Supplementary Information

# Metal-free direct construction of sulfenylated pyrazoles via the NaOH promoted sulfenylation of pyrazolones with aryl thiols

Xiaoxia Liu‡, Huanhuan Cui‡, Daoshan Yang, Shicui Dai, Tiantian Zhang, Jingyu Sun, Wei Wei*, 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, China.*

**Phone: +86 537 4458317; Fax: +86 537 4458317.* E-mail: weiweiqfnu@163.com; huawang_qfnu@126.com, website: http://wang.qfnu.edu.cn.

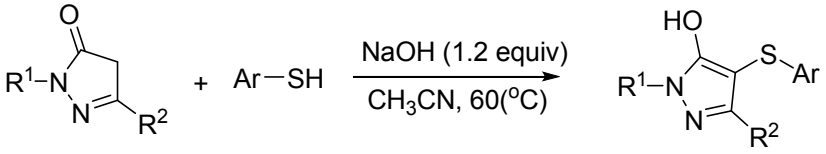
‡ *Authors with equal contribution.*

# Contents

## 1. General information

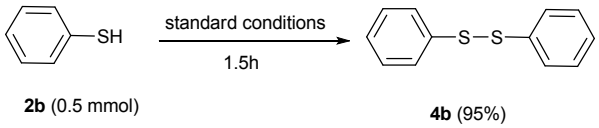
All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a Bruker Avance III 500 spectrometer with TMS as internal standard (500 MHz $^{1}H$, 125 MHz $^{13}C$) at room temperature, the chemical shifts ($\delta$) were expressed in ppm and $J$ values were given in Hz. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). 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 on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200 - 300 mesh).

## 2. General procedure for NaOH promoted sulfenylation of pyrazolones with aryl thiols for the synthesis of sulfenylated pyrazoles



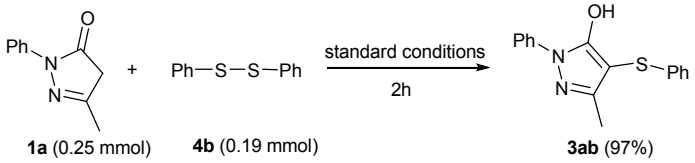

To a mixture of pyrazolone **1** (0.25 mmol, 43.6 mg), aryl thiol **2** (0.375 mmol, 46.6 mg), NaOH (0.3 mmol, 12.0 mg), and $CH_3CN$ (2 mL) in a 25 mL round-bottomed flack at room temperature under air. The reaction vessel was allowed to stir at 60 °C for 2-5h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products.

## 3. The reaction of thiophenol 2b was conducted independently under the standard conditions




To a mixture of thiophenol **2b** (0.5 mmol, 51.1 vl), NaOH (0.3 mmol, 12.0 mg), and $CH_3CN$ (2 mL) in a 25 mL round-bottomed flack at room temperature under air. The reaction vessel was allowed to stir at 60 °C for 1.5h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of petroleum ether to give the desired product **4b** in 95% yield (52.1 mg, 0.238 mmol).

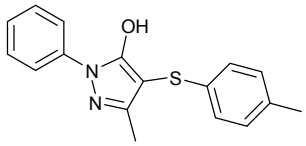
## 4. The reaction of pyrazolone 1a and diphenyl sulfide 4b was conducted under the standard conditions




To a mixture of pyrazolone **1a** (0.25 mmol, 43.6 mg), diphenyl sulfide **4b** (0.19

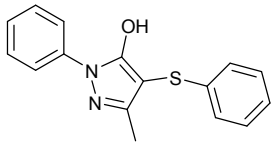
mmol, 41.5 mg), NaOH (0.3 mmol, 12.0 mg), and $CH_3CN$ (2 mL) in a 25 mL round-bottomed flack at room temperature under air. The reaction vessel was allowed to stir at 60 °C for 2h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3ab** in 97% yield (71.6mg, 0.243 mmol).

**5. Characterization data of products 3aa-3ha**



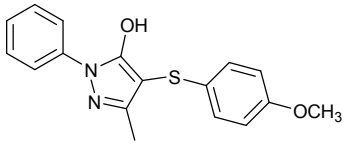

**(3aa)**

**3-methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-ol**,[1] Compound **3aa** was obtained in 99% yield (73.3 mg, 0.248 mmol) according to the general procedure (2h). White solid, mp: 178.8-179.7 °C. $^1$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.16 (s, 1H), 7.75 (d, $J$ = 8.2 Hz, 2H), 7.48 (t, $J$ = 7.8 Hz, 2H), 7.28 (t, $J$ = 7.4 Hz, 1H), 7.10 (d, $J$ = 8.2 Hz, 2H), 7.00 (d, $J$ = 8.1 Hz, 2H), 2.24 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.5, 138.7, 135.3, 134.8, 130.1, 129.4, 126.1, 125.8, 121.2, 88.6, 20.9, 12.8. HRMS (ESI) calcd for $C_{17}H_{17}N_2OS$ $(M + H)^+$ 297.1062, found 297.1067.



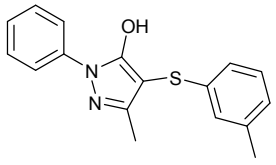

**(3ab)**

**3-methyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5-ol**[2], Compound **3ab** was obtained in 96% yield (67.9 mg, 0.241 mmol) according to the general procedure (3h). White solid, mp: 170.1-171.6 °C. $^1$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.16 (s, 1H), 7.75 (d, $J$ = 7.7 Hz, 2H), 7.48 (t, $J$ = 7.6 Hz, 2H), 7.29 (t, $J$ = 7.9 Hz, 3H), 7.13 (t, $J$ = 7.4 Hz, 1H), 7.09 (d, $J$ = 7.6 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.6, 138.9, 138.6, 129.5, 129.4, 126.2, 125.4, 125.4, 121.2, 87.9, 12.8. HRMS (ESI) calcd for $C_{16}H_{15}N_2OS$ $(M + H)^+$ 283.0905, found 283.0907.



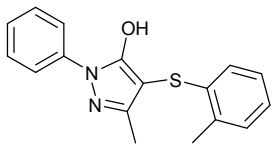
**(3ac)**

**4-(4-methoxyphenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**[2], Compound **3ac** was obtained in 91% yield (70.7 mg, 0.227 mmol) according to the general procedure (4h). White solid, mp: 164.5-164.7 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.11 (s, 1H), 7.73 (d, $J$ = 7.7 Hz, 2H), 7.49-7.45 (m, 2H), 7.27 (t, $J$ = 7.4 Hz, 1H), 7.09 (t, $J$ = 8.8 Hz, 2H), 6.90-6.87 (m, 2H), 3.71 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 158.0, 152.3, 138.7, 132.5, 129.4, 129.2, 128.2, 126.1, 121.1, 115.3, 89.7, 55.6, 12.8. HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2S$ $(M + H)^+$ 313.1011, found 313.1015.



**(3ad)**

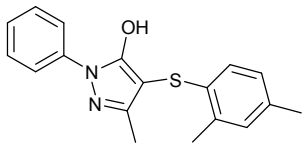
**3-methyl-1-phenyl-4-(m-tolylthio)-1H-pyrazol-5-ol**, Compound **3ad** was obtained in 85% yield (63.3 mg, 0.214 mmol) according to the general procedure (4h). White solid, mp: 179.6-181.0 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.16 (s, 1H), 7.76 (t, $J$ = 1.1 Hz, 2H), 7.49-7.46 (m, 2H), 7.28 (t, $J$ = 7.4 Hz, 1H), 7.17 (t, $J$ = 7.6 Hz, 1H), 6.94 (d, $J$ = 8.2 Hz, 2H), 6.85 (d, $J$ = 8.0 Hz, 1H), 2.25 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.5, 138.8, 138.7, 138.7, 129.4, 129.4, 126.3, 126.1, 125.8, 122.5, 121.1, 88.2, 21.5, 12.8. HRMS (ESI) calcd for $C_{17}H_{17}N_2OS$ $(M + H)^+$ 297.1062, found 297.1061.



**(3ae)**

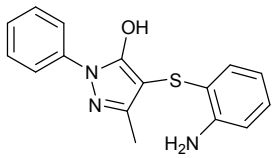
**3-methyl-1-phenyl-4-(o-tolylthio)-1H-pyrazol-5-ol**[1], Compound **3ae** was obtained in 97% yield (71.8 mg, 0.242 mmol) according to the general procedure (2h). White solid, mp: 190.7-190.8 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.16 (s, 1H), 7.76 (d, $J$ = 7.6 Hz, 2H), 7.48 (t, $J$ = 7.6 Hz, 2H), 7.29 (t, $J$ = 7.4 Hz, 1H), 7.18 (d, $J$ = 7.3

Hz, 1H), 7.10 (t, *J* = 6.7 Hz, 1H), 7.05-7.01 (m, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.8, 152.7, 138.6, 137.7, 134.0, 130.5, 129.4, 127.0, 126.2, 125.0, 124.1, 121.2, 87.0, 19.7, 12.8. HRMS (ESI) calcd for $C_{17}H_{17}N_2OS$ $(M + H)^+$ 297.1062, found 297.1063.



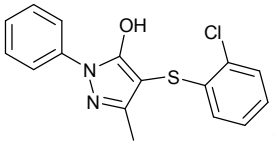

**(3af)**

**4-(2,4-dimethylphenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**, Compound **3af** was obtained in 90% yield (69.8 mg, 0.225 mmol) according to the general procedure (4h). White solid, mp: 190.0-190.4 $^{o}$C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.11 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H), 2.09 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.6, 138.6, 134.3, 134.1, 134.1, 131.3, 129.4, 127.6, 126.1, 124.7, 121.1, 87.6, 20.7, 19.7, 12.7. HRMS (ESI) calcd for $C_{18}H_{19}N_2OS$ $(M + H)^+$ 311.1218, found 311.1214.



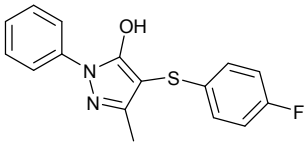

**(3ag)**

**4-(2-aminophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**, Compound **3ag** was obtained in 97% yield (72.1 mg, 0.243 mmol) according to the general procedure (2h). Gray solid, mp: 182.9-183.1 $^{o}$C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 7.71 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 6.7 Hz, 1H), 6.99-6.96 (m, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 3.85 (s, 2H), 2.20 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 159.2, 152.6, 148.4, 138.1, 132.7, 129.4, 128.9, 125.9, 120.6, 119.1, 117.1, 115.4, 92.3, 12.6. HRMS (ESI) calcd for $C_{16}H_{16}N_3OS$ $(M + H)^+$ 298.1014, found 298.1013.



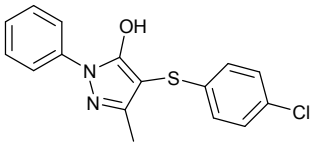
**(3ah)**

**4-(2-chlorophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**, Compound **3ah** was obtained in 87% yield (68.6 mg, 0.217 mmol) according to the general procedure (2h). White solid, mp: 182.0-182.3 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.32 (s, 1H), 7.77 (t, $J$ = 1.0 Hz, 2H), 7.49 (t, $J$ = 7.6 Hz, 2H), 7.46-7.44 (m, 1H), 7.30 (t, $J$ = 7.4 Hz, 1H), 7.28-7.24 (m, 1H), 7.17-7.14 (m, 1H), 6.78 (d, $J$ = 7.7 Hz, 1H), 2.11 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.3, 152.6, 138.5, 137.7, 129.9, 129.4, 129.4, 128.2, 126.5, 126.3, 125.7, 121.4, 85.8, 12.7. HRMS (ESI) calcd for $C_{16}H_{14}ClN_2OS$ $(M + H)^+$ 317.0515, found 317.0517.



**(3ai)**

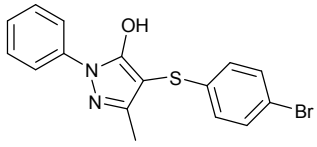
**4-(4-fluorophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**[1], Compound **3ai** was obtained in 98% yield (73.9 mg, 0.246 mmol) according to the general procedure (3h). White solid, mp: 170.8-171.1 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.26 (s, 1H), 7.74 (d, $J$ = 7.7 Hz, 2H), 7.48 (t, $J$ = 7.6 Hz, 2H), 7.28 (t, $J$ = 7.4 Hz, 1H), 7.15 (t, $J$ = 9.2 Hz, 4H), 2.14 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 160.9 (d, $J$ = 240.4 Hz), 157.4, 152.4, 138.6, 134.3 (d, $J$ = 2.8 Hz), 129.4, 127.7 (d, $J$ = 7.9 Hz), 126.2, 121.2, 116.5 (d, $J$ = 21.9 Hz), 88.5, 12.5. HRMS (ESI) calcd for $C_{16}H_{14}FN_2OS$ $(M + H)^+$ 301.0811, found 301.0815.



**(3aj)**

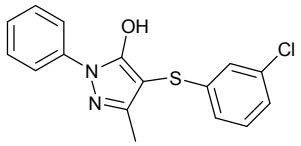
**4-(4-chlorophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**[2], Compound **3aj** was obtained in 91% yield (71.8 mg, 0.227 mmol) according to the general procedure (2h). White solid, mp: 179.1-181.1 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.26 (s,

1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.2, 152.4, 138.5, 138.1, 130.0, 129.4, 129.4, 127.0, 126.2, 121.2, 87.3, 12.7. HRMS (ESI) calcd for $C_{16}H_{14}ClN_2OS$ $(M + H)^+$ 317.0515, found 317.0513.



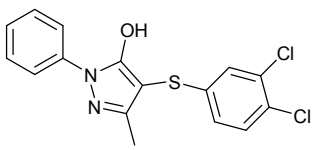
**(3ak)**

**4-(4-bromophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**[2], Compound **3ak** was obtained in 84% yield (76.2 mg, 0.212 mmol) according to the general procedure (3h). White solid, mp: 194.1-194.3 $^{o}$C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.34 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 8.4 Hz, 4H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.7, 152.4, 138.7, 138.6, 132.3, 129.4, 127.4, 126.2, 121.2, 118.1, 87.3, 12.8. HRMS (ESI) calcd for $C_{16}H_{14}BrN_2OS$ $(M + H)^+$ 361.0010, found 361.0011.



**(3al)**

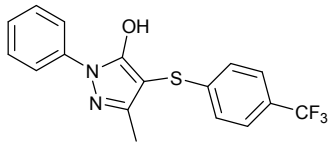
**4-(3-chlorophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**[1], Compound **3al** was obtained in 92% yield (72.9 mg, 0.231 mmol) according to the general procedure (2h). White solid, mp: 182.1-182.9 $^{o}$C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.33 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.33-7.28 (m, 2H), 7.20-7.18 (m, 1H), 7.07-7.05 (m, 2H), 2.14 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.7, 152.4, 141.8, 138.5, 134.3, 131.2, 129.4, 126.3, 125.4, 124.5, 124.0, 121.3, 87.0, 12.7. HRMS (ESI) calcd for $C_{16}H_{14}ClN_2OS$ $(M + H)^+$ 317.0515, found 317.0517.



**(3am)**

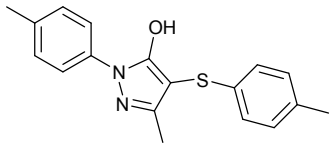
**4-(3,4-dichlorophenylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol**, Compound **3am**

was obtained in 89% yield (77.7 mg, 0.222 mmol) according to the general procedure (2h). White solid, mp: 89.2-90.3 °C. $^1$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 7.75 (d, $J$ = 7.6 Hz, 2H), 7.53 (d, $J$ = 8.5 Hz, 1H), 7.48 (t, $J$ = 7.6 Hz, 2H), 7.30-7.27 (m, 2H), 7.06-7.04 (m, 1H), 2.14 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.4, 140.5, 138.4, 132.2, 131.4, 129.4, 127.8, 126.5, 126.3, 125.5, 121.2, 87.0, 12.7. HRMS (ESI) calcd for $C_{16}H_{13}Cl_2N_2OS$ $(M + H)^+$ 351.0126, found 351.0121.



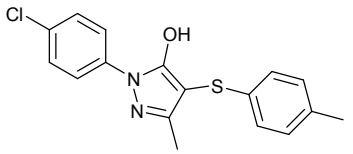
**(3an)**

**3-methyl-1-phenyl-4-(4-(trifluoromethyl)phenylthio)-1H-pyrazol-5-ol**, Compound **3an** was obtained in 97% yield (84.8 mg, 0.242 mmol) according to the general procedure (4h). White solid, mp: 198.9-199.3 °C. $^1$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.40 (s, 1H), 7.76 (d, $J$ = 7.6 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.49 (t, $J$ = 7.6 Hz, 2H), 7.30 (t, $J$ = 7.4 Hz, 1H), 7.27 (d, $J$ = 8.3 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.4, 145.0, 138.5, 129.4, 128.8 (d, $J$ = 132.5Hz), 126.2 (q, $J$ = 3.8 Hz), 125.8 (d, $J$ = 31.7 Hz), 125.4, 124.8 (d, $J$ = 269.9 Hz), 121.3, 88.3, 12.7. HRMS (ESI) calcd for $C_{17}H_{14}F_3N_2OS$ $(M + H)^+$ 351.0779, found 351.0781.



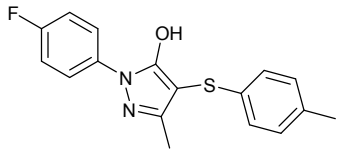
**(3ba)**

**3-methyl-1-p-tolyl-4-(p-tolylthio)-1H-pyrazol-5-ol**[2], Compound **3ba** was obtained in 93% yield (72.2 mg, 0.233 mmol) according to the general procedure (4h). White solid, mp: 98.9-100.7 °C. $^1$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.07 (s, 1H), 7.61 (d, $J$ = 8.5 Hz, 2H), 7.27 (d, $J$ = 8.4 Hz, 2H), 7.10 (d, $J$ = 8.2 Hz, 2H), 6.99 (d, $J$ = 8.2 Hz, 2H), 2.33 (s, 3H), 2.24 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 156.3, 152.0, 136.3, 135.4, 135.3, 134.7, 130.1, 129.8, 125.7, 121.2, 88.2, 21.0, 20.9, 12.8. HRMS (ESI) calcd for $C_{18}H_{19}N_2OS$ $(M + H)^+$ 311.1218, found 311.1215.



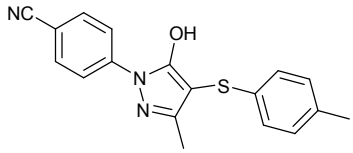

**(3ca)**

**1-(4-chlorophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol**, Compound **3ca** was obtained in 98% yield (81.2 mg, 0.246 mmol) according to the general procedure (2h). White solid, mp: 89.7-90.1 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.38 (s, 1H), 7.80-7.79 (m, 2H), 7.54-7.53 (m, 2H), 7.10 (d, $J$ = 8.2 Hz, 2H), 6.99 (d, $J$ = 8.2 Hz, 2H), 2.24 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 157.5, 152.9, 137.5, 135.1, 134.8, 130.1, 130.1, 129.4, 125.8, 122.4, 88.8, 20.9, 12.8. HRMS (ESI) calcd for $C_{17}H_{16}ClN_2OS$ $(M + H)^+$ 331.0672, found 331.0677.




**(3da)**

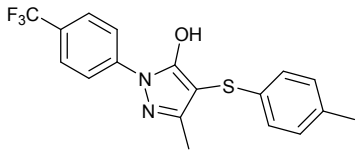
**1-(4-fluorophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol**, Compound **3da** was obtained in 81% yield (64.0 mg, 0.204 mmol) according to the general procedure (2h). White solid, mp: 151.8-152.4 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.21 (s, 1H), 7.78-7.75 (m, 2H), 7.32 (t, $J$ = 8.9 Hz, 2H), 7.10 (d, $J$ = 8.1 Hz, 2H), 6.99 (d, $J$ = 8.2 Hz, 2H), 2.24 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 160.2 (d, $J$ = 241.4 Hz), 156.9, 152.4, 135.2, 135.1, 134.8, 130.1, 125.8, 123.3 (d, $J$ = 8.0 Hz), 116.1 (d, $J$ = 22.6 Hz), 88.5, 20.9, 12.8. HRMS (ESI) calcd for $C_{17}H_{16}FN_2OS$ $(M + H)^+$ 315.0967, found 315.0969.




**(3ea)**

**4-(5-hydroxy-3-methyl-4-(p-tolylthio)-1H-pyrazol-1-yl)benzonitrile**[1], Compound **3ea** was obtained in 77% yield (61.7 mg, 0.192 mmol) according to the general procedure (2h). White solid, mp: 184.2-184.6 °C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.67 (s, 1H), 8.02 (d, $J$ = 8.9 Hz, 2H), 7.93 (d, $J$ = 8.8 Hz, 2H), 7.10 (d, $J$ = 8.2 Hz, 2H), 7.00 (d, $J$ = 8.2 Hz, 2H), 2.23 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR ($^{d6}$DMSO, 125

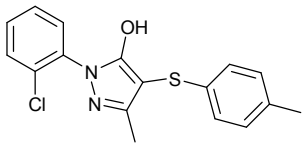
MHz, ppm): 158.7, 154.2, 142.0, 135.0, 134.8, 133.9, 130.2, 125.9, 120.2, 119.2, 107.6, 89.4, 20.9, 12.8. HRMS (ESI) calcd for $C_{18}H_{16}N_3OS$ $(M + H)^+$ 322.1014, found 322.1016.




**(3fa)**

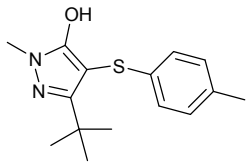
**3-methyl-4-(p-tolylthio)-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-ol**,

Compound **3fa** was obtained in 87% yield (79.2 mg, 0.218 mmol) according to the general procedure (2h). White solid, mp: 173.6-174.2 $^oC$. $^1H$ NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 12.49 (s, 1H), 8.03 (d, $J$ = 8.7 Hz, 2H), 7.85 (d, $J$ = 8.8 Hz, 2H), 7.10 (d, $J$ = 8.2 Hz, 2H), 7.01 (d, $J$ = 8.2 Hz, 2H), 2.24 (s, 3H), 2.14 (s, 3H); $^{13}C$ NMR ($^{d6}$DMSO, 125 MHz, ppm): 158.3, 153.9, 141.7, 134.9 (d, $J$ = 16.0 Hz), 130.2, 127.9, 126.7(q, $J$ = 3.3 Hz), 125.9, 124.7 (d, $J$ = 270.2 Hz), 121.4, 120.5, 89.3, 20.9, 12.8. HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2OS$ $(M + H)^+$ 365.0935, found 365.0933.




**(3ga)**

**1-(2-chlorophenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol**, Compound **3ga** was obtained in 90% yield (74.6 mg, 0.226 mmol) according to the general procedure (5h). White solid, mp: 98.7-100.1 $^oC$. $^1H$ NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 11.86 (s, 1H), 7.67-7.65 (m, 1H), 7.56-7.48 (m, 3H), 7.11 (d, $J$ = 8.1 Hz, 2H), 7.00 (d, $J$ = 8.0 Hz, 2H), 2.25 (s, 3H), 2.08 (s, 3H); $^{13}C$ NMR ($^{d6}$DMSO, 125 MHz, ppm): 158.4, 152.4, 135.8, 135.6, 134.6, 131.9, 131.0, 130.6, 130.5, 130.1, 128.4, 125.5, 86.4, 20.9, 12.8. HRMS (ESI) calcd for $C_{17}H_{16}ClN_2OS$ $(M + H)^+$ 331.0672, found 331.0677.




**(3ha)**

**3-tert-butyl-1-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol**, Compound **3ha** was

obtained in 90% yield (62.3 mg, 0.226 mmol) according to the general procedure (4h). White solid, mp: 211.4-211.6 $^{o}$C. $^{1}$H NMR ($^{d6}$DMSO, 500 MHz, ppm): $\delta$ 11.14 (s, 1H), 7.06 (d, $J$ = 8.2 Hz, 2H), 6.86 (d, $J$ = 8.2 Hz, 2H), 3.52 (s, 3H), 2.22 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR ($^{d6}$DMSO, 125 MHz, ppm): 159.1, 157.2, 136.7, 134.0, 129.8, 124.9, 82.4, 33.9, 33.8, 29.6, 20.9. HRMS (ESI) calcd for $C_{15}H_{21}N_2OS$ $(M + H)^+$ 277.1375, found 277.1371.

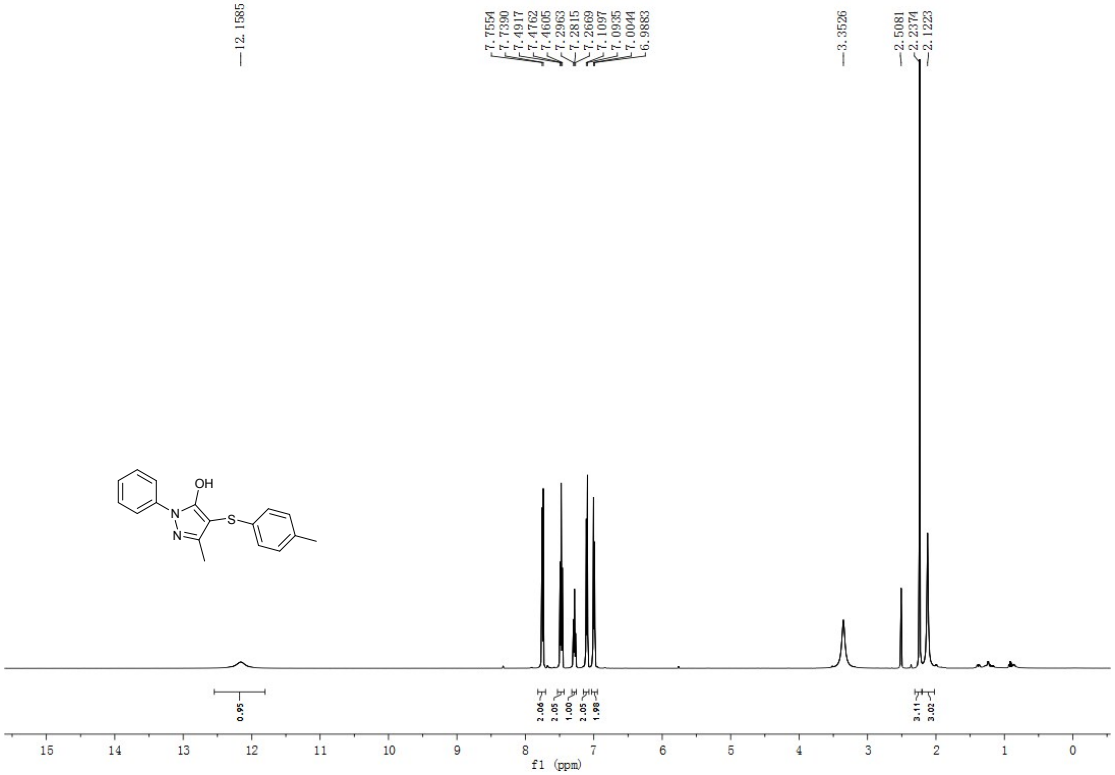
## 6. Reference

[1] X. Zhao, L. Zhang, T. Li, G. Liu, H. Wang and K. Lu, *Chem. Commun.,* 2014, **50**, 13121.

[2] V. B. Purohit, S. C. Karad, K. H. Patel and D. K. Raval, *Tetrahedron,* 2016, **72**, 1114.

## 7.Copies of NMR spectra for compounds 3aa-3ha

**3aa**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7.0935
7.0044
6.9883
3.3526
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2.2374
2.1223
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S
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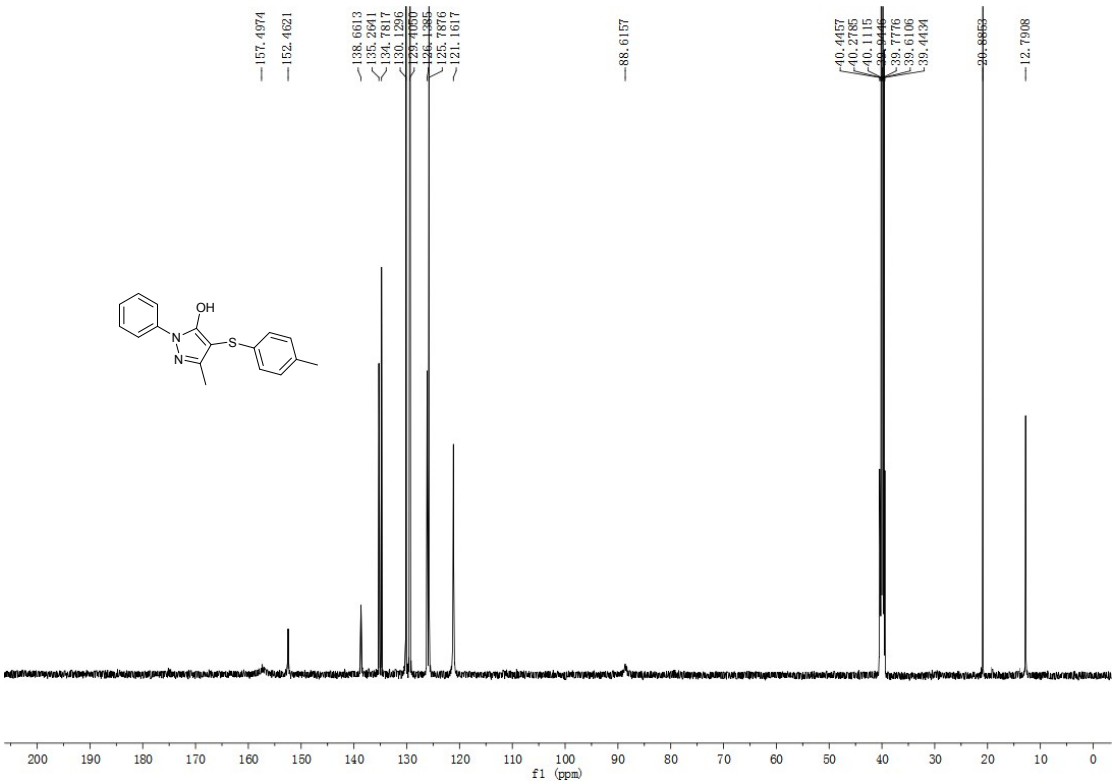
2.05
1.00
2.05
1.98
3.11
3.03
f1 (ppm)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88.6157
40.4457
40.2785
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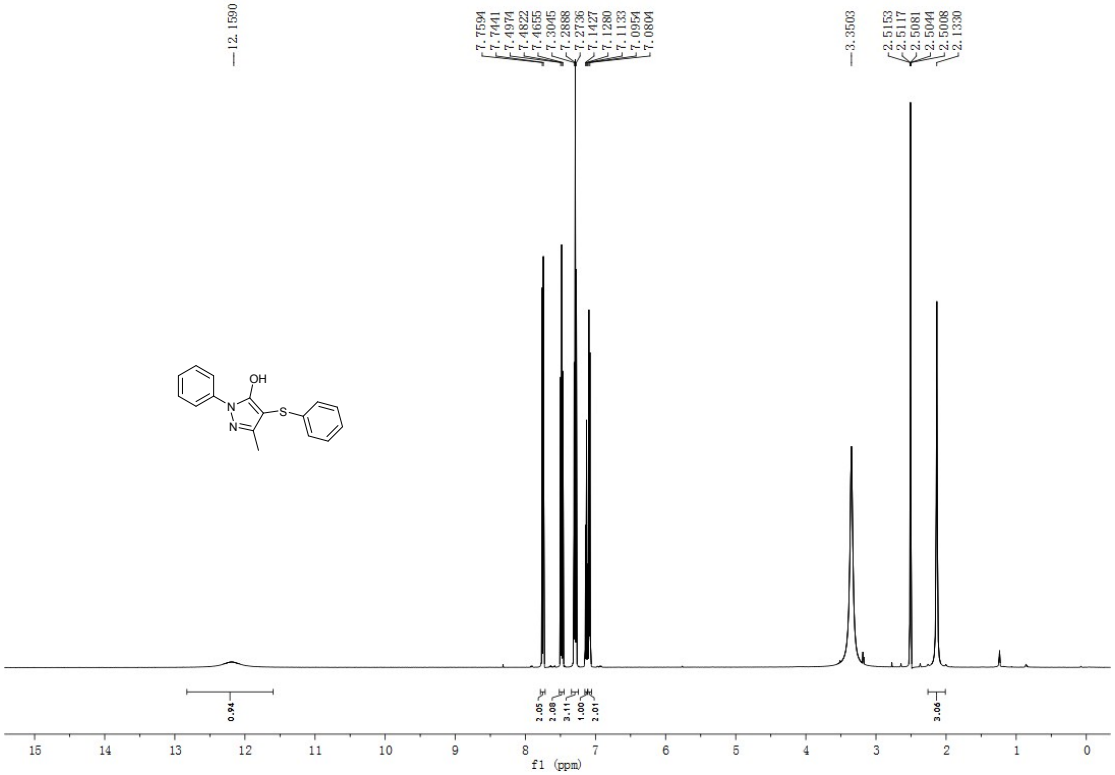
N
S
f1 (ppm)

**3ab**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7.1133
7.0954
7.0804
3.3503
2.5153
2.5117
2.5081
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2.1330
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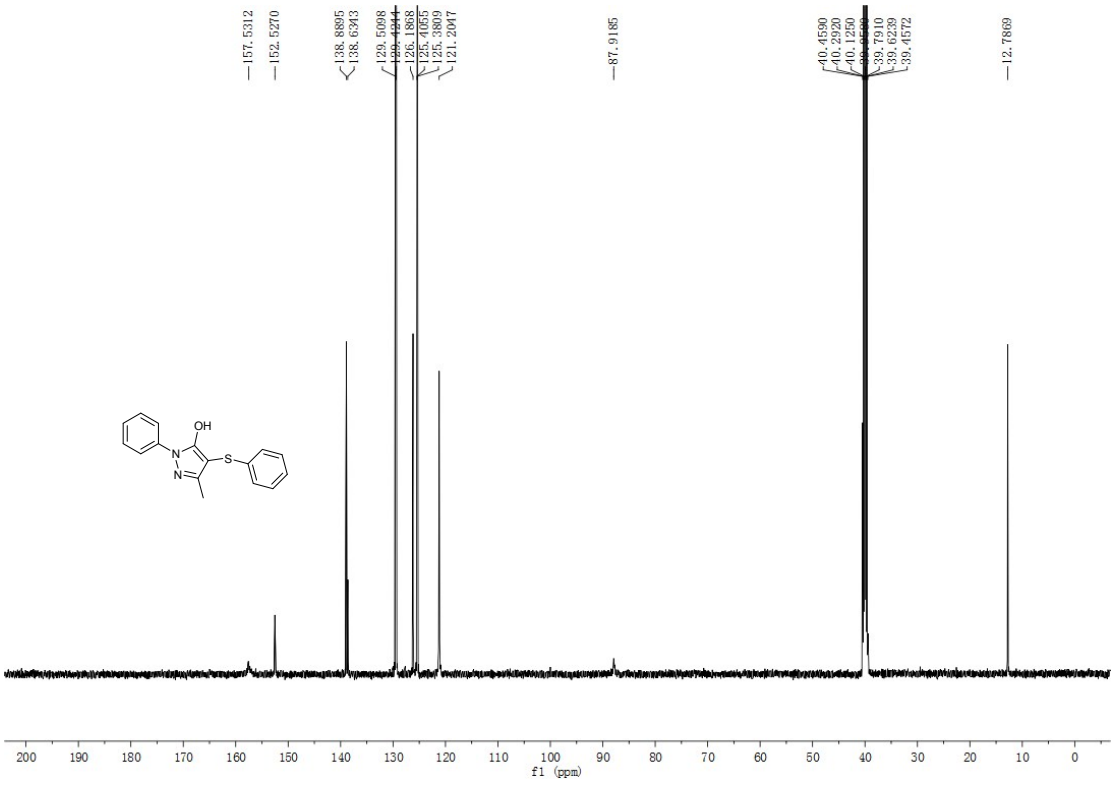
1.00
2.01
3.04
f1 (ppm)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125.3809
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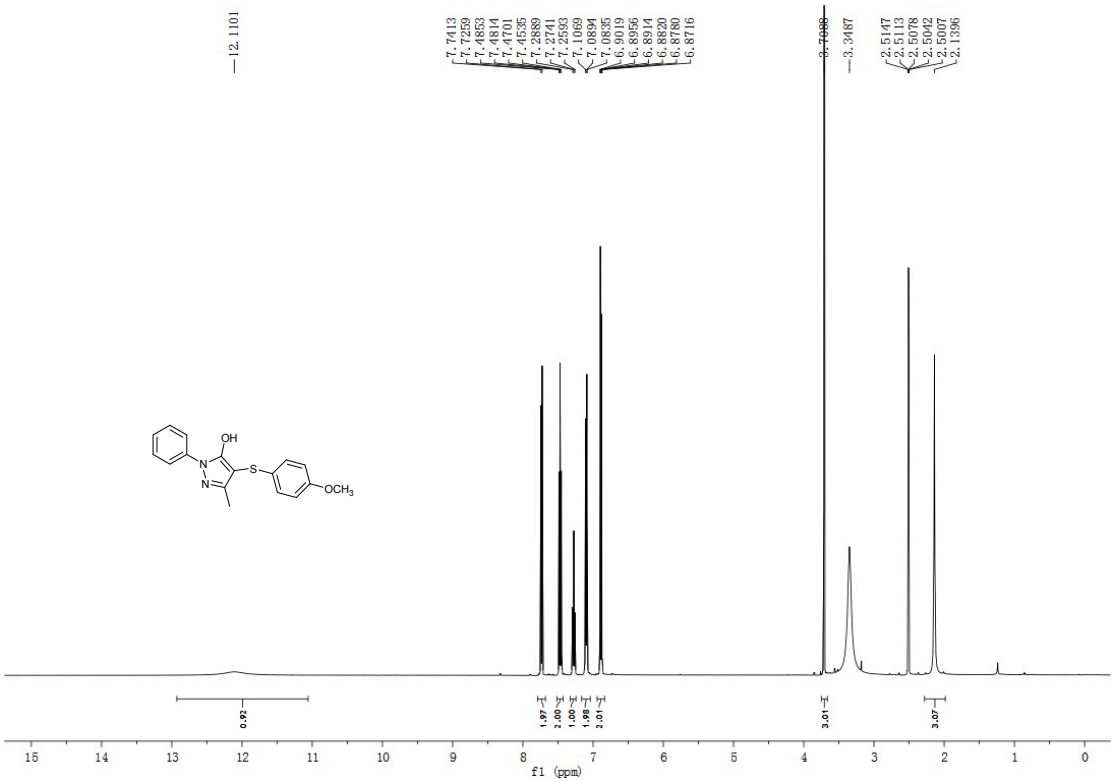
40.2920
40.1250
39.7910
39.6239
39.4572
12.7869
f1 (ppm)

**3ac**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7.1069
7.0894
7.0835
6.9019
6.8956
6.8914
6.8820
6.8780
6.8716
3.7988
3.3487
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2.5113
2.5078
2.5042
2.5007
2.1396
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1.00
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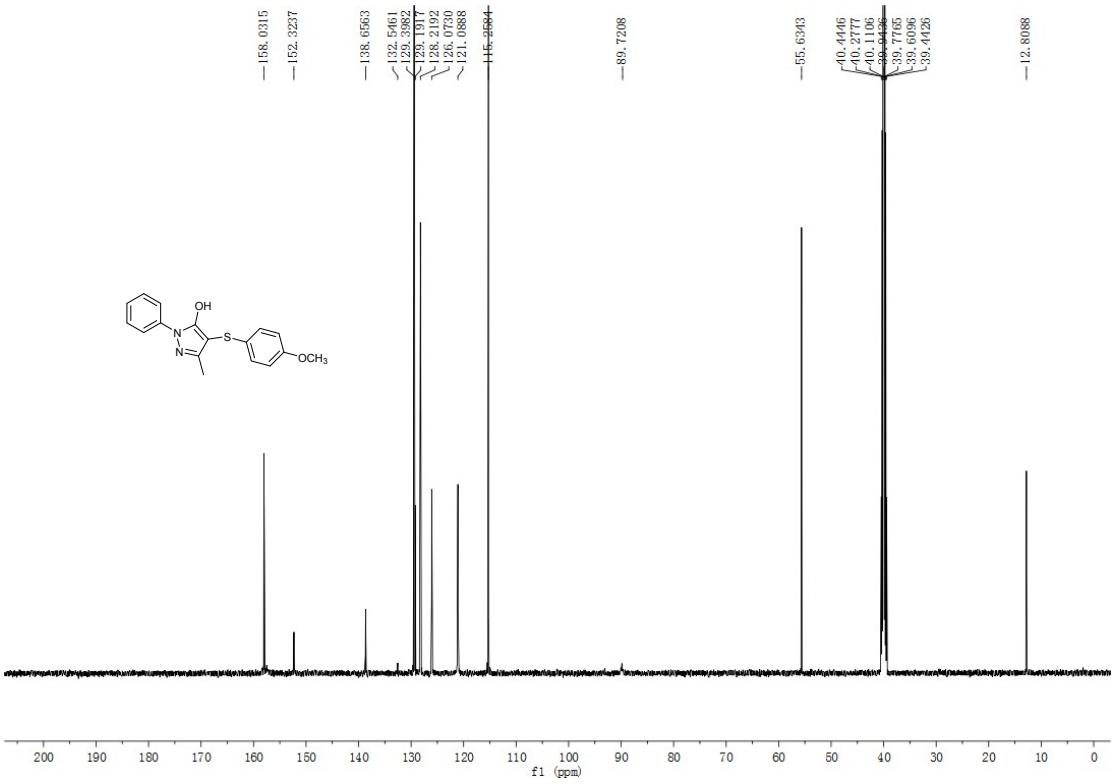
2.01
3.01
3.07
f1 (ppm)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55.6343
40.4446
40.2777
40.1106
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39.4426
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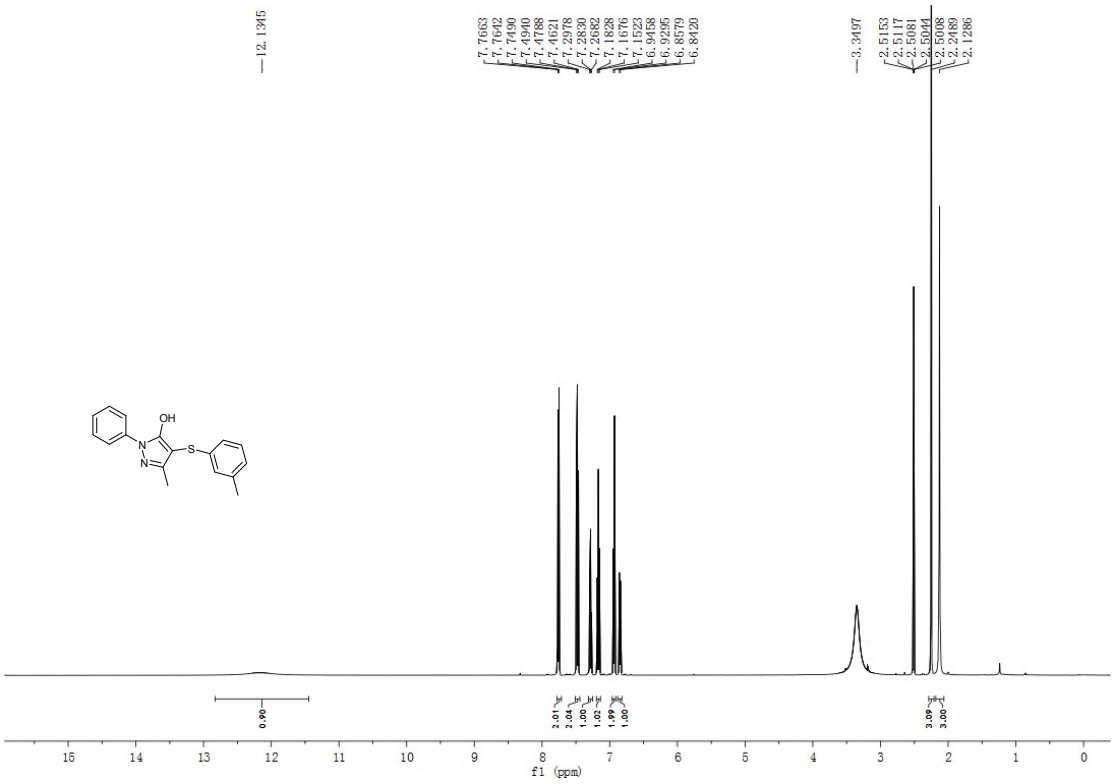
N
S
OCH3
f1 (ppm)

**3ad**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7.1828
7.1676
7.1523
6.9458
6.9295
6.8579
6.8420
3.3497
2.5153
2.5117
2.5081
2.5044
2.5008
2.2489
2.1286
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S
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1.99
1.00
3.09
3.00
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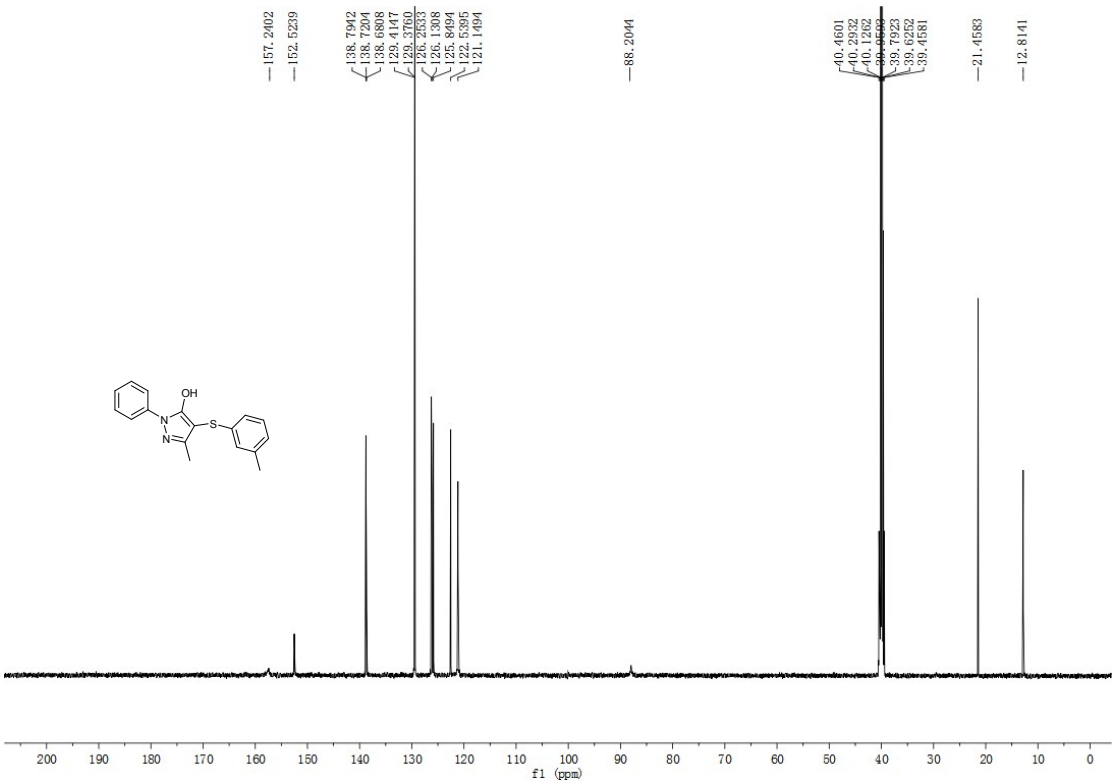
f1 (ppm)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39.7923
39.6252
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N
N
S
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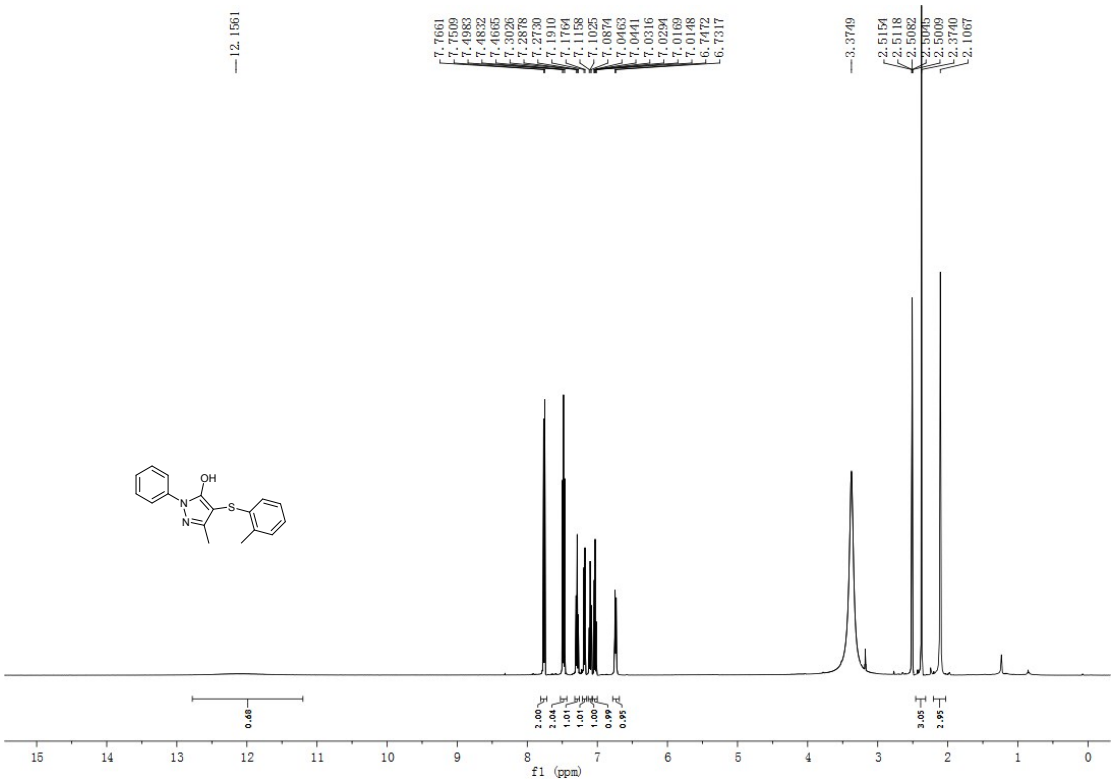
f1 (ppm)

**3ae**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7.0148
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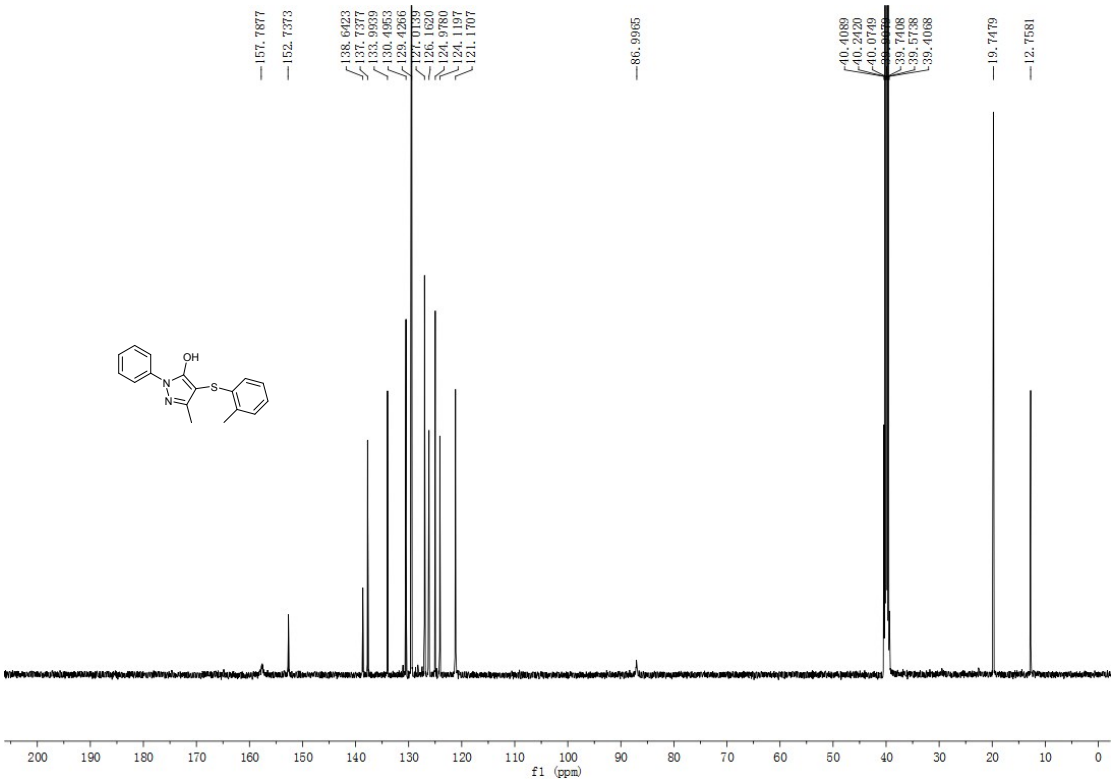
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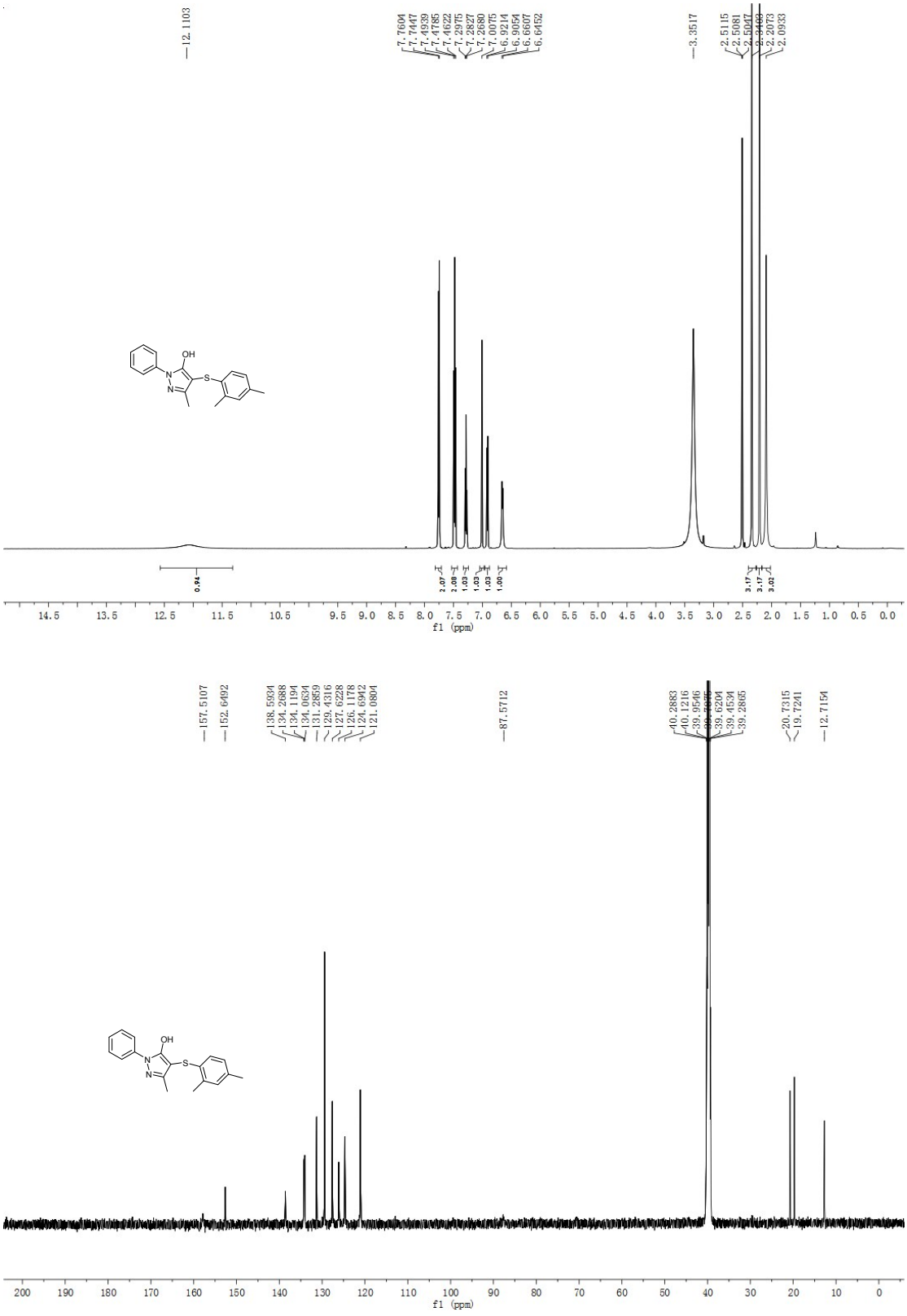
N
N
S
f1 (ppm)

**3af**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6.6452
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2.5115
2.5081
2.5047
2.3468
2.2073
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1.00
3.17
3.17
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f1 (ppm)
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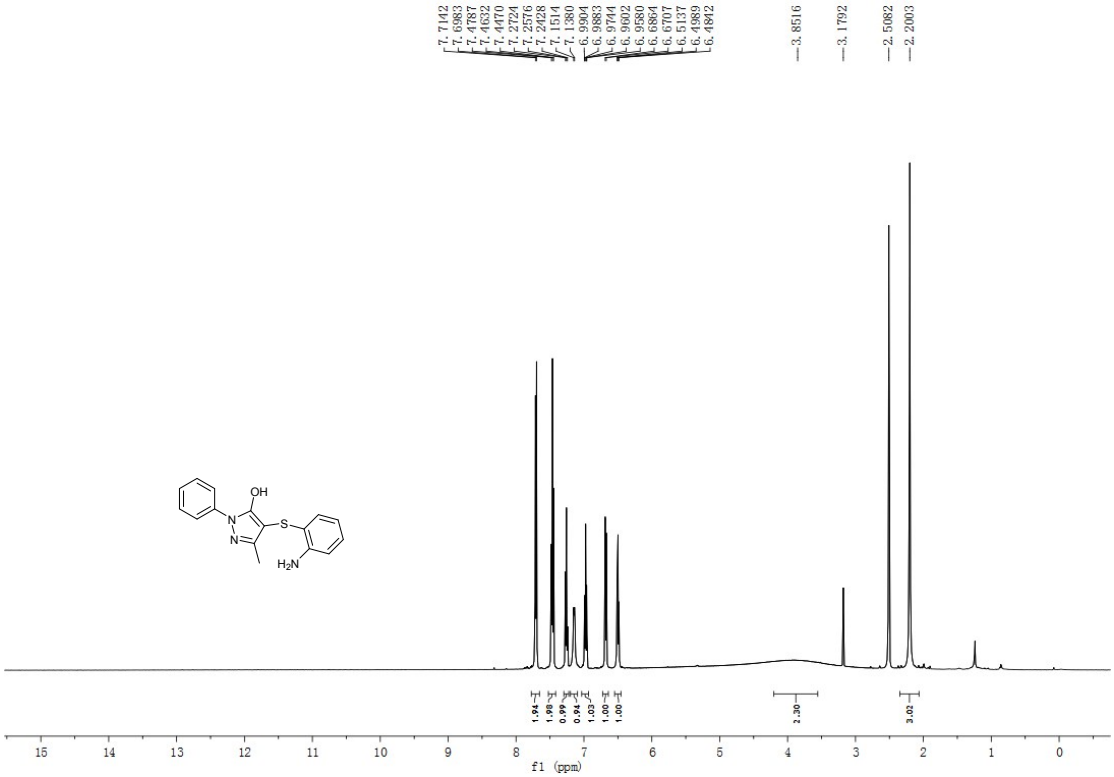
S
f1 (ppm)

**3ag**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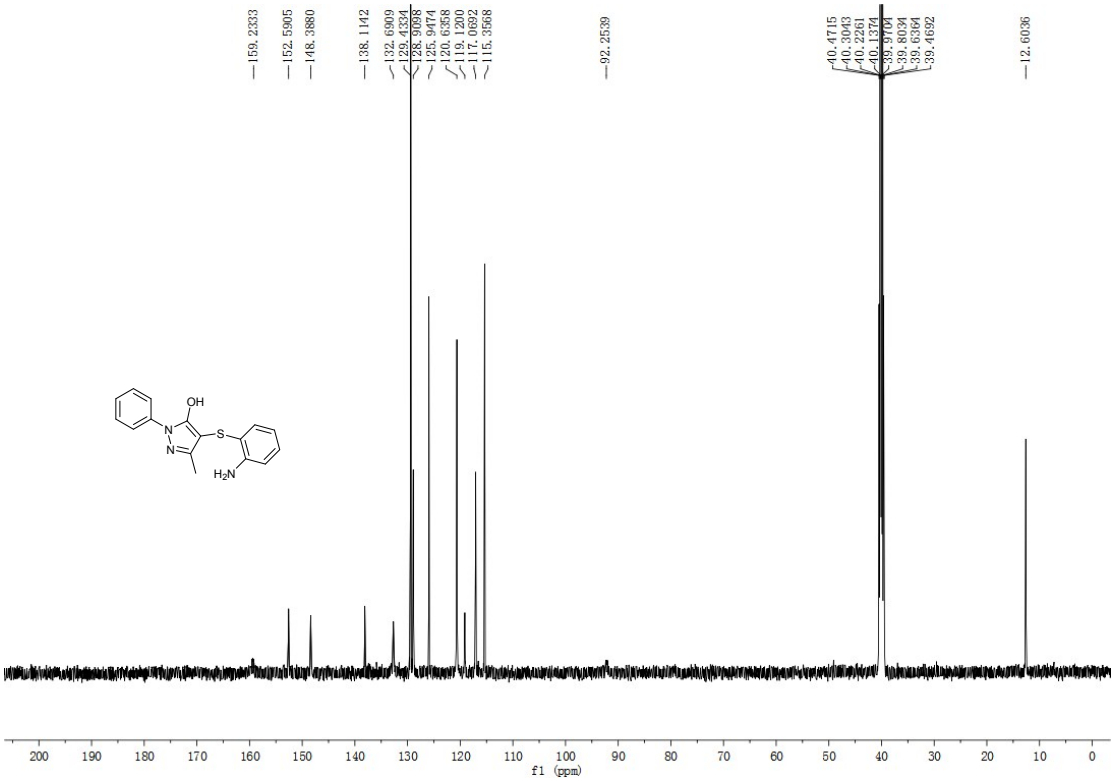
f1 (ppm)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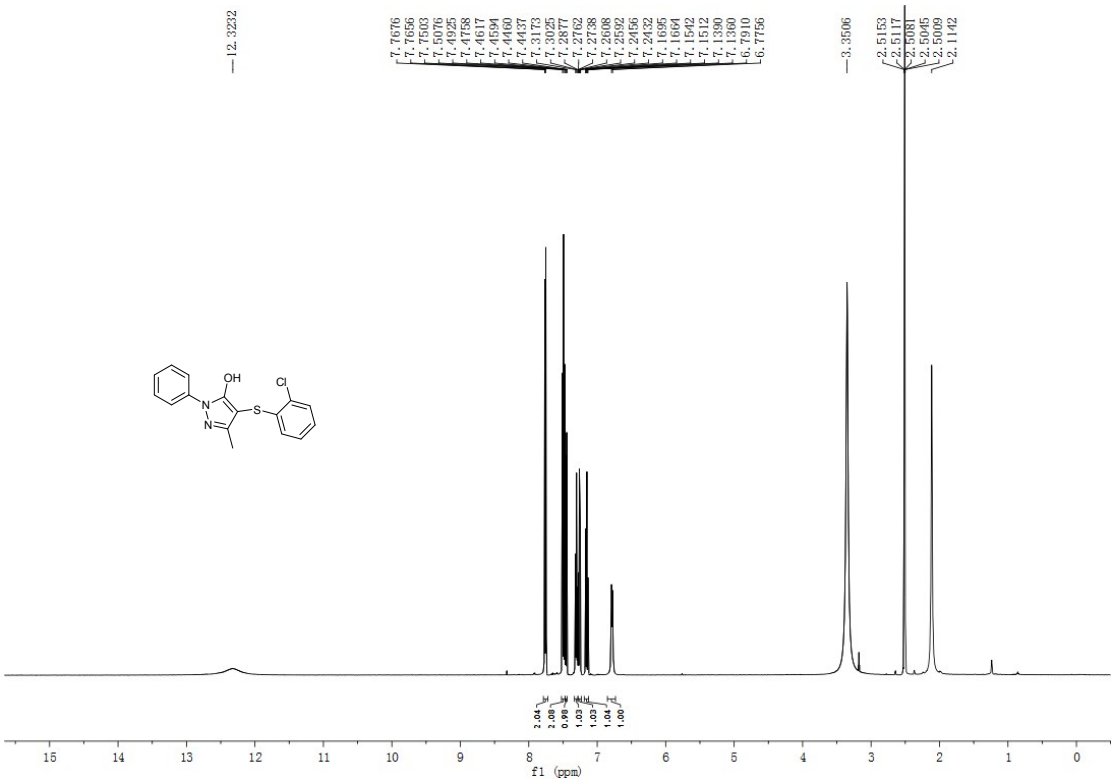
N
S
H2N
f1 (ppm)

**3ah**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2.5045
2.5009
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OH
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S
N
N
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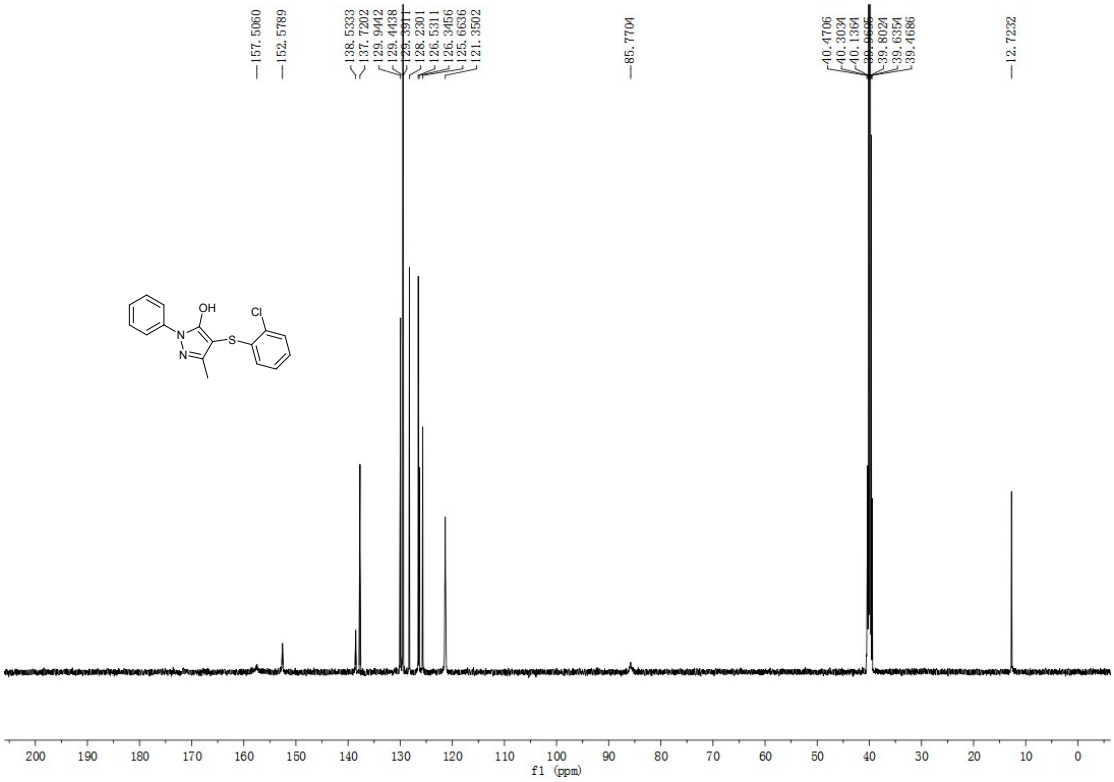
1.00
f1 (ppm)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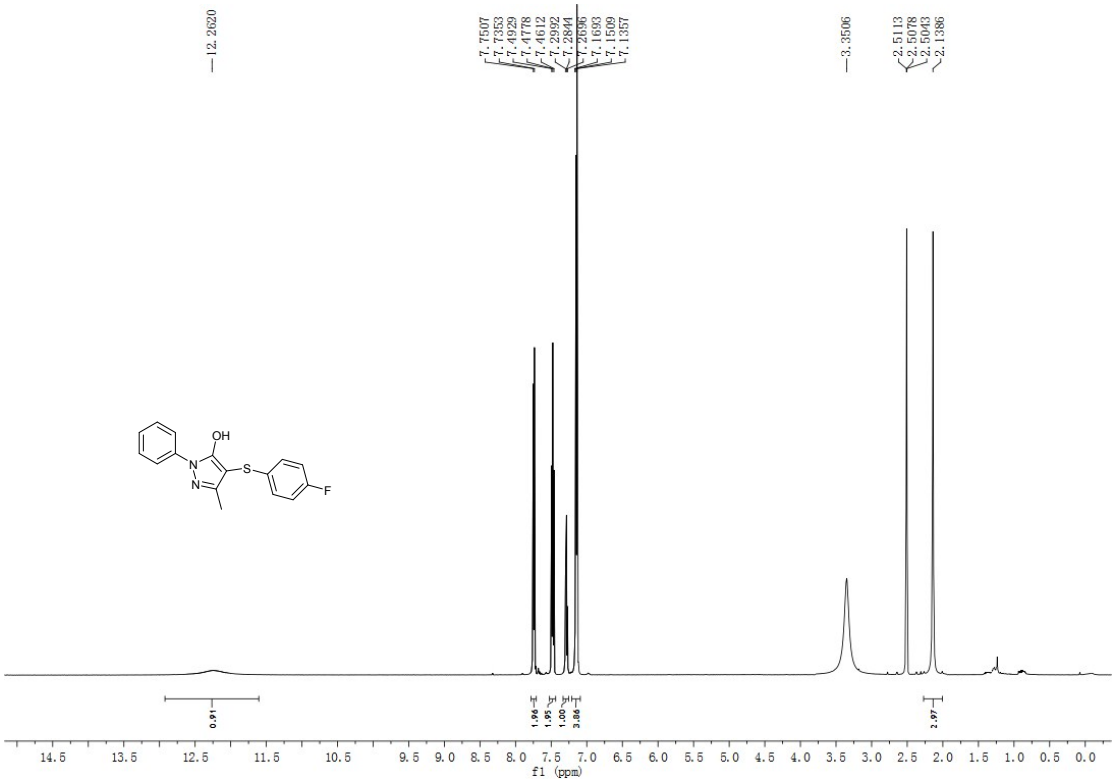
OH
Cl
S
N
N
f1 (ppm)

**3ai**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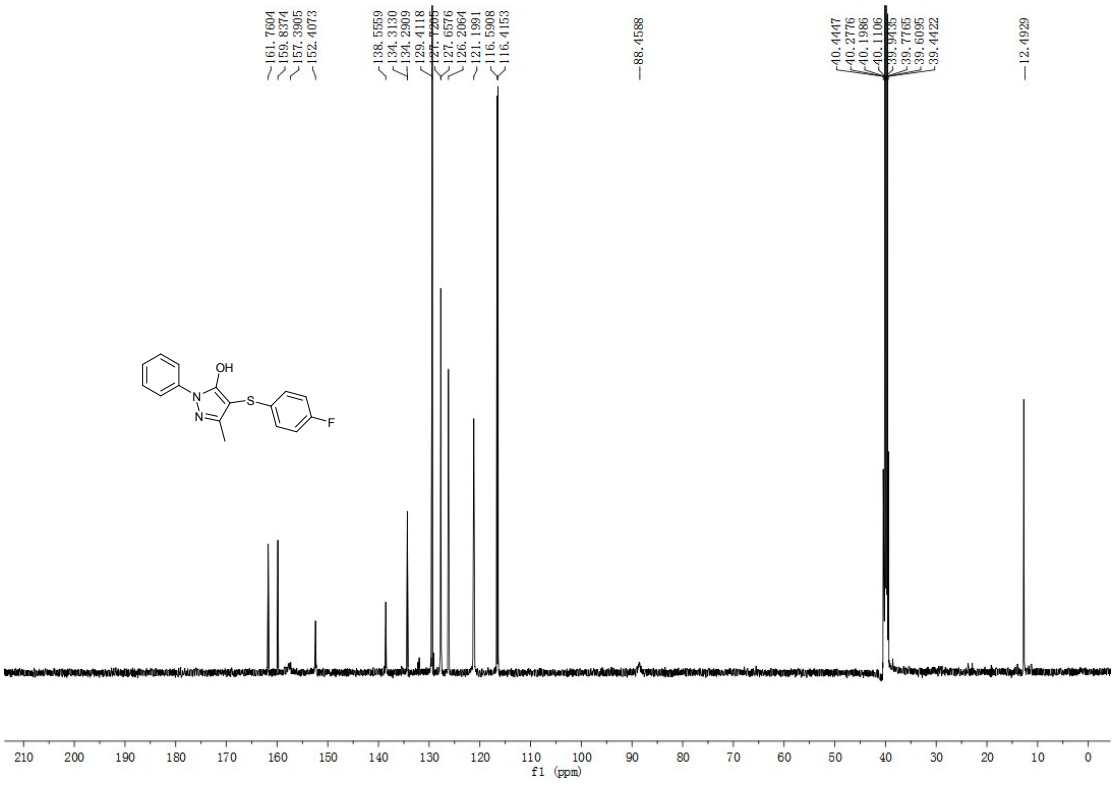
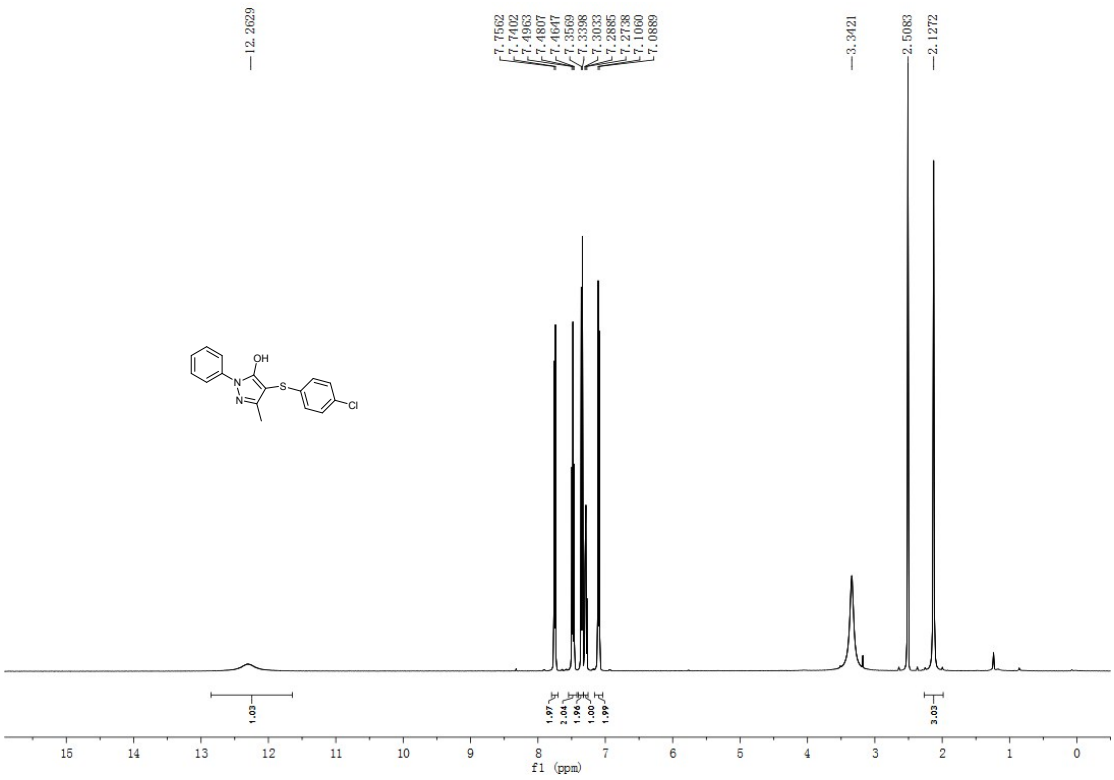
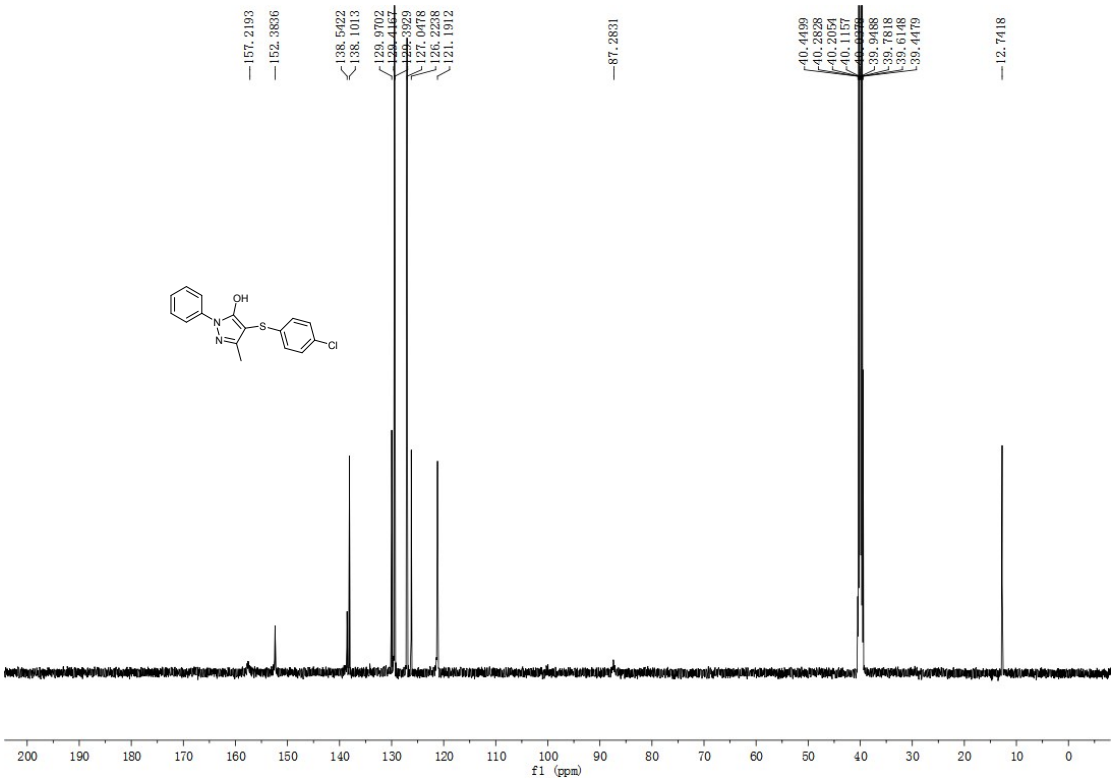
7.7353
7.4929
7.4778
7.4612
7.2992
7.2844
7.2696
7.1693
7.1509
7.1357
3.3506
2.5113
2.5078
2.5043
2.1386
OH
N
N
S
F
f1 (ppm)

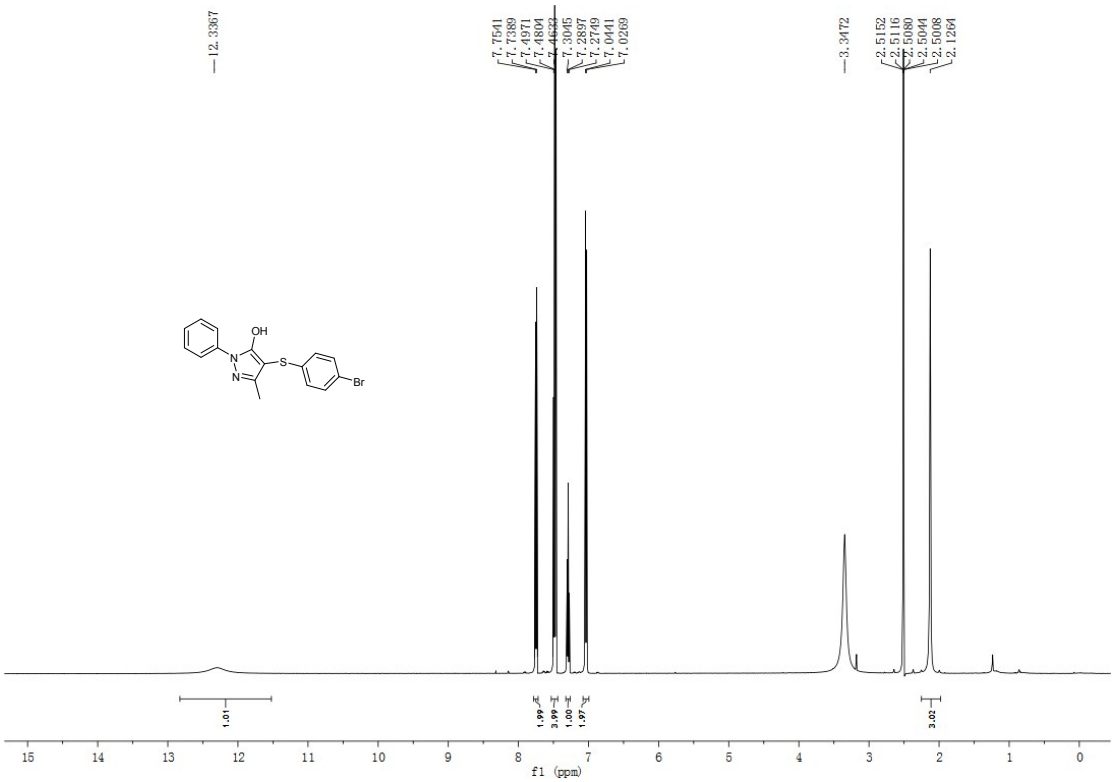

161.7604
159.8374
157.3905
152.4073
138.5559
134.3130
134.2909
129.4118
127.7205
127.6576
126.2064
121.1991
116.5908
116.4153
88.4588
40.4447
40.2776
40.1986
40.1106
39.9435
39.7765
39.6095
39.4422
12.4929
OH
N
N
S
F
f1 (ppm)

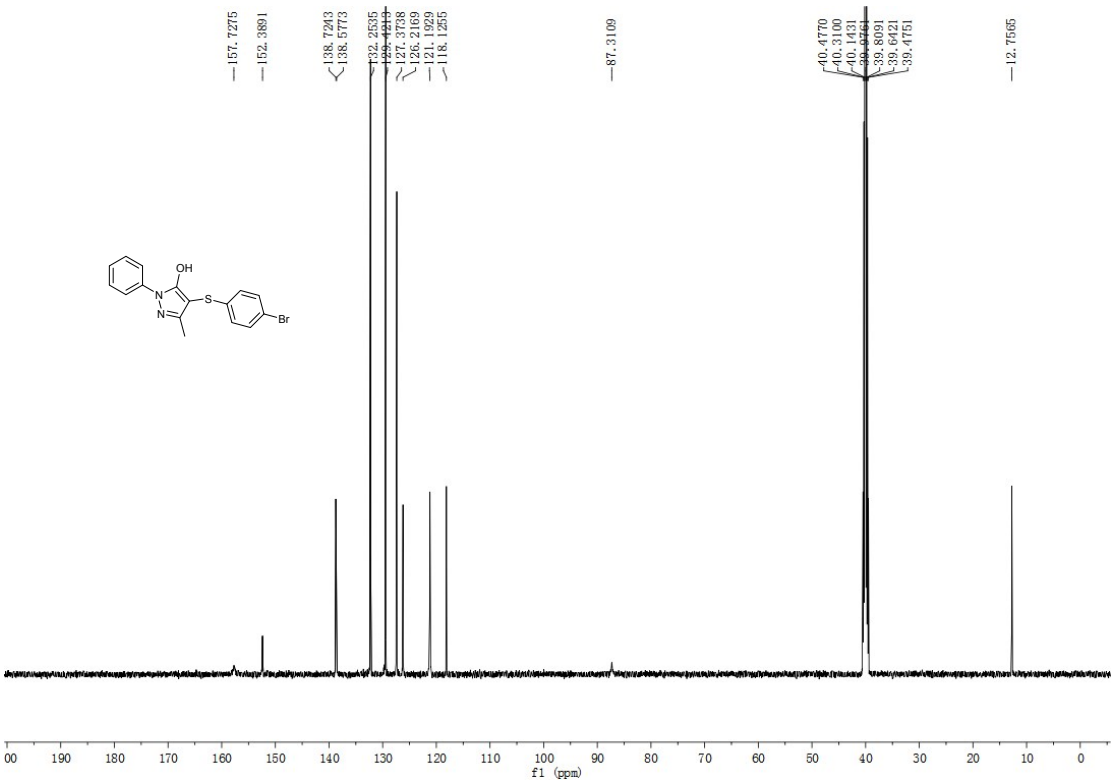
**3aj**


12.2629
7.7562
7.7402
7.4963
7.4807
7.4647
7.3569
7.3398
7.3033
7.2885
7.2738
7.1060
7.0889
3.3421
2.5083
2.1272
OH
N
N
S
Cl
1.03
1.97
2.04
1.96
1.00
1.99
3.03
f1 (ppm)

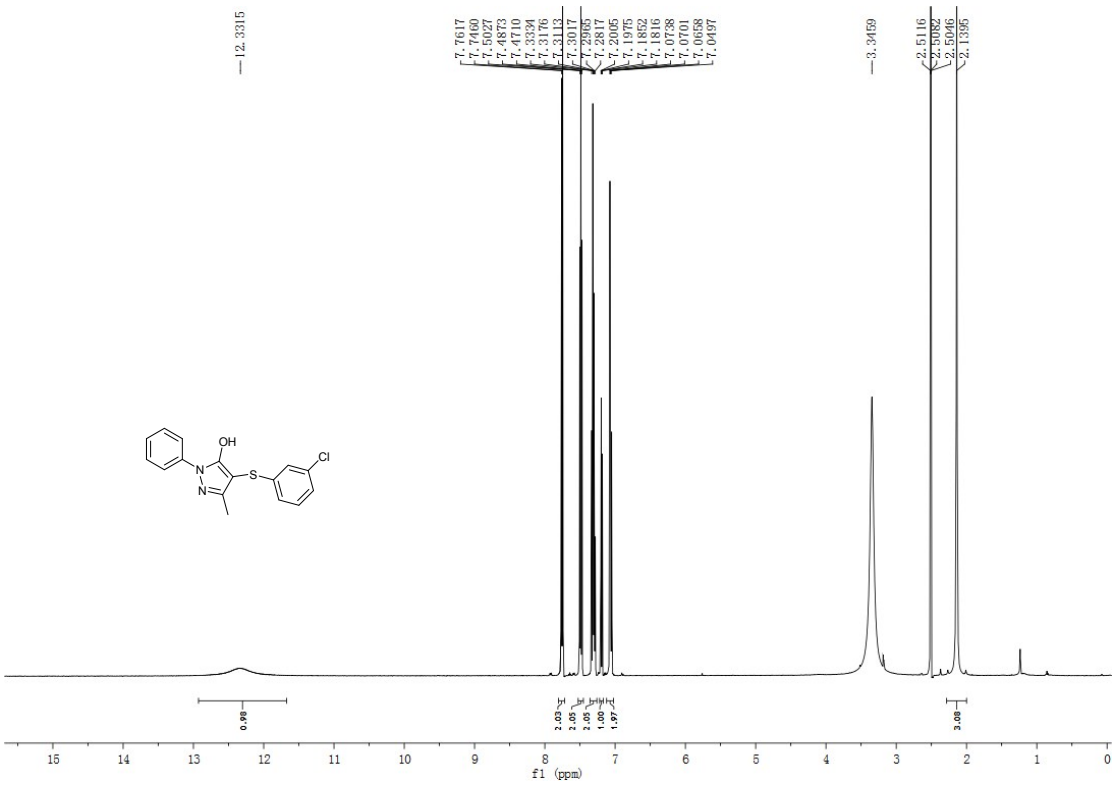

157.2193
152.3836
138.5422
138.1013
129.9702
129.4167
129.3929
127.0478
126.2238
121.1912
87.2831
40.4499
40.2828
40.2054
40.1157
39.9488
39.7818
39.6148
39.4479
12.7418
OH
N
N
S
Cl
f1 (ppm)

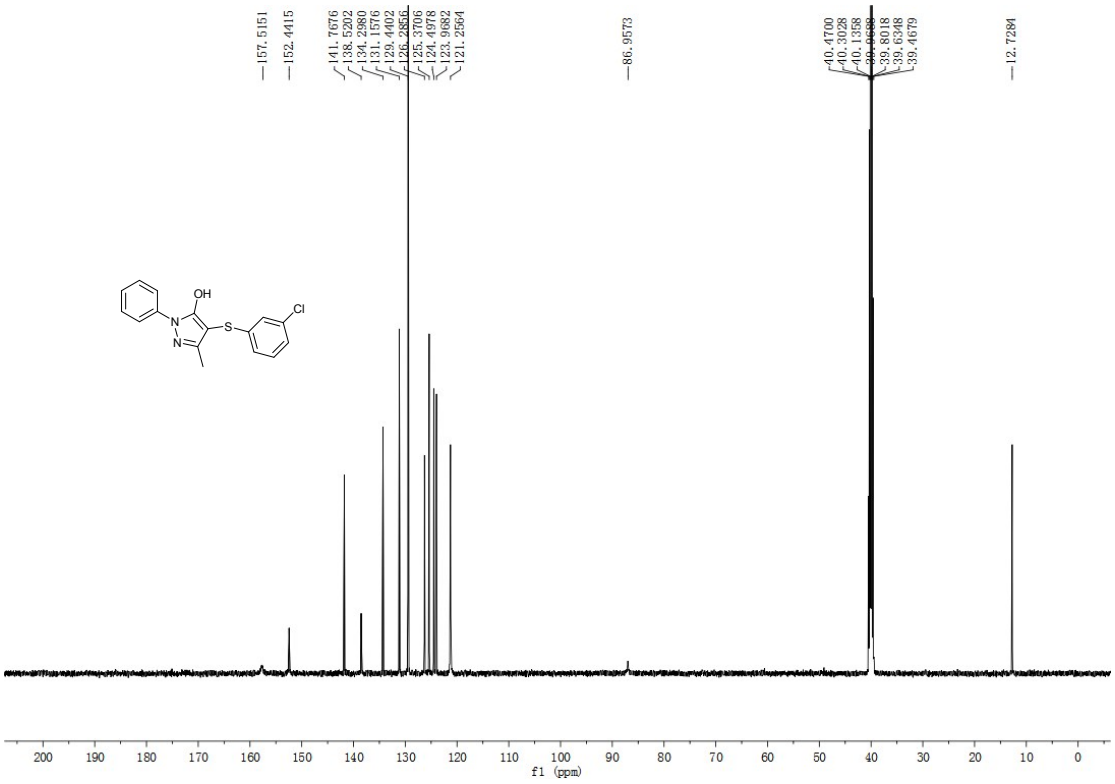
**3ak**


12.3367
7.7541
7.7389
7.4971
7.4804
7.4632
7.3045
7.2897
7.2749
7.0441
7.0269
3.3472
2.5152
2.5116
2.5080
2.5044
2.5008
2.1264
OH
N
N
S
Br
1.01
1.99
3.99
1.00
1.97
3.02
f1 (ppm)

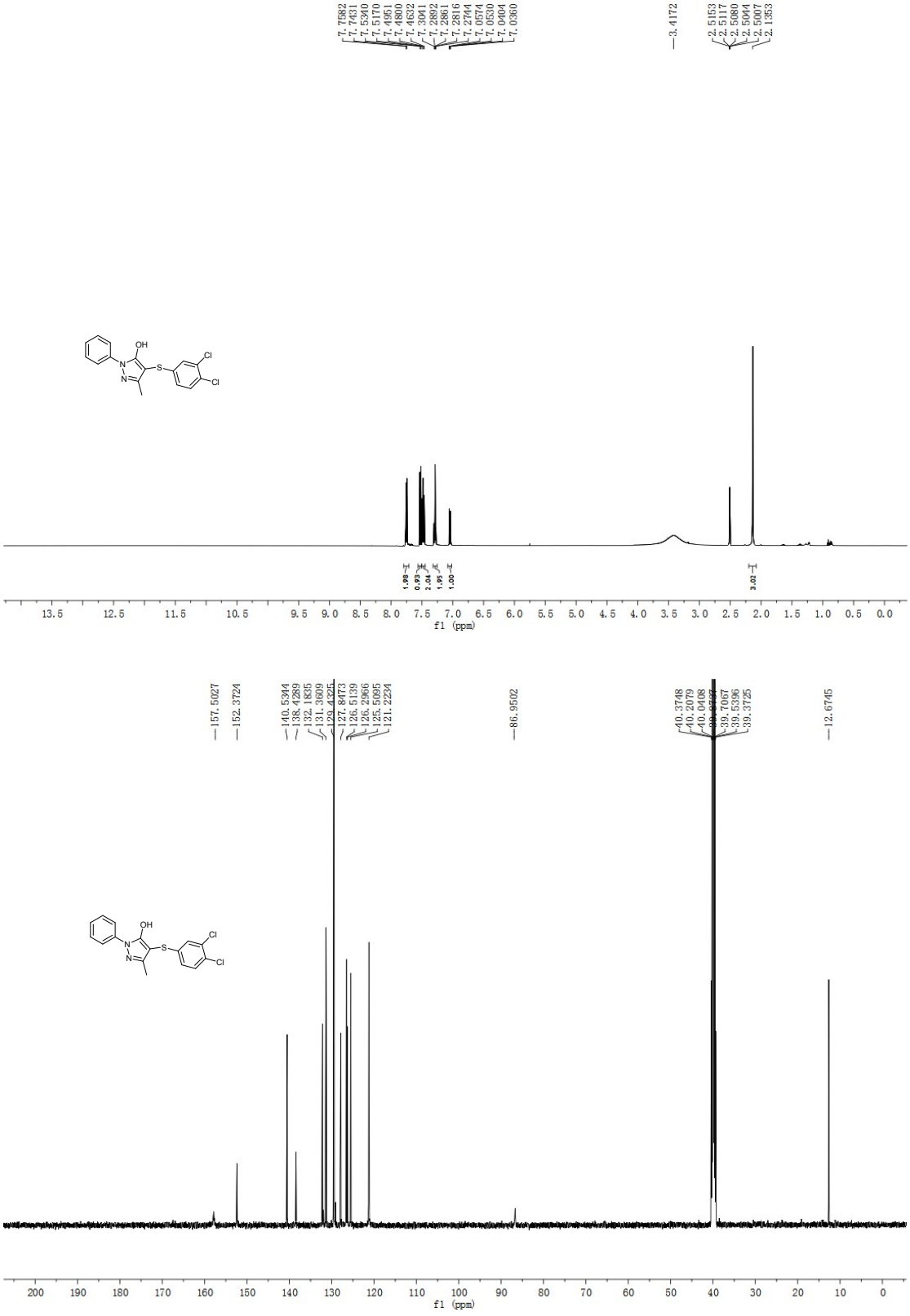

157.7275
152.3891
138.7243
138.5773
132.2535
128.4213
127.3738
126.2169
121.1929
118.1255
87.3109
40.4770
40.3100
40.1431
39.8091
39.6421
39.4751
12.7565
OH
N
N
S
Br
f1 (ppm)

**3al**

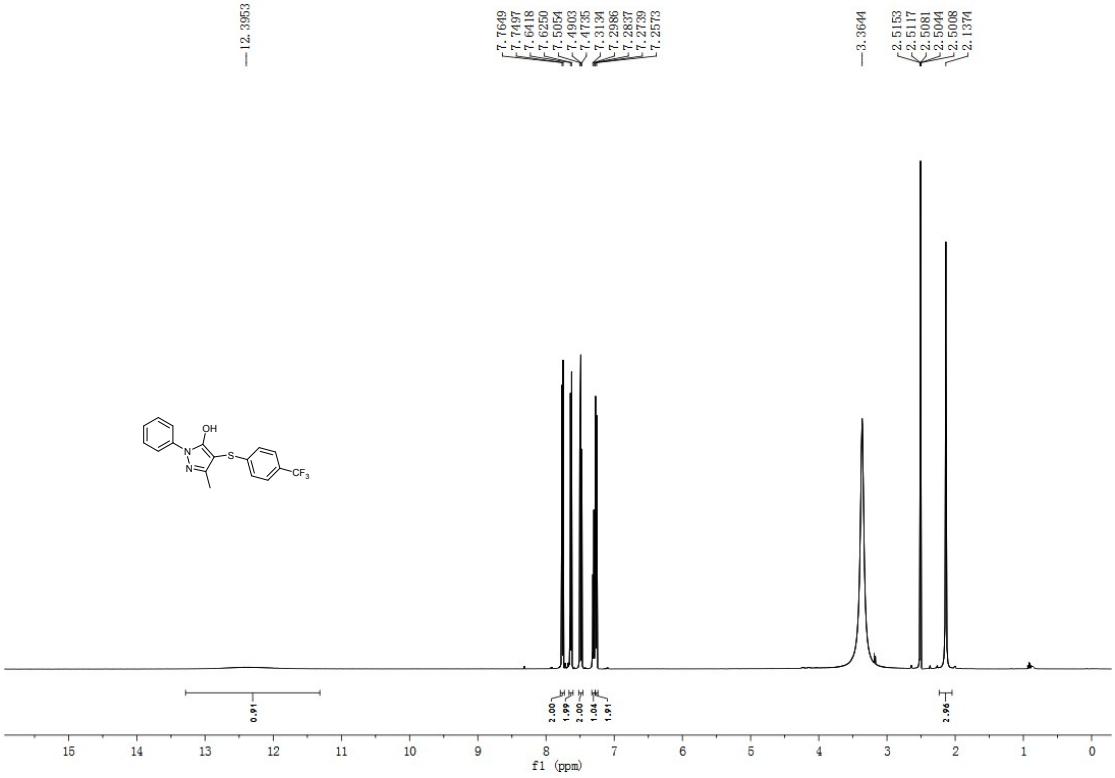

12.3315
7.7617
7.7460
7.5027
7.4873
7.4710
7.3334
7.3176
7.3113
7.3017
7.2965
7.2817
7.2005
7.1975
7.1852
7.1816
7.0738
7.0701
7.0658
7.0497
3.3459
2.5116
2.5082
2.5046
2.1395
OH
N
N
S
Cl
0.98
2.03
2.05
2.05
1.00
1.97
3.09
f1 (ppm)

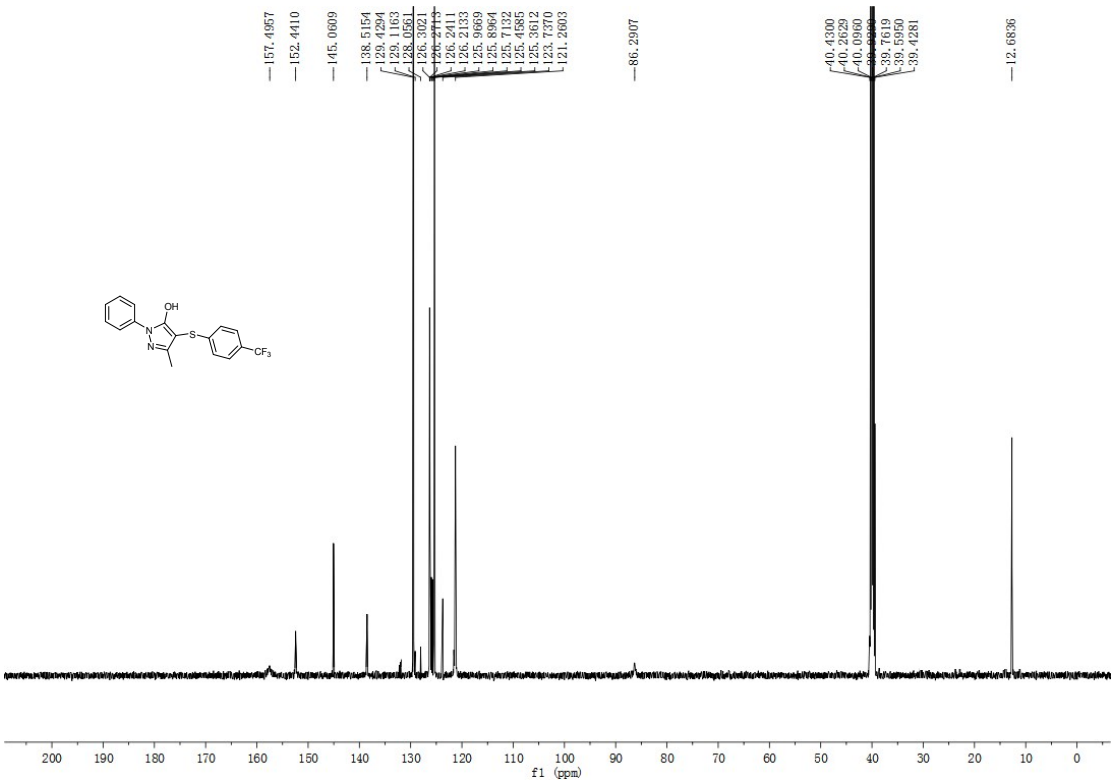

157.5151
152.4415
141.7676
138.5202
134.2980
131.1576
129.4402
126.2856
125.3706
124.4978
123.9682
121.2564
86.9573
40.4700
40.3028
40.1358
39.9688
39.8018
39.6348
39.4679
12.7284
OH
N
N
S
Cl
f1 (ppm)

**3am**

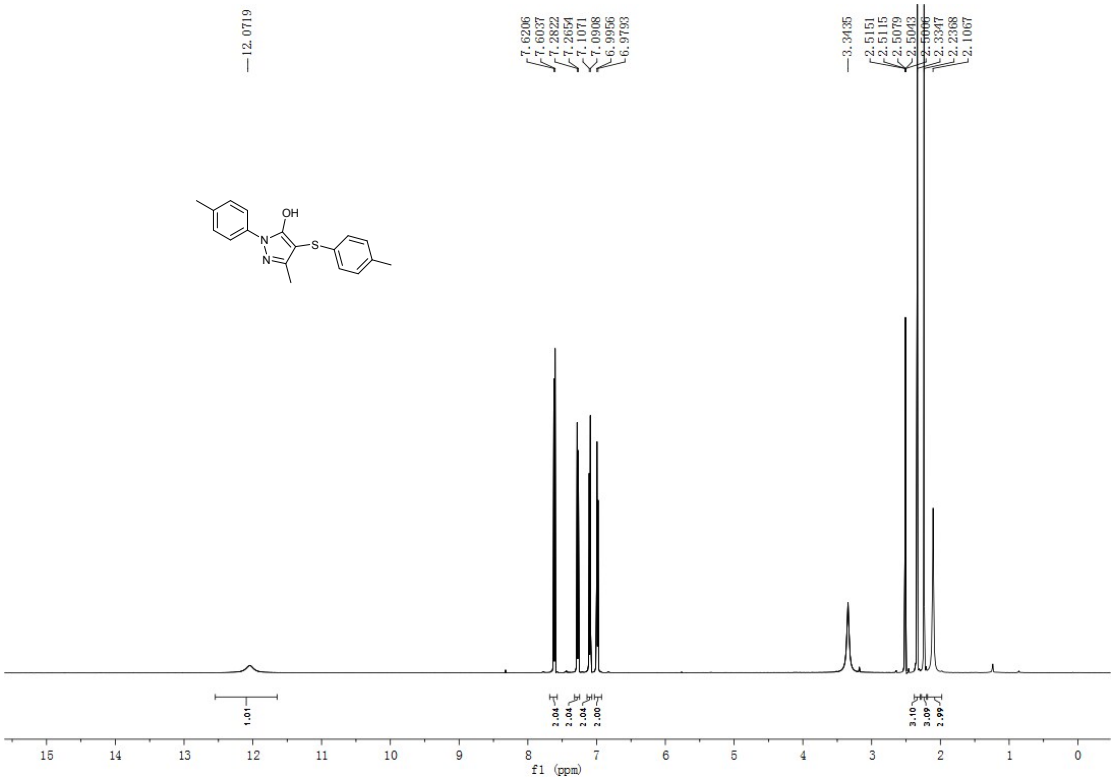

7.7582
7.7431
7.5340
7.5170
7.4951
7.4800
7.4632
7.3041
7.2892
7.2861
7.2816
7.2744
7.0574
7.0530
7.0404
7.0360
3.4172
2.5153
2.5117
2.5080
2.5044
2.5007
2.1353
OH
N
N
S
Cl
Cl
1.98
0.93
2.04
1.95
1.00
3.02
f1 (ppm)
157.5027
152.3724
140.5344
138.4289
132.1835
131.3609
129.4325
127.8473
126.5139
126.2966
125.5095
121.2234
86.9502
40.3748
40.2079
40.0408
39.7067
39.5396
39.3725
12.6745
f1 (ppm)

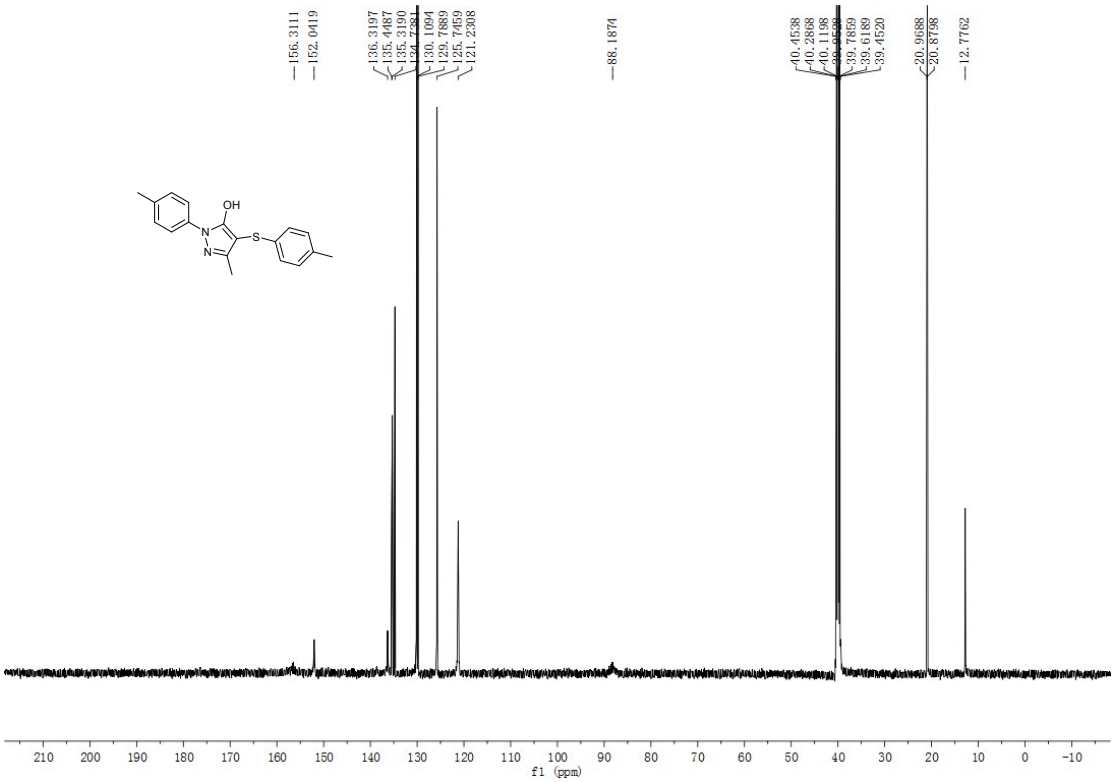
**3an**


12.3953
7.7649
7.7497
7.6418
7.6250
7.5054
7.4903
7.4735
7.3134
7.2986
7.2837
7.2739
7.2573
3.3644
2.5153
2.5117
2.5081
2.5044
2.5008
2.1374
OH
N
N
S
CF3
0.91
2.00
1.99
2.00
1.04
1.91
2.94
f1 (ppm)

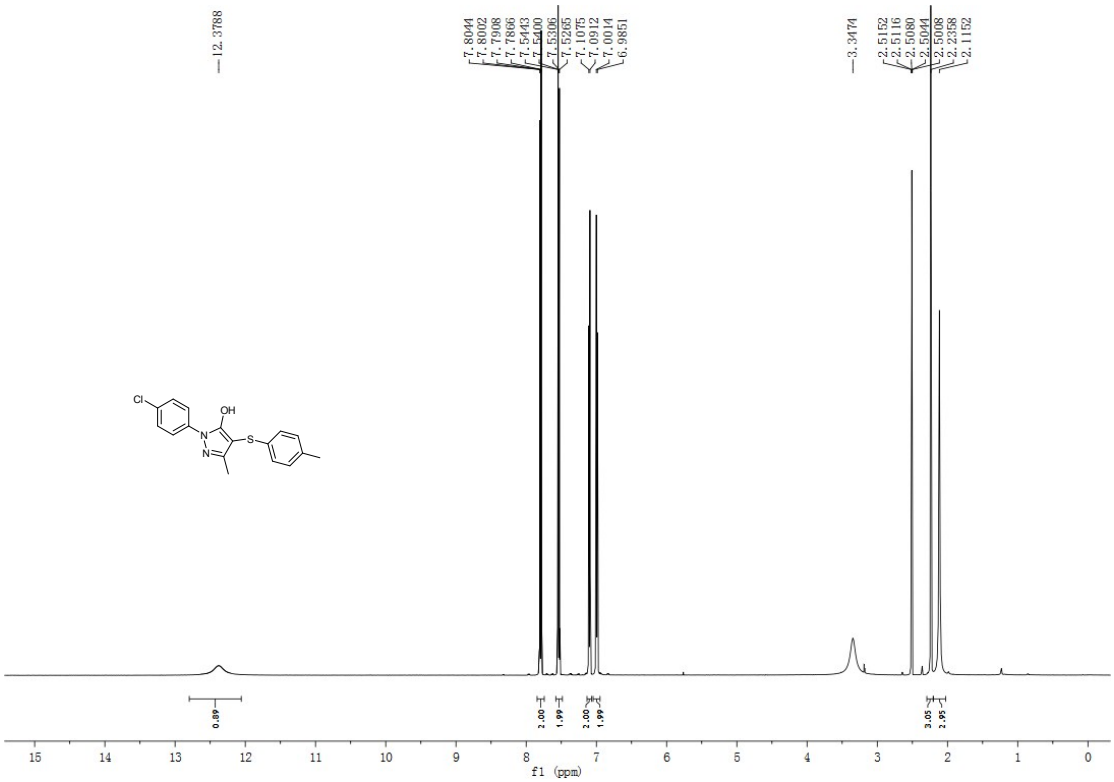

157.4957
152.4410
145.0609
138.5154
129.4294
129.1163
128.1951
126.3021
126.2115
126.2111
126.2033
125.9669
125.8964
125.7122
125.4815
125.3612
123.7370
121.2603
86.2907
40.4300
40.2629
40.0960
39.7619
39.5950
39.4281
12.6836
OH
N
N
S
CF3
f1 (ppm)

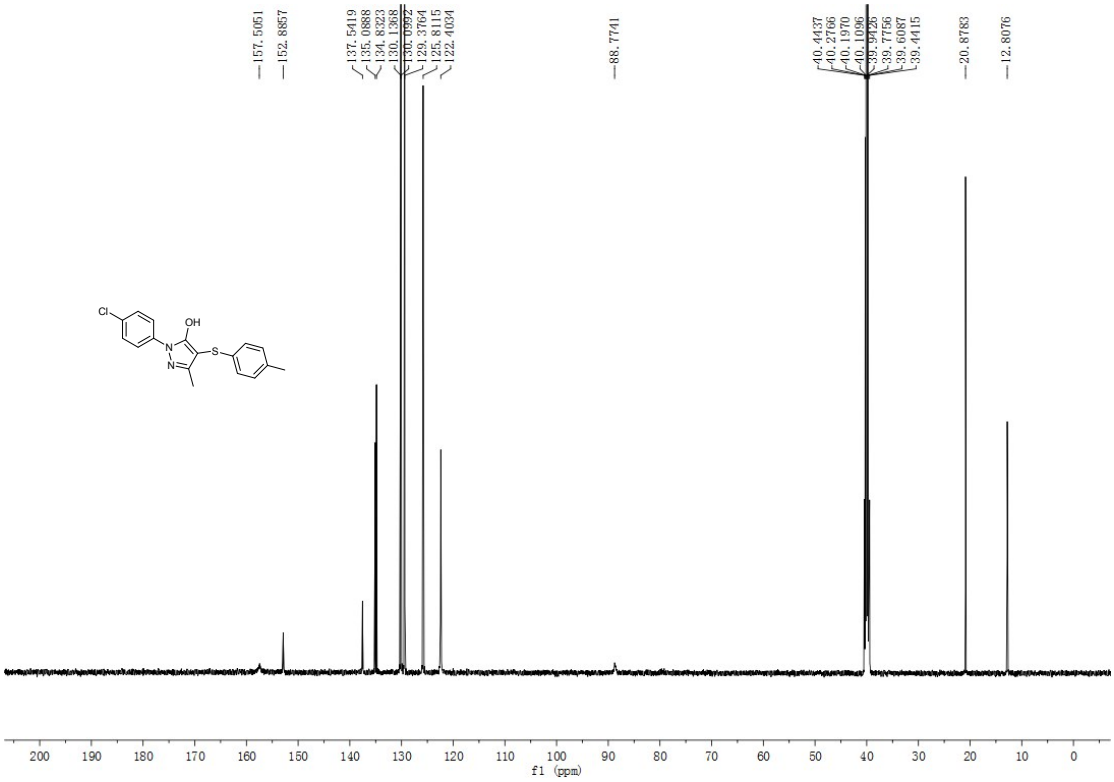
**3ba**


12.0719
7.6206
7.6037
7.2822
7.2654
7.1071
7.0908
6.9956
6.9793
3.3435
2.5151
2.5115
2.5079
2.5043
2.3347
2.2368
2.1067
OH
N
N
S
1.01
2.04
2.04
2.04
2.00
3.10
3.09
2.97
f1 (ppm)

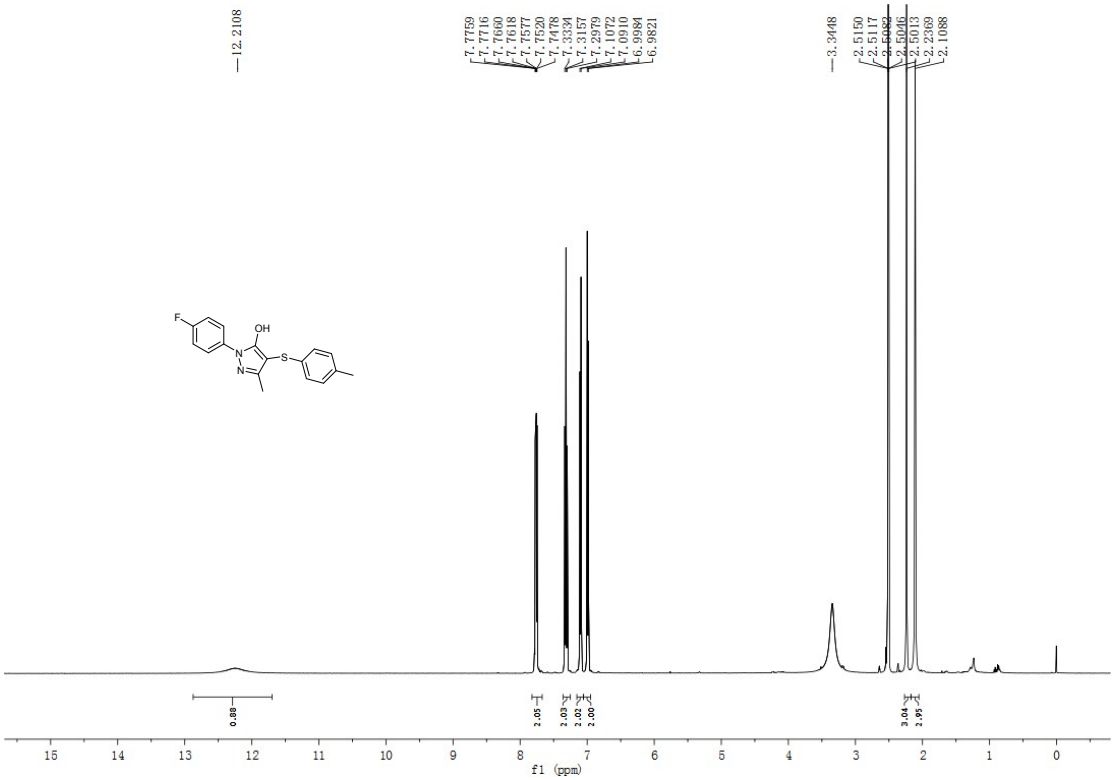

156.3111
152.0419
136.3197
135.4087
135.3190
134.7381
130.1094
129.7889
125.7459
121.2308
88.1874
40.4538
40.2868
40.1198
39.7859
39.6189
39.4520
20.9688
20.8798
12.7762
OH
N
N
S
f1 (ppm)

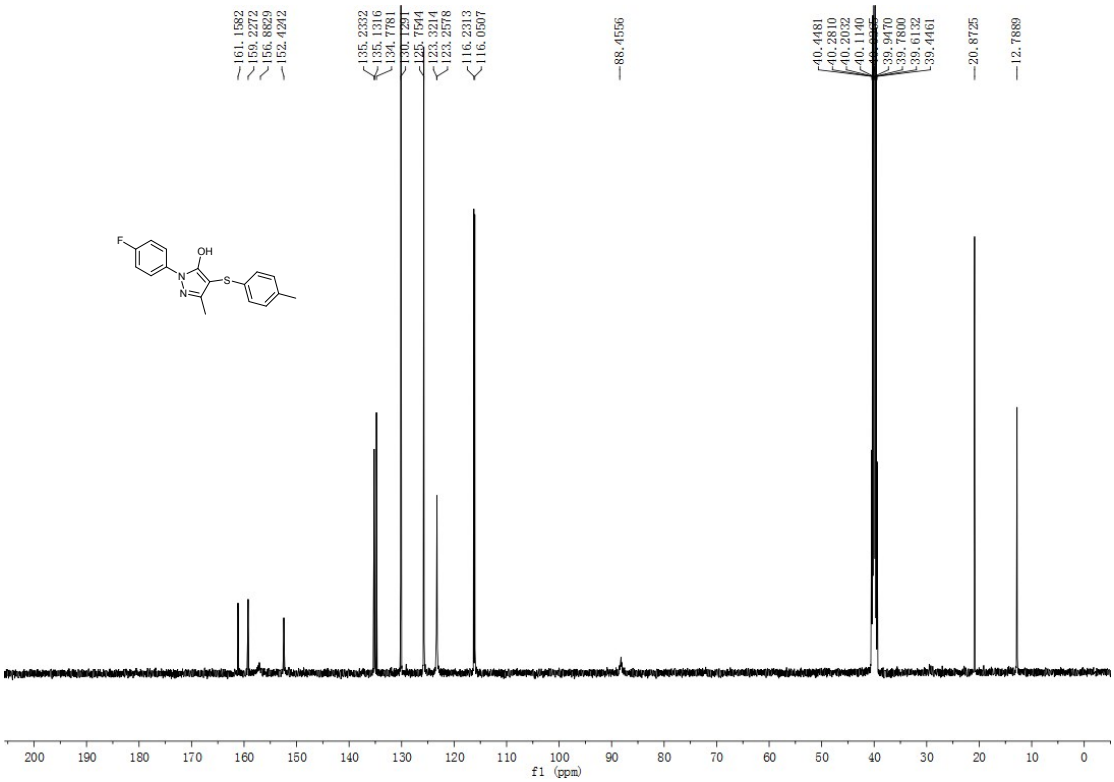
**3ca**


12.3788
7.8044
7.8002
7.7908
7.7866
7.5443
7.5400
7.5306
7.5285
7.1075
7.0912
7.0014
6.9851
3.3474
2.5152
2.5116
2.5080
2.5044
2.5008
2.2358
2.1152
Cl
OH
N
N
S
0.89
2.00
1.99
2.00
1.99
3.05
2.95
f1 (ppm)

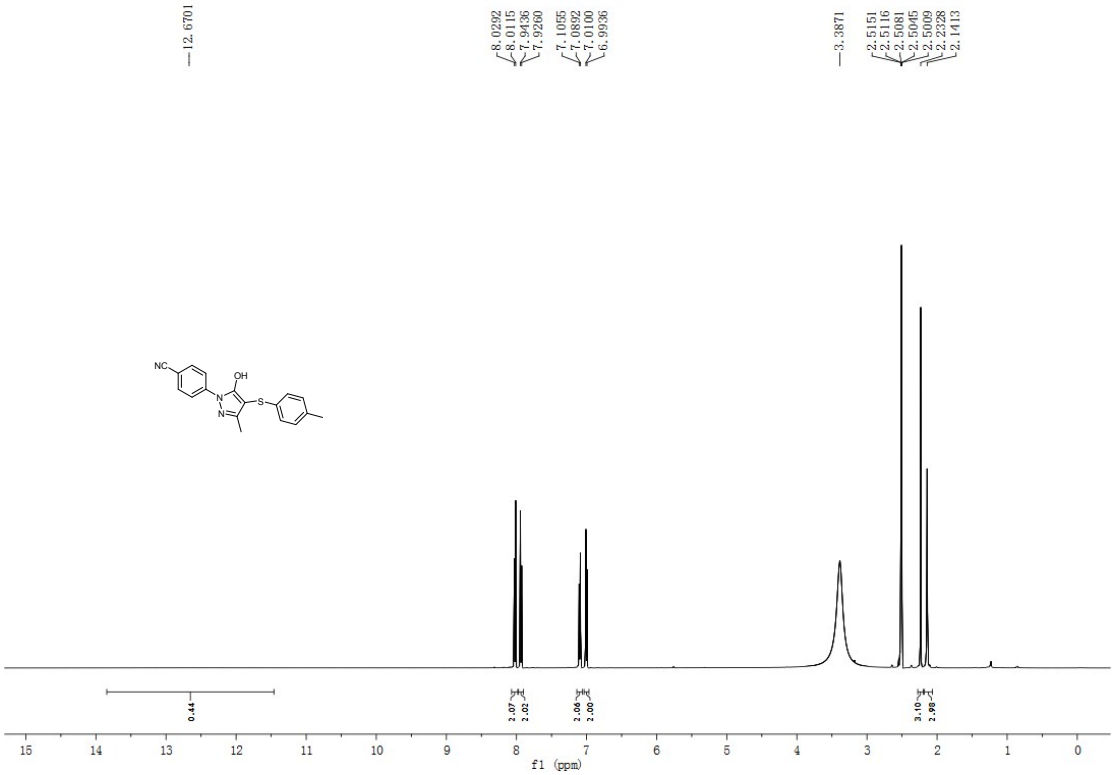

157.5051
152.8857
137.5419
135.0888
134.8323
130.1368
130.0992
129.3764
125.8115
122.4034
88.7741
40.4437
40.2766
40.1970
40.1096
39.9126
39.7756
39.6087
39.4415
20.8783
12.8076
Cl
OH
N
N
S
f1 (ppm)

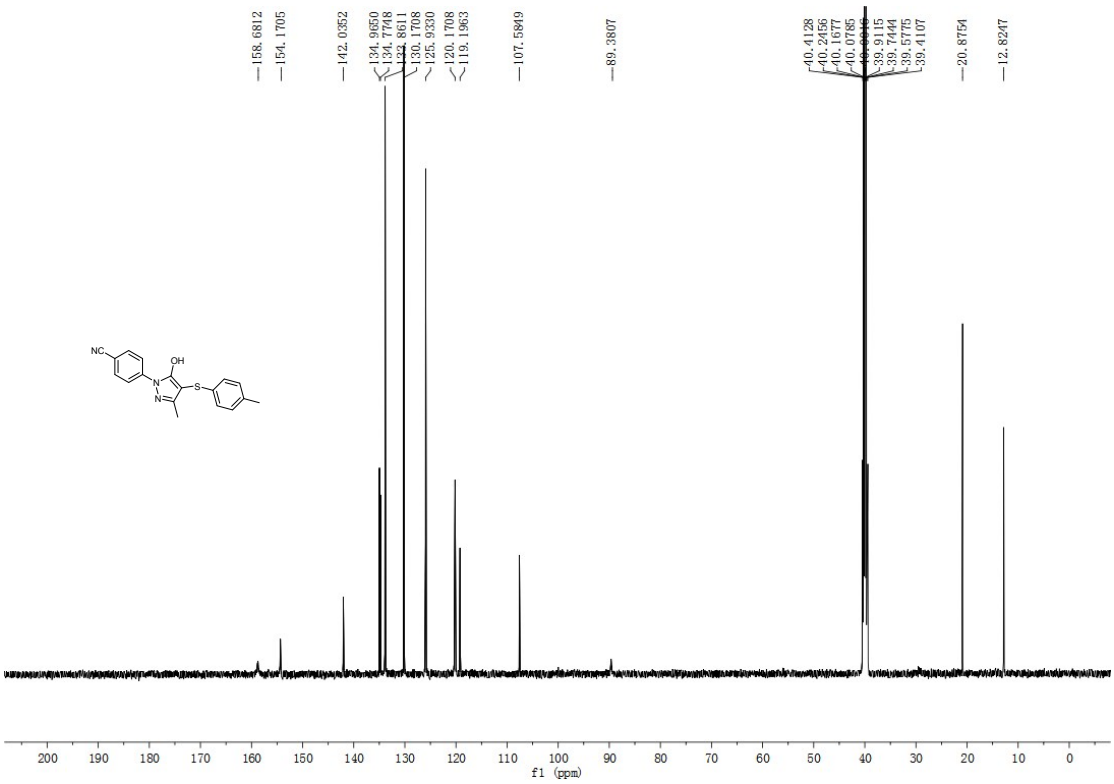
**3da**


12.2108
7.7759
7.7716
7.7660
7.7618
7.7577
7.7520
7.7478
7.3334
7.3157
7.2979
7.1072
7.0910
6.9984
6.9821
3.3448
2.5150
2.5117
2.5046
2.5013
2.2369
2.1088
F
OH
N
N
S
0.88
2.05
2.03
2.02
2.00
3.04
2.95
f1 (ppm)

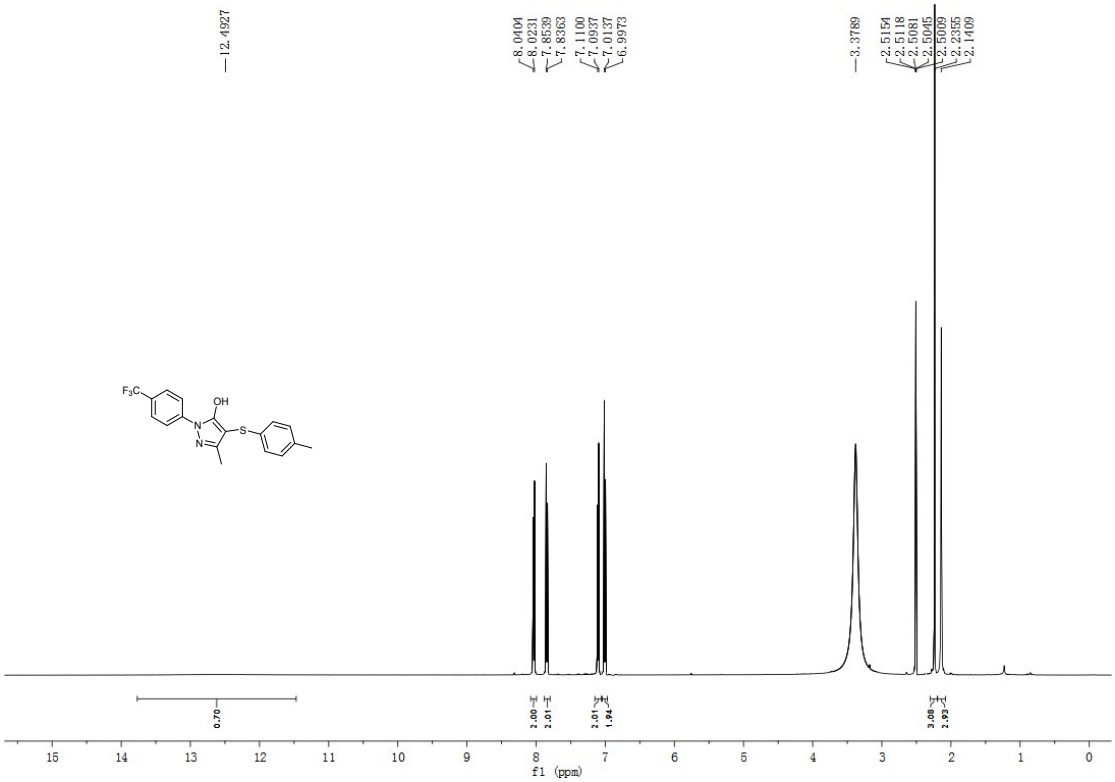

161.1582
159.2272
156.8829
152.4242
135.2332
135.1316
134.7781
130.1291
125.7544
123.3214
123.2578
116.2313
116.0507
88.4556
40.4481
40.2810
40.2032
40.1140
39.9470
39.7800
39.6132
39.4461
20.8725
12.7889
F
OH
N
N
S
f1 (ppm)

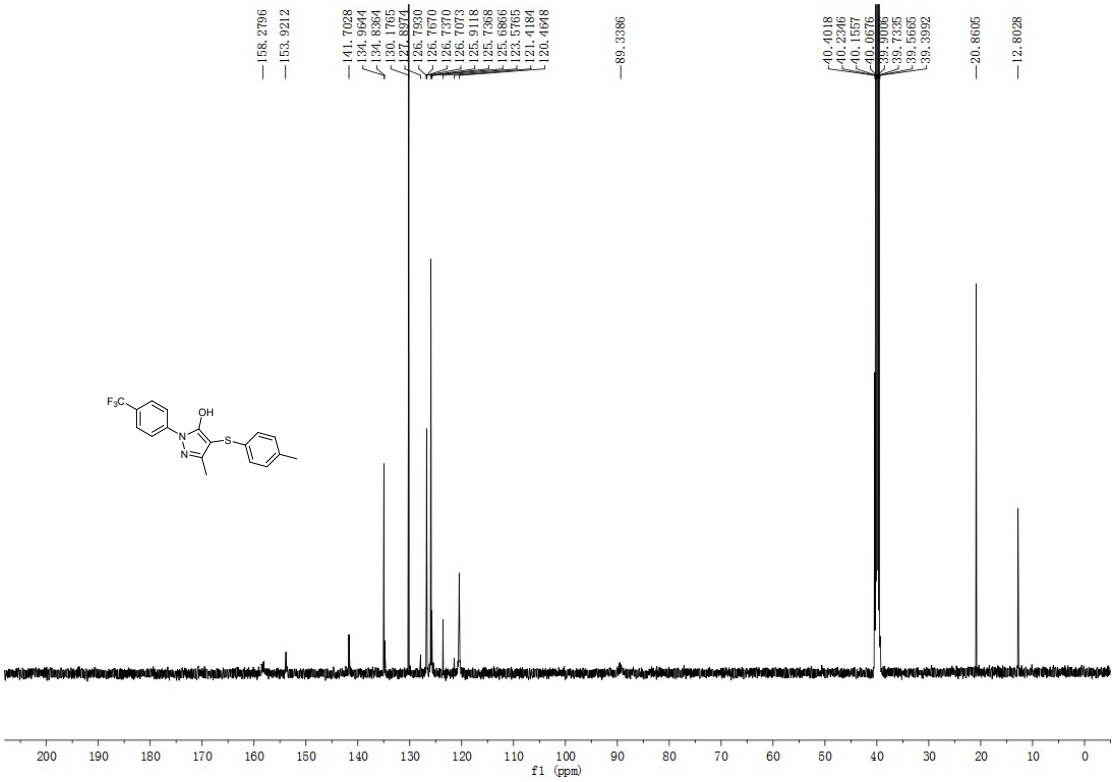
**3ea**


12.6701
8.0292
8.0115
7.9436
7.9260
7.1055
7.0892
7.0100
6.9936
3.3871
2.5151
2.5116
2.5081
2.5045
2.5009
2.2328
2.1413
NC
OH
N
N
S
0.44
2.07
2.02
2.06
2.00
3.10
2.98
f1 (ppm)

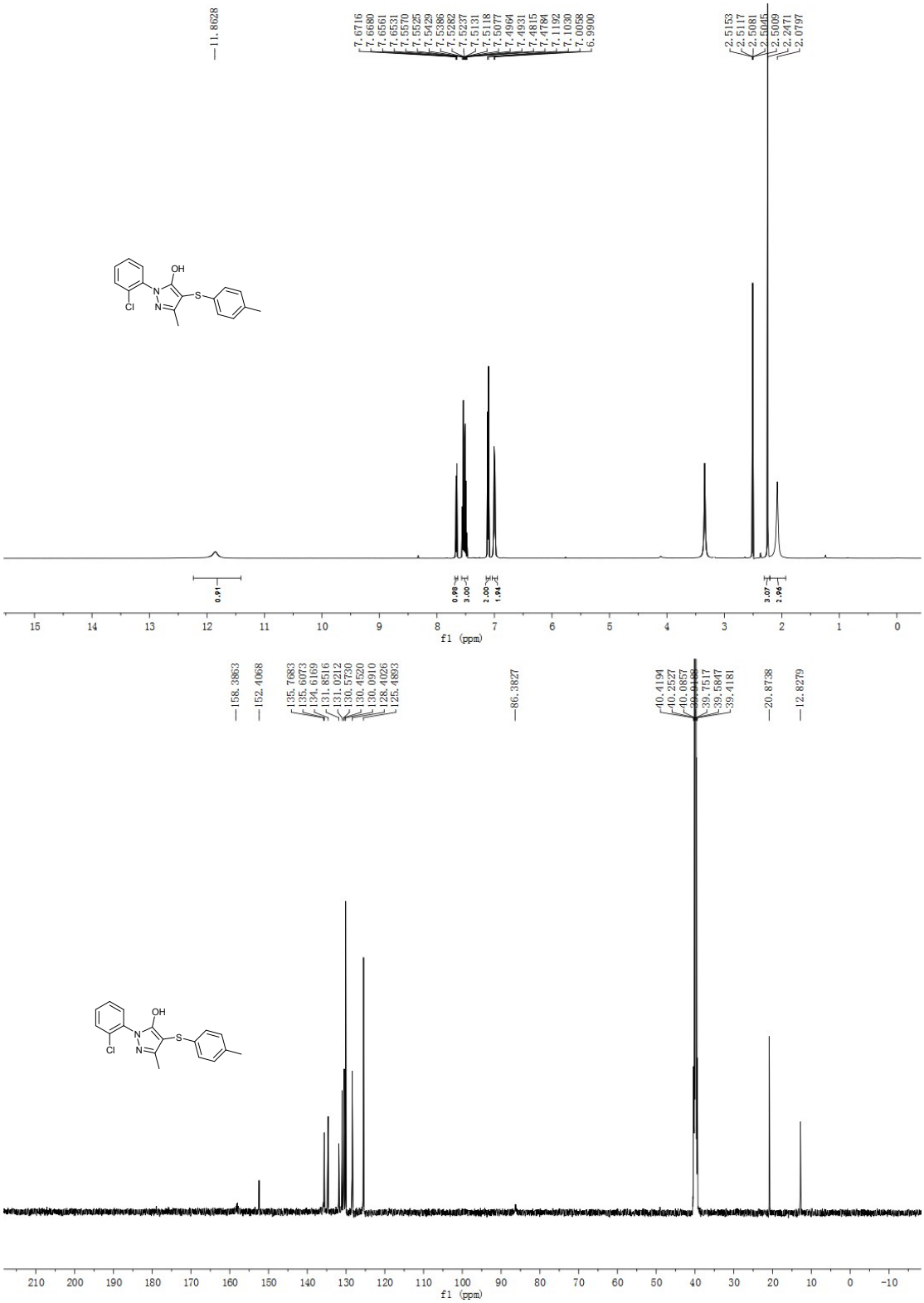

158.6812
154.1705
142.0352
134.9650
134.7748
132.8611
130.1708
125.9330
120.1708
119.1963
107.5849
89.3807
40.4128
40.2456
40.1677
40.0785
39.9115
39.7444
39.5775
39.4107
20.8754
12.8247
NC
OH
N
N
S
f1 (ppm)

**3fa**

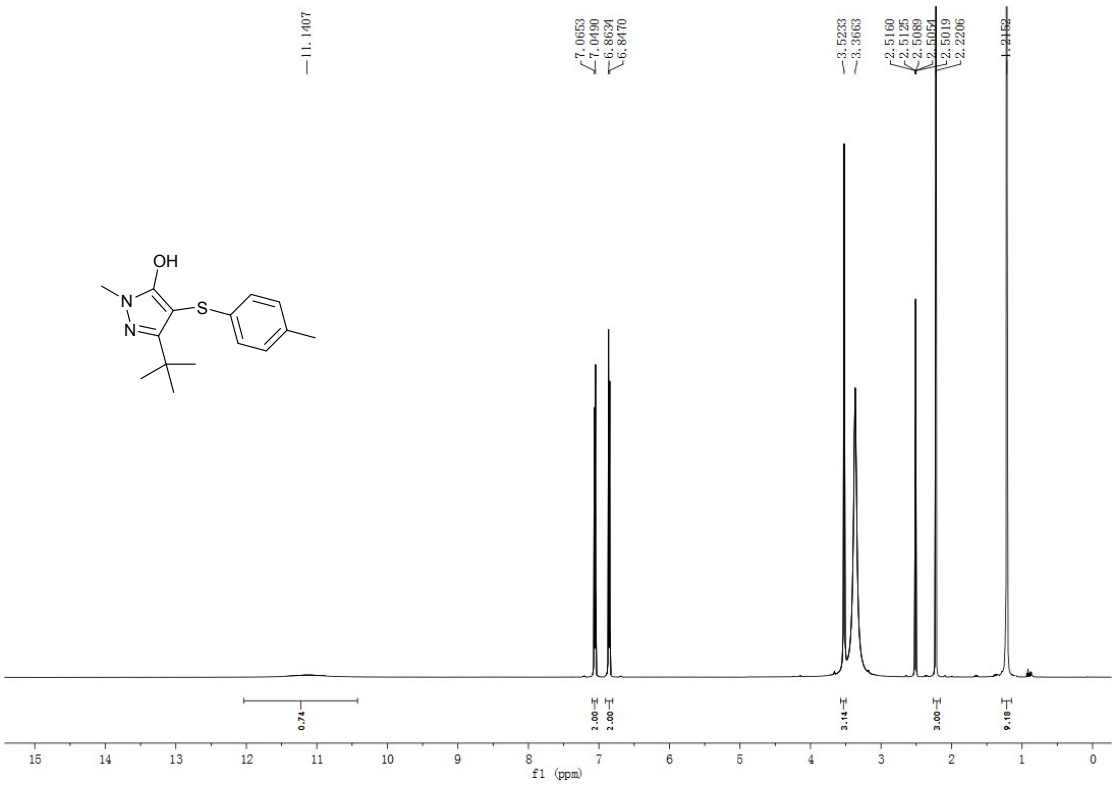

12.4927
8.0404
8.0231
7.8539
7.8363
7.1100
7.0937
7.0137
6.9973
3.3789
2.5154
2.5118
2.5081
2.5045
2.5009
2.2395
2.1409
f1 (ppm)

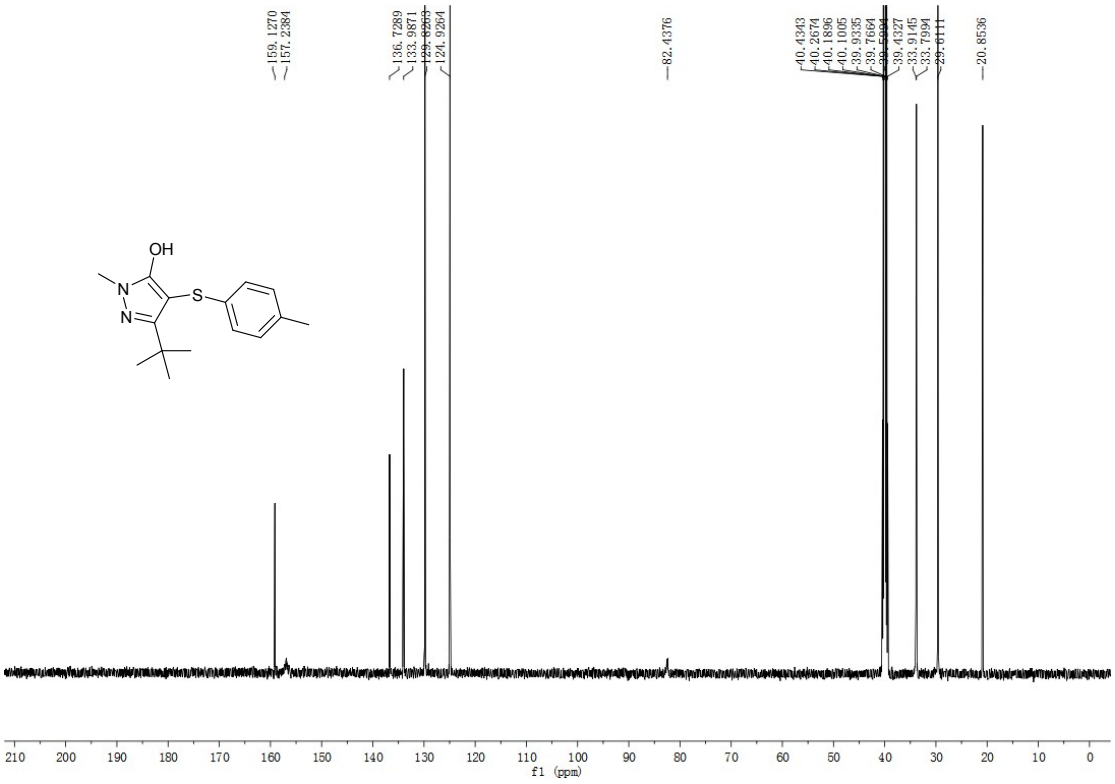

158.2796
153.9212
141.7028
134.9644
134.8364
130.1765
127.8974
126.7930
126.7670
126.7370
126.7073
125.9118
125.7368
125.6866
123.5765
121.4184
120.4648
89.3386
40.4018
40.2346
40.1557
40.0676
39.9006
39.7335
39.5665
39.3992
20.8605
12.8028
f1 (ppm)

**3ga**


11.8628
7.6716
7.6680
7.6561
7.6531
7.5570
7.5525
7.5429
7.5386
7.5282
7.5237
7.5131
7.5118
7.5077
7.4964
7.4931
7.4815
7.4784
7.1192
7.1030
7.0058
6.9900
2.5153
2.5117
2.5081
2.5045
2.5009
2.2471
2.0797
OH
N
N
Cl
S
0.91
0.98
3.00
2.05
1.94
3.07
2.06
f1 (ppm)
158.3863
152.4068
135.7683
135.6073
134.6169
131.8516
131.0212
130.5730
130.4520
130.0910
128.4026
125.4893
86.3827
40.4194
40.2527
40.0857
39.9188
39.7517
39.5847
39.4181
20.8738
12.8279
f1 (ppm)

**3ha**


11.1407
7.0653
7.0490
6.8634
6.8470
3.5233
3.3663
2.5160
2.5125
2.5089
2.5054
2.5019
2.2206
1.3162
OH
N
N
S
0.74
2.00
2.00
3.14
3.00
9.18
f1 (ppm)


159.1270
157.2384
136.7289
133.9871
125.8263
124.9264
82.4376
40.4343
40.2674
40.1896
40.1005
39.9335
39.7664
39.4327
33.5145
33.3994
29.6111
20.8536
OH
N
N
S
f1 (ppm)