Supporting Information

Copper-catalyzed reactions of α,β-unsaturated *N*-tosylhydrazones with diaryliodonium salts to construct *N*-arylpyrazoles and diaryl sulfones

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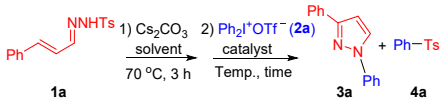
1. General experiment information

All reactions were carried out in dried glassware with magnetic stirring. Solvents used in the reactions were distilled from appropriate drying agents prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded respectively at 400MHz and 100MHz (600MHz and 150MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. High resolution mass spectra were obtained on Bruker Daltonics micrOTOF-Q II spect-rometer in ESI mode. Melting points were recorded using Reichert melting point apparatus and temperatures were uncorrected. All the reagents were obtained from commercial supplier and used as received, without further purification unless otherwise noted.

2. Optimization of reaction and control experiments

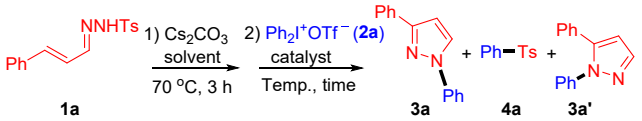
Table 1. Optimization of reaction conditions. [a]

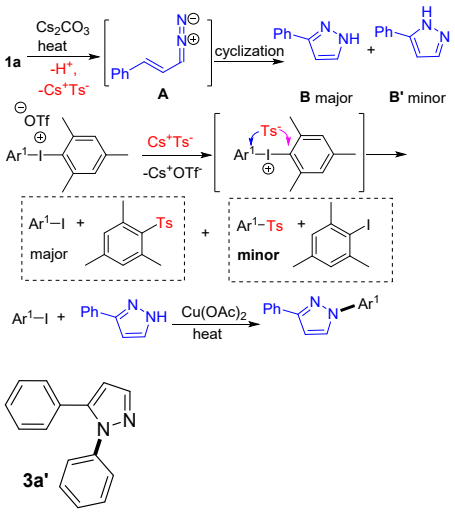


entry	catalyst	solvent	T (°C)/ t (h)	**3a** [b]	4a [b]
1	-	DCE	70/12	< 5	90
2	$Cu(OTf)_2$	DCE	70/12	25	91
3	CuI	DCE	70/12	30	91
4	$Cu(BF_4)(CN)_4$	DCE	70/12	15	95
5	$Cu(OAc)_2$	DCE	70/12	40	90
6	$Cu(OAc)_2$	Dioxane	70/12	45	91
7	$Cu(OAc)_2$	CH_3CN	70/12	30	92
8[c,d]	$Cu(OAc)_2$	DMF	70/12	75	90
9[c,d]	$Cu(OAc)_2$	DMSO	70/12	60	90
10[c,d]	$Cu(OAc)_2$	DMF	110/12	80	95
11[c,d]	$Cu(OAc)_2$	DMF	130/24	95	96

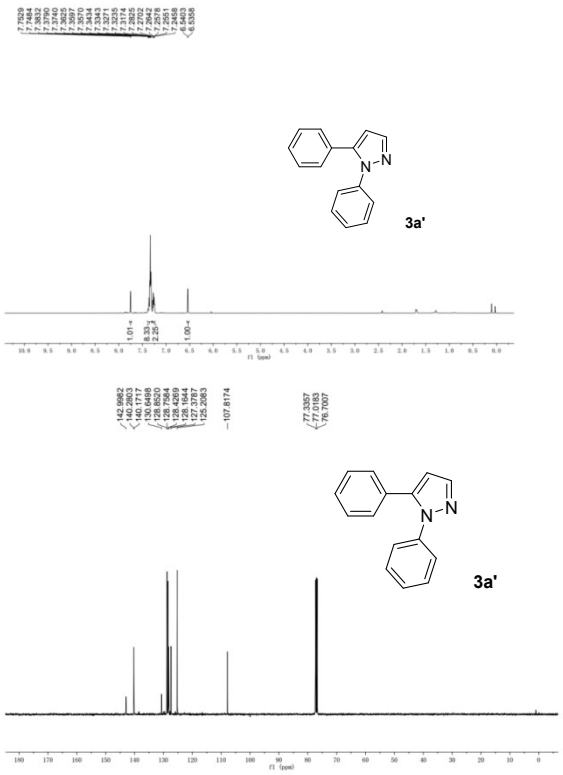
[a] Reaction conditions: α, β-unsaturated *N*-tosylhydrazone **1a** (0.1 mmol, 1.0 equiv), Cs_2CO_3 (0.15 mmol, 1.5 equiv) in 1 mL of solvent at 70 °C for 3 hours. And then, diaryliodonium salt **2a** (0.1 mmol, 1.0 equiv) and copper catalyst (0.005 mmol, 5 mmol%) were added, reacting at 70 °C, 110 °C and 130 °C for 12 hours or 24 hours. [b] Isolated yield. [c] The regioselectivity of **3a/3a'** >20:1. [d] Determined by ^{1}H NMR analysis of the crude reaction mixture.

the 1,5-diphenyl-pyrazole **3a'** was minor isomer.

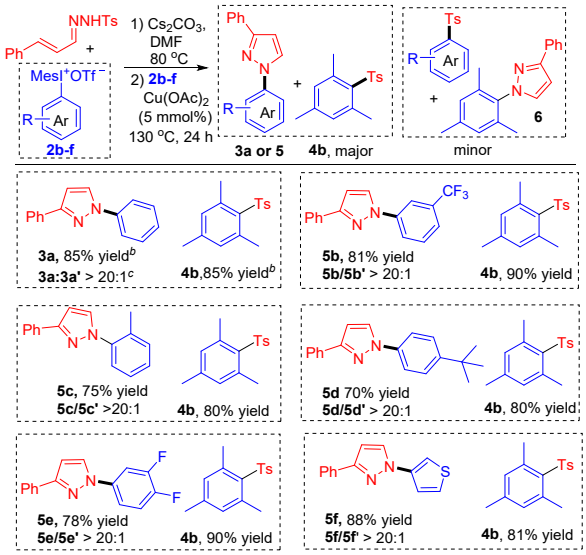




1,5-diphenyl-pyrazole (3a') R_f = 0.60 (EA/PE = 1:10), oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.30 (m, 8H), 7.29 – 7.24 (m, 2H), 6.54 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 140.28, 140.17, 130.65, 128.85, 128.76, 128.43, 128.16, 127.38, 125.21, 107.82. HRMS calcd for $C_{15}H_{12}N_2$ [M+H] $^+$: 221.1079, found: 221.1083.



Scheme 2. Substrate Scope of unsymmetrical diaryliodonium salts (for detail)



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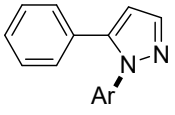
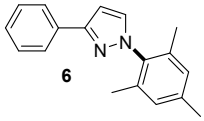


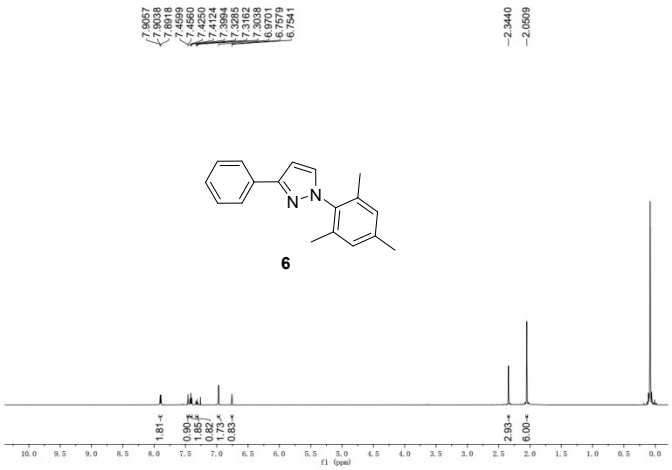
5'

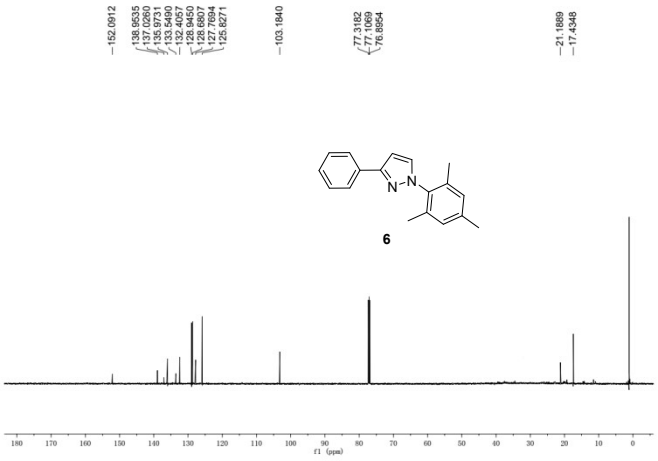
Compound **6** was a minor product



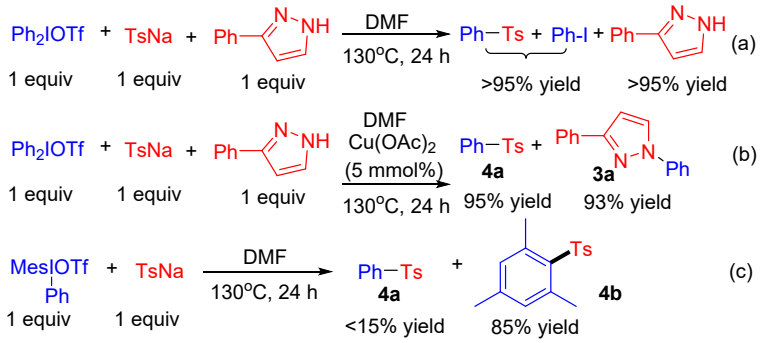
6

1-mesityl-3-phenyl-pyrazole (6) R_f = 0.65 (EA/PE = 1:10), white solid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 2H), 6.77 – 6.74 (m, 1H), 2.34 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 152.09, 138.95, 137.03, 135.97, 133.55, 132.41, 128.95, 128.68, 127.77, 125.83, 103.18, 21.19, 17.43. HRMS calcd for $C_{18}H_{18}N_2$ [M+H]$^+$: 263.1548, found: 263.1539.





Scheme 3.Control Experiments

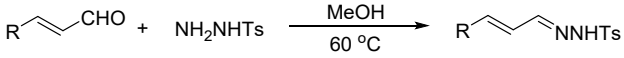


In Scheme 3 (a), it demonstrates that the nucleophilicity of *p*-toluenesulfonyl anion (Ts^-) is stronger than that of 3-phenyl-pyrazole.

In Scheme 3 (b), While adding $Cu(OAc)_2$ as catalyst, it provided biphenyl sulfide in 95% yield, and *N*-arylpyrazole in 93% yield. It shows that $Cu(OAc)_2$ catalyzed the coupling reaction of iodobenzene with 3-phenylpyrazole,

In Scheme 3 (c), it demonstrates that the bond cleavage of I-mesityl is faster than that of I-phenyl in the mesityl phenyliodonium salts because the intermediate Ar^+ formed *in situ* from 2,4,6-trimethylphenyl are more stable than phenyl ion.

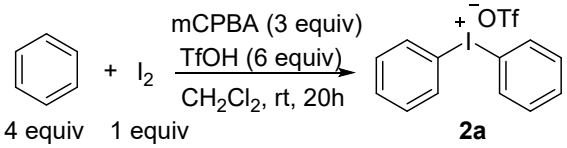
3. Synthesis of α,β-unsaturated tosylhydrazones[1]



α,β-unsaturated aldehydes（5 mmol）was dropped to a solution of pure 4-methylbenzenesylfonhydrazide (5 mmol) in methanol (5 mL). The mixture was stirred and heated to 60 °C until the α,β-unsaturated aldehydes was completely dissolved. After approximately 0.5-3 hour the crude products was obtained as precipitates. The precipitate was washed by using petroleum ether and dried in *vacuo* to afford the pure products. The reaction provides the α,β-unsaturated tosylhydrazones in about 70-99% yields.

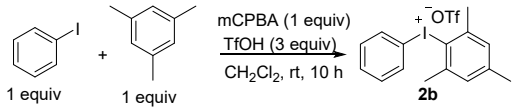
4. Synthesis of diphenyliodonium triflate reagents[2]

4.1 Synthesis of Di(phenyl)iodonium Triflate (2a)



Iodine (2 mmol), benzene (8 mmol), and MCPBA (8 mmol) were dissolved in 10 mL of CH_2Cl_2. Then, TfOH (12 mmol) was added to the mixture and the solution was stirred at 40 °C for 15 min. After the solvents were evaporated in vacuo, the residue was submitted to flash chromatography to give **2a** as solid in 65% yield.

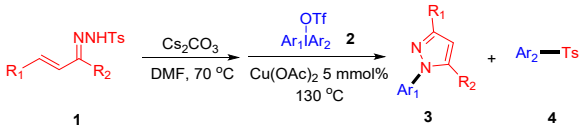
4.2 Synthesis of unsymmetrical arylphenyliodonium salts Triflate (2b) by in Situ Anion Exchange



Iodobenzene (2.5mmol), mCPBA10 (2.5 mmol), and 2,4,6-trimethylphen (2.5 mmol) were dissolved in CH_2Cl_2 (10 mL) and 2,2,2-trifluoroethanol (10 mL). Then, TfOH (2.5 mmol) was added to the solution and the mixture was stirred at r.t. for 10 h and the solution was concentrated in vacuo. Et_2O (1 mL) was added and the mixture was stirred at r.t. for 10 min to precipitate. The precipitate was filtered off, washed with Et_2O, and dried to give salt **2b** in 90%.

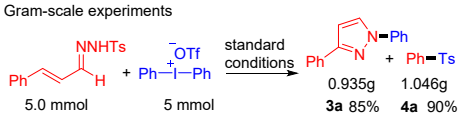
5. General Procedure for the domino reaction and gram scale reaction

5.1 General Procedure for the domino reaction



α, β-unsaturated *N*-tosylhydrazones **1** (0.1 mmol, 1 equiv), Cs_2CO_3 (0.15 mmol) and DMF (1 mL) were added to a tube. The mixture was stirred at 70 °C for 2-3 h. The reaction mixture was cooled to room temperature. And then, the di(phenyl)iodonium triflate (**2a**, 0.1 mmol, 1 equiv) and Cu(OAc)2 (0.005 mmol, 0.05 equiv) were added to this tube. The mixture was heated at 130 °C in a preheated oil bath for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL water and extracted with ethyl acetate (3×10 mL). The combined organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatograph on silica gel (ethyl acetate/petroleum ether as the eluent) to afford the target products **3** and **4**.

5.2 General Procedure for the gram scale reaction



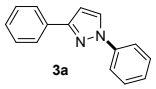
α, β-unsaturated *N*-tosylhydrazones **1a** (5 mmol, 1 equiv), Cs_2CO_3 (7.5 mmol) and DMF (10 mL) were added to a tube. The mixture was stirred at 70 °C for 4 h. The reaction mixture was cooled to room temperature. And then, the di(phenyl)iodonium triflate (**2a**, 5 mmol, 1 equiv) and Cu(OAc)2 (0.25 mmol, 0.05 equiv) were added to this tube. The mixture was heated at 130 °C in a preheated oil bath for 30 hours. The reaction mixture was cooled to room temperature, diluted with 50 mL water and extracted with ethyl acetate (3×20 mL). The combined organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatograph on silica gel (ethyl acetate/petroleum ether as the eluent) to afford the target products **3a** and **4a**.

6. References

1 a) A. J. Xia,; T. R. Kang, L. He, L. M. Chen, W. Y. Li, J. L. Yang, Q. Z. Liu, *Angew. Chem., Int. Ed*., 2016, ***55***, 1441; (b) X. Nie, Y. Wang, L. Yang, Z. Yang, T. Kang, *Tetrahedron Lett.*, 2017, ***58***, 3003.;(c) L.Zeng, X.-Q. Guo, Z.-J. Yang, Y. Gan, L.-M. Chen, T.-R. Kang, *Tetrahedron Lett.*, 2019, ***60***, 150943; d) L.-M. Chen, J. Zhao, A.-J. Xia, X.-Q. Guo, Y. Gan, C. Zhou, Z.-J. Yang, J. Yang, T.-R. Kang. *Org. Biomol. Chem*., 2019, ***17***, 8561.

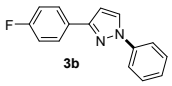
2 a)M. Bielawski, B. Olofsson, Chem. Commun. 2007, 2521;b) M. Bielawski, M. Zhu, B. Olofsson, Adv. synth. Catal. 2007, 349, 2610; c) M. Bielawski, B. Olofsson, Org. Synth. 2009, 86, 308-314.

7. ^{1}H NMR, ^{13}C NMR data of compounds



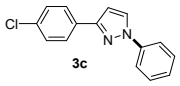
3a

1,3-diphenyl-1H-pyrazole (3a) R_f = 0.70 (EA/PE = 1:10), yield 92%, white solid. m.p.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.81 – 7.76 (m, 2H), 7.51 – 7.41 (m, 4H), 7.38 – 7.27 (m, 2H), 6.79 (d, *J* = 2.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.94, 140.26, 133.15, 129.40, 128.64, 128.00, 127.96, 126.31, 125.84, 119.05, 105.01. HRMS calcd for $C_{15}H_{12}N_2$ [M+H] $^{+}$: 221.1079, found: 221.1082.



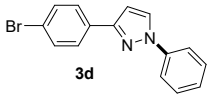
3b

3-(4-fluorophenyl)-1-phenyl-1H-pyrazole (3b) R_f = 0.75 (EA/PE = 1:10), yield 91%, white solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 2.4 Hz, 1H), 7.91-7.89 (m, 2H), 7.80 – 7.73 (m, 2H), 7.51 – 7.43 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.72 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 162.85 (d, *J* = 246.7Hz), 152.11, 140.22, 129.54, 128.21, 127.64, 127.58, 126.51, 119.11, 115.67 (d, *J* = 21.6Hz), 104.92. HRMS calcd for $C_{15}H_{11}FN_2$ [M+H] $^{+}$: 239.0985, found: 239.0987.



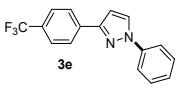
3c

3-(4-chlorophenyl)-1-phenyl-1H-pyrazole (3c) R_f = 0.72 (EA/PE = 1:5), yield 88%, white solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.78 – 7.75 (m, 2H), 7.49 – 7.45 (m, 2H), 7.42 – 7.39 (m, 2H), 7.33 – 7.29 (m, 1H), 6.75 (d, *J* = 2.5 Hz, 1H).
^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 151.87, 140.17, 133.82, 131.73, 129.56, 128.92, 128.27, 127.16, 126.61, 119.16, 105.07.HRMS calcd for $C_{15}H_{11}ClN_2$ [M+H] $^{+}$: 225.0689, found: 255.0693.



3d

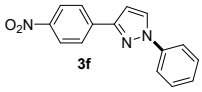
3-(4-bromophenyl)-1-phenyl-1H-pyrazole (3d) R_f = 0.6 (EA/PE = 1:5), yield 86%, white solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.78 – 7.75 (m, 2H), 7.57 – 7.54 (m, 2H), 7.49 – 7.46 (m, 2H), 7.33 – 7.29 (m, 1H), 6.75 (d, *J* = 2.5 Hz, 1H).
^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 151.88, 140.16, 132.19, 131.86, 129.56, 128.26, 127.46, 126.62, 122.03, 119.15, 105.06. HRMS calcd for $C_{15}H_{11}BrN_2$ [M+H] $^{+}$: 299.0184, found: 299.0188.



3e

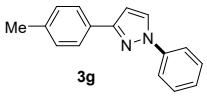
1-phenyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole (3e) R_f = 0.68 (EA/PE = 1:5), yield 83%, white solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 2.5 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.35 – 7.31 (m, 1H), 6.82 (d, *J* = 2.5 Hz, 1H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 151.50, 140.10, 136.64, 129.83 (d, *J* = 32.4 Hz), 129.60, 128.43, 126.82, 126.01, 125.71 (d, *J* = 3.9 Hz), 124.39 (d, *J* = 271.8 Hz), 119.25, 105.48. HRMS calcd for $C_{16}H_{11}F_3N_2$ [M+H] $^+$: 289.0953, found: 289.0950.



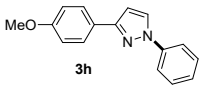
3f

3-(4-nitrophenyl)-1-phenyl-1H-pyrazole (3f) R_f = 0.30 (EA/PE = 1:10), yield 95%, yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.32 – 8.26 (m, 2H), 8.10 – 8.05 (m, 2H), 8.04 – 7.99 (m, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.38 – 7.32 (m, 1H), 6.90 – 6.85 (m, 1H).
^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 150.60, 147.35, 139.94, 139.47, 129.65, 128.74, 127.12, 126.30, 124.21, 119.35, 105.98. HRMS calcd for $C_{15}H_{11}N_3O_2$[M+H] $^+$: 266.0930, found: 266.0935.



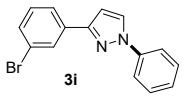
3g

1-phenyl-3-(p-tolyl)-1H-pyrazole (3g) R_f = 0.51 (EA/PE = 1:20), yield 93%, white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.70-7.67 (m, 2H), 7.42 – 7.35 (m, 2H), 7.23 – 7.14 (m, 3H), 6.67 (d, *J* = 2.5 Hz, 1H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.01, 140.29, 137.81, 130.34, 129.39, 129.34, 127.87, 126.21, 125.74, 119.02, 104.85, 21.32. HRMS calcd for $C_{16}H_{14}N_2$[M+H] $^+$: 235.1235, found: 235.1242.



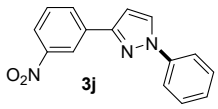
3h

3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole (3h) R_f = 0.55 (EA/PE = 1:5), yield 85%, white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 2.5 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.76 (dd, *J* = 8.6, 1.1 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.29 (d, *J* = 6.3 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.71 (d, *J* = 2.5 Hz, 1H), 3.86 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.60, 152.77, 140.26, 129.41, 127.91, 127.11, 126.17, 125.93, 118.95, 114.05, 104.60, 55.34. HRMS calcd for $C_{16}H_{14}N_2O$[M+H] $^+$: 251.1184, found: 251.1187.



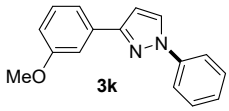
3i

3- (3-bromophenyl)-1-phenyl-1H-pyrazole (3i) R_f = 0.68 (EA/PE = 1:5), yield 85%, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (t, *J* = 1.8 Hz, 1H), 7.95 (d, *J* = 2.5 Hz, 1H), 7.83 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.50 – 7.45 (m, 3H), 7.33 (t, *J* = 1.1 Hz, 2H), 6.76 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 151.48, 140.12, 135.29, 130.96, 130.29, 129.57, 128.86, 128.29, 126.69, 124.45, 122.96, 119.19, 105.24. HRMS calcd for $C_{15}H_{11}BrN_2$ [M+H] $^+$: 299.0184, found: 299.0188.



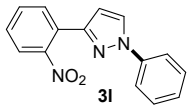
3j

3-(3-nitrophenyl)-1-phenyl-1H-pyrazole (3j) R_f = 0.48 (EA/PE = 1:10), yield 92%, yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.22 (dd, *J* = 45.0, 7.3 Hz, 2H), 8.03 – 7.98 (m, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 1H), 6.88 – 6.83 (m, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 150.61, 148.78, 139.97, 135.03, 131.61, 129.63, 128.64, 126.96, 122.63, 120.70, 119.25, 105.39. HRMS calcd for $C_{15}H_{11}N_3O_2$[M+H] $^+$: 266.0930, found: 266.0938.



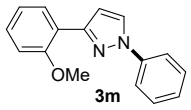
3k

3-(3-methoxyphenyl)-1-phenyl-1H-pyrazole (3k) R_f = 0.58 (EA/PE = 1:5), yield 95%, yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.52 – 7.45 (m, 4H), 7.37 – 7.33 (m, 1H), 7.30 (tt, *J* = 7.6, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 160.01, 152.87, 140.28, 134.57, 129.76, 129.51, 128.08, 126.46, 119.17, 118.53, 114.08, 111.03, 105.29, 55.43. HRMS calcd for $C_{16}H_{14}N_2O$[M+H] $^+$: 251.1184, found: 251.1189.



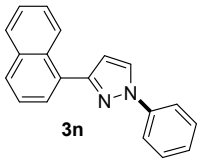
3l

3-(2-nitrophenyl)-1-phenyl-1H-pyrazole (3l) R_f = 0.45 (EA/PE = 1:10), yield 90%, Fuchsia oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.75 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.63 – 7.59 (m, 1H), 7.49 – 7.44 (m, 3H), 7.33 – 7.28 (m, 1H), 6.62 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 149.28, 148.32, 139.91, 131.92, 130.87, 129.55, 128.75, 127.97, 127.25, 126.86, 123.78, 119.20, 107.06. HRMS calcd for $C_{15}H_{11}N_3O_2$[M+H] $^+$: 266.0930, found: 266.0936.



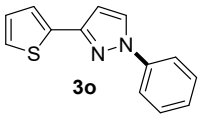
3m

3-(2-methoxyphenyl)-1-phenyl-1H-pyrazole (3m) R_f = 0.46 (EA/PE = 1:10), yield 88%, white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 2.5 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.47 – 7.43 (m, 2H), 7.29 – 7.27 (m, 1H), 7.19 (d, *J* = 35.5 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.08 – 7.07 (m, 1H), 6.83 (ddd, *J* = 8.2, 2.6, 0.8 Hz, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 159.95, 152.25, 140.11, 138.56, 130.80, 129.76, 129.56, 127.98, 126.46, 120.87, 119.44, 119.03, 113.84, 111.46, 105.11, 55.33. HRMS calcd for $C_{16}H_{14}N_2O$[M+H] $^+$: 251.1184, found: 251.1187.



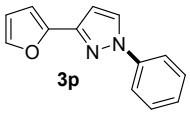
3n

3-(naphthalen-1-yl)-1-phenyl-1H-pyrazole (3n) R_f = 0.78 (EA/PE = 1:5), yield 84%, yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.68 – 8.64 (m, 1H), 8.07 (d, *J* = 2.4 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.84 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.81 – 7.78 (m, 1H), 7.57 – 7.52 (m, 3H), 7.52 – 7.48 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.6 Hz). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 152.98, 140.32, 134.10, 131.48, 131.22, 129.55, 128.72, 128.43, 127.34, 126.50, 126.47, 126.33, 125.92, 125.46, 119.17, 108.95. HRMS calcd for $C_{19}H_{14}N_2$ [M+H] $^+$: 271.1235, found: 271.1238.



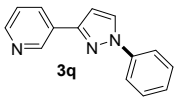
3o

1-phenyl-3-(thiophen-2-yl)-1H-pyrazole (3o) R_f = 0.50 (EA/PE = 1:10), yield 75%, yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 2.4 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7. 46 (t, *J* = 8.0 Hz, 2H), 7.42 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.09 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.68 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 148.32, 140.05, 136.44, 129.51, 128.09, 127.55, 126.50, 125.02, 124.29, 119.16, 105.17. HRMS calcd for $C_{13}H_{10}N_2S$[M+H] $^+$: 227.0643, found: 227.0647.



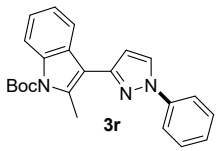
3p

3-(furan-2-yl)-1-phenyl-1H-pyrazole (3p) R_f = 0.75(EA/PE = 1:5), yield 84%, colourless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 2.5 Hz, 1H), 7.75 – 7.73 (m, 2H), 7.50 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.78 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.8 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 148.61, 145.52, 142.23, 140.04, 129.51, 127.96, 126.64, 119.35, 111.48, 106.56, 105.05. HRMS calcd for $C_{13}H_{10}N_2O$[M+H] $^+$: 211.0871, found: 211.0877.



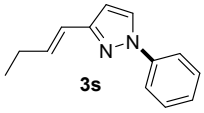
3q

3-(1-phenyl-1H-pyrazol-3-yl)pyridine (3q) R_f = 0.42 (EA/PE = 1:2), yield 75%, yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.58 (d, *J* = 3.6 Hz, 1H), 8.25 – 8.21 (m, 1H), 8.00 (d, *J* = 2.5 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.51 – 7.46 (m, 2H), 7.36 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.34 – 7.30 (m, 1H), 6.83 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 150.02, 149.10, 147.40, 140.07, 133.08, 129.59, 128.41, 126.81, 125.42, 123.68, 119.23, 105.17. HRMS calcd for $C_{14}H_{11}N_3$ [M+H] $^+$: 222.1031, found: 222.1037.



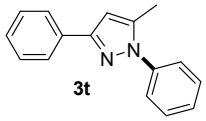
3r

tert-butyl 2-methyl-3-(1-phenyl-1H-pyrazol-3-yl)-1H-indole-1-carboxylate (3r) R_f = 0.80 (EA/PE = 1:3), yield 84%, white solid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 2.4 Hz, 1H), 7.97 – 7.94 (m, 1H), 7.84 – 7.80 (m, 2H), 7.50 – 7.46 (m, 2H), 7.33 – 7.26 (m, 3H), 6.72 – 6.70 (m, 1H), 2.85 (s, 3H), 1.73 (s, 9H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 150.86, 147.32, 140.32, 136.04, 135.65, 129.51, 128.92, 127.12, 126.28, 123.81, 123.01, 119.85, 118.93, 115.34, 113.27, 108.39, 83.96, 28.40, 15.39. HRMS calcd for $C_{23}H_{23}N_3O_2$ [M+H] $^+$: 374.1869, found: 374.1872.



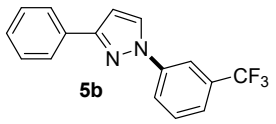
3s

(E)-3-(but-1-en-1-yl)-1-phenyl-1H-pyrazole (3s) R_f = 0.65 (EA/PE = 1:10), yield 92%, colourless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 2.5, 0.6 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.45 – 7.41 (m, 2H), 7.27 – 7.24 (m, 1H), 6.53 – 6.48 (m, 2H), 6.39 (dt, *J* = 16.0, 6.3 Hz, 1H), 2.29 – 2.23 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 152.75, 140.22, 135.38, 129.46, 127.62, 126.14, 120.93, 118.92, 104.43, 25.97, 13.38. HRMS calcd for $C_{13}H_{14}N_2$ [M+H] $^+$: 199.1235, found: 199.1238.



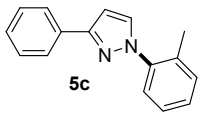
3t

5-methyl-1,3-diphenyl-1H-pyrazole (3t) R_f = 0.63 (EA/PE = 1:10), yield 65%, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.47 (m, 4H), 7.43 – 7.36 (m, 3H), 7.32 (tt, *J* = 6.8, 1.3 Hz, 1H), 6.54 (s, 1H), 2.39 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.53, 140.15, 139.98, 133.37, 129.09, 128.56, 127.75, 127.61, 125.73, 125.00, 104.38, 12.59. HRMS calcd for $C_{16}H_{14}N_2$ [M+H] $^+$: 235.1235, found: 235.1233.



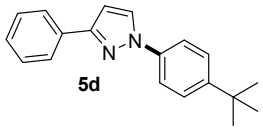
5b

3-phenyl-1-(3-(trifluoromethyl)phenyl)-1H-pyrazole (5b) R_f = 0.55(EA/PE = 1:10), yield 81%, oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 8.03 – 7.99 (m, 1H), 7.98 – 7.90 (m, 3H), 7.63 – 7.52 (m, 2H), 7.48 – 7.42 (m, 2H), 7.39 – 7.35 (m, 1H), 6.83 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 153.66, 140.57, 132.74, 132.09 (d, *J* = 32.4 Hz) 130.13, 129.90 (d, *J* = 4.3 Hz), 128.81, 128.44, 128.03, 125.99, 122.81 (d, *J* = 3.0 Hz), 121.79, 115.85 (q, *J* = 3.7 Hz), 105.89. HRMS calcd for $C_{16}H_{11}F_3N_2$ [M+H] $^+$: 289.0953, found: 289.0958.



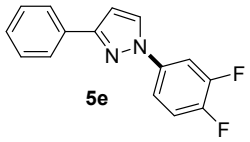
5c

3-phenyl-1-(o-tolyl)-1H-pyrazole (5c) R_f = 0.70 (EA/PE = 1:20), yield 75%, oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.89 (m, 2H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.32 (ddt, *J* = 14.5, 6.3, 1.8 Hz, 4H), 6.76 (d, *J* = 2.4 Hz, 1H), 2.33 (s, 3H).^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 152.36, 140.10, 133.83, 133.37, 131.99, 131.45, 128.70, 128.48, 127.91, 126.71, 126.20, 125.84, 103.63, 18.32. HRMS calcd for $C_{16}H_{14}N_2$ [M+H] $^+$: 235.1235, found: 235.1237.



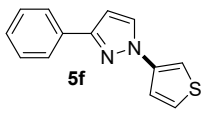
5d

1-(4-(tert-butyl)phenyl)-3-phenyl-1H-pyrazole (5d) R_f = 0.65 (EA/PE = 1:20), yield 70%, white solid.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 3H), 7.70 – 7.67 (m, 2H), 7.50 – 7.47 (m, 2H), 7.46 – 7.42 (m, 2H), 7.34 (tt, *J* = 6.9, 1.2 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 152.75, 149.58, 137.98, 133.32, 128.71, 128.06, 128.00, 126.35, 125.88, 118.98, 104.81, 34.65, 31.45. HRMS calcd for $C_{19}H_{20}N_2$ [M+H] $^+$: 277.1705, found: 277.1713.



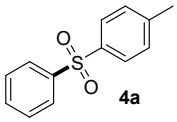
5e

1-(3,4-difluorophenyl)-3-phenyl-1H-pyrazole (5e) R_f = 0.70 (EA/PE = 1:10), yield78%, yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 – 7.89 (m, 2H), 7.89 (d, *J* = 2.5 Hz, 1H), 7.69 (ddd, *J* = 11.3, 6.9, 2.7 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.38 – 7.35 (m, 1H), 7.28-7.23 (m, 1H), 6.79 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 153.46, 150.68 (dd, *J* = 249.2, 13.5 Hz), 148.76 (dd, *J* = 248.0, 12.7 Hz), 136.82 (dd, *J* = 8.4, 2.4 Hz), 132.74, 128.81, 128.40, 128.09, 125.93, 117.91 (d, *J* = 18.6 Hz), 114.36 (dd, *J* = 5.7, 3.3 Hz), 109.00 (d, *J* = 21.7 Hz), 105.71. HRMS calcd for $C_{15}H_{10}F_2N_2$ [M+H] $^+$: 257.0890, found: 257.0894.



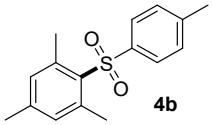
5f

3-phenyl-1-(thiophen-3-yl)-1H-pyrazole (5f) R_f = 0.55 (EA/PE = 1:10), yield 88%, white solid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 – 7.89 (m, 2H), 7.83 (d, *J* = 2.6 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.39 (dd, *J* = 5.1, 3.3 Hz, 1H), 7.36 – 7.32 (m, 1H), 6.73 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 152.62, 139.97, 133.06, 128.85, 128.74, 128.12, 126.51, 125.92, 120.40, 110.68, 104.54. HRMS calcd for $C_{13}H_{10}N_2S$[M+H] $^+$: 226.0565, found: 226.0569.



4a

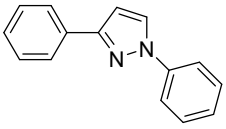
1-methyl-4-(phenylsulfonyl)benzene (4a) R_f = 0.45 (EA/PE = 1:5), white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.46 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.13, 142.02, 138.68, 132.96, 129.89, 129.19, 127.72, 127.49, 21.55. HRMS calcd for $C_{13}H_{12}O_2S[M+H]^+$: 233.0636, found: 233.0639.



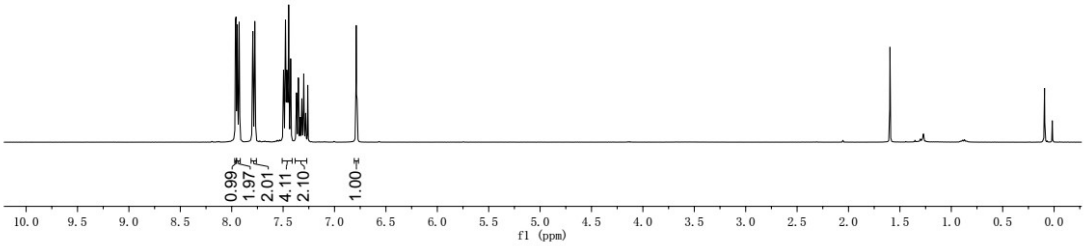
4b

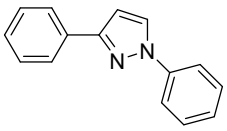
1,3,5-trimethyl-2-tosylbenzene (4b) R_f = 0.45 (EA/PE = 1:10), white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 2H), 6.94 (s, 2H), 2.60 (s, 6H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 143.46, 143.27, 140.69, 140.03, 134.22, 132.25, 129.55, 126.39, 22.92, 21.63, 21.10. HRMS calcd for $C_{16}H_{18}O_2S[M+H]^+$: 275.1106, found: 275.1112.

8. NMR spectra for compounds

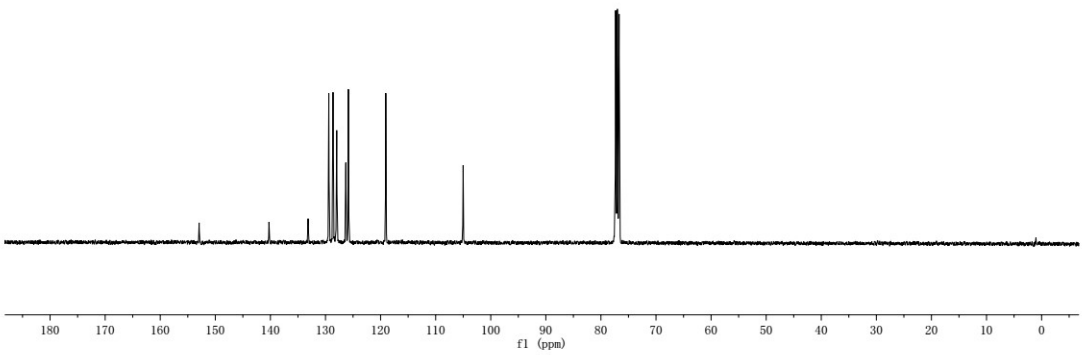


3a





3a




7.9490
7.9451
7.9102
7.9063
7.9012
7.8990
7.8976
7.8956
7.8903
7.8866
7.7743
7.7726
7.7601
7.4879
7.4754
7.4643
7.4615
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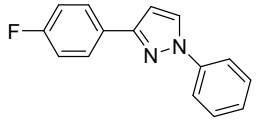
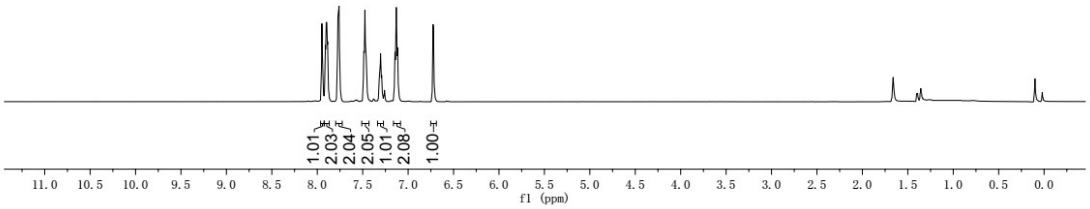
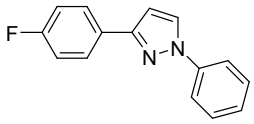
7.1302
7.1191
7.1157
6.7257
6.7217


F
N
N

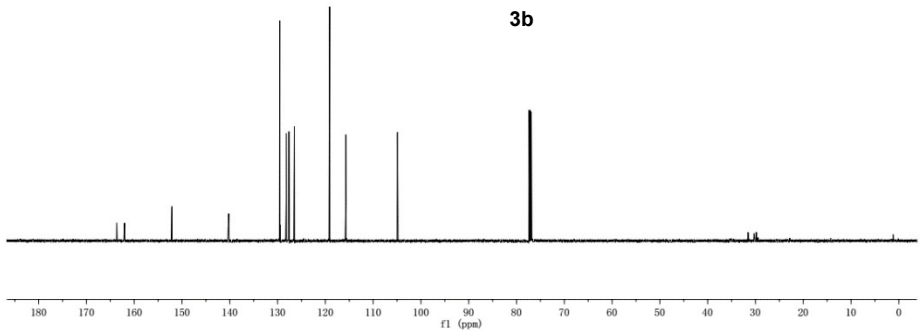
3b


1.01
2.03
2.04
2.05
1.01
2.08
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

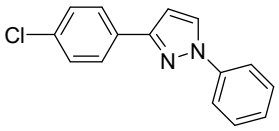

163.6675
162.0330
152.1149
140.2216
129.5414
128.2068
127.6366
127.5831
126.5074
119.1105
115.7369
115.5939
104.9154
77.3504
77.1390
76.9269


F
N
N

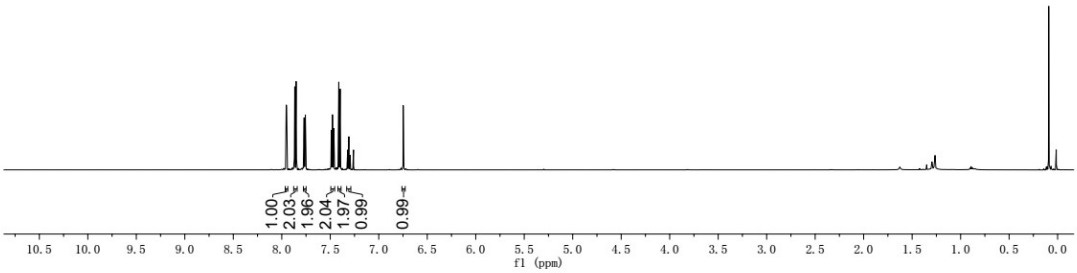
3b

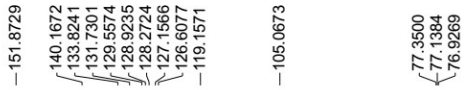

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

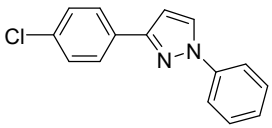

7.9543
7.9501
7.8704
7.8663
7.8630
7.8553
7.8520
7.8479
7.7739
7.7712
7.7693
7.7660
7.7598
7.7584
7.7567
7.7551
7.7514
7.4926
7.4896
7.4862
7.4771
7.4754
7.4660
7.4629
7.4594
7.4162
7.4088
7.4011
7.3937
7.3224
7.3206
7.3189
7.3082
7.2976
7.2959
7.2941
6.7478
6.7436


Cl
N
N

3c


1.00
2.03
1.96
2.04
1.97
0.99
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

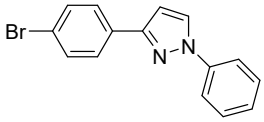

151.8729
140.1672
133.8241
131.7301
129.5574
128.9235
128.2724
127.1566
126.6077
119.1571
105.0673
77.3500
77.1384
76.9269


Cl
N
N

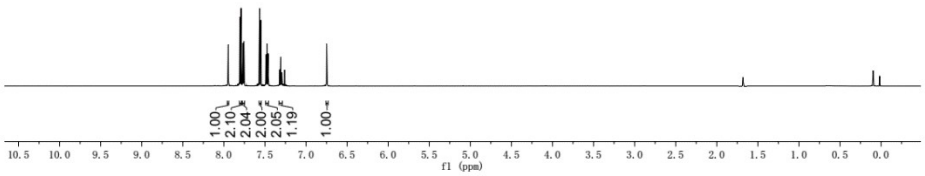
3c

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

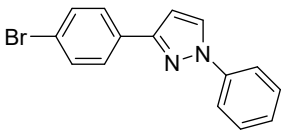

7.9504
7.9463
7.8086
7.8046
7.8013
7.7936
7.7903
7.7863
7.7699
7.7680
7.7647
7.7586
7.7571
7.7554
7.7537
7.5684
7.5644
7.5611
7.5534
7.5501
7.5461
7.4910
7.4879
7.4845
7.4754
7.4737
7.4643
7.4612
7.4578
7.3221
7.3203
7.3185
7.3079
7.2973
7.2955
7.2938
6.7481
6.7439


Br
N
N

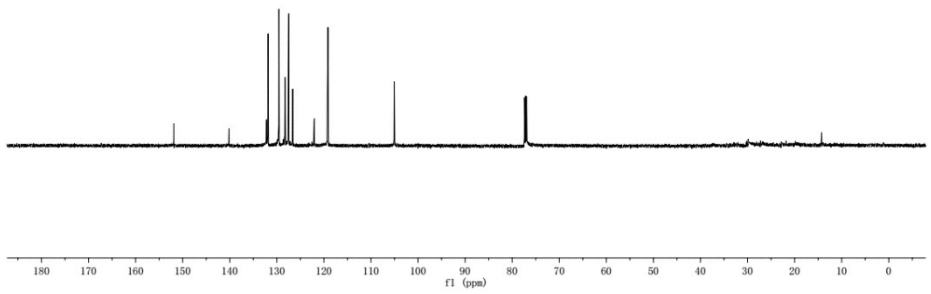
3d


1.00
2.10
2.04
2.00
2.05
1.19
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

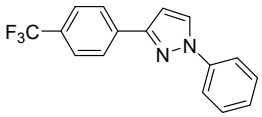

151.8758
140.1643
132.1903
131.8616
129.5568
128.2643
127.4645
126.6152
122.0317
119.1467
105.0630
77.3698
77.1588
76.9463


Br
N
N

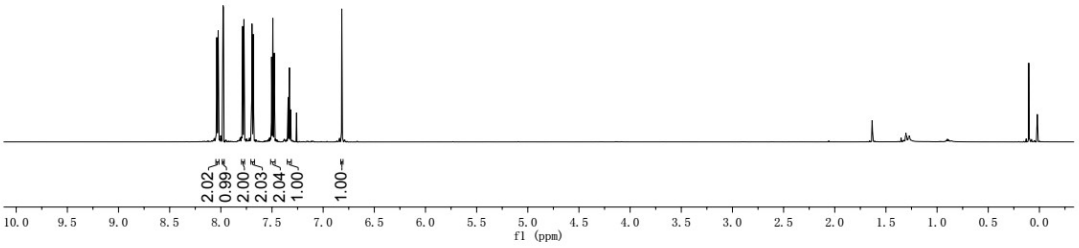
3d

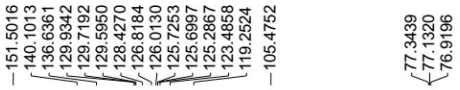

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

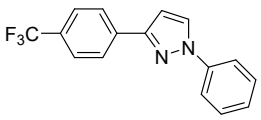

8.0395
8.0261
7.9783
7.9742
7.7885
7.7867
7.7757
7.7741
7.7726
7.6957
7.6822
7.5042
7.4917
7.4902
7.4776
7.3418
6.8181
6.8140


F3C
N
N

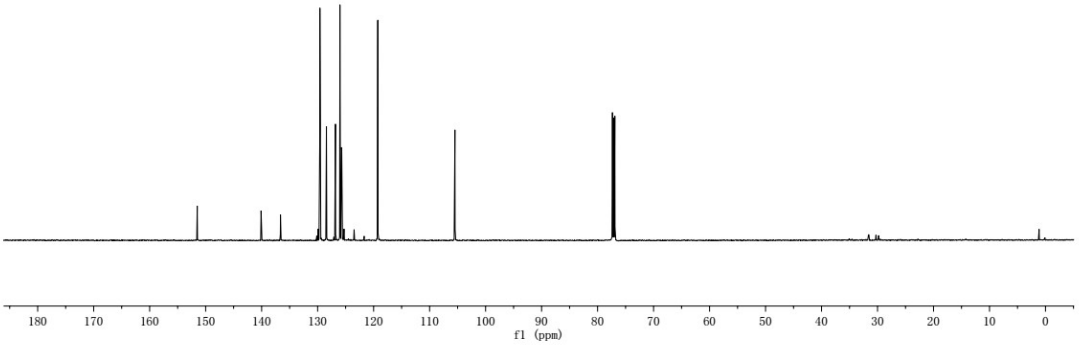
3e


2.02
0.99
2.00
2.03
2.04
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

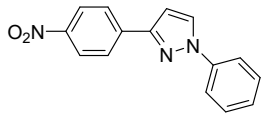

151.5016
140.1013
136.6361
129.9342
129.7192
129.5950
128.4270
126.8184
126.0130
125.7253
125.6997
125.2867
123.4858
119.2524
105.4752
77.3439
77.1320
76.9196


F3C
N
N

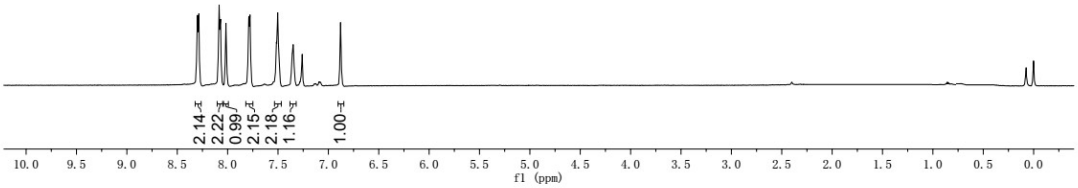
3e

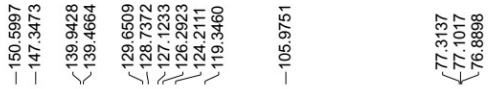

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.2996
8.2853
8.0841
8.0724
8.0700
8.0167
8.0128
7.7887
7.7764
7.5153
7.5030
7.4919
7.3603
7.3499
7.3379
6.8791
6.8753


O2N
N
N

3f


2.14
2.22
0.99
2.15
2.18
1.16
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.5997
147.3473
139.9428
139.4664
129.6509
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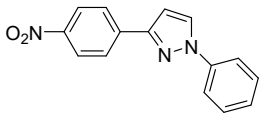
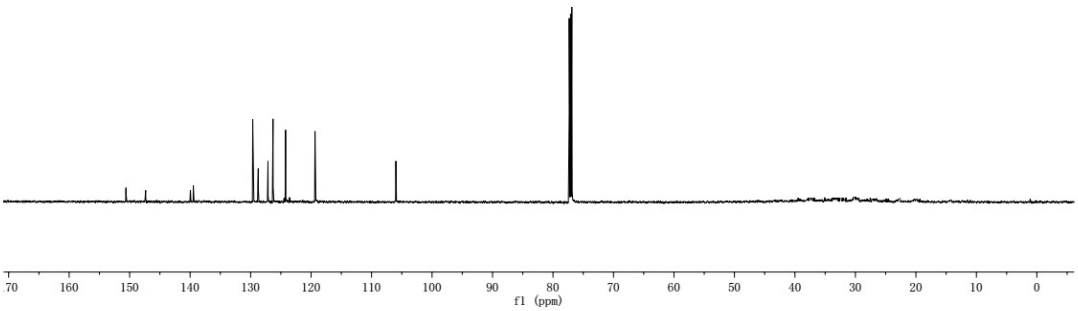
127.1233
126.2923
124.2111
119.3460
105.9751
77.3137
77.1017
76.8898

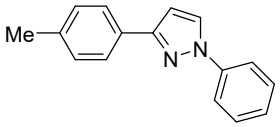

O2N
N
N

3f

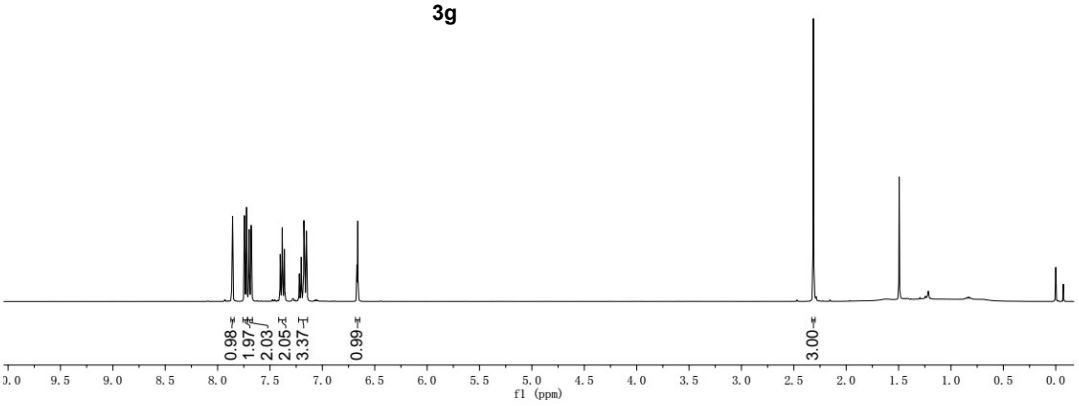

70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.8632
7.8570
7.7441
7.7238
7.7022
7.6993
7.6945
7.6803
7.6780
7.4023
7.3835
7.3814
7.3623
7.2203
7.2018
7.1766
7.1717
6.6623

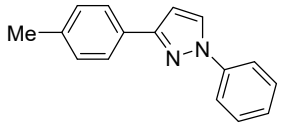

2.3137


Me
N
N

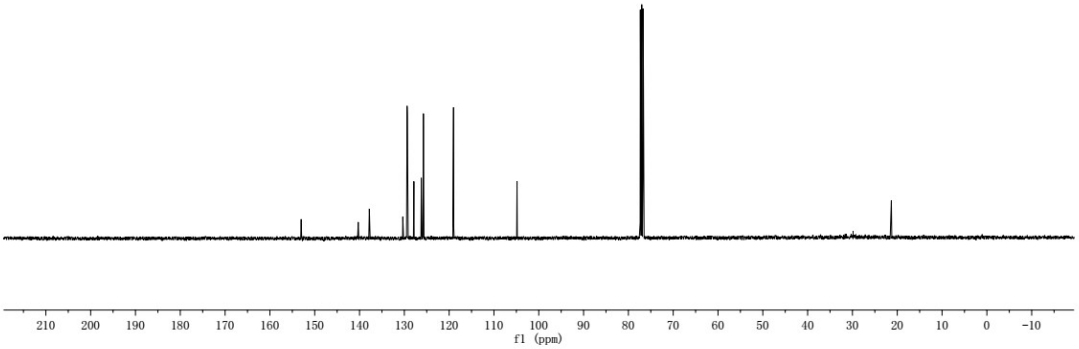
3g

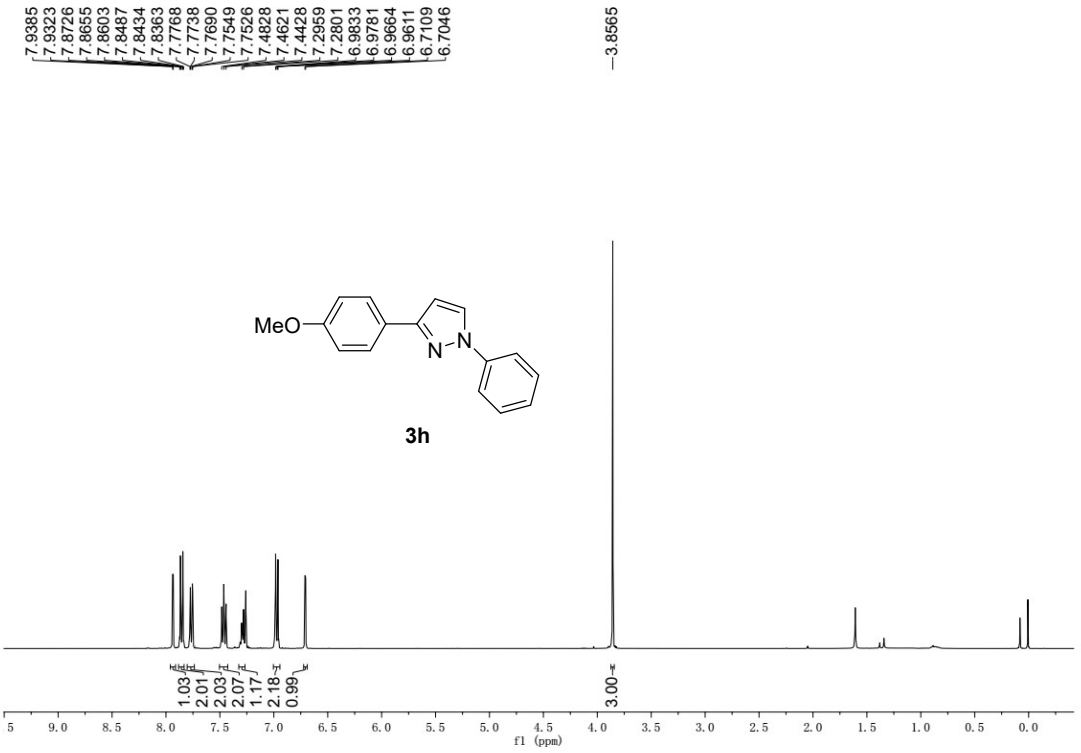

0.98
1.97
2.03
2.05
3.37
0.99
3.00
f1 (ppm)


153.0131
140.2869
137.8091
130.3385
129.3888
129.3367
127.8720
126.2139
125.7421
119.0203
104.8506
77.3373
77.0198
76.7024
21.3170

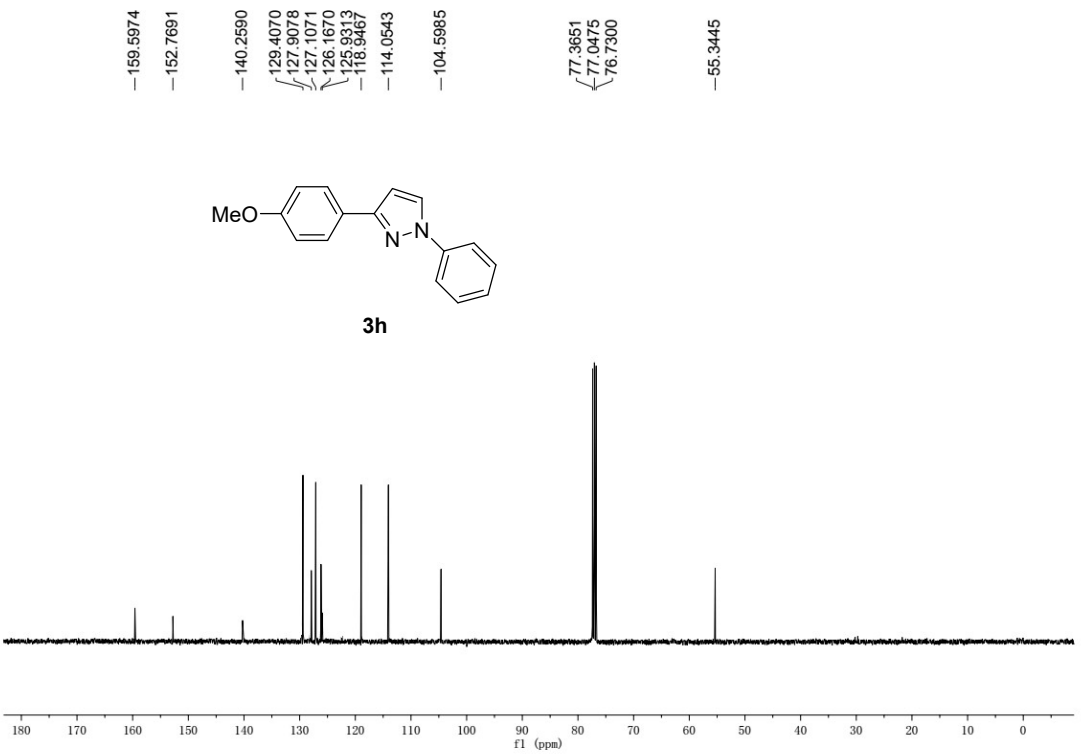

Me
N
N

3g


f1 (ppm)


7.9385
7.9323
7.8726
7.8655
7.8603
7.8487
7.8434
7.8363
7.7768
7.7738
7.7690
7.7549
7.7526
7.4828
7.4621
7.4428
7.2959
7.2801
6.9833
6.9781
6.9664
6.9611
6.7109
6.7046
3.8565
MeO
N
N
1.03
2.01
2.03
2.07
1.17
2.18
0.99
3.00
f1 (ppm)

3h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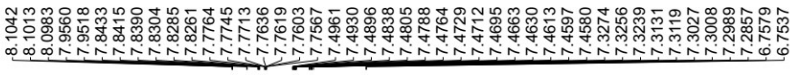
152.7691
140.2590
129.4070
127.9078
127.1071
126.1670
125.9313
118.9467
114.0543
104.5985
77.3651
77.0475
76.7300
55.3445
MeO
N
N
f1 (ppm)

3h


8.1042
8.1013
8.0983
7.9560
7.9518
7.8433
7.8415
7.8390
7.8304
7.8285
7.8261
7.7764
7.7745
7.7713
7.7636
7.7619
7.7603
7.7567
7.4961
7.4930
7.4896
7.4838
7.4805
7.4788
7.4764
7.4729
7.4712
7.4695
7.4663
7.4630
7.4613
7.4597
7.4580
7.3274
7.3256
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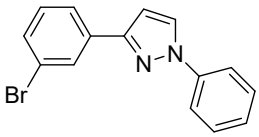
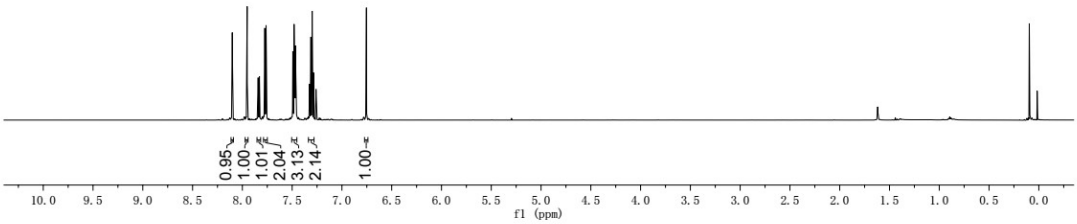
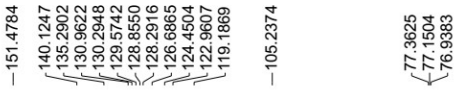
7.3131
7.3119
7.3027
7.3008
7.2989
7.2857
6.7579
6.7537


Br
N
N

3i


0.95
1.00
1.01
2.04
3.13
2.14
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.4784
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135.2902
130.9622
130.2948
129.5742
128.8550
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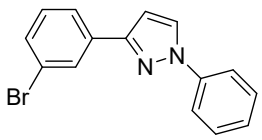
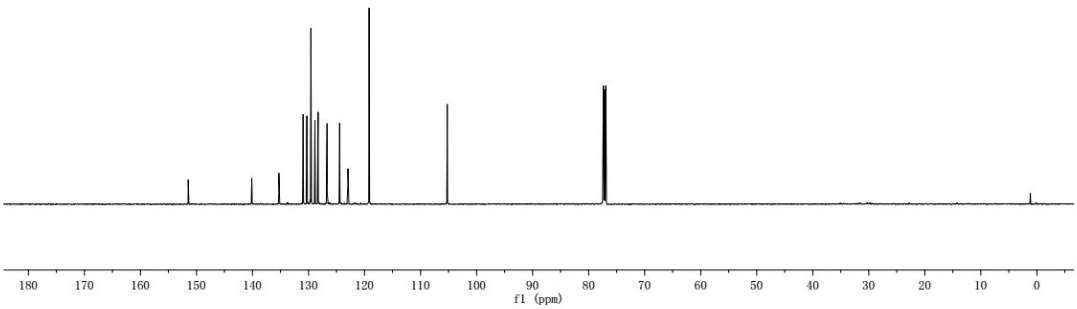
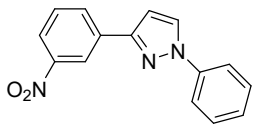
126.6865
124.4504
122.9607
119.1869
105.2374
77.3625
77.1504
76.9383


Br
N
N

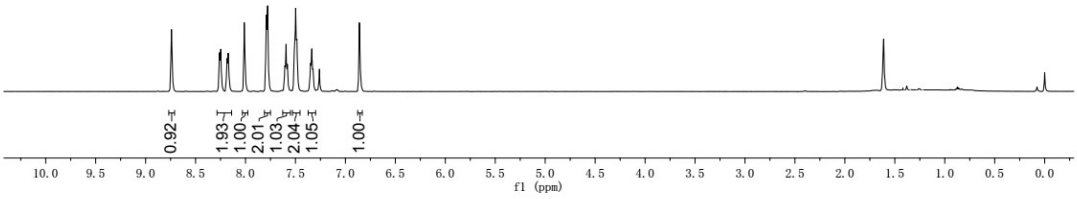
3i

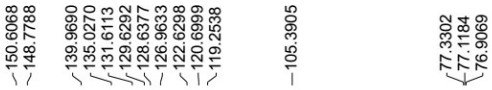

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

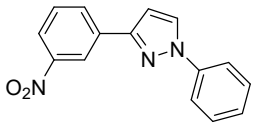

8.7410
8.2604
8.2478
8.1849
8.1733
8.0125
8.0094
7.7911
7.7788
7.6070
7.5940
7.5810
7.5107
7.4982
7.4851
7.3486
7.3365
7.3254
6.8601
6.8572


O2N
N
N

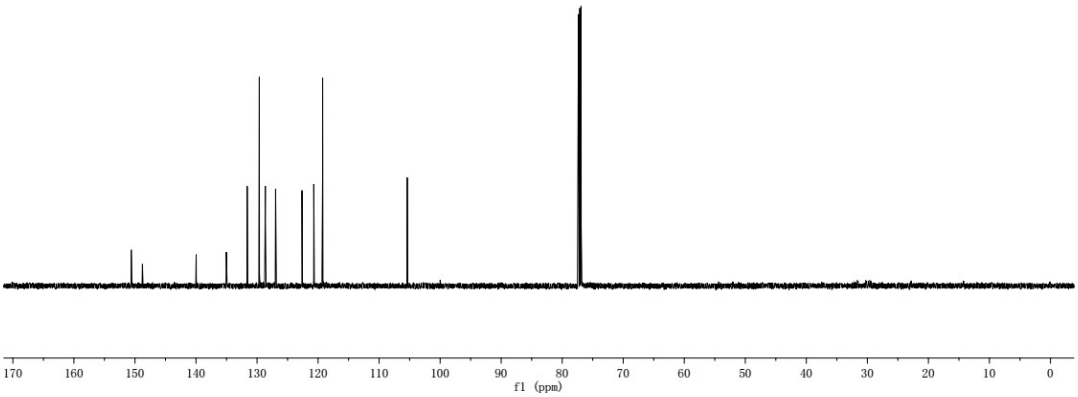
3j

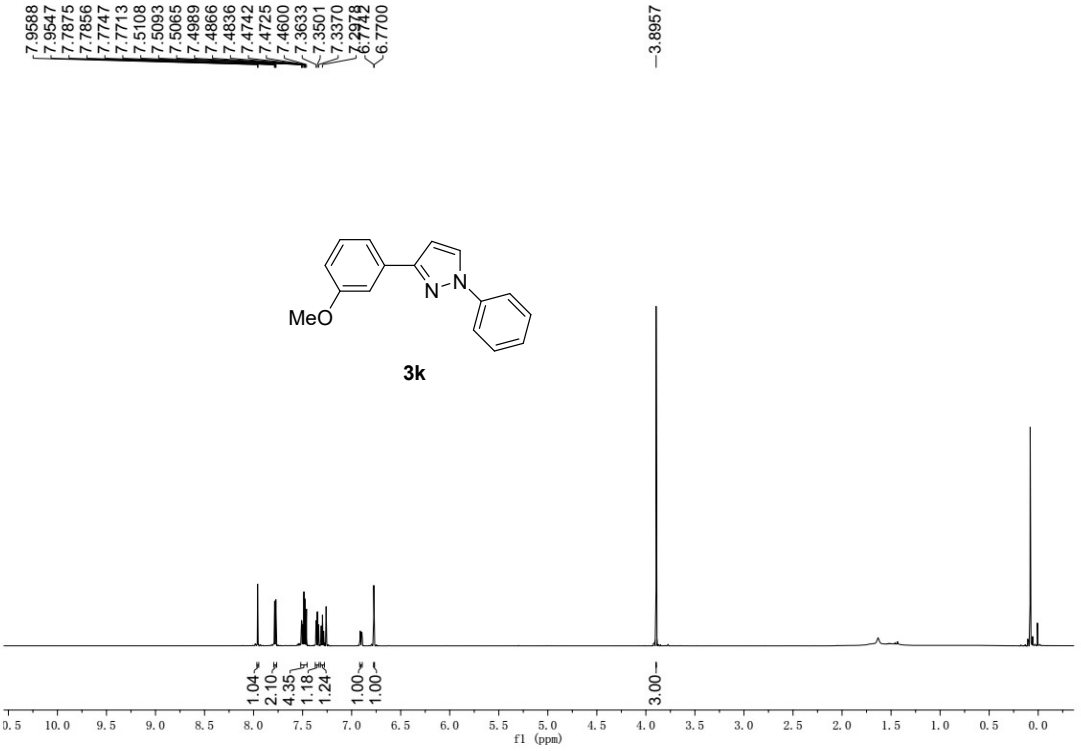

0.92
1.93
1.00
2.01
1.03
2.04
1.05
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

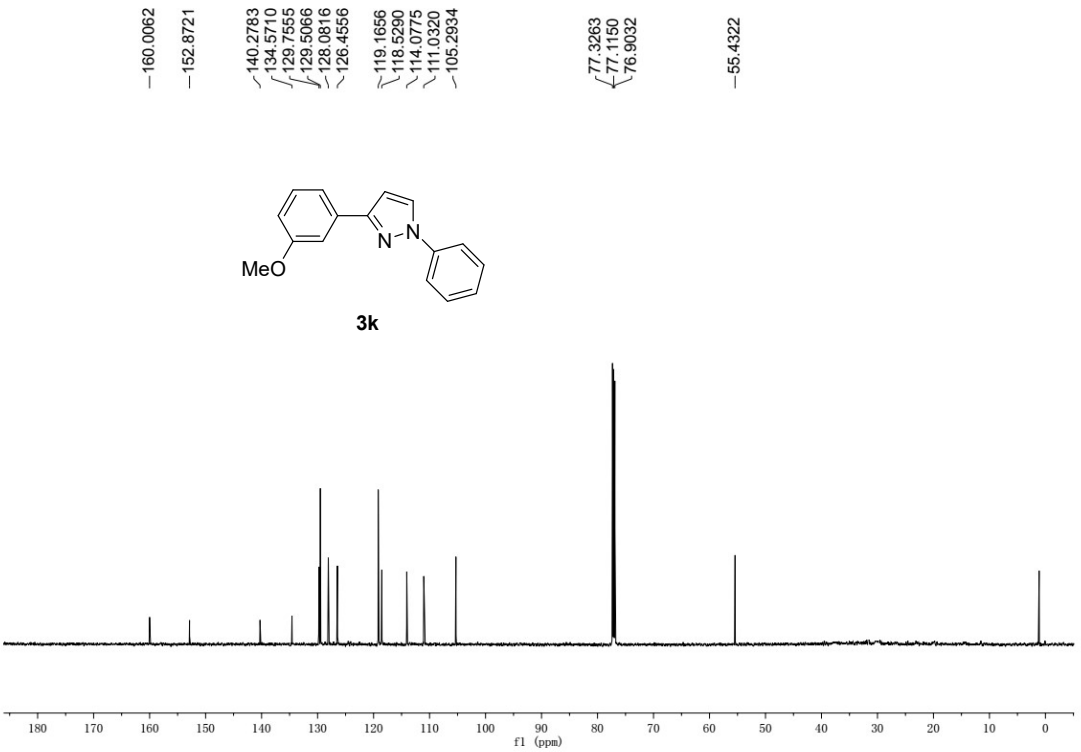

150.6068
148.7788
139.9690
135.0270
131.6113
129.6292
128.6377
126.9633
122.6298
120.6999
119.2538
105.3905
77.3302
77.1184
76.9069


O2N
N
N

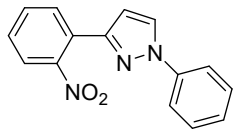
3j


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

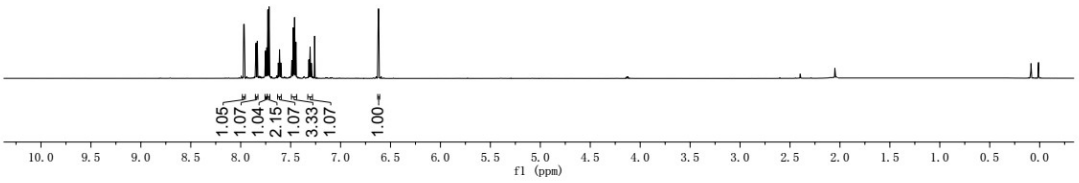

7.9588
7.9547
7.7875
7.7856
7.7747
7.7713
7.5108
7.5093
7.5065
7.4989
7.4866
7.4836
7.4742
7.4725
7.4600
7.3633
7.3501
7.3370
6.7742
6.7700
3.8957
MeO
N
N
3k
1.04
2.10
4.35
1.18
1.24
1.00
1.00
3.00
f1 (ppm)

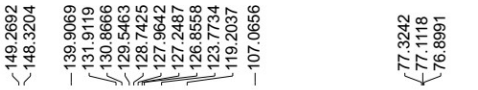

160.0062
152.8721
140.2783
134.5710
129.7555
129.5066
128.0816
126.4556
119.1656
118.5290
114.0775
111.0320
105.2934
77.3263
77.1150
76.9032
55.4322
MeO
N
N
3k
f1 (ppm)

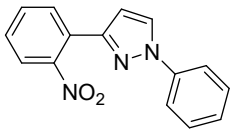

7.9701
7.9693
7.9660
7.9652
7.8489
7.8466
7.8359
7.8337
7.7546
7.7525
7.7411
7.7390
7.7330
7.7318
7.7302
7.7283
7.7272
7.7249
7.7189
7.7175
7.7157
7.7140
7.7104
7.6255
7.6236
7.6111
7.6098
7.5969
7.4905
7.4892
7.4881
7.4869
7.4769
7.4742
7.4706
7.4646
7.4609
7.4593
7.4491
7.4468
7.3176
7.3157
7.3050
7.3035
7.2929
6.6222
6.6180


N
N
NO2

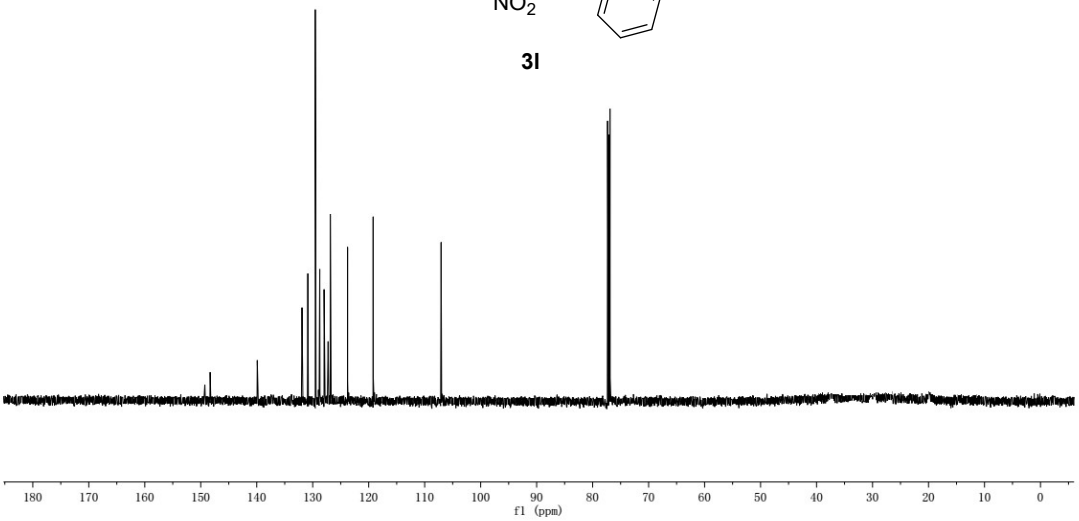
3l


1.05
1.07
1.04
2.15
1.07
3.33
1.07
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

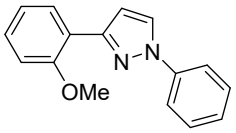

149.2692
148.3204
139.9069
131.9119
130.8666
129.5463
128.7425
127.9642
127.2487
126.8558
123.7734
119.2037
107.0656
77.3242
77.1118
76.8991


N
N
NO2

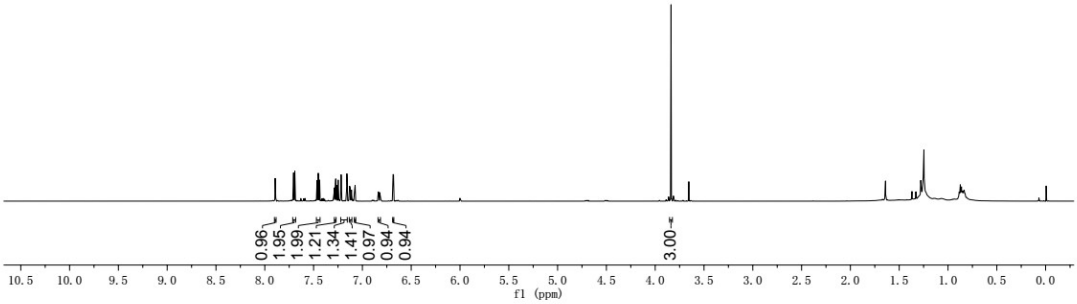
3l


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

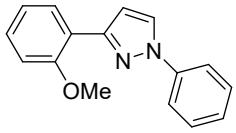

7.8937
7.8894
7.7069
7.7050
7.7016
7.6956
7.6941
7.6924
7.6907
7.4679
7.4648
7.4614
7.4556
7.4524
7.4506
7.4474
7.4412
7.4381
7.4347
7.2864
7.2780
7.2733
7.2176
7.1585
7.1310
7.1245
7.1232
7.1118
7.1106
7.0783
7.0746
7.0716
6.8366
6.8353
6.8324
6.8310
6.8230
6.8216
6.8187
6.8174
6.6855
6.6813
3.8376


N
N
OMe

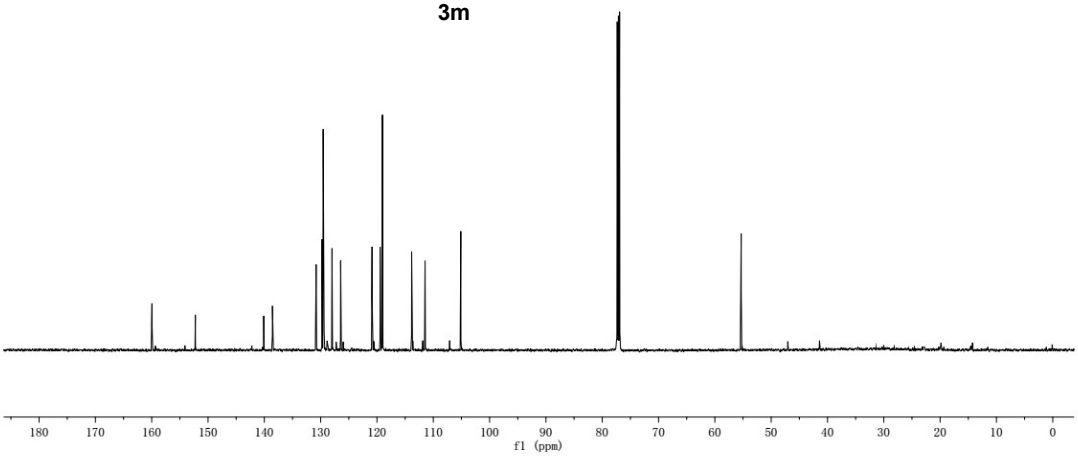
3m


0.96
1.95
1.99
1.21
1.34
1.41
0.97
0.94
0.94
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

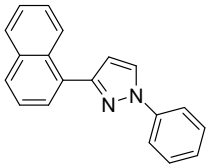

159.9540
152.2522
140.1088
138.5641
130.7968
129.7571
129.5563
127.9850
126.4565
120.8718
119.4374
119.0338
113.8427
111.4575
105.1135
77.3397
77.1282
76.9168
55.3252


N
N
OMe

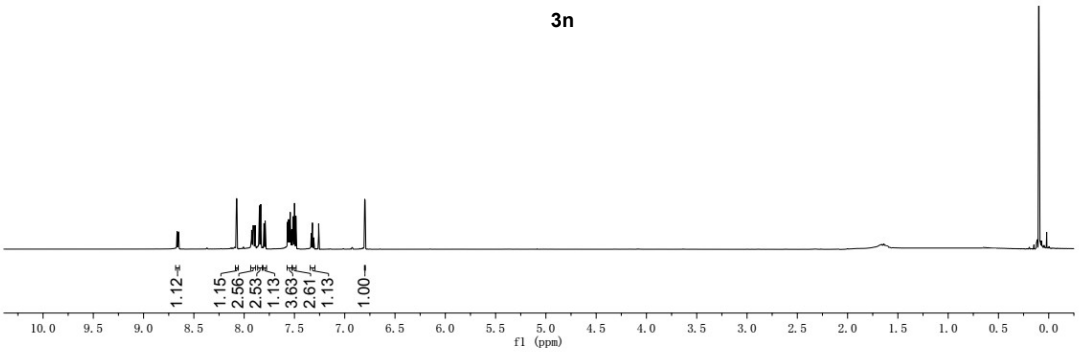
3m

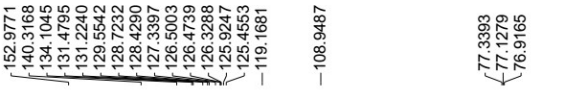

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

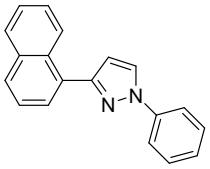

8.6674
8.6653
8.6638
8.6558
8.6513
8.0762
8.0722
7.9258
7.9220
7.9132
7.9101
7.9051
7.8913
7.8495
7.8477
7.8350
7.8335
7.8028
7.8009
7.7911
7.7891
7.5703
7.5654
7.5626
7.5583
7.5567
7.5542
7.5515
7.5489
7.5448
7.5416
7.5385
7.5289
7.5265
7.5177
7.5151
7.5121
7.5087
7.4996
7.4981
7.4884
7.4855
7.3335
7.3212
7.3087
6.8017
6.7977



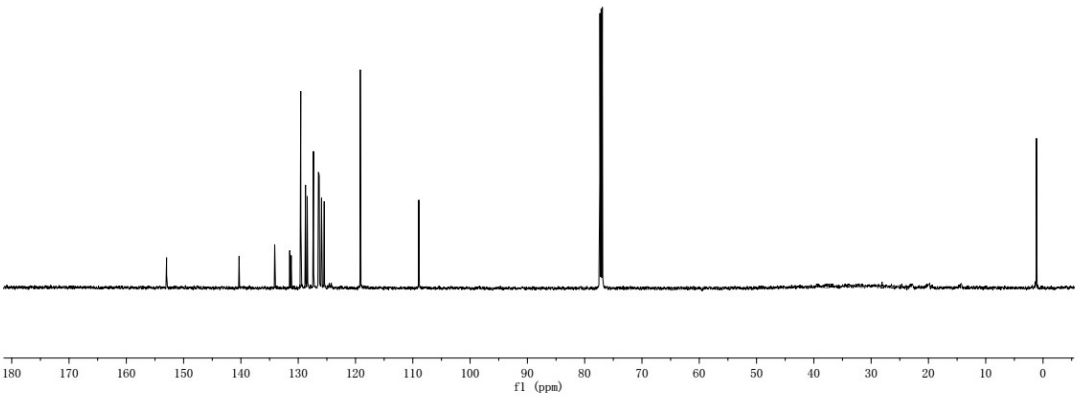
3n

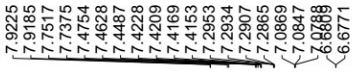

1.12
1.15
2.56
2.53
1.13
3.63
2.61
1.13
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

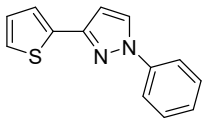

152.9771
140.3168
134.1045
131.4795
131.2240
129.5542
128.7232
128.4290
127.3397
126.5003
126.4739
126.3288
125.9247
125.4553
119.1681
108.9487
77.3393
77.1279
76.9165



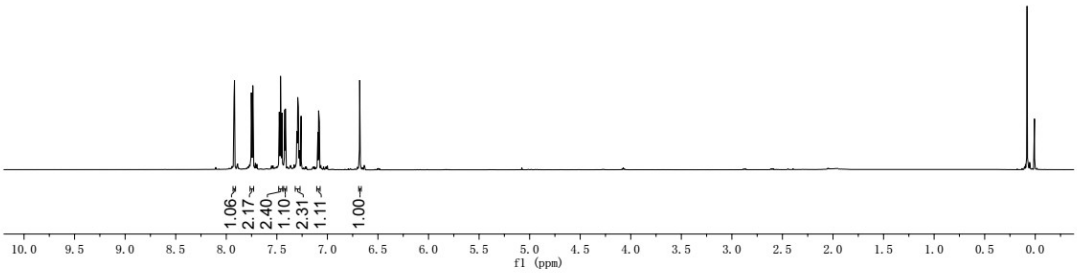
3n

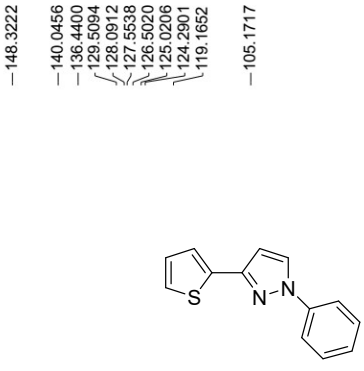

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.9225
7.9185
7.7517
7.7375
7.4754
7.4628
7.4487
7.4228
7.4209
7.4169
7.4153
7.2953
7.2934
7.2907
7.2865
7.0869
7.0847
6.6809
6.6771



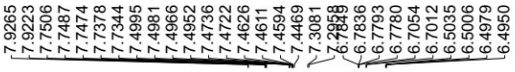
3o


1.06
2.17
2.40
1.10
2.31
1.11
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.3222
140.0456
136.4400
129.5094
128.0912
127.5538
126.5020
125.0206
124.2901
119.1652
105.1717
77.3267
77.1155
76.9040

3o

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.9265
7.9223
7.7506
7.7487
7.7474
7.7378
7.7344
7.4995
7.4981
7.4966
7.4952
7.4736
7.4722
7.4626
7.4611
7.4594
7.4469
7.3081
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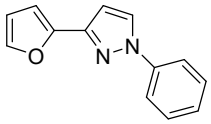
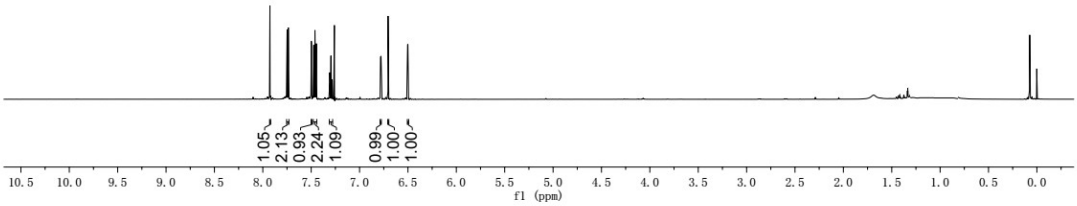
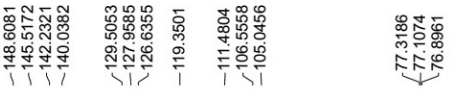
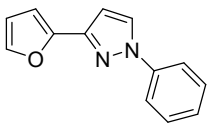
6.7054
6.7012
6.5035
6.5006
6.4979
6.4950



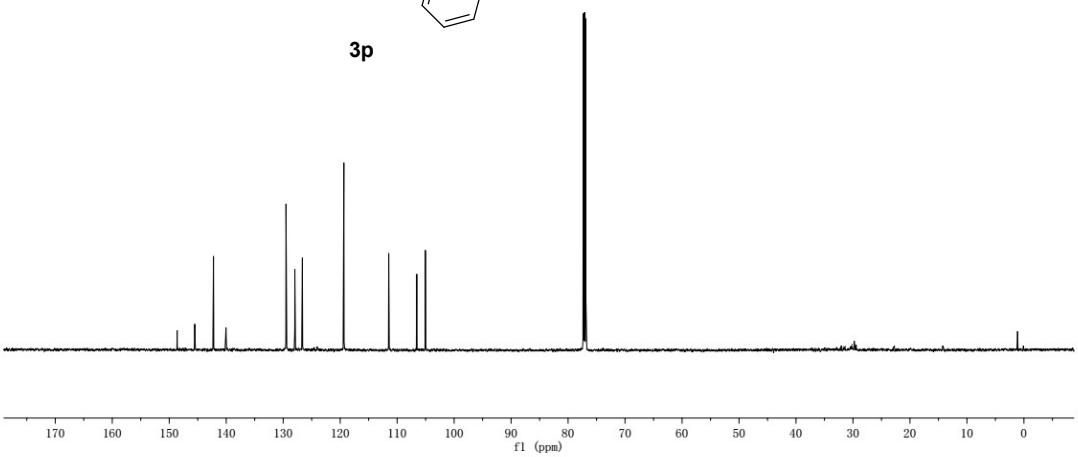
3p


1.05
2.13
0.93
2.24
1.09
0.99
1.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

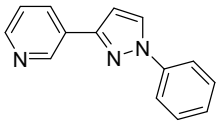

148.6081
145.5172
142.2321
140.0382
129.5053
127.9585
126.6355
119.3501
111.4804
106.5558
105.0456
77.3186
77.1074
76.8961



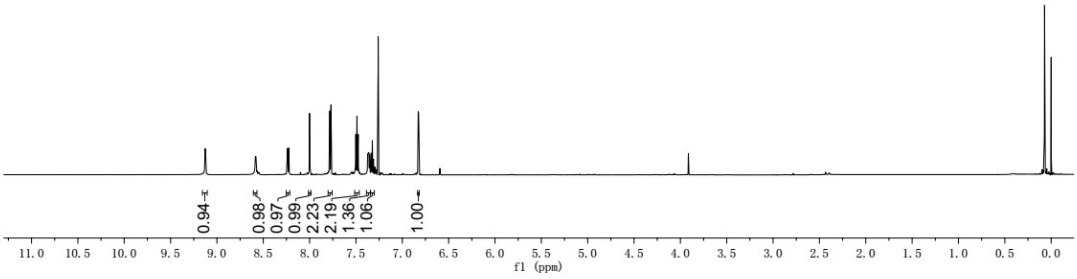
3p


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

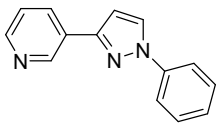

9.1266
8.5850
8.5789
8.2402
8.2372
8.2338
8.2271
8.2240
8.2206
8.0007
7.9965
7.7839
7.7820
7.7787
7.7711
7.7695
7.7677
7.5018
7.4986
7.4893
7.4877
7.4781
7.4752
7.3743
7.3664
7.3612
7.3532
7.3373
7.3357
7.3339
7.3233
7.3218
7.3110
7.3092
6.8281
6.8239



3q

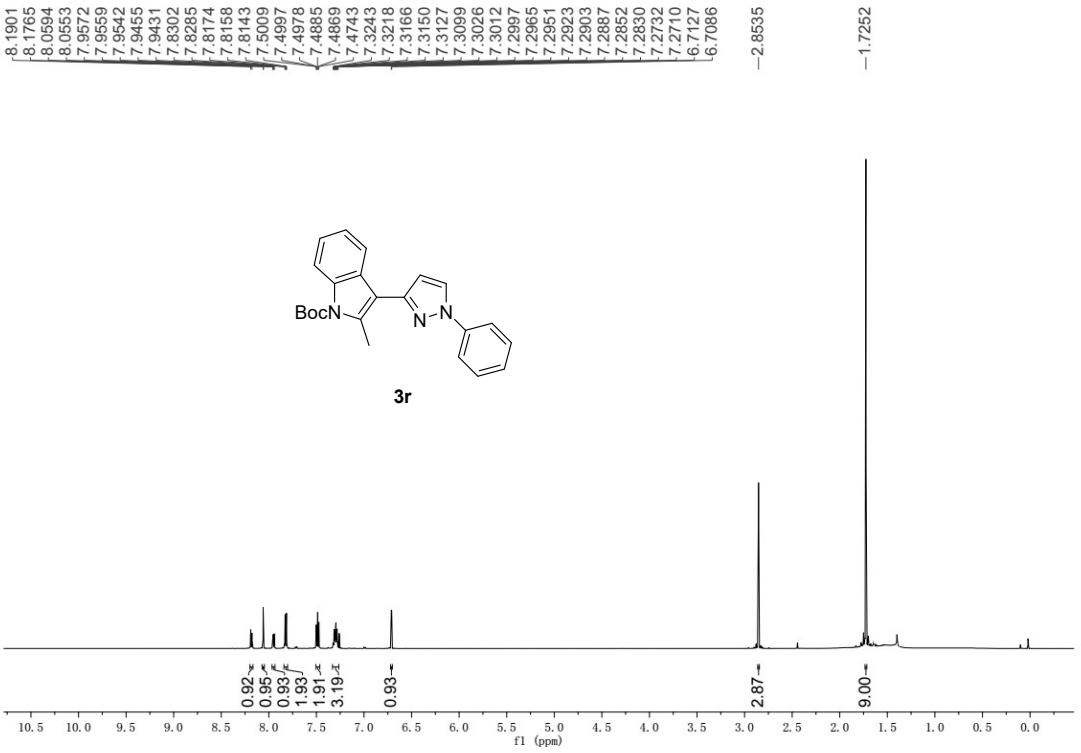

0.94
0.98
0.97
0.99
2.23
2.19
1.36
1.06
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.0241
149.0984
147.4002
140.0716
133.0740
129.5921
128.4068
126.8068
125.4131
123.6760
119.2323
105.1745
77.3129
77.1010
76.8893



3q

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.0553
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7.9559
7.9542
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7.9431
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7.8285
7.8174
7.8158
7.8143
7.5009
7.4997
7.4978
7.4885
7.4869
7.4743
7.3243
7.3218
7.3166
7.3150
7.3127
7.3099
7.3026
7.3012
7.2997
7.2965
7.2951
7.2923
7.2903
7.2887
7.2852
7.2830
7.2732
7.2710
7.7127
6.7086
2.8535
1.7252
BocN
N
N
3r
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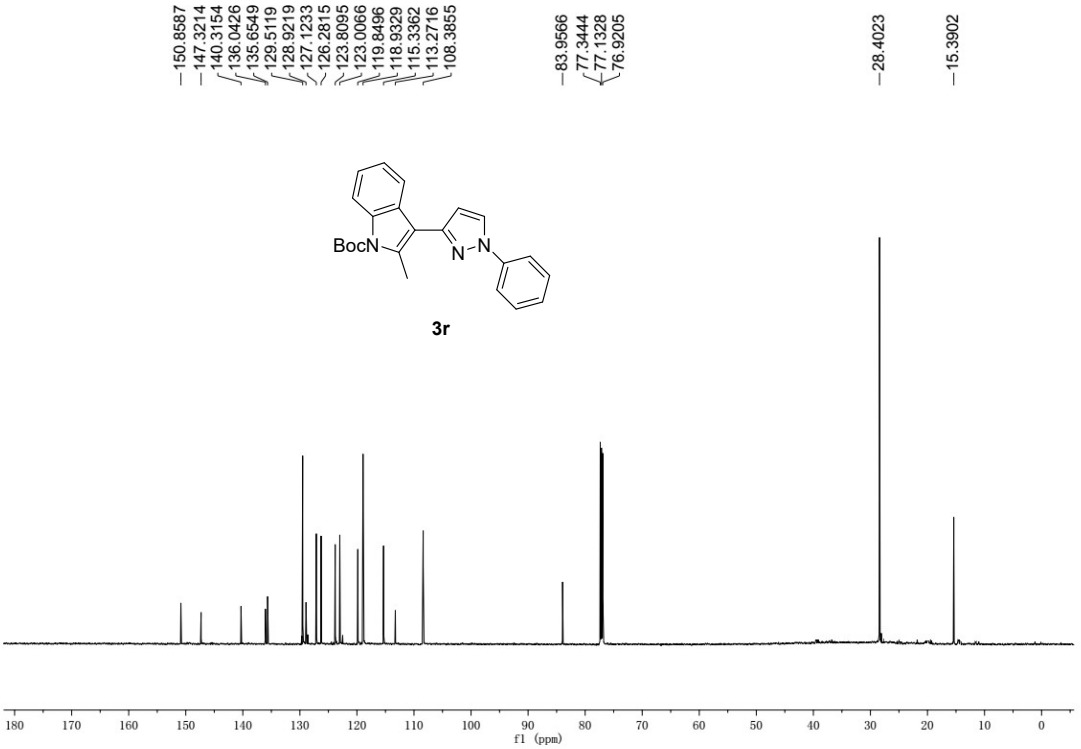
0.95
0.93
1.93
1.91
3.19
0.93
2.87
9.00
f1 (ppm)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140.3154
136.0426
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128.9219
127.1233
126.2815
123.8095
123.0066
119.8496
118.9329
115.3362
113.2716
108.3855
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28.4023
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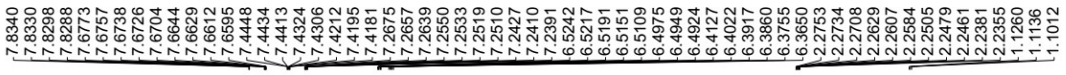
BocN
N
N
3r
f1 (ppm)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7.6738
7.6726
7.6704
7.6644
7.6629
7.6612
7.6595
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7.4434
7.4413
7.4324
7.4306
7.4212
7.4195
7.4181
7.2675
7.2657
7.2639
7.2550
7.2533
7.2519
7.2510
7.2427
7.2410
7.2391
6.5242
6.5217
6.5191
6.5151
6.5109
6.4975
6.4949
6.4924
6.4127
6.4022
6.3917
6.3860
6.3755
6.3650
2.2753
2.2734
2.2708
2.2629
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2.2505
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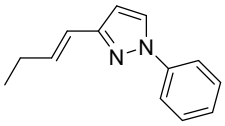
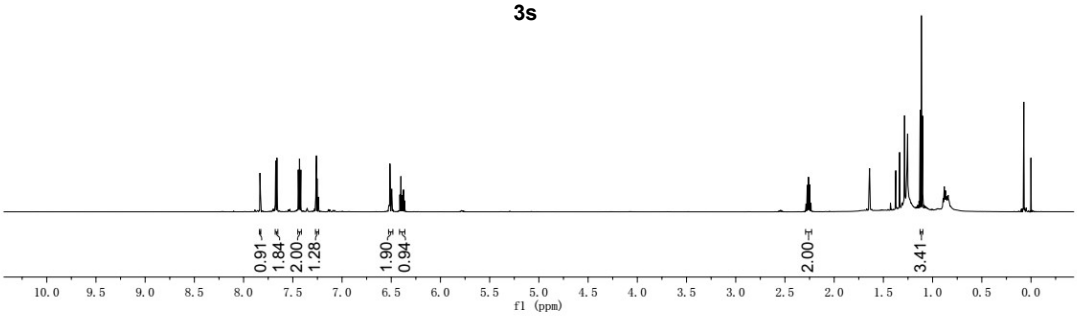
2.2461
2.2381
2.2355
1.1260
1.1136
1.1012



3s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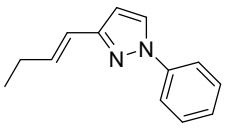
2.00
1.28
1.90
0.94
2.00
3.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.7531
140.2211
135.3848
129.4578
127.6231
126.1397
120.9327
118.9200
104.4277
77.3191
77.1079
76.8966
25.9709
13.3821



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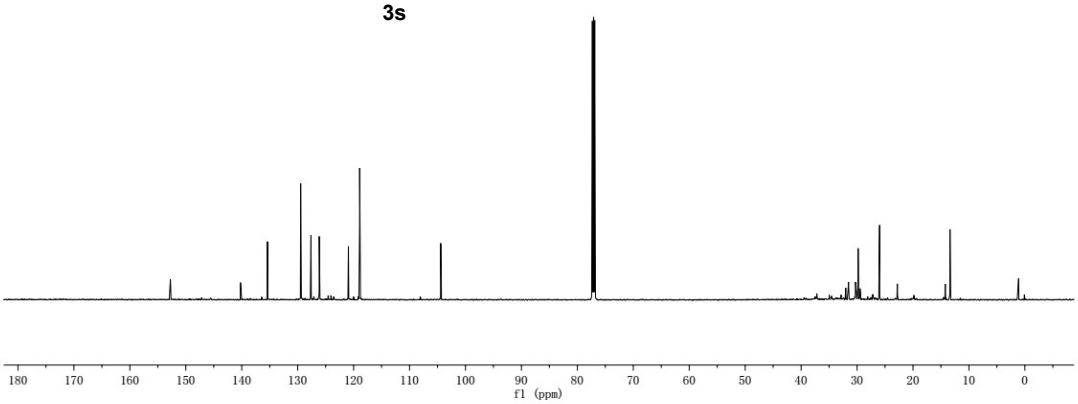
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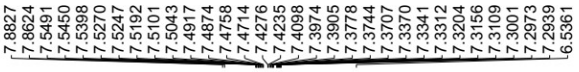
f1 (ppm)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7.5491
7.5450
7.5398
7.5270
7.5247
7.5192
7.5101
7.5043
7.4917
7.4874
7.4758
7.4714
7.4276
7.4235
7.4098
7.3974
7.3905
7.3778
7.3744
7.3707
7.3370
7.3341
7.3312
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7.2939
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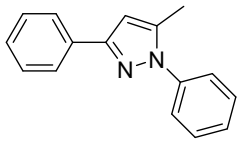
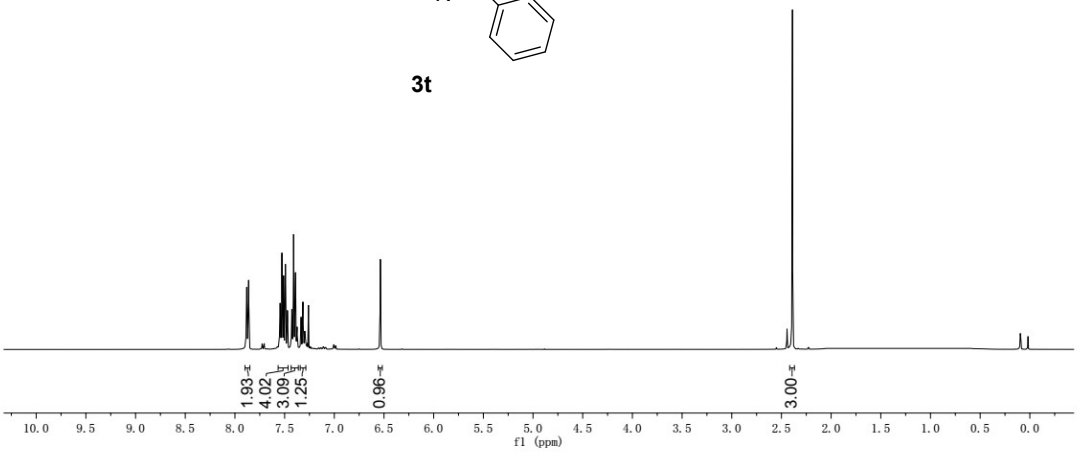
2.3907
2.3892



3t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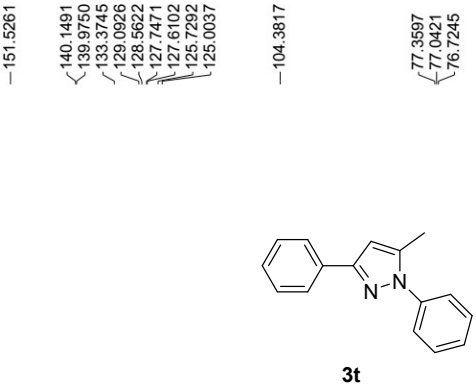
4.02
3.09
1.25
0.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.1491
139.9750
133.3745
129.0926
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127.6102
125.7292
125.0037
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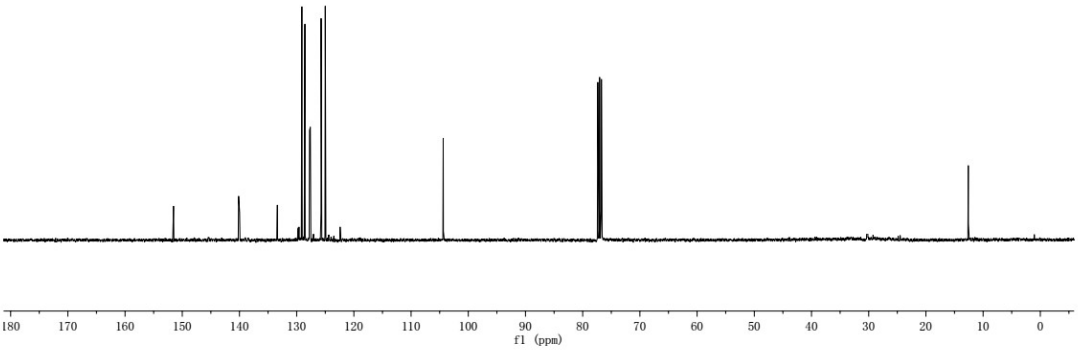
77.0421
76.7245
12.5893

3t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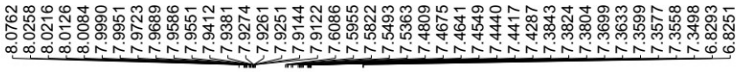
f1 (ppm)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8.0084
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7.9951
7.9723
7.9689
7.9586
7.9551
7.9412
7.9381
7.9274
7.9261
7.9251
7.9144
7.9122
7.6086
7.5955
7.5822
7.5493
7.5363
7.4809
7.4675
7.4641
7.4549
7.4440
7.4417
7.4287
7.3843
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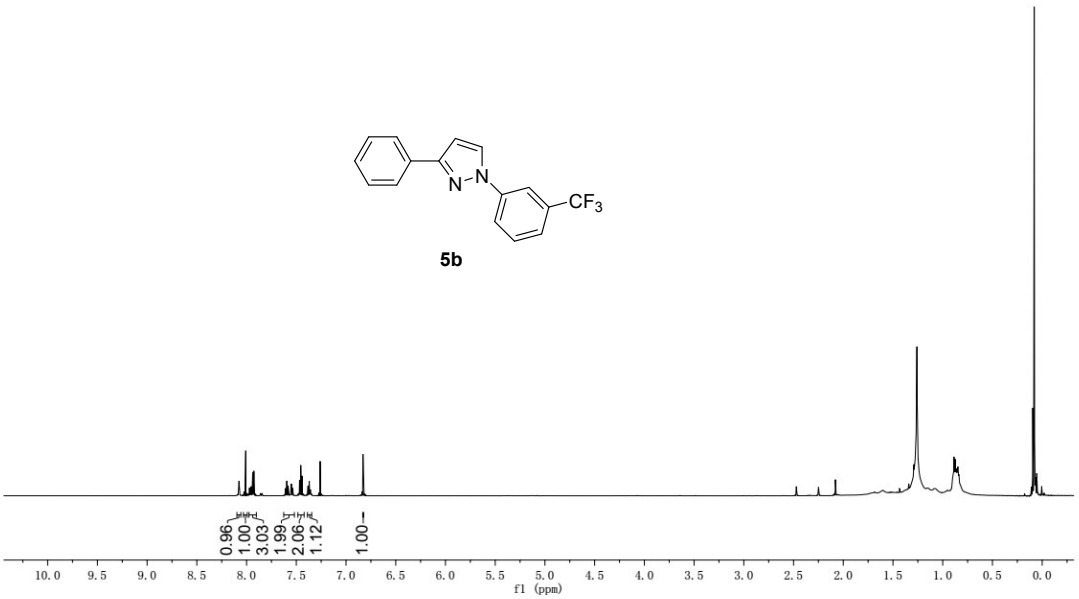
7.3699
7.3633
7.3599
7.3577
7.3558
7.3498
6.8293
6.8251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N
CF3
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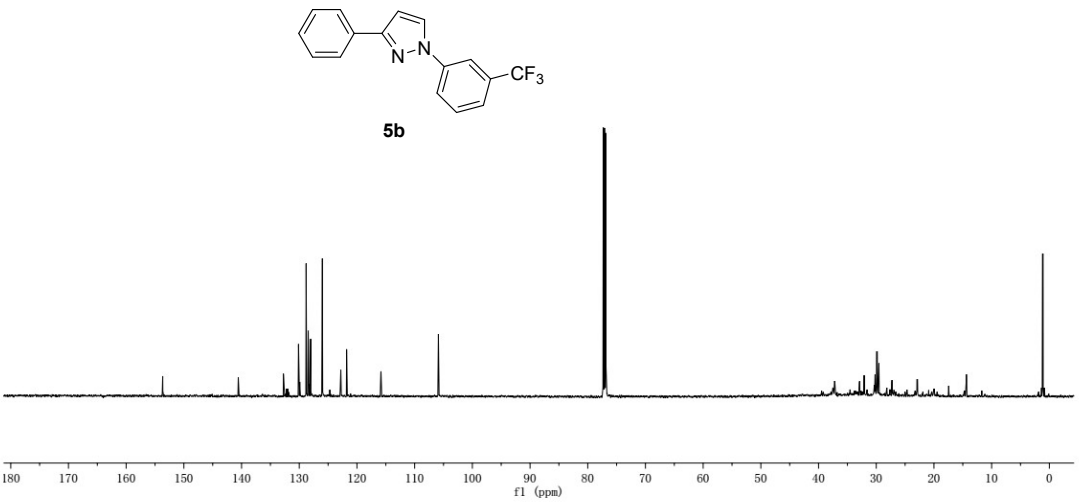
3.03
1.99
2.06
1.12
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5b


153.6629
140.5670
132.7428
132.2007
131.9862
130.1343
129.9097
129.8810
128.8092
128.4448
128.0261
125.9940
122.8159
122.7958
121.7923
115.8807
115.8558
115.8344
115.8102
105.8862
77.3082
77.0970
76.8857


N
N
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5b


7.9108
7.9086
7.9052
7.8994
7.8982
7.8968
7.8948
7.8919
7.6313
7.6274
7.4323
7.4294
7.4199
7.4157
7.4094
7.4067
7.4039
7.4017
7.3460
7.3393
7.3378
7.3334
7.3300
7.3275
7.3237
7.3164
7.3122
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7.3041
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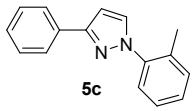
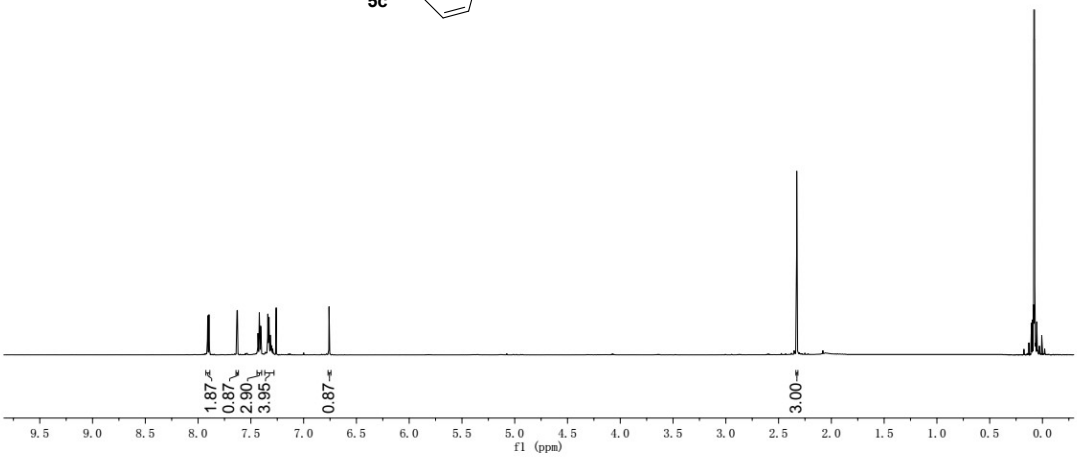
6.7555
2.3280



5c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0.87
2.90
3.95
0.87
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.3619
140.0980
133.8279
133.3700
131.9884
131.4517
128.6986
128.4773
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126.7096
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125.8385
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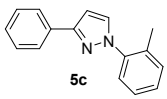
77.1020
76.8900
18.3243



5c

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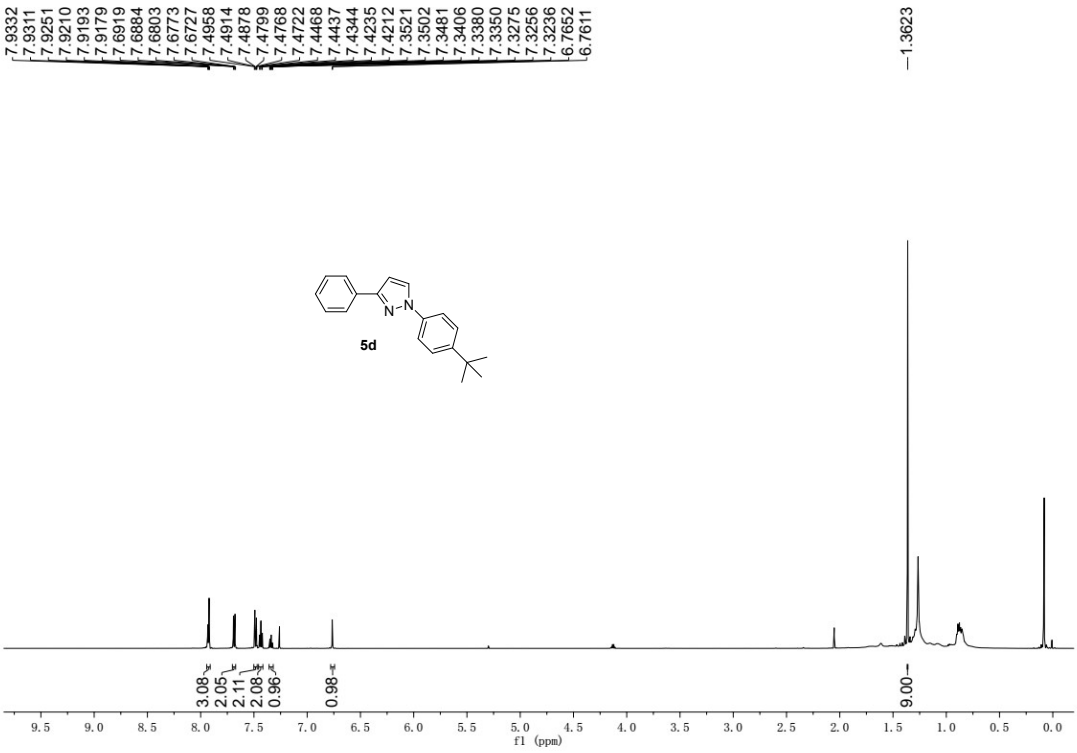
f1 (ppm)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7.9210
7.9193
7.9179
7.6919
7.6884
7.6803
7.6773
7.6727
7.4958
7.4914
7.4878
7.4799
7.4768
7.4722
7.4468
7.4437
7.4344
7.4235
7.4212
7.3521
7.3502
7.3481
7.3406
7.3380
7.3350
7.3275
7.3256
7.3236
6.7652
6.7611
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5d
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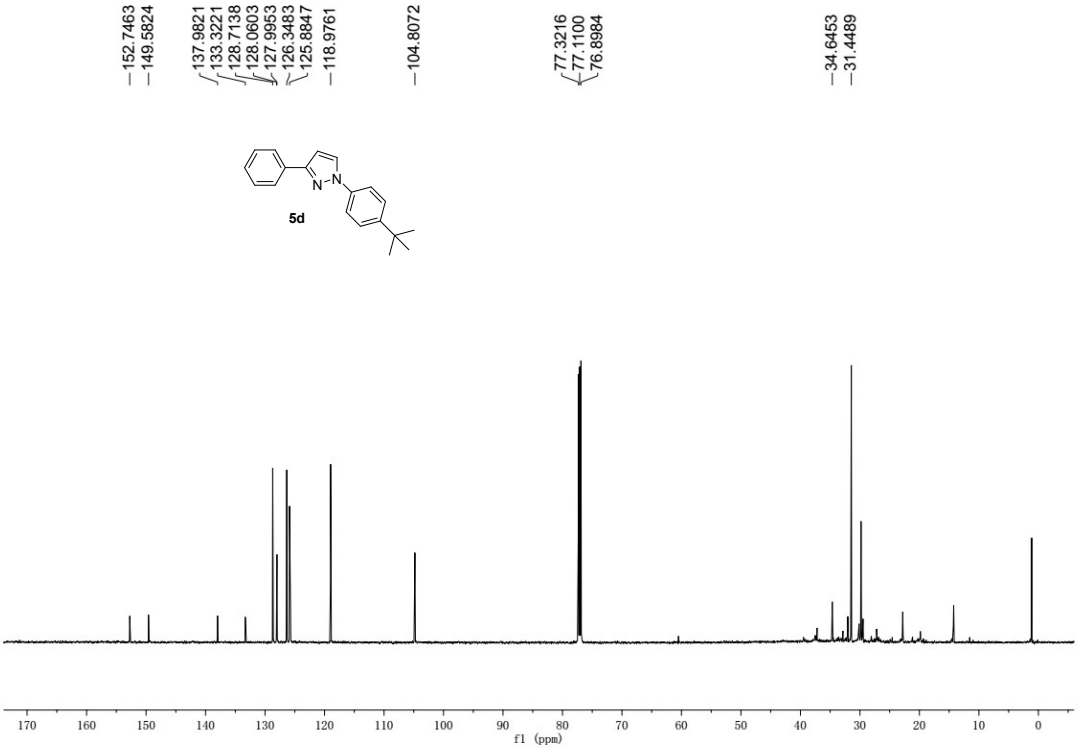
2.05
2.11
2.08
0.96
0.98
9.00
f1 (ppm)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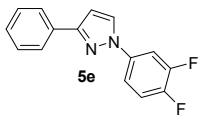
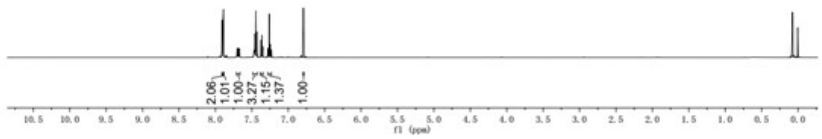
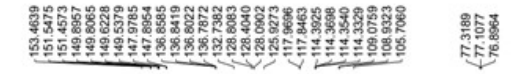
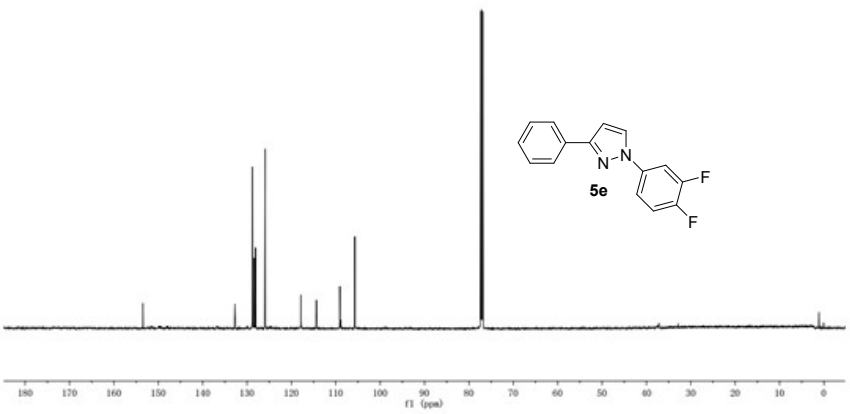
76.8984
34.6453
31.4489
5d
f1 (ppm)


5e






5e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7.9040
7.8982
7.8970
7.8956
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7.8297
7.8254
7.4521
7.4497
7.4449
7.4437
7.4412
7.4324
7.4251
7.4224
7.4195
7.4172
7.3956
7.3901
7.3870
7.3816
7.3563
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7.3296
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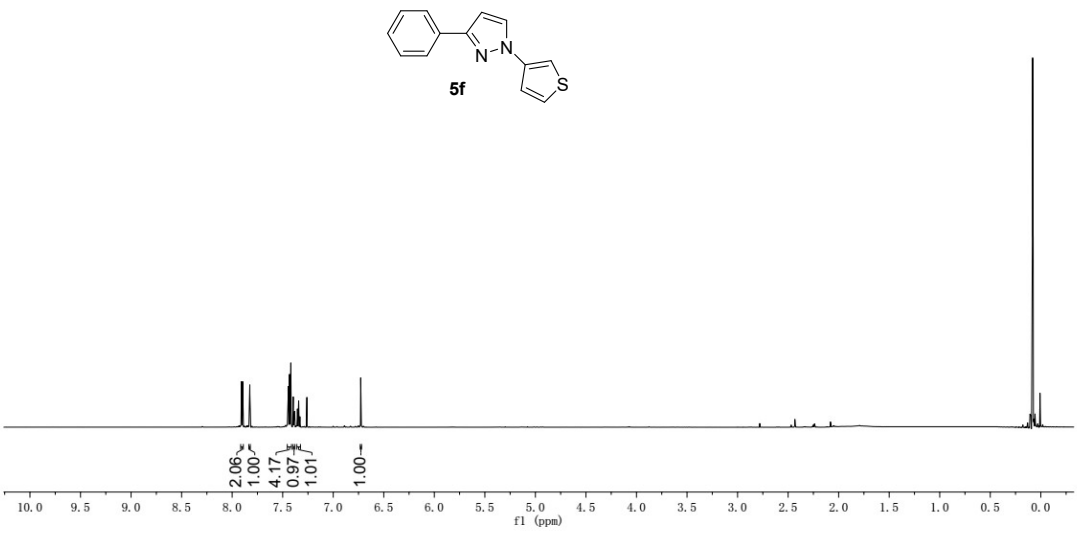
6.7242


5f
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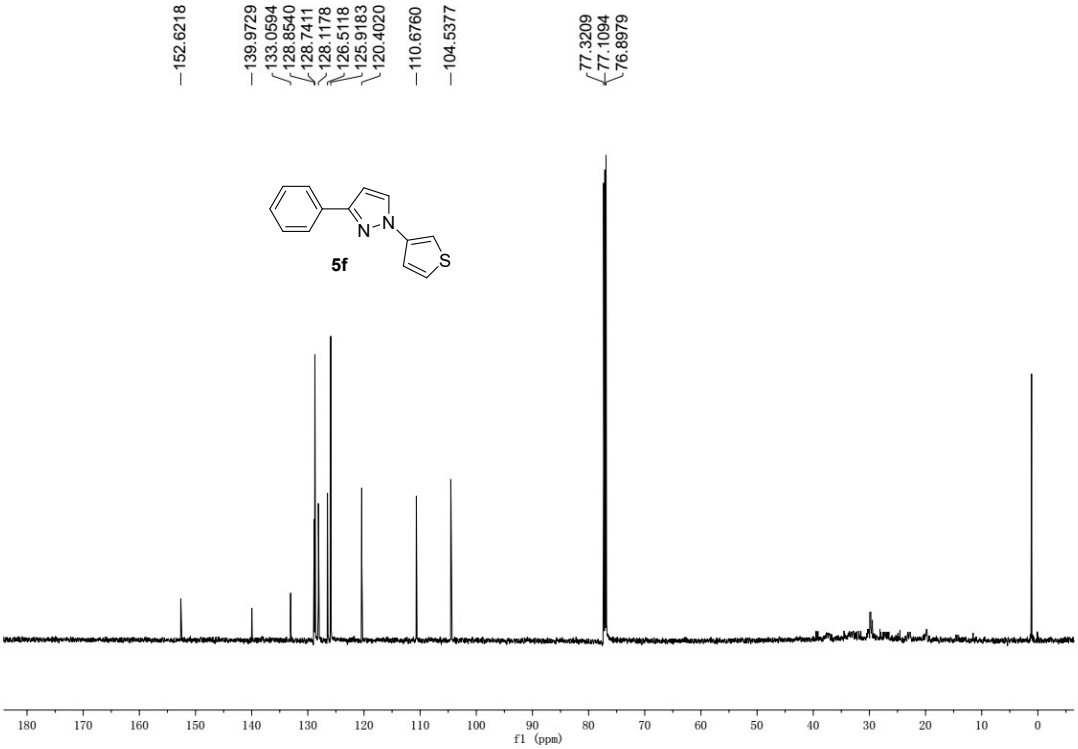
1.00
4.17
0.97
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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120.4020
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104.5377
77.3209
77.1094
76.8979
5f
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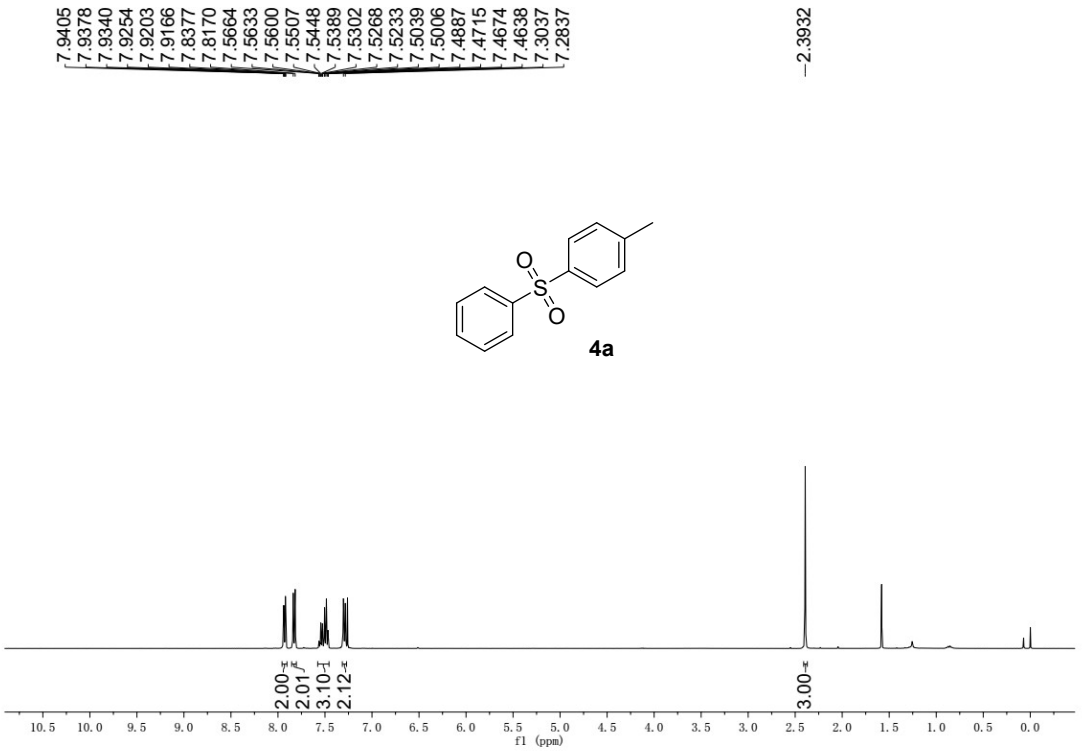
f1 (ppm)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7.5600
7.5507
7.5448
7.5389
7.5302
7.5268
7.5233
7.5039
7.5006
7.4887
7.4715
7.4674
7.4638
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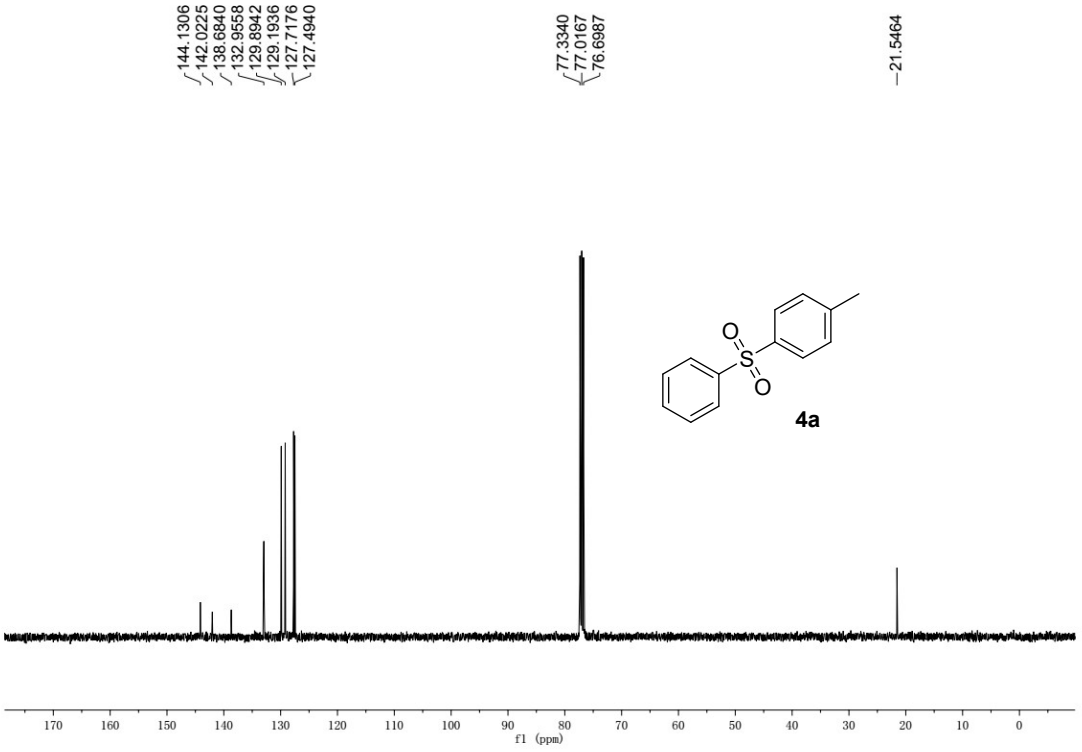
7.2837
2.3932
4a
2.00
2.01
3.10
2.12
3.00
f1 (ppm)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127.7176
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77.3340
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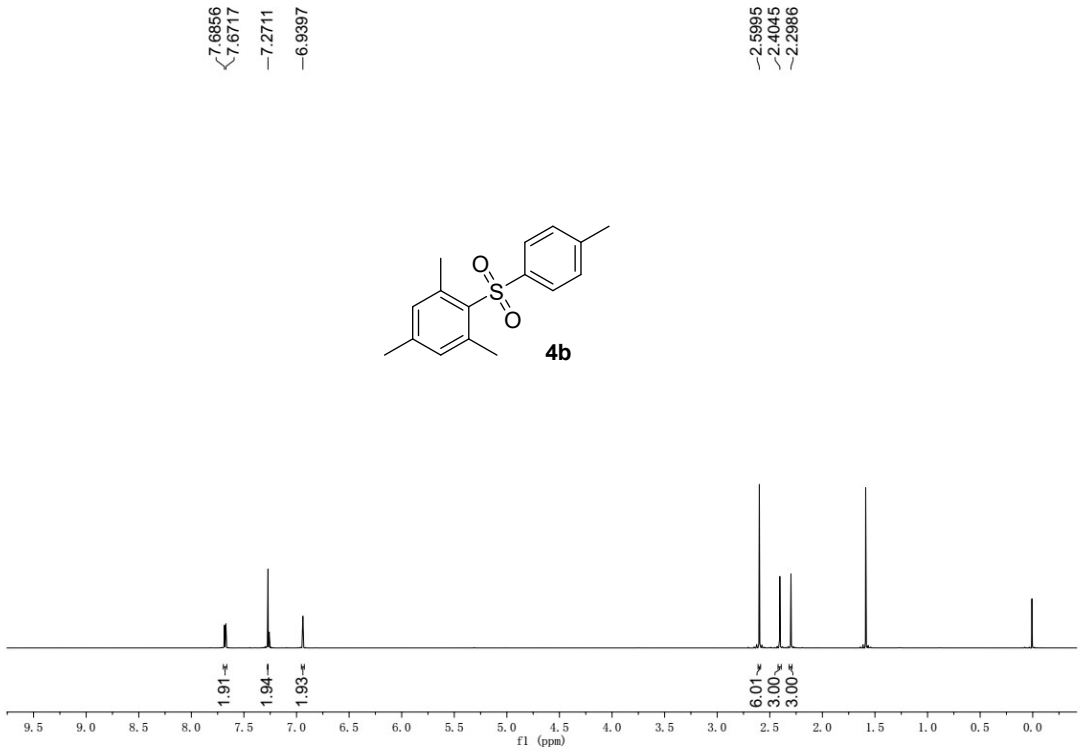
76.6987
21.5464
4a
f1 (ppm)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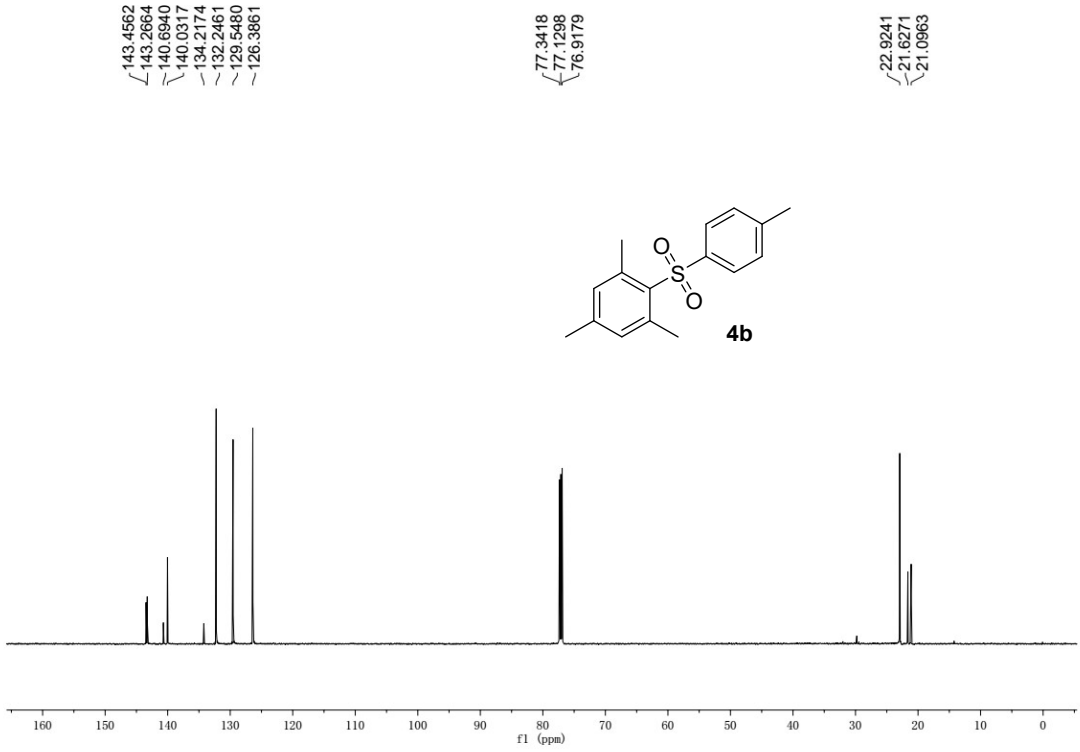
7.2711
6.9397
2.5995
2.4045
2.2986
4b
1.91
1.94
1.93
6.01
3.00
3.00
f1 (ppm)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129.5480
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77.3418
77.1298
76.9179
22.9241
21.6271
21.0963
4b
f1 (ppm)

9. X-Ray Structure of 3i

Compound **3i** (CCDC 1899449) contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

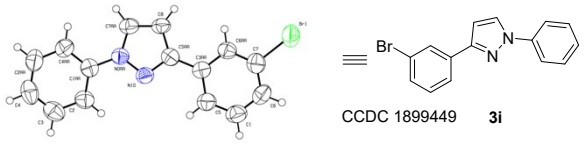

Table S1. Crystal data and structure refinement for Compound **3i**

Identification code	**3i**
Empirical formula	$C_{15}H_{11}BrN_2$
Formula weight	299.17
Temperature/K	292.95(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.5406(3)
b/Å	8.3315(5)
c/Å	27.8631(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1286.21(12)
Z	4
ρ_{calc}g/cm^3	1.545
μ/mm^{-1}	4.199
F(000)	600.0
Crystal size/mm^3	0.7 × 0.6 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.084 to 145.704
Index ranges	-4 ≤ h ≤ 6, -9 ≤ k ≤ 10, -34 ≤ l ≤ 34
Reflections collected	7593
Independent reflections	2447 [R_{int} = 0.0656, R_{sigma} = 0.0467]
Data/restraints/parameters	2447/0/163
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0804, wR_2 = 0.2372
Final R indexes [all data]	R_1 = 0.0917, wR_2 = 0.2596
Largest diff. peak/hole / e Å^{-3}	1.18/-1.18
Flack parameter	-0.01(4)

10. X-Ray Structure of 4b

Compound **4b** (CCDC 1910849) contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

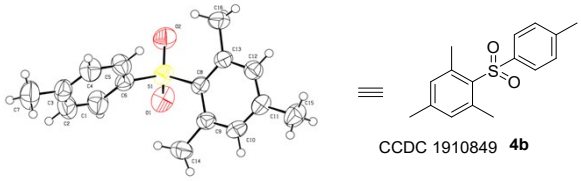

Table S2. Crystal data and structure refinement for Compound **4b**

Identification code	**4b**
Empirical formula	$C_{16}H_{18}O_2S$
Formula weight	274.36
Temperature/K	295.13(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.1266(3)
b/Å	24.3656(8)
c/Å	7.7718(2)
α/°	90
β/°	110.298(4)
γ/°	90
Volume/Å^3	1443.33(9)
Z	4
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	1.948
F(000)	584.0
Crystal size/mm^3	0.7 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.256 to 145.726
Index ranges	-9 ≤ h ≤ 9, -29 ≤ k ≤ 29, -6 ≤ l ≤ 9
Reflections collected	8456
Independent reflections	2802 [R_{int} = 0.0314, R_{sigma} = 0.0274]
Data/restraints/parameters	2802/0/176
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0556, wR_2 = 0.1556
Final R indexes [all data]	R_1 = 0.0645, wR_2 = 0.1680
Largest diff. peak/hole / e Å^{-3}	0.39/-0.32