Supporting Information

Electrocatalytic Three-Component Synthesis of 4-Halopyrazoles with Sodium Halide as Halogen Source

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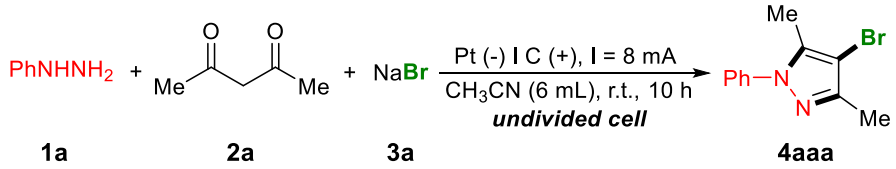
1. General Information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anode electrode is graphite (15 mm × 10 mm × 2 mm) and cathode electrode is platinum electrode (15 mm ×10 mm × 0.1 mm). The instrument for cyclic voltammetrys is CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in CH_3CN) as counter and reference electrode. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. ^{1}H NMR spectra were recorded at 500 MHz, ^{13}C NMR spectra were recorded at 125 MHz and ^{19}F NMR spectra were recorded at 471 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1} H NMR: $CDCl_3$ 7.26 ppm, ^{13}C NMR: $CDCl_3$ 77.0 ppm), the chemical shifts (δ) were expressed in ppm and J values were given in Hz. HRMS were performed on a spectrometer operating on ESI-TOF.

2. Experimental Section

Table S1. Optimization of the reaction conditions

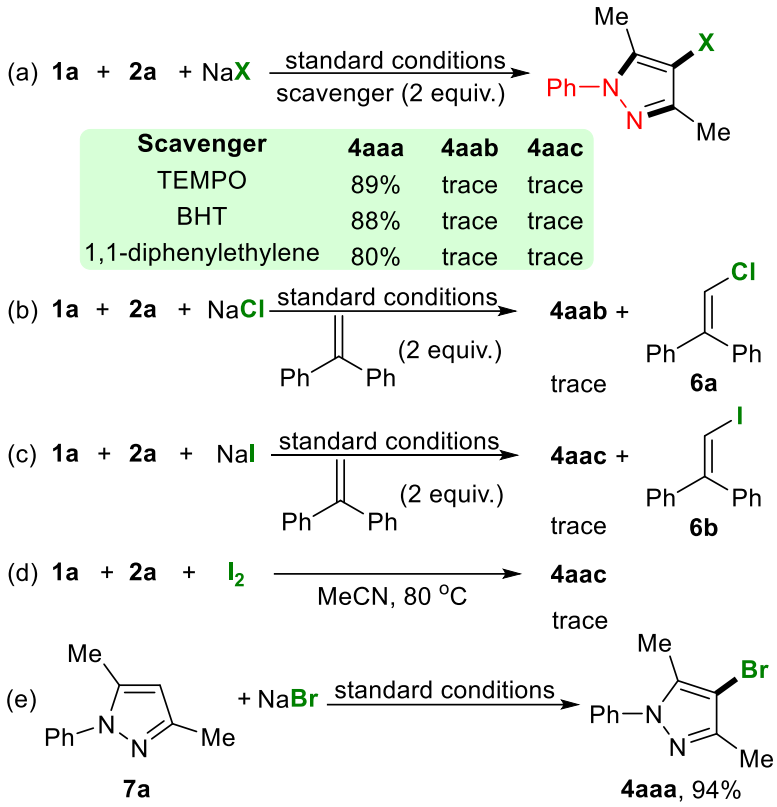


1a **2a** **3a** **4aaa**

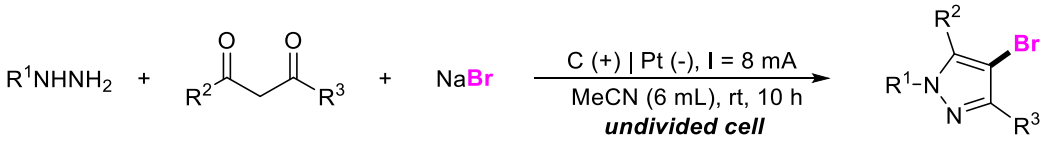
Entry	Variation from the standard reaction conditions	Yield[b]
1	**None**	**96%**
2	C(+)|C(-) instead of C(+)|Pt (-)	76%
3	C(+)|Cu(-) instead of C(+)|Pt (-)	80%
4	C(+)|Ni(-) instead of C(+)|Pt (-)	31%
5	Pt(+)|Pt(-) instead of C(+)|Pt (-)	89%
6	Pt(+)|Mg(-) instead of C(+)|Pt (-)	79%
7	Pt(+)|Fe(-) instead of C(+)|Pt (-)	72%
8	Pt(+)|Zn (-) instead of C(+)|Pt (-)	86%
9	NH_4Br instead of NaBr	90%
10	TBAB instead of NaBr	73%
11	NBS instead of NaBr	76%
12	$MgBr_2$ instead of NaBr	44%
13	CsBr instead of NaBr	51%
14	EtOH instead of MeCN	79%
15	DMF instead of MeCN	23%
16	DMSO instead of MeCN	36%
17	DCE instead of MeCN	*trace*
18	THF instead of MeCN	*trace*
19	1.0 equiv. of NaBr	84%
20	4 mL MeCN instead of 6 ml	93%
21	5 mA, 10 h instead of 8 mA, 10 h	56%
22	15 mA, 4 h instead of 8 mA, 10 h	78%
23	Without electric current	*N.D.*[c]

[a]Conditions: C (15 mm × 10 mm × 2 mm) as the anode, Pt (15 mm × 10 mm × 0.1 mm) as the cathode, constant current = 8 mA, **1a** (0.5 mmol), **2a** (0.5 mmol), **3** (1 mmol), MeCN (6 mL), room temperature, in air, 10 h, undivided cell; [b]GC yields using dodecane as an internal reference. [c]No desired product.

Scheme S1 Control Experiments

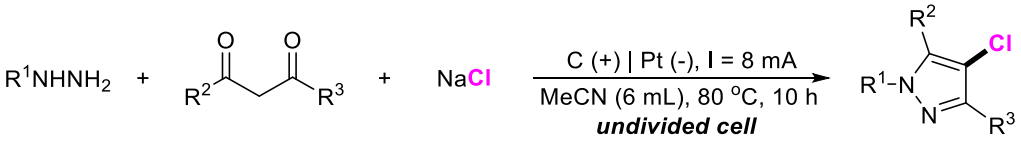


2.1 General experimental procedure A for Compounds 4aaa-4aca



In an undivided three-necked flask (25 mL) equipped with a stir bar, hydrazine (0.5 mmol), diacetone (0.5 mmol), NaBr (1.0 mmol) and MeCN (6 mL) were added. The flask was equipped with platinum electrode (15 mm × 10 mm × 0.1 mm) as cathode, graphite (15 mm × 10 mm × 2 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under room temperature for 10 h. After completion, the solvent was concentrated under reduced pressure, and the pure products **4aaa-4aca** were obtained by flash chromatography on silica gel.

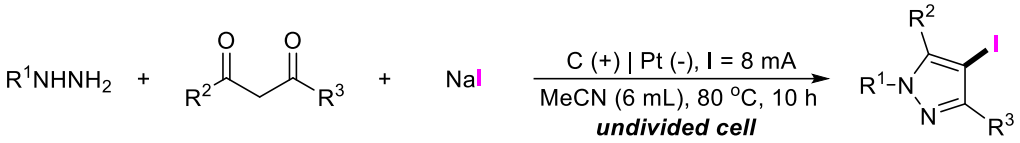
2.2 General experimental procedure B for Compounds 4aab-4bab



In an undivided three-necked flask (25 mL) equipped with a stir bar, hydrazine (0.5 mmol), diacetone (0.5 mmol), NaCl (1.0 mmol) and MeCN (6 mL) were added. The flask was equipped with platinum electrode (15 mm × 10 mm × 0.1 mm) as cathode, graphite (15 mm × 10 mm × 2 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA

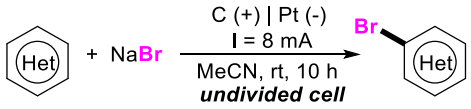
under 80 °C for 10 h. After completion, the solvent was concentrated under reduced pressure, and the pure products **4aab-4bab** were obtained by flash chromatography on silica gel.

2.3 General experimental procedure C for Compound 4aac



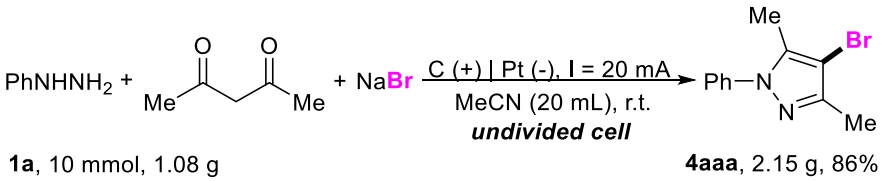
In an undivided three-necked flask (25 mL) equipped with a stir bar, hydrazine (0.5 mmol), diacetone (0.5 mmol), NaI (2.0 mmol) and MeCN (6 mL) were added. The flask was equipped with platinum electrode (15 mm × 10 mm × 0.1 mm) as cathode, graphite (15 mm × 10 mm × 2 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under 80 °C for 10 h. After completion, the solvent was concentrated under reduced pressure, and the pure product **4aac** was obtained by flash chromatography on silica gel.

2.4 General experimental procedure D for Compounds 5aa-6da



In an undivided three-necked flask (25 mL) equipped with a stir bar, aromatic heterocycles (0.5 mmol), NaBr (1.0 mmol) and MeCN (6 mL) were added. The flask was equipped with platinum electrode (15 mm × 10 mm × 0.1 mm) as cathode, graphite (15 mm × 10 mm × 2 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA for 10 h. After completion, the solvent was concentrated under reduced pressure, and the pure products **5aa-6da** were obtained by flash chromatography on silica gel.

2.5 Large-scale synthesis of 4aaa



1a, 10 mmol, 1.08 g

4aaa, 2.15 g, 86%

In an undivided three-necked flask (25 mL) equipped with a stir bar, hydrazine (10 mmol), diacetone (10 mmol), NaBr (20 mmol) and MeCN (20 mL) were added. The flask was equipped with platinum electrode (15 mm × 10 mm × 0.1 mm) as cathode, graphite (15 mm × 10 mm × 2 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under room temperature for 72 h. After completion, the solvent was concentrated under reduced pressure, and the pure product **4aaa** was obtained by flash chromatography on silica gel in the yield of 86%.

2.6 Cyclic voltammetry experiment:

CV measurements were performed on a CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in CH_3CN) as counter and reference electrode. Cyclic voltammograms of reactants and their mixtures in 0.1 M Bu_4NBF_4/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in CH_3CN) as counter and reference electrode at 50 mV/s scan rate: a) NaBr (20 mmol/L), b) NaCl (20 mmol/L), MeCN (9.5 mL), H_2O (0.5 mL), c) NaI (20 mmol/L), d) **7a** (20 mmol/L).

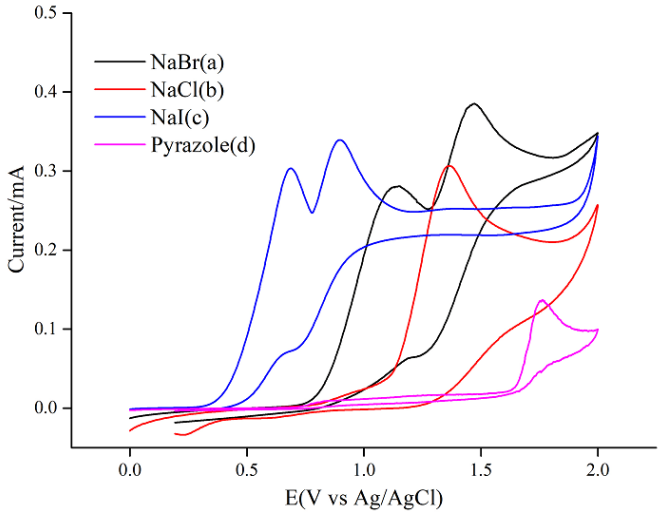
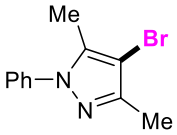
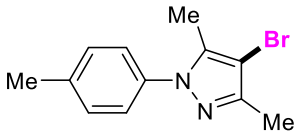


Figure S1 Cyclic voltammetry experiment

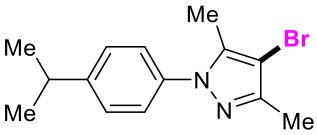
3. Characterization data of products 4aaa-4iab and 5aa-6da



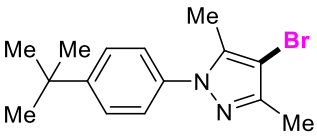
4-bromo-3,5-dimethyl-1-phenyl-1H-pyrazole **(4aaa)**[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 3H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.50, 138.72, 136.45, 128.13, 126.77, 123.60, 95.33, 11.34, 10.73.



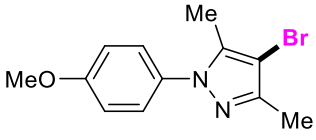
4-bromo-3,5-dimethyl-1-(p-tolyl)-1H-pyrazole **(4baa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 4H), 2.39 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.27, 137.80, 137.47, 137.39, 129.72, 124.59, 96.03, 21.13, 12.38, 11.69; HRMS: calcd for $C_{12}H_{14}BrN_2$ $[M+H]^+$ 265.0340, found 265.0344.



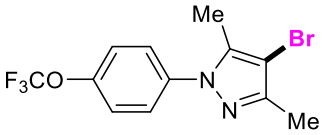
4-bromo-1-(4-isopropylphenyl)-3,5-dimethyl-1H-pyrazole **(4caa):** ^{13}C NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 4H), 2.97-2.94 (m, 1H), 2.29 (s, 6H), 1.27 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.74, 147.26, 137.59, 137.45, 127.14, 124.66, 95.98, 33.84, 23.97, 12.38, 11.70; HRMS: calcd for $C_{14}H_{18}BrN_2$ $[M+H]^+$ 293.0653, found 293.0651.



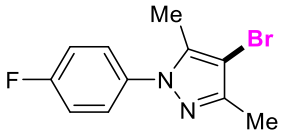
4-bromo-1-(4-(tert-butyl)phenyl)-3,5-dimethyl-1H-pyrazole **(4daa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.29 (s, 6H), 1.34 (s, 9H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 150.94, 147.25, 137.41, 137.29, 126.07, 124.27, 96.03, 34.69, 31.34, 12.40, 11.72; HRMS: calcd for $C_{15}H_{20}BrN_2$ $[M+H]^+$ 307.0810, found 307.0813.



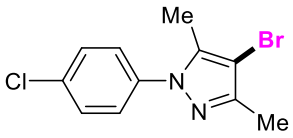
4-bromo-1-(4-methoxyphenyl)-3,5-dimethyl-1H-pyrazole **(4eaa)**[2]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.18, 147.12, 137.66, 132.95, 126.31, 114.28, 95.65, 55.57, 12.34, 11.53.



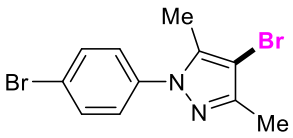
4-bromo-3,5-dimethyl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrazole **(4faa)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.26, 148.10, 138.28, 137.56, 125.88, 121.73, 120.42 (q, $J_{C\text{-}F}$ = 258.3 Hz), 96.93, 12.31, 11.74; ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.02; HRMS: calcd for $C_{12}H_{11}BrF_3N_2O$ $[M+H]^+$ 335.0007, found 335.0004.



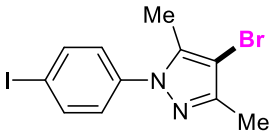
4-bromo-1-(4-fluorophenyl)-3,5-dimethyl-1H-pyrazole **(4gaa)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.17-7.14 (m, 2H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161. 91 (d, $J_{C\text{-}F}$ = 248.5 Hz, 2H), 147.70, 137.64, 135.96, 126.64 (d, $J_{C\text{-}F}$ = 1.1 Hz), 116.21 (d, $J_{C\text{-}F}$ = 23.1 Hz), 96.37, 12.36, 11.65; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.39; HRMS: calcd for $C_{11}H_{11}BrFN_2$ $[M+H]^+$ 269.0090, found 269.0088.



4-bromo-1-(4-chlorophenyl)-3,5-dimethyl-1H-pyrazole **(4haa)** [3]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.41-7.36 (m, 2H), 2.30 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.58, 139.82, 137.52, 129.19, 127.83, 124.69, 96.38, 12.39, 11.78.

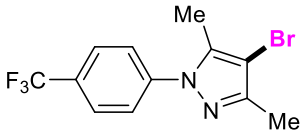


4-bromo-1-(4-bromophenyl)-3,5-dimethyl-1H-pyrazole **(4iaa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.05, 138.83, 137.47, 132.32, 125.96, 121.40, 96.96, 12.40, 11.86; HRMS: calcd for $C_{11}H_{11}Br_2N_2$ $[M+H]^+$ 328.9289, found 328.9291.

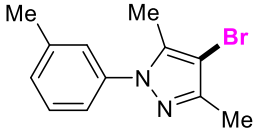


4-bromo-1-(4-iodophenyl)-3,5-dimethyl-1H-pyrazole **(4jaa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz,

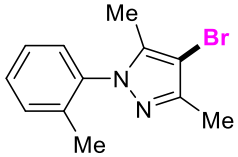
$CDCl_3$) δ 148.11, 139.52, 138.30, 137.45, 126.14, 97.02, 92.63, 12.40, 11.88; HRMS: calcd for $C_{11}H_{11}BrIN_2$ $[M+H]^+$ 376.9150, found 376.9142.



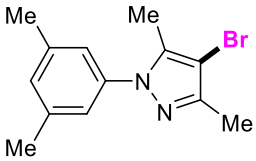
4-bromo-3,5-dimethyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole **(4kaa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.62, 142.56, 137.58, 129.44 (d, $J_{C\text{-}F}$ = 33.0 Hz), 126.41(d, $J_{C\text{-}F}$ = 3.8 Hz), 124.17, 123.80 (d, $J_{C\text{-}F}$ = 274.8 Hz), 97.75, 12.38, 12.05; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.46; HRMS: calcd for $C_{12}H_{11}BrF_3N_2$ $[M+H]^+$ 319.0058, found 319.0064.



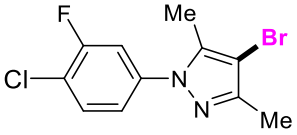
4-bromo-3,5-dimethyl-1-(m-tolyl)-1H-pyrazole **(4laa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J = 8.0 Hz, 1H), 7.24 (s, 1H), 7.17 (t, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.39, 139.73, 139.38, 137.47, 128.86, 128.61, 125.41, 121.63, 96.22, 21.37, 12.39, 11.77; HRMS: calcd for $C_{12}H_{14}BrN_2$ $[M+H]^+$ 265.0340, found 265.0344.



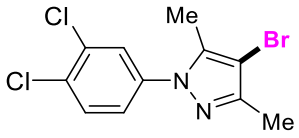
4-bromo-3,5-dimethyl-1-(o-tolyl)-1H-pyrazole **(4maa):**^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.07, 138.61, 138.44, 136.08, 131.01, 129.38, 127.79, 126.64, 94.54, 17.26, 12.43, 10.72; HRMS: calcd for $C_{12}H_{14}BrN_2$ $[M+H]^+$ 265.0340, found 265.0344.



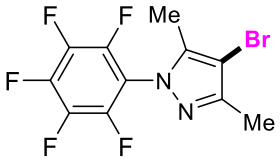
4-bromo-1-(3,5-dimethylphenyl)-3,5-dimethyl-1H-pyrazole **(4naa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 3H), 2.35 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.22, 139.67, 138.98, 137.43, 129.52, 122.45, 96.03, 21.27, 12.38, 11.76; HRMS: calcd for $C_{13}H_{16}BrN_2$ $[M+H]^+$ 279.0473, found 279.0478.



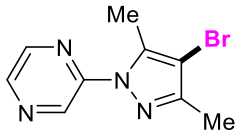
4-bromo-1-(3-chloro-4-fluorophenyl)-3,5-dimethyl-1H-pyrazole **(4oaa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 6.5 Hz, 1H), 7.28 (t, J = 8.5 Hz, 1H), 7.23 (t, J = 8.5 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.38 (d, $J_{C\text{-}F}$ = 251.0 Hz), 148.23, 137.66, 136.36 (d, $J_{C\text{-}F}$ = 0.4 Hz), 127.04, 124.22 (d, $J_{C\text{-}F}$ = 7.4 Hz), 121.77(d, $J_{C\text{-}F}$ = 19.0 Hz), 116.92 (d, $J_{C\text{-}F}$ = 22.7 Hz), 97.01, 12.35, 11.75; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.76-115.80 (m, 1F); HRMS: calcd for $C_{11}H_{10}BrClFN_2$ $[M+H]^+$ 302.9700, found 302.9767.



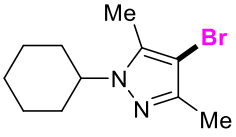
4-bromo-1-(3,4-dichlorophenyl)-3,5-dimethyl-1H-pyrazole **(4paa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 5.5 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.52, 139.01, 137.59, 133.25, 131.76, 130.76, 126.20, 123.30, 97.48, 12.38, 11.94; HRMS: calcd for $C_{11}H_{10}BrCl_2N_2$ $[M+H]^+$ 318.9404, found 318.9401.



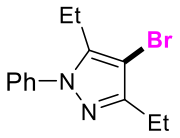
4-bromo-3,5-dimethyl-1-(perfluorophenyl)-1H-pyrazole **(4qaa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.52, 145.0-144.9 (m), 143.08-142.87 (m), 140.29, 139.03-138.77 (m), 136.99-136.79 (m), 96.86, 12.55, 10.37; ^{19}F NMR (471 MHz, $CDCl_3$) δ -145.05--145.09 (m), -151.1--151.20 (m), -160.4--160.52 (m); HRMS: calcd for $C_{11}H_7BrF_5N_2$ $[M+H]^+$ 340.9713, found 340.9710.



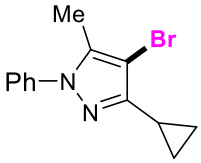
2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)pyrazine **(4raa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.45 (s, 1H), 8.35 (s, 1H), 2.66 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.76, 149.41, 141.19, 141.11, 139.77, 138.01, 99.92, 13.55, 12.61; HRMS: calcd for $C_9H_{10}BrN_4$ $[M+H]^+$ 253.0089, found 253.0092.



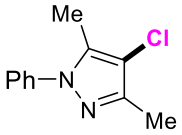
4-bromo-1-cyclohexyl-3,5-dimethyl-1H-pyrazole **(4saa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (t, J = 10.5 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 1.92-1.86 (m, 6H), 1.69 (t, J = 7.0 Hz, 1H), 1.38-1.25 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.30, 135.83, 93.59, 58.46, 32.65, 25.75, 25.15, 12.38, 10.26; HRMS: calcd for $C_{11}H_{18}BrN_2$ $[M+H]^+$ 257.0653, found 257.0658.



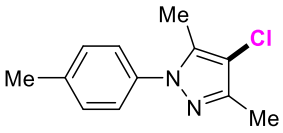
4-bromo-3,5-diethyl-1-phenyl-1H-pyrazole **(4aba)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.38 (m, 3H), 7.33-7.32 (m, 2H), 2.64-2.60 (m, 4H), 1.22 (t, *J* = 7.5 Hz, 3H), 1.04 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.42, 141.91, 138.90, 128.17, 127.08, 124.27, 93.32, 19.39, 17.64, 11.98, 11.88; HRMS: calcd for $C_{13}H_{16}BrN_2$ $[M+H]^+$ 279.0497, found 279.0495.



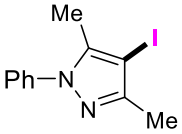
4-bromo-3-cyclopropyl-5-methyl-1-phenyl-1H-pyrazole **(4aca):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 2.28 (s, 3H), 1.80-1.74 (m, 1H), 0.87 (d, *J* = 8.0 Hz, 2H), 0.71 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.76, 140.71, 139.94, 128.87, 127.52, 124.69, 96.62, 12.37, 6.98, 6.93; HRMS: calcd for $C_{13}H_{14}BrN_2$ $[M+H]^+$ 277.0340, found 277.0346.



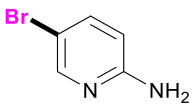
4-chloro-3,5-dimethyl-1-phenyl-1H-pyrazole **(4aab)**[2]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.41-7.37 (m, 3H), 2.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.07, 139.75, 135.73, 129.20, 127.75, 124.56, 109.82, 11.44, 10.86.



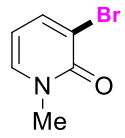
4-chloro-3,5-dimethyl-1-(p-tolyl)-1H-pyrazole **(4bab)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.26 (m, 4H), 2.40 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.77, 137.74, 137.30, 135.71, 129.73, 124.50, 109.47, 21.13, 11.43, 10.78; HRMS: calcd for $C_{12}H_{14}ClN_2$ $[M+H]^+$ 221.0846, found 221.0849.



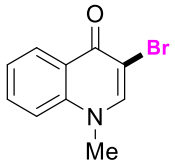
3-cyclopropyl-5-methyl-1-phenyl-4-thiocyanato-1H-pyrazole **(4aac)**[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.5 Hz, 2H), 7.39-7.35 (m, 3H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.76, 140.89, 139.89, 129.18, 127.92, 124.80, 65.41, 14.18, 13.51.



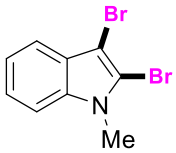
5-bromopyridin-2-amine **(5aa)**[4]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 2.5 Hz, 1 H), 7.36 (dd, J_1 = 7.5 Hz, J_2 = 2.5 Hz, 1H), 6.50 (d, J = 7.5 Hz, 1H), 3.53 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.05, 148.71, 140.14, 110.07, 108.31.



3-bromo-1-methylpyridin-2(1H)-one **(5ba)**[5]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.49 (d, J = 8.5 Hz, 1 H), 6.41 (d, J = 8.5 Hz, 1H), 4.53 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.53, 142.58, 138.14, 121.90, 97.67, 37.74.



3-bromo-1-methylquinolin-4(1H)-one **(5ca)**[6]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 2.0 Hz, 1H), 7.93 (s, 1H), 7.76 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 1H), 7.28 (d, J = 7.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.44, 143.92, 138.58, 135.40, 129.93, 126.48, 118.35, 117.34, 105.47, 40.92.



2,3-dibromo-1-methyl-1H-indene **(5da)**[7]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 1H), 7.28-7.23 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H,), 3.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.34, 126.96, 122.90, 120.80, 118.87, 114.90, 109.62, 92.68, 32.36.

4. References

[1] Bondarenko, O. B.; Karetnikov, G. L.; Komarov, A. I.; Pavlov, A. I.; Nikolaeva, S. N. *Journal of Organic Chemistry*, **2021**, *86*, 322.

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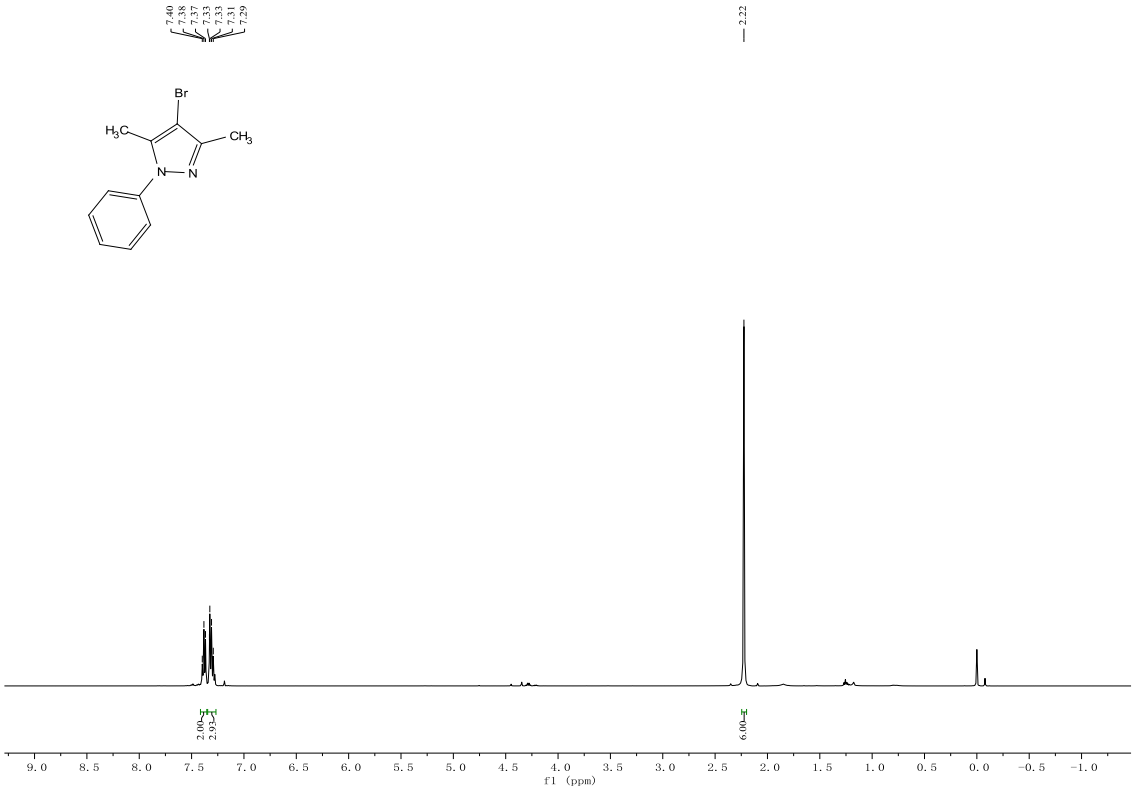
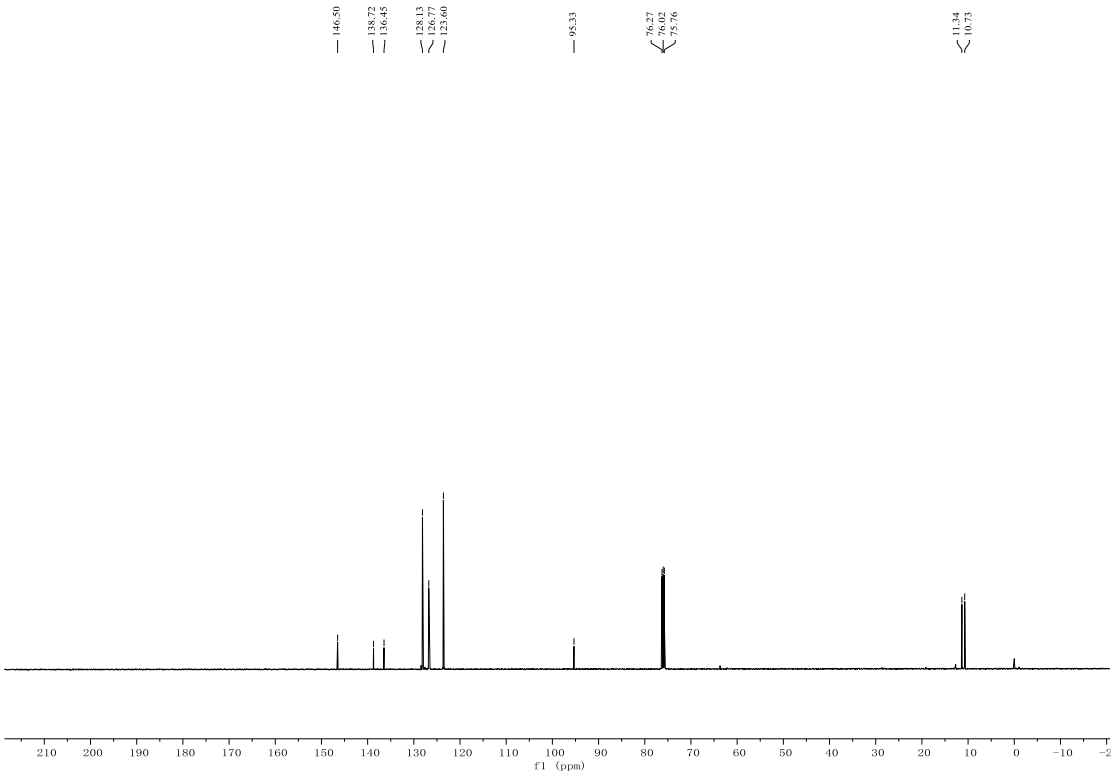
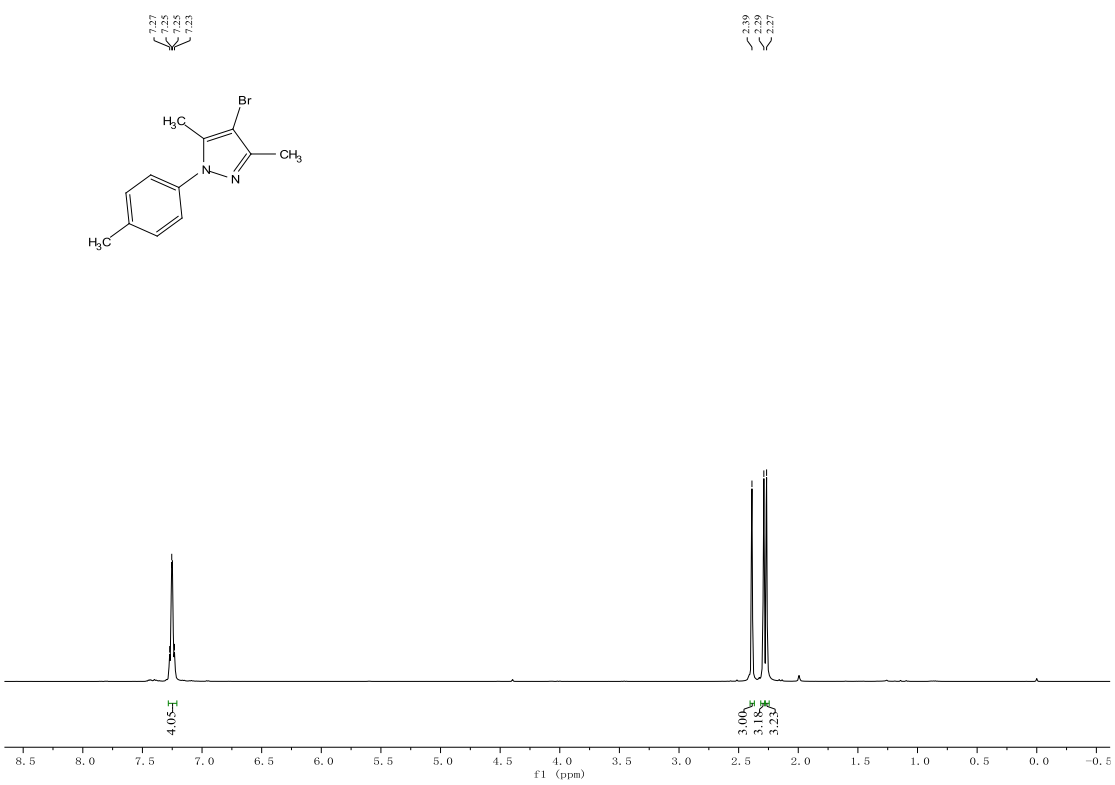
5. ^{1}H and ^{13}C NMR spectra of products



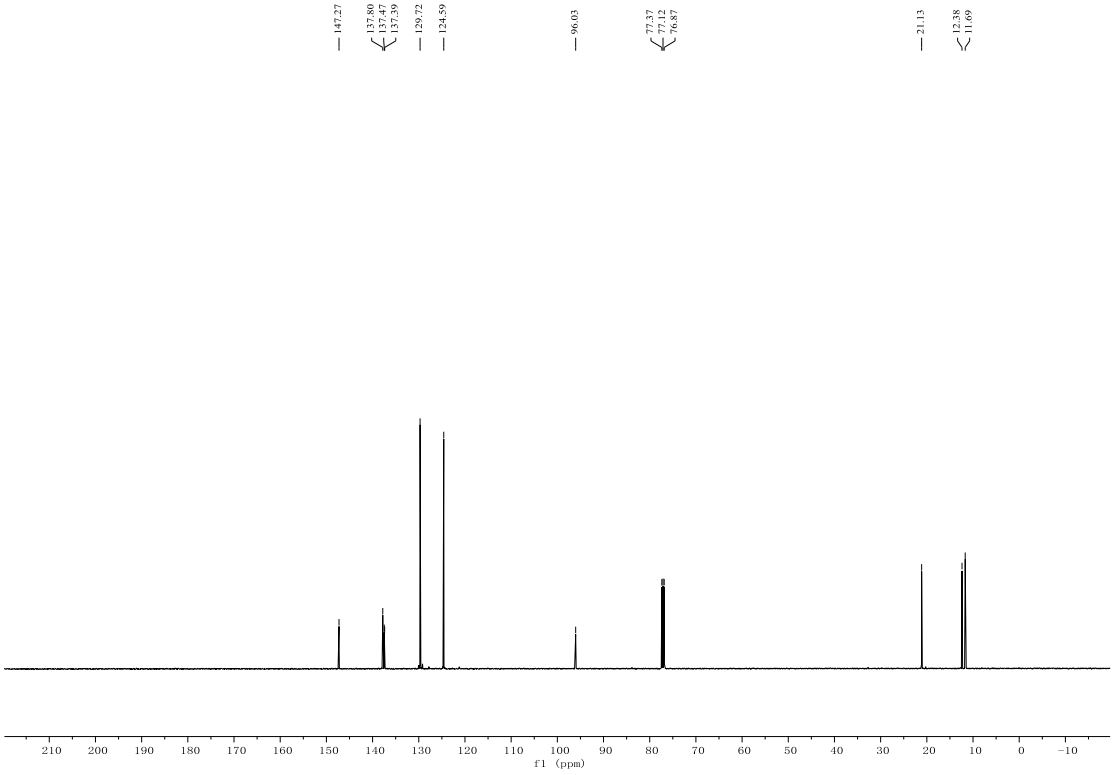
^{1}H NMR of compound **4aaa**



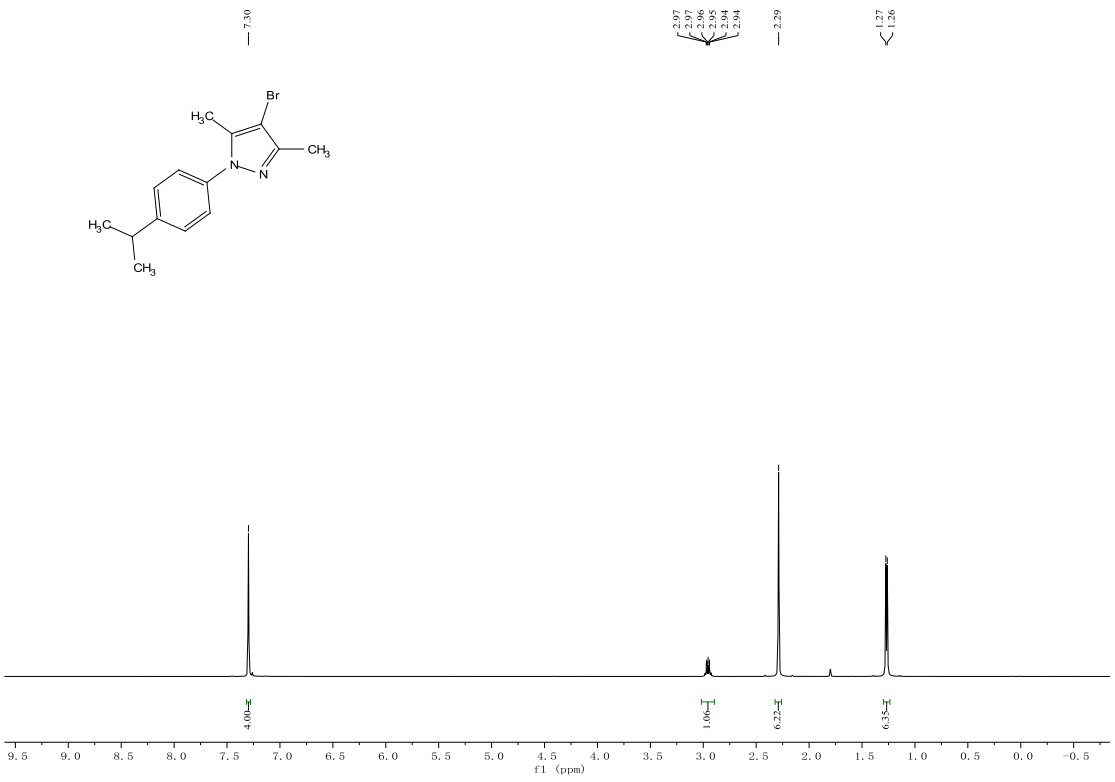
^{13}C NMR of compound **4aaa**



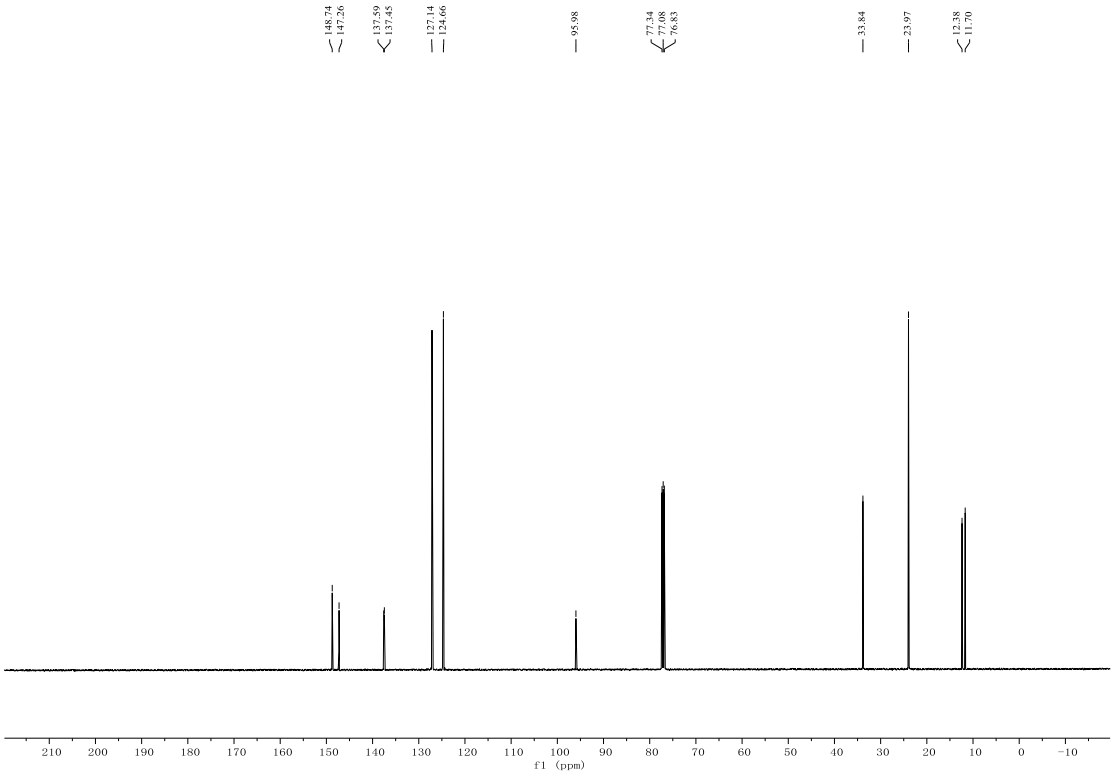
^{1}H NMR of compound **4baa**



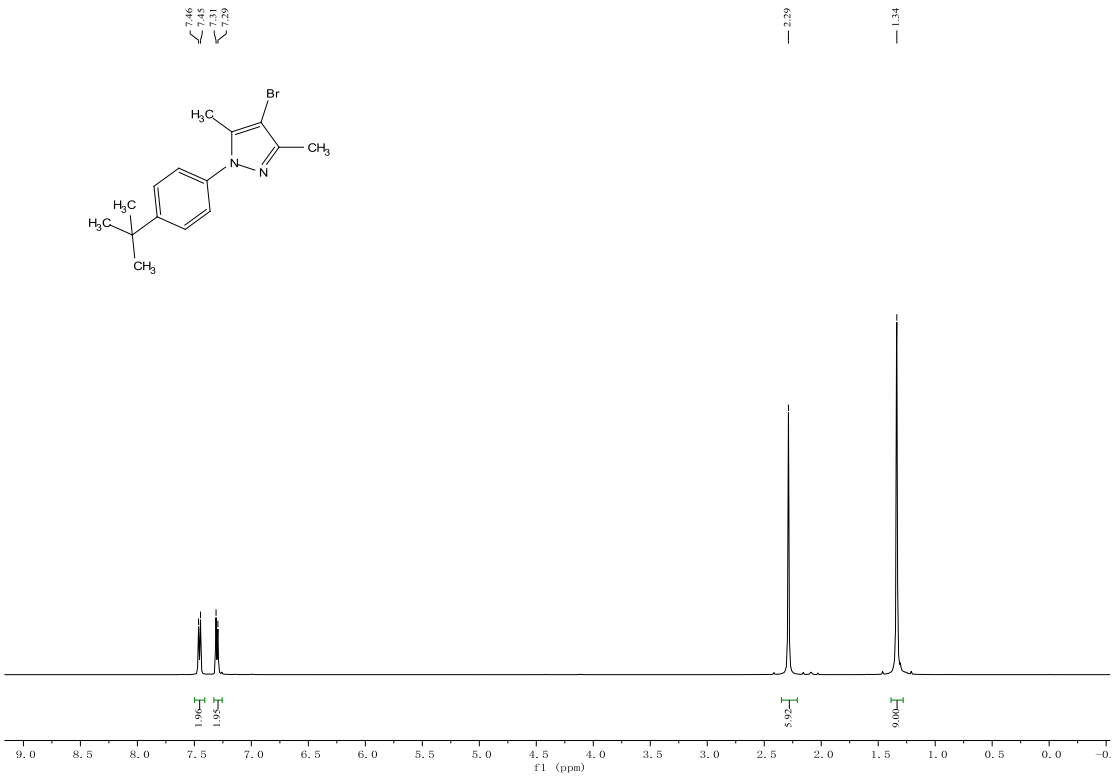
^{13}C NMR of compound **4baa**



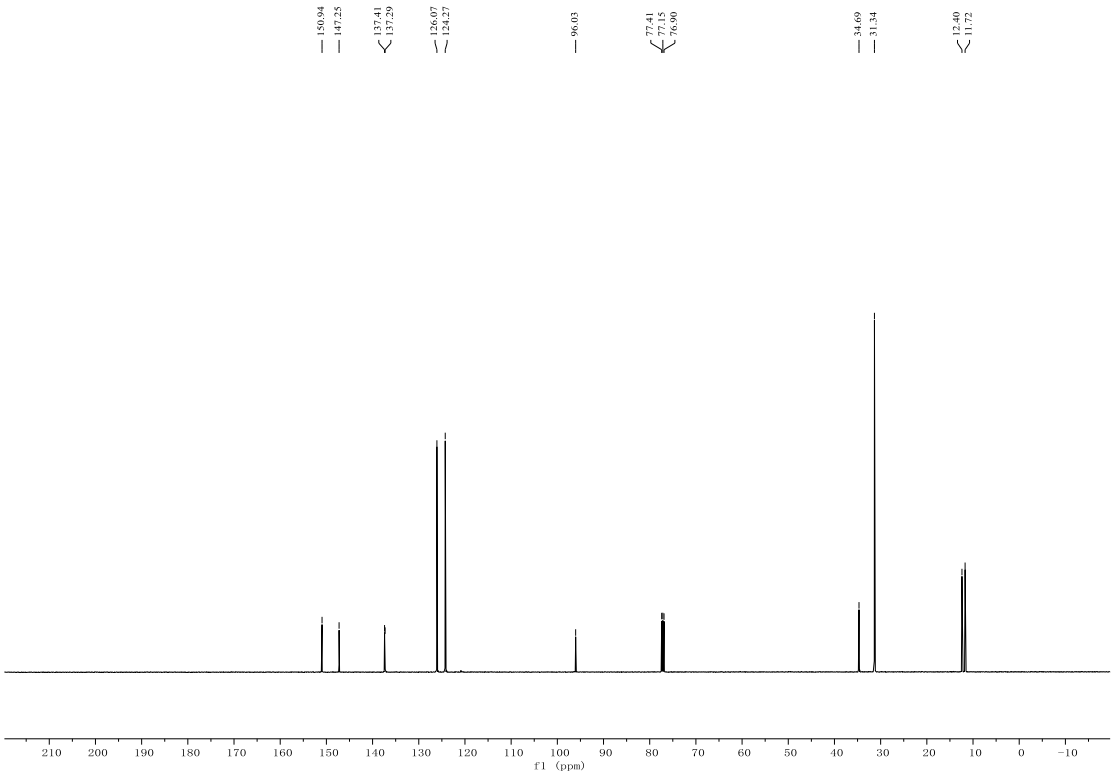
^{1}H NMR of compound **4caa**



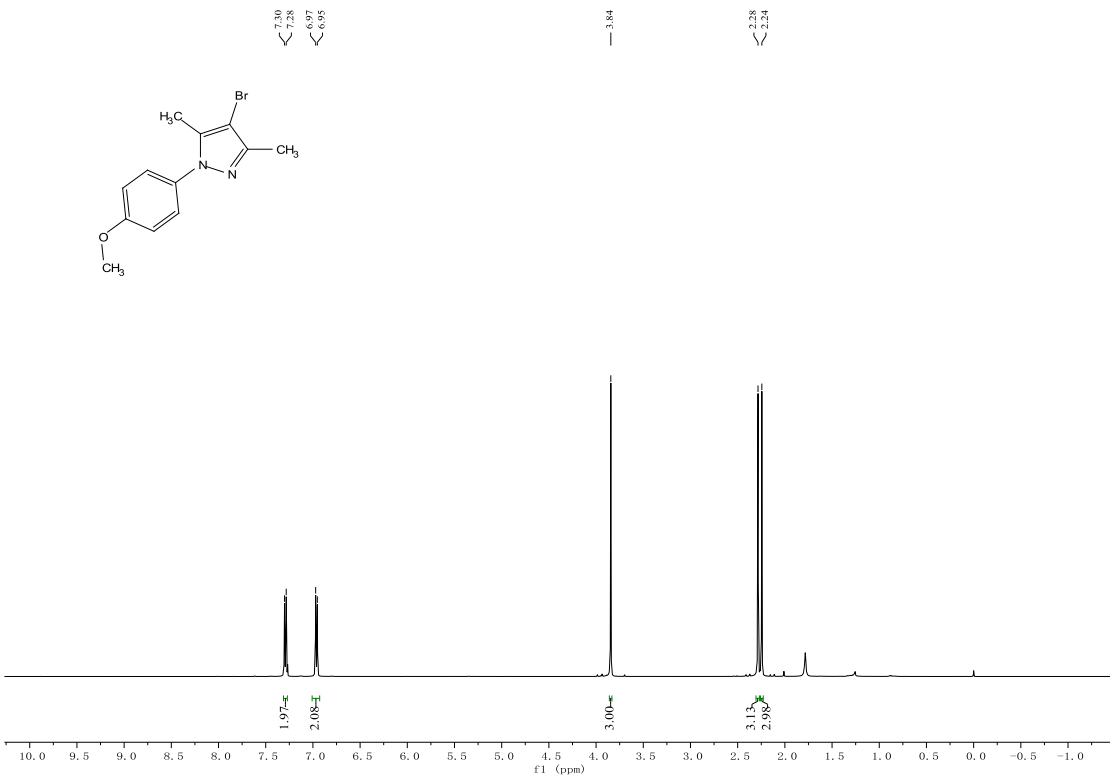
^{13}C NMR of compound **4caa**



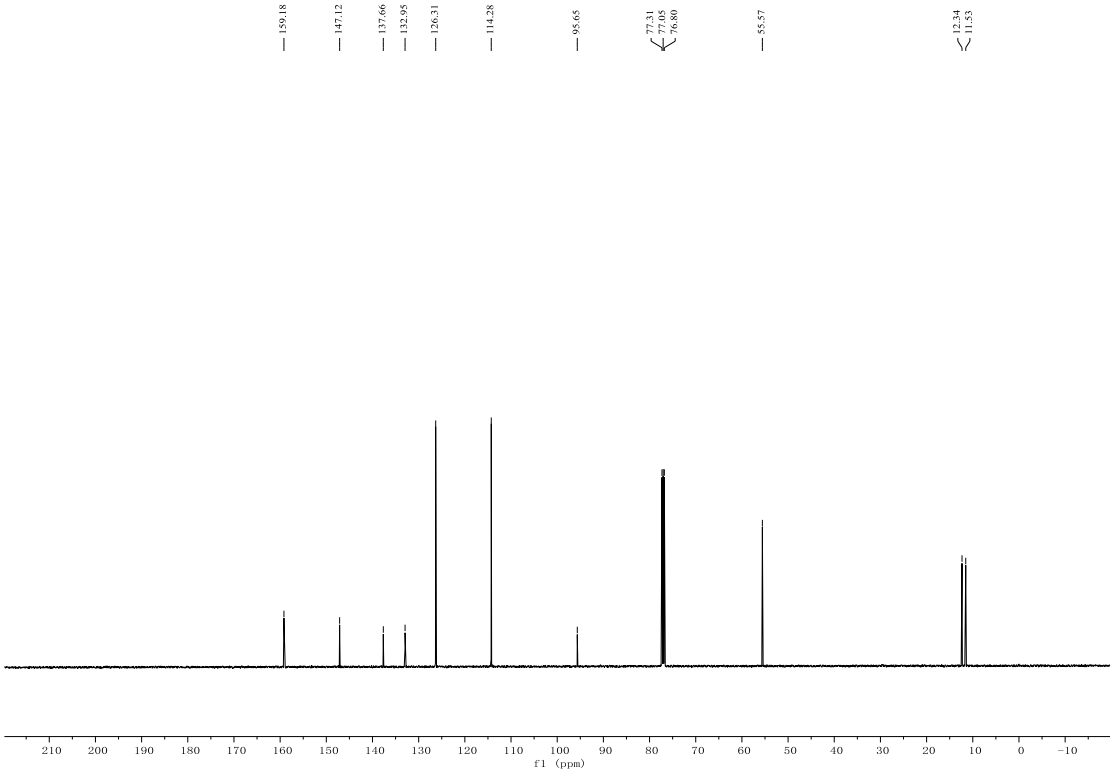
^{1}H NMR of compound **4daa**



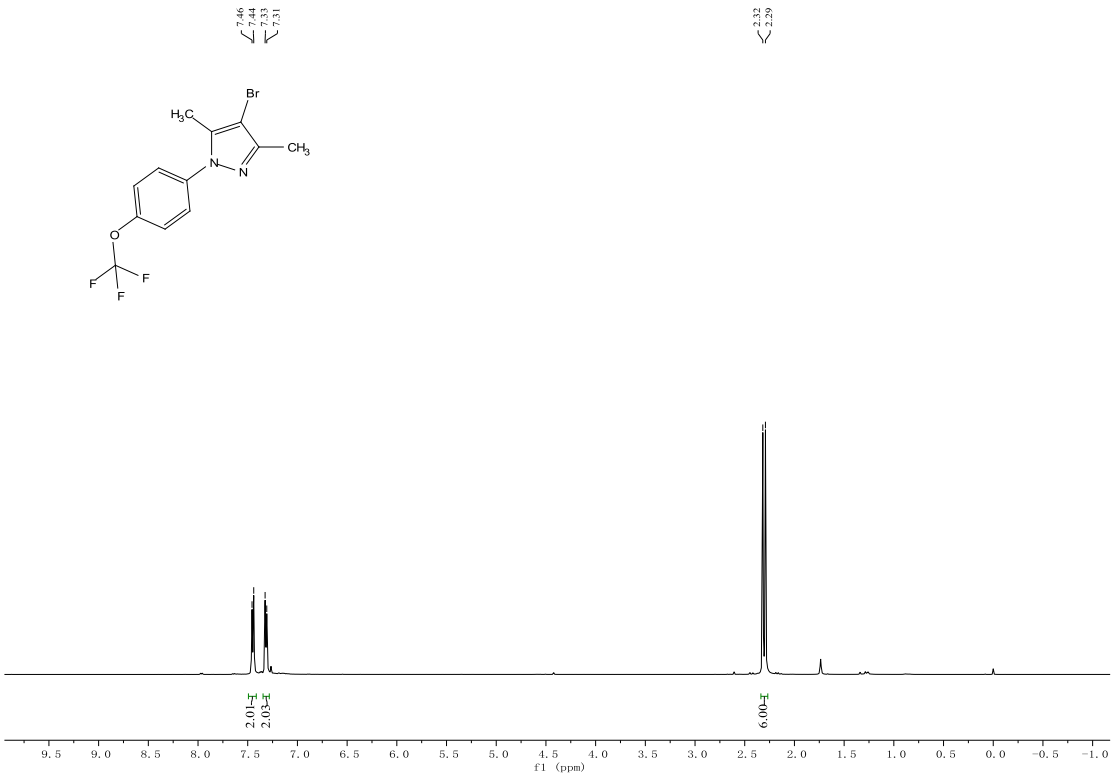
^{13}C NMR of compound **4daa**



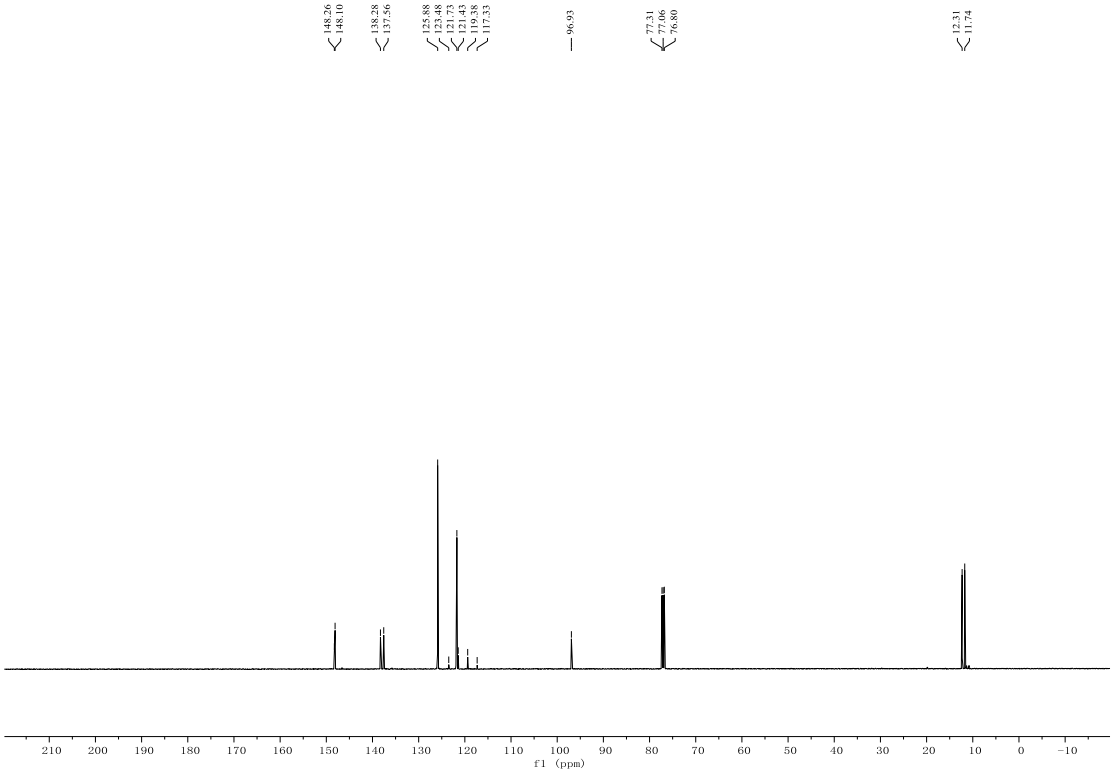
^{1}H NMR of compound **4eaa**



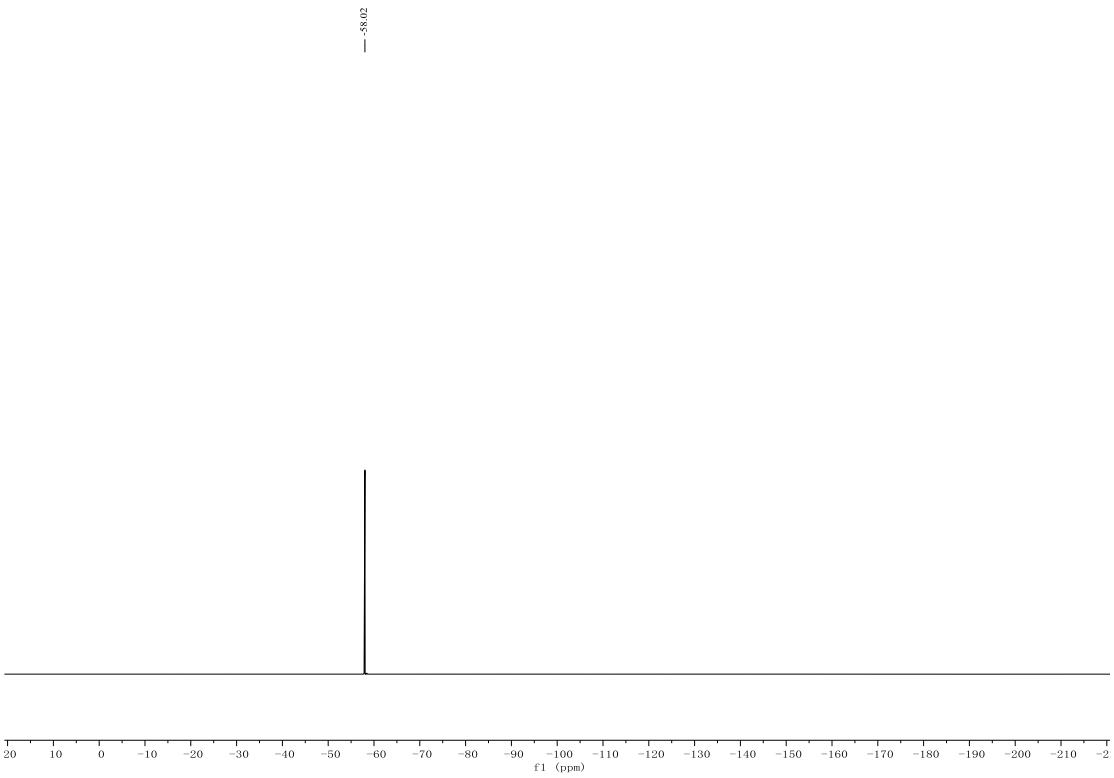
^{13}C NMR of compound **4eaa**



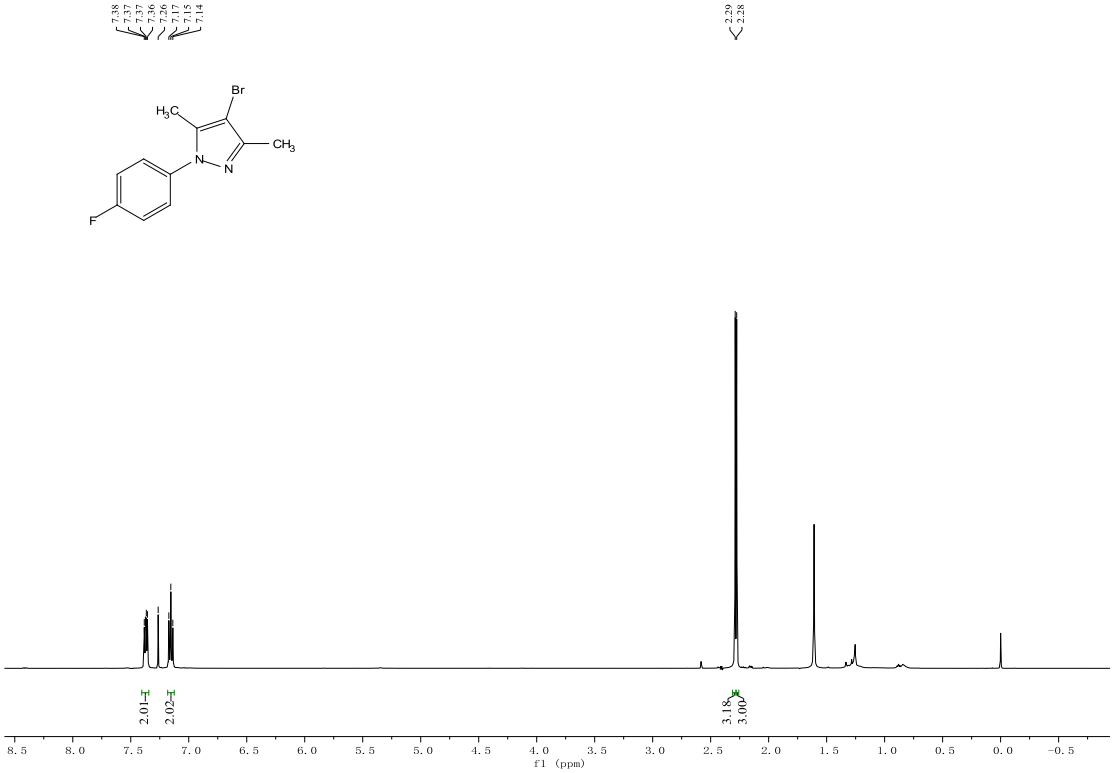
^{1}H NMR of compound **4faa**



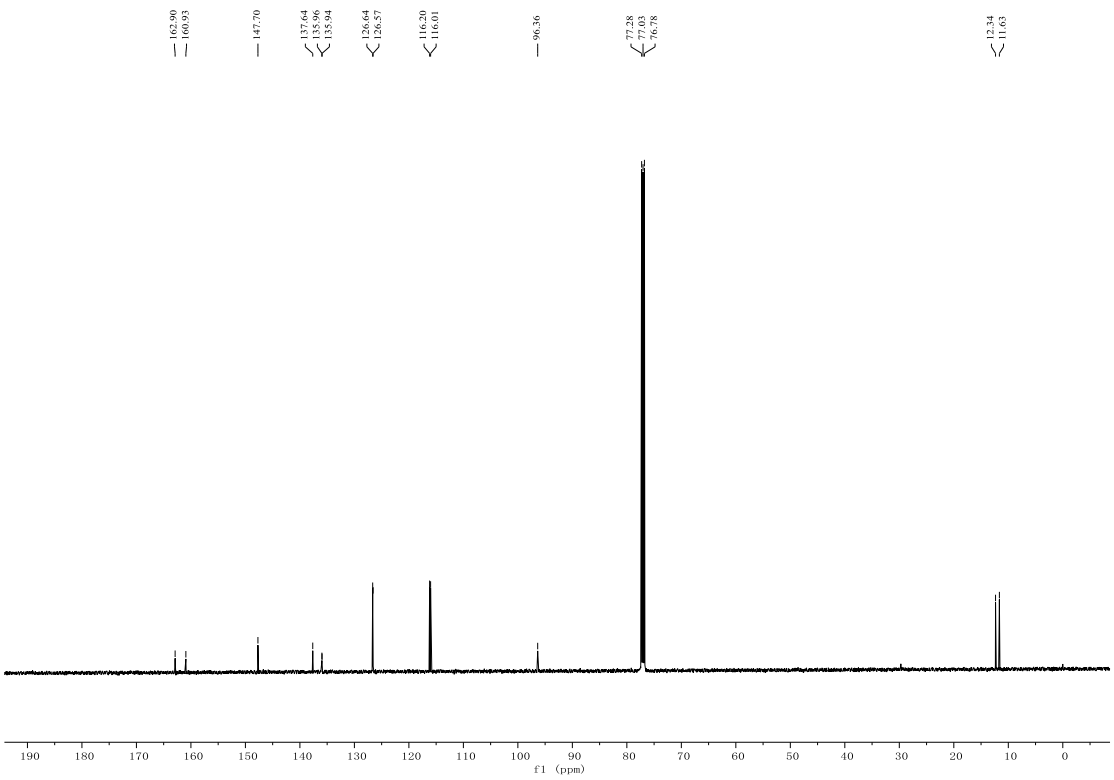
^{13}C NMR of compound **4faa**



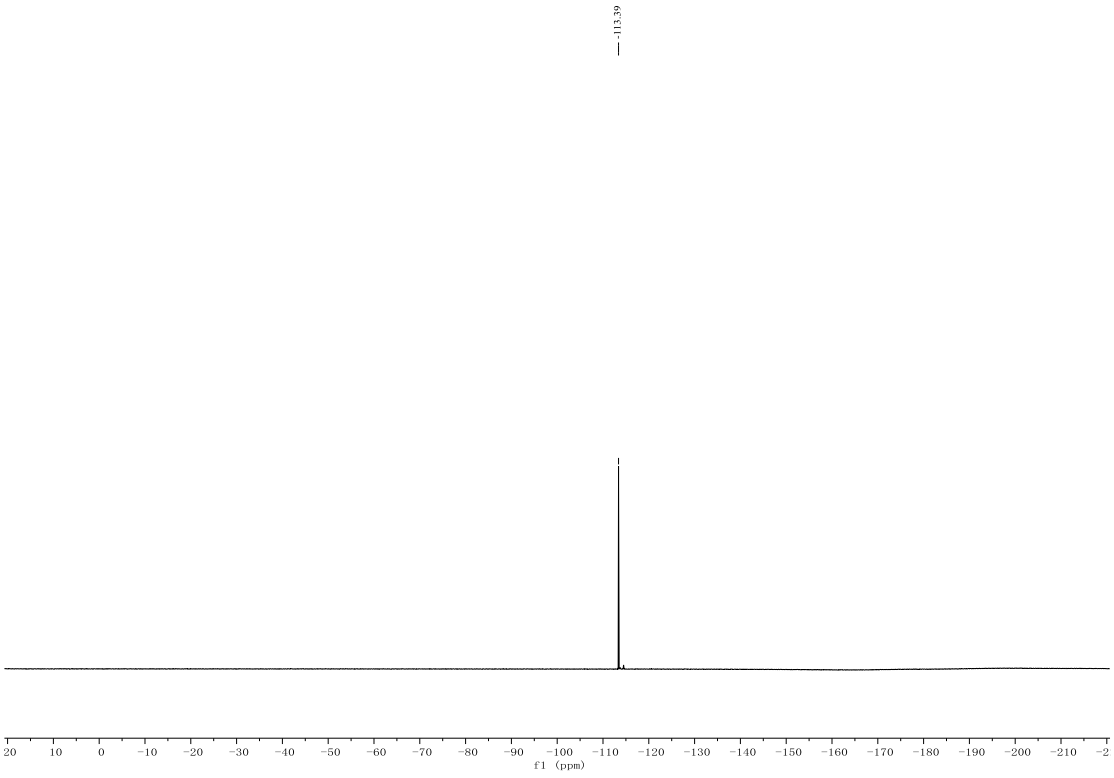
^{19}F NMR of compound **4faa**



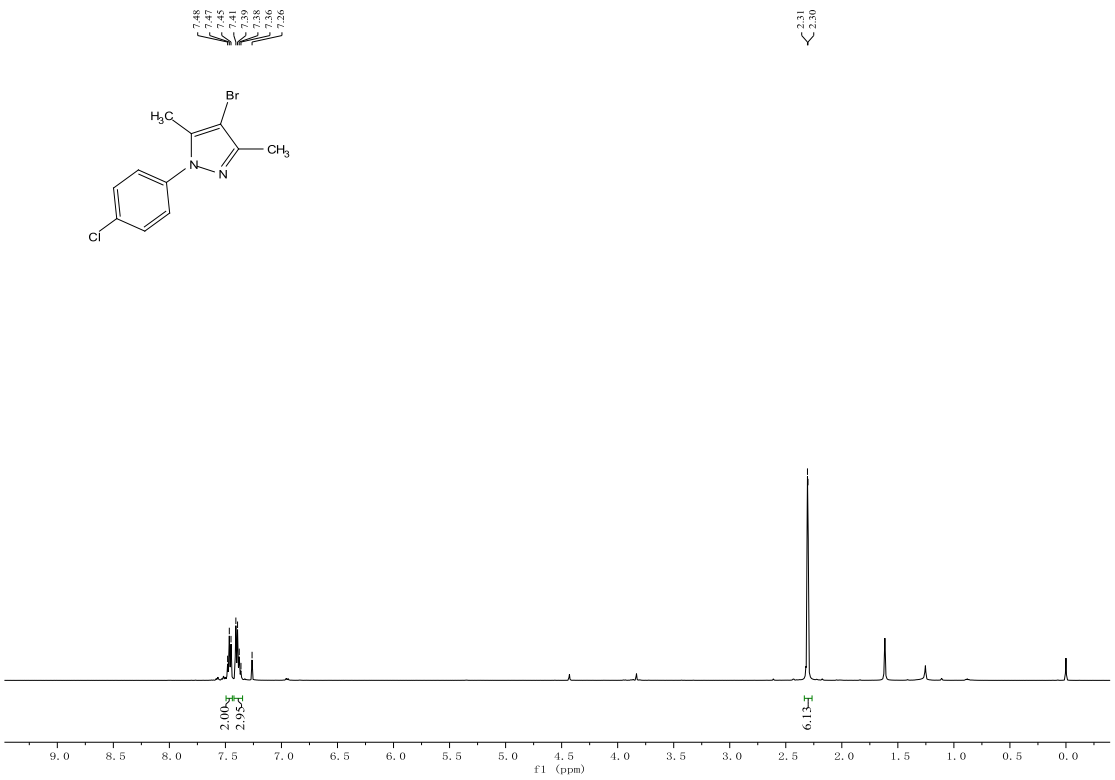
^{1}H NMR of compound **4gaa**



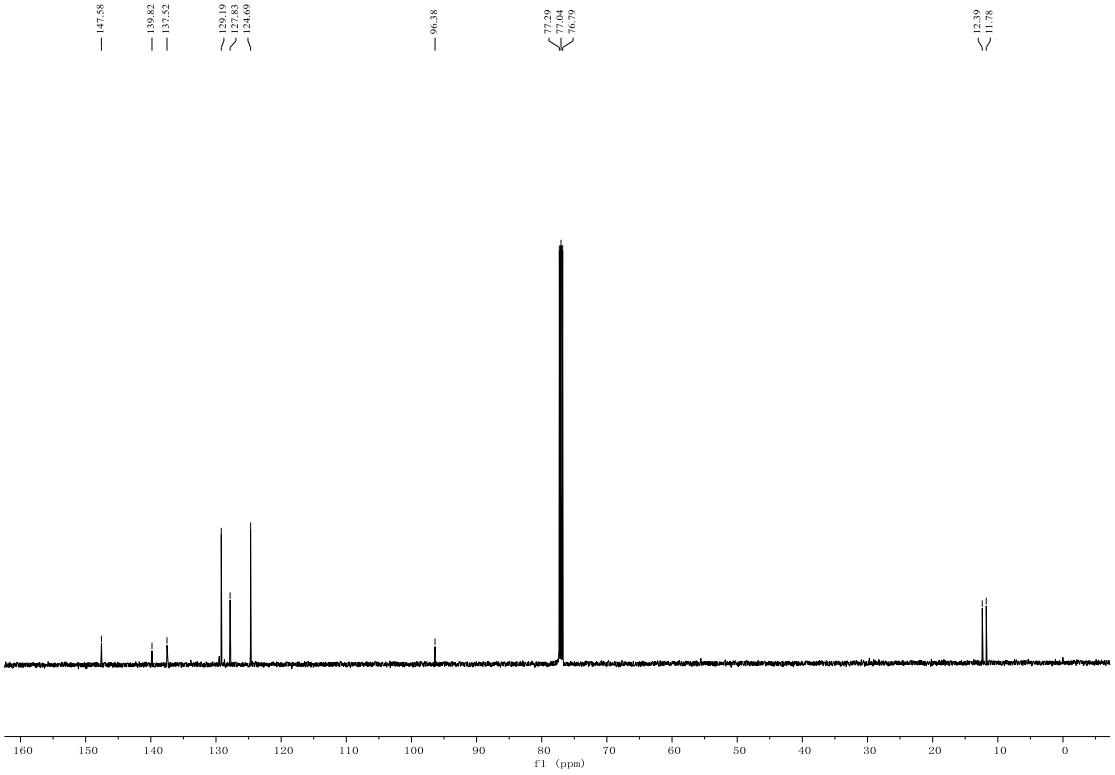
^{13}C NMR of compound **4gaa**



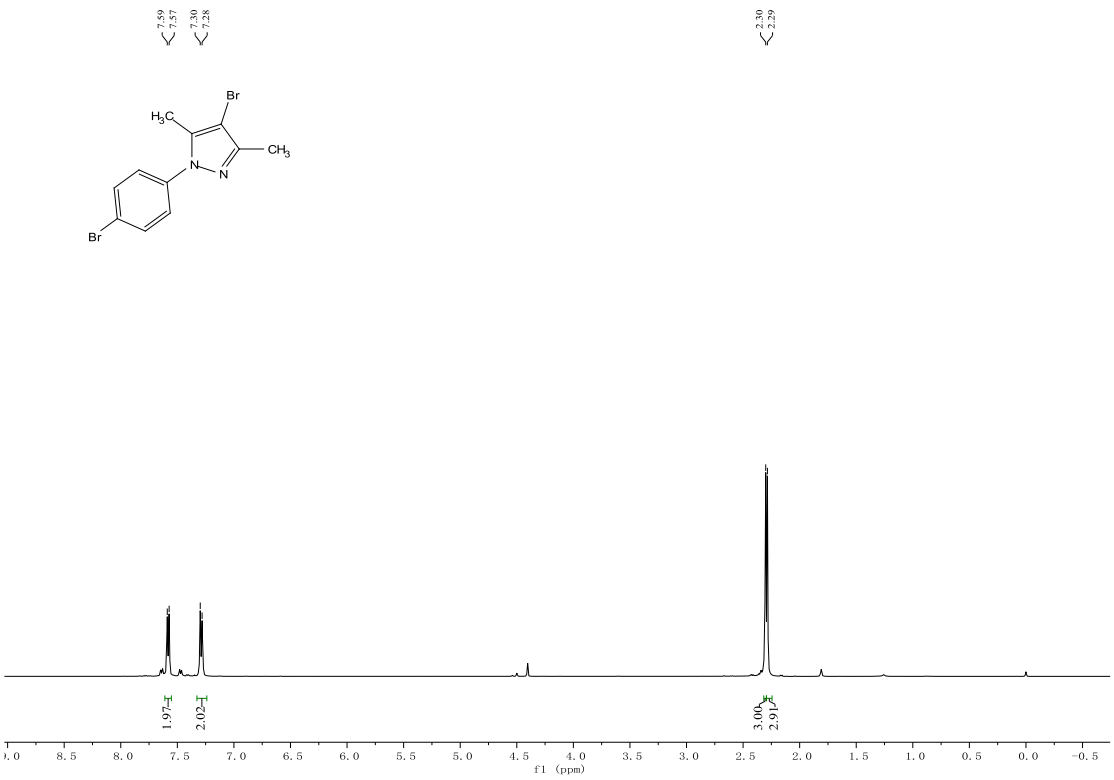
^{19}F NMR of compound **4gaa**



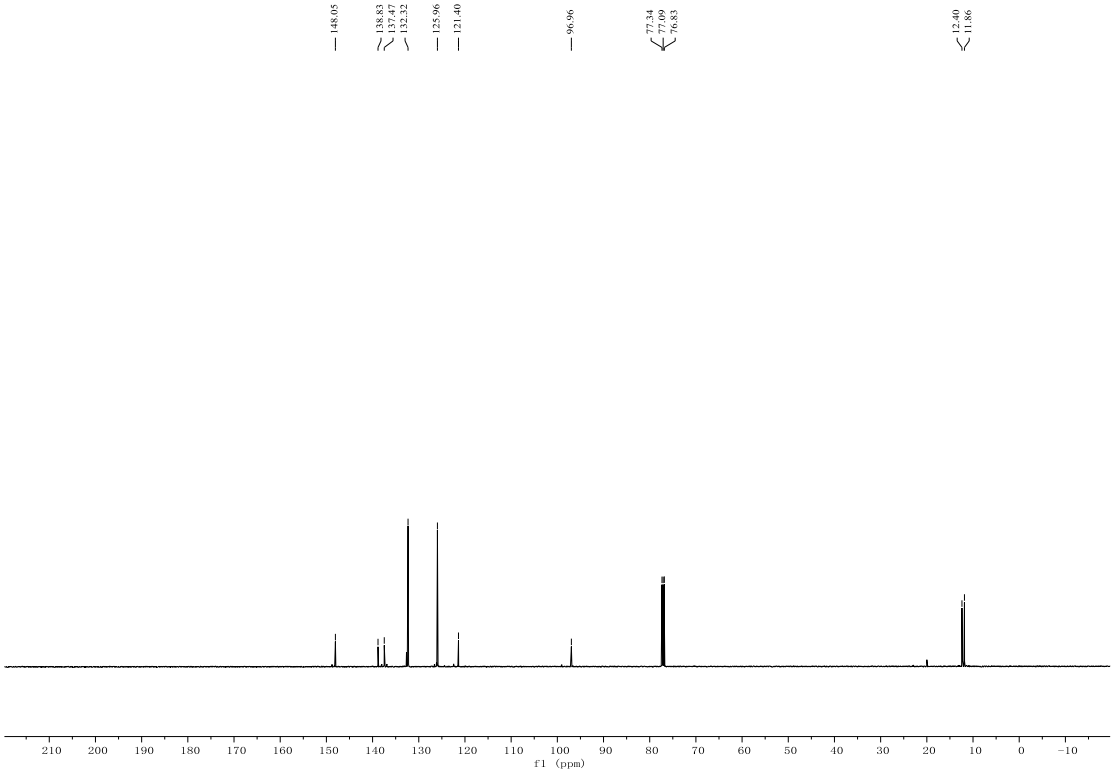
^{1}H NMR of compound **4haa**



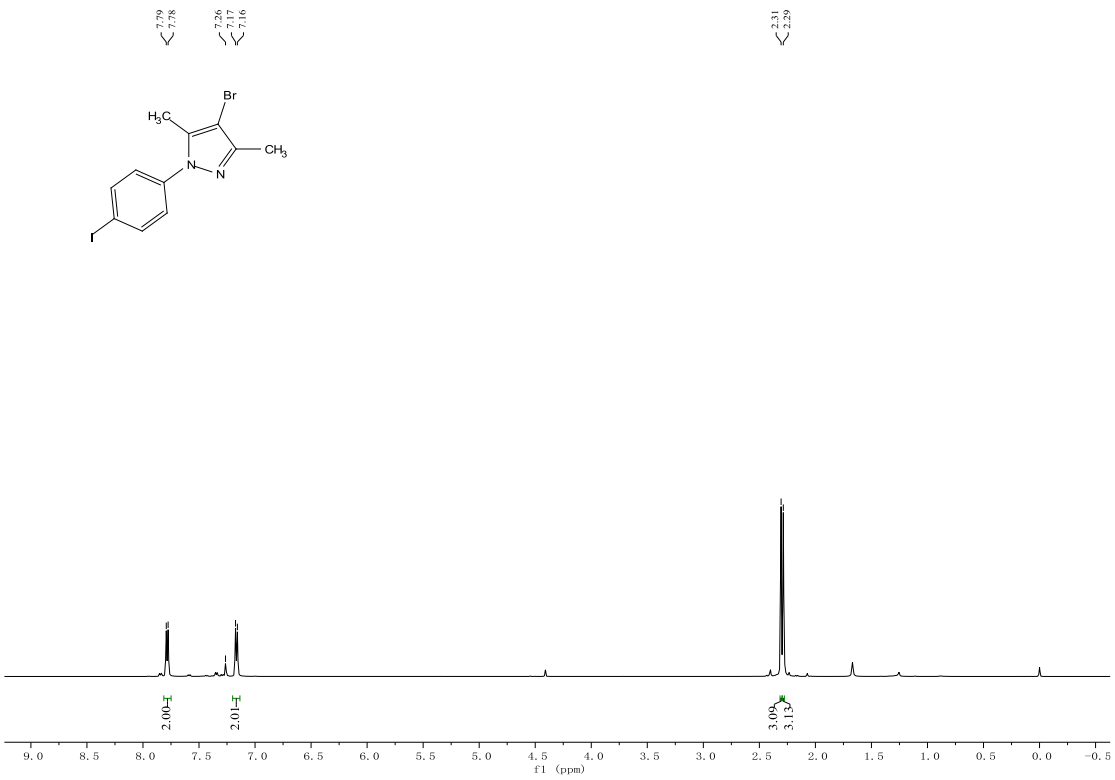
^{13}C NMR of compound **4haa**



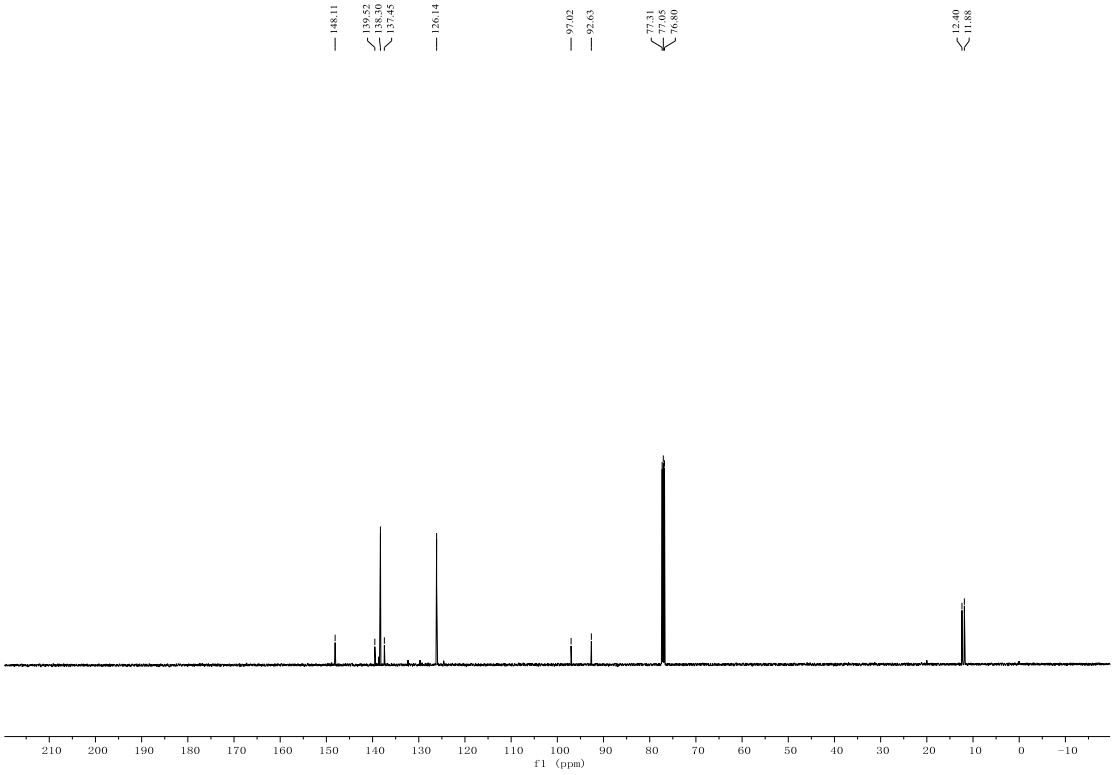
^{1}H NMR of compound **4iaa**



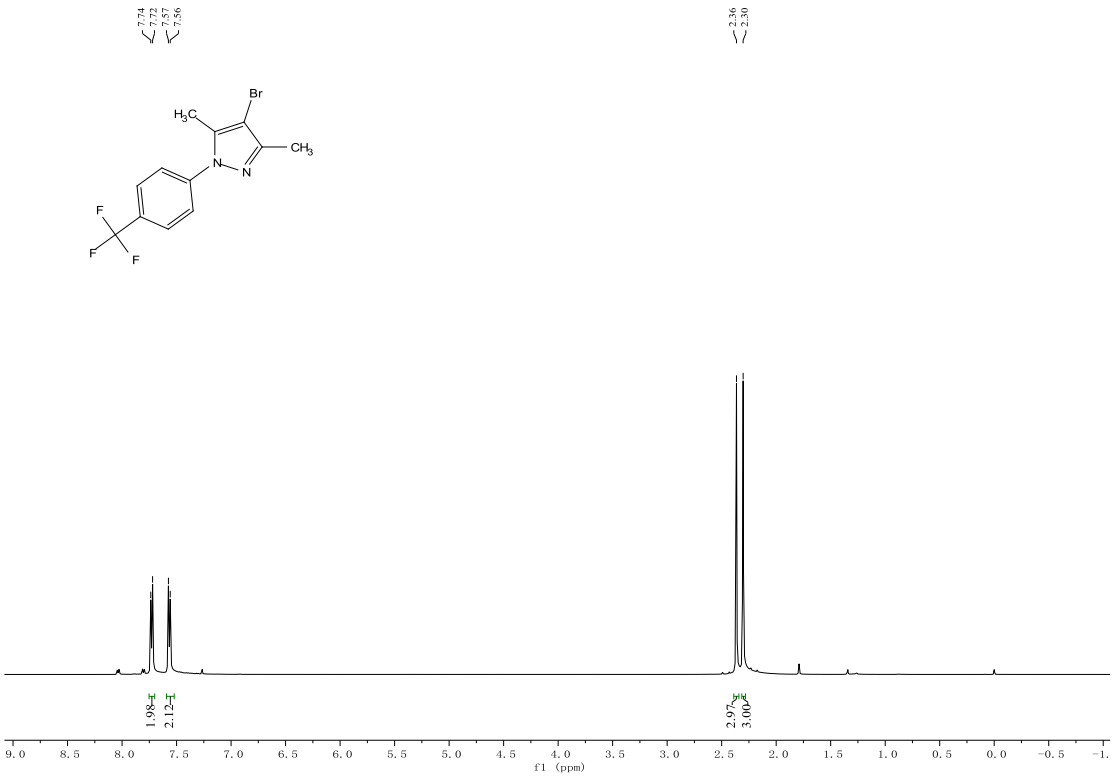
^{13}C NMR of compound **4iaa**



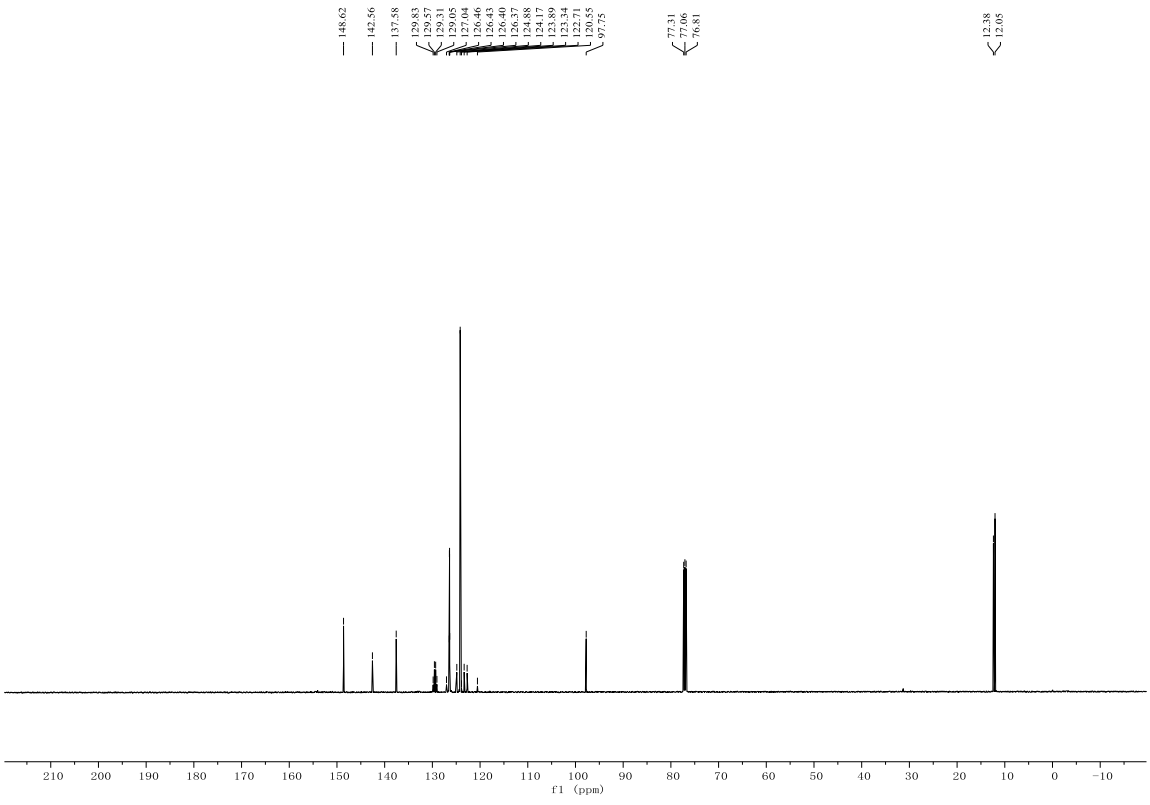
^{1}H NMR of compound **4jaa**



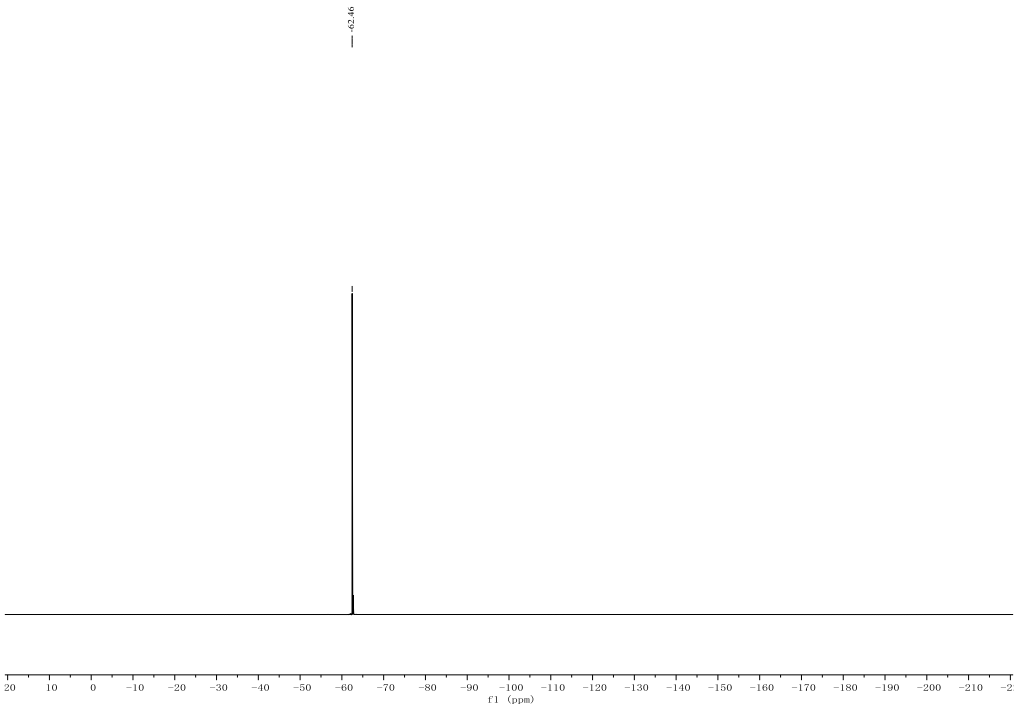
^{13}C NMR of compound **4jaa**



^{1}H NMR of compound **4kaa**



^{13}C NMR of compound **4kaa**



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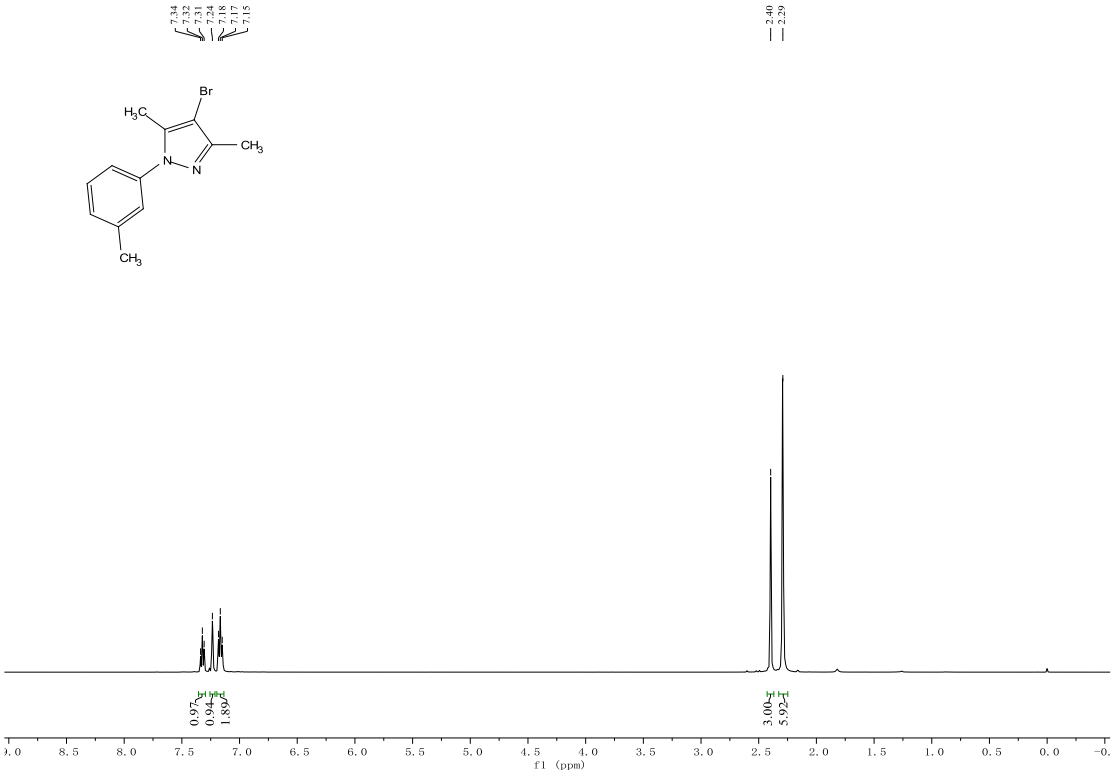

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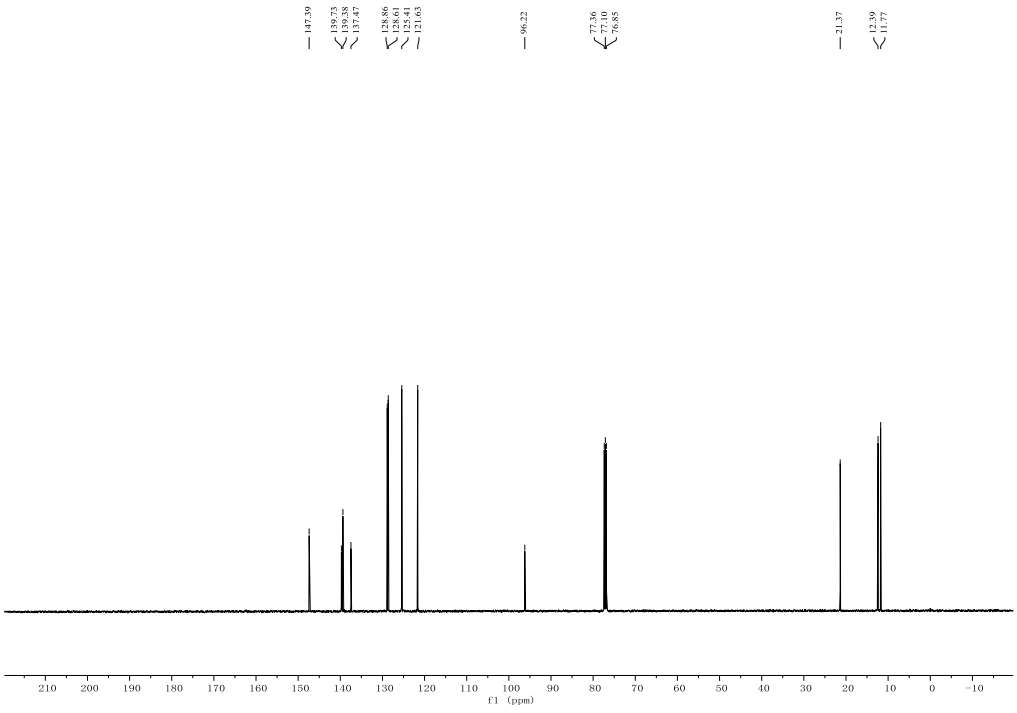
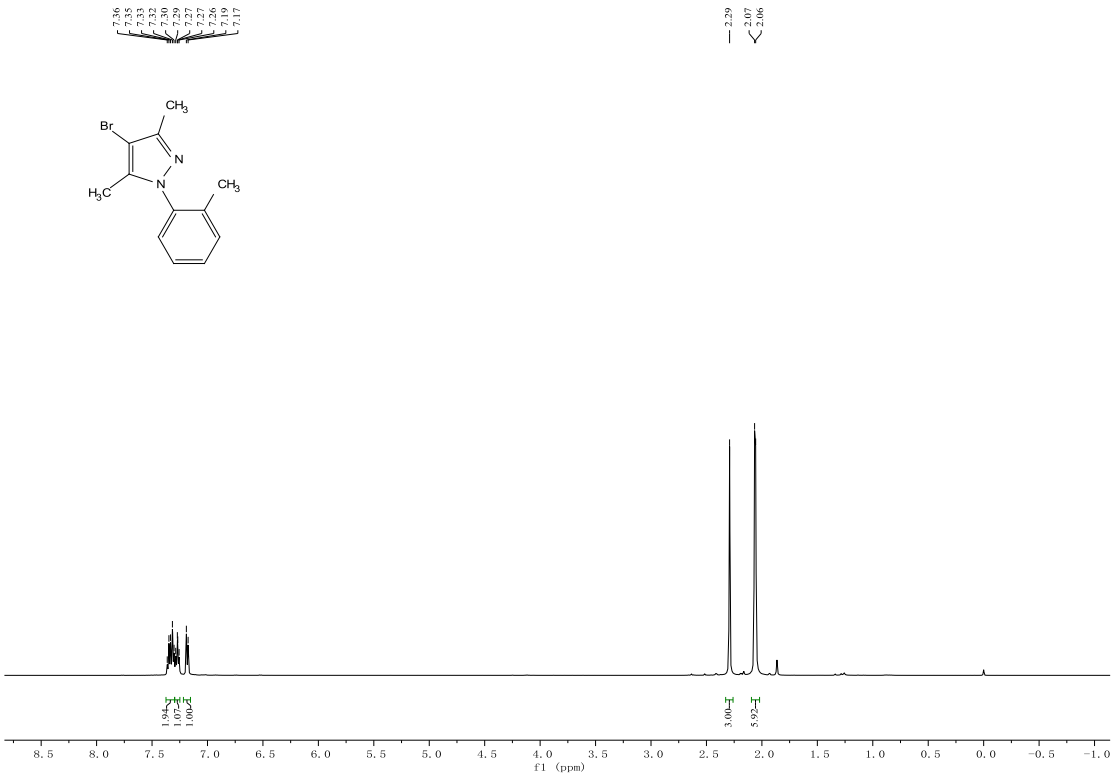
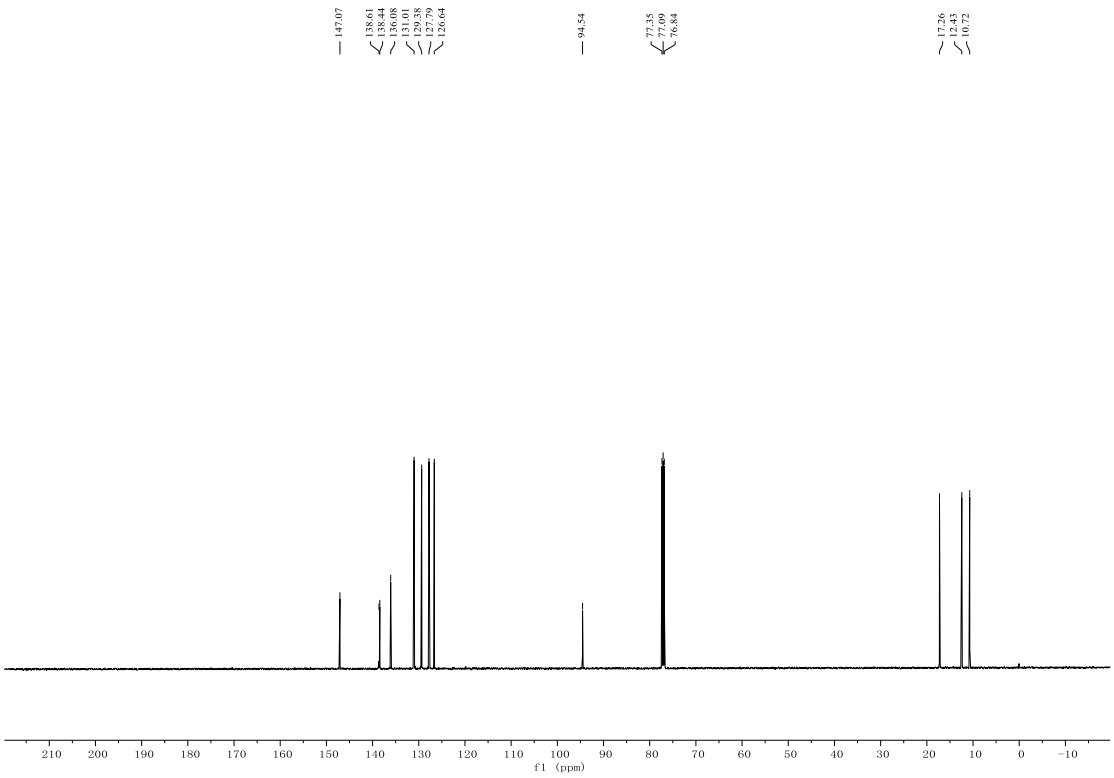


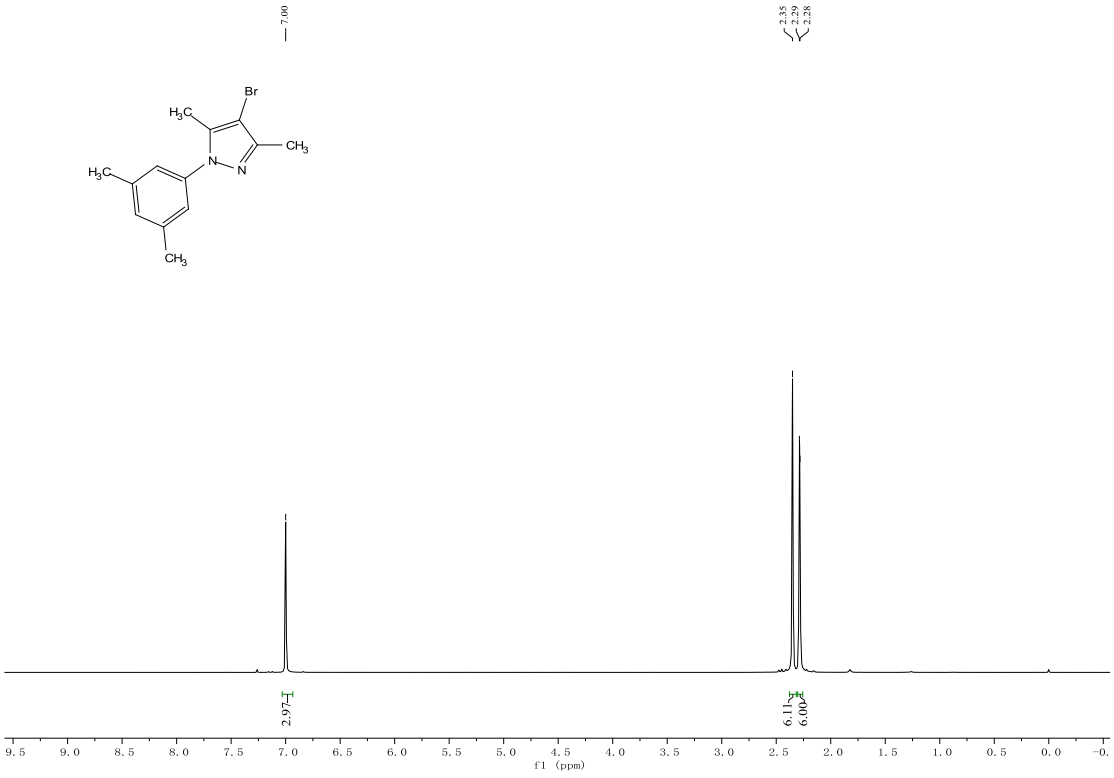
^{13}C NMR of compound **4laa**



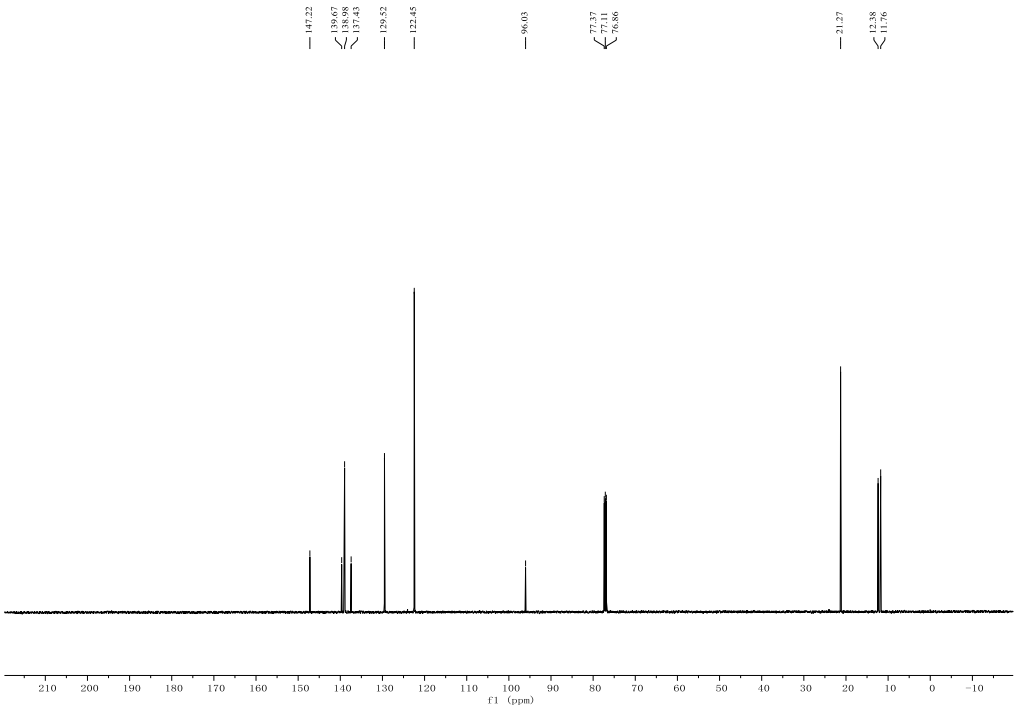
^{1}H NMR of compound **4maa**



^{13}C NMR of compound **4maa**



^{1}H NMR of compound **4naa**



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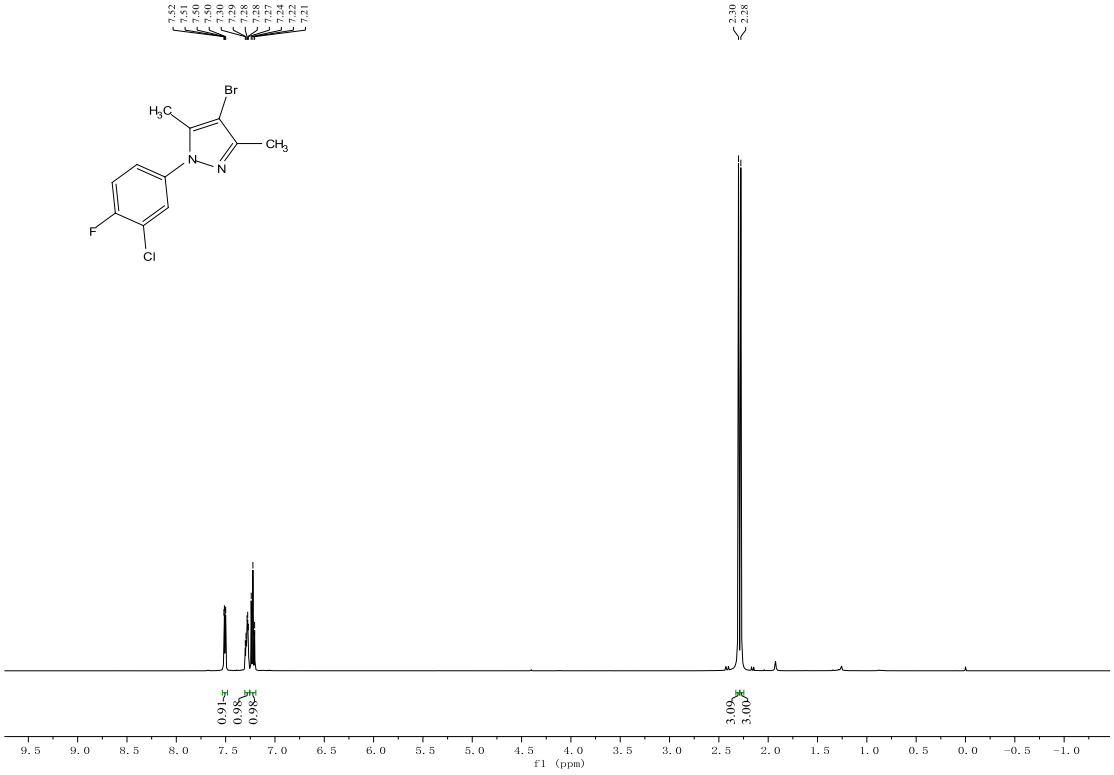
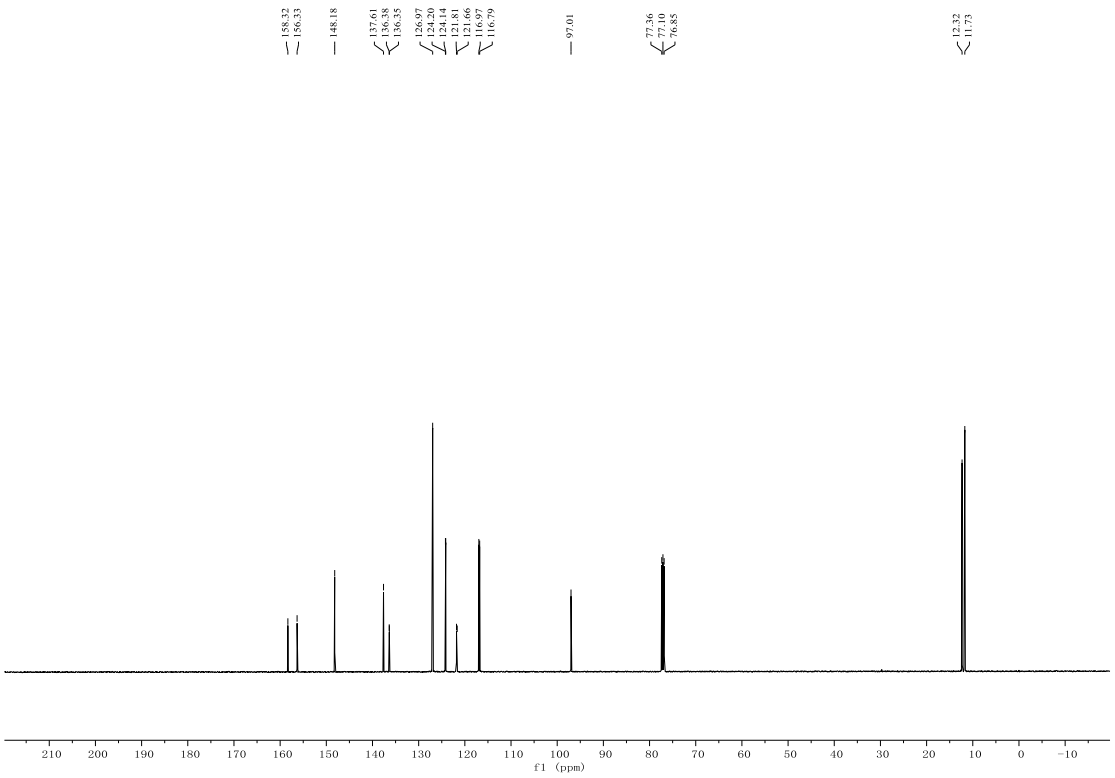
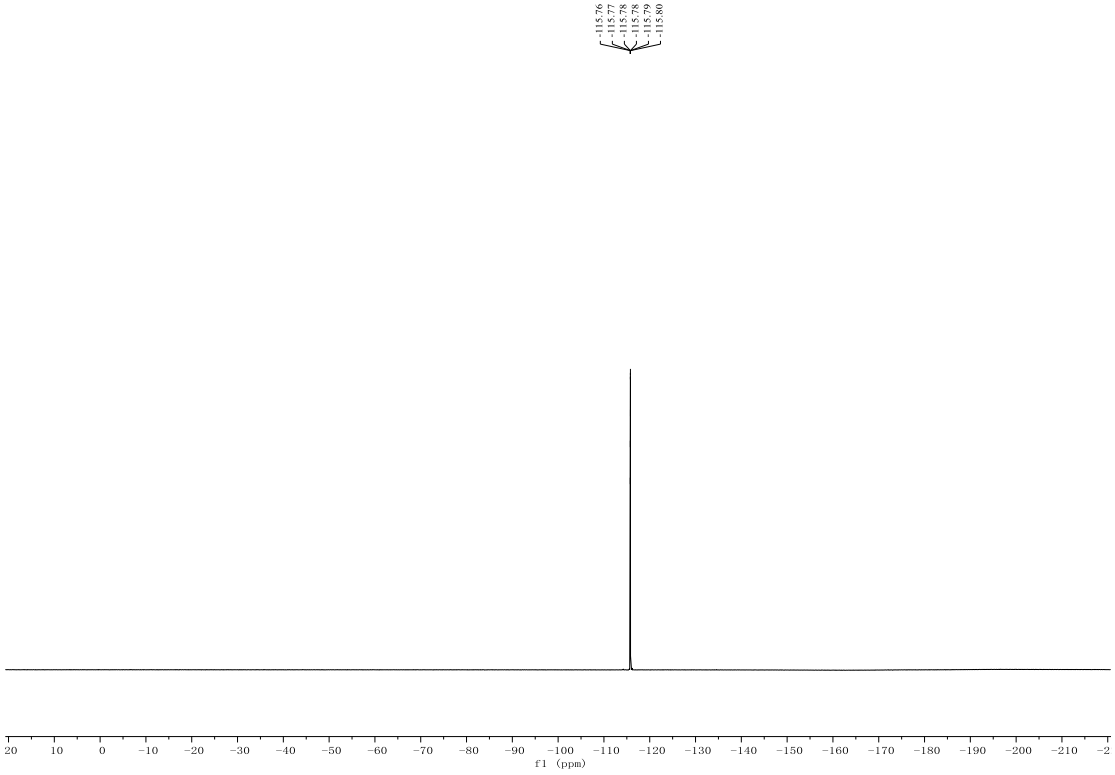


^{1}H NMR of compound **4oaa**



^{13}C NMR of compound **4oaa**



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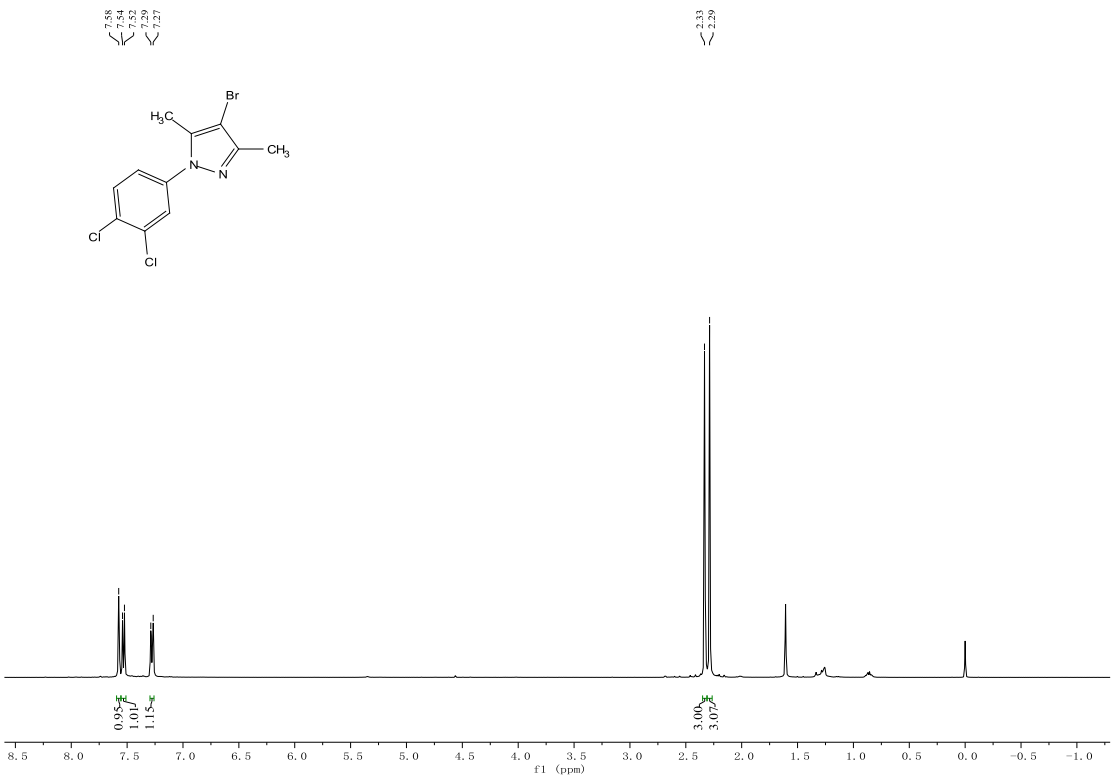
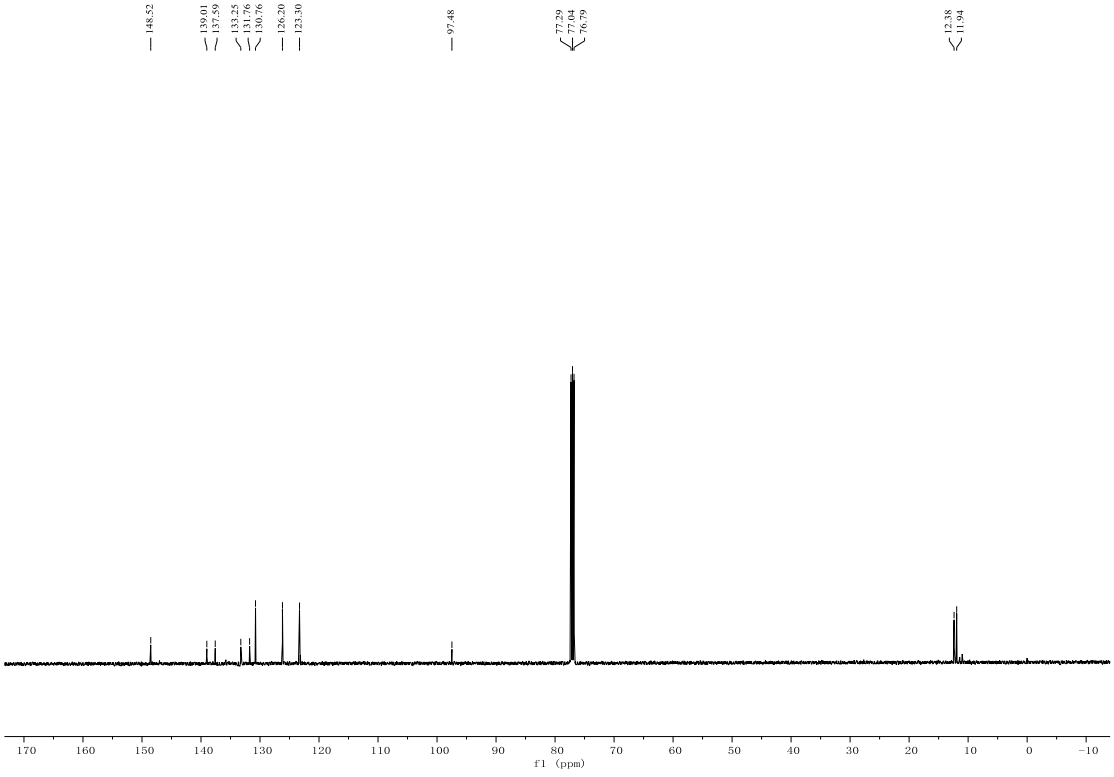
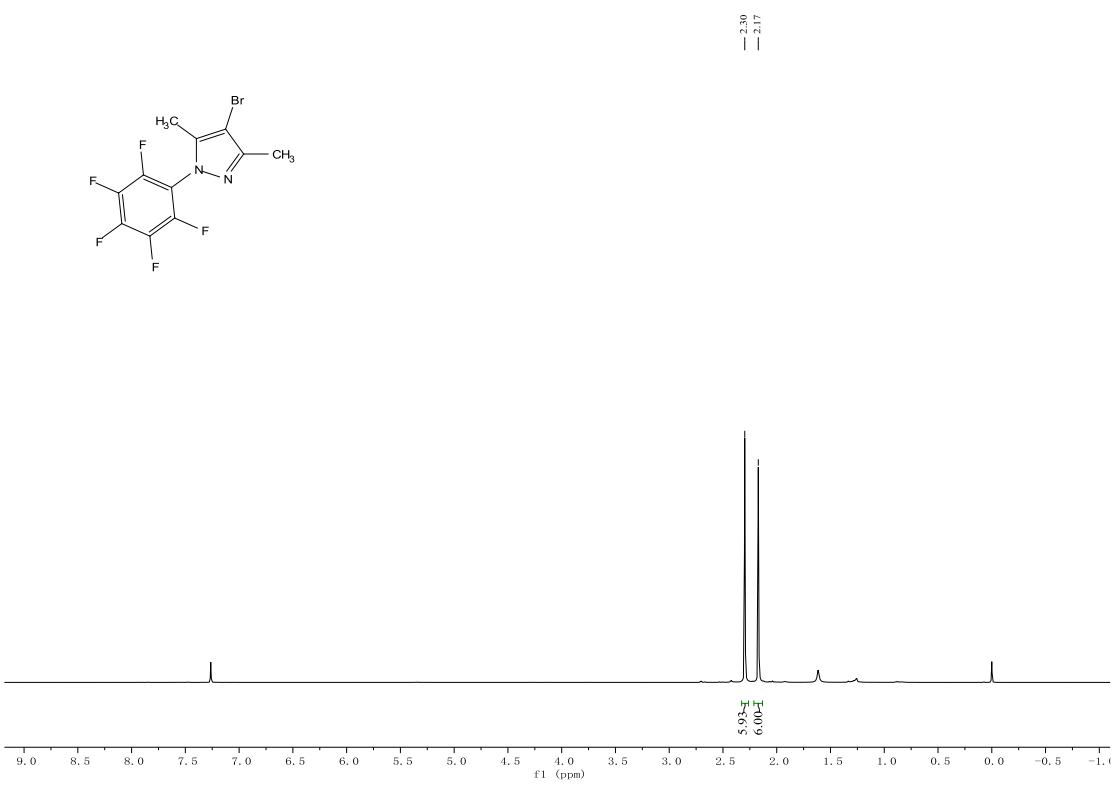


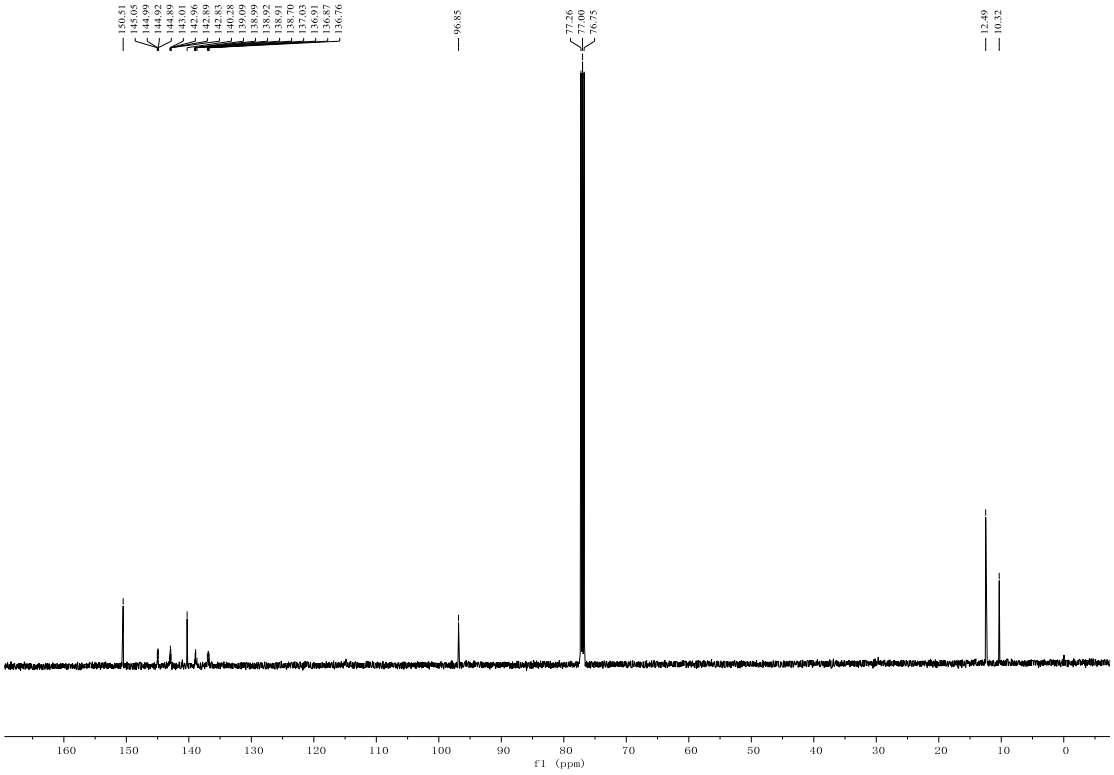
^{1}H NMR of compound **4paa**



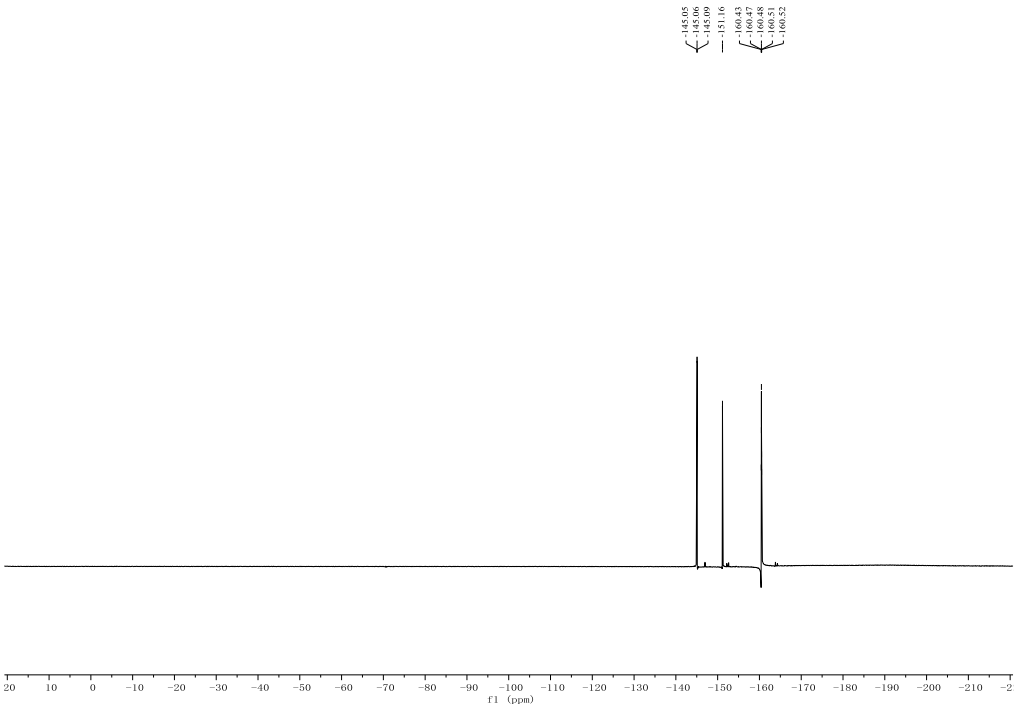
^{13}C NMR of compound **4paa**



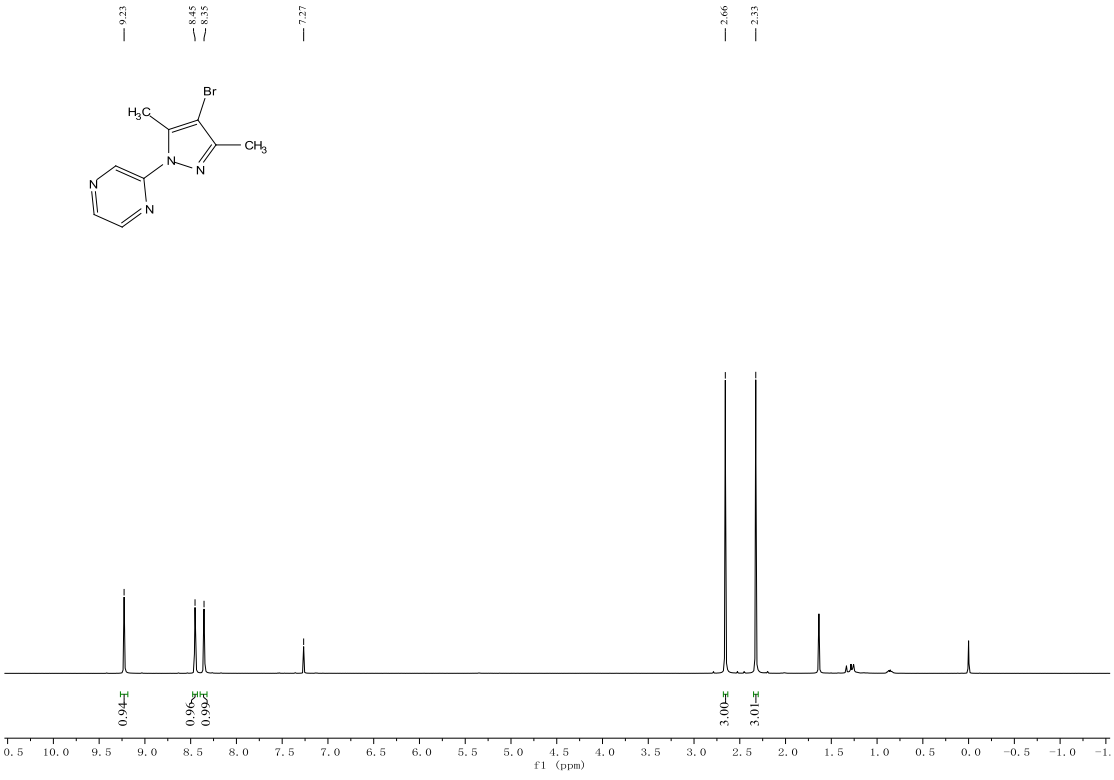
^{1}H NMR of compound **4qaa**



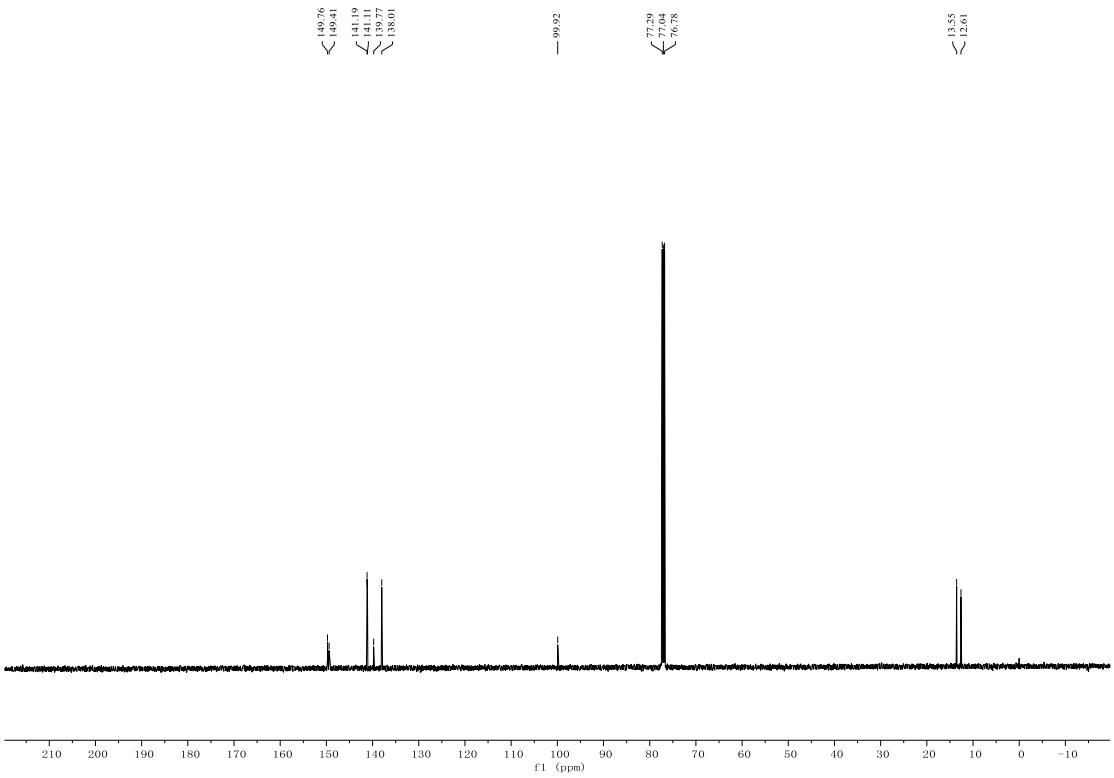
^{13}C NMR of compound **4qaa**



^{19}F NMR of compound **4qaa**



^{1}H NMR of compound **4raa**



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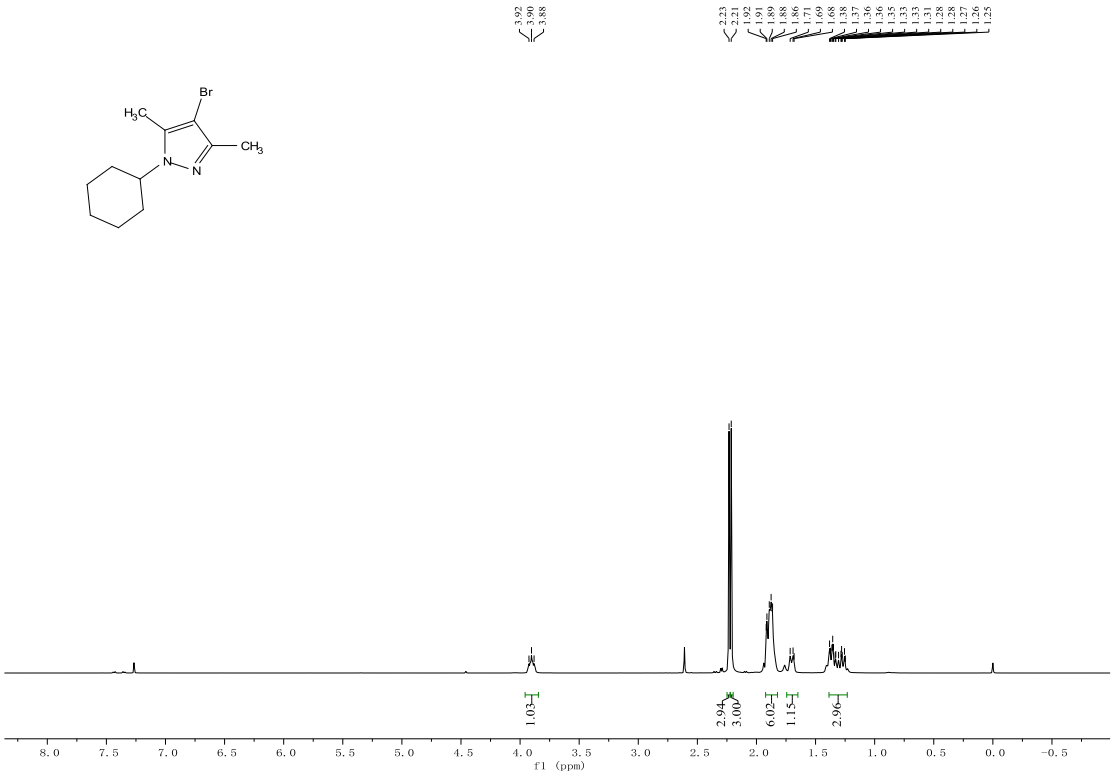

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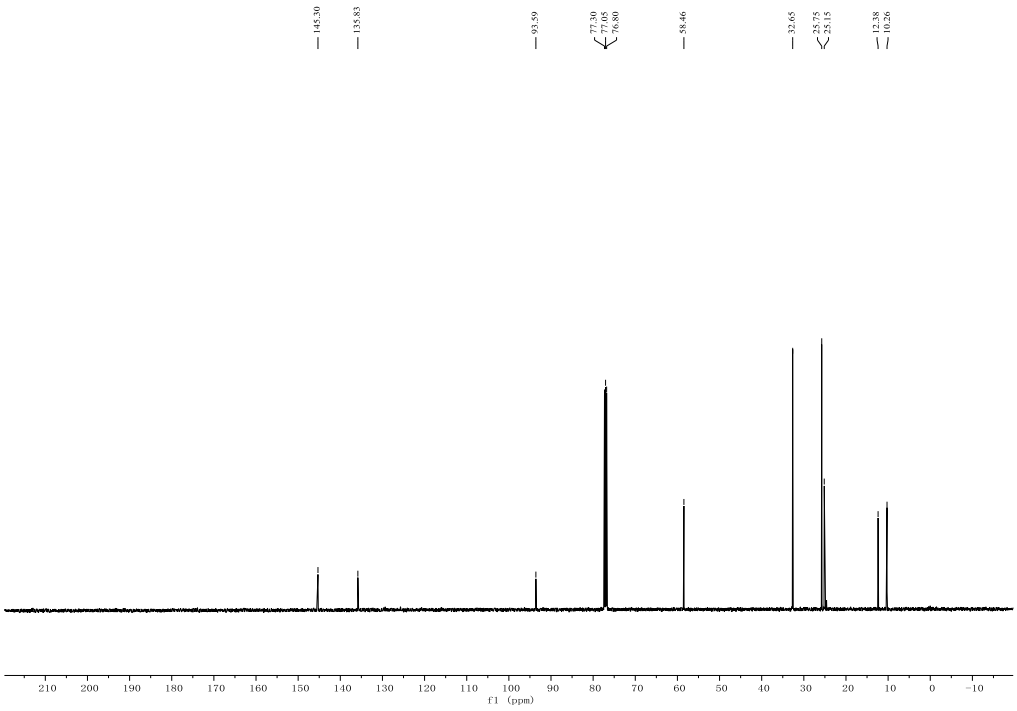

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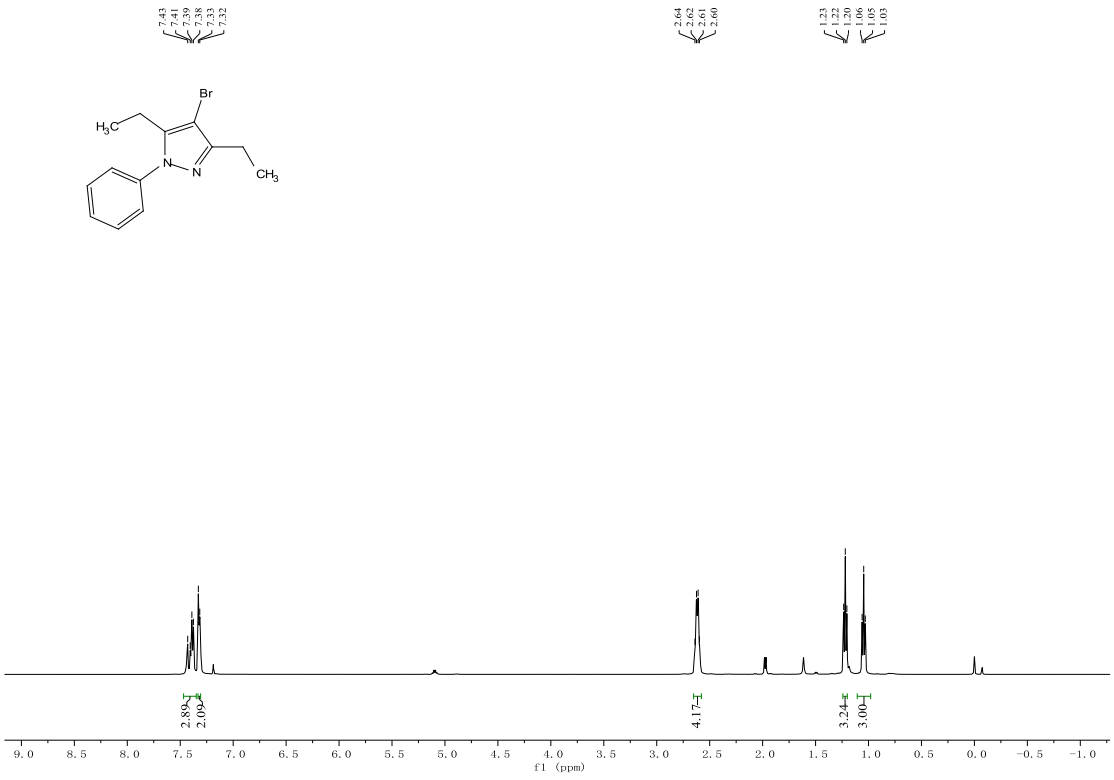
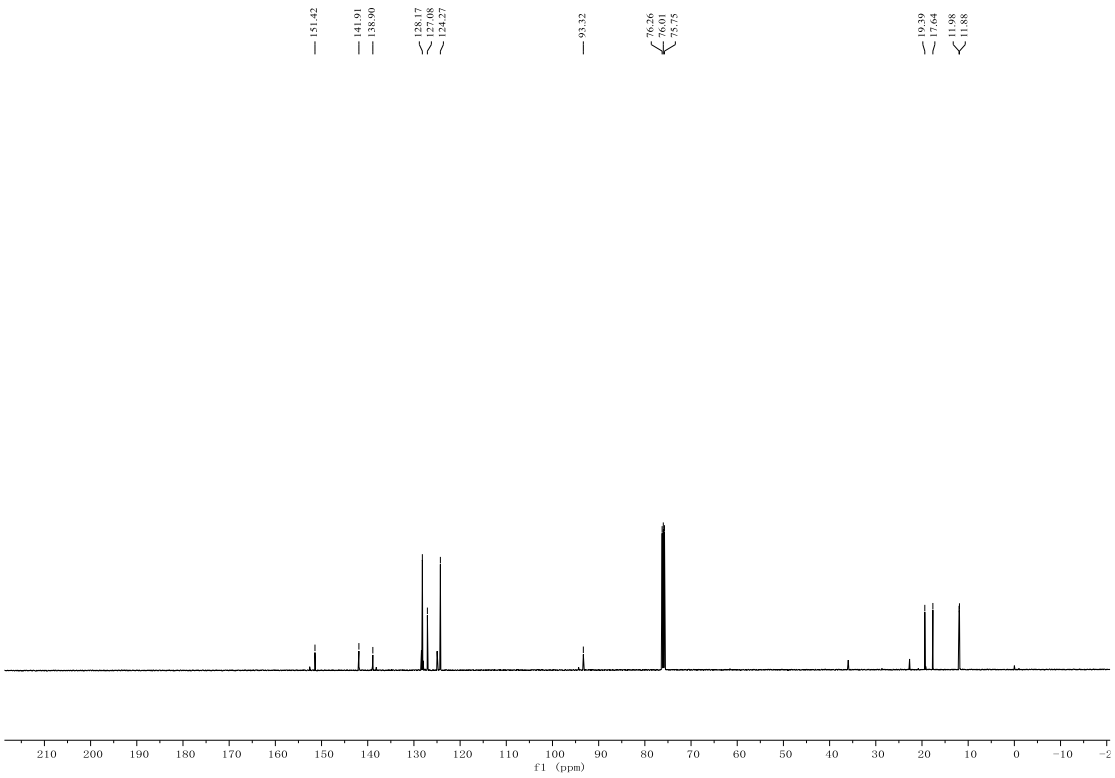
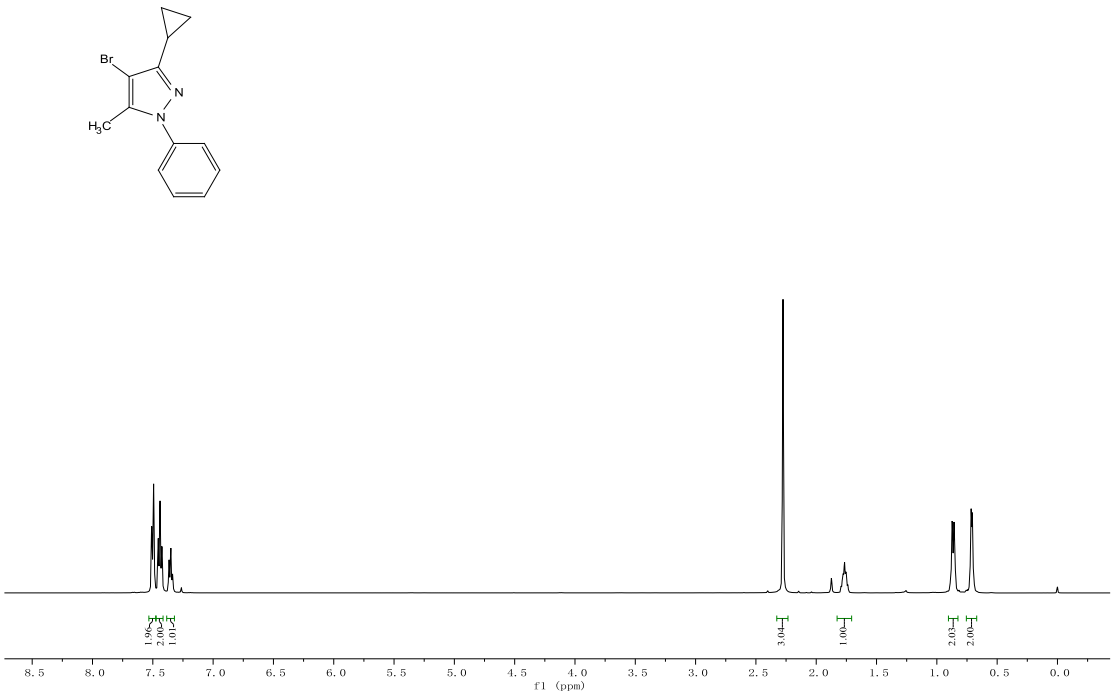


^{1}H NMR of compound **4aba**



^{13}C NMR of compound **4aba**



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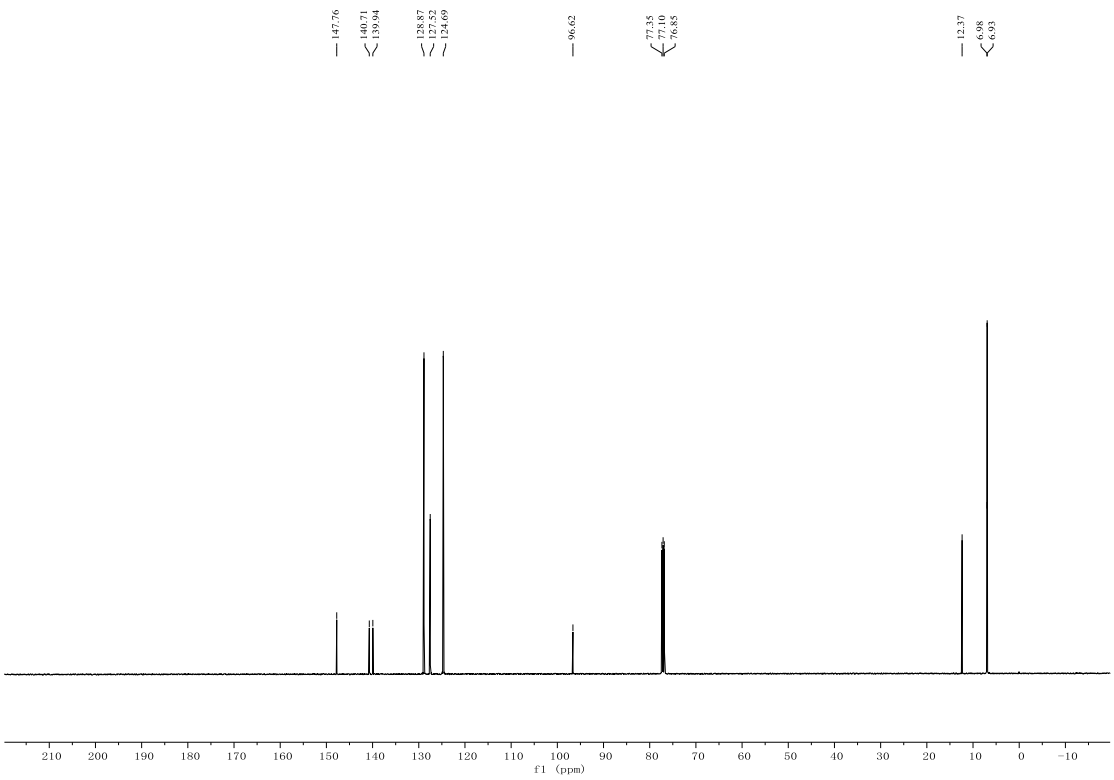

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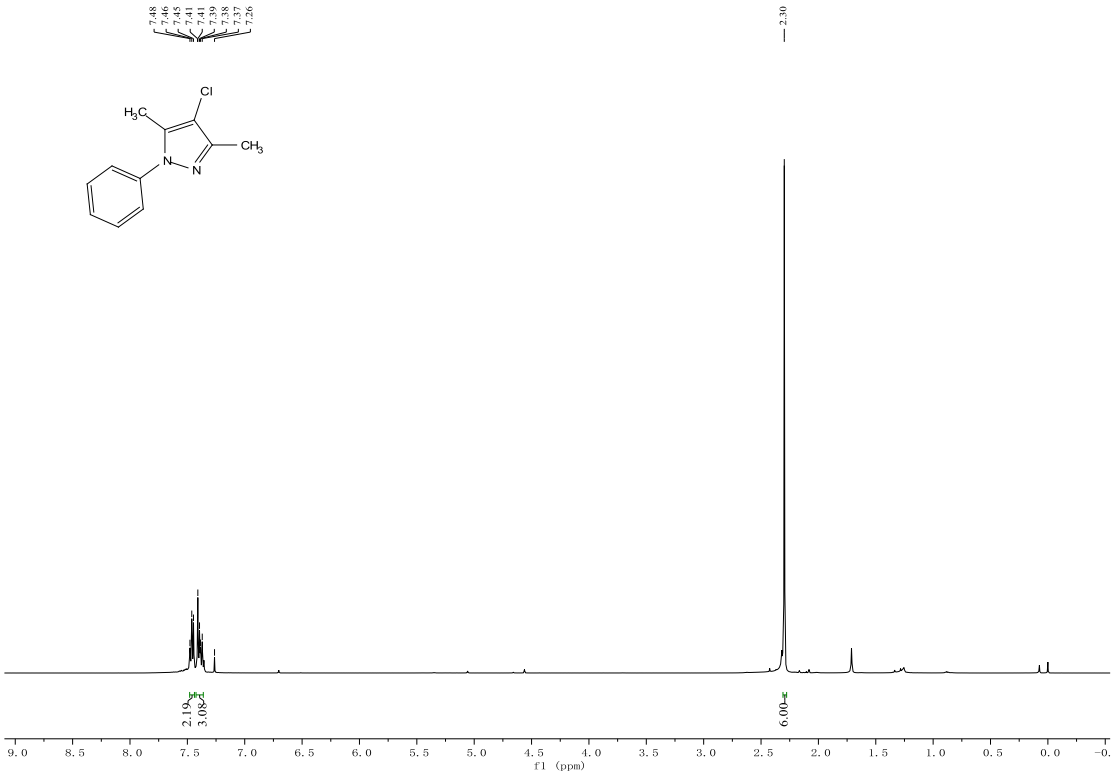

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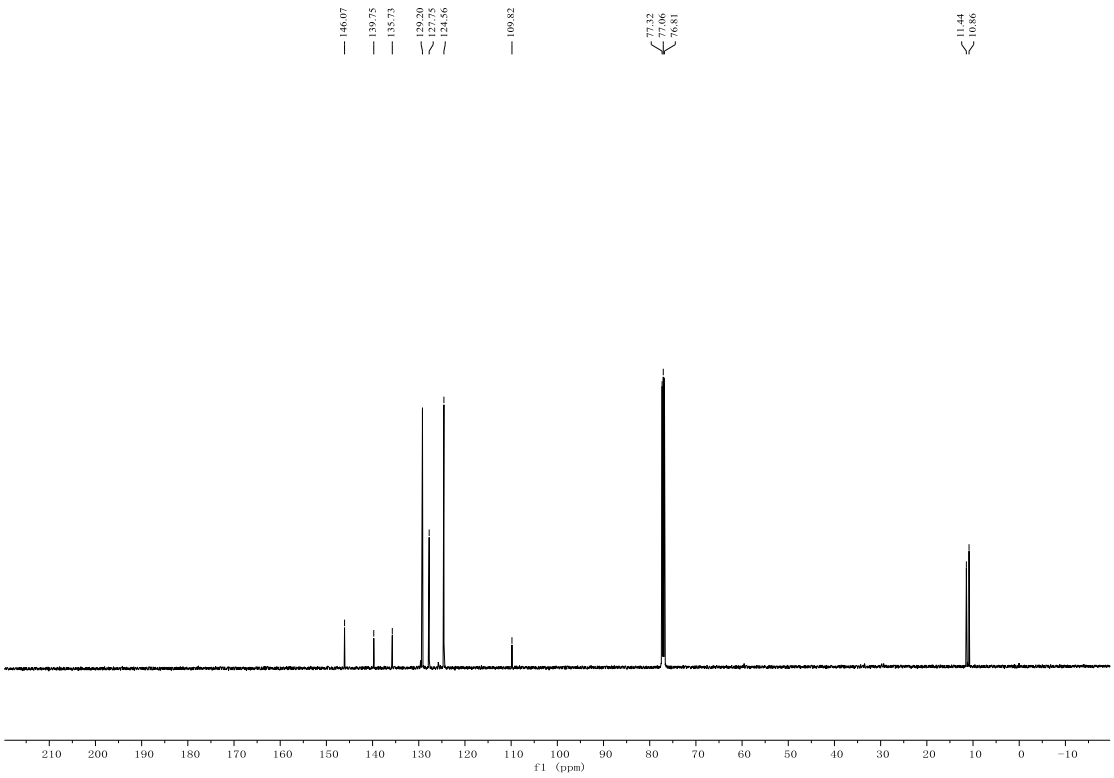

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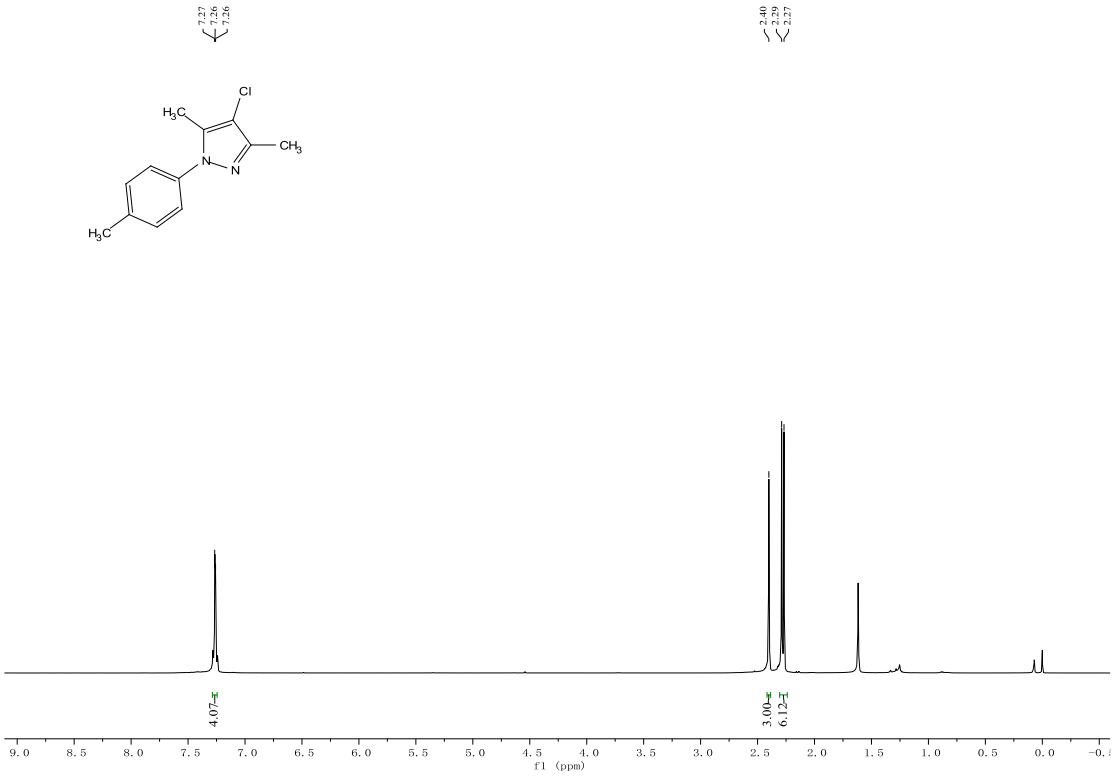

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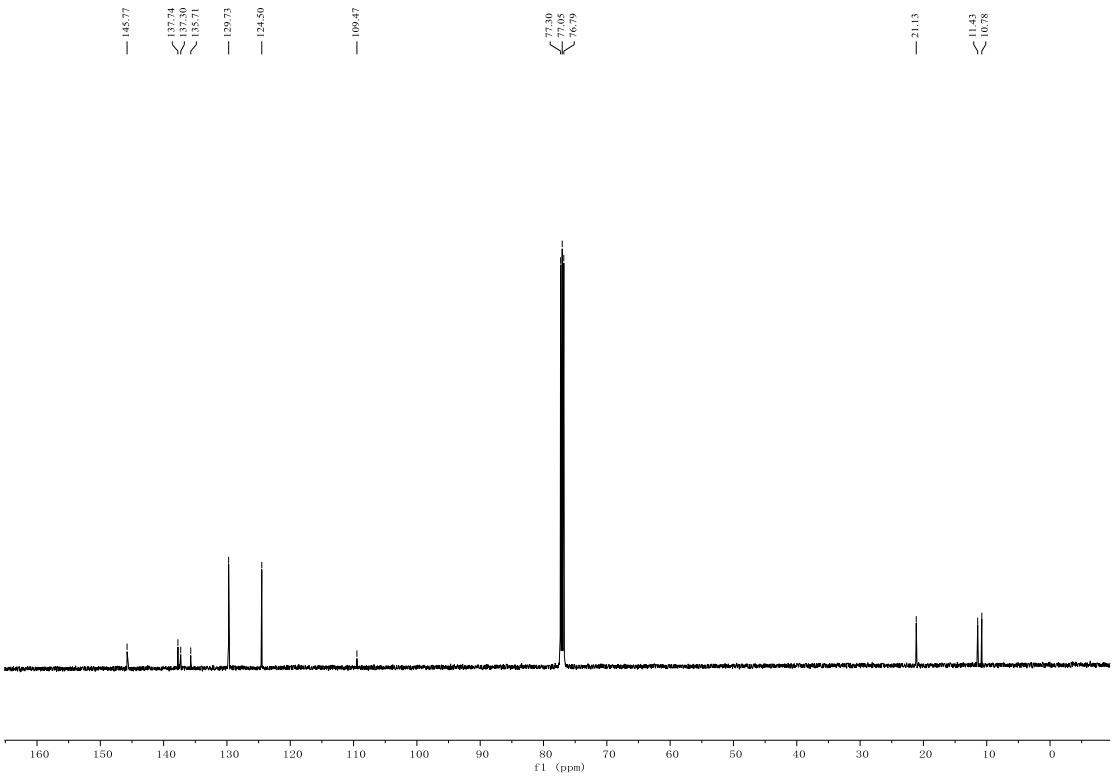

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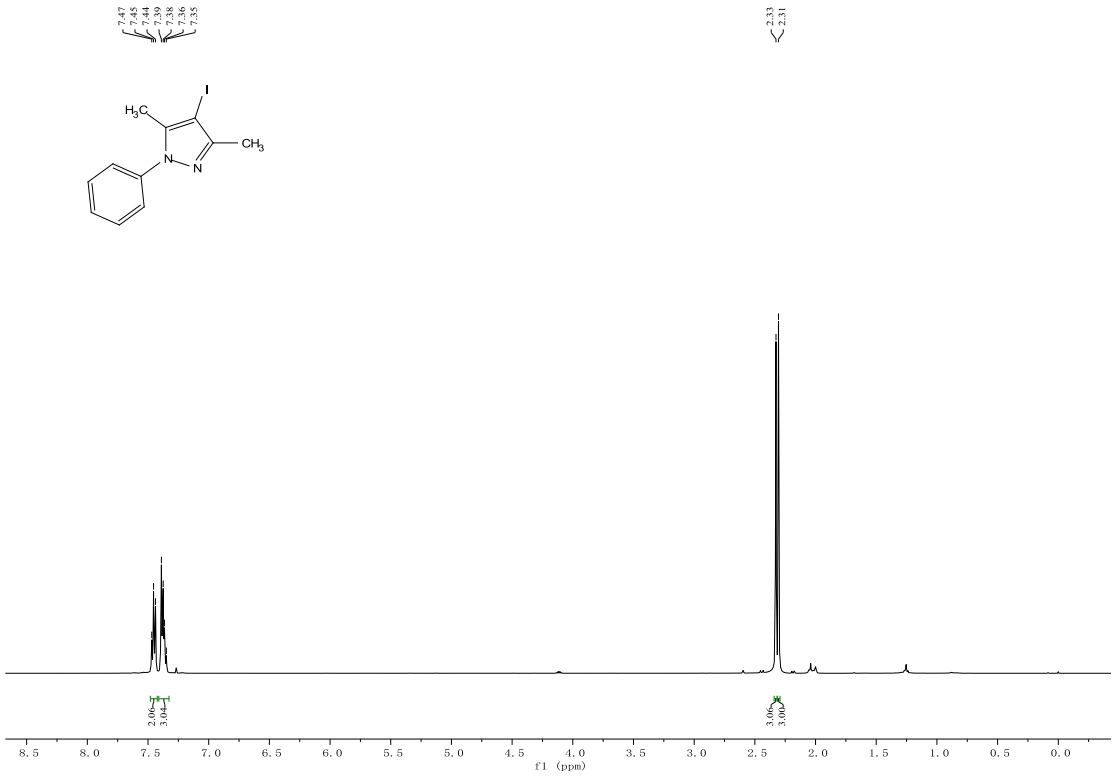

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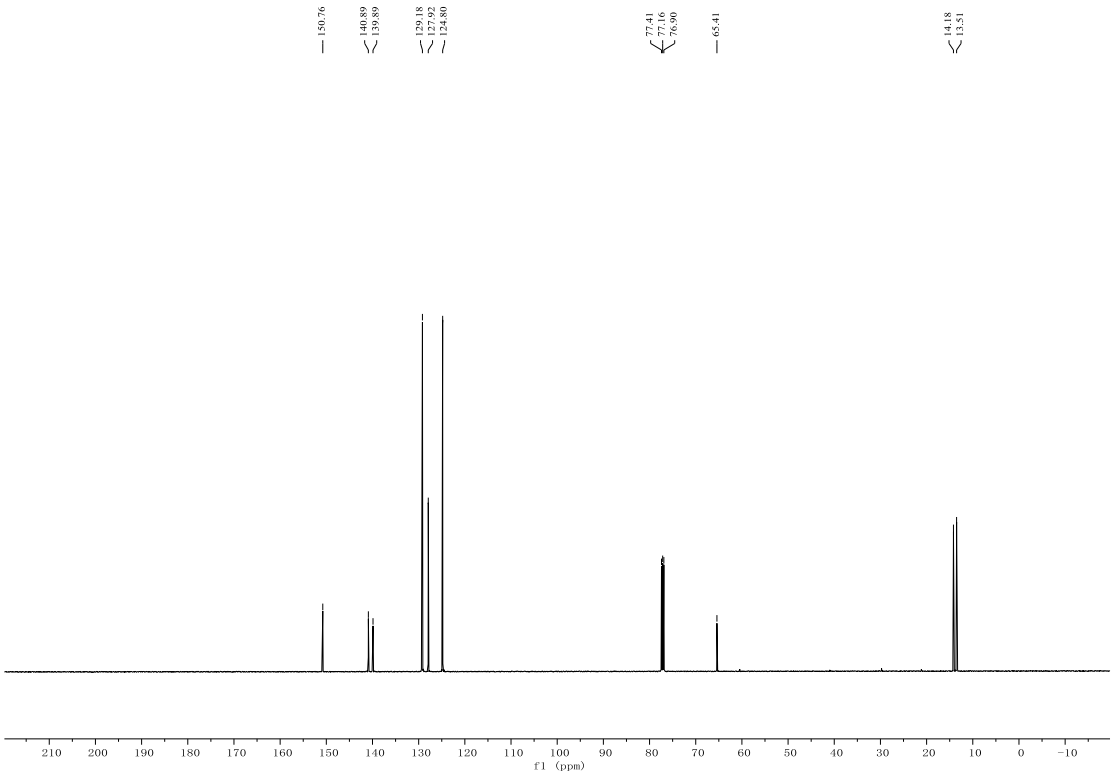

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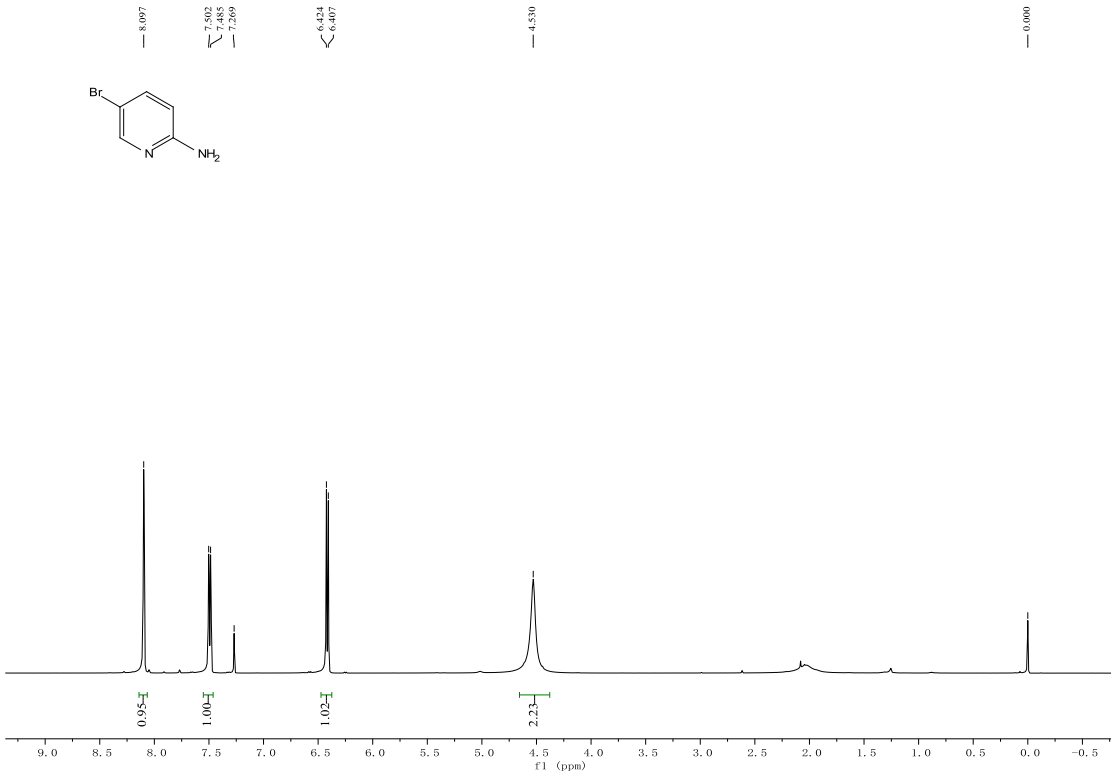

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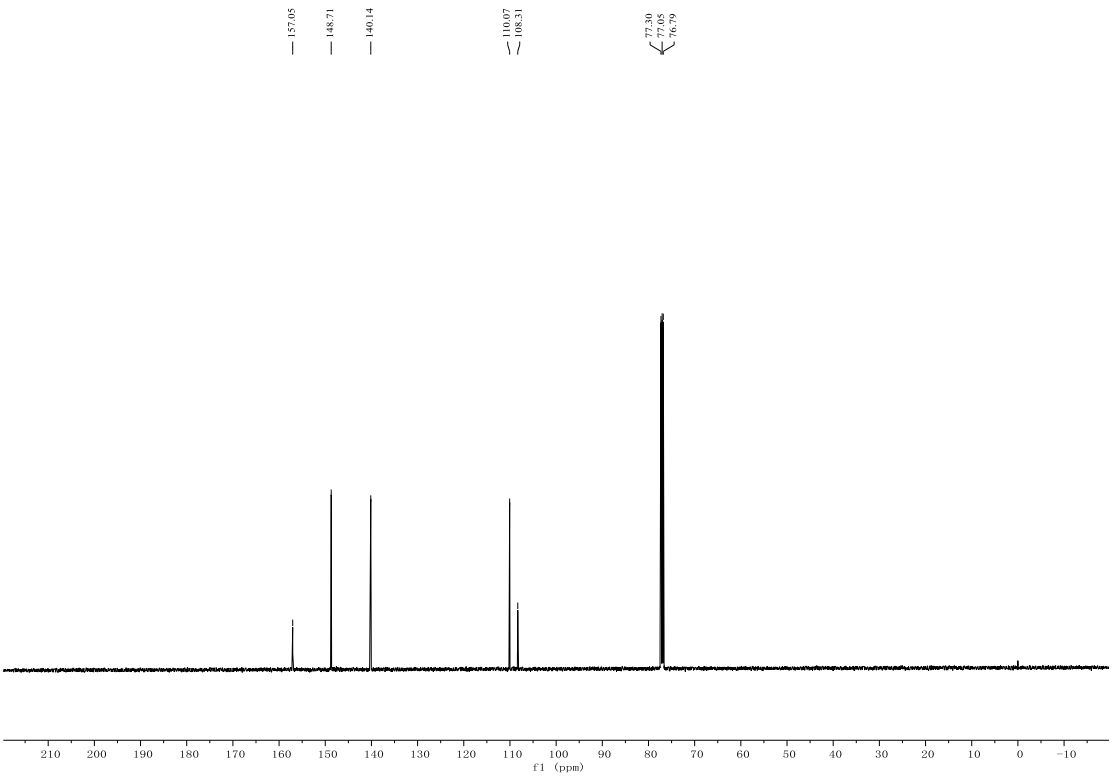
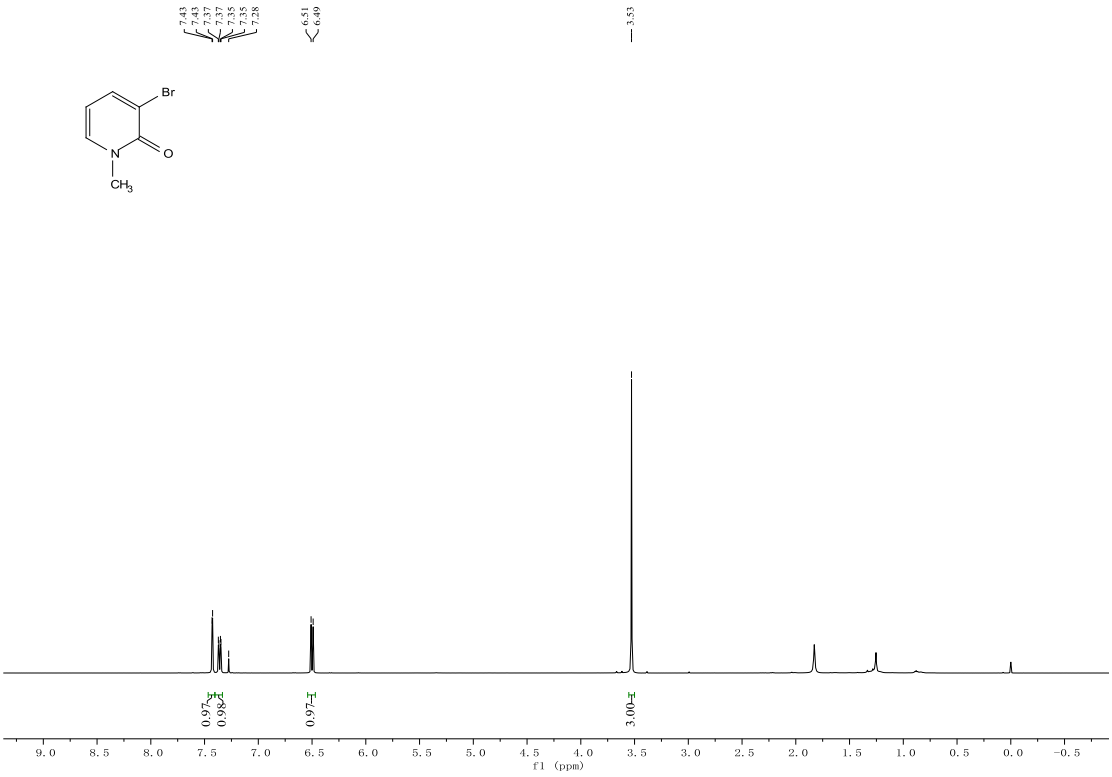
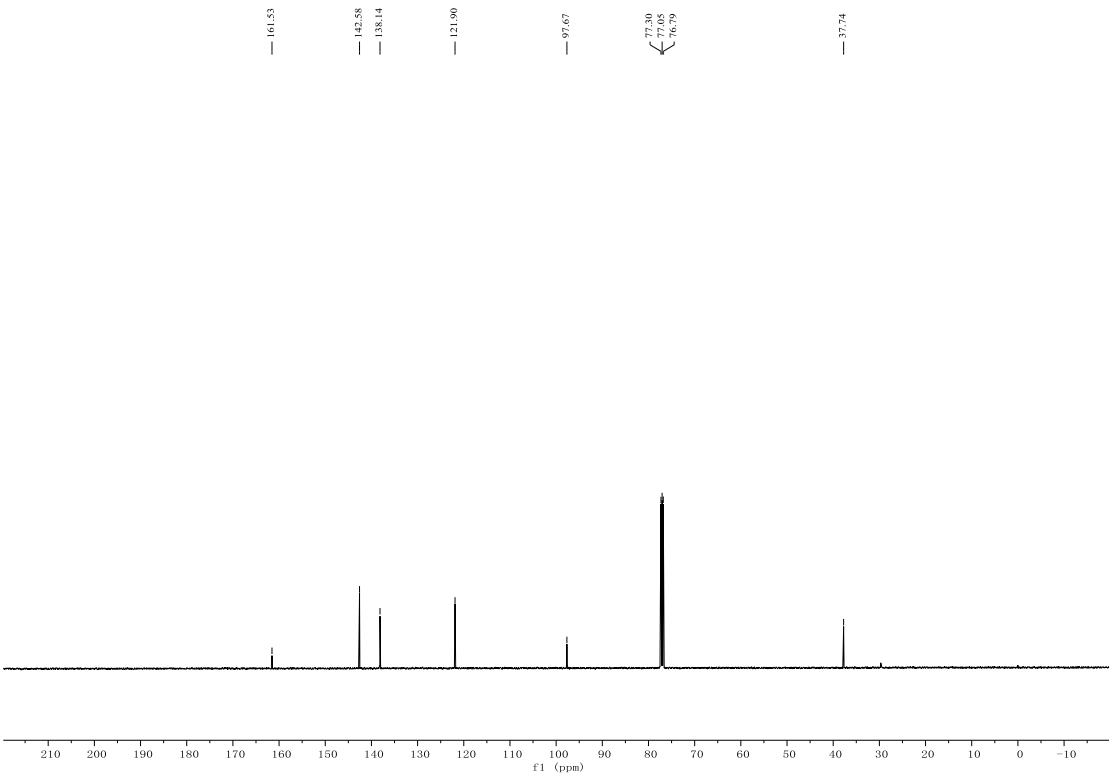


^{13}C NMR of compound **5aa**



^{1}H NMR of compound **5ba**



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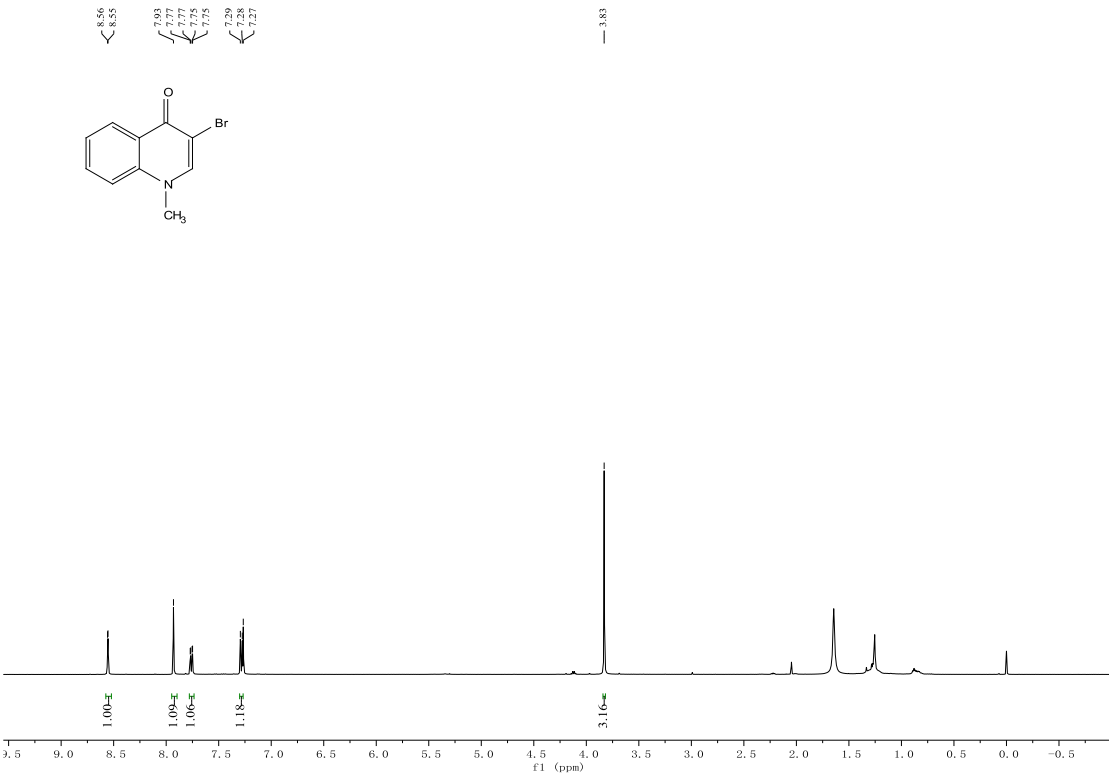

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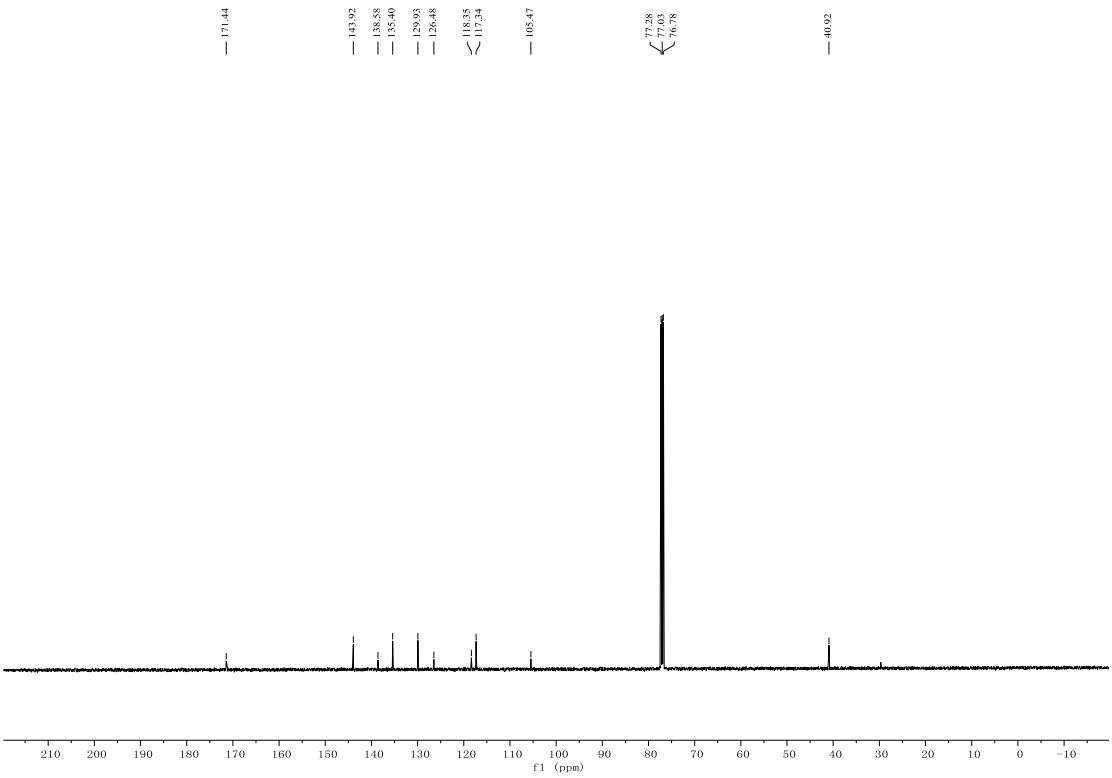

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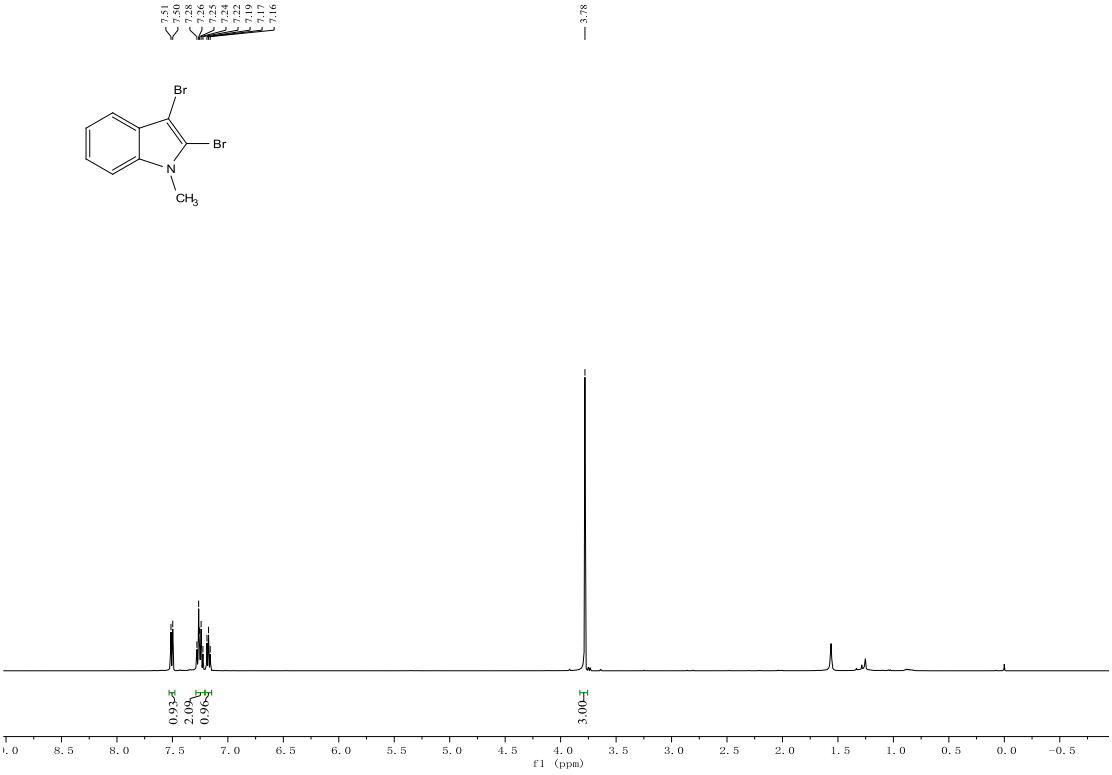

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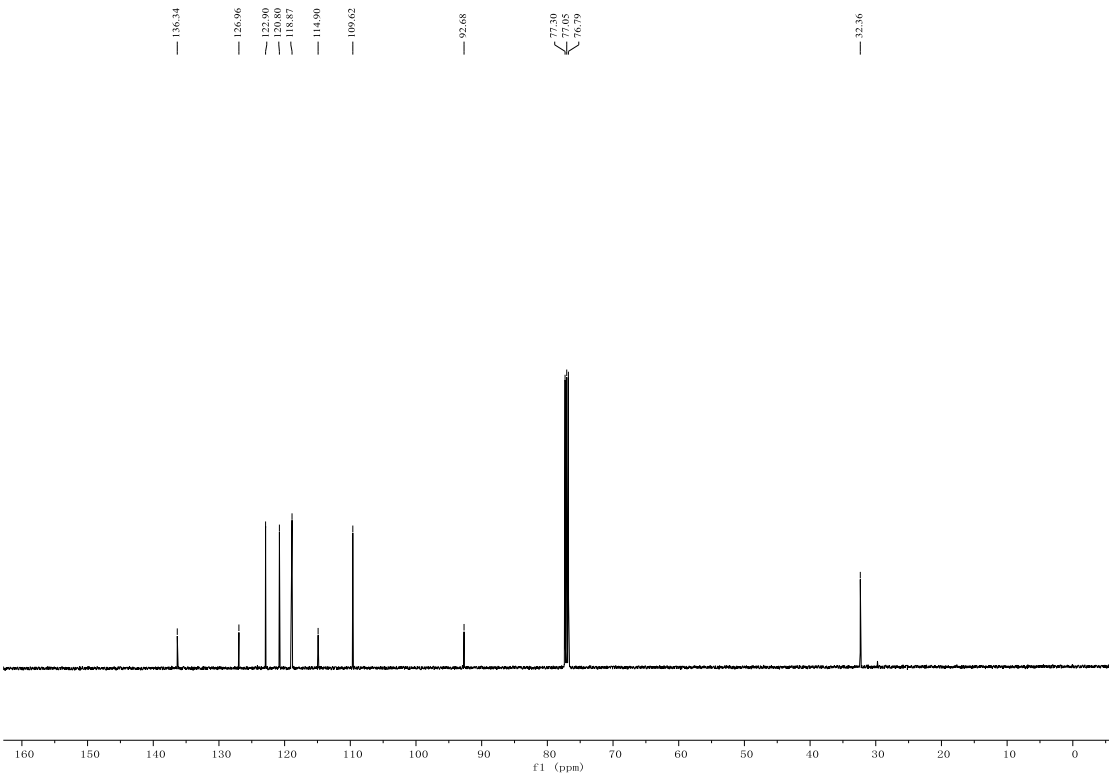

^{13}C NMR of compound **5da**