

Organic photoredox-catalyzed oxidative azolation of unactivated fluoroarenes

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1. Reagents

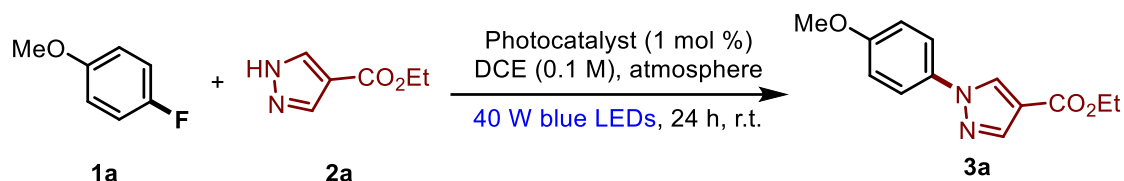
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

2. Instruments

NMR spectra were recorded on Varian Inova-400 MHz, Inova-300 MHz, Bruker DRX-400 or Bruker DRX-500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. HRMS analysis were carried out using a Bruker micrOTOF-Q instrument or a TOF-MS instrument. LC-MS analysis carried out using a Agilent Technologies 1260 Zinfinity. The fluorescence quenching experiment was carried out on Hitachi F-2500 fluorescence spectrophotometer. The reactor was 3.0 cm from 40 W blue LEDs.

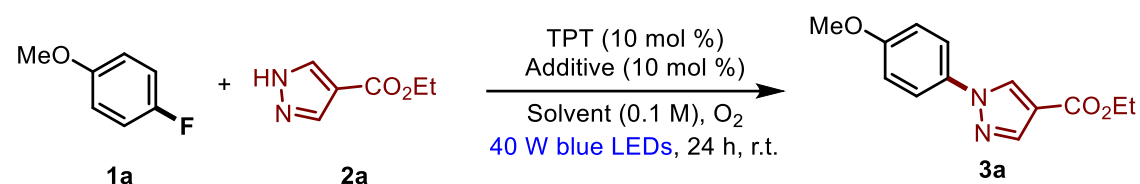
3. Optimization of reaction conditions

Table S-1: Influence of photocatalyst and reaction atmosphere^a



Entry	Photocatalyst	Atmosphere	Solvent	Yield (%) ^b
1 ^c	TPT	Air	DCE	22
2	<i>fac</i> -Ir(ppy) ₃	Air	DCE	0
3	Ir(df(CF ₃)ppy) ₂ (dtbbpy)PF ₆	Air	DCE	0
4	Ir(ppy) ₂ (dtbbpy)PF ₆	Air	DCE	0
5	Ru(bpy) ₃ Cl ₂	Air	DCE	0
6	Fluorescein	Air	DCE	0
7	Eosin Y	Air	DCE	0
8	DDQ	Air	DCE	trace
9 ^c	TPT	Ar	DCE	18
10 ^c	TPT	O ₂	DCE	35

^aReaction conditions: **1a** (0.1 mmol), **2a** (3.0 equiv), Photocatalyst (1 mol %), DCE (1 mL) at room temperature using irradiation with 40 W blue LEDs for 24 h. ^bIsolated yields. ^cPhotocatalyst (10 mol %).

Table S-2: Influence of additives and solvent^a

Entry	Photocatalyst	Additive	Atmosphere	Solvent	Yield (%) ^b
1	TPT	AgSbF ₆	O ₂	DCE	24
2	TPT	Fe(OTf) ₂	O ₂	DCE	19
3	TPT	Cu(OTf) ₂	O ₂	DCE	62
4	TPT	CuCl ₂	O ₂	DCE	27
5	TPT	CuO	O ₂	DCE	11
6	TPT	CuI	O ₂	DCE	22
7	TPT	CuBr	O ₂	DCE	26
8	TPT	Cu(OTf) ₂	O ₂	MeCN	trace
9	TPT	Cu(OTf) ₂	O ₂	DMF	trace
10	TPT	Cu(OTf) ₂	O ₂	DMSO	trace
11	TPT	Cu(OTf) ₂	O ₂	HFIP	14
12	TPT	Cu(OTf) ₂	O ₂	<i>n</i> -hexane	17
13	TPT	Cu(OTf) ₂	O ₂	DCM	67
14 ^c	TPT	Cu(OTf) ₂	O ₂	DCM	78

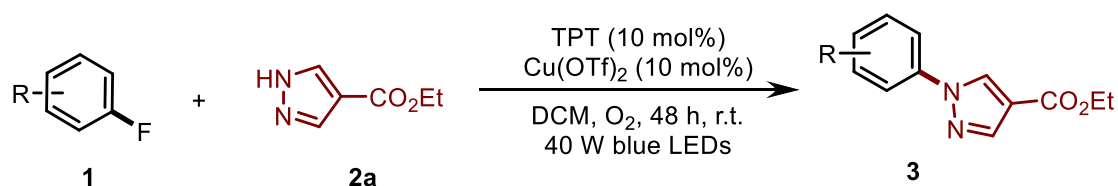
^aReaction conditions: **1a** (0.1 mmol), **2a** (3.0 equiv), TPT (10 mol %), Additive (10 mol %), Solvent (1 mL) at room temperature using irradiation with 40 W blue LEDs for 24 h. ^bIsolated yields. ^cReaction for 48 h.

4. General procedure for the synthesis of 3a-3q

The photochemical reaction setup is shown in Fig. S1. All the reactions were carried out under the blue light irradiation using a Geao Chemical 450-460 nm lamp. Ambient temperature throughout the course of the reaction was maintained by a cooling fan. The reaction vial was placed proximately 3-5 cm away from the Kessillight source (Fig. S1)

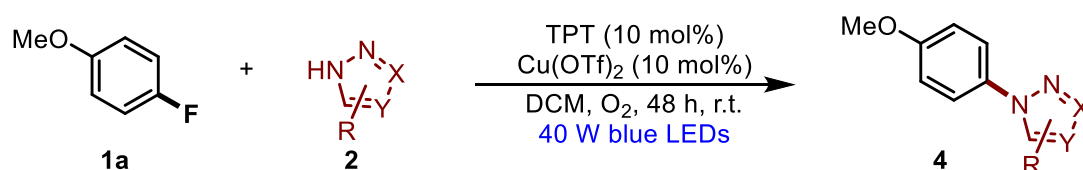


Figure S1: Photochemical reaction setup



A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole derivatives **1** (0.1 mmol, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (0.3 mmol, 3.0 equiv), TPT (4.0 mg, 10.0 mol%), Cu(OTf)₂ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tube was evacuated and backfilled with oxygen atmosphere (three times), then the mixture was stirred and irradiated by a 40 W blue LED at room temperature for 48 h. After the indicated reaction time, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1-20:1) to give the product **3**.

5. General procedure for the synthesis of 4a-4i



A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole **1a** (0.1 mmol, 12.6 mg, 1.0 equiv), pyrazole derivatives **2** (0.3 mmol, 3.0 equiv), TPT (4.0 mg, 10.0 mol%), Cu(OTf)₂ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tube was evacuated and backfilled with oxygen atmosphere (three times), then the mixture was stirred and irradiated by a 40 W blue LED at room temperature for 48 h. After the indicated reaction time, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1-20:1) to give the product **4**.

6. Gram-scale synthesis of **3a**

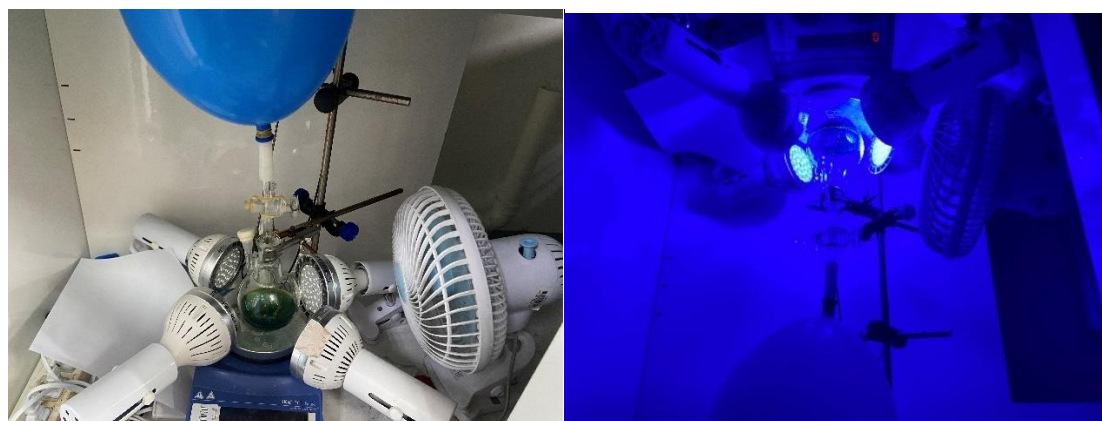
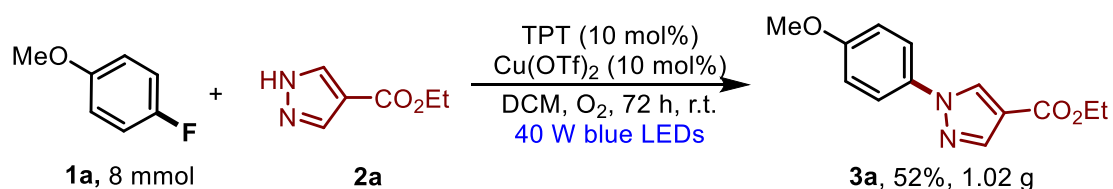


Figure S2: Photochemical reaction setup

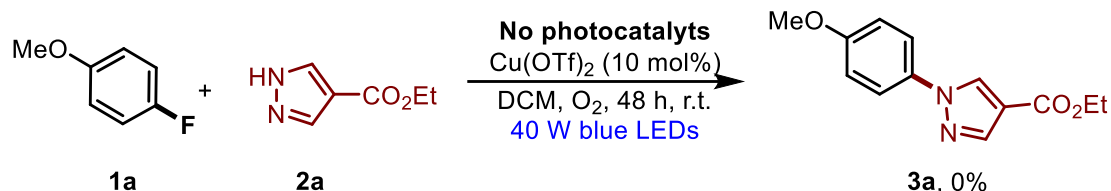


A dried 200 mL round-bottomed flask equipped with a magnetic stir bar was charged with 4-fluoroanisole derivatives **1a** (8.0 mmol, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (24.0 mmol, 3.0 equiv), TPT (320 mg, 10.0 mol%), Cu(OTf)₂ (288 mg, 10 mol%), and DCM (50 mL). The round-bottomed flask was evacuated and backfilled with oxygen atmosphere (three times), then the mixture was stirred and irradiated by 4 × 40 W blue LEDs at room temperature for 72 h. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with saturated NaCl solution, dried with anhydrous Na₂SO₄, and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column

chromatography on silica gel (petroleum ether/EtOAc) to afford desired product **3a** (1.02 g) in 52% yield.

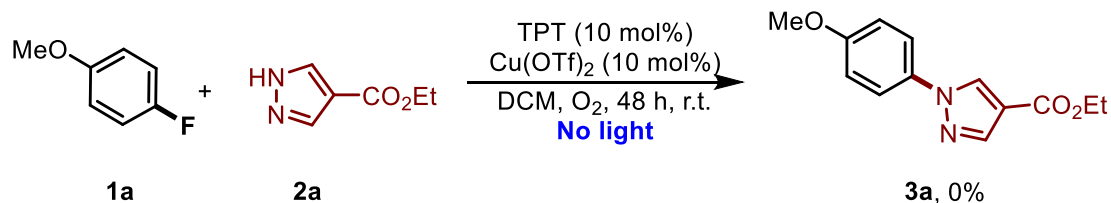
7. Control experiment

7.1 Reaction without photocatalyst



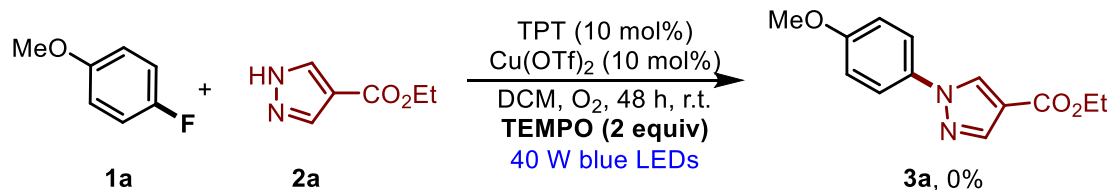
A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole **1a** (0.1 mmol, 12.6 mg, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (0.3 mmol, 3.0 equiv), Cu(OTf)₂ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tube was evacuated and backfilled with oxygen atmosphere (three times), then the mixture was stirred and irradiated by a 40 W blue LED at room temperature for 48 h. ¹H NMR showed no formation of the desired product, indicating that a photocatalyst was required for conversion.

7.2 Reaction without light



A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole **1a** (0.1 mmol, 12.6 mg, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (0.3 mmol, 3.0 equiv), TPT (4.0 mg, 10.0 mol%), Cu(OTf)₂ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tube was evacuated and backfilled with oxygen atmosphere (three times), then the mixture was stirred at room temperature for 48 h. ¹H NMR showed no formation of the desired product, indicating that the light's was required for conversion.

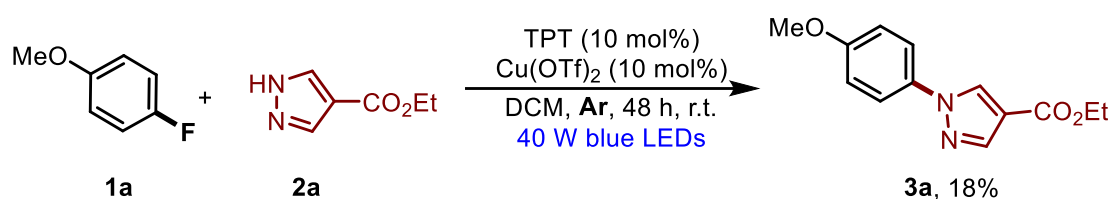
7.3 Reaction with TEMPO



A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole **1a** (0.1 mmol, 12.6 mg, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (0.3 mmol, 3.0 equiv), Cu(OTf)₂ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tube was evacuated and backfilled with oxygen atmosphere (three times), then the mixture was stirred and irradiated by a 40 W blue LED at room temperature for 48 h. ¹H NMR shows no desired product formation suggesting that the reaction proceeds through the radical mechanism.

7.4 Reaction without O₂

d) Reaction without O₂



A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole **1a** (0.1 mmol, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (0.3 mmol, 3.0 equiv), TPT (4.0 mg, 10.0 mol%), Cu(OTf)₂ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tube was evacuated and backfilled with Ar atmosphere (three times), then the mixture was stirred and irradiated by a 40 W blue LED at room temperature for 48 h. After the indicated reaction time, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1-20:1) to give the product **3a** (4.4 mg).

8. Mechanism experiment

8.1 Fluorescence Quenching Experiments^[1]

Test conditions for quenching reaction (I_0 and I are respective fluorescence intensities in the absence and presence of the indicated concentrations of the quenchers):

TPT: 1.6 mg dissolved in 50 mL DCM (0.00008 M)

Quencher: 36.2 mg of **Cu(OTf)₂** dissolved in 25 mL DCM (0.004 M)

14.1 mg of **2a** dissolved in 25 mL DCM (0.004 M)

12.6 mg of **1a** dissolved in 25 mL DCM (0.004 M)

General procedure:

1 mL of prepared solution containing TPT was added to a cuvette, keep the total volume at 4 mL, **Quenchers** and DCM were added as the following table:

Entry	TPT	Quencher	DCM	Concentration of quencher
1	1 mL	0 mL	3 mL	0 M
2	1 mL	0.25 mL	2.75 mL	2.5×10^{-4} M
3	1 mL	0.5 mL	2.5 mL	5.0×10^{-4} M
4	1 mL	0.75 mL	2.25 mL	7.5×10^{-4} M
5	1 mL	1 mL	2 mL	1×10^{-3} M

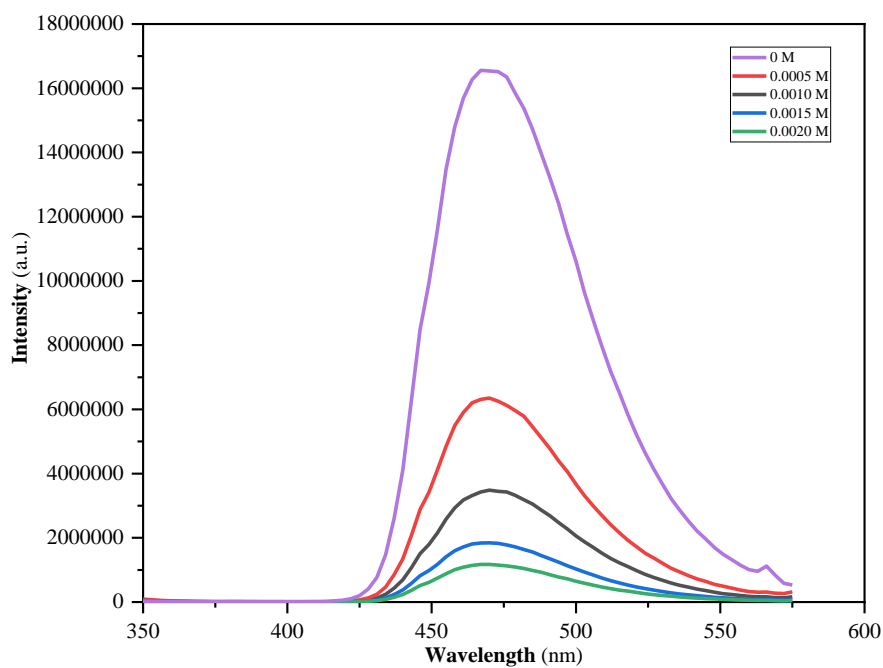


Figure S-1. Fluorescence quenching experiments with **1a**

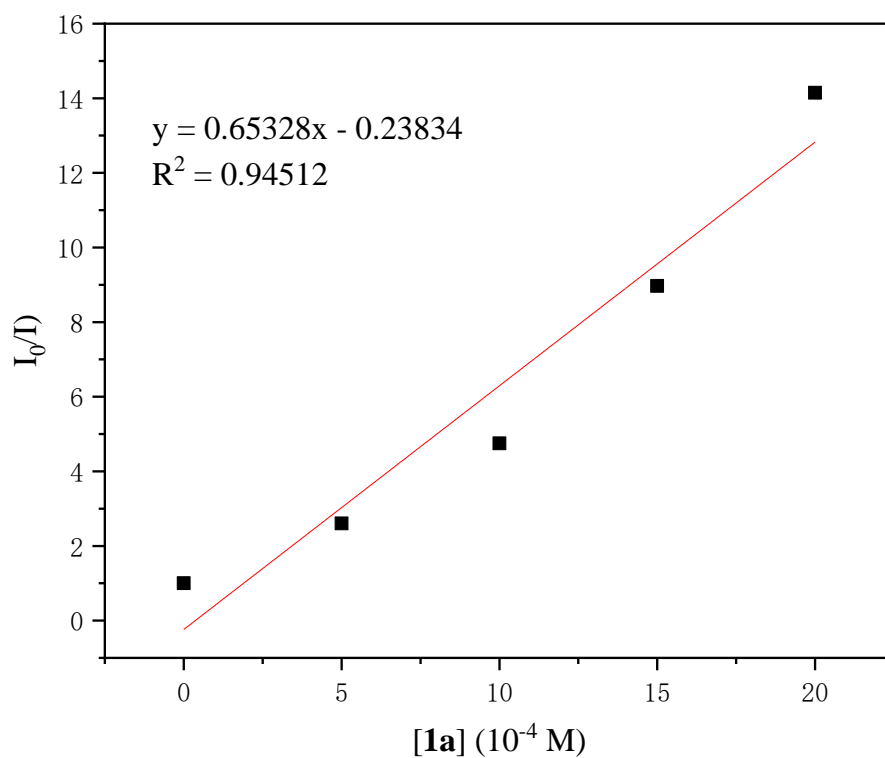


Figure S-2. Stern-Volmer plots of **1a**

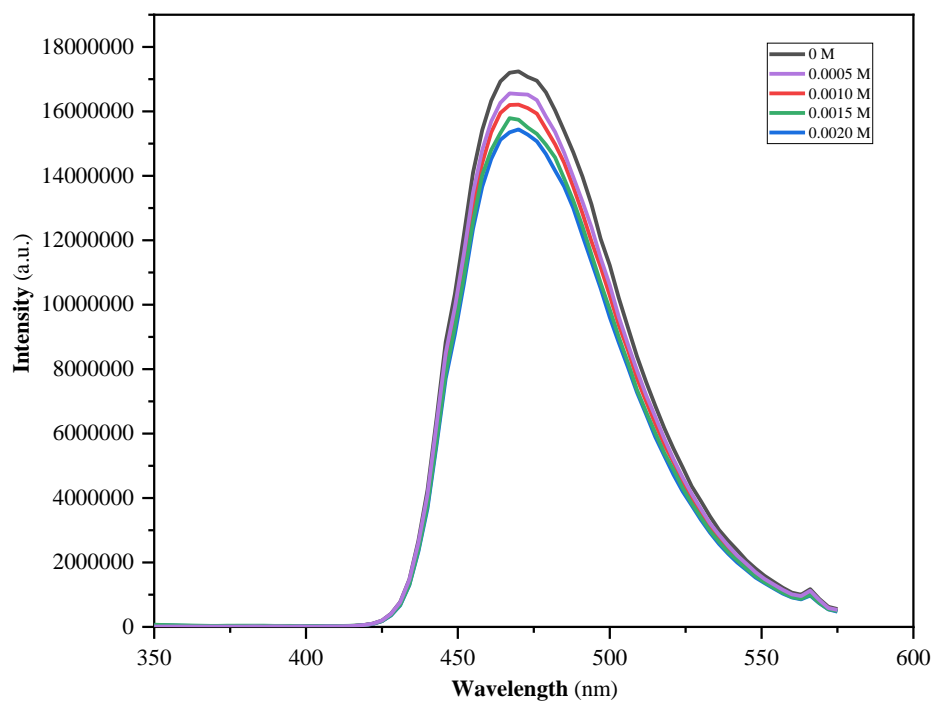


Figure S-3. Fluorescence quenching experiments with **2a**

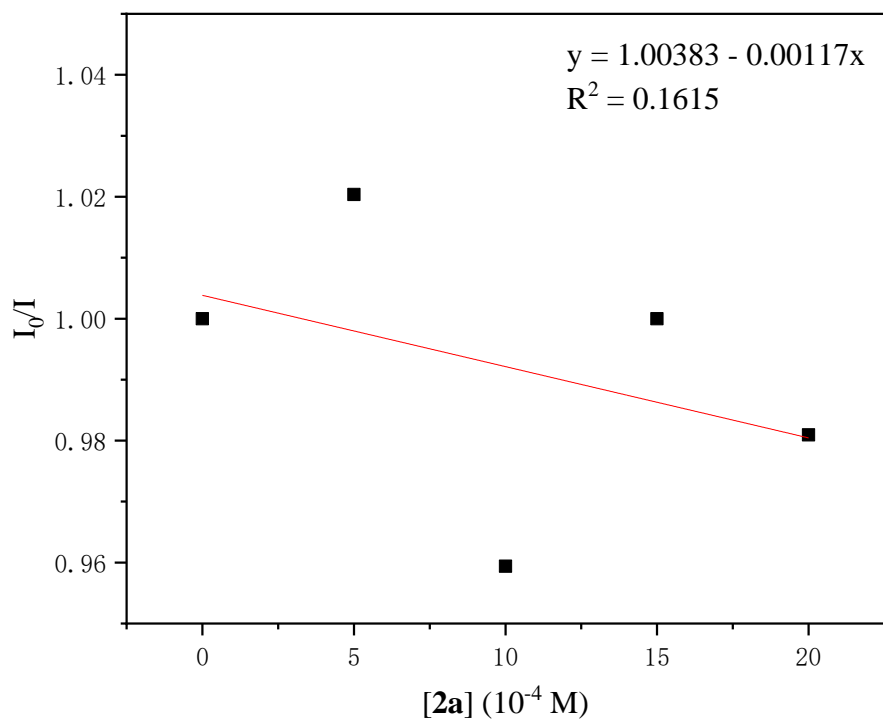


Figure S-4. Stern-Volmer plots of **2a**

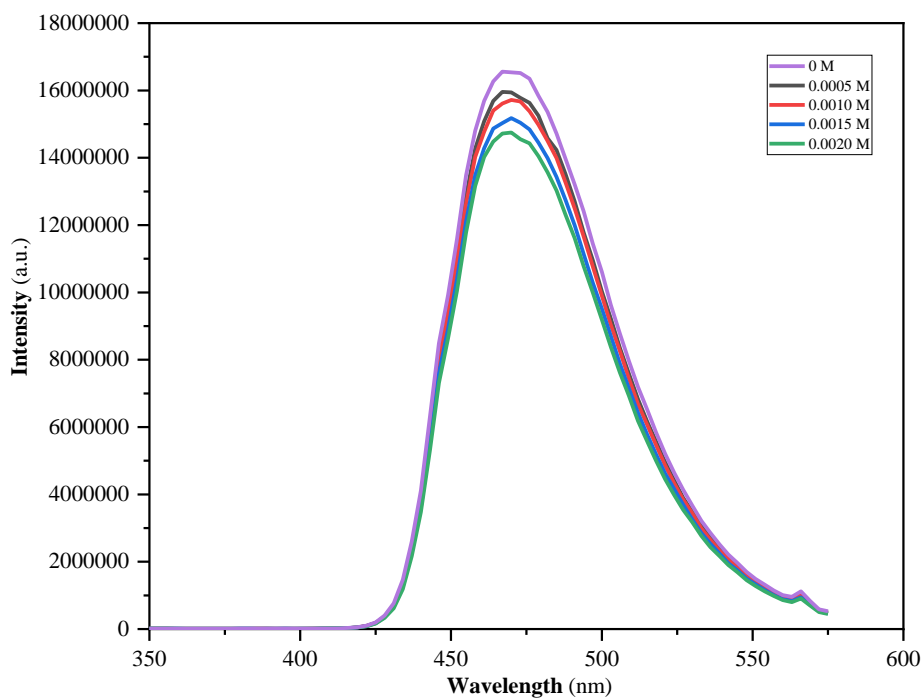


Figure S-5. Fluorescence quenching experiments with $\text{Cu}(\text{OTf})_2$

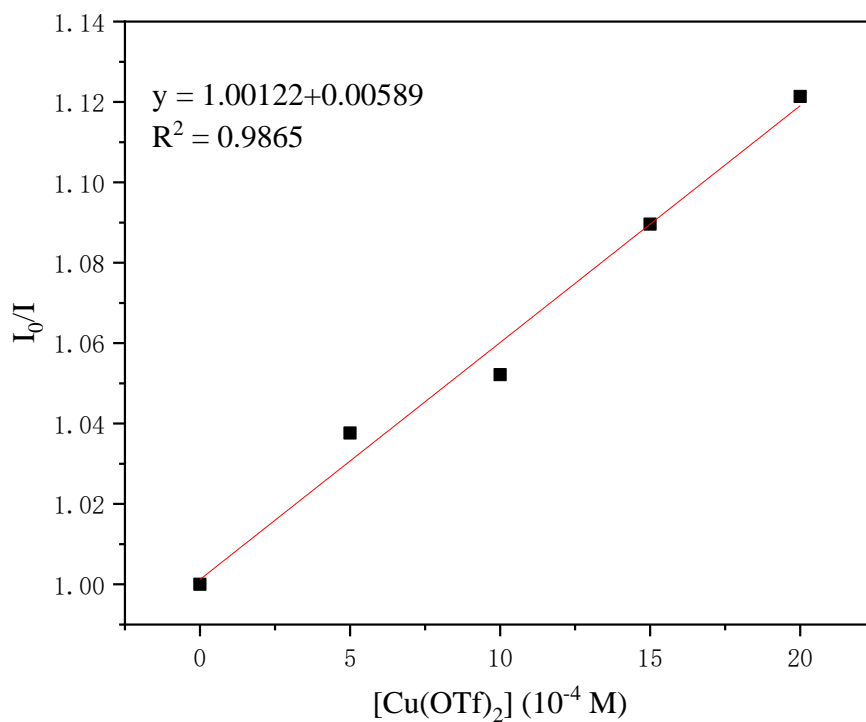
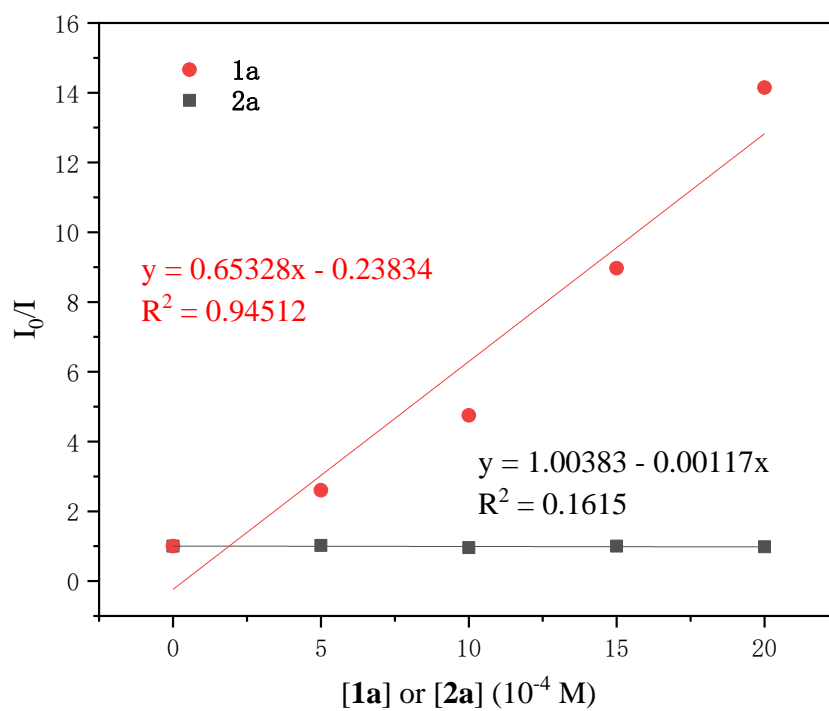


Figure S-6. Stern-Volmer plots of Cu(OTf)₂



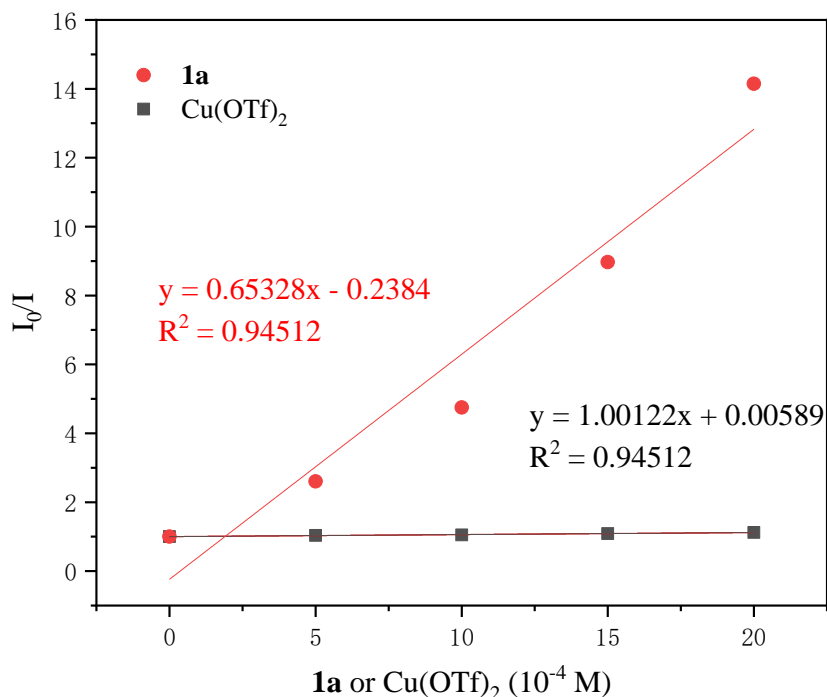


Figure S-7. Quenching efficiency of **1a**, **2a**, and $\text{Cu}(\text{OTf})_2$

Inference: The results can clearly show that **1a** quench TPT more effectively than that of **2a** and $\text{Cu}(\text{OTf})_2$

8.2 Light ON-OFF experiment

Eight standard reaction mixtures were added to six dry 25 ml Schlenk tubes. A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-fluoroanisole **1a** (0.1 mmol, 1.0 equiv), ethyl 1H-pyrazole-4-carboxylate **2a** (0.3 mmol, 3.0 equiv), TPT (4.0 mg, 10.0 mol%), $\text{Cu}(\text{OTf})_2$ (3.6 mg, 10 mol%), and DCM (1.0 mL). The tubes were evacuated and backfilled with argon (three times). Then the mixtures were stirred and irradiated by a 40 W blue LED at room temperature. After two hours, the blue LED was turned off and one Schlenk tube was removed from the irradiator for treatment. The remaining seven Schlenk tubes were stirred for two hours in the absence of light. Then one Schlenk tube was removed for treatment and the blue LED was turned back on to irradiate the remaining six reactions. After another two hours, the blue LED was

turned off and one Schlenk tube was removed for treatment. The remaining five reactions were stirred under no light for another two hours. Next, one Schlenk tube was removed for processing and the blue LED was turned back on to irradiate the remaining four reactions. Two hours later, the blue LED was turned off and one Schlenk tube was removed for processing, and the remaining three Schlenk tube was stirred for two hours in the absence of light. Then, Schlenk tube was removed for processing. Repeat the previous operation until the last reaction is processed. The crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to afford desired products **3a**. The yield of **3a** was measured by weight of the product. The nature of the graph indicates that the azolation process is light dependent as no formation of desired product was observed in the absence of the light.

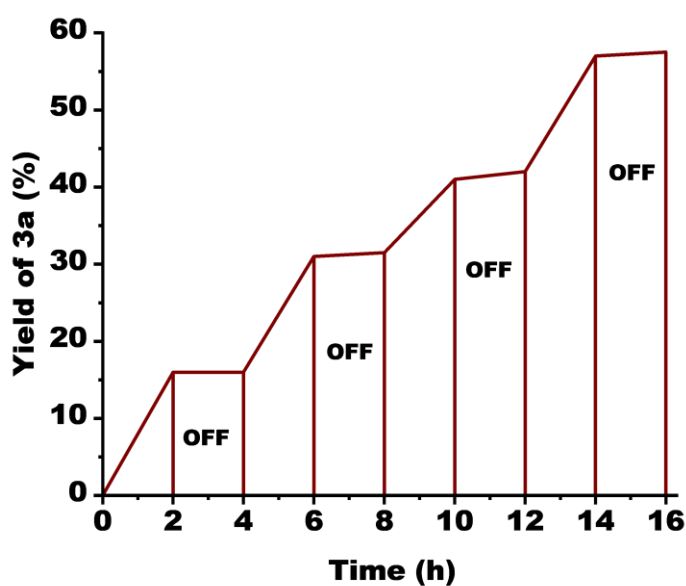


Figure S-8 Light ON-OFF experiment

8.3 UV-experiments

Step 1: 0.1 mmol of **1a**, TPT, and [**1a** (0.1 mmol, 1 eq)+TPT (0.34 eq)] in 1 mL of DCM.

Step 2: put 1 μ l of Step 1 solution into a cuvette containing 2 mL of DCM. Finally, the absorption spectra of these solutions were analysed (Figure S-9) using a UV-Vis spectrophotometer. (UV-3600, Shimadzu, Japan).

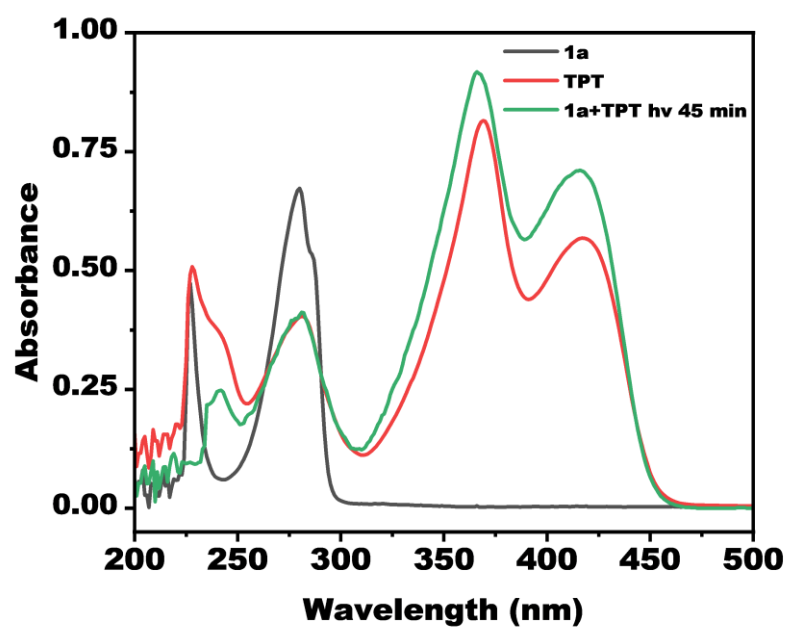
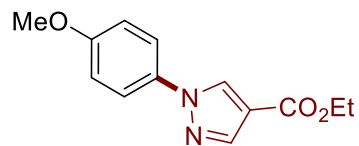


Figure S-9 UV-experiments

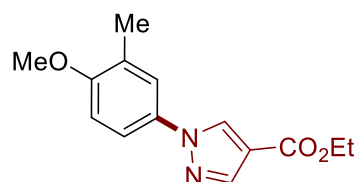
9. Characterization data of products

Ethyl 1-(4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3a)



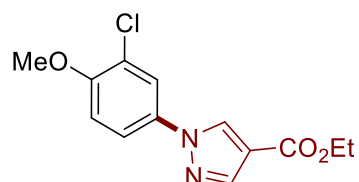
White solid, m.p. 65-68 °C. Isolated yield: 19.2 mg, 78%. **¹H NMR** (400 MHz, CDCl₃) δ 8.30 (s, 1H), 8.07 (s, 1H), 7.60 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 163.1, 159.1, 142.0, 133.2, 130.1, 121.4, 116.7, 114.8, 60.5, 55.7, 14.5. **HRMS** Calcd for C₁₃H₁₅N₂O₃ [M+H]⁺: 247.1077; Found: 247.1085.

Ethyl 1-(4-methoxy-3-methylphenyl)-1H-pyrazole-4-carboxylate (3b)



White solid, m.p. 78-81 °C. Isolated yield: 13.5 mg, 52%. **¹H NMR** (400 MHz, CDCl₃) δ 8.29 (s, 1H), 8.06 (s, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 2.27 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 163.1, 157.3, 141.9, 132.7, 130.1, 128.2, 122.6, 118.4, 116.5, 110.4, 60.5, 55.8, 16.5, 14.5. **HRMS** Calcd for C₁₄H₁₇N₂O₃ [M+H]⁺: 261.1234; Found: 261.1229.

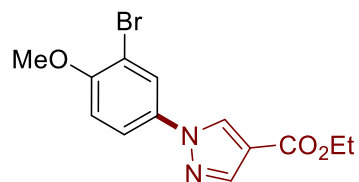
Ethyl 1-(3-chloro-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3c)



White solid, m.p. 67-71 °C. Isolated yield: 15.4 mg, 55%. **¹H NMR** (400 MHz, CDCl₃) δ 8.30 (s, 1H), 8.07 (s, 1H), 7.76 (d, *J* = 2.7 Hz, 1H), 7.55 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 162.9, 154.6, 142.3, 133.3, 130.1, 123.6, 122.2, 119.1,

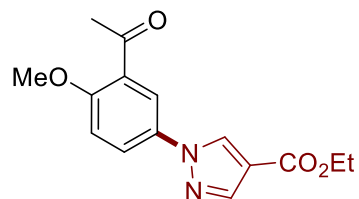
117.1, 112.5, 60.6, 56.6, 14.5. **HRMS** Calcd for $C_{13}H_{14}ClN_2O_3$ $[M+H]^+$: 281.0687; Found: 281.0677.

Ethyl 1-(3-bromo-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3d)



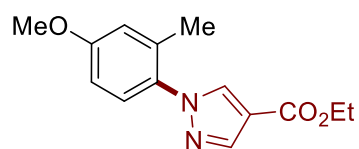
White solid, m.p. 97-99 °C. Isolated yield: 23.3 mg, 72%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.06 (s, 1H), 7.92 (d, $J = 2.7$ Hz, 1H), 7.59 (dd, $J = 8.8, 2.7$ Hz, 1H), 6.96 (d, $J = 8.9$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 3.93 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 155.5, 142.3, 133.6, 130.0, 125.2, 119.9, 117.1, 112.4, 112.2, 60.6, 56.7, 14.5. **HRMS** Calcd for $C_{13}H_{14}BrN_2O_3$ $[M+H]^+$: 325.0182; Found: 325.0187.

Ethyl 1-(3-acetyl-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3e)



White solid, m.p. 91-93 °C. Isolated yield: 21.9 mg, 76%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.07 (s, 1H), 8.00 (d, $J = 2.9$ Hz, 1H), 7.88 (dd, $J = 8.9, 2.9$ Hz, 1H), 7.08 (d, $J = 9.0$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 3.97 (s, 3H), 2.65 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.5, 162.9, 158.2, 142.3, 133.1, 130.1, 128.6, 125.3, 121.4, 117.0, 113.0, 60.6, 56.2, 32.0, 14.5. **HRMS** Calcd for $C_{15}H_{17}N_2O_4$ $[M+H]^+$: 289.1183; Found: 289.1189.

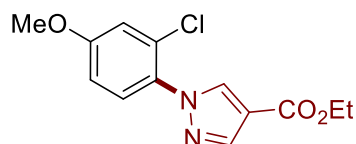
Ethyl 1-(4-methoxy-2-methylphenyl)-1H-pyrazole-4-carboxylate (3f)



Yellow oil. Isolated yield: 21.1 mg, 81%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.02 (s, 1H), 7.21 (d, $J = 8.6$ Hz, 1H), 6.82 (d, $J = 2.9$ Hz, 1H), 6.78 (dd, $J = 8.6, 2.9$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 2.17 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H).

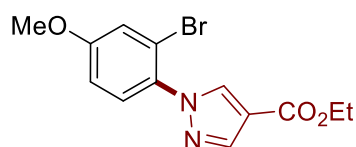
^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 160.0, 141.6, 135.6, 134.3, 132.5, 127.4, 116.4, 115.8, 111.8, 60.4, 55.6, 18.1, 14.5. **HRMS** Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 261.1234; Found: 261.1241.

Ethyl 1-(2-chloro-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3g)



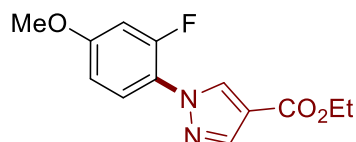
Yellow oil. Isolated yield: 23.5 mg, 84%. ^1H NMR (400 MHz, CDCl_3) δ 8.21 (s, 1H), 8.08 (s, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 6.89 (dd, J = 8.8, 2.8 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 160.3, 141.9, 134.9, 130.8, 130.0, 128.7, 116.2, 115.6, 113.6, 60.5, 56.0, 14.5. **HRMS** Calcd for $\text{C}_{13}\text{H}_{14}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 281.0687; Found: 281.0696.

Ethyl 1-(2-bromo-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3h)



Yellow oil. Isolated yield: 26.9 mg, 83%. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 8.09 (s, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 2.8 Hz, 1H), 6.93 (dd, J = 8.8, 2.8 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 160.5, 141.9, 135.1, 132.4, 129.0, 119.9, 118.6, 116.1, 114.1, 60.5, 56.0, 14.5. **HRMS** Calcd for $\text{C}_{13}\text{H}_{14}\text{BrN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 325.0182; Found: 325.0177.

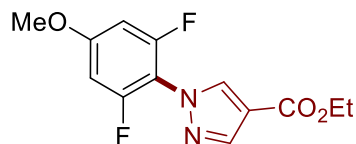
Ethyl 1-(2-fluoro-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3i)



White solid, m.p. 68-70 °C. Isolated yield: 23.0 mg, 87%. ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, J = 2.3 Hz, 1H), 8.08 (s, 1H), 7.71 (t, J = 9.1 Hz, 1H), 6.83 – 6.73 (m, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -122.49. ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 160.1 (d, J = 10.2 Hz), 154.7 (d, J = 249.5 Hz), 141.8, 133.9 (d, J = 8.1 Hz), 125.7 (d, J = 2.0 Hz), 121.2 (d, J = 10.8

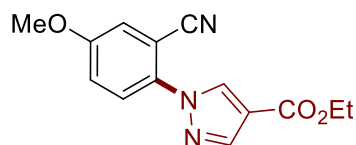
Hz), 116.7, 110.7 (d, $J = 3.0$ Hz), 102.7 (d, $J = 23.9$ Hz), 60.5, 56.0, 14.5. **HRMS** Calcd for $C_{13}H_{14}FN_2O_3$ $[M+H]^+$: 265.0983; Found: 265.0987.

Ethyl 1-(2,6-difluoro-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3j)



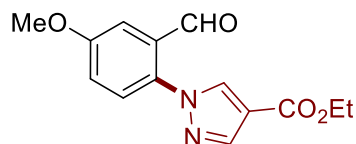
Colourless oil. Isolated yield: 25.2 mg, 89%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.09 (s, 1H), 6.61 (s, 1H), 6.59 (s, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.97. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 161.2 (t, $J = 13.2$ Hz), 158.2 (dd, $J = 252.8, 6.0$ Hz), 142.5, 136.1, 129.4 (d, $J = 168.3$ Hz), 116.5, 98.7 (dd, $J = 24.1, 2.8$ Hz), 60.6, 56.3, 14.5. **HRMS** Calcd for $C_{13}H_{13}F_2N_2O_3$ $[M+H]^+$: 283.0889; Found: 283.0884.

Ethyl 1-(2-cyano-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3k)



White solid, m.p. 102-105 °C. Isolated yield: 23.1 mg, 85%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.15 (s, 1H), 7.61 (d, $J = 9.2$ Hz, 1H), 7.26 – 7.21 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.89 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 159.2, 142.9, 134.8, 133.1, 126.7, 120.4, 118.4, 117.6, 116.0, 107.9, 60.7, 56.2, 14.5. **HRMS** Calcd for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1030; Found: 272.1038.

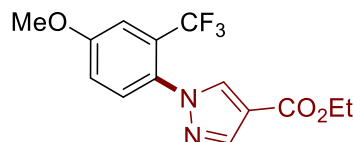
Ethyl 1-(2-formyl-4-methoxyphenyl)-1H-pyrazole-4-carboxylate (3l)



White solid, m.p. 137-139 °C. Isolated yield: 19.8 mg, 72%. **1H NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.23 (s, 1H), 8.13 (s, 1H), 7.50 (dd, $J = 3.0, 0.8$ Hz, 1H), 7.41 (d, $J = 8.7$ Hz, 1H), 7.21 (dd, $J = 8.7, 3.0$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.91 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.1, 162.7, 160.1, 142.7,

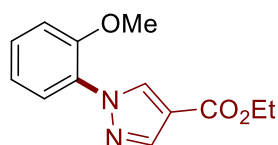
135.1, 134.4, 131.8, 126.9, 121.5, 117.3, 111.7, 60.7, 56.1, 14.5. **HRMS** Calcd for $C_{14}H_{15}N_2O_4$ $[M+H]^+$: 275.1026; Found: 275.1038.

Ethyl 1-(4-methoxy-2-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3m)



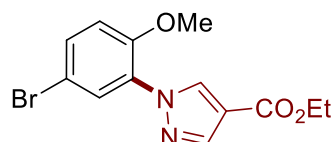
Yellow oil. Isolated yield: 24.8 mg, 79%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.41 (d, $J = 8.7$ Hz, 1H), 7.27 (d, $J = 2.9$ Hz, 1H), 7.13 (dd, $J = 8.7, 2.9$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.73. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 160.2, 142.0, 135.4 (d, $J = 1.8$ Hz), 130.7, 127.7 (d, $J = 31.7$ Hz), 129.6 – 124.9 (m), 122.6 (d, $J = 273.8$ Hz), 117.5, 116.4, 112.9 (q, $J = 5.1$ Hz), 60.6, 56.1, 14.5. **HRMS** Calcd for $C_{14}H_{14}F_3N_2O_3$ $[M+H]^+$: 315.0951; Found: 315.0958.

Ethyl 1-(2-methoxyphenyl)-1H-pyrazole-4-carboxylate (3n)^[2]



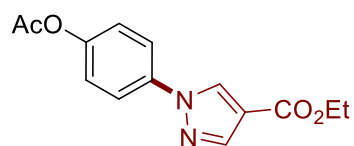
Colorless liquid. Isolated yield: 17.7 mg, 72 %. **1H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (s, 1H), 7.72 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.36 – 7.28 (m, 1H), 7.09 – 7.02 (m, 2H), 4.32 (q, $J = 7.1$ Hz, 2H), 3.88 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 151.3, 141.4, 135.1, 129.0, 125.3, 121.2, 115.8, 112.3, 60.3, 56.0, 14.5.

Ethyl 1-(2-methoxyphenyl)-1H-pyrazole-4-carboxylate (3o)



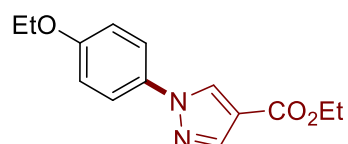
Yellow solid, m.p. 95-97 °C. Isolated yield: 21.5 mg, 66%. **1H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (s, 1H), 7.64 (dd, $J = 8.1, 0.7$ Hz, 1H), 7.23 – 7.18 (m, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 3.92 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 151.6, 141.5, 134.9, 128.0, 126.2, 124.4, 121.9, 116.2, 115.9, 60.4, 56.4, 14.5. **HRMS** Calcd for $C_{13}H_{14}BrN_2O_3$ $[M+H]^+$: 325.0182; Found: 325.0186.

Ethyl 1-(4-acetoxyphenyl)-1H-pyrazole-4-carboxylate (3q)



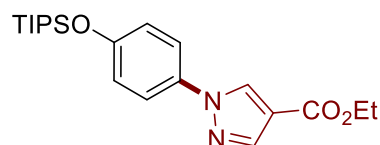
White solid, m.p. 94-96 °C. Isolated yield: 20.8 mg, 76 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.36 (s, 1H), 8.08 (s, 1H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.20 (d, $J = 9.0$ Hz, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.31 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.3, 162.8, 149.8, 142.4, 137.1, 130.1, 122.9, 120.7, 117.2, 60.6, 21.2, 14.5. **HRMS** Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 275.1026; Found: 275.1036.

Ethyl 1-(4-ethoxyphenyl)-1H-pyrazole-4-carboxylate (3r)



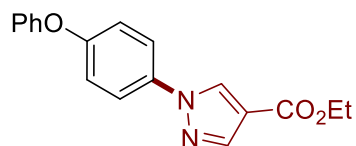
White solid, m.p. 62-63 °C. Isolated yield: 17.0 mg, 64%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (s, 1H), 8.06 (s, 1H), 7.58 (d, $J = 9.0$ Hz, 2H), 6.97 (d, $J = 9.0$ Hz, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 4.07 (q, $J = 7.0$ Hz, 2H), 1.44 (t, $J = 7.0$ Hz, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 177.9, 163.1, 158.5, 142.0, 130.1, 121.4, 116.7, 115.3, 64.0, 60.5, 14.9, 14.6. **HRMS** Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 261.1234; Found: 261.1245.

Ethyl 1-(4-((triisopropylsilyl)oxy)phenyl)-1H-pyrazole-4-carboxylate (3s)



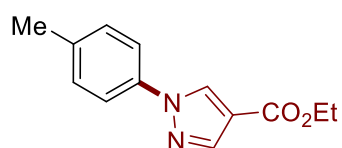
Colourless oil. Isolated yield: 15.1 mg, 39%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (s, 1H), 8.06 (s, 1H), 7.53 (d, $J = 8.9$ Hz, 2H), 6.96 (d, $J = 8.9$ Hz, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.33 – 1.22 (m, 3H), 1.11 (d, $J = 7.3$ Hz, 18H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.1, 155.9, 142.0, 133.4, 130.1, 121.3, 120.8, 116.7, 60.5, 18.0, 14.6, 12.8. **HRMS** Calcd for $\text{C}_{21}\text{H}_{33}\text{N}_2\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 389.2255; Found: 389.2268.

Ethyl 1-(4-phenoxyphenyl)-1H-pyrazole-4-carboxylate (3t)^[3]



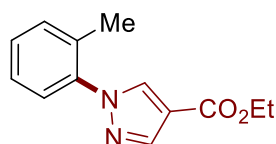
White solid, m.p. 108-110 °C. Isolated yield: 19.1 mg, 62%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 (d, $J = 0.7$ Hz, 1H), 8.08 (s, 1H), 7.70 – 7.59 (m, 2H), 7.40 – 7.32 (m, 2H), 7.17 – 7.11 (m, 1H), 7.11 – 7.06 (m, 2H), 7.06 – 7.01 (m, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.9, 156.9, 156.8, 142.2, 135.0, 130.1, 130.0, 123.9, 121.4, 119.5, 119.2, 116.9, 60.5, 14.5.

Ethyl 1-(p-tolyl)-1H-pyrazole-4-carboxylate (3u)^[4]



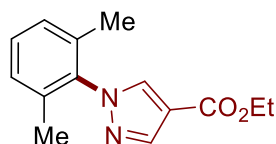
Brown solid. Mp: 68-70 °C. Isolated yield: 15.6 mg, 68 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.28 (s, 1H), 8.00 (s, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 7.5$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.30 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.0, 142.1, 137.6, 137.3, 130.2, 130.0, 119.6, 116.8, 60.5, 21.1, 14.5.

Ethyl 1-(o-tolyl)-1H-pyrazole-4-carboxylate (3v)^[5]



Yellow oil. Isolated yield: 10.0 mg, 42%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (dd, $J = 7.9, 0.6$ Hz, 2H), 7.40 – 7.26 (m, 4H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.24 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (101 MHz, Chloroform-*d*) δ 163.2, 141.7, 139.3, 134.0, 133.8, 131.6, 129.3, 126.9, 126.1, 116.0, 60.5, 18.1, 14.5.

Ethyl 1-(2,6-dimethylphenyl)-1H-pyrazole-4-carboxylate (3w)

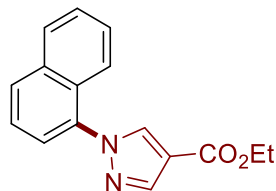


Yellow oil. Isolated yield: 15.6 mg, 64%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (s, 1H), 8.05 (s, 1H), 7.29 – 7.24 (m, 1H), 7.23 – 7.12 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 2.35 (s, 3H), 2.06 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.2,

141.6, 139.4, 138.8, 134.3, 133.0, 130.8, 126.1, 124.1, 115.9, 60.4, 20.4, 14.5, 14.4.

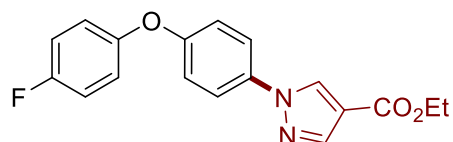
HRMS Calcd for $C_{14}H_{17}N_2O_2$ $[M+H]^+$: 245.1285; Found: 245.1289.

Ethyl 1-(naphthalen-1-yl)-1H-pyrazole-4-carboxylate (3x)^[3]



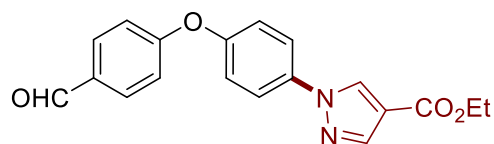
White solid, m.p. 104-106 °C. Isolated yield: 10.6 mg, 44%. **¹H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.23 (s, 1H), 8.00 – 7.90 (m, 2H), 7.80 – 7.72 (m, 1H), 7.58 – 7.51 (m, 4H), 4.36 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (100 MHz, $CDCl_3$) δ 163.1, 142.2, 136.5, 135.1, 134.4, 129.9, 128.9, 128.4, 127.7, 127.0, 125.1, 123.5, 122.9, 116.3, 60.6, 14.5.

Ethyl 1-(4-(4-fluorophenoxy)phenyl)-1H-pyrazole-4-carboxylate (3y)



White solid, 77-79 °C. Isolated yield: 26.7 mg, 82 %. **¹H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.08 (s, 1H), 7.64 (d, $J = 9.0$ Hz, 2H), 7.12 – 6.98 (m, 6H), 4.33 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H). **¹⁹F NMR** (376 MHz, $CDCl_3$) δ -119.11. **¹³C NMR** (100 MHz, $CDCl_3$) δ 162.9, 159.3 (d, $J = 242.7$ Hz), 157.3, 152.5 (d, $J = 2.8$ Hz), 142.2, 135.0, 130.1, 121.5, 120.9 (d, $J = 8.1$ Hz), 119.0, 117.4 – 116.1 (m), 60.6, 14.5. **HRMS** Calcd for $C_{18}H_{16}FN_2O_3$ $[M+H]^+$: 327.1139; Found: 327.1147.

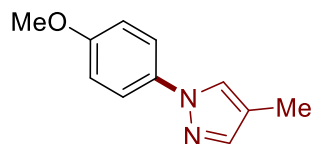
Ethyl 1-(4-(4-formylphenoxy)phenyl)-1H-pyrazole-4-carboxylate (3z)



White solid, 85-87 °C. Isolated yield: 25.2 mg, 75 %. **¹H NMR** (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.38 (d, $J = 0.6$ Hz, 1H), 8.09 (s, 1H), 7.90 – 7.84 (m, 2H), 7.78 – 7.70 (m, 2H), 7.23 – 7.15 (m, 2H), 7.14 – 7.07 (m, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (100 MHz, $CDCl_3$) δ 190.8, 162.9, 162.7, 154.6, 142.4, 136.3, 132.2,

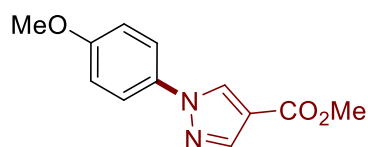
131.9, 130.2, 121.61, 121.4, 118.0, 117.2, 60.6, 14.5. **HRMS** Calcd for C₁₉H₁₇N₂O₄ [M+H]⁺: 337.1183; Found: 337.1187.

1-(4-methoxyphenyl)-4-methyl-1H-pyrazole (4a)



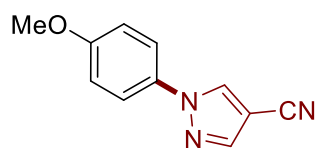
White solid, m.p. 52-54 °C. Isolated yield: 9.6 mg, 51 %. **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (s, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.49 (s, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 2.15 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 158.1, 141.4, 134.3, 125.6, 120.6, 117.9, 114.6, 55.7, 9.1. **HRMS** Calcd for C₁₁H₁₃N₂O [M+H]⁺: 189.1022; Found: 189.1018.

Methyl 1-(4-methoxyphenyl)-1H-pyrazole-4-carboxylate (4b)



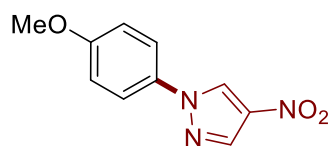
White solid, 115-116 °C. Isolated yield: 12.8 mg, 55 %. **¹H NMR** (400 MHz, CDCl₃) δ 8.31 (s, 1H), 8.07 (s, 1H), 7.60 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 163.5, 159.2, 142.0, 133.2, 130.2, 121.4, 116.3, 114.8, 55.8, 51.7. **HRMS** Calcd for C₁₂H₁₃N₂O₃ [M+H]⁺: 233.0921; Found: 233.0931.

1-(4-methoxyphenyl)-1H-pyrazole-4-carbonitrile (4c)



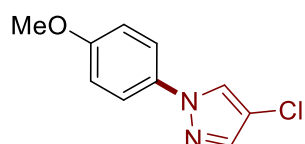
White solid, 76-78 °C. Isolated yield: 12.5 mg, 63 %. **¹H NMR** (400 MHz, CDCl₃) δ 8.20 (d, *J* = 0.6 Hz, 1H), 7.95 (s, 1H), 7.56 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 159.6, 143.1, 132.5, 131.8, 121.7, 114.9, 113.3, 94.0, 55.8. **HRMS** Calcd for C₁₁H₁₀N₃O [M+H]⁺: 200.0818; Found: 200.0826.

1-(4-methoxyphenyl)-4-nitro-1H-pyrazole (4d)



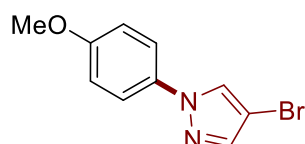
White solid, m.p. 124-126 °C. Isolated yield: 11.6 mg, 53 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.52 (d, $J = 0.6$ Hz, 1H), 8.23 (s, 1H), 7.60 (d, $J = 9.1$ Hz, 2H), 7.01 (d, $J = 9.0$ Hz, 2H), 3.87 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.9, 141.4, 136.6, 132.3, 125.9, 121.6, 115.0, 55.8. **HRMS** Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 200.0818; Found: 200.0826.

4-chloro-1-(4-methoxyphenyl)-1H-pyrazole (4e)



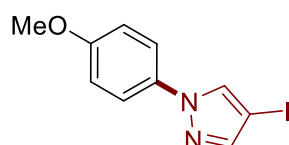
White solid, m.p. 75-78 °C. Isolated yield: 7.3 mg, 35 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.61 (s, 1H), 7.53 (d, $J = 9.0$ Hz, 2H), 6.97 (d, $J = 9.0$ Hz, 2H), 3.85 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.0, 158.8, 157.1, 139.1, 125.1, 120.9, 114.8, 55.7. **HRMS** Calcd for $\text{C}_{10}\text{H}_{10}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 209.0476; Found: 209.0481.

4-bromo-1-(4-methoxyphenyl)-1H-pyrazole (4f)



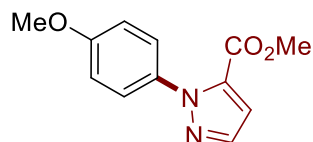
White solid, m.p. 81-83 °C. Isolated yield: 9.3 mg, 37 %. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (s, 1H), 7.64 (s, 1H), 7.53 (d, $J = 9.0$ Hz, 2H), 6.97 (d, $J = 9.0$ Hz, 2H), 3.85 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.8, 141.2, 133.6, 127.3, 121.0, 114.8, 95.2, 55.7. **HRMS** Calcd for $\text{C}_{10}\text{H}_{10}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 252.9971; Found: 252.9978.

4-iodo-1-(4-methoxyphenyl)-1H-pyrazole (4g)



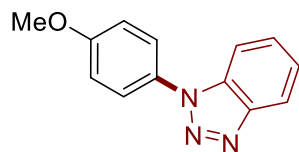
White solid, m.p. 105-107 °C. Isolated yield: 12.3 mg, 41 %. **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.68 (s, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.1, 158.8, 145.7, 133.5, 131.5, 121.0, 114.7, 55.7. **HRMS** Calcd for C₁₀H₁₀IN₂O [M+H]⁺: 300.9832; Found: 300.9838.

Ethyl 1-(4-methoxyphenyl)-1H-pyrazole-5-carboxylate (4h)



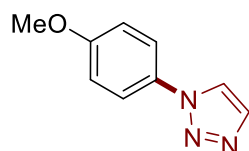
White solid, m.p. 61-63 °C. Isolated yield: 15.0 mg, 61 %. **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.00 – 6.92 (m, 3H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 162.5, 159.2, 145.0, 133.5, 128.6, 122.0, 114.7, 110.3, 61.2, 55.7, 14.5. **HRMS** Calcd for C₁₃H₁₅N₂O₃ [M+H]⁺: 247.1077; Found: 247.1085.

1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (4i)



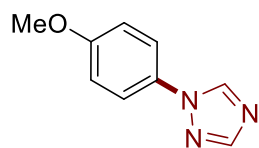
White solid, m.p. 70-73 °C. Isolated yield: 10.1 mg, 45 %. **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.12 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 160.0, 146.5, 132.8, 130.14, 128.12, 124.8, 124.4, 120.4, 115.1, 110.4, 55.8. **HRMS** Calcd for C₁₃H₁₅N₂O₃ [M+H]⁺: 226.0975; Found: 226.0983.

1-(4-methoxyphenyl)-1H-1,2,3-triazole (4j)^[6]



Beige solid, m.p. 80-82 °C. Isolated yield: 11.4 mg, 65 %. **¹H NMR** (400 MHz, CDCl₃) δ 7.90 (d, *J* = 1.1 Hz, 1H), 7.79 (d, *J* = 1.1 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.05 – 6.96 (m, 2H), 3.84 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 159.9, 134.2, 130.4, 122.3, 122.1, 114.8, 55.6.

1-(4-methoxyphenyl)-1H-1,2,4-triazole (4k)^[7]



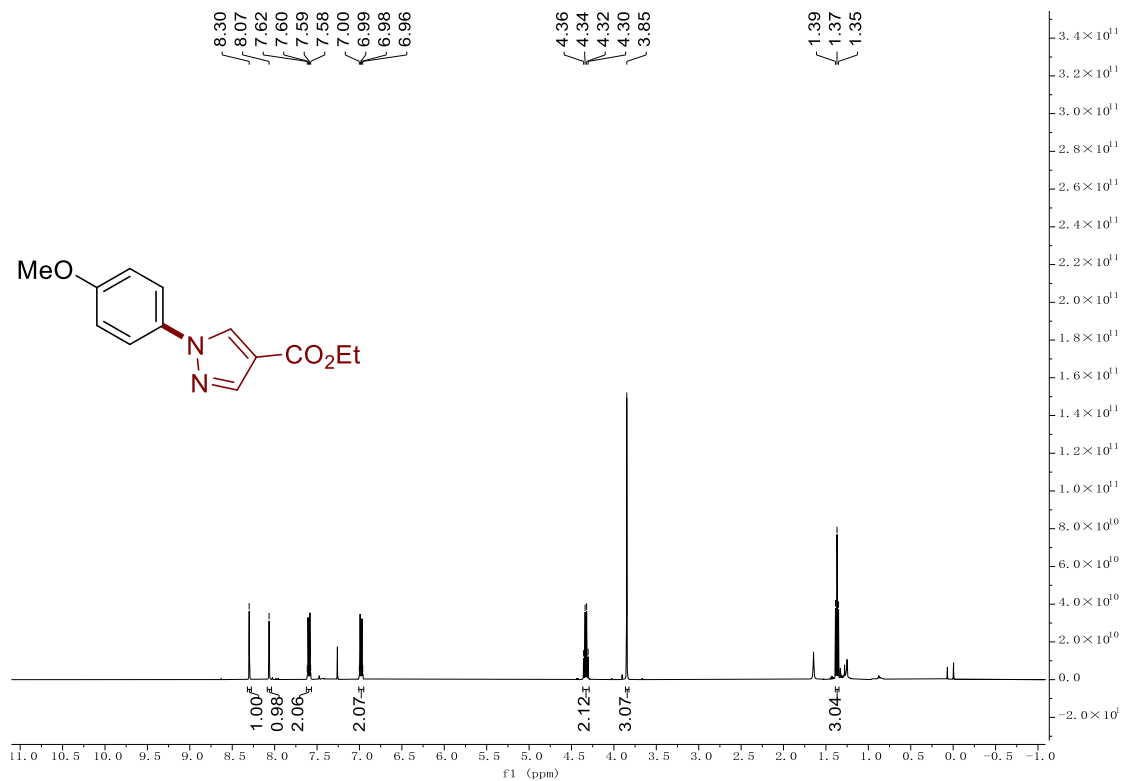
White solid. Mp: 96-97 °C. Isolated yield: 10.0 mg, 54 %. ¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1H), 8.05 (s, 1H), 7.54 (dd, *J* = 9.1, 1.0 Hz, 2H), 6.98 (dd, *J* = 9.0, 1.2 Hz, 2H), 3.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 152.4, 140.9, 130.5, 121.9, 114.9, 55.7.

10. References

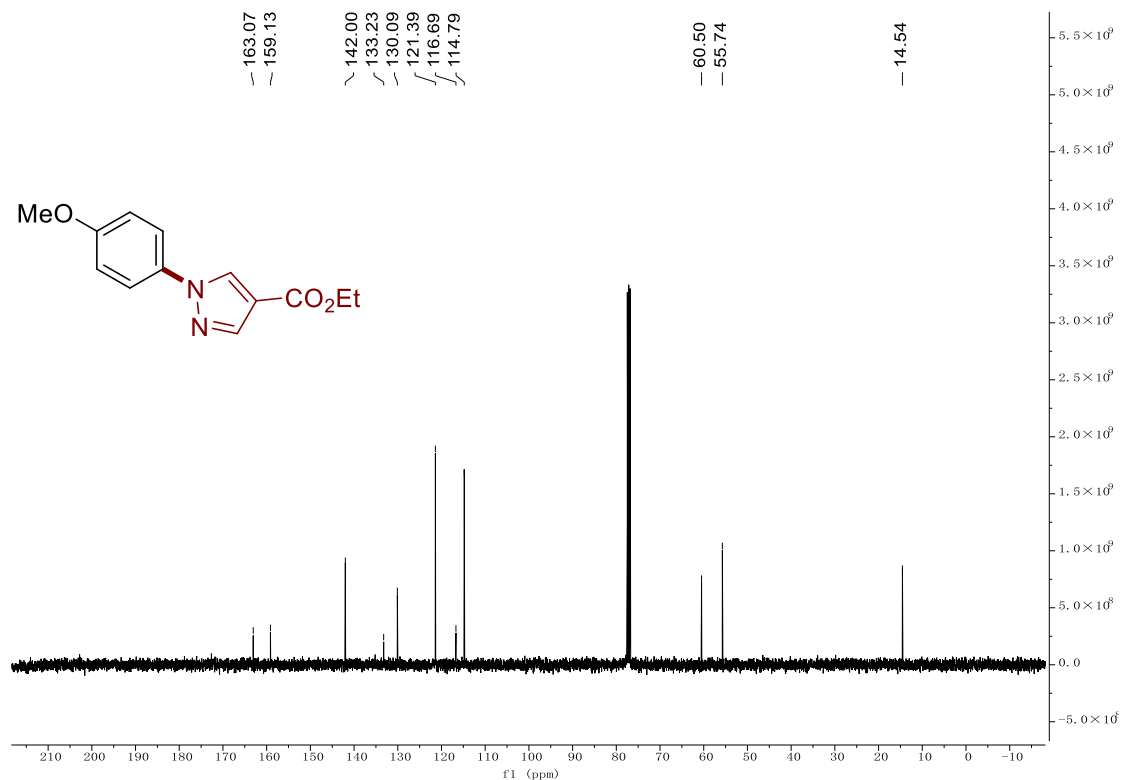
- [1] C. Wang, X.-J. Zhang, Y.-W. Zhao, Q. Liu, H. Cheng, Z. Huang, Y. Zhao, *Org. Chem. Front.* **2023**, *10*, 335–341.
- [2] Q. Zhang, L.-G. Meng, K. Wang, L. Wang, *Org. Lett.* **2015**, *17*, 872-875.
- [3] P. P. Sen, S. R. Roy, *Org. Lett.* **2023**, *25*, 1895-1900.
- [4] S. B. Annes, R. Saritha, S. Subramanian, B. Shankar, S. Ramesh, *Green Chemistry* **2020**, *22*, 2388-2393.
- [5] Q. Zhang, L.-G. Meng, K. Wang, L. Wang, *Org. Lett.* **2015**, *17*, 872-875.
- [6] V. V. Voronin, M. S. Ledovskaya, K. S. Rodygin, V. P. Ananikov, *Eur. J. Org. Chem.* **2021**, *2021*, 5640-5648.
- [7] J. C. Antilla, J. M. Baskin, T. E. Barder, S. L. Buchwald, *J. Org. Chem.* **2004**, *69*, 5578-5587.

11. NMR spectra

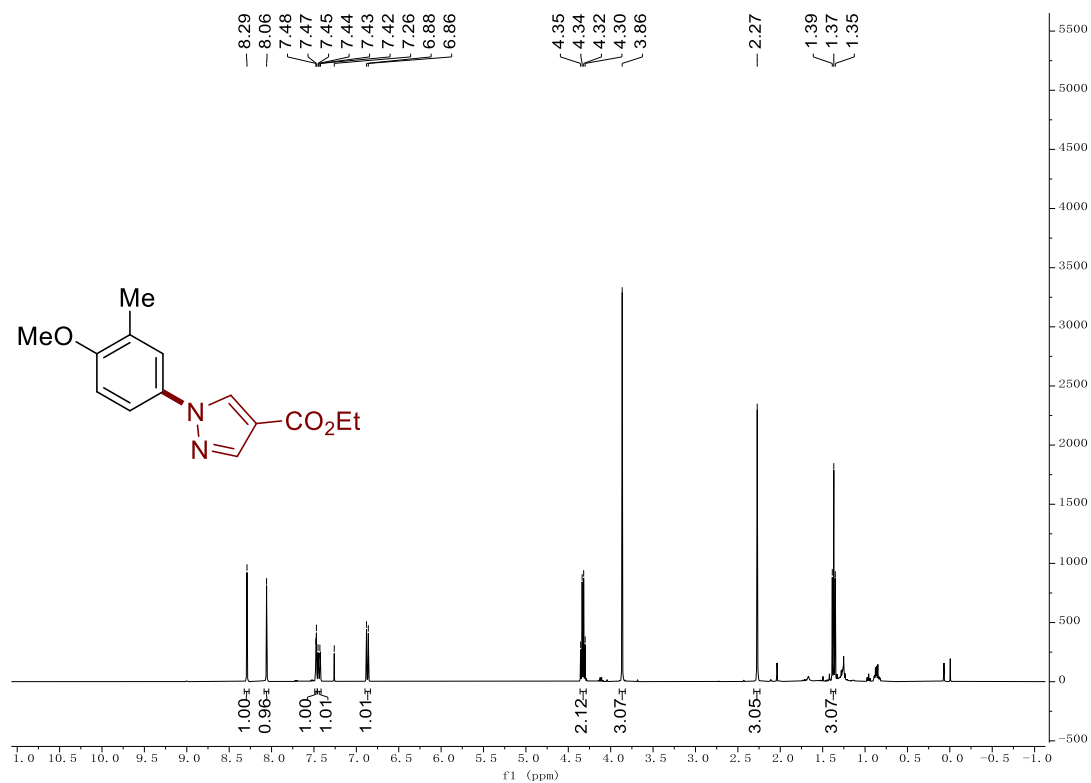
¹H NMR Spectrum of 3a (400 MHz, CDCl₃)



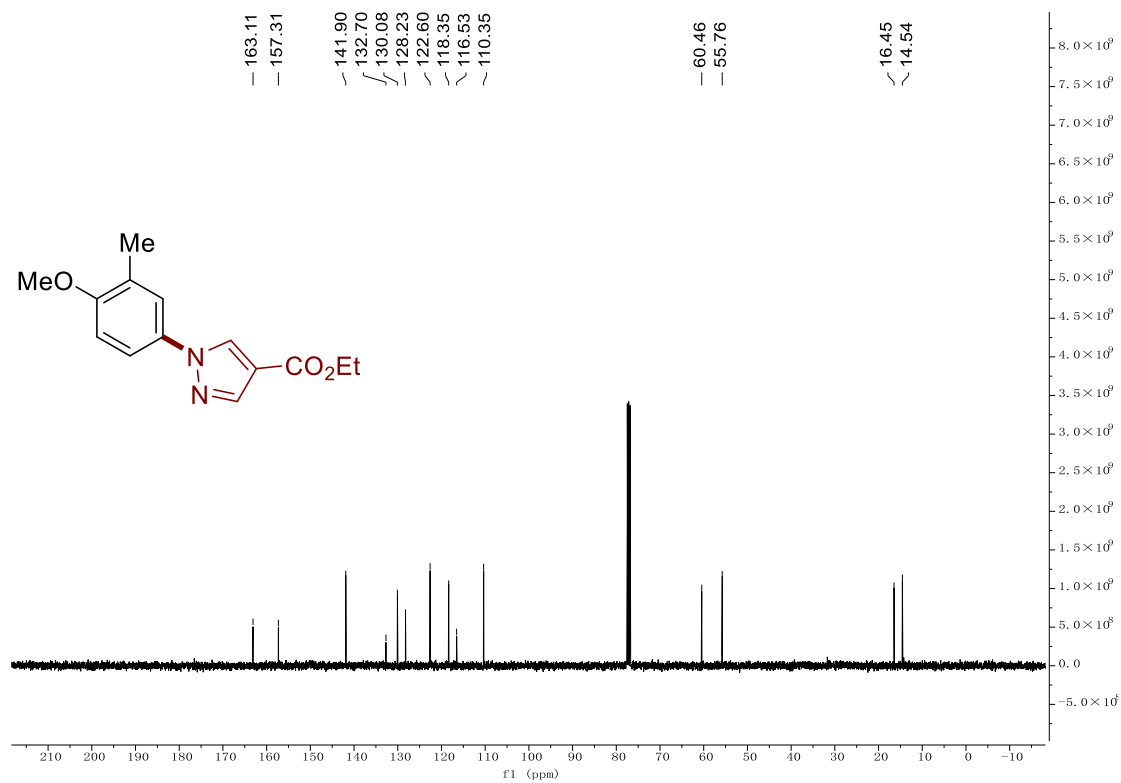
¹³C NMR Spectrum of 3a (400 MHz, CDCl₃)



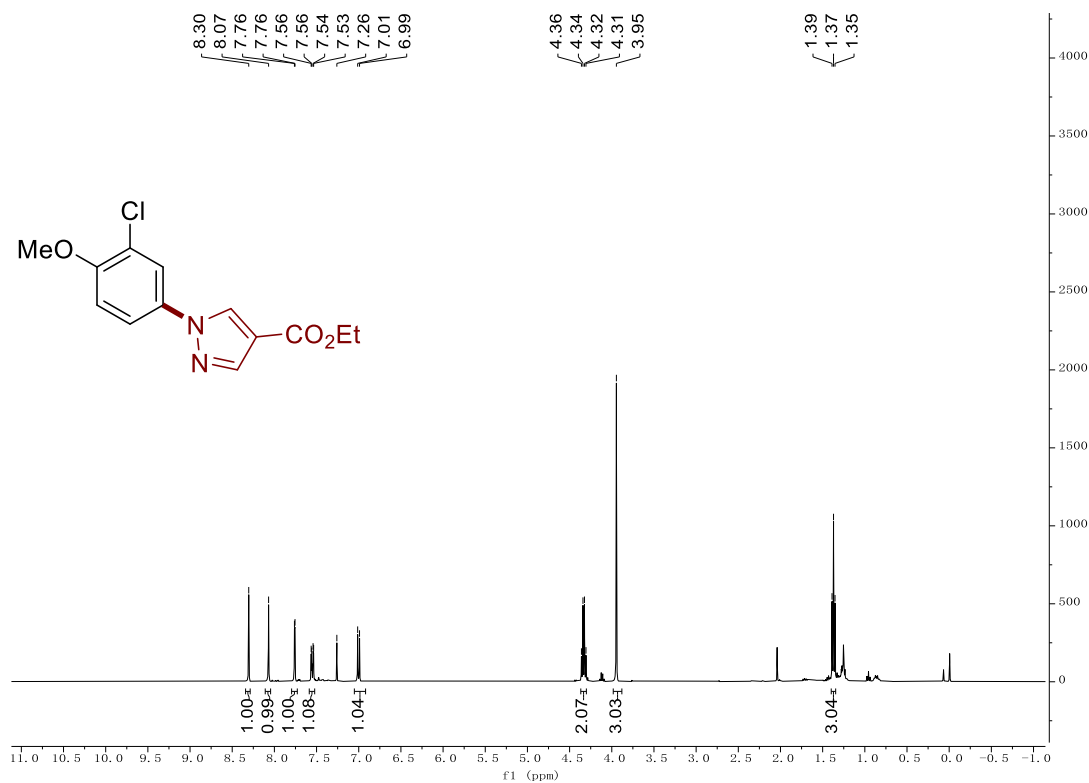
¹H NMR Spectrum of 3b (400 MHz, CDCl₃)



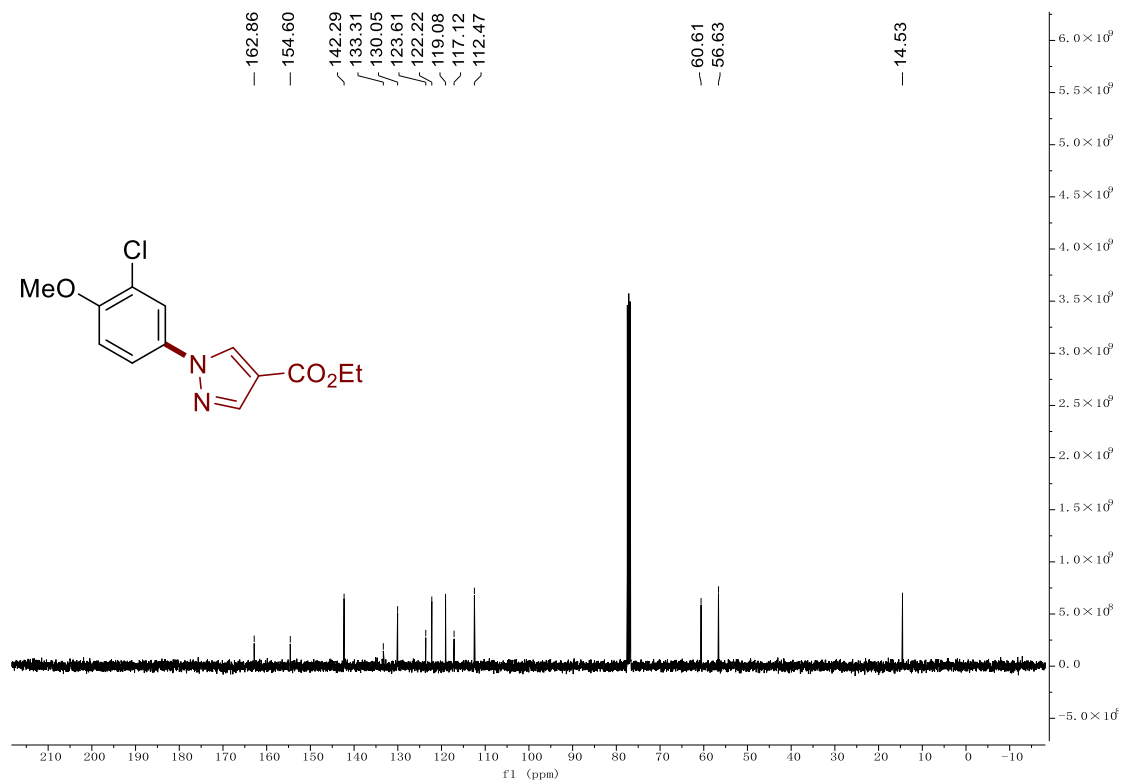
¹³C NMR Spectrum of 3b (400 MHz, CDCl₃)



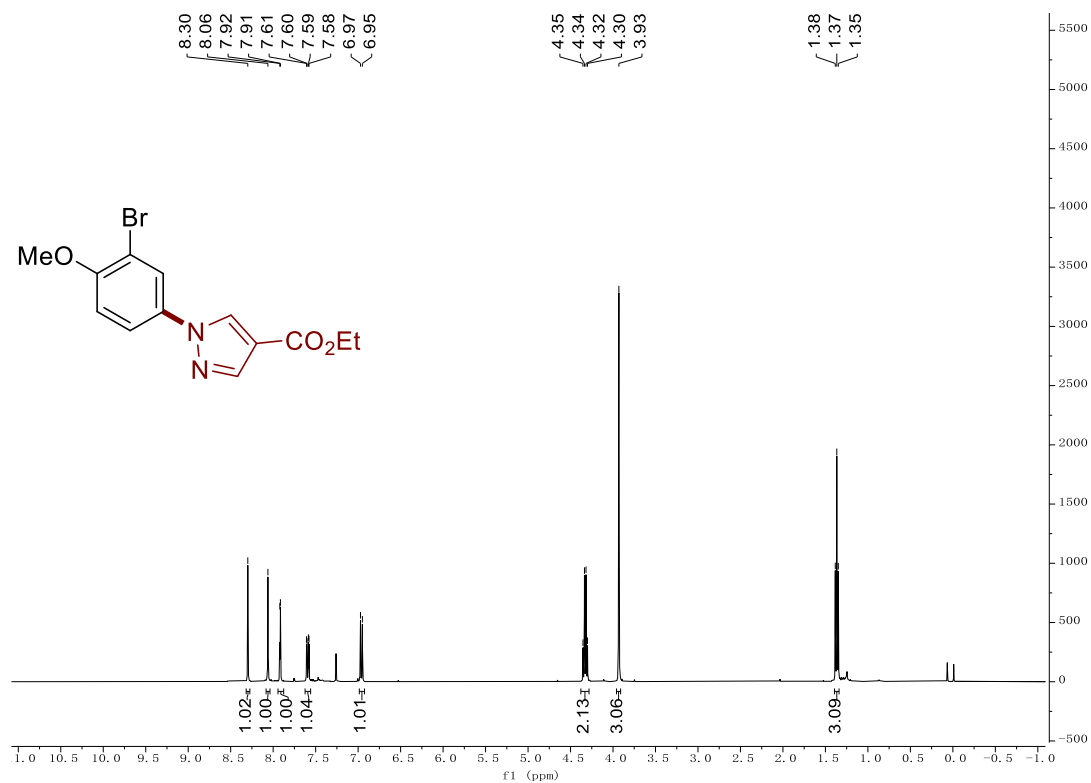
¹H NMR Spectrum of 3c (400 MHz, CDCl₃)



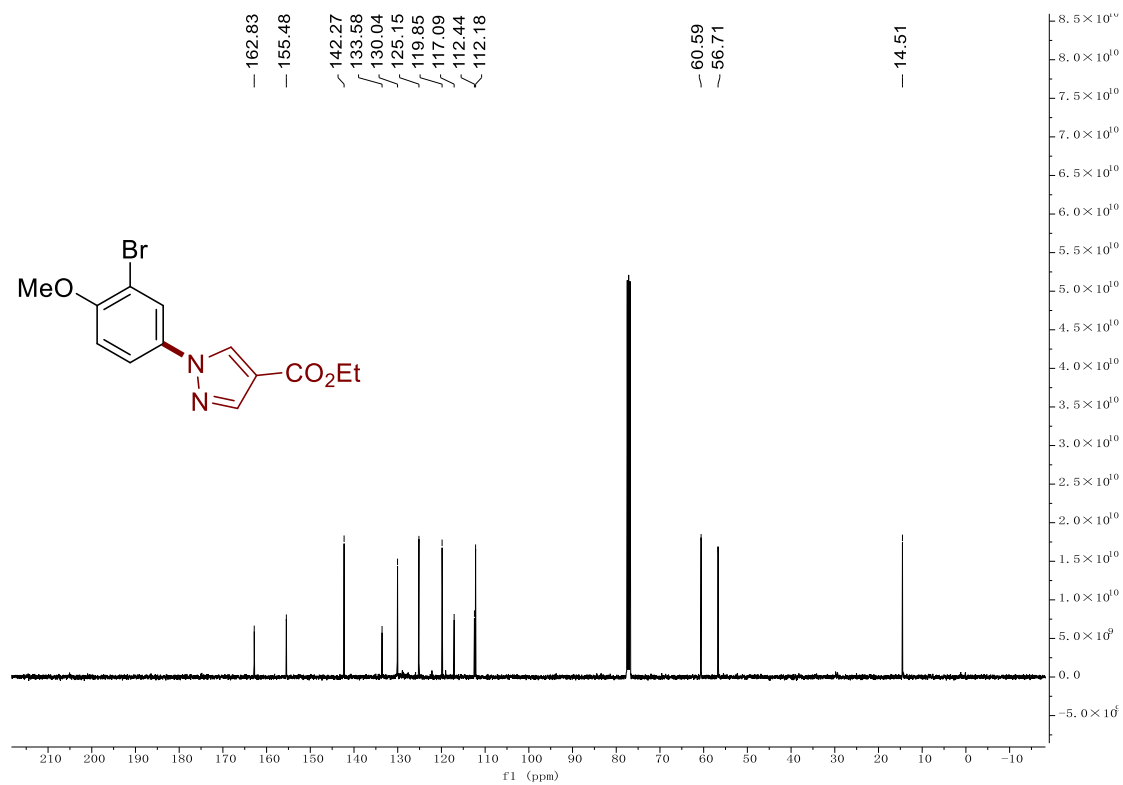
¹³C NMR Spectrum of 3c (400 MHz, CDCl₃)



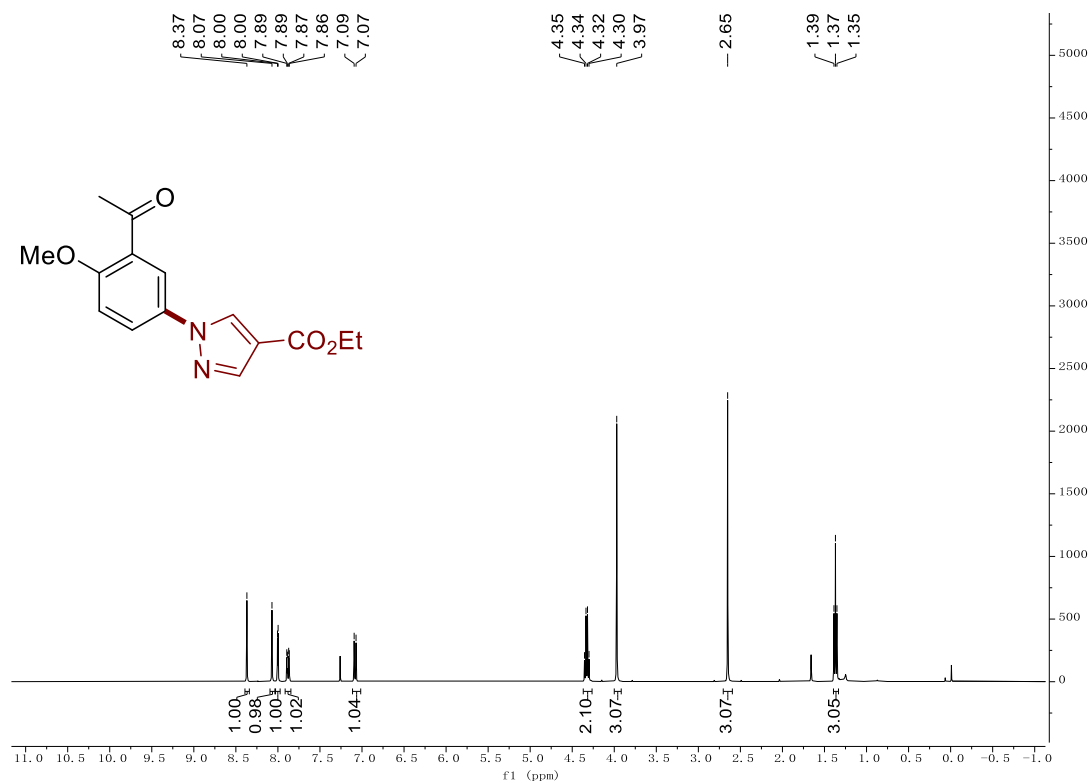
¹H NMR Spectrum of 3d (400 MHz, CDCl₃)



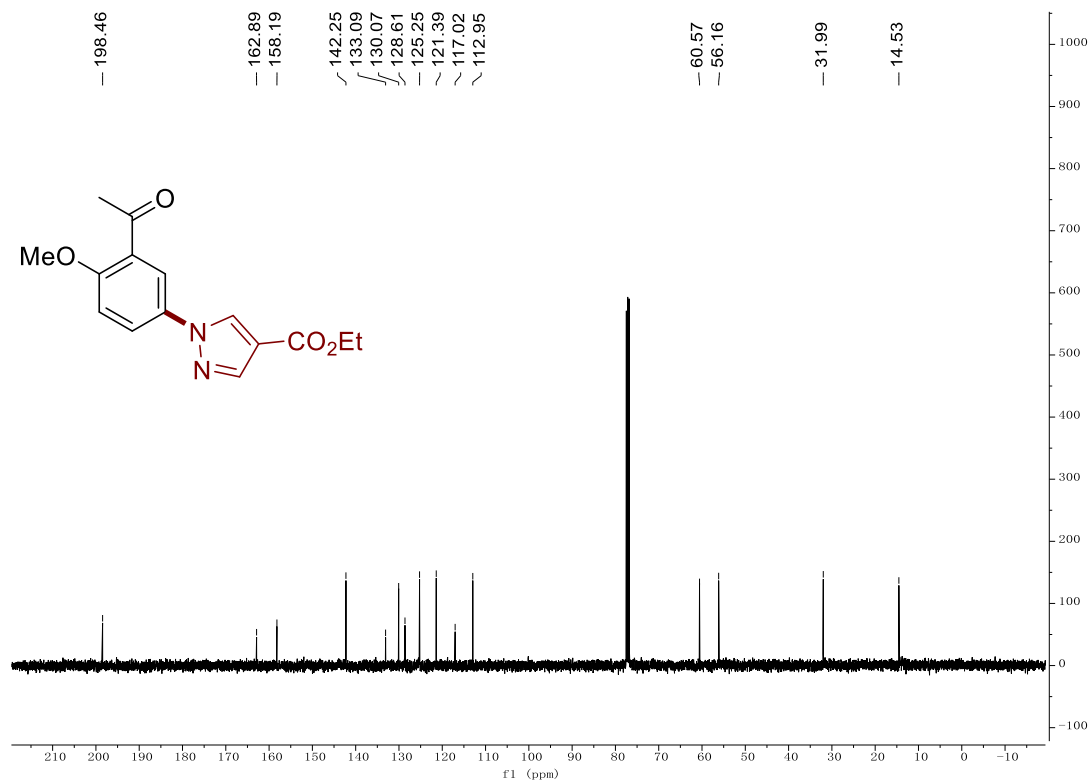
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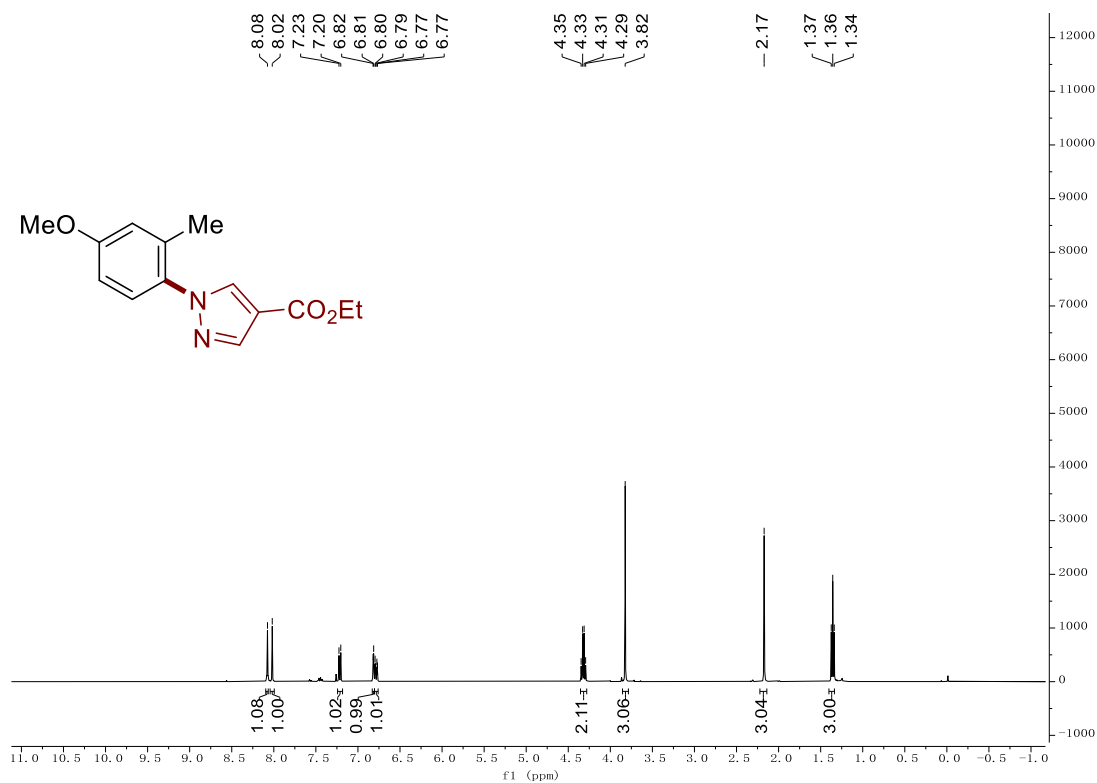
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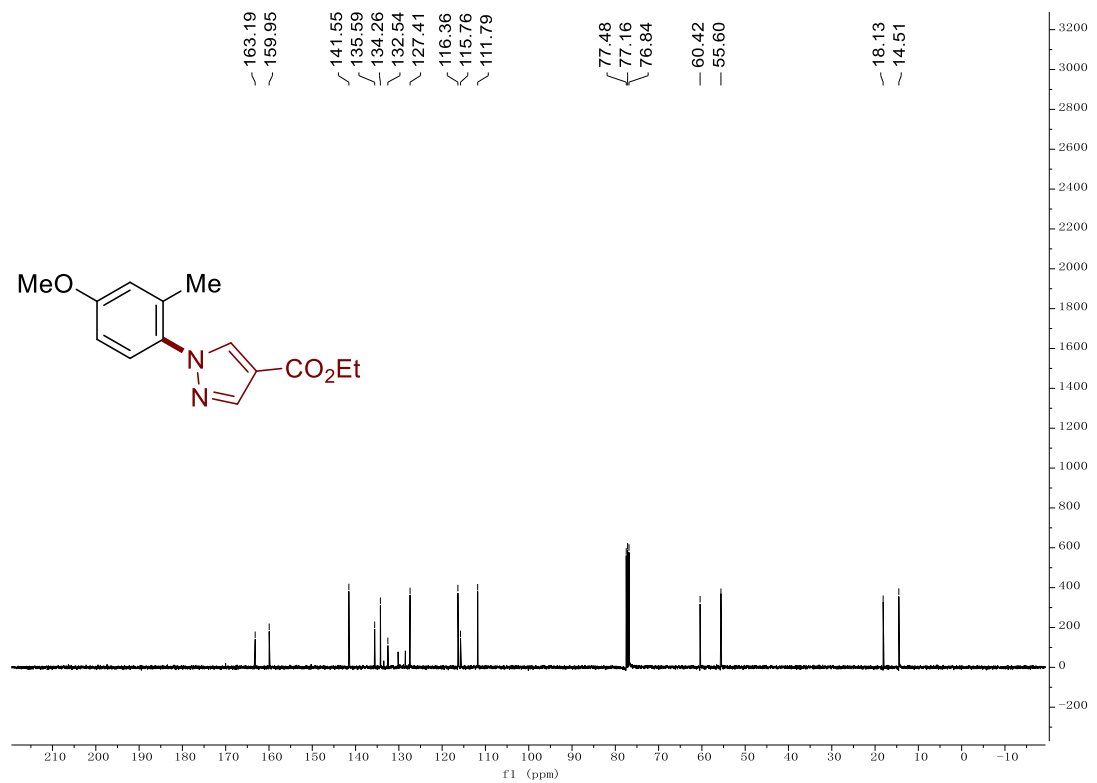
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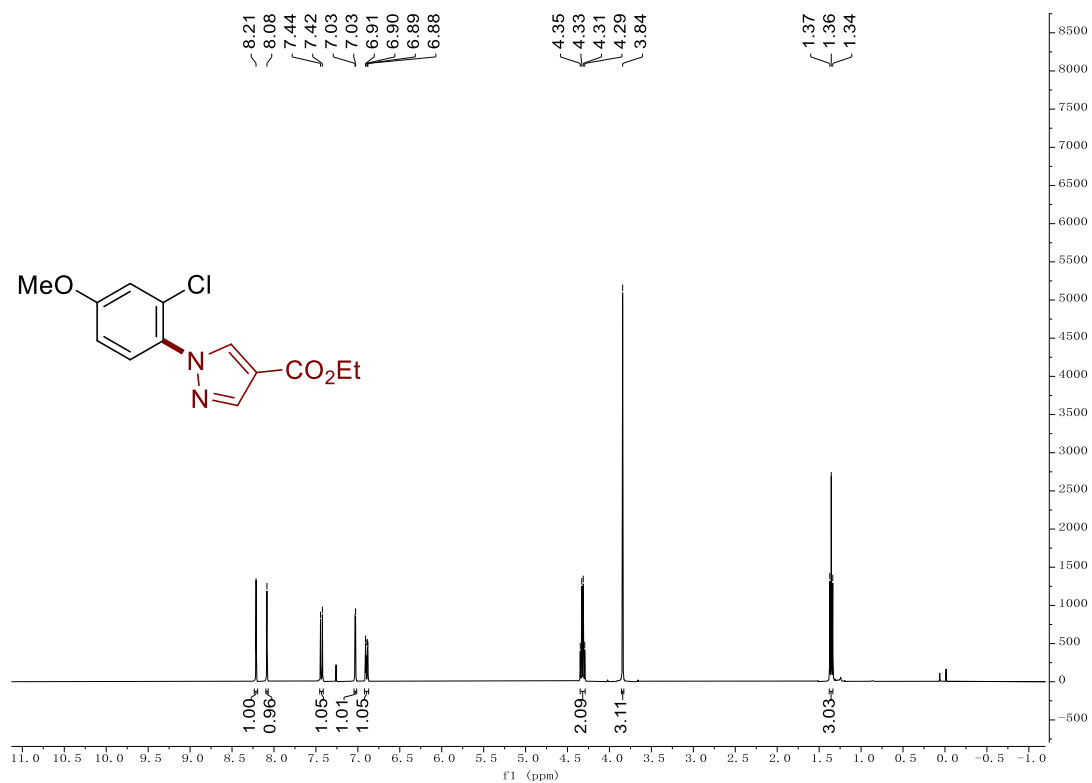
¹H NMR Spectrum of 3f (400 MHz, CDCl₃)



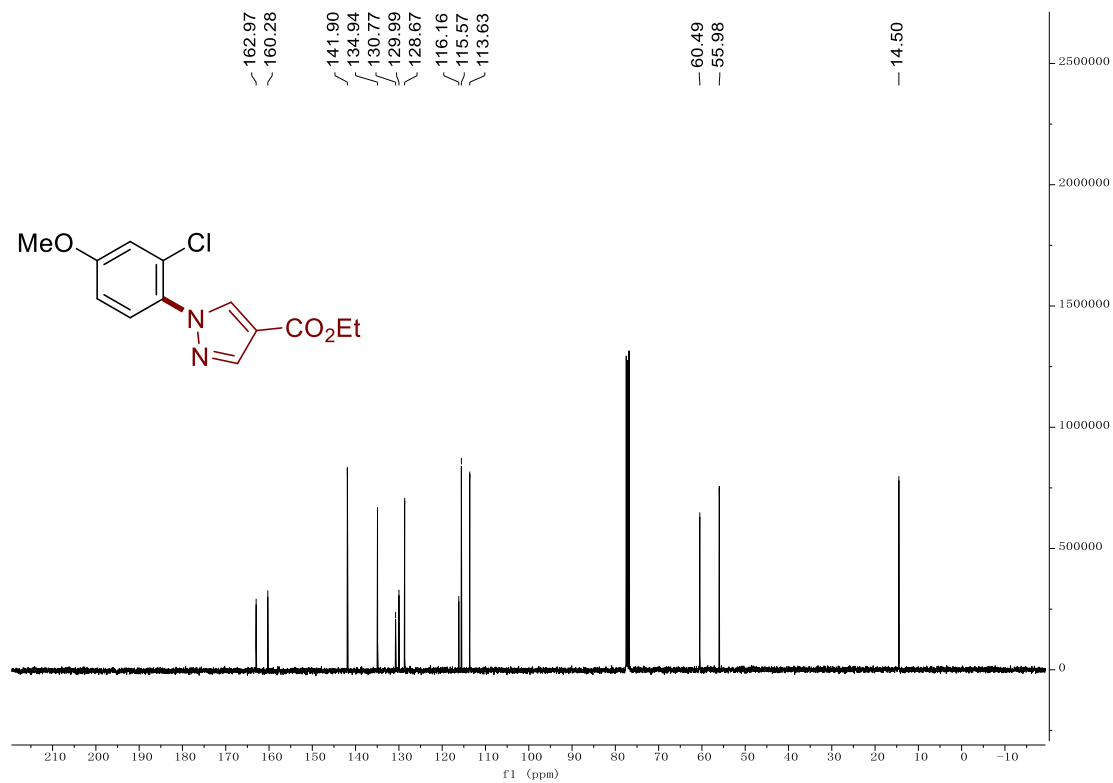
¹³C NMR Spectrum of 3f (400 MHz, CDCl₃)



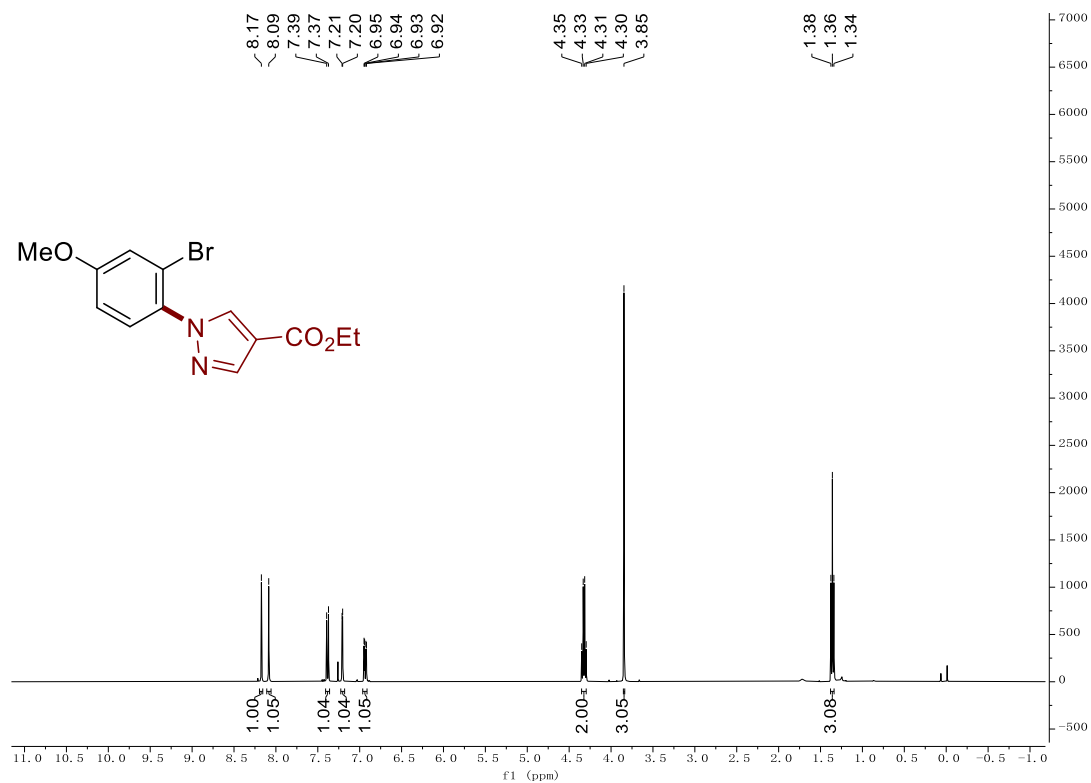
¹H NMR Spectrum of 3g (400 MHz, CDCl₃)



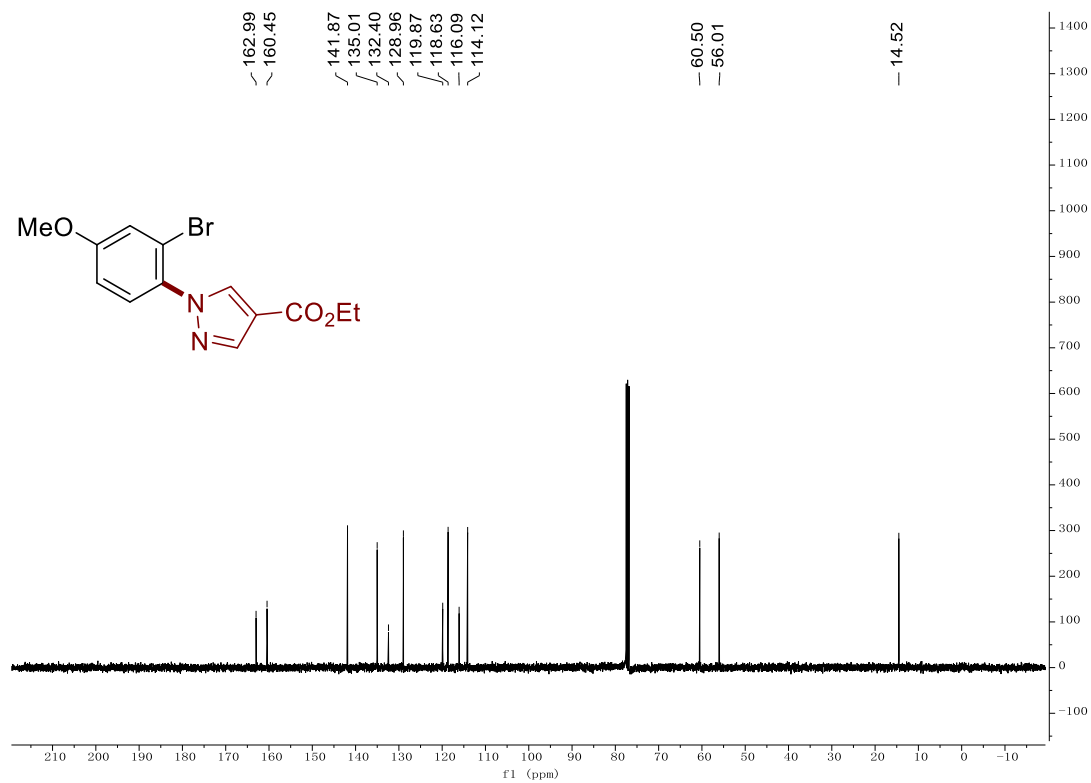
¹³C NMR Spectrum of 3g (400 MHz, CDCl₃)



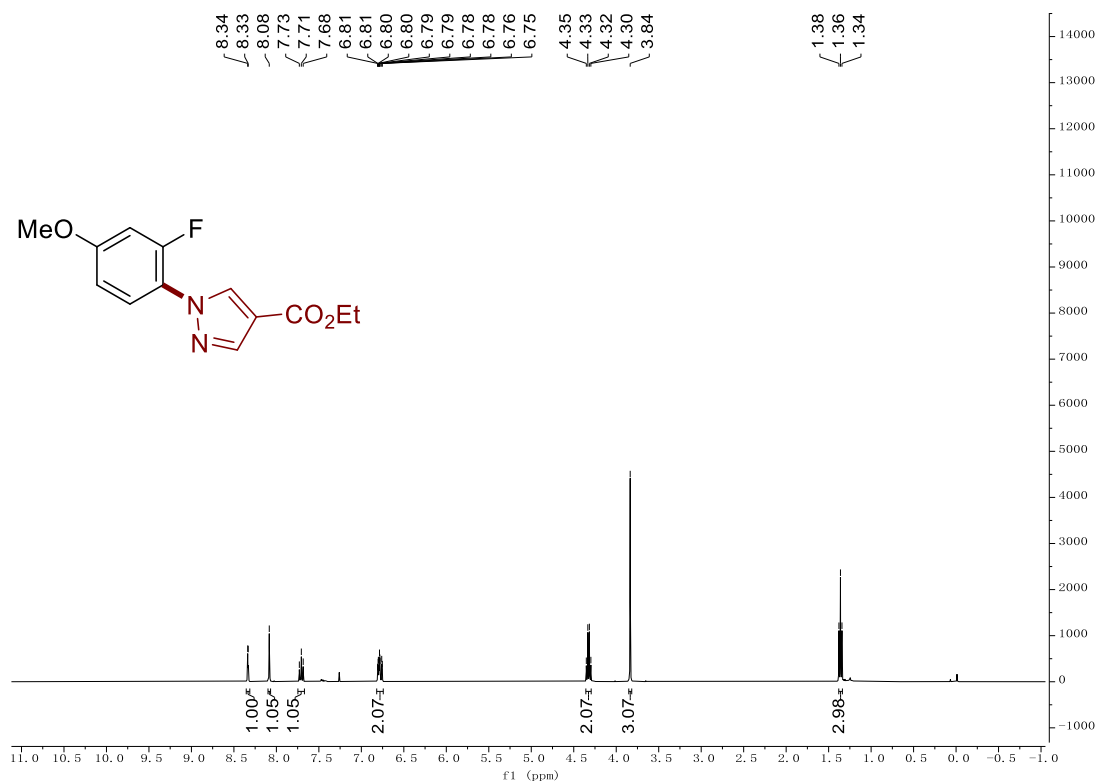
¹H NMR Spectrum of 3h (400 MHz, CDCl₃)



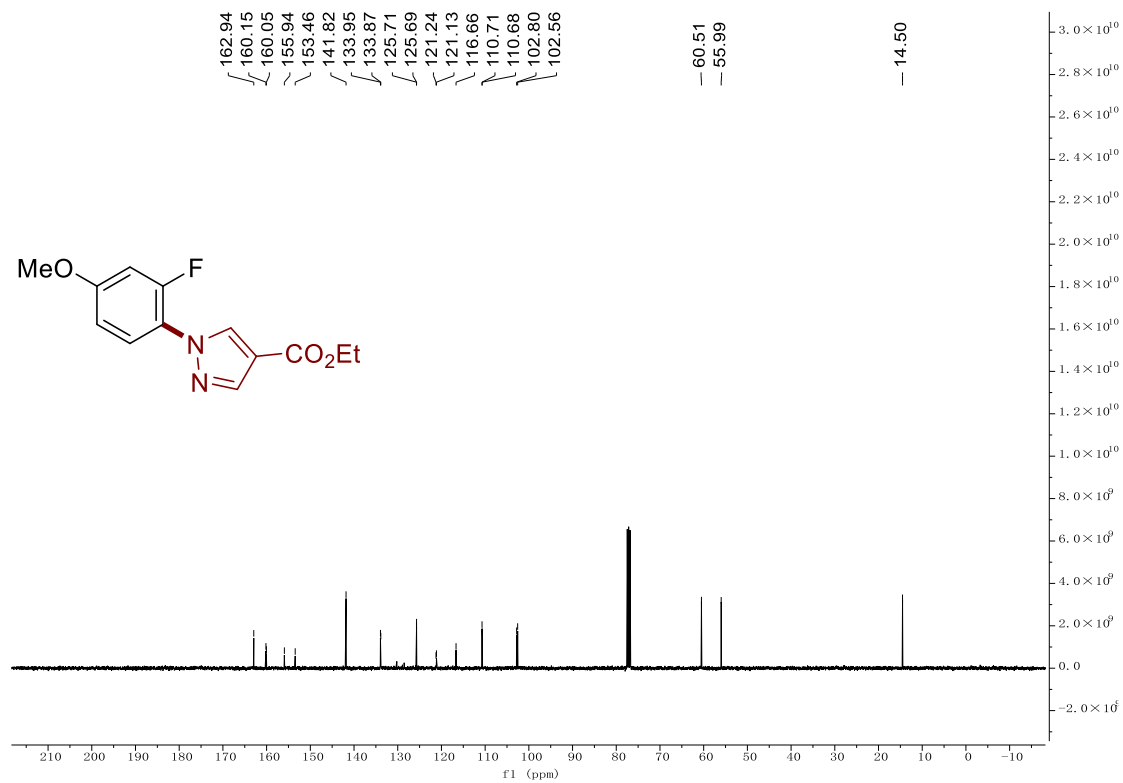
¹³C NMR Spectrum of 3h (400 MHz, CDCl₃)



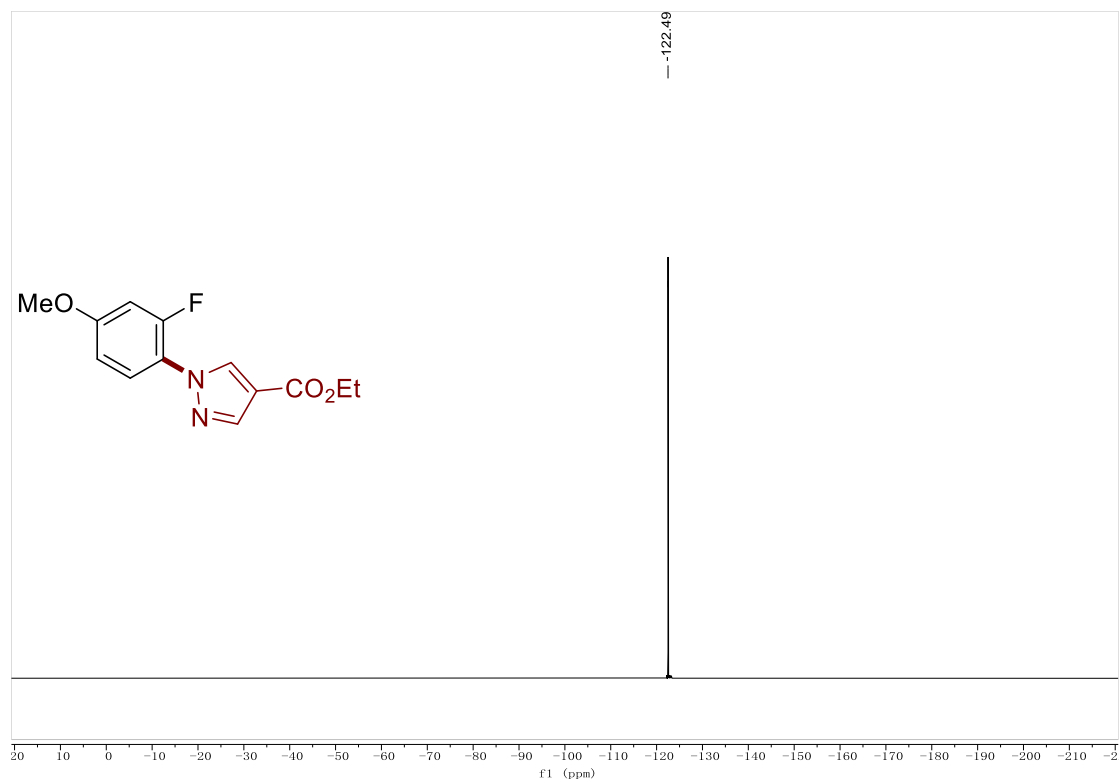
¹H NMR Spectrum of 3i (400 MHz, CDCl₃)



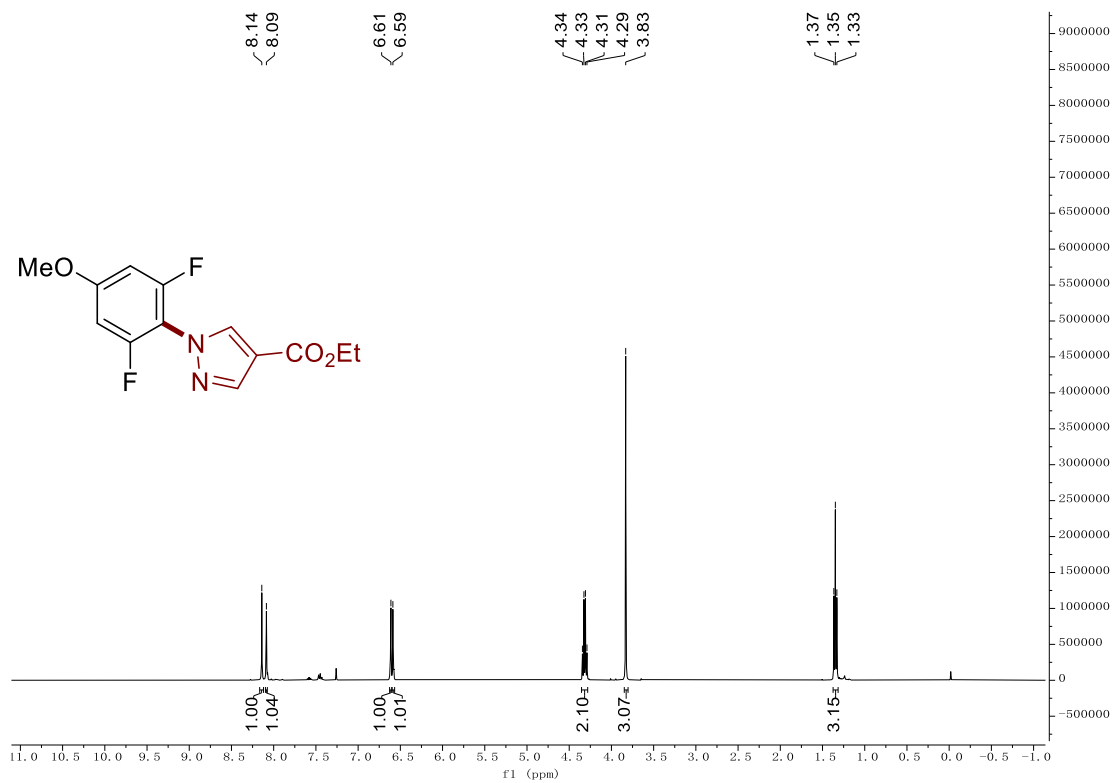
¹³C NMR Spectrum of 3i (400 MHz, CDCl₃)



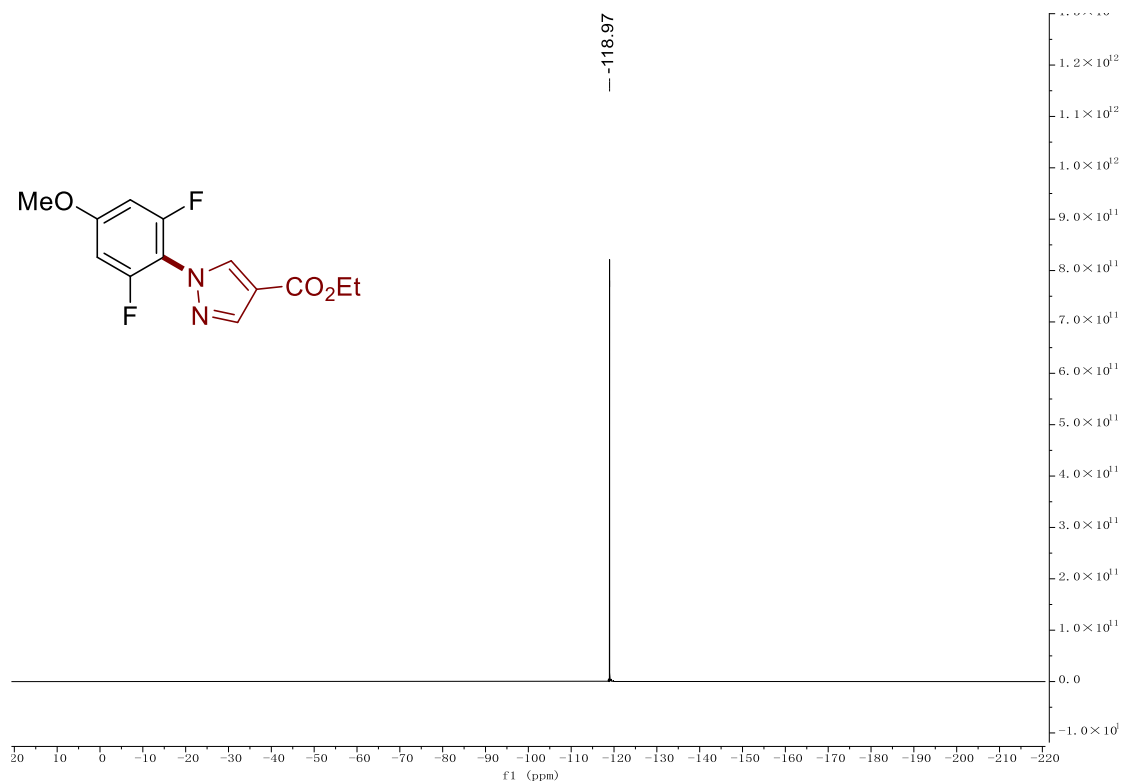
^{19}F NMR Spectrum of 3i (400 MHz, CDCl_3)



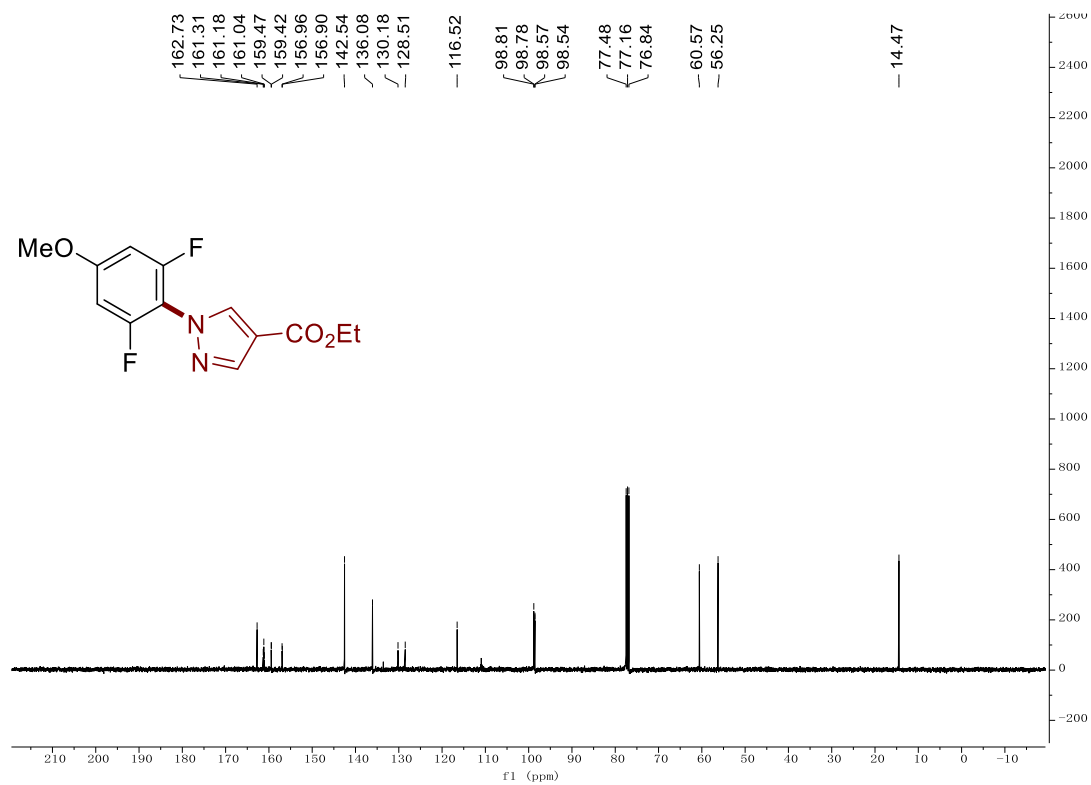
^1H NMR Spectrum of 3j (400 MHz, CDCl_3)



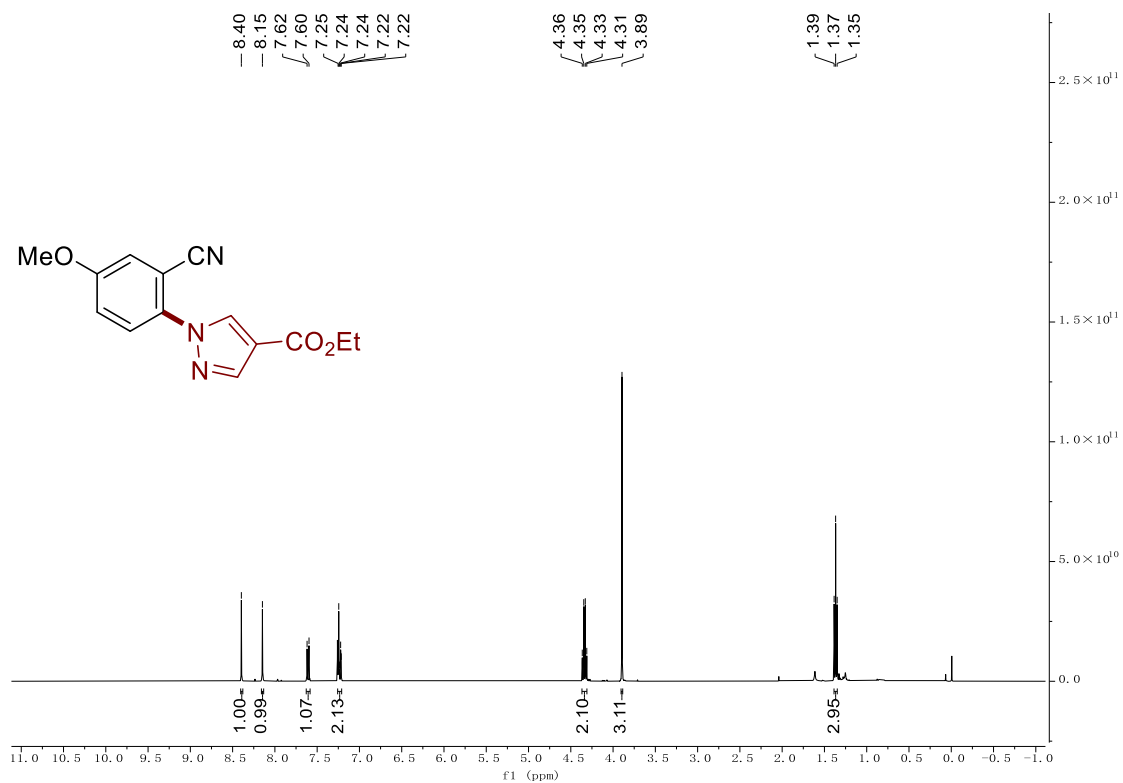
¹³C NMR Spectrum of 3j (400 MHz, CDCl₃)



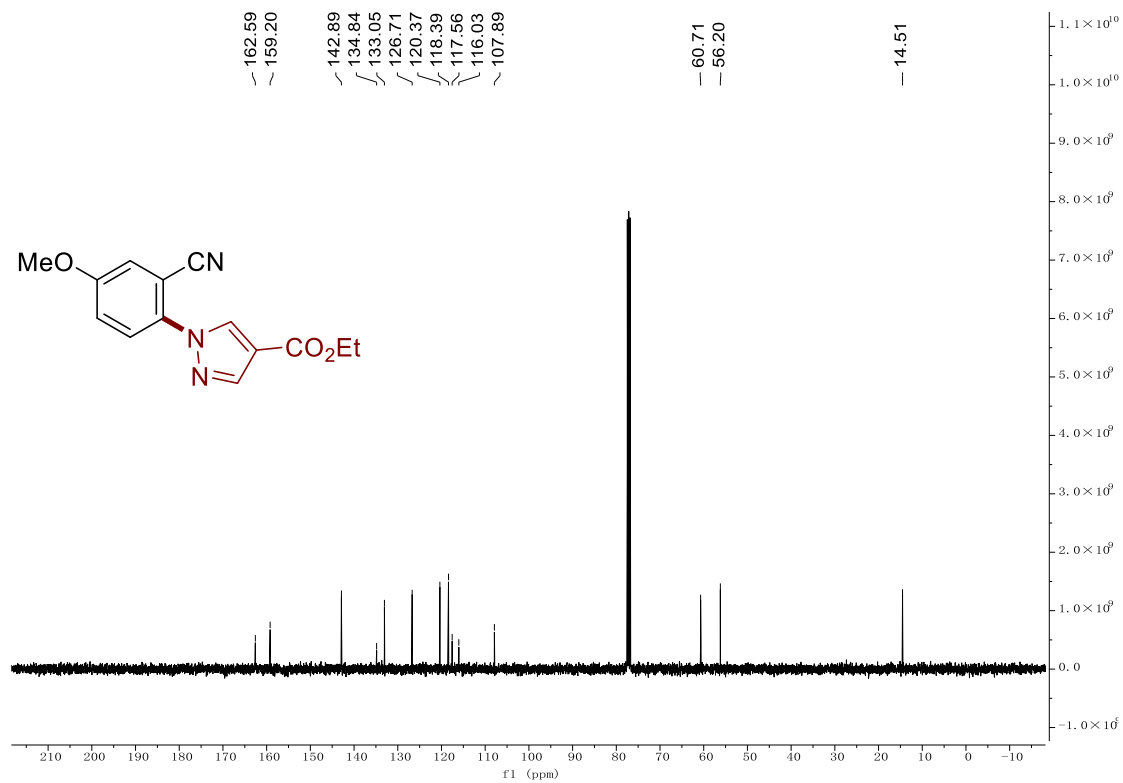
¹⁹F NMR Spectrum of 3j (400 MHz, CDCl₃)



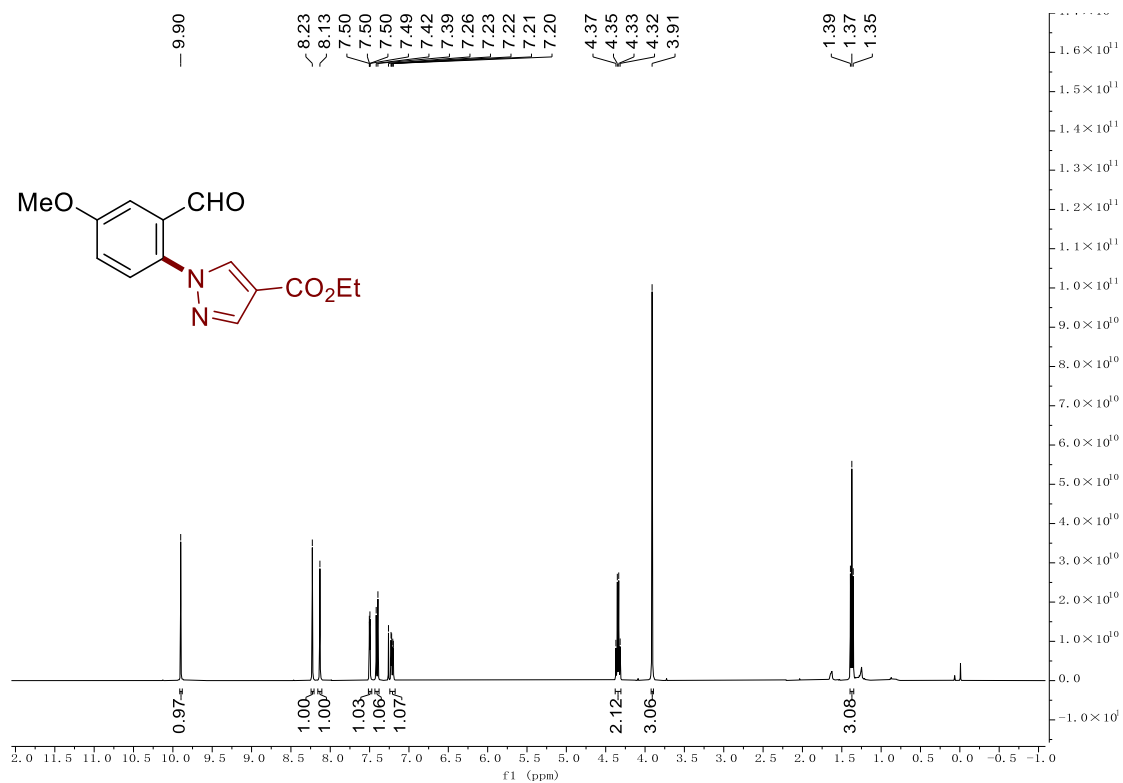
¹H NMR Spectrum of 3k (400 MHz, CDCl₃)



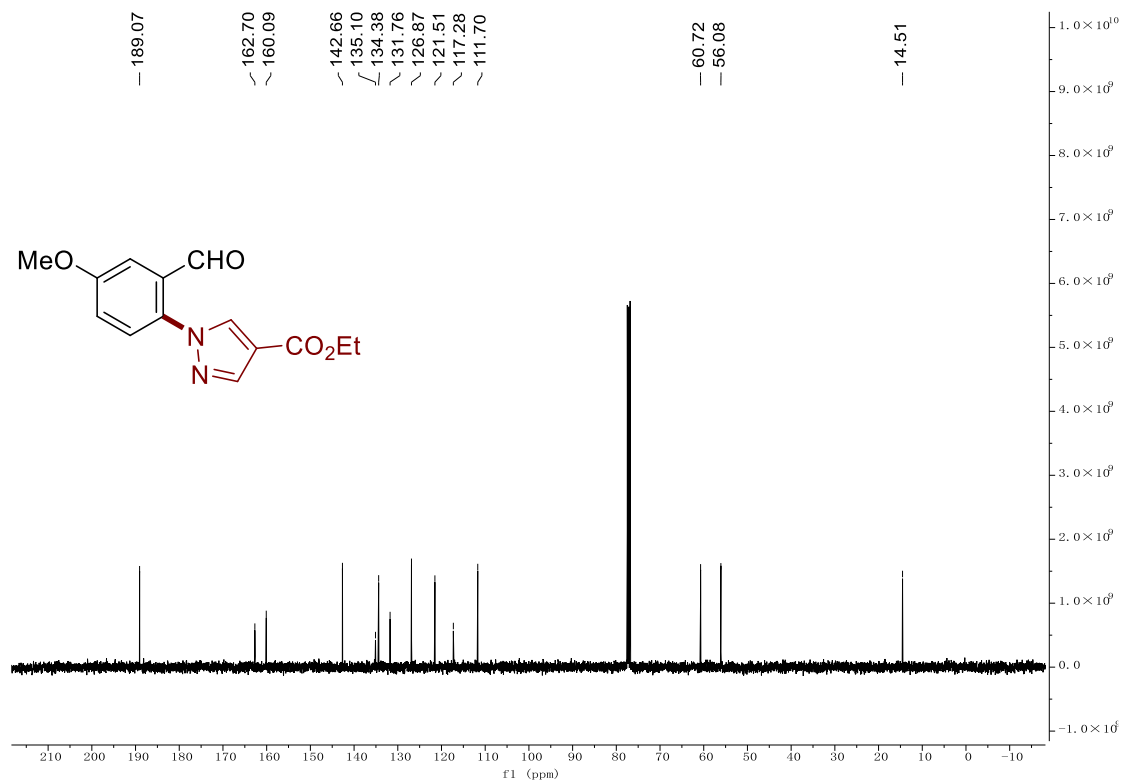
¹³C NMR Spectrum of 3k (400 MHz, CDCl₃)



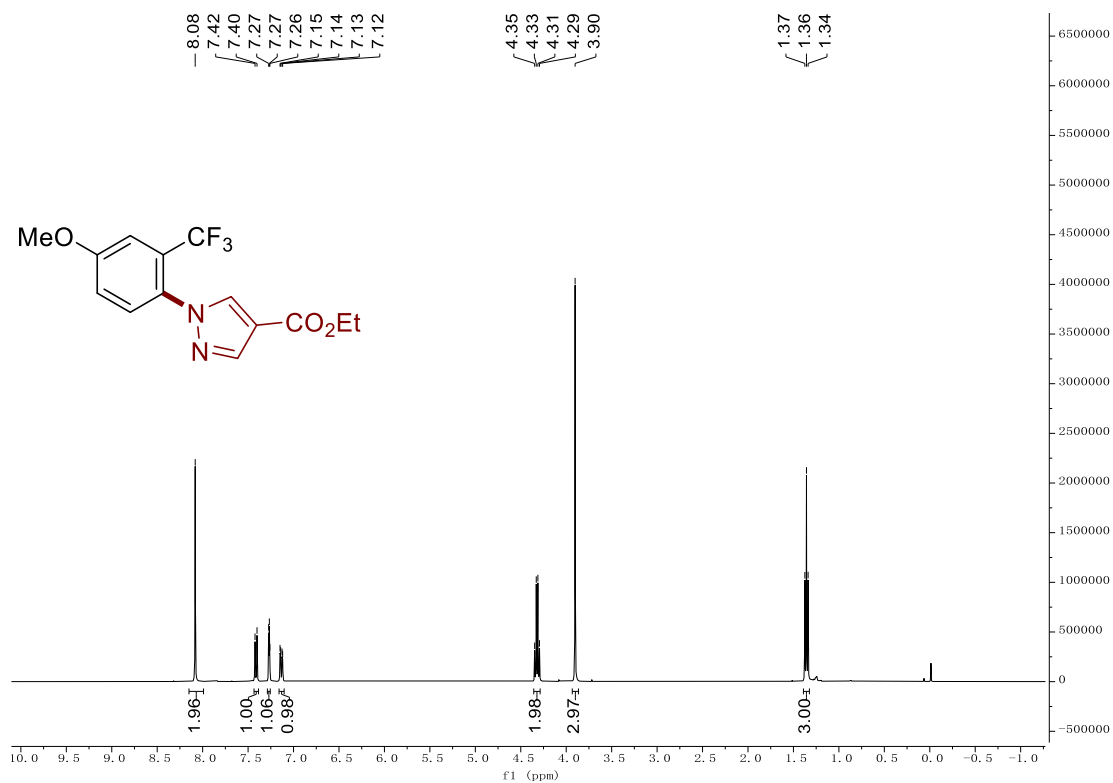
¹H NMR Spectrum of 31 (400 MHz, CDCl₃)



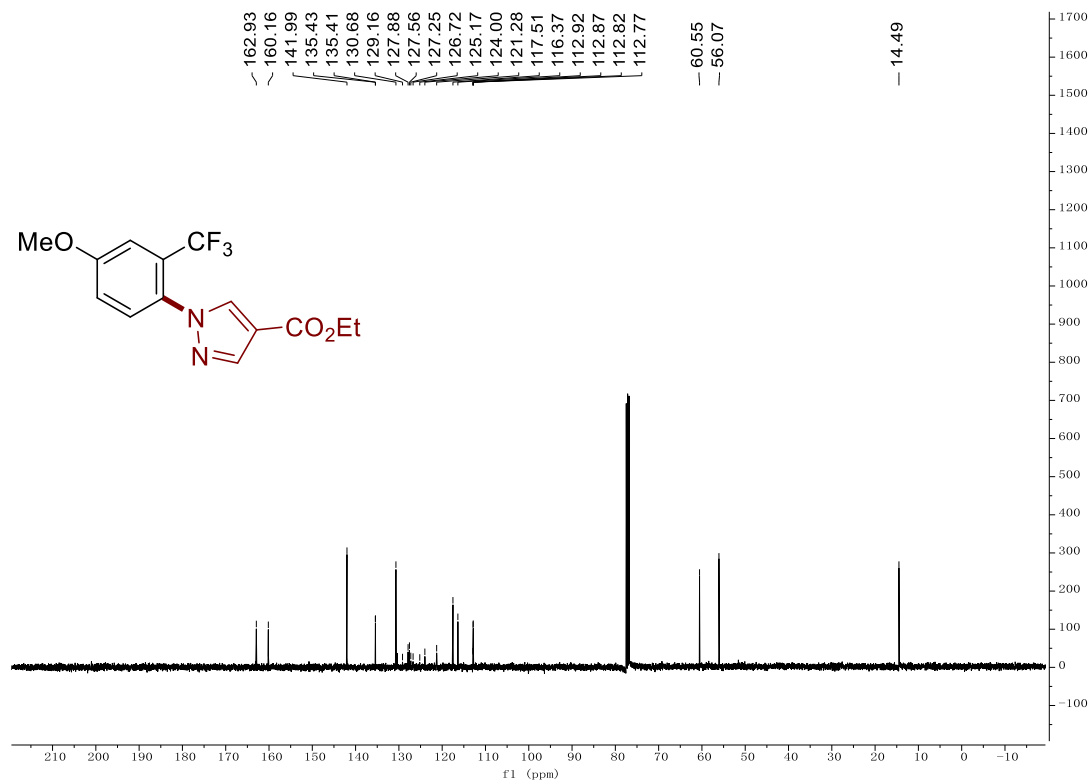
¹³C NMR Spectrum of 31 (400 MHz, CDCl₃)



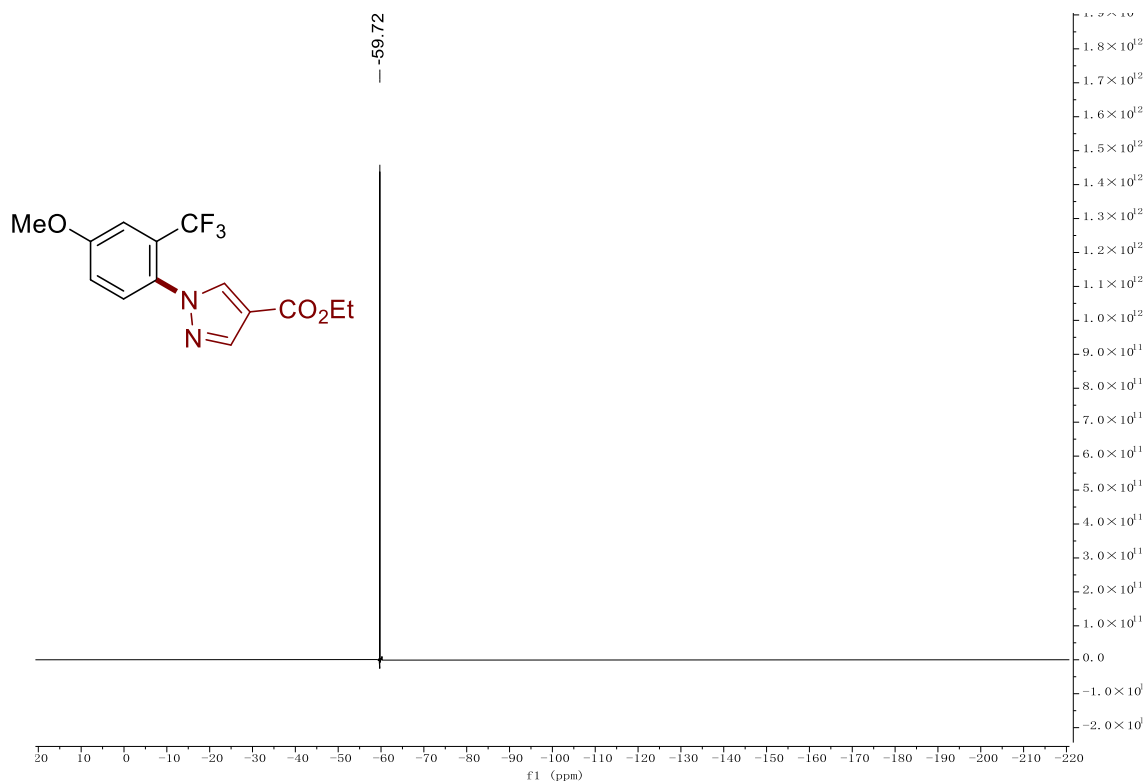
¹H NMR Spectrum of 3m (400 MHz, CDCl₃)



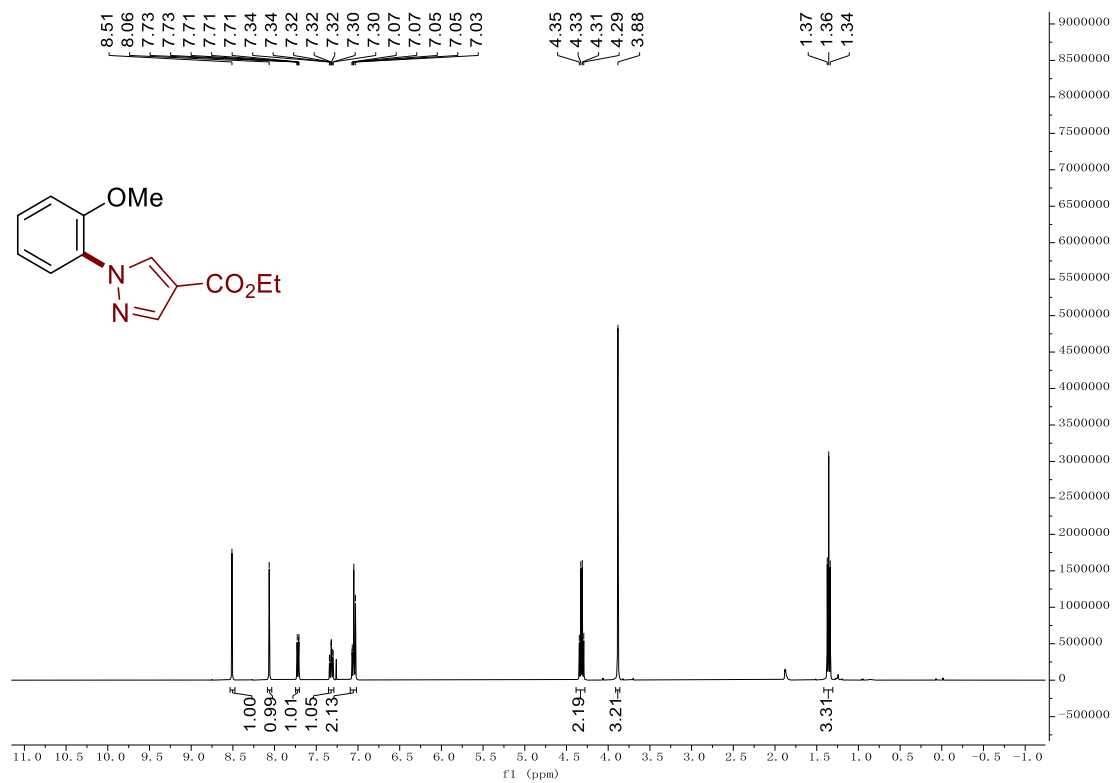
¹³C NMR Spectrum of 3m (400 MHz, CDCl₃)



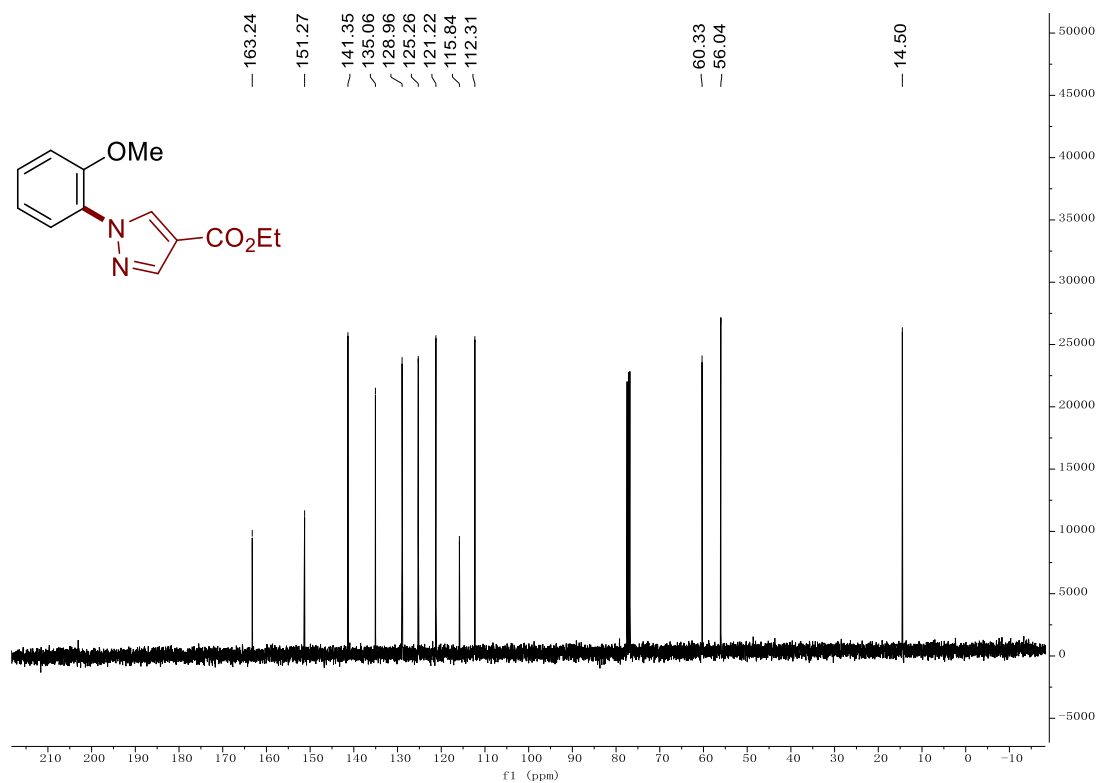
¹⁹F NMR Spectrum of 3m (400 MHz, CDCl₃)



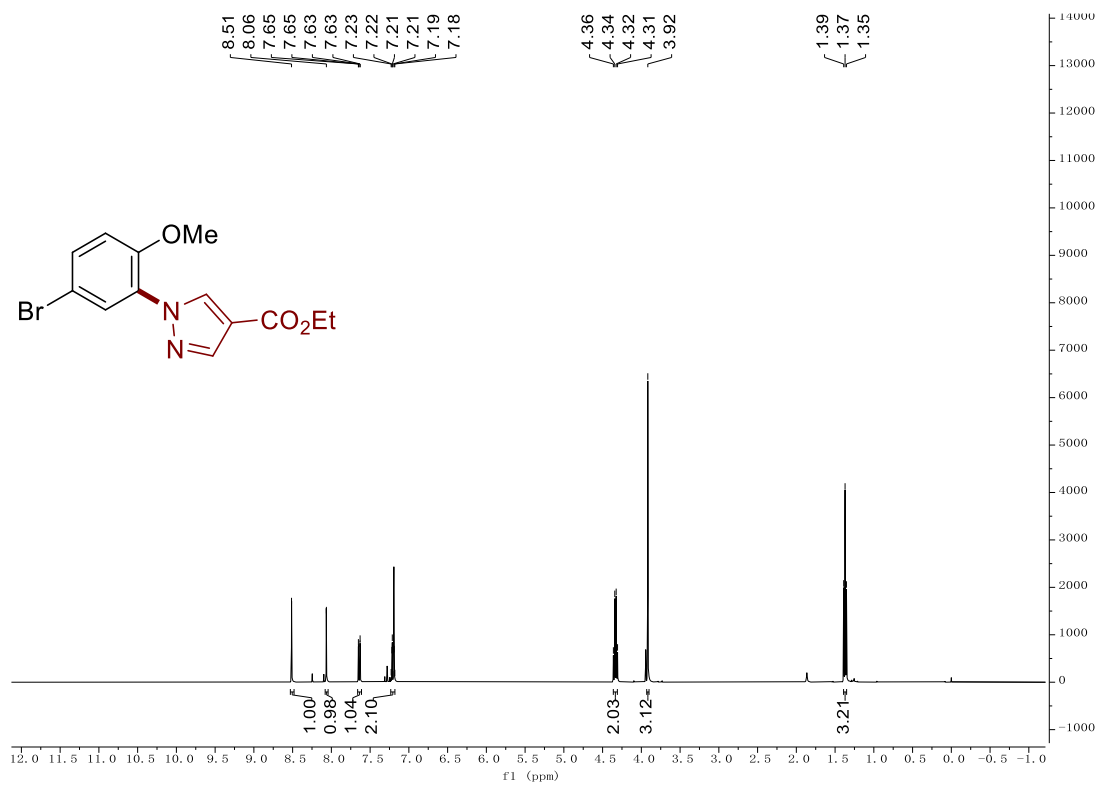
¹H NMR Spectrum of 3n (400 MHz, CDCl₃)



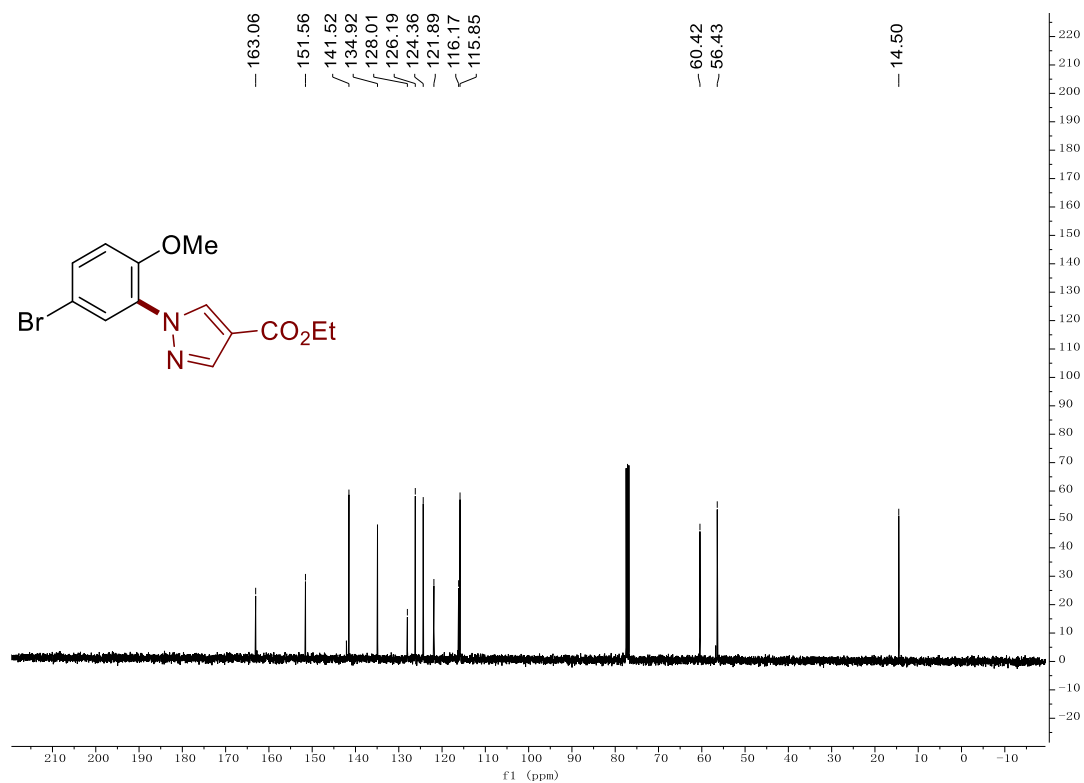
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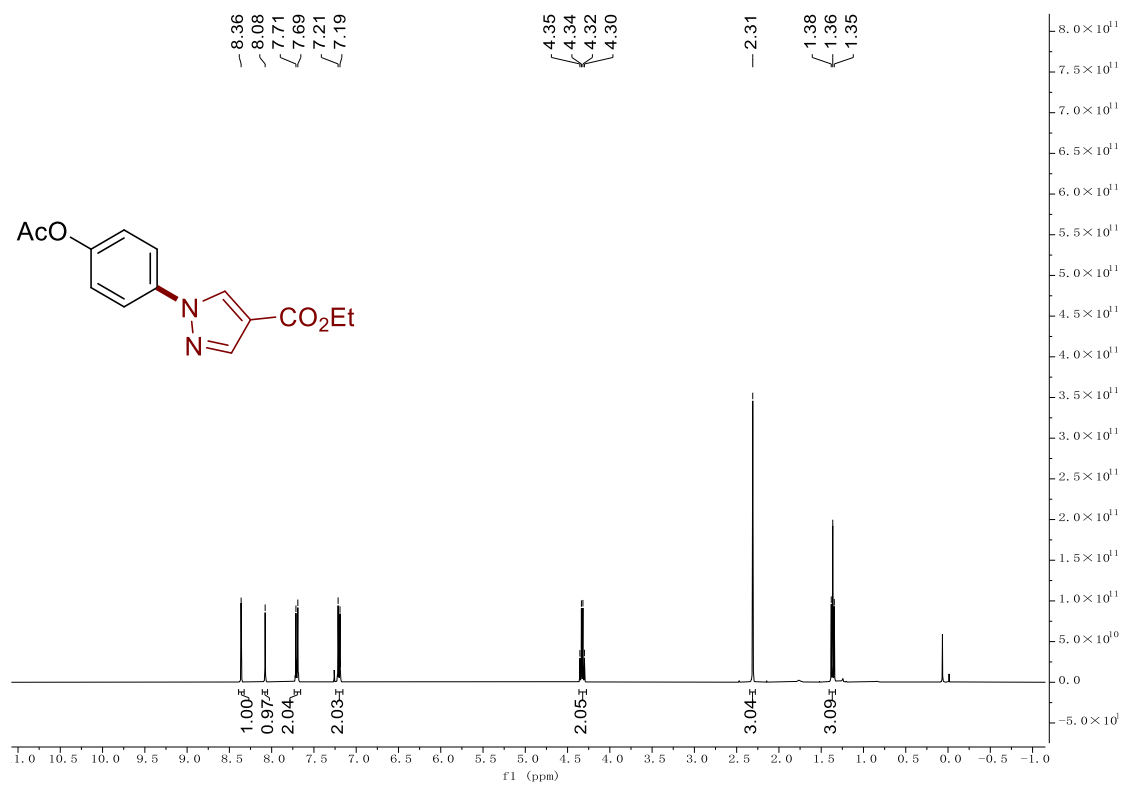
¹H NMR Spectrum of 3o (400 MHz, CDCl₃)



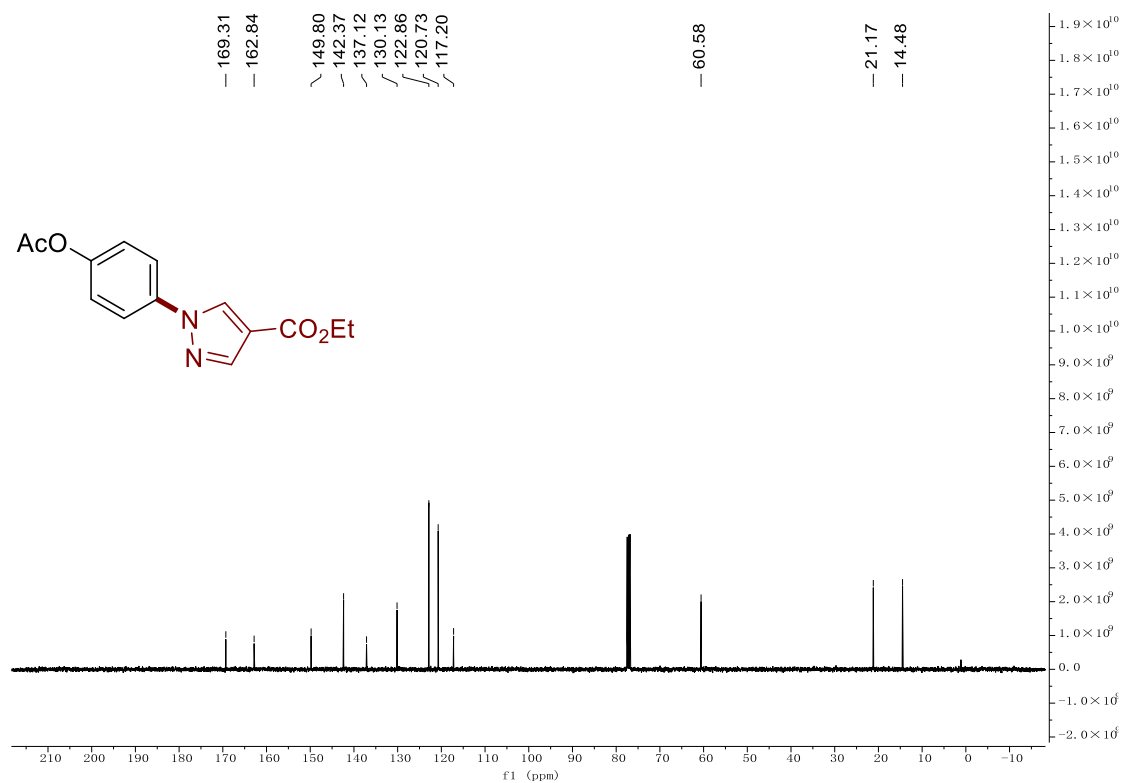
¹³C NMR Spectrum of 3o (400 MHz, CDCl₃)



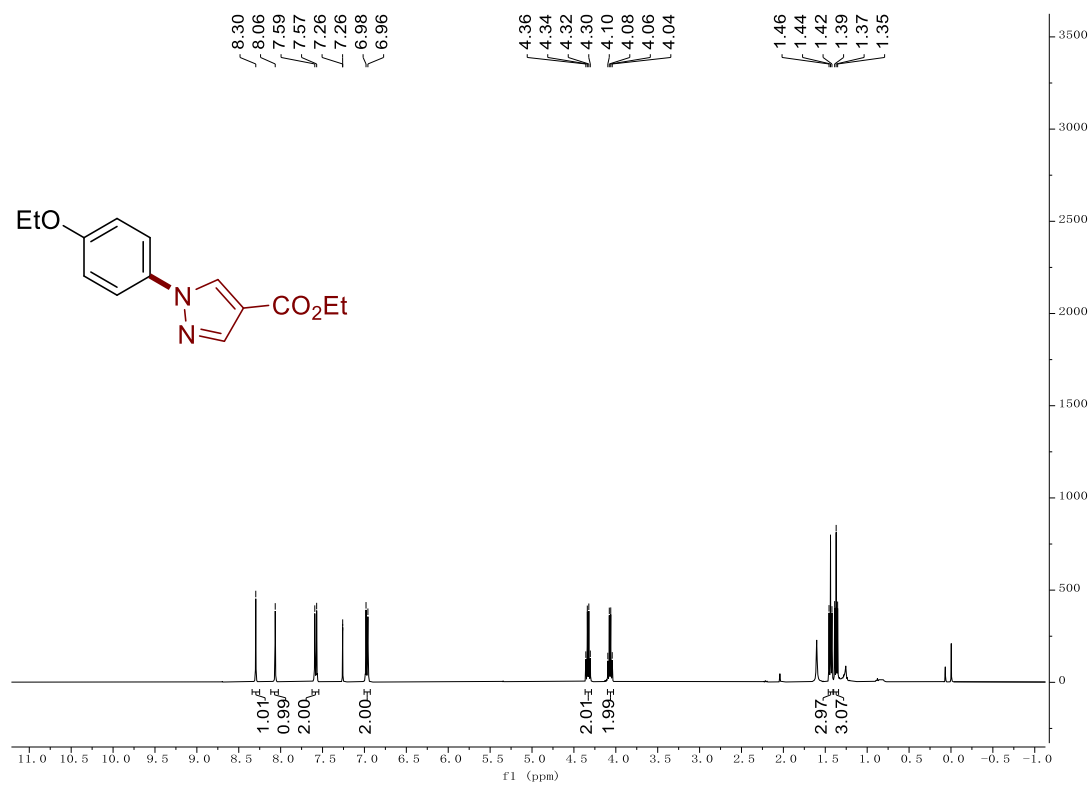
¹H NMR Spectrum of 3q (400 MHz, CDCl₃)



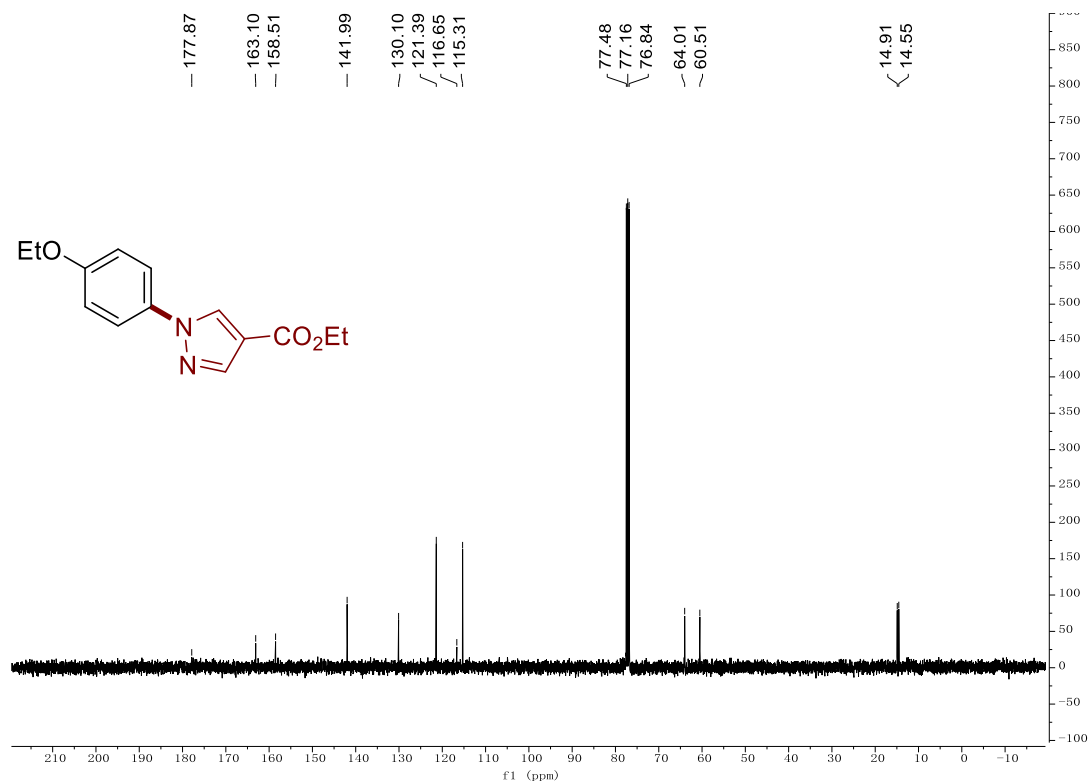
¹³C NMR Spectrum of 3q (400 MHz, CDCl₃)



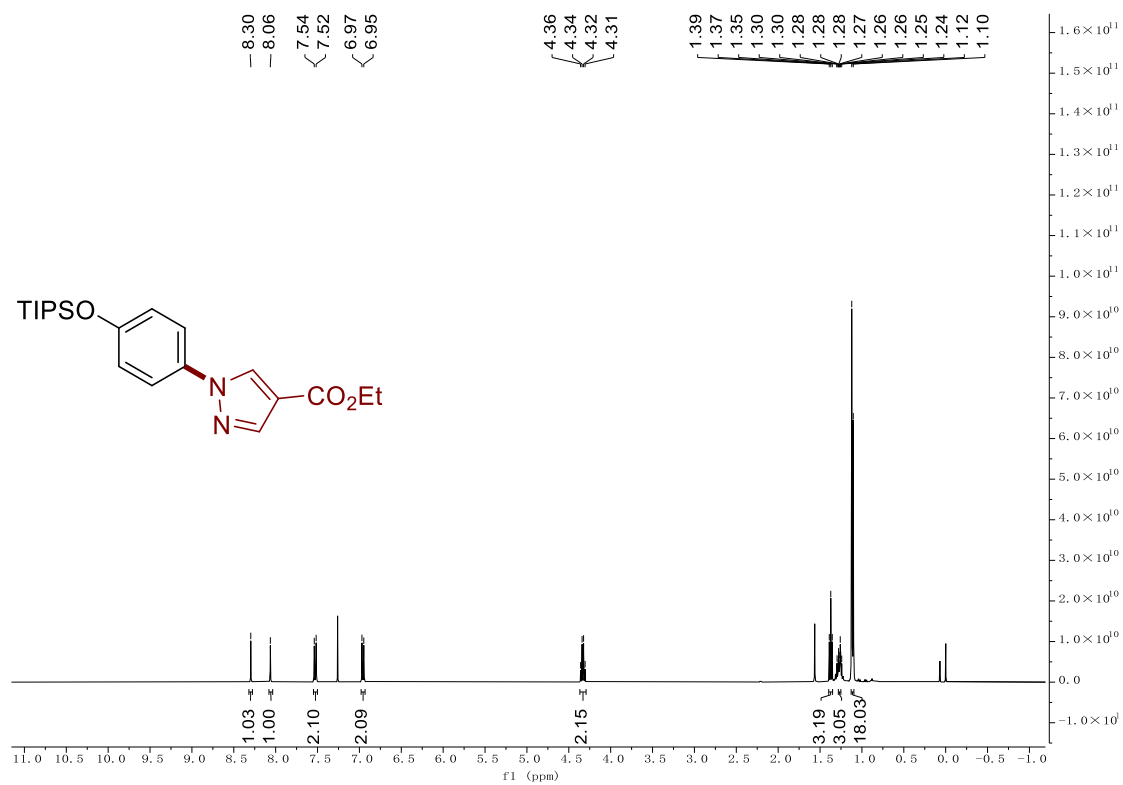
¹H NMR Spectrum of 3r (400 MHz, CDCl₃)



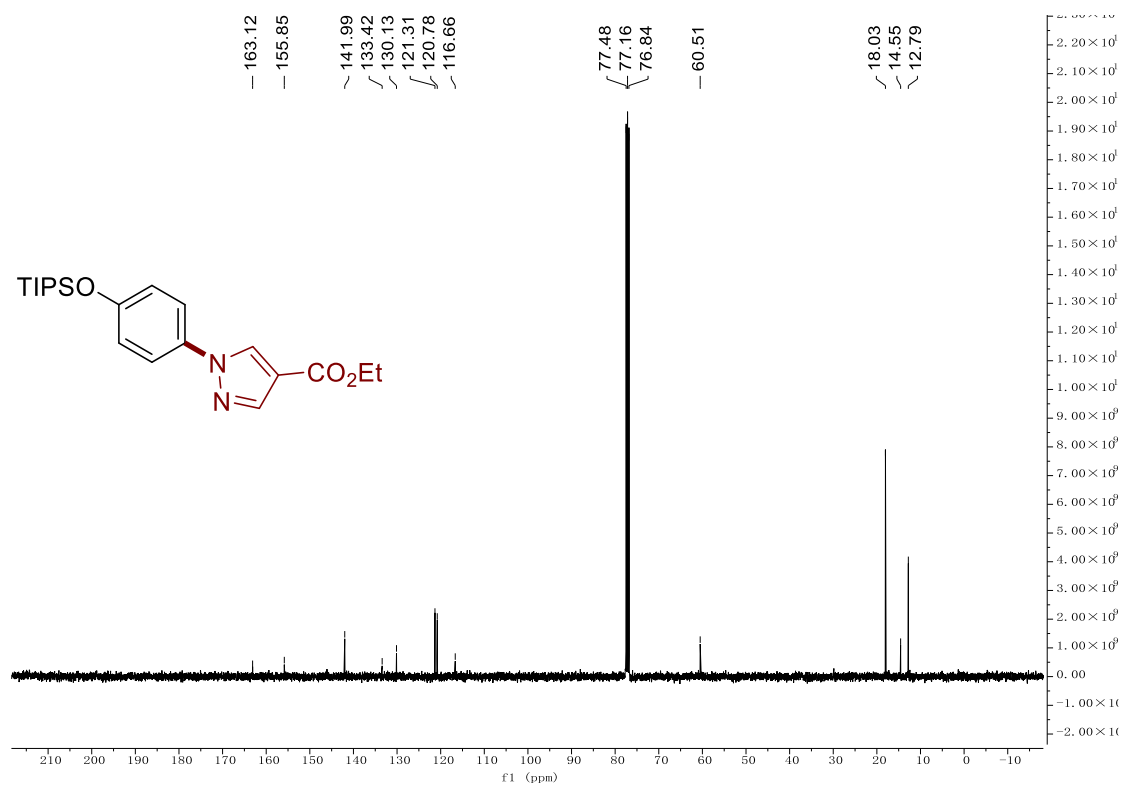
¹³C NMR Spectrum of 3r (400 MHz, CDCl₃)



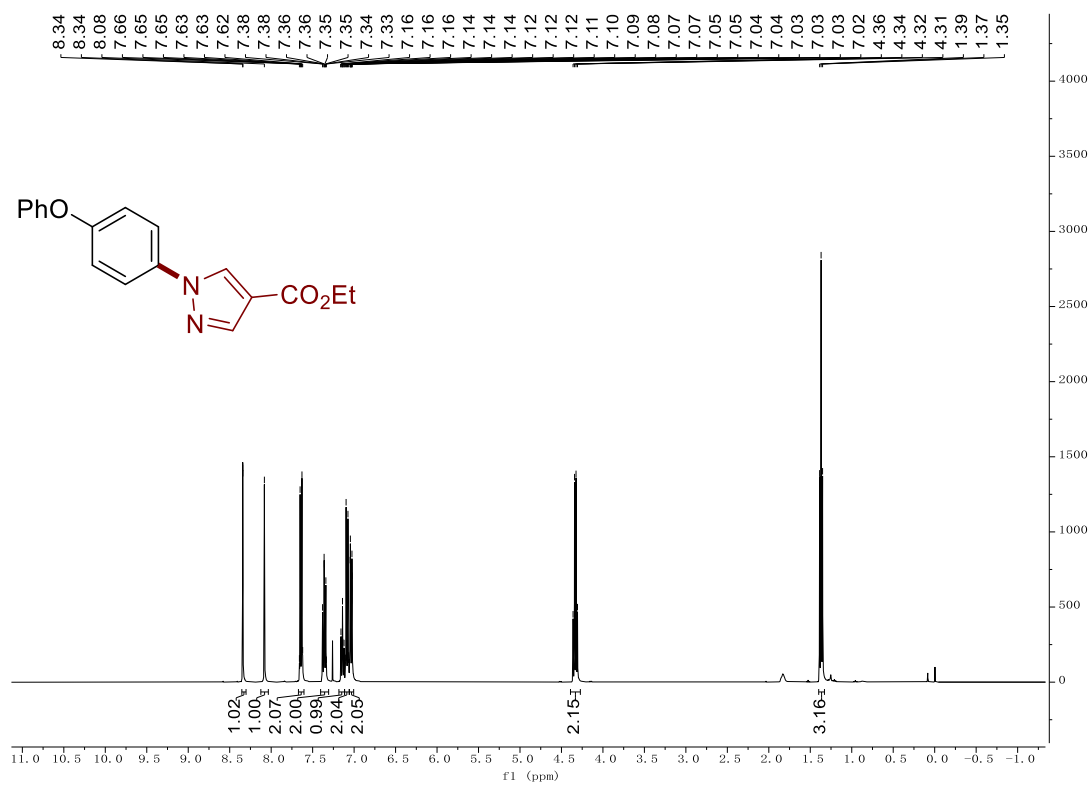
¹H NMR Spectrum of 3s (400 MHz, CDCl₃)



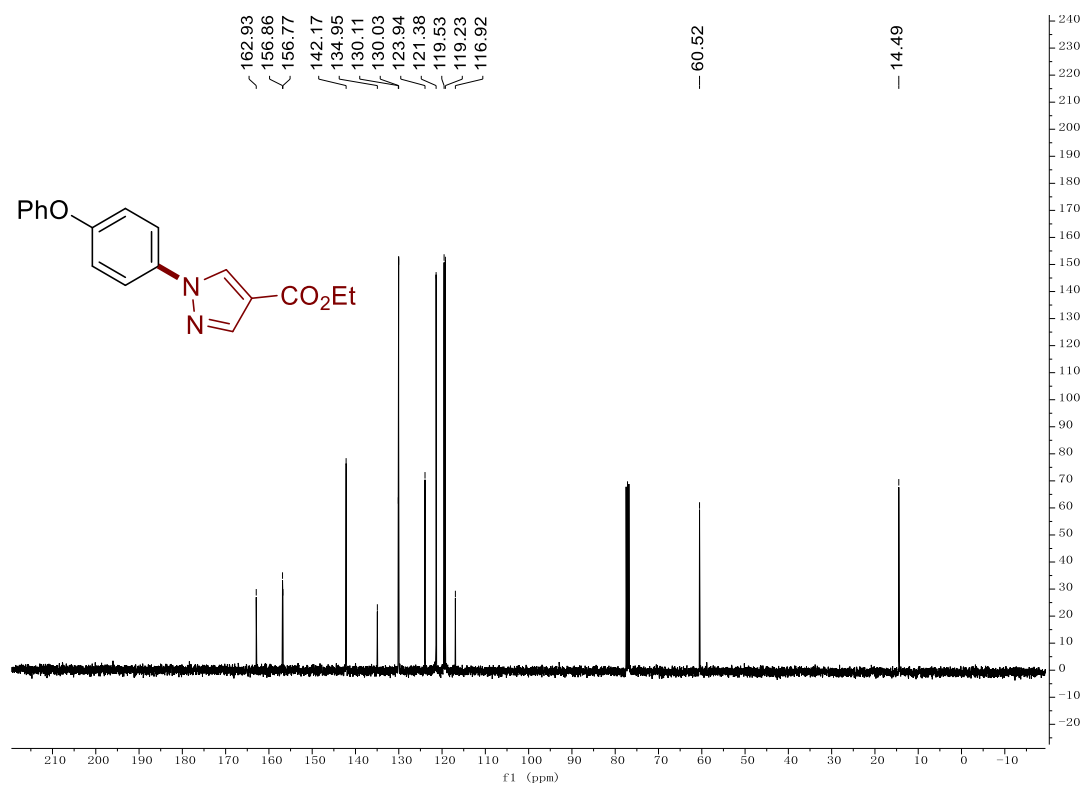
¹³C NMR Spectrum of 3s (400 MHz, CDCl₃)



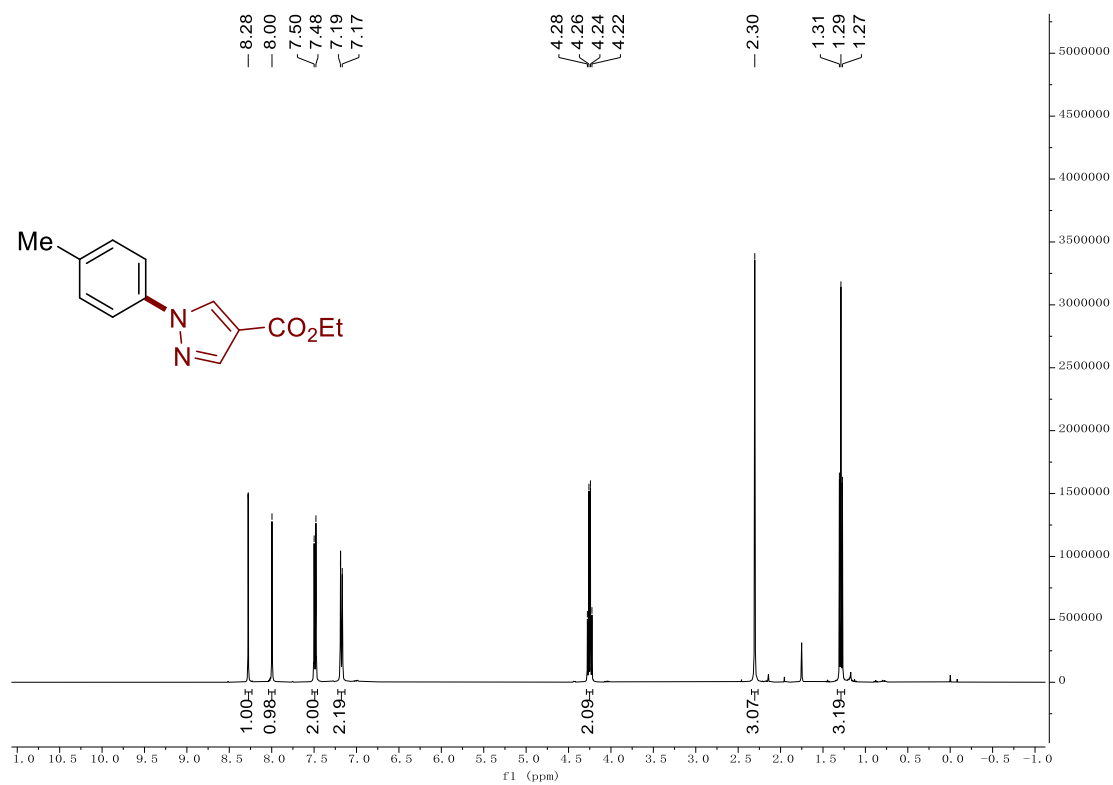
¹H NMR Spectrum of 3t (400 MHz, CDCl₃)



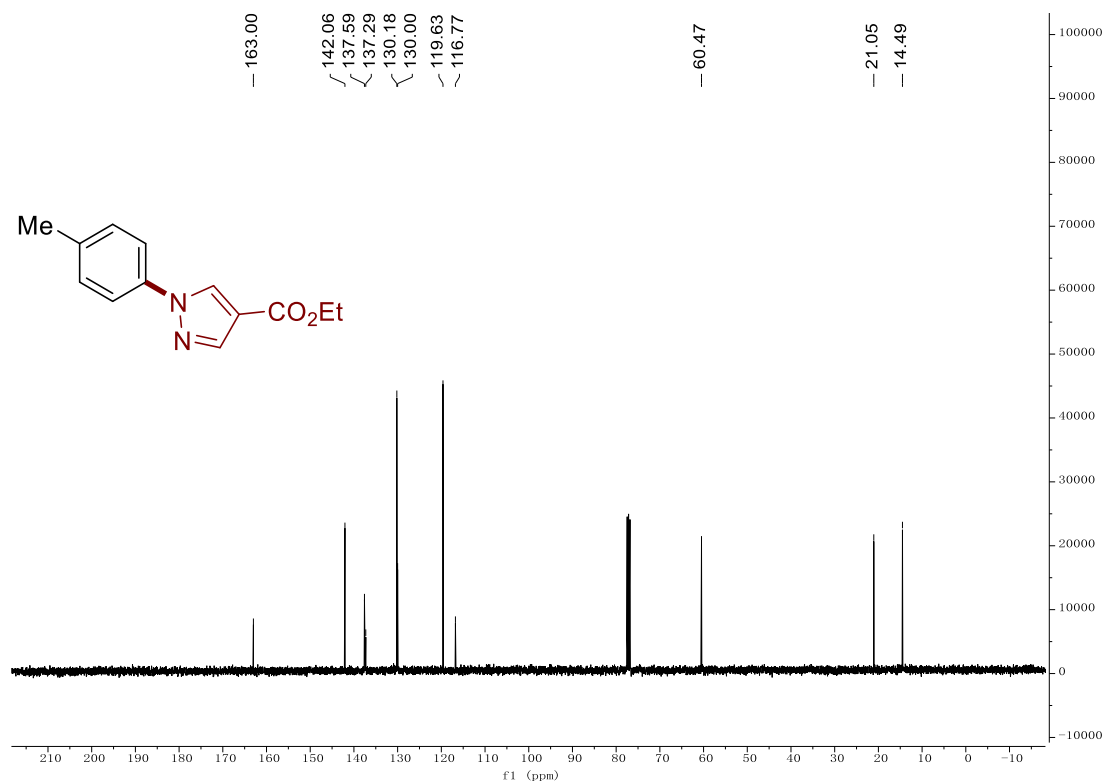
¹³C NMR Spectrum of 3t (400 MHz, CDCl₃)



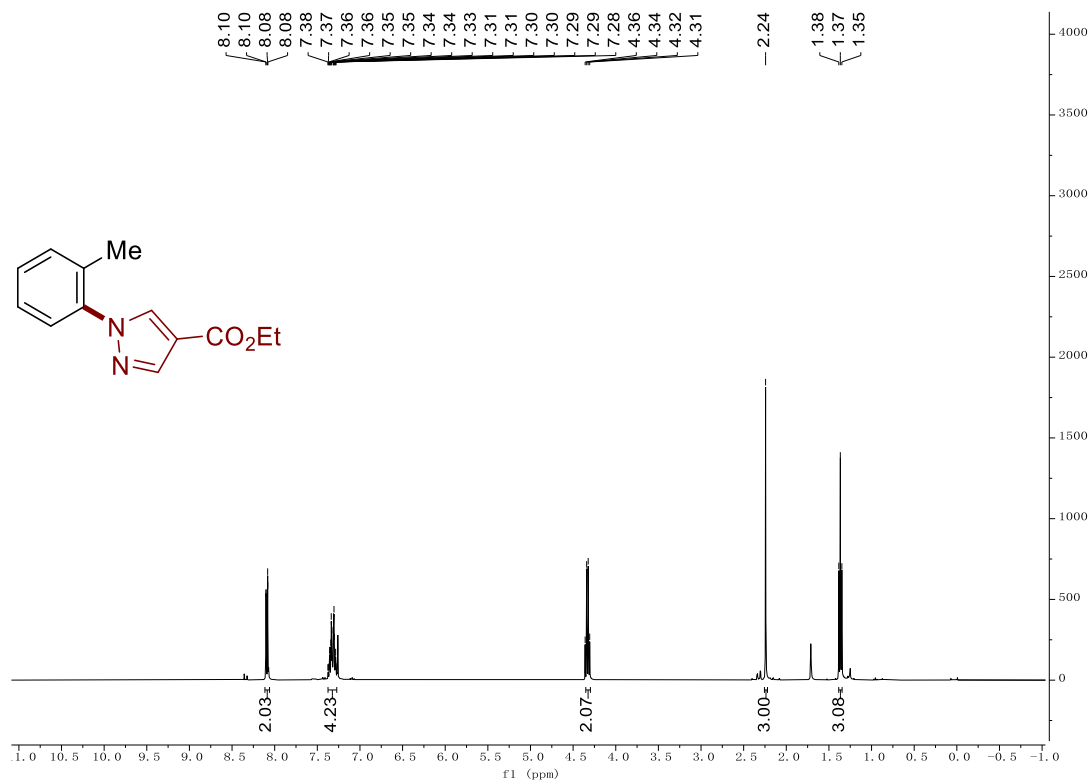
¹H NMR Spectrum of 3u (400 MHz, CDCl₃)



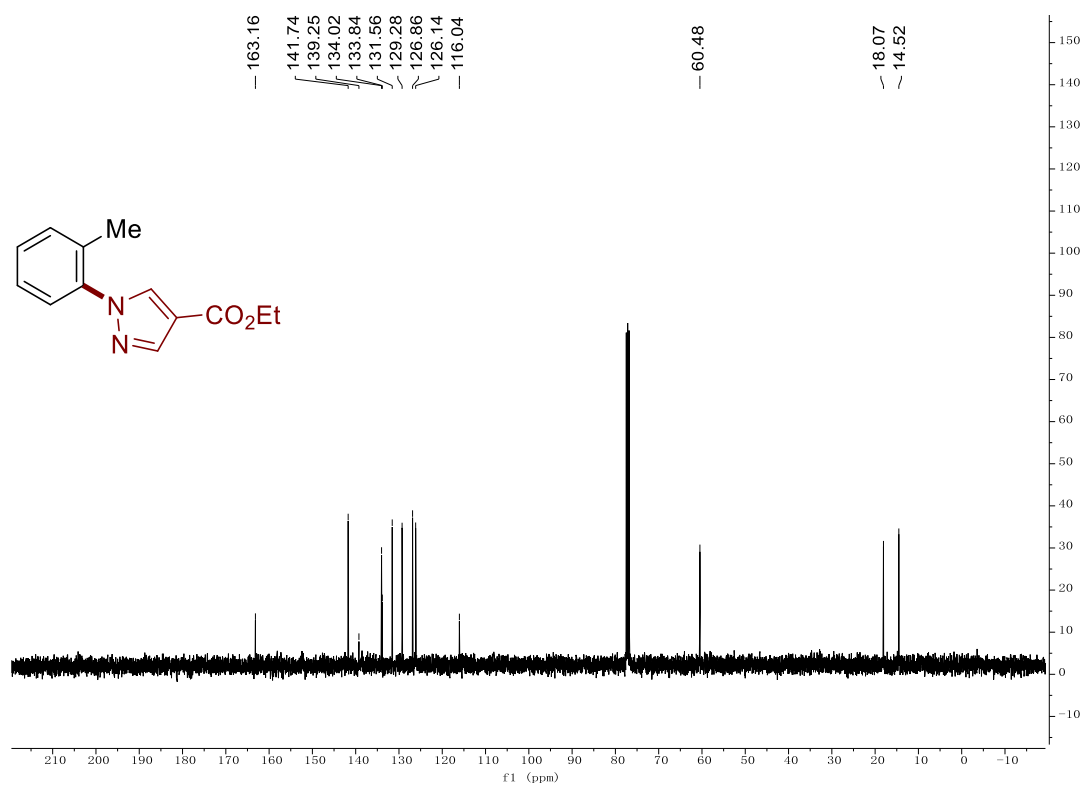
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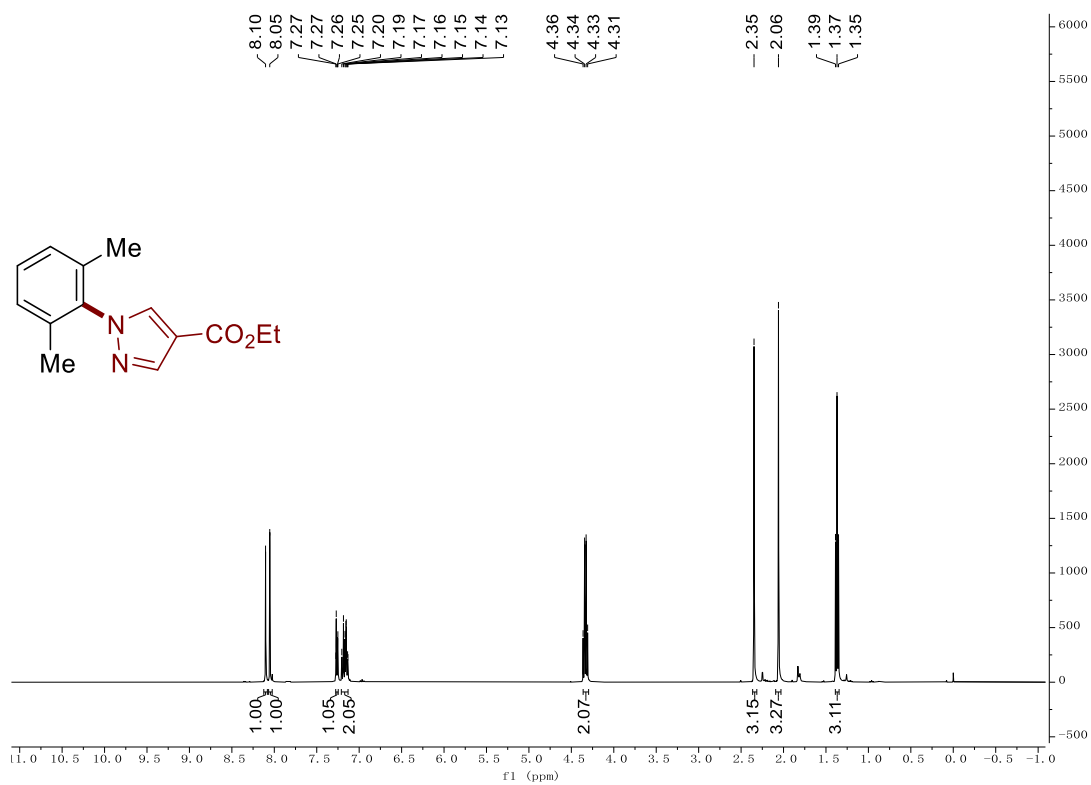
¹H NMR Spectrum of 3v (400 MHz, CDCl₃)



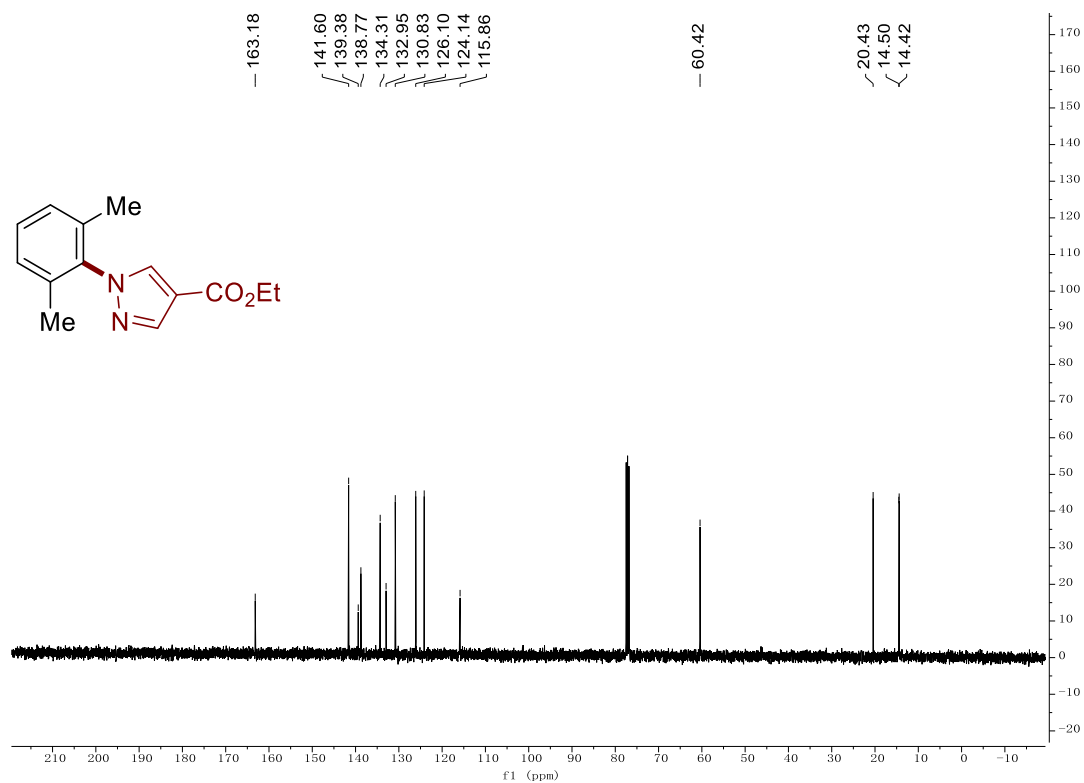
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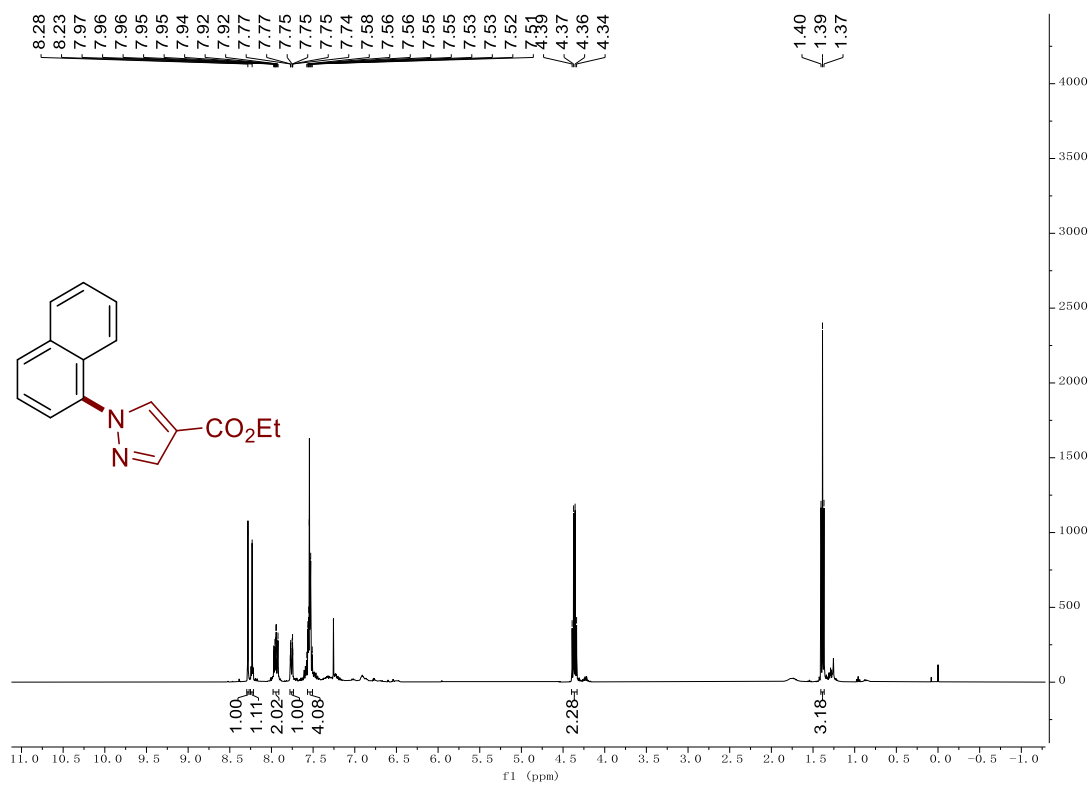
¹H NMR Spectrum of 3w (400 MHz, CDCl₃)



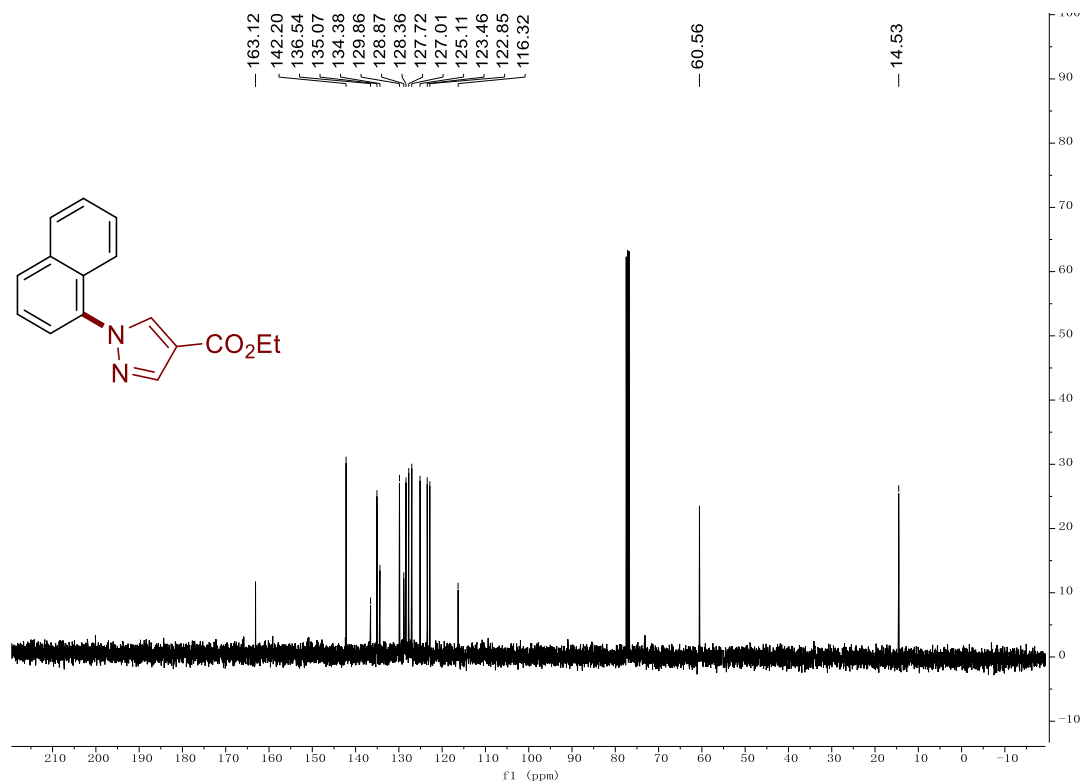
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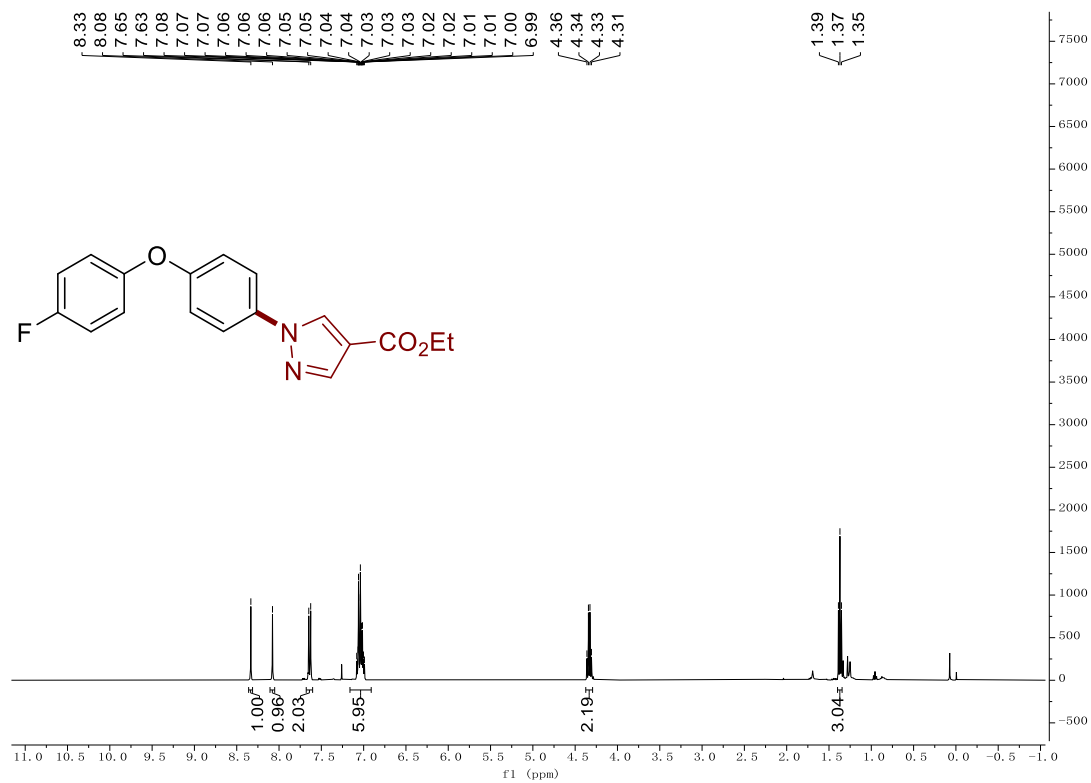
¹H NMR Spectrum of 3x (400 MHz, CDCl₃)



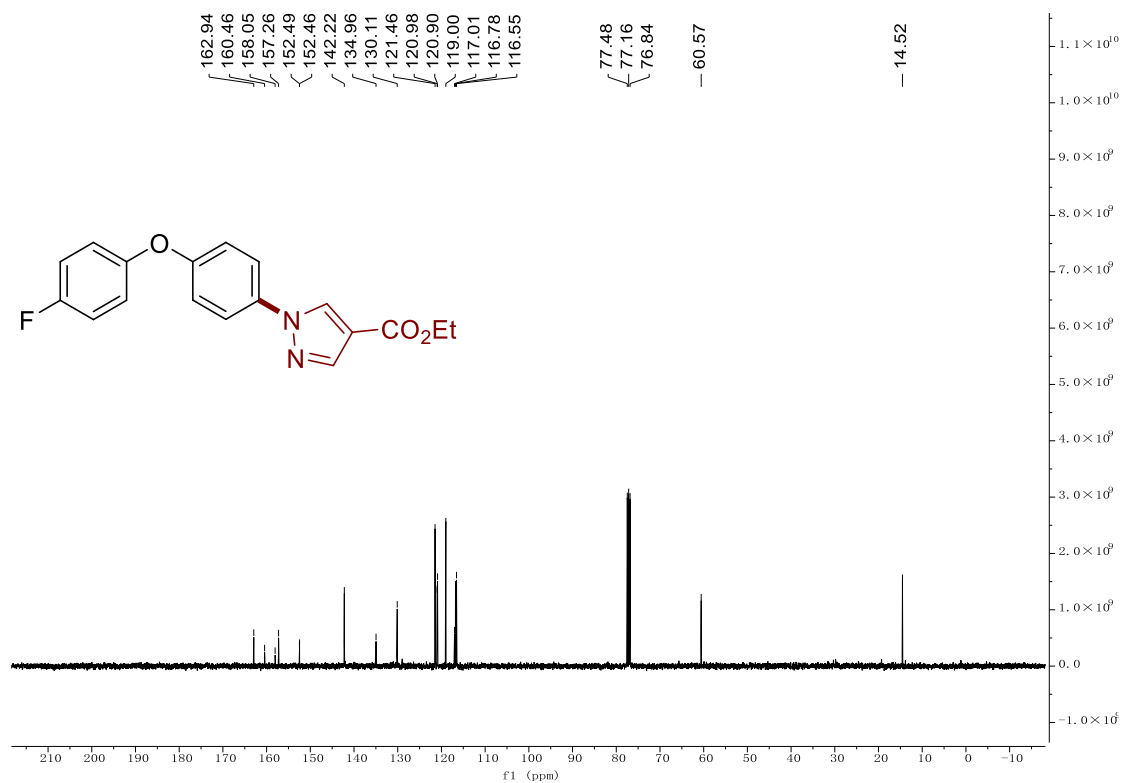
¹³C NMR Spectrum of 3x (400 MHz, CDCl₃)



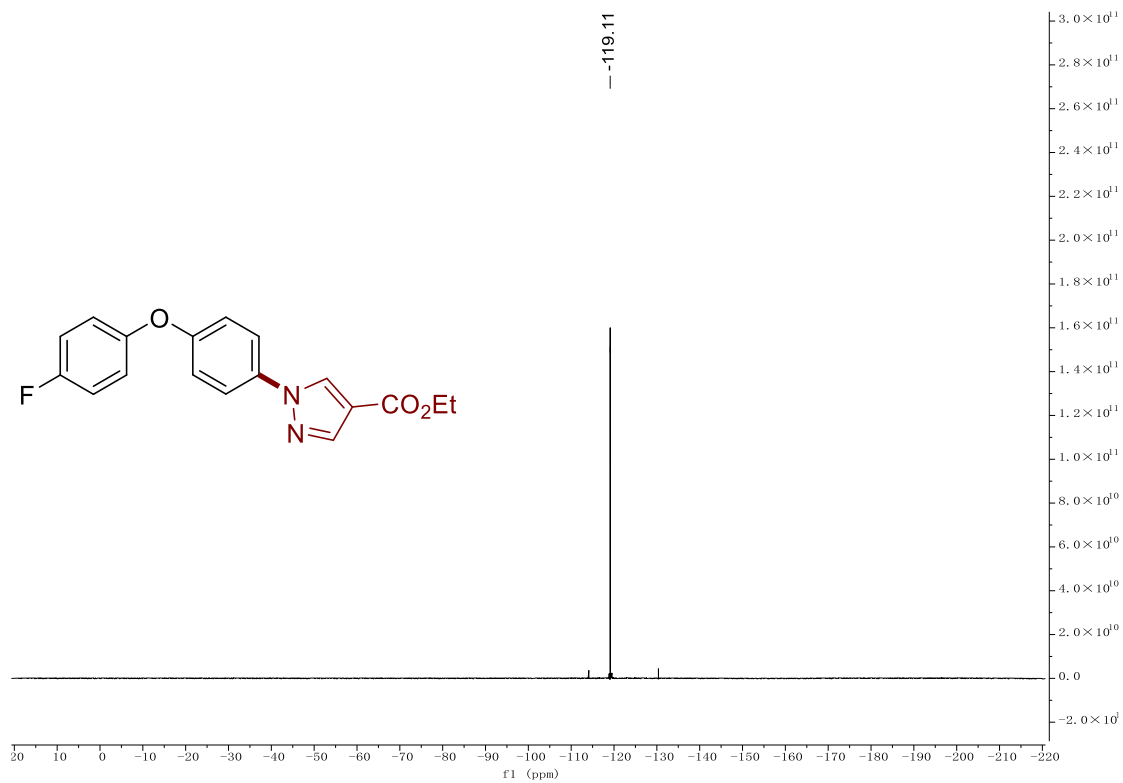
¹H NMR Spectrum of 3y (400 MHz, CDCl₃)



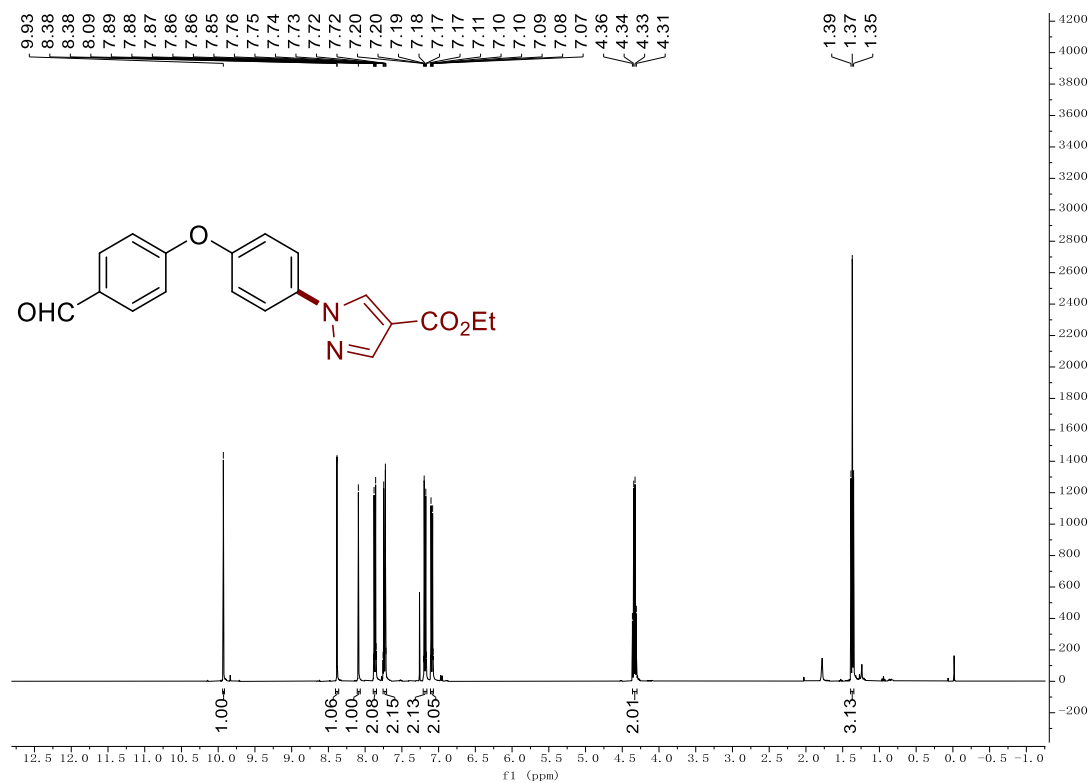
¹³C NMR Spectrum of 3y (400 MHz, CDCl₃)



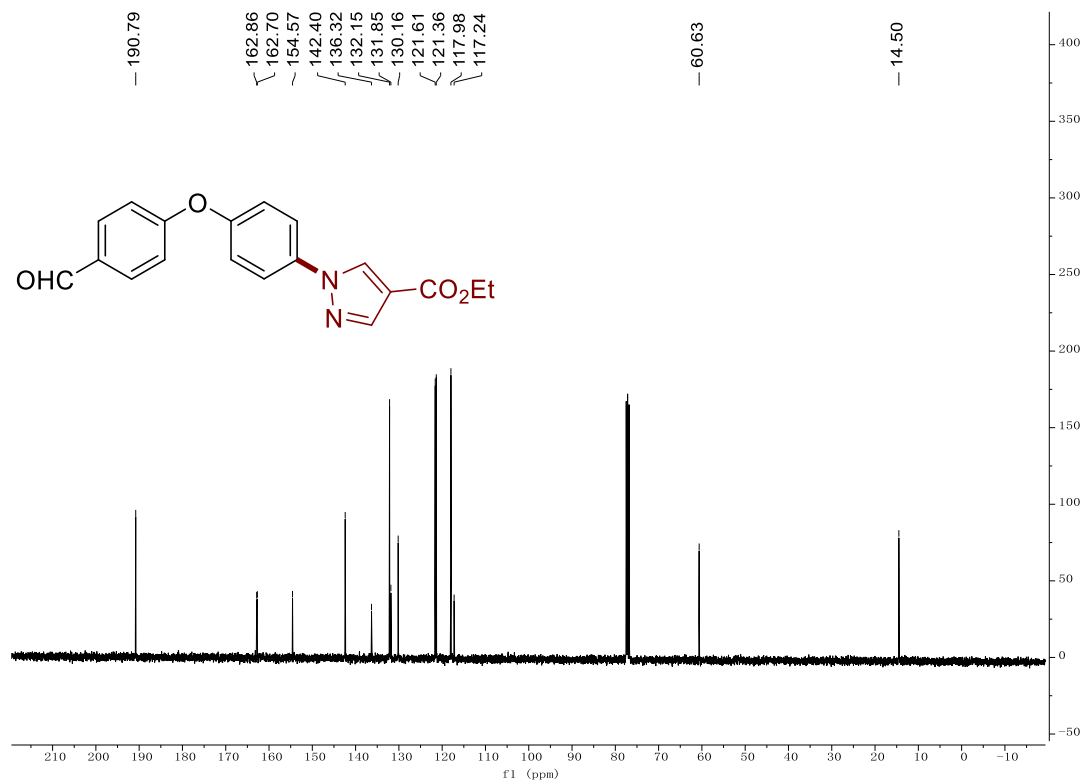
¹⁹F NMR Spectrum of 3y (400 MHz, CDCl₃)



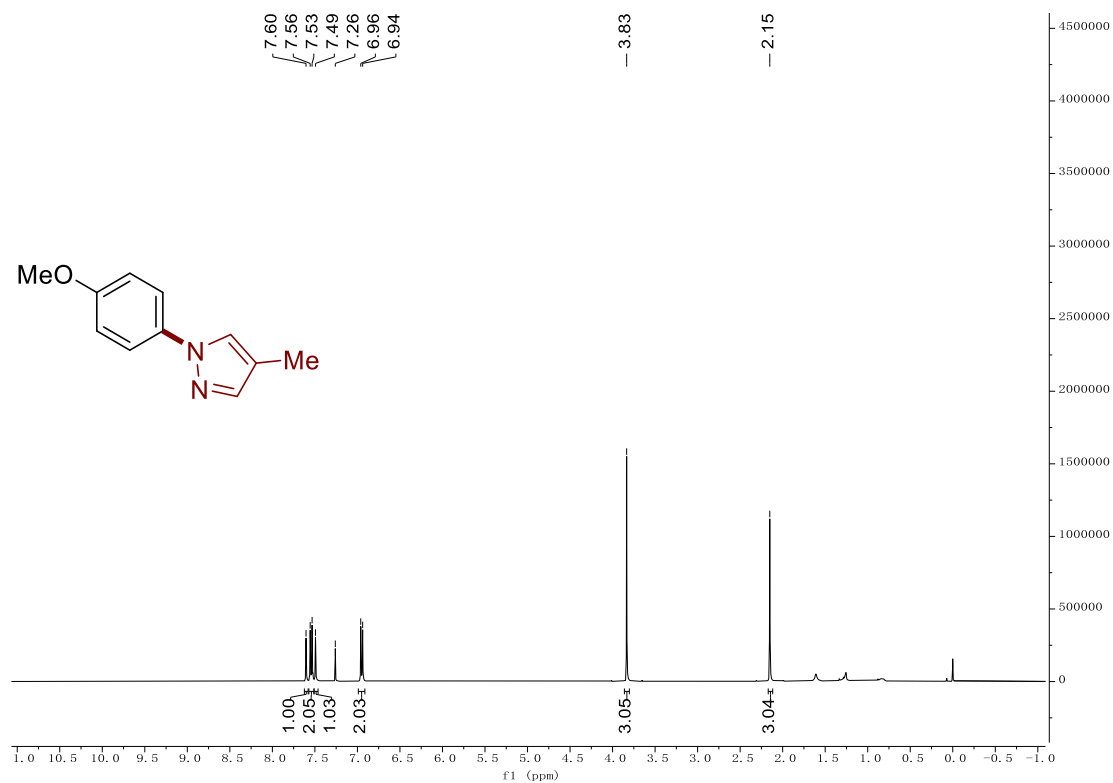
¹H NMR Spectrum of 3z (400 MHz, CDCl₃)



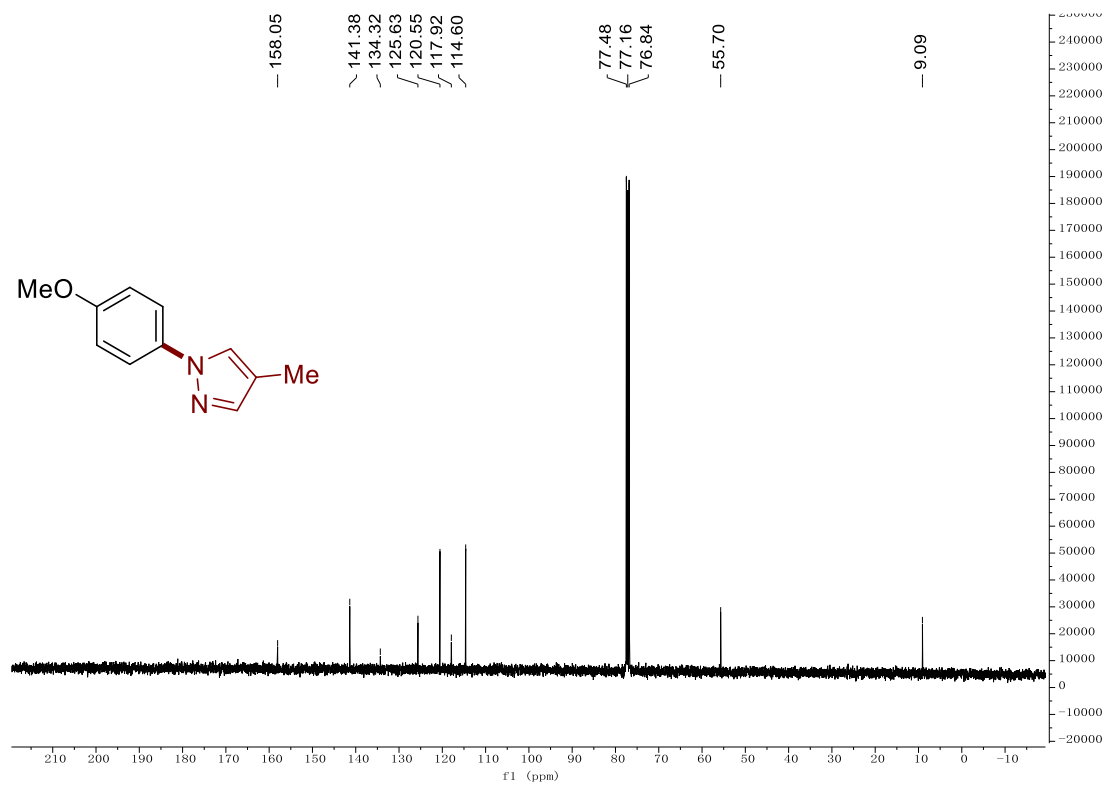
¹³C NMR Spectrum of 3z (400 MHz, CDCl₃)



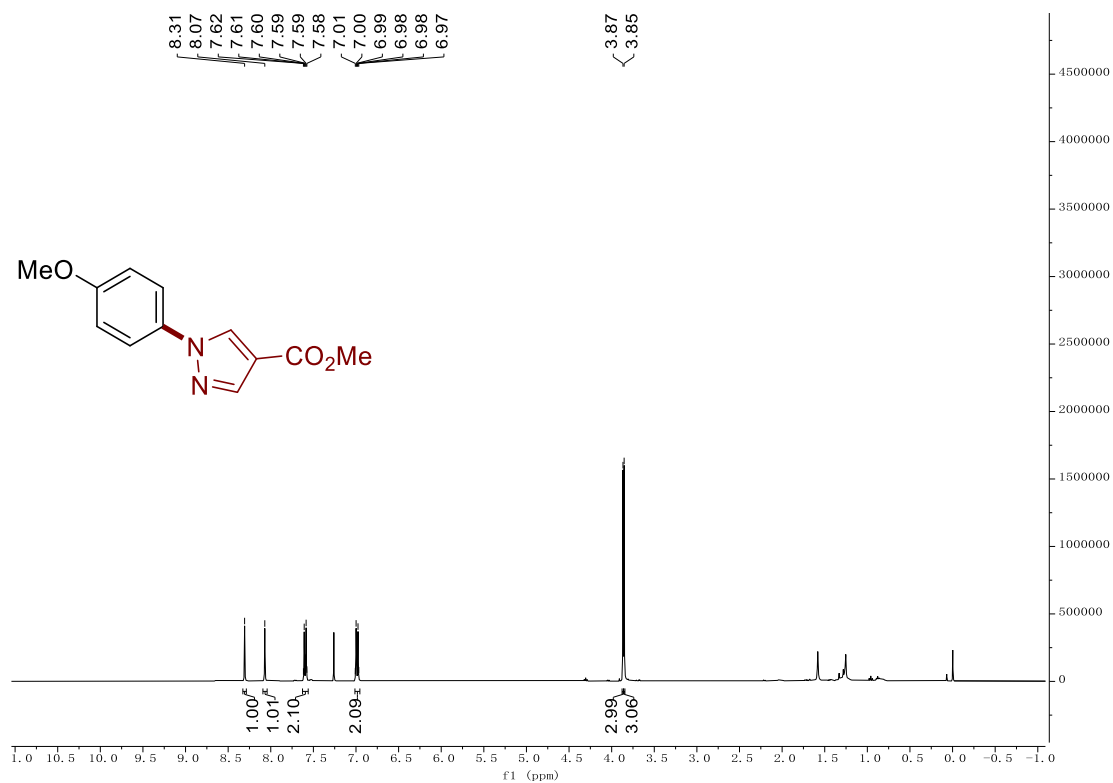
¹H NMR Spectrum of 4a (400 MHz, CDCl₃)



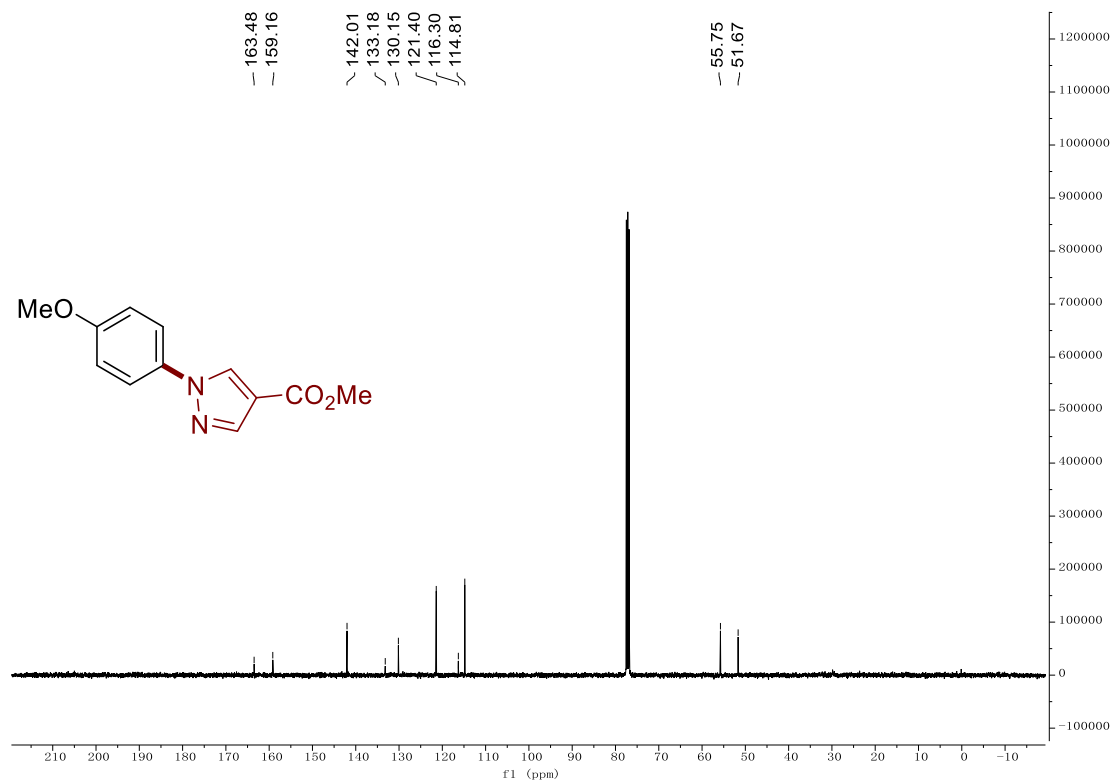
¹³C NMR Spectrum of 4a (400 MHz, CDCl₃)



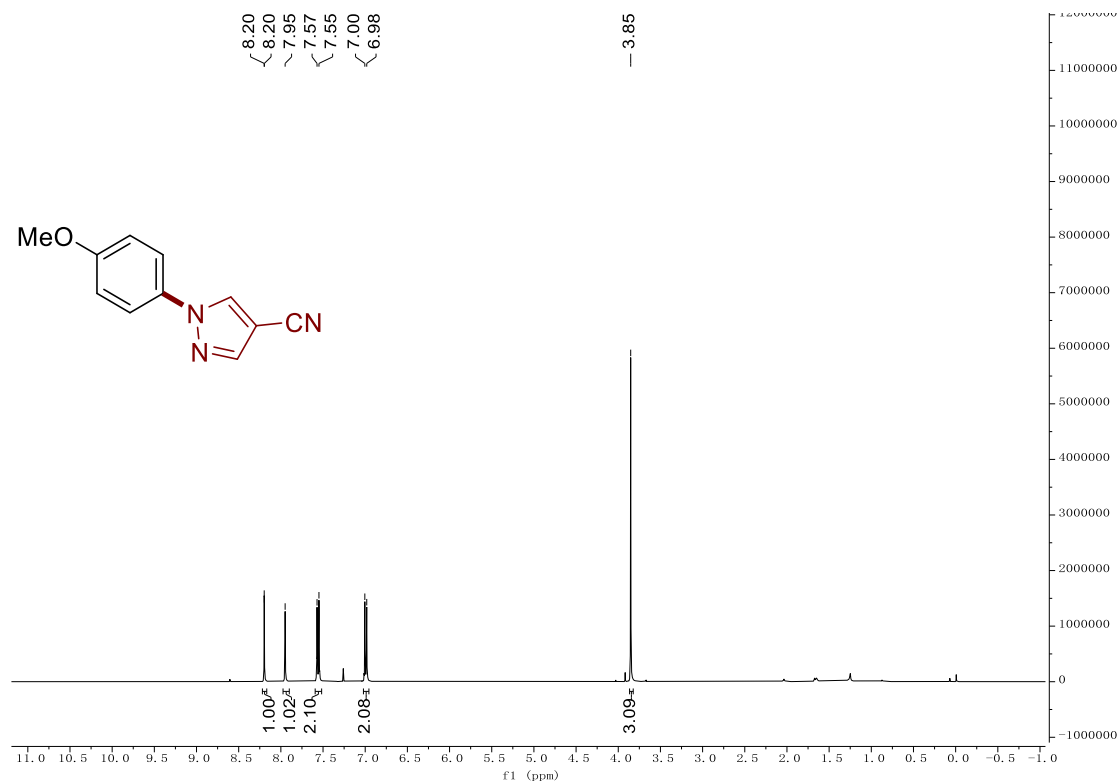
¹H NMR Spectrum of 4b (400 MHz, CDCl₃)



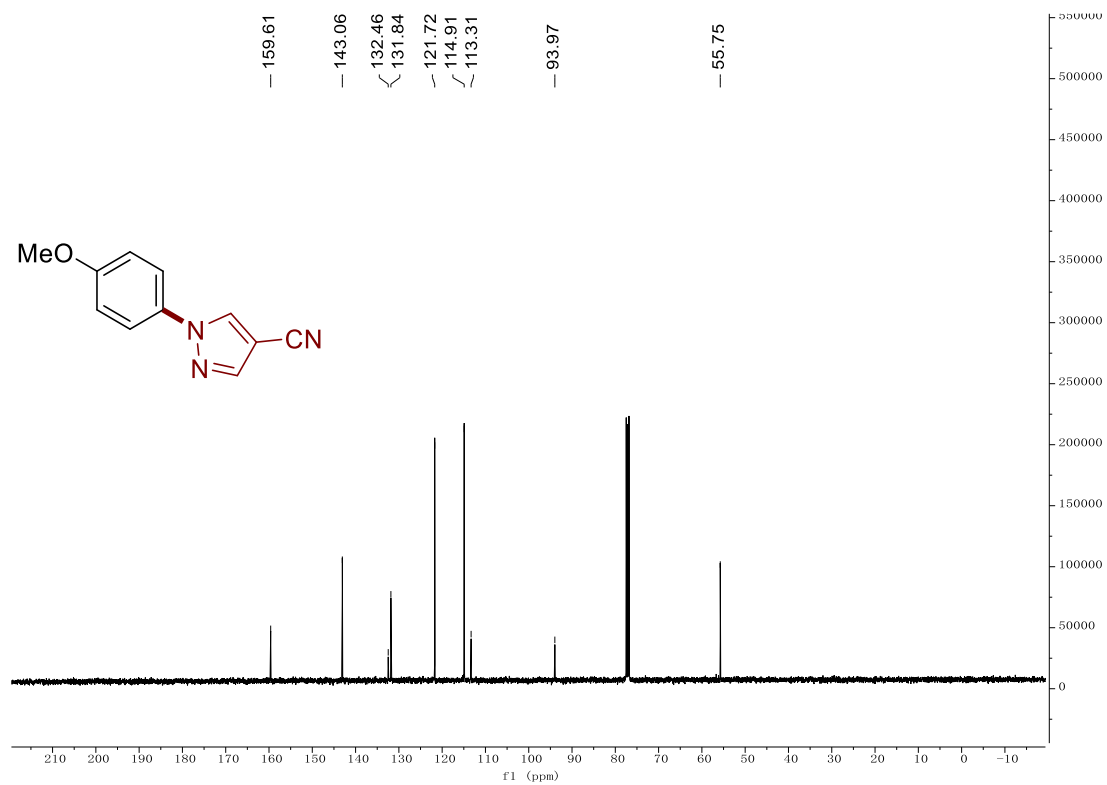
¹³C NMR Spectrum of 4b (400 MHz, CDCl₃)



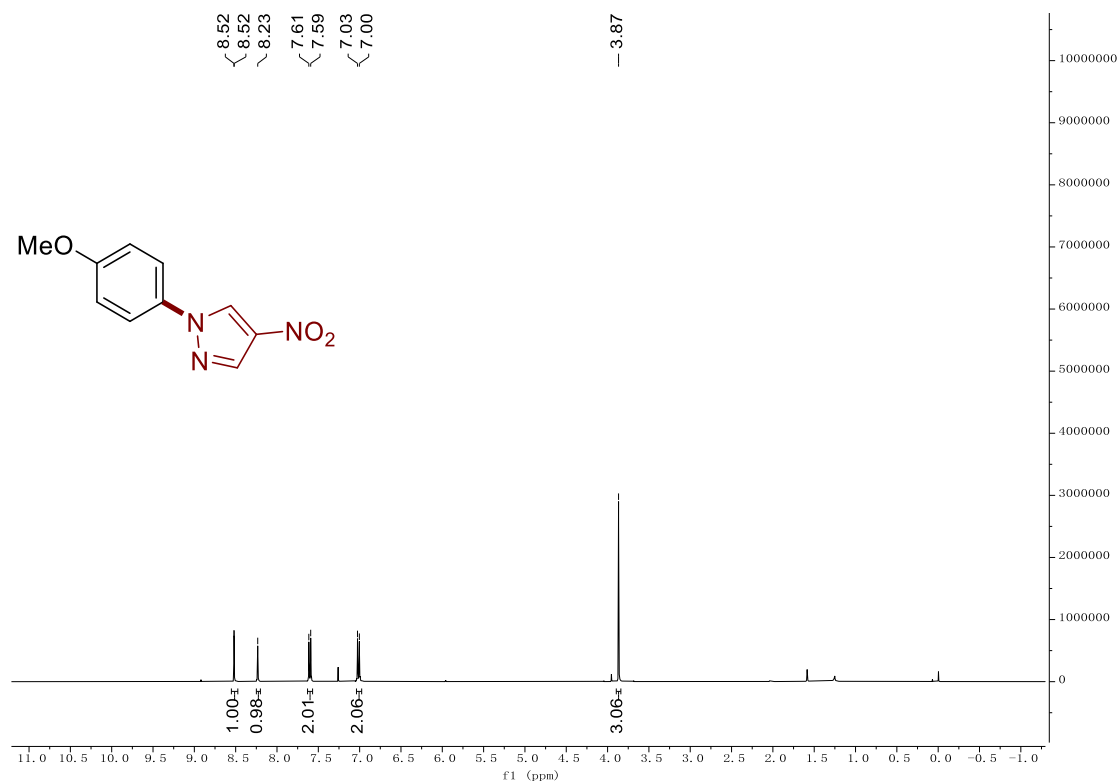
¹H NMR Spectrum of 4c (400 MHz, CDCl₃)



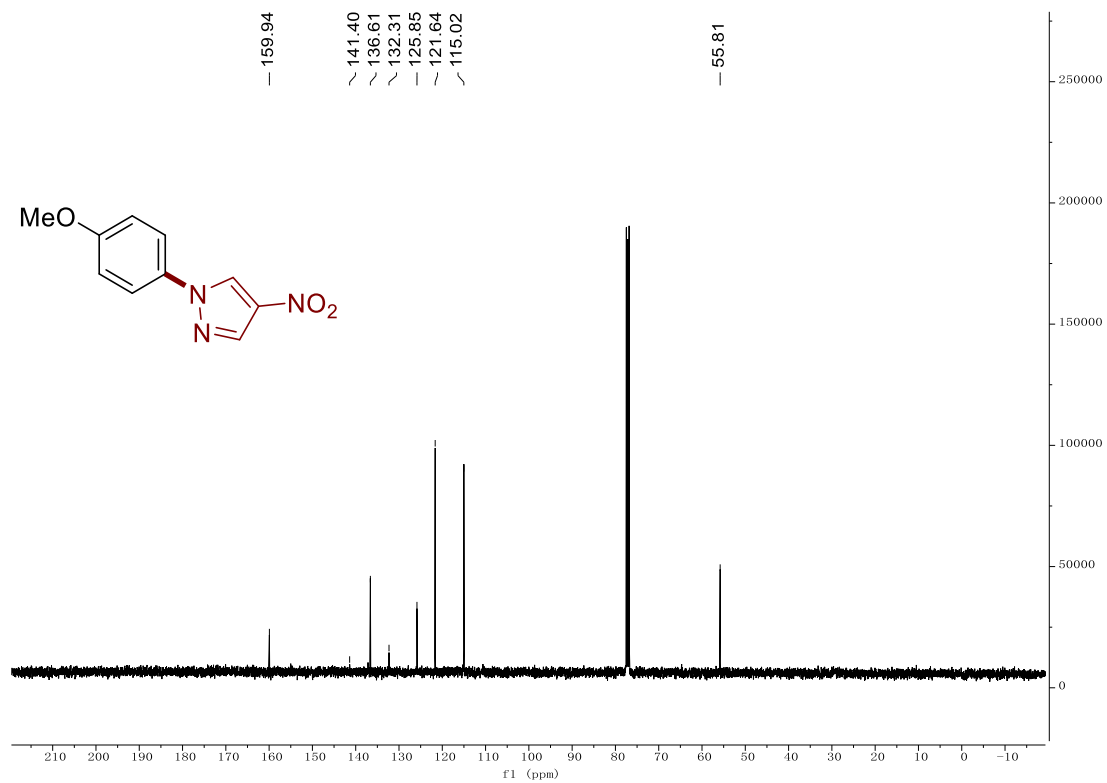
¹³C NMR Spectrum of 4c (400 MHz, CDCl₃)



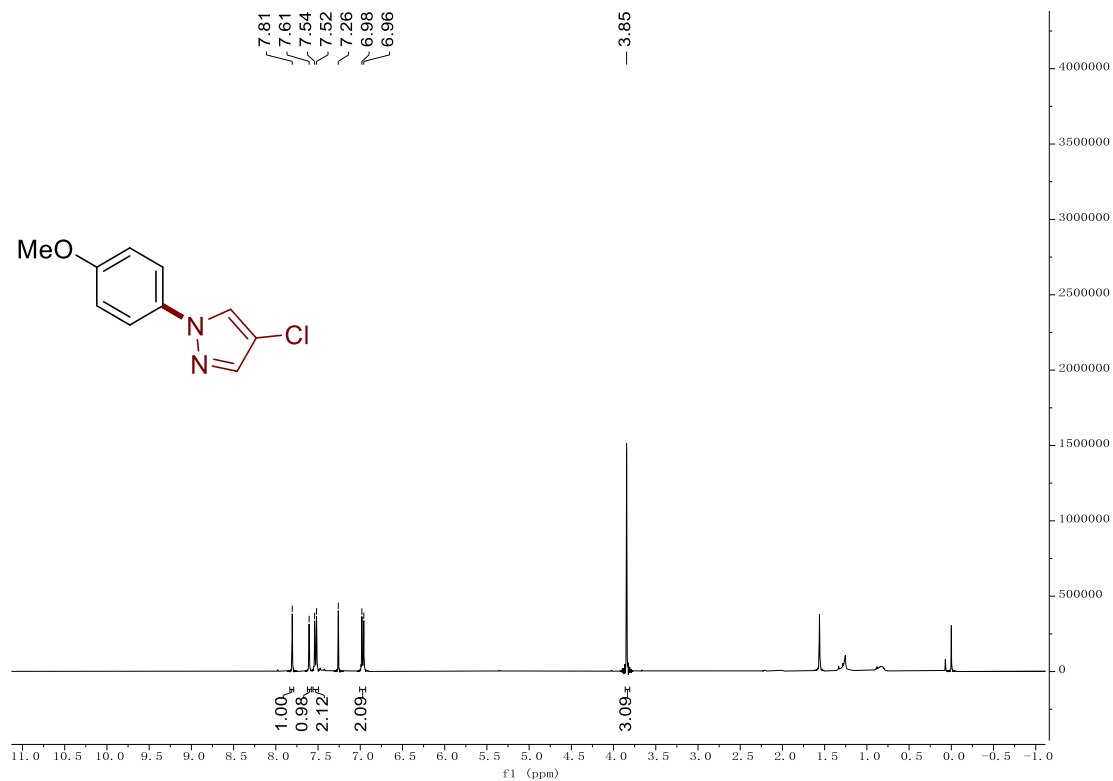
¹H NMR Spectrum of 4d (400 MHz, CDCl₃)



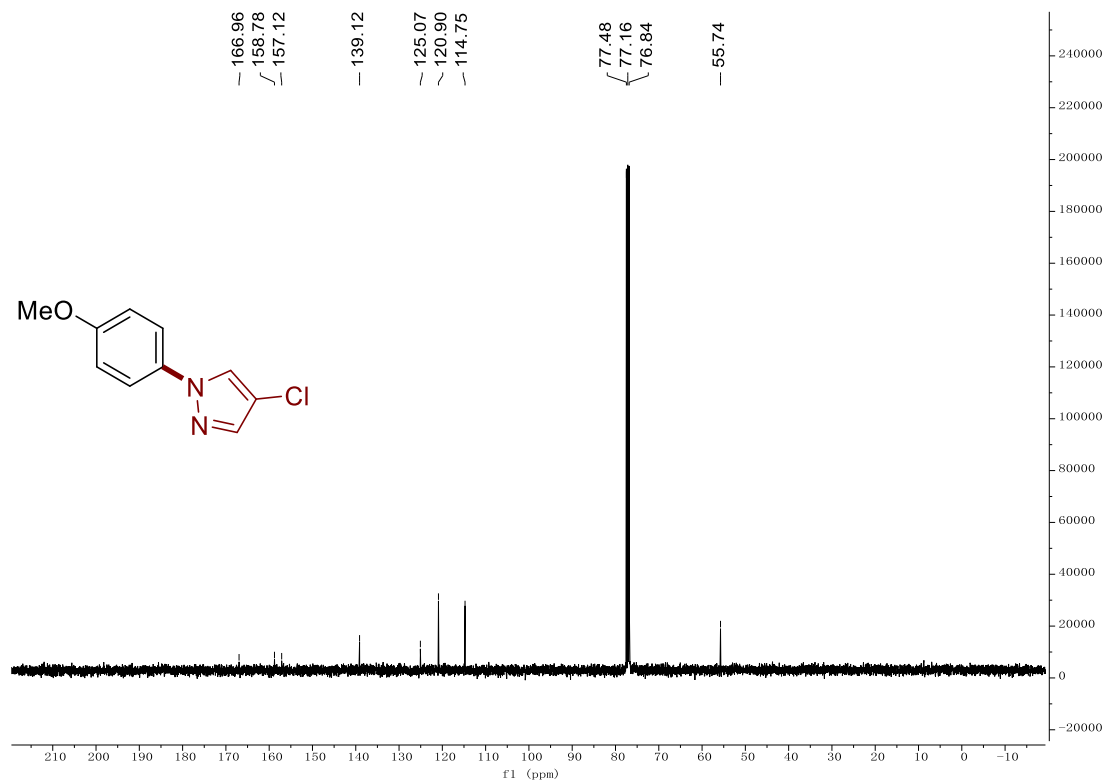
¹³C NMR Spectrum of 4d (400 MHz, CDCl₃)



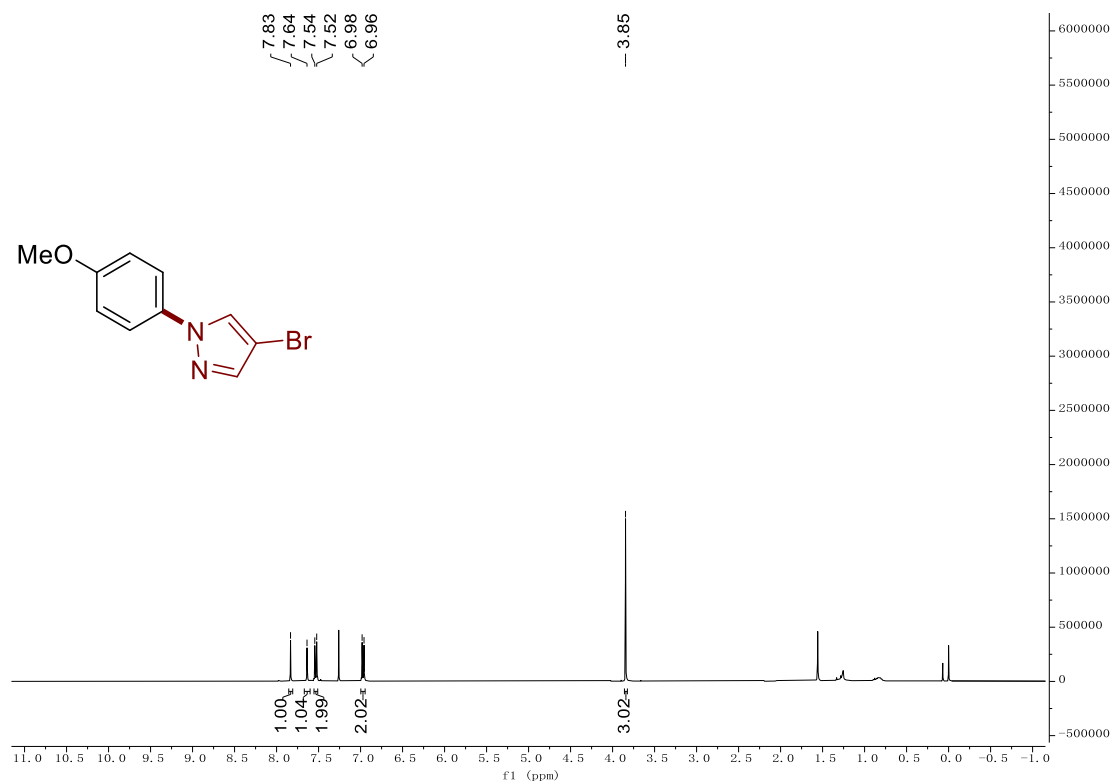
¹H NMR Spectrum of 4e (400 MHz, CDCl₃)



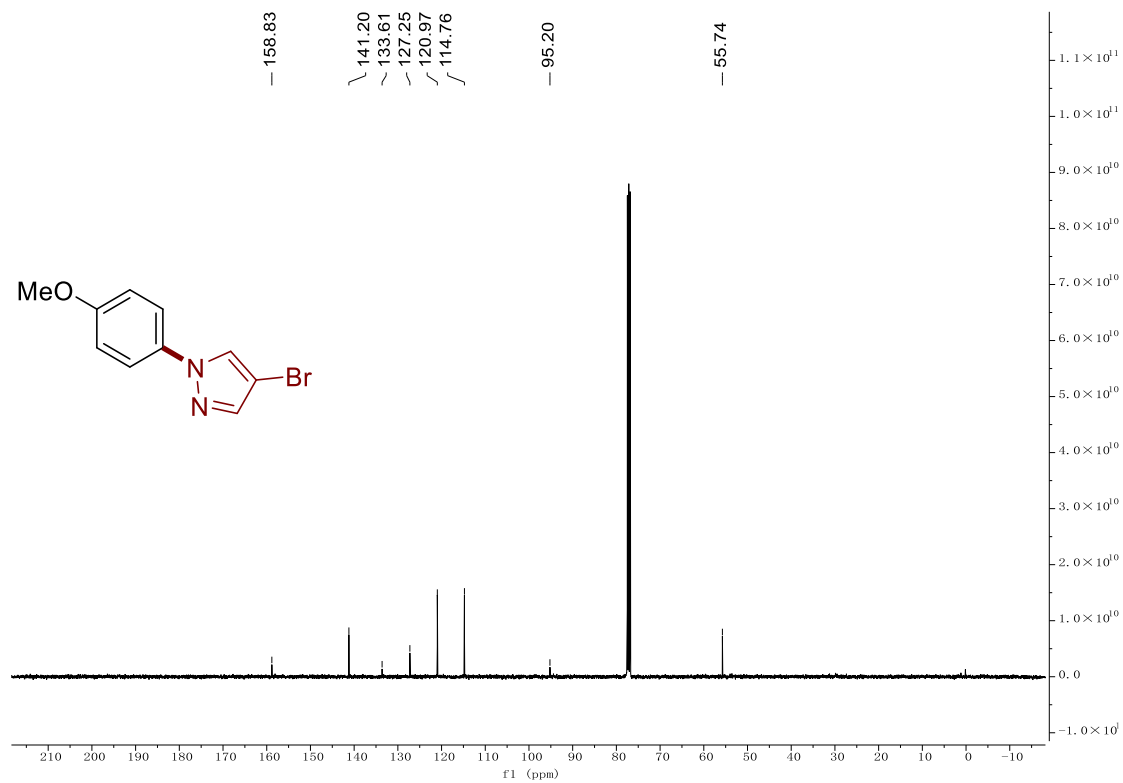
¹³C NMR Spectrum of 4e (400 MHz, CDCl₃)



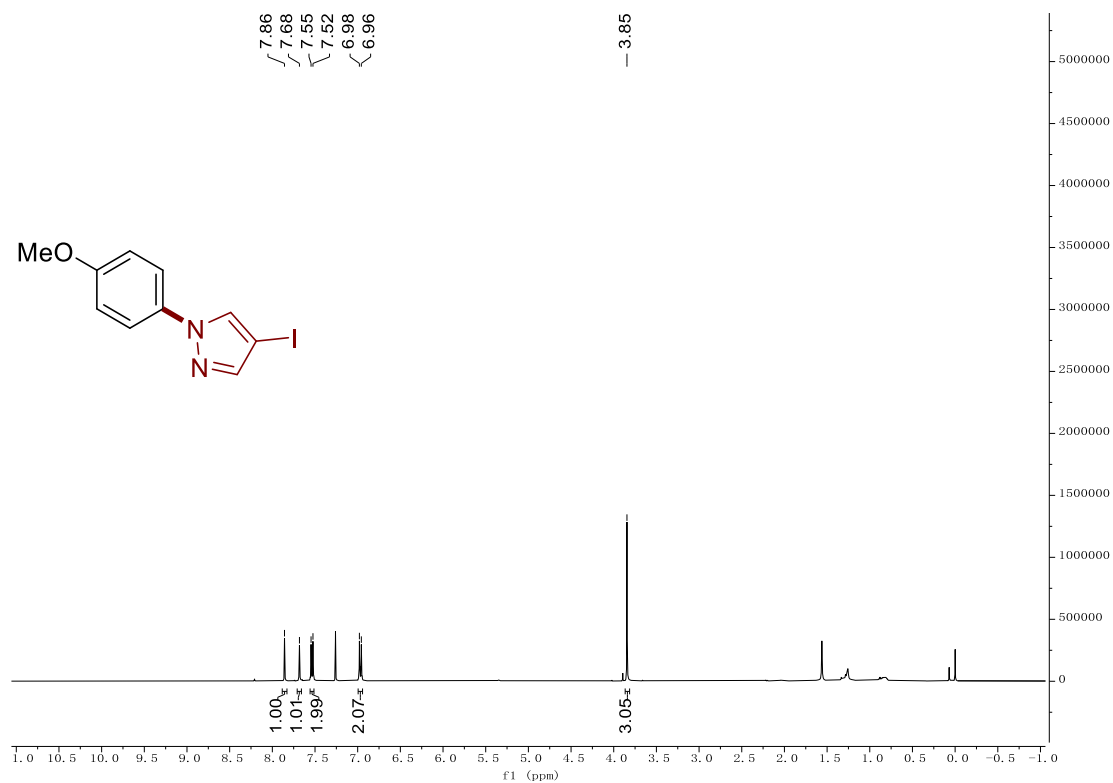
¹H NMR Spectrum of 4f (400 MHz, CDCl₃)



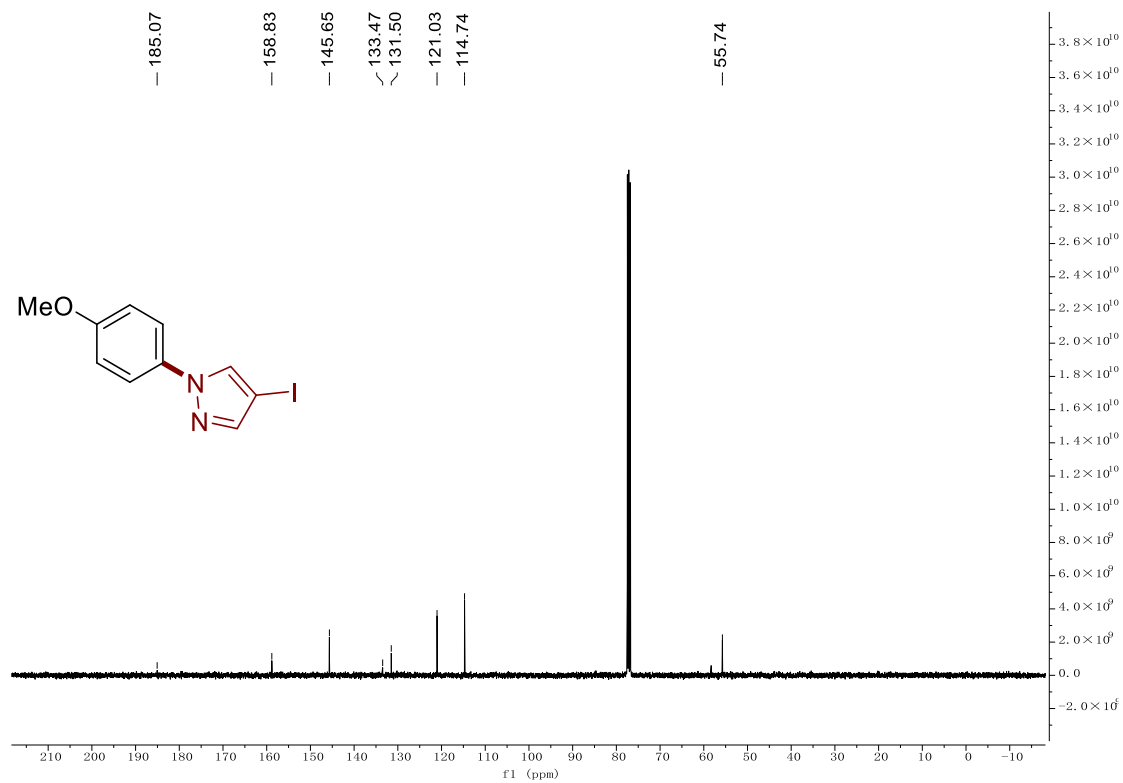
¹³C NMR Spectrum of 4f (400 MHz, CDCl₃)



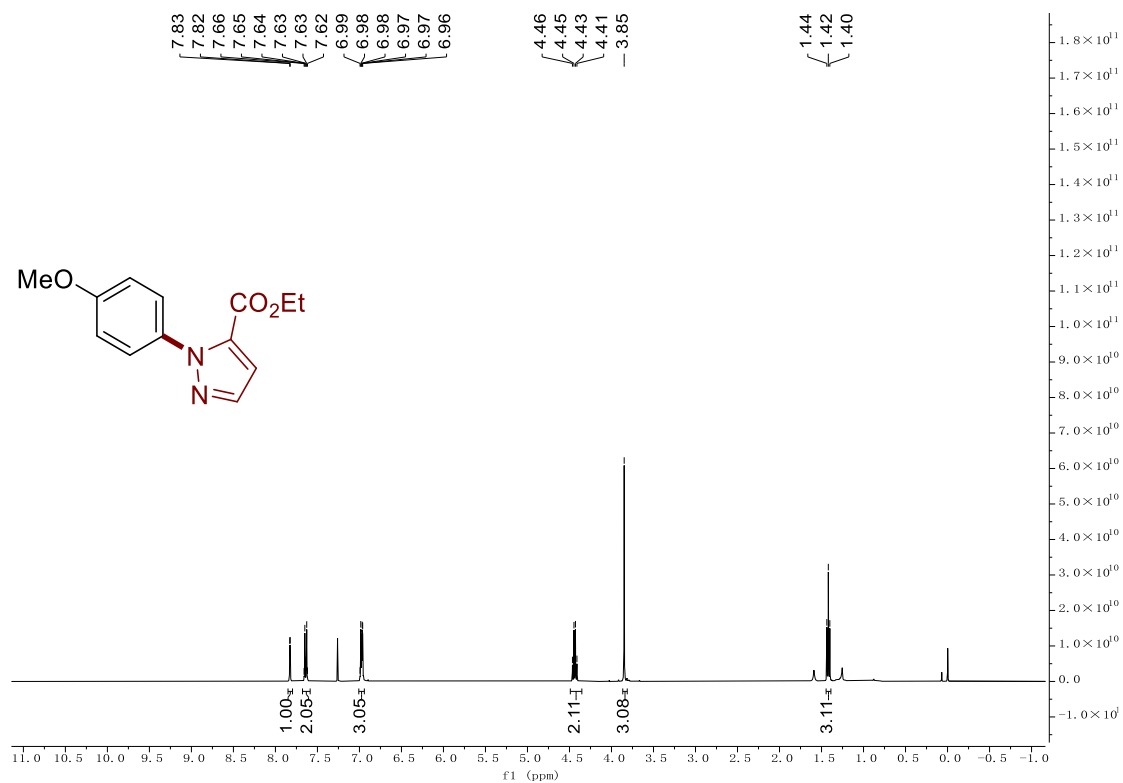
¹H NMR Spectrum of 4g (400 MHz, CDCl₃)



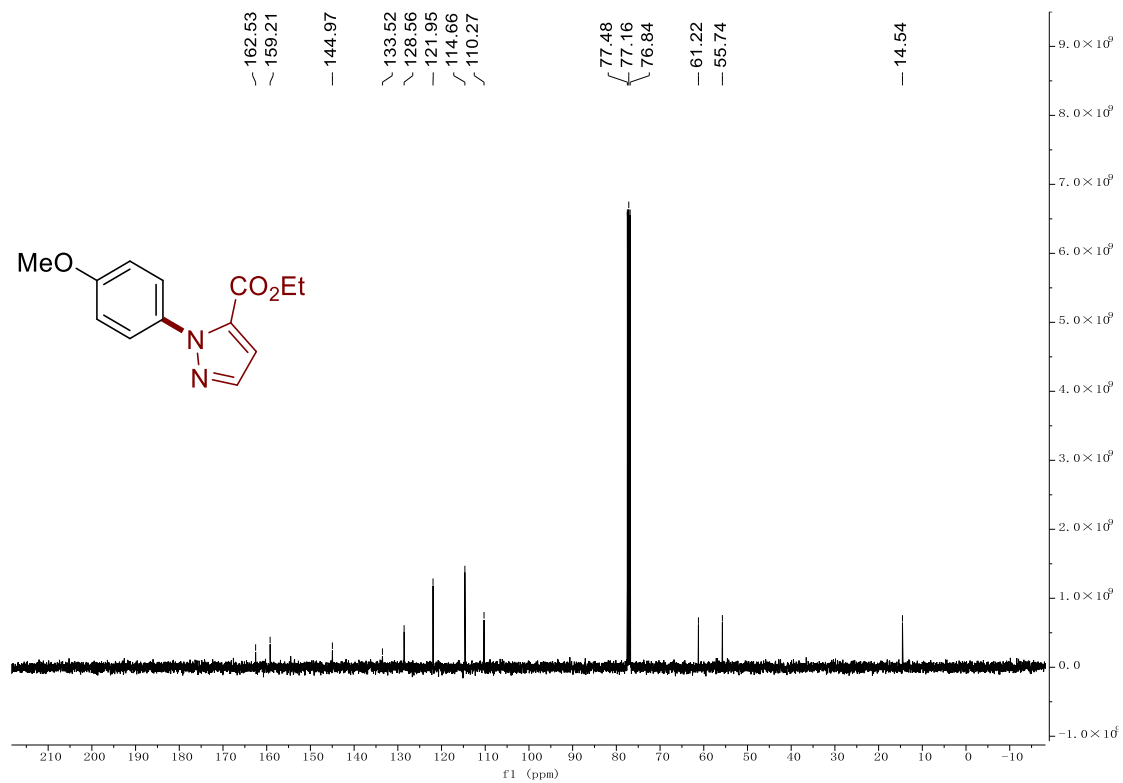
¹³C NMR Spectrum of 4g (400 MHz, CDCl₃)



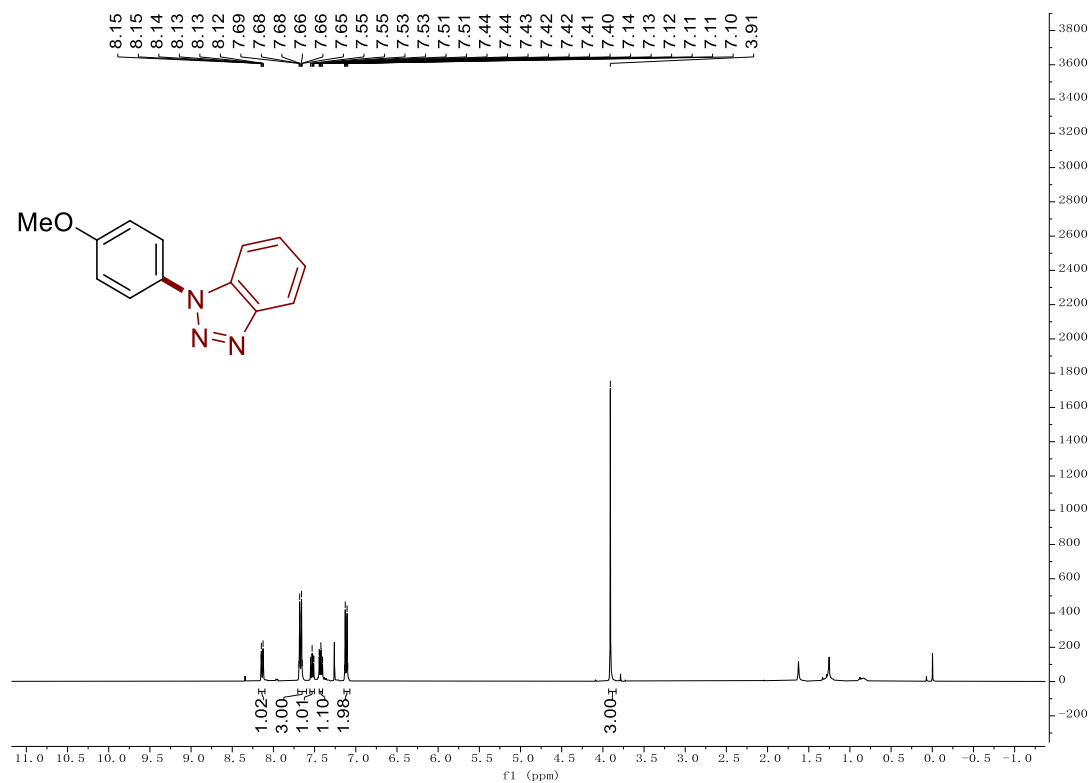
¹H NMR Spectrum of 4h (400 MHz, CDCl₃)



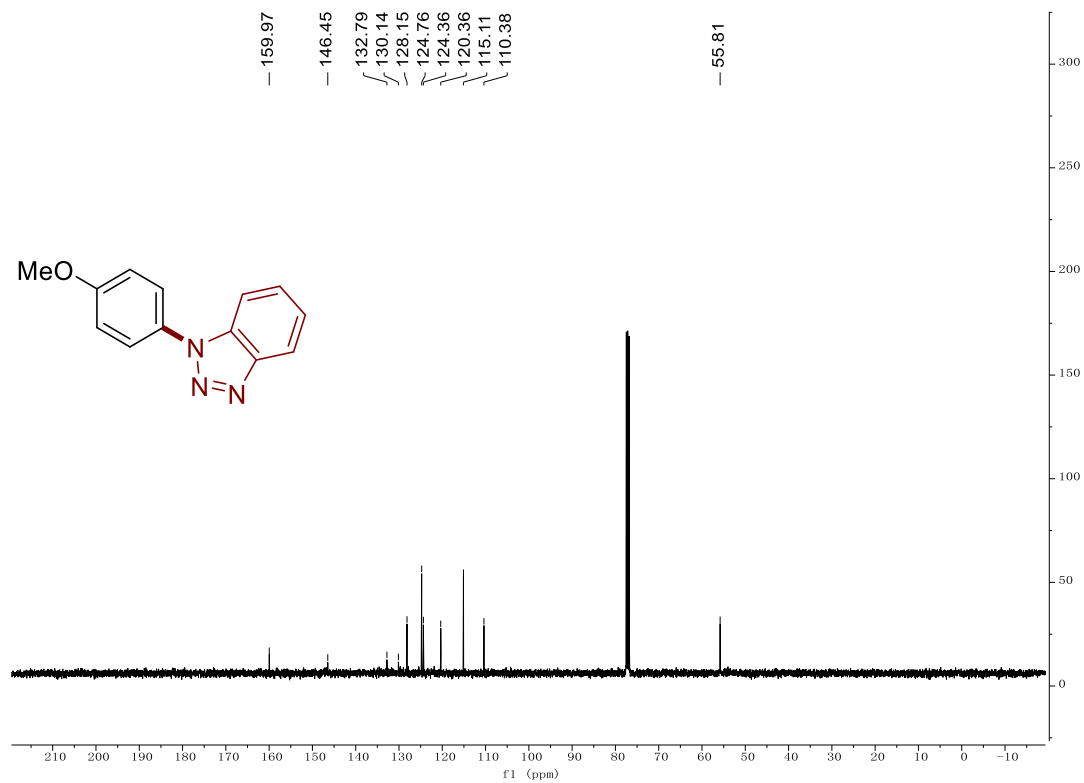
¹³C NMR Spectrum of 4h (400 MHz, CDCl₃)



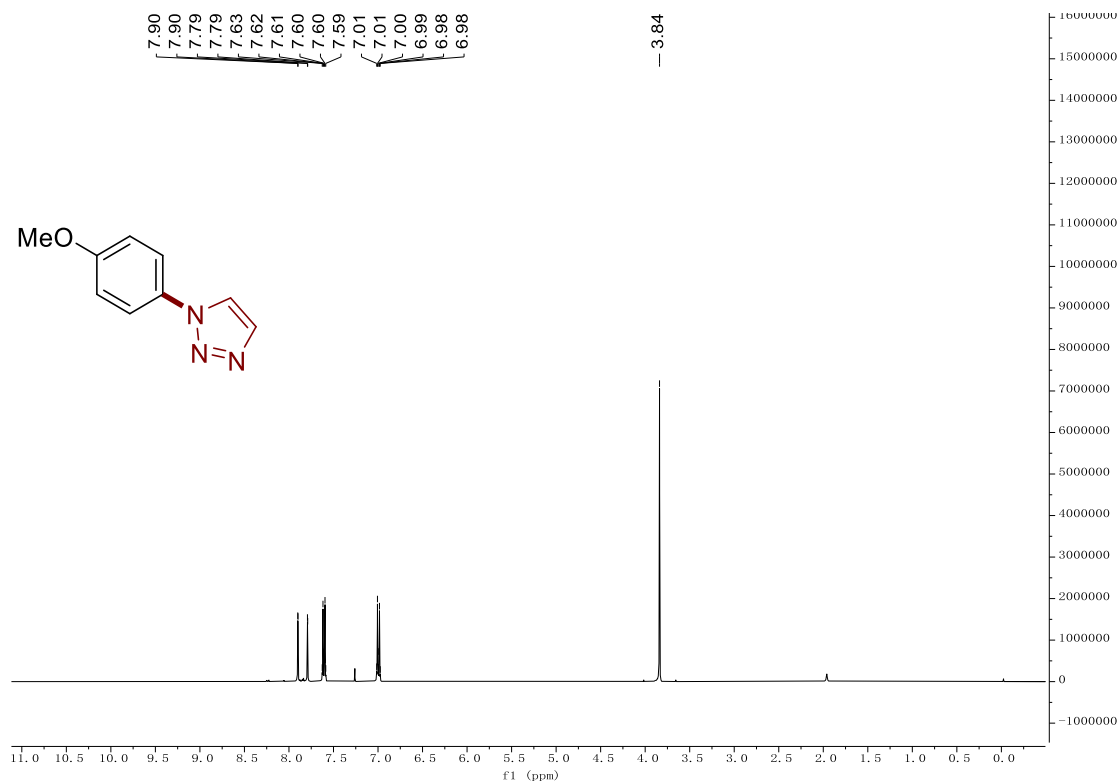
¹H NMR Spectrum of 4i (400 MHz, CDCl₃)



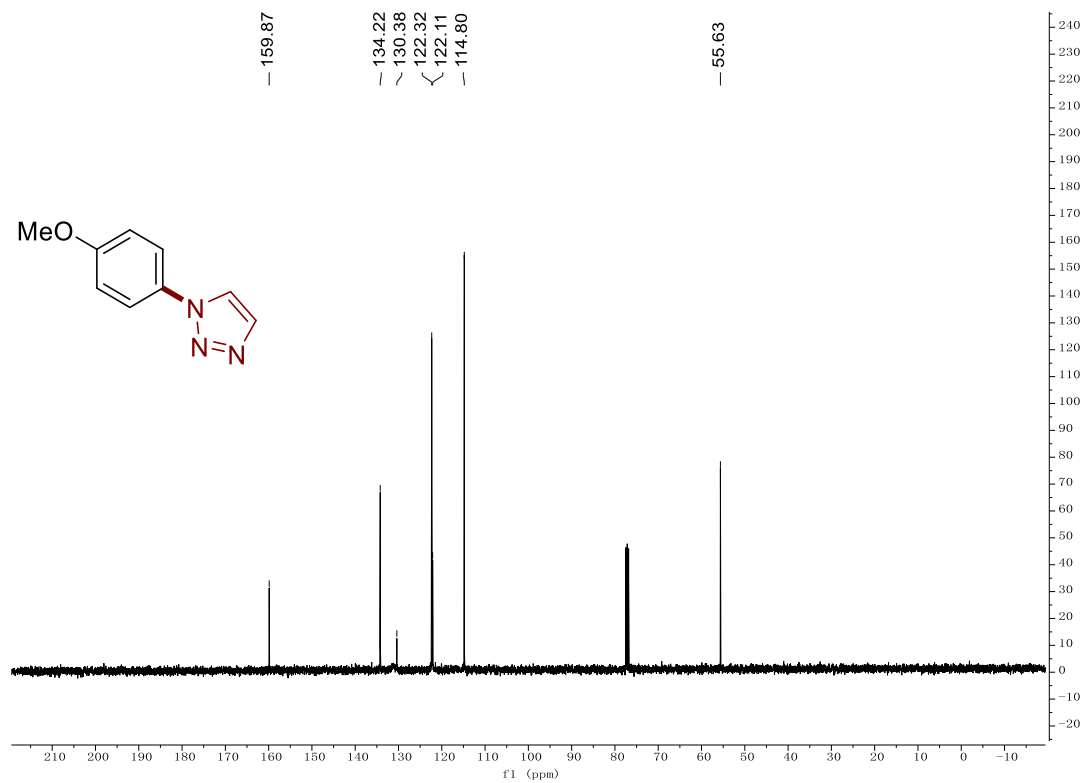
¹³C NMR Spectrum of 4i (400 MHz, CDCl₃)



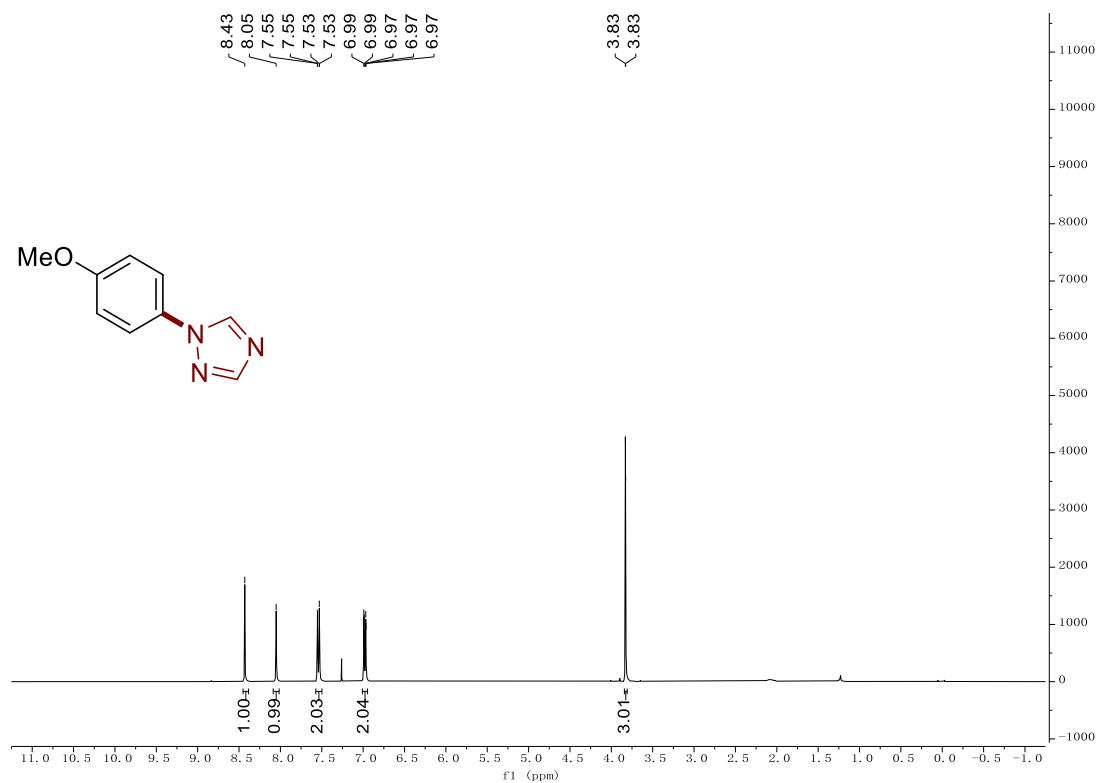
¹H NMR Spectrum of 4j (400 MHz, CDCl₃)



¹³C NMR Spectrum of 4j (400 MHz, CDCl₃)



¹H NMR Spectrum of 4k (400 MHz, CDCl₃)



¹³C NMR Spectrum of 4k(400 MHz, CDCl₃)

