Supporting Information

Photoredox-Catalyzed C(sp^2)-H Trifluoromethylarion of 3-Methylene-isoindolin-1-ones under Metal-Free Conditions

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1. General information

All solvents were obtained from a commercial source and were purified by using standard methods. Commercial reagents were used as received without further purification, unless otherwise stated. 3-Methylene-2-phenylisoindolin-1-one derivatives were prepared according to the reported procedures.[1-6]

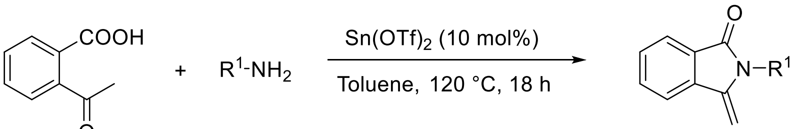
All glassware was thoroughly oven-dried before use. For all experiments, if heating is required, the heat source is an oil bath. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 and chemical shifts are reported in δ (ppm) referenced to residual undeuterated solvent signal for ^{1}H NMR (7.26 ppm) and ^{13}C NMR (77.16 ppm). The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD-MS-MS quadrupole mass spectrometer. Fluorescence emission spectra were measured on an Agilent Cary Eclipse fluorescence spectrophotometer. The light source for the photocatalytic reaction is manufactured by GeAo Chem (24 W blue LEDs, 450-465 nm). A fan was used to maintain the reaction temperature at room temperature. The reactions were carried out in a borosilicate glass vessel and the distance from the light source to the irradiation vessel is about 1 cm.

Reaction set-up (large scale)

Reaction set-up (small scale)

2. Synthesis of starting materials

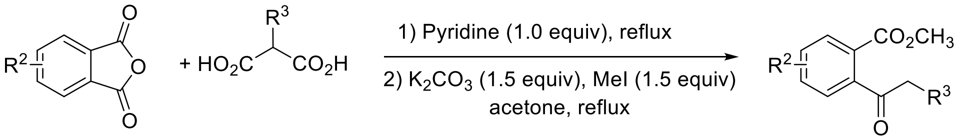
Procedure A:



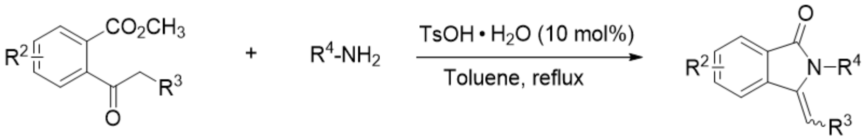
1

2-Acetyl-carboxylic acid (1.0 equiv), $Sn(OTf)_2$ (10 mol %), amines (1.2 equiv) and toluene were add to a round-bottom flask equipped with stir bar. The reaction mixture was then heated to 120 ℃ under air in an oil bath (TLC tracking detection). After being cooled down to room temperature, the reaction was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, which was further purified by silica gel column chromatography on silica gel to afford substrates **1**[1].

Procedure B:



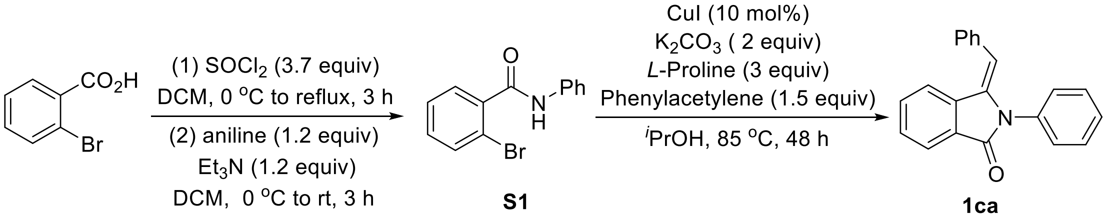
A mixture of phthalic anhydride derivatives (1.2 equiv), malonic acid (1.0 equiv) and pyridine (1.0 equiv) were refluxed until starting materials was consumed. Upon completion, the resulting mixture was cooled to room temperature, and water was added and the mixture was further stirred for 30 min. The solution was treated with concentrated HCl to pH 3-4 and extracted with ethyl acetate. The organic layers were combined, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to obtain the crude product without further purification. The obtained 2-acetylbenzoic acid derivatives were dissolved in acetone, followed by the addition of anhydrous K_2CO_3 (1.5 equiv) and MeI (1.5 equiv). The reaction mixture was stirred under reflux. Upon completion, the resulting mixture was cooled to room temperature, acetone removed on a rotary evaporator, the resulted solid was dissolved in ethyl acetate and mixed with distilled water, extracted with ethyl acetate. The organic phase was dried by anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on a silica gel to afford the corresponding methyl 2-acylbenzoate derivatives.



1

To a suspension of methyl 2-acylbenzoate derivatives (1.0 equiv) in toluene was added amines (1.2 equiv) and *p*-toluenesulfonic acid monohydrate (10 mol%). The reaction mixture was stirred under reflux using a Dean–Stark water separator until the reaction was completed as determined by TLC. After being cooled down to room temperature, the reaction was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, which was further purified by silica gel column chromatography on silica gel to afford substrates **1**. [2]

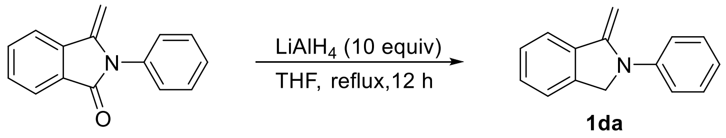
Procedure C:



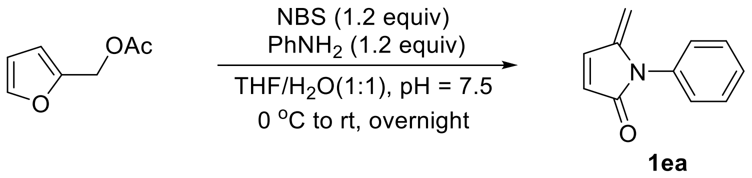
To a solution of 2-bromobenzoic acid (2.0 g, 10 mmol) in anhydrous CH_2Cl_2 (10 mL) was added $SOCl_2$ (4.4 g, 37.0 mmol) at 0 °C. The reaction mixture was then heated to reflux under an oil bath for 3 h. Upon completion of the reaction, the resulting mixture was cooled to room temperature, the solvent was concentrated in vacuo, and the residue was used directly without purification.

To a solution of aniline (12.0 mmol) and Et_3N (12.0 mmol) in anhydrous CH_2Cl_2 was added a solution of acyl chloride in 5 mL CH_2Cl_2 at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for another 3 h. Upon completion of the reaction, the reaction was quenched with saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, which was further purified by silica gel column chromatography on silica gel to afford intermediate **S1**.[3]

To a solution of **S1** in anhydrous ^{i}PrOH (20.0 mL) was added phenylacetylene (1.2 g, 1.5 equiv), CuI (153.0 mg, 10 mol%), *L*-Proline (2.8 g, 3.0 equiv) and K_2CO_3 (2.2 g, 2.0 equiv) successively at room temperature. Then the reaction mixture was warmed to 85 °C and stirred for another 3 h. Upon completion of the reaction, the reaction was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) on silica gel to afford obtain the target product **1ca**. [4]

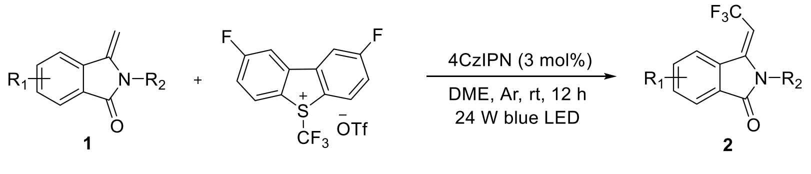


To a solution of 3-methyleneisoindoline-1-one (331 mg, 1.0 equiv) in anhydrous THF (10 mL) was added $LiAlH_4$ (10 equiv) in 5 batches at 0 ^{o}C. Then the reaction mixture was heated to reflux overnight. Upon completion of the reaction, the reaction was quenched with H_2O (1.0 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, the residue was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) on silica gel to afford obtain the target product **1da**. [5]

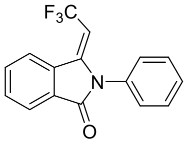


To a solution of furfuryl acetate (378.0 mg, 1.0 equiv) in THF (30 mL) and sodium phosphate buffer (30 mL) was added *N*-bromosuccinimide (213.6 mg, 1.2 equiv) at 0 ^{o}C, and the reaction mixture was stirred at the same temperature for 1 h. Then phenylamine (111.8 mg, 1.2 equiv) was added to the reaction mixture and allowed to warm room temperature stirred overnight. Upon completion of the reaction, the reaction was quenched with H_2O (10.0 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, the residue was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) on silica gel to afford obtain the target product **1ea**. [6]

3. General procedure for the synthesis of trifluoromethyl isoind-olinone 2

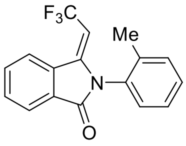


To a screw-capped vial with a magnetic stirring bar were added 4CzIPN (2.4 mg, 0.003 mmol, 3 mol%), **1** (0.1 mmol, 1.0 equiv), Umemoto's reagent (0.12 mmol, 1.2 equiv) in an argon-filled glovebox. After DME (1.0 mL) was added into the vial via a syringe, the vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The resulting mixture was stirred upon 24 W blue LED irradiation under argon atmosphere for 12 hours. After completion of the reaction, the crude mixture was purified by flash chromatography to afford the pure products **2a-2ba**.



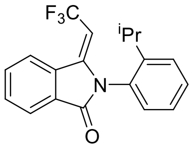
2a

(*E*)-2-phenyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2a). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. Yellow oil (20.1 mg, 70% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.71 – 7.65 (m, 1H), 7.60 – 7.53 (m, 2H), 7.52 – 7.47 (m, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 5.30 (q, *J* = 9.2 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.5, 146.5 (q, *J* = 6.1 Hz), 133.6, 133.4, 132.5, 131.7, 130.0, 130.0, 129.4, 128.9, 125.2 (q, *J* = 5.7 Hz), 124.2 (q, *J* = 266.5 Hz), 124.1, 97.0 (q, *J* = 38.6 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for $[C_{16}H_{11}F_3NO]^+$: 290.0787, found: 290.0779.



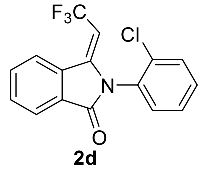
2b

(*E*)-2-(*O*-tolyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2b). Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. White solid (26.0 mg, 86% yield), m.p. 117.7 – 117.8 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (d, *J* = 7.6 Hz, 1H), 8.01 – 7.95 (m, 1H), 7.74 (td, *J* = 7.6, 1.2 Hz, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 5.05 (q, *J* = 9.0 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.2, 145.9 (q, *J* = 6.1 Hz), 137.5, 133.3, 132.6, 132.3, 131.7, 131.7, 130.15, 130.06, 129.5, 127.6, 125.2 (q, *J* = 5.5 Hz), 124.2 (q, *J* = 266.5 Hz), 124.1, 96.7 (q, *J* = 38.6 Hz), 17.7; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for $[C_{17}H_{13}F_3NO]^+$: 304.0944, found: 304.0952.



2c

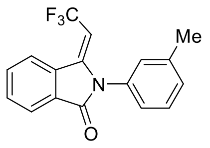
(*E*)-2-(2-isopropylphenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2c). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. Colorless oil (26.0 mg, 76% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.72 – 7.66 (m, 1H), 7.51 (d, *J* = 4.0 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.04 (q, *J* = 9.0 Hz, 1H), 2.79 – 2.68 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.7, 148.2, 146.9 (q, *J* = 6.0 Hz), 133.3, 132.6, 131.7, 130.9, 130.5, 130.1, 129.6, 127.5, 127.4, 125.2 (q, *J* = 5.6 Hz), 124.2 (q, *J* = 266.5 Hz), 124.2, 97.0 (q, *J* = 38.7 Hz), 28.6, 24.1, 23.7; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.4 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for $[C_{19}H_{17}F_3NO]^+$: 332.1257, found: 332.1261.



2d

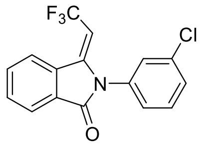
(*E*)-2-(2-chlorophenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2d). Petroleum ether/ethyl acetate (30:1, v/v) as the eluent. White solid (26.0 mg, 81% yield), m.p. 159.1 – 159.4 °C. **^{1}H NMR (400 MHz, CDCl3)** δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.71 – 7.66 (m, 1H), 7.65 – 7.59 (m, 1H), 7.52 – 7.44 (m, 2H), 7.41 – 7.34 (m, 1H), 5.02 (t, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.8, 145.0 (q, *J* = 6.1 Hz), 134.0, 133.4, 132.5, 131.6, 131.3, 131.2, 131.2, 131.0, 129.7, 128.3, 125.2 (q, *J* = 5.7 Hz), 124.2, 124.1 (q, *J* = 266.7 Hz), 96.8 (q, *J* = 38.7 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.5 (s); **HRMS (ESI)** m/z: [M+H]$^+$

calcd for [$C_{16}H_{10}ClF_3NO$]$^+$: 324.0398, found: 324.0393.



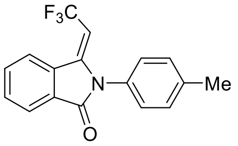
2e

(*E*)-2-(*m*-tolyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2e). Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. White solid (22.0 mg, 73% yield), m.p. 85.6 – 86.9 °C. **^{1}HNMR (400 MHz, CDCl$_3$)** δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), δ 7.73 (td, *J* = 7.6, 1.2 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.49 – 7.40 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.28 (q, *J* = 9.0 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.6, 146.6 (q, *J* = 6.0 Hz), 140.2, 133.4, 133.3, 132.4, 131.7, 130.3, 130.0, 129.8, 129.5, 125.9, 125.1 (q, *J* = 5.6 Hz), 124.2 (q, *J* = 266.6 Hz), 124.1, δ 97.0 (q, *J* = 38.6 Hz), 21.5; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{17}H_{13}F_3NO$]$^+$: 304.0944, found: 304.0935.



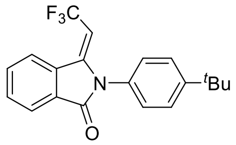
2f

(*E*)-2-(3-chlorophenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2f). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. White solid (19.0 mg, 59% yield), m.p. 108.3 – 108.9 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), δ 7.75 (td, *J* = 7.6, 0.8 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.54 – 7.47 (m, 2H), 7.34 (d, *J* = 12.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 5.30 (q, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.2, 146.1 (q, *J* = 5.9 Hz), 135.6, 134.7, 133.6, 132.4, 131.9, 134.0, 129.7, 129.7, 129.3, 127.3, 125.3 (q, *J* = 5.6 Hz), 124.2, 124.1 (q, *J* = 266.8 Hz), 97.2 (q, *J* = 38.8 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.4 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{16}H_{10}ClF_3NO$]$^+$: 324.0398, found: 324.0387.



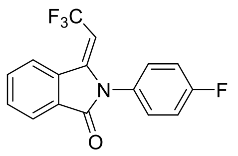
2g

(*E*)-2-(*p*-tolyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2g). Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. White solid (16.0 mg, 53% yield), m.p. 136.7 – 138.3 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), δ 7.72 (td, *J* = 7.6, 1.2 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 5.30 (q, *J* = 9.2 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.6, 146.6 (q, *J* =6.0 Hz), 139.5, 133.3, 132.5, 131.6, 130.8, 130.7, 130.1, 128.7, 125.1 (q, *J* = 5.6 Hz), 124.3 (q, *J* = 266.6 Hz), 124.1, 96.9 (q, *J* = 38.6 Hz), 21.4; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{17}H_{13}F_3NO$]$^+$: 304.0944, found: 304.0947.



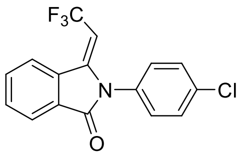
2h

(*E*)-2-(4-(*tert*-butyl)phenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2h). Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. Colourless oil (23.0 mg, 70% yield).**^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.70 – 7.64 (m, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 5.33 (q, *J* = 9.1 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.6, 152.4, 146.6 (q, *J* = 6.2 Hz), 133.3, 132.5, 131.6, 130.7, 130.1, 128.3, 127.0, 125.1 (q, *J* = 5.7 Hz), 124.3 (q, *J* = 266.6 Hz), 124.1, 97.0 (q, *J* = 38.5 Hz), 35.0, 31.5; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{20}H_{19}F_3NO$]$^+$: 346.1413, found: 346.1420.



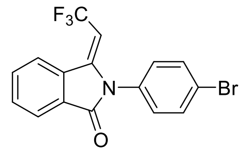
2i

(*E*)-2-(4-fluorophenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2i). Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. White solid (23.0 mg, 74% yield), m.p. 116.8 – 116.9 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), δ 7.73 (td, *J* = 7.6, 1.2 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 5.24 (q, *J* = 9.0 Hz, 1H) ; **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.5, 162.9 (d, *J* = 248.3 Hz), 146.5 (q, *J* = 6.0 Hz), 133.5, 132.4, 131.8, 130.9 (d, *J* = 8.7 Hz), 129.8, 129.4 (d, *J* = 3.3 Hz), 125.2 (q, *J* = 5.6 Hz), 124.2, 124.1 (q, *J* = 266.8 Hz), 117.2 (d, *J* = 23.0 Hz), 97.1 (q, *J* = 38.7 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.4 (s), -111.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{16}H_{10}F_4NO$]$^+$: 308.0693, found: 308.0696.



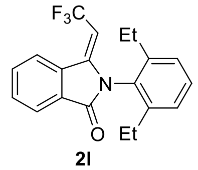
2j

(*E*)-2-(4-chlorophenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2j). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. White solid (21.0 mg, 65% yield), m.p. 155.9 – 156.5 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), δ 7.72 (td, *J* = 7.6, 0.8 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.26 (m, 2H), 5.29 (q, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.3, 146.3 (q, *J* =5.4 Hz), 135.5, 133.6, 132.5, 132.1, 131.9, 130.4, 130.3, 129.8, 125.3 (q, *J* = 5.8 Hz), 124.2, 124.09 (q, *J* =266.3 Hz), 97.1 (q, *J* = 38.7 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.4 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{16}H_{10}ClF_3NO$]$^+$: 324.0398, found: 324.0408.



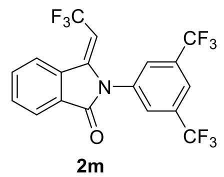
2k

(*E*)-2-(4-bromophenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2k). Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. White solid (24.0 mg, 66% yield), m.p. 164.0 – 164.7 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), δ 7.74 (td, *J* = 7.6, 1.2 Hz, 1H), 7.72 – 7.65 (m, 3H), 7.24 – 7.18 (m, 2H), 5.29 (q, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.3, 146.2 (q, *J* = 5.8 Hz), 133.6, 133.4, 132.6, 132.4, 131.9, 130.6, 129.7, 125.3 (q, *J* = 5.6 Hz), 124.2, 124.1 (q, *J* = 266.7 Hz), 123.5, 97.1 (q, *J* = 38.7 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.4 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{16}H_{10}BrF_3NO$]$^+$: 367.9892, found: 367.9900.



2l

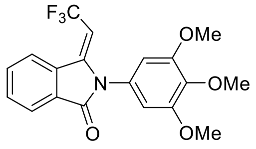
(*E*)-2-(2,6-diethylphenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2l). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. Colorless oil (24.0 mg, 70% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), δ 7.75 (td, *J* = 7.6, 1.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.47 – 7.40 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 4.97 (q, *J* = 9.2 Hz, 1H), 2.46 – 2.34 (m, 4H), 1.15 (t, *J* = 7.6 Hz, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.6, 145.8 (q, *J* = 6.1 Hz), 143.1, 133.3, 132.5, 131.7, 130.3, 130.2, 130.0, 127.2, 125.3 (q, *J* = 5.6 Hz), 124.2 (q, *J* = 266.5 Hz). 124.2, 96.5 (q, *J* = 38.6 Hz), 24.3, 14.4; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.4 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{20}H_{19}F_3NO$]$^+$: 346.1413, found: 346.1421.



2m

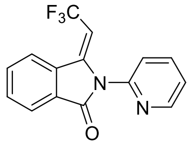
(*E*)-2-(3,5-bis(trifluoromethyl)phenyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2m). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. White solid (17.0 mg, 49% yield), m.p. 122.2 – 122.6 °C. **^{1}H NMR (400**

MHz, CDCl$_3$) δ 8.15 (d, *J* = 7.6 Hz, 1H), 8.05 – 7.97 (m, 2H), 7.84 (s, 2H), δ 7.80 (td, *J* = 7.6, 1.2 Hz, 1H), 7.76 – 7.70 (m, 1H), 5.27 (q, *J* = 8.6 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.0, 145.7 (q, *J* = 5.9 Hz), 135.3, 134.1, 133.8 (q, *J* = 34.2 Hz), 132.3 (d, *J* = 5.5 Hz), 129.5 (d, *J* = 3.2 Hz), 129.1, 125.5 (q, *J* = 5.7 Hz), 124.5, 133.8 (q, *J* = 34.3 Hz), 123.7 (q, *J* = 267.1 Hz). 123.3 (q, *J* = 3.6 Hz), 122.8 (q, *J* = 271.5 Hz), 97.3 (q, *J* = 39.1 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.6 (s), -62.9 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [C$_{18}$H$_9$F$_9$NO]$^+$: 426.0535, found: 426.0535.



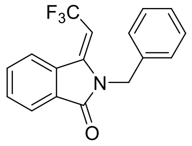
2n

(*E*)-3-(2,2,2-trifluoroethylidene)-2-(3,4,5-trimethoxyphenyl)isoindolin-1-one (2n). Petroleum ether/ethyl acetate (20:1, v/v) as the eluent. White solid (21.0 mg, 53% yield), m.p. 200.6 – 201.3 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), δ 7.73 (td, *J* = 7.6, 1.2 Hz, 1H), 7.70 – 7.65 (m, 1H), 6.51 (s, 2H), 5.34 (q, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 18.9 Hz, 9H) 3.91 (s, 3H), 3.87 (s, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.5, 154.2, 146.6 (q, *J* = 6.1 Hz), 138.8, 133.4, 132.38, 131.73, 129.88, 128.90, 125.13 (q, *J* = 5.5 Hz), 124.21 (q, *J* = 266.7 Hz), 124.10, 106.29, 97.23 (q, *J* = 38.6 Hz), 61.04, 56.43; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [C$_{19}$H$_{17}$F$_3$NO$_4$]$^+$: 380.1104, found: 380.1104.



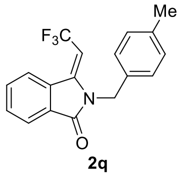
2o

(*E*)-2-(pyridin-2-yl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2o). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. White solid (8.0 mg, 27% yield), m.p. 140.4 – 141.0 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.69 (d, *J* = 4.8 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.03 – 7.88 (m, 2H), 7.78 – 7.71 (m, 1H), 7.71 – 7.64 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.35 (m, 1H), 5.95 (q, *J* = 9.4 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.2, 149.6, 148.1, 144.0 (q, *J* = 6.2 Hz), 138.9, 133.8, 132.6, 131.6, 129.4, 125.3 (q, *J* = 11.4, 5.7 Hz), 124.3, δ 124.1 (q, *J* = 267.1 Hz), 123.6, 123.4, 98.6 (q, *J* = 38.4 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.5 (s). **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [C$_{15}$H$_{10}$F$_3$N$_2$O]$^+$: 291.0740, found: 291.0730.



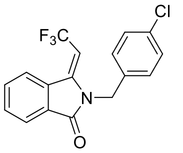
2p

(*E*)-2-benzyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2p). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. Yellow oil (25.0 mg, 83% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.98 – 7.85 (m, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.36 – 7.26 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 2H), 5.40 (q, *J* = 9.0 Hz, 1H), 4.99 (s, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.0, 144.4 (q, *J* = 6.1 Hz), 135.5, 133.3, 132.7, 131.4, 123.0, 129.1, 128.0, 127.0, 125.1 (q, *J* = 5.5 Hz), 124.0 (q, *J* = 266.8 Hz). 124.0, 96.5 (q, *J* = 38.7 Hz), 43.5; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [C$_{17}$H$_{13}$F$_3$NO]$^+$: 304.0944, found: 304.0953.

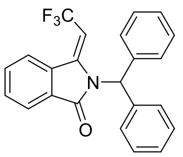


2q

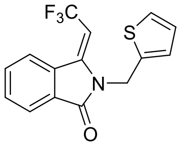
(*E*)-2-(4-methylbenzyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2q). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. Colorless oil (18.0 mg, 57% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.97 – 7.90 (m, 1H), δ 7.67 (td, *J* = 7.6, 1.6 Hz, 1H), 7.62 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 – 7.07 (m, 4H), 5.41 (q, *J* = 9.0 Hz, 1H), 4.94 (s, 2H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.0, 144.5 (q, *J* = 6.0 Hz), 137.7, 133.2, 132.7, 132.5, 131.4, 130.1, 129.8, 127.0, 125.0 (q, J = 5.6 Hz), 124.0 (q, J = 266.7 Hz), 123.9, 96.5 (q, J = 38.7 Hz), 43.3, 21.2; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.2 (d, J = 9.0 Hz); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{18}H_{15}F_3NO]^+$: 318.1100, found: 318.1095.


2r

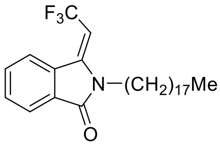
(*E*)-2-(4-chlorobenzyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2r). Petroleum ether/ethyl acetate (45:1, v/v) as the eluent. White solid (24.0 mg, 71% yield), m.p. 122.5 – 123.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), δ 7.69 (td, J = 7.6, 1.6 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.34 (q, J = 8.8 Hz, 1H), 4.95 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.0, 144.3 (q, J = 6.0 Hz), 134.0, 133.9, 133.4, 132.6, 131.6, 129.8, 129.3, 128.4, 125.2 (q, J = 5.6 Hz), 124.0, 122.5, 96.5 (q, J = 38.8 Hz), 42.9; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{17}H_{12}ClF_3NO]^+$: 338.0554, found: 338.0560.


2s

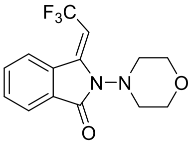
(*E*)-2-benzhydryl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2s). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. Colorless oil (29.0 mg, 77% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 7.2 Hz, 1H), δ 7.68 (td, J = 7.6, 1.2 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.41 – 7.29 (m, 10H), 7.14 (s, 1H), 5.41 (q, J = 9.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.2, 143.7 (q, J = 6.1 Hz), 137.2, 133.3, 132.8, 131.3, 129.6, 128.8, 128.6, 128.1, 125.1 (q, J = 5.8 Hz), 124.0, 123.8 (q, J = 266.9 Hz), 99.2 (q, J = 38.6 Hz), 58.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.4 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{23}H_{17}F_3NO]^+$: 380.1257, found: 380.1248.


2t

(*E*)-2-(thiophen-2-ylmethyl)-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2t). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. White solid (20.0 mg, 65% yield), m.p. 115.8 – 116.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), δ 7.67 (td, J = 7.6, 1.2 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.24 (dd, J = 5.0, 1.1 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 6.96 (dd, J = 5.2, 3.6 Hz, 1H), 5.58 (q, J = 8.8 Hz, 1H), 5.13 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.5, 144.1 (q, J = 6.0 Hz), 138.0, 133.3, 132.7, 131.5, 129.8, 127.2, 126.5, 125.8, 125.1 (q, J = 5.7 Hz), 124.0, 124.0 (q, J = 266.8 Hz), 96.2 (q, J = 38.9 Hz), 38.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{15}H_{11}F_3NOS]^+$: 310.0508, found: 310.0516.

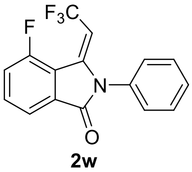

2u

(*E*)-2-octadecyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2u). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. White solid (29.0 mg, 63% yield), m.p. 64.8 – 65.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.61 – 7.56 (m, 1H), 5.44 (q, J = 9.0 Hz, 1H), 3.74 (t, J = 7.4 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.37 – 1.23 (m, 30H), 0.87 (t, J = 6.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.8, 144.8 (q, J = 6.0 Hz), 132.9, 132.6, 131.3, 130.3, 124.9 (q, J = 5.7 Hz), 124.3 (q, J = 266.4 Hz), 123.6, 95.0 (q, J = 38.7 Hz), 39.8, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 27.9, 27.1, 22.8, 14.2; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -52.9 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{28}H_{43}F_3NO]^+$: 466.3291, found: 466.3283.



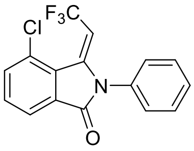
2v

(*E*)-2-morpholino-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2v). Petroleum ether/ethyl acetate (30:1, v/v) as the eluent. White solid (20.0 mg, 67% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.00 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H), δ 7.67 (td, J = 7.6, 1.2 Hz, 1H), 7.64 – 7.59 (m, 1H), 6.16 (q, J = 9.6 Hz, 1H), 4.07 – 3.96 (m, 4H), 3.71 (td, J = 11.6, 2.0 Hz, 2H), 2.84 (d, J = 10.4 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.4, 142.8 (q, J = 6.1 Hz), 133.3, 131.5, 130.6, 129.0, 125.1 (d, J = 5.5 Hz), 124.7 (q, J = 266.1 Hz), 123.4, 96.2 (q, J = 38.5 Hz), 67.5, 51.6; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{14}H_{14}F_3N_2O_2$]$^+$: 299.1002, found: 299.1006.



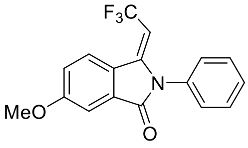
2w

(*E*)-4-fluoro-2-phenyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2w). Petroleum ether/ethyl acetate (30:1, v/v) as the eluent. Colorless oil (17.0 mg, 55% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 (d, J = 7.6 Hz, 1H), 7.71 (td, J = 8.0, 2.8 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.47 (m, 1H), 7.37 – 7.29 (m, 3H), 5.32 (q, J = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.2, 158.9 (d, J = 261.4 Hz), 145.8 – 145.4 (m), 135.4 (d, J = 7.7 Hz), 134.7 (d, J = 1.2 Hz), 133.1, 130.1, 129.6, 129.0, 124.0 (q, J = 266.6 Hz), 121.8 – 121.1 (m), 119.4 (d, J = 18.9 Hz), 116.8 (d, J = 12.8 Hz), 97.8 (q, J = 38.8 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.5 (s), -115.7 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{16}H_{10}F_4NO$]$^+$: 308.0693, found: 308.0684.



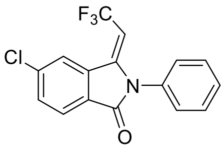
2x

(*E*)-4-chloro-2-phenyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2x). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. White solid (23.0 mg, 71% yield), m.p. 154.6 – 155.2 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.03 (d, J = 7.2 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.31 (d, J = 7.2 Hz, 2H), 5.32 (q, J = 9.2 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.0, 144.9 (q, J = 6.3 Hz), 134.7, 134.0, 133.4, 133.2, 132.4, 130.1, 129.5, 128.9, 125.8, 124.1 (q, J = 266.7 Hz), 123.7 (q, J = 5.8 Hz), 97.4 (q, J = 38.9 Hz); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{16}H_{10}ClF_3NO$]$^+$: 324.0398, found: 324.0398.



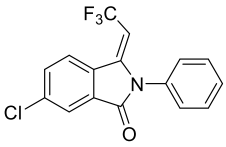
2y

(*E*)-6-methoxy-2-phenyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2y). Petroleum ether/ethyl acetate (20:1, v/v) as the eluent. White solid (17.0 mg, 53% yield), m.p. 146.3 – 146.5 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.99 (d, J = 8.7 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 (d, J = 2.5 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.23 (dd, J = 8.7, 2.5 Hz, 1H), 5.19 (q, J = 9.1 Hz, 1H), 3.94 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.5, 162.7, 146.3 (q, J = 6.1 Hz), 133.7, 132.2, 130.0, 129.3, 129.0, 126.5 (q, J = 5.6 Hz), 124.9, 124.4 (q, J = 266.2 Hz).120.8, 107.3, 95.7 (q, J = 38.5 Hz), 56.1; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: [M+H]$^+$ calcd for [$C_{17}H_{13}F_3NO_2$]$^+$: 320.0893, found: 320.0894.



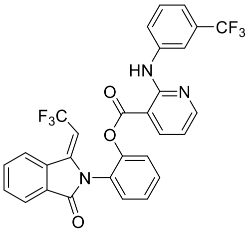
2z

(*E*)-5-chloro-2-phenyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2z). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. White solid (25.0 mg, 77% yield), m.p. 146.9 – 147.4 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.06 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.35 – 7.28 (m, 2H), 5.34 (q, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.4, 145.4 (q, *J* = 5.9 Hz), 134.0, 133.9, 133.3, 132.1, 130.2, 129.6, 128.8, 128.3, 125.5 (q, *J* = 6.1 Hz), 125.2, 98.0 (q, *J* = 39.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{16}H_{10}ClF_3NO]^+$: 324.0398, found: 324.0389.



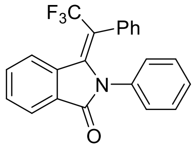
2aa

(*E*)-6-chloro-2-phenyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2aa). Petroleum ether/ethyl acetate (50:1, v/v) as the eluent. White solid (22.0 mg, 68% yield), m.p. 80.2 – 80.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.53 – 7.45 (m, 1H), 7.31 (d, *J* = 7.2 Hz, 2H), 5.32 (q, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.2, 145.6 (q, *J* = 5.9 Hz), 138.3, 133.5, 133.3, 131.7, 130.1, 129.6, 128.8, 126.4 (q, *J* = 5.8 Hz), 124.3, 124.0 (q, *J* = 268.4 Hz), 117.2 (d, *J* = 22.9 Hz), 97.6 (q, *J* = 38.7 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.3 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{16}H_{10}ClF_3NO]^+$: 324.0398, found: 324.0406.



2ba

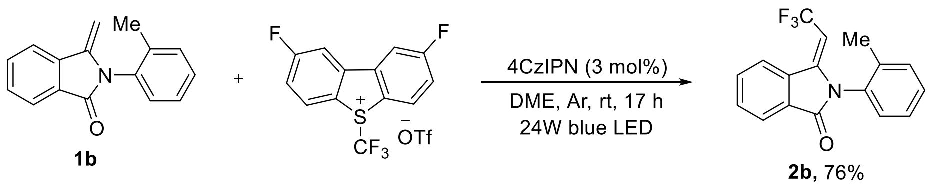
(*E*)-2-(1-oxo-3-(2,2,2-trifluoroethylidene)isoindolin-2-yl)phenyl 2-((3-(trifluoromethyl)phenyl)amino)nicotinate (2ba). Petroleum ether/ethyl acetate (20:1, v/v) as the eluent. Yellow solid (27.0 mg, 47% yield), m.p. 170.7 – 171.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.97 (s, 1H), 8.34 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.49 (m, 6H), 7.47 – 7.37 (m, 2H), 7.28 (M, 1H), 6.61 (dd, *J* = 7.6, 4.8 Hz, 1H), 5.66 (q, *J* = 9.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.6, 164.8, 156.1, 154.1, 147.3, 142.0 (q, *J* = 5.4 Hz), 140.5, 134.0, 137.0, 133.6, 131.6, 131.4, 131.1 (d, *J* = 1.2 Hz), 130.6, 129.3, 127.6, 127.4, 126.7, 124.5, 123.9, 123.4 (dd, *J* = 270.6, 183.7 Hz), 123.3, 120.1, 119.5 (q, *J* = 3.8 Hz), 117.6 (q, *J* = 3.9 Hz), 114.2, 106.1, 93.0 (q, *J* = 39.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -52.2 (s), -62.6 (s); **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{29}H_{18}F_6N_3O_3]^+$: 570.1247, found: 570.1262.



2-phenyl-3-(2,2,2-trifluoro-1-phenylethylidene)isoindolin-1-one(2ca). Petroleum ether/ethyl acetate (20:1, v/v) as the eluent. Yellow oil (10.0 mg, 27% yield). *E/Z* = 1:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.40 (m, 11H), 7.24 – 7.20 (m, 1H), 7.04 – 7.00 (m, 4H), 6.98 – 6.94 (m, 2H), 6.88 (s, 1H), 6.87 (s, 1H), 6.85 – 6.80 (m, 2H), 5.86 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.6, 168.5, 137.7, 137.4, 136.6, 134.9, 133.6 (d, *J* = 2.2 Hz), 133.4, 132.9, 132.5 (q, *J* = 2.2 Hz), 131.9, 131.7, 131.1, 130.6, 129.8, 129.6, 129.5, 129.3, 129.1, 129.0, 128.8, 128.6, 128.4, 128.4, 128.3, 128.4, 128.2, 127.8, 127.5, 127.4 (q, *J* = 2.5 Hz), 125.7 (q, *J* = 7.6 Hz), 125.2, 124.2, 123.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -54.3 (s), -54.7 (s). **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{22}H_{15}F_3NO]^+$: 366.1100, found: 366.1100.

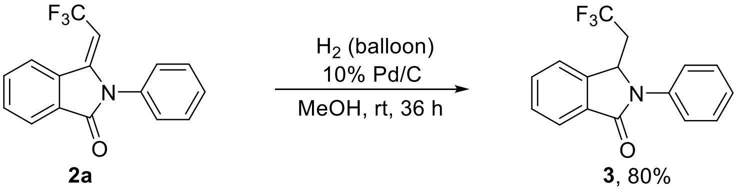
4. Large-scale synthesis and transformation of products

4.1 Scale-up reaction

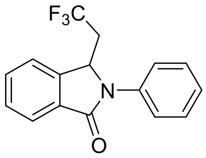


To a round-bottom flask with a stirring bar were added 4CzIPN (23.7 mg, 0.03 mmol, 3 mol%), **1b** (1 mmol, 1.0 equiv), Umemoto's reagent (1.2 mmol, 1.2 equiv) in an argon-filled glovebox. After DME (10.0 mL) being added into the vial via a syringe, the vial was sealed with a cap containing a rubber stopper and removed from the glovebox. The resulting mixture was stirred upon 24 W blue LED irradiation under argon. After completion of the reaction, the crude mixture was purified by flash chromatography (Petroleum ether/ethyl acetate = 50:1, v/v) to afford the pure product **2b** (231 mg, 76%).

4.2 Transformation of product 2a

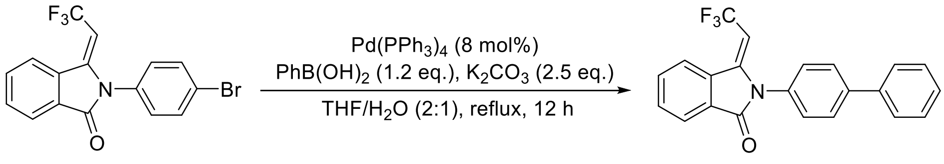


According to literature report,[7] to a Schlenk tube equipped with a magnetic stir bar were added **2a** (28.9 mg, 0.1 mmol), MeOH (3 mL) and 10 % Pd/C (5.6 mg), then replacement of hydrogen (balloon). The resulting mixture was stirred at room temperature for 36 hours. After the solvent was removed under reduced pressure, saturated brine (5 mL) was added and the aqueous layer was extracted with EtOAc (5 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography (Petroleum ether/ethyl acetate = 8:1, v/v) to afford white solid **3** (23.3 mg, 80% yield).



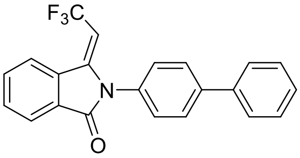
2-phenyl-3-(2,2,2-trifluoroethyl)isoindolin-1-one. Petroleum ether/ethyl acetate (8:1, v/v) as the eluent. White solid (23.1 mg, 80% yield), m.p. 150.8 – 151.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.61 – 7.54 (m, 3H), 7.52 – 7.46 (m, 2H), 7.32 – 7.27 (m, 1H), 5.43 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.55 – 2.40 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.7, 143.1, 136.1, 132.7, 132.0, 129.6, 129.6, 126.3, 125.6 (q, *J* = 275.8 Hz), 124.5, 123.9, 123.2 (q, *J* = 5.6 Hz), 55.6 (d, *J* = 3.1 Hz), 36.6 (q, *J* = 28.2 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.1 (s). **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{16}H_{13}F_3NO]^+$: 292.0944, found: 292.0946.

4.2 Transformation of product 2k



2k **4**, 82%

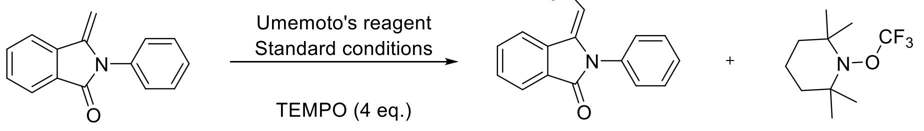
According to literature report,[8] to a Schlenk tube equipped with a magnetic stir bar were added **2k** (36.7 mg, 0.1 mmol), $Pd(PPh_3)_4$ (8 mmol%), $PhB(OH)_2$ (1.2 equiv), K_2CO_3 (2.5 equiv) and THF/H_2O (2:1, 2 mL), then replacement of hydrogen (balloon). The resulting mixture was stirred at room temperature for 12 hours. After the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography (petroleum ether as the eluent) to afford white solid **4** (38 mg, 82% yield).



(*E*)-2-([1,1'-biphenyl]-4-yl)-3-(2,2,2-trifluoroethylidene)isoin-dolin-1-one. Petroleum ether/ethyl acetate (40:1, v/v) as the eluent. White solid (38.0 mg, 82% yield), m.p. 126.2 – 127.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.79 – 7.62 (m, 6H), 7.52 – 7.46 (m, 2H), 7.44 – 7.36 (m, 3H), 5.40 (q, *J* = 9.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.6, 146.4 (q, *J* = 6.0 Hz), 142.4, 140.1, 133.4, 132.5, 132.5, 131.7, 123.0, 129.2, 129.1, 128.8, 128.0, 127.4, 125.2 (q, *J* = 5.6 Hz), 124.2, 124.2 (q, *J* = 266.7 Hz), 97.1 (q, *J* = 38.5 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -53.3 (s). **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $[C_{22}H_{15}F_3NO]^+$: 366.1100, found: 366.1094.

5. Radical trapping experiments

5.1 Radical trapping experiment with TEMPO



1a **2a**, 0% **5**

To a screw-capped vial with a stirring bar were added 4CzIPN (2.4 mg, 0.003 mmol), 3-methylene-2-phenylisoindolin-1-one **1a** (22.1 mg, 0.1 mmol), Umemoto's reagent (52.6 mg, 0.12 mmol) and TEMPO (62.5 mg, 0.4 mmol) in an argon-filled glovebox. After DME (1 mL) was added into the vial via a syringe, the vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The resulting mixture was stirred upon 24 W blue LED irradiation under argon balloon for 12 hours. HRMS (ESI): compound **5**, $[M+H]^+$ calcd for $[C_{10}H_{19}F_3NO]$: 226.1413, found: 226.1408.

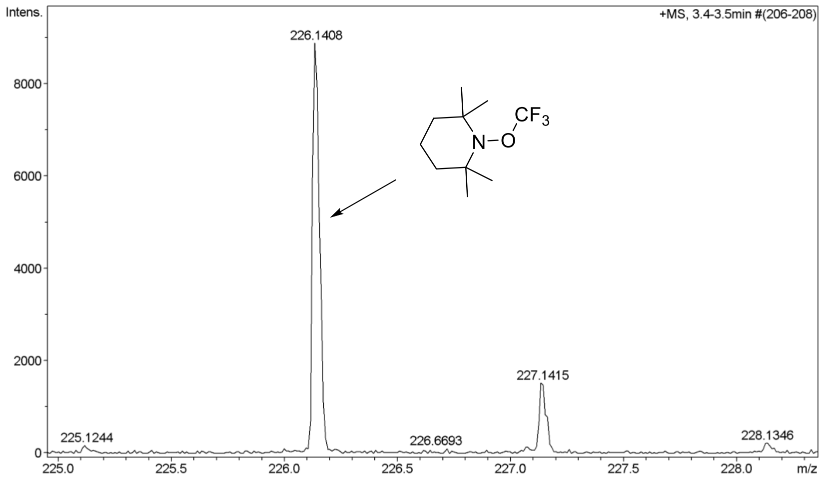
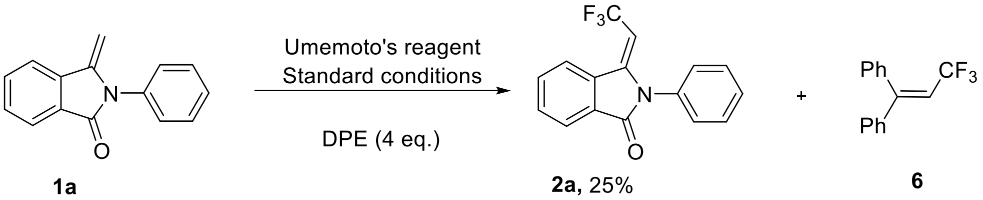


Figure S1 3-Methylene-2-phenylisoindolin-1-one **1a** and Umemoto's reagent under standard conditions with TEMPO (4.0 equiv).

5.2 Radical trapping experiment with DPE



To a screw-capped vial with a stirring bar were added 3-methylene-2-phenylisoindolin-1-one **1a** (22.1 mg, 0.1 mmol), Umemoto's reagent (52.6 mg, 0.12 mmol) and DPE (72.1 mg, 0.4 mmol) in an argon-filled glovebox. After DME (1 mL) was added into the vial via a syringe, the vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The resulting mixture was stirred upon 24 W blue LED irradiation under argon balloon for 12 hours. HRMS (ESI): compound **6**, $[M+H]^+$ calcd for $[C_{15}H_{12}F_3]$: 249.0886, found: 249.0881.

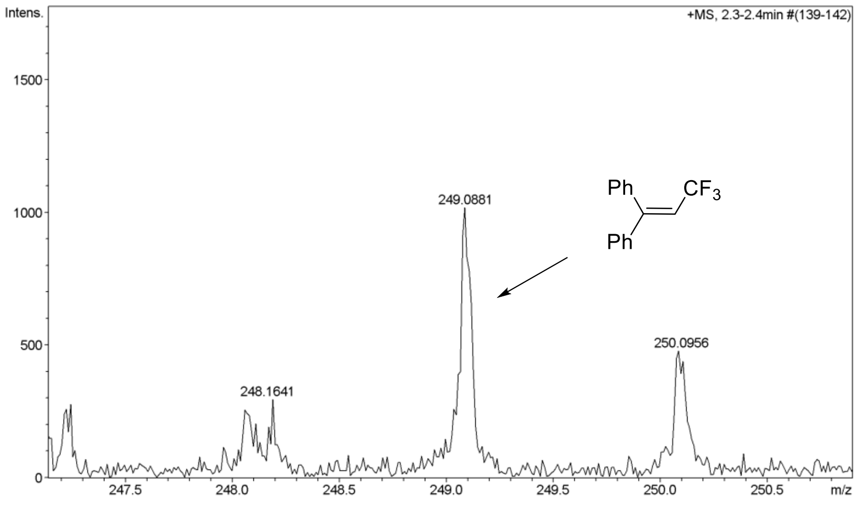


Figure S2 3-Methylene-2-phenylisoindolin-1-one **1a** and Umemoto's reagent under standard conditions with DPE (4.0 equiv).

6. Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 1.25 μM 4CzIPN, in degassed dry DME at room temperature. The solutions were irradiated at 390 nm and fluorescence was measured from 450 nm to 700 nm. Control experiments showed that the excited state 4CzIPN* was mainly quenched by Umemoto's reagent.

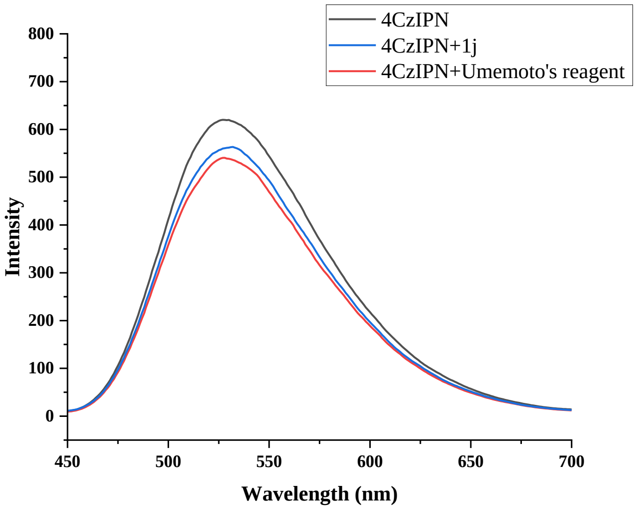


Figure S3 Fluorescence quenching of excited 4CzIPN with 2-(4-chlorophenyl)-3-methyleneisoindolin-1-one **1j**, Umemoto's reagent in DME (excitation wavelength: 390 nm). 4CzIPN (1.25 μM) in DME (black line), 4CzIPN (1.25 μM) with 2-(4-chlorophenyl)-3-methyleneisoindolin-1-one **1j** (5.0 mM) in DME (blue line), 4CzIPN (1.25 μM) with Umemoto's reagent (5.0 mM) in DME (red line).

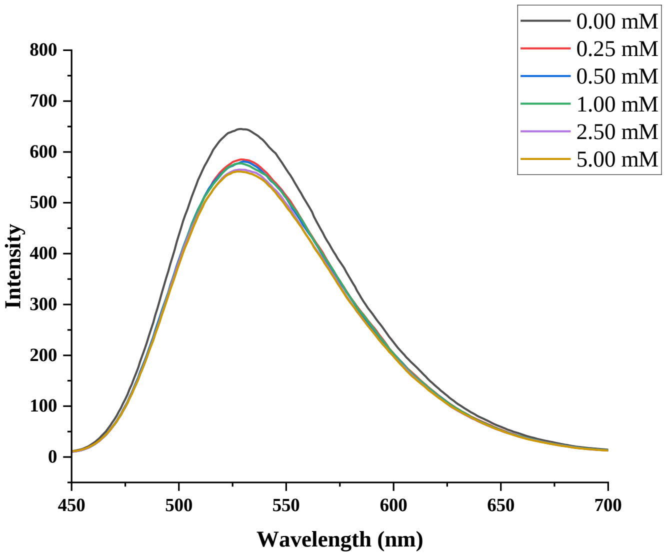


Figure S4 Fluorescence quenching data with 4CzIPN and variable **1j** (10^{-3} M).

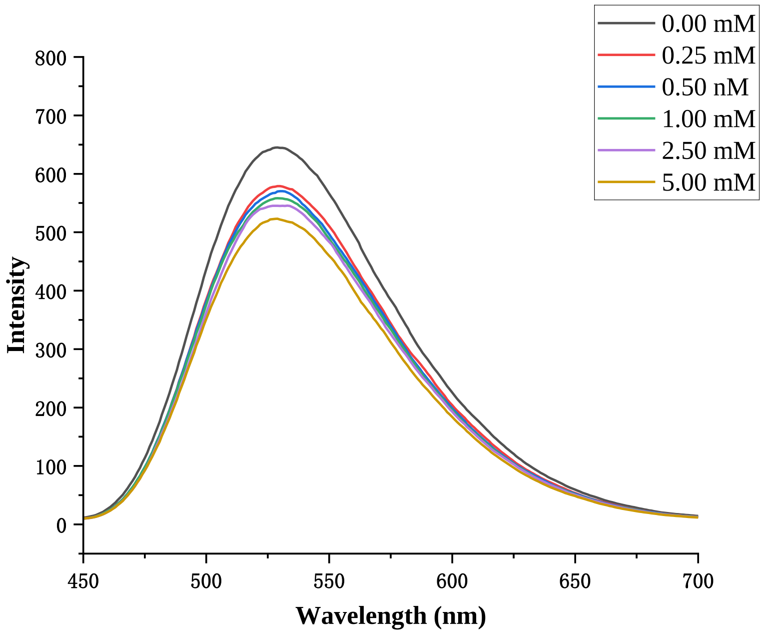


Figure S5 Fluorescence quenching data with 4CzIPN and variable Umemoto's reagent (10^{-3} M).

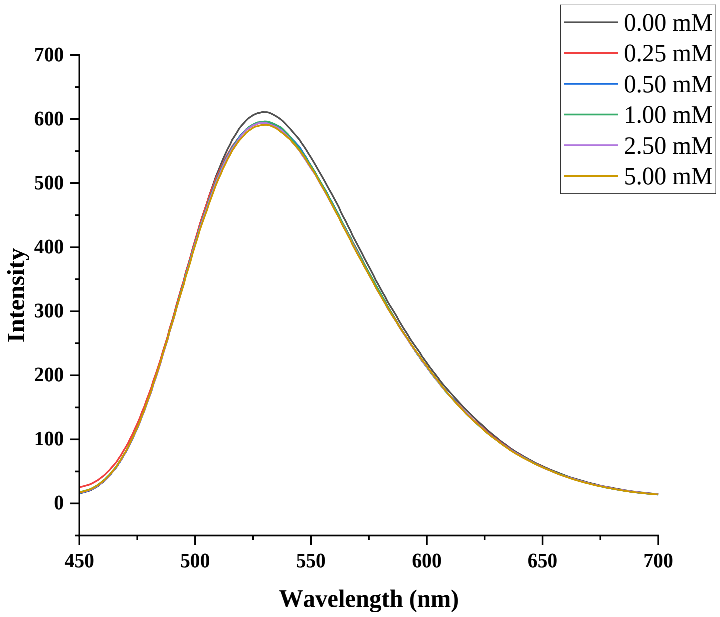


Figure 6 Fluorescence quenching data with 4CzIPN and variable dibenzothiophene (10^{-3} M).

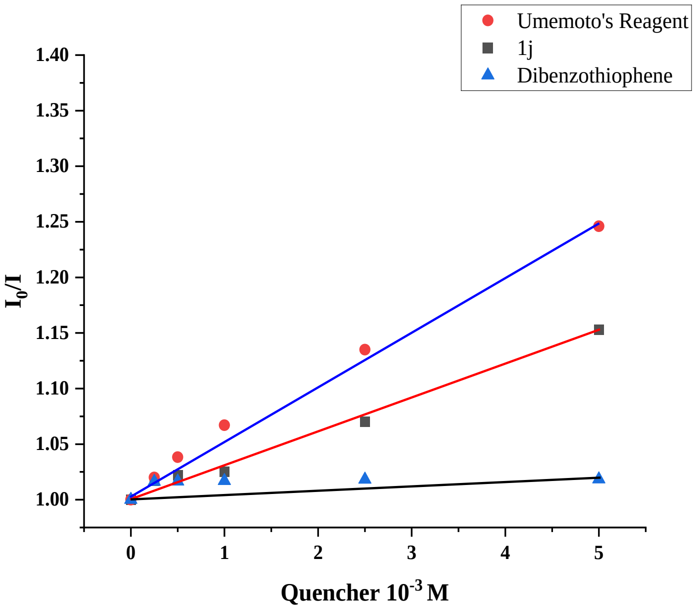


Figure S7 Stern-Volmer plots of 4CzIPN and three quenchers. I_0 and I are luminescence intensities in the absence and presence of the indicated concentrations (10^{-3} M) of the corresponding quencher.

These results suggested that the excited photocatalyst 4CzIPN was primarily quenched by Umemoto's reagent, while 2-(4-chlorophenyl)-3-methyleneisoindolin-1-one **1j** and dibenzothiophene showed much less effect.

7. X-Ray Crystal Data of 2i

The product **2i** (20 mg) was resolved in CH_2Cl_2 and layered with Petroleum ether to obtained **2i** as colorless crystals suitable for X-ray diffraction analysis. The intensity data were collected on an a Rigaku Gemini diffractometer (Xcalibur, Eos) using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The crystal structure (ORTEP representation, 50% thermal probability ellipsoids) and the data were outlined in **Table S1**.

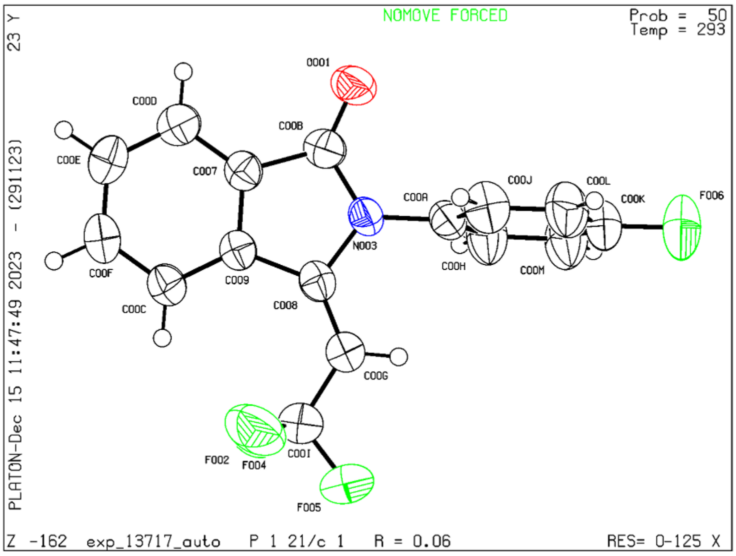


Table S1. Crystal data and structure refinement for **2i** (CCDC 2314640)

Empirical formula	$C_{16}H_9F_4NO$
Formula weight	307.24
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P 21/c
a/Å	16.1519(17)
b/Å	9.9600 (11)
c/Å	8.6943(9)
α/°	90
β/°	98.929(10)
γ/°	90
Volume/$Å^3$	1381.7(3)
Z	4
ρ_{calc}g/cm^3	1.467
μ/mm^{-1}	0.124
F(000)	624.0
Crystal size/mm^3	0.26 × 0.25 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.822 to 58.302
Index ranges	$-21 \le h \le 20$, $-13 \le k \le 8$, $-10 \le l \le 11$
Reflections collected	6389
Independent reflections	3175 [R_{int} = 0.0321, R_{sigma} = 0.0632]
Data/restraints/parameters	3175/0/200
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0673, wR_2 = 0.1207
Final R indexes [all data]	R_1 = 0.1372, wR_2 = 0.1507
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.21

8. References

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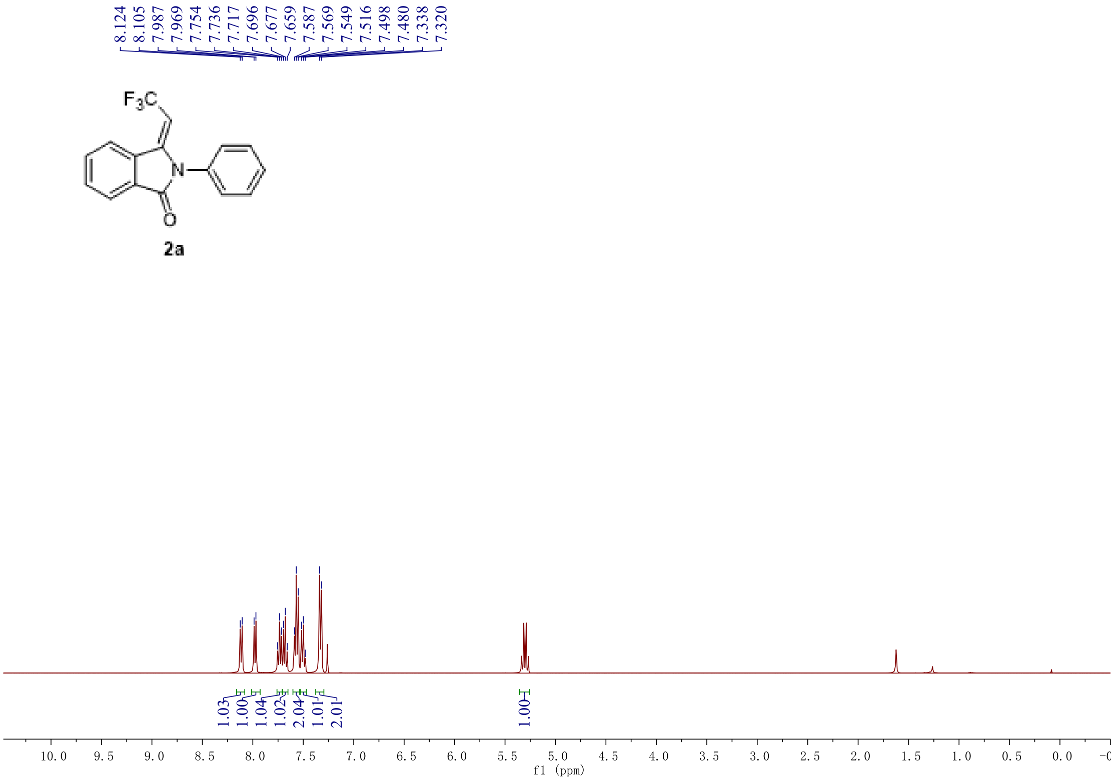
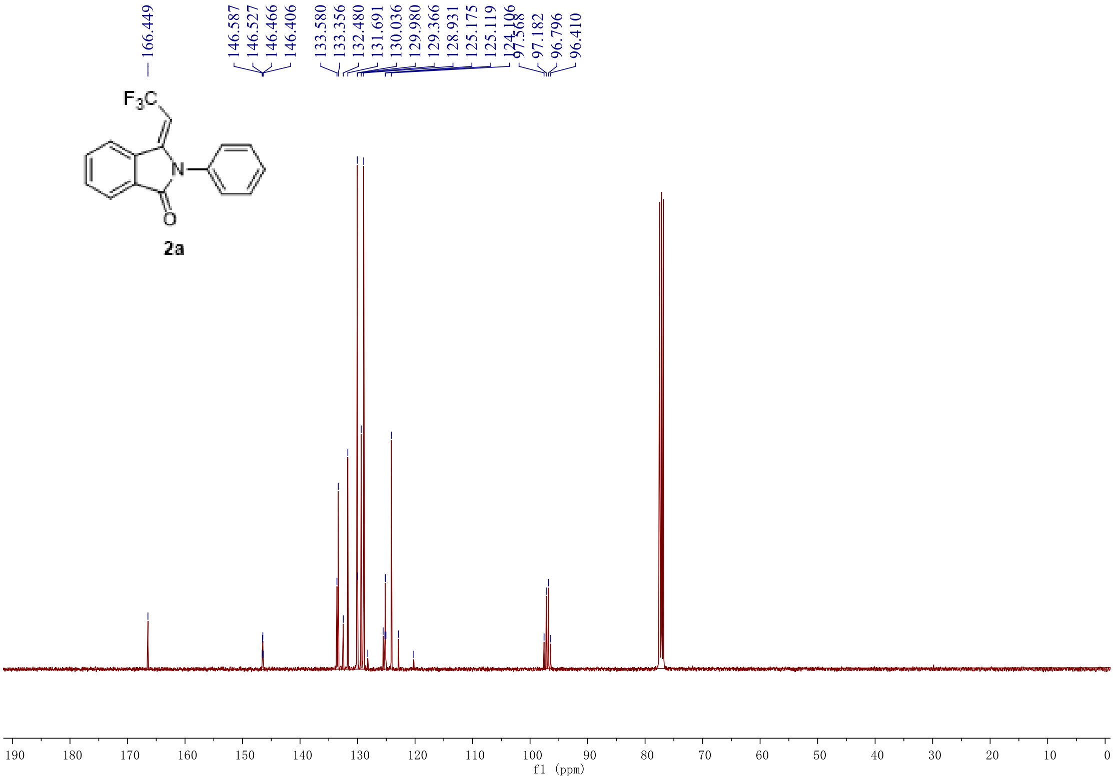
9. NMR Spectra

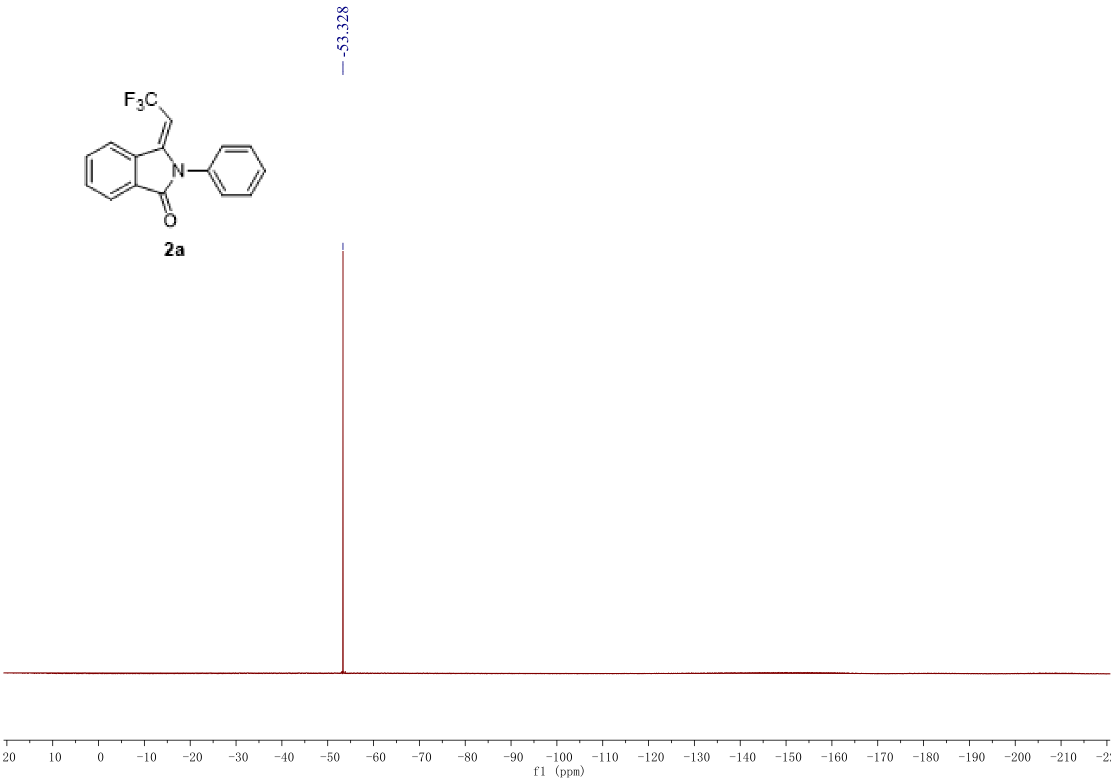
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2a



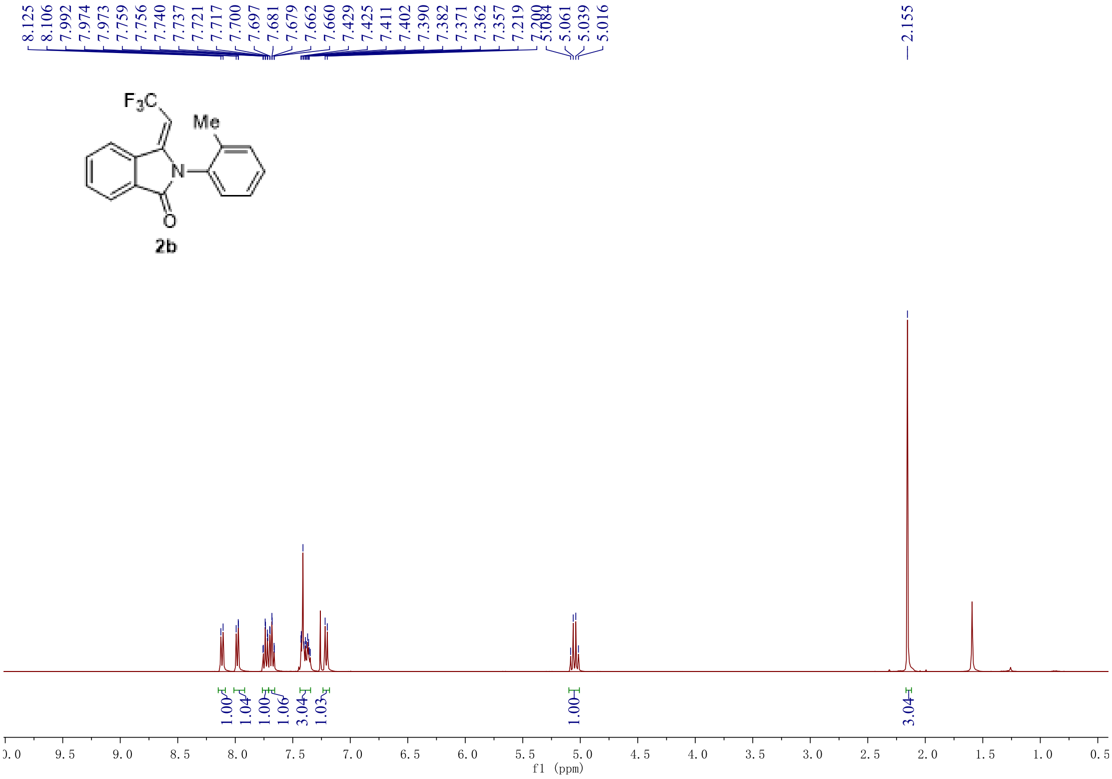
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2a



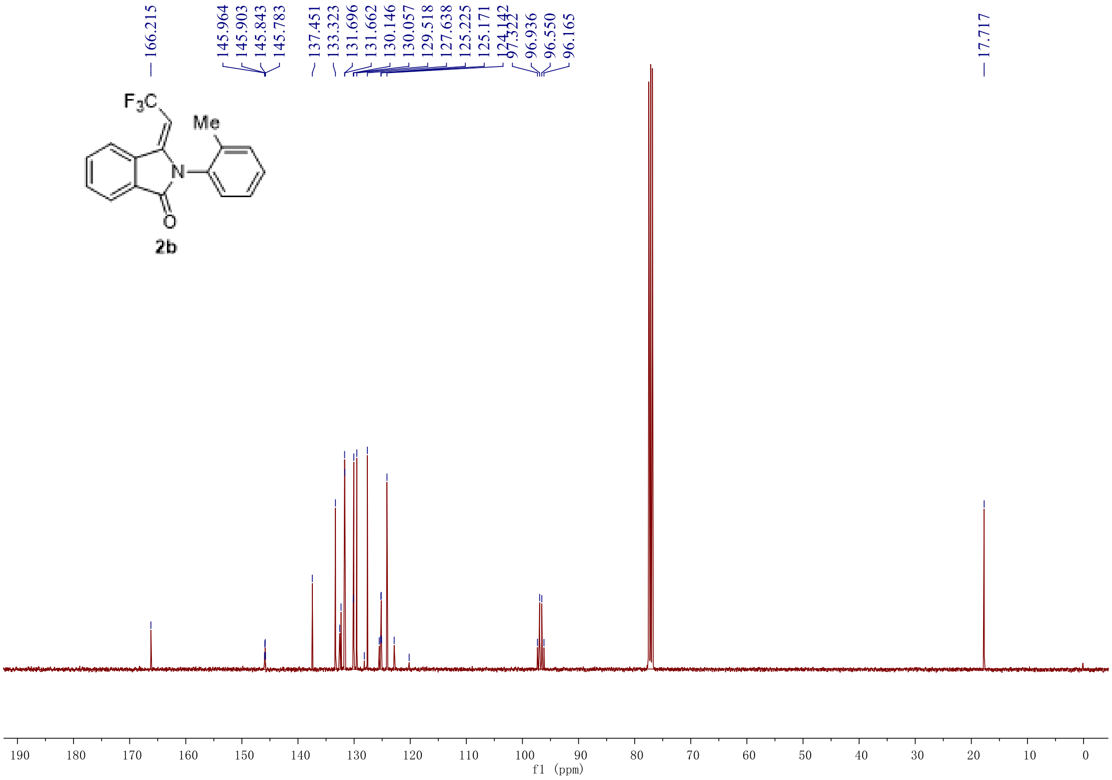
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2a



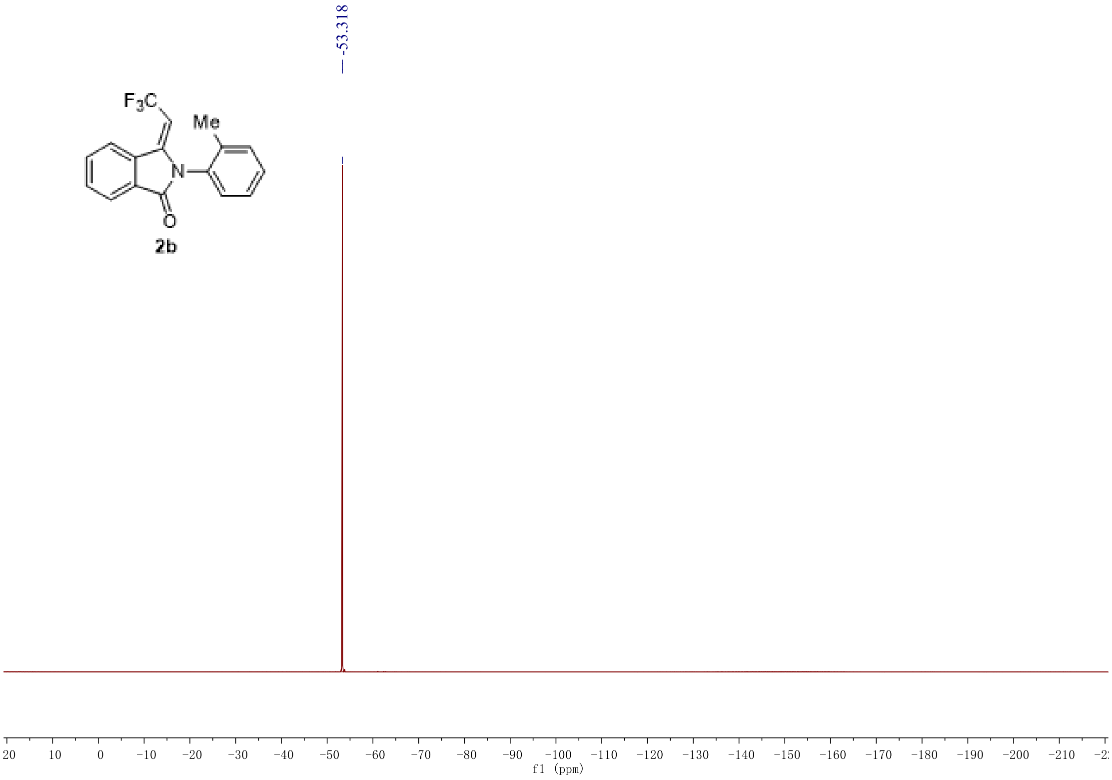
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2b



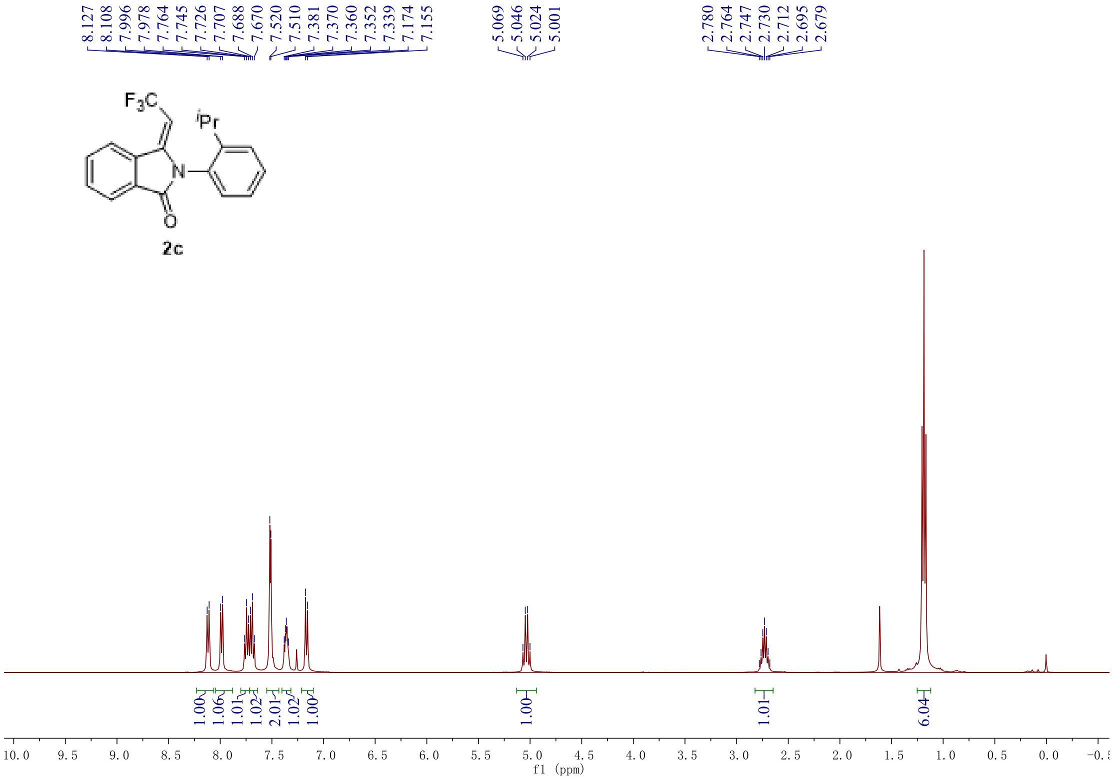
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2b



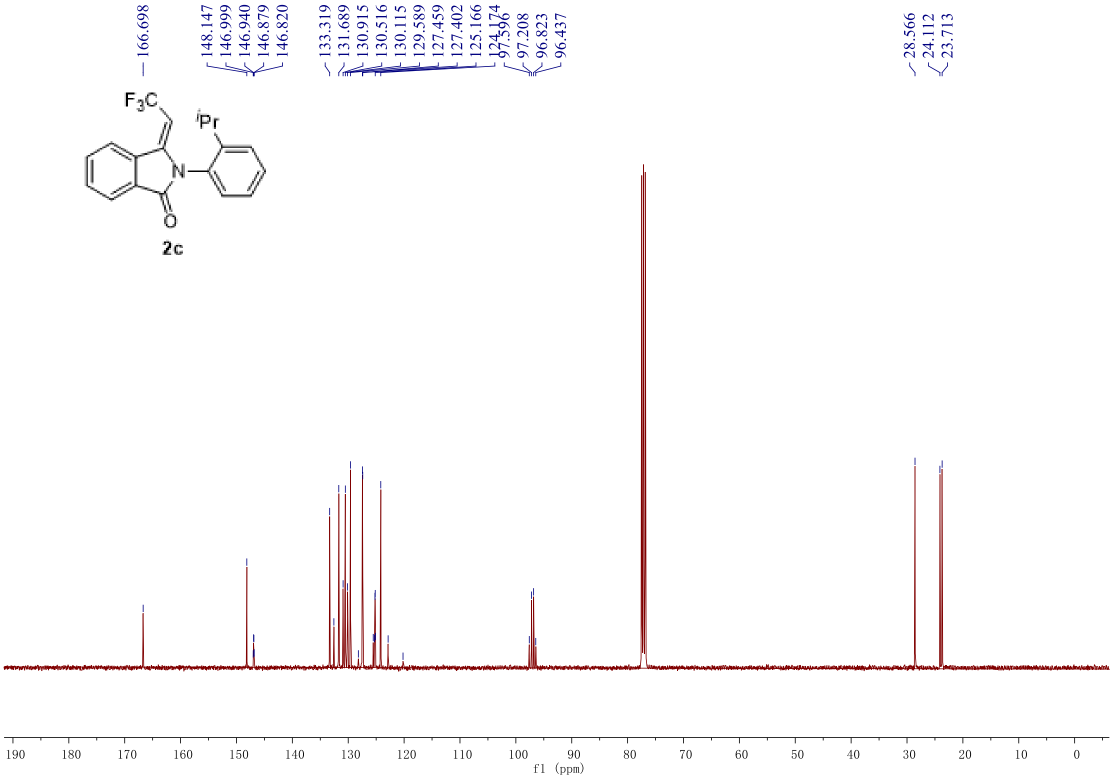
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2b



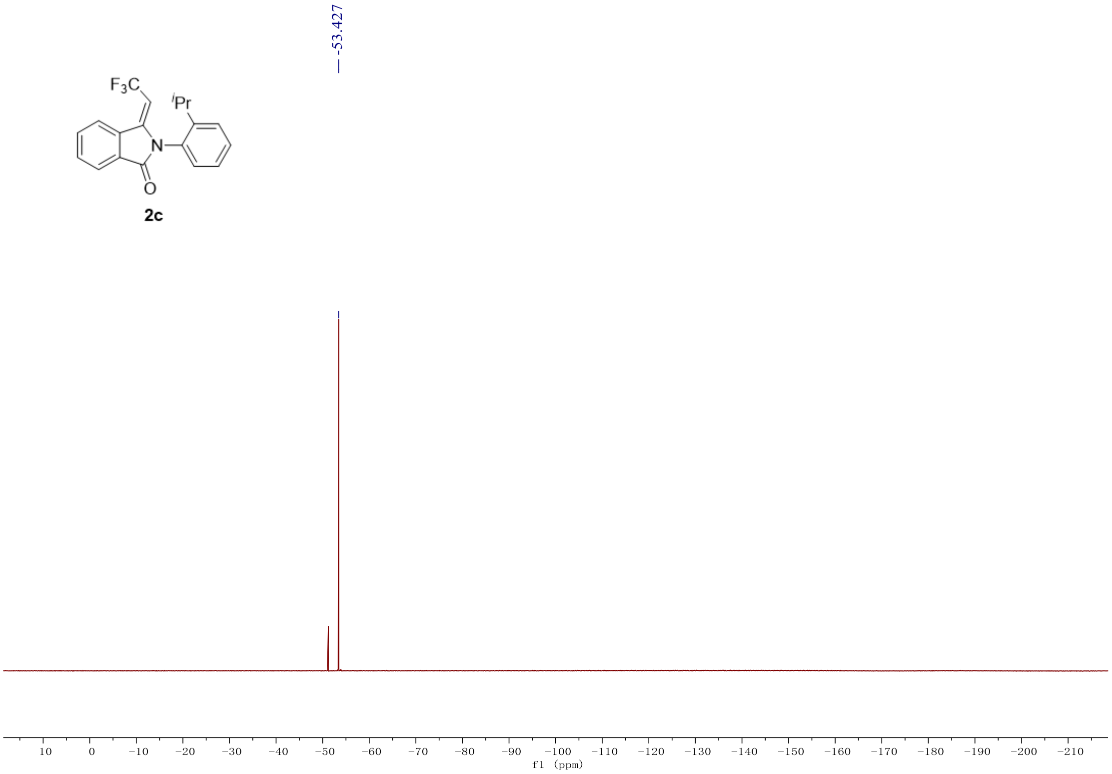
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2c



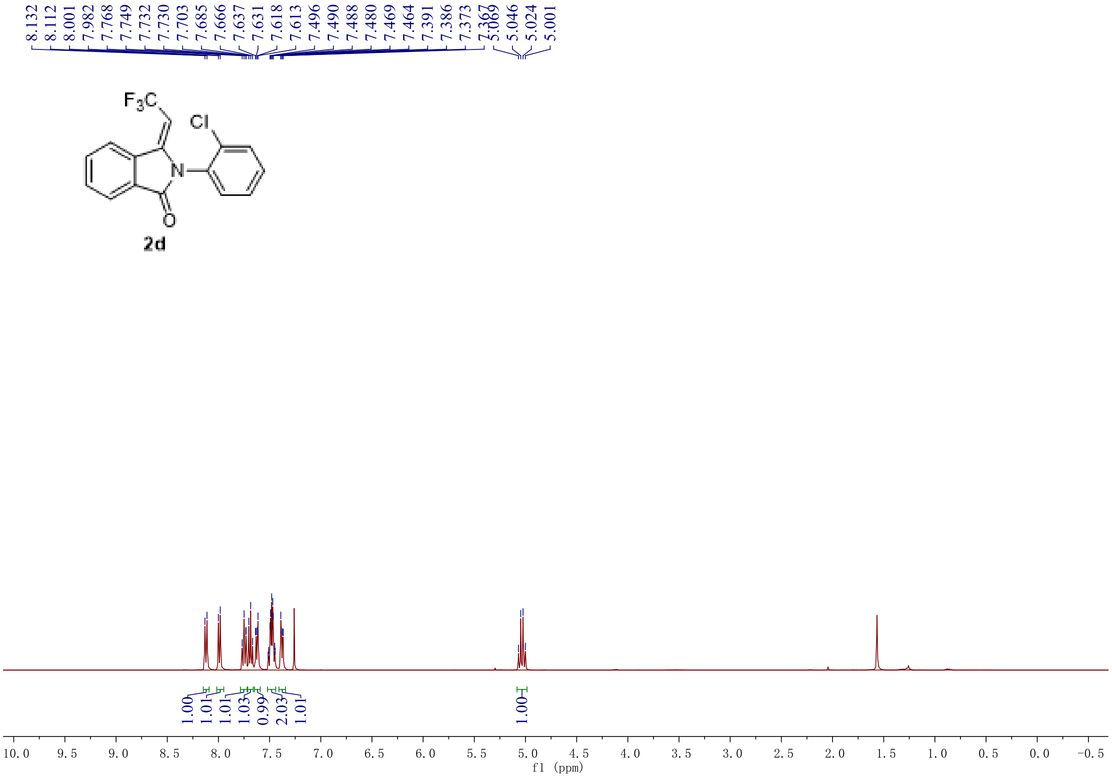
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2c



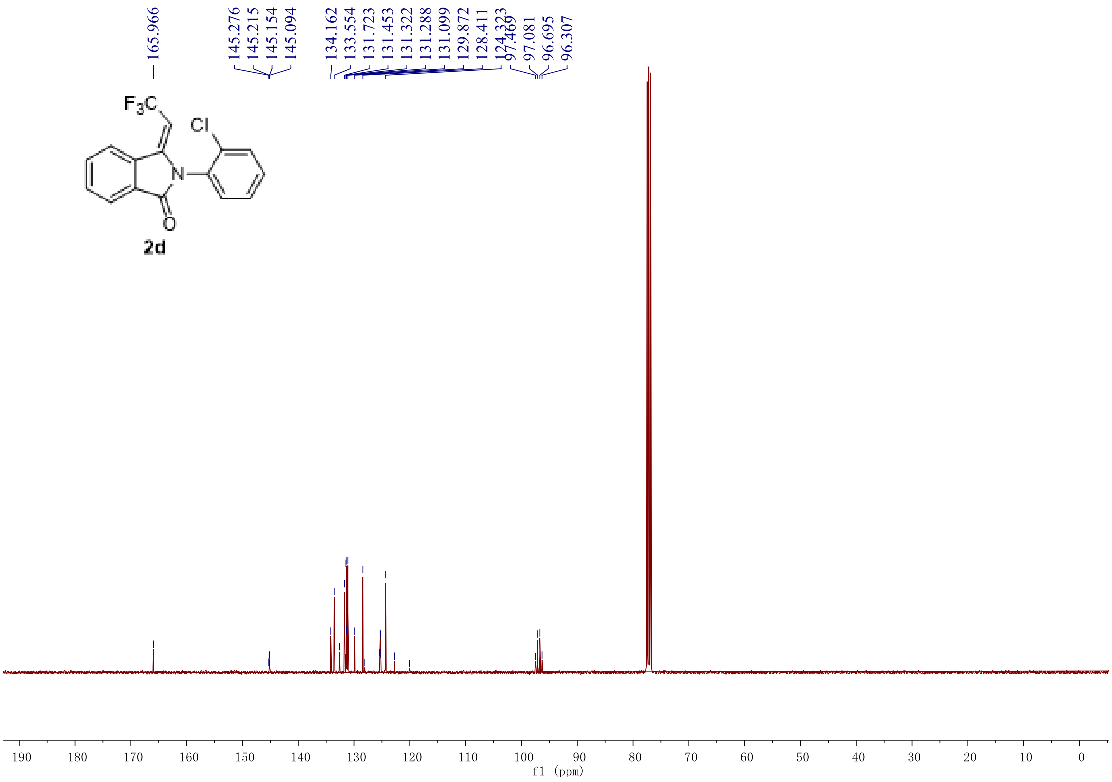
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2c



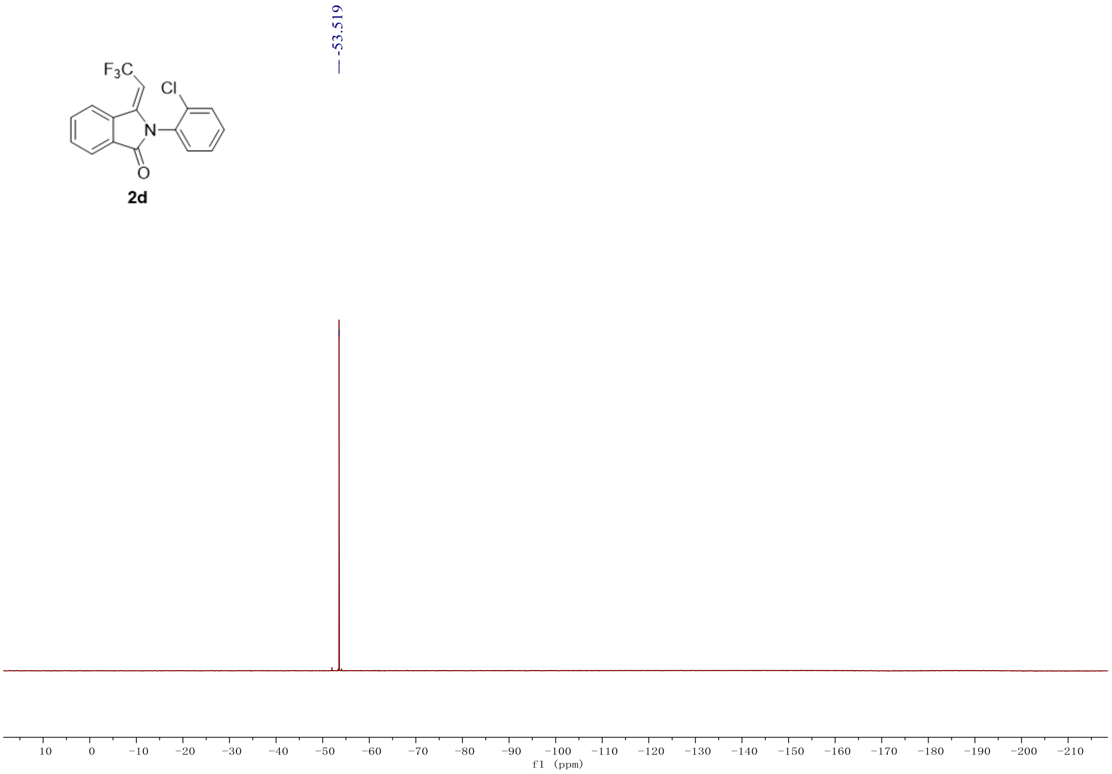
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2d



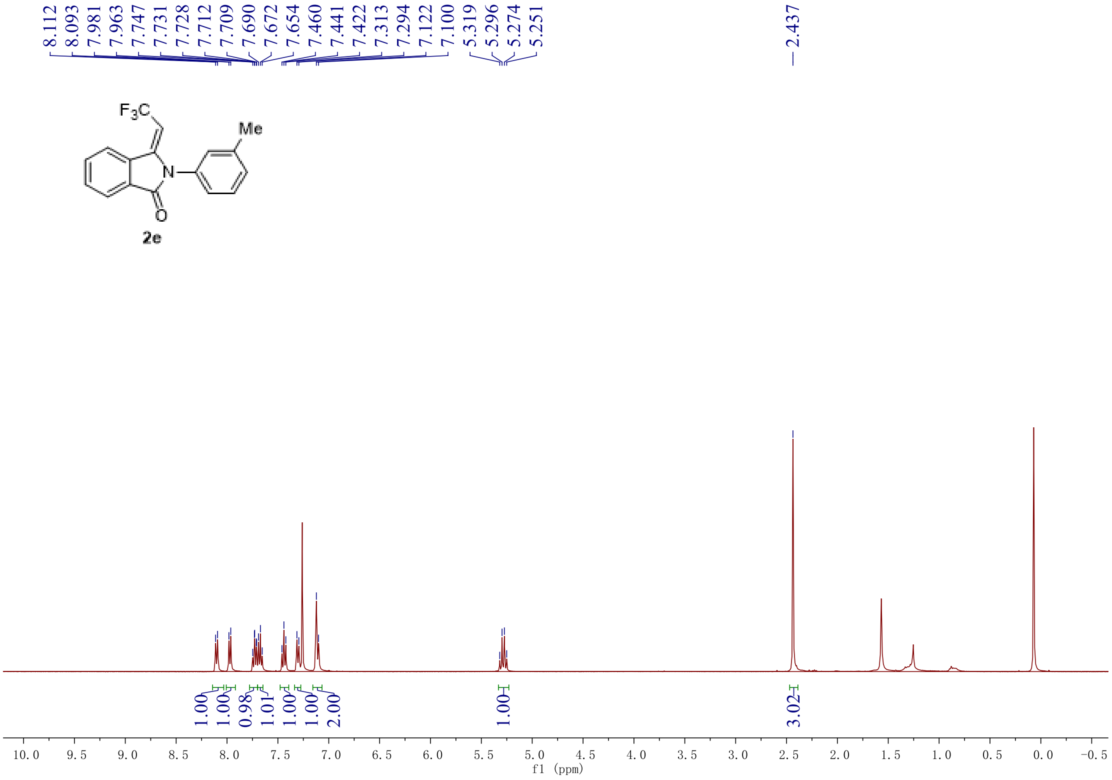
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2d



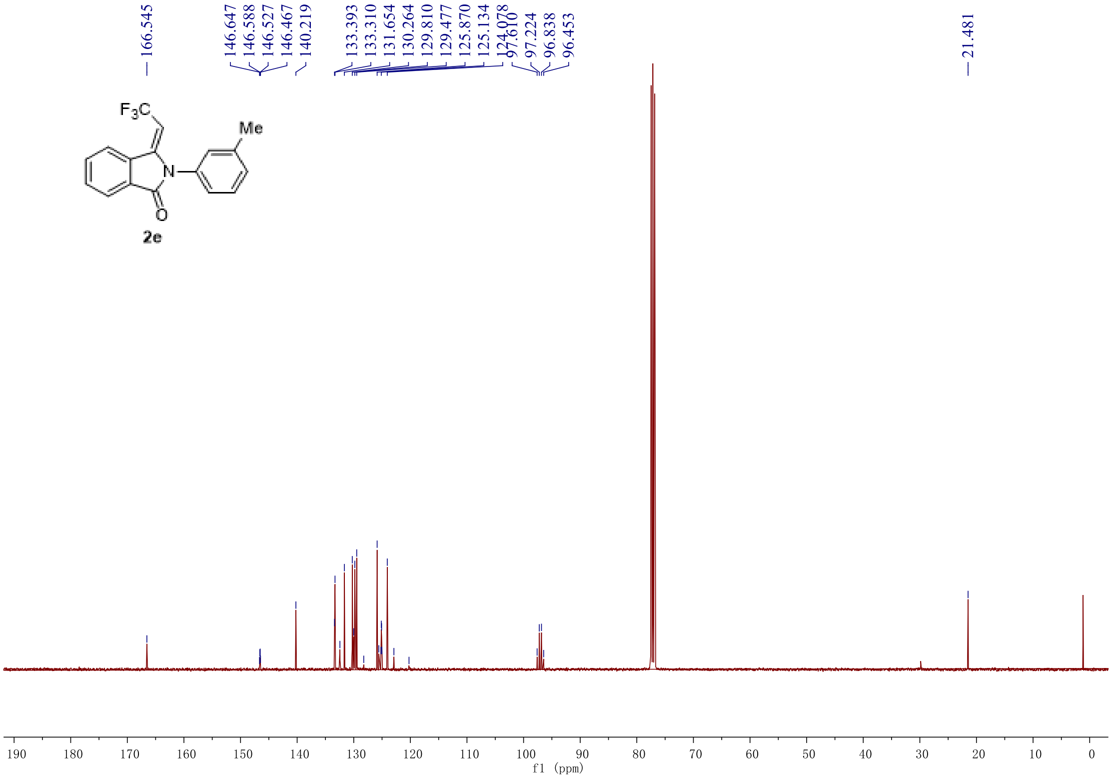
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2d



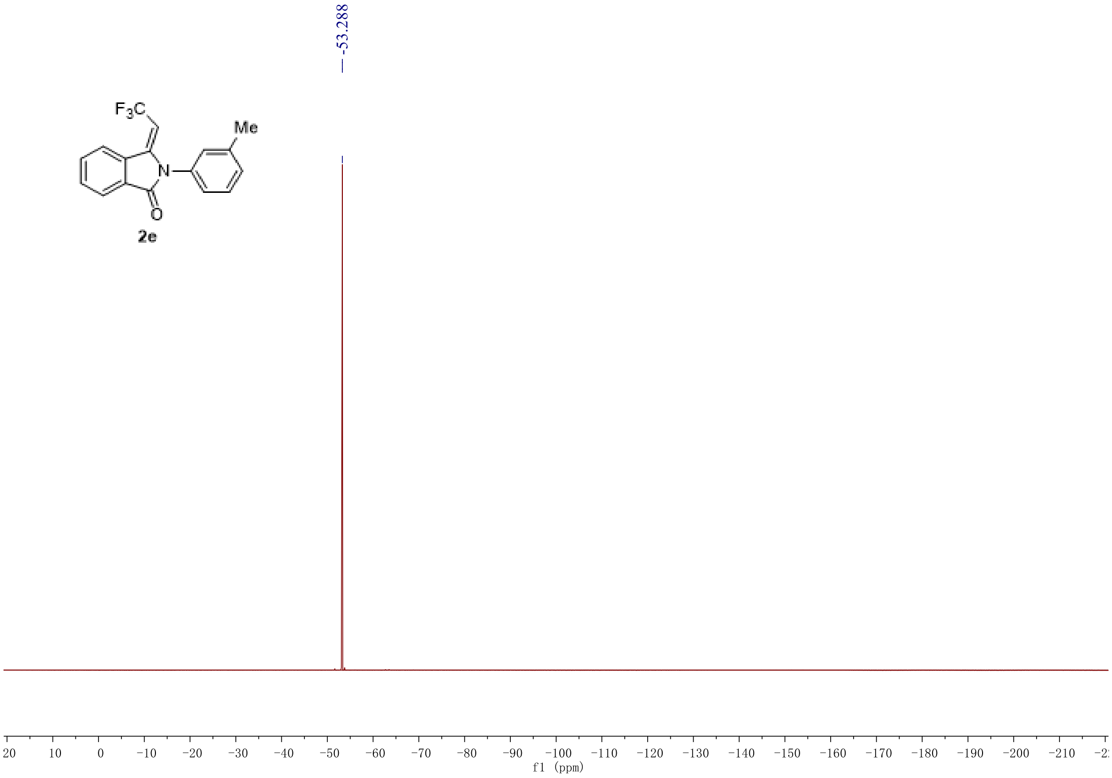
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2e



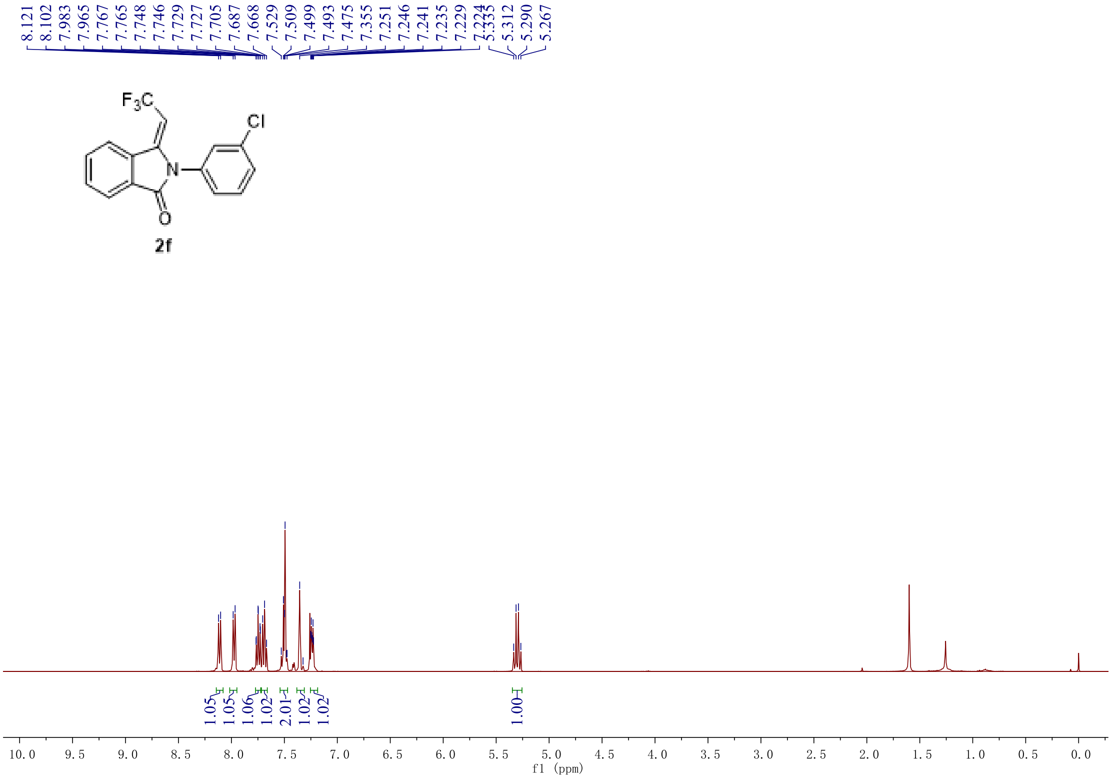
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2e



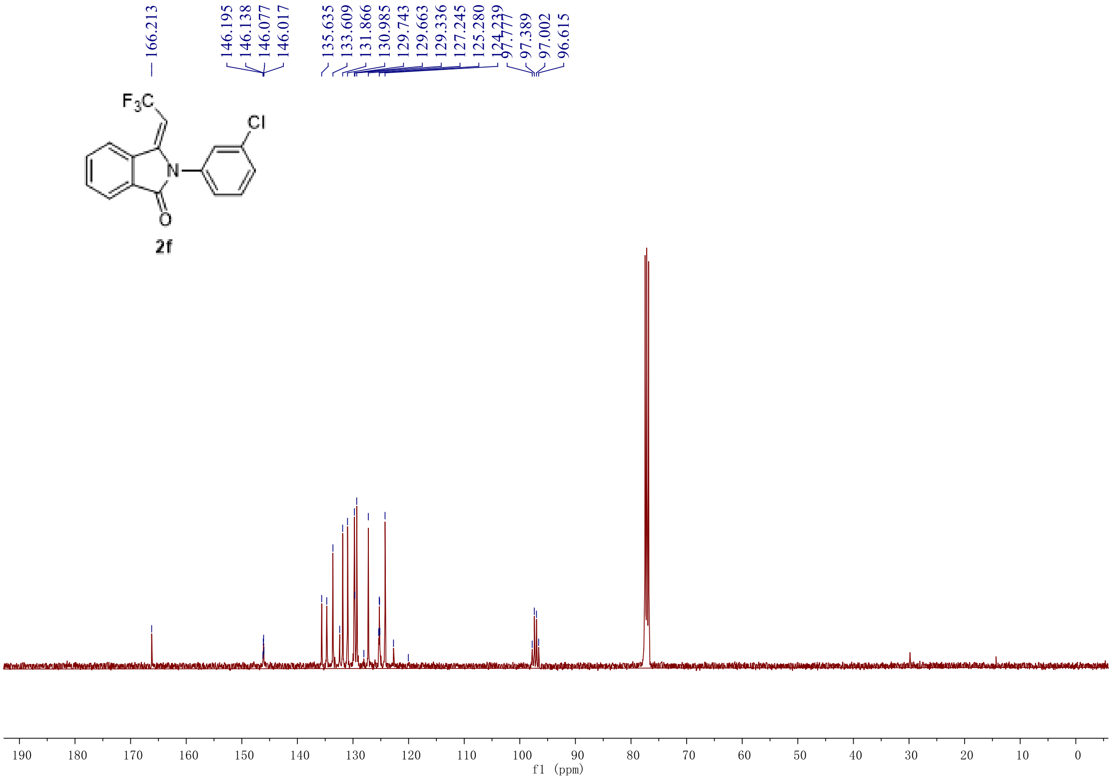
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2e



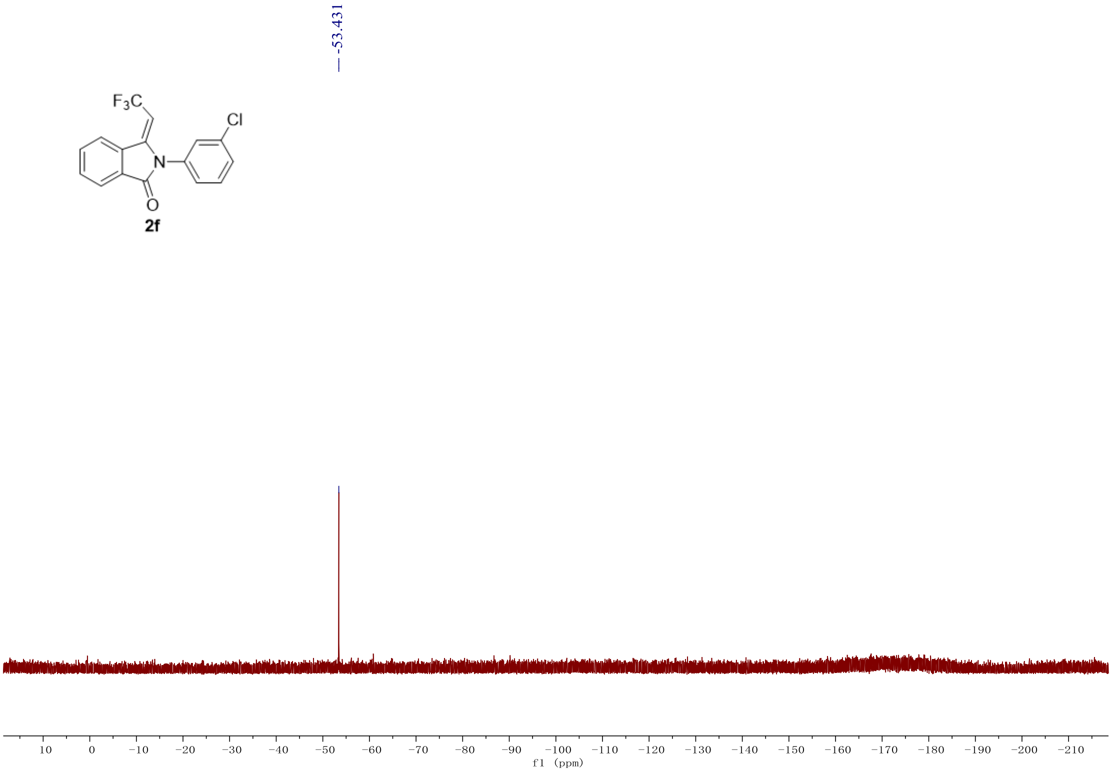
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2f



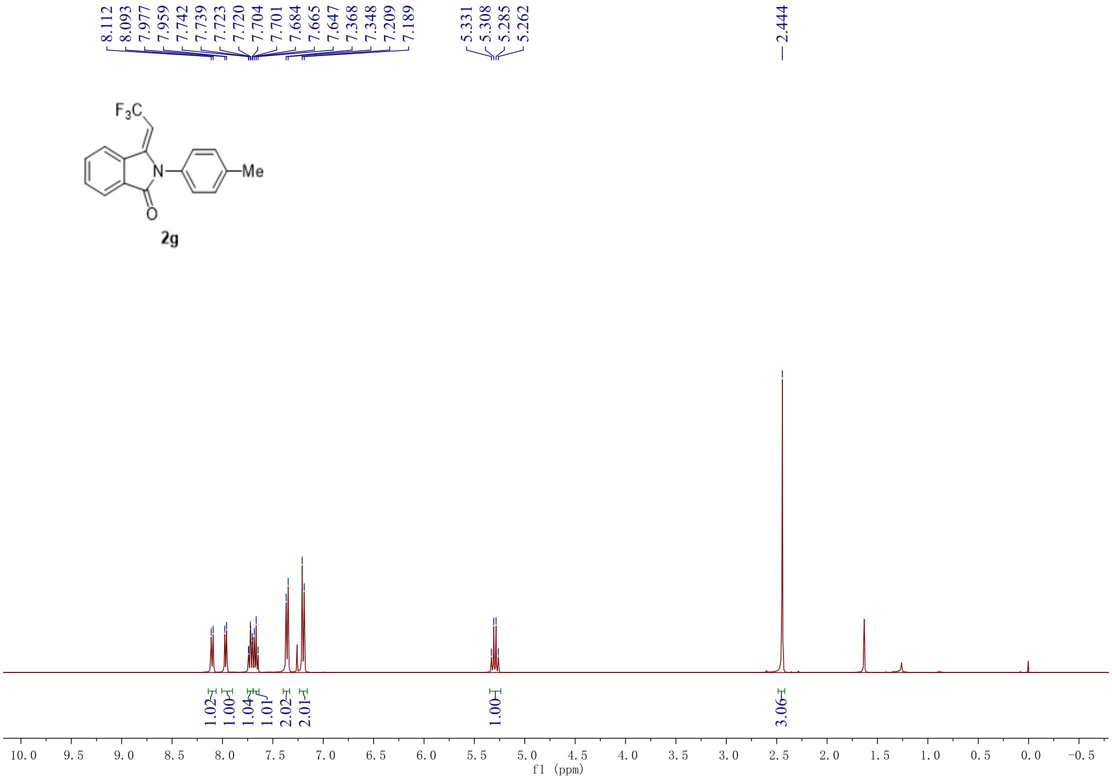
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2f



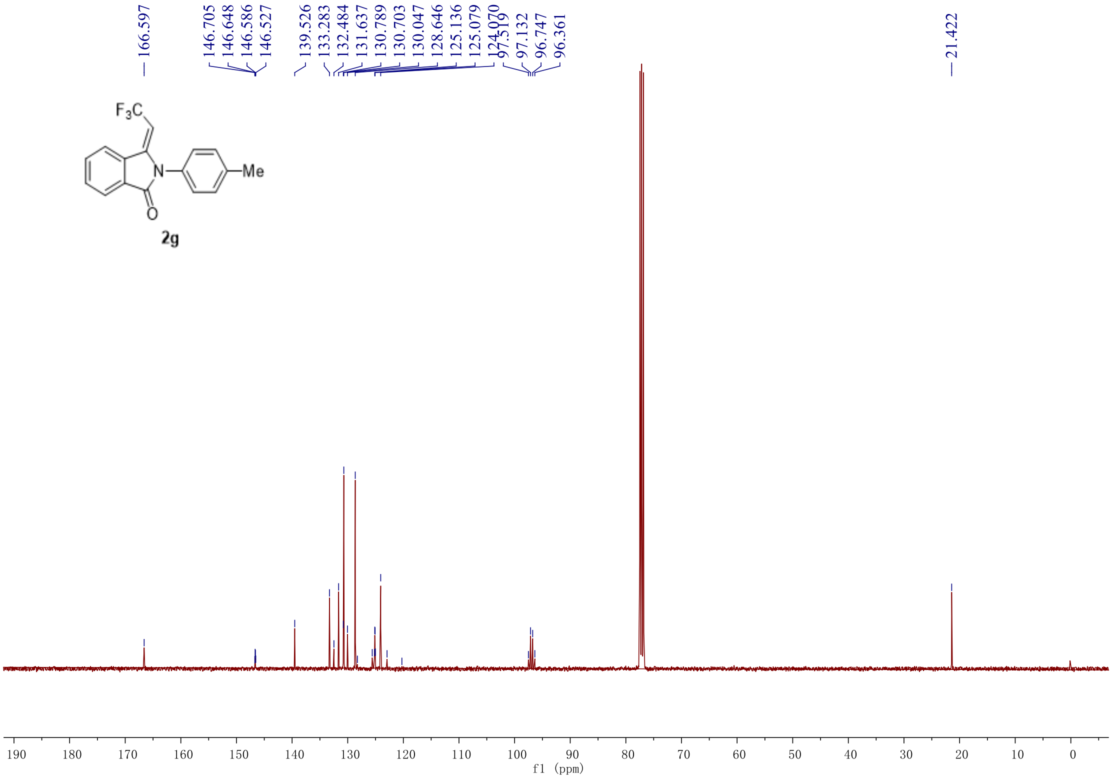
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2f



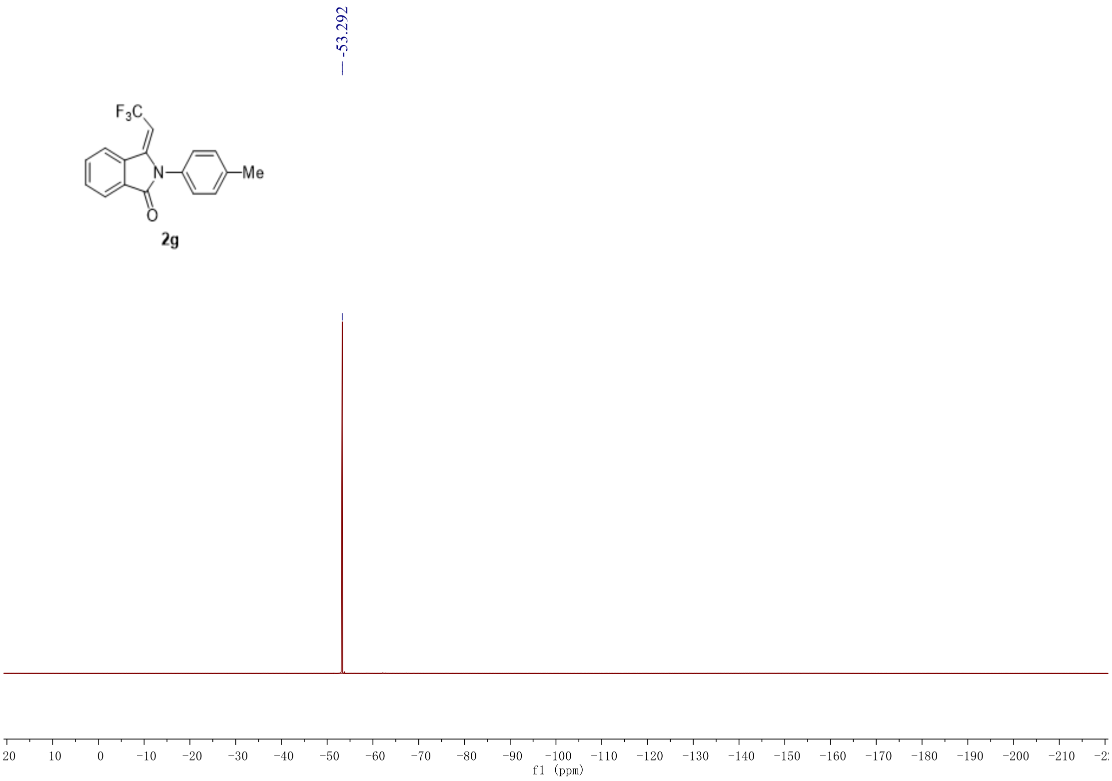
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2g



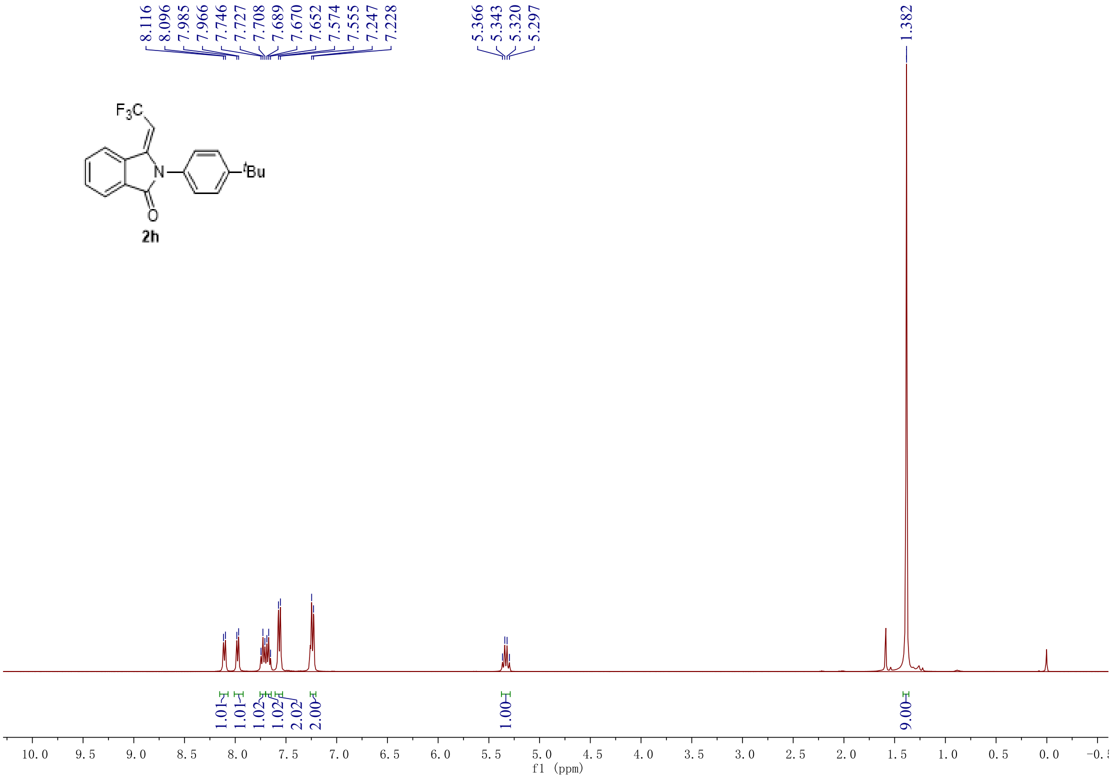
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2g



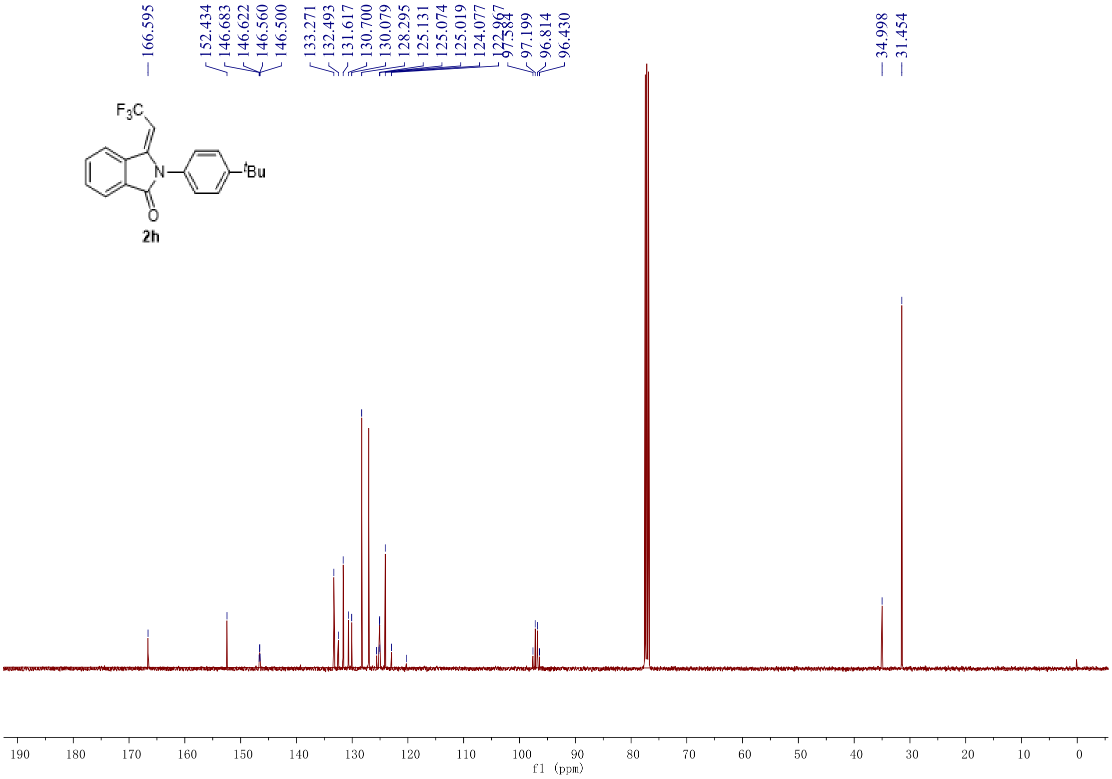
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2g



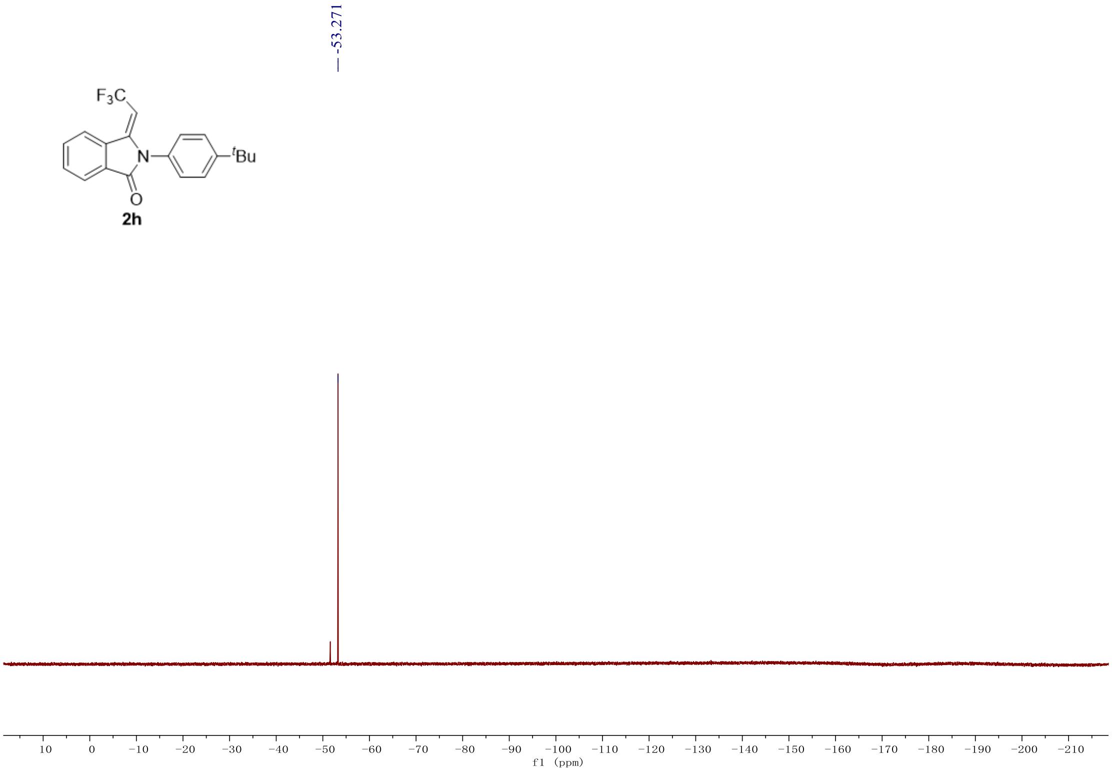
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2h



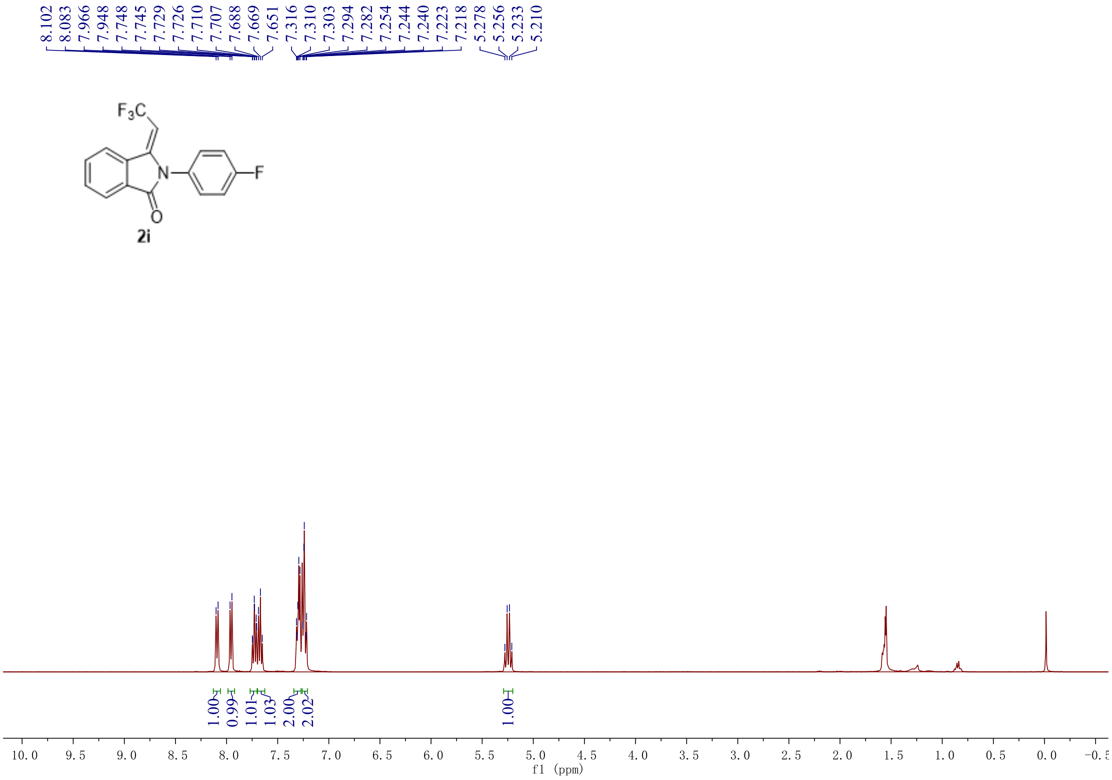
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2h



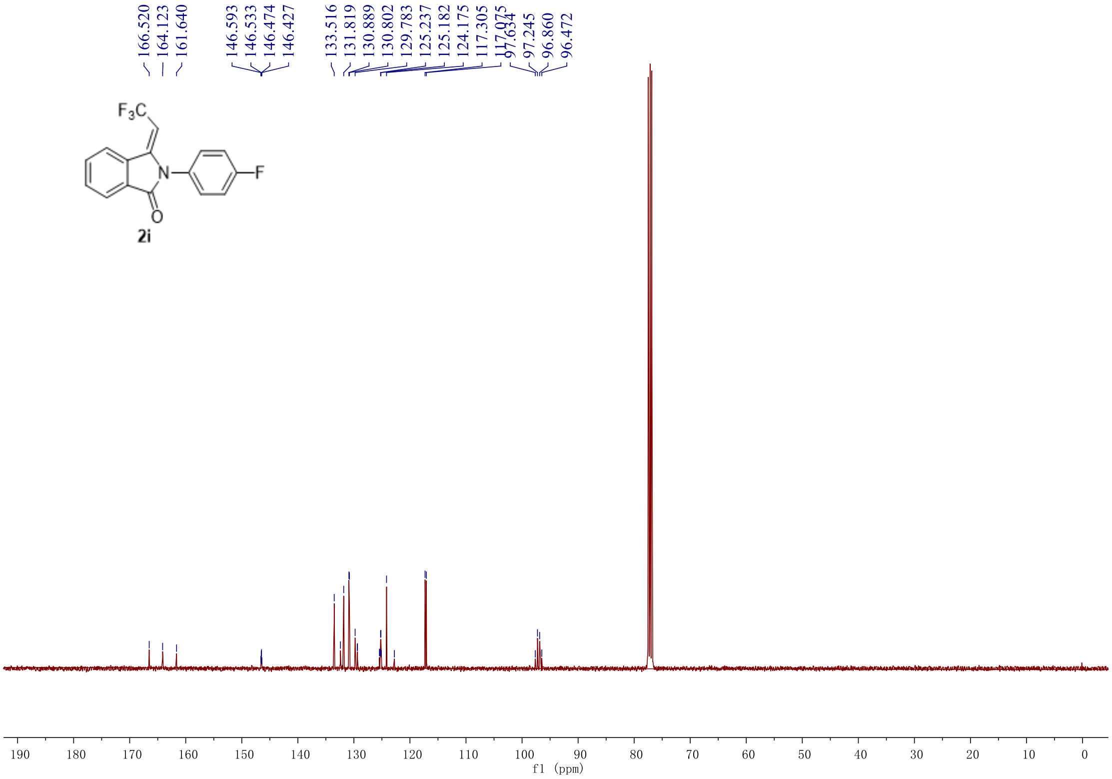
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2h



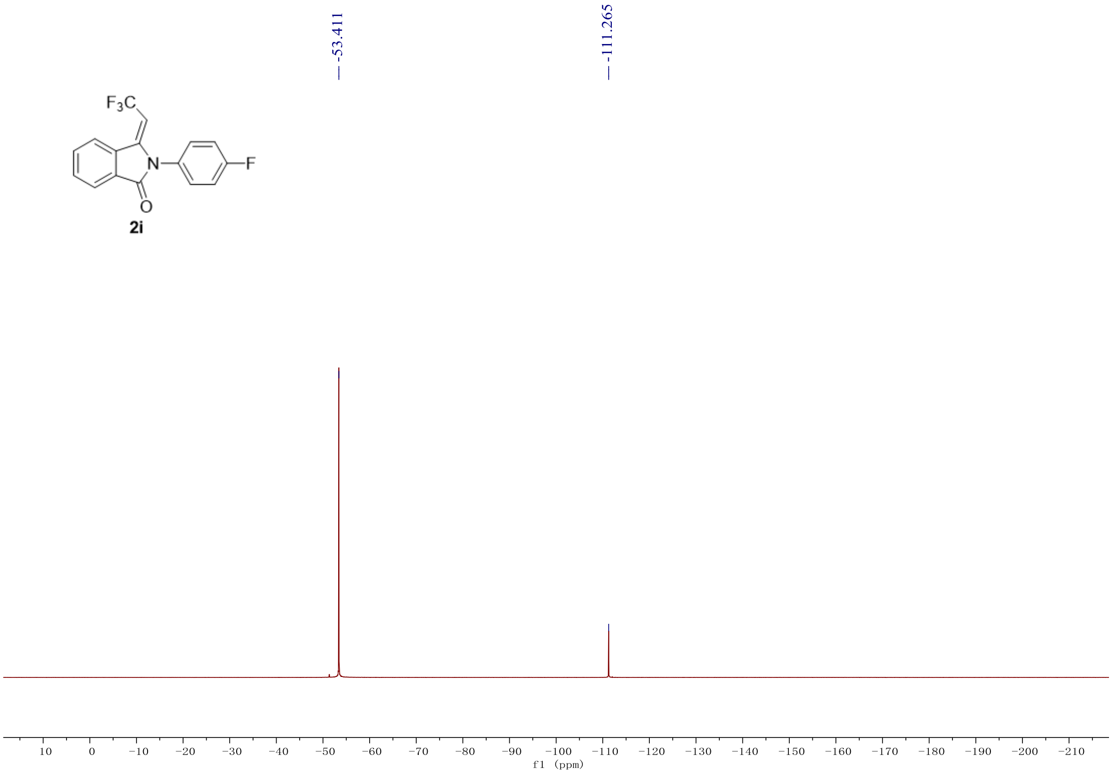
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2i



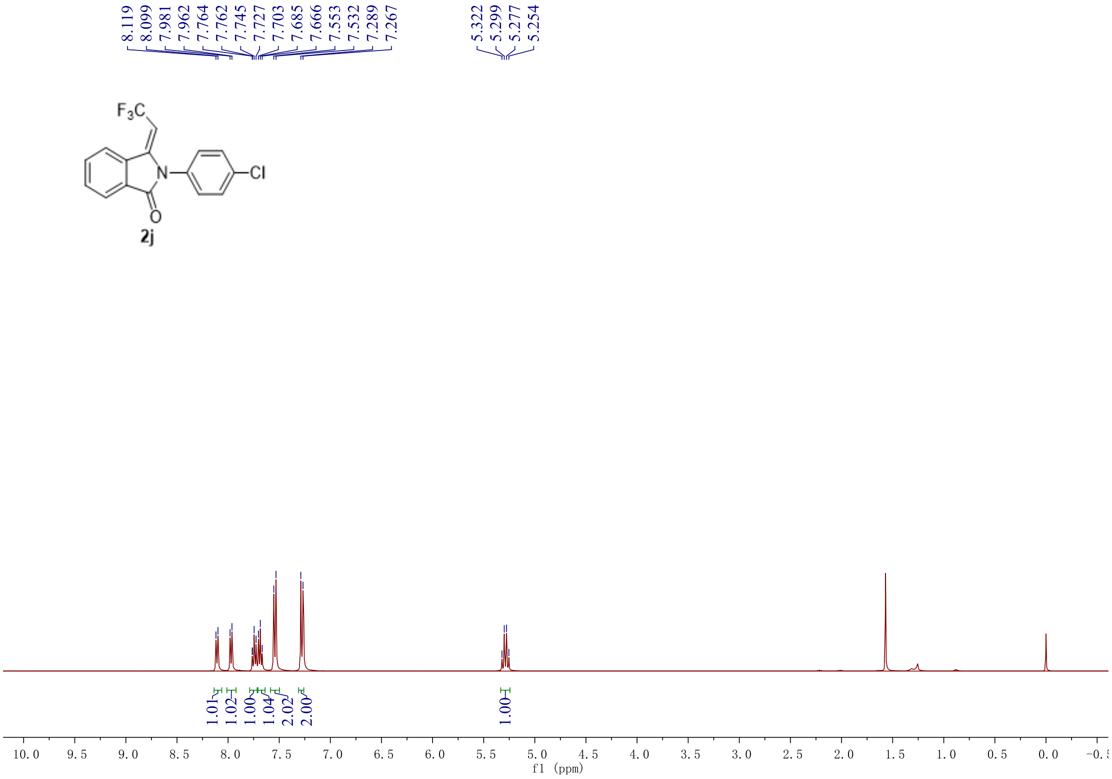
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2i



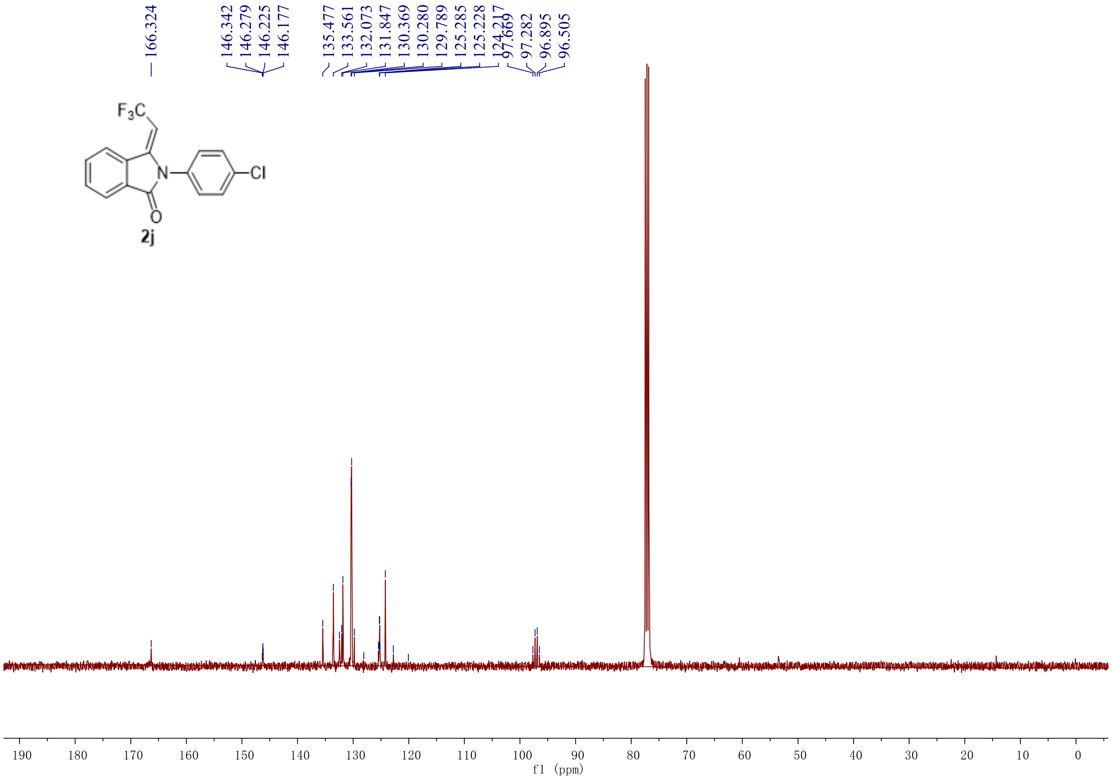
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2i



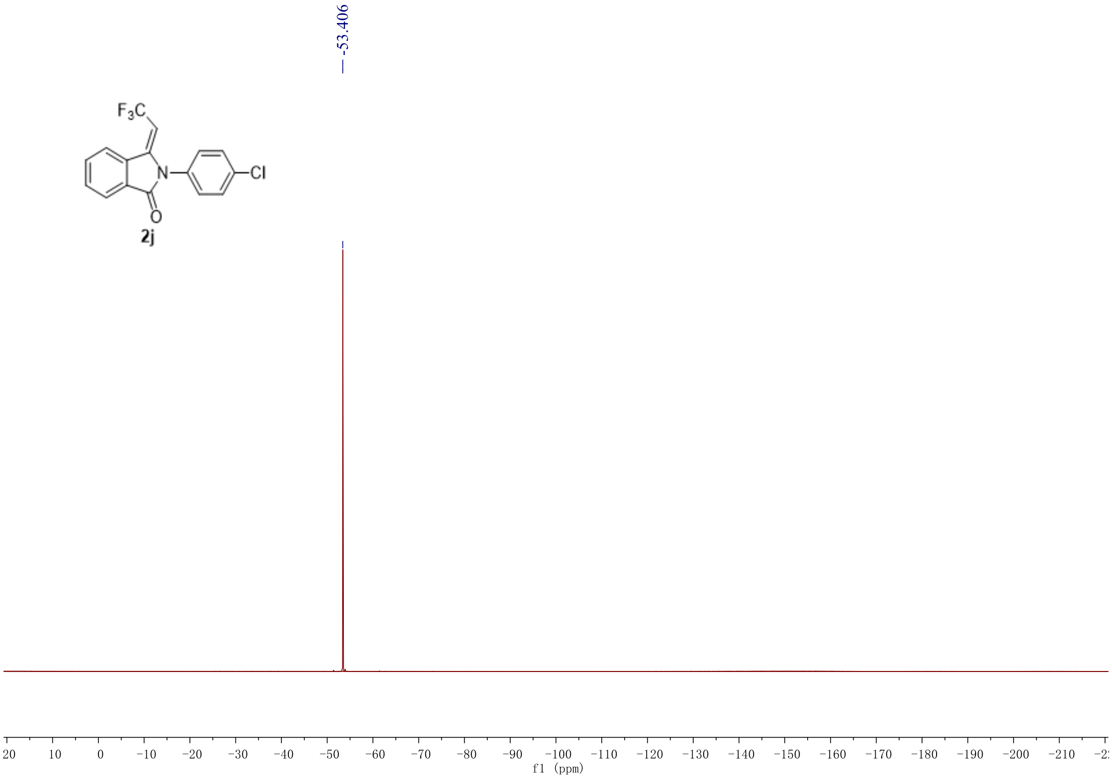
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2j



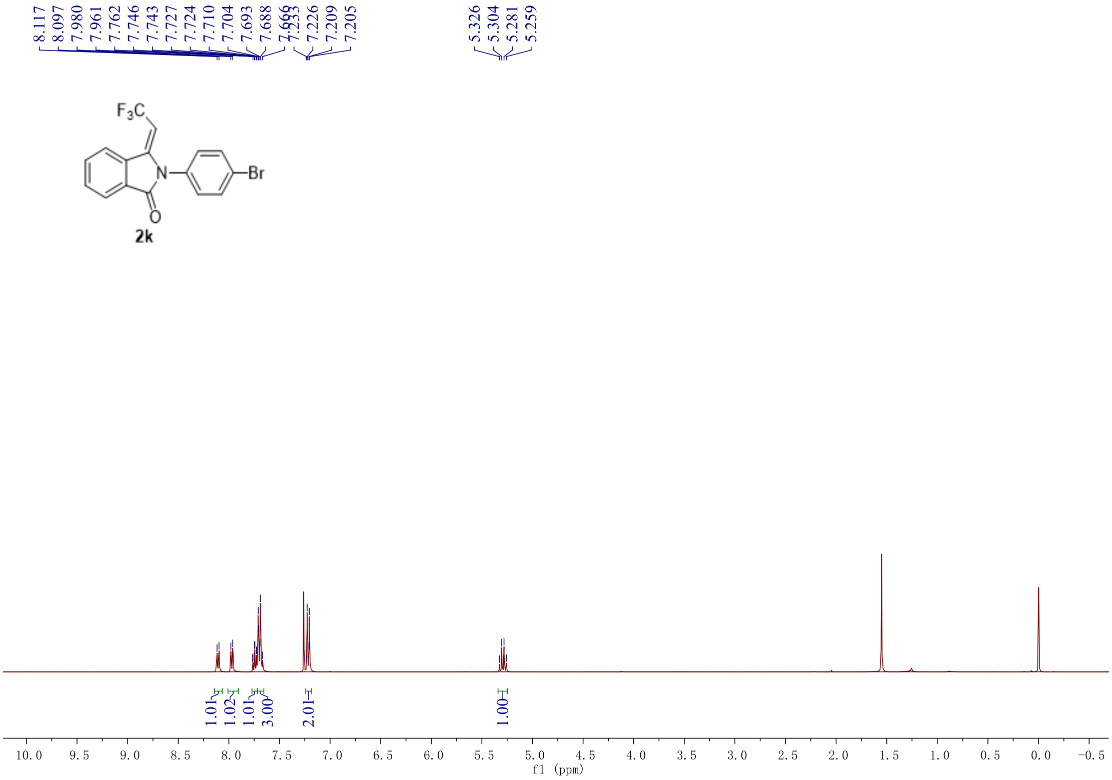
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2j



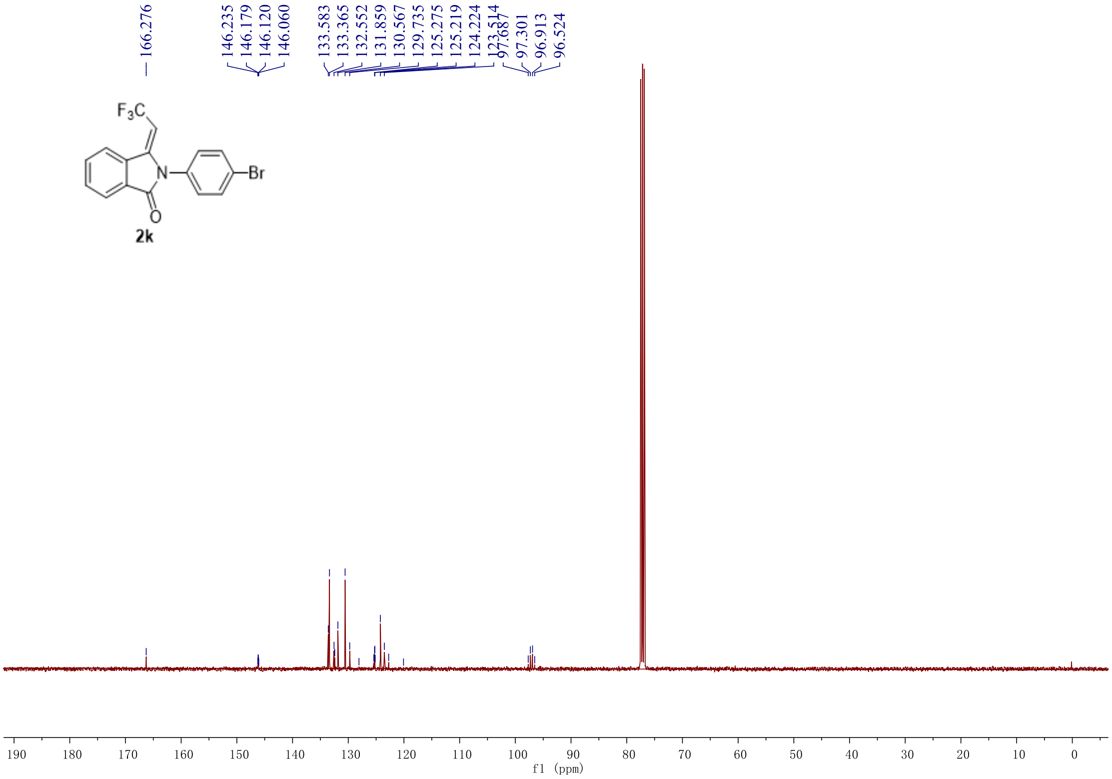
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2j



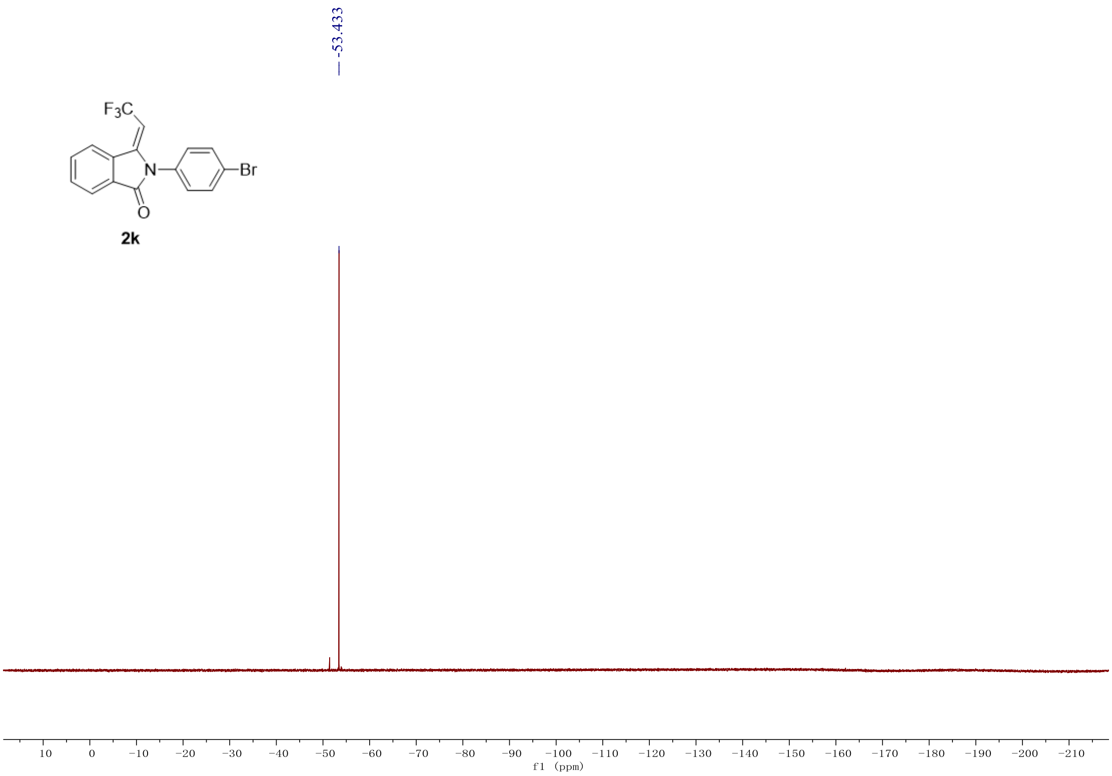
^1H NMR spectrum (400 MHz, $CDCl_3$) of compound 2k



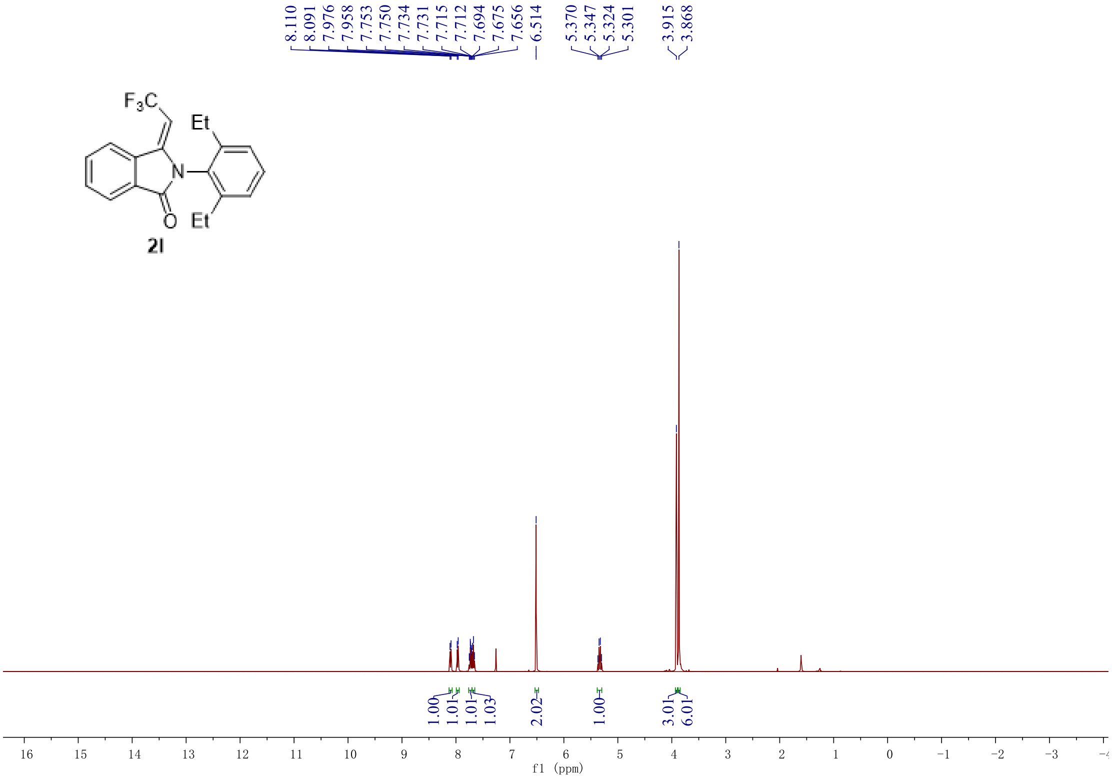
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2k



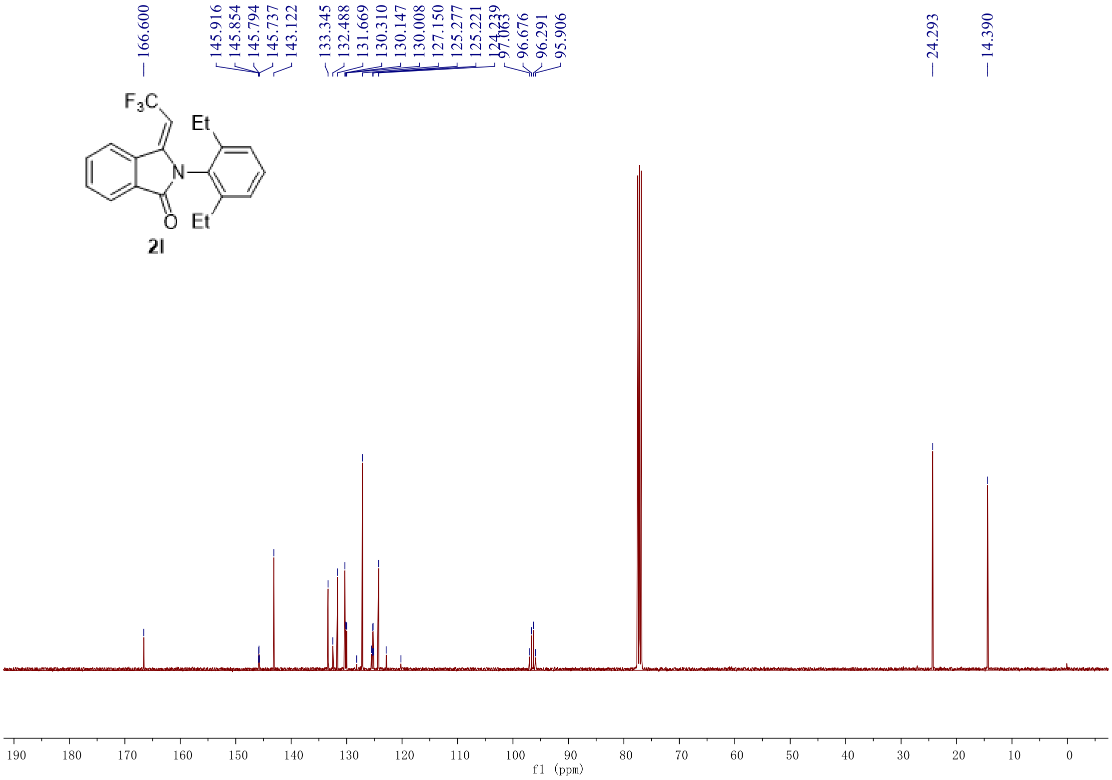
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2k



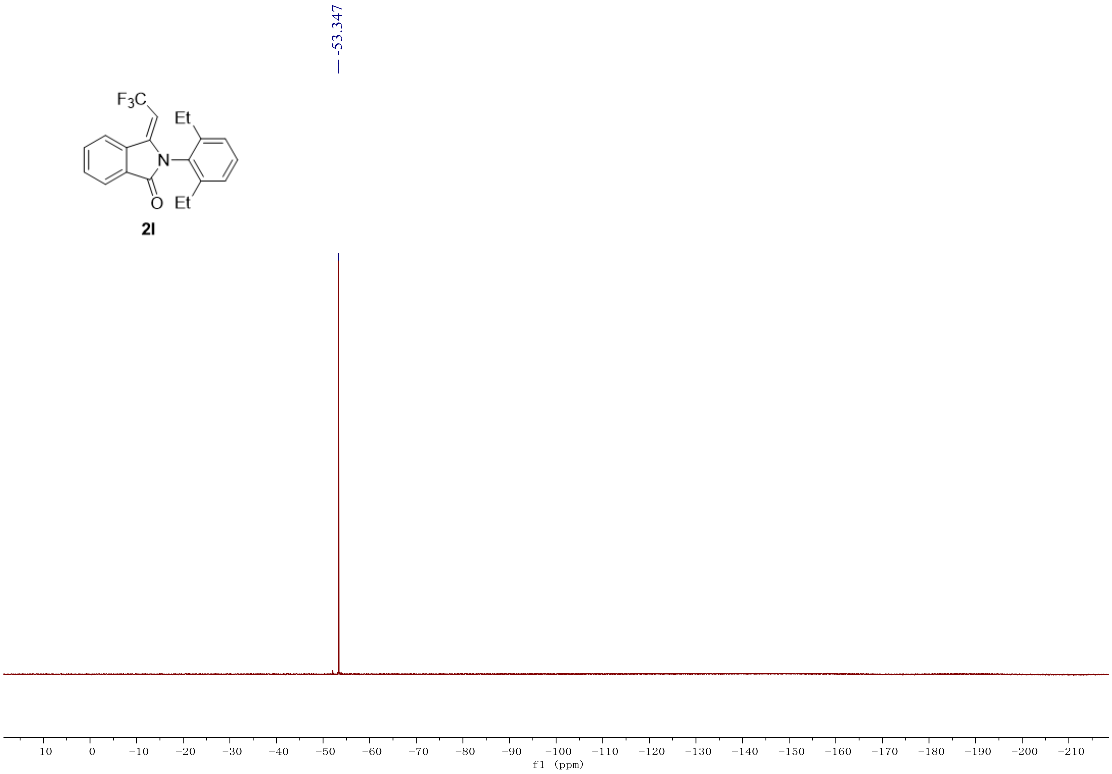
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2l



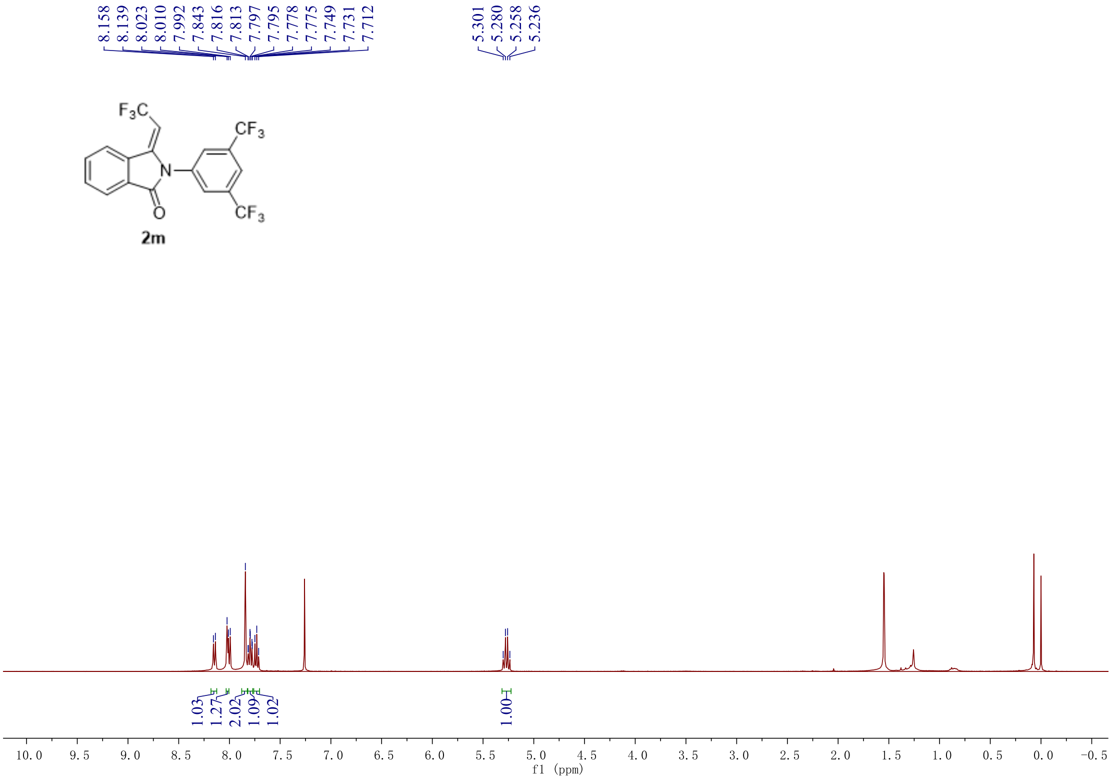
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2l



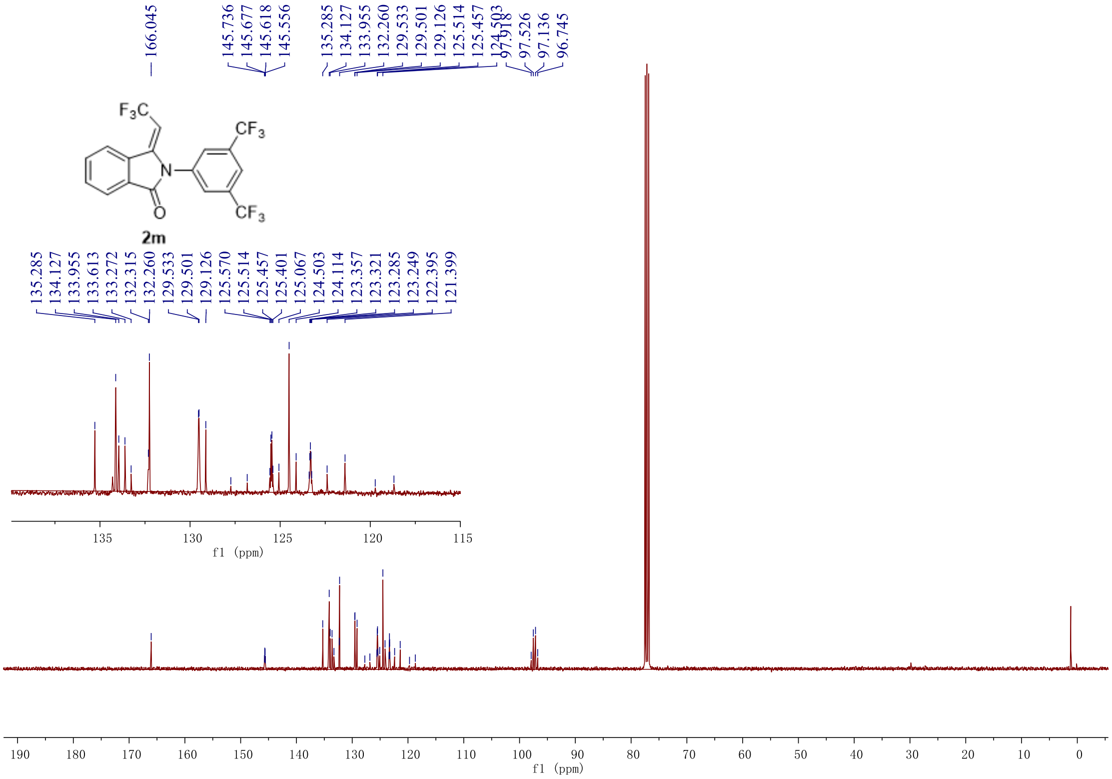
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2l



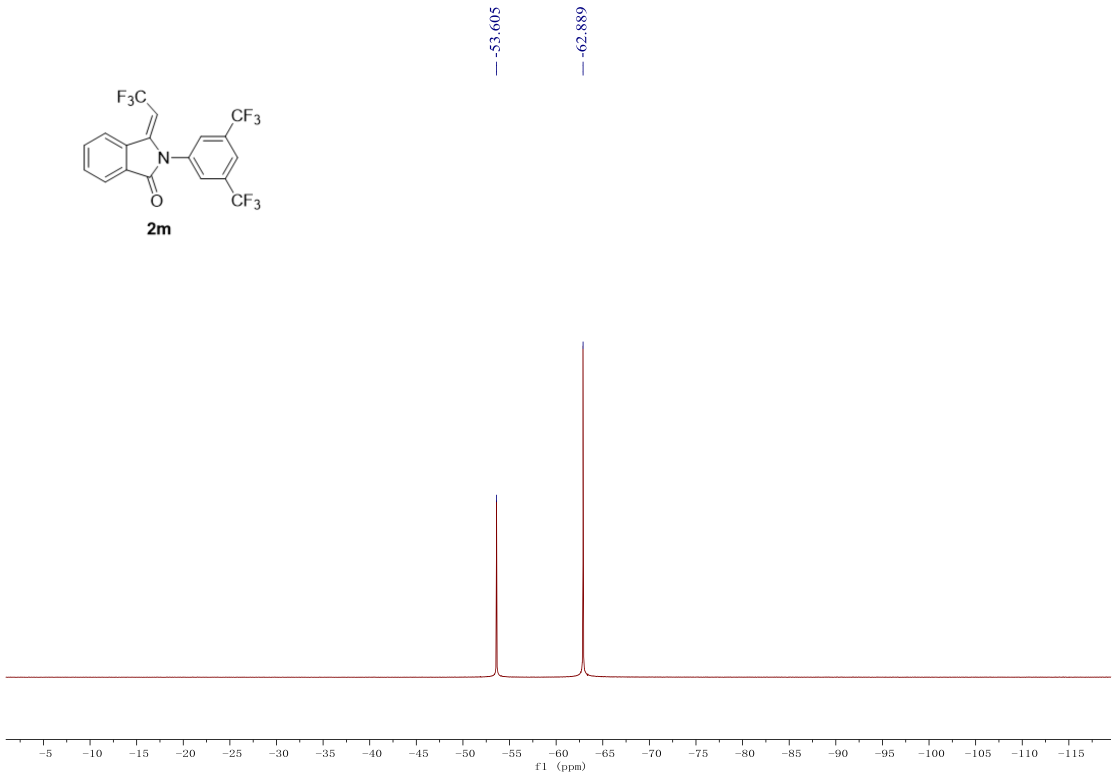
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2m



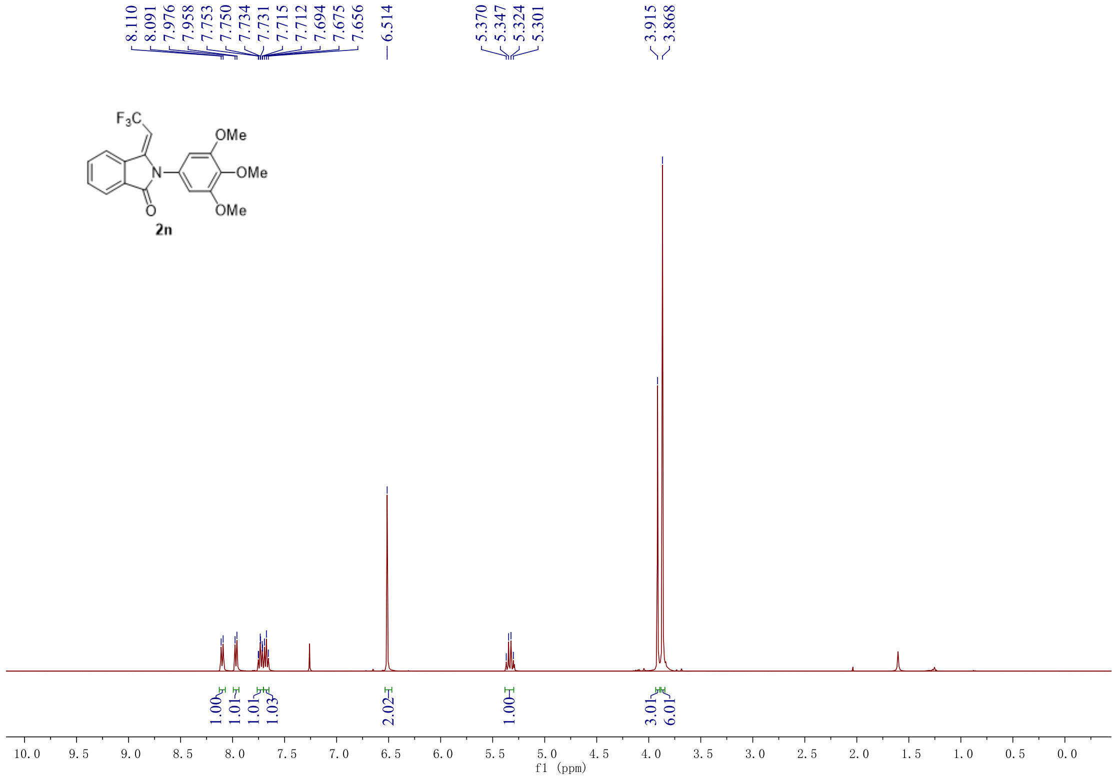
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2m



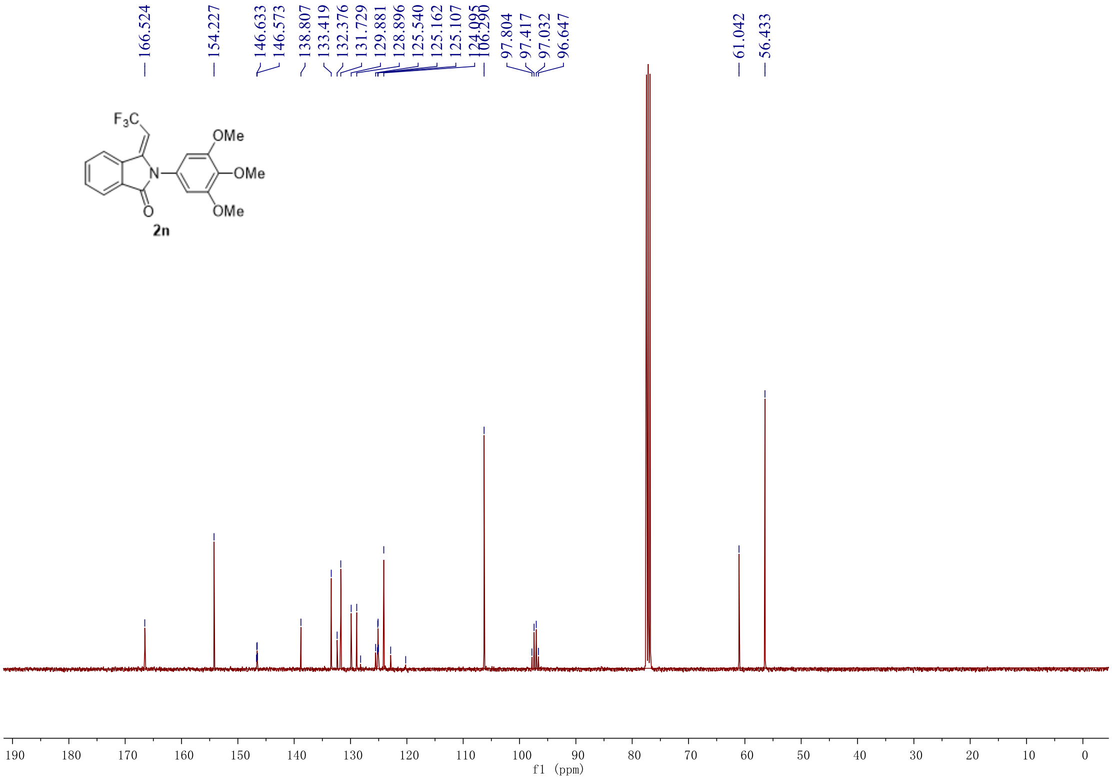
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2m



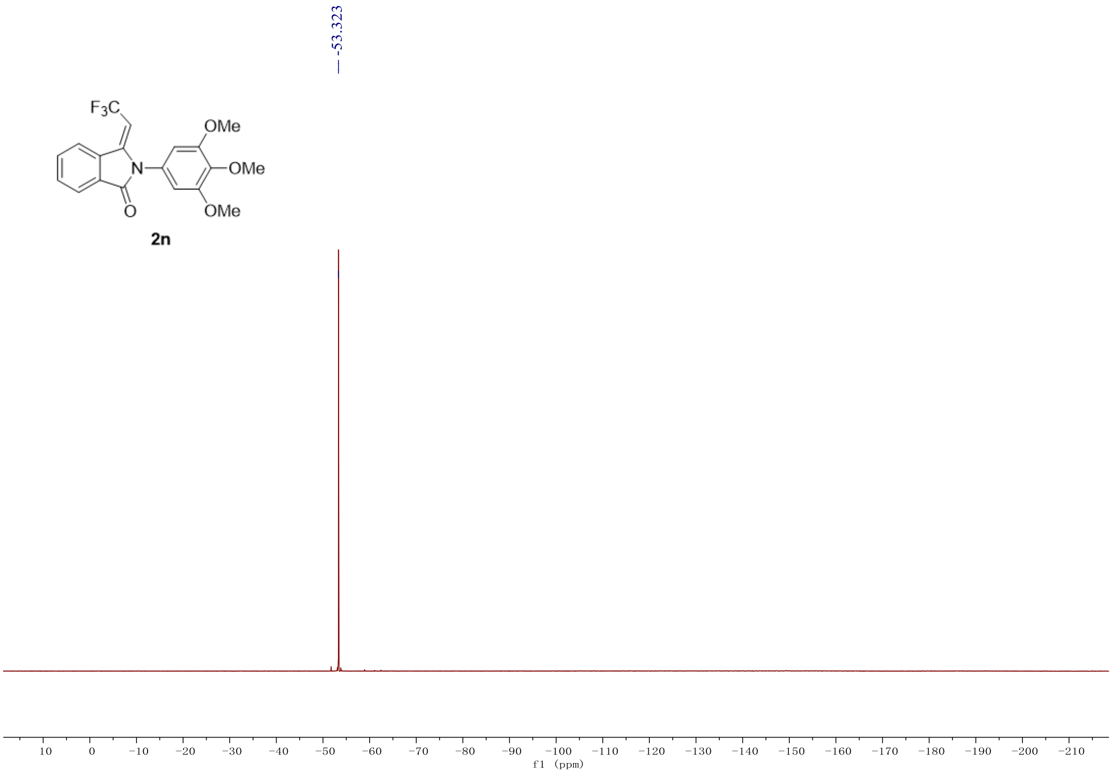
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2n



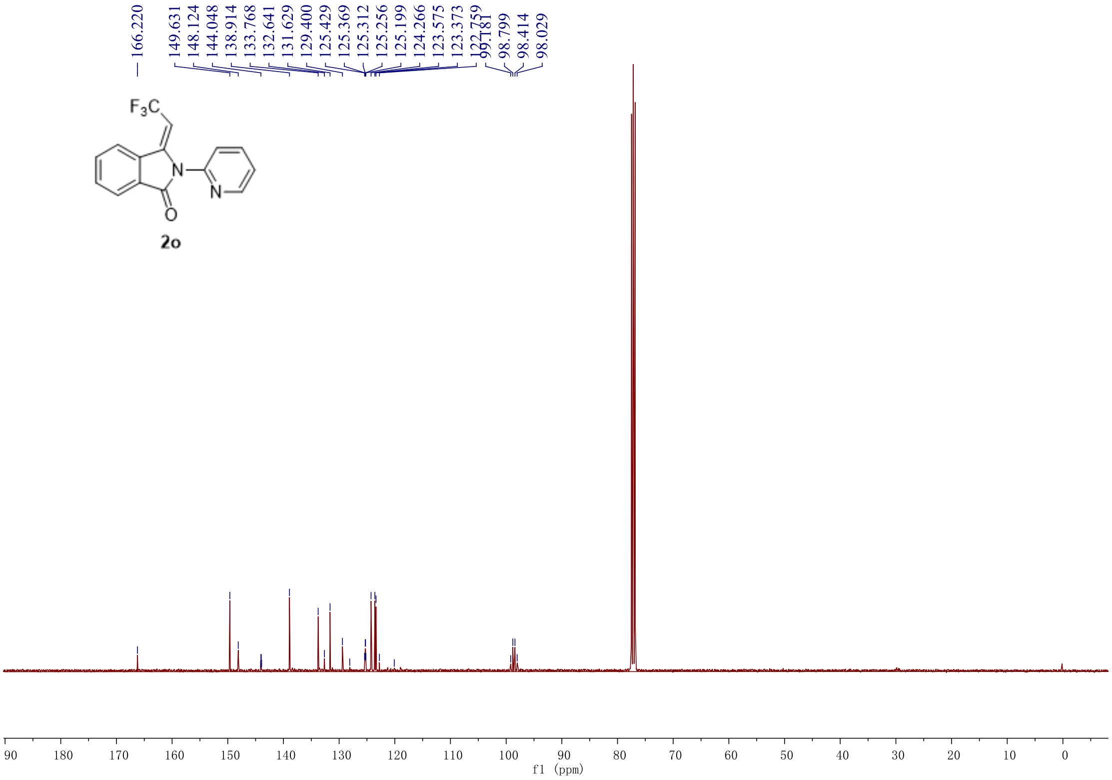
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2n



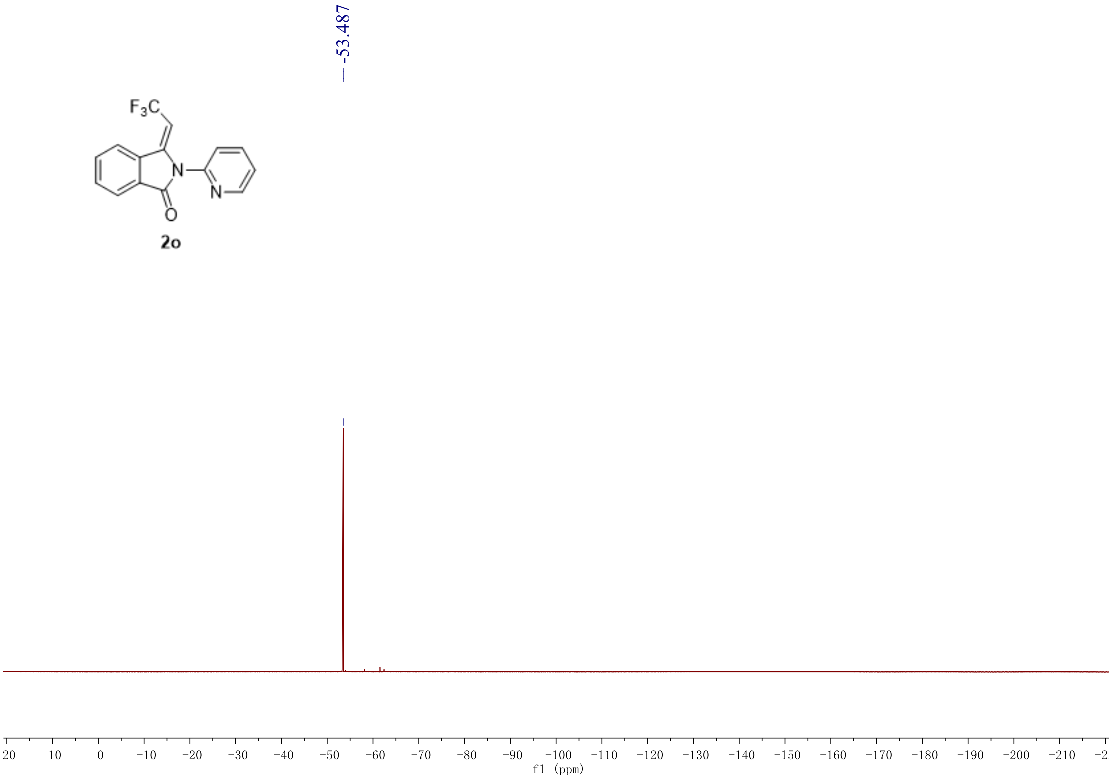
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2n



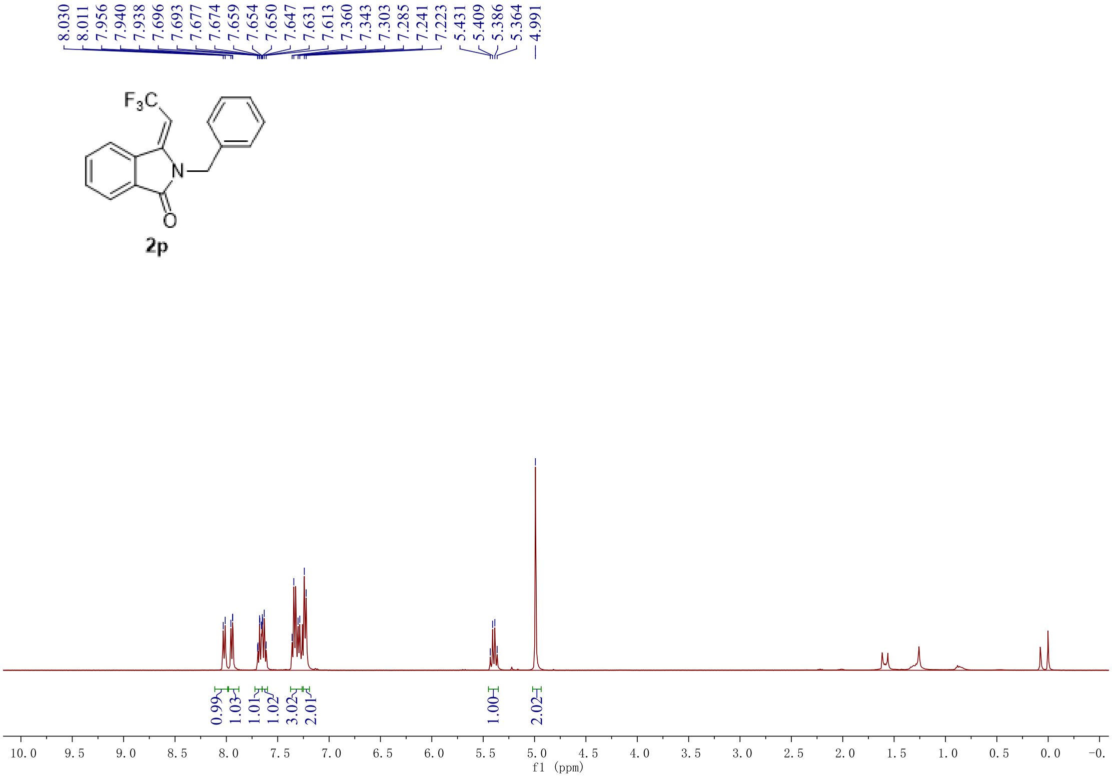
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2o



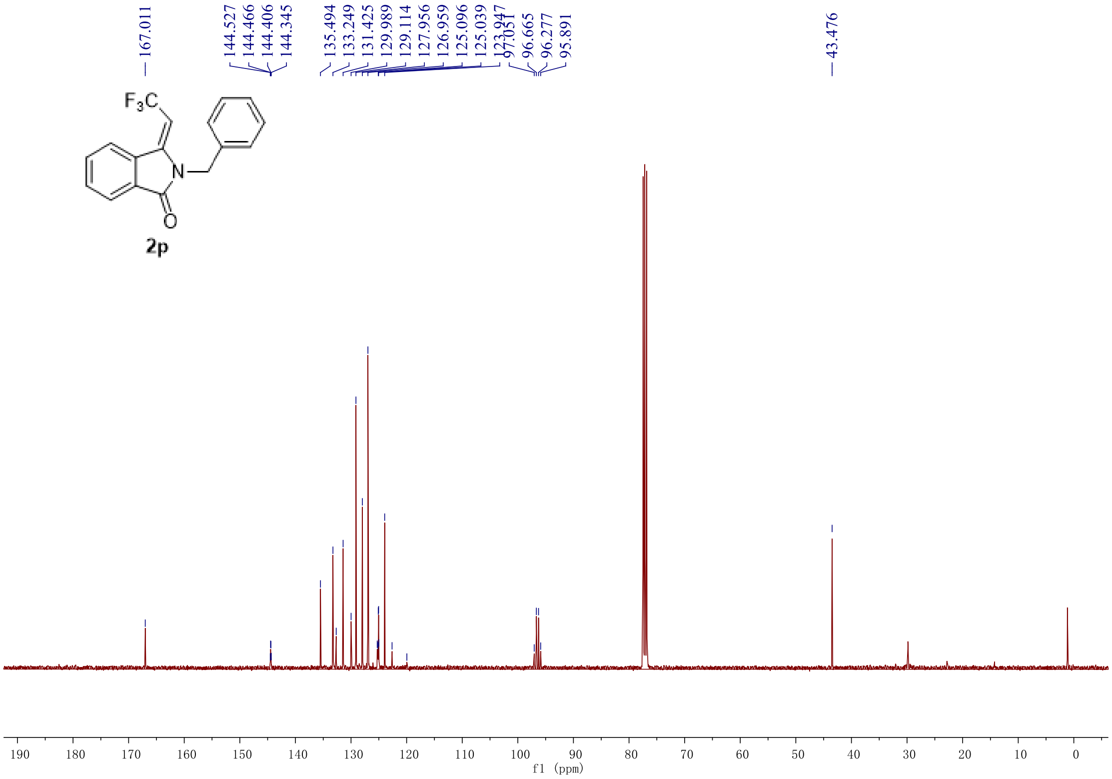
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2o



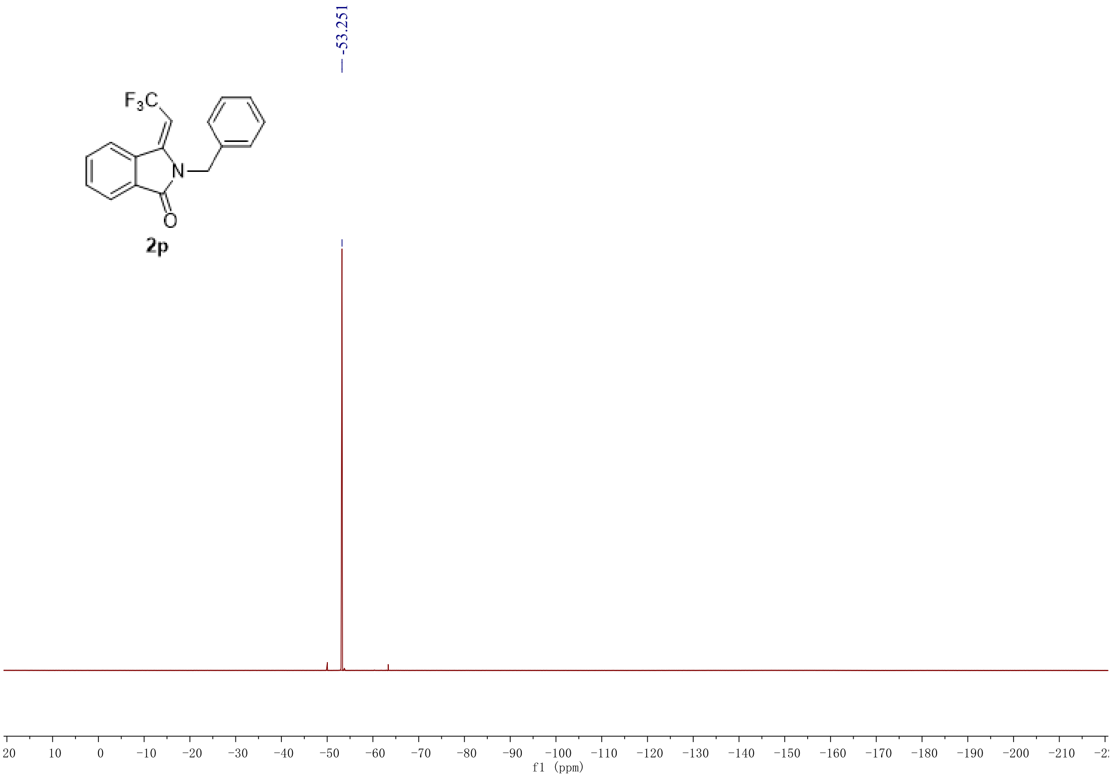
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2p



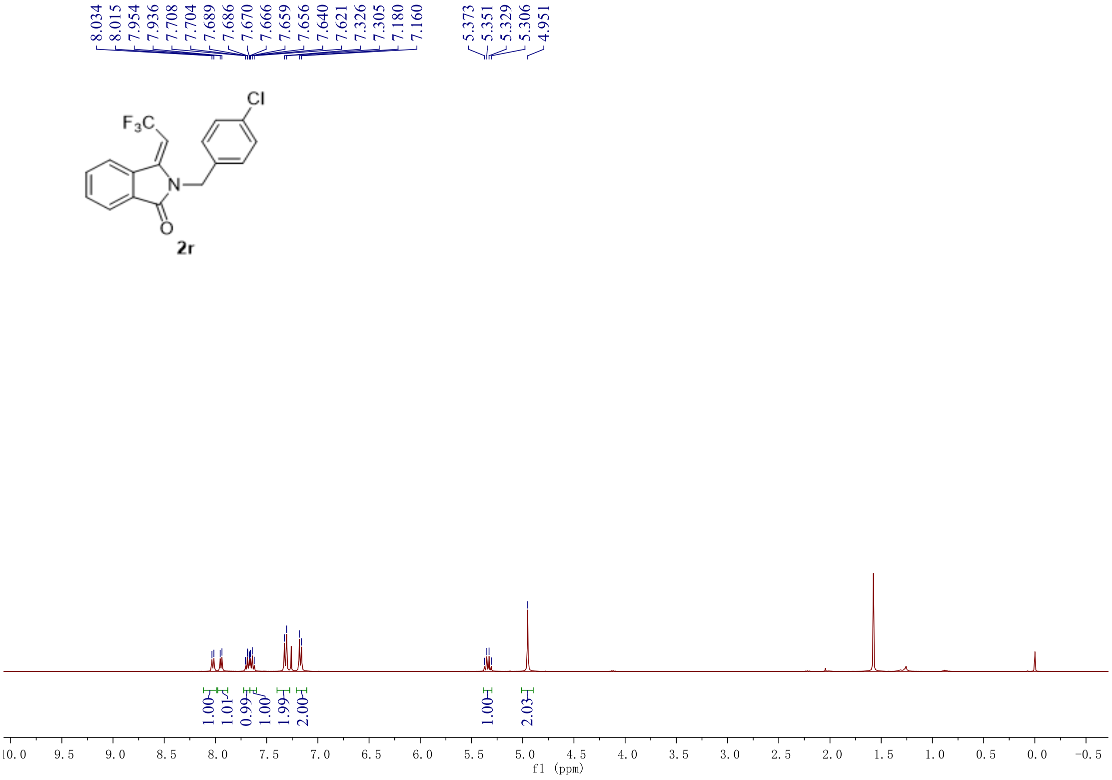
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2p



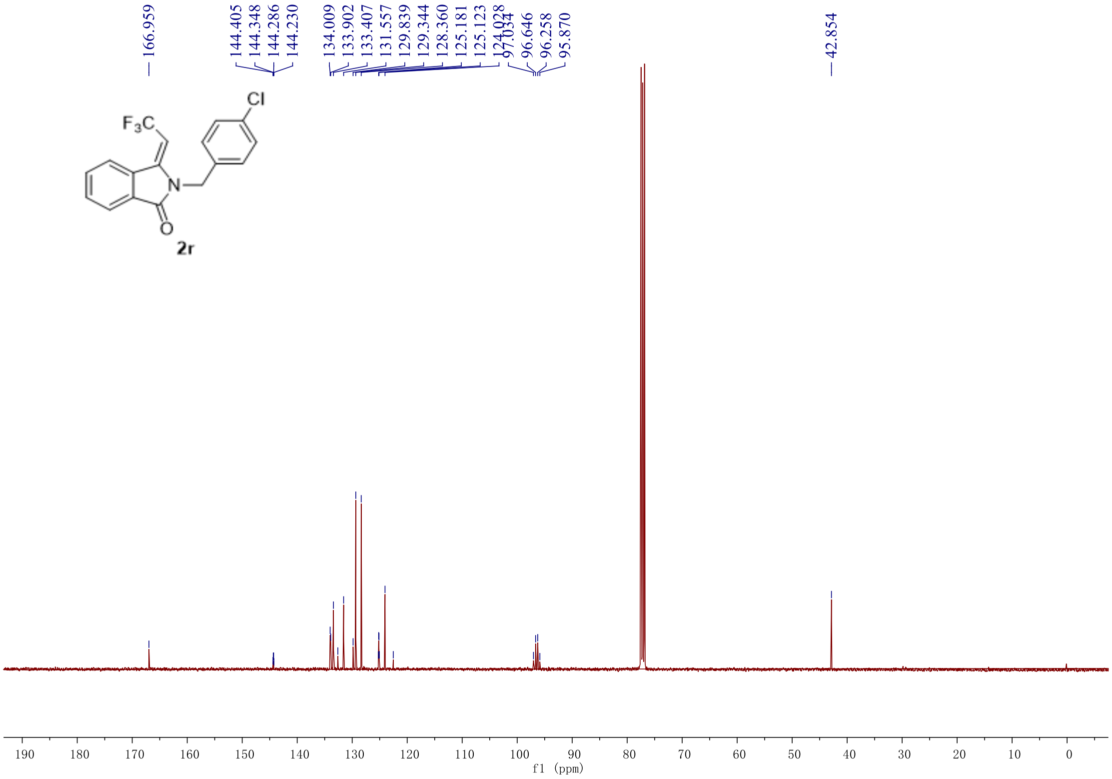
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2p



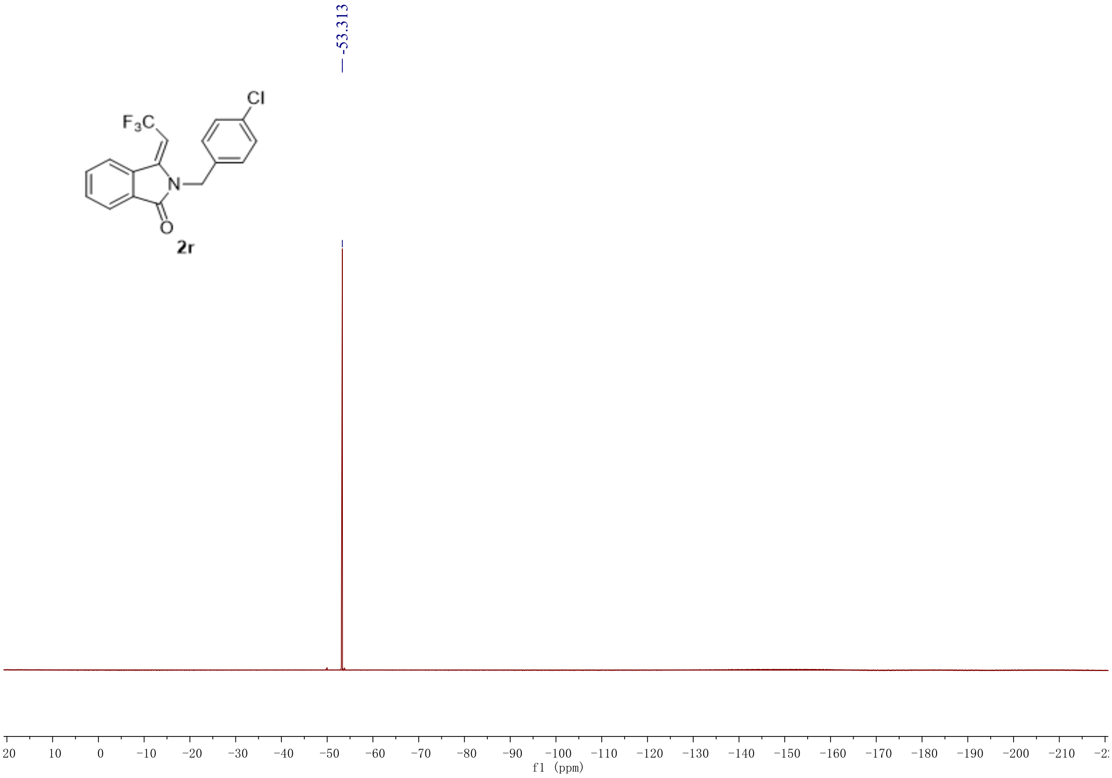
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2r



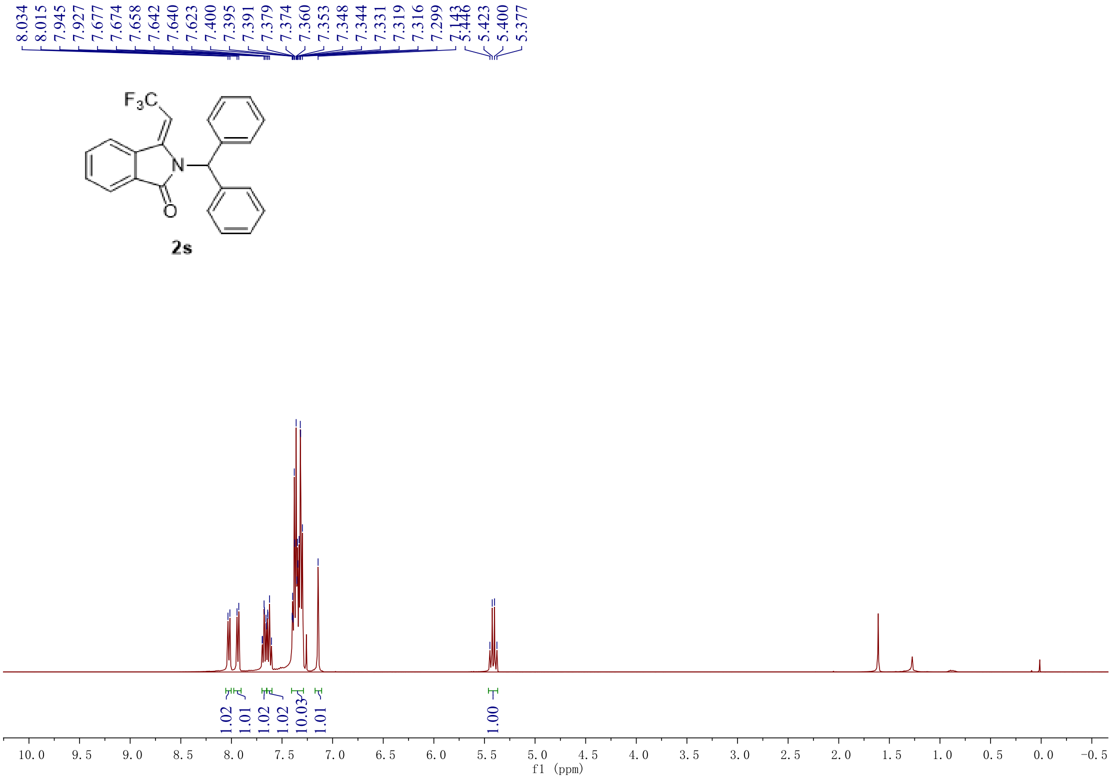
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2r



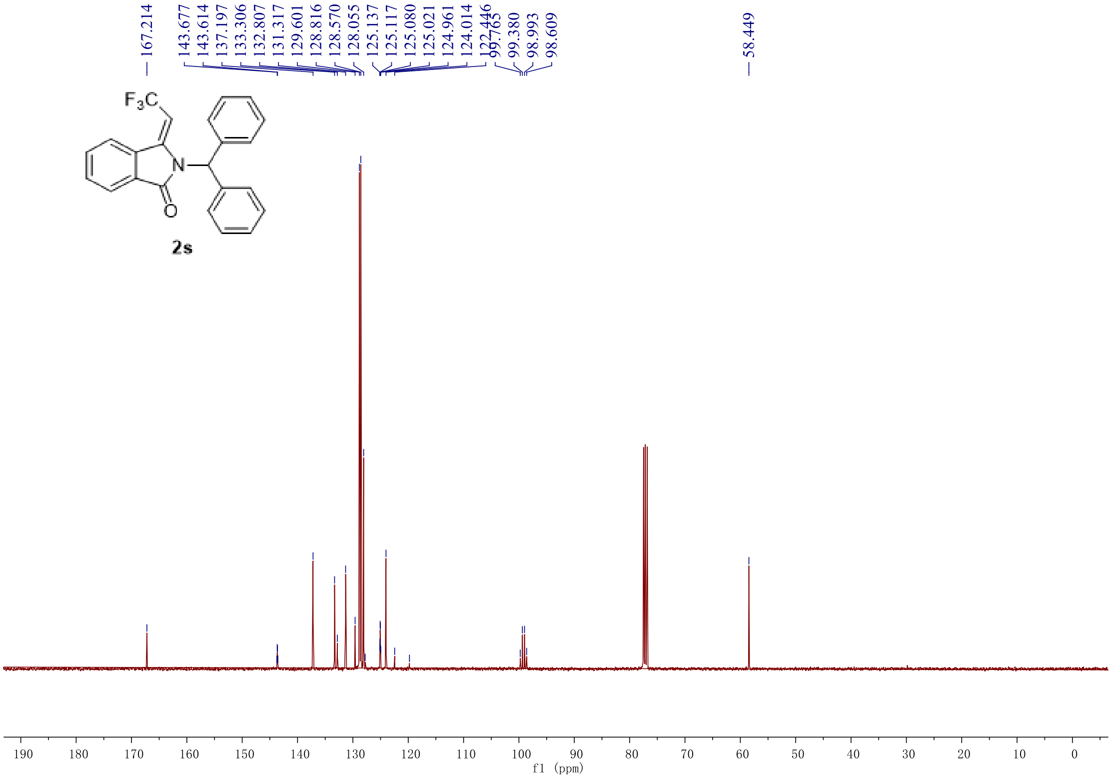
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2r



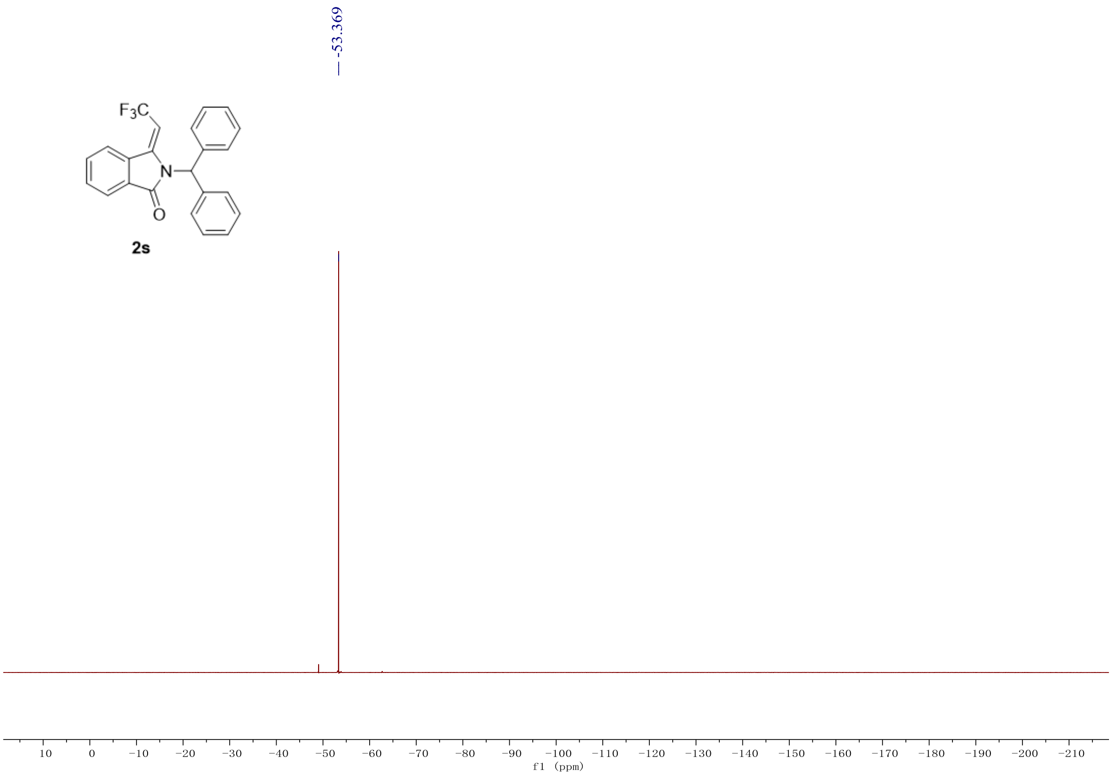
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2s



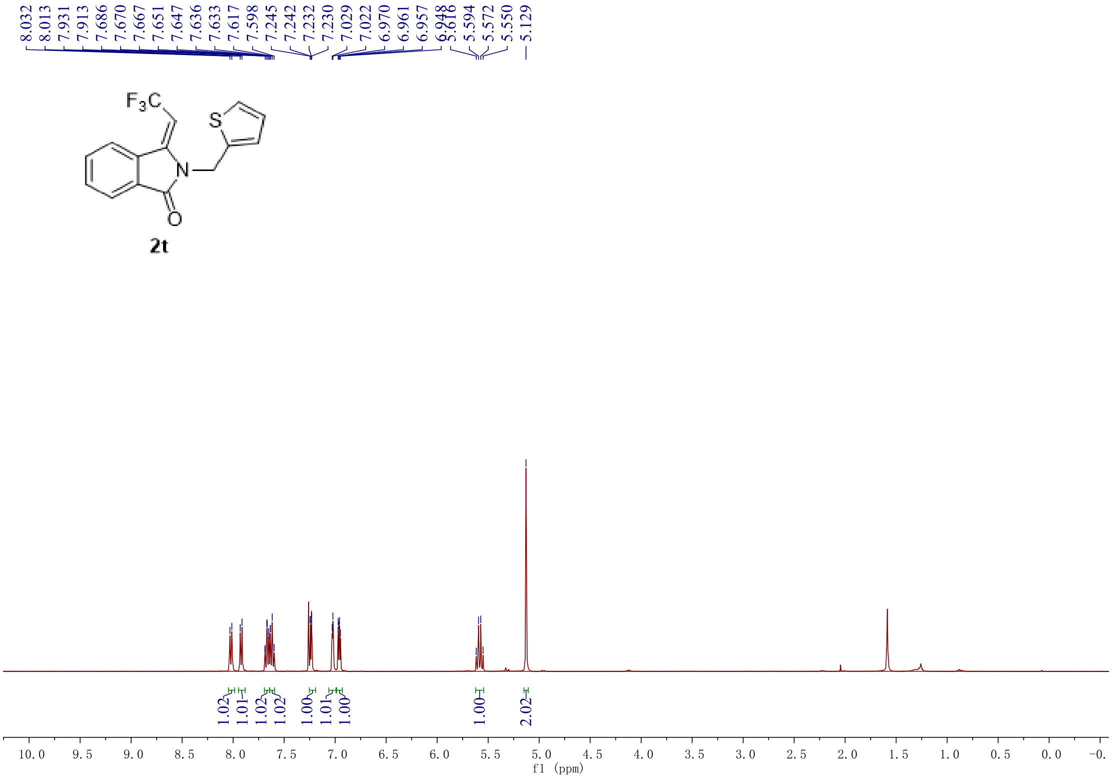
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2s



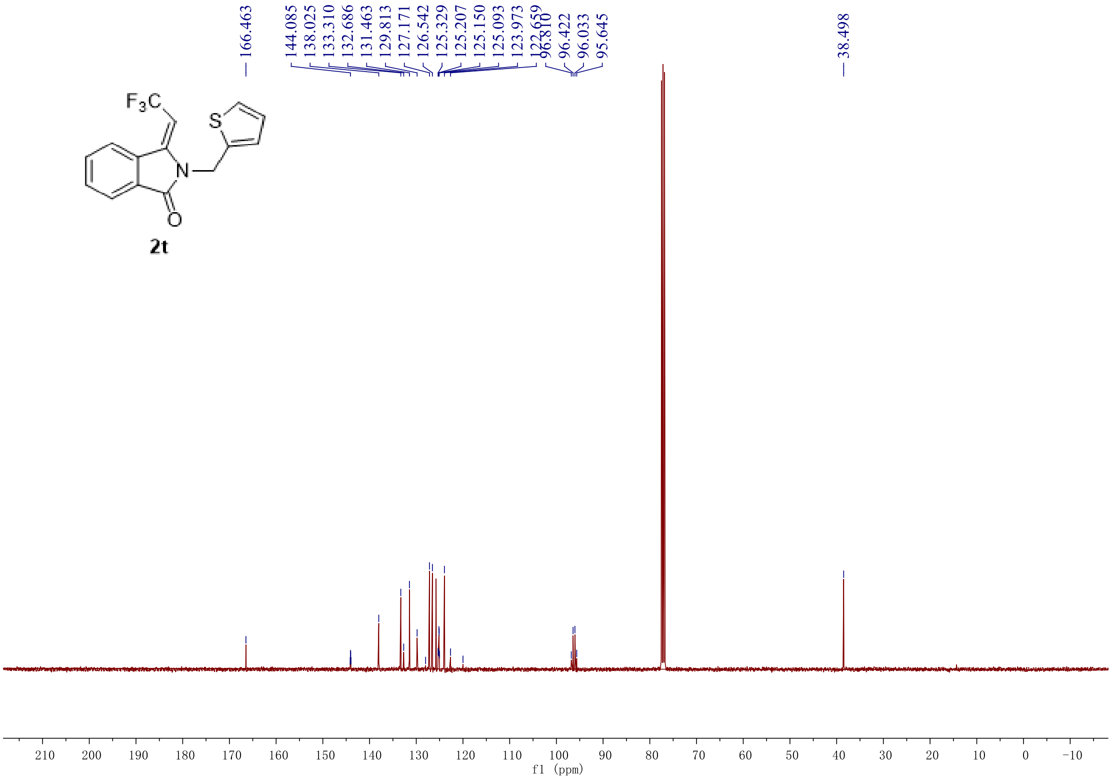
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2s



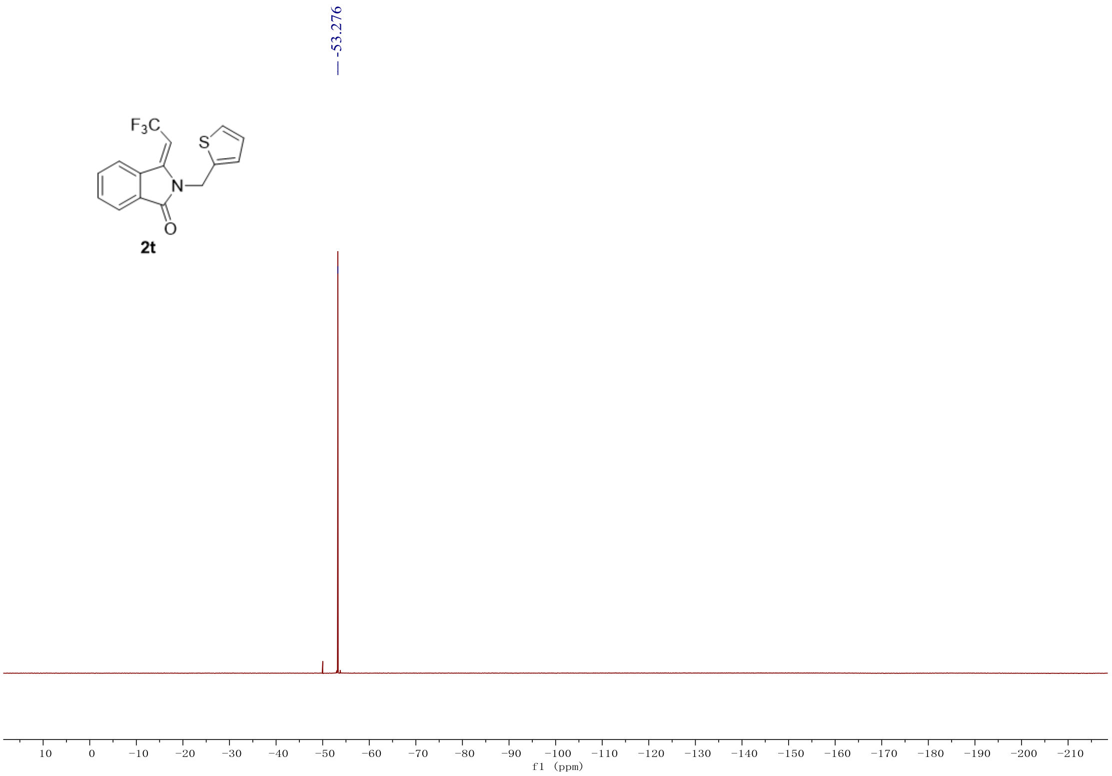
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2t



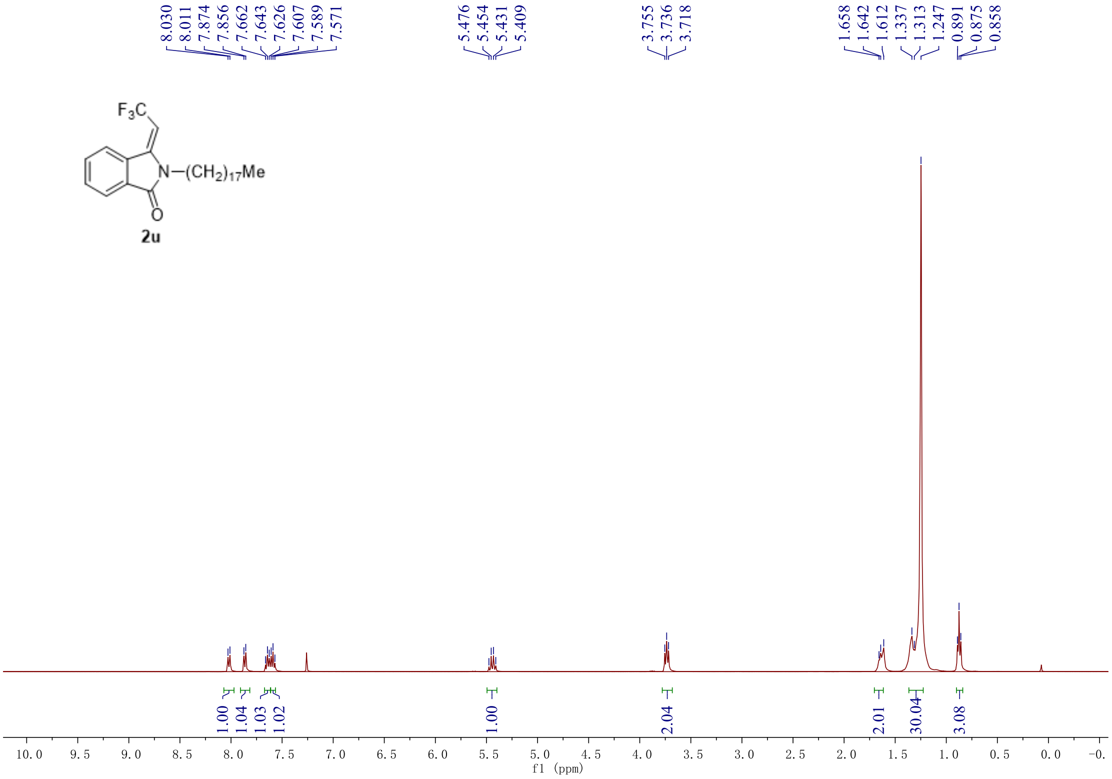
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2t



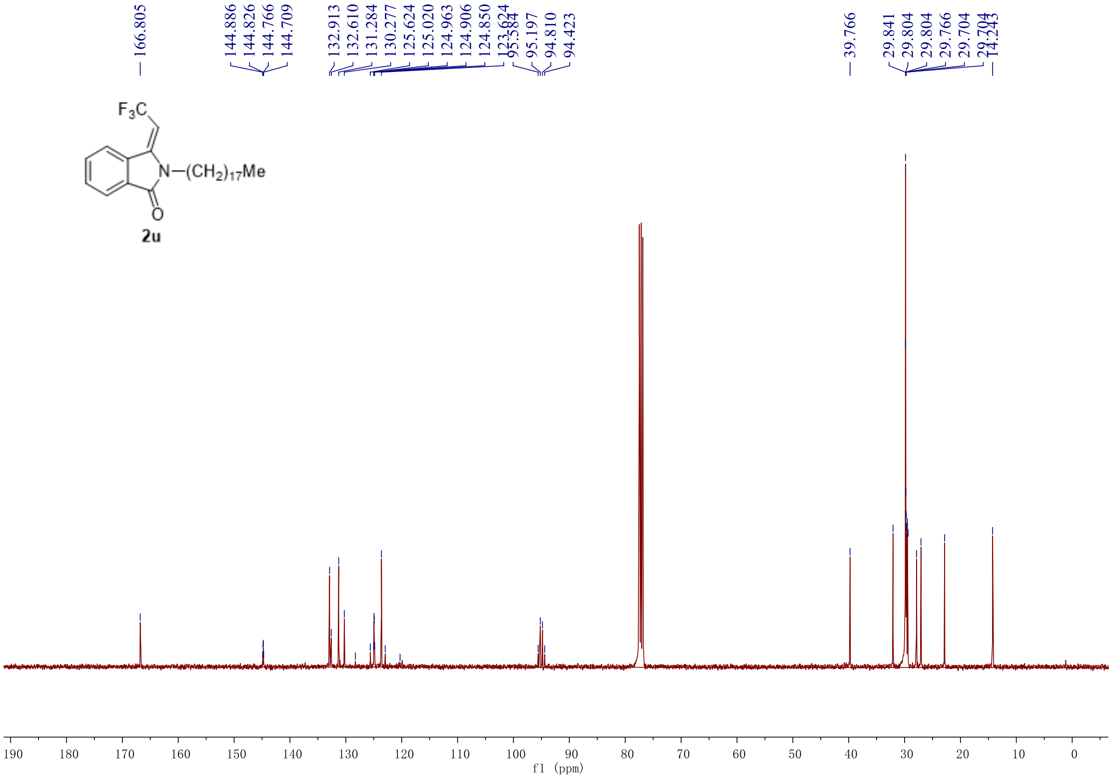
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2t



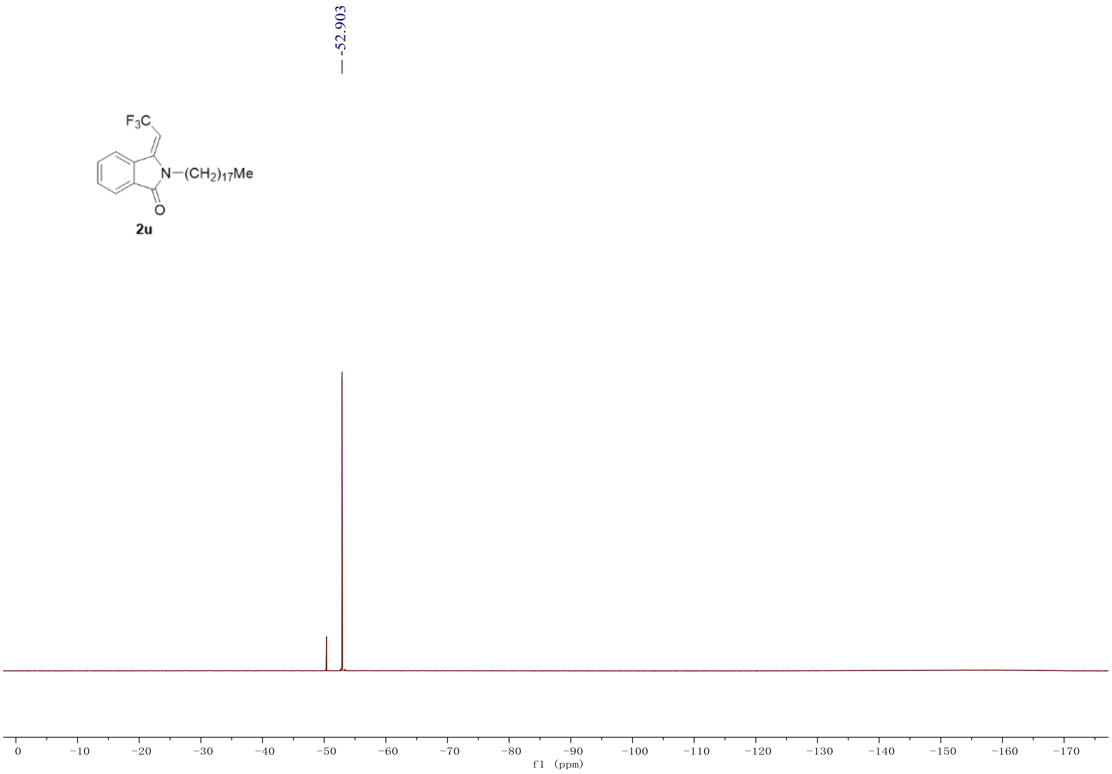
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2u



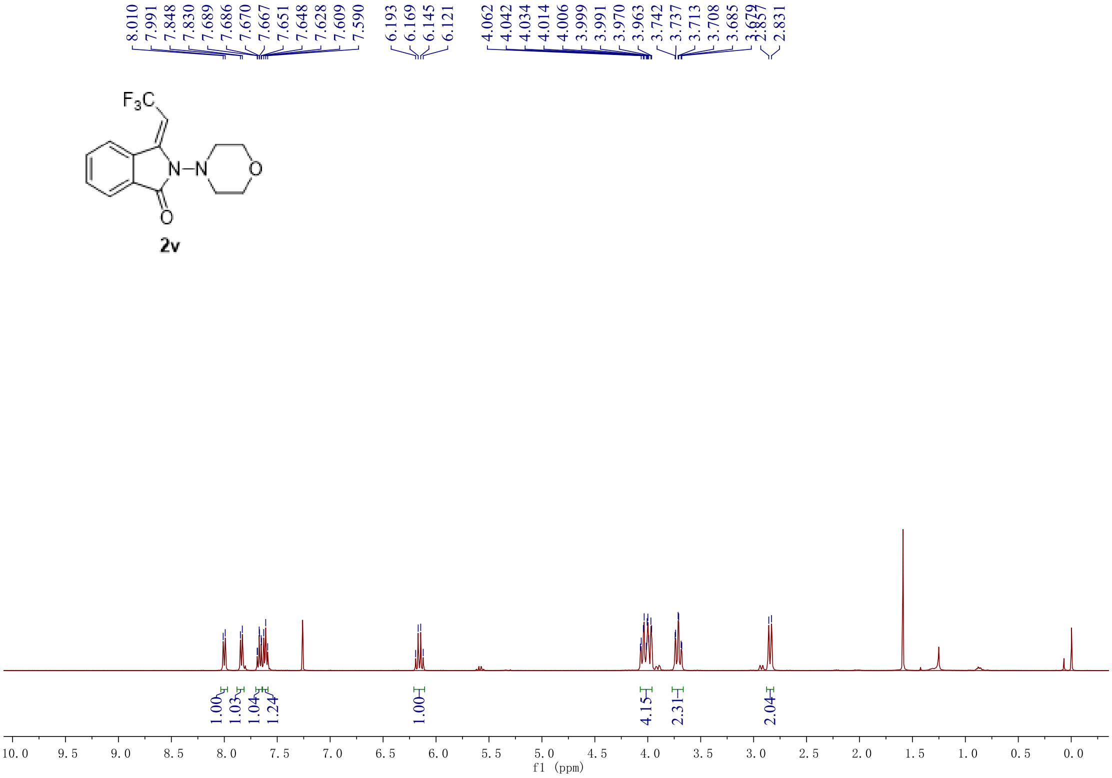
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2u



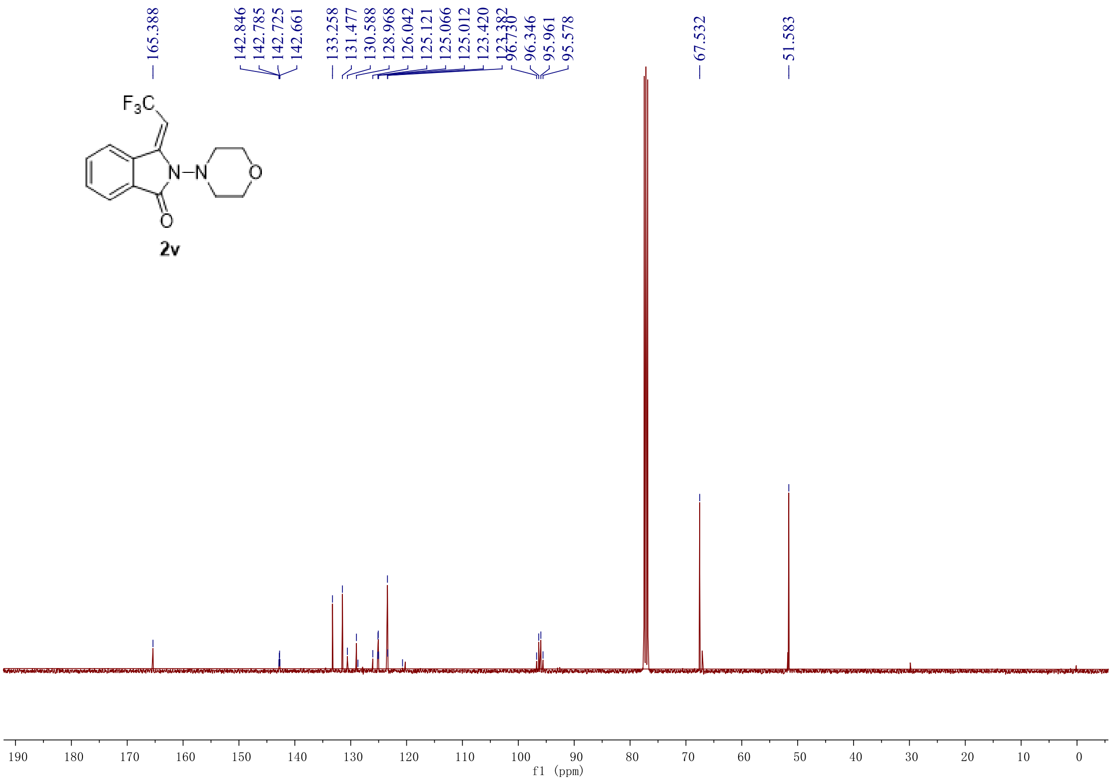
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2u



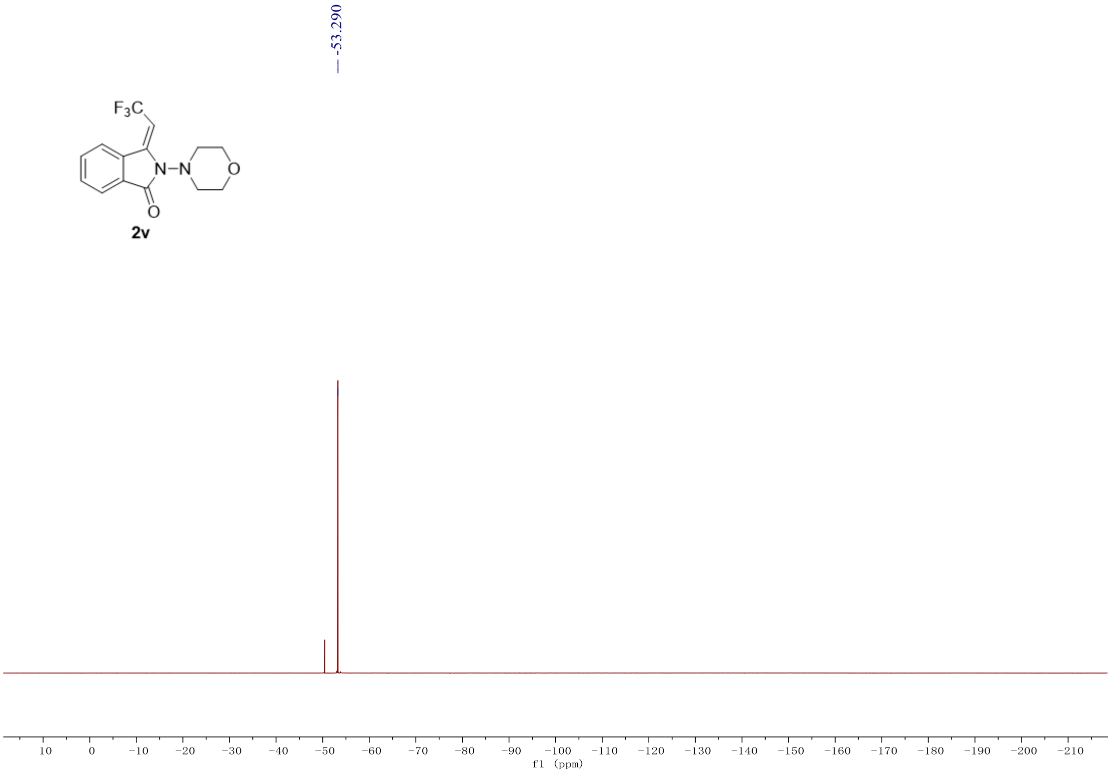
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2v



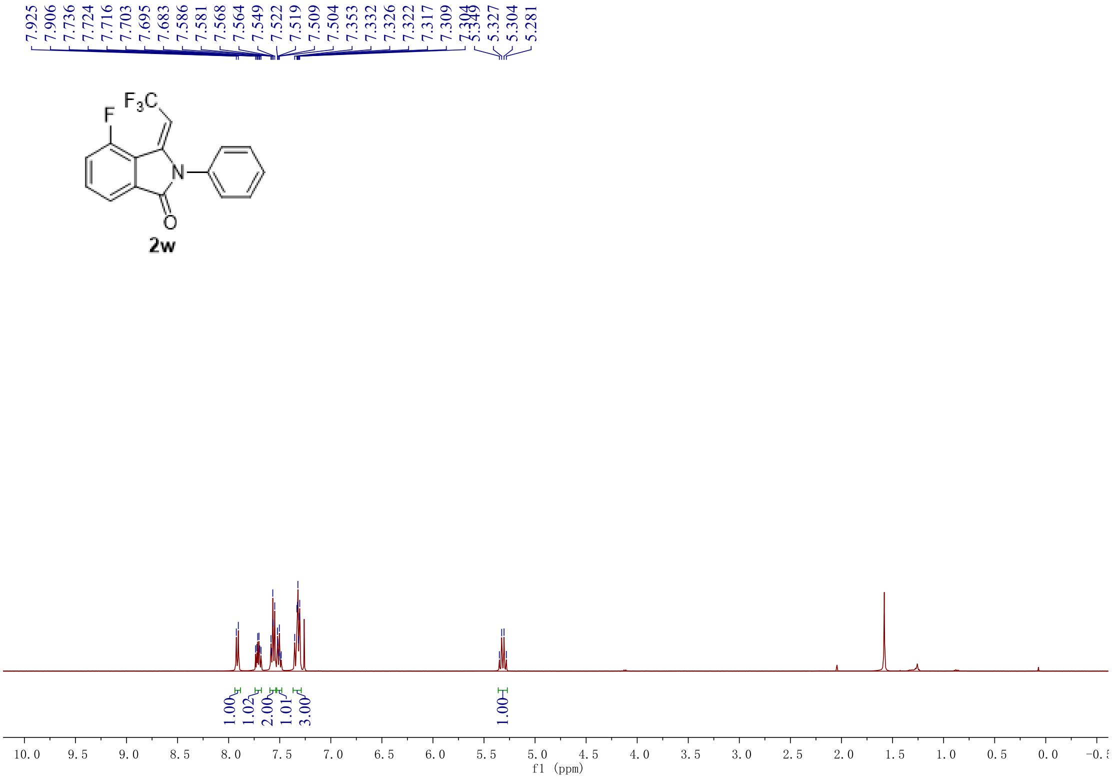
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2v



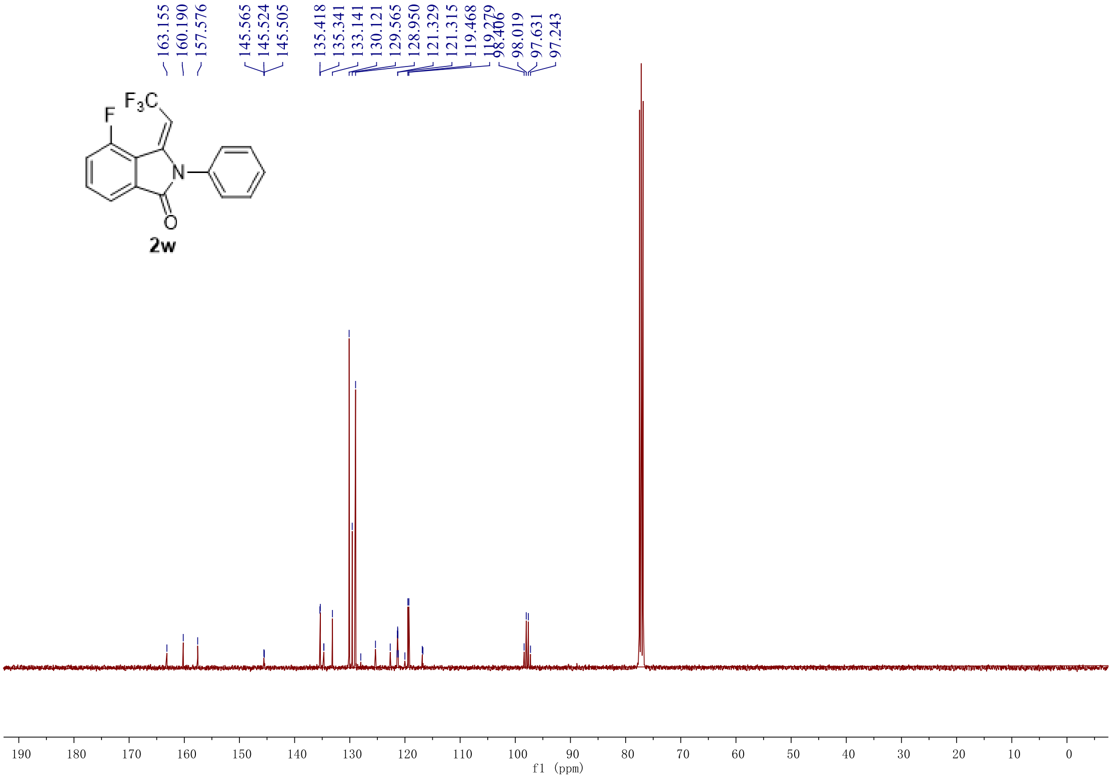
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2v



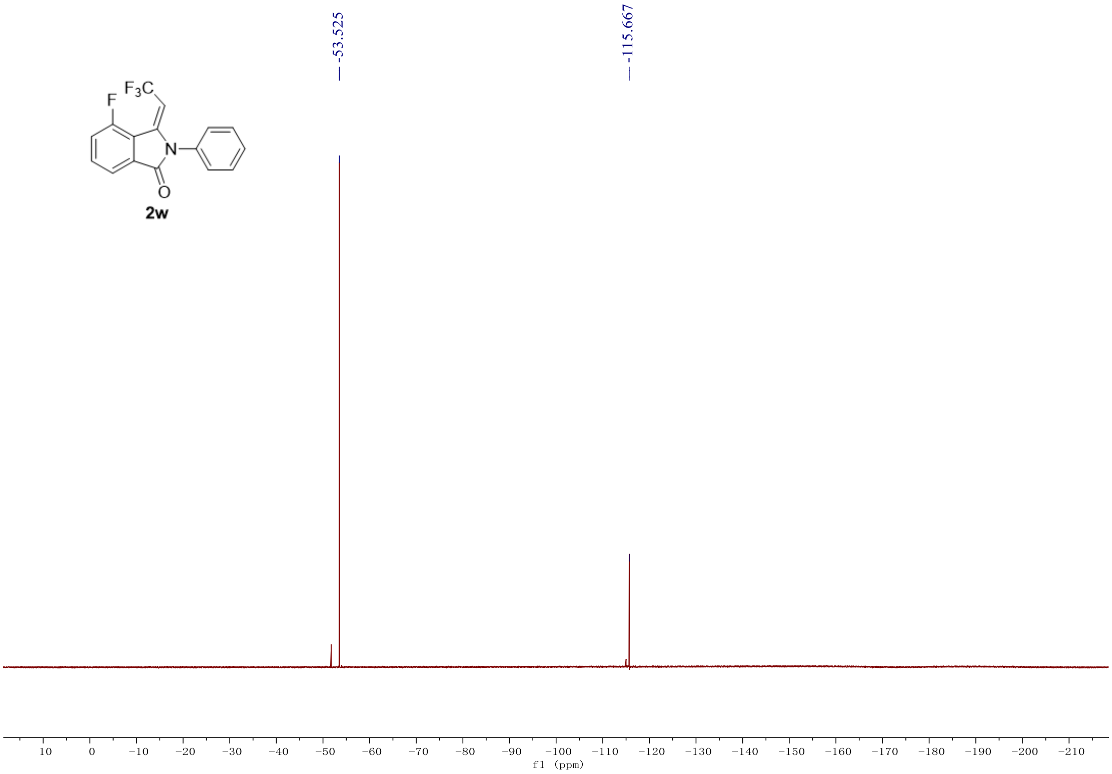
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2w



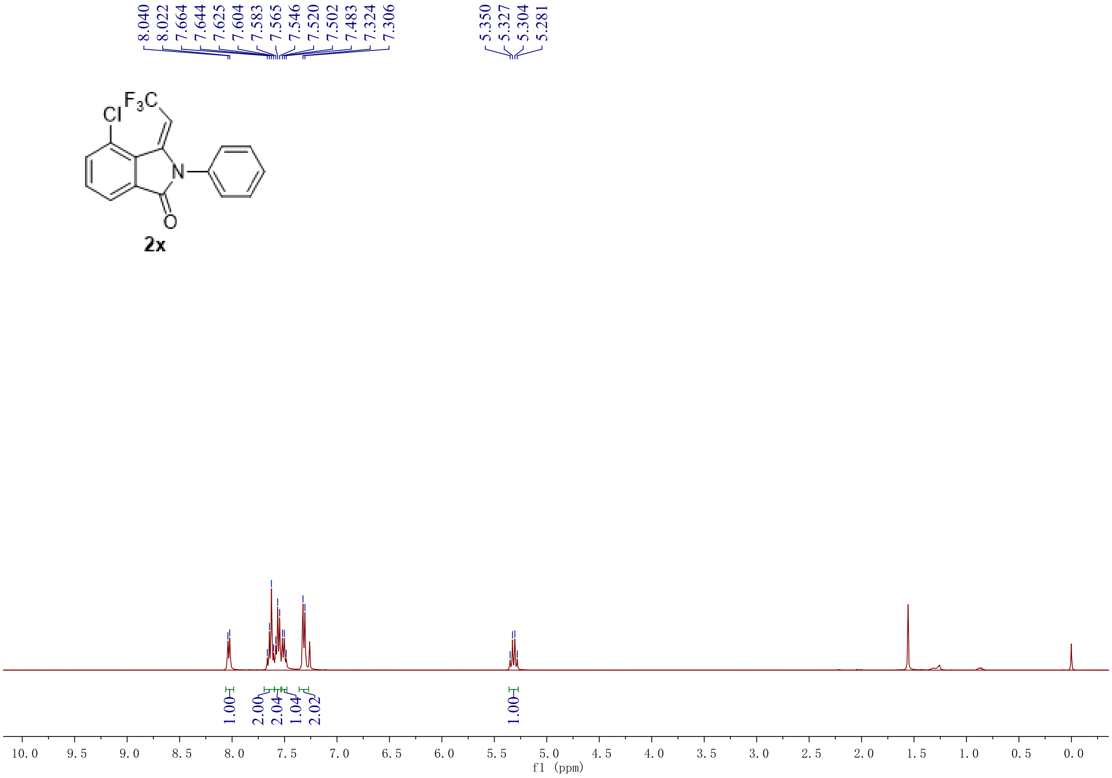
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2w



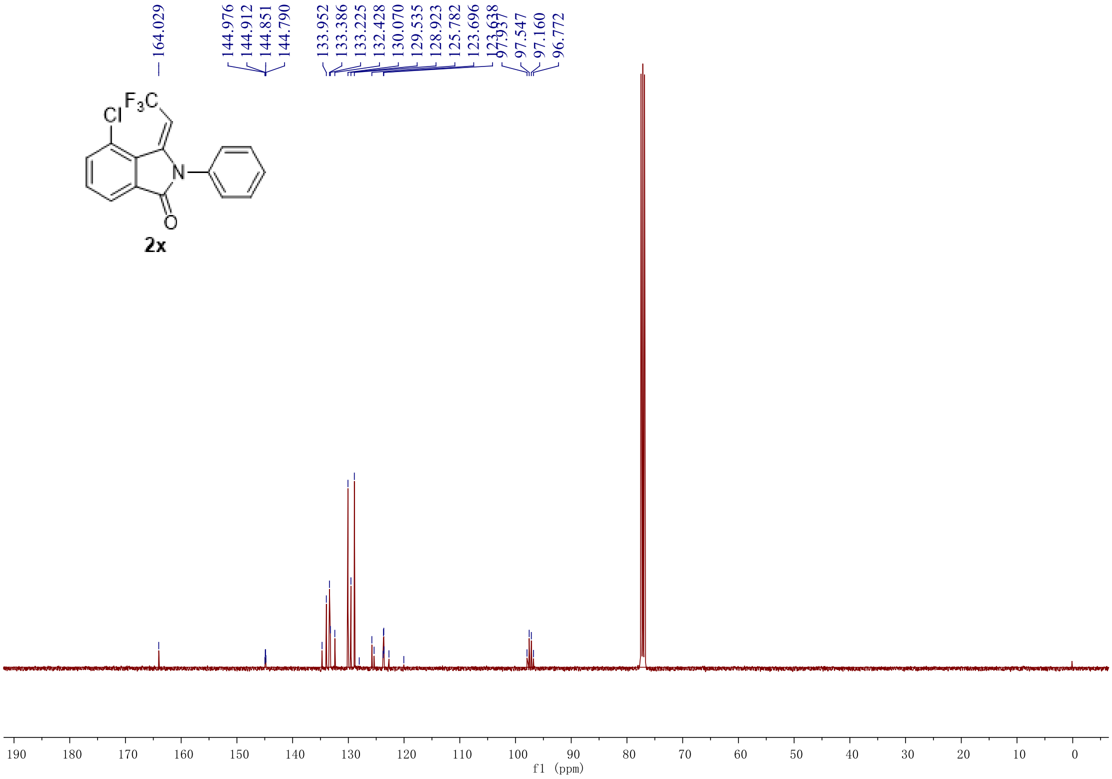
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2w



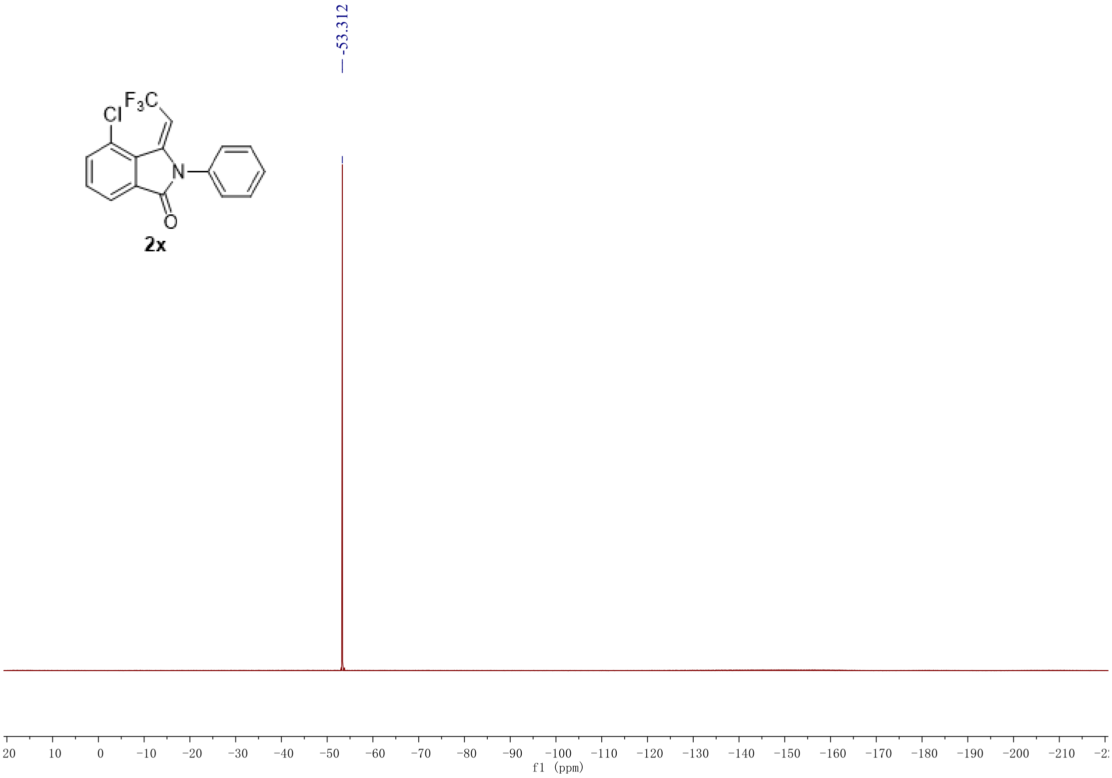
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2x



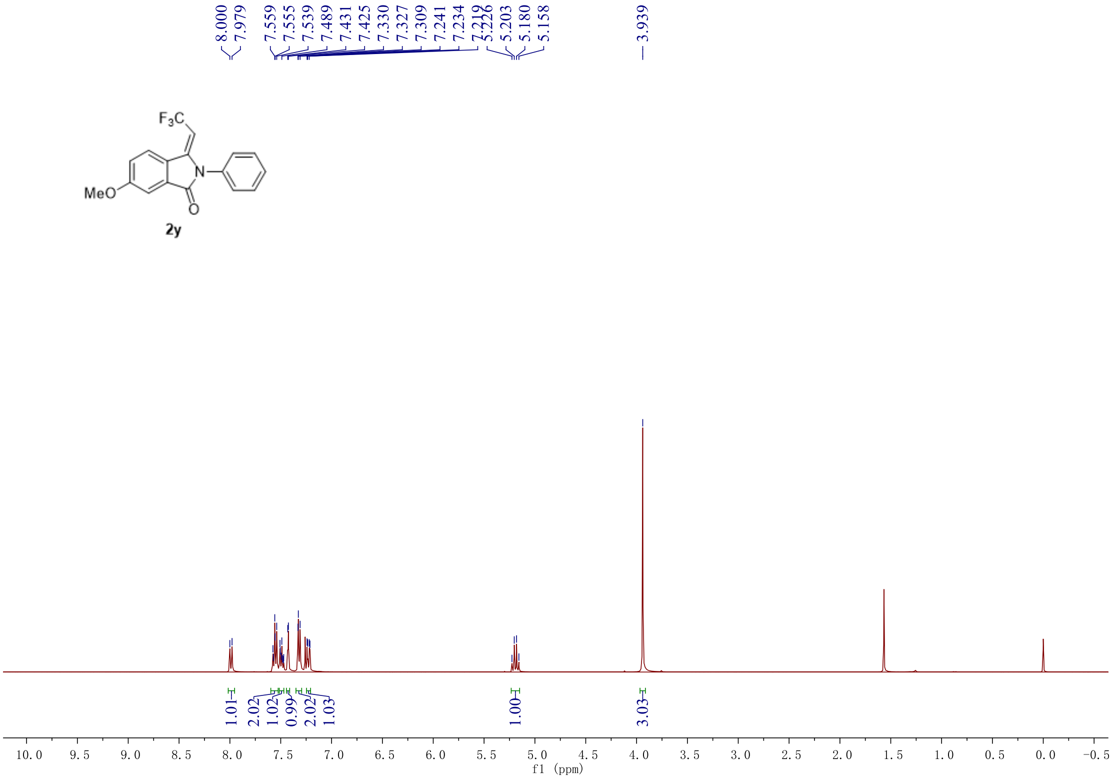
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2x



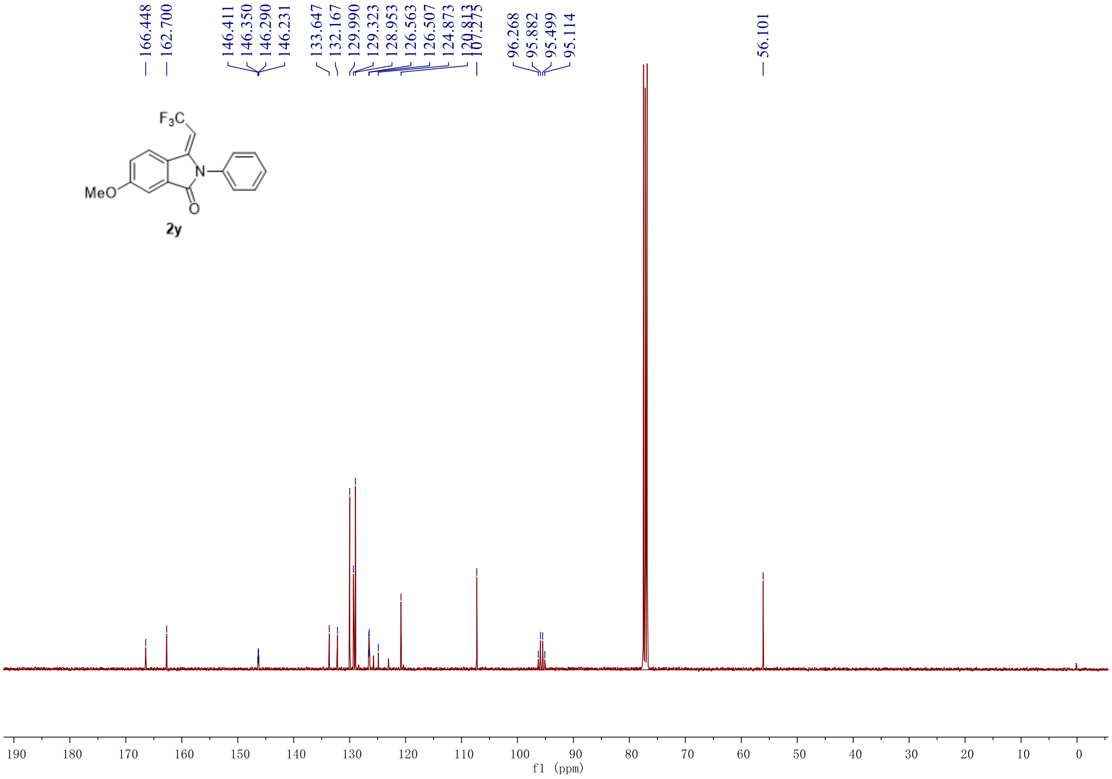
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2x



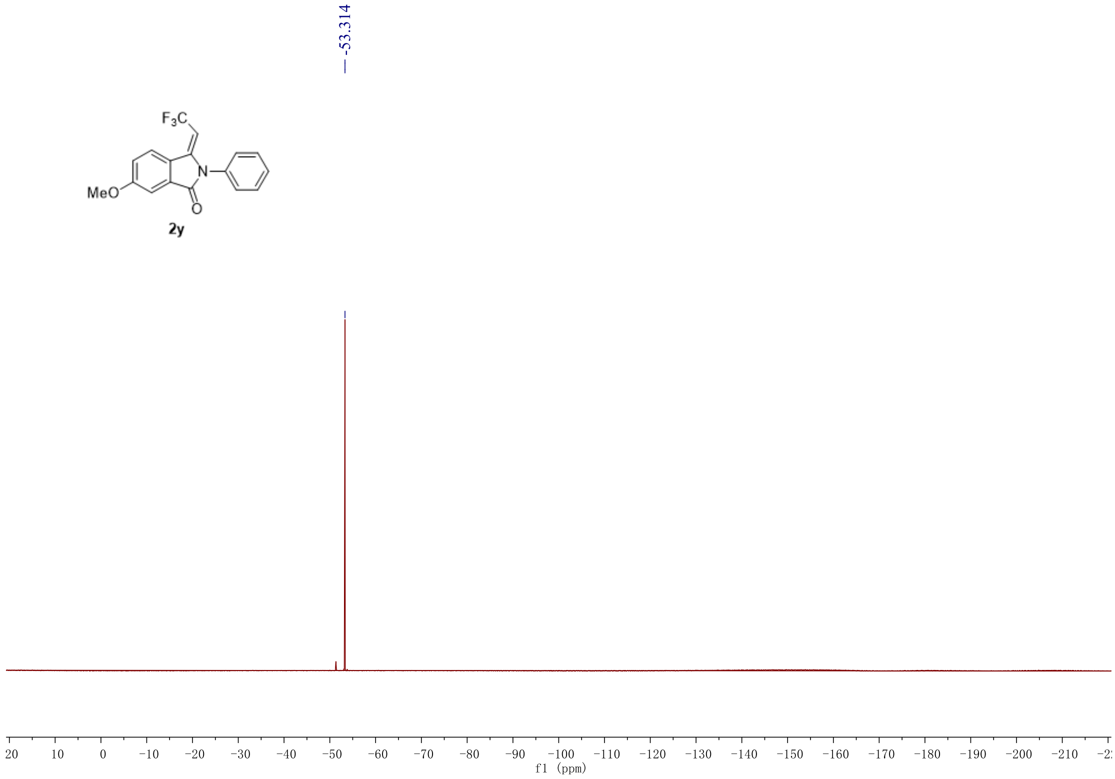
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2y



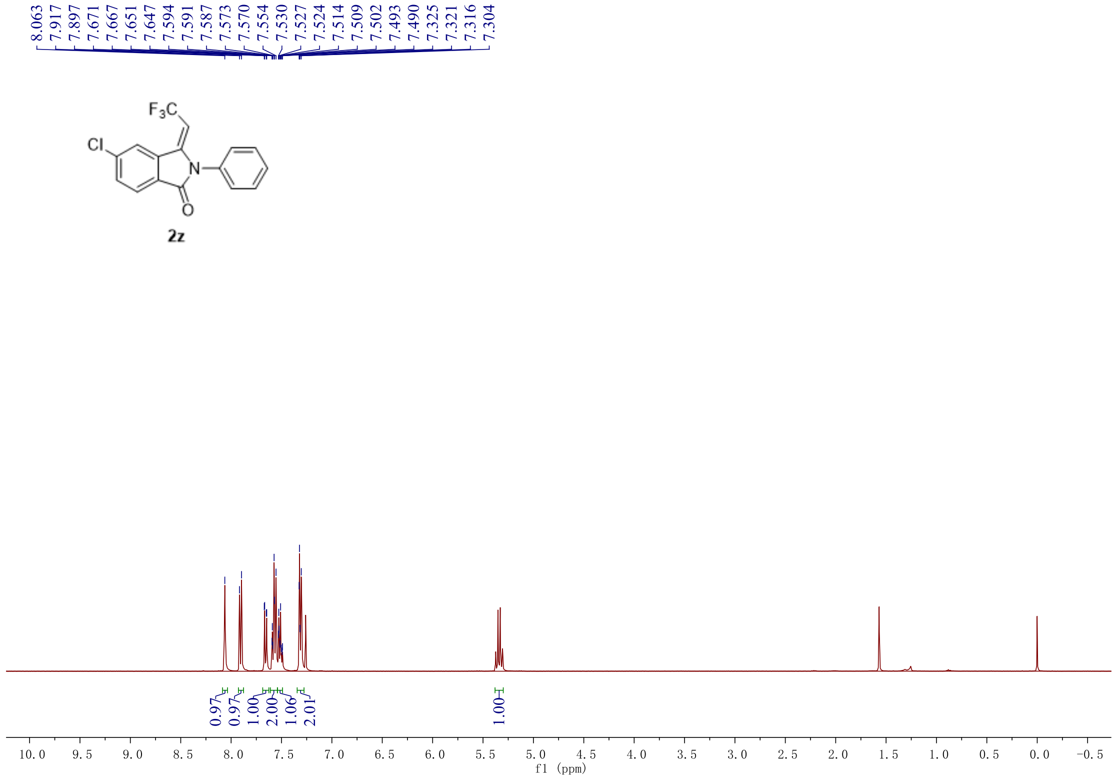
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2y



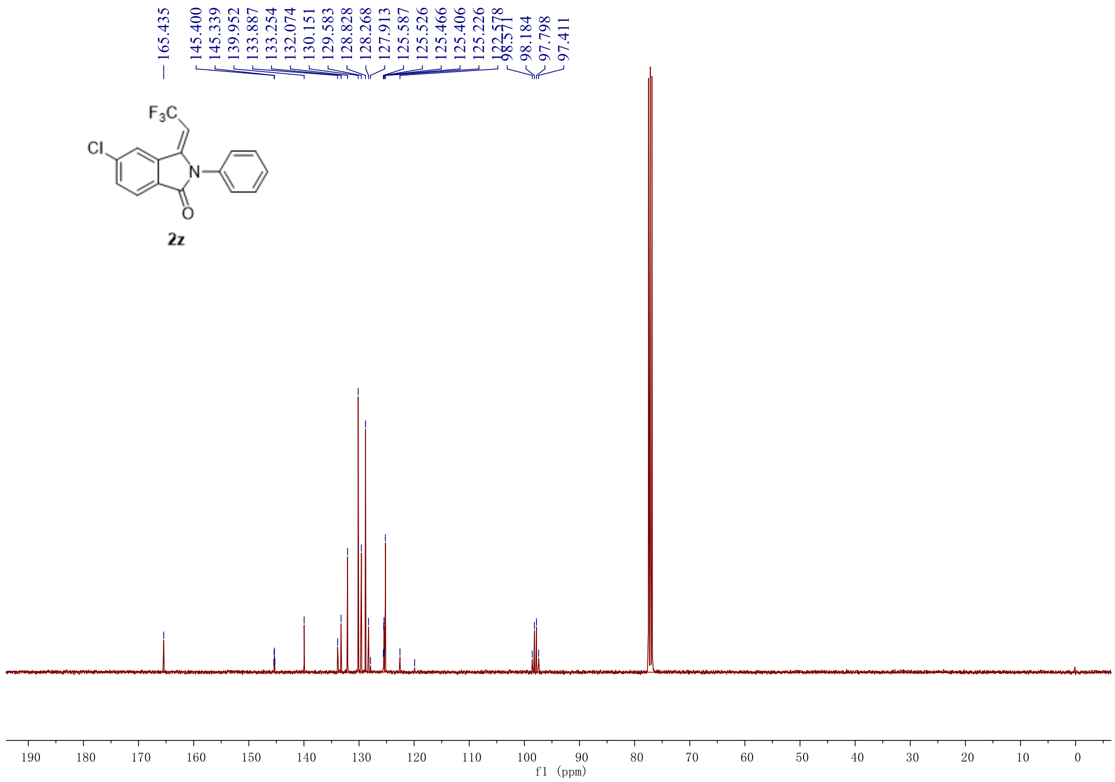
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2y



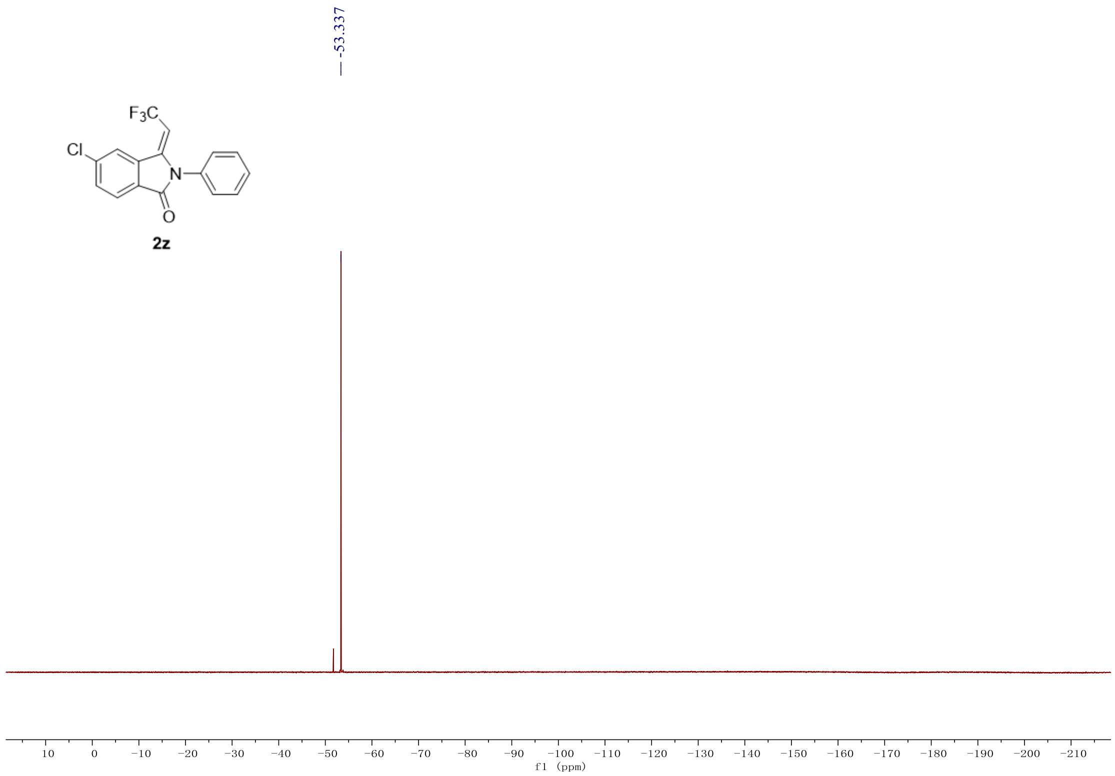
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2z



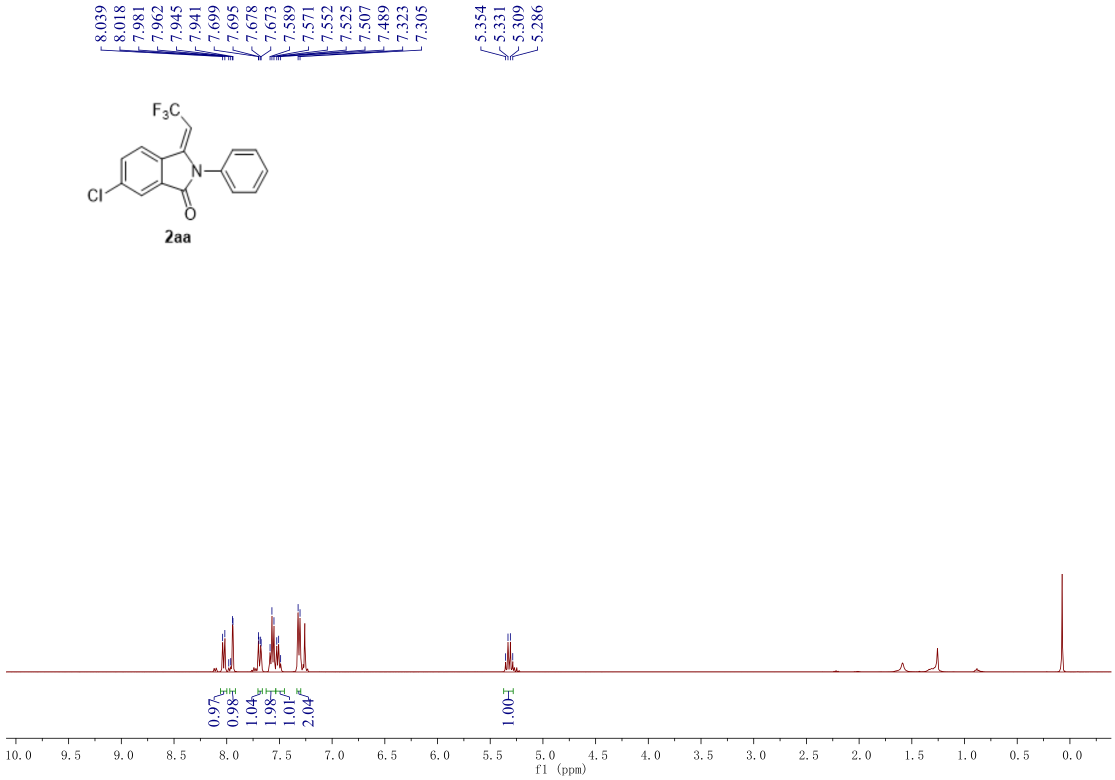
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2z



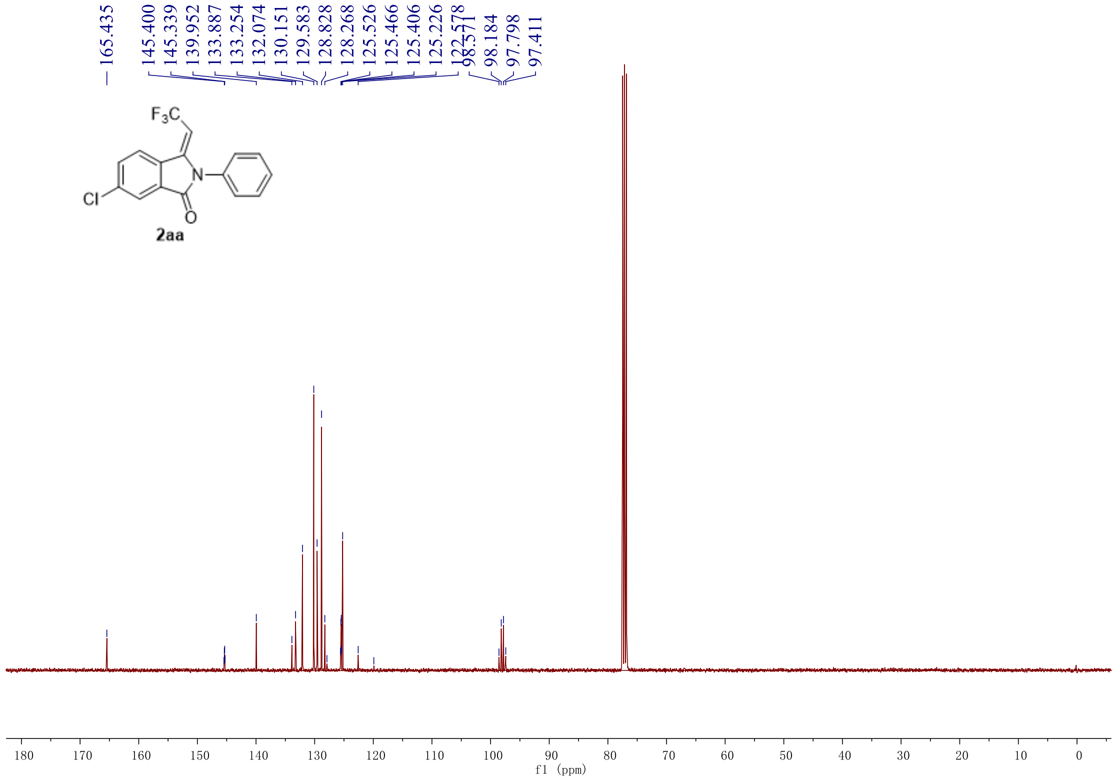
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2z



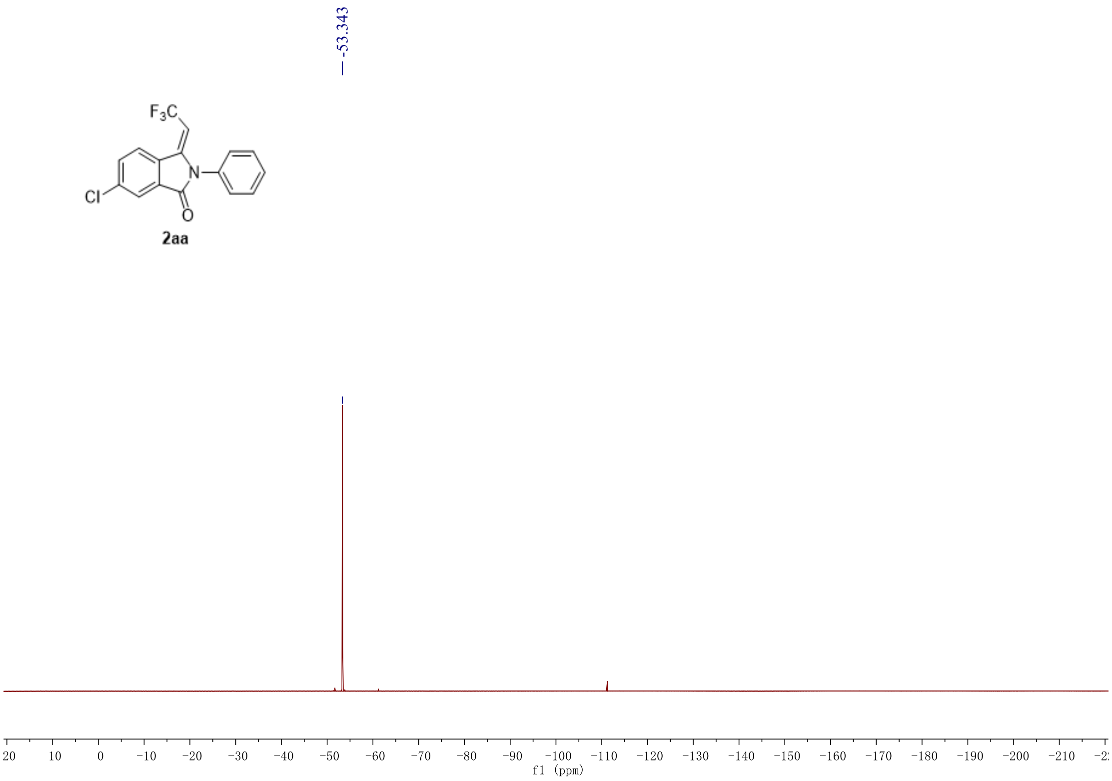
^1H NMR spectrum (400 MHz, $CDCl_3$) of compound 2aa



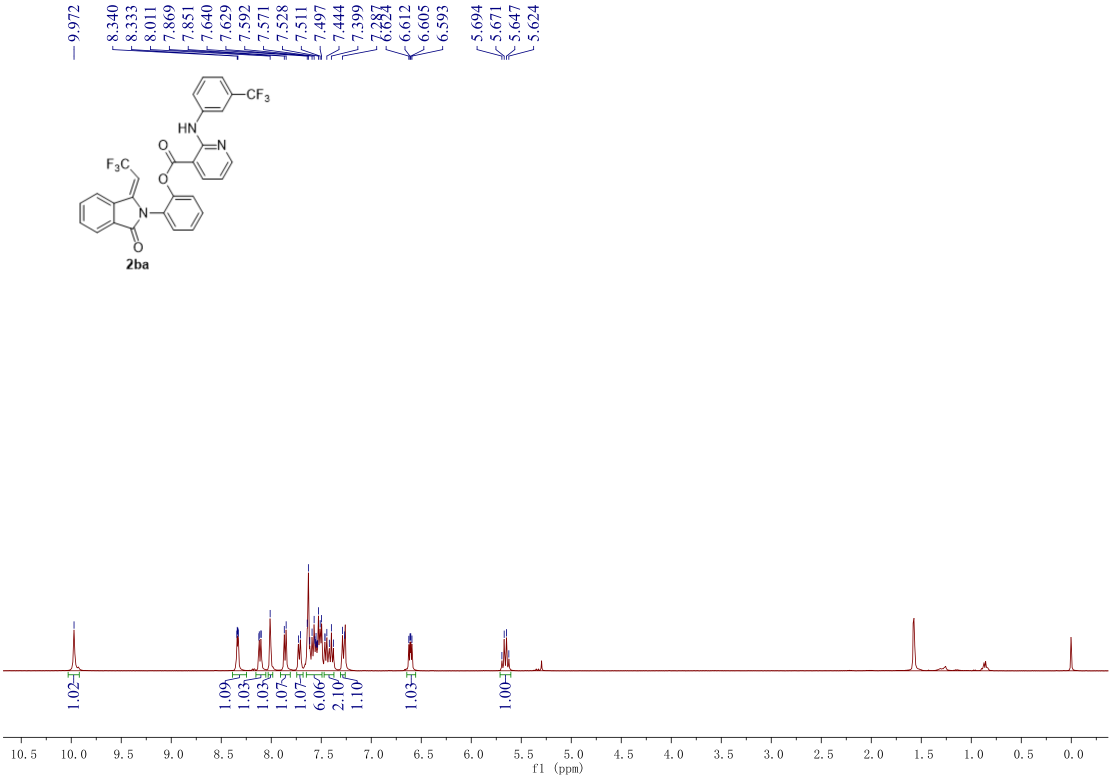
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2aa



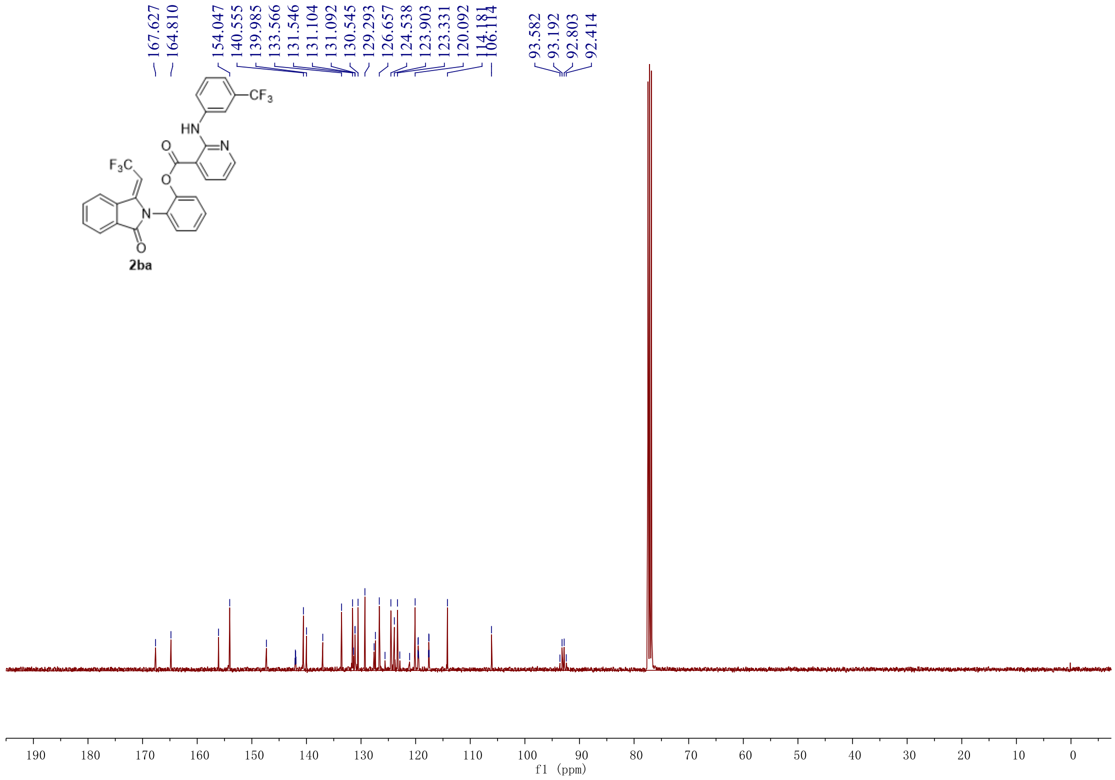
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2aa



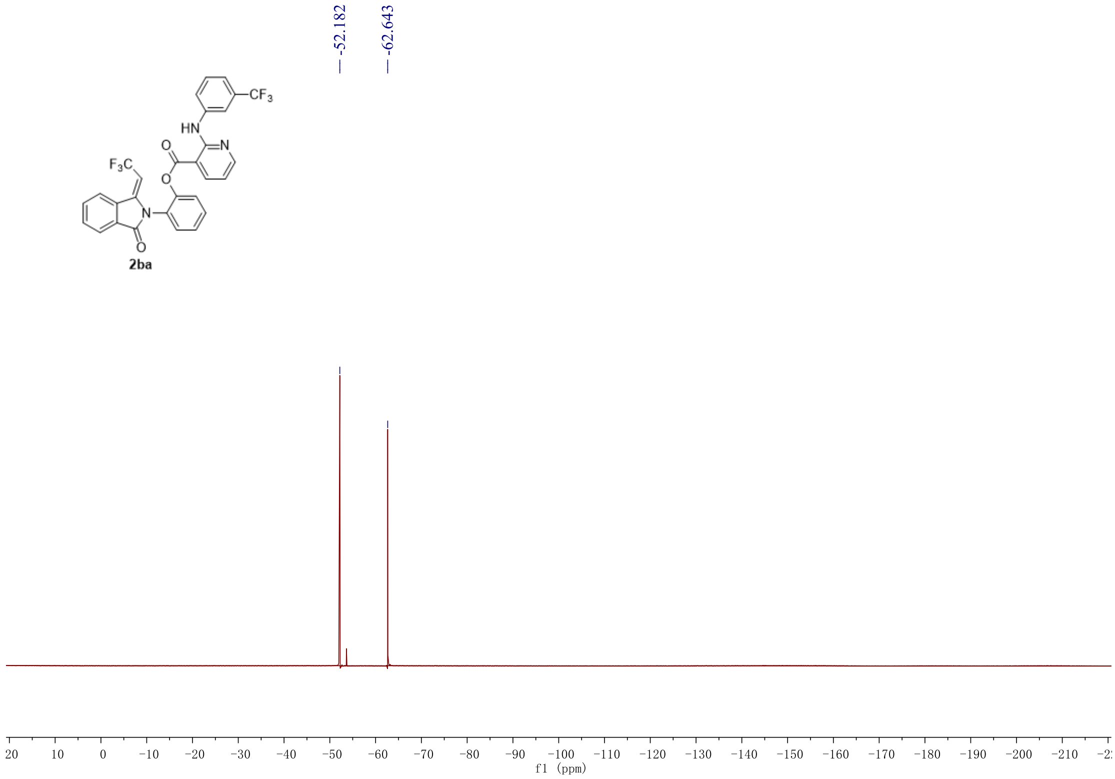
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2ba



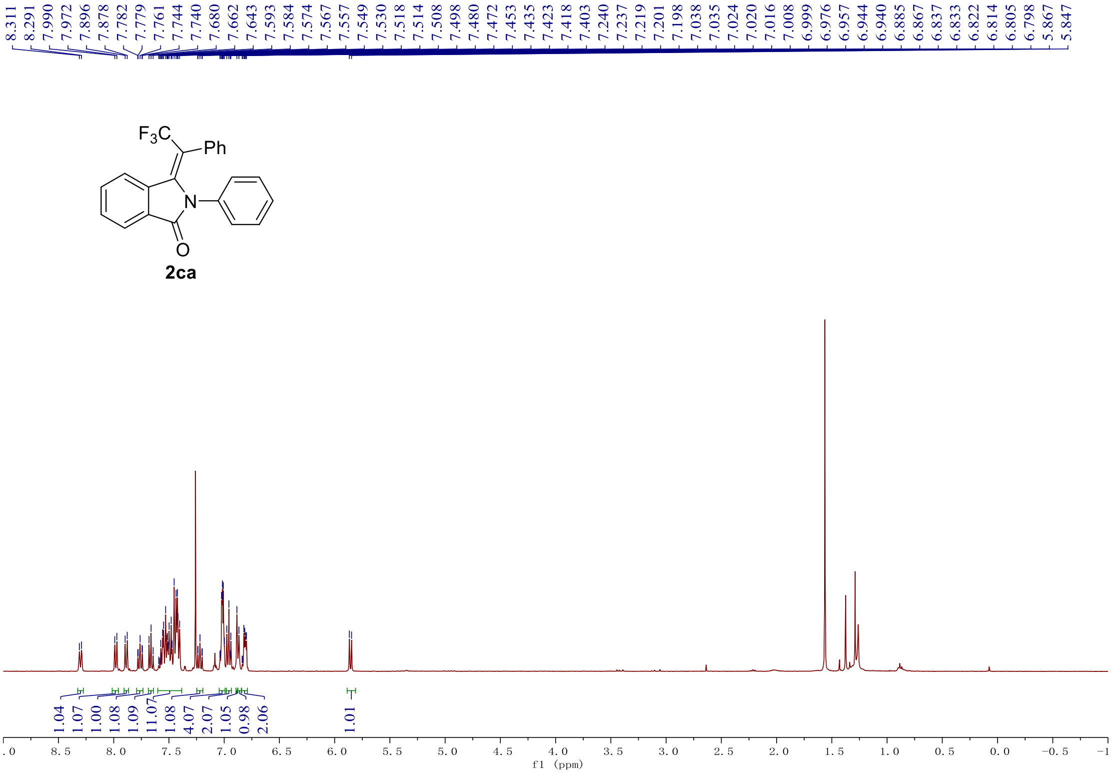
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2ba



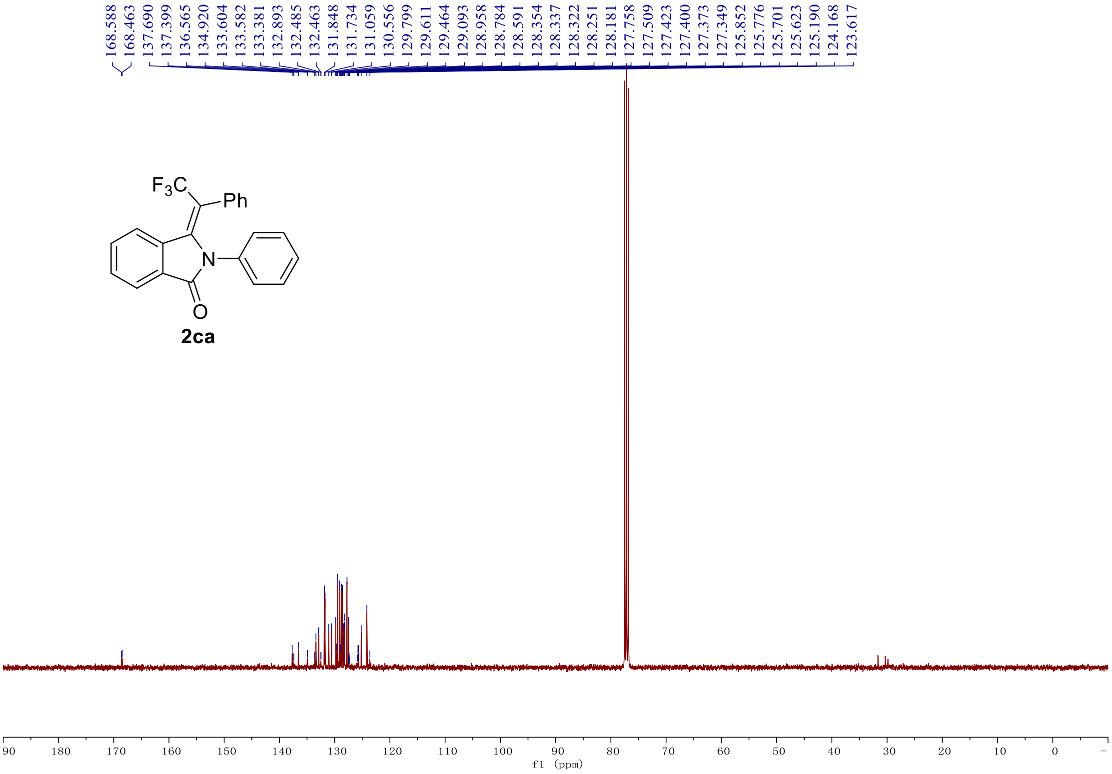
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 2ba



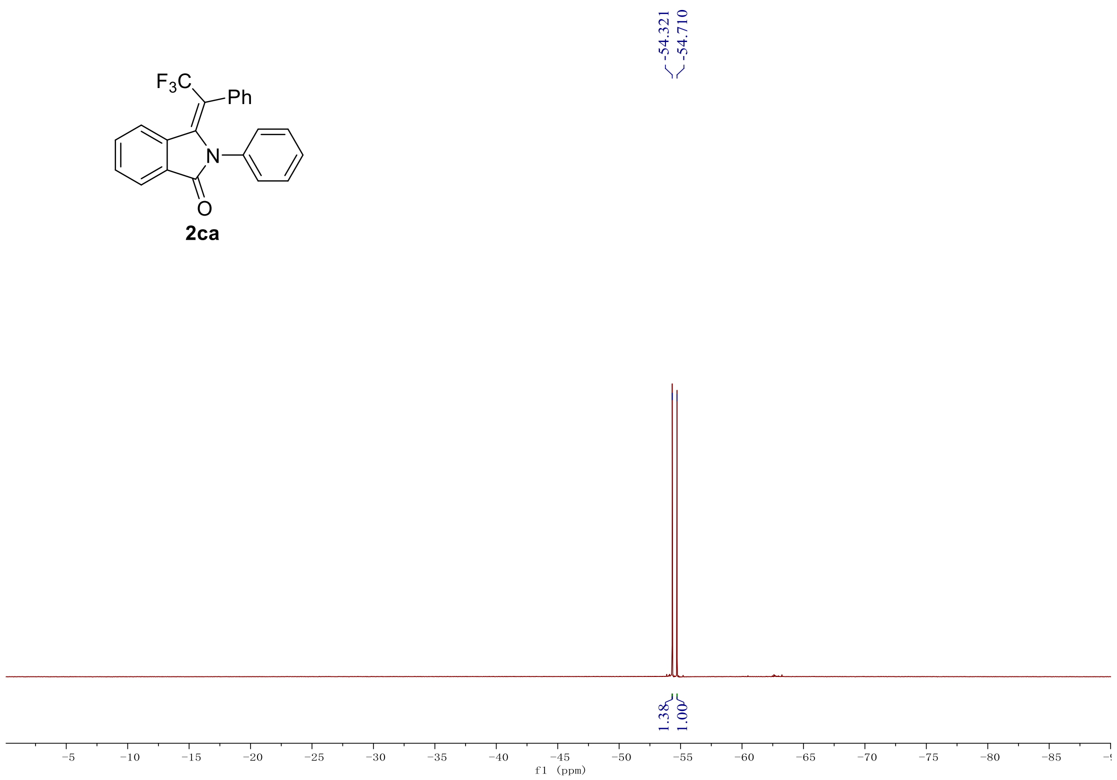
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound 2ca



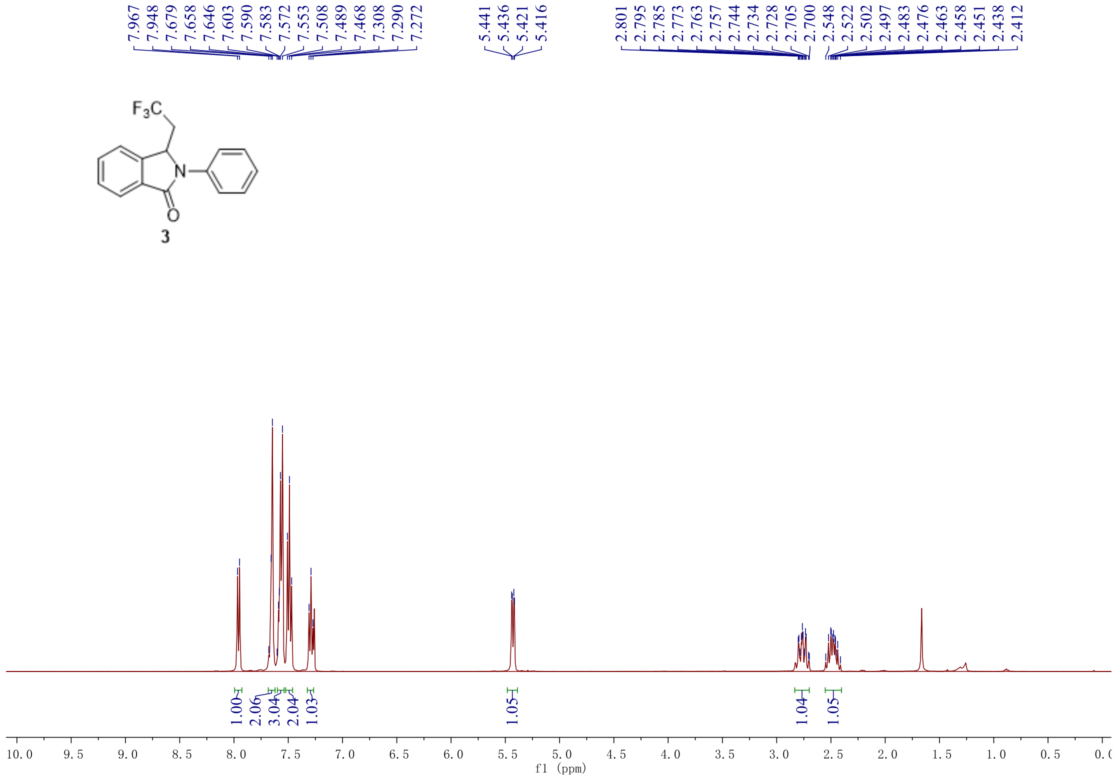
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 2ca



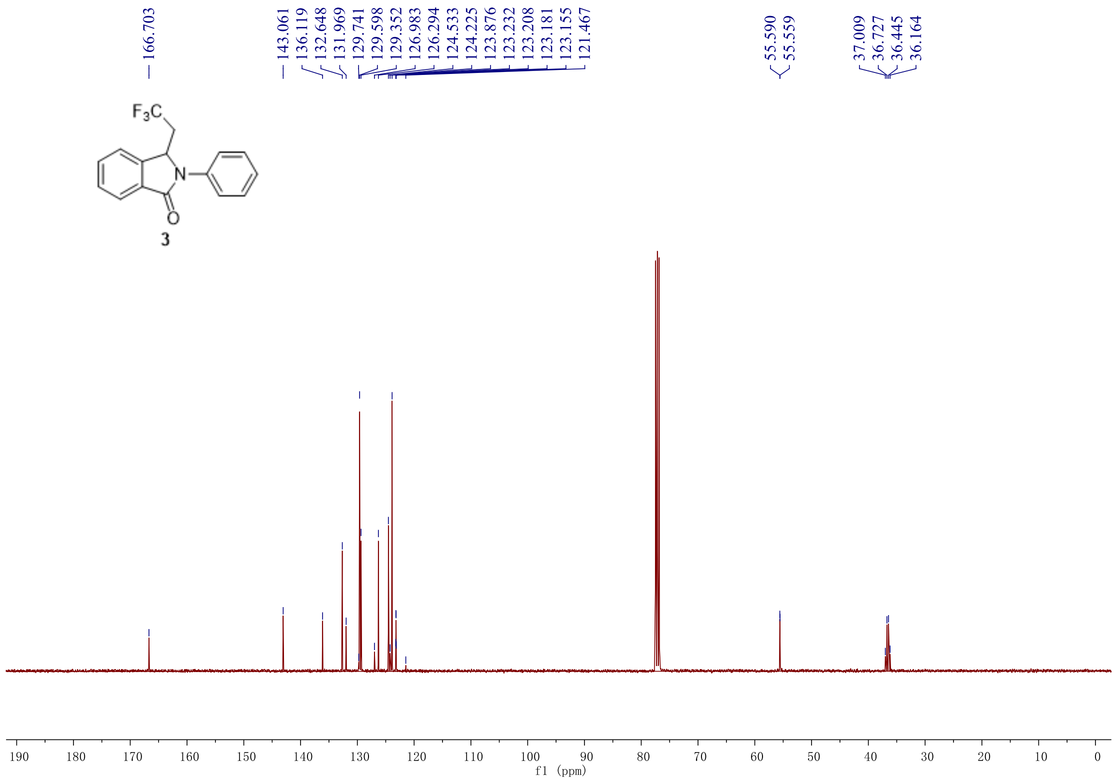
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 2ca



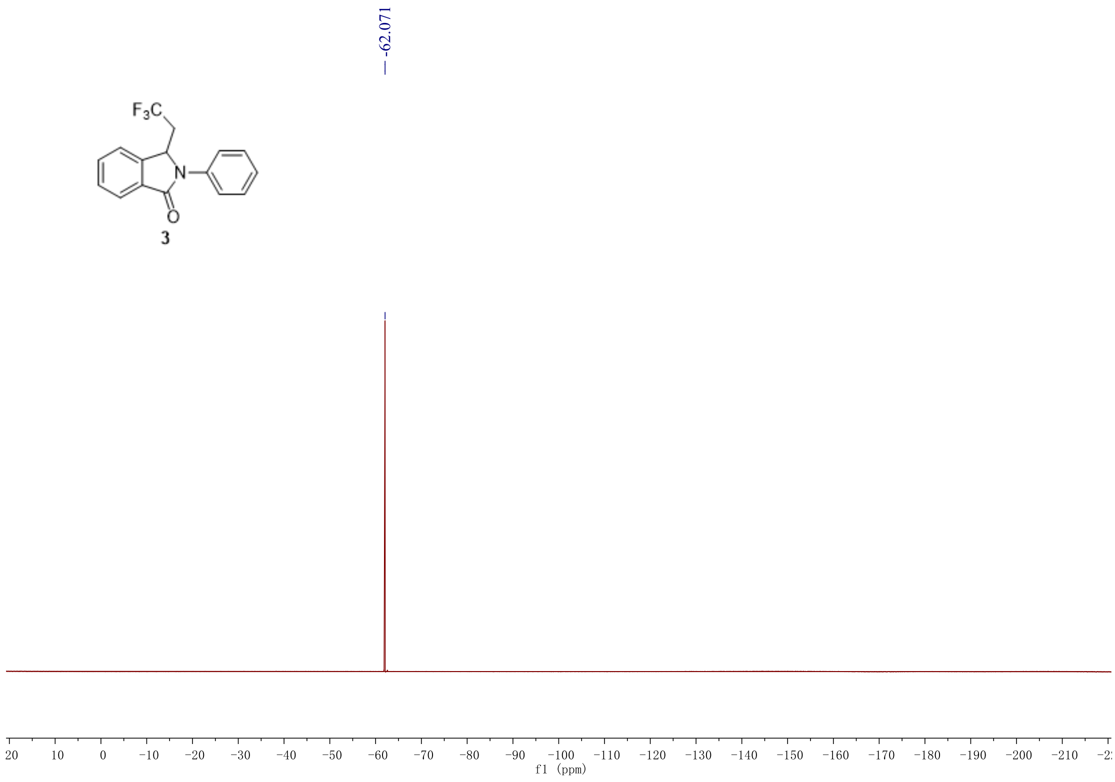
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 3



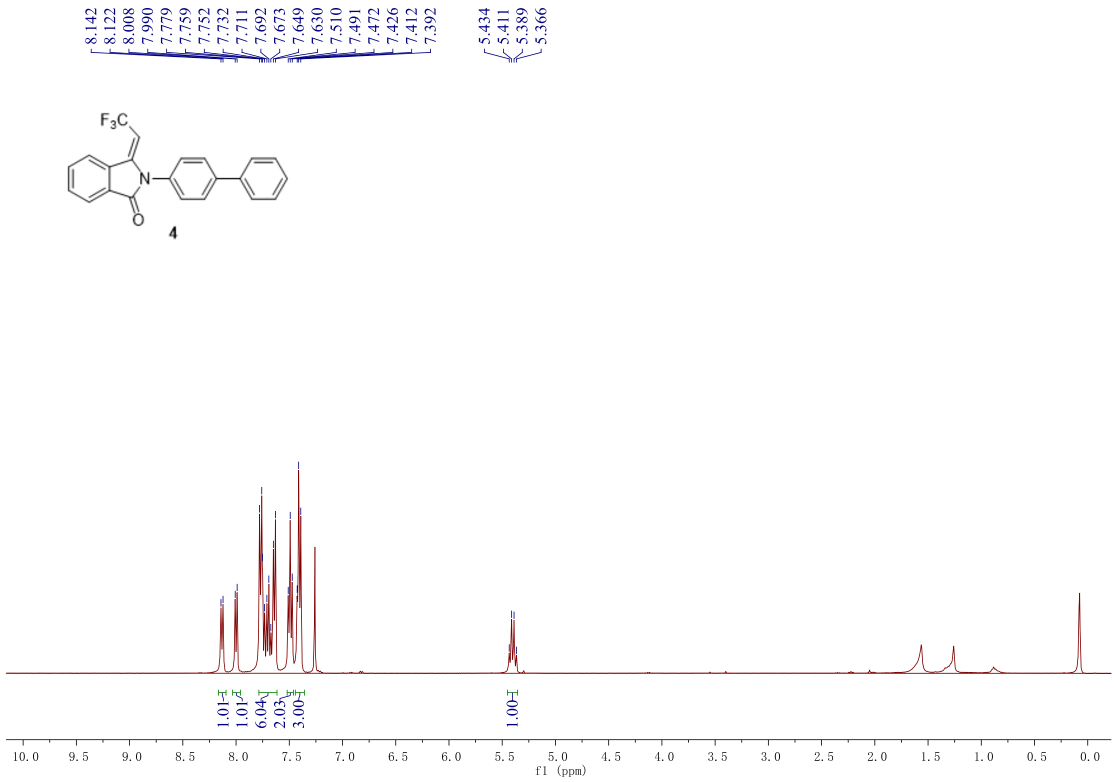
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 3



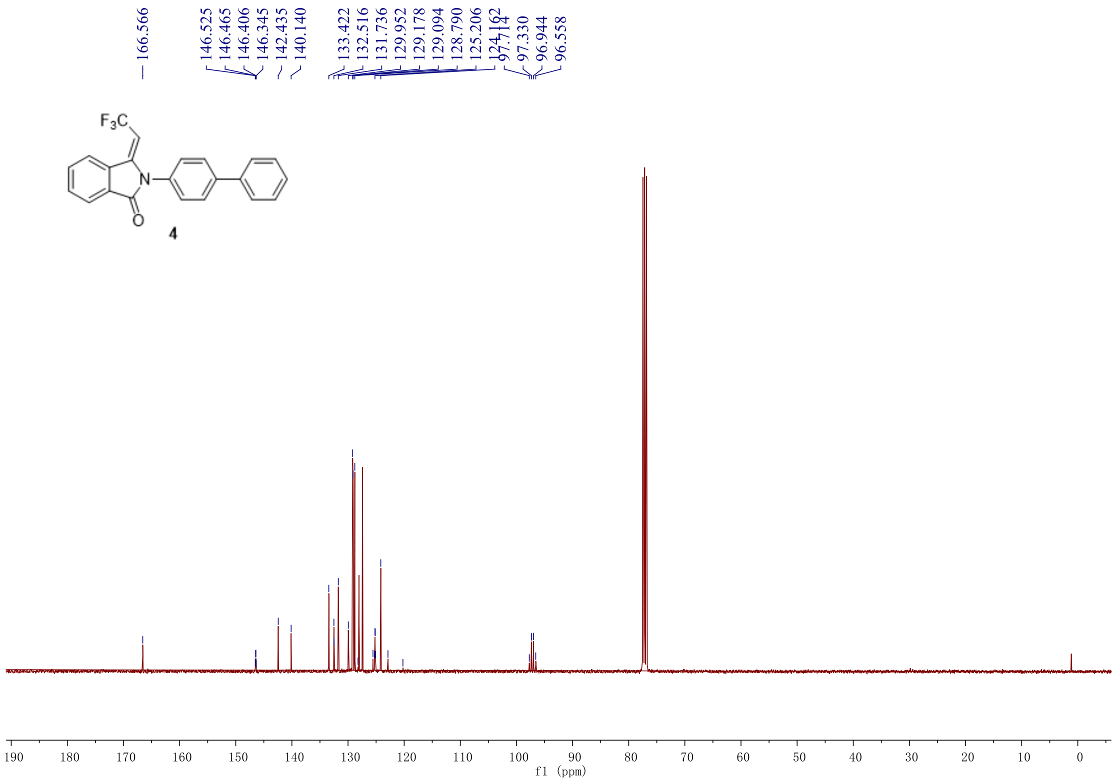
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound 3



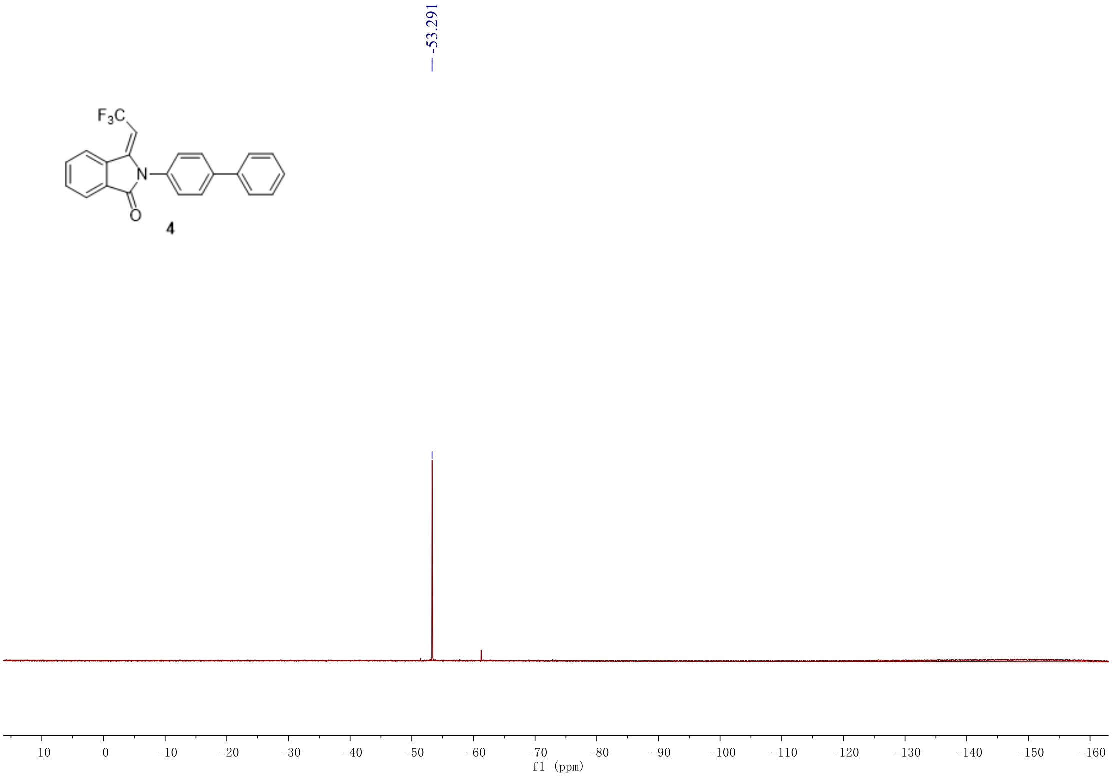
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 4



^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound 4



^{19}F NMR spectrum (376 MHz, CDCl$_3$) of compound 4



4

F3C
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f1 (ppm)