Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Domino Sonogashira coupling/metal carbene-involved annulation enabled by Pd/Cu relay catalysis: rapid assembly of indazole-containing biheteroaryls

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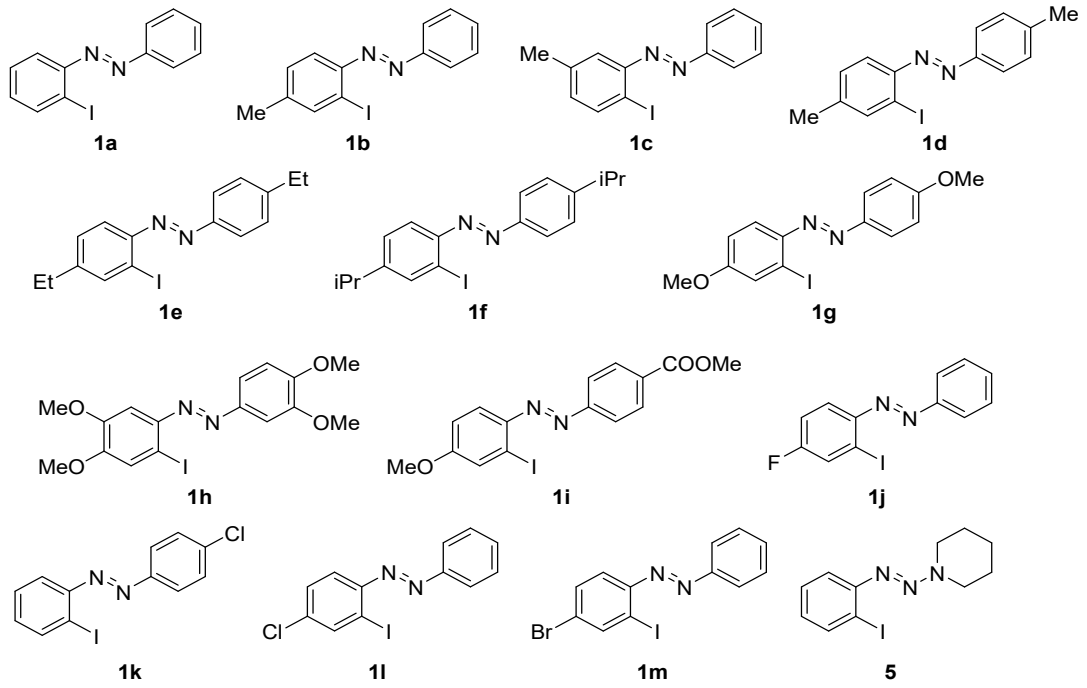
1. General Information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube, solvents were purified by standard method. Unless specified, all metal complexes, reagents, and starting materials were purchased from commercial sources and used as received. Metal salts were stored in a nitrogen atmosphere dry box. Acetonitrile, methanol, toluene, THF, Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 MHz or 600 MHz spectrometers. ^1H and ^{13}C-NMR chemical shifts were determined relative to internal standard TMS at 0.0, $CDCl_3$ (δ (^1H), 7.26 ppm; δ (^{13}C), 77.16 ppm). The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integrations. High-resolution mass spectra (HRMS) were recorded on an Agilent 6545B series Q-TOF LCMS with electronspray ionization (ESI).

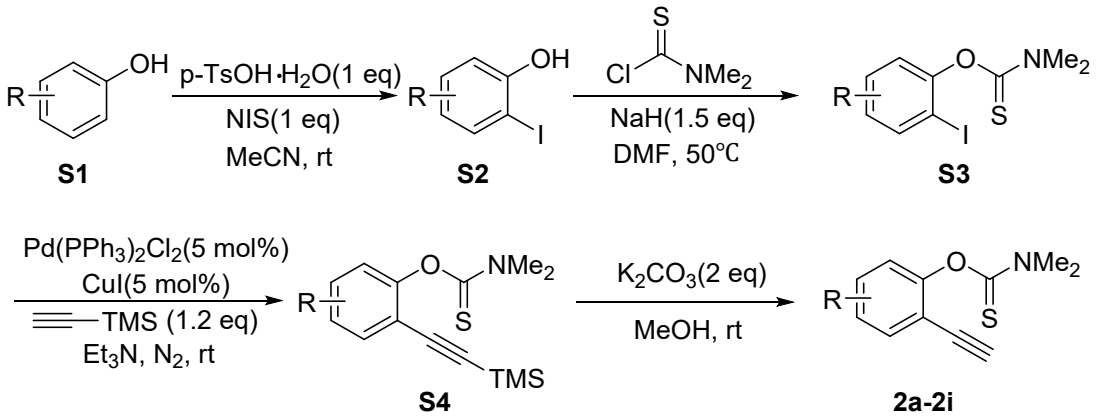
2. Known Starting Materials and General Synthetic Procedure

2.1 Substrate 1a-1m:



All starting materials **1a-1m and 5** are known compounds. Starting materials **(1a-1m, 5)** were prepared according to the literature. [1]

2.2 General Procedure for the Synthesis of 2a-2i[2]:



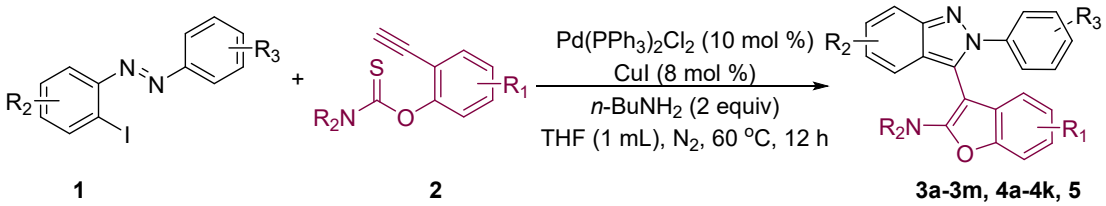
To a solution of the corresponding phenol **S1** (10 mmol, 1.0 equiv) in CH_3CN (2 M) at room temperature was added p-TsOH monohydrate (10 mmol, 1.0 equiv). After 10 min, added NIS (10 mmol, 1 equiv) to the reaction mixture. The mixture was

stirred for 8 h at room temperature and quenched by addition of aqueous Na_2SO_3 solution. It was acidified by addition of aqueous HCl (1 M), the organic solvent was evaporated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried with $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc: 6/1), giving the expected product **S2** (81– 93% yields).

To a solution of **S2** (10 mmol) in DMF (30 mL) containing NaH (15 mmol, 1.5 equiv) was added thiocarbamoyl chloride (15 mmol, 1.5 equiv) in one portion. The temperature rose rapidly to 50 ℃, and the mixture was stirred at this temperature for 5 h. Once the reaction was completed, water was added (30 mL) and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with 5% HCl (20 mL), 1 M NaOH (20 mL), and brine (20 mL),dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc: 5/1), giving the expected product **S3** (68 – 79% yields).

To a **S3** (10 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$(0.5 mmol, 0.05equiv), and copper(I) iodide (0.5 mmol, 0.05 equiv) in 30 mL of triethylamine, a solution of trimethylsilyl acetylene (12 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for overnight under N_2 atmosphere. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator. A portion of the crude product(S4) was directly subjected for the next step. A mixture of **S4** (10 mmol), anhydrous potassium carbonate (20 mmol, 2equiv) in anhydrous MeOH (30 mL) was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure, and the residue was mixed with 20 mL of aqueous sodium bicarbonate and extracted with EtOAc (20 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc:20/1), giving the expected product **2a-2i** (65 – 84% yields).

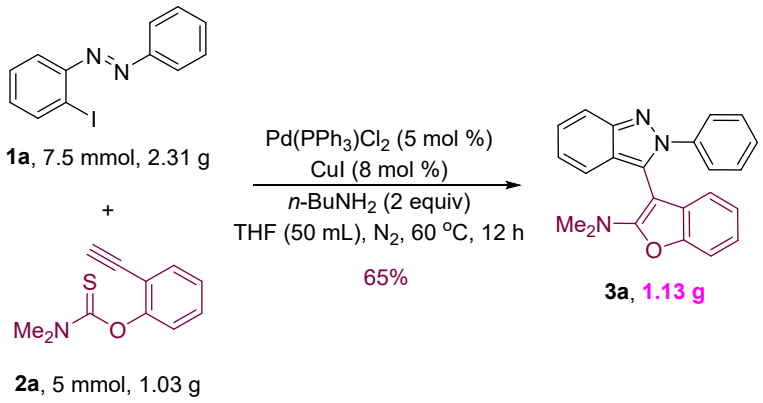
3. General Procedure for Domino reaction



1 **2** **3a-3m, 4a-4k, 5**

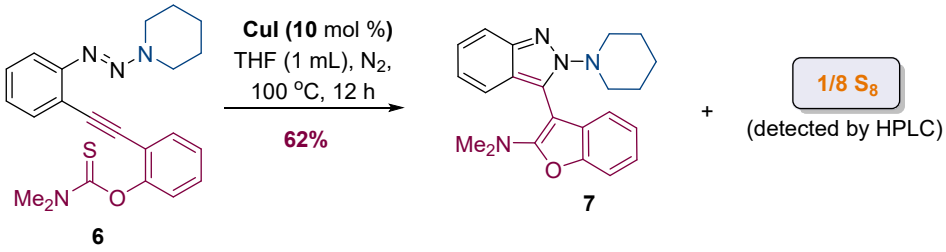
General procedure: **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$(14.1 mg, 0.02 mmol, 10 mol%), and copper(I) iodide (3.1 mg, 0.016 mmol, 8 mol%) in 1 mL of THF, a solution of triethylamine (54 uL, 0.4 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred at 60 ℃ for 12 h under N_2 atmosphere. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography (petroleum: ether/EtOAc = 30/1-10/1), giving the expected product **3a-3m, 4a-4k, 5**.

4. Gram-Scale Reaction for the Synthesis of 3a



1a (2.31 g, 7.5 mmol, 1.5 equiv), **2a** (1.03 g, 5.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$(175.5 mg, 0.25 mmol, 5 mol %), and copper(I) iodide (76.2 mg, 0.4 mmol, 8 mol%) in 50 mL of THF, a solution of triethylamine (1.33 mL, 10.0 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred at 60 ℃ for 12 h under N_2 atmosphere. After the reaction was completed, the solvent was evaporated and the organic product purified by column chromatography (petroleum: ether/EtOAc = 30/1-10/1), giving the expected product **3a** (1.13 g, 65%) as a yellow solid.

5. Mechanistic studies



The treatment of intermediate **6** with CuI (10 mol %) at 100 °C for 12 h delivered the desired biheteroaryl **7** in 62% yield (Figure 5b). In this reaction, the elemental sulfur was also detected by HPLC. See below:

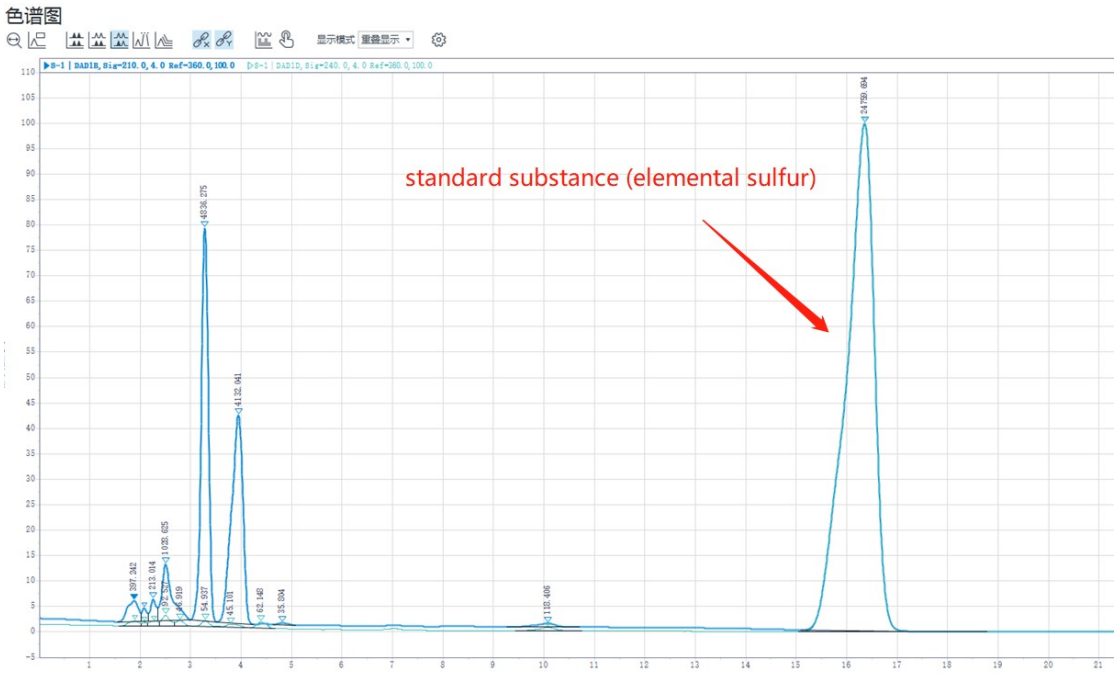


Fig. S1 Standard substance (elemental sulfur) by HPLC analysis

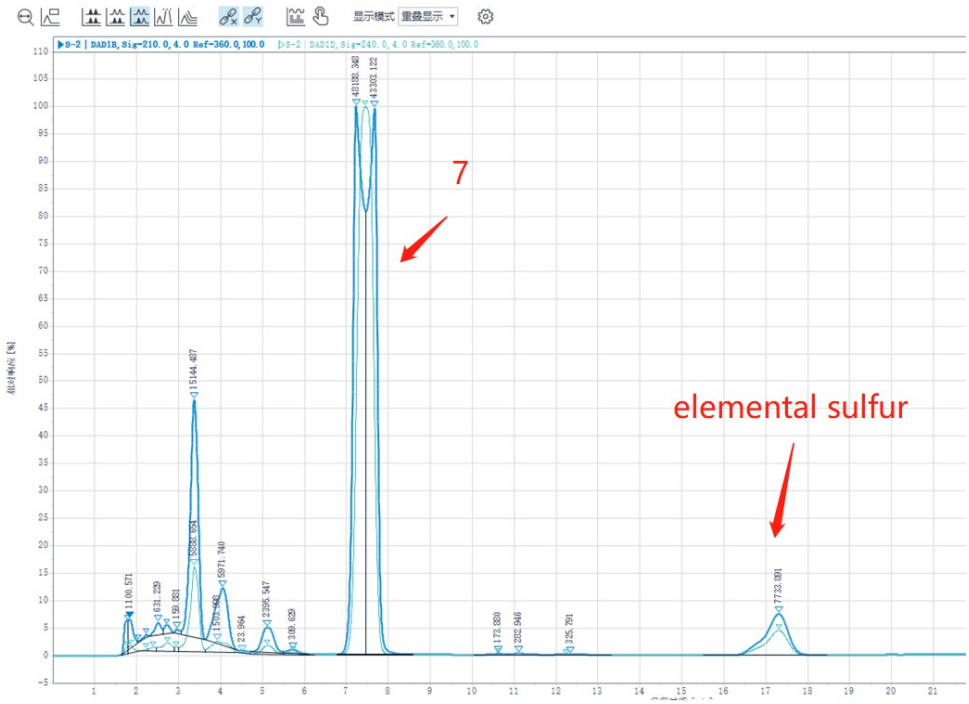


Fig. S2 The reaction mixture by HPLC analysis

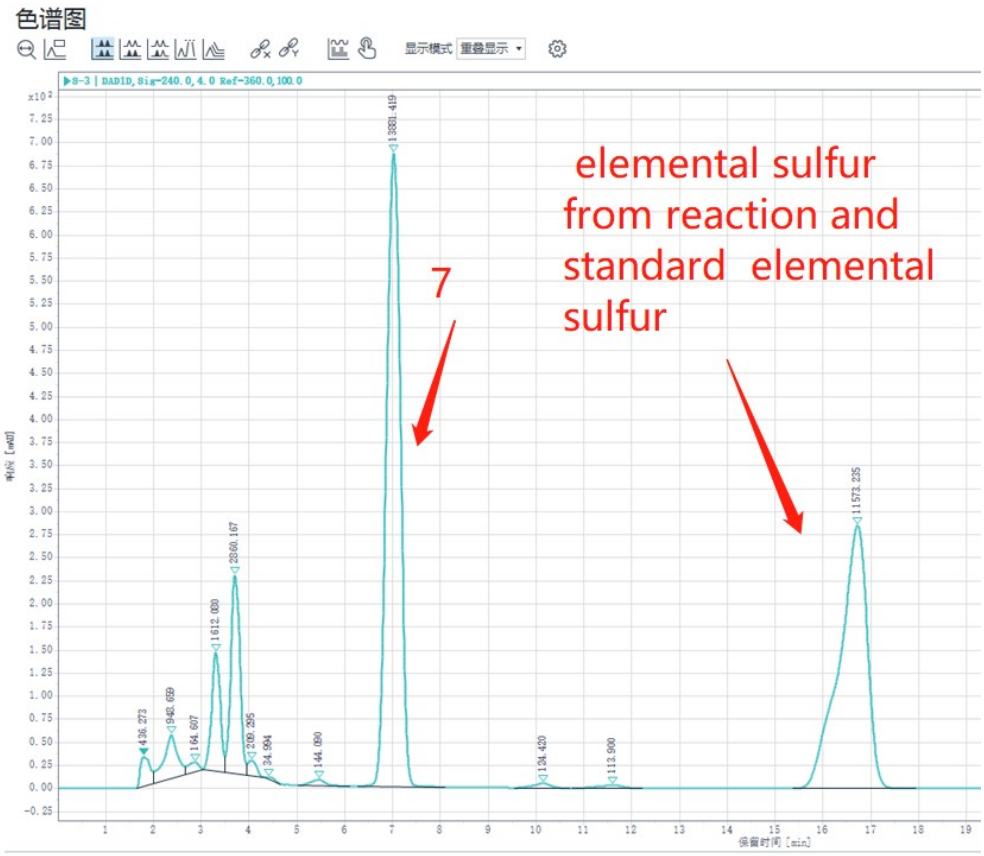
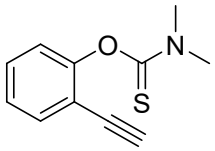


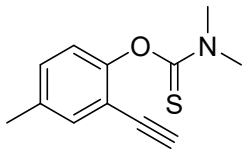
Fig. S3 The reaction mixture and standard substance (elemental sulfur) by HPLC analysis

6. Characterization of Products



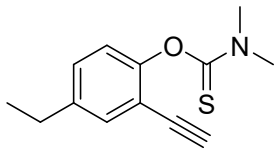
2a

***O*-(2-Ethynylphenyl) dimethylcarbamothioate** (**2a**) Yield 82%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.54 (dd, J = 7.7, 1.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.22 (td, J = 7.6, 1.2 Hz, 1H), 7.12 (dd, J = 8.2, 1.2 Hz, 1H), 3.47 (s, 3H), 3.39 (s, 3H), 3.20 (s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 187.0, 155.3, 133.7, 129.8, 126.0, 124.0, 117.0, 81.9, 78.8, 43.4, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}NOS^+$ 206.0634; Found: 206.0641.



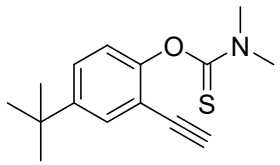
2b

***O*-(2-Ethynyl-4-methylphenyl) dimethylcarbamothioate** (**2b**) Yield 88%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.34 (d, J = 2.2 Hz, 1H), 7.18 (dd, J = 8.3, 2.2 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 3.46 (s, 3H), 3.37 (s, 3H), 3.16 (s, 1H), 2.33 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 187.3, 153.2, 135.7, 134.0, 130.6, 123.5, 116.5, 81.5, 78.9, 43.4, 38.9, 20.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}NOS^+$ 220.0791; Found: 220.0794.



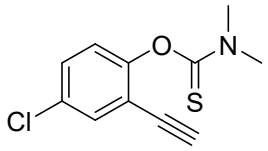
2c

***O*-(4-Ethyl-2-ethynylphenyl) dimethylcarbamothioate** (**2c**) Yield 36%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.36 (d, J = 2.3 Hz, 1H), 7.21 (dd, J = 8.3, 2.2 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 3.46 (s, 3H), 3.37 (s, 3H), 3.17 (s, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 187.3, 153.3, 141.9, 132.8, 129.4, 123.6, 116.5, 81.4, 79.1, 43.4, 38.9, 28.2, 15.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}NOS^+$ 234.0947; Found: 234.0954.



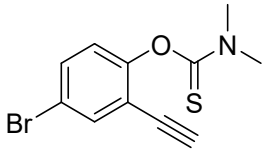
2d

***O*-(4-(Tert-butyl)-2-ethynylphenyl) dimethylcarbamothioate** (**2d**) Yield 57%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.74 (d, J = 2.5 Hz, 1H), 7.61 (dd, J = 8.6, 2.5 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 3.67 (s, 3H), 3.58 (s, 3H), 3.38 (s, 1H), 1.52 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 187.2, 153.0, 148.8, 130.7, 127.1, 123.2, 116.0, 81.2, 79.4, 43.4, 38.9, 34.6, 31.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}NOS^+$ 262.1260; Found: 262.1268.



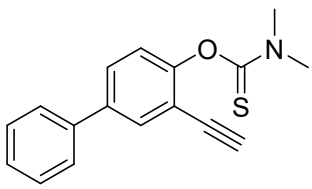
2e

***O*-(4-Chloro-2-ethynylphenyl) dimethylcarbamothioate** (**2e**) Yield 46%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.49 (d, J = 2.6 Hz, 1H), 7.34 (dd, J = 8.7, 2.6 Hz, 1H), 7.06 (d, J = 8.7 Hz, 1H), 3.45 (s, 3H), 3.37 (s, 3H), 3.24 (s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.6, 153.8, 133.2, 131.2, 129.9, 125.3, 118.5, 83.1, 77.6, 43.5, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}ClNOS^+$ 240.0244; Found: 240.0246.



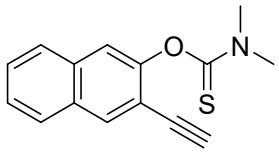
2f

***O*-(4-Bromo-2-ethynylphenyl) dimethylcarbamothioate** (**2f**) Yield 44%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.65 (d, J = 2.5 Hz, 1H), 7.49 (dd, J = 8.7, 2.5 Hz, 1H), 7.00 (d, J = 8.7 Hz, 1H), 3.45 (s, 3H), 3.37 (s, 3H), 3.24 (s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.5, 154.3, 136.1, 132.8, 125.6, 119.0, 118.8, 83.2, 77.5, 43.5, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}BrNOS^+$ 283.9739; Found: 283.9735.



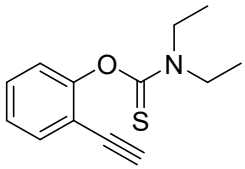
2g

***O*-(3-Ethynyl-[1,1'-biphenyl]-4-yl) dimethylcarbamothioate** (**2g**) Yield 41%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.76 (d, J = 2.3 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.46 – 7.41 (m, 2H), 7.39 – 7.33 (m, 1H), 7.20 (d, J = 8.5 Hz, 1H), 3.49 (s, 3H), 3.41 (s, 3H), 3.23 (s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 187.0, 154.6, 139.6, 139.2, 132.3, 129.0, 128.5, 127.8, 127.2, 124.3, 117.2, 82.0, 78.9, 43.5, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NOS^+$ 282.0947; Found:282.0954.



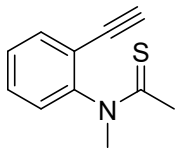
2h

***O*-(3-Ethynylnaphthalen-2-yl) dimethylcarbamothioate** (**2h**) Yield 64%, white solid, (Eluent: petroleum ether/ethyl acetate= 15/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 8.33 (dd, J = 8.4, 1.1 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.59 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.51 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.32 (d, J = 8.9 Hz, 1H), 3.64 (s, 1H), 3.49 (s, 3H), 3.44 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.9, 154.4, 134.1, 131.2, 129.7, 128.3, 127.5, 126.3, 126.1, 122.7, 112.6, 86.9, 43.4, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NOS^+$ 256.0791; Found:256.0794.



2i

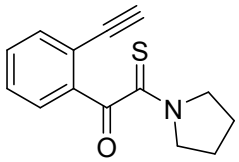
O-**(2-Ethynylphenyl) diethylcarbamothioate** (**2i**) Yield 79%, white solid, (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.53 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 (ddd, J = 8.2, 7.5, 1.7 Hz, 1H), 7.21 (td, J = 7.6, 1.2 Hz, 1H), 7.11 (dd, J = 8.2, 1.1 Hz, 1H), 3.90 (q, J = 7.1 Hz, 2H), 3.73 (q, J = 7.1 Hz, 2H), 3.18 (s, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.1, 155.3, 133.7, 129.8, 125.9, 123.9, 117.1, 81.9, 79.1, 48.5, 44.5, 13.5, 11.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}NOS^+$ 234.0947; Found:234.0951.



2j

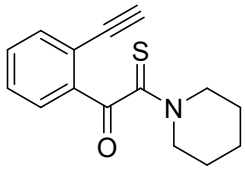
***N*-(2-Ethynylphenyl)-*N*-methylethanethioamide** (**2j**) Yield 55%, white solid, (Eluent: petroleum ether/ethyl acetate= 5/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ

7.59 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.45 (td, *J* = 7.7, 1.6 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.20 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.71 (d, *J* = 0.7 Hz, 3H), 3.29 (s, 1H), 2.37 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** *δ* 202.1, 147.9, 134.1, 130.5, 128.8, 126.1, 119.8, 83.3, 78.5, 44.6, 33.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}NS^+$ 190.0685; Found: 190.0687.



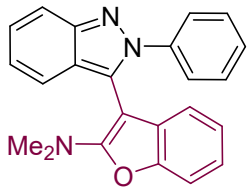
2k

1-(2-Ethynylphenyl)-2-(pyrrolidin-1-yl)-2-thioxoethan-1-one (**2k**) Yield 52%, cyan solid, (Eluent: petroleum ether/ethyl acetate= 10/1). **^{1}H NMR (600 MHz, Chloroform-d)** *δ* 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.47 (td, *J* = 7.6, 1.5 Hz, 1H), 3.86 (tdd, *J* = 5.5, 2.6, 1.2 Hz, 2H), 3.81 – 3.72 (m, 2H), 3.35 (s, 1H), 2.16 – 2.02 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** *δ* 192.5, 187.3, 137.0, 135.0, 132.6, 131.0, 129.2, 121.5, 83.5, 81.5, 51.8, 51.5, 26.1, 24.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NOS^+$ 244.0791; Found:244.0791.



2l

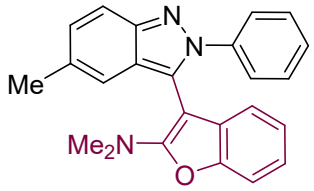
1-(2-Ethynylphenyl)-2-(piperidin-1-yl)-2-thioxoethan-1-one (**2l**) Yield 50%, cyan solid, (Eluent: petroleum ether/ethyl acetate= 10/1). **^{1}H NMR (600 MHz, Chloroform-d)** *δ* 7.97 – 7.93 (m, 1H), 7.61 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.45 (td, *J* = 7.6, 1.4 Hz, 1H), 4.17 (t, *J* = 5.6 Hz, 2H), 3.69 – 3.59 (m, 2H), 3.41 (s, 1H), 1.85 – 1.80 (m, 2H), 1.78 (ddd, *J* = 10.9, 8.1, 4.9 Hz, 2H), 1.73 (tq, *J* = 8.4, 5.4, 4.4 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** *δ* 194.7, 186.0, 136.7, 135.5, 132.7, 131.1, 129.0, 121.9, 83.9, 81.8, 53.4, 48.4, 26.1, 25.2, 24.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NOS^+$ 258.0947; Found:258.0947.



3a

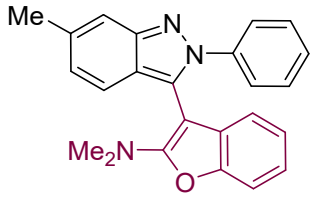
***N*,*N*-Dimethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine** (**3a**) was obtained as a yellow solid (62 mg, 88%). (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** *δ* 7.81 (dt, *J* = 9.0, 1.0 Hz, 1H), 7.58 (ddt, *J* = 8.0, 6.8, 1.3 Hz, 3H), 7.39 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 7.09 (ddd, *J* = 8.5, 6.5, 0.9

Hz, 1H), 7.05 – 7.01 (m, 2H), 6.92 – 6.88 (m, 1H), 2.68 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.0, 149.5, 149.2, 140.7, 131.8, 129.1, 128.6, 128.1, 127.2, 124.6, 124.3, 123.3, 122.0, 121.2, 120.7, 118.0, 117.0, 109.6, 81.0, 39.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N_3O^+$ 354.1601; Found: 354.1596.



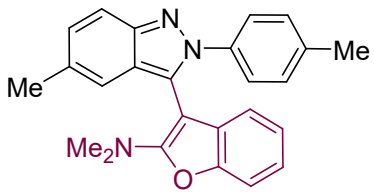
3b

***N*,*N*-Dimethyl-3-(5-methyl-2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine** (**3b**) was obtained as a yellow solid (62 mg, 84%). (Eluent: petroleum ether/ethyl acetate= 20/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.72 (dd, J = 8.8, 0.9 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 3H), 7.21 (dd, J = 8.9, 1.6 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.95 – 6.92 (m, 1H), 2.67 (s, 6H), 2.41 (d, J = 1.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.9, 149.5, 148.2, 140.8, 132.0, 131.4, 130.1, 129.0, 127.9, 127.5, 124.6, 124.5, 123.3, 120.6, 119.0, 117.7, 117.0, 109.6, 81.1, 39.0, 21.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{21}N_3NaO^+$ 390.1577; Found: 390.1580.



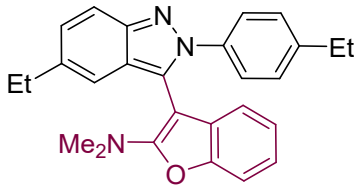
3c

***N*,*N*-Dimethyl-3-(6-methyl-2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine** (**3c**) was obtained as a yellow solid (60 mg, 82%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (400 MHz, Chloroform-d)** δ 7.57 (d, J = 8.2 Hz, 3H), 7.47 (d, J = 8.6 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.03 (dq, J = 5.7, 2.9, 2.3 Hz, 2H), 6.96 – 6.87 (m, 2H), 2.67 (d, J = 2.1 Hz, 6H), 2.49 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.9, 149.8, 149.5, 140.8, 137.1, 131.9, 129.0, 128.3, 127.9, 125.0, 124.5, 123.3, 122.7, 120.7, 120.7, 117.0, 116.2, 109.6, 81.1, 39.1, 22.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}N_3O^+$ 368.1757; Found: 368.1758.



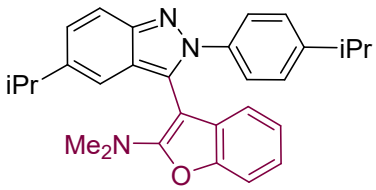
3d

***N*,*N*-Dimethyl-3-(5-methyl-2-(p-tolyl)-2*H*-indazol-3-yl)benzofuran-2-amine** (**3d**) was obtained as a yellow solid (55 mg, 72%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.71 (dd, J = 8.8, 0.9 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.30 – 7.27 (m, 2H), 7.20 (dd, J = 8.9, 1.6 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.07 – 7.02 (m, 2H), 6.94 – 6.92 (m, 1H), 2.68 (s, 6H), 2.40 (d, J = 1.2 Hz, 3H), 2.33 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.9, 149.5, 148.0, 138.3, 137.8, 132.2, 131.3, 129.9, 129.5, 127.3, 124.6, 124.3, 123.2, 120.6, 119.0, 117.6, 117.0, 109.5, 81.0, 39.0, 21.9, 21.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O^+$ 382.1914; Found: 382.1916.



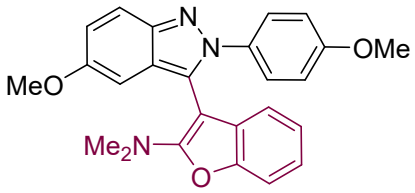
3e

3-(5-Ethyl-2-(4-ethylphenyl)-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (**3e**) was obtained as a yellow solid (68 mg, 72%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.71 (dd, J = 8.9, 0.9 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.32 (dd, J = 1.7, 1.0 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 (dd, J = 8.9, 1.6 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.07 – 7.02 (m, 2H), 6.96 – 6.92 (m, 1H), 2.71 (q, J = 7.5 Hz, 2H), 2.67 (s, 6H), 2.63 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.0, 149.5, 148.2, 144.1, 138.5, 137.8, 132.1, 129.0, 128.3, 127.6, 124.4, 124.4, 123.2, 120.6, 117.7, 117.7, 117.1, 109.5, 81.3, 39.0, 29.3, 28.5, 15.7, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}N_3O^+$ 410.2227; Found: 410.2231.



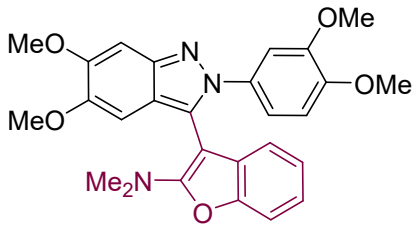
3f

3-(5-Isopropyl-2-(4-isopropylphenyl)-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (**3f**) was obtained as a yellow solid (60 mg, 69%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.75 (dd, J = 8.9, 0.9 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.36 – 7.33 (m, 1H), 7.32 – 7.28 (m, 2H), 7.21 – 7.16 (m, 2H), 7.09 – 7.02 (m, 2H), 6.99 – 6.91 (m, 1H), 2.97 (p, J = 6.9 Hz, 1H), 2.90 (p, J = 6.9 Hz, 1H), 2.66 (s, 6H), 1.29 (dd, J = 6.9, 2.2 Hz, 6H), 1.22 (dd, J = 6.9, 2.8 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.0, 149.5, 148.7, 148.3, 142.3, 138.6, 132.0, 127.7, 127.68, 126.9, 124.4, 124.3, 123.2, 120.6, 117.7, 117.2, 116.3, 109.5, 81.6, 39.0, 34.4, 33.9, 24.2, 24.04, 24.03, 24.00. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{32}N_3O^+$ 438.2540; Found: 438.2539.



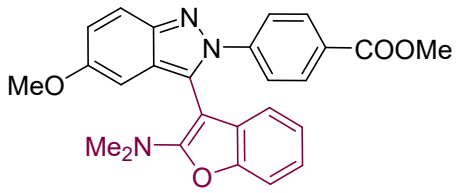
3g

3-(5-Methoxy-2-(4-methoxyphenyl)-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (**3g**) was obtained as a yellow solid (66 mg, 80%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.70 (dd, J = 9.3, 0.7 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.32 – 7.28 (m, 1H), 7.12 – 7.02 (m, 3H), 6.97 – 6.92 (m, 1H), 6.87 – 6.81 (m, 2H), 6.72 (dd, J = 2.4, 0.7 Hz, 1H), 3.77 (d, J = 6.5 Hz, 6H), 2.70 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.0, 157.9, 155.3, 149.5, 145.7, 134.0, 132.1, 127.0, 125.6, 124.1, 123.3, 121.9, 120.5, 119.3, 117.0, 114.1, 109.5, 96.9, 81.0, 55.5, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_3^+$ 414.1812; Found: 414.1808.



3h

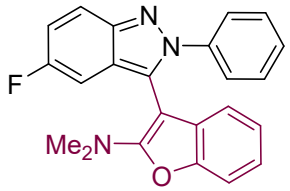
3-(2-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (**3h**) was obtained as a yellow solid (62 mg, 65%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.30 – 7.27 (m, 1H), 7.12 (s, 1H), 7.09 – 7.01 (m, 4H), 6.97 – 6.92 (m, 1H), 6.74 (d, J = 8.6 Hz, 1H), 6.69 (s, 1H), 3.99 (s, 3H), 3.83 (d, J = 8.0 Hz, 6H), 3.52 (s, 3H), 2.67 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.0, 152.3, 149.4, 148.8, 148.3, 148.3, 145.2, 133.8, 132.6, 127.2, 123.5, 120.6, 119.0, 116.7, 116.2, 110.7, 109.6, 108.1, 97.5, 95.9, 80.3, 56.1, 56.1, 56.1, 55.8, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}N_3O_5^+$ 474.2023; Found: 474.2021.



3i

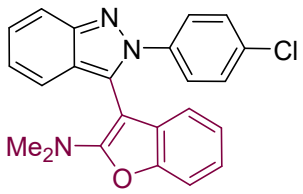
Methyl-4-(3-(2-(dimethylamino)benzofuran-3-yl)-5-methoxy-2*H*-indazol-2-yl)benzoate (**3i**) was obtained as a yellow solid (51 mg, 58%). (Eluent: petroleum

ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.60 (d, J = 8.7 Hz, 2H), 7.30 – 7.23 (m, 3H), 6.92 – 6.87 (m, 1H), 6.68 – 6.61 (m, 3H), 6.51 – 6.47 (m, 1H), 6.28 (d, J = 2.4 Hz, 1H), 3.48 (s, 3H), 3.35 (s, 3H), 2.28 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.5, 157.9, 155.6, 149.5, 146.5, 144.4, 131.7, 130.6, 129.0, 127.5, 124.6, 123.9, 123.5, 123.0, 120.8, 119.5, 116.9, 109.7, 96.7, 80.6, 55.6, 52.4, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}N_3O_4^+$ 442.1761; Found:442.1762.



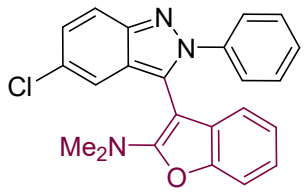
3j

3-(5-Fluoro-2-phenyl-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (3j) was obtained as a yellow solid (68 mg, 92%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (400 MHz, Chloroform-d)** δ 7.79 (dd, *J* = 9.6, 4.4 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.21 – 7.12 (m, 2H), 7.04 (dd, *J* = 6.2, 3.2 Hz, 2H), 6.88 (dd, *J* = 6.1, 3.1 Hz, 1H), 2.69 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.50 (d, *J* = 240.6 Hz), 158.0, 149.5, 146.5, 140.6, 131.7, 129.1, 128.8 (d, *J* = 8.6 Hz), 128.2, 124.5, 123.5 (d, *J* = 11.1 Hz), 123.4, 120.8, 120.1 (d, *J* = 9.6 Hz), 118.8 (d, *J* = 29.1 Hz), 116.9, 109.6, 103.5, 103.3, 80.5, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}FN_3O^+$ 372.1507; Found:372.1507.



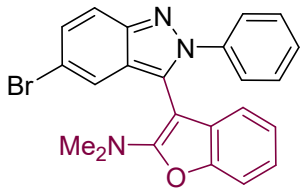
3k

3-(2-(4-Chlorophenyl)-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (3k) was obtained as a yellow solid (64 mg, 83%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.79 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.37 (ddd, *J* = 8.8, 6.6, 1.1 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.09 (ddd, *J* = 8.6, 6.5, 0.9 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.89 – 6.85 (m, 1H), 2.71 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.9, 149.4, 149.2, 139.2, 133.7, 131.6, 129.1, 128.6, 127.3, 125.6, 124.3, 123.3, 122.1, 121.0, 120.7, 117.8, 116.8, 109.6, 80.3, 39.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}ClN_3O^+$ 388.1211; Found:388.1214.



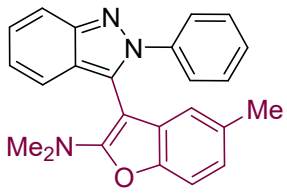
3l

3-(5-Chloro-2-phenyl-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (3l) was obtained as a yellow solid (68 mg, 88%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (400 MHz, Chloroform-d)** δ 7.78 (dd, J = 9.2, 2.1 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.41 – 7.28 (m, 5H), 7.07 (dt, J = 5.8, 2.3 Hz, 2H), 6.91 (dd, J = 5.9, 3.0 Hz, 1H), 2.69 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.0, 149.5, 147.5, 140.4, 131.7, 129.1, 128.6, 128.5, 128.3, 127.6, 124.6, 124.5, 123.4, 120.8, 119.7, 119.6, 116.8, 109.7, 80.1, 39.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}ClN_3O^+$ 388.1211; Found:388.1212.



3m

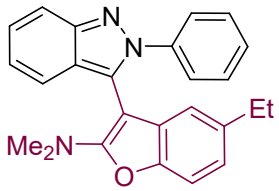
3-(5-Bromo-2-phenyl-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (3m) was obtained as a yellow solid (81 mg, 94%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (400 MHz, Chloroform-d)** δ 7.78 – 7.66 (m, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.35 (ddd, J = 28.5, 19.8, 7.4 Hz, 5H), 7.05 (dd, J = 6.0, 3.0 Hz, 2H), 6.92 – 6.85 (m, 1H), 2.69 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.0, 149.4, 147.5, 140.4, 131.7, 130.8, 129.1, 128.3, 125.4, 124.5, 123.5, 123.2, 120.9, 119.8, 116.8, 115.4, 109.7, 80.0, 39.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}BrN_3O^+$ 432.0706; Found:432.0709.



4a

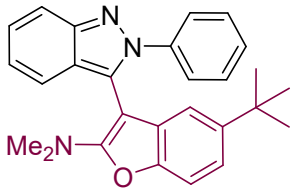
***N*,*N*-5-Trimethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine (4a)** was obtained as a yellow solid (60 mg, 82%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.82 (dt, J = 8.7, 1.0 Hz, 1H), 7.58 (ddt, J = 8.0, 5.2, 1.9 Hz, 3H), 7.36 (dddd, J = 10.9, 8.0, 6.4, 1.4 Hz, 3H), 7.33 – 7.29 (m, 1H), 7.16 (d, J = 8.2 Hz, 1H), 7.10 (ddd, J = 8.4, 6.5, 0.9 Hz, 1H), 6.84 (dd, J = 8.3,

1.7 Hz, 1H), 6.74 – 6.71 (m, 1H), 2.64 (s, 6H), 2.27 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.2, 149.2, 147.9, 140.7, 132.8, 132.0, 129.0, 128.8, 128.0, 127.1, 124.6, 124.2, 121.9, 121.6, 121.2, 118.0, 117.2, 109.1, 80.8, 39.0, 21.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{21}N_3NaO^+$ 390.1577; Found:390.1577.



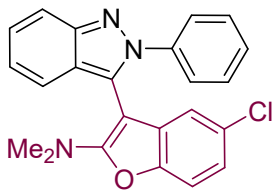
4b

5-Ethyl-*N*,*N*-dimethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine (**4b**) was obtained as a yellow solid (55 mg, 72%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (400 MHz, Chloroform-d)** δ 7.82 (d, J = 8.8 Hz, 1H), 7.60 (dt, J = 7.8, 3.4 Hz, 3H), 7.41 – 7.27 (m, 4H), 7.18 (d, J = 8.2 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.86 (dd, J = 8.3, 1.8 Hz, 1H), 6.70 (d, J = 2.0 Hz, 1H), 2.68 (s, 6H), 2.55 (q, J = 7.6 Hz, 2H), 1.12 (t, J = 7.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.2, 149.2, 148.0, 140.8, 139.4, 131.7, 129.0, 128.9, 128.0, 127.1, 124.7, 124.2, 121.9, 121.3, 120.6, 117.9, 116.1, 109.1, 81.1, 39.1, 29.0, 16.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O^+$ 382.1914; Found:382.1915.



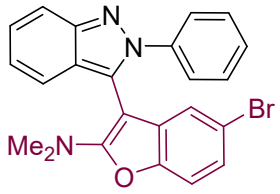
4c

5-(Tert-butyl)-*N*,*N*-dimethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine (**4c**) was obtained as a yellow solid (71 mg, 87%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.83 (dd, J = 8.7, 1.0 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.61 (dt, J = 8.4, 1.1 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.32 – 7.27 (m, 1H), 7.19 (d, J = 8.5 Hz, 1H), 7.10 (ddd, J = 8.5, 6.5, 0.9 Hz, 1H), 7.06 (dd, J = 8.5, 2.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 2.75 (s, 6H), 1.18 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.3, 149.1, 147.7, 146.3, 140.9, 130.8, 129.1, 129.0, 127.9, 127.2, 124.6, 124.1, 121.9, 121.2, 118.1, 117.8, 114.0, 108.7, 81.6, 39.3, 34.7, 31.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}N_3O^+$ 410.2227; Found:410.2225.



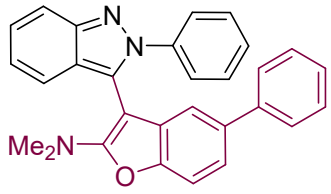
4d

5-Chloro-*N*,*N*-dimethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine (4d) was obtained as a yellow solid (40 mg, 52%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.81 (dt, J = 8.8, 0.9 Hz, 1H), 7.57 – 7.52 (m, 3H), 7.39 – 7.35 (m, 3H), 7.35 – 7.31 (m, 1H), 7.17 (d, J = 8.5 Hz, 1H), 7.12 (ddd, J = 8.5, 6.5, 0.9 Hz, 1H), 6.97 (dd, J = 8.5, 2.1 Hz, 1H), 6.84 (d, J = 2.2 Hz, 1H), 2.68 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.7, 149.1, 147.7, 140.4, 133.5, 129.0, 128.9, 128.1, 127.6, 127.1, 124.5, 124.1, 122.2, 120.7, 120.3, 118.0, 116.3, 110.3, 80.0, 38.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}ClN_3O^+$ 388.1211; Found:388.1213.



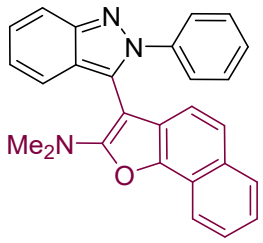
4e

5-Bromo-*N*,*N*-dimethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine (4e) was obtained as a yellow solid (50 mg, 58%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.82 (dt, J = 8.9, 1.0 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.39 – 7.35 (m, 3H), 7.35 – 7.31 (m, 1H), 7.15 – 7.08 (m, 3H), 6.99 (d, J = 1.9 Hz, 1H), 2.68 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.7, 149.2, 148.2, 140.5, 134.1, 129.1, 128.2, 127.7, 127.2, 124.6, 124.3, 123.2, 122.3, 120.8, 119.3, 118.1, 116.6, 110.9, 80.0, 38.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}BrN_3O^+$ 432.0706; Found:432.0711.



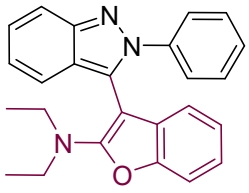
4f

***N*,*N*-Dimethyl-5-phenyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine (4f)** was obtained as a yellow solid (69 mg, 81%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.82 (dt, J = 8.8, 0.9 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.60 (dt, J = 8.5, 1.1 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.39 – 7.29 (m, 7H), 7.26 – 7.23 (m, 2H), 7.11 – 7.07 (m, 2H), 2.70 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.5, 149.2, 149.2, 141.8, 140.8, 137.0, 132.3, 129.1, 128.7, 128.5, 128.1, 127.4, 127.2, 126.8, 124.7, 124.3, 122.1, 121.1, 120.2, 118.0, 115.5, 109.6, 81.0, 39.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}N_3O^+$ 430.1914; Found:430.1915.



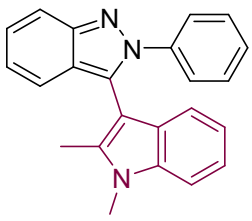
4g

***N*,*N*-Dimethyl-3-(2-phenyl-2*H*-indazol-3-yl)naphtho[1,2-b]furan-2-amine** (**4g**) was obtained as a yellow solid (70 mg, 87%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.87 (ddt, J = 12.9, 8.3, 1.0 Hz, 2H), 7.57 – 7.51 (m, 5H), 7.40 (ddd, J = 8.8, 6.5, 1.1 Hz, 1H), 7.31 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.20 (ddd, J = 8.5, 1.3, 0.6 Hz, 1H), 7.13 – 7.07 (m, 2H), 2.64 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.1, 149.3, 146.1, 140.5, 131.2, 129.4, 129.0, 128.8, 128.1, 127.3, 126.7, 125.9, 125.7, 125.3, 124.8, 124.2, 122.9, 122.6, 121.4, 121.2, 118.0, 111.1, 82.1, 39.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{22}N_3O^+$ 404.1757; Found:404.1759.



4h

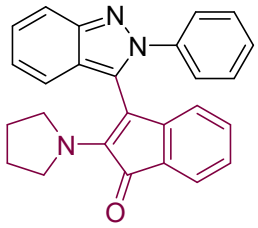
***N*,*N*-Diethyl-3-(2-phenyl-2*H*-indazol-3-yl)benzofuran-2-amine** (**4h**) was obtained as a yellow solid (35 mg, 46%). (Eluent: petroleum ether/ethyl acetate= 20/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.82 (dd, J = 8.7, 1.1 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.39 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.11 – 7.06 (m, 1H), 7.06 – 7.04 (m, 2H), 6.97 – 6.92 (m, 1H), 3.09 (dq, J = 14.2, 7.1 Hz, 2H), 2.97 (dq, J = 14.2, 7.1 Hz, 2H), 0.83 (t, J = 7.1 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.0, 149.5, 149.3, 140.7, 132.1, 129.1, 128.6, 128.0, 127.1, 124.7, 123.7, 123.2, 121.9, 121.2, 120.5, 118.0, 116.9, 109.5, 81.0, 43.3, 13.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O^+$ 382.1914; Found:382.1913.



4i

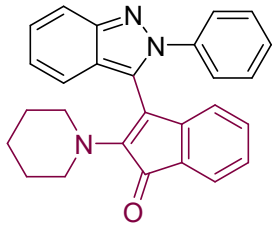
(1,2-Dimethyl-1*H*-indol-3-yl)-2-phenyl-2*H*-indazole (**4i**) was obtained as a yellow solid (33 mg, 49%). (Eluent: petroleum ether/ethyl acetate= 10/1). **^{1}H NMR (600**

MHz, Chloroform-d) δ 7.74 (dt, J = 8.8, 1.0 Hz, 1H), 7.40 (tt, J = 8.2, 1.2 Hz, 3H), 7.29 – 7.27 (m, 1H), 7.25 – 7.19 (m, 3H), 7.19 – 7.16 (m, 2H), 7.13 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 6.97 (ddd, J = 7.9, 6.8, 0.9 Hz, 2H), 3.60 (s, 3H), 1.89 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.3, 141.0, 137.1, 136.3, 130.6, 129.0, 127.7, 127.3, 127.0, 124.9, 123.3, 121.6, 121.6, 121.5, 120.3, 119.3, 117.9, 109.1, 101.9, 30.0, 11.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N_3^+$ 338.1652; Found: 338.1655.



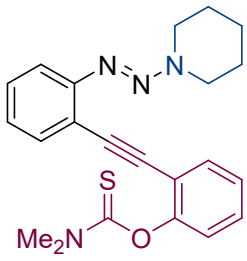
4k

3-(2-Phenyl-2*H*-indazol-3-yl)-2-(pyrrolidin-1-yl)-1*H*-inden-1-one (**4k**) was obtained as a purple solid (26 mg, 33%). (Eluent: petroleum ether/ethyl acetate= 15/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.82 – 7.76 (m, 3H), 7.59 (dt, J = 8.5, 1.1 Hz, 1H), 7.42 (dd, J = 8.5, 7.1 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.27 (m, 1H), 7.10 (ddd, J = 8.5, 6.5, 0.9 Hz, 1H), 7.03 (td, J = 7.5, 1.2 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.23 (d, J = 7.4 Hz, 1H), 3.29 – 3.22 (m, 2H), 3.17 (dt, J = 10.8, 6.0 Hz, 2H), 1.68 – 1.59 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 193.9, 150.3, 149.2, 141.2, 140.8, 135.6, 129.8, 129.3, 128.3, 127.2, 126.7, 124.6, 124.1, 123.7, 123.2, 122.2, 121.1, 118.1, 117.2, 104.0, 49.6, 25.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}N_3O^+$ 392.1757; Found: 392.1753.



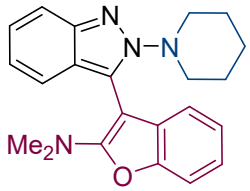
4l

3-(2-Phenyl-2*H*-indazol-3-yl)-2-(piperidin-1-yl)-1*H*-inden-1-one (**4l**) was obtained as a purple solid (24 mg, 30%). (Eluent: petroleum ether/ethyl acetate= 15/1). **^{1}H NMR (600 MHz, Chloroform-d)** δ 7.81 (dt, J = 8.8, 0.9 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.62 (dt, J = 8.4, 1.1 Hz, 1H), 7.45 (dd, J = 8.5, 7.0 Hz, 2H), 7.38 (ddd, J = 8.6, 6.5, 1.1 Hz, 2H), 7.29 (dt, J = 7.1, 0.9 Hz, 1H), 7.13 (ddd, J = 8.4, 6.6, 0.9 Hz, 1H), 7.06 (td, J = 7.5, 1.2 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.39 (dd, J = 7.4, 0.8 Hz, 1H), 3.07 – 3.03 (m, 2H), 2.66 – 2.62 (m, 2H), 1.43 – 1.31 (m, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 194.5, 149.5, 147.6, 144.4, 140.6, 135.2, 129.2, 129.1, 128.7, 127.4, 127.3, 125.3, 124.4, 123.7, 123.2, 122.5, 121.1, 118.3, 118.2, 111.8, 49.3, 26.1, 24.0.HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}N_3O^+$ 406.1914; Found: 406.1913.



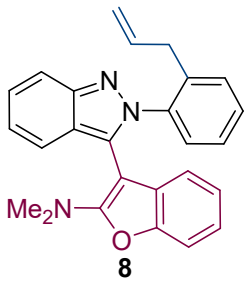
6

(*E*)-O-(2-((2-(piperidin-1-yldiazenyl)phenyl)ethynyl)phenyl) dimethylcarbamothioate (**6**) was obtained as a red solid (41 mg, 52%). (Eluent: petroleum ether/ethyl acetate= 30/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.54 (dd, J = 7.7, 1.7 Hz, 1H), 7.45 (dd, J = 8.3, 1.2 Hz, 1H), 7.41 (dd, J = 7.7, 1.5 Hz, 1H), 7.36 (td, J = 7.9, 1.7 Hz, 1H), 7.28 (ddd, J = 8.3, 7.3, 1.5 Hz, 1H), 7.23 (td, J = 7.6, 1.2 Hz, 1H), 7.18 (dd, J = 8.1, 1.2 Hz, 1H), 7.10 (td, J = 7.5, 1.2 Hz, 1H), 3.84 (s, 4H), 3.44 (s, 3H), 3.37 (s, 3H), 1.71 (d, J = 11.0 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 187.3, 154.6, 152.0, 132.9, 132.9, 129.3, 128.7, 125.9, 125.13, 123.9, 118.7, 118.2, 117.3, 92.8, 88.4, 43.4, 39.0, 24.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}N_4OS^+$ 393.1744; Found:393.1744.



7

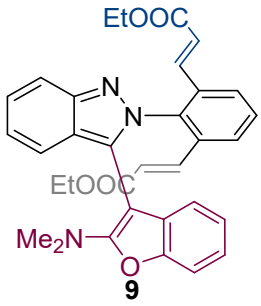
***N*,*N*-Dimethyl-3-(2-(piperidin-1-yl)-2*H*-indazol-3-yl)benzofuran-2-amine** (**7**) was obtained as a yellow solid (45 mg, 62%). (Eluent: petroleum ether/ethyl acetate= 15/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.72 (dt, J = 8.7, 1.0 Hz, 1H), 7.50 (dt, J = 8.4, 1.1 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.10 – 7.02 (m, 3H), 7.00 – 6.95 (m, 1H), 3.32 – 3.24 (m, 4H), 2.87 (s, 6H), 1.65 (p, J = 5.8 Hz, 4H), 1.50 (q, J = 5.8 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.2, 149.6, 145.8, 132.0, 126.2, 126.0, 122.9, 121.3, 121.2, 121.0, 120.3, 117.4, 117.3, 109.4, 80.7, 56.4, 39.5, 26.2, 23.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}N_4O^+$ 361.2023; Found:361.2026.



8

3-(2-(2-Allylphenyl)-2*H*-indazol-3-yl)-*N*,*N*-dimethylbenzofuran-2-amine (**8**) was obtained as a yellow solid (38 mg, 48%). (Eluent: petroleum ether/ethyl acetate=

10/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.80 (dt, J = 8.7, 1.0 Hz, 1H), 7.61 (dt, J = 8.4, 1.1 Hz, 1H), 7.37 (ddd, J = 8.8, 6.6, 1.1 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.29 (dd, J = 7.3, 1.4 Hz, 1H), 7.26 (q, J = 3.7, 2.7 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.17 (td, J = 7.5, 1.8 Hz, 1H), 7.12 (ddd, J = 8.4, 6.5, 0.9 Hz, 1H), 7.03 – 6.98 (m, 2H), 6.93 – 6.89 (m, 1H), 5.69 (ddt, J = 16.9, 10.0, 6.8 Hz, 1H), 5.01 – 4.83 (m, 2H), 3.14 (d, J = 6.7 Hz, 2H), 2.74 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.5, 149.4, 149.0, 139.1, 136.8, 136.1, 131.7, 130.2, 130.1, 129.1, 127.4, 126.9, 126.4, 123.2, 123.1, 121.9, 121.1, 120.7, 118.1, 117.1, 116.9, 109.6, 81.5, 39.5, 35.4, 29.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}N_3O^+$ 394.1914; Found:394.1922.



9

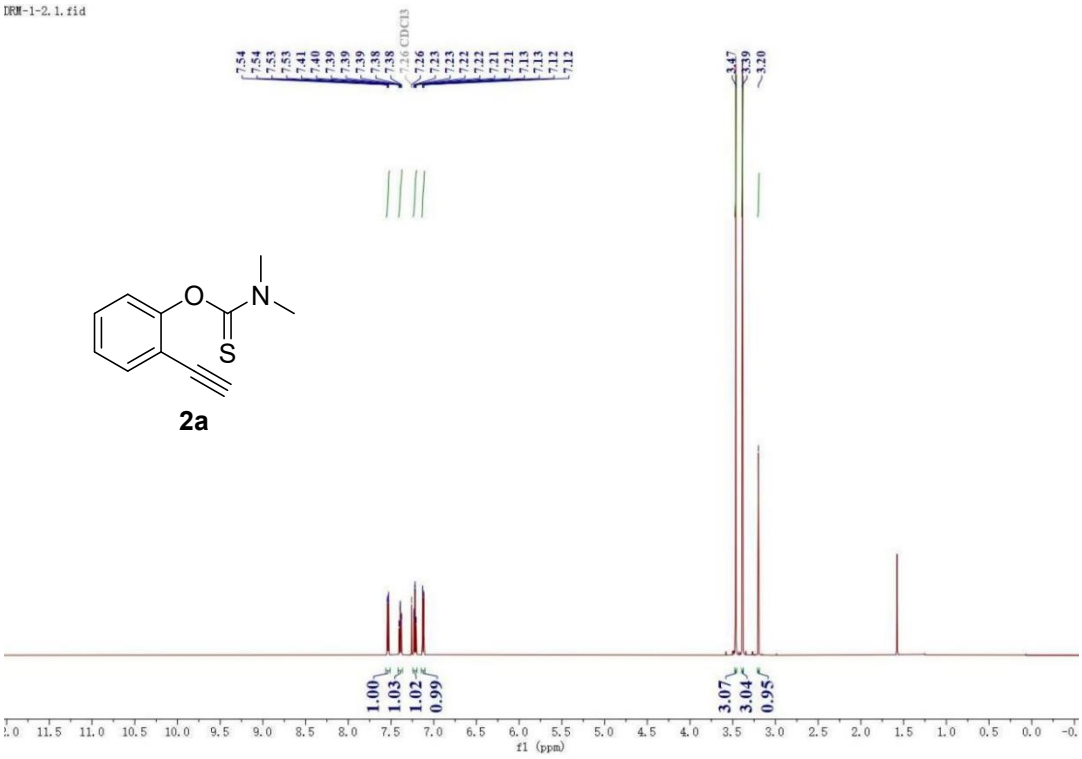
Diethyl-3,3'-(2-(3-(2-(dimethylamino)benzofuran-3-yl)-2*H*-indazol-2-yl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (**9**) was obtained as a yellow solid (78 mg, 71%). (Eluent: petroleum ether/ethyl acetate= 5/1).**^{1}H NMR (600 MHz, Chloroform-d)** δ 7.83 (dd, J = 8.8, 1.1 Hz, 1H), 7.77 (dd, J = 8.0, 1.3 Hz, 1H), 7.65 (dd, J = 8.5, 1.1 Hz, 1H), 7.50 (dd, J = 7.9, 1.3 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.43 – 7.38 (m, 2H), 7.19 – 7.14 (m, 2H), 7.00 (ddd, J = 9.2, 7.8, 1.5 Hz, 2H), 6.94 (td, J = 7.5, 1.0 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 5.89 (d, J = 16.0 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.53 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.3, 165.6, 159.0, 149.7, 149.6, 139.7, 138.9, 138.8, 133.5, 133.4, 132.5, 130.3, 129.5, 128.0, 127.6, 127.5, 122.7, 122.7, 122.6, 121.5, 121.4, 120.9, 120.6, 118.4, 118.4, 109.6, 84.8, 60.7, 60.4, 40.5, 14.3, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{32}N_3O_5^+$ 550.2336; Found:550. 2345.

7. References

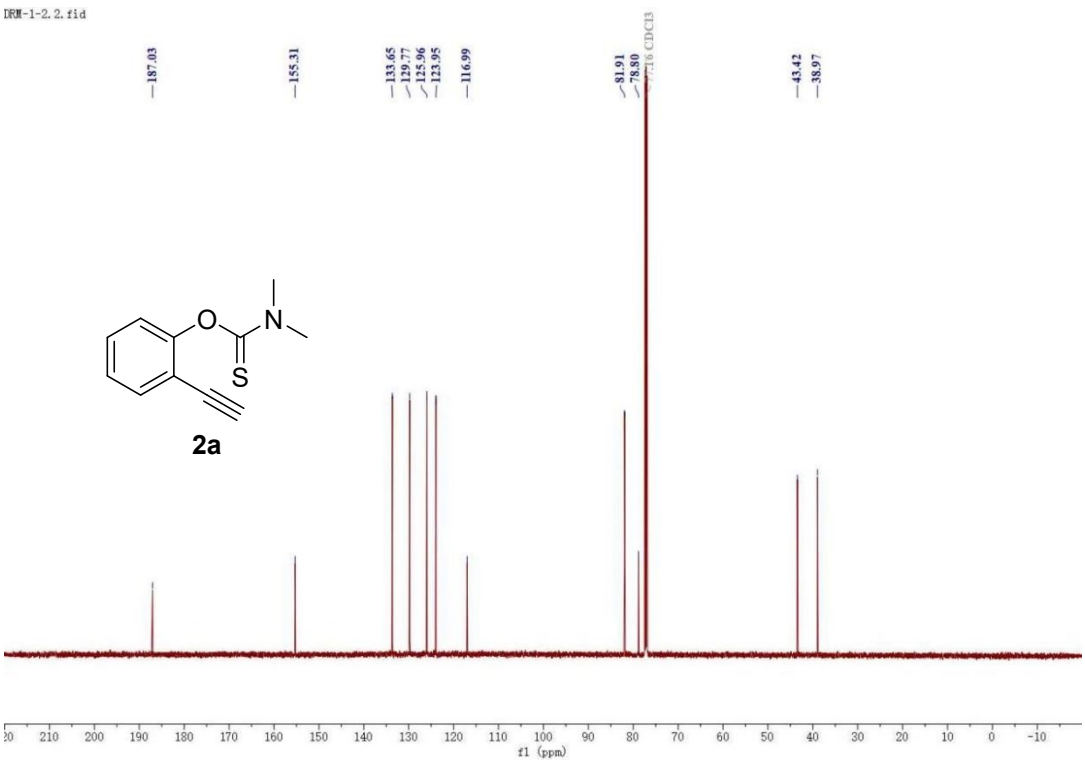
[1] (a) Ma .X.-T.; Tian. S.-K. *Adv. Synth. Catal.* **2013**, *335*, 337–340; (b) Das, U.; S.; Ben-David, Y.; Diskin-Posner, Y.; Milstein. D. *Adv. Synth. Catal.* **2021**, *363*, 3744-3749; (c) Qiu, S.; Gao, X.; Zhu, S. *Chem. Sci.* **2021**, *12*, 13730–13736.
[2] Li, X.; Chen, H.; Xuan, Q.; Mai, S.; Lan, Yu.; Song, Q. *Org. Lett.* **2021**, *23*, 3518–3523.

8. NMR Spectra

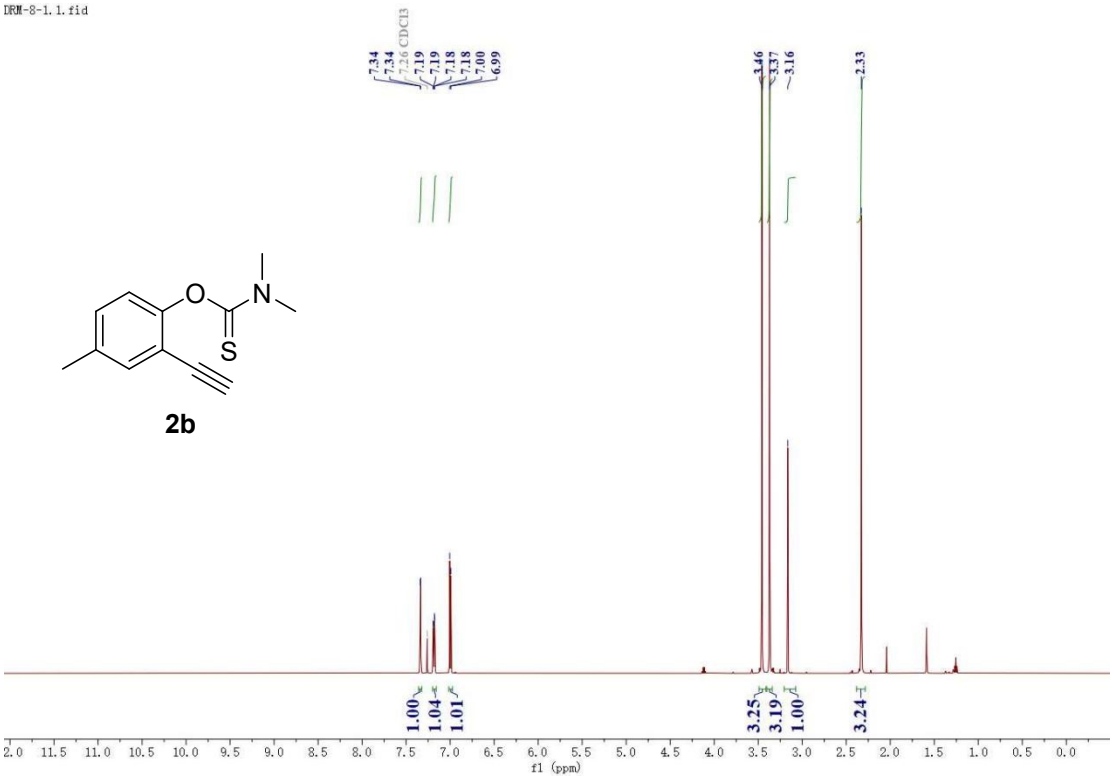
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2a



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2a

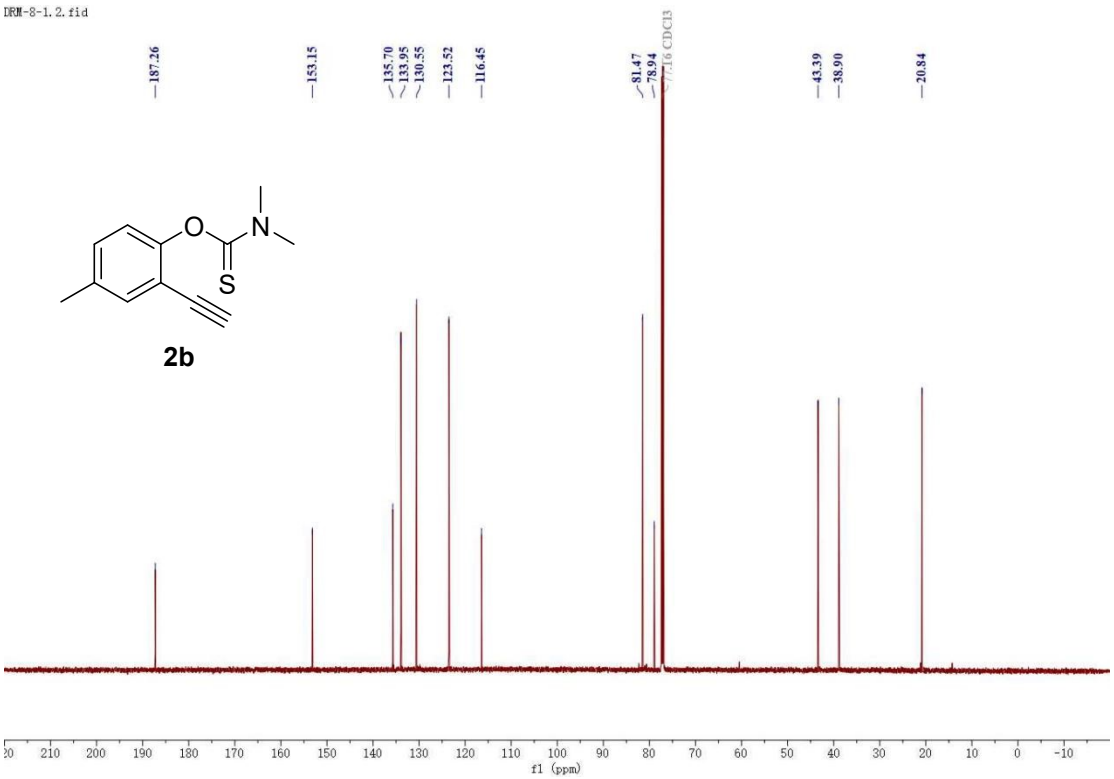


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2b



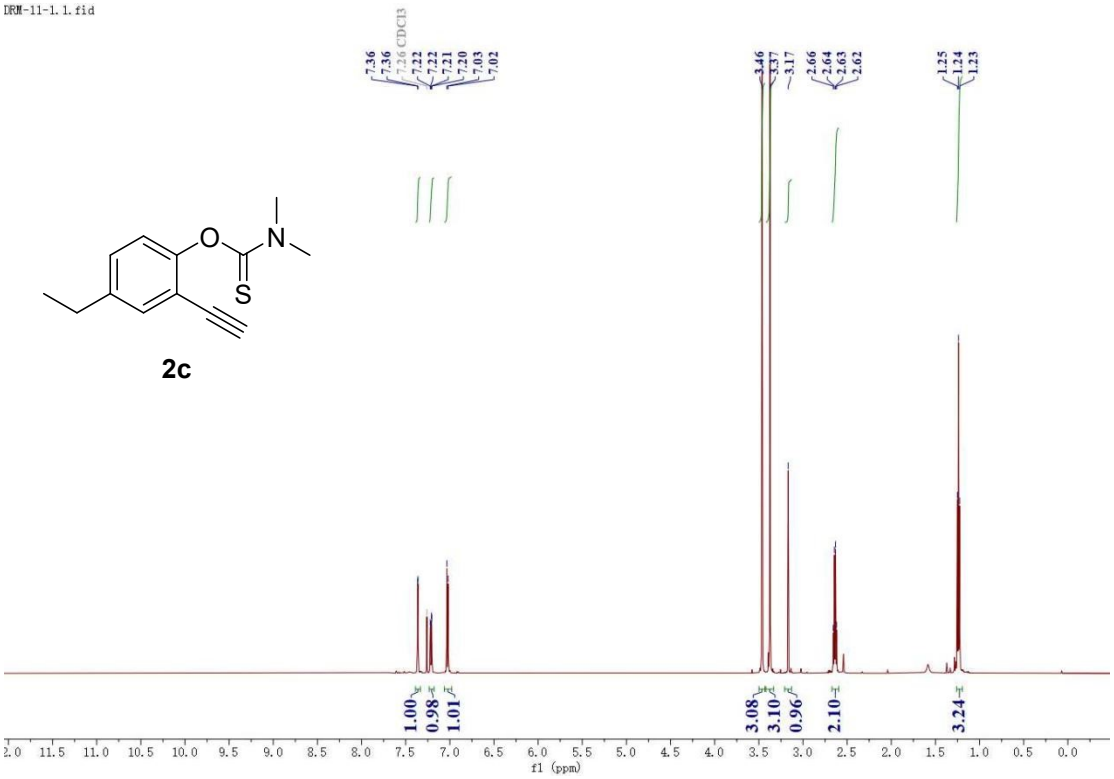
2b

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2b



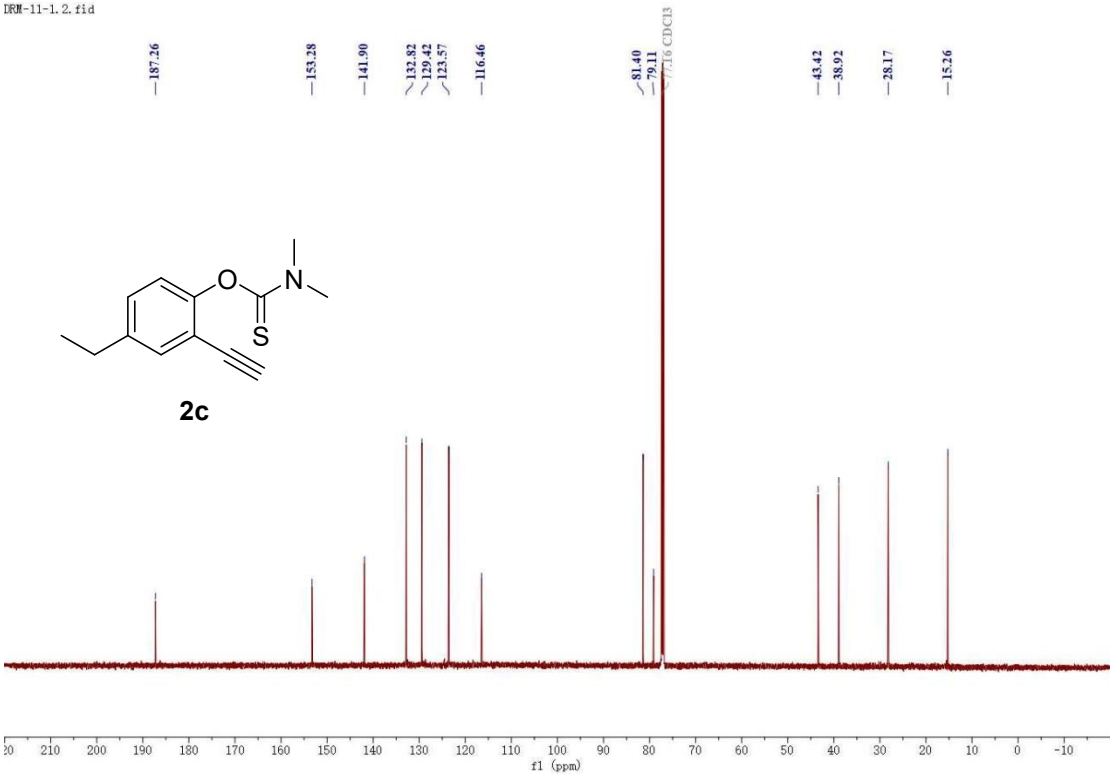
2b

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



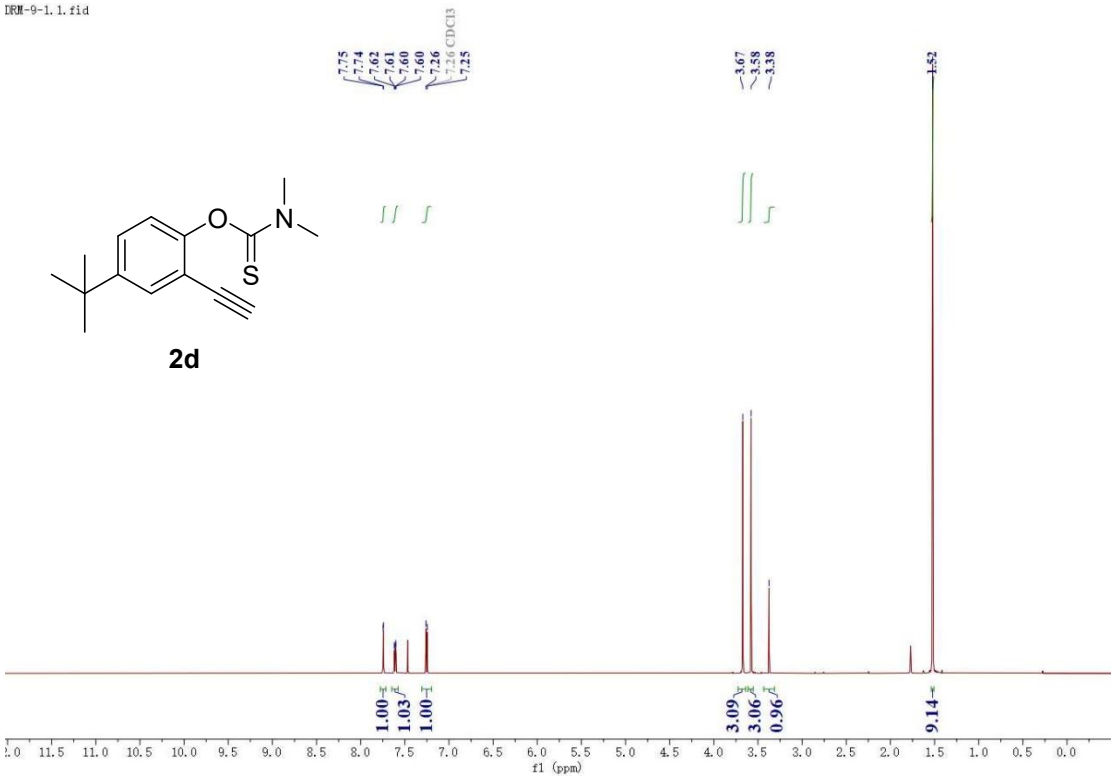
2c

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2c



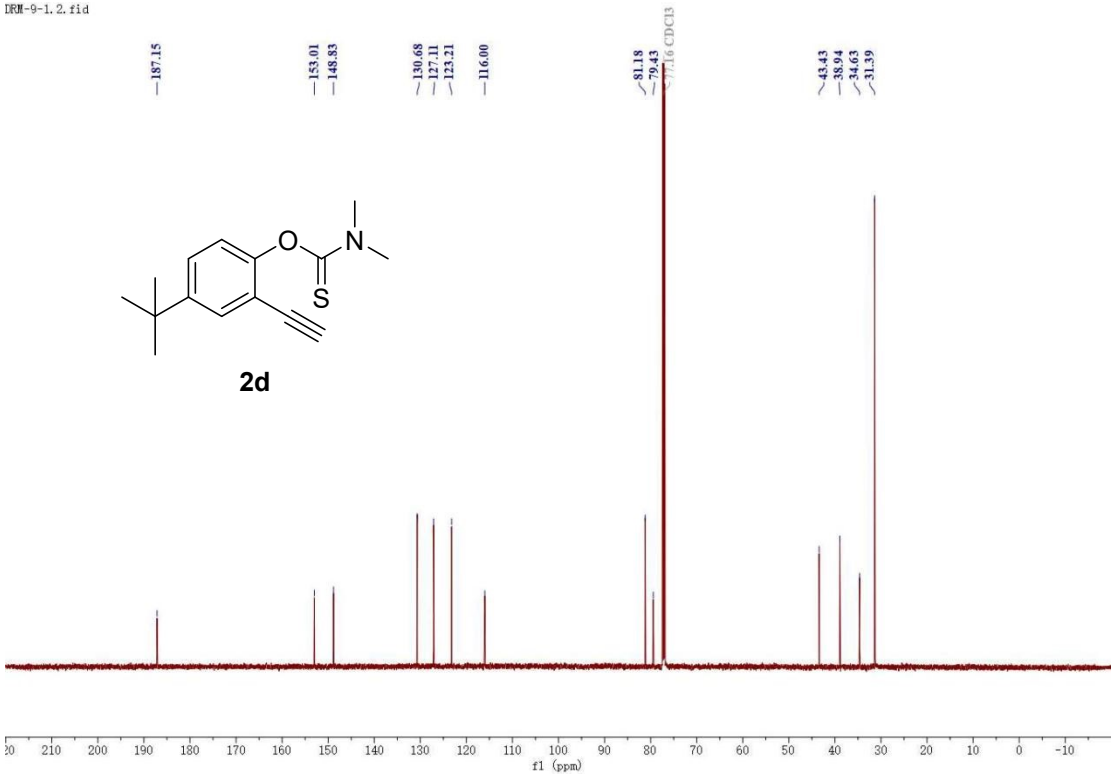
2c

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



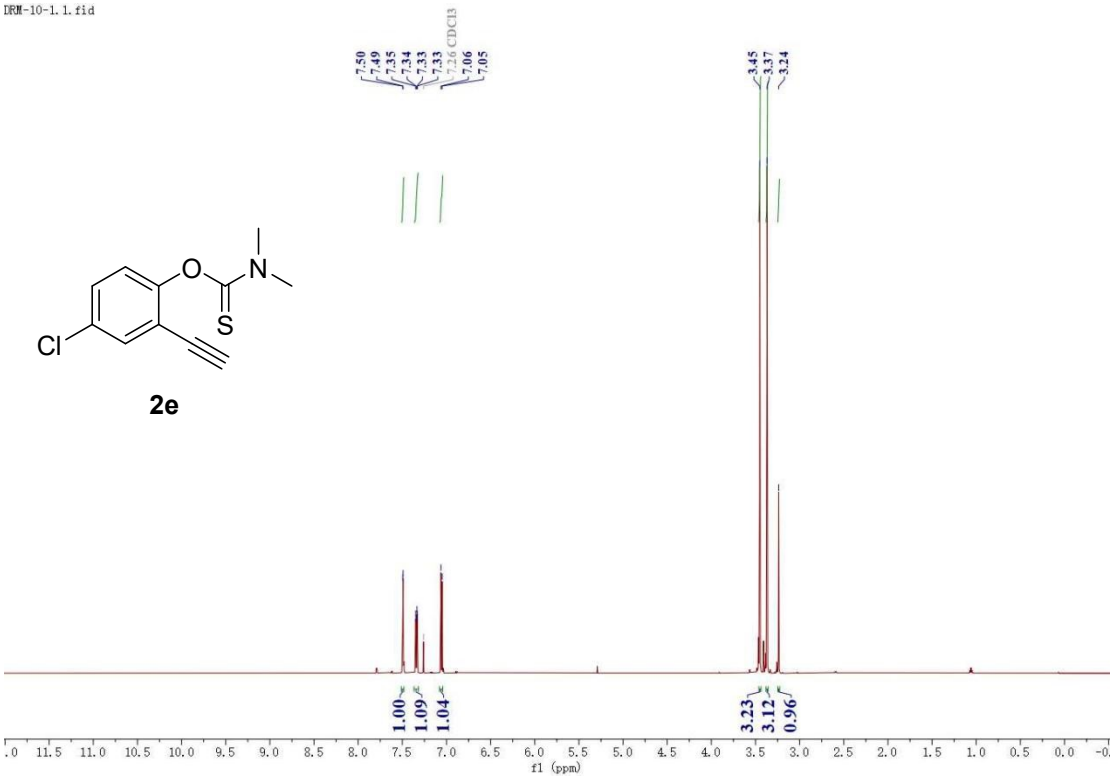
2d

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2d



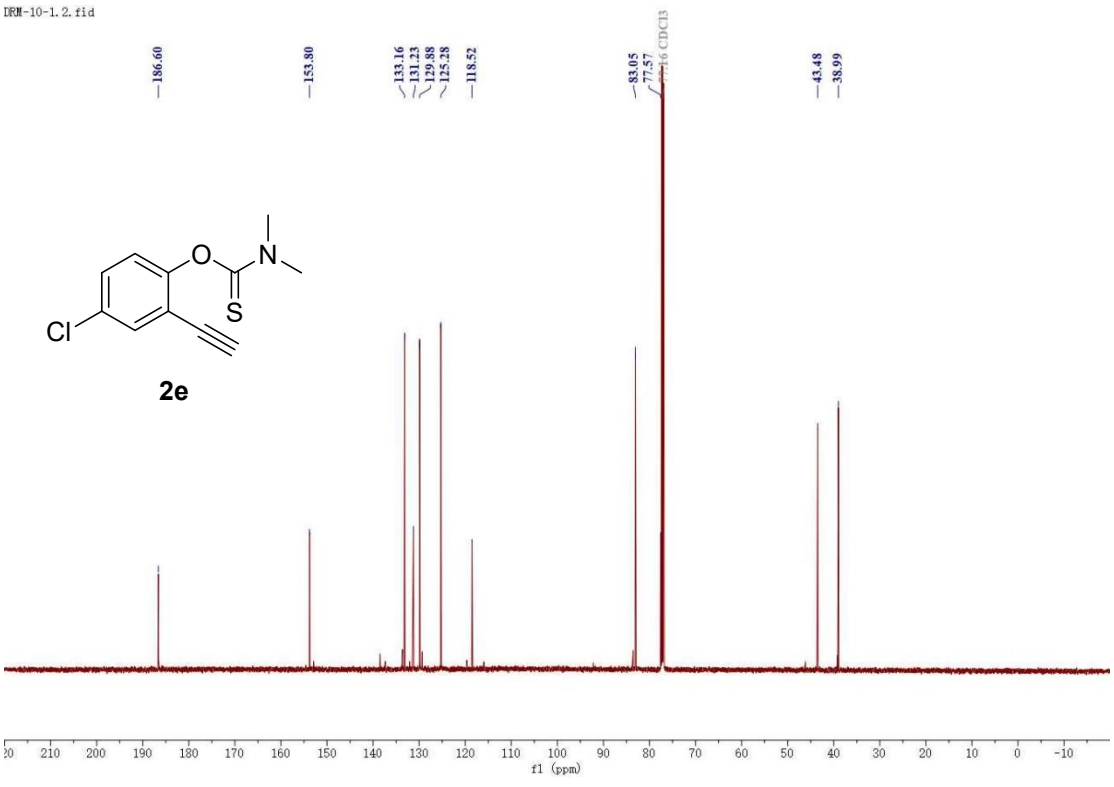
2d

^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2e



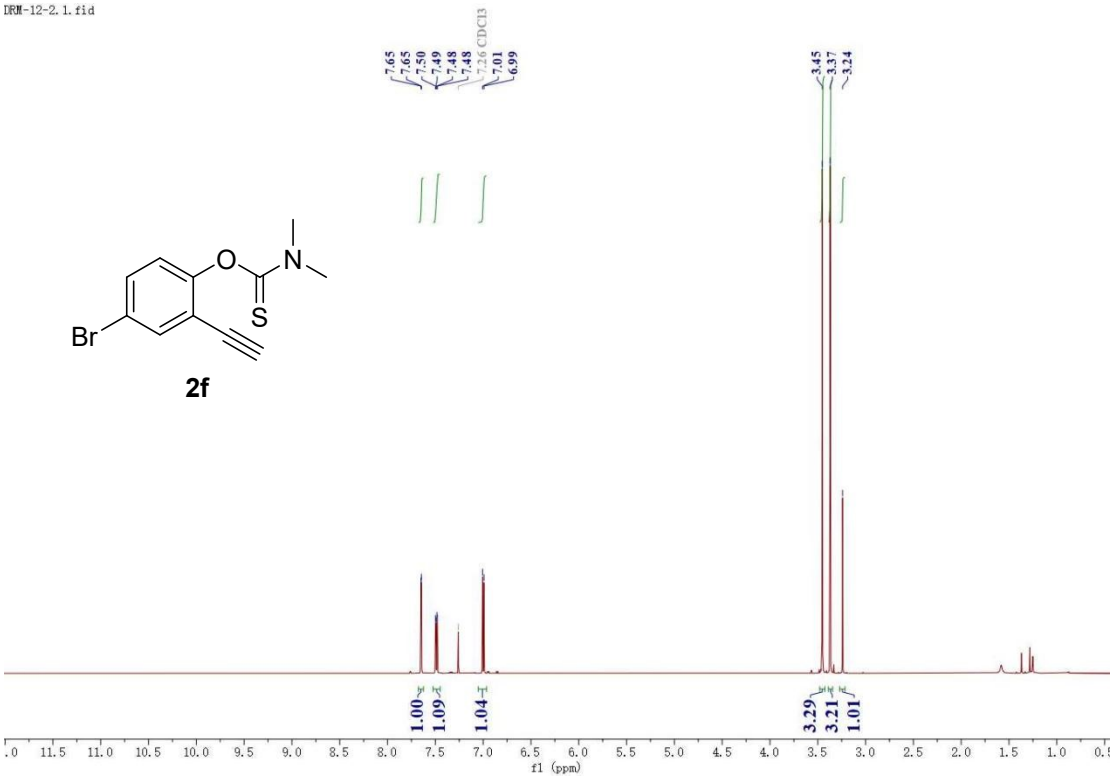
2e

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2e



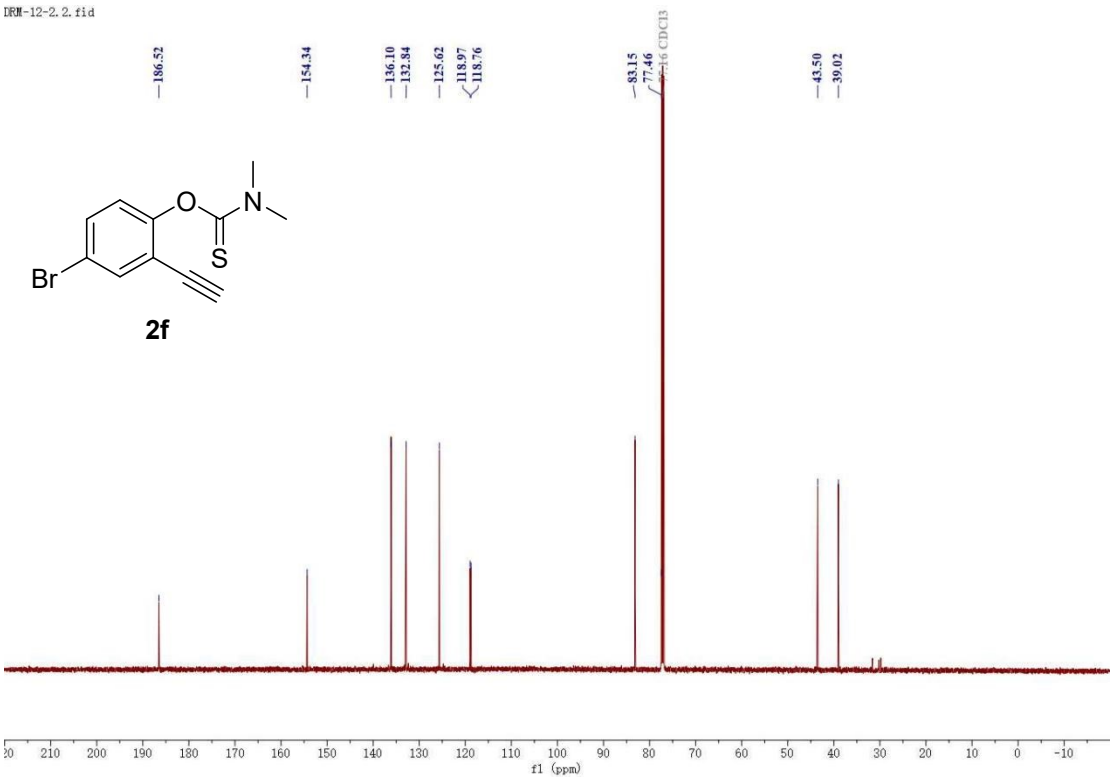
2e

^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2f



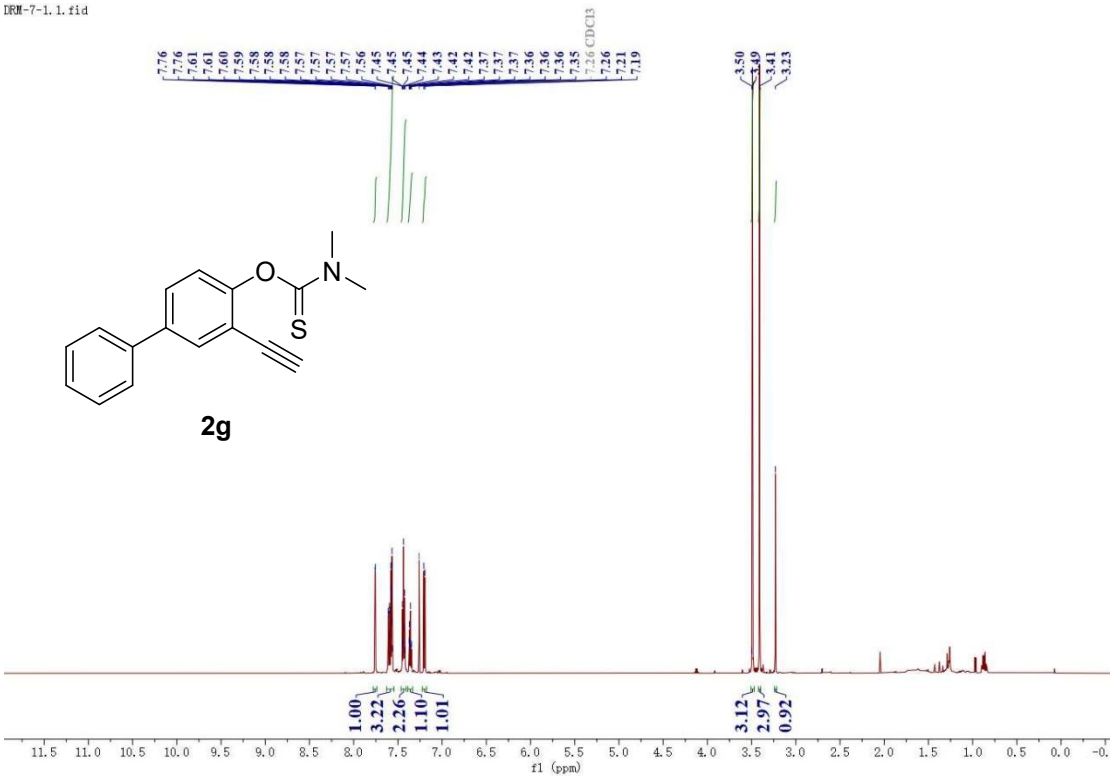
2f

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2f

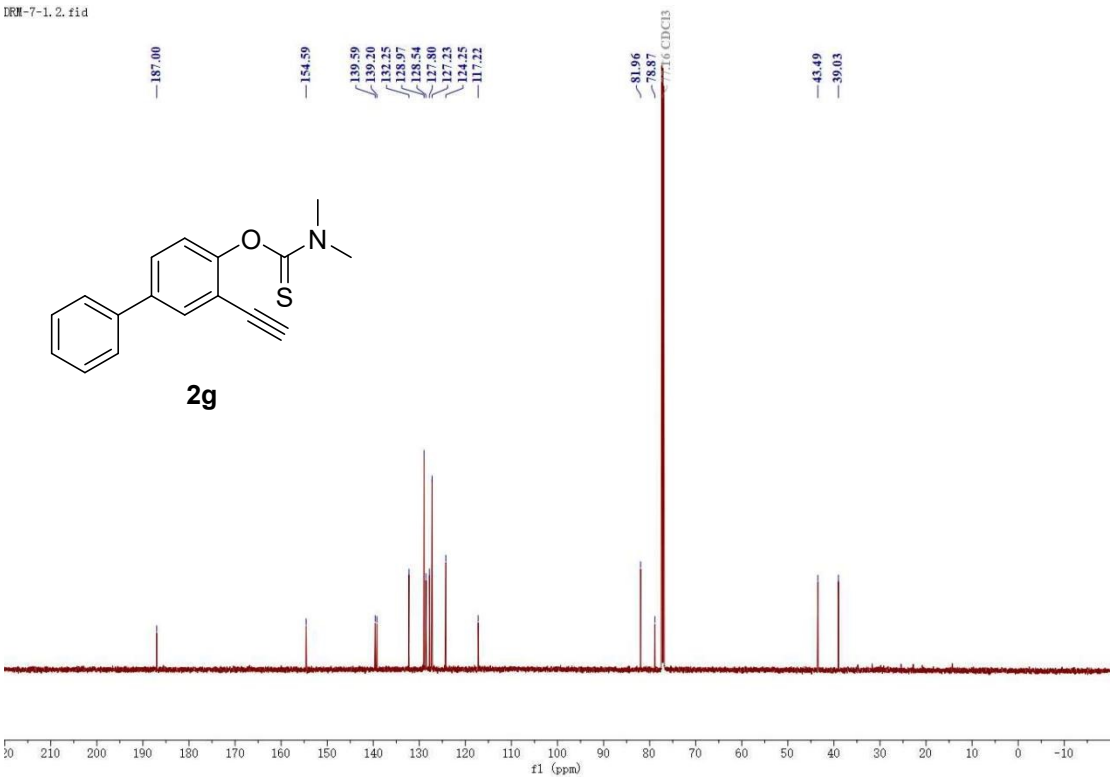


2f

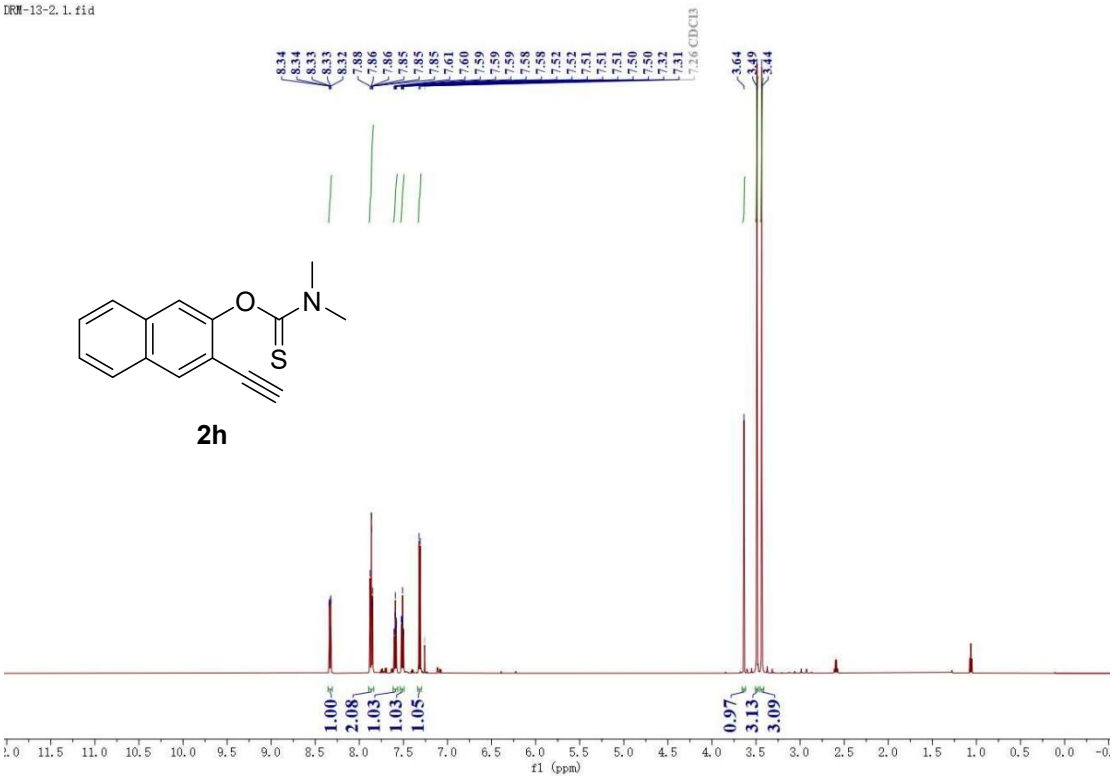
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2g



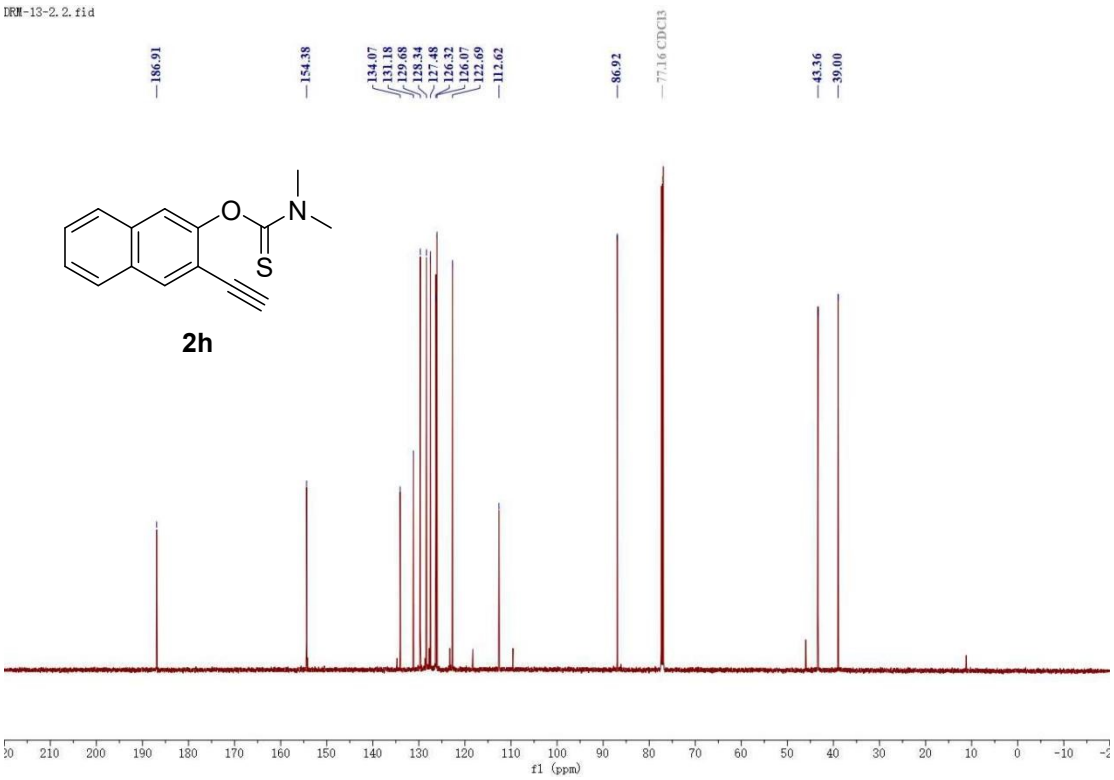
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2g



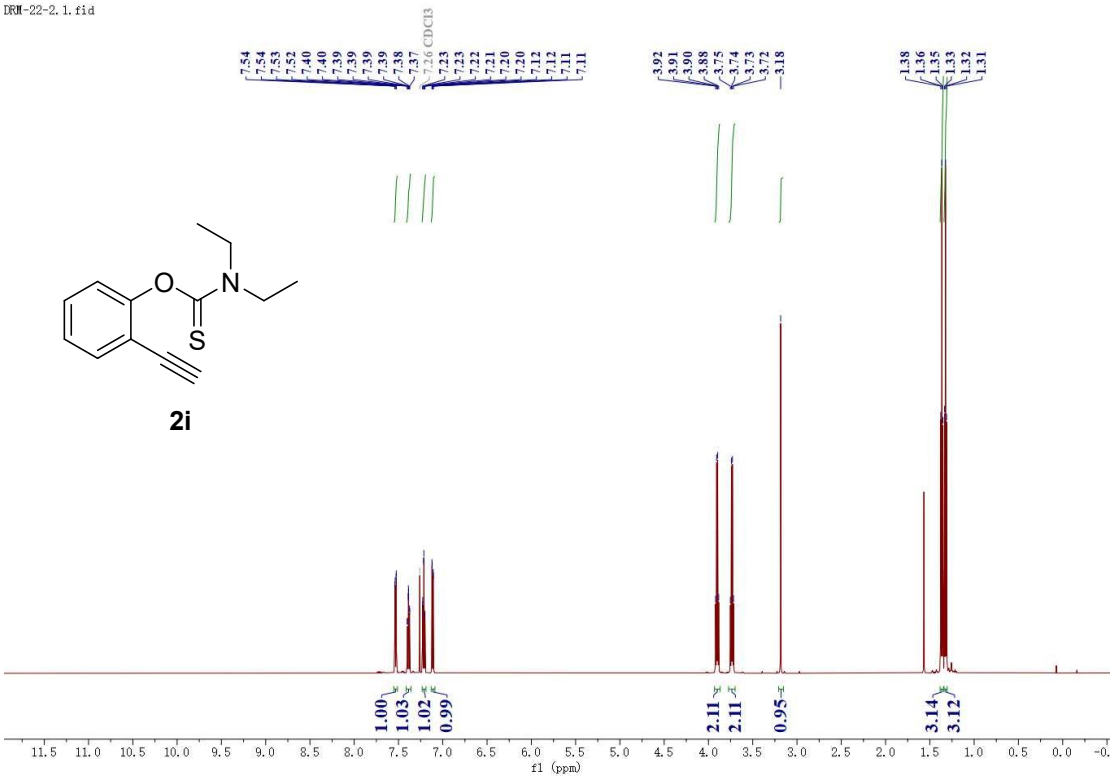
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2h



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2h

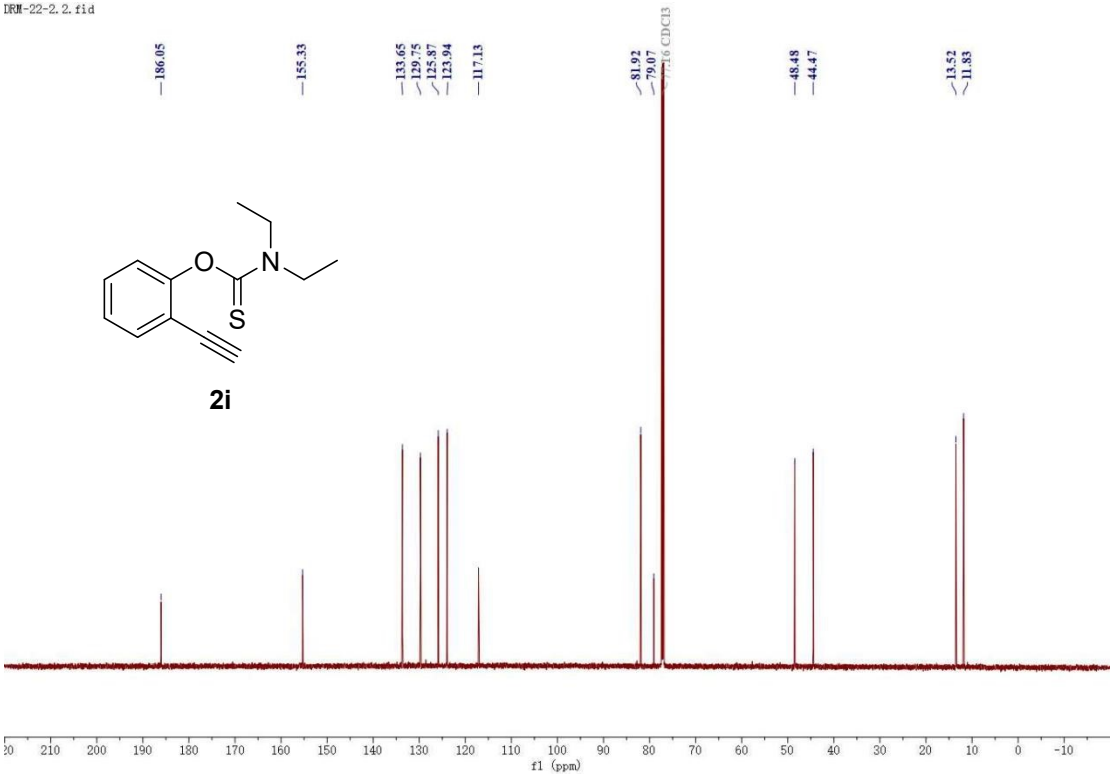


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2i



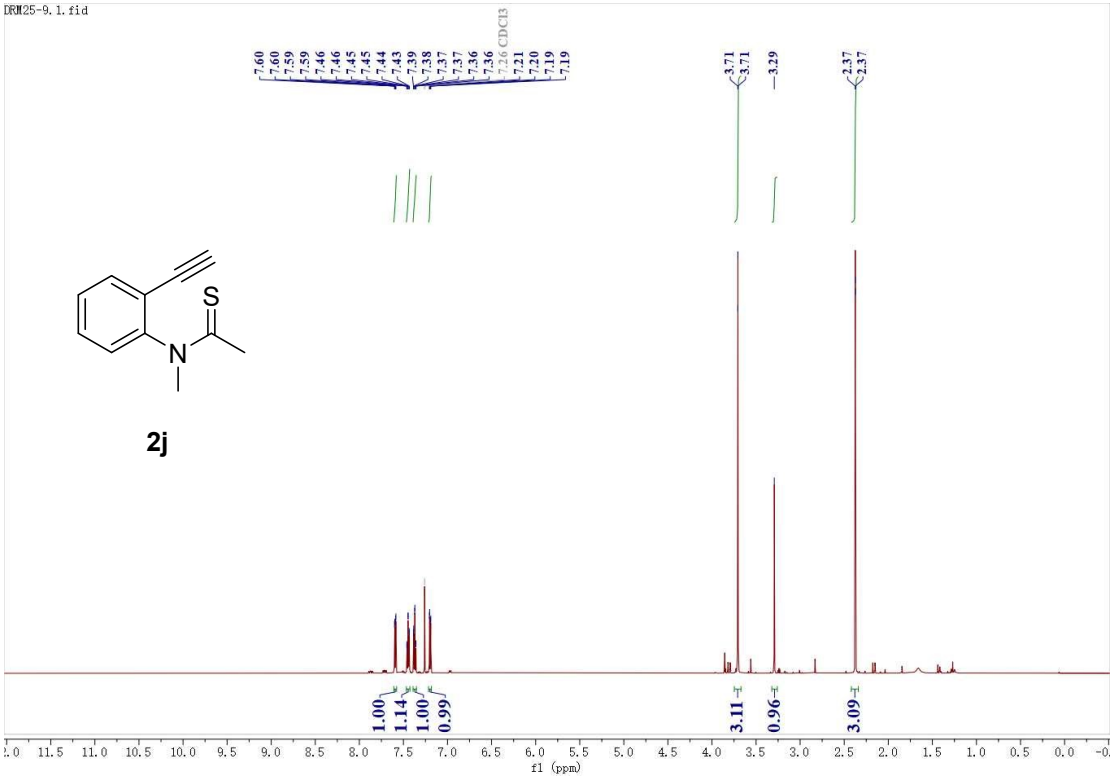
2i

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2i



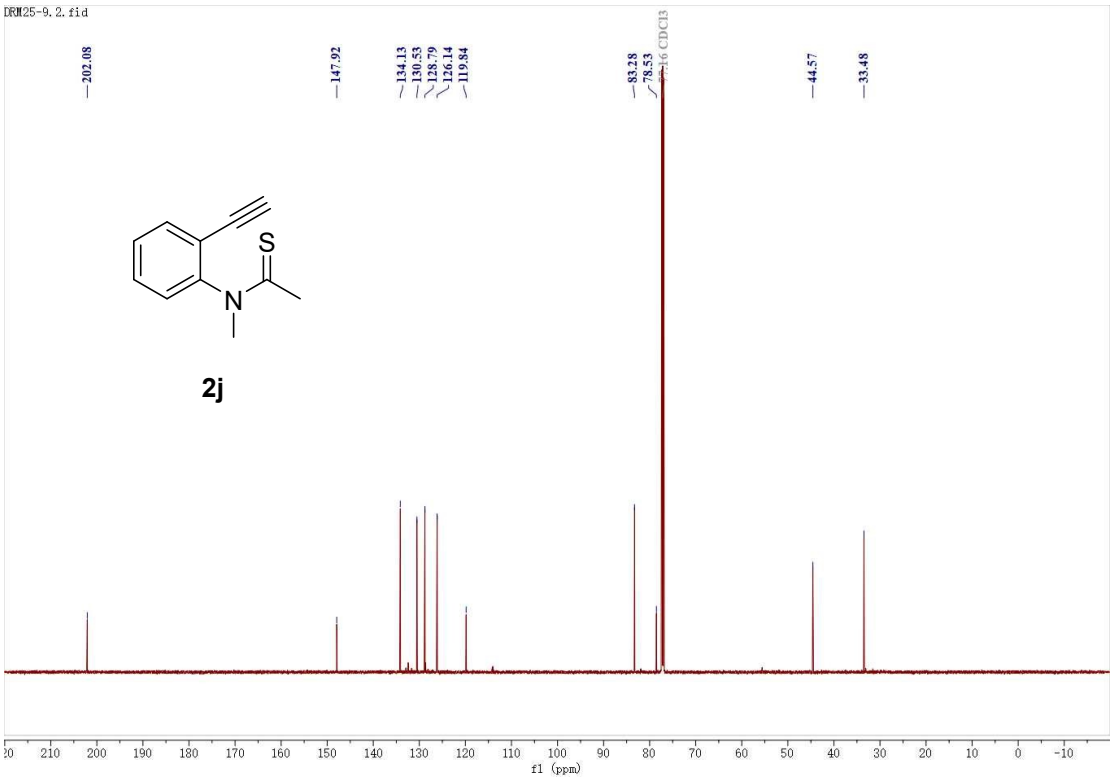
2i

^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2j



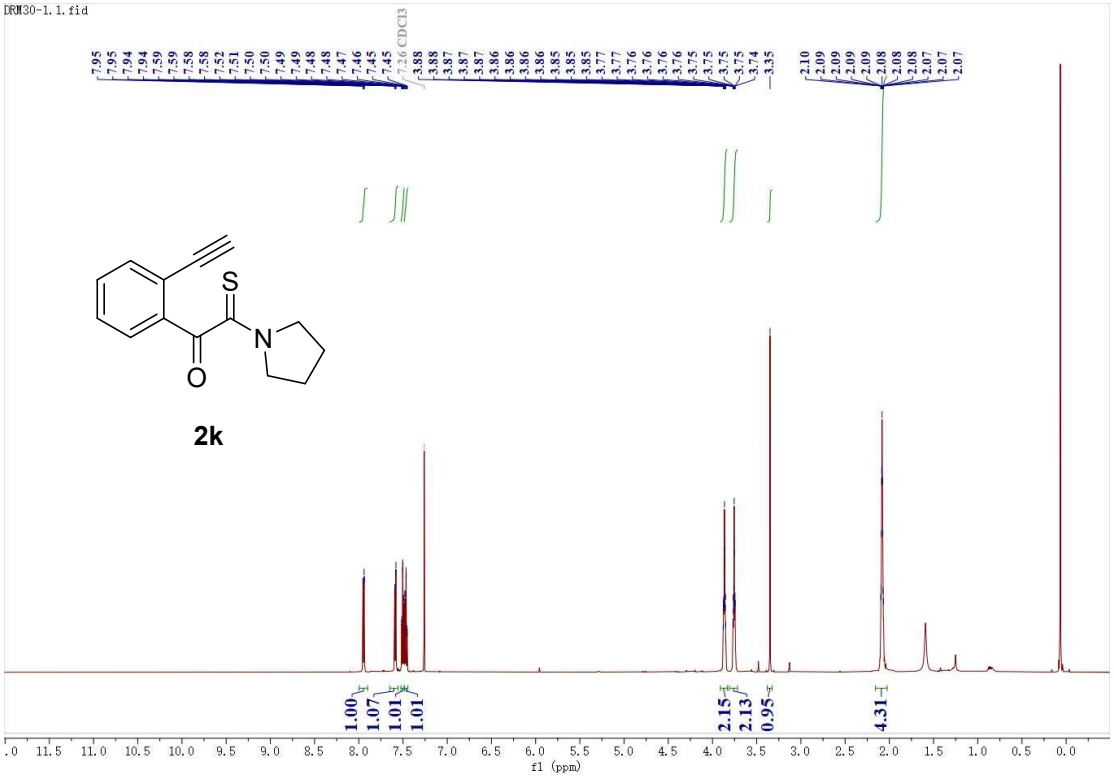
2j

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2j

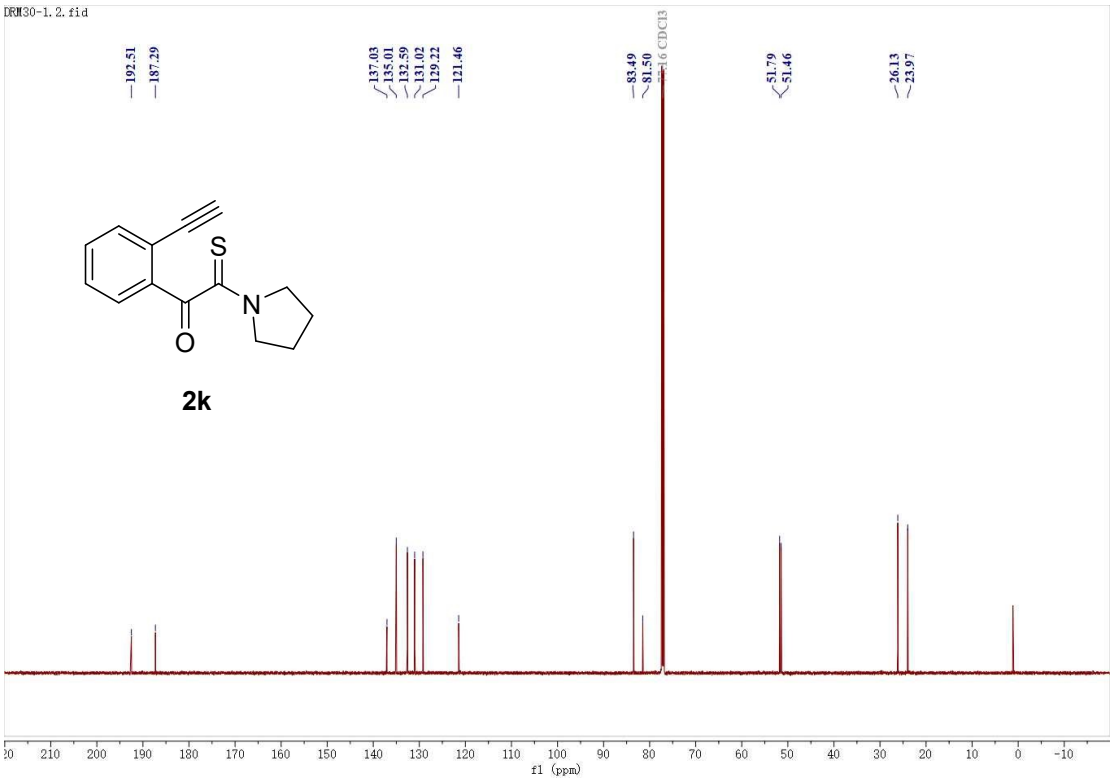


2j

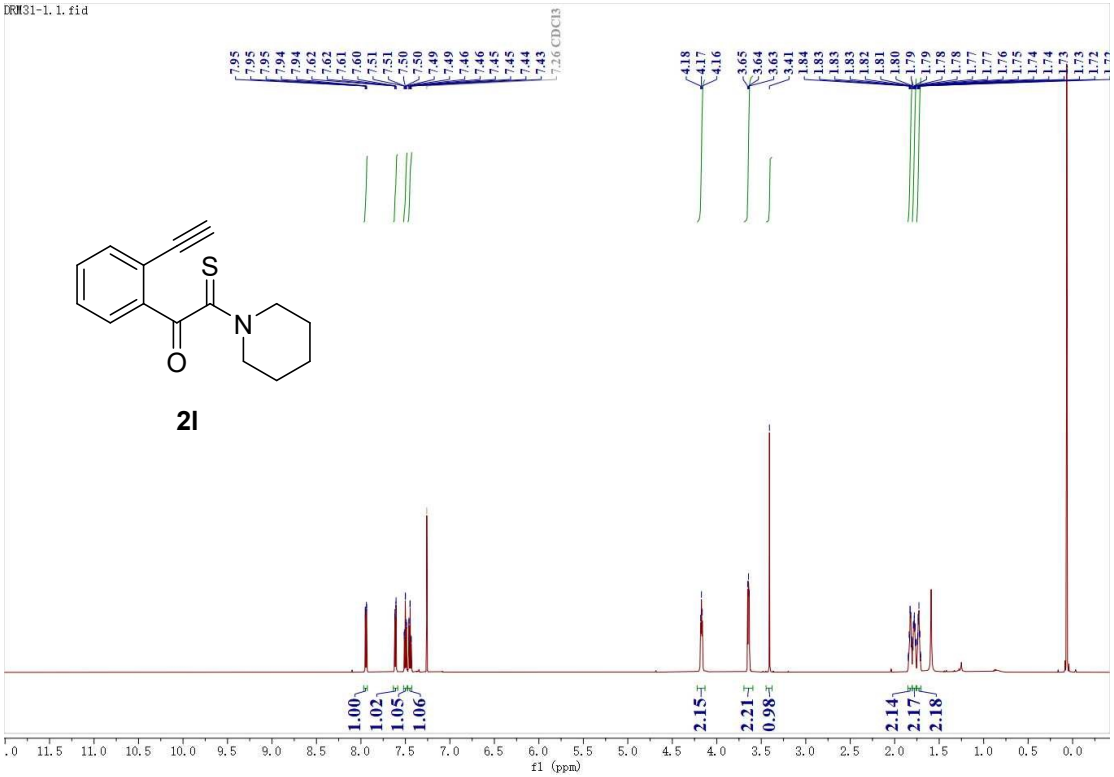
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2k



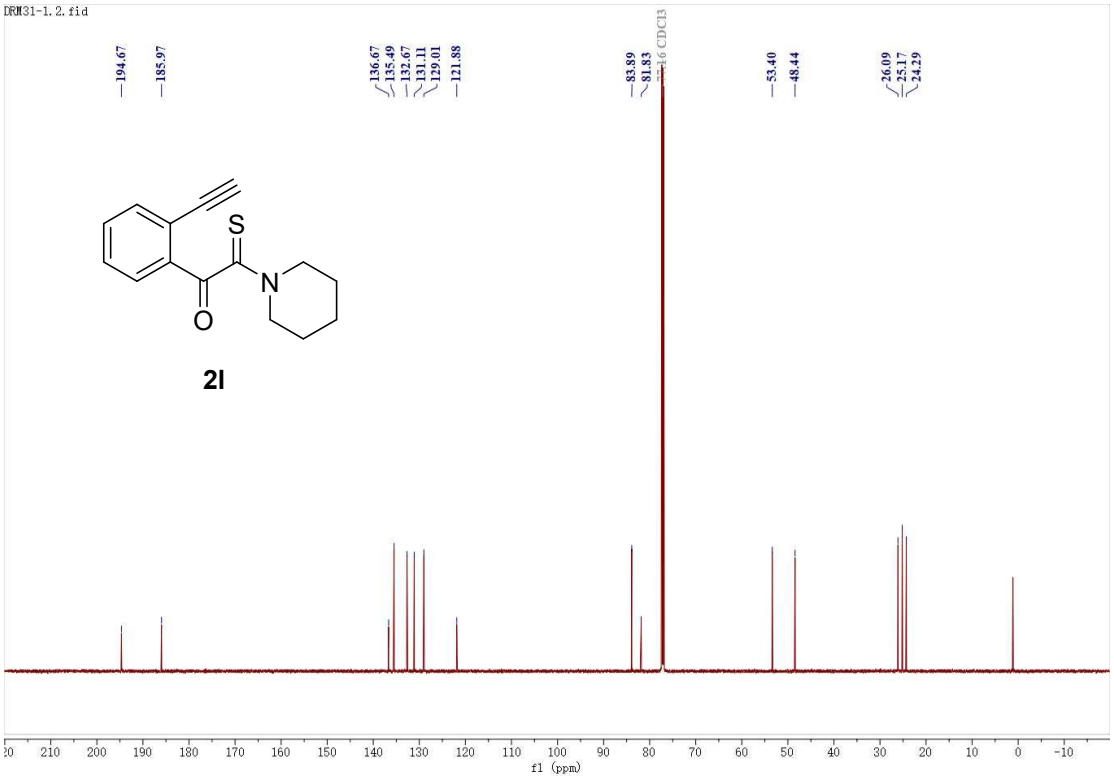
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2k



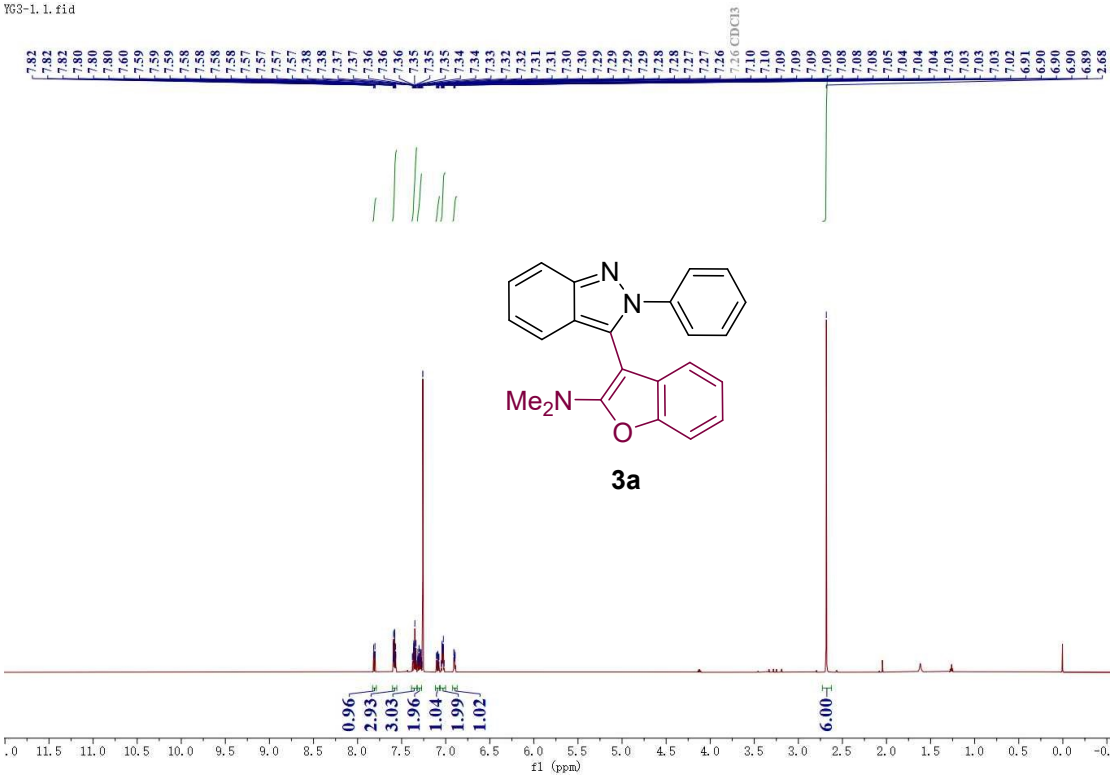
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2l



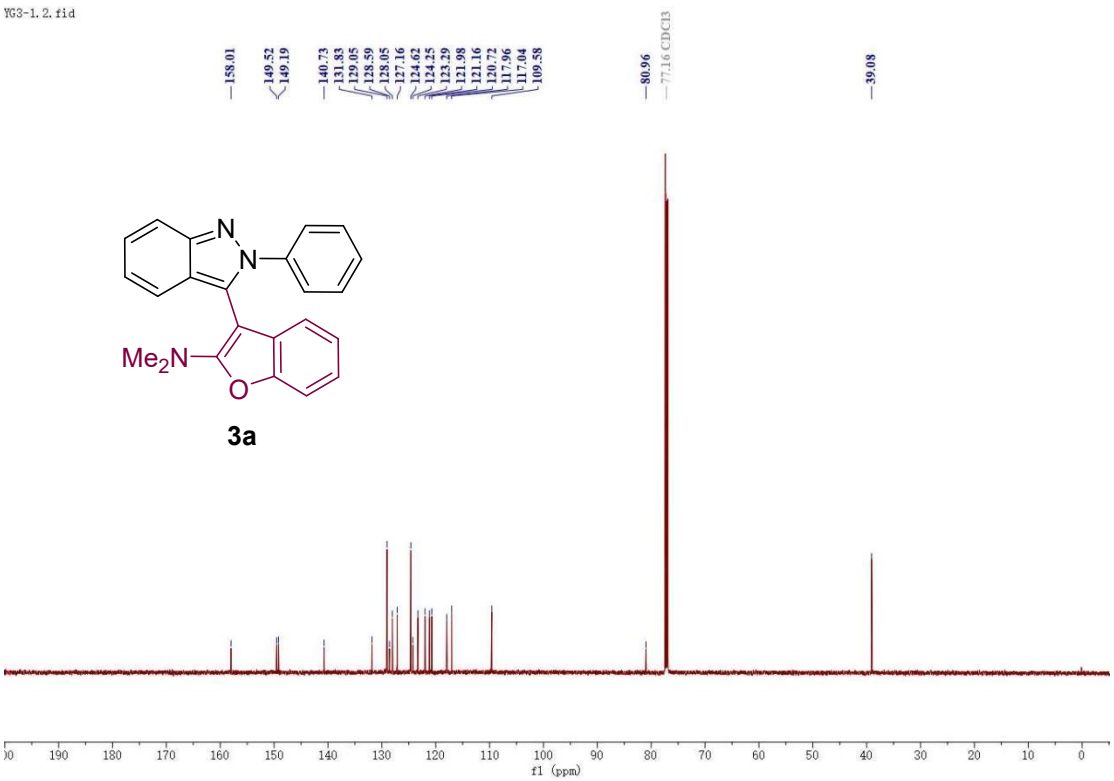
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 2l



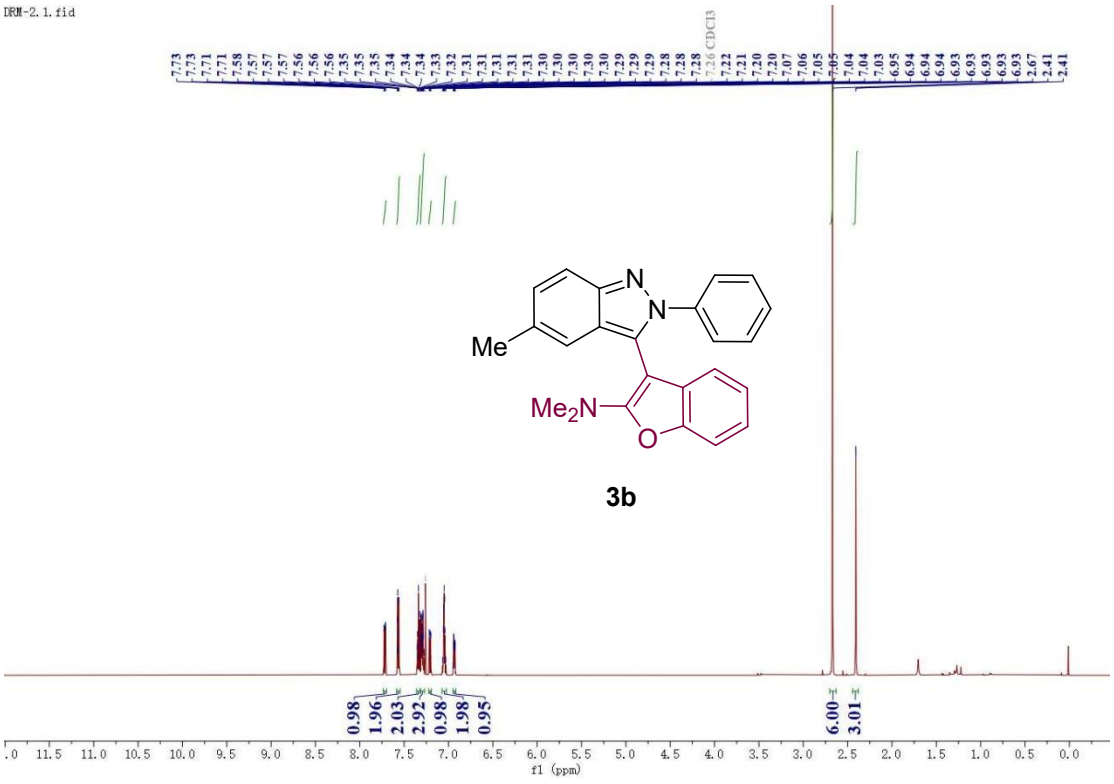
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3a



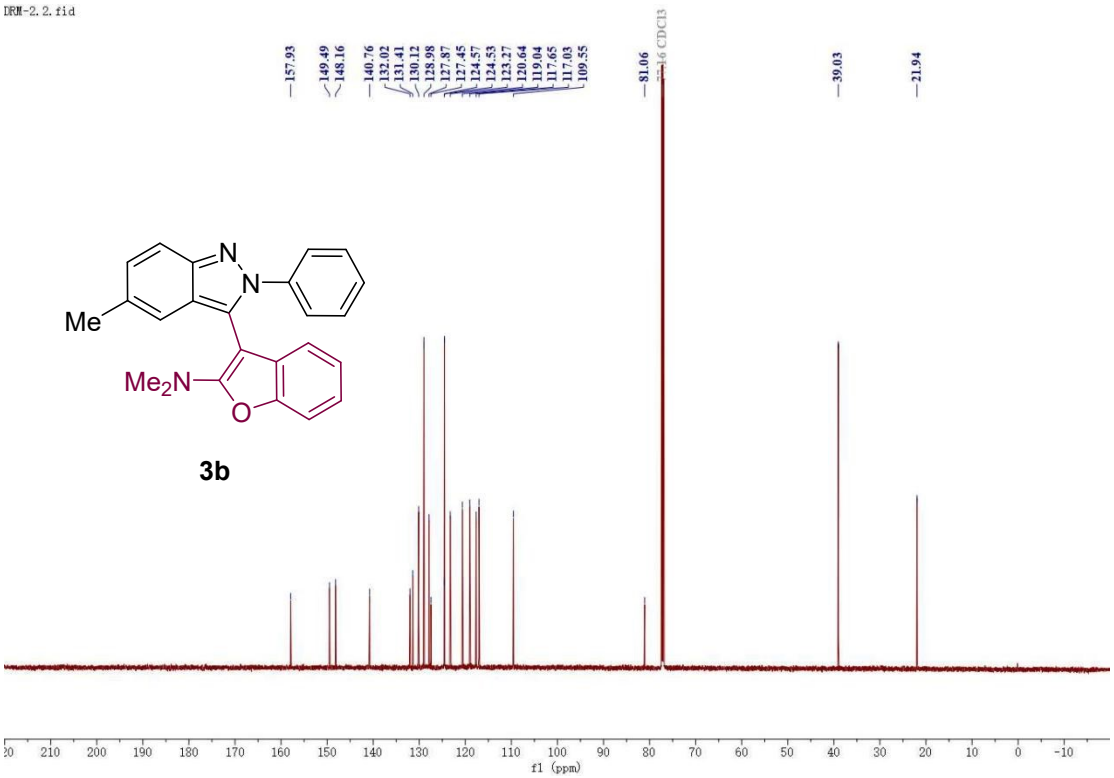
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3a



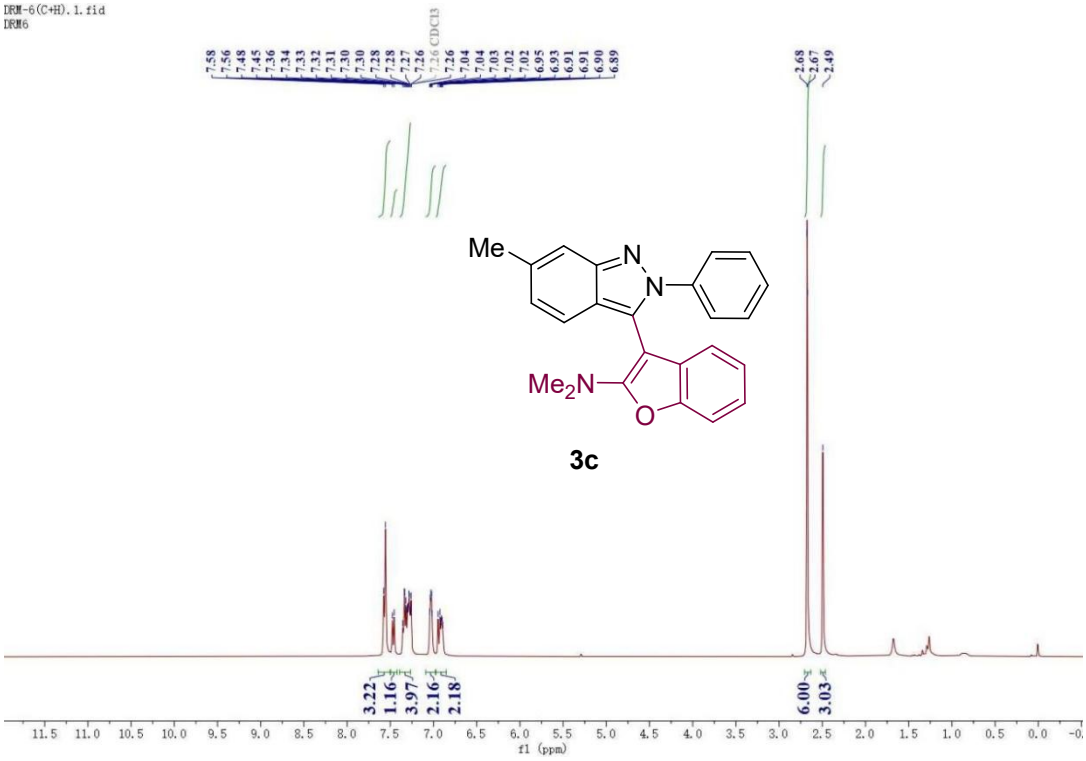
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3b



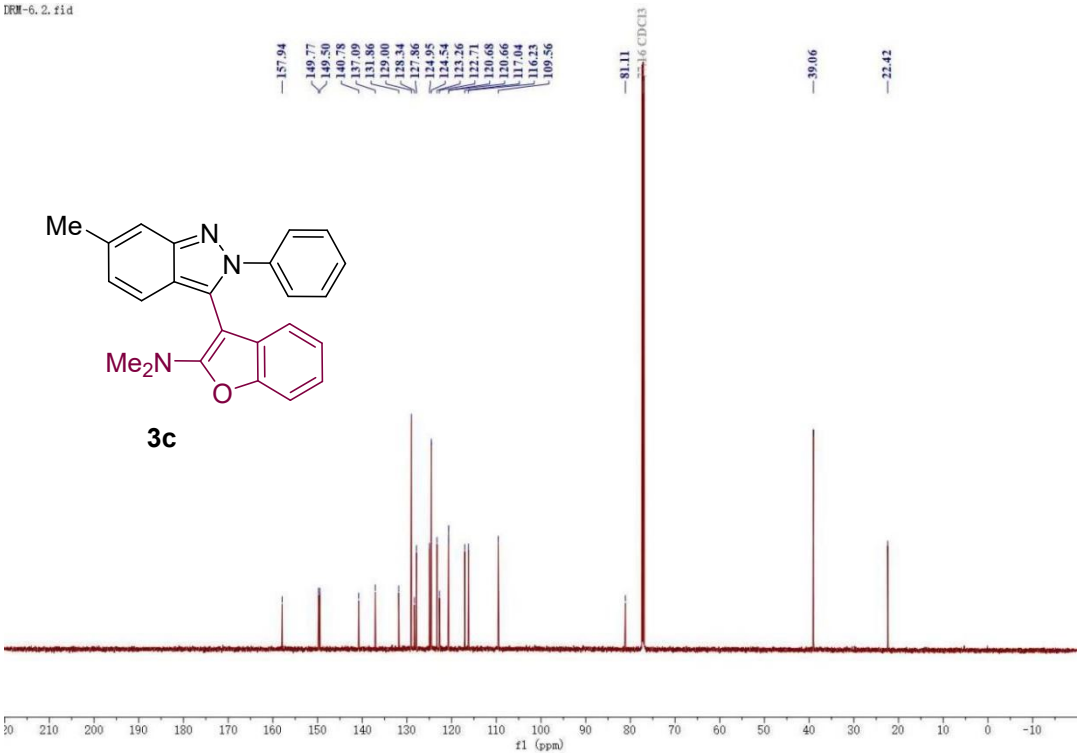
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3b



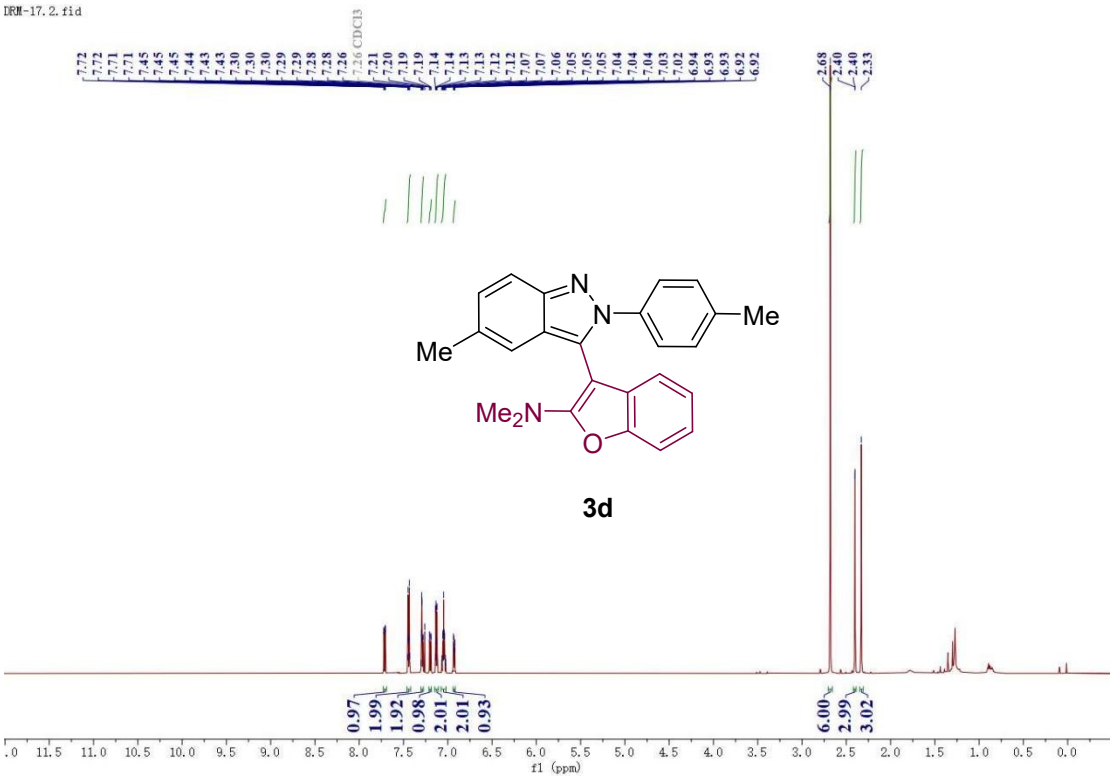
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3c



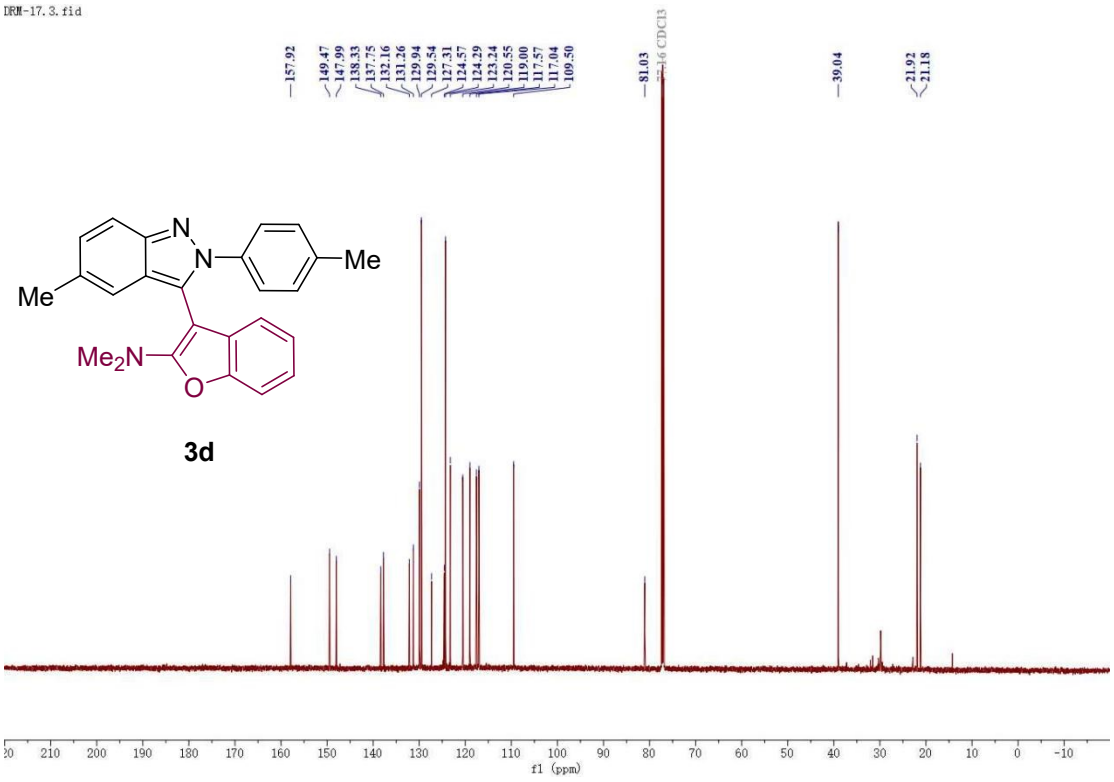
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3c



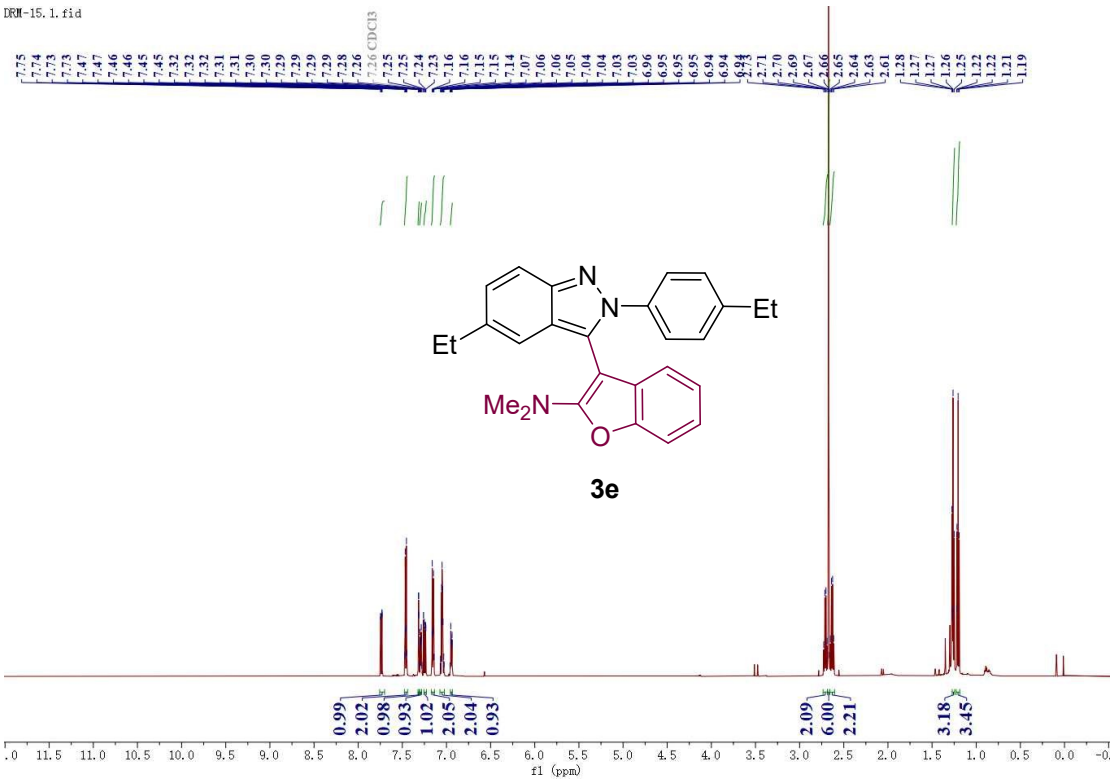
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3d



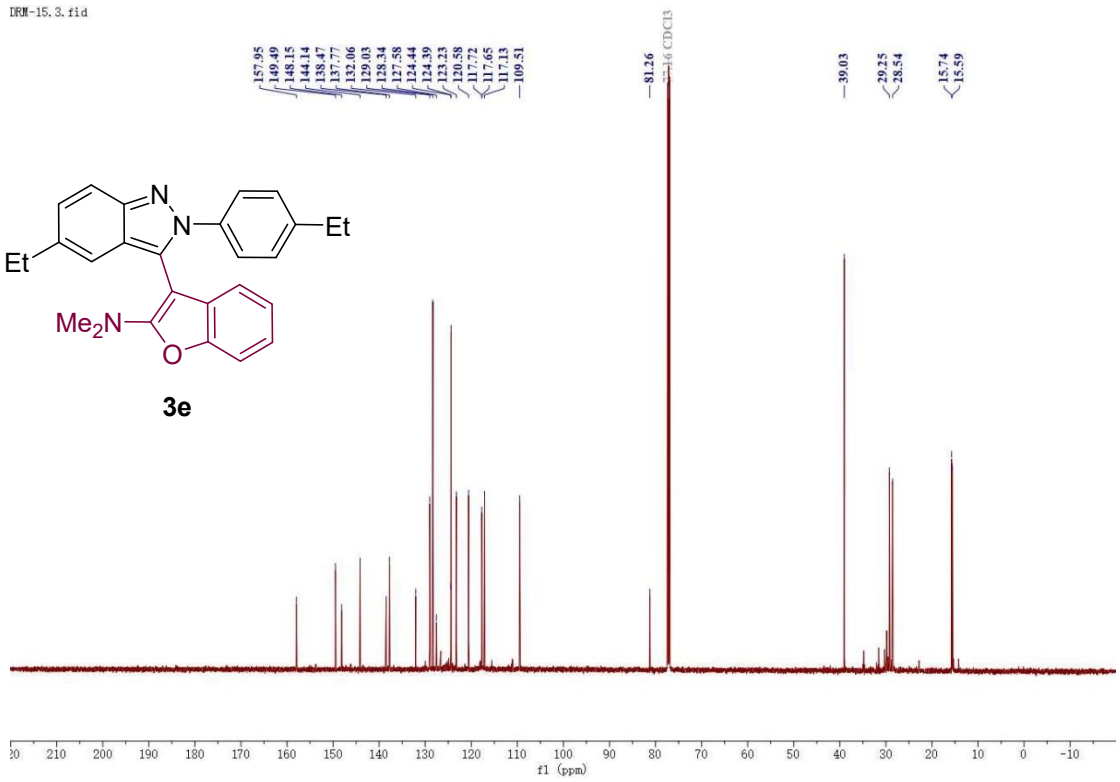
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3d



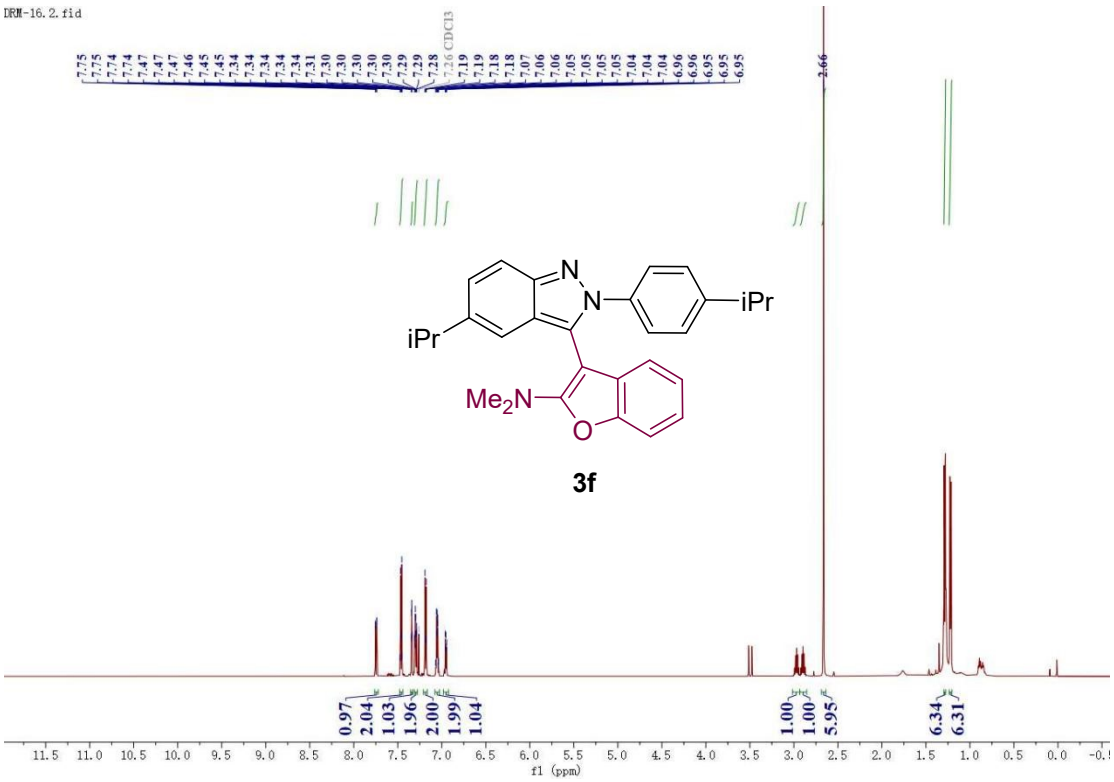
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3e



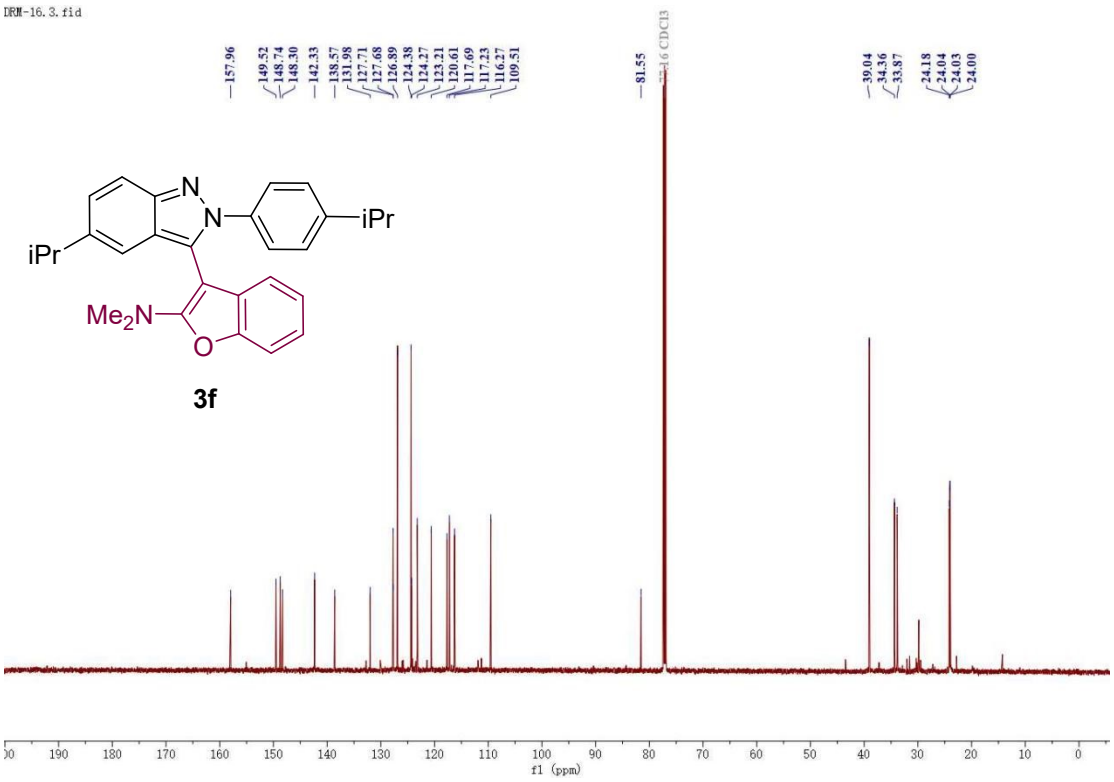
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3e



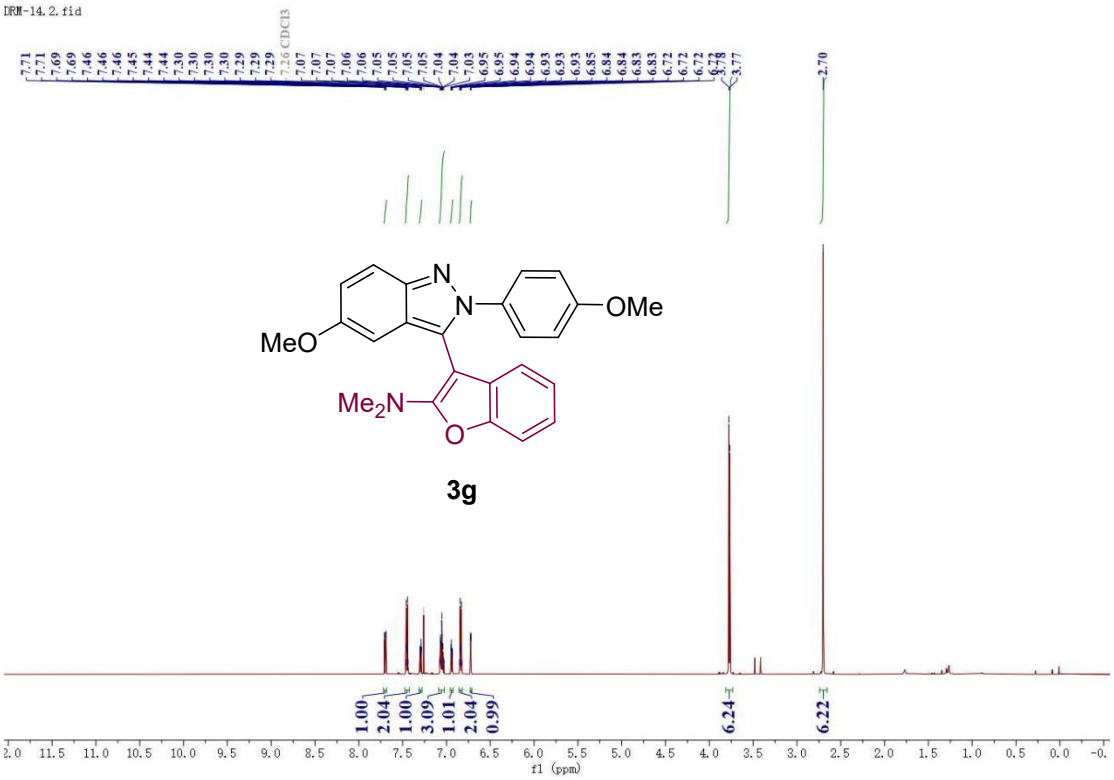
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3f



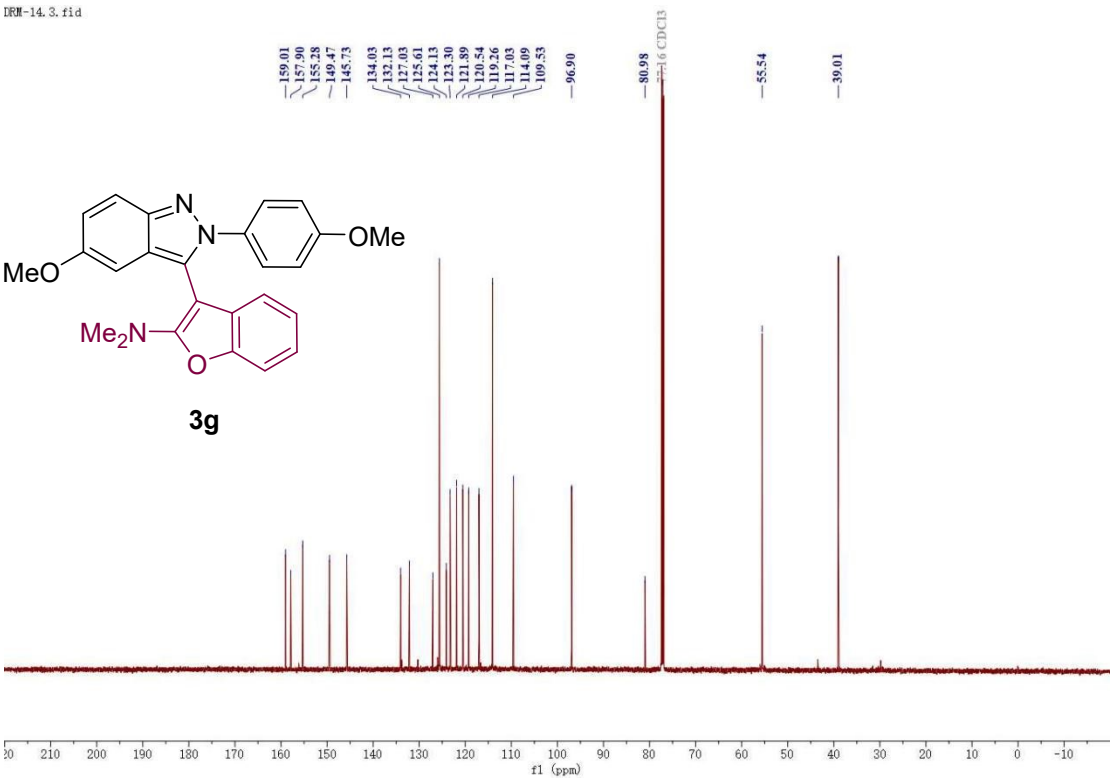
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3f



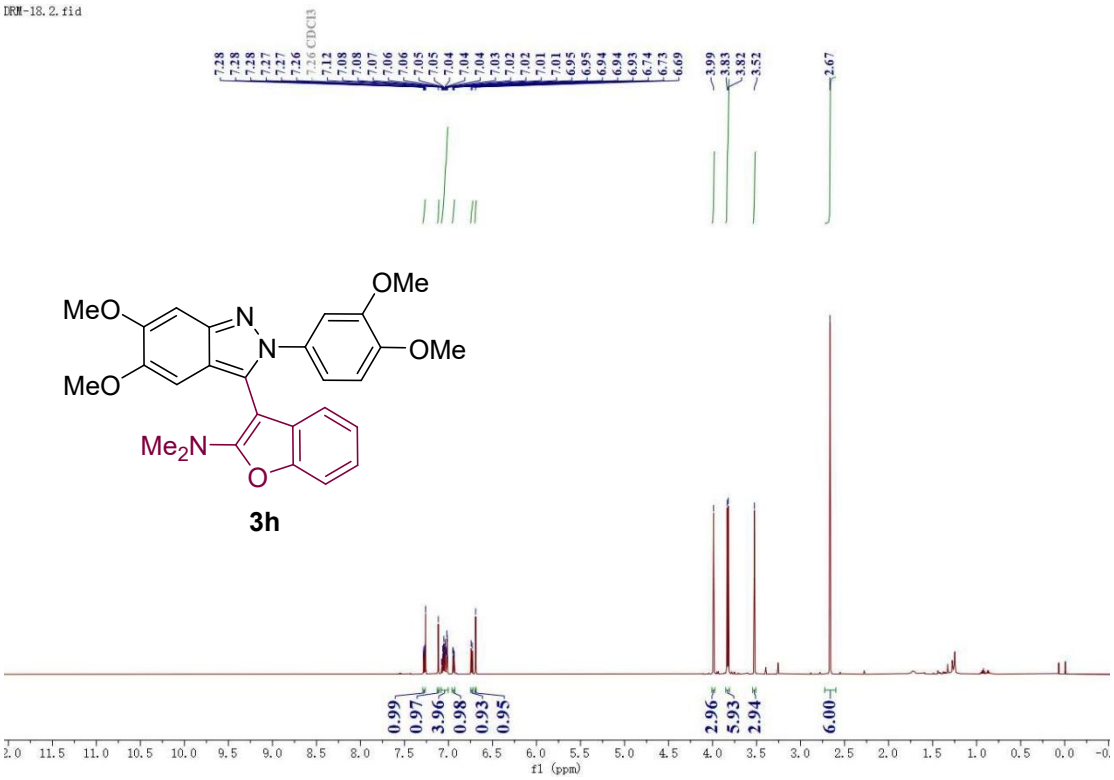
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3g



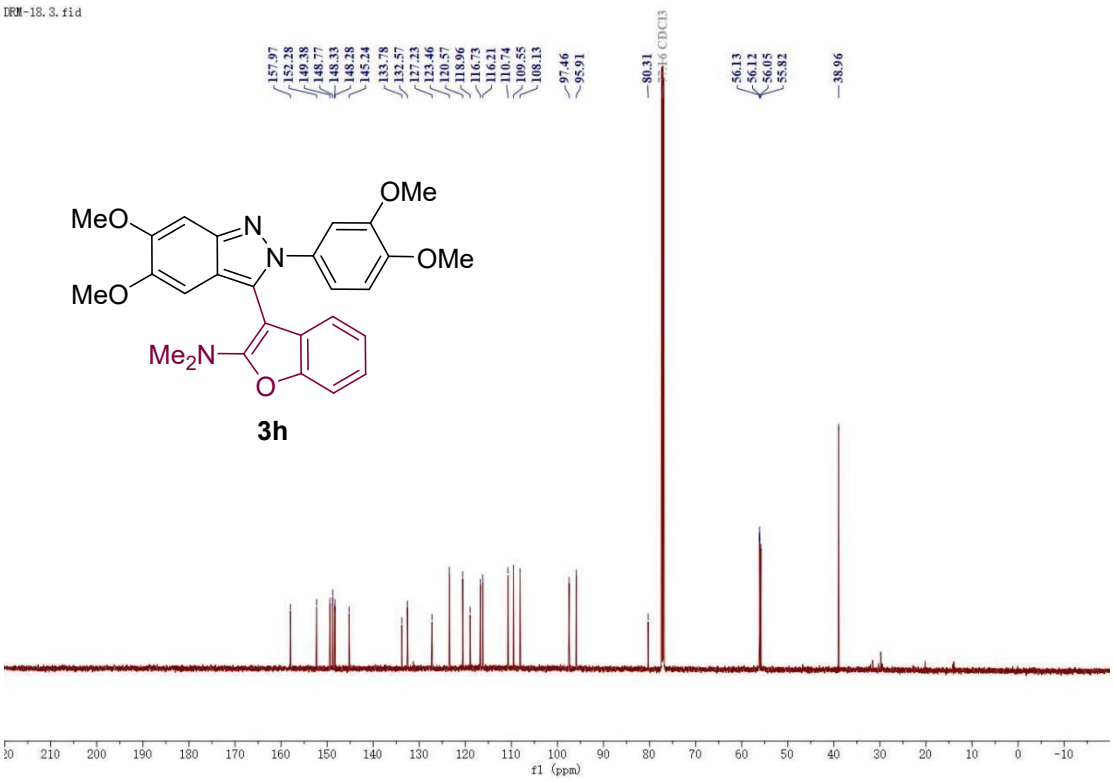
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3g



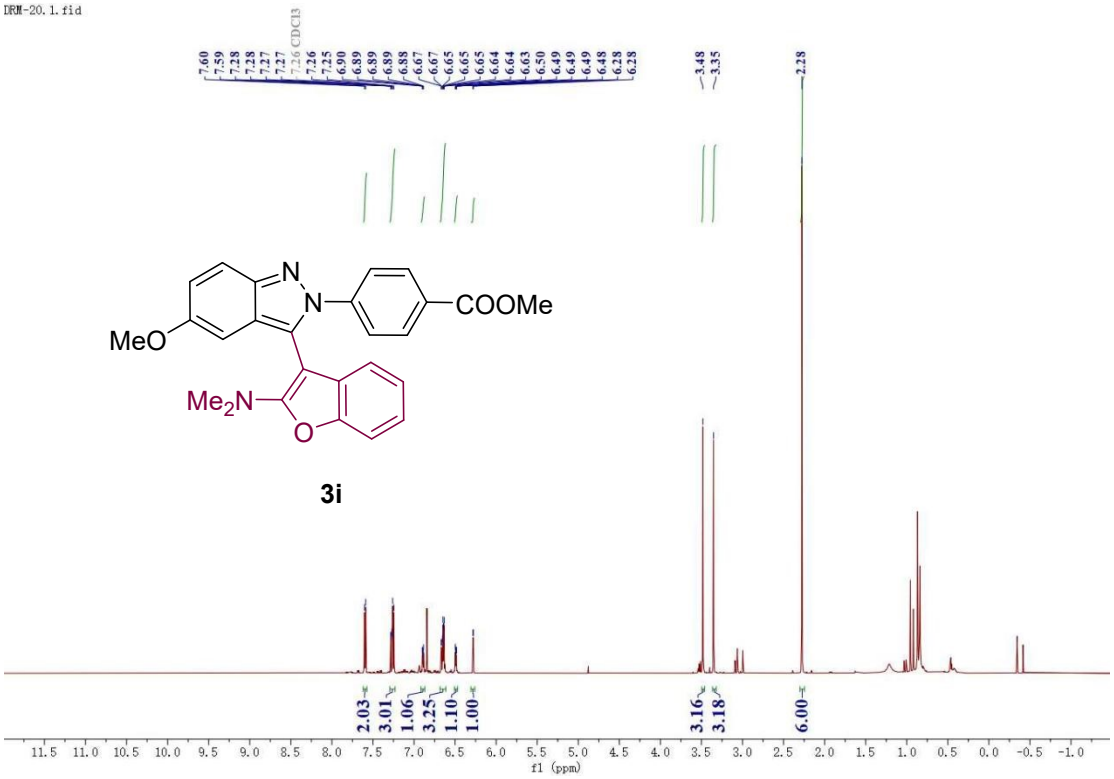
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3h



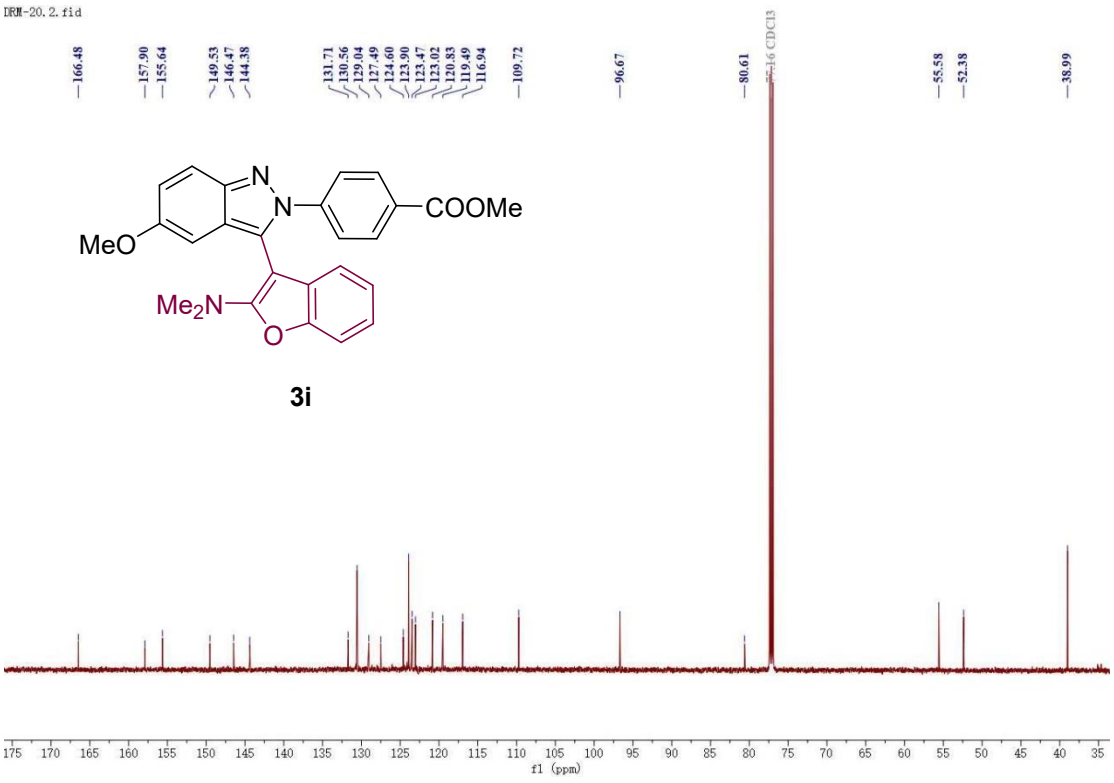
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3h



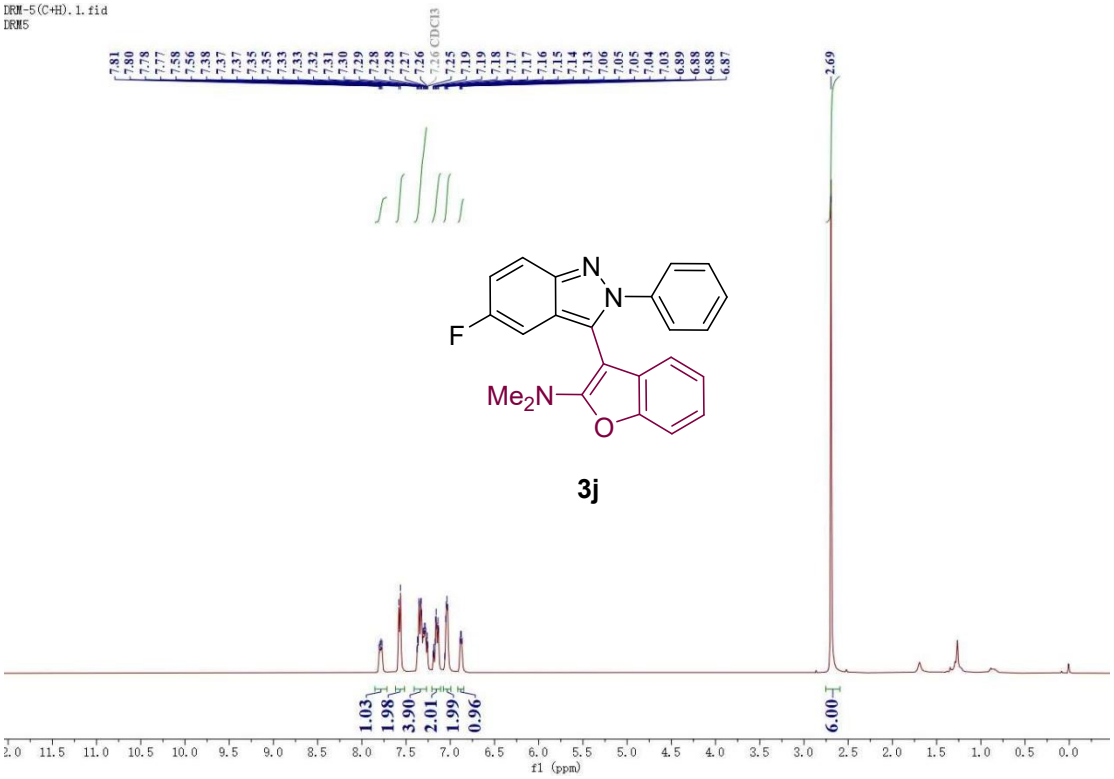
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3i



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3i

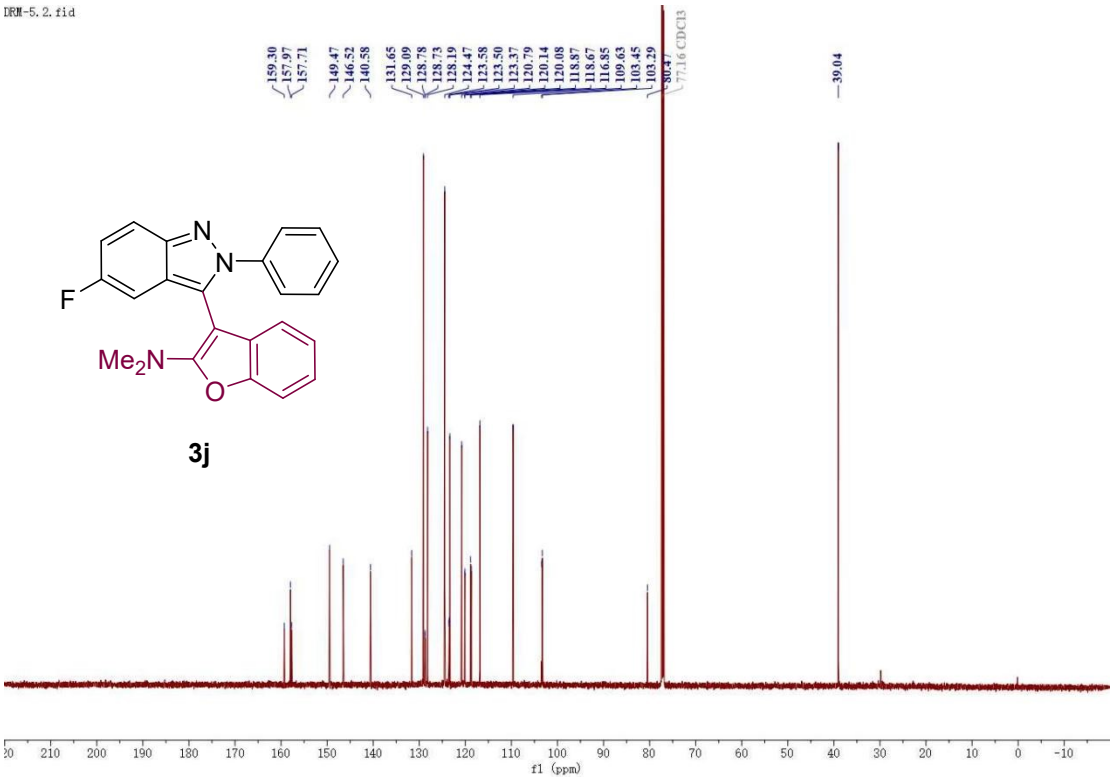


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3j



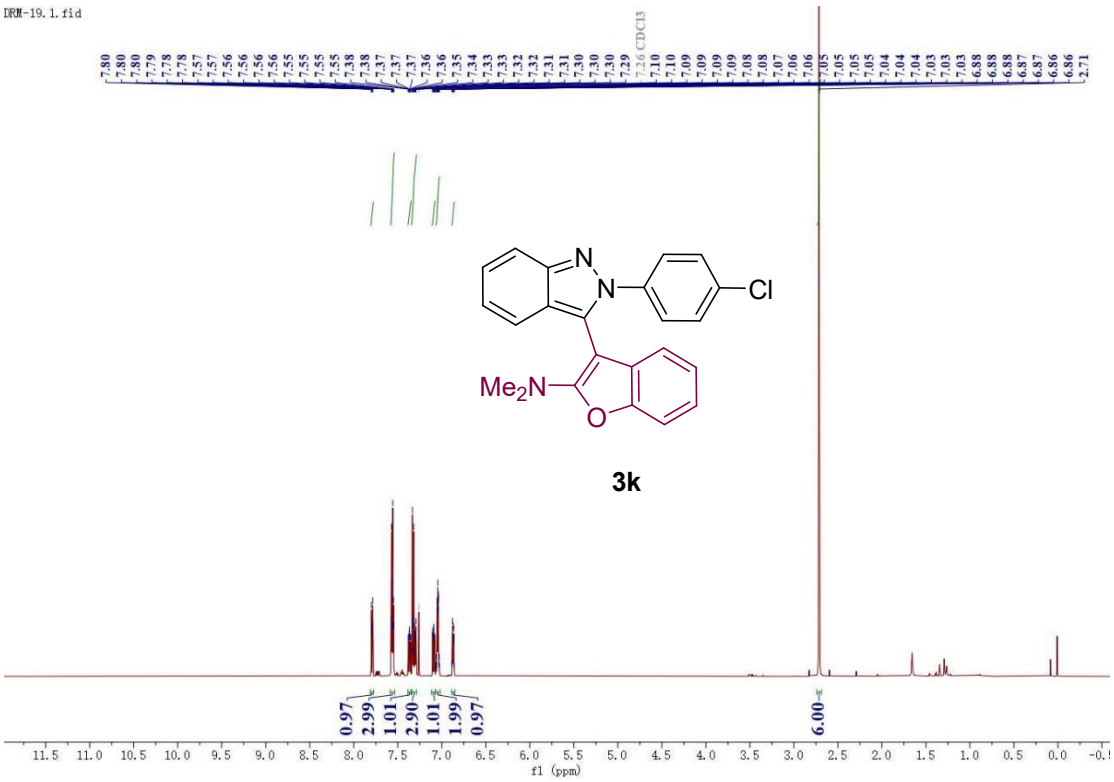
3j

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3j

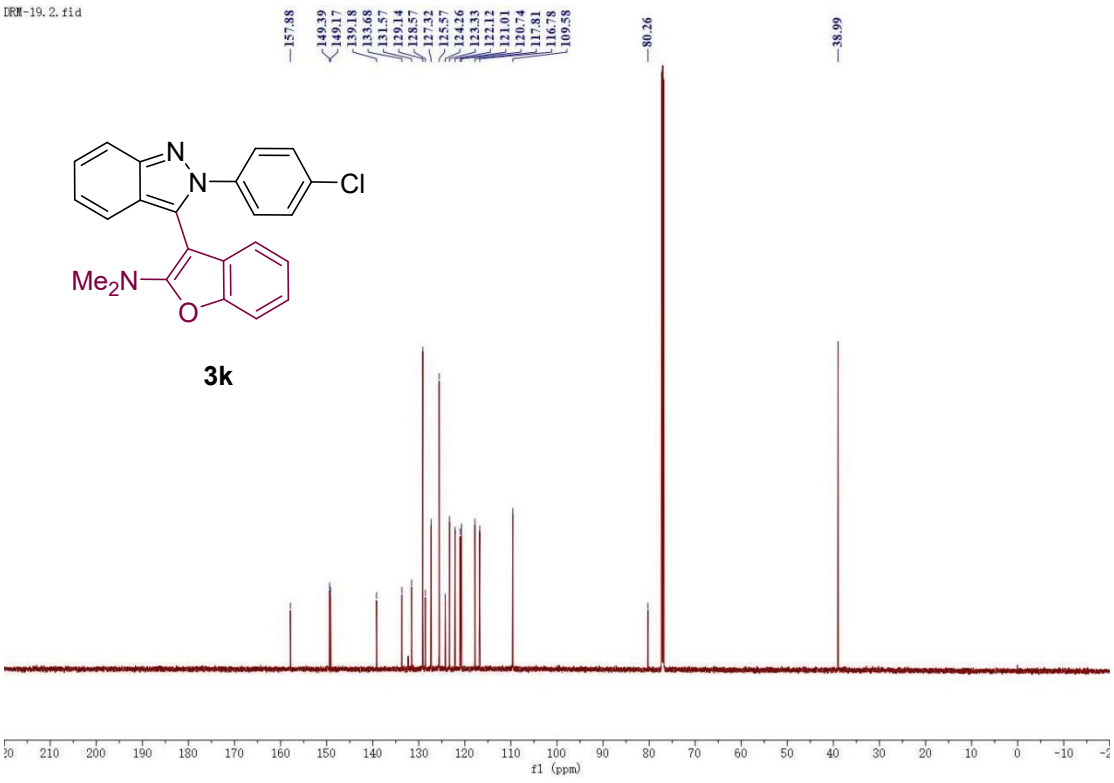


3j

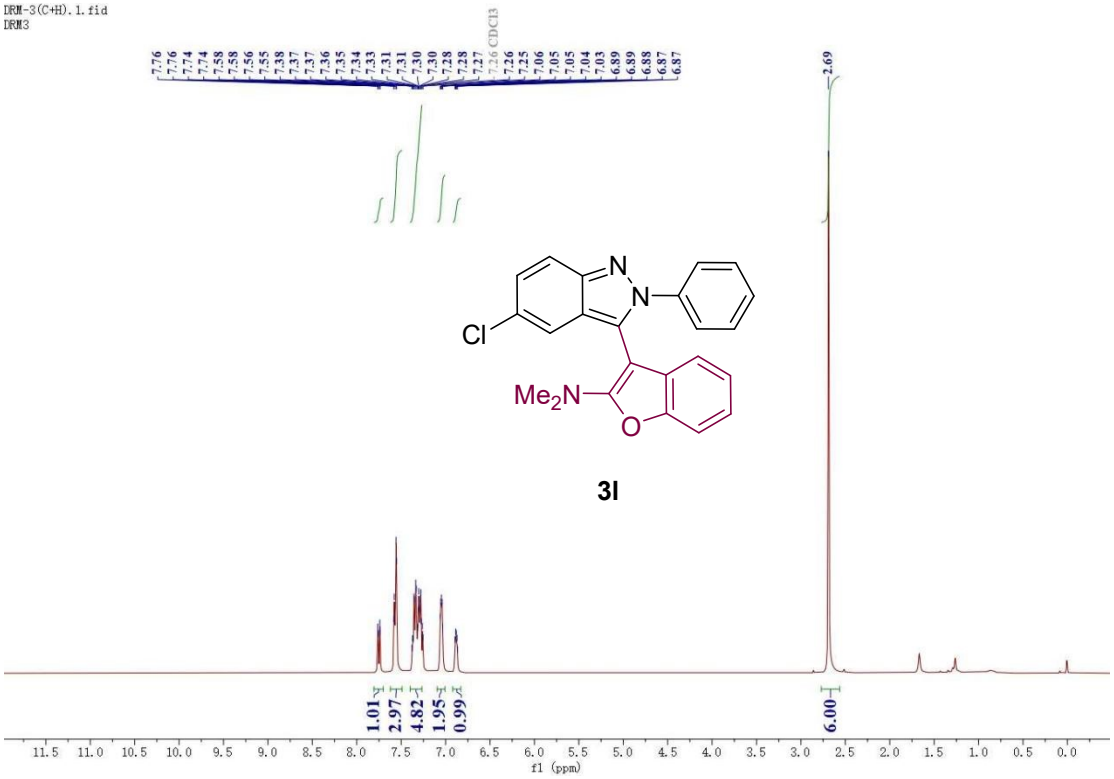
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3k



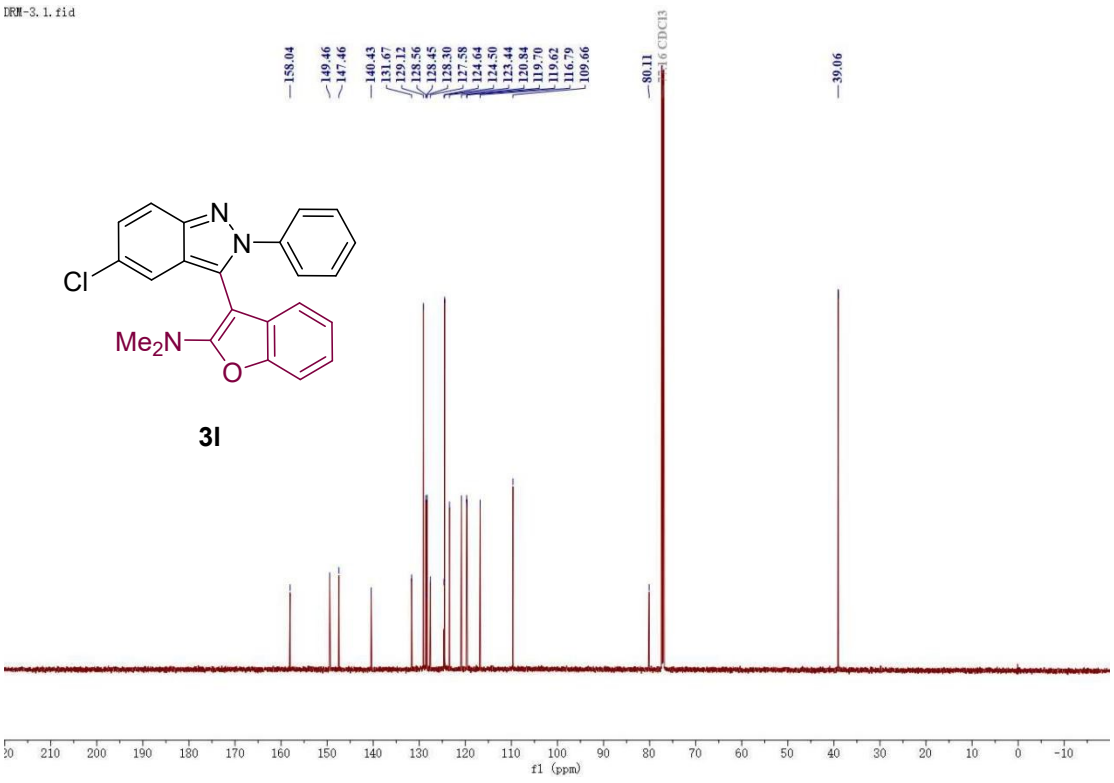
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3k



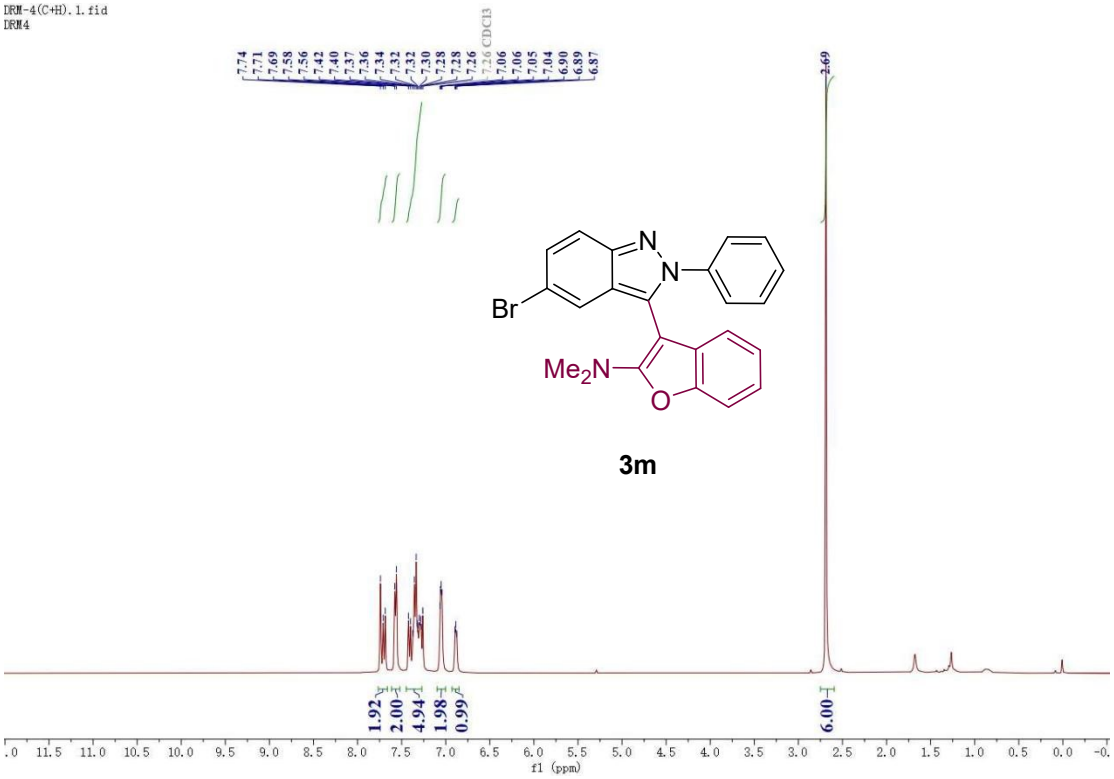
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3l



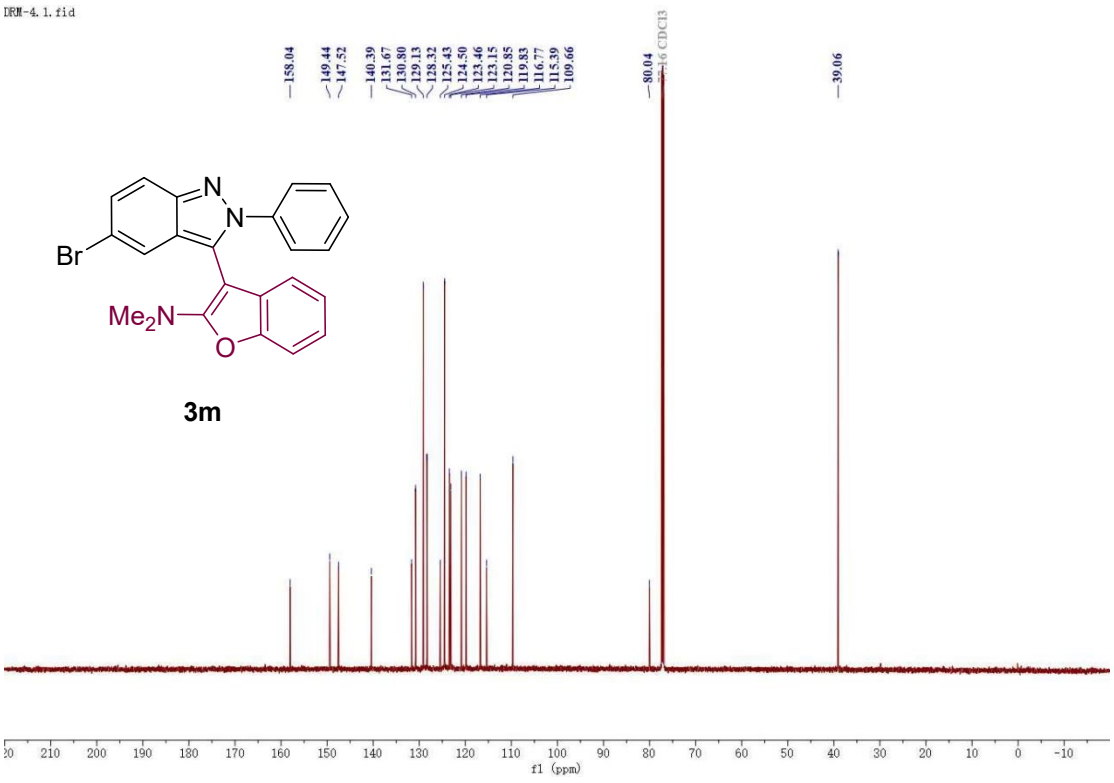
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3l



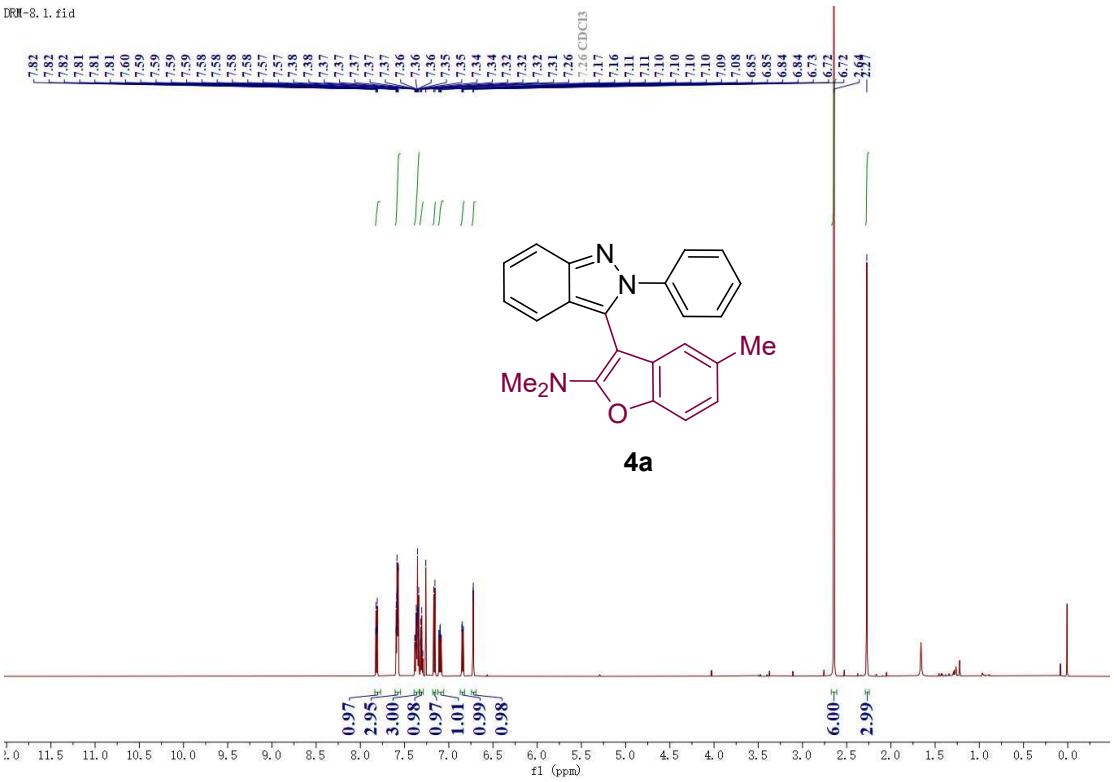
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3m



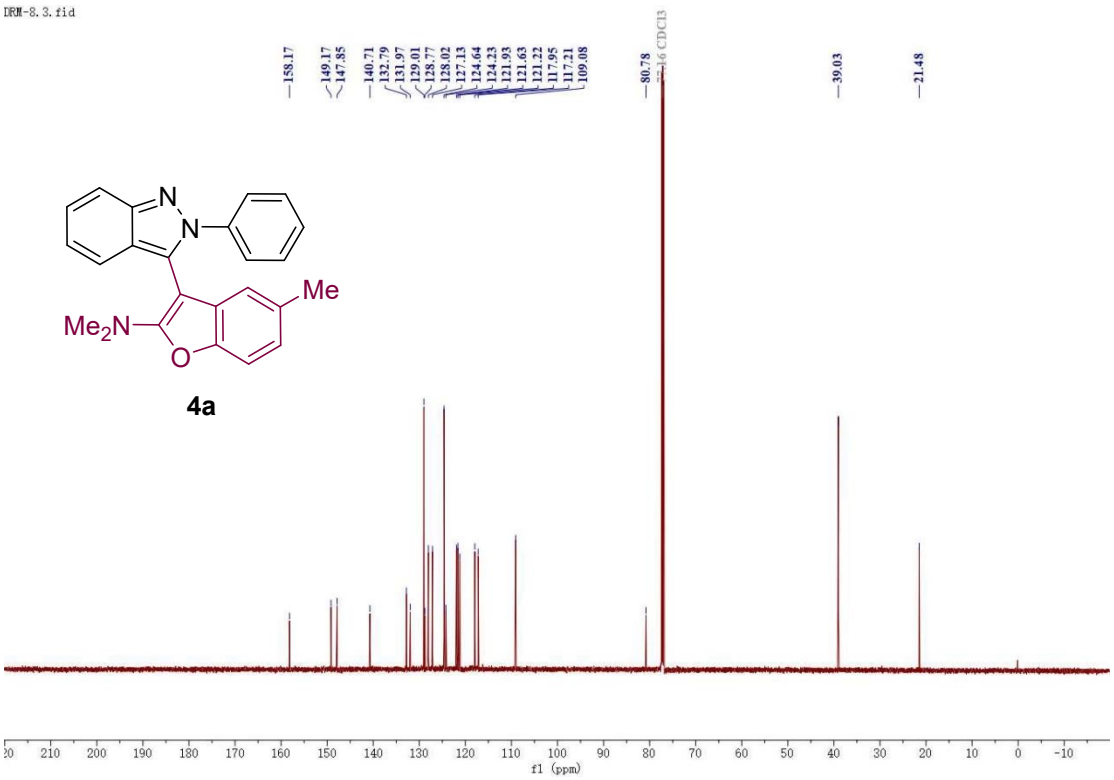
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3m



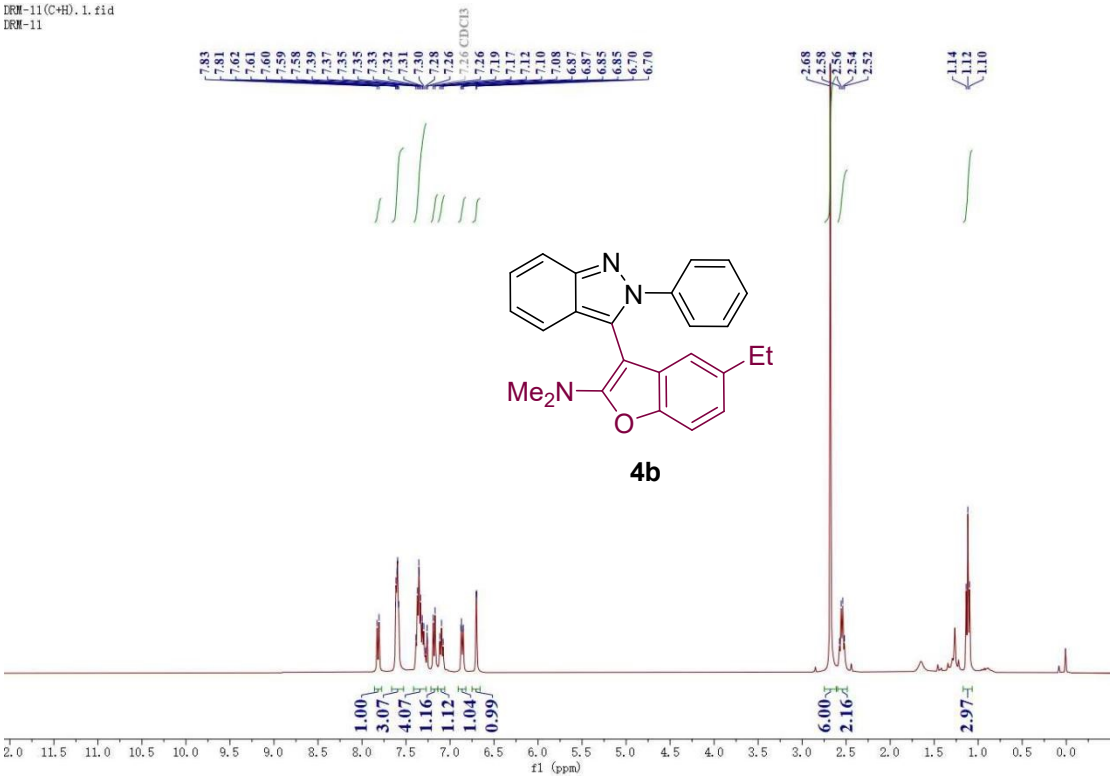
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4a



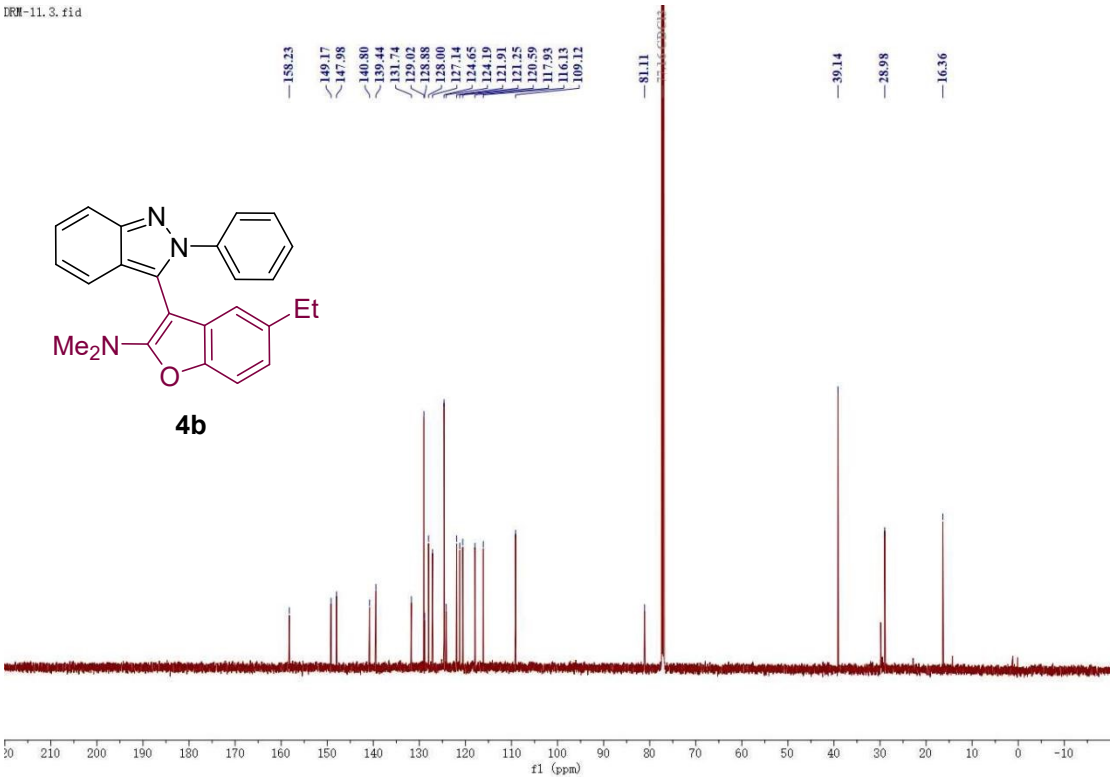
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4a



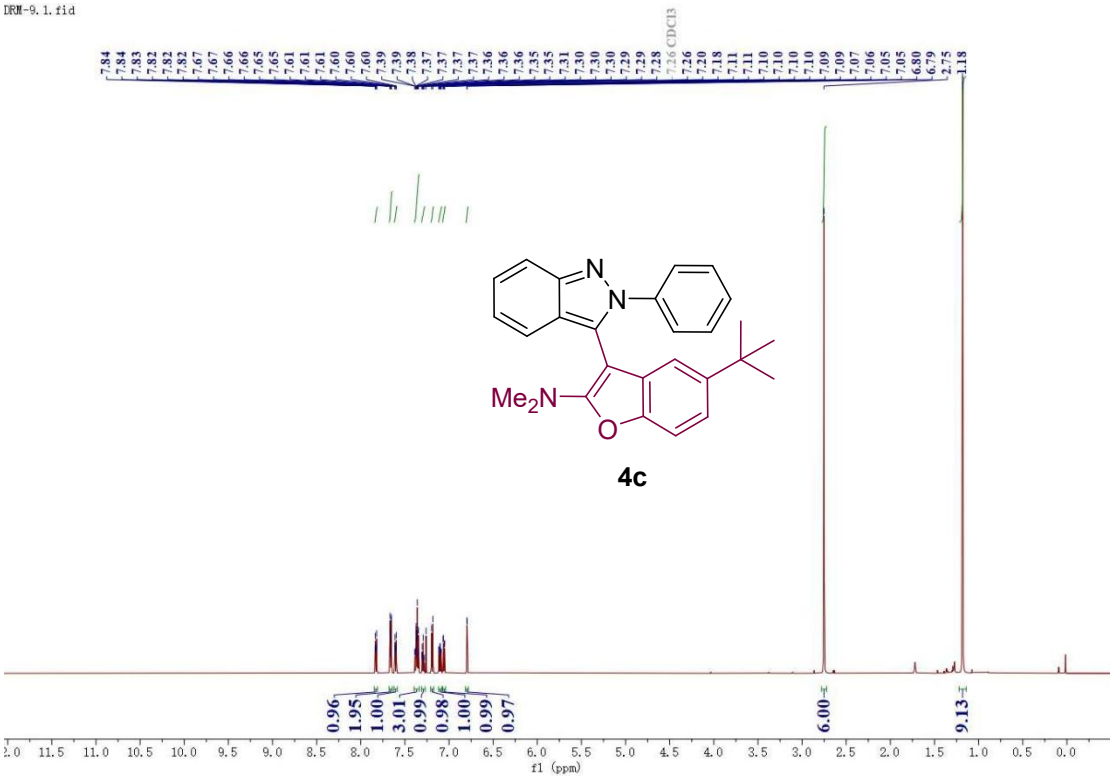
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4b



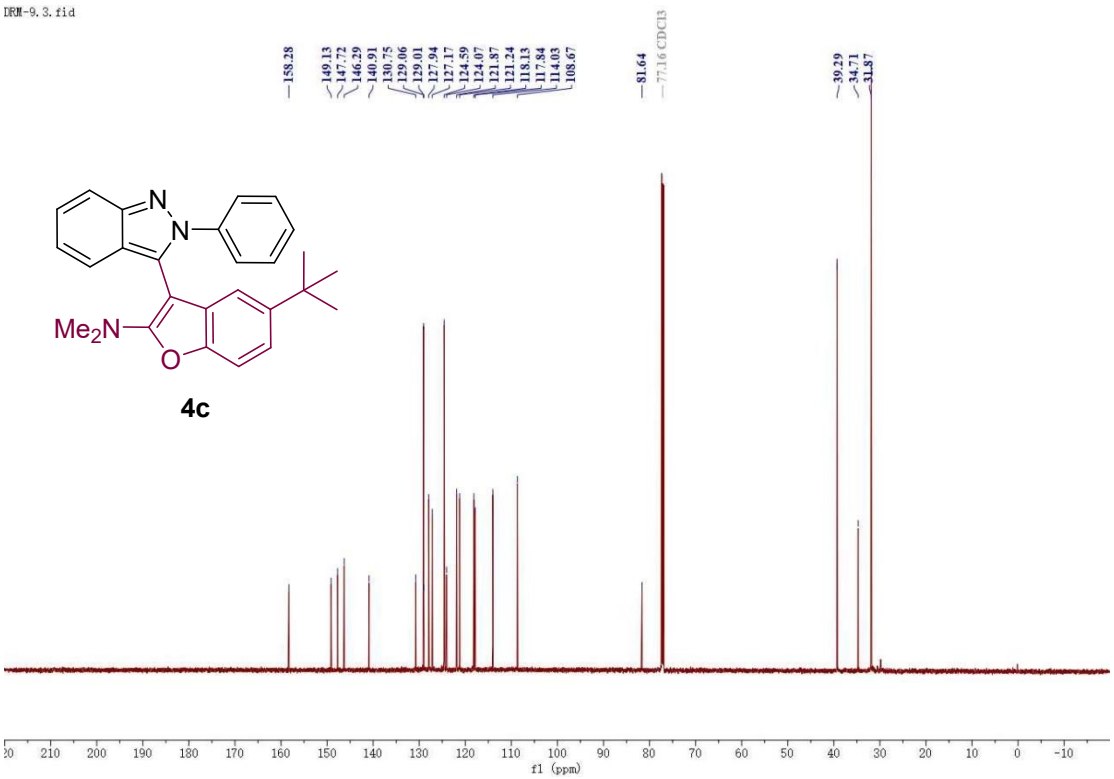
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4b



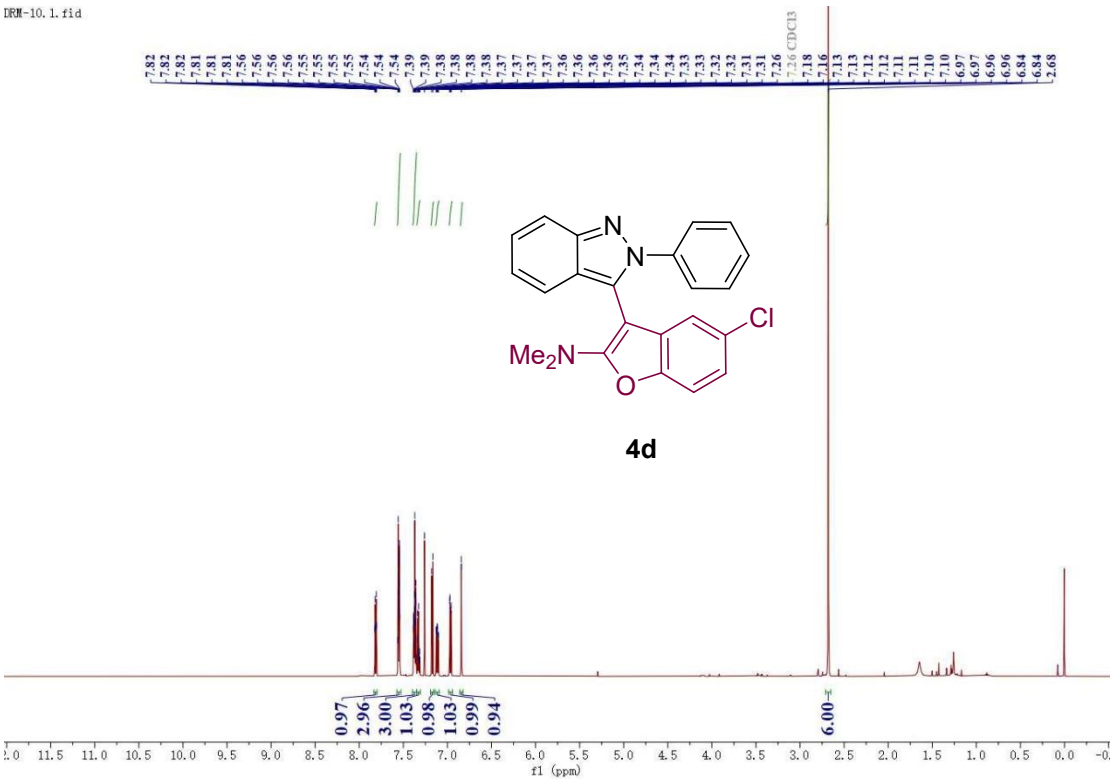
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4c



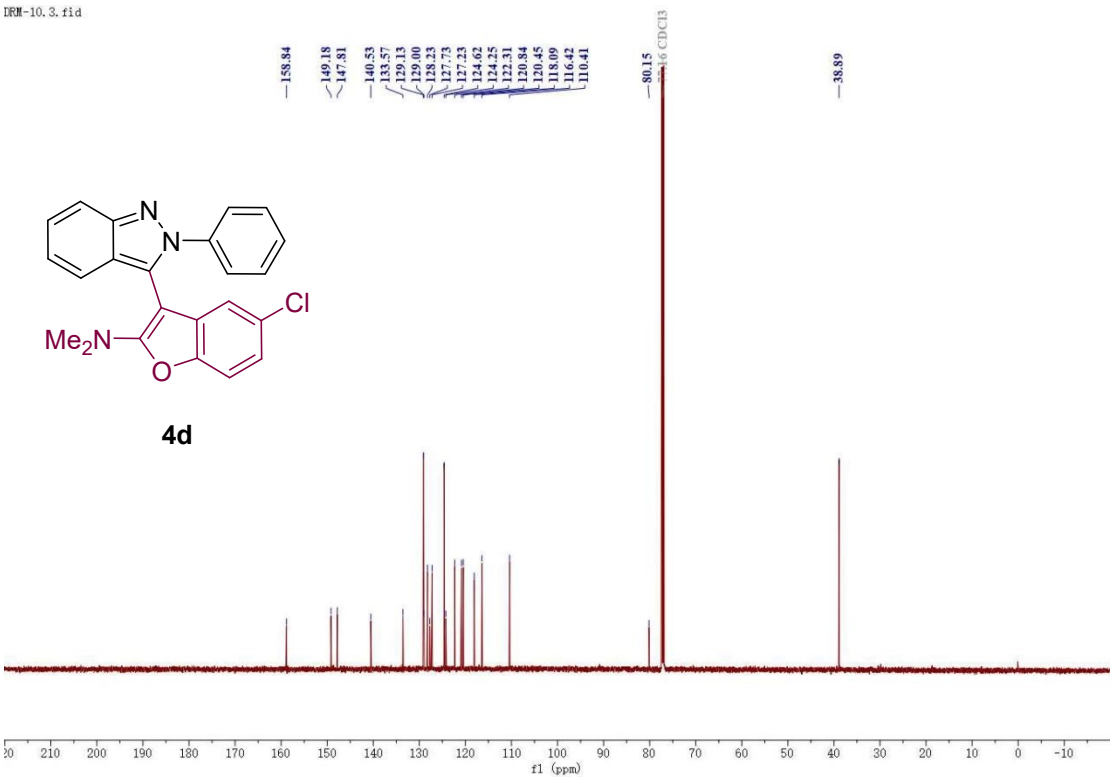
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4c



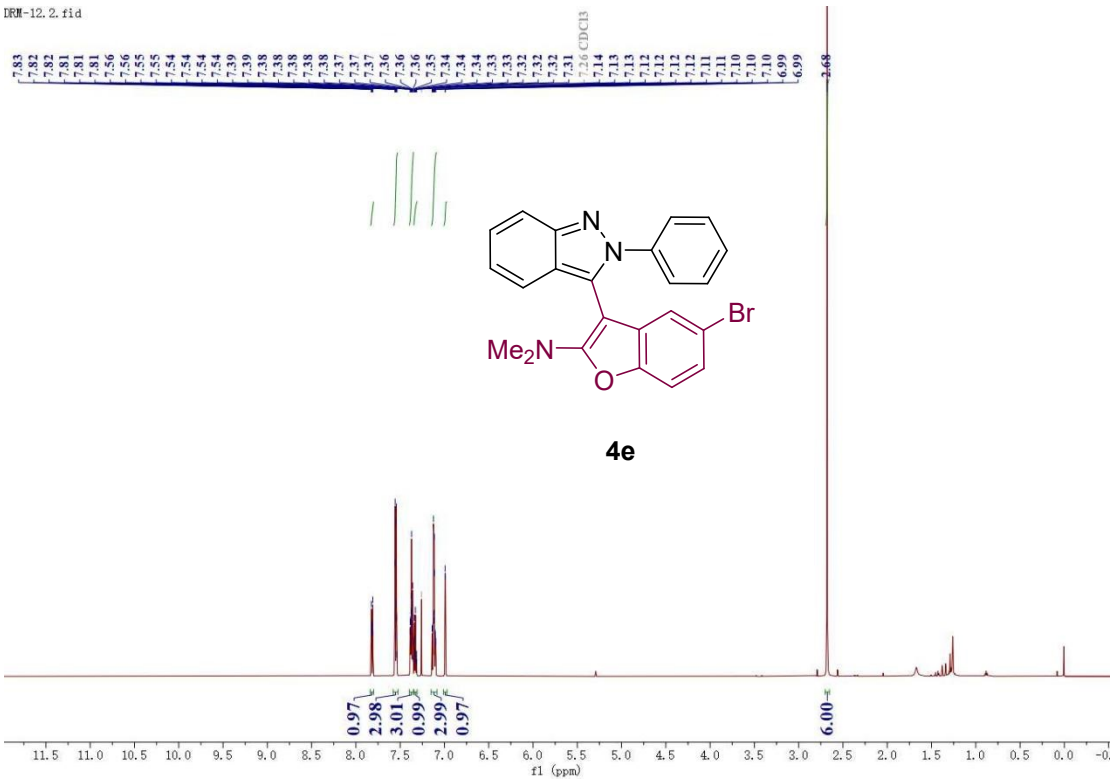
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4d



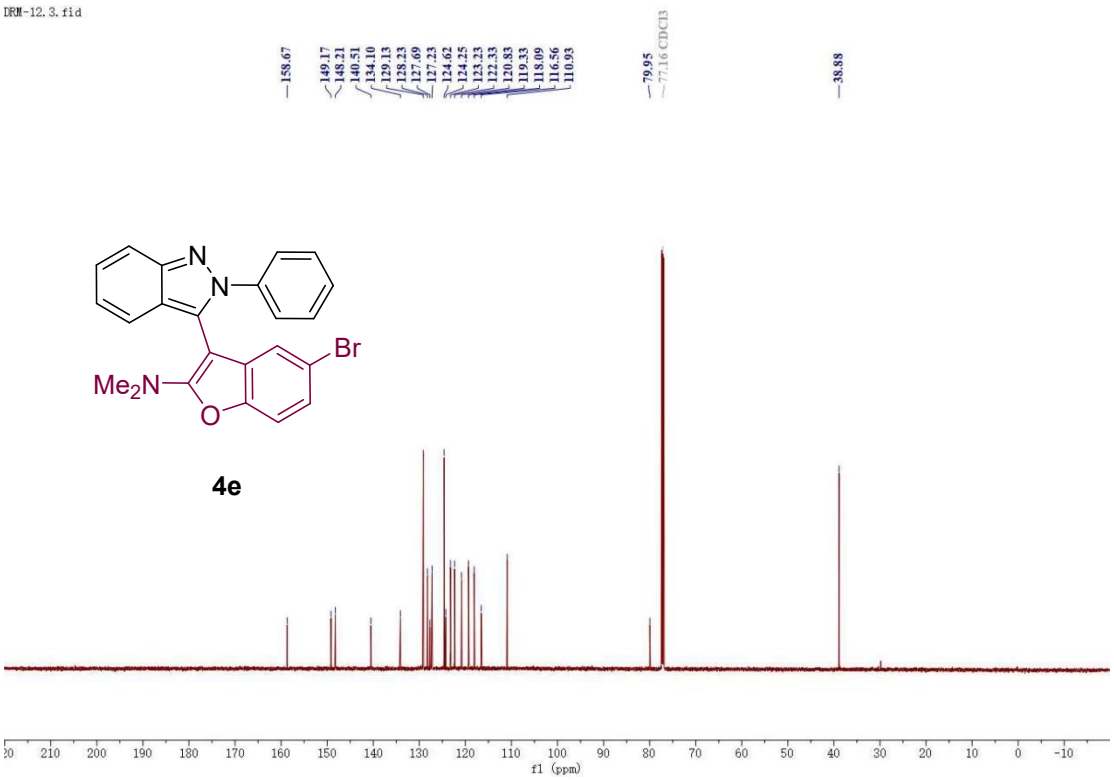
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4d



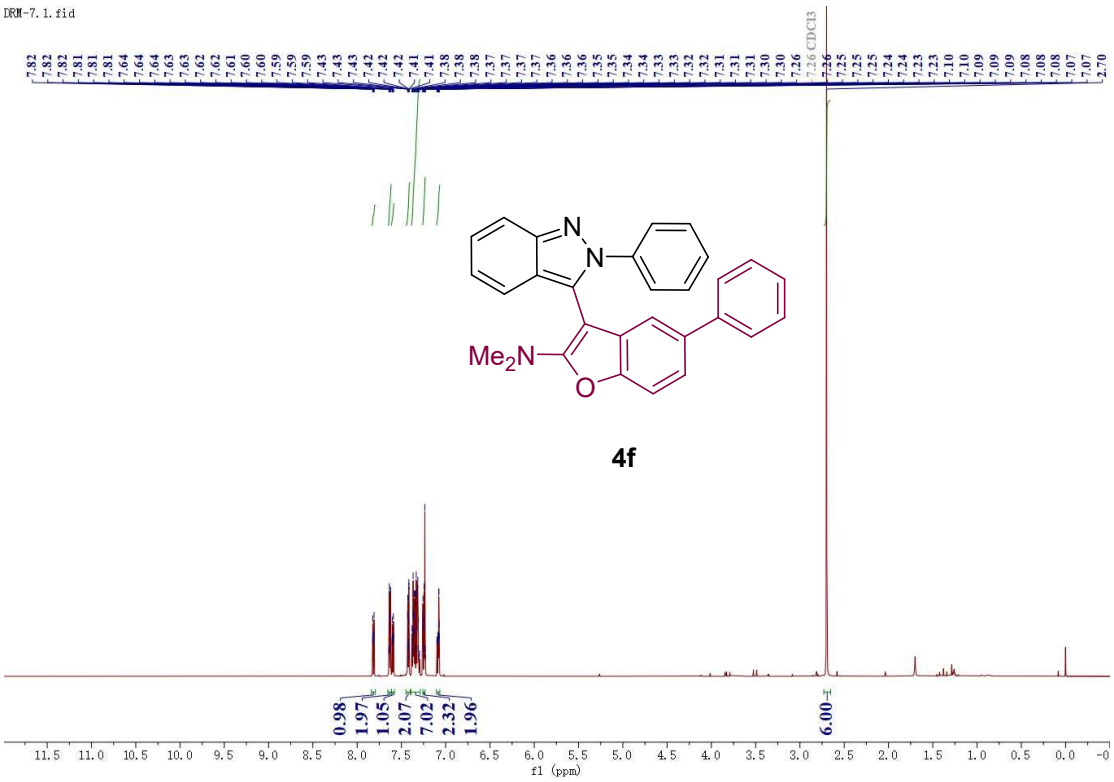
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4e



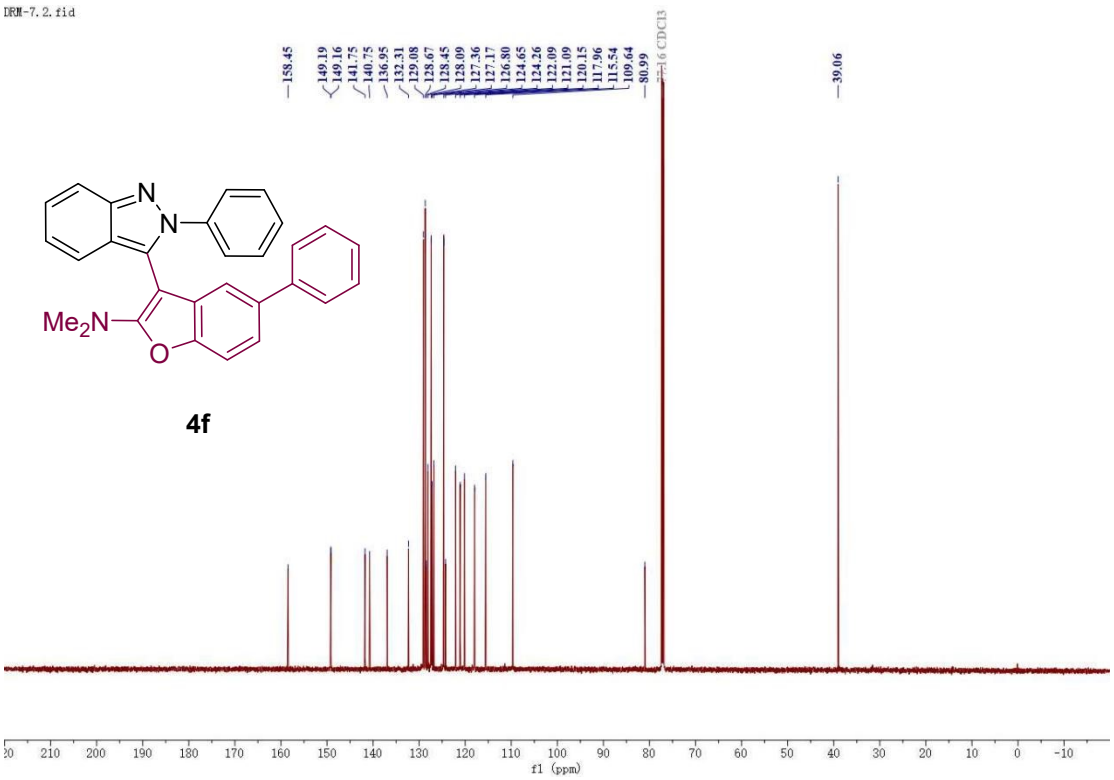
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4e



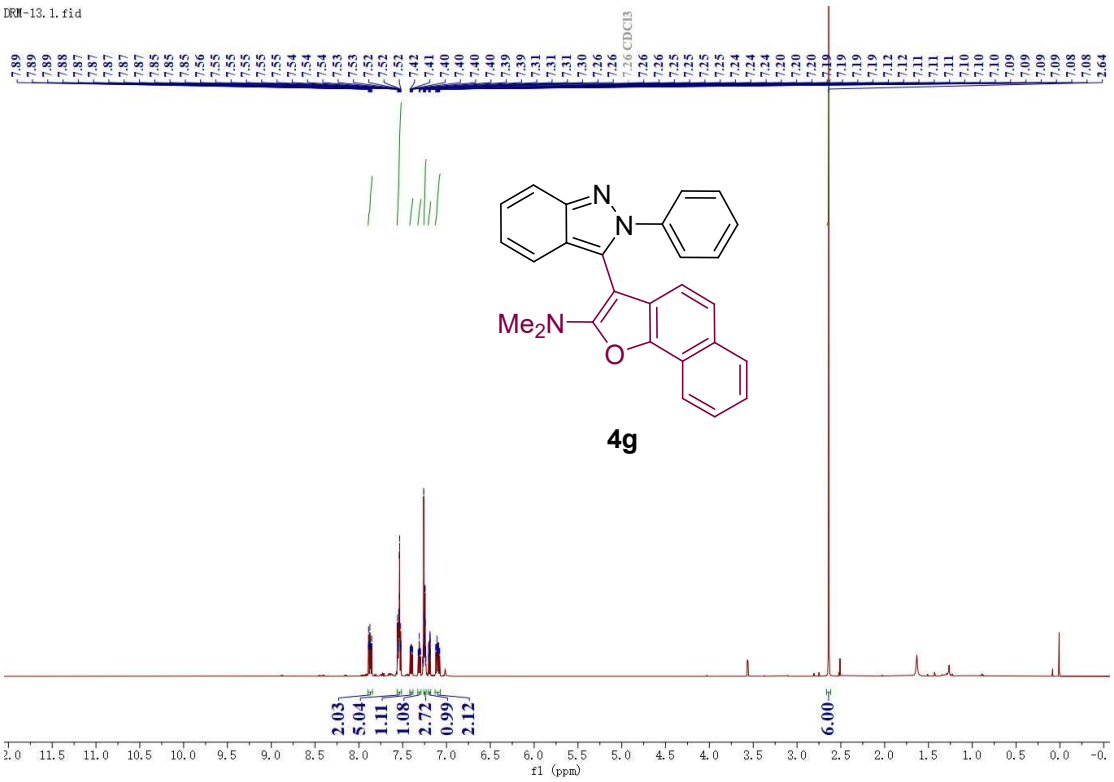
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4f



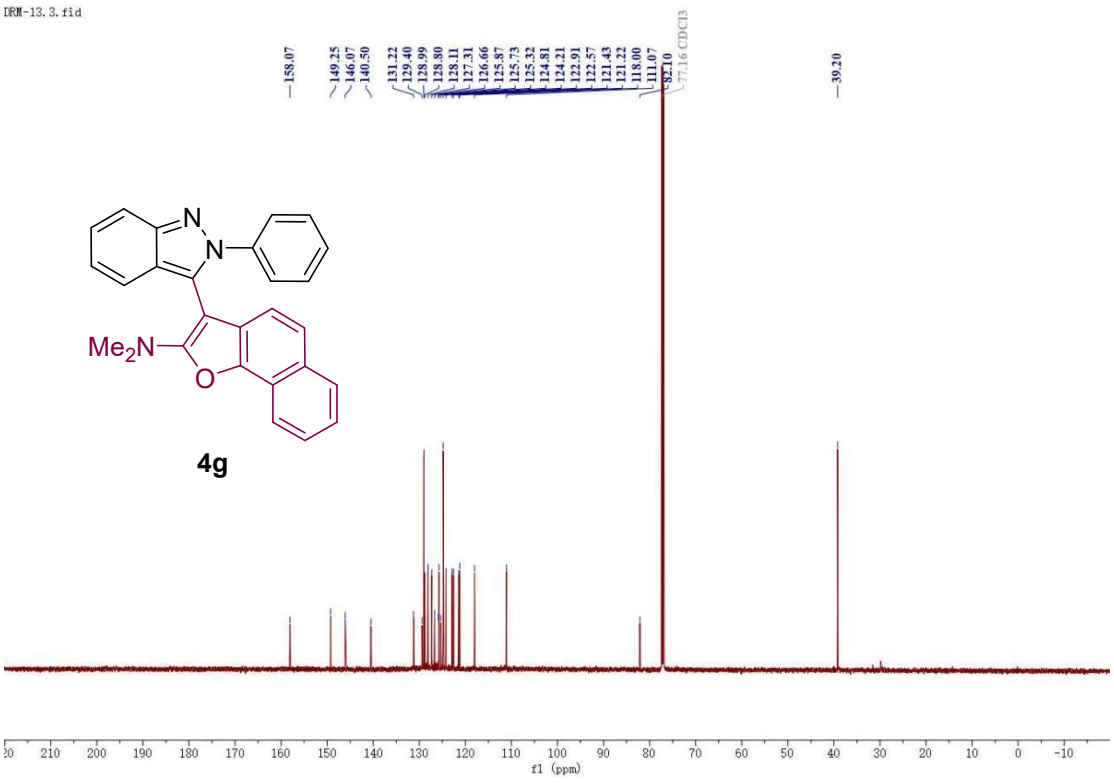
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4f



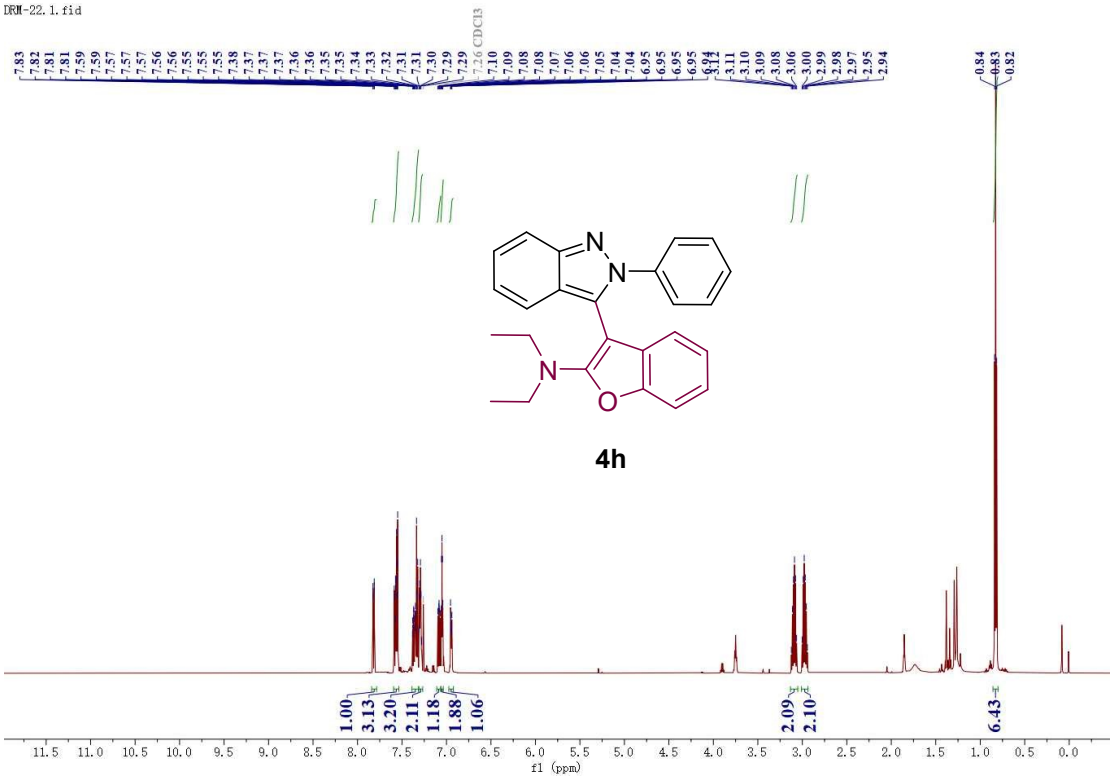
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4g



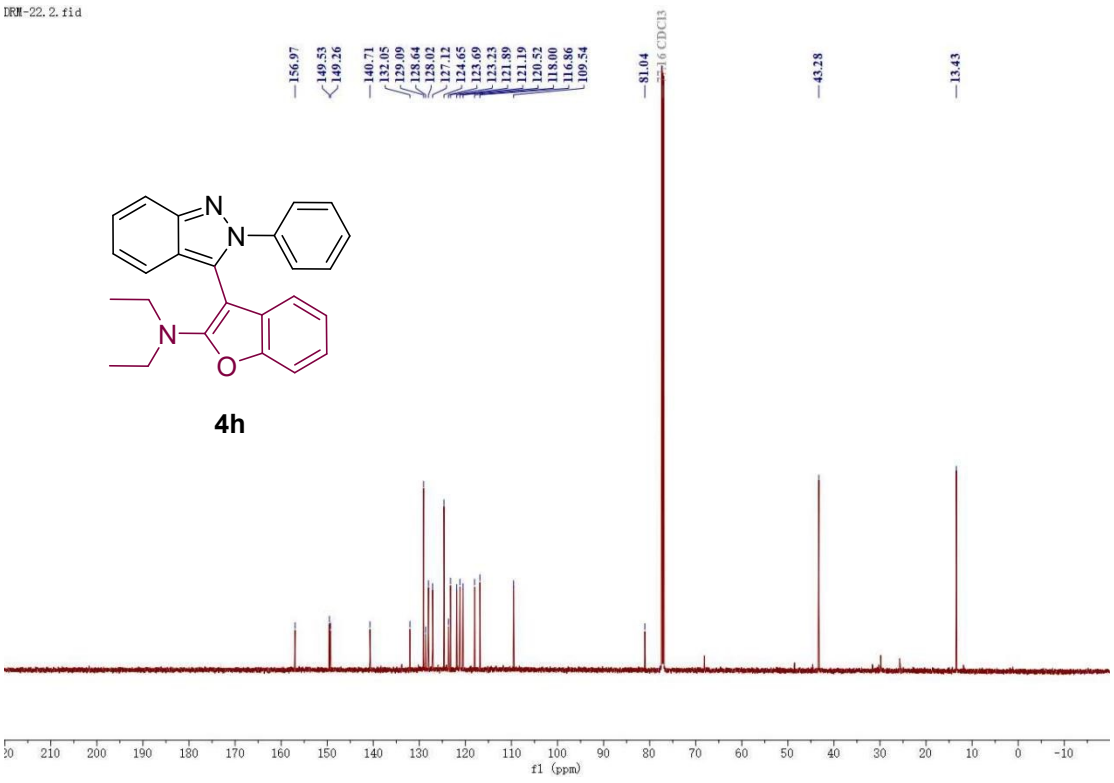
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4g



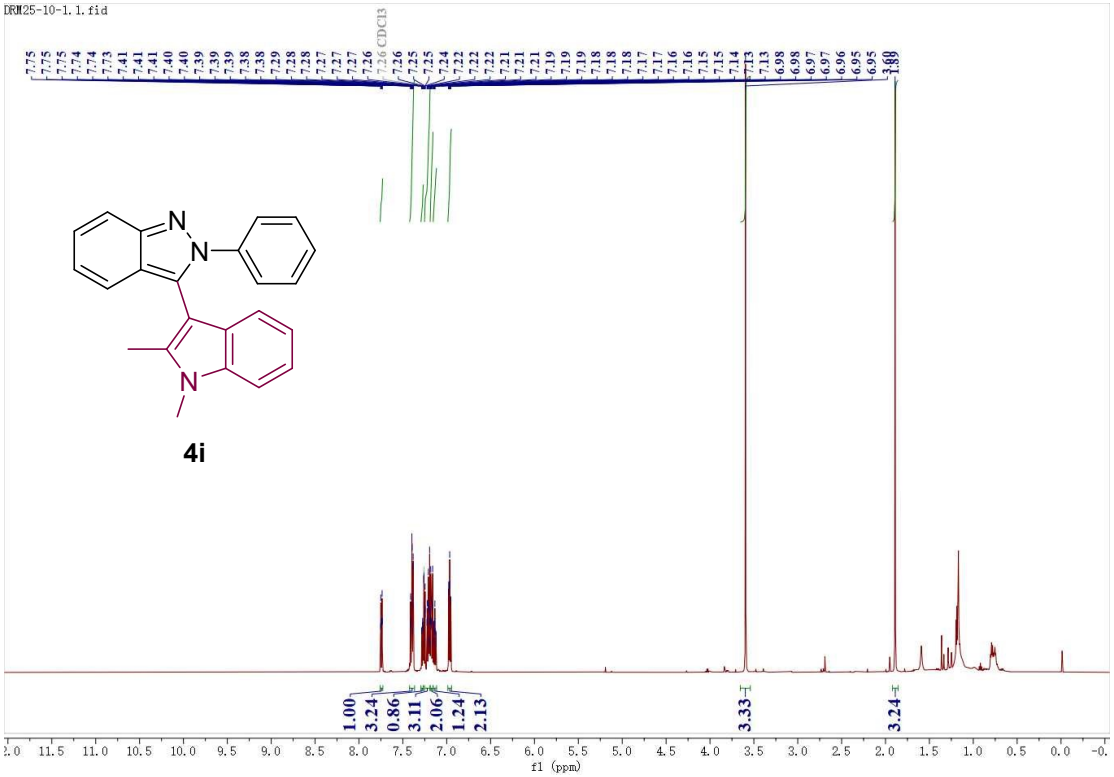
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4h



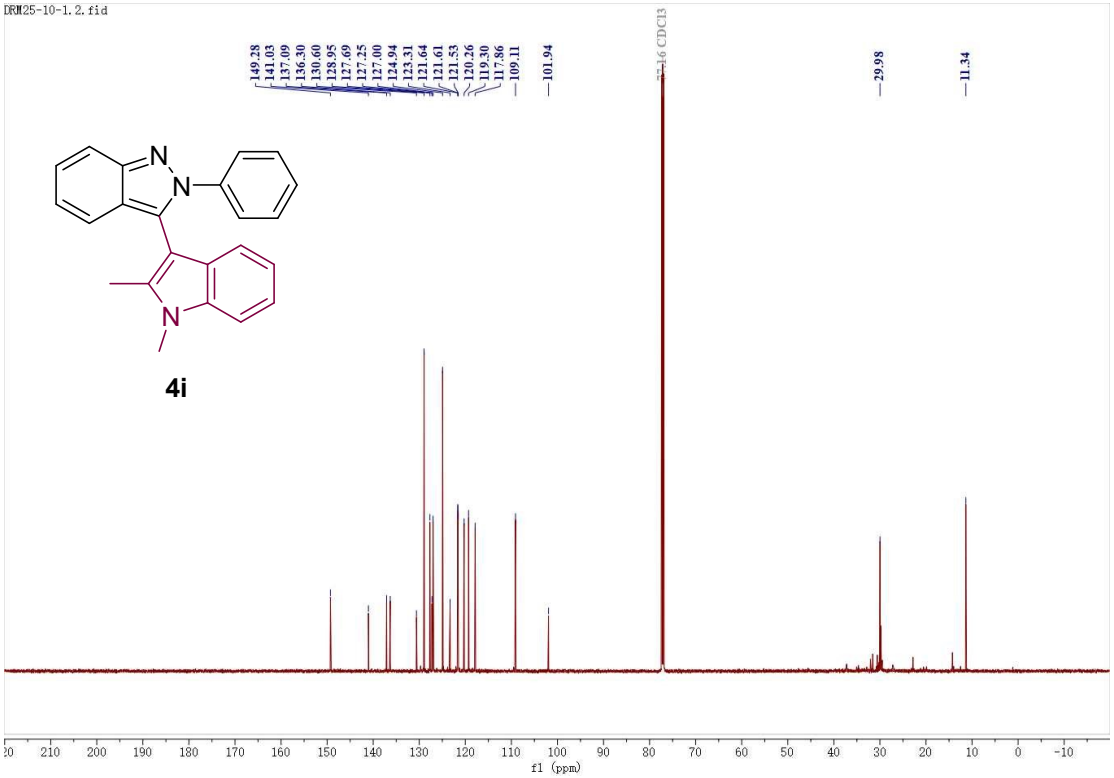
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4h



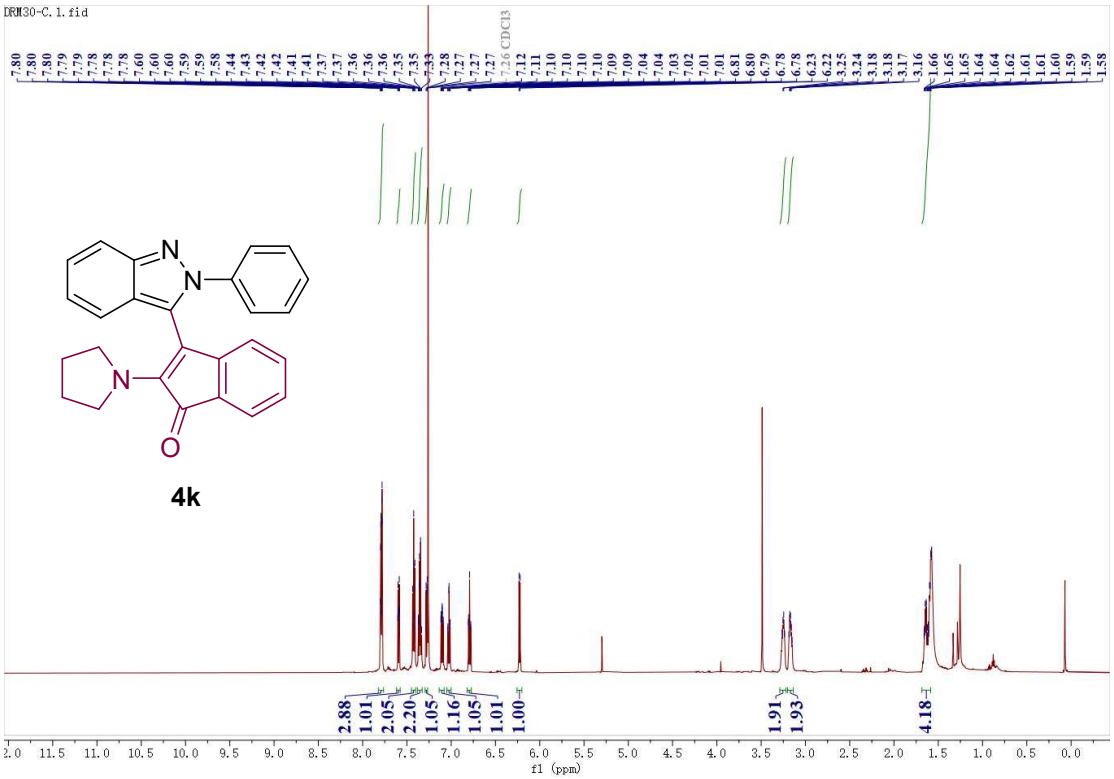
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4i



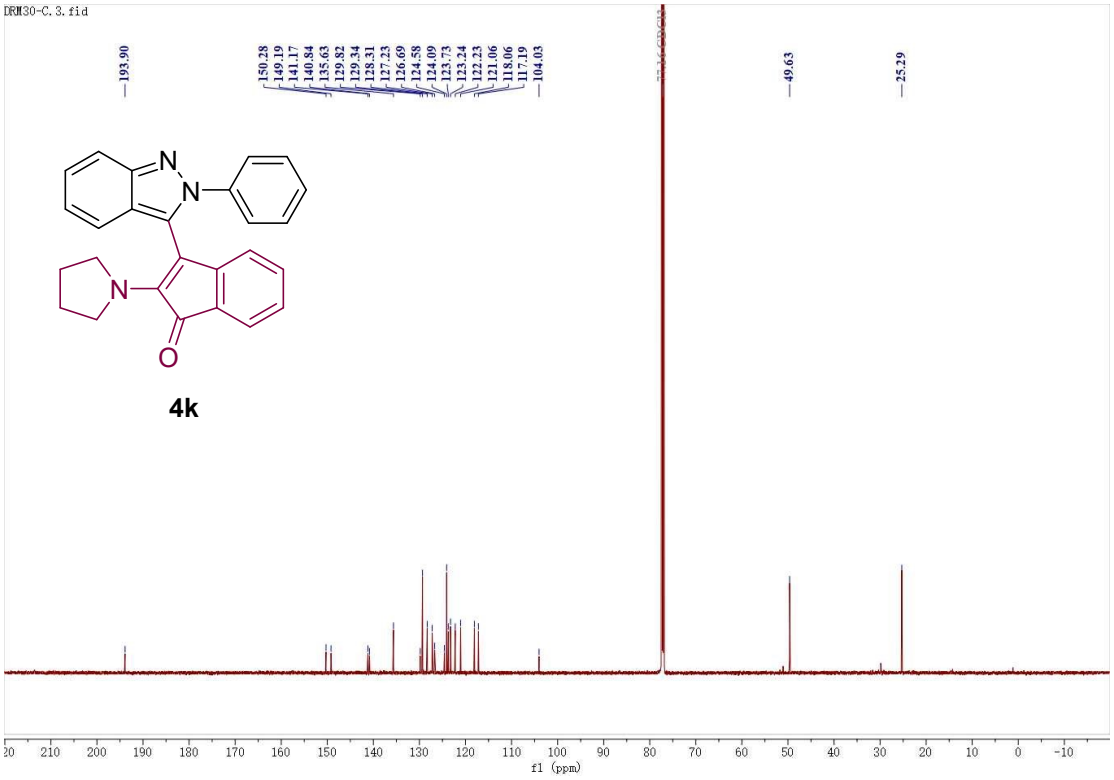
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4i



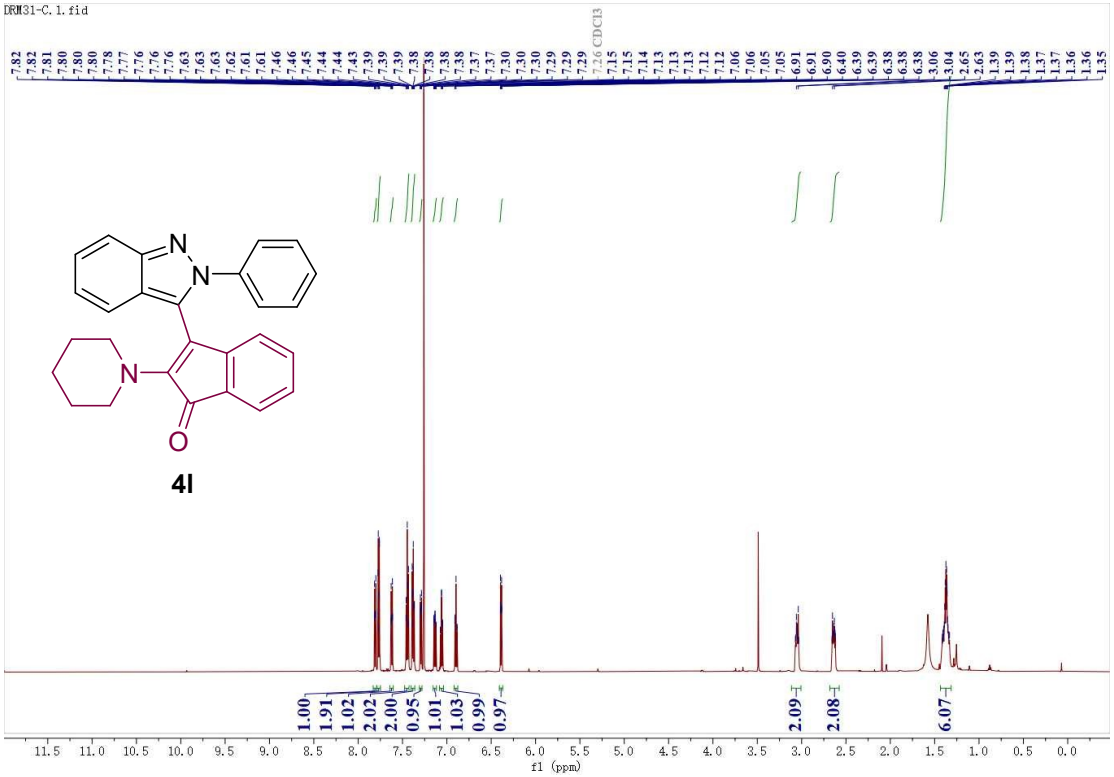
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4k



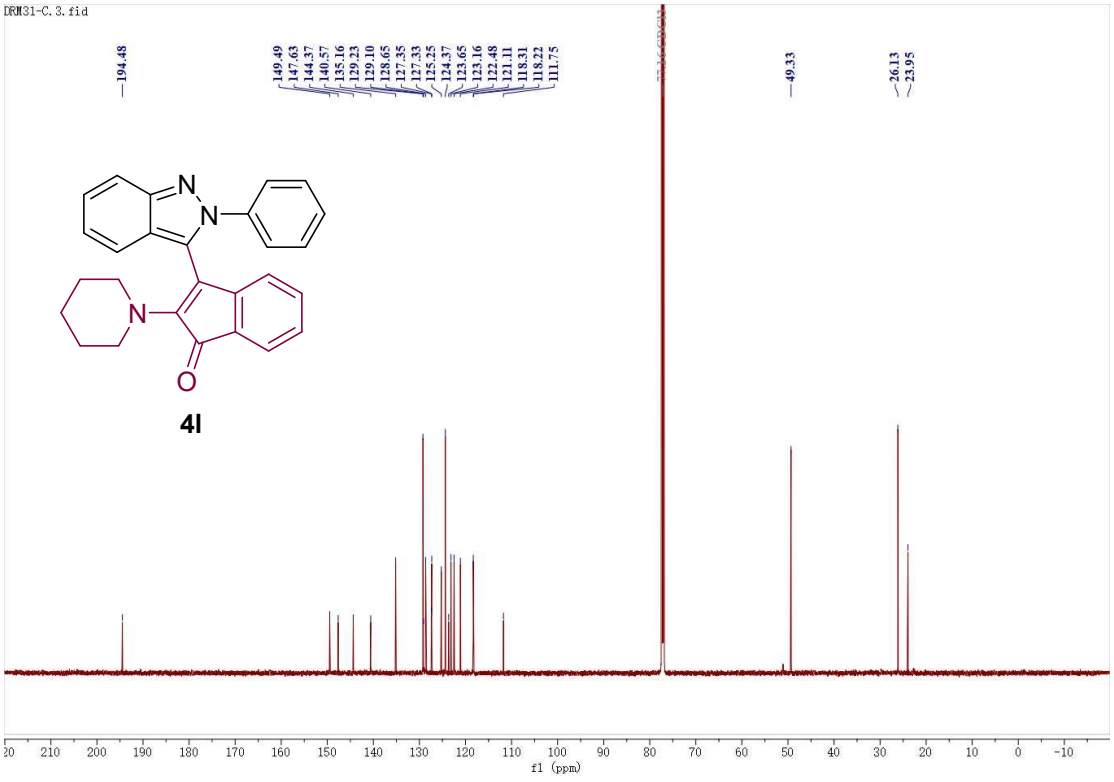
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4k



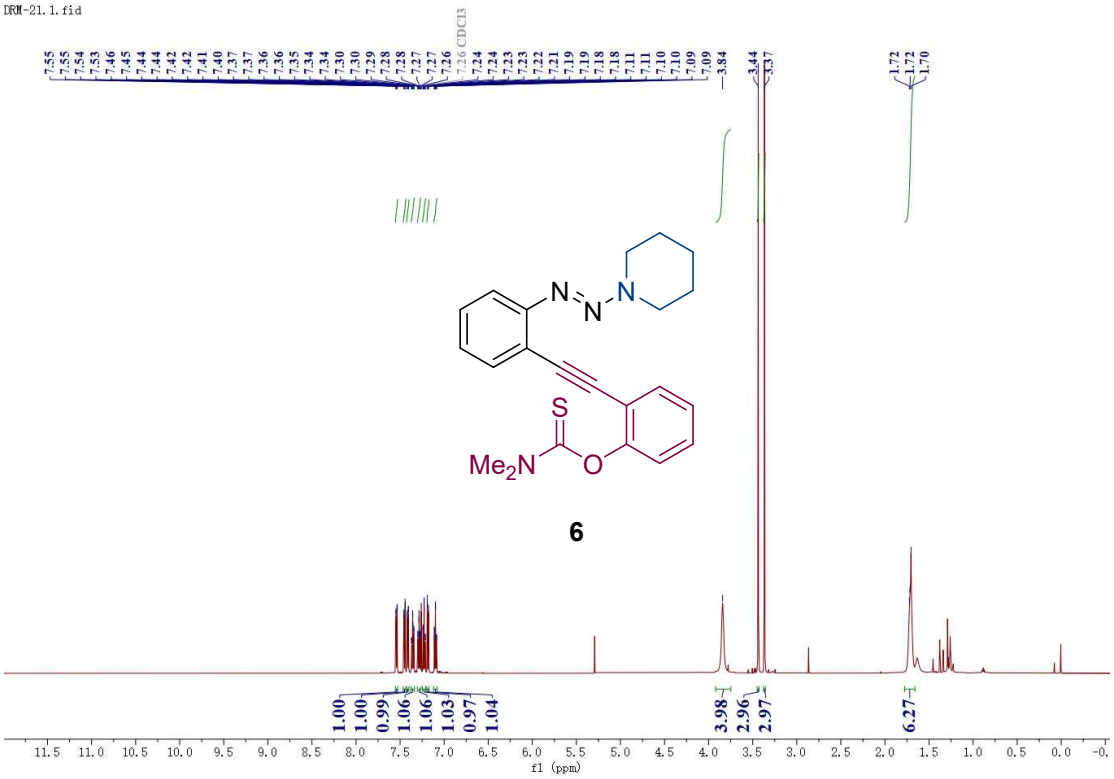
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4l



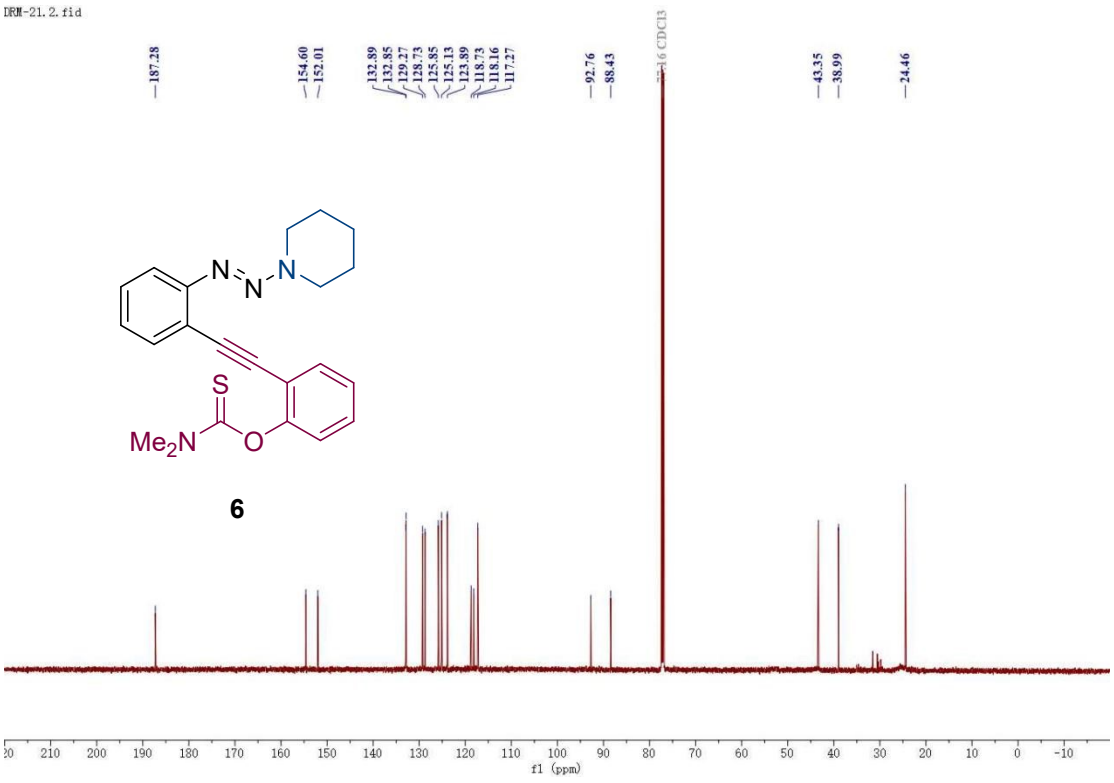
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4l



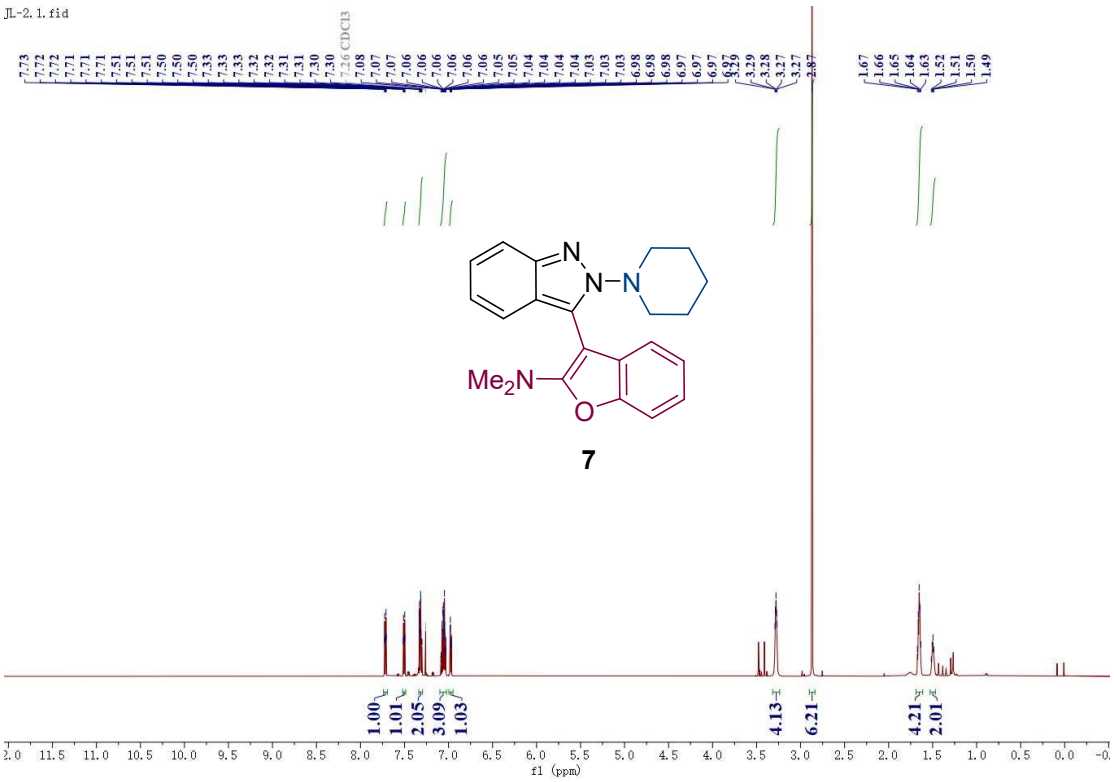
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 6



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 6

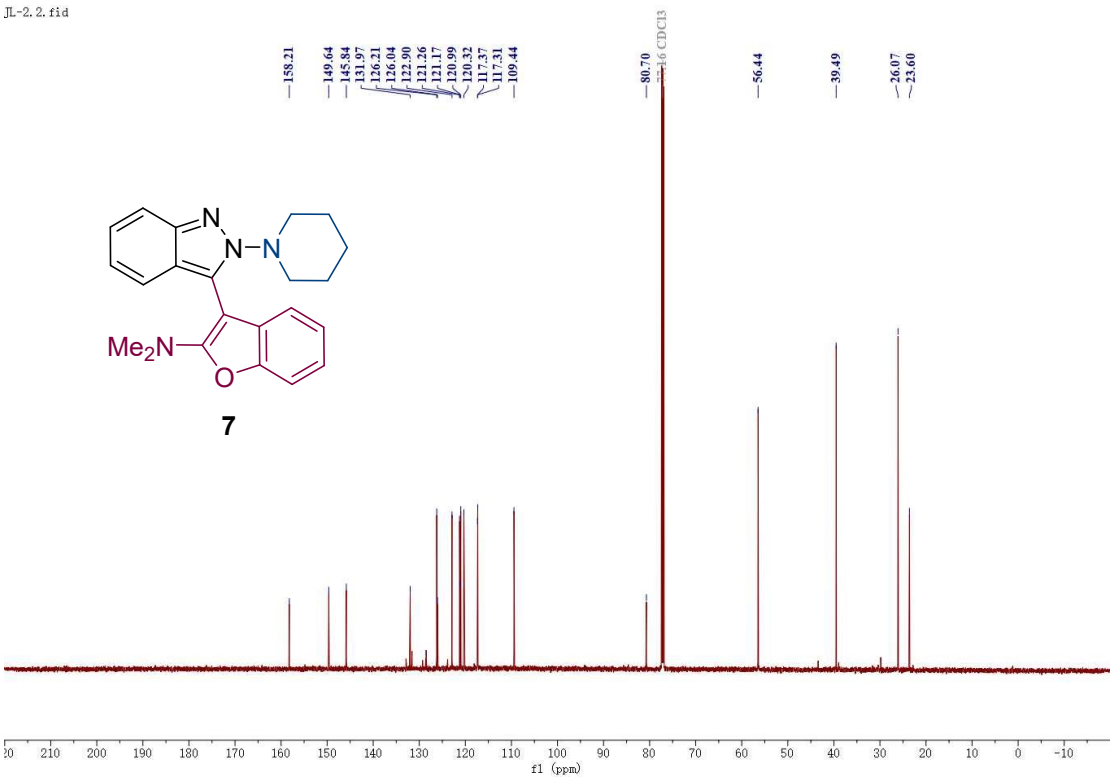


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 7



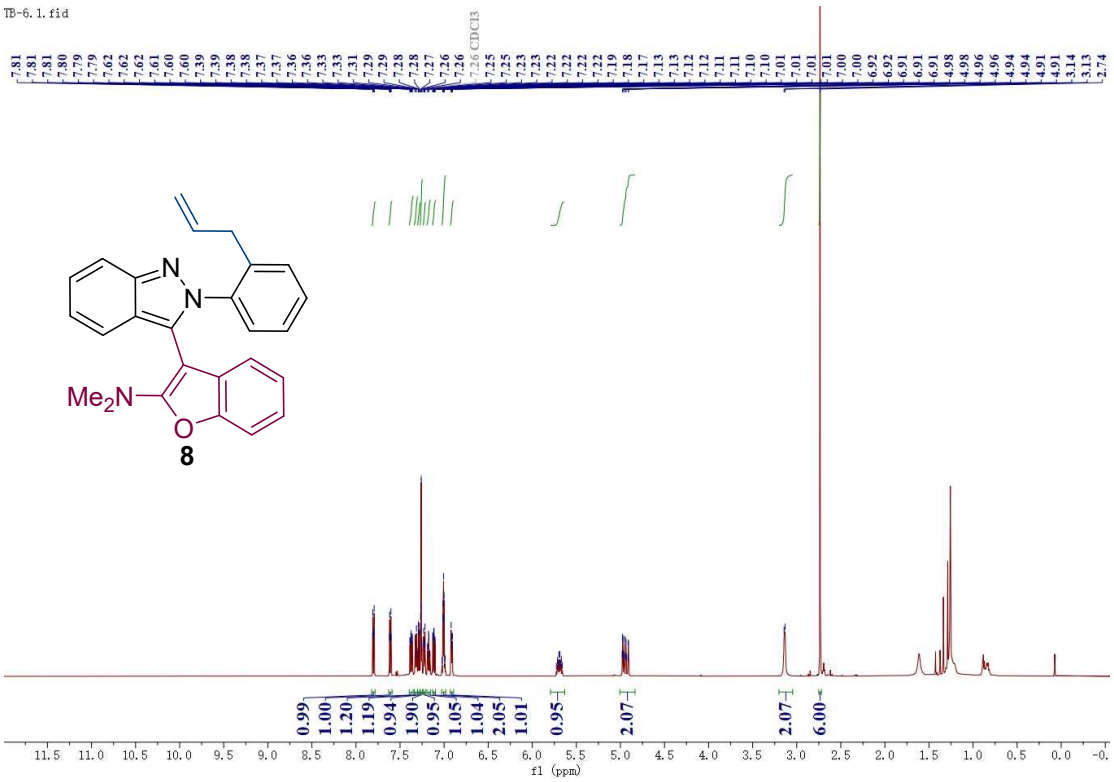
7

^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 7

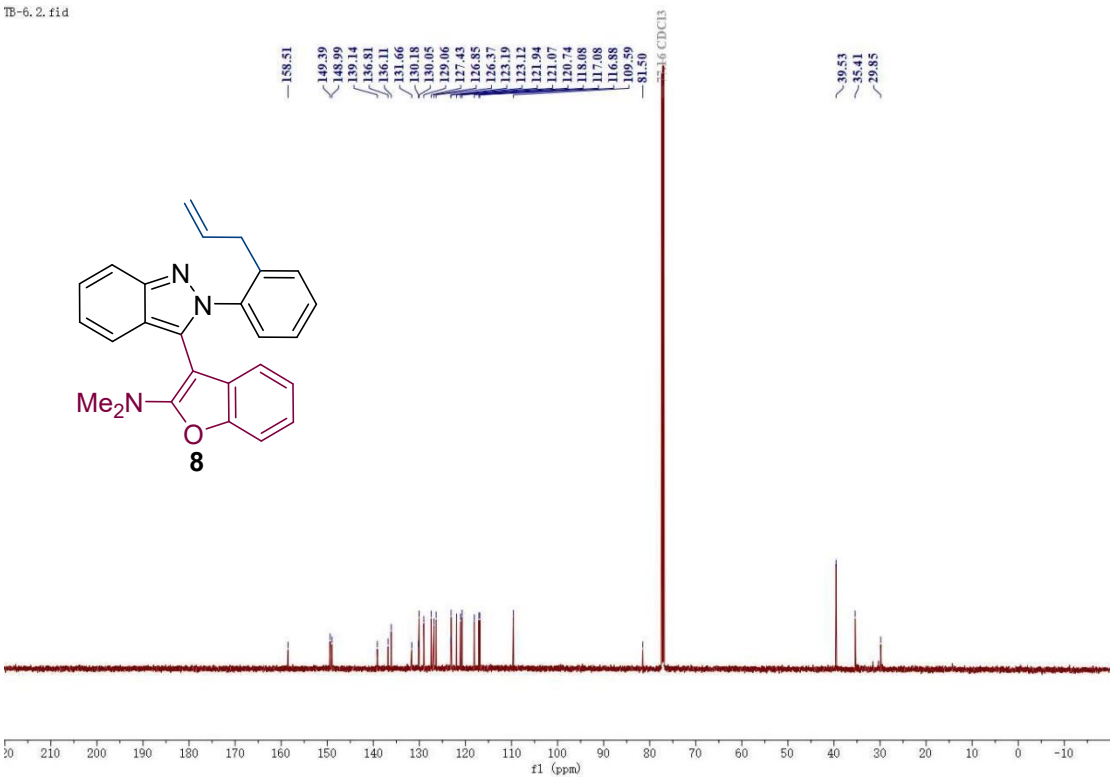


7

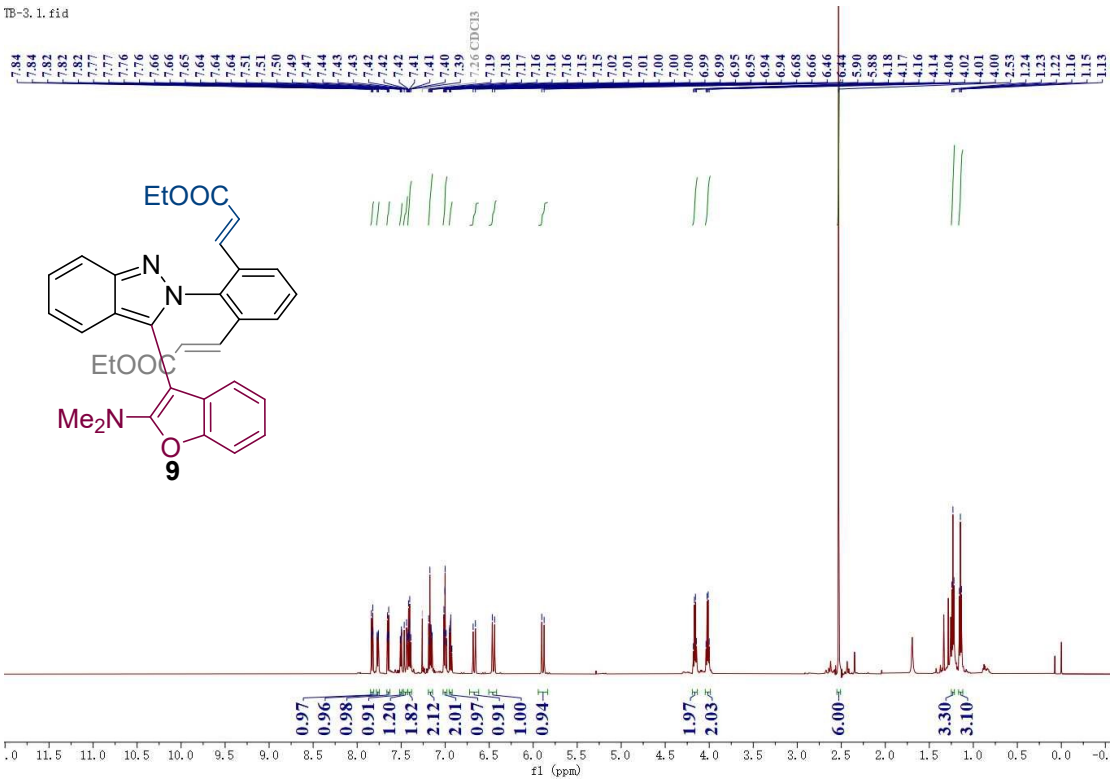
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 8



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 8



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 9



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 9