Supporting Information

Electrochemical radical Csp^2-H/N-H cyclization of arylhydrazones to 1*H*-indazoles with H_2 evolution

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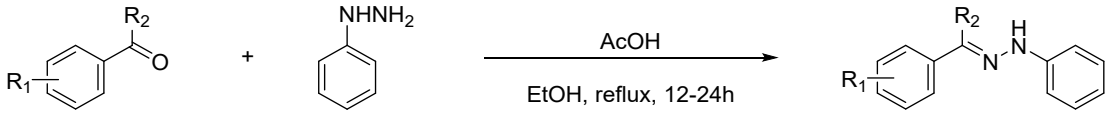
General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anodic electrode was graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (boiling point is between 60-90 ℃). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). All chemical shifts were reported relative to tetramethylsilane and solvent peaks. And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz).

Experimental procedure

General Procedure A for the Preparation of Hydrazone Substrates A[1,2]:

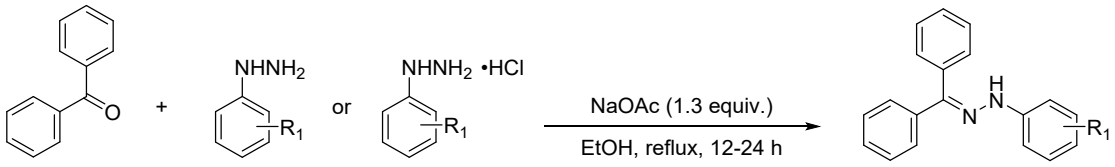


To a solution of ketone (3.0 mmol, 1.0 equiv.) in 5.0 mL of EtOH, a few drops of AcOH were added to the mixture and stirred for 10-15 min. Then phenyl hydrazine (3.6 mmol, 1.2 equiv.) was added in, and the reaction mixture was heated to reflux until TLC indicated the most disappearance of starting material. Then the solvent was removed under the reduced pressure, and the resulting residue was purified through silica gel column chromatography to provide the hydrazone substrate.

In some cases, the reaction mixture solidified in several hours from a clear solution. The reaction was cooled to 0 ^{o}C for 30 min, then filtered and washed with cooled MeOH to give the pure product.

In some other cases, some products were easy to be decomposed especially those products which were liquid, so it should be taken to reaction in a few hours, such as **3e**.

General Procedure A for the Preparation of Hydrazone Substrates B[1,2]:



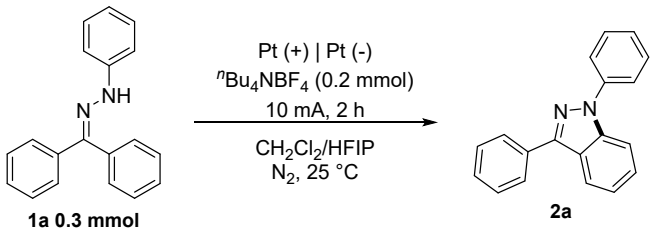
To a solution of ketone (3.0 mmol, 1.0 equiv.) in 5.0 mL of EtOH, NaOAc (3.9 mmol, 1.3 equiv.) was added to the mixture and hydrazine hydrochloride (3.6 mmol, 1.2 equiv.). The reaction mixture was stirred for 10-15 min and then heated to reflux. After the TLC indicated the most disappearance of starting material, the solvent was removed under the reduced pressure, and the resulting residue was purified through silica gel column chromatography to provide the hydrazone substrate .

In some other cases, some products were easy to be decomposed especially those products which were liquid, so it should be taken to reaction in a few hours, such as **2c, 2d**.

General Procedure A for the Preparation of other substrates:

The synthesis methods of other substrates are derived from references

General Procedure B for the Synthesis of 1H-Indazoles:

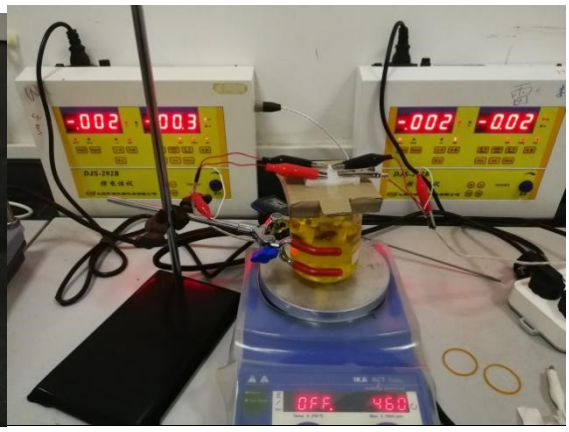


In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, hydrazone substrate 1 (0.30 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.20 mmol) and HFIP/CH_2Cl_2 (6 mL/4 mL) were combined and added. The bottle was equipped with platinum plates (15 mm× 15 mm× 0.3 mm) as the anode and the cathode and then charged with nitrogen. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether: DCM or petroleum ether: ethyl acetate as the eluent.

Procedure for gram scale synthesis of 2q： In an oven-dried beaker (250 mL) equipped with a stir bar, **1q** (1.994 g, 6 mmol), $^{n}Bu_4NBF_4$ (1.312 g, 4.0 mmol) and HFIP/CH_2Cl_2 (120 mL/80 mL) were combined and added. The bottle was equipped with two platinum plates (15 mm× 15 mm× 0.3 mm) as the anode and two platinum plates (15 mm× 15 mm× 0.3 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under air atmosphere at room temperature for 20 h. When the reaction finished, the beaker was washed with CH_2Cl_2 (30 mL x 3) and concentrated. The pure product was obtained by flash column chromatography on silica gel (hexane: ethyl acetate = 80:1). White solid was obtained in 60% isolated yield (1.3 g). Because the solvent is easy to volatilize, the solvent can be replenished in an appropriate proportion (DCM/HFIP 2:3) to keep it at about 180 mL.

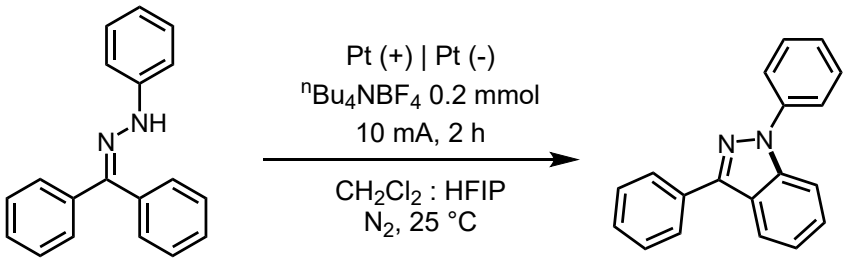
Procedure for gram scale synthesis of 2w： In an oven-dried beaker (250 mL) equipped with a stir bar, **1w** (1.890 g, 8 mmol), $^{n}Bu_4NBF_4$ (1.312 g, 4.0 mmol) and HFIP/CH_2Cl_2 (120 mL/80 mL) were combined and added. The bottle was equipped with two platinum plates (15

mm× 15 mm× 0.3 mm) as the anode and two platinum plates (15 mm× 15 mm× 0.3 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA under air atmosphere at room temperature for 22.5 h. When the reaction finished, the beaker was washed with CH_2Cl_2 (25 mL x 3) and concentrated. The pure product was obtained by flash column chromatography on silica gel (hexane: ethyl acetate = 80:1). Yellow oil was obtained in 52% isolated yield (0.9840 g). Because the solvent is easy to volatilize, the solvent can be replenished in an appropriate proportion (DCM/HFIP 2:3) to keep it at about 180 mL.



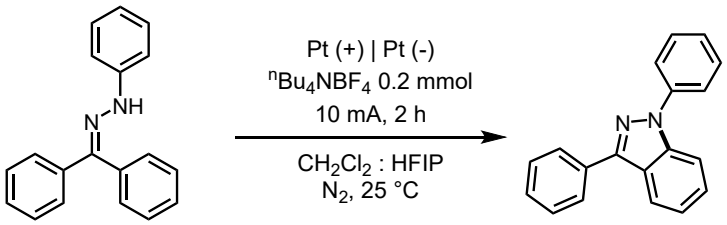
Extra optimization tables

Table 1. Optimization of different alcohols



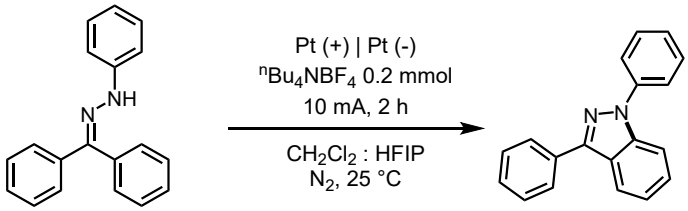
Entry	Variation	Yield[b]
1	DCM 4 mL 6 mL MeOH	n.d.
2	DCM 4 mL 6 mL Ethylene glycol	n.d.
3	DCM 4 mL 6 mL isopropanol	n.d.

Table 2. Optimization of different organic acid



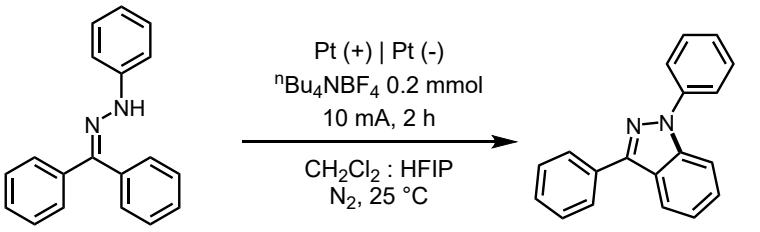
Entry	Variation	Yield[b]
1	DCM 10 mL 3.0 mmol Benzoic acid	n.d.
2	DCM 4 mL 6 mL AcOH	n.d.
3	MeOH 5 mL 5 mL AcOH	n.d.

Table 3. Optimization of different co-solvent



Entry	Variation	Yield[b]
1	DMSO instead of DCM	n.d.
2	MeCN instead of DCM	trace
3	THF instead of DCM	trace

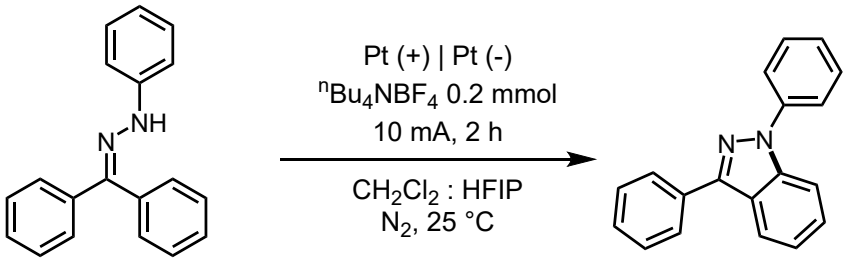
Table 4. Optimization of different fluorinated species



Entry	Variation	Yield[b]
1	DCM 9 mL 1 mL TFA	18 %
2	DCM 9 mL 1 mL HFIP	43 %
3	DCM 4 mL 6 mL HFIP	77 %
4	DCM 4 mL 6 mL TFE	75 %

[b] Yields of 2a were determined by gas chromatography (GC) analysis by using biphenyl as the internal standard

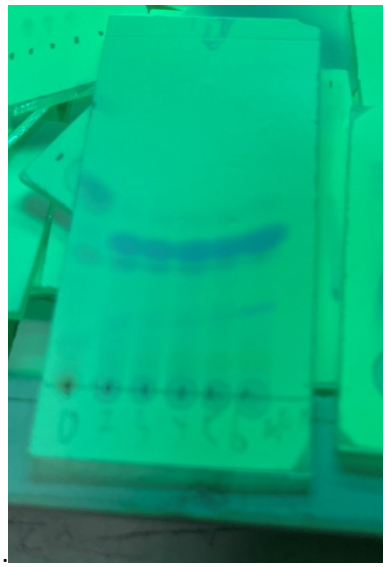
Table 5. Optimization of the amount of HFIP



Entry	Variation	Yield[b]
1	DCM 10 mL 3.0 equiv HFIP	12 %
2	DCM 9 mL 1 mL HFIP	43 %
3	DCM 8 mL 2 mL HFIP	64 %
4	DCM 7 mL 3 mL HFIP	70 %
5	DCM 6 mL 4 mL HFIP	74 %
6	DCM 5 mL 5 mL HFIP	74%
7	DCM 4 mL 6 mL HFIP	76 %

[b] Yields of 2a were determined by gas chromatography (GC) analysis by using biphenyl as the

internal standard



Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. The scan rate was 0.10 V/s, ranging from 0.0 V to 3.0 V.

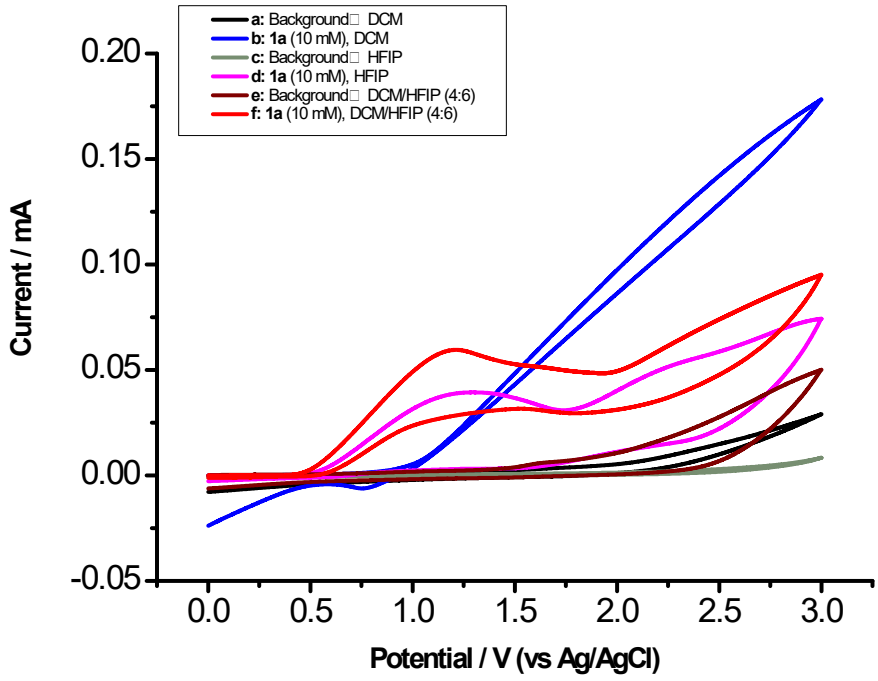


Figure S1. Cyclic voltammograms of related compounds (10 mM) in corresponding solvent containing 0.1 mmol $^{n}Bu_4NBF_4$. a : background, DCM; b : **1a** (10 mM), DCM; c : background, HFIP; d : **1a** (10 mM), HFIP; e : background, DCM / HFIP (4 : 6); f : **1a** (10 mM), DCM / HFIP (4 : 6);.

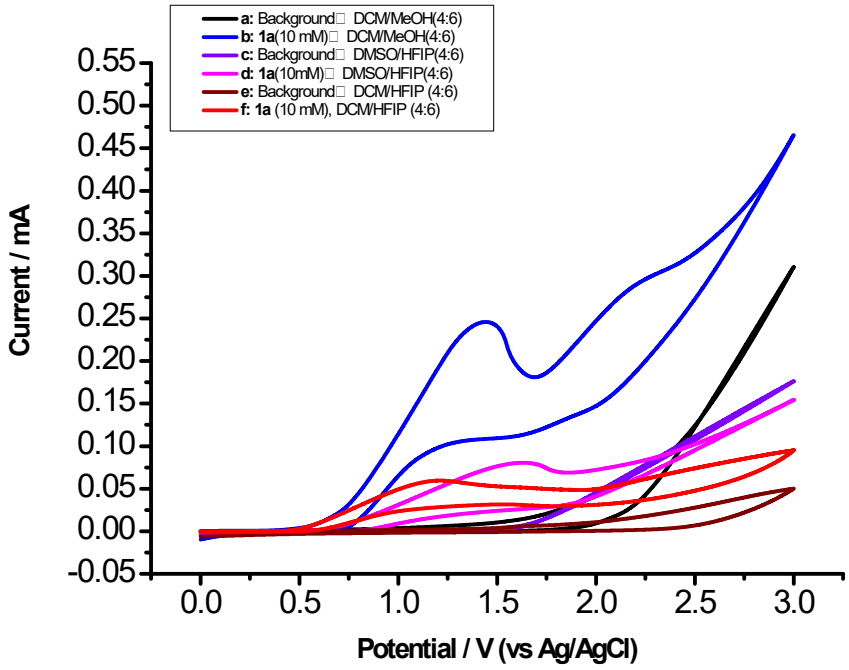


Figure S2. Cyclic voltammograms of related compounds (10 mM) in mixture solvent containing 0.1 mmol $^{n}Bu_4NBF_4$. a : background, DCM / MeOH (4 : 6); b : **1a** (10 mM), DCM / MeOH (4 : 6); c : background, DMSO / HFIP (4 : 6); d : **1a** (10 mM), DMSO / HFIP (4 : 6); e : background, DCM / HFIP (4 : 6); f : **1a** (10 mM), DCM / HFIP (4 : 6).

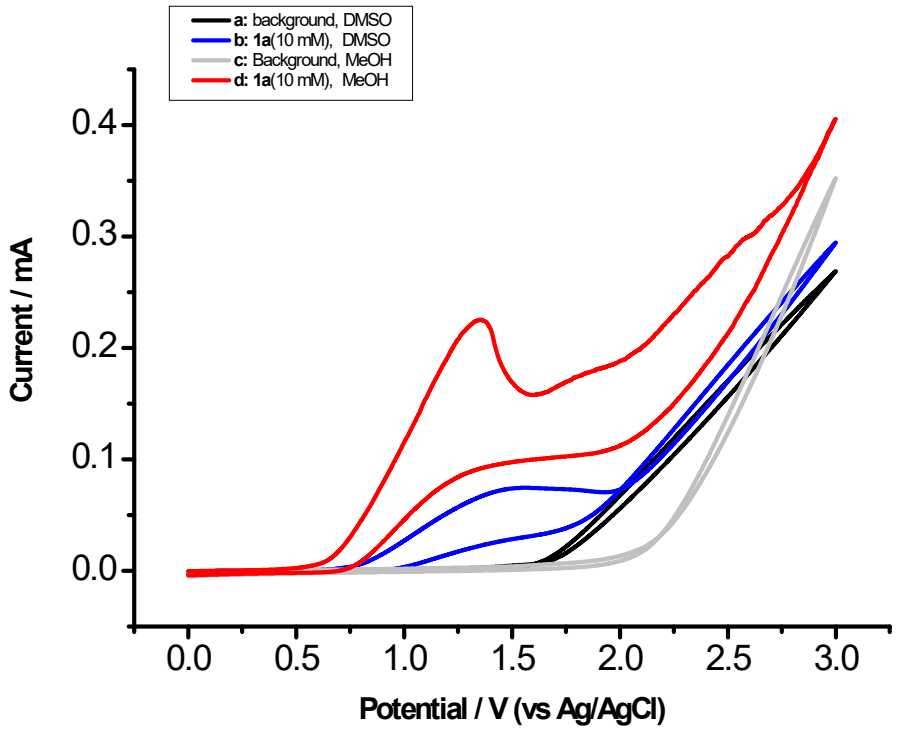
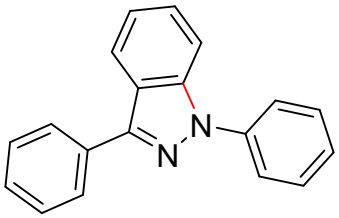


Figure S3. Cyclic voltammograms of related compounds (10 mM) in single solvent containing 0.1 mmol $^{n}Bu_4NBF_4$. a : background, DMSO; b : **1a** (10 mM), DMSO; c : background, MeOH; d : **1a** (10 mM), MeOH.

Detail descriptions for products

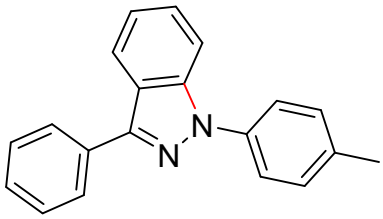


1,3-Diphenyl-1*H*-indazole (2a).[2]

White solid was obtained in 78% isolated yield, 63.3 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.07 (m, 1H), 8.05−8.03 (m, 2H), 7.81−7.76 (m, 3H), 7.56−7.51 (m, 4H), 7.46−7.41 (m, 2H), 7.38−7.34 (m, 1H), 7.30−7.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 140.5, 140.3, 133.4, 129.6, 129.0, 128.4, 127.9, 127.2, 126.8, 123.3, 123.1, 122.1, 121.7, 110.8.

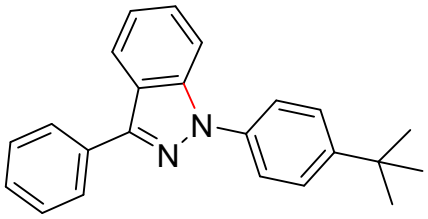


3-Phenyl-1-(*p*-tolyl)-1*H*-indazole (2b).[2]

White solid was obtained in 77% isolated yield, 65.7 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.03 (m, 3H), 7.72 (d, J = 8.4 Hz, 1H), 7.66–7.64 (m, 2H), 7.53−7.50 (m, 2H), 7.43−7.40 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.4, 137.7, 136.7, 133.4, 130.1, 128.9, 128.3, 127.9, 127.1, 123.1, 123.0, 121.9, 121.6, 110.8, 21.2.



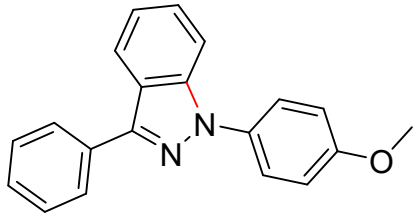
1-(4-Isopropylphenyl)-3-phenyl-1*H*-indazole (2c).[2]

White solid was obtained in 56% isolated yield, 55.2 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.03 (m, 3H), 7.74 (d, J = 8.4 Hz, 1H), 7.70−7.68 (m, 2H), 7.55−7.49 (m, 4H), 7.43−7.39 (m, 2H), 7.25 (t, J = 8.0 Hz, 1H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 145.8, 140.4, 137.6, 133.4, 128.9, 128.3, 127.8, 127.0, 126.5, 123.0, 122.8, 121.9, 121.6, 110.8, 34.8, 31.5.

HRMS (ESI) m/z calculated for $C_{23}H_{22}N_2$ $[M+H]^+$: 327.1856, found: 327.1860.

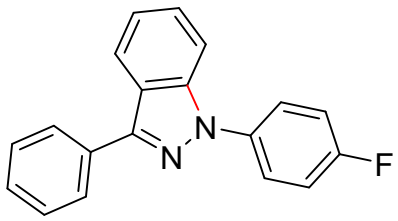


1-(4-Methoxyphenyl)-3-phenyl-1*H*-indazole (2d).[2]

After the condensation of diphenyl ketone (0.5 mmol) and hydrazine salt (0.75 mmol), prepared according to General Procedure **B** was complete, the reaction mixture was concentrated and the resulting crude hydrazone (**1d**) was directly subjected to the General Procedure **C** and the time delayed to 3.5 h. White solid was obtained in 59% isolated yield, 88.7 mg, 0.5 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.07 (m, 1H), 8.05–8.03 (m, 2H), 7.70–7.66 (m, 3H), 7.55–7.51(m, 2H), 7.46–7.41 (m, 2H), 7.30–7.26 (m, 1H, overlapped with the peak of chloroform), 7.09–7.06 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 145.7, 140.7, 133.4, 133.3, 129.0, 128.3, 127.9, 127.1, 125.0, 122.8, 121.8, 121.6, 114.7, 110.6, 55.8.



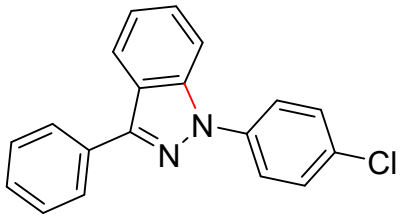
1-(4-Fluorophenyl)-3-phenyl-1*H*-indazole (2e).[2]

White solid was obtained in 76% isolated yield, 67.1 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$)) δ 8.08–8.06 (m, 1H), 8.03–8.01 (m, 2H), 7.76–7.71 (m, 2H), 7.69–7.67 (m, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.47–7.41 (m, 2H), 7.30-7.26 (m, 1H), 7.25–7.21 (m, 2H, overlapped with the peak of chloroform).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 247.5 Hz), 146.3, 140.5, 136.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.2, 129.0, 128.5, 127.9, 127.4, 124.9 (d, $J_{C\text{-}F}$ = 9.1 Hz), 123.1, 122.1, 121.8, 116.4 (d, $J_{C\text{-}F}$ = 23.2 Hz), 110.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.90.

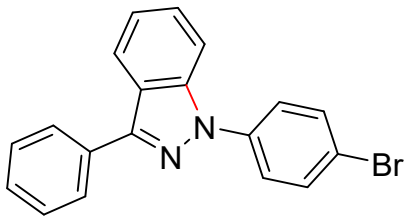


1-(4-Chlorophenyl)-3-phenyl-1*H*-indazole (2f).[2]

White solid was obtained in 78% isolated yield, 71.0 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (m, 1H), 8.02−8.00 (m, 2H), 7.75−7.71 (m, 3H), 7.55−7.42 (m, 6H), 7.31−7.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 140.3, 138.8, 133.0, 132.1, 129.7, 129.0, 128.6, 127.9, 127.5, 124.0, 123.4, 122.3, 121.9, 110.6.

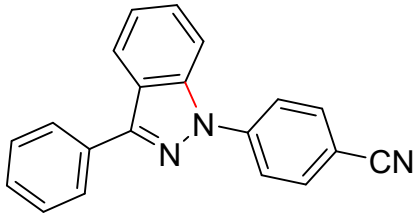


1-(4-Bromophenyl)-3-phenyl-1*H*-indazole (2g).[2]

White solid was obtained in 85% isolated yield, 88.7 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (m, 1H), 8.03−8.01 (m, 2H), 7.74−7.64 (m, 5H), 7.55−7.51 (m, 2H), 7.48−7.42 (m, 2H), 7.31−7.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 140.2, 139.3, 133.0, 132.6, 129.0, 128.6, 127.9, 127.5, 124.3, 123.4, 122.3, 121.9, 119.9, 110.6.

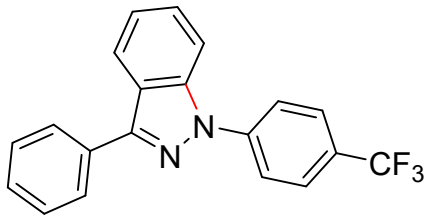


4-(3-Phenyl-1*H*-indazol-1-yl)benzonitrile (2h).[2]

White solid was obtained in 86% isolated yield, 76.2 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 8.02−7.94 (m, 4H), 7.83−7.78 (m, 3H), 7.56−7.45 (m, 4H), 7.34 (t, J = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 143.8, 140.0, 133.6, 132.5, 129.1, 129.0, 128.1, 127.9, 124.1, 123.0, 122.2, 122.0, 118.7, 110.8, 109.1.



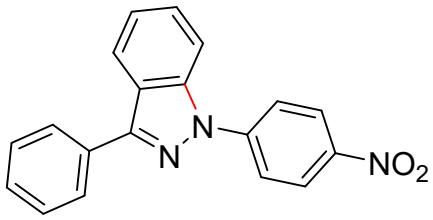
3-Phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-indazole (2i).[2]

White solid was obtained in 66% isolated yield,66.7 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.08 (m, 1H), 8.04− 8.02 (m, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.81 (t, J = 8.0 Hz, 3H), 7.56−7.44 (m, 4H), 7.34−7.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 143.1, 140.2, 132.8, 129.1, 128.8, 128.2 (q, $J_{C\text{-}F}$ = 32.3 Hz), 128.0, 127.8, 126.8 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.1 (q, $J_{C\text{-}F}$ = 273.7 Hz), 123.8, 122.6, 122.3, 122.0, 110.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.12.

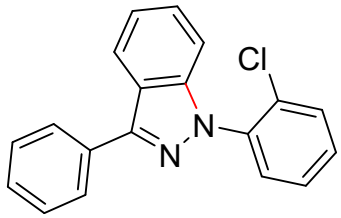


1-(4-Nitrophenyl)-3-phenyl-1*H*-indazole (2j).[2]

yellow solid was obtained in 50% isolated yield, 47.3 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41−8.38 (m, 2H), 8.10 (d, J = 8.0 Hz, 1H), 8.04−8.01 (m, 4H), 7.88 (d, J = 8.4 Hz, 1H), 7.57−7.53 (m, 3H), 7.50−7.46 (m, 1H), 7.36 (t, J = 7.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 145.4, 144.9, 140.1, 132.4, 129.1, 128.3, 128.0, 125.4, 124.4, 123.2, 122.3, 121.5, 110.9.

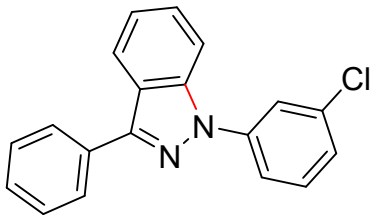


1-(2-Chlorophenyl)-3-phenyl-1*H*-indazole (2k).[2]

colorless oil was obtained in 73% isolated yield, 66.8 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 8.05−8.04 (m, 2H), 7.60−7.55 (m, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.42−7.39 (m, 4H), 7.29−7.24 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 141.9, 137.1, 133.2, 131.6, 130.8, 129.9, 129.8, 128.9, 128.4, 127.84, 127.82, 127.0, 122.2, 121.9, 121.5, 110.9.

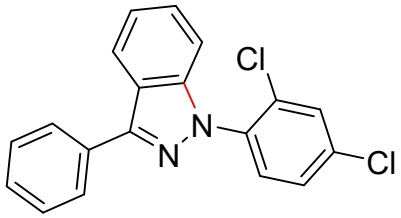


1-(3-Chlorophenyl)-3-phenyl-1*H*-indazole (2l).[2]

colorless oil was obtained in 80% isolated yield, 73.0 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.05 (m, 1H), 8.03−8.01 (m, 2H), 7.83 (t, J = 2.0 Hz, 1H), 7.77−7.75 (m, 1H), 7.70−7.67 (m, 1H), 7.54−7.51 (m, 2H), 7.48−7.42 (m, 3H), 7.32−7.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 141.3, 140.2, 135.2, 132.9, 130.5, 129.0, 128.6, 127.9, 127.6, 126.6, 123.5, 123.0, 122.4, 121.9, 120.6, 110.6.

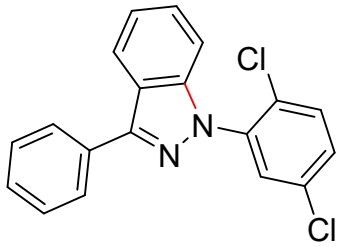


1-(2,4-Dichlorophenyl)-3-phenyl-1*H*-indazole (2m).[2]

colorless oil was obtained in 86% isolated yield, 87.5 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.07 (m, 1H), 8.03−8.01 (m, 2H), 7.62 (d, J = 2.4 Hz, 1H), 7.53−7.49 (m, 3H), 7.44−7.39 (m, 3H), 7.30−7.26 (m, 1H), 7.25−7.22 (m, 1H, overlapped with the peak of chloroform).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 141.8, 135.9, 135.1, 133.0, 132.4, 130.6, 130.5, 129.0, 128.6, 128.2, 127.9, 127.3, 122.3, 122.1, 121.6, 110.8.

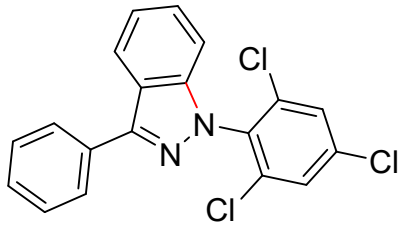


1-(2,5-Dichlorophenyl)-3-phenyl-1*H*-indazole (2n).[2]

White solid was obtained in 92% isolated yield, 93.5 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 1H), 8.04−8.02 (m, 2H), 7.61−7.60 (m, 1H), 7.55−7.51 (m, 3H), 7.46−7.38 (m, 3H), 7.31−7.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 141.7, 138.0, 133.3, 132.9, 131.6, 129.9, 129.8, 129.7, 129.0, 128.7, 127.9, 127.3, 122.4, 122.2, 121.6, 111.0.

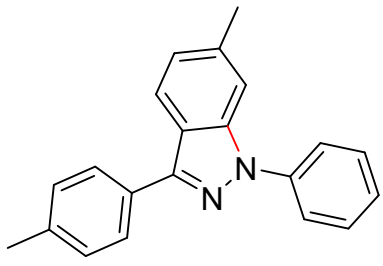


3-Phenyl-1-(2,4,6-trichlorophenyl)-1*H*-indazole (2o).[2]

colorless oil was obtained in 60% isolated yield, 67.3 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.11 (m, 1H), 8.05−8.03 (m, 2H), 7.56−7.51 (m, 4H), 7.47−7.42 (m, 2H), 7.34−7.30 (m, 1H), 7.12−7.10 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 141.9, 136.5, 136.2, 133.7, 133.0, 129.0, 128.9, 128.7, 127.9, 127.6, 122.2, 122.1, 121.7, 109.9.

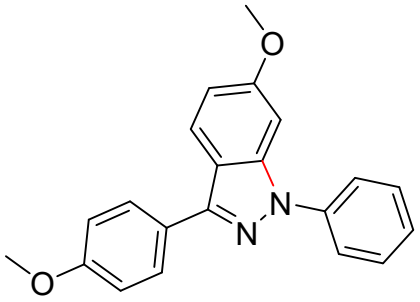


6-Methyl-1-phenyl-3-(p-tolyl)-1*H*-indazole (2p).[2]

White solid was obtained in 80% isolated yield, 71.6 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8 Hz, 3H), 7.78−7.76 (m, 2H), 7.55−7.51 (m, 3H), 7.36−7.31 (m, 3H), 7.09 (d, J = 7.2 Hz, 1H), 2.49 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 141.0, 140.3, 138.2, 137.6, 130.5, 129.6, 129.5, 127.7, 126.6, 124.1, 123.1, 121.4, 121.3, 110.2, 22.2, 21.5.

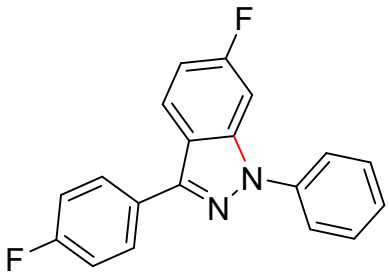


6-Methoxy-3-(4-methoxyphenyl)-1-phenyl-1*H*-indazole (2q).[2]

White solid was obtained in 67% isolated yield, 66.3 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.76–7.74 (m, 2H), 7.54–7.50 (m, 2H), 7.35–7.31 (m, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.03–7.01 (m, 2H), 6.88 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.83-3.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 159.8, 145.9, 141.6, 140.2, 129.5, 128.9, 126.6, 125.8, 123.0, 122.4, 117.7, 114.3, 113.4, 91.9, 55.6, 55.4.



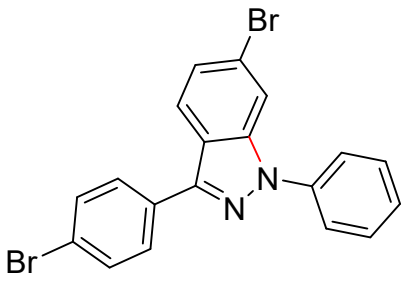
6-Fluoro-3-(4-fluorophenyl)-1-phenyl-1*H*-indazole (2r).[2]

White solid was obtained in 48% isolated yield, 44.0 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (dd, *J* = 8.8, 5.2 Hz, 1H), 8.11 –8.06 (m, 2H), 7.86–7.83 (m, 2H), 7.69 (dd, *J* = 10, 2.4 Hz, 1H), 7.65–7.61 (m, 2H), 7.49–7.39 (m, 3H), 7.26 (td, *J* = 9.2, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.6 (d, $J_{C\text{-}F}$ = 25.3 Hz), 161.1 (d, $J_{C\text{-}F}$ = 24.2 Hz), 144.5, 140.1 (d, $J_{C\text{-}F}$ = 12.1 Hz), 139.2, 129.9, 129.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.2, 123.5 (d, $J_{C\text{-}F}$ = 12.1 Hz), 122.5, 119.3, 116.2 (d, $J_{C\text{-}F}$ =22.2 Hz), 112.1 (d, $J_{C\text{-}F}$ =26.3 Hz), 97.0 (d, $J_{C\text{-}F}$ = 27.3 Hz).

^{19}F NMR (376 MHz, DMSO) δ -112.80, -113.01.

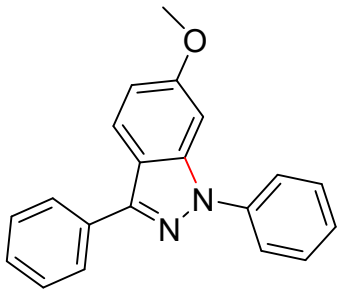


6-Bromo-3-(4-bromophenyl)-1-phenyl-1*H*-indazole (2t).[2]

White solid was obtained in 45% isolated yield, 57.8 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.2 Hz, 1H), 7.88−7.86 (m, 3H), 7.74−7.72 (m, 2H), 7.66−7.64 (m, 2H), 7.60−7.56 (m, 2H), 7.44−7.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 141.2, 139.5, 132.2, 131.7, 129.8, 129.2, 127.5, 125.8, 123.3, 122.8, 122.6, 121.9, 121.7, 113.8.

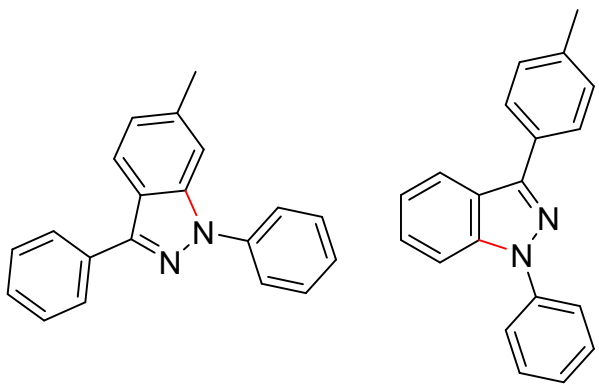


6-Methoxy-1,3-diphenyl-1*H*-indazole (2u).[2]

White solid was obtained in 47% isolated yield, 42.3 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−8.00 (m, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.78−7.76 (m, 2H), 7.57−7.49 (m, 4H), 7.43−7.35 (m, 2H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.93 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 146.2, 141.7, 140.2, 133.3, 129.6, 128.9, 128.4, 127.8, 126.8, 123.2, 122.5, 117.8, 113.7, 91.9, 55.7.



6-Methyl-1,3-diphenyl-1*H*-indazole (2t and 1-phenyl-3-(p-tolyl)-1*H*-indazole (2t′).[3]

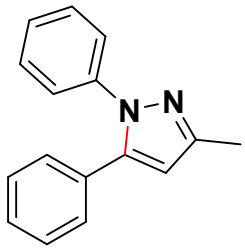
White solid was obtained in 76% isolated yield, 64.6 mg 2t:2t' = 78:22 by ^{1}H NMR, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.02 (m, 1.80H), 7.96−7.92 (m, 1.19H), 7.79−7.75 (m, 2.19H), 7.56−7.50 (m, 4.40H), 7.45−7.33 (m, 2.49H), 7.29−7.25 (m, 1.19H), 7.11 (d, J = 8.4 Hz, 0.76H), 2.51 (s, 2.33H), 2.43 (s, 0.65H);

^{13}C NMR (101 MHz, $CDCl_3$) :

2t: δ 146.0, 141.0, 140.3, 137.6, 133.4, 129.5, 128.9, 128.3, 127.8, 126.7, 124.2, 123.2, 121.4, 121.3, 110.3, 22.2;

2t′: δ 146.3, 140.4, 140.3, 138.3, 130.4, 129.7, 129. 6, 127.8, 127.2, 126.7, 123.3, 123.1, 121.91, 121. 8, 110.7, 21.5.

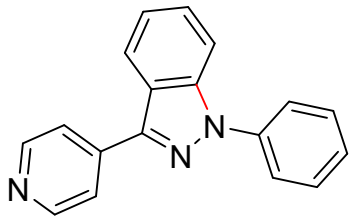


3-methyl-1,5-diphenyl-1*H*-pyrazole (2v).[4]

Yellow solid was obtained in 62% isolated yield, 43.7 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 10H), 6.31 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 143.8, 140.2, 130.8, 128.9, 128.7, 128.5, 128.2, 127.2, 125.2, 107.8, 13.7.

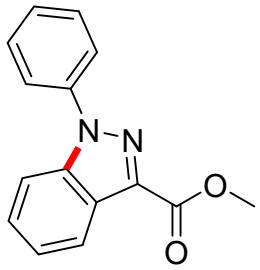


1-phenyl-3-(pyridin-4-yl)-1H-indazole (2z).[1]

White solid was obtained in 25 % isolated yield, 42.3 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.2 Hz, 2H), 8.13−8.11 (m, 1H) , 8.00−7.98 (m, 2H), 7.82−7.78 (m, 3H), 7.61−7.57 (m, 2H), 7.52−7.48 (m, 1H), 7.45−7.41 (m, 1H), 7.38−7.34 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 143.1, 141.0, 140.7, 139.8, 129.7, 127.6, 127.5, 123.4, 123.0, 122.9, 121.9, 121.1, 111.2.

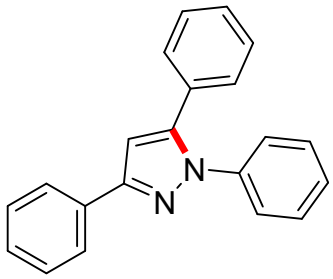


Methyl 1-phenyl-1H-indazole-3-carboxylate (3a).[8]

White solid was obtained in 12 % isolated yield, 9.2 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35−8.33 (m, 1H), 7.76−7.73 (m, 3H), 7.59−7.55 (m, 2H), 7.52−7.44 (m, 2H), 7.42−7.38 (m, 1H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 140.5, 139.3, 136.9, 129.7, 128.2, 127.8, 124.7, 124.1, 123.9, 122.6, 111.0, 52.4.

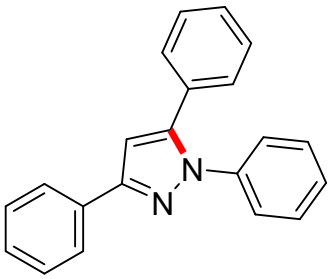


6-Methoxy-1,3-diphenyl-1*H*-indazole (3b).[9]

White solid was obtained in 18 % isolated yield, 16.0 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.92 (m, 2H), 7.45−7.41 (m, 2H), 7.38−7.26 (m, 11H), 6.82 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 144.5, 140.2, 133.1, 130.7, 129.0, 128.8, 128.8, 128.6, 128.4, 128.1, 127.5, 125.9, 125.4, 105.3.



6-Methoxy-1,3-diphenyl-1*H*-indazole (3c).[9]

White solid was obtained in 7 % isolated yield, 6.5 mg, 0.3 mmol scale

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.92 (m, 2H), 7.45−7.42 (m, 2H), 7.39−7.27 (m, 11H), 6.83 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 144.5, 140.2, 133.1, 130.7, 129.1, 128.9, 128.8, 128.6, 128.4, 128.1, 127.6, 125.9, 125.4, 105.3.

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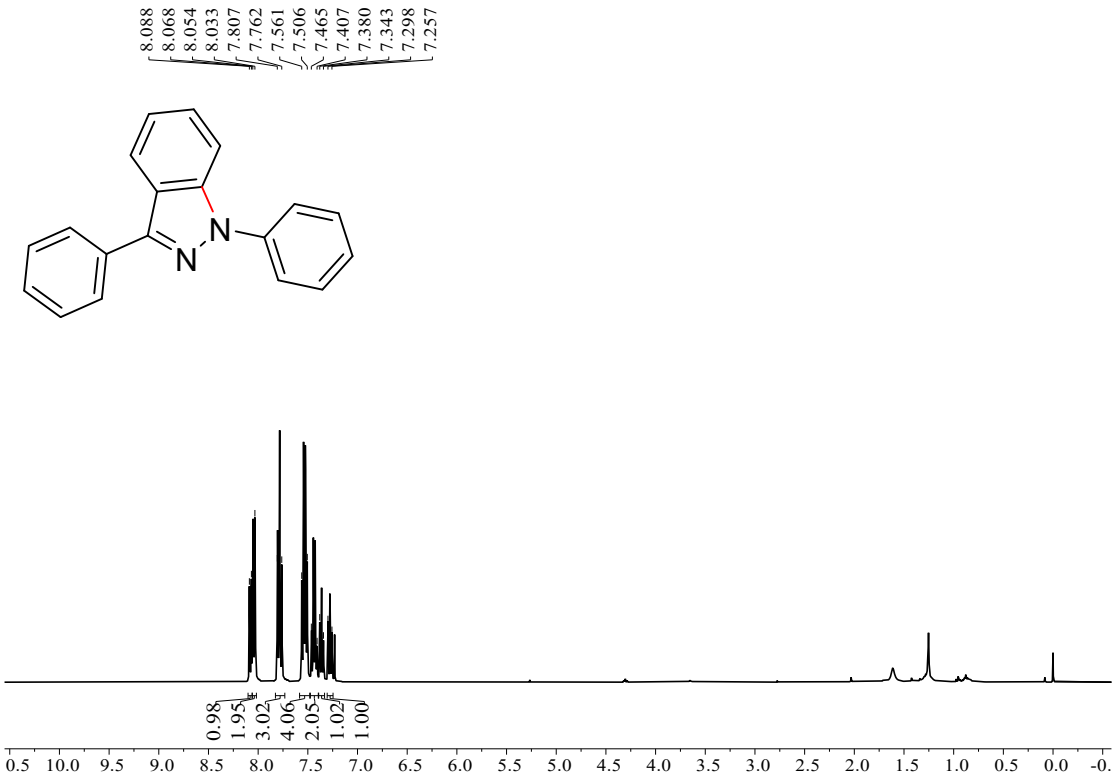
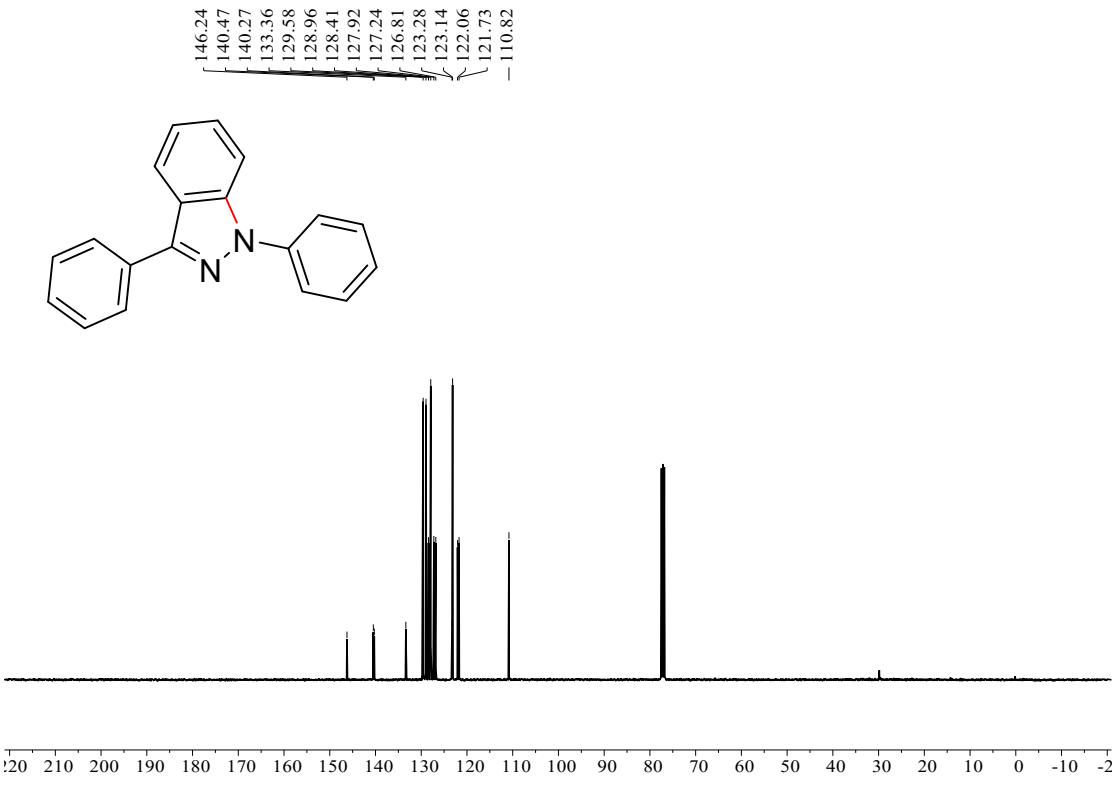
Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

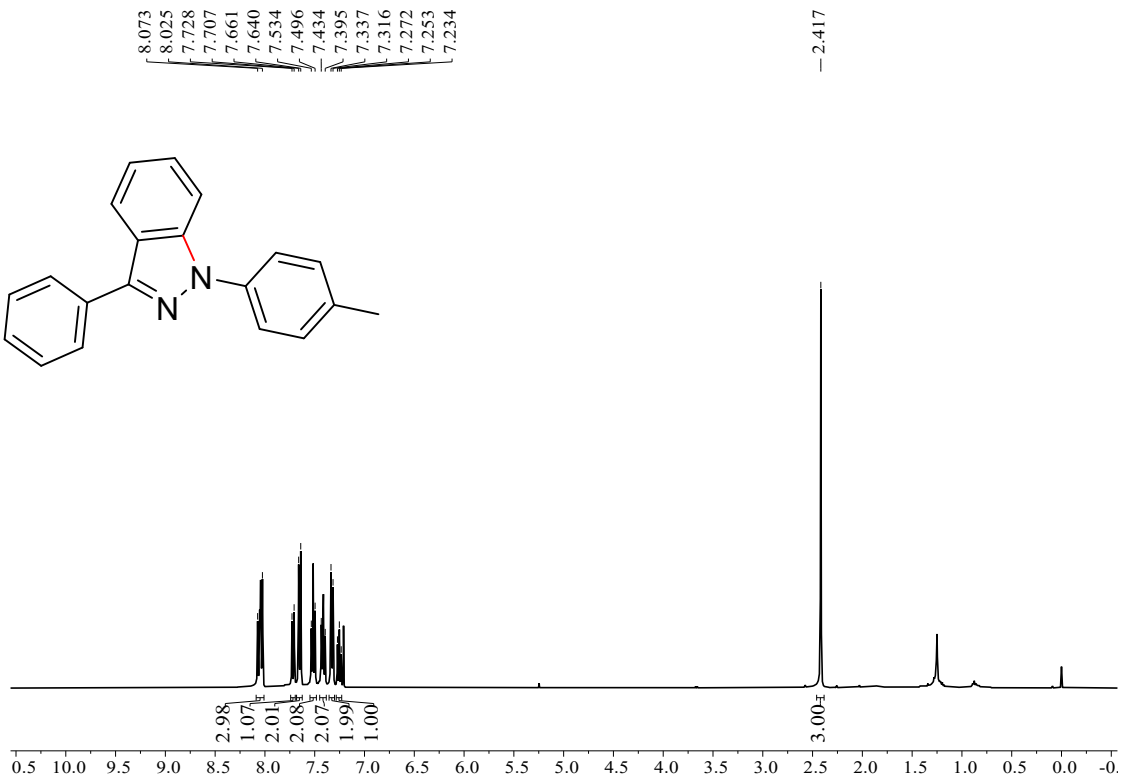
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2a



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2a



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



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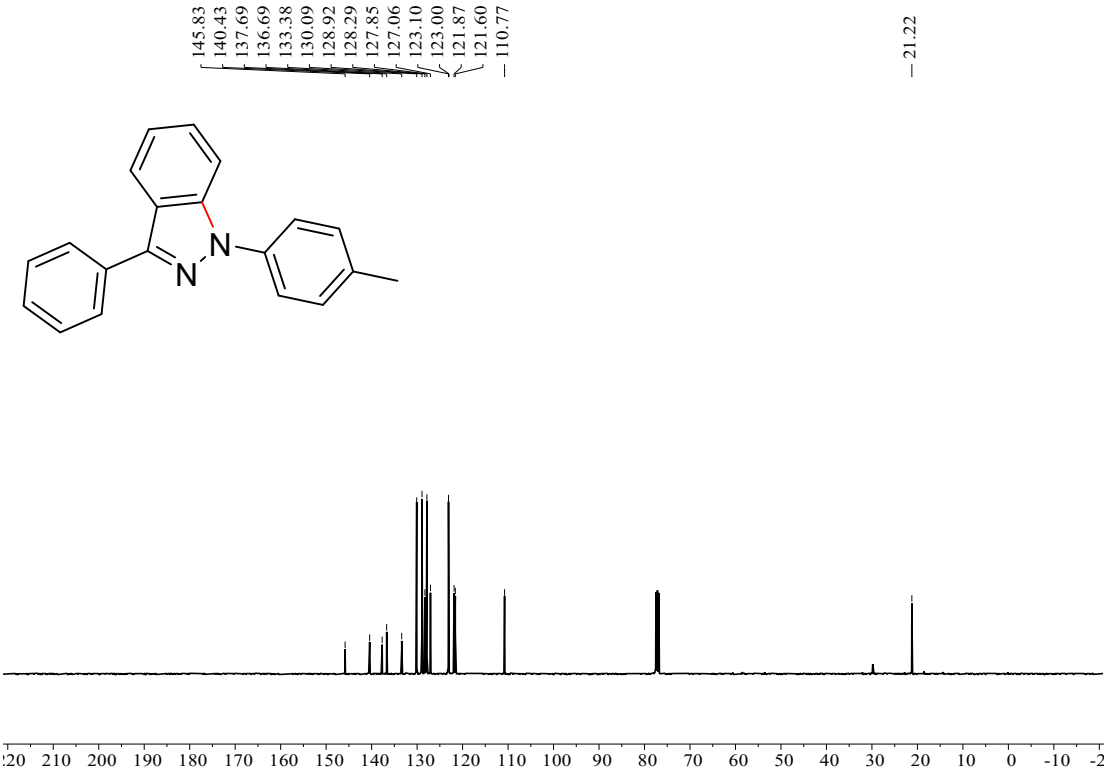
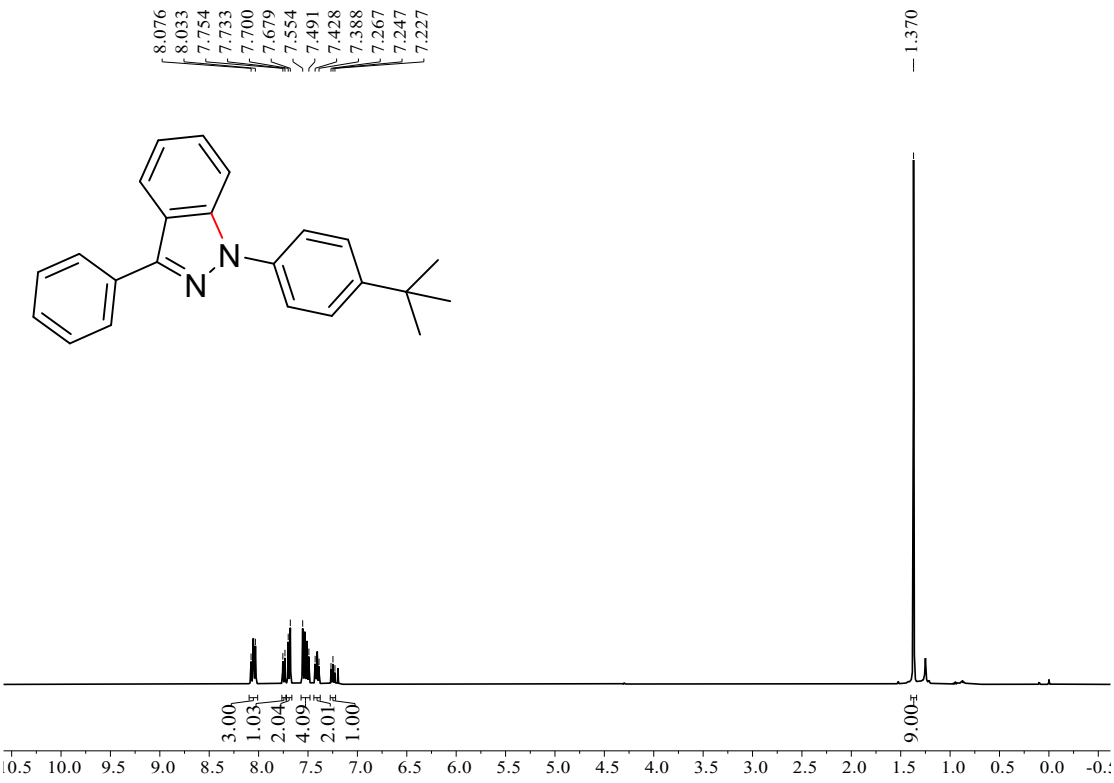
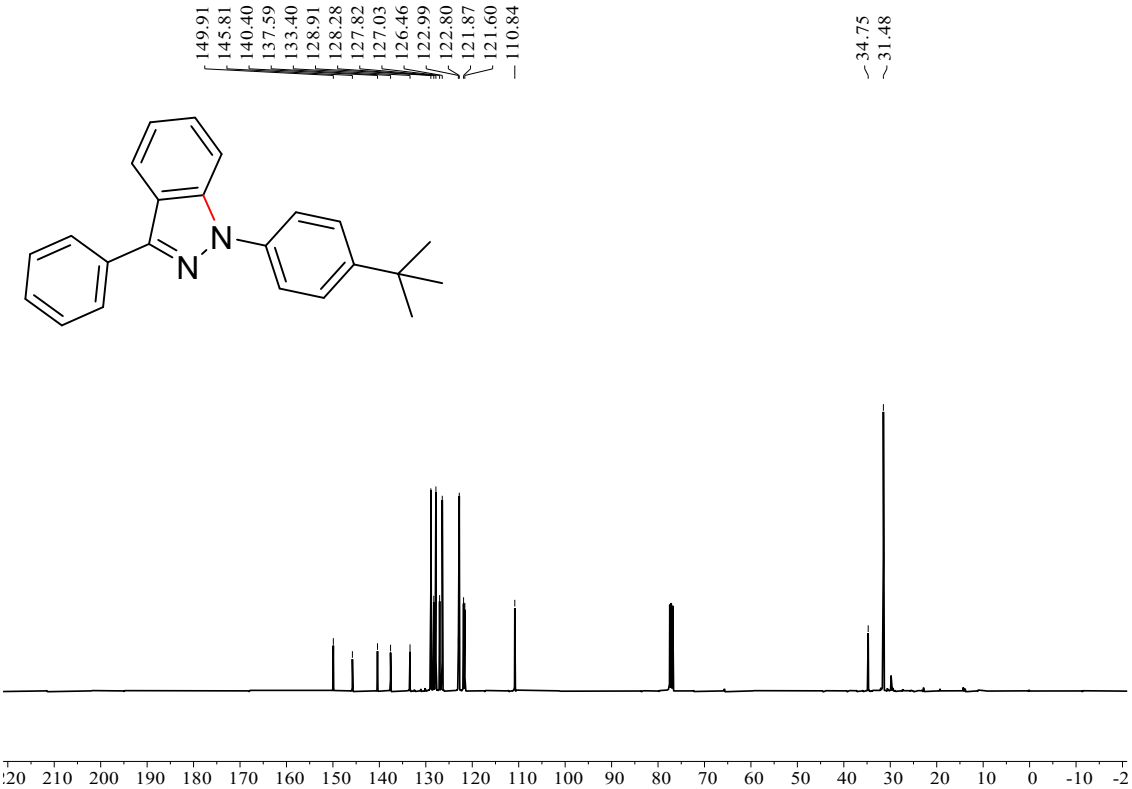


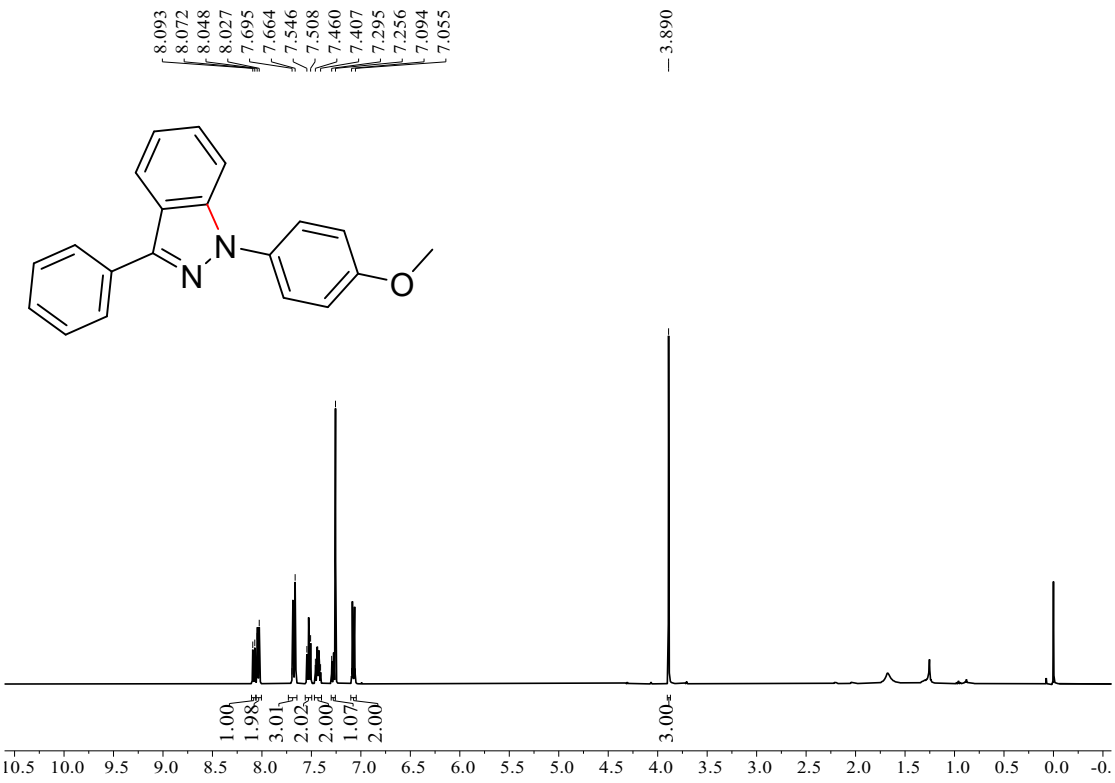
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2c



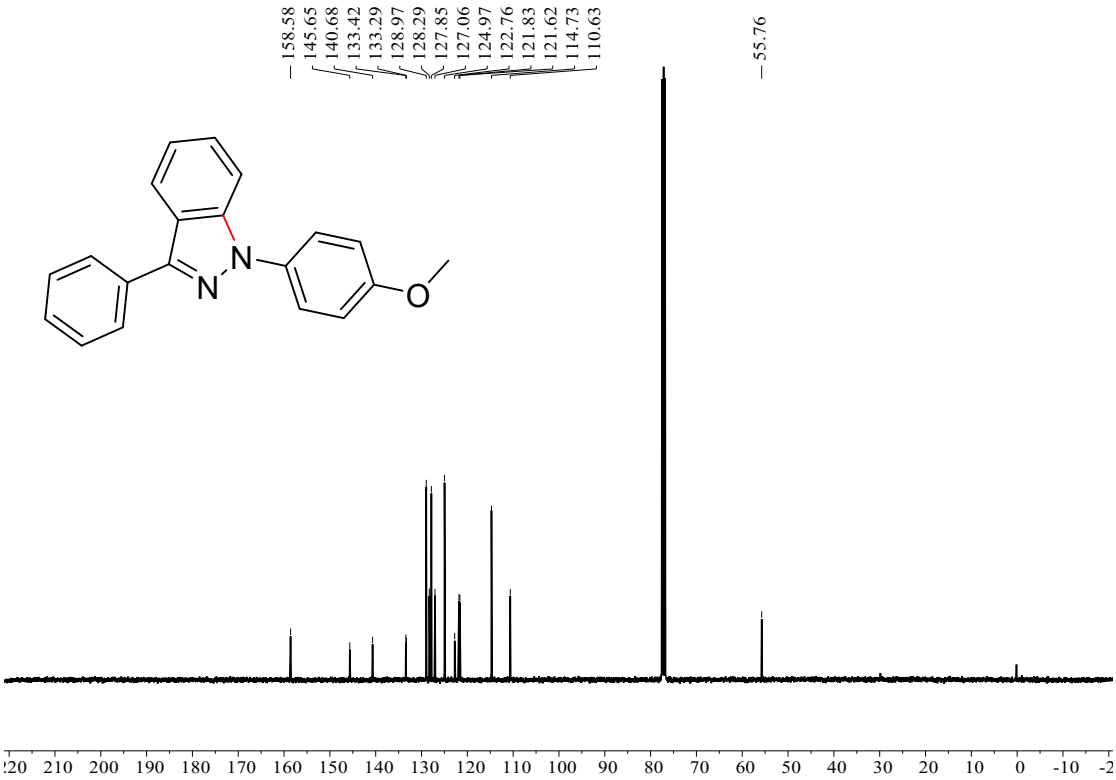
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2c



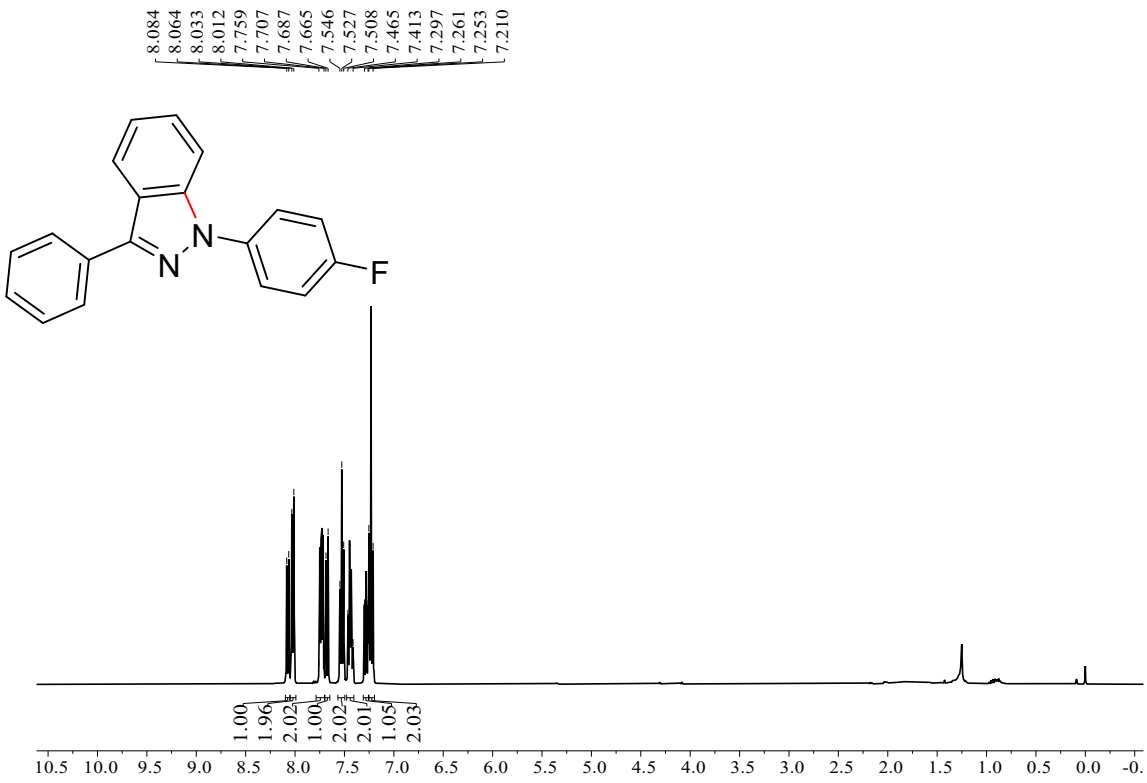
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2d



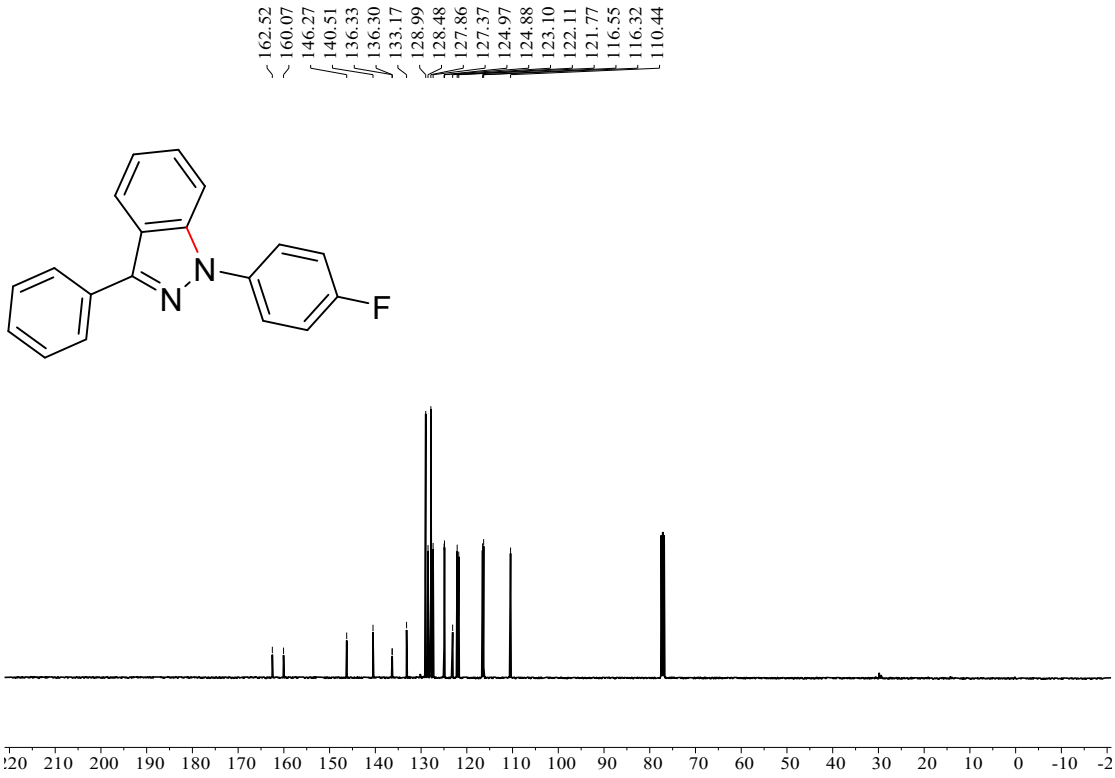
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2d



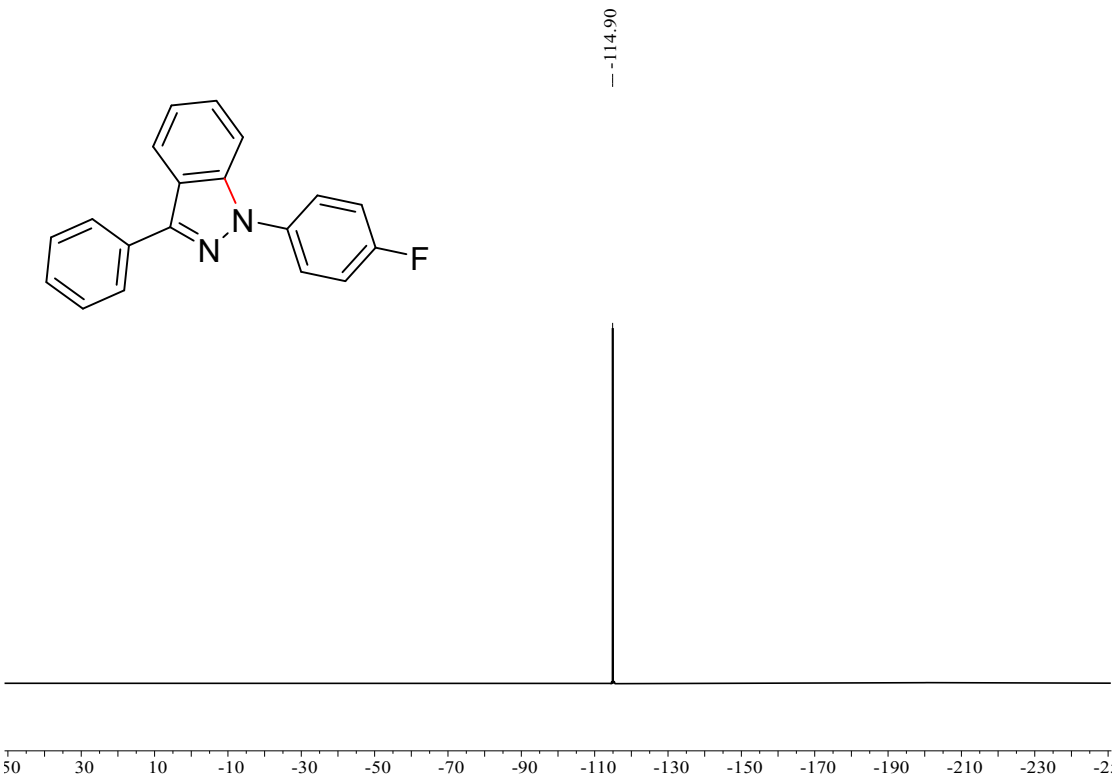
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2e



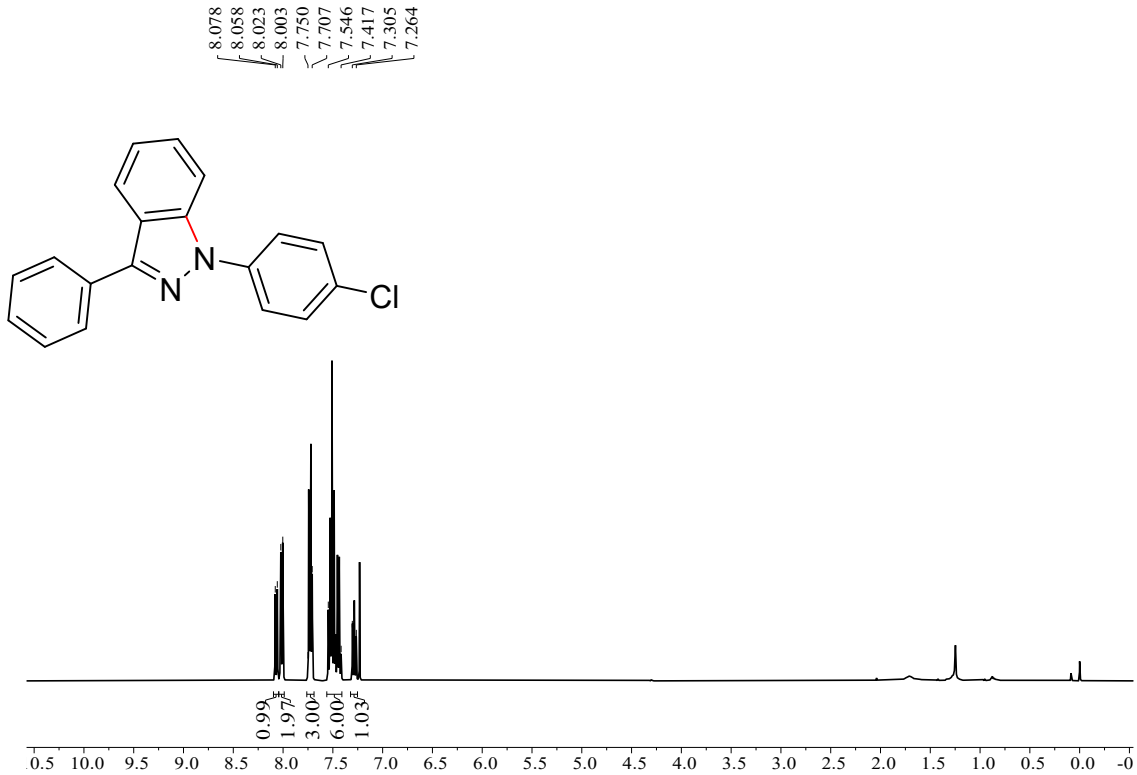
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2e



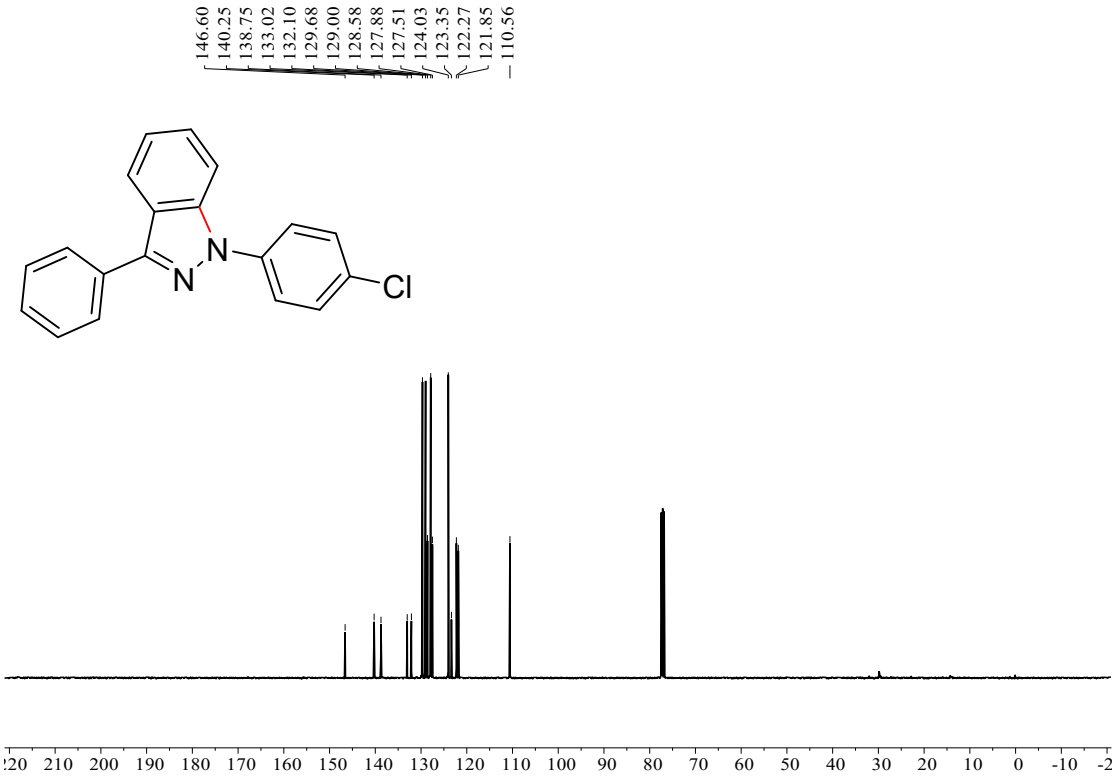
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2e



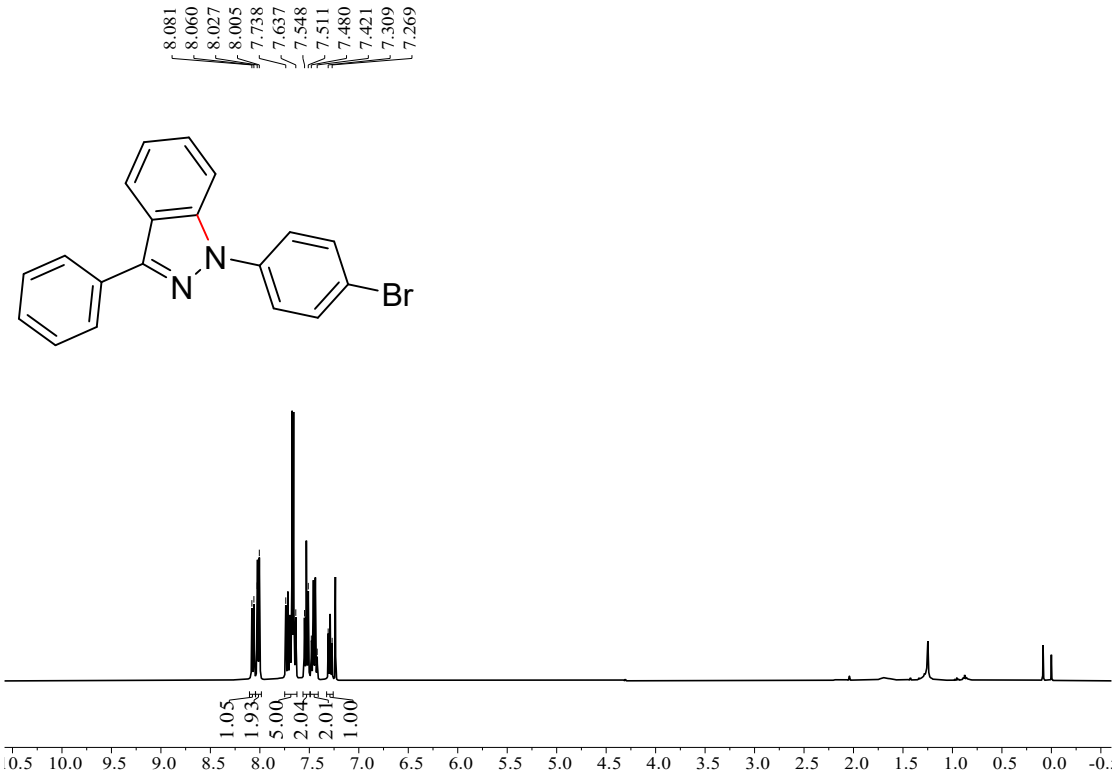
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2f



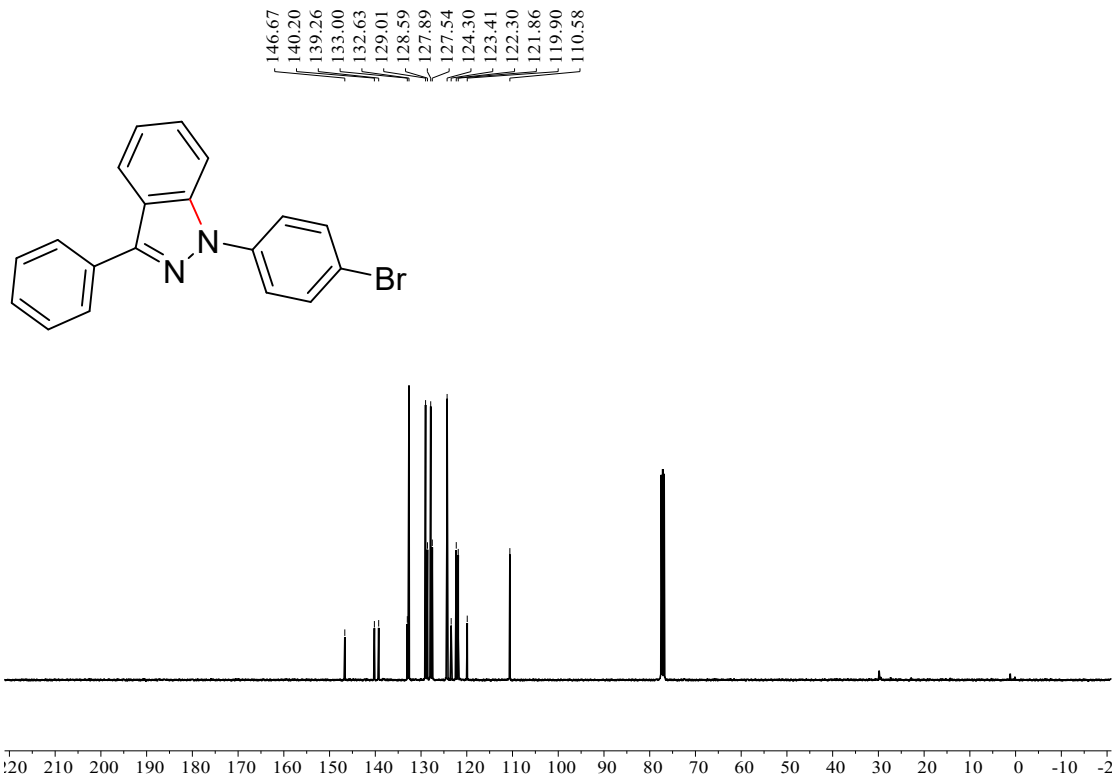
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2f



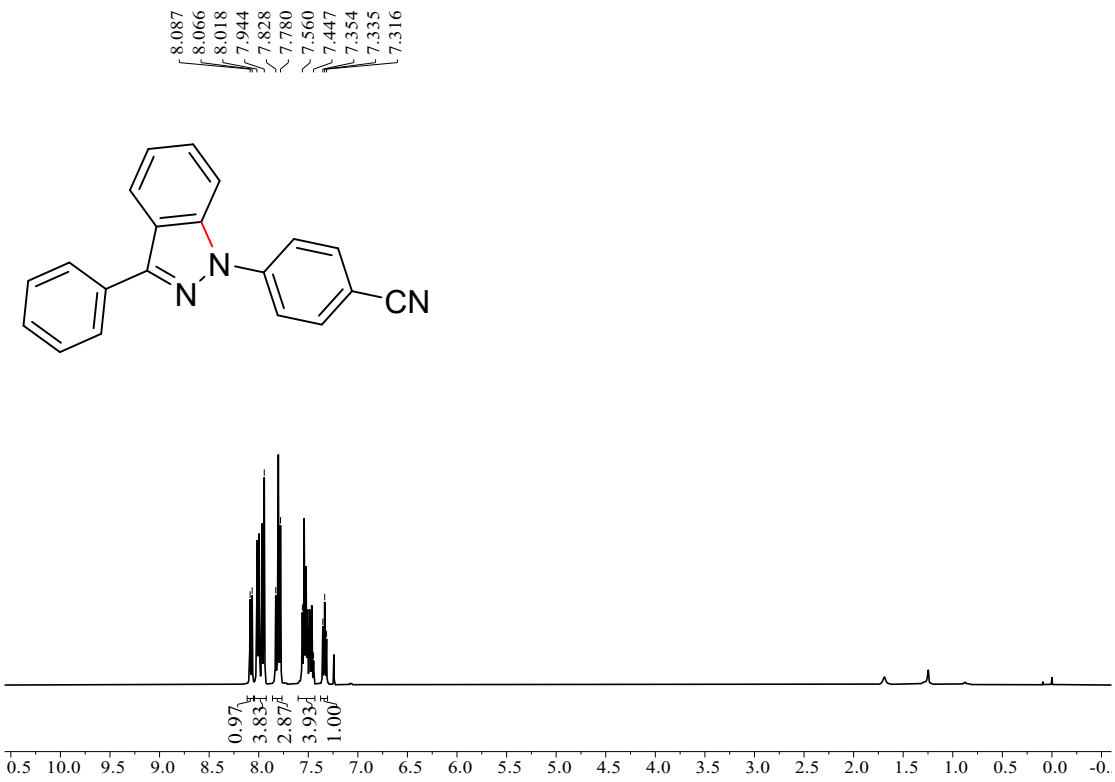
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2g



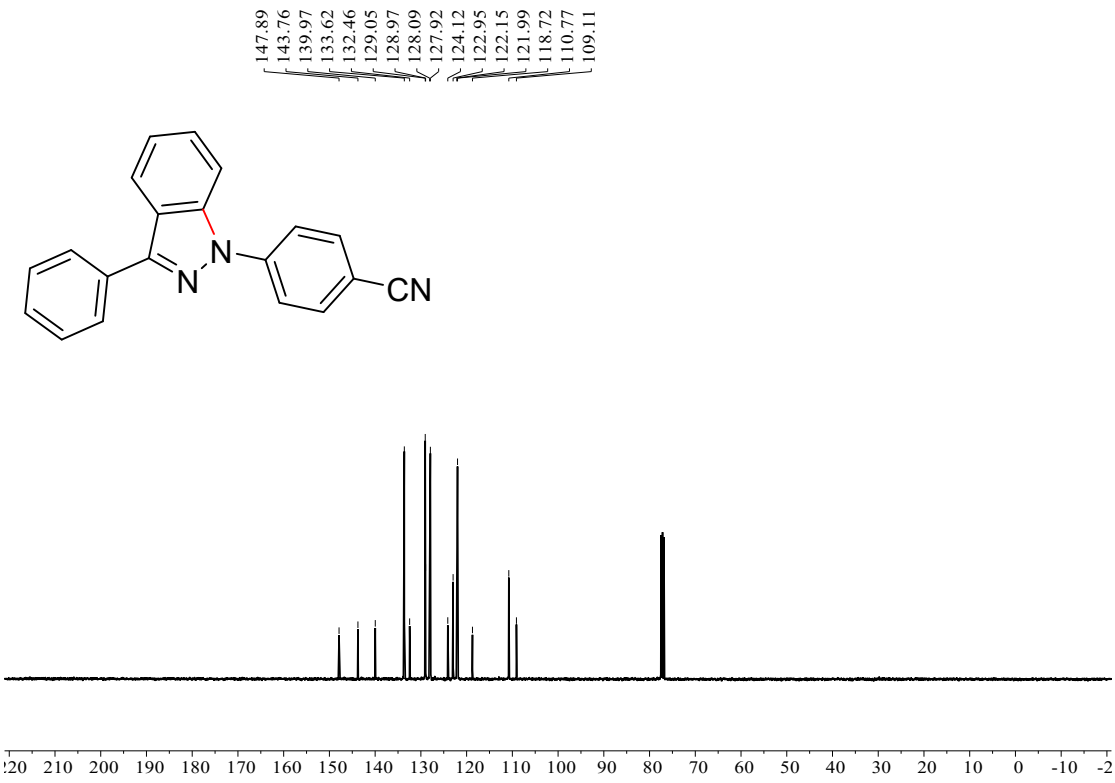
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2g



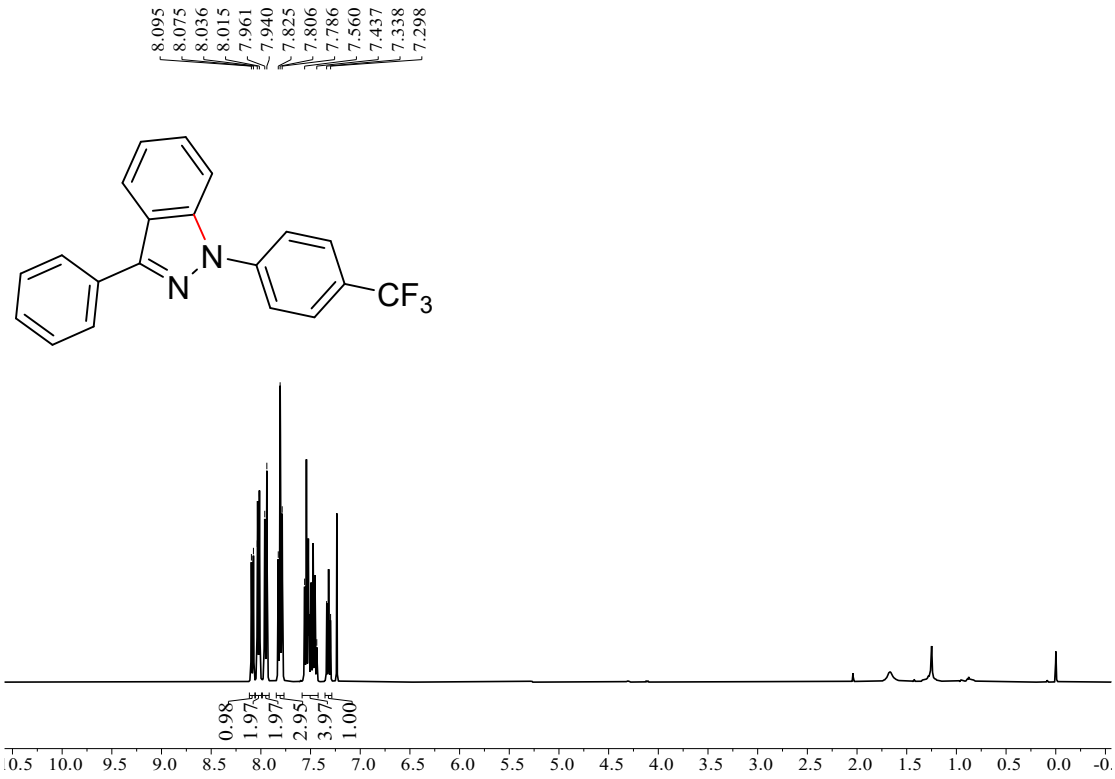
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2h



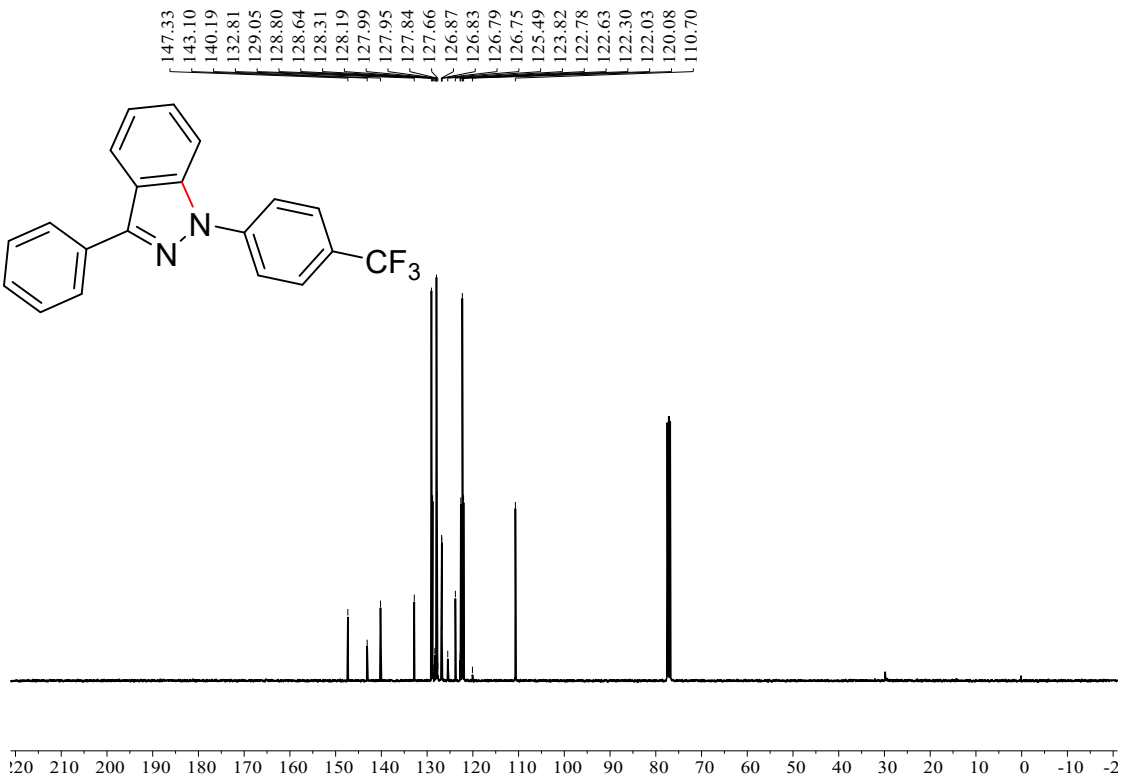
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2h



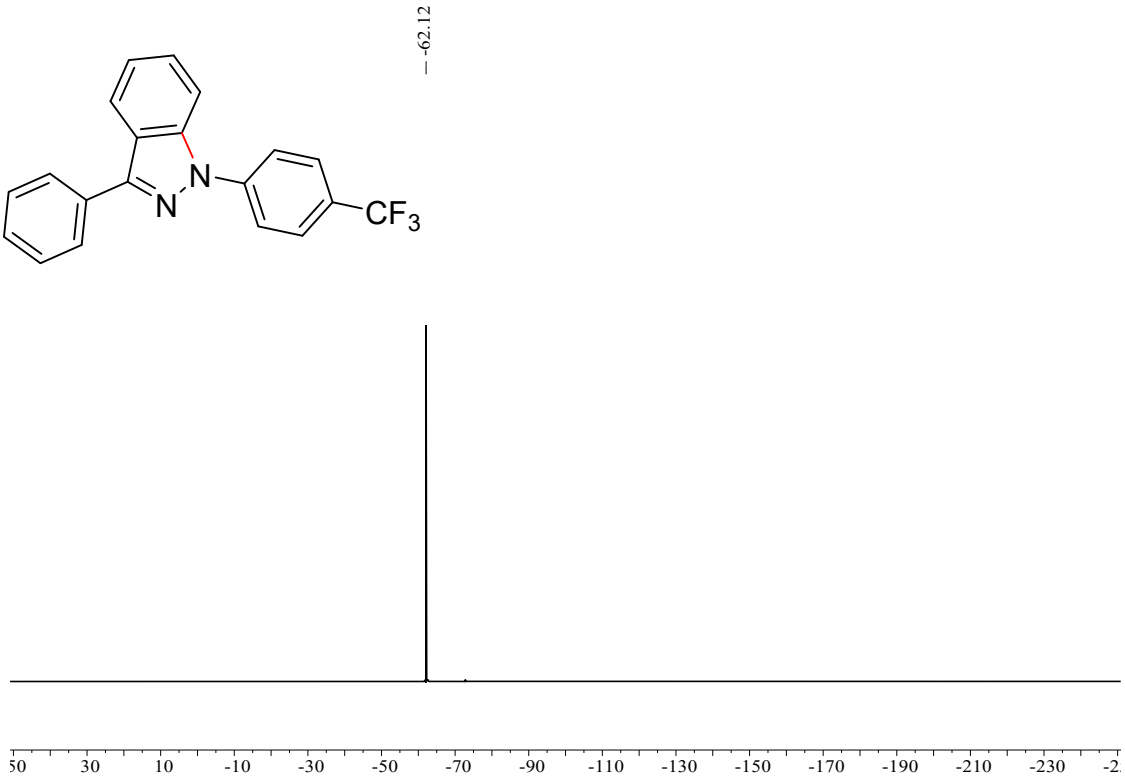
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2i



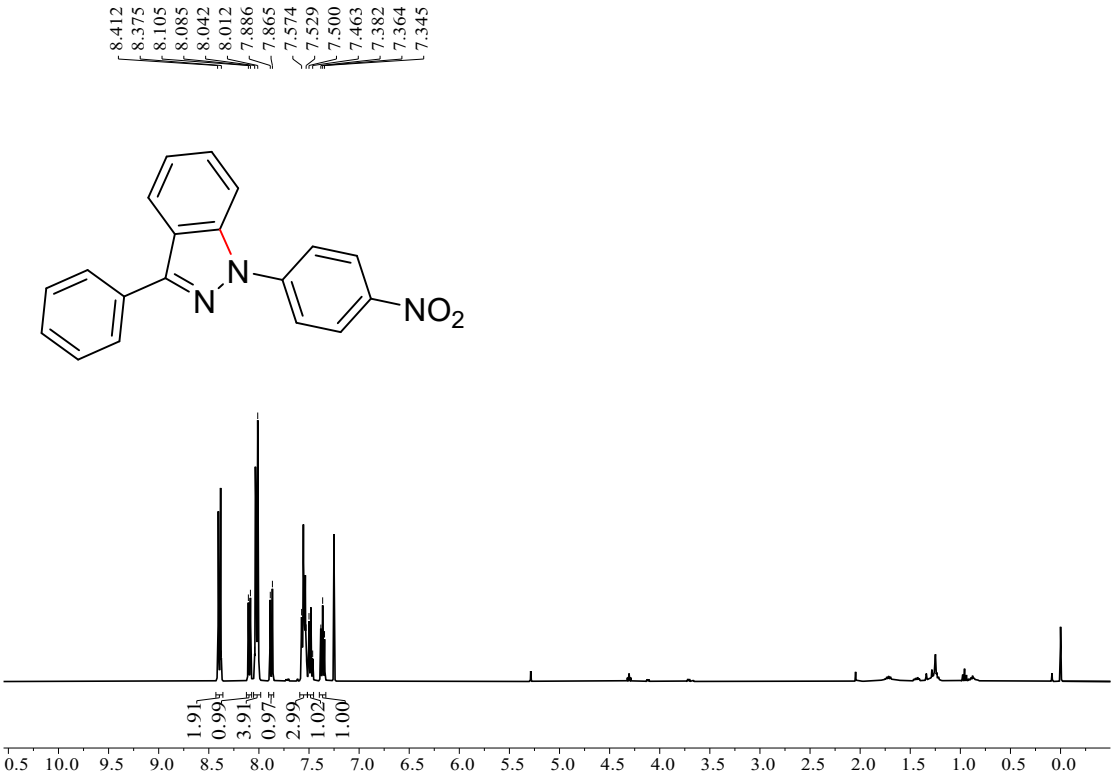
^{13}C NMR(101 MHz, $CDCl_3$) spectrum of 2i



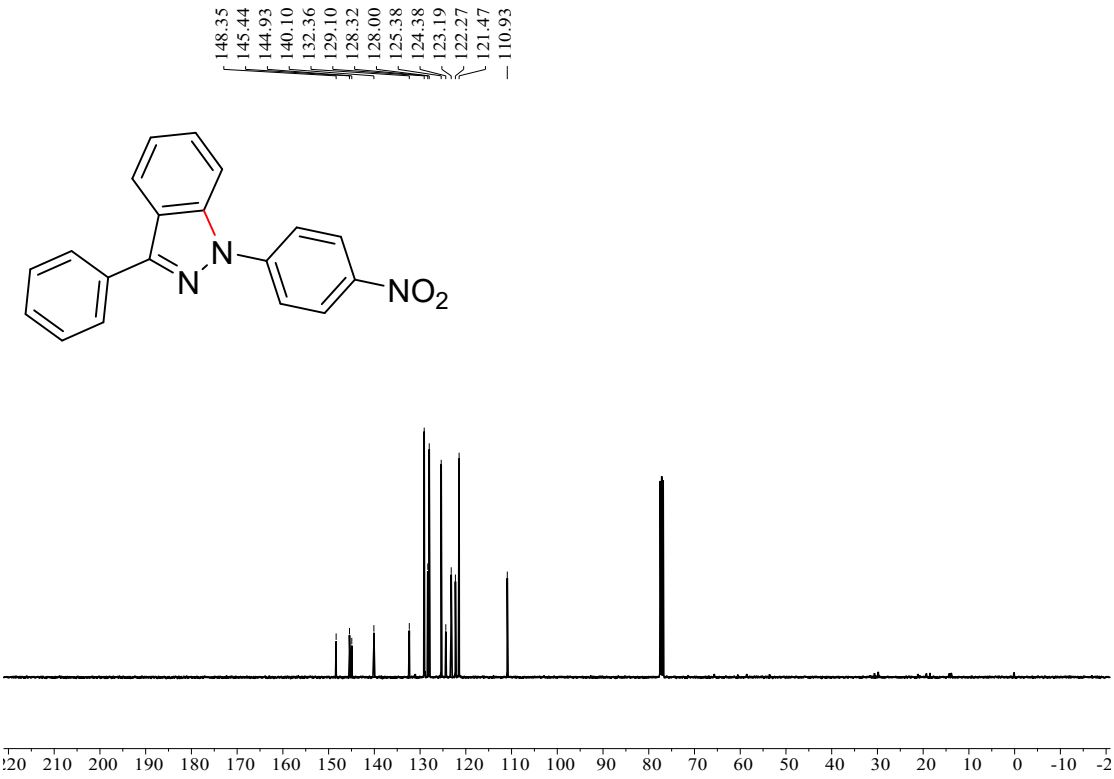
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2i



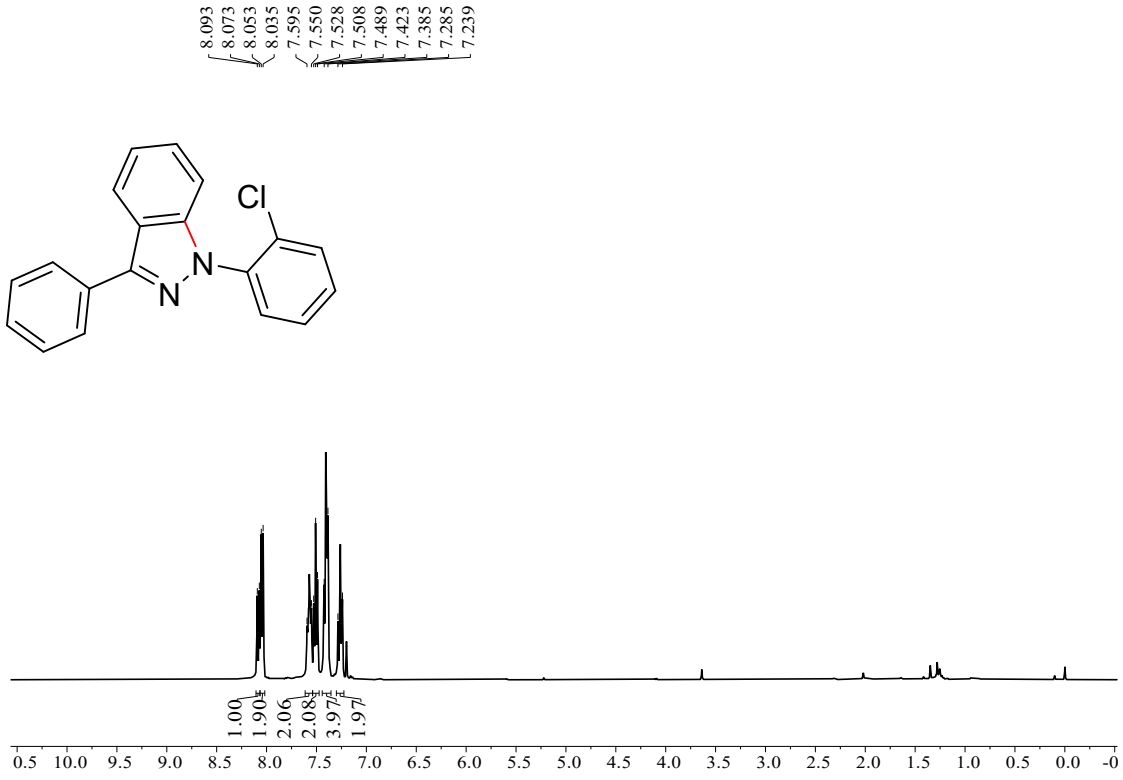
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2j



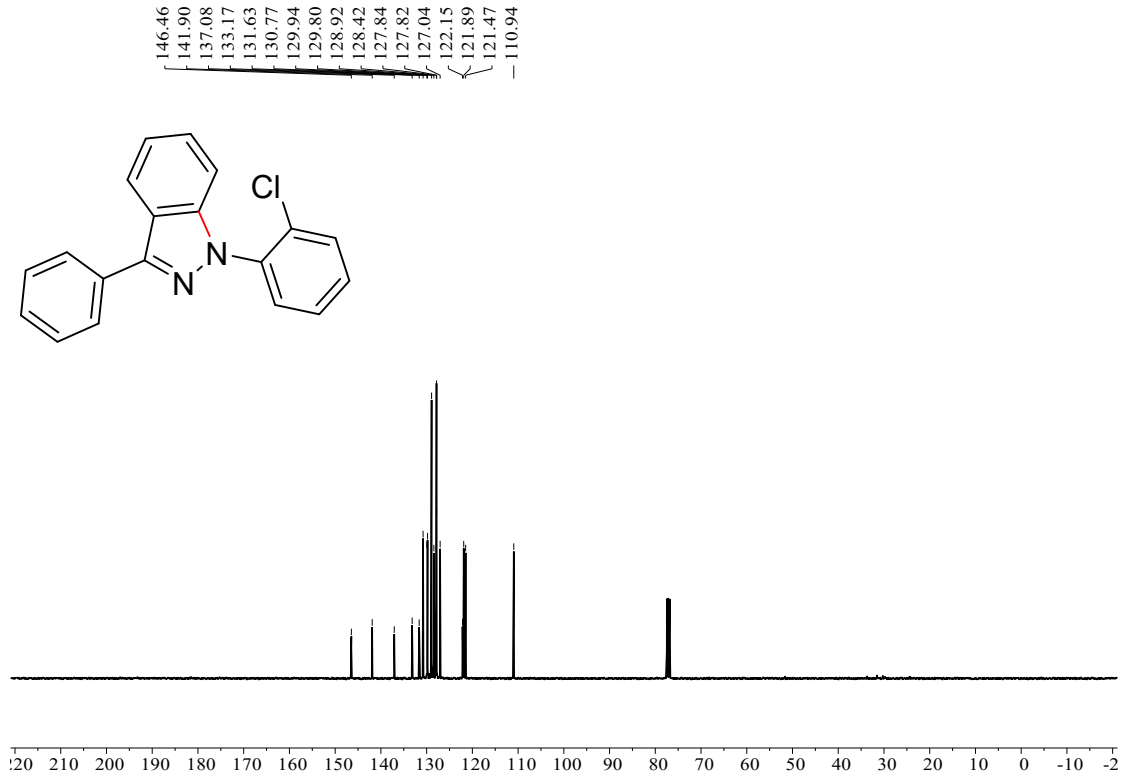
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2j



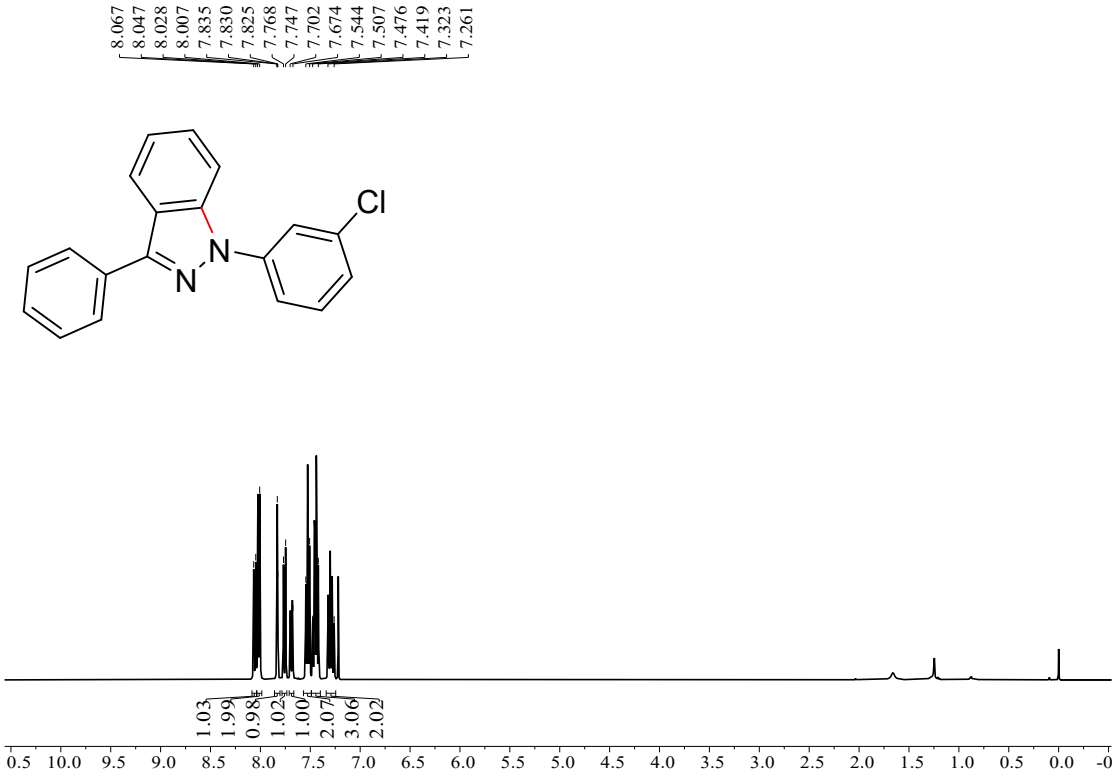
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2k



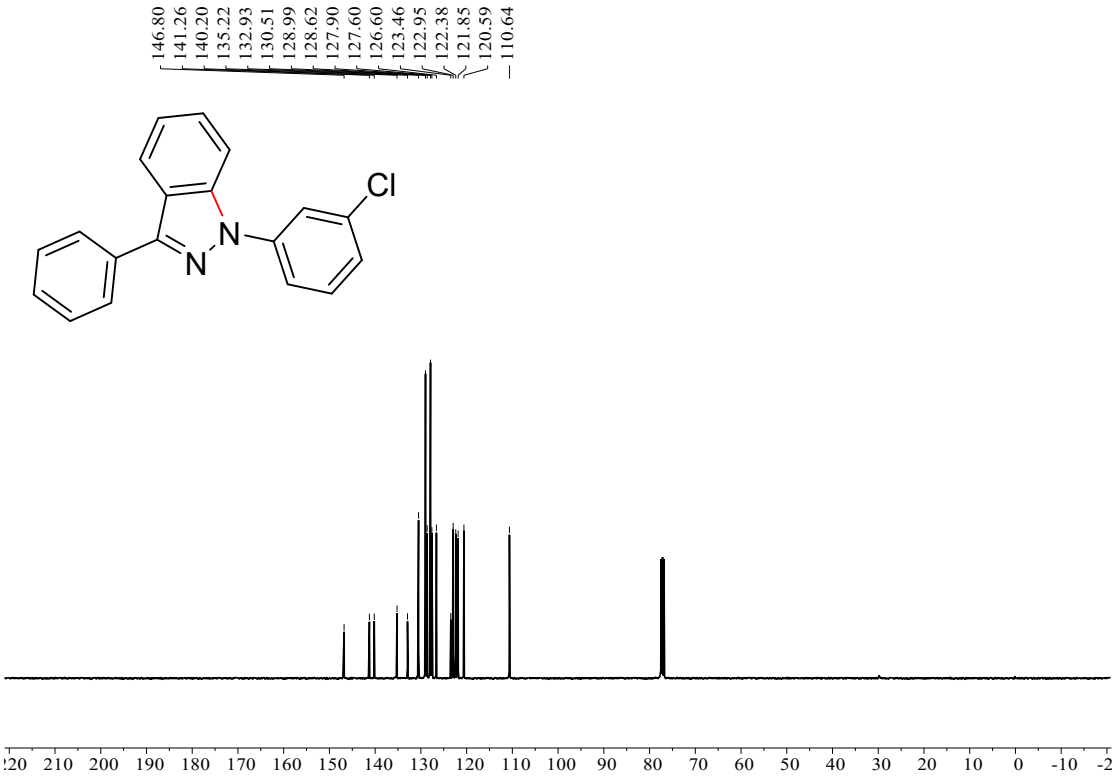
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2k



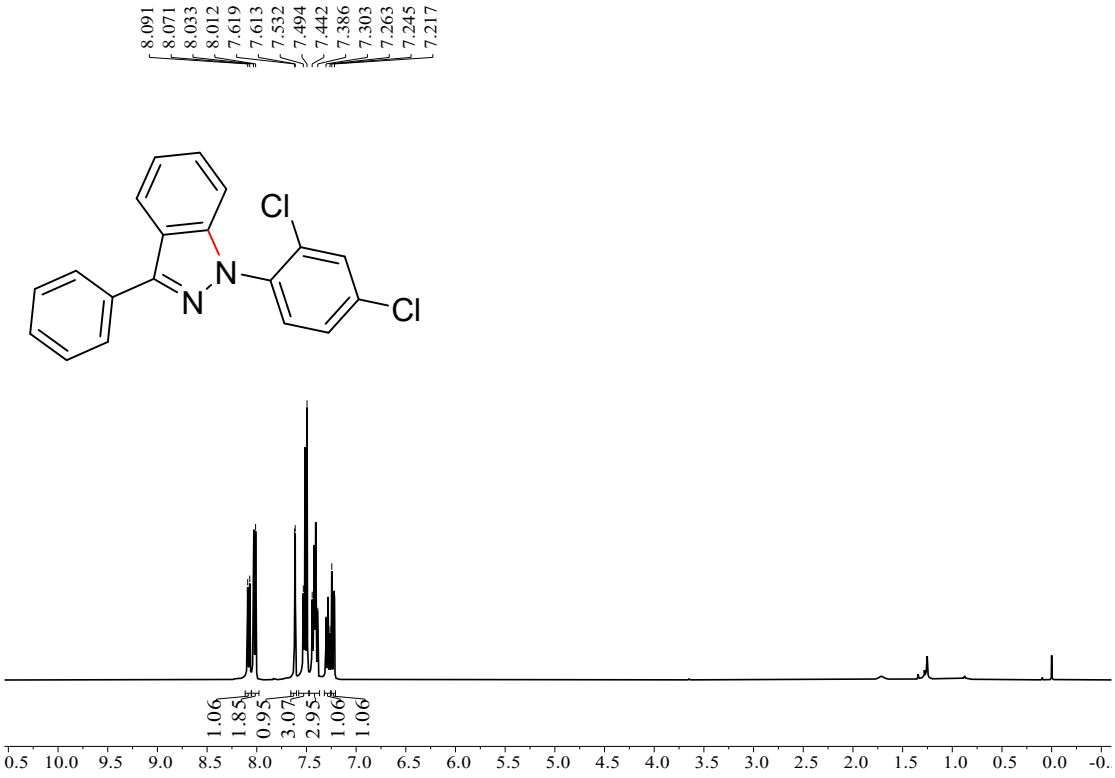
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2l



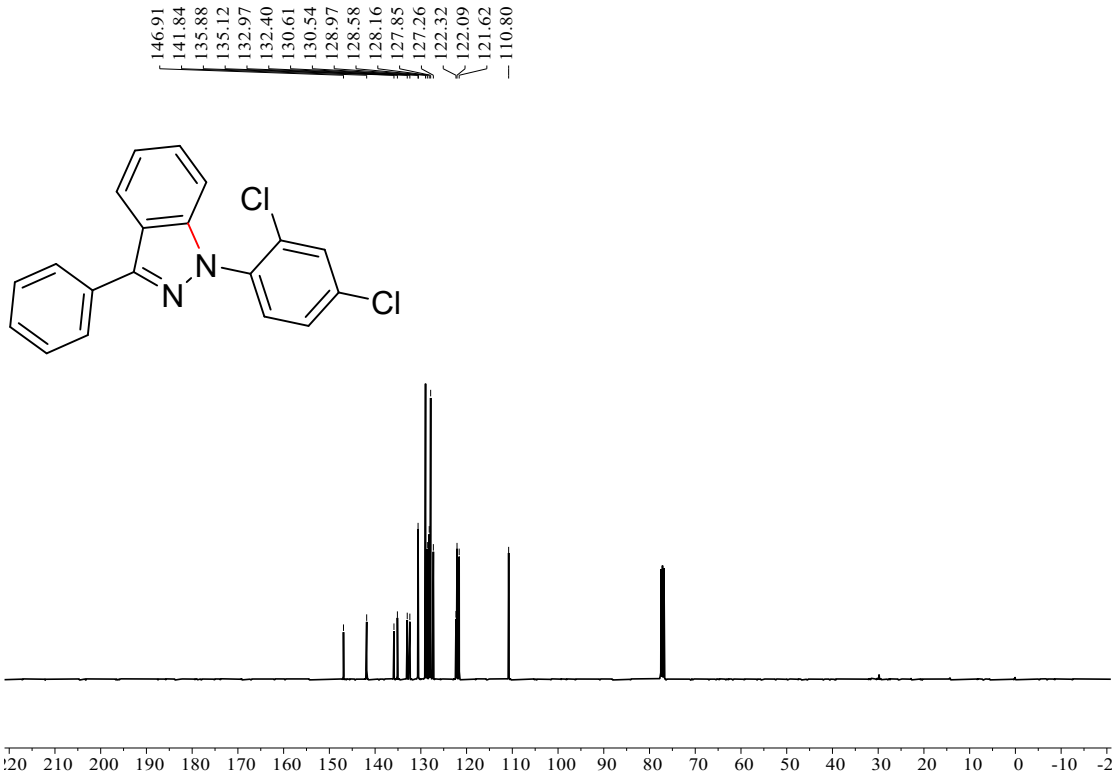
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2l



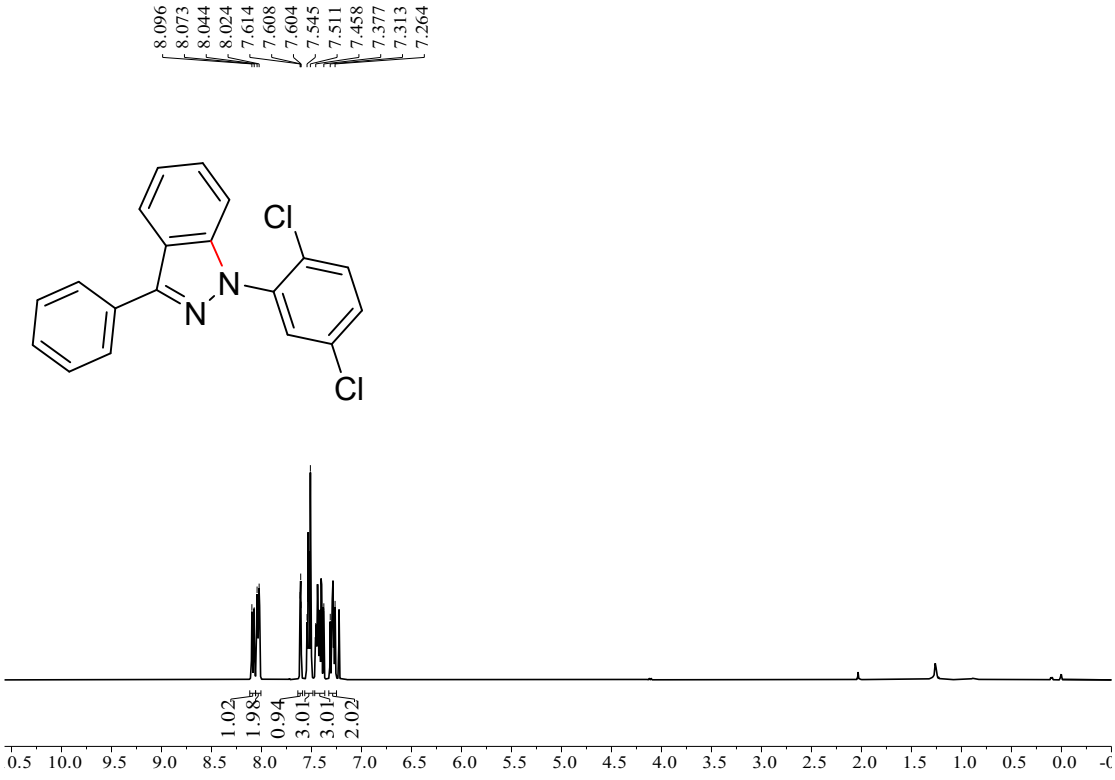
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2m



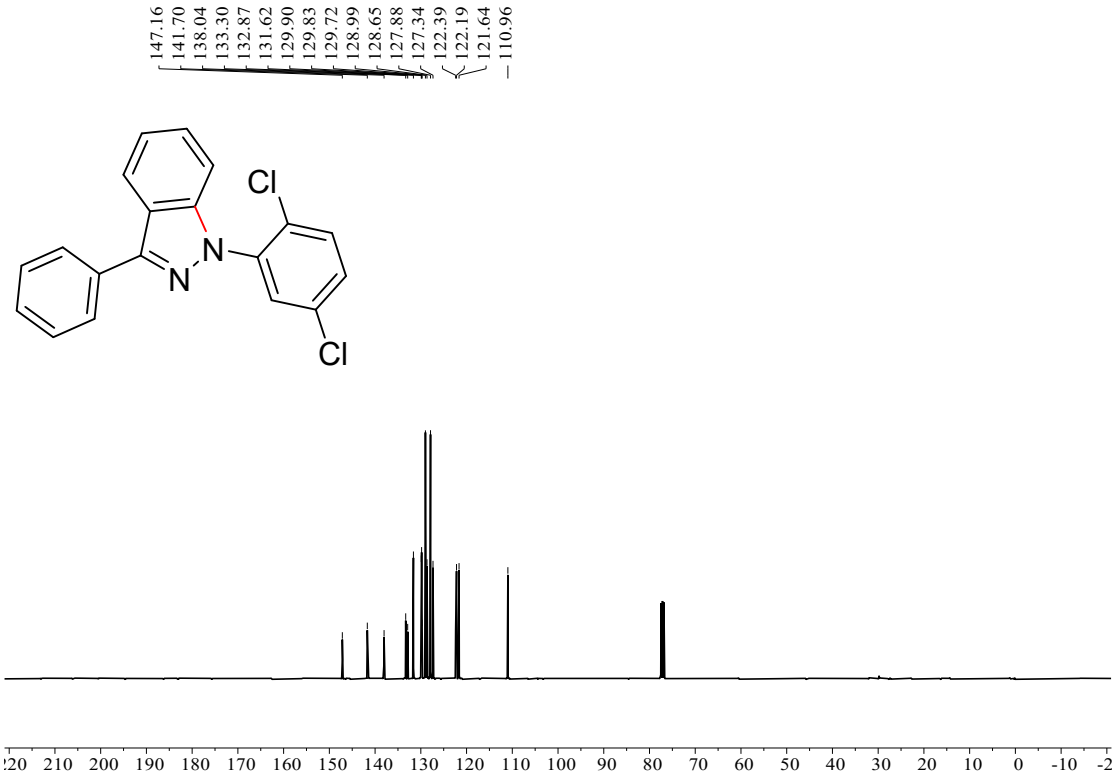
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2m



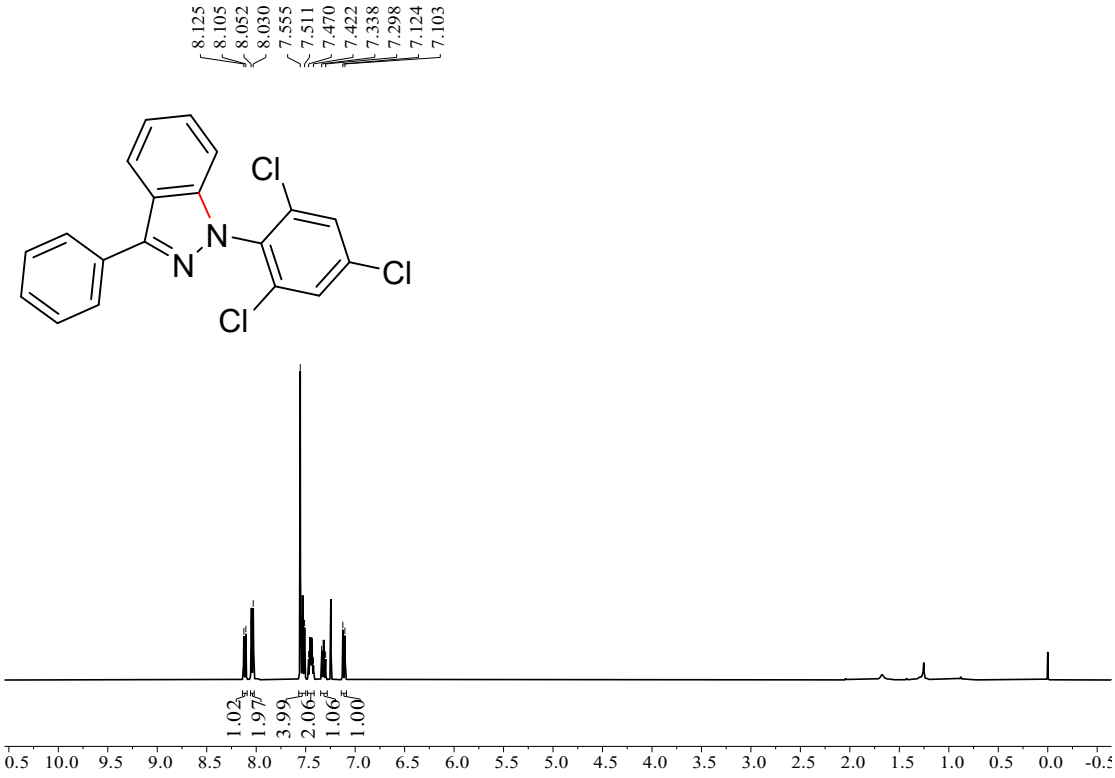
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2n



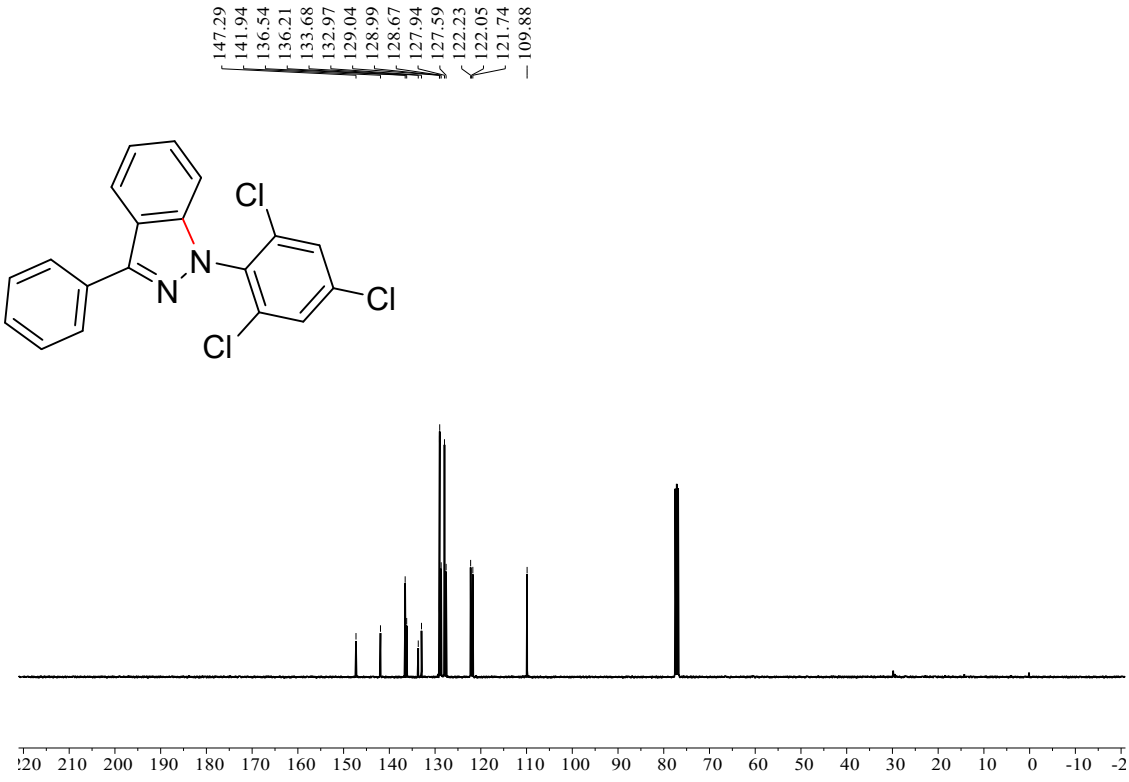
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2n



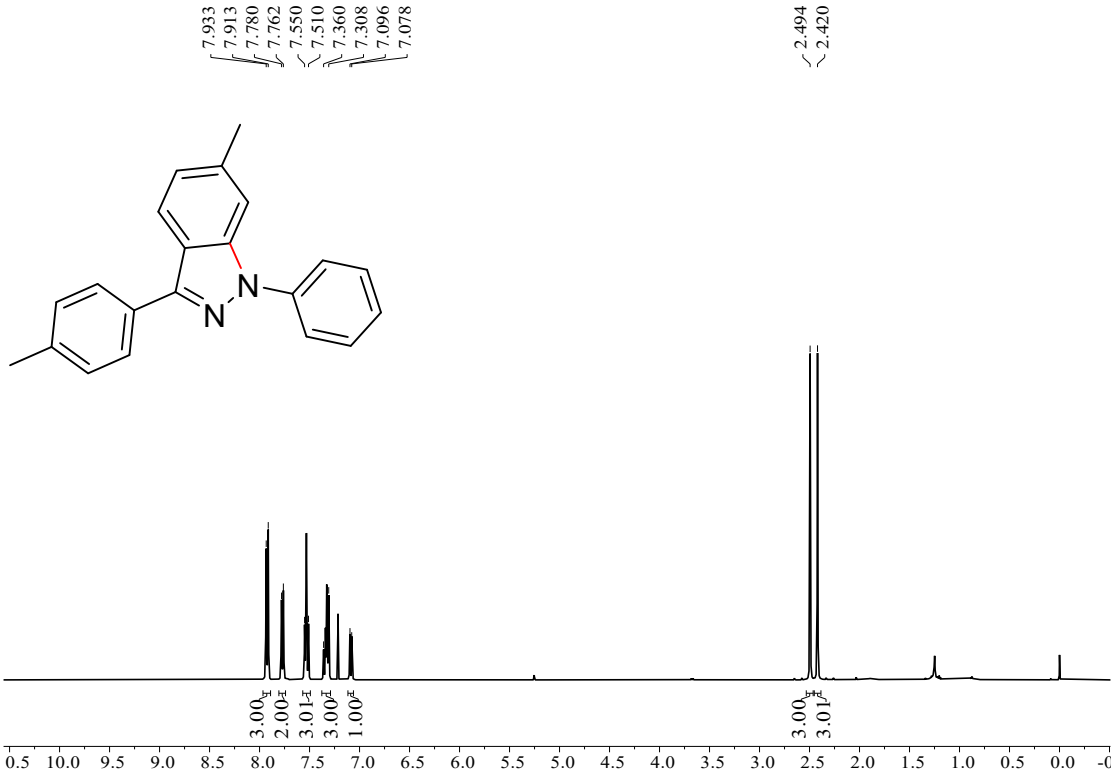
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2o



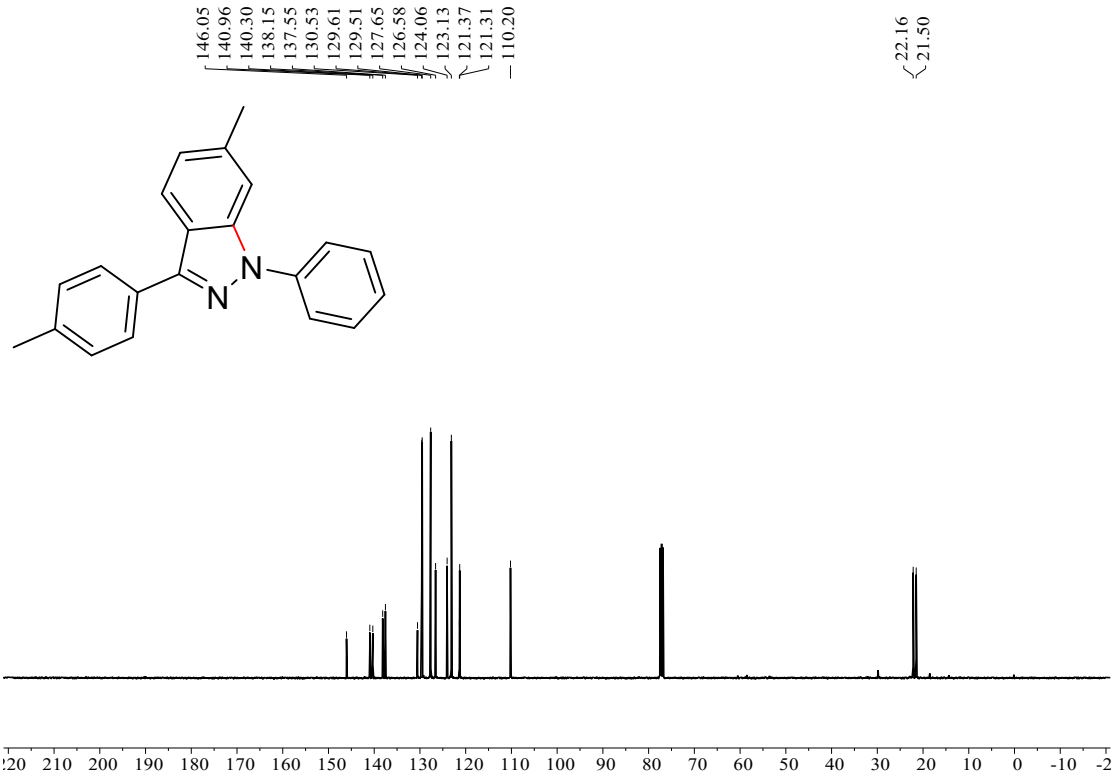
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2o



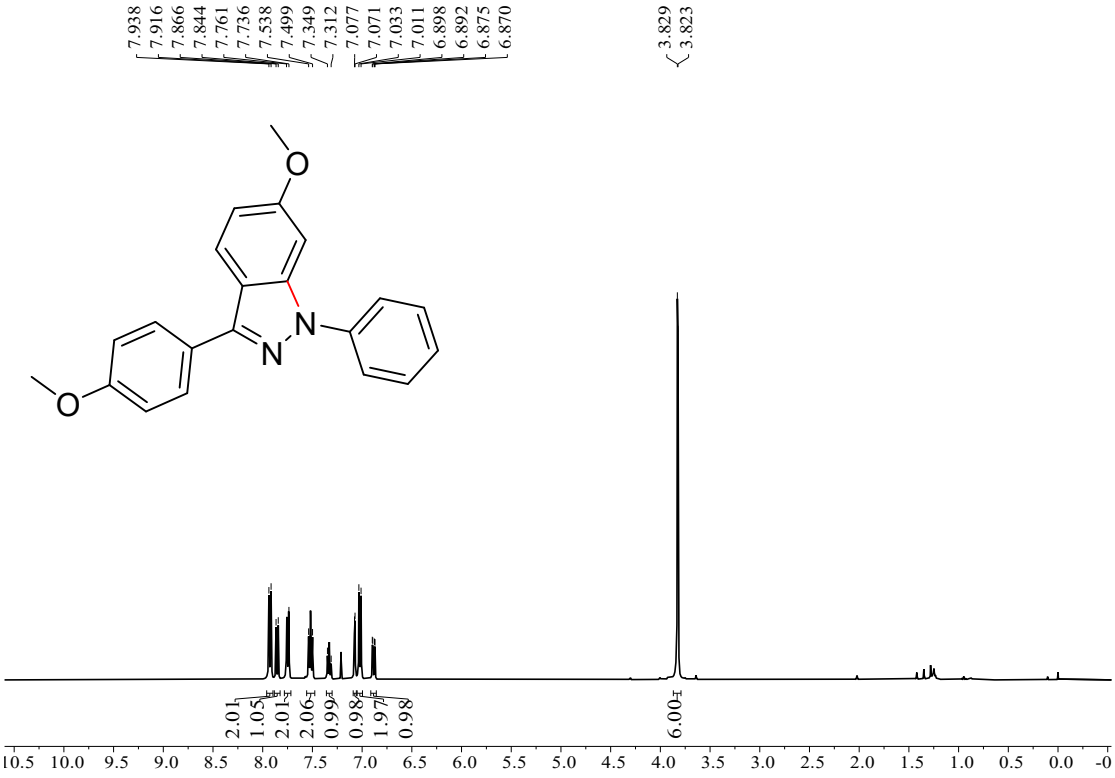
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2p



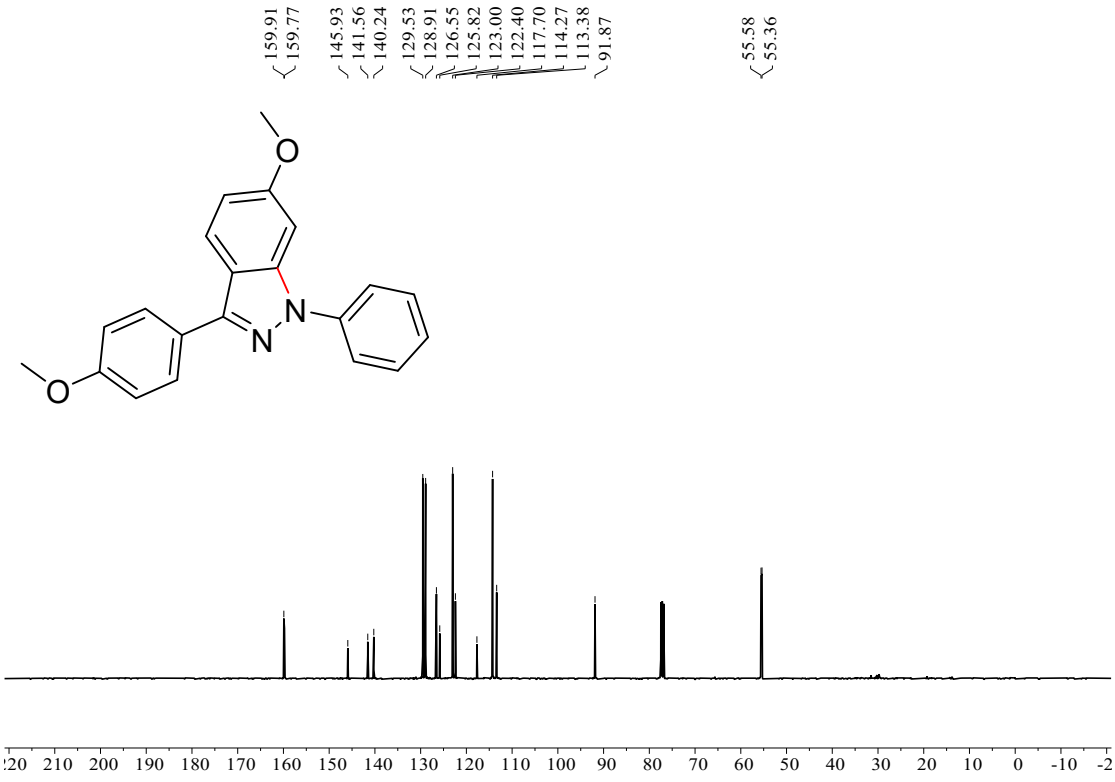
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2p



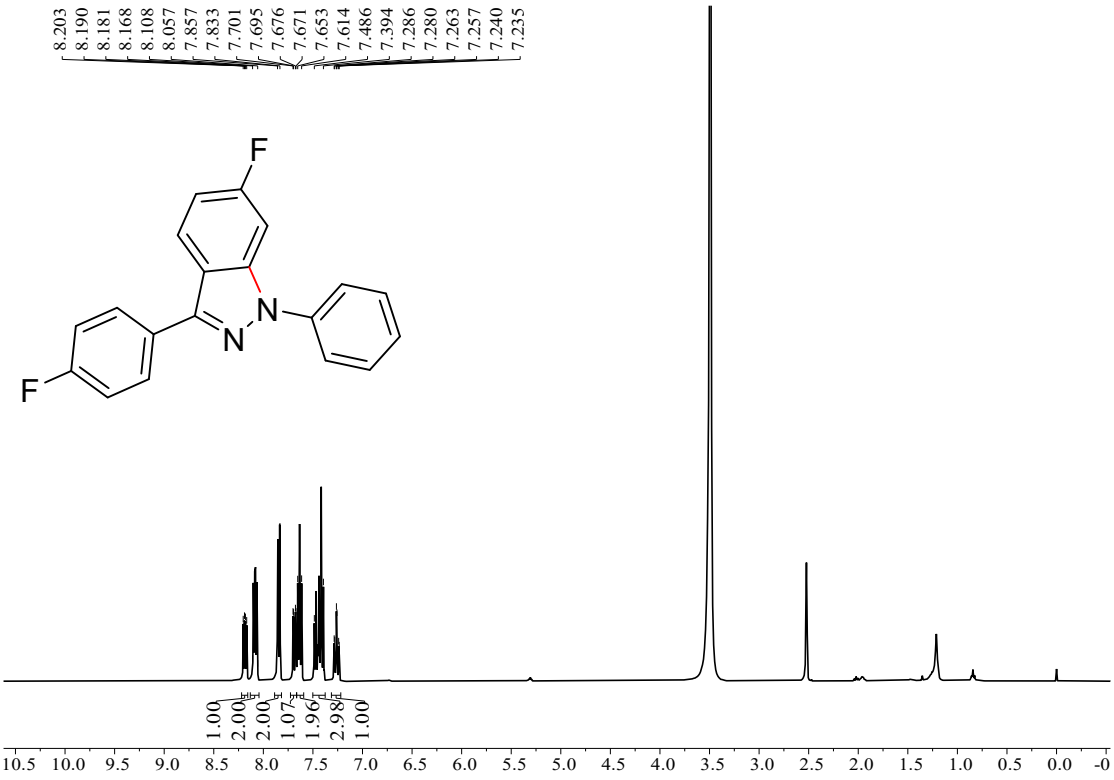
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2q



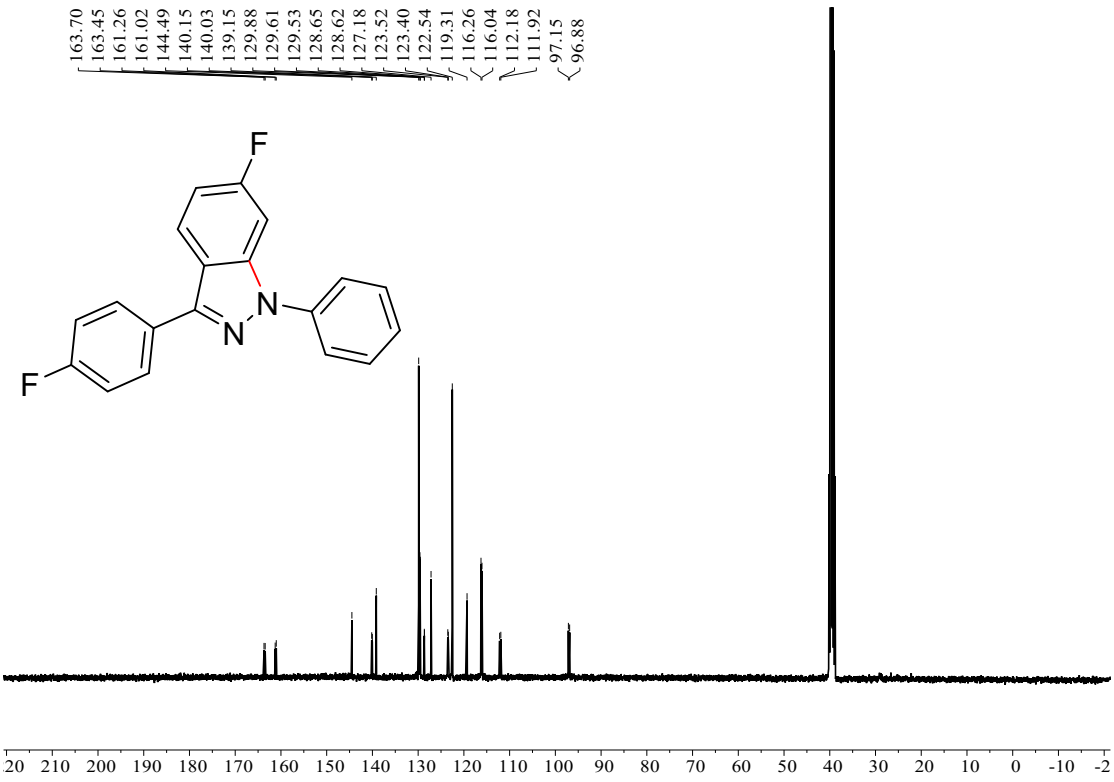
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2q



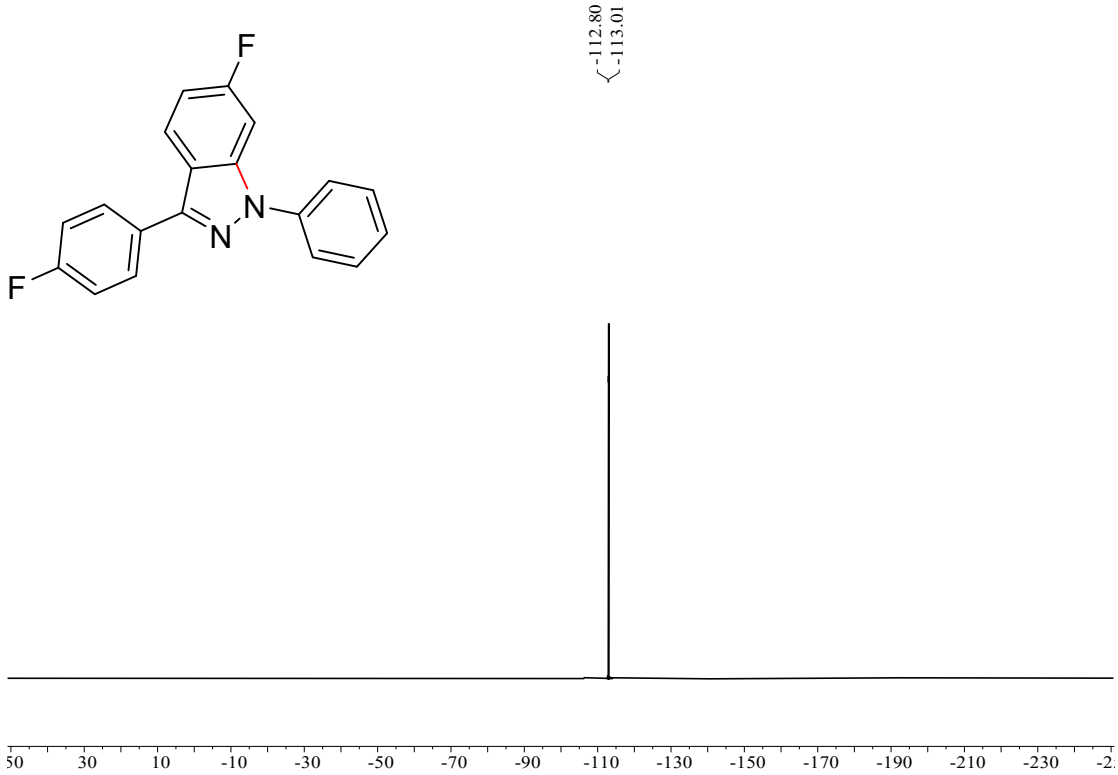
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 2r



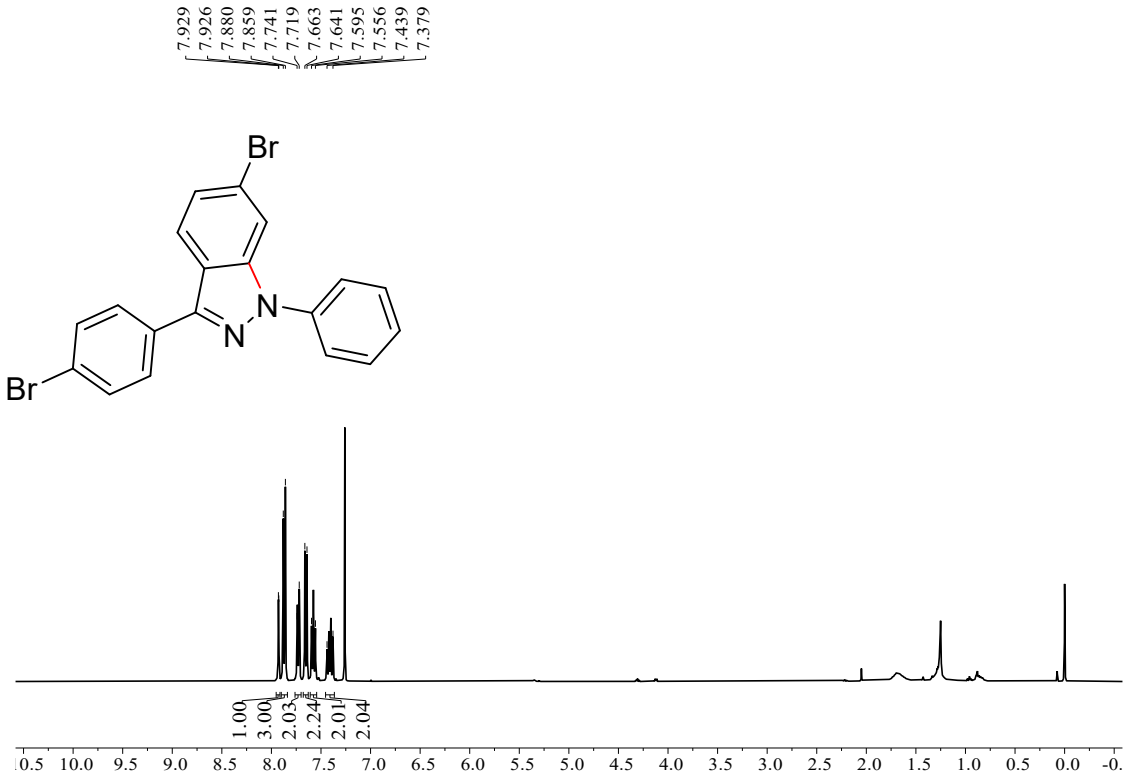
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of 2r



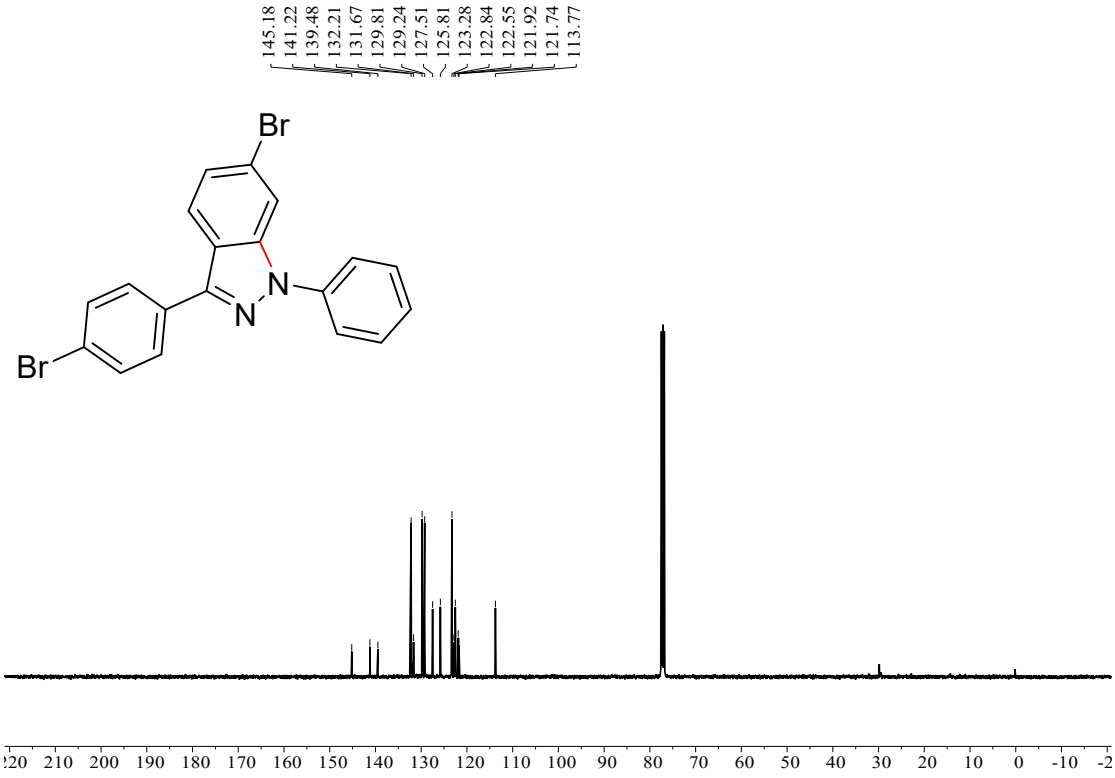
^{19}F NMR (376 MHz, DMSO-d_6) spectrum of 2r



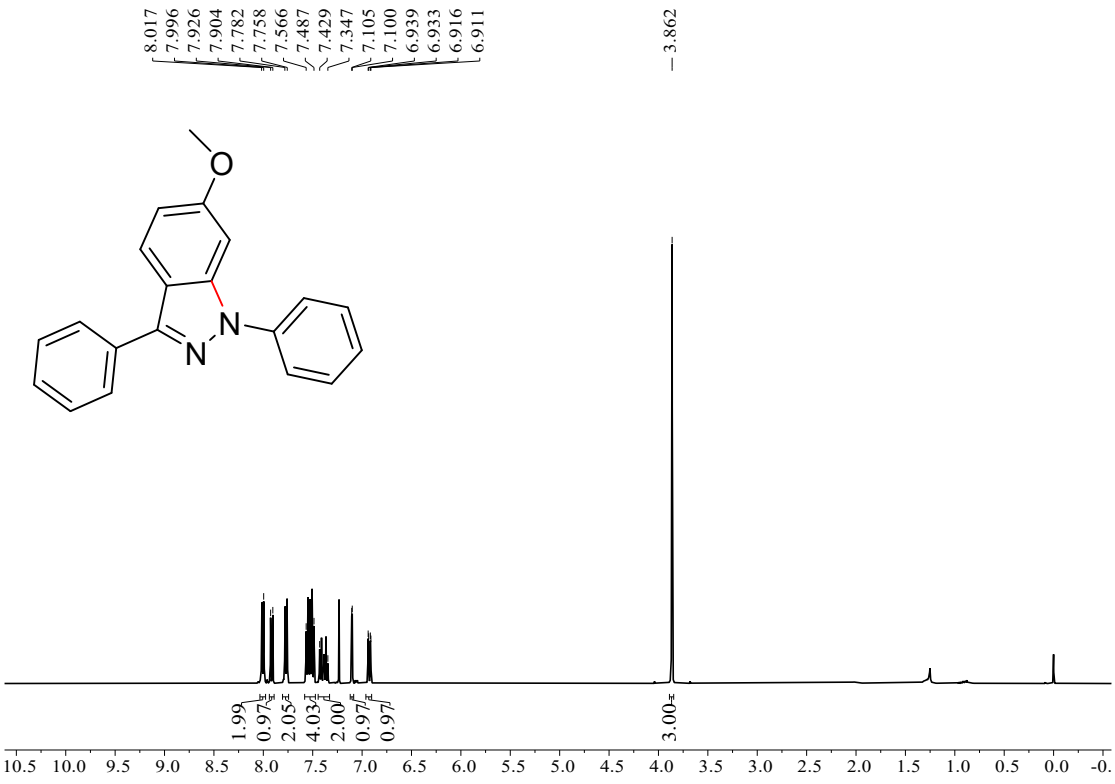
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2s



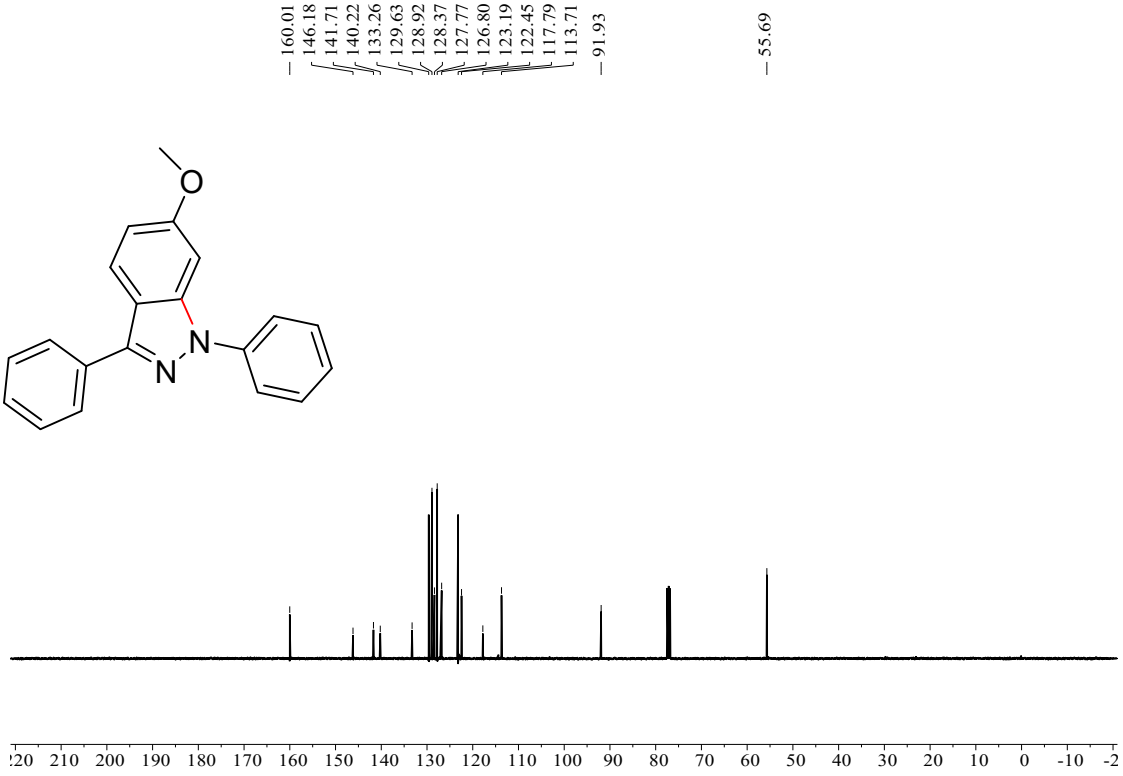
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2s



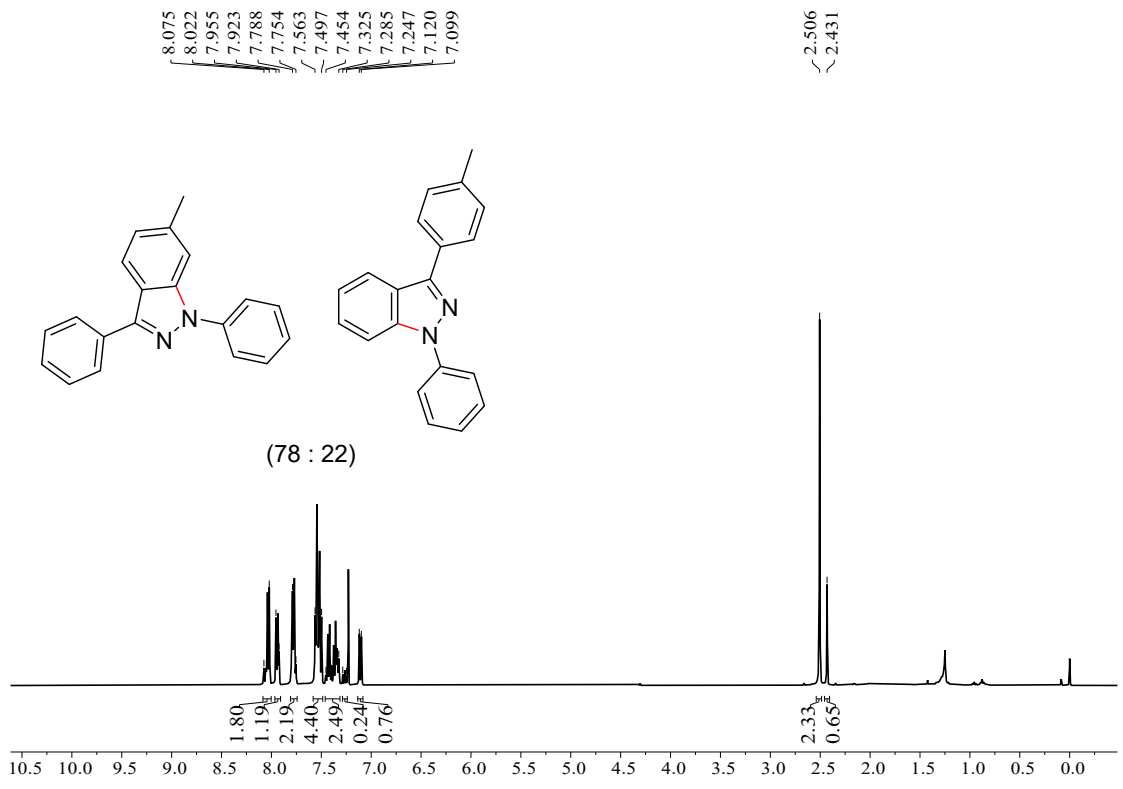
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2u



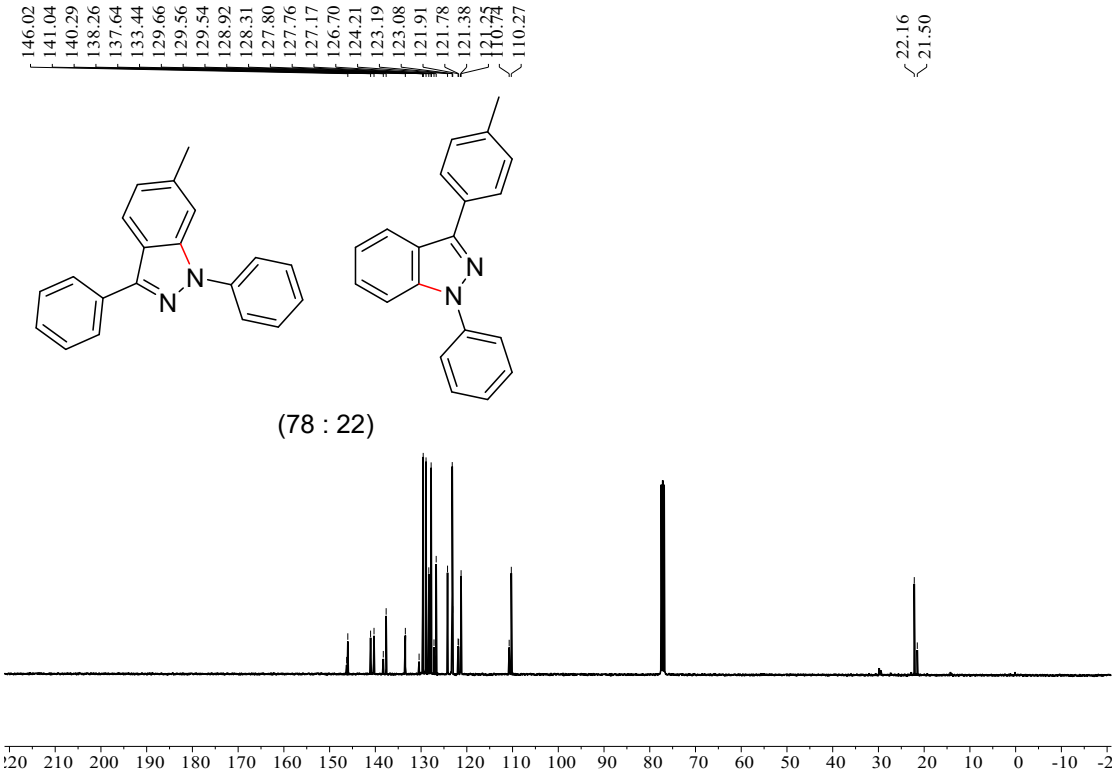
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2u



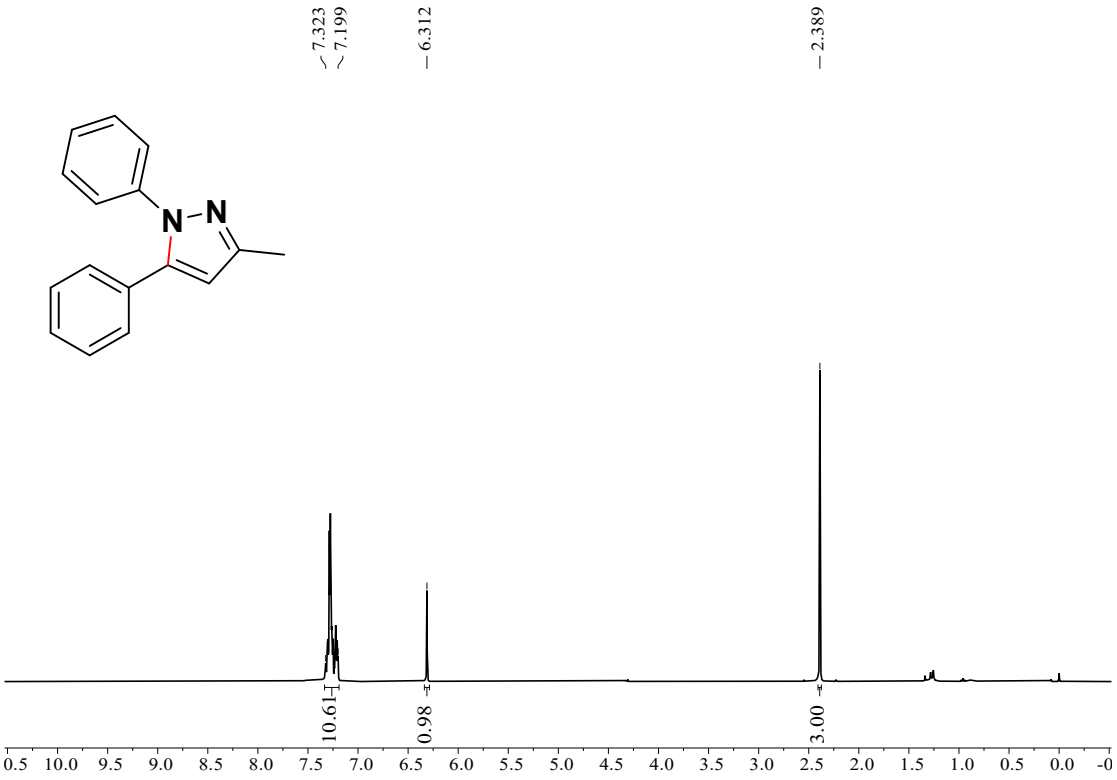
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2t and 2t′



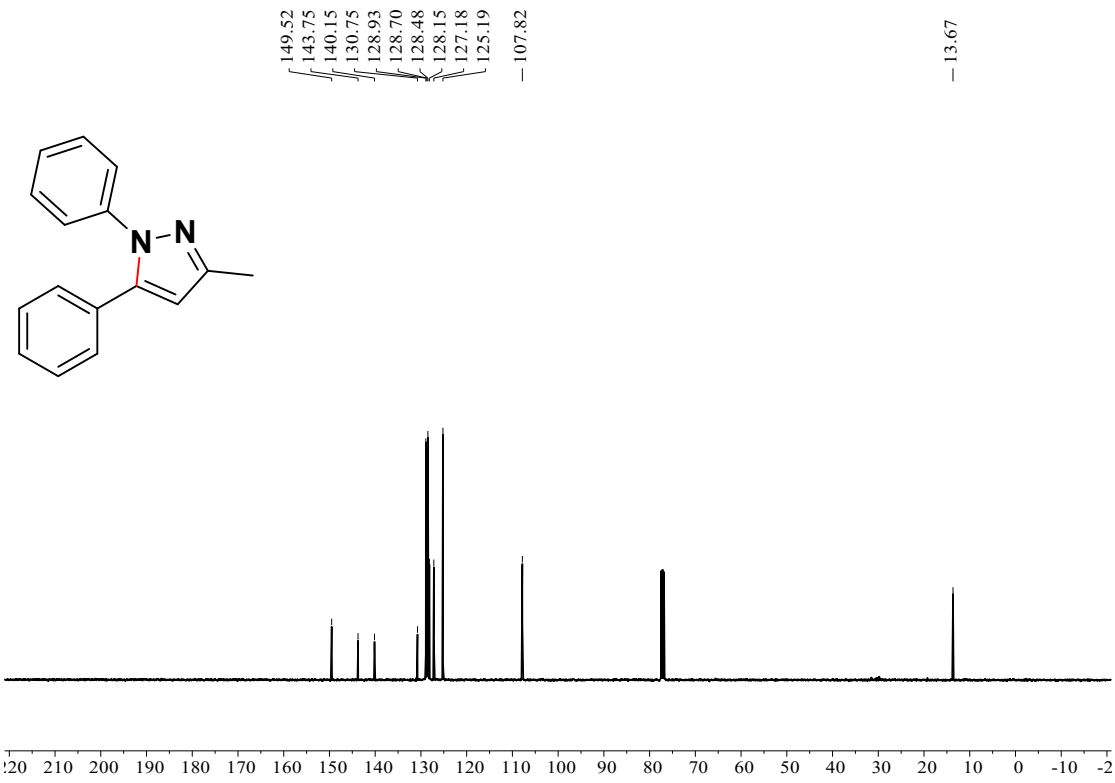
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2t and 2t′



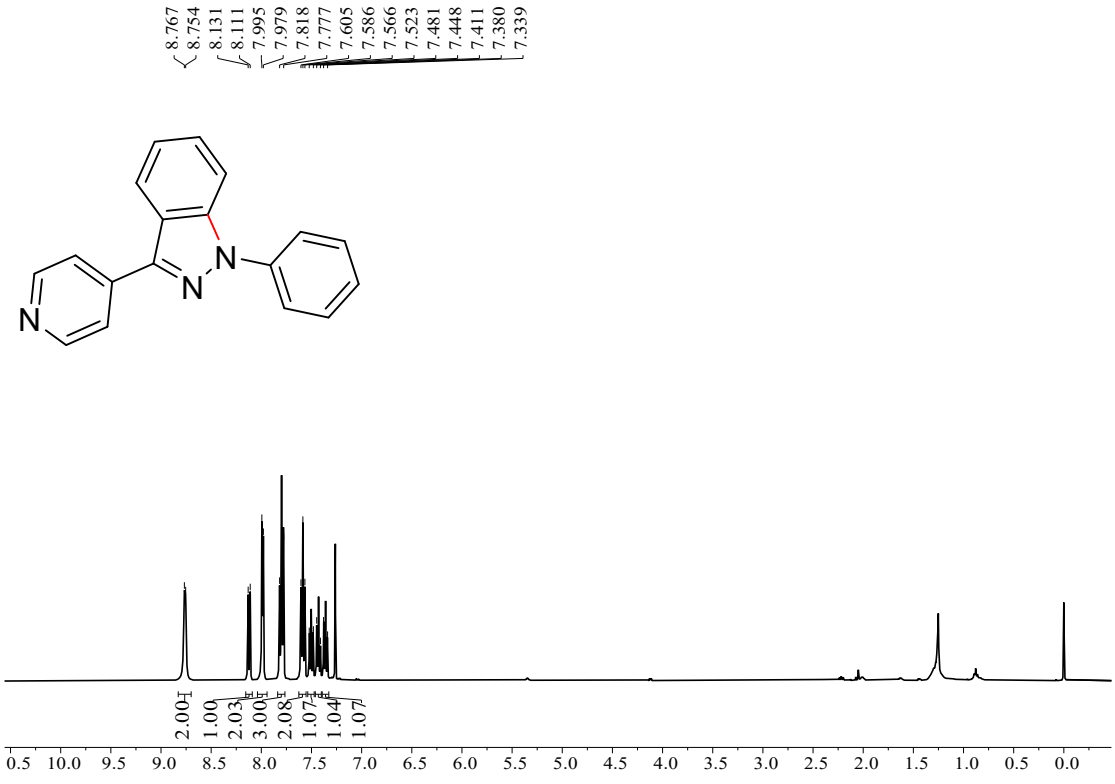
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2v



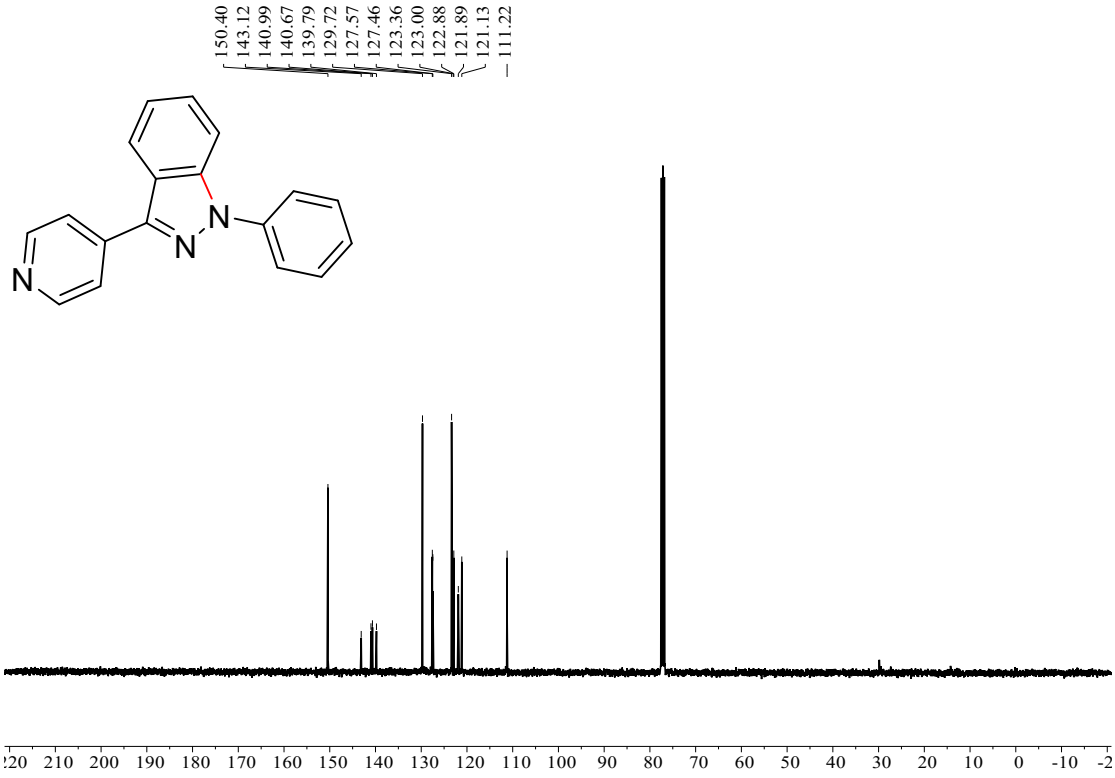
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2v



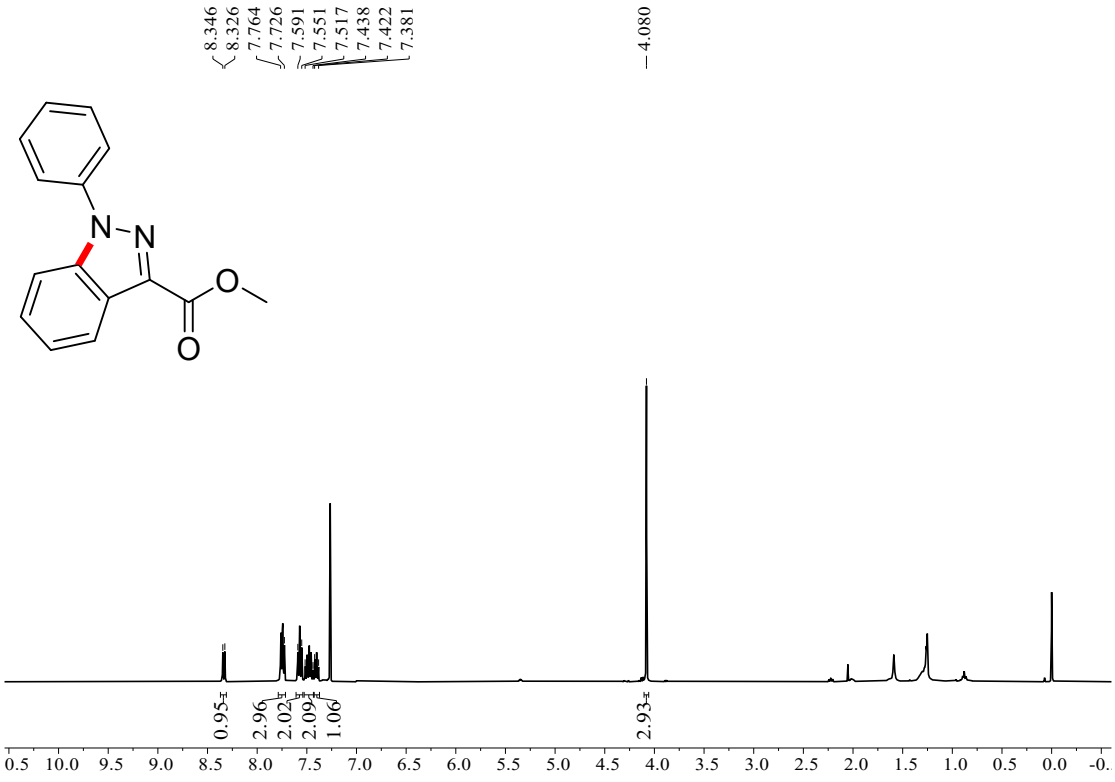
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2z



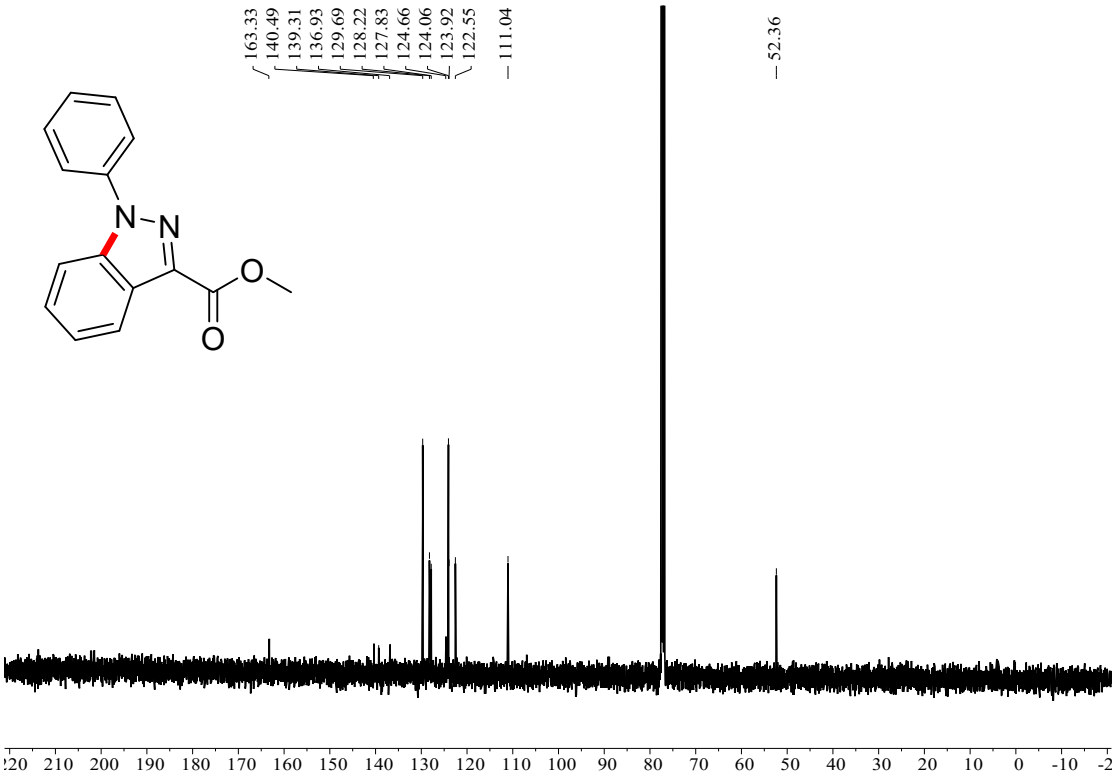
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2z



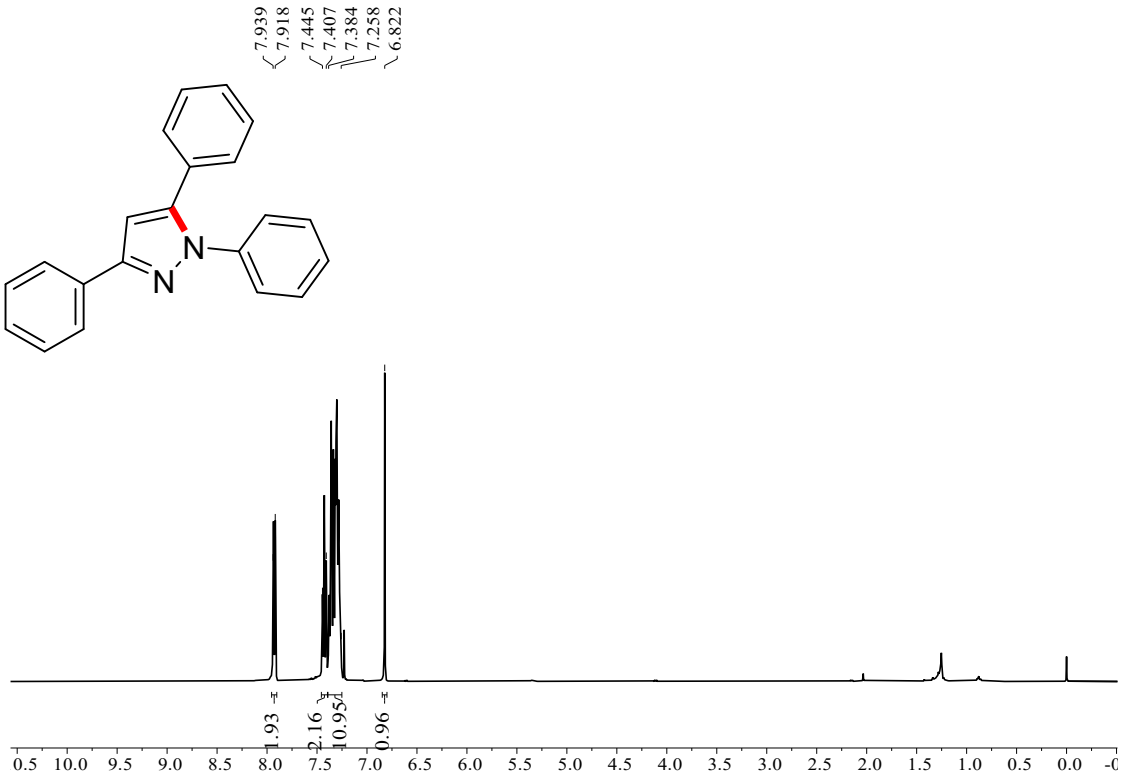
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a



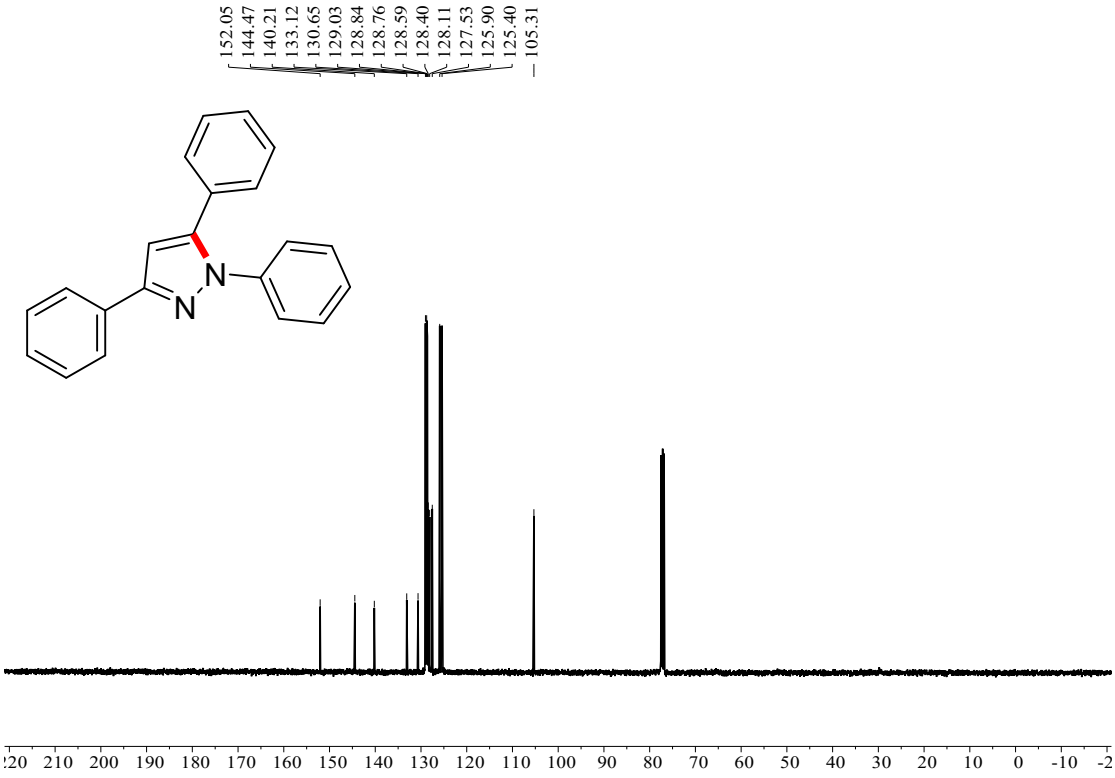
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3a



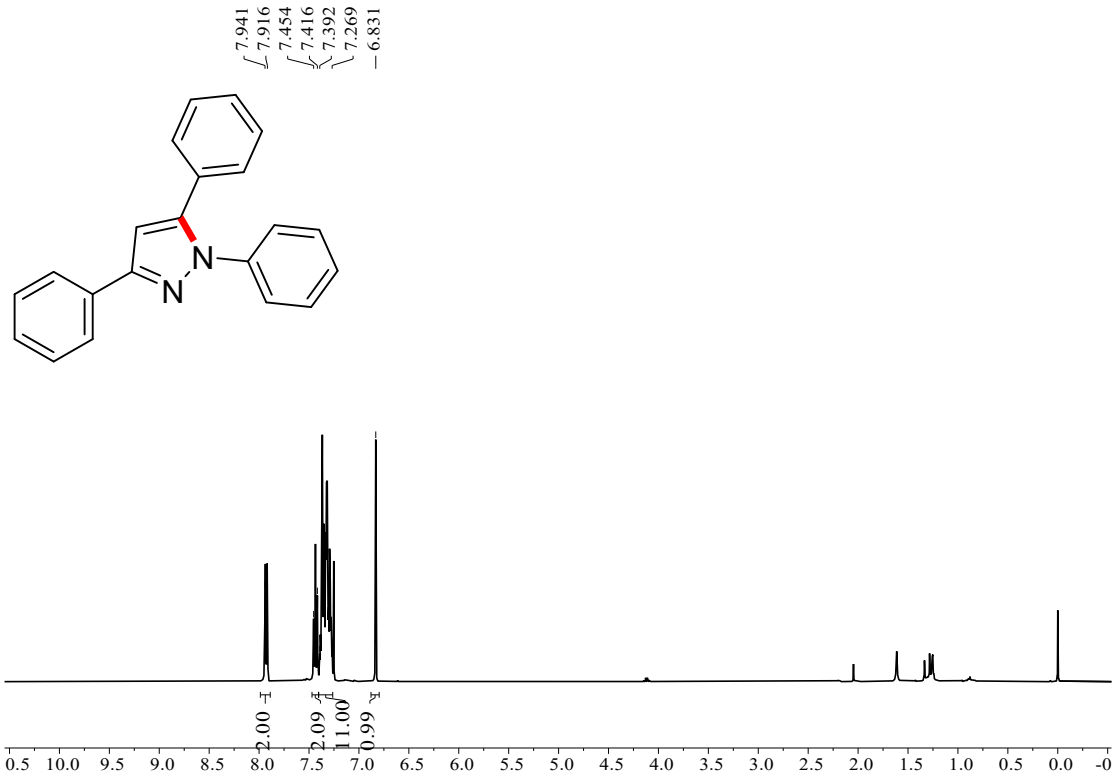
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3b



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



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3c