Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Visible Light-Induced C(sp^3)–H Azolation of Ethers *via* Radical-Polar Crossover

Cheng Huang,*[a,b] Yu-Shu Qin,[a,b] Chen-Lu Wang,[a] Peng Xiao,[a] Sheng Tang,[a] Hong-Jun Liu,[a] Zhenhong Wei[a], and Hu Cai*[a]

[a]School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi 330031, P. R. China.

[b]These authors contributed equally to this work.

*Corresponding Author(s): Cheng Huang: huangcheng@ncu.edu.cn; Hu Cai: caihu@ncu.edu.cn;

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1. General Information

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received. All ethers were distilled using standard literature procedures to remove radical inhibitors prior to use. ^{1}H NMR spectra were recorded using Agilent ProPulse AM-400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were recorded at 376 MHz using $CDCl_3$ as solvent. Mass spectra were recorded using an Agilent 7890-5975C spectrometer. EPR spectra were recorded by X Band on a Bruker E500 spectrometer. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products visualized by UV detection.

2. Reaction Setup

A homemade four-channel LEDs were employed as the irradiation apparatus (4 × 4 array, for each channel electrical input 3.2 V × 600 mA × 4 blue LEDs, 405 ± 10 nm, light intensity 200~600 mW/cm^2, CN204522959U), and Pyrex tubes were used as the reaction vessel. The distance from the LEDs to Pyrex tubes was less than 5 mm. No filter was used during irradiation. Low-temperature Pump was used to maintain 20 ~ 30 ℃ in reactor.

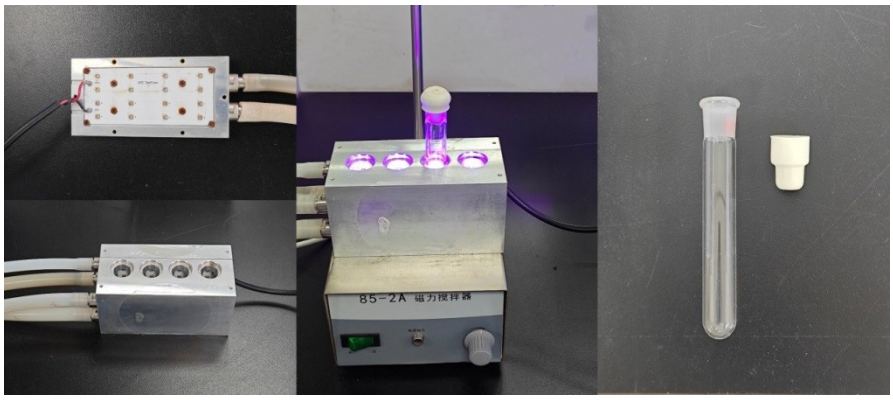
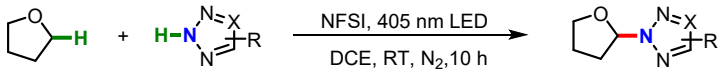


Figure S1. 405 nm Blue LED

3. General Experimental Procedure for C(sp^3)–H Azolation of Ethers



1a **2** **3**

A 10 mL reaction tube with magnetic stirring bar was charged with THF **1a** (12.5mmol, 125 equiv), azole **2** (0.1 mmol, 1.0 equiv), NFSI (0.2 mmol, 2.0 equiv) and 2.0 mL of 1,2-Dichloroethane. The reaction tube was sealed and the resulting mixed solution was strictly deaerated with N_2 for 30 minutes, then the solution was irradiated by blue LED (λ = 405 nm) at room temperature for 10 h. After reaction, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired product.

4. Radical Trapping Reactions

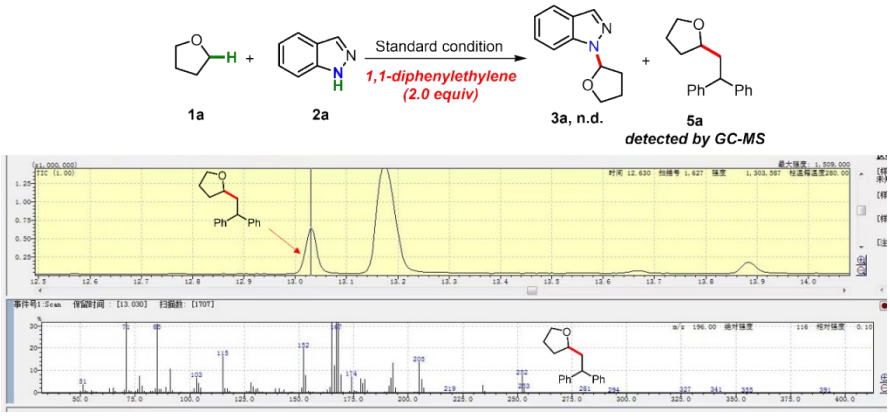
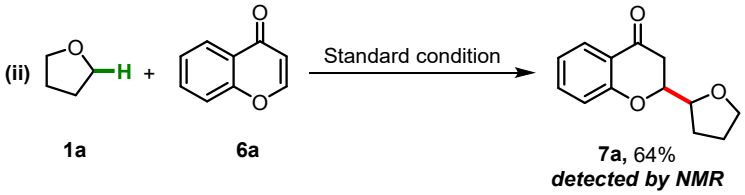


Figure S2 GC-MS of the crude reaction mixture



The 1:1 mixture of diastereomers **7a** was obtained: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.01 (td, J = 10.9, 5.9 Hz, 2H), 4.40 (M, 1H), 4.14 (M, 1H), 3.98 – 3.80 (m, 2H), 2.94 – 2.61 (m, 2H), 2.14 – 1.84 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1(1), 192.0(6), 161.3(7), 161.3(5), 136.0, 135.9, 126.9, 126.8, 121.3, 118.1, 118.0, 79.8, 79.6(8), 79.6(5), 79.5, 69.0, 68.9, 39.9, 39.1, 27.6, 27.5, 25.9, 25.7. HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{13}H_{15}O_3$ 219.1016; Found: 219.1016.

5. Electron Paramagnetic Resonance (EPR) Spectroscopy Experiments

EPR spectra were recorded by X Band on a Bruker E500 spectrometer. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.852 GHz. Typical spectrometer parameters are shown as follows, Center field set: 3510 G; Sweep width: 100G; Number of Points: 1024; Attenuation:10 dB; Modulation frequency: 100 kHz; Modulation Amplitude: 1.0 G; Conver Time :20.00 ms; Sweep Time: 20.48 s.

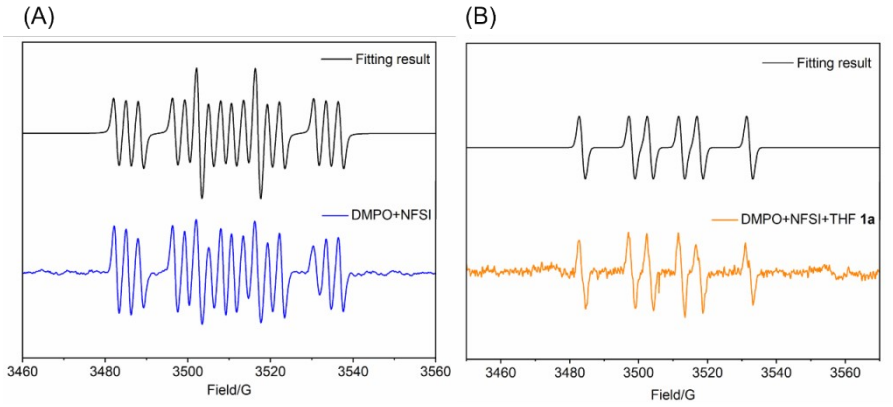


Figure S3. (A) A solution containing DMPO (0.2 M), NFSI (0.1 M), and CH_3CN was irradiated for 15 mins with 405 nm LED under N_2 atmosphere; (B) A solution containing DMPO (0.2 M), NFSI (0.1 M), CH_3CN, and THF (1 M) was irradiated for 15 mins with 405 nm LED under N_2 atmosphere.

6. Light on/ off Reaction

Eight parallel reaction mixtures in 10 mL reaction tube with magnetic stirring bar was charged with tetrahydrofuran **1a** (12.5mmol, 125 equiv), 3-phenyl-1*H*-pyrazole **2m** (0.1 mmol), NFSI (0.2 mmol, 2.0 equiv), and 2.0 mL of DCE. The reaction tube was sealed and the resulting mixed solution was strictly deaerated with N_2 for 30 minutes. These reaction tubes were labeled by **A, B, C, D, E, F, G,** and **H**.

The reaction **A** was irradiated by 405 nm LED for 1 h at room temperature. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product was determined by ^{1}H NMR spectroscopy and the product **3m** was obtained in 19% yield.

The reaction **B** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **B** was stirred in the absence of light for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product **3m** was determined by ^{1}H NMR spectroscopy and the product was obtained in 26% yield.

The reaction **C** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **C** was stirred in the absence of light for 1 h. Then, the reaction **C** was irradiated by 405 nm LED for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product was determined by ^{1}H NMR spectroscopy and the product **3m** was obtained in 40% yield.

The reaction **D** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **D** was stirred in the absence of light for 1 h. Then, the reaction **D** was irradiated by 405 nm LED for 1 h. Then, the reaction **D** was stirred in the absence of light for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product **3m** was determined by ^{1}H NMR spectroscopy and the product was obtained in 49% yield.

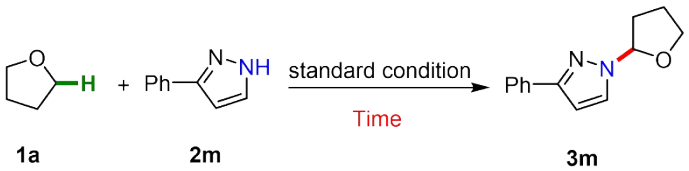
The reaction **E** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **E** was stirred in the absence of light for 1 h. Then, the reaction **E** was irradiated by 405 nm LED for 1 h. Then, the reaction **E** was stirred in the absence of light for 1 h. Then, the reaction **E** was irradiated by 405 nm LED for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product was determined by ^{1}H NMR spectroscopy and the product **3m** was obtained in 58% yield.

The reaction **F** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **F** was stirred in the absence of light for 1 h. Then, the reaction **F** was irradiated by 405 nm LED for 1 h. Then, the reaction **F** was stirred in the absence of light for 1 h. Then, the reaction **F** was irradiated by 405 nm LED for 1 h. Then, the reaction **F** was stirred in the absence of light for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product was determined by ^{1}H NMR spectroscopy and the product **3m** was obtained in 61% yield.

The reaction **G** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **G** was stirred in the absence of light for 1 h. Then, the reaction **G** was irradiated by

405 nm LED for 1 h. Then, the reaction **G** was stirred in the absence of light for 1 h. Then, the reaction **G** was irradiated by 405 nm LED for 1 h. Then, the reaction **G** was stirred in the absence of light for 1 h. Then, the reaction **G** was irradiated by 405 nm LED for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product was determined by ^{1}H NMR spectroscopy and the product **3m** was obtained in 78% yield.

The reaction **H** was irradiated by 405 nm LED for 1 h at room temperature. Then, the reaction **H** was stirred in the absence of light for 1 h. Then, the reaction **H** was irradiated by 405 nm LED for 1 h. Then, the reaction **H** was stirred in the absence of light for 1 h. Then, the reaction **H** was irradiated by 405 nm LED for 1 h. Then, the reaction **H** was stirred in the absence of light for 1 h. Then, the reaction **H** was irradiated by 405 nm LED for 1 h. Then, the reaction **H** was stirred in the absence of light for 1 h. After reaction, 0.1 mmol of diphenylacetonitrile as the internal standard was added into the mixture. Upon removal of solvent under vacuum, the yield of the desired product was determined by ^{1}H NMR spectroscopy and the product **3m** was obtained in 81% yield.



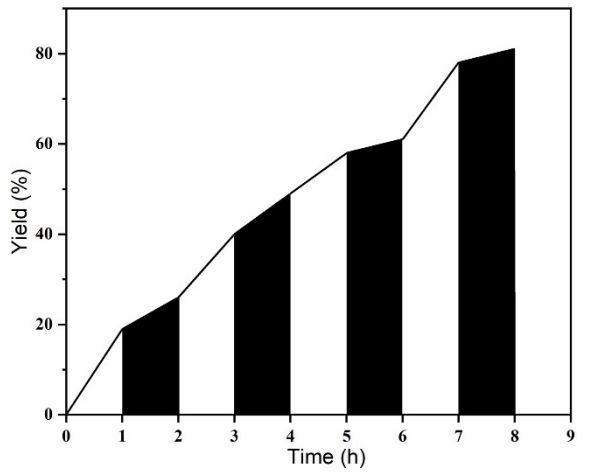


Figure S4. Profile of the reaction with the light on/off over time.

7. Continuous-Flow Reaction

A 10 mL reaction tube with magnetic stirring bar was charged with THF **1a** (25.0 mmol, 25 equiv), 3-phenyl-1*H*-pyrazole **2m** (1.0 mmol, 1.0 equiv), NFSI (630 mg, 2.0 equiv) and 4.0 mL of 1,2-Dichloroethane. The 6 mL mixture was swirled until homogeneous, placed in 10 mL disposable syringe and mounted on a syringe pump. The mixture liquid feed was pumped into the flow reactor under blue LED (λ = 405 nm) irradiation at room temperature for 10 h. After reaction, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired product **3m** in 84% yield.

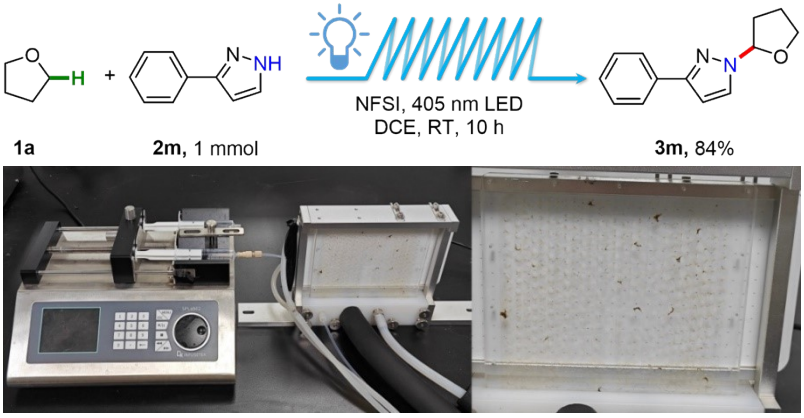
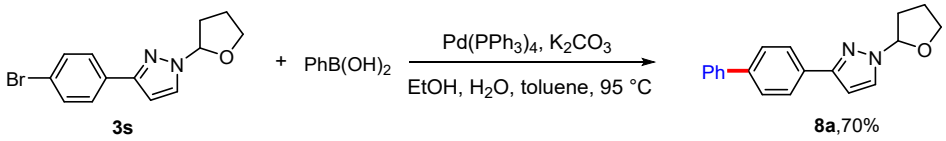
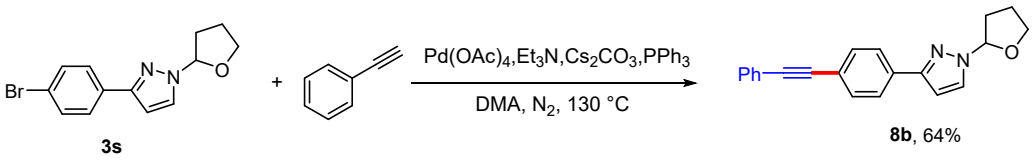


Figure S5. Continuous-Flow Reaction Setup

8. Experimental Procedure for Diversification



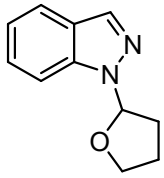
8a was prepared according to the modified literature methods.[1] In an oven-dried round bottom flask, 3-(4-Bromophenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole **3s** (88 mg, 0.3 mmol, 1.0 equiv) was taken in a mixture of 2.0 mL EtOH, 1 mL water and 3 mL toluene and degassed for 20 mins. To the resulting mixture, Phenylboronic acid (54.9 mg, 0.4 mmol, 1.5 equiv), K_2CO_3 (165 mg, 1.2 mmol, 4.0 equiv) and $Pd(PPh_3)_4$ (2.7 mg, 0.024 mmol, 0.8 mol%) were added successively at room temperature. The resulting mixture was stirred at 95 °C (oil bath) under positive argon pressure for 12 h. The reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, concentrated *in vacuo* to obtain a black oil which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to obtain 3-([1,1'-Biphenyl]-4-yl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole **8a** as a yellow oil.



8b was prepared according to the modified literature procedure.[2] 3-(4-Bromophenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole **3s** (0.5 mmol, 1.0 equiv), Phenylacetylene (0.75 mmol, 1.5 equiv), $Pd(OAc)_2$ (5.6 mg, 5 mol%), PPh_3 (52.5 mg, 0.4 equiv), Cs_2CO_3 (162.6 mg, 1.0 equiv) and Et_3N (1.0 mmol, 2.0 equiv) were added in an oven-dried 10mL test tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then DMA (4.0 mL) was added in the test tube via syringe. The resulting mixture was stirred at 130 °C (oil bath) under positive argon pressure for 3h. After cooling to room temperature, the solvent diluted with 10 mL ethyl acetate and washed with 5 mL brine and dried over anhydrous Na_2SO_4. After the solvent was evaporated *in vacuo*, the residues were purified by column chromatography, eluting with petroleum ether/ethyl acetate = 5:1 to afford **8b** as a yellow oil.

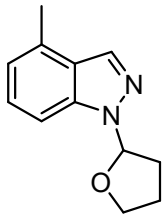
9. Characterization Data for All Compounds

1-(Tetrahydrofuran-2-yl)-1*H*-indazole (3a)



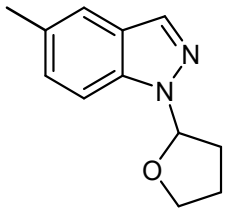
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 14.7 mg, yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.37 (d, J = 3.0 Hz, 1H), 4.07 – 3.94 (m, 2H), 2.98 – 2.88 (m, 1H), 2.46 – 2.34 (m, 2H), 2.16 – 2.03 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.0, 126.6, 124.7, 121.2, 121.0, 109.7, 86.9, 68.8, 30.3, 25.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O$ 189.1022; Found: 189.1022.

4-Methyl-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3b)



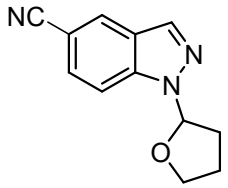
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 14.6 mg, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 6.94 (d, J = 7.0 Hz, 1H), 6.38 (dd, J = 6.5, 3.2 Hz, 1H), 4.08 – 3.96 (m, 2H), 2.98 – 2.90 (m, 1H), 2.60 (s, 3H), 2.47 – 2.34 (m, 2H), 2.16 – 2.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 132.7, 131.4, 126.7, 125.1, 121.1, 107.1, 87.0, 68.7, 30.2, 25.1, 18.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O$ 203.1179; Found: 203.1179.

5-Methyl-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3c)



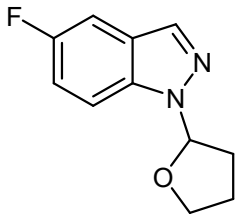
The compound was prepared according to the General procedure. Yellow oil R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 12.3 mg, yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.48 (d, J = 9.2 Hz, 2H), 7.22 (dd, J = 8.5, 1.4 Hz, 1H), 6.35 (dd, J = 6.7, 3.2 Hz, 1H), 4.05 – 3.94 (m, 2H), 2.96 – 2.87 (m, 1H), 2.44 (d, J = 5.1 Hz, 3H), 2.41 – 2.33 (m, 2H), 2.15 – 2.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 133.4, 130.6, 128.7, 125.1, 120.0, 109.4, 86.9, 68.7, 30.2, 25.1, 21.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O$ 203.1179; Found: 203.1178.

1-(Tetrahydrofuran-2-yl)-1*H*-indazole-5-carbonitrile (3d)



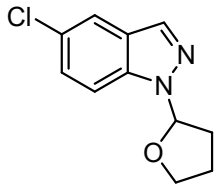
The compound was prepared according to the General procedure. Yellow oil R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 10.2 mg, yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.69 – 7.60 (m, 1H), 7.50 (dd, J = 8.7, 1.4 Hz, 1H), 6.31 (dd, J = 6.6, 2.8 Hz, 1H), 3.97 (dd, J = 9.9, 3.7 Hz, 2H), 2.92 – 2.81 (m, 1H), 2.42 – 2.25 (m, 2H), 2.15 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 134.6, 128.6, 127.4, 124.2, 119.6, 111.1, 104.6, 87.4, 69.1, 30.5, 24.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{12}N_3O$ 214.0975; Found: 214.0977.

5-Fluoro-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3e)



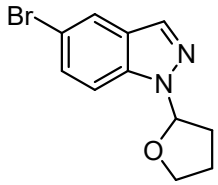
The compound was prepared according to the General procedure. Yellow oil R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 14.8 mg, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.54 (dd, J = 9.1, 4.1 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.16 (td, J = 9.0, 2.4 Hz, 1H), 6.33 (dd, J = 6.6, 3.1 Hz, 1H), 4.05 – 3.94 (m, 2H), 2.98 – 2.88 (m, 1H), 2.46 – 2.31 (m, 2H), 2.15 – 2.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (J_{C-F} = 239.4 Hz), 136.8, 133.5 (J_{C-F} = 6.1 Hz), 124.7 (J_{C-F} = 10.1Hz), 116.1 (J_{C-F} = 28.3Hz), 110.9 (J_{C-F} = 10.1 Hz), 105.0 (J_{C-F} = 24.2 Hz), 87.2, 68.8, 30.3, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.74 (td, J = 8.7, 4.1 Hz). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}FN_2O$ 207.0928; Found: 207.0930.

5-Chloro-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3f)



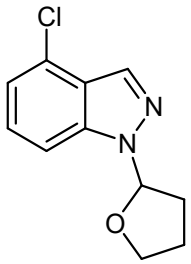
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 15.4 mg, yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.64 (s, 1H), 7.50 (d, J = 8.9 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 6.29 (d, J = 3.4 Hz, 1H), 3.98 (t, J = 6.8 Hz, 2H), 2.95 – 2.82 (m, 1H), 2.41 – 2.29 (m, 2H), 2.12 – 2.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 133.1, 127.2, 126.7, 125.5, 120.1, 110.9, 87.2, 68.8, 30.3, 24.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}ClN_2O$ 223.0633; Found: 223.0638.

5-Bromo-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3g)



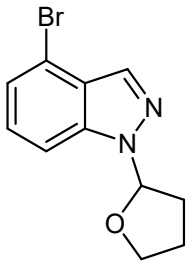
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 22.4 mg, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 (d, J = 0.7 Hz, 1H), 7.51 – 7.42 (m, 2H), 6.32 (dd, J = 6.4, 3.0 Hz, 1H), 4.00 (t, J = 6.6 Hz, 2H), 3.00 – 2.85 (m, 1H), 2.46 – 2.29 (m, 2H), 2.17 – 2.04 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 133.0, 129.6, 126.2, 123.4, 114.2, 111.2, 87.2, 68.8, 30.3, 24.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}BrN_2O$ 267.0128; Found: 267.0128.

4-Chloro-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3h)



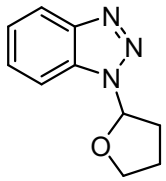
The compound was prepared according to the General procedure. Yellow oil R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 13.8 mg, yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.28 (dd, J = 13.8, 5.6 Hz, 1H), 7.13 (d, J = 7.4 Hz, 1H), 6.33 (dd, J = 6.5, 2.9 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.00 – 2.86 (m, 1H), 2.46 – 2.32 (m, 2H), 2.18 – 2.03 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 132.5, 127.2, 126.5, 124.0, 120.8, 108.5, 87.3, 68.9, 30.4, 24.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}ClN_2O$ 223.0633; Found: 223.0632.

4-Bromo-1-(tetrahydrofuran-2-yl)-1*H*-indazole (3i)



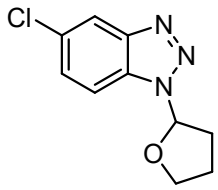
The compound was prepared according to the General procedure. Yellow oil R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 14.0 mg, yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 7.0 Hz, 1H), 7.20 (dd, J = 8.3, 7.5 Hz, 1H), 6.30 (dd, J = 6.6, 3.0 Hz, 1H), 4.07 – 3.91 (m, 2H), 2.98 – 2.85 (m, 1H), 2.45 – 2.30 (m, 2H), 2.16 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 133.9, 127.4, 125.7, 124.0, 114.5, 109.0, 87.4, 68.9, 30.4, 24.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}BrN_2O$ 267.0128; Found: 267.0130.

1-(Tetrahydrofuran-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (3j)



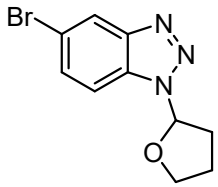
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 14.3 mg, yield 76%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 6.71 (dd, J = 7.0, 2.7 Hz, 1H), 4.03 – 3.89 (m, 2H), 2.84 – 2.74 (m, 1H), 2.51 (d, J = 7.6 Hz, 1H), 2.30 – 2.22 (m, 1H), 2.15 – 2.03 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.9, 132.9, 128.1, 124.8, 119.7, 111.5, 87.5, 69.2, 30.9, 24.8. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{10}H_{12}N_3O$ 190.0975; Found: 190.0975.

5-Chloro-1-(tetrahydrofuran-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (3k)



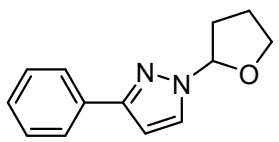
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 15.0 mg, yield 67%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 6.6 Hz, 1H), 3.97 – 3.89 (m, 2H), 2.81 – 2.73 (m, 1H), 2.48 (d, J = 13.3 Hz, 1H), 2.27 – 2.18 (m, 1H), 2.14 – 2.04 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.5, 131.7, 129.3, 128.6, 118.9, 113.15, 87.9, 69.3, 31.0, 24.6. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{10}H_{11}ClN_3O$ 224.0585; Found: 224.0585.

5-Bromo-1-(tetrahydrofuran-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (3l)



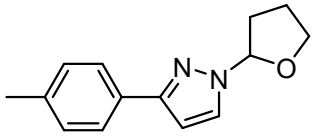
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 18.7 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.43 (d, J = 9.0 Hz, 1H), 6.57 – 6.50 (m, 1H), 4.30 (dd, J = 13.9, 7.7 Hz, 1H), 4.12 (dd, J = 14.4, 7.1 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.55 – 2.39 (m, 2H), 2.19 – 2.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 142.9, 130.5, 120.9, 120.3, 119.9, 94.4, 70.4, 32.4, 24.2. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{10}H_{11}BrN_3O$ 268.0080; Found: 268.0080.

3-Phenyl-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3m)



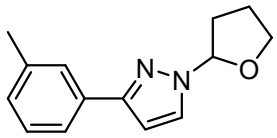
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 19.2 mg, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 2.3 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.34 – 7.25 (m, 1H), 6.58 (d, J = 2.2 Hz, 1H), 6.03 (dd, J = 6.6, 2.5 Hz, 1H), 4.25 – 4.13 (m, 1H), 4.07 – 3.96 (m, 1H), 2.73 – 2.62 (m, 1H), 2.42 – 2.29 (m, 1H), 2.28 – 2.16 (m, 1H), 2.12 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 133.6, 129.1, 128.5, 127.6, 125.7, 102.9, 90.2, 69.3, 31.9, 24.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O$ 215.1179; Found: 215.1182.

1-(Tetrahydrofuran-2-yl)-3-(*p*-tolyl)-1*H*-pyrazole (3n)



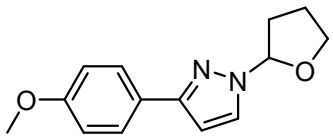
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 18.0 mg, yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 2.3 Hz, 1H), 7.22 – 7.17 (m, 2H), 6.54 (d, J = 2.2 Hz, 1H), 6.02 (dd, J = 6.6, 2.5 Hz, 1H), 4.22 – 4.14 (m, 1H), 4.05 – 3.97 (m, 1H), 2.73 – 2.62 (m, 1H), 2.37 (s, 3H), 2.36 – 2.28 (m, 1H), 2.27 – 2.17 (m, 1H), 2.09 – 1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 137.3, 129.2, 129.0, 125.5(9), 125.5(8), 102. 7, 90.2, 69.3, 31.9, 24.4, 21.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}N_2O$ 229.1335; Found: 229.1340.

1-(Tetrahydrofuran-2-yl)-3-(*m*-tolyl)-1*H*-pyrazole (3o)



The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 17.8 mg, yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.63 – 7.56 (m, 2H), 7.32 – 7.25 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.56 (d, J = 2.4 Hz, 1H), 6.03 (dd, J = 6.6, 2.5 Hz, 1H), 4.22 – 4.15 (m, 1H), 4.05 – 3.98 (m, 1H), 2.72 – 2.62 (m, 1H), 2.40 (s, 3H), 2.37 – 2.29 (m, 1H), 2.28 – 2.18 (m, 1H), 2.10 – 2.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 138.1, 133.5, 129.0, 128.4(1), 128.3(8), 126.3, 122.9, 102.9, 90.3, 69.3, 32.0, 24.3, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}N_2O$ 229.1335; Found: 229.1341.

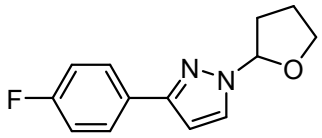
3-(4-Methoxyphenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3p)



The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 21.2 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.5 Hz, 2H), 7.53 (s, 1H), 6.91 (d, J = 8.5 Hz, 2H), 6.47 (s, 1H), 6.03 – 5.94 (m, 1H), 4.15 (dd, J = 13.7, 7.8 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.81 (s, 3H), 2.67 – 2.59 (m, 1H), 2.38 – 2.26 (m, 1H), 2.24 – 2.14 (m, 1H), 2.06 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3,

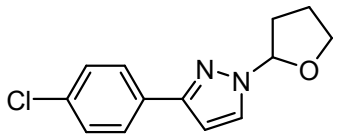
151.75, 129.1, 127.0, 126.4, 114.0, 102.4, 90.2, 69.3, 55.3, 31.9, 24.4. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{17}N_2O_2$ 245.1285; Found: 245.1287.

3-(4-Fluorophenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3q)



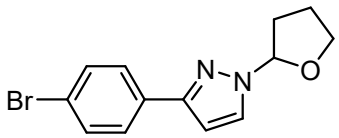
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 19.4 mg, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.52 (s, 1H), 6.01 (dd, *J* = 6.6, 2.6 Hz, 1H), 4.21 – 4.13 (m, 1H), 4.04 – 3.97 (m, 1H), 2.70 – 2.62 (m, 1H), 2.38 – 2.30 (m, 1H), 2.26 – 2.18 (m, 1H), 2.10 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (J_{C-F} = 247.5 Hz),157.7 (J_{C-F} =100.0 Hz), 151.0, 129.3, 127.3 (J_{C-F} = 8.1 Hz), 115.4 (J_{C-F} = 21.2 Hz), 102.7, 90.2, 69.3, 31.9, 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.65 – -115.07 (m). HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{14}FN_2O$ 233.1085; Found: 233.1085.

3-(4-Chlorophenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3r)



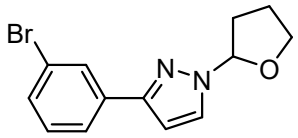
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 21.8 mg, yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.01 (dd, *J* = 6.6, 2.6 Hz, 1H), 4.20 – 4.14 (m, 1H), 4.04 – 3.98 (m, 1H), 2.68 – 2.61 (m, 1H), 2.39 – 2.31 (m, 1H), 2.26 – 2.17 (m, 1H), 2.09 – 2.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 133.3, 132.2, 129.3, 128.7, 126.9, 102.8, 90.3, 69.3, 31.9, 24.3. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{14}ClN_2O$ 249.0789; Found: 249.0789.

3-(4-Bromophenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3s)



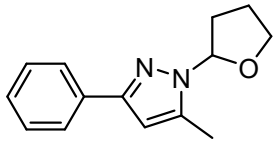
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 24.2 mg, yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 6.52 (d, *J* = 1.8 Hz, 1H), 5.99 (d, *J* = 6.4 Hz, 1H), 4.15 (dd, *J* = 13.6, 7.9 Hz, 1H), 4.04 – 3.94 (m, 1H), 2.68 – 2.59 (m, 1H), 2.39 – 2.28 (m, 1H), 2.24 – 2.15 (m, 1H), 2.10 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 132.6, 131.7, 129.4, 127.3, 121.5, 102.9, 90.3, 69.4, 32.0, 24.4. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{14}BrN_2O$ 293.0284; Found: 293.0284.

3-(3-Bromophenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3t)



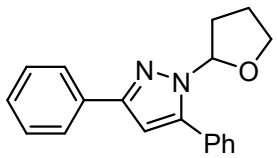
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 25.1 mg, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 2.3 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.29 – 7.18 (m, 1H), 6.55 (d, J = 2.3 Hz, 1H), 6.01 (dd, J = 6.6, 2.4 Hz, 1H), 4.17 (td, J = 8.0, 5.5 Hz, 1H), 4.01 (dd, J = 15.1, 7.4 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.41 – 2.29 (m, 1H), 2.29 – 2.16 (m, 1H), 2.12 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 135.7, 130.4, 130.1, 129.4, 128.6, 124.2, 122.7, 103.0, 90.3, 69.3, 31.9, 24.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}BrN_2O$ 293.0284; Found: 293.0284.

5-Methyl-3-phenyl-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3u)



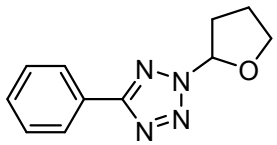
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 19.2 mg, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.38 (dd, J = 10.2, 5.1 Hz, 2H), 7.32 – 7.25 (m, 1H), 6.34 (s, 1H), 5.98 (dd, J = 7.0, 2.8 Hz, 1H), 4.10 (dd, J = 14.8, 7.3 Hz, 1H), 3.97 (dd, J = 7.6, 6.1 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.54 – 2.46 (m, 1H), 2.42 (d, J = 14.3 Hz, 3H), 2.34 – 2.25 (m, 1H), 2.11 – 2.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 140.3, 133.9, 128.4, 127.4, 125.6, 103.4, 86.3, 68.7, 30.3, 25.2, 11.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}N_2O$ 229.1335; Found: 229.1335.

3,5-Diphenyl-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3v)



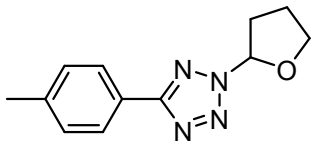
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 15.6 mg, yield 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.3 Hz, 2H), 7.62 (d, J = 7.0 Hz, 2H), 7.52 – 7.37 (m, 5H), 7.32 (t, J = 7.3 Hz, 1H), 6.63 (s, 1H), 6.00 (dd, J = 7.2, 2.7 Hz, 1H), 4.29 (dd, J = 14.4, 7.6 Hz, 1H), 4.01 (dd, J = 13.9, 7.5 Hz, 1H), 2.92 – 2.77 (m, 1H), 2.69 – 2.55 (m, 1H), 2.33 – 2.17 (m, 1H), 2.14 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 145.7, 133.6, 129.3, 128.7, 128.6, 128.5, 127.7, 125.7, 103.6, 86.6, 69.1, 31.0, 25.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O$ 291.1492; Found: 291.1492.

5-Phenyl-2-(tetrahydrofuran-2-yl)-2*H*-tetrazole (3w)



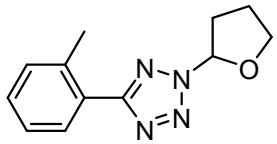
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 18.1 mg, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 2H), 7.47 (dd, *J* = 4.4, 1.4 Hz, 3H), 6.59 – 6.55 (m, 1H), 4.31 – 4.23 (m, 1H), 4.13 (dd, *J* = 14.3, 7.1 Hz, 1H), 2.76 – 2.64 (m, 1H), 2.56 – 2.44 (m, 2H), 2.22 – 2.10 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 130.3, 128.8, 127.4, 126.9, 91.6, 70.2, 31.8, 24.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_4O$ 217.1084; Found: 217.1084.

2-(Tetrahydrofuran-2-yl)-5-(*p*-tolyl)-2*H*-tetrazole (3x)



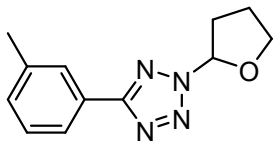
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 20.7 mg, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.55 (dd, *J* = 6.4, 2.1 Hz, 1H), 4.31 – 4.24 (m, 1H), 4.12 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.54 – 2.45 (m, 2H), 2.40 (s, 3H), 2.19 – 2.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 140.5, 129.5, 126.8, 124.6, 91.6, 70.2, 31.8, 24.0, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_4O$ 231.1240; Found: 231.1240.

2-(Tetrahydrofuran-2-yl)-5-(*o*-tolyl)-2*H*-tetrazole (3y)



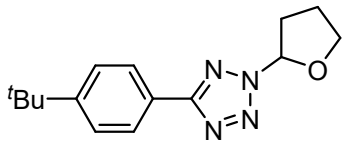
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 18.6 mg, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.27 (m, 3H), 6.60 (dd, *J* = 6.2, 1.6 Hz, 1H), 4.32 – 4.24 (m, 1H), 4.18 – 4.09 (m, 1H), 2.72 – 2.66 (m, 1H), 2.63 (s, 3H), 2.54 – 2.47 (m, 2H), 2.23 – 2.10 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 137.4, 131.3, 129.9, 129.5, 126.4, 126.0, 91.5, 70.2, 31.9, 24.0, 21.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_4O$ 231.1240; Found: 231.1240.

2-(Tetrahydrofuran-2-yl)-5-(*m*-tolyl)-2*H*-tetrazole (3z)



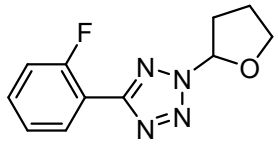
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 20.8 mg, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 6.56 (dd, *J* = 6.4, 2.0 Hz, 1H), 4.32 – 4.22 (m, 1H), 4.18 – 4.10 (m, 1H), 2.73 – 2.65 (m, 1H), 2.55 – 2.46 (m, 2H), 2.42 (s, 3H), 2.22 – 2.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 138.6, 131.1, 128.7, 127.5, 127.2, 124.0, 91.6, 70.2, 31.8, 24.0, 21.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_4O$ 231.1240; Found: 231.1240.

5-(4-(*tert*-butyl)Phenyl)-2-(tetrahydrofuran-2-yl)-2*H*-tetrazole (3aa)



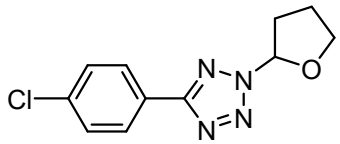
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 24.2 mg, yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.54 – 7.48 (m, 2H), 6.56 (dd, J = 6.5, 2.1 Hz, 1H), 4.33 – 4.21 (m, 1H), 4.17 – 4.07 (m, 1H), 2.76 – 2.62 (m, 1H), 2.57 – 2.41 (m, 2H), 2.23 – 2.08 (m, 1H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 153.6, 126.7, 125.8, 91.6, 70.2, 34.9, 31.8, 31.2, 24.0. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{21}N_4O$ 273.1710; Found: 273.1710.

5-(2-Fluorophenyl)-2-(tetrahydrofuran-2-yl)-2*H*-tetrazole (3ab)



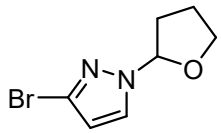
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 19.7 mg, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (td, J = 7.6, 1.6 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.32 – 7.19 (m, 2H), 6.62 (dd, J = 6.3, 1.8 Hz, 1H), 4.34 – 4.26 (m, 1H), 4.15 (dd, J = 14.5, 8.0 Hz, 1H), 2.77 – 2.66 (m, 1H), 2.61 – 2.45 (m, 2H), 2.25 – 2.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (J_{C-F} = 256.5 Hz), 131.9 (J_{C-F} = 8.08 Hz), 130.0 (J_{C-F} = 3.0 Hz), 124.4 (J_{C-F} = 4.0 Hz), 116.6 (J_{C-F} = 21.2 Hz), 115.6 (J_{C-F} = 12.1 Hz), 91.9, 70.3, 31.9, 24.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.60 – -111.69 (m). HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{11}H_{12}FN_4O$ 235.0990; Found: 235.0990.

5-(4-Chlorophenyl)-2-(tetrahydrofuran-2-yl)-2*H*-tetrazole (3ac)



The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 23.2 mg, yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 6.56 (d, J = 5.4 Hz, 1H), 4.26 (dd, J = 13.9, 7.7 Hz, 1H), 4.13 (dd, J = 14.6, 7.5 Hz, 1H), 2.77 – 2.61 (m, 1H), 2.57 – 2.41 (m, 2H), 2.21 – 2.10 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 136.4, 129.1, 128.2, 125.9, 91.8, 70.2, 31.8, 24.0. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{11}H_{12}ClN_4O$ 251.0694; Found: 251.0694.

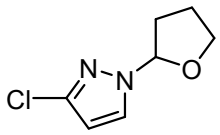
4-Bromo-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3ad)



The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 19.4 mg, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.46 (s, 1H), 5.94 – 5.87 (m, 1H), 4.07 (dd, J = 13.7, 7.9 Hz, 1H), 3.95 (q, J = 7.5 Hz, 1H),

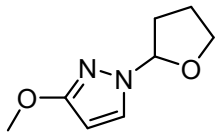
2.58 – 2.50 (m, 1H), 2.33 – 2.22 (m, 1H), 2.15 – 2.05 (m, 1H), 2.04 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 128.1, 93.4, 90.6, 69.4, 31.6, 24.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_7H_{10}BrN_2O$ 216.9971; Found: 216.9966.

4-Chloro-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3ae)



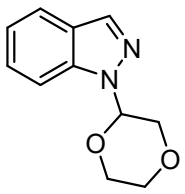
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 14.6 mg, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.43 (s, 1H), 5.92 – 5.85 (m, 1H), 4.12 – 4.04 (m, 1H), 3.96 (q, *J* = 7.5 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.32 – 2.22 (m, 1H), 2.15 – 2.05 (m, 1H), 2.04 – 1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 125.9, 110.2, 90.6, 69.3, 31.6, 24.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_7H_{10}ClN_2O$ 173.0476; Found: 173.0474.

4-Methoxy-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (3af)



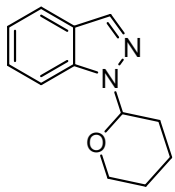
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 14.5 mg, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.20 (s, 1H), 5.85 (dd, *J* = 6.7, 2.8 Hz, 1H), 4.04 (dd, *J* = 14.1, 7.8 Hz, 1H), 3.94 (dd, *J* = 14.7, 7.4 Hz, 1H), 3.72 (s, 3H), 2.62 – 2.53 (m, 1H), 2.32 – 2.21 (m, 1H), 2.19 – 2.08 (m, 1H), 2.05 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1 127.6, 112.5, 90.4, 69.0, 58.8, 31.0, 24.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_8H_{13}N_2O_2$ 169.0972; Found: 169.0970.

1-(1,4-Dioxan-2-yl)-1*H*-indazole (3ag)



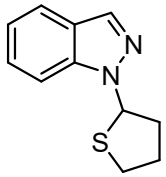
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 12.5 mg, yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 5.73 (dd, *J* = 9.4, 2.3 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.82 – 3.69 (m, 1H), 2.66 – 2.52 (m, 1H), 2.16 – 2.07 (m, 1H), 1.79 – 1.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 133.9, 126.5, 121.2, 121.0, 110.0, 85.3, 67.5, 29.4, 25.1, 22.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_2$ 205.0972; Found: 205.0972.

1-(Tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (3ah)



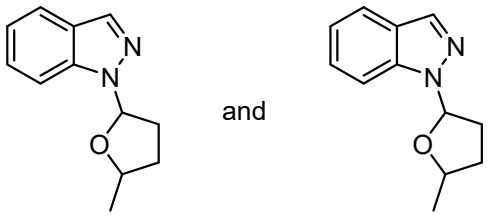
The compound was prepared according to the General procedure. Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 9.2 mg, yield 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 6.7 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 5.80 – 5.65 (m, 1H), 4.02 (d, J = 10.1 Hz, 1H), 3.78 – 3.68 (m, 1H), 2.65 – 2.52 (m, 1H), 2.18 – 2.03 (m, 2H), 1.83 – 1.70 (m, 2H), 1.65 (d, J = 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 134.0, 126.6, 124.7, 121.3, 121.1, 110.1, 85.3, 67.6, 29.5, 25.2, 22.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O$ 203.1179; Found: 203.1179.

1-(Tetrahydrothiophen-2-yl)-1*H*-indazole (3ai)



The compound was prepared according to the General procedure. Yellow oil R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 10.8 mg, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.35 (dd, J = 6.8, 4.2 Hz, 1H), 3.34 – 3.26 (m, 1H), 3.06 – 2.98 (m, 1H), 2.87 – 2.79 (m, 1H), 2.67 – 2.56 (m, 1H), 2.45 – 2.35 (m, 1H), 2.29 – 2.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 134.0, 126.3, 124.6, 121.2, 121.0, 109.5, 65.6, 36.8, 33.8, 30.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2S$ 205.0794; Found: 205.0790.

1-(5-Methyltetrahydrofuran-2-yl)-1*H*-indazole (3aj)



diastereoisomer 1 diastereoisomer 2

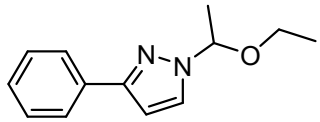
A 1:1 mixture of diastereomers **3aj** (the title compounds) was obtained according to the General procedure. 12.5 mg, combined yield 62%.

Diastereoisomer 1: Colorless oil R_f = 0.7 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.37 (dd, J = 9.8, 5.4 Hz, 1H), 7.19 – 7.11 (m, 1H), 6.42 (dd, J = 6.6, 3.6 Hz, 1H), 4.40 – 4.27 (m, 1H), 3.06 – 2.94 (m, 1H), 2.54 – 2.39 (m, 2H), 1.74 – 1.60 (m, 1H), 1.33 – 1.21 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 133.9, 126.6, 124.7, 121.1, 121.0, 109.7, 86.7, 76.1, 32.8, 30.4, 20.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O$ 203.1179; Found: 203.1177.

Diastereoisomer 2: Yellow oil R_f = 0.6 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, CDCl3) δ 8.01 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.36 (t, J = 7.4 Hz,

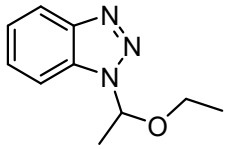
1H), 7.14 (t, J = 7.4 Hz, 1H), 6.30 (d, J = 6.9 Hz, 1H), 4.32 – 4.21 (m, 1H), 2.94 – 2.82 (m, 1H), 2.41 (t, J = 15.4 Hz, 1H), 2.18 (s, 1H), 2.13 – 2.03 (m, 1H), 1.24 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 139.9, 134.0, 126.5, 124.6, 121.1, 121.0, 109.7, 86.8, 77.4, 32.5, 31.4, 21.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O$ 203.1179; Found: 203.1177.

1-(1-Ethoxyethyl)-3-phenyl-1*H*-pyrazole (3ak)



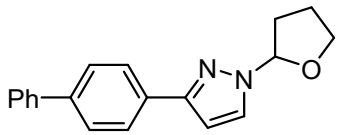
The compound was prepared according to the General procedure. Colorless oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 11.6 mg, yield 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 1.5 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.29 (dd, J = 15.3, 8.1 Hz, 1H), 6.64 (d, J = 1.4 Hz, 1H), 5.58 (q, J = 6.0 Hz, 1H), 3.56 – 3.47 (m, 1H), 3.45 – 3.36 (m, 1H), 1.71 (d, J = 6.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 133.5, 128.6, 127.6, 127.2, 125.7, 103.7, 87.6, 64.1, 22.2, 14.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O$ 217.1335; Found: 217.1337.

1-(1-Ethoxyethyl)-1*H*-benzo[*d*][1,2,3]triazole (3al)



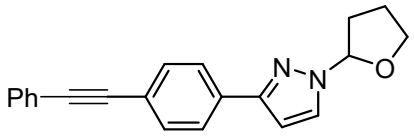
The compound was prepared according to the General procedure. Colorless oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 9.2 mg, yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, J = 8.8 Hz, 1H), 7.80 (t, J = 8.7 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.43 – 7.35 (m, 1H), 6.34 – 6.21 (m, 1H), 3.59 – 3.47 (m, 1H), 3.32 – 3.20 (m, 1H), 1.94 – 1.81 (m, 3H), 1.20 – 1.06 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 131.1, 127.4, 124.2, 120.1, 111.2, 87.1, 64.4, 21.2, 14.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{14}N_3O$ 192.1131; Found: 192.1133.

3-([1,1'-Biphenyl]-4-yl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (8a)



Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 20.3 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.65 (d, J = 8.3 Hz, 4H), 7.59 (d, J = 2.4 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.32 (m, 1H), 6.61 (d, J = 2.4 Hz, 1H), 6.04 (dd, J = 6.6, 2.5 Hz, 1H), 4.26 – 4.16 (m, 1H), 4.10 – 3.97 (m, 1H), 2.75 – 2.64 (m, 1H), 2.41 – 2.31 (m, 1H), 2.30 – 2.20 (m, 1H), 2.13 – 1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 140.9, 140.3, 132.7, 129.3, 128.8, 127.3, 127.0, 126.1, 103.0, 90.3, 69.4, 32.0, 24.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O$ 291.1492; Found: 291.1493.

3-(4-(Phenylethynyl)phenyl)-1-(tetrahydrofuran-2-yl)-1*H*-pyrazole (8b)

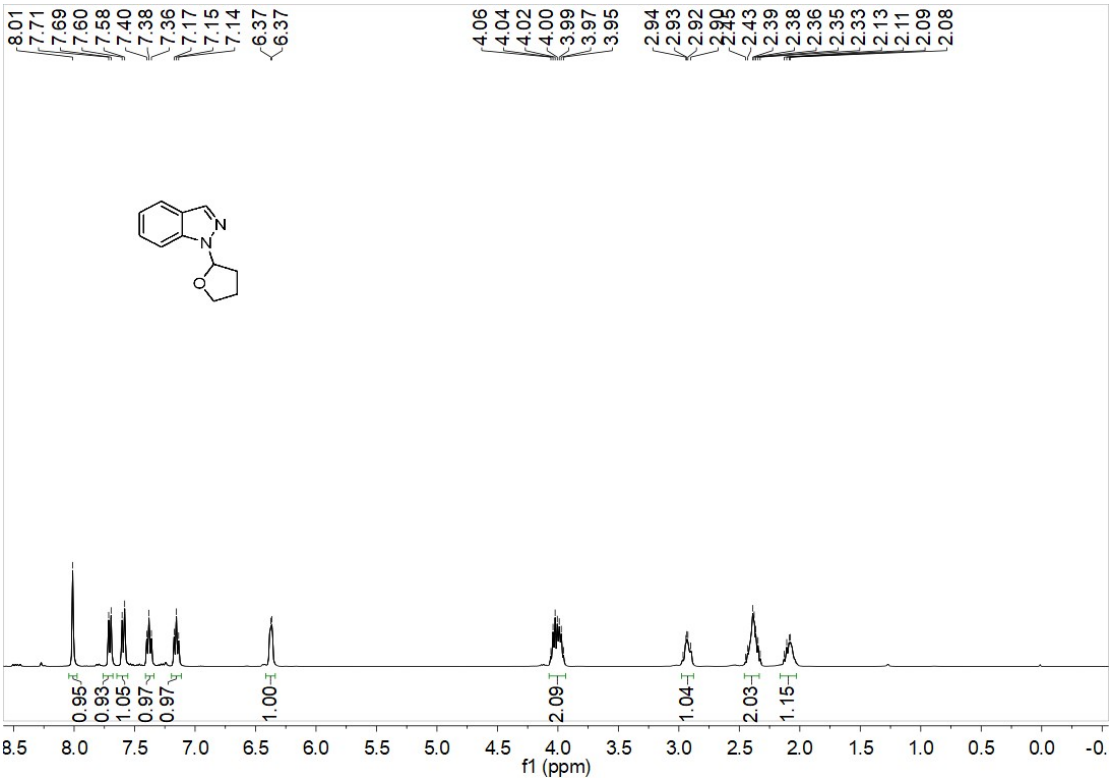


Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate 4:1); 20.1 mg, yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 2H), 7.59 – 7.50 (m, 5H), 7.38 – 7.29 (m, 3H), 6.57 (d, J = 2.4 Hz, 1H), 6.00 (dd, J = 6.6, 2.5 Hz, 1H), 4.19 – 4.12 (m, 1H), 3.99 (dd, J = 15.1, 7.4 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.38 – 2.27 (m, 1H), 2.26 – 2.14 (m, 1H), 2.07 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 133.5, 131.8, 131.6, 129.3, 128.3, 128.2, 125.5, 123.3, 122.2, 103.1, 90.3, 89.9, 89.6, 69.3, 31.9, 24.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O$ 315.1492; Found: 315.1495.

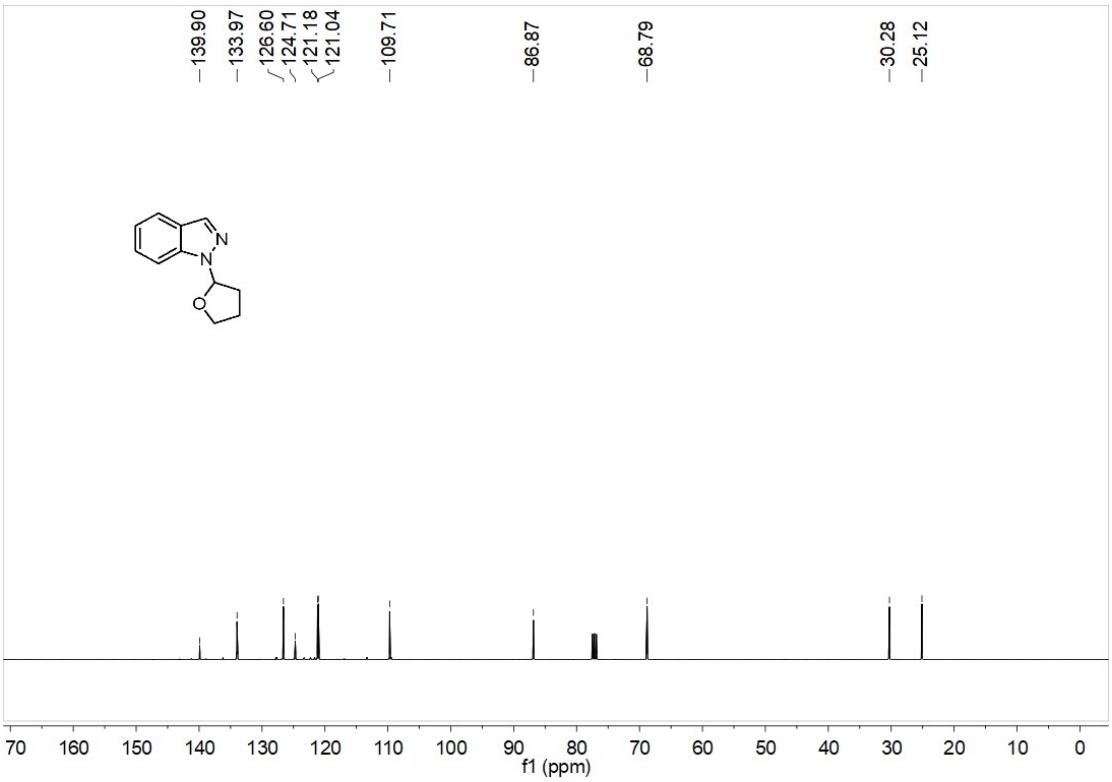
10. References

1. A. Ray Choudhury and S. Mukherjee, *Chem. Sci.*, 2016, **7**, 6940-6945.
2. S. Batsyts, E. G. Hübner, J. C. Namyslo, M. Gjikaj and A. Schmidt, *Org. Biomol. Chem.*, 2019, **17**, 4102-4114.

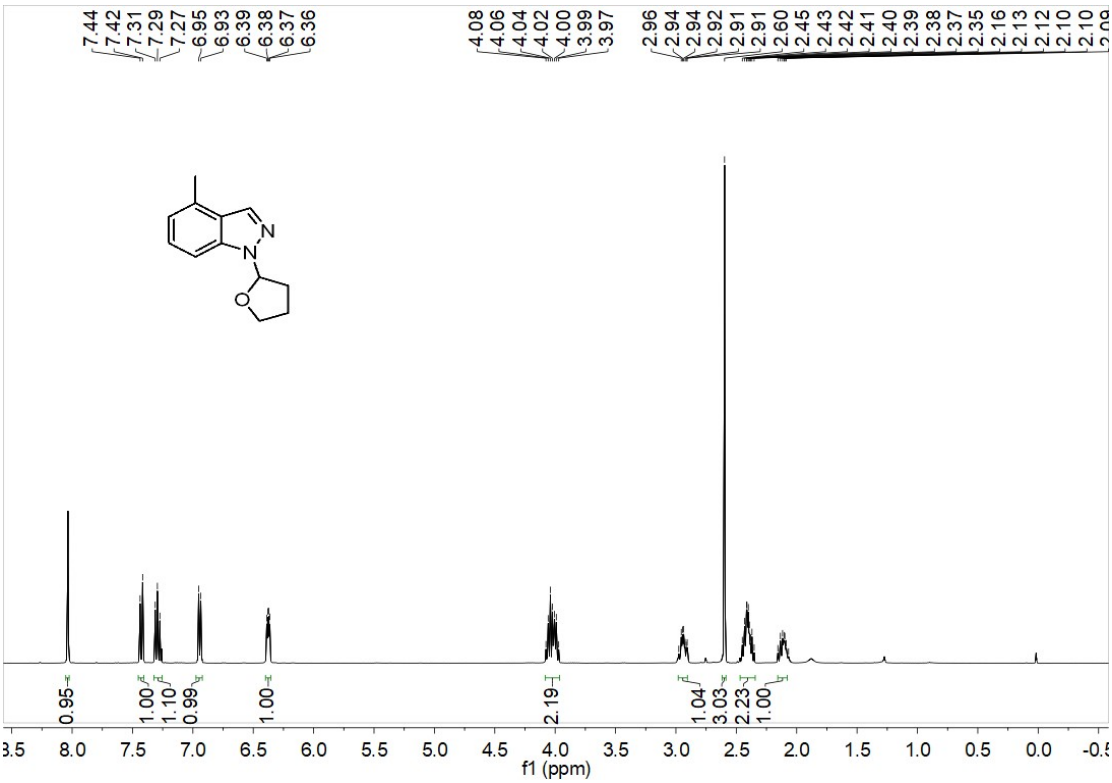
11. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR



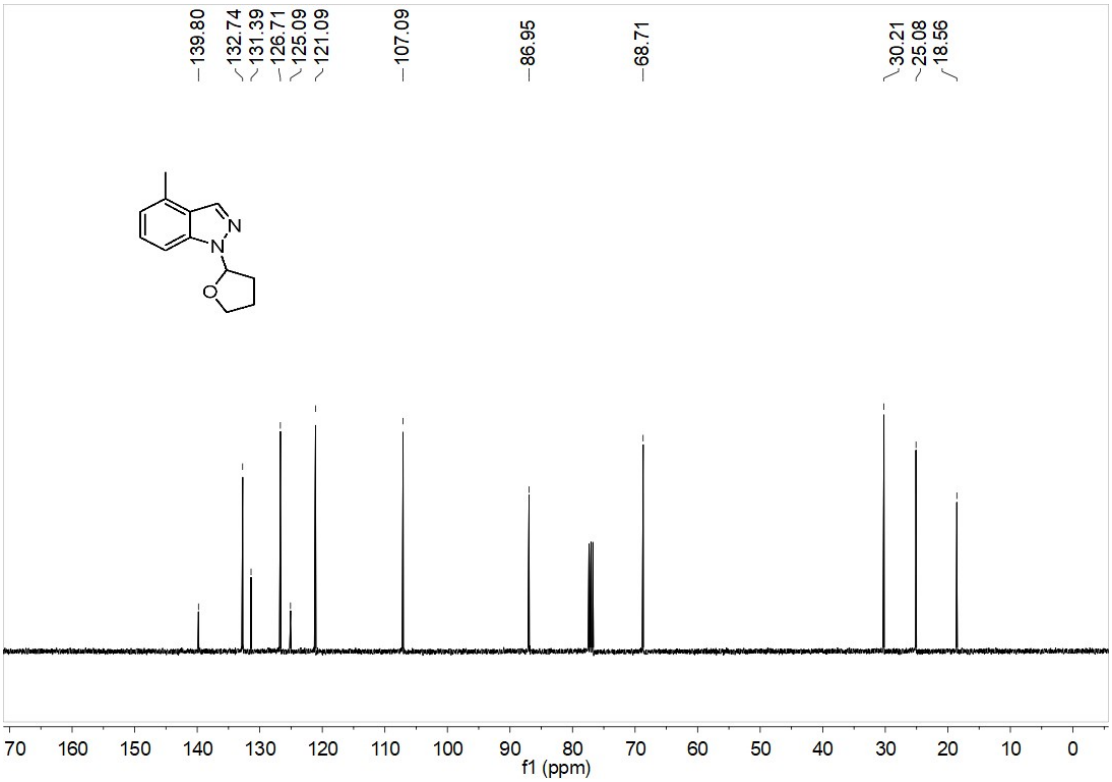
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



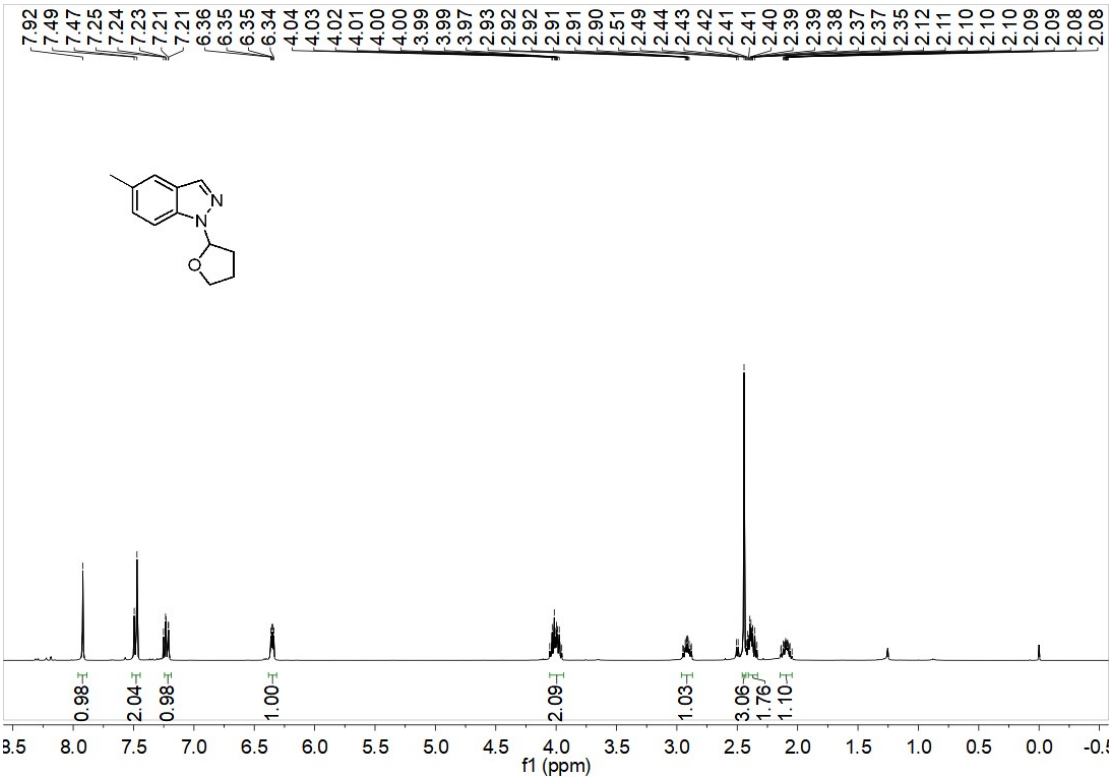
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



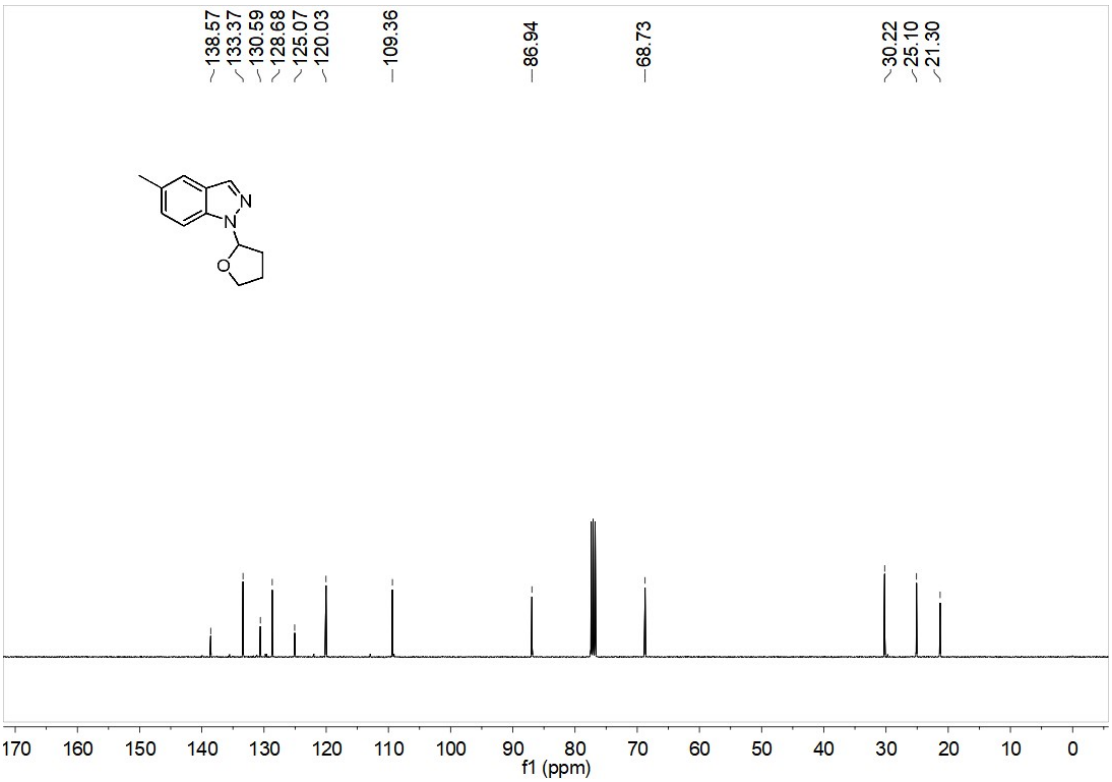
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



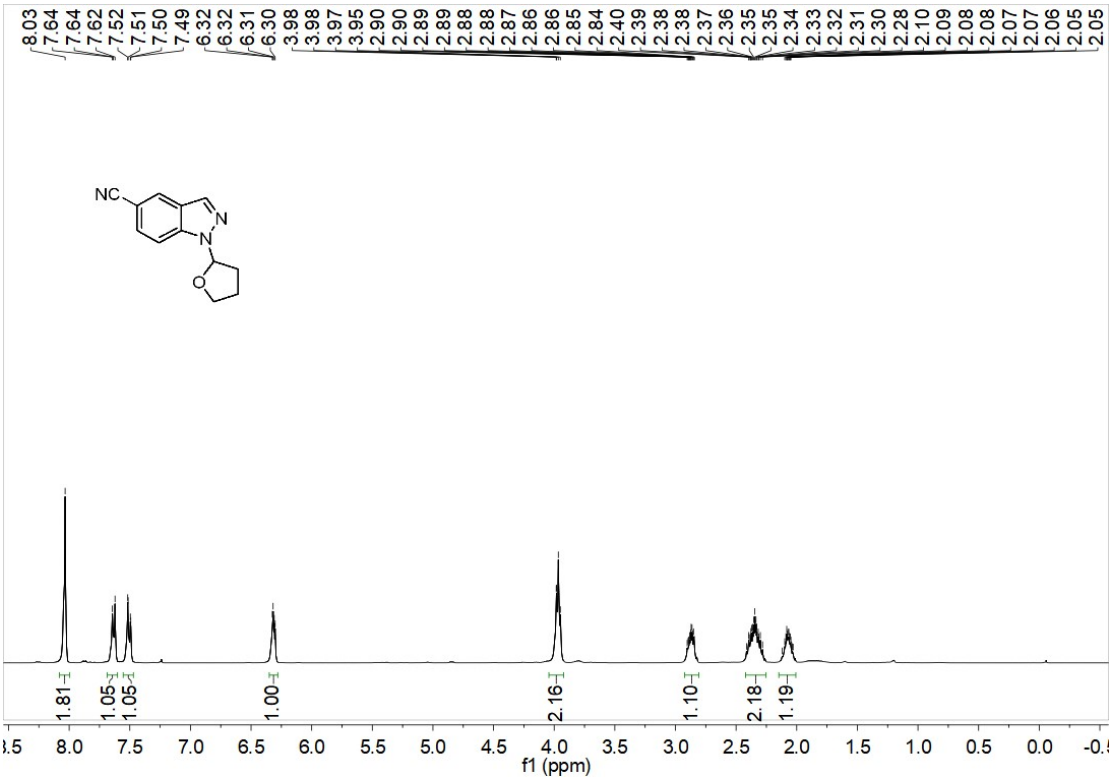
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



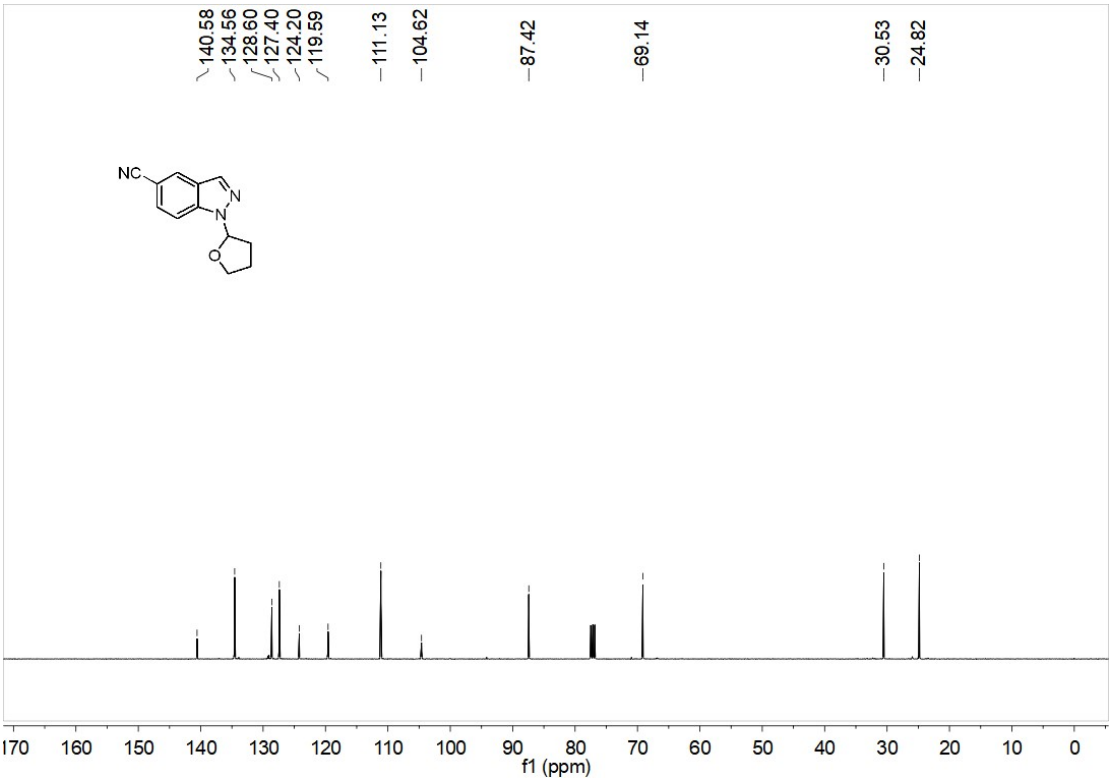
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



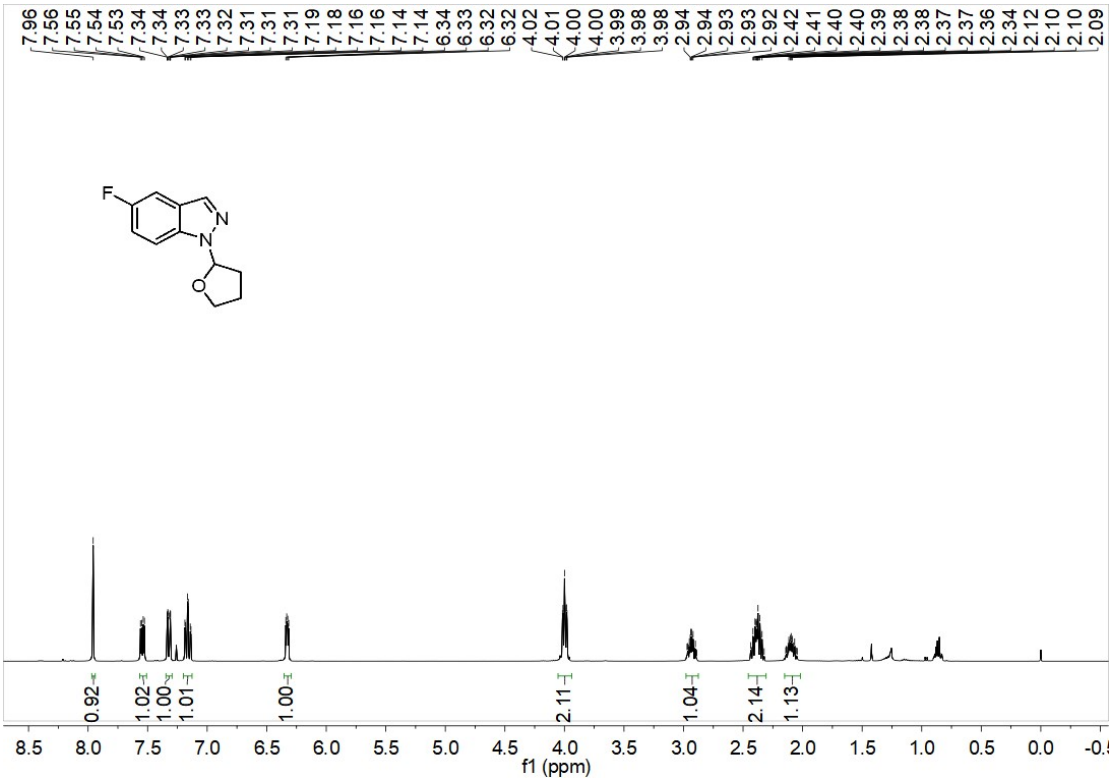
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



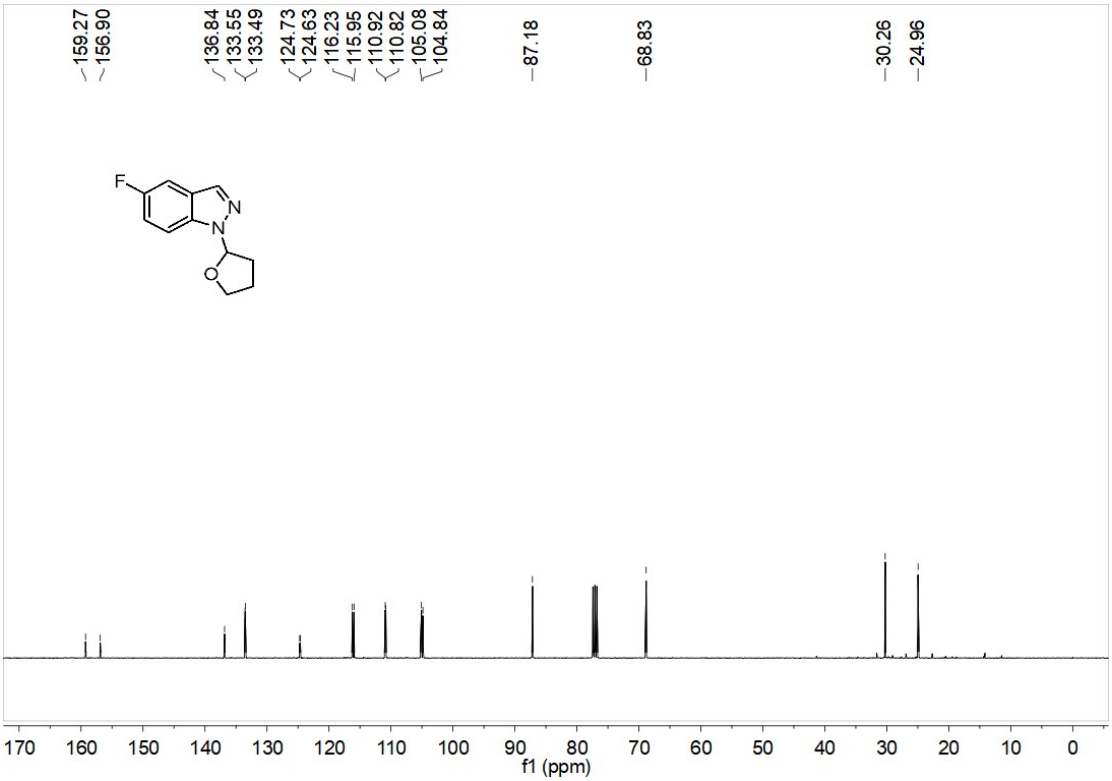
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



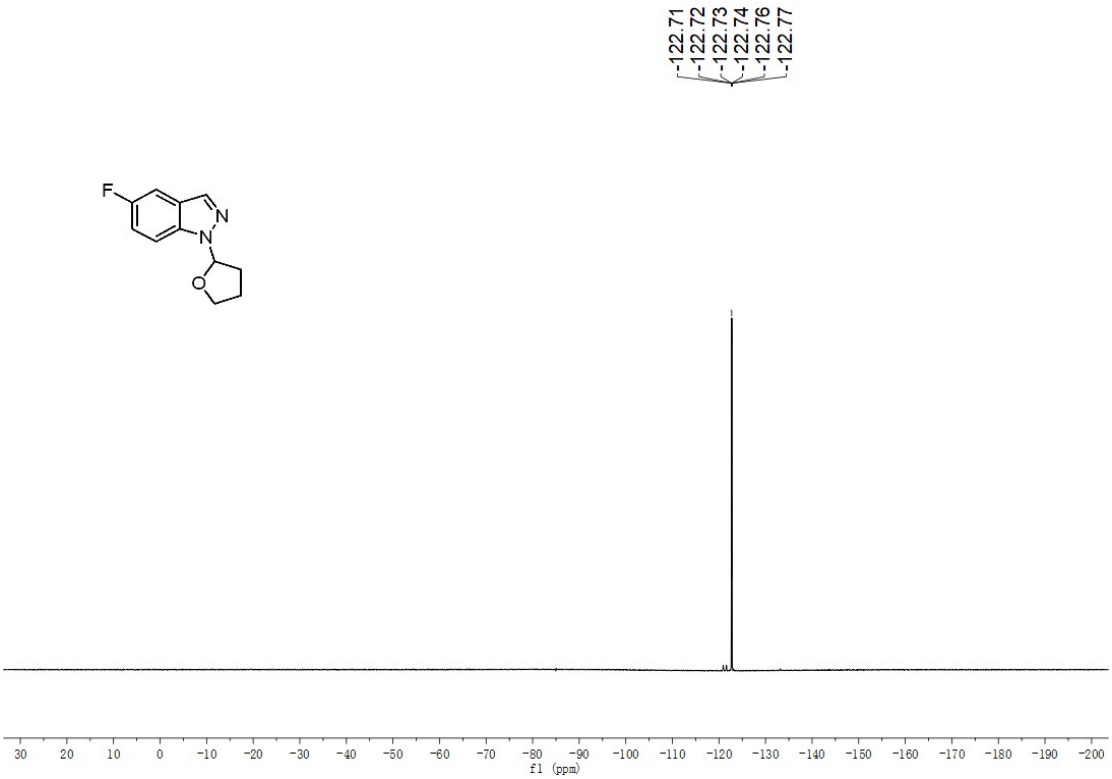
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



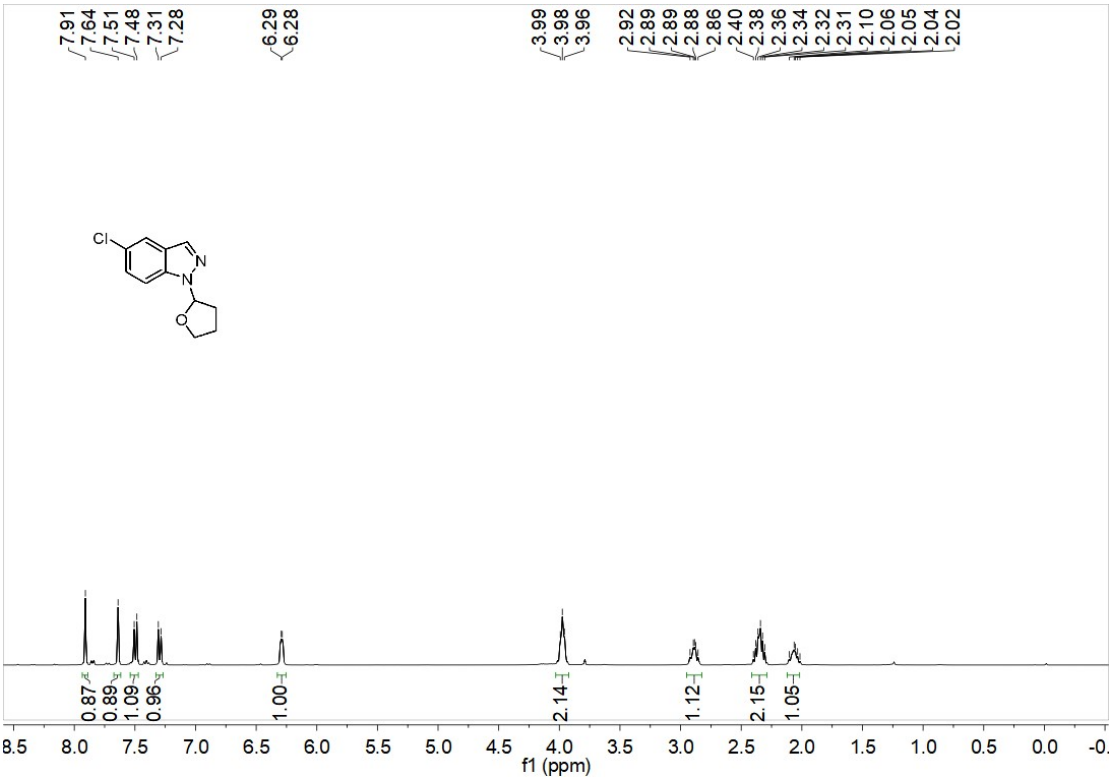
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



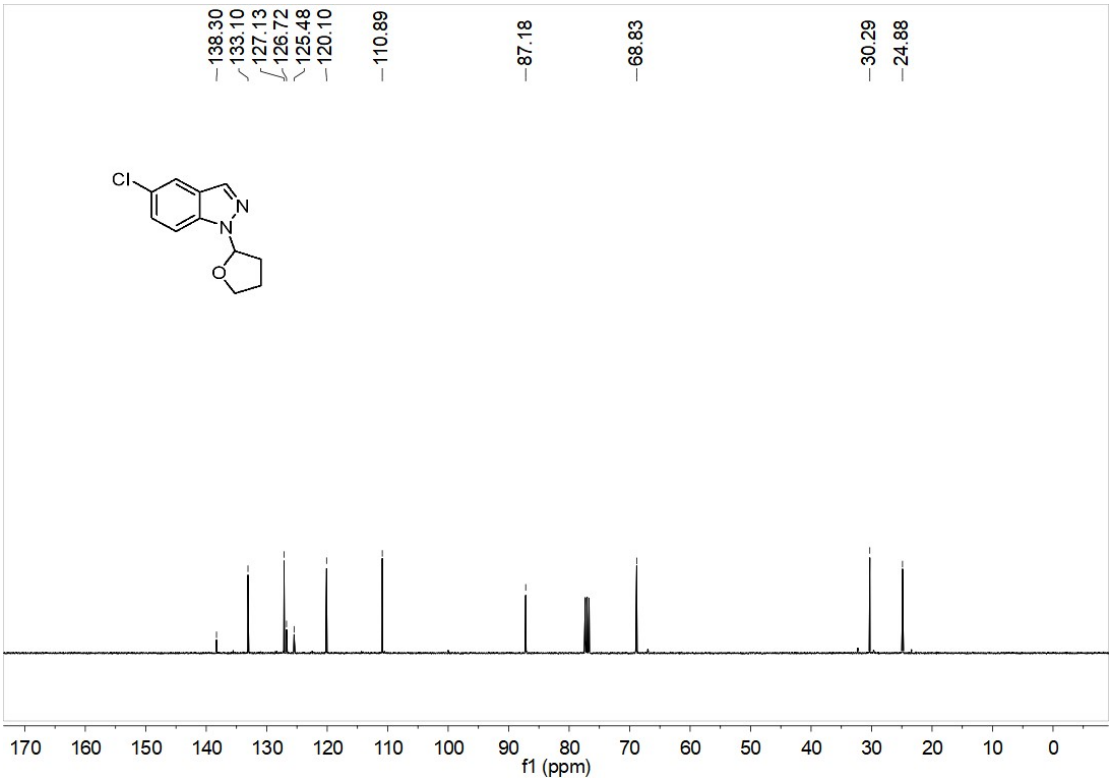
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



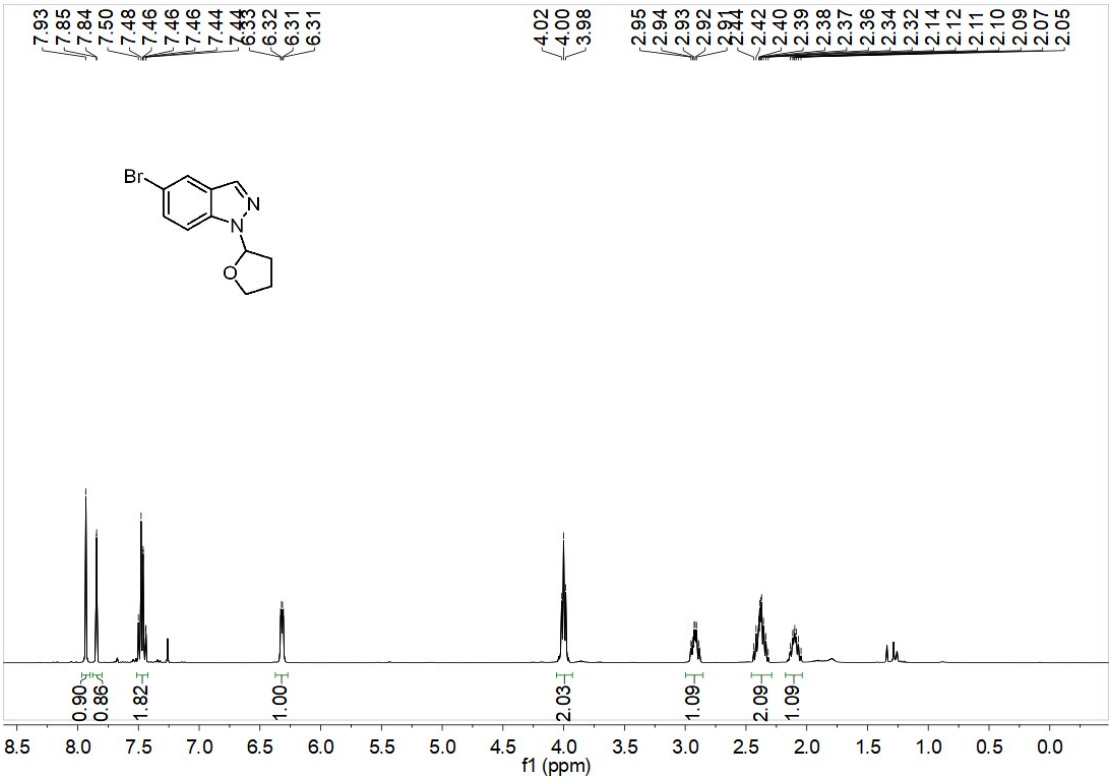
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



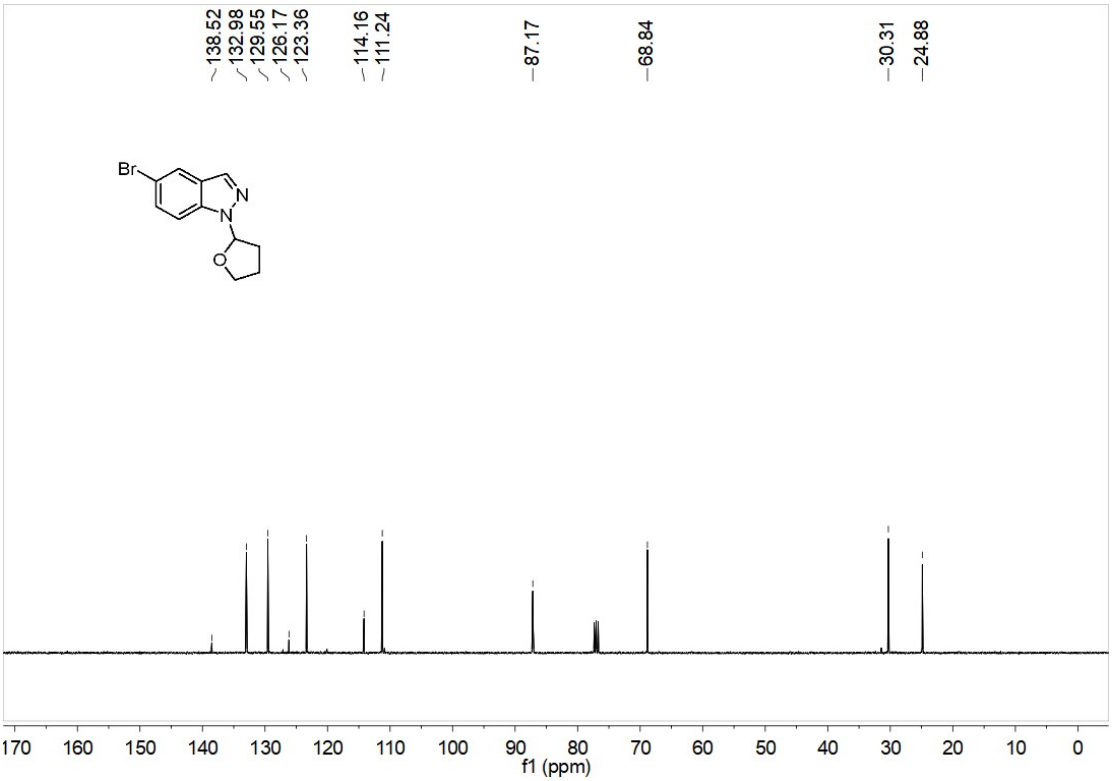
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



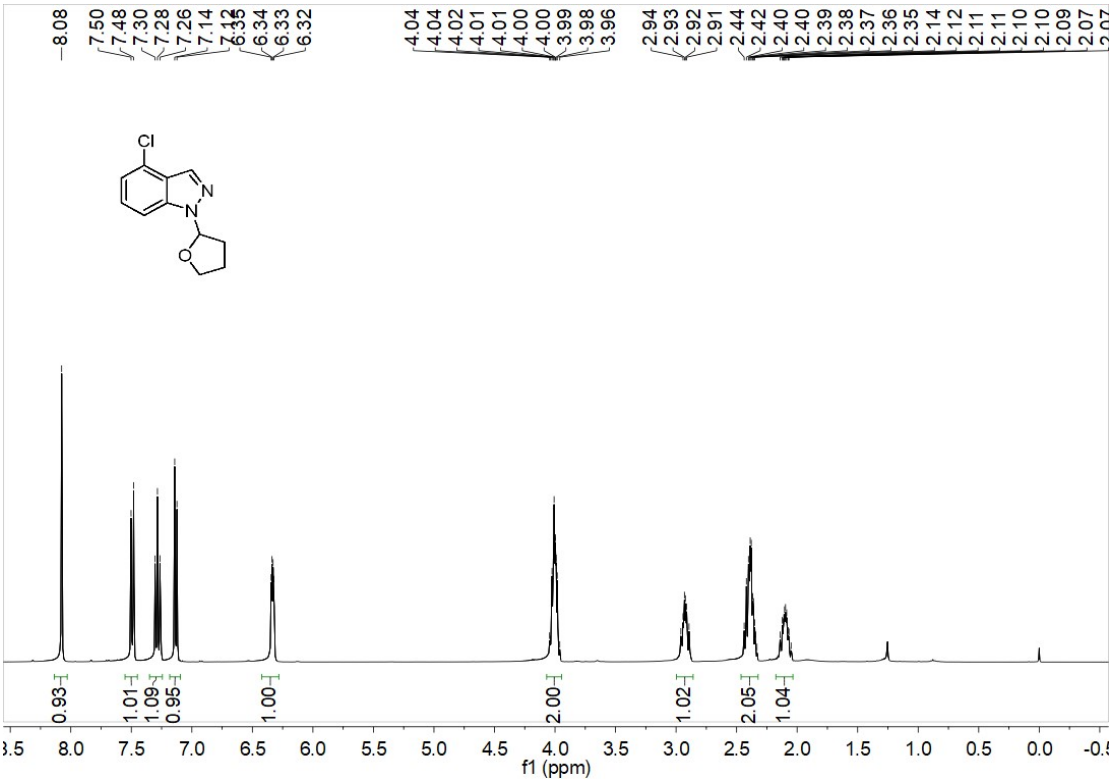
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



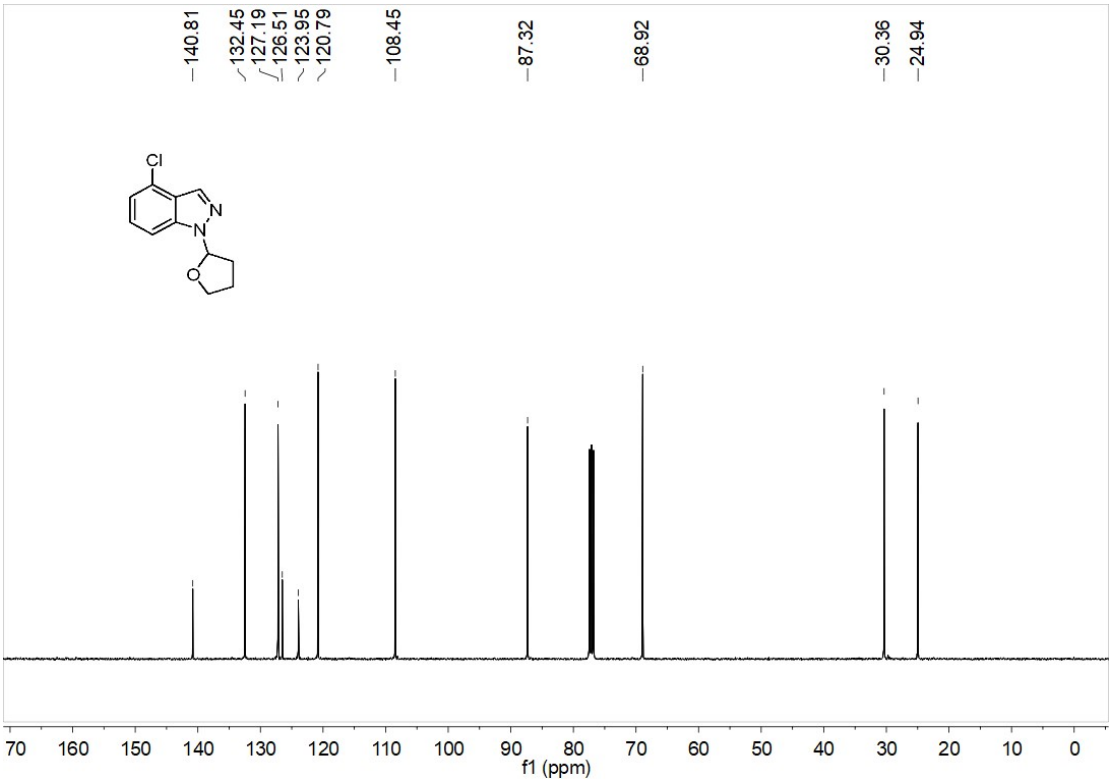
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



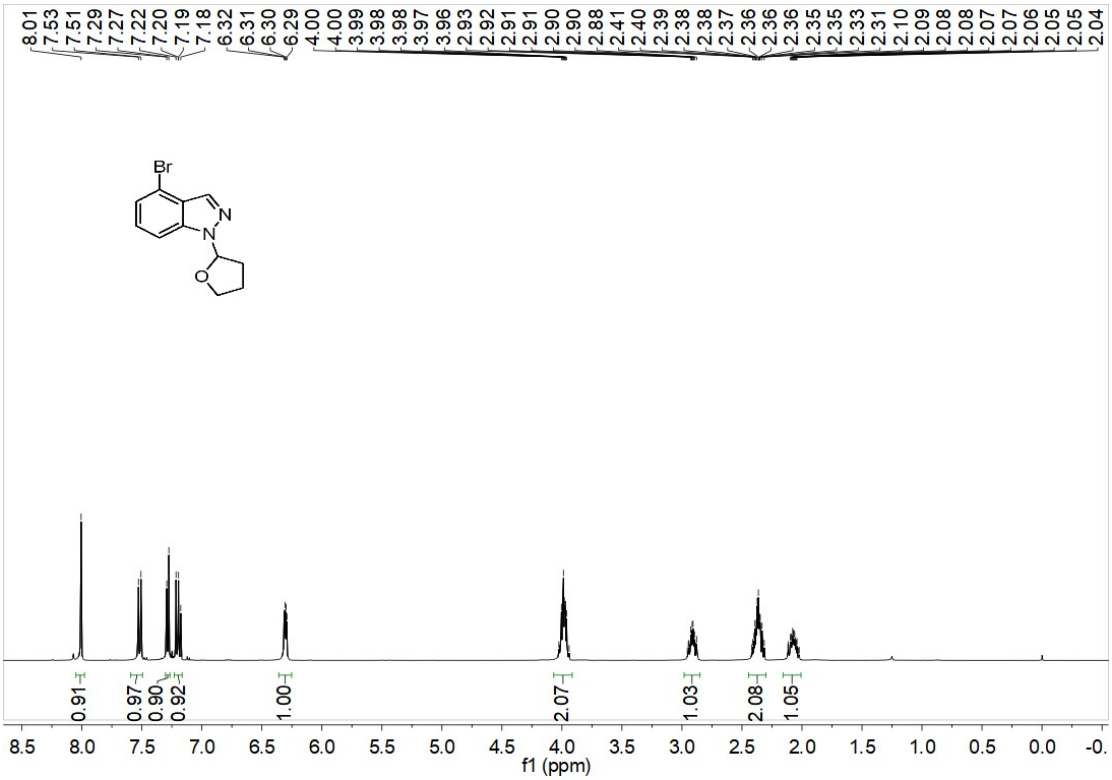
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



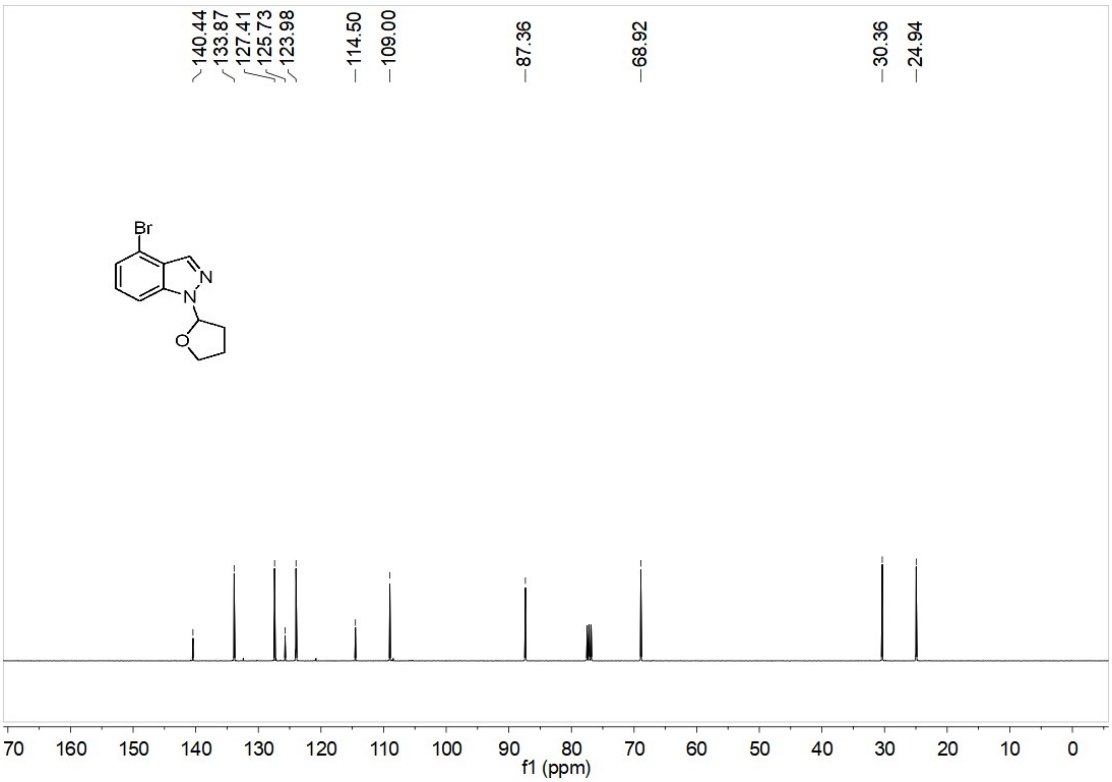
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



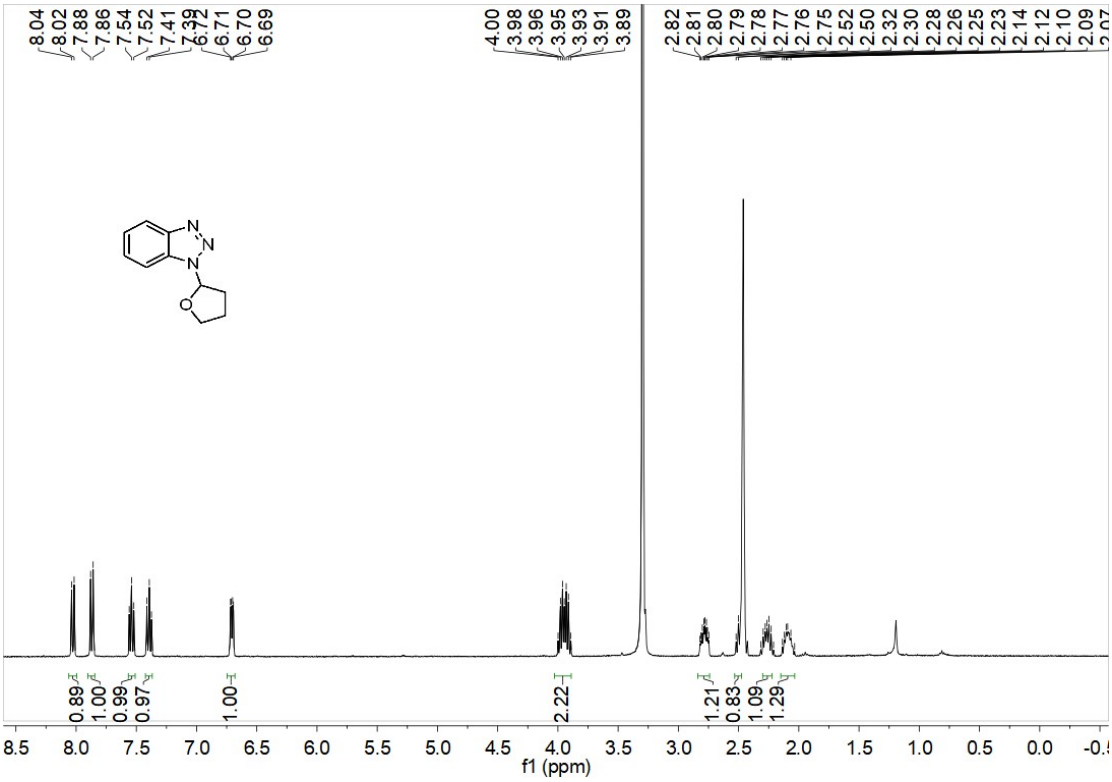
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



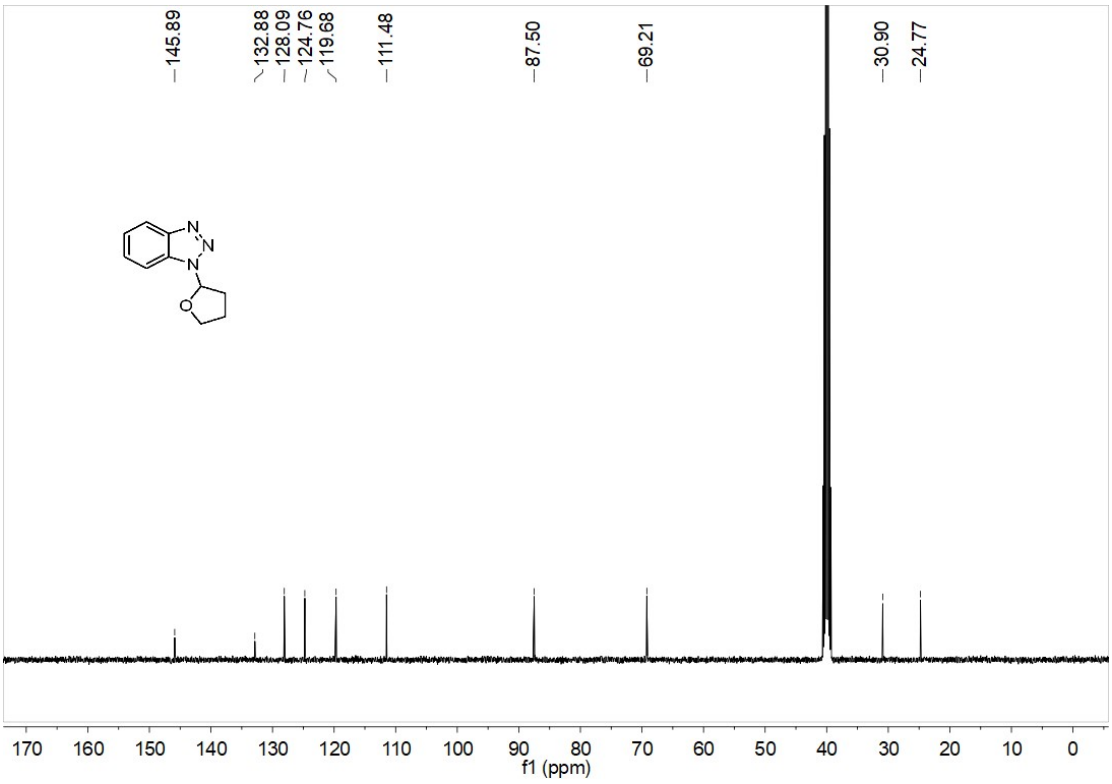
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



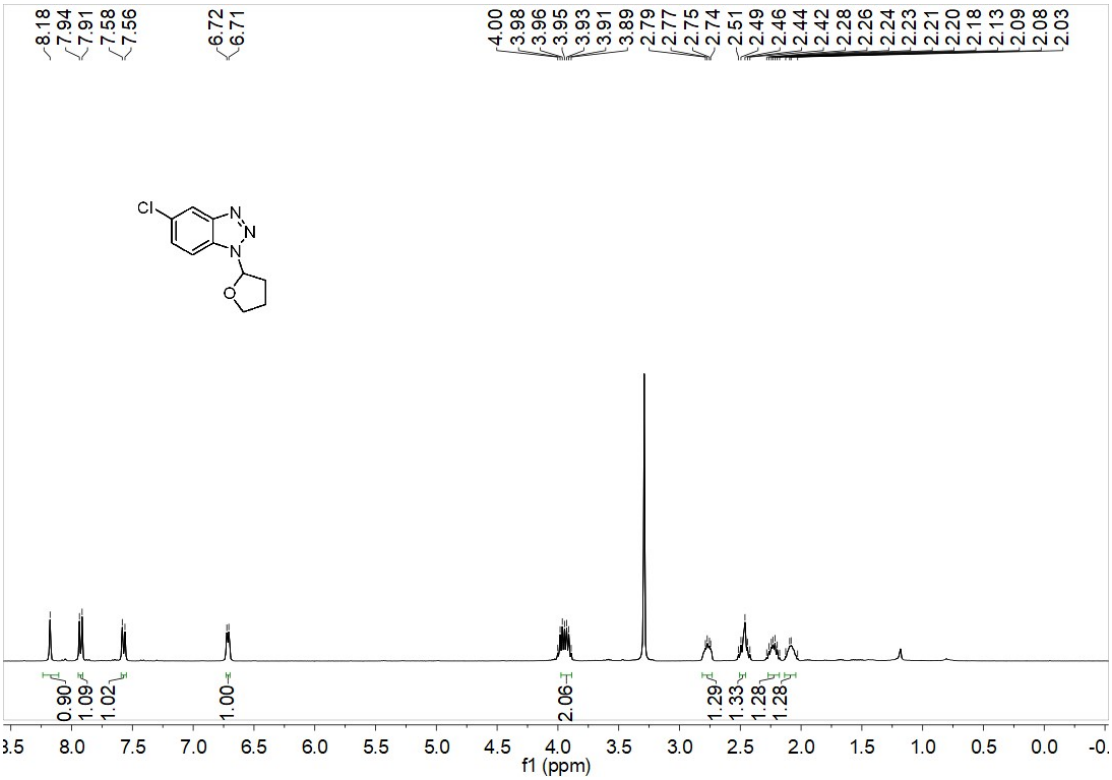
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



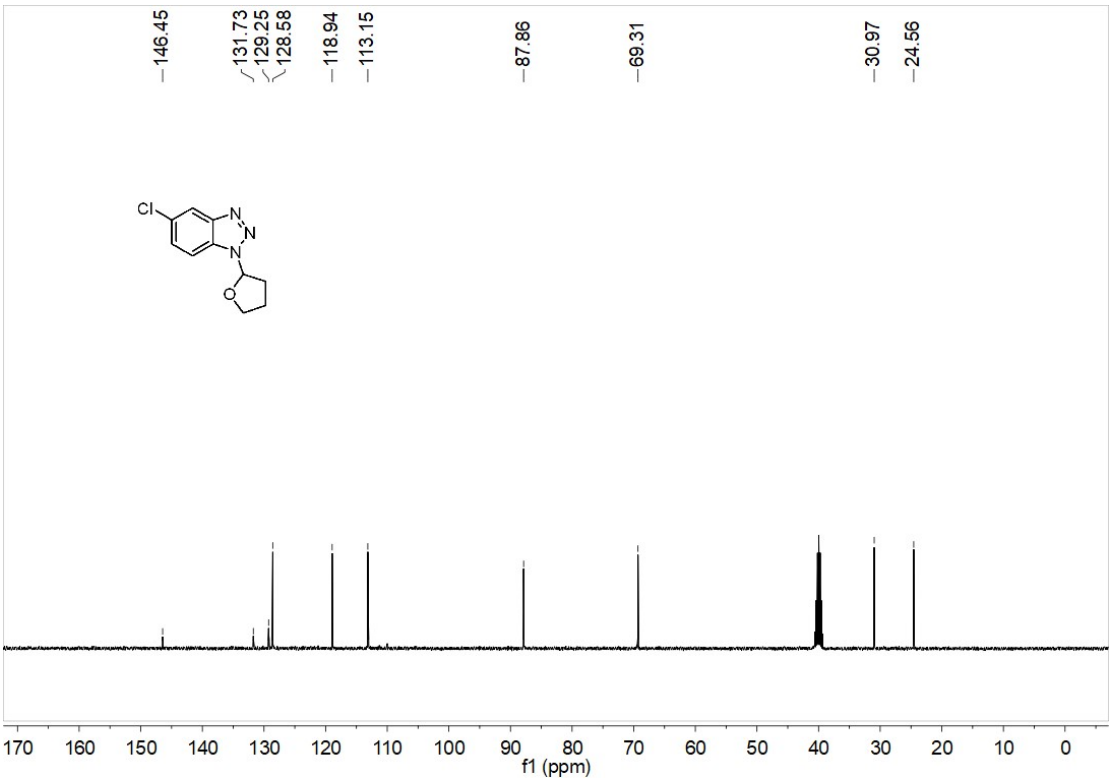
^{1}H NMR (400 MHz, DMSO-d_6) of **3j**



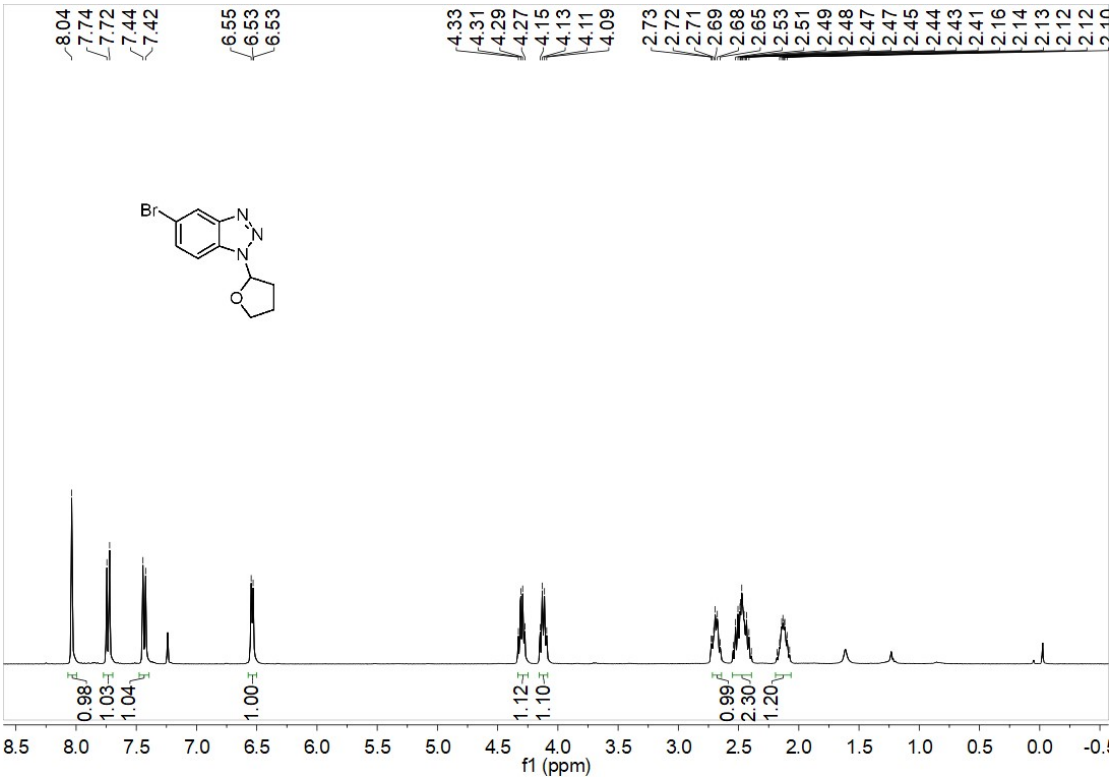
^{13}C NMR (101 MHz, DMSO-d_6) of **3j**



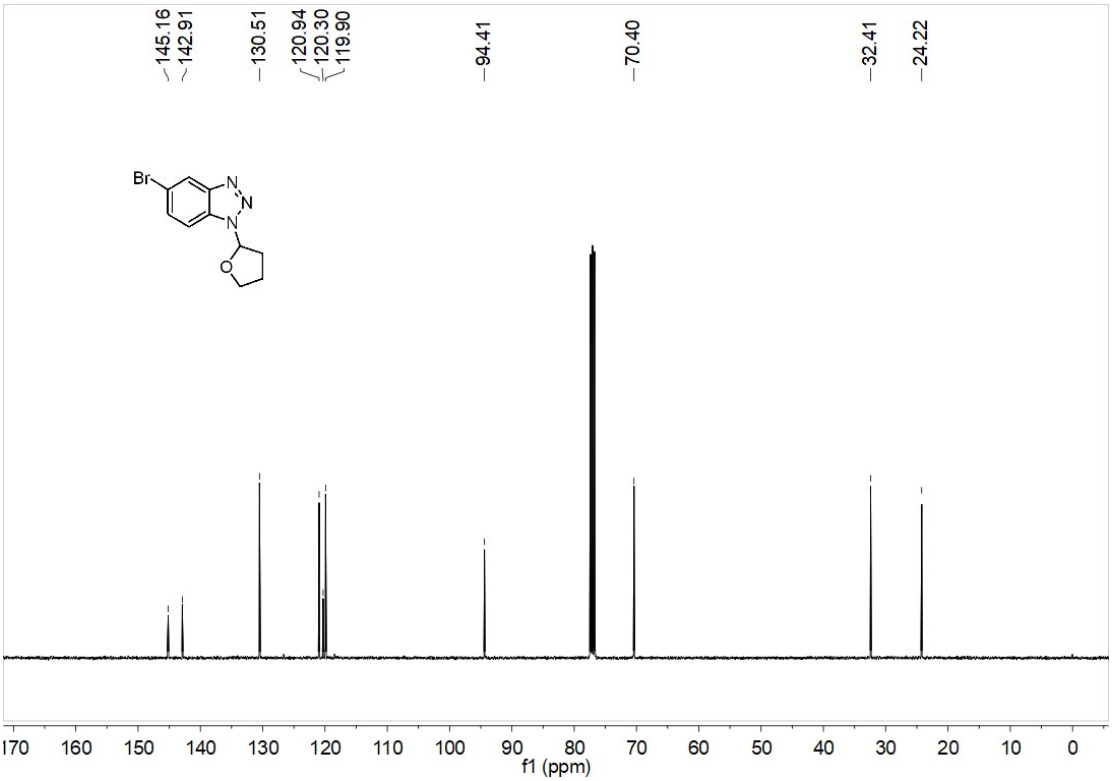
^{1}H NMR (400 MHz, DMSO-d_6) of **3k**



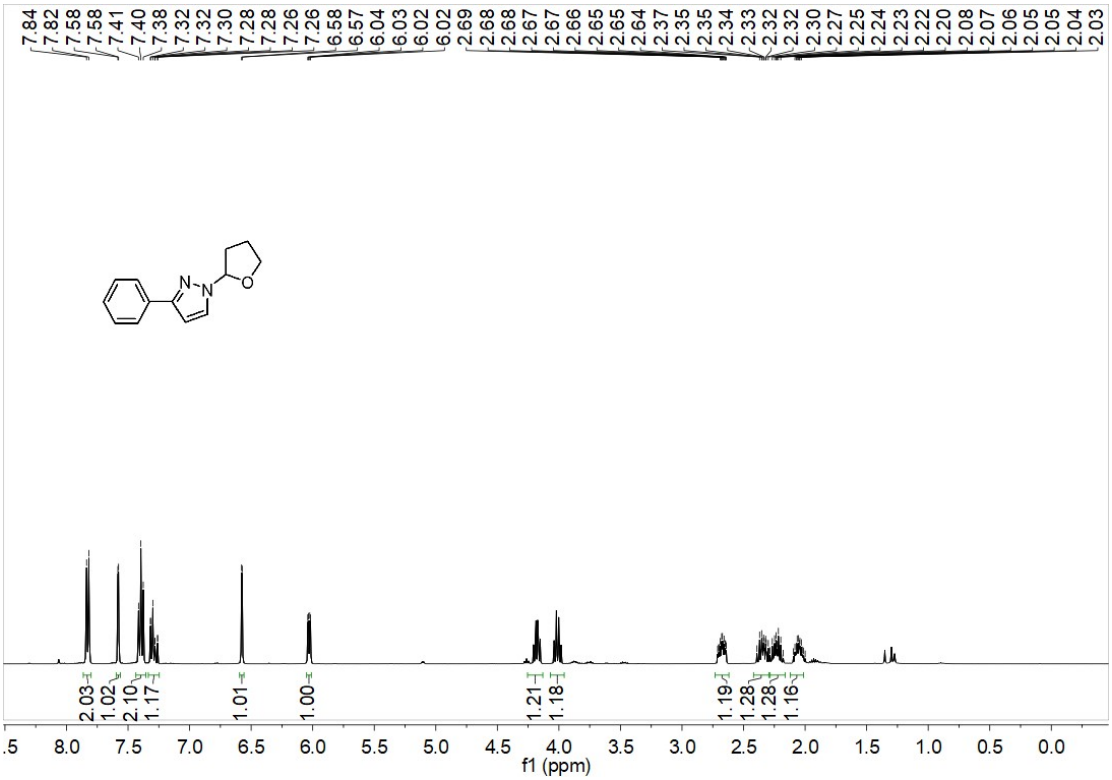
^{13}C NMR (101 MHz, DMSO-d_6) of **3k**



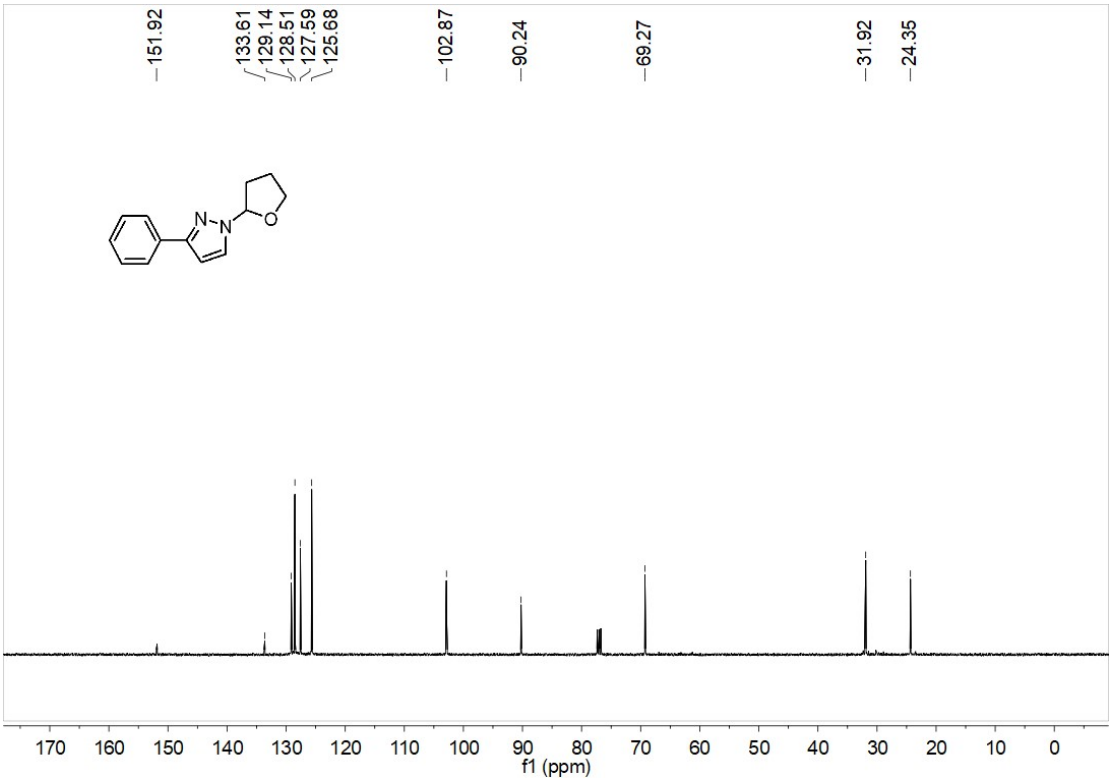
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



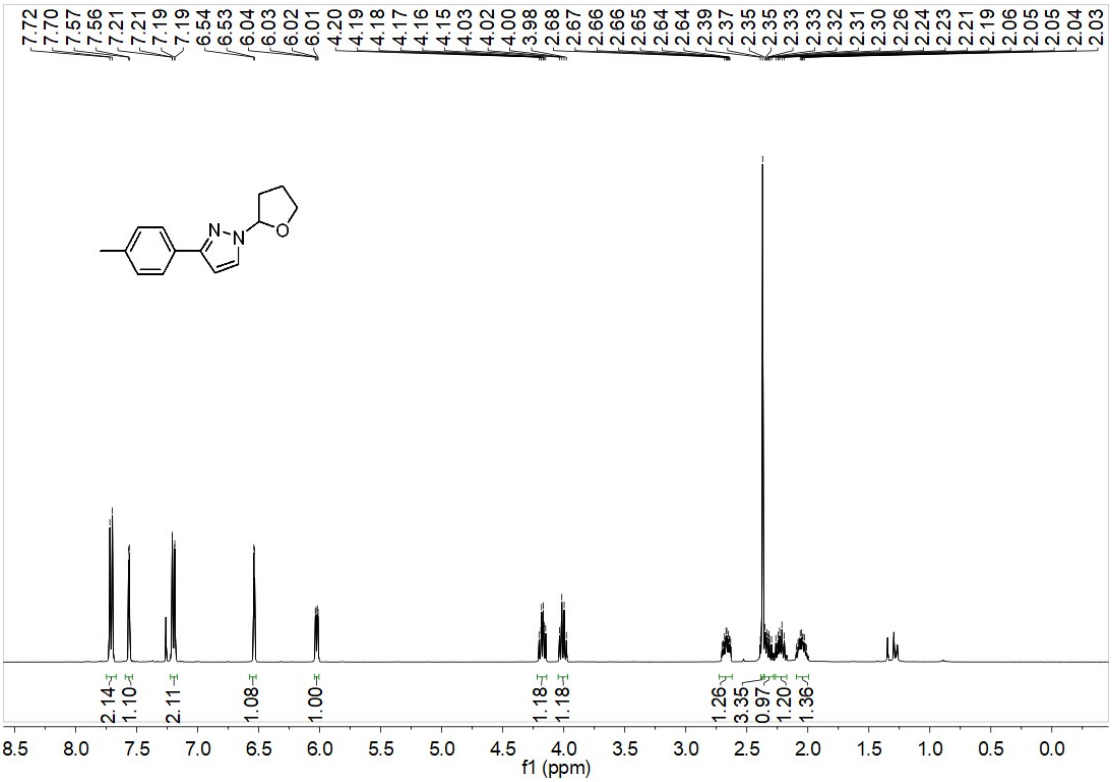
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



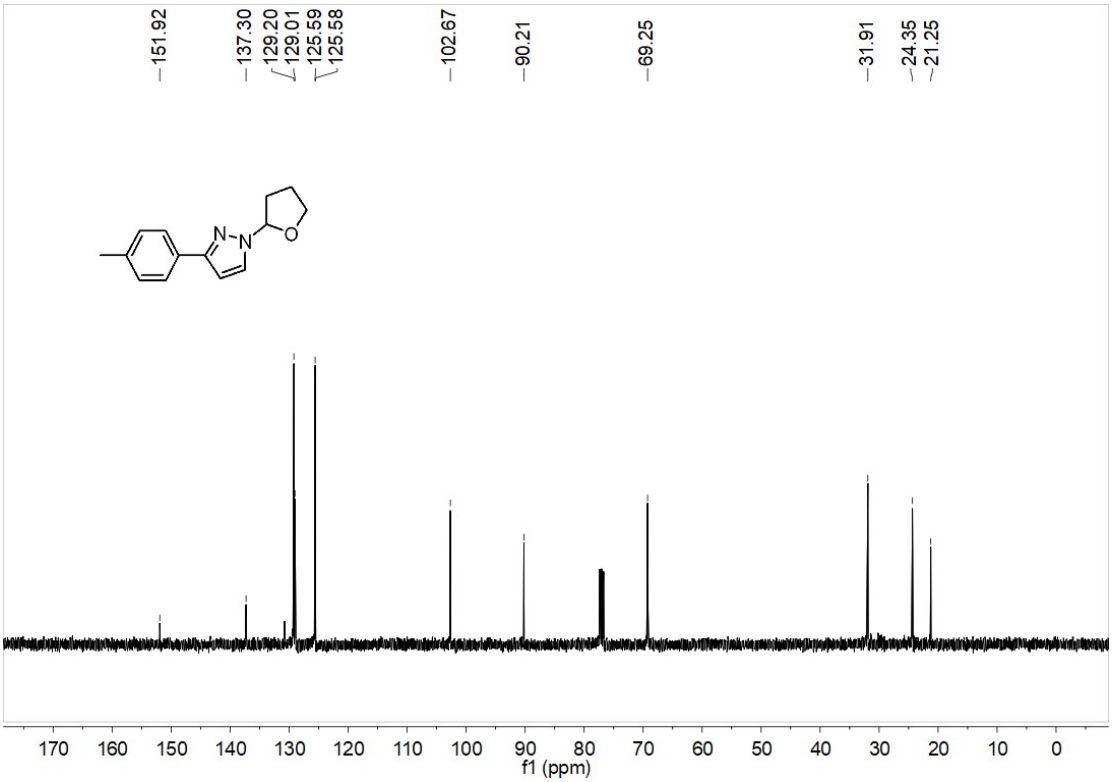
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



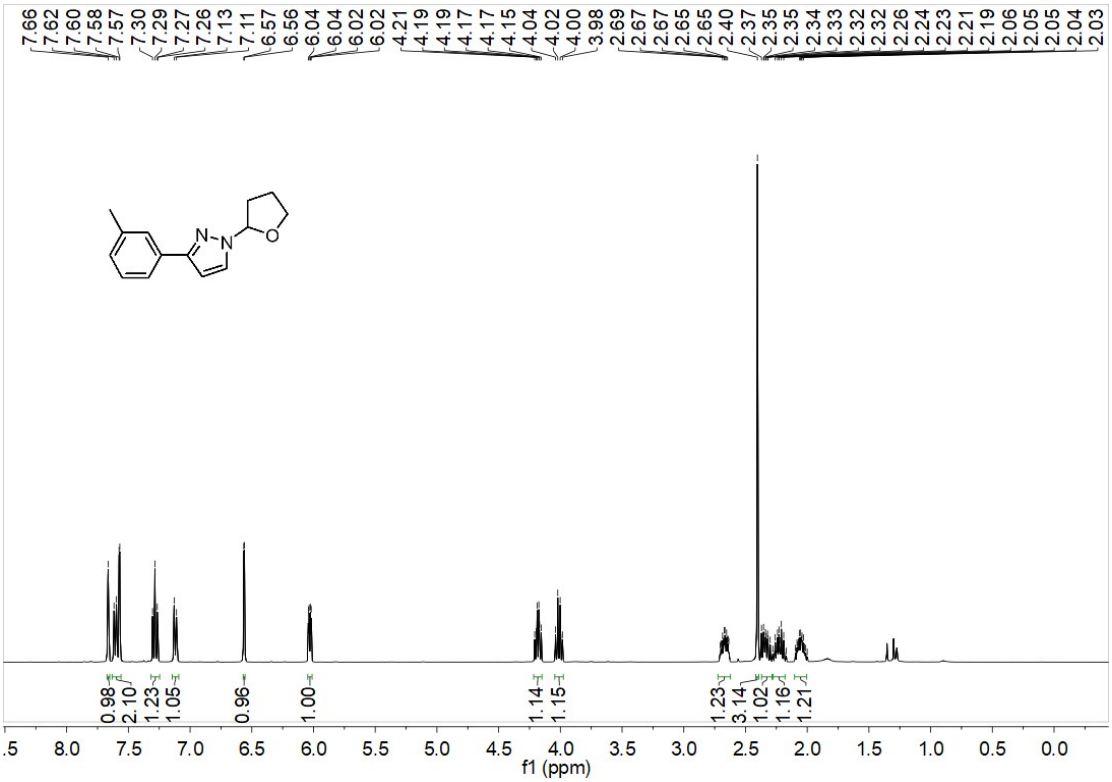
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



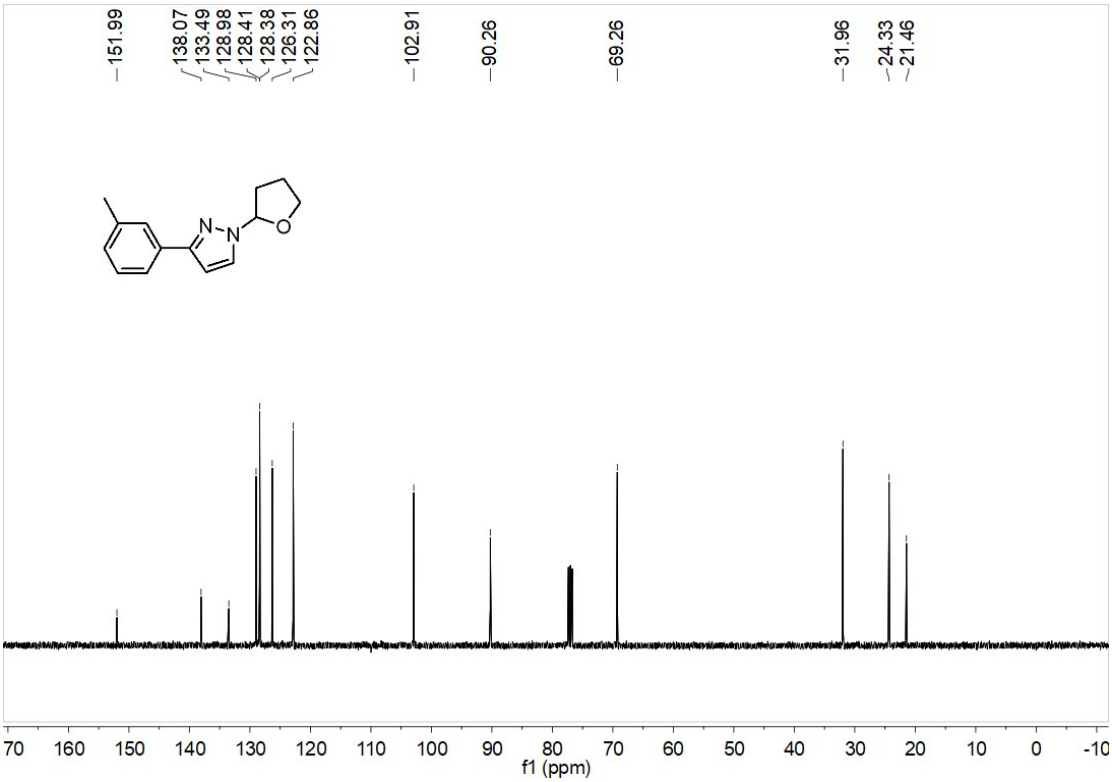
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



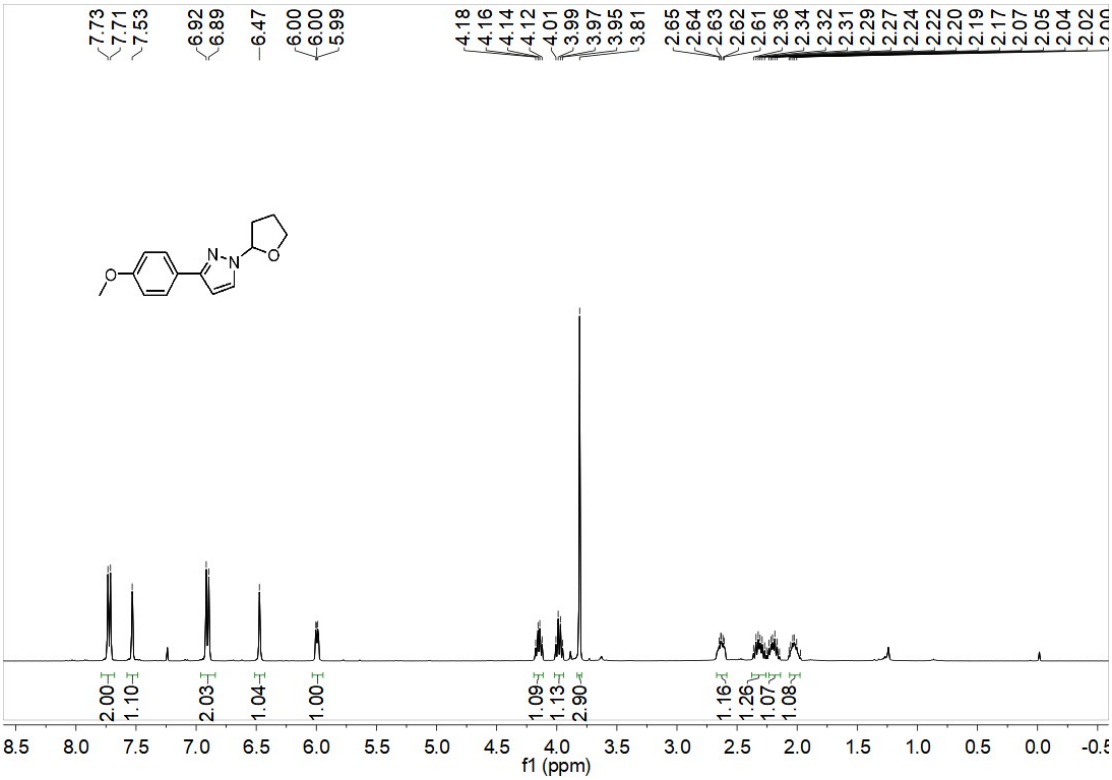
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



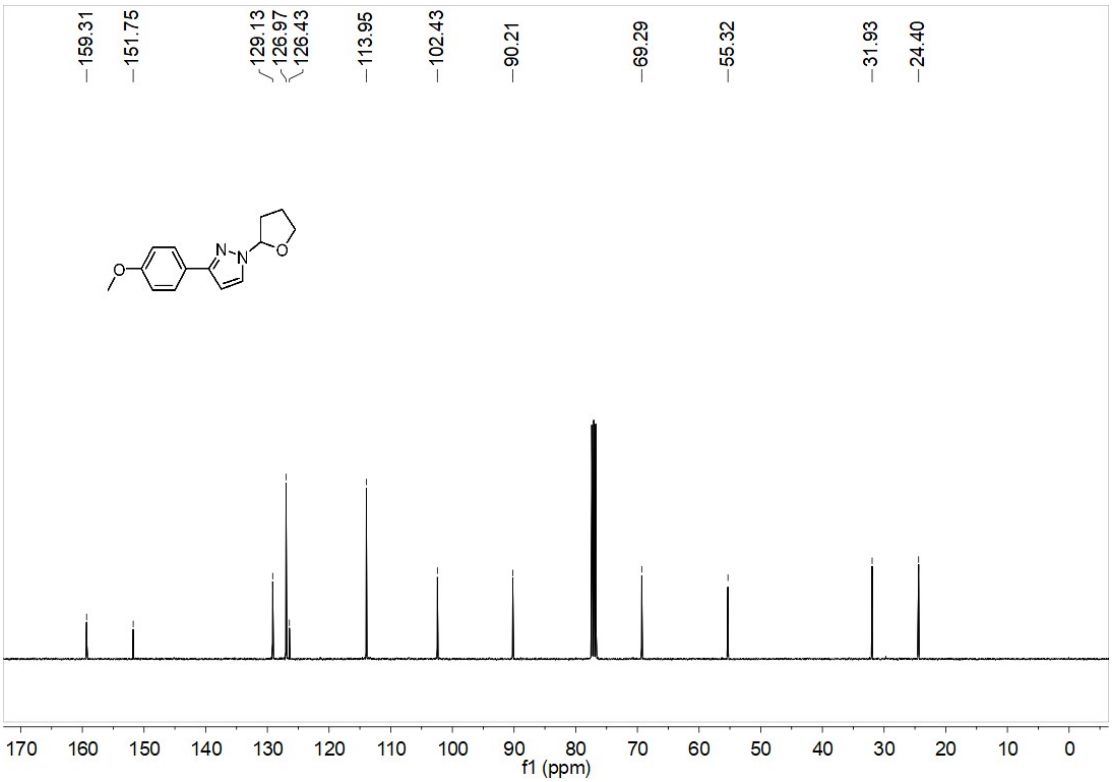
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



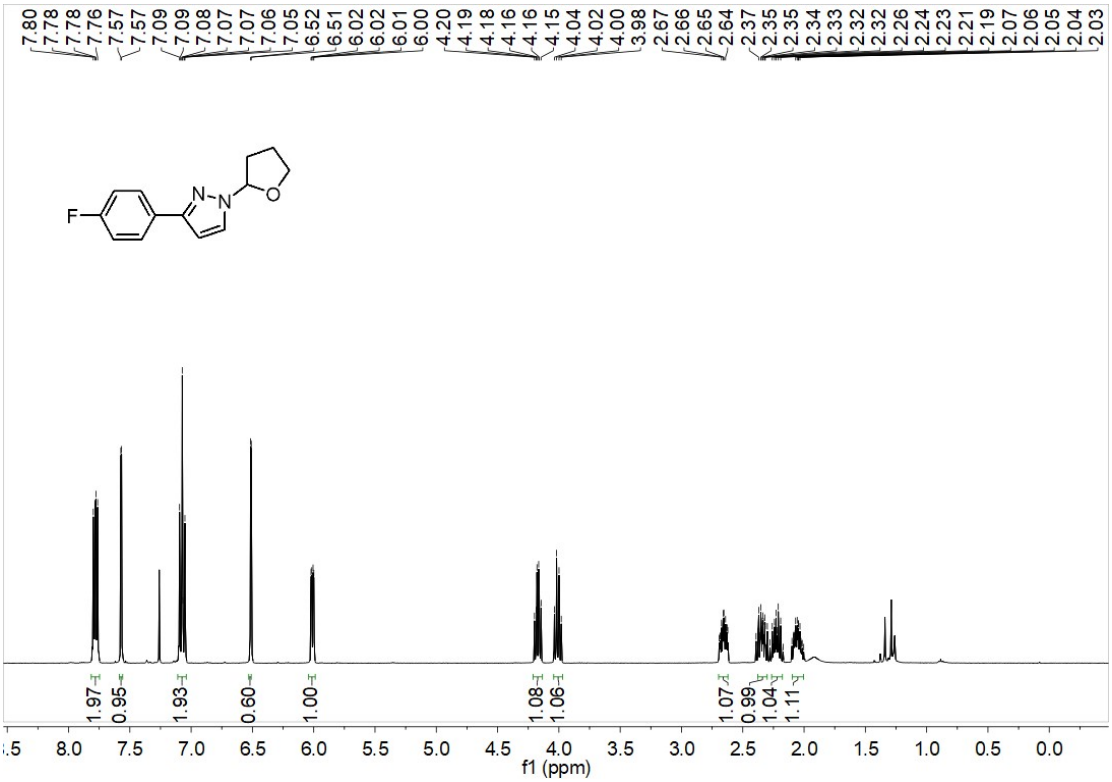
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



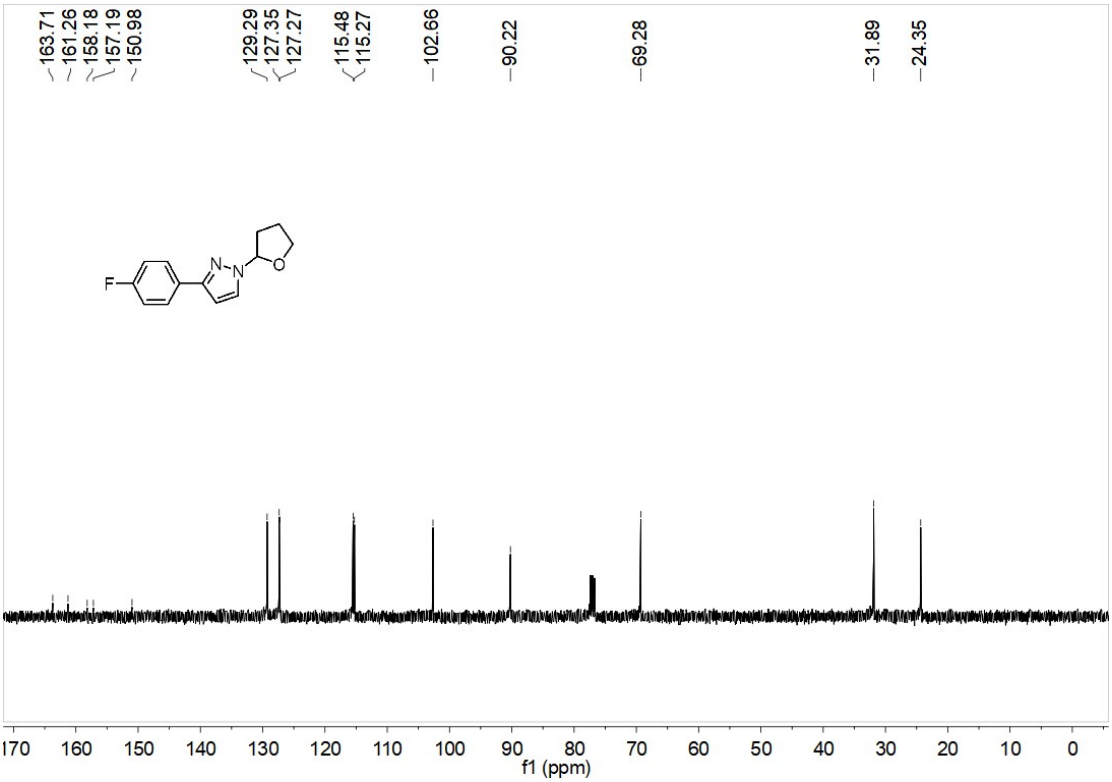
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



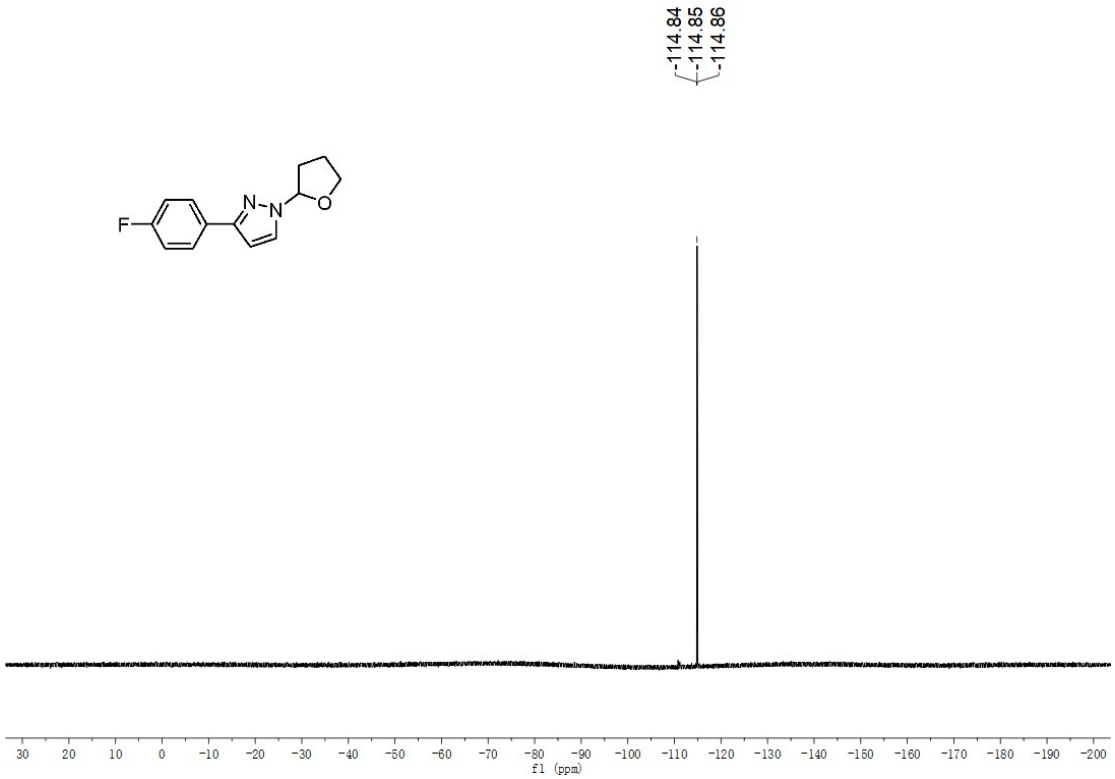
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



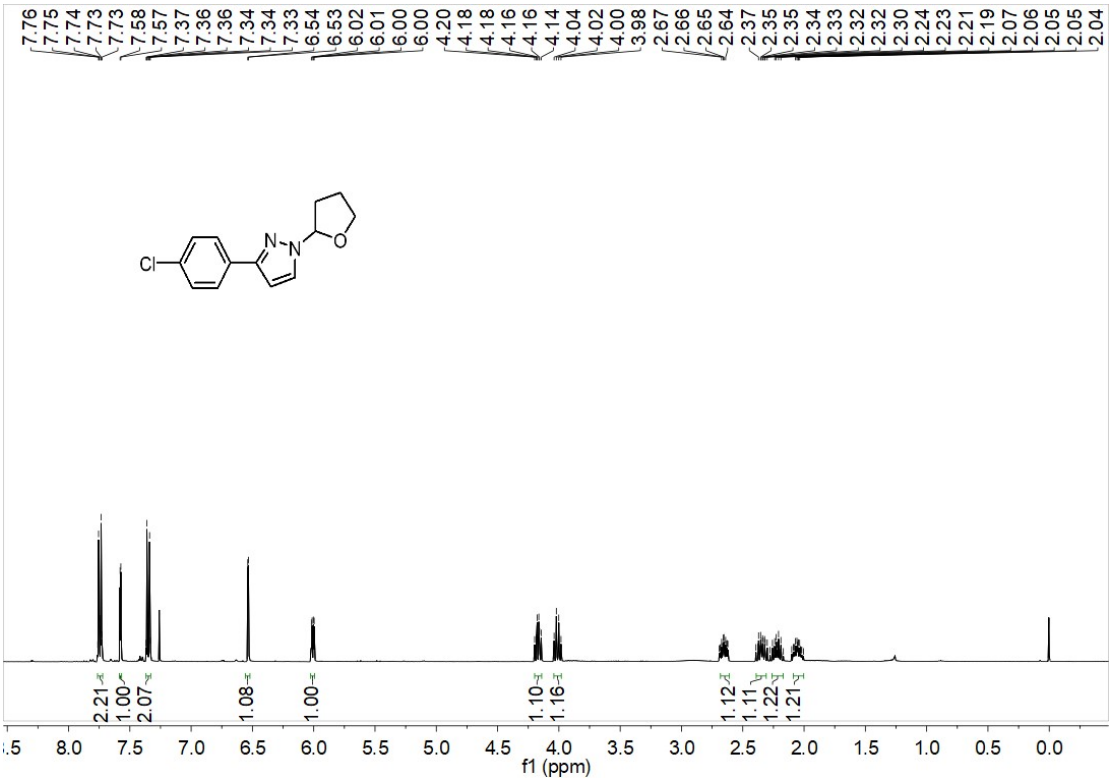
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



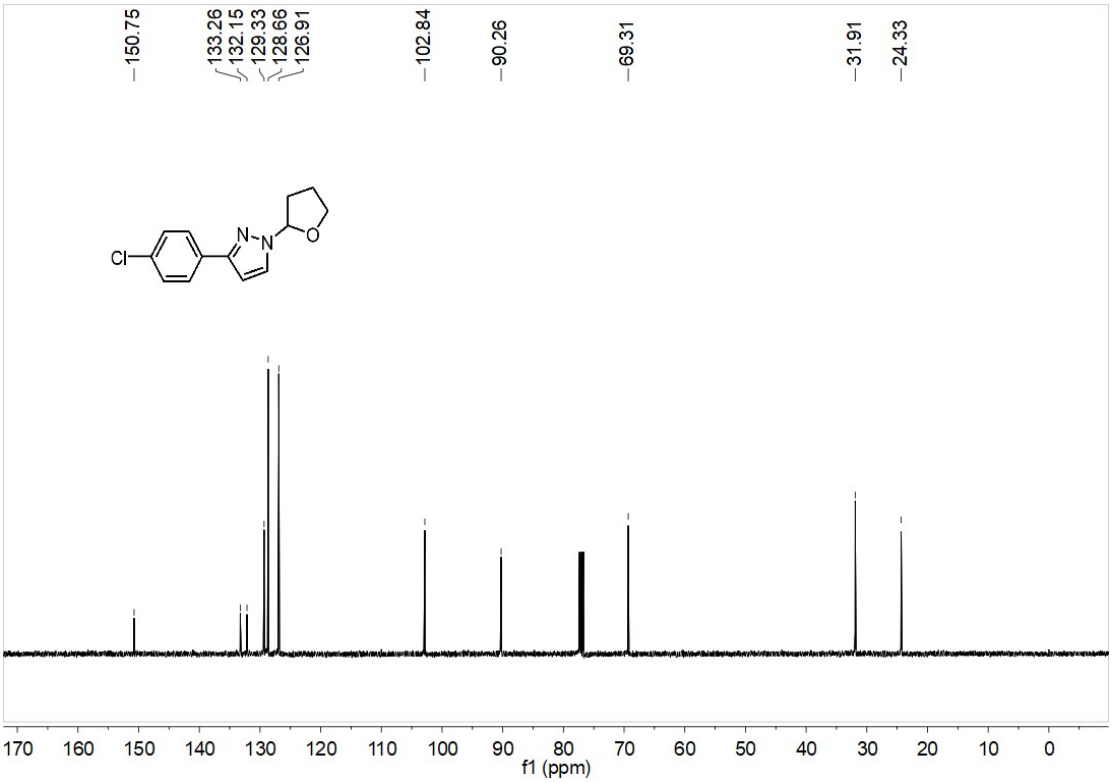
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



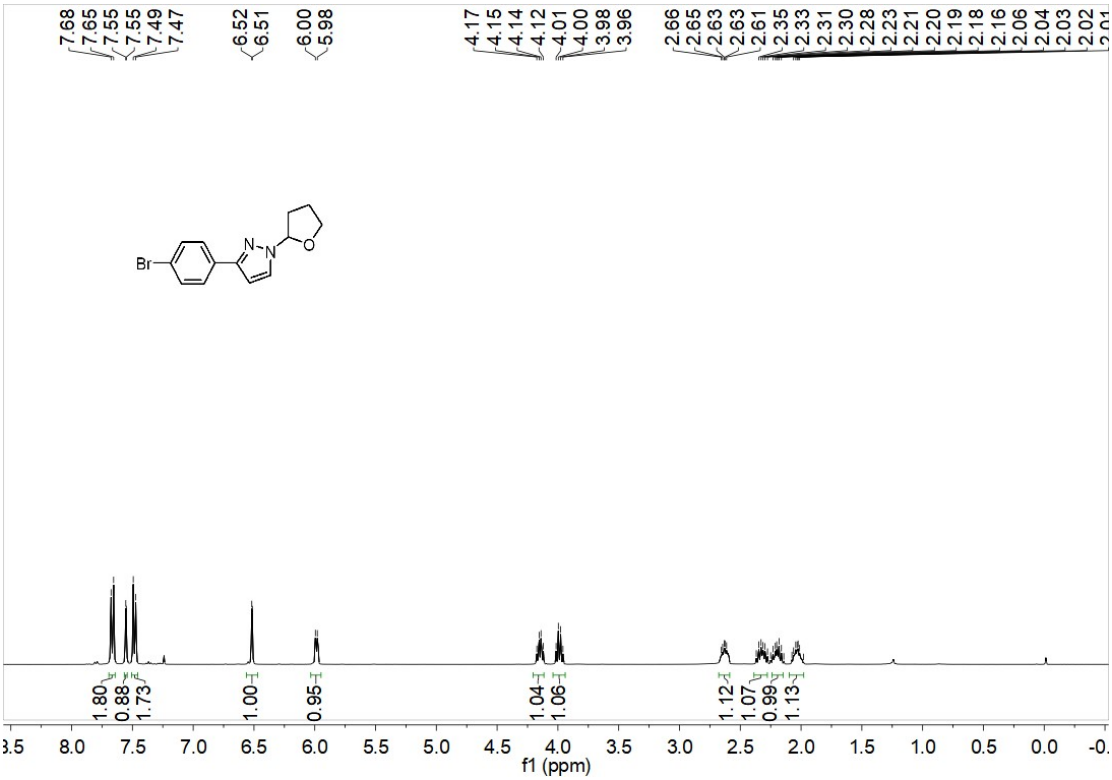
^{19}F NMR (376 MHz, $CDCl_3$) of **3q**



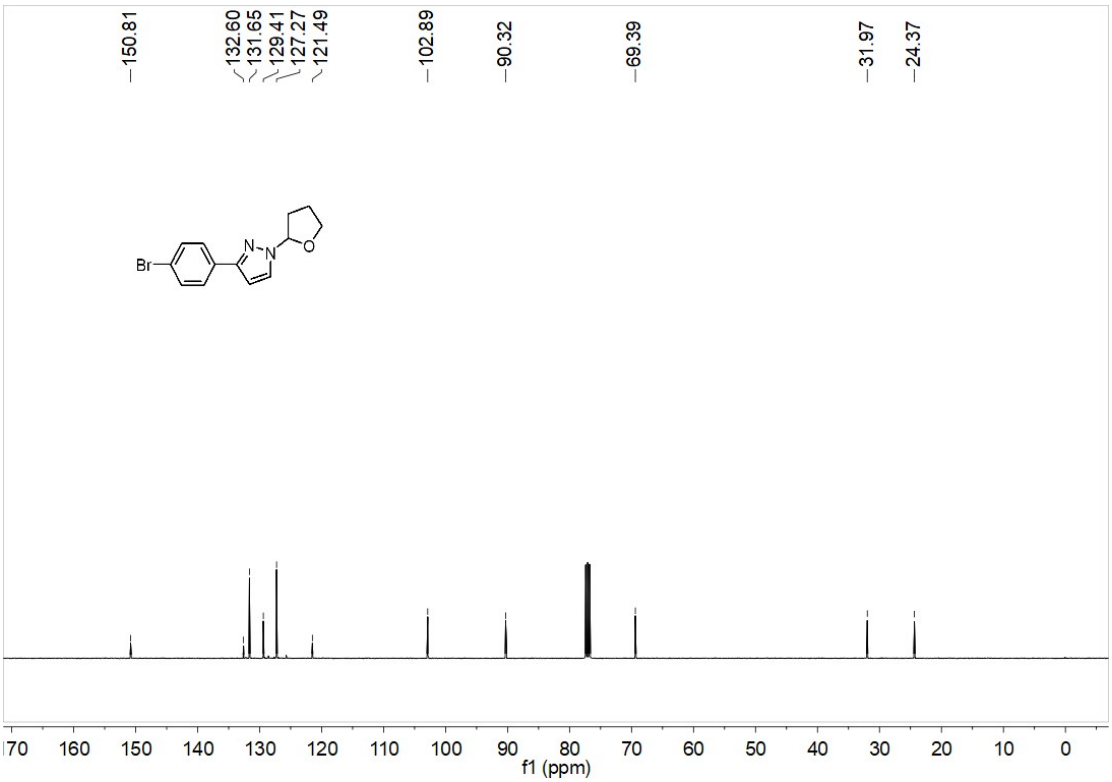
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



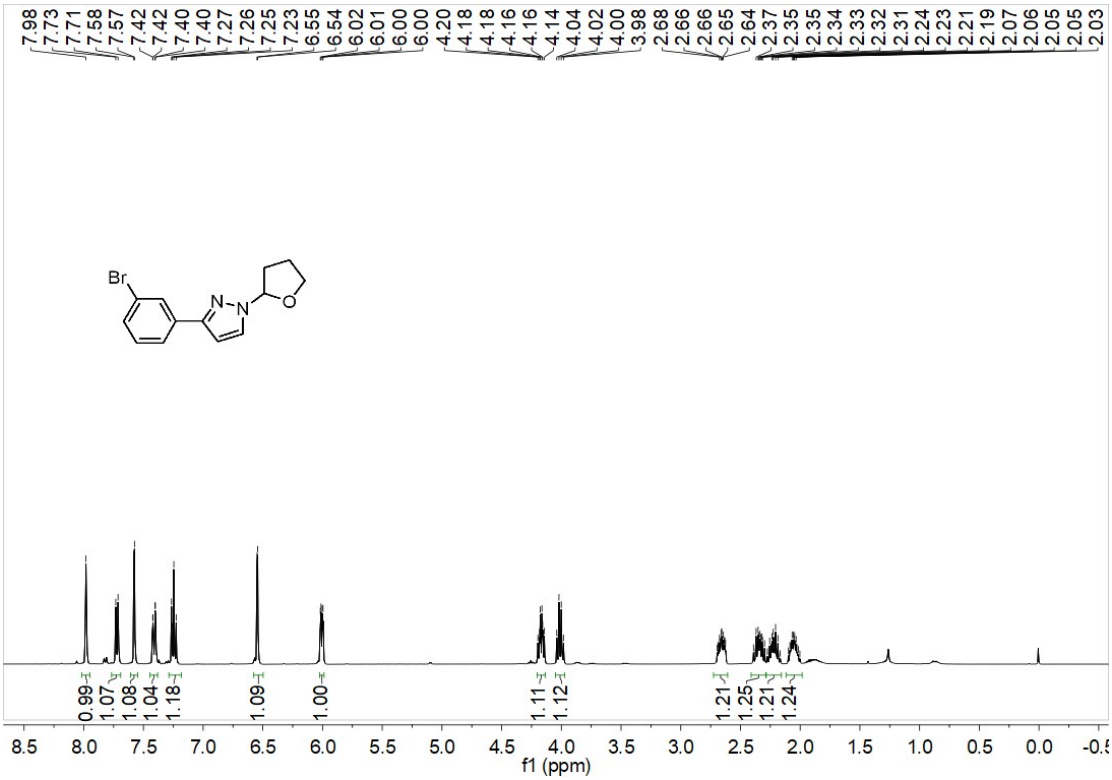
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



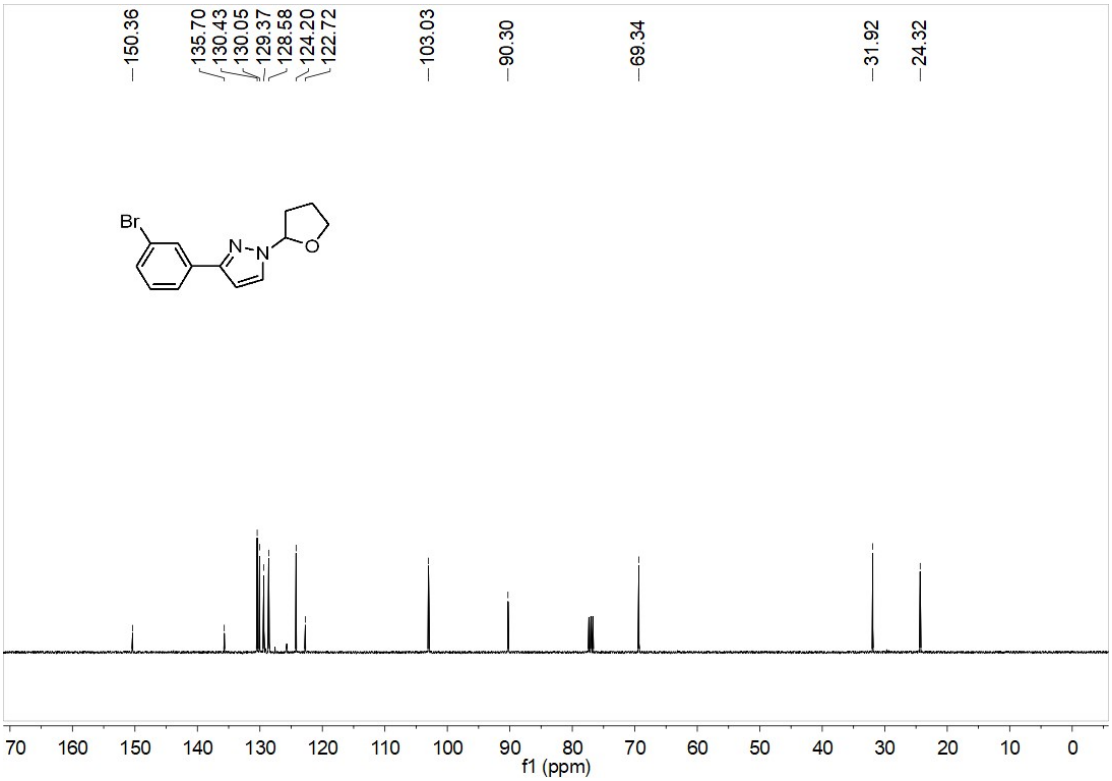
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



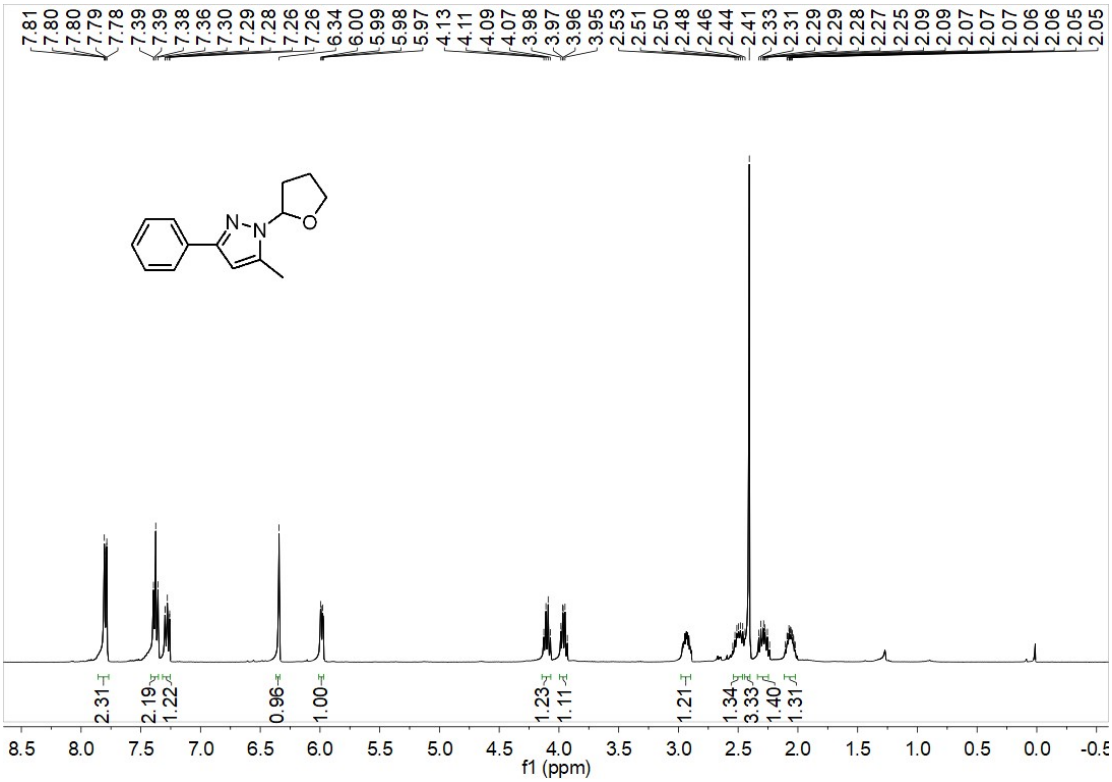
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



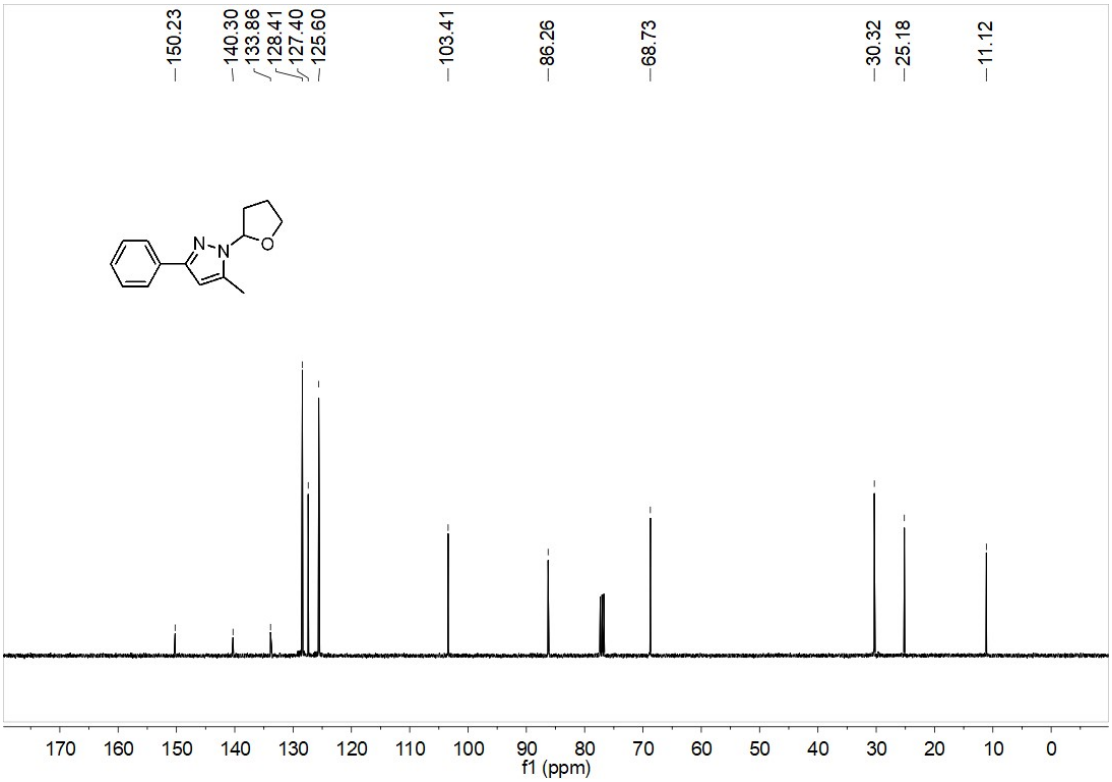
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



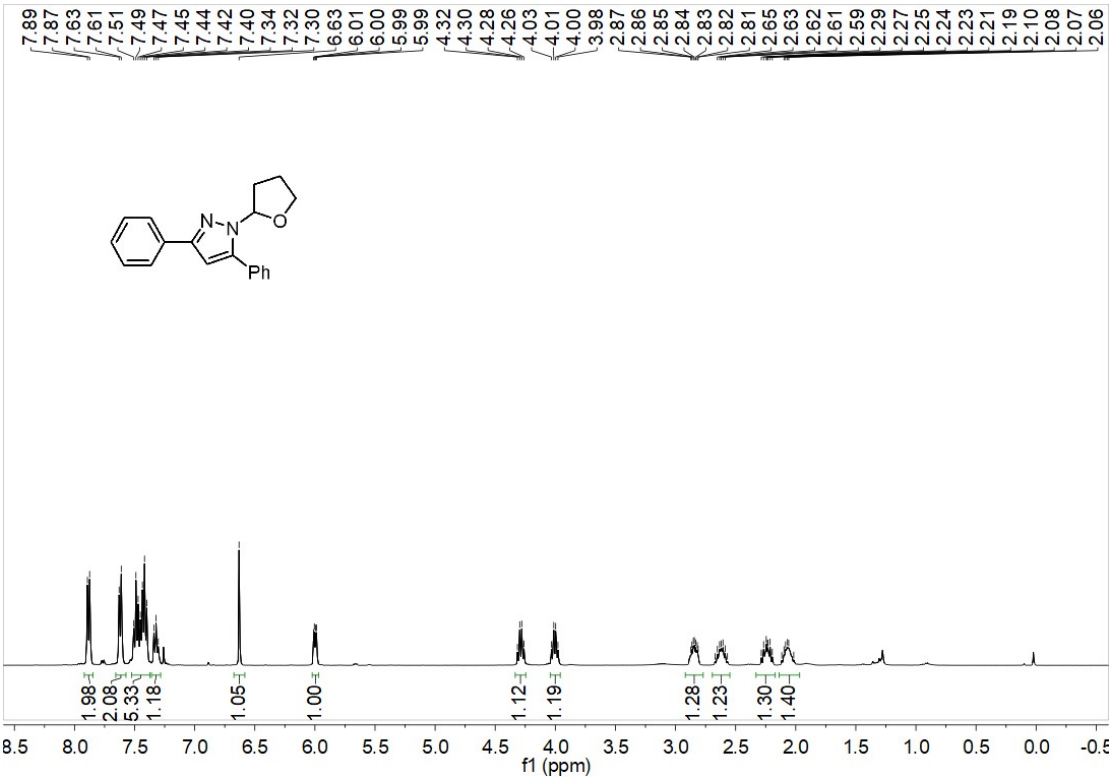
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



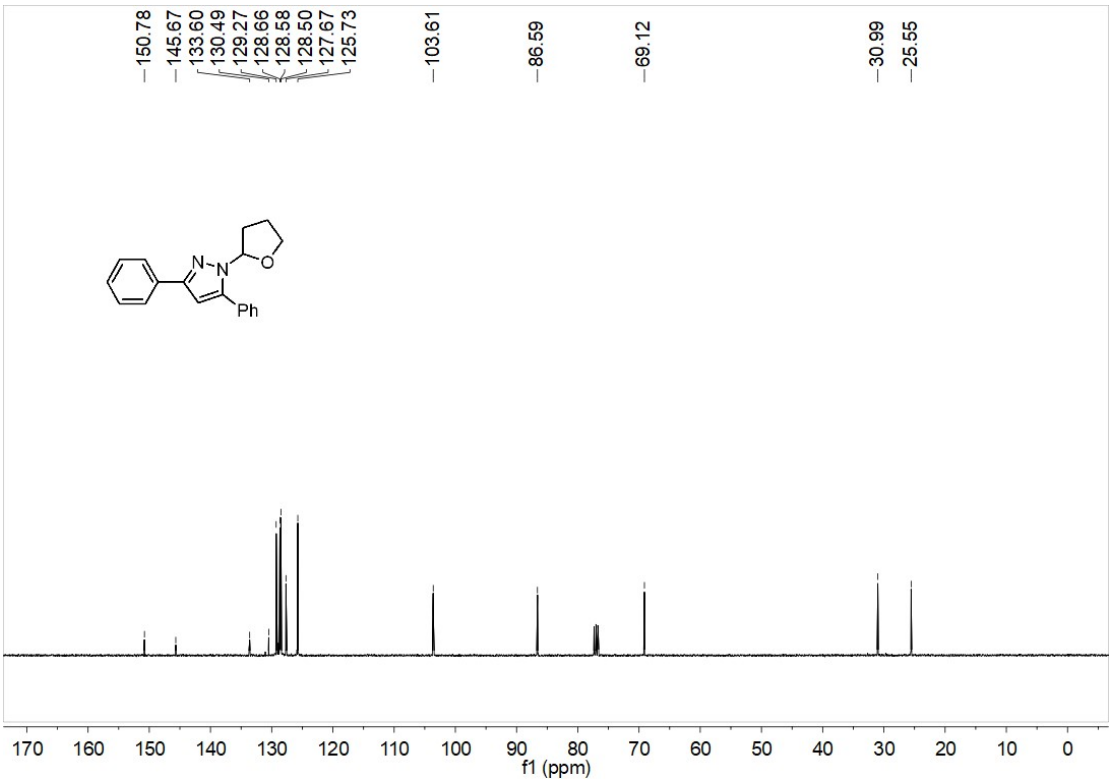
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



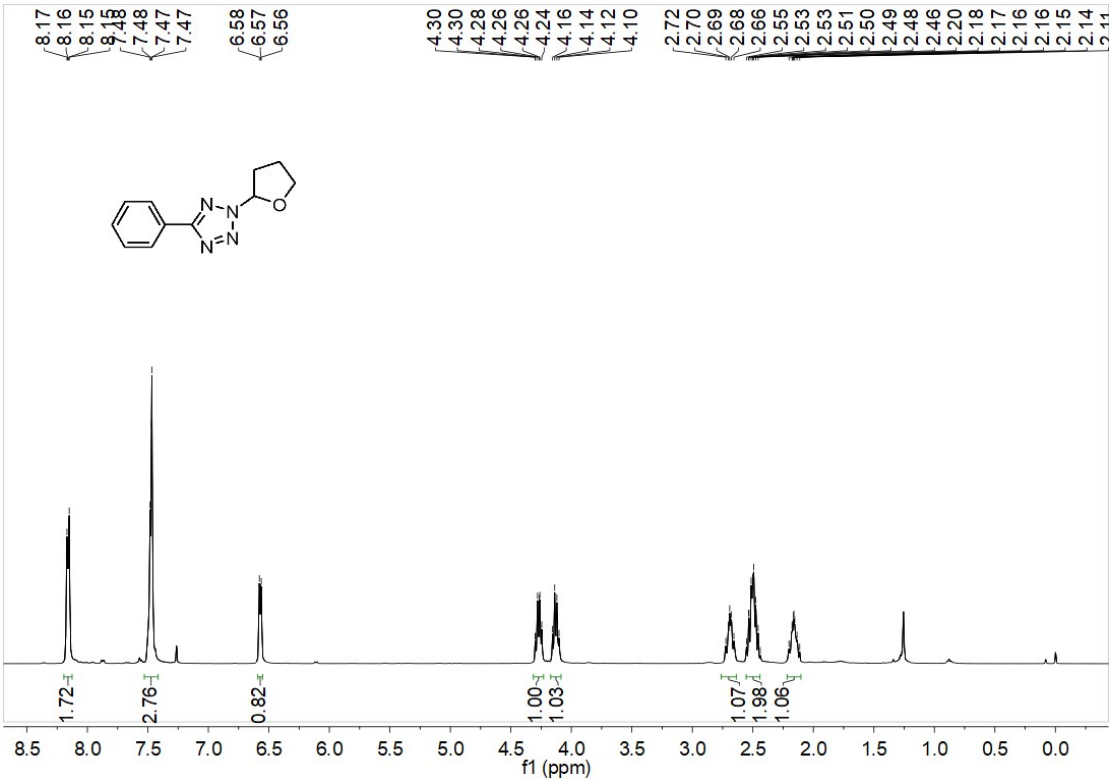
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



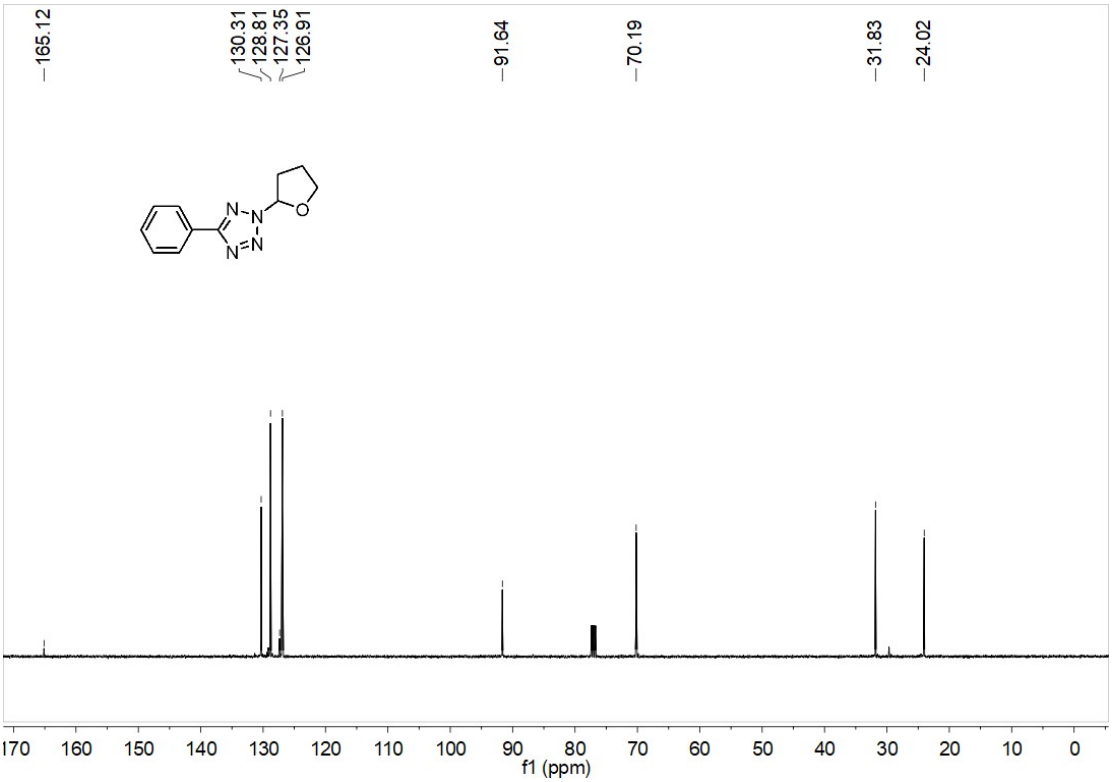
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



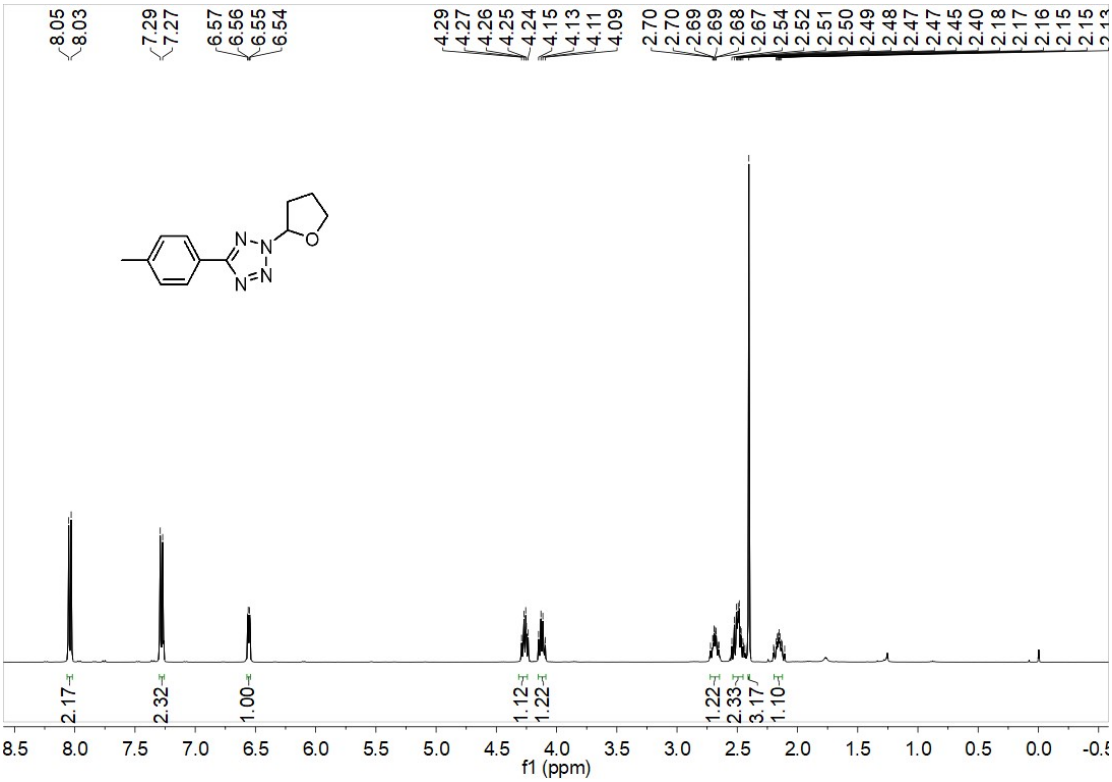
^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



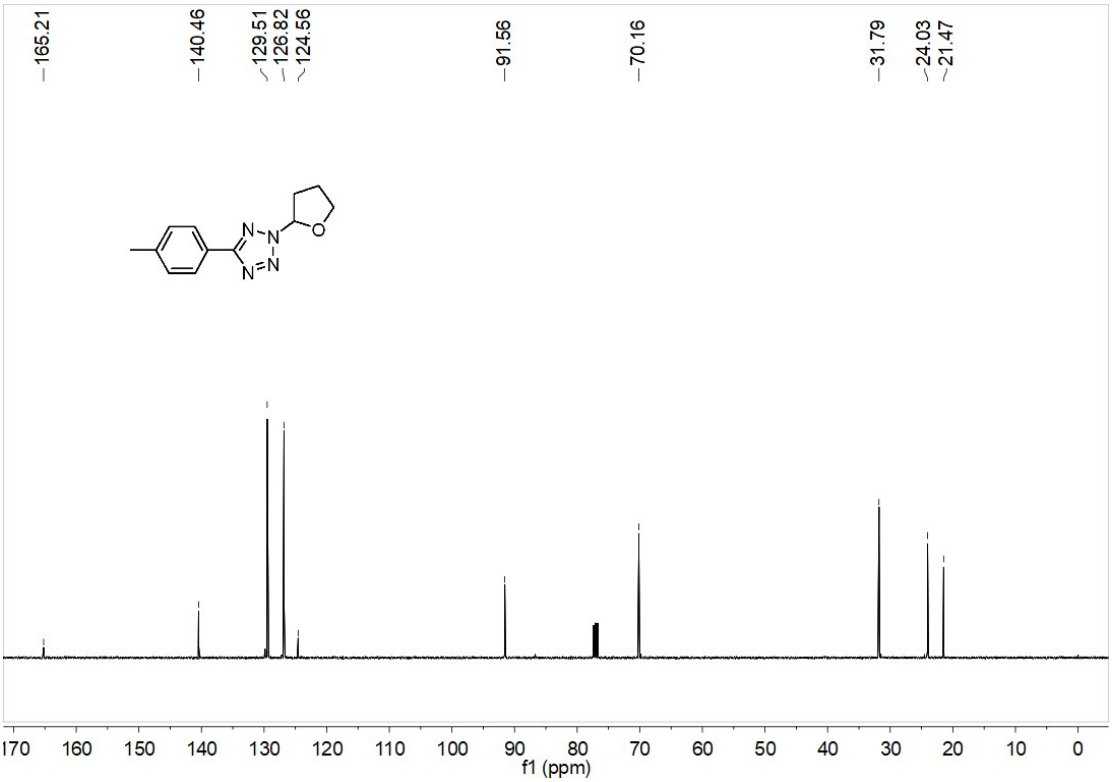
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



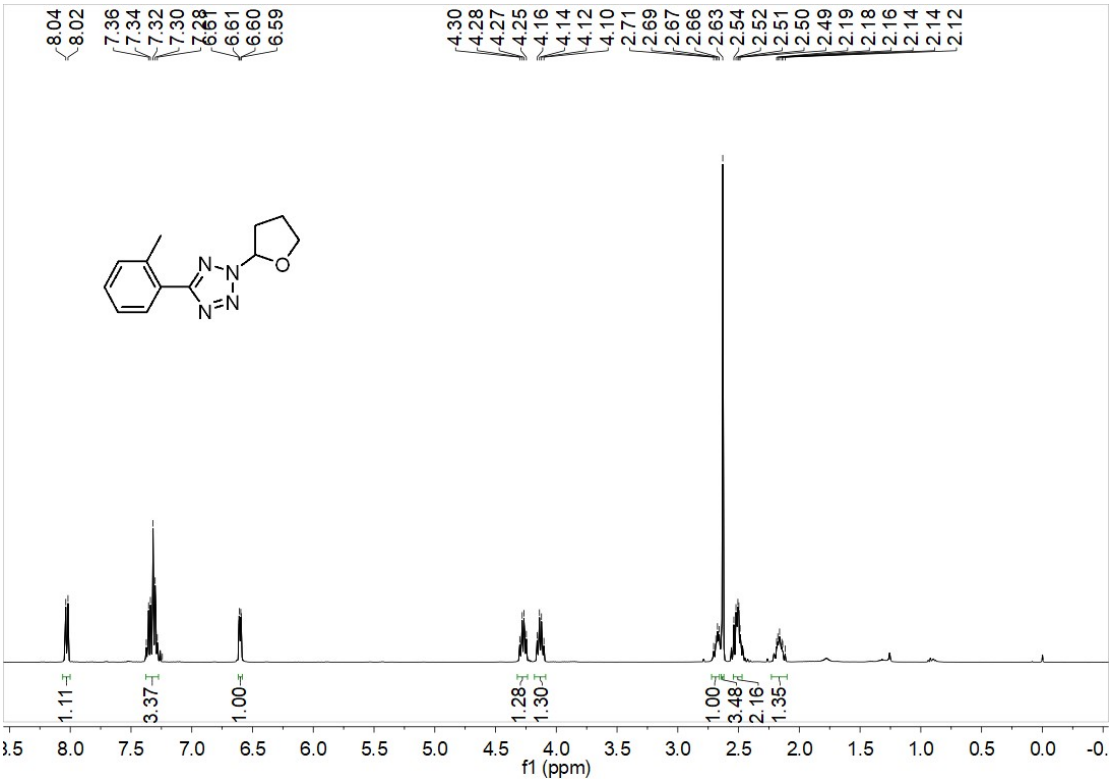
^{13}C NMR (101 MHz, $CDCl_3$) of **3w**



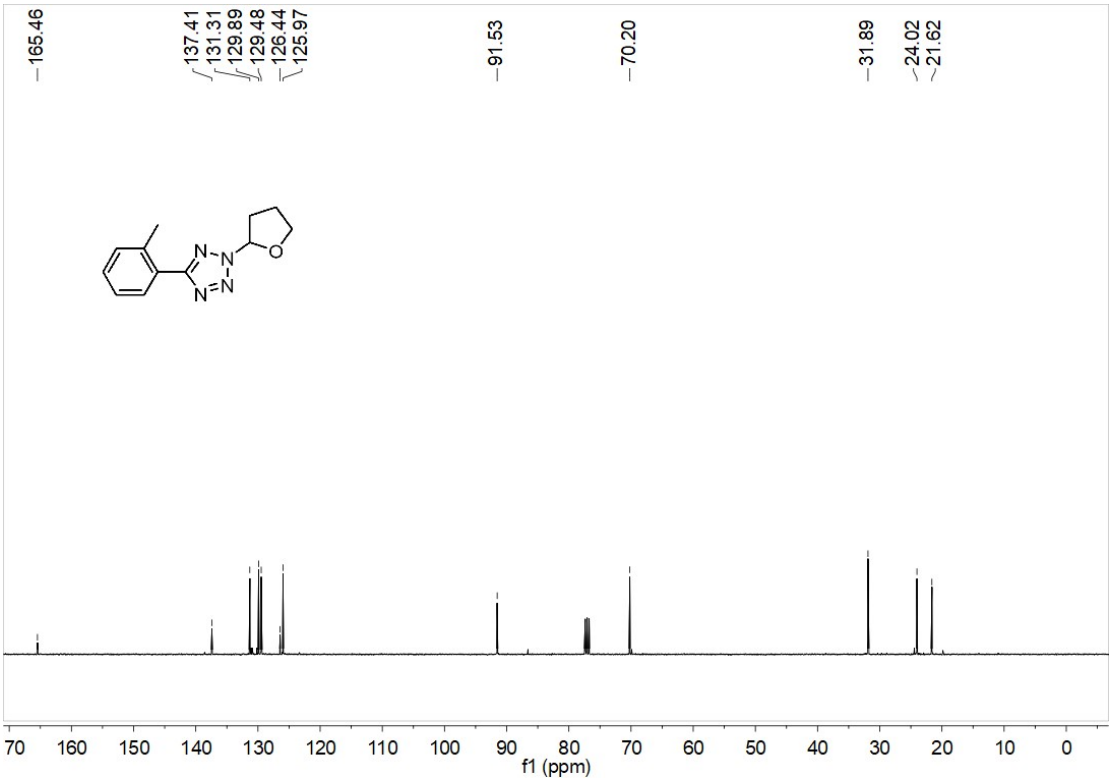
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



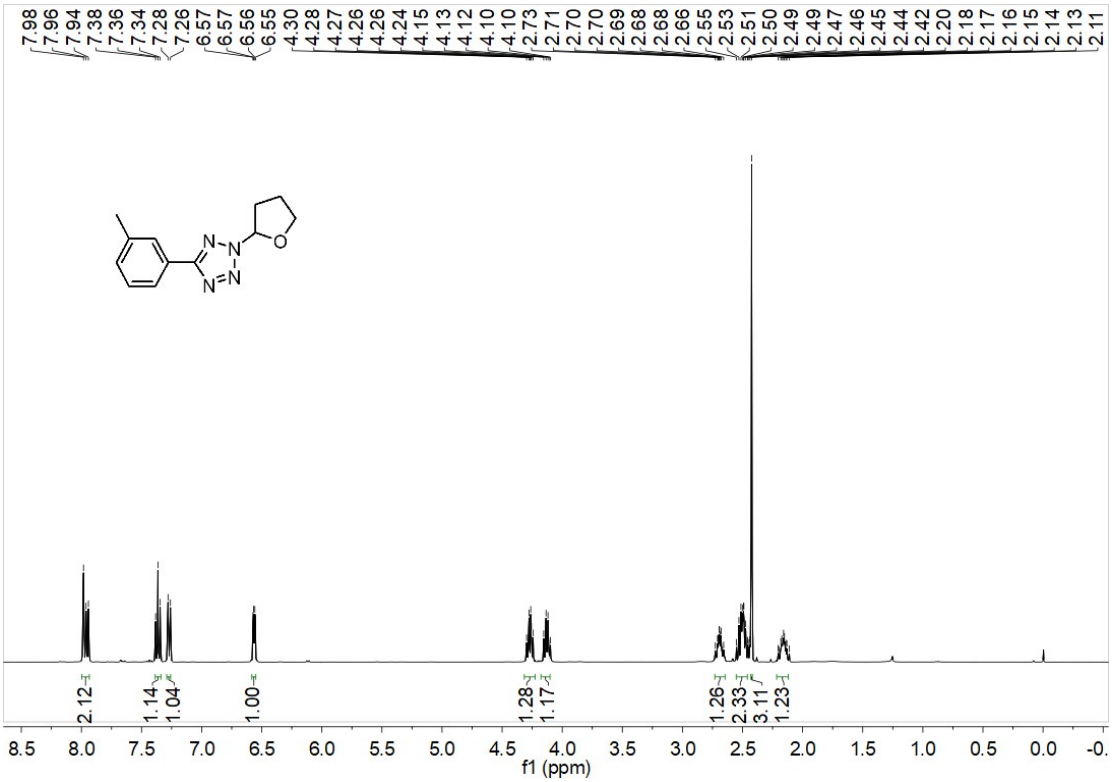
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



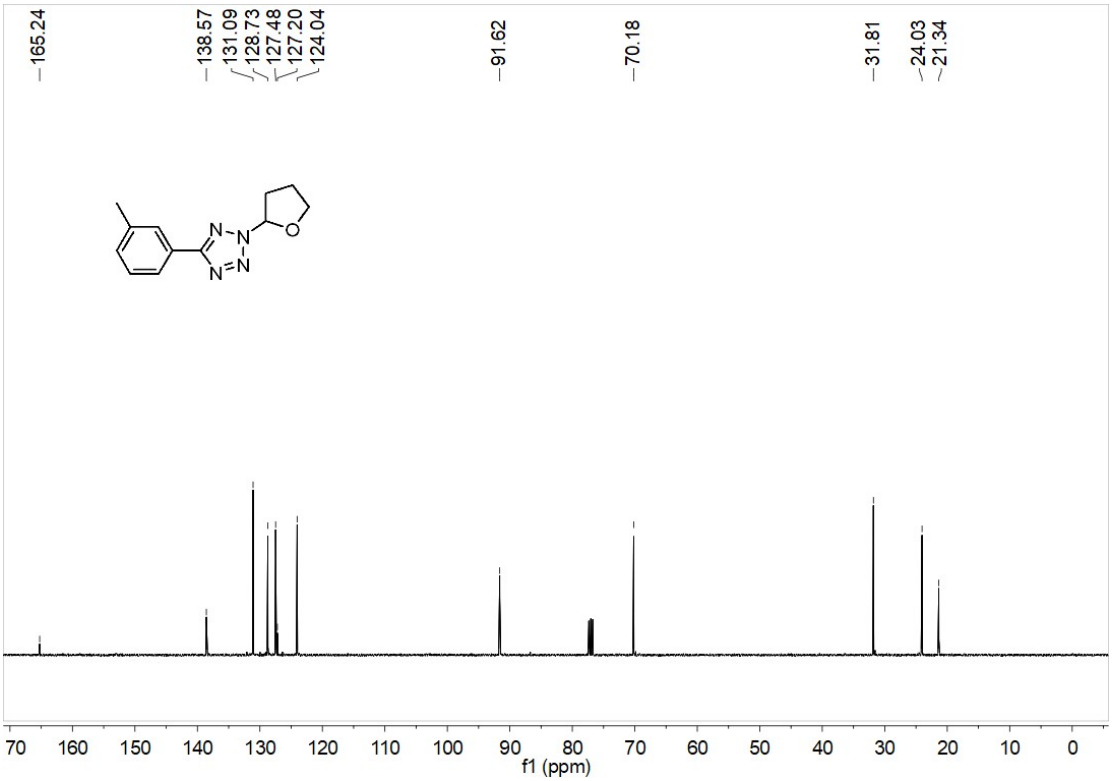
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



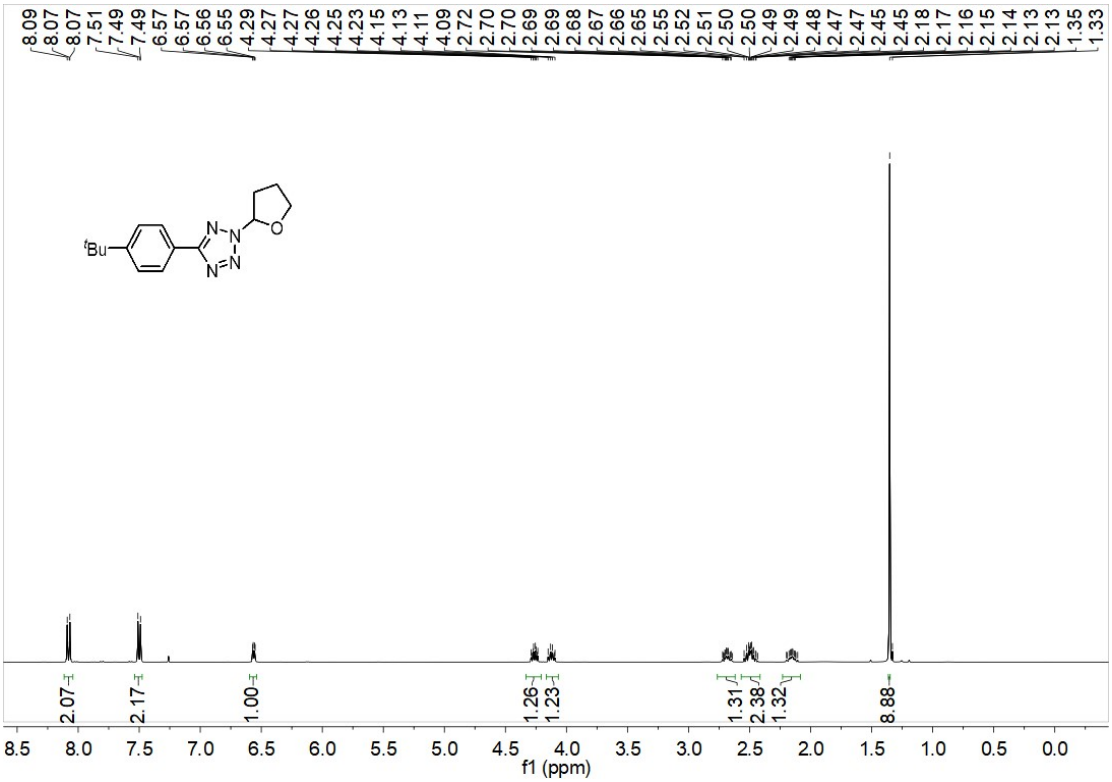
^{13}C NMR (101 MHz, $CDCl_3$) of **3y**



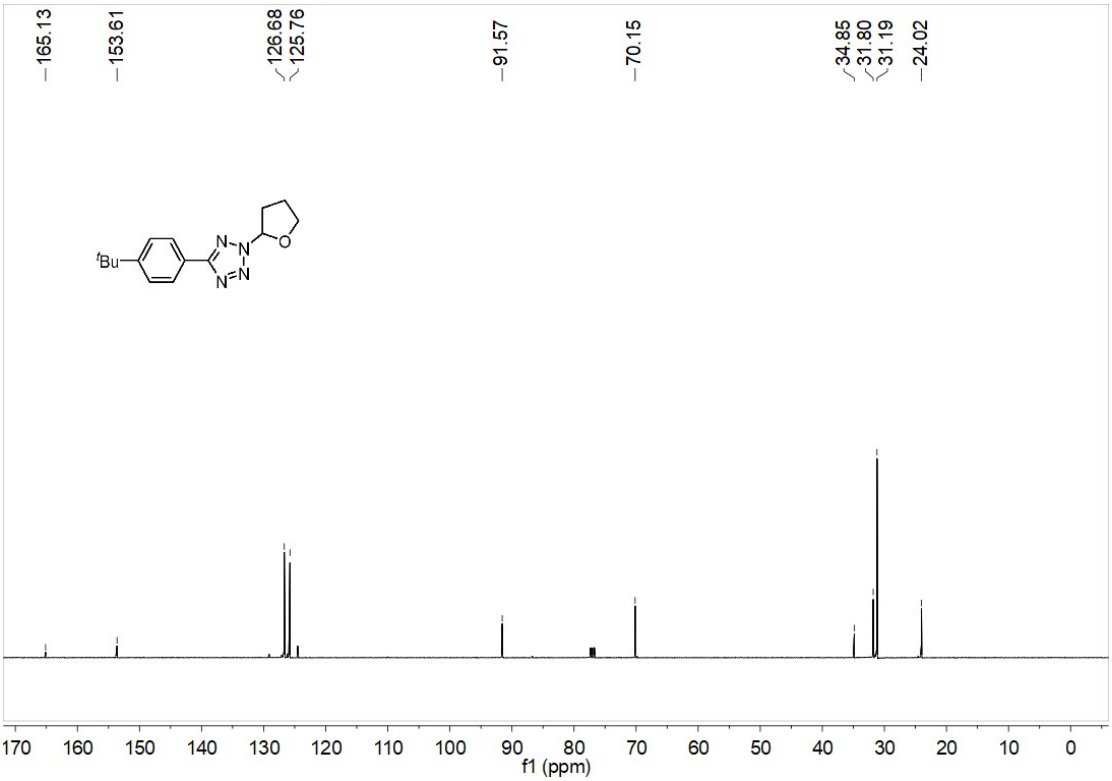
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



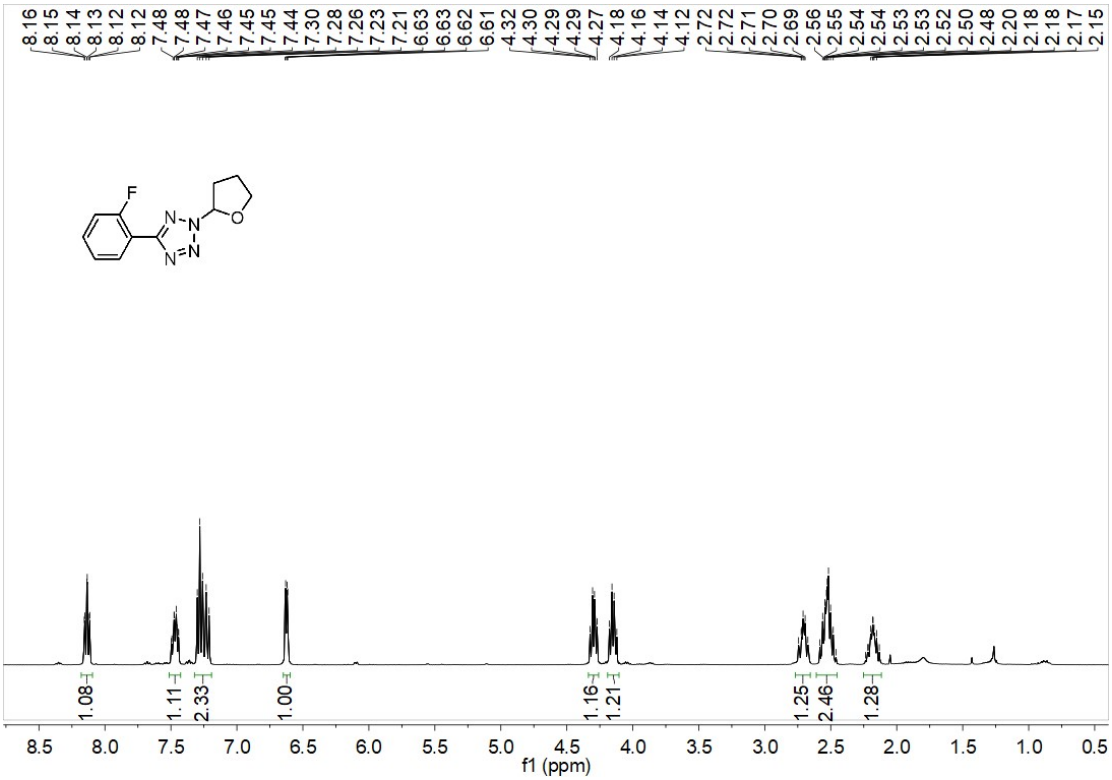
^{13}C NMR (101 MHz, $CDCl_3$) of **3z**



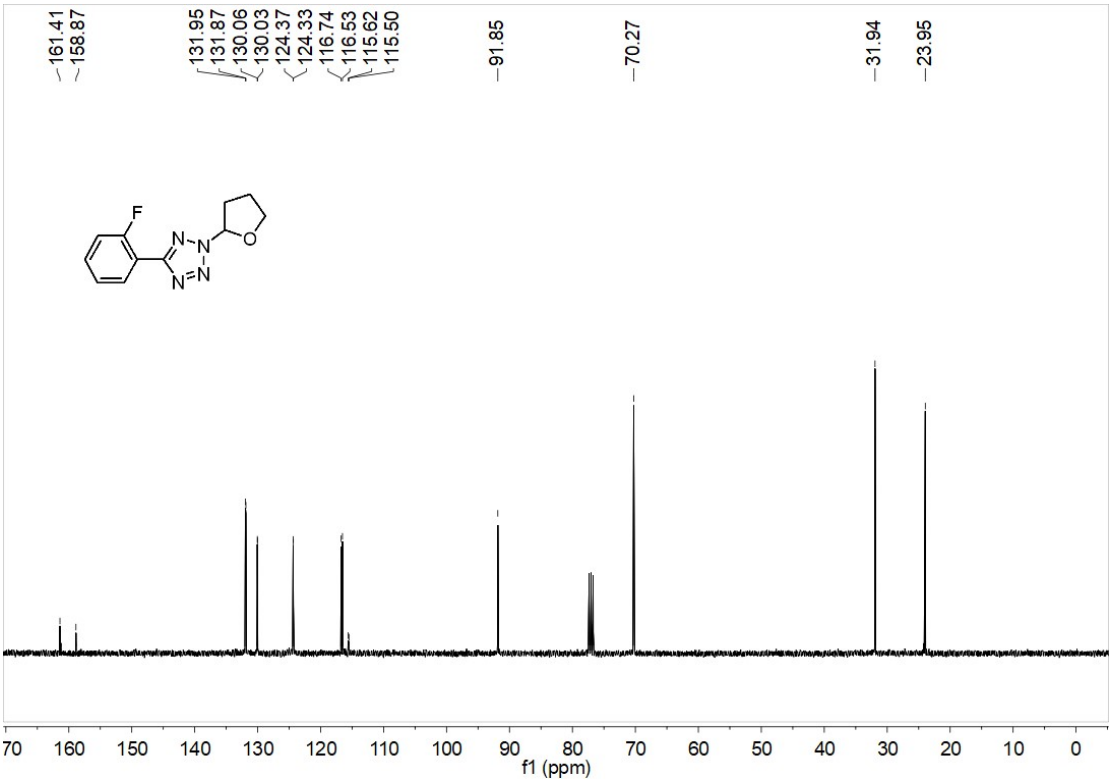
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



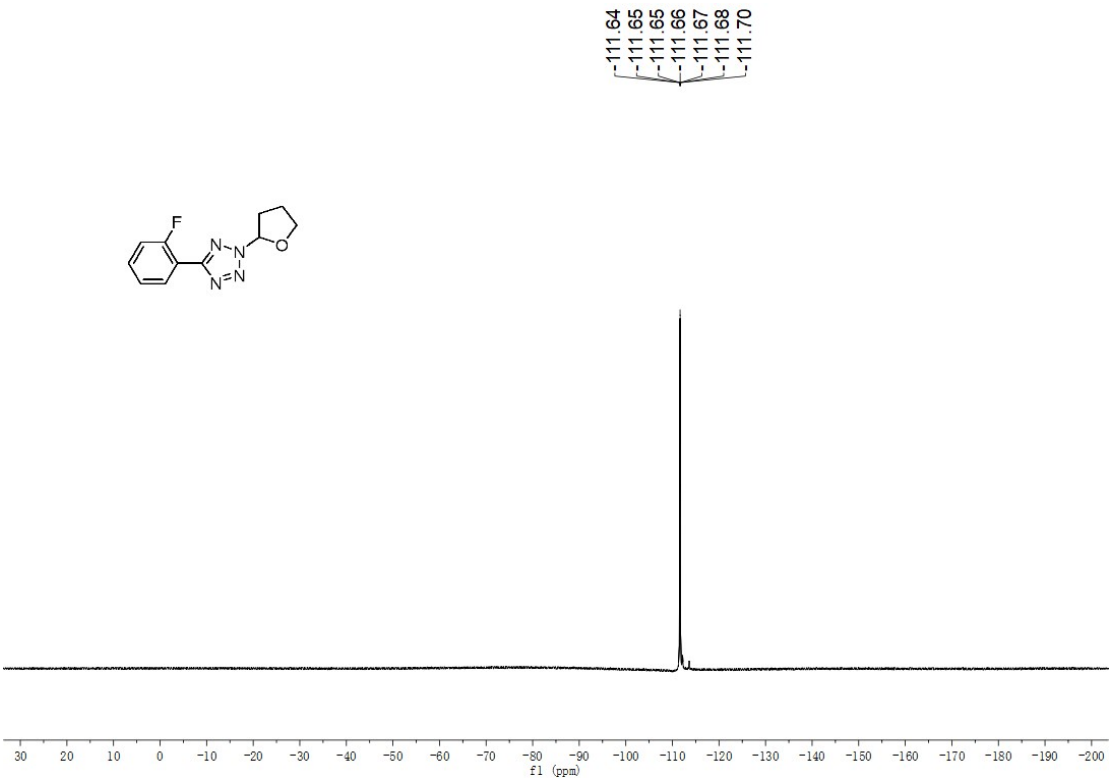
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



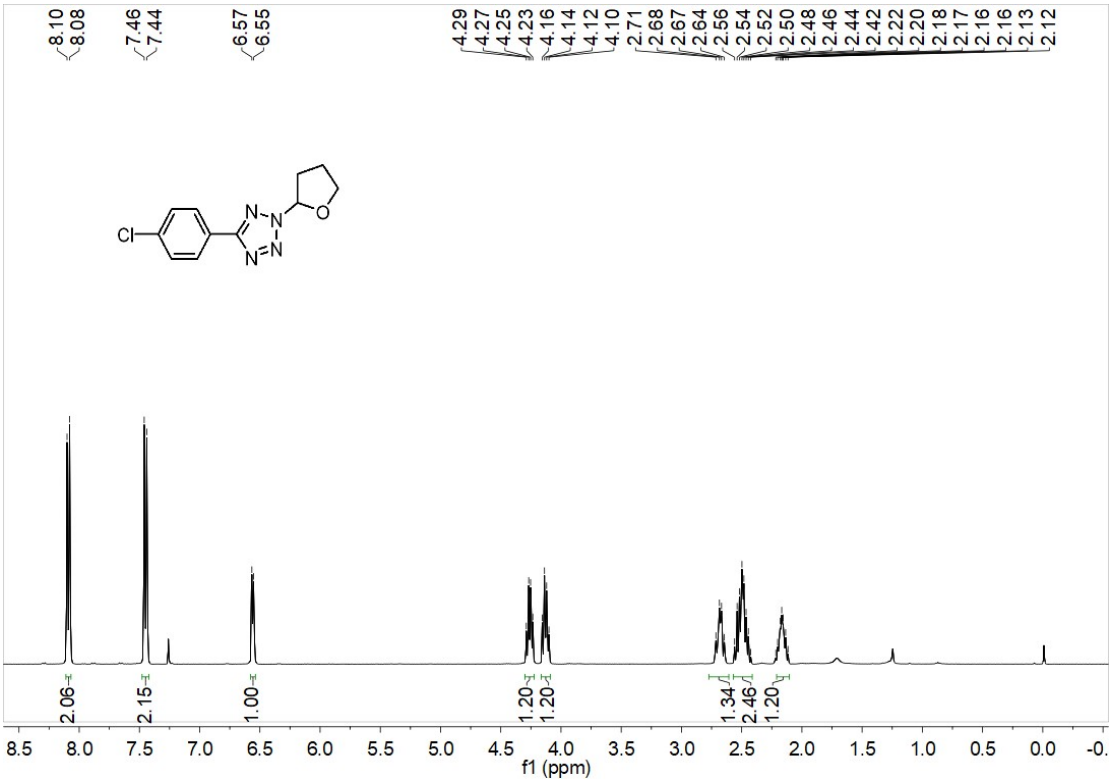
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



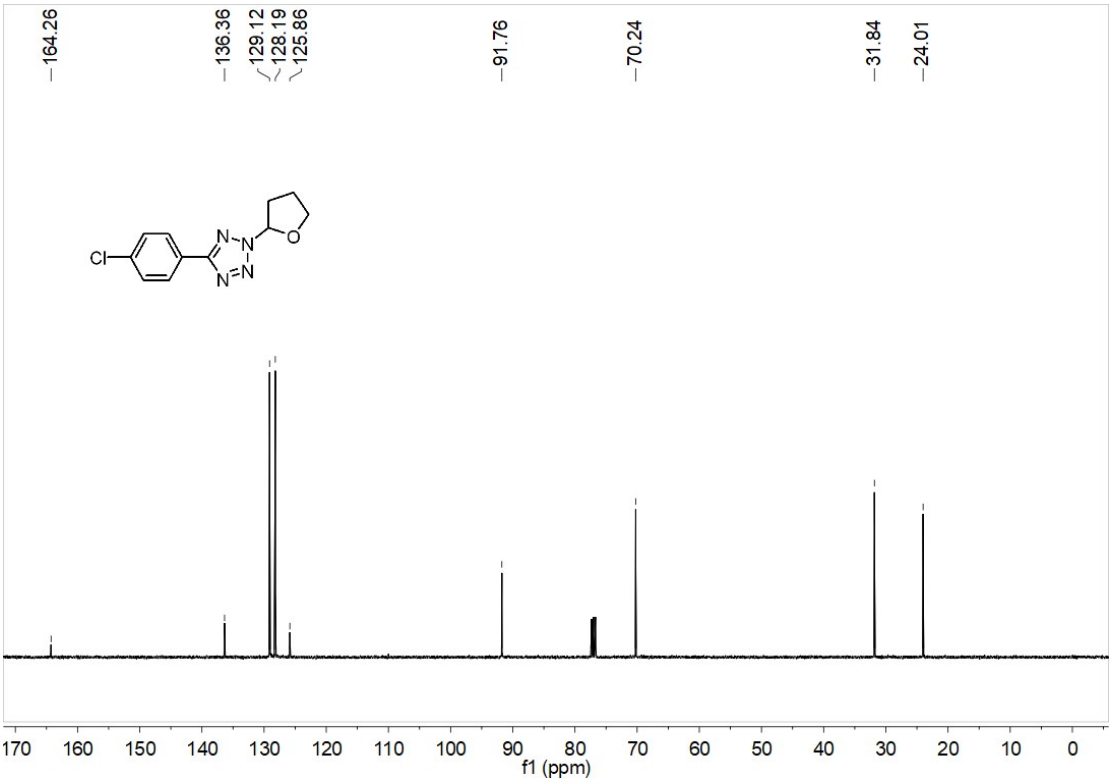
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



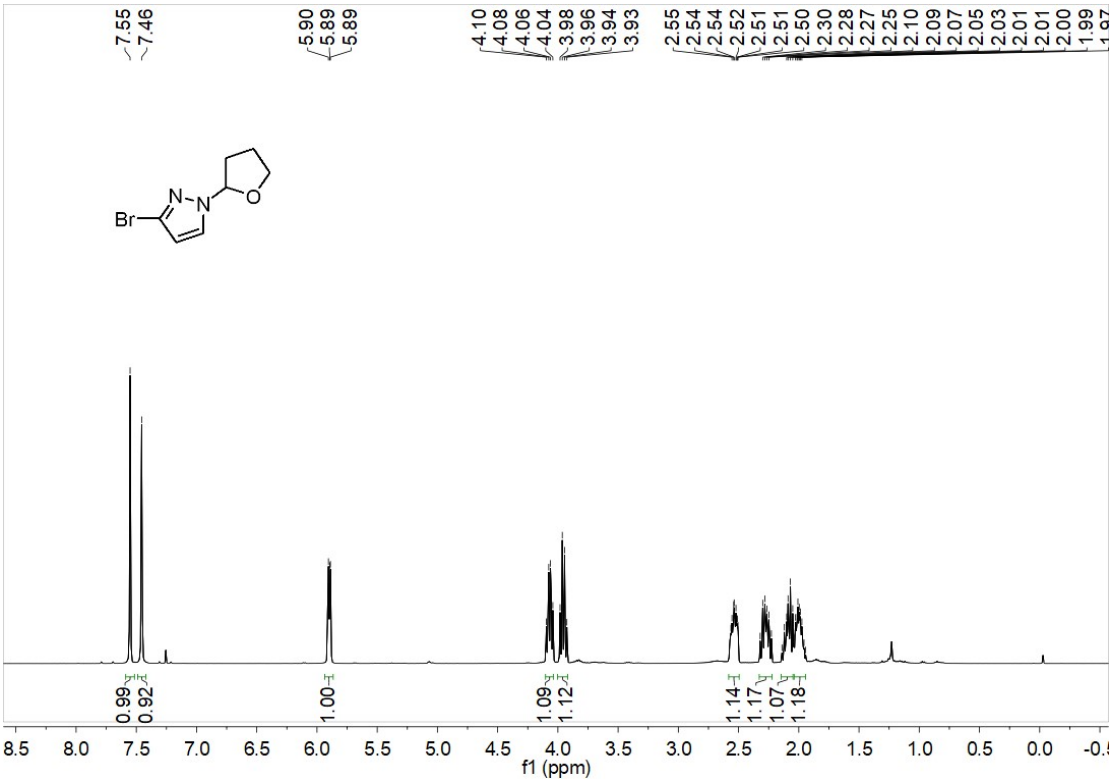
^{19}F NMR (376 MHz, $CDCl_3$) of **3ab**



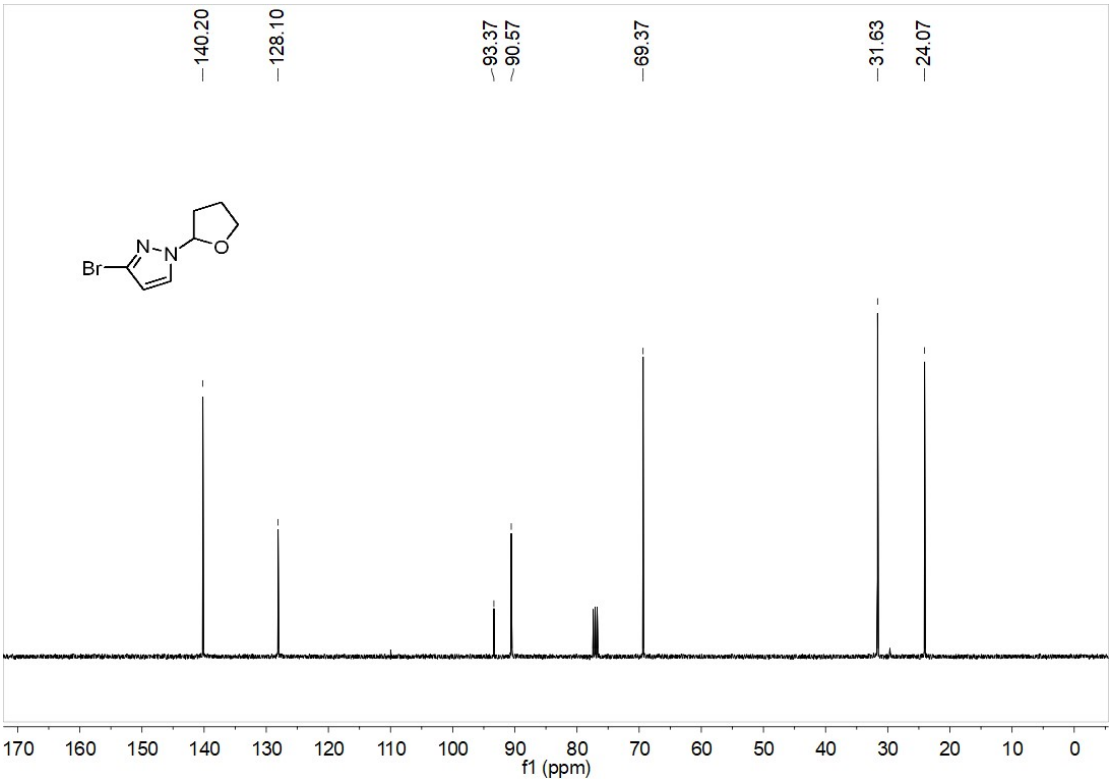
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



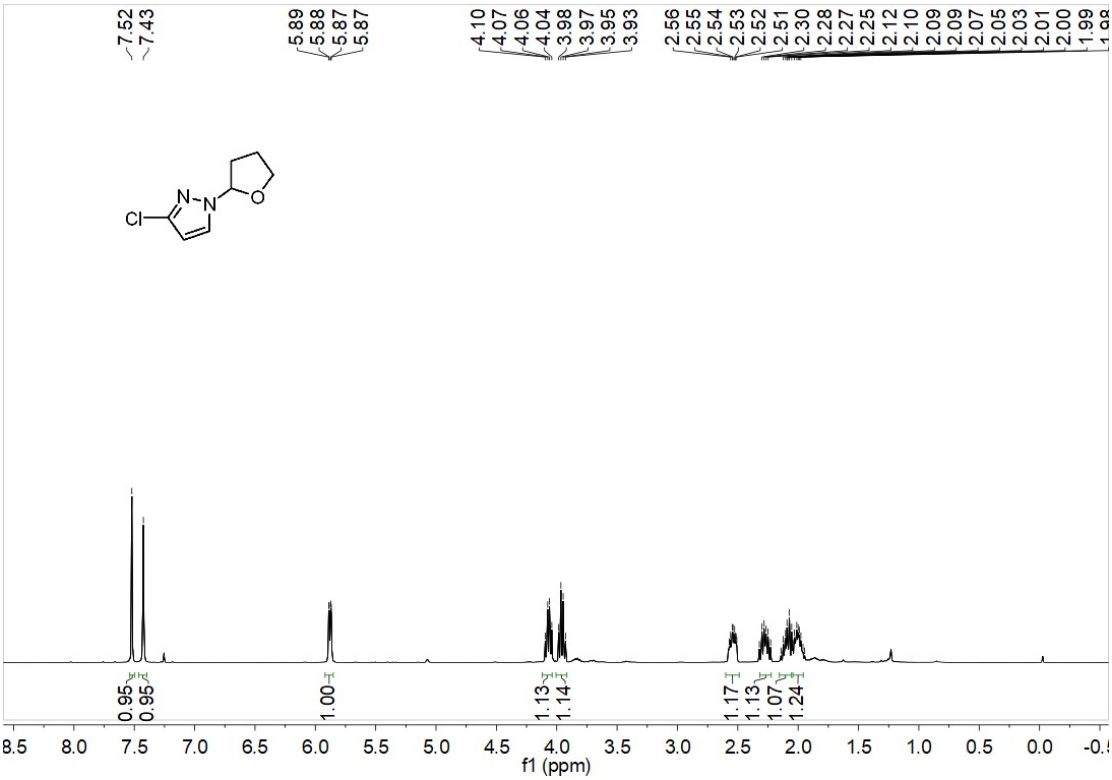
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



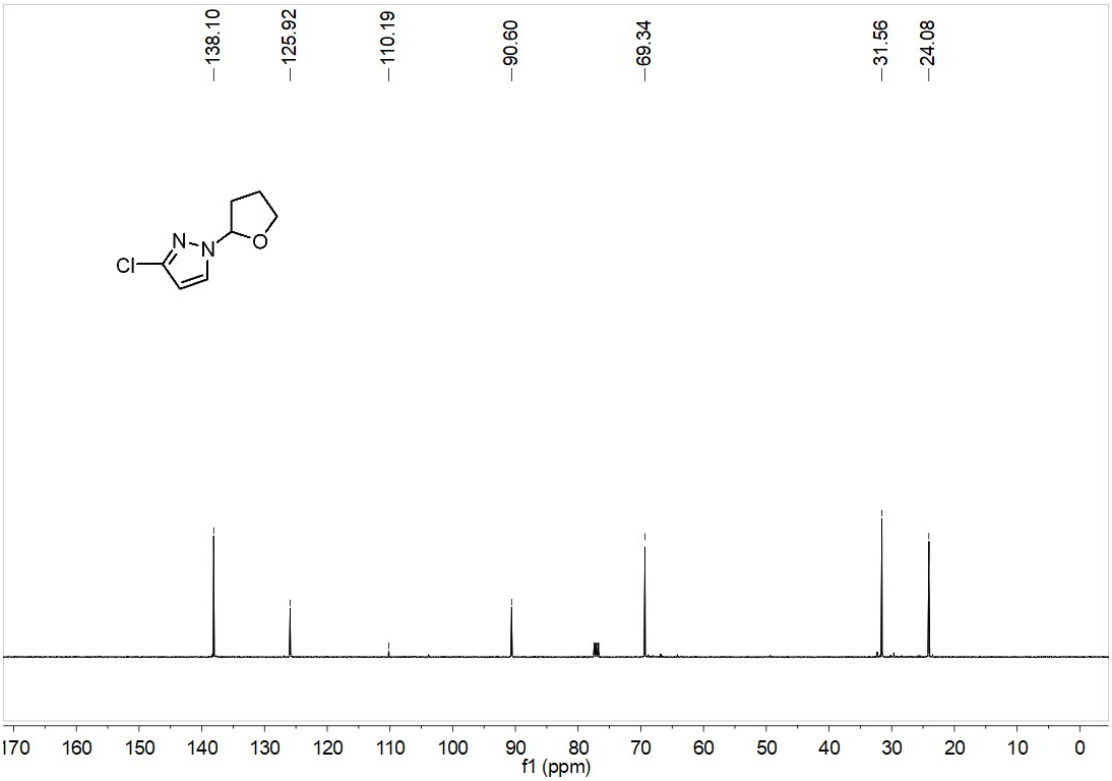
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



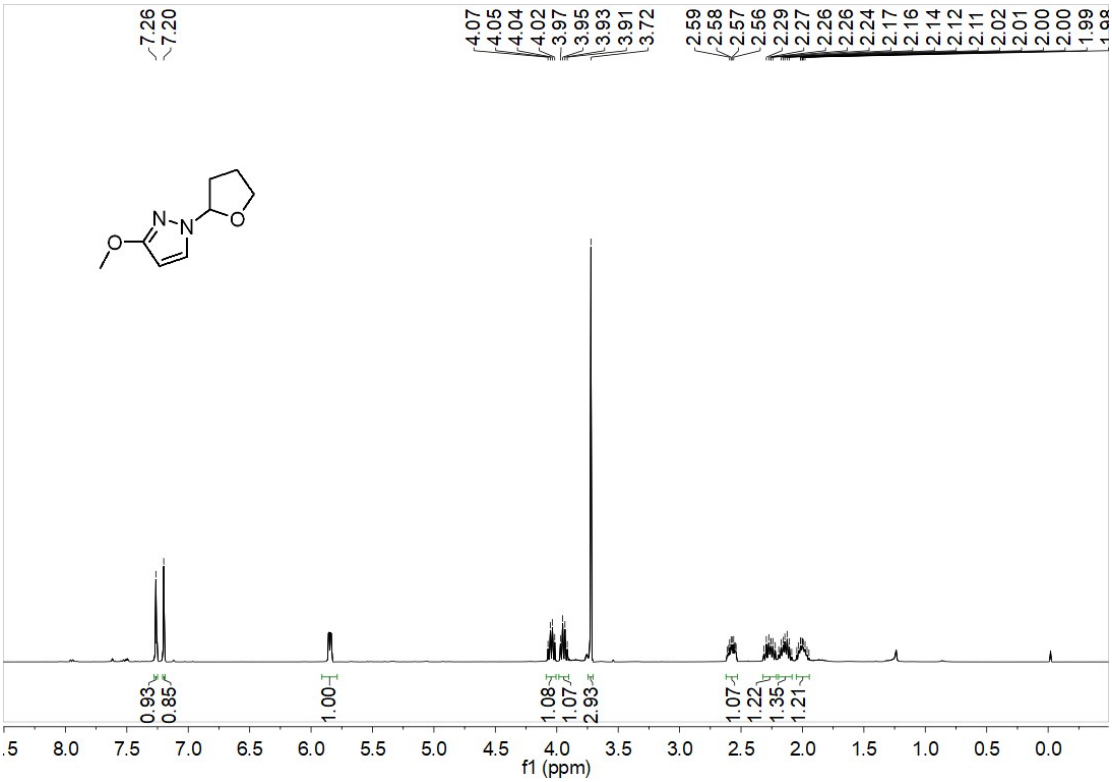
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



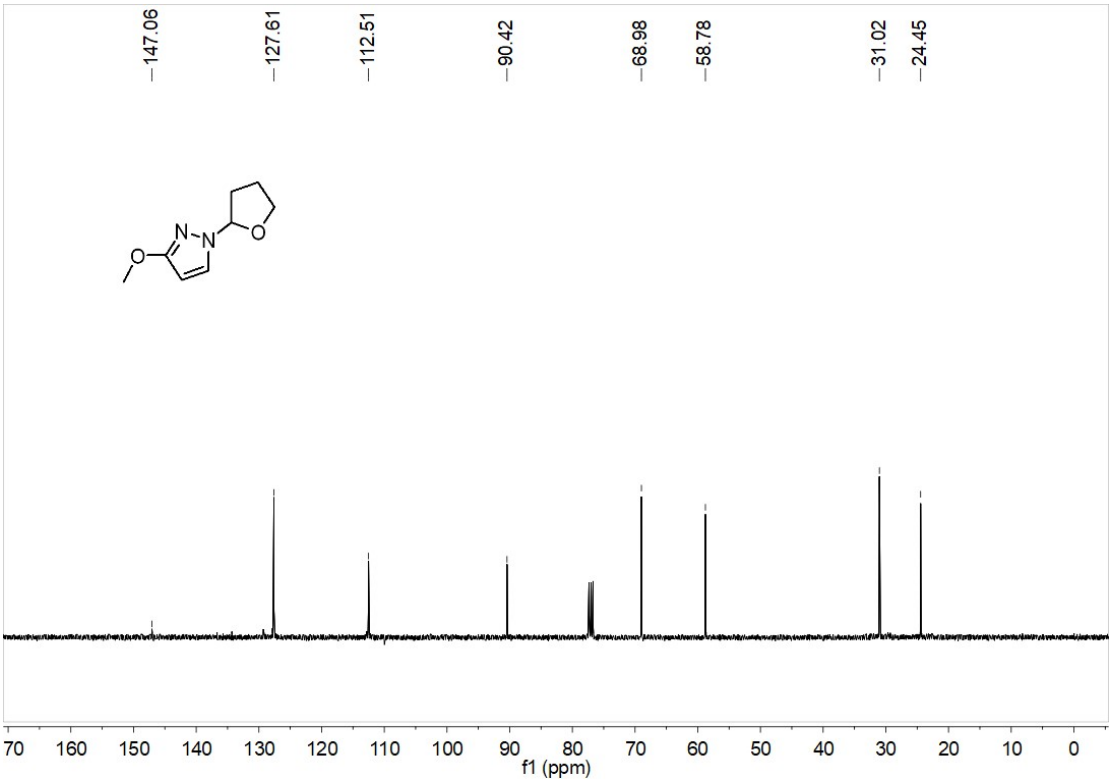
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



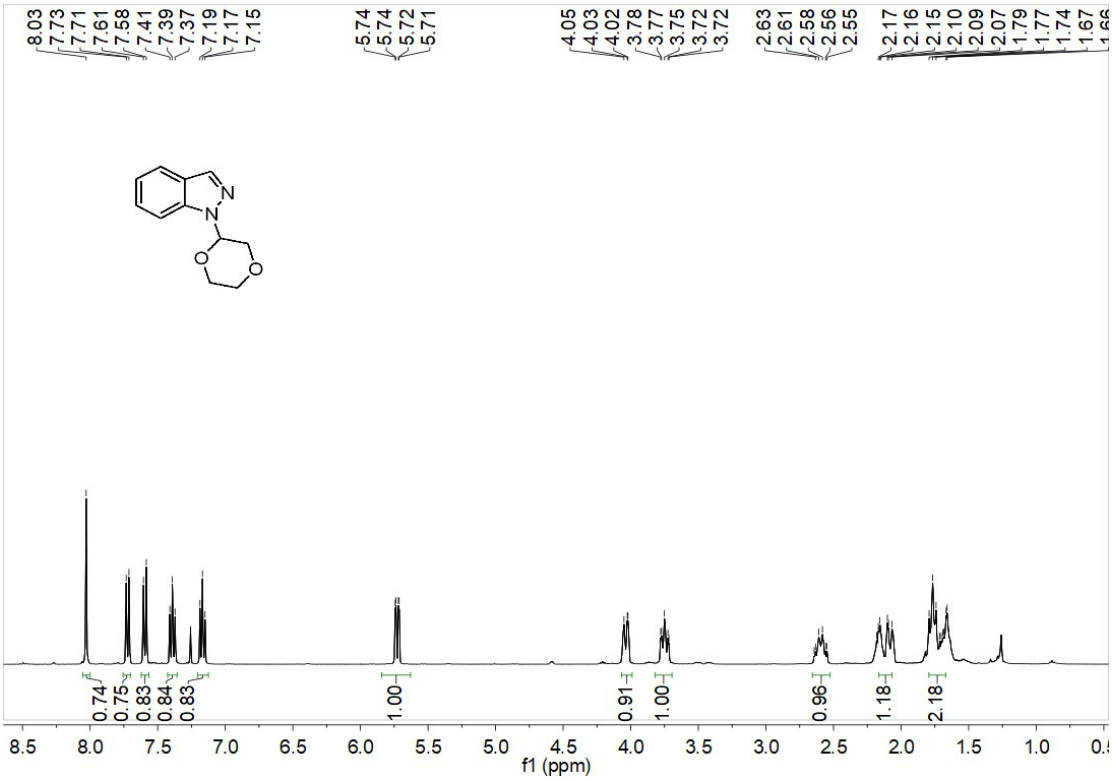
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



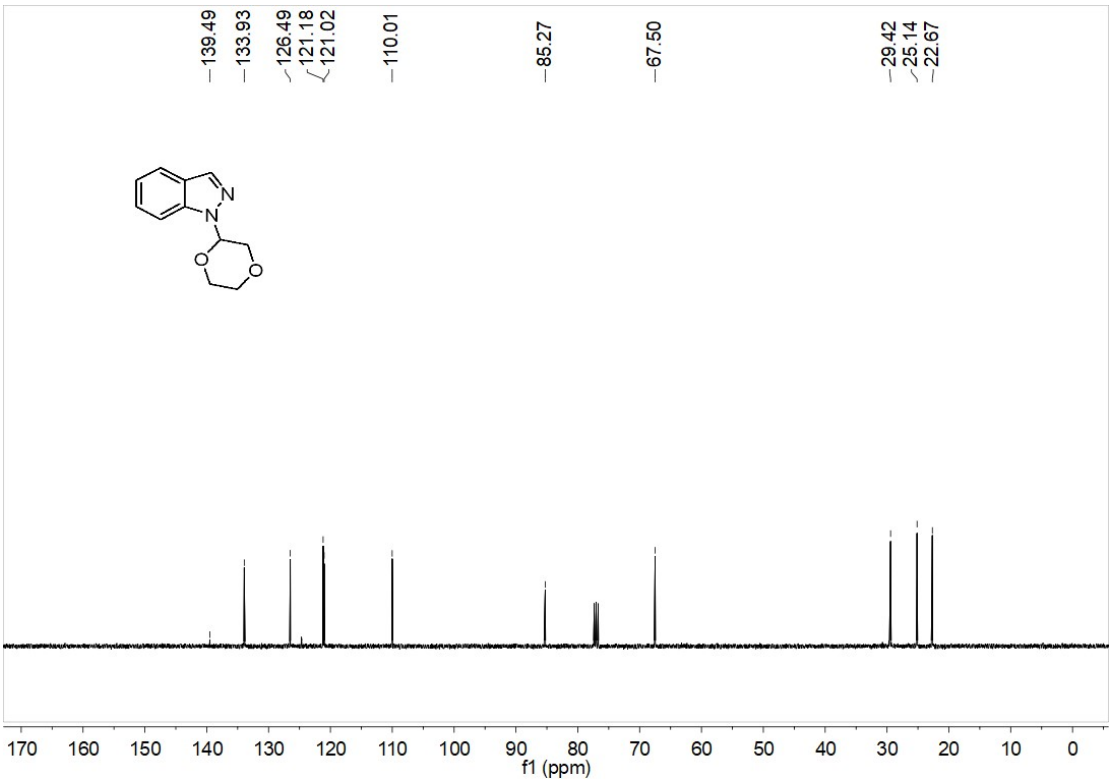
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



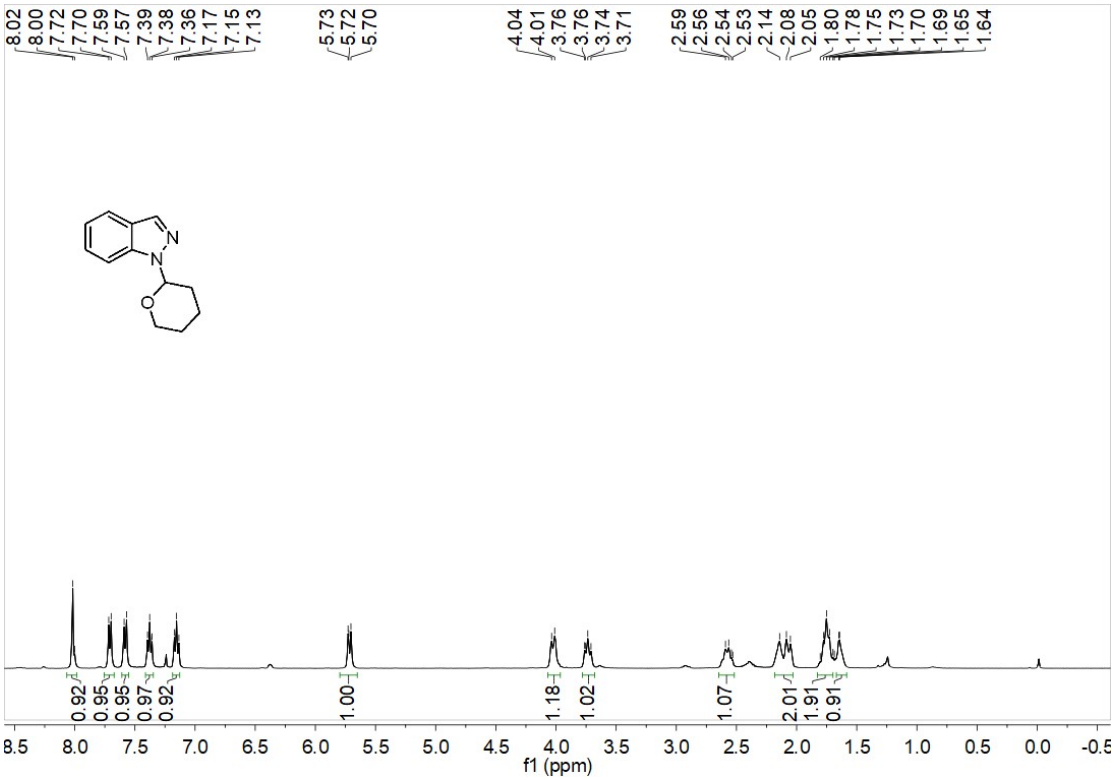
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



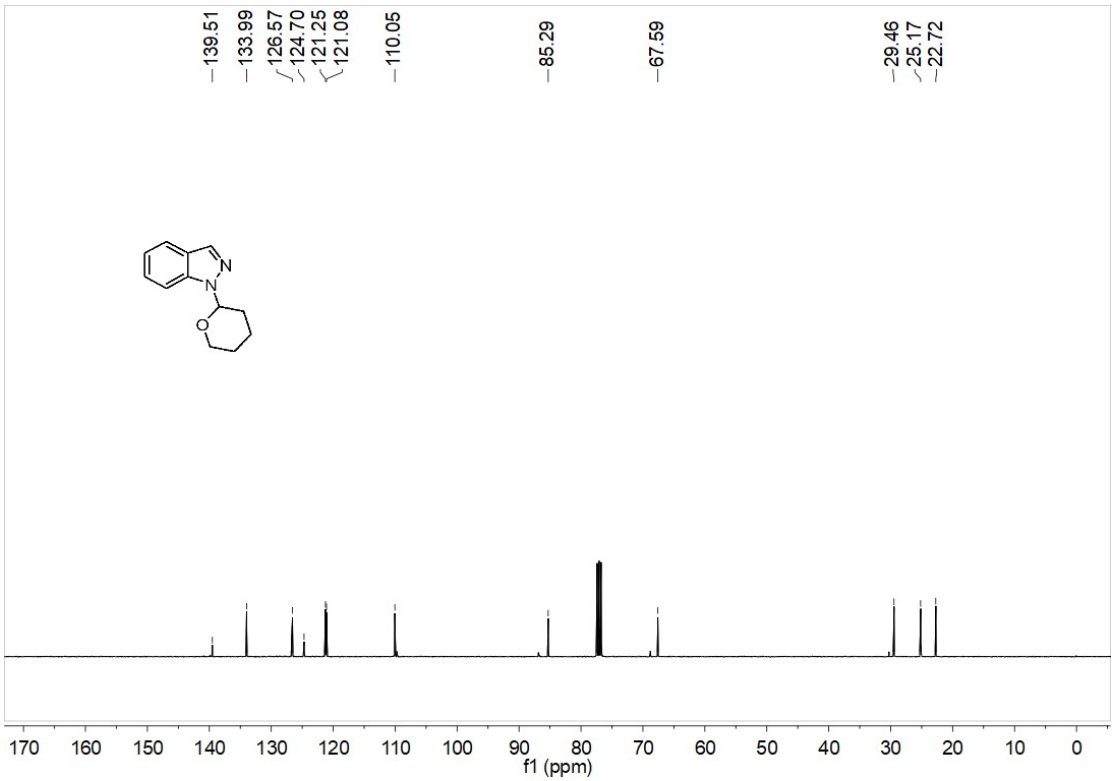
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



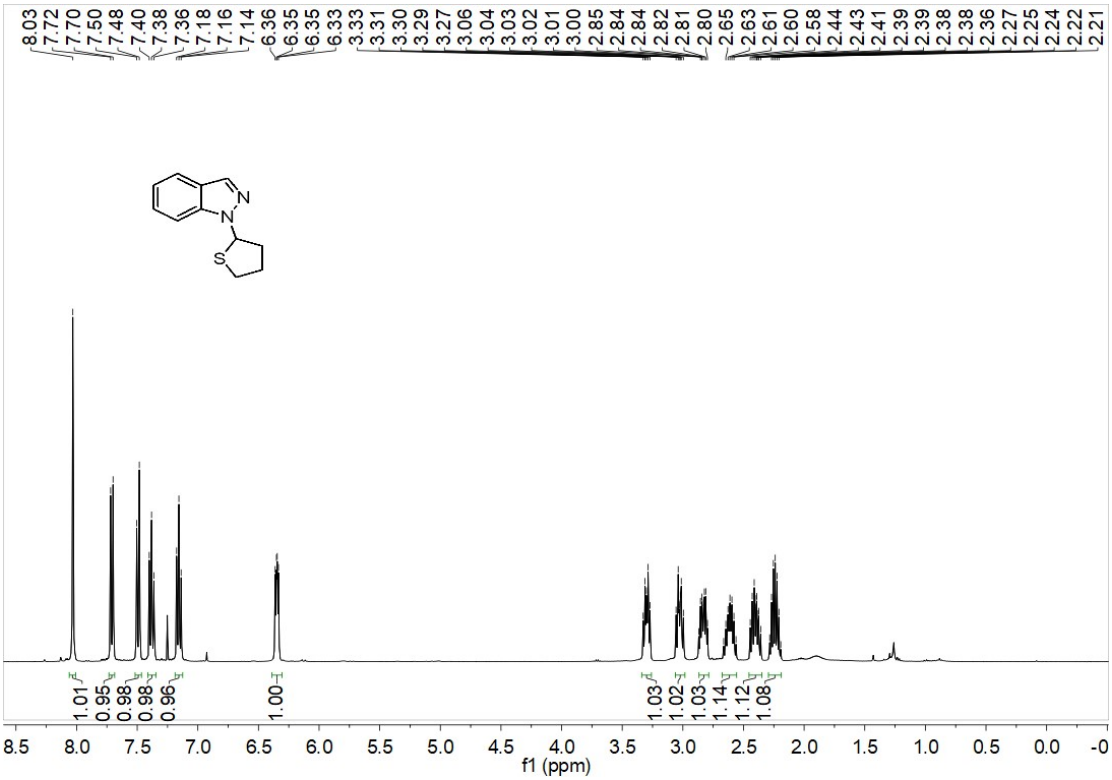
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



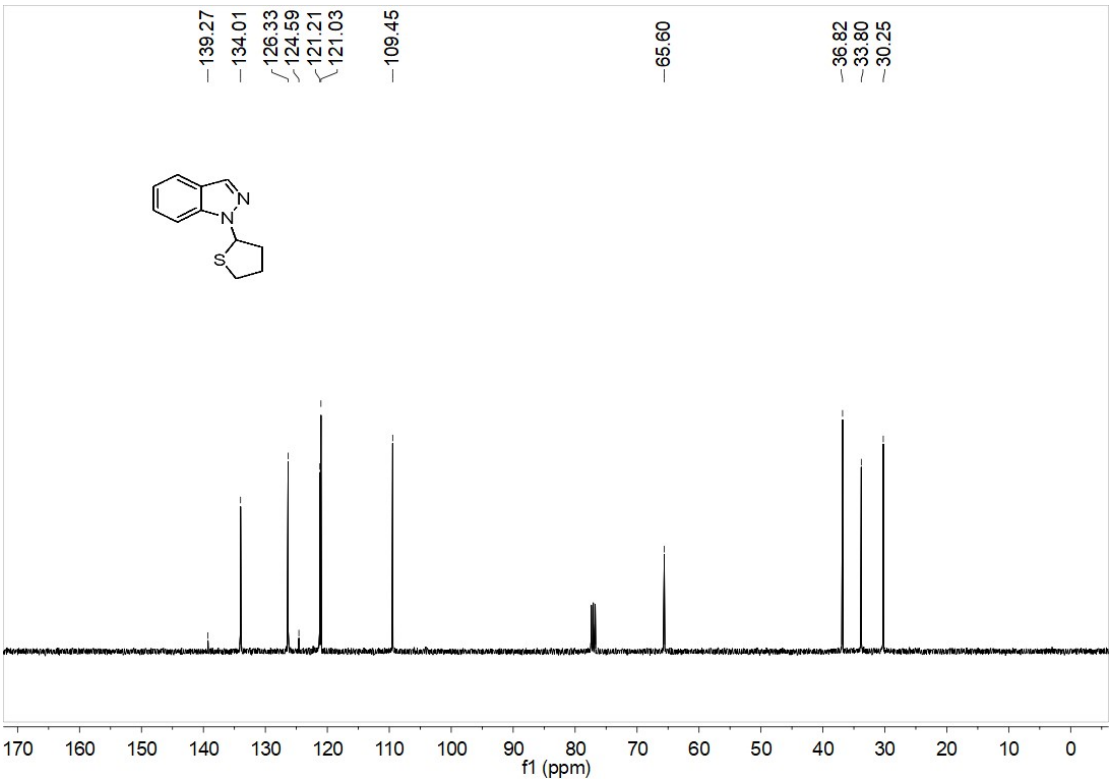
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



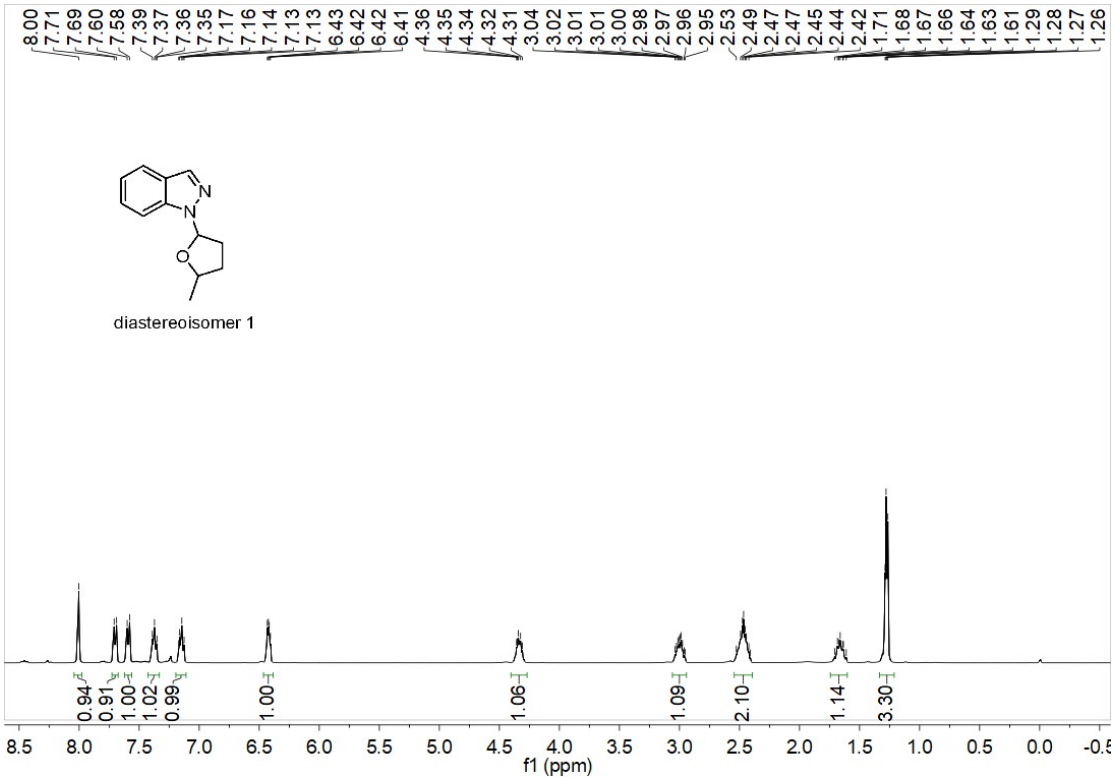
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**



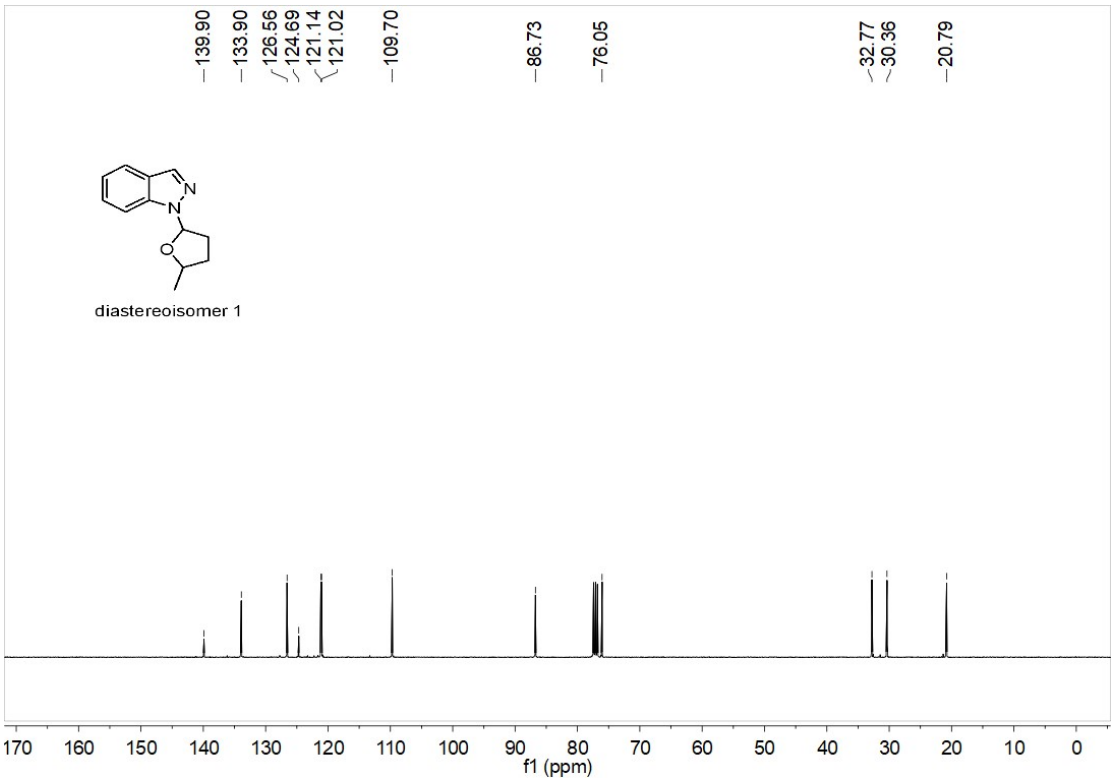
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



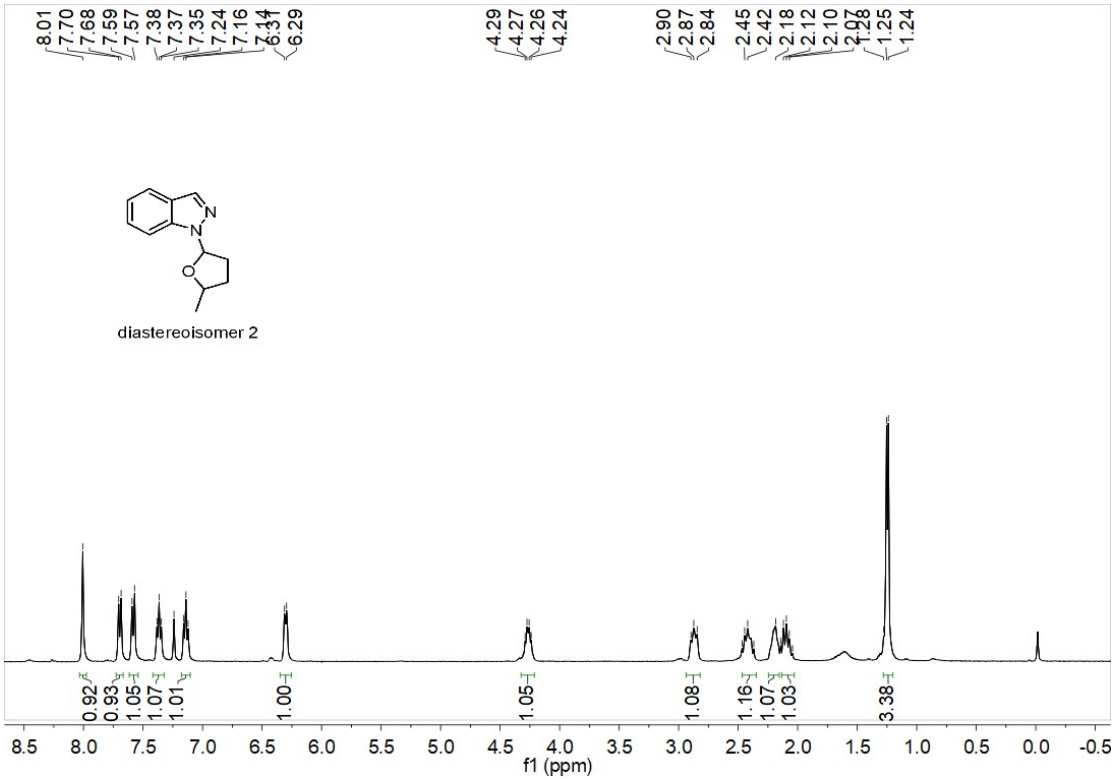
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



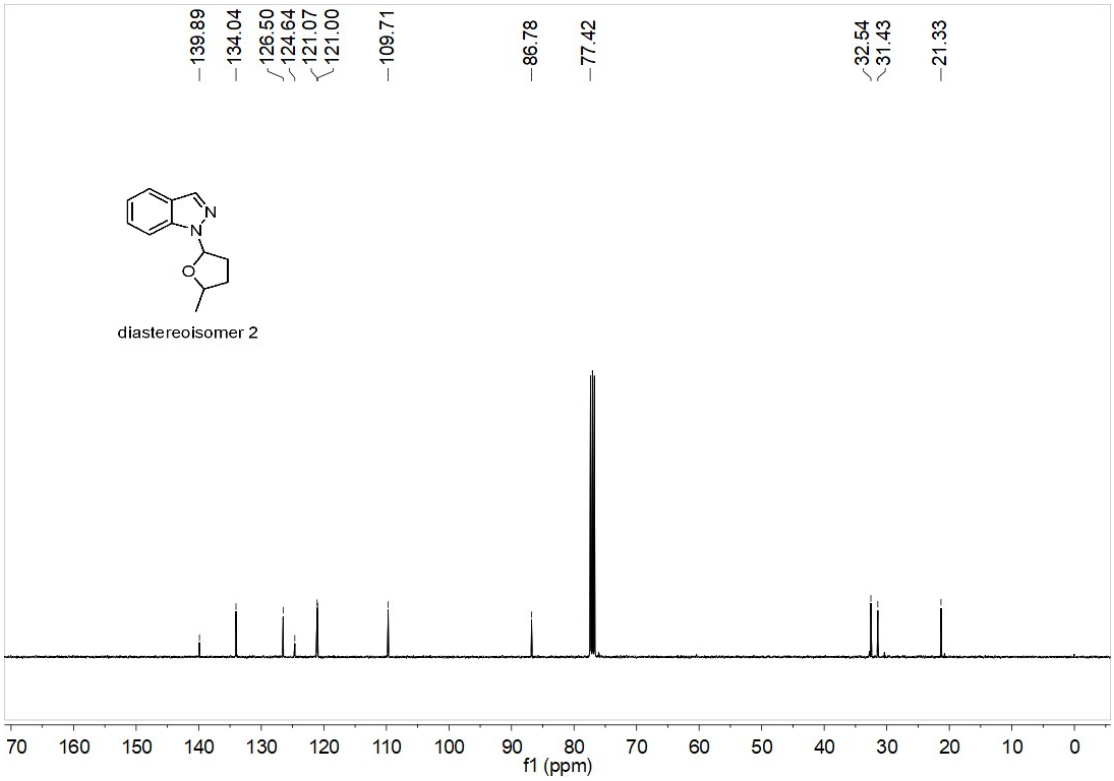
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



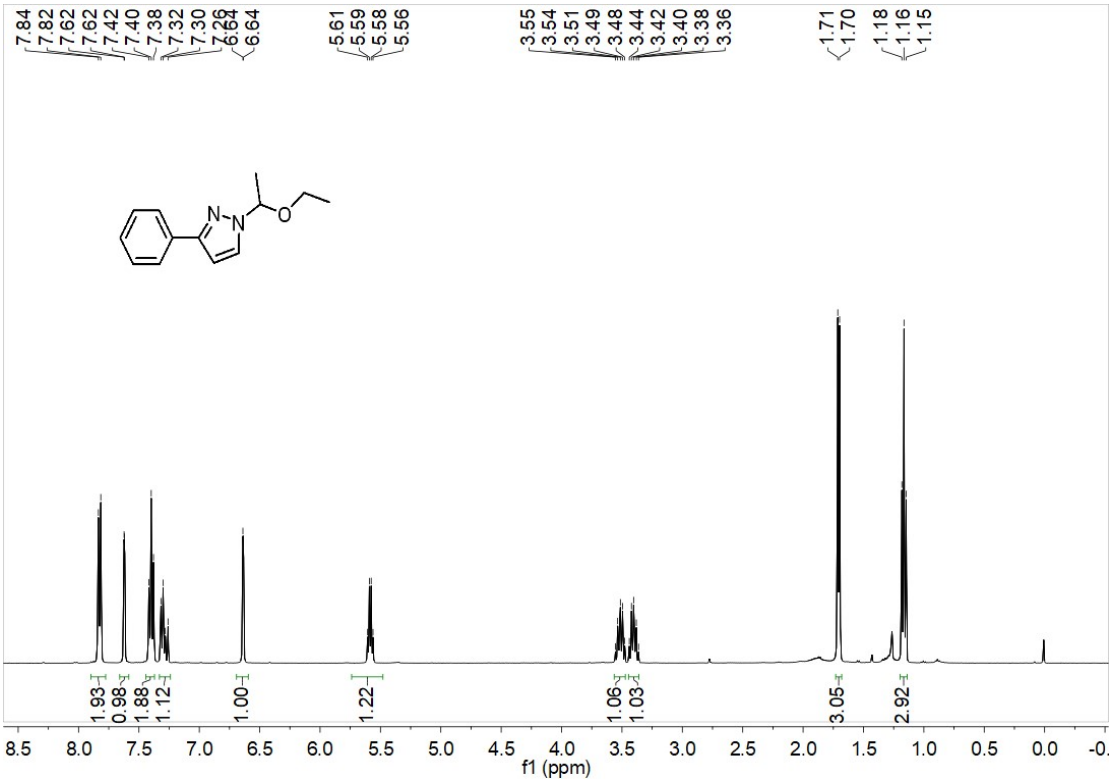
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



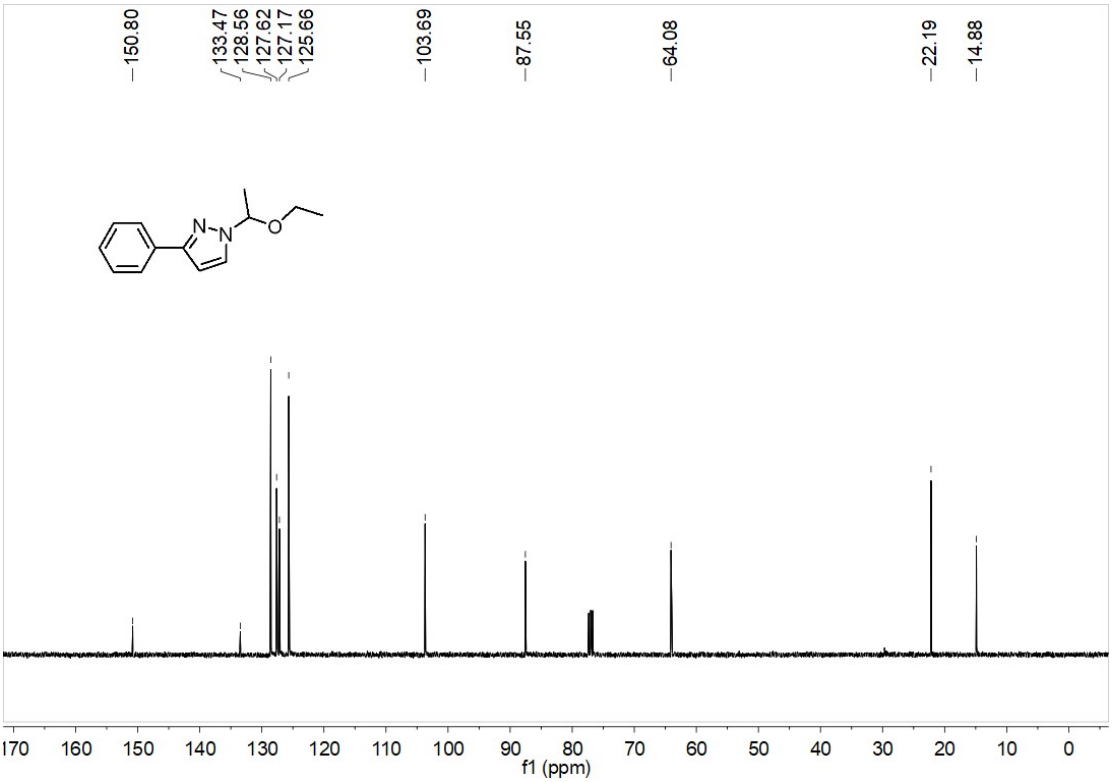
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



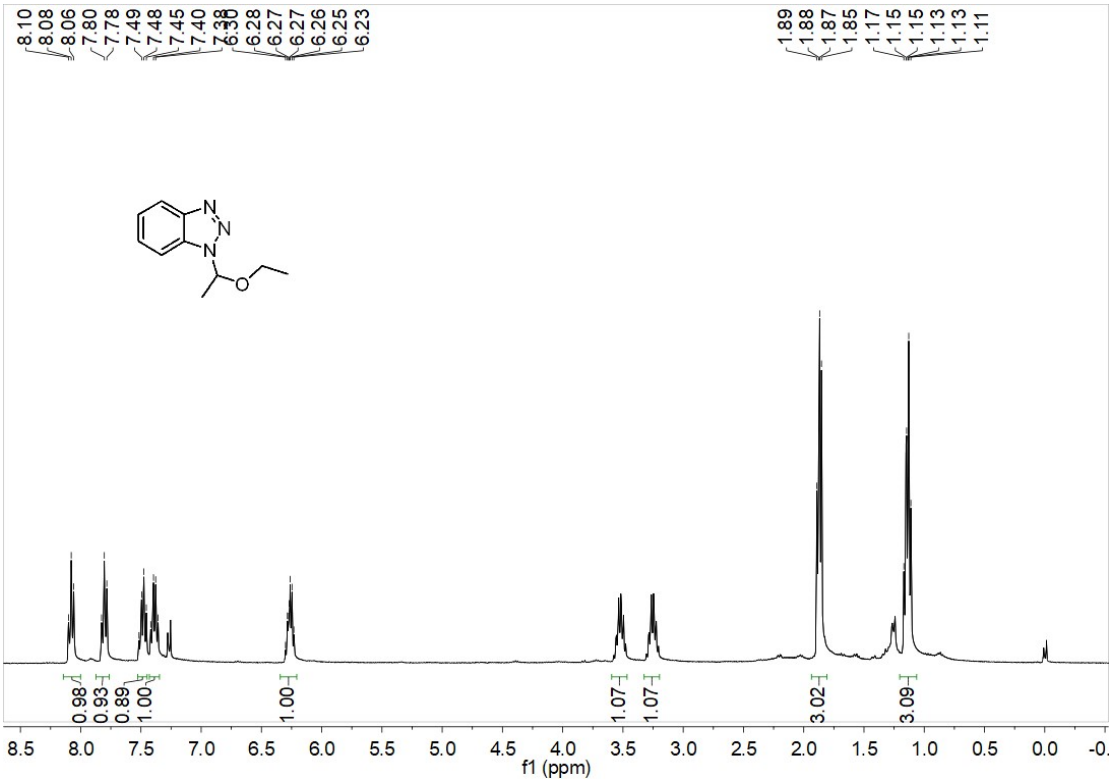
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



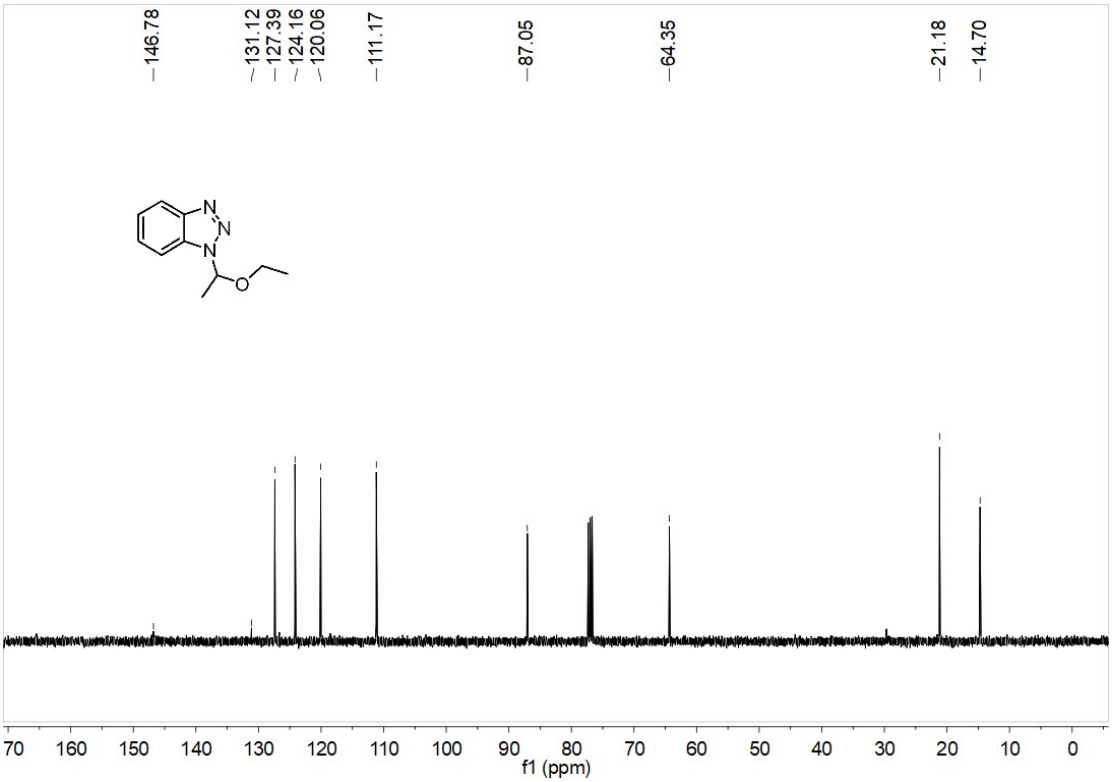
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



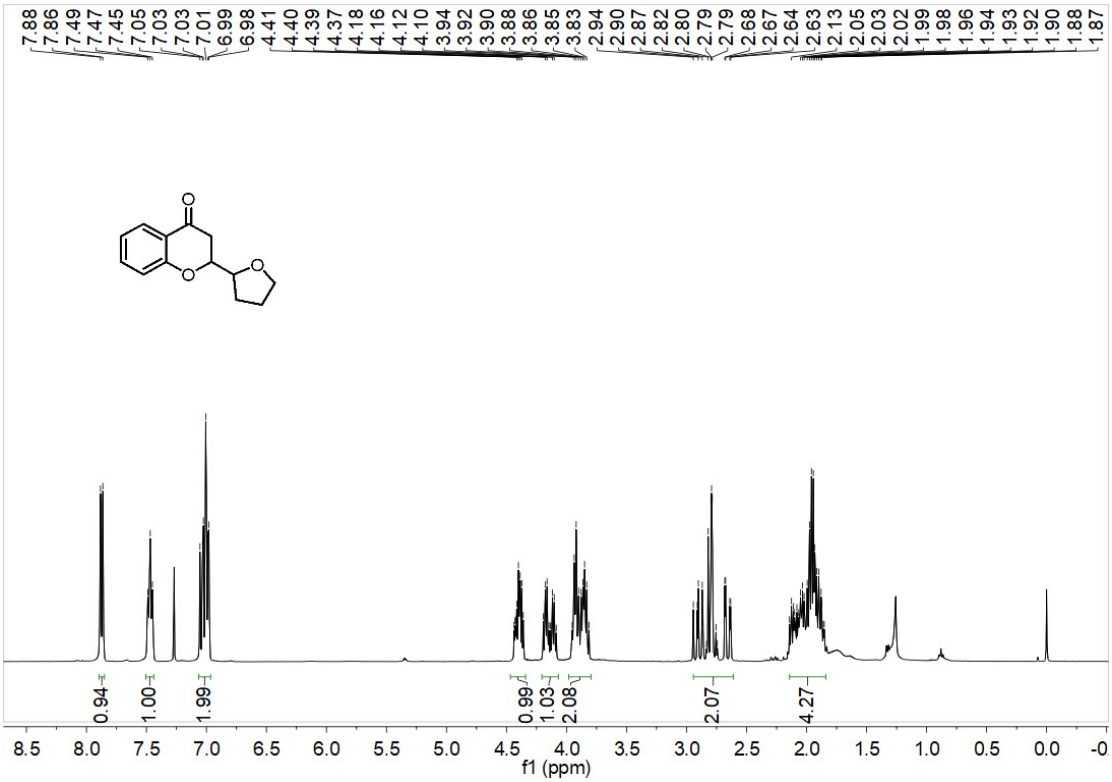
^{13}C NMR (101 MHz, $CDCl_3$) of **3ak**



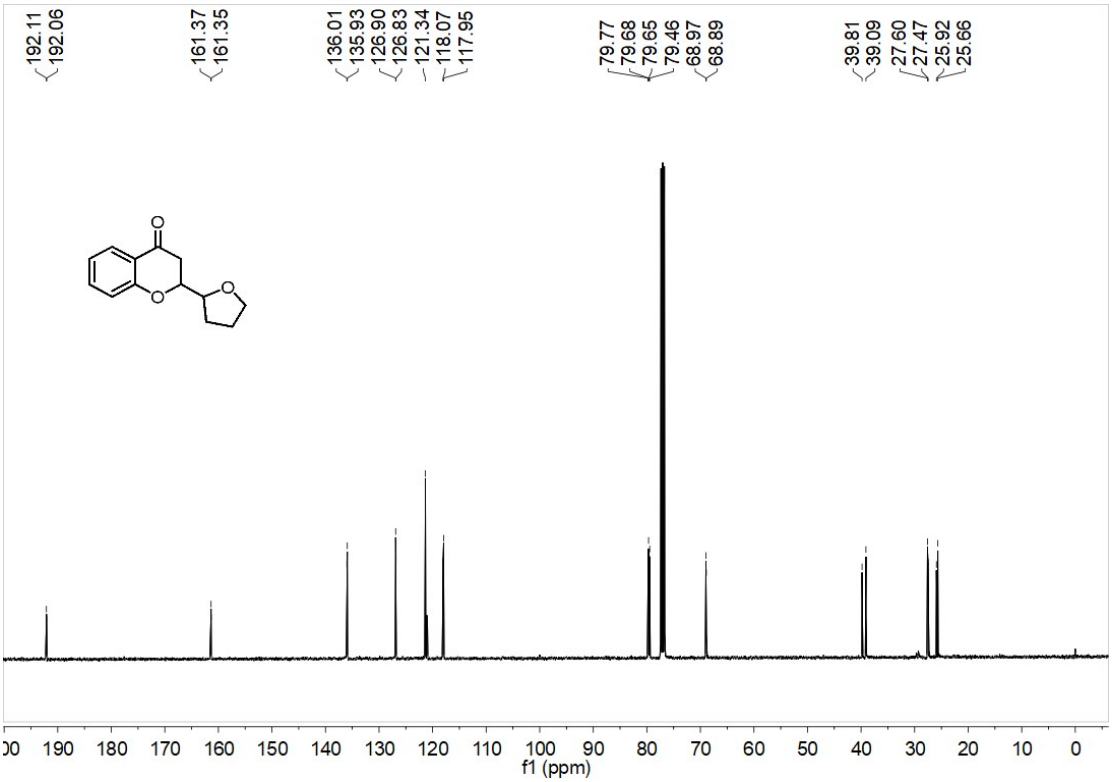
^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



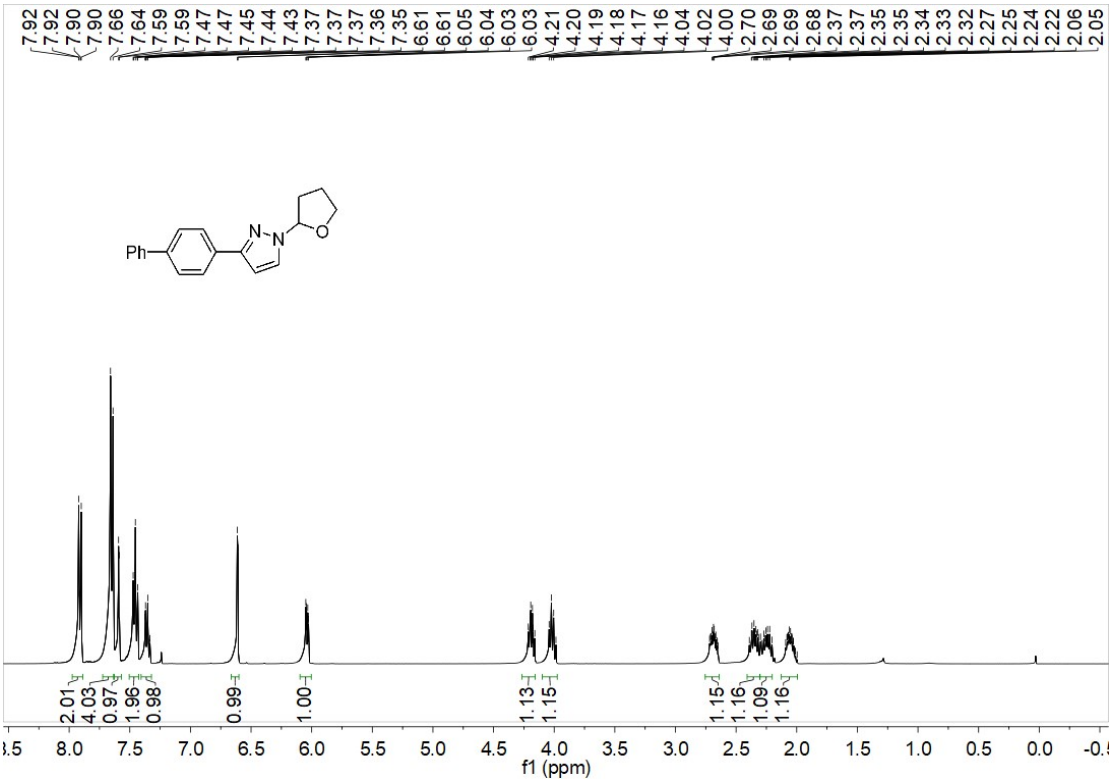
^{13}C NMR (101 MHz, $CDCl_3$) of **3al**



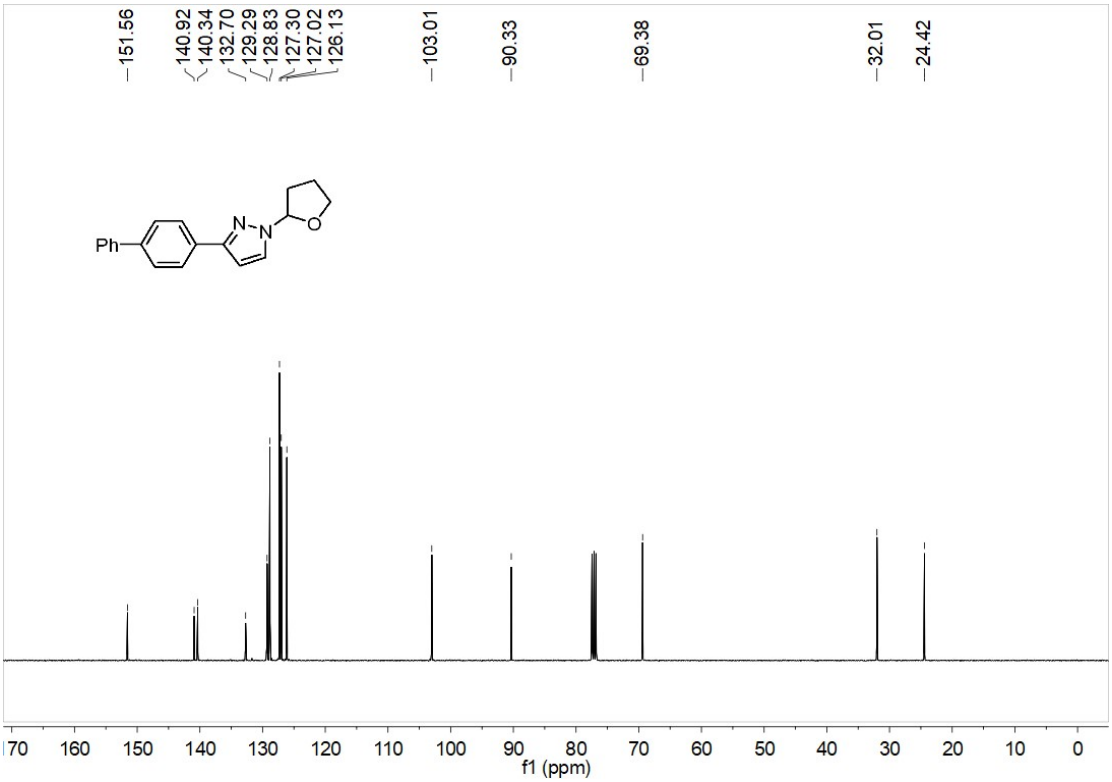
^{1}H NMR (400 MHz, $CDCl_3$) of **7a**



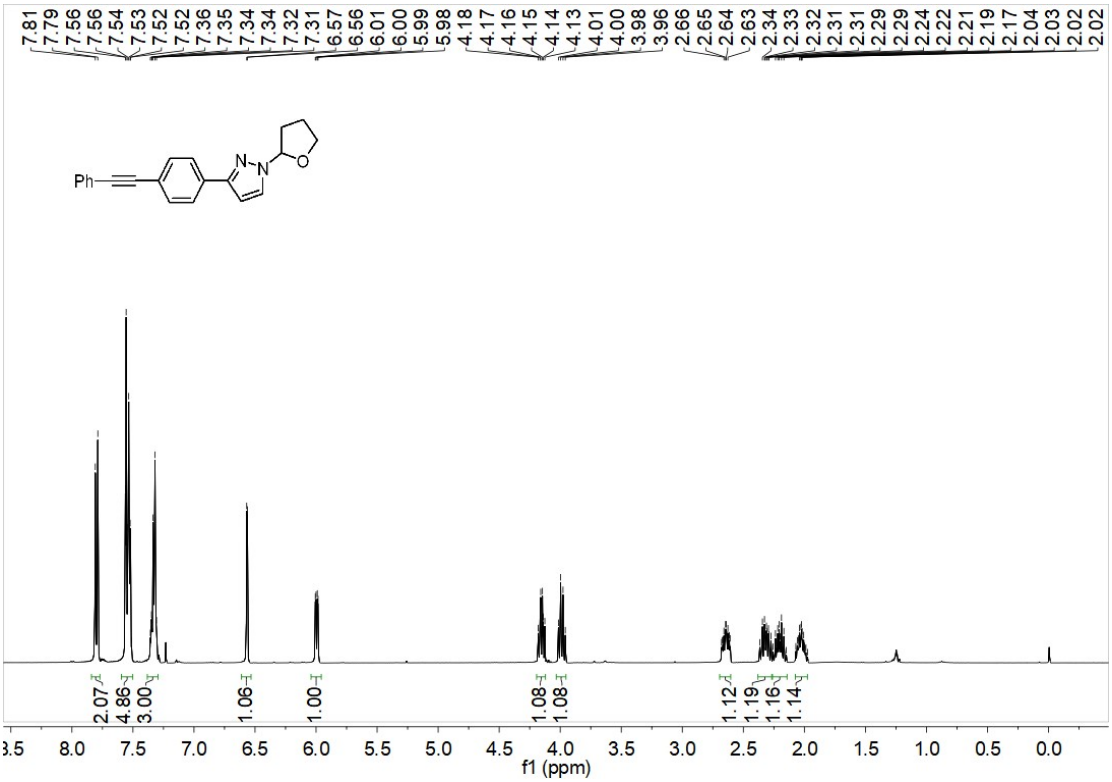
^{13}C NMR (101 MHz, $CDCl_3$) of **7a**



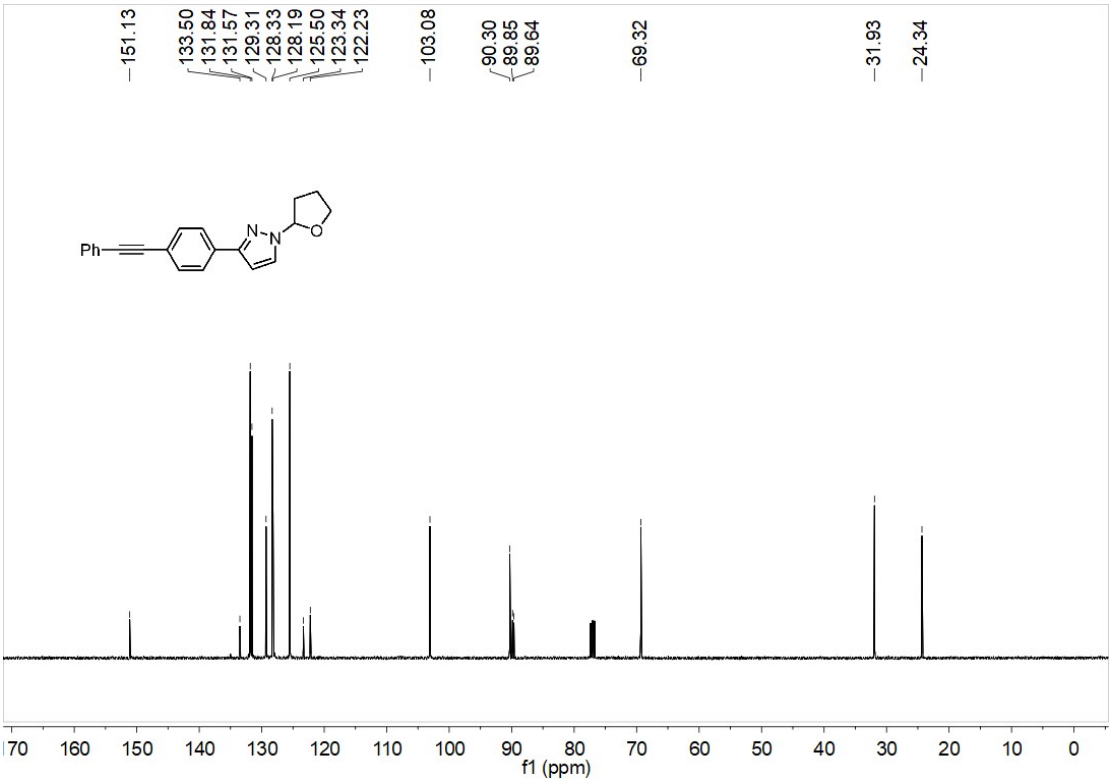
^{1}H NMR (400 MHz, $CDCl_3$) of **8a**



^{13}C NMR (101 MHz, $CDCl_3$) of **8a**



^{1}H NMR (400 MHz, $CDCl_3$) of **8b**



^{13}C NMR (101 MHz, $CDCl_3$) of **8b**