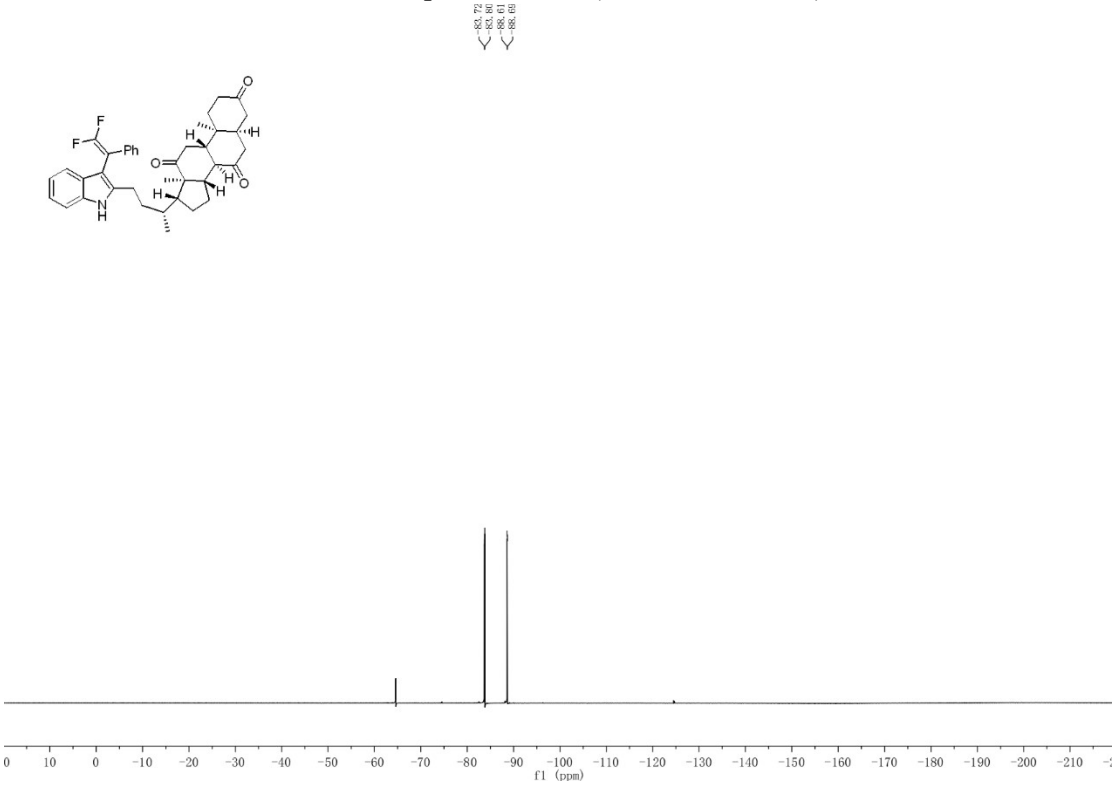
^{1}H NMR spectra of **3as** (400 MHz, $CDCl_3$)



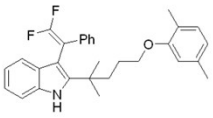
^{13}C NMR spectra of **3as** (100 MHz, $CDCl_3$)

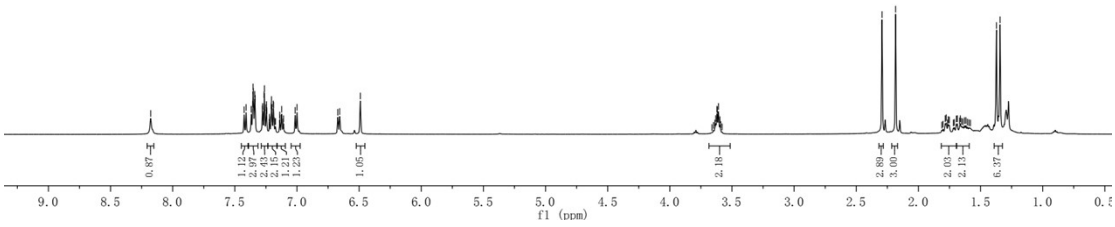


^{19}F NMR spectra of **3as** (470 MHz, $CDCl_3$)

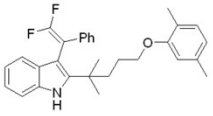


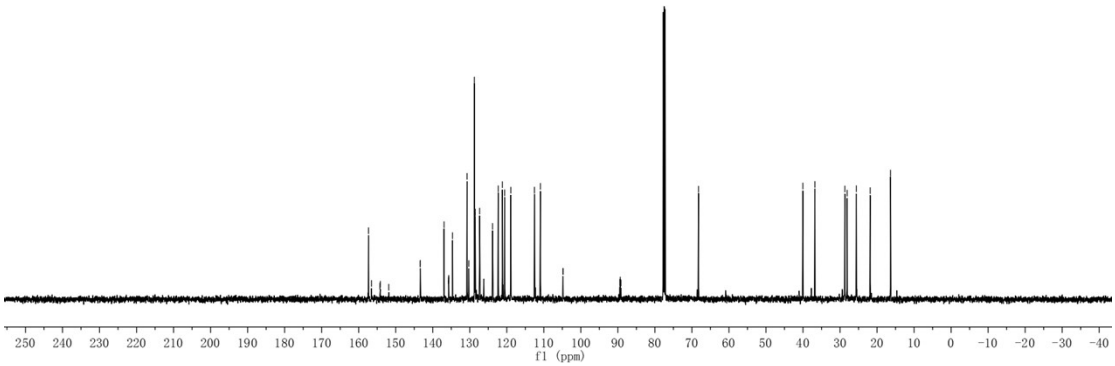
^{1}H NMR spectra of **3at** (500 MHz, $CDCl_3$)



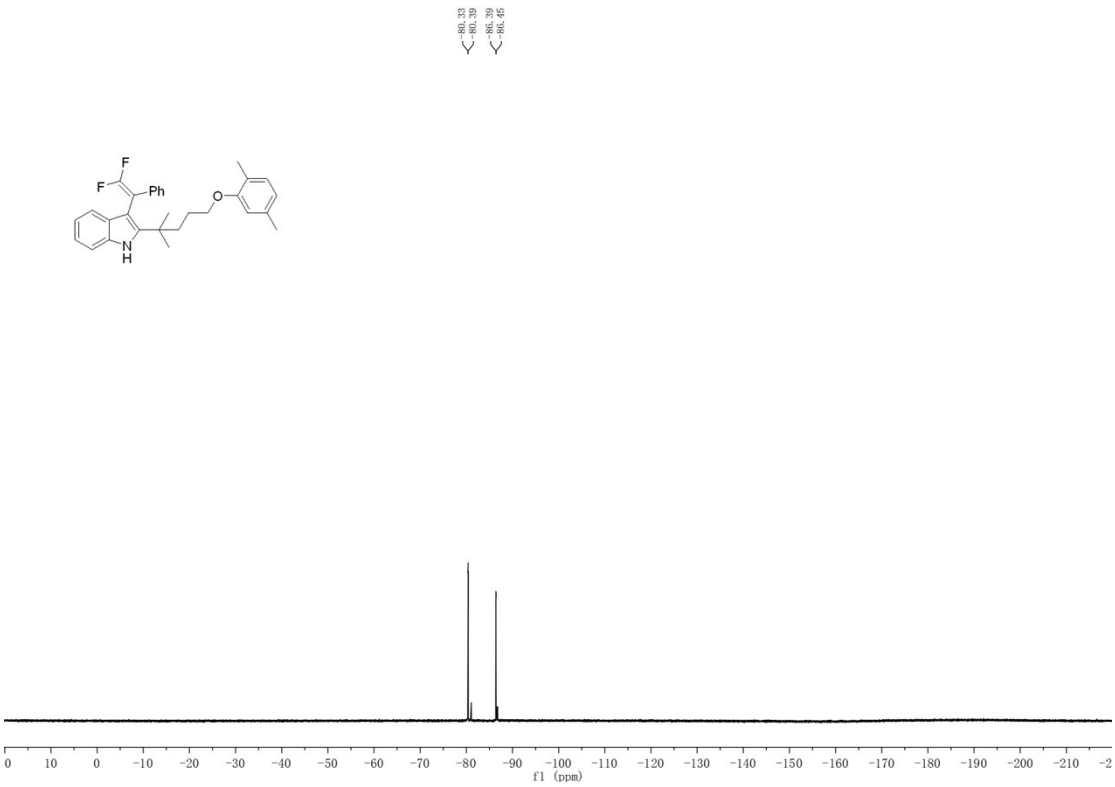


^{13}C NMR spectra of **3at** (125 MHz, $CDCl_3$)

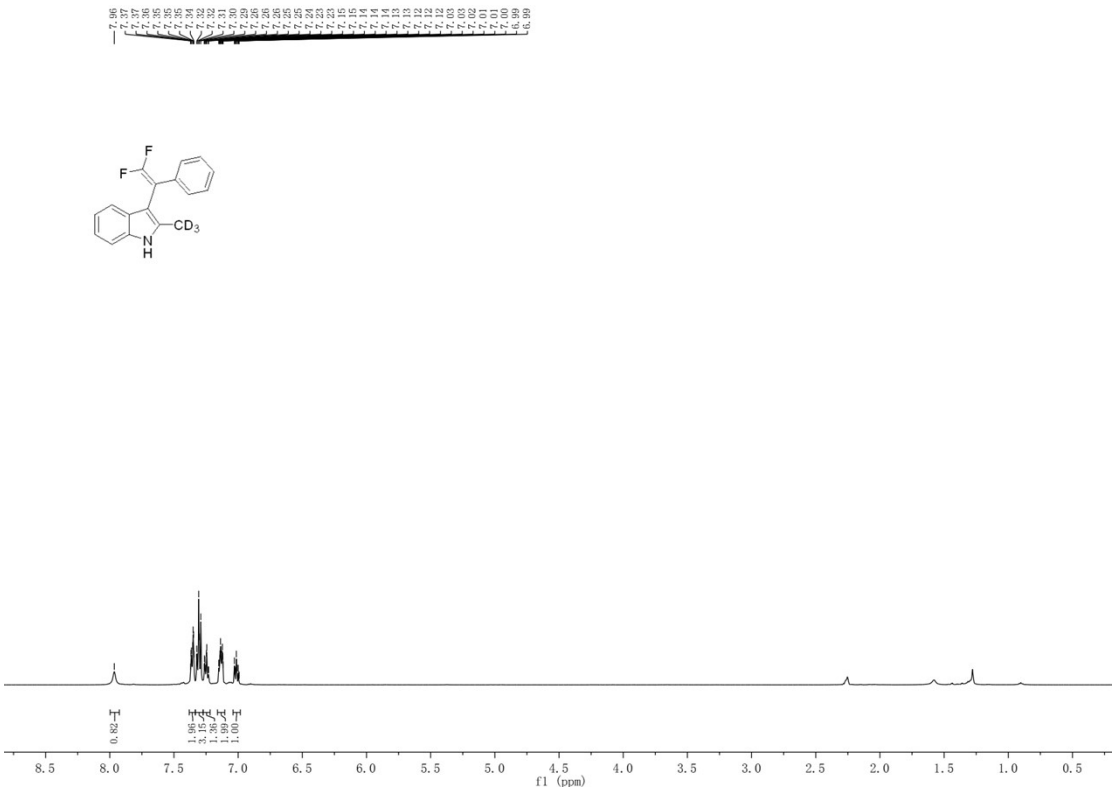




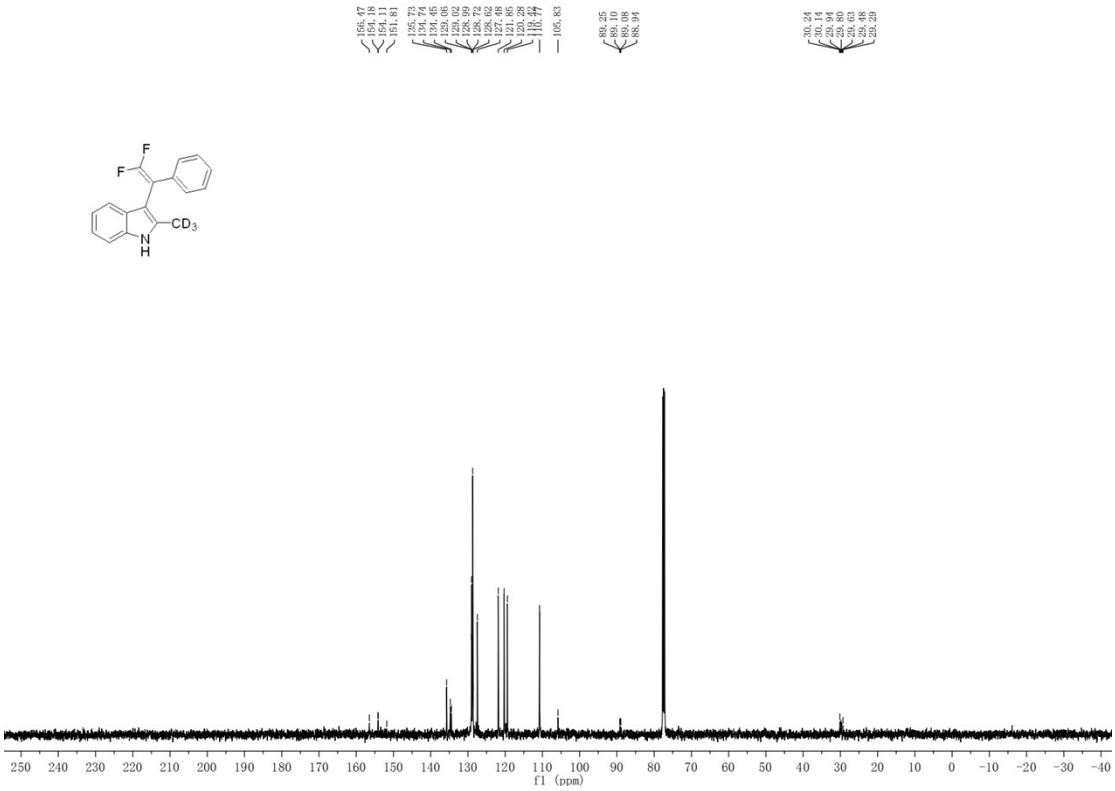
^{19}F NMR spectra of **3at**(470 MHz, $CDCl_3$)



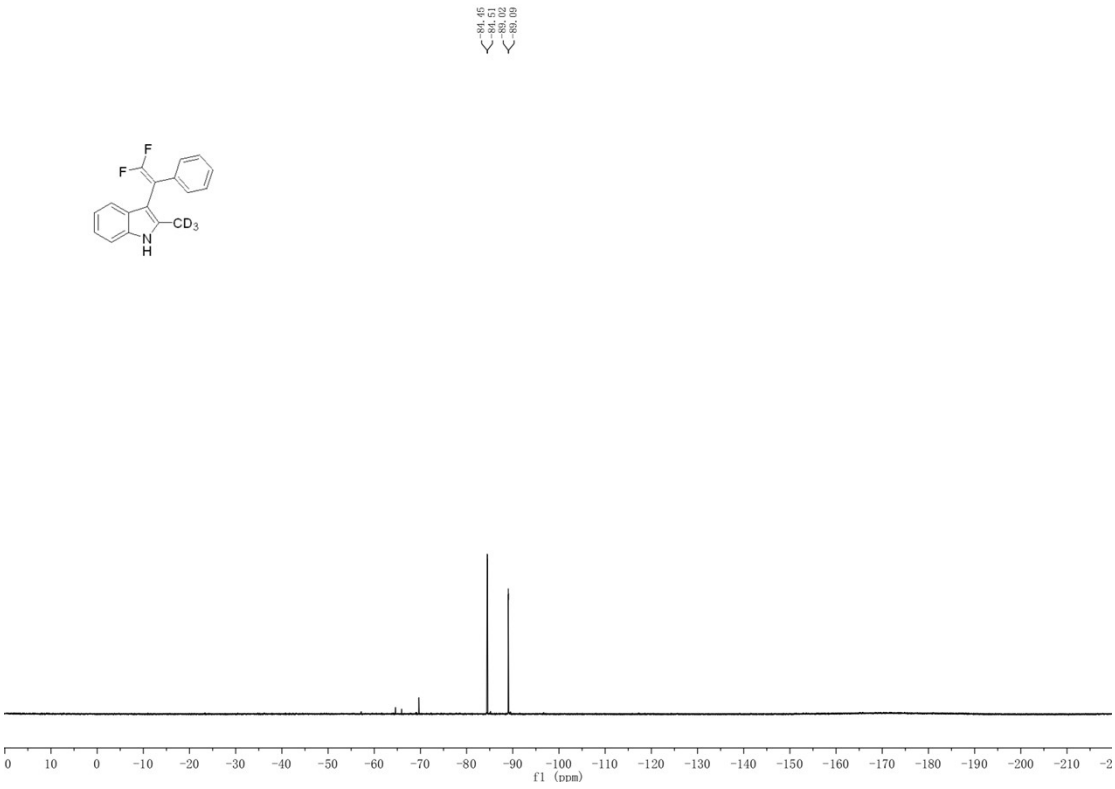
^{1}H NMR spectra of **3au** ($CDCl_3$)



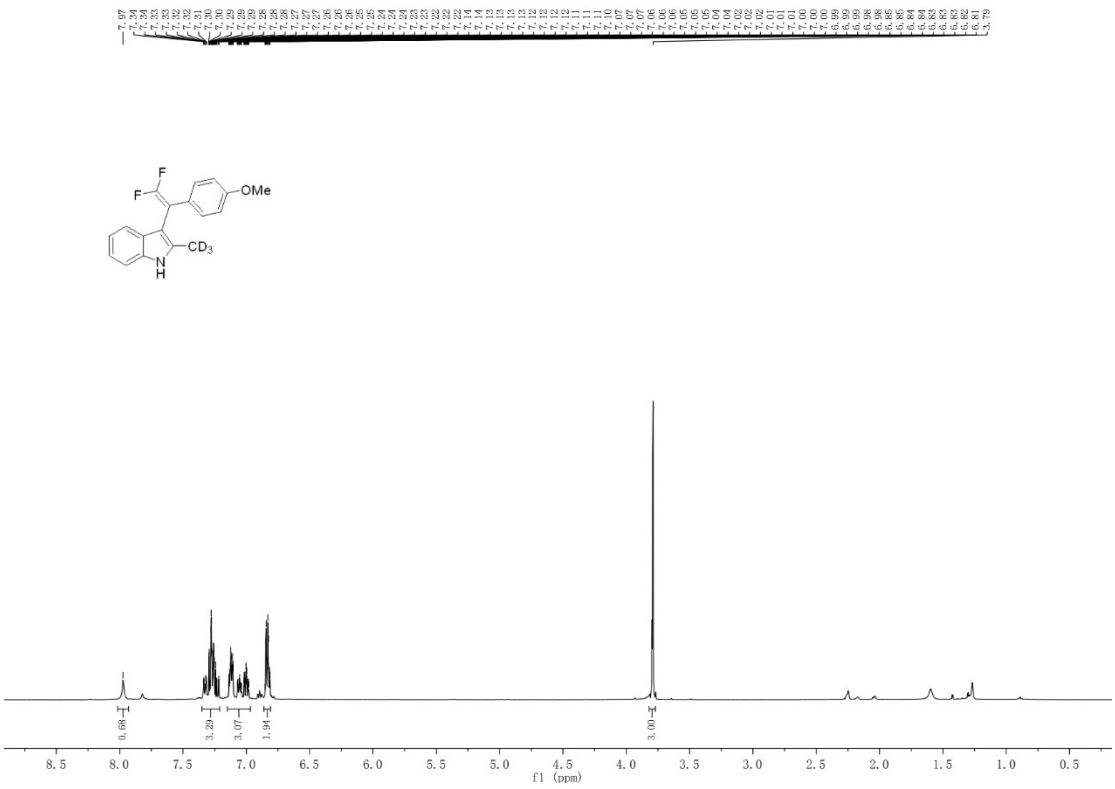
^{13}C NMR spectra of **3au** (125 MHz, $CDCl_3$)



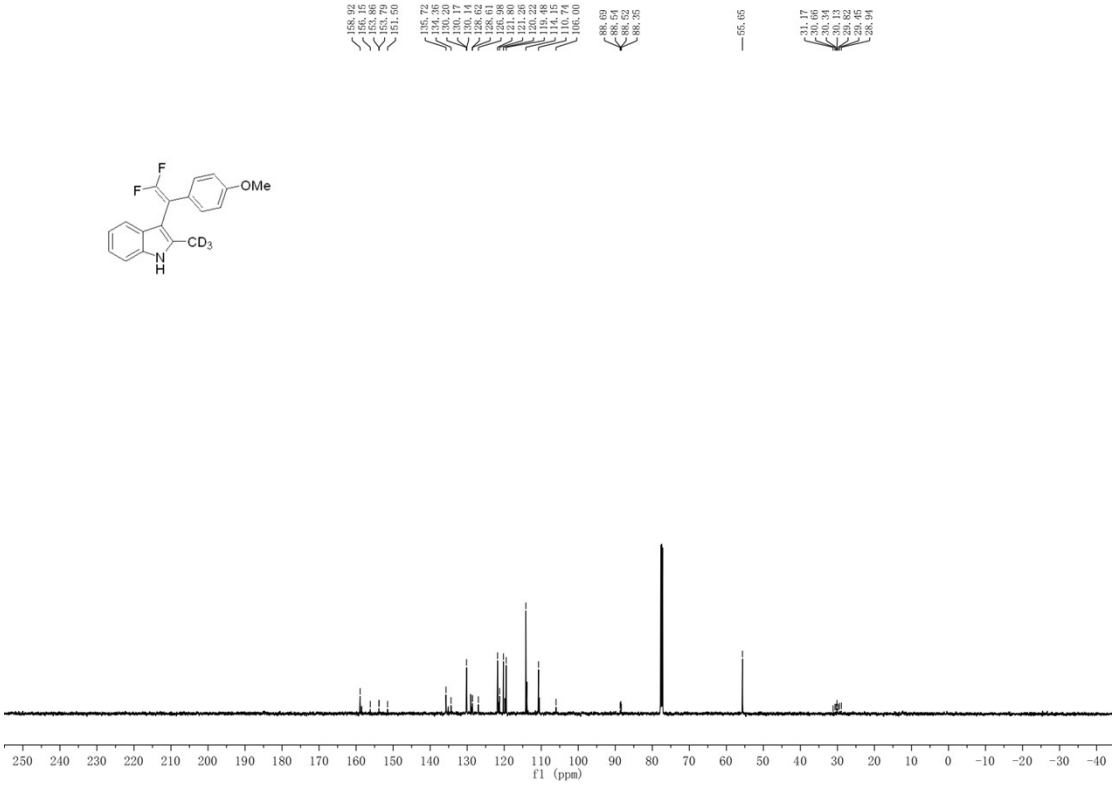
^{19}F NMR spectra of **3au** (470 MHz, $CDCl_3$)



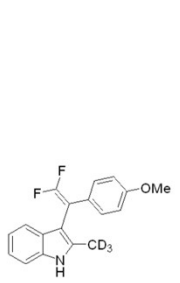
^{1}H NMR spectra of **3av** (500 MHz, $CDCl_3$)

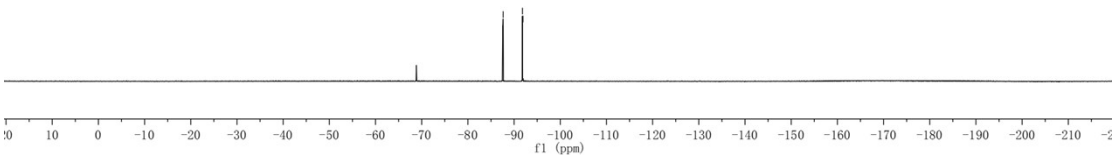


^{13}C NMR spectra of **3av** (125 MHz, $CDCl_3$)

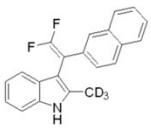


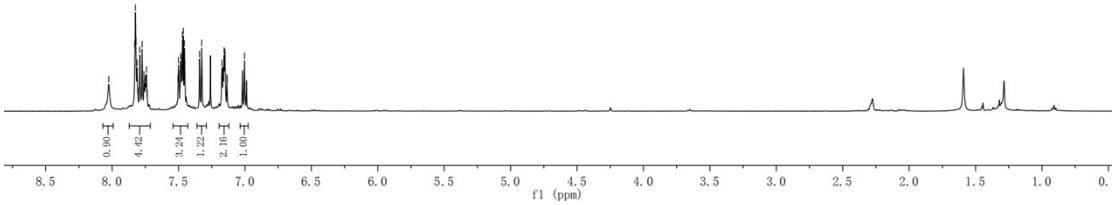
^{19}F NMR spectra of **3av** (376 MHz, DMSO-d_6)



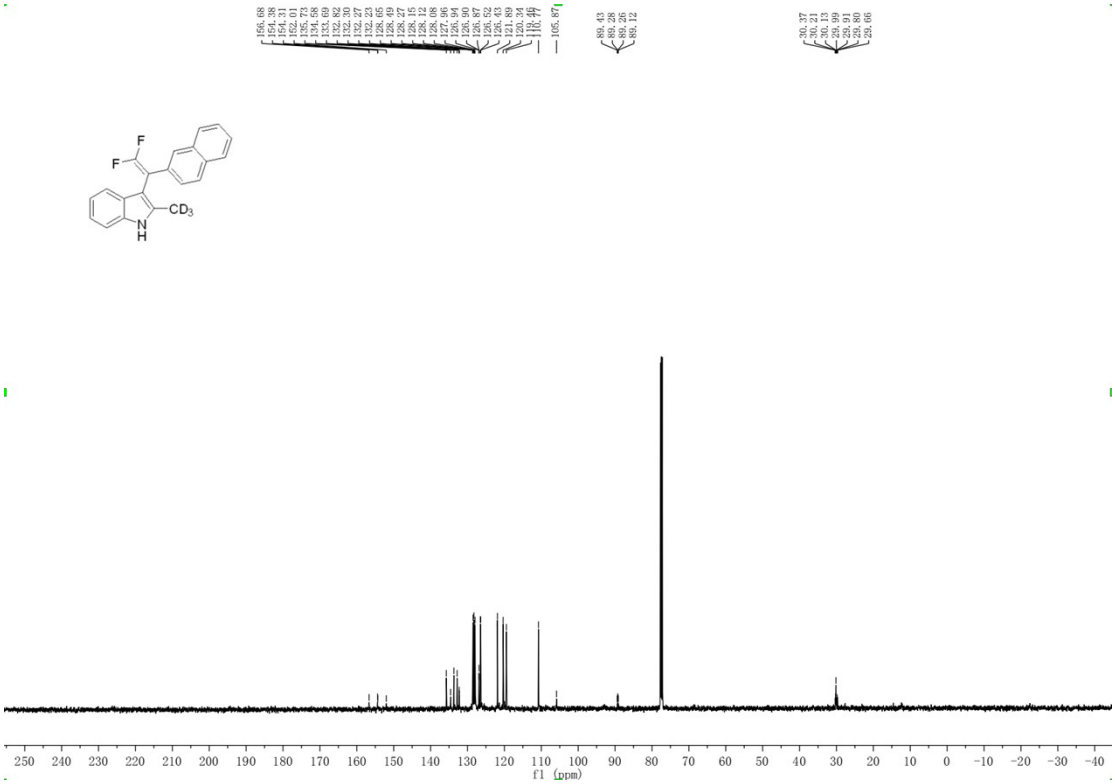


^{1}H NMR spectra of **3aw** (500 MHz, $CDCl_3$)

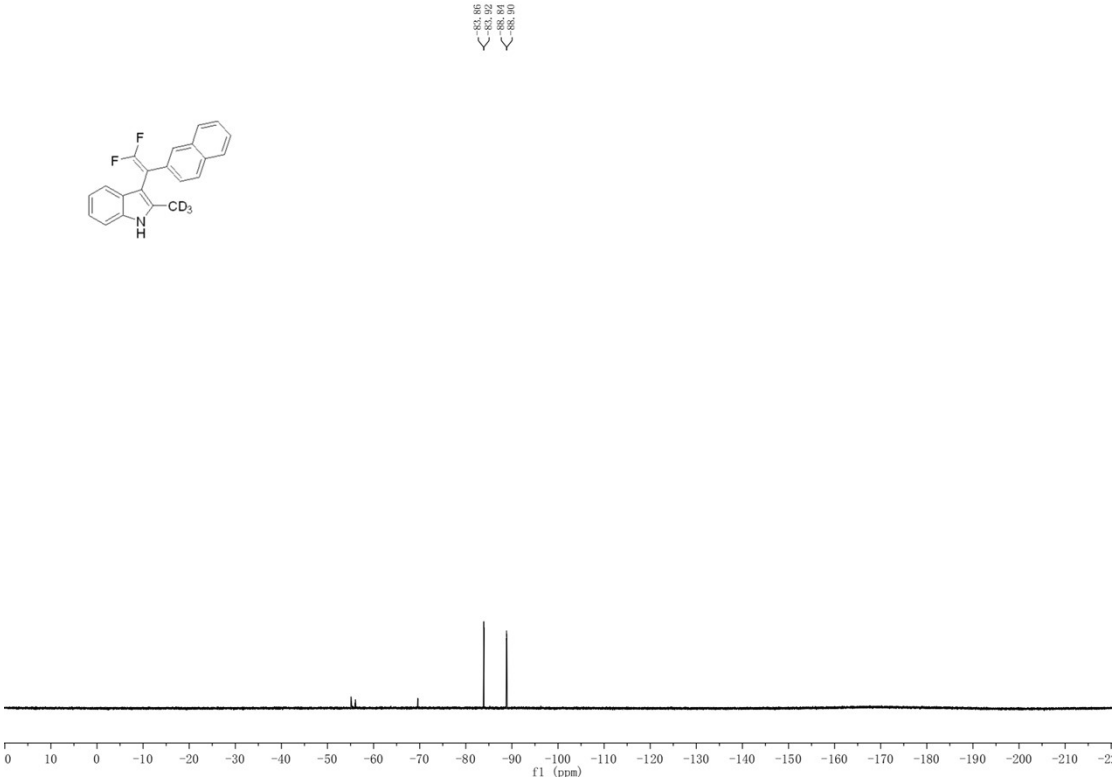




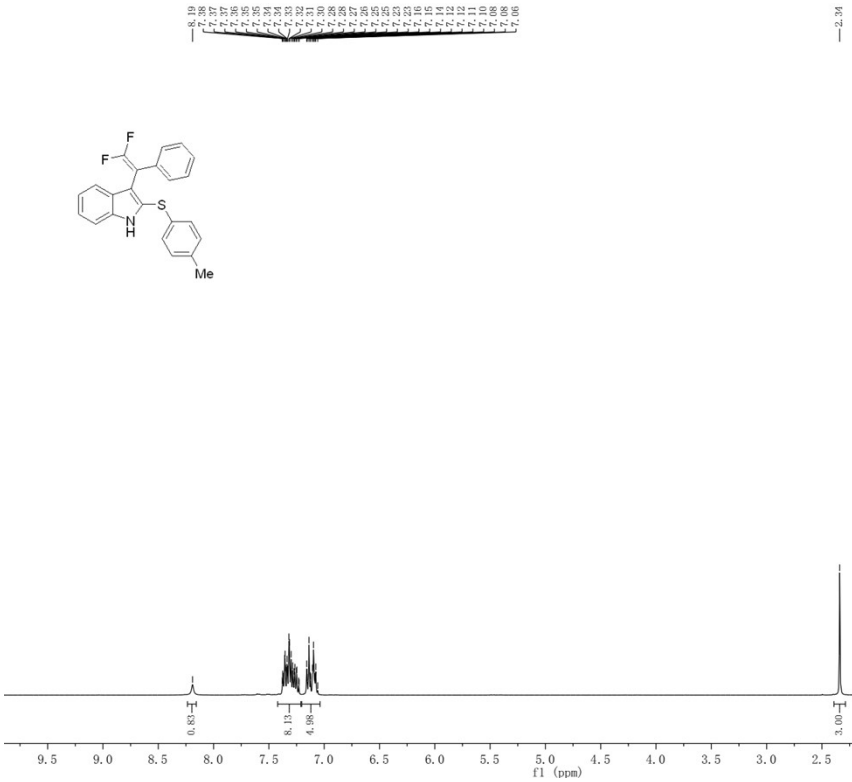
^{13}C NMR spectra of **3aw** (125 MHz, $CDCl_3$)



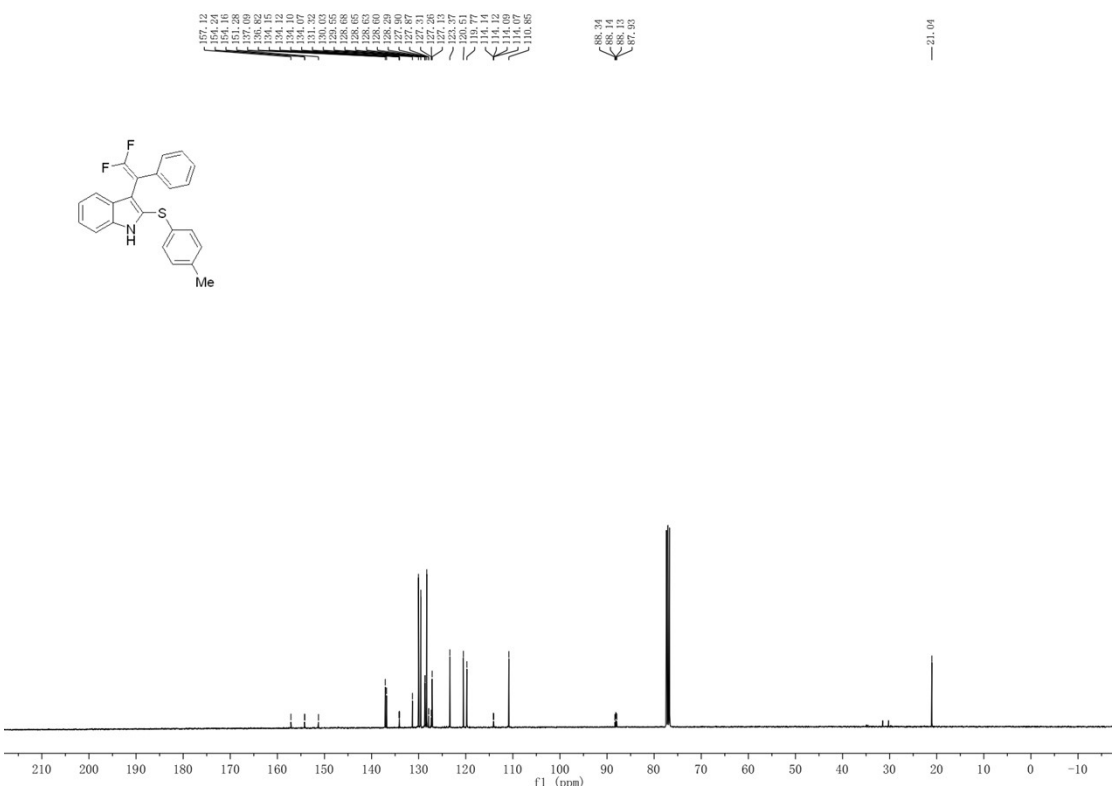
^{19}F NMR spectra of **3aw** (470 MHz, $CDCl_3$)



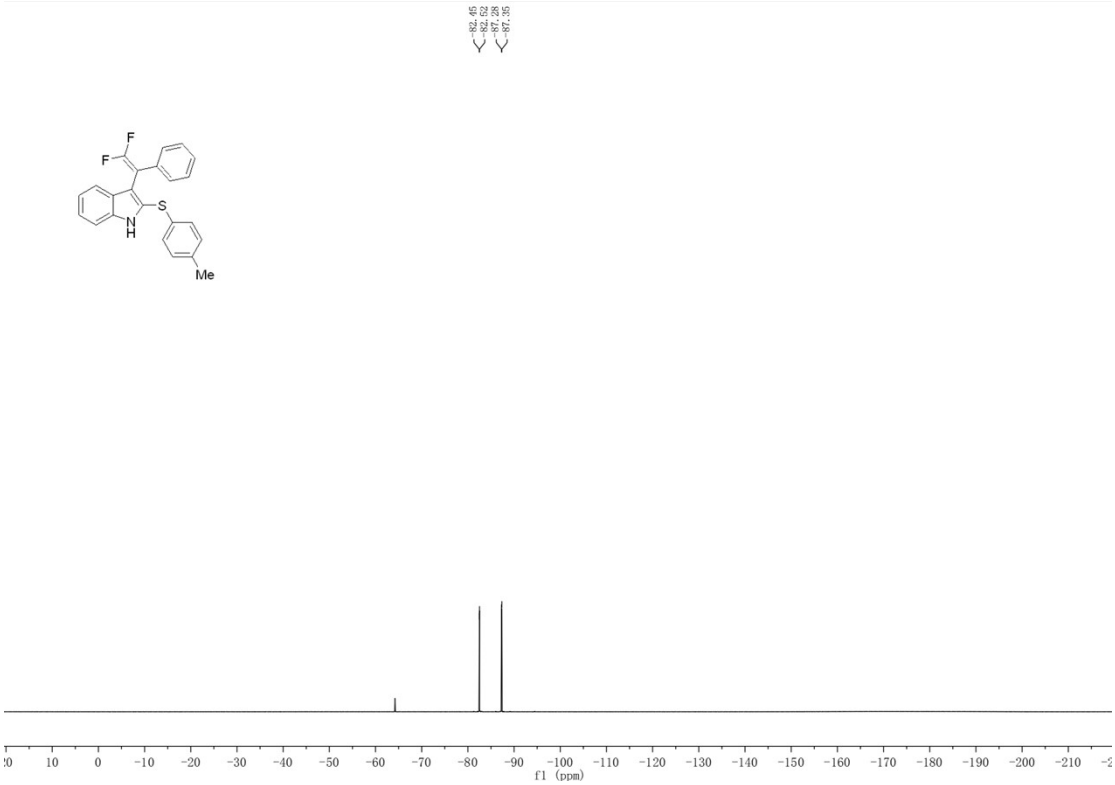
^{1}H NMR spectra of **5a** (400 MHz, $CDCl_3$)



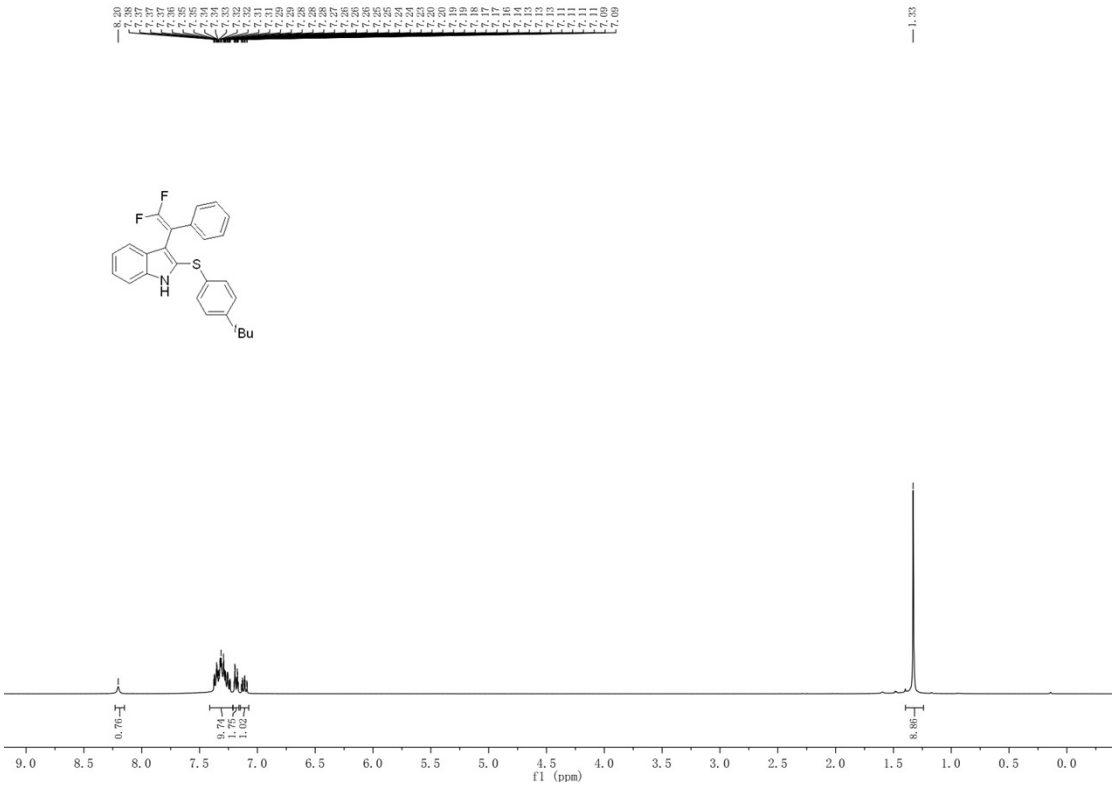
^{13}C NMR spectra of **5a** (100 MHz, $CDCl_3$)



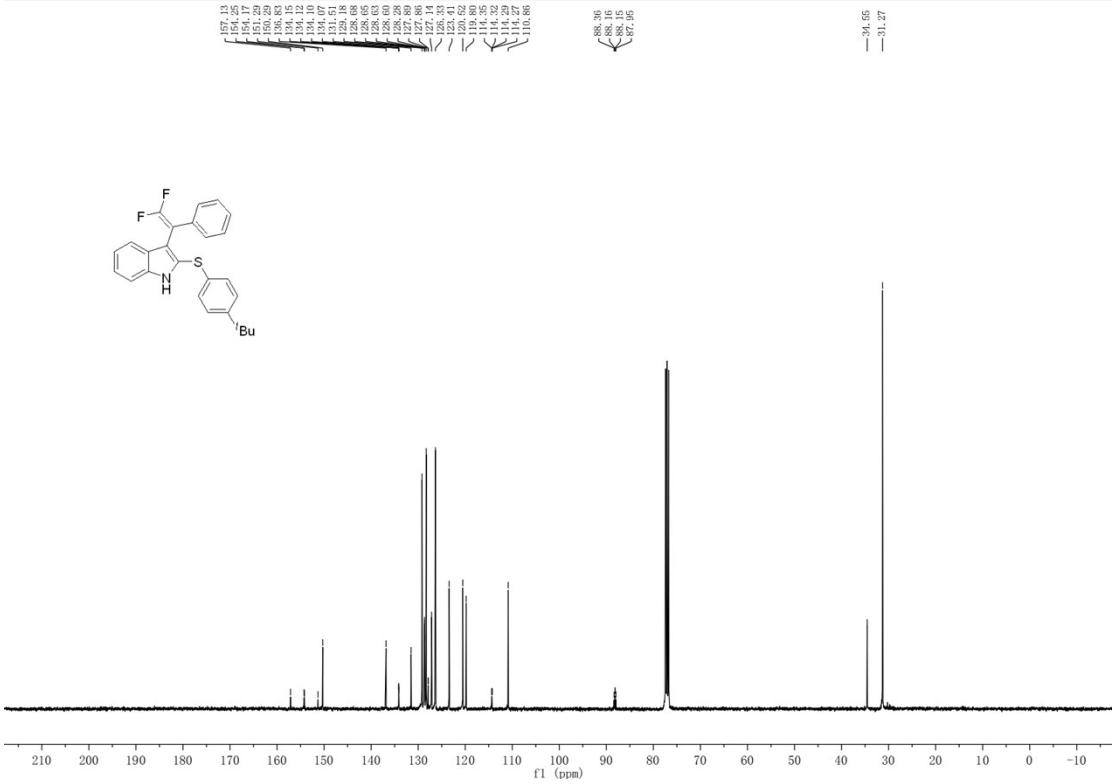
^{19}F NMR spectra of **5a** (376 MHz, $CDCl_3$)



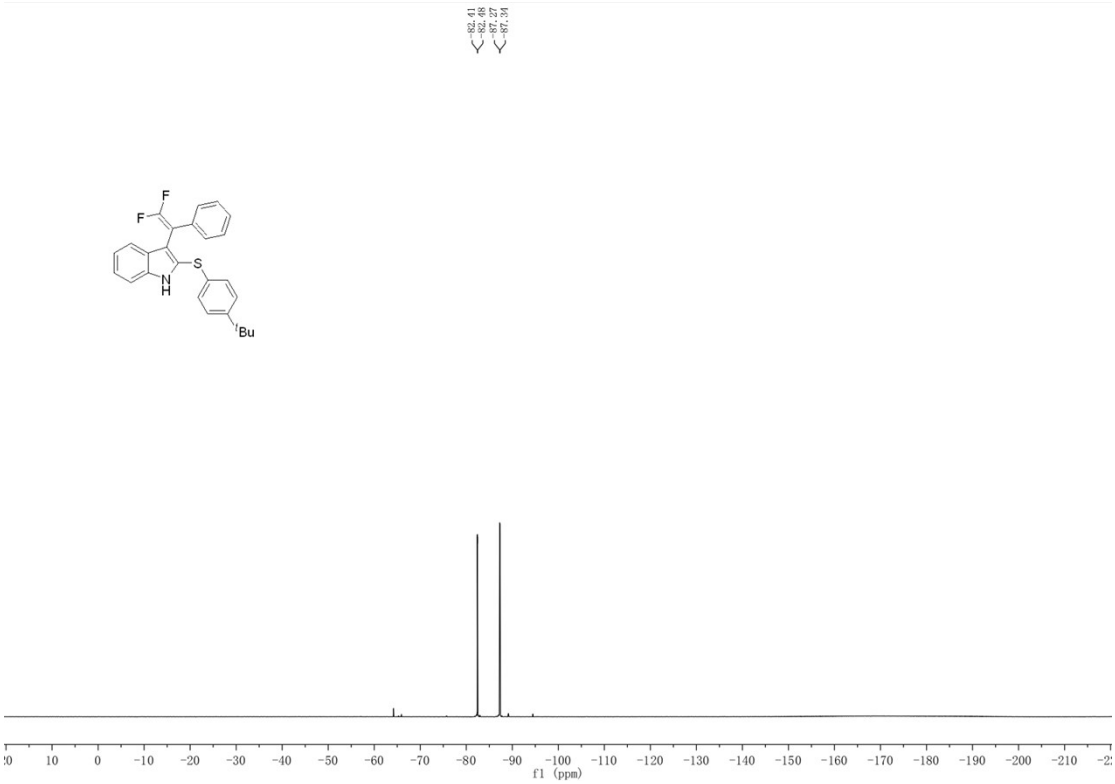
^{1}H NMR spectra of **5b** (400 MHz, $CDCl_3$)



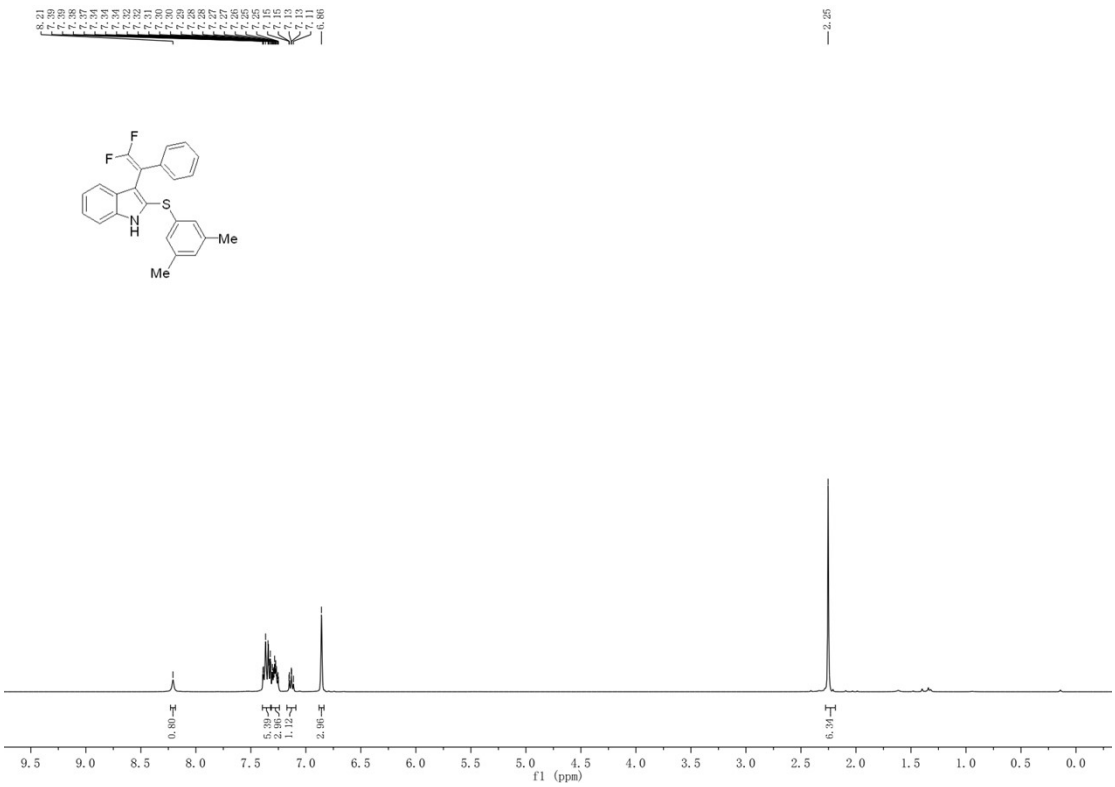
^{13}C NMR spectra of **5b** (100 MHz, $CDCl_3$)



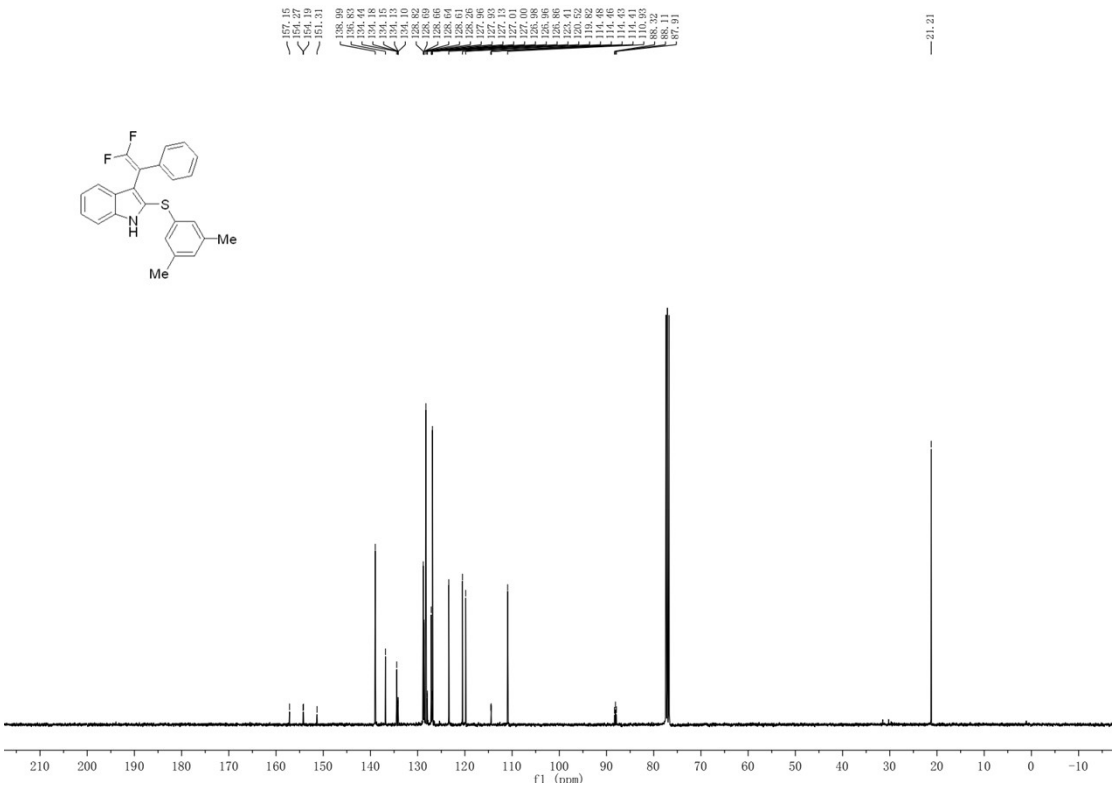
^{19}F NMR spectra of **5b** (376 MHz, $CDCl_3$)



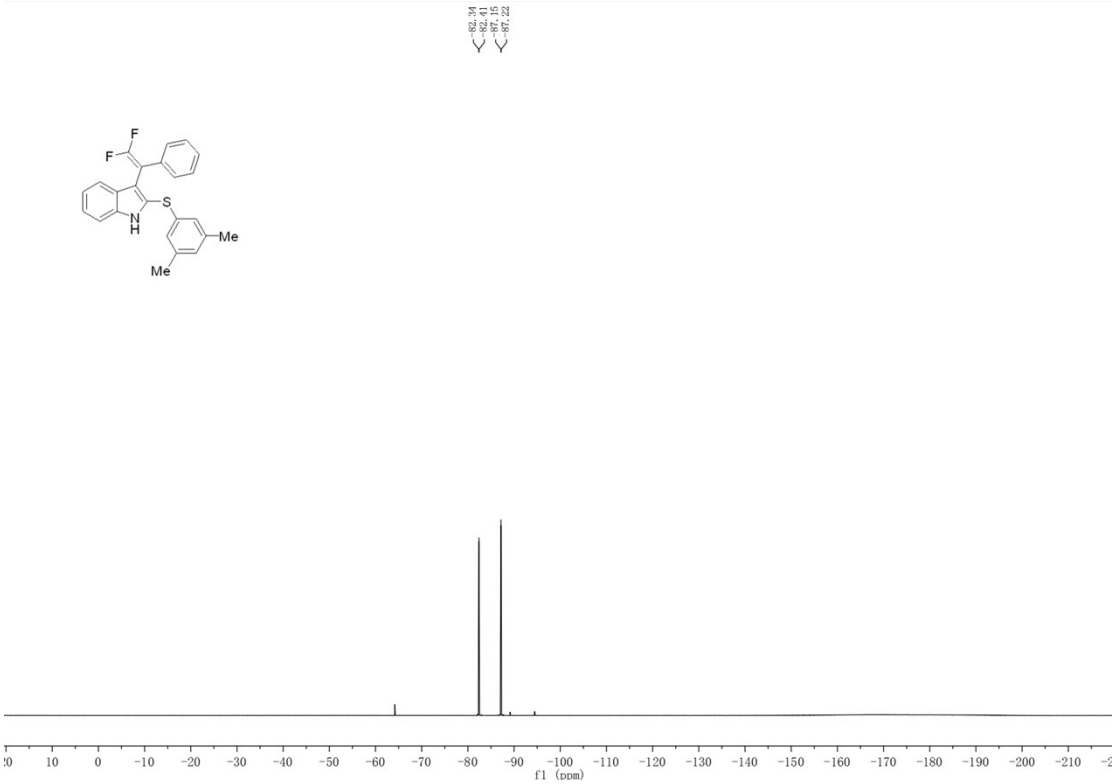
^{1}H NMR spectra of **5c** (400 MHz, $CDCl_3$)



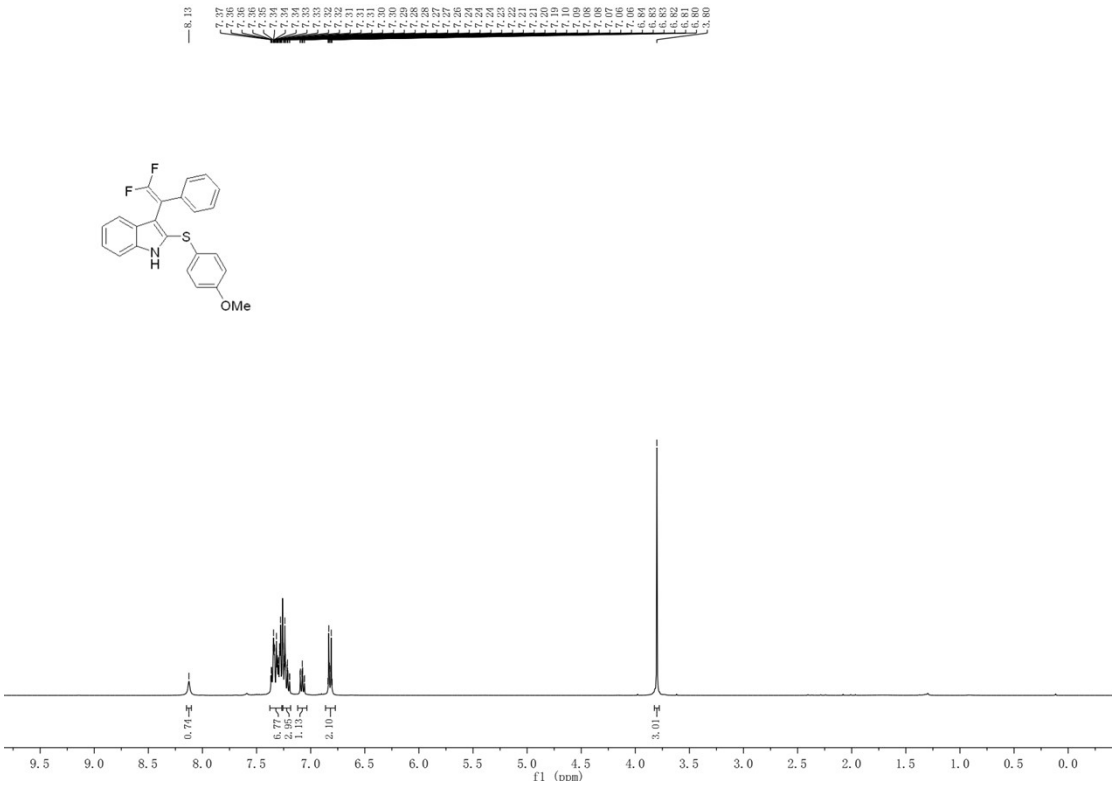
^{13}C NMR spectra of **5c** (100 MHz, $CDCl_3$)



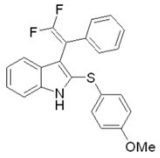
^{19}F NMR spectra of **5c** (376 MHz, $CDCl_3$)

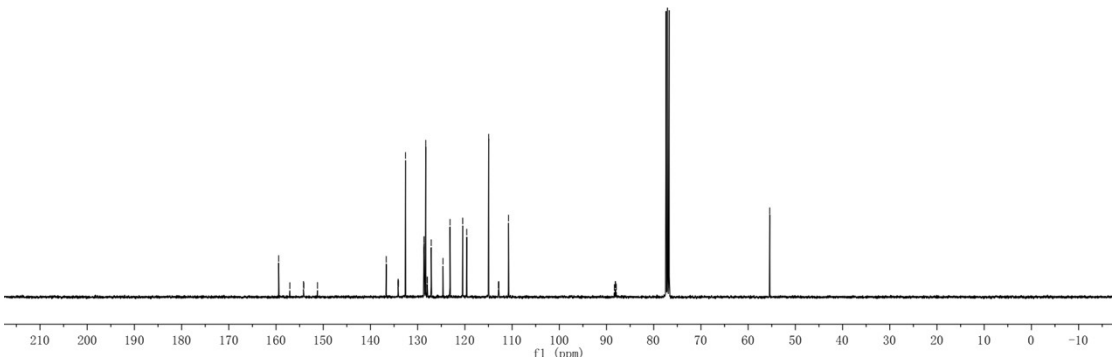


^{1}H NMR spectra of **5d** (400 MHz, $CDCl_3$)

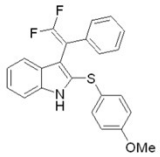


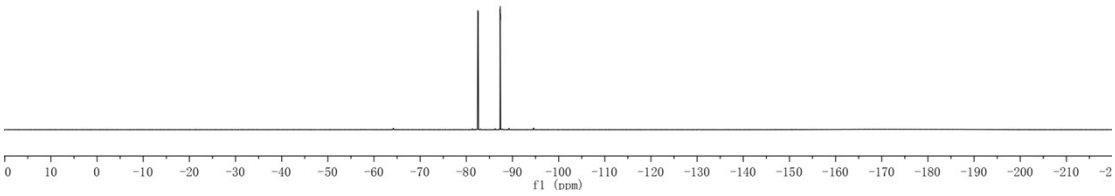
^{13}C NMR spectra of **5d** (100 MHz, $CDCl_3$)



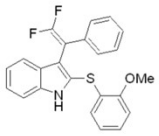


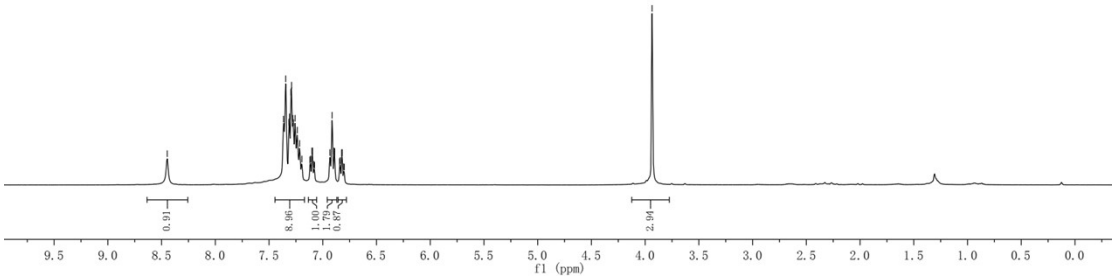
^{19}F NMR spectra of **5d** (376 MHz, $CDCl_3$)



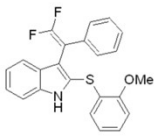


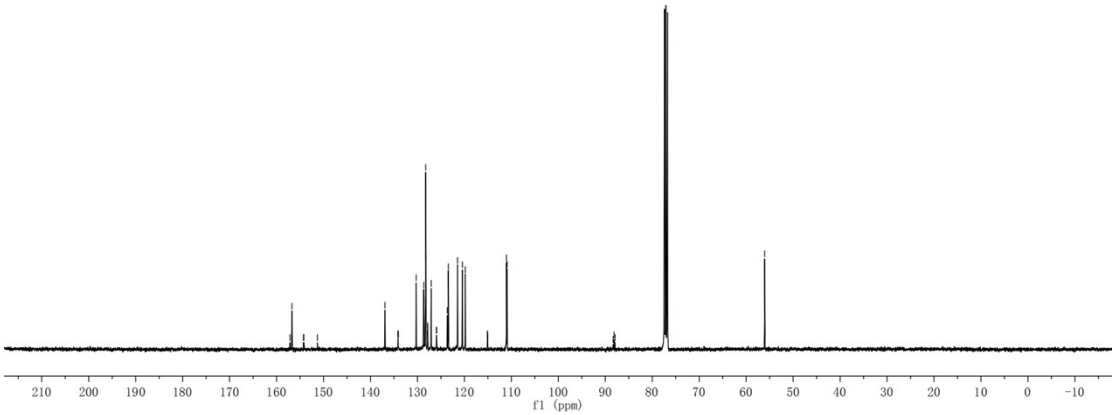
^{1}H NMR spectra of **5e** (400 MHz, $CDCl_3$)



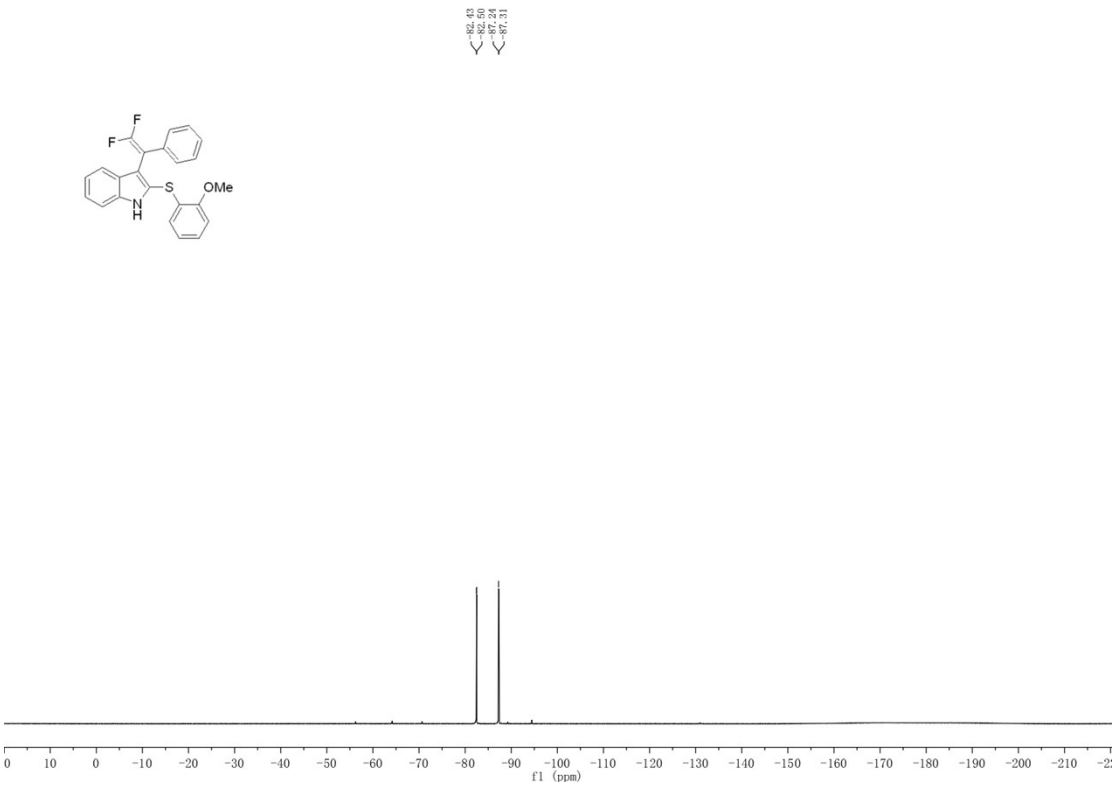


^{13}C NMR spectra of **5e** (100 MHz, $CDCl_3$)

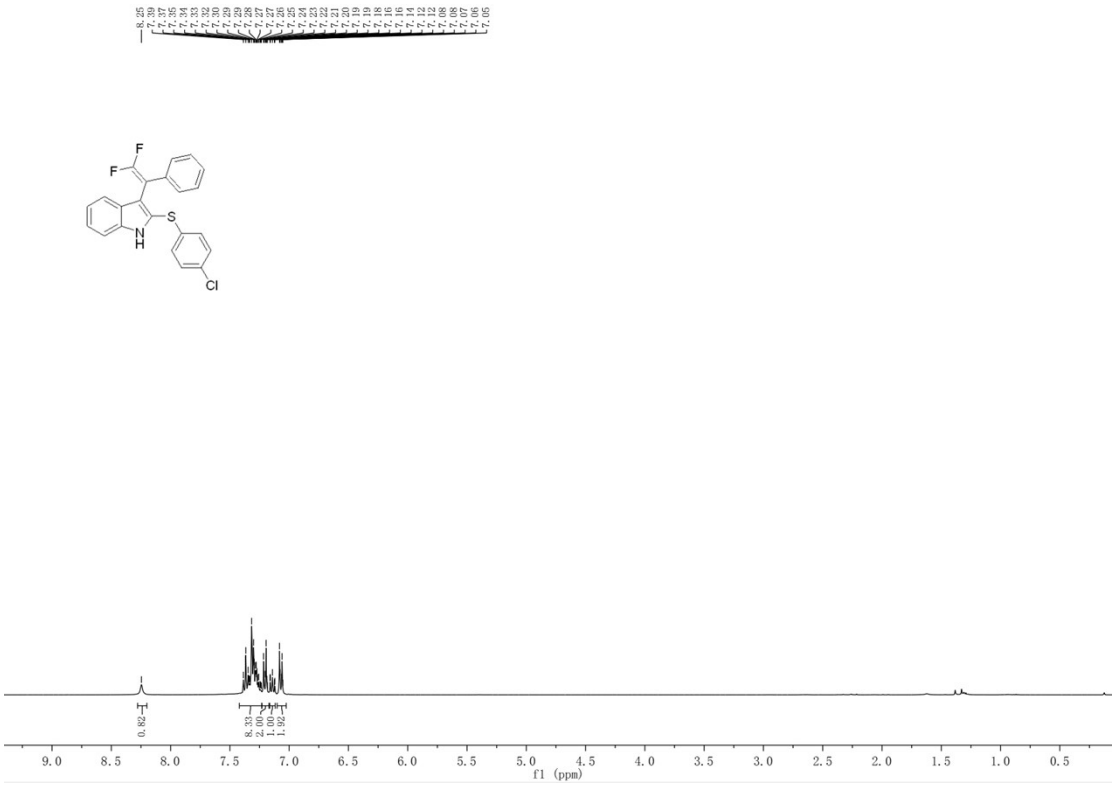




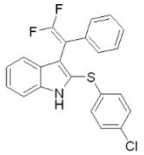
^{19}F NMR spectra of **5e** (376 MHz, $CDCl_3$)

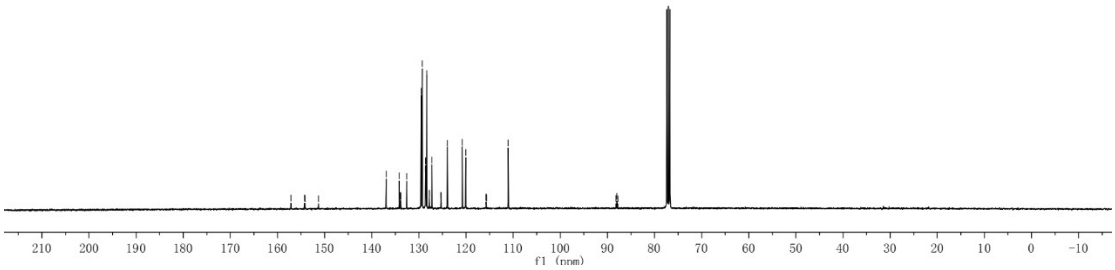


^{1}H NMR spectra of **5f** (400 MHz, $CDCl_3$)

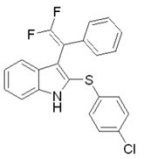


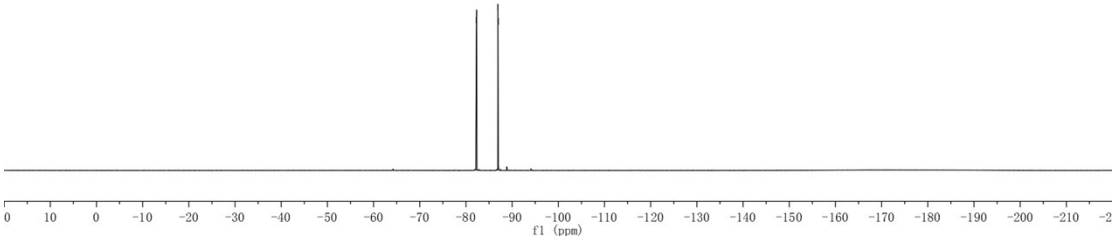
^{13}C NMR spectra of **5f** (100 MHz, $CDCl_3$)



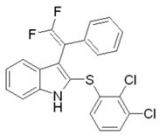


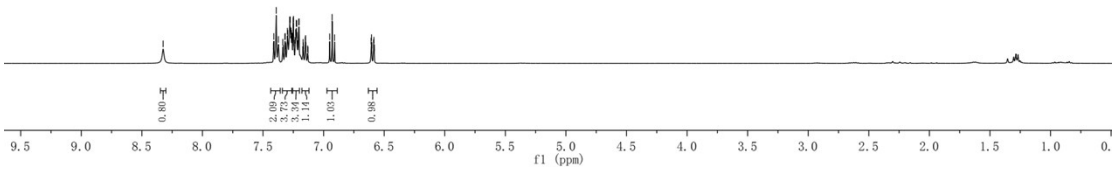
^{19}F NMR spectra of **5f** (376 MHz, $CDCl_3$)



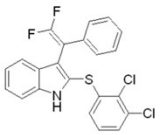


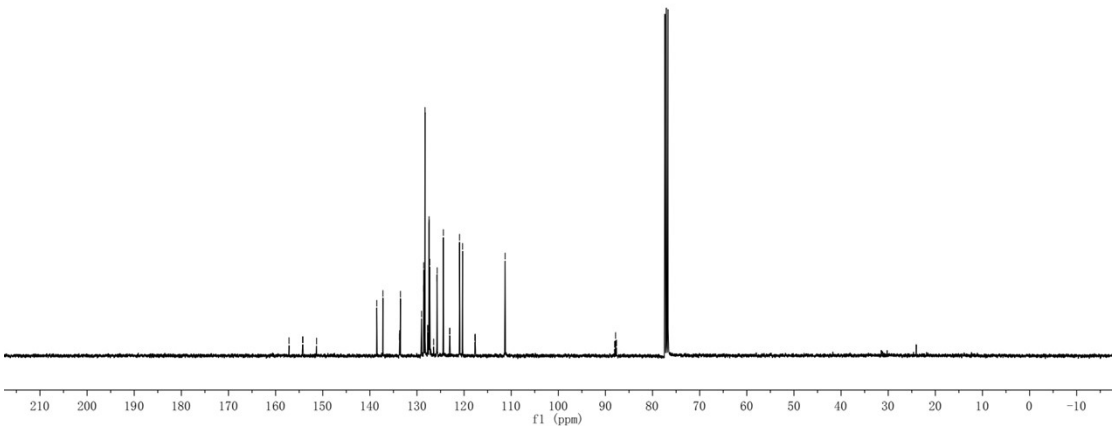
^{1}H NMR spectra of **5g** (400 MHz, $CDCl_3$)



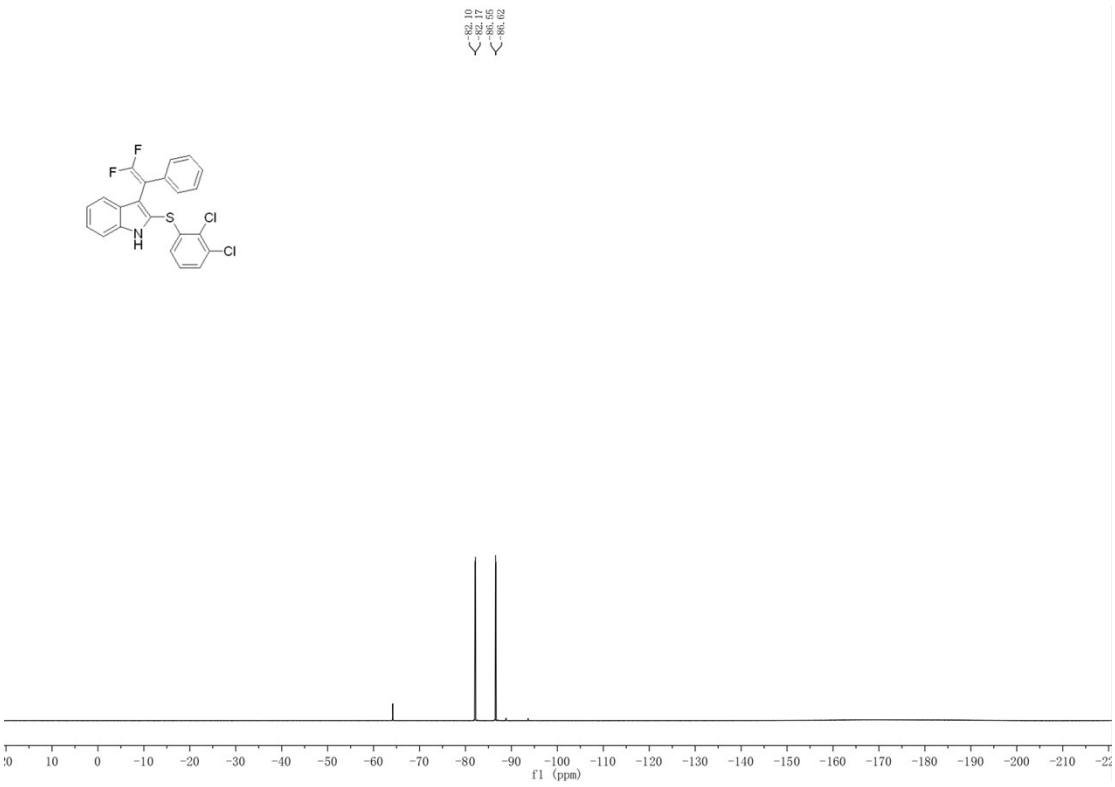


^{13}C NMR spectra of **5g** (100 MHz, $CDCl_3$)

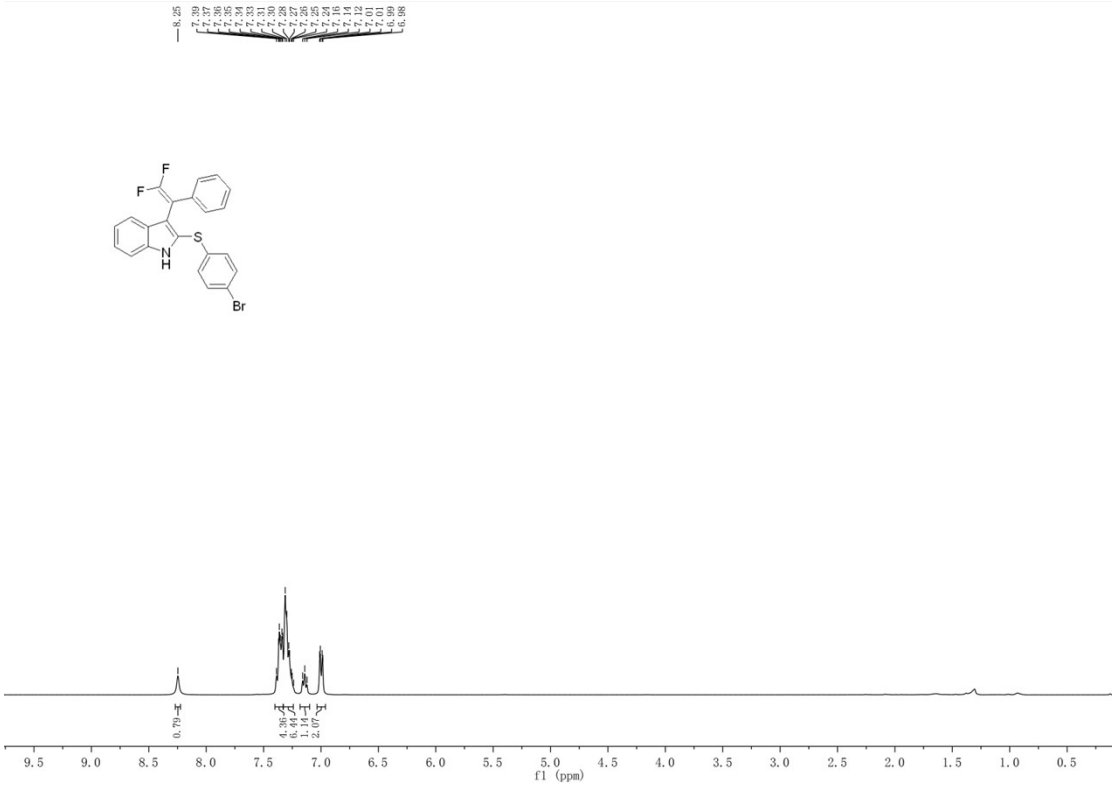




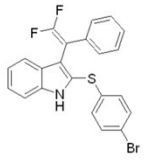
^{19}F NMR spectra of **5g** (376 MHz, $CDCl_3$)

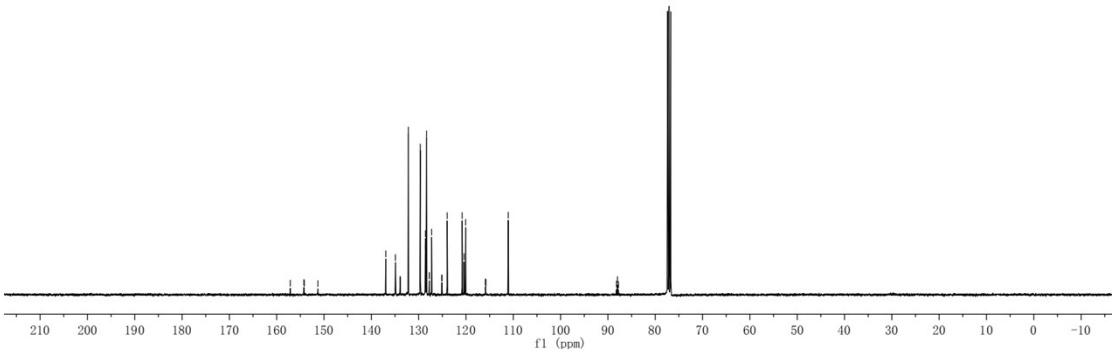


^{1}H NMR spectra of **5h** (400 MHz, $CDCl_3$)

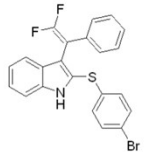


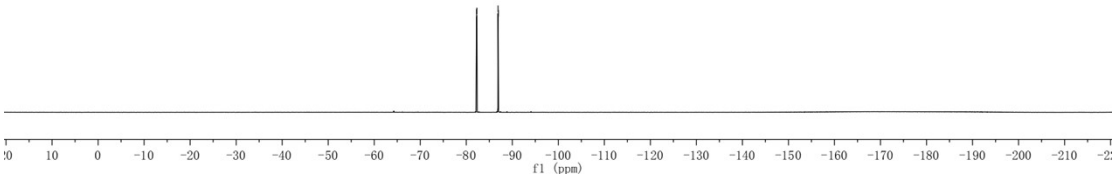
^{13}C NMR spectra of **5h** (100 MHz, $CDCl_3$)



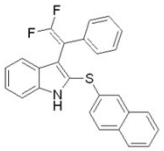


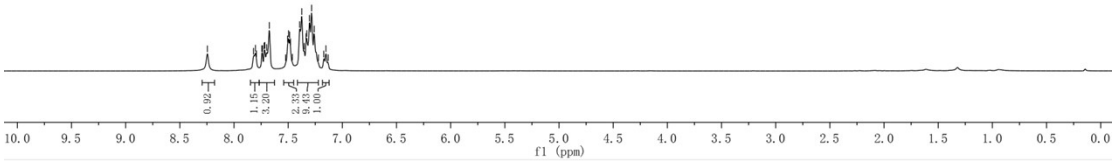
^{19}F NMR spectra of **5h** (376 MHz, $CDCl_3$)



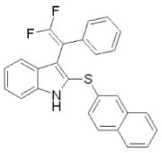


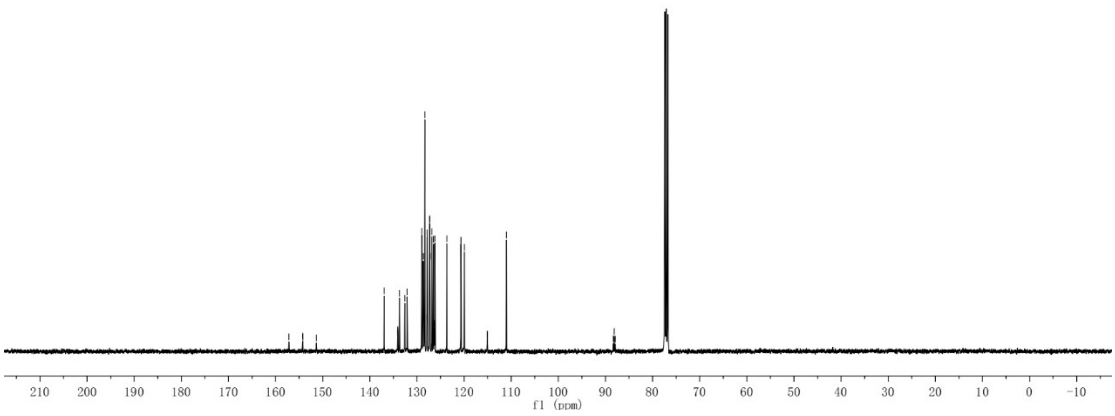
^{1}H NMR spectra of **5i** (400 MHz, $CDCl_3$)



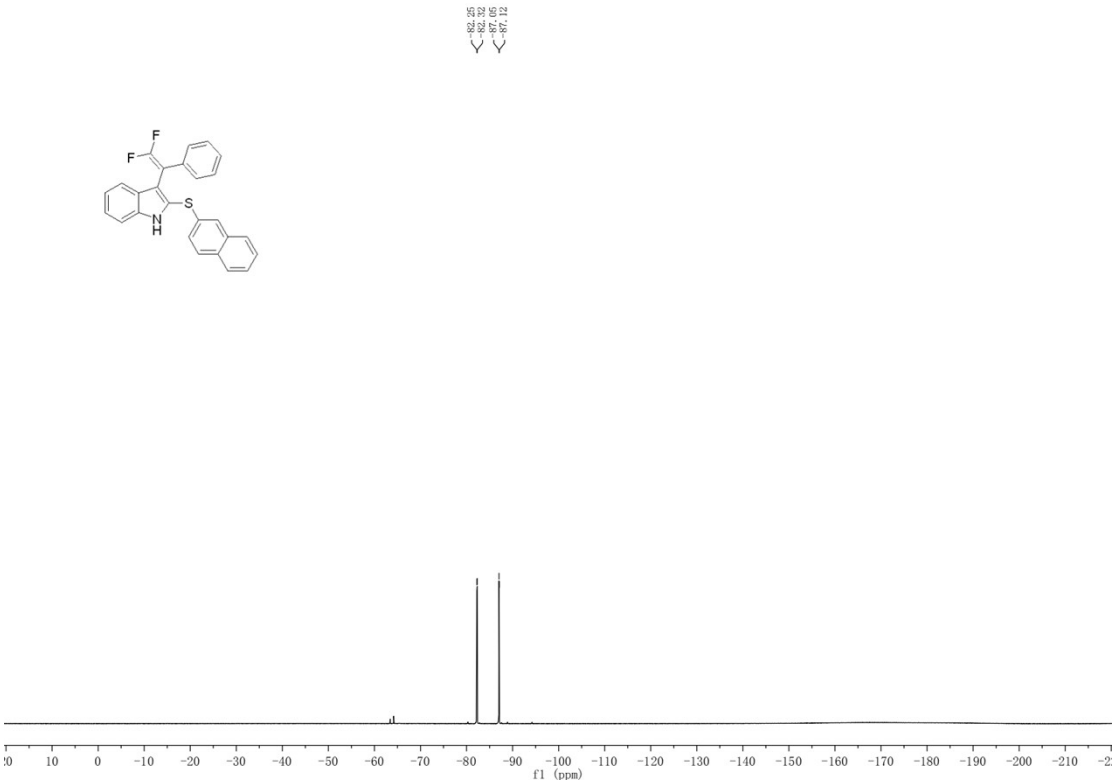


^{13}C NMR spectra of **5i** (100 MHz, $CDCl_3$)

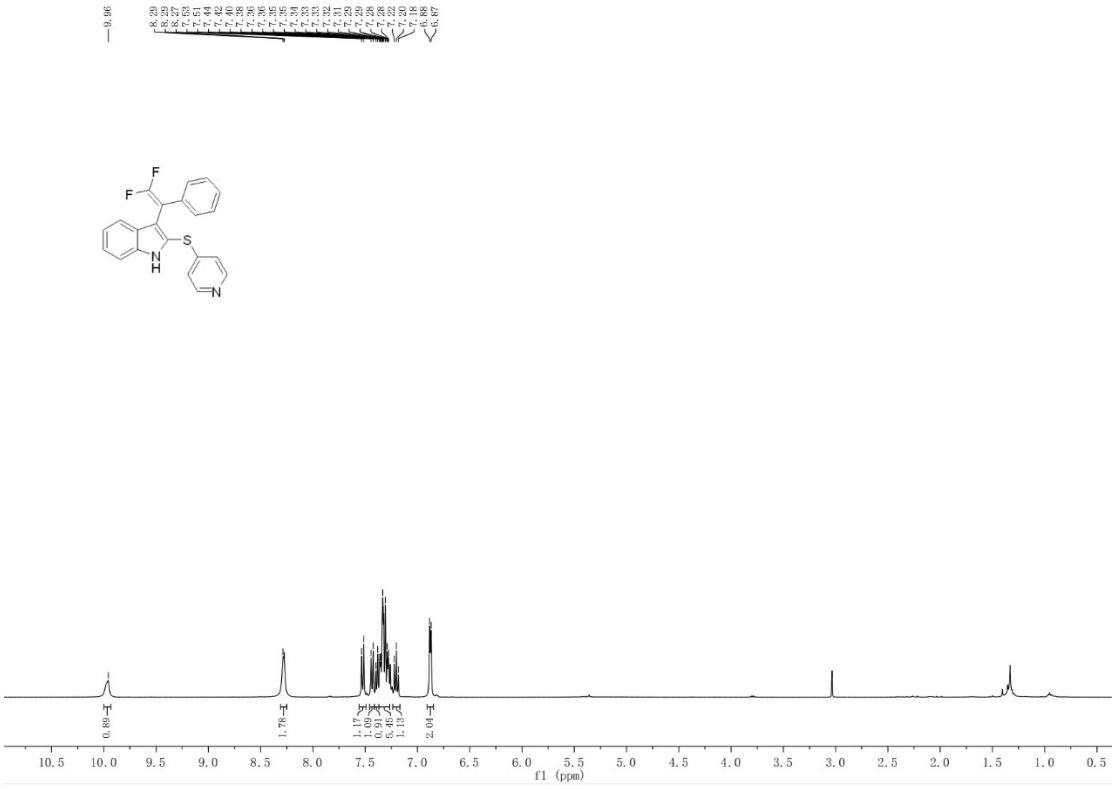




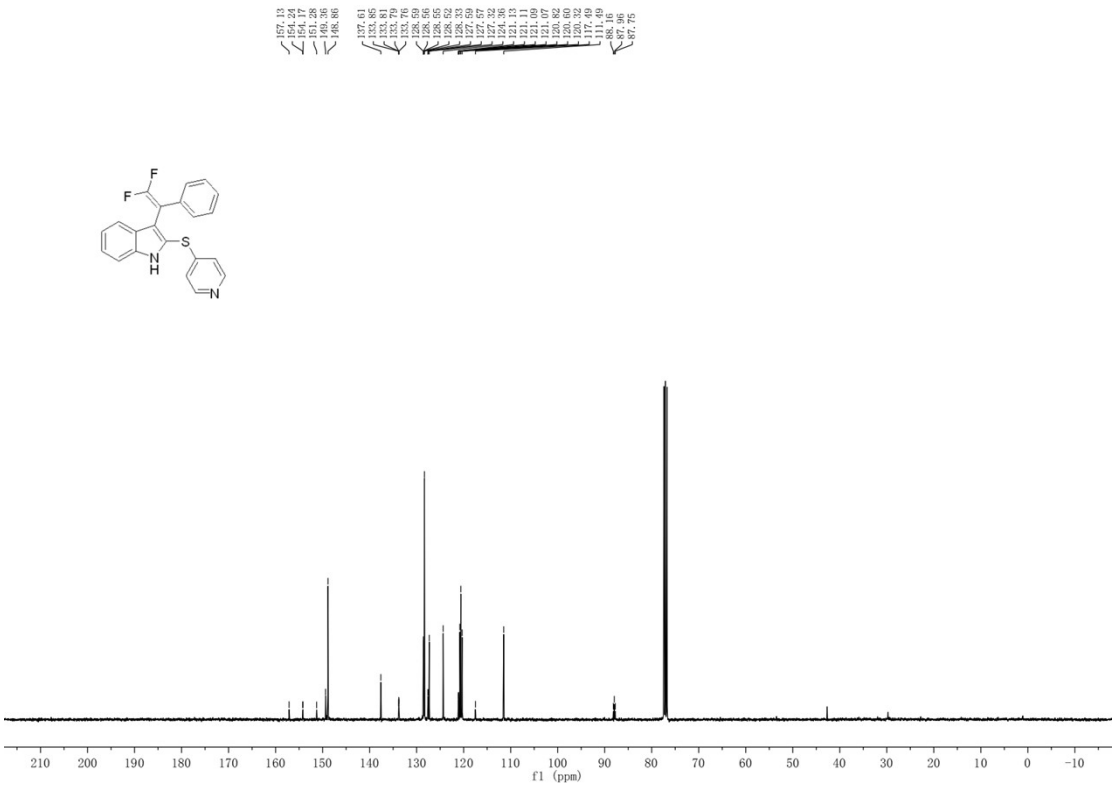
^{19}F NMR spectra of **5i** (376 MHz, $CDCl_3$)



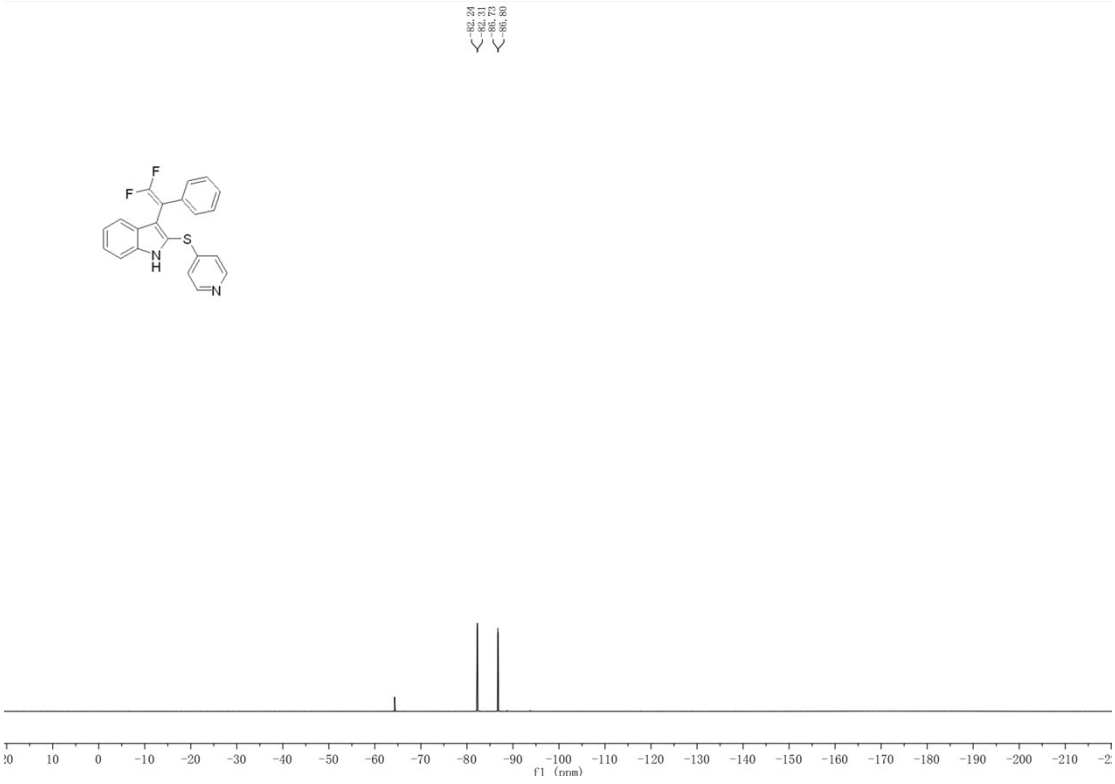
^{1}H NMR spectra of **5j** (400 MHz, $CDCl_3$)



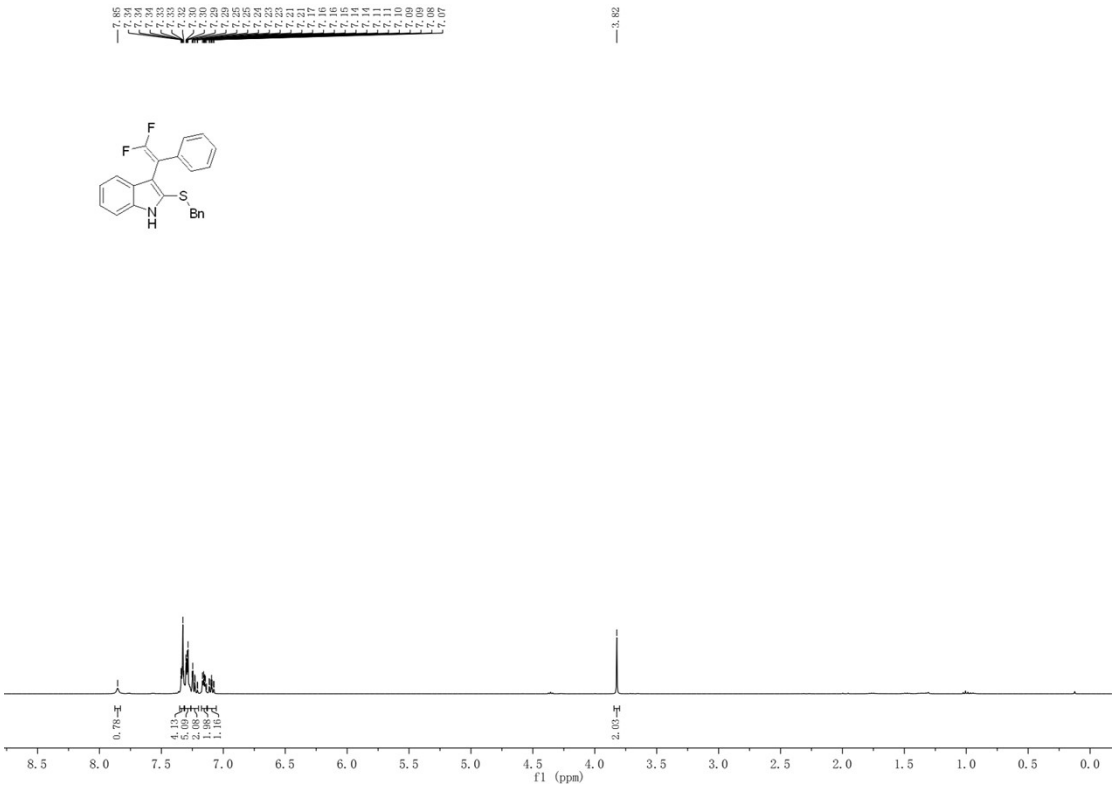
^{13}C NMR spectra of **5j** (100 MHz, $CDCl_3$)



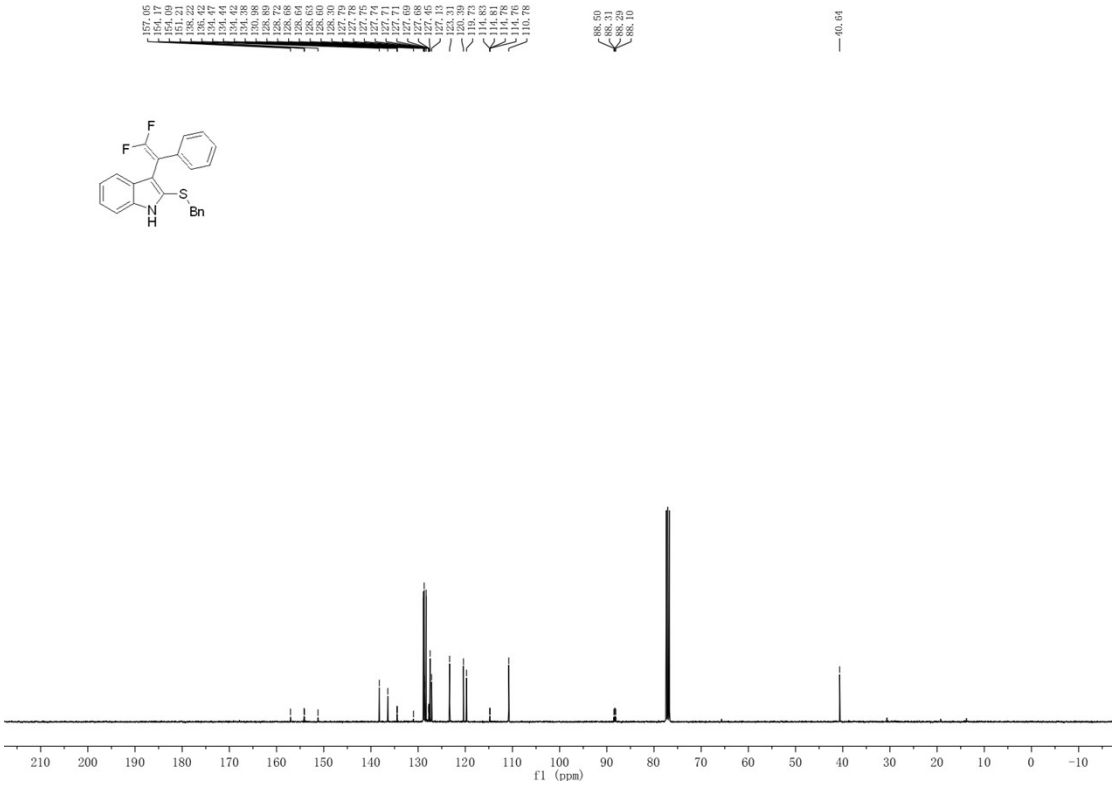
^{19}F NMR spectra of **5j** (376 MHz, $CDCl_3$)



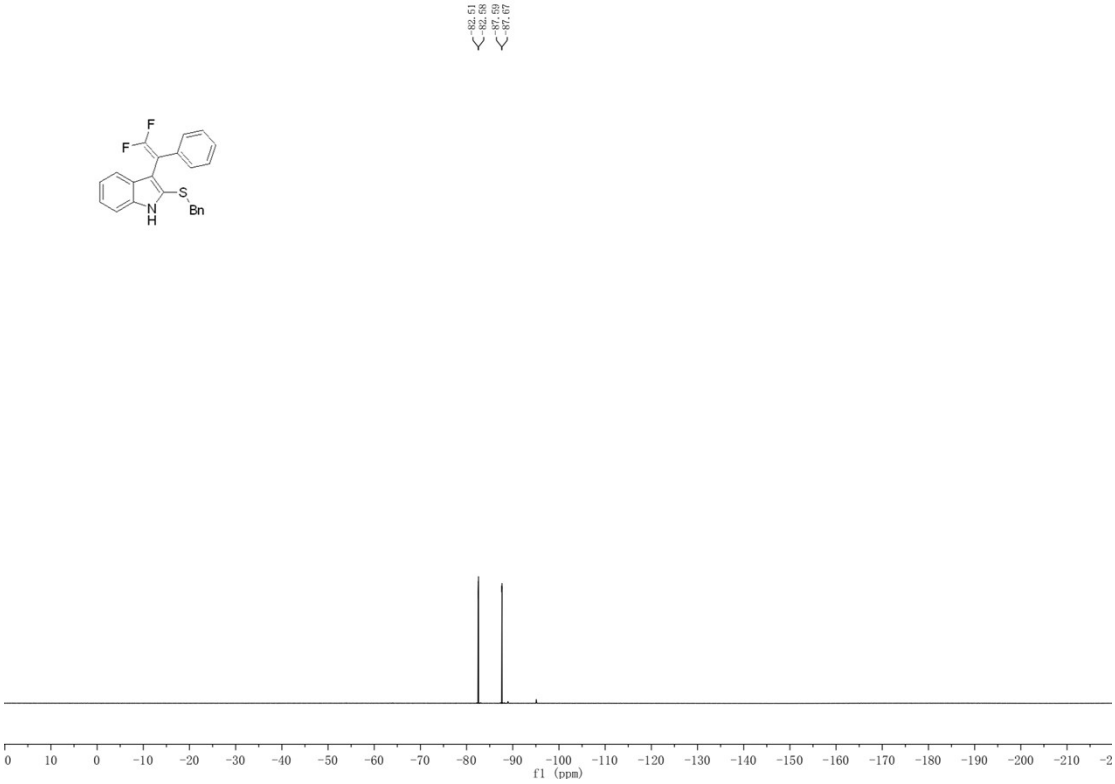
^{1}H NMR spectra of **5k** (400 MHz, $CDCl_3$)



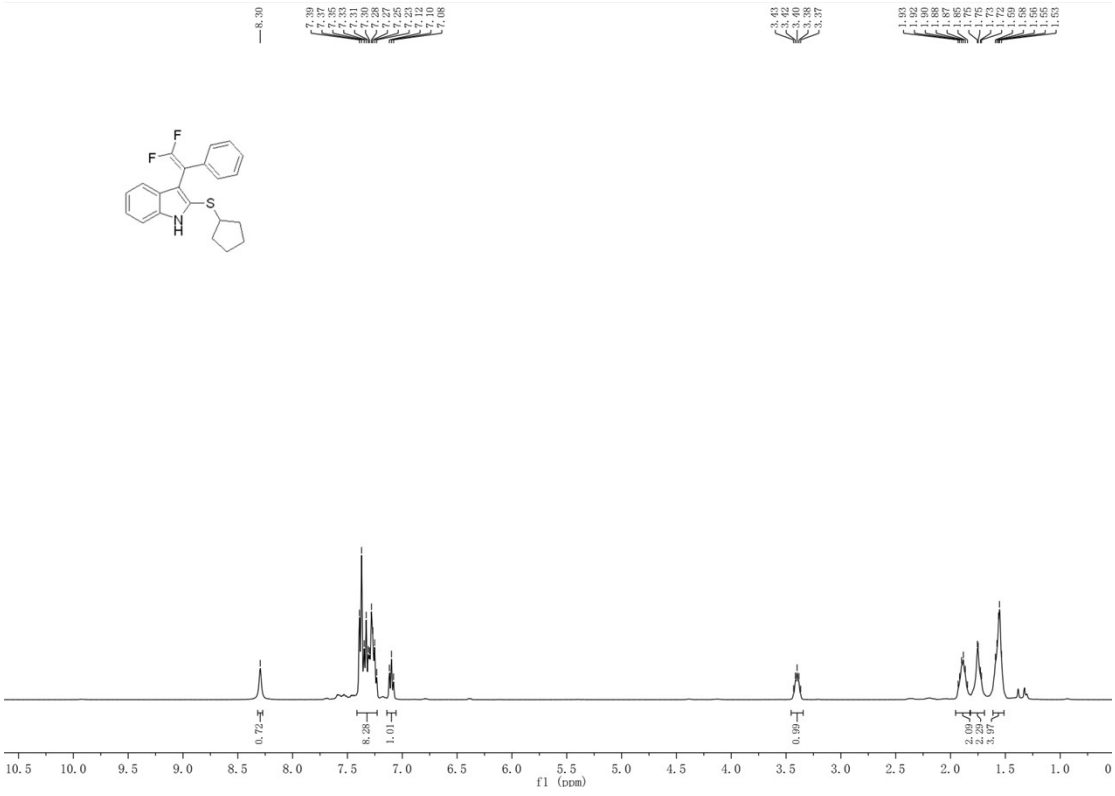
^{13}C NMR spectra of **5k** (100 MHz, $CDCl_3$)



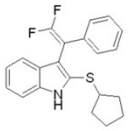
^{19}F NMR spectra of **5k** (376 MHz, $CDCl_3$)

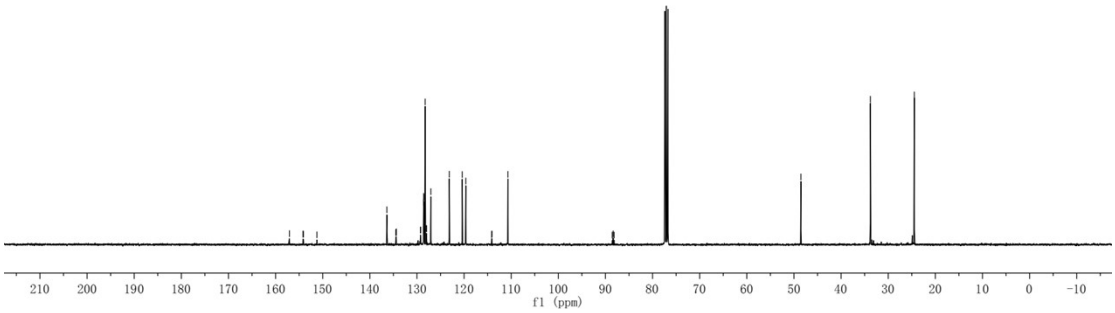


^{1}H NMR spectra of **5l** (400 MHz, $CDCl_3$)

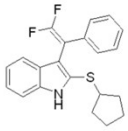


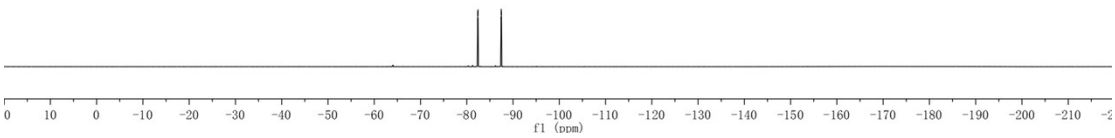
^{13}C NMR spectra of **5l** (100 MHz, $CDCl_3$)



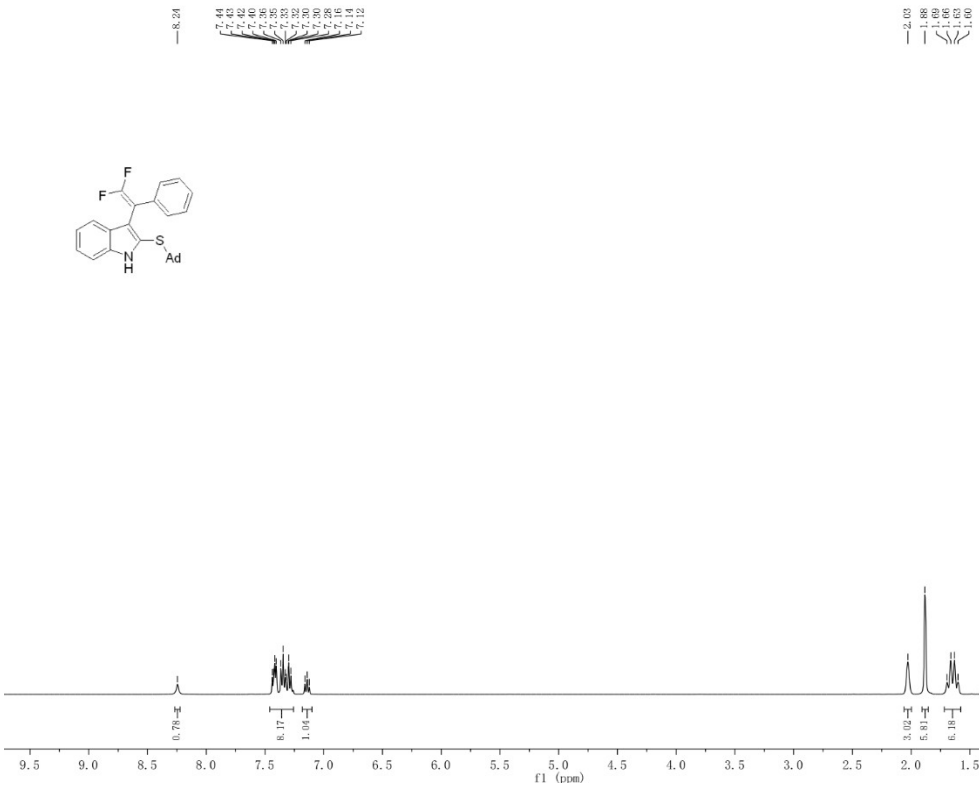


^{19}F NMR spectra of **5l** (376 MHz, $CDCl_3$)

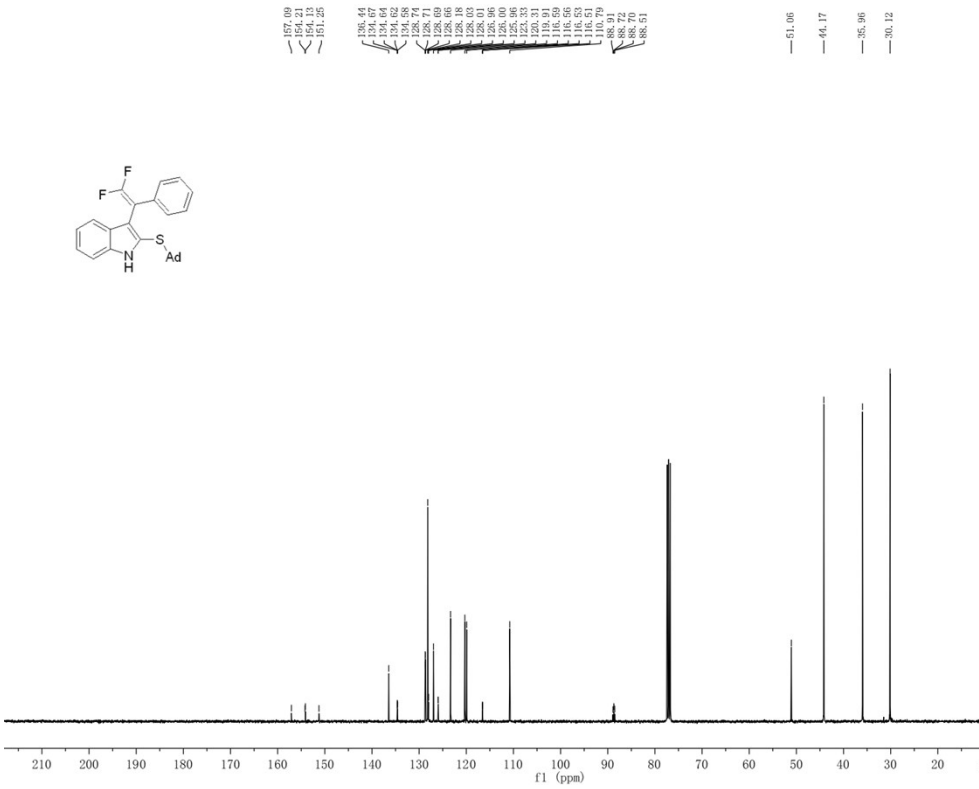




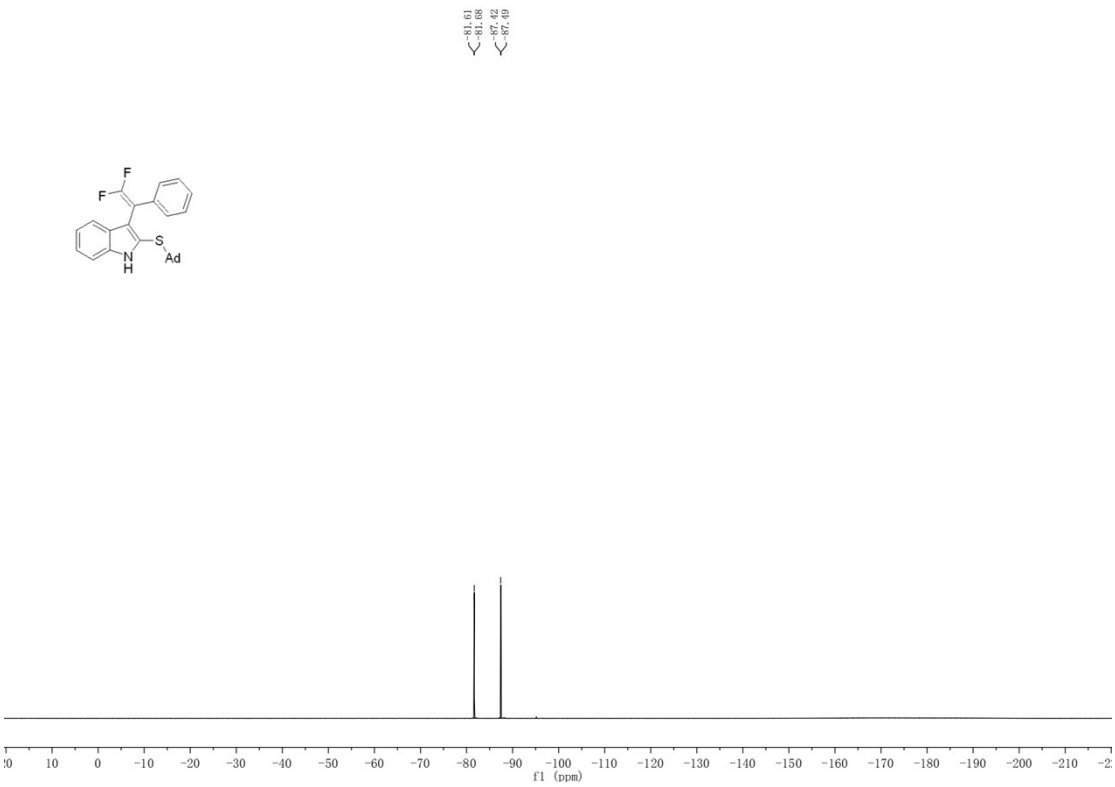
^{1}H NMR spectra of **5m** (400 MHz, $CDCl_3$)



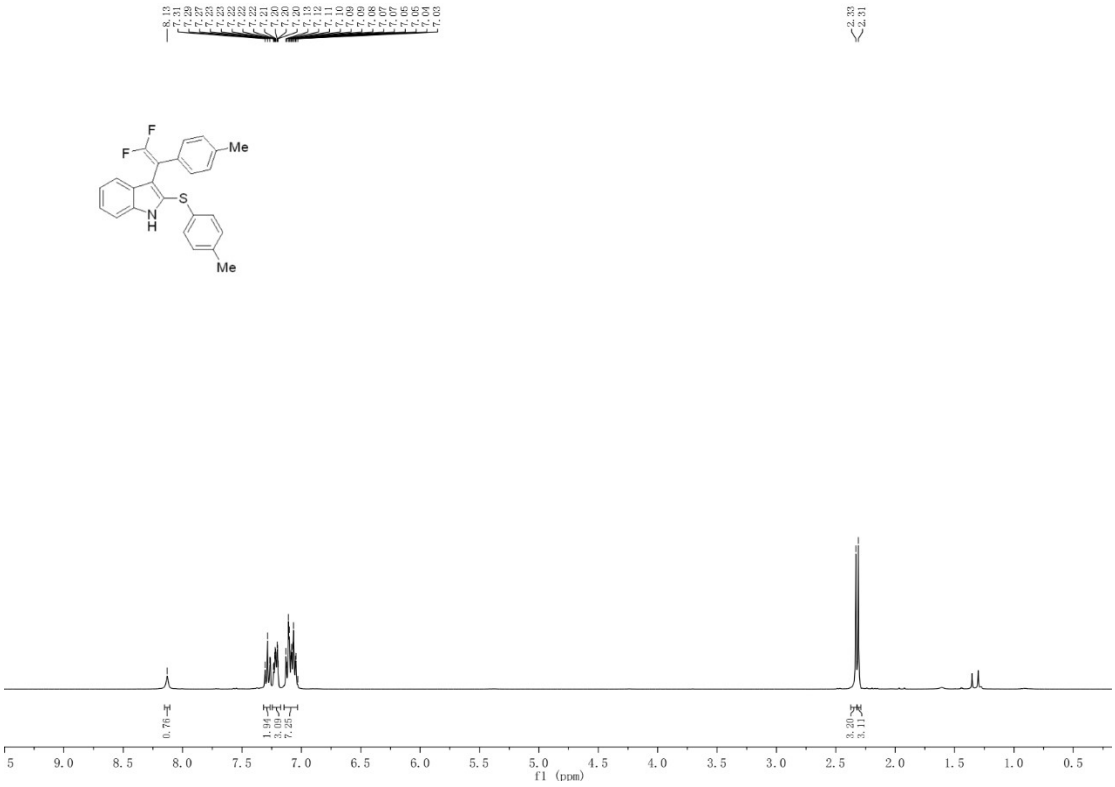
^{13}C NMR spectra of **5m** (100 MHz, $CDCl_3$)



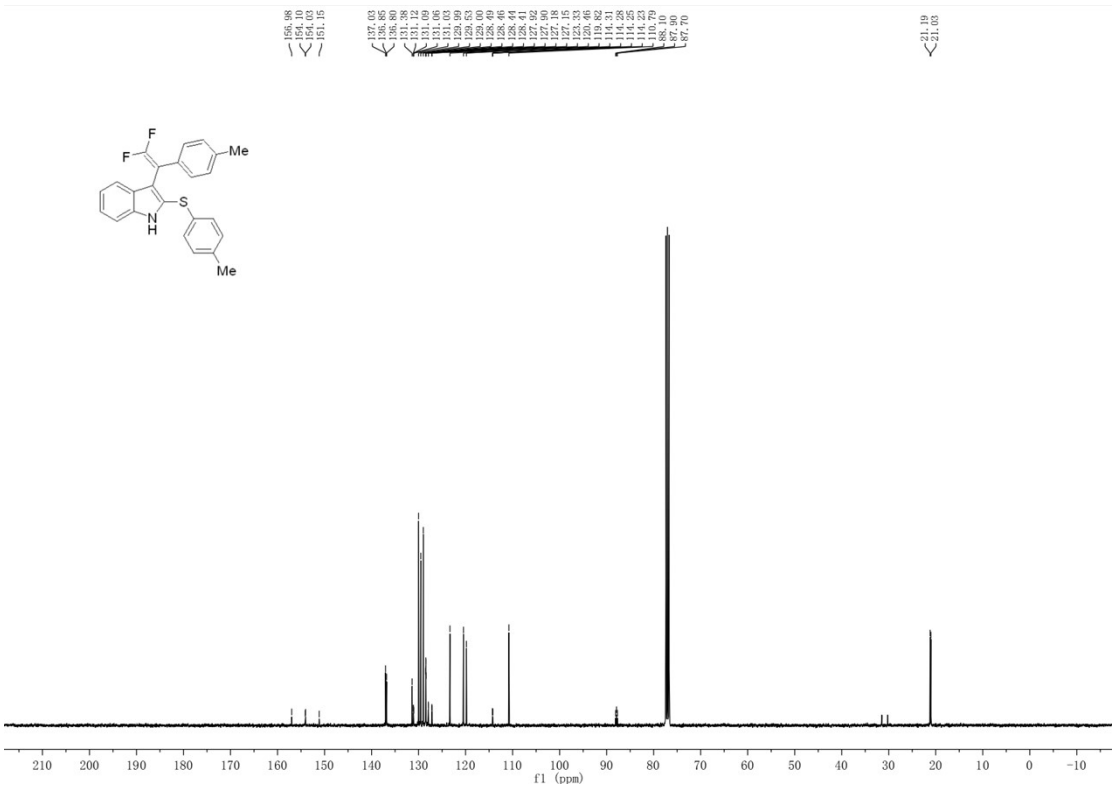
^{19}F NMR spectra of **5m** (376 MHz, $CDCl_3$)



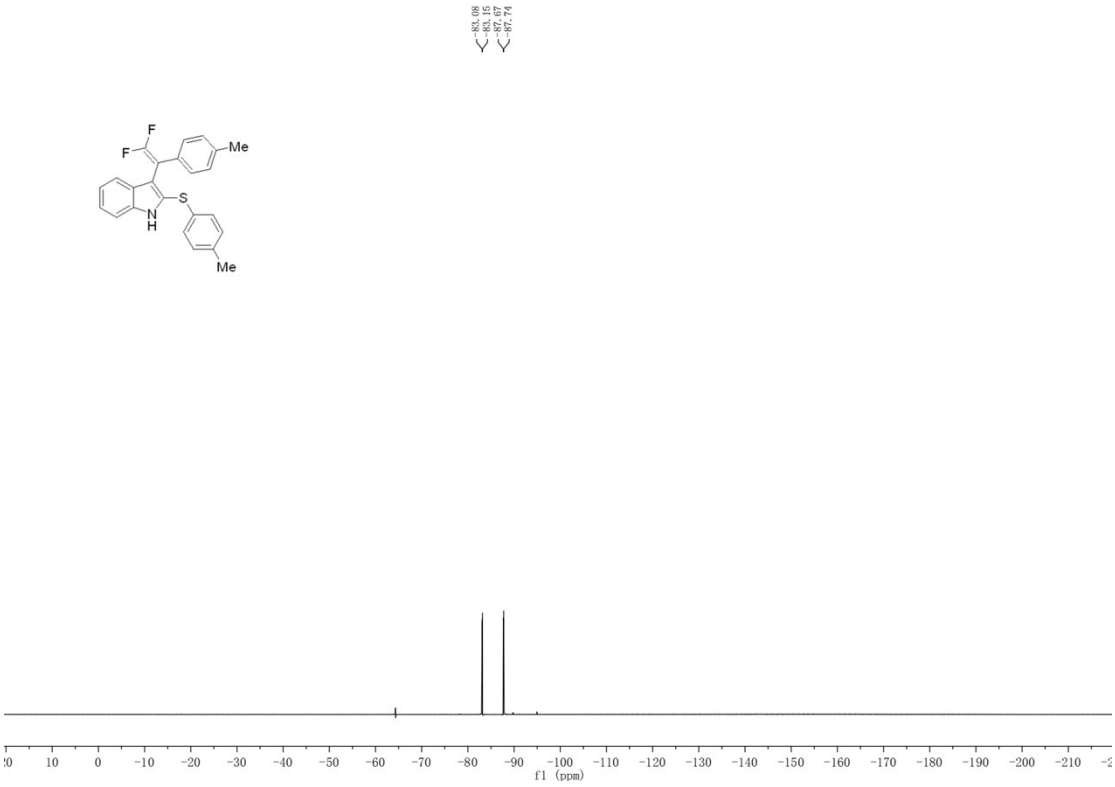
^{1}H NMR spectra of **5n** (400 MHz, $CDCl_3$)



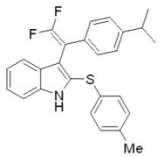
^{13}C NMR spectra of **5n** (100 MHz, $CDCl_3$)

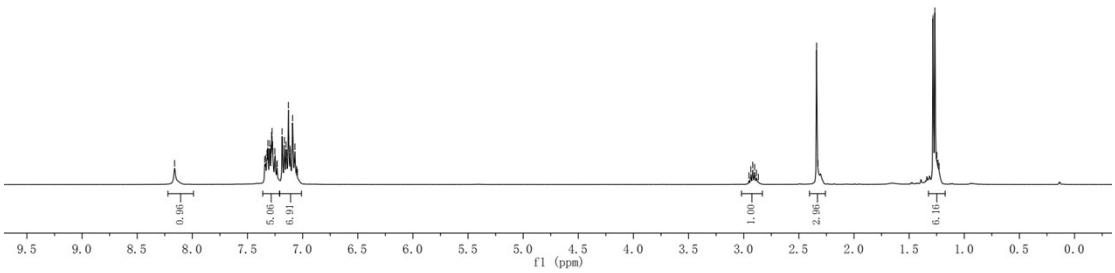


^{19}F NMR spectra of **5n** (376 MHz, $CDCl_3$)

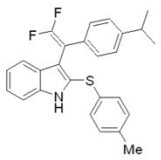


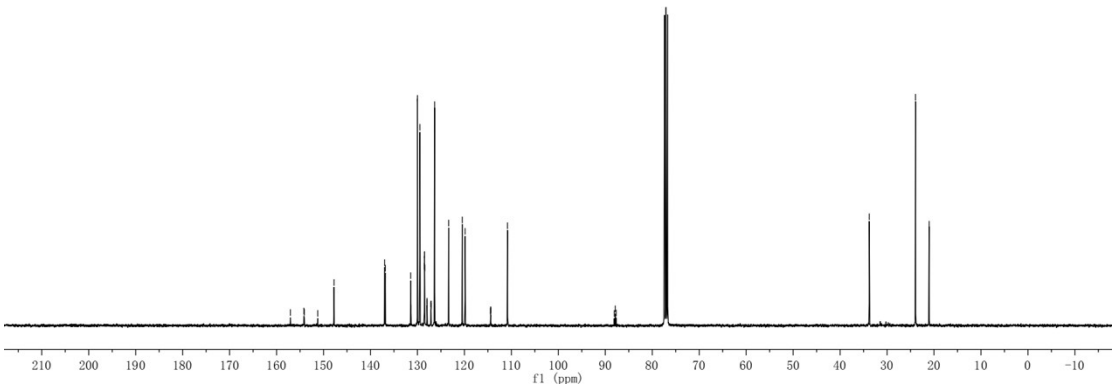
^{1}H NMR spectra of **5o** (400 MHz, $CDCl_3$)



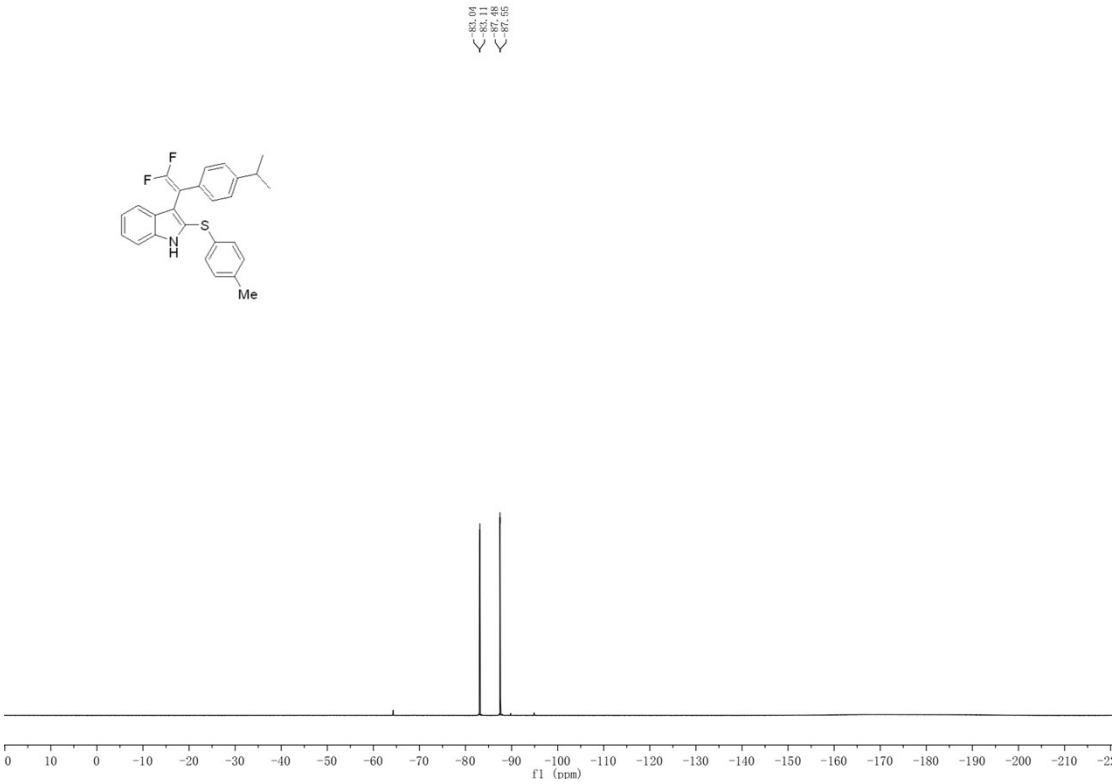


^{13}C NMR spectra of **5o** (100 MHz, $CDCl_3$)

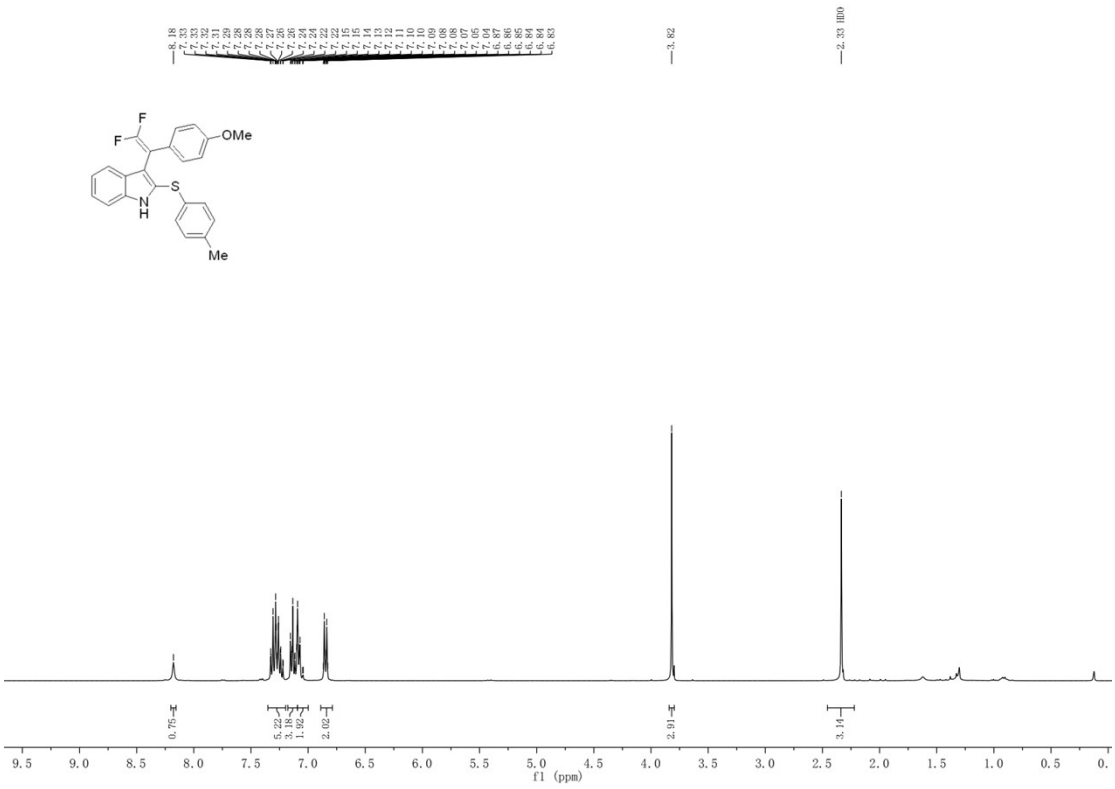




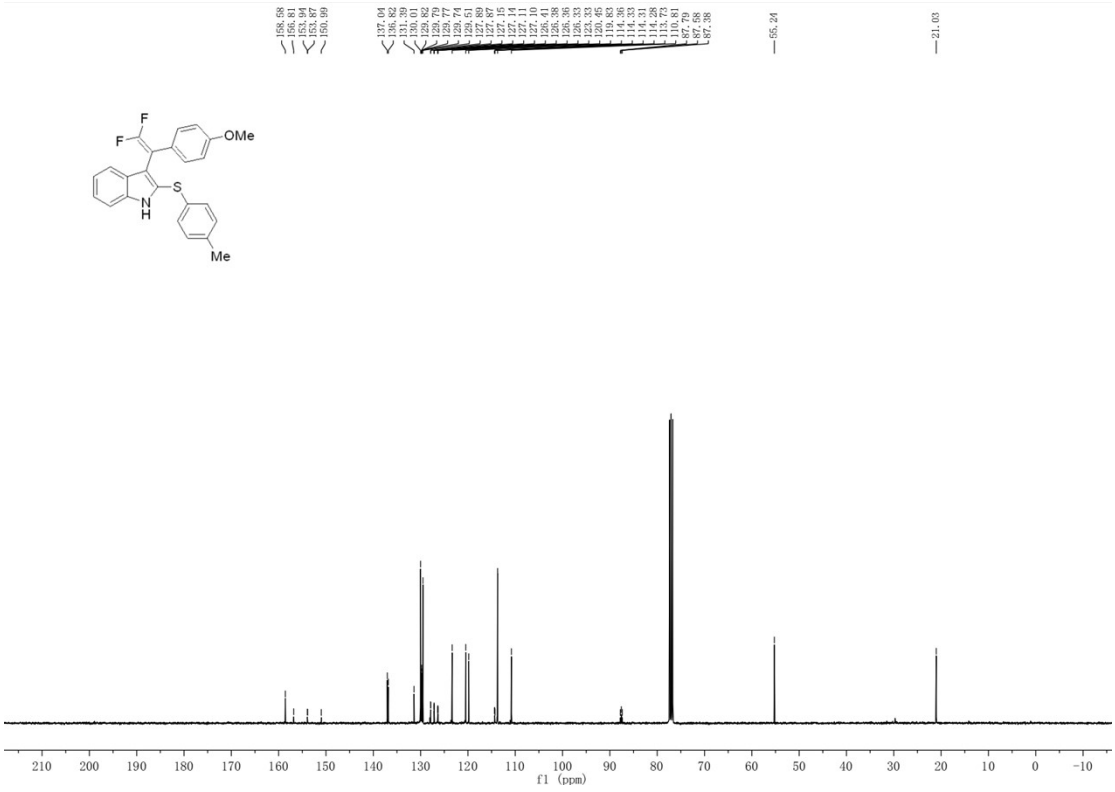
^{19}F NMR spectra of **5o** (376 MHz, $CDCl_3$)



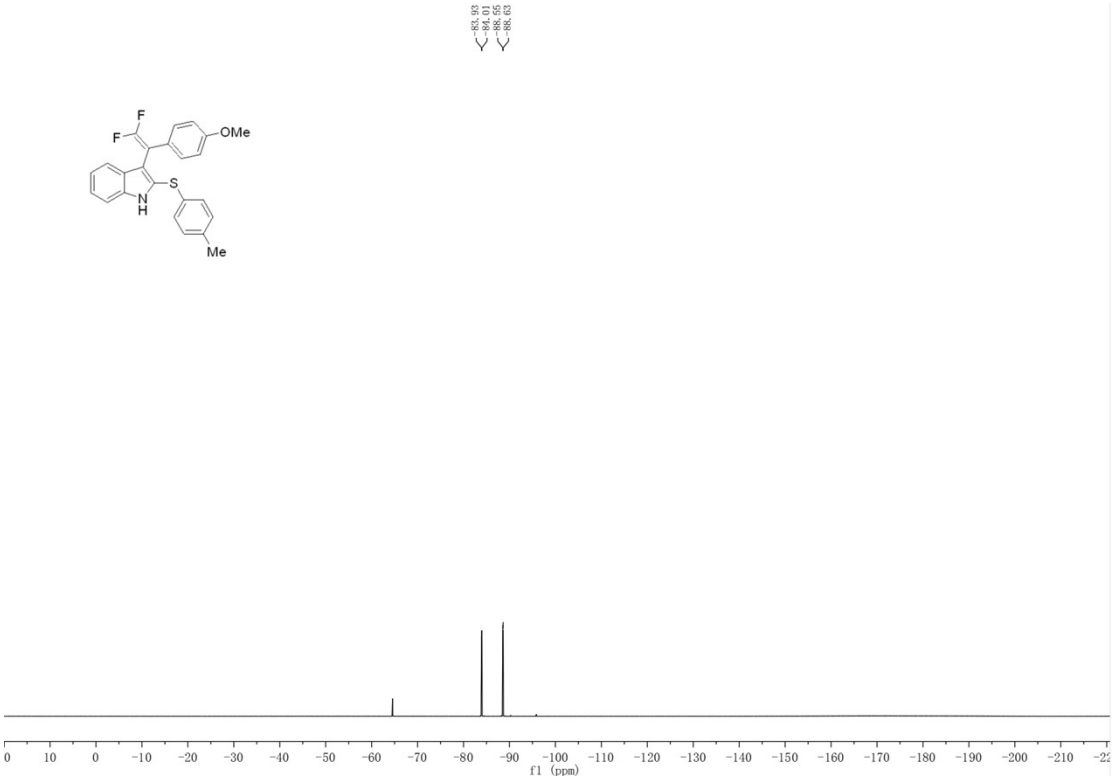
^{1}H NMR spectra of **5p** (400 MHz, $CDCl_3$)



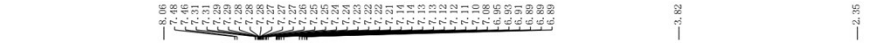
^{13}C NMR spectra of **5p** (100 MHz, $CDCl_3$)

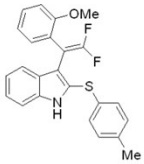


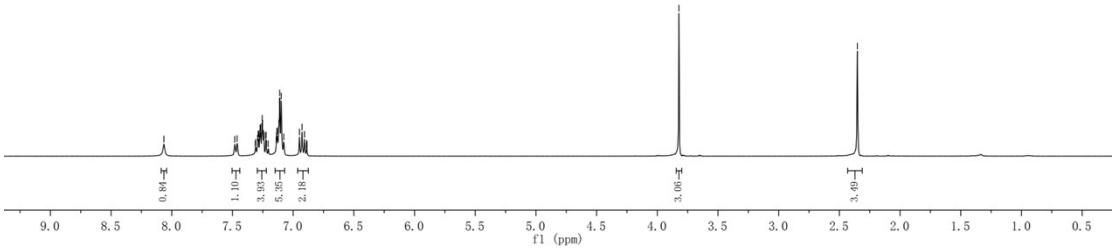
^{19}F NMR spectra of **5p** (376 MHz, $CDCl_3$)



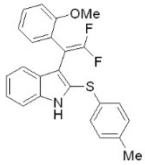
^{1}H NMR spectra of **5q** (400 MHz, $CDCl_3$)

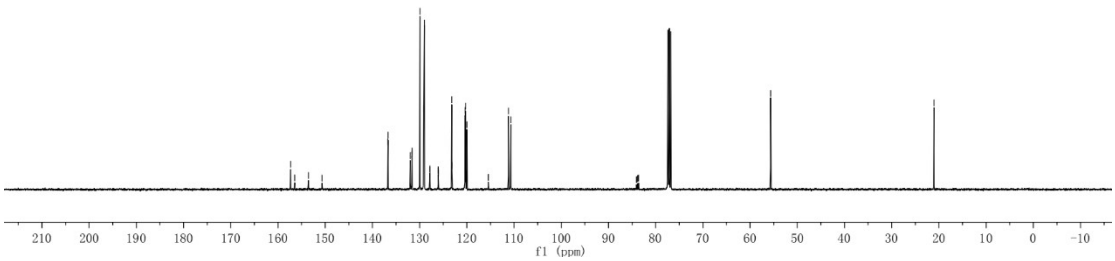




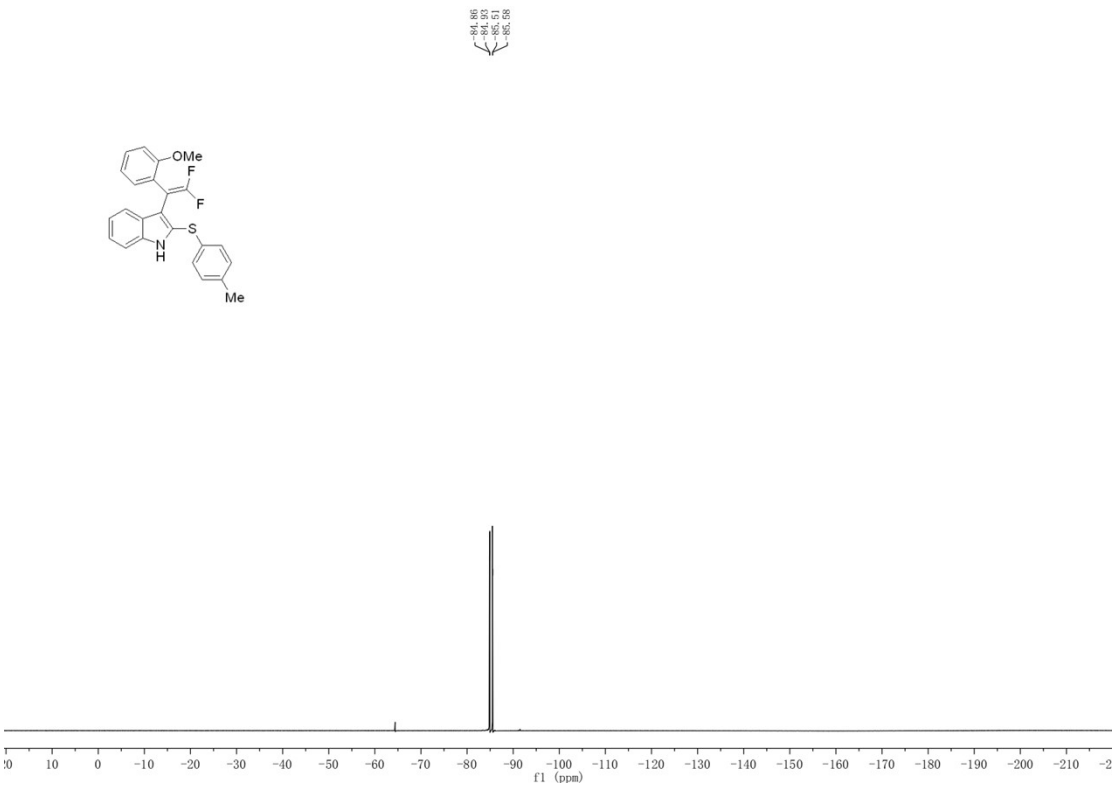


^{13}C NMR spectra of **5q** (100 MHz, $CDCl_3$)

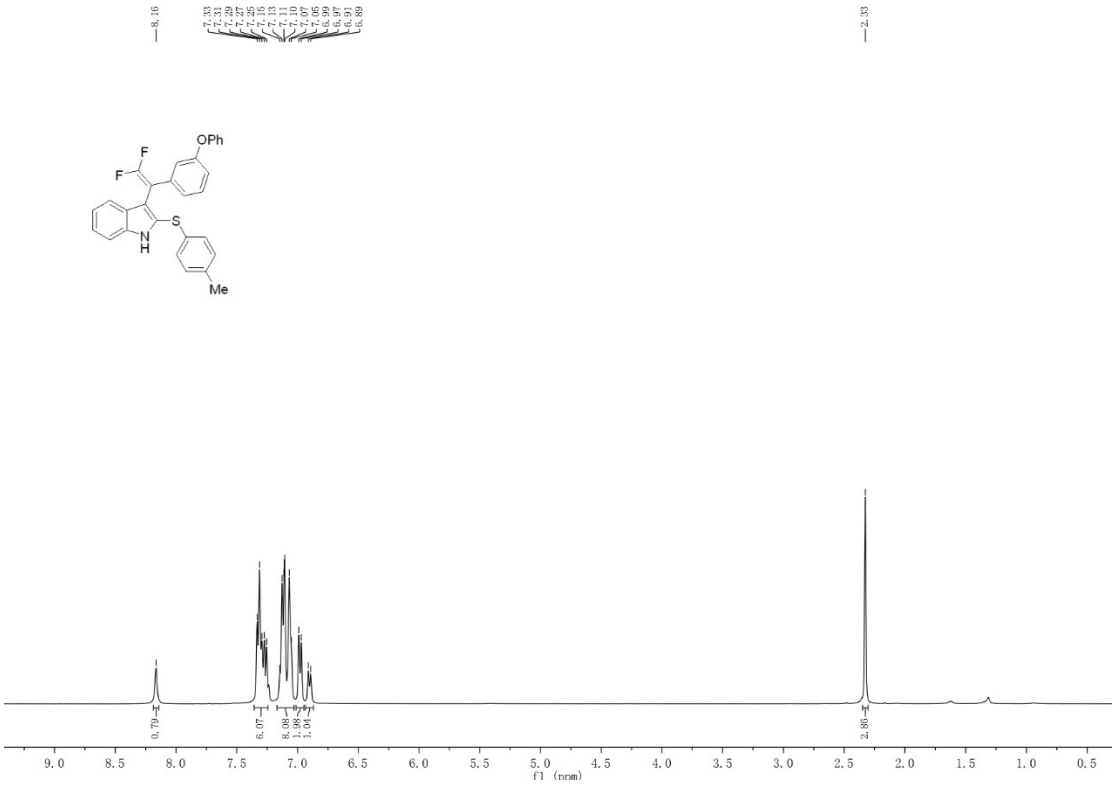




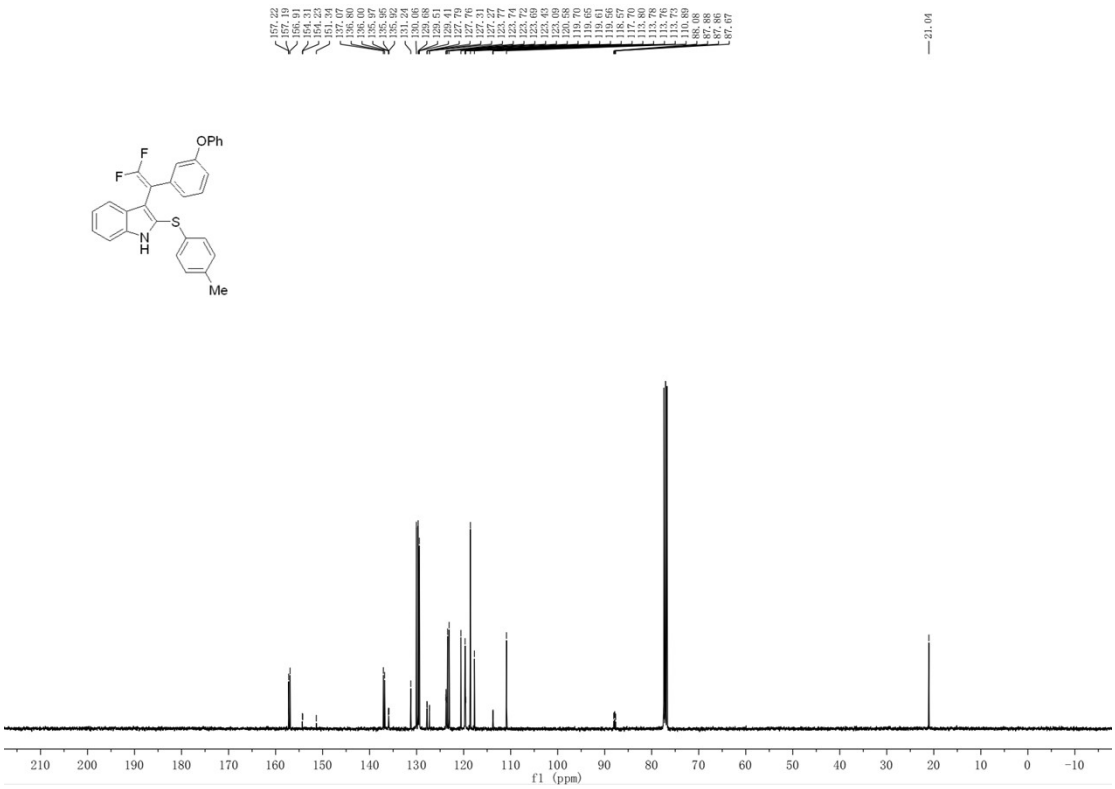
^{19}F NMR spectra of **5q** (376 MHz, $CDCl_3$)



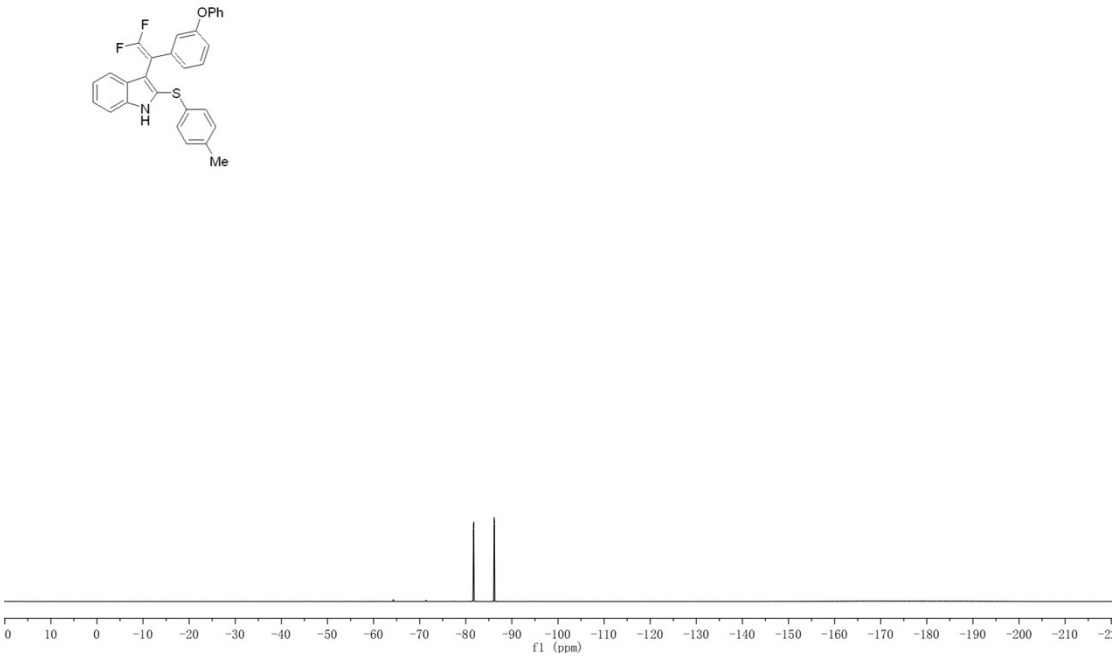
^{1}H NMR spectra of **5r** (400 MHz, $CDCl_3$)



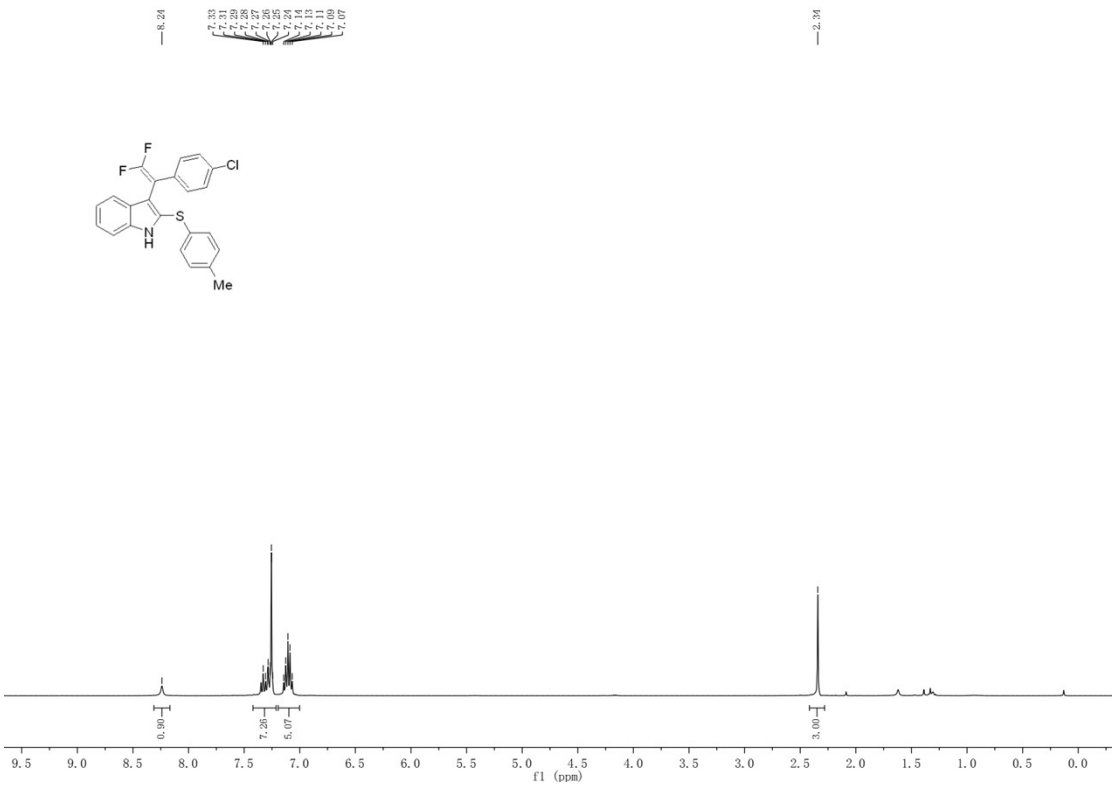
^{13}C NMR spectra of **5r** (100 MHz, $CDCl_3$)



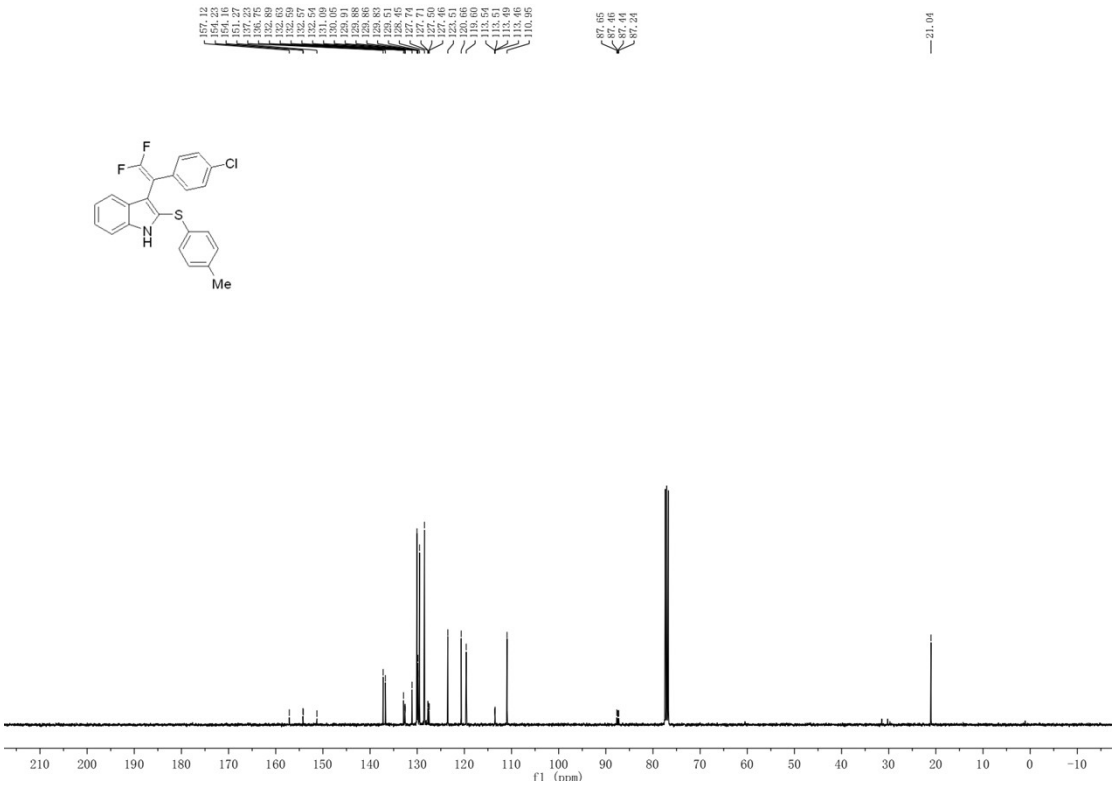
^{19}F NMR spectra of **5r** (376 MHz, $CDCl_3$)



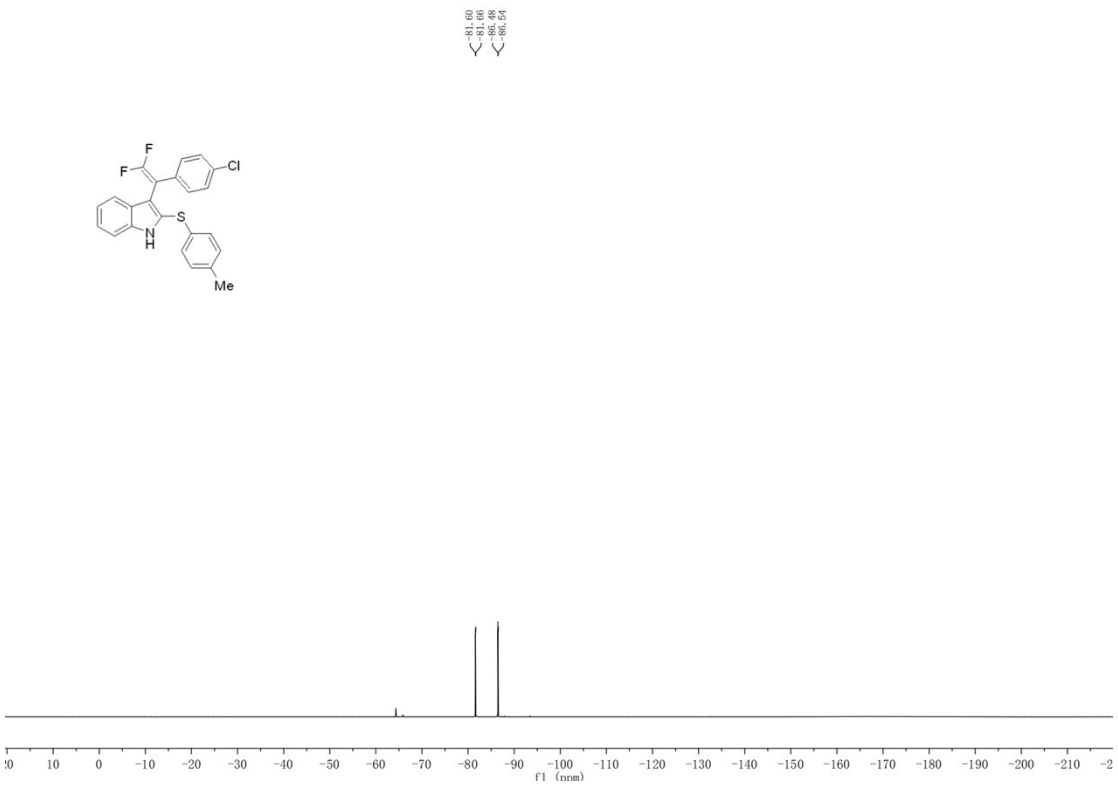
^{1}H NMR spectra of **5s** (400 MHz, $CDCl_3$)



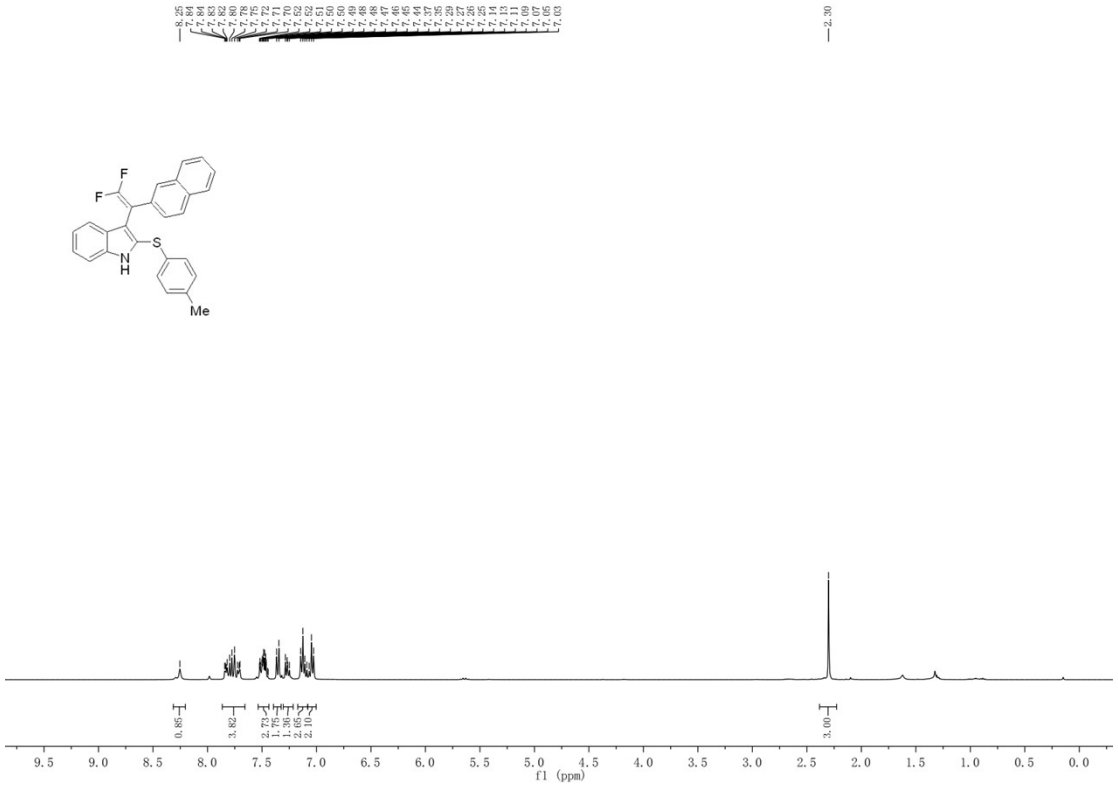
^{13}C NMR spectra of **5s** (100 MHz, $CDCl_3$)



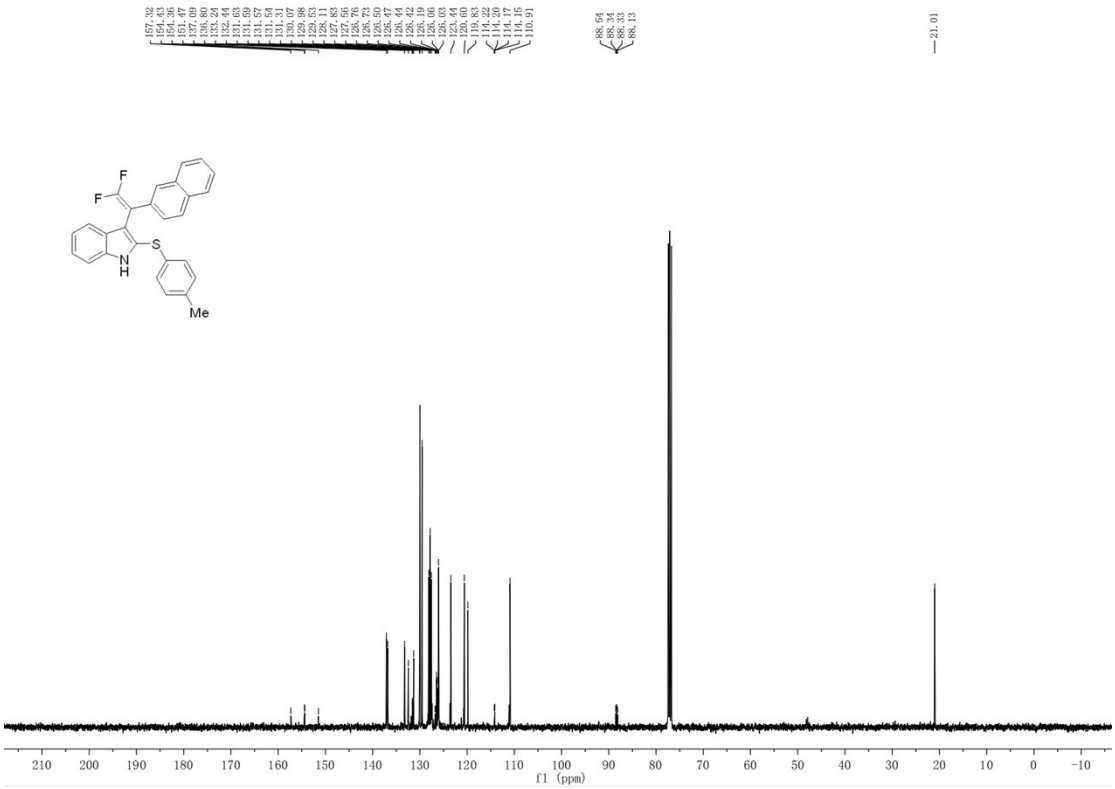
^{19}F NMR spectra of **5s** (376 MHz, $CDCl_3$)



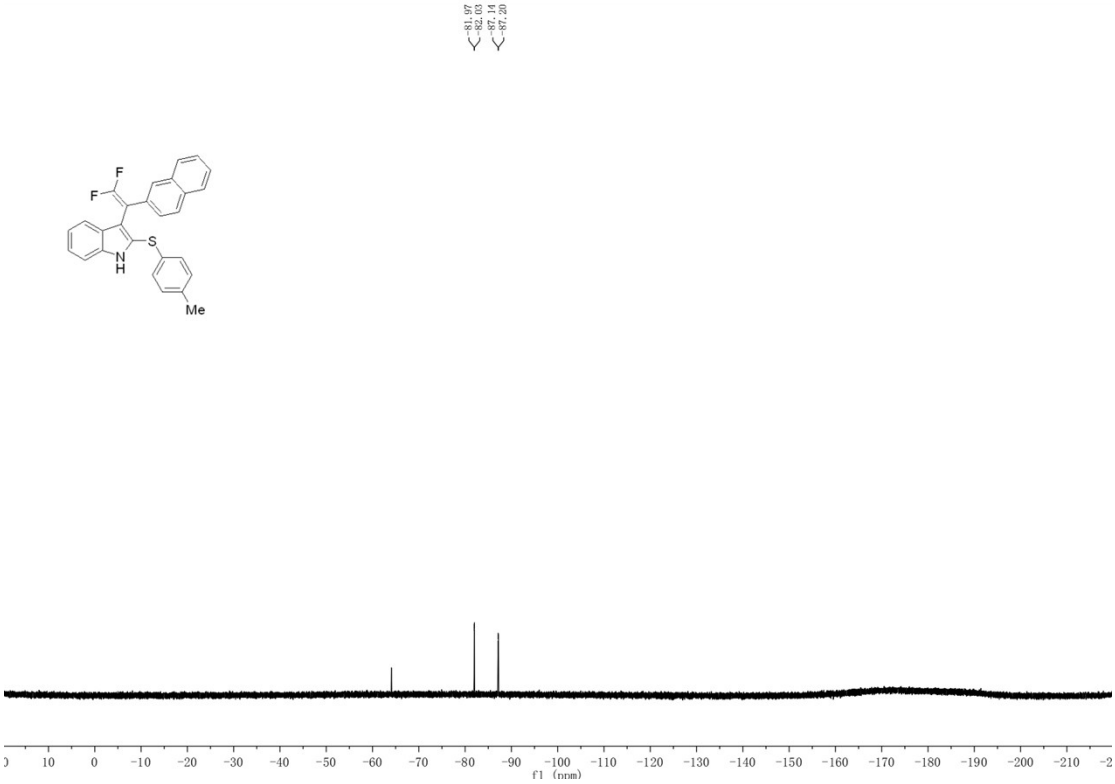
^{1}H NMR spectra of **5t** (400 MHz, $CDCl_3$)



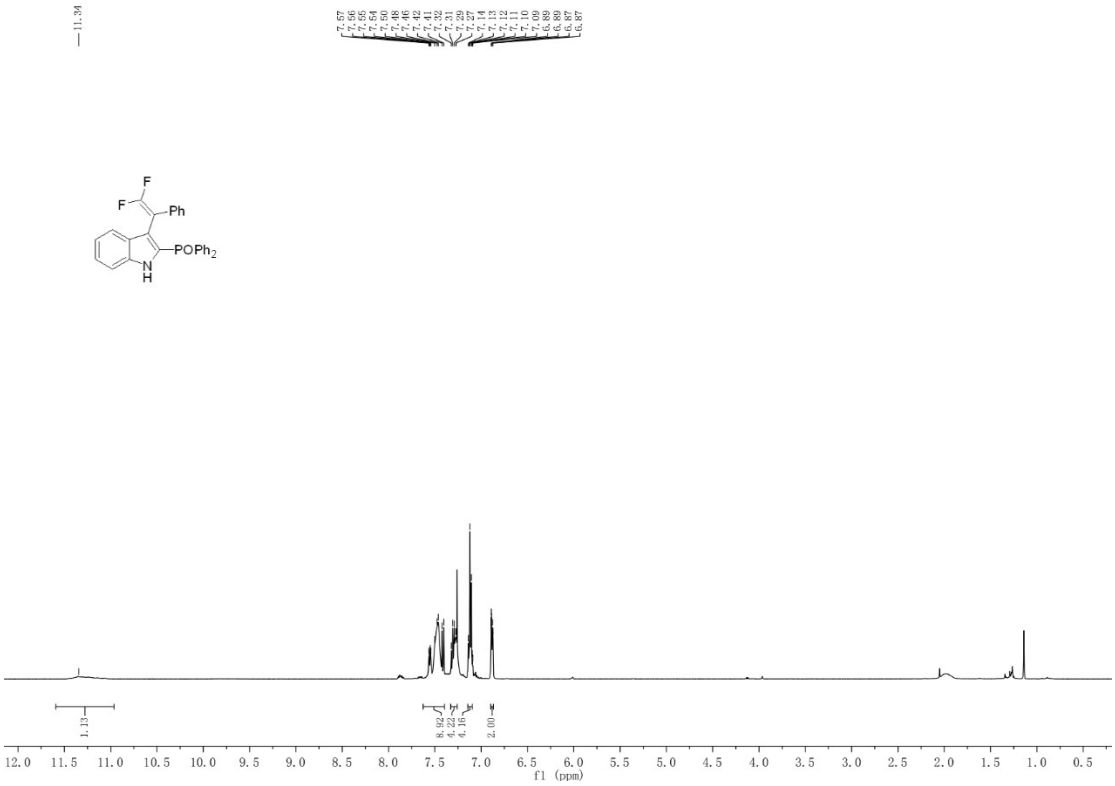
^{13}C NMR spectra of **5t** (100 MHz, $CDCl_3$)



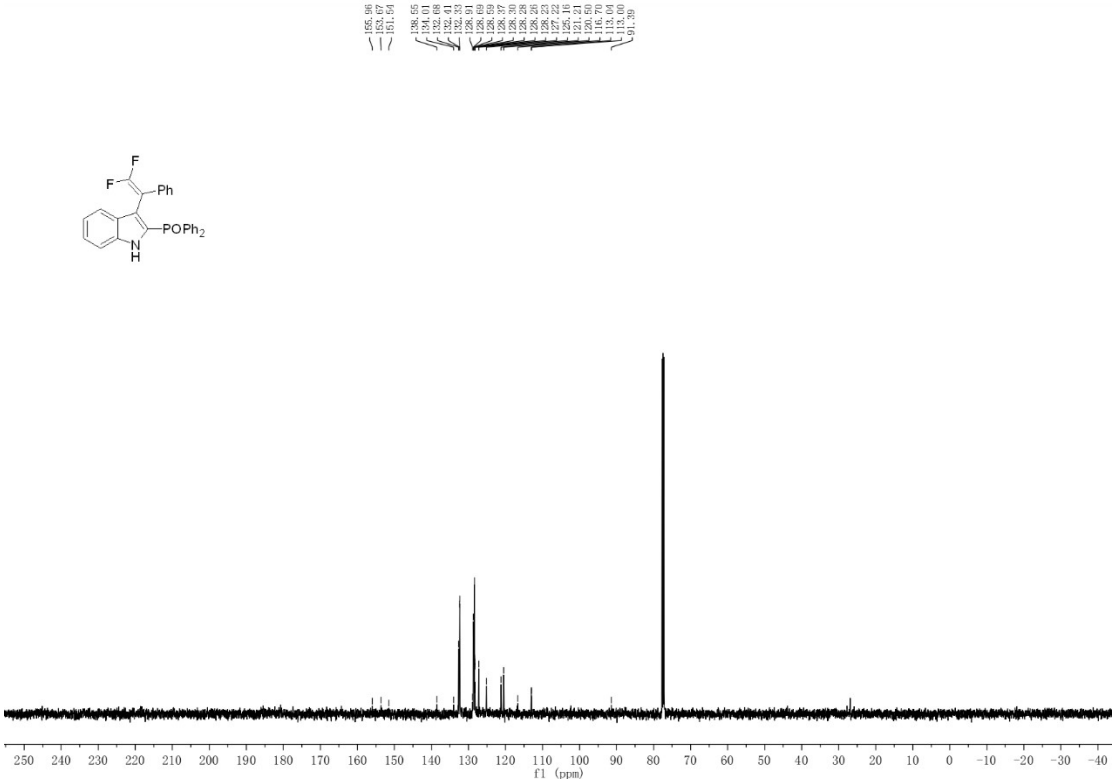
^{19}F NMR spectra of **5t** (376 MHz, $CDCl_3$)



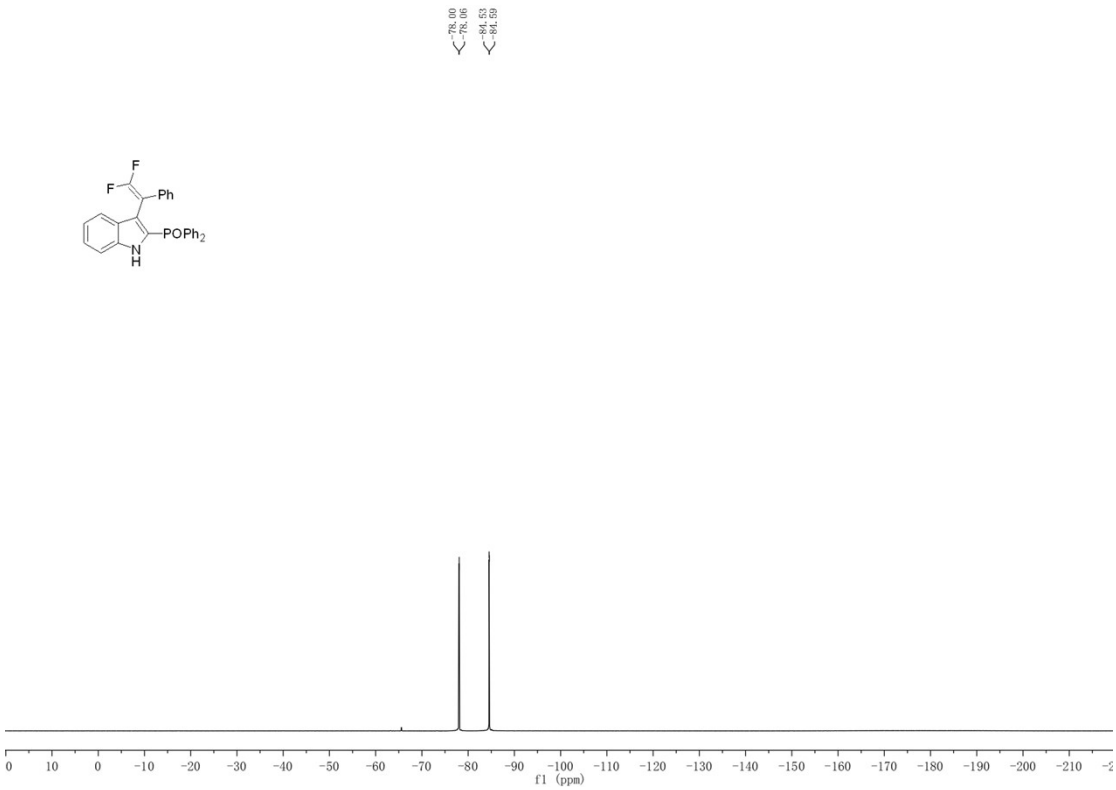
^{1}H NMR spectra of **6** (500 MHz, $CDCl_3$)



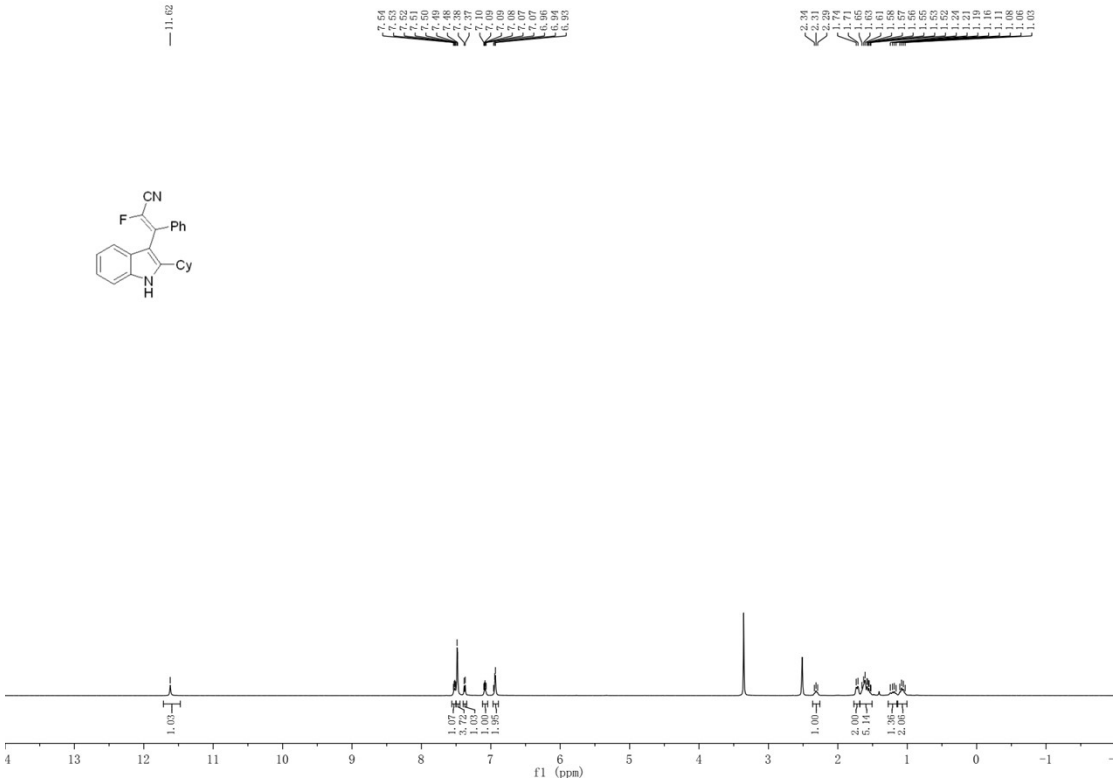
^{13}C NMR spectra of **6** (125 MHz, $CDCl_3$)



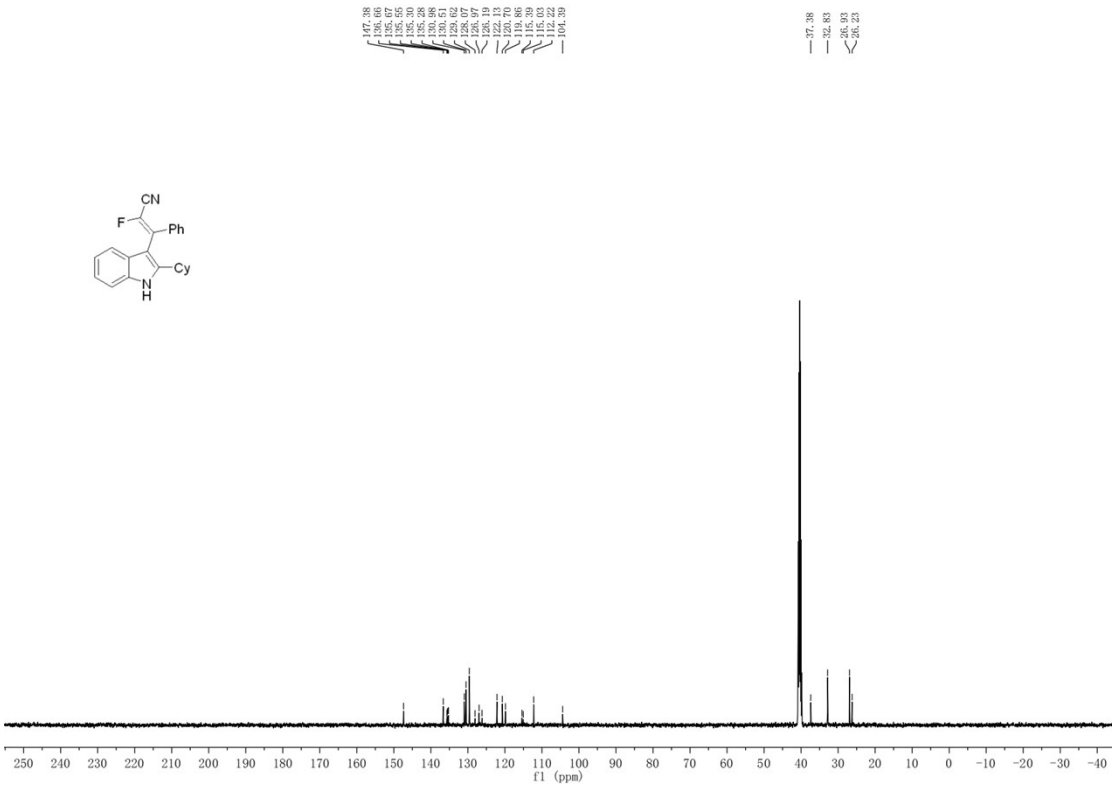
^{19}F NMR spectra of **6** (376 MHz, $CDCl_3$)



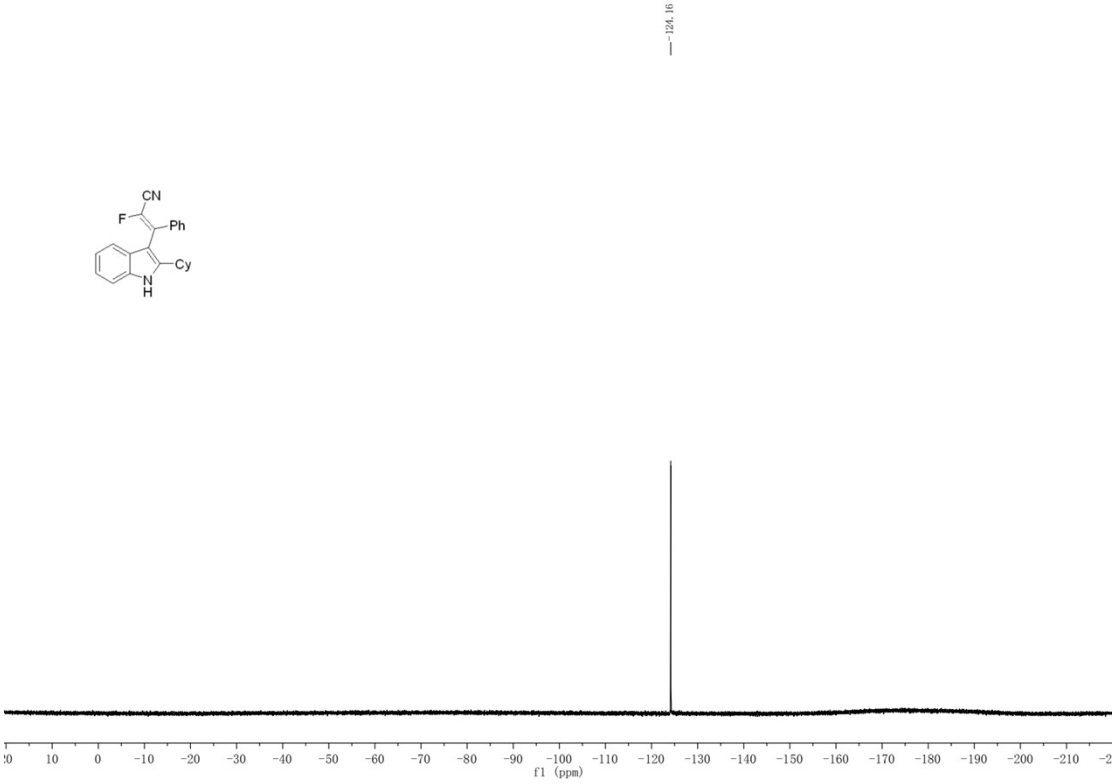
^{1}H NMR spectra of **7** (500 MHz, DMSO-d_6)



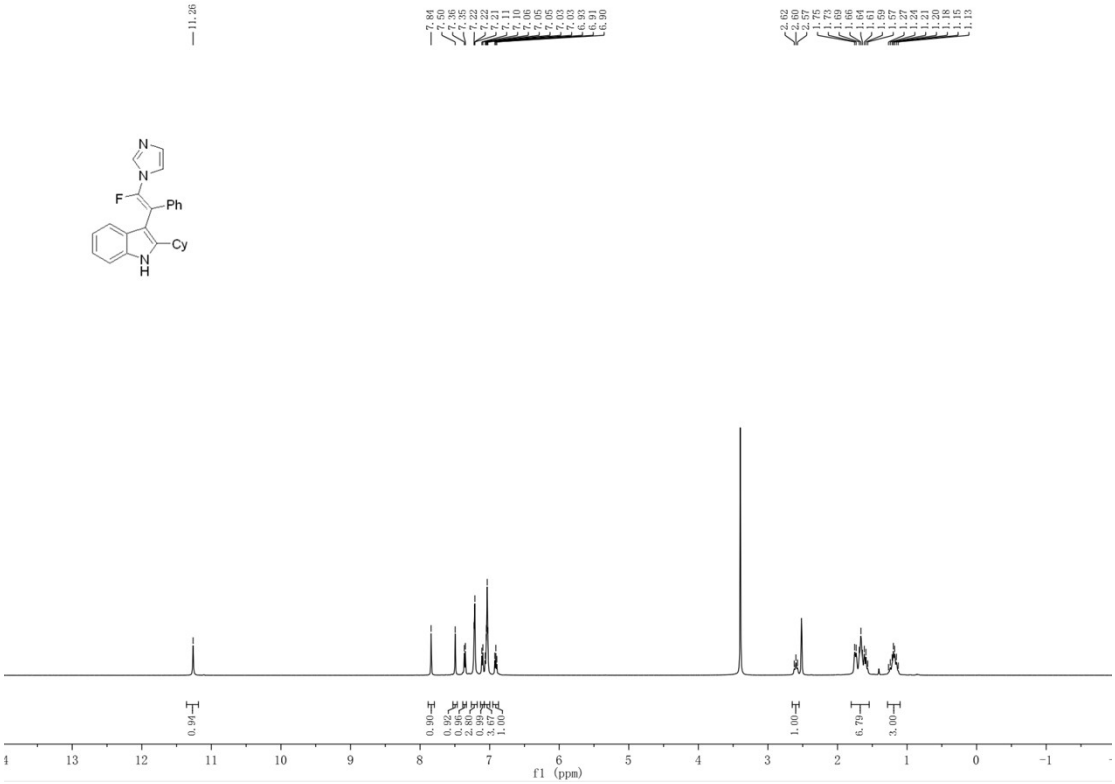
^{13}C NMR spectra of **7** (125 MHz, DMSO-d_6)



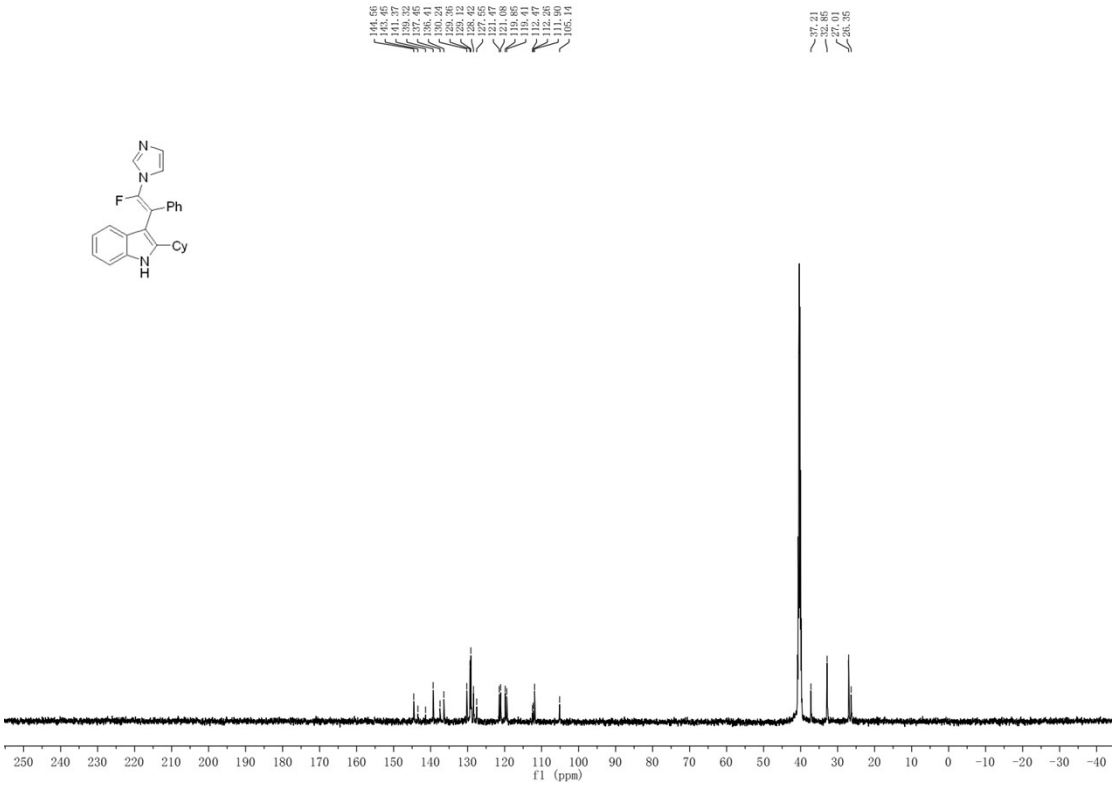
^{19}F NMR spectra of **7** (470 MHz, DMSO-d_6)



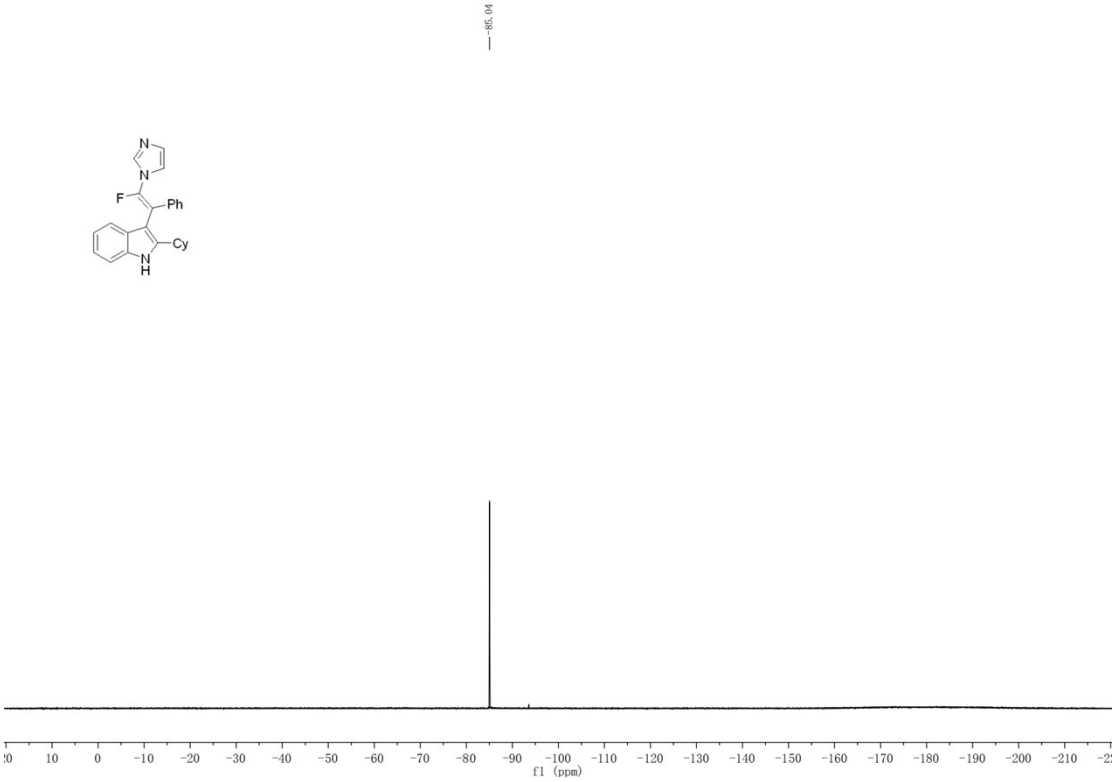
^{1}H NMR spectra of **8** (500 MHz, DMSO-d_6)



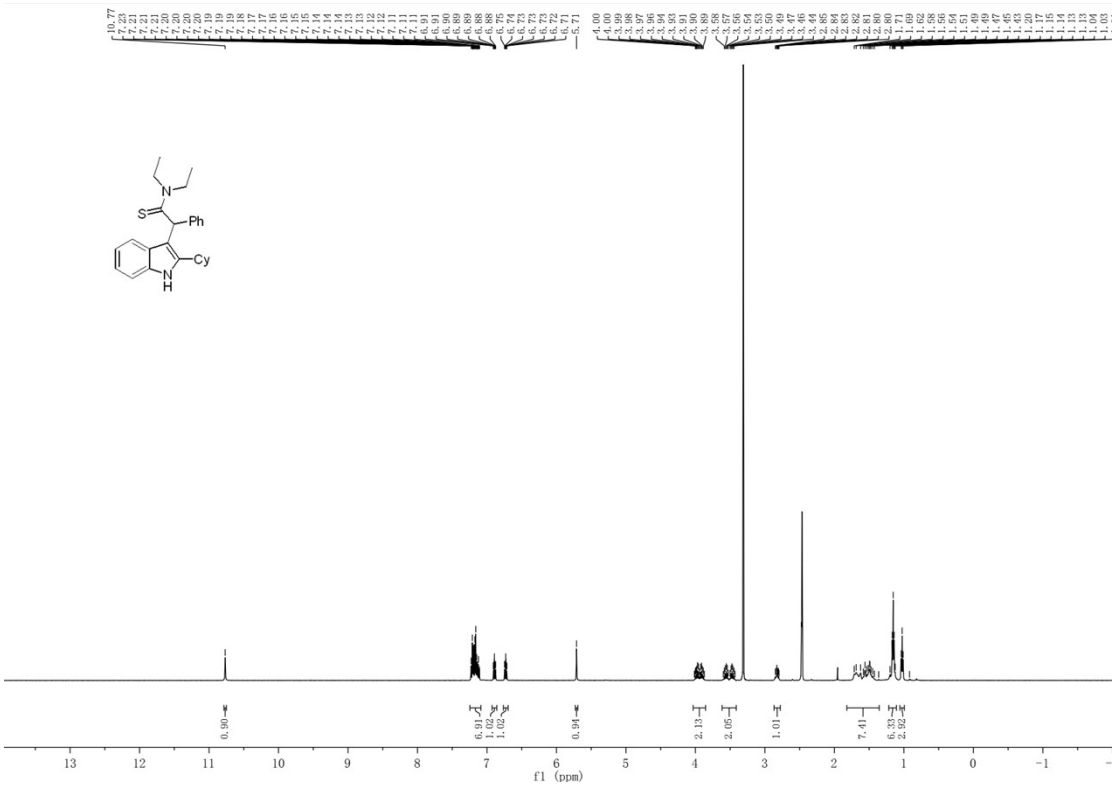
^{13}C NMR spectra of **8** (125 MHz, DMSO-d_6)



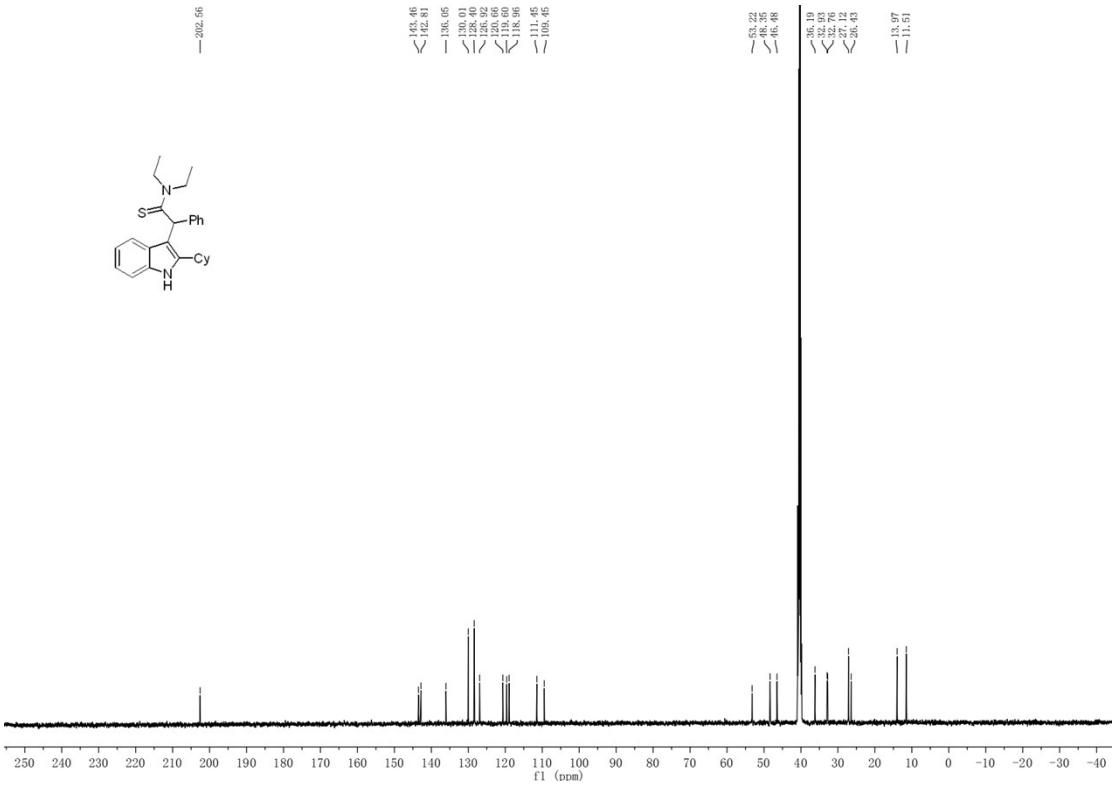
^{19}F NMR spectra of **8** (470 MHz, DMSO-d_6)



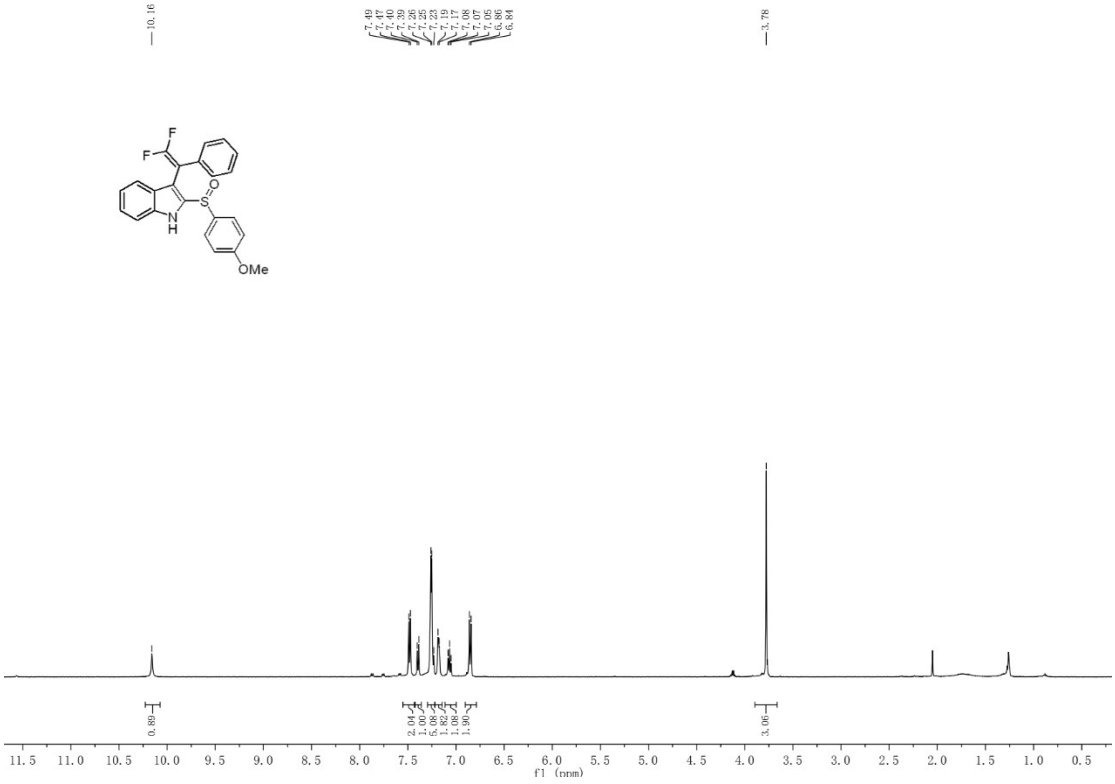
^{1}H NMR spectra of **9** (500 MHz, DMSO-d_6)



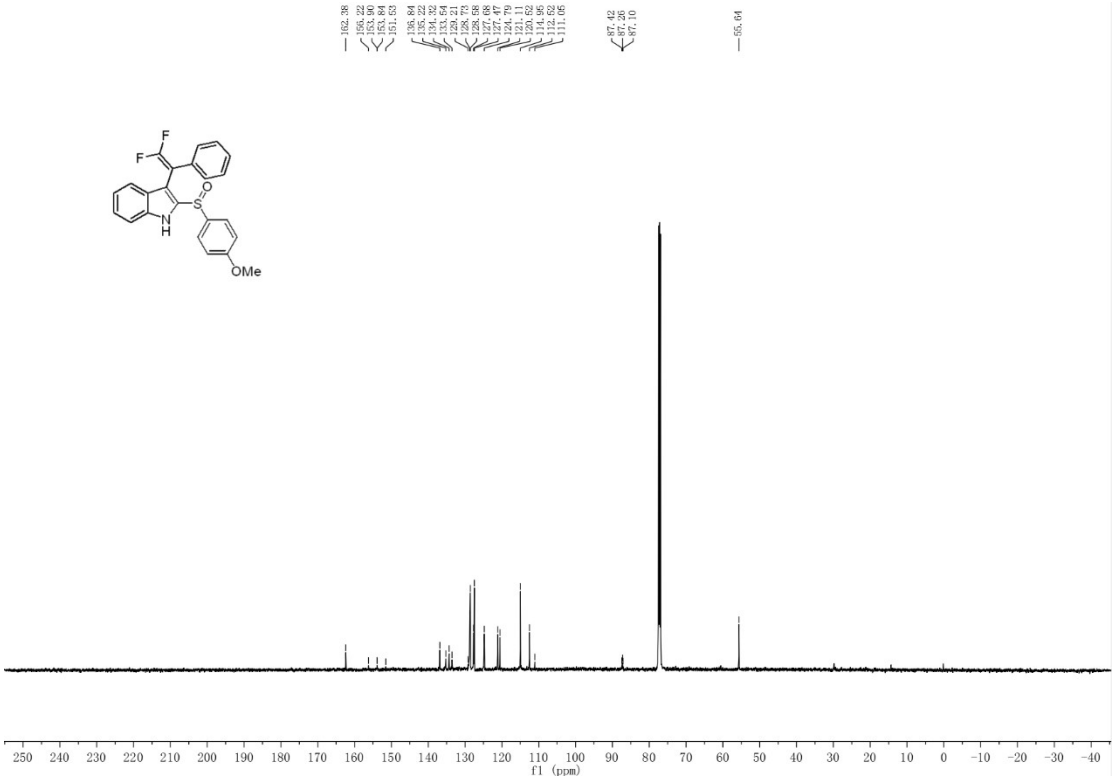
^{13}C NMR spectra of **9** (125 MHz, DMSO-d_6)



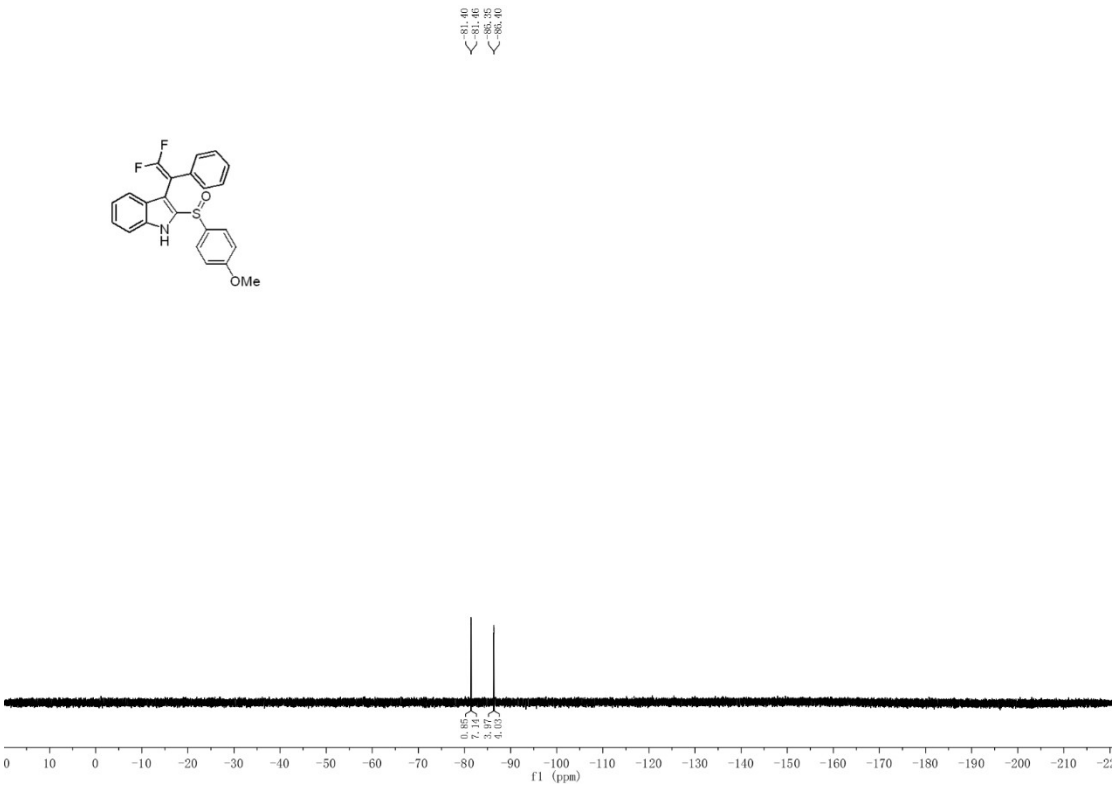
^{1}H NMR spectra of **10** (500 MHz, CDCl3)



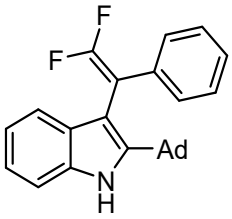
^{13}C NMR spectra of **10** (125 MHz, $CDCl_3$)



^{19}F NMR spectra of **10** (376 MHz, $CDCl_3$)



10. X-Ray Crystallographic Data of compound 3n



(CCDC: 2478297)

The single crystal suitable for X-ray diffraction experiment was obtained by diffusion method of petroleum ether/ dichloromethane containing the compound **3n**.

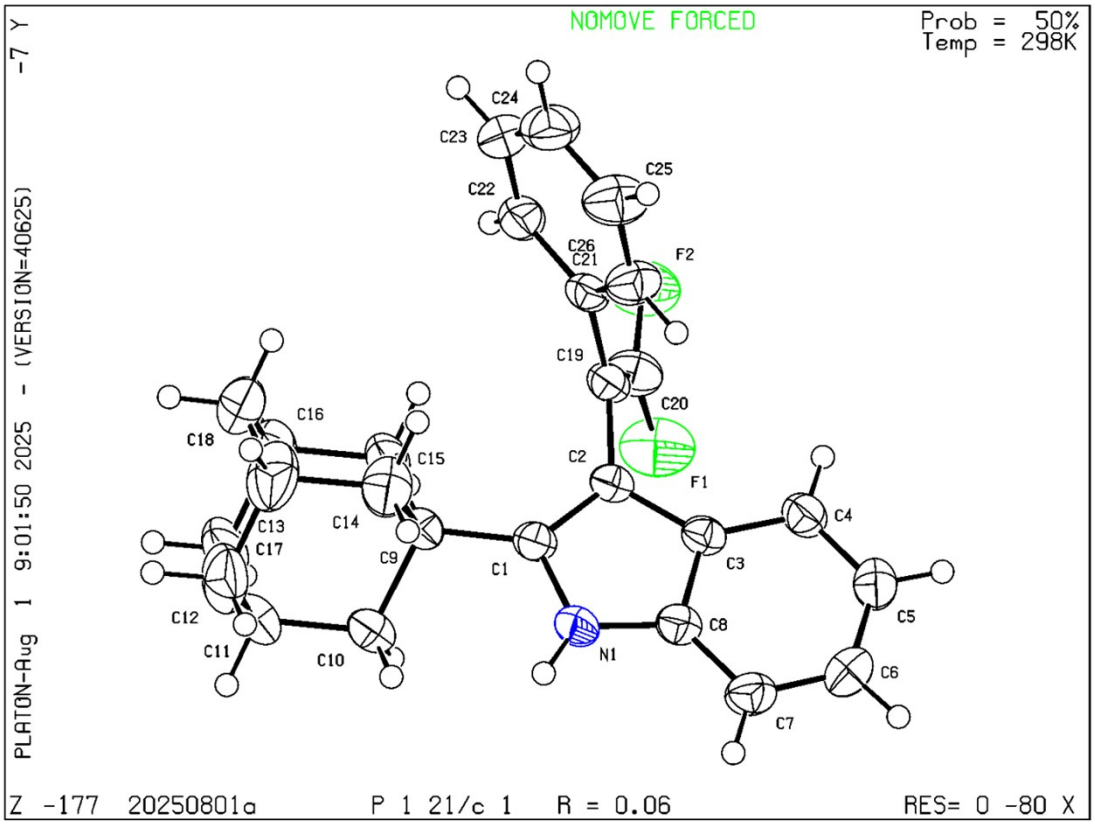


Figure **S5**. X-ray structure of **3n** (at 50% probability level).

Table S2. X-Ray crystallographic data of **3n**.

CCDC	**2478297**
	$C_{26}H_{25}F_2N$
Formula weight	389.47
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	13.2095(8)
Formula	7.0242(4)
c (Å)	22.2707(13)
α (°)	90
β (°)	101.622(2)

γ (°)	90
Volume (Å^3)	2024.0(2)
Z	4
Crystal size, mm^3	0.13×0.12×0.10
Density (g/cm^3)	1.278
Absorption coefficient (mm^{-1})	0.086
Temp. (K)	298(2)
Total reflns.	5734
Indepnt. reflns.	5734
Final R indices [I > 2σ(I)]	R1= 0.0621, wR2 = 0.1249
R indices (all data)	R1= 0.0954, wR2 = 0.1395