Silver-catalysed [3 + 2] annulation reaction of aryldiazonium salts with allenes enabled by boronate direction

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General Information

^{1}H, ^{13}C and ^{19}F were recorded on Bruker AV 400 MHz and JEOL AV 400 MHz instrument at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Meanwhile, ^{1}H, ^{13}C and ^{19}F were recorded on JEOL AV 600 MHz instrument at 600 MHz (^{1}H NMR), 151 MHz (^{13}C NMR), as well as 565 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker mior OTOF-QII instrument. X-ray structural analysis was conducted on a Bruker APEX-II CCD instrument.

Materials: Tetrahydrofuran (THF) and toluene were distilled from sodium/ benzophenone; CH_2Cl_2 (DCM) was distilled from CaH_2; Acetonitrile (MeCN), Methyl *tert*-butyl ether (MTBE), *N,N*-dimethylformamide (DMF), 1,4-Dioxane, 2-Allenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) , trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-yn-1-yl)silane (**10a**) were purchased from commercial sources. Allenylboronates (**1b**–**1e**[1], **1f**–**1j**[2]), 4,4,5,5-tetramethyl-2-(3-phenylprop-2-yn-1-yl)-1,3,2-dioxaborolane (**10b**[3] were prepared according to the corresponding literature. All commercially available reagents were used without further purification.

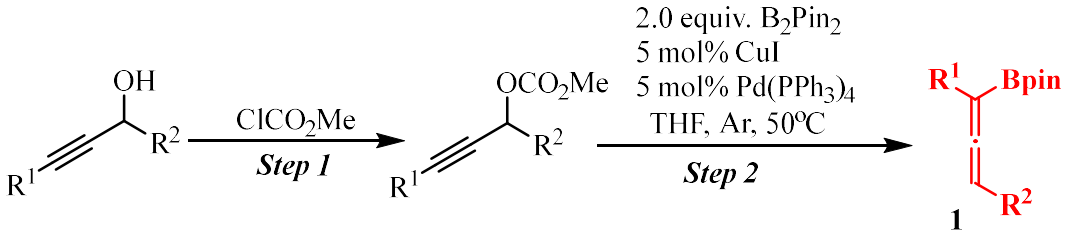
Analytical thin layer chromatography was performed on 0.20 mm silica gel plates. Silica gel (200–300 mesh) was used for flash chromatography. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

Important Safety Note

Handling of aryl diazonium salts should be done in a well-ventilated fume cupboard. No incidents occurred handling of these reagents during this study, yet the readers should be aware of carcinogenicity and explosiveness of the herein described diazonium salts. General safety precautions when working with diazonium salts should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment.

Experimental Procedure

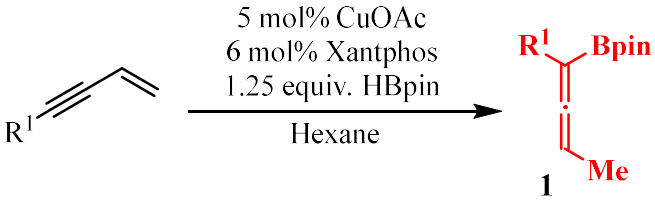
General procedure for the synthesis of allenylboronates. (Method 1).



Step 1: Compounds **1b–1e** were synthesized according to previously reported procedure[1]. A flask was charged with the propargylic alcohol (1.0 equiv., 10 mmol) and CH_2Cl_2 (20 mL) and cooled to 0 °C. Pyridine (4.0 equiv., 40 mmol) and $ClCO_2Me$ (2.0 equiv., 20 mmol) were subsequently added to the solution. The reaction was stirred for 10 hours, after which it was quenched by the addition of H_2O. The mixture was extracted with CH_2Cl_2 and the combined organic phases were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo*. The product was purified with flash column chromatography (pentane:EtOAc 25:1) as clear oil.

Step 2: Inside a glove box, a 50 mL Schlenk tube equipped with a Teflon coated stirring bar was charged with copper iodide (5 mol%, 47.6 mg, 0.25 mmol), $Pd(PPh_3)_4$ (5 mol%, 289 mg, 0.25 mmol), B_2pin_2 (2.0 equiv., 2.54 g, 10 mmol) and THF (20 mL). The mixture was pre-stirred for 10-15 seconds after which the non-terminal propargylic carbonate (5 mmol) was added to the mixture. The vial was then closed, brought outside the glove box and heated to 50 °C for 16 hours. After the reaction was finished the content of the vial was washed out with pentane and concentrated under reduced pressure. The remaining content was dissolved in pentane and purified by flash column chromatography. ***Caution:*** A rapid column chromatography (within 10 minutes) was required to receive reproducible results due to the relatively low stability of the allenyl-Bpin products on silica.

General procedure for the synthesis of allenylboronates. (Method 2).



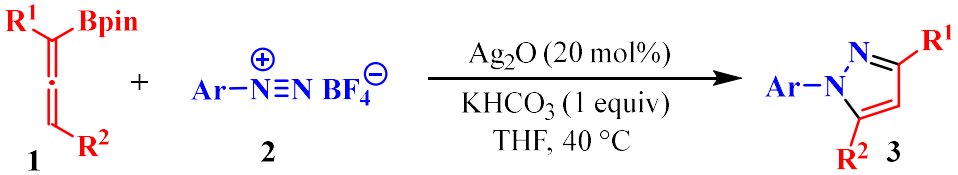
Compounds **1f–1j** were synthesized according to previously reported procedure[2]. An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with Xantphos (CAS:161265-03-8, 6 mol%, 0.12 mmol, 70 mg), CuOAc (5 mol%, 0.1 mmol, 12.3 mg), and hexane (10 mL) in a nitrogen-filled glove box. The mixture was allowed to stir for 30 min under N_2 at 22 °C. HBpin (CAS: 25015-63-8, 2.5 equiv., 2.5 mmol, 320 mg) and 1,3-enyne (1.0 equiv., 2 mmol) were added to the Schlenk tube. The resulting mixture was allowed to stir at 22 °C for 15 h. The mixture was concentrated in vacuo,

affording yellow oil residue, which was purified by silica gel chromatography (100:1 hexanes/ethyl acetate) to afford allenylboronate **1** as colorless oil. Rapid silica gel chromatography (10 min) is imperative for reproducible results because the allenylboronates decompose readily on silica gel.

General procedure for the synthesis of 4,4,5,5-tetramethyl-2-(3-phenylprop-2-yn-1-yl)-1,3,2-dioxaborolane (10b).

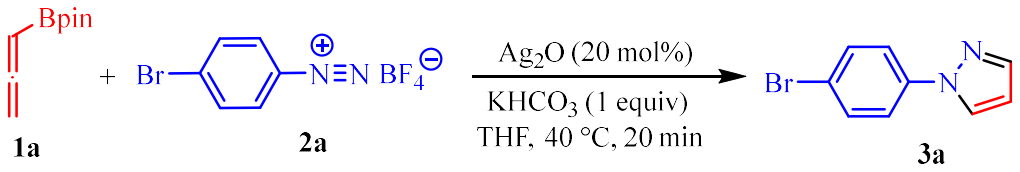
Compound **10b** was synthesized according to previously reported procedure[3]. Dry THF (20 mL, 0.5 M) and ethynylbenzene (1.0 equiv., 10 mmol, 1.02 g) were added to a nitorgen purged round bottom flask. The reaction was cooled to -78 °C before the dropwise addition of n-butyllithium (1.1 equiv., 11 mmol, 6.9 mL, 1.6 M in hexane) over a period of 5 minutes. After stirring for 1 hour, 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (CAS:70557-99-2, 1.0 equiv., 10 mmol, 2.68 g) was added dropwise. The reaction was kept cold for 6 hours before warming up to room temperature overnight. Once complete, the reaction was quenched with water and EtOAc. After separating the layers, the aqueous layer was washed with EtOAc (3 x 15 mL) collecting the organic layer each time. The organic layer was then washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting yellow oil was then carried forward crude in the borylation reaction.

General procedure for the synthesis of *N*^{1}-Aryl pyrazoles from the corresponding aryl diazonium salts and allenylboronates.



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with aryl diazonium salts **2** (0.4 mmol), Ag_2O (20 mol%, 9.2 mg, 0.04 mmol), $KHCO_3$ (1.0 equiv., 20 mg, 0.2 mmol), then THF (1 mL) was added. After that, allenylboronate **1** (1.0 equiv., 20 mg, 0.2 mmol) was added in 1 mL of THF slowly in 3 minutes. The resulting mixture was allowed to stir at 40 ºC in Argon atmosphere for 0.3 – 10 hours. Then the mixture was quenched with sat. NH_4Cl (aq.), filtered through a Celite plug, and rinsed with ethyl acetate. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding *N*^{1}-Aryl pyrazoles **3**.

Reaction Optimization



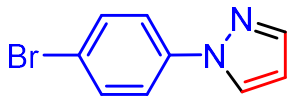
1a **2a** **3a**

Table S1

Entry[a]	Variation from the standard conditions	Yield[b]
1	none	86
2	Ag_2CO_3 instead of Ag_2O	56
3	AgOAc instead of Ag_2O	64
4	AgF instead of Ag_2O	41
5	$AgPF_6$ instead of Ag_2O	14
6	PPh_3AuOTf instead of Ag_2O	trace
7	$Cu(OTf)_2$ instead of Ag_2O	nd
8	$PdCl_2(MeCN)_2$ instead of Ag_2O	trace
9	$Zn(OAc)_2$ instead of Ag_2O	nd
10	10 mol% of Ag_2O was employed	69
11	50 mol% of Ag_2O was employed	78
12	K_2CO_3 instead of $KHCO_3$	55
13	KOAc instead of $KHCO_3$	68
14	$NaHCO_3$ instead of $KHCO_3$	63
15	MTBE instead of THF	6
16	DMF instead of THF	58
17	MeCN instead of THF	nd
18	1,4-dioxane instead of THF	27
19	25 °C instead of 40 °C	43
20	**1a** was added in one portion	50

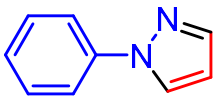
[a] General reaction procedure: To a mixture of phenyl diazonium salt **2a** (81 mg, 0.3 mmol), catalyst (0.04 mmol), and base (0.2 mmol) in 1 mL of solvent was added the allenyl boronate **1a** (33 mg, 0.2 mmol) in 1 mL of solvent slowly in 3 minutes, and the mixture reacted at 40 °C for 20 minutes unless otherwise noted. [b] Yield of isolated pyrazole **3a**. ***Safety note:*** Handling of aryl diazonium salts should be done in a well-ventilated fume cupboard.

Characterization Data



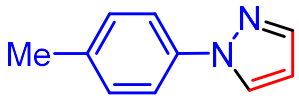
3a

1-(4-bromophenyl)-1*H*-pyrazole (3a).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3a** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as orange solid (38 mg, 86%). Reaction time for this compound is 20 min. M.p.: 69-70 ºC. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.72 (s, 1H), 7.65 – 7.53 (m, 4H), 6.47 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.5, 139.3, 132.6, 126.7, 120.7, 119.7, 108.1. **HRMS (ESI-TOF)**: calcd. for $C_9H_8BrN_2$ (M+H): 222.9871, found: *m/z* 222.9871.



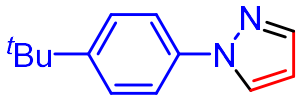
3b

1-phenyl-1*H*-pyrazole (3b).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3b** by column chromatography on silica gel (petroleum ether/EtOAc, 50:1, v/v) as red oil (15 mg, 52%). Reaction time for this compound is 1 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.94 – 7.84 (m, 1H), 7.73 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.42 (q, *J* = 7.6 Hz, 2H), 7.25 (q, *J* = 7.2 Hz, 1H), 6.43 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.2, 140.3, 129.5, 126.9, 126.5, 119.3, 107.7. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_2$ (M+H): 145.0766, found: *m/z* 145.0768.



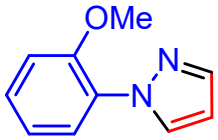
3c

1-(*p*-tolyl)-1*H*-pyrazole (3c).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3c** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (22 mg, 69%). Reaction time for this compound is 1 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 6.0 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 10.2 Hz, 2H), 6.47 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.9, 138.1, 136.4, 130.0, 126.8, 119.3, 21.0. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_{11}N_2$ (M+H): 159.0922, found: *m/z* 159.0920.



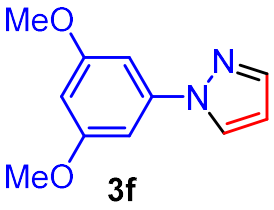
3d

1-[4-(*tert*-butyl)phenyl]-1*H*-pyrazole (3d).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3d** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (24 mg, 60%). Reaction time for this compound is 4 h. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 2.5 Hz, 1H), 7.72 (s, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.45 (s, 1H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.6, 140.8, 137.8, 126.7, 126.3, 119.0, 107.3, 34.5, 31.4. **HRMS (ESI-TOF)**: calcd. for $C_{13}H_{17}N_2$ (M+H): 201.1392, found: *m/z* 201.1391.



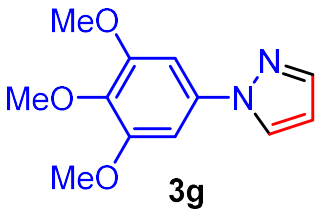
3e

1-(2-methoxyphenyl)-1*H*-pyrazole (3e).[4b] For 0.2 mmol scales, the standard procedure was followed to provide **3e** by column chromatography on silica gel (petroleum ether/EtOAc, 15:1, v/v) as red oil (22 mg, 61%). Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.05 (q, *J* = 7.9 Hz, 2H), 6.43 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.4, 140.2, 131.7, 129.8, 128.1, 125.4, 121.3, 112.3, 106.3, 56.0. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_{11}N_2O$ (M+H): 175.0871, found: *m/z* 175.0871.



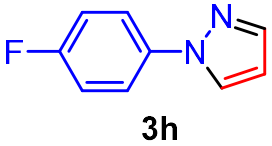
3f

1-(3,5-dimethoxyphenyl)-1*H*-pyrazole (3f).[4c] For 0.2 mmol scales, the standard procedure was followed to provide **3f** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as red oil (24 mg, 56%). Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.71 (s, 1H), 6.87 (s, 2H), 6.45 (s, 1H), 6.39 (s, 1H), 3.85 (s, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 161.5, 141.9, 141.1, 127.1, 107.7, 98.6, 97.8, 55.7. **HRMS (ESI-TOF)**: calcd. for $C_{11}H_{13}N_2O_2$ (M+H): 205.0977, found: *m/z* 205.0973.



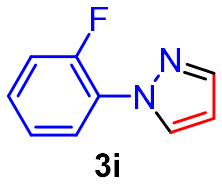
3g

1-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole (3g). For 0.2 mmol scales, the standard procedure was followed to provide **3g** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as an orange solid (32 mg, 67%). M.p.: 61-62 °C. Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 1.4 Hz, 1H), 6.90 (s, 2H), 6.55 – 6.39 (m, 1H), 3.92 (s, 6H), 3.86 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.8, 141.0, 136.7, 136.5, 127.1, 107.7, 97.3, 61.2, 56.4. **HRMS (ESI-TOF)**: calcd. for $C_{12}H_{15}N_2O_3$ (M+H): 235.1083, found: *m/z* 235.1083.



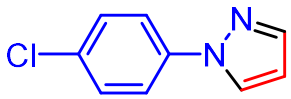
3h

1-(4-fluorophenyl)-1*H*-pyrazole (3h).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3h** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (27 mg, 84%). Reaction time for this compound is 3 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.17 – 7.09 (m, 2H), 6.46 (t, *J* = 2.1 Hz, 1H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -115.90. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 161.2 (d, *J* = 245.8 Hz), 141.2, 136.7, 127.0, 121.1 (d, *J* = 8.2 Hz), 116.3 (d, *J* = 22.9 Hz), 107.8. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_2F$ (M+H): 163.0672, found: *m/z* 163.0664.



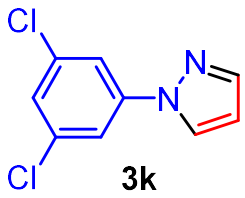
3i

1-(2-fluorophenyl)-1*H*-pyrazole (3i).[4d] For 0.2 mmol scales, the standard procedure was followed to provide **3i** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (22 mg, 67%). Reaction time for this compound is 3 h. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.9 Hz, 1H), 7.93 – 7.83 (m, 1H), 7.73 (s, 1H), 7.28 – 7.21 (m, 3H), 6.47 (s, 1H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -125.05. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.6 (d, *J* = 248.5 Hz), 140.9, 130.9 (d, *J* = 10.5 Hz), 128.5 (d, *J* = 9.4 Hz), 127.8 (d, *J* = 7.9 Hz), 125.0 (d, *J* = 3.8 Hz), 124.5, 116.9 (d, *J* = 20.6 Hz), 107.6. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_2F$ (M+H): 163.0672, found: *m/z* 163.0672.



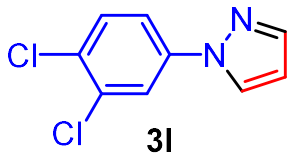
3j

1-(4-chlorophenyl)-1*H*-pyrazole (3j).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3j** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as yellow solid (0.2 mmol, 33 mg, 92%). This compound was also prepared on a 10 mmol scale, and 1.32 g of **3j** was obtained in 74% yield. M.p.: 53-54 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 2.5 Hz, 1H), 7.72 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.47 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.5, 138.8, 132.0, 129.6, 126.8, 120.4, 108.1. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_2Cl$ (M+H): 179.0376, found: *m/z* 179.0375.



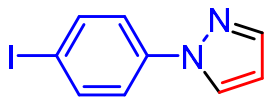
3k

1-(3,5-dichlorophenyl)-1*H*-pyrazole (3k). For 0.2 mmol scales, the standard procedure was followed to provide **3k** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red solid (33 mg, 78%). M.p.: 60-61 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.73 (s, 1H), 7.63 (s, 2H), 7.25 (d, *J* = 1.8 Hz, 1H), 6.49 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.1, 141.6, 135.9, 126.9, 126.3, 117.5, 108.7. **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_2Cl_2$ (M+H): 212.9986, found: *m/z* 212.9984.



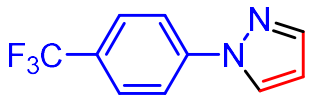
3l

1-(3,4-dichlorophenyl)-1*H*-pyrazole (3l).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3l** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as yellow solid (37 mg, 88%). M.p.: 76-77 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.54 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 6.49 (dd, *J* = 2.6, 1.7 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.9, 139.4, 133.6, 131.1, 130.1, 126.8, 121.0, 118.1, 108.5. **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_2Cl_2$ (M+H): 212.9986, found: *m/z* 212.9987.



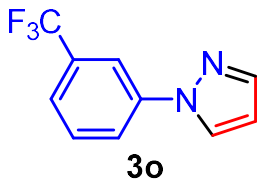
3m

1-(4-iodophenyl)-1*H*-pyrazole (3m).[4e] For 0.2 mmol scales, the standard procedure was followed to provide **3m** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red solid (44 mg, 81%). M.p.: 85-86 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.73 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.48 (t, *J* = 2.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.6, 140.0, 138.5, 126.7, 120.9, 108.2, 90.6. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_2I$ (M+H): 270.9732, found: *m/z* 270.9736.



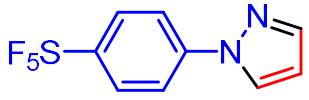
3n

1-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (3n).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3n** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as white solid (40 mg, 93%). M.p.: 92-93 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 6.52 (dd, *J* = 2.6, 1.7 Hz, 1H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -62.11. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.6, 142.1, 128.3 (q, *J* = 33.3 Hz), 126.9, 124.0 (q, *J* = 271.8 Hz), 118.9, 108.6. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_9N_2F_3$ (M+H): 213.0640, found: *m/z* 213.0636.



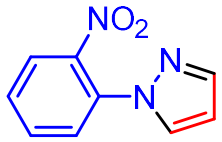
3o

1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazole (3o). For 0.2 mmol scales, the standard procedure was followed to provide **3o** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (36 mg, 84%). Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.96 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.74 (s, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 6.50 (t, *J* = 2.1 Hz, 1H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -62.68. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.8, 140.6, 132.1 (q, *J* = 32.9 Hz), 130.2, 126.9, 123.8 (q, *J* = 272.4 Hz), 123.0 (q, *J* = 3.8 Hz), 122.0, 116.1 (q, *J* = 3.8 Hz), 108.5. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_9N_2F_3$ (M+H): 213.0640, found: *m/z* 213.0639.



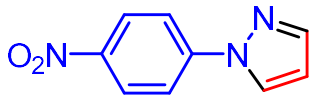
3p

1-[4-(pentafluoro-λ^6-sulfanyl)phenyl]-1*H*-pyrazole (3p).[4f] For 0.2 mmol scales, the standard procedure was followed to provide **3p** by column chromatography on silica gel (petroleum ether/EtOAc, 50:1, v/v) as yellow solid (40 mg, 74%). M.p.: 77-78 ºC. Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 2.6 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 3H), 7.76 (s, 1H), 6.56 – 6.48 (m, 1H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ 84.43 (p, *J* = 150.2 Hz), 63.51 (d, *J* = 149.4 Hz). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.3 (p, *J* = 18.0 Hz), 142.3, 142.0, 127.6 (p, *J* = 4.8 Hz), 126.9, 118.4, 108.9. **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_2SF_5$ (M+H): 271.0328, found: *m/z* 271.0327.



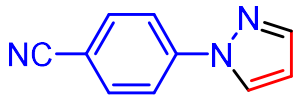
3q

1-(2-nitrophenyl)-1*H*-pyrazole (3q).[4g] For 0.2 mmol scales, the standard procedure was followed to provide **3q** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as yellow solid (34 mg, 90%). M.p.: 87-88 ºC. Reaction time for this compound is 3 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.74 (dd, *J* = 11.6, 2.1 Hz, 2H), 7.68 (td, *J* = 7.8, 1.5 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52 (td, *J* = 7.8, 1.3 Hz, 1H), 6.50 (dd, *J* = 2.5, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.7, 142.5, 133.6, 133.1, 129.8, 128.5, 126.3, 125.2, 108.3. **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_3O_2$ (M+H): 190.0617, found: *m/z* 190.0615.



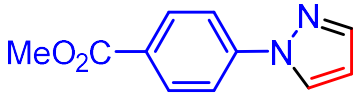
3r

1-(4-nitrophenyl)-1*H*-pyrazole (3r).[4h] The standard procedure was followed to provide **3r** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as white solid (0.2 mmol, 36 mg, 95%). This compound was also prepared on a 10 mmol scale, and 2.65 g of 3r was obtained in 87% yield. M.p.: 169-170 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.33 (dd, *J* = 9.9, 2.0 Hz, 2H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.88 (dd, *J* = 9.1, 2.5 Hz, 2H), 7.79 (s, 1H), 6.55 (t, *J* = 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.5, 142.9, 127.2, 126.8, 125.5, 118.7, 109.5. **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_3O_2$ (M+H): 190.0617, found: *m/z* 190.0610.



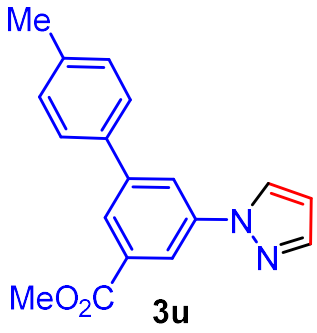
3s

4-(1*H*-pyrazol-1-yl)benzonitrile (3s).[4h] For 0.2 mmol scales, the standard procedure was followed to provide **3s** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as white solid (30 mg, 91%). M.p.: 88-89 ºC. Reaction time for this compound is 2 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.79 – 7.69 (m, 3H), 6.59 – 6.47 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.1, 142.6, 133.8, 126.9, 119.1, 118.5, 109.7, 109.2. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_8N_3$ (M+H): 170.0718, found: *m/z* 170.0715.



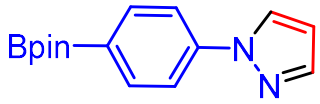
3t

methyl 4-(1*H*-pyrazol-1-yl)benzoate (3t).[4h] For 0.2 mmol scales, the standard procedure was followed to provide **3t** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as red solid (38 mg, 94%). M.p.: 114-115 ºC. Reaction time for this compound is 3 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.99 (d, *J* = 2.6 Hz, 1H), 7.90 – 7.65 (m, 3H), 6.49 (t, *J* = 2.1 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 166.5, 143.4, 142.0, 131.3, 127.8, 127.0, 118.4, 108.6, 52.3. **HRMS (ESI-TOF)**: calcd. for $C_{11}H_{11}N_2O_2$ (M+H): 203.0821, found: *m/z* 203.0817.



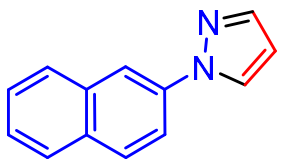
3u

methyl 4'-methyl-5-(1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-3-carboxylate (3u). For 0.2 mmol scales, the standard procedure was followed to provide **3u** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as yellow oil (45 mg, 76%). Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.24 (t, *J* = 1.8 Hz, 1H), 8.18 (dt, *J* = 7.6, 1.8 Hz, 2H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.51 (t, *J* = 2.2 Hz, 1H), 3.97 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 166.5, 143.1, 141.6, 140.8, 138.3, 136.4, 131.9, 129.8, 127.1, 127.1, 125.9, 122.0, 118.1, 108.2, 52.6, 21.3. **HRMS (ESI-TOF)**: calcd. for $C_{18}H_{17}N_2O_2$ (M+H): 293.1290, found: *m/z* 293.1286.



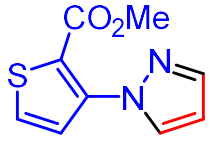
3v

1-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1*H*-pyrazole (3v).[4i] For 0.2 mmol scales, the standard procedure was followed to provide **3v** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as white solid (25 mg, 47%). M.p.: 76-77 °C. Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 2.5 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.72 (s, 1H), 7.71 (s, 1H), 6.54 – 6.44 (m, 1H), 1.36 (s, 12H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.3, 141.5, 136.2, 126.8, 118.1, 108.0, 84.1, 25.0. **HRMS (ESI-TOF)**: calcd. for $C_{15}H_{20}N_2O_2B$ (M+H): 271.1618, found: *m/z* 271.1622.



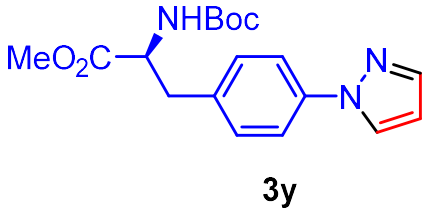
3w

1-(naphthalen-2-yl)-1*H*-pyrazole (3w).[4a] For 0.2 mmol scales, the standard procedure was followed to provide **3w** by column chromatography on silica gel (petroleum ether/EtOAc, 15:1, v/v) as grey solid (17 mg, 43%). M.p.: 83-84 °C. Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 2.2 Hz, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.79 (d, *J* = 1.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.46 (m, 1H), 6.60 – 6.46 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.4, 137.7, 133.7, 132.0, 129.6, 128.1, 127.9, 127.1, 126.0, 118.7, 116.5, 107.9. **HRMS (ESI-TOF)**: calcd. for $C_{13}H_{11}N_2$ (M+H): 195.0922, found: *m/z* 195.0924.



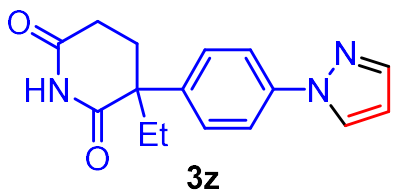
3x

methyl 3-(1*H*-pyrazol-1-yl)thiophene-2-carboxylate (3x). For 0.2 mmol scales, the standard procedure (1.0 equiv. K_2CO_3 instead of $KHCO_3$) was followed to provide **3x** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as red solid (25.2 mg, 60%). M.p.: 40-41 °C. Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.71 (s, 1H), 7.53 (dd, *J* = 5.4, 1.3 Hz, 1H), 7.45 (dd, *J* = 5.3, 1.3 Hz, 1H), 6.43 (s, 1H), 3.85 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 161.4, 143.0, 141.3, 132.7, 130.6, 126.9, 119.0, 106.7, 52.4. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_2O_2S$ (M+H): 209.0385, found: *m/z* 209.0384.



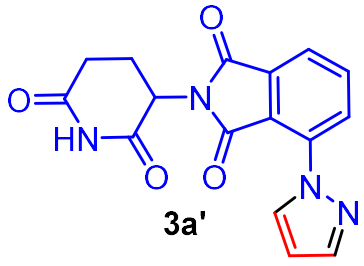
3y

methyl (S)-3-[4-(1*H*-pyrazol-1-yl)phenyl]-2-[(*tert*-butoxycarbonyl)amino]propan-oate (3y). For 0.2 mmol scales, the standard procedure was followed to provide **3y** by column chromatography on silica gel (petroleum ether/EtOAc, 2:1, v/v) as white solid (47 mg, 67%). M.p.: 112-113 °C. Reaction time for this compound is 6 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.8 Hz, 1H), 7.71 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.53 – 6.41 (m, 1H), 5.01 (d, *J* = 8.2 Hz, 1H), 4.60 (q, *J* = 7.7, 7.1 Hz, 1H), 3.72 (s, 3H), 3.12 (ddd, *J* = 45.1, 13.8, 5.9 Hz, 2H), 1.42 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 172.3, 155.2, 141.2, 139.3, 134.4, 130.4, 126.8, 119.4, 107.7, 80.2, 54.5, 52.4, 37.9, 28.4. **HRMS (ESI-TOF)**: calcd. for $C_{18}H_{23}N_3O_4Na$ (M+Na): 368.1586, found: *m/z* 368.1581.



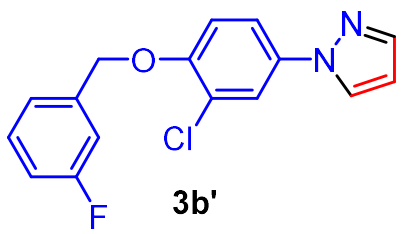
3z

3-[4-(1*H*-pyrazol-1-yl)phenyl]-3-ethylpiperidine-2,6-dione (3z). For 0.2 mmol scales, the standard procedure was followed to provide **3z** by column chromatography on silica gel (petroleum ether/EtOAc, 2:1, v/v) as red solid (35 mg, 62%). M.p.: 136-137 °C. Reaction time for this compound is 6 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.92 (d, *J* = 2.5 Hz, 1H), 7.73 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.47 (s, 1H), 2.63 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.43 (ddd, *J* = 18.3, 13.5, 4.1 Hz, 2H), 2.26 (td, *J* = 14.1, 13.6, 4.4 Hz, 1H), 2.07 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.95 (dq, *J* = 14.6, 7.4 Hz, 1H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 175.0, 172.1, 141.5, 139.6, 136.9, 127.5, 126.8, 119.7, 108.0, 50.9, 33.0, 29.3, 27.1, 9.1. **HRMS (ESI-TOF)**: calcd. for $C_{16}H_{18}N_3O_2$ (M+H): 284.1399, found: *m/z* 284.1397.



3a'

2-(2,6-dioxopiperidin-3-yl)-4-(1*H*-pyrazol-1-yl)isoindoline-1,3-dione (3a'). For 0.2 mmol scales, the standard procedure was followed to provide **3a'** by column chromatography on silica gel (petroleum ether/EtOAc, 1:1, v/v) as yellow solid (29 mg, 44%). M.p.: 220-221 °C. Reaction time for this compound is 8 h. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.16 (s, 1H), 8.58 (d, *J* = 2.6 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 8.00 (t, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 1H), 7.87 (d, *J* = 1.7 Hz, 1H), 6.59 (t, *J* = 2.2 Hz, 1H), 5.19 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.89 (ddd, *J* = 17.0, 13.9, 5.4 Hz, 1H), 2.61 (dt, *J* = 17.0, 3.1 Hz, 1H), 2.54 (dd, *J* = 13.3, 4.5 Hz, 1H), 2.11 – 2.03 (m, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 173.3, 170.2, 166.7, 165.9, 142.7, 137.4, 136.7, 133.8, 133.4, 130.3, 122.2, 120.5, 108.0, 49.7, 31.4, 22.4. **HRMS (ESI-TOF)**: calcd. for $C_{16}H_{13}N_4O_4$ (M+H): 325.0937, found: *m/z* 325.0935.

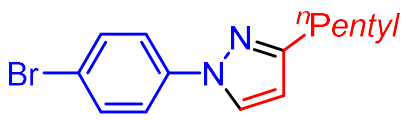


3b'

1-[3-chloro-4-[(3-fluorobenzyl)oxy]phenyl]-1*H*-pyrazole (3b'). For 0.2 mmol scales, the standard procedure was followed to provide **3b'** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as white solid (45 mg, 75%). M.p.: 72-73 °C. Reaction time for this compound is 6 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 7.51 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.36 (q, *J* = 6.7, 5.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.07 – 6.97 (m, 2H), 6.45 (s, 1H), 5.18 (s, 2H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -112.37. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 246.9 Hz), 152.5, 141.2, 138.9, 134.7, 130.4 (d, *J* = 8.0 Hz), 126.9, 124.2, 122.6, 121.9, 118.6, 115.1 (d, *J* = 21.2 Hz), 114.5, 114.1 (d, *J* = 22.2 Hz), 107.8, 70.5. **HRMS (ESI-TOF)**: calcd. for $C_{16}H_{13}N_2OFCl$ (M+H): 303.0700, found: *m/z* 303.0698.

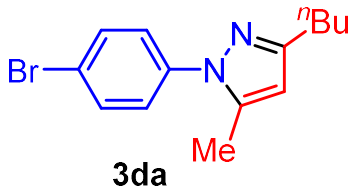
3ba

1-(4-bromophenyl)-3-methyl-1*H*-pyrazole (3ba). For 0.2 mmol scales, the standard procedure was followed to provide **3ba** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as brown solid (32 mg, 68%). M.p.: 92-93 °C. Reaction time for this compound is 4 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.4 Hz, 1H), 7.52 (s, 4H), 6.25 (d, *J* = 2.4 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.1, 139.3, 132.5, 127.3, 120.2, 119.0, 108.1, 13.8. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_{10}N_2Br$ (M+H): 237.0027, found: *m/z* 237.0029.



3ca

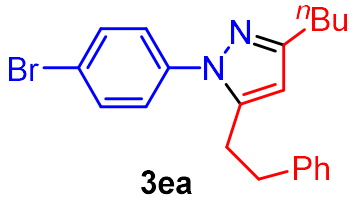
1-(4-bromophenyl)-3-pentyl-1*H*-pyrazole (3ca). For 0.2 mmol scales, the standard procedure was followed to provide **3ca** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (28 mg, 48%). Reaction time for this compound is 8 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.4 Hz, 1H), 7.52 – 7.55 (m, 4H), 6.27 (d, *J* = 2.4 Hz, 1H), 2.69 (t, *J* = 7.8 Hz, 2H), 1.79 – 1.62 (m, 2H), 1.47 – 1.22 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 156.0, 139.4, 132.4, 127.2, 120.3, 119.0, 107.0, 31.7, 29.4, 28.5, 22.6, 14.1. **HRMS (ESI-TOF)**: calcd. for $C_{14}H_{18}N_2Br$ (M+H): 293.0653, found: *m/z* 293.0658.



3da

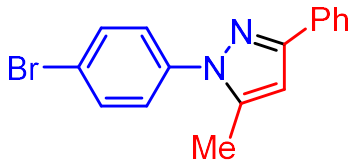
1-(4-bromophenyl)-3-butyl-5-methyl-1*H*-pyrazole (3da). For 0.2 mmol scales, the standard procedure was followed to provide **3da** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red oil (28 mg, 48%). Reaction time for this compound is 8 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (dq, *J* = 9.0, 2.1 Hz, 2H), 7.32 (dq, *J* = 8.9, 2.1 Hz, 2H), 6.01 (s, 1H), 2.62 (q, *J* = 6.4, 4.8 Hz, 2H), 2.31 (s, 3H), 1.76 – 1.54 (m, 2H), 1.44 – 1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ

154.4, 139.3, 139.1, 132.2, 126.2, 120.8, 106.5, 31.9, 28.0, 22.7, 14.0, 12.6. **HRMS (ESI-TOF)**: calcd. for $C_{14}H_{18}N_2Br$ (M+H): 293.0653, found: *m/z* 293.0646.



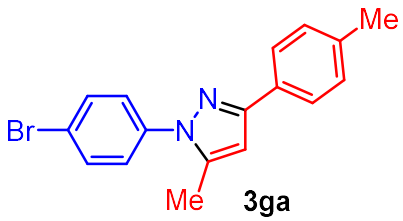
3ea

1-(4-bromophenyl)-3-butyl-5-phenethyl-1*H*-pyrazole (3ea). For 0.2 mmol scales, the standard procedure was followed to provide **3ea** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red solid (34 mg, 44%). Reaction time for this compound is 8 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 6.1 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.07 (s, 1H), 2.89 (q, *J* = 4.7 Hz, 4H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.65 (t, *J* = 7.7 Hz, 2H), 1.45 – 1.32 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 154.3, 143.5, 140.7, 139.0, 132.2, 128.6, 128.4, 126.9, 126.5, 121.2, 105.0, 35.2, 31.9, 28.5, 28.1, 22.6, 14.1. **HRMS (ESI-TOF)**: calcd. for $C_{21}H_{24}N_2Br$ (M+H): 383.1123, found: *m/z* 383.1125.



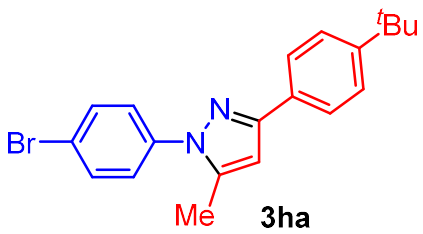
3fa

1-(4-bromophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (3fa). The standard procedure was followed to provide **3fa** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as yellow oil (0.2 mmol, 29 mg, 46%). This compound was also prepared on a 4 mmol scale, and 0.52 g of **3fa** was obtained in 42% yield. Reaction time for this compound is 8 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 6.7 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.41 (dd, *J* = 11.1, 8.1 Hz, 4H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.53 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 152.0, 140.3, 139.1, 133.2, 132.3, 128.7, 128.1, 126.4, 125.8, 121.3, 105.0, 12.8. **HRMS (ESI-TOF)**: calcd. for $C_{16}H_{14}N_2Br$ (M+H): 313.0340, found: *m/z* 313.0344.



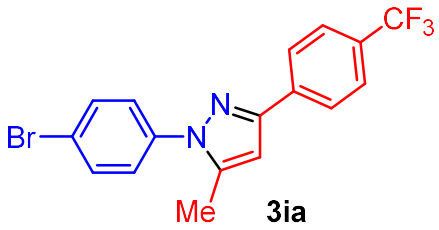
3ga

1-(4-bromophenyl)-5-methyl-3-(*p*-tolyl)-1*H*-pyrazole (3ga). For 0.2 mmol scales, the standard procedure (1.0 equiv. K_2CO_3 instead of $KHCO_3$) was followed to provide **3ga** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as yellow solid (27 mg, 41%). M.p.: 90-91 °C. Reaction time for this compound is 10 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.50 (s, 1H), 2.38 (s, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 152.0, 140.1, 139.1, 137.8, 132.3, 130.3, 129.4, 126.4, 125.7, 121.2, 104.8, 21.4, 12.8. **HRMS (ESI-TOF)**: calcd. for $C_{17}H_{16}N_2Br$ (M+H): 327.0497, found: *m/z* 327.0497.



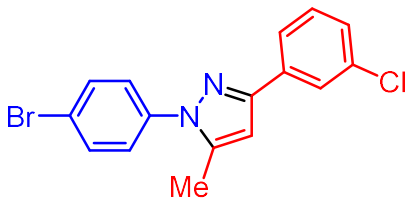
3ha

1-(4-bromophenyl)-3-[4-(*tert*-butyl)phenyl]-5-methyl-1*H*-pyrazole (3ha). For 0.2 mmol scales, the standard procedure was followed to provide **3ha** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as yellow solid (29 mg, 40%). M.p.: 117-118 °C. Reaction time for this compound is 10 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.42 (t, *J* = 8.2 Hz, 4H), 6.50 (s, 1H), 2.38 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 152.0, 151.1, 140.1, 139.1, 132.3, 130.4, 126.4, 125.6, 125.5, 121.1, 104.9, 34.7, 31.4, 12.8. **HRMS (ESI-TOF)**: calcd. for $C_{20}H_{22}N_2Br$ (M+H): 369.0966, found: *m/z* 369.0966.



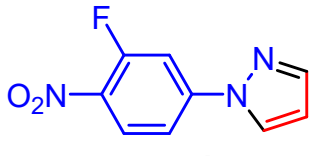
3ia

1-(4-bromophenyl)-5-methyl-3-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (3ia). For 0.2 mmol scales, the standard procedure was followed to provide **3ia** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as yellow oil (35 mg, 46%). Reaction time for this compound is 10 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.88 – 7.54 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 1H), 2.39 (s, 3H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -62.33. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 150.5, 140.7, 138.8, 136.7, 132.4, 129.8 (q, *J* = 32.5 Hz), 126.4, 126.2 (q, *J* = 271.8 Hz), 125.9, 125.7 (q, *J* = 3.9 Hz), 121.7, 105.2, 12.7. **HRMS (ESI-TOF)**: calcd. for $C_{17}H_{13}N_2F_3Br$ (M+H): 381.0214, found: *m/z* 381.0215.



3ja

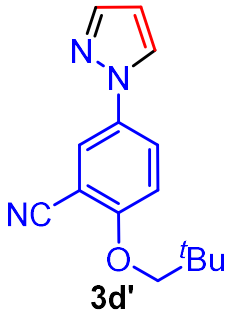
1-(4-bromophenyl)-3-(3-chlorophenyl)-5-methyl-1*H*-pyrazole (3ja). For 0.2 mmol scales, the standard procedure was followed to provide **3ja** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as red oil (33 mg, 48%). Reaction time for this compound is 10 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 8.7, 3.1 Hz, 2H), 7.41 (dd, *J* = 8.8, 3.0 Hz, 2H), 7.33 (td, *J* = 7.8, 3.1 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 150.6, 140.5, 138.9, 135.0, 134.7, 132.4, 130.0, 128.0, 126.4, 125.9, 123.9, 121.5, 105.0, 12.7. **HRMS (ESI-TOF)**: calcd. for $C_{16}H_{13}N_2ClBr$ (M+H): 346.9951, found: *m/z* 346.9950.



3c'

1-(3-fluoro-4-nitrophenyl)-1*H*-pyrazole (3c'). For 0.2 mmol scales, the standard procedure was followed to provide **3c'** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as yellow solid (35 mg, 84%). M.p.: 133-134 °C. Reaction time for this compound is 5 h. **^{1}H**

NMR (600 MHz, Chloroform-*d*) δ 8.28 – 8.16 (m, 1H), 8.01 (d, *J* = 2.7 Hz, 1H), 7.80 (s, 1H), 7.73 (dd, *J* = 12.1, 2.3 Hz, 1H), 7.62 (ddd, *J* = 9.0, 2.3, 1.2 Hz, 1H), 6.60 – 6.53 (m, 1H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -112.84. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 156.8 (d, *J* = 265.8 Hz), 145.2 (d, *J* = 10.3 Hz), 143.3, 134.5, 128.0, 127.2, 113.4 (d, *J* = 3.7 Hz), 110.0, 108.2 (d, *J* = 25.9 Hz). **HRMS (ESI-TOF)**: calcd. for $C_9H_7N_3O_2F$ (M+H): 208.0522, found: *m/z* 208.0521.

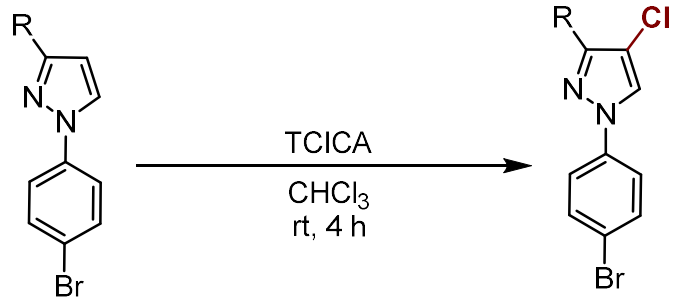


3d'

2-(neopentyloxy)-5-(1*H*-pyrazol-1-yl)benzonitrile (3d'). For 0.2 mmol scales, the standard procedure was followed to provide **3d'** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as yellow solid (46 mg, 90%). M.p.: 88-89 °C. Reaction time for this compound is 8 h. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 3H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.05 – 6.89 (m, 1H), 6.46 (t, *J* = 2.1 Hz, 1H), 3.71 (s, 2H), 1.08 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.6, 141.5, 133.7, 126.8, 125.3, 124.2, 115.6, 113.2, 108.2, 102.7, 79.3, 32.2, 26.6. **HRMS (ESI-TOF)**: calcd. for $C_{15}H_{18}N_3O$ (M+H): 256.1450, found: *m/z* 256.1454.

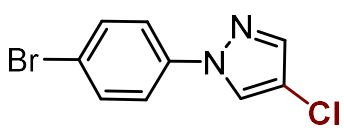
Synthetic Transformations

General procedure for the synthesis of 4- chlorinated *N*[1]-Aryl pyrazoles from the corresponding *N*[1]-Aryl pyrazoles.



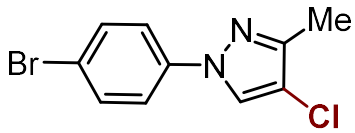
3a or **3ba** **4a or 4b**

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with *N*[1]-Aryl pyrazole **3a** (0.2 mmol, 44.4 mg, 1.0 equiv.) or **3ba** (0.2 mmol, 23.4 mg, 1.0 equiv.), TCICA (0.24 mmol, 1.2 equiv., 55.8 mg, CAS: 87-90-1), then chloroform (2 mL) was added. The resulting mixture was allowed to stir at room temperature for 4 hours in Argon atmosphere. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding 4-chlorinated *N*[1]-Aryl pyrazoles.



4a

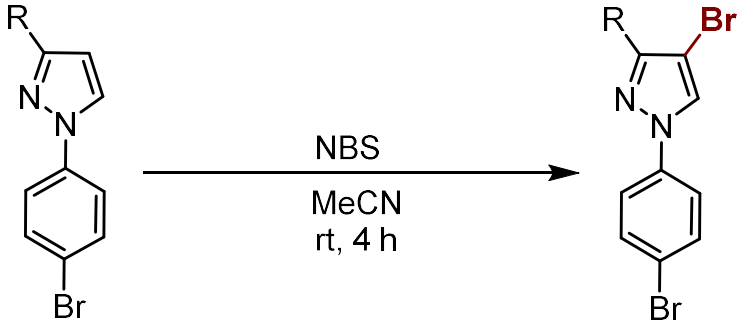
1-(4-bromophenyl)-4-chloro-1*H*-pyrazole (4a).[5] For 0.2 mmol scales, the standard procedure was followed to provide **4a** by column chromatography on silica gel (petroleum ether/EtOAc, 30:1, v/v) as yellow solid (49 mg, 95%). M.p.: 84-85 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.63 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 9.1 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.9, 138.8, 132.7, 124.8, 120.4, 120.4, 113.0. **HRMS (ESI-TOF)**: calcd. for $C_9H_7N_2ClBr$ (M+H): 256.9481, found: *m/z* 256.9480.



4b

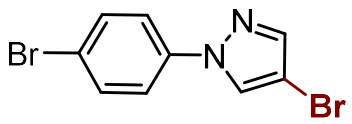
1-(4-bromophenyl)-4-chloro-3-methyl-1*H*-pyrazole (4b). For 0.1 mmol scales, the standard procedure was followed to provide **4b** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as white solid (27 mg, 95%). M.p.: 84-85 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 148.3, 138.8, 132.6, 124.8, 120.0, 119.7, 112.4, 11.3. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_9N_2ClBr$ (M+H): 270.9638, found: *m/z* 270.9636.

General procedure for the synthesis of 4-brominated N^1-Aryl pyrazoles from the corresponding N^1-Aryl pyrazoles.



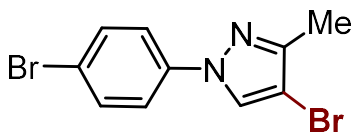
3a or **3ba** or **3fa** or **3d'** → **4c** or **4d** or **4e** or **8**

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with N^1-Aryl pyrazole **3a** (0.2 mmol, 44.4 mg, 1.0 equiv.) or **3ba** (0.2 mmol, 23.4 mg, 1.0 equiv.), or **3fa** (0.2 mmol, 62.4 mg, 1.0 equiv.) or **3d'** (0.2 mmol, 51 mg, 1.0 equiv.), NBS (0.24 mmol, 42.7 mg, 1.2 equiv., CAS: 128-08-5), then acetonitrile (2 mL) was added. The resulting mixture was allowed to stir at room temperature for 4 hours in argon atmosphere. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding 4-brominated N^1-Aryl pyrazoles.



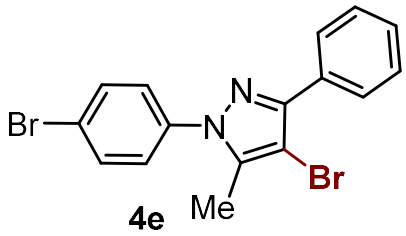
4c

4-bromo-1-(4-bromophenyl)-1*H*-pyrazole (4c).[5] For 0.2 mmol scales, the standard procedure was followed to provide **4c** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as red solid (51 mg, 85%). M.p.: 60-61 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.63 (s, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.9, 138.8, 132.7, 124.8, 120.4, 120.4, 113.0. **HRMS (ESI-TOF)**: calcd. for $C_9H_7N_2Br_2$ (M+H): 300.8976, found: *m/z* 300.8974.



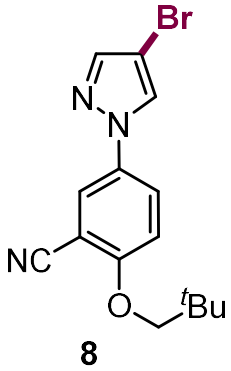
4d

4-bromo-1-(4-bromophenyl)-3-methyl-1*H*-pyrazole (4d). For 0.1 mmol scales, the standard procedure was followed to provide **4d** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as white solid (28 mg, 88%). M.p.: 91-92 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.83 (d, J = 6.1 Hz, 1H), 7.54 (dd, J = 6.2, 2.6 Hz, 2H), 7.49 (dd, J = 6.0, 2.8 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 149.8, 138.8, 132.6, 127.2, 120.1, 119.8, 97.2, 12.2. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_9N_2Br_2$ (M+H): 314.9132, found: *m/z* 314.9129.



4e

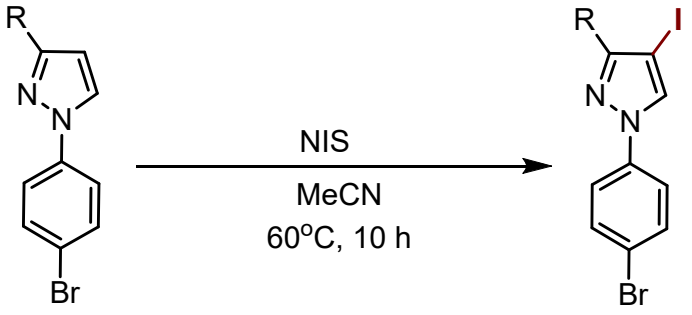
4-bromo-1-(4-bromophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (4e). For 0.2 mmol scales, the standard procedure was followed to provide **4e** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as yellow oil (58 mg, 74%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.37 (m, 3H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 149.4, 139.0, 138.8, 132.5, 132.0, 128.5, 128.5, 127.9, 126.4, 122.0, 94.9, 12.1. **HRMS (ESI-TOF)**: calcd. for $C_{16}H_{13}N_2Br_2$ (M+H): 390.9445, found: *m/z* 390.9447.



8

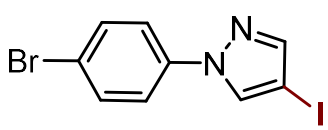
5-(4-bromo-1*H*-pyrazol-1-yl)-2-(neopentyloxy)benzonitrile (8). For 0.2 mmol scales, the standard procedure was followed to provide **8** by column chromatography on silica gel (petroleum ether/EtOAc, 8:1, v/v) as yellow solid (35 mg, 52%). M.p.: 102-103 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 2.2 Hz, 1H), 7.82 (t, *J* = 2.5 Hz, 1H), 7.78 (dt, *J* = 9.1, 2.5 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.03 (dd, *J* = 9.1, 2.2 Hz, 1H), 3.73 (d, *J* = 2.1 Hz, 2H), 1.10 (d, *J* = 1.9 Hz, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 160.0, 141.9, 133.1, 127.0, 125.1, 124.2, 115.4, 113.2, 102.9, 96.2, 79.4, 32.2, 26.6. **HRMS (ESI-TOF)**: calcd. for $C_{15}H_{11}N_3OBr$ (M+H): 334.0555, found: *m/z* 334.0560.

General procedure for the synthesis of 4-iodinated -*N*^{1}-Aryl pyrazoles from the corresponding *N*^{1}-Aryl pyrazoles.



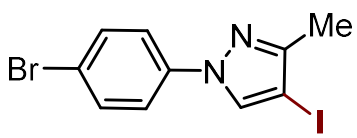
3a or **3ba** **4f** or **4g**

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with *N*^{1}-Aryl pyrazole **3a** (0.2 mmol, 44.4 mg, 1.0 equiv.) or **3ba** (0.2 mmol, 23.4 mg, 1.0 equiv.), NIS (0.6 mmol, 135 mg, 3.0 equiv., CAS: 516-12-1), then acetonitrile (2 mL) was added. The resulting mixture was allowed to stir at 60 °C for 10 hours in argon atmosphere. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding 4- iodinated *N*^{1}-Aryl pyrazoles.



4f

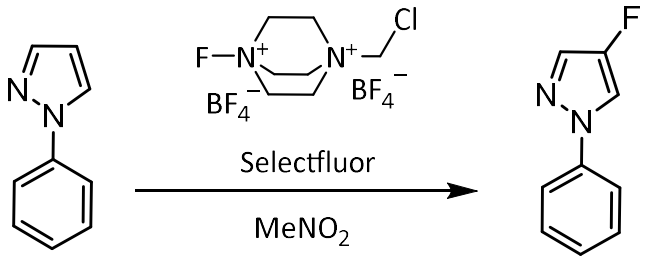
1-(4-bromophenyl)-4-iodo-1*H*-pyrazole (4f). For 0.2 mmol scales, the standard procedure was followed to provide **4f** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as white solid (60 mg, 86%). M.p.: 109-110 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 2.8 Hz, 1H), 7.70 (s, 1H), 7.56 (dd, *J* = 9.0, 2.6 Hz, 2H), 7.51 (dd, *J* = 9.0, 2.7 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.3, 138.5, 132.7, 131.3, 120.5, 120.4, 59.6. **HRMS (ESI-TOF)**: calcd. for $C_9H_7N_2BrI$ (M+H): 348.8837, found: *m/z* 348.8837.



4g

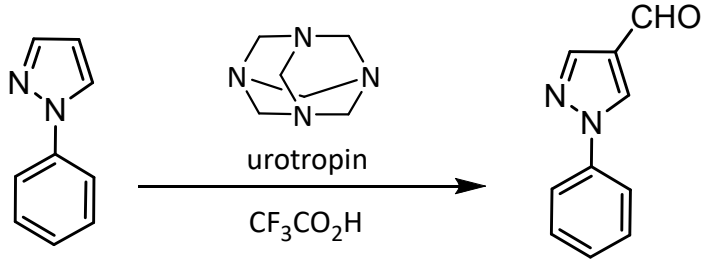
1-(4-bromophenyl)-4-iodo-3-methyl-1*H*-pyrazole (4g). For 0.2 mmol scales, the standard procedure was followed to provide **4g** by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as white solid (69 mg, 95%). M.p.: 90-91 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.1, 138.6, 132.6, 131.8, 120.1, 119.8, 63.3, 13.8. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_9N_2BrI$ (M+H): 362.8994, found: *m/z* 362.8997.

General Procedure for electrophilic and nucleophilic functionalizations of *N*[1]-Aryl pyrazoles.[6-9]



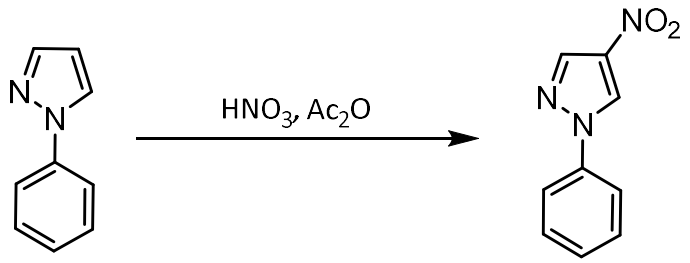
3a **5a**

A dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with 1-phenyl-1*H*-pyrazole **3a** (0.50 mmol, 72.0 mg, 1.0 equiv.), Selectfluor (1.0 mmol, 354.3 mg, 2.0 equiv.), Na_2CO_3 (0.20 mmol, 21.2 mg, 40 mol%) and $MeNO_2$ (2.0 mL) was stirred at 80 °C for 48 h under air. The reaction mixture was cooled to room temperature and then filtered through a pad of Celite and concentrated under reduced pressure. The residue was then charged on silica gel column and eluted with a mixture of ethyl acetate/petroleum ether (1:40) to give the desired product **5a**. **4-Fluoro-1-phenyl-1*H*-pyrazole (5a).** Yellow solid (33 mg, 50%). M.p.: 37-38 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 4.3 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -175.06. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.2 (d, *J* = 248.6 Hz), 140.1, 129.5, 128.5 (d, *J* = 13.7 Hz), 126.7, 118.7, 113.0 (d, *J* = 28.4 Hz). **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_2F$ (M+H): 163.0672, found: *m/z* 163.0670.



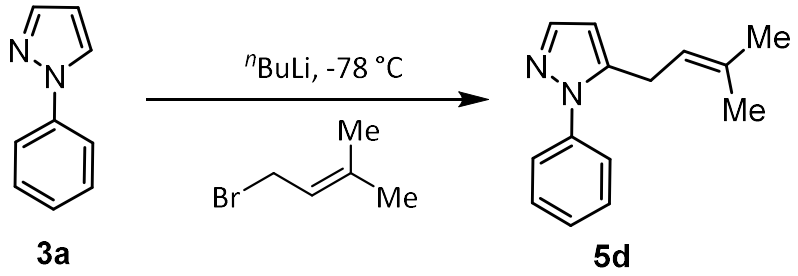
3a **5b**

To a 100 mL round-bottom flask, 1.00 mmol of 1-phenyl-1*H*-pyrazoles **3a** (2.0 mmol, 288.1 mg, 1.0 equiv.), hexamethylenetetramine (3.0 mmol, 420.6 mg, 1.5 equiv.) and trifluoracetic acid (5 mL) were added. The reaction was heated under reflux with stirring for 12 h. At the end of the reaction, the resulting solution was neutralized with a 10% $NaHCO_3$ solution in an ice bath and the precipitate was filtered off under vacuum. **1-Phenyl-1*H*-pyrazole-4-carbaldehyde (5b).** White solid (179 mg, 52%). M.p.: 84-85 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 8.44 (s, 1H), 8.17 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 184.0, 141.7, 139.2, 130.0, 129.7, 128.0, 125.7, 119.8. **HRMS (ESI-TOF)**: calcd. for $C_{10}H_9N_2O$ (M+H): 173.0715, found: *m/z* 173.0718.



3a **5c**

1-Phenyl-1*H*-pyrazole **3a** (72 mg, 0.5 mmol) was added to a cold mixture (-10 °C) of acetic anhydride (2 mL) and conc. HNO_3 (0.1 mL) and stirring was continued at ambient temperature for 4 hrs. The reaction mixture quenched with cold water and filtered. Isolation of the filter cake, which was then charged on silica gel column and eluted with a mixture of ethyl acetate/petroleum ether (1:10) to give the desired product **5c**. **4-Nitro-1-phenyl-1*H*-pyrazole (5c).** White solid (23 mg, 61%). M.p.: 127-128 ºC. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 8.26 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.7, 136.7, 129.9, 128.7, 125.8, 120.1, 119.8. **HRMS (ESI-TOF)**: calcd. for $C_9H_8N_3O_2$ (M+H): 190.0617, found: *m/z* 190.0612.

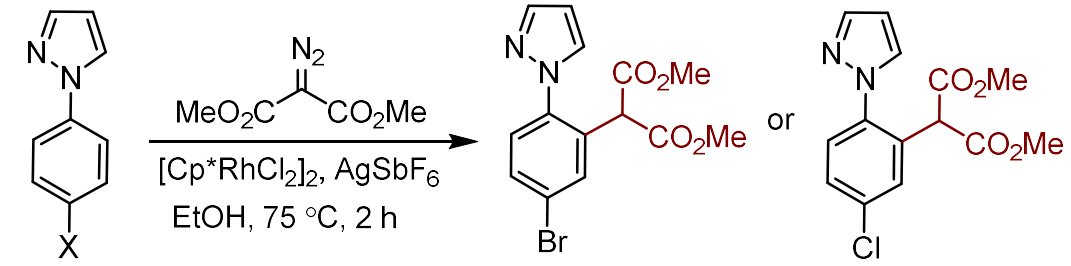


3a **5d**

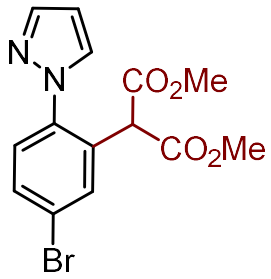
A dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with 1-phenyl-1*H*-pyrazole **3a** (1.0 mmol, 144.2 mg, 1 equiv.) and dry THF were loaded to the flask, and the mixture was cooled to −78 °C. To the stirred solution ^{n}BuLi (1.2 mmol, 0.75 mL, 1.2 equiv., 1.6 M in THF) was added dropwise. When the addition was finished, the mixture was stirred for 1 hour at the same temperature. Then, a solution of 3-methyl-2-butyenyl bromide (1.2 mmol, 178.8 mg, 1.2 equiv.) in THF was added dropwise. The mixture was stirred for 2 h at the same temperature. The cooling bath was removed, and the mixture was stirred at rt for 12 h. The reaction mixture was diluted with a saturated solution of ammonium chloride and concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with a sodium bicarbonate solution (3 times). The organic layer was separated, dried over sodium sulfate, and concentrated under reduced pressure. The residue was then charged on silica gel column and eluted with a mixture of ethyl acetate/petroleum ether (1:10) to give the desired product **5d**. **5-(3-methylbut-2-en-1-yl)-1-phenyl-1*H*-pyrazole (5d).** Yellow liquid (144 mg, 68%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.44 (d, *J* = 5.8 Hz, 4H), 7.37 (dt, *J* = 8.5, 4.4 Hz, 1H), 6.19 (s, 1H), 5.23 (t, *J* = 6.9 Hz, 1H), 3.34 (d, *J* = 7.0 Hz, 2H), 1.70 (s, 3H), 1.56 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.8, 139.9, 133.9, 129.0, 127.7, 125.4, 120.2, 105.8, 25.6, 25.5, 17.7. **HRMS**

(ESI-TOF): calcd. for $C_{14}H_{17}N_2$ (M+H): 213.1392, found: *m/z* 213.1389.

General Procedure for the Rh(III)-Catalyzed *ortho* C–H Functionalization of Arenes with Diazo Compounds.[10]

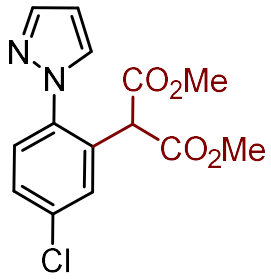


A dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with 1-aryl-1*H*-pyrazole **3a** (0.2 mmol, 44.4 mg, 1.0 equiv.) or **3j** (0.2 mmol, 35.6 mg, 1.0 equiv.), $[Cp^*RhCl_2]_2$ (2 μmol, 1 mg, 1mol%), $AgSbF_6$ (10 μmol, 3 mg, 5mol%), and EtOH (2 mL) under Ar. After the reaction mixture was stirred at room temperature for 1 h, diazo compound (0.24 mmol, 38 mg, 1.2 equiv.) was then added in one pot, and the mixture was stirred at 75 °C for 2 h. The reaction mixture was cooled to room temperature and then filtered through a pad of Celite and concentrated under reduced pressure. The residue was then charged on silica gel column and eluted with a mixture of ethyl acetate/petroleum ether (1:8) to give the desired product **6a** or **6b**.



6a

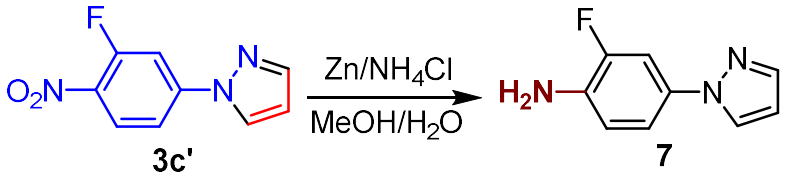
dimethyl 2-[5-bromo-2-(1*H*-pyrazol-1-yl)phenyl]malonate (6a). For 0.2 mmol scales, the standard procedure was followed to provide **6a** by column chromatography on silica gel (petroleum ether/EtOAc, 5:1, v/v) as white solid (58 mg, 78%). M.p.: 92-93 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.2 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 4.94 (s, 1H), 3.73 (s, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 168.1, 141.6, 138.8, 133.5, 132.3, 131.1, 130.6, 127.4, 122.4, 107.5, 53.3, 52.1. **HRMS (ESI-TOF)**: calcd. for $C_{14}H_{14}N_2O_4Br$ (M+H): 353.0137, found: *m/z* 353.0139.



6b

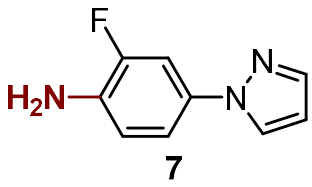
dimethyl 2-[5-chloro-2-(1*H*-pyrazol-1-yl)phenyl]malonate (6b). For 0.2 mmol scales, the standard procedure was followed to provide **6b** by column chromatography on silica gel (petroleum ether/EtOAc, 25:1, v/v) as white solid (45 mg, 73%). M.p.: 74-75 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 2.0 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 6.45 (t, *J* = 2.2 Hz, 1H), 4.93 (s, 1H), 3.73 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.1, 141.6, 138.3, 134.5, 131.1, 130.6, 130.4, 129.3, 127.2, 107.4, 53.2, 52.2. **HRMS (ESI-TOF)**: calcd. for $C_{14}H_{14}N_2O_4Cl$ (M+H): 309.0642, found: *m/z* 309.0645.

General Procedure for the synthesis of aromatic amine (7) from nitroarene (3c').



3c' 7

A dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with 1-(3-fluoro-4-nitrophenyl)-1*H*-pyrazole **3c'** (1.0 equiv., 30.7 mg, 0.1 mmol), zinc powder (10 equiv., 65.4 mg, 1 mmol), ammonium chloride (15 equiv., 80 mg, 1.5 mmol), MeOH (2 mL) and H_2O (1 mL). After the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was then charged on silica gel column and eluted with a mixture of ethyl acetate/petroleum ether (1:2) to give the desired product **7**.

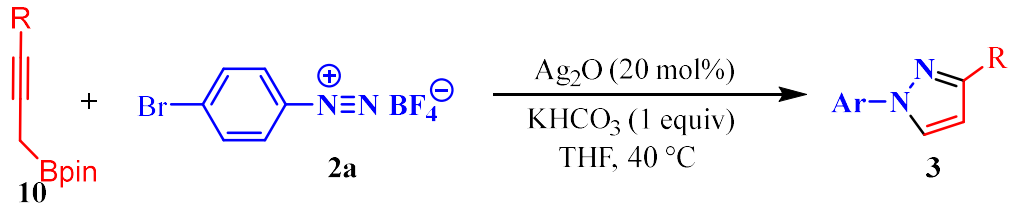


7

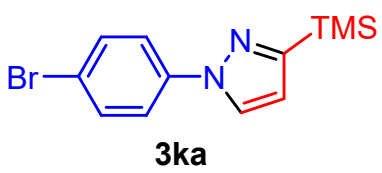
2-fluoro-4-(1*H*-pyrazol-1-yl)aniline (7). For 0.1 mmol scales, the standard procedure was followed to provide **7** by column chromatography on silica gel (petroleum ether/EtOAc, 2:1, v/v) as yellow oil (15 mg, 55%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.4 Hz, 1H), 7.66 (s, 1H), 7.37 (d, *J* = 13.1 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.81 (t, *J* = 8.9 Hz, 1H), 6.46 – 6.38 (m, 1H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -132.79. **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.4 (d, *J* = 240.0 Hz), 140.7, 133.3 (d, *J* = 12.8 Hz), 132.3 (d, *J* = 8.7 Hz), 126.8, 117.0 (d, *J* = 4.6 Hz), 115.6 (d, *J* = 3.6 Hz), 108.0 (d, *J* = 23.1 Hz), 107.3. **HRMS (ESI-TOF)**: calcd. for $C_9H_9N_3F$ (M+H): 178.0781, found: *m/z* 178.0782.

Mechanistic studies.

General procedure for the synthesis of *N*^{1}-Aryl pyrazoles from the corresponding aryl diazonium salts and propargynyl borates.

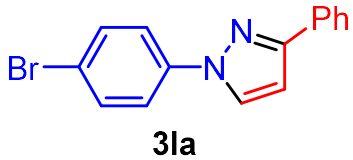


An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with aryl diazonium salts **2** (0.4 mmol, 2.0 equiv., 108 mg), Ag_2O (0.04 mmol, 20 mol%, 9.2 mg), $KHCO_3$ (0.2 mmol, 1.0 equiv., 20 mg), then THF (1 mL) was added. After that, propargynyl borates **10** (0.2 mmol, 1.0 equiv.) in 1 mL THF was added slowly in 3 minutes. The resulting mixture was allowed to stir at 40 ºC in Argon atmosphere for 8 hours. Then the mixture was filtered through a Celite plug, rinsed with ethyl acetate. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding *N*^{1}-Aryl pyrazoles **3**.



3ka

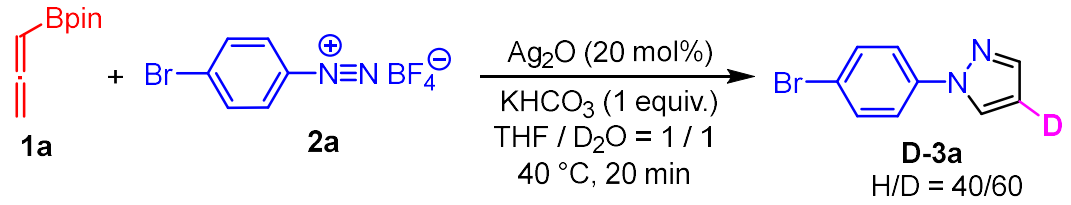
1-(4-bromophenyl)-3-(trimethylsilyl)-1*H*-pyrazole (3ka). For 0.2 mmol scales, the standard procedure was followed to provide **3ka** by column chromatography on silica gel (petroleum ether/EtOAc, 50:1, v/v) as yellow oil (28 mg, 47%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.4 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 2.4 Hz, 1H), 0.34 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 155.7, 139.5, 132.4, 126.8, 121.0, 119.5, 114.0, -1.0. **HRMS (ESI-TOF)**: calcd. for $C_{12}H_{16}N_2BrSi$ (M+H): 295.0266, found: *m/z* 295.0262.



3la

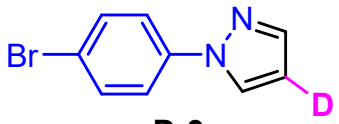
1-(4-bromophenyl)-3-phenyl-1*H*-pyrazole (3la). For 0.2 mmol scales, the standard procedure was followed to provide **3la** by column chromatography on silica gel (petroleum ether/EtOAc, 10:1, v/v) as white solid (19 mg, 33%). M.p.: 124-125ºC. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 2H), 7.90 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 6.7 Hz, 1H), 6.78 (d, *J* = 2.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.3, 139.3, 133.0, 132.5, 128.8, 128.3, 128.0, 126.0, 120.5, 119.5, 105.6. **HRMS (ESI-TOF)**: calcd. for $C_{15}H_{12}N_2Br$ (M+H): 299.0184, found: *m/z* 299.0182.

General procedure for the synthesis of 4-Deuterated *N*^{1}-Aryl pyrazoles from the corresponding aryl diazonium salt and allenylboronate.



1a 2a D-3a H/D = 40/60

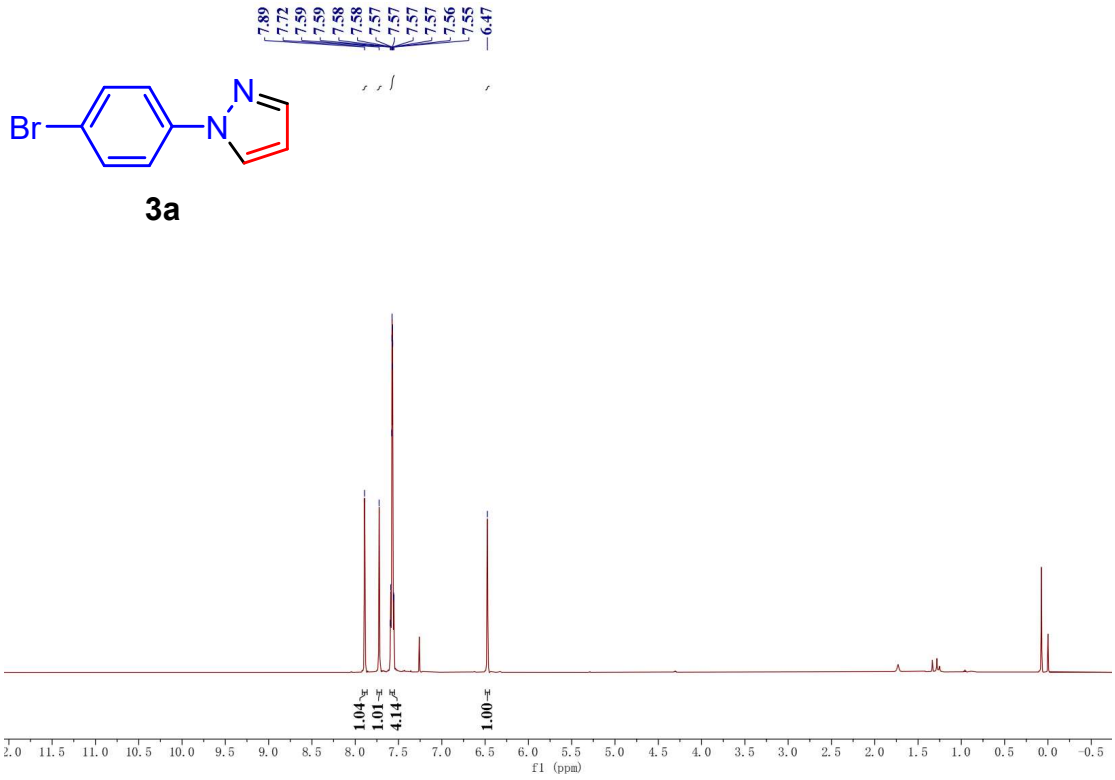
Deuterium Labeling Experiments: An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with aryl diazonium salts **2** (0.4 mmol), Ag_2O (20 mol%, 9.2 mg), $KHCO_3$ (1.0 equiv., 20 mg), then THF (1 mL) and D_2O (2 mL) were added. After that, allenylboronate **1a** (1.0 equiv., 0.2 mmol) was added in 1 mL of THF slowly in 3 minutes. The resulting mixture was allowed to stir at 40 °C in Argon atmosphere for 20 minutes. Then the mixture was filtered through a Celite plug, rinsed with ethyl acetate. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding 4-Deuterated *N*^{1}-Aryl pyrazoles **D-3a**. The H/D ratios of the product was determined by **^{1}H NMR** analysis. (H/D = 40/60)



D-3a

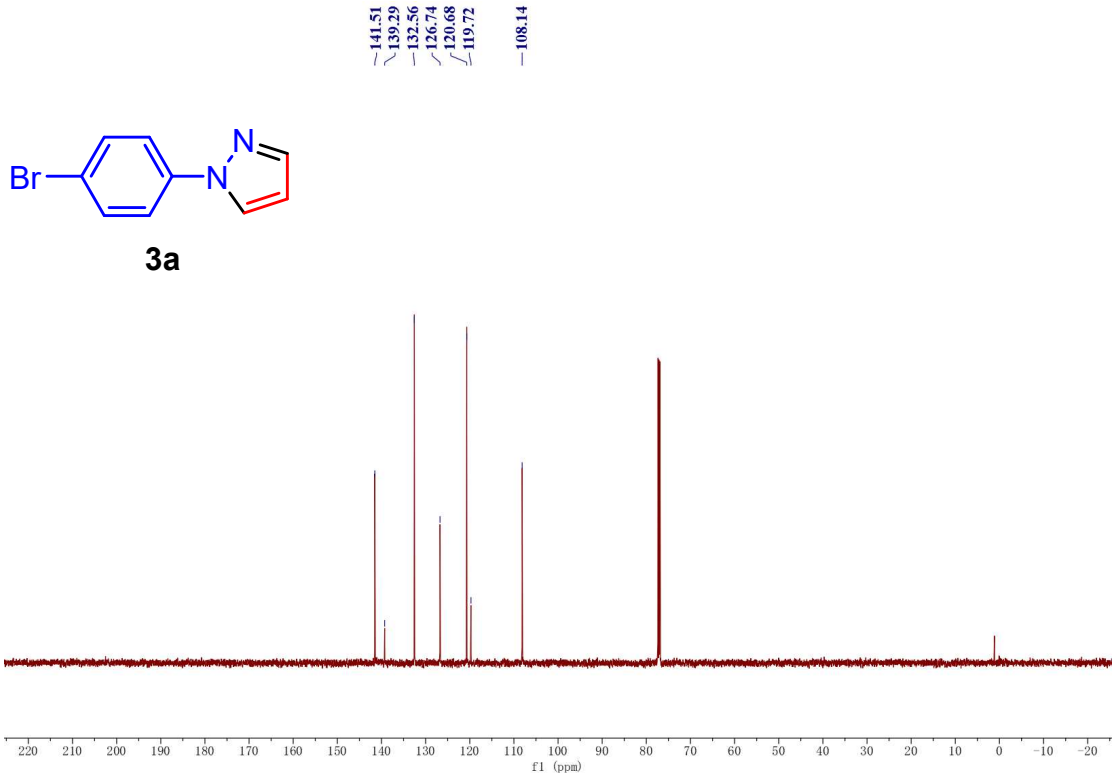
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 4.7 Hz, 1H), 7.72 (d, *J* = 3.5 Hz, 1H), 7.66 – 7.39 (m, 4H), 6.48 (d, *J* = 3.3 Hz, 0.4H).

NMR Spectra



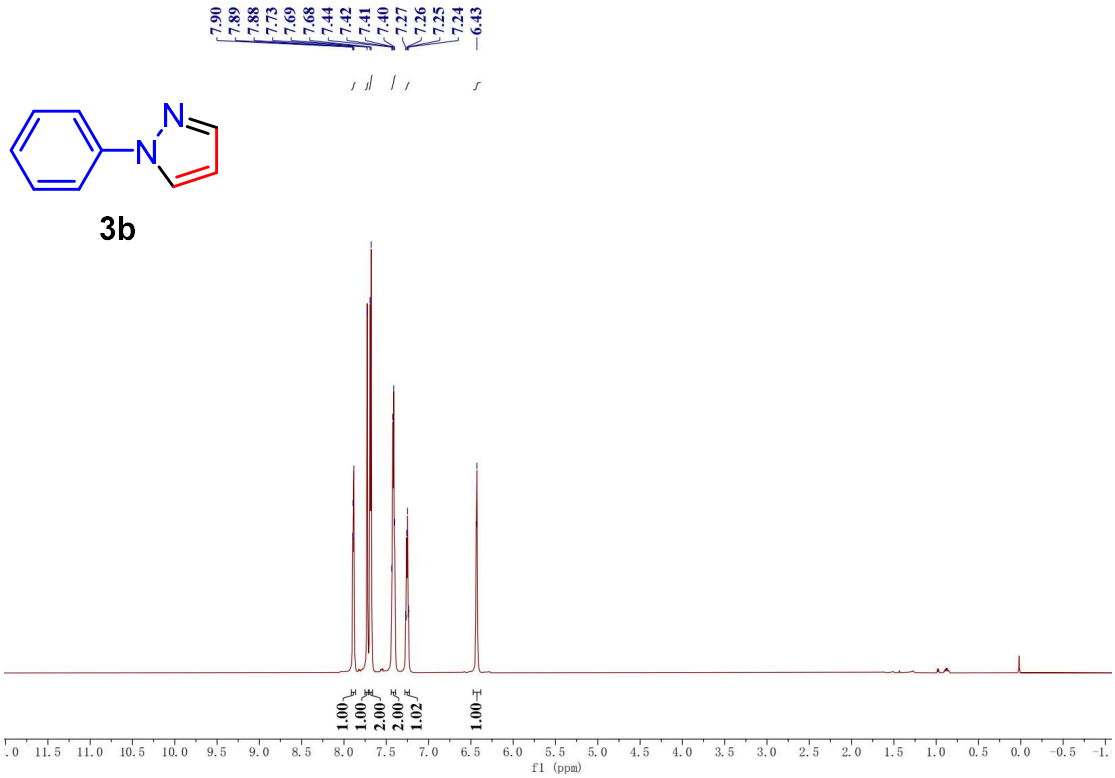
3a

^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3a**

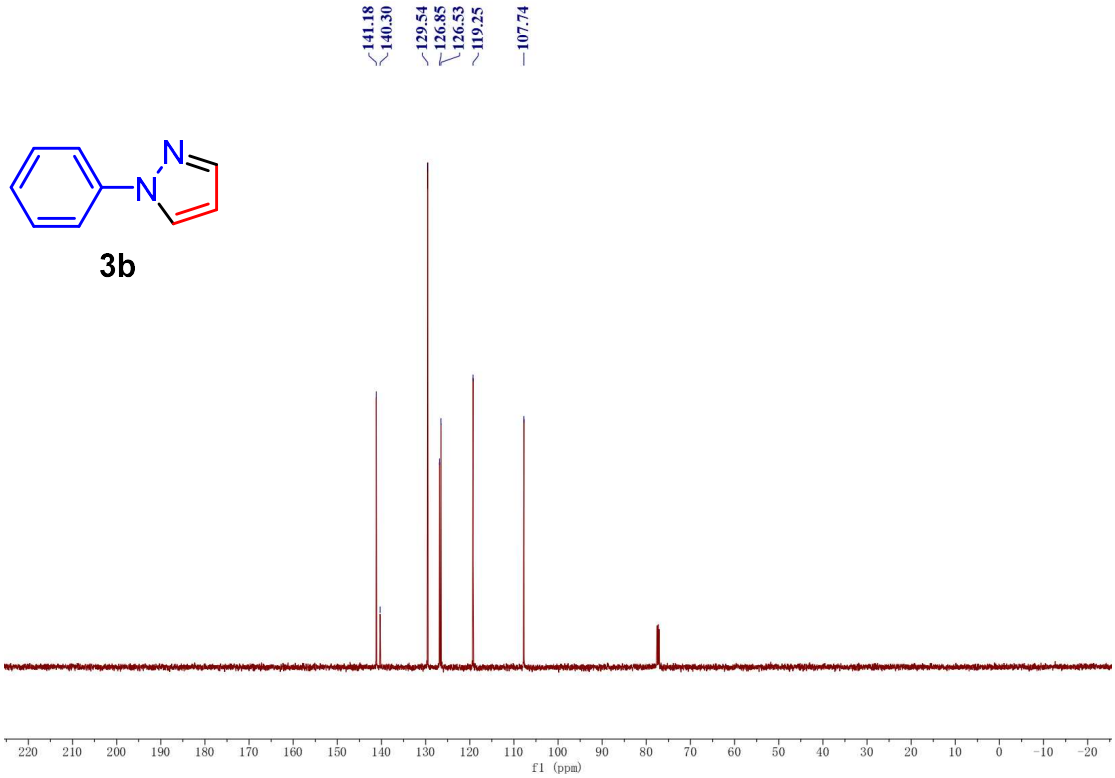


3a

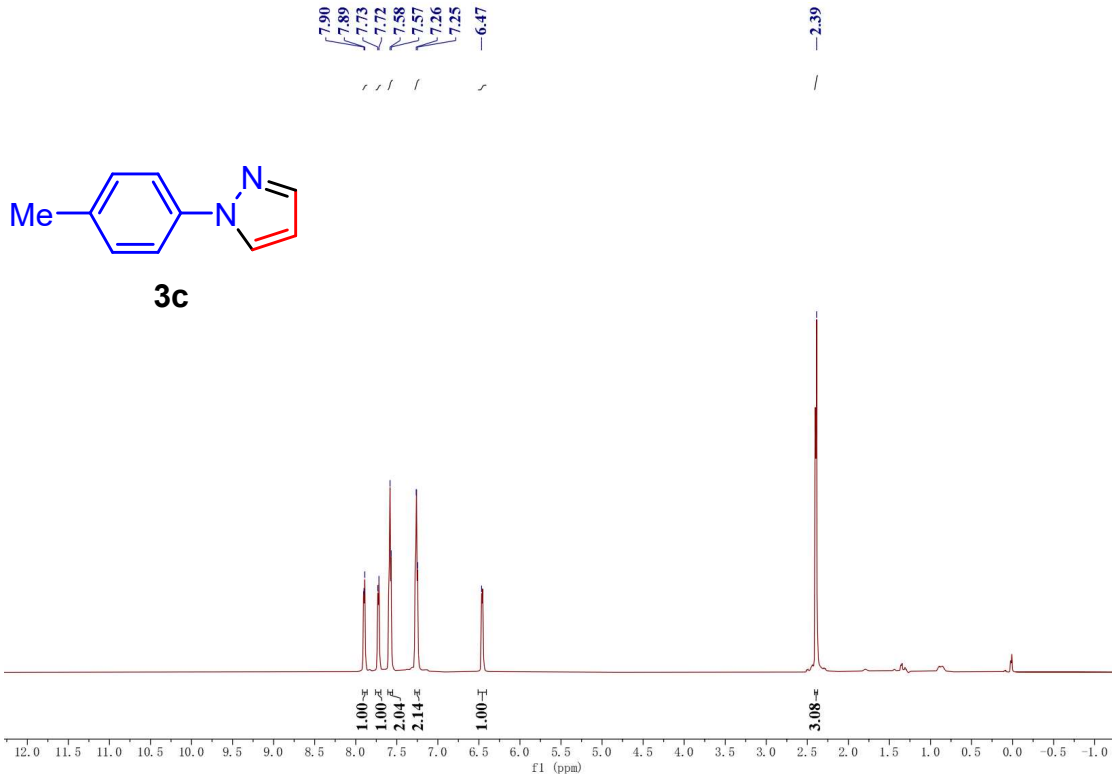
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3a**



^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3b**

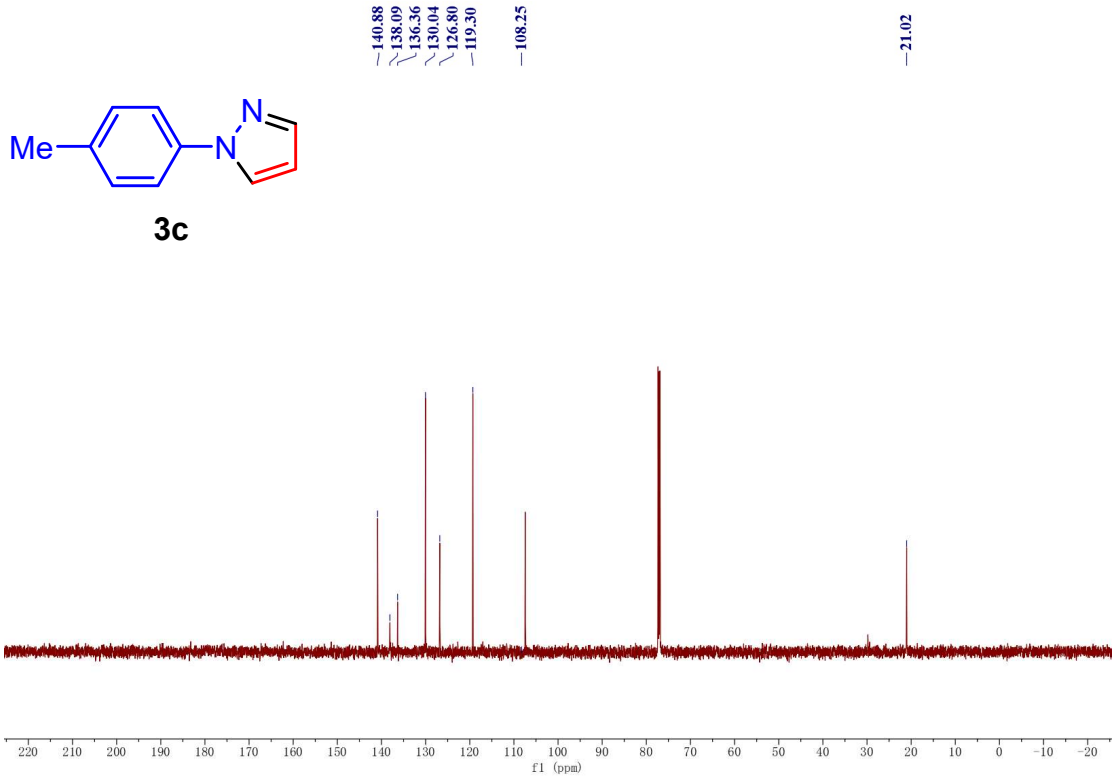


^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3b**



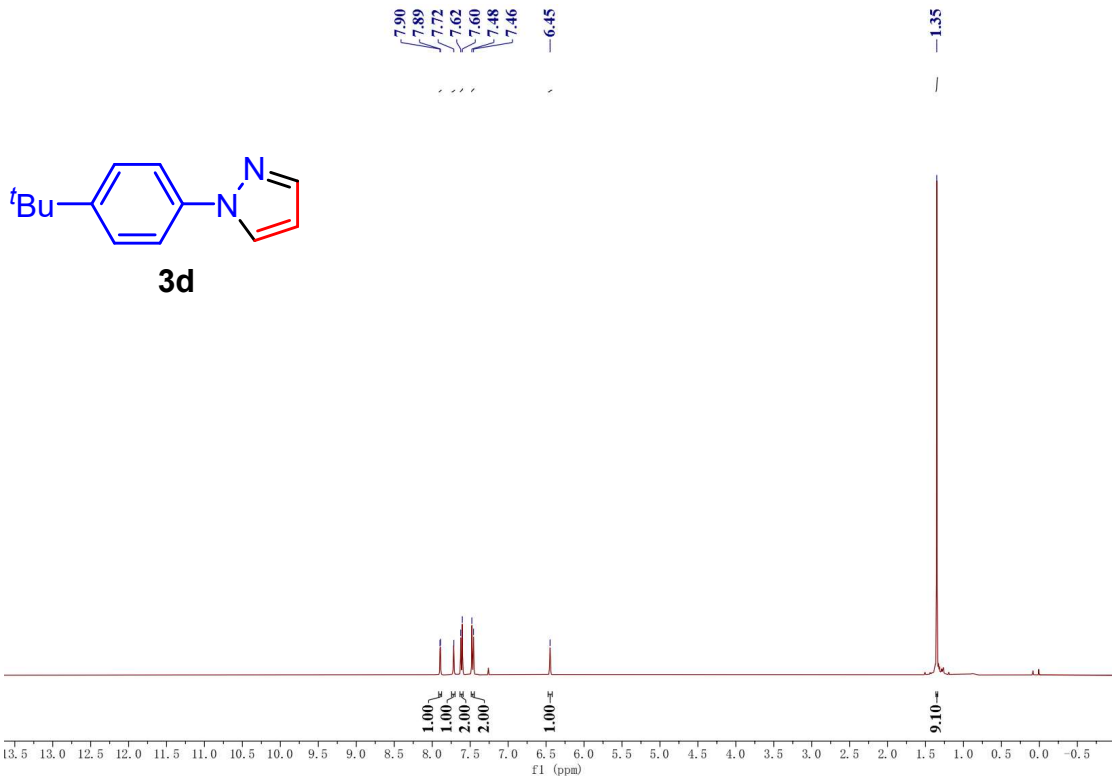
3c

^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3c**

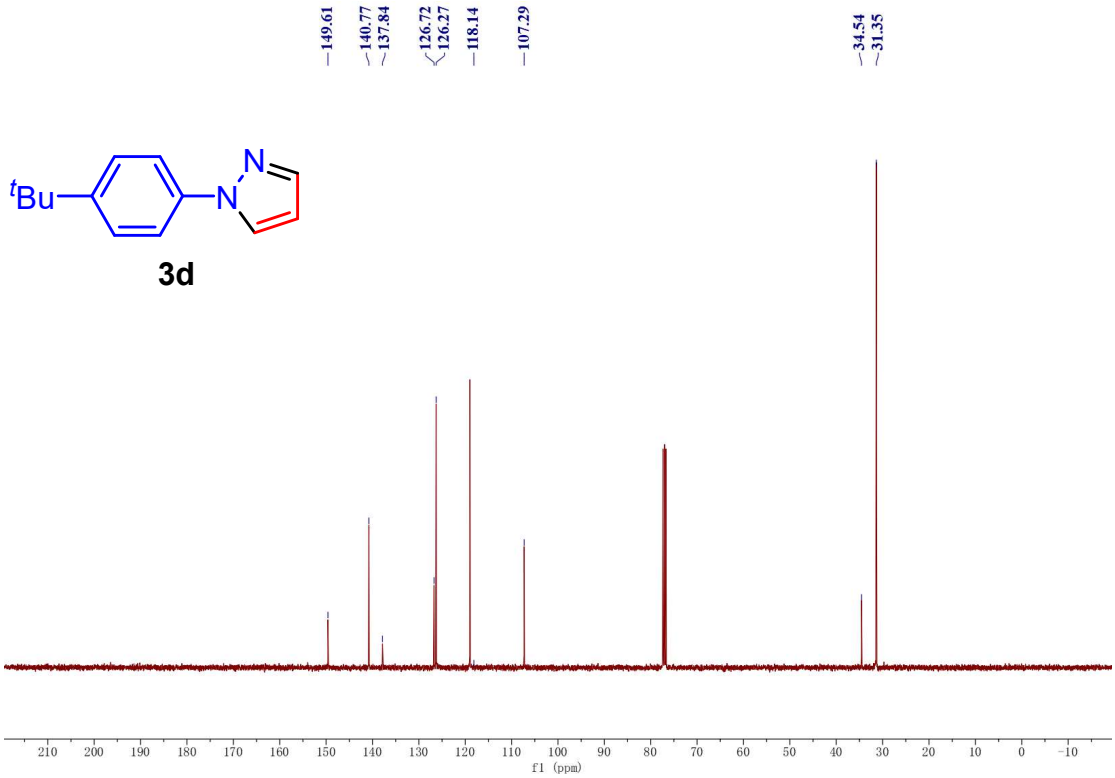


3c

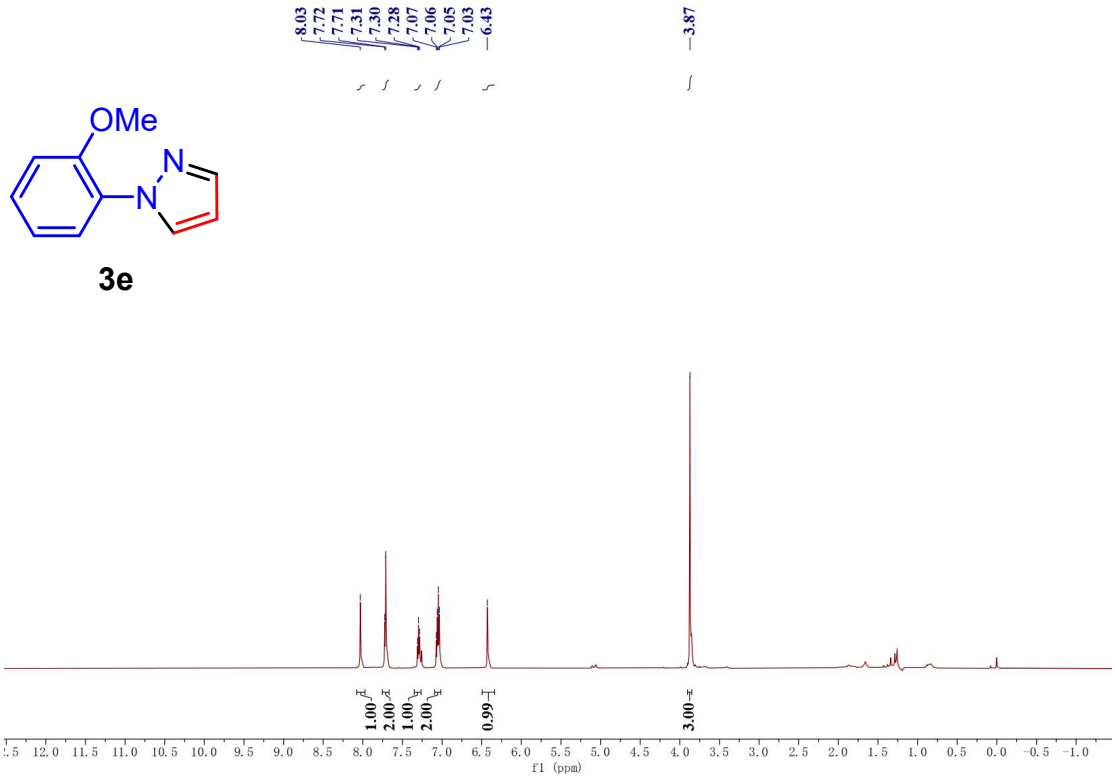
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3c**



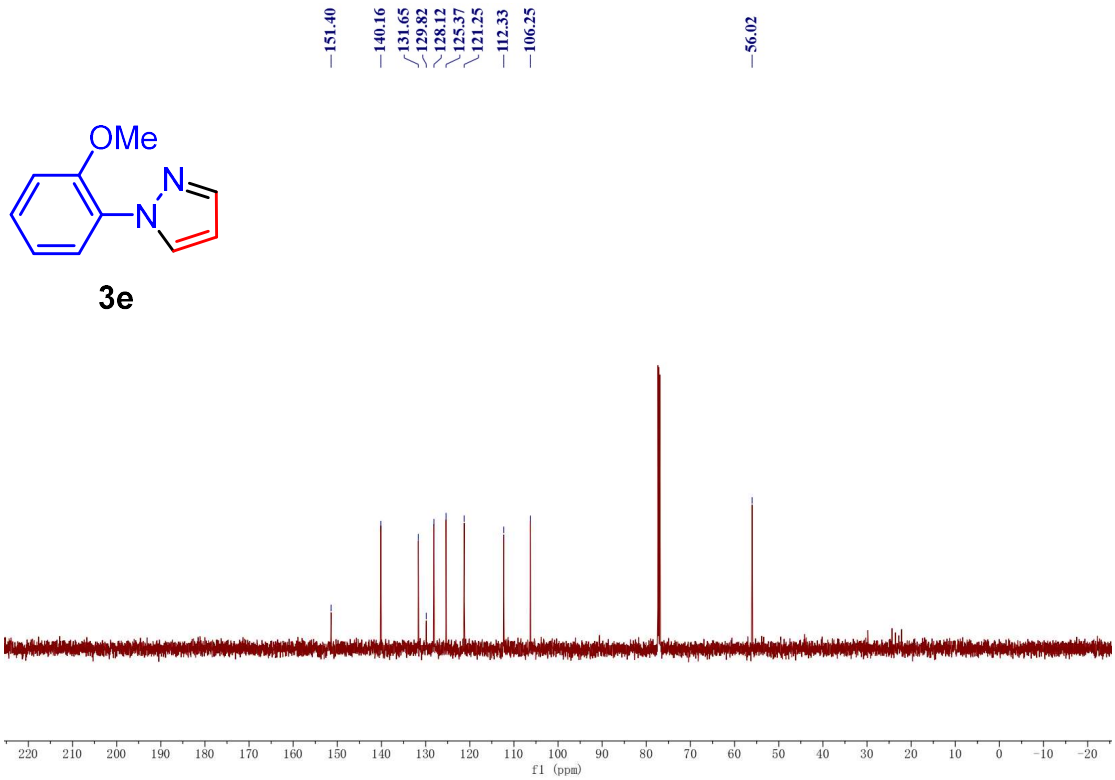
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **3d**



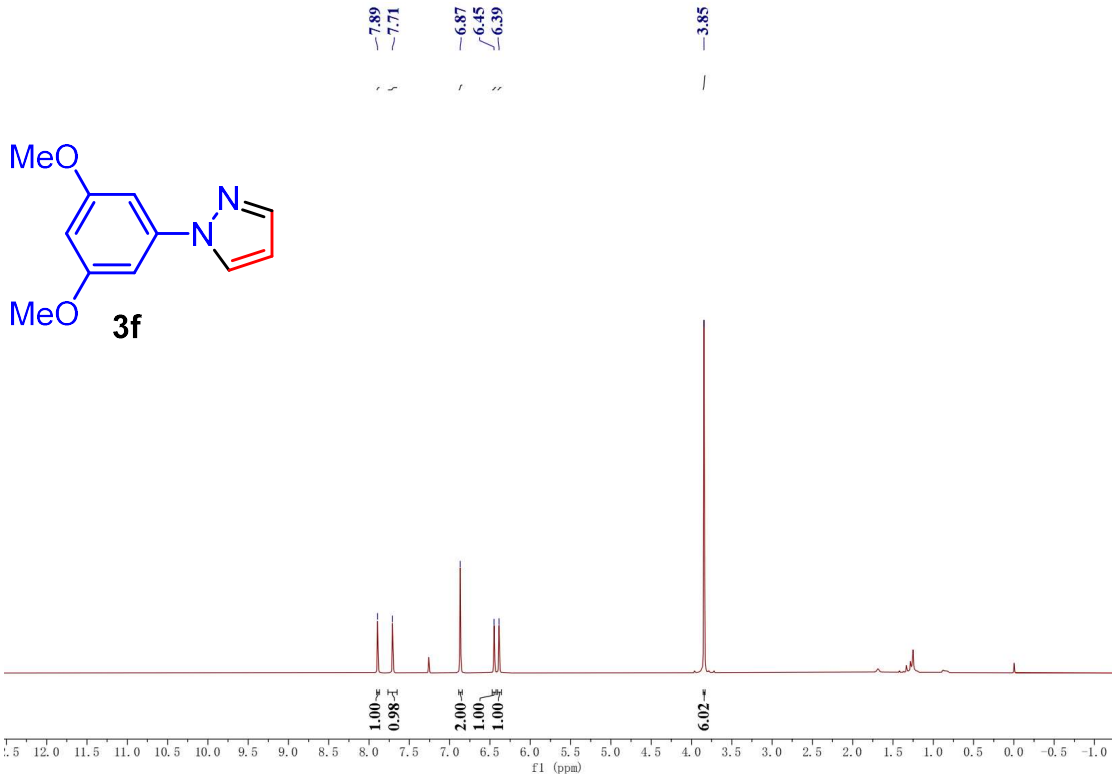
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **3d**



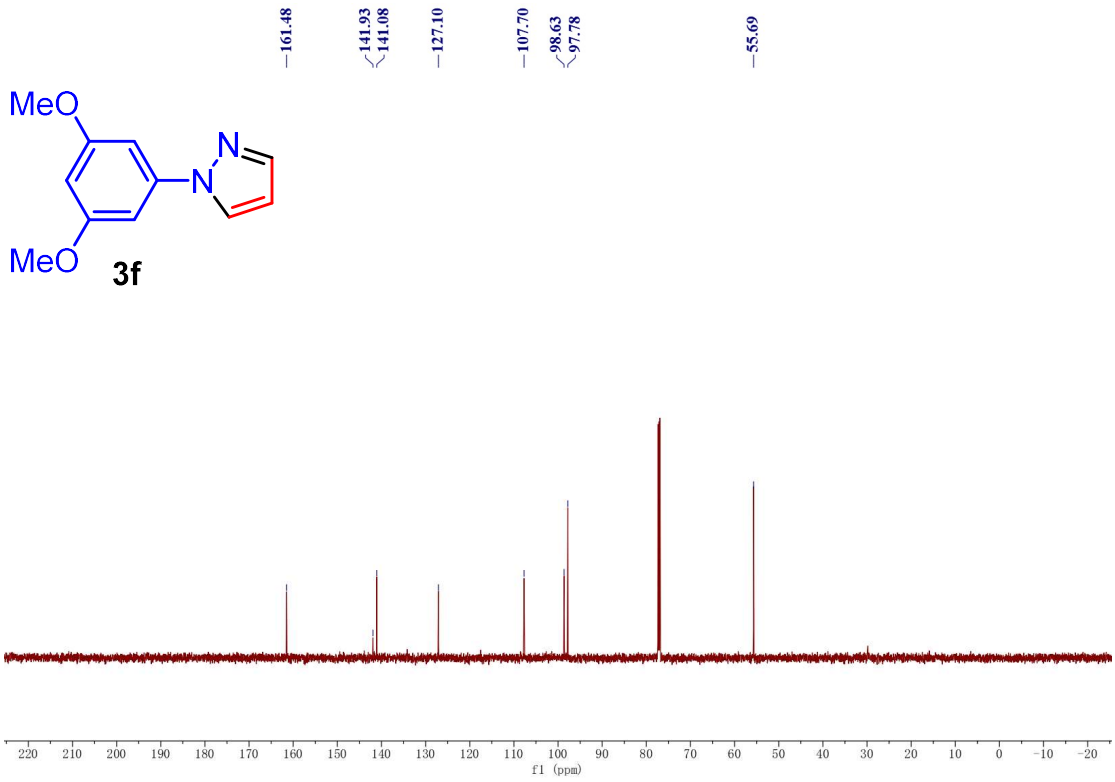
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3e**



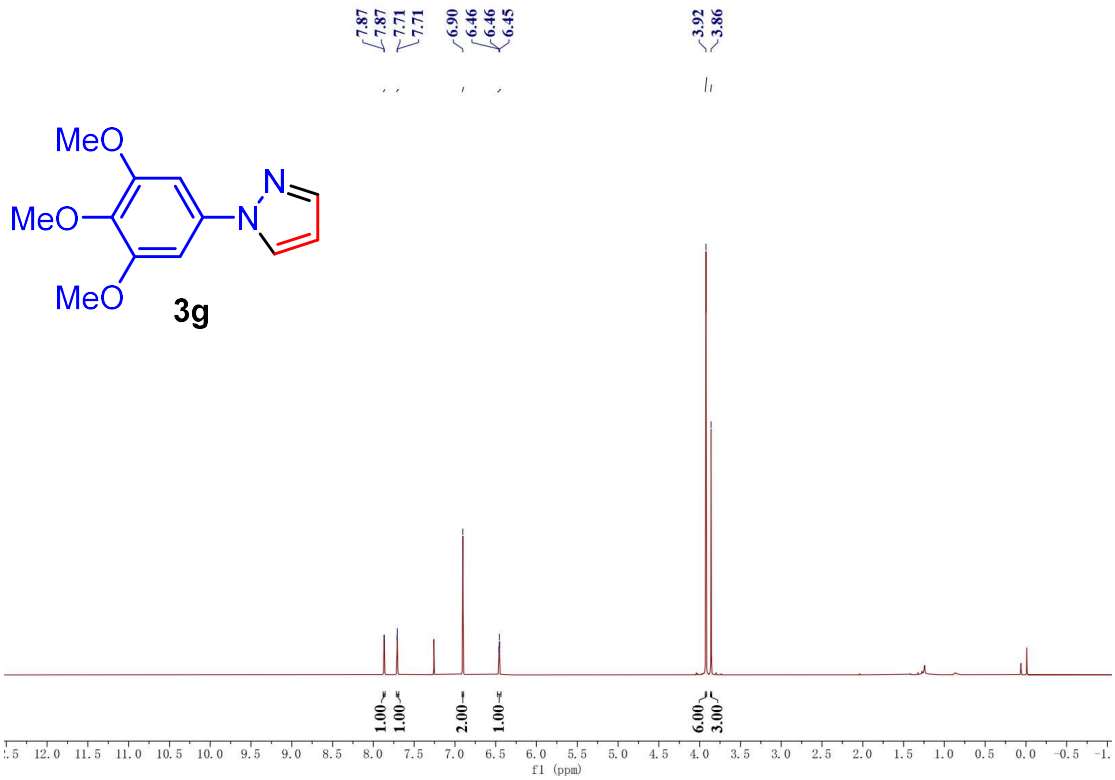
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3e**



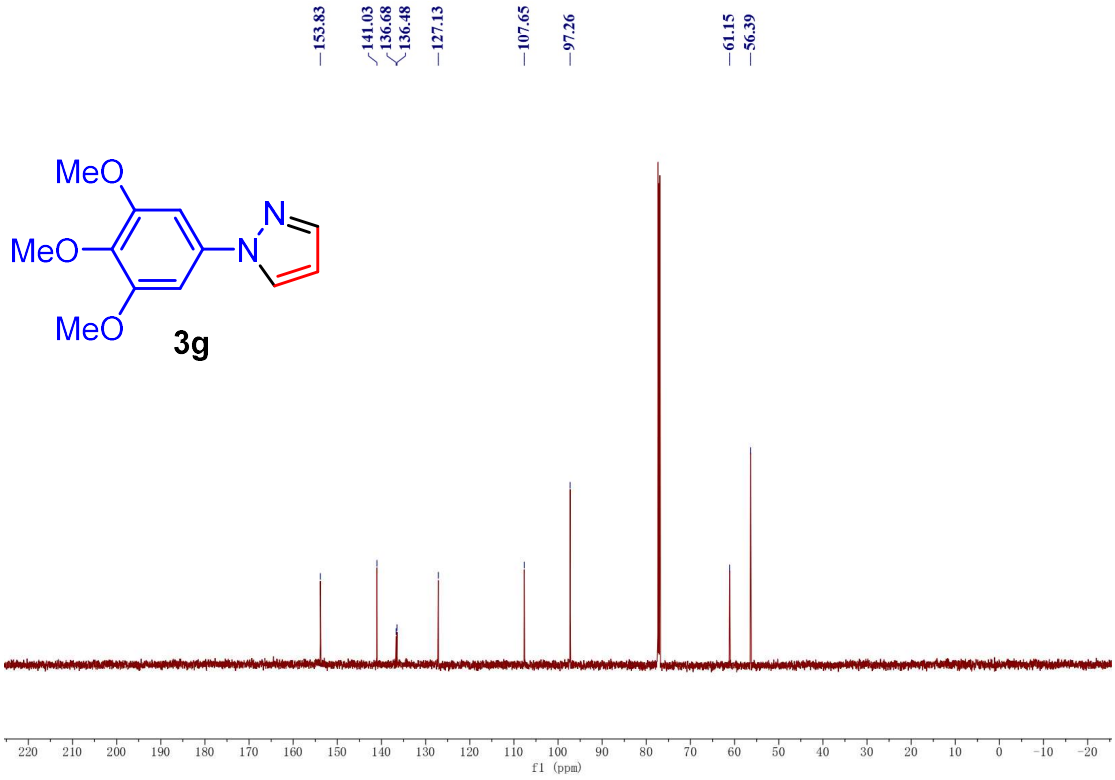
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3f**



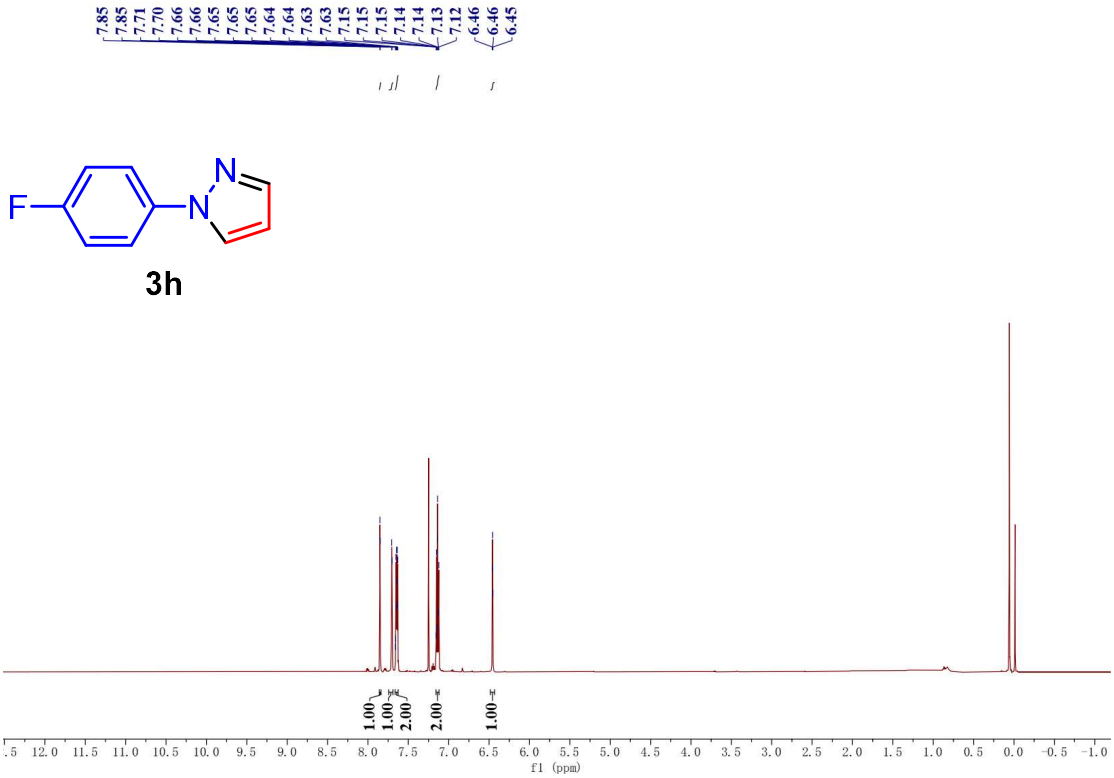
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3f**



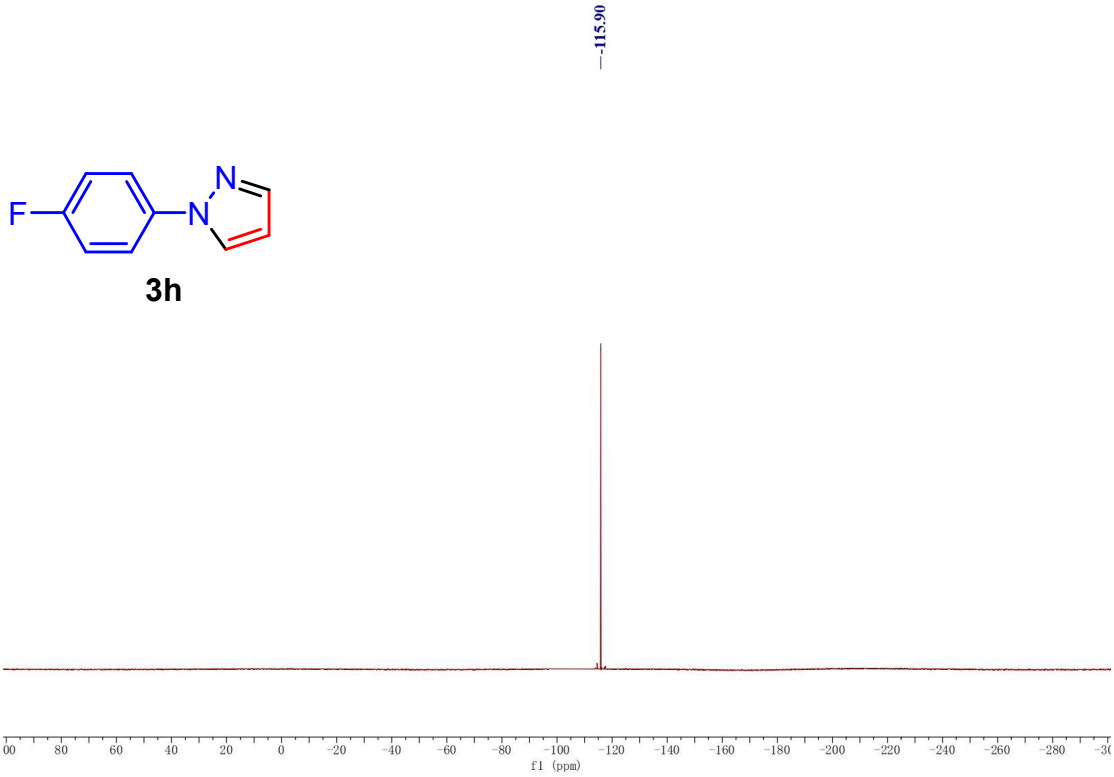
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3g**



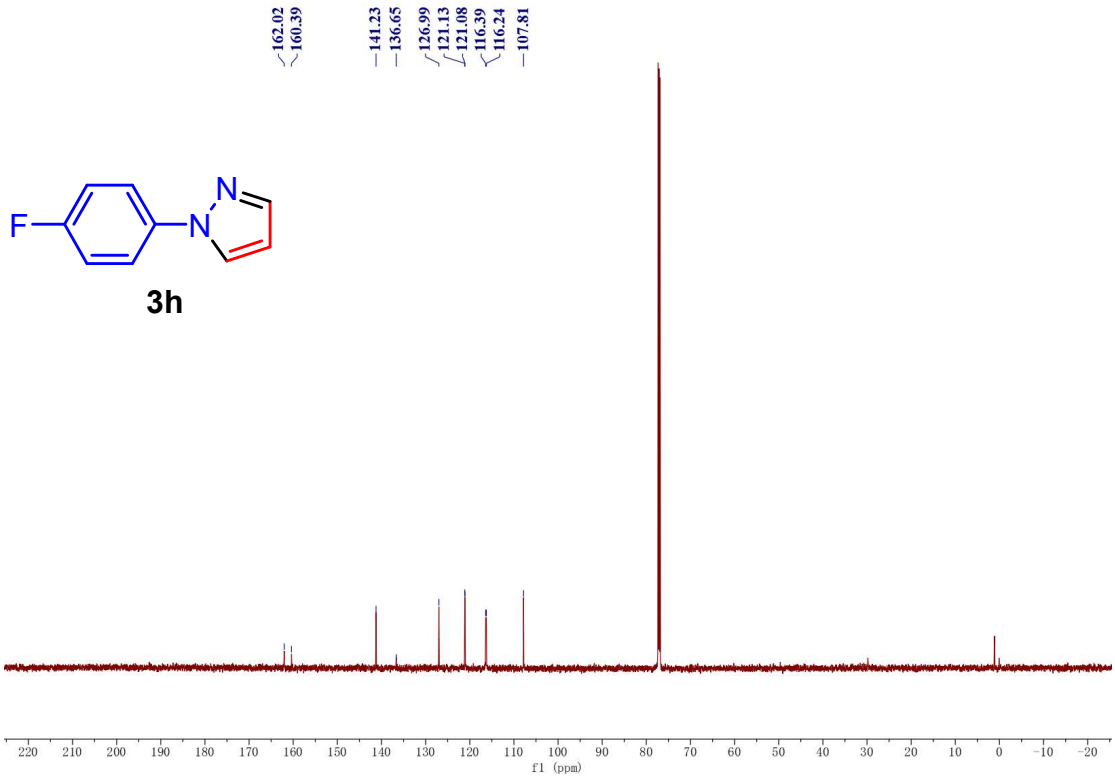
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3g**



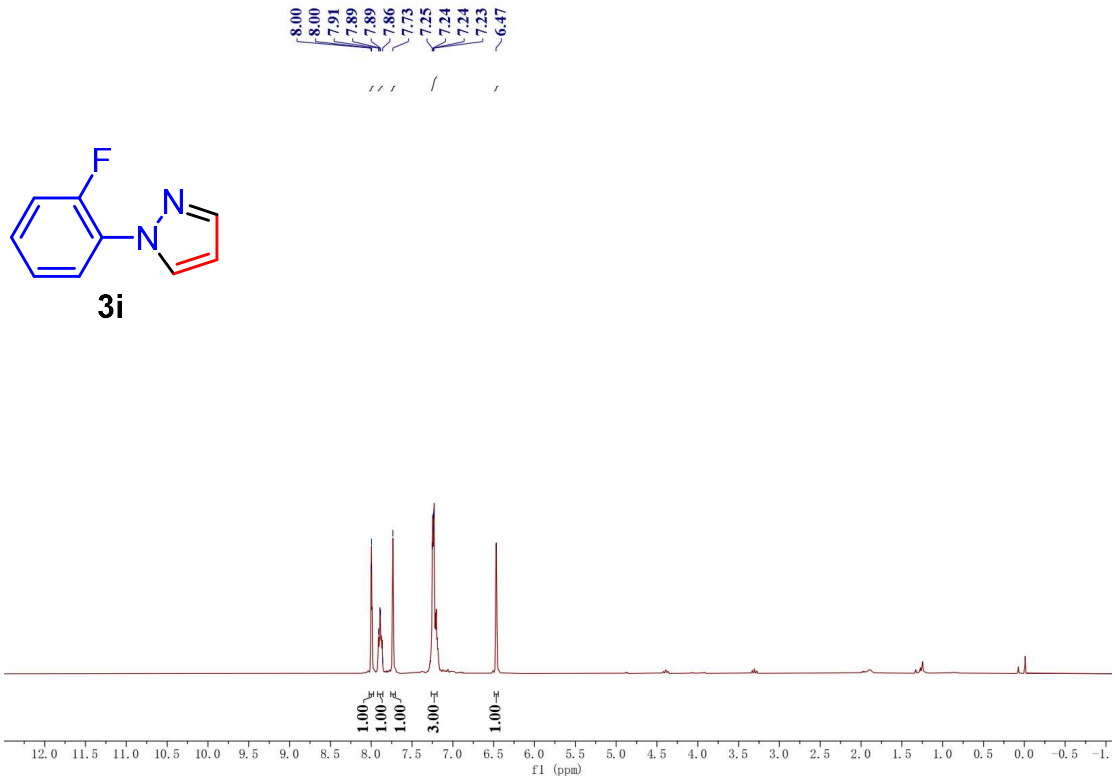
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3h**



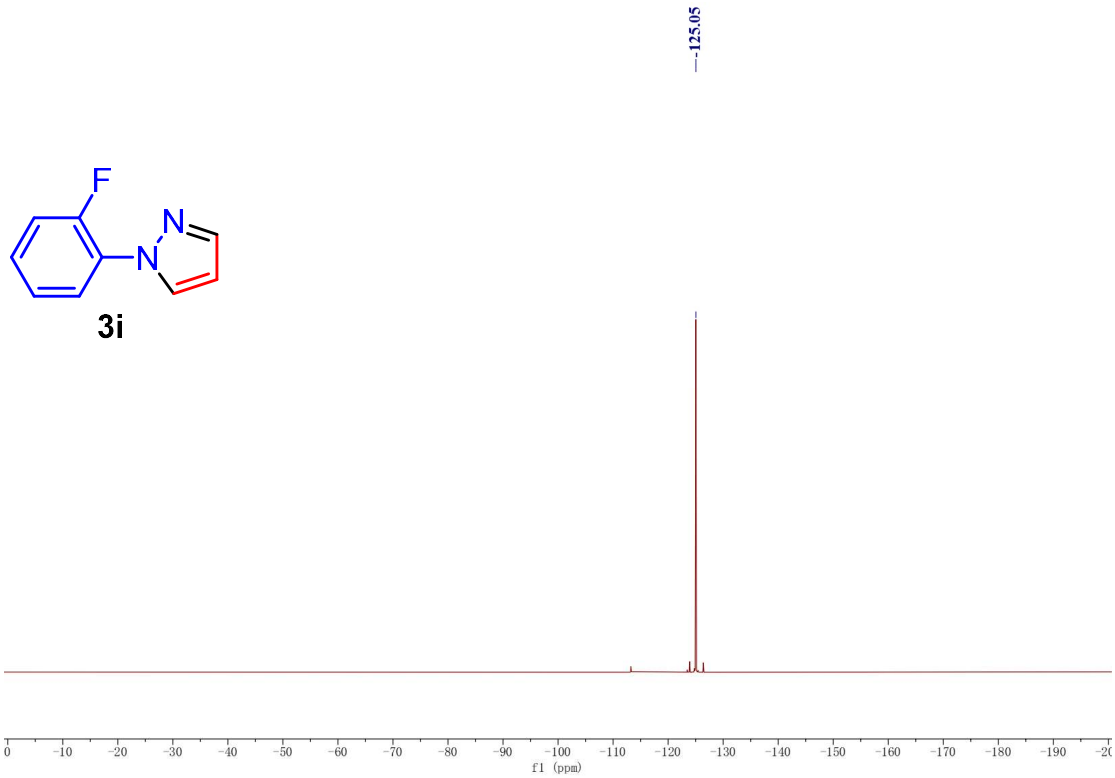
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **3h**



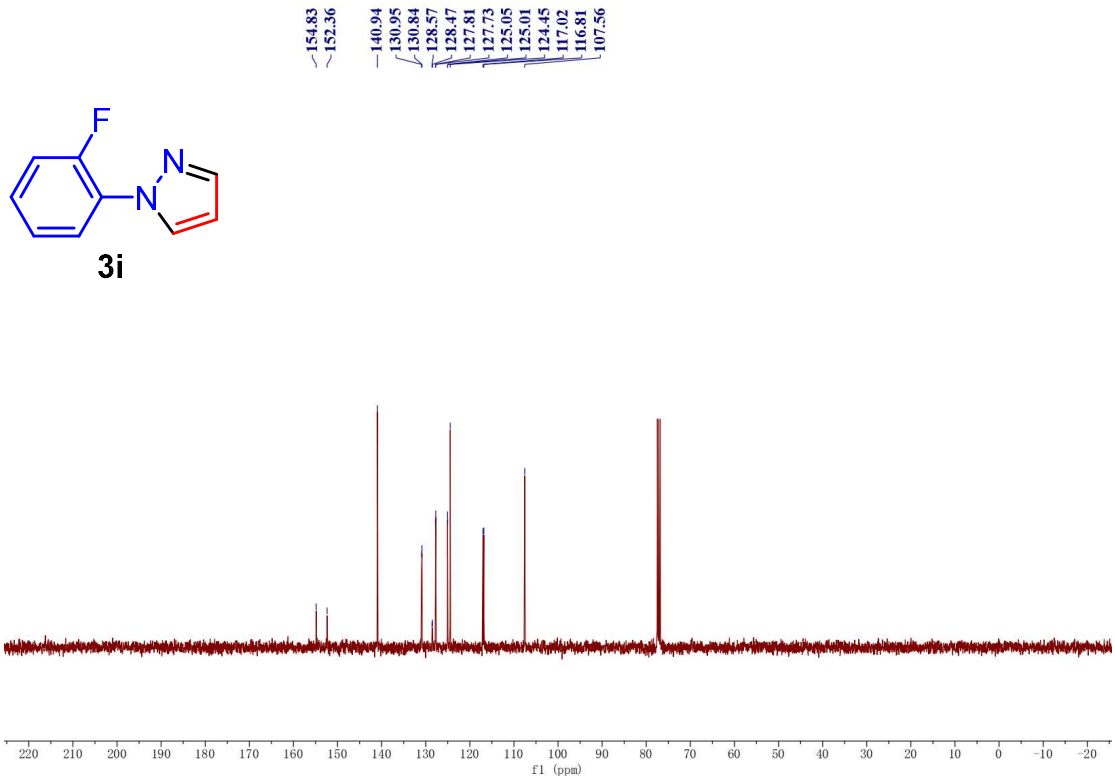
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3h**



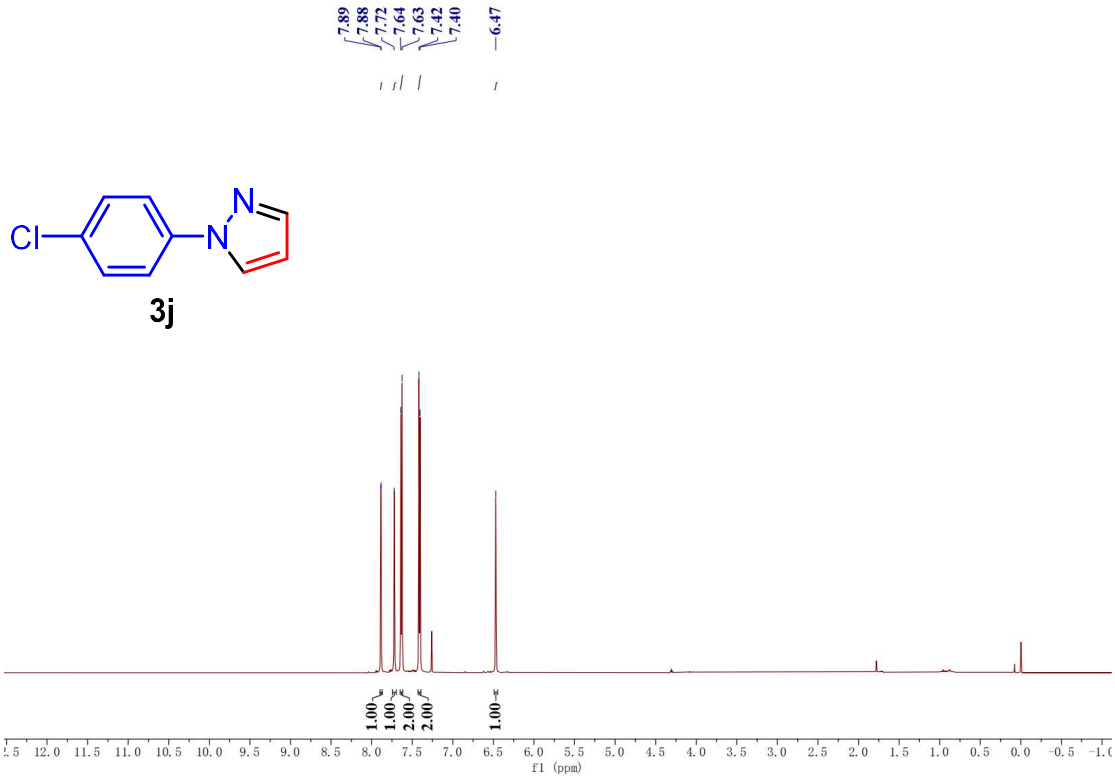
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **3i**



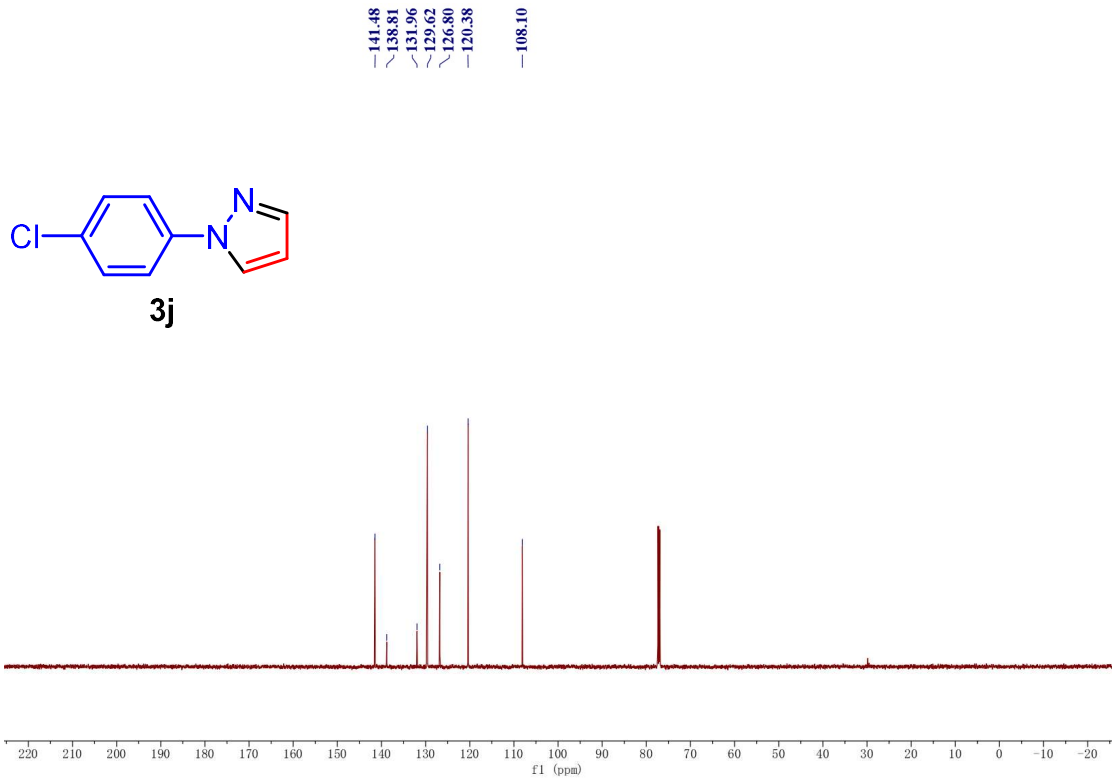
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of **3i**



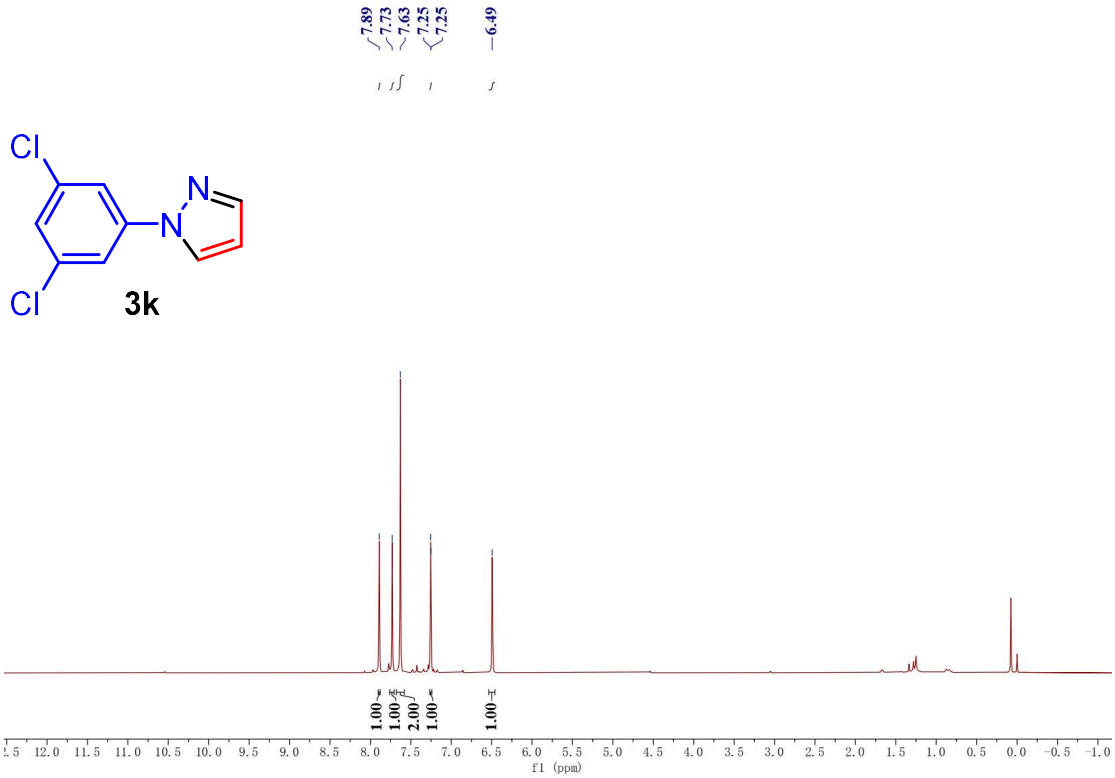
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **3i**



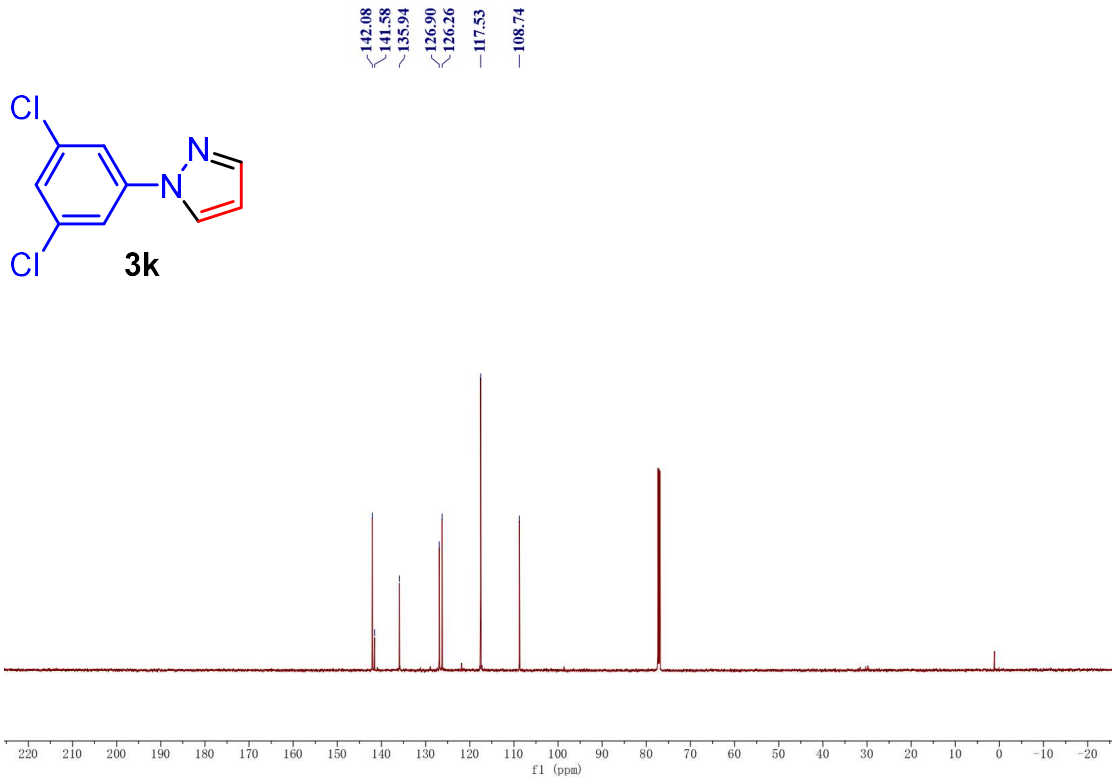
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3j**



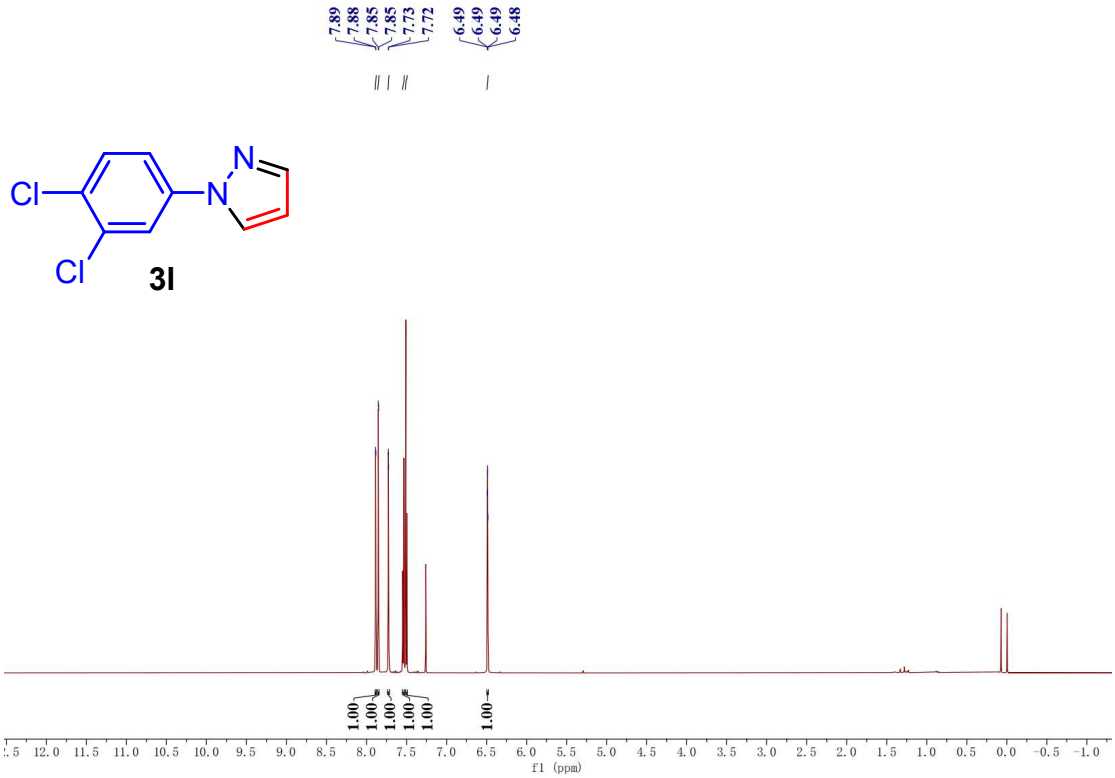
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3j**



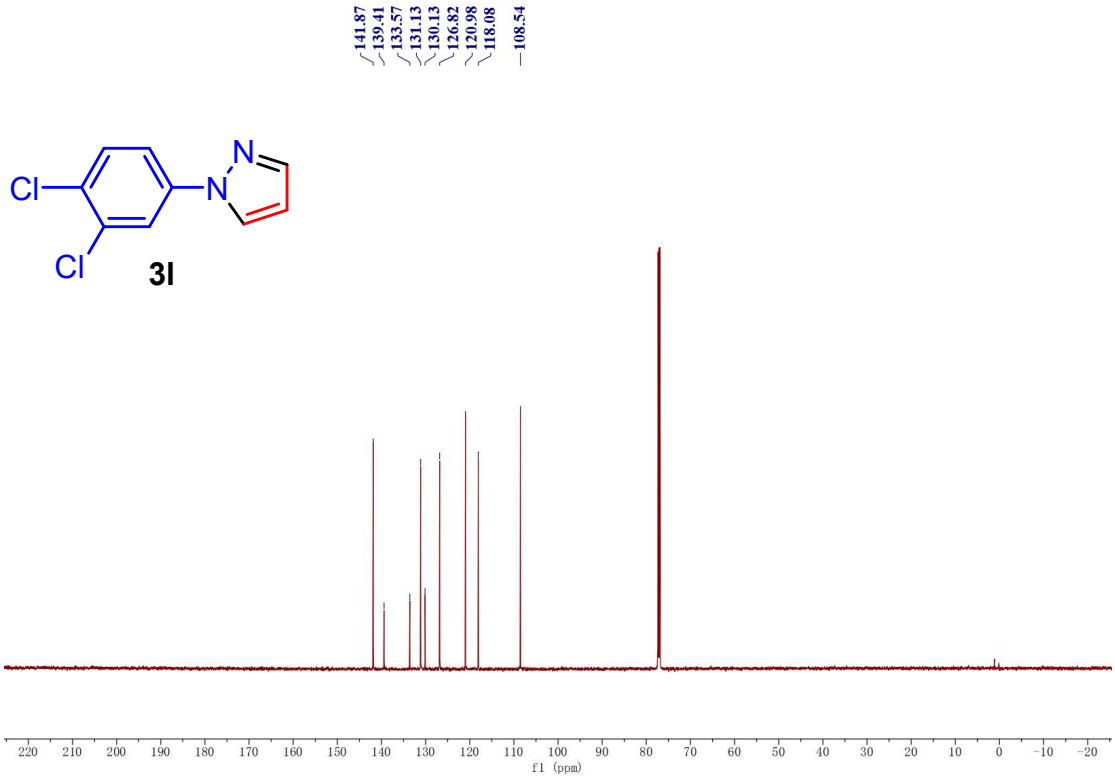
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3k**



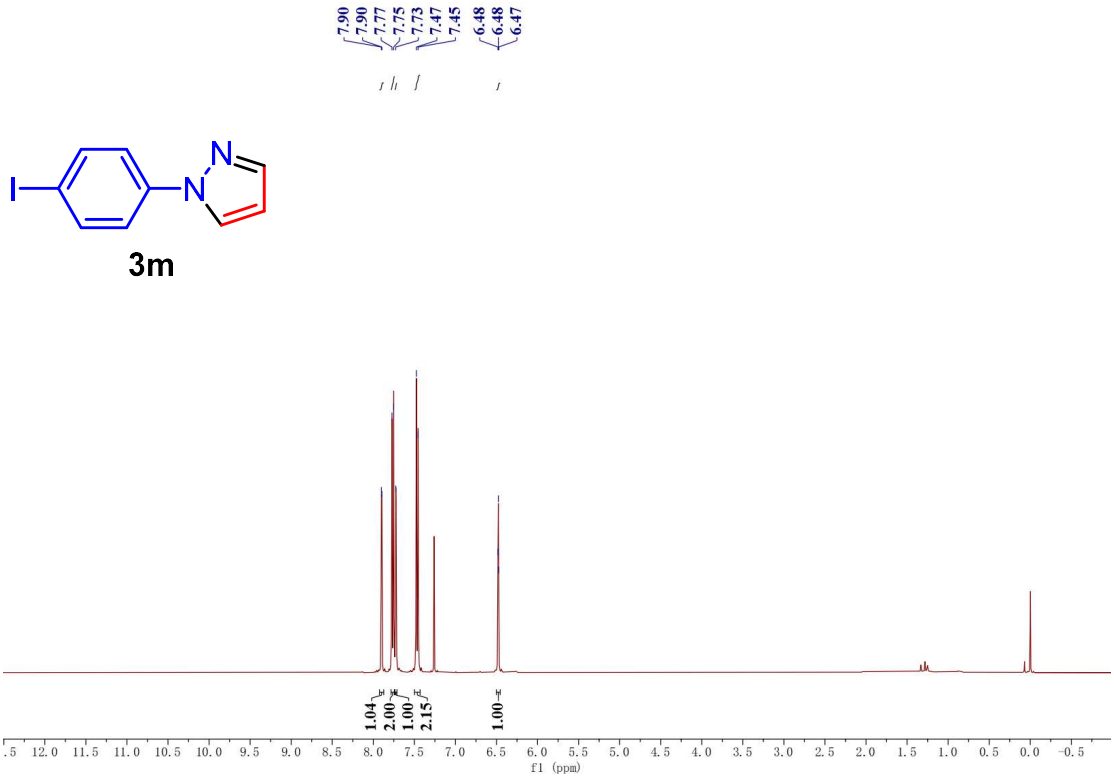
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3k**



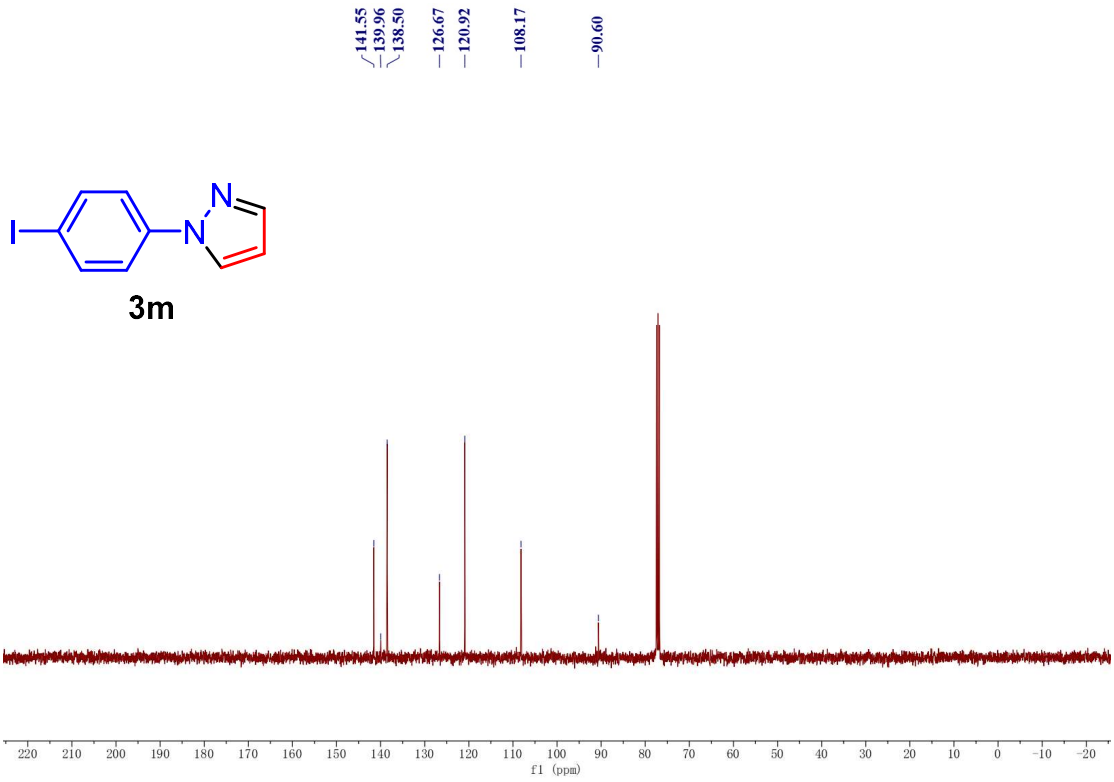
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3l**



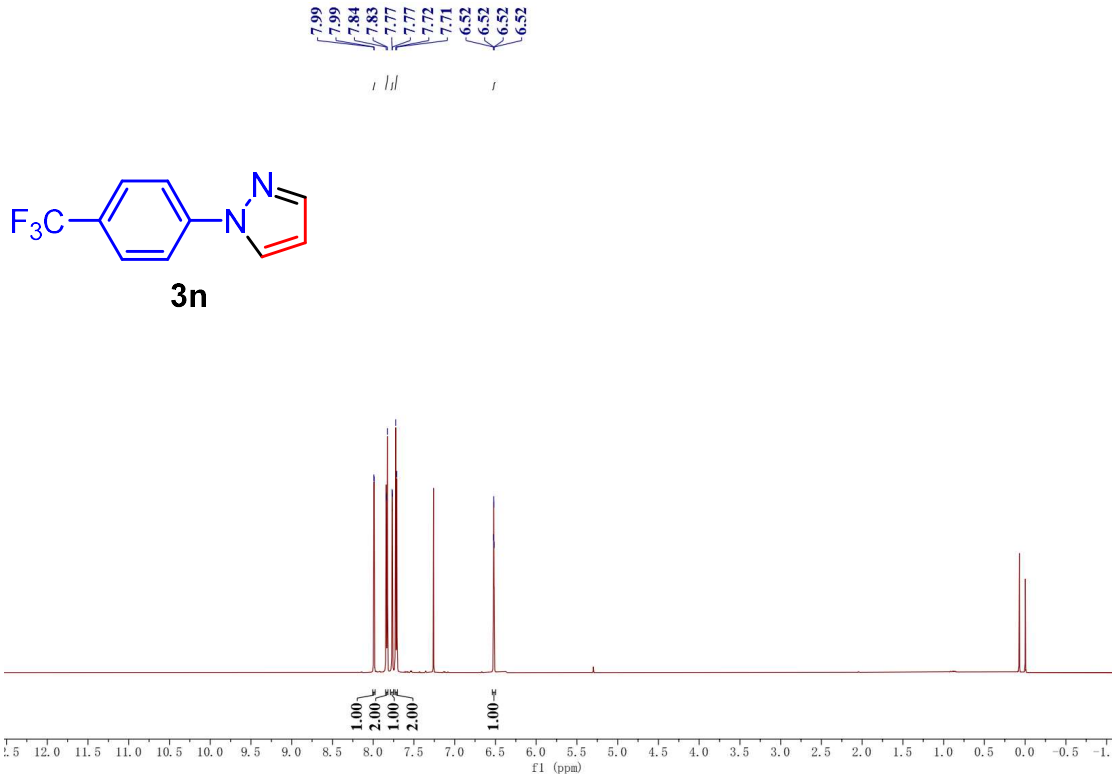
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3l**



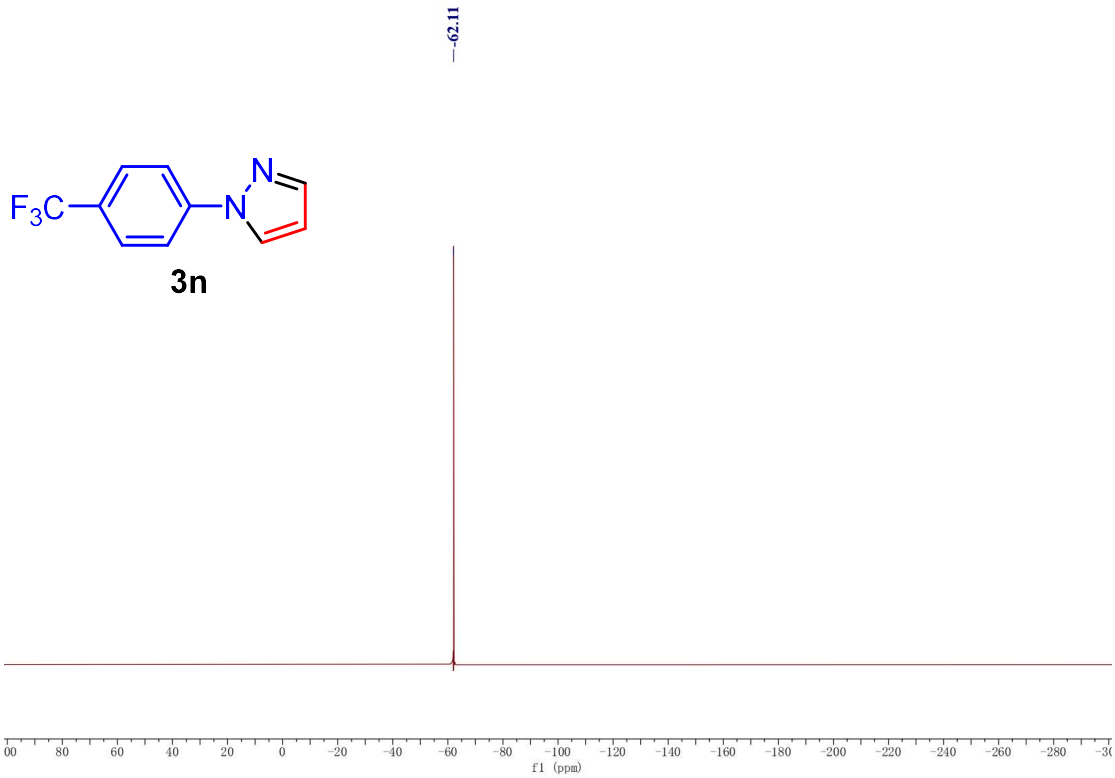
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **3m**



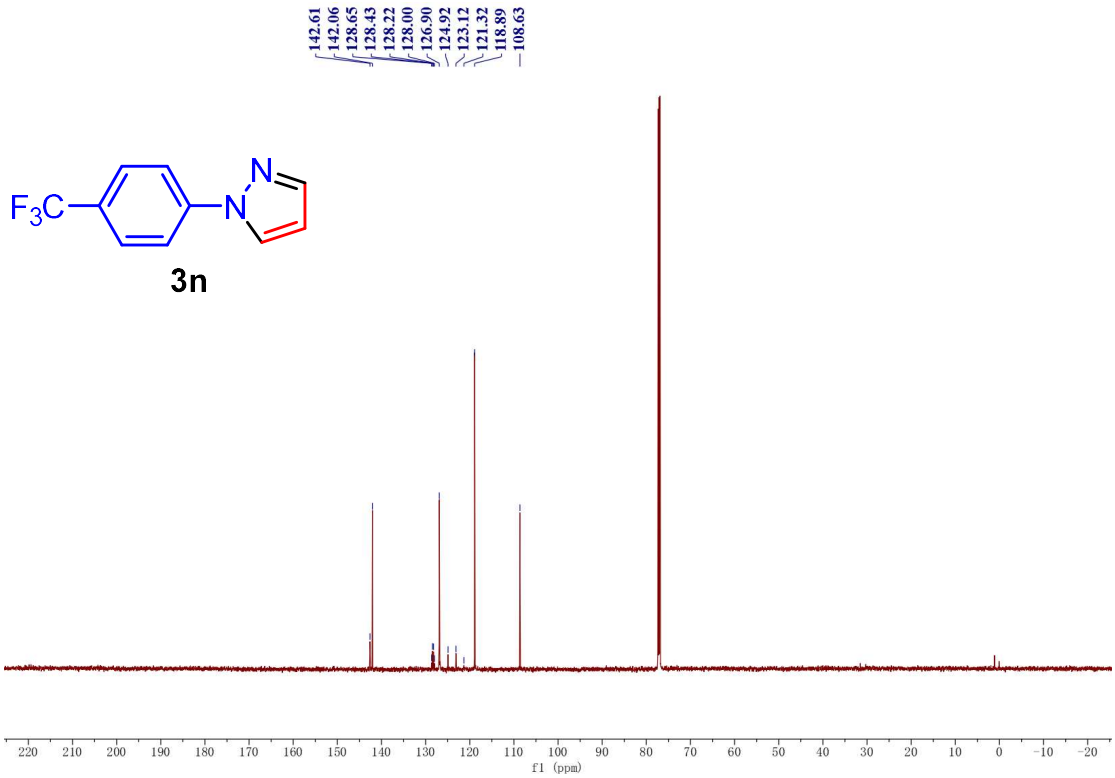
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **3m**



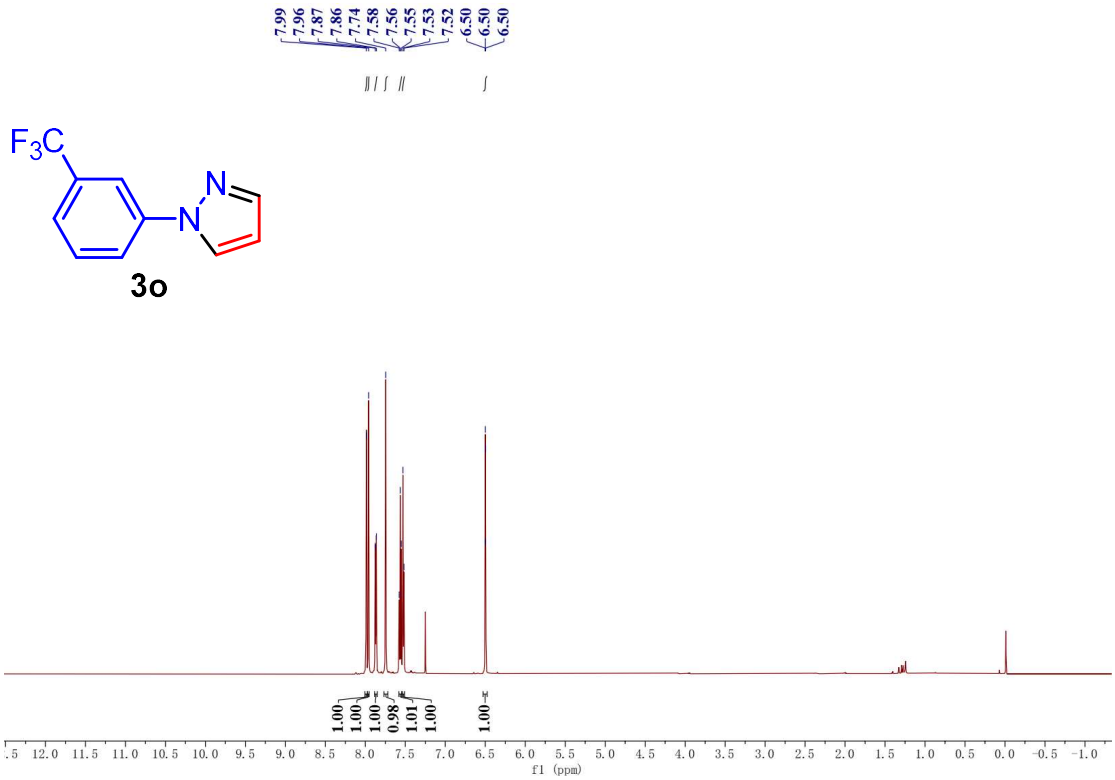
[1]H NMR (600 MHz, Chloroform-*d*) spectrum of **3n**



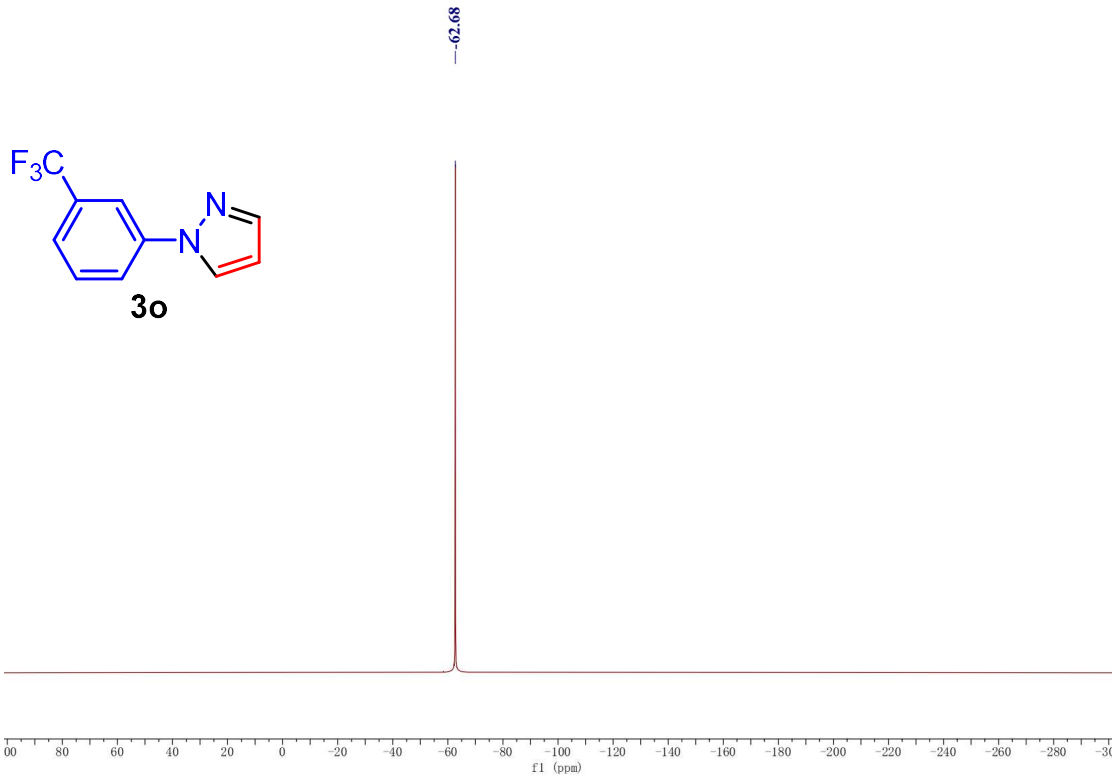
[19]F NMR (565 MHz, Chloroform-*d*) spectrum of **3n**



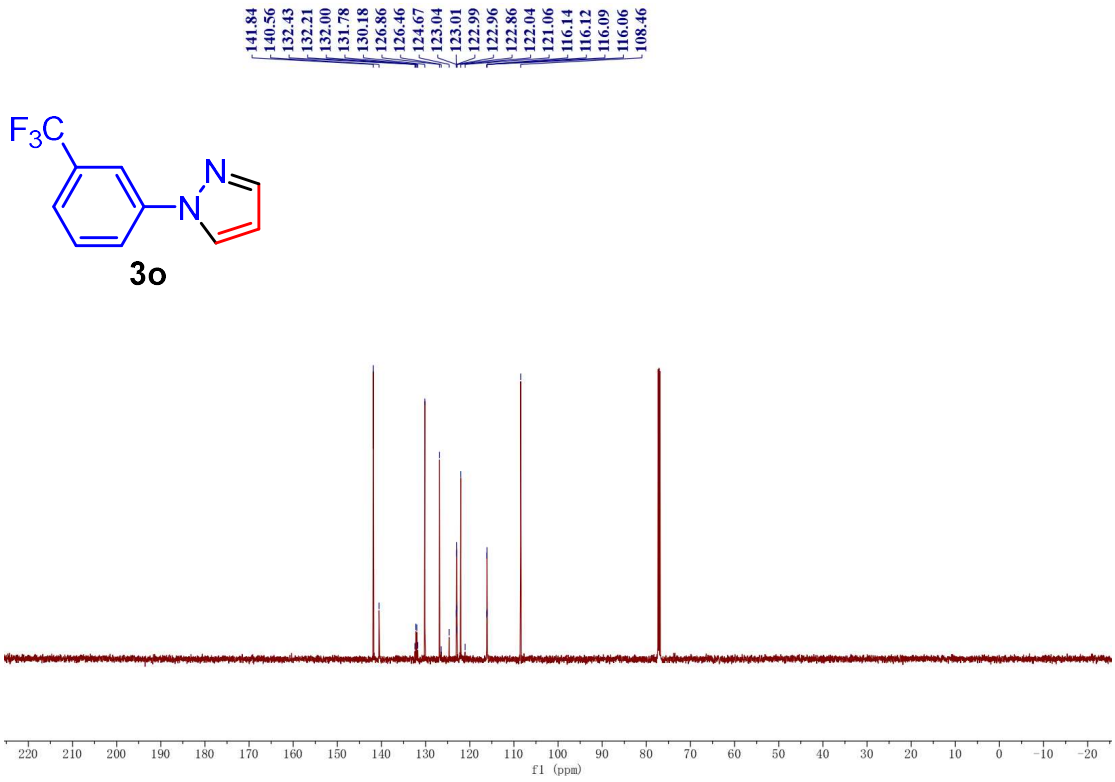
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3n**



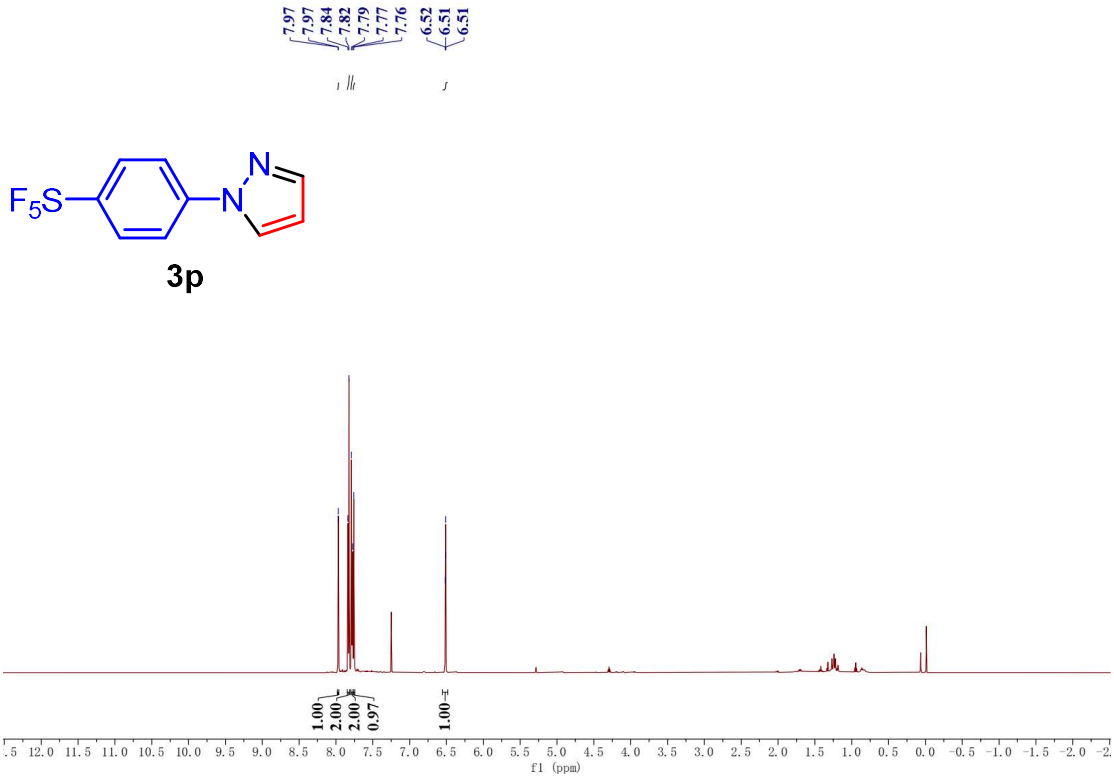
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3o**



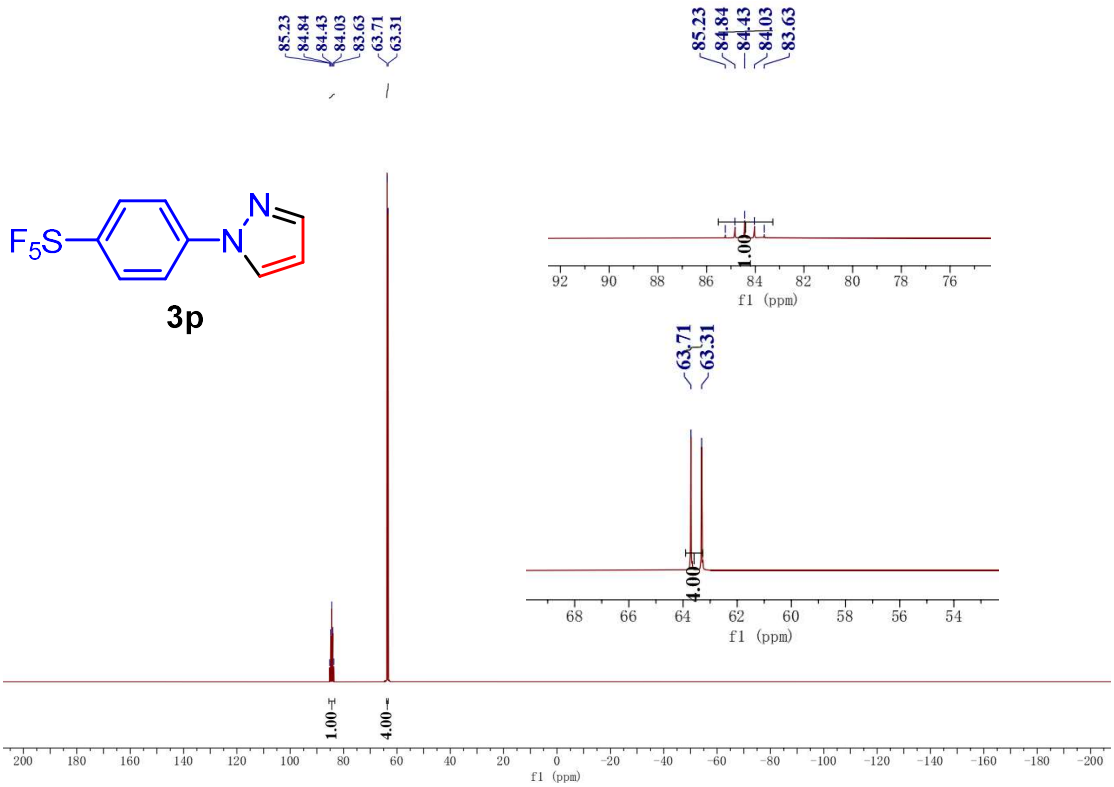
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **3o**



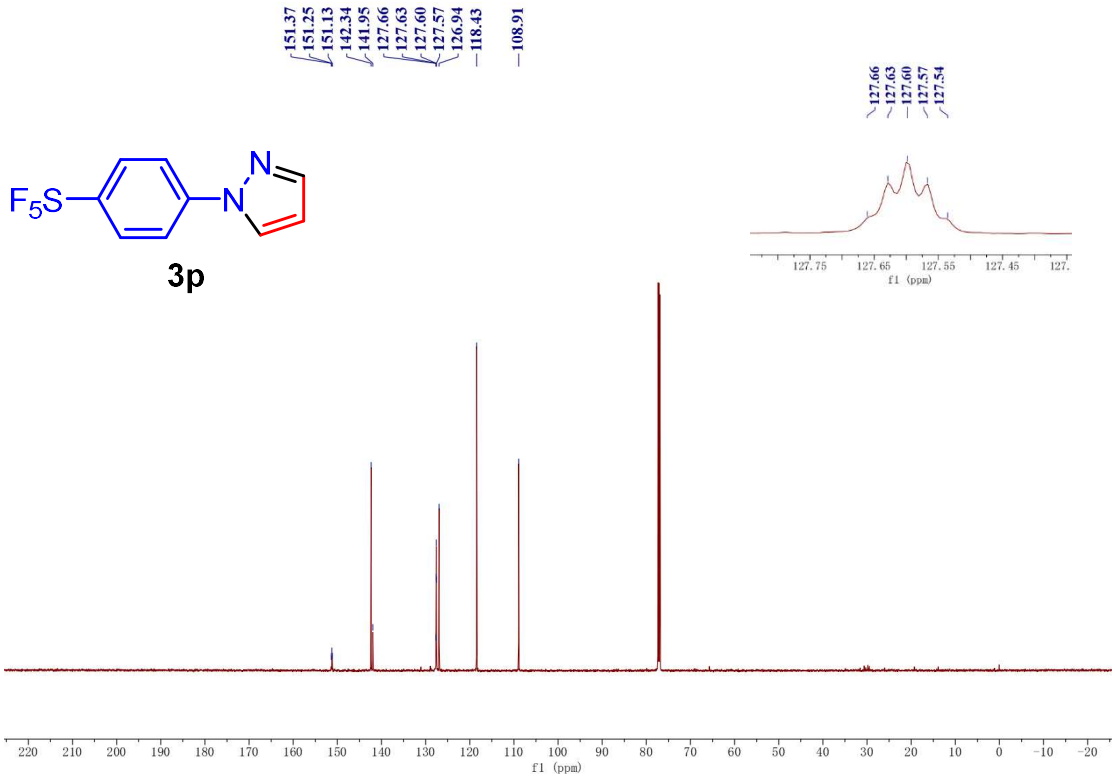
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3o**



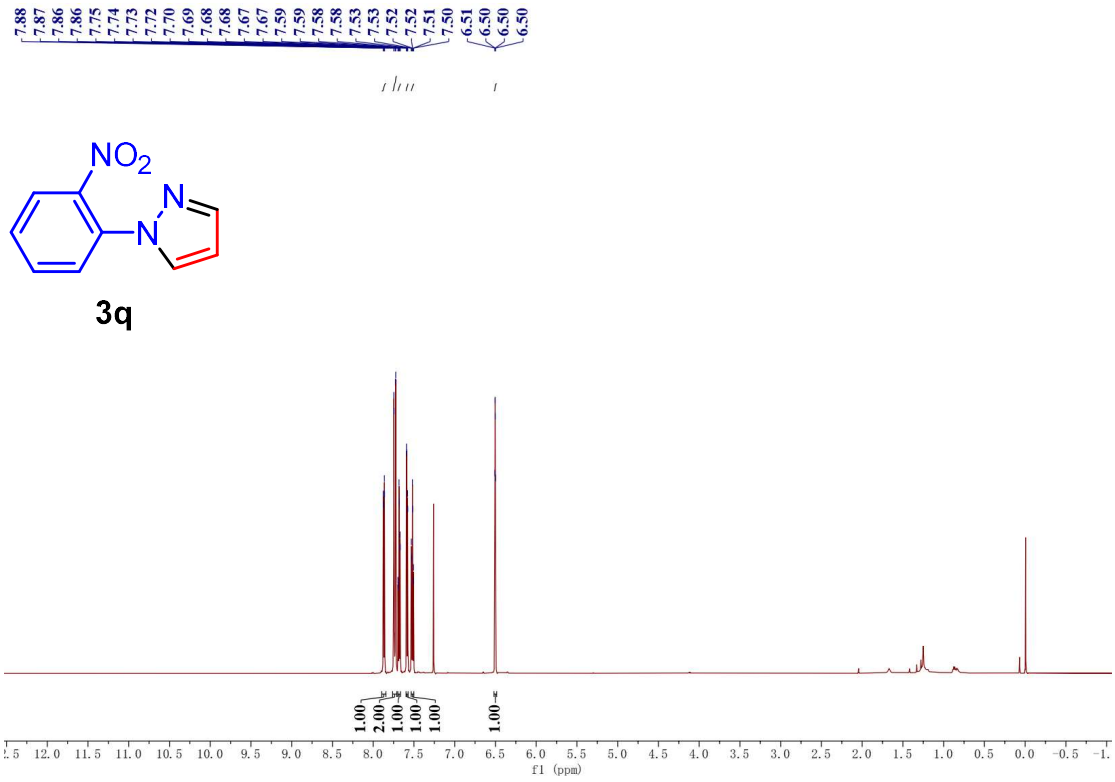
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3p**



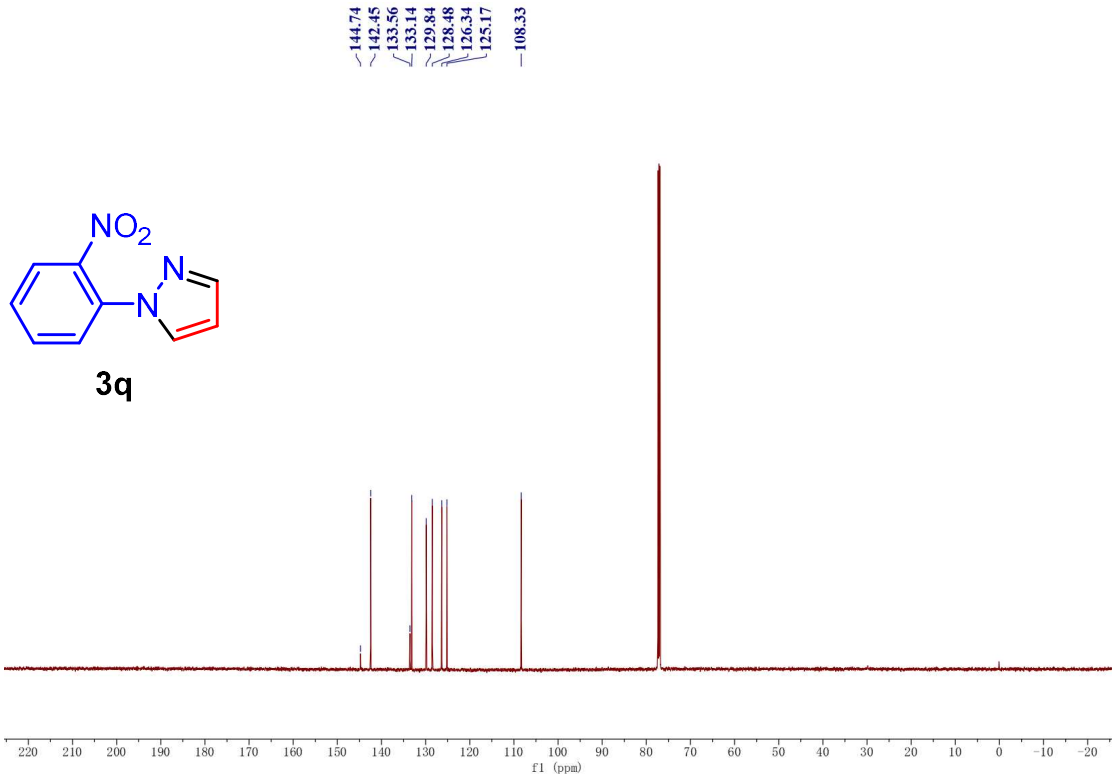
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **3p**



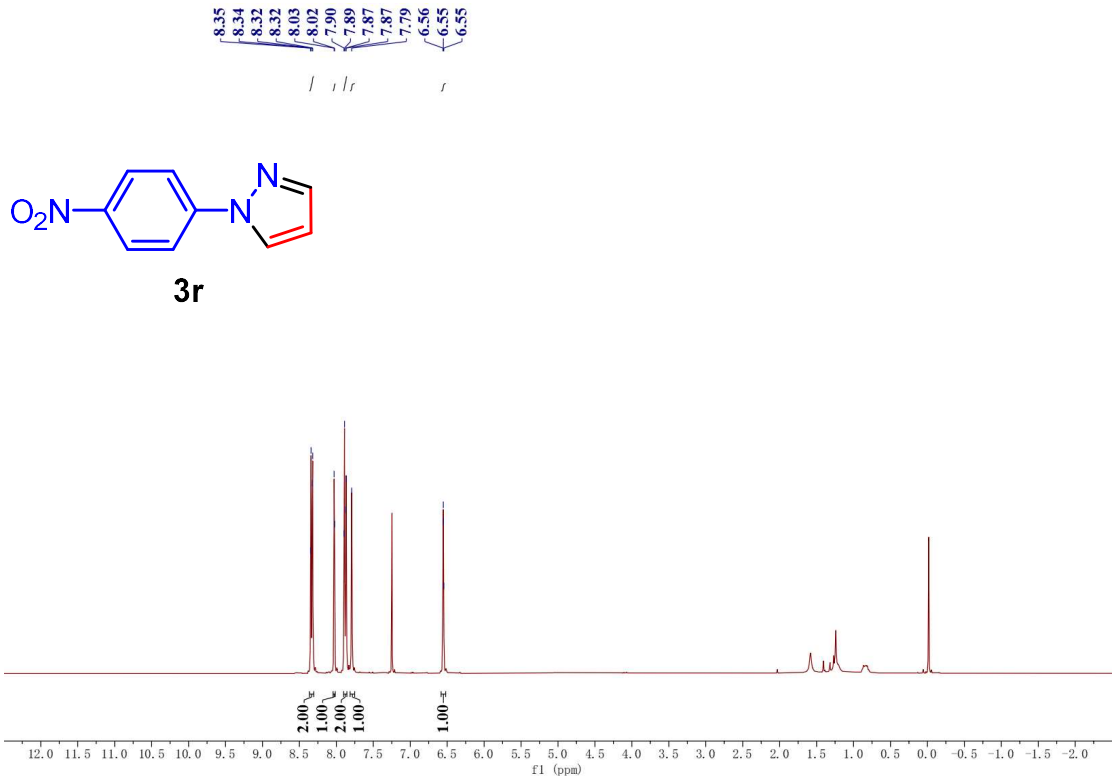
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3p**



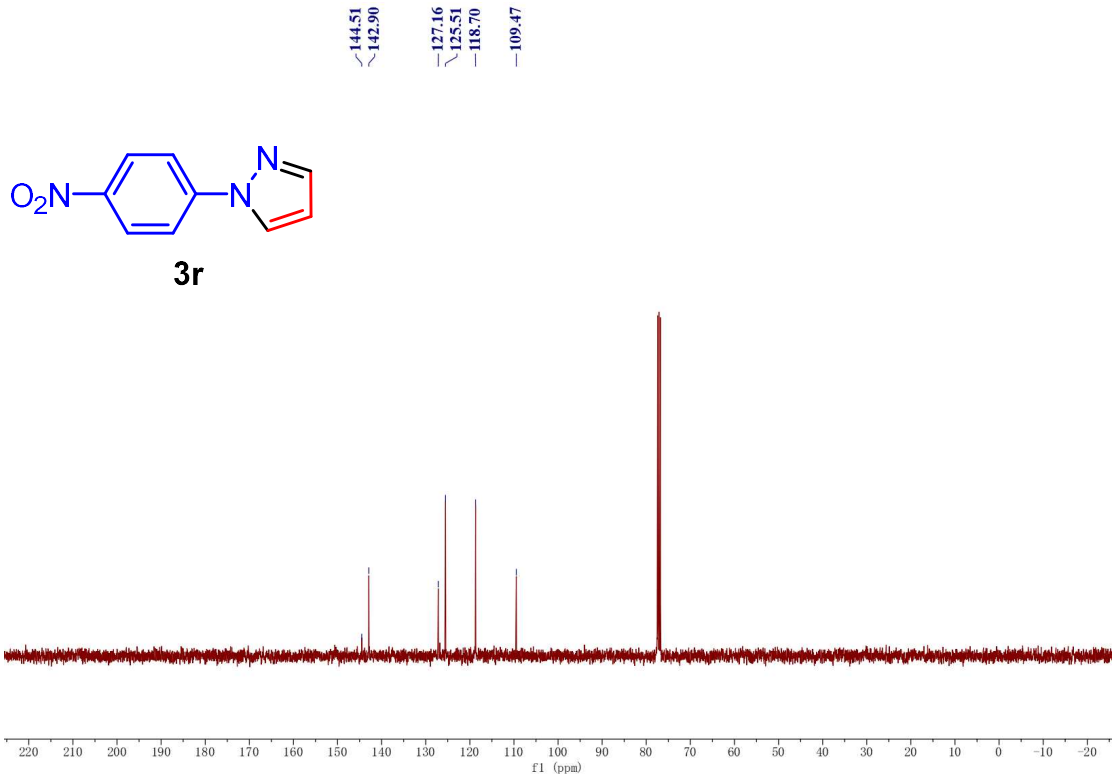
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3q**



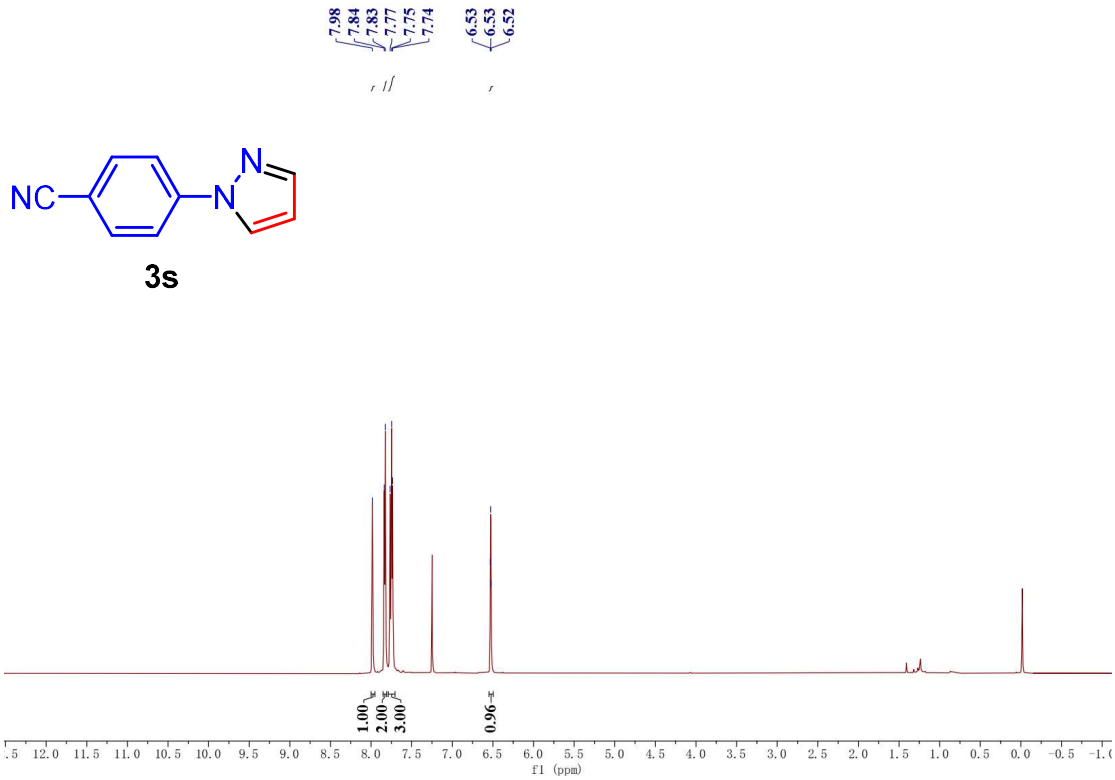
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3q**



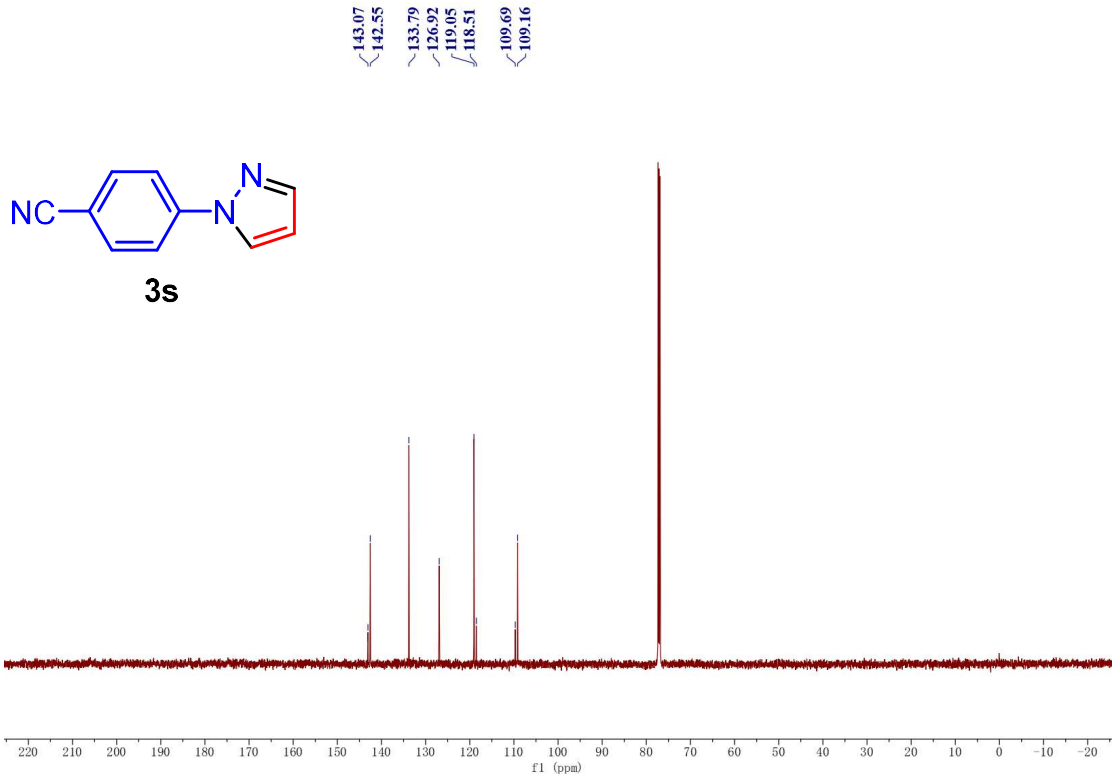
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **3r**



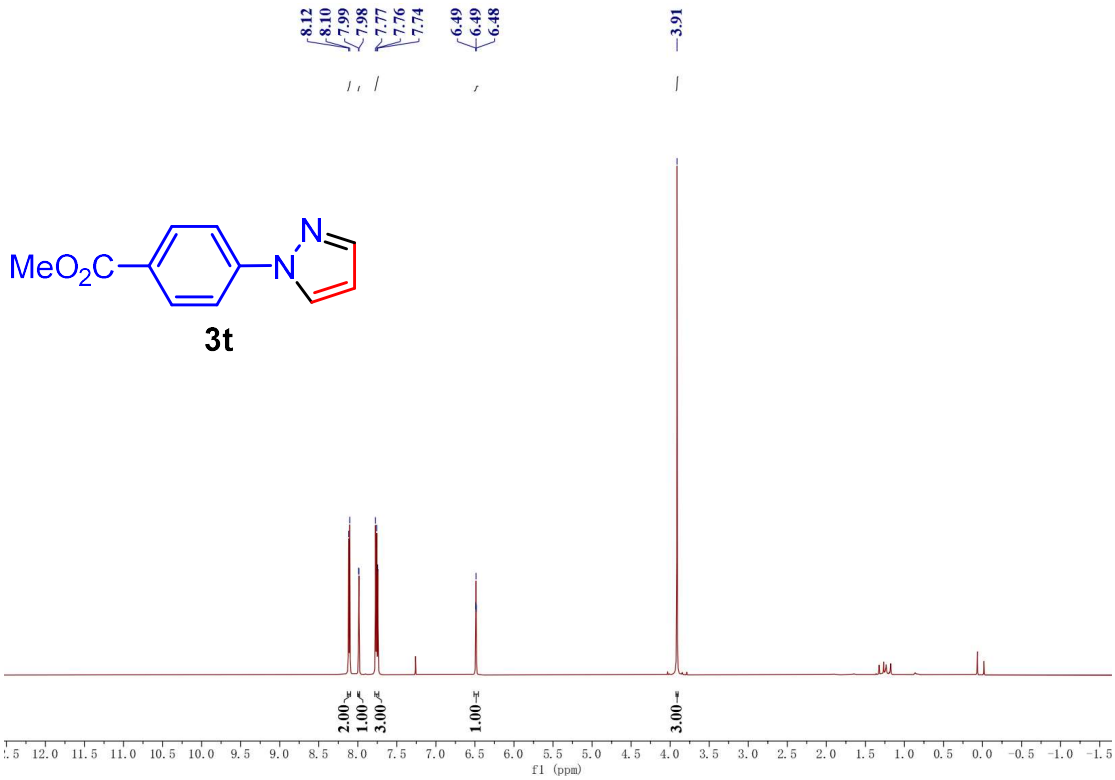
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **3r**



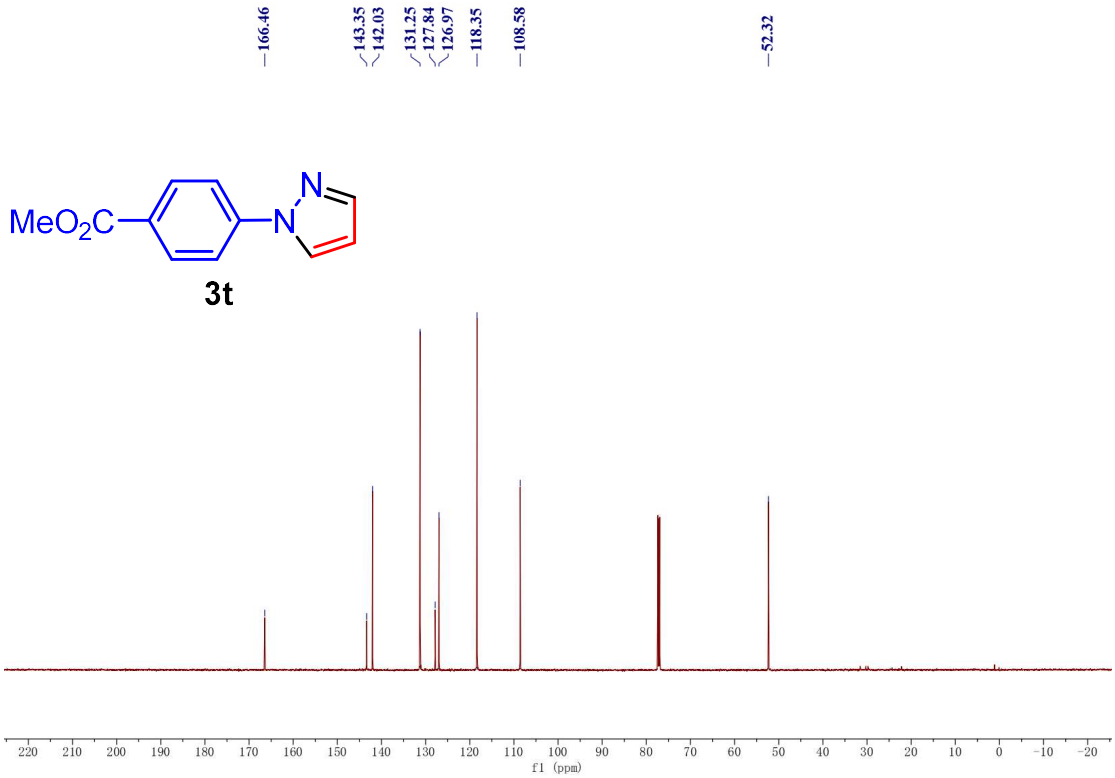
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3s**



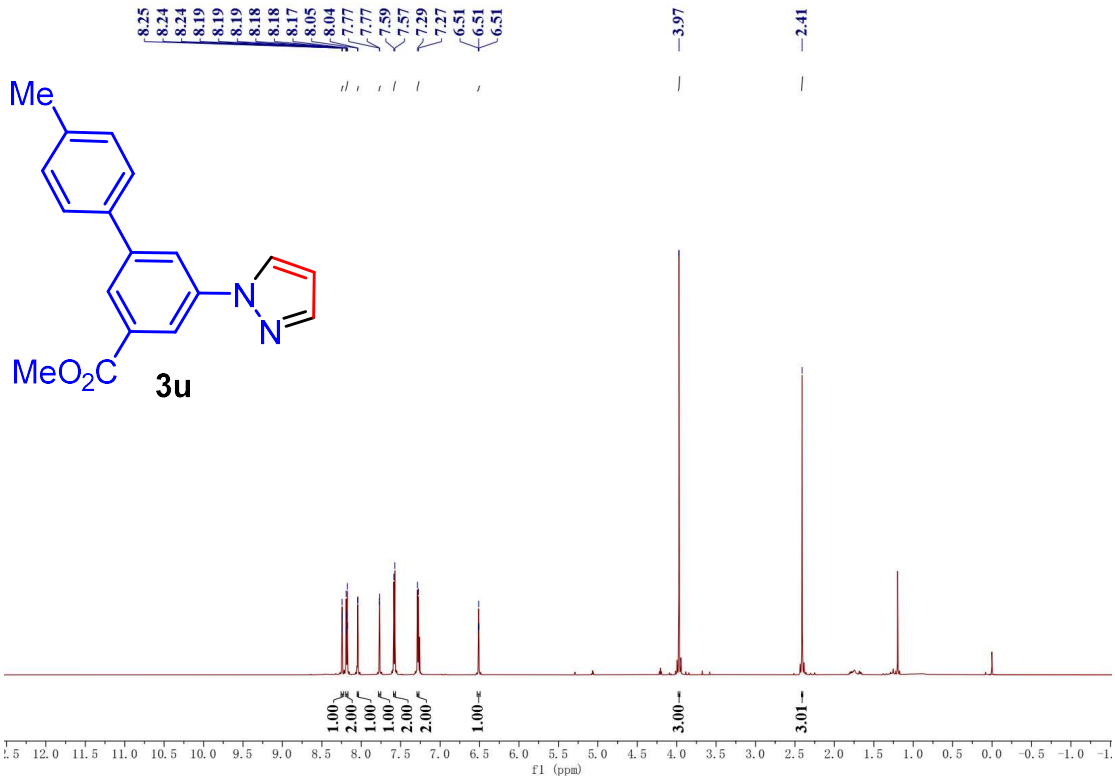
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3s**



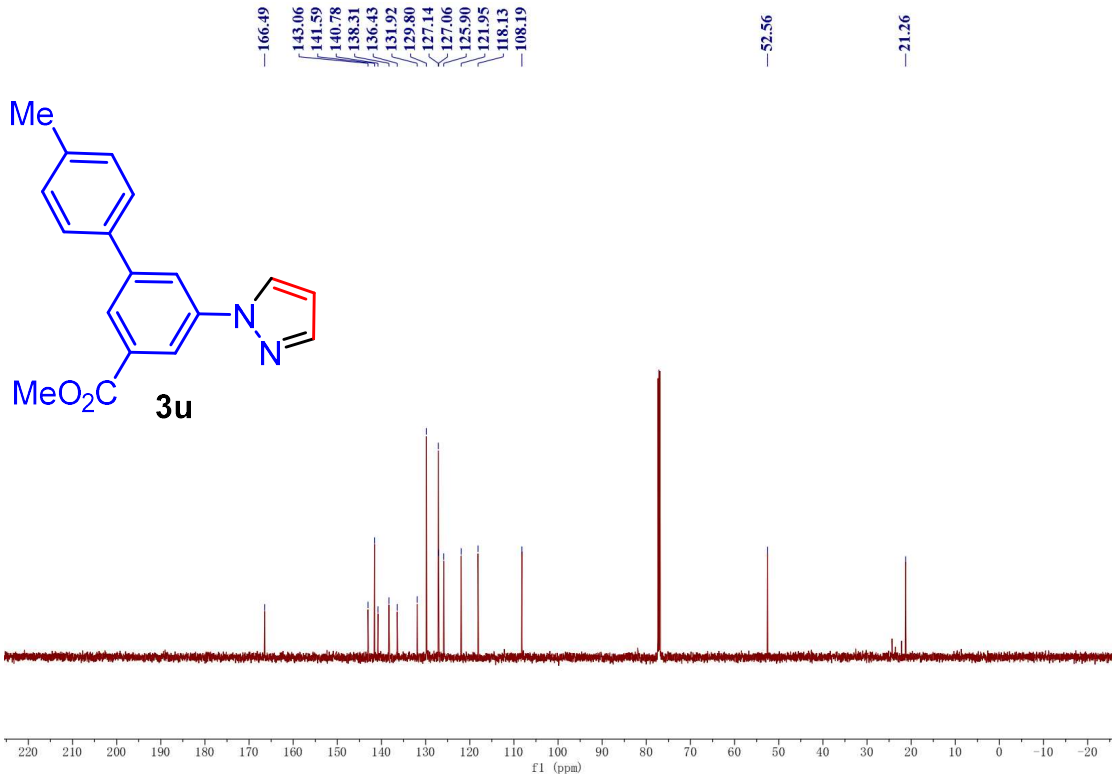
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3t**



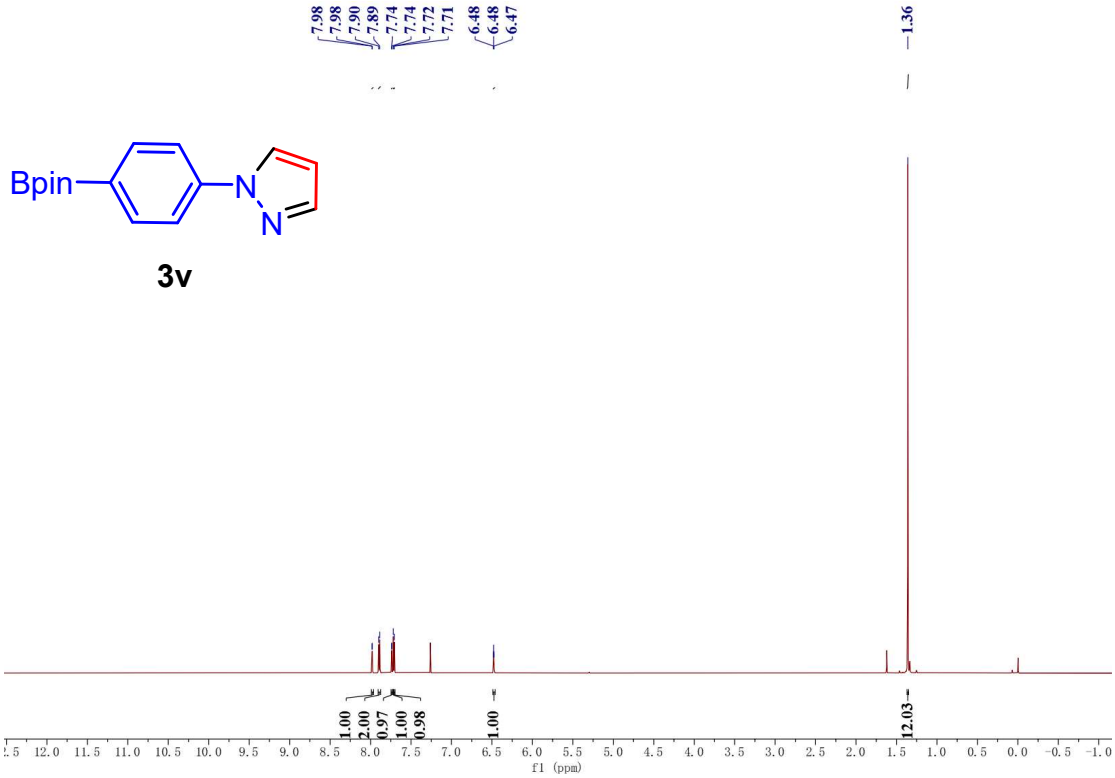
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3t**



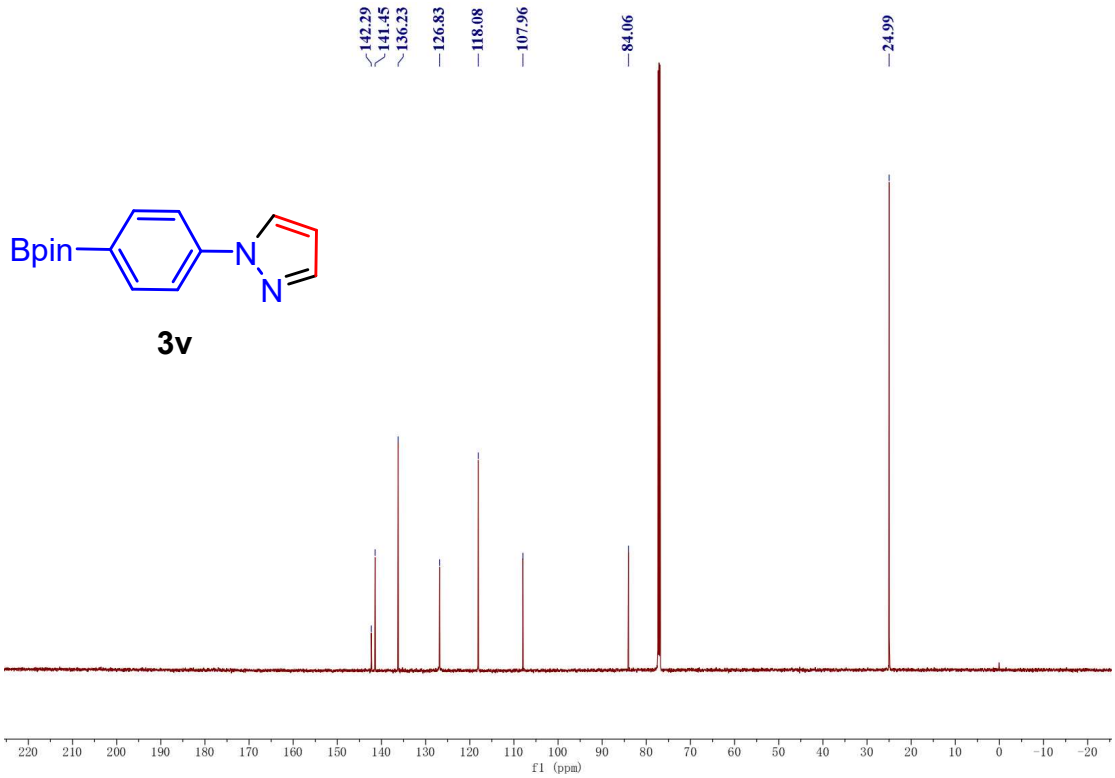
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3u**



^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3u**

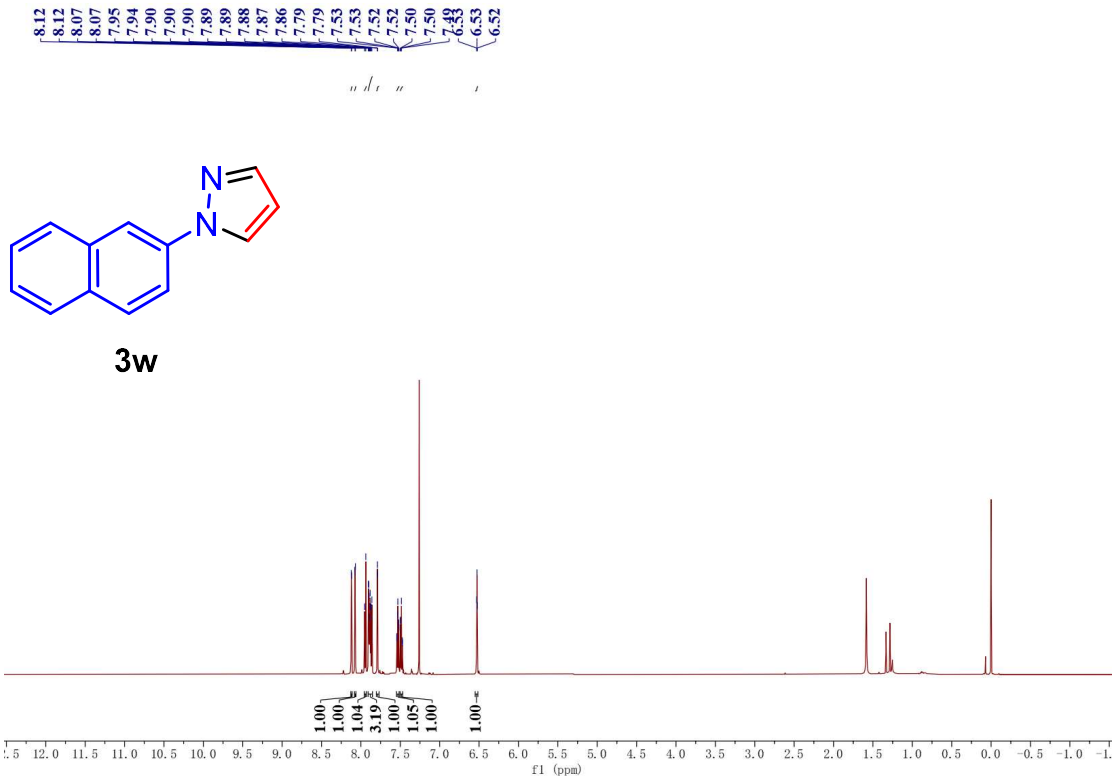


^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3v**



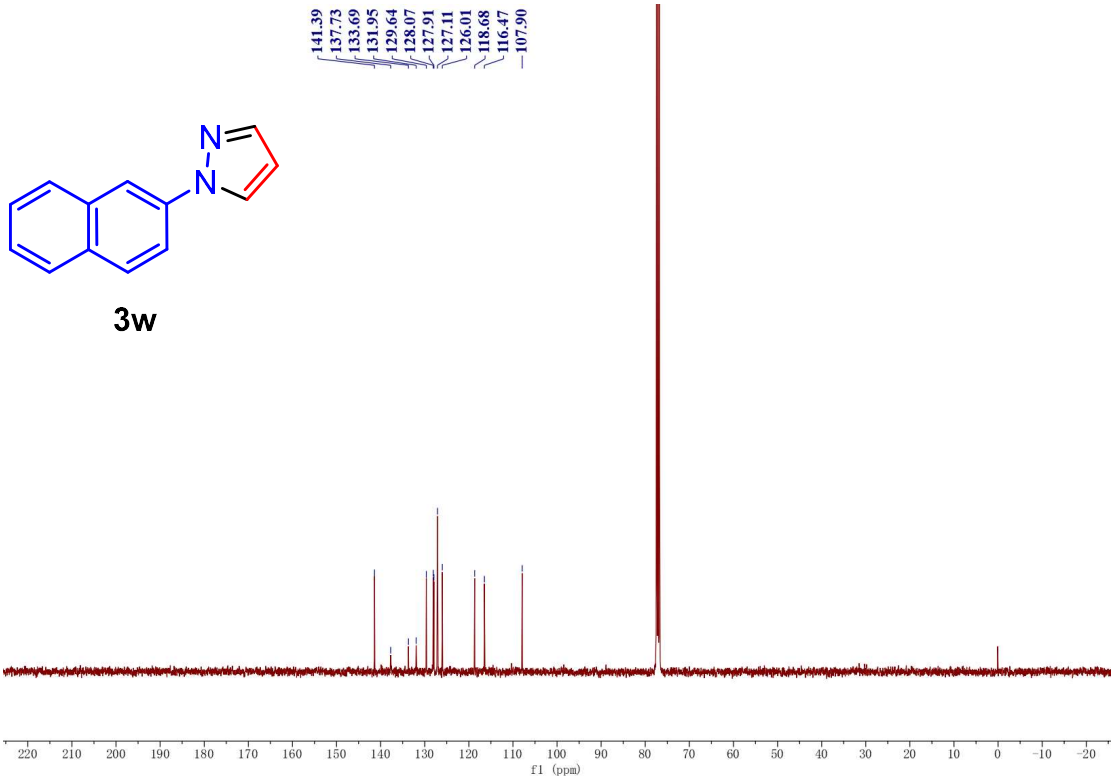
3v

^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3v**



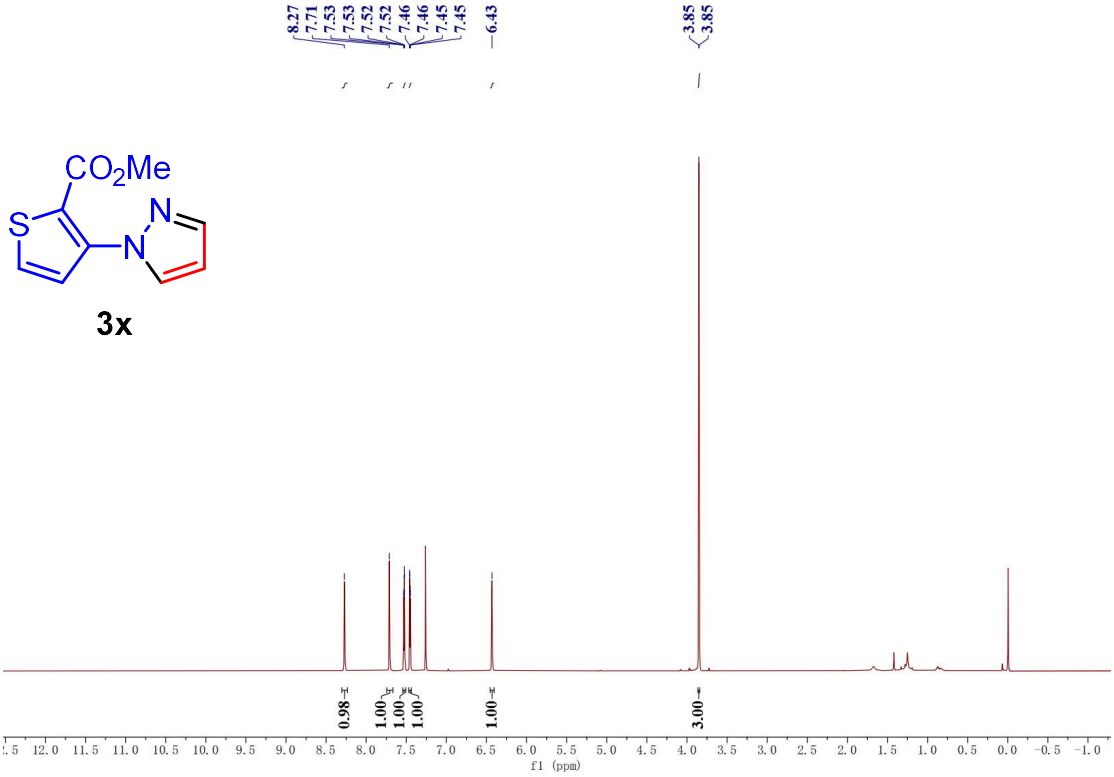
3w

^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3w**



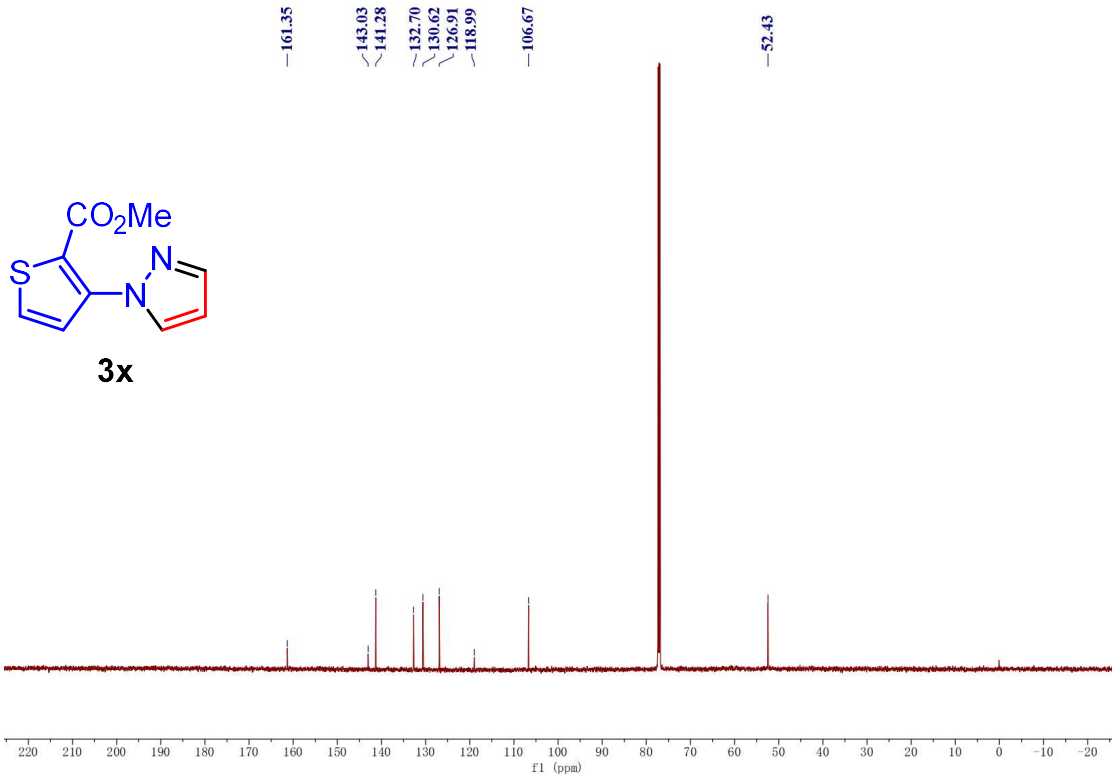
3w

^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3w**

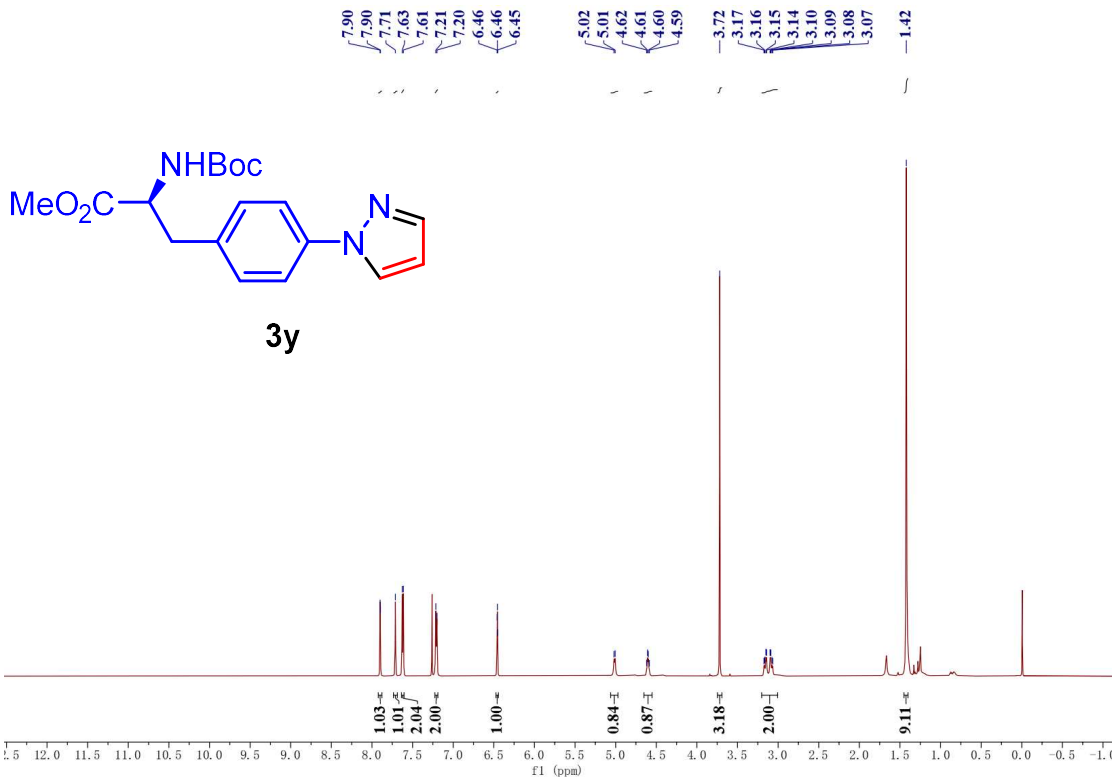


3x

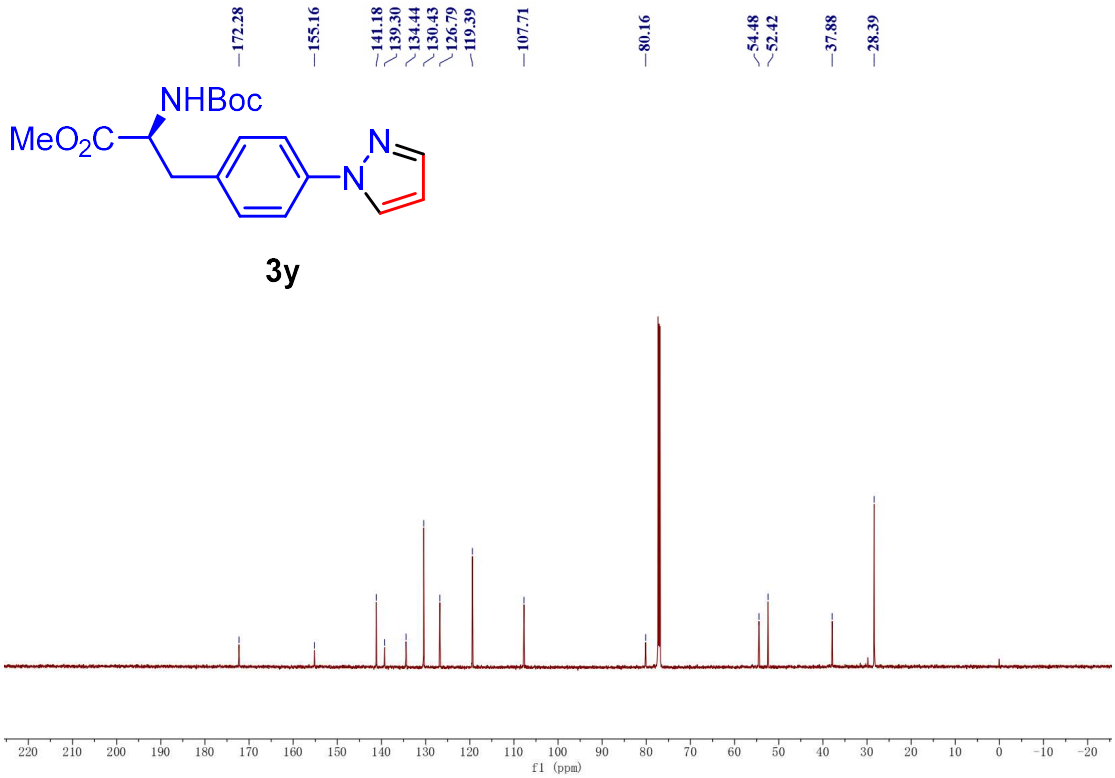
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3x**



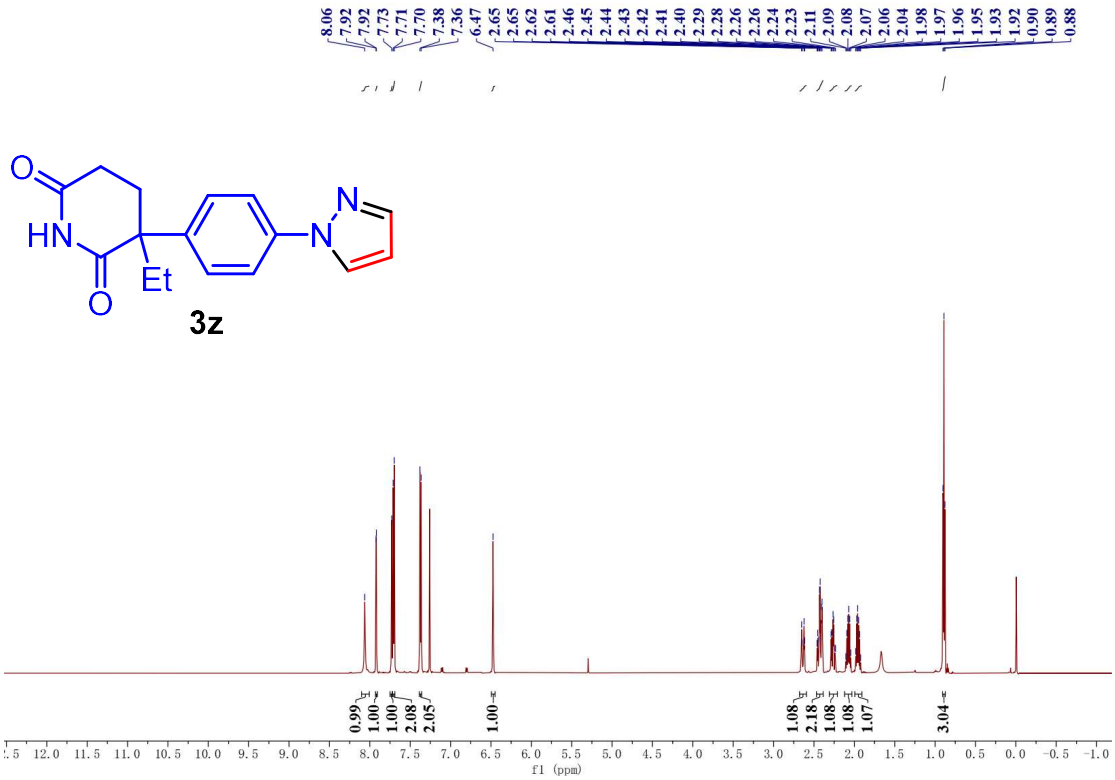
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3x**



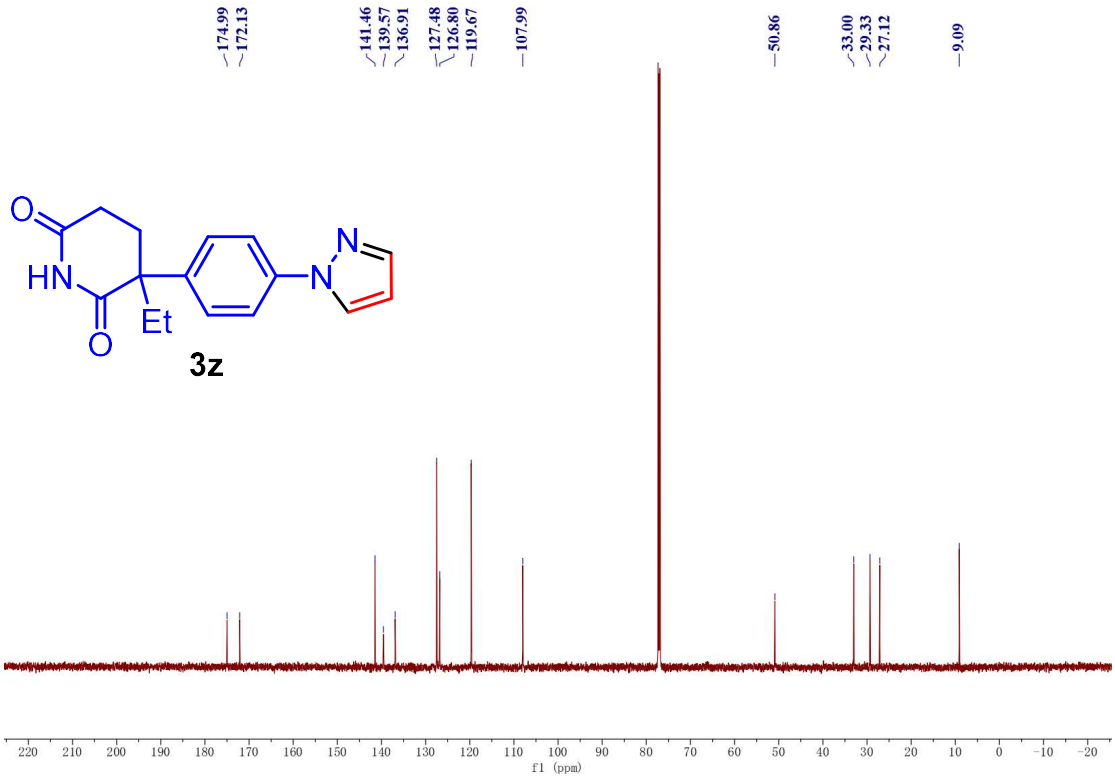
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3y**



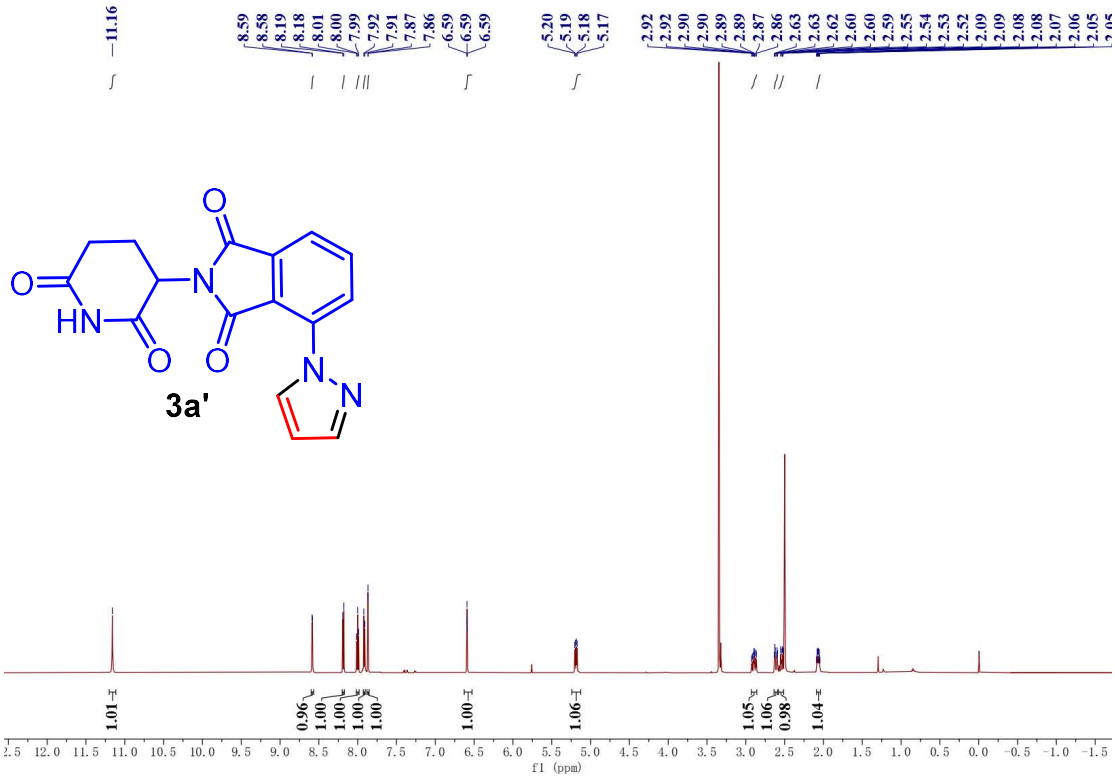
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3y**



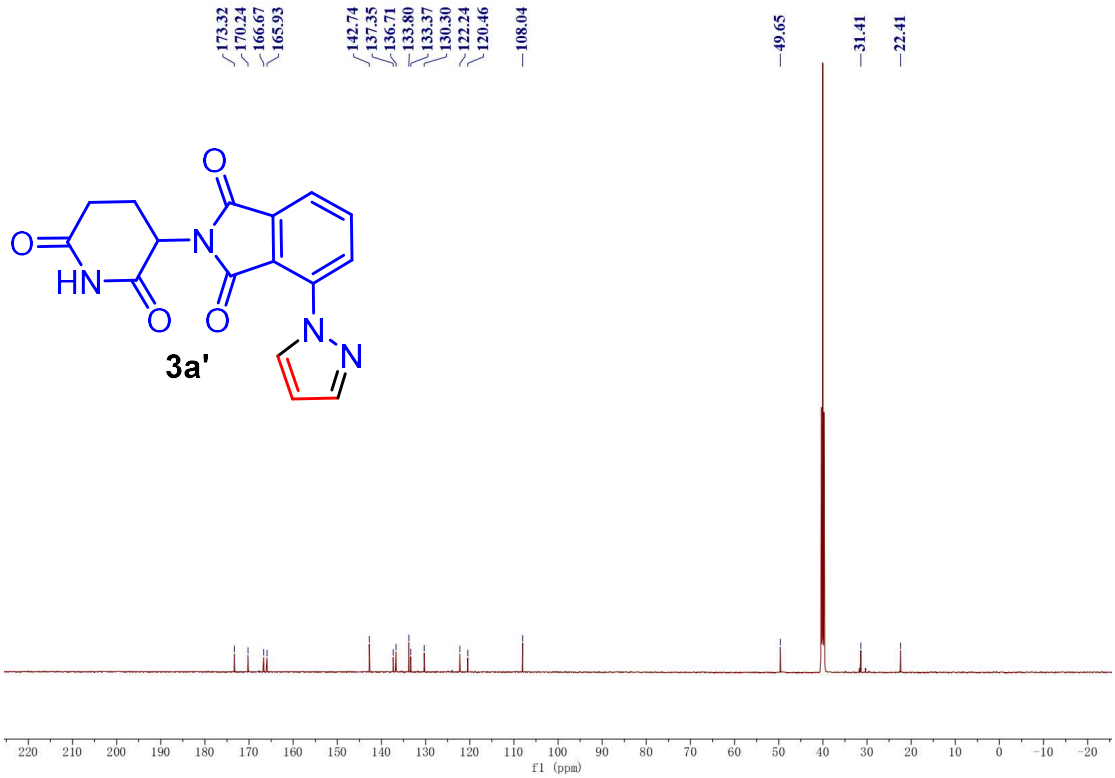
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3z**



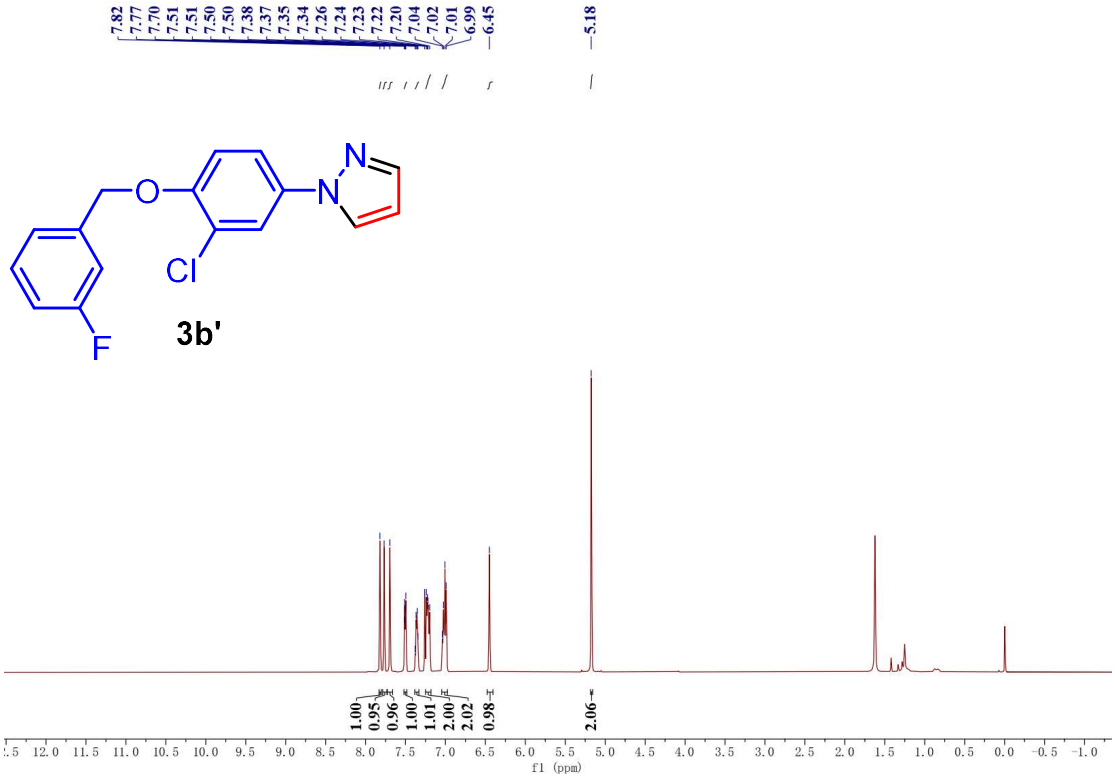
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3z**



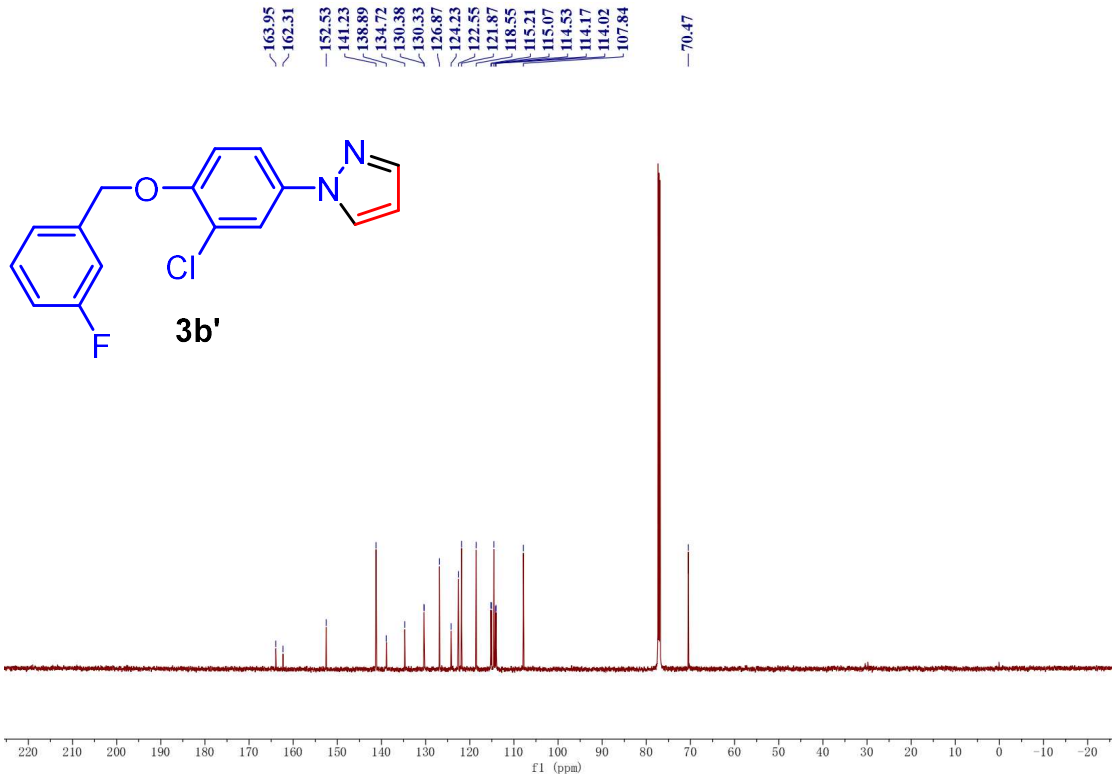
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of **3a'**



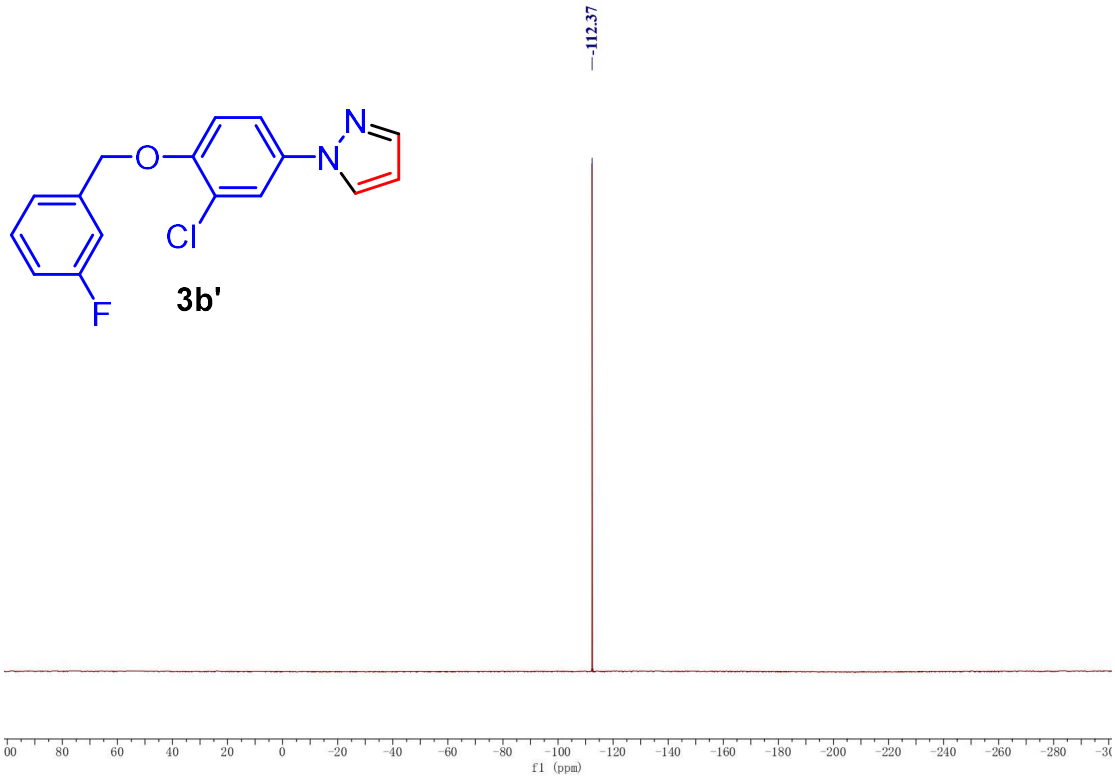
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of **3a'**



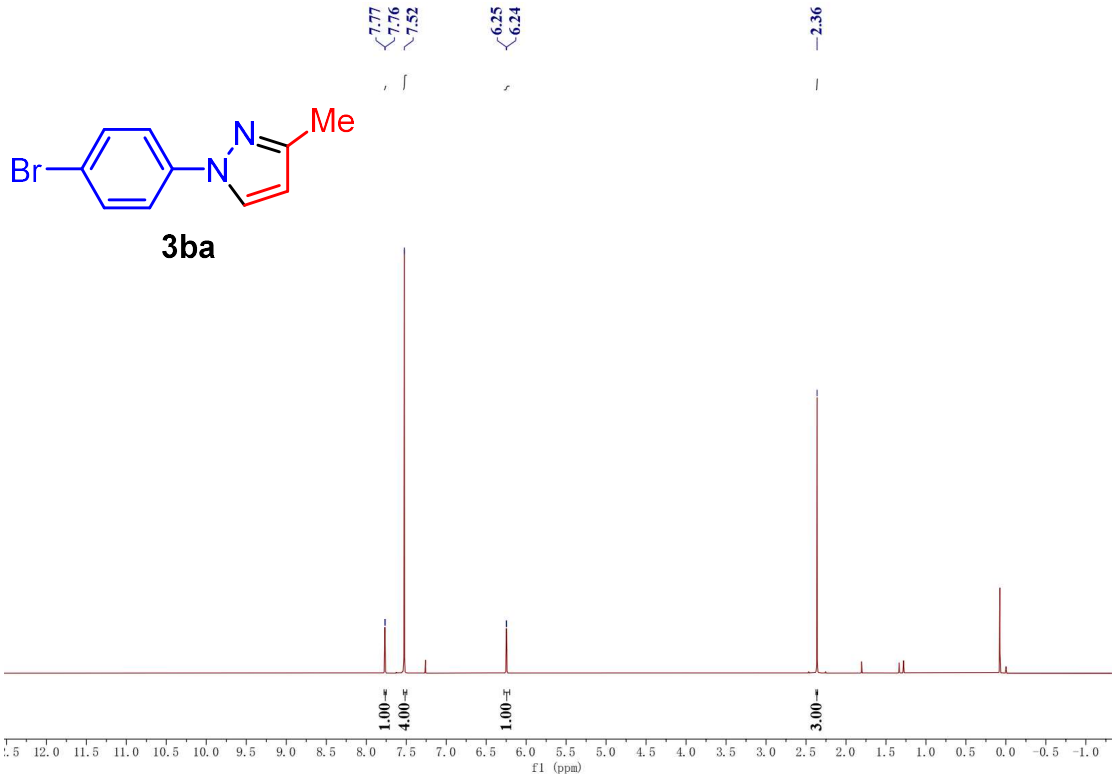
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3b'**



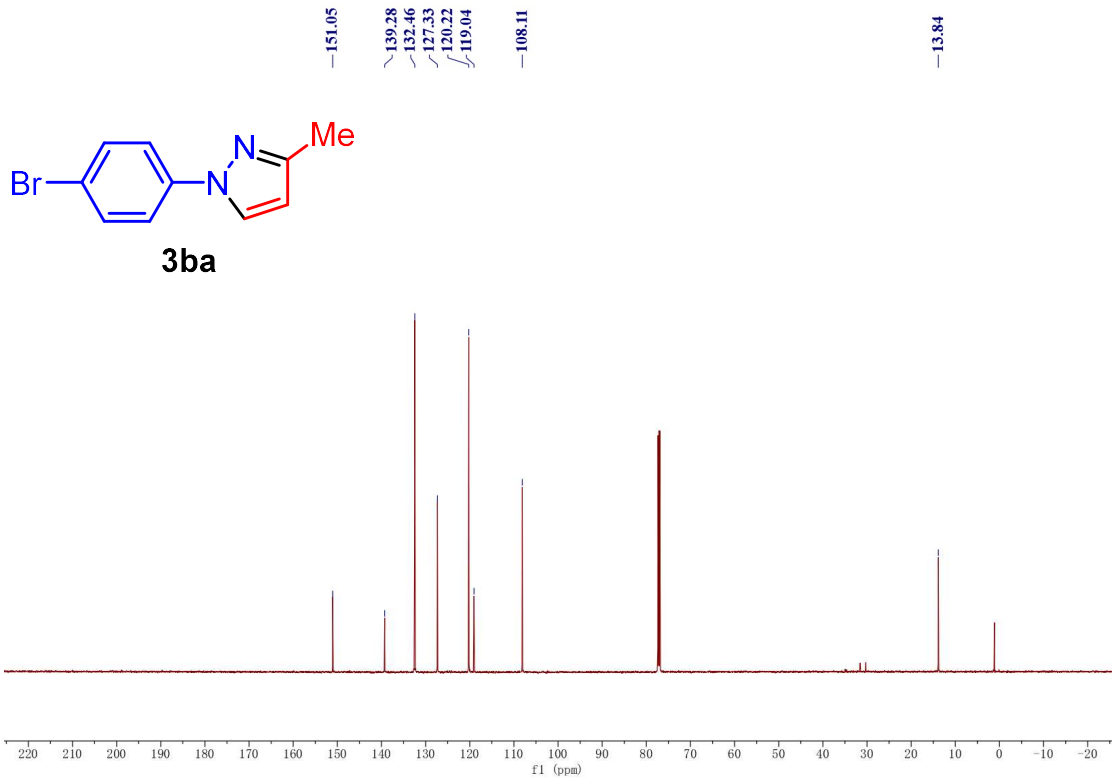
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3b'**



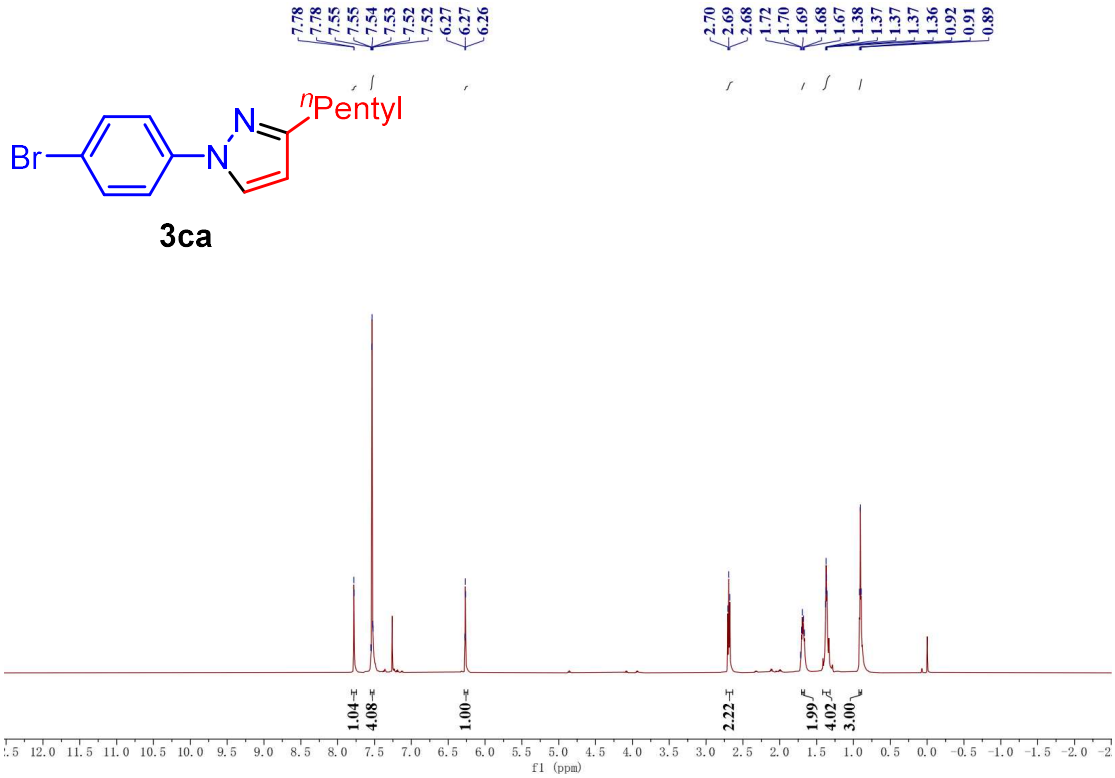
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **3b'**



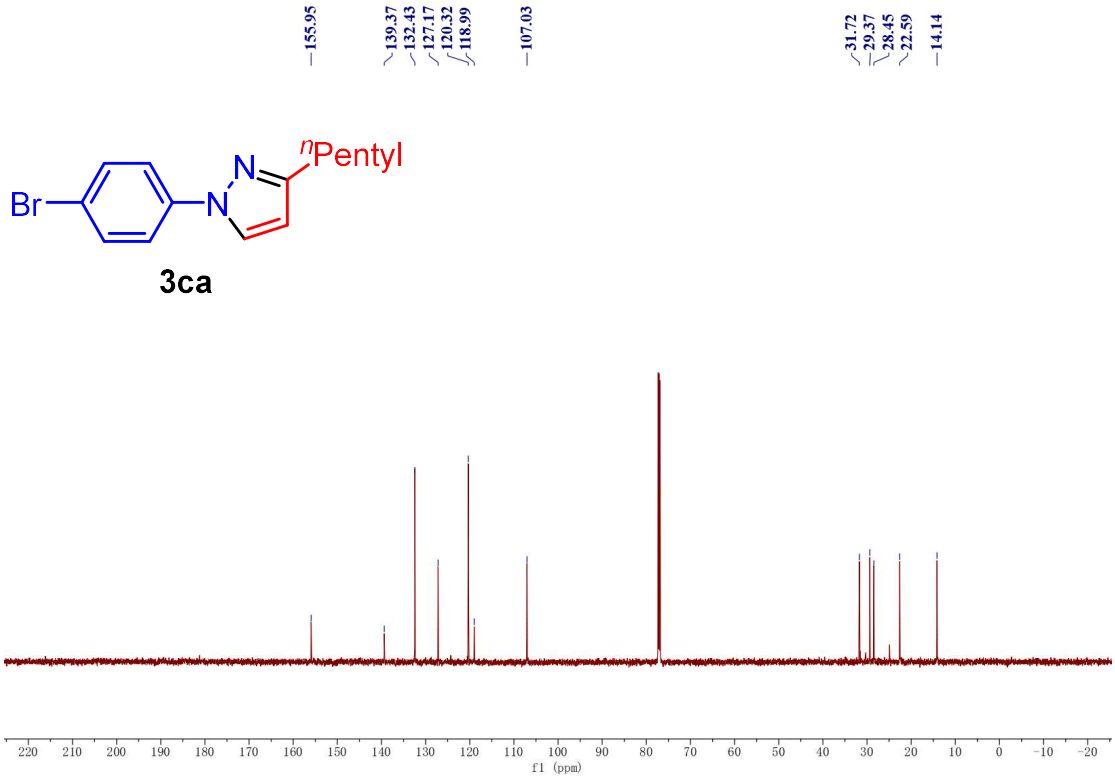
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ba**



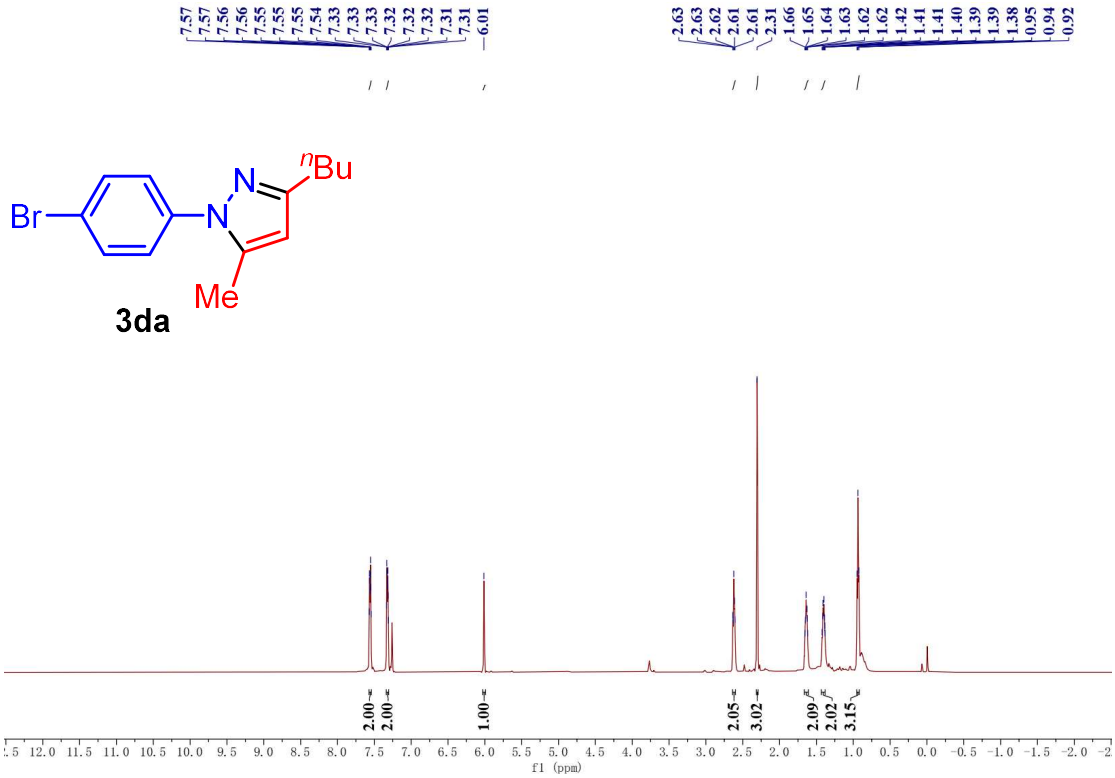
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ba**



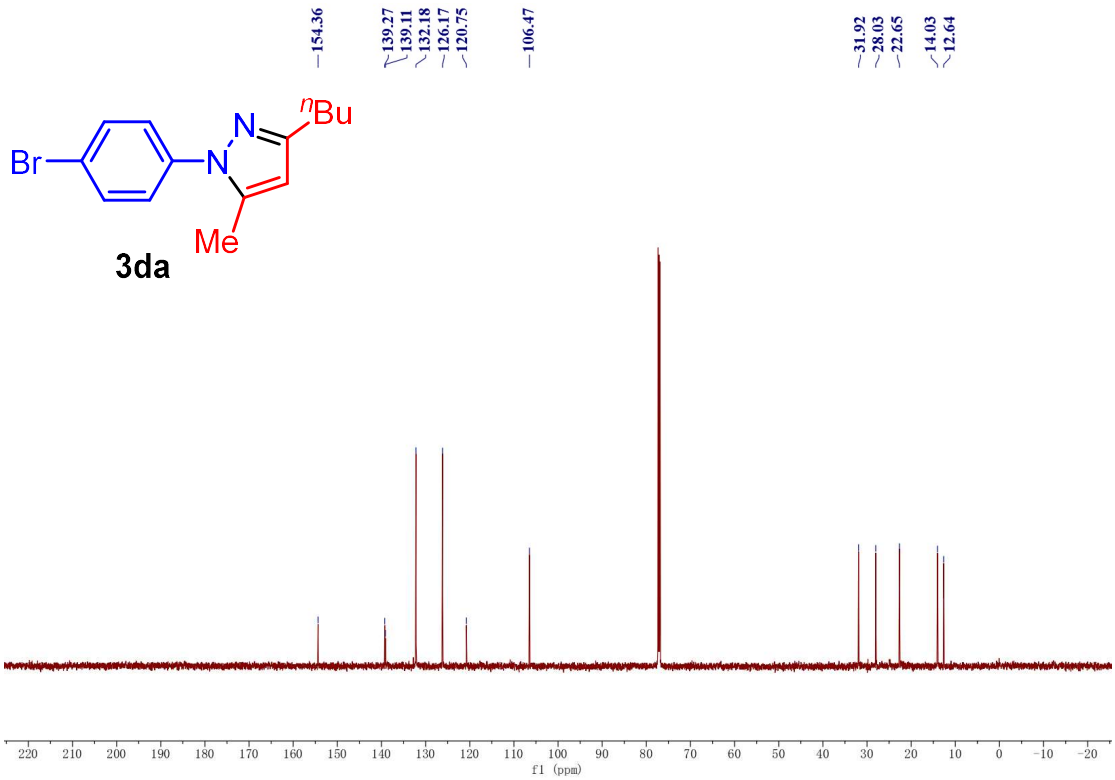
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ca**



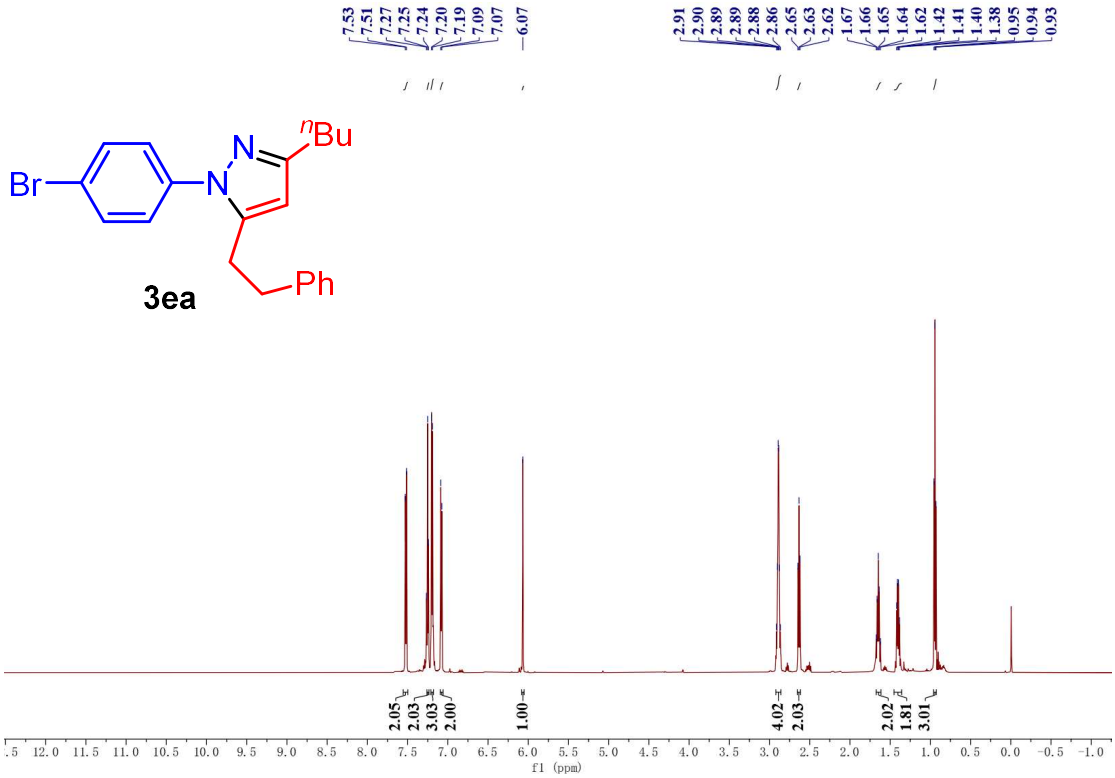
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ca**



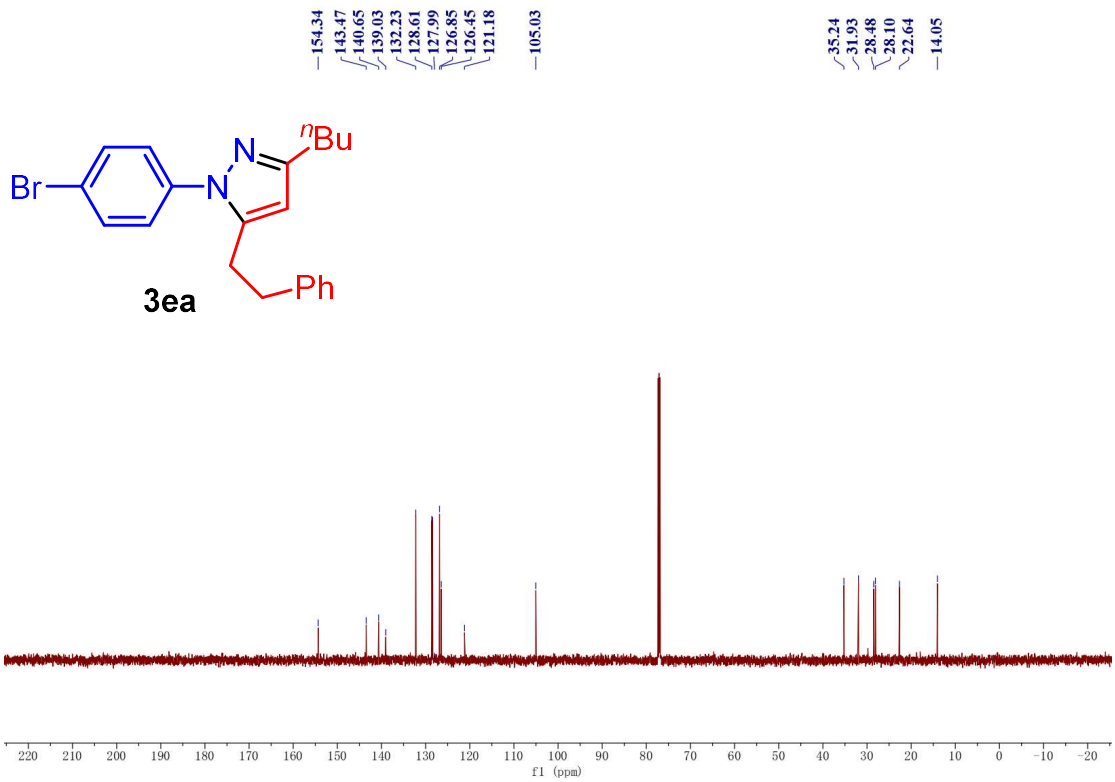
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3da**



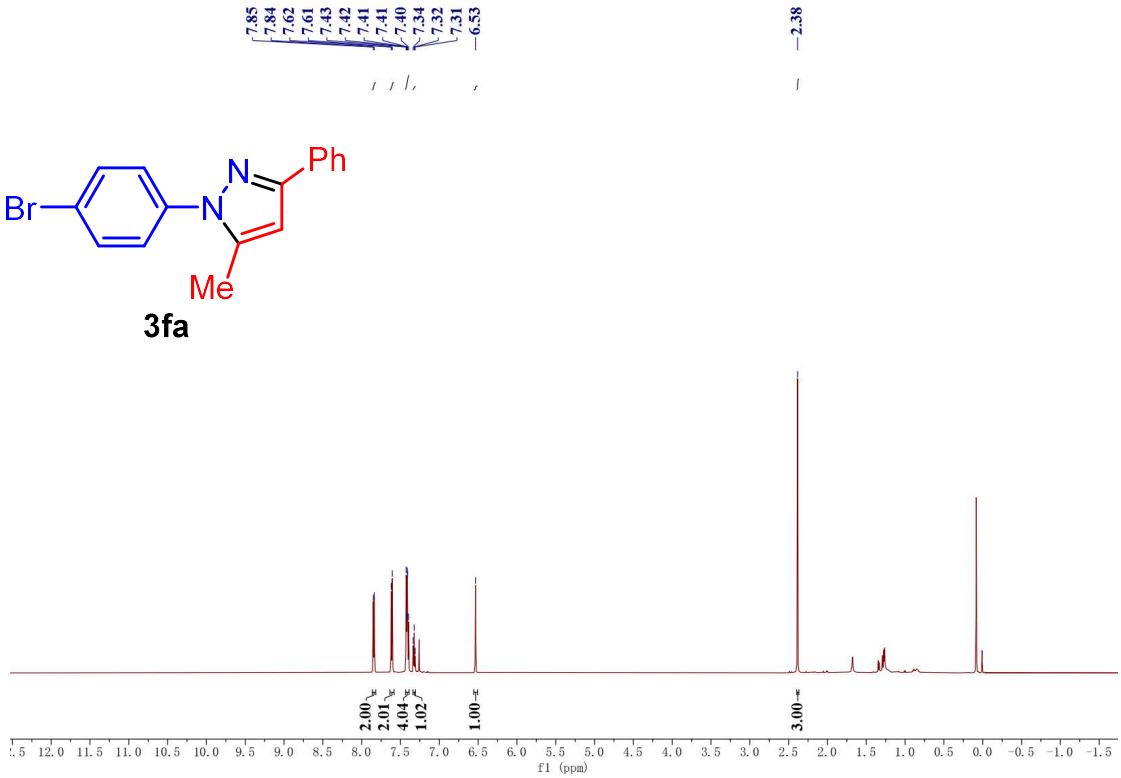
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3da**



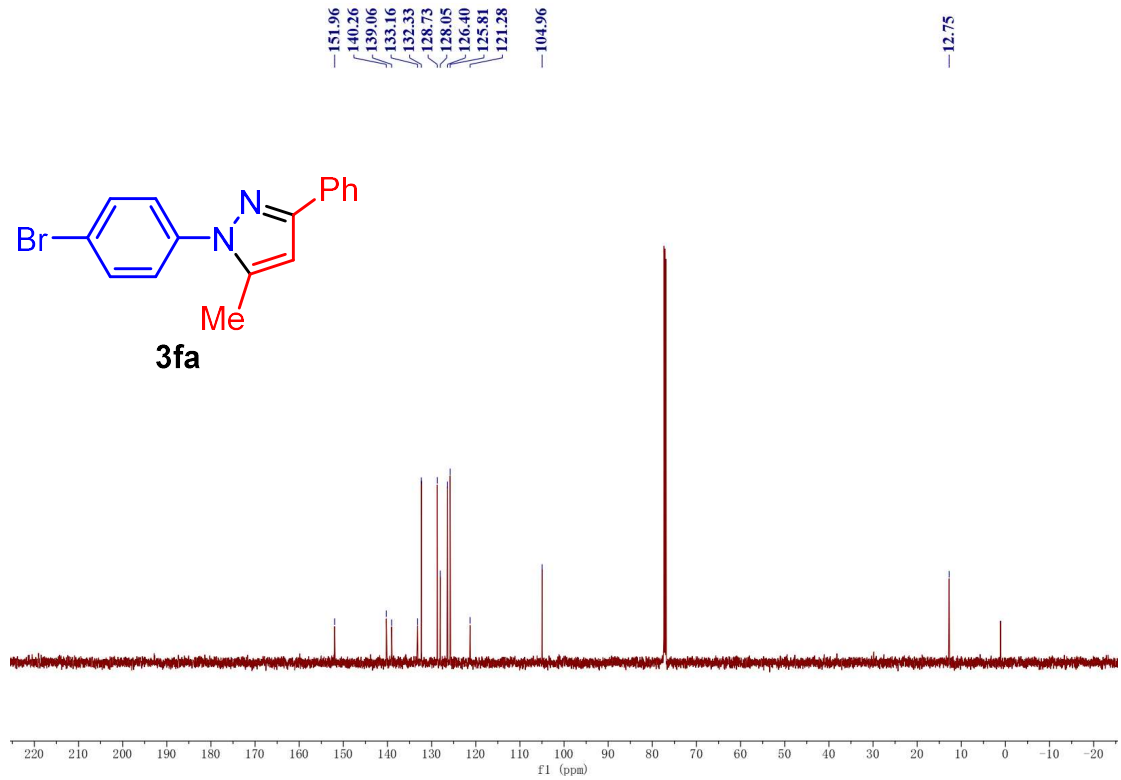
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ea**



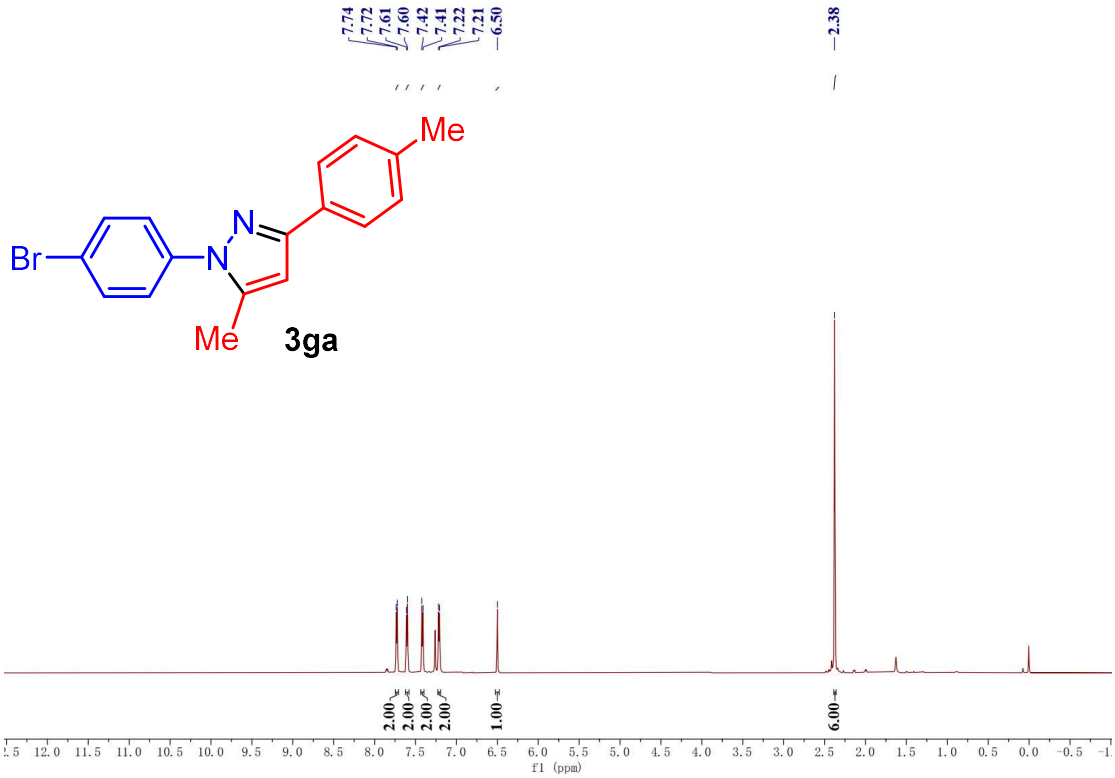
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ea**



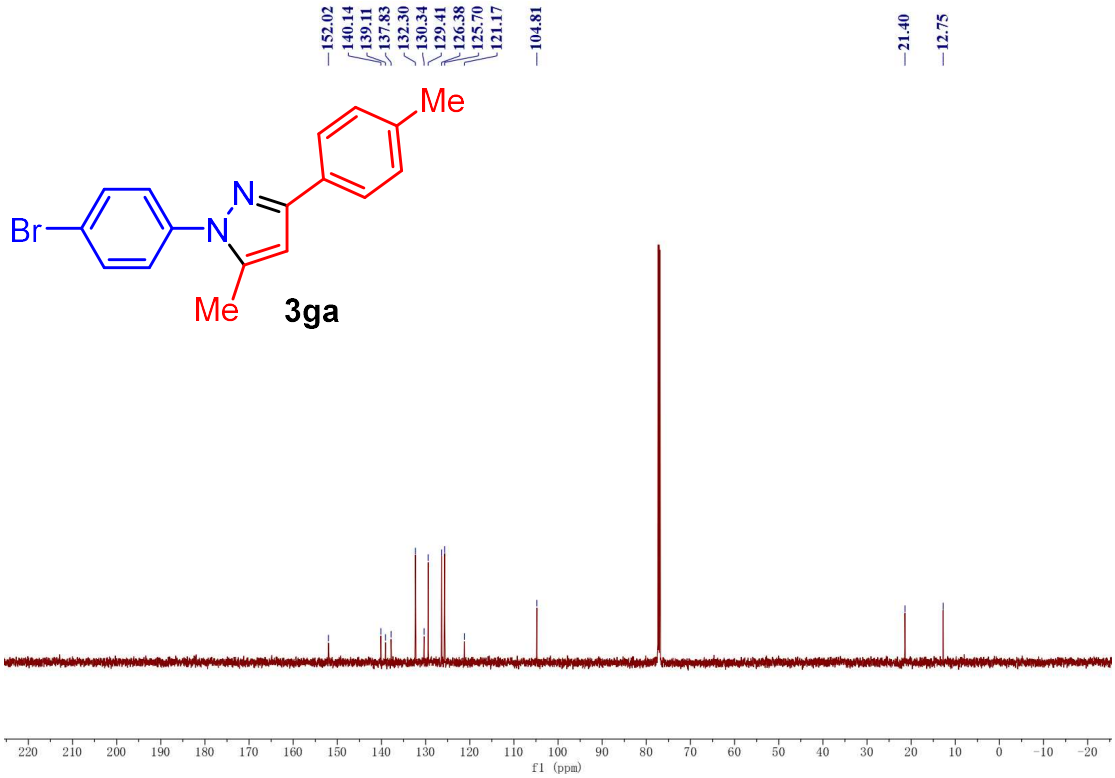
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3fa**



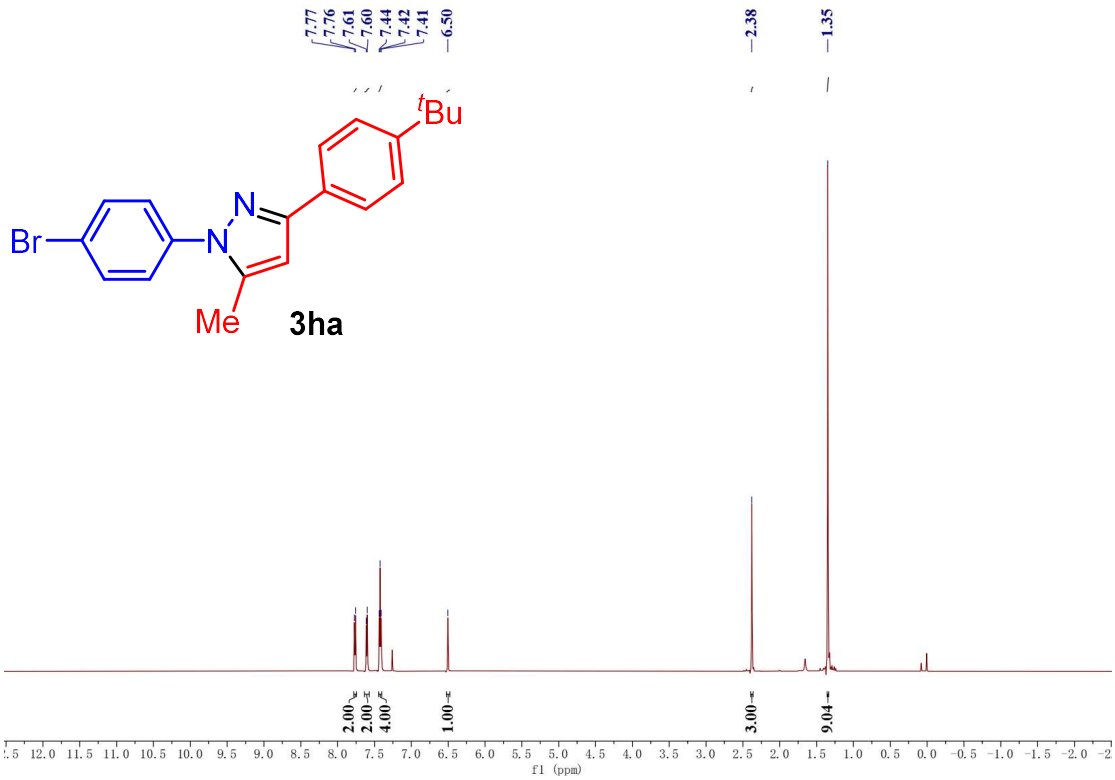
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3fa**



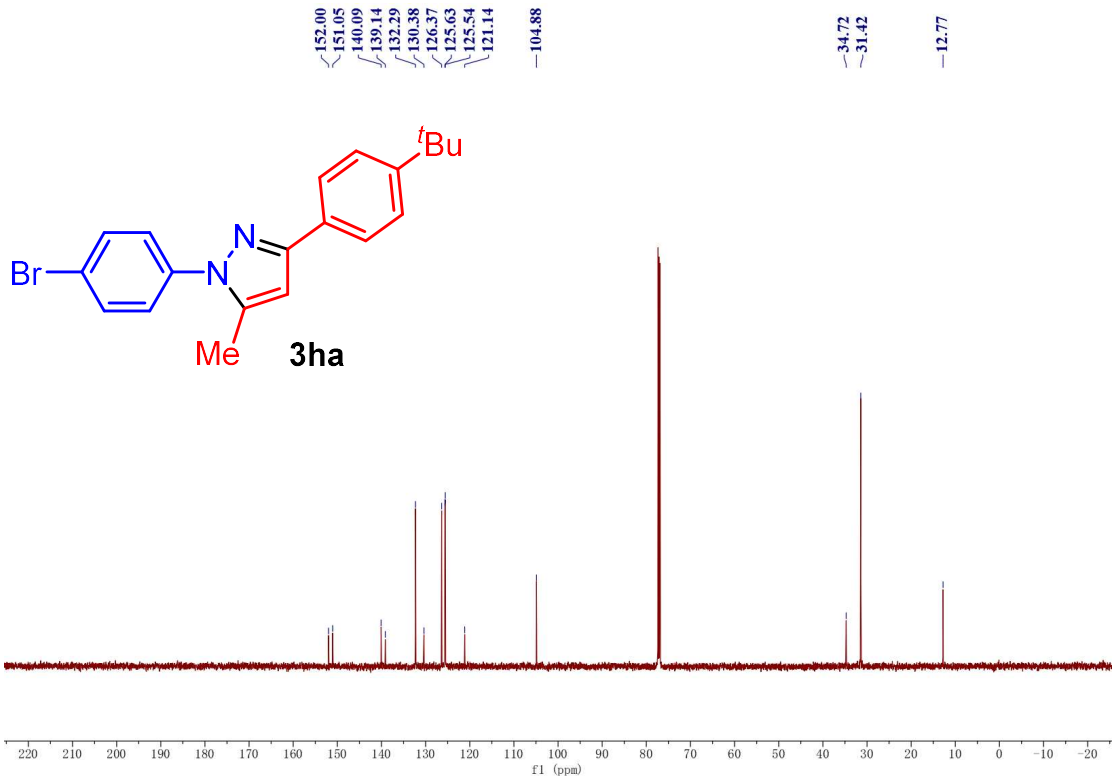
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ga**



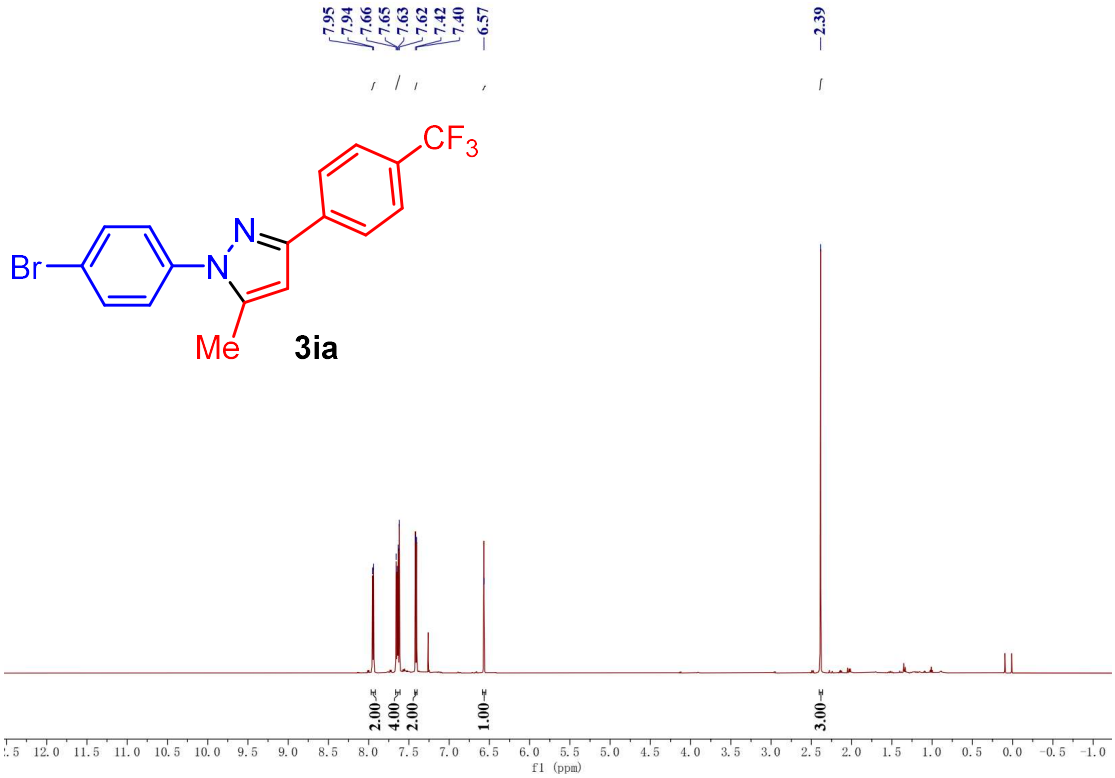
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ga**



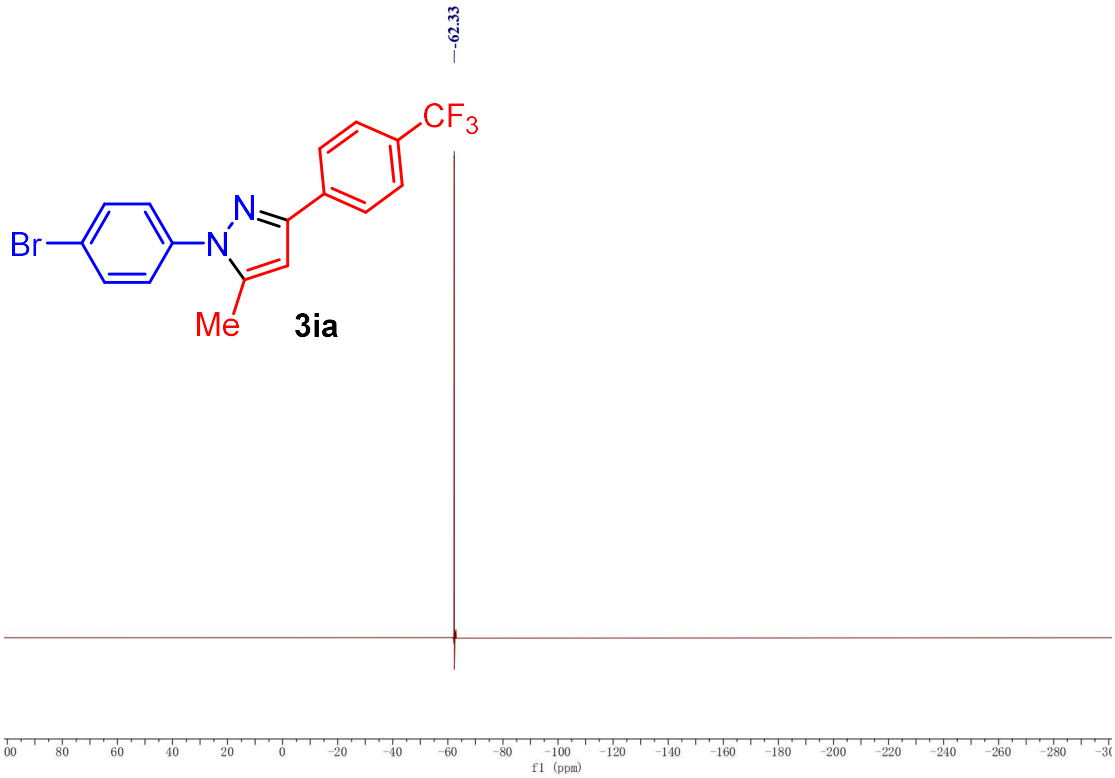
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ha**



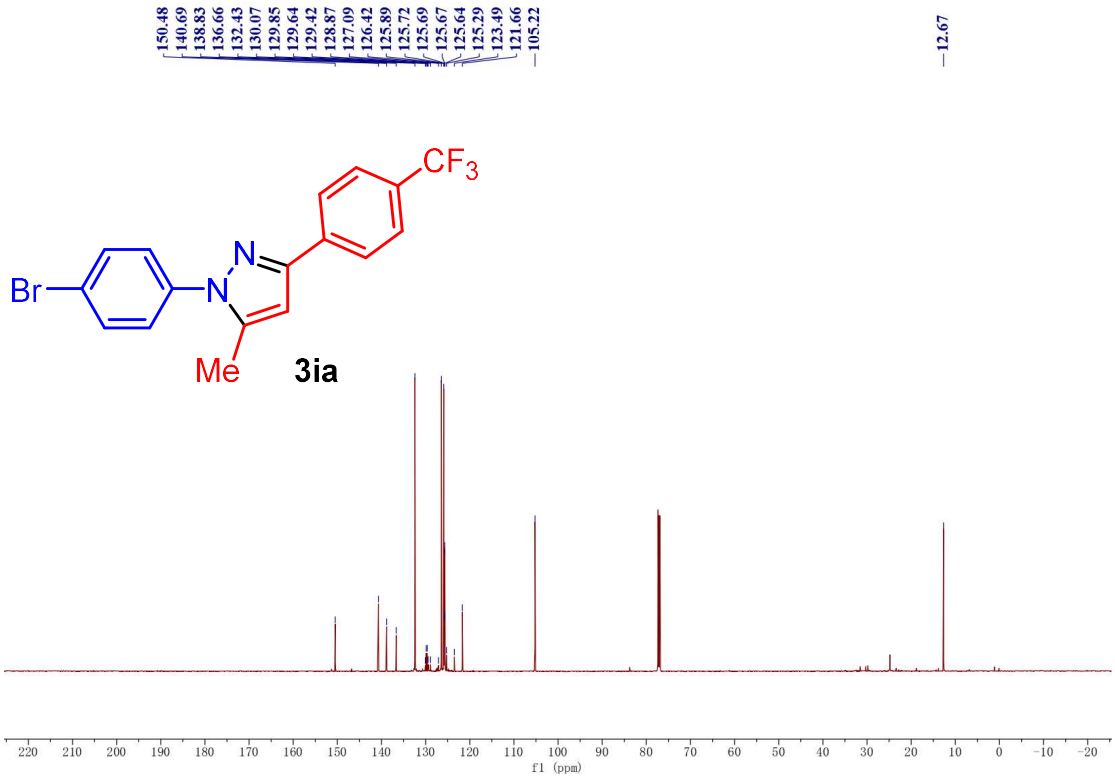
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ha**



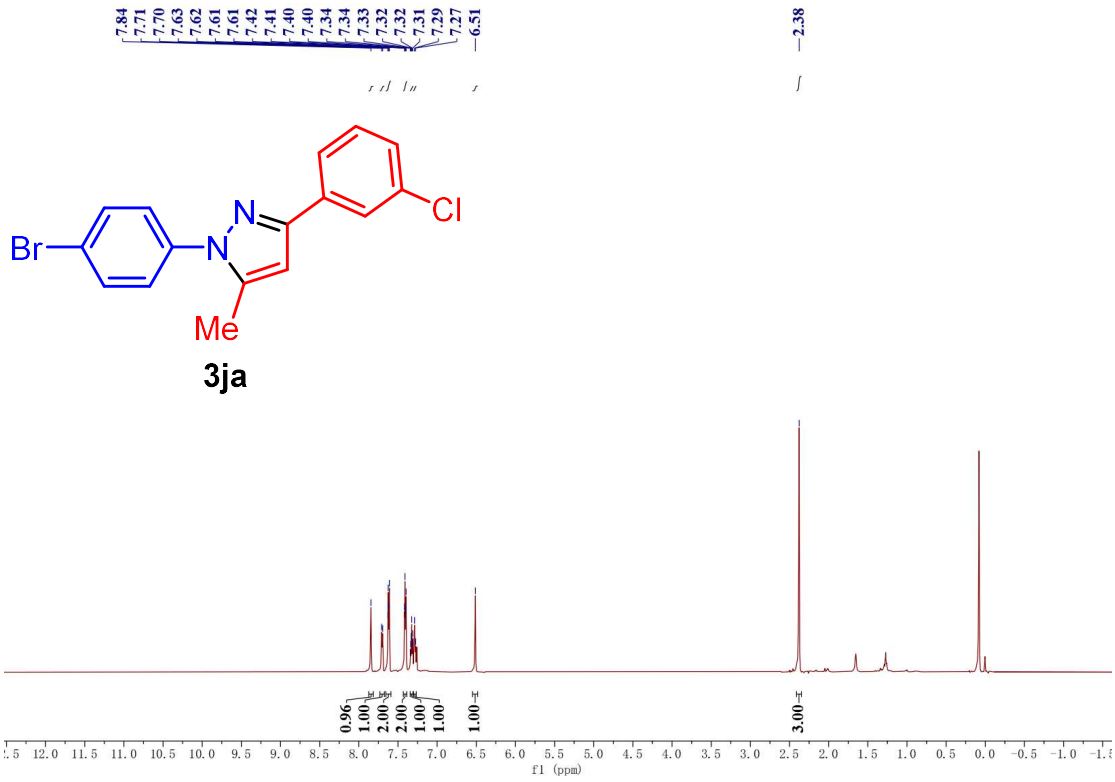
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ia**



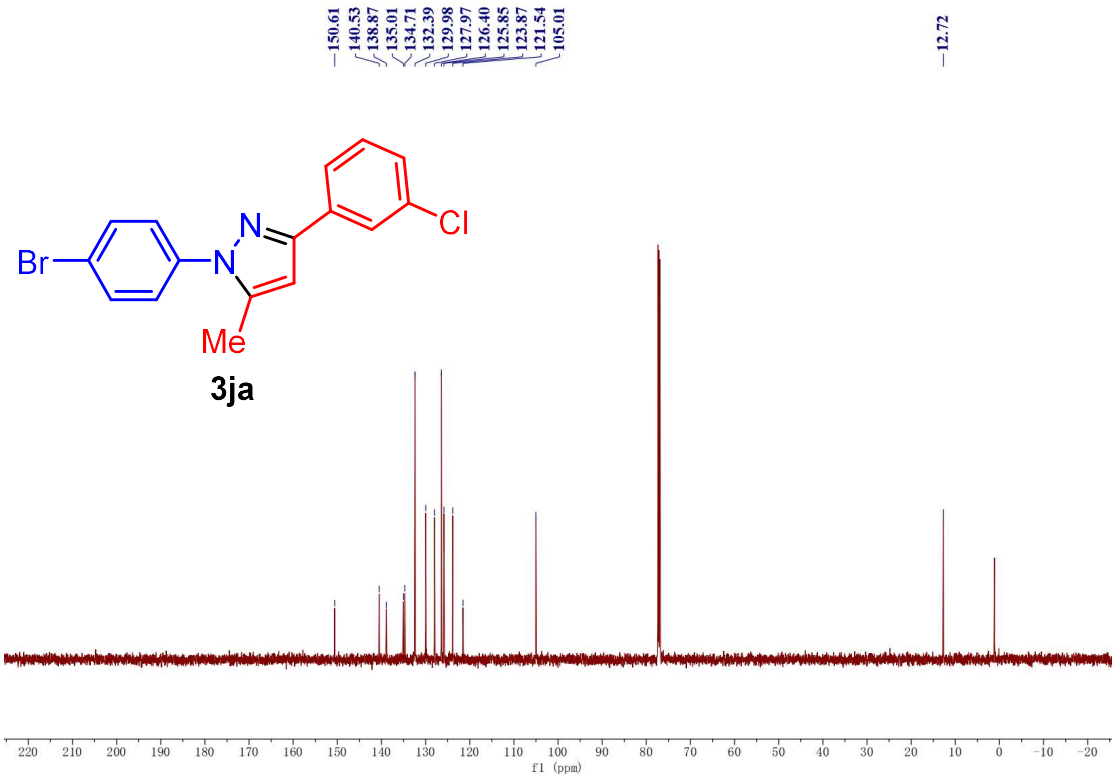
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **3ia**



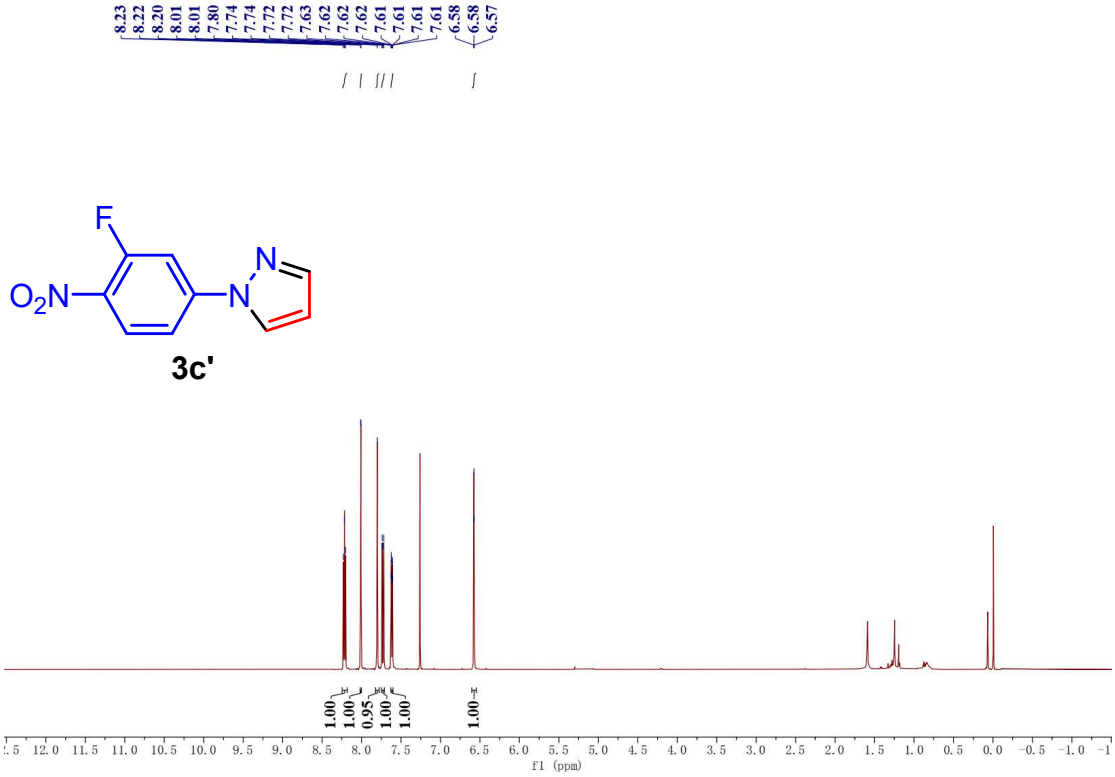
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ia**



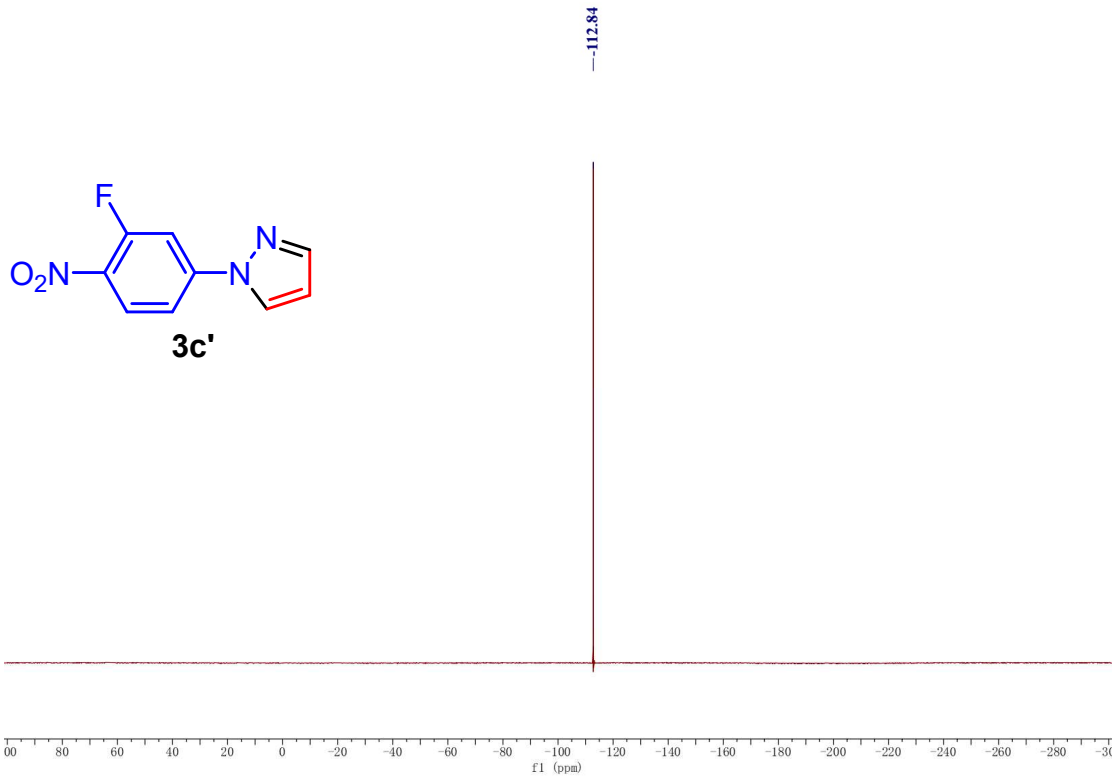
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ja**



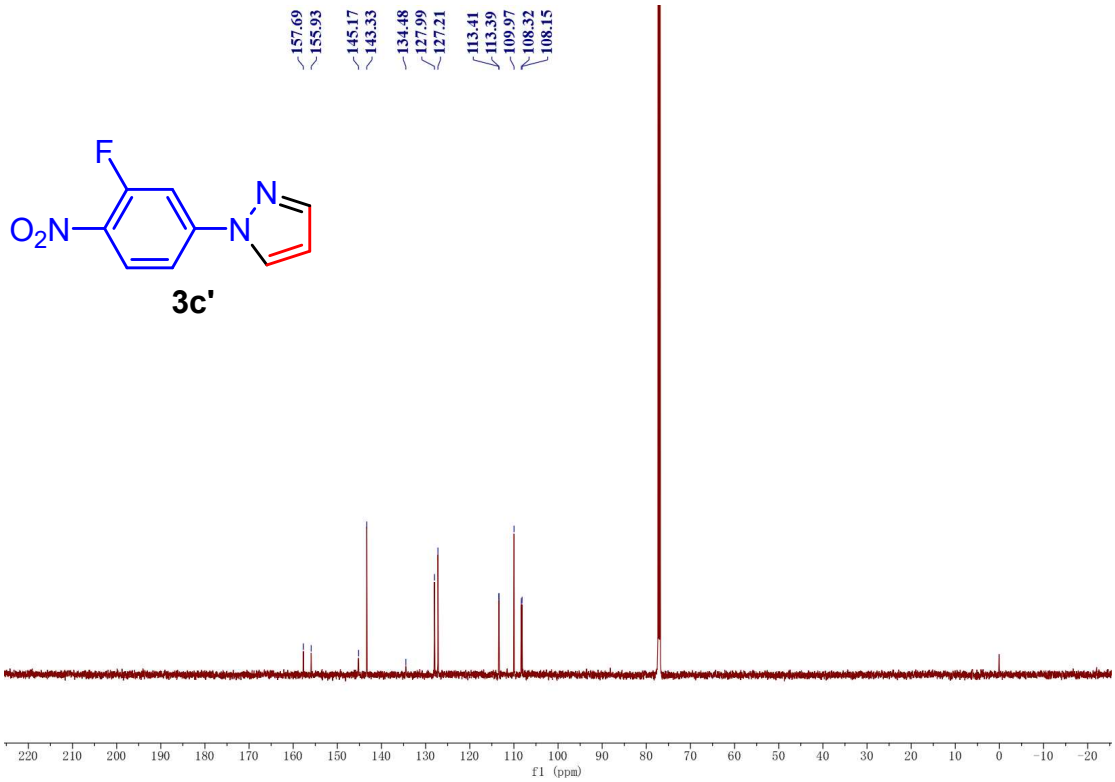
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ja**



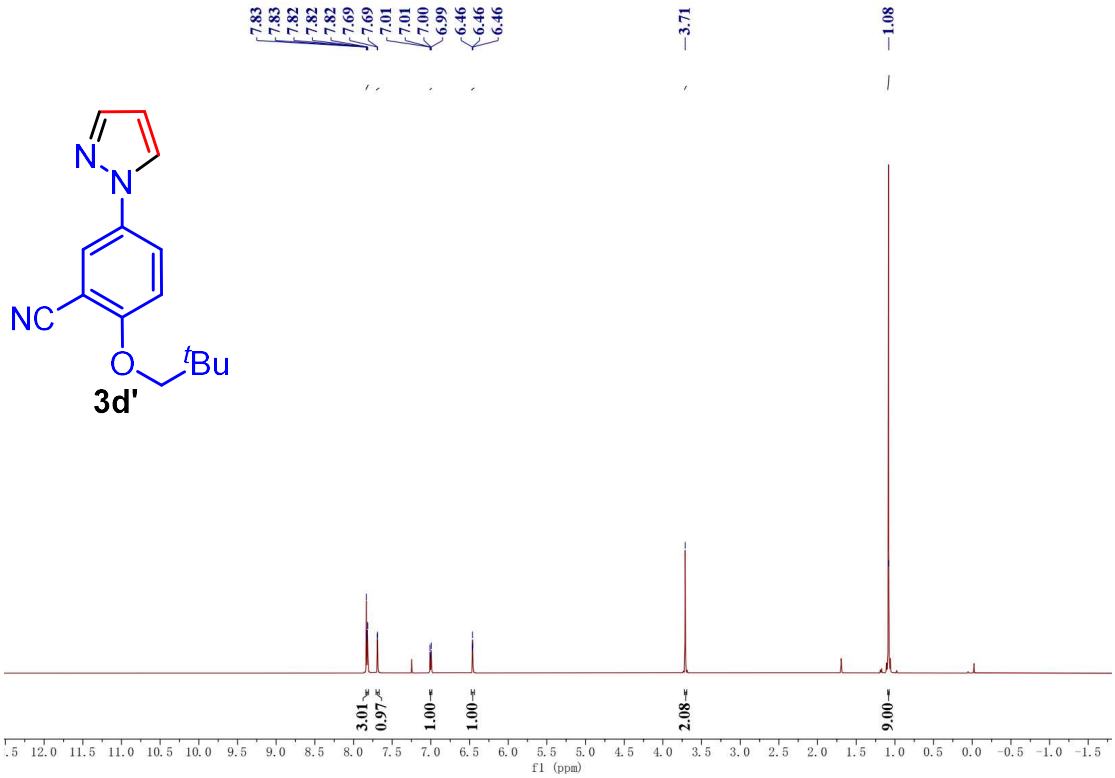
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3c'**



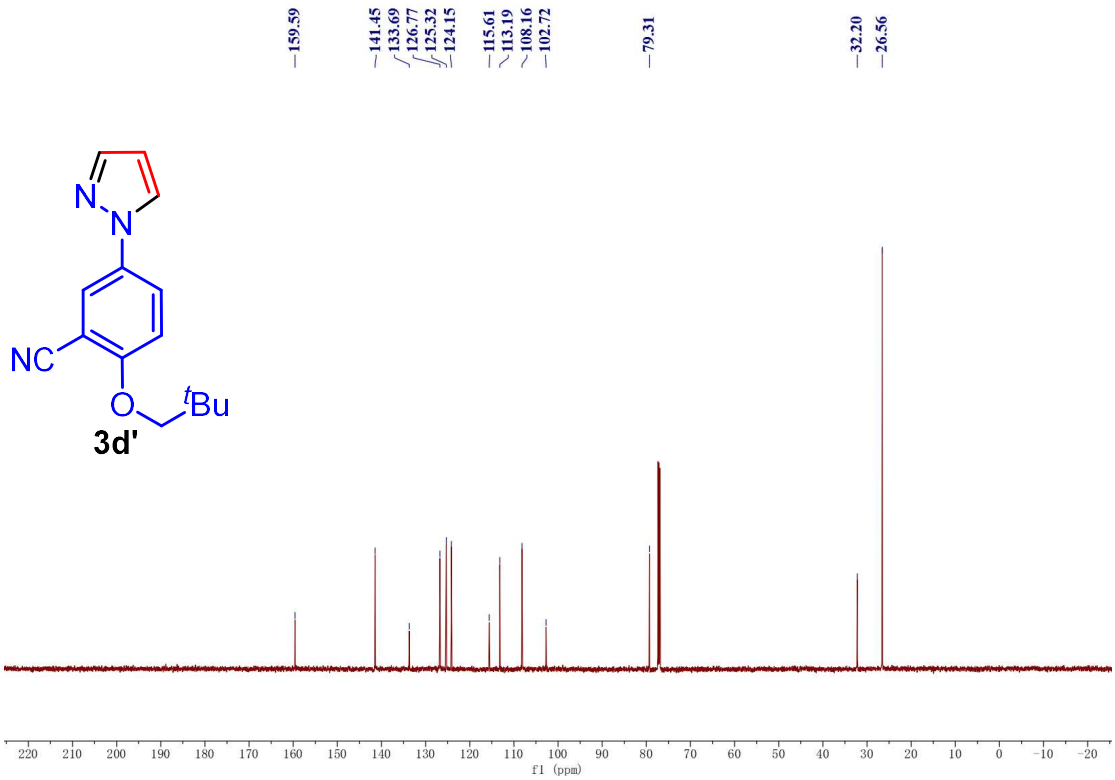
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **3c'**



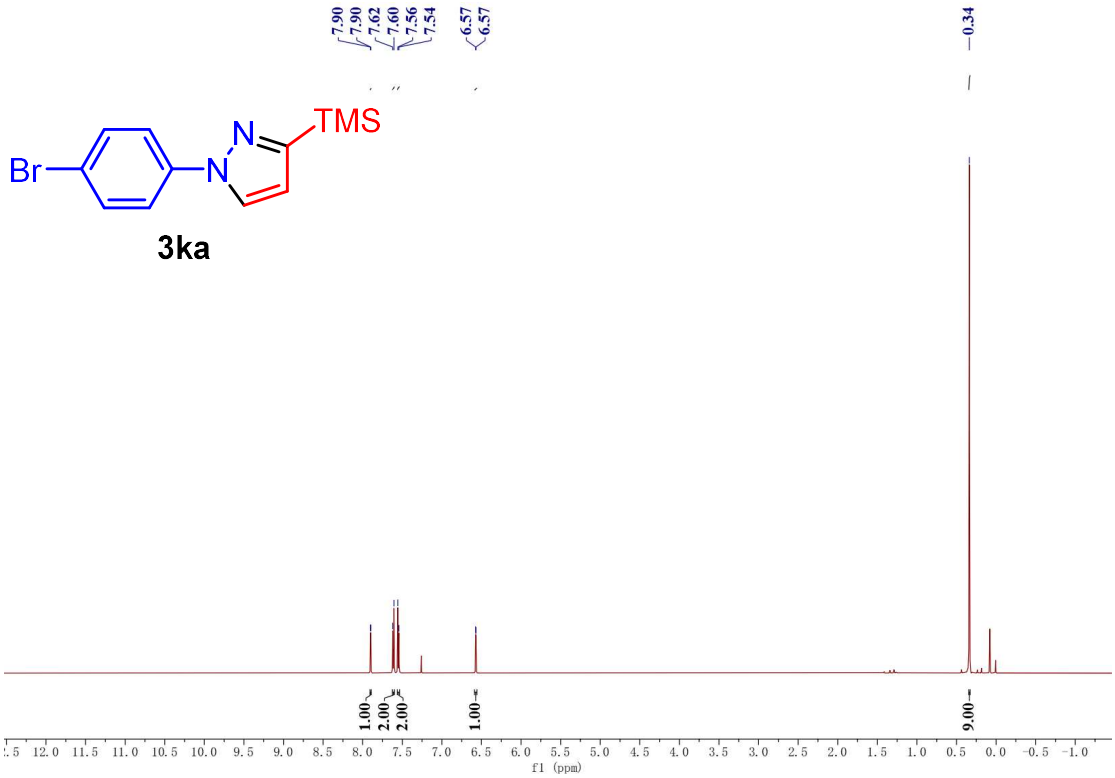
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3c'**



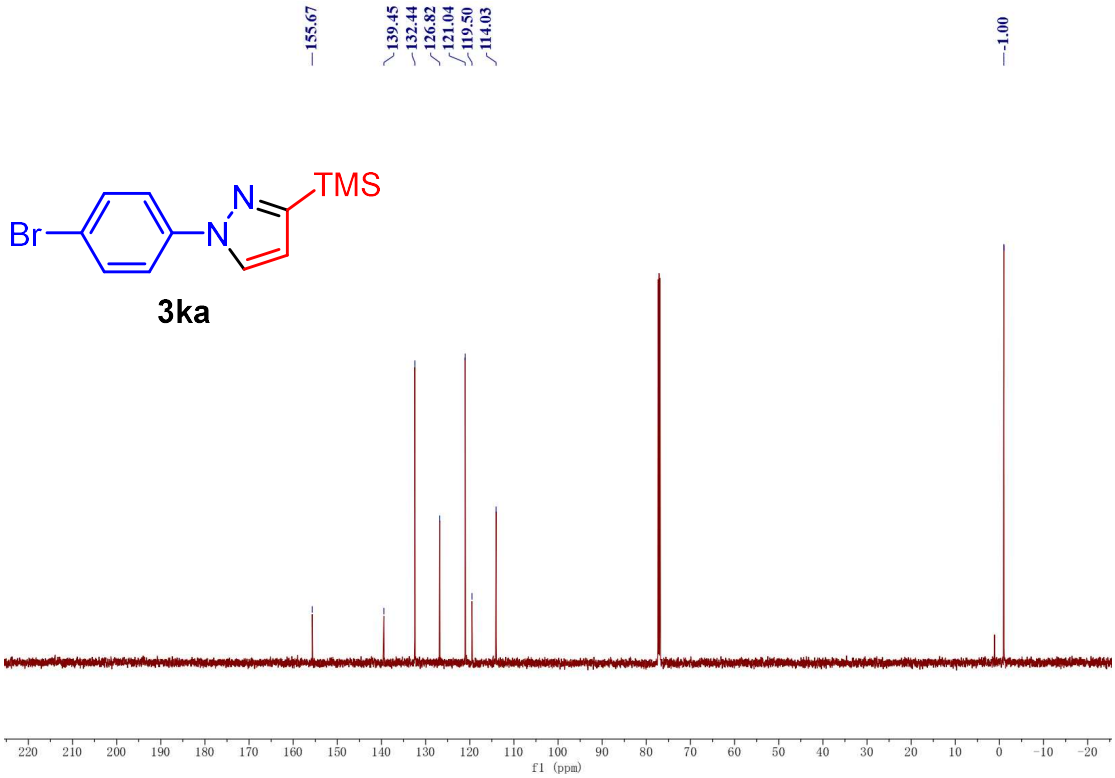
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3d'**



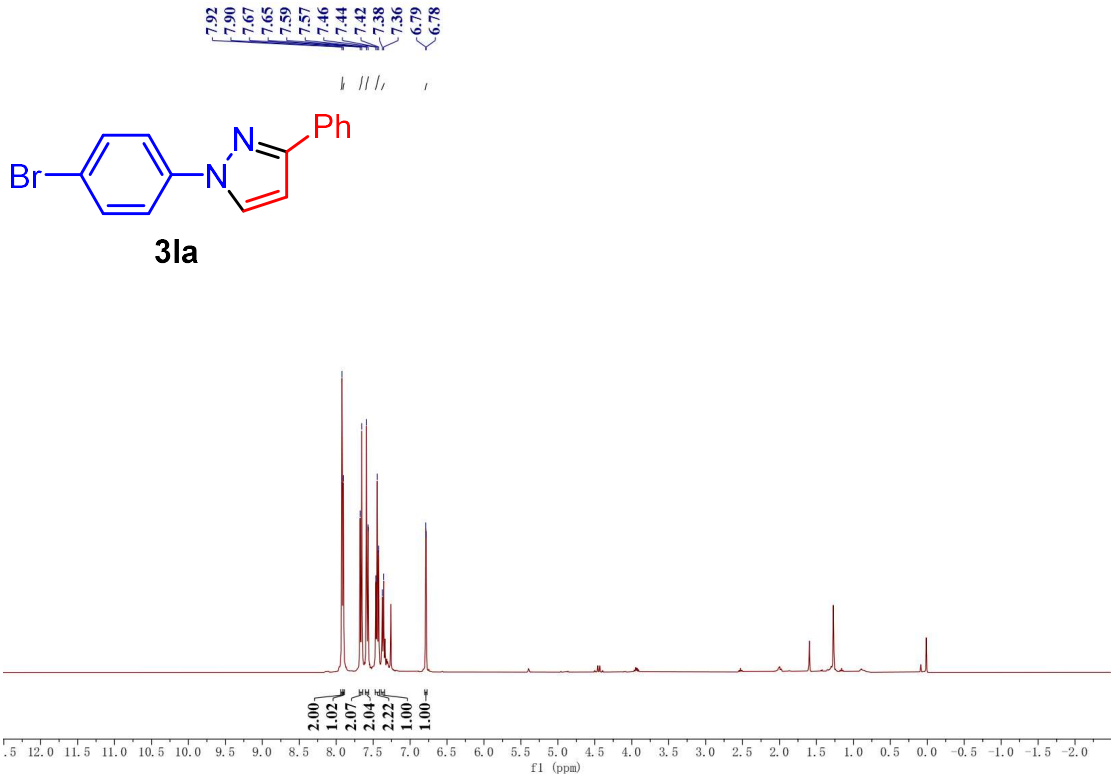
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3d'**



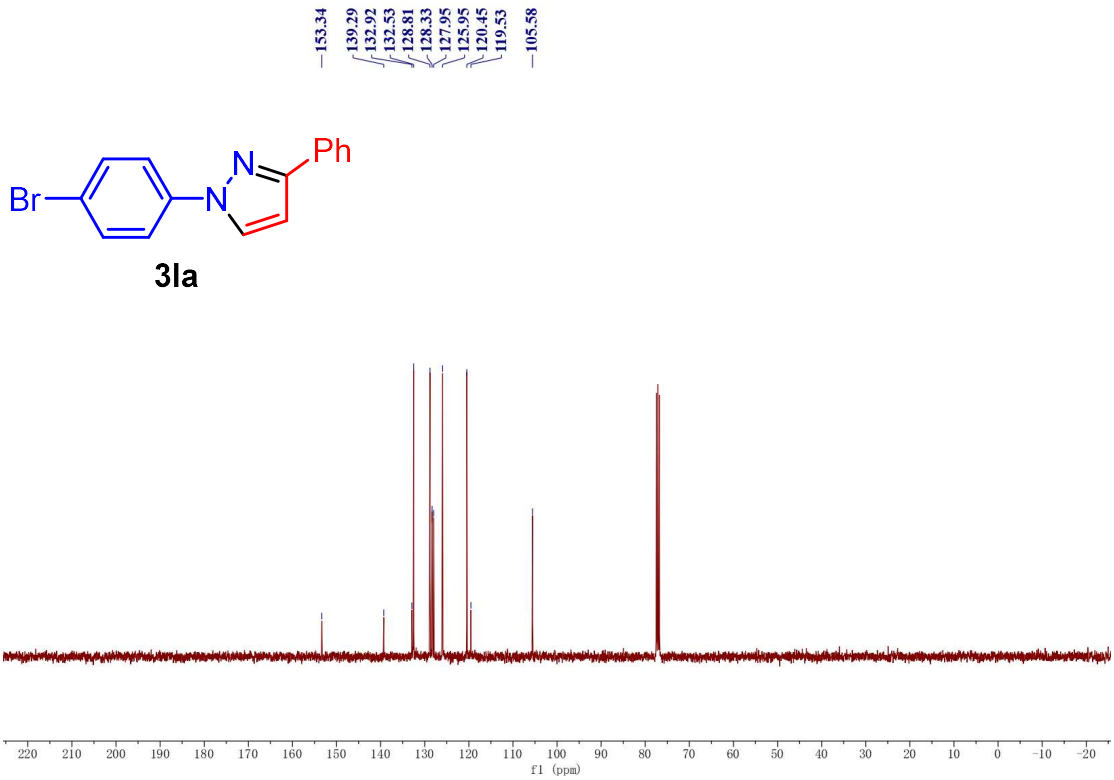
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **3ka**



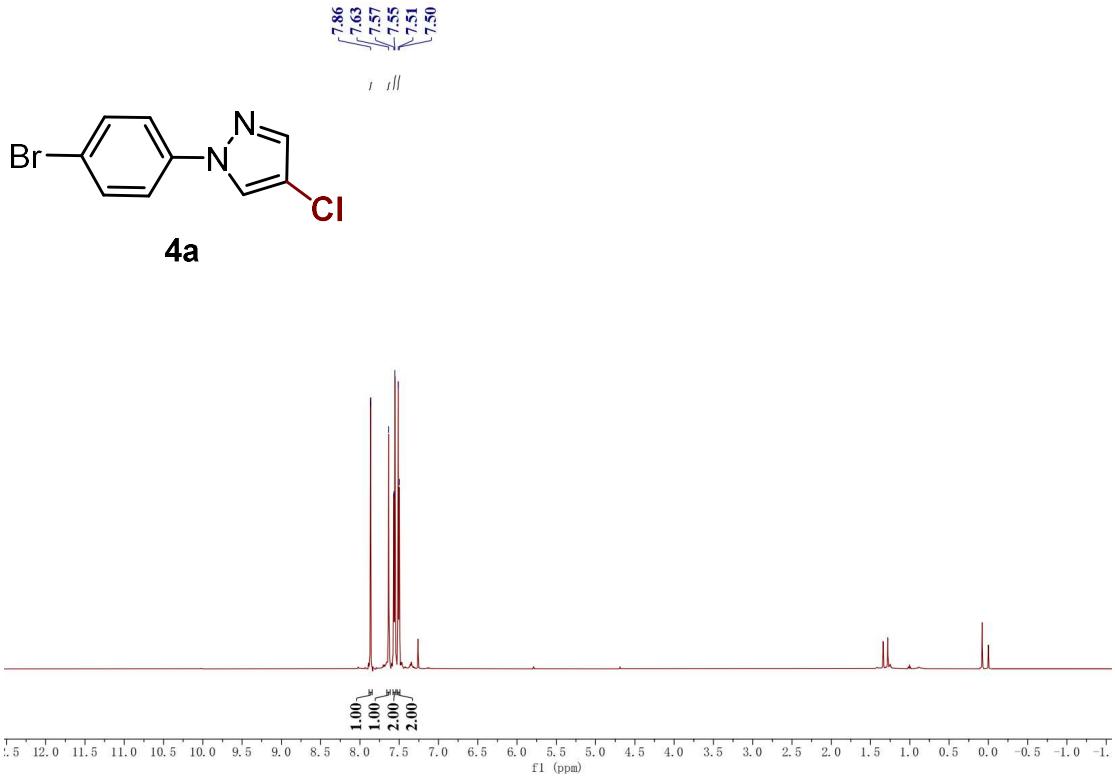
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **3ka**



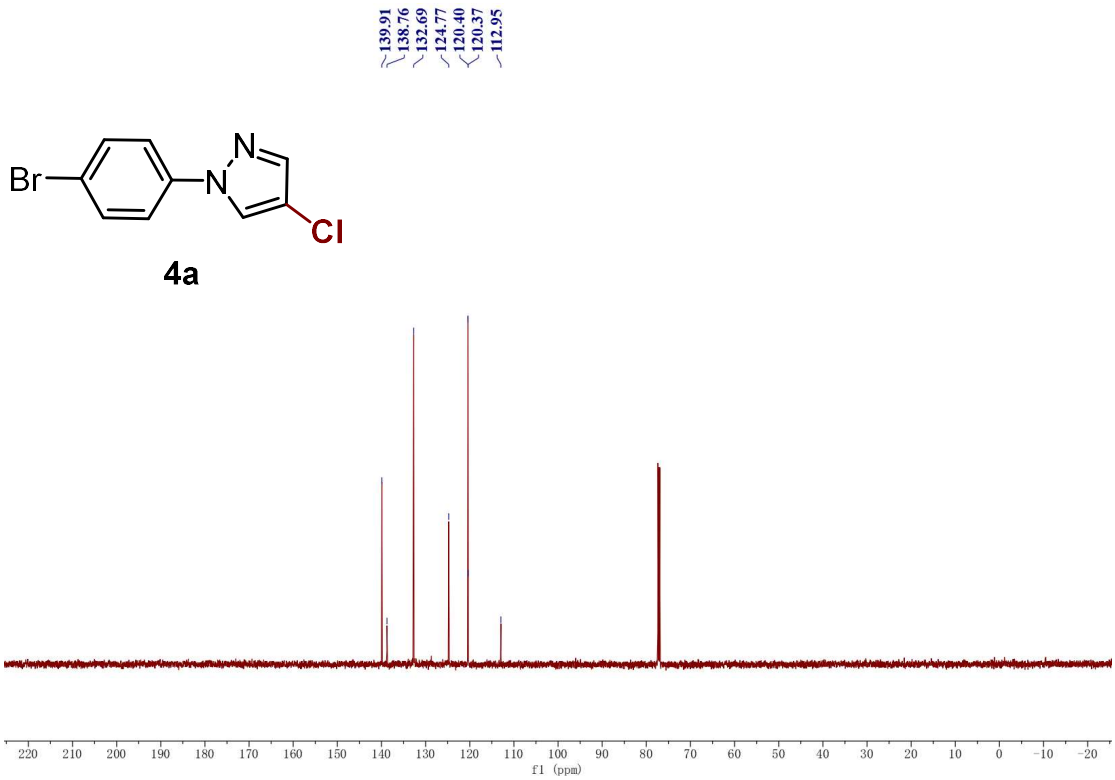
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **3la**



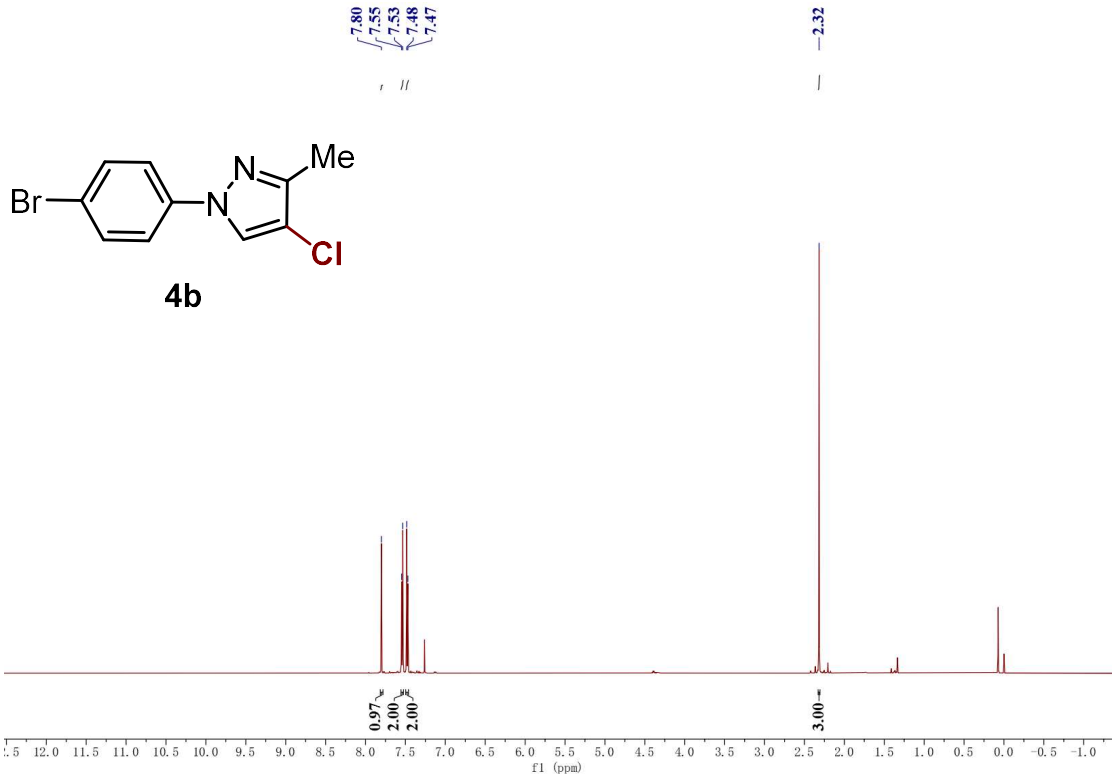
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **3la**



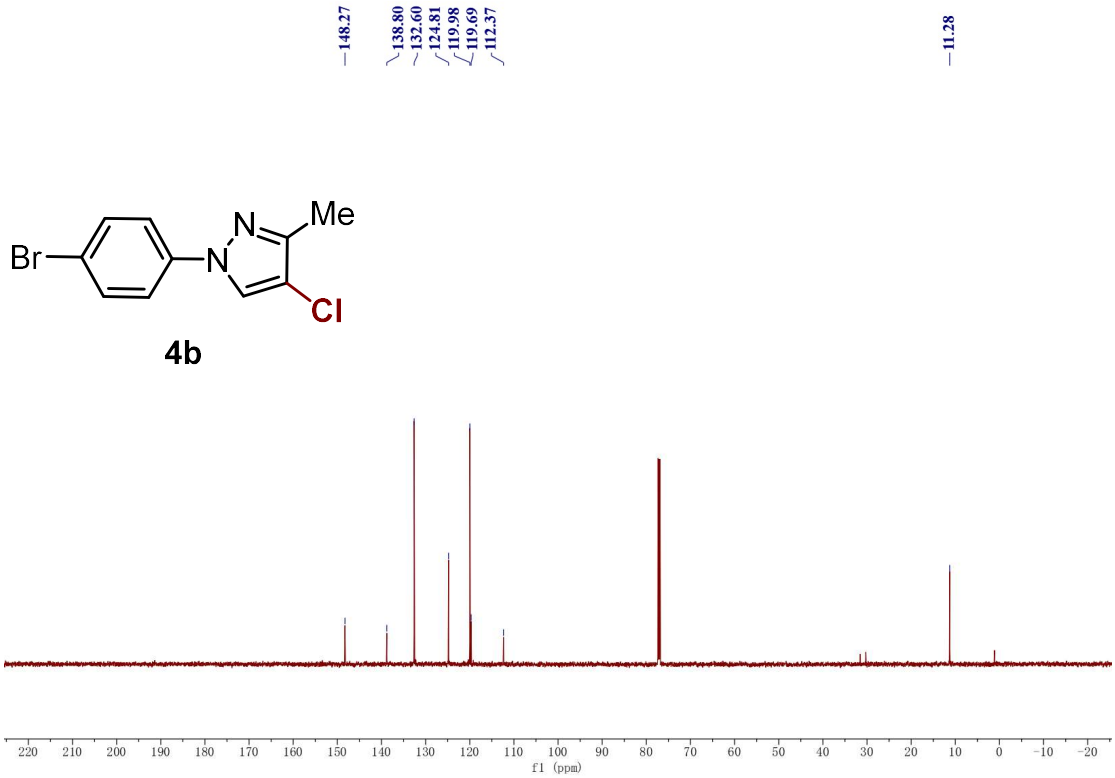
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4a**



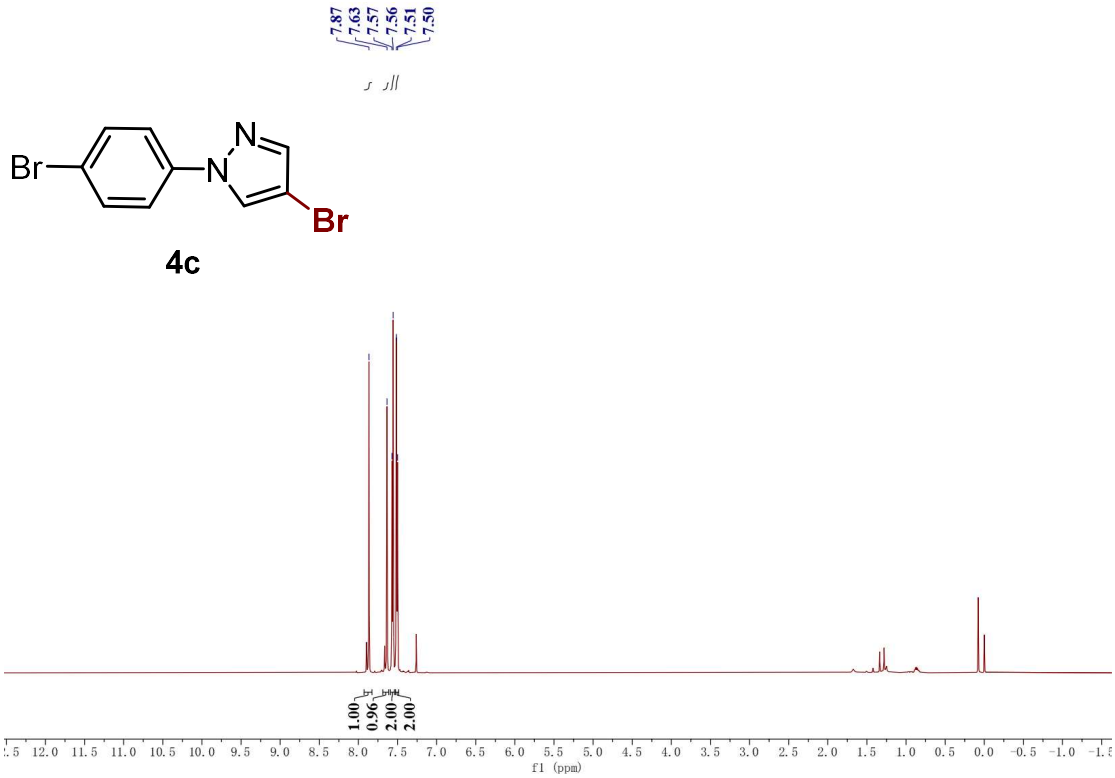
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4a**



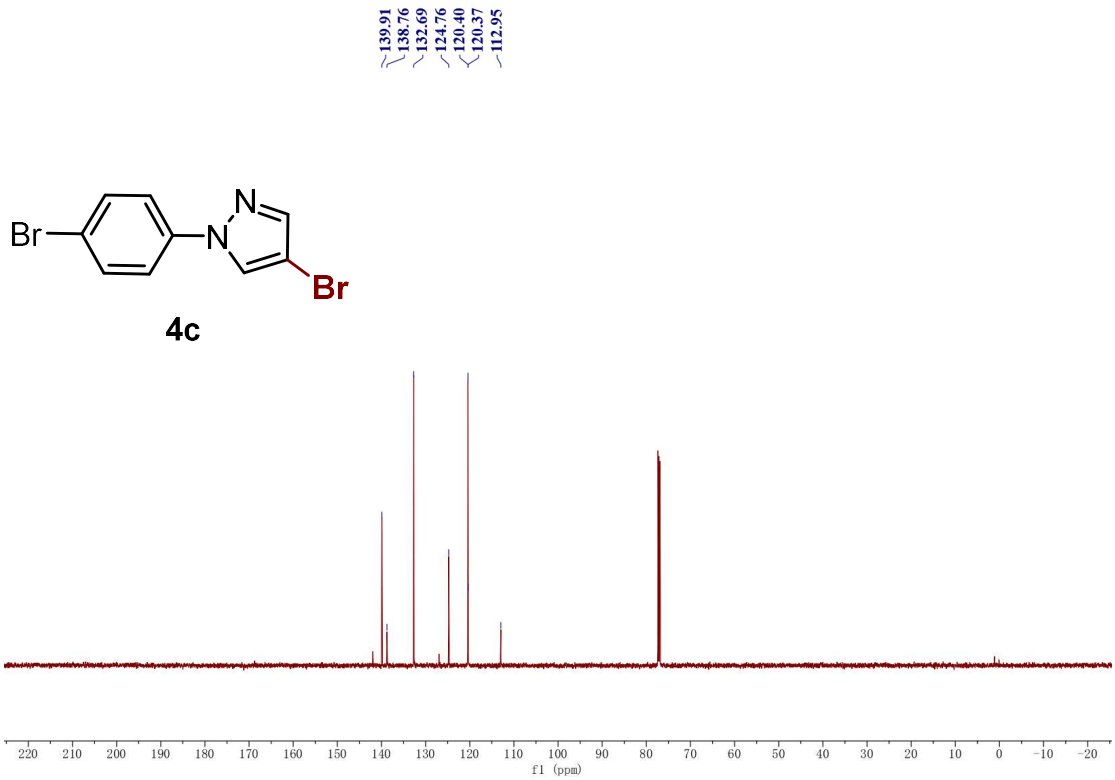
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4b**



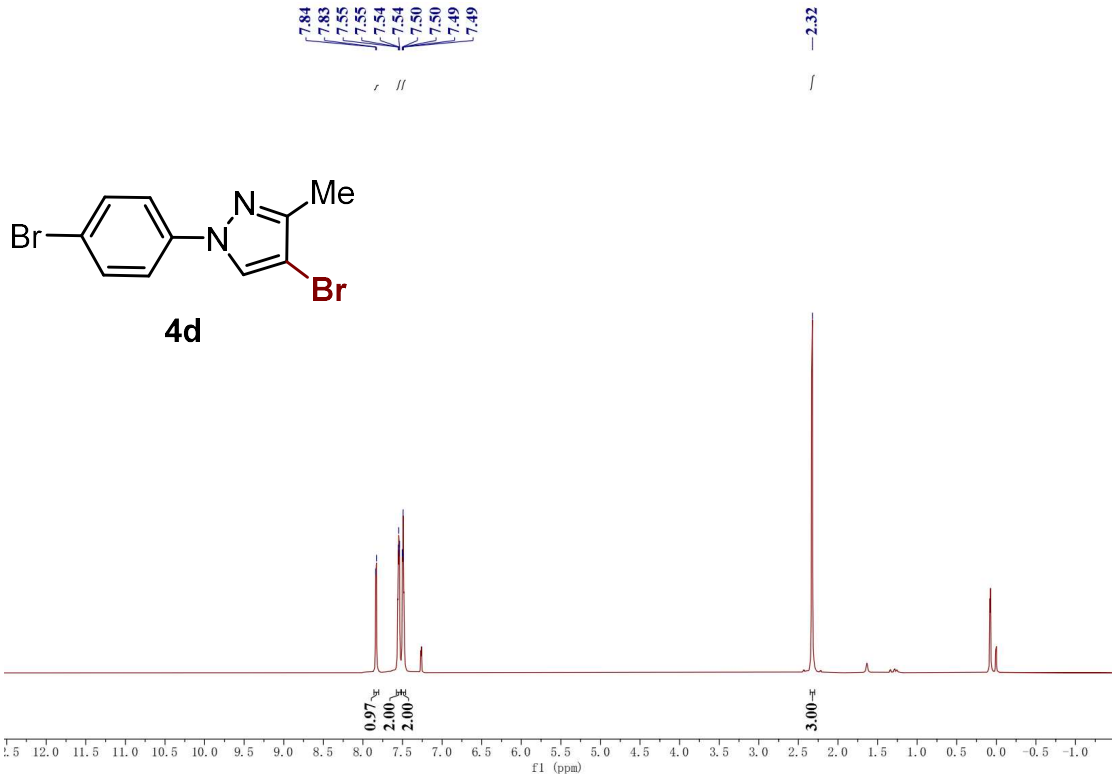
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4b**



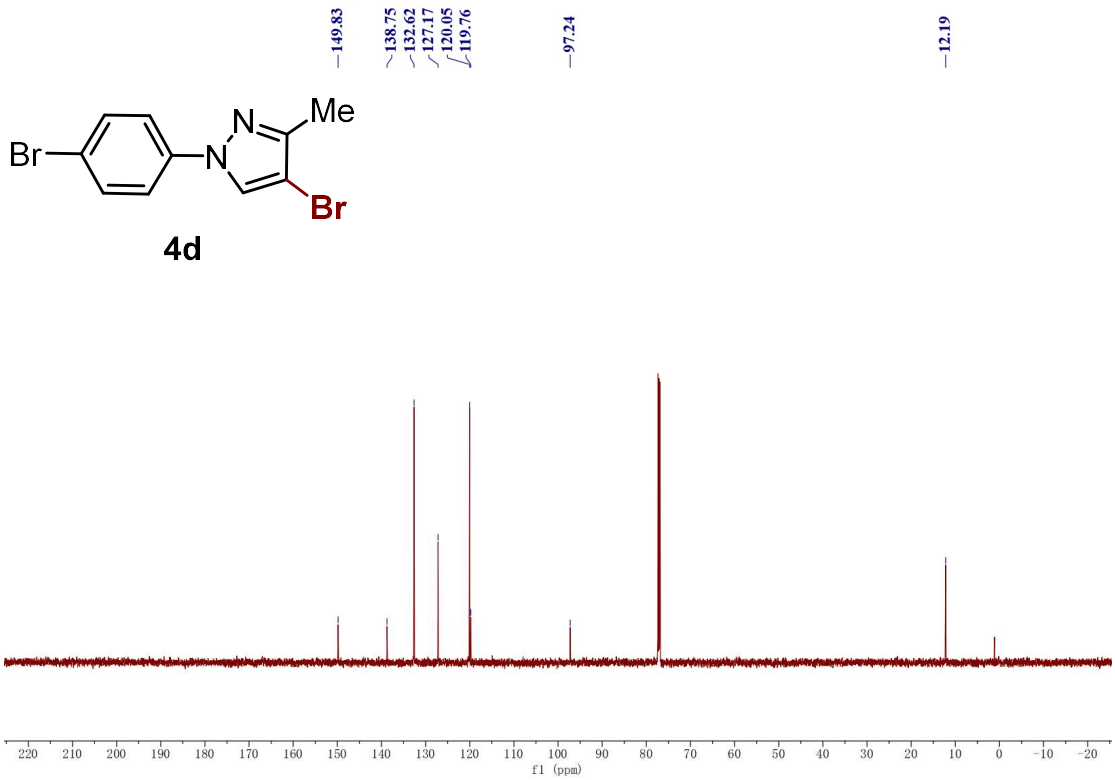
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4c**



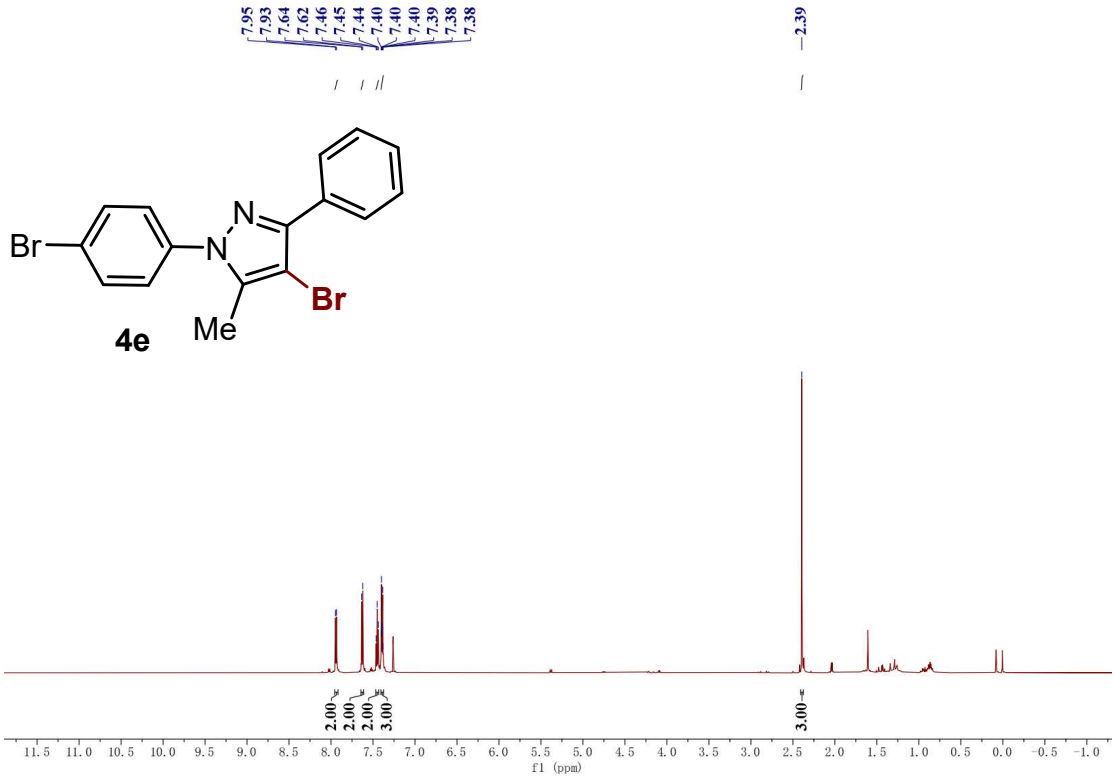
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4c**



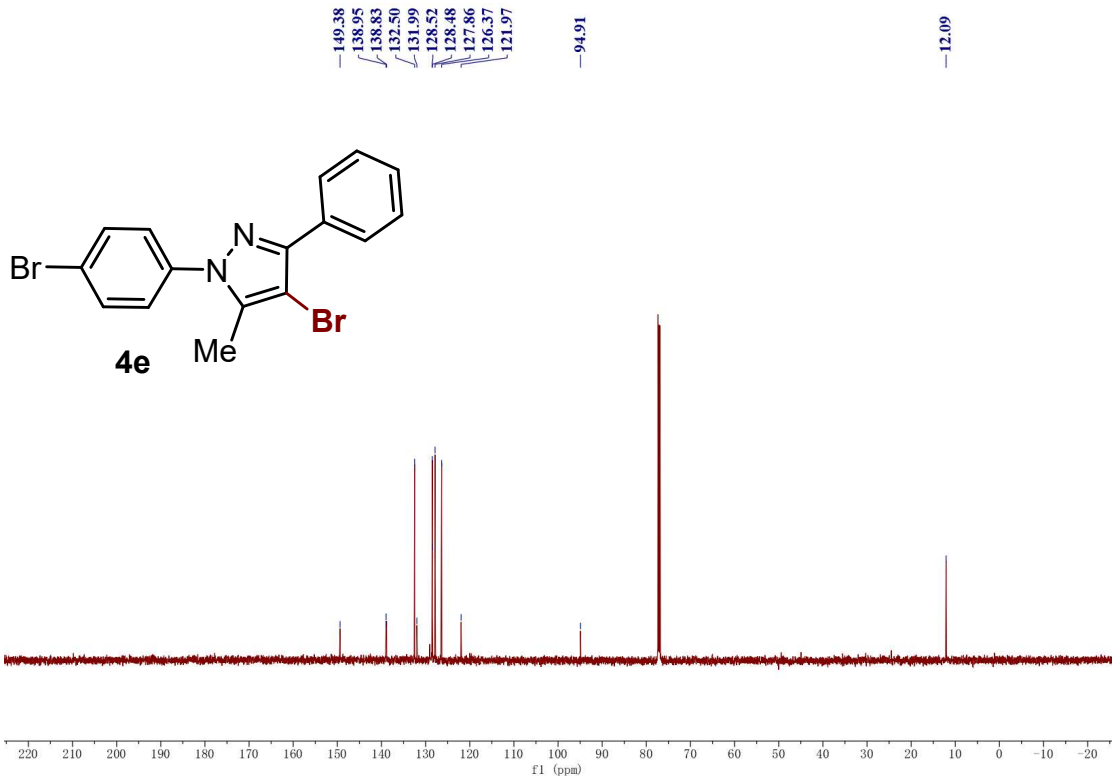
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4d**



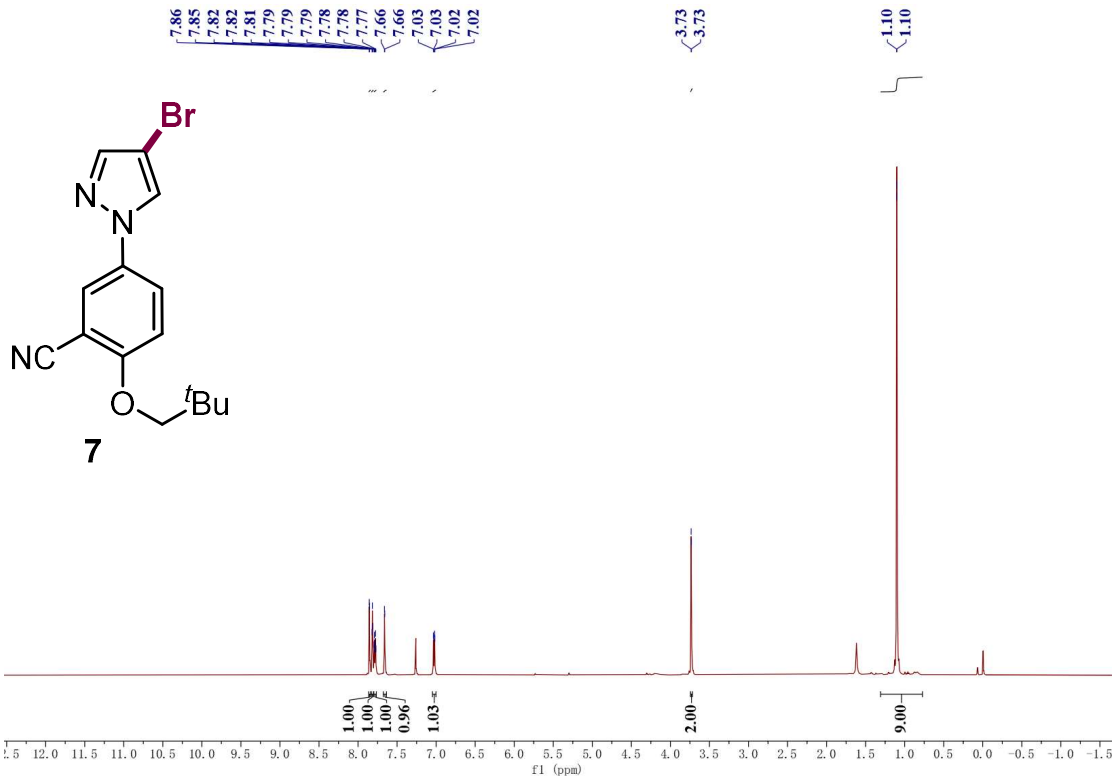
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4d**



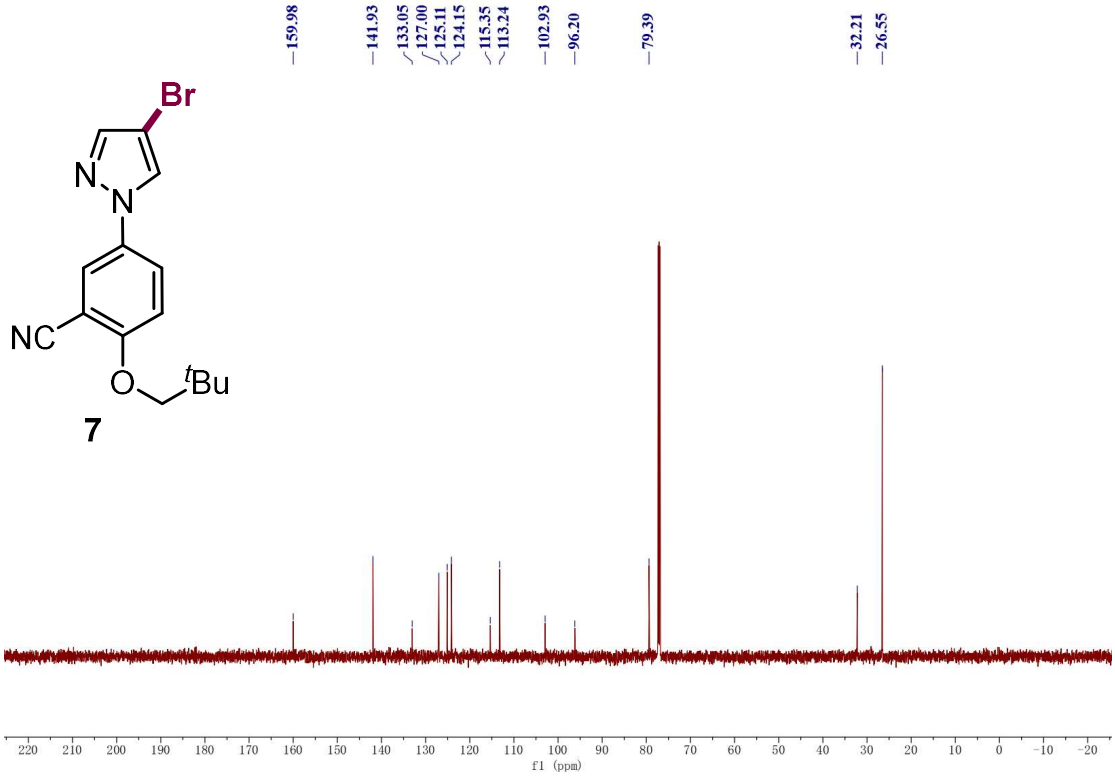
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4e**



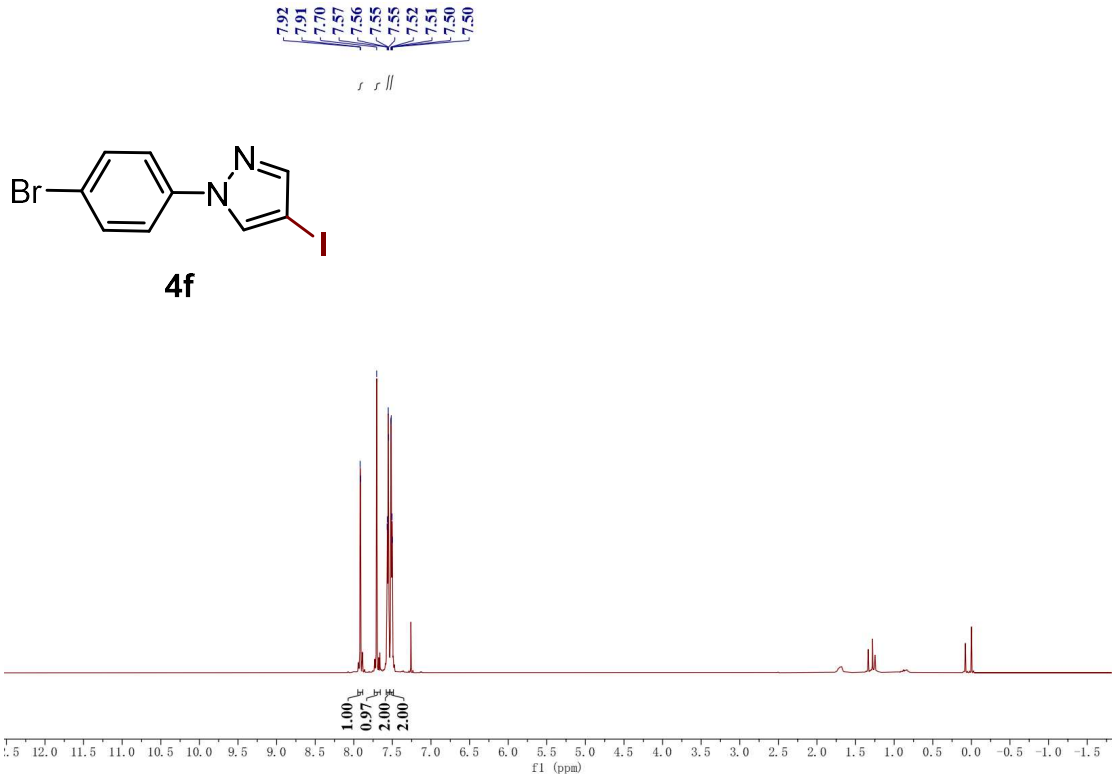
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4e**



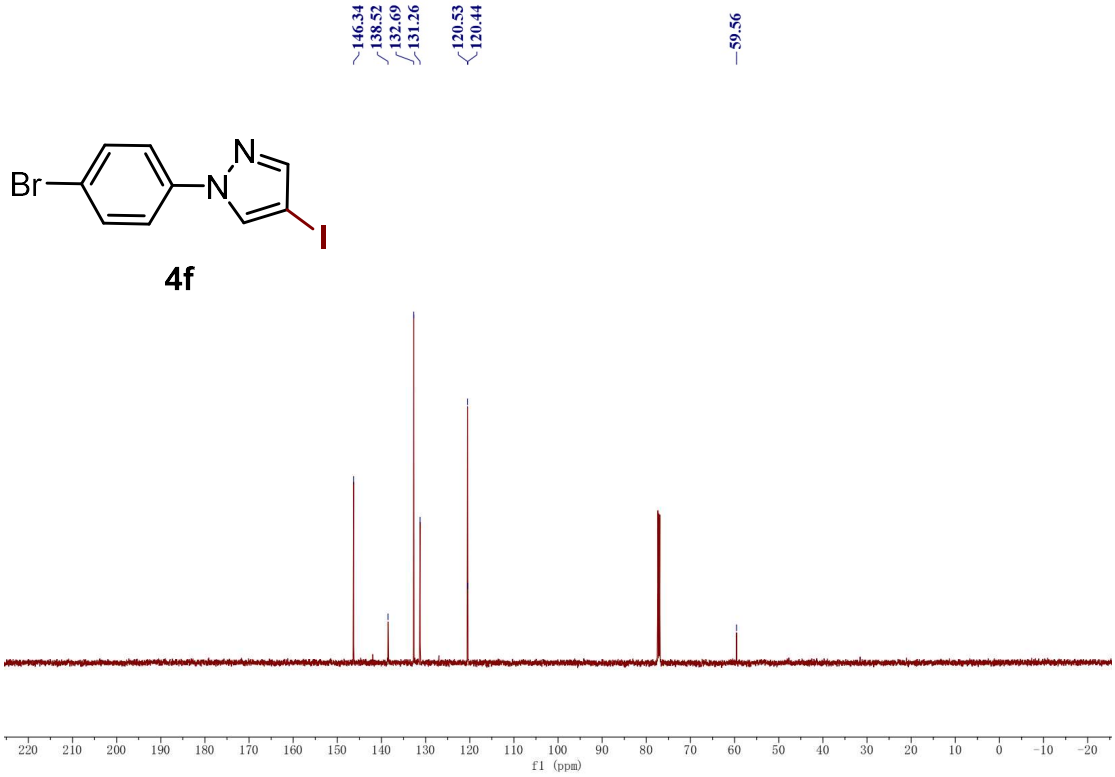
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **7**



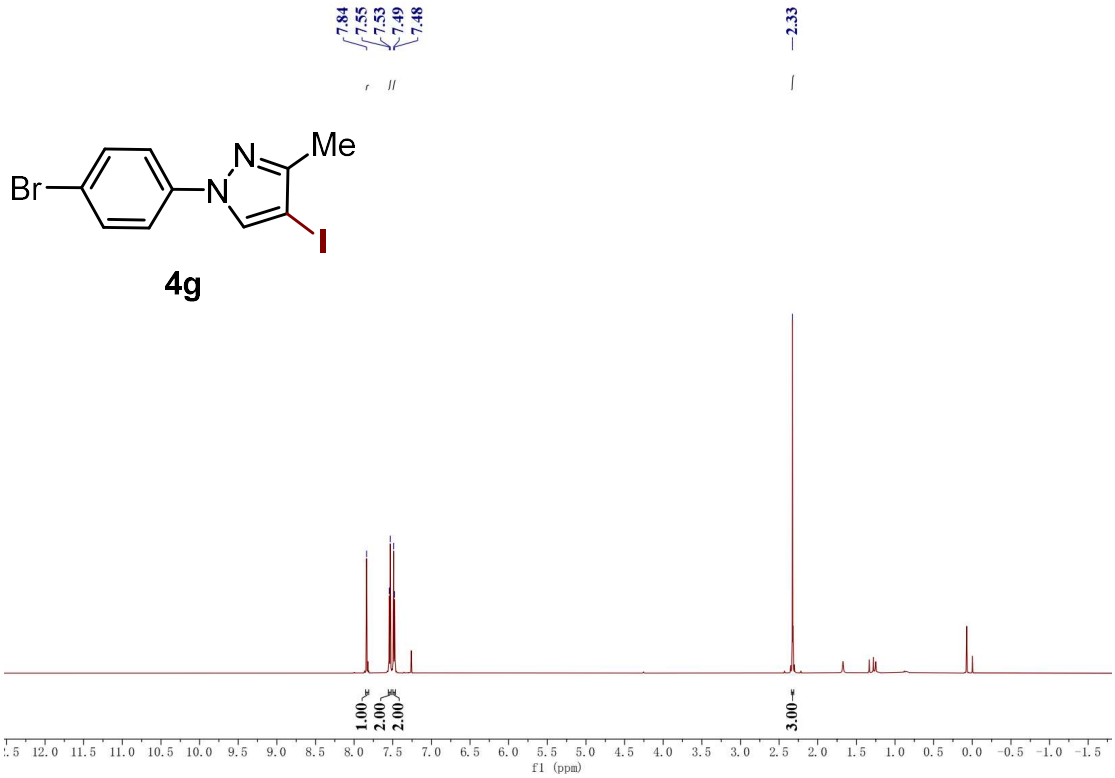
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **7**



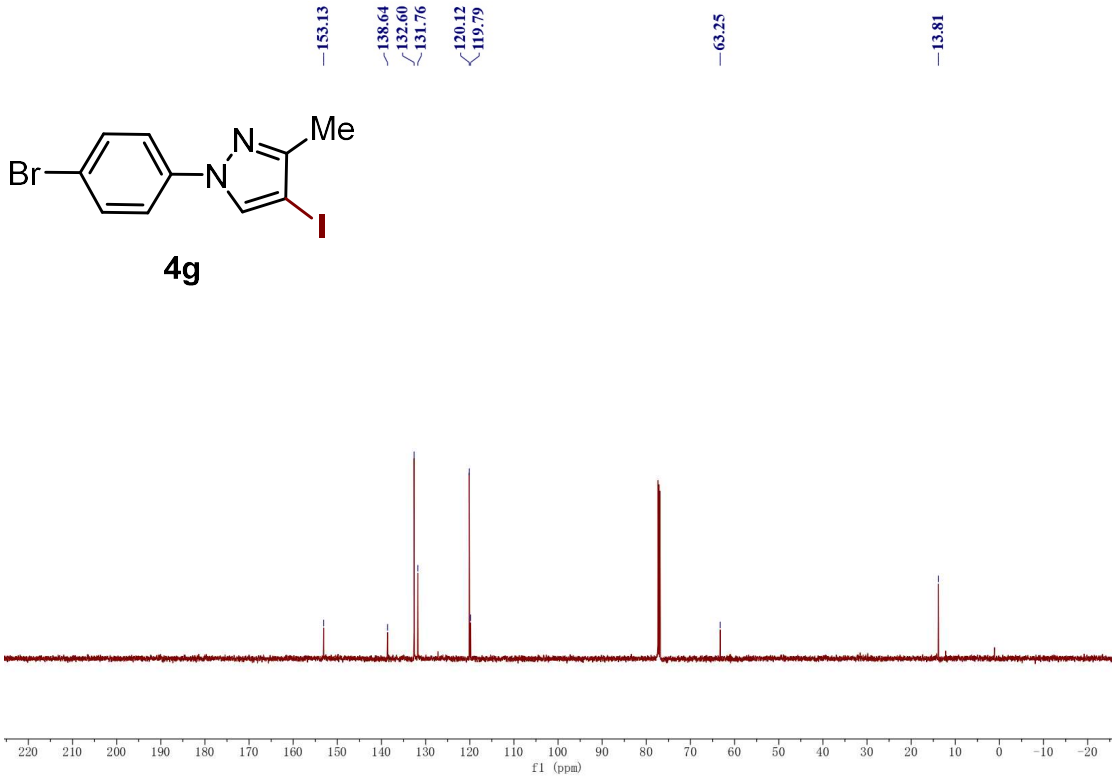
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4f**



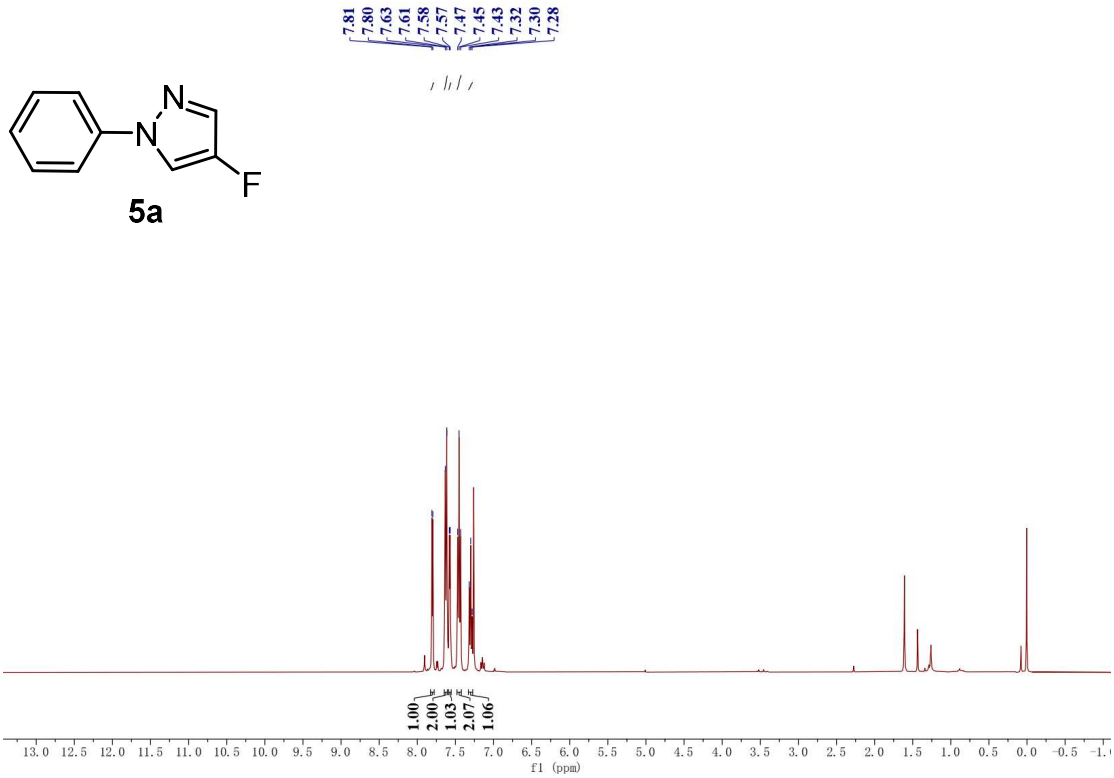
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4f**



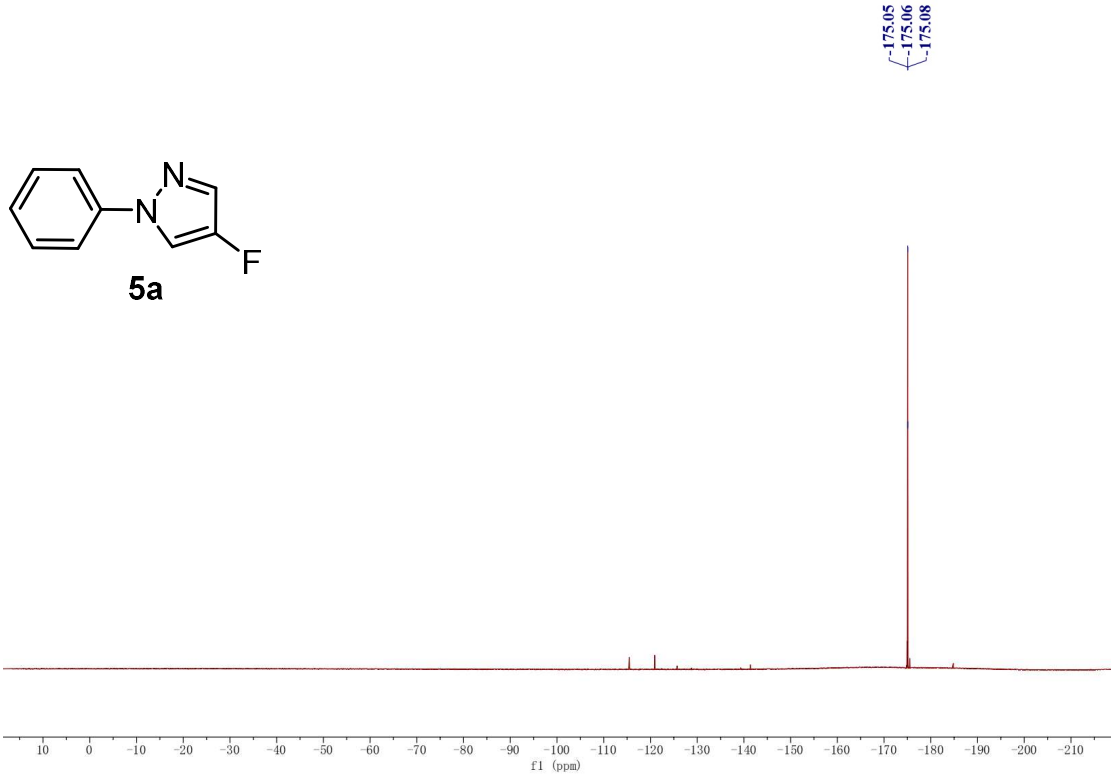
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **4g**



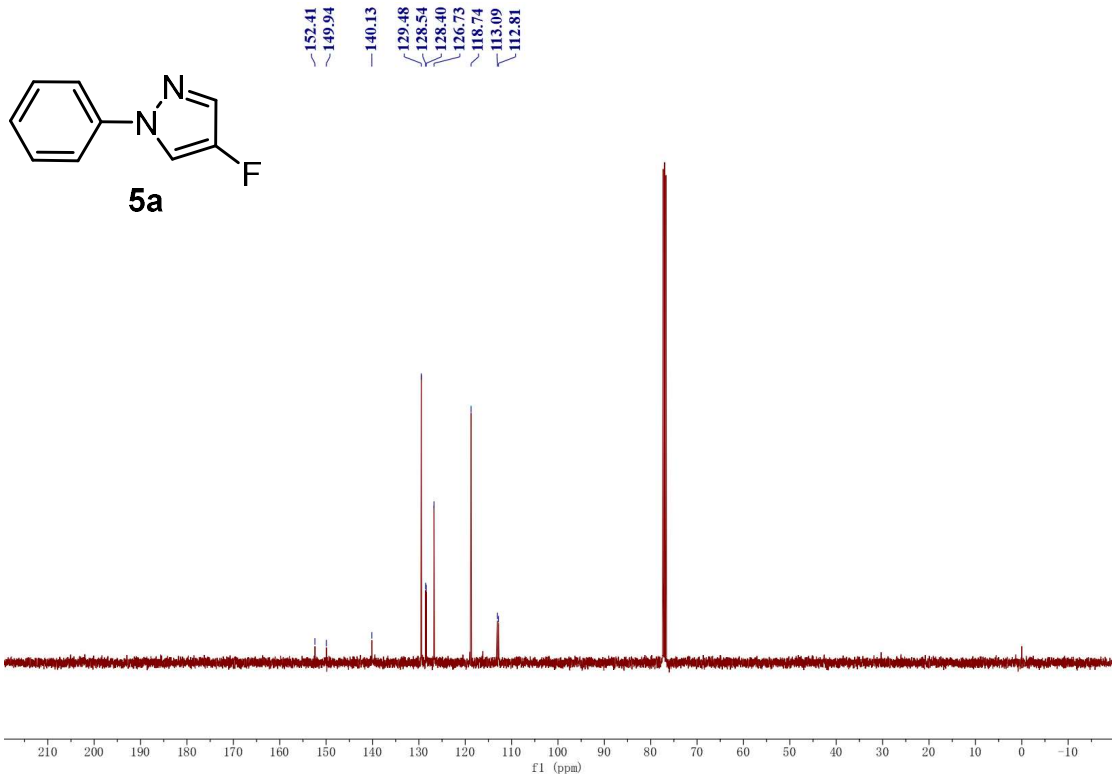
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **4g**



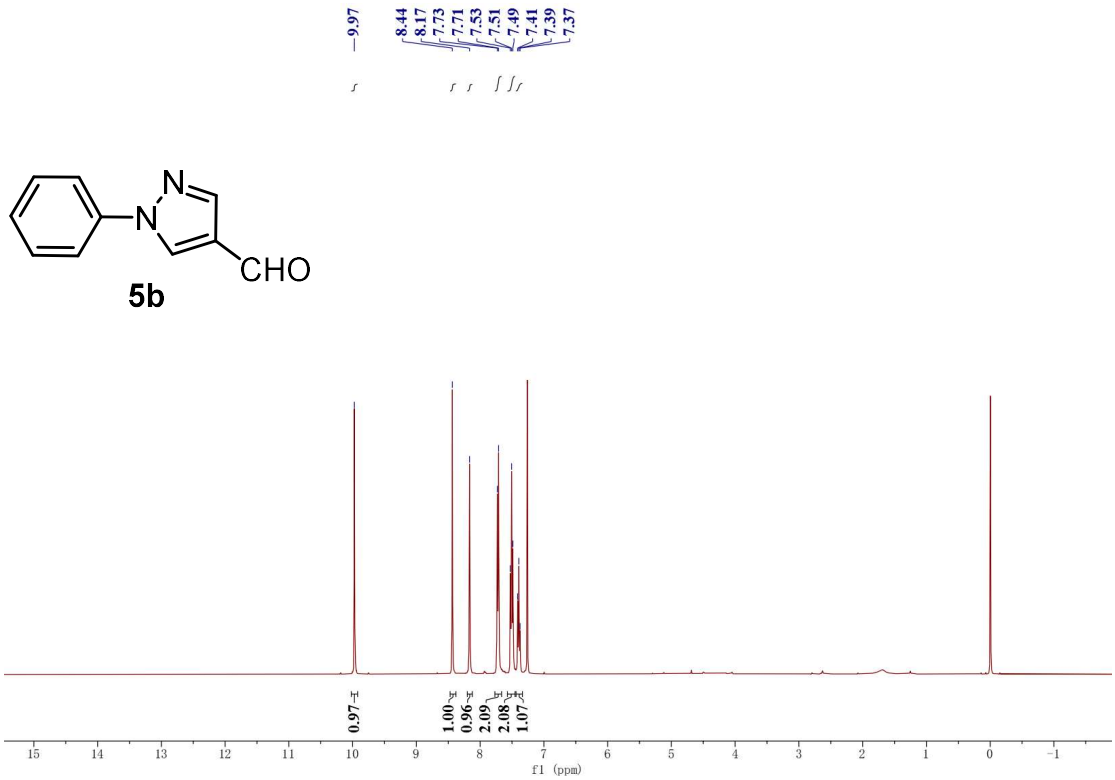
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **5a**



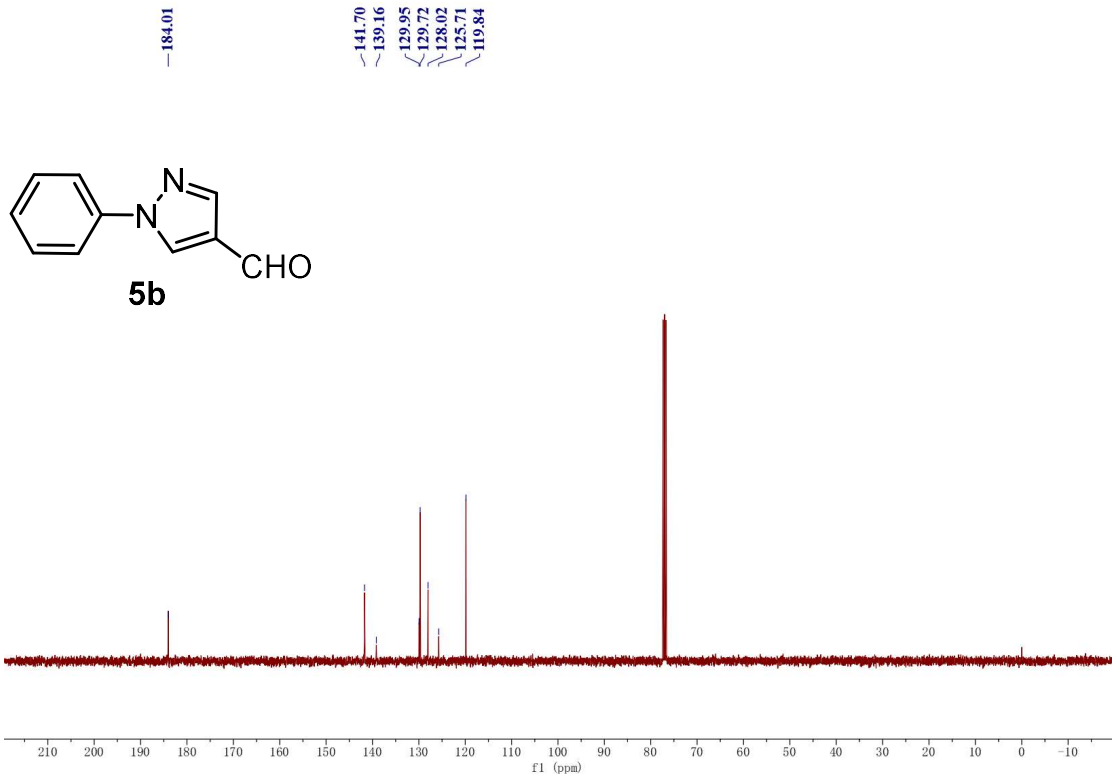
^{19}F NMR (367 MHz, Chloroform-*d*) spectrum of **5a**



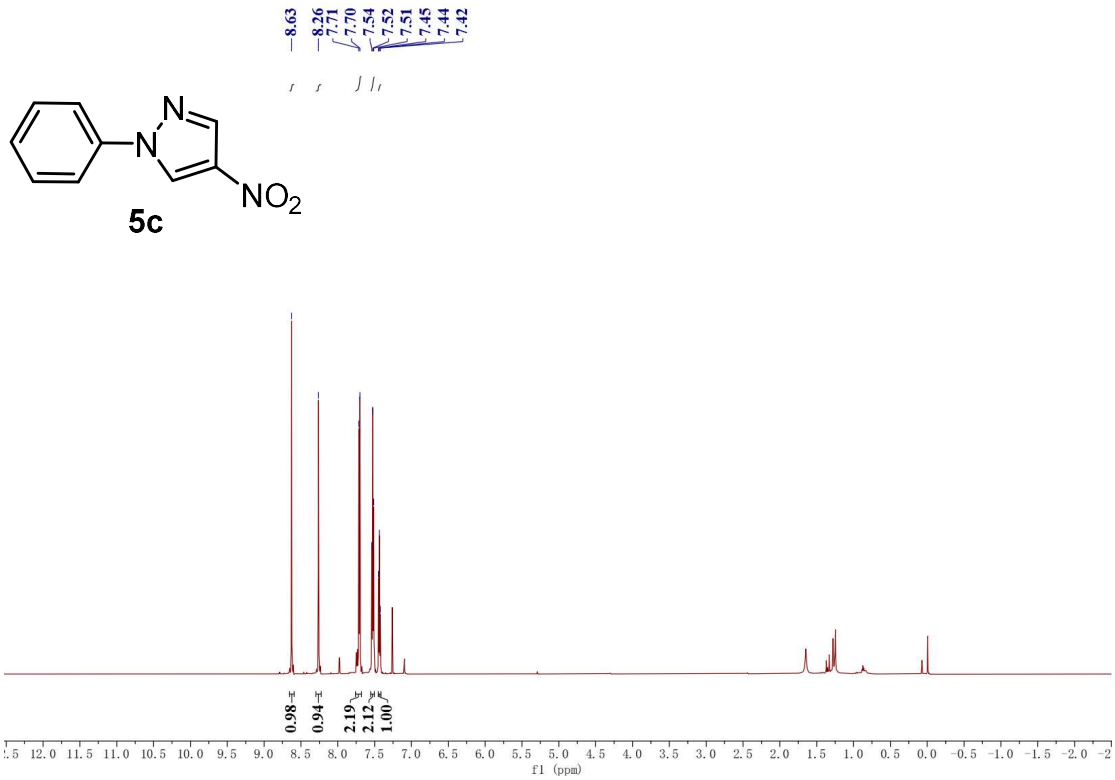
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **5a**



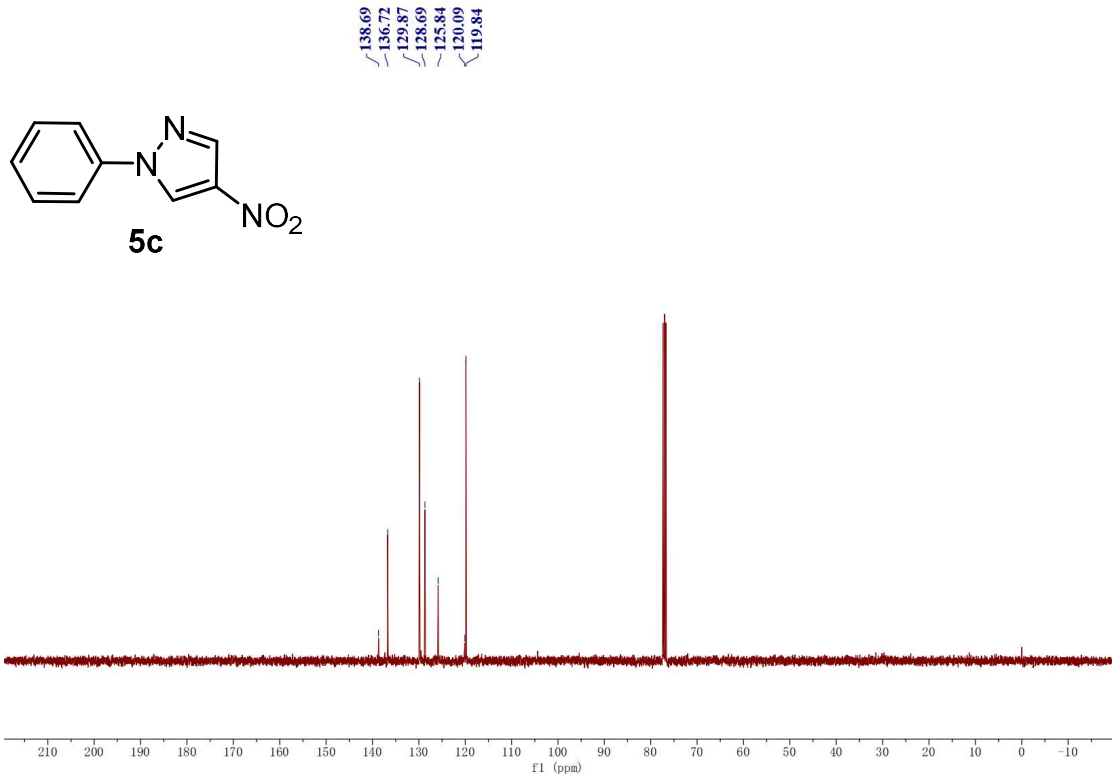
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **5b**



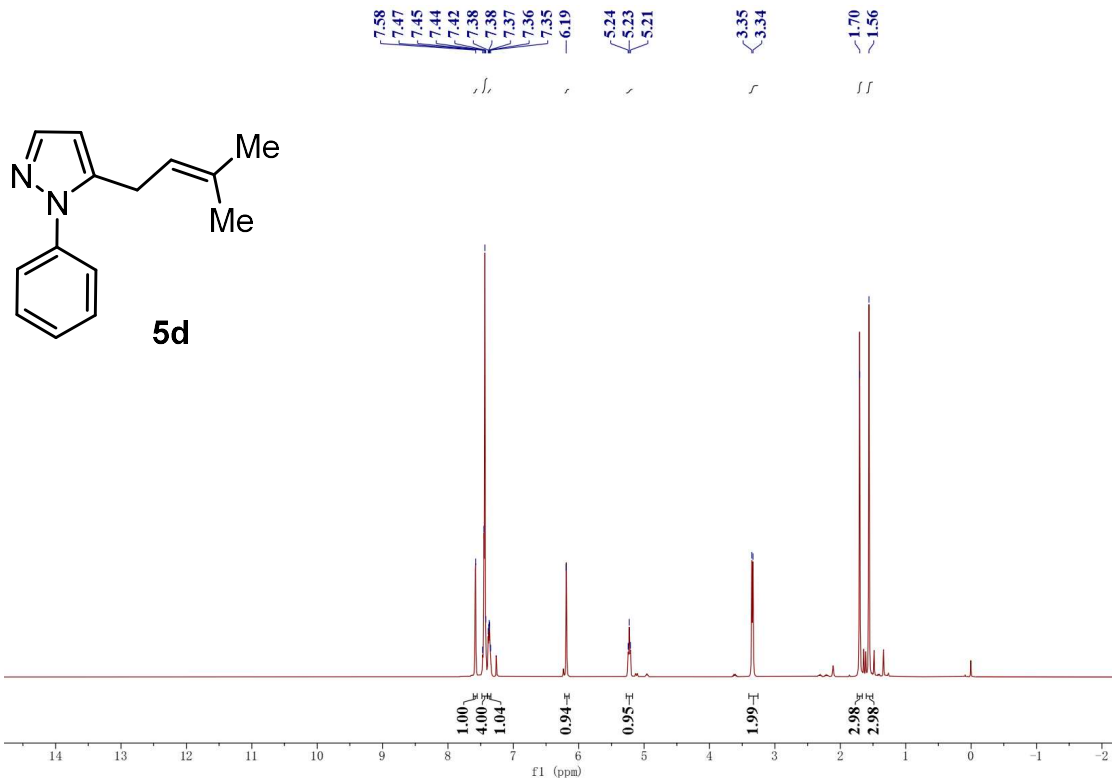
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **5b**



^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **5c**



^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **5c**



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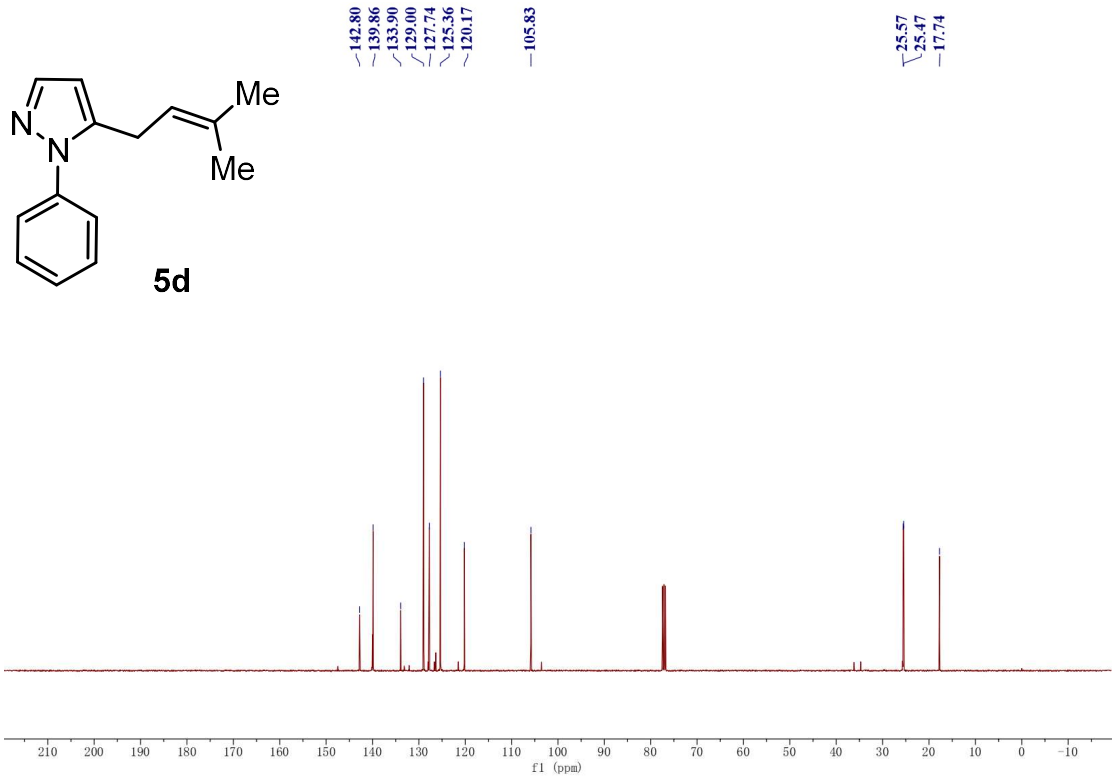
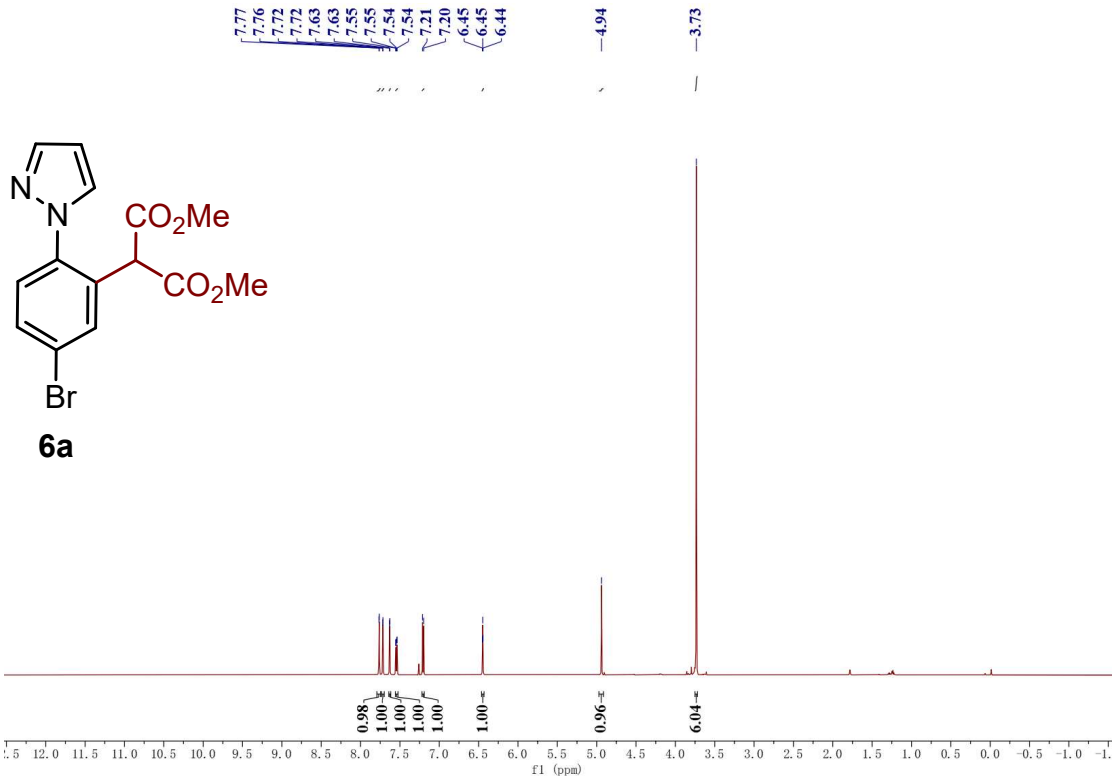
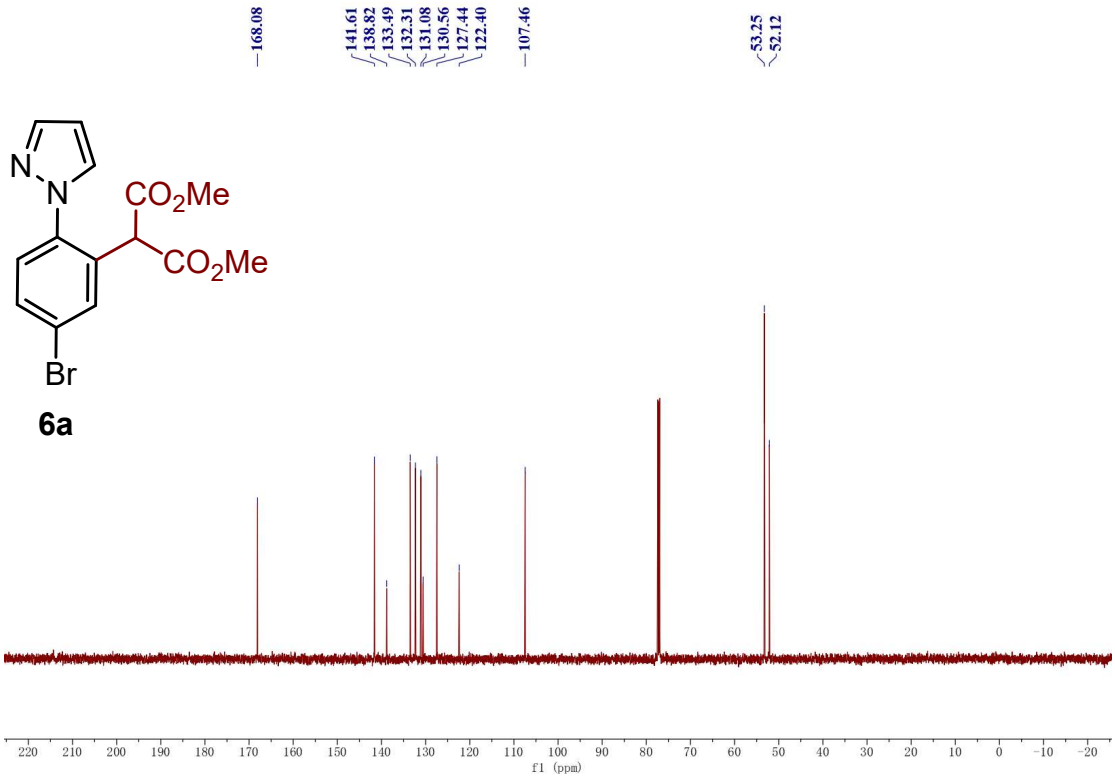


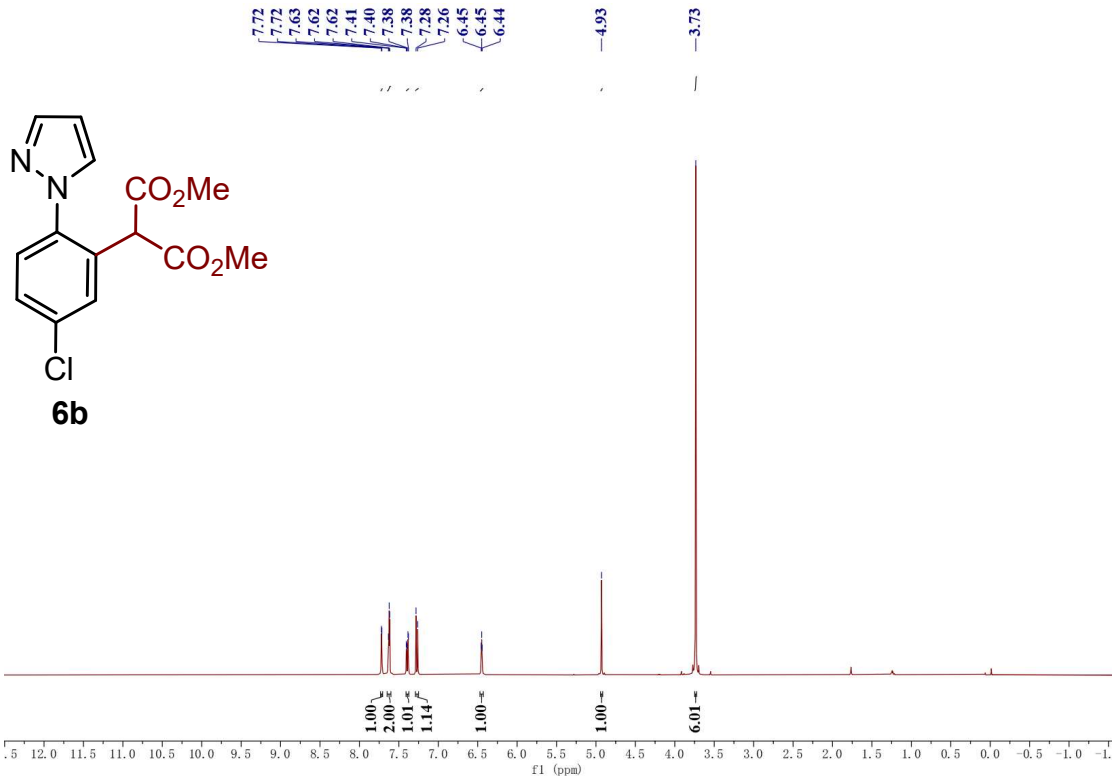
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **5d**



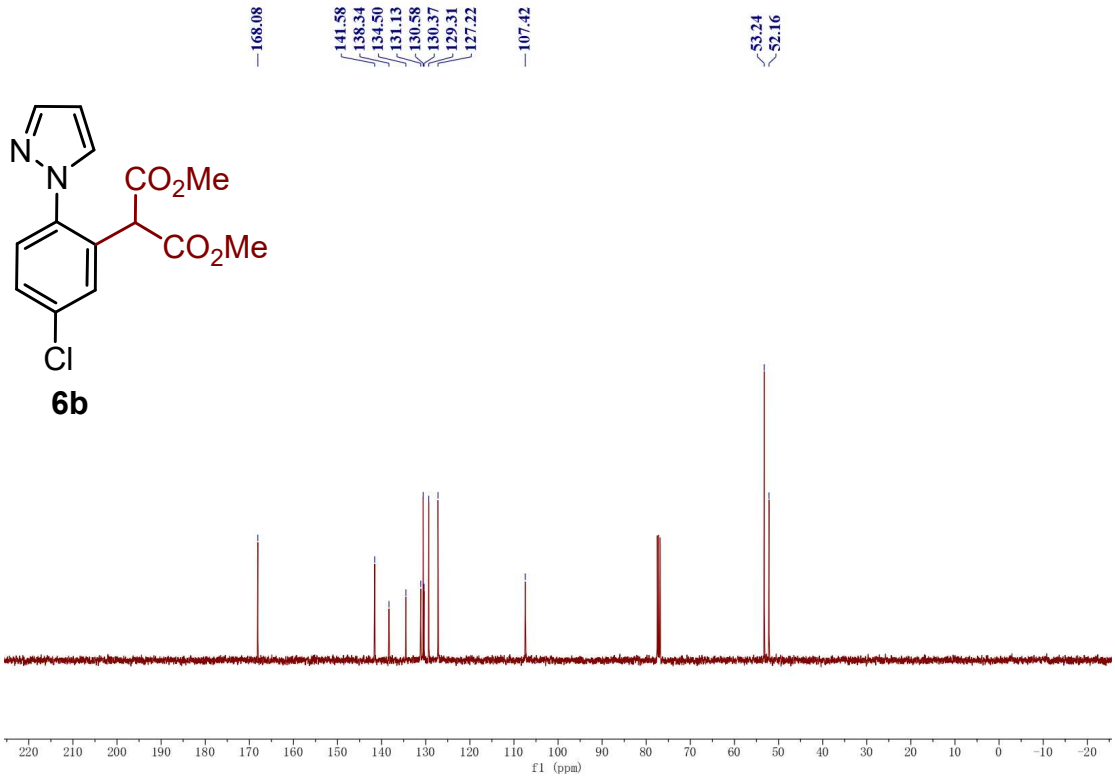
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **6a**



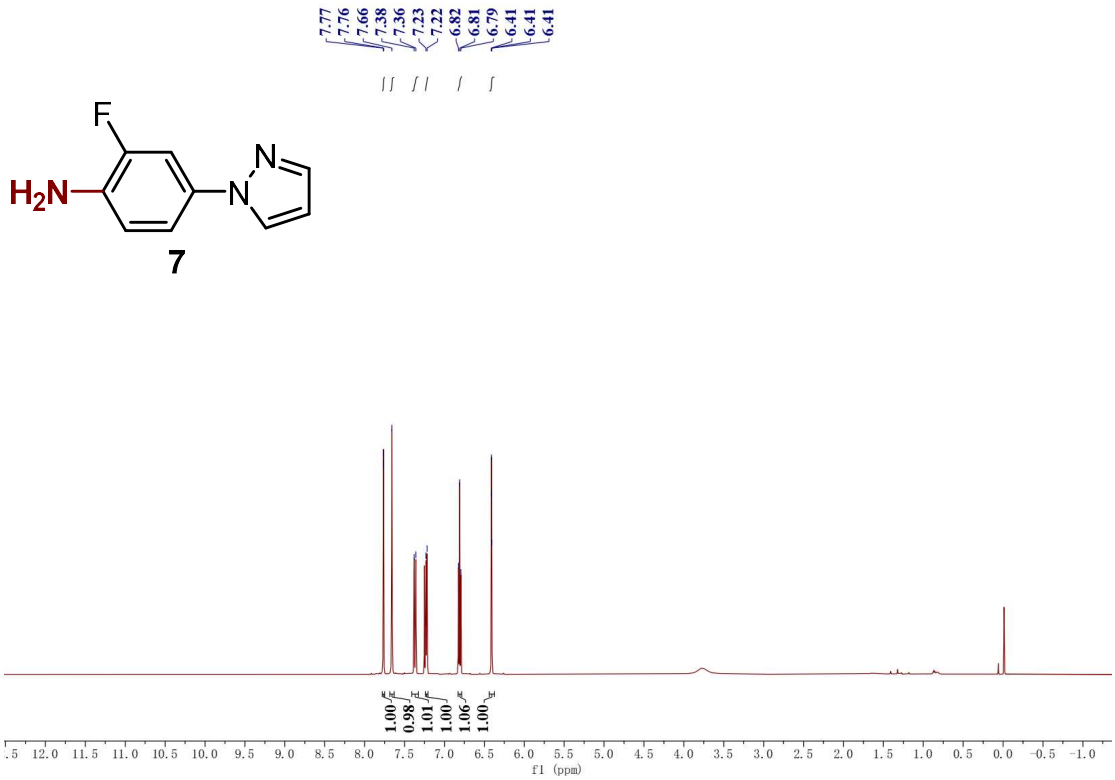
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **6a**



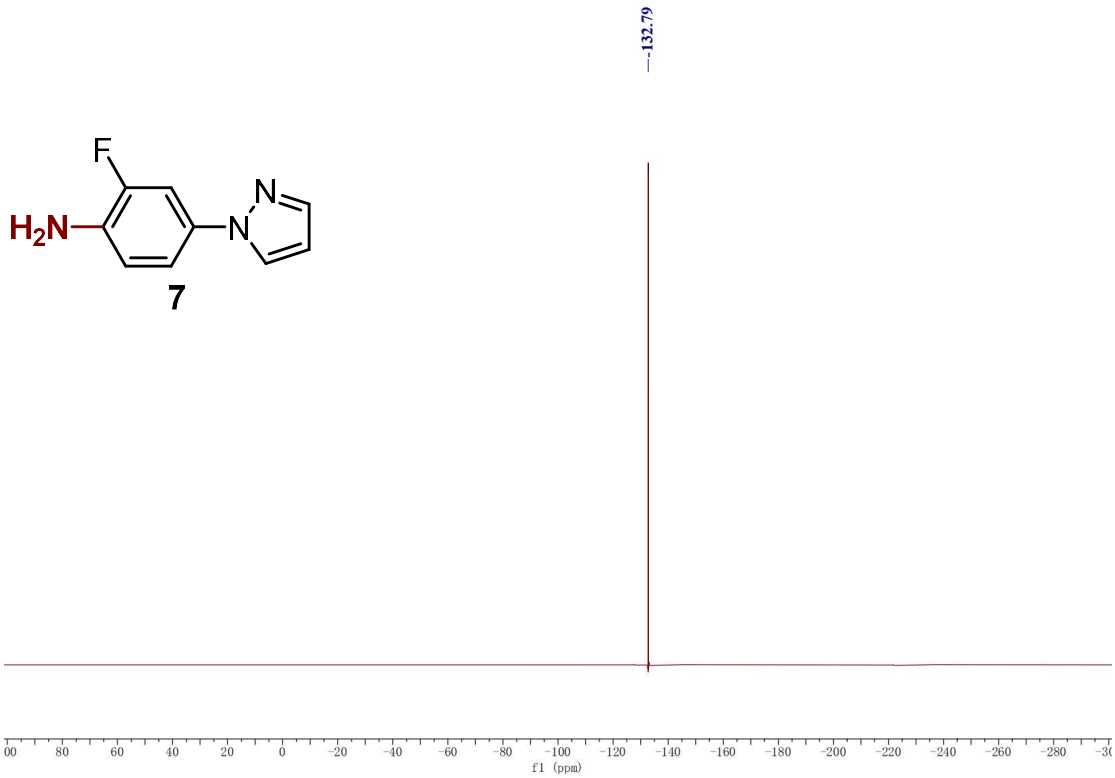
^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of **6b**



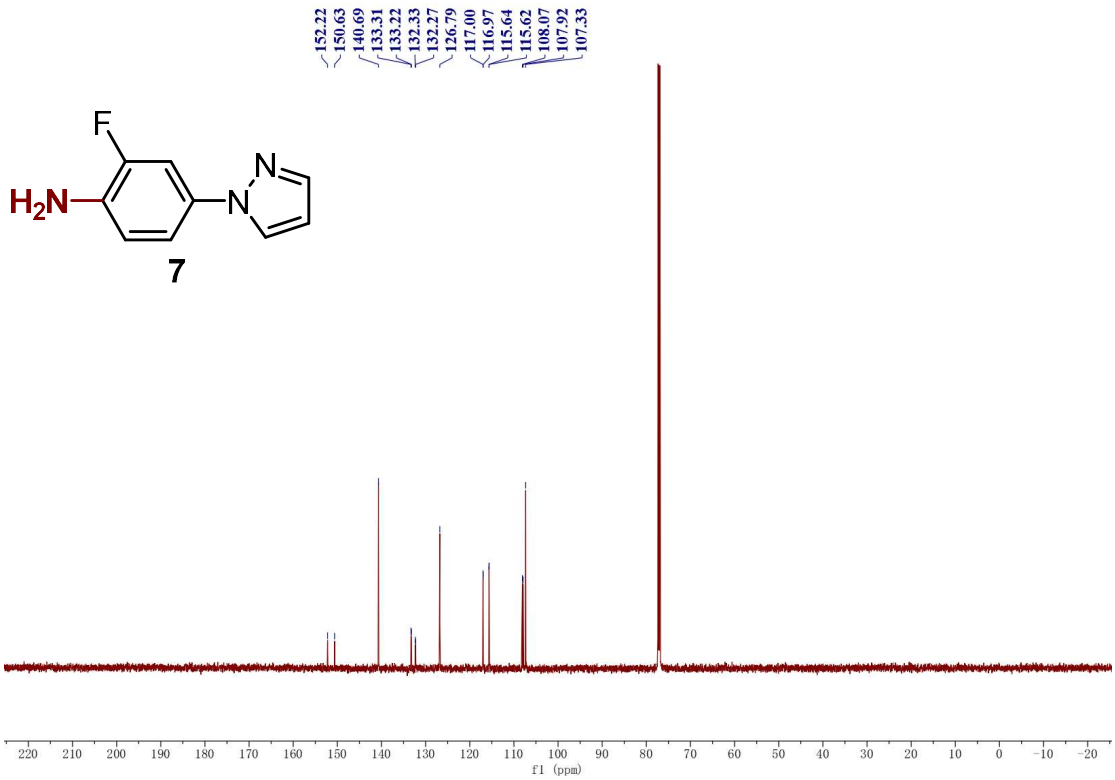
^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of **6b**



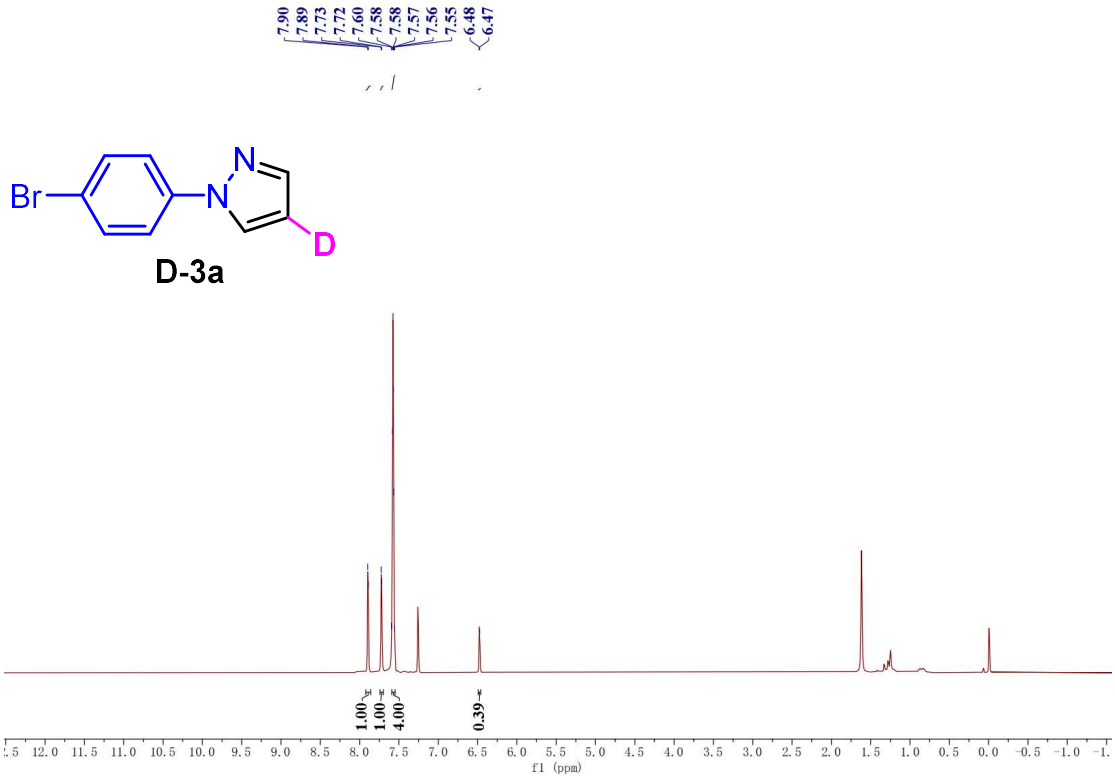
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **7**



^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **7**



^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of **7**



^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of **D-3a**

X-Ray crystallographic data

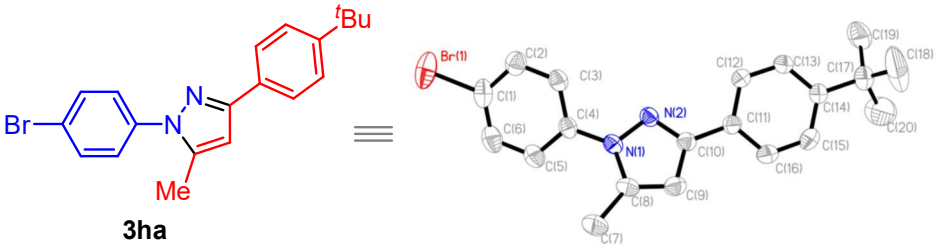
For the crystallization process, vacuum dried pure sample for **3r, 3ha** and **3la** (around 20-30 mg) was taken in a vial and dissolved in 1 mL of DCM and 5 mL hexane. The vial was kept around room temperature for slow evaporation. After 1-2 days, we could find colorless, needle shape crystal, which was picked up from the vial and performed single crystal XRD study.

The X-ray crystallographic structures for **3r, 3ha** and **3la**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, number 2090718, 2090719 and 2090720.

3r

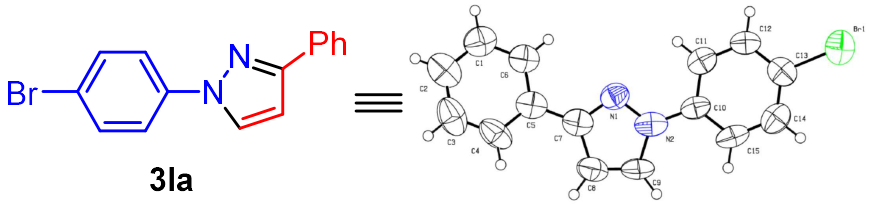
Empirical formula	$C_9H_7N_3O_2$
Formula weight	189.18
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.9272(4)
b/Å	10.2579(6)
c/Å	11.4955(6)
α/°	90
β/°	93.872(2)
γ/°	90
Volume/Å^3	814.99(8)
Z	4
ρ_{calc}g/cm^3	1.542
μ/mm^{-1}	0.114
F(000)	392.0
Crystal size/mm^3	0.29 × 0.23 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.328 to 50.04
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	15108
Independent reflections	1437 [R_{int} = 0.1380, R_{sigma} = 0.0439]
Data/restraints/parameters	1437/0/127
Goodness-of-fit on F^2	1.079

Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1245
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1281
Largest diff. peak/hole / e Å^{-3}	0.28/-0.43



3ha

Empirical formula	$C_{20}H_{21}BrN_2$
Formula weight	369.30
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.6106(9)
b/Å	7.0096(9)
c/Å	35.036(5)
α/°	90
β/°	93.871(4)
γ/°	90
Volume/Å^3	1864.8(4)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	2.206
F(000)	760.0
Crystal size/mm^3	0.32 × 0.19 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.662 to 59.174
Index ranges	-9 ≤ h ≤ 10, -9 ≤ k ≤ 9, -48 ≤ l ≤ 48
Reflections collected	40261
Independent reflections	5233 [R_{int} = 0.0836, R_{sigma} = 0.0610]
Data/restraints/parameters	5233/48/212
Goodness-of-fit on F^2	0.992
Final R indexes [I>=2σ (I)]	R_1 = 0.0616, wR_2 = 0.1484
Final R indexes [all data]	R_1 = 0.1705, wR_2 = 0.1957
Largest diff. peak/hole / e Å^{-3}	0.47/-0.40



3la

Empirical formula	$C_{15}H_{11}BrN_2$
Formula weight	299.17
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	8.3864(19)
b/Å	26.396(6)
c/Å	5.7779(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1279.0(5)
Z	4
ρ_{calc}g/cm^3	1.554
μ/mm^{-1}	3.196
F(000)	600.0
Crystal size/mm^3	0.32 × 0.26 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.096 to 50.042
Index ranges	$-9 \le h \le 9$, $-28 \le k \le 31$, $-6 \le l \le 6$
Reflections collected	17590
Independent reflections	2241 [R_{int} = 0.1607, R_{sigma} = 0.1292]
Data/restraints/parameters	2241/1/140
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1036
Final R indexes [all data]	R_1 = 0.1559, wR_2 = 0.1333
Largest diff. peak/hole / e Å^{-3}	0.34/-0.23
Flack parameter	-0.01(3)

Computational Results

All the calculations were performed using the Gaussian 16 program.[11] The geometry optimizations and frequencies were calculated in B3LYP[12] functional employing a mixed basis set of Stuttgart-Dresden effective core potential (SDD)[13] on sliver and a 6-31G(d,p) basis set on the remaining atoms. The SMD[14] solvation model was used to account for the effects of tetrahydrofuran environment. Optimized geometries were verified by frequency computations as minima (zero imaginary frequencies) or transition structures (a single imaginary frequency). More accurate electronic energies were obtained at B3LYP-D3(BJ)[15] /6-311+G(2d,p)+SDD(Ag) level of theory. Gibbs free energies were corrected using Truhlar et al.'s quasi-harmonic treatment[16] by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}, and concentration was corrected from 1 atm to 1mol/L. This was implemented using GoodVibes.[17] Non-covalent interaction analysis was performed by NCIPLOT[18] and displayed via PyMOL.[19] All energetics reported throughout the text are in kcal/mol and the bond lengths are in angstroms (Å). Structures were generated using CYLview.[20]

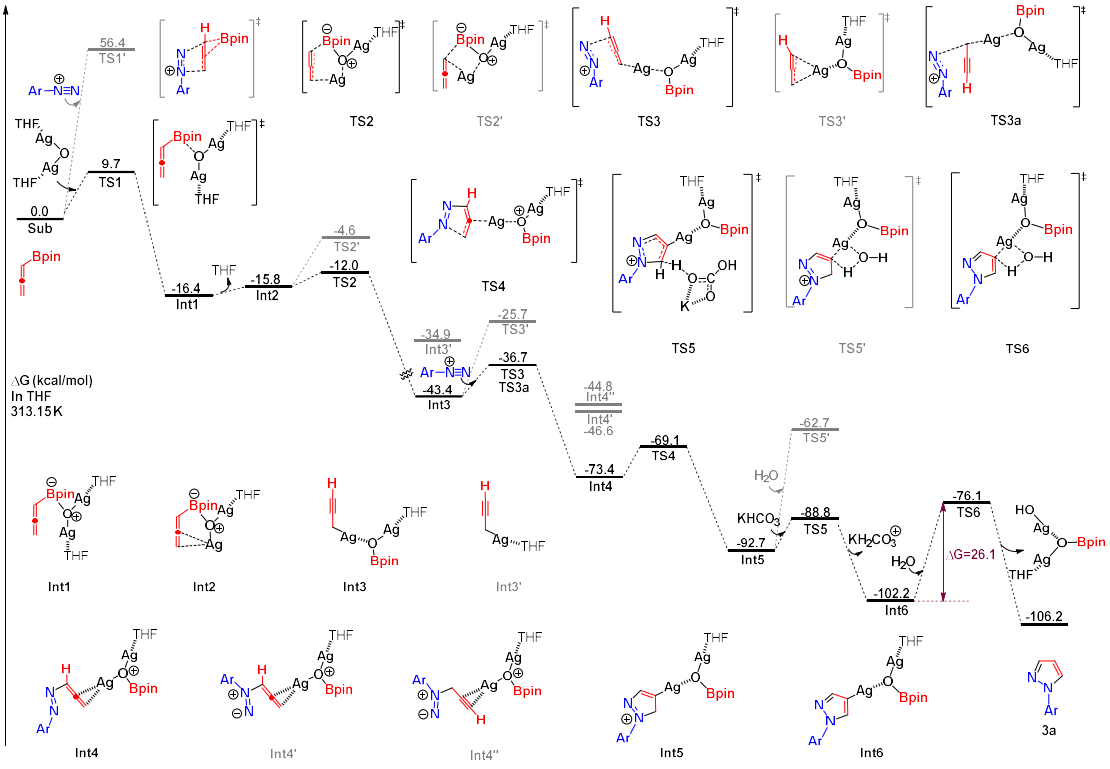


Fig. S1 Calculated free energy profiles for annulation reaction of allenylboronate **1a** and aryl diazonium salt **2a**.

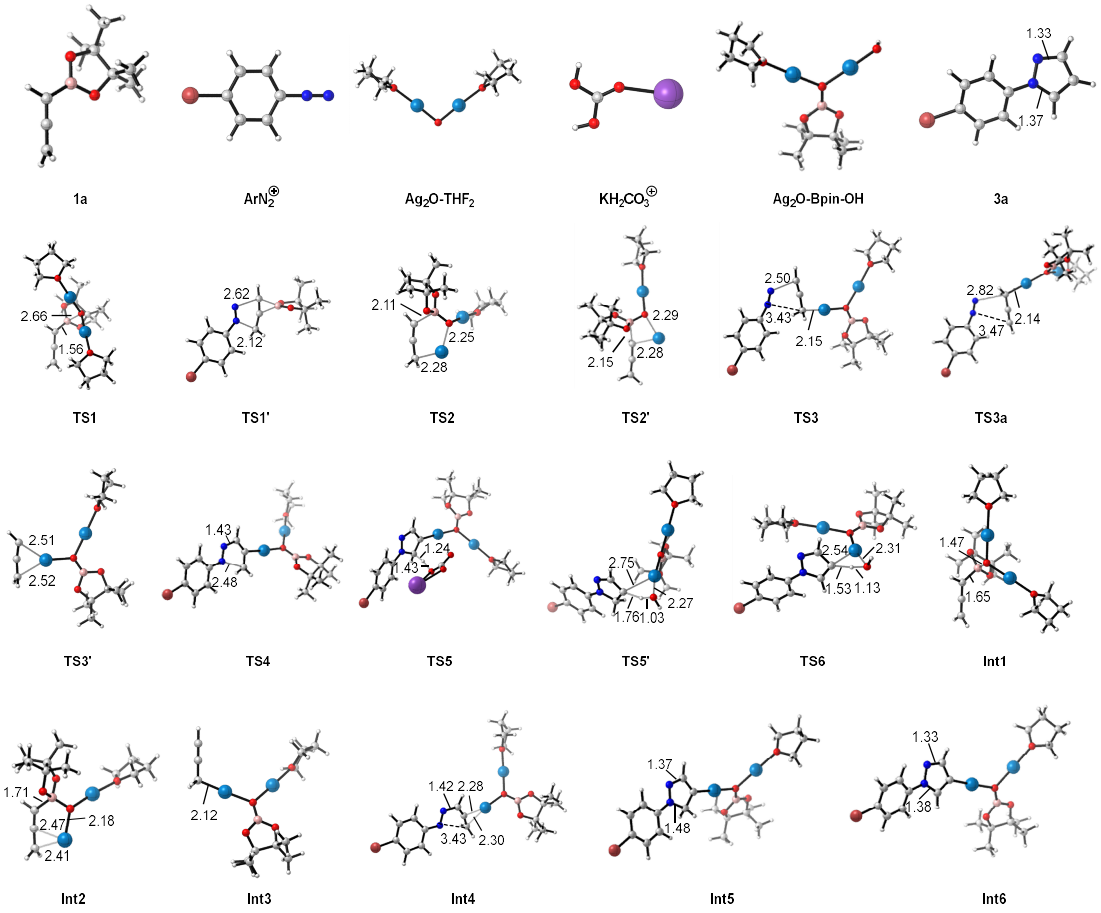


Fig. S2 Calculated structures of substrates, transition states, intermediates and products for annulation reaction of allenylboronate **1a** and aryl diazonium salt **2a**.

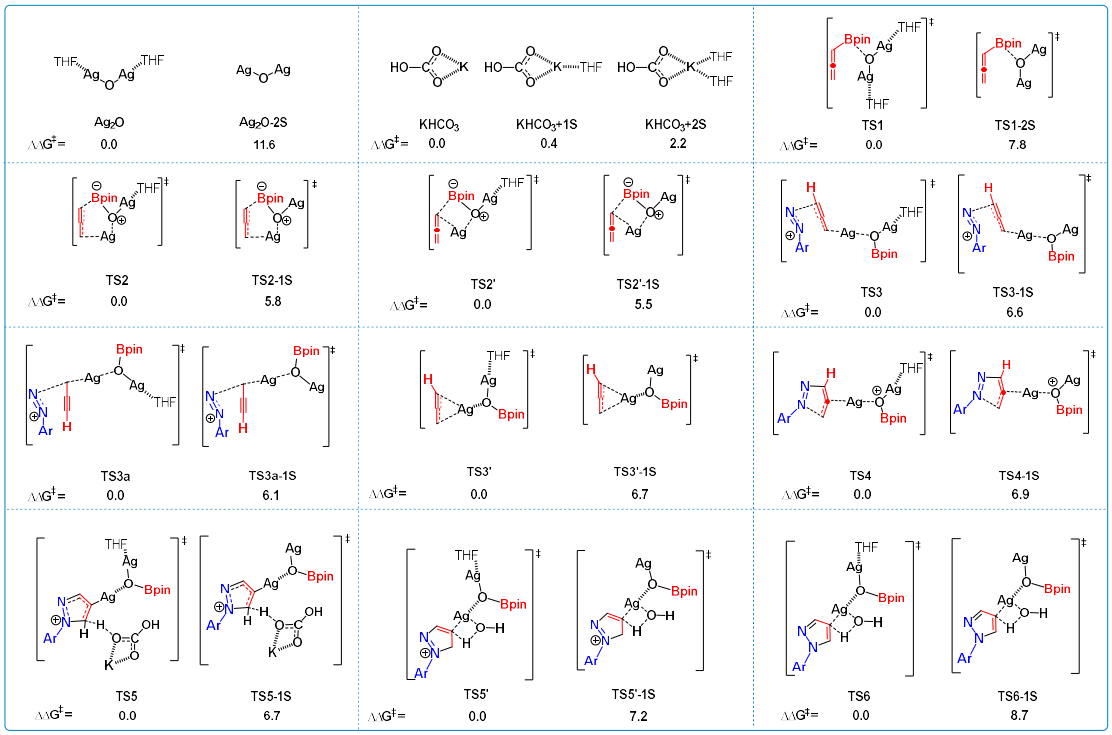


Fig. S3 Calculated free energies of transition states and substrates under different coordination

numbers of tetrahydrofuran.

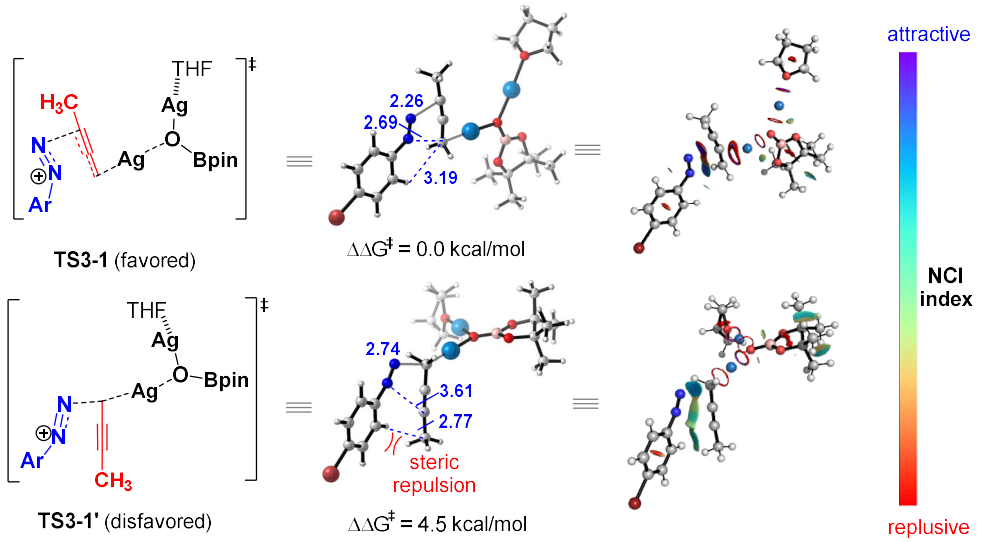


Fig. S4 Noncovalent interaction analysis (blue, strong attraction; green, weak interaction; and red, strong repulsion) for stereo-controlling transition states in annulation reaction of allenylboronate **1b** and aryl diazonium salt **2a**, together with their relative free energies (kcal/mol) and bond lengths (Å).

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B3LYP/6-31G(d,p)+SDD(Ag)-SMD Calculated Cartesian Coordinates and Single Point Energies Calculated Using the B3LYP-D3(BJ)/6-311+G(2d,p)+SDD(Ag)-SMD//B3LYP/6-31G(d,p)+SDD(Ag)-SMD

1a

C	-3.35745	-0.27598	-0.02983
C	-2.30907	-1.04266	-0.22744
H	-2.48265	-2.09177	-0.47685
C	-4.39333	0.49343	0.17041
H	-4.82798	0.61109	1.1612
H	-4.85518	1.04534	-0.64595
C	0.94821	0.87444	0.00178
C	1.43289	-0.6281	0.03043
B	-0.84406	-0.53404	-0.11918
O	-0.48951	0.7432	0.23582
O	0.22817	-1.35163	-0.37588
C	1.7891	-1.12813	1.43485
H	1.92149	-2.21367	1.40378
H	2.72024	-0.68158	1.79578
H	0.99597	-0.90512	2.15459
C	2.55264	-0.9673	-0.94854
H	3.45862	-0.39973	-0.71274
H	2.79523	-2.03193	-0.87508
H	2.26876	-0.75628	-1.98144
C	1.53453	1.76506	1.09283
H	2.62164	1.84127	0.98838
H	1.11779	2.77341	1.00785
H	1.30642	1.38844	2.09194
C	1.10964	1.54198	-1.36853
H	0.57711	2.4976	-1.36392
H	2.16099	1.73861	-1.59825
H	0.68955	0.92549	-2.16881

Zero-point correction= 0.228111 (Hartree/Particle)
Thermal correction to Energy= 0.242483
Thermal correction to Enthalpy= 0.243474
Thermal correction to Gibbs Free Energy= 0.186762
SCF Done: E(RB3LYP) = -527.573685601
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.191189

3a

C	0.89958	-1.19035	0.16455
C	-0.49282	-1.17443	0.16606
C	-1.17882	0.03282	-0.00875
C	-0.4675	1.22406	-0.19123
C	0.92602	1.21132	-0.17999
C	1.59751	0.00416	-0.0027
H	1.42958	-2.126	0.30189
H	-1.05096	-2.09219	0.30435
H	-0.98797	2.16037	-0.35939
H	1.47555	2.13475	-0.3223
N	-3.2859	-1.09942	-0.29569
N	-2.59686	0.03799	-0.00067
C	-4.56689	-0.75759	-0.1883
Br	3.51413	-0.01433	0.00658
C	-3.43559	1.07732	0.29211
C	-4.72275	0.59875	0.17824
H	-3.05932	2.04781	0.5773
H	-5.63928	1.14552	0.34384
H	-5.33516	-1.49522	-0.38135

Zero-point correction= 0.142064 (Hartree/Particle)
Thermal correction to Energy= 0.152449
Thermal correction to Enthalpy= 0.153441
Thermal correction to Gibbs Free Energy= 0.102770
SCF Done: E(RB3LYP) = -3030.97833764
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.107009

ArN_2^+

C	-0.07416	-1.22784	0.
C	-1.4573	-1.24259	0.
C	-2.12053	0.	0.
C	-1.4573	1.24259	0.
C	-0.07416	1.22784	0.
C	0.60257	0.	0.
H	0.47384	-2.16188	0.
H	-2.01514	-2.17126	0.
H	-2.01514	2.17126	0.
H	0.47384	2.16188	0.
N	-4.60395	0.	0.
N	-3.49033	0.	0.
Br	2.49222	0.	0.

Zero-point correction= 0.088921 (Hartree/Particle)
Thermal correction to Energy= 0.097293
Thermal correction to Enthalpy= 0.098285

Thermal correction to Gibbs Free Energy= 0.052615
SCF Done: E(RB3LYP) = -2914.58276067
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.056525

THF

C	-1.16723	-0.4274	0.13247
O	0.00006	-1.25523	-0.00015
C	1.16733	-0.42727	-0.13228
C	0.73261	0.99525	0.22899
C	-0.73277	0.99511	-0.22907
H	-1.95447	-0.81827	-0.52309
H	-1.53499	-0.47649	1.16898
H	1.95435	-0.81798	0.52364
H	1.53551	-0.47644	-1.16863
H	0.79268	1.14991	1.31244
H	1.34448	1.75876	-0.25945
H	-1.34475	1.75862	0.25924
H	-0.79289	1.14954	-1.31255

Zero-point correction= 0.116709 (Hartree/Particle)
Thermal correction to Energy= 0.122061
Thermal correction to Enthalpy= 0.123052
Thermal correction to Gibbs Free Energy= 0.086607
SCF Done: E(RB3LYP) = -232.546605287
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.090419

Ag_2O-2S

O	0.	0.	1.22902
Ag	0.	-1.5379	-0.1046
Ag	0.	1.5379	-0.1046

Zero-point correction= 0.002213 (Hartree/Particle)
Thermal correction to Energy= 0.006641
Thermal correction to Enthalpy= 0.007633
Thermal correction to Gibbs Free Energy= -0.029766
SCF Done: E(RB3LYP) = -369.242405988
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: -0.025931

Ag_2O

O	-0.00747	-2.08684	-0.10523
Ag	-1.5449	-0.80023	-0.03063
Ag	1.58093	-0.862	-0.05279
O	-3.2718	0.53368	0.04963
C	-4.12841	0.68292	1.21918
C	-3.87969	1.16736	-1.11729
C	-5.0957	1.79975	0.84596

H	-4.64574	-0.26732	1.39735
H	-3.48598	0.9098	2.07328
C	-5.2791	1.57965	-0.66432
H	-3.25944	2.02818	-1.39019
H	-3.87658	0.44639	-1.93853
H	-4.64279	2.77789	1.04109
H	-6.03215	1.73353	1.40553
H	-5.62917	2.47193	-1.18931
H	-5.99362	0.76989	-0.84638
O	3.36629	0.39133	-0.00426
C	3.86232	1.16516	-1.13858
C	4.09161	0.73777	1.21163
C	4.81486	2.19326	-0.53232
H	4.373	0.47382	-1.818
H	3.00415	1.60615	-1.65176
C	5.33393	1.47319	0.7227
H	3.45042	1.37729	1.82959
H	4.30129	-0.19025	1.7488
H	4.26962	3.10102	-0.25246
H	5.6105	2.47008	-1.22844
H	5.72702	2.15801	1.47833
H	6.12111	0.75877	0.45866

Zero-point correction= 0.239597 (Hartree/Particle)
Thermal correction to Energy= 0.258281
Thermal correction to Enthalpy= 0.259273
Thermal correction to Gibbs Free Energy= 0.182488
SCF Done: E(RB3LYP) = -834.393150633
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.193972

H_2O

O	-0.32762	-0.52738	-0.33746
H	0.63808	-0.47384	-0.33746
H	-0.59951	0.40081	-0.33746

Zero-point correction= 0.021180 (Hartree/Particle)
Thermal correction to Energy= 0.024159
Thermal correction to Enthalpy= 0.025150
Thermal correction to Gibbs Free Energy= 0.001744
SCF Done: E(RB3LYP) = -76.4669292954
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.004963

$KHCO_3$

C	-1.01678	0.03897	0.00087
O	-2.39989	0.08202	-0.0021
H	-2.67515	-0.84773	-0.00125

O	-0.44166	1.15393	0.00163
O	-0.48979	-1.11035	0.00171
K	1.86456	-0.02058	-0.00073

Zero-point correction= 0.027785 (Hartree/Particle)
Thermal correction to Energy= 0.033569
Thermal correction to Enthalpy= 0.034560
Thermal correction to Gibbs Free Energy= -0.004141
SCF Done: E(RB3LYP) = -864.539782720
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: -0.000437

$KH_2CO_3^+$

H	-2.14962	1.69945	-0.0171
C	-1.28246	0.02607	0.0089
O	-1.52186	-1.27804	0.00229
O	-0.15205	0.4814	0.04186
O	-2.39634	0.75694	-0.02403
K	2.36247	-0.00462	-0.00912
H	-2.48061	-1.45041	-0.02389

Zero-point correction= 0.040009 (Hartree/Particle)
Thermal correction to Energy= 0.046361
Thermal correction to Enthalpy= 0.047352
Thermal correction to Gibbs Free Energy= 0.006791
SCF Done: E(RB3LYP) = -864.975251599
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.010754

$KHCO_3$-1S

C	3.53188	0.07517	0.09652
O	4.86712	0.31561	0.386
H	4.95758	1.2795	0.33565
O	3.18956	-1.13086	0.10686
O	2.82061	1.09185	-0.14233
K	0.73286	-0.45661	-0.50639
O	-1.88747	-0.83676	-0.90153
C	-2.52229	-2.12154	-1.11491
C	-2.88373	0.21452	-0.94131
C	-4.02433	-1.87238	-0.98711
H	-2.26119	-2.48551	-2.118
H	-2.13367	-2.82952	-0.37535
C	-4.15051	-0.43095	-1.50081
H	-3.04353	0.59237	0.07771
H	-2.50242	1.03336	-1.56055
H	-4.33405	-1.93272	0.0621
H	-4.61356	-2.59176	-1.56163
H	-5.05782	0.07434	-1.15983

H	-4.13685	-0.41314	-2.59625

Zero-point correction= 0.145296 (Hartree/Particle)
Thermal correction to Energy= 0.158833
Thermal correction to Enthalpy= 0.159824
Thermal correction to Gibbs Free Energy= 0.095615
SCF Done: E(RB3LYP) = -1097.10287585
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.10715

$KHCO_3$-2S

C	2.05705	-2.0312	0.07763
O	3.34765	-2.44496	0.39647
H	3.77827	-2.57769	-0.46196
O	1.31233	-1.80197	1.05906
O	1.79667	-1.92649	-1.15349
K	-0.32976	-0.45435	-0.52912
O	-2.96276	-0.0431	-0.15917
C	-3.78176	0.95541	-0.81432
C	-3.75197	-0.75618	0.82373
C	-5.07751	1.0338	-0.00679
H	-3.22874	1.90047	-0.83984
H	-3.97263	0.6353	-1.84764
C	-5.20739	-0.40045	0.52603
H	-3.5358	-1.82568	0.73298
H	-3.4576	-0.4246	1.82901
H	-5.92733	1.34962	-0.61751
H	-4.96876	1.74056	0.82335
H	-5.61165	-1.06153	-0.24866
H	-5.84311	-0.47905	1.41178
O	1.44281	1.59792	-0.26667
C	2.59852	1.46383	-1.1338
C	1.88231	1.72112	1.10802
C	3.81992	1.37424	-0.21352
H	2.47488	0.56741	-1.74999
H	2.64315	2.34549	-1.78649
C	3.34891	2.13695	1.03333
H	1.2404	2.45581	1.6049
H	1.77368	0.74911	1.60842
H	4.71564	1.80153	-0.67268
H	4.02654	0.32874	0.03885
H	3.43306	3.21892	0.87951
H	3.90323	1.87193	1.93781

Zero-point correction= 0.263529 (Hartree/Particle)
Thermal correction to Energy= 0.284258
Thermal correction to Enthalpy= 0.285249

Thermal correction to Gibbs Free Energy= 0.203011

SCF Done: E(RB3LYP) = -1329.66610751

Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.216988

Ag_2O-Bpin-OH

Ag	-1.06304	2.59024	-0.00516
C	-3.48437	-1.51541	-0.17685
C	-2.35845	-2.55	0.22487
B	-1.46483	-0.44942	-0.00049
O	-2.83244	-0.23835	0.07406
O	-1.14198	-1.80117	-0.05707
C	-2.34262	-3.83786	-0.59356
H	-1.52196	-4.47961	-0.25663
H	-3.2769	-4.39371	-0.46279
H	-2.20187	-3.64018	-1.65838
C	-2.34842	-2.87685	1.72322
H	-3.2066	-3.49247	2.00897
H	-1.43689	-3.43429	1.96102
H	-2.35834	-1.96726	2.33176
C	-3.83412	-1.55545	-1.66956
H	-4.38739	-2.46229	-1.93182
H	-4.4619	-0.69232	-1.91126
H	-2.93629	-1.50567	-2.29343
C	-4.75708	-1.58822	0.6621
H	-5.46466	-0.82416	0.32459
H	-5.24062	-2.56453	0.55221
H	-4.55538	-1.41671	1.7216
O	-0.54071	0.53062	-0.0171
Ag	1.4958	-0.02872	-0.016
O	3.59252	-0.56669	-0.01514
C	4.45805	-0.53948	1.16481
C	4.3566	-0.92403	-1.21014
C	5.87516	-0.62598	0.60835
H	4.2497	0.38214	1.71331
H	4.20205	-1.40242	1.78922
C	5.68287	-1.45071	-0.67476
H	3.77441	-1.66035	-1.76912
H	4.48308	-0.02052	-1.81651
H	6.56132	-1.09346	1.31868
H	6.25276	0.37351	0.36811
H	5.60287	-2.51694	-0.4378
H	6.4931	-1.31565	-1.39538
O	-1.49629	4.57205	-0.03367
H	-1.72076	4.79441	0.88105

Zero-point correction= 0.316675 (Hartree/Particle)
Thermal correction to Energy= 0.342539
Thermal correction to Enthalpy= 0.343530
Thermal correction to Gibbs Free Energy= 0.252011
SCF Done: E(RB3LYP) = -1089.25231747
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.264954

Bpin-AgO

C	2.97239	1.08143	-0.23906
C	3.87796	-0.15514	0.14024
B	1.67719	-0.81811	-0.0139
O	1.64707	0.58908	0.06296
O	2.99949	-1.27174	-0.11914
C	5.14179	-0.31497	-0.70336
H	5.80633	0.54795	-0.58657
H	5.69076	-1.20578	-0.38029
H	4.90776	-0.43293	-1.76375
C	4.24008	-0.19473	1.63241
H	4.68388	-1.16808	1.86421
H	4.96328	0.58184	1.90118
H	3.35183	-0.07205	2.26004
C	3.00834	1.40938	-1.7389
H	2.21613	2.13055	-1.96495
H	3.9639	1.85007	-2.04058
H	2.83404	0.51475	-2.3448
C	3.23001	2.34784	0.57551
H	4.25361	2.70948	0.42931
H	2.54698	3.141	0.25273
H	3.06998	2.18124	1.64315
O	0.61961	-1.62122	0.01058
Ag	-1.26052	-0.79365	0.06356
O	-3.28581	-0.03139	0.10959
C	-4.21313	-0.14575	-1.01232
C	-3.74362	0.99218	1.0519
C	-5.49791	0.49498	-0.50528
H	-3.79494	0.39326	-1.87027
H	-4.30177	-1.20671	-1.25681
C	-4.96594	1.62605	0.38996
H	-3.98987	0.48535	1.99061
H	-2.9232	1.69336	1.22264
H	-6.07639	-0.22511	0.08325
H	-6.12397	0.85721	-1.32448
H	-5.69498	1.9664	1.12928
H	-4.66749	2.48498	-0.22019

Zero-point correction= 0.303449 (Hartree/Particle)
Thermal correction to Energy= 0.324167
Thermal correction to Enthalpy= 0.325158
Thermal correction to Gibbs Free Energy= 0.248440
SCF Done: E(RB3LYP) = -866.346774231
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.258187

Int1

C	-0.88554	-2.84472	3.14972
C	-0.0042	-1.91746	2.88367
C	-1.77077	-3.79131	3.38731
H	-2.81488	-3.56397	3.60112
C	0.67487	-2.34965	-0.68627
C	2.0328	-2.33685	0.12526
B	0.34892	-1.24935	1.41131
O	-0.2928	-2.00743	0.30285
O	1.80919	-1.31712	1.09969
C	3.26982	-1.97655	-0.70425
H	4.15969	-1.9851	-0.06446
H	3.43561	-2.6987	-1.51216
H	3.18425	-0.97964	-1.1443
C	2.29827	-3.66866	0.8542
H	2.55392	-4.47822	0.16163
H	3.14203	-3.53244	1.53952
H	1.43309	-3.9757	1.44617
C	0.65072	-1.29404	-1.81087
H	1.30766	-1.55829	-2.64771
H	-0.37128	-1.21618	-2.19892
H	0.9436	-0.30792	-1.4371
C	0.30801	-3.71143	-1.28883
H	-0.63988	-3.63133	-1.83376
H	1.06915	-4.05985	-1.99694
H	0.18147	-4.46992	-0.51302
O	-0.07003	0.16237	1.48251
Ag	1.51745	1.38335	0.85046
Ag	-1.96016	0.31703	0.60758
H	0.53254	-1.49819	3.74335
H	-1.49654	-4.8463	3.38835
O	-3.97749	0.5713	-0.18998
C	-4.36634	0.07515	-1.50559
C	-5.15743	0.73004	0.66338
C	-5.85054	0.39924	-1.60878
H	-3.73956	0.58122	-2.24377
H	-4.17776	-1.00404	-1.54598

C	-6.32689	0.19379	-0.16162
H	-4.98715	0.17947	1.59167
H	-5.25594	1.79737	0.88739
H	-6.36189	-0.25066	-2.32329
H	-5.99329	1.43973	-1.92003
H	-6.47877	-0.8718	0.03962
H	-7.25662	0.72211	0.06334
O	3.07688	2.81986	0.29687
C	4.17783	3.19524	1.17814
C	3.29715	3.33883	-1.0505
C	4.9024	4.31045	0.43406
H	3.74686	3.49911	2.13515
H	4.81645	2.31724	1.32947
C	4.71866	3.89617	-1.03481
H	3.15221	2.52015	-1.75985
H	2.54745	4.11594	-1.23633
H	5.95174	4.38402	0.73026
H	4.41865	5.27432	0.62584
H	5.43809	3.11523	-1.30304
H	4.83606	4.72795	-1.7338

Zero-point correction= 0.466955 (Hartree/Particle)
Thermal correction to Energy= 0.501730
Thermal correction to Enthalpy= 0.502722
Thermal correction to Gibbs Free Energy= 0.388050
SCF Done: E(RB3LYP) = -1362.01552170
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.407758

Int2

C	-2.42345	2.36783	1.77692
C	-2.32173	1.07458	1.75254
H	-2.78131	0.51658	2.57146
C	-2.46739	3.71476	1.70336
H	-1.7663	4.32617	2.27117
H	-3.3524	4.22195	1.32009
C	-2.55254	-1.81613	-0.43189
C	-1.69339	-2.20713	0.83535
B	-1.61907	0.15561	0.48896
O	-2.76283	-0.42019	-0.25168
O	-0.91225	-1.03023	1.05923
C	-0.75458	-3.40095	0.63452
H	-0.19883	-3.59709	1.55895
H	-1.31105	-4.31141	0.38328
H	-0.02795	-3.21088	-0.15958
C	-2.56798	-2.46871	2.07672

H	-3.10288	-3.42285	2.0124
H	-1.92588	-2.5014	2.96374
H	-3.30549	-1.675	2.22039
C	-1.79095	-2.05118	-1.75294
H	-1.68771	-3.11599	-1.99275
H	-2.34622	-1.57343	-2.56754
H	-0.79507	-1.60055	-1.71905
C	-3.91481	-2.51416	-0.52038
H	-4.43986	-2.18552	-1.42453
H	-3.80926	-3.60402	-0.57527
H	-4.54721	-2.2694	0.33639
O	-0.6996	0.95769	-0.29858
Ag	1.21705	0.12932	-0.17095
Ag	-1.19302	3.08352	-0.24286
O	3.28978	-0.5749	-0.15912
C	4.01763	-0.92029	1.06148
C	3.97775	-1.10318	-1.33147
C	5.13905	-1.85317	0.60819
H	4.39797	0.01155	1.4937
H	3.31532	-1.38211	1.75979
C	5.38799	-1.40703	-0.84175
H	3.45572	-2.00707	-1.66729
H	3.92544	-0.34297	-2.11463
H	4.80247	-2.89498	0.63276
H	6.02363	-1.76236	1.24328
H	5.87452	-2.17497	-1.44829
H	6.00402	-0.50171	-0.86694

Zero-point correction= 0.348727 (Hartree/Particle)
Thermal correction to Energy= 0.375790
Thermal correction to Enthalpy= 0.376782
Thermal correction to Gibbs Free Energy= 0.284754
SCF Done: E(RB3LYP) = -1129.44774087
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.297069

Int3

C	-0.89483	4.58187	2.00533
C	-0.01881	5.22256	2.5577
H	0.74709	5.78454	3.04363
C	-1.93172	3.8195	1.34995
H	-2.21455	4.28406	0.39797
H	-2.83047	3.766	1.97569
C	-3.3154	-2.29487	-0.49315
C	-2.14208	-3.32302	-0.23879
B	-1.42782	-1.1832	0.18269

O	-2.81254	-1.09035	0.14859
O	-0.9793	-2.44985	-0.18059
C	-1.93063	-4.34979	-1.34785
H	-1.08961	-5.00248	-1.0917
H	-2.81777	-4.98003	-1.4696
H	-1.70879	-3.87315	-2.30512
C	-2.24411	-4.0275	1.1199
H	-3.06437	-4.75135	1.14089
H	-1.31124	-4.56642	1.31338
H	-2.39582	-3.31	1.93225
C	-3.51449	-1.96469	-1.97781
H	-3.95098	-2.80552	-2.52535
H	-4.19549	-1.1124	-2.06474
H	-2.56945	-1.69264	-2.45811
C	-4.65102	-2.66815	0.14415
H	-5.39117	-1.89018	-0.06897
H	-5.02881	-3.61097	-0.2652
H	-4.56933	-2.76734	1.22864
O	-0.61104	-0.17053	0.52635
Ag	1.47179	-0.49304	0.55206
Ag	-1.31891	1.83031	0.94036
O	3.618	-0.77083	0.58696
C	4.40462	-0.94615	1.8072
C	4.49352	-0.62736	-0.57757
C	5.8067	-1.27973	1.31294
H	4.37676	-0.00766	2.37198
H	3.93361	-1.73868	2.39327
C	5.89596	-0.47811	0.00404
H	4.38798	-1.53121	-1.18718
H	4.15523	0.23961	-1.14984
H	5.89628	-2.35296	1.11386
H	6.57147	-0.99669	2.04027
H	6.65954	-0.85791	-0.67911
H	6.11204	0.57456	0.21464

Zero-point correction= 0.349027 (Hartree/Particle)
Thermal correction to Energy= 0.377284
Thermal correction to Enthalpy= 0.378276
Thermal correction to Gibbs Free Energy= 0.280676
SCF Done: E(RB3LYP) = -1129.49038962
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.295708

Int3'

C	3.50623	-0.58225	0.06027
C	2.81525	0.67942	-0.06493

H	3.07591	1.18009	-1.00412
C	4.08783	-1.64624	0.16586
H	4.59835	-2.57873	0.25828
Ag	0.7101	0.42101	-0.0432
H	3.07274	1.35327	0.75984
O	-1.49834	0.16349	-0.02208
C	-2.18403	-0.51217	-1.10848
C	-2.19377	-0.22432	1.19148
C	-3.67102	-0.42117	-0.74141
H	-1.91288	0.00218	-2.0321
H	-1.838	-1.55251	-1.15671
C	-3.67738	-0.22513	0.8013
H	-1.85093	-1.22137	1.49631
H	-1.92821	0.50063	1.96288
H	-4.20377	-1.32418	-1.04924
H	-4.1387	0.43169	-1.2395
H	-4.21598	-1.0214	1.32077
H	-4.14528	0.72626	1.06629

Zero-point correction= 0.163068 (Hartree/Particle)
Thermal correction to Energy= 0.174819
Thermal correction to Enthalpy= 0.175811
Thermal correction to Gibbs Free Energy= 0.120184
SCF Done: E(RB3LYP) = -495.675649728
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.126849

Int4

C	7.5338	-2.38818	0.96421
C	6.1918	-2.03645	0.92668
C	5.80158	-0.82063	0.33521
C	6.76879	0.03036	-0.21865
C	8.11728	-0.31531	-0.18409
C	8.48437	-1.52268	0.40889
H	7.8419	-3.32385	1.41715
H	5.44062	-2.69365	1.34978
H	6.44915	0.96284	-0.67287
H	8.86492	0.34315	-0.61095
N	3.60517	-1.09593	0.78867
N	4.46885	-0.36227	0.23936
C	2.25971	-0.66621	0.62944
Br	10.3295	-2.01291	0.46474
C	1.7605	0.82261	-1.49139
C	1.85675	0.10877	-0.36446
H	1.57522	-1.08367	1.35945
H	1.66907	0.33239	-2.46166

H	1.91425	1.902	-1.48654
C	-3.17777	4.21124	-0.14627
C	-4.50612	3.56191	0.41654
B	-3.00057	1.92726	-0.13563
O	-2.24538	3.08738	-0.10395
O	-4.35489	2.16299	0.02281
C	-5.79529	4.10465	-0.19155
H	-6.65542	3.58701	0.24487
H	-5.90416	5.1728	0.02219
H	-5.82651	3.96137	-1.27372
C	-4.5902	3.5877	1.94668
H	-4.76134	4.60033	2.32327
H	-5.42729	2.96046	2.26851
H	-3.67685	3.1981	2.40707
C	-3.29149	4.64117	-1.61296
H	-3.93401	5.51911	-1.72631
H	-2.29615	4.89896	-1.98777
H	-3.69255	3.83693	-2.23769
C	-2.6097	5.34929	0.69532
H	-1.6879	5.72227	0.23758
H	-3.3177	6.18258	0.74795
H	-2.37638	5.02613	1.71202
O	-2.46432	0.69612	-0.30713
Ag	-3.83695	-0.93017	-0.26761
Ag	-0.35283	0.62965	-0.59844
O	-5.18614	-2.62696	-0.239
C	-5.52631	-3.36708	0.97633
C	-6.12659	-2.94918	-1.31786
C	-6.43629	-4.48778	0.4931
H	-4.5902	-3.70602	1.42597
H	-6.03939	-2.68655	1.66511
C	-7.19738	-3.81704	-0.66205
H	-6.50843	-2.01152	-1.72841
H	-5.56673	-3.4858	-2.09065
H	-7.0961	-4.84616	1.28694
H	-5.8419	-5.33141	0.1267
H	-8.00865	-3.19362	-0.27213
H	-7.62239	-4.53469	-1.36778

Zero-point correction= 0.442713 (Hartree/Particle)
Thermal correction to Energy= 0.479691
Thermal correction to Enthalpy= 0.480683
Thermal correction to Gibbs Free Energy= 0.360624
SCF Done: E(RB3LYP) = -4044.14904009
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.380324

Int4'

N	3.785	-0.94517	0.81835
N	4.58728	-0.15081	0.3724
C	2.28137	-0.75367	0.71912
C	1.74527	0.61766	-1.44247
C	1.8158	-0.09664	-0.30994
H	1.70327	-1.14319	1.54708
H	1.63463	0.13171	-2.41134
H	1.91529	1.69412	-1.43053
C	-3.11995	4.0617	-0.1448
C	-4.46652	3.44935	0.41598
B	-2.99034	1.7752	-0.09923
O	-2.21178	2.91903	-0.07581
O	-4.34094	2.04134	0.04473
C	-5.73865	4.00888	-0.21198
H	-6.61325	3.51654	0.22502
H	-5.82666	5.08239	-0.01627
H	-5.76347	3.84901	-1.29198
C	-4.56257	3.50001	1.9446
H	-4.71585	4.5216	2.30432
H	-5.41526	2.89526	2.26856
H	-3.66122	3.09868	2.41843
C	-3.21132	4.47019	-1.61917
H	-3.83266	5.36051	-1.75217
H	-2.20724	4.69921	-1.98929
H	-3.62558	3.66545	-2.23458
C	-2.53493	5.20065	0.68369
H	-1.60147	5.54638	0.22819
H	-3.22538	6.04956	0.71653
H	-2.31729	4.889	1.70742
O	-2.48477	0.52809	-0.25044
Ag	-3.96252	-1.00933	-0.24011
Ag	-0.37392	0.41276	-0.53463
O	-5.43894	-2.59271	-0.21262
C	-5.93746	-3.19288	1.02549
C	-6.34773	-2.88679	-1.32701
C	-6.93545	-4.24345	0.5594
H	-5.07555	-3.59337	1.56411
H	-6.41382	-2.40923	1.62549
C	-7.54614	-3.58344	-0.68756
H	-6.59692	-1.94539	-1.82223
H	-5.80836	-3.53547	-2.02461
H	-7.67744	-4.46862	1.32921

H	-6.41713	-5.17058	0.29267
H	-8.3044	-2.84921	-0.39644
H	-8.00601	-4.30195	-1.37008
C	4.17248	-2.17776	1.53679
C	3.37379	-3.3188	1.4917
C	5.39027	-2.1714	2.21574
C	3.80035	-4.4782	2.14245
H	2.43973	-3.32966	0.94023
C	5.81292	-3.32105	2.8756
H	5.99382	-1.27041	2.21777
C	5.01144	-4.46423	2.83131
H	3.19402	-5.37584	2.10513
H	6.75218	-3.32421	3.41664
Br	5.59128	-6.0462	3.73501

Zero-point correction= 0.442313 (Hartree/Particle)
Thermal correction to Energy= 0.479239
Thermal correction to Enthalpy= 0.480231
Thermal correction to Gibbs Free Energy= 0.359811
SCF Done: E(RB3LYP) = -4044.10619635
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.380124

Int4''

N	3.52014	-0.53025	-2.2157
N	4.12077	-1.19118	-1.40412
C	1.36703	-1.23876	0.28174
C	1.98718	-0.17563	-2.07795
C	1.50645	-0.69828	-0.81048
H	1.37593	-1.74404	1.22809
H	1.46192	-0.63367	-2.9188
H	1.89081	0.91114	-2.13379
C	-2.74214	3.79694	0.11769
C	-4.20738	3.41173	0.5731
B	-3.02574	1.5246	0.03597
O	-2.05807	2.50746	0.16151
O	-4.31278	2.02481	0.12801
C	-5.32006	4.22183	-0.08435
H	-6.29284	3.87474	0.27847
H	-5.22805	5.28298	0.16861
H	-5.30814	4.12089	-1.1716
C	-4.38489	3.40758	2.09568
H	-4.3759	4.42229	2.50425
H	-5.34906	2.95171	2.34124
H	-3.59915	2.82933	2.59162
C	-2.6706	4.29127	-1.33153

H	-3.11272	5.2859	-1.44009
H	-1.62121	4.35254	-1.63638
H	-3.18458	3.60874	-2.01554
C	-2.01438	4.76711	1.04255
H	-1.00829	4.96056	0.65698
H	-2.54302	5.72443	1.09316
H	-1.91845	4.36845	2.05465
O	-2.73726	0.21666	-0.15908
Ag	-4.36423	-1.15289	-0.20144
Ag	-0.67863	-0.32758	-0.22823
O	-5.95349	-2.6199	-0.25157
C	-6.53471	-3.2188	0.95062
C	-6.81497	-2.86157	-1.41434
C	-7.55703	-4.21392	0.41944
H	-5.71779	-3.66912	1.51937
H	-7.00129	-2.42415	1.54374
C	-8.07443	-3.50942	-0.84531
H	-6.99571	-1.9046	-1.90952
H	-6.27047	-3.52706	-2.09197
H	-8.34591	-4.4139	1.14849
H	-7.07056	-5.16108	0.16336
H	-8.81126	-2.7441	-0.58028
H	-8.53265	-4.19666	-1.56038
C	4.14293	0.04286	-3.43407
C	3.39371	0.61292	-4.46412
C	5.53507	-0.02267	-3.5171
C	4.04603	1.12009	-5.59001
H	2.31349	0.66953	-4.42777
C	6.18867	0.4864	-4.63374
H	6.088	-0.47571	-2.70222
C	5.43486	1.05399	-5.6632
H	3.4688	1.55917	-6.39536
H	7.26985	0.44126	-4.69843
Br	6.32631	1.75449	-7.20196

Zero-point correction= 0.442263 (Hartree/Particle)
Thermal correction to Energy= 0.479507
Thermal correction to Enthalpy= 0.480499
Thermal correction to Gibbs Free Energy= 0.360061
SCF Done: E(RB3LYP) = -4044.10280901
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.379695

Int5

C	-7.6019	-1.17482	0.56321
C	-6.26593	-1.37885	0.88574

C	-5.27507	-0.64083	0.22282
C	-5.61768	0.29841	-0.75762
C	-6.95715	0.50075	-1.07783
C	-7.9383	-0.23691	-0.41602
H	-8.37157	-1.74232	1.07333
H	-5.99143	-2.10113	1.64463
H	-4.8573	0.87216	-1.27487
H	-7.22545	1.22658	-1.83651
N	-3.53023	-1.7129	1.41294
N	-3.91046	-0.84071	0.54579
C	-2.16281	-1.66489	1.51364
Br	-9.77402	0.03907	-0.85546
C	-2.75103	-0.11846	-0.01621
C	-1.58614	-0.72131	0.6825
H	-1.69157	-2.3451	2.20984
H	-2.85812	0.95619	0.17601
H	-2.71766	-0.26552	-1.10272
C	2.62251	3.92028	0.285
C	4.05391	3.50992	-0.24827
B	2.77444	1.64094	0.10731
O	1.86444	2.68627	0.11269
O	4.08791	2.08022	0.03714
C	5.22465	4.17923	0.46522
H	6.16828	3.82025	0.04189
H	5.19068	5.26542	0.33229
H	5.2283	3.9596	1.53494
C	4.20096	3.66757	-1.76628
H	4.24168	4.72051	-2.06033
H	5.13258	3.19021	-2.08588
H	3.37399	3.19119	-2.30198
C	2.60879	4.2492	1.78241
H	3.11204	5.19769	1.99192
H	1.57114	4.33391	2.11987
H	3.0937	3.46378	2.37039
C	1.93412	5.03038	-0.50319
H	0.94852	5.23186	-0.07135
H	2.51502	5.95726	-0.45749
H	1.79536	4.75833	-1.55169
O	2.42438	0.33737	0.16362
Ag	3.99733	-1.08402	0.0278
Ag	0.38028	-0.18829	0.42314
O	5.53207	-2.60002	-0.16122
C	5.99864	-3.10908	-1.45054
C	6.47625	-2.95597	0.90367

C	7.01196	-4.18437	-1.08502
H	5.12414	-3.47588	-1.99269
H	6.45599	-2.28275	-2.00667
C	7.65624	-3.60766	0.18617
H	6.73932	-2.04447	1.44566
H	5.96071	-3.64649	1.57867
H	7.73269	-4.35399	-1.8886
H	6.5033	-5.12953	-0.86733
H	8.40666	-2.85478	-0.07628
H	8.13454	-4.36938	0.8064

Zero-point correction= 0.446715 (Hartree/Particle)
Thermal correction to Energy= 0.482128
Thermal correction to Enthalpy= 0.483120
Thermal correction to Gibbs Free Energy= 0.368057
SCF Done: E(RB3LYP) = -4044.18528982
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.385804

Int6

C	7.0545	-0.69145	-0.26247
C	5.70032	-0.99176	-0.38657
C	4.74727	0.03644	-0.40121
C	5.16586	1.37017	-0.2955
C	6.52005	1.67152	-0.15959
C	7.4549	0.6387	-0.14458
H	7.78556	-1.49226	-0.25094
H	5.37395	-2.02091	-0.47201
H	4.44688	2.18084	-0.33495
H	6.83561	2.70571	-0.07894
N	2.99492	-1.49769	-1.00137
N	3.37619	-0.28007	-0.52417
C	1.66412	-1.45891	-0.97718
Br	9.31864	1.05276	0.0356
C	2.28141	0.49101	-0.2065
C	1.12683	-0.22814	-0.48303
H	2.41197	1.47871	0.2113
C	-3.28215	4.4482	-0.01902
C	-4.69719	3.94929	0.4786
B	-3.31599	2.15905	0.08699
O	-2.46473	3.25368	0.13127
O	-4.65499	2.53281	0.14517
C	-5.89158	4.58459	-0.22752
H	-6.8216	4.16491	0.16971
H	-5.91384	5.66617	-0.05804
H	-5.87107	4.40173	-1.30402

C	-4.86958	4.04856	1.99937
H	-4.96702	5.08735	2.32896
H	-5.7788	3.51353	2.29129
H	-4.02516	3.59625	2.52857
C	-3.26445	4.82074	-1.50671
H	-3.80847	5.75056	-1.69845
H	-2.22726	4.9619	-1.82596
H	-3.70324	4.02998	-2.12314
C	-2.66506	5.57099	0.81009
H	-1.68463	5.8351	0.40086
H	-3.29279	6.46778	0.78056
H	-2.52705	5.27678	1.85273
O	-2.90308	0.88031	0.00058
Ag	-4.37875	-0.63125	0.00882
Ag	-0.83587	0.34861	-0.23999
O	-5.85035	-2.21668	0.002
C	-6.48759	-2.76179	1.20048
C	-6.24951	-2.9723	-1.18645
C	-7.57866	-3.68374	0.66914
H	-5.72849	-3.30504	1.77403
H	-6.85847	-1.92063	1.79096
C	-6.96596	-4.2033	-0.64164
H	-6.91054	-2.33425	-1.78287
H	-5.34744	-3.1991	-1.75946
H	-8.49357	-3.11665	0.46735
H	-7.8146	-4.4824	1.37657
H	-7.71362	-4.58045	-1.3436
H	-6.2474	-5.00402	-0.43722
H	1.11909	-2.32989	-1.32437

Zero-point correction= 0.435590 (Hartree/Particle)
Thermal correction to Energy= 0.470844
Thermal correction to Enthalpy= 0.471836
Thermal correction to Gibbs Free Energy= 0.354808
SCF Done: E(RB3LYP) = -4043.76530164
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.374909

TS1

C	-1.08652	-2.31524	2.63466
C	0.0132	-1.79852	2.14088
C	-2.18395	-2.8414	3.11787
H	-3.16617	-2.53412	2.7612
C	1.33389	-3.74205	-0.84318
C	2.65293	-3.22335	-0.13591
B	0.79899	-2.40162	0.92937

O	0.30527	-3.41055	0.13217
O	2.15534	-2.20221	0.77204
C	3.67742	-2.58584	-1.07262
H	4.53636	-2.23274	-0.49213
H	4.04544	-3.31331	-1.8042
H	3.25622	-1.73351	-1.60938
C	3.33651	-4.28467	0.73728
H	3.79413	-5.07538	0.13458
H	4.12579	-3.80656	1.32601
H	2.62987	-4.74479	1.43438
C	0.99191	-2.98348	-2.13124
H	1.73296	-3.16496	-2.91673
H	0.02204	-3.33718	-2.49895
H	0.90237	-1.91151	-1.92528
C	1.28933	-5.24934	-1.09053
H	0.32695	-5.51729	-1.53837
H	2.07795	-5.55434	-1.78685
H	1.40099	-5.82202	-0.16714
O	0.14754	-0.29406	-0.55589
Ag	1.15905	1.40946	-0.21032
Ag	-1.77603	0.29069	-0.42866
H	0.42371	-0.91319	2.63153
H	-2.15768	-3.60931	3.88959
O	-3.88617	0.85068	-0.31856
C	-4.82825	0.69925	-1.41996
C	-4.59281	1.14388	0.9253
C	-6.11696	1.33403	-0.91155
H	-4.39699	1.19257	-2.29427
H	-4.95144	-0.36974	-1.63094
C	-6.07547	0.99664	0.58755
H	-4.24339	0.44599	1.69021
H	-4.33263	2.16564	1.22311
H	-6.99834	0.93149	-1.41711
H	-6.09399	2.41857	-1.06388
H	-6.40462	-0.03457	0.75403
H	-6.69798	1.65853	1.19479
O	2.33194	3.21807	0.14546
C	2.77892	3.65594	1.46172
C	2.97757	4.00126	-0.90425
C	3.42228	5.01586	1.21705
H	1.90471	3.68289	2.11671
H	3.49794	2.92358	1.84751
C	4.03003	4.84156	-0.18408
H	3.39306	3.30815	-1.63994

H	2.20852	4.61756	-1.3829
H	4.16617	5.25889	1.97992
H	2.66059	5.80314	1.21143
H	4.9777	4.29597	-0.12257
H	4.21155	5.79041	-0.69504

Zero-point correction= 0.467833 (Hartree/Particle)
Thermal correction to Energy= 0.502344
Thermal correction to Enthalpy= 0.503336
Thermal correction to Gibbs Free Energy= 0.389546
SCF Done: E(RB3LYP) = -1361.97461249
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.408389

TS1-2S

C	1.20148	-2.25968	-1.13207
C	-0.0385	-1.90512	-1.35018
C	2.46184	-2.69758	-0.99283
H	3.26671	-2.29405	-1.60557
C	-2.80563	-0.50221	0.81408
C	-2.97088	0.27557	-0.56082
B	-1.0161	-0.92519	-0.55141
O	-1.71888	-1.42727	0.52417
O	-1.67987	0.09158	-1.20865
C	-3.23925	1.77289	-0.4224
H	-3.29698	2.22855	-1.41658
H	-4.19335	1.9547	0.0839
H	-2.44718	2.27393	0.13736
C	-4.01101	-0.35185	-1.49903
H	-5.03019	-0.22573	-1.1208
H	-3.94862	0.13617	-2.47681
H	-3.82564	-1.42017	-1.64503
C	-2.35621	0.38634	1.97967
H	-3.11822	1.12921	2.23746
H	-2.19429	-0.24553	2.86007
H	-1.40631	0.8716	1.73754
C	-4.02362	-1.3279	1.23033
H	-3.79833	-1.86553	2.1569
H	-4.88724	-0.68181	1.42105
H	-4.30167	-2.06478	0.47366
O	0.51114	0.47433	0.74581
Ag	1.30044	2.07919	-0.22576
Ag	2.10169	-0.8579	0.51551
H	-0.523	-2.42989	-2.18322
H	2.67658	-3.59308	-0.41225

Zero-point correction= 0.230472 (Hartree/Particle)

Thermal correction to Energy= 0.250139
Thermal correction to Enthalpy= 0.251131
Thermal correction to Gibbs Free Energy= 0.178007
SCF Done: E(RB3LYP) = -896.827405389
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.186007

TS1'

C	-5.52395	-1.62421	-1.4782
C	-4.20222	-1.58565	-1.05504
C	-3.5997	-0.34237	-0.82472
C	-4.28562	0.8548	-1.01106
C	-5.60845	0.81119	-1.44539
C	-6.21436	-0.4245	-1.67021
H	-6.00711	-2.57812	-1.65448
H	-3.64401	-2.50134	-0.8969
H	-3.81236	1.81345	-0.8476
H	-6.15327	1.73435	-1.6035
N	-1.41972	-1.18264	-0.37671
N	-2.22352	-0.34848	-0.38824
C	0.41944	0.13616	0.94895
Br	-8.02768	-0.48152	-2.253
C	-1.69726	1.52606	0.45116
C	-0.49538	0.97736	0.87937
H	-2.44938	1.75172	1.20317
H	-1.65154	2.20061	-0.40114
H	1.16849	-0.60931	1.14609
O	1.58332	2.56392	0.25752
C	2.278	3.69183	0.93667
B	1.04538	1.82988	1.25014
O	1.39487	2.12377	2.51663
C	2.31701	4.13865	3.51956
H	2.45347	3.64669	4.48666
H	3.07035	4.92763	3.4332
H	1.32724	4.59804	3.50394
C	3.79382	2.33934	2.57619
H	4.65507	3.01281	2.56996
H	3.77276	1.82201	3.53914
H	3.93299	1.59302	1.78894
C	1.31685	4.87861	0.87015
H	1.77573	5.77269	1.30048
H	1.0785	5.08843	-0.17614
H	0.38224	4.67937	1.4024
C	2.49312	3.12245	2.40028
C	3.5556	3.98674	0.16359

H	3.3035	4.33773	-0.841
H	4.12376	4.77664	0.66415
H	4.19231	3.10547	0.06949

Zero-point correction= 0.316236 (Hartree/Particle)
Thermal correction to Energy= 0.340095
Thermal correction to Enthalpy= 0.341086
Thermal correction to Gibbs Free Energy= 0.260150
SCF Done: E(RB3LYP) = -3442.08717847
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.26828

TS2

C	-1.6758	1.92667	1.8822
C	-1.59622	0.66306	1.91473
H	-1.72755	-0.02427	2.7388
C	-1.70279	3.27815	1.57572
H	-0.89359	3.90522	1.95203
H	-2.67268	3.77467	1.53374
C	-3.05676	-1.84512	-0.49433
C	-2.02472	-2.55619	0.47174
B	-1.37879	-0.33997	0.07578
O	-2.75623	-0.45295	-0.31313
O	-0.91257	-1.64437	0.46026
C	-1.53257	-3.92379	-0.00933
H	-0.82133	-4.33601	0.71523
H	-2.36064	-4.63523	-0.10322
H	-1.02458	-3.85288	-0.97389
C	-2.55128	-2.69589	1.91017
H	-3.30944	-3.48251	1.98805
H	-1.71872	-2.96429	2.56935
H	-2.98924	-1.76526	2.27661
C	-2.81698	-2.1922	-1.97473
H	-3.09412	-3.22547	-2.21002
H	-3.42747	-1.52862	-2.59612
H	-1.76968	-2.04196	-2.2522
C	-4.52903	-2.08469	-0.15305
H	-5.16455	-1.54554	-0.86408
H	-4.78576	-3.14809	-0.21715
H	-4.7743	-1.72788	0.84984
O	-0.51895	0.46782	-0.66668
Ag	1.49101	0.05049	-0.32284
Ag	-1.08906	2.63757	-0.52201
O	3.61833	-0.3044	-0.06777
C	4.34637	-0.02509	1.17177
C	4.39682	-1.18824	-0.9308

C	5.5885	-0.91219	1.11339
H	4.59255	1.04191	1.17358
H	3.68652	-0.24657	2.01395
C	5.81907	-1.08132	-0.39714
H	3.99827	-2.20545	-0.84087
H	4.27158	-0.83753	-1.95781
H	5.38667	-1.88293	1.57816
H	6.43679	-0.454	1.62766
H	6.41394	-1.96462	-0.64233
H	6.3174	-0.19935	-0.81364

Zero-point correction= 0.347683 (Hartree/Particle)
Thermal correction to Energy= 0.374605
Thermal correction to Enthalpy= 0.375597
Thermal correction to Gibbs Free Energy= 0.283539
SCF Done: E(RB3LYP) = -1129.44056232
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.295986

TS2-1S

C	-1.67675	1.65235	-1.63796
C	-0.4698	1.29465	-1.75172
H	0.25863	1.47587	-2.5285
C	-2.99366	1.90663	-1.27585
H	-3.78095	1.40454	-1.83955
H	-3.24741	2.91973	-0.96212
C	2.40128	1.28607	0.73568
C	2.75257	0.31985	-0.46904
B	0.43417	0.32641	-0.04732
O	0.983	1.47553	0.59975
O	1.52434	-0.42038	-0.63506
C	3.88416	-0.67101	-0.18806
H	4.0519	-1.30016	-1.06936
H	4.82229	-0.14906	0.02998
H	3.64919	-1.32599	0.65425
C	3.06073	1.07167	-1.77321
H	4.0482	1.54381	-1.7397
H	3.05524	0.36011	-2.60563
H	2.32142	1.84705	-1.98197
C	2.65985	0.64072	2.10874
H	3.72859	0.52644	2.31881
H	2.22863	1.28093	2.88513
H	2.1844	-0.34173	2.18342
C	3.09004	2.65112	0.68362
H	2.77901	3.25213	1.54485
H	4.18024	2.54975	0.72406

H	2.82511	3.20285	-0.22103
O	-0.59111	-0.41951	0.50968
Ag	-0.13269	-2.43849	-0.11444
Ag	-2.56637	0.63263	0.54968

Zero-point correction= 0.228875 (Hartree/Particle)
Thermal correction to Energy= 0.248687
Thermal correction to Enthalpy= 0.249678
Thermal correction to Gibbs Free Energy= 0.176957
SCF Done: E(RB3LYP) = -896.863443760
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.184269

TS2'

C	3.87436	-0.82179	1.0814
C	2.56836	-0.73977	1.18948
H	2.14189	-0.91089	2.18338
C	5.18746	-0.76545	0.91669
H	5.78237	-1.64329	0.67713
H	5.72343	0.17491	1.03856
C	1.8038	2.37126	-0.84727
C	1.24796	2.51839	0.63032
B	1.13885	0.27874	-0.04531
O	1.96464	0.95447	-1.00061
O	0.58931	1.25768	0.84406
C	0.22248	3.64054	0.81804
H	-0.12168	3.6538	1.85814
H	0.66129	4.62087	0.60108
H	-0.65193	3.50348	0.17752
C	2.35396	2.68042	1.68615
H	2.84131	3.65882	1.61807
H	1.90613	2.59596	2.68223
H	3.1144	1.90299	1.59415
C	0.79878	2.84257	-1.91438
H	0.66747	3.93015	-1.9132
H	1.16973	2.547	-2.90135
H	-0.18016	2.37478	-1.77188
C	3.1509	3.05585	-1.09321
H	3.4634	2.89061	-2.13016
H	3.08633	4.1381	-0.93333
H	3.93012	2.6536	-0.44207
O	0.32625	-0.79647	-0.43124
Ag	-1.70583	-0.50126	-0.17171
Ag	1.99081	-2.36914	-0.28956
O	-3.8601	-0.31814	0.0712
C	-4.53494	-0.29118	1.36586

C	-4.78917	0.03338	-1.00202
C	-6.02006	-0.2857	1.0243
H	-4.20633	-1.16795	1.92896
H	-4.22969	0.61769	1.89672
C	-6.05205	0.51068	-0.29017
H	-4.31575	0.79632	-1.62463
H	-4.96358	-0.86716	-1.6009
H	-6.61809	0.17163	1.81639
H	-6.37913	-1.30797	0.86415
H	-5.99307	1.58514	-0.08658
H	-6.94894	0.32075	-0.88482

Zero-point correction= 0.346945 (Hartree/Particle)
Thermal correction to Energy= 0.374366
Thermal correction to Enthalpy= 0.375358
Thermal correction to Gibbs Free Energy= 0.280923
SCF Done: E(RB3LYP) = -1129.42735984
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.29458

TS2'-1S

C	-2.44432	1.81271	-0.89323
C	-1.62824	0.80556	-1.09565
H	-1.53742	0.43164	-2.11998
C	-3.15768	2.89737	-0.6344
H	-4.21429	2.85153	-0.38248
H	-2.70485	3.88657	-0.68517
C	1.42648	1.87219	0.92111
C	1.81972	1.6303	-0.59555
B	0.09406	0.16688	0.03459
O	0.1922	1.15365	1.06309
O	1.17836	0.3721	-0.88715
C	3.32204	1.48314	-0.85126
H	3.49746	1.29456	-1.91611
H	3.8609	2.3986	-0.58322
H	3.75235	0.65217	-0.28714
C	1.25755	2.69495	-1.55066
H	1.75955	3.65961	-1.42265
H	1.41888	2.36527	-2.5826
H	0.18484	2.83589	-1.40769
C	2.43689	1.25831	1.90737
H	3.39118	1.79595	1.9145
H	2.01463	1.30319	2.91655
H	2.63304	0.20687	1.67475
C	1.19354	3.33874	1.29291
H	0.91422	3.40936	2.3498

H	2.09913	3.93812	1.14672
H	0.38543	3.77844	0.70426
O	-0.26749	-1.15632	0.31056
Ag	1.41254	-2.36064	-0.19488
Ag	-2.52117	-0.73206	0.31428

Zero-point correction= 0.228413 (Hartree/Particle)
Thermal correction to Energy= 0.248592
Thermal correction to Enthalpy= 0.249583
Thermal correction to Gibbs Free Energy= 0.174385
SCF Done: E(RB3LYP) = -896.851284220
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.183408

TS3

C	8.06802	-1.47331	0.0733
C	7.00682	-2.36262	0.01664
C	5.70229	-1.83823	-0.04615
C	5.43703	-0.46188	-0.05731
C	6.51058	0.4158	-0.0025
C	7.81087	-0.09655	0.06458
H	9.08314	-1.84843	0.12404
H	7.16884	-3.43459	0.02047
H	4.41552	-0.10439	-0.10707
H	6.33428	1.48475	-0.0101
N	4.07371	-3.71264	-0.12898
N	4.65366	-2.74115	-0.09556
C	1.57221	-3.61321	-0.18337
Br	9.27456	1.10803	0.14893
C	1.715	-0.98118	-0.098
C	1.57461	-2.38698	-0.14449
H	1.34217	-4.65587	-0.21727
H	2.17803	-0.55054	-0.99084
H	2.17004	-0.60999	0.8251
C	-2.32493	4.06392	-0.28268
C	-3.79469	3.75144	0.2081
B	-2.61004	1.80326	-0.038
O	-1.64431	2.79949	-0.03725
O	-3.90003	2.31893	-0.03745
C	-4.89938	4.46475	-0.56568
H	-5.87666	4.17277	-0.16777
H	-4.80752	5.55087	-0.46231
H	-4.87833	4.2137	-1.62827
C	-3.98343	3.96339	1.71508
H	-3.97711	5.02534	1.97797
H	-4.9492	3.54543	2.01602

H	-3.20094	3.46019	2.29155
C	-2.23871	4.33513	-1.78955
H	-2.67875	5.30162	-2.05252
H	-1.18637	4.3481	-2.08986
H	-2.74614	3.55586	-2.36666
C	-1.60642	5.16516	0.49136
H	-0.59475	5.29513	0.0936
H	-2.13177	6.12012	0.38721
H	-1.52413	4.9271	1.554
O	-2.33023	0.48497	-0.03847
Ag	-3.94914	-0.87315	0.03272
Ag	-0.28851	-0.20271	-0.07565
O	-5.54489	-2.33407	0.10006
C	-6.37413	-2.58854	1.28241
C	-6.16084	-2.91402	-1.09284
C	-7.64762	-3.23413	0.74159
H	-5.81009	-3.25838	1.93944
H	-6.54394	-1.63676	1.79138
C	-7.16485	-3.91987	-0.54693
H	-6.64689	-2.11128	-1.65904
H	-5.36091	-3.35298	-1.69358
H	-8.39467	-2.46841	0.50811
H	-8.08254	-3.93236	1.46064
H	-7.97354	-4.11291	-1.25598
H	-6.66818	-4.86868	-0.31769

Zero-point correction= 0.438455 (Hartree/Particle)
Thermal correction to Energy= 0.476191
Thermal correction to Enthalpy= 0.477183
Thermal correction to Gibbs Free Energy= 0.354756
SCF Done: E(RB3LYP) = -4044.08568512
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.375548

TS3-1S

C	-7.27768	-0.39192	0.47249
C	-6.41664	-1.37469	0.93447
C	-5.04732	-1.25608	0.63058
C	-4.52518	-0.19142	-0.11655
C	-5.40024	0.78421	-0.5725
C	-6.76281	0.67541	-0.27427
H	-8.33689	-0.45689	0.692
H	-6.7802	-2.21526	1.51475
H	-3.46363	-0.14243	-0.32644
H	-5.02446	1.61879	-1.1523
N	-3.83863	-3.19303	1.60717

N	-4.20134	-2.2491	1.09923
C	-1.35603	-3.69572	1.586
Br	-7.95108	2.01622	-0.89815
C	-1.05828	-1.42186	0.28498
C	-1.15204	-2.65	0.97943
H	-1.32822	-4.6225	2.11628
H	-1.41603	-0.56298	0.86162
H	-1.48221	-1.44927	-0.72337
C	3.76676	2.68613	1.08249
C	5.05099	2.41337	0.20035
B	3.59078	0.64225	0.06019
O	2.83706	1.67269	0.59851
O	4.93591	0.98346	-0.06387
C	6.38162	2.67801	0.89775
H	7.20774	2.44521	0.21799
H	6.46888	3.73213	1.18043
H	6.49849	2.06668	1.79506
C	5.01266	3.12622	-1.15623
H	5.14924	4.20621	-1.04796
H	5.82361	2.74383	-1.78413
H	4.06648	2.94826	-1.67661
C	3.99276	2.41193	2.57403
H	4.63644	3.16933	3.03108
H	3.02781	2.43013	3.08992
H	4.44601	1.42911	2.73729
C	3.13345	4.06065	0.89037
H	2.24559	4.14854	1.52472
H	3.83072	4.85385	1.17914
H	2.82779	4.22592	-0.14497
O	3.11252	-0.56025	-0.31211
Ag	4.73704	-1.76162	-1.13383
Ag	1.03063	-1.00743	0.00286

Zero-point correction= 0.319852 (Hartree/Particle)
Thermal correction to Energy= 0.350307
Thermal correction to Enthalpy= 0.351298
Thermal correction to Gibbs Free Energy= 0.249056
SCF Done: E(RB3LYP) = -3811.50707035
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.263701

TS3a

C	8.4529	0.19172	1.09457
C	7.22147	0.37624	1.70086
C	6.07088	-0.00573	0.98379
C	6.11509	-0.56517	-0.302

C	7.35822	-0.75039	-0.88666
C	8.51067	-0.36976	-0.18808
H	9.35713	0.48078	1.61692
H	7.13808	0.80261	2.69409
H	5.19436	-0.83026	-0.80862
H	7.42655	-1.18252	-1.87774
N	4.00565	0.36058	2.32124
N	4.85604	0.1778	1.61249
C	1.51562	0.25761	0.99713
Br	10.20377	-0.62123	-1.00146
C	2.90827	0.20498	-1.25663
C	2.24824	0.22469	-0.22958
H	1.65291	-0.64008	1.60843
H	3.34481	0.2088	-2.23123
H	1.70541	1.16029	1.58569
Ag	-0.58011	0.34787	0.56893
C	-3.60354	3.80512	-0.49973
C	-5.00874	3.09968	-0.33411
B	-3.31739	1.57537	-0.05324
O	-2.69407	2.81041	0.05232
O	-4.65333	1.68935	-0.41893
C	-6.02361	3.41631	-1.42856
H	-6.95396	2.87132	-1.23834
H	-6.25936	4.48545	-1.44257
H	-5.65847	3.12784	-2.41655
C	-5.63502	3.32302	1.04771
H	-5.98726	4.35153	1.17074
H	-6.49413	2.65465	1.16216
H	-4.92432	3.10297	1.8504
C	-3.20384	4.01464	-1.9654
H	-3.80393	4.79618	-2.44092
H	-2.15366	4.31967	-2.00789
H	-3.31276	3.09366	-2.54658
C	-3.43867	5.10626	0.28012
H	-2.43324	5.50803	0.11826
H	-4.15826	5.85777	-0.06091
H	-3.57387	4.95661	1.3534
O	-2.70222	0.39758	0.17232
Ag	-3.88198	-1.3508	0.03961
O	-5.02745	-3.1819	-0.10825
C	-5.88419	-3.6957	0.9594
C	-5.30255	-3.87758	-1.36922
C	-6.38352	-5.03331	0.43091
H	-5.27517	-3.76472	1.86356

H	-6.70206	-2.9844	1.12164
C	-6.51191	-4.76246	-1.07705
H	-5.48198	-3.12565	-2.14132
H	-4.40978	-4.45744	-1.62503
H	-7.32915	-5.32598	0.89365
H	-5.64467	-5.81897	0.62127
H	-7.44057	-4.2224	-1.28897
H	-6.49905	-5.67479	-1.67805

Zero-point correction= 0.438644 (Hartree/Particle)
Thermal correction to Energy= 0.476401
Thermal correction to Enthalpy= 0.477393
Thermal correction to Gibbs Free Energy= 0.354427
SCF Done: E(RB3LYP) = -4044.08569710
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.375564

TS3a-1S

C	-7.45387	-1.07652	-0.11364
C	-6.22695	-1.65682	0.17518
C	-5.13179	-0.80871	0.40777
C	-5.22774	0.58325	0.36729
C	-6.46644	1.15146	0.09845
C	-7.56262	0.3184	-0.14562
H	-8.31434	-1.70604	-0.30824
H	-6.1092	-2.7339	0.21545
H	-4.35351	1.19446	0.55448
H	-6.57246	2.22933	0.07392
N	-3.32865	-2.32004	1.08911
N	-3.89661	-1.41316	0.7099
C	-0.70902	-1.51307	0.76342
Br	-9.24951	1.10198	-0.53438
C	-2.014	0.47589	-0.36408
C	-1.40703	-0.44917	0.16044
H	-0.77905	-1.5598	1.85323
H	-2.37914	1.33432	-0.88437
H	-0.84095	-2.48633	0.28413
Ag	1.37113	-1.05682	0.39093
C	4.19383	2.78612	0.44667
C	5.48301	2.23792	-0.28905
B	3.97018	0.54042	0.04594
O	3.24181	1.69874	0.25663
O	5.3276	0.79534	-0.13588
C	6.80975	2.65925	0.33495
H	7.63906	2.21826	-0.22759
H	6.92581	3.74738	0.3019

H	6.89275	2.33224	1.37358
C	5.48936	2.53101	-1.79383
H	5.65869	3.59232	-1.99787
H	6.29802	1.96314	-2.26474
H	4.54666	2.23535	-2.26463
C	4.38768	2.95364	1.95825
H	5.04641	3.79563	2.19059
H	3.41539	3.14524	2.42255
H	4.80801	2.05088	2.41214
C	3.60517	4.06009	-0.15202
H	2.71118	4.3514	0.4086
H	4.32197	4.88547	-0.09144
H	3.31935	3.92337	-1.19712
O	3.45733	-0.70449	0.00733
Ag	4.99897	-2.12372	-0.58505

Zero-point correction= 0.319636 (Hartree/Particle)
Thermal correction to Energy= 0.350103
Thermal correction to Enthalpy= 0.351095
Thermal correction to Gibbs Free Energy= 0.248609
SCF Done: E(RB3LYP) = -3811.50776804
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.263594

TS3'

C	1.98774	-4.31614	-0.03988
C	3.23786	-3.77856	-0.20829
H	3.69002	-3.73711	-1.19607
C	0.74915	-4.59953	0.11614
H	0.29704	-5.58244	0.21157
H	3.9041	-3.65861	0.64237
C	1.8432	3.14098	0.25648
C	3.10322	2.27294	-0.14079
B	1.24597	0.93847	0.01031
O	0.74355	2.23578	-0.04314
O	2.63031	0.91817	0.09785
C	4.34775	2.51441	0.70892
H	5.15678	1.85835	0.37199
H	4.69262	3.54906	0.61024
H	4.16417	2.30757	1.76542
C	3.45558	2.37031	-1.63048
H	3.87975	3.34657	-1.88404
H	4.19878	1.6039	-1.871
H	2.57788	2.20022	-2.2618
C	1.77473	3.45077	1.7571
H	2.53798	4.17511	2.05695

H	0.79336	3.8765	1.989
H	1.90252	2.54566	2.35887
C	1.66011	4.42188	-0.55255
H	0.75528	4.94199	-0.22147
H	2.50751	5.09973	-0.40589
H	1.55999	4.21669	-1.62053
O	0.47017	-0.16085	-0.01917
Ag	1.31469	-2.15905	-0.03651
Ag	-1.62435	0.10477	-0.02492
O	-3.77584	0.34028	-0.02419
C	-4.62441	0.17877	1.15802
C	-4.59072	0.48574	-1.22959
C	-6.03301	-0.01347	0.60472
H	-4.25058	-0.67473	1.72831
H	-4.53287	1.08901	1.76034
C	-5.99177	0.78302	-0.7096
H	-4.15381	1.2876	-1.8293
H	-4.54778	-0.45513	-1.78946
H	-6.79373	0.3484	1.30067
H	-6.22304	-1.07302	0.40368
H	-6.1073	1.85446	-0.51418
H	-6.76232	0.47477	-1.4204

Zero-point correction= 0.347284 (Hartree/Particle)
Thermal correction to Energy= 0.375164
Thermal correction to Enthalpy= 0.376156
Thermal correction to Gibbs Free Energy= 0.279897
SCF Done: E(RB3LYP) = -1129.46068799
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.294258

TS3'-1S

C	-4.14332	-1.5716	0.04817
C	-3.44838	-2.75244	0.02019
H	-3.30986	-3.28707	-0.91621
C	-4.58506	-0.36991	0.07178
H	-5.62027	-0.04192	0.09352
H	-3.27969	-3.31354	0.9359
C	3.24289	-0.3153	0.20208
C	2.58574	-1.70024	-0.18459
B	0.96319	-0.09431	0.0138
O	2.15871	0.61904	-0.06851
O	1.17736	-1.46135	0.0939
C	3.05358	-2.89128	0.6468
H	2.53012	-3.79576	0.32085
H	4.12751	-3.06034	0.51577

H	2.85037	-2.74896	1.7103
C	2.69983	-2.02391	-1.67945
H	3.72539	-2.28049	-1.96164
H	2.05987	-2.88186	-1.90736
H	2.371	-1.18321	-2.29827
C	3.5729	-0.20274	1.69545
H	4.4218	-0.83562	1.97103
H	3.83503	0.83466	1.92633
H	2.71701	-0.48332	2.31702
C	4.45522	0.08127	-0.63536
H	4.82875	1.05661	-0.30648
H	5.26597	-0.64463	-0.51416
H	4.20948	0.15344	-1.69706
O	-0.24196	0.50229	0.01446
Ag	-2.09576	-0.61485	0.03354
Ag	-0.13619	2.66124	-0.06945

Zero-point correction= 0.228704 (Hartree/Particle)
Thermal correction to Energy= 0.249390
Thermal correction to Enthalpy= 0.250382
Thermal correction to Gibbs Free Energy= 0.173051
SCF Done: E(RB3LYP) = -896.882560710
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.183051

TS4

C	7.83808	-1.27434	0.81768
C	6.46661	-1.38917	0.99847
C	5.59175	-0.6104	0.21921
C	6.10324	0.27845	-0.73649
C	7.47784	0.39712	-0.92232
C	8.33116	-0.38223	-0.14171
H	8.51907	-1.87007	1.41505
H	6.06555	-2.07447	1.73644
H	5.41469	0.87244	-1.32895
H	7.87409	1.08424	-1.66099
N	3.68611	-1.43393	1.16619
N	4.18701	-0.65333	0.33033
C	2.2603	-1.42542	1.23985
Br	10.2189	-0.23161	-0.38457
C	2.05096	0.29479	-0.51143
C	1.60708	-0.59266	0.42446
H	1.83603	-2.10481	1.96549
H	2.12086	0.01821	-1.56365
H	2.20898	1.34471	-0.26332
C	-2.67743	3.8899	-0.0111

C	-4.18472	3.47199	0.22763
B	-2.87615	1.60628	-0.00695
O	-1.9708	2.63222	0.21256
O	-4.17602	2.06113	-0.14775
C	-5.2018	4.2028	-0.64315
H	-6.20887	3.83584	-0.42075
H	-5.18538	5.27831	-0.43917
H	-5.01191	4.04764	-1.70732
C	-4.60411	3.53812	1.70046
H	-4.69279	4.5712	2.04895
H	-5.58042	3.05689	1.81452
H	-3.89048	3.0164	2.34578
C	-2.38947	4.31361	-1.45569
H	-2.83903	5.28323	-1.68865
H	-1.30711	4.40017	-1.593
H	-2.76545	3.57784	-2.17338
C	-2.13637	4.93275	0.96171
H	-1.08665	5.14163	0.73188
H	-2.69136	5.87215	0.87196
H	-2.19527	4.59127	1.99729
O	-2.51955	0.30356	-0.07667
Ag	-4.10162	-1.11519	-0.16785
Ag	-0.43253	-0.11237	0.12349
O	-5.65723	-2.6164	-0.2419
C	-6.144	-3.35635	0.92232
C	-6.52324	-2.85121	-1.4017
C	-7.09435	-4.3936	0.34006
H	-5.27412	-3.7768	1.43225
H	-6.65622	-2.65376	1.58925
C	-7.70659	-3.645	-0.8551
H	-6.79769	-1.88083	-1.8221
H	-5.94244	-3.41728	-2.1372
H	-7.84123	-4.71556	1.06968
H	-6.53759	-5.27341	0.0006
H	-8.49747	-2.96786	-0.51621
H	-8.12585	-4.315	-1.60946

Zero-point correction= 0.442608 (Hartree/Particle)
Thermal correction to Energy= 0.478623
Thermal correction to Enthalpy= 0.479615
Thermal correction to Gibbs Free Energy= 0.363261
SCF Done: E(RB3LYP) = -4044.14278956
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.380982

TS4-1S

C	7.16926	-1.031	-0.00133
C	5.83823	-1.42472	-0.01096
C	4.82187	-0.45212	-0.00232
C	5.152	0.91004	0.01584
C	6.48526	1.31059	0.0257
C	7.48062	0.33374	0.01698
H	7.95822	-1.77466	-0.00791
H	5.57619	-2.47653	-0.02506
H	4.35522	1.64707	0.02229
H	6.74099	2.36377	0.04011
N	3.10492	-1.95282	-0.02569
N	3.44417	-0.75114	-0.01039
C	1.69806	-2.19682	-0.03248
Br	9.314	0.86732	0.03033
C	1.1305	0.20542	-0.00571
C	0.88662	-1.13595	-0.02196
H	1.41625	-3.24011	-0.04537
H	1.16277	0.78481	-0.92867
H	1.15916	0.76337	0.9305
C	-4.10541	2.79976	-0.16988
C	-5.50156	2.14505	0.18504
B	-3.88483	0.52497	-0.00702
O	-3.17404	1.70716	0.09821
O	-5.25499	0.73416	-0.10561
C	-6.67339	2.62312	-0.6657
H	-7.58637	2.10033	-0.36298
H	-6.84097	3.69582	-0.52556
H	-6.50955	2.43268	-1.72836
C	-5.85294	2.24126	1.67363
H	-6.1061	3.26572	1.96144
H	-6.72234	1.60833	1.87722
H	-5.02731	1.89948	2.3055
C	-3.96498	3.15272	-1.65479
H	-4.5897	4.00872	-1.92608
H	-2.92282	3.41489	-1.86165
H	-4.23723	2.3092	-2.29675
C	-3.71676	3.99489	0.69459
H	-2.73493	4.36845	0.38657
H	-4.43728	4.81036	0.57482
H	-3.66268	3.73118	1.75294
O	-3.34026	-0.71059	-0.01142
Ag	-4.96052	-2.19037	-0.00381
Ag	-1.21673	-0.88341	-0.01846

Zero-point correction= 0.323961 (Hartree/Particle)
Thermal correction to Energy= 0.352840
Thermal correction to Enthalpy= 0.353832
Thermal correction to Gibbs Free Energy= 0.255379
SCF Done: E(RB3LYP) = -3811.56396032
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.269256

TS5

N	-3.33473	-1.61075	-0.06799
N	-3.02037	-2.48645	0.8585
C	-2.1555	-0.93975	-0.55569
C	-1.67348	-2.51511	0.94664
C	-1.04391	-1.6122	0.0729
H	-2.14732	-0.68069	-1.61421
H	-1.22247	-3.20075	1.6517
H	-2.21379	0.17117	-0.01305
C	-2.14344	1.69074	1.76293
O	-0.84066	1.40924	2.0395
O	-2.83777	2.16787	2.66681
O	-2.55972	1.43657	0.56033
K	-5.11691	1.83783	1.3327
H	-0.41893	1.05788	1.23699
C	5.0321	-3.51324	-0.09092
C	6.0632	-2.35595	0.22217
B	3.97412	-1.48239	-0.1327
O	3.75112	-2.83464	0.06788
O	5.32425	-1.16842	-0.19208
C	7.36699	-2.42207	-0.56728
H	8.00509	-1.57433	-0.29747
H	7.9155	-3.34054	-0.33441
H	7.1922	-2.38494	-1.64461
C	6.35828	-2.19985	1.71852
H	6.96487	-3.02712	2.09863
H	6.91439	-1.27059	1.87716
H	5.43656	-2.14905	2.30649
C	5.10121	-4.00504	-1.54139
H	6.01209	-4.58105	-1.72936
H	4.24236	-4.65375	-1.73952
H	5.06773	-3.17142	-2.24984
C	5.07976	-4.69749	0.86963
H	4.31867	-5.43173	0.58675
H	6.05496	-5.19331	0.82735
H	4.88896	-4.39223	1.90064
O	2.98969	-0.56597	-0.25795

Ag	3.59043	1.46413	-0.35776
Ag	0.94972	-1.14685	-0.10708
C	-4.68202	-1.22456	-0.27632
C	-5.01755	-0.43608	-1.38624
C	-5.67097	-1.59783	0.64744
C	-6.3346	-0.01354	-1.5676
H	-4.2691	-0.15098	-2.11571
C	-6.98845	-1.18163	0.46068
H	-5.40799	-2.20471	1.50545
C	-7.31283	-0.38985	-0.64477
H	-6.58864	0.59349	-2.42905
H	-7.74939	-1.47512	1.17527
Br	-9.11713	0.18032	-0.90198
O	4.15102	3.55223	-0.44271
C	4.20101	4.42976	0.72692
C	4.82823	4.17581	-1.58415
C	4.55177	5.79744	0.15735
H	3.22563	4.38009	1.21652
H	4.9731	4.05547	1.40855
C	5.47514	5.43695	-1.01779
H	5.5431	3.45613	-1.98992
H	4.06539	4.39776	-2.33757
H	5.0366	6.43488	0.90069
H	3.64966	6.30453	-0.20114
H	6.48509	5.21852	-0.6555
H	5.54143	6.22838	-1.76817

Zero-point correction= 0.472135 (Hartree/Particle)
Thermal correction to Energy= 0.514384
Thermal correction to Enthalpy= 0.515376
Thermal correction to Gibbs Free Energy= 0.383536
SCF Done: E(RB3LYP) = -4908.73773412
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.404232

TS5-1S

N	-2.63635	-1.01255	0.96215
N	-2.29393	-0.93315	2.22678
C	-1.50974	-0.72469	0.10913
C	-0.96363	-0.70441	2.27113
C	-0.37944	-0.59677	0.99794
H	-1.4505	-1.29073	-0.82073
H	-0.4914	-0.62704	3.24148
H	-1.74074	0.41877	-0.29787
C	-2.04028	2.70696	-0.03782
O	-0.77058	2.87136	0.42637

O	-2.88645	3.55046	0.277
O	-2.26455	1.66622	-0.77985
K	-4.92684	2.08245	-0.608
H	-0.21628	2.1518	0.07903
C	5.54154	-2.51276	-0.44813
C	6.61858	-1.36152	-0.31857
B	4.49843	-0.49055	-0.18027
O	4.32392	-1.85032	0.00691
O	5.80719	-0.16497	-0.52341
C	7.72469	-1.39172	-1.3682
H	8.40987	-0.55306	-1.20755
H	8.30554	-2.31659	-1.29204
H	7.32574	-1.3144	-2.38186
C	7.22287	-1.25752	1.08637
H	7.89484	-2.09395	1.29947
H	7.80211	-0.33158	1.15842
H	6.44594	-1.2342	1.85695
C	5.29834	-2.95049	-1.89696
H	6.14702	-3.51358	-2.29626
H	4.41644	-3.59763	-1.92955
H	5.11418	-2.09234	-2.55075
C	5.79259	-3.73107	0.43478
H	4.98964	-4.4612	0.29179
H	6.73728	-4.21613	0.16848
H	5.82391	-3.46625	1.49376
O	3.53311	0.44153	-0.04601
Ag	4.3991	2.43581	-0.24339
Ag	1.55388	-0.1242	0.48103
C	-4.00039	-1.06187	0.58016
C	-4.3443	-1.37722	-0.74232
C	-5.00137	-0.75366	1.51469
C	-5.68418	-1.37678	-1.13204
H	-3.58437	-1.62994	-1.47227
C	-6.34031	-0.76211	1.1265
H	-4.73156	-0.50481	2.53387
C	-6.67434	-1.07183	-0.19512
H	-5.94518	-1.62585	-2.15434
H	-7.11059	-0.52534	1.85165
Br	-8.50878	-1.08186	-0.72536

Zero-point correction= 0.353355 (Hartree/Particle)
Thermal correction to Energy= 0.388483
Thermal correction to Enthalpy= 0.389474
Thermal correction to Gibbs Free Energy= 0.275690
SCF Done: E(RB3LYP) = -4676.15892320

Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.292275

TS5'

N	-3.15379	-1.89439	-0.11194
N	-2.4525	-2.61292	0.69572
C	-2.51598	-1.85198	-1.45194
C	-1.35522	-3.08115	0.01637
C	-1.28979	-2.67638	-1.31064
H	-3.21681	-2.25457	-2.19461
H	-0.67007	-3.70935	0.57178
H	-2.30628	-0.81023	-1.72266
Ag	1.19075	-1.56738	-1.75638
C	0.18269	2.9257	-1.38368
C	1.50647	3.54026	-0.77413
B	1.63262	1.25134	-0.78753
O	0.57359	1.5433	-1.63582
O	2.12147	2.37799	-0.14357
C	1.28892	4.61559	0.28599
H	2.25644	4.96658	0.65873
H	0.76157	5.47676	-0.13712
H	0.7152	4.23874	1.13534
C	2.48636	4.0412	-1.84158
H	2.12322	4.95137	-2.32791
H	3.4448	4.27048	-1.36562
H	2.66243	3.28448	-2.61247
C	-0.97893	2.88836	-0.38371
H	-1.37025	3.88975	-0.18205
H	-1.79174	2.28649	-0.80231
H	-0.67653	2.4383	0.56699
C	-0.27405	3.55264	-2.69749
H	-1.18417	3.05491	-3.04786
H	-0.50543	4.61406	-2.56161
H	0.4842	3.45908	-3.47775
O	2.12572	0.00791	-0.61451
Ag	3.87441	-0.19687	0.56347
O	0.66401	-3.30053	-3.12351
H	-0.20922	-3.21978	-2.59211
H	0.47988	-3.01599	-4.03259
O	5.65536	-0.4944	1.75784
C	7.02237	-0.32794	1.25248
C	5.64897	-0.51977	3.22047
C	7.87675	-0.08631	2.49439
H	7.2923	-1.25115	0.72973
H	7.0259	0.50542	0.54586

C	7.09363	-0.81565	3.59815
H	5.31953	0.4603	3.58382
H	4.93377	-1.28462	3.5316
H	7.93648	0.98464	2.71458
H	8.892	-0.46914	2.36631
H	7.33378	-0.45425	4.60099
H	7.28476	-1.89335	3.56094
C	-4.35765	-1.26551	0.28784
C	-5.06159	-0.48092	-0.63441
C	-4.83616	-1.43024	1.59577
C	-6.24503	0.14253	-0.24825
H	-4.7016	-0.35031	-1.64832
C	-6.01785	-0.80682	1.97834
H	-4.28808	-2.04081	2.30268
C	-6.71362	-0.02396	1.05428
H	-6.7904	0.75037	-0.96064
H	-6.39055	-0.9327	2.98829
Br	-8.33456	0.83304	1.58437

Zero-point correction= 0.469444 (Hartree/Particle)
Thermal correction to Energy= 0.507214
Thermal correction to Enthalpy= 0.508206
Thermal correction to Gibbs Free Energy= 0.386248
SCF Done: E(RB3LYP) = -4120.62038238
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.406821

TS5'-1S

C	5.66699	0.36535	-1.43786
C	4.47075	1.06815	-1.35827
C	3.75056	1.07587	-0.15495
C	4.22804	0.38438	0.96534
C	5.42668	-0.31906	0.88254
C	6.13653	-0.32406	-0.31751
H	6.22639	0.3589	-2.36607
H	4.09715	1.6076	-2.22
H	3.67921	0.38549	1.8998
H	5.79653	-0.85539	1.74863
N	2.02541	2.41736	-1.06718
N	2.53025	1.78815	-0.0628
C	0.8517	3.00519	-0.66368
Br	7.77929	-1.28938	-0.43213
C	1.66089	1.93867	1.13085
C	0.52844	2.77876	0.6672
H	2.23627	2.41109	1.93706
Ag	-2.1013	1.91401	0.85974

C	-2.11454	-2.70283	1.41981
C	-2.80068	-3.22755	0.09408
B	-2.80462	-0.92903	0.14335
O	-1.88569	-1.29419	1.11299
O	-3.47264	-2.02569	-0.39323
C	-3.84136	-4.32354	0.29848
H	-4.27225	-4.60893	-0.66663
H	-3.3824	-5.216	0.73606
H	-4.65399	-3.99557	0.94999
C	-1.79282	-3.64632	-0.98187
H	-1.28182	-4.57594	-0.71477
H	-2.32383	-3.81109	-1.92465
H	-1.03691	-2.87243	-1.14784
C	-3.04338	-2.75016	2.63826
H	-3.21704	-3.77695	2.9731
H	-2.57924	-2.19851	3.46167
H	-4.0122	-2.28839	2.42387
C	-0.77613	-3.35452	1.75232
H	-0.37305	-2.91995	2.67275
H	-0.89859	-4.42985	1.91698
H	-0.0428	-3.20598	0.95676
O	-3.04735	0.33386	-0.25906
Ag	-4.57216	0.27444	-1.82347
O	-1.54715	3.62868	2.23837
H	-0.66431	3.51693	1.72941
H	-1.93552	4.47702	1.9727
H	0.31347	3.57627	-1.41003
H	1.34853	0.94796	1.48318

Zero-point correction= 0.350835 (Hartree/Particle)
Thermal correction to Energy= 0.381408
Thermal correction to Enthalpy= 0.382400
Thermal correction to Gibbs Free Energy= 0.279695
SCF Done: E(RB3LYP) = -3888.04080263
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.294932

TS6

C	-5.68001	-0.4154	-0.49791
C	-4.50251	-0.96483	-1.00029
C	-3.47818	-1.35787	-0.12705
C	-3.64445	-1.19331	1.25549
C	-4.82765	-0.65583	1.7604
C	-5.83609	-0.26927	0.87997
H	-6.46952	-0.11682	-1.1786
H	-4.37294	-1.0977	-2.06742

H	-2.85238	-1.46862	1.94307
H	-4.94946	-0.53191	2.83068
N	-1.9171	-1.6678	-1.93402
N	-2.28778	-1.91542	-0.64433
C	-0.77573	-2.34423	-2.07748
Br	-7.45984	0.47776	1.5729
C	-1.37674	-2.73878	-0.02222
C	-0.3565	-3.06653	-0.91069
H	-1.5517	-3.05961	0.99614
Ag	1.92087	-2.21362	-0.17959
C	5.97108	0.1941	0.90687
C	5.4192	1.65859	1.13042
B	3.73684	0.28053	0.40046
O	4.74585	-0.58302	0.80678
O	4.1393	1.6116	0.43977
C	6.26784	2.7693	0.51788
H	5.7982	3.74011	0.70718
H	7.26695	2.78827	0.96567
H	6.37351	2.65034	-0.56261
C	5.12448	1.9716	2.60275
H	6.0438	2.08385	3.18539
H	4.56761	2.91203	2.66291
H	4.51647	1.1874	3.0644
C	6.71855	0.02974	-0.4225
H	7.68717	0.53851	-0.40892
H	6.89672	-1.03513	-0.60164
H	6.1344	0.421	-1.26131
C	6.81143	-0.36186	2.05307
H	7.12923	-1.38227	1.81576
H	7.7119	0.24234	2.20555
H	6.25013	-0.3929	2.98937
O	2.51382	-0.12483	0.01787
Ag	1.01875	1.2298	-0.58248
O	1.78288	-4.51084	-0.39918
H	0.78799	-4.05579	-0.69791
H	2.2329	-4.78916	-1.21209
O	-0.58792	2.534	-1.21255
C	-1.13334	3.61833	-0.39959
C	-1.48569	2.22464	-2.33146
C	-2.17819	4.27204	-1.29401
H	-1.57696	3.18727	0.50514
H	-0.30218	4.27154	-0.12326
C	-2.72971	3.07399	-2.08415
H	-0.96431	2.50277	-3.25352

H	-1.67729	1.14908	-2.32783
H	-1.70508	4.99445	-1.96775
H	-2.94496	4.78967	-0.71233
H	-3.21209	3.36531	-3.0204
H	-3.45541	2.51924	-1.4804
H	-0.27858	-2.29745	-3.04173

Zero-point correction= 0.454535 (Hartree/Particle)
Thermal correction to Energy= 0.492355
Thermal correction to Enthalpy= 0.493346
Thermal correction to Gibbs Free Energy= 0.369915
SCF Done: E(RB3LYP) = -4120.20262777
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.392

TS6-1S

C	-5.96613	-0.68495	-0.85218
C	-4.83291	-1.46145	-0.62261
C	-3.76791	-0.94808	0.12966
C	-3.84533	0.35165	0.64765
C	-4.98356	1.12579	0.42819
C	-6.03496	0.60223	-0.32123
H	-6.78761	-1.08816	-1.43382
H	-4.76817	-2.46603	-1.02207
H	-3.01916	0.77362	1.20896
H	-5.0371	2.13109	0.83061
N	-2.35149	-2.80767	-0.45325
N	-2.62207	-1.74476	0.36
C	-1.22777	-3.31955	0.04226
Br	-7.59645	1.67024	-0.63157
C	-1.672	-1.6196	1.3415
C	-0.7253	-2.63093	1.19514
H	-1.76189	-0.84761	2.093
Ag	1.49843	-1.70375	0.86067
C	2.92188	2.73276	1.33866
C	3.64236	3.03766	-0.03608
B	3.0219	0.82658	0.06602
O	2.30294	1.44029	1.08199
O	3.9338	1.69809	-0.52875
C	4.9504	3.81462	0.07851
H	5.3809	3.9619	-0.91745
H	4.779	4.80289	0.51757
H	5.68484	3.28558	0.68957
C	2.72013	3.70459	-1.06374
H	2.49734	4.74152	-0.79521
H	3.21584	3.70683	-2.03973

H	1.7743	3.16331	-1.1643
C	3.90195	2.53973	2.502
H	4.3689	3.48358	2.79911
H	3.35717	2.14363	3.36445
H	4.69288	1.82791	2.24609
C	1.83242	3.72753	1.72891
H	1.38258	3.42643	2.68044
H	2.24966	4.73156	1.85876
H	1.03893	3.77442	0.97991
O	2.86829	-0.45233	-0.31656
Ag	4.04606	-0.91926	-2.06641
O	1.30782	-3.1363	2.73618
H	0.2707	-3.02618	2.09559
H	1.69512	-4.00425	2.54494
H	-0.80651	-4.19477	-0.44195

Zero-point correction= 0.335392 (Hartree/Particle)
Thermal correction to Energy= 0.366146
Thermal correction to Enthalpy= 0.367137
Thermal correction to Gibbs Free Energy= 0.262013
SCF Done: E(RB3LYP) = -3887.61999962
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.279354

TS3-1

C	7.79442	-2.04447	-0.23283
C	6.48794	-2.50848	-0.14771
C	5.43737	-1.58087	-0.15553
C	5.6694	-0.20862	-0.24639
C	6.97949	0.25592	-0.332
C	8.02563	-0.66741	-0.32419
H	8.62173	-2.74488	-0.22783
H	6.27863	-3.5705	-0.07608
H	4.83229	0.48127	-0.25003
H	7.17809	1.31869	-0.40404
N	3.62886	-3.08674	0.00956
N	4.07716	-2.00879	-0.07194
C	1.37033	-3.10243	0.10011
Br	9.82185	-0.03718	-0.44133
C	1.81922	-0.54066	-0.06134
C	1.44212	-1.8648	0.02844
H	2.09593	-0.12534	-1.02909
H	2.16271	-0.01788	0.82988
C	-2.47937	4.02831	-0.11596
C	-3.94816	3.68775	0.35999
B	-2.75214	1.75838	0.04833

O	-1.7912	2.75787	0.08421
O	-4.04375	2.26292	0.06075
C	-5.05577	4.42182	-0.38916
H	-6.03174	4.10901	-0.00425
H	-4.9707	5.5037	-0.2444
H	-5.03098	4.21121	-1.46038
C	-4.14126	3.84155	1.87326
H	-4.1417	4.89311	2.17486
H	-5.10524	3.40733	2.15623
H	-3.35699	3.32248	2.43303
C	-2.39191	4.35575	-1.61113
H	-2.83982	5.32775	-1.83762
H	-1.33919	4.38997	-1.9085
H	-2.89199	3.59506	-2.21874
C	-1.76945	5.10326	0.70101
H	-0.75871	5.25648	0.30935
H	-2.30238	6.05726	0.63364
H	-1.68642	4.82462	1.75364
O	-2.45591	0.44222	0.00756
Ag	-4.08033	-0.91915	-0.01163
Ag	-0.36901	-0.09136	-0.01607
C	1.28602	-4.55611	0.1845
H	0.24997	-4.90982	0.24386
H	1.75079	-5.01053	-0.69668
H	1.81805	-4.91147	1.07318
O	-5.67466	-2.38199	-0.05692
C	-6.57353	-2.65691	1.06932
C	-6.23043	-2.91886	-1.29904
C	-7.82276	-3.26738	0.4389
H	-6.05663	-3.35344	1.73721
H	-6.7592	-1.71741	1.59513
C	-7.27756	-3.92396	-0.83992
H	-6.6725	-2.09316	-1.86812
H	-5.4036	-3.35307	-1.86594
H	-8.54455	-2.48384	0.18598
H	-8.30763	-3.9786	1.11173
H	-8.04769	-4.08349	-1.59845
H	-6.80835	-4.88674	-0.61128

Zero-point correction= 0.467338 (Hartree/Particle)
Thermal correction to Energy= 0.506526
Thermal correction to Enthalpy= 0.507518
Thermal correction to Gibbs Free Energy= 0.383416
SCF Done: E(RB3LYP) = -4083.43140416
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.402775

TS3-1'

C	-7.59379	-0.33653	-2.73723
C	-6.23821	-0.10331	-2.90237
C	-5.39592	-0.29763	-1.79055
C	-5.86466	-0.7178	-0.53843
C	-7.22352	-0.95342	-0.39393
C	-8.07265	-0.75874	-1.48975
H	-8.2694	-0.19351	-3.57215
H	-5.83141	0.21889	-3.85412
H	-5.16535	-0.84831	0.27797
H	-7.61525	-1.28167	0.56124
N	-3.02851	0.14201	-2.40857
N	-4.04431	-0.06741	-1.96987
C	-1.16562	0.23458	-0.40331
Br	-9.9309	-1.07424	-1.28242
C	-3.01003	-0.02267	1.48706
C	-2.16328	0.08964	0.61275
H	-1.26716	1.15065	-0.9935
Ag	0.7577	0.44958	0.51852
C	3.35957	4.06581	2.12152
C	4.79925	3.41871	2.20877
B	3.23718	1.81418	1.70973
O	2.59109	3.01747	1.46501
O	4.49061	1.99683	2.28228
C	5.60958	3.80905	3.44129
H	6.57818	3.29901	3.42284
H	5.79983	4.88719	3.45654
H	5.0992	3.53261	4.36637
C	5.63234	3.63252	0.93923
H	5.95789	4.67222	0.83928
H	6.52514	3.00116	0.98733
H	5.07076	3.35865	0.04064
C	2.72011	4.29845	3.49584
H	3.20462	5.11879	4.03377
H	1.66574	4.55778	3.3588
H	2.76992	3.39977	4.11853
C	3.2728	5.33601	1.28033
H	2.2397	5.69792	1.26469
H	3.8984	6.12779	1.70536
H	3.58529	5.16146	0.24855
O	2.71252	0.60585	1.42517
Ag	3.89593	-1.09858	1.81901
C	-3.90476	-0.13042	2.64059

H	-4.76761	0.54057	2.54981
H	-4.29019	-1.15026	2.75798
H	-3.38492	0.13102	3.57126
H	-1.06021	-0.64033	-1.05259
O	5.04287	-2.89946	2.17516
C	6.21452	-3.29352	1.38619
C	4.97997	-3.66678	3.41819
C	6.985	-4.26437	2.27816
H	5.84715	-3.76652	0.46974
H	6.77378	-2.39011	1.13135
C	5.88273	-4.86604	3.16519
H	5.34901	-3.03701	4.23578
H	3.93158	-3.91789	3.59467
H	7.71384	-3.72406	2.89117
H	7.51828	-5.01539	1.69049
H	6.26812	-5.28896	4.0961
H	5.33635	-5.64786	2.62698

Zero-point correction= 0.467395 (Hartree/Particle)
Thermal correction to Energy= 0.506939
Thermal correction to Enthalpy= 0.507931
Thermal correction to Gibbs Free Energy= 0.380527
SCF Done: E(RB3LYP) = -4083.42405164
Thermal correction to Gibbs free energy (ZPG) from GoodVibes: 0.402515