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Supporting Information

An Organic Photoredox Catalyst Promoted Para-Selective C-H Amination of Aryl Oximes

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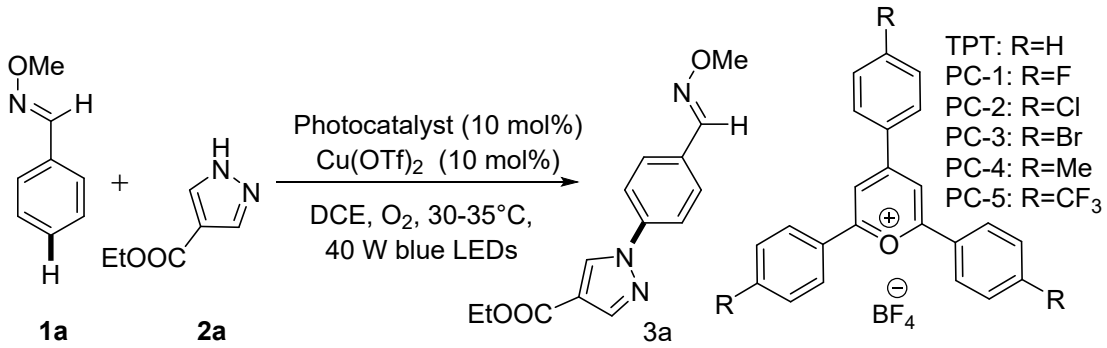
Supplementary Methods

Reagents: Unless otherwise noted, all reagents purchased from commercial suppliers and used without further purification. Column chromatography purifications performed using 200–300 and 300-400 mesh silica gel.

Instruments: NMR spectra 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, dt = doublet of triplets, brs = broad singlet, m = multiplet. HRMS analysis carried out using a Bruker micrOTOF–Q instrument or a TOF–MS instrument. The UV–visdiffuse reflection spectroscopy (DRS) were measured on a Shimadzu UV-3600 spectrophotometer at room temperature. LC-MS analysis carried out using a Agilent Technologies 1260 Znfinity. Cyclic voltammetry was performed on the Autolab 302N. The fluorescence quenching experiment was carried out on Hitachi F-2500 fluorescence spectrophotometer. The XPS test was operated on X-ray photoelectron spectrometer (EXCALAB 250 XI).

Optimization Studies

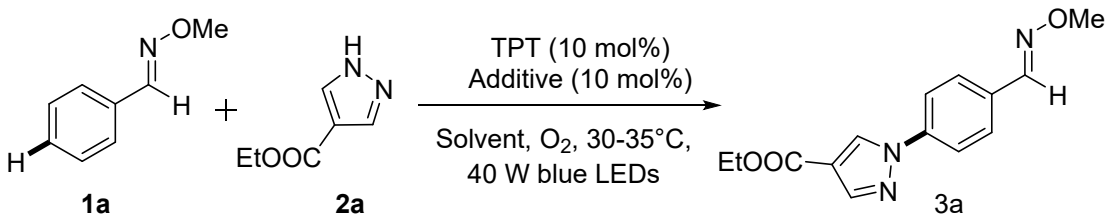
Table S-1: Influence of the Photocatalyst.[a]



Entry	Photocatalyst	Yield
1	**TPT**	**83 %**
2	Acr^{+}-Mes BF_4^-	62 %
3	Eosin Y	trace
4	*fac*-Ir(III)$(ppy)_3$	trace
5	4CZIPN	trace
6	Rose Bengal	trace
7	PC-1	57 %
8	PC-2	50 %
9	PC-3	43 %
10	PC-4	77 %
11	PC-5	44 %

[a] Reaction condition: 1a (0.1 mmol), 2a (0.2 mmol), Photocatalyst (10 mol %), $Cu(OTf)_2$ (10 mol %), DCE (1 mL) , O_2 , at 30-35°C under 40 W blue LEDs irradiation for 12 h. Isolated yields.

Table S-2: Influence of the Additive, Solvent. [a]



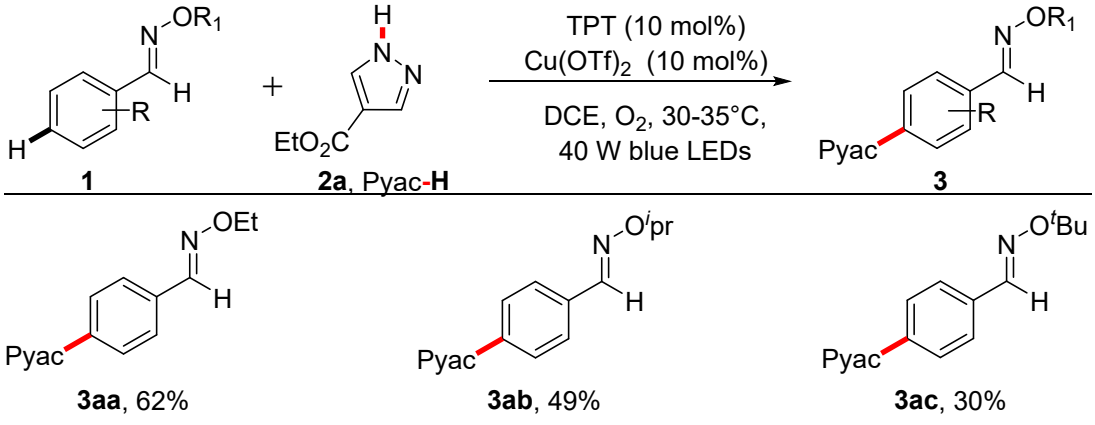
Entry	Additive	Solvent	Yield
1	$Cu(OAc)_2$	DCE	42 %
2	CuO	DCE	64 %
3	Cu_2Br	DCE	70 %
4	Cu_2O	DCE	45 %
5	$Fe(OTf)_3$	DCE	73 %
6	LiOTf	DCE	trace
7	$Cu(OTf)_2$	DCM	78 %
8	$Cu(OTf)_2$	MeCN	56 %
9	$Cu(OTf)_2$	Acetone	57 %
10	$Cu(OTf)_2$	DMF	0 %
11	$Cu(OTf)_2$	HFIP	0 %
12	none	DCE	0 %
13[b]	$Cu(OTf)_2$	DCE	0 %
14[c]	$Cu(OTf)_2$	DCE	0 %
15[d]	$Cu(OTf)_2$	DCE	31 %

[a] Reaction condition: 1a (0.1 mmol), 2a (0.2 mmol), TPT (10 mol %), Additive (10 mol %), Solvent (1 mL) , O_2 , at 30-35°C under 40 W blue LEDs irradiation for 12 h.

[b] No TPT. [c] Dark. [d] Ar. Isolated yields.

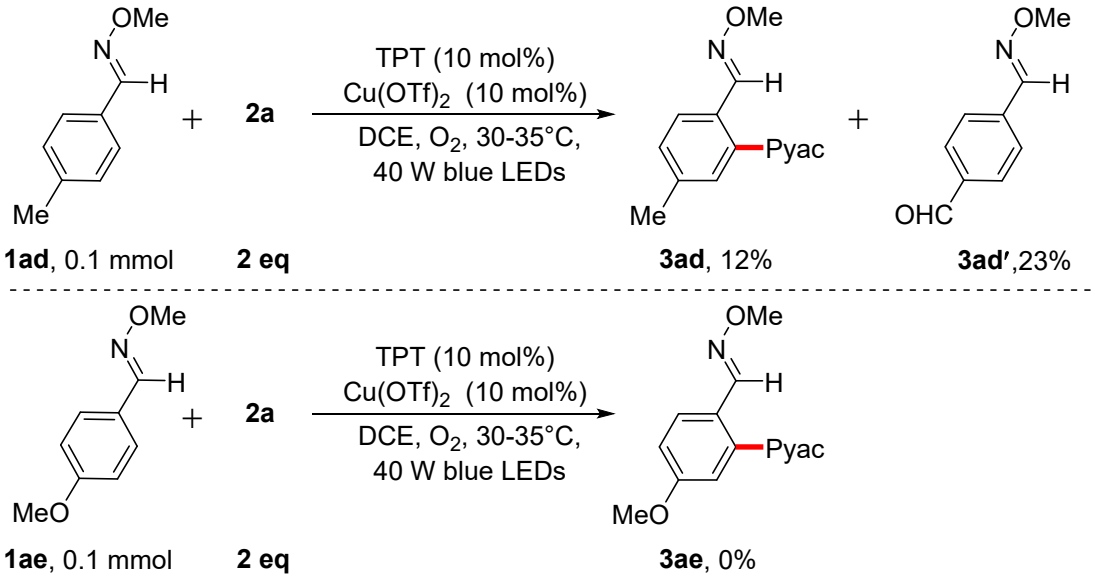
Other substrates

Scheme S1. Substrate scope of the oxime ether derivatives.[a]



[a]Reaction condition: **1** (0.1 mmol), **2a** (0.2 mmol), TPT (10 mol %), $Cu(OTf)_2$ (10 mol%), DCE (1 mL) , O_2, at 30-35°C under 40 W blue LEDs irradiation for 12 h. Isolated yields.

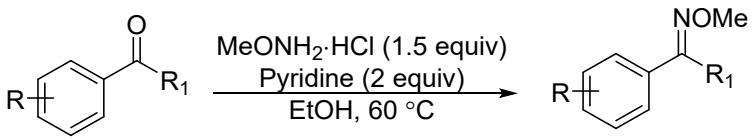
Scheme S2. Oxime protected 4-methylbenzaldehyde and 4-methoxybenzaldehyde as substrate.



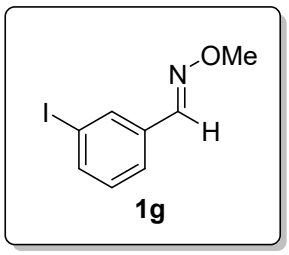
Preparation of substrates

2a-2o, 7 were purchased from commercial sources and used without further purification. **1a-1x** were prepared according to reported methods[1]. These compounds **1a-1f**, **1k-1q**, **1s-1u**, **1x** were known.

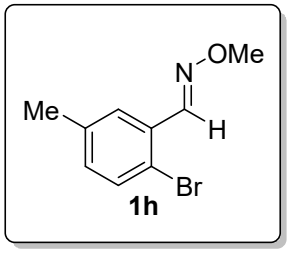
Preparation of *O*-methyl aryl oximes 1a-1x[1]



To a solution of Ketones (22.0 mmol) and pyridine (5.0 mL, 61.8 mmol) in EtOH (10 Ml) was added NH_2OMe•HCl (2.29 g, 33.0 mmol) in one portion and the reaction mixture was stirred at 60 °C for 6 h. The reaction was quenched by adding water and extracted twice with ethyl acetate. The combined extracts were washed with aqueous HCl and brine, and dried over $MgSO_4$. The solvents were removed under reduced pressure. Further recrystallization was conducted from ethyl acetate-hexane to provide *O*-methyl ketoximes. [1]

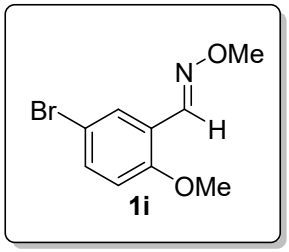


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 3.4 Hz, 2H), 7.68 (ddd, *J* = 7.9, 1.8, 1.1 Hz, 1H), 7.51 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 138.7, 135.6, 134.4, 130.4, 126.4, 94.6, 62.4. **HRMS** Calcd for C_8H_8INONa $[M+Na]^+$: 283.9548; Found:283.9541.



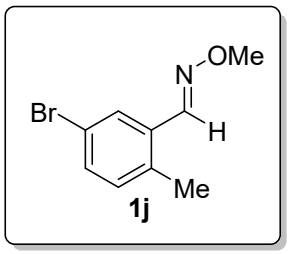
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.00 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 148.3, 137.7, 132.9, 132.2, 131.2, 128.0, 120.7, 62.3, 21.0. **HRMS** Calcd for $C_9H_{10}BrNONa$ $[M+Na]^+$: 249.9843; Found: 249.9842.



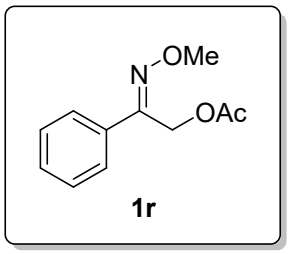
1i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 3.97 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 143.4, 133.4, 128.9, 122.7, 113.3, 112.8, 62.1, 55.8. **HRMS** Calcd for $C_9H_{10}BrNO_2Na$ $[M+Na]^+$: 265.9793; Found: 265.9797.



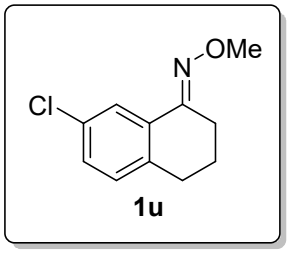
1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 3.99 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.1, 135.5, 132.4, 132.4, 129.2, 120.0, 62.3, 19.3. **HRMS** Calcd for $C_9H_{10}BrNONa$ $[M+Na]^+$: 249.9843; Found: 249.9847.



1r

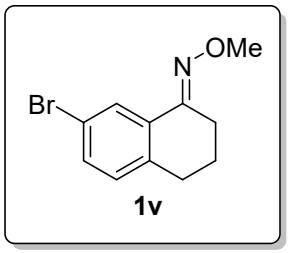
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.43 – 7.31 (m, 3H), 5.22 (s, 2H), 4.02 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 153.6, 133.5, 129.4, 128.5, 126.9, 62.6, 56.5, 20.7. **HRMS** Calcd for $C_{11}H_{13}NO_3Na$ $[M+Na]^+$: 230.0793; Found: 230.0787.



1u

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.3 Hz, 1H), 7.19 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 3.99 (s, 3H), 2.70 (t, *J* = 6.7 Hz, 4H), 1.82 (dt, *J* = 12.4, 6.5

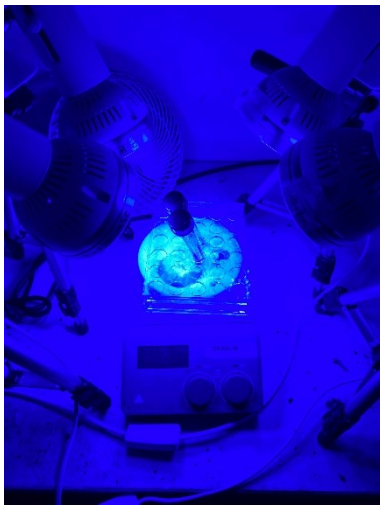
Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 137.9, 132.4, 132.3, 130.0, 129.0, 124.1, 62.3, 29.3, 24.0, 21.4. **HRMS** Calcd for $C_{11}H_{12}ClNONa$ $[M+Na]^+$: 232.0505; Found: 232.0511.

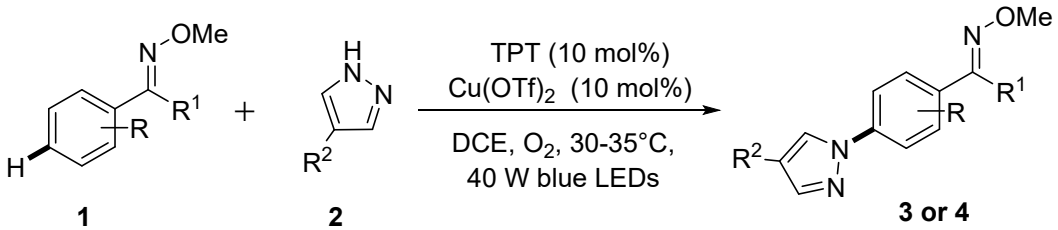


1v

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 2.1 Hz, 1H), 7.34 (dd, J = 8.1, 2.2 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 3.99 (s, 3H), 2.69 (q, J = 6.4 Hz, 4H), 1.82 (p, J = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 138.3, 132.8, 131.8, 130.3, 127.1, 120.3, 62.3, 29.4, 24.0, 21.3. **HRMS** Calcd for $C_{11}H_{12}BrNONa$ $[M+Na]^+$: 276.0000; Found: 276.0003.

Procedures for preparation 3 and **4.**

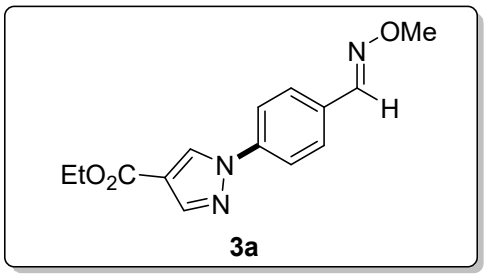




1 **2** **3 or 4**

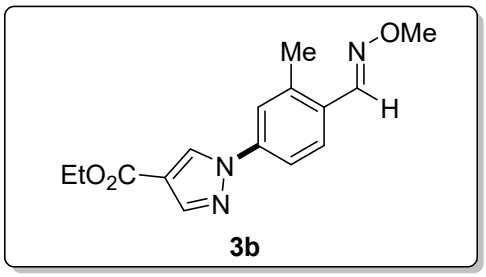
General Procedure for para C-H Amination of Aryl Oximes : A mixture of 1 (0.1 mmol, 1.0 eq), Pyrazole 2 (0.2 mmol, 2.0 eq), TPT (4.0 mg, 10 mol%), $Cu(OTf)_2$ (3.6 mg, 10 mol%) and DCE (1 ml) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 12 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.



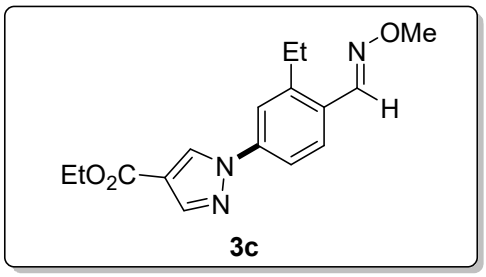
3a

Yellow solid, isolated yield: 22.6 mg, 83%. Mp: 102-104℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.10 (s, 1H), 8.07 (s, 1H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 147.3, 142.4, 140.0, 131.4, 129.9, 128.2, 119.5, 117.3, 62.2, 60.5, 14.4. **HRMS** Calcd for $C_{14}H_{15}N_3O_3Na$ $[M+Na]^+$: 296.1011; Found: 296.1010.



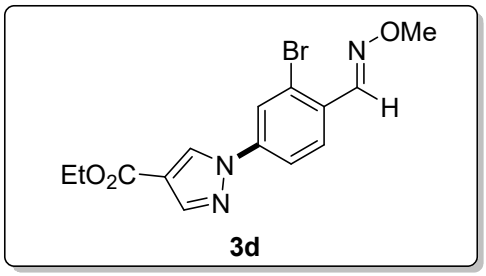
3b

Yellow solid, isolated yield: 19.8 mg, 69%. Mp: 81-83℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.30 (s, 1H), 8.08 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 2.46 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 146.3, 142.3, 139.7, 138.4, 129.9, 129.6, 127.9, 121.3, 117.1, 116.8, 62.1, 60.5, 19.9, 14.4. **HRMS** Calcd for $C_{15}H_{17}N_3O_3Na$ $[M+Na]^+$: 310.1168; Found: 310.1169.



3c

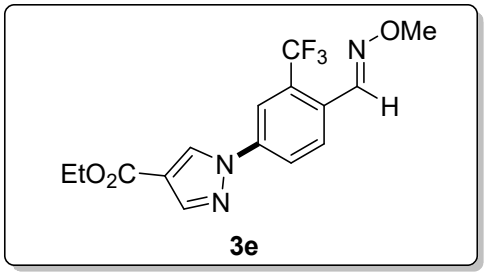
Yellow solid, isolated yield: 21.1 mg, 70%. Mp: 65-66℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.31 (s, 1H), 8.08 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 145.9, 144.7, 142.4, 140.0, 129.9, 129.0, 128.1, 120.0, 117.2, 117.0, 62.2, 60.6, 26.4, 15.6, 14.5. **HRMS** Calcd for $C_{16}H_{20}N_3O_3$ $[M+H]^+$: 302.1505; Found: 302.1496.



3d

White solid, isolated yield: 17.6 mg, 50%. Mp: 151-152℃

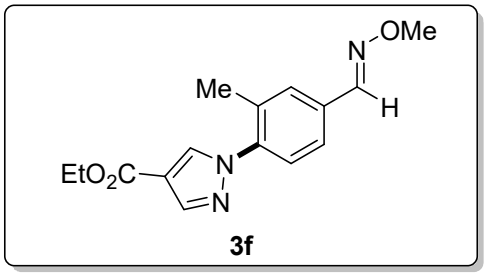
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.09 (s, 1H), 7.98 (d, *J* = 2.3 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.63 (dd, *J* = 8.7, 1.7 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 146.8, 142.7, 140.5, 130.5, 129.9, 128.3, 124.4, 123.6, 118.0, 117.7, 62.5, 60.7, 14.4. **HRMS** Calcd for $C_{14}H_{14}BrN_3O_3Na$ $[M+Na]^+$: 374.0116; Found: 374.0124.



3e

White solid, isolated yield: 19.1 mg, 56%. Mp: 155-157℃

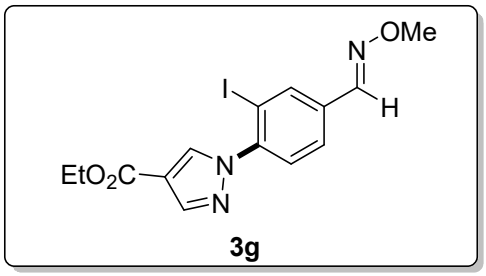
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.40 (q, *J* = 2.3 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.12 (s, 1H), 8.07 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 144.1 (q, *J* = 1.8 Hz), 143.0, 139.8, 130.2(C-F $^2J_{C\text{-}F}$ = 31.5 Hz), 123.0, 129.9(C-F $^2J_{C\text{-}F}$ = 31.5 Hz), 129.5 (C-F $^2J_{C\text{-}F}$ = 31.5 Hz), 129.3 (d, *J* = 1.5 Hz), 129.2(C-F $^2J_{C\text{-}F}$ = 31.5 Hz), 129.0, 127.5(C-F $^1J_{C\text{-}F}$ = 272.7 Hz), 124.8(C-F $^1J_{C\text{-}F}$ = 272.7 Hz), 122.1, 122.0(C-F $^1J_{C\text{-}F}$ = 272.7 Hz), 119.3(C-F $^1J_{C\text{-}F}$ = 272.7 Hz), 118.0, 116.9 (q, *J* = 5.9 Hz), 62.7, 60.8, 14.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.81 (d, *J* = 1.9 Hz). **HRMS** Calcd for $C_{15}H_{14}F_3N_3O_3Na$ $[M+Na]^+$: 364.0885; Found: 364.0881.



3f

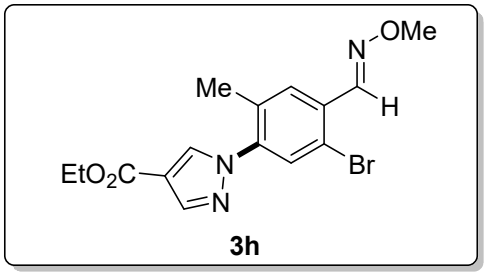
White solid, isolated yield: 24.7 mg, 86%. Mp: 83-84℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 4.1 Hz, 2H), 8.06 (s, 1H), 7.56 (s, 1H), 7.50 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.28 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 147.4, 141.8, 139.9, 133.9, 133.8, 132.9, 129.8, 126.2, 125.4, 116.2, 62.2, 60.4, 18.2, 14.4. **HRMS** Calcd for $C_{15}H_{17}N_3O_3Na$ $[M+Na]^+$: 310.1168; Found: 310.1164.



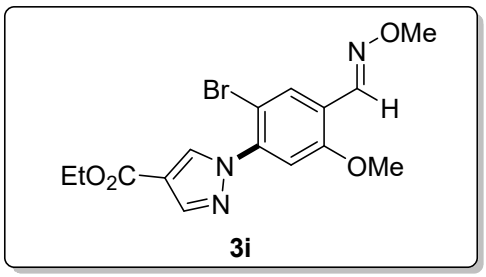
3g

Yellow solid, isolated yield: 16.0 mg, 40%. Mp: 93-94℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 8.12 (s, 1H), 8.00 (s, 1H), 7.65 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 0H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 145.6, 143.1, 142.2, 138.2, 134.8, 134.5, 127.9, 127.5, 116.5, 93.9, 62.5, 60.5, 14.4. **HRMS** Calcd for $C_{14}H_{14}IN_3O_3Na$ $[M+Na]^+$: 421.9978; Found: 421.9970.



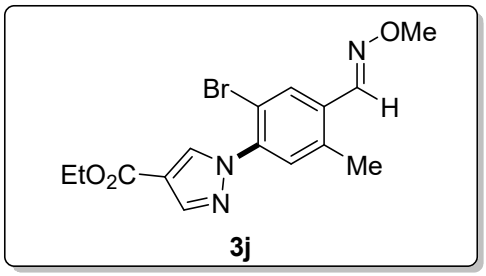
3h

Yellow solid, isolated yield: 25.2 mg, 69%. Mp: 96-98℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.09 (d, *J* = 5.3 Hz, 2H), 7.82 (s, 1H), 7.55 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 2.24 (d, *J* = 0.9 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 146.9, 142.2, 140.6, 133.8, 132.8, 131.9, 130.0, 129.9, 120.7, 116.6, 62.5, 60.6, 18.1, 14.5. **HRMS** Calcd for $C_{15}H_{16}BrN_3O_3Na$ $[M+Na]^+$: 388.0273; Found: 388.0265.



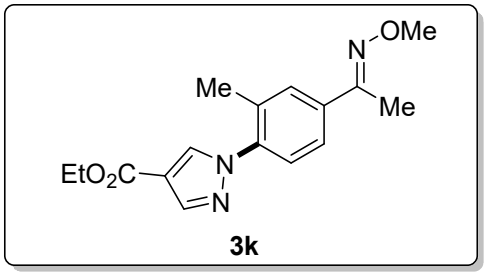
3i

Yellow solid, isolated yield: 19.8 mg, 52%. Mp: 132-133℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.01 (s, 1H), 7.43 (d, *J* = 2.8 Hz, 1H), 7.37 (s, 1H), 7.24 (d, *J* = 2.8 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 13.9 Hz, 7H), 1.36 (t, *J* = 7.1 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 160.6, 143.5, 142.4, 136.4, 133.1, 130.9, 123.0, 120.6, 116.6, 109.4, 62.6, 60.6, 56.2, 14.5. **HRMS** Calcd for $C_{15}H_{16}BrN_3O_4Na$ $[M+Na]^+$: 404.0222; Found: 404.0225.



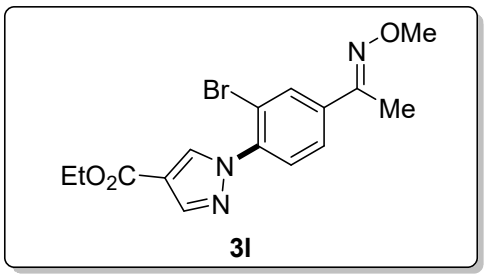
3j

White solid, isolated yield: 20.1 mg, 55%. Mp: 100-101℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.24 (s, 1H), 8.10 (s, 1H), 8.06 (s, 1H), 7.36 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.38 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 144.9, 142.2, 139.1, 137.2, 134.7, 132.6, 131.5, 129.9, 116.4, 115.1, 62.5, 60.6, 19.2, 14.5. **HRMS** Calcd for $C_{15}H_{17}BrN_3O_3$ $[M+H]^+$: 366.0453; Found: 366.0456.



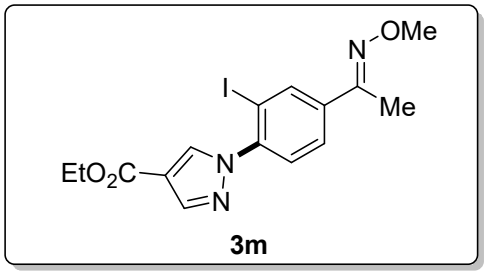
3k

Yellow liquid, isolated yield: 27.1 mg, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.08 (s, 1H), 7.63 (s, 1H), 7.56 (dd, *J* = 8.2, 2.7 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 153.7, 141.9, 139.6, 137.4, 134.0, 133.6, 129.1, 126.0, 124.6, 116.2, 62.2, 60.5, 18.4, 14.5, 12.7. **HRMS** Calcd for $C_{16}H_{19}N_3O_3Na$ $[M+Na]^+$: 324.1324; Found: 324.1327.



3l

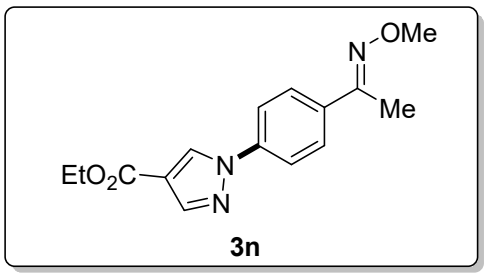
Yellow solid, isolated yield: 26.6 mg, 73%. Mp: 121-123℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.12 (s, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 2.22 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 152.1, 142.2, 139.2, 138.8, 134.8, 131.3, 127.9, 125.9, 118.32, 116.5, 62.5, 60.6, 14.5, 12.4. **HRMS** Calcd for $C_{15}H_{16}BrN_3O_3Na$ $[M+Na]^+$: 388.0273; Found: 388.0278.



3m

Yellow liquid, isolated yield: 20.1 mg, 50%.

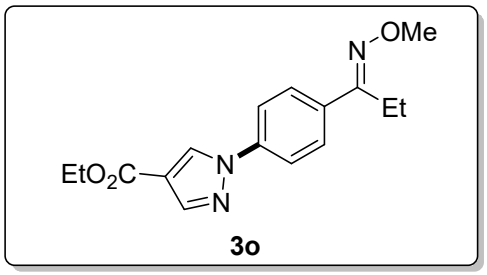
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.9 Hz, 1H), 8.20 (s, 1H), 8.12 (s, 1H), 7.72 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 2.21 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 152.0, 142.8, 142.2, 139.2, 137.7, 134.6, 127.6, 126.7, 116.5, 93.8, 62.5, 60.6, 14.5, 12.5. **HRMS** Calcd for $C_{15}H_{16}IN_3O_3Na$ $[M+Na]^+$: 436.0314; Found: 436.0317.



3n

Yellow solid, isolated yield: 16.6 mg, 58%. Mp: 110-112℃.

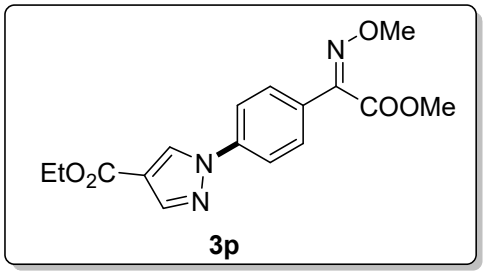
^{1}H NMR (400 MHz, $CDCl_3$ δ 8.42 (s, 1H), 8.10 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 2.24 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 153.5, 142.5, 139.8, 135.9, 130.0, 127.4, 119.4, 117.3, 62.2, 60.6, 14.5, 12.6. **HRMS** Calcd for $C_{15}H_{17}N_3O_3Na$ $[M+Na]^+$: 310.1168; Found: 310.1165.



3o

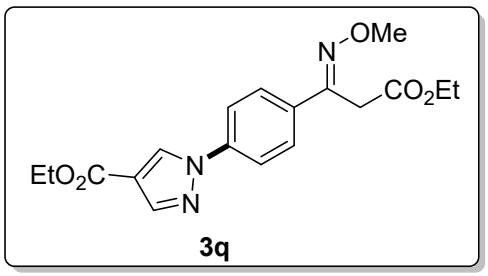
White solid, isolated yield: 15.1 mg, 50%. Mp: 109-112℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.10 (s, 1H), 7.76 (d, *J* = 9.1 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 158.6, 142.5, 139.7, 134.9, 130.0, 127.6, 119.5, 117.3, 62.2, 60.6, 19.9, 14.5, 11.2. **HRMS** Calcd for $C_{16}H_{20}N_3O_3$ $[M+H]^+$: 302.1505; Found: 302.1491.



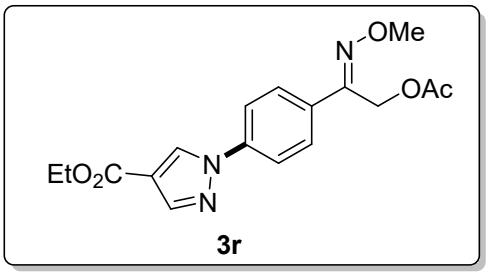
3p

White solid, isolated yield: 27.1 mg, 82%. Mp: 116-119℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.10 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 3H), 3.91 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 162.8, 148.0, 142.6, 134.0, 131.0, 130.0, 128.4, 118.9, 117.5, 64.0, 60.7, 53.2, 14.5. **HRMS** Calcd for $C_{16}H_{17}N_3O_5Na$ $[M+Na]^+$: 354.1066; Found: 354.1063.



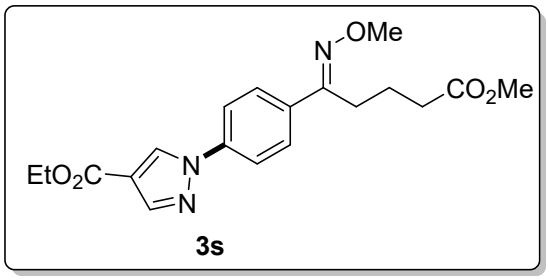
3q

Yellow solid, isolated yield: 26.9 mg, 75%. Mp: 105-107℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.09 (s, 1H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 3.77 (s, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 162.9, 150.3, 142.6, 140.0, 134.6, 130.1, 127.6, 119.5, 117.4, 62.6, 61.4, 60.7, 33.1, 14.5, 14.2. **HRMS** Calcd for $C_{18}H_{21}N_3O_5Na$ $[M+Na]^+$: 382.1379; Found: 382.1375.



3r

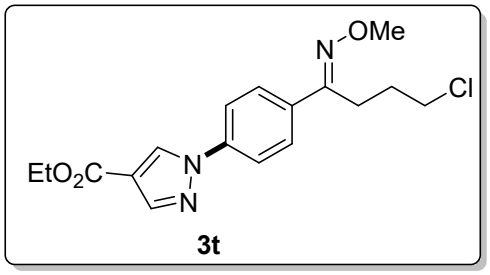
Yellow solid, isolated yield: 26.9 mg, 78%. Mp: 117-119℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.09 (s, 1H), 7.71 (s, 4H), 5.22 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 1.99 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 162.8, 152.5, 142.5, 134.0, 132.7, 130.0, 128.3, 119.3, 117.4, 62.8, 60.6, 56.3, 20.8, 14.5. **HRMS** Calcd for $C_{17}H_{19}N_3O_5Na$ $[M+Na]^+$: 368.1222; Found: 368.1218.



3s

Yellow solid, isolated yield: 22.8 mg, 61%. Mp: 90-91℃.

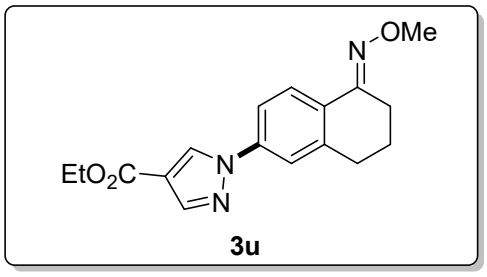
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.08 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 3.65 (s, 3H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.36 (t, *J* = 7.3 Hz, 2H), 1.86 (p, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 162.8, 156.3, 142.4, 139.7, 134.5, 129.9, 127.5, 119.4, 117.2, 62.1, 60.5, 51.6, 33.4, 25.4, 21.7, 14.4. **HRMS** Calcd for $C_{19}H_{23}N_3O_5Na$ $[M+Na]^+$: 396.1535; Found: 396.1548.



3t

White solid, isolated yield: 25.5 mg, 73%. Mp: 114-116℃.

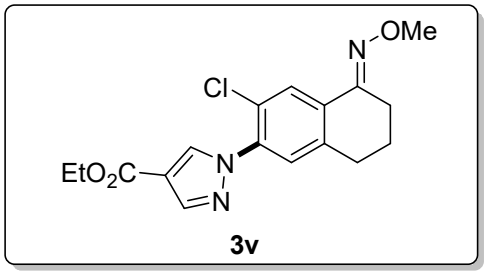
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.10 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.21 – 2.77 (m, 2H), 2.09 – 1.97 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 156.0, 142.5, 139.9, 134.6, 130.0, 127.5, 119.5, 117.3, 62.3, 60.6, 44.8, 29.6, 24.0, 14.5. **HRMS** Calcd for $C_{17}H_{20}ClN_3O_3Na$ $[M+Na]^+$: 372.1091; Found: 372.1087.



3u

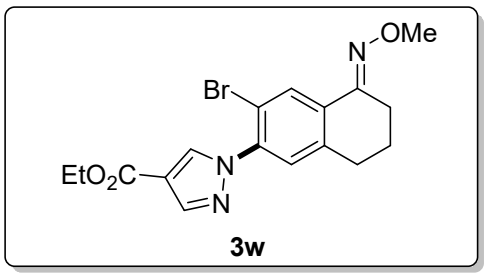
Yellow solid, isolated yield: 18.2 mg, 58%. Mp: 134-136℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.49 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.84 – 2.76 (m, 2H), 2.74 (t, *J* = 6.6 Hz, 2H), 1.87 (dt, *J* = 12.7, 6.5 Hz, 2H), 1.37 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 153.2, 142.4, 141.2, 139.4, 130.2, 130.0, 125.9, 119.4, 117.4, 117.2, 62.3, 60.6, 30.0, 24.2, 21.3, 14.5. **HRMS** Calcd for $C_{17}H_{19}N_3O_3Na$ $[M+Na]^+$: 336.1324; Found: 336.1330.



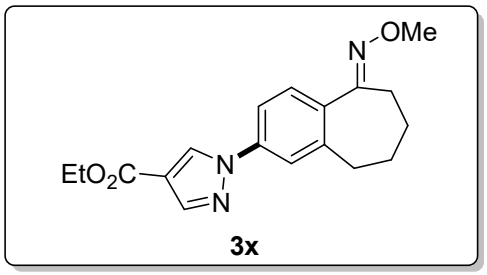
3v

Yellow solid, isolated yield: 17.7 mg, 51%. Mp: 110-112℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.14 (s, 1H), 8.10 (s, 1H), 7.39 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 2.73 (dt, *J* = 10.3, 6.3 Hz, 4H), 1.85 (p, *J* = 6.5 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 152.0, 142.2, 139.3, 136.9, 134.7, 132.7, 127.3, 126.4, 125.7, 116.5, 62.5, 60.6, 29.2, 23.9, 21.1, 14.5. **HRMS** Calcd for $C_{17}H_{18}ClN_3O_3Na$ $[M+Na]^+$: 370.0934; Found: 370.0930.



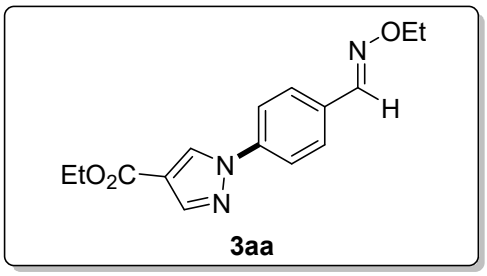
3w

Yellow solid, isolated yield: 24.6 mg, 63%. Mp: 138-141℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 4.3 Hz, 2H), 8.09 (s, 1H), 7.30 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.77 – 2.64 (m, 4H), 1.84 (dt, *J* = 12.3, 6.5 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 151.8, 142.0, 139.8, 138.5, 134.7, 133.0, 123.0, 127.8, 116.3, 115.5, 62.4, 60.5, 29.2, 23.8, 20.9, 14.5. **HRMS** Calcd for $C_{17}H_{19}BrN_3O_3$ $[M+H]^+$: 392.0610; Found: 392.0591.



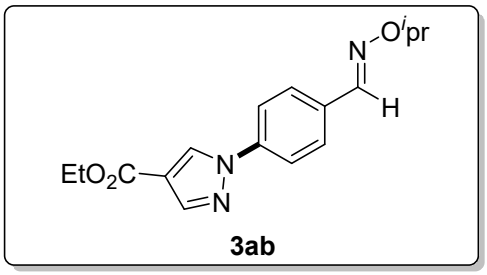
3x

Yellow solid, isolated yield: 15.4 mg, 47%. Mp: 125-127℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s,1H), 8.09 (s,1H), 7.53 (s, 1H), 7.52 (t, *J* = 1.3 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 2.80 (t, *J* = 6.7 Hz, 2H), 2.73 – 2.61 (m, 2H), 1.79 (p, *J* = 6.8 Hz, 2H), 1.61 (p, *J* = 6.4 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 161.0, 142.3, 141.4, 139.9, 135.5, 130.1, 129.1, 120.0, 117.3, 117.1, 62.1, 60.6, 32.0, 26.4, 25.9, 21.5, 14.5. **HRMS** Calcd for $C_{18}H_{21}N_3O_3Na$ $[M+Na]^+$: 350.1481; Found: 350.1479.



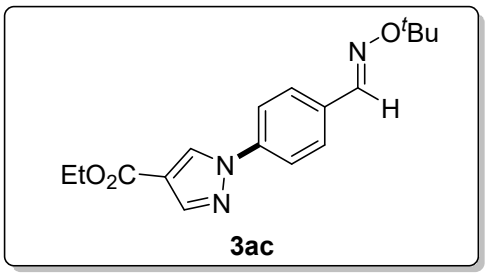
3aa

White solid, isolated yield: 17.8 mg, 62%. Mp: 100-102℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.09 (s, 1H), 8.06 (s, 1H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 147.1, 142.5, 140.1, 131.8, 130.0, 128.2, 119.6, 117.3, 70.11, 60.6, 14.7, 14.5. **HRMS** Calcd for $C_{15}H_{17}N_3O_3Na$ $[M+Na]^+$: 310.1168; Found: 310.1169.



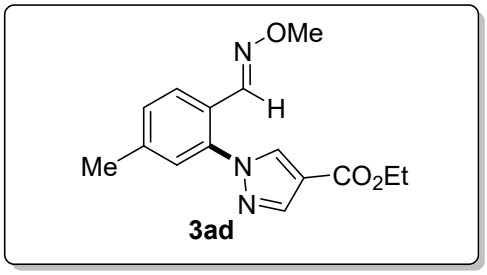
3ab

White solid, isolated yield: 14.8 mg, 49%. Mp: 101-102℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.09 (s, 1H), 8.05 (s, 1H), 7.71 (d, *J* = 9.2 Hz, 2H), 7.67 (d, *J* = 9.3 Hz, 2H), 4.46 (m, *J* = 6.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 6.3 Hz, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 146.6, 142.5, 140.0, 132.1, 130,0, 128.2, 119.6, 117.3, 76.2, 60.6, 21.8, 14.5. **HRMS** Calcd for $C_{16}H_{19}N_3O_3Na$ $[M+Na]^+$: 324.1324; Found: 324.1320.



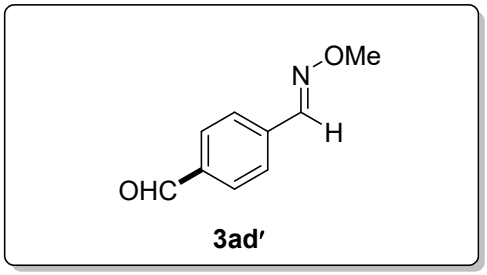
3ac

White solid, isolated yield: 9.5 mg, 30%. Mp: 95-97℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.10 (s, 1H), 8.05 (s, 1H), 7.70 (s, 4H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.37 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 146.0, 142.5, 139.8, 132.6, 130.0, 128.1, 119.6, 117.3, 79.7, 60.6, 27.7, 14.5. **HRMS** Calcd for $C_{17}H_{21}N_3O_3Na$ $[M+Na]^+$: 338.1481; Found: 338.1483.



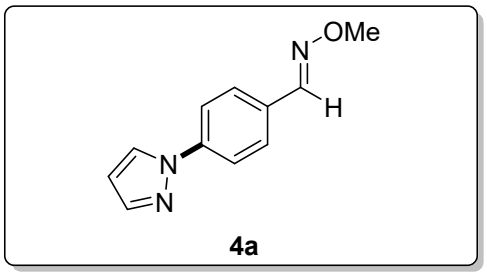
3ad

White solid, isolated yield: 3.4 mg, 12%. Mp: 115-117℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.93 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.20 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.41 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 144.6, 142.4, 141.2, 138.3, 134.5, 130.2, 127.2, 126.5, 125.0, 116.7, 62.3, 60.6, 21.3, 14.5. **HRMS** Calcd for $C_{15}H_{17}N_3O_3Na$ $[M+Na]^+$: 310.1168; Found: 310.1173.



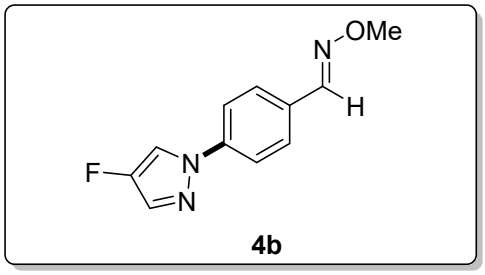
3ad′

White liquid, isolated yield: 3.8 mg, 23%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.09 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 4.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8, 147.4, 138.0, 137.0, 130.2, 127.6, 62.6. **HRMS** Calcd for $C_9H_9NO_2Na$ $[M+Na]^+$: 186.0531; Found: 186.0536.



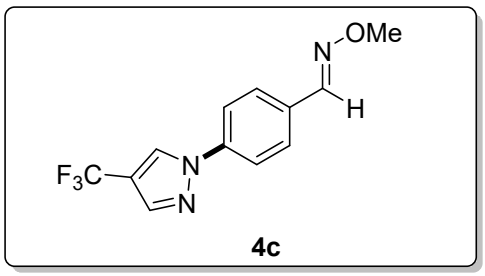
4a

Yellow solid, isolated yield: 12.7 mg, 63%. Mp: 50-51℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.94 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 141.6, 130.4, 128.3, 126.8, 119.2, 108.1, 62.2. **HRMS** Calcd for $C_{11}H_{12}N_3O$ $[M+H]^+$: 202.0980; Found: 202.0980.



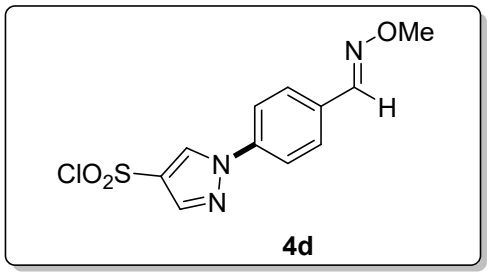
4b

White solid, isolated yield: 12.7 mg, 58%. Mp: 102-103℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.81 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.66 (d, *J* = 9.1 Hz, 2H), 7.62 (d, *J* = 9.1 Hz, 2H), 7.58 (dd, *J* = 4.3, 0.8 Hz, 1H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 150.2, 147.5, 140.9, 130.7, 129.1 (d, *J* = 13.9 Hz), 128.3, 118.7, 113.0 (d, *J* = 28.3 Hz), 62.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -174.27. **HRMS** Calcd for $C_{11}H_{11}FN_3O$ $[M+H]^+$: 220.0886; Found: 220.0891.



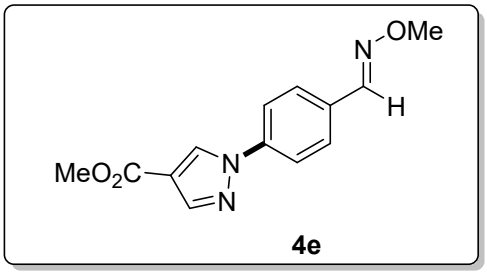
4c

Yellow solid, isolated yield: 17.5 mg, 65%. Mp: 51-52℃.
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 8.26 (s, 1H), 8.20 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.8, 139.6, 138.5 (q, *J* = 2.7 Hz), 131.0, 128.5 (q, *J* = 3.8 Hz), 128.1, 126.7 (C-F $^1J_{C\text{-}F}$ = 264.5 Hz), 124.0 (C-F $^1J_{C\text{-}F}$ = 264.5 Hz), 121.4 (C-F $^1J_{C\text{-}F}$ = 264.5 Hz), 119.30, 118.8 (C-F $^1J_{C\text{-}F}$ = 264.5 Hz), 114.7 (C-F $^2J_{C\text{-}F}$ = 37.3 Hz), 114.3 (C-F $^2J_{C\text{-}F}$ = 37.3 Hz), 113.9 (C-F $^2J_{C\text{-}F}$ = 37.3 Hz), 113.6 (C-F $^2J_{C\text{-}F}$ = 37.3 Hz), 61.7. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -55.16. **HRMS** Calcd for $C_{12}H_{11}F_3N_3O$ $[M+H]^+$: 270.0854; Found: 270.0849.



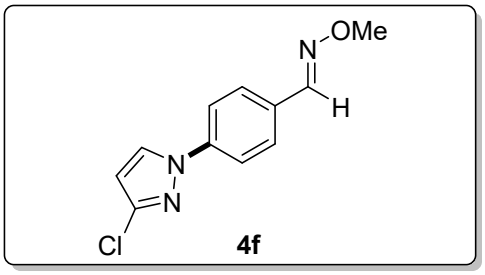
4d

White liquid,, isolated yield: 15.5 mg, 52%.
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 1H), 8.25 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 9.3 Hz, 3H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 148.0, 140.4, 139.4, 133.2, 129.8, 128.1, 126.12, 118.6, 61.7. **HRMS** Calcd for $C_{11}H_{11}ClSN_3O_3$ $[M+H]^+$: 300.0210; Found: 300.0215.



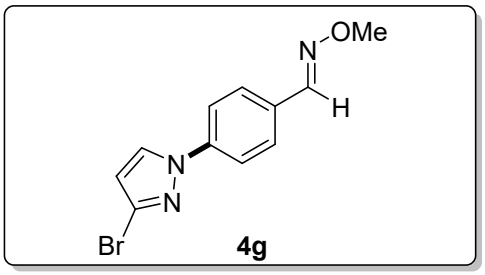
4e

Yellow solid, isolated yield: 20.2 mg, 78%. Mp: 104-106℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.09 (s, 1H), 8.06 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.67 (d, *J* = 8.9 Hz, 2H), 3.98 (s, 3H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 147.3, 142.5, 140.1, 131.6, 130.1, 128.3, 119.6, 117.0, 62.3, 51.7. **HRMS** Calcd for $C_{13}H_{13}N_3O_3Na$ $[M+Na]^+$: 282.0855; Found: 282.0857.



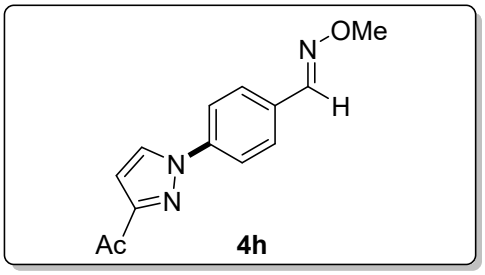
4f

White solid, isolated yield: 14.3 mg, 61%. Mp: 94-96℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 1.9 Hz, 1H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 141.0, 139.3, 132.2, 127.7, 127.3, 125.1, 107.1, 62.3. **HRMS** Calcd for $C_{11}H_{10}ClN_3Ona$ $[M+Na]^+$: 258.0410; Found: 258.0411.



4g

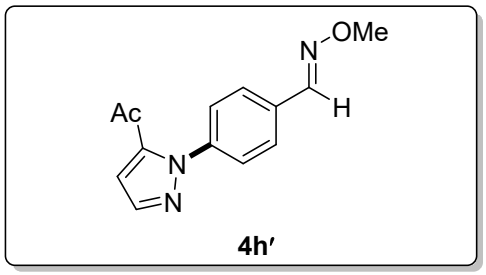
White solid, isolated yield: 19.8 mg, 71%. Mp: 110-112℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 1.9 Hz, 1H), 3.99 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 141.9, 139.9, 132.3, 127.6, 125.8, 112.7, 111.0, 62.3. **HRMS** Calcd for $C_{11}H_{10}ClN_3Ona$ $[M+Na]^+$: 301.9905; Found: 301.9899.



4h

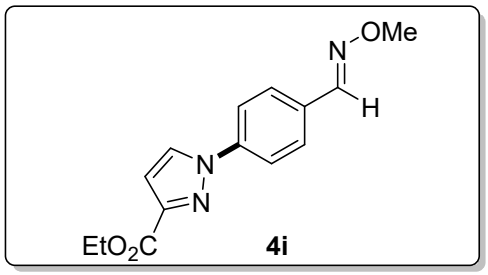
White solid, isolated yield: 8.9 mg, 36.5%. Mp: 139-143℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.95 (d, *J* = 2.6 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 2.6 Hz, 1H), 4.00 (s, 3H), 2.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 152.9, 147.4, 140.5, 131.6, 128.6, 128.3, 119.8, 108.4, 62.3, 26.7. **HRMS** Calcd for $C_{13}H_{13}N_3O_2Na$ $[M+Na]^+$: 266.0905; Found: 266.0903.



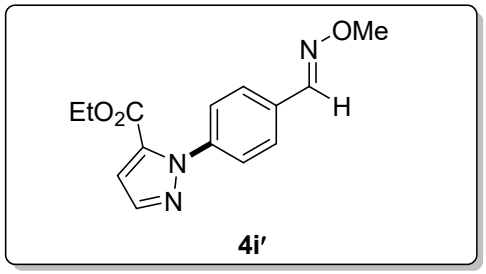
4h′

White solid, isolated yield: 8.9 mg, 36.5%. Mp: 125-127℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 2.0 Hz, 1H), 3.99 (s, 3H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.7, 147.6, 141.6, 134.0, 139.8, 132.5, 127.3, 126.2, 113.4, 62.3, 28.9. **HRMS** Calcd for $C_{13}H_{13}N_3O_2Na$ $[M+Na]^+$: 266.0905; Found: 266.0909.



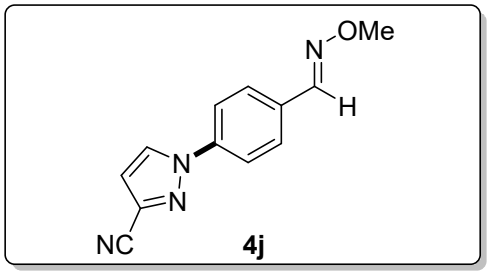
4i

White solid, isolated yield: 15.3 mg, 56%. Mp: 86-87℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 2.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 147.6, 141.3, 140.0, 133.6, 132.6, 127.2, 126.3, 113.0, 62.3, 61.4, 14.1. **HRMS** Calcd for $C_{14}H_{15}N_3O_3Na$ $[M+Na]^+$: 296.1011; Found: 296.1008.



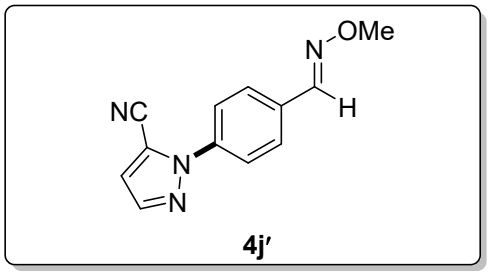
4i′

White solid, isolated yield: 7.6 mg, 28%. Mp: 81-82℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.95 (d, *J* = 2.6 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 2.5 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 147.4, 145.7, 140.5, 131.6, 128.4, 128.2, 120.2, 110.8, 62.3, 61.4, 14.5. **HRMS** Calcd for $C_{14}H_{15}N_3O_3Na$ $[M+Na]^+$: 296.1011; Found: 296.1013.



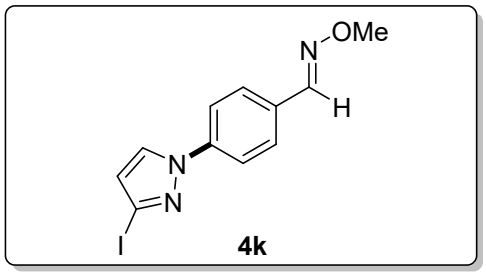
4j

White solid, isolated yield: 10.1 mg, 44.6%. Mp: 110-112℃.
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (s, 1H), 8.05 (d, J = 2.1 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 2.1 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.7, 141.5, 138.8, 132.5, 128.0, 123.4, 117.4, 113.6, 111.2, 61.9. **HRMS** Calcd for $C_{12}H_{11}N_4O$ $[M+H]^+$: 227.0933; Found: 227.0936.



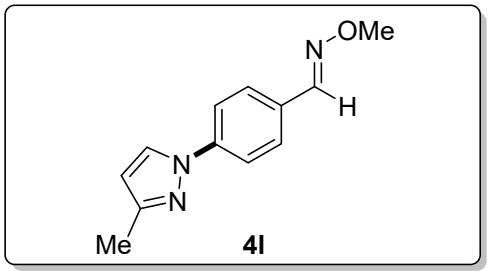
4j′

White solid, isolated yield: 1.7 mg, 7.4%. Mp: 104-106℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.00 (d, J = 2.6 Hz, 1H), 7.72 (s, 4H), 6.88 (d, J = 2.6 Hz, 1H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 139.8, 132.4, 128.4, 128.2, 126.8, 120.0, 113.8, 113.2, 62.4. **HRMS** Calcd for $C_{12}H_{11}N_4O$ $[M+H]^+$: 227.0933; Found: 227.0936.



4k

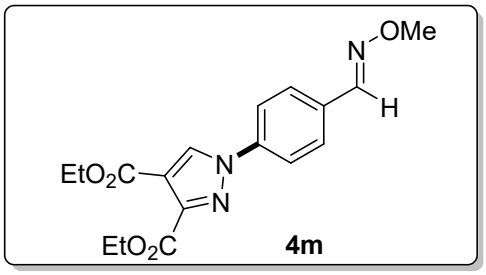
White solid, isolated yield: 20.9 mg, 64%. Mp: 112-114℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.75 – 7.66 (m, 3H), 7.56 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 1.9 Hz, 1H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 143.1, 141.1, 132.5, 127.5, 126.5, 118.0, 80.5, 62.4. **HRMS** Calcd for $C_{11}H_{11}IN_3O$ $[M+H]^+$: 327.9947; Found: 327.9952.



4l

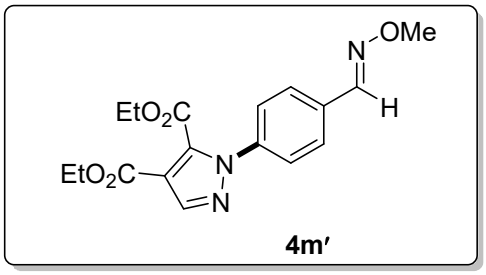
Yellow liquid, isolated yield: 8.2 mg, 38%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.58 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 3.99 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 141.0, 140.4, 138.9, 131.43, 127.8, 124.9, 107.6, 62.3, 12.7. **HRMS** Calcd for $C_{12}H_{13}N_3Ona$ $[M+Na]^+$: 238.0956; Found: 238.0949.



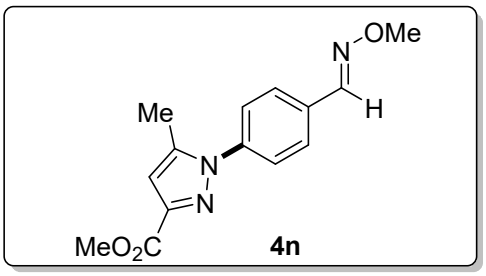
4m

White solid, isolated yield: 12.1 mg, 35%. Mp: 112-113℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.05 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 4.34 (p, *J* = 7.1 Hz, 4H), 3.99 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 161.0, 147.2, 141.7, 139.9, 137.0, 133.0, 127.9, 124.2, 116.2, 63.0, 62.4, 61.0, 14.4, 13.9. **HRMS** Calcd for $C_{17}H_{19}N_3O_5Na$ $[M+Na]^+$: 368.1222; Found: 368.1212.



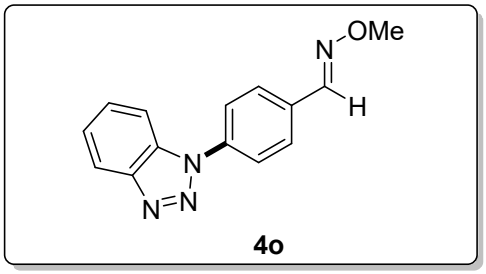
4m′

White solid, isolated yield: 12.1 mg, 35%. Mp: 102-103℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.07 (s, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.99 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.1, 161.6, 147.2, 145.6, 139.6, 132.3, 131.4, 128.3, 120.2, 116.9, 62.4, 62.1, 61.2, 14.4, 14.3. **HRMS** Calcd for $C_{17}H_{19}N_3O_5Na$ $[M+Na]^+$: 368.1222; Found: 368.1217.



4n

White solid, isolated yield: 15.3 mg, 56%. Mp: 121-123℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.81 (s, 1H), 3.98 (s, 3H), 3.78 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 149.5, 147.7, 141.2, 133.6, 132.3, 127.3, 126.2, 112.7, 62.3, 52.1, 13.5. **HRMS** Calcd for $C_{14}H_{16}N_3O_3$ $[M+H]^+$: 274.1192; Found: 274.1182.

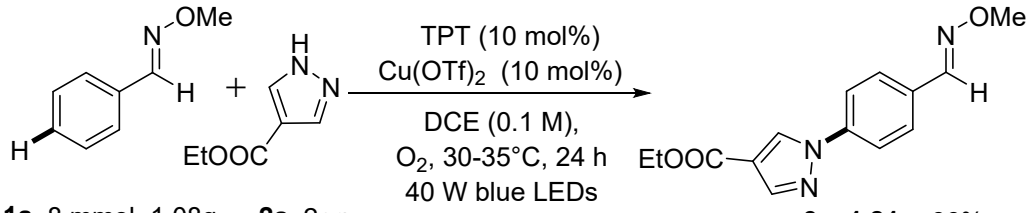


4o

White solid, isolated yield: 11.8 mg, 47%. Mp: 60-61℃.
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.38 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.01 – 7.94 (m, 3H), 7.91 (d, J = 8.7 Hz, 2H), 7.68 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H), 7.53 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.8, 145.9, 137.2, 132.1, 131.6, 128.9, 128.4, 124.9, 122.8, 119.8, 111.1, 61.8. **HRMS** Calcd for $C_{14}H_{12}N_4Ona$ $[M+Na]^+$: 275.0909; Found: 275.0901.

Application

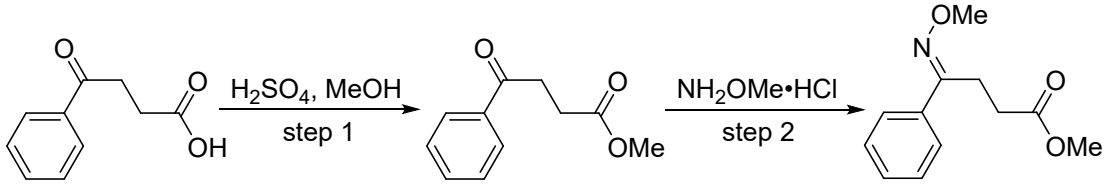
Gram scale reaction



1a, 8 mmol, 1.08g **2a**, 2eq **3a**, **1.81g**, 66%

A mixture of **1a** (8 mmol, 1.08g, 1.0 eq), **2a** (16 mmol, 2.24g, 2.0 eq), TPT (320 mg, 10 mol%), $Cu(OTf)_2$ (288 mg, 10 mol%) and DCE (80 ml) in a 250 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 24 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 = 10:1) to give the product **3a** (1.81g, 66%).

General procedures for preparation of 5.



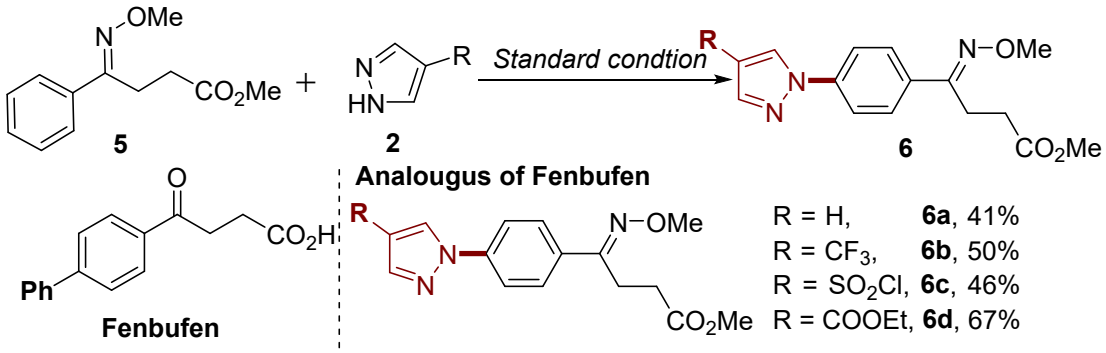
Fenbufen precursor **5sm** **5**

Step 1: To a well-stirred mixture of Fenbufen precursor (10 mmol), alcohol (11 mmol),

acetonitrile (20 mmol) and sulfuric acid (98%, 12 mmol, 0.7 mL) was added at room temperature. Slowly heated to 80-85 °C and maintained between 80-85°C for 16-18 h. The reaction mixture cooled and added to 20% sodium carbonate solution (100 mL). The reaction mass was extracted in CH_2Cl_2 (50 mL × 2). The combined organic layer was washed with water (100 mL), dried over sodium sulfate, and concentrated under reduced pressure to obtain corresponding ester **5sm** (97-99%) as the only product. **5sm** analytical data are consistent with the literature.[2]

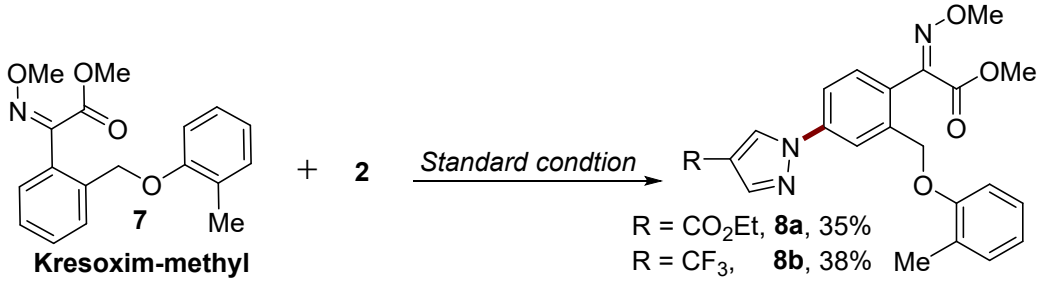
Step 2: To a solution of **5sm** (22.0 mmol) and pyridine (5.0 mL, 61.8 mmol) in EtOH (10 mL) was added NH_2OMe•HCl (2.29 g, 33.0 mmol) in one portion and the reaction mixture was stirred at 60 °C for 6 h. The reaction was quenched by adding water and extracted twice with ethyl acetate. The combined extracts were washed with aqueous HCl and brine, and dried over $MgSO_4$. The solvents were removed under reduced pressure. Further recrystallization was conducted from ethyl acetate-hexane to provide **5**. **5** analytical data are consistent with the literature. [3]

Synthesis of fenbufen precursor analogues.

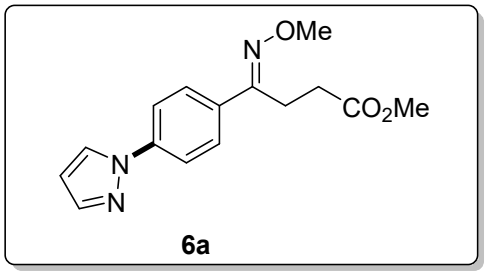


A mixture of **5** (0.2 mmol, 1.0 eq), Pyrazole 2 (0.4 mmol, 2.0 eq), TPT (8.0 mg, 10 mol%), $Cu(OTf)_2$ (7.2 mg, 10 mol%) and DCE (2 mL) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 12 h. After the 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 = 10:1) to give the product.

Synthesis of Kresoxim-methyl derivatives.

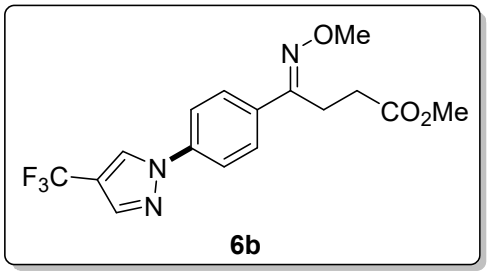


A mixture of **7** (0.2 mmol, 1.0 eq), Pyrazole 2 (0.4 mmol, 2.0 eq), TPT (8.0 mg, 10 mol%), $Cu(OTf)_2$ (7.2 mg, 10 mol%) and DCE (2 mL) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 18 h. After the 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) to give the product **8a-8b**.



Yellow liquid, isolated yield: 23.5 mg, 41%.

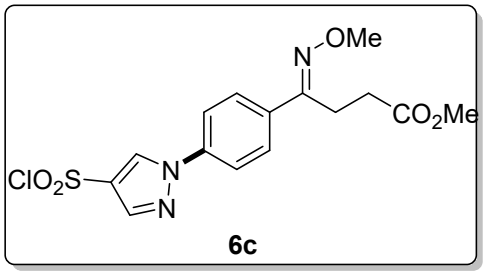
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.5 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.70 (d, *J* = 9.0 Hz, 2H), 6.47 (t, *J* = 2.1 Hz, 1H), 4.00 (s, 3H), 3.66 (s, 3H), 3.05 (t, *J* = 8.1 Hz, 2H), 2.58 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 155.9, 141.5, 140.8, 133.2, 127.5, 126.8, 119.0, 108.1, 62.3, 51.9, 30.7, 22.3. **HRMS** Calcd for $C_{15}H_{17}N_3O_3Na$ $[M+Na]^+$: 310.1168; Found: 310.1167.



Yellow liquid, isolated yield: 35.5 mg, 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.91 (s, 1H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 2H), 4.01 (s, 3H), 3.66 (s, 3H), 3.05 (t, *J* = 8.2 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 155.6, 139.8, 138.6 (q, *J* = 2.7 Hz), 134.7, 127.7, 126.5 (C-F $1J_{C\text{-}F}$ = 265.8 Hz), 126.3 (q, *J* = 3.8 Hz), 123.8 (C-F $1J_{C\text{-}F}$ = 265.8 Hz), 121.2(C-F $1J_{C\text{-}F}$ = 265.8 Hz), 119.6, 118.5(C-F $1J_{C\text{-}F}$ = 265.8 Hz), 116.5 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 116.1 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 115.7 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 115.3

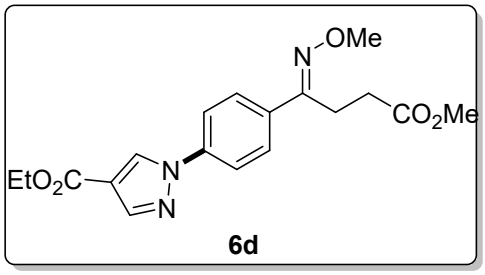
(C-F $2J_{C\text{-}F}$ = 38.5 Hz), 62.4, 51.9, 30.7, 22.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -56.8. **HRMS** Calcd for $C_{16}H_{16}F_3N_3O_3Na$ $[M+Na]^+$: 378.1041; Found: 378.1041.



6c

White liquid, isolated yield: 35.4 mg, 46%.

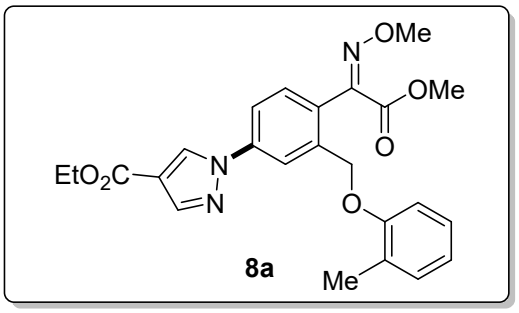
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.17 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 4.02 (s, 3H), 3.67 (s, 3H), 3.06 (t, *J* = 8.3 Hz, 2H), 2.60 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 155.4, 139.6, 138.8, 135.9, 129.3, 128.9, 127.9, 120.1, 62.6, 52.0, 30.6, 22.3. **HRMS** Calcd for $C_{15}H_{16}ClSN_3O_5Na$ $[M+Na]^+$: 408.0397; Found: 408.0395.



6d

White solid, isolated yield: 48.1 mg, 67%. Mp: 99-101℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.10 (s, 1H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.66 (s, 3H), 3.09 – 3.01 (m, 2H), 2.61 – 2.56 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 162.8, 155.7, 142.5, 139.9, 134.4, 130.0, 127.6, 119.5, 117.4, 62.4, 60.6, 51.9, 30.7, 22.3, 14.5. **HRMS** Calcd for $C_{18}H_{21}N_3O_5Na$ $[M+Na]^+$: 382.1379; Found: 382.1377.

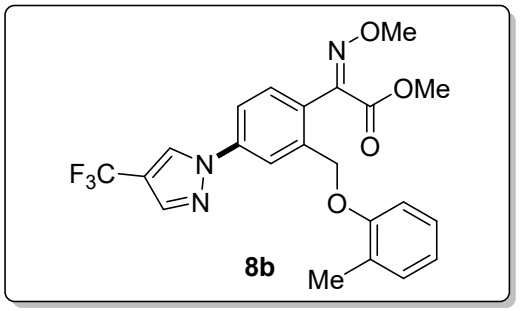


8a

White solid, isolated yield: 31.6 mg, 35%. Mp: 124-127℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (s, 1H), 8.07 (s, 1H), 7.74 (s, 1H), 7.65 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.47 (td, *J* = 7.5, 1.6 Hz, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 4.98 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.71 (s, 3H), 2.18 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.7, 162.2, 155.2, 148.9, 141.3, 134.9, 132.3, 130.7,

129.8, 129.4, 128.9, 128.2, 127.9, 127.3, 121.6, 117.6, 115.8, 111.8, 68.3, 63.3, 59.9, 52.5, 15.8, 14.3. **HRMS** Calcd for $C_{24}H_{25}N_3O_6Na$ $[M+Na]^+$: 474.1641; Found: 474.1652.



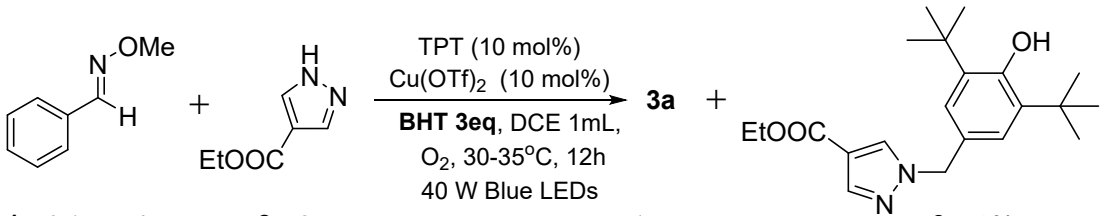
8b

Yellow liquid, isolated yield: 34.0 mg, 38%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.86 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.41 (td, J = 7.5, 1.5 Hz, 1H), 7.35 (dd, J = 8.7, 2.8 Hz, 1H), 7.22 (dd, J = 7.5, 1.5 Hz, 1H), 6.83 (d, J = 8.8 Hz, 1H), 5.01 (s, 2H), 4.04 (s, 3H), 3.84 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 156.2, 149.4, 137.9 (q, J = 2.7 Hz), 135.2, 132.8, 129.8, 129.2, 128.8, 128.7, 128.0, 127.7, 126.8 (C-F $1J_{C\text{-}F}$ = 266.2 Hz), 126.4 (q, J = 3.8 Hz), 124.0 (C-F $1J_{C\text{-}F}$ = 266.2 Hz), 122.9, 121.4 (C-F $1J_{C\text{-}F}$ = 266.2 Hz), 118.7 (C-F $1J_{C\text{-}F}$ = 266.2 Hz), 118.5, 115.6 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 115.3 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 114.9 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 114.5 (C-F $2J_{C\text{-}F}$ = 38.5 Hz), 111.8, 68.7, 64.0, 53.1, 16.5. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -54.8. **HRMS** Calcd for $C_{22}H_{20}F_3N_3O_4Na$ $[M+Na]^+$: 470.1304; Found: 470.1311.

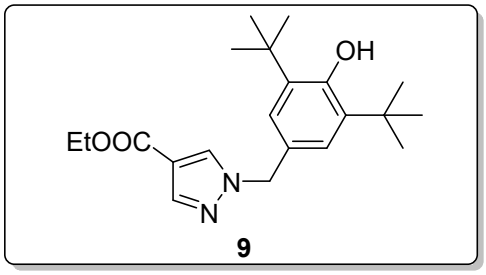
Control experiments

Free radical trapping experiment.



1a, 0.1 mmol **2a**, 2 eq trace **9**, 56%

A mixture of 1a (0.1 mmol, 1.0 eq), 2a (0.2 mmol, 2.0 eq), TPT (4.0 mg, 10 mol%), $Cu(OTf)_2$ (3.6 mg, 10 mol%), BHT (67.0 mg, 3.0 eq) and DCE (1 mL) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 12 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 = 10:1) to give the product **9**.



9

White solid, isolated yield: 20.1 mg, 56%. Mp: 132-136℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.82 (s, 1H), 7.07 (s, 2H), 5.27 (s, 1H), 5.20 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.42 (s, 18H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 154.2, 141.1, 136.6, 132.5, 125.9, 125.3, 115.4, 60.3, 57.0, 34.5, 30.3, 14.5. **HRMS** Calcd for $C_{21}H_{30}N_2O_3Na$ $[M+Na]^+$: 381.2154; Found: 381.2152.

Fluorescence Quenching Experiments

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 Acetone (0.00008 M)

Quencher: 36.2 mg of $Cu(OTf)_2$ dissolved in 25 mL Acetone (0.004 M)

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

13.5 mg of **1a** dissolved in 25 mL Acetone (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 DCE were added as the following table:

Entry	TPT	quenchers	Acetone	Total volume
1	1 ml	0 ml	3 ml	4 ml
2	1 ml	0.25 ml	2.75 ml	4 ml
3	1 ml	0.5 ml	2.5 ml	4 ml
4	1 ml	0.75 ml	2.25 ml	4 ml
5	1 ml	1 ml	2 ml	4 ml

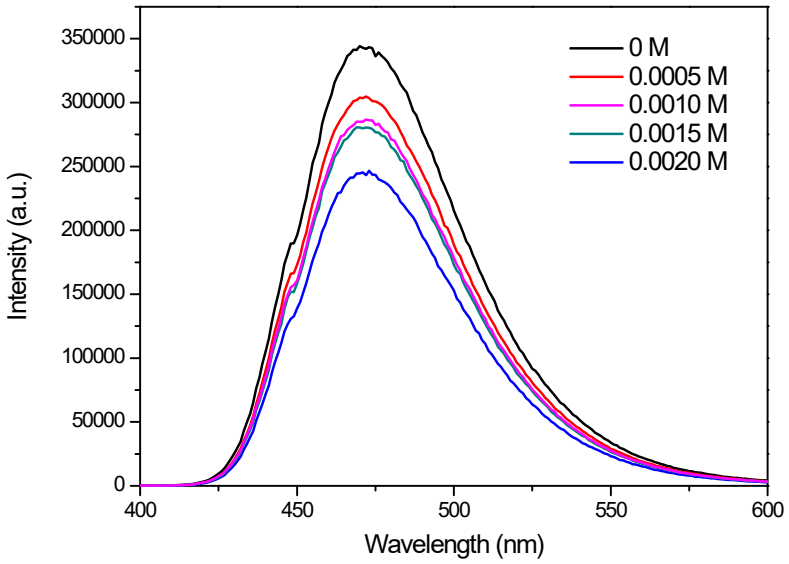


Figure S-1. Fluorescence quenching experiments with **2a**

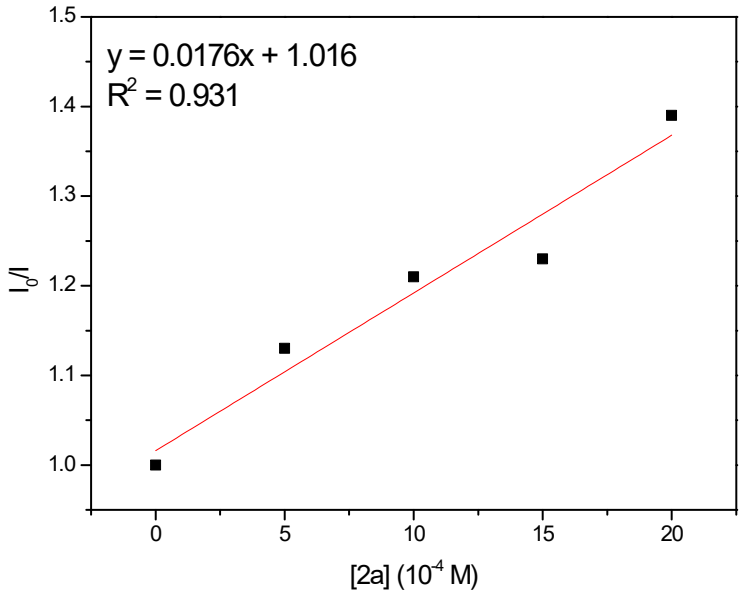


Figure S-2. Stern-Volmer plots of **2a**

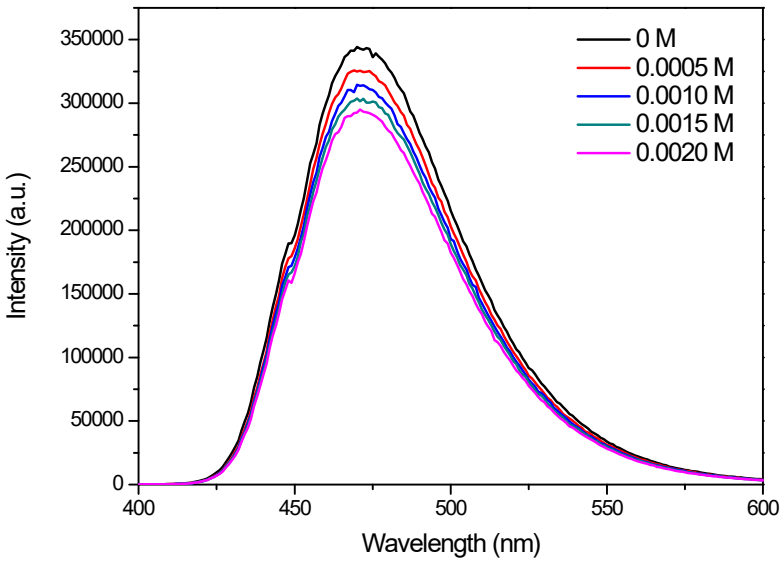


Figure S-3. Fluorescence quenching experiments with **1a**

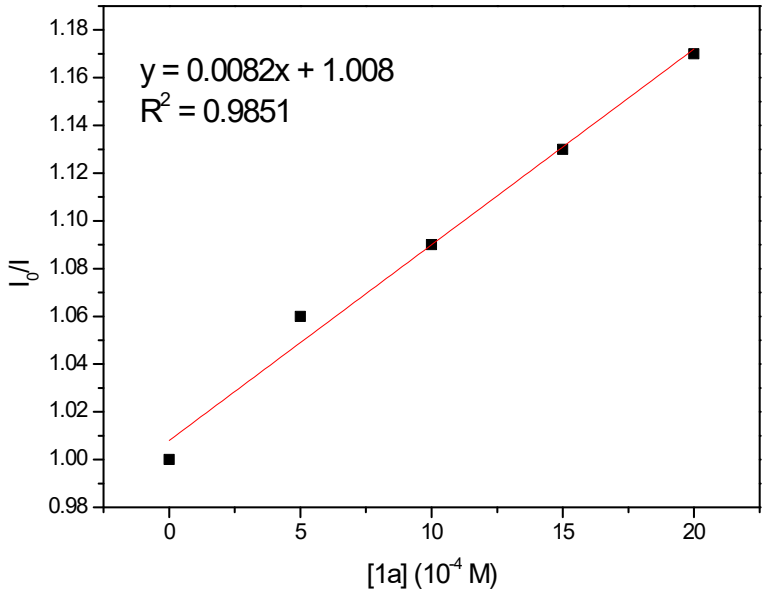


Figure S-4. Stern-Volmer plots of **1a**

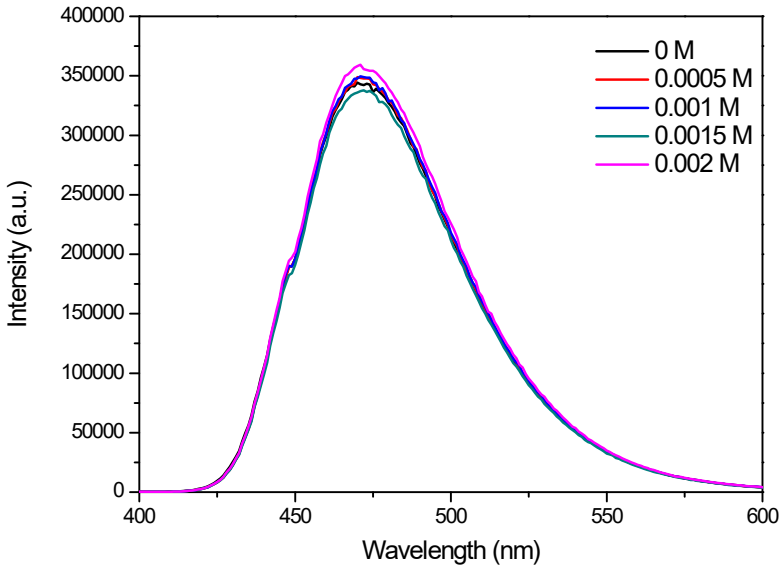


Figure S-5. Fluorescence quenching experiments with **$Cu(OTf)_2$**

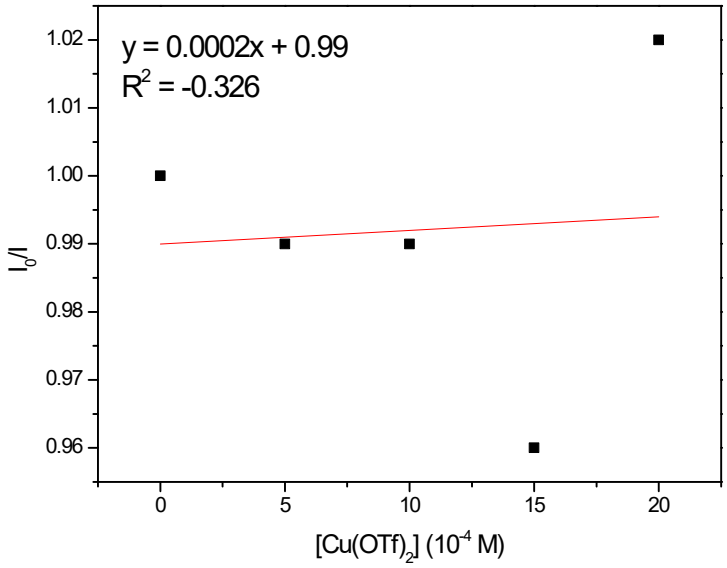


Figure S-6. Stern-Volmer plots of **$Cu(OTf)_2$**

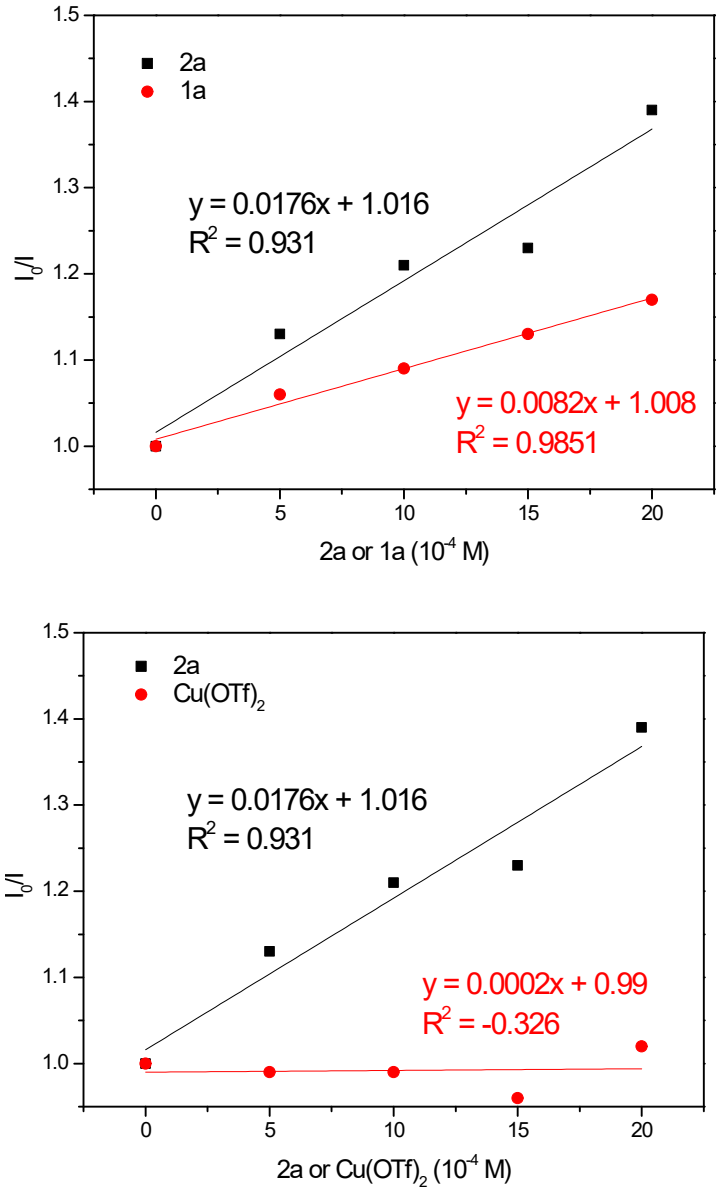


Figure S-7. Quenching efficiency of **2a**, **1a**, and $Cu(OTf)_2$

Inference: The results can clearly show that **2a** quench DCFS more effectively than that of **1a** and $Cu(OTf)_2$.

Quantum Yield Measurement

The measured method was designed according to a published procedure by Ackermann with slight modifications [4].

The solutions were prepared and stored in the dark:

Preparation of potassium ferrioxalate solution: 295 mg of solid potassium ferrioxalate, 140 µL H_2SO_4 were diluted with H_2O to a finale volume of 50 mL.

Preparation of buffer solution:

4.95 g NaOAc and 1 mL H_2SO_4 were diluted with H_2O to a finale volume of 100 mL. Using the same setup as for catalytic reactions 0.7 mL of the potassium ferrioxalate solution were irradiated for 20 sec. The sample solution was added to of 1.4 mL of the buffer solution containing 0.7 mg 1,10-phenanthroline. The solution was diluted with H_2O to a finale volume of 3.5 mL. Subsequently the absorbance of this solution was determined at 510 nm. The same procedure was followed for a nonirradiated sample.

Calculation Number of Photons:

Abs of Fe^{2+} (at 510 nm) = 3.629 (after irradiation of 20 sec)

Abs of Fe^{2+} (at 510 nm) = 0.053 (no irradiation)

ΔAbs of Fe^{2+} (at 510 nm) = 3.629-0.053 = 3.576

$$[Fe^{2+}] = \frac{\Delta Abs\ of\ Fe^{2+}\ (at\ 510\ nm)}{e_{510nm} \times 1}$$

$$[Fe^{2+}] = \frac{3.576}{11100 M^{-1} cm^{-1} \times 1\ cm} = 3.222 \times 10^{-4} M$$

$$n_{(Fe^{2+})} = 3.222\ M \times 0.0035\ L = 1.128 \times 10^{-6}$$

with quantum yield of 0.9 for the absorption of Fe^{3+}:

$$n_{(photons)} = 1.253 \times 10^{-6}$$

$$n_{(photons)} = 6.265 \times 10^{-8}\ mol/s$$

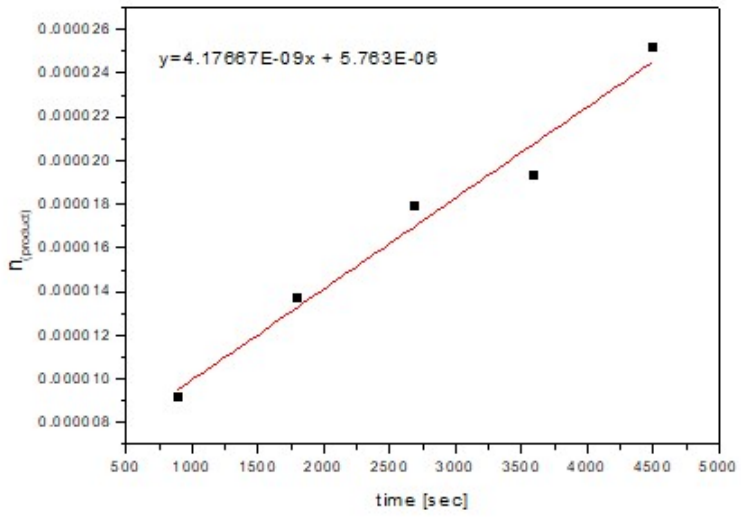
The initial rate of the amination was determined to be $4.177 \times 10^{-9}\ mol/s$.

$$\text{Quantum Yield} = \frac{n_{priduct}/s}{Photons/s} = \frac{4.177 \times 10^{-9}}{6.265 \times 10^{-8}} = 0.067$$

Determination Initial Rate:

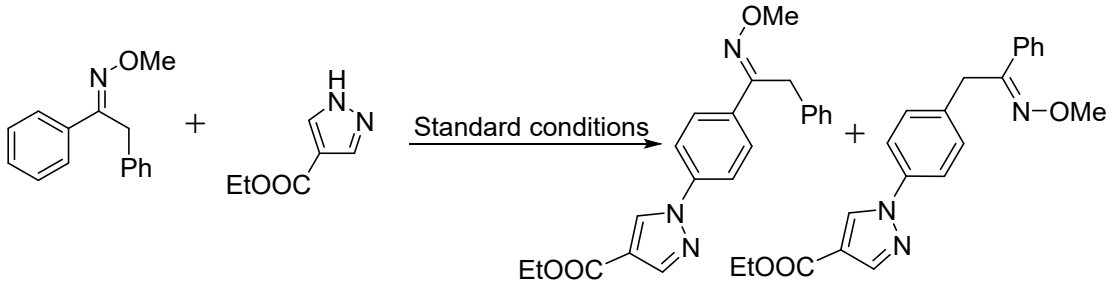
Product formation was monitored by ^{1}H-spectroscopy using mesitylene as internal standard.

Time in s	900	1800	2700	3600	4500
Yield by ^{1}H [%]	9.17	13.70	17.86	19.31	25.16
$n_{(product)}◊10^{-5}$	0.917	1.370	1.786	1.931	2.516



Preliminary mechanistic studies

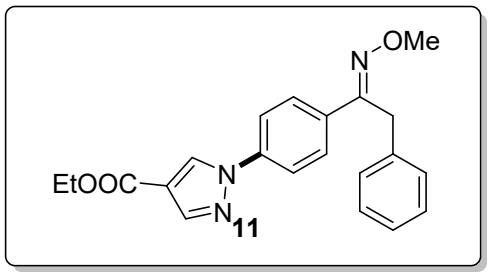
Selective C-H amination.



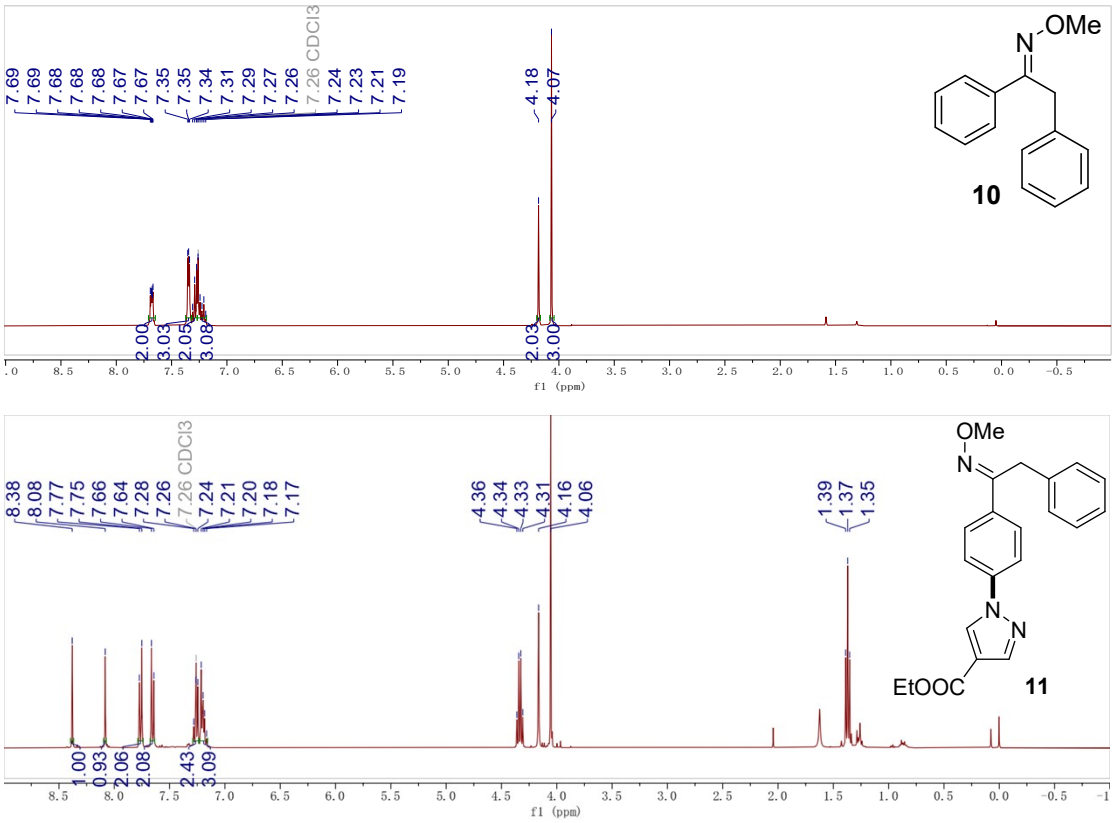
10, 0.1 mmol **2a**, 2 eq **11**, 69% **12**, trace

A mixture of **10** (0.1 mmol, 1.0 eq), **2a** (0.2 mmol, 2.0 eq), TPT (4.0 mg, 10 mol%), $Cu(OTf)_2$ (3.6 mg, 10 mol%) and DCE (1 ml) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 12 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 = 10:1) to give the product **11**

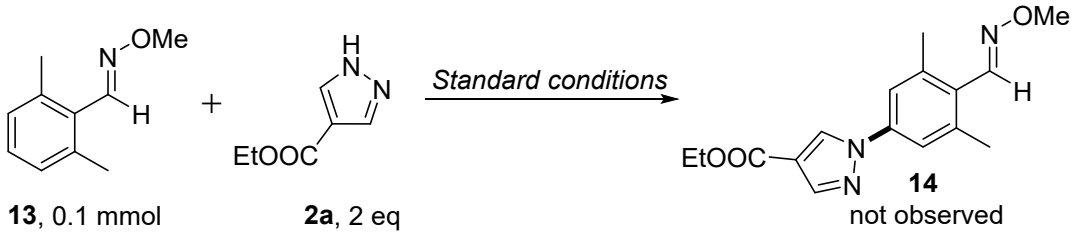
(25.1mg, 69%), but **12** was not detected.



Yellow solid, isolated yield: 25.1 mg, 69%. Mp: 110-112℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.08 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.17 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.16 (s, 2H), 4.06 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 155.0, 142.5, 139.8, 136.5, 134.9, 130.0, 128.8, 128.5, 127.9, 126.6, 119.4, 117.3, 62.4, 60.6, 32.5, 14.5. **HRMS** Calcd for $C_{21}H_{21}N_3O_3Na$ $[M+Na]^+$: 386.1481; Found: 386.1490.



Non-reactive substrate.



A mixture of **13** (0.1 mmol, 1.0 eq), **2a** (0.2 mmol, 2.0 eq), TPT (4.0 mg, 10 mol%),

$Cu(OTf)_2$ (3.6 mg, 10 mol%) and DCE (1 ml) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 12 h. After the reaction, **14** was not detected.

UV-experiments

Step 1: 0.1 mmol of 1a, 2a, 3a, TPT, $Cu(OTf)_2$ and (1a (0.1 mmol 1 eq)+TPT (0.34 eq)) in 1 ml of DCE.

Step 2: put 1µl of **Step 1** solution into a cuvette containing 2ml of DCE.

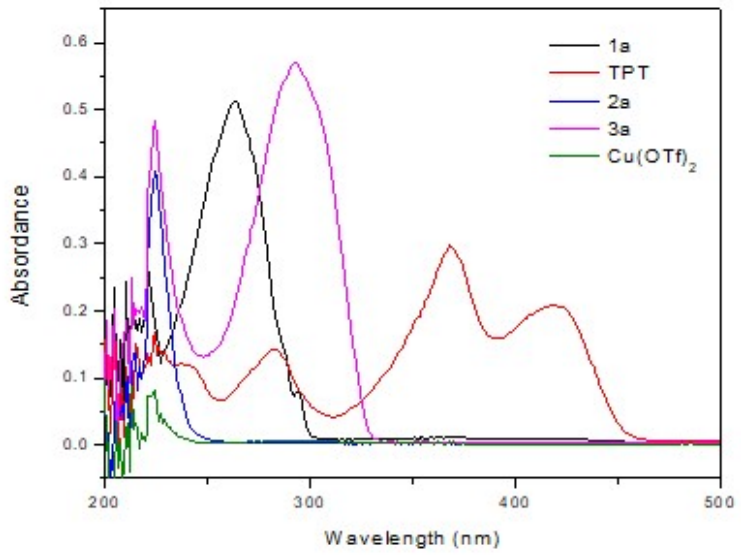


Figure S-8. UV Spectra of 1a, 2a, 3a, TPT and $Cu(OTf)_2$ in DCE

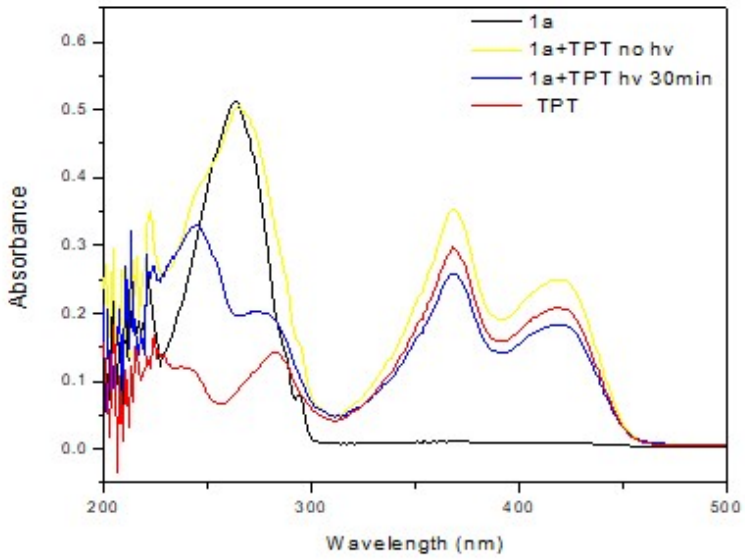
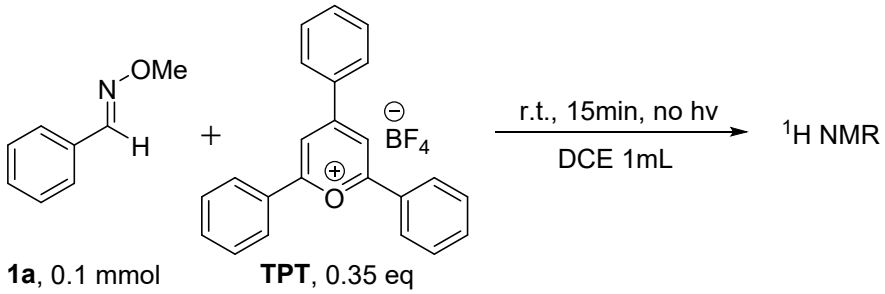
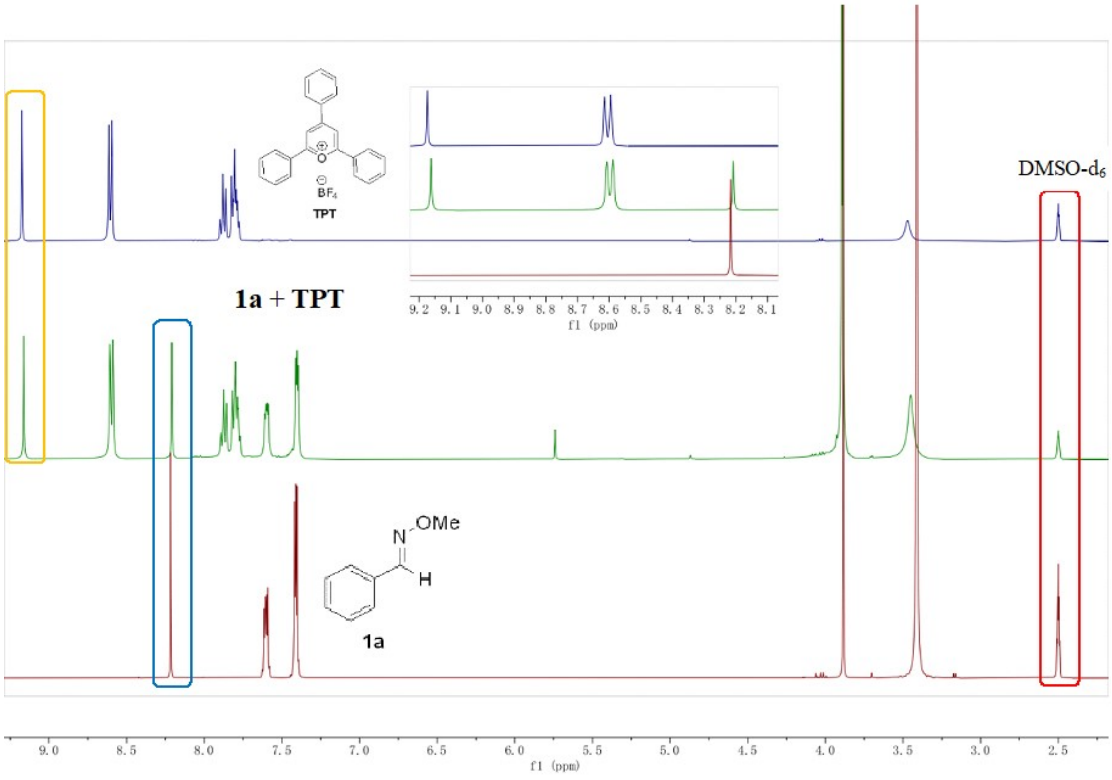


Figure S-9. UV Spectra of 1a, 1a + TPT and TPT in DCE

^{1}H NMR experiments



A mixture of **1a** (0.1 mmol, 1.0 eq), TPT (13.5 mg, 0.34 eq) and DCE (1 ml) in a 15 ml glass vial sealed. The reaction vessel was stirred for 15 minutes. After the reaction, then direct analysis by ^{1}NMR spectroscopy.



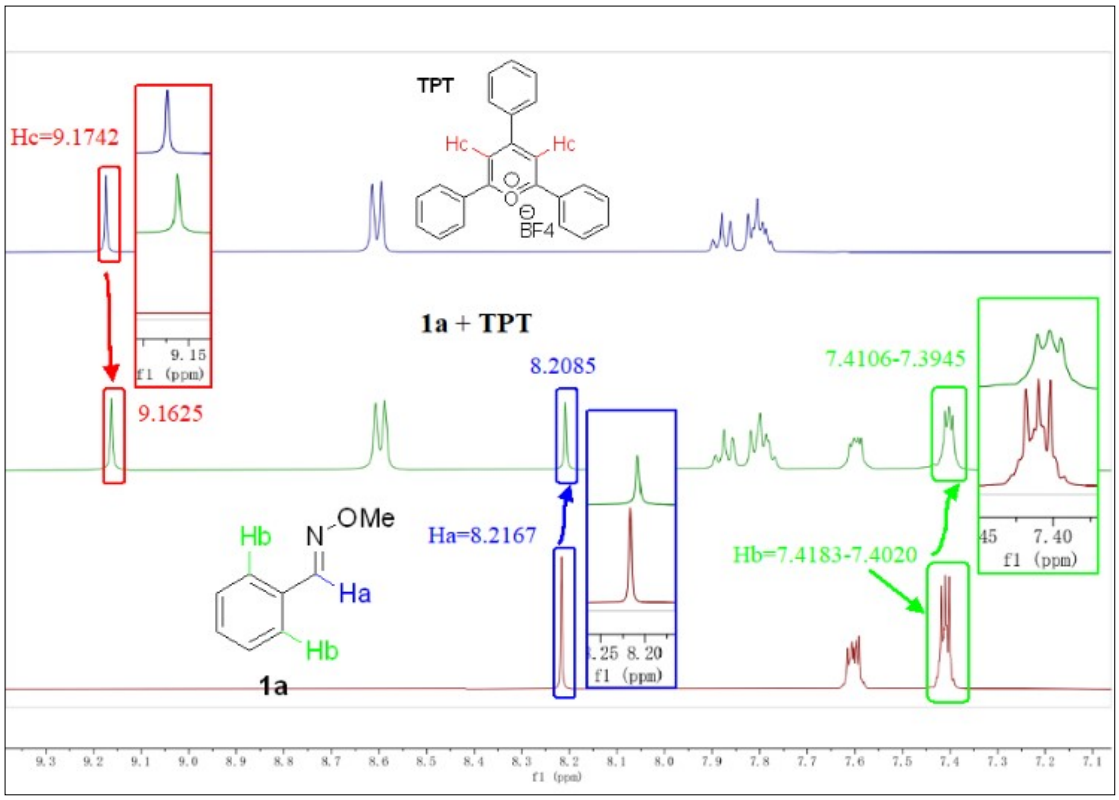
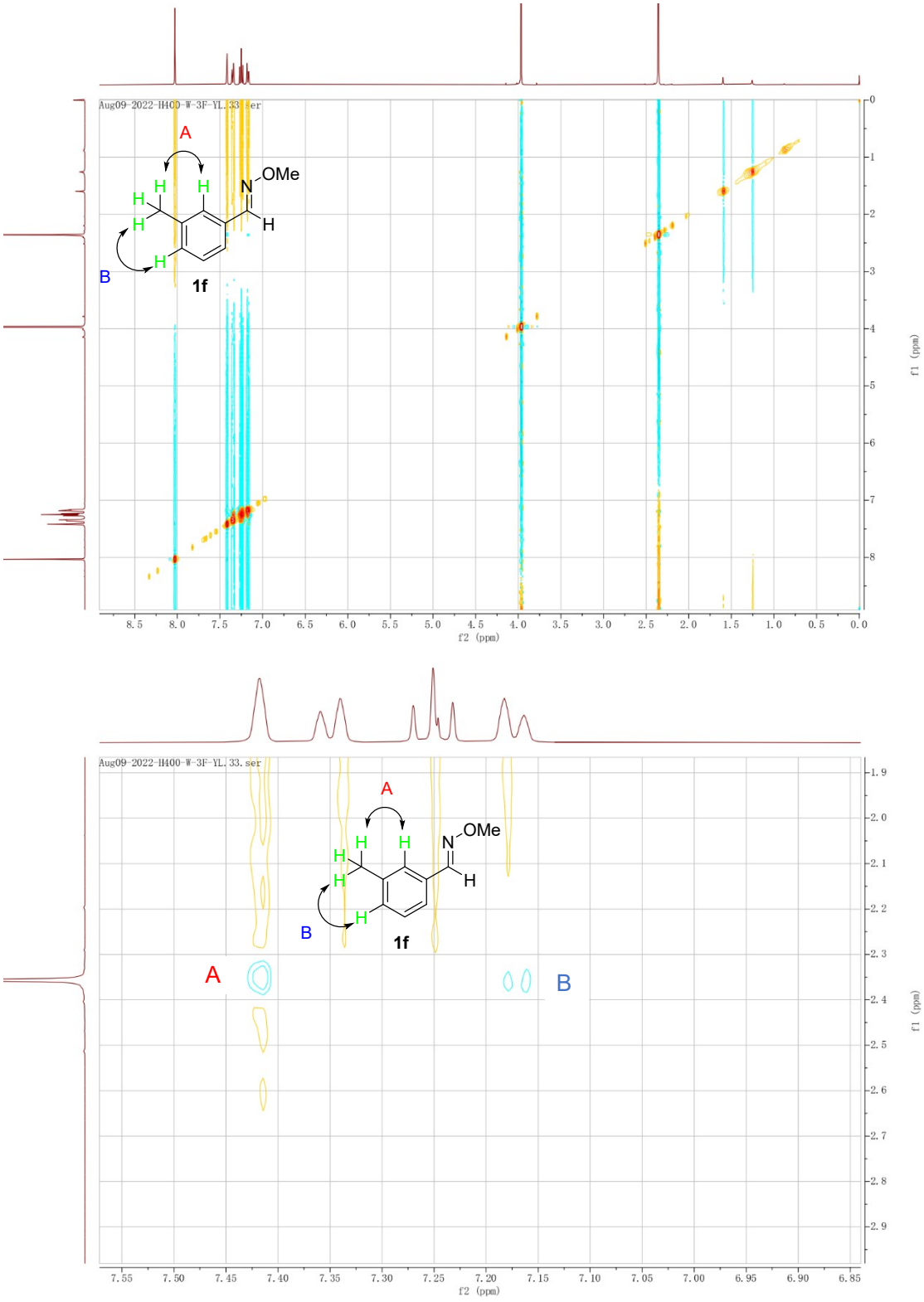
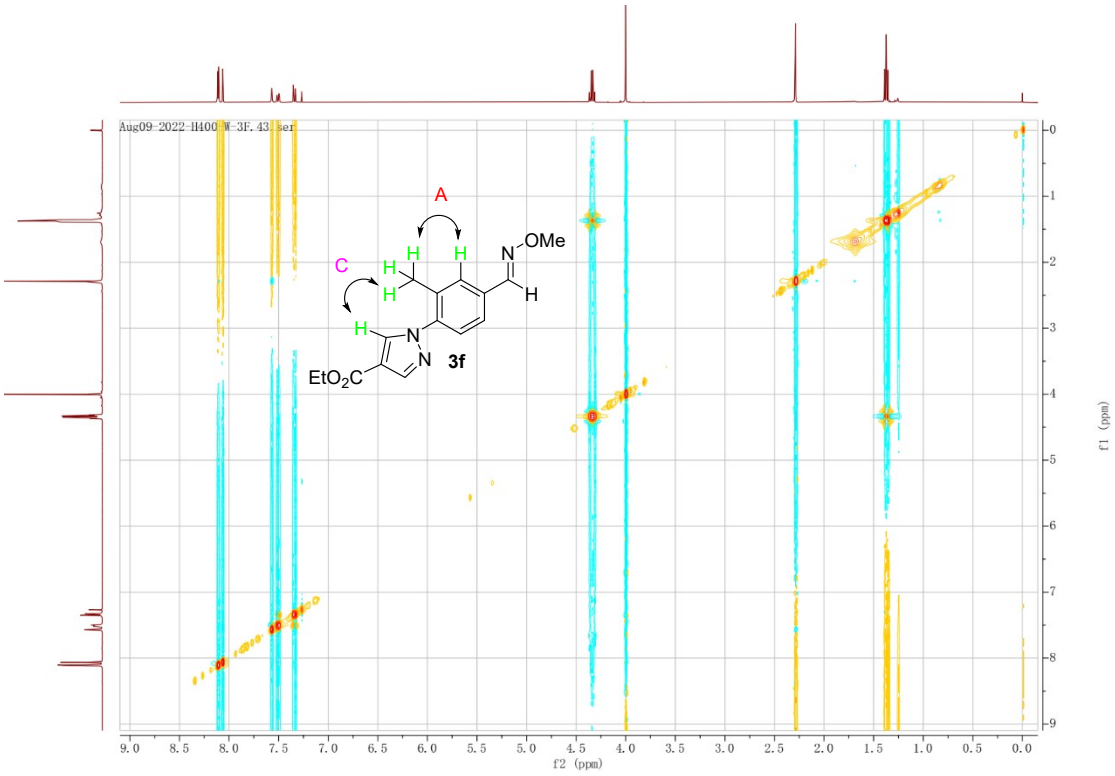
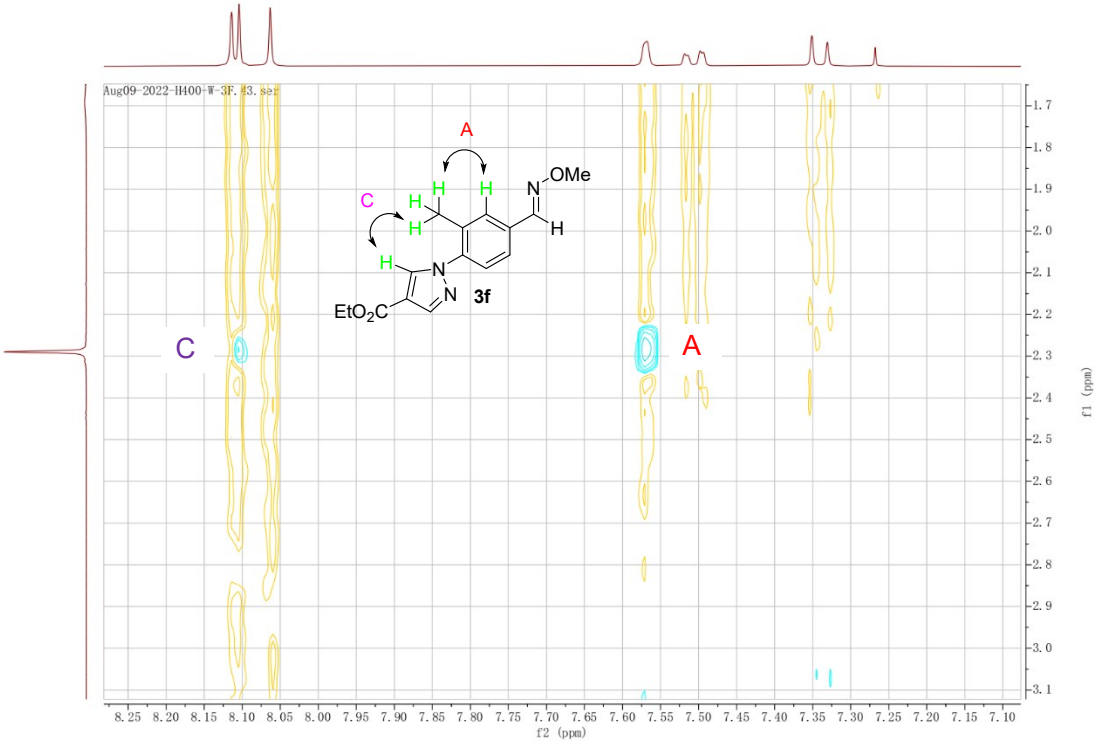


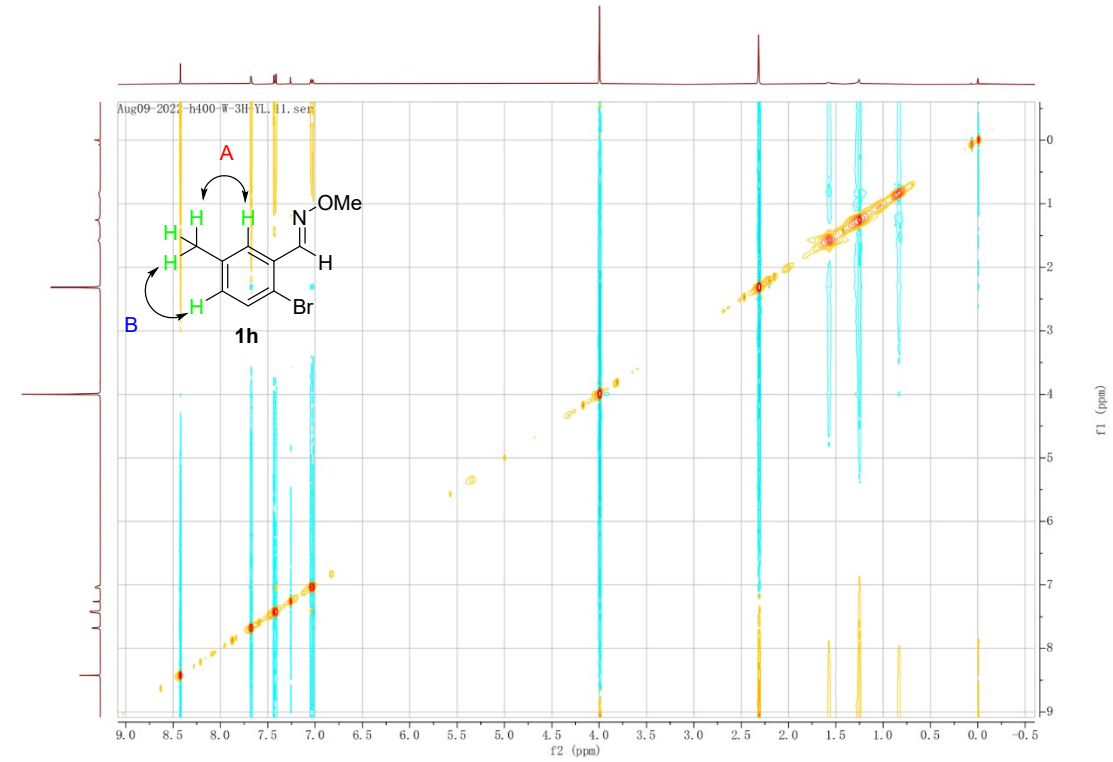
Figure S-10. [1]H NMR Spectra of **1a** and **TPT** in DMSO-*d*6

NOESY analysis of 3f, 3h and 3v.




A
C
OMe
3f
f2 (ppm)
f1 (ppm)


A
C
OMe
3f
C
A
f2 (ppm)
f1 (ppm)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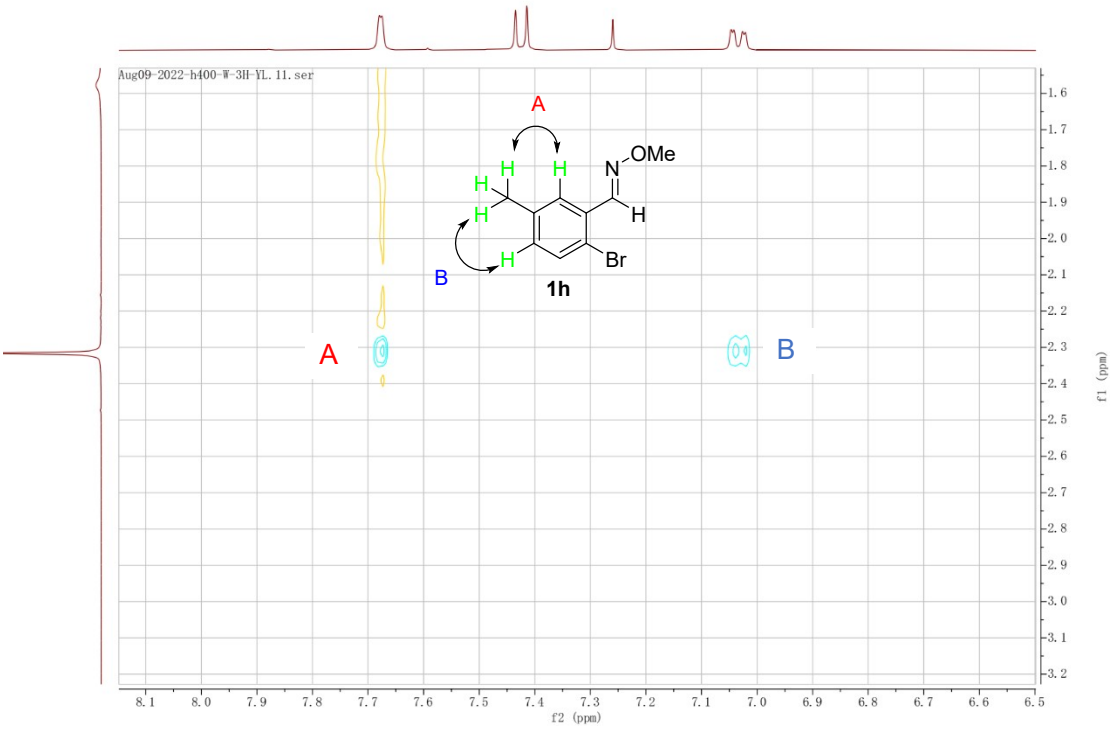
A
B
OMe
N
H
Br
1h
f2 (ppm)
f1 (ppm)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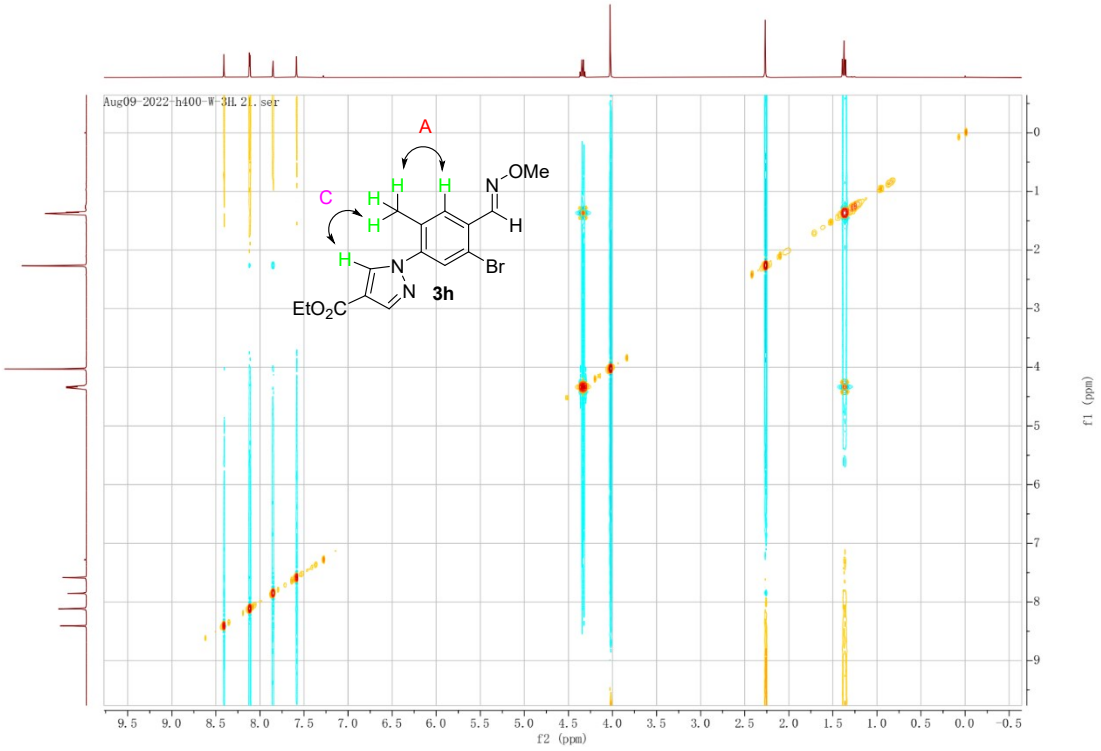
A
B
OMe
N
H
Br
1h
f2 (ppm)
f1 (ppm)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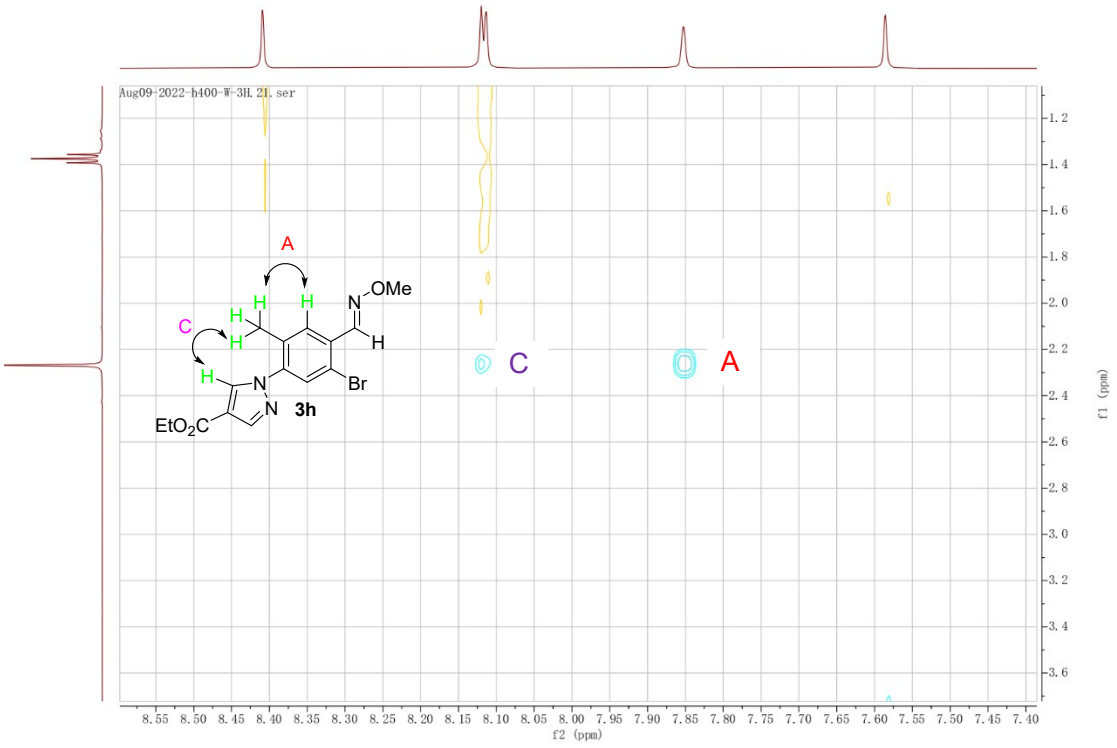
A
C
H
H
H
H
N
OMe
H
Br
N
N
H
EtO2C
3h
f2 (ppm)
f1 (ppm)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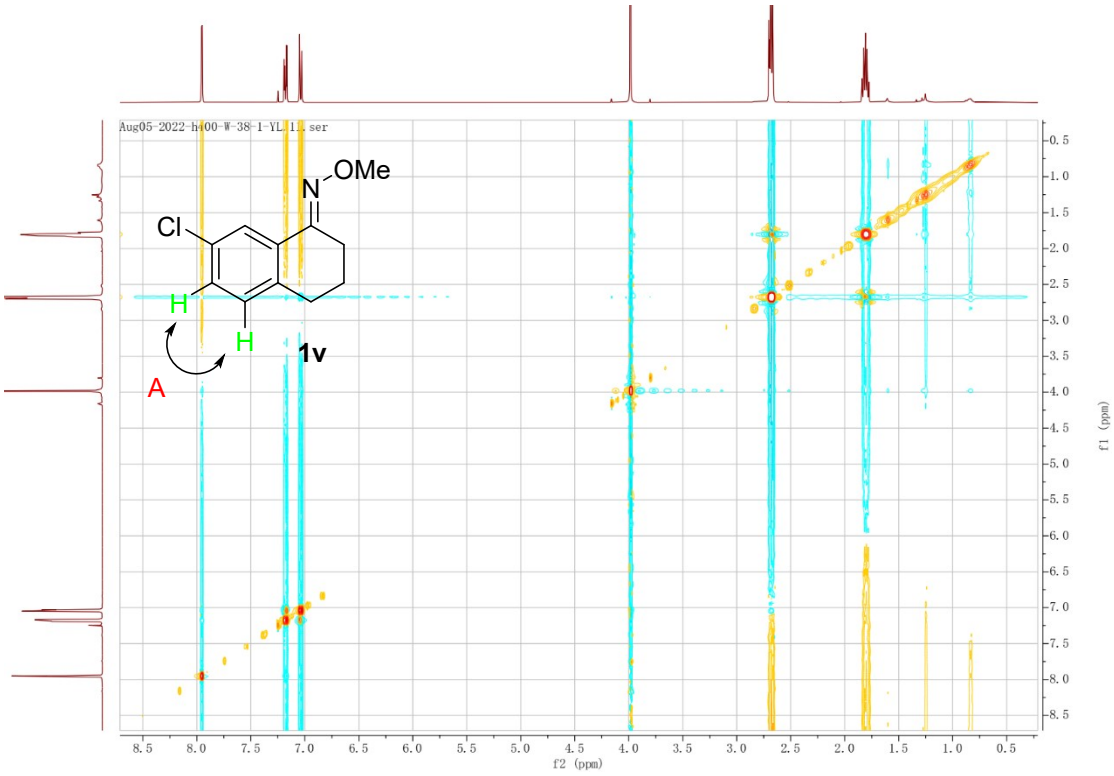
A
C
H
H
H
H
N
OMe
H
Br
N
N
H
EtO2C
3h
C
A
f2 (ppm)
f1 (ppm)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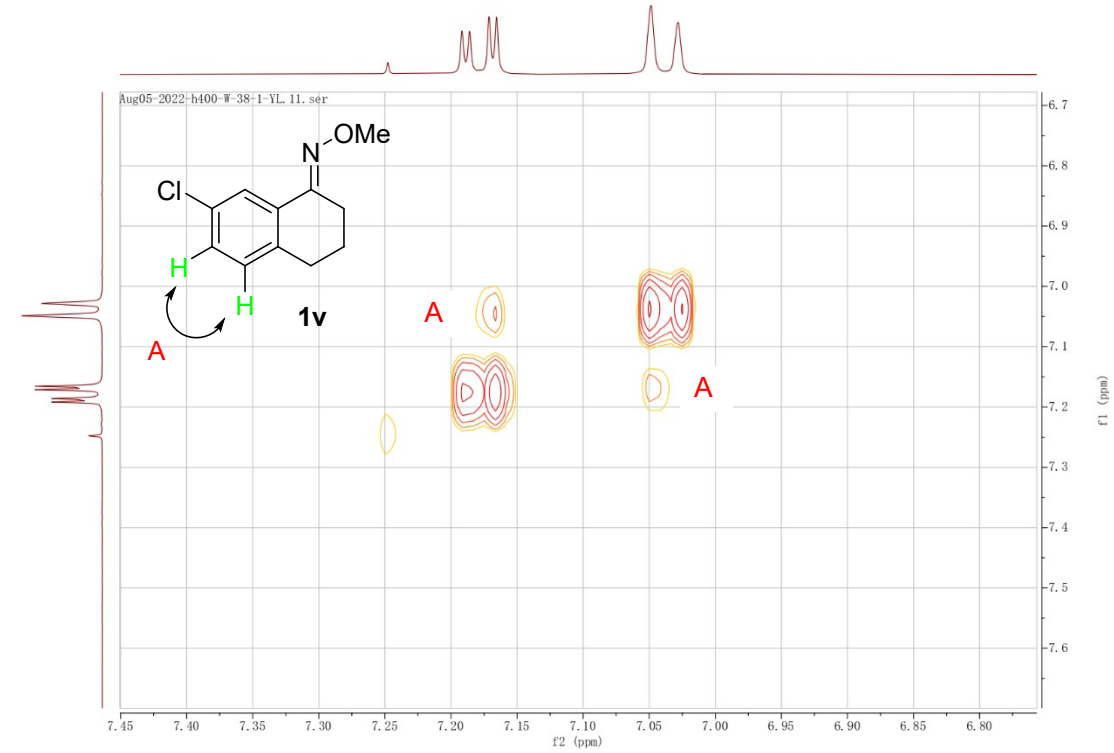
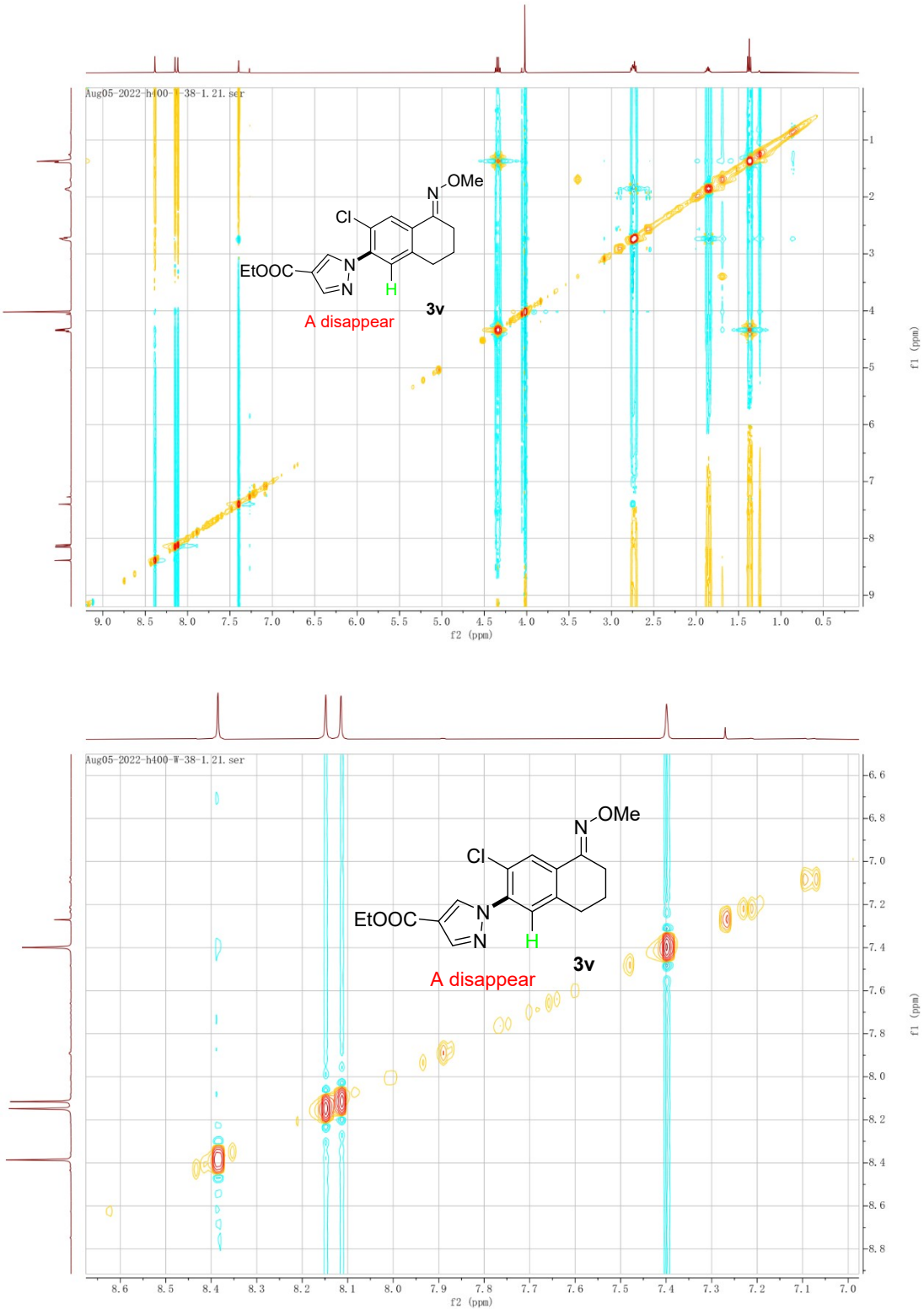
N
OMe
Cl
H
H
1v
A
f2 (ppm)
f1 (ppm)


Aug05-2022-h400-W-38-1-YL-11.ser
N
OMe
Cl
H
H
1v
A
A
A
f2 (ppm)
f1 (ppm)



The characterization of $Cu^{2+}$by XPS

A mixture of **1p** (0.1 mmol, 1.0 eq), **2a** (0.2 mmol, 2.0 eq), TPT (4.0 mg, 10 mol%),

$Cu(OTf)_2$ (3.6 mg, 10 mol%) and DCE (1 ml) in a 15 ml glass vial sealed under **argon** atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 12 h. The reaction mixture was directed dried by oil pump, and then transformed into glove box. The reaction mixture was direct by X-ray photoelectron spectroscopy. The result listed below.

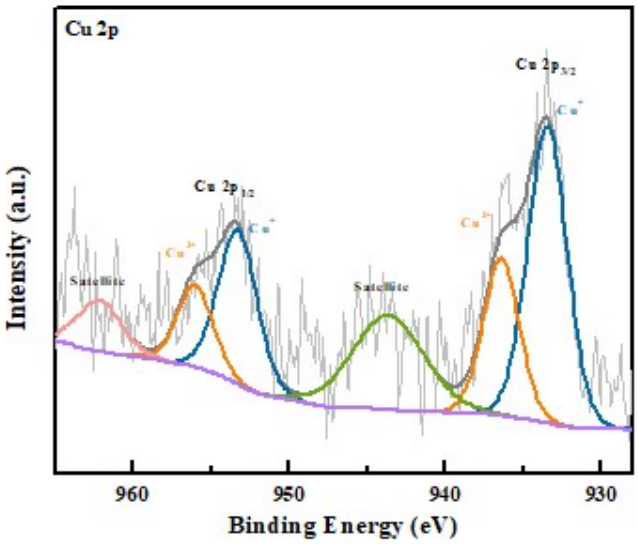
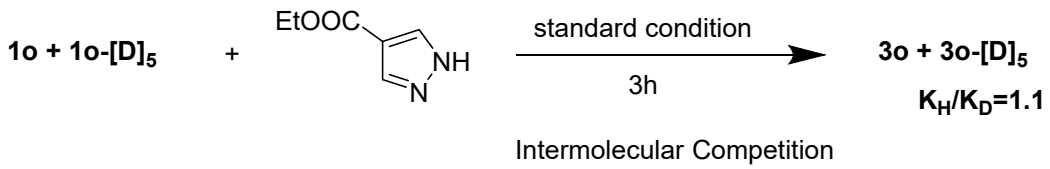


Figure S-11.XPS of Cu

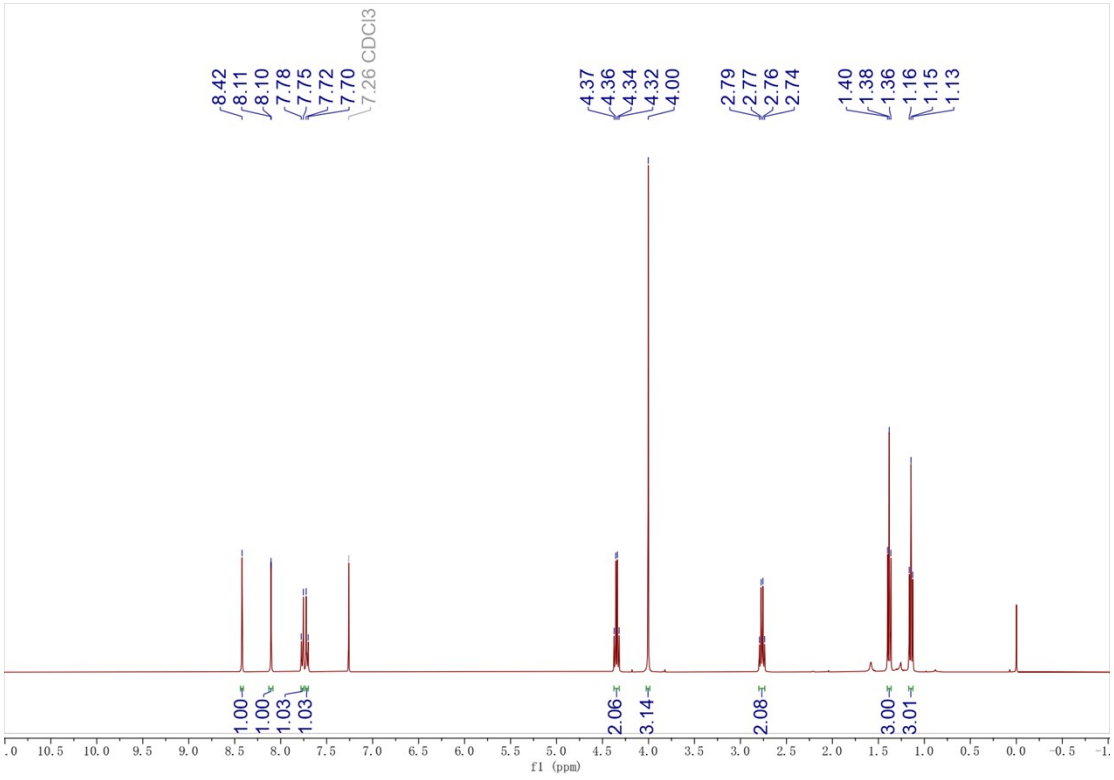
In order to explain the mechanism more favorably, the XPS spectrum was used to further analyze the catalyst residue after the reaction, and the photoelectron peaks at 933.5 and 953.5 eV correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. It shows that in addition to Cu $^{2+}$, Cu $^{+}$ also exists in the catalytic system[5][6]. And then the two peaks at 933.5 and 953.5 eV split into four peaks, two of them at 936.4 and 955.9 eV ascribing to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ orbits of Cu $^{2+}$, and the other two peaks at 933.4 and 953.4 eV corresponding to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ orbits of Cu $^{+}$.

KIE experiments



KIE by intermolecular competion: A mixture of **1o** (0.1 mmol, 1.0 eq) and **1o-[D]$_5$** (0.1

mmol, 1.0 eq), **2a** (0.4 mmol, 2.0 eq), TPT (8.0 mg, 10 mol%), $Cu(OTf)_2$ (7.2 mg, 10 mol%) and DCE (2 ml) in a 15 ml glass vial sealed under oxygen atmosphere. The reaction vessel was exposed to 40 w blue LEDs irradiation at room temperature stirring for 3 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 = 10:1) to give the product. The results determined by ^1H NMR spectroscopy.



Effect of Light: On/Off Plot

According to the general procedure, a reaction containing mesitylene as internal standard was set up and placed in front of the LEDs. The reaction was sequentially stirred under visible light irradiation and in the absence of light. Every two hours an aliquot of 50 μL was removed via syringe and analyzed by ^1H-NMR spectroscopy. After a total of 8 h the determined yields were plotted against the reaction time.

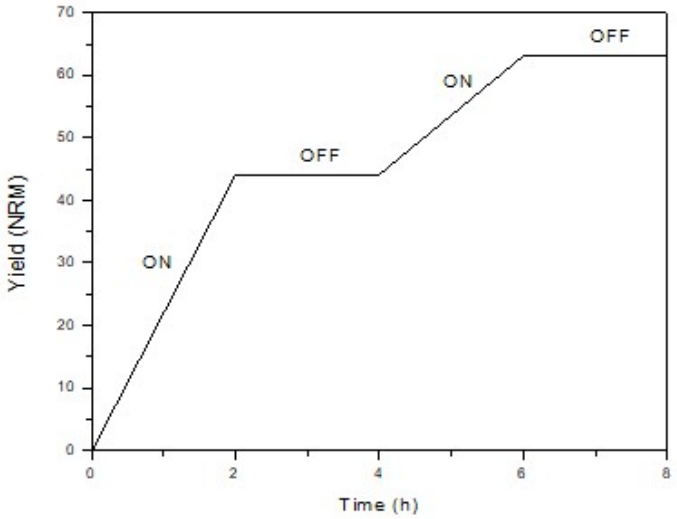


Figure S-12. Effect of visible light irradiation.

References

[1] N. Wang, L. Liu, W. Xu, M. Zhang, Z. Huang, D. Shi, Y. Zhao, *Org. Lett.* **2019**, *21*, 365-368.

[2] G. Xiao, C. Xie, Q. Guo, G. Zi, G. Hou, Y. Huang, *Org Lett.* **2022**, *24*, 2722-2727.

[3] B. Hasdemir, O. Sacan, H. Yasa, H. B. Kucuk, A. S. Yusufoglu, R. Yanardag, *Arch Pharm (Weinheim)* **2018**, *351*.

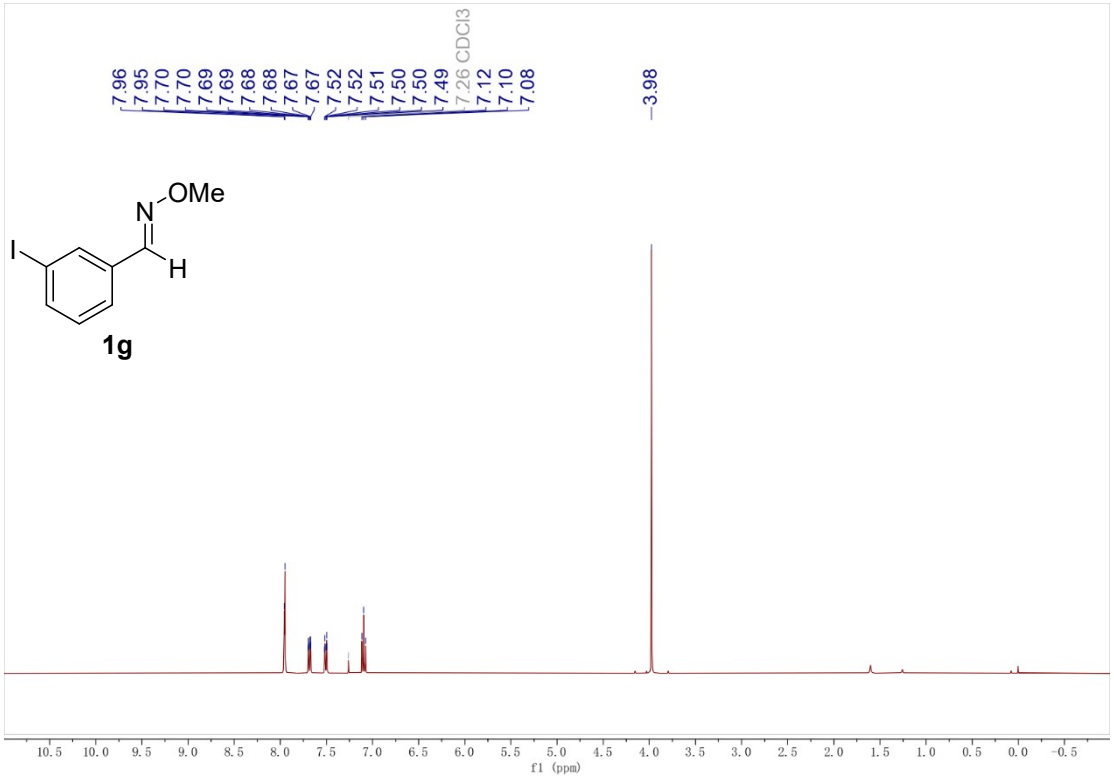
[4] P. Gandeepan, J. Koeller, K. Korvorapun, J. Mohr, L. Ackermann, *Angew. Chem. Int. Ed.* **2019**, *58*, 9820-9825.

[5] X. Han, H. Sheng, C. Yu, T. W. Walker, G. W. Huber, J. Qiu, S. Jin, *ACS Catal.* **2020**, *10*, 6741-6752.

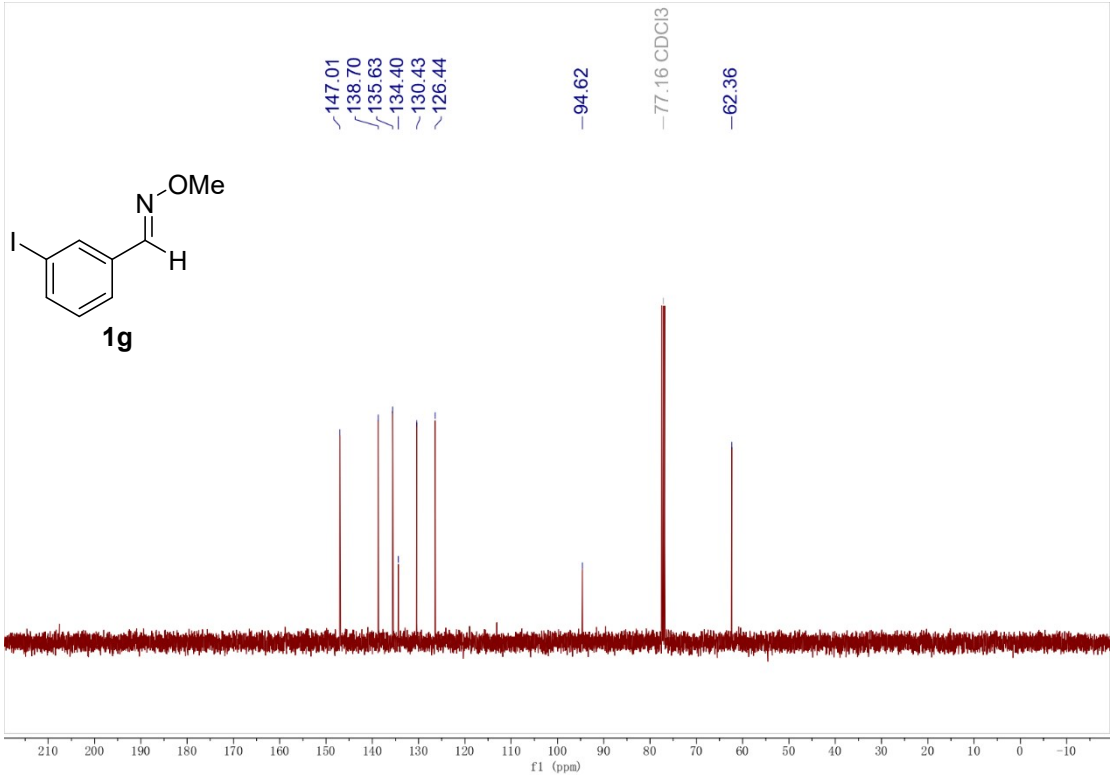
[6] S. Wu, X. Huang, H. Zhang, Z. Wei, M. Wang, *ACS Catal.* **2021**, *12*, 58-65.

NMR spectra

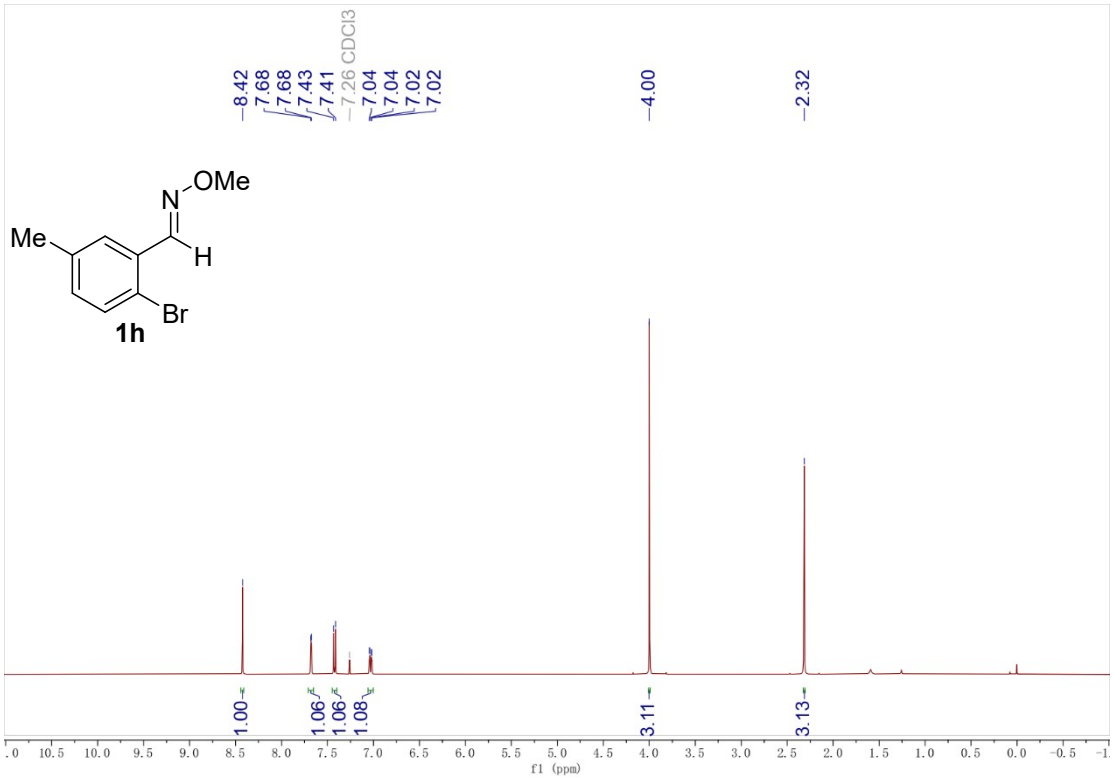
^{1}H NMR of 1g



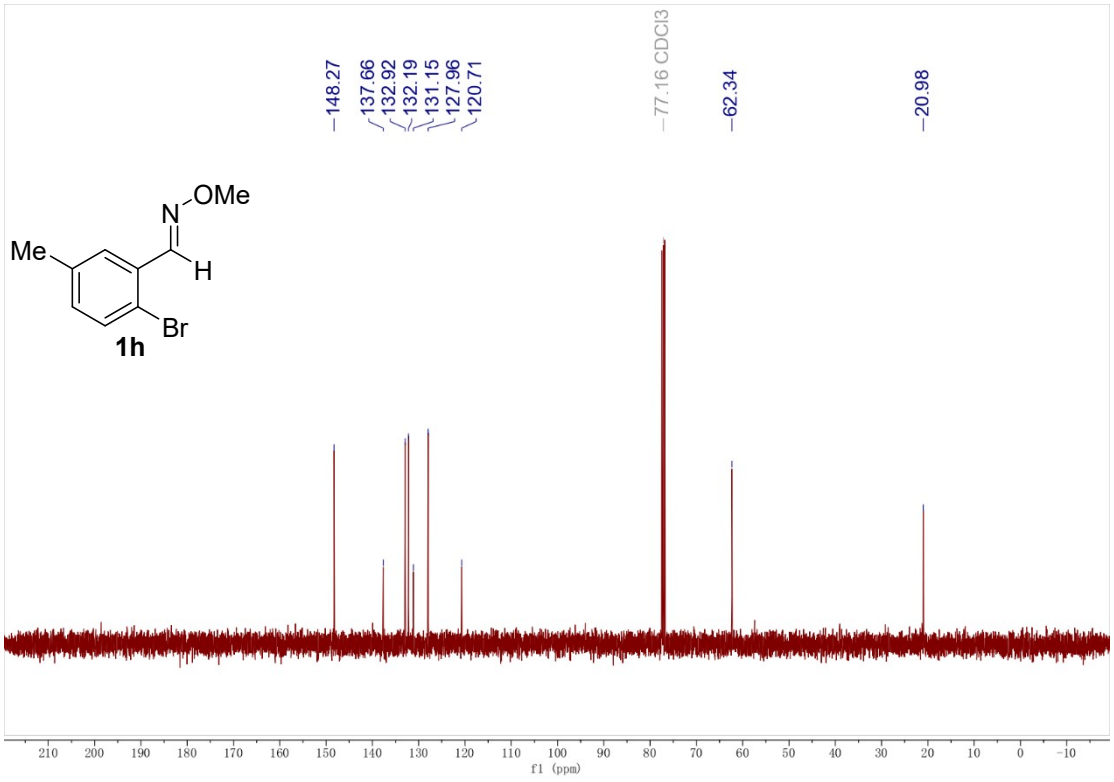
^{13}C NMR of 1g



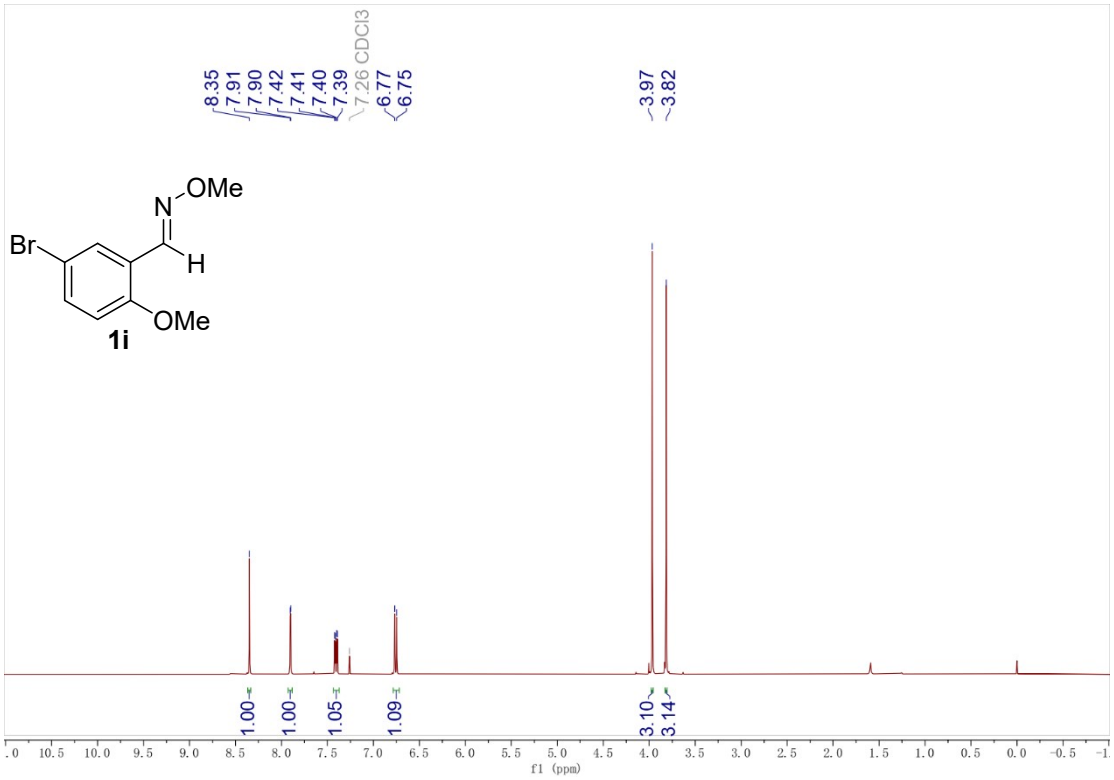
^{1}H NMR of 1h



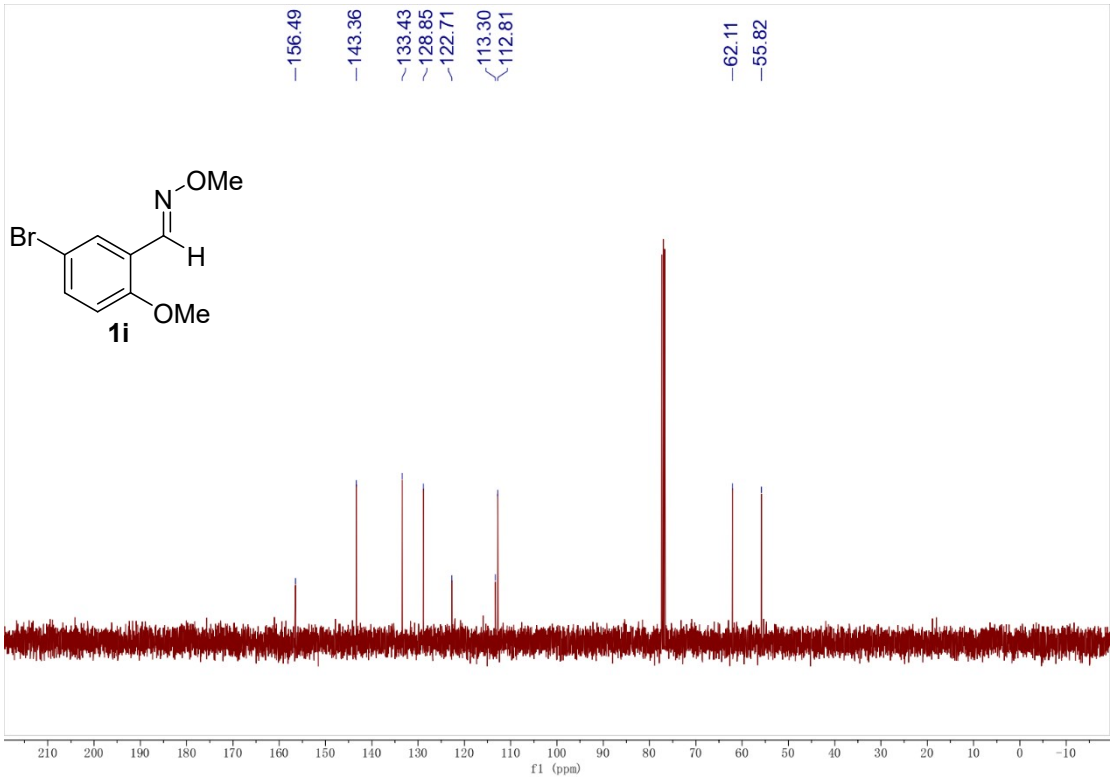
^{13}C NMR of 1h



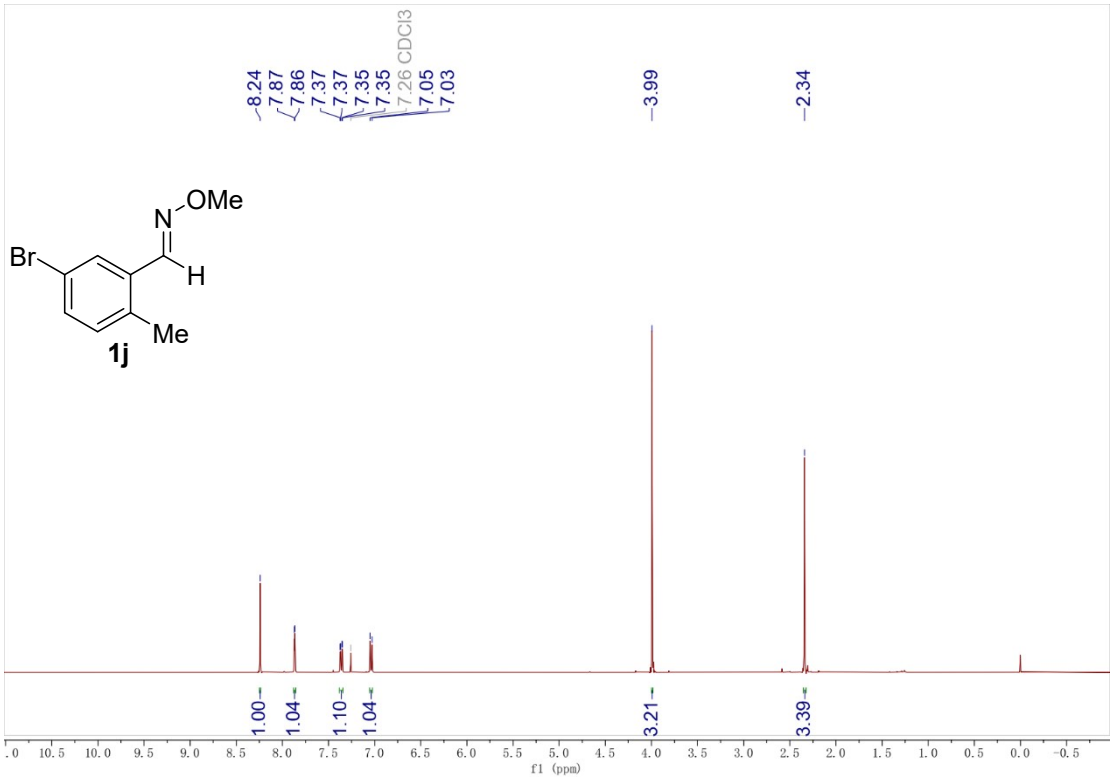
^{1}H NMR of 1i



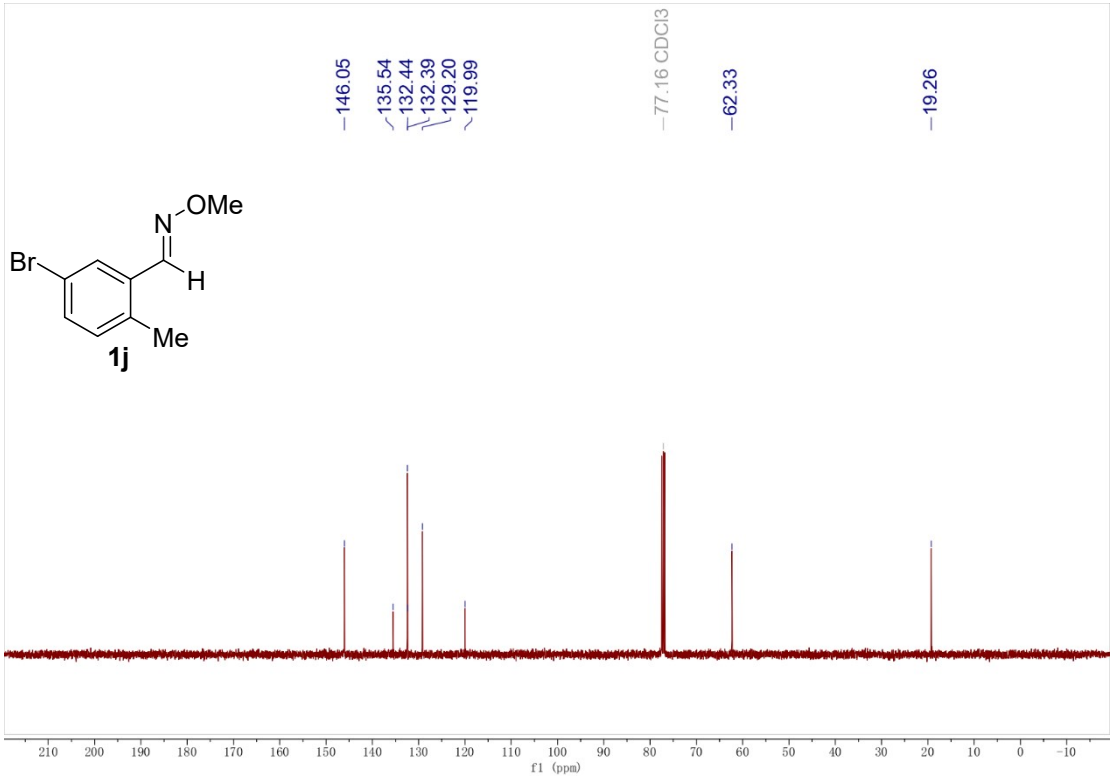
^{13}C NMR of 1i



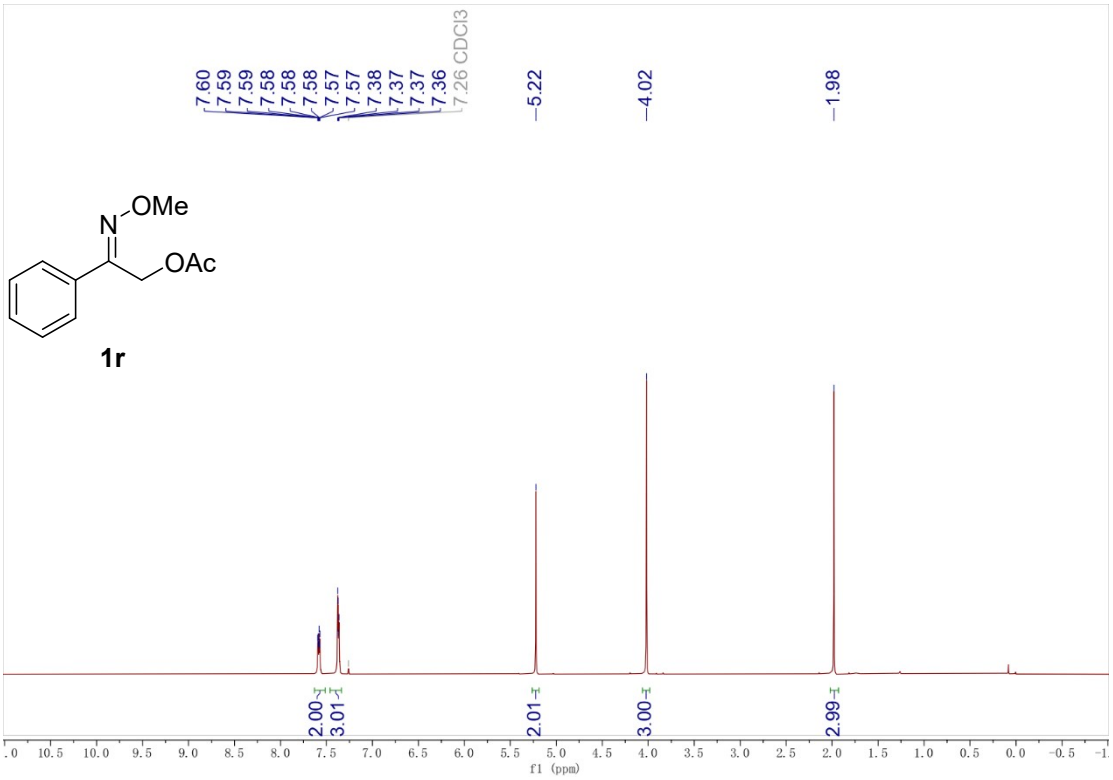
^{1}H NMR of 1j



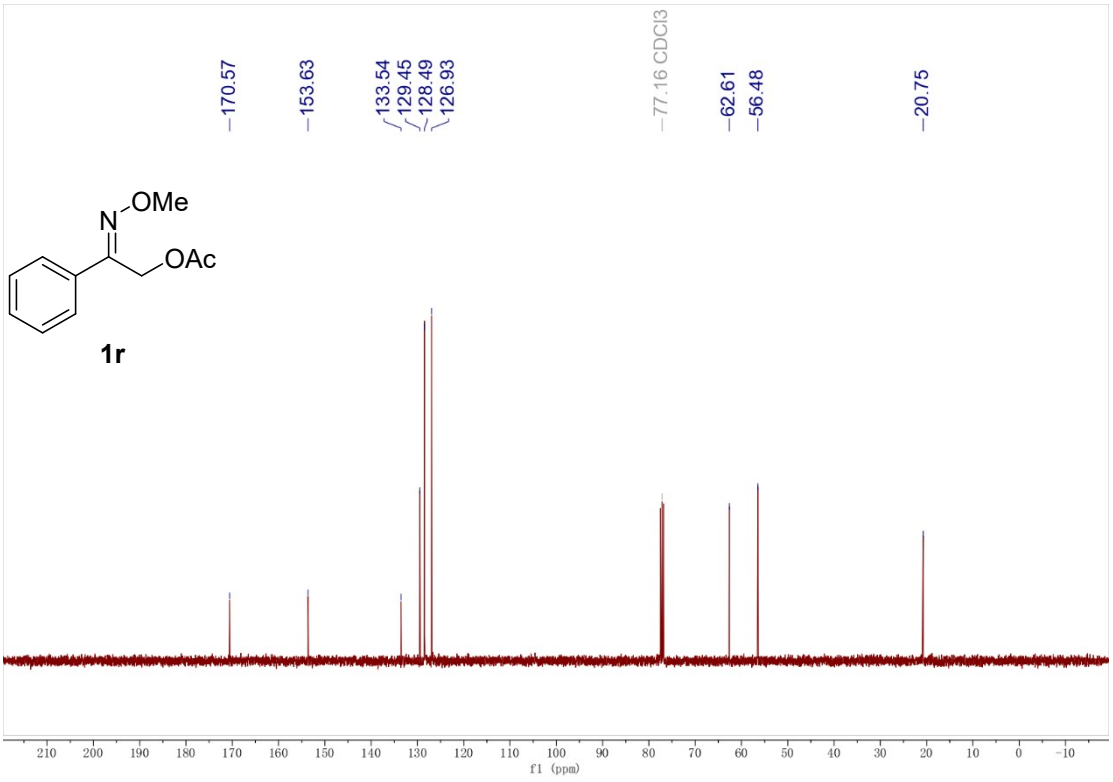
^{13}C NMR of 1j



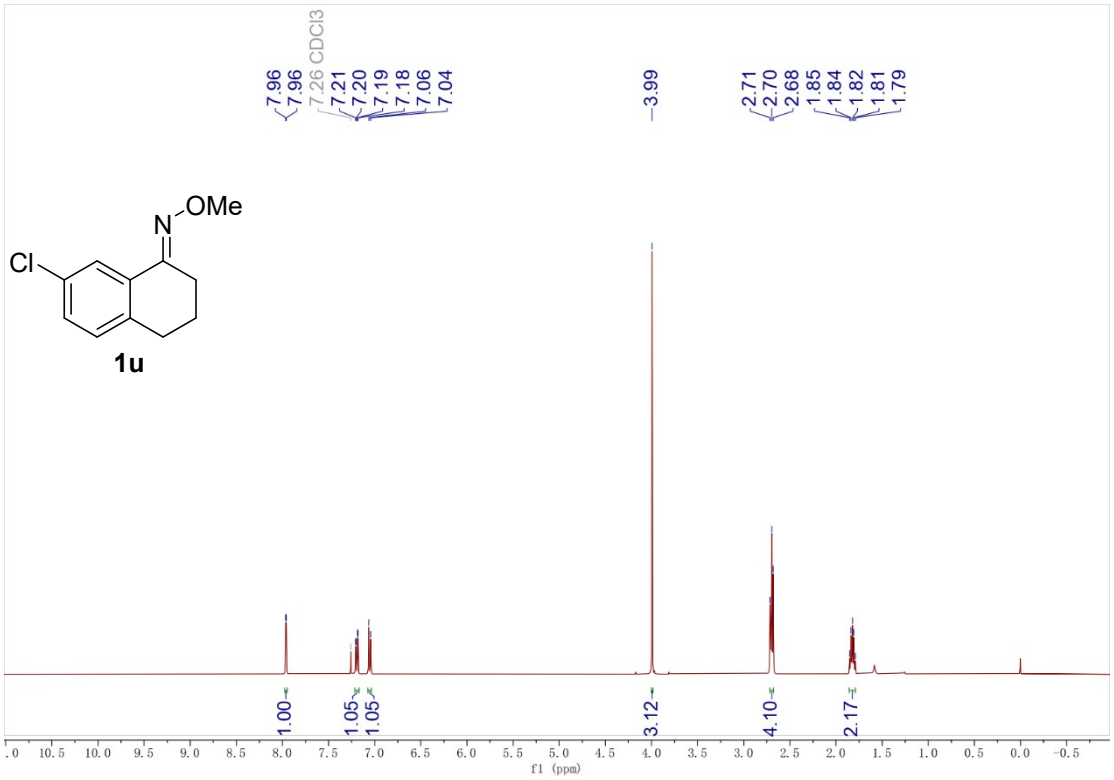
^{1}H NMR of 1r



^{13}C NMR of 1r



^{1}H NMR of 1u



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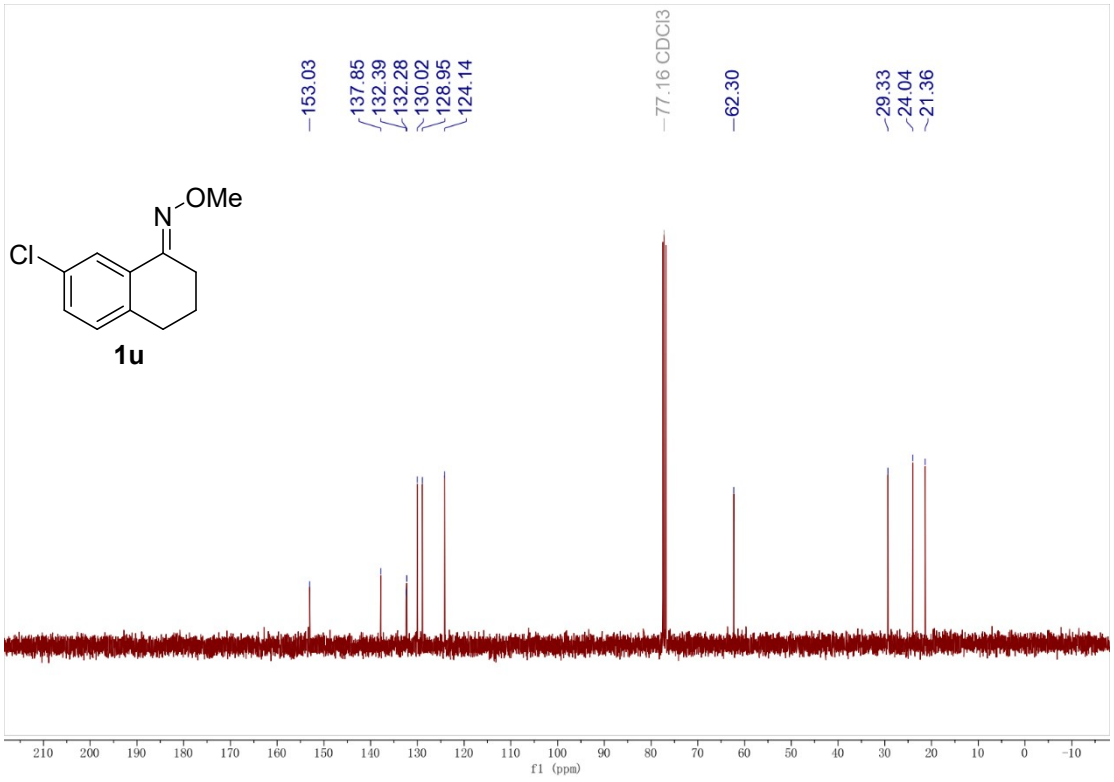
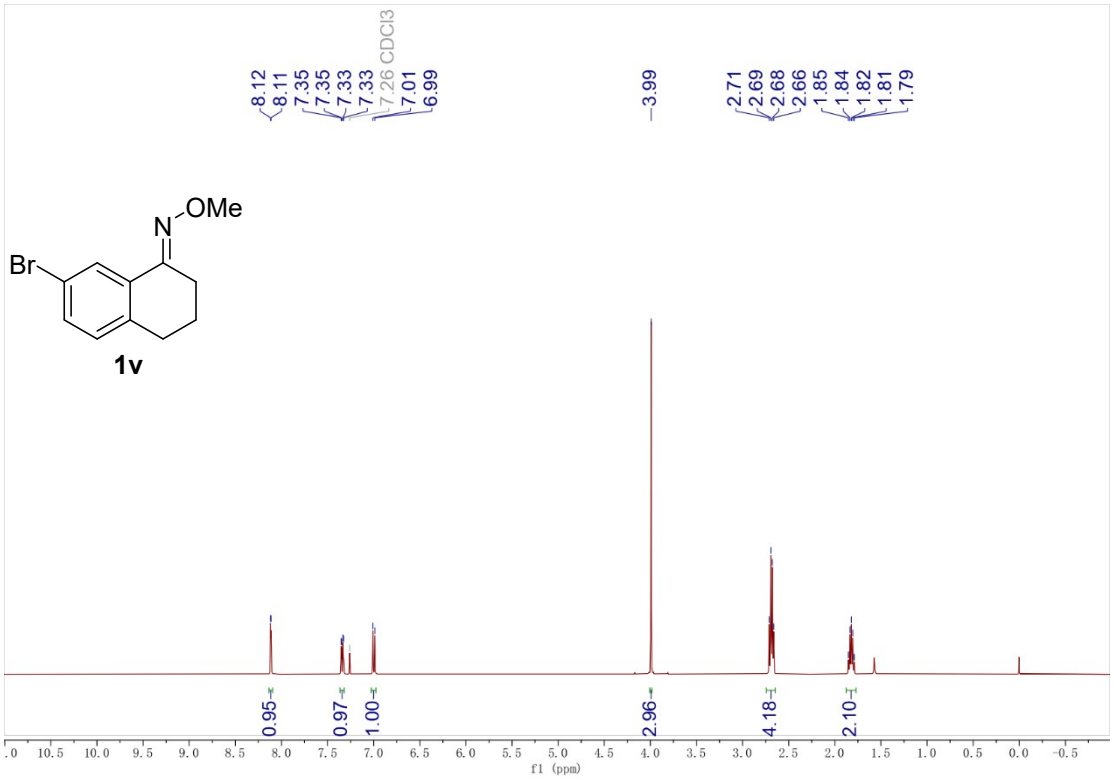


^{1}H NMR of 1v



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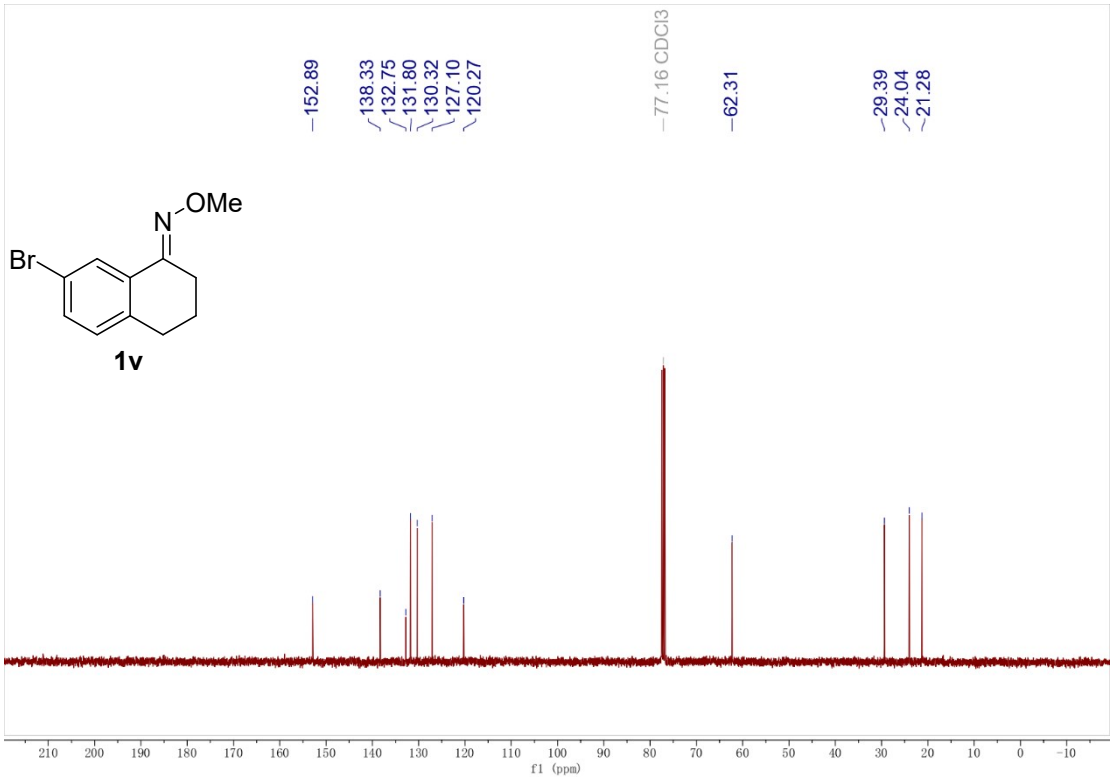
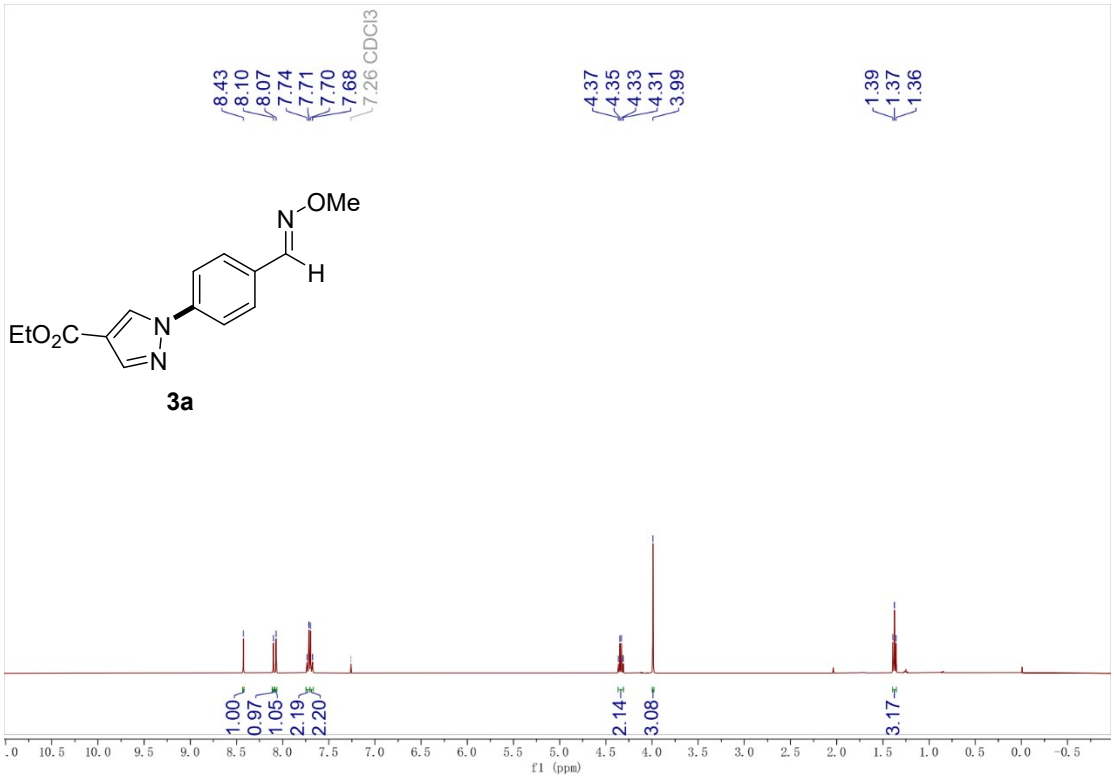


^{1}H NMR of 3a



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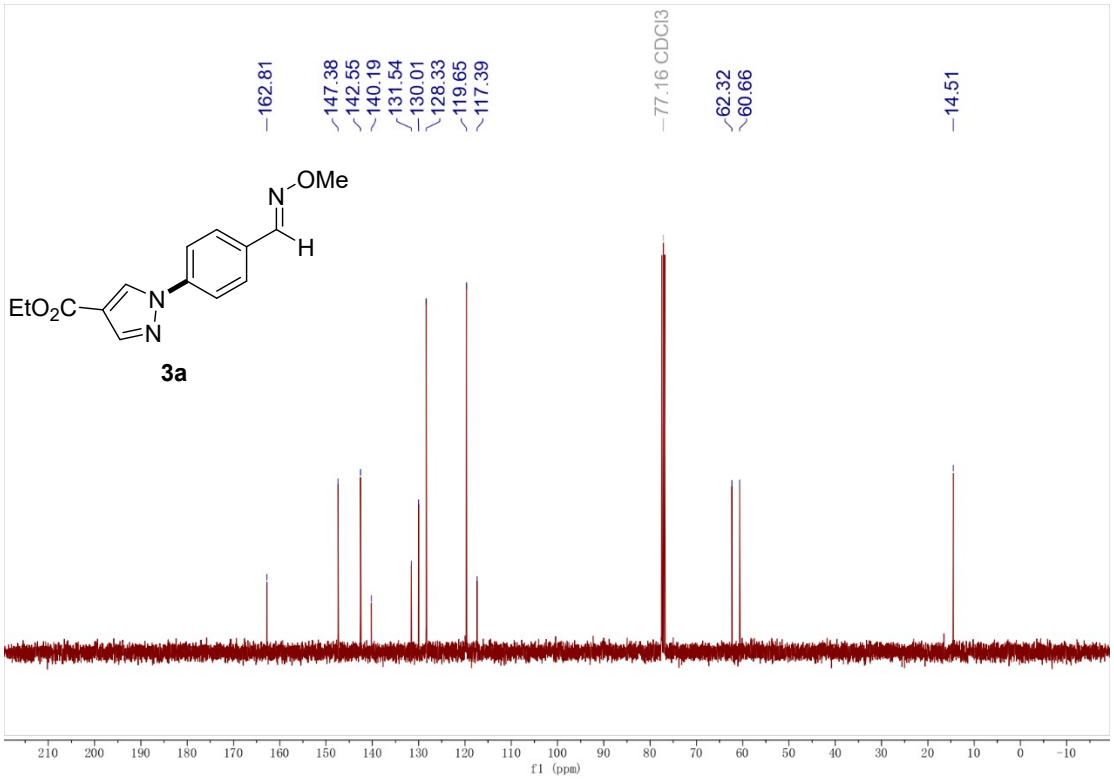
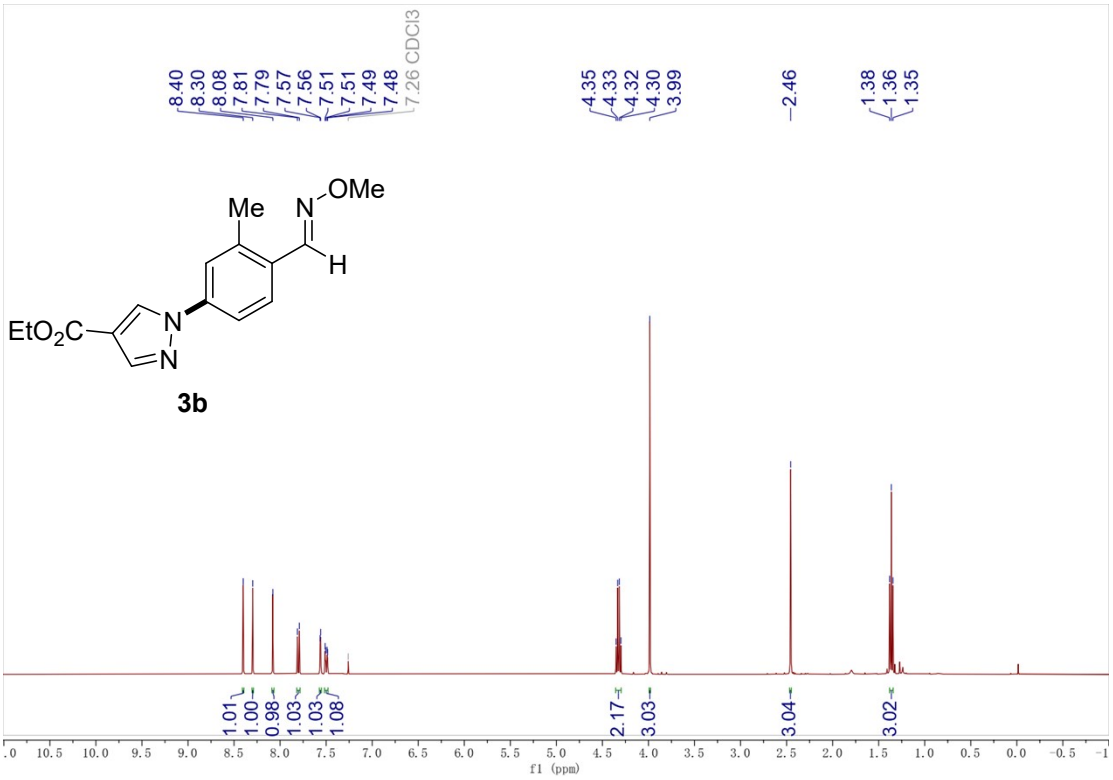
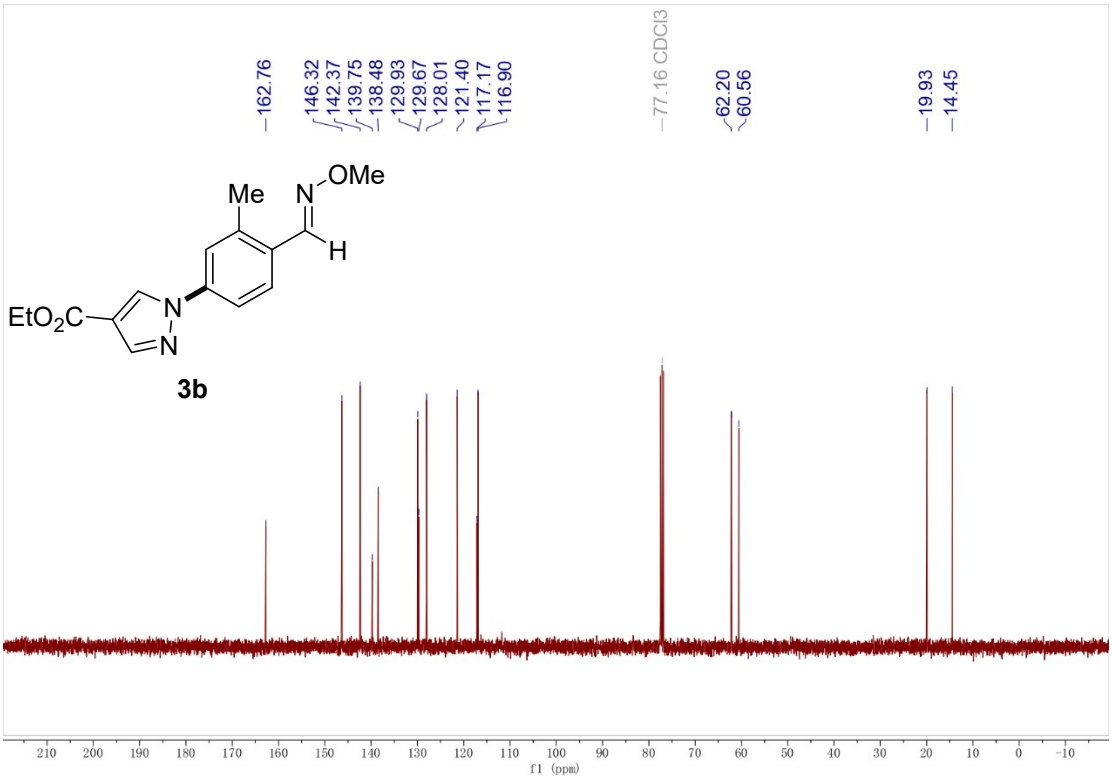


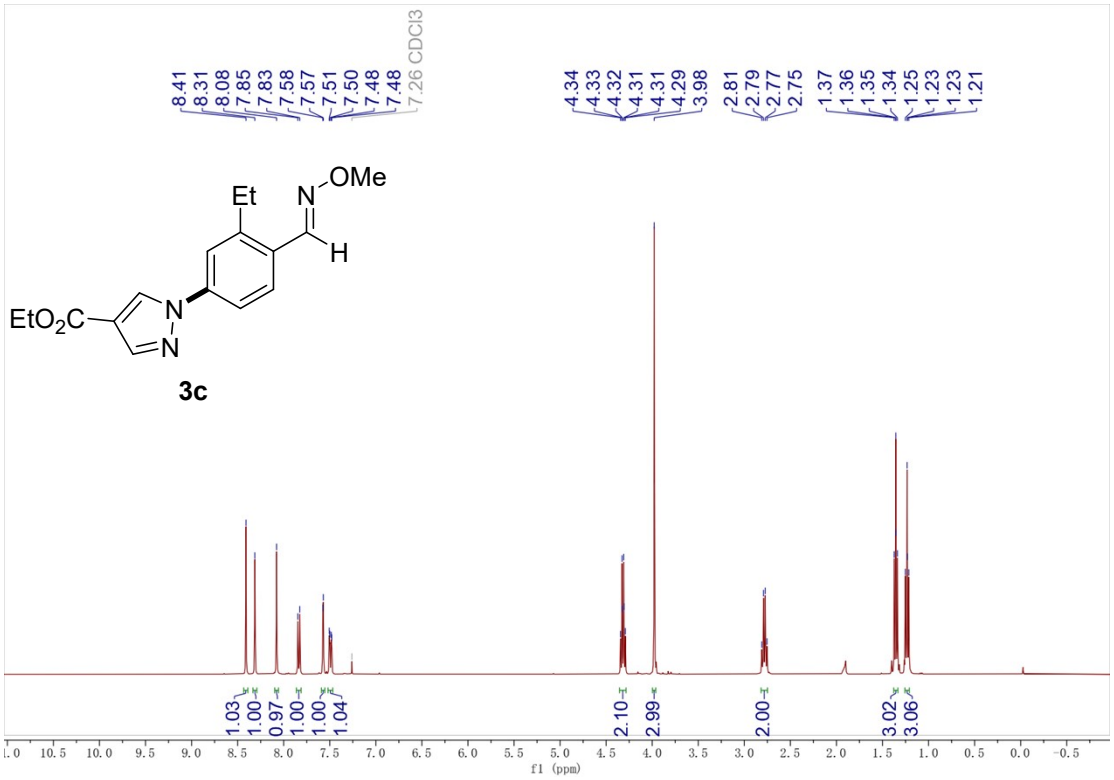
^{1}H NMR of 3b



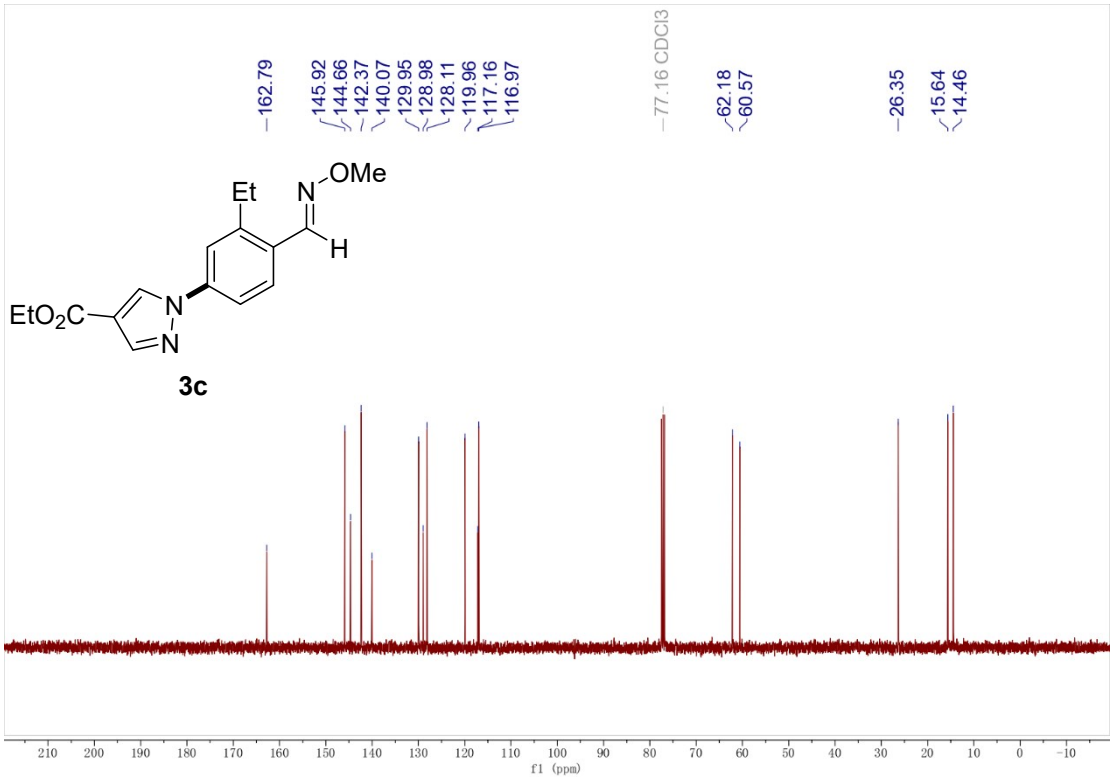
^{13}C NMR of 3b



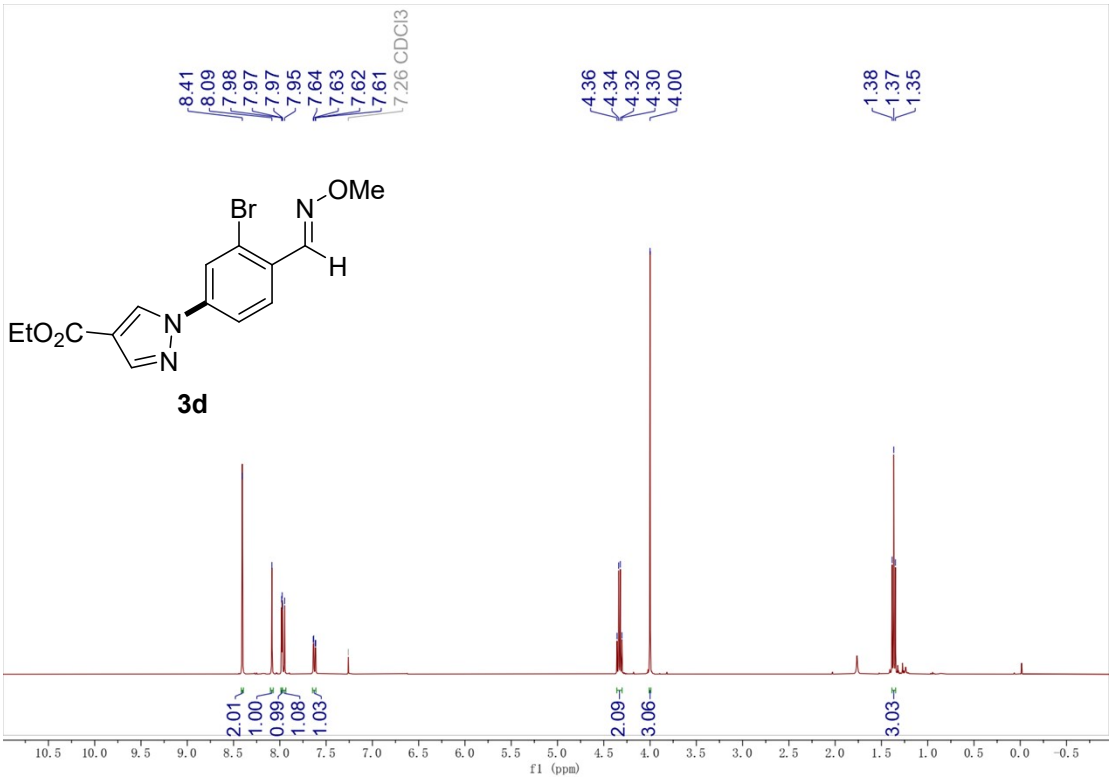
^{1}H NMR of 3c



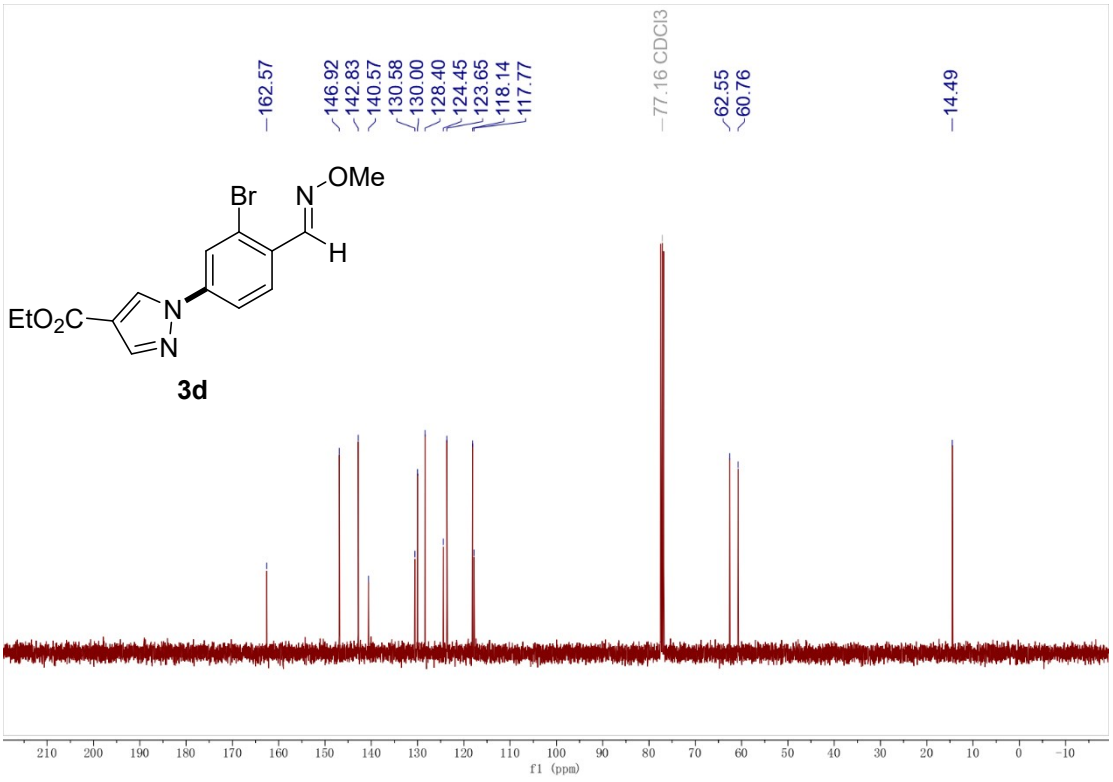
^{13}C NMR of 3c



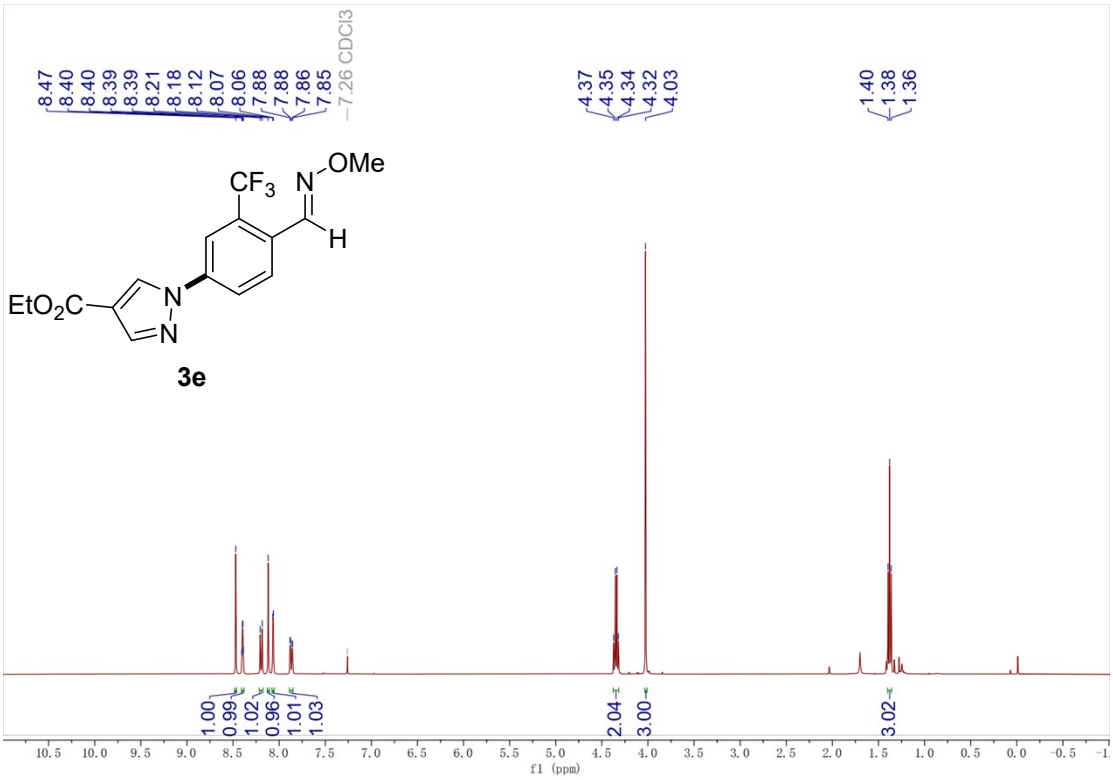
^{1}H NMR of 3d



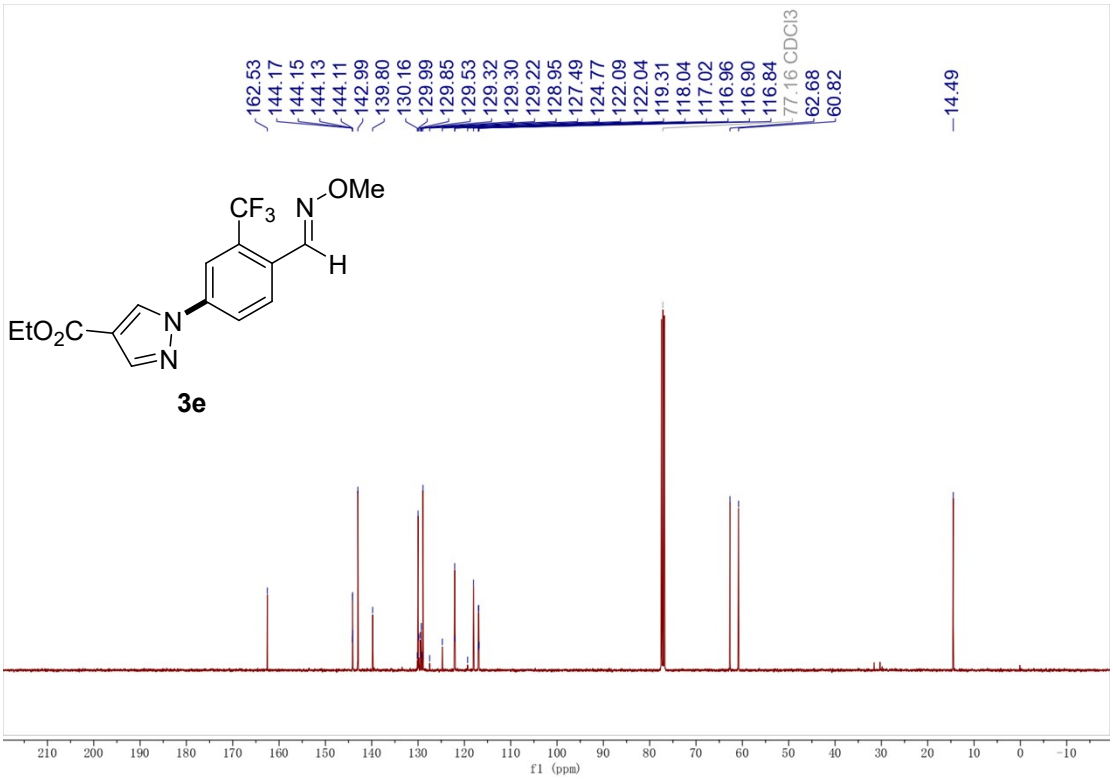
^{13}C NMR of 3d



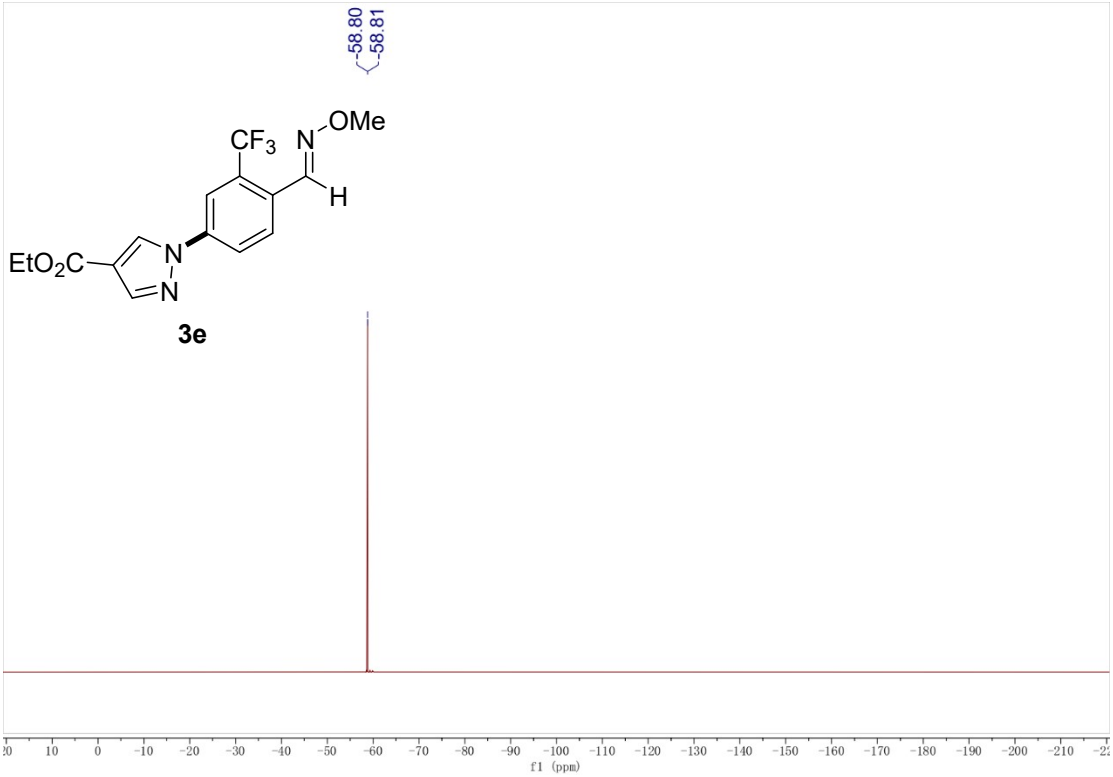
^{1}H NMR of 3e



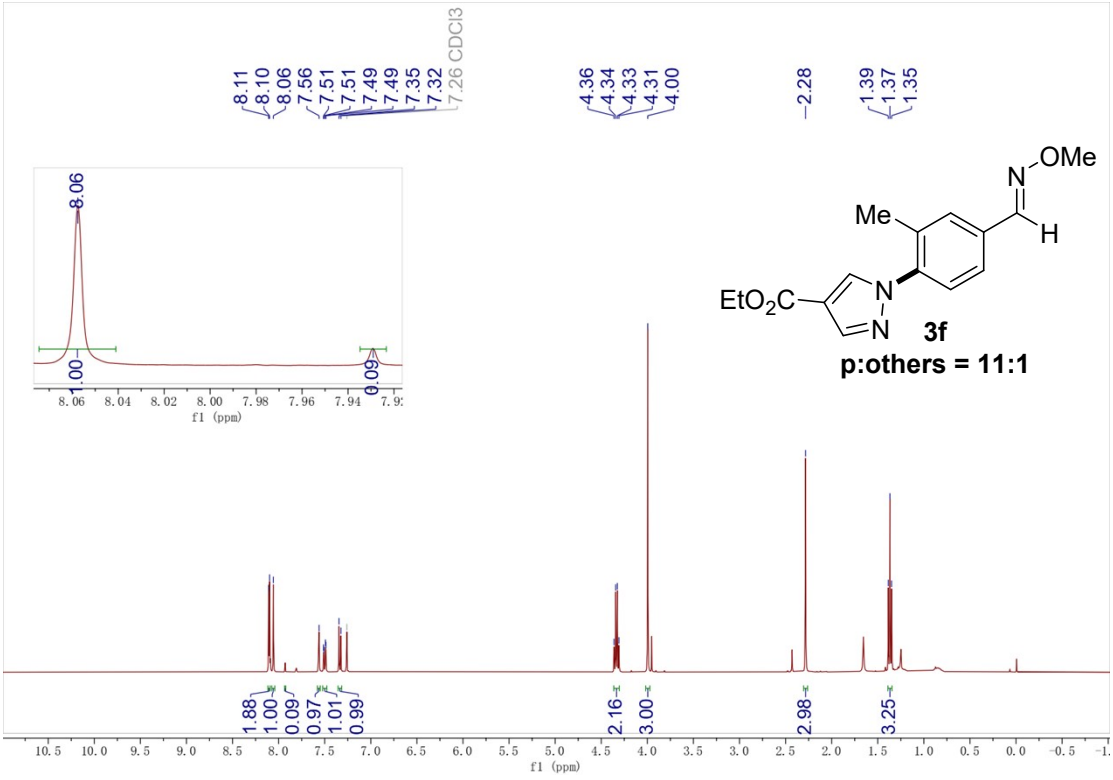
^{13}C NMR of 3e



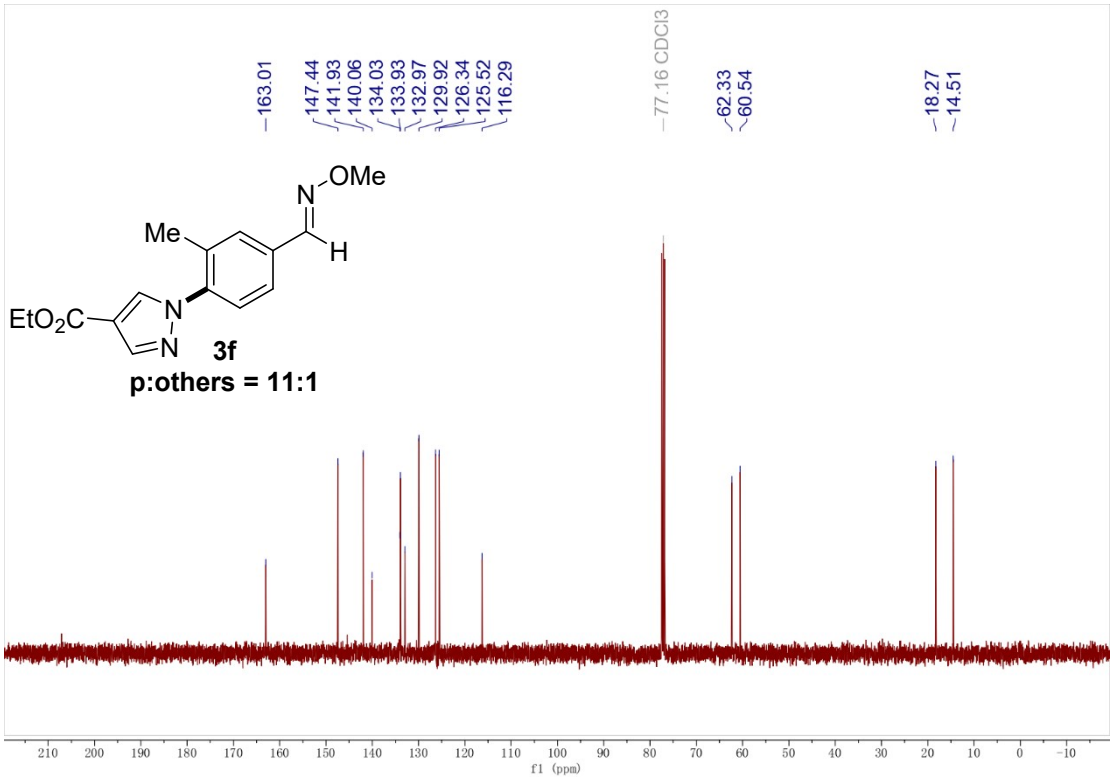
^{19}F NMR of 3e



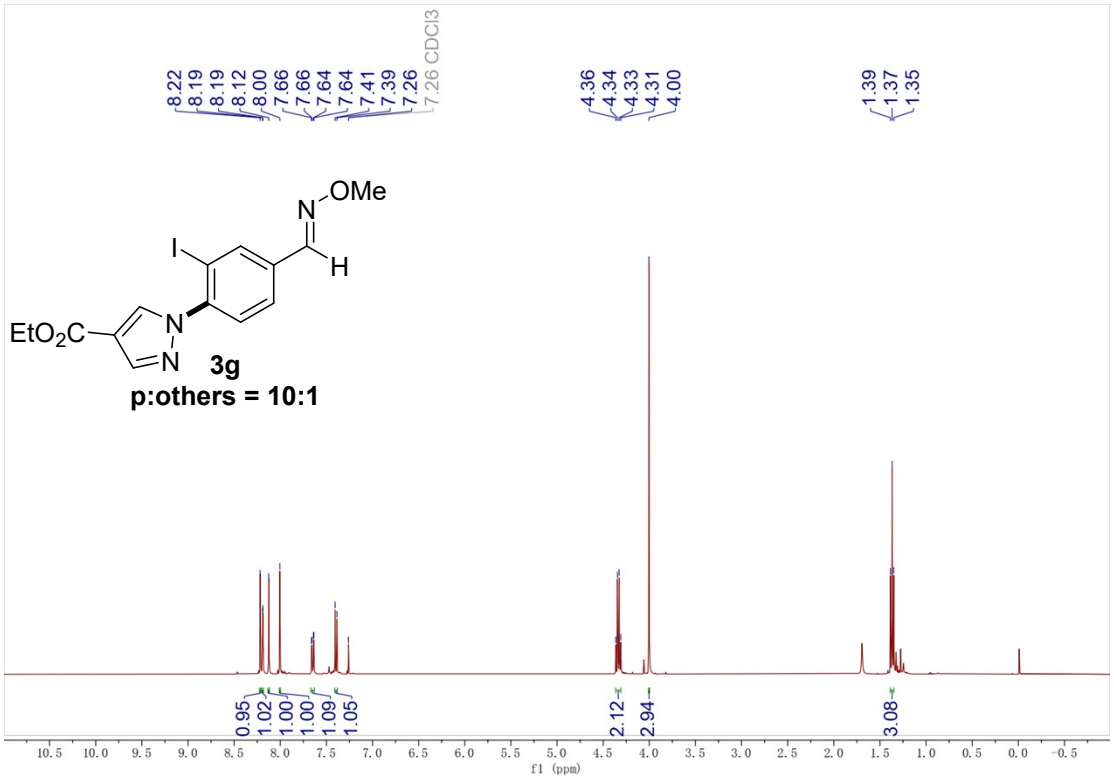
^{1}H NMR of 3f



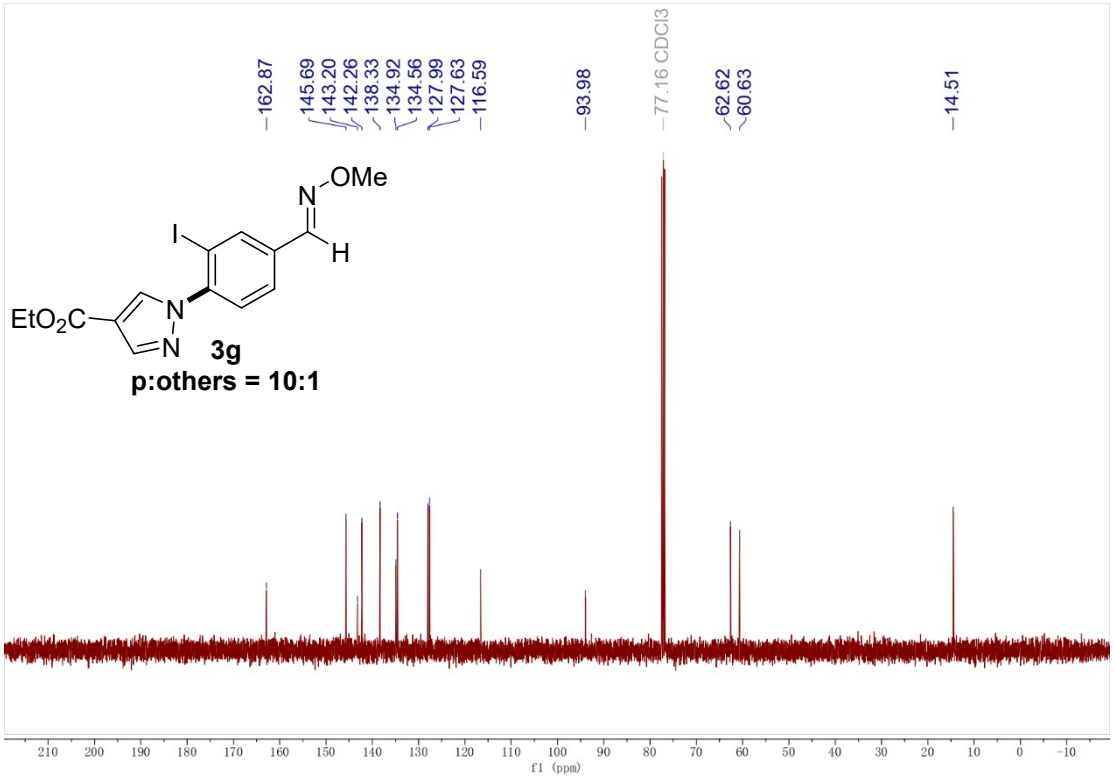
^{13}C NMR of 3f



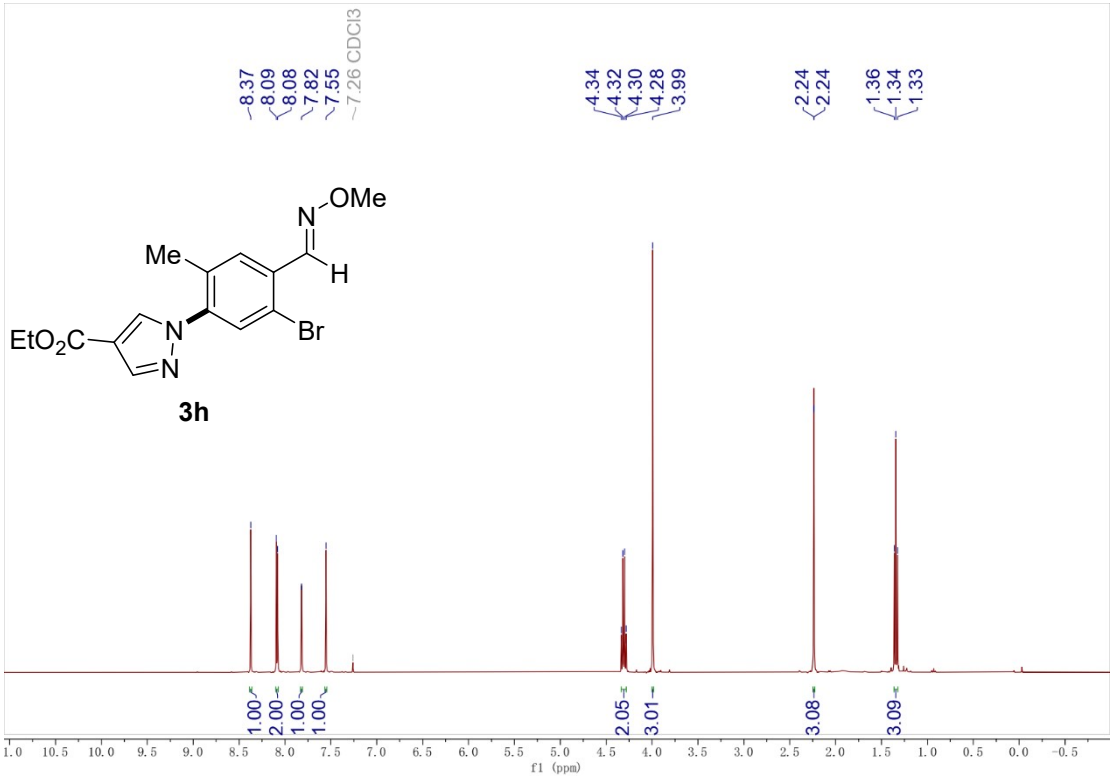
^{1}H NMR of 3g



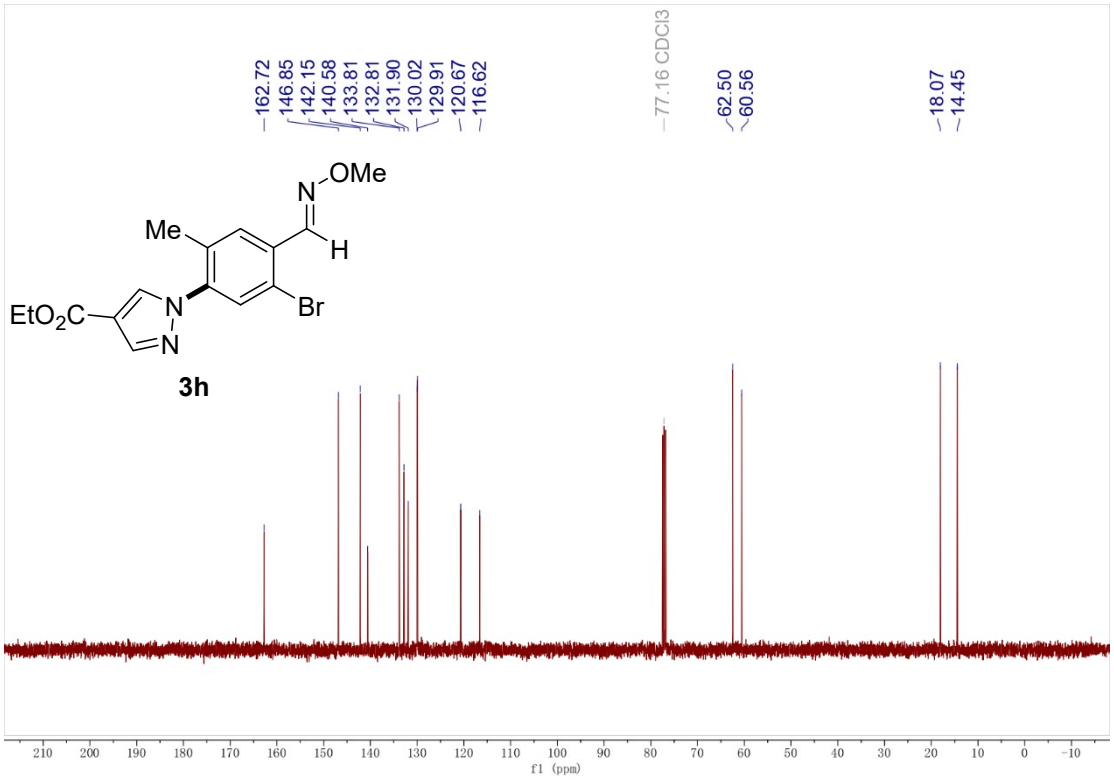
^{13}C NMR of 3g



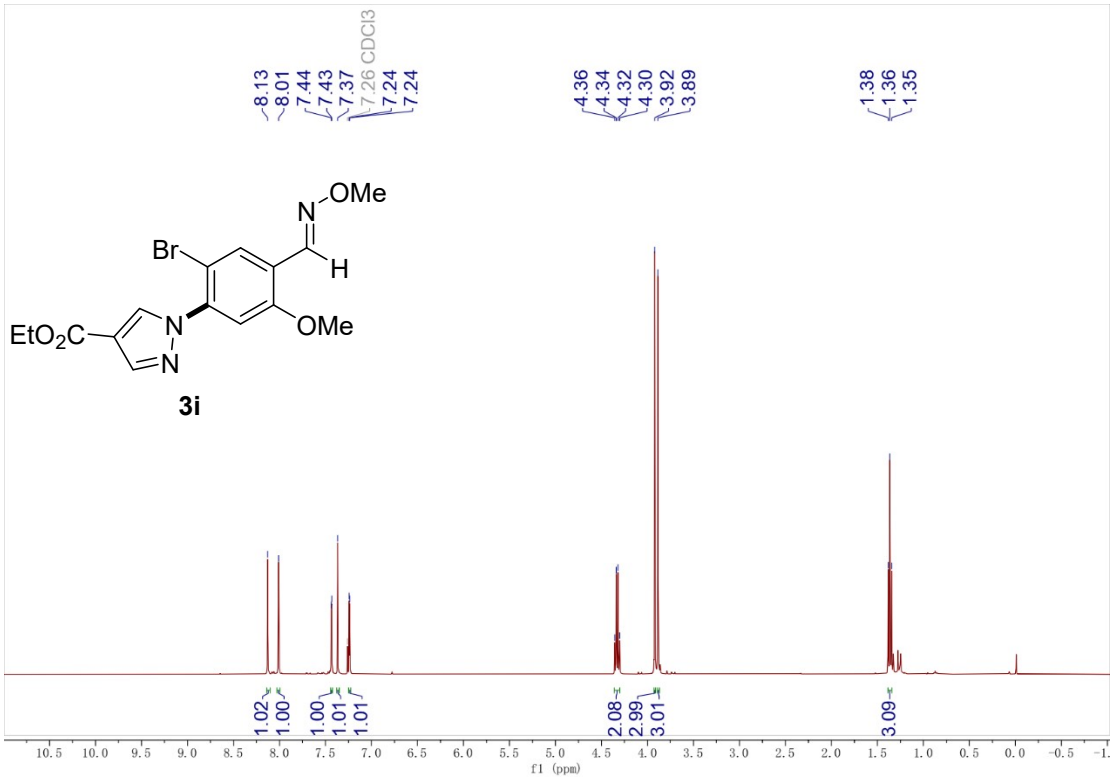
^{1}H NMR of 3h



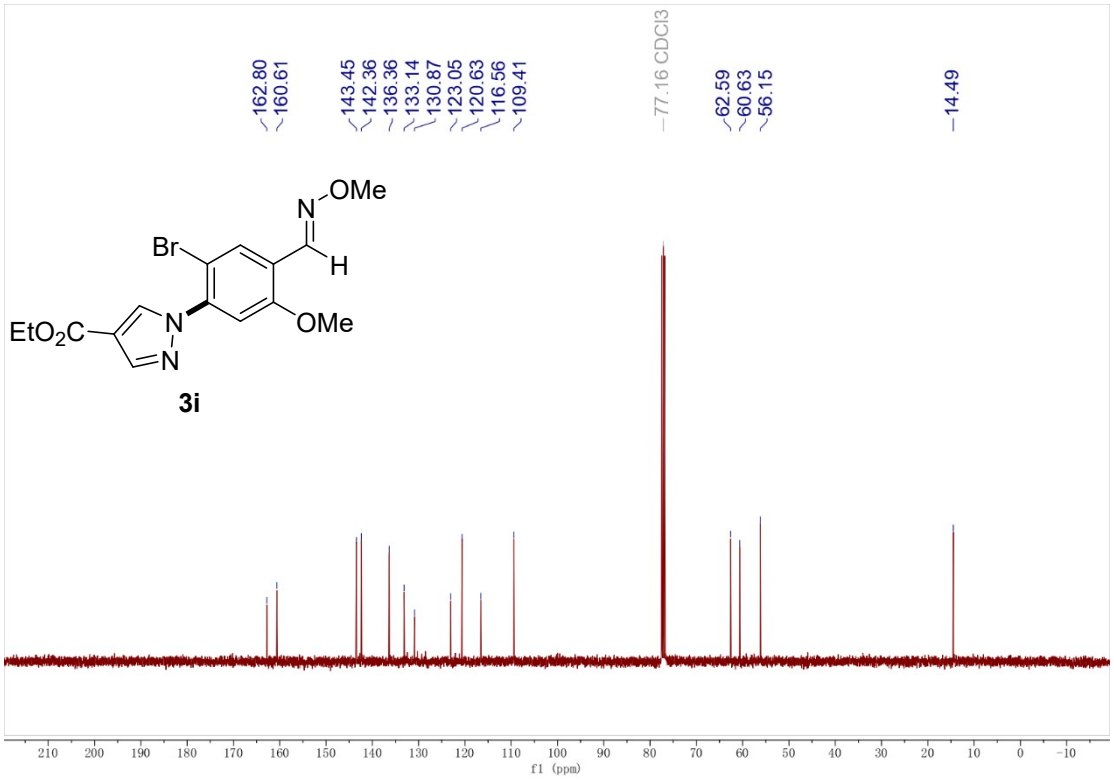
^{13}C NMR of 3h



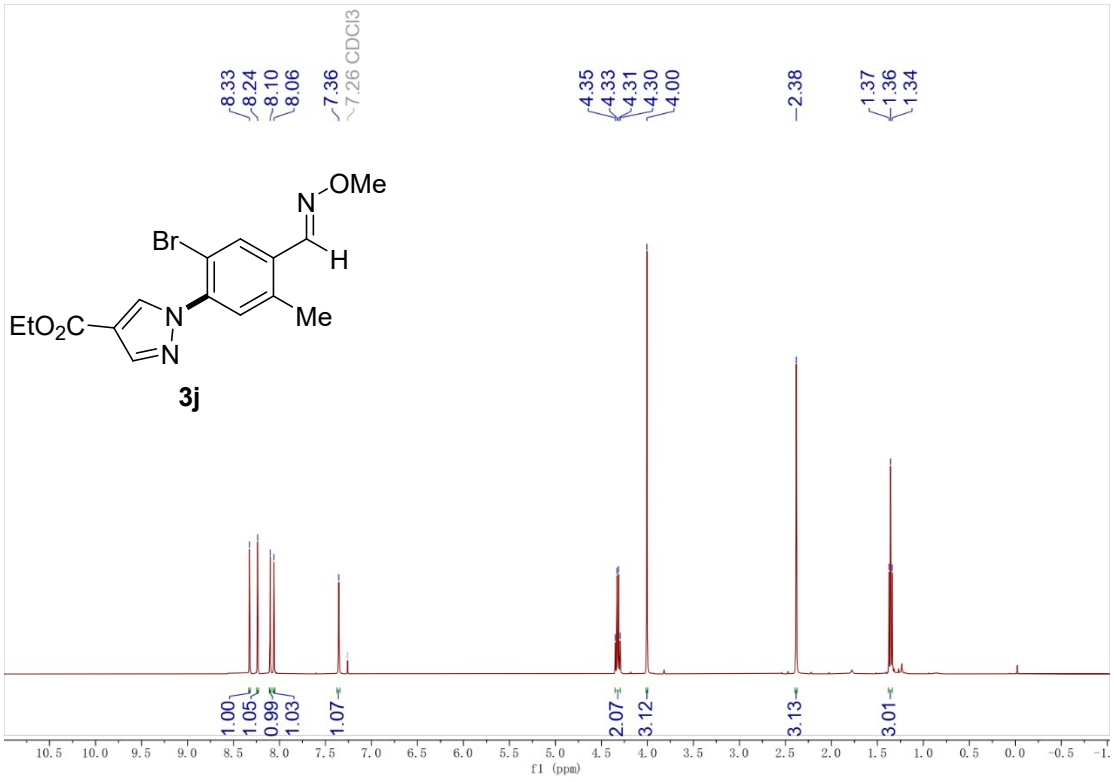
^{1}H NMR of 3i



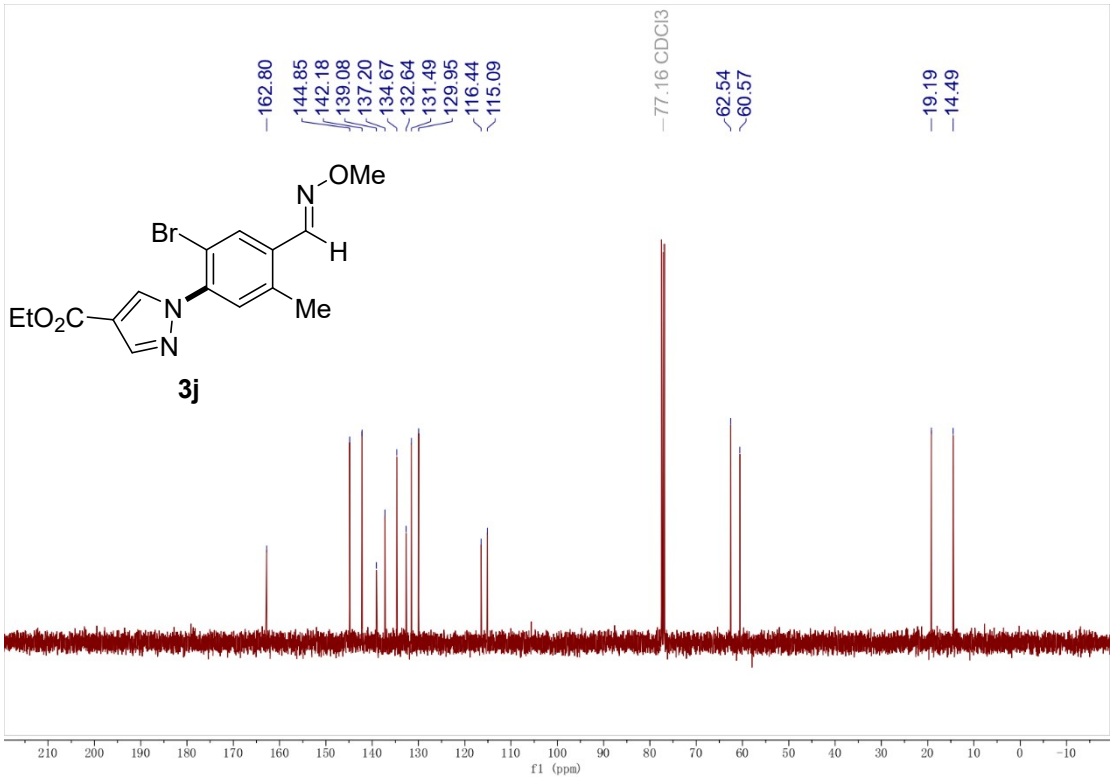
^{13}C NMR of 3i



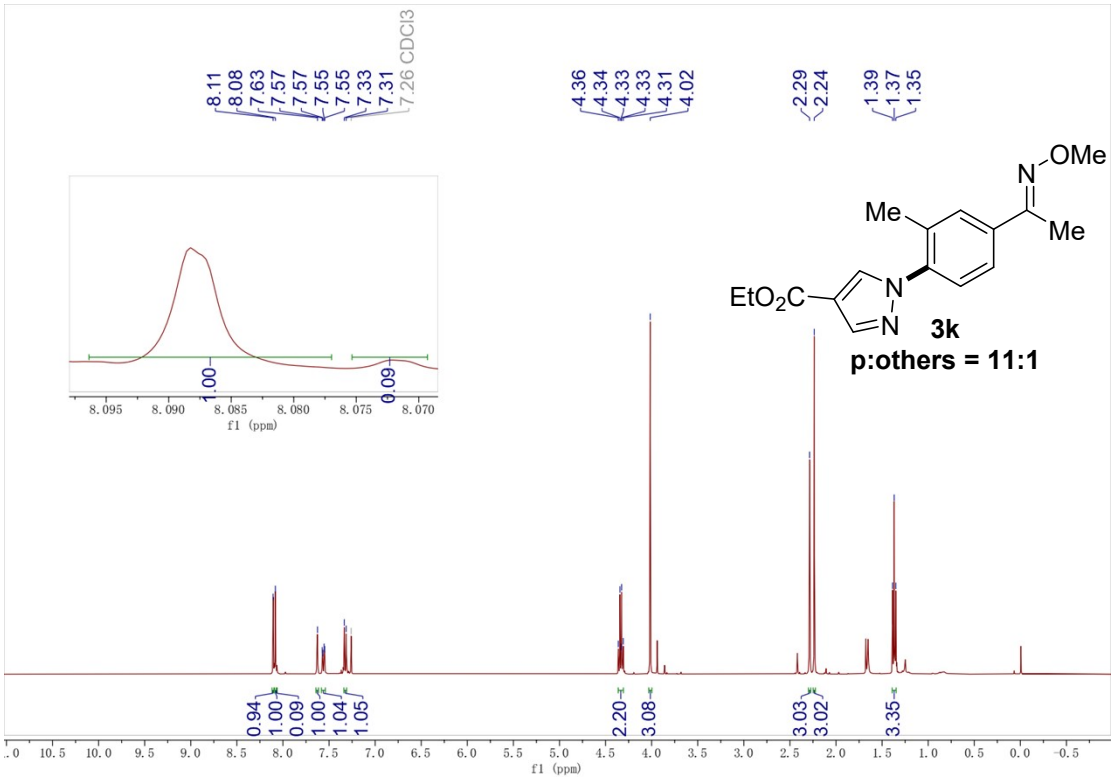
^{1}H NMR of 3j



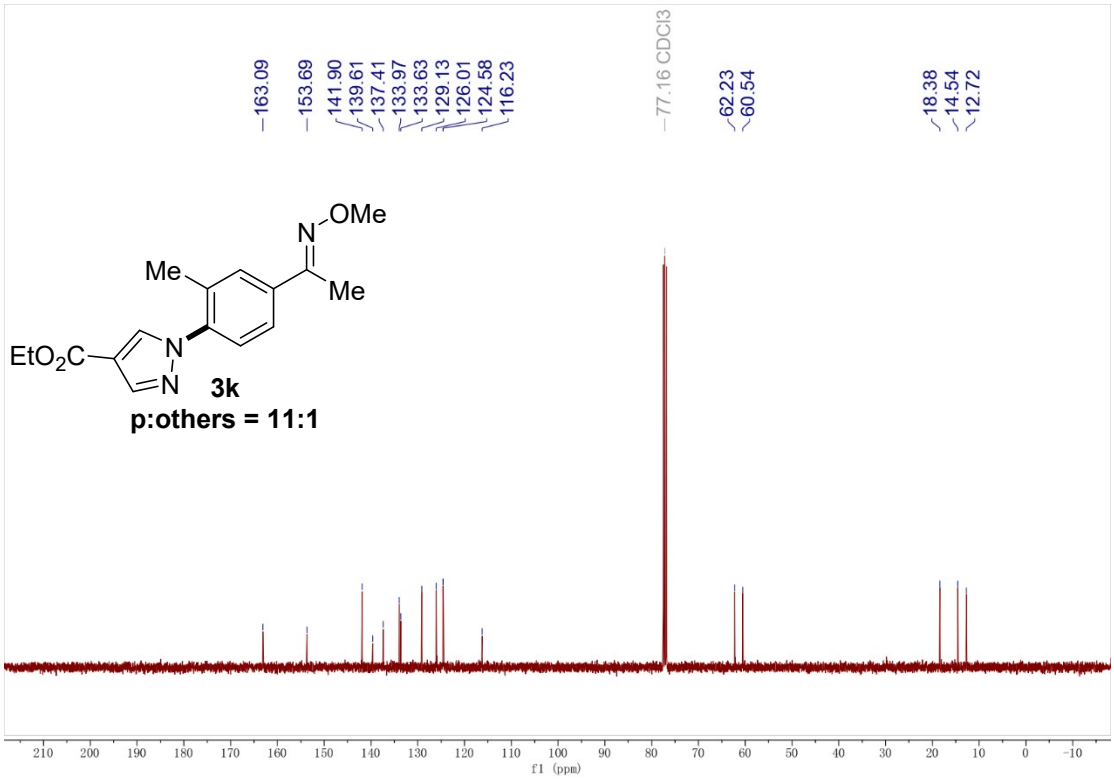
^{13}C NMR of 3j



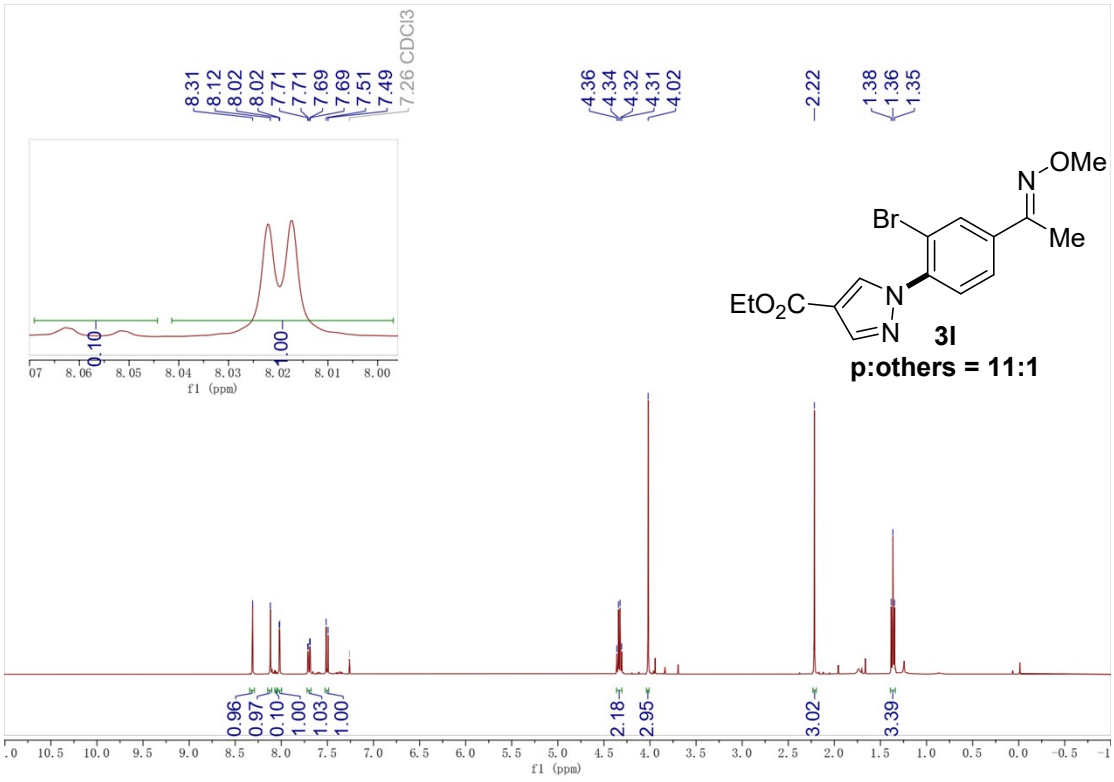
^{1}H NMR of 3k



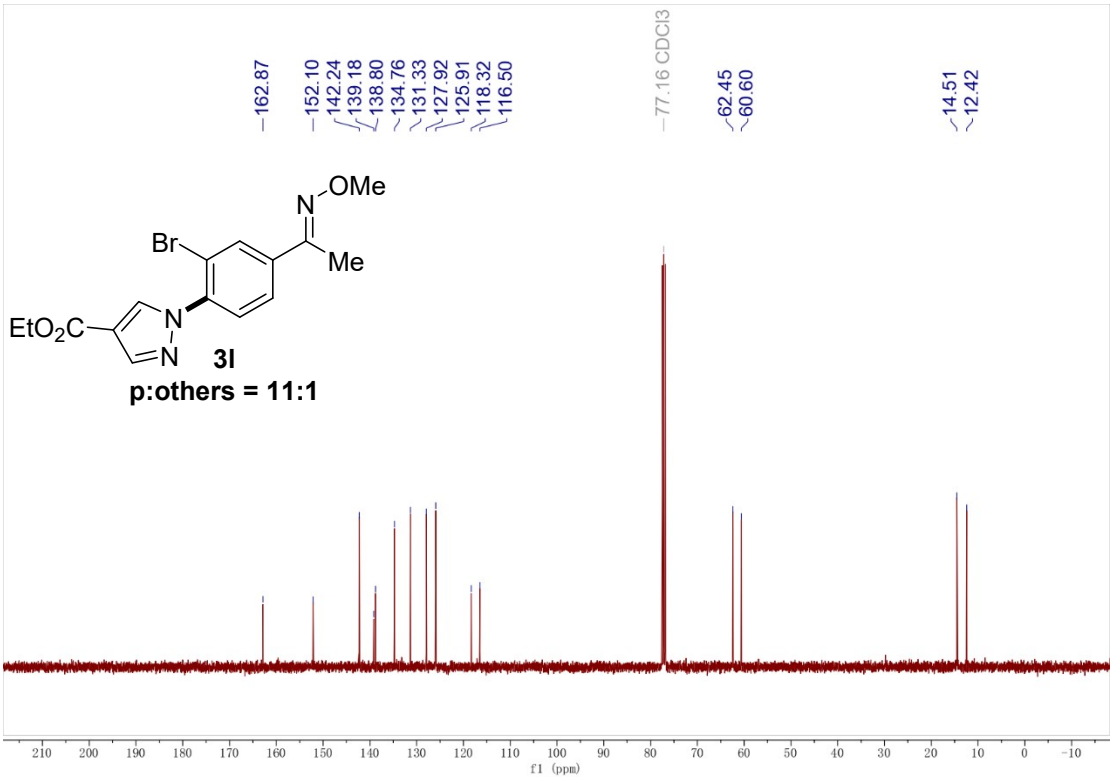
^{13}C NMR of 3k



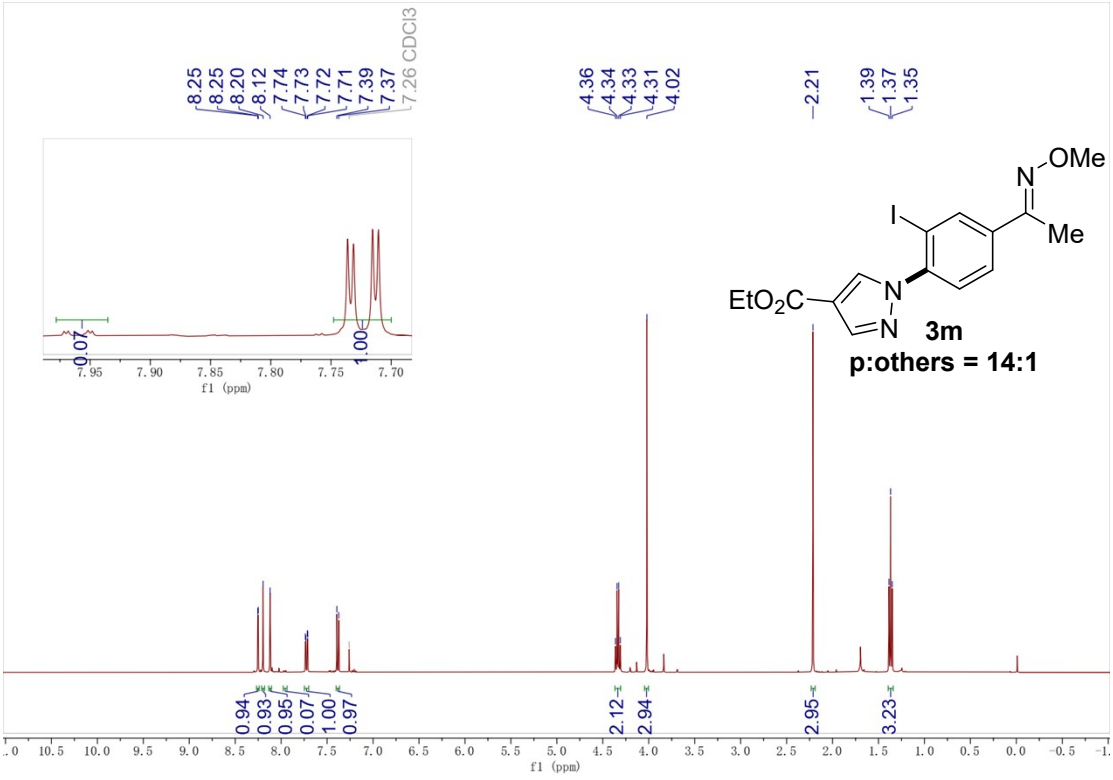
^{1}H NMR of 3l



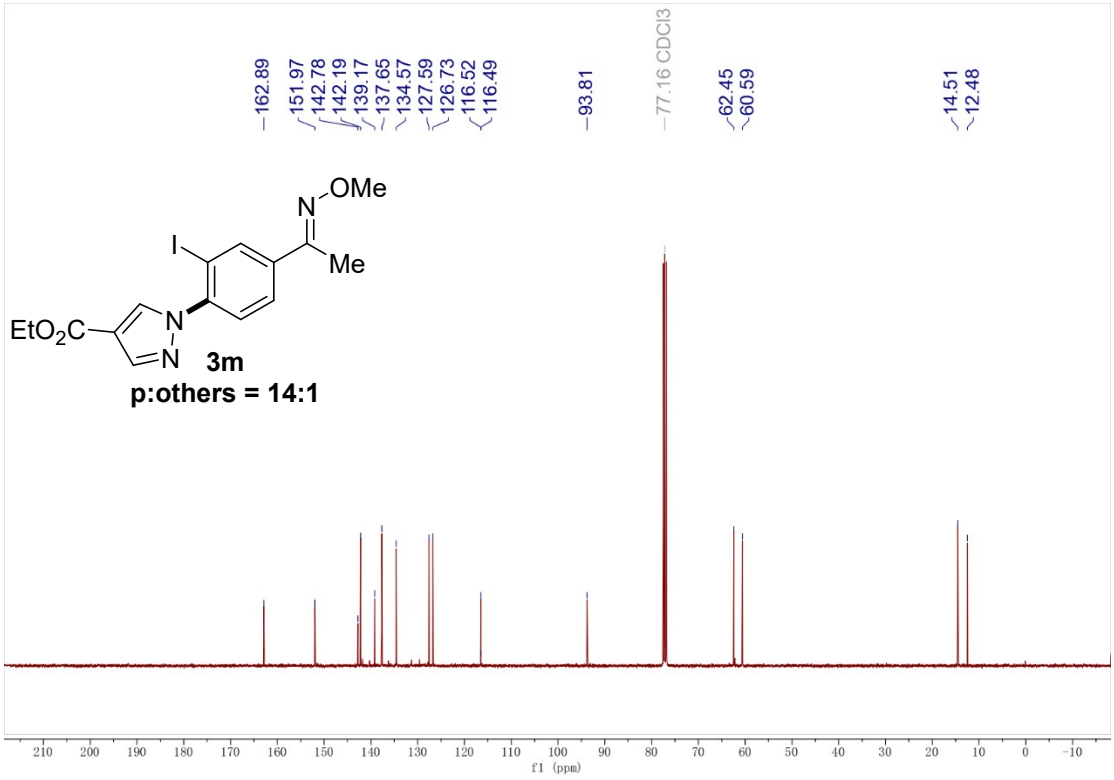
^{13}C NMR of 3l



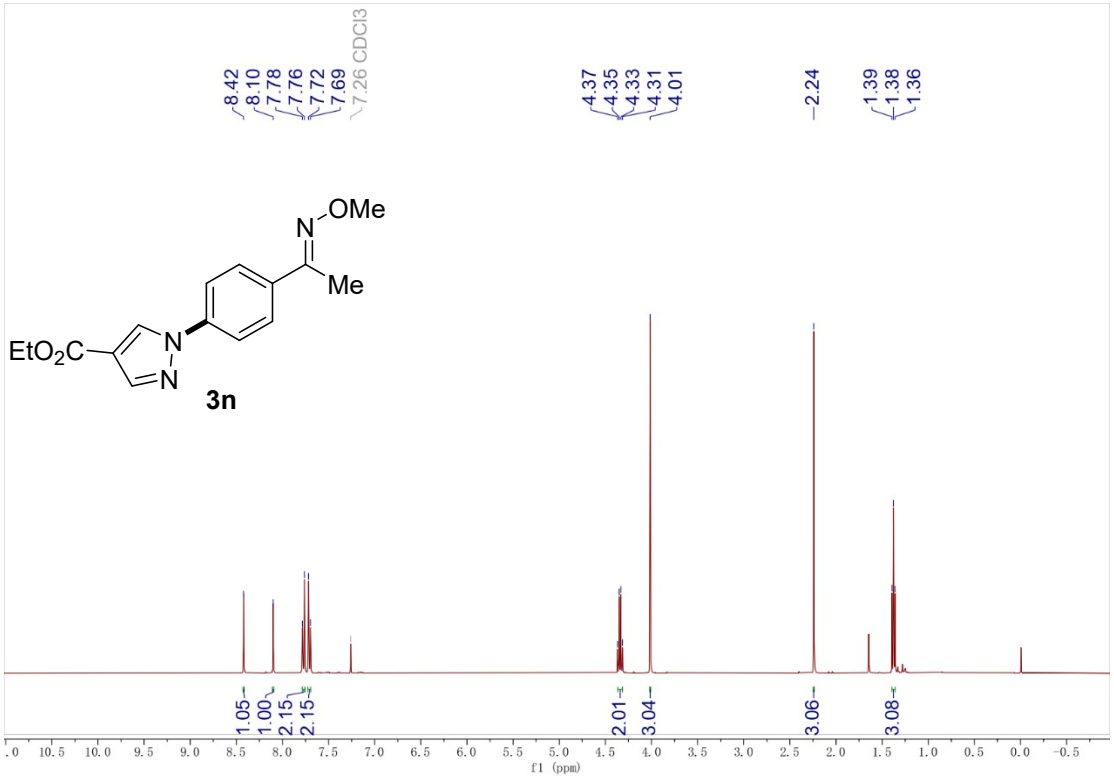
^{1}H NMR of 3m



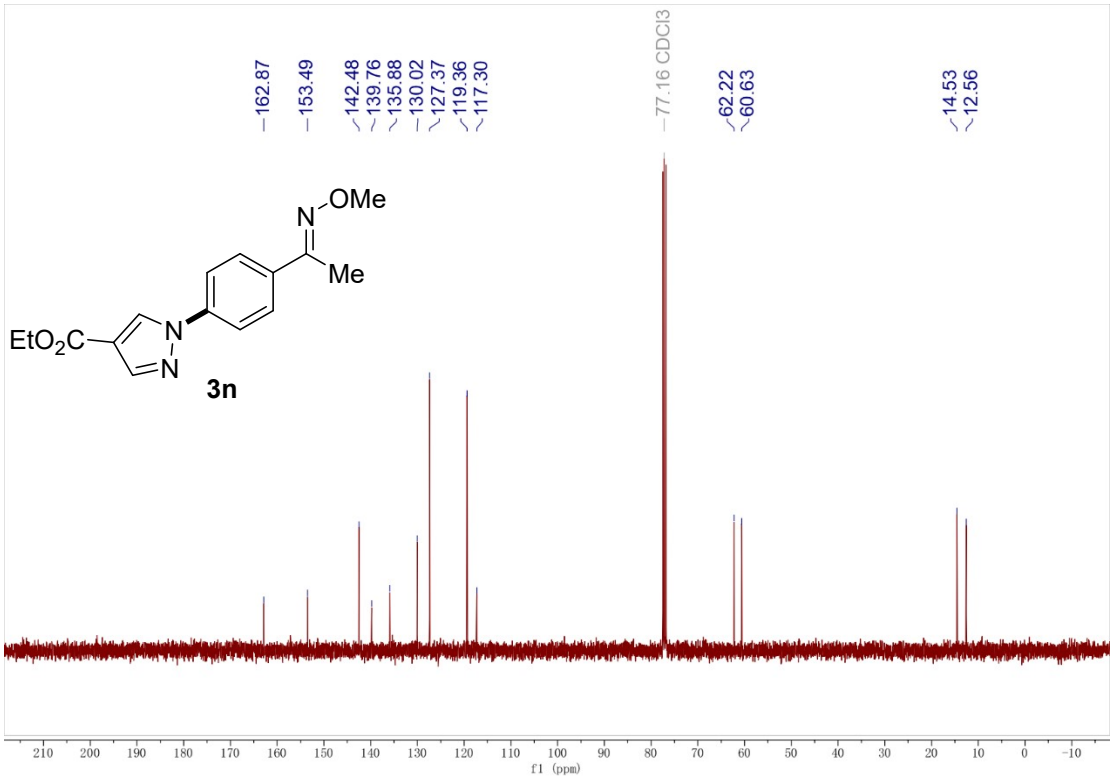
^{13}C NMR of 3m



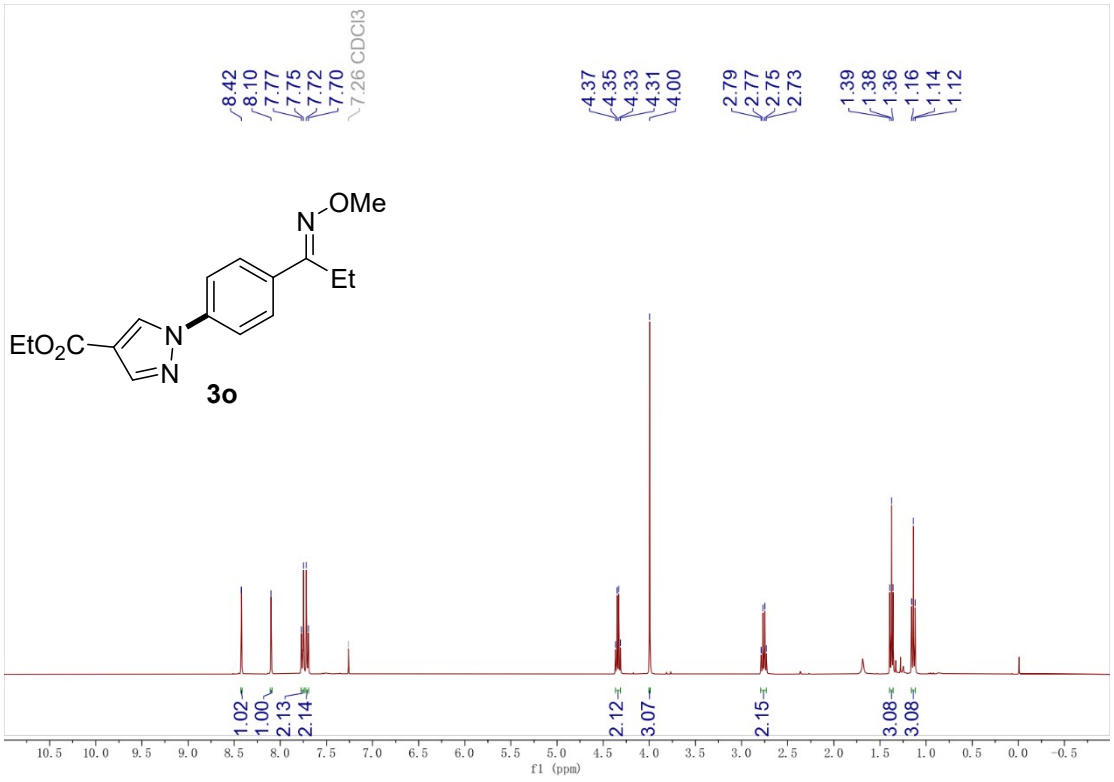
^{1}H NMR of 3n



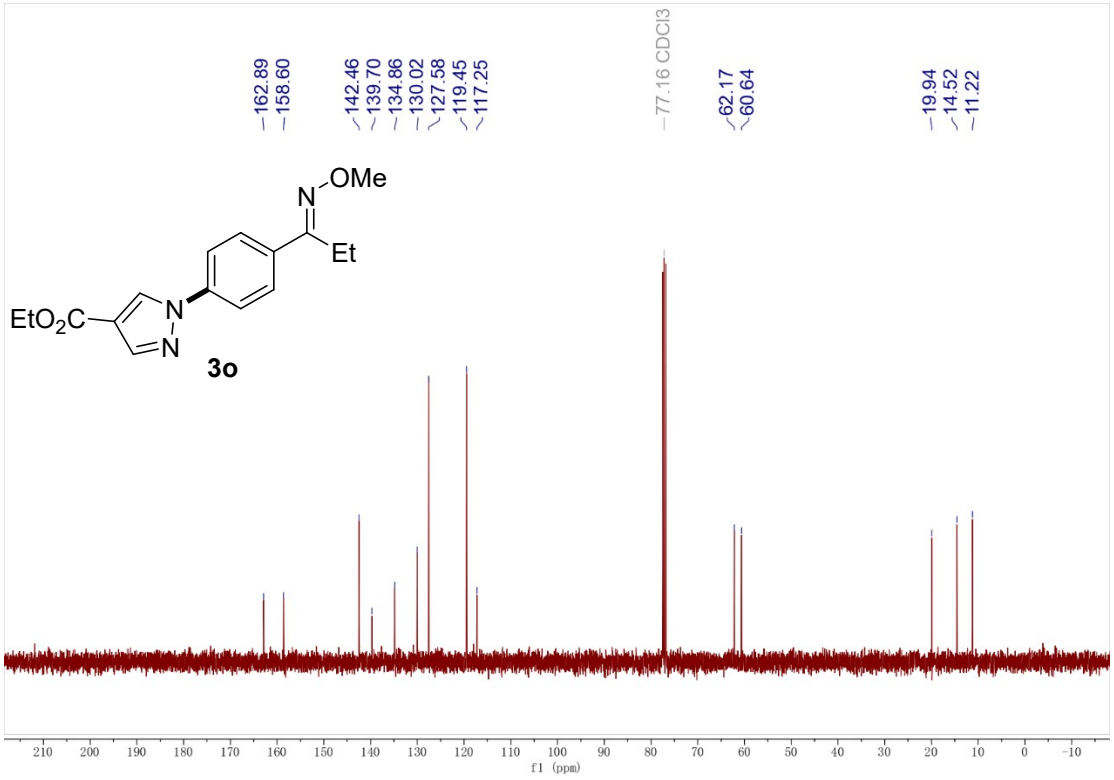
^{13}C NMR of 3n



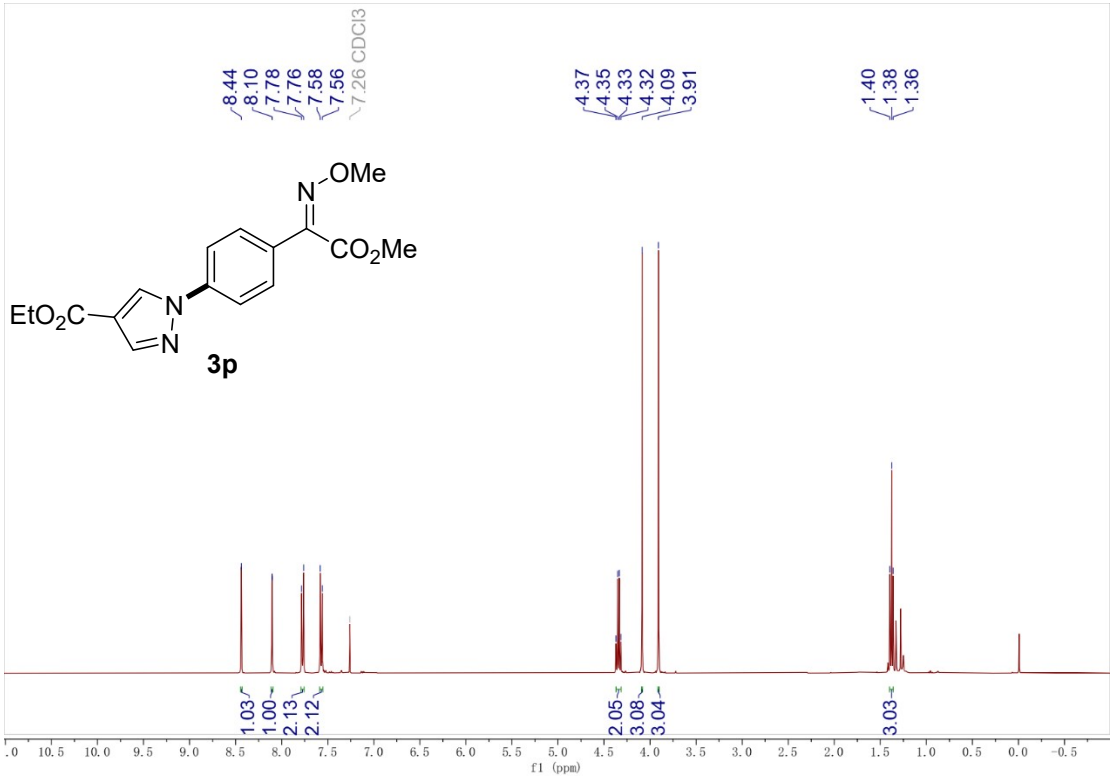
^{1}H NMR of 3o



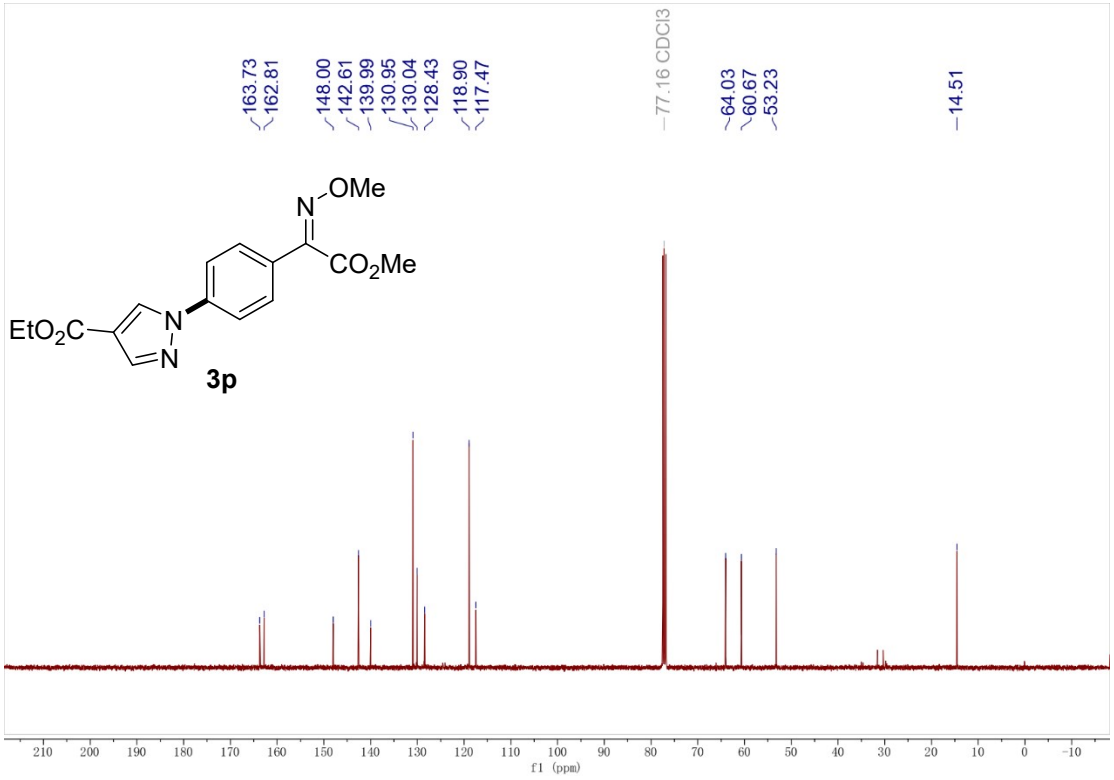
^{13}C NMR of 3o



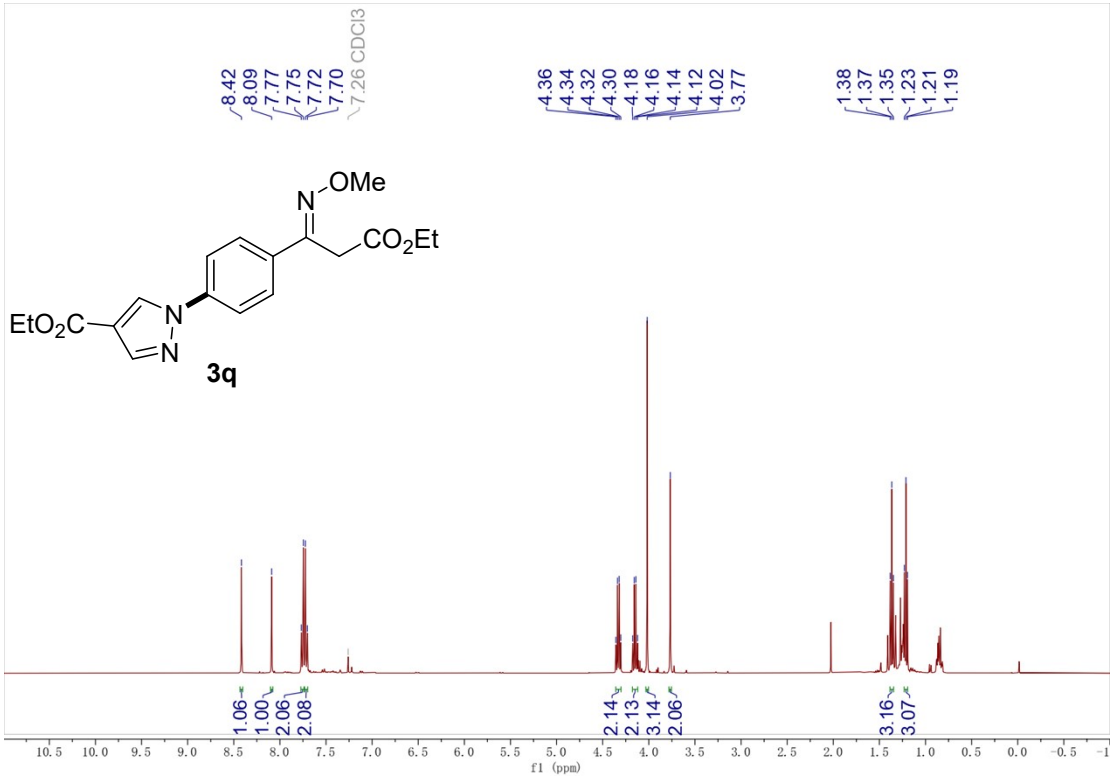
^{1}H NMR of 3p



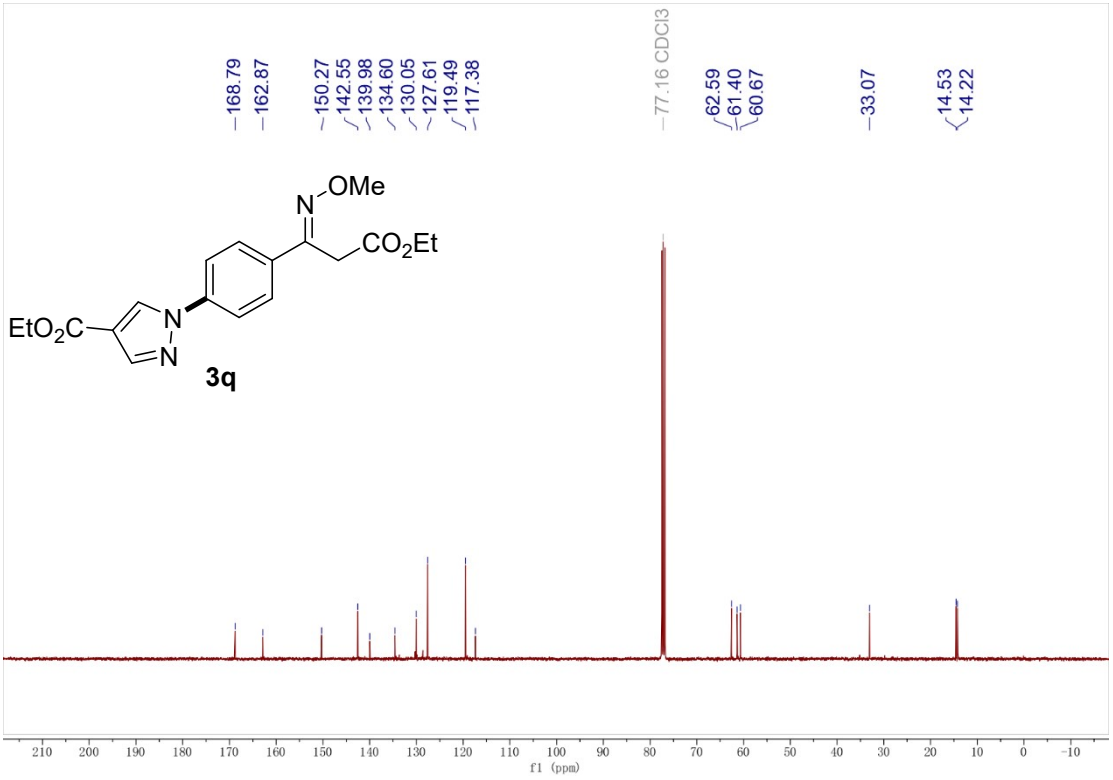
^{13}C NMR of 3p



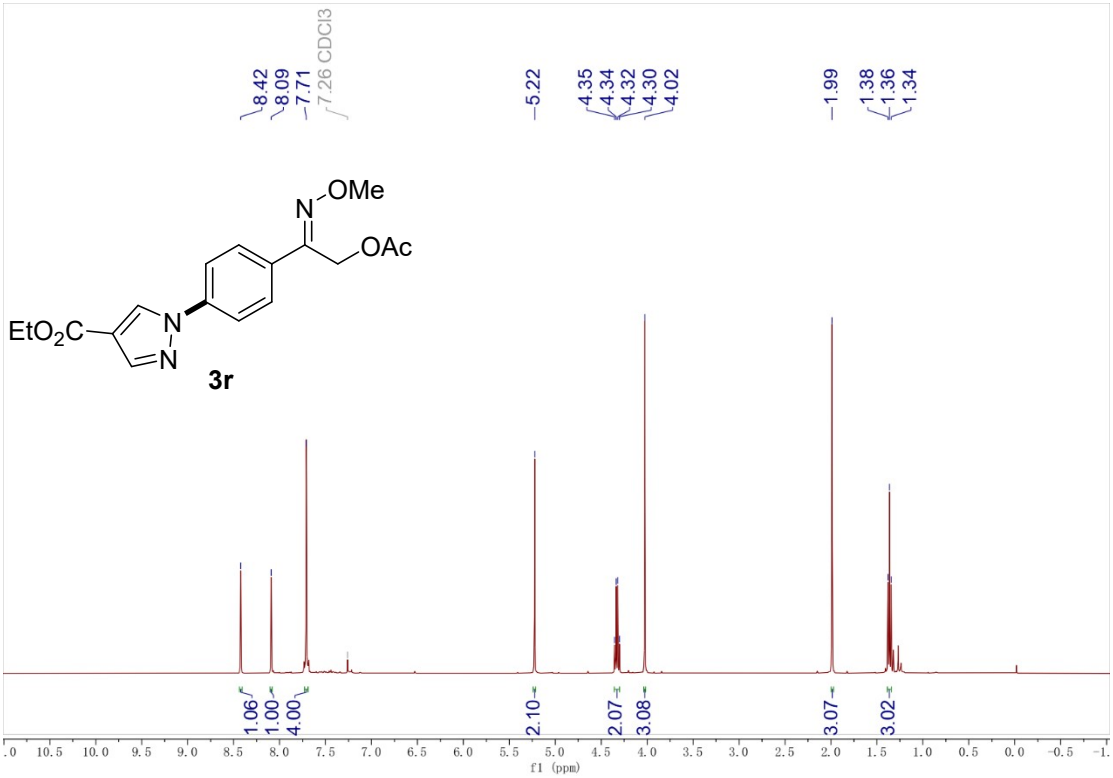
^{1}H NMR of 3q



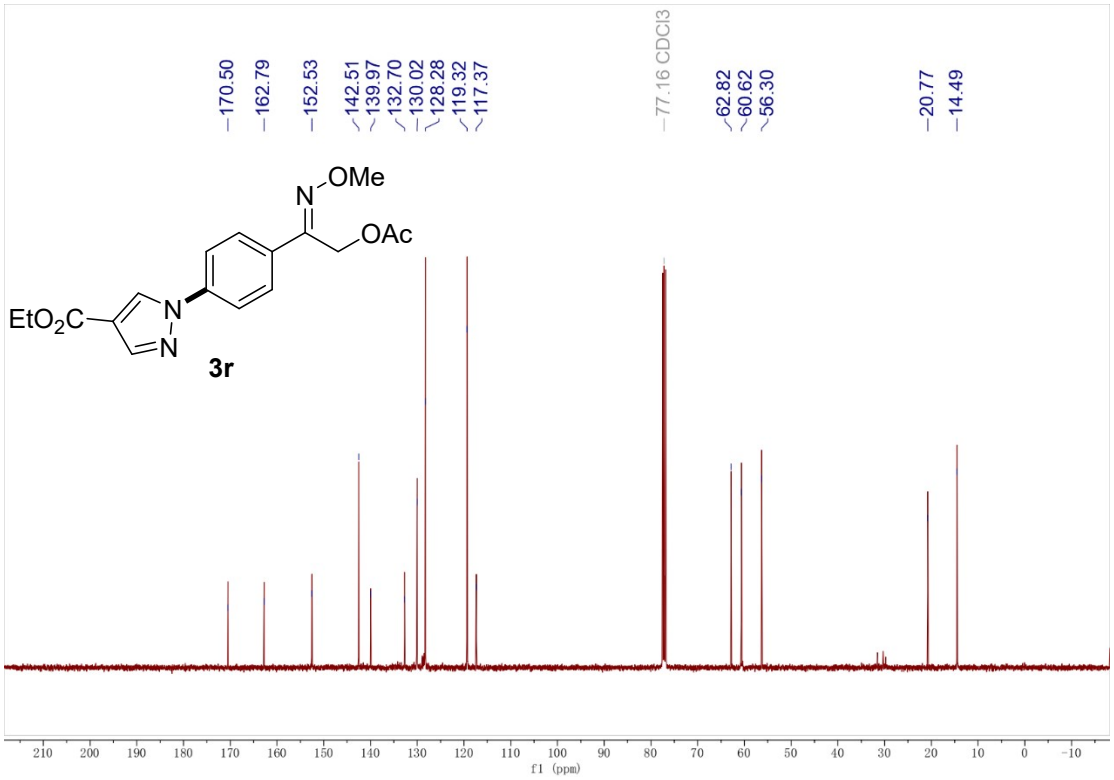
^{13}C NMR of 3q



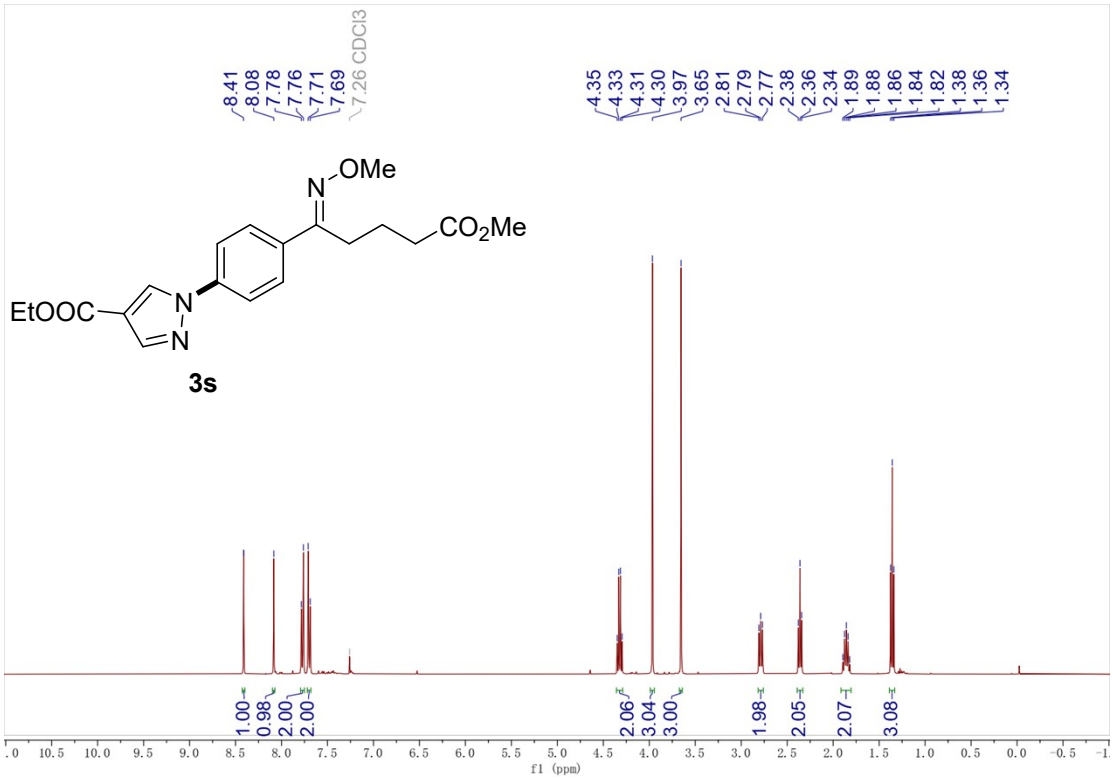
^{1}H NMR of 3r



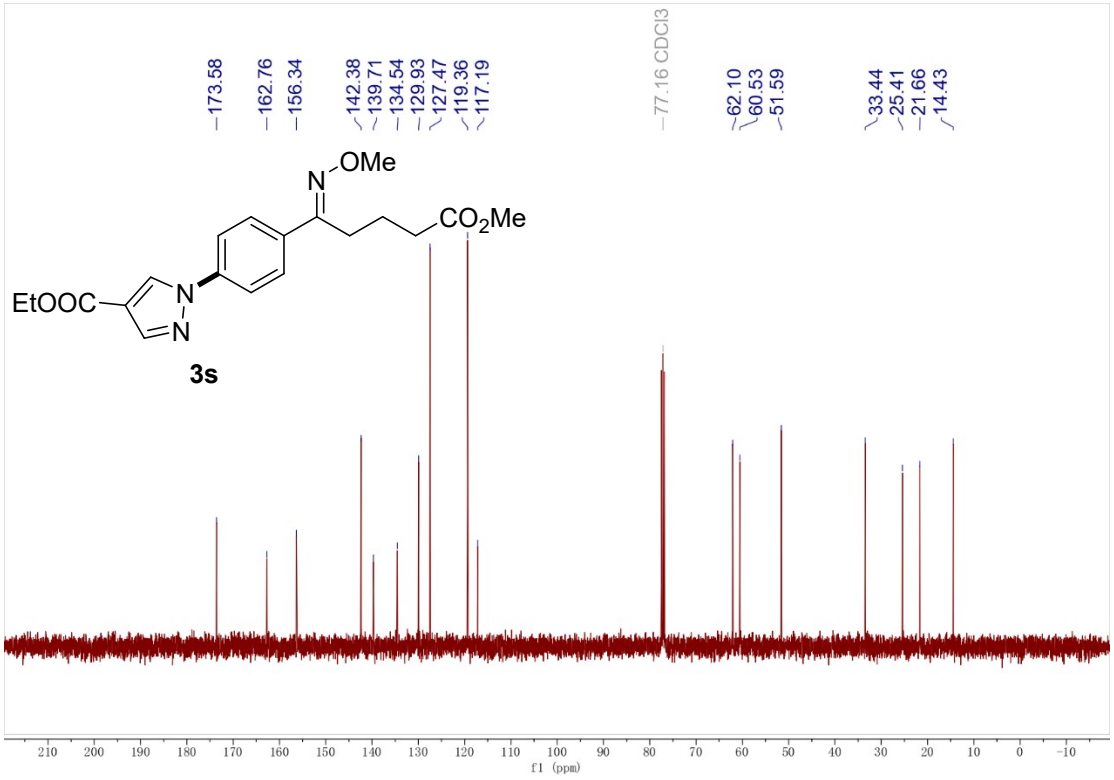
^{13}C NMR of 3r



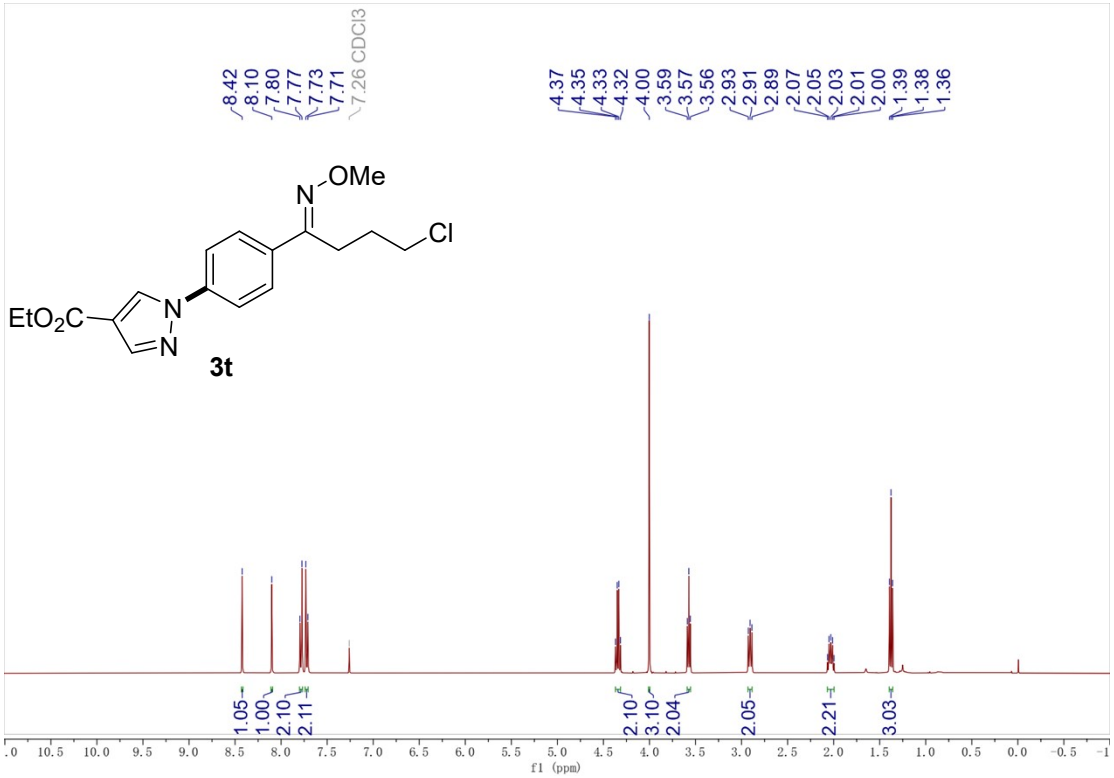
^{1}H NMR of 3s



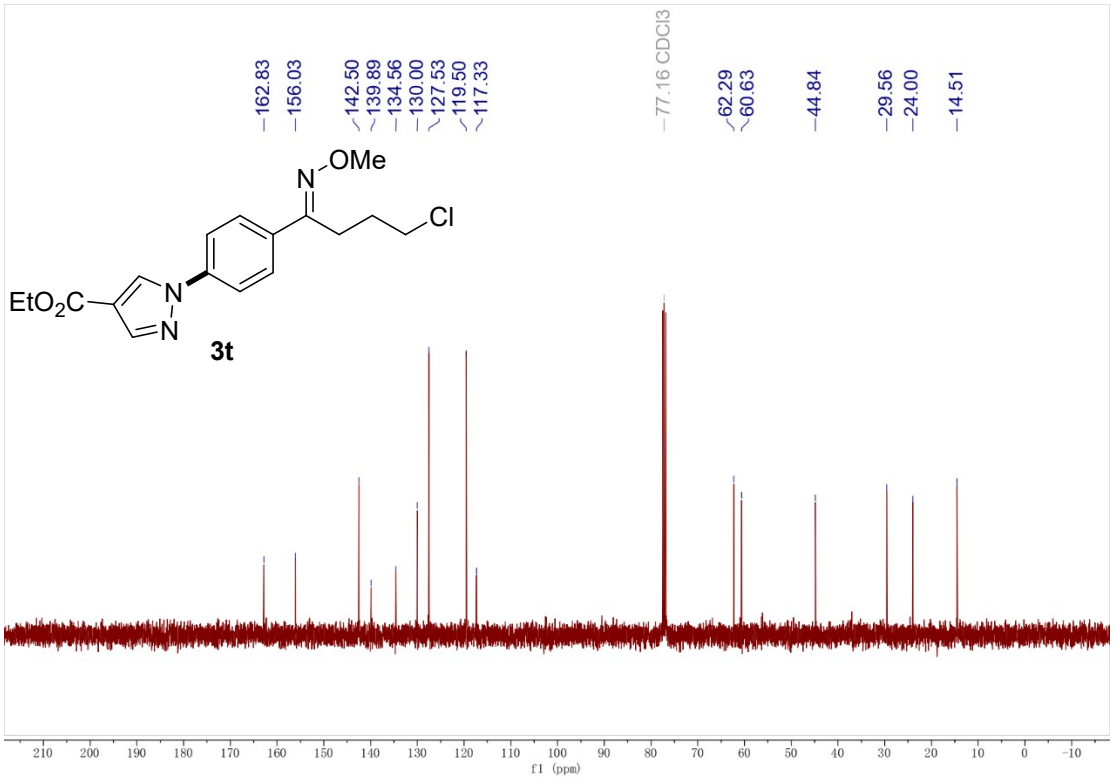
^{13}C NMR of 3s



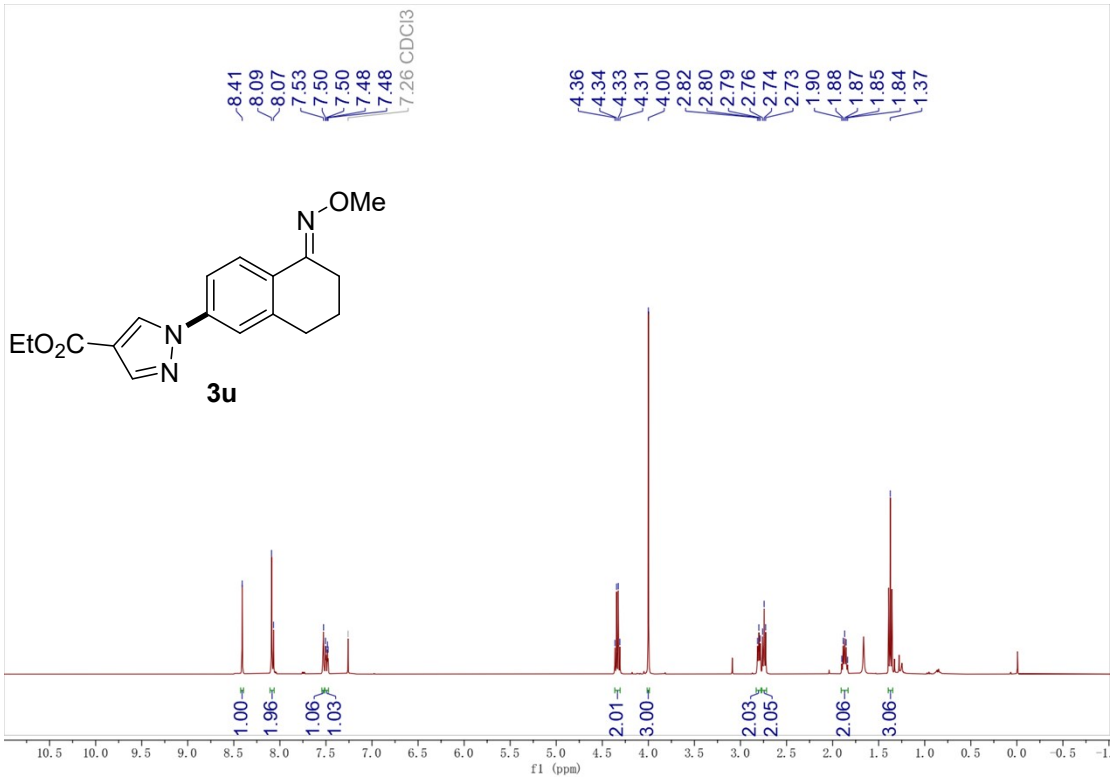
^{1}H NMR of 3t



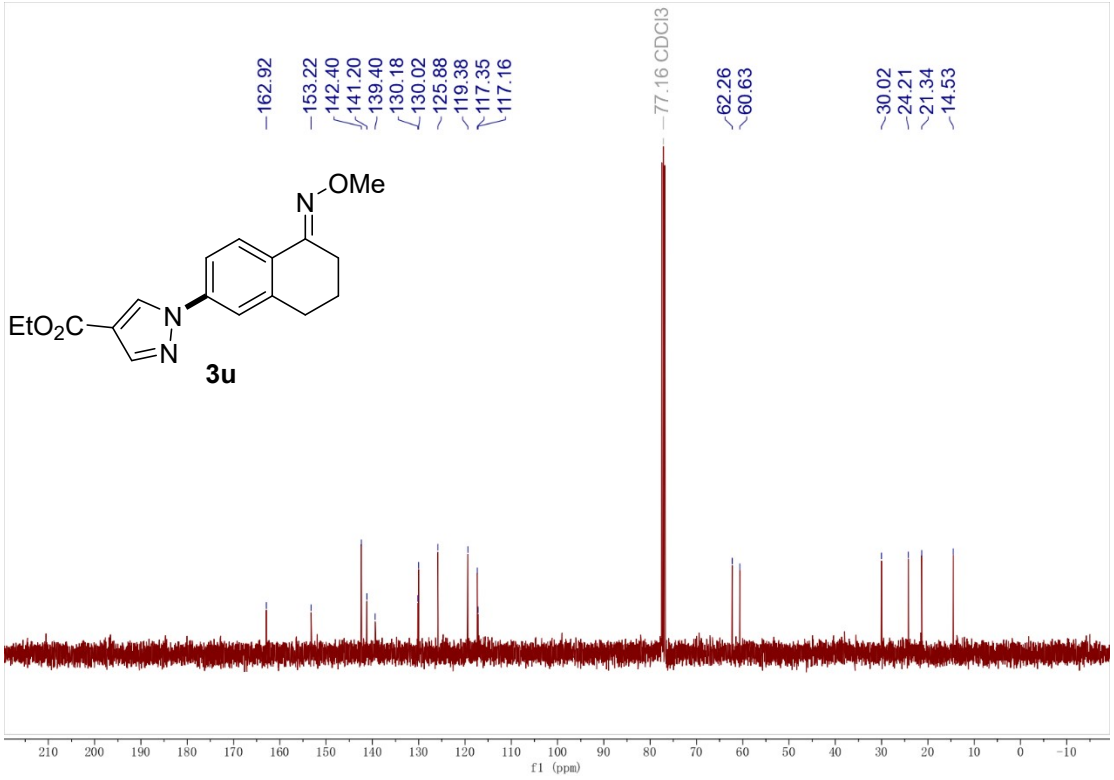
^{13}C NMR of 3t



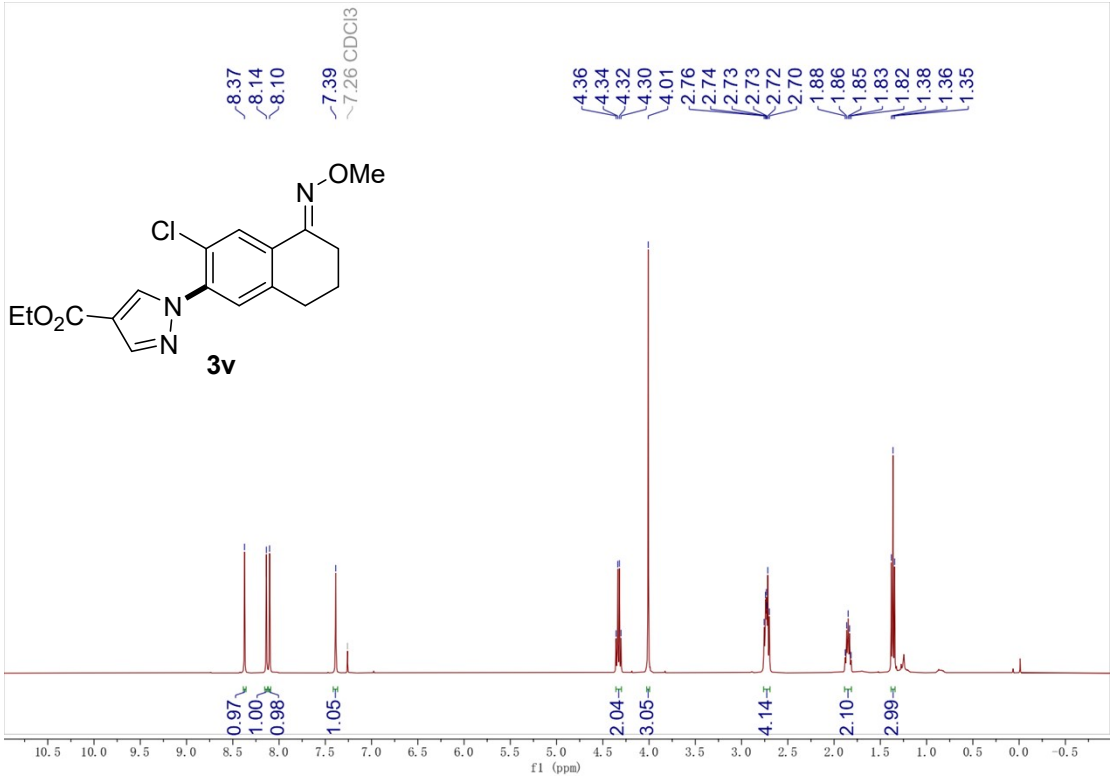
^{1}H NMR of 3u



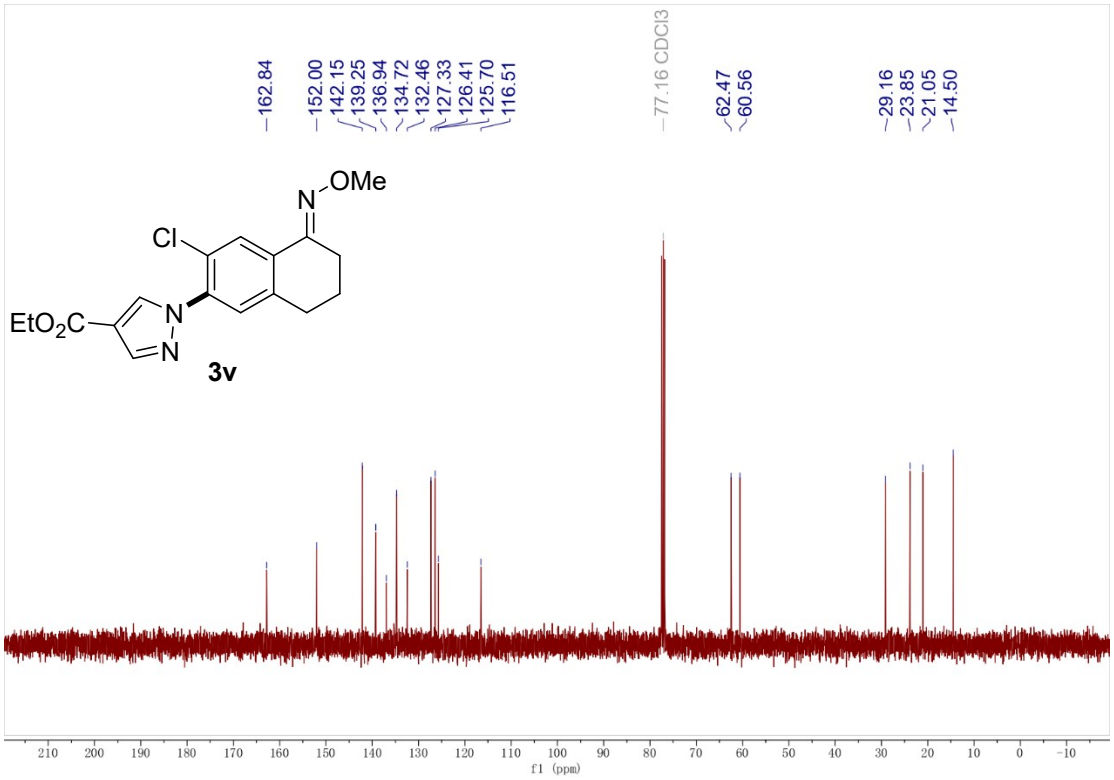
^{13}C NMR of 3u



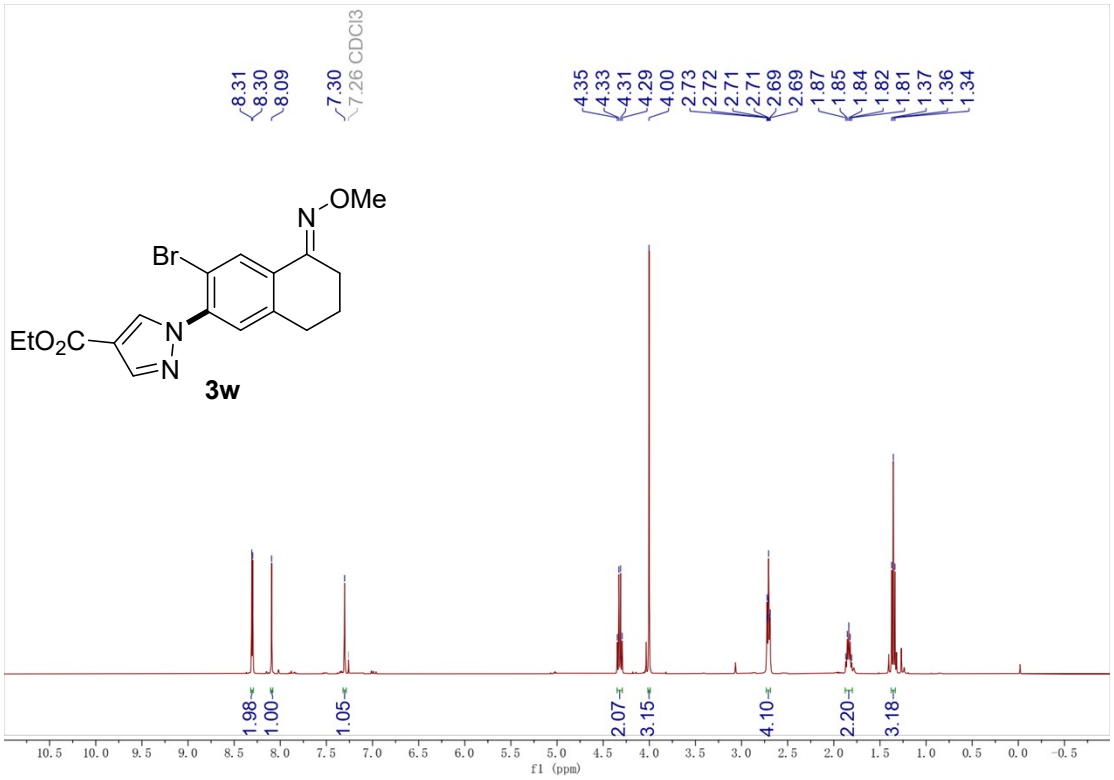
^{1}H NMR of 3v



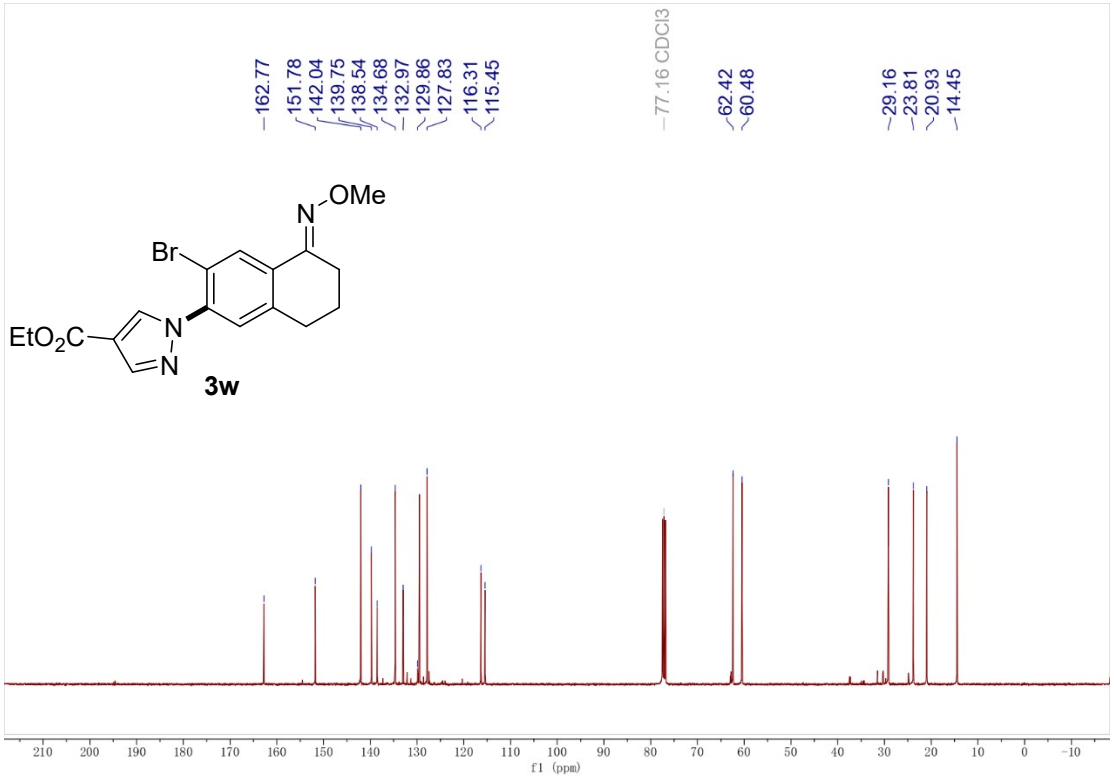
^{13}C NMR of 3v


162.84
152.00
142.15
139.25
136.94
134.72
132.46
127.33
126.41
125.70
116.51
77.16 CDCl3
62.47
60.56
29.16
23.85
21.05
14.50
OMe
N
Cl
EtO2C
N
N
3v
f1 (ppm)

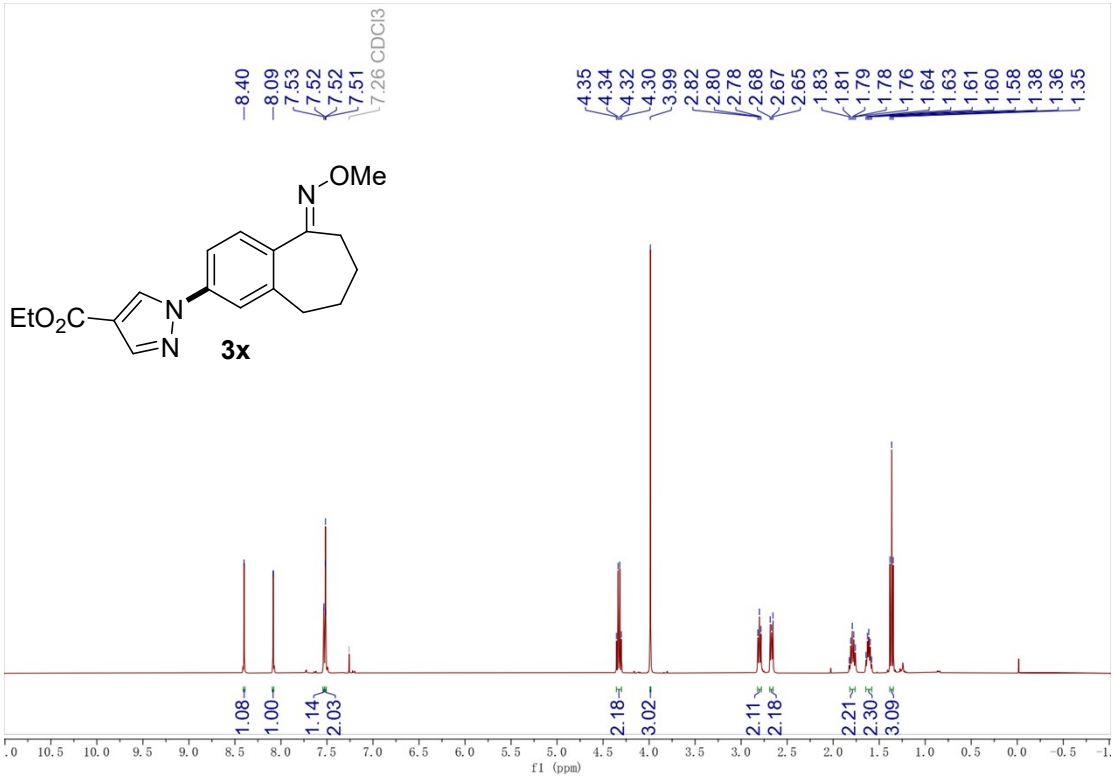
^{1}H NMR of 3w


8.31
8.30
8.09
7.30
7.26 CDCl3
4.35
4.33
4.31
4.29
4.00
2.73
2.72
2.71
2.71
2.69
2.69
1.87
1.85
1.84
1.82
1.81
1.37
1.36
1.34
OMe
N
Br
EtO2C
N
N
3w
1.98
1.00
1.05
2.07
3.15
4.10
2.20
3.18
f1 (ppm)

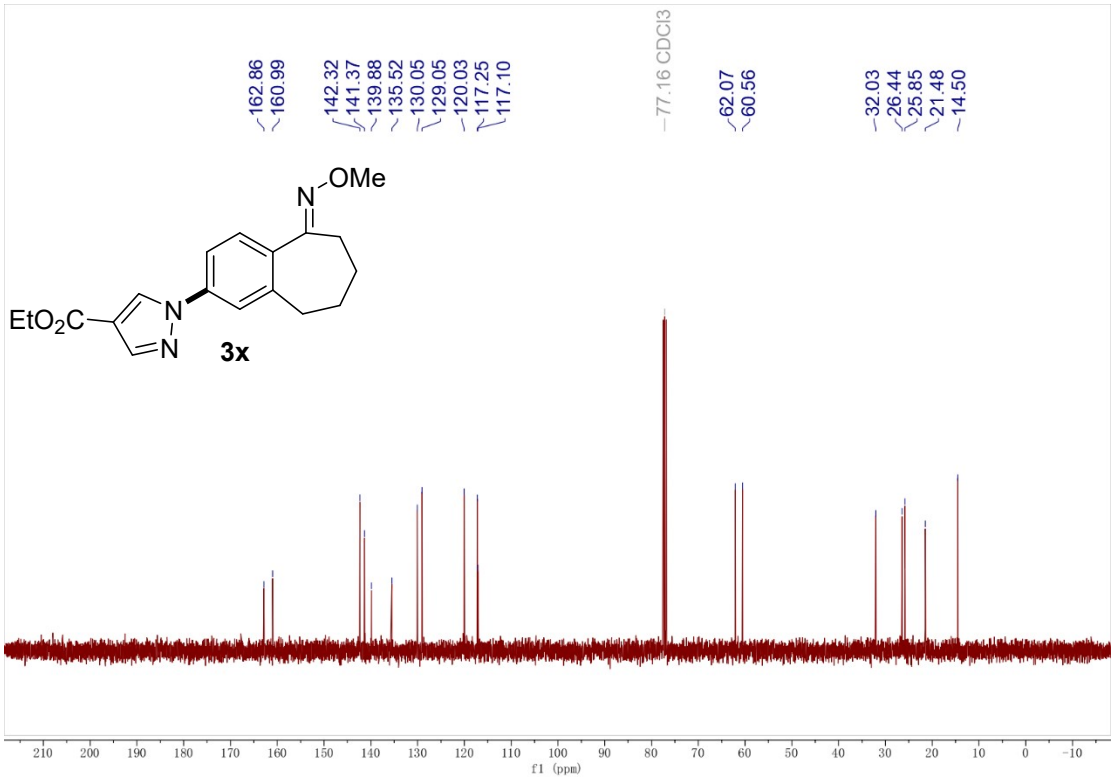
^{13}C NMR of 3w



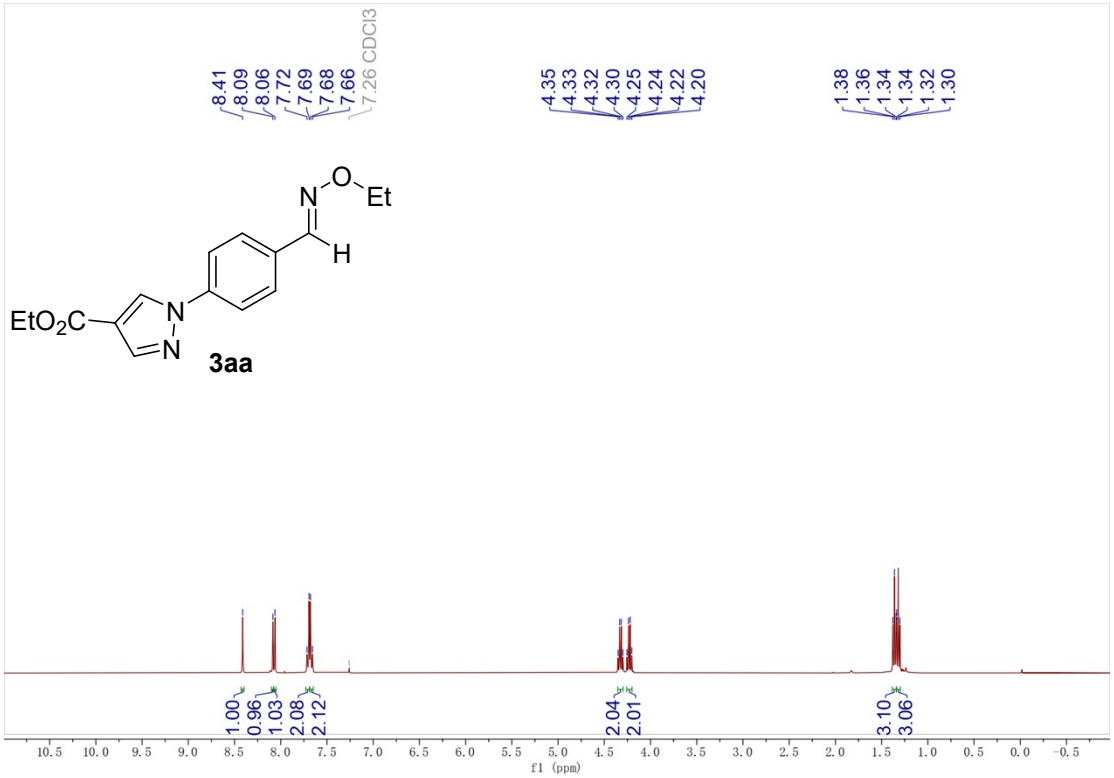
^{1}H NMR of 3x



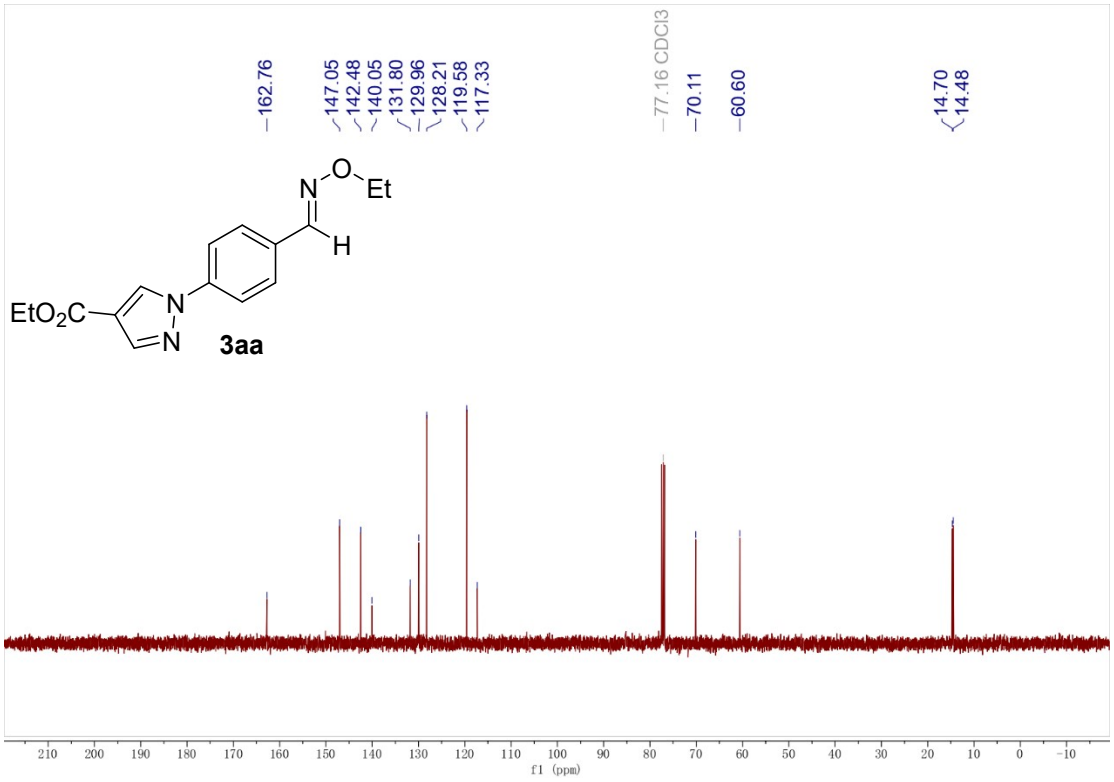
^{13}C NMR of 3x



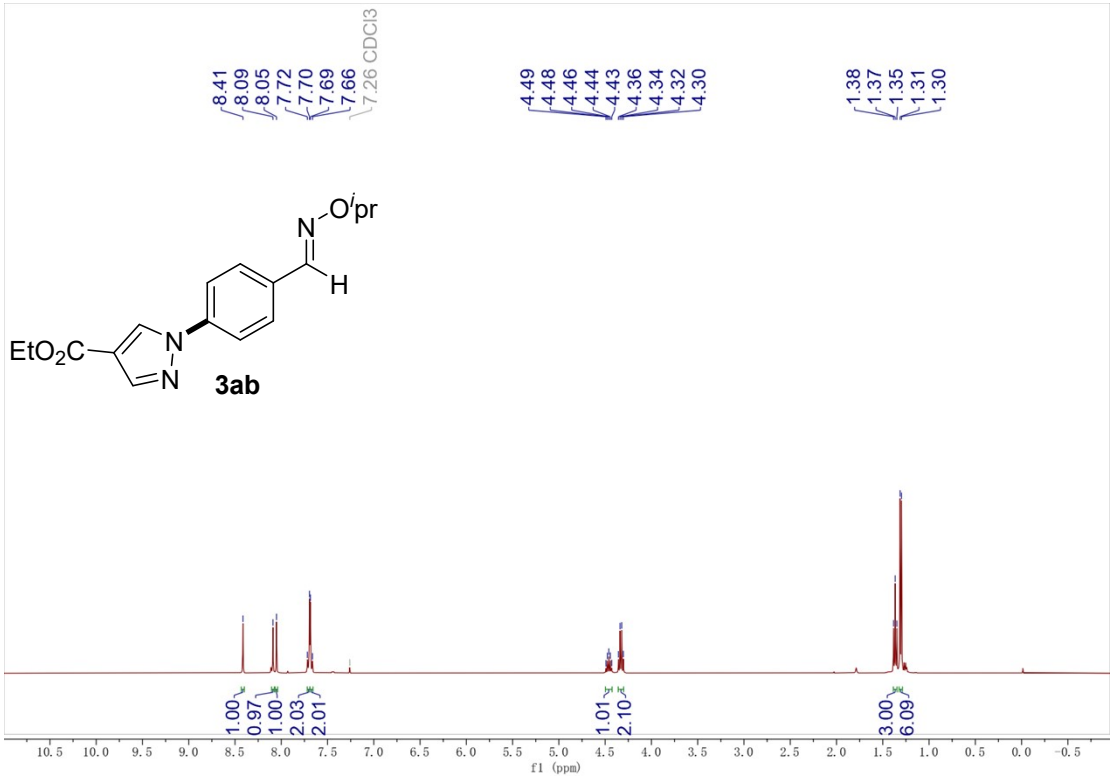
^{1}H NMR of 3aa



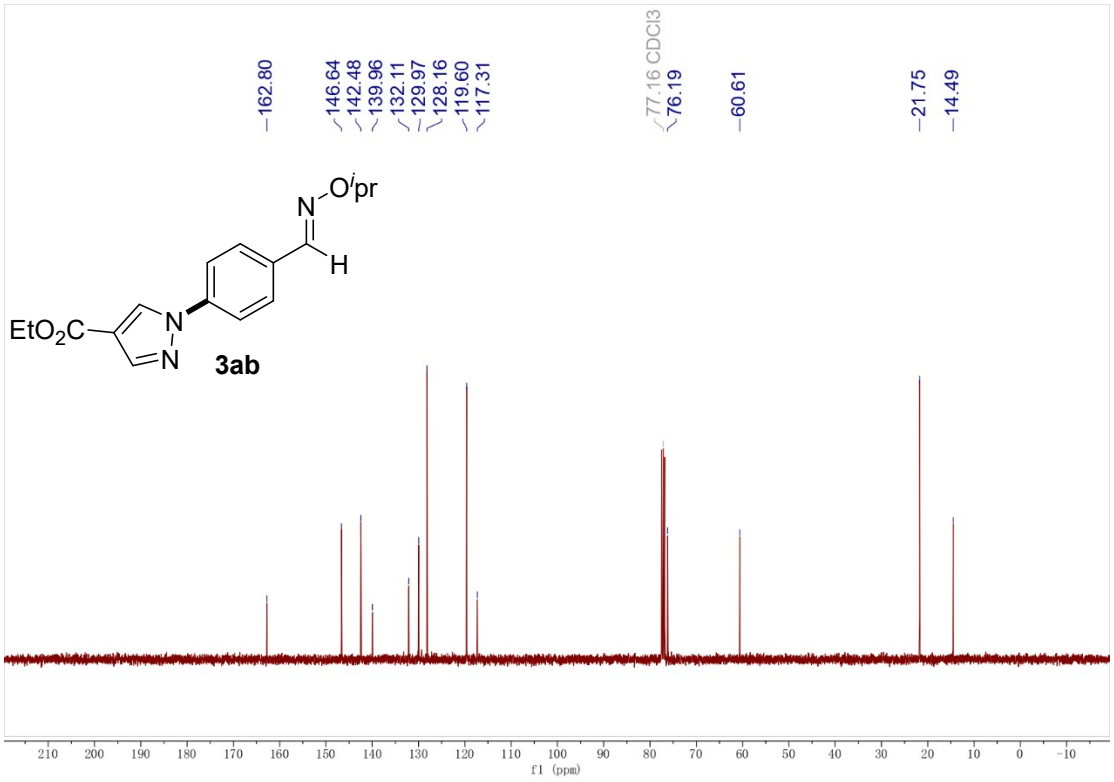
^{13}C NMR of 3aa



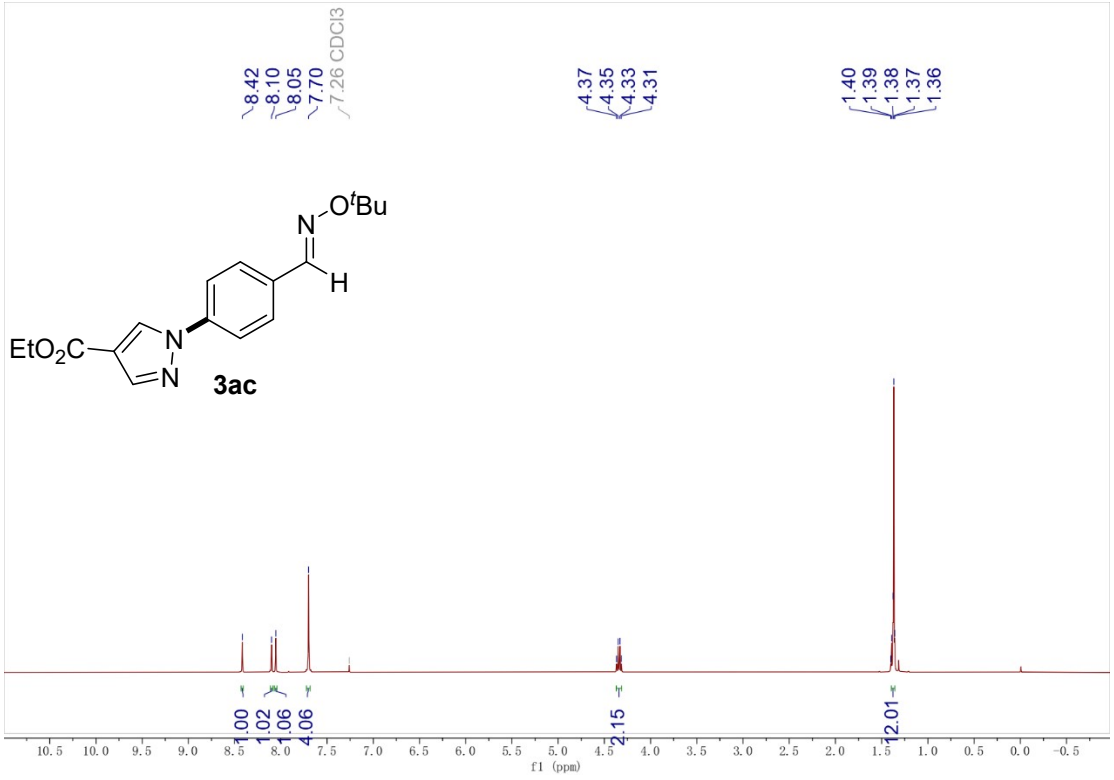
^{1}H NMR of 3ab



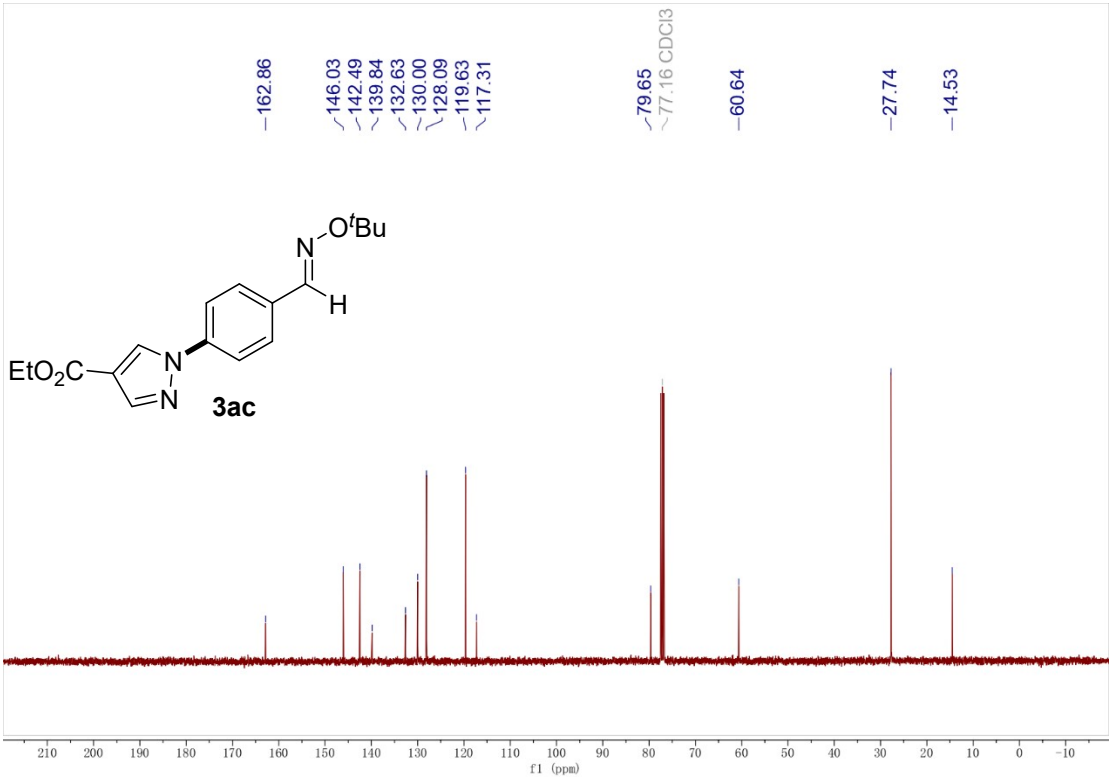
^{13}C NMR of 3ab



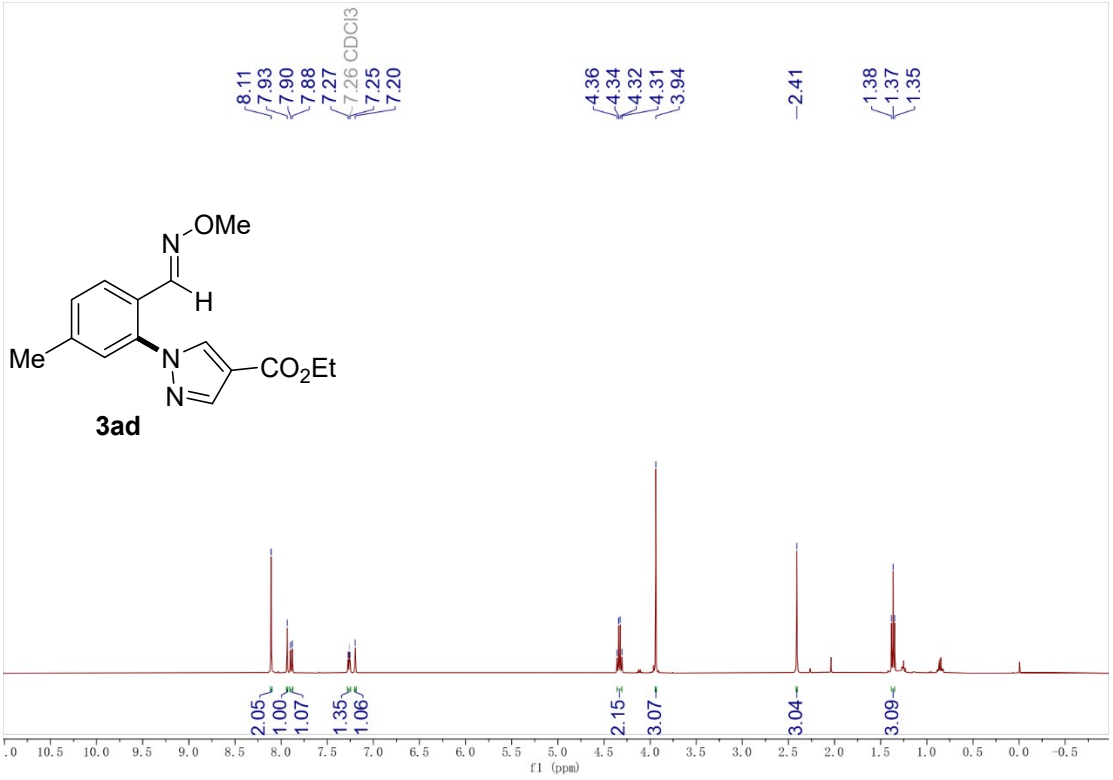
^{1}H NMR of 3ac



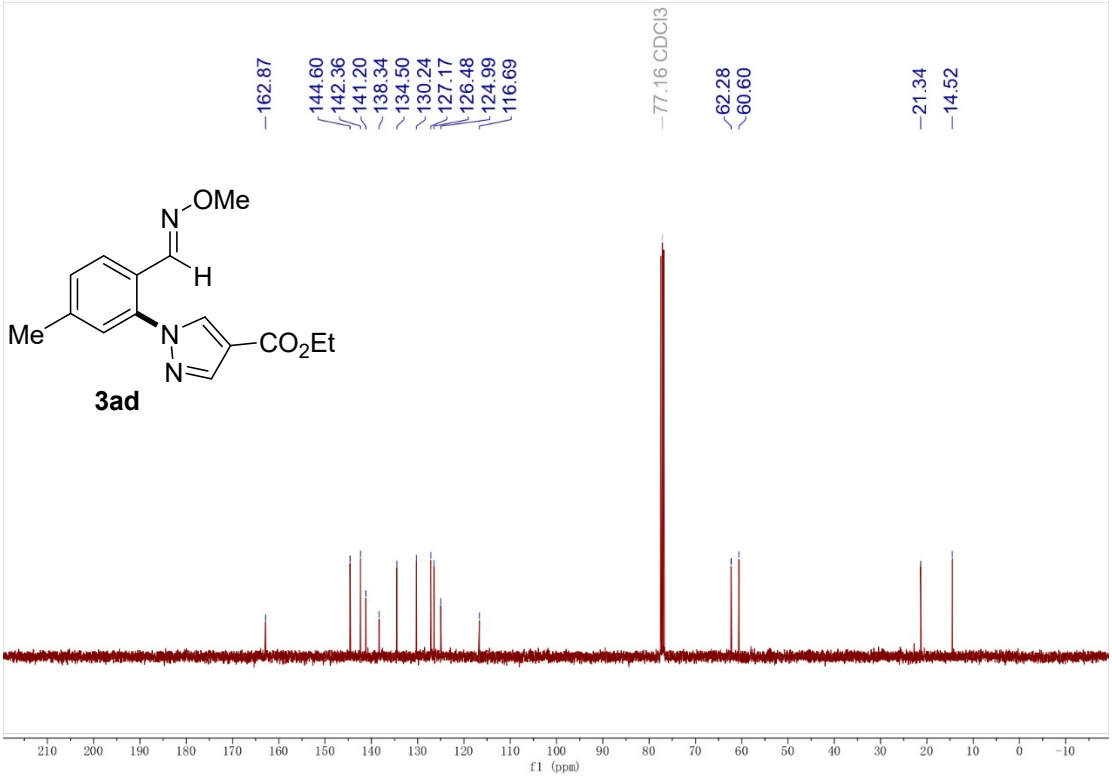
^{13}C NMR of 3ac



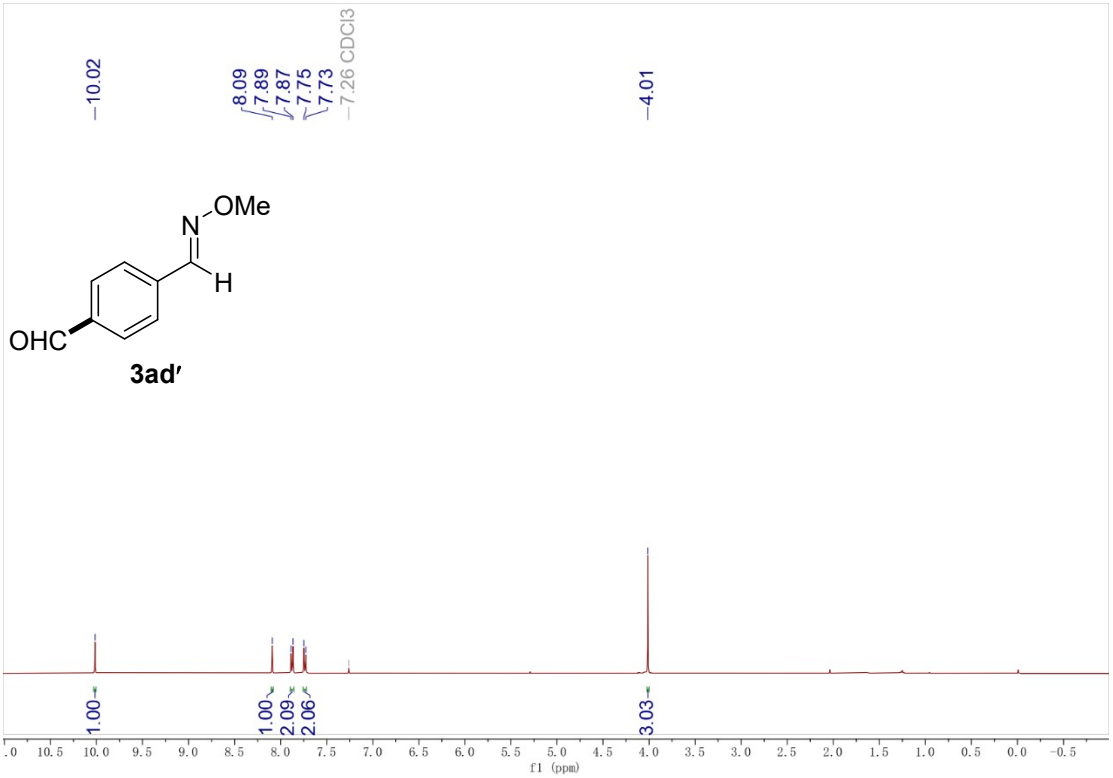
^{1}H NMR of 3ad



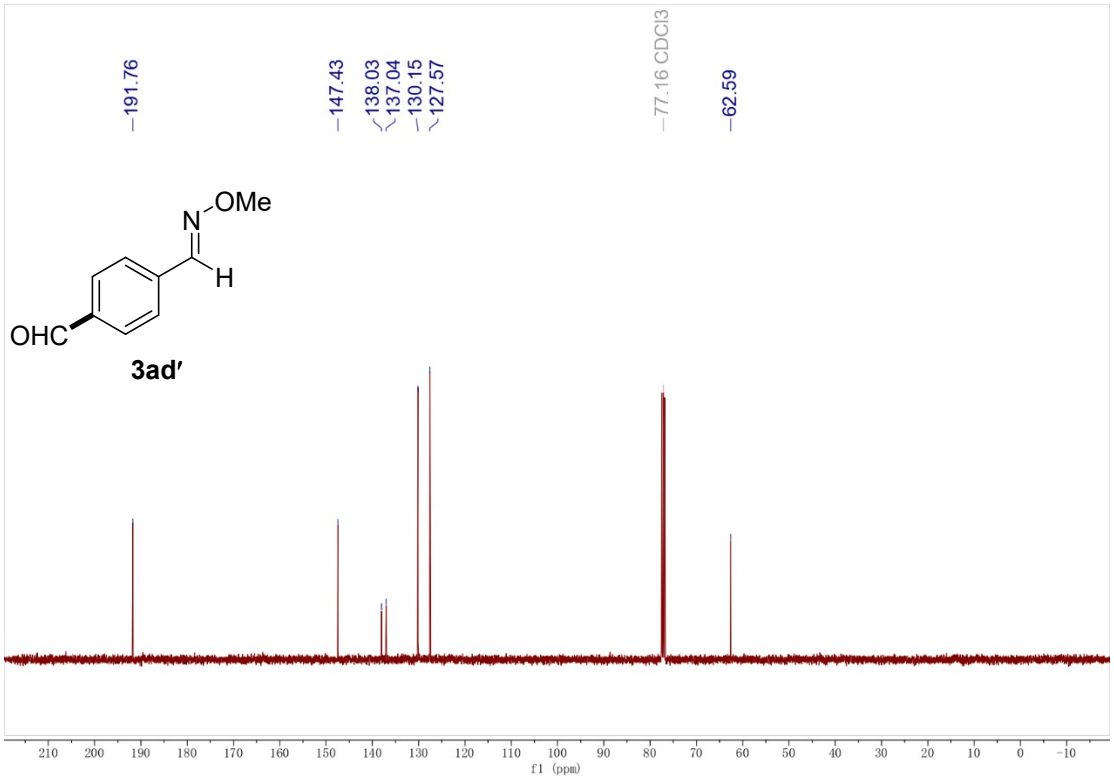
^{13}C NMR of 3ad



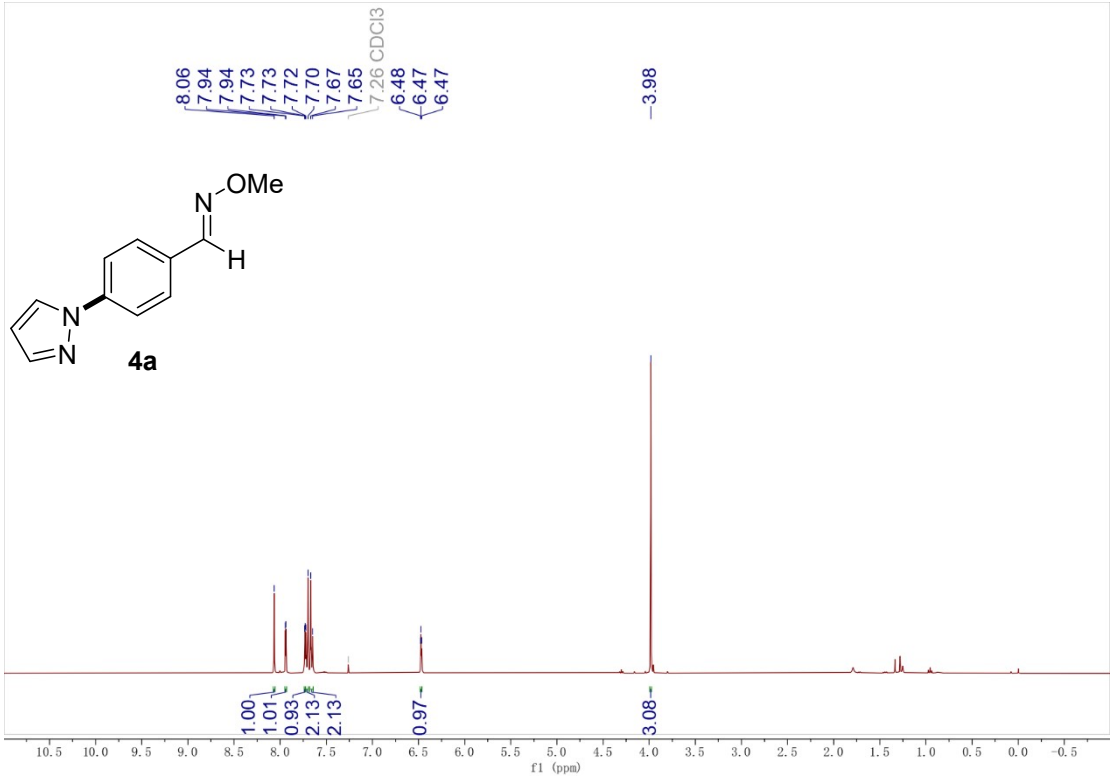
^{1}H NMR of 3ad'



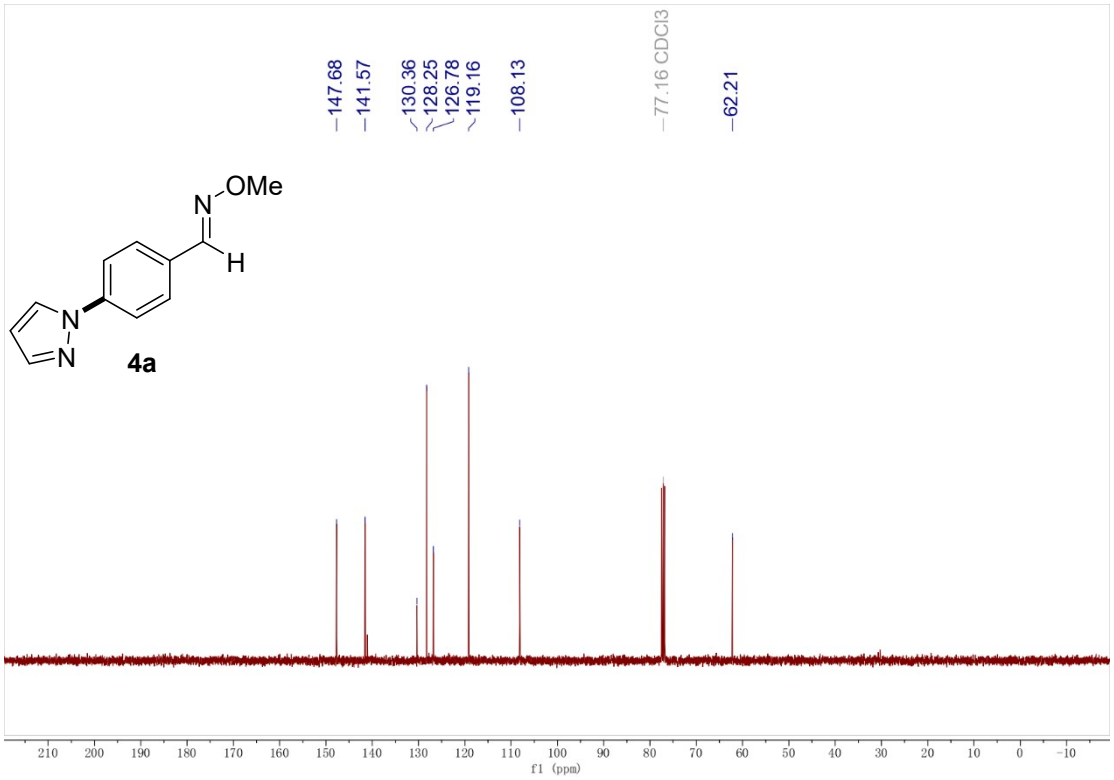
^{13}C NMR of 3ad'


191.76
147.43
138.03
137.04
130.15
127.57
77.16 CDCl3
62.59
N
OMe
H
OHC
3ad′
f1 (ppm)

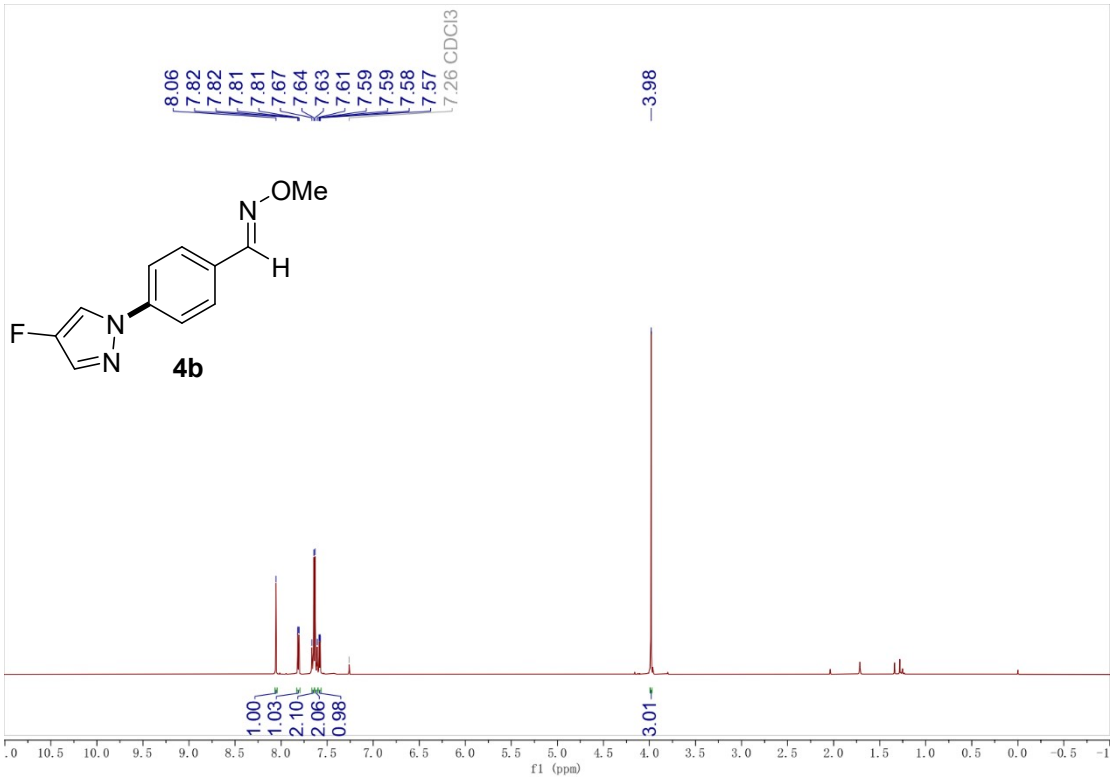
^{1}H NMR of 4a


8.06
7.94
7.94
7.73
7.73
7.72
7.70
7.67
7.65
7.26 CDCl3
6.48
6.47
6.47
3.98
N
OMe
H
N
N
4a
1.00
1.01
0.93
2.13
2.13
0.97
3.08
f1 (ppm)

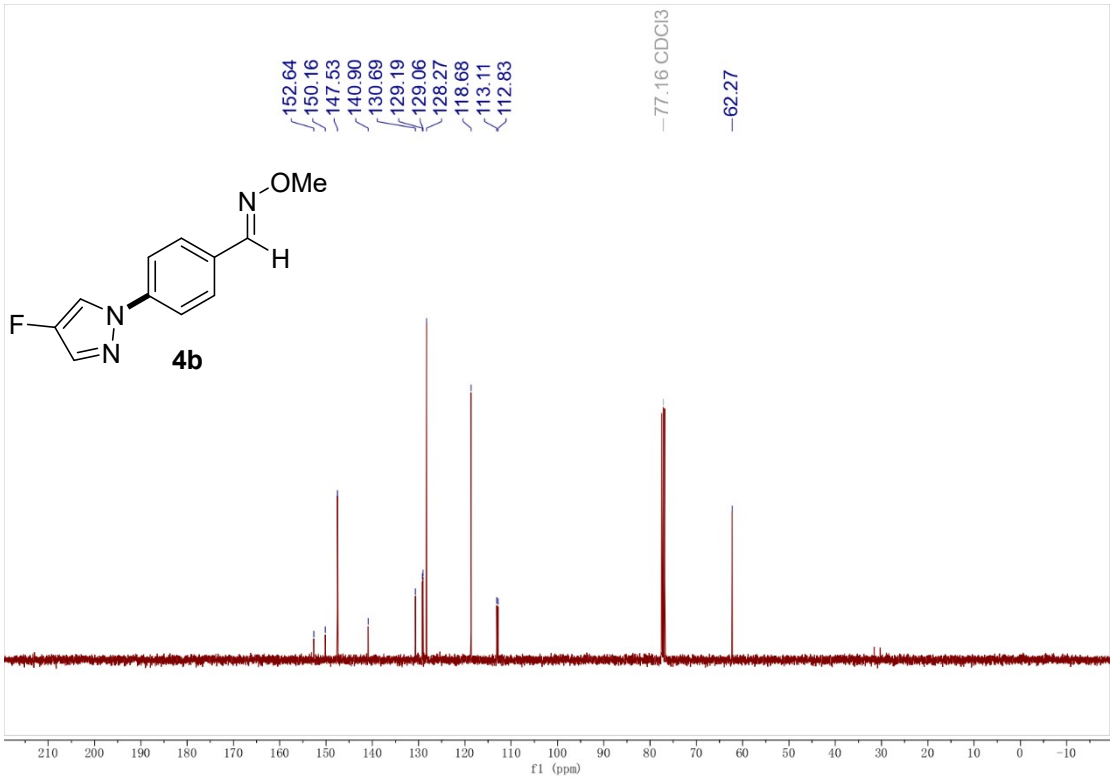
^{13}C NMR of 4a



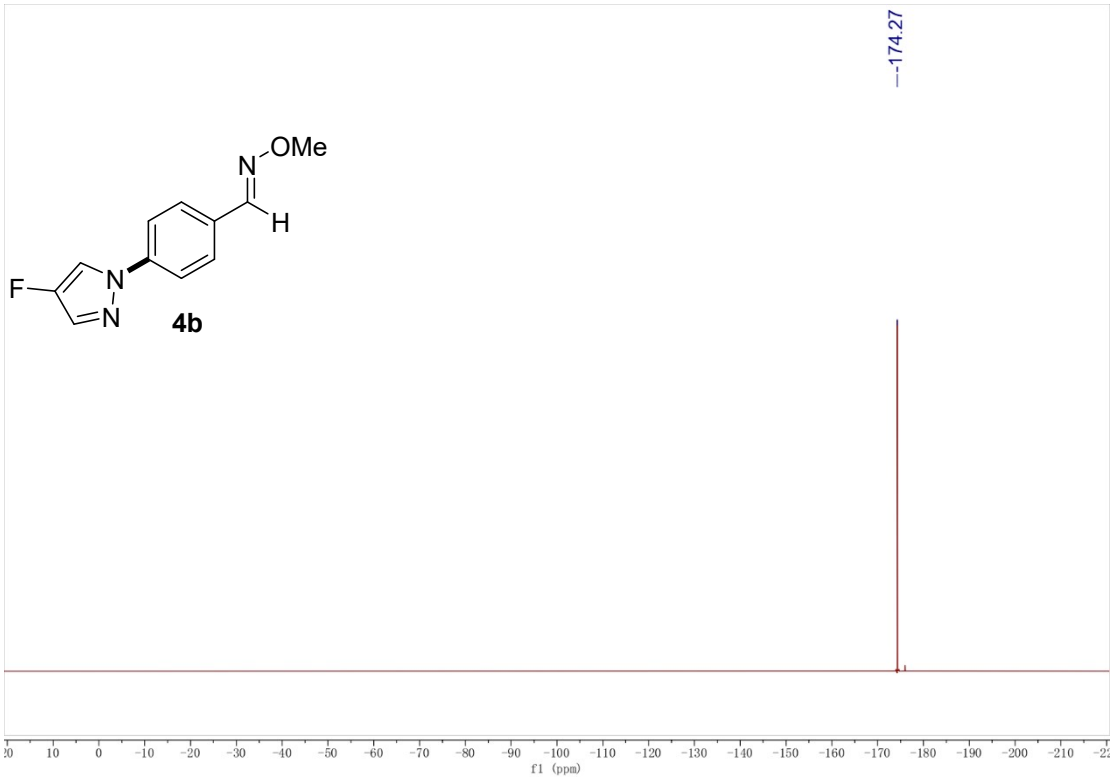
^{1}H NMR of 4b



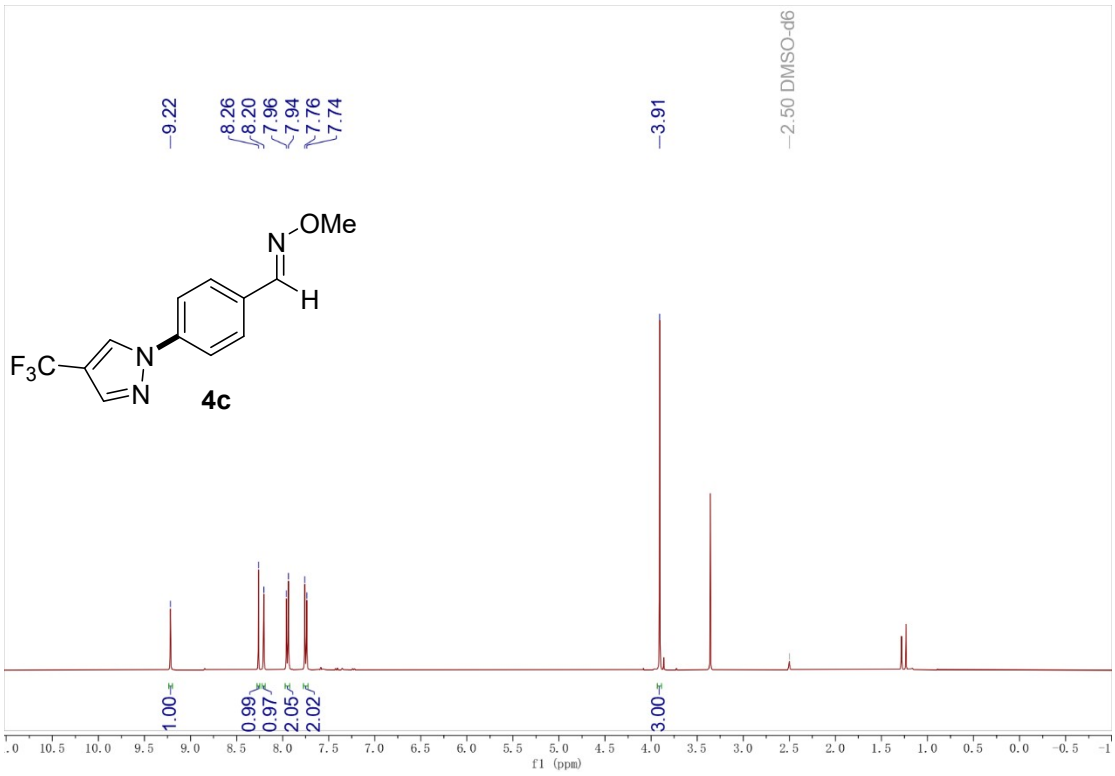
^{13}C NMR of 4b



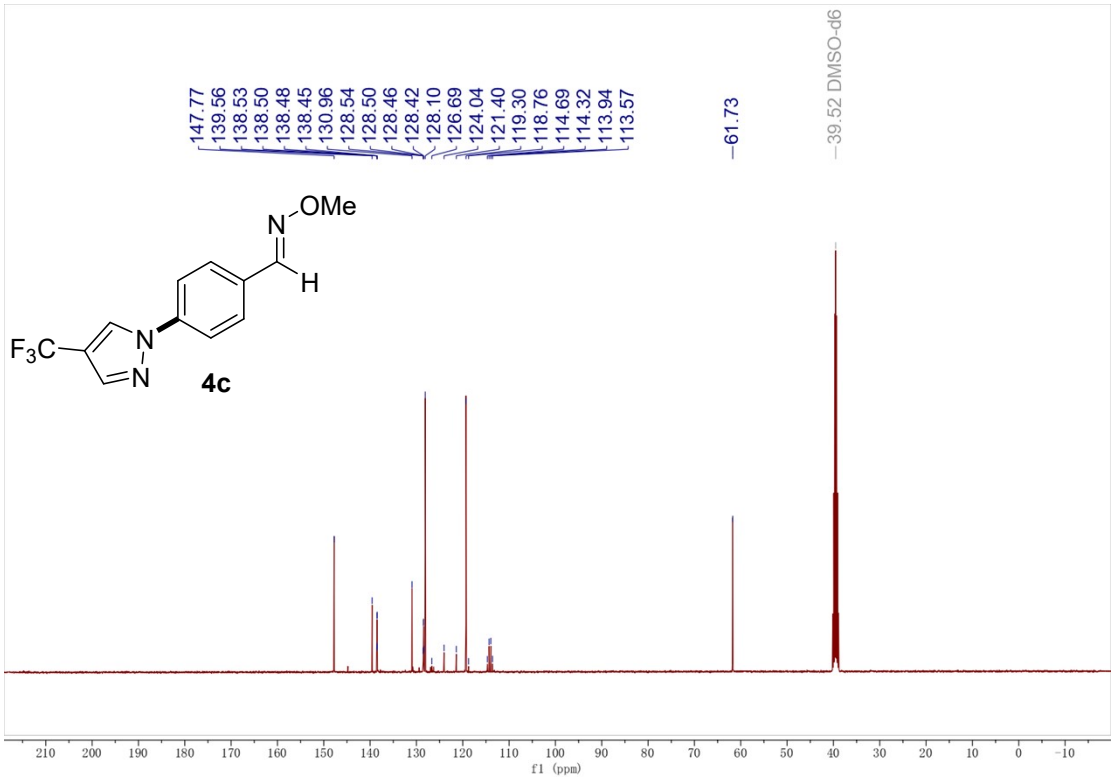
^{19}F NMR of 4b



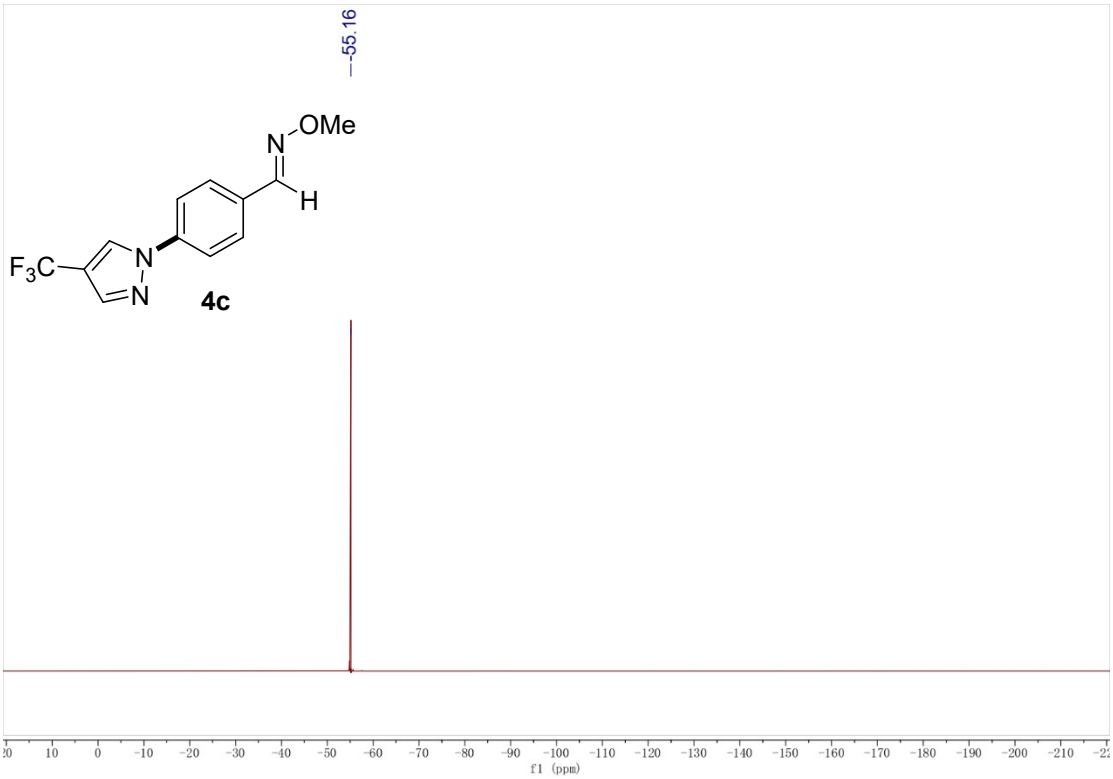
^{1}H NMR of 4c



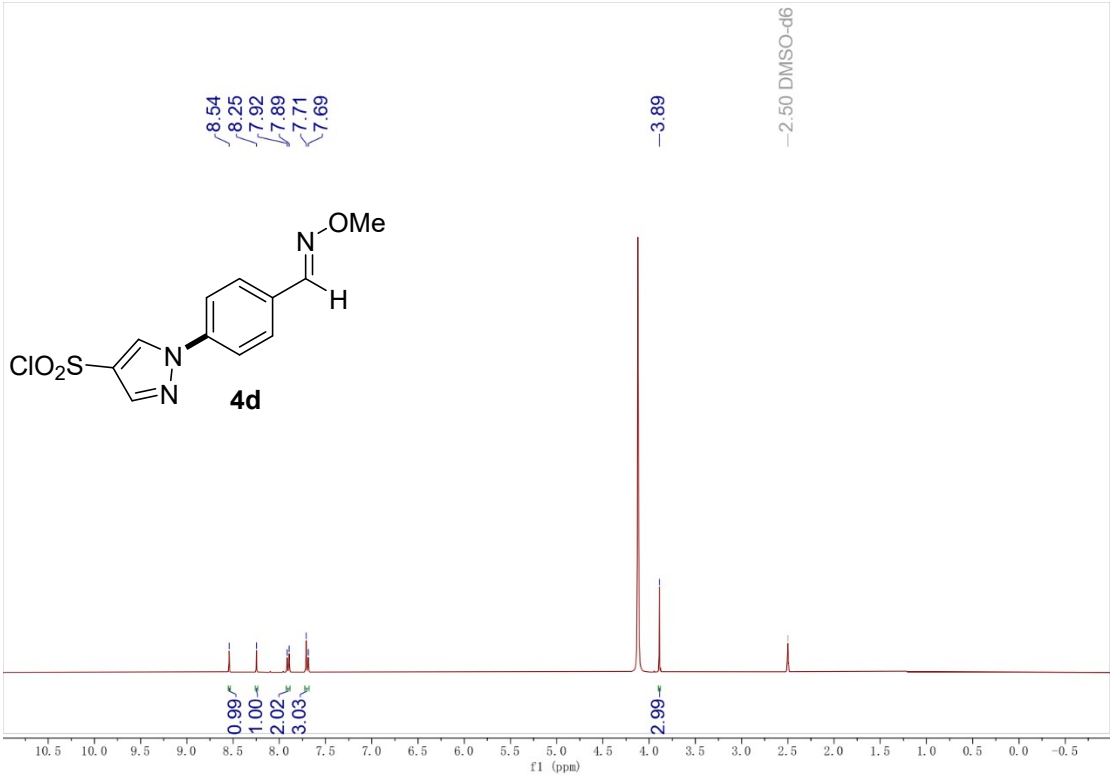
^{13}C NMR of 4c



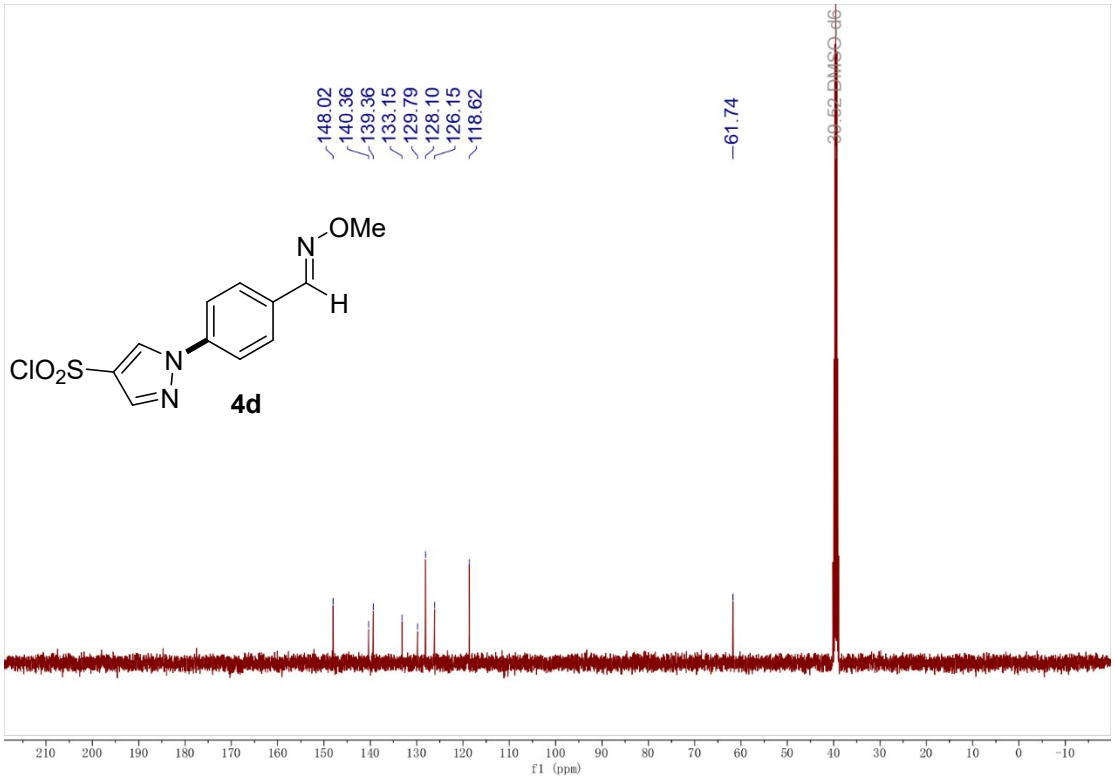
^{19}F NMR of 4c



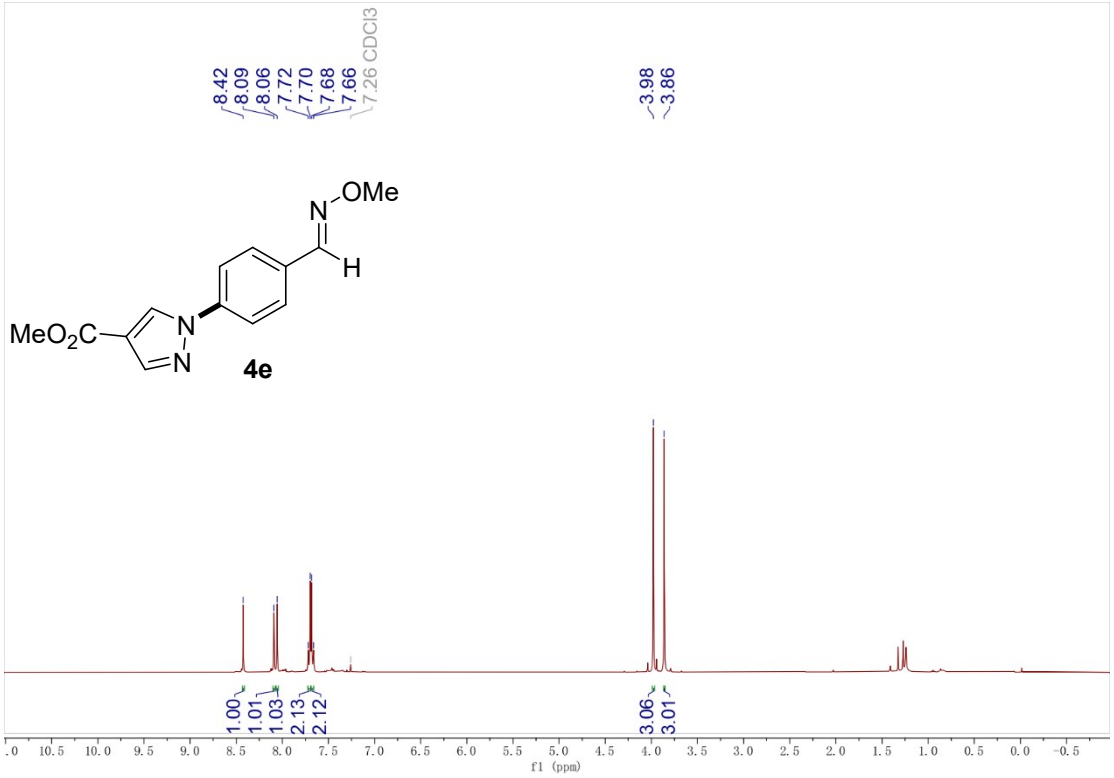
^{1}H NMR of 4d



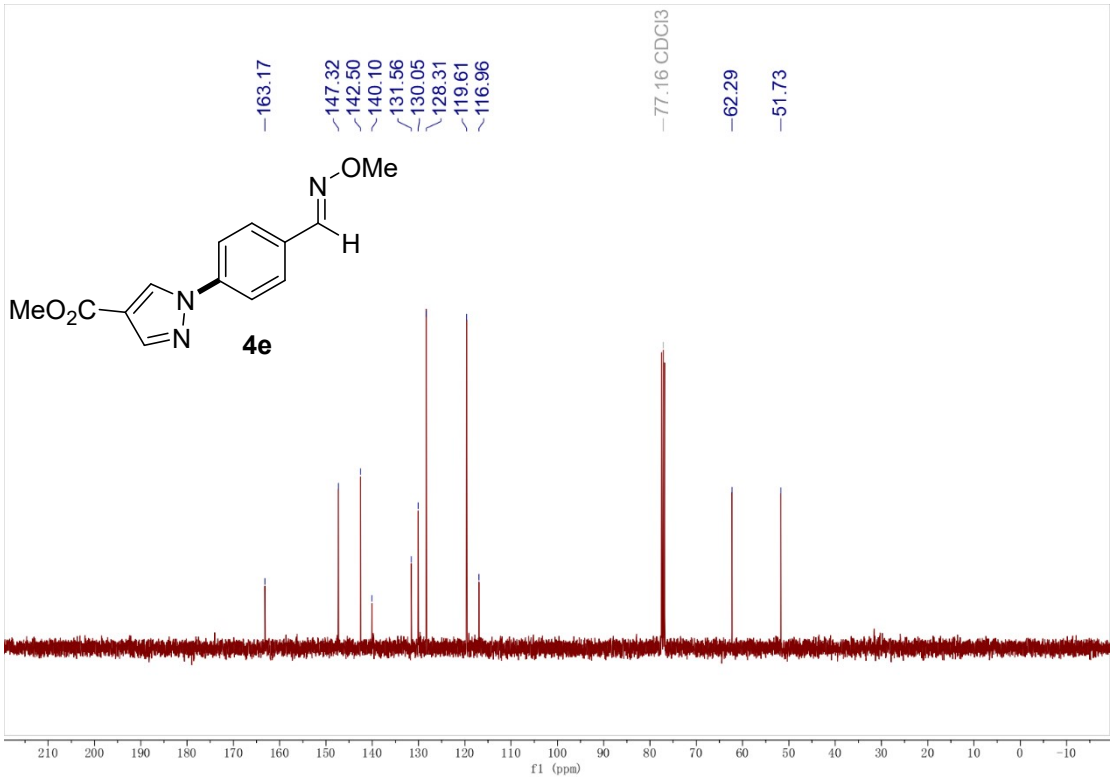
^{13}C NMR of 4d



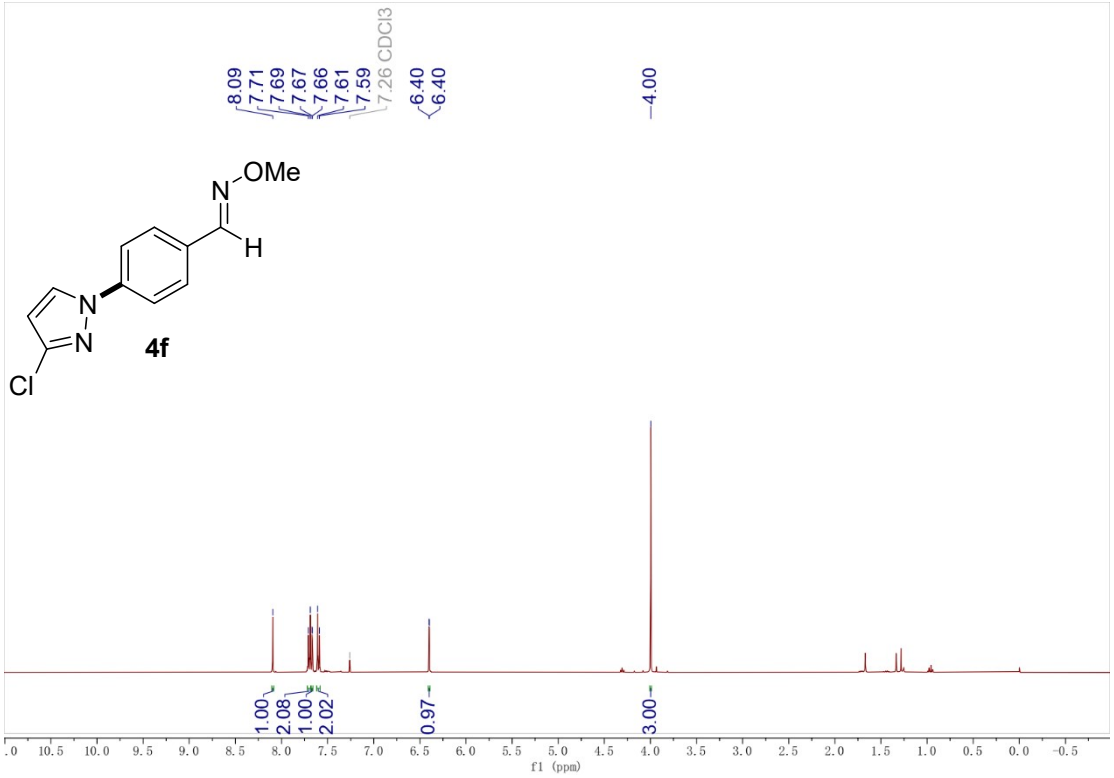
^{1}H NMR of 4e



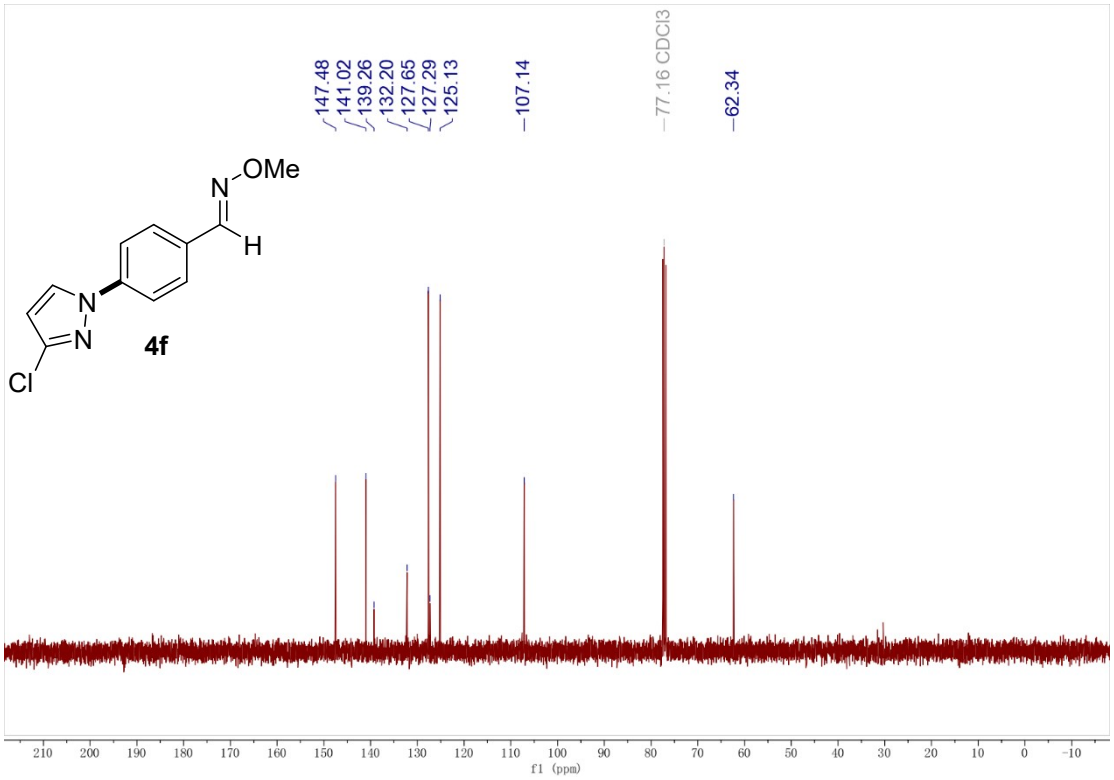
^{13}C NMR of 4e



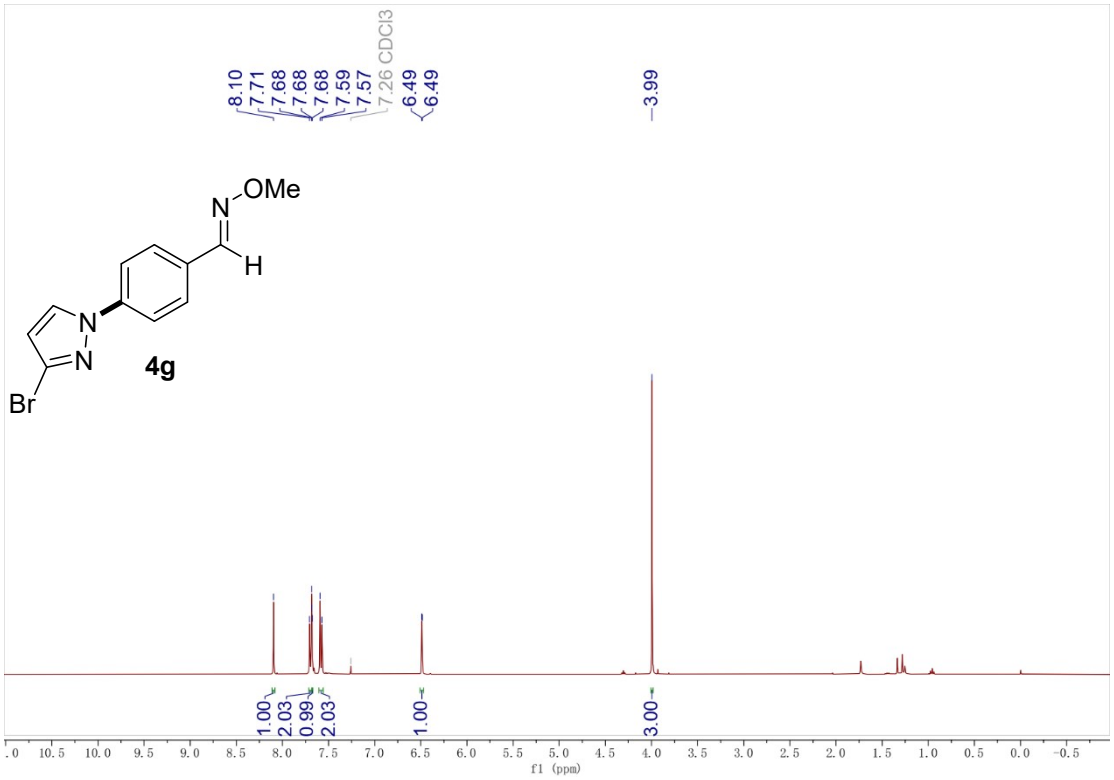
^{1}H NMR of 4f



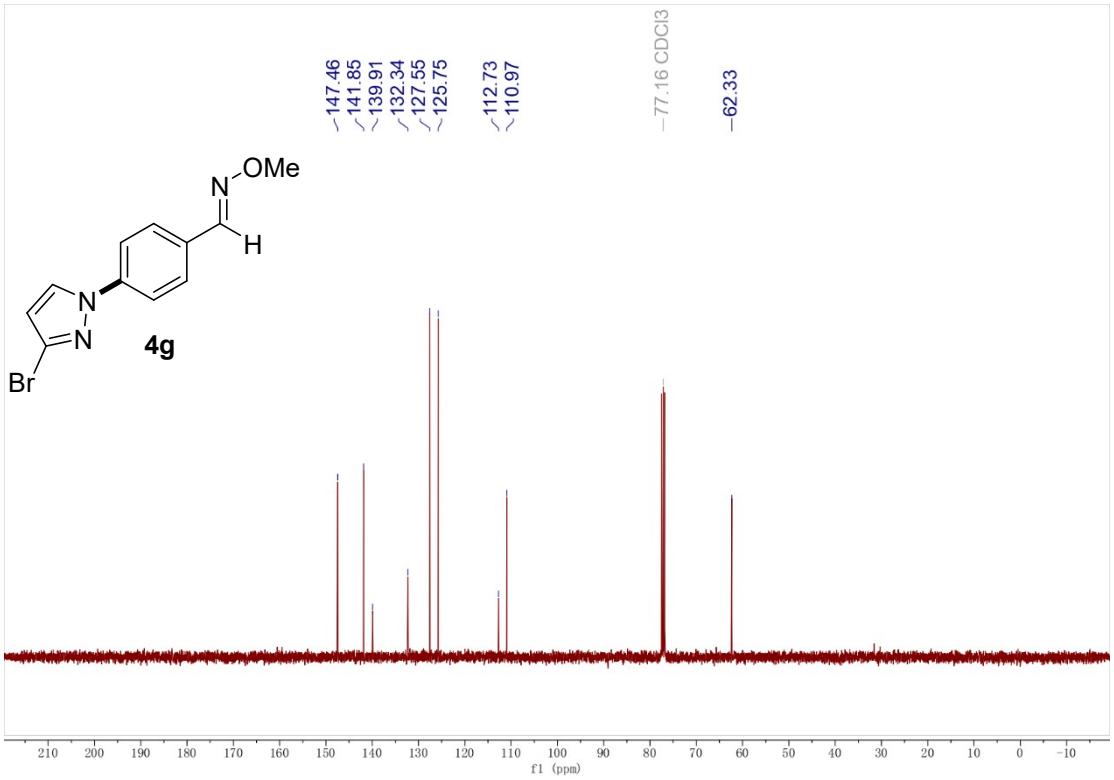
^{13}C NMR of 4f



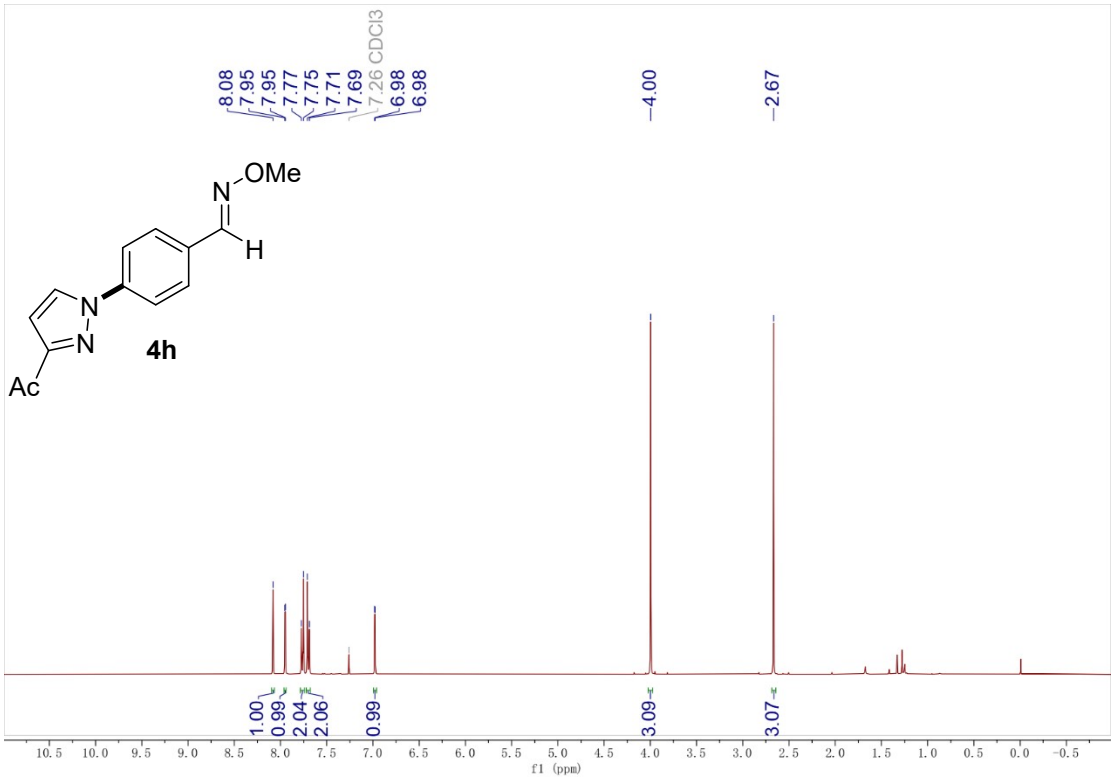
^{1}H NMR of 4g



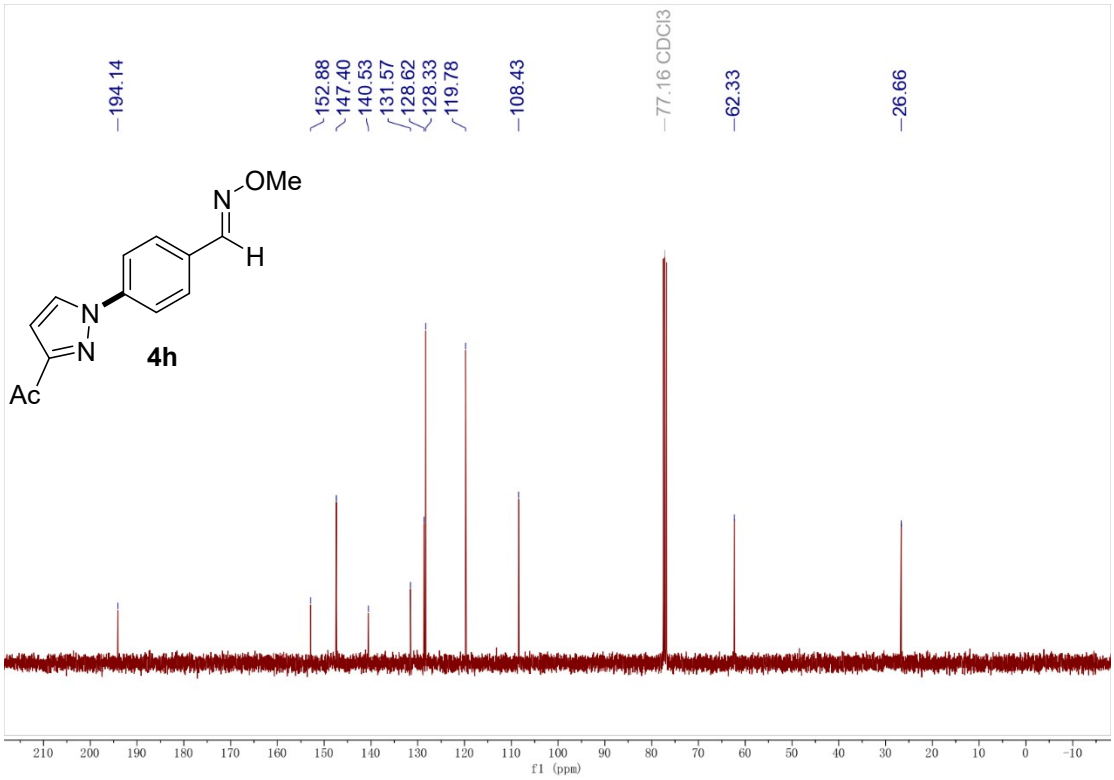
^{13}C NMR of 4g



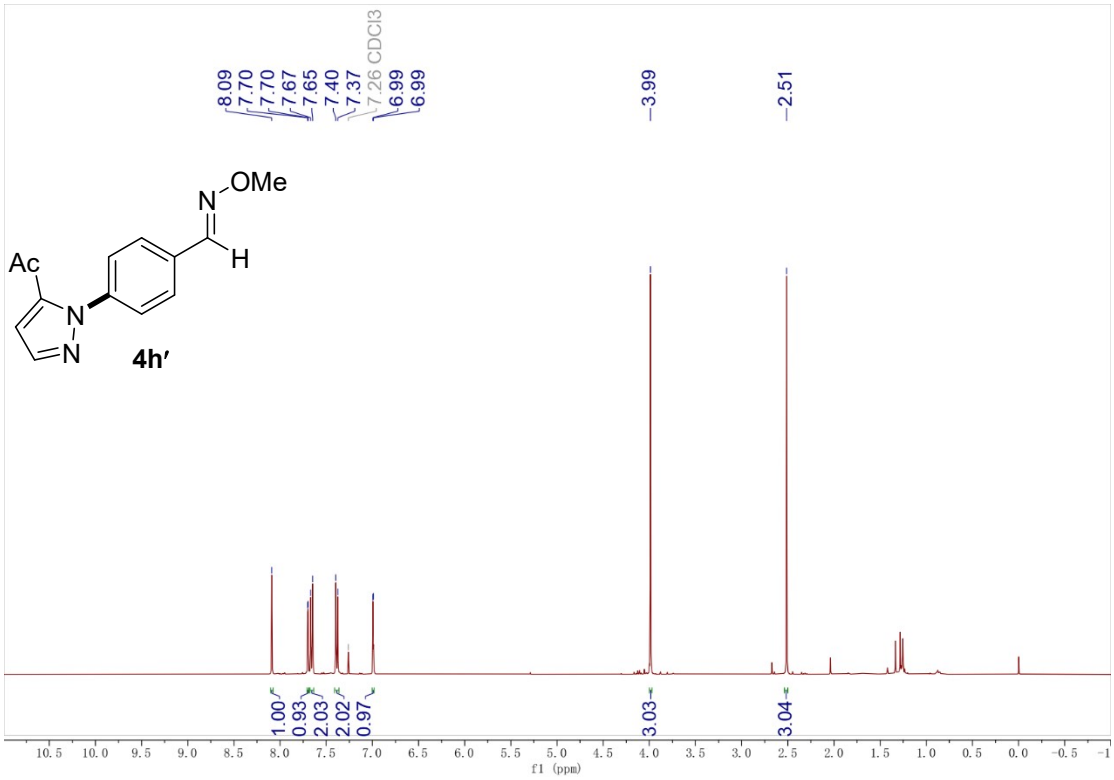
^{1}H NMR of 4h



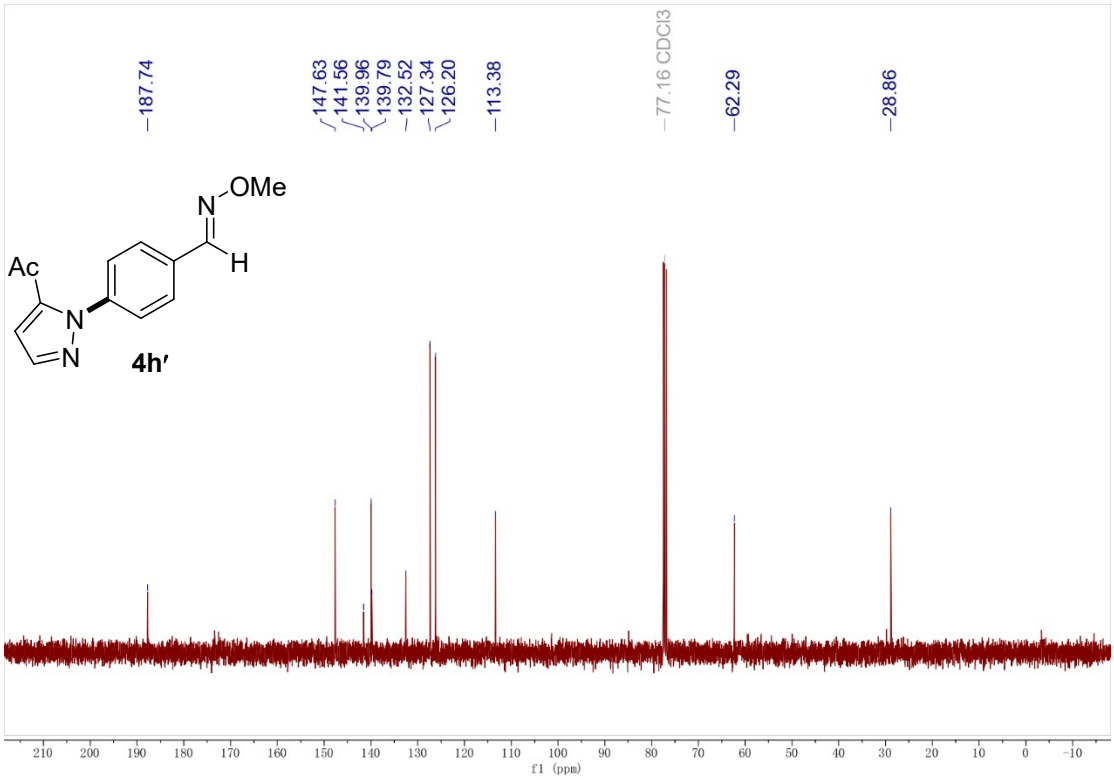
^{13}C NMR of 4h



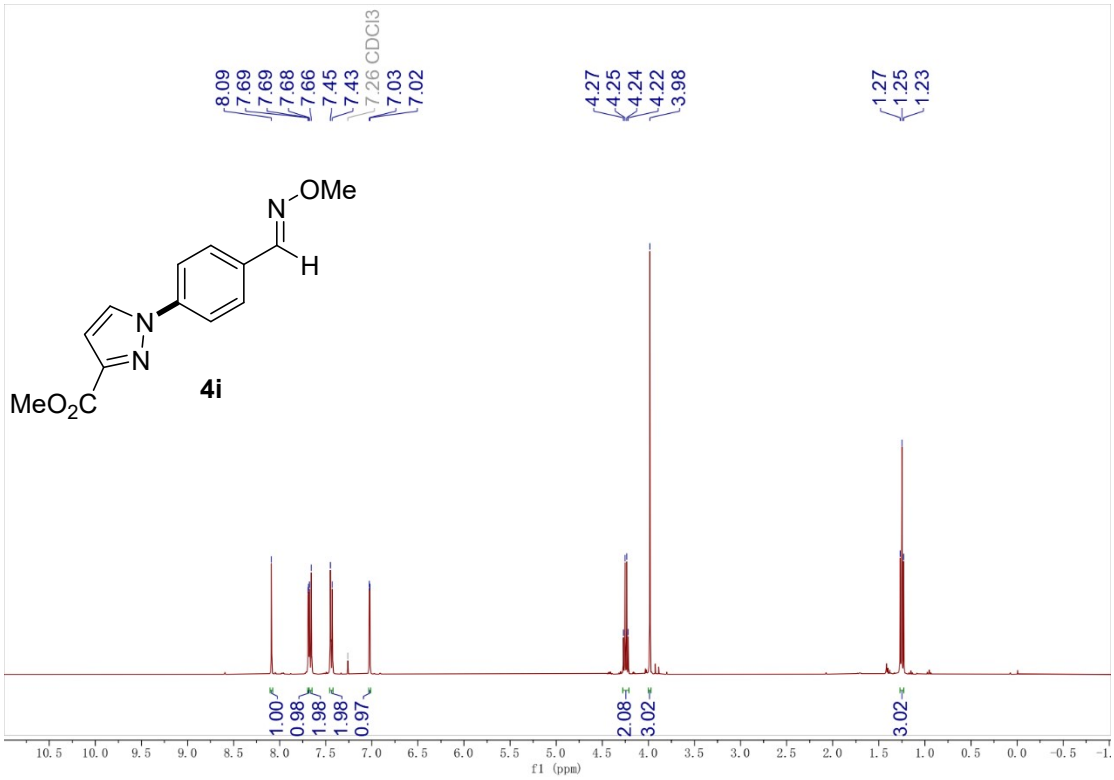
^{1}H NMR of 4h'



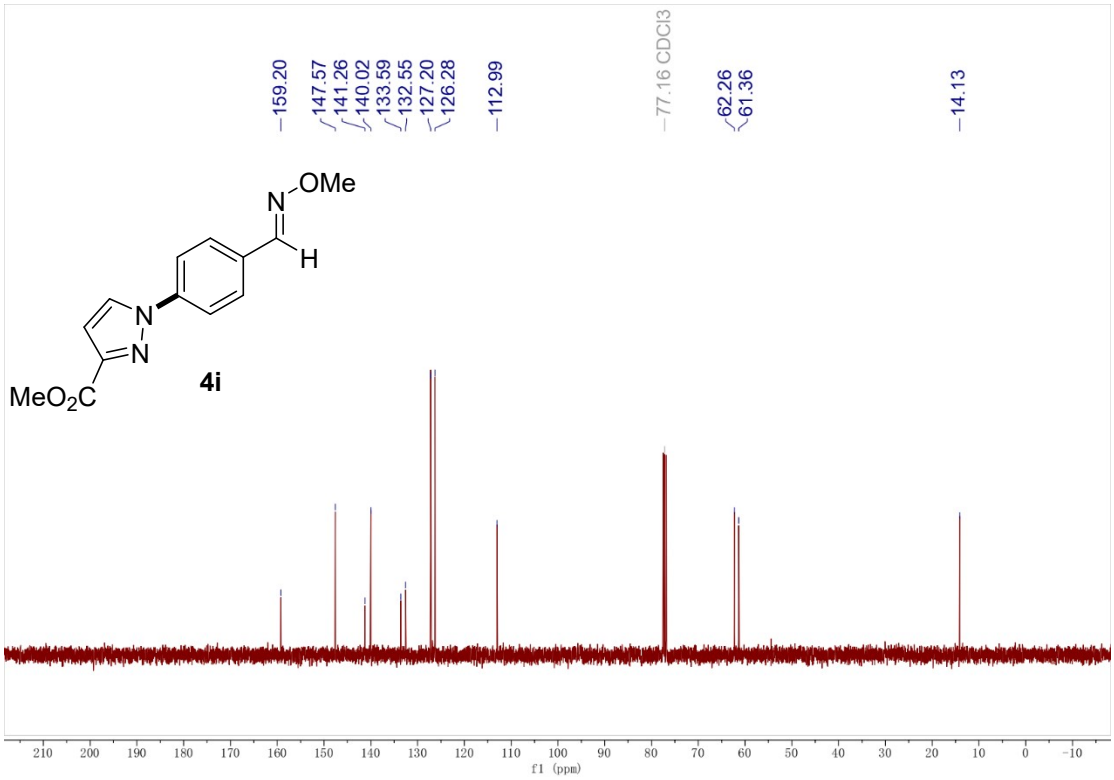
^{13}C NMR of 4h'



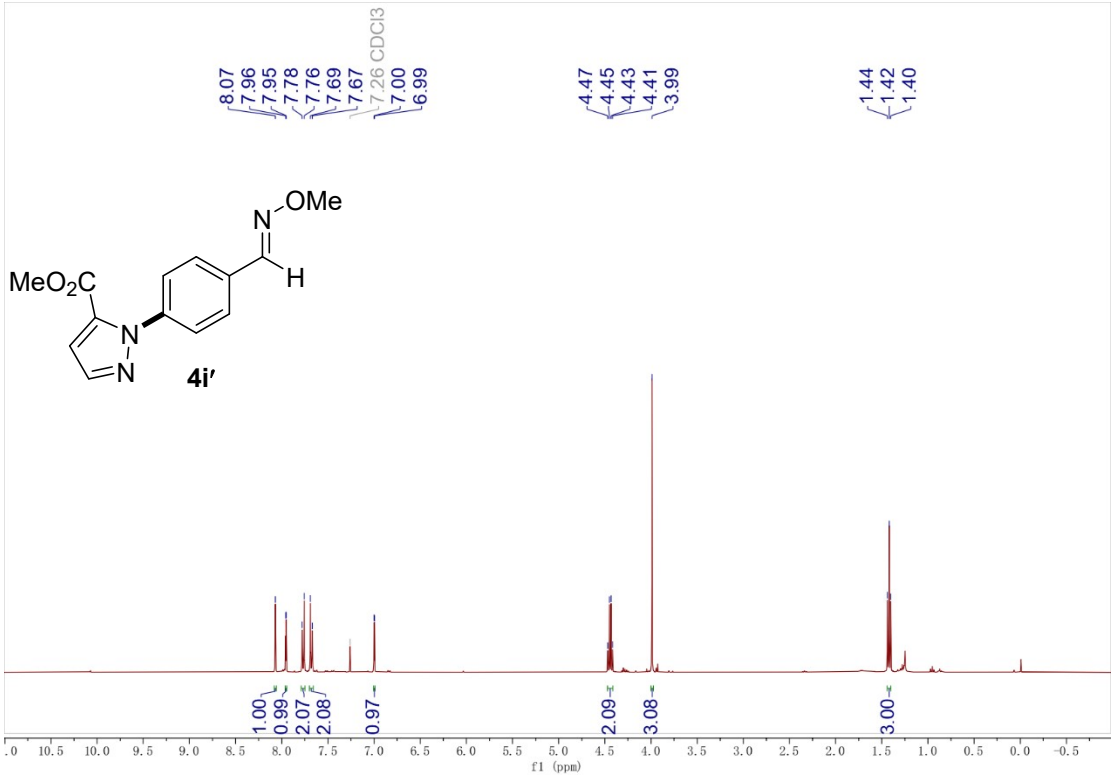
^{1}H NMR of 4i



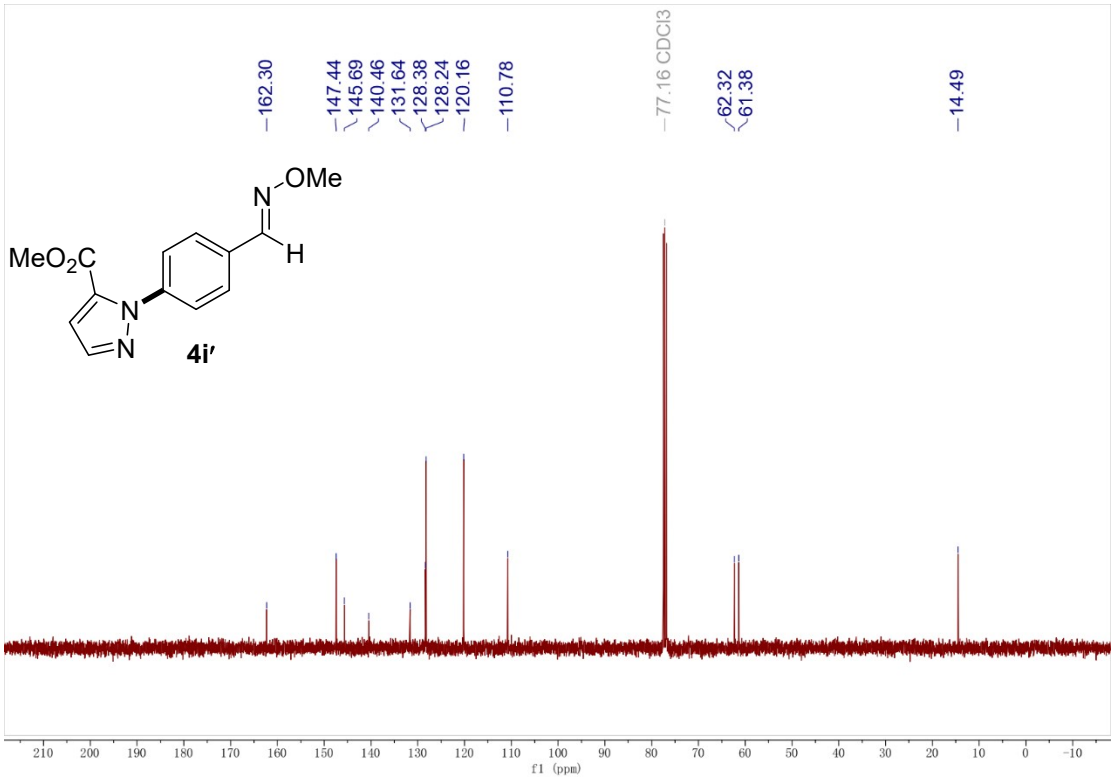
^{13}C NMR of 4i



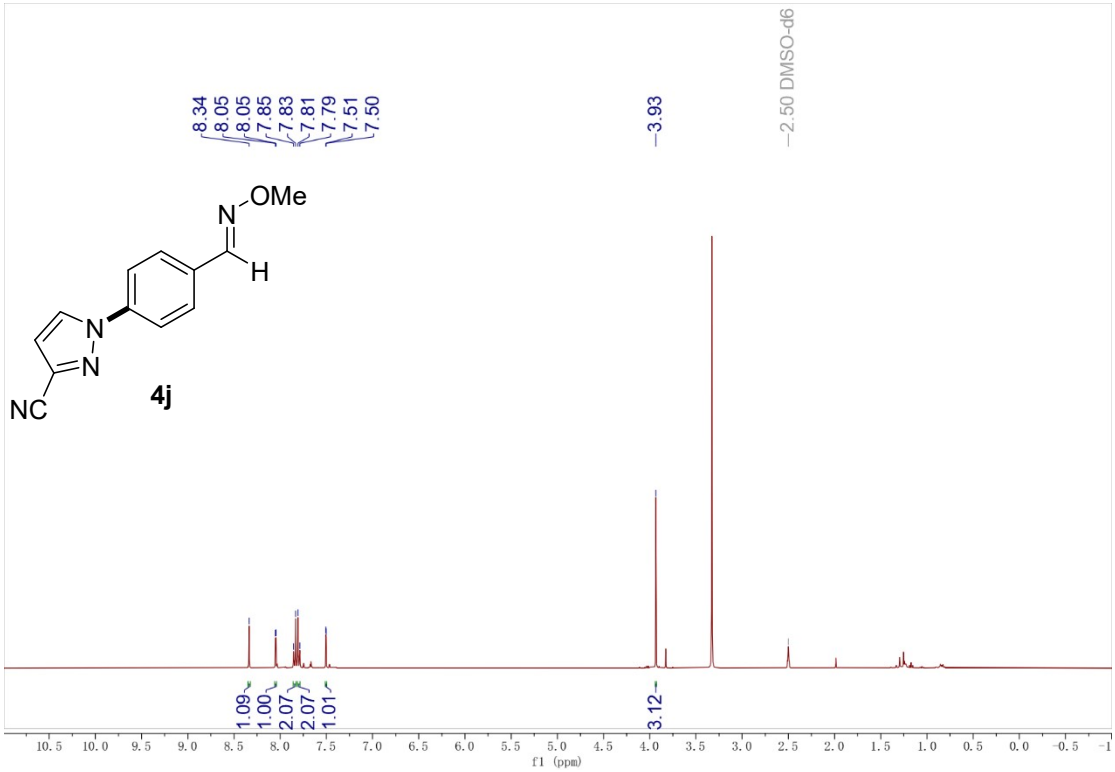
^{1}H NMR of 4i'



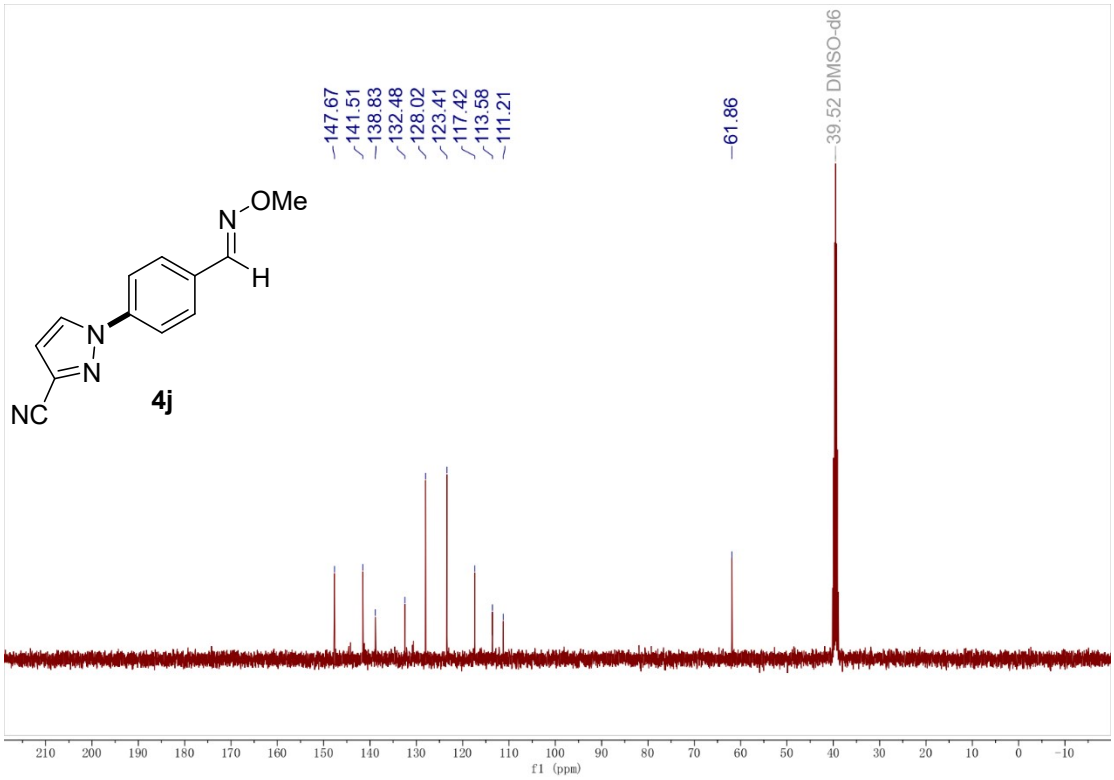
^{13}C NMR of 4i'



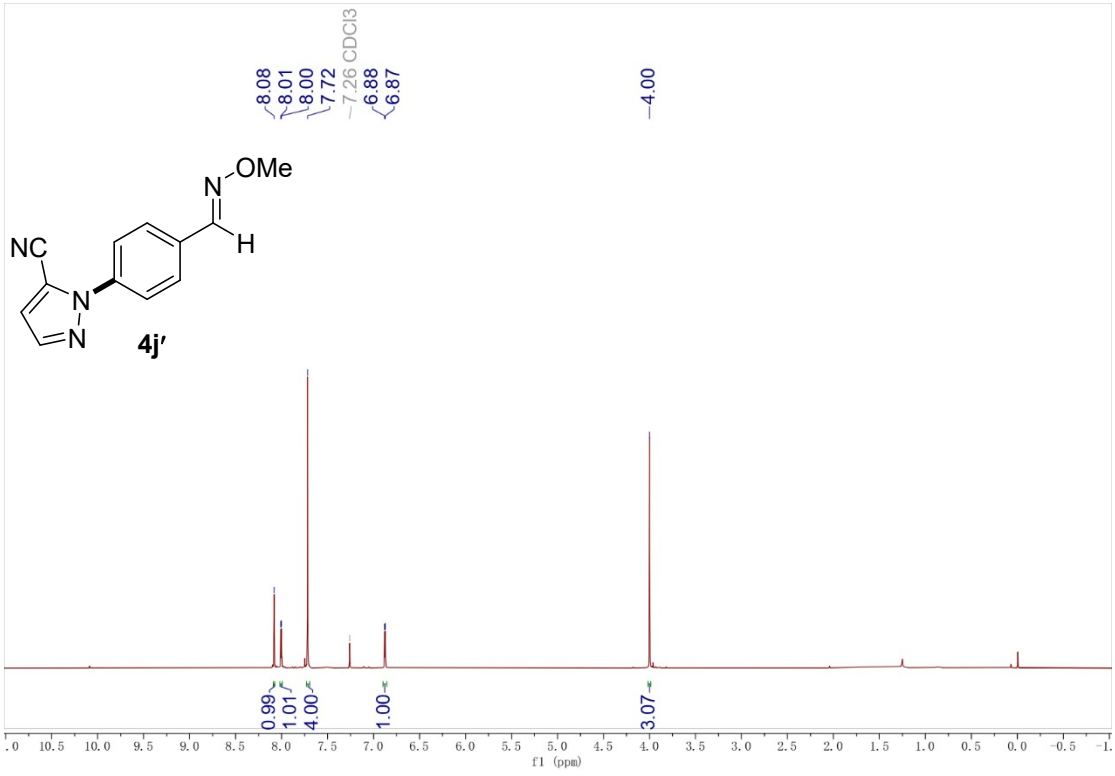
^{1}H NMR of 4j



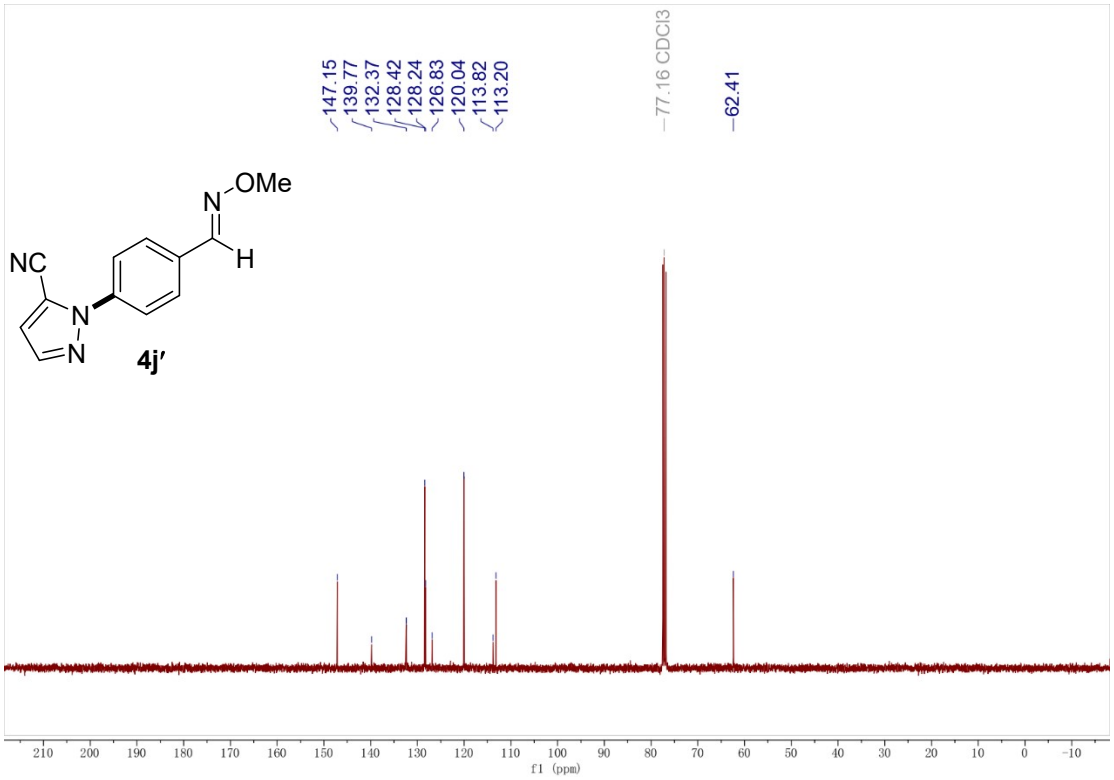
^{13}C NMR of 4j



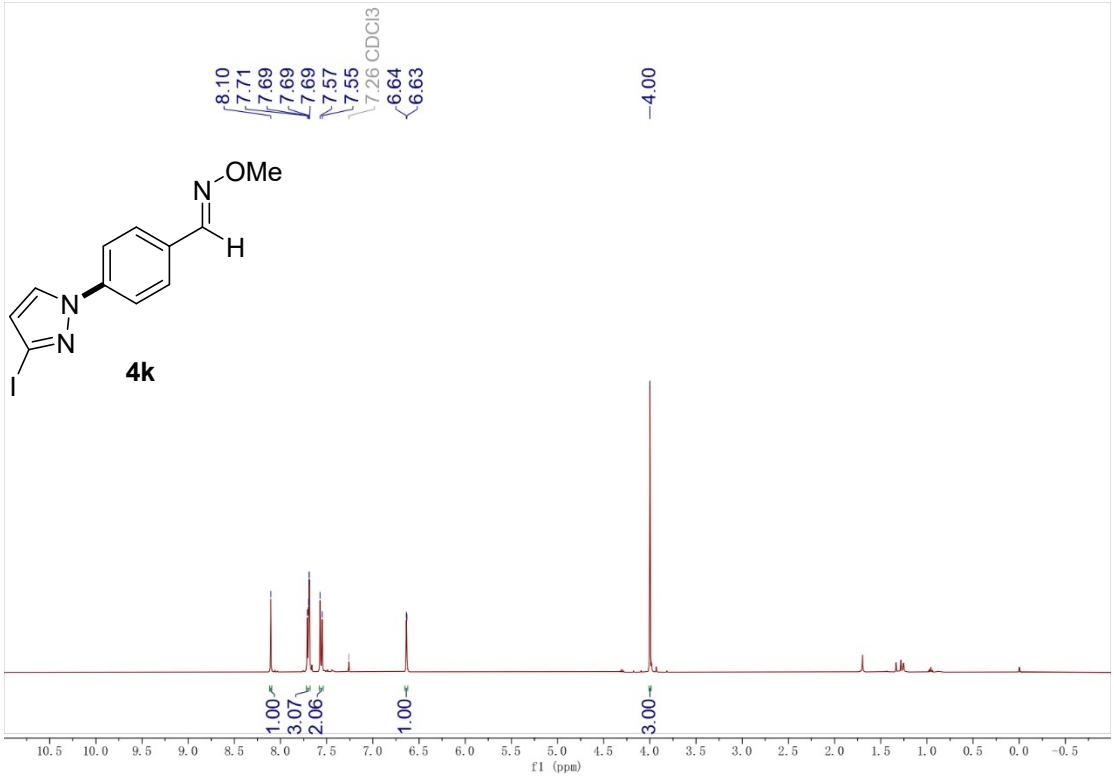
^{1}H NMR of 4j'



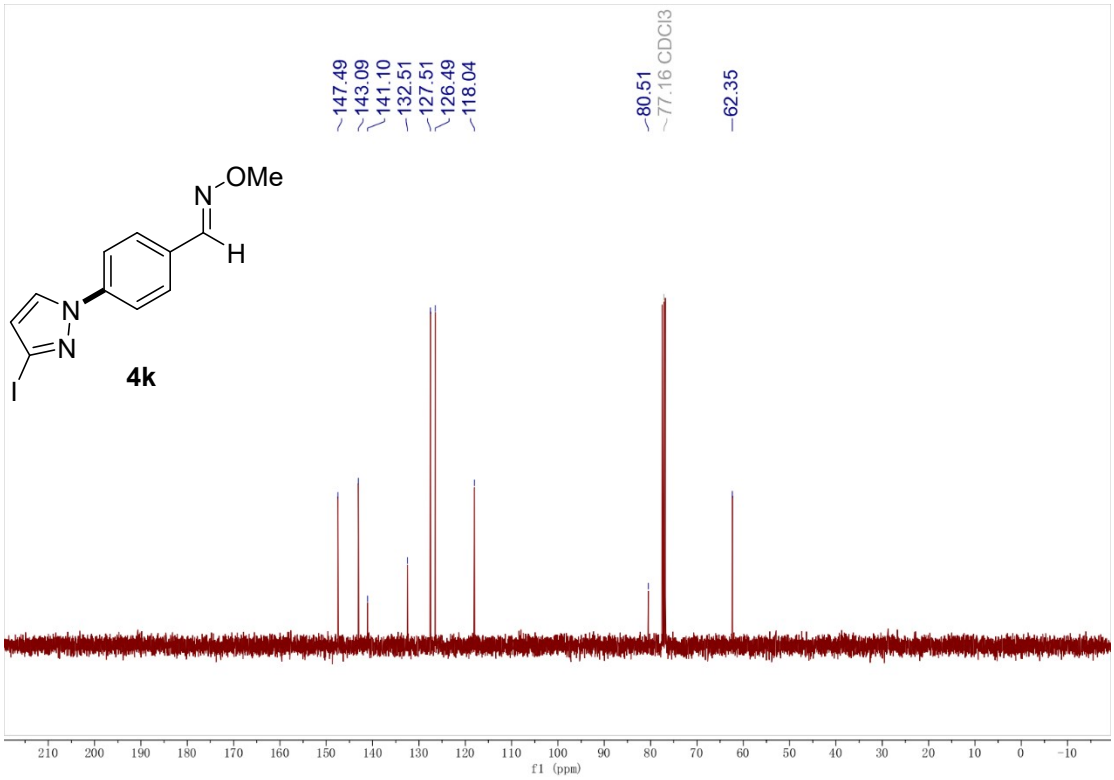
^{13}C NMR of 4j'



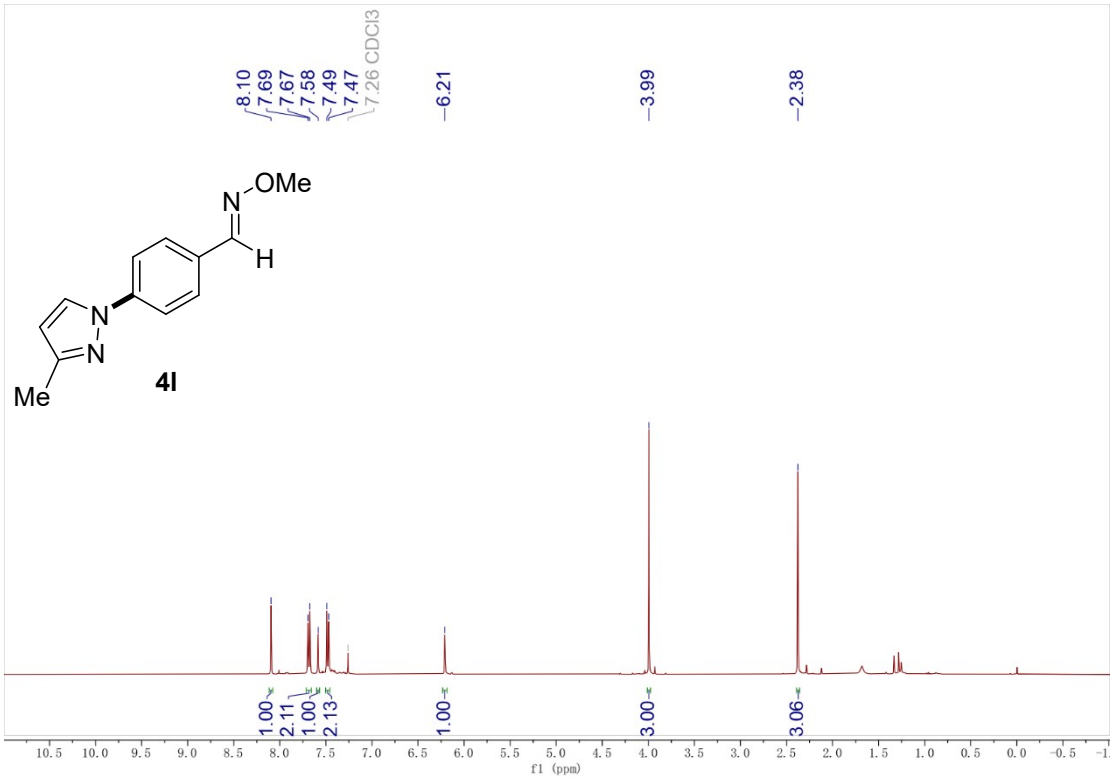
^{1}H NMR of 4k



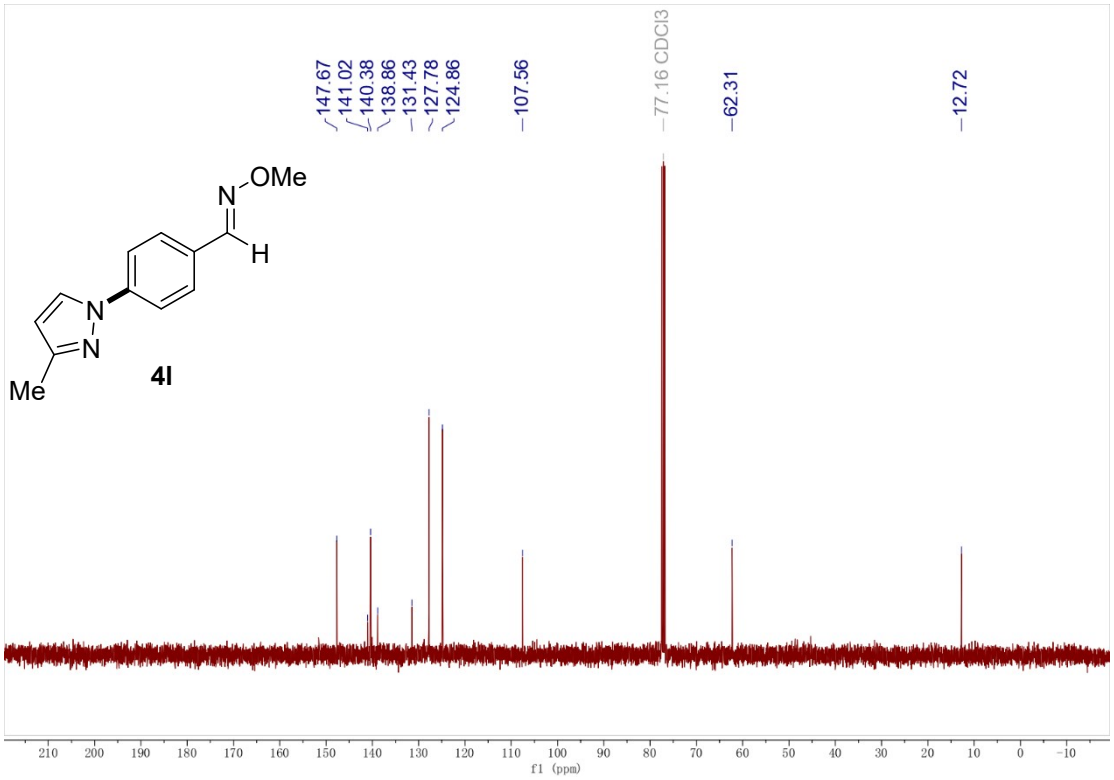
^{13}C NMR of 4k



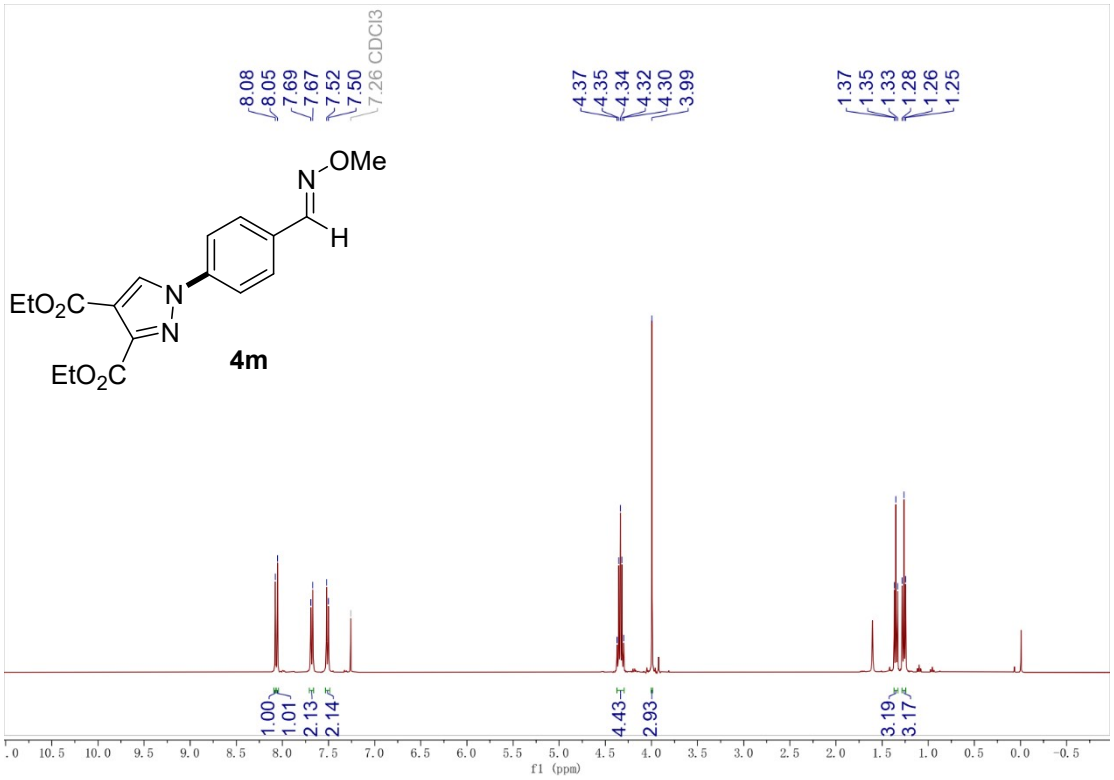
^{1}H NMR of 4l



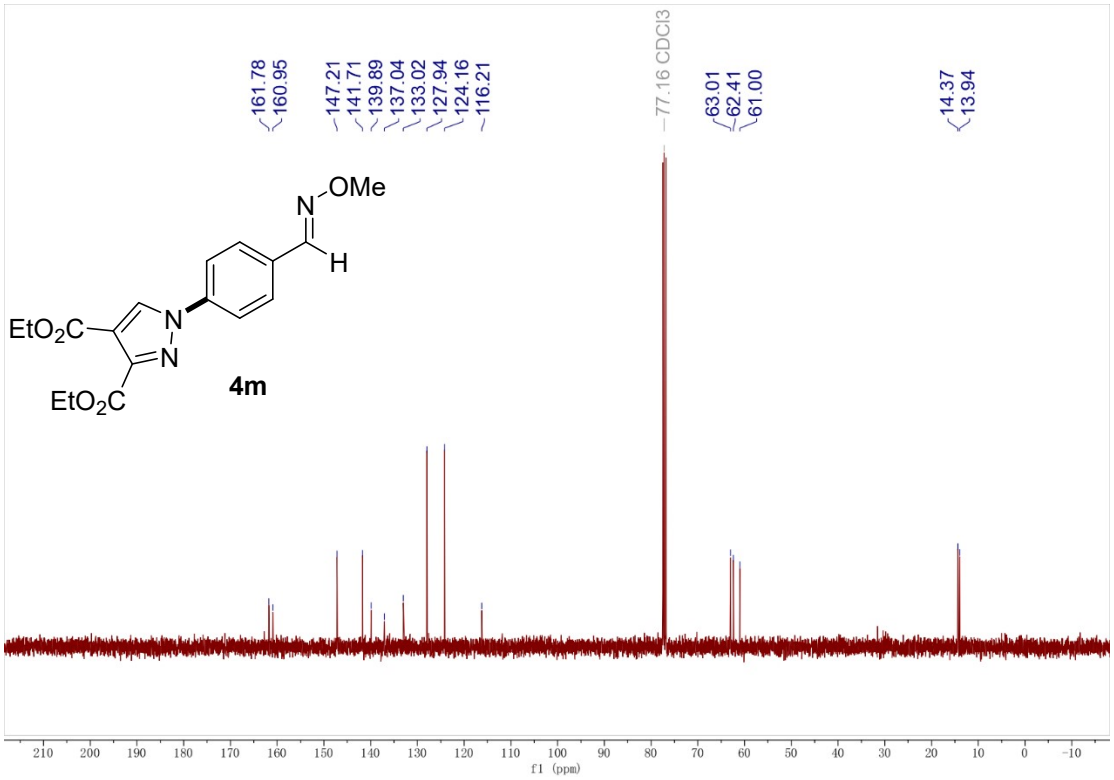
^{13}C NMR of 4l



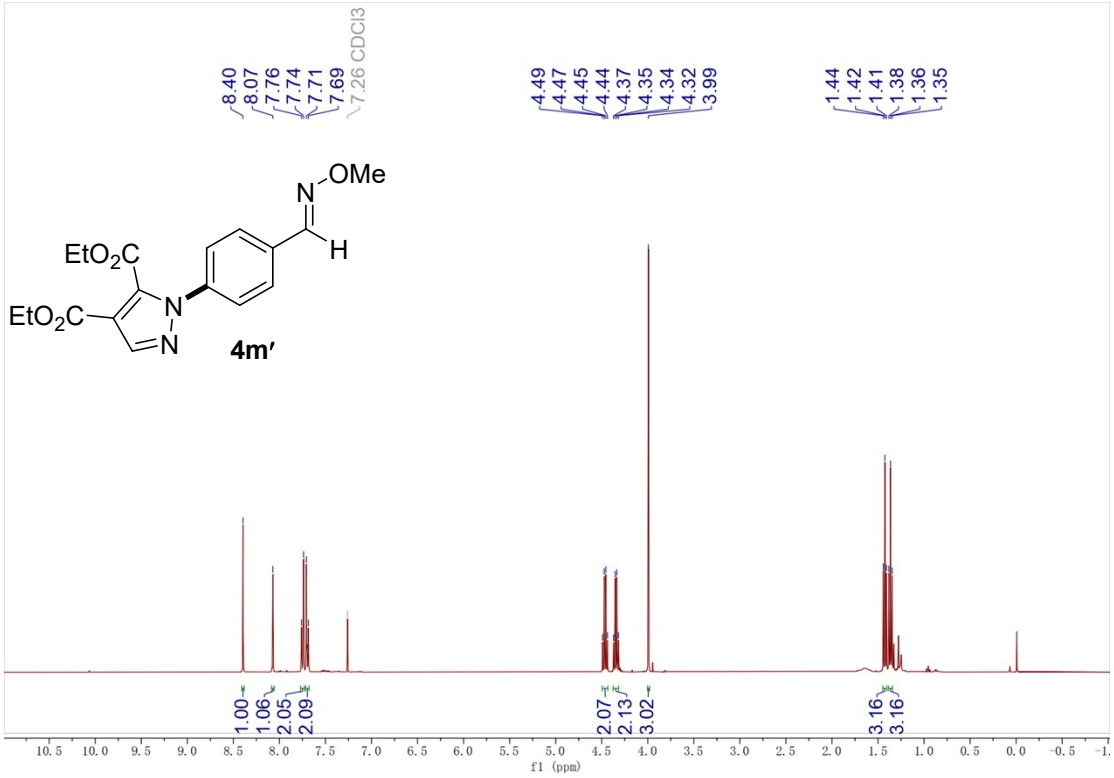
^{1}H NMR of 4m



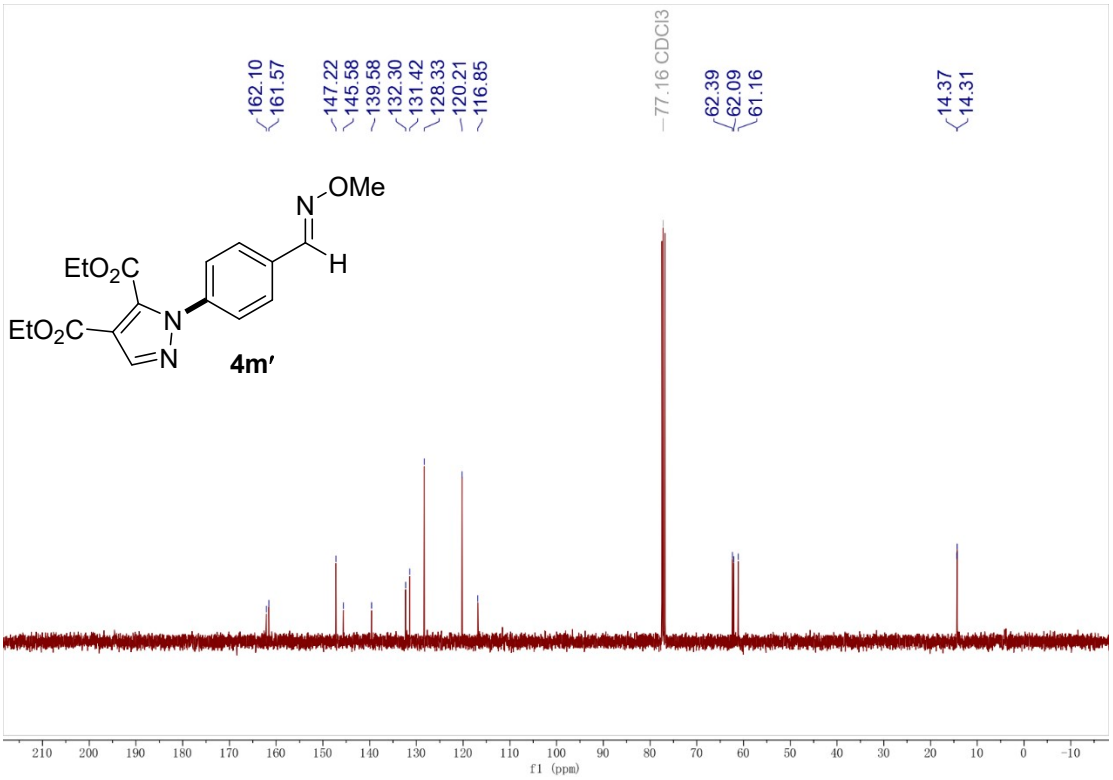
^{13}C NMR of 4m



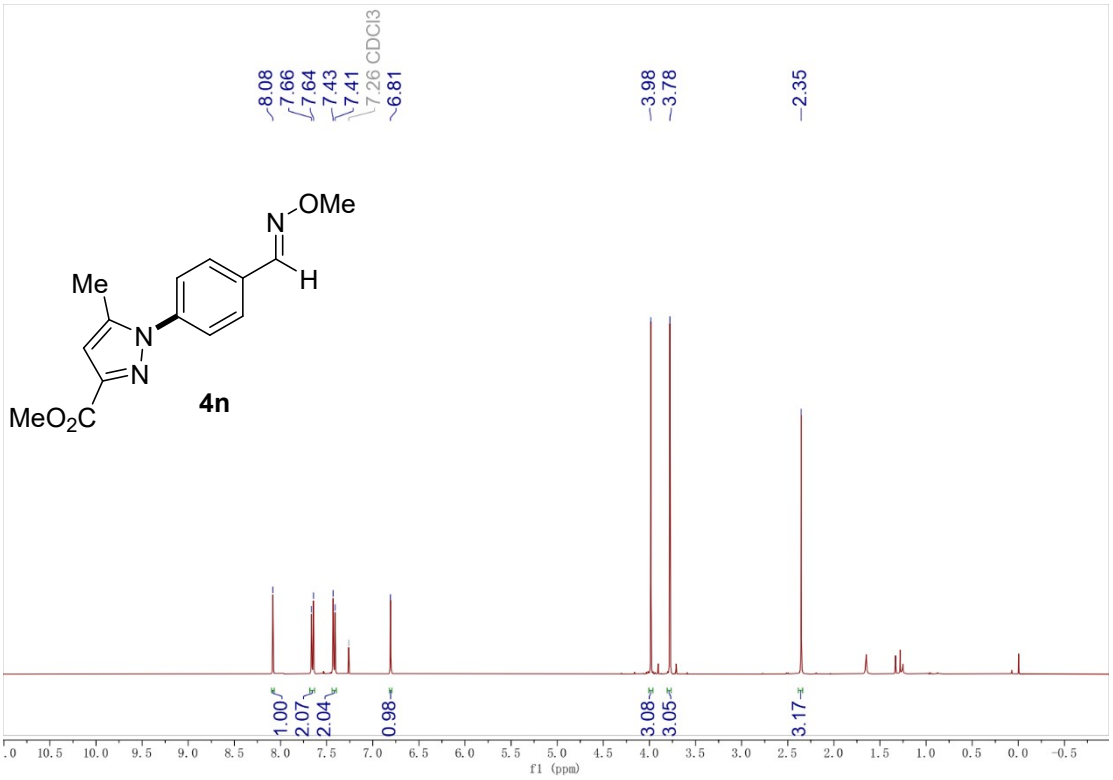
^{1}H NMR of 4m'



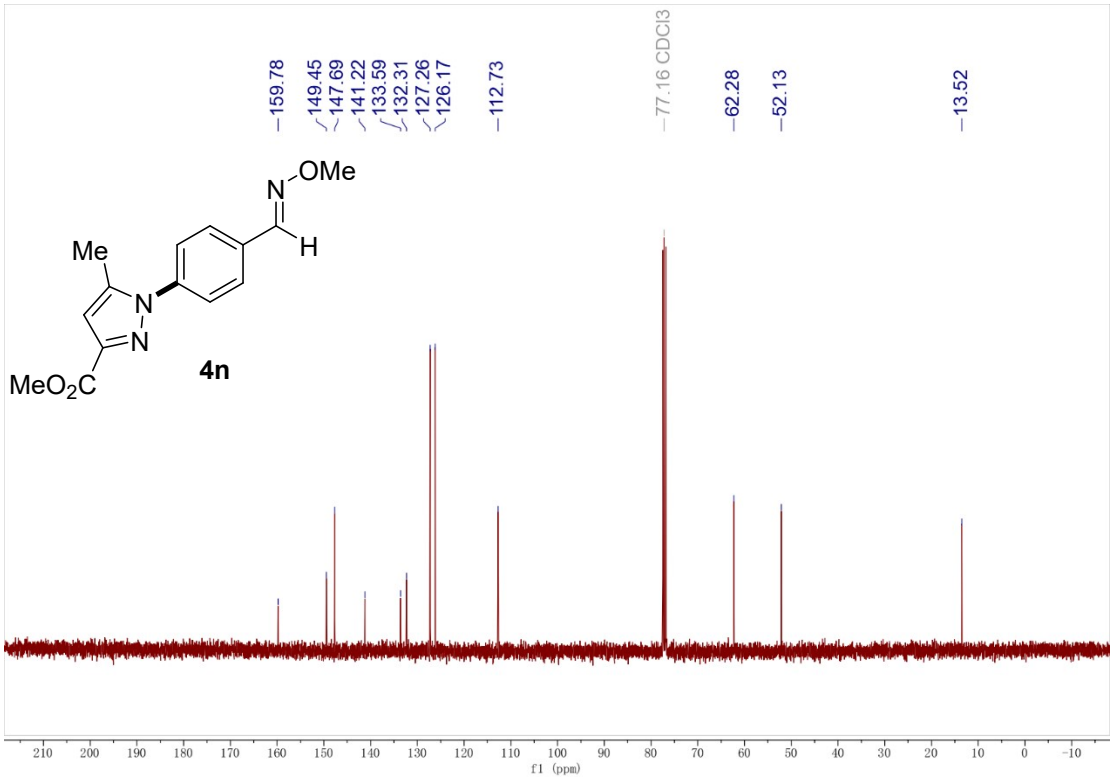
^{13}C NMR of 4m'



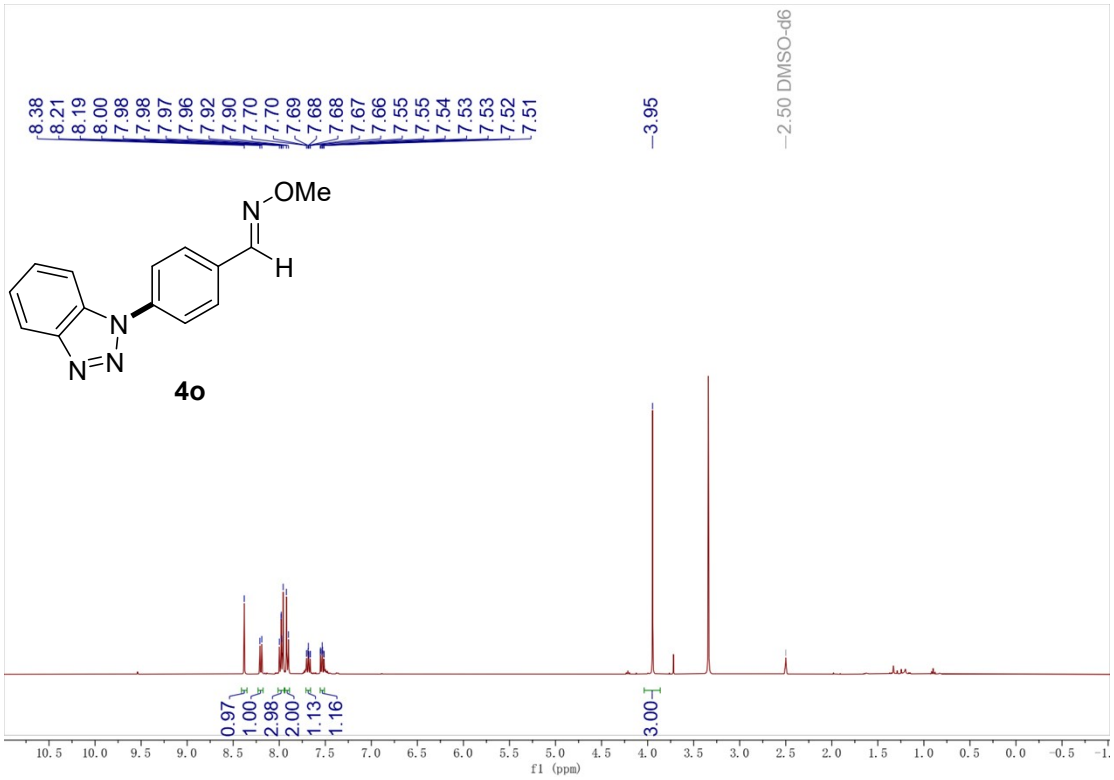
^{1}H NMR of 4n



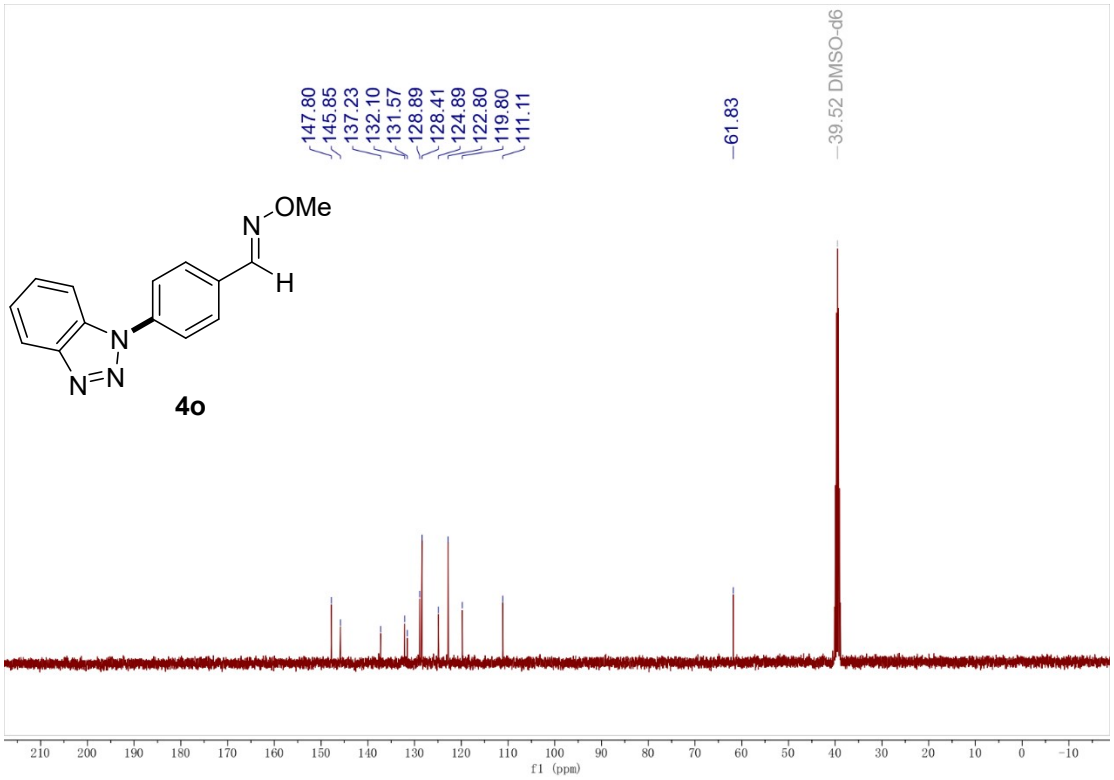
^{13}C NMR of 4n



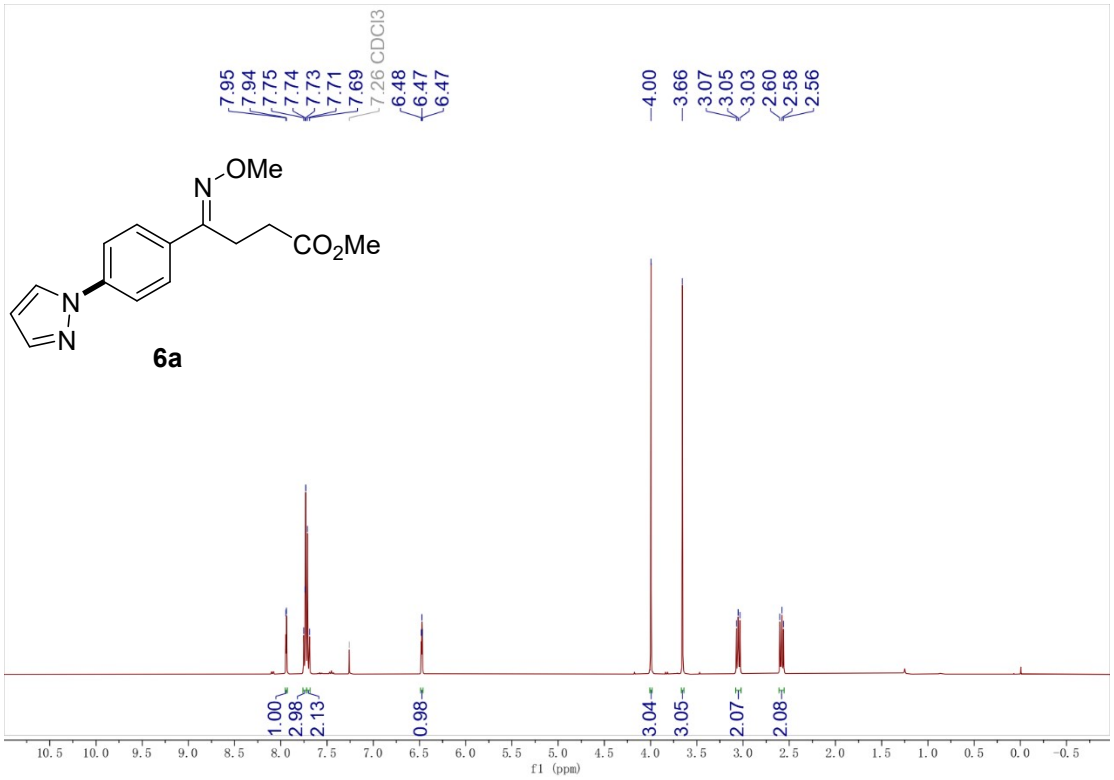
^{1}H NMR of 4o



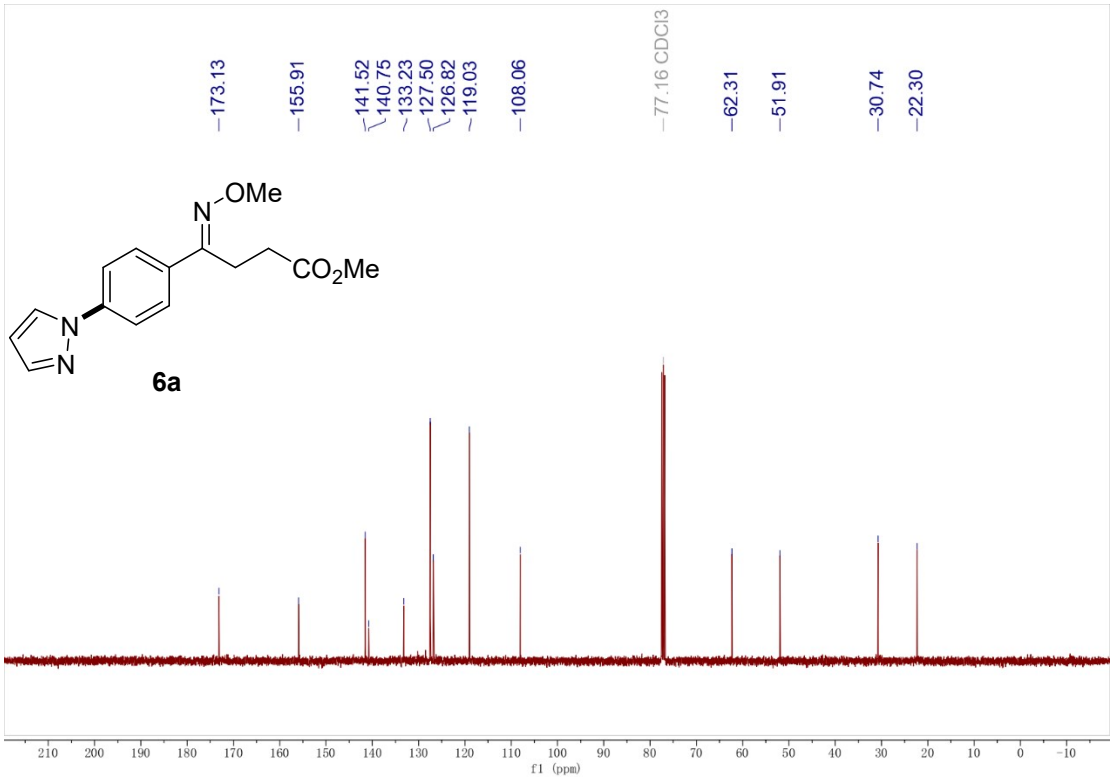
^{13}C NMR of 4o



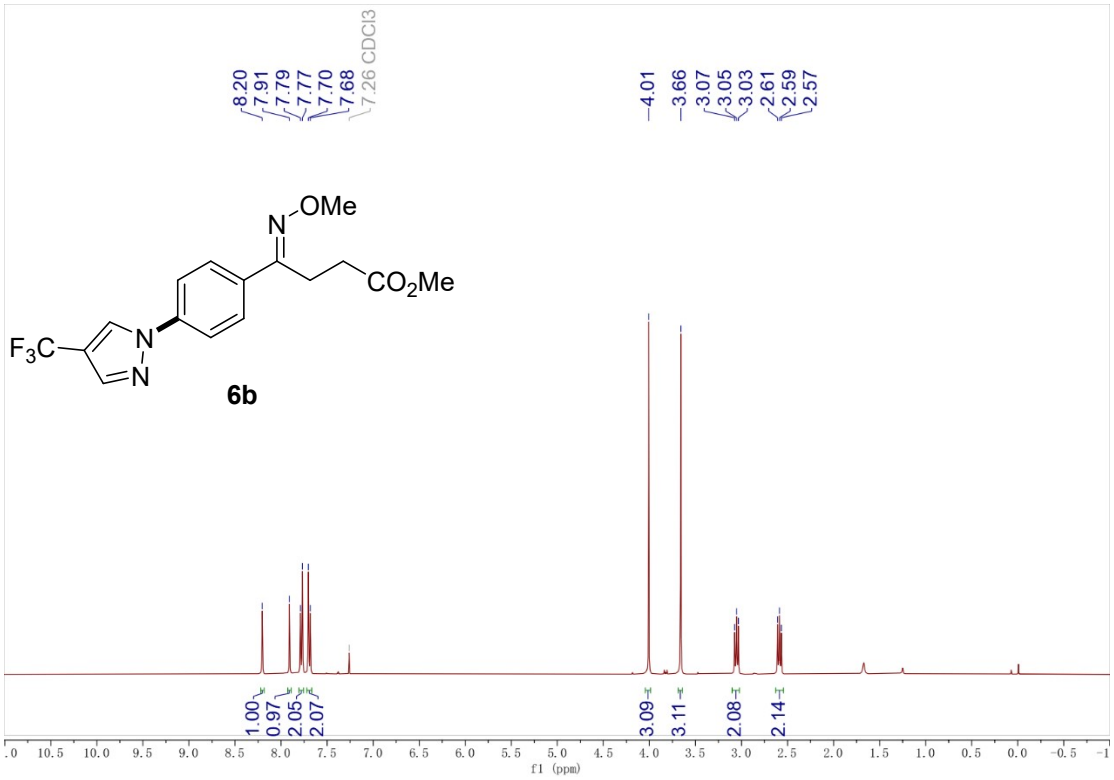
^{1}H NMR of 6a



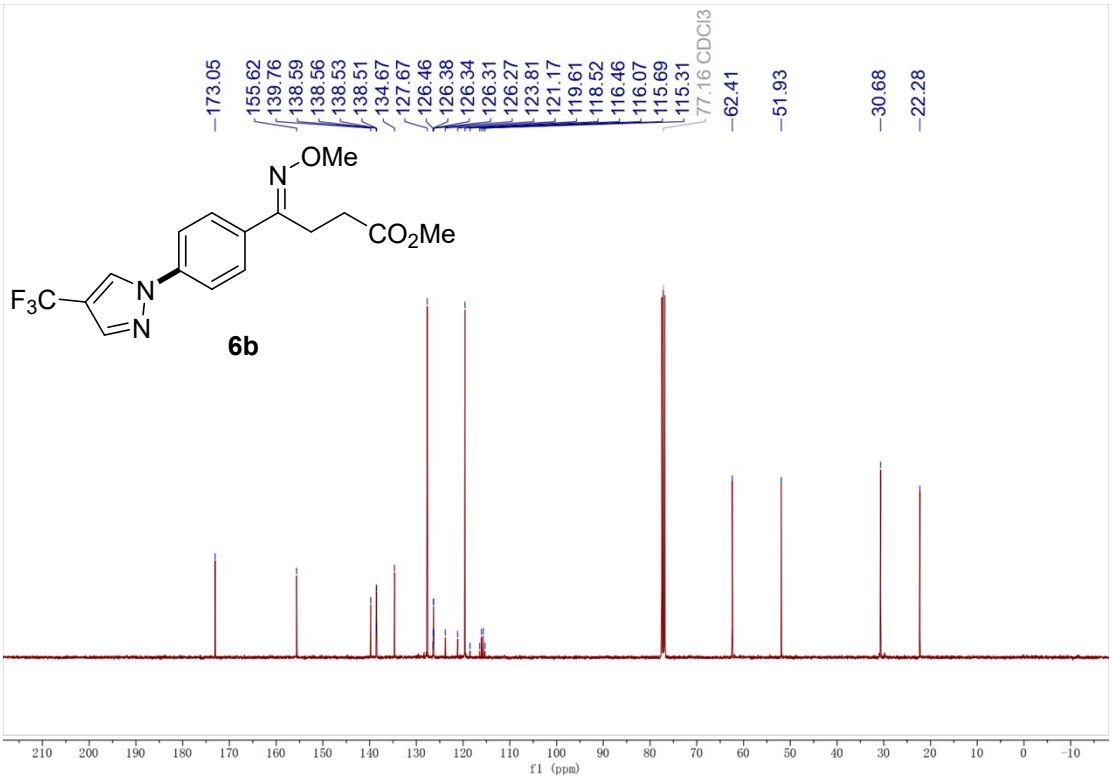
^{13}C NMR of 6a



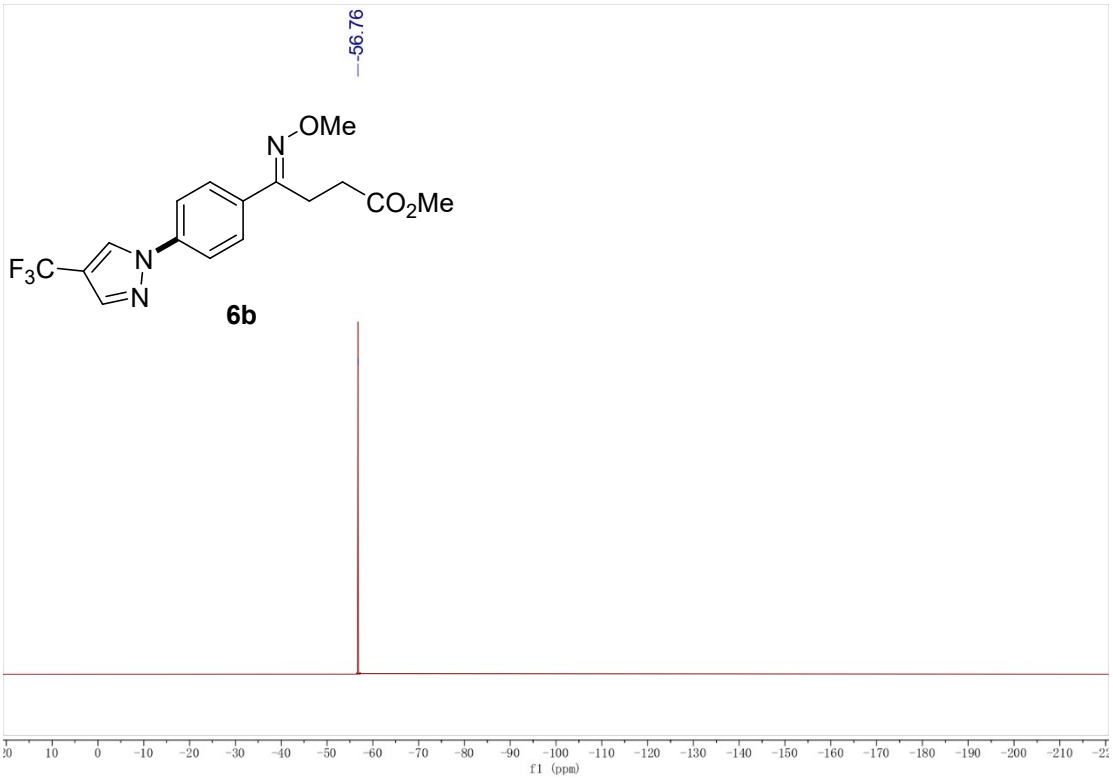
^{1}H NMR of 6b



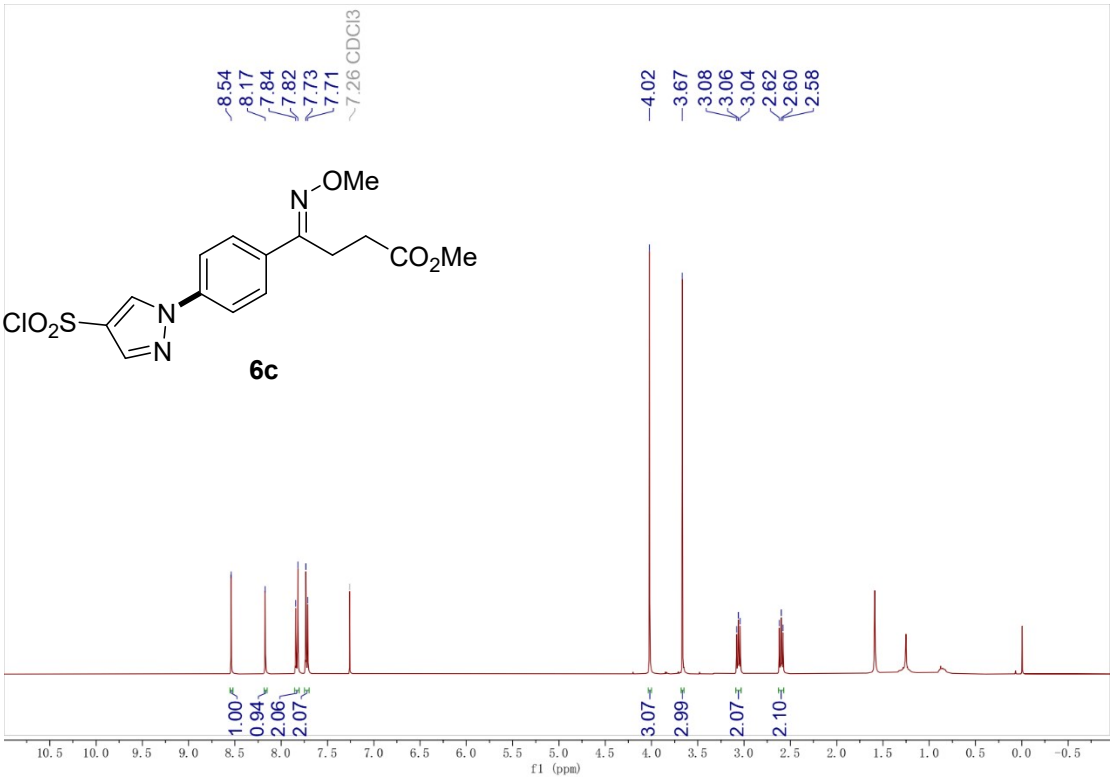
^{13}C NMR of 6b



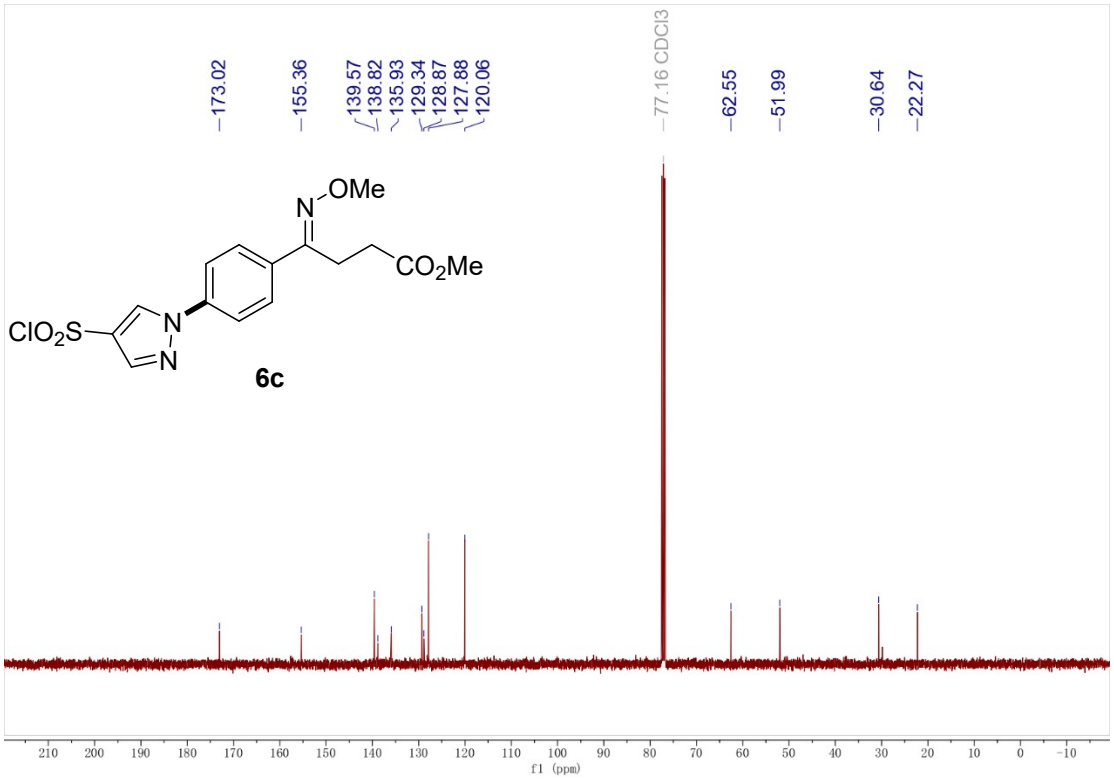
^{19}F NMR of 6b



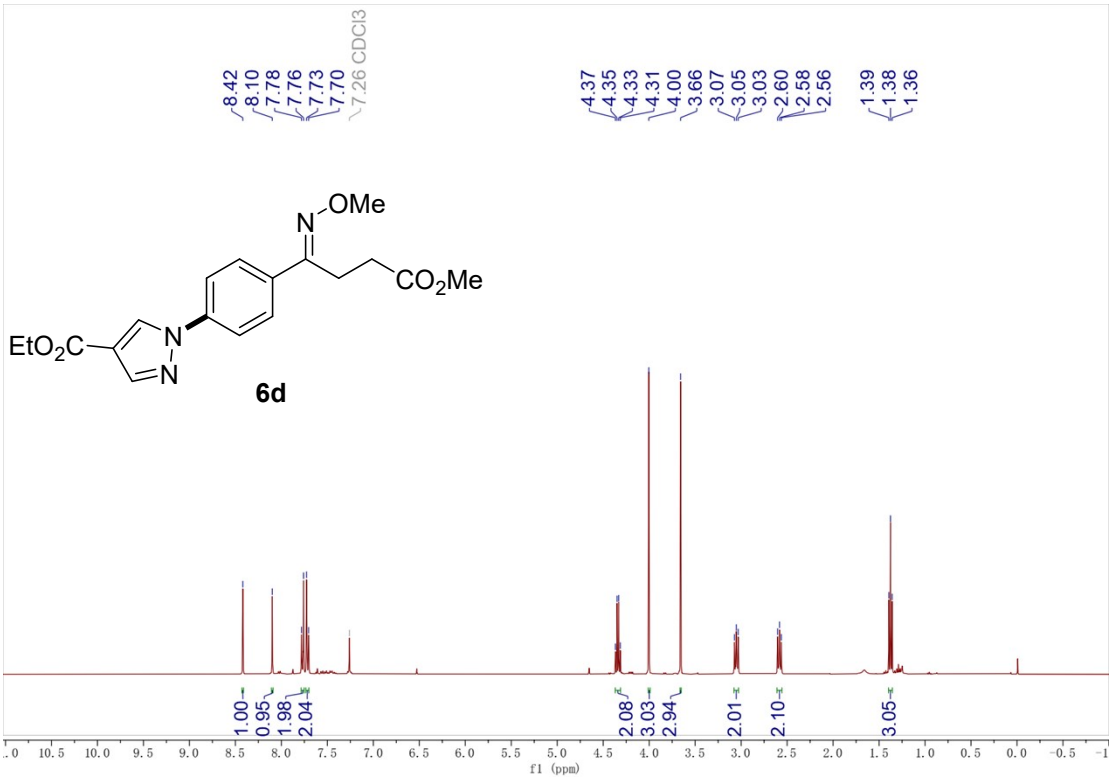
^{1}H NMR of 6c



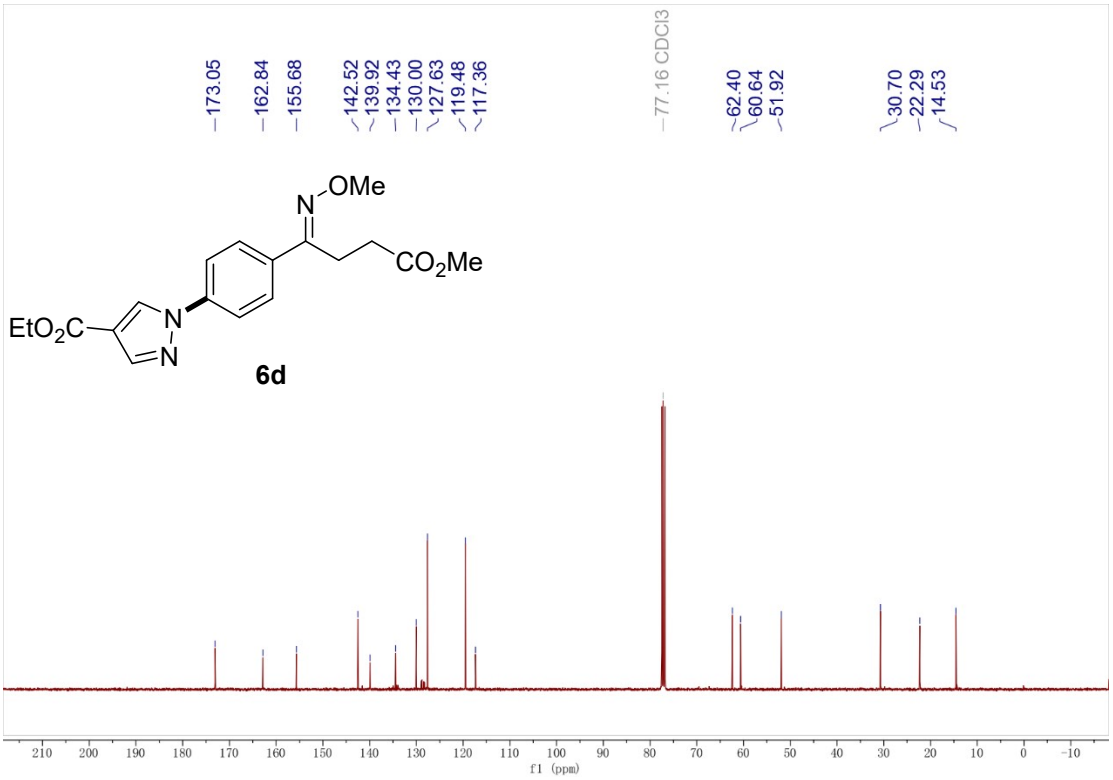
^{13}C NMR of 6c



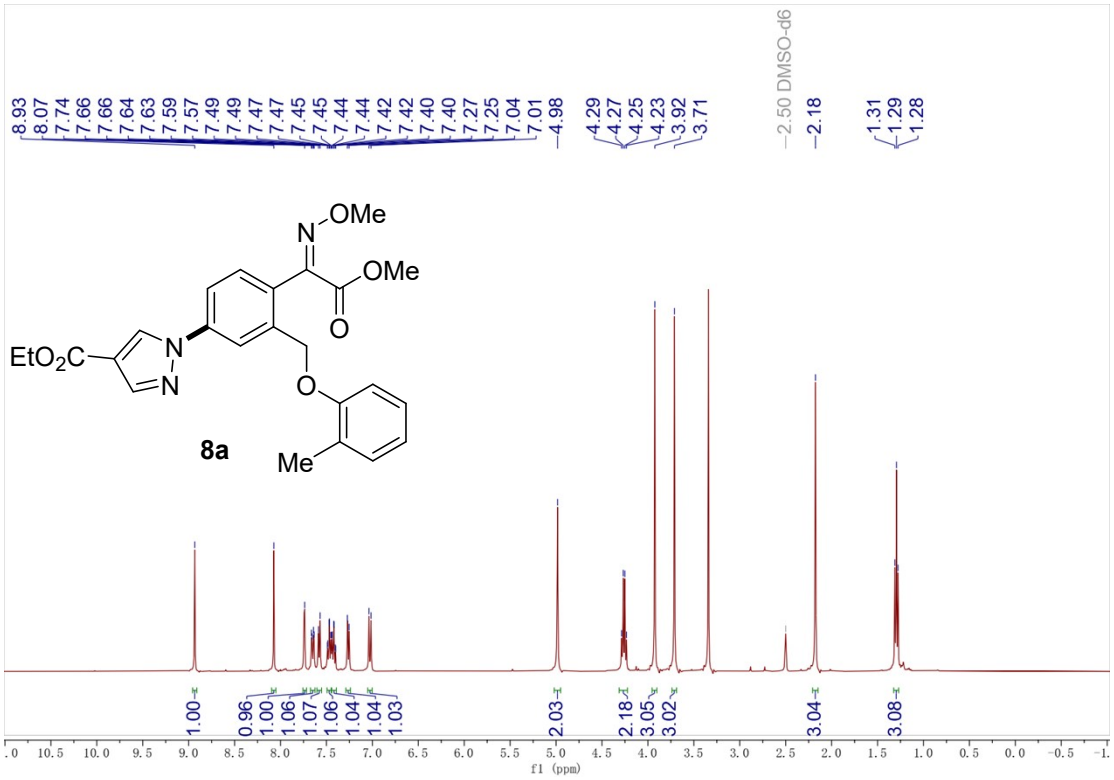
^{1}H NMR of 6d



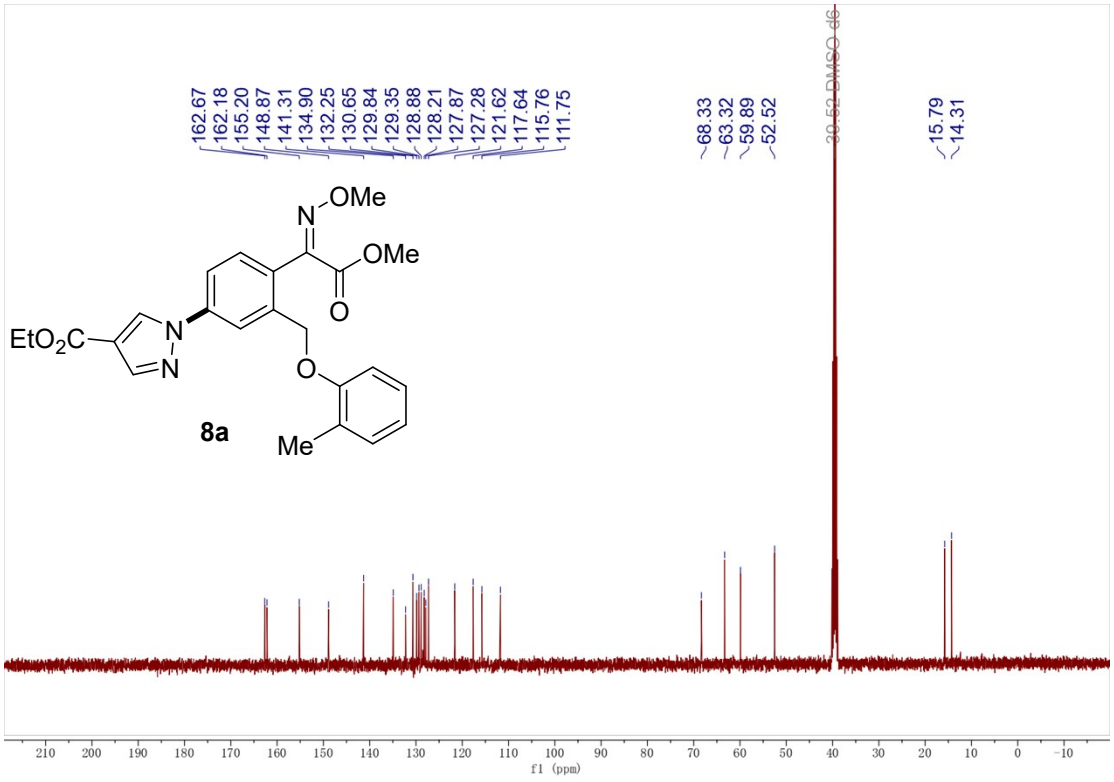
^{13}C NMR of 6d



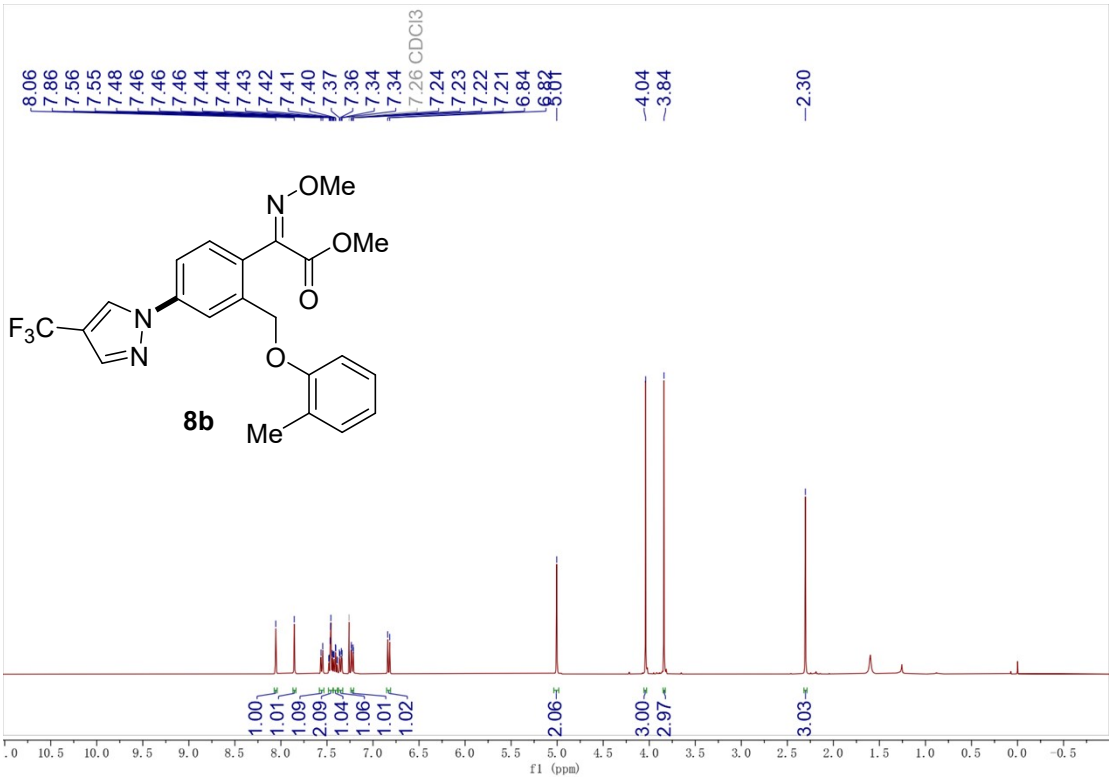
^{1}H NMR of 8a



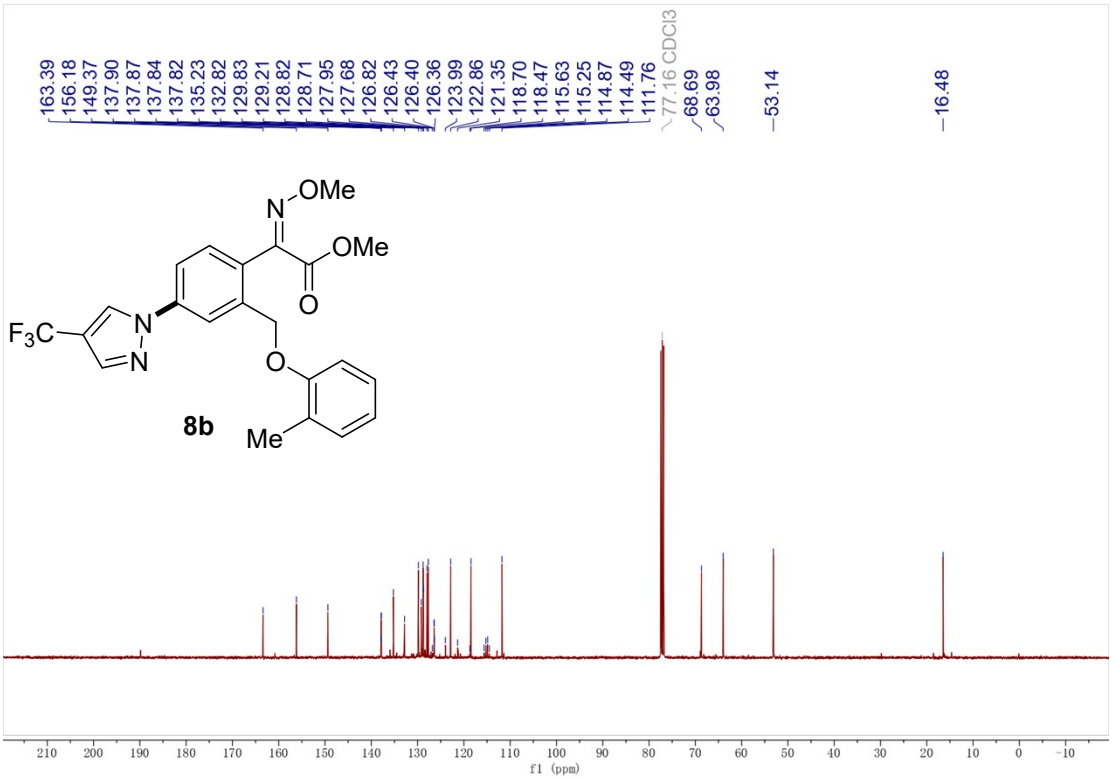
^{13}C NMR of 8a



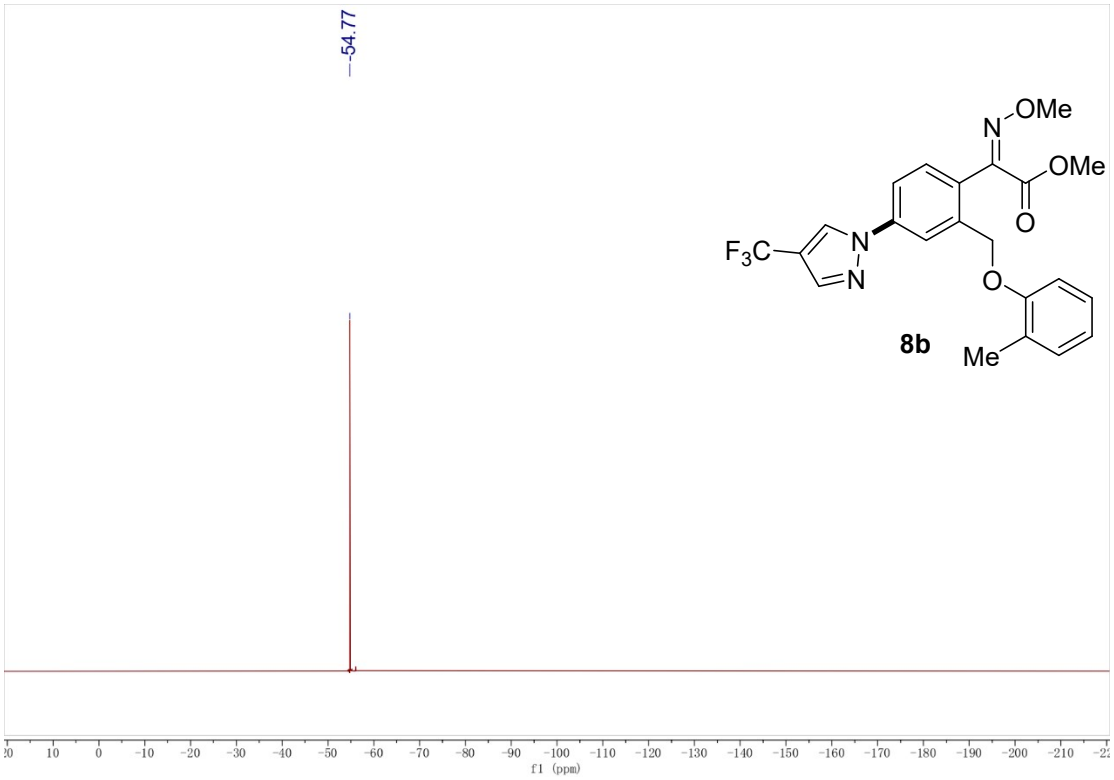
^{1}H NMR of 8b



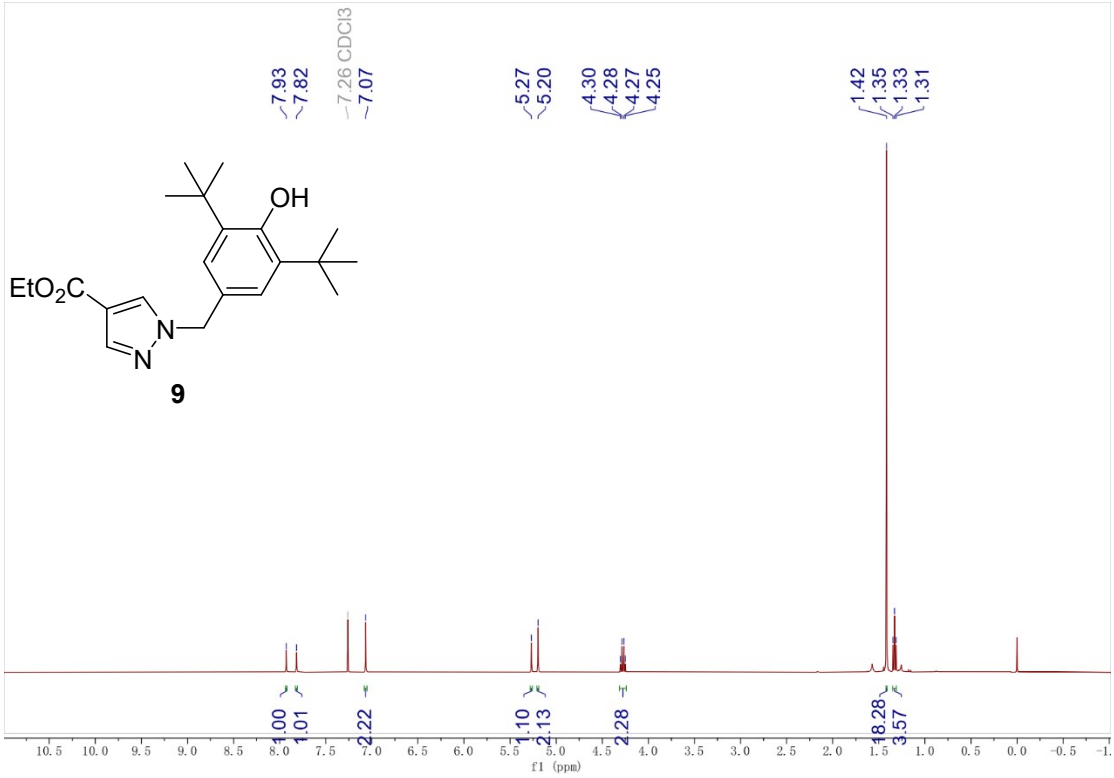
^{13}C NMR of 8b



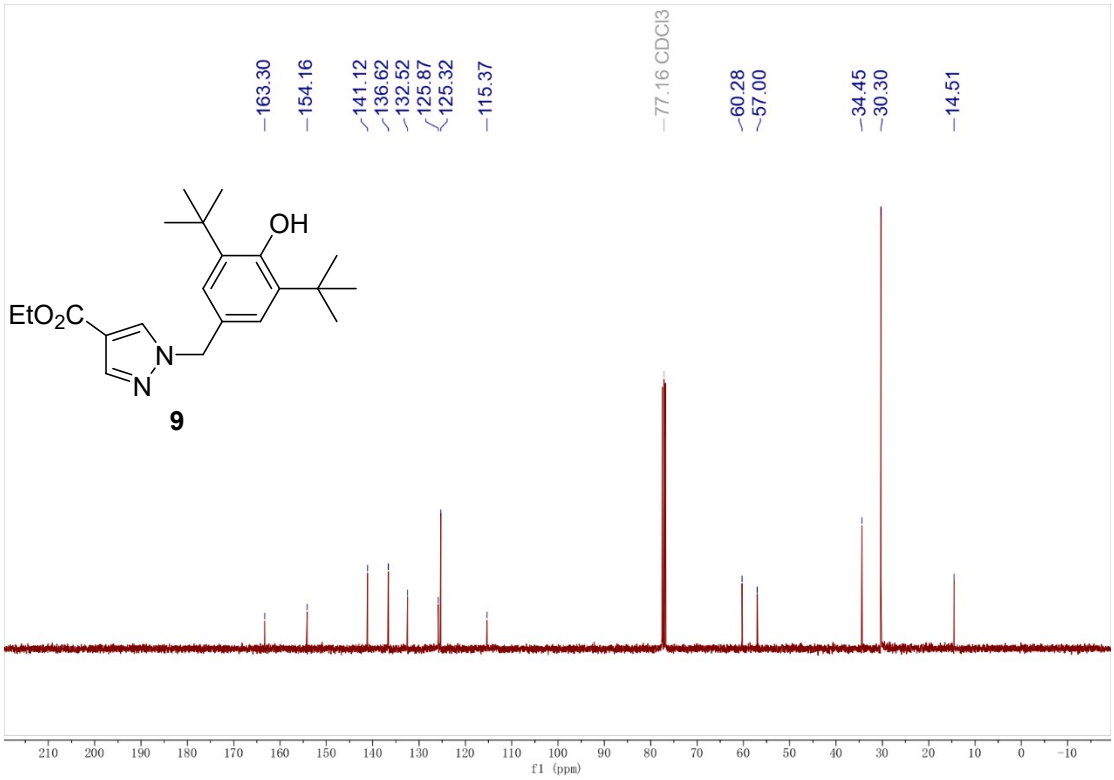
^{19}F NMR of 8b



^{1}H NMR of 9



^{13}C NMR of 9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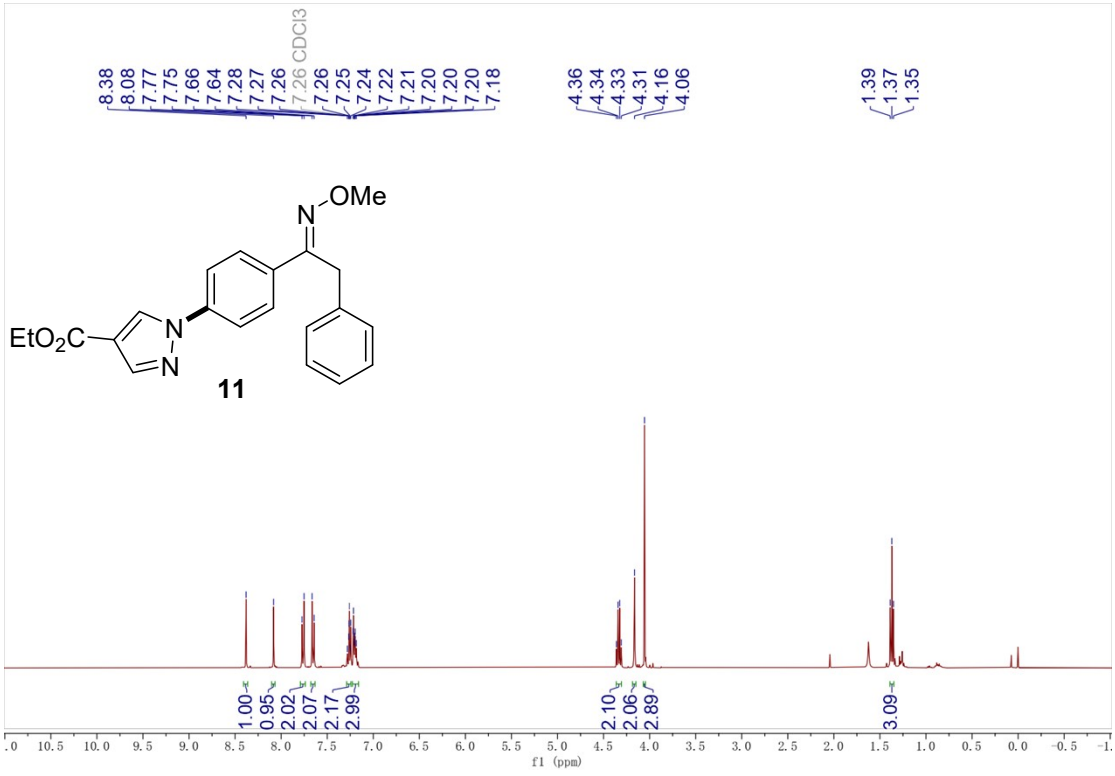
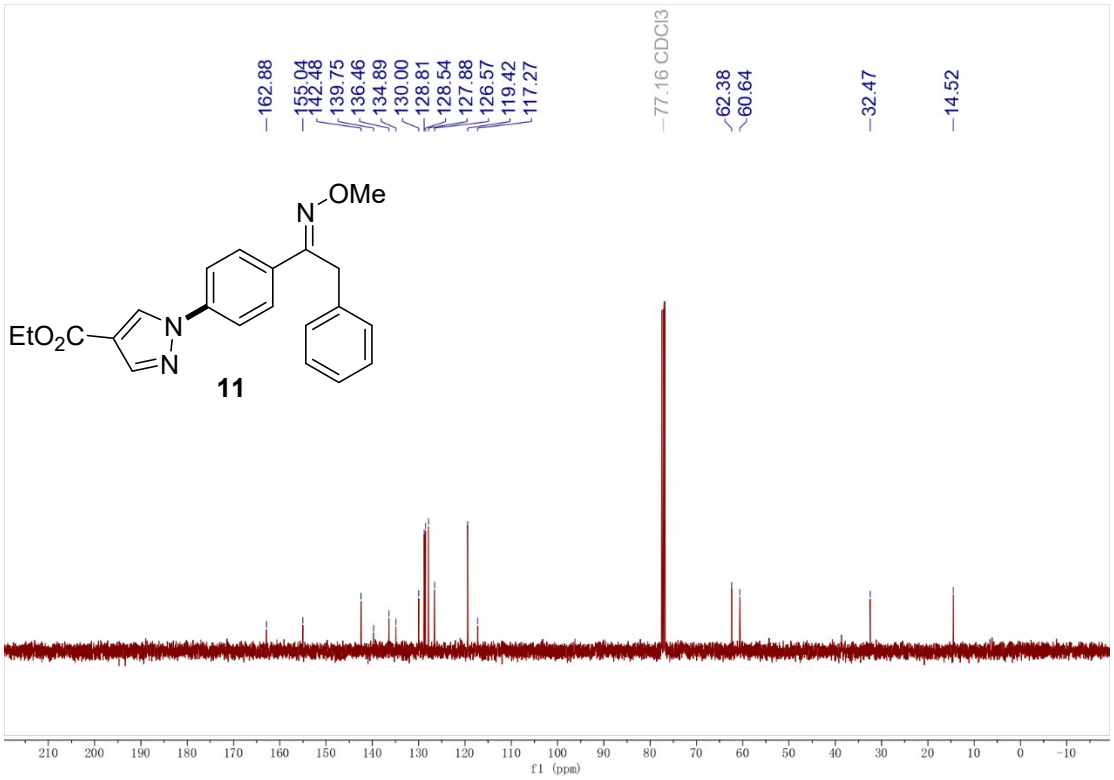
154.16
141.12
136.62
132.52
125.87
125.32
115.37
77.16 CDCl3
60.28
57.00
34.45
30.30
14.51
OH
EtO2C
N
N
9
f1 (ppm)

^{1}H NMR of 11


8.38
8.08
7.77
7.75
7.66
7.64
7.28
7.27
7.26
7.26 CDCl3
7.26
7.25
7.24
7.22
7.21
7.20
7.20
7.20
7.18
4.36
4.34
4.33
4.31
4.16
4.06
1.39
1.37
1.35
N
OMe
EtO2C
N
N
11
1.00
0.95
2.02
2.07
2.17
2.99
2.10
2.06
2.89
3.09
f1 (ppm)

^{13}C NMR of 11


162.88
155.04
142.48
139.75
136.46
134.89
130.00
128.81
128.54
127.88
126.57
119.42
117.27
77.16 CDCl3
62.38
60.64
32.47
14.52
N
OMe
EtO2C
N
N
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)