Supporting Information

Metal-Free Iodine-Catalyzed Direct Cross-Dehydrogenative Coupling (CDC) Between Pyrazoles and Thiols

Daoshan Yang,* Pengfei Sun, Wei Wei, Lingduan Meng, Lingchao He, Baokai Fang, Wei Jiang, and Hua Wang*

The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, P. R. China.

Fax: +86-5374458306

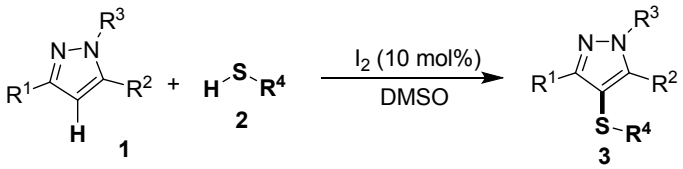
E-mail: *yangdaoshan@tsinghua.org.cn; huawang_qfnu@126.com*

Table of contents

General information

All commercially available reagent-grade chemicals were purchased from chemical suppliers and used as received without further purification unless otherwise stated. pyrazoles were prepared according to previous literatures.[1] Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using either tetramethylsilane (TMS) as the internal standard in $CDCl_3$ (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.24 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm) or tetramethylsilane (TMS) as the internal standard in DMSO-d_6 (1HNMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0 ppm). The chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t) and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer. Column chromatography was performed on silica gel (200-300 mesh).

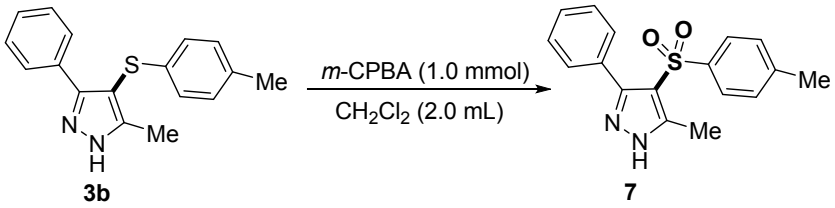
General experimental procedures for synthesis of C-4 sulfenylated pyrazoles



A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with iodine (5 mg, 0.02 mmol), substituted various pyrazole (**1**) (0.2 mmol), thiols (**2**) (0.24 mmol), and DMSO (2 mL). The tube was sealed, and then the mixture was

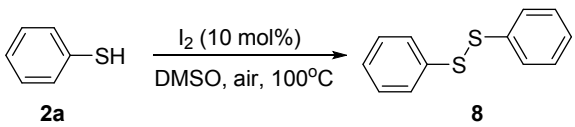
stirred under air atmosphere at 100 °C for 18 h. After completion of the reaction, the resulting solution was cooled down to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**3**).

General procedure for synthesis of compounds 7[2]



A solution of **3b** (0.3 mmol) in 2 mL CH_2Cl_2 was cooled to 0 ºC. Then, *m*-CPBA (0.104g, 0.6 mmol) dissolved in 2 mL CH_2Cl_2 was added drop wise to the stirred solution of **3b**. The reaction progress was monitored by TLC. After completion of the reaction, the resulting solution was cooled to room temperature , and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product **7** in 73% yield as a white solid.

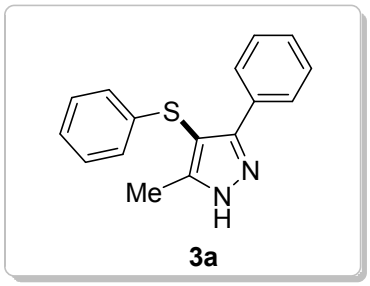
General procedure for synthesis of compounds 5



A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with iodine (5 mg, 0.02 mmol), benzenethiol (0.24 mmol), and DMSO (2 mL). The tube was sealed, and then the mixture was stirred under air atmosphere at 100 °C for 18 h. After

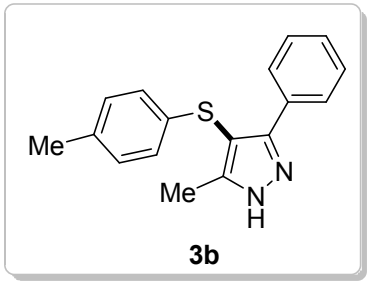
completion of the reaction, the resulting solution was cooled down to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**8**).

Characterization data of products 3a-3ae, 4 and 5



3a

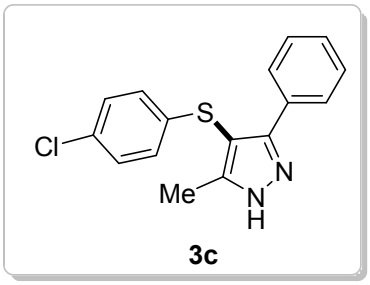
5-Methyl-3-phenyl-4-(phenylthio)-1*H*-pyrazole (3a). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 50 mg, 94% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 11.46 (s, br, 1H), 7.78 (dd, 2H, J = 5.0 Hz), 7.35-7.34 (m, 3H), 7.24 (t, 2H, J = 10.0 Hz), 7.12 (t, 1H, J = 10.0 Hz), 7.07 (d, 2H, J = 10.0 Hz), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.7, 149.5, 138.6, 129.0, 128.6, 128.5, 128.2, 127.9, 125.3, 124.9, 102.8, 10.6. HRMS m/z calcd. for $C_{16}H_{15}N_2S[M+H]^+$: 267.0950, found: 267.0948.



3b

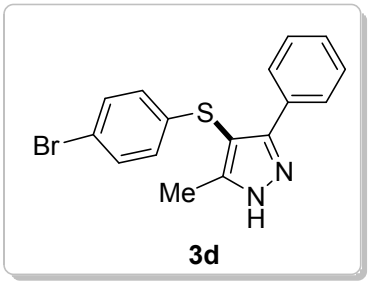
5-Methyl-3-phenyl-4-(*p*-tolylthio)-1*H*-pyrazole (3b). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 51 mg, 92% yield. (petroleum ether/ethyl acetate = 3:1,

Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.71 (dd, 2H, J = 10.0 Hz), 7.30-7.26 (m, 3H), 6.96 (d, 2H, J = 10.0 Hz), 6.88 (d, 2H, J = 10.0 Hz), 2.22 (s, 3H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.3, 149.6, 134.9, 134.7, 131.1, 129.7, 128.6, 127.8, 125.5, 103.4, 20.9, 10.7. HRMS m/z calcd. for $C_{17}H_{17}N_2S$ $[M+H]^+$: 281.1107, found: 281.1110.



3c

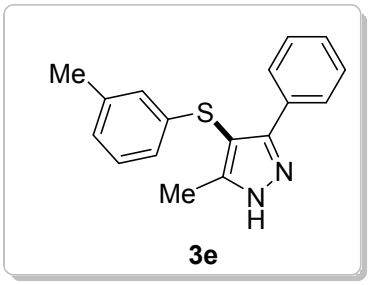
4-(4-Chlorophenylthio)-5-methyl-3-phenyl-1*H*-pyrazole (3c). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 52 mg, 87% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.74 (dd, 2H, J = 10.0 Hz), 7.38-7.35 (m, 3H), 7.18 (d, 2H, J = 10.0 Hz), 6.97 (d, 2H, J = 10.0 Hz), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.3, 149.7, 137.1, 130.9, 130.8, 129.1, 128.8, 128.6, 127.6, 126.6, 102.6, 10.8. HRMS m/z calcd. for $C_{16}H_{14}ClN_2S$ $[M+H]^+$: 301.0561, found: 301.0564.



3d

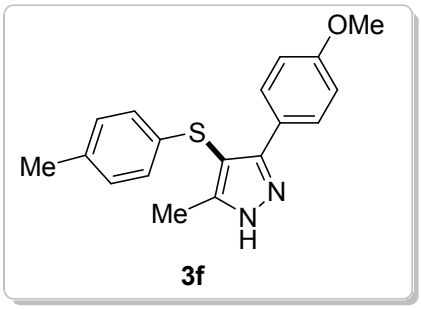
4-(4-Bromophenylthio)-5-methyl-3-phenyl-1*H*-pyrazole (3d). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 61 mg, 89% yield. (petroleum ether/ethyl

acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.74 (dd, 2H, J = 10.0 Hz), 7.38-7.36 (m, 3H), 7.32 (d, 2H, J = 10.0 Hz), 6.91 (d, 2H, J = 10.0 Hz), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.3, 149.8, 137.8, 131.9, 130.7, 128.8, 128.6, 127.6, 126.9, 118.5, 10.8. HRMS m/z calcd. for $C_{16}H_{14}BrN_2S$ $[M+H]^+$: 345.0061, 347.0041, found: 345.0052, 347.0059.



3e

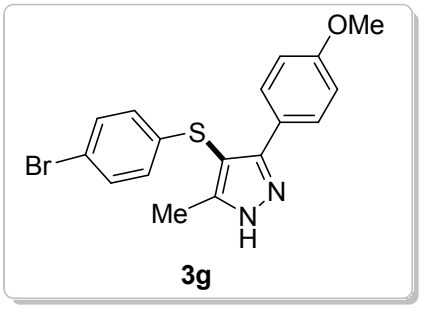
5-Methyl-3-phenyl-4-(*m*-tolylthio)-1*H*-pyrazole (3e). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 48 mg, 86% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.78 (dd, 2H, J = 10.0 Hz), 7.40-7.36 (m, 3H), 7.11 (t, 1H, J = 10.0 Hz), 6.92 (d, 2H, J = 10.0 Hz), 6.90 (s, 1H), 6.83 (d, 2H, J = 10.0 Hz), 2.29 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 150.8, 150.0, 138.8, 138.3, 130.9, 130.8, 128.8, 128.7, 128.6, 127.6, 125.9, 122.3, 103.0, 21.4, 10.9. HRMS m/z calcd. for $C_{17}H_{17}N_2S$ $[M+H]^+$: 281.1107, found: 281.1105.



3f

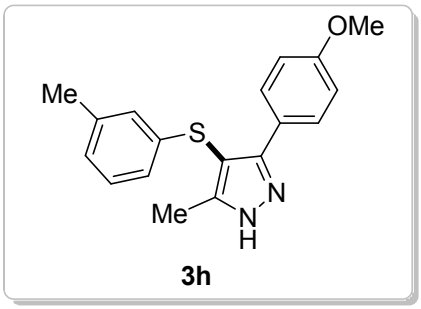
3-(4-Methoxyphenyl)-5-methyl-4-(*p*-tolylthio)-1*H*-pyrazole (3f). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 55 mg, 89% yield. (petroleum ether/ethyl

acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 12.00 (br, s, 1H), 7.71 (d, 2H, J = 5.0 Hz), 7.06 (d, 2H, J = 10.0 Hz), 6.99 (d, 2H, J = 10.0 Hz), 6.85 (d, 2H, J = 5.0 Hz), 3.80 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 159.9, 150.9, 149.9, 135.2, 134.6, 129.8, 129.2, 125.5, 123.5, 113.9, 102.7, 55.2, 20.9, 10.9. HRMS m/z calcd. for $C_{18}H_{19}N_2OS$ $[M+H]^+$: 311.1213, found: 311.1214.



3g

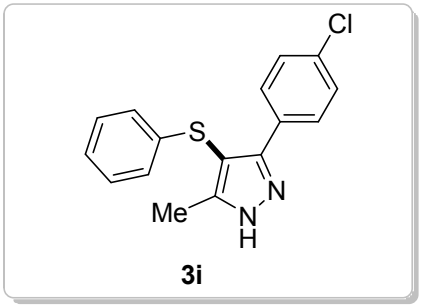
4-(4-Bromophenylthio)-3-(4-methoxyphenyl)-5-methyl-1*H*-pyrazole (3g). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 65 mg, 88% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 12.36 (br, s, 1H), 7.66 (d, 2H, J = 10.0 Hz), 7.31 (d, 2H, J = 10.0 Hz), 6.91 (d, 2H, J = 5.0 Hz), 6.84 (d, 2H, J = 5.0 Hz), 3.80 (s, 3H), 2.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 160.0, 151.0, 149.9, 138.0, 132.0, 129.1, 126.8, 123.1, 118.5, 114.0, 101.7, 55.2, 10.8. HRMS m/z calcd. for $C_{17}H_{16}BrN_2OS$ $[M+H]^+$: 376.0245, 378.0224, found: 376.0047, 378.0231.



3h

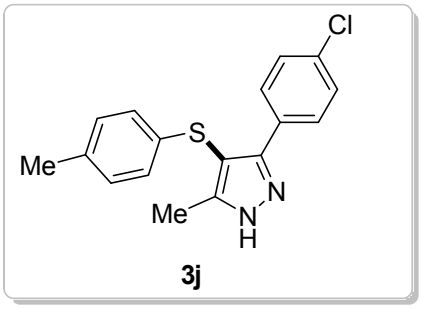
3-(4-Methoxyphenyl)-5-methyl-4-(*m*-tolylthio)-1*H*-pyrazole (3h). Eluent petroleum

ether/ethyl acetate (4:1). Brown solid, 52 mg, 84% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.5). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 11.8 (br, s, 1H), 7.71 (d, 2H, J = 5.0 Hz), 7.13 (t, 1H, J = 10.0 Hz), 6.98-6.93 (m, 2H), 6.84 (d, 3H, J = 5.0 Hz), 3.80 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 159.9, 151.1, 150.0, 138.8, 138.6, 129.2, 128.9, 125.9, 125.8, 123.5, 122.3, 113.9, 102.3, 55.2, 21.5, 10.9. HRMS m/z calcd. for $C_{18}H_{19}N_2OS$ $[M+H]^+$: 311.1213, found: 311.1214.



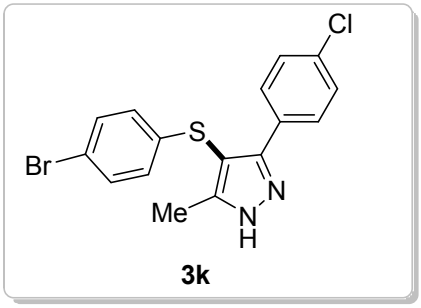
3i

3-(4-Chlorophenyl)-5-methyl-4-(phenylthio)-1*H*-pyrazole (3i). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 83 mg, 92% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.70 (d, 2H, J = 10.0 Hz), 7.29-7.23 (m, 4H), 7.14 (t, 1H, J = 10.0 Hz), 7.06 (d, 2H, J = 10.0 Hz), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.2, 149.1, 138.2, 134.7, 129.4, 129.1, 129.0, 128.7, 125.4, 125.2, 103.2, 10.5. HRMS m/z calcd. for $C_{16}H_{14}ClN_2S$ $[M+H]^+$: 301.0561, found: 301.0564.



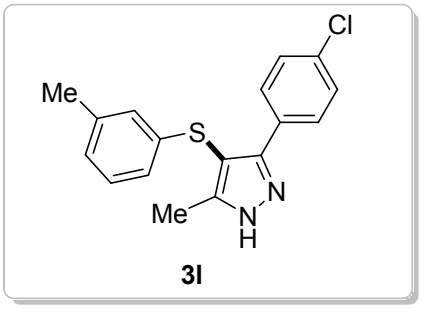
3j

3-(4-Chlorophenyl)-5-methyl-4-(*p*-tolylthio)-1*H*-pyrazole (3j). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 53 mg, 85% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.78 (d, 2H, J = 10.0 Hz), 7.34 (d, 2H, J = 10.0 Hz), 7.04 (d, 2H, J = 10.0 Hz), 6.94 (d, 2H, J = 10.0 Hz), 2.34 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 50.9, 148.8, 135.0, 134.5, 129.8, 129.4, 129.0, 128.7, 128.6, 128.5, 103.7, 20.9, 10.6. HRMS m/z calcd. for $C_{17}H_{16}ClN_2S$ $[M+H]^+$: 315.0717, found: 315.0719.



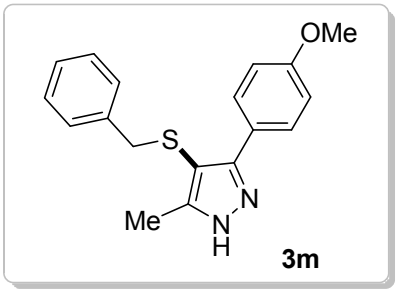
3k

4-(4-Bromophenylthio)-3-(4-chlorophenyl)-5-methyl-1*H*-pyrazole (3k). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 65 mg, 86% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.5). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.71 (d, 2H, J = 10.0 Hz), 7.33 (dd, 4H, J = 10.0 Hz), 6.98 (d, 2H, J = 10.0 Hz), 2.28 (s, 3H). ^{13}C NMR (,$CDCl_3$,125 MHz, ppm) δ 151.1, 148.8, 137.4, 134.8, 132.0, 129.6, 128.8, 128.7, 126.9, 125.6, 118.7, 10.6. HRMS m/z calcd. for $C_{16}H_{13}BrClN_2S$ $[M+H]^+$: 378.9671, 380.9651, found: 378.9680, 380.9654.



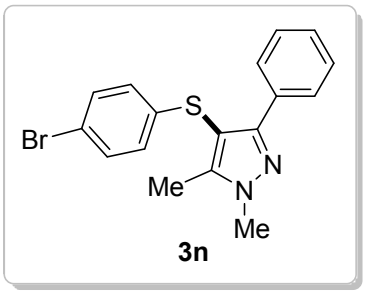
3l

3-(4-Chlorophenyl)-5-methyl-4-(*m*-tolylthio)-1*H*-pyrazole (3l). Eluent petroleum ether/ethyl acetate (4:1). Brown solid, 53 mg, 85% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 10.3 (br, s, 1H), 7.71 (d, 2H, J = 10.0 Hz), 7.29 (d, 2H, J = 10.0 Hz), 7.12 (dd, 1H, J = 5.0 Hz, J = 10.0 Hz), 6.94 (d, 1H, J = 10.0 Hz), 6.90 (s, 1H), 6.80 (d, 2H, J = 10.0 Hz), 2.29 (s, 3H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$ 125 MHz, ppm) δ 151.1, 150.0, 138.9, 137.9, 134.6, 129.7, 129.0, 128.9, 128.7, 126.1, 125.9, 122.3, 103.3, 21.5, 10.6. HRMS m/z calcd. for $C_{17}H_{16}ClN_2S$ $[M+H]^+$: 315.0717, found: 315.0719.



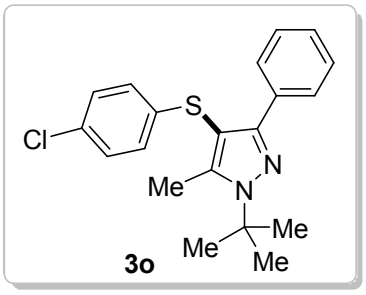
3m

3-(4-Methoxyphenyl)-5-methyl-4-(phenethylthio)-1*H*-pyrazole (3m). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 42 mg, 65% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR (,$CDCl_3$ 500 MHz, ppm) δ 11.7 (br, s, 1H), 7.87 (d, 2H, J = 10.0 Hz), 7.28-7.25 (m, 2H), 7.20 (t, 1H, J = 10.0 Hz), 7.06 (d, 2H, J = 10.0 Hz), 6.91 (d, 2H, J = 10.0 Hz), 6.80 (d, 2H, J = 10.0 Hz), 3.86 (s, 3H), 2.76 (d 2H, J = 10.0 Hz), 2.70 (d, 2H, J = 10.0 Hz), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 159.7, 150.0, 148.5, 140.4, 129.2, 128.5, 128.4, 126.2, 124.2, 113.8, 105.4, 55.2, 37.5, 36.0, 10.9. HRMS m/z calcd. for $C_{19}H_{21}N_2OS$ $[M+H]^+$: 325.1369, found: 325.1365.



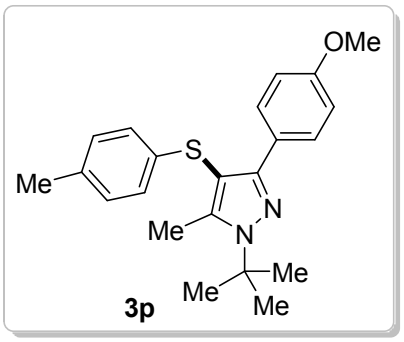
3n

4-(4-Bromophenylthio)-1,5-dimethyl-3-phenyl-1*H*-pyrazole (3n). Eluent petroleum ether/ethyl acetate (4:1). White solid, 64 mg, 90% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.85 (d, 2H, J = 10.0 Hz), 7.38-7.32 (m, 5H), 6.92 (d, 2H, J = 10.0 Hz), 3.94 (s, 3H), 2.33 (d 2H, J = 10.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 152.8, 145.2, 138.3, 132.5, 131.9, 128.3, 128.1, 127.5, 126.8, 118.4, 101.9, 37.2, 10.0. HRMS m/z calcd. for $C_{17}H_{16}BrN_2S$ $[M+H]^+$: 359.0212, 361.0197, found: 359.0215, 361.0219.

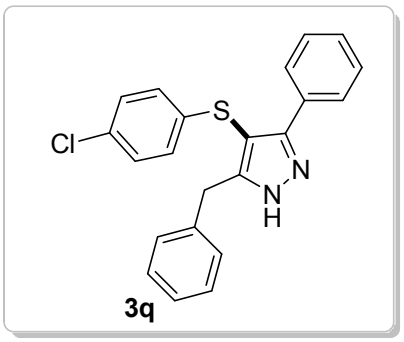


3o

5-*tert*-Butyl-4-(4-chlorophenylthio)-3-phenyl-1*H*-pyrazole (3o). Eluent petroleum ether/ethyl acetate (4:1). White solid, 53 mg, 77% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.32 (d, 2H, J = 10.0 Hz), 7.35-7.33 (m, 3H), 7.17 (d, 2H, J = 10.0 Hz), 6.95 (d, 2H, J = 10.0 Hz), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 1148.1, 141.0, 127.0, 125.9, 123.9, 123.8, 122.3, 120.6, 118.5, 114.4, 114.2, 113.8, 58.5, 18.5, 15.3. HRMS m/z calcd. for $C_{19}H_{20}ClN_2S$ $[M+H]^+$: 343.1030, found: 343.1038.

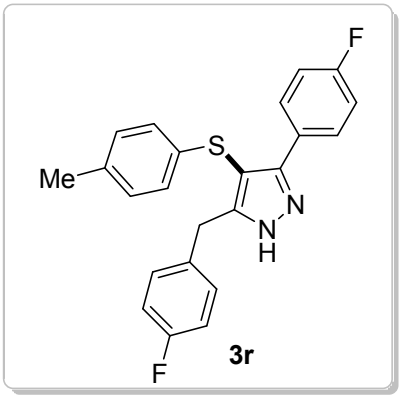


5-*tert*-Butyl-3-(4-methoxyphenyl)-4-(*p*-tolylthio)-1*H*-pyrazole (3p). Eluent petroleum ether/ethyl acetate (5:1). White solid, 57 mg, 82% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 13.1 (br, s, 1H), 7.64 (d, 2H, J = 5.0 Hz), 7.04 (d, 2H, J = 10.0 Hz), 6.92 (d, 2H, J = 5.0 Hz), 6.83 (d, 2H, J = 10.0 Hz), 3.78 (s, 3H), 2.20 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 159.7, 158.6, 147.8, 140.9, 131.5, 128.9, 124.9, 121.5, 120.6, 114.3, 113.6, 55.3, 44.7, 30.1, 27.4. HRMS m/z calcd. for $C_{21}H_{25}N_2OS$ $[M+H]^+$: 353.1682, found: 353.1685.

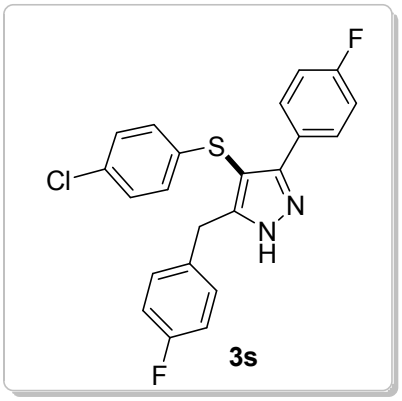


5-Benzyl-4-(4-chlorophenylthio)-3-phenyl-1*H*-pyrazole (3q). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 59 mg, 78% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.73 (d, 2H, J = 10.0 Hz), 7.36-7.33 (m, 3H), 7.21-7.18 (m, 3H), 7.15 (d, 2H, J = 10.0 Hz), 7.11 (d, 2H, J = 10.0 Hz), 6.89 (d, 2H, J = 10.0 Hz), 4.00 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ

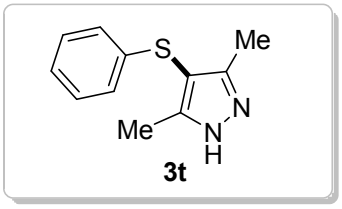
1152.9, 150.7, 137.4, 136.9, 130.7, 130.3, 128.93, 128.91, 128.8, 128.7, 128.6, 127.5, 126.63, 126.61, 102.4, 31.9. HRMS m/z calcd. for $C_{22}H_{18}ClN_2S$ $[M+H]^+$: 377.0874, found: 377.0883.



5-(4-Fluorobenzyl)-3-(4-fluorophenyl)-4-(p-tolylthio)-1*H*-pyrazole (3r). Eluent petroleum ether/ethyl acetate (5:1). White solid, 63 mg, 80% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.70 (d, 2H, J = 10.0 Hz), 7.10 (d, 2H, J = 5.0 Hz), 7.00 (d, 2H, J = 10.0 Hz), 6.90 (d, 2H, J = 5.0 Hz), 6.88 (d, 2H, J = 10.0 Hz), 6.77 (d, 2H, J = 10.0 Hz), 3.97 (s, 2H), 2.29 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.6 (d, J_{CF} = 245.0 Hz), 159.9, 158.2, 134.1 (d, J_{CF} = 7.5 Hz), 134.6, 129.9, 129.8, 129.6, 129.3, 128.8, 125.5, 123.2, 114.0, 113.98, 113.94, 102.4, 31.1, 20.9. HRMS m/z calcd. for $C_{23}H_{19}F_2N_2S$ $[M+H]^+$: 393.1232, found: 393.1236.

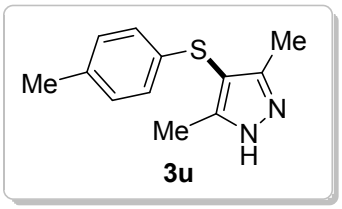


4-(4-Chlorophenylthio)-5-(4-fluorobenzyl)-3-(4-fluorophenyl)-1*H*-pyrazole (3s). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 62 mg, 75% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.64 (d, 2H, J = 10.0 Hz), 7.09 (d, 2H, J = 10.0 Hz), 7.04 (d, 2H, J = 10.0 Hz), 6.85 (dd, 4H, J = 5.0 Hz), 6.69 (d, 2H, J = 10.0 Hz), 3.92 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 160.1 (d, J_{CF} = 243.0 Hz), 158.2, 153.5, 150.3, 137.1 (d, J_{CF} = 7.5 Hz), 130.5, 129.8, 129.6, 128.9, 128.8, 126.5, 122.7, 114.1, 113.8, 101.4, 31.2. HRMS m/z calcd. for $C_{22}H_{16}ClF_2N_2S$ $[M+H]^+$: 413.0685, found: 413.0689.



3t

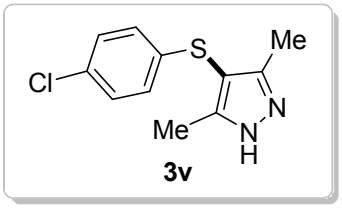
3,5-Dimethyl-4-(phenylthio)-1*H*-pyrazole (3t). Eluent petroleum ether/ethyl acetate (4:1). White solid, 38 mg, 93% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.24 (dd, 2H, J = 5.0 Hz, J = 10.0 Hz), 7.12 (dd, 2H, J = 10.0 Hz), 7.04 (d, 2H, J = 10.0 Hz), 2.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 148.9, 138.6, 128.9, 125.3, 124.8, 104.2, 103.7, 11.1. HRMS m/z calcd. for $C_{11}H_{13}N_2S$ $[M+H]^+$: 205.0794, found: 205.0799.



3u

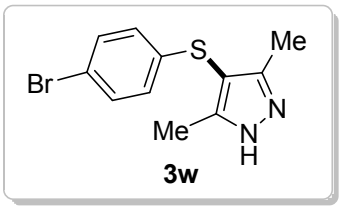
3,5-Dimethyl-4-(*p*-tolylthio)-1*H*-pyrazole (3u). Eluent petroleum ether/ethyl acetate (4:1). White solid, 41 mg, 95% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3).

^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.08 (d, 2H, J = 5.0 Hz, J = 10.0 Hz), 6.97 (d, 2H, J = 5.0 Hz), 2.37 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (,$CDCl_3$ 125 MHz, ppm) δ 148.8, 135.0, 134.7, 129.7, 125.6, 104.3, 20.9, 11.2. HRMS m/z calcd. for $C_{12}H_{15}N_2S$ $[M+H]^+$: 219.0950, found: 219.0959.



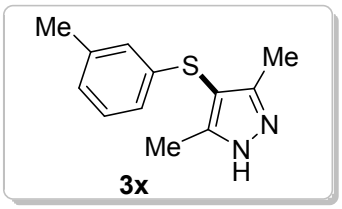
3v

4-(4-Chlorophenylthio)-3,5-dimethyl-1*H*-pyrazole (3v). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 43 mg, 91% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 10.9 (br, s, 1H), 7.19 (d, 2H, J = 10.0 Hz), 6.94 (d, 2H, J = 10.0 Hz), 2.33 (s, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 148.9, 137.1, 130.7, 129.0, 126.6, 103.5, 11.1. HRMS m/z calcd. for $C_{11}H_{12}ClN_2S$ $[M+H]^+$: 239.0404, found: 239.0408.



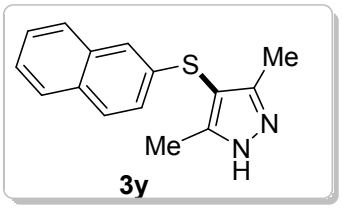
3w

4-(4-Bromophenylthio)-3,5-dimethyl-1*H*-pyrazole (3w). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 52 mg, 93% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 12.5 (br, s, 1H), 7.34 (d, 2H, J = 10.0 Hz), 6.90 (d, 2H, J = 10.0 Hz), 2.35 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 148.9, 137.9, 131.9, 126.9, 118.4, 103.3, 11.1. HRMS m/z calcd. for $C_{11}H_{12}BrN_2S$ $[M+H]^+$: 282.9905, 284.9884, found: 282.9914, 284.9890.



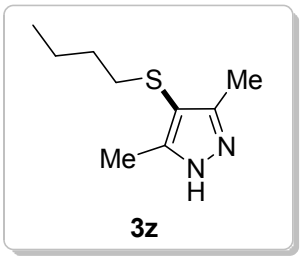
3x

3,5-Dimethyl-4-(*m*-tolylthio)-1*H*-pyrazole (3x). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 40 mg, 92% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 12.0 (br, s, 1H), 7.24 (dd, 2H, J = 5.0 Hz, J = 10.0 Hz), 6.94 (d, 2H, J = 10.0 Hz), 6.83 (d, 2H, J = 5.0 Hz), 2.37 (s, 6H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 148.9, 138.7, 138.3, 128.8, 125.9, 125.8, 122.4, 21.5, 11.2. HRMS m/z calcd. for $C_{12}H_{15}N_2S$ $[M+H]^+$: 219.0950, found: 219.0959.



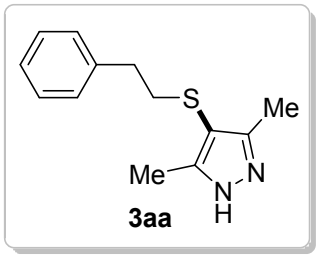
3y

3,5-Dimethyl-4-(naphthalen-2-ylthio)-1*H*-pyrazole (3y). Eluent petroleum ether/ethyl acetate (4:1). White solid, 48 mg, 96% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 12.1(br, s, 1H), 7.82 (d, 1H, J = 10.0 Hz), 7.77 (d, 1H, J = 10.0 Hz), 7.71 (d, 1H, J = 5.0 Hz), 7.49-7.44 (m, 3H), 7.31 (d, 1H, J = 10.0 Hz), 2.46 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 149.0, 144.5, 136.3, 133.9, 131.4, 128.6, 127.8, 126.9, 126.6, 125.2, 124.3, 122.7, 104.2, 103.4, 12.3. HRMS m/z calcd. for $C_{15}H_{15}N_2S$ $[M+H]^+$: 255.0950, found: 255.0956.



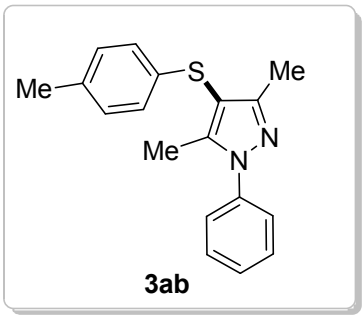
3z

4-(Butylthio)-3,5-dimethyl-1*H*-pyrazole (3z). Eluent petroleum ether/ethyl acetate (4:1). Yellow solid, 23 mg, 62% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 10.6 (br, s, 1H), 2.51 (t, 2H, J = 5.0 Hz, J = 10.0 Hz), 2.35 (s, 6H), 1.48-1.40 (m, 4H), 0.90 (t, 3H, J = 5.0 Hz, J = 10.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 147.8, 146.2, 106.7, 36.1, 31.7, 21.7, 13.7, 12.9, 11.2. HRMS m/z calcd. for $C_9H_{17}N_2S$ $[M+H]^+$: 185.1107, found: 185.1101.



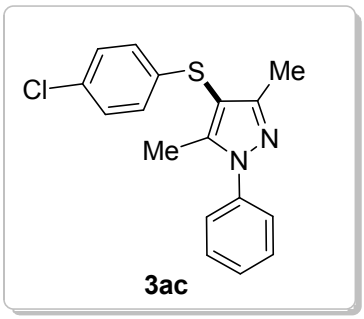
3aa

3,5-Dimethyl-4-(phenethylthio)-1*H*-pyrazole (3aa). Eluent petroleum ether/ethyl acetate (4:1). White solid, 83 mg, 94% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.4). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 11.40 (br, s, 1H), 7.32 (dd, 2H, J = 5.0 Hz, J = 10.0 Hz), 7.24 (d, 2H, J = 5.0 Hz, J = 10.0 Hz), 7.18 (d, 1H, J = 5.0 Hz), 286-2.79 (m, 4H), 2.41 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 148.1, 140.5, 128.5, 128.4, 126.3, 106.5, 37.5, 36.4, 11.3. HRMS m/z calcd. for $C_{13}H_{17}N_2S$ $[M+H]^+$: 233.1107, found: 233.1105.



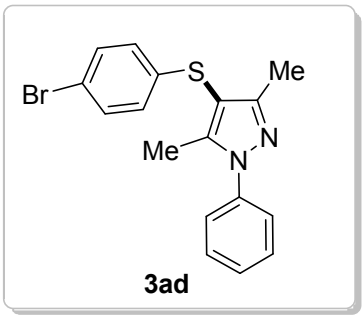
3ab

3,5-Dimethyl-1-phenyl-4-(*p*-tolylthio)-1*H*-pyrazole (3ab). Eluent petroleum ether/ethyl acetate (30:1). White solid, 48 mg, 82% yield. (petroleum ether/ethyl acetate = 25:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.53-7.49 (m, 4H), 7.43-7.40 (m, 1H), 7.08 (d, 2H, J = 10.0 Hz, J = 10.0 Hz), 7.01 (d, 2H, J = 10.0 Hz), 2.38 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.1, 144.0, 139.8, 134.8, 134.7, 129.7, 129.2, 127.8, 125.8, 124.7, 106.7, 20.9, 12.1, 11.6. HRMS m/z calcd. for $C_{18}H_{19}N_2S$ $[M+H]^+$: 295.1263, found: 295.1269.



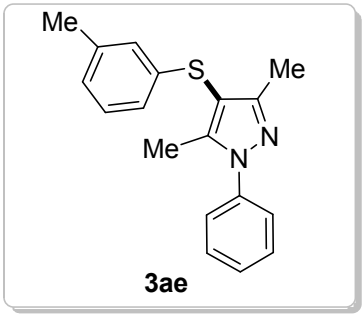
3ac

4-(4-Chlorophenylthio)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (3ac). Eluent petroleum ether/ethyl acetate (30:1). White solid, 54 mg, 86% yield. (petroleum ether/ethyl acetate = 25:1, Rf= 0.3). ^{1}H NMR $CDCl_3$ (, 500 MHz, ppm) δ 7.53-7.49 (m, 4H), 7.44-7.41 (m, 1H), 7.22 (d, 2H, J = 10.0 Hz, J = 10.0 Hz), 7.01 (d, 2H, J = 10.0 Hz), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.1, 144.2, 139.7, 137.0, 130.8, 129.2, 129.0, 127.9, 126.7, 124.7, 105.8, 12.1, 11.5. HRMS m/z calcd. for $C_{17}H_{16}ClN_2S$ $[M+H]^+$: 315.0717, found: 315.0713.



3ad

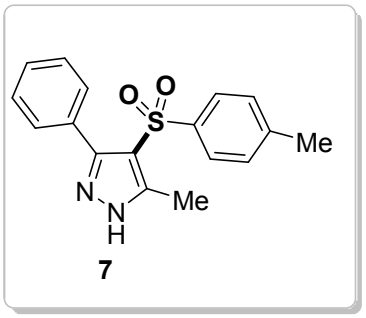
4-(4-Bromophenylthio)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (3ad). Eluent petroleum ether/ethyl acetate (30:1). White solid, 61 mg, 85% yield. (petroleum ether/ethyl acetate = 25:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.52-7.49 (m, 4H), 7.44-7.42 (m, 1H), 7.37 (d, 2H, J = 10.0 Hz), 6.95 (d, 2H, J = 10.0 Hz), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.1, 144.2, 139.7, 137.7, 131.9, 129.2, 128.0, 127.0, 126.7, 124.7, 118.5, 105.6, 12.1, 11.5. HRMS m/z calcd. for $C_{17}H_{16}BrN_2S$ $[M+H]^+$: 359.0218, 361.0197, found: 359.0215, 361.0194.



3ae

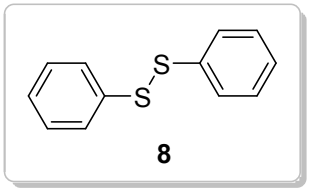
3,5-Dimethyl-1-phenyl-4-(*m*-tolylthio)-1*H*-pyrazole (3ae). Eluent petroleum ether/ethyl acetate (30:1). White solid, 52 mg, 88% yield. (petroleum ether/ethyl acetate = 25:1, Rf= 0.3). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.52-7.51 (m, 4H), 7.43-7.41 (m, 1H), 7.15 (dd, 1H, J = 5.0 Hz, J = 10.0 Hz), 6.95 (d, 2H, J = 10.0 Hz), 6.86 (d, 1H, J = 10.0 Hz), 2.38 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.2, 144.1, 139.8, 138.7, 138.1, 129.2, 128.8, 127.8, 126.0, 125.9, 124.7, 122.5, 106.2, 21.5, 12.1, 11.6. HRMS m/z calcd. for $C_{18}H_{19}N_2S$ $[M+H]^+$:

295.1263, found: 295.1269.



7

5-Methyl-3-phenyl-4-tosyl-1*H*-pyrazole (7). Eluent petroleum ether/ethyl acetate (3:1). White solid, 68mg, 73% yield. (petroleum ether/ethyl acetate = 3:1, Rf= 0.2). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.42-7.38 (m, 5H), 7.34-7.31 (m, 2H), 7.09 (d, 2H, J = 10.0 Hz), 2.33 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 171.4, 150.6, 145.7, 143.6, 140.0, 130.2, 129.9, 129.35, 129.31, 128.0, 126.7, 117.8, 21.8, 11.3. HRMS m/z calcd. for $C_{14}H_{10}N_2O_2S$ $[M+H]^+$: 313.1005, found: 313.1009.



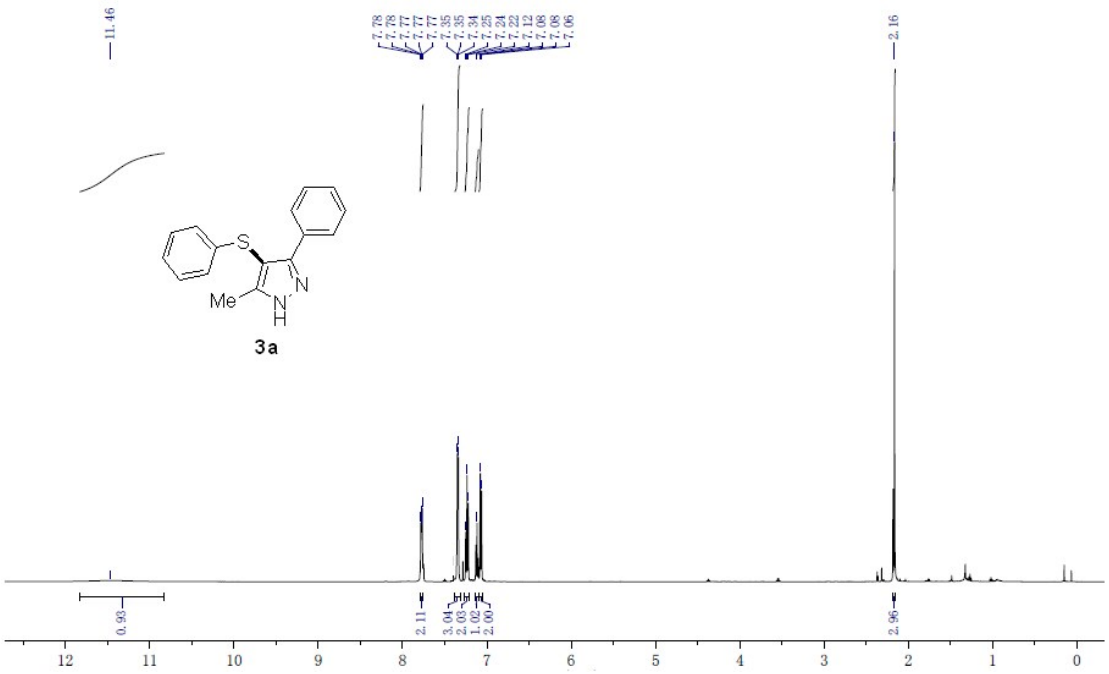
8

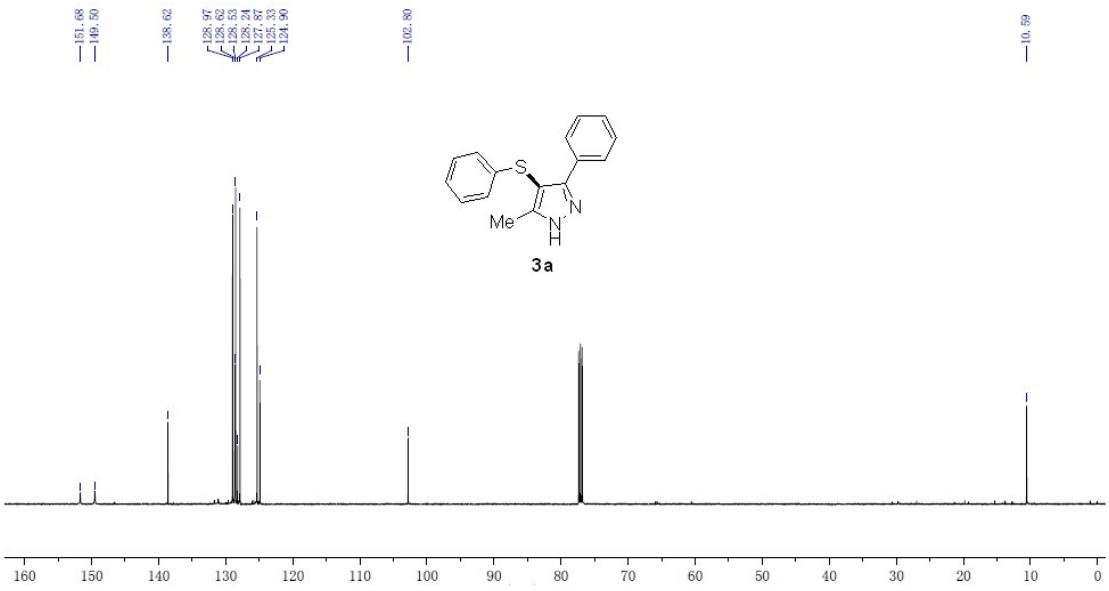
1,2-Diphenyldisulfane (8). Eluent petroleum ether/ethyl acetate (50:1). White solid, 25.6 mg, 98% yield. (petroleum ether/ethyl acetate = 50:1, Rf= 0.8). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.55 (d, 4H, J = 10.0 Hz), 7.34 (dd, 4H, J = 5.0 Hz, J = 10.0 Hz), 7.27 (dd, 2H, J = 5.0 Hz, J = 10.0 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 137.1, 129.1, 127.5, 127.2.

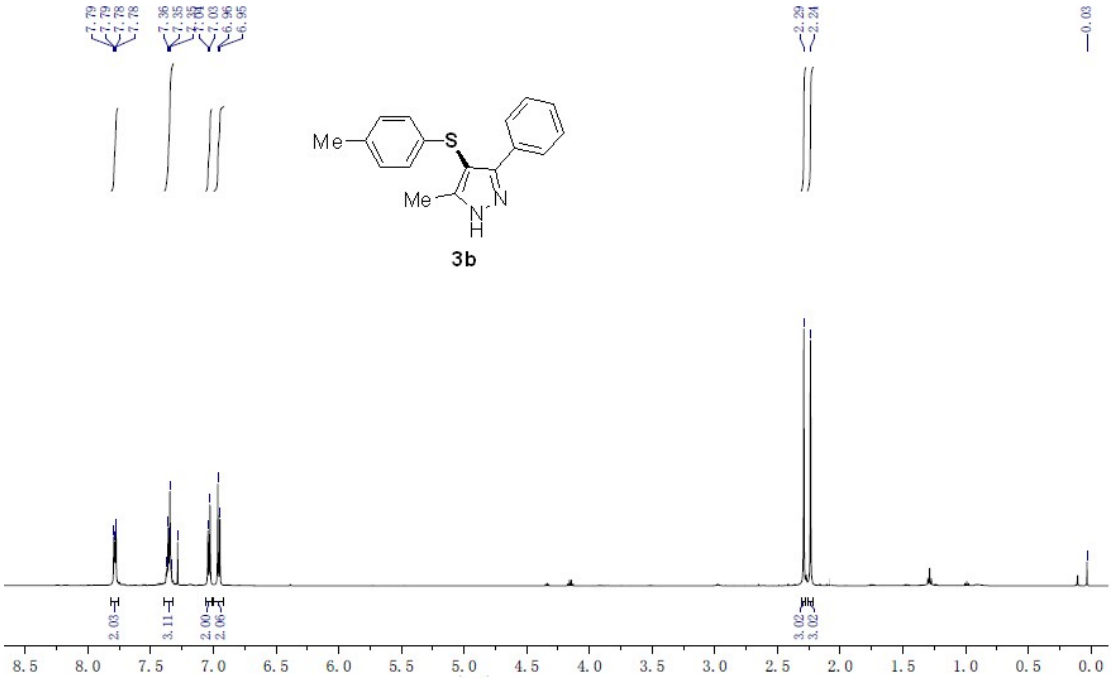
Reference

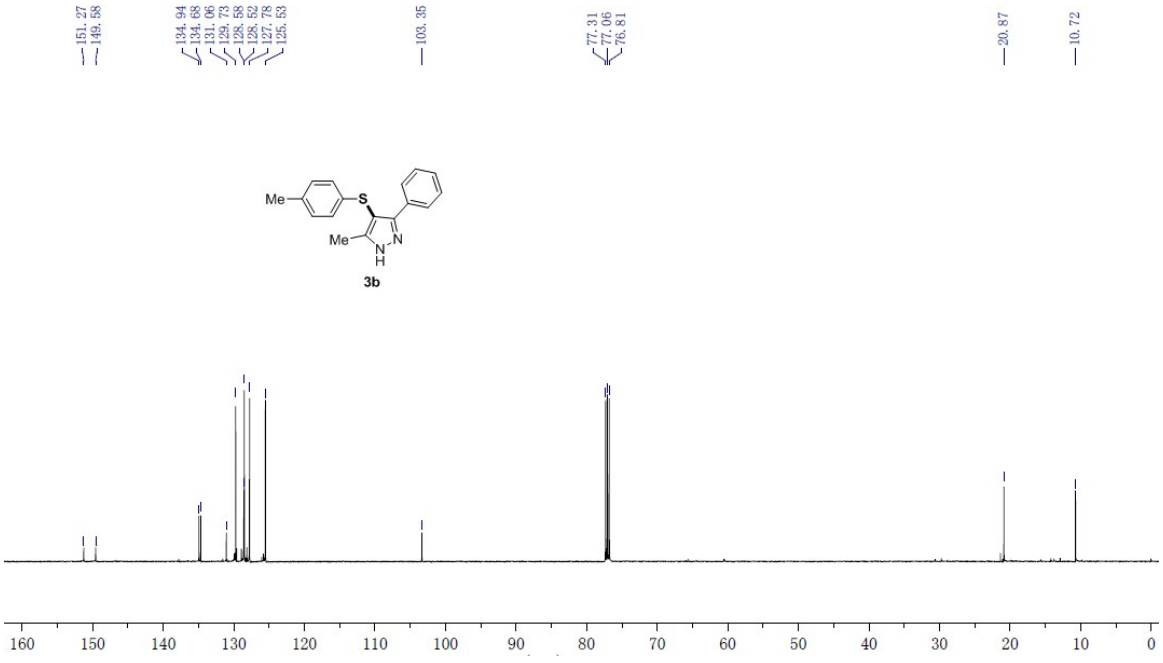
1 (a) J. Wen, Y. Fu, R.-Y. Zhang, J. Zhang, S.-Y. Chen, X.-Q. Yu, *Tetrahedron.,* 2011, **67**, 9618; (b) L. Wang, X. Yu, X. Feng, M. Bao, *J. Org. Chem.,* 2013, **78**, 1693.

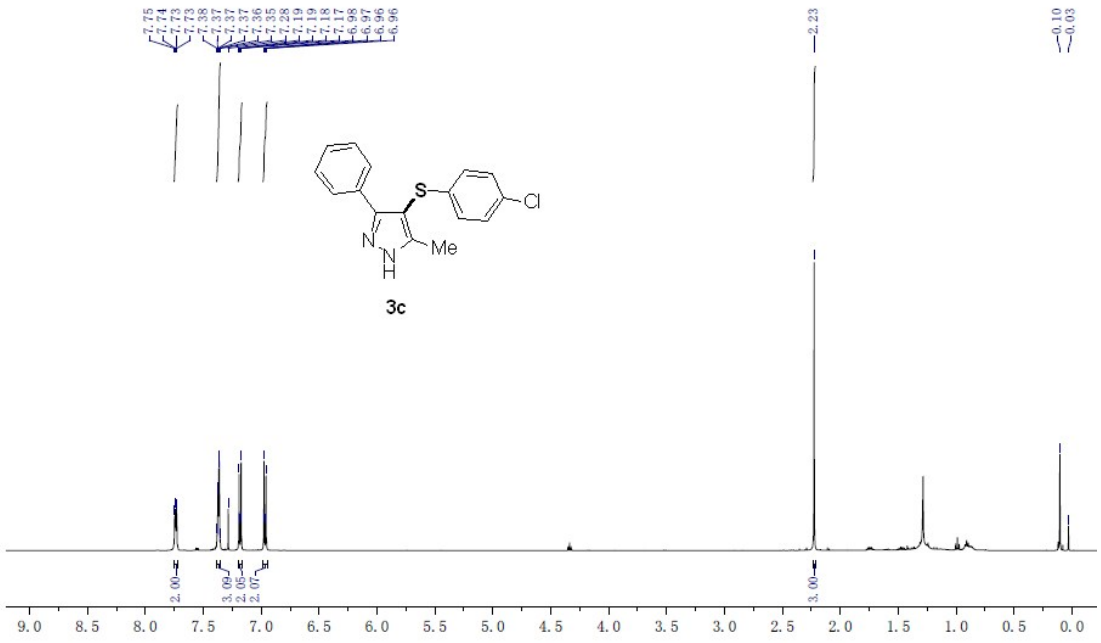
2 D. C. Mohan, S. N. Rao, C. Ravi, S. Adimurthy, *Asian J. Org. Chem.,* 2014, **3**, 609.

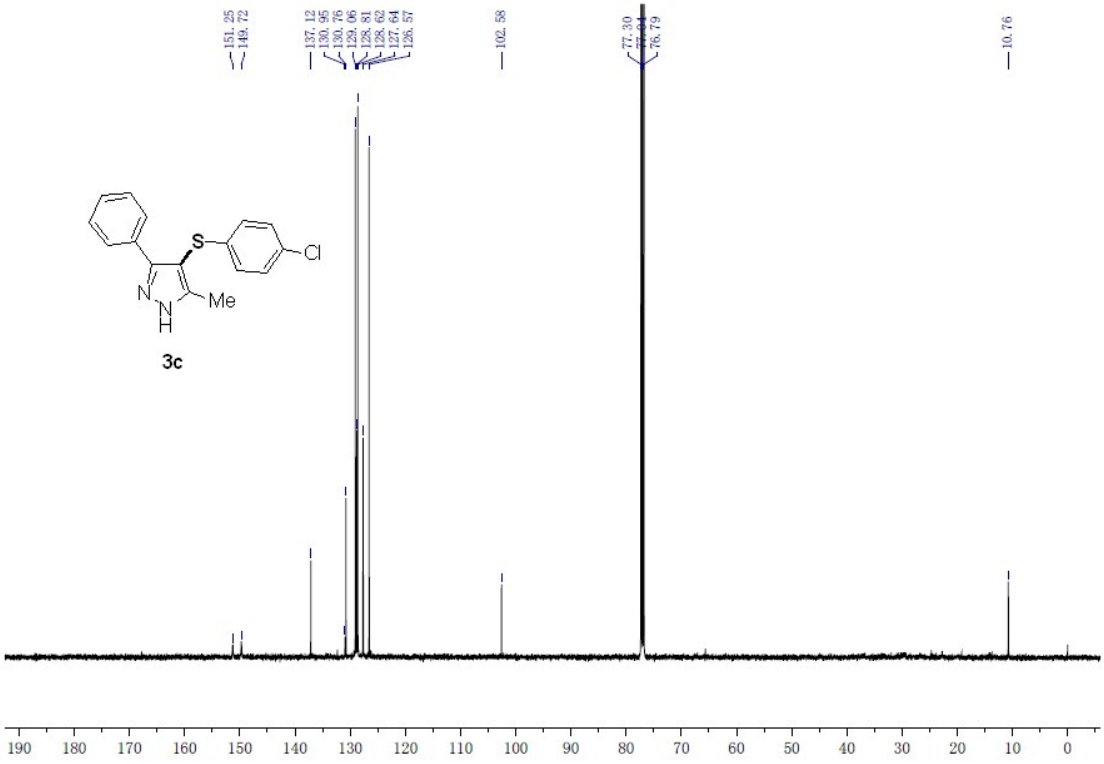

11.46
7.78
7.78
7.77
7.77
7.77
7.77
7.35
7.34
7.25
7.24
7.22
7.12
7.06
7.06
7.06
2.16
S
Me
N
N
H
3a
0.93
2.11
3.04
2.03
1.02
2.00
2.96
12
11
10
9
8
7
6
5
4
3
2
1
0

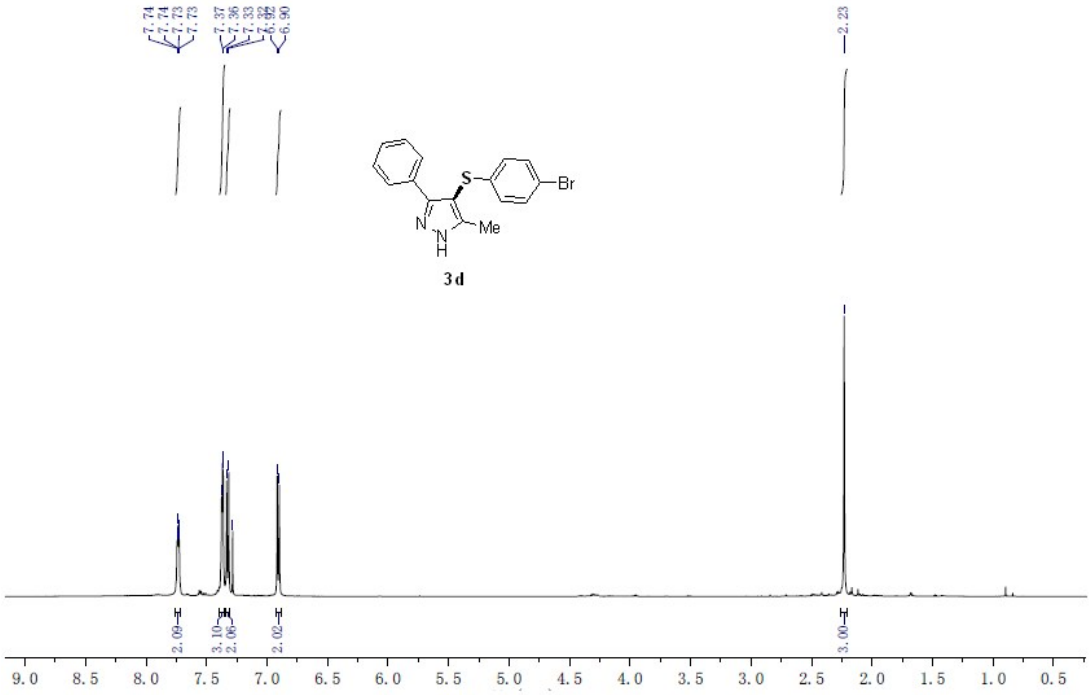

151.68
149.50
138.62
128.97
128.62
128.53
128.24
127.87
125.33
124.90
102.80
10.59
S
Me
N
N
H
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.79
7.79
7.78
7.78
7.36
7.35
7.03
6.96
6.95
2.29
2.24
0.03
Me
S
Me
N
N
H
3b
2.03
3.11
2.00
2.06
3.02
3.02
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

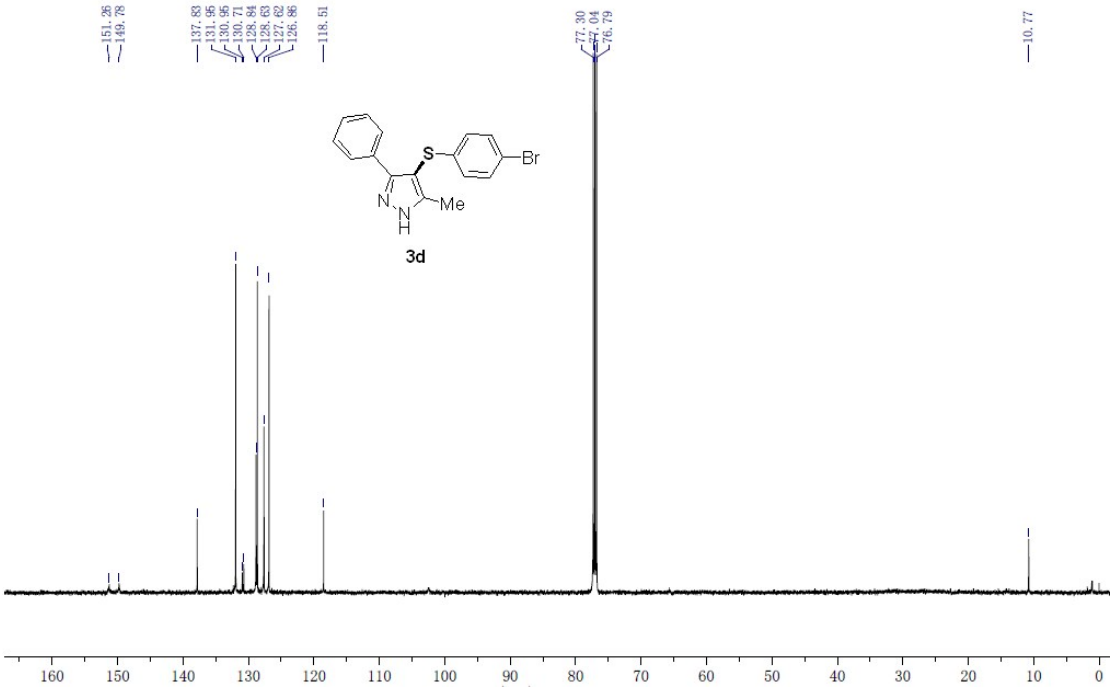

151.27
149.58
134.94
134.68
131.06
129.73
128.58
128.52
127.78
125.53
103.35
77.31
77.06
76.81
20.87
10.72
Me
S
Me
N
N
H
3b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.75
7.74
7.73
7.73
7.38
7.37
7.37
7.37
7.36
7.35
7.28
7.19
7.19
7.18
7.17
6.98
6.97
6.96
6.96
2.23
0.10
0.03
S
Cl
N
N
H
Me
3c
2.00
3.09
2.05
2.07
3.00
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

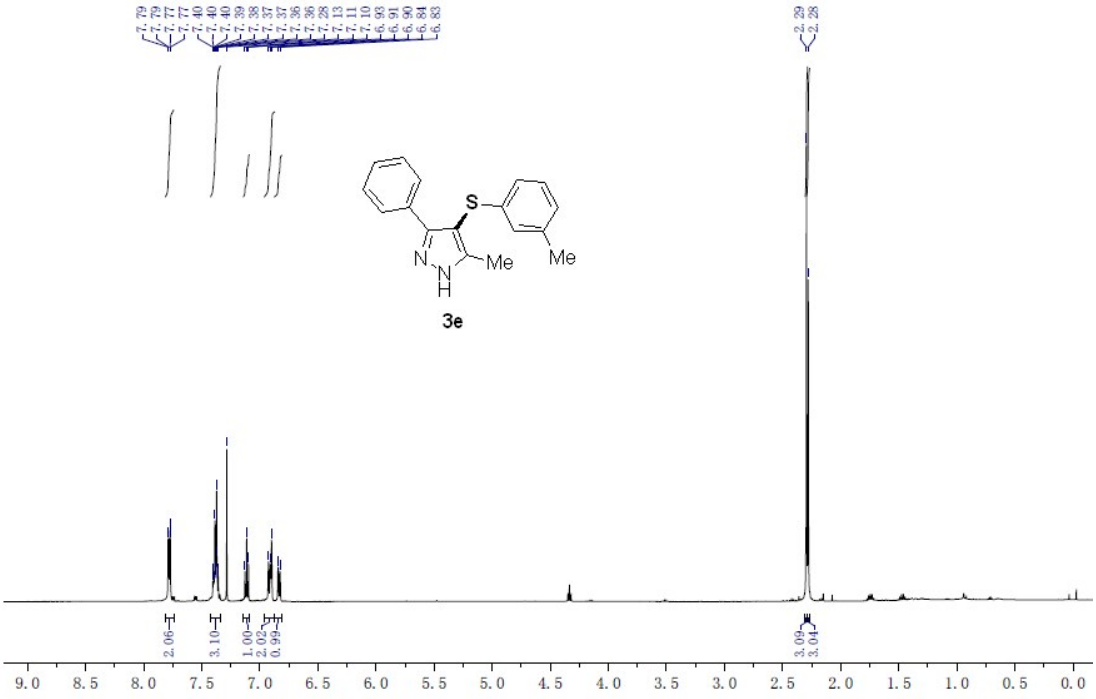

151.25
149.72
137.12
130.95
130.76
129.06
128.81
128.62
127.64
126.57
102.58
77.30
77.04
76.79
10.76
S
Cl
N
N
H
Me
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

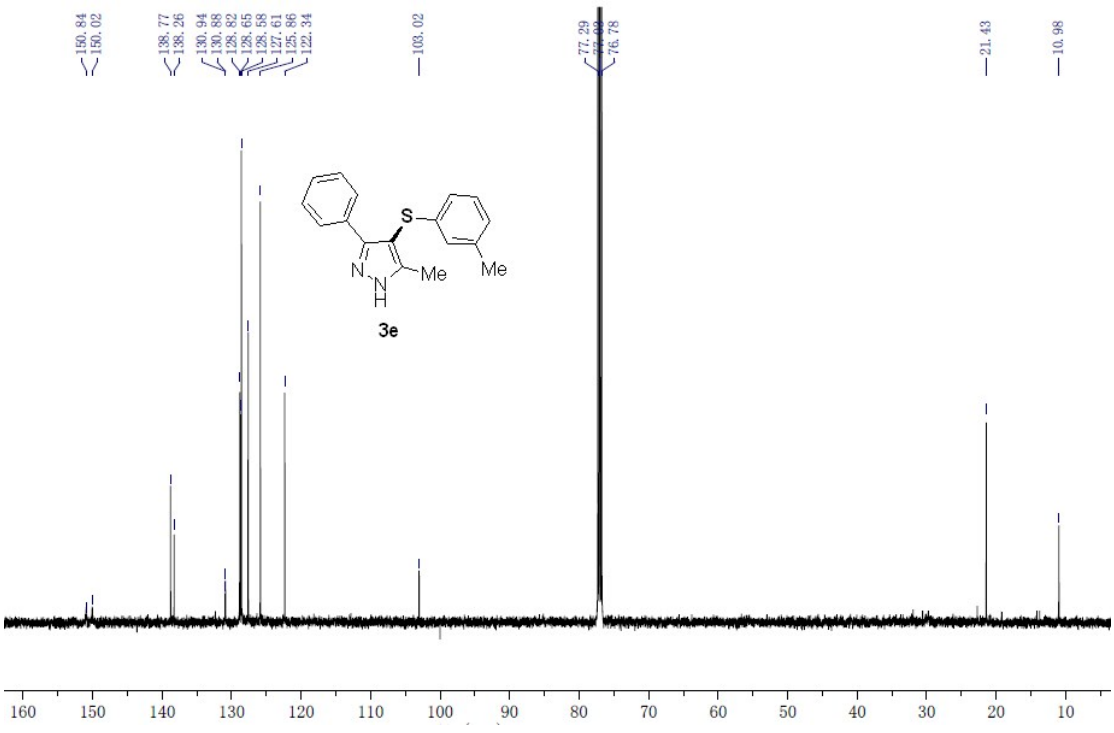

7.74
7.74
7.73
7.73
7.37
7.36
7.33
7.32
6.92
6.90
2.23
S
Br
N
N
H
Me
2.09
3.10
2.06
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

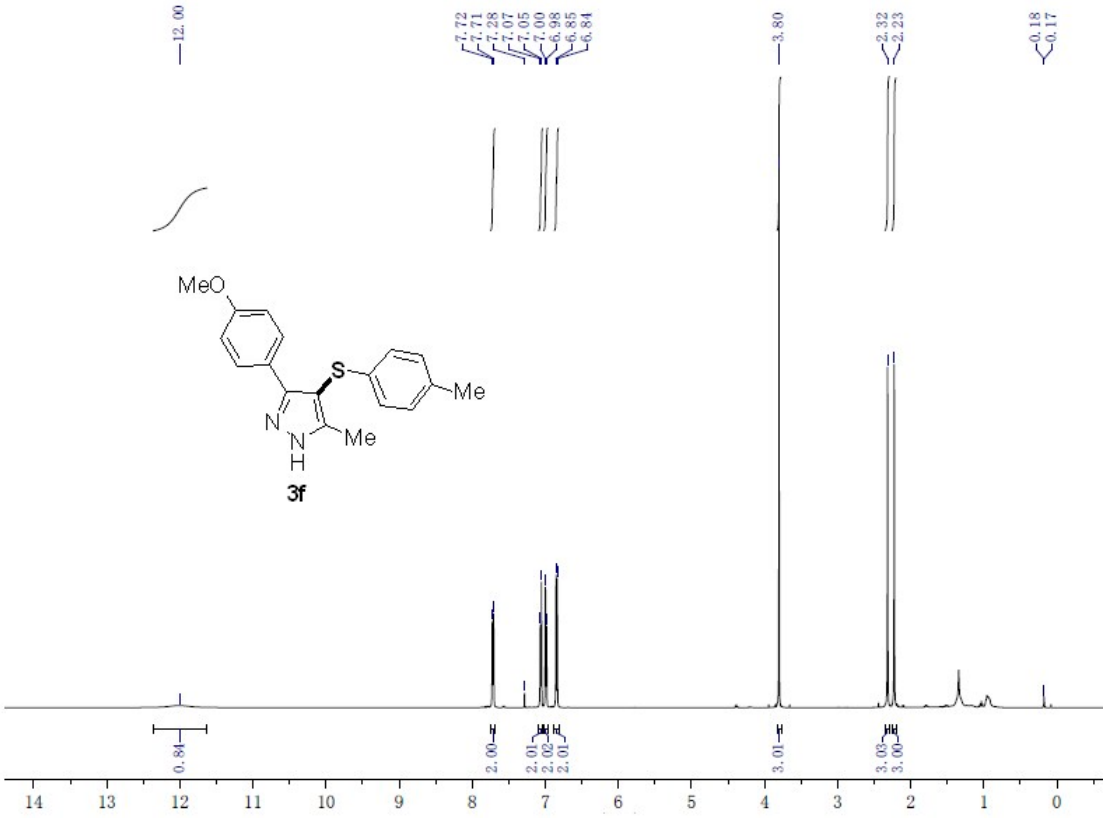
3d

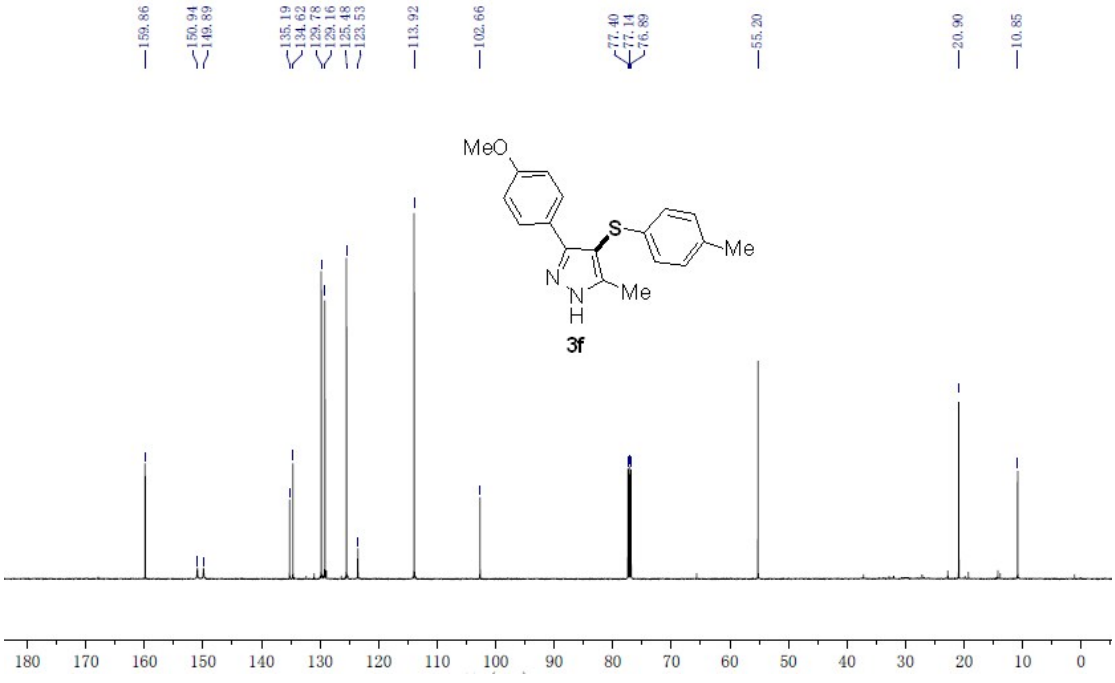

151.26
149.78
137.83
131.95
130.95
130.71
128.84
128.63
127.62
126.86
118.51
77.30
77.04
76.79
10.77
S
Br
N
N
H
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

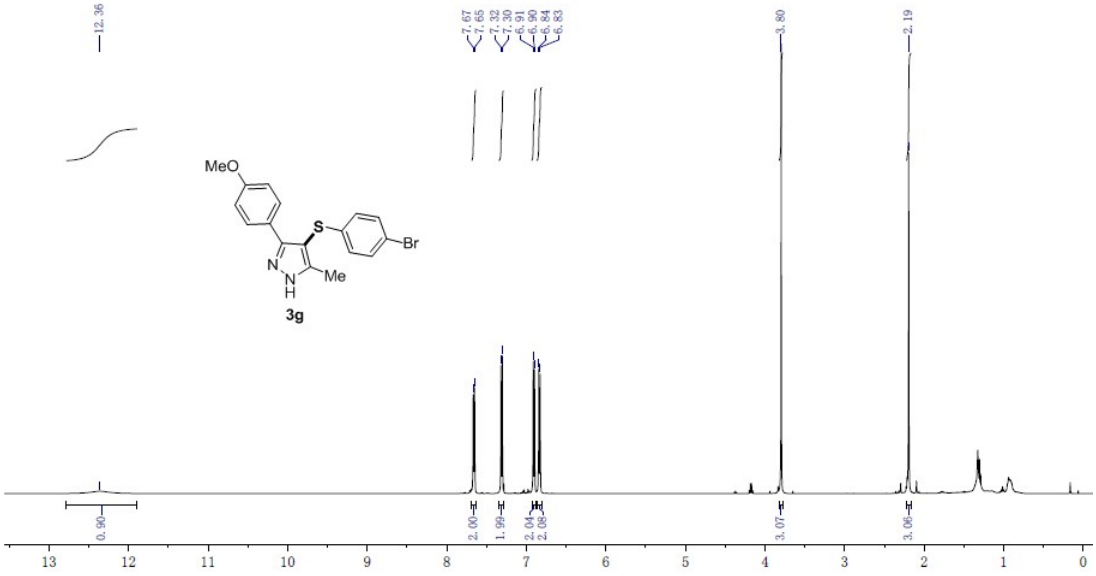
3d

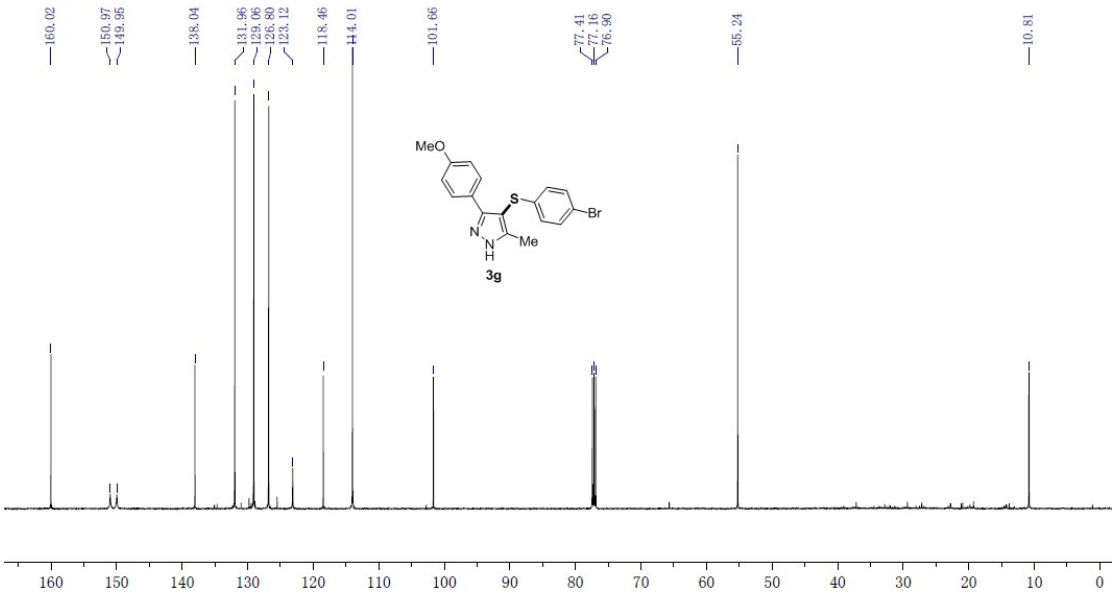

7.79
7.79
7.77
7.77
7.40
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.28
7.13
7.11
7.10
6.93
6.91
6.90
6.84
6.83
2.29
2.28
S
N
N
H
Me
Me
3e
2.06
3.10
1.00
2.02
0.99
3.09
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

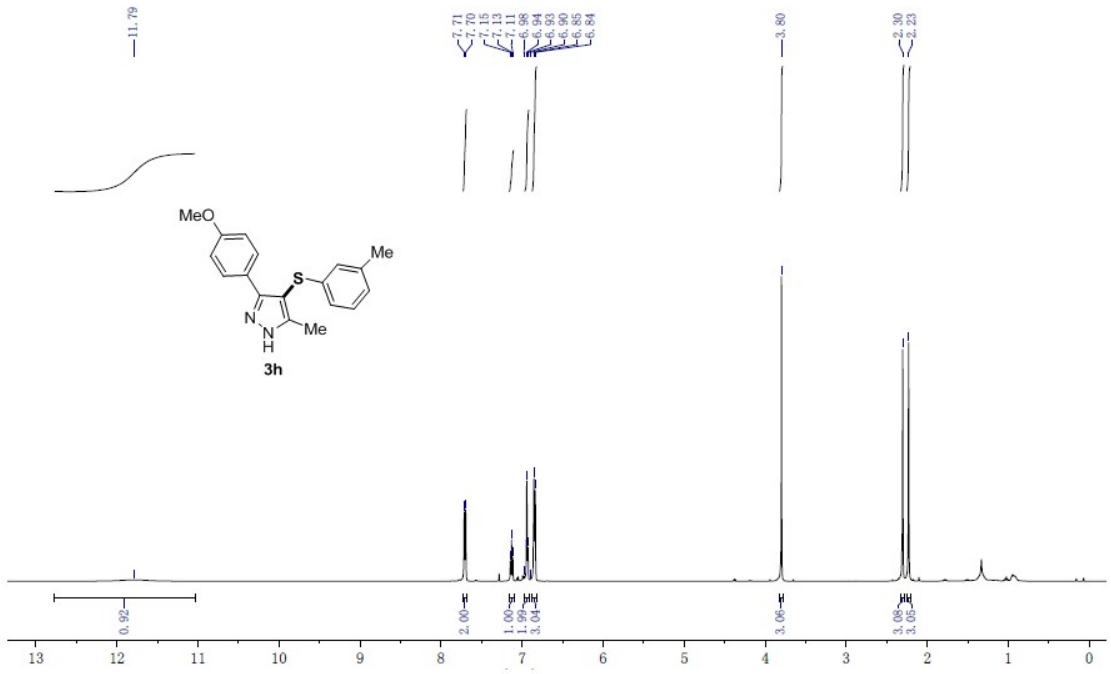

150.84
150.02
138.77
138.26
130.94
130.88
128.82
128.65
128.58
127.61
125.86
122.34
103.02
77.29
77.09
76.78
21.43
10.98
S
N
N
H
Me
Me
3e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

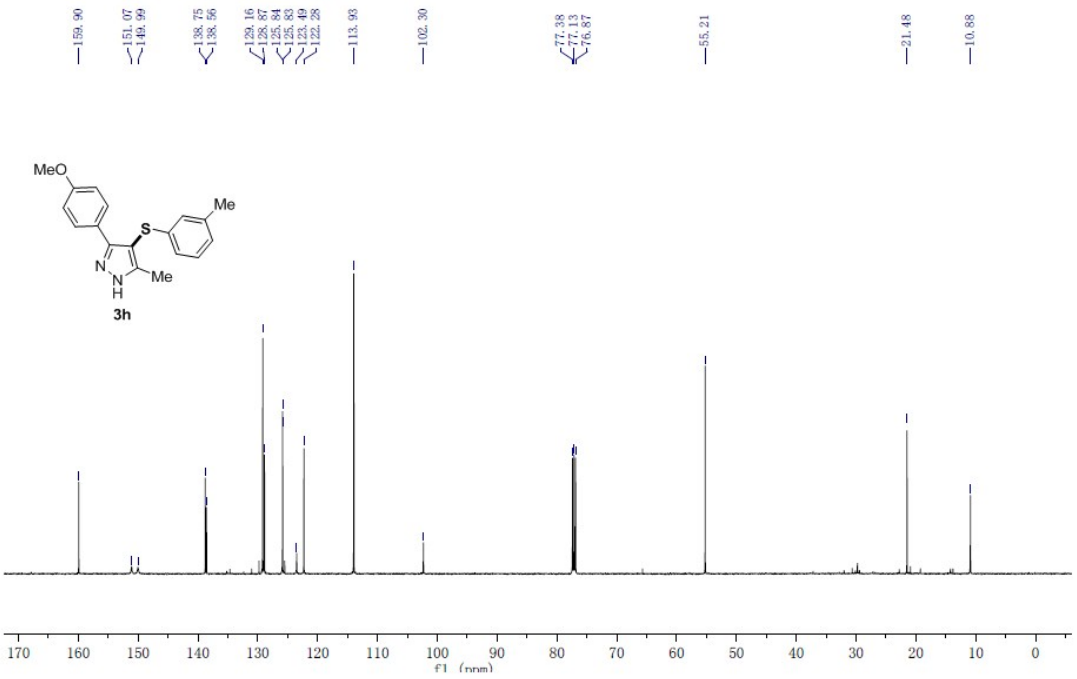

12.00
7.72
7.71
7.28
7.07
7.05
7.00
6.98
6.85
6.84
3.80
2.32
2.23
0.18
0.17
MeO
S
Me
N
N
H
Me
3f
0.84
2.00
2.01
2.02
2.01
3.01
3.03
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

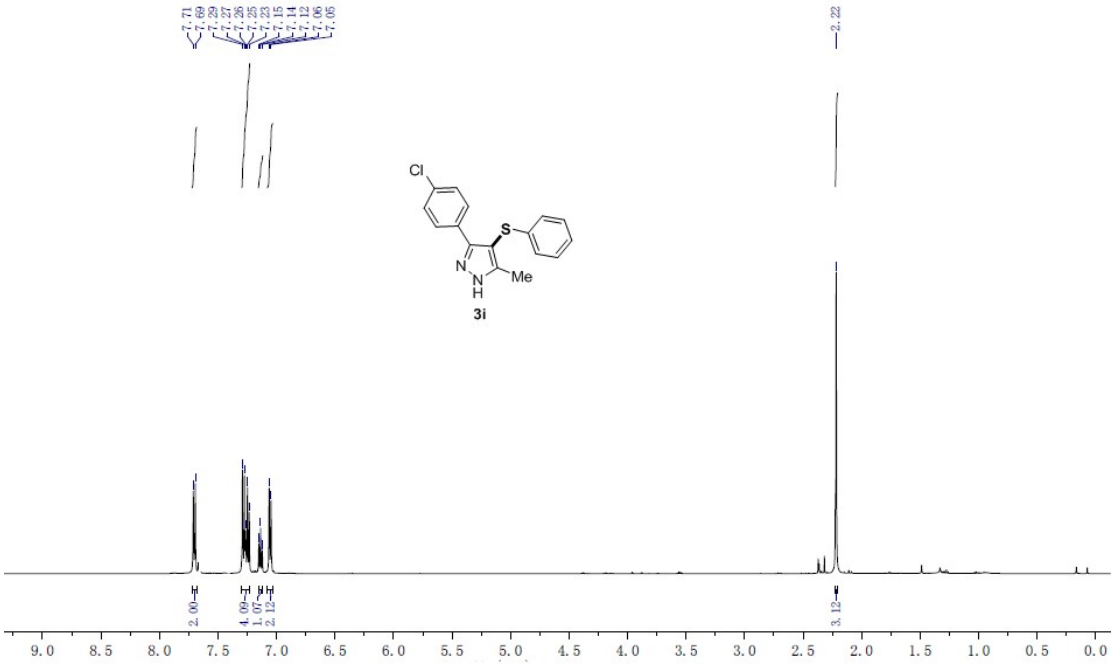

159.86
150.94
149.89
135.19
134.62
129.78
129.16
125.48
123.53
113.92
102.66
77.40
77.14
76.89
55.20
20.90
10.85
MeO
S
Me
N
N
H
Me
3f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

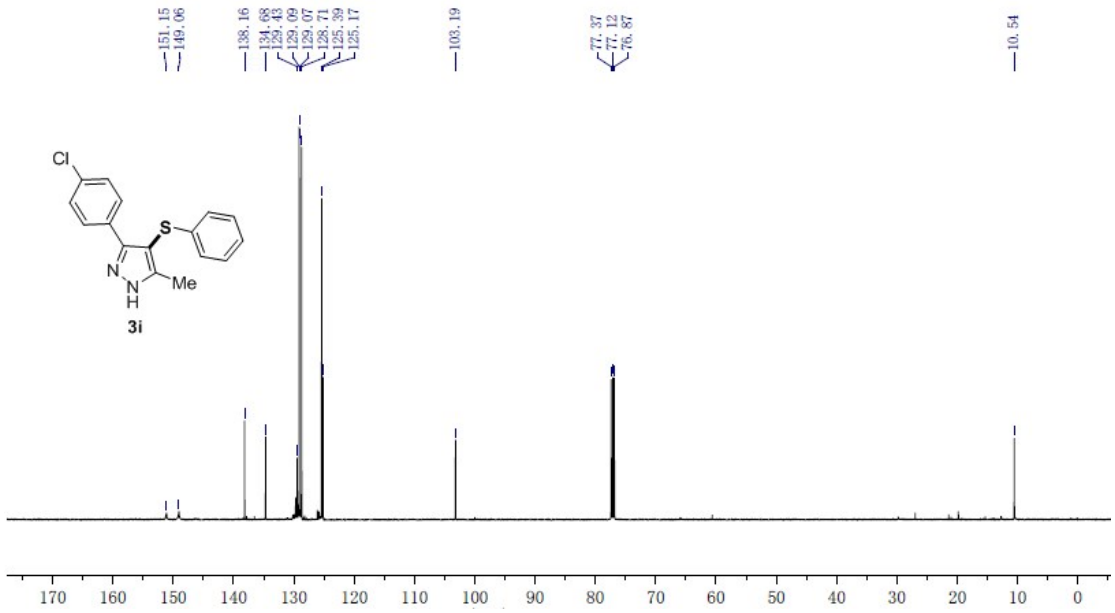

12.36
7.67
7.65
7.32
7.30
6.91
6.90
6.84
6.83
3.80
2.19
MeO
S
Br
N
N
H
Me
3g
0.90
2.00
1.99
2.04
2.08
3.07
3.06
13
12
11
10
9
8
7
6
5
4
3
2
1
0

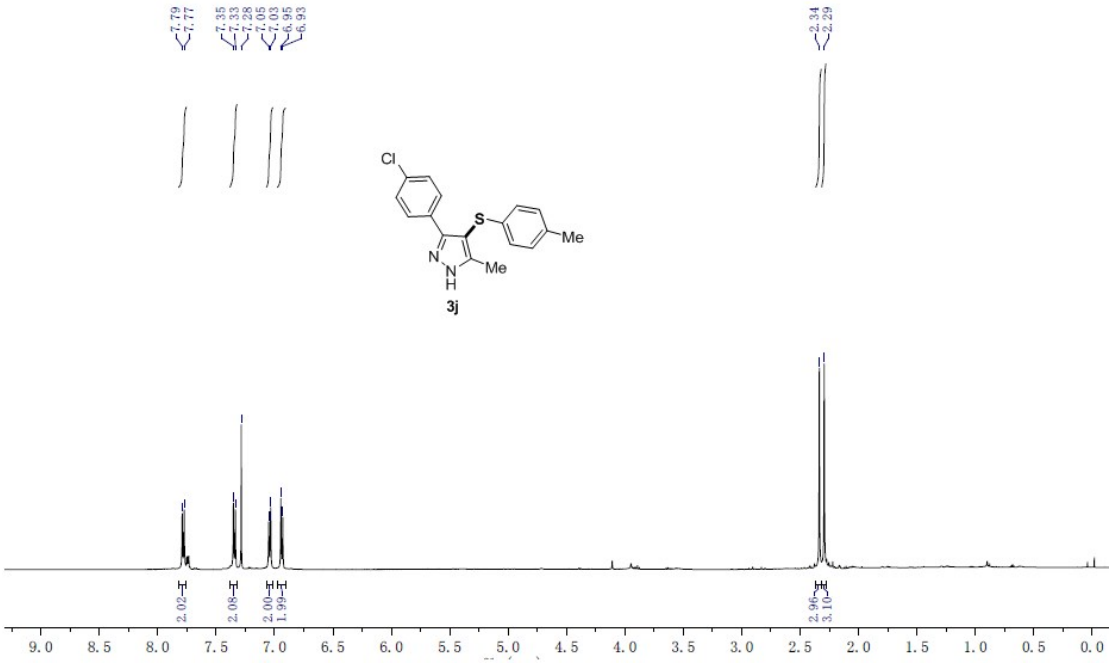

160.02
150.97
149.95
138.04
131.96
129.06
126.80
123.12
118.46
114.01
101.66
77.41
77.16
76.90
55.24
10.81
MeO
S
Br
N
N
H
Me
3g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

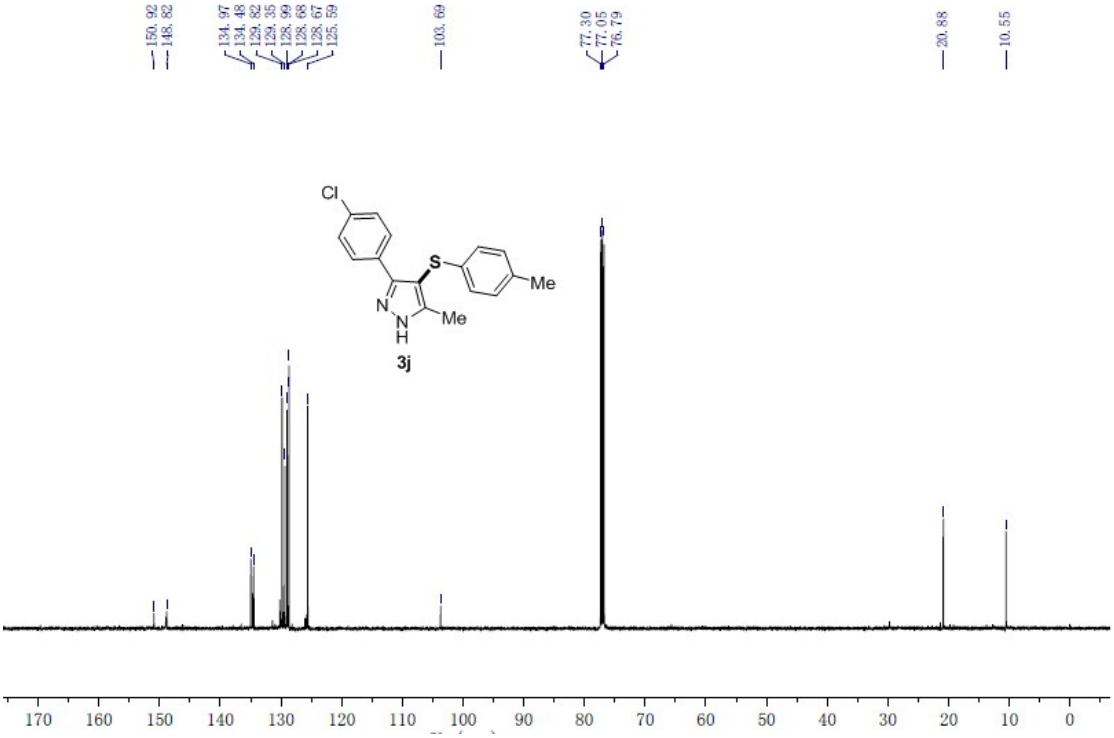

11.79
7.71
7.70
7.15
7.13
7.11
6.98
6.94
6.93
6.90
6.85
6.84
3.80
2.30
2.23
MeO
Me
S
N
N
H
Me
3h
0.92
2.00
1.00
1.99
3.04
3.06
3.08
3.09
13
12
11
10
9
8
7
6
5
4
3
2
1
0

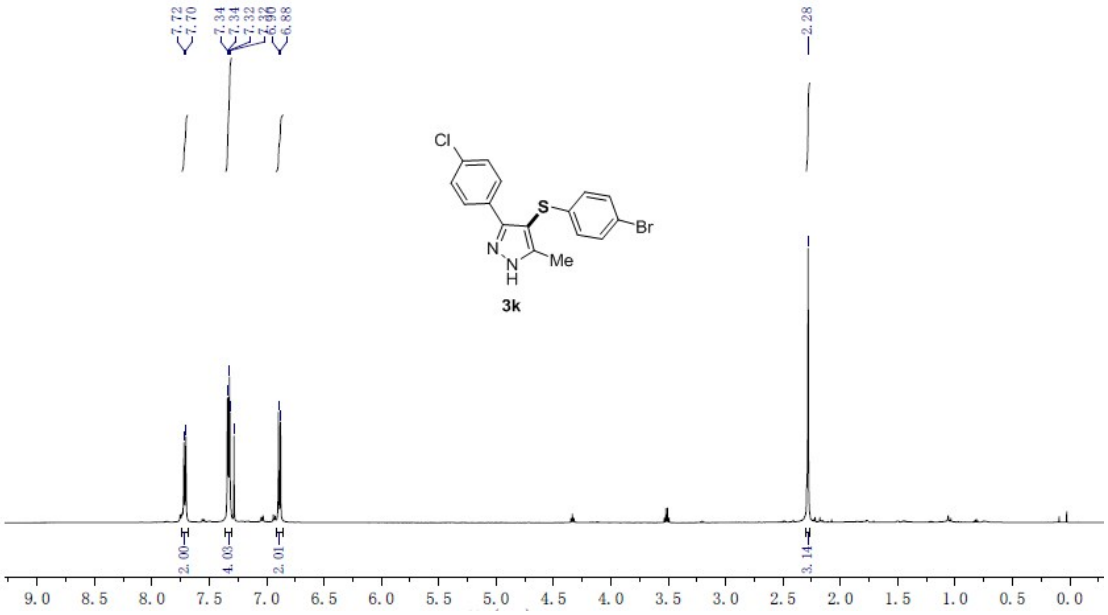

159.90
151.07
149.99
138.75
138.56
129.16
128.87
125.84
125.83
123.49
122.28
113.93
102.30
77.38
77.13
76.87
55.21
21.48
10.88
MeO
Me
S
N
N
H
Me
3h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

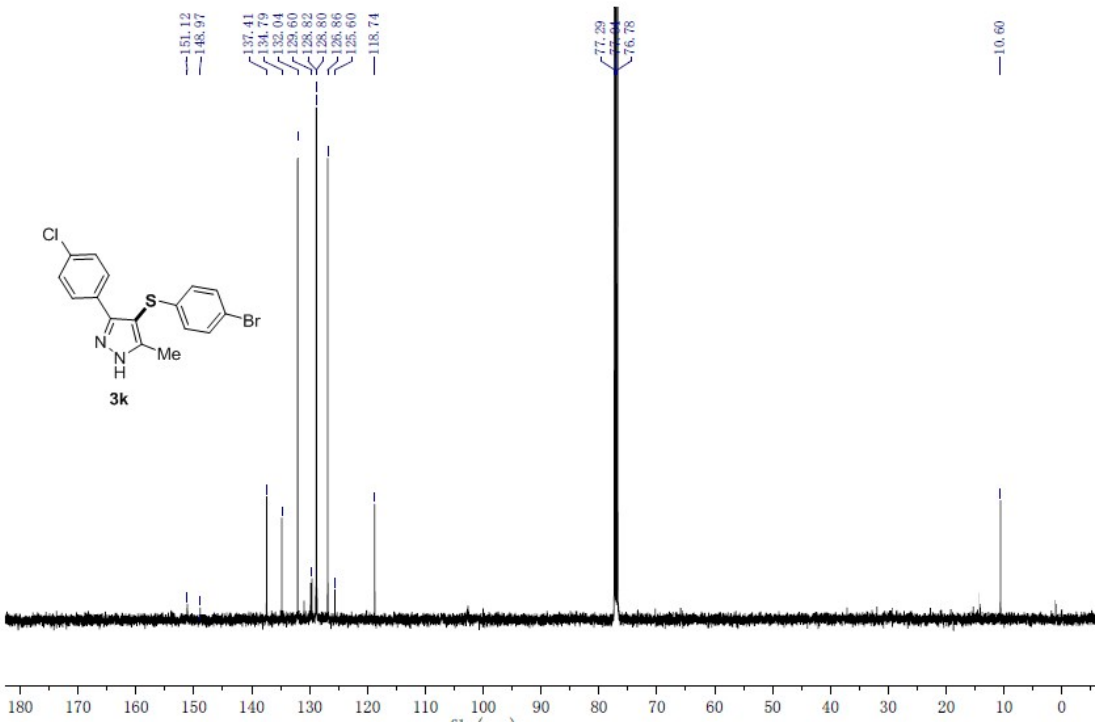

7.71
7.69
7.29
7.27
7.26
7.25
7.23
7.15
7.14
7.12
7.06
7.05
2.22
Cl
S
N
N
H
Me
3i
2.00
4.09
1.07
2.12
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

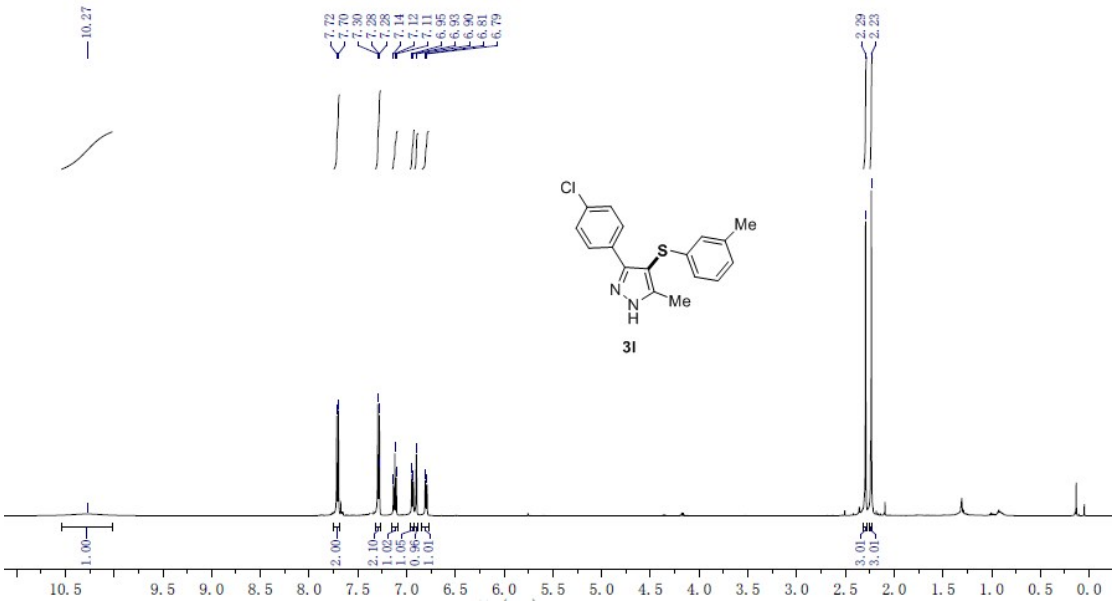

151.15
149.06
138.16
134.68
129.43
129.09
129.07
128.71
125.39
125.17
103.19
77.37
77.12
76.87
10.54
Cl
S
N
N
H
Me
3i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

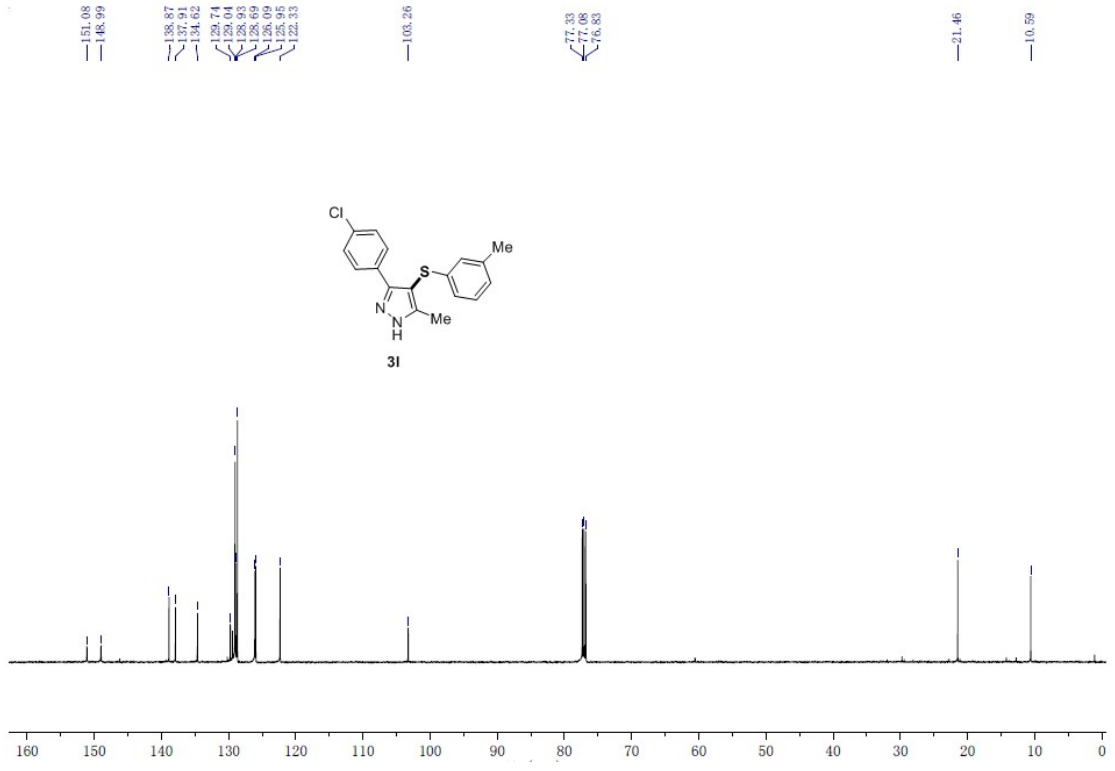

7.79
7.77
7.35
7.33
7.28
7.05
7.03
6.95
6.93
2.34
2.29
Cl
S
Me
N
N
H
Me
3j
2.02
2.08
2.00
1.99
2.96
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

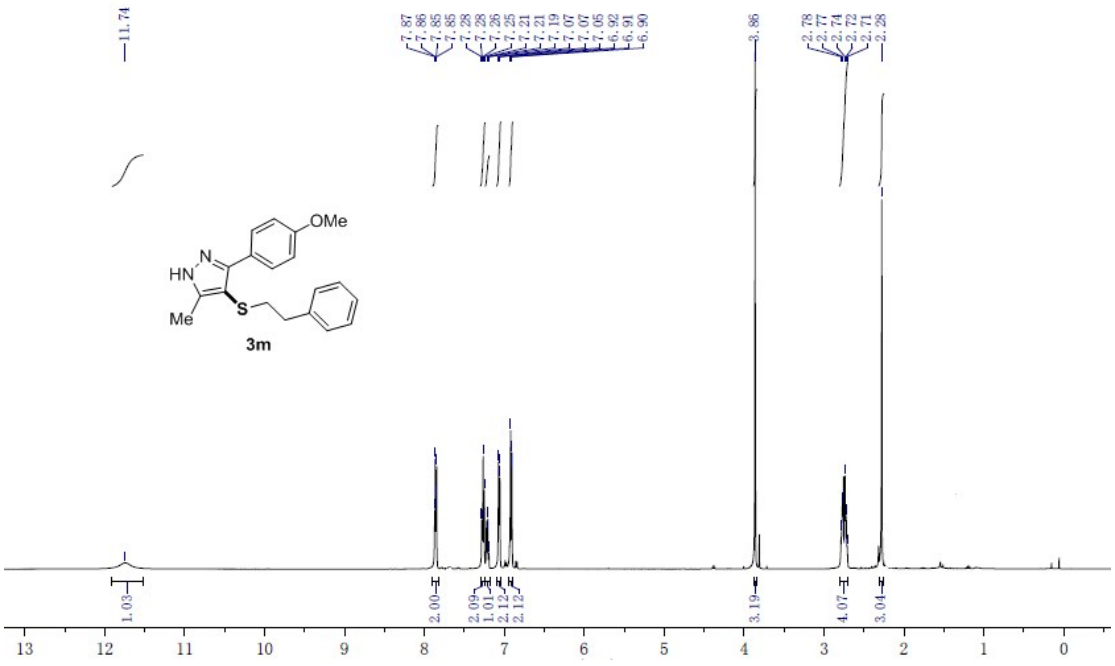

150.92
148.82
134.97
134.48
129.82
129.35
128.99
128.68
128.67
125.59
103.69
77.30
77.05
76.79
20.88
10.55
Cl
S
Me
N
N
H
Me
3j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

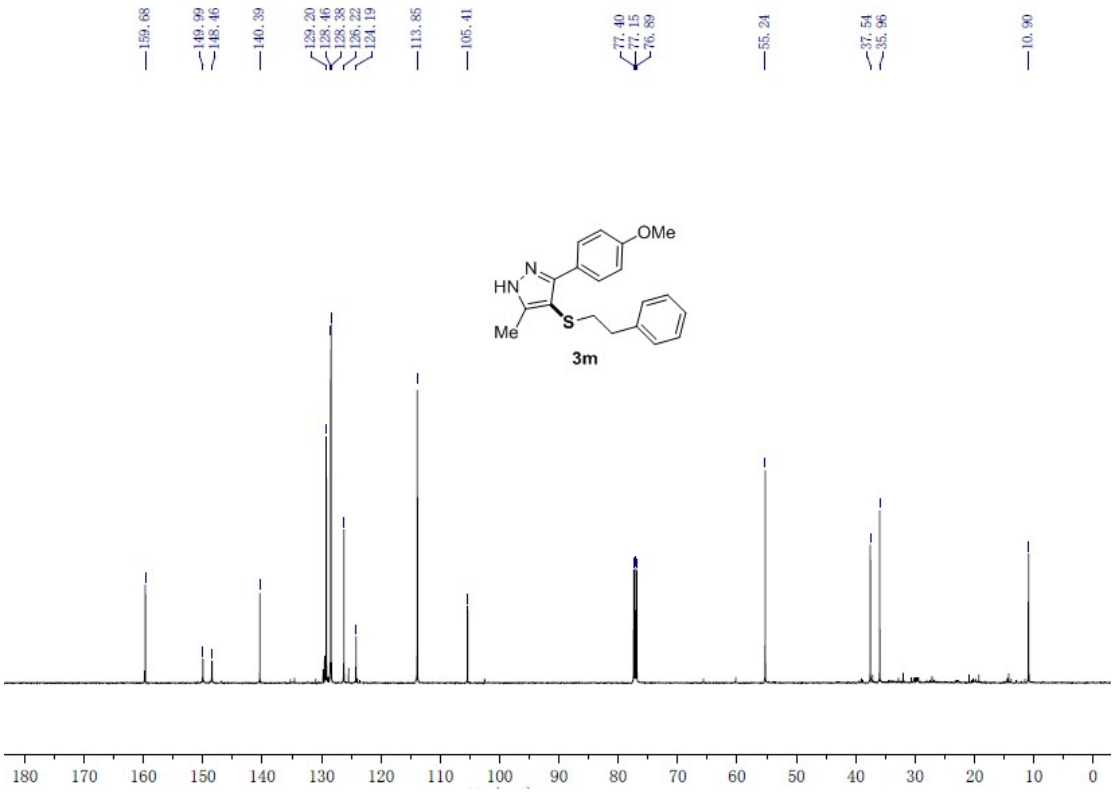

7.72
7.70
7.34
7.34
7.32
6.90
6.88
2.28
Cl
S
Br
N
N
H
Me
3k
2.00
4.03
2.01
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

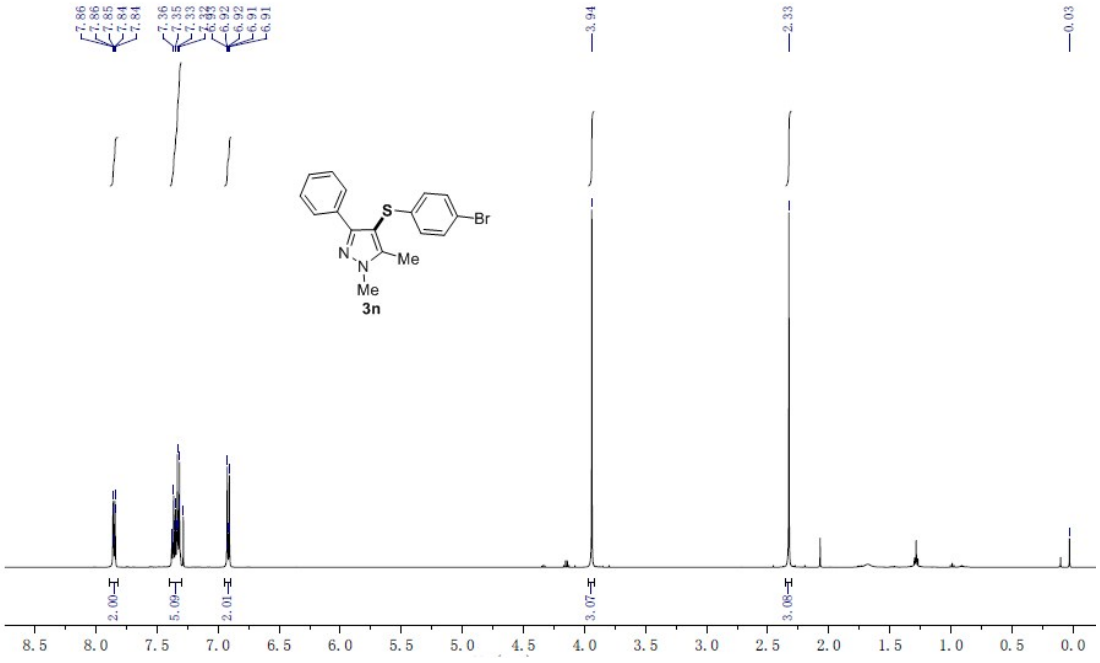

151.12
148.97
137.41
134.79
132.04
129.60
128.82
128.80
126.86
125.60
118.74
77.29
76.78
10.60
Cl
S
Br
N
N
H
Me
3k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

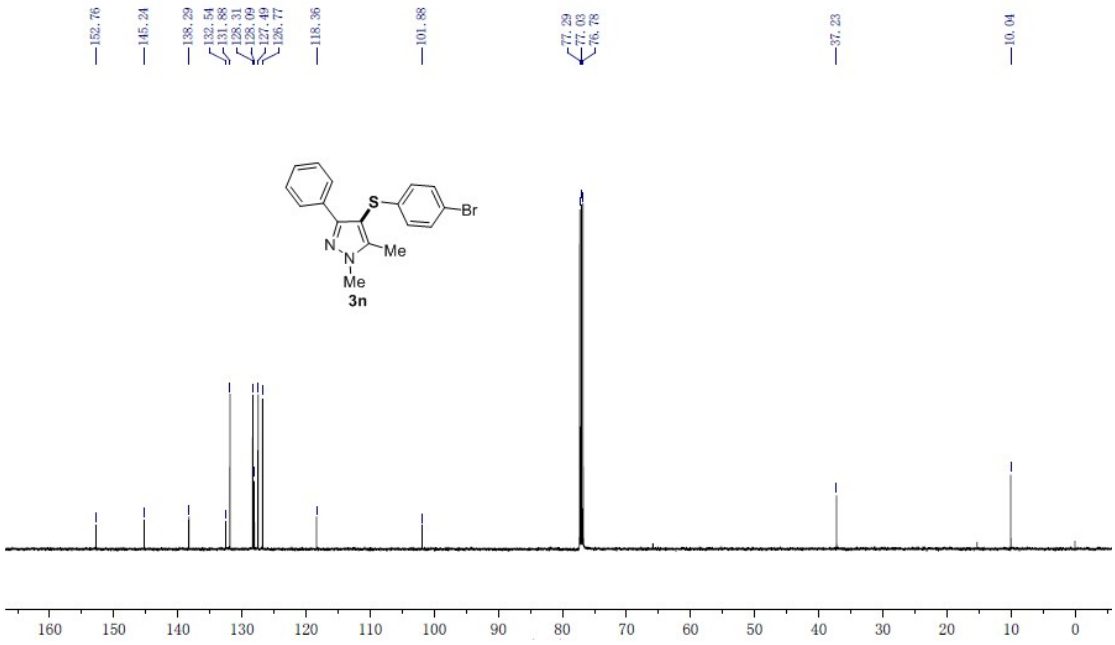

10.27
7.72
7.70
7.30
7.28
7.28
7.14
7.12
7.11
6.95
6.93
6.90
6.81
6.79
2.29
2.23
Cl
Me
S
N
N
H
Me
3l
1.00
2.00
2.10
1.02
1.05
0.96
1.01
3.01
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

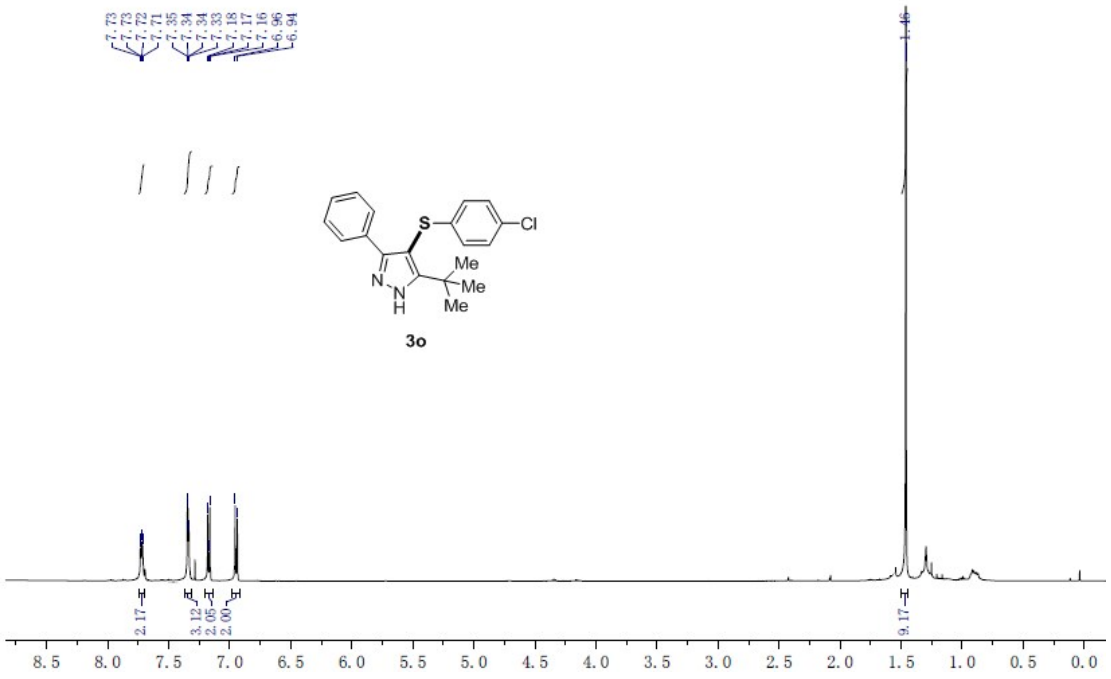

151.08
148.99
138.87
137.91
134.62
129.74
129.04
128.93
128.69
126.09
125.95
122.33
103.26
77.33
77.08
76.83
21.46
10.59
Cl
Me
S
N
N
H
Me
3l
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

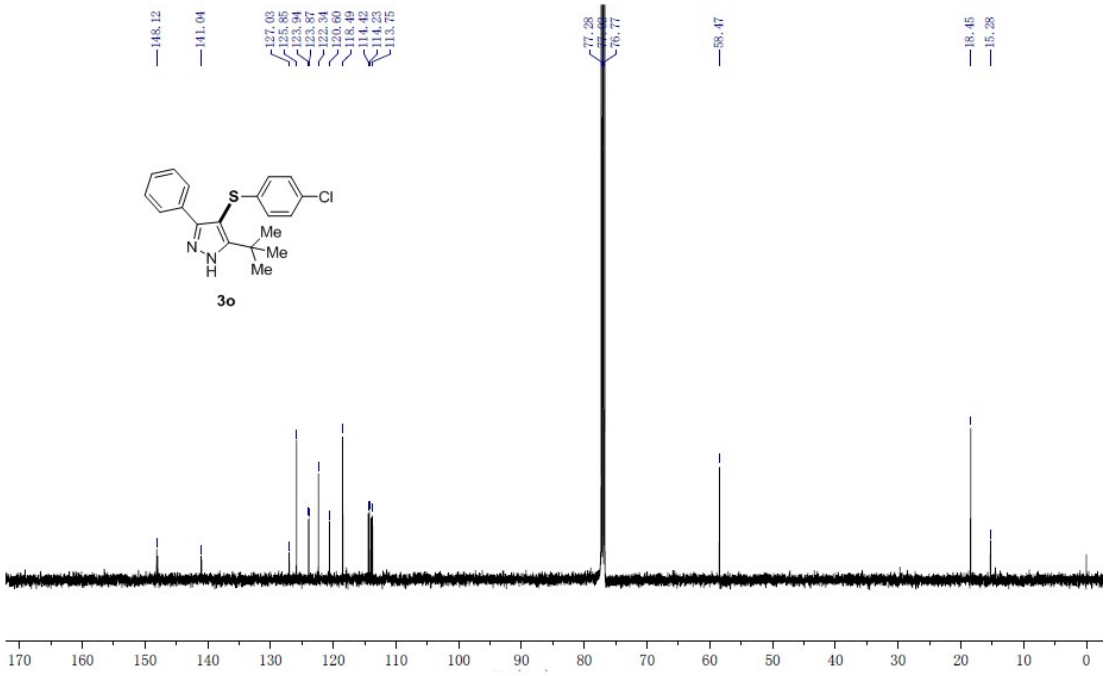

11.74
7.87
7.86
7.85
7.85
7.28
7.26
7.25
7.21
7.21
7.19
7.07
7.07
7.05
6.92
6.91
6.90
3.86
2.78
2.77
2.74
2.72
2.71
2.28
OMe
HN
N
Me
S
3m
1.03
2.00
2.09
1.01
2.12
2.12
3.19
4.07
3.04
13
12
11
10
9
8
7
6
5
4
3
2
1
0

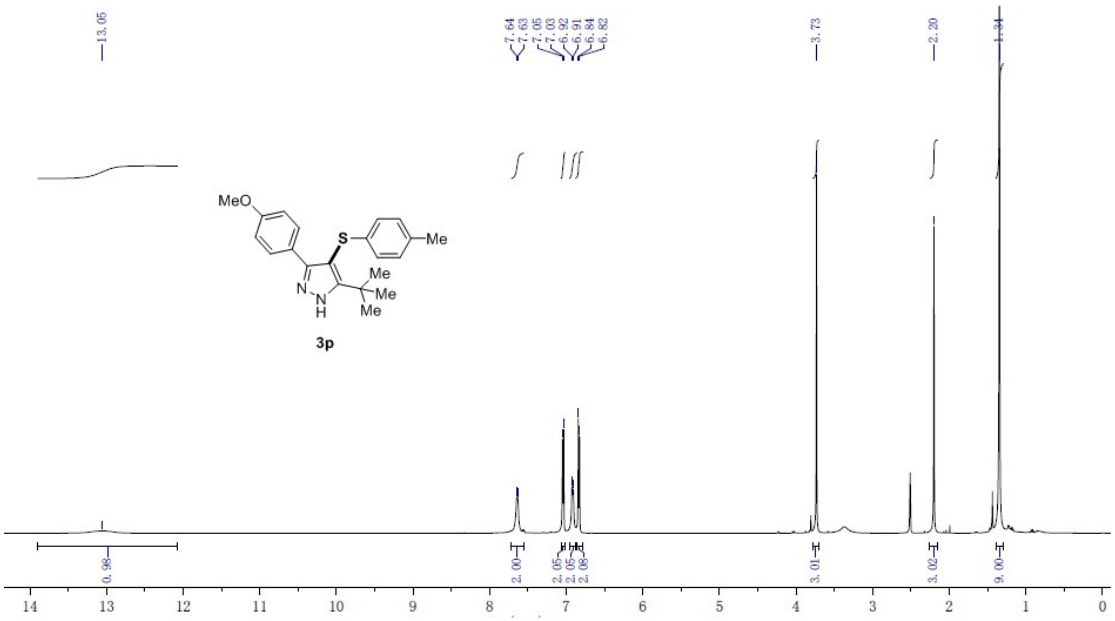

159.68
149.99
148.46
140.39
129.20
128.46
128.38
126.22
124.19
113.85
105.41
77.40
77.15
76.89
55.24
37.54
35.96
10.90
OMe
HN
N
Me
S
3m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

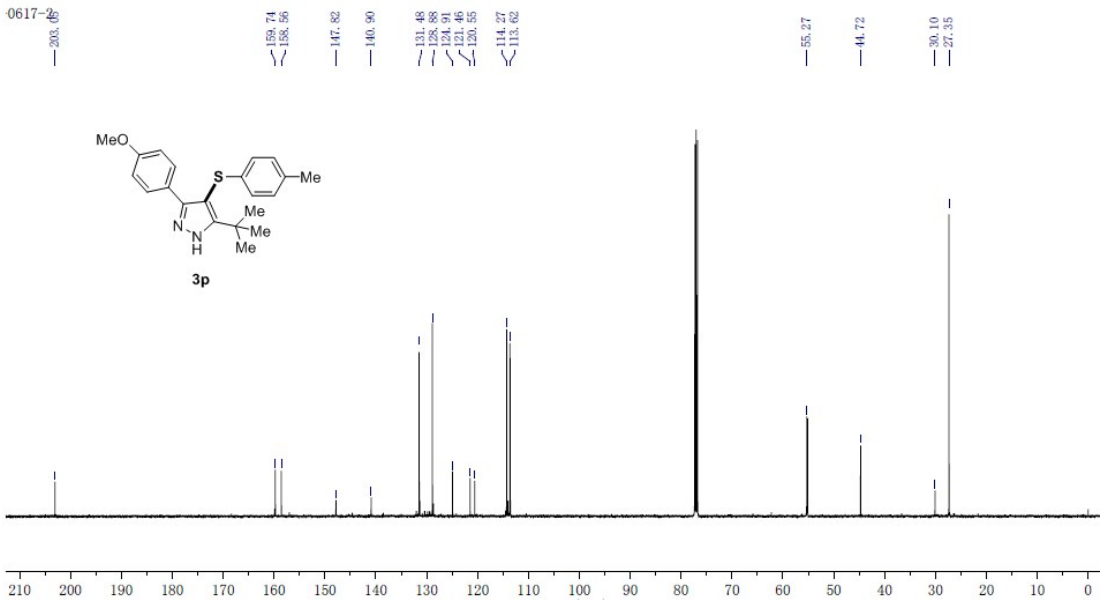

7.86
7.86
7.85
7.84
7.84
7.36
7.35
7.33
6.92
6.92
6.91
6.91
3.94
2.33
0.03
S
Br
N
N
Me
Me
3n
2.00
5.09
2.01
3.07
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

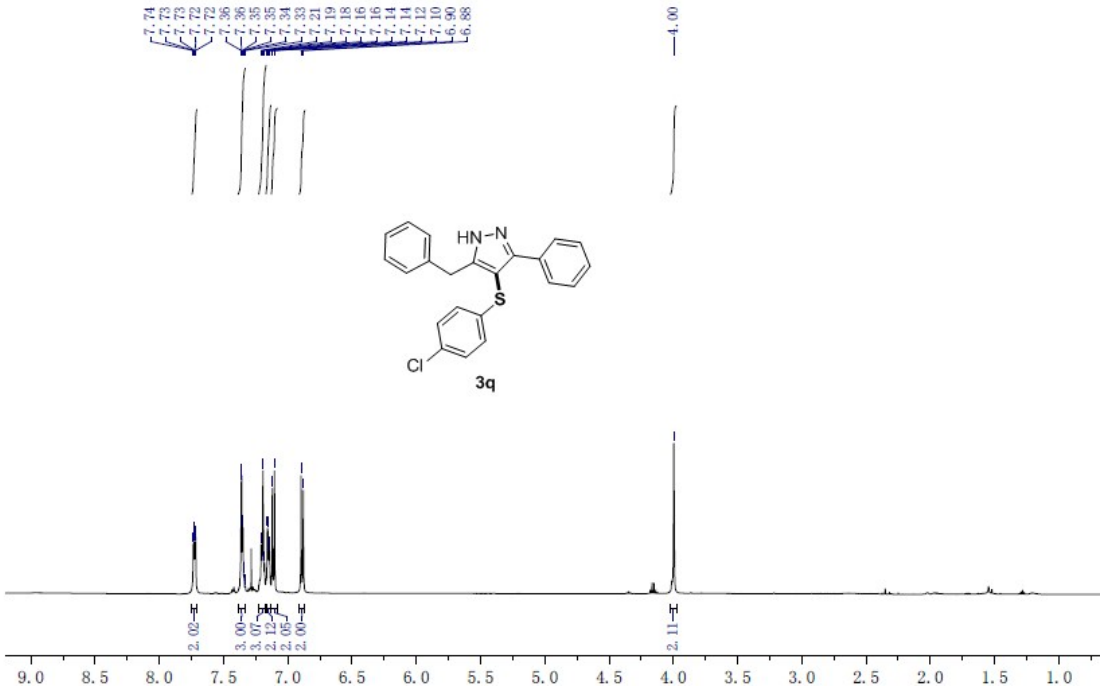

152.76
145.24
138.29
132.54
131.88
128.31
128.09
127.49
126.77
118.36
101.88
77.29
77.03
76.78
37.23
10.04
S
Br
N
N
Me
Me
3n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

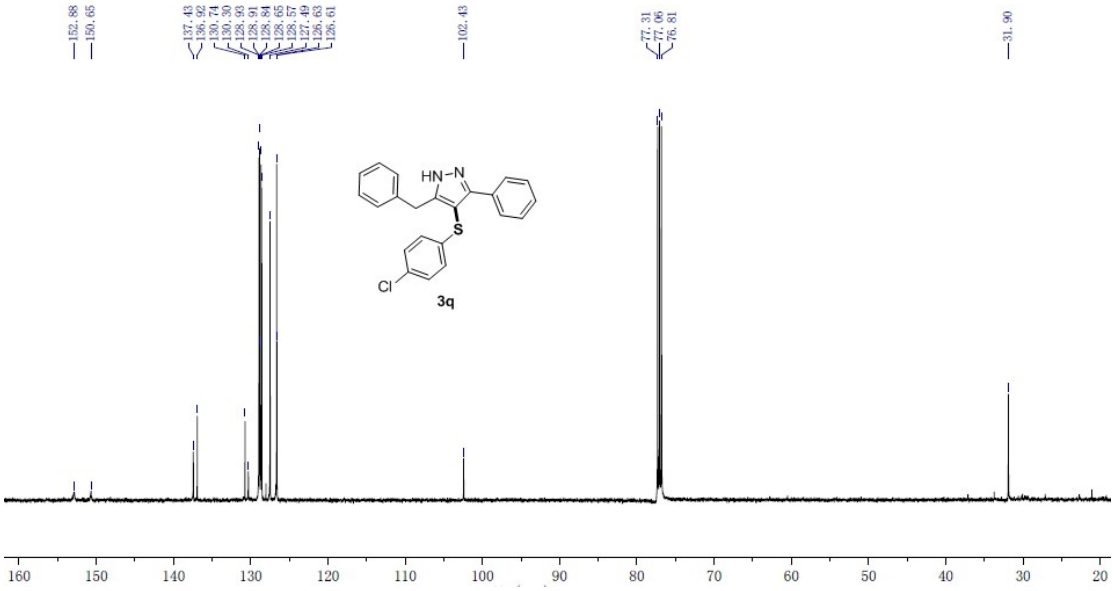

7.73
7.73
7.72
7.71
7.35
7.34
7.34
7.33
7.18
7.17
7.16
6.96
6.94
1.46
S
Cl
Me
Me
Me
N
N
H
3o
2.17
3.12
2.05
2.00
9.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

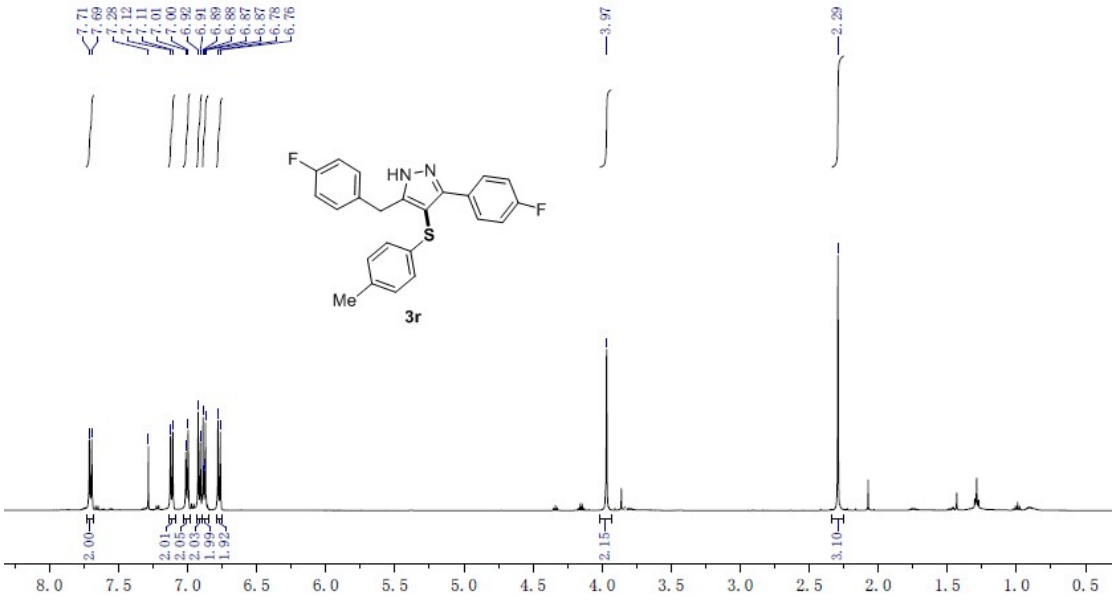

148.12
141.04
127.03
125.85
123.94
123.87
122.34
120.60
118.49
114.42
114.23
113.75
77.28
77.02
76.77
58.47
18.45
15.28
S
Cl
Me
Me
Me
N
N
H
3o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

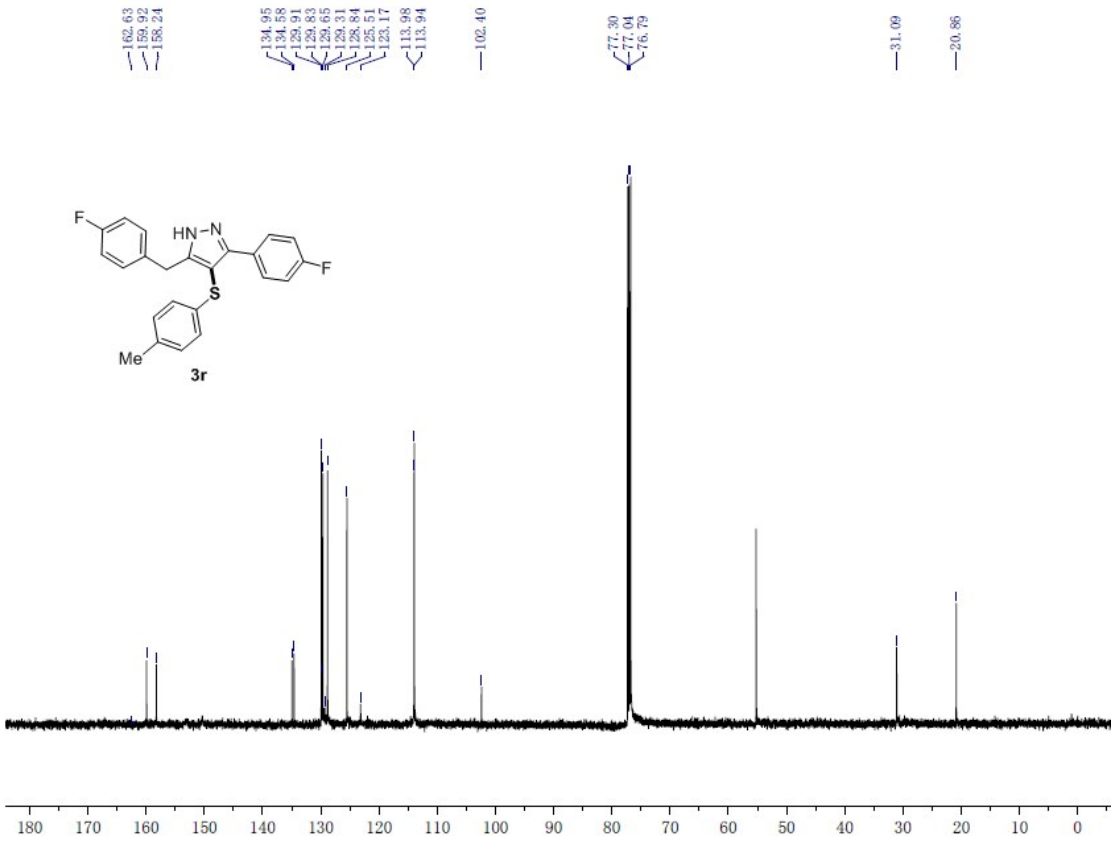

13.05
7.64
7.63
7.06
7.03
6.92
6.91
6.84
6.82
3.73
2.20
1.34
MeO
S
Me
N
N
H
Me
Me
Me
3p
0.98
2.00
2.05
2.05
2.08
3.01
3.02
9.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

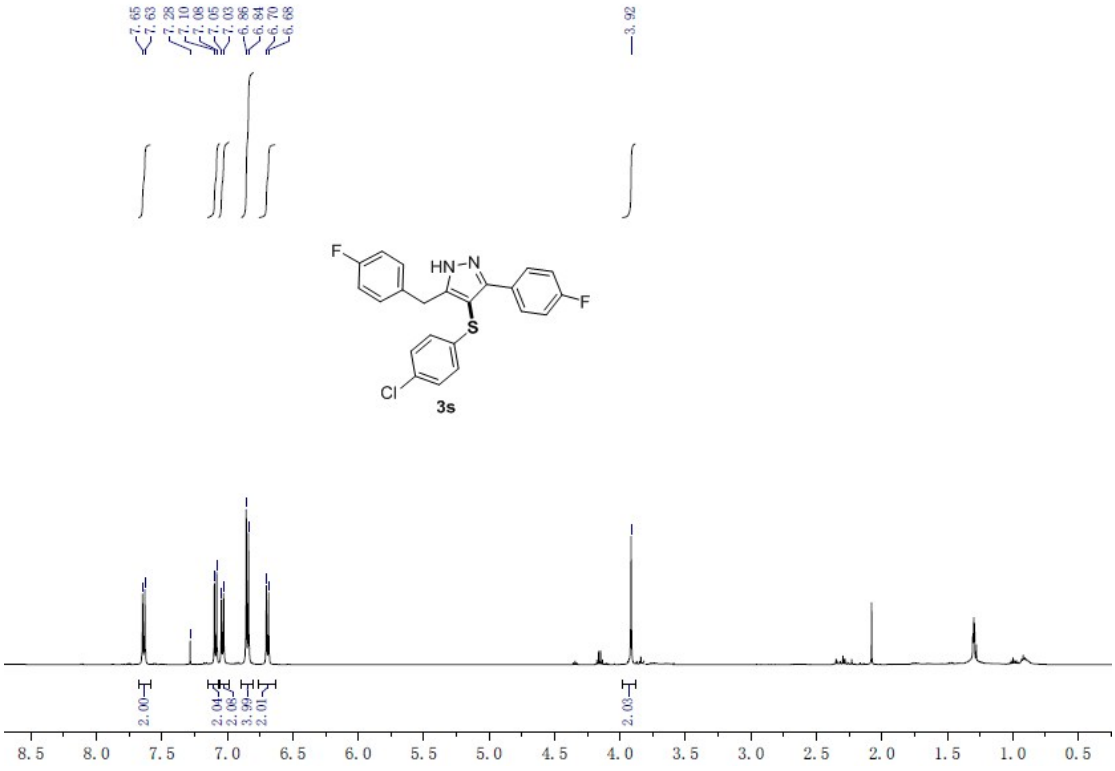

0617-2
203.05
159.74
158.56
147.82
140.90
131.48
128.88
124.91
121.46
120.55
114.27
113.62
55.27
44.72
30.10
27.35
MeO
S
Me
N
N
H
Me
Me
Me
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

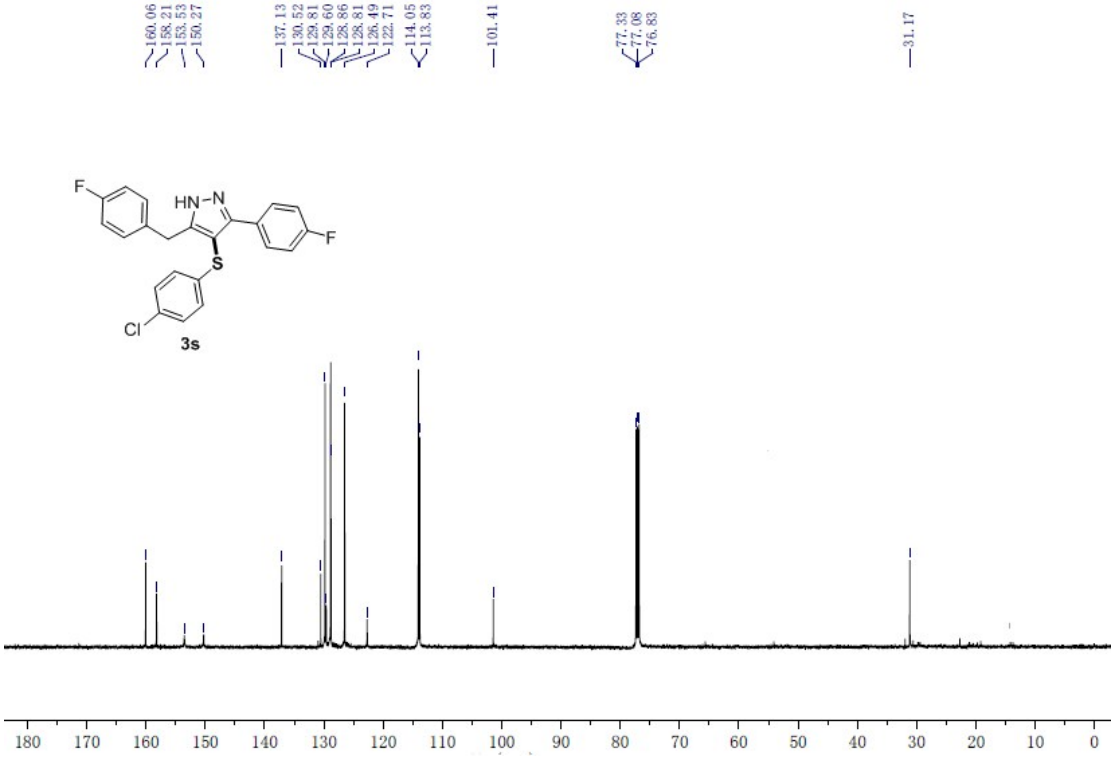

7.74
7.73
7.73
7.72
7.72
7.36
7.36
7.35
7.35
7.34
7.33
7.21
7.19
7.18
7.16
7.16
7.14
7.14
7.12
7.10
6.90
6.88
4.00
HN-N
S
Cl
3q
2.02
3.00
3.07
2.12
2.05
2.00
2.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

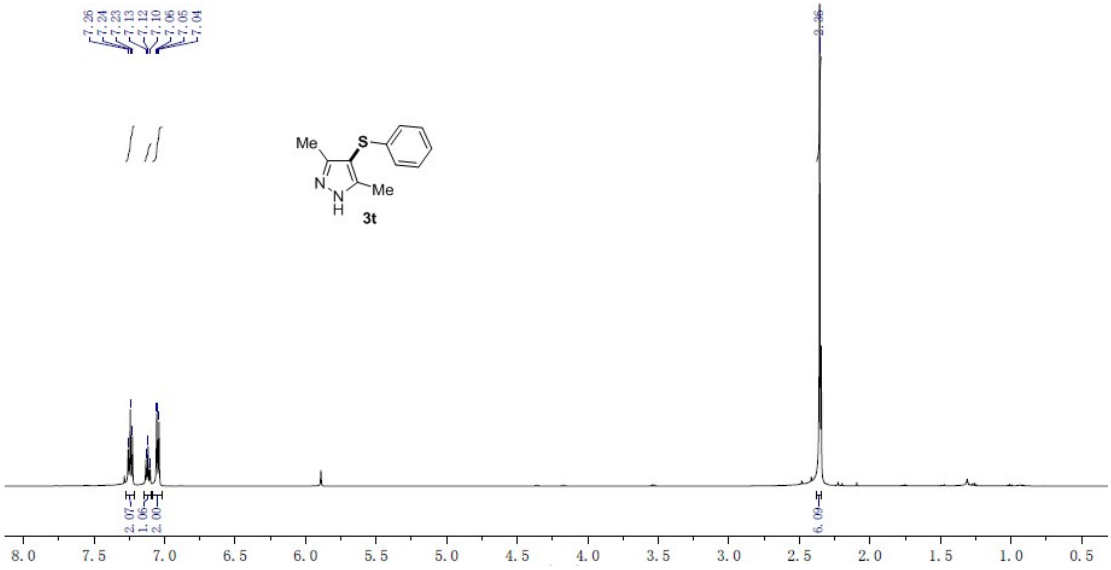

152.88
150.65
137.43
136.92
130.74
130.30
129.93
129.54
128.84
128.65
128.57
127.49
126.63
126.61
102.43
77.31
77.06
76.81
31.90
HN-N
S
Cl
3q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

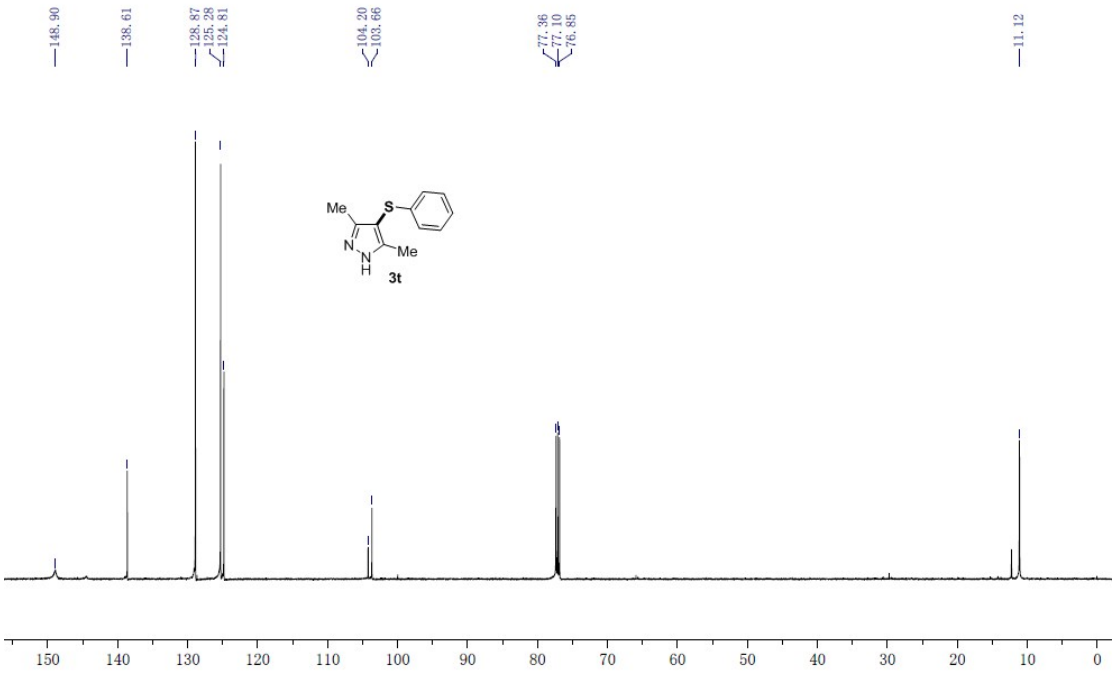

7.71
7.69
7.28
7.12
7.11
7.01
7.00
6.92
6.91
6.89
6.88
6.87
6.87
6.78
6.76
3.97
2.29
F
HN–N
F
S
Me
3r
2.00
2.01
2.05
2.03
1.99
1.92
2.15
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

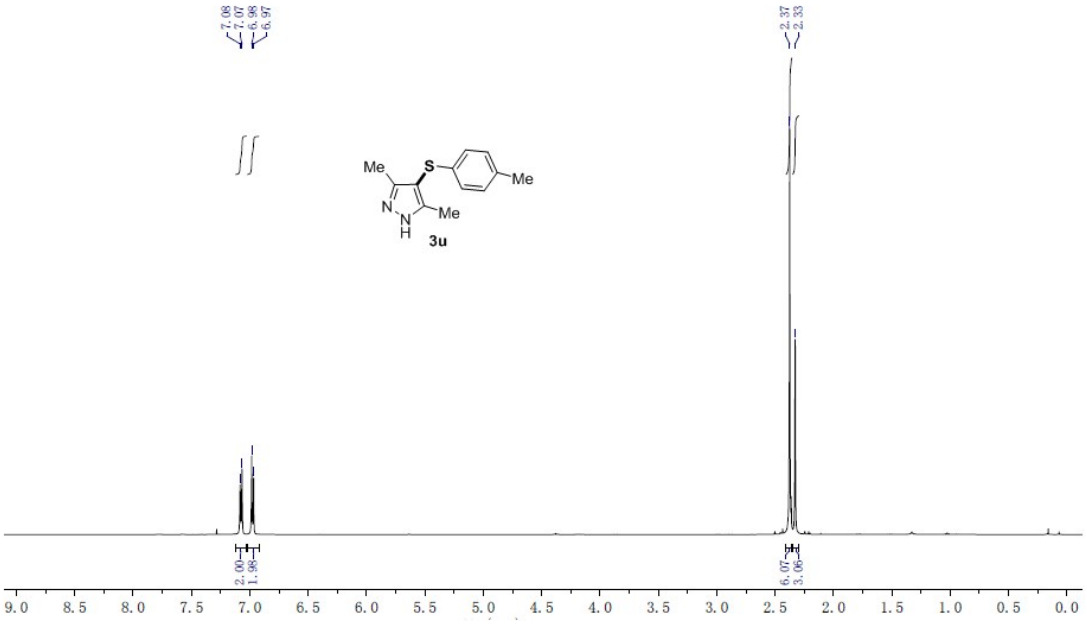

162.63
159.92
158.24
134.95
134.58
129.91
129.83
129.65
129.31
128.84
125.51
123.17
113.98
113.94
102.40
77.30
77.04
76.79
31.09
20.86
F
HN–N
F
S
Me
3r
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

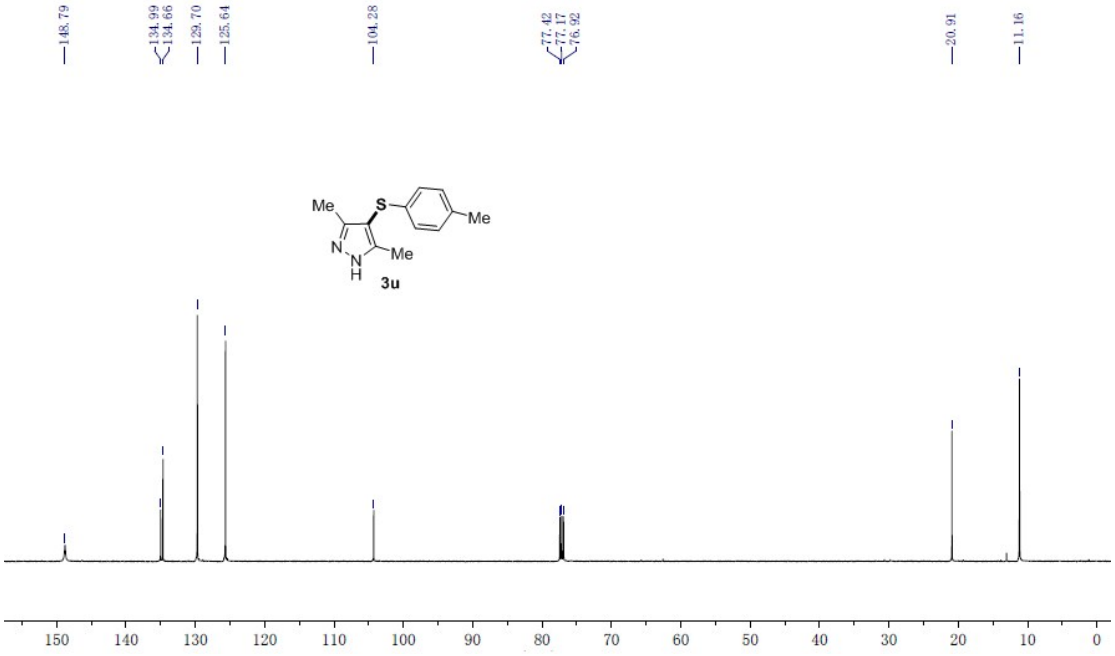

7.65
7.63
7.28
7.10
7.08
7.05
7.03
6.86
6.84
6.70
6.68
3.92
F
HN-N
F
S
Cl
3s
2.00
2.04
2.06
3.99
2.01
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

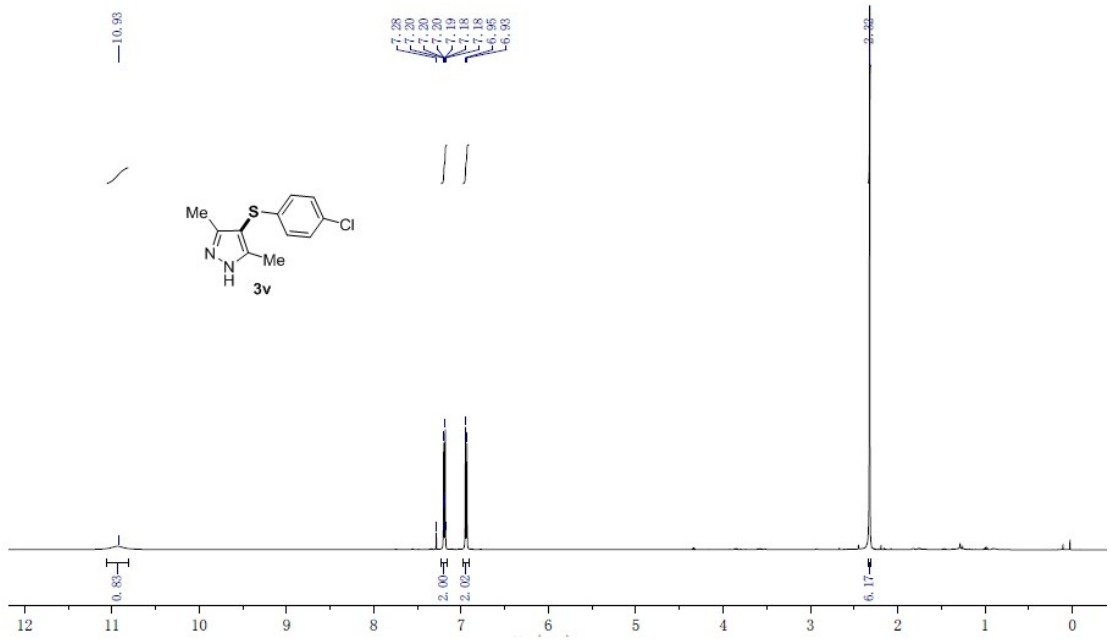

160.06
158.21
153.53
150.27
137.13
130.52
129.81
129.60
128.86
128.81
126.49
122.71
114.05
113.83
101.41
77.33
77.08
76.83
31.17
F
HN-N
F
S
Cl
3s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

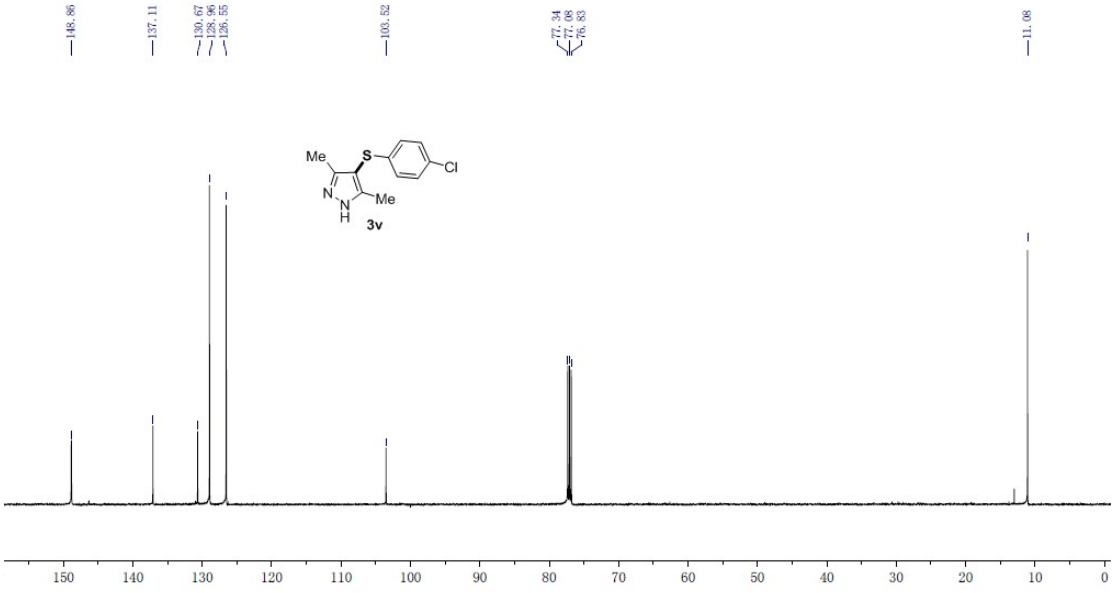

7.26
7.24
7.23
7.13
7.12
7.10
7.06
7.05
7.04
2.36
Me
S
N
H
Me
3t
2.07
1.06
2.00
6.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

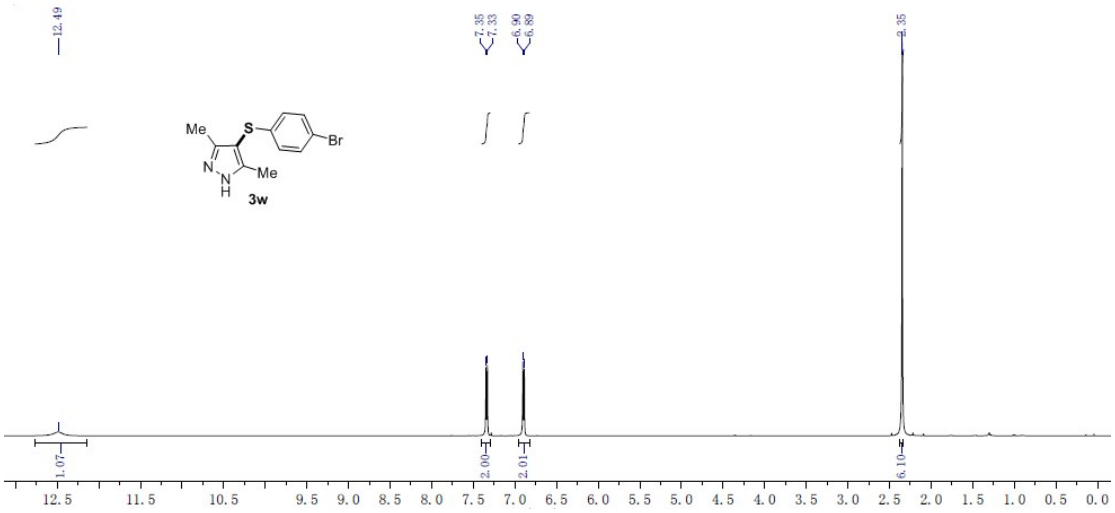

148.90
138.61
128.87
125.28
124.81
104.20
103.66
77.36
77.10
76.85
11.12
Me
S
N
H
Me
3t
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

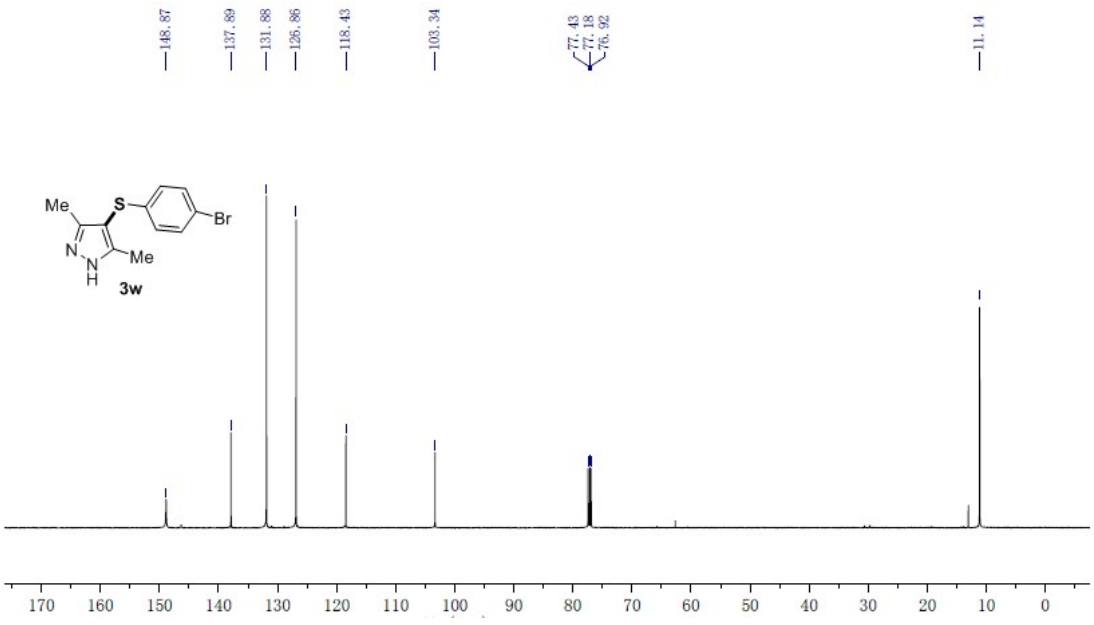

7.08
7.07
6.98
6.97
2.37
2.33
Me
S
Me
N
N
H
Me
3u
2.00
1.98
6.07
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

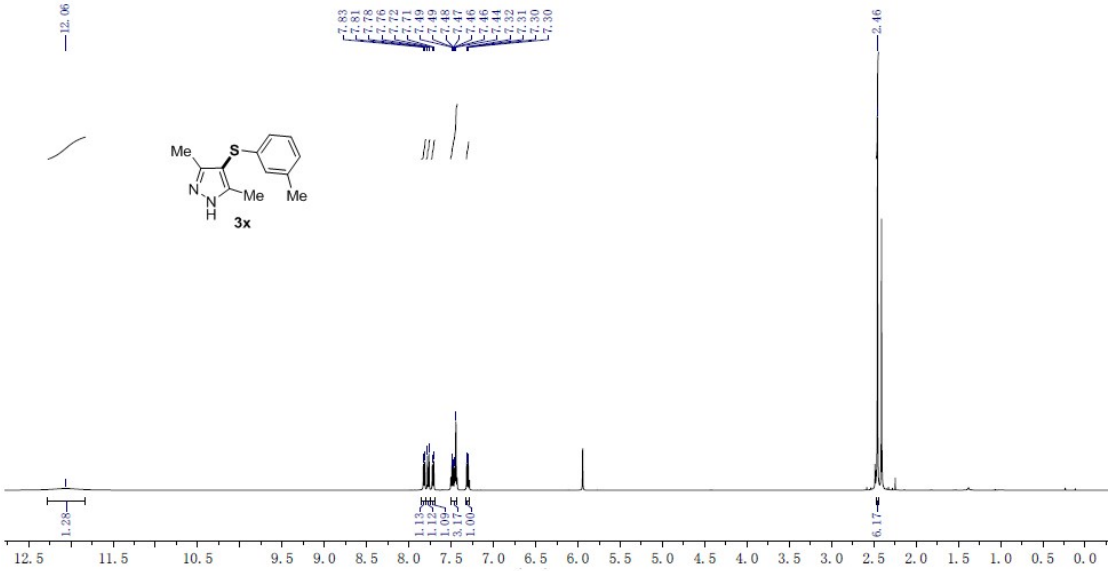

148.79
134.99
134.66
129.70
125.64
104.28
77.42
77.17
76.92
20.91
11.16
Me
S
Me
N
N
H
Me
3u
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

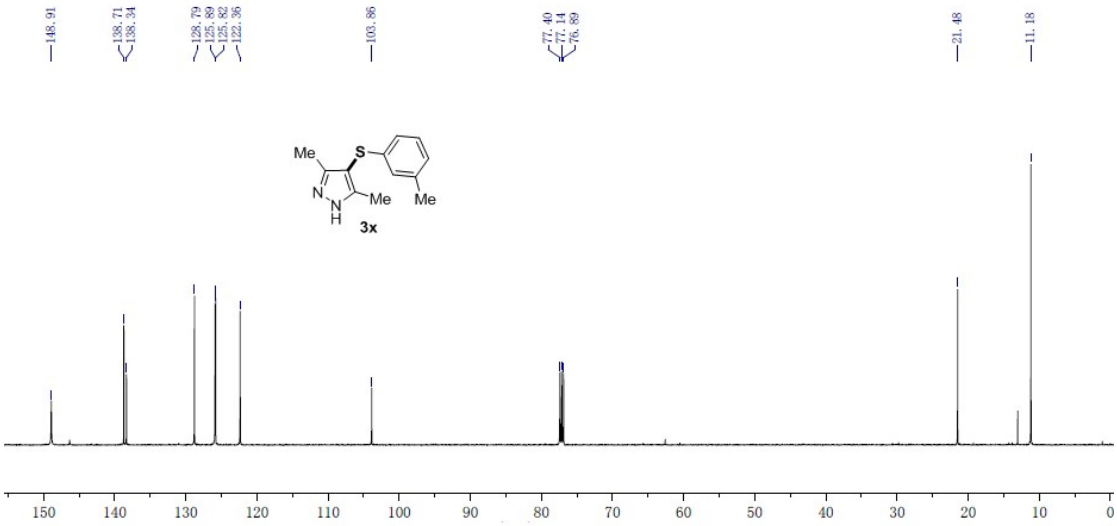

10.93
7.28
7.20
7.20
7.20
7.19
7.18
7.18
6.95
6.93
2.32
Me
S
Cl
N
N
H
Me
3v
0.83
2.00
2.02
6.17
12
11
10
9
8
7
6
5
4
3
2
1
0

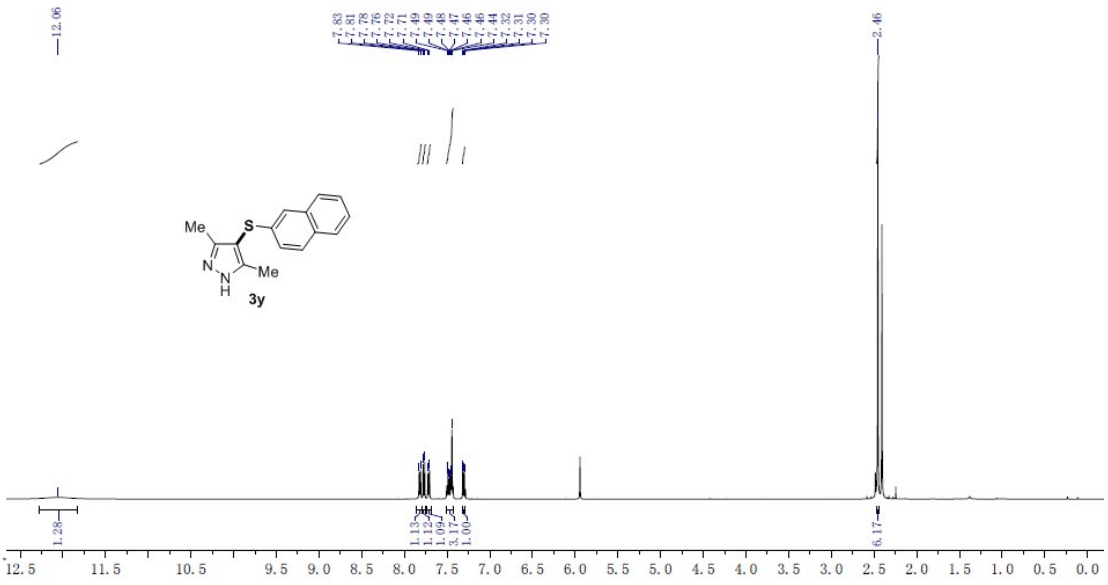

148.86
137.11
130.67
128.96
126.55
103.52
77.34
77.08
76.83
11.08
Me
S
Cl
N
N
H
Me
3v
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

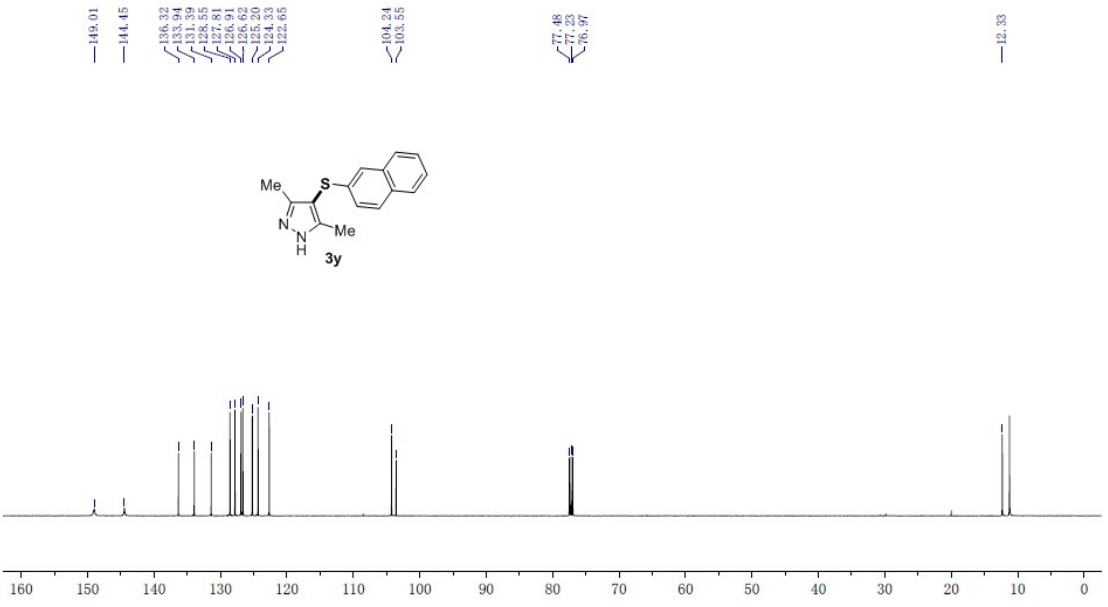

12.49
7.35
7.33
6.90
6.89
2.35
Me
S
Br
N
N
H
Me
3w
1.07
2.00
2.01
6.10
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

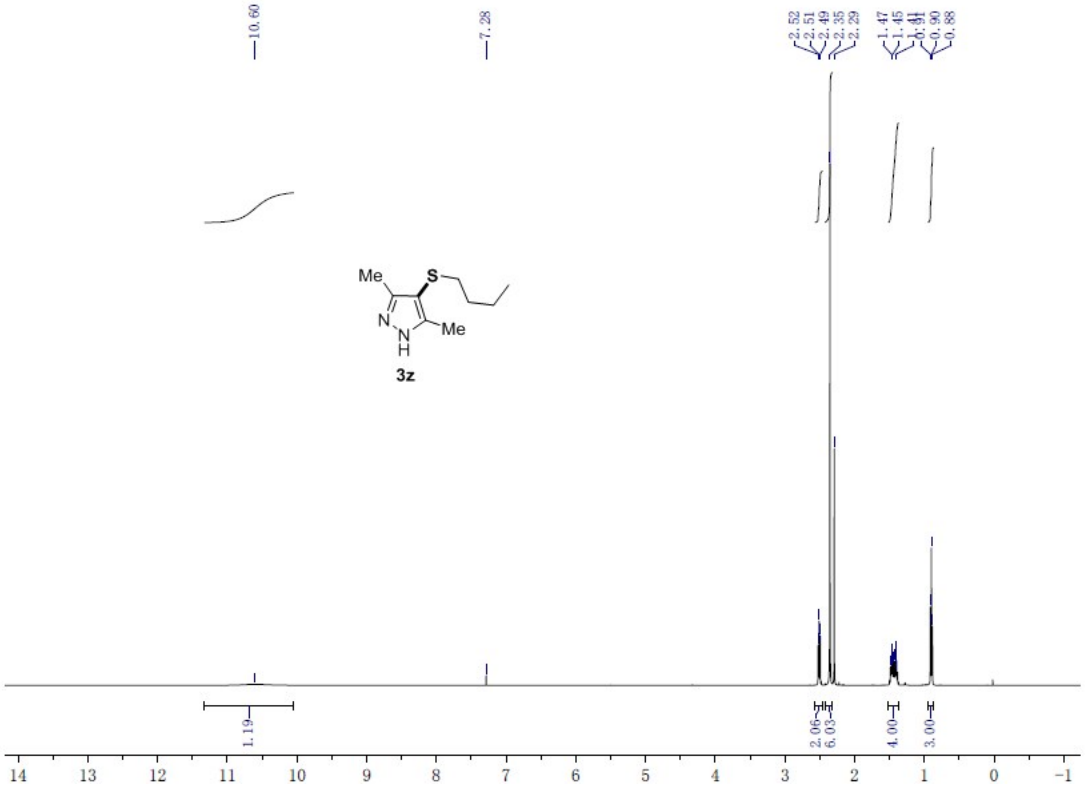

148.87
137.89
131.88
126.86
118.43
103.34
77.43
77.18
76.92
11.14
Me
S
Br
N
N
H
Me
3w
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

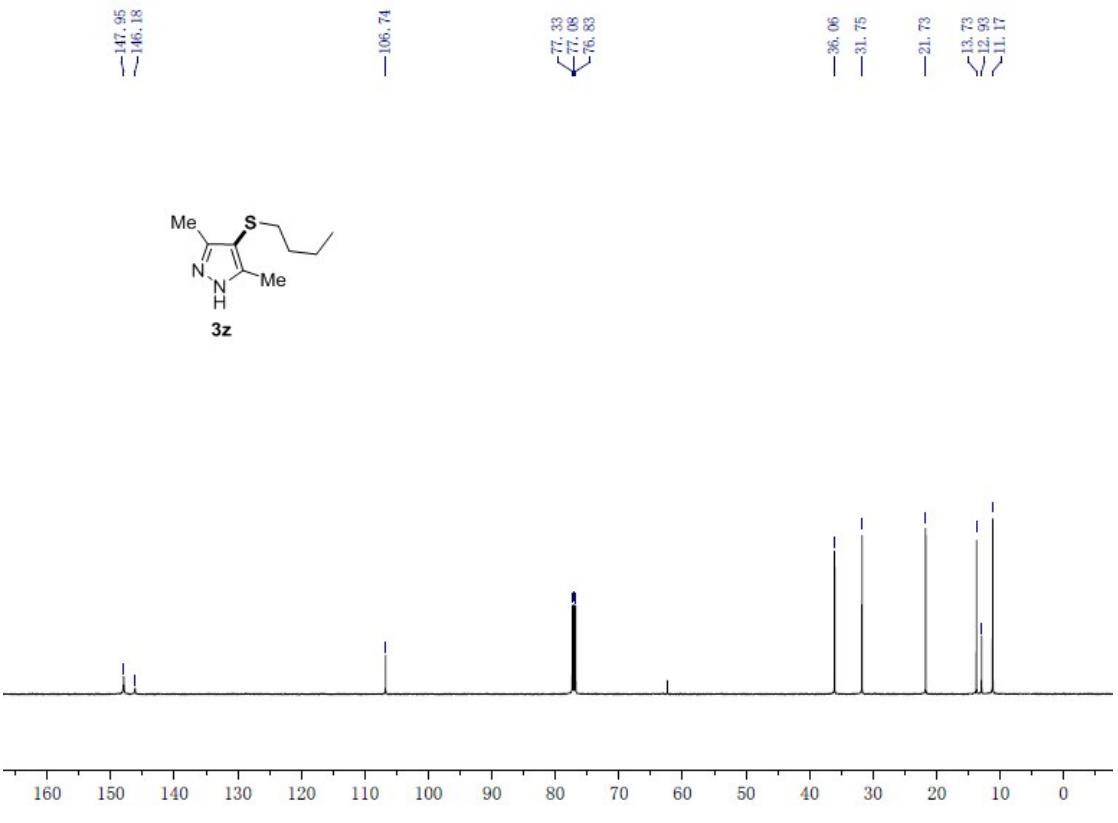

12.06
7.83
7.81
7.78
7.76
7.72
7.71
7.49
7.48
7.47
7.46
7.46
7.44
7.32
7.31
7.30
7.30
2.46
Me
S
N
N
H
Me
Me
3x
1.28
1.13
1.12
1.09
3.17
1.00
6.17
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

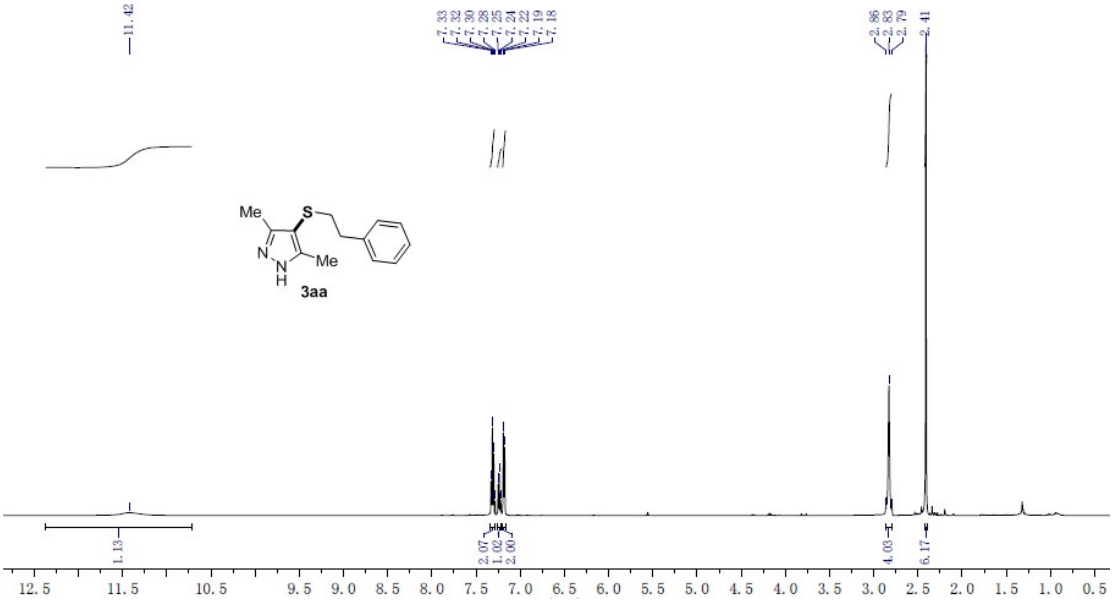

148.91
138.71
138.34
128.79
125.89
125.82
122.36
103.86
77.40
77.14
76.89
21.48
11.18
Me
S
N
N
H
Me
Me
3x
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

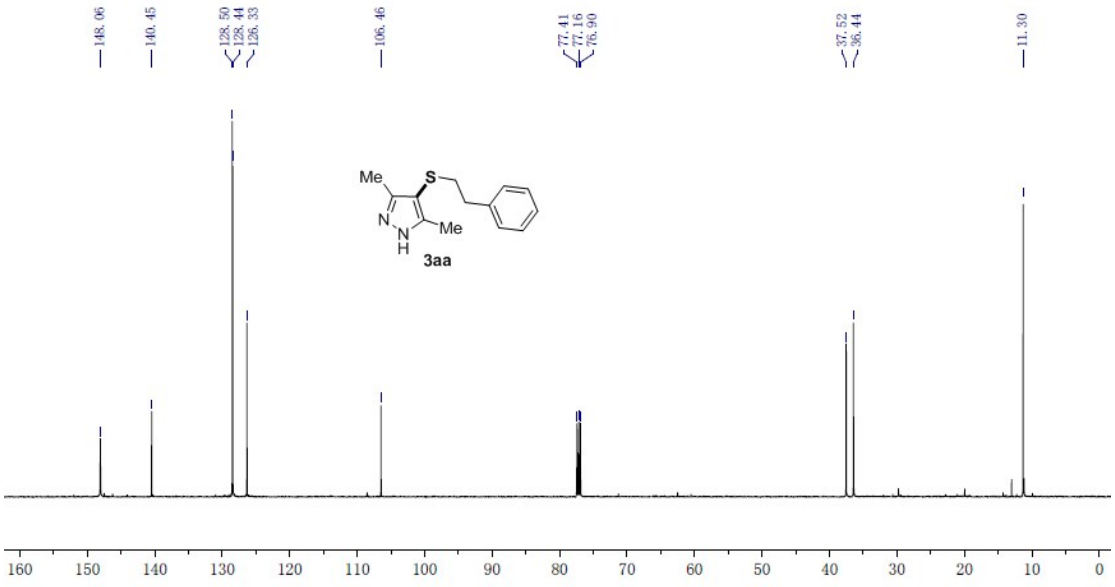

12.06
7.83
7.81
7.78
7.76
7.72
7.71
7.49
7.48
7.47
7.46
7.46
7.44
7.32
7.31
7.30
7.30
2.46
Me
S
N
N
H
Me
3y
1.28
1.13
1.21
1.09
3.17
1.00
6.17
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

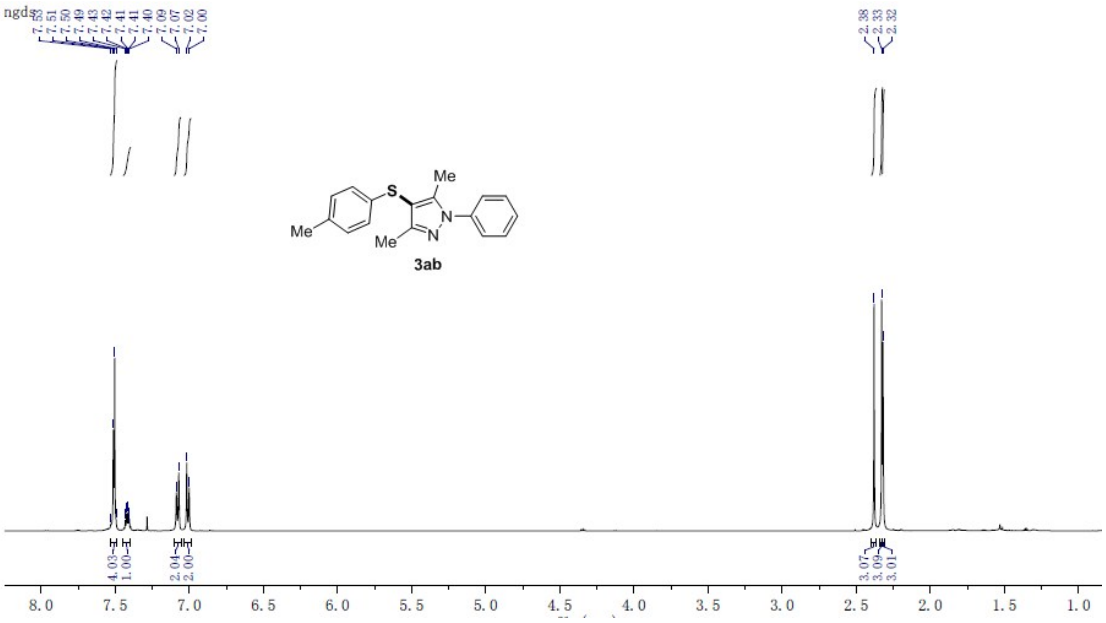

149.01
144.45
136.32
133.94
131.99
128.55
127.81
126.91
126.62
125.20
124.33
122.65
104.24
103.55
77.48
77.23
76.97
12.33
Me
S
N
N
H
Me
3y
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

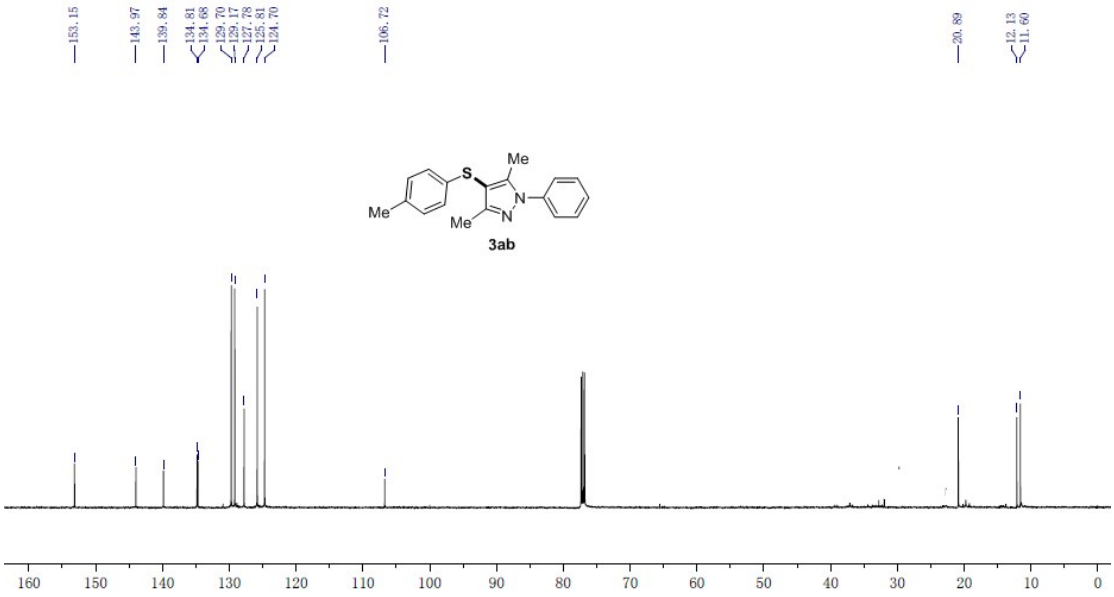

10.60
7.28
2.52
2.51
2.49
2.35
2.29
1.47
1.45
0.91
0.90
0.88
Me
S
N
N
H
Me
3z
1.19
2.06
6.03
4.00
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

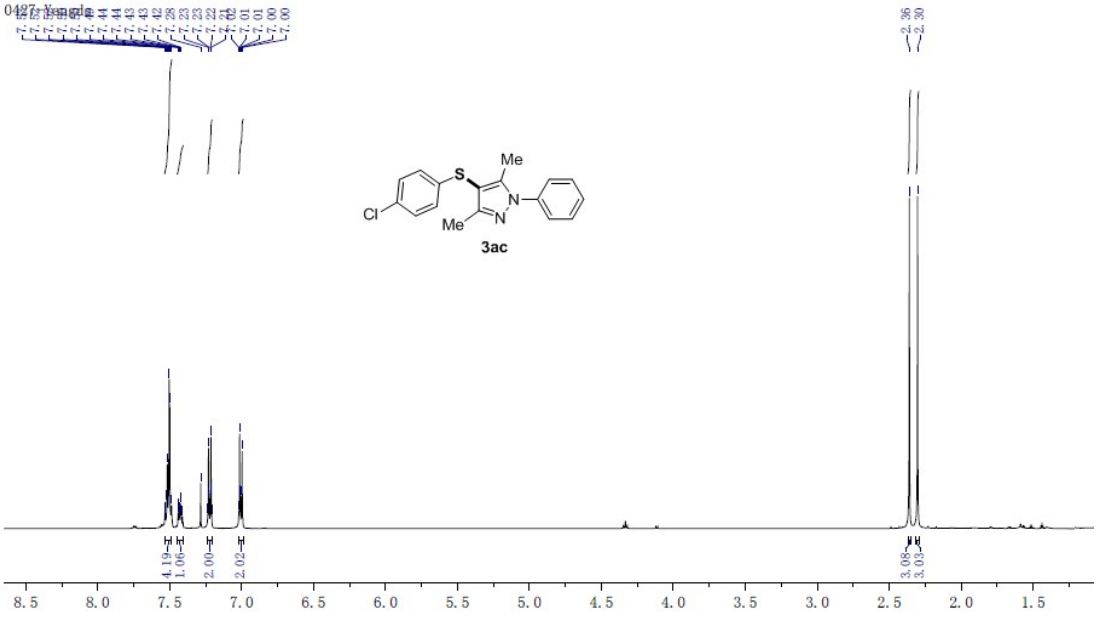

147.95
146.18
106.74
77.33
77.08
76.83
36.06
31.75
21.73
13.73
12.93
11.17
Me
S
N
N
H
Me
3z
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

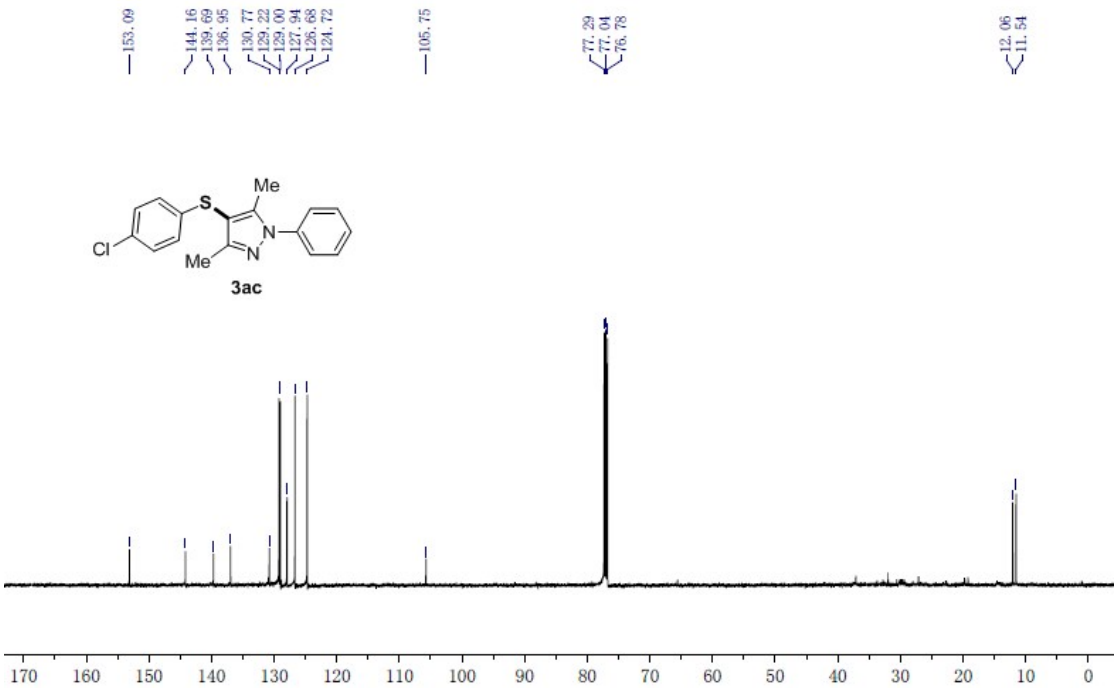

11.42
7.33
7.32
7.30
7.28
7.25
7.24
7.22
7.19
7.18
2.86
2.83
2.79
2.41
Me
S
N
N
H
Me
3aa
1.13
2.07
1.02
2.00
4.03
6.17
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

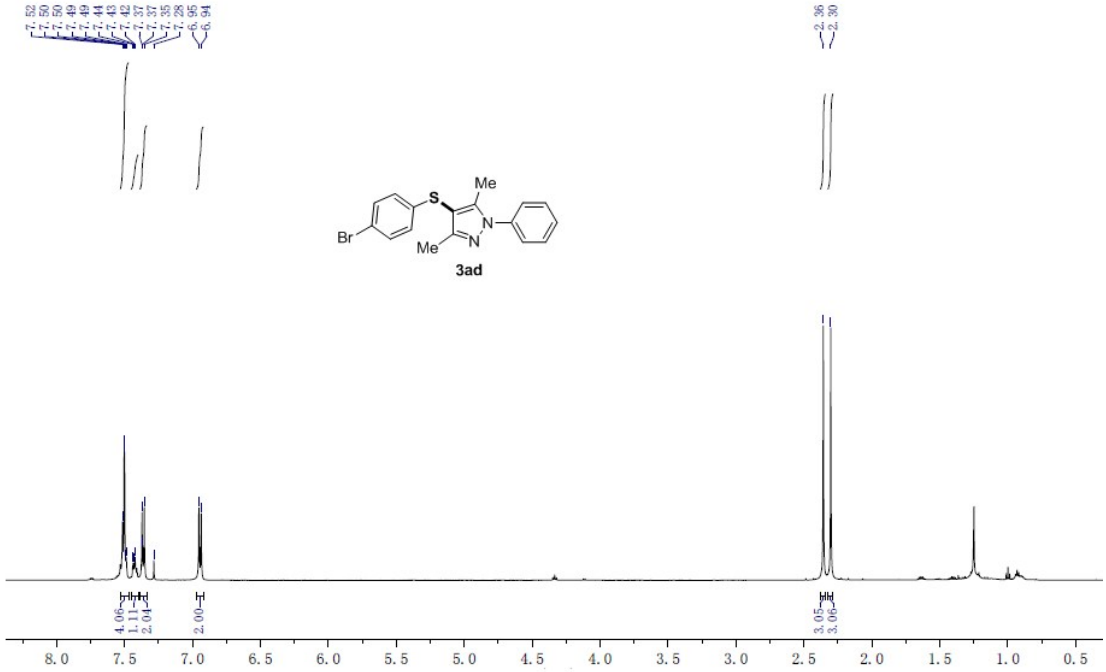

148.06
140.45
128.50
128.44
126.33
106.46
77.41
77.16
76.90
37.52
36.44
11.30
Me
S
N
N
H
Me
3aa
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

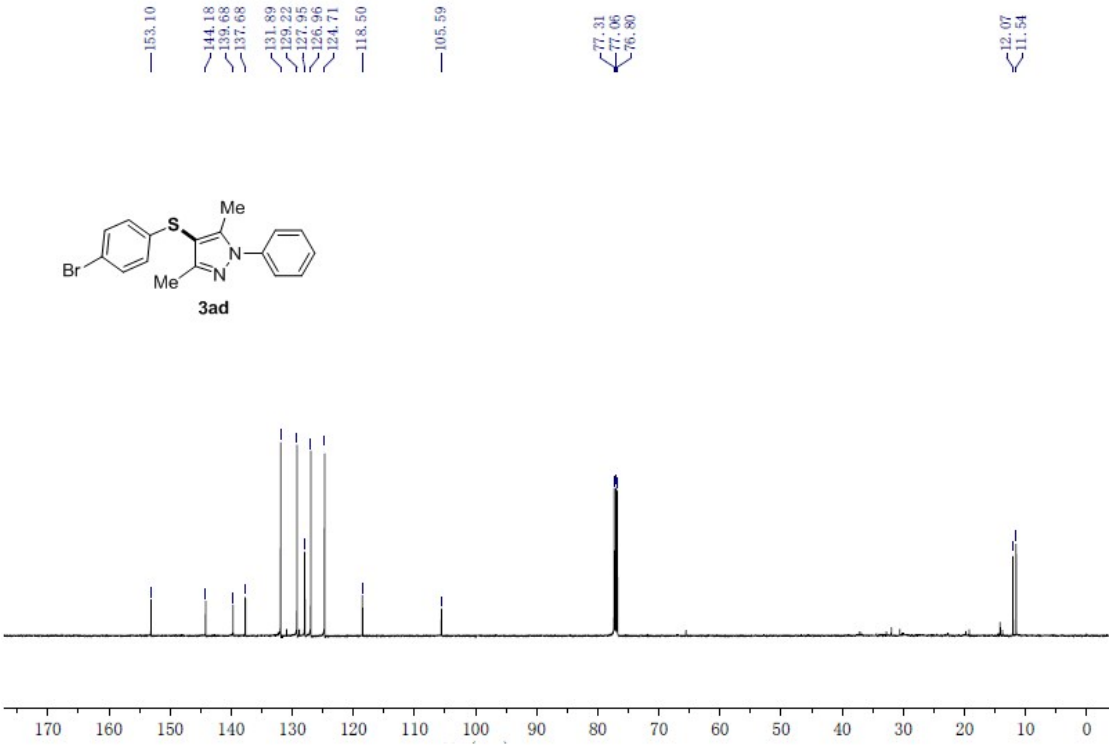

ngds
7.53
7.51
7.50
7.49
7.43
7.42
7.41
7.41
7.40
7.09
7.07
7.02
7.00
2.38
2.33
2.32
Me
S
N
Me
N
Me
3ab
4.03
1.00
2.04
2.00
3.07
3.09
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

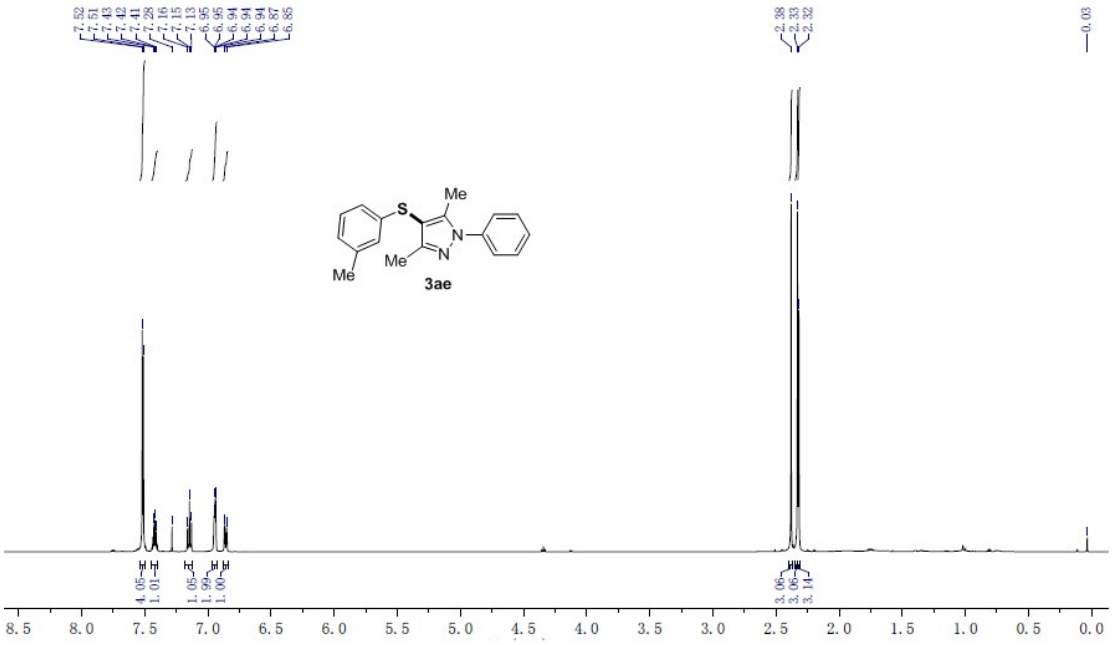

153.15
143.97
139.84
134.81
134.68
129.70
129.17
127.78
125.81
124.70
106.72
20.89
12.13
11.60
Me
S
N
Me
N
Me
3ab
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

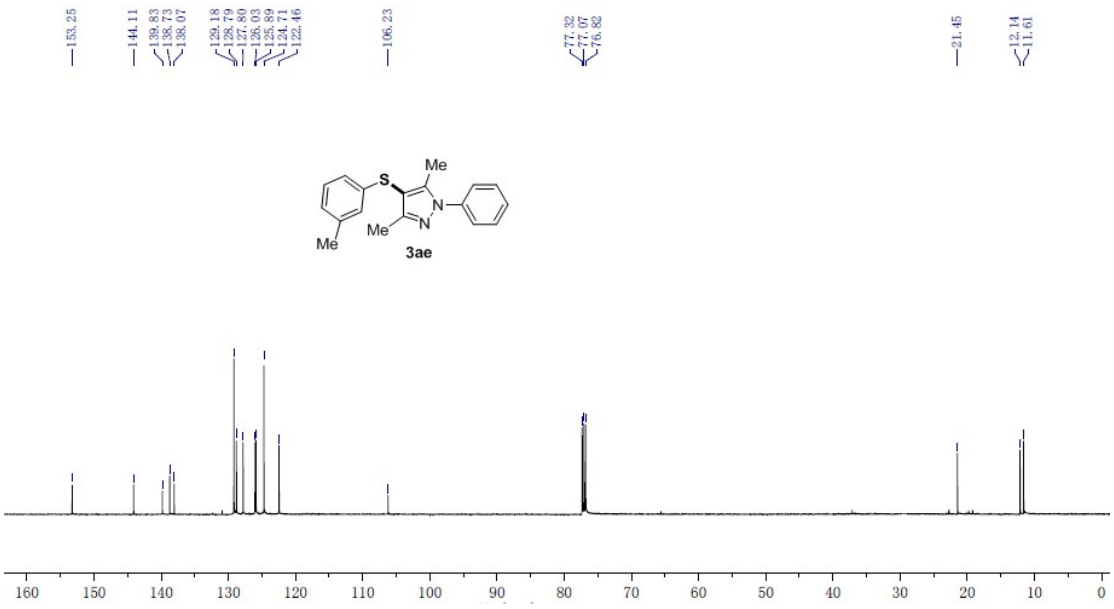

Me
S
Cl
N
Me
3ac

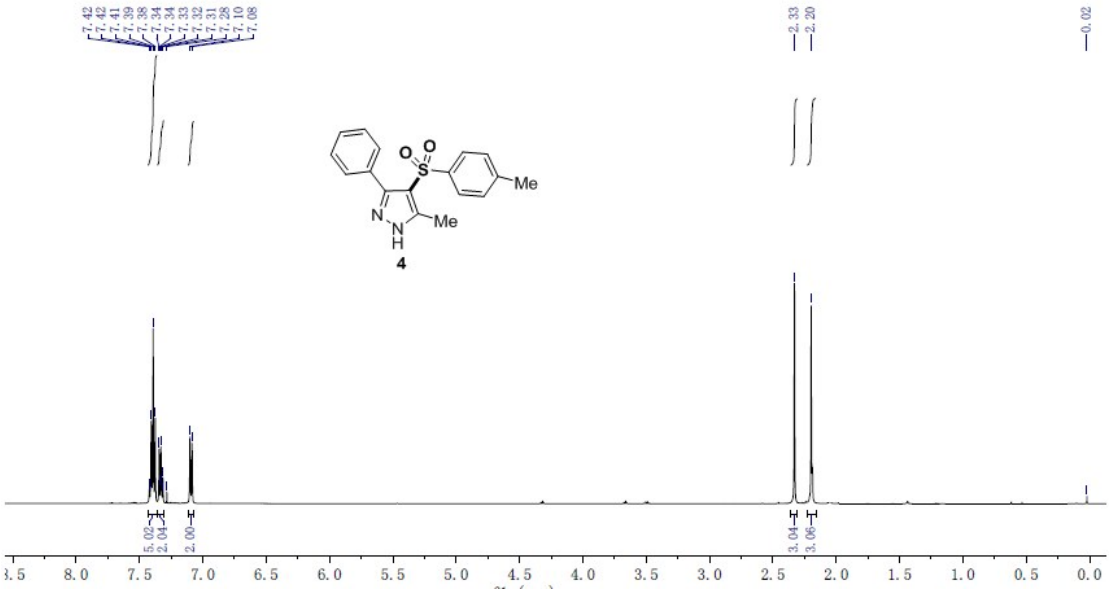

Me
S
Cl
N
Me
3ac

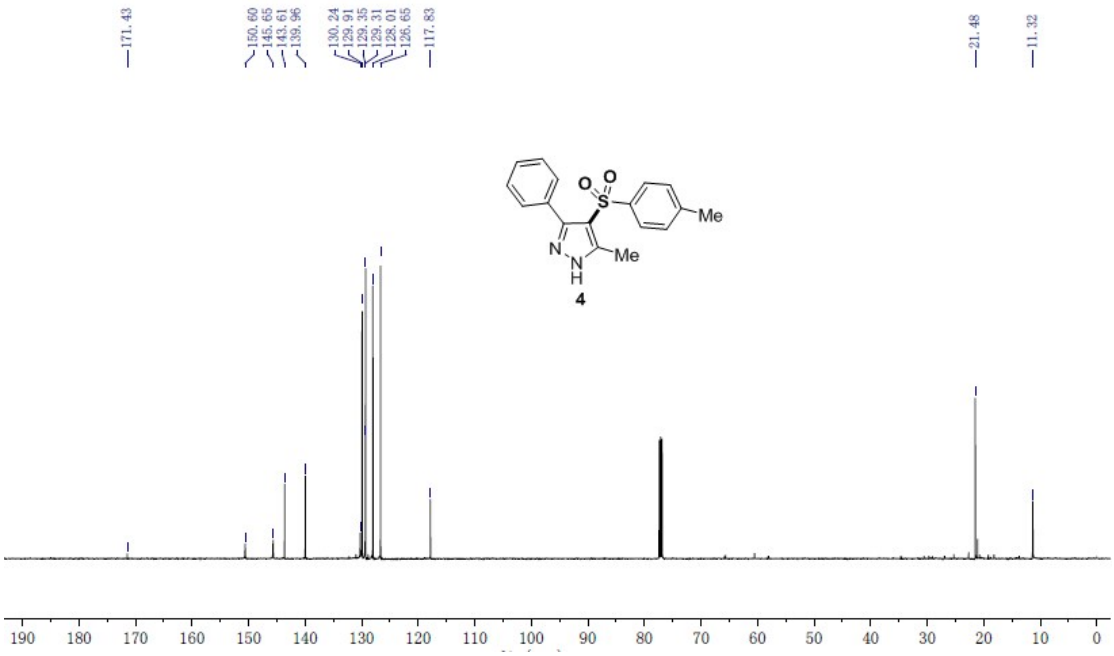

7.52
7.50
7.50
7.49
7.49
7.44
7.43
7.42
7.37
7.37
7.35
7.28
6.95
6.94
2.36
2.30
Me
S
Br
N
Me
N
3ad
4.06
1.11
2.04
2.00
3.05
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

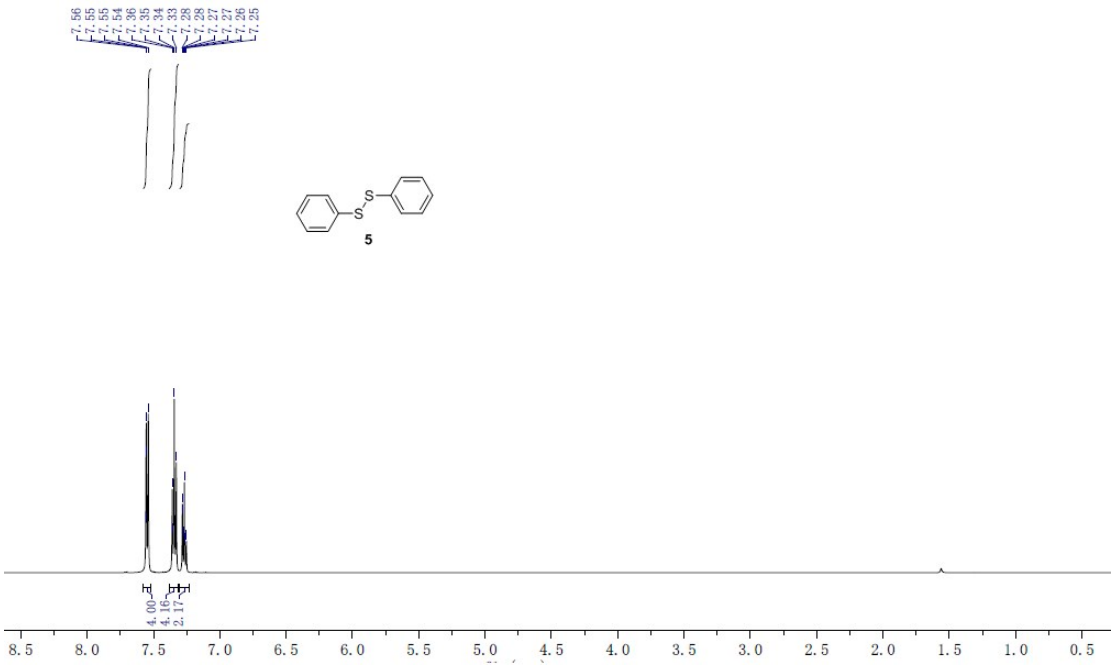

153.10
144.18
139.68
137.68
131.89
129.22
127.95
126.96
124.71
118.50
105.59
77.31
77.06
76.80
12.07
11.54
Me
S
Br
N
Me
N
3ad
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

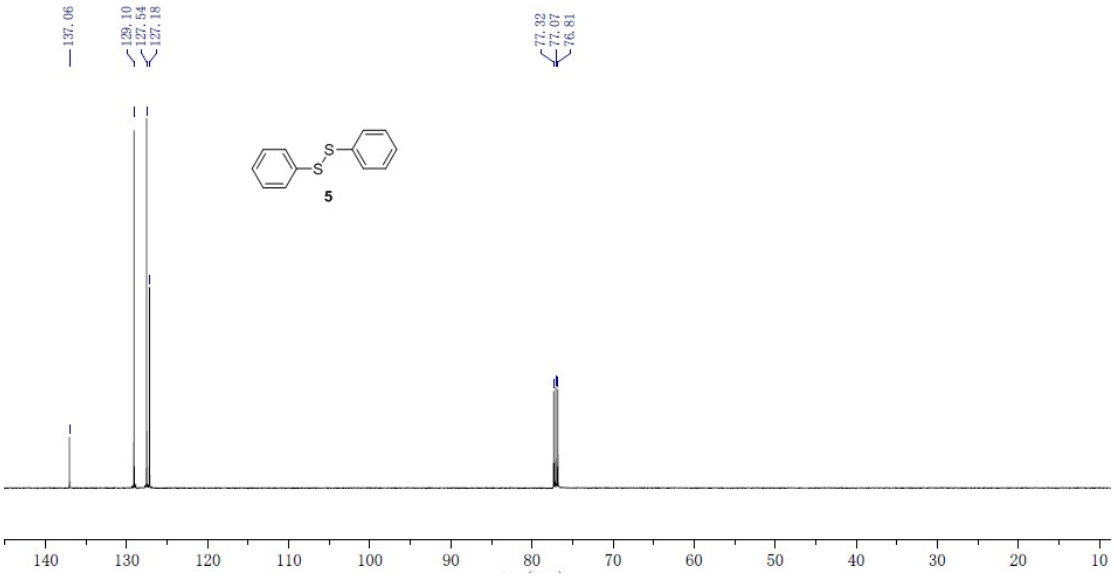

7.52
7.51
7.43
7.42
7.41
7.28
7.16
7.15
7.13
6.95
6.95
6.94
6.94
6.94
6.87
6.85
2.38
2.33
2.32
0.03
Me
S
N
N
Me
Me
3ae
4.05
1.01
1.05
1.99
1.00
3.06
3.06
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


153.25
144.11
139.83
138.73
138.07
129.18
128.79
127.80
126.03
125.89
124.71
122.46
106.23
77.32
77.07
76.82
21.45
12.14
11.61
Me
S
N
N
Me
Me
3ae
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.42
7.42
7.41
7.39
7.38
7.34
7.34
7.33
7.32
7.31
7.28
7.10
7.08
2.33
2.20
0.02
Me
Me
4
5.02
2.04
2.00
3.04
3.06

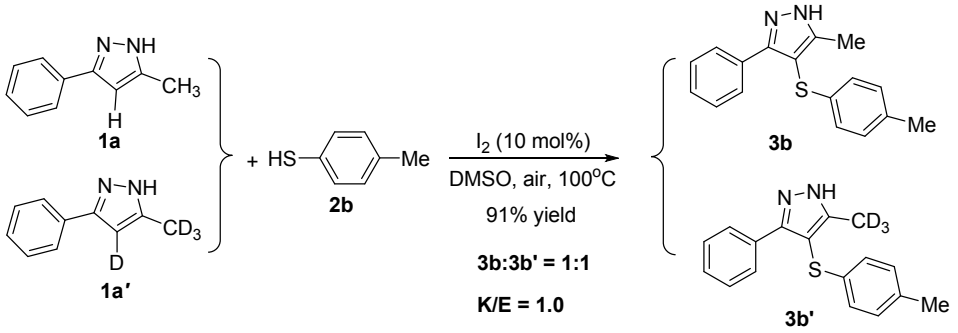

171.43
150.60
145.65
143.61
139.96
130.24
129.91
129.35
129.31
128.01
126.65
117.83
21.48
11.32
Me
Me
4


7.56
7.55
7.55
7.55
7.54
7.36
7.35
7.34
7.33
7.28
7.28
7.27
7.27
7.26
7.25
5
4.00
4.16
2.17
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


137.06
129.10
127.54
127.18
77.32
77.07
76.81
5
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Kinetic Isotopic Effect (KIE) Studies:

A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with iodine (5 mg, 0.02 mmol), 5-methyl-3-phenyl-1*H*-pyrazole **1a** (0.1 mmol), **1a**-d_4 (0.2 mmol), benzenethiol **2a** (0.24 mmol), and DMSO (2 mL). The tube was sealed, and then the mixture was stirred under air atmosphere at 100 °C for 18 h. After completion of the reaction, the resulting solution was cooled down to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product , the product was analyzed by ^{1}H-NMR (500 MHz) (Figure S1). The result was summarized in equation S1:



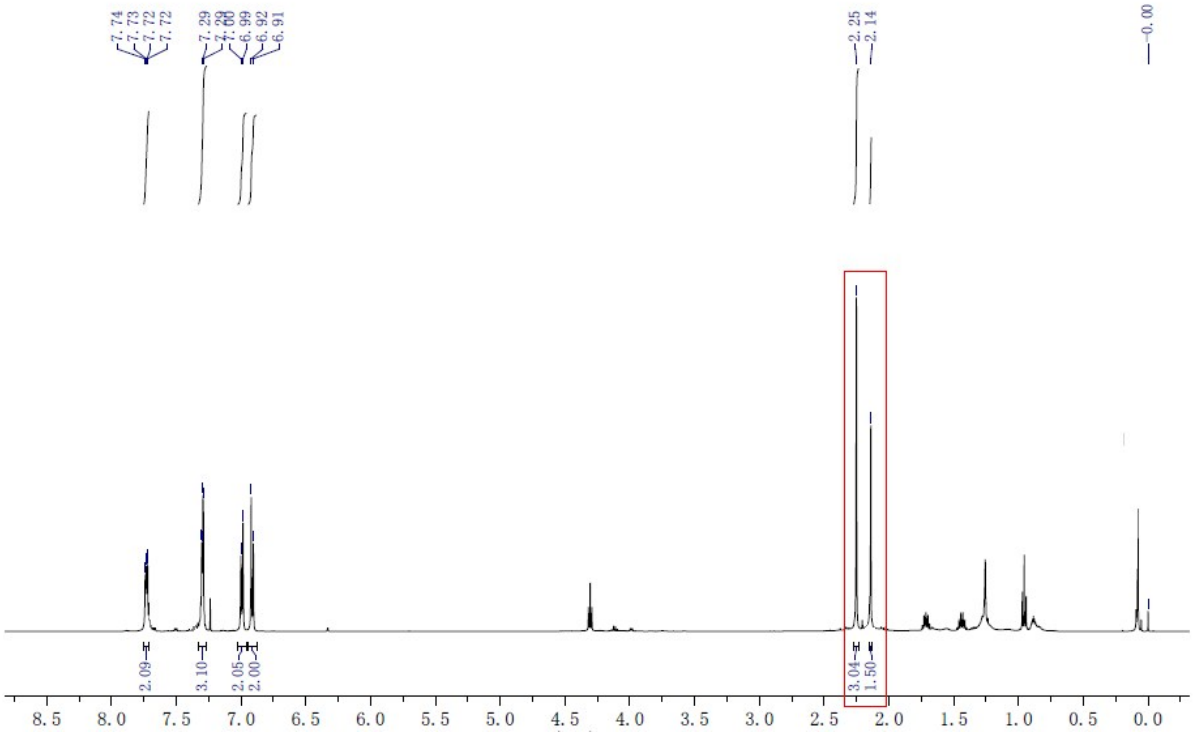


Figure S1. The 1H-NMR spectrum of **3b** and **3b**-d_3