Supporting Information

$K_2S_2O_8$-Promoted Direct Thiocyanation of Pyrazolin-5-ones with Ammonium Thiocyanate at Room Temperature

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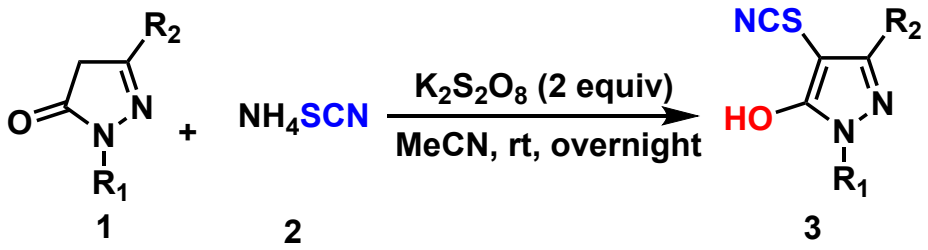
Contents

1. General information

All reactions were performed in flame-dried glassware. Liquids and solutions were transferred with syringes. All solvents and chemical reagents were obtained from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal in CD_3OD or in $CDCl_3$. Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer. Column chromatography on silica gel (200−300 mesh) was used for the routine purification of the reaction products. The column output was monitored by TLC on silica gel (100−200 mesh) precoated on glass plates (15 × 50 mm), and spots were visualized by UV light at 254 nm. Commercially available chemicals were obtained from Acros Organics, Alfa Aesar, Adamas-beta, and J&K. Starting materials (pyrazolones) were prepared according to the literature procedures.[1, 2]

2. General procedures for synthesis of C-4 thiocyanated pyrazoles 3

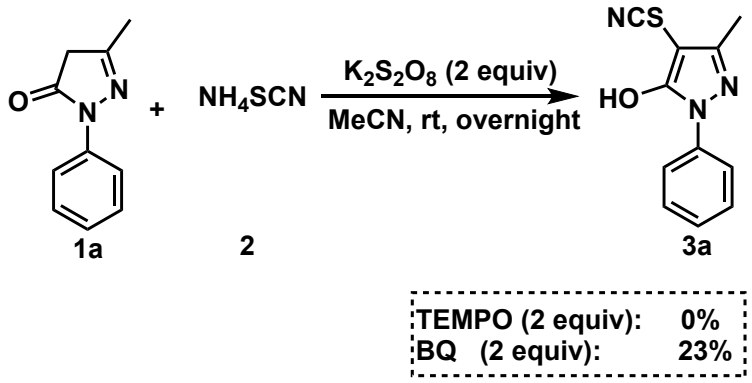


Acetonitrile (2 mL) was added to a mixture of pyrazolone **1** (0.2 mmol), ammonium thiocyanate **2** (0.6 mmol), and $K_2S_2O_8$ (0.4 mmol) in a 10 mL round-bottomed flask at room temperature. The reaction vessel was allowed to stir at room temperature overnight. After completion of the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by silica gel column by using dichloromethane and methanol as a mixed eluent to provide the desired products **3a**-**u**.

Gram-scale synthesis of 3a: Acetonitrile (30 mL) was added to a mixture of pyrazolone **1a** (10 mmol, 1.74 g), ammonium thiocyanate **2** (30 mmol, 2.28 g),

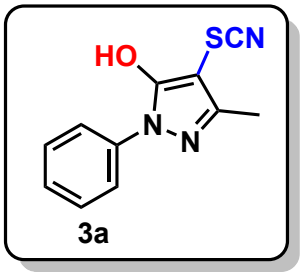
$K_2S_2O_8$ (20 mmol, 5.4 g) in a 100 mL round-bottomed flask at room temperature. The reaction vessel was allowed to stir at room temperature overnight. After completion of the reaction, the resulting mixture was concentrated under vacuum and the resulting residue was purified by silica gel column using a mixture of dichloromethane and methanol as eluent to provide the desired product **3a** (1.97g, 85%) .

3. Radical trapping experiments

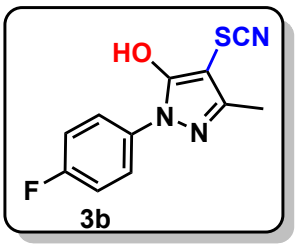


Acetonitrile (2 mL) was added to a mixture of pyrazolone **1a** (0.2 mmol), ammonium thiocyanate **2** (0.6 mmol), $K_2S_2O_8$ (0.4 mmol), TEMPO (62.5 mg, 2.0 equiv) or BQ (43.2 mg, 2.0 equiv) in a 10 mL round-bottomed flask at room temperature. The reaction vessel was allowed to stir at room temperature overnight. After completion of the reaction, the resulting mixture was concentrated under vacuum and the resulting residue was purified by silica gel column using a mixture of dichloromethane and methanol as eluent to provide the desired product **3a**.

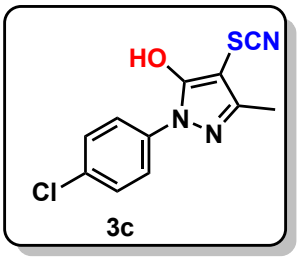
4.Characterization data of products 3a-3u



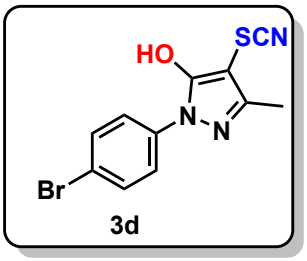
Methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-ol (3a). Compound **3a** was obtained in 89% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.24 (dd, *J* = 12.6, 5.4 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.65, 151.38, 134.99, 129.11 (2C), 127.44, 122.07 (2C), 110.76, 82.20, 11.55. HRMS (ESI) calcd for $C_{11}H_8N_3OS$ $(M-H)^-$ 230.0394, found 230.0388.



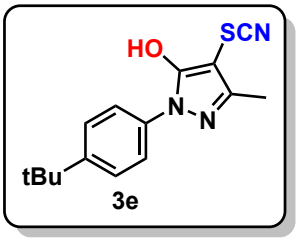
(4-Fluorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3b). Compound **3b** was obtained in 82% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.77 (s, 1H), 7.36 (dd, *J* = 8.8, 4.6 Hz, 2H), 6.97 (t, *J* = 8.4 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.25, 160.41(d, J_{CF}= 34.0 Hz) , 151.58, 131.28 (d, J_{CF} = 3.8 Hz), 124.26 (d, J_{CF} = 8.8 Hz), 116.00 (d, J_{CF}= 23.9 Hz), 110.88, 81.80, 11.70; ^{19}F NMR (471 MHz, Methanol-d_4) δ -116.53 (s, 1F). HRMS (ESI) calcd for $C_{11}H_8FN_3OS$ $(M-H)^-$ 248.0299, found 248.0295.



1-(4-Chlorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3c). Compound **3c** was obtained in 77% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.64 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 158.59, 151.42, 135.42, 131.29, 128.32 (2C), 122.38 (2C), 110.69, 79.10, 10.44. HRMS (ESI) calcd for $C_{11}H_7ClN_3OS$ $(M-H)^-$ 264.0004, found 263.9998.

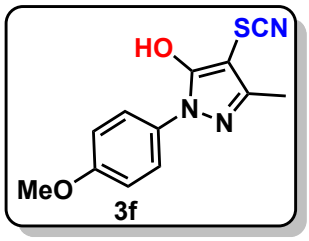


1-(4-Bromophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3d). Compound **3d** was obtained in 94% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.85 (s, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 9.8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.62, 152.17, 134.28, 132.18 (2C), 123.19 (2C), 120.70, 110.88, 82.14, 11.87. HRMS (ESI) calcd for $C_{11}H_7BrN_3OS$ $(M-H)^-$ 307.9499, found 307.9495.



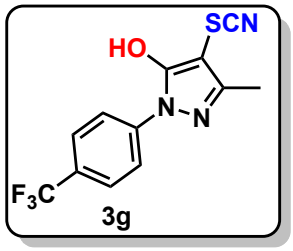
1-(4-(*Tert*-butyl)phenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3e). Compound **3e** was obtained in 71% yield according to the general procedure. Yellow solid. ^{1}H

NMR (400 MHz, Chloroform-*d*) δ 11.44 (s, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 9.9 Hz, 2H), 2.28 (s, 3H), 1.26 (s, 9H, -tBu). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.20, 150.35, 150.20, 131.92, 125.60 (2C), 121.33 (2C), 110.34, 34.19, 30.83, 10.97. HRMS (ESI) calcd for $C_{15}H_{16}N_3OS$ $(M-H)^-$ 286.1020, found 286.1013.



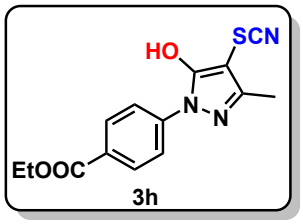
3f

1-(4-Methoxyphenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3f). Compound **3f** was obtained in 78% yield according to the general procedure. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 2.27 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.43, 158.89, 150.50, 127.78, 124.42 (2C), 114.25 (2C), 110.93, 81.77, 55.52, 11.46. HRMS (ESI) calcd for $C_{12}H_{10}N_3O_2S$ $(M-H)^-$ 260.0499, found 260.0497.

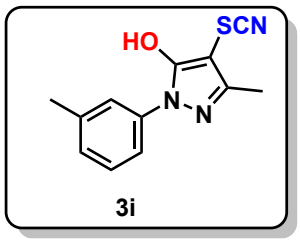


3g

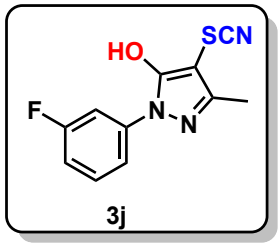
3-**Methyl-4-thiocyanato-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazol-5-ol (3g).** Compound **3g** was obtained in 77% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 163.14, 153.88, 142.88, 127.79 (q, J_{CF}= 32.8 Hz), 126.95 (q, J_{CF}= 3.8 Hz, 2C), 124.53, 121.51 (2C), 113.39, 78.32, 12.70; ^{19}F NMR (471 MHz, Methanol-d_4) δ -63.88 (s, 3F). HRMS (ESI) calcd for $C_{12}H_7F_3N_3OS$ $(M-H)^-$ 298.0267, found 298.0262.



Ethyl 4-(5-hydroxy-3-methyl-4-thiocyanato-1*H*-pyrazol-1-yl)benzoate (3h). Compound **3h** was obtained in 78% yield according to the general procedure. Yellow solid. ^{1}H NMR (600 MHz, Methanol-d_4) δ 8.06 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Methanol-d_4) δ 165.59, 159.97, 152.19, 141.19, 129.63 (2C), 126.73, 119.43 (2C), 111.00, 78.34, 60.41, 12.81, 10.69. HRMS (ESI) calcd for $C_{14}H_{14}N_3O_3S$ $(M+H)^+$ 304.0750, found 304.0748.

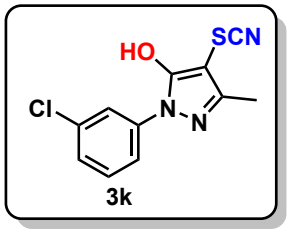


3-**Methyl-4-thiocyanato-1-(m-tolyl)-1*H*-pyrazol-5-ol (3i).** Compound **3i** was obtained in 81% yield according to the general procedure. Yellow solid. ^{1}H NMR (600 MHz, Methanol-d_4) δ 7.44 (d, J = 1.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, Methanol-d_4) δ 158.82, 150.84, 138.64, 136.33, 128.21, 127.01, 122.05, 118.63, 110.73, 79.35, 19.65, 10.24. HRMS (ESI) calcd for $C_{12}H_{12}N_3OS$ $(M+H)^+$ 246.0696, found 246.0699.

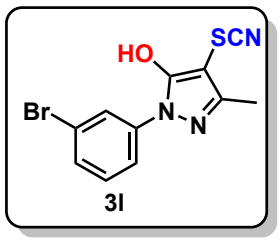


1-(3-Fluorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3j). Compound **3j** was obtained in 82% yield according to the general procedure. Yellow solid. ^{1}H NMR

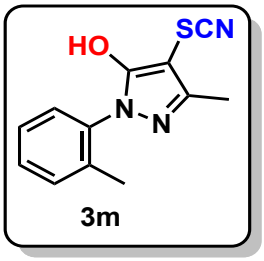
(500 MHz, Methanol-d_4) δ 7.53 (d, J = 8.8 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.04 (td, J = 8.1, 2.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 163.27, 161.33, 158.86, 151.68, 138.23 (d, J_{CF}= 11.3 Hz), 129.81 (d, J_{CF}= 10.1 Hz), 116.03 (d, J_{CF}= 3.8 Hz), 112.25 (d, J_{CF}= 21.4 Hz), 110.67, 107.75 (d, J_{CF}= 26.5 Hz), 79.22, 10.42; ^{19}F NMR (471 MHz, Methanol-d_4) δ -113.88 (s, 1F). HRMS (ESI) calcd for $C_{11}H_7FN_3OS$ $(M-H)^-$ 248.0299, found 248.0293.



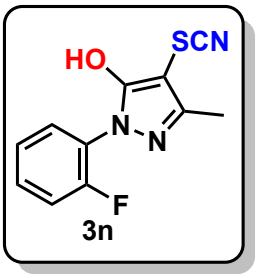
1-(3-Chlorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3k). Compound **3k** was obtained in 79% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.74 (s, 1H), 7.33 (dd, J = 8.8, 4.6 Hz, 2H), 6.94 (t, J = 8.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.25, 160.54, 151.58, 131.29, 124.29, 124.22, 116.10, 115.91, 110.88, 81.80, 11.70. HRMS (ESI) calcd for $C_{11}H_7ClN_3OS$ $(M-H)^-$ 264.0004, found 263.9997.



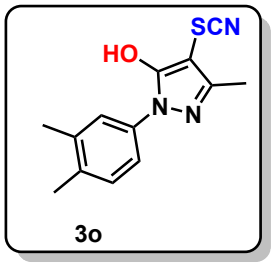
1-(3-Bromophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3l). Compound **3l** was obtained in 82% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.91 (t, J = 2.0 Hz, 1H), 7.68 (ddd, J = 8.1, 2.1, 1.0 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.35 (t, J = 8.1 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 159.31, 152.21, 138.44, 130.28, 129.00, 123.84, 122.01, 119.59, 111.12, 79.69, 10.93. HRMS (ESI) calcd for $C_{11}H_7BrN_3OS$ $(M-H)^-$ 307.9499, found 307.9492.



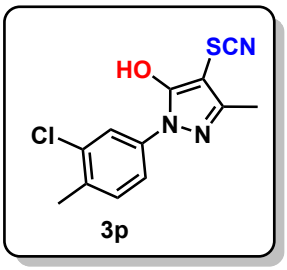
3-Methyl-4-thiocyanato-1-(o-tolyl)-1*H*-pyrazol-5-ol (3m). Compound **3m** was obtained in 84% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.73 (s, 1H), 7.26 (s, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.09 (td, *J* = 7.6, 1.5 Hz, 1H), 6.92 – 6.87 (m, 1H), 2.14 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.03, 150.67, 136.32, 133.36, 131.14, 129.81, 127.60, 126.67, 111.05, 80.63, 17.64, 11.32. HRMS (ESI) calcd for $C_{12}H_{10}N_3OS$ $(M-H)^-$ 244.0550, found 244.0545.



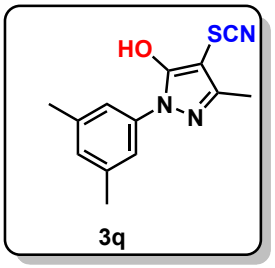
1-(2-Fluorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3n). Compound **3n** was obtained in 82% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.49 – 7.44 (m, 2H), 7.29 (t, *J* = 8.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 160.11, 157.75, 155.74, 151.42, 130.07 (d, J_{CF}= 7.6 Hz), 128.17, 124.04 (d, J_{CF}= 3.8 Hz), 115.84 (d, J_{CF} = 18.9 Hz), 111.03, 77.32, 10.44; ^{19}F NMR (471 MHz, Methanol-d_4) δ -122.56 (s, 1F). HRMS (ESI) calcd for $C_{11}H_7FN_3OS$ $(M-H)^-$ 248.0299, found 248.0293.



1-(3,4-Dimethylphenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3o). Compound **3o** was obtained in 83% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.98 (s, 1H), 7.11 – 7.07 (m, 1H), 7.06 – 6.99 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.52, 150.60, 137.56, 136.28, 132.63, 130.01, 123.39, 119.74, 110.80, 81.95, 19.74, 19.37, 11.42. HRMS (ESI) calcd for $C_{13}H_{14}N_3OS$ $(M+H)^+$ 260.0852, found 260.0856.

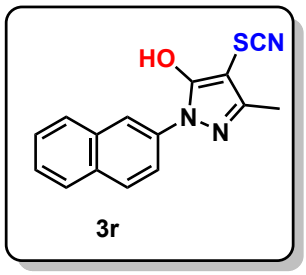


1-(3-Chloro-4-methylphenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3p). Compound **3p** was obtained in 95% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 2.2 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.53, 151.81, 135.07, 134.50, 134.04, 131.10, 122.15, 119.78, 111.03, 81.70, 19.65, 11.80. HRMS (ESI) calcd for $C_{12}H_{11}ClN_3OS$ $(M+H)^+$ 280.0306, found 280.0332.

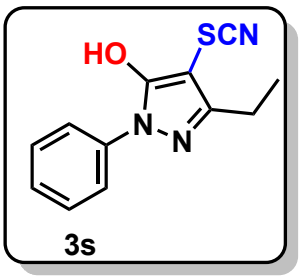


1-(3,5-Dimethylphenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-ol (3q). Compound **3q** was obtained in 87% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.94 (s, 2H), 6.81 (s, 1H), 2.32 (s, 3H), 2.15 (s, 6H, -2CH_3). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.46, 150.83, 138.92 (2C), 134.81,

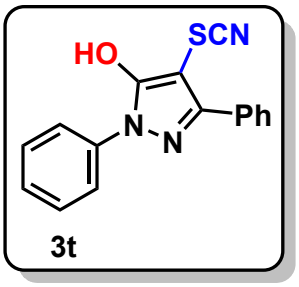
129.17, 119.89 (2C), 110.70, 82.03, 21.17, 11.44. HRMS (ESI) calcd for $C_{13}H_{14}N_3OS$ $(M+H)^+$ 260.0852, found 260.0857.



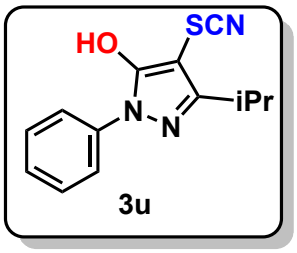
3-Methyl-1-(naphthalen-2-yl)-4-thiocyanato-1*H*-pyrazol-5-ol (3r). Compound **3r** was obtained in 87% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Methanol-d_4) δ 8.09 (d, J = 2.1 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.80 (dd, J = 8.8, 2.2 Hz, 1H), 7.53 (ddd, J = 7.5, 5.6, 1.8 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 148.47, 140.95, 123.56, 122.59, 121.27, 118.00, 116.97, 116.69, 115.89, 115.36, 109.67, 108.92, 100.36, 69.42, 8.64. HRMS (ESI) calcd for $C_{15}H_{12}N_3OS$ $(M+H)^+$ 282.0696, found 282.0699.



Ethyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-ol (3s). Compound **3s** was obtained in 94% yield according to the general procedure. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.39 (s, 1H), 7.31 (d, J = 7.5 Hz, 2H), 7.20 (d, J = 8.0 Hz, 3H), 2.67 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.71, 156.45, 134.97, 129.02 (2C), 127.37, 122.15 (2C), 111.01, 81.30, 19.83, 12.52. HRMS (ESI) calcd for $C_{12}H_{10}N_3OS$ $(M-H)^-$ 244.0550, found 244.0547.



1,3-Diphenyl-4-thiocyanato-1*H*-pyrazol-5-ol (3t). Compound **3t** was obtained in 93% yield according to the general procedure. Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.53 (s, 1H), 7.65 – 7.57 (m, 2H), 7.45 – 7.36 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.20 (dt, *J* = 14.3, 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.27, 152.29, 135.65, 130.46, 129.00, 128.82, 128.44, 128.31, 127.52, 122.33, 111.62, 80.48. HRMS (ESI) calcd for $C_{16}H_{10}N_3OS$ $(M-H)^-$ 292.0550, found 292.0544.



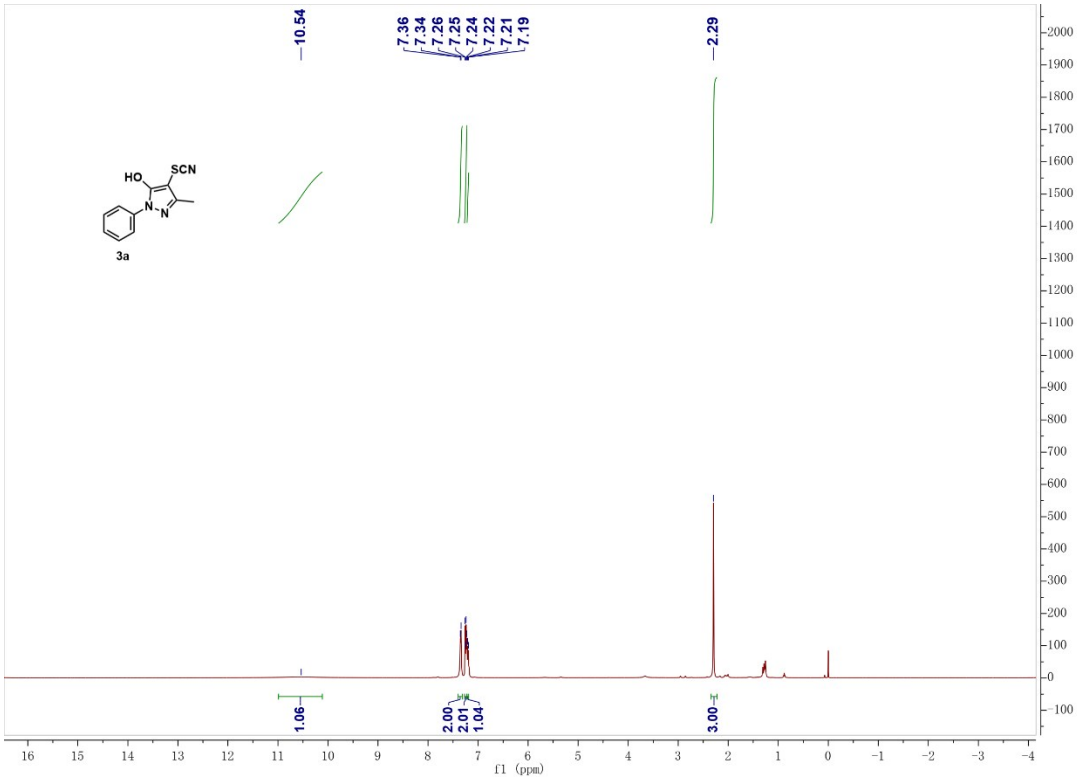
Isopropyl-4-thiocyanato-1-(m-tolyl)-1*H*-pyrazol-5-ol (3u). Compound **3u** was obtained in 89% yield according to the general procedure. Yellow solid. ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.32 (m, 1H), 3.25 (p, *J* = 7.0 Hz, 1H), 1.40 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 159.38, 158.40, 136.51, 128.29, 126.45, 122.08, 111.06, 77.73, 26.84, 19.61. HRMS (ESI) calcd for $C_{13}H_{14}N_3OS$ $(M+H)^+$ 260.0852, found 260.0853.

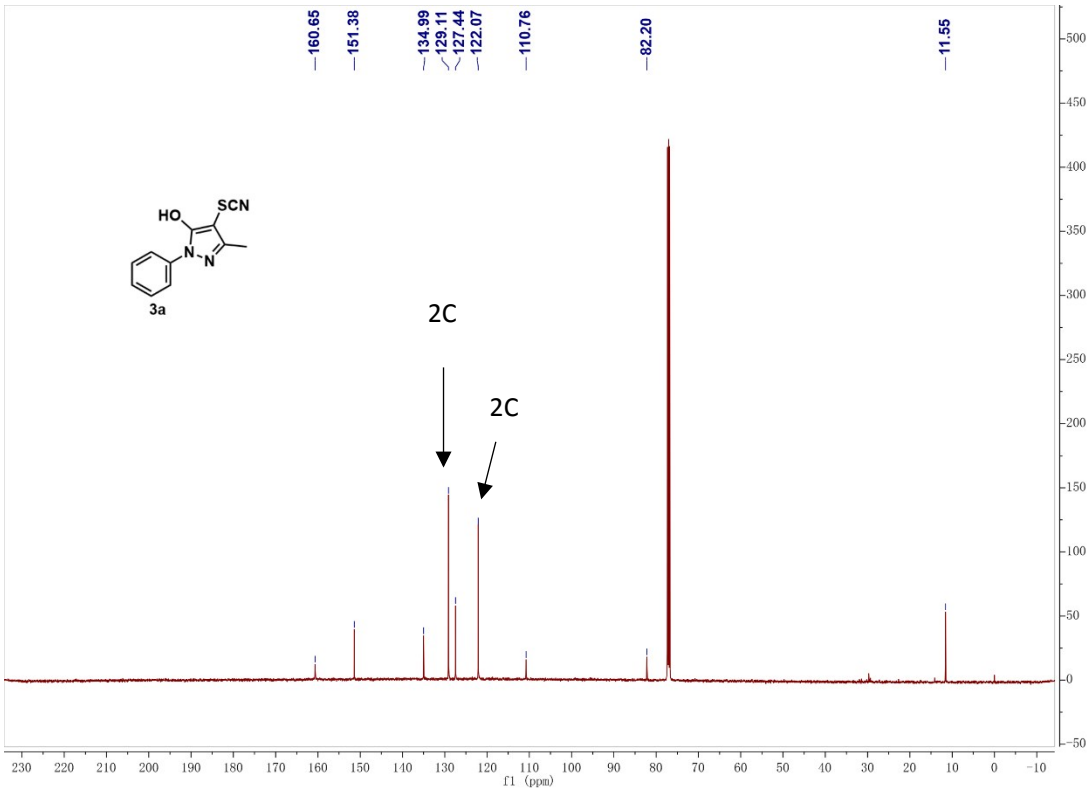
5. Reference

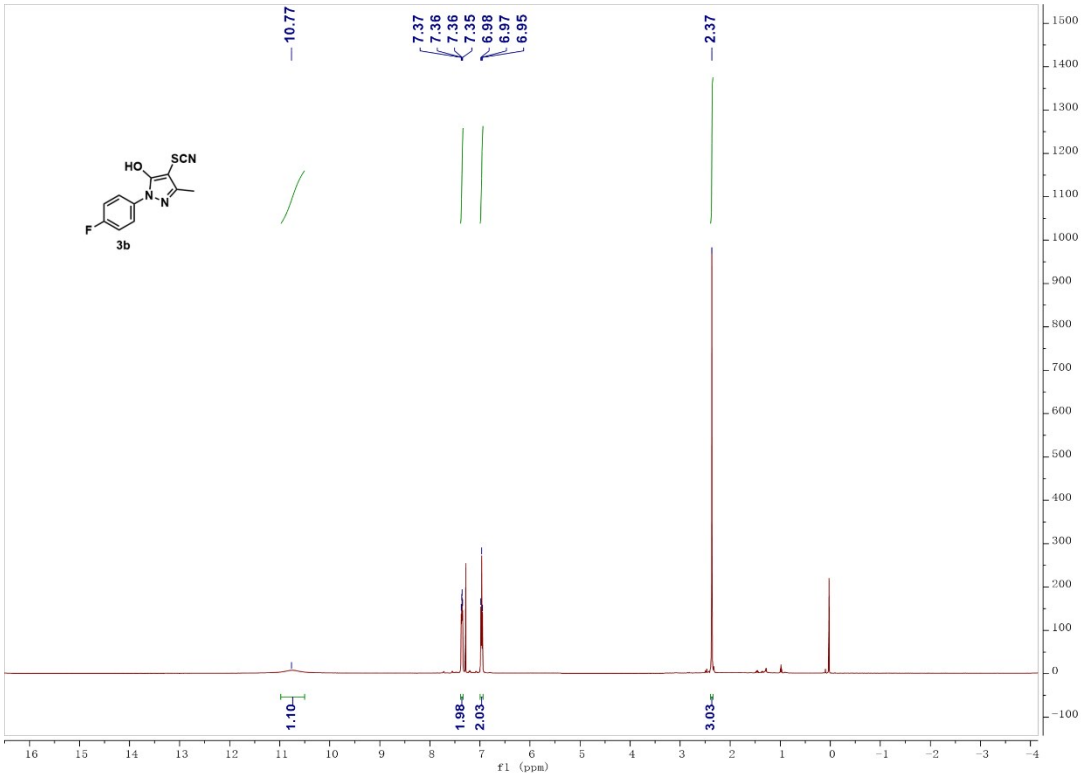
1. Y.-Y. Huang, H.-C. Lin, K.-M. Cheng, W.-N. Su, K.-C. Sung, T.-P. Lin, J.-J. Huang, S.-K. Lin and F. F. Wong, *Tetrahedron.*, 2009, **65**, 9592.

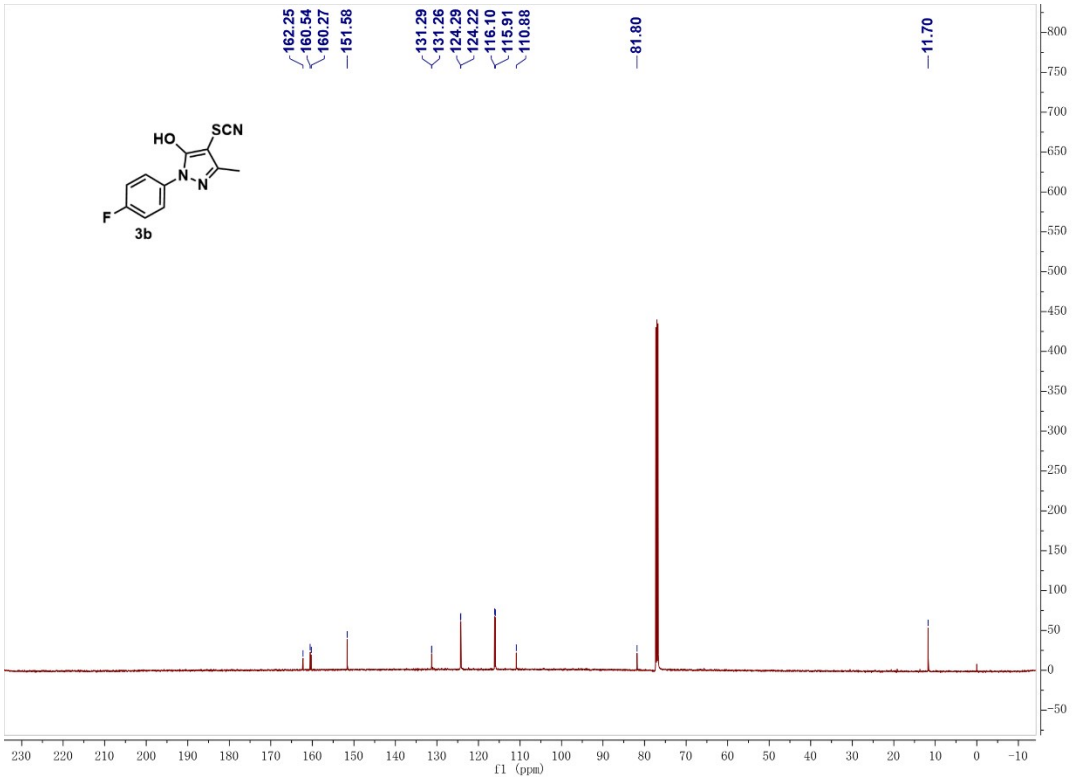
2. X.-j. Wang, J. Tan and K. Grozinger, *Tetrahedron Lett.*, 2000, **41**, 4713.

6. Copies of NMR spectra for compounds 3a−3u

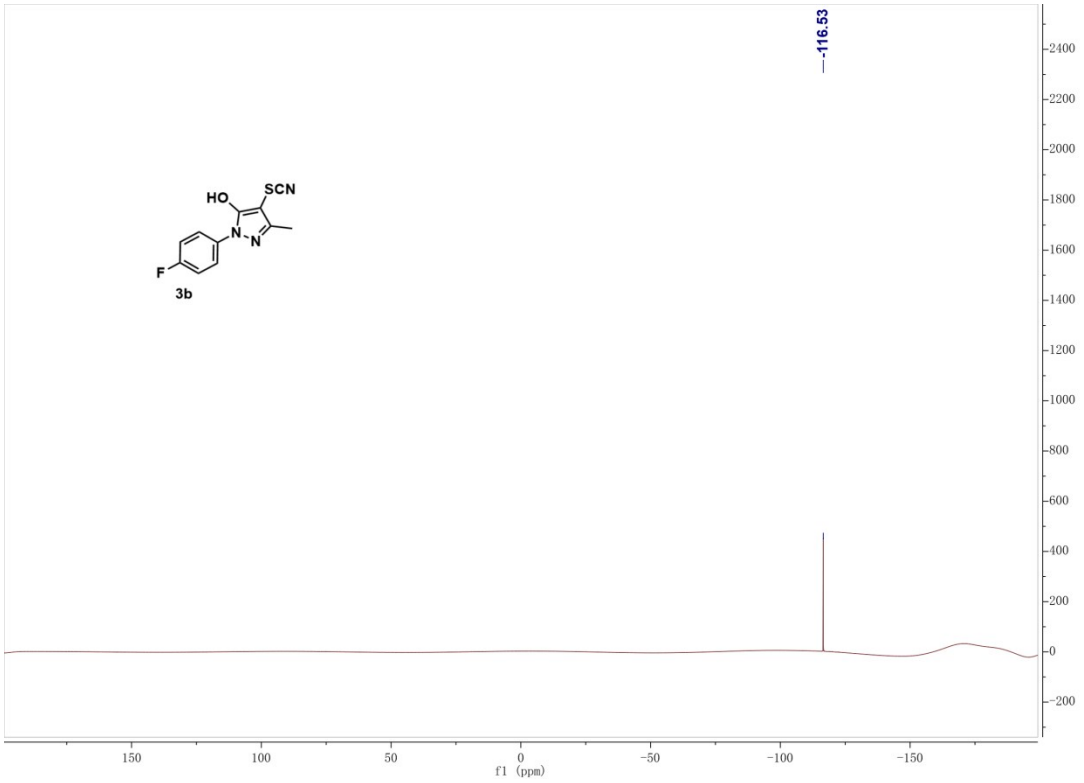


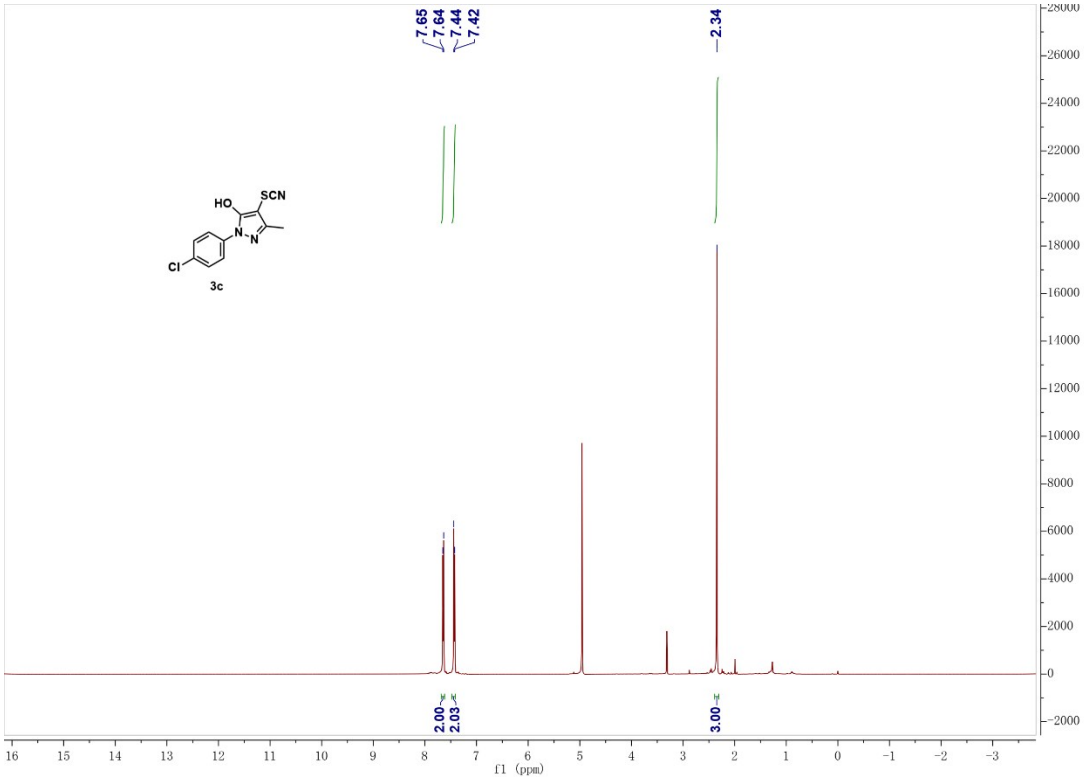


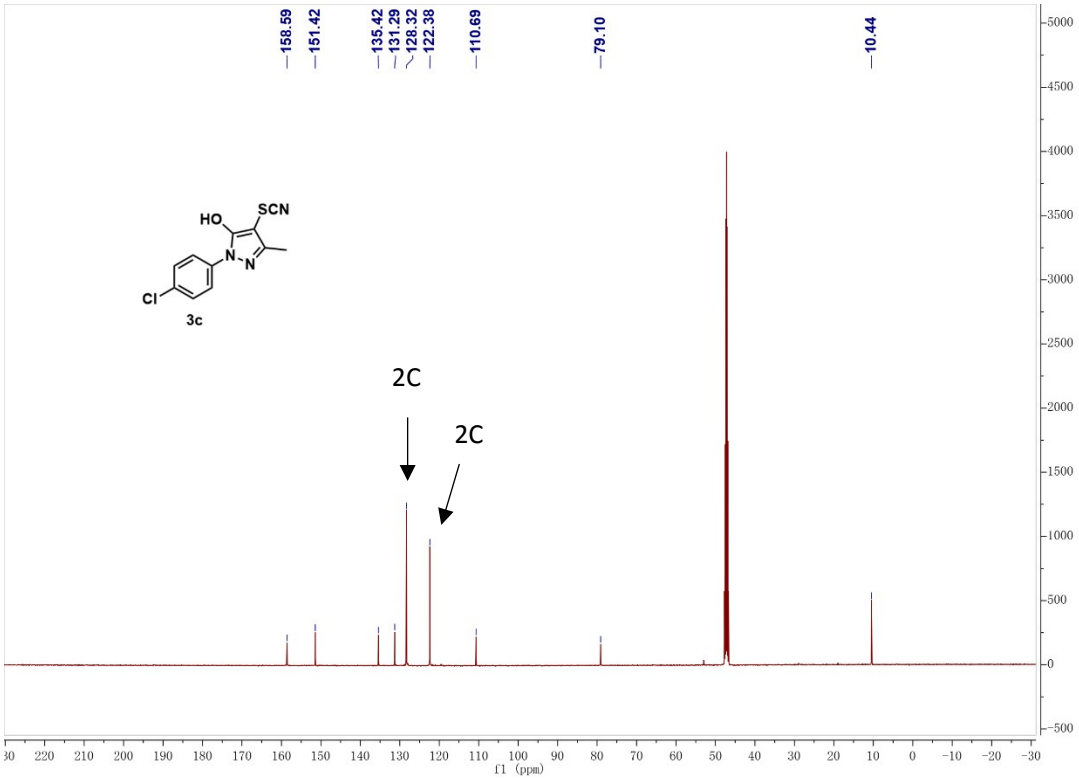


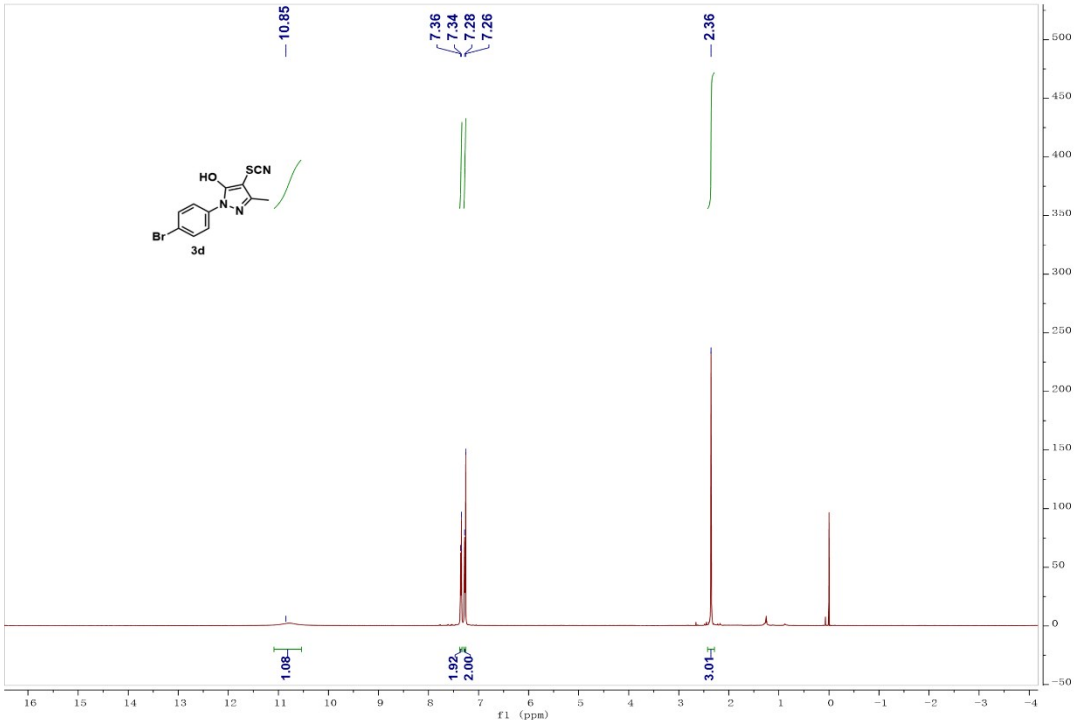


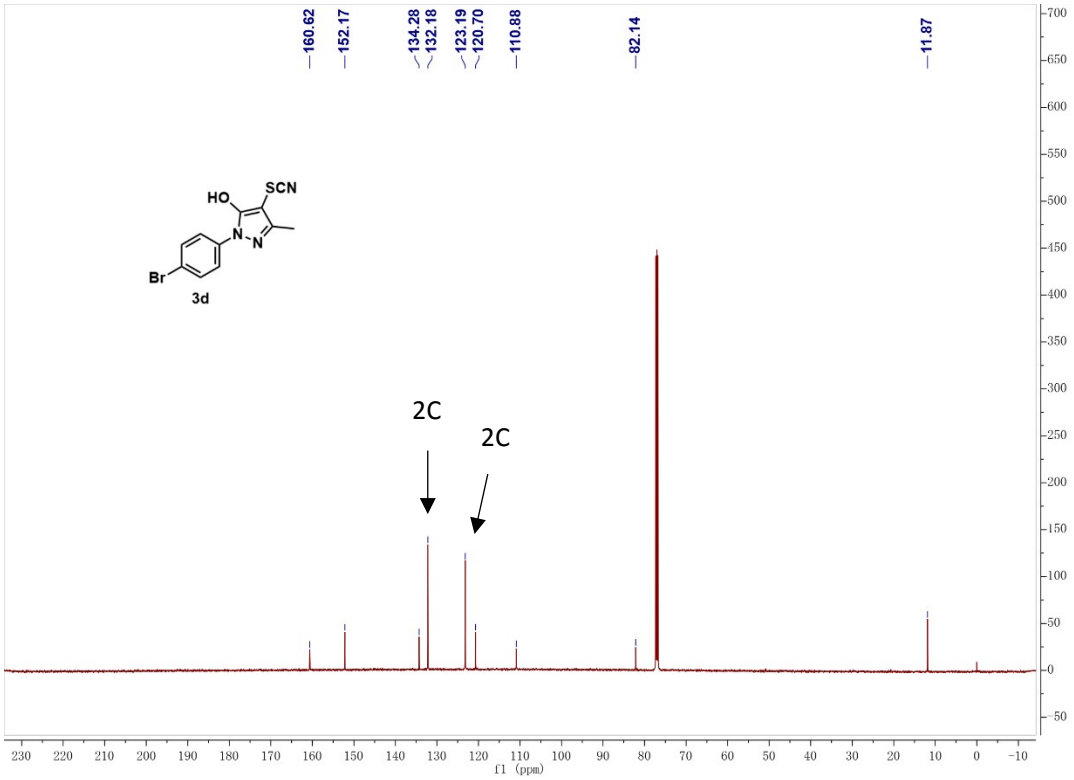
^{19}F NMR spectrum of **3b**:

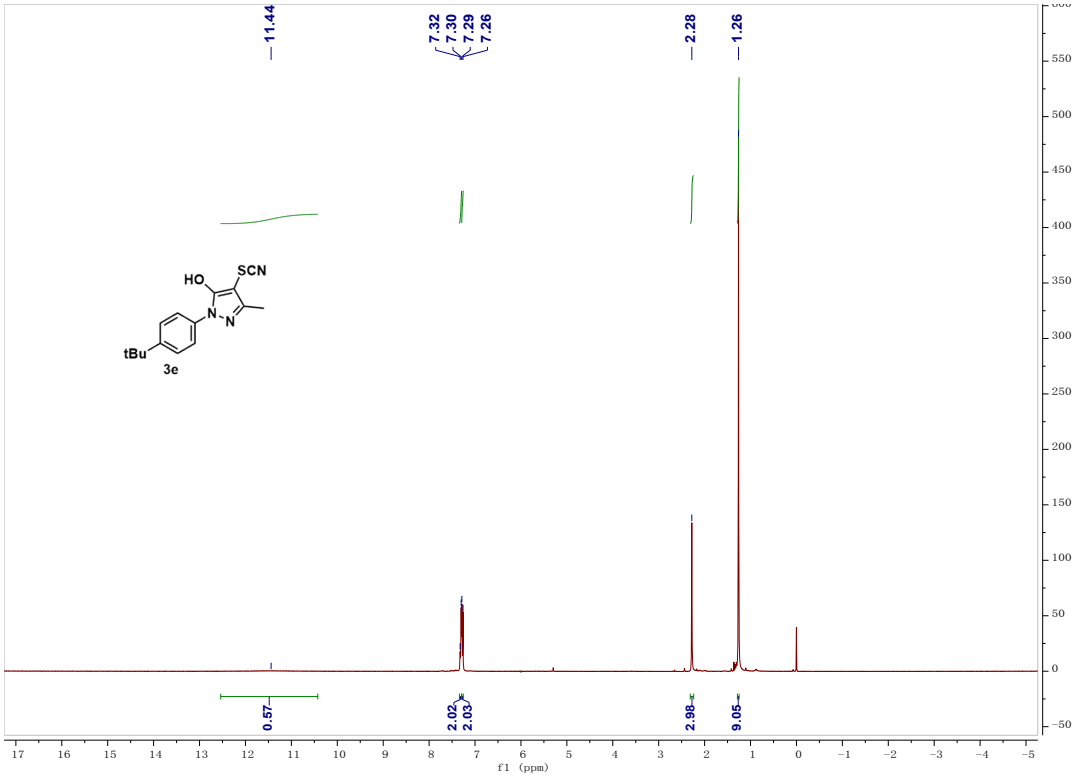

-116.53
HO
SCN
N
N
F
3b
f1 (ppm)

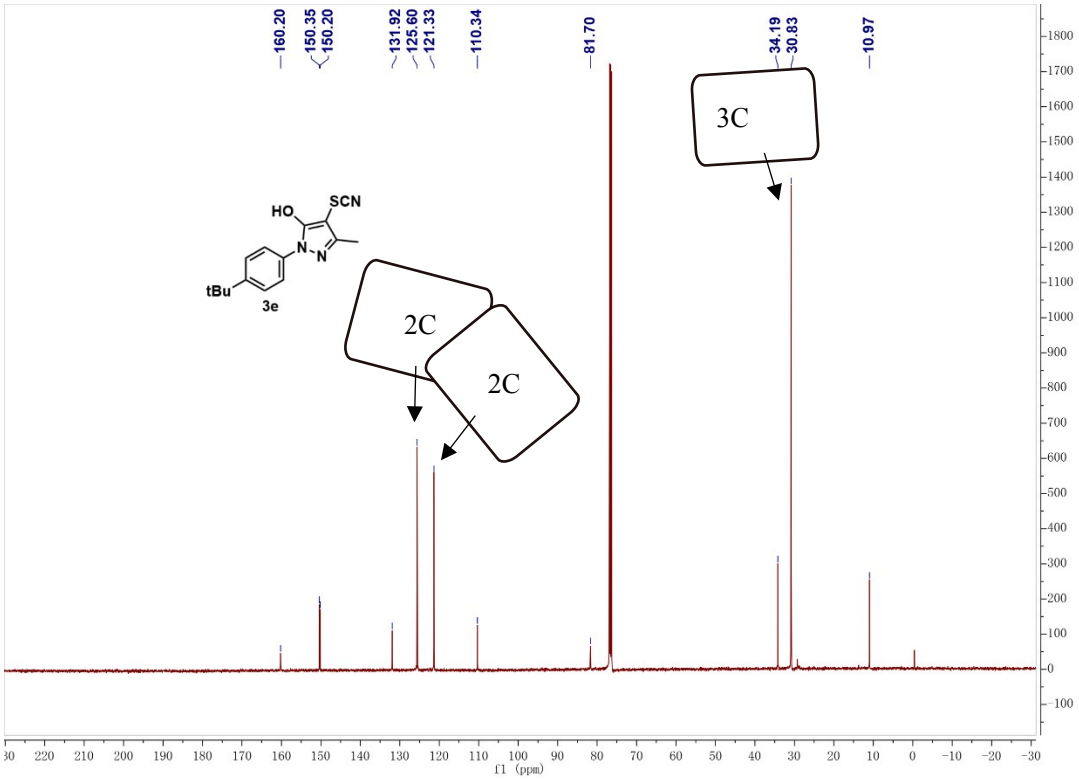

7.65
7.64
7.44
7.42
2.34
HO
SCN
N
N
Cl
3c
2.00
2.03
3.00
f1 (ppm)

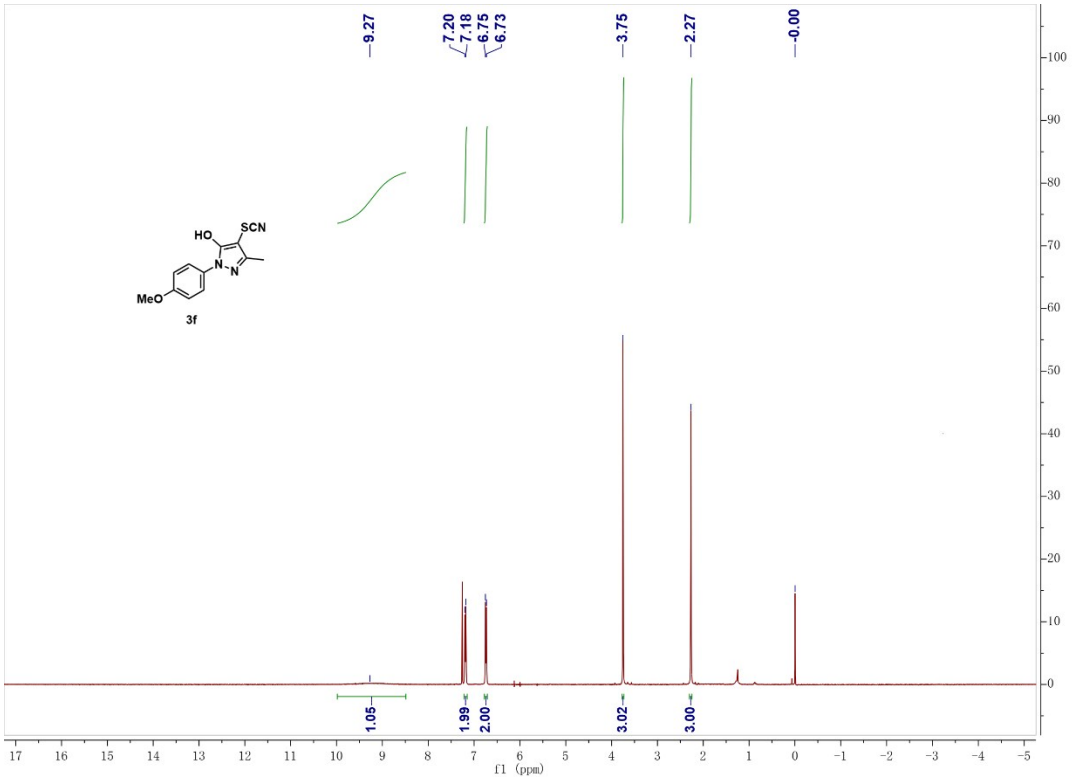

158.59
151.42
135.42
131.29
128.32
122.38
110.69
79.10
10.44
HO
SCN
N
N
Cl
3c
2C
2C
f1 (ppm)

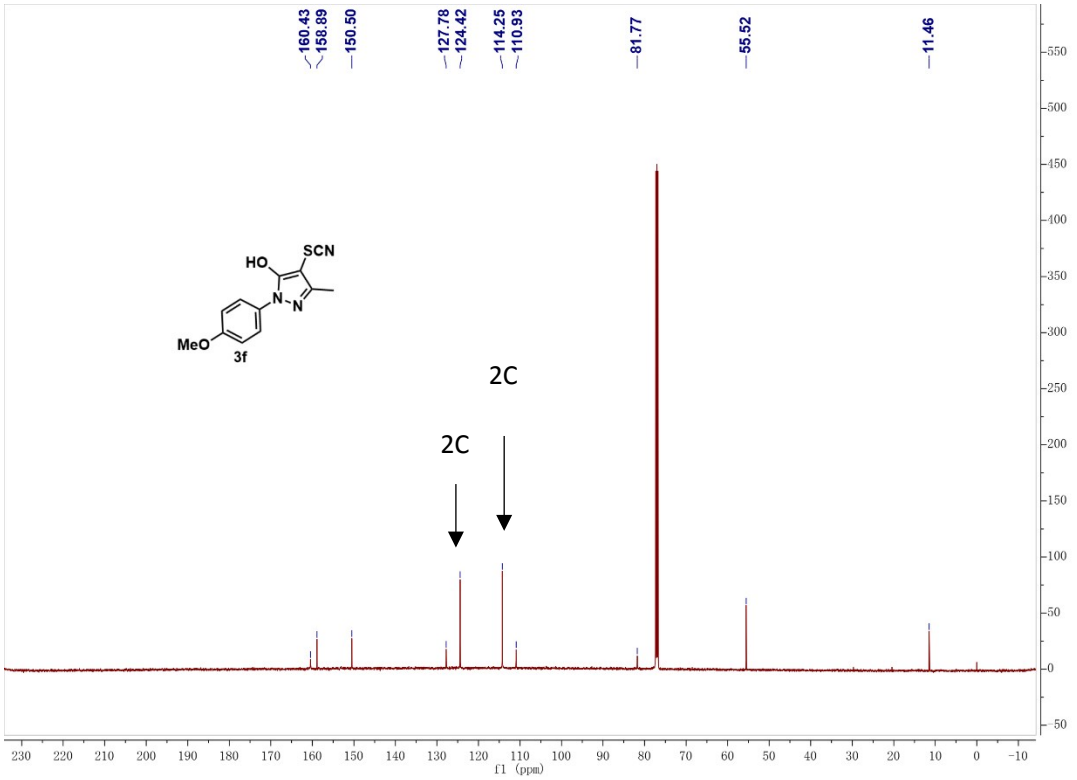

10.85
7.36
7.34
7.28
7.26
2.36
HO
SCN
N
N
Br
3d
1.08
1.92
2.00
3.01
f1 (ppm)

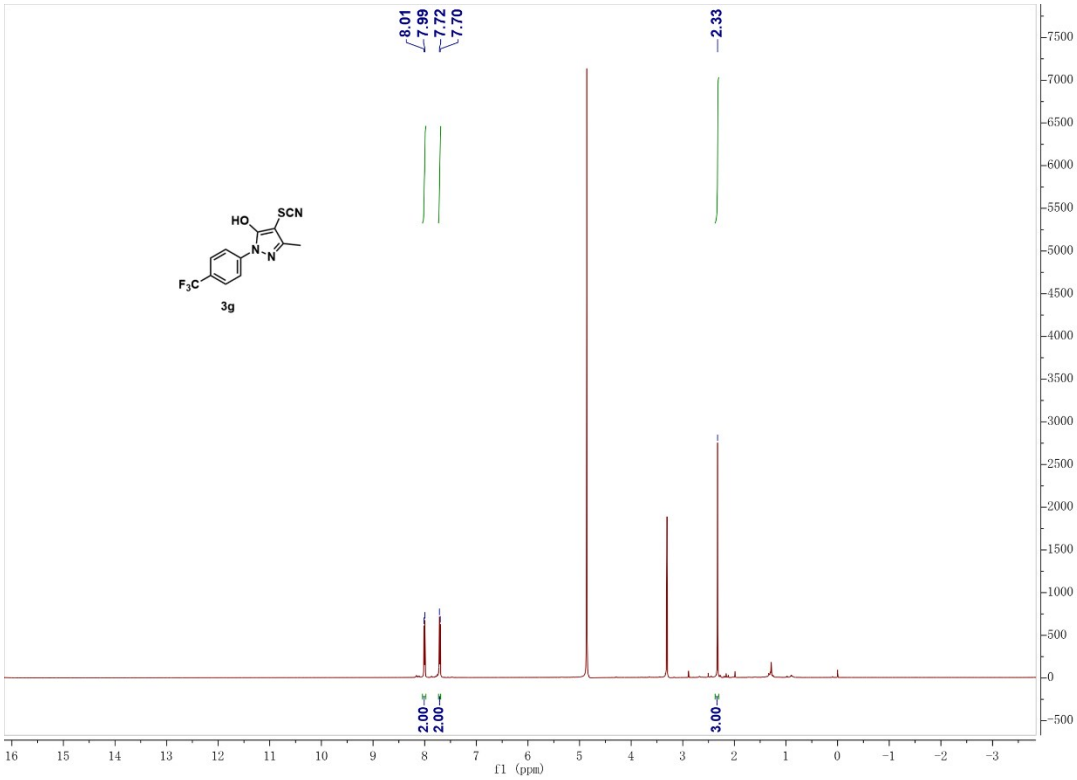

160.62
152.17
134.28
132.18
123.19
120.70
110.88
82.14
11.87
HO
SCN
N
N
Br
3d
2C
2C
f1 (ppm)

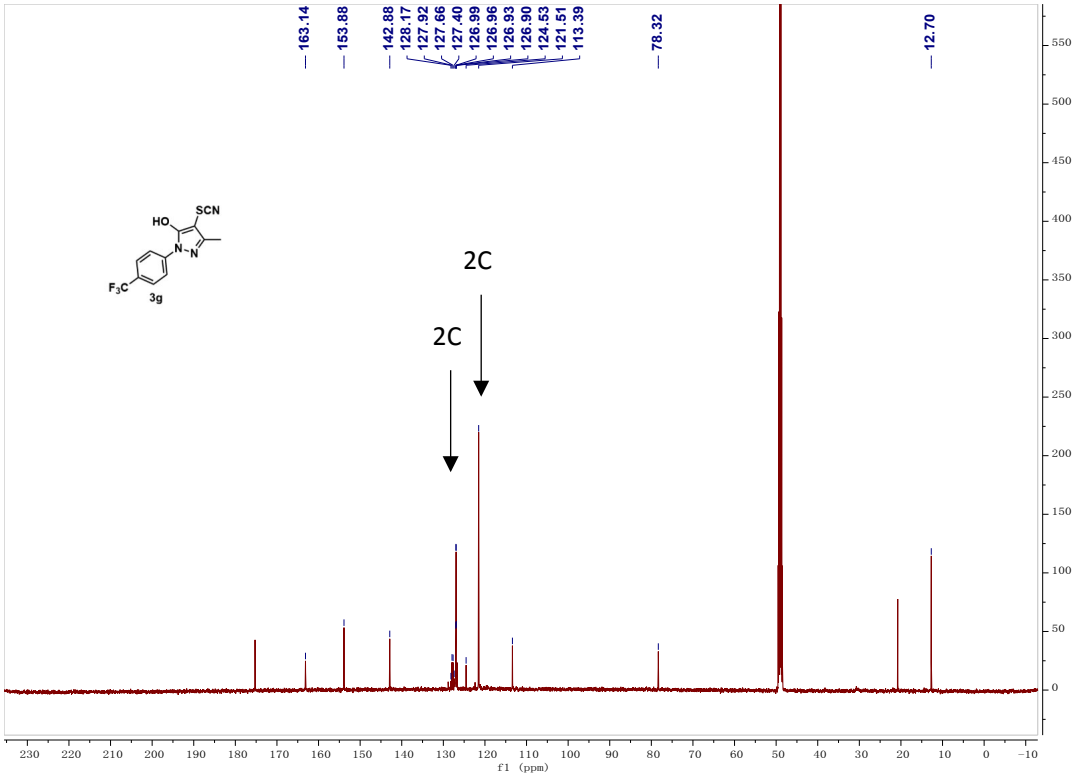

11.44
7.32
7.30
7.29
7.26
2.28
1.26
HO
SCN
N
N
tBu
3e
0.57
2.02
2.03
2.98
9.05
f1 (ppm)


160.20
150.35
150.20
131.92
125.60
121.33
110.34
81.70
34.19
30.83
10.97
3C
2C
2C
HO
SCN
tBu
3e
f1 (ppm)

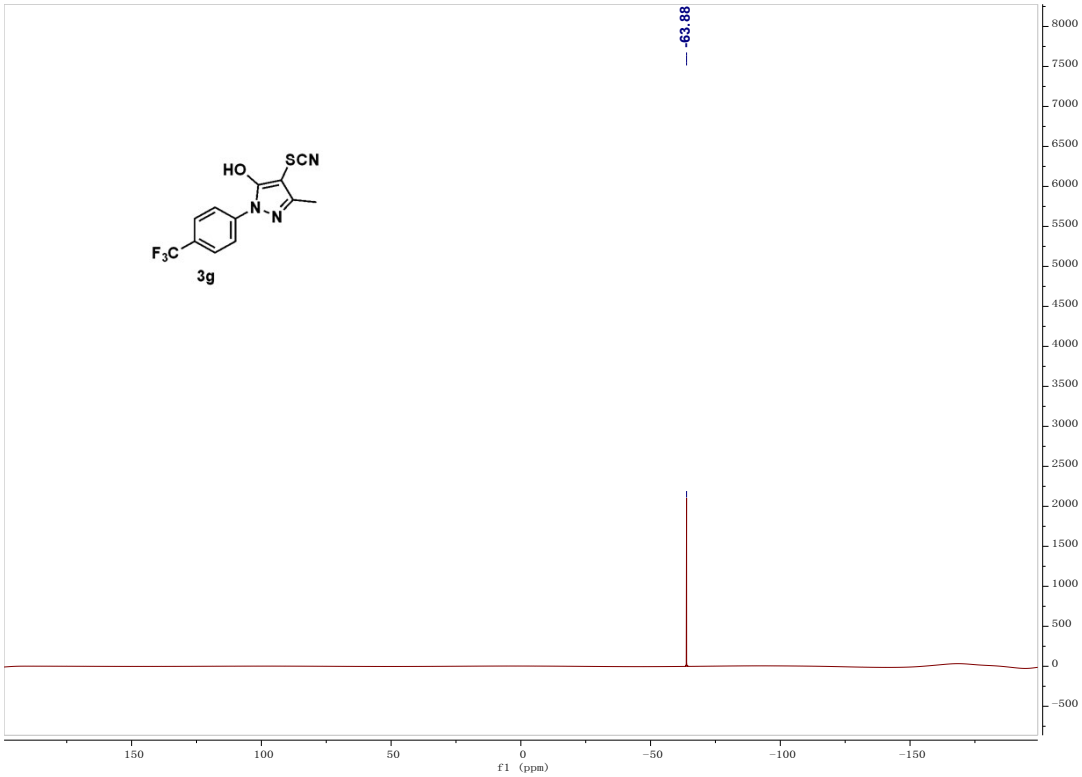

9.27
7.20
7.18
6.75
6.73
3.75
2.27
0.00
HO
SCN
MeO
3f
1.05
1.99
2.00
3.02
3.00
f1 (ppm)

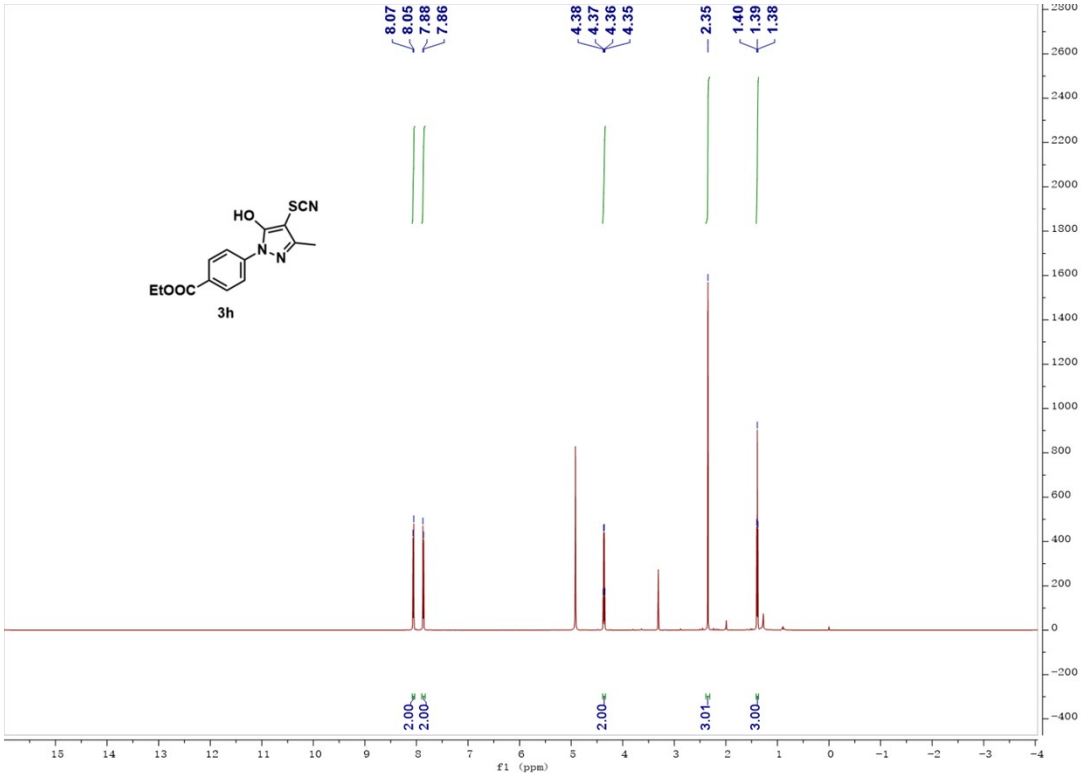

160.43
158.89
150.50
127.78
124.42
114.25
110.93
81.77
55.52
11.46
HO
SCN
N
N
MeO
3f
2C
2C
f1 (ppm)

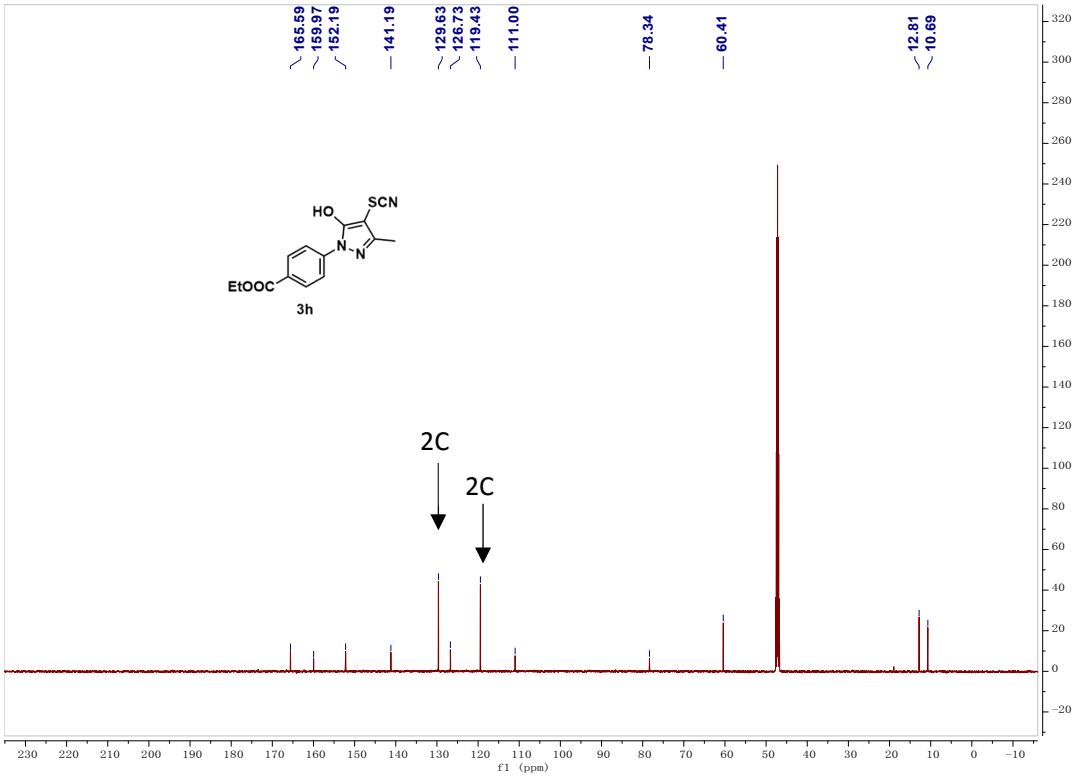

8.01
7.99
7.72
7.70
2.33
HO
SCN
N
N
F3C
3g
2.00
2.00
3.00
f1 (ppm)

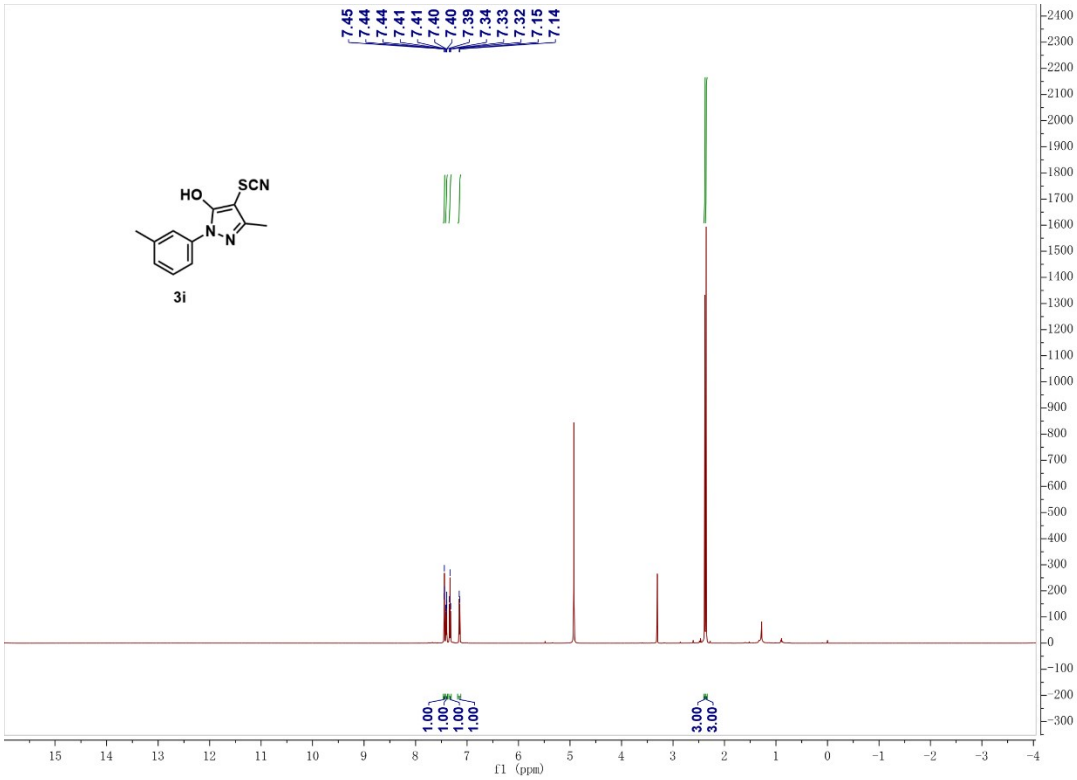


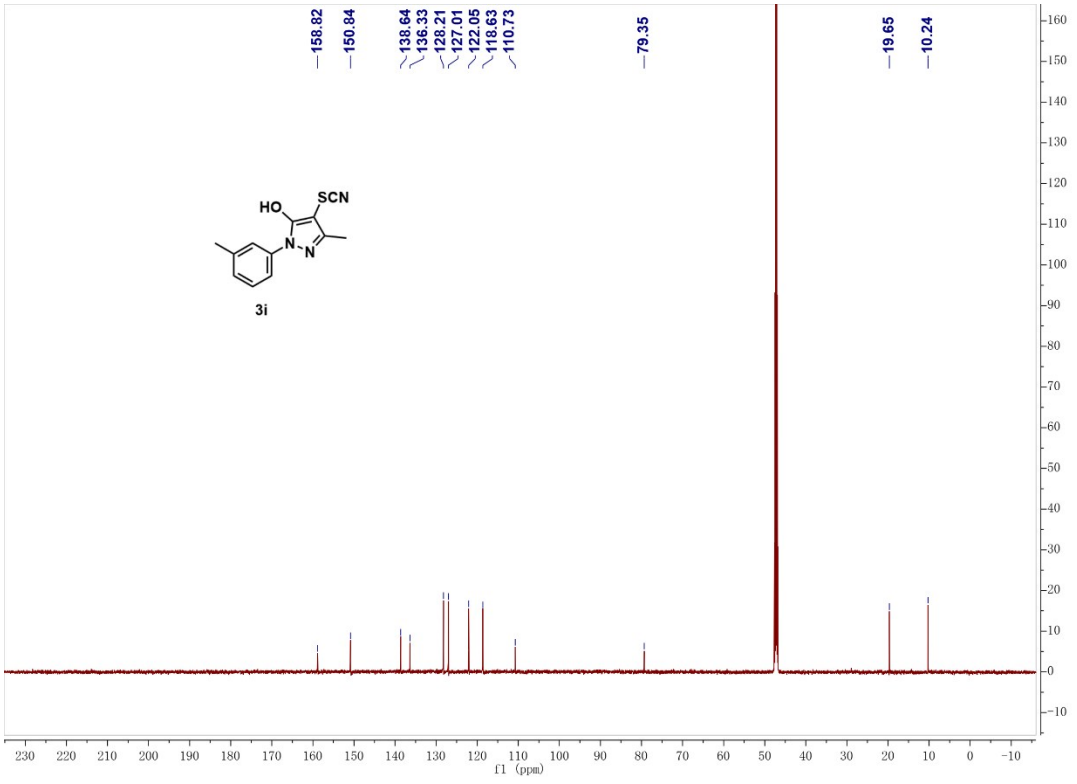
^{19}F NMR spectrum of 3g：




8.07
8.05
7.88
7.86
4.38
4.37
4.36
4.35
2.35
1.40
1.39
1.38
HO
SCN
N
N
EtOOC
3h
2.00
2.00
2.00
3.01
3.00
f1 (ppm)


165.59
159.97
152.19
141.19
129.63
126.73
119.43
111.00
78.34
60.41
12.81
10.69
HO
SCN
N
N
EtOOC
3h
2C
2C
f1 (ppm)


7.45
7.44
7.44
7.41
7.41
7.40
7.40
7.39
7.34
7.33
7.32
7.15
7.14
HO
SCN
N
N
3i
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


158.82
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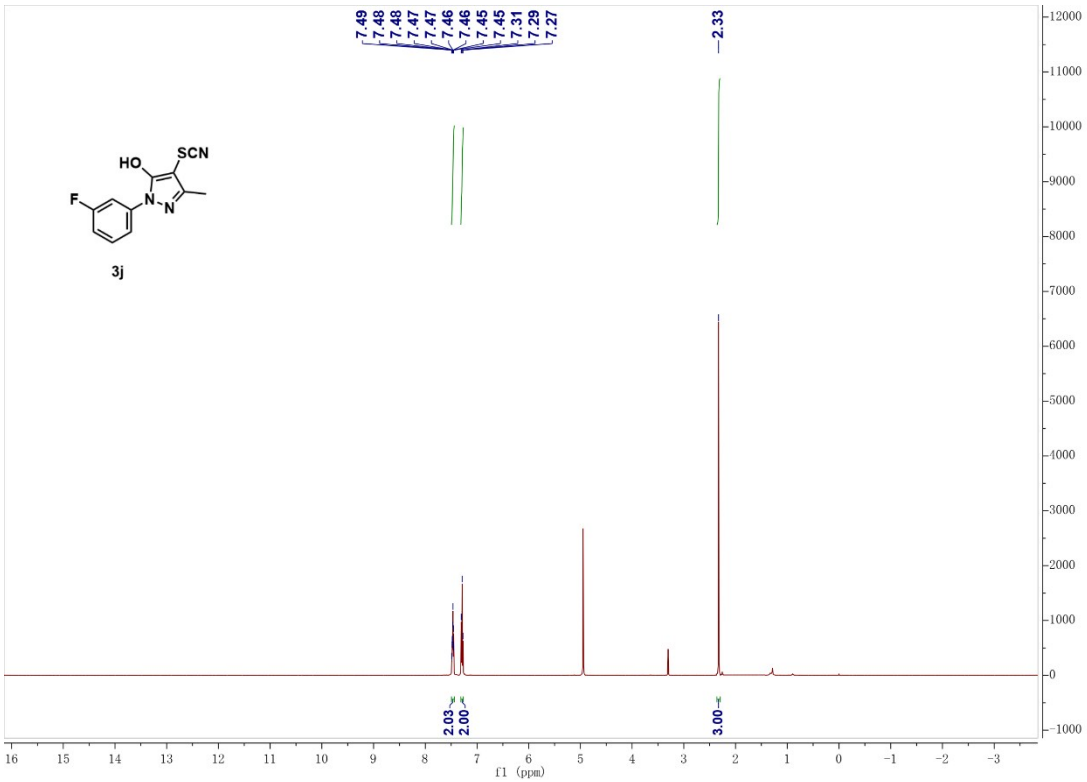
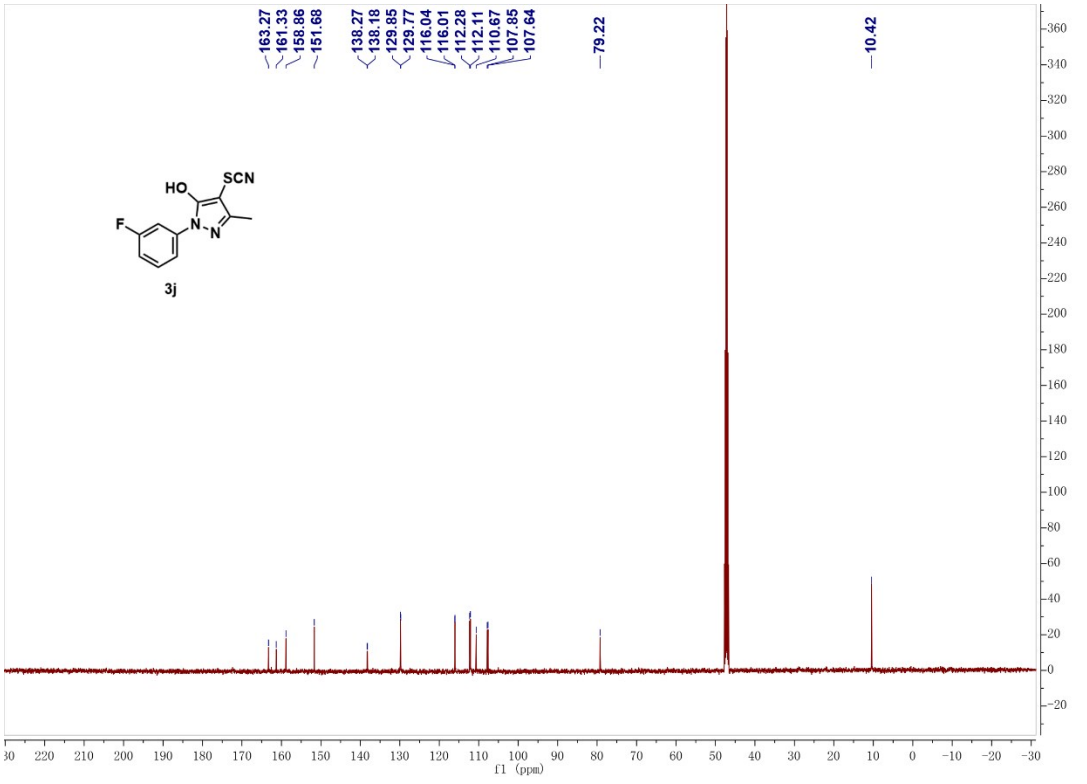
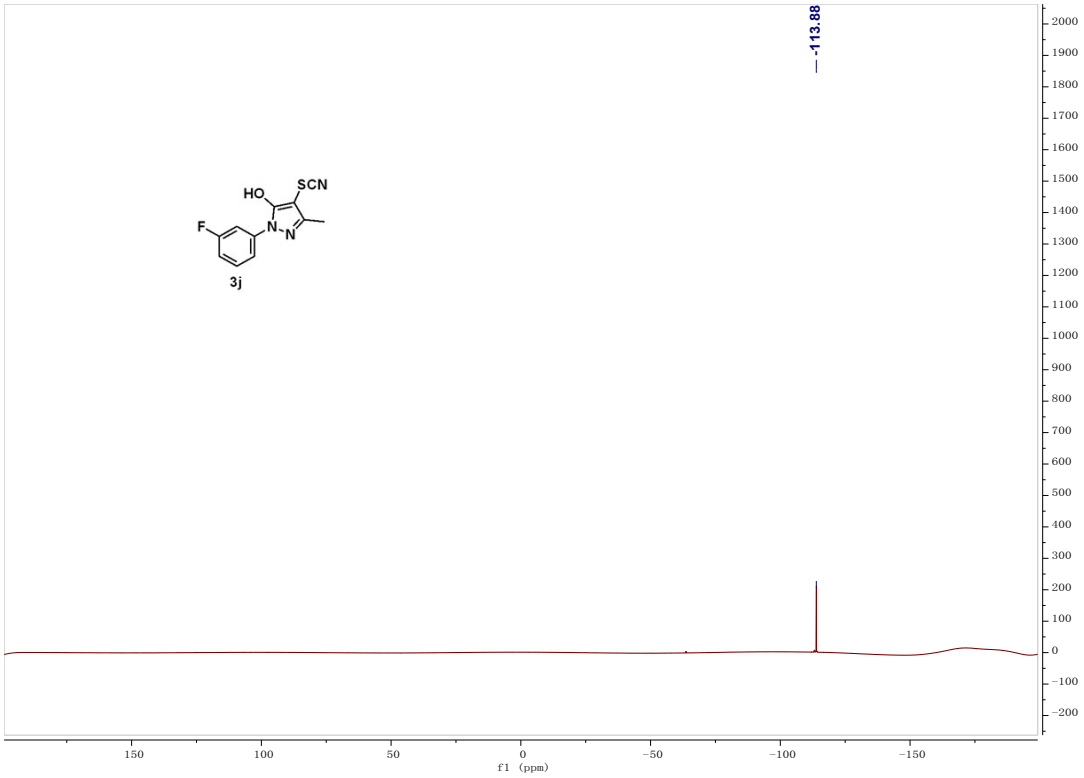
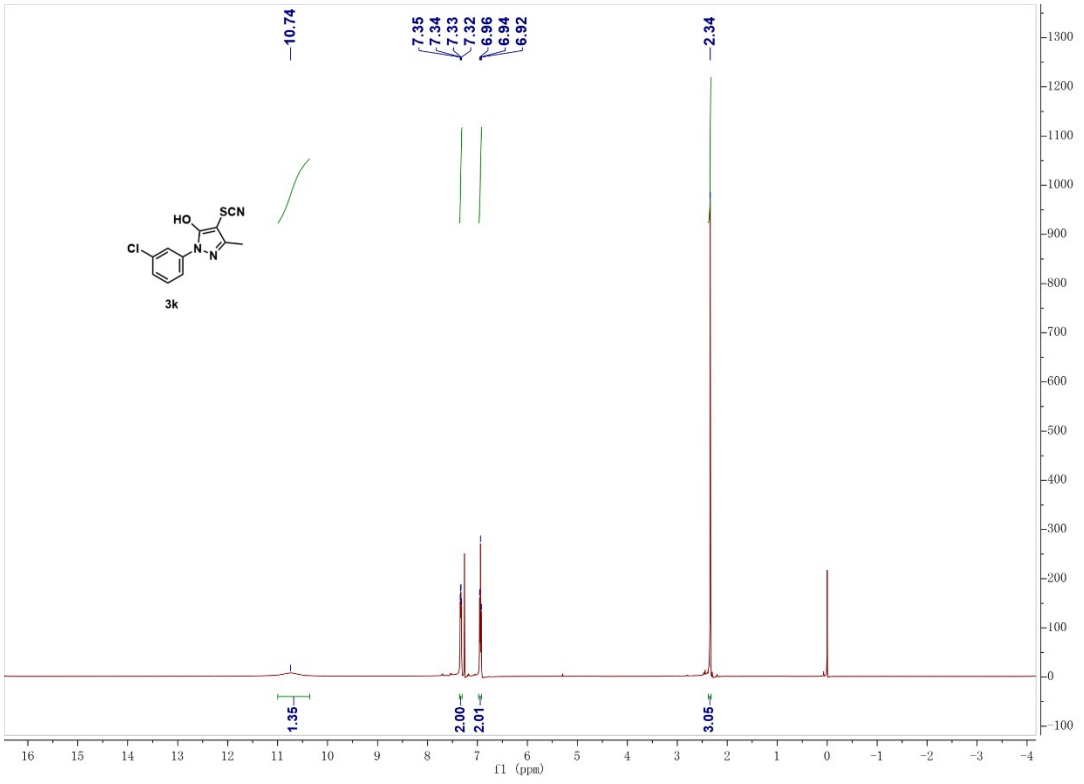
138.64
136.33
128.21
127.01
122.05
118.63
110.73
79.35
19.65
10.24
HO
SCN
N
N
3i
f1 (ppm)

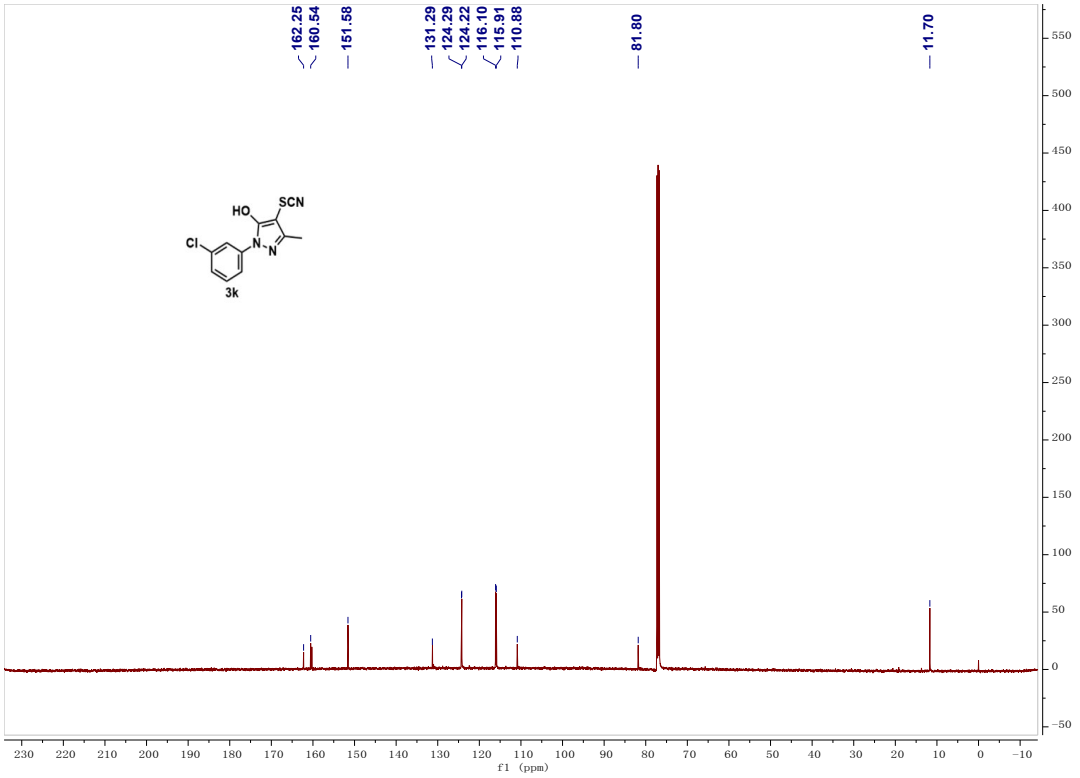




^{19}F NMR spectrum of **3j**：


-113.88
HO
SCN
F
N
N
3j
f1 (ppm)


10.74
7.35
7.34
7.33
7.32
6.96
6.94
6.92
2.34
HO
SCN
Cl
N
N
3k
1.35
2.00
2.01
3.05
f1 (ppm)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151.58
131.29
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124.22
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115.91
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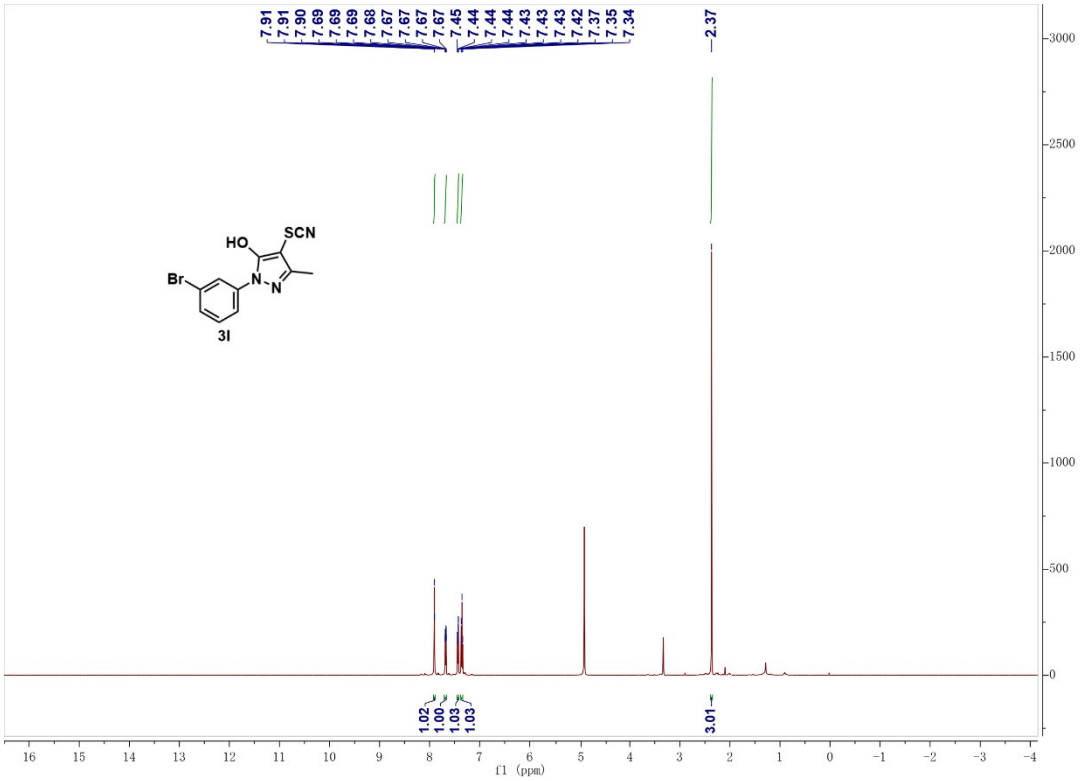
81.80
11.70
HO
SCN
Cl
N
N
3k
f1 (ppm)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7.90
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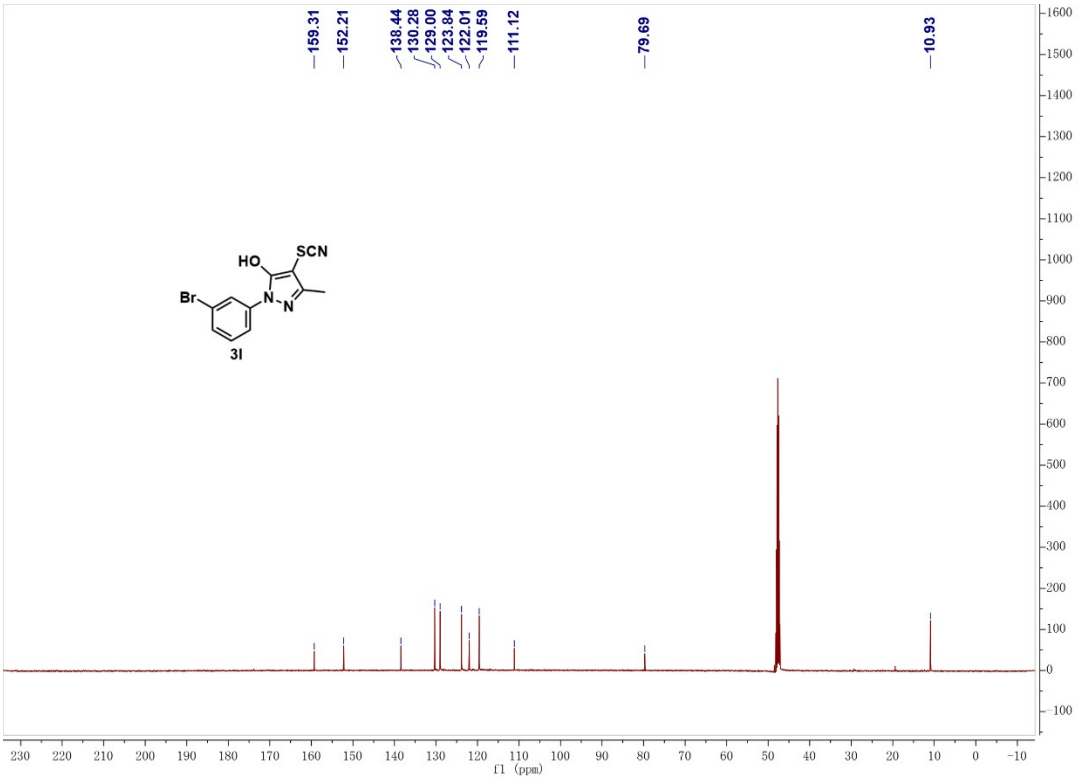
7.69
7.68
7.67
7.67
7.67
7.67
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.37
7.35
7.34
2.37
HO
SCN
Br
N
N
3l
1.02
1.00
1.03
1.03
3.01
f1 (ppm)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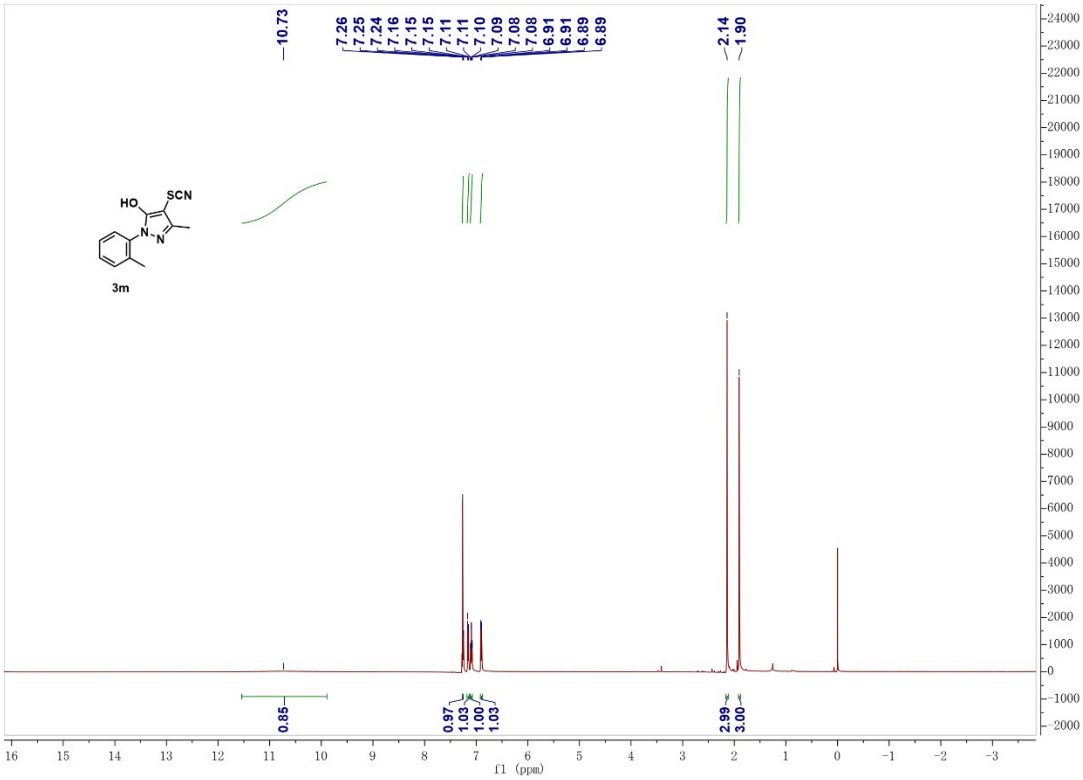
111.12
79.69
10.93
HO
SCN
Br
N
N
3l
f1 (ppm)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7.15
7.15
7.11
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7.10
7.09
7.08
7.08
6.91
6.91
6.89
6.89
2.14
1.90
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SCN
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N
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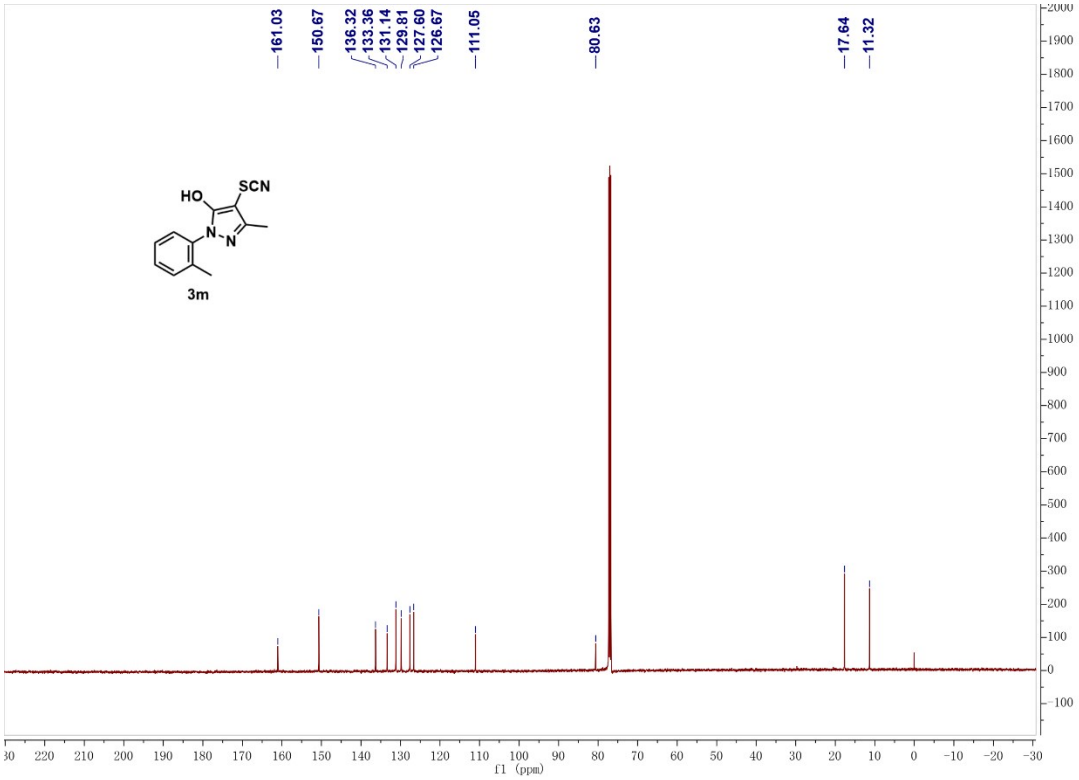
0.97
1.03
1.00
1.03
2.99
3.00
f1 (ppm)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131.14
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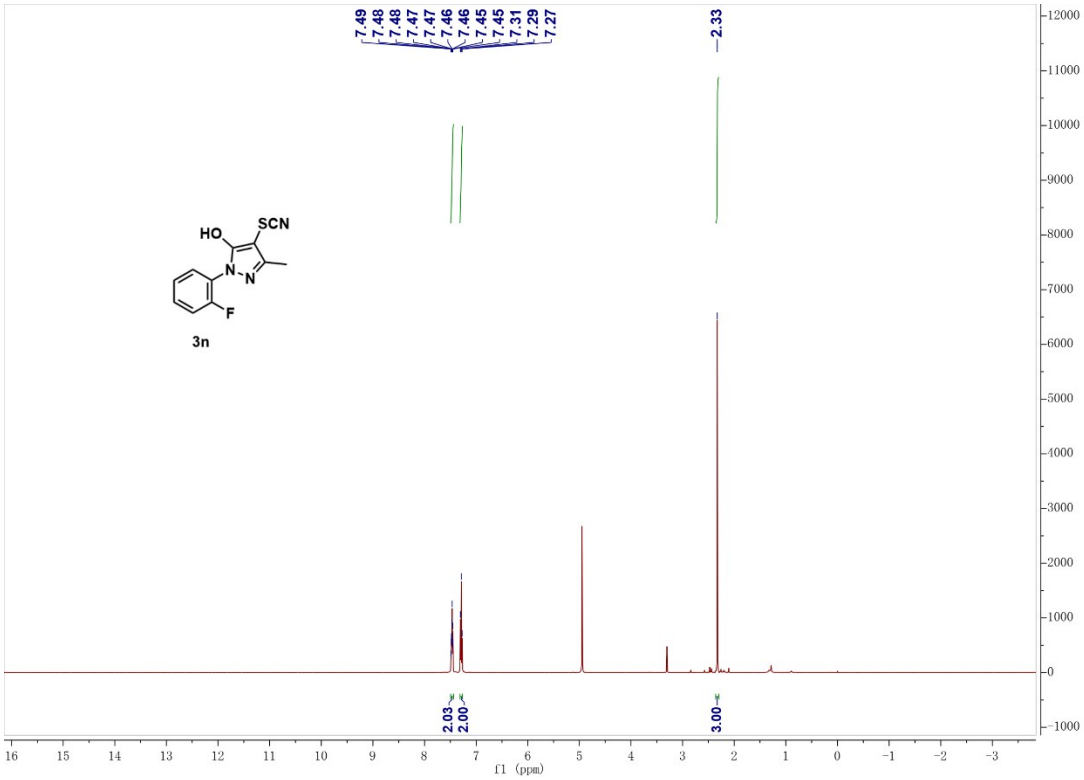
111.05
80.63
17.64
11.32
HO
SCN
N
N
3m
f1 (ppm)


7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
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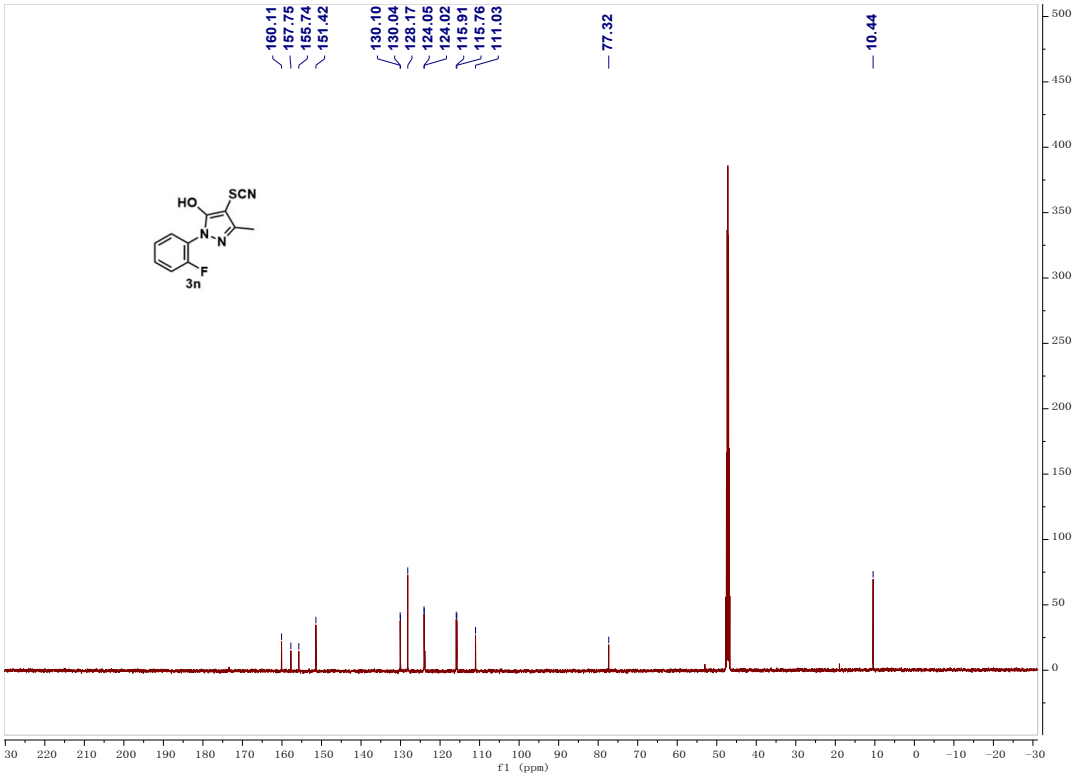
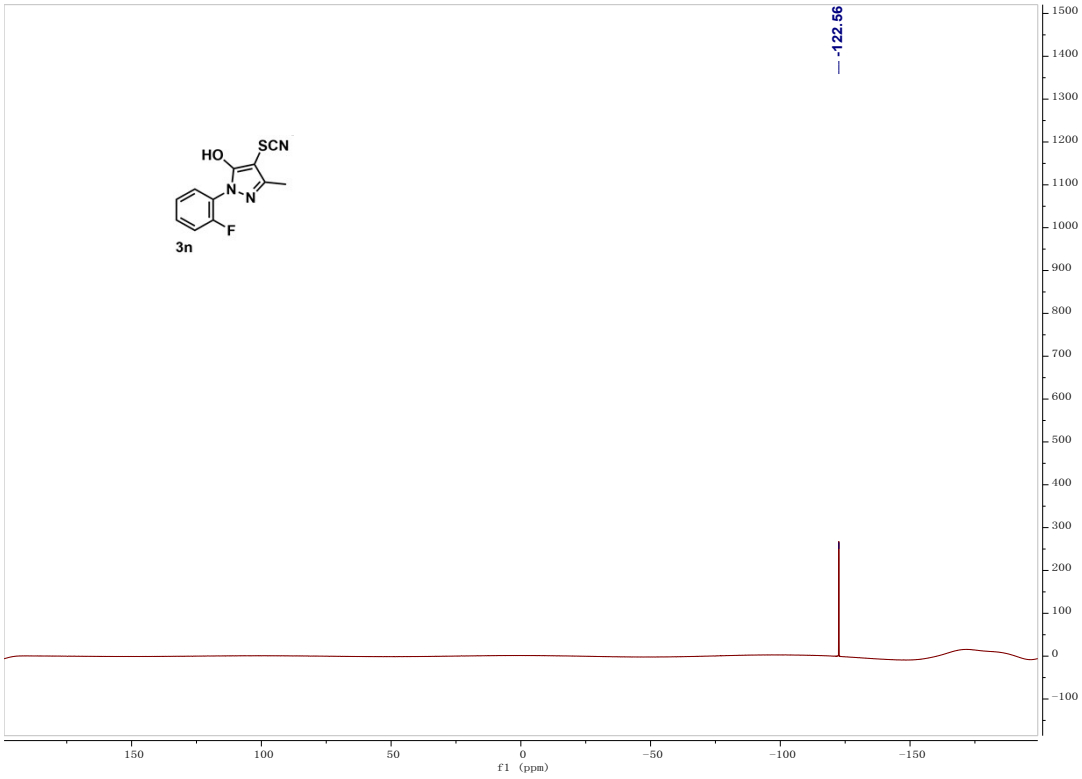
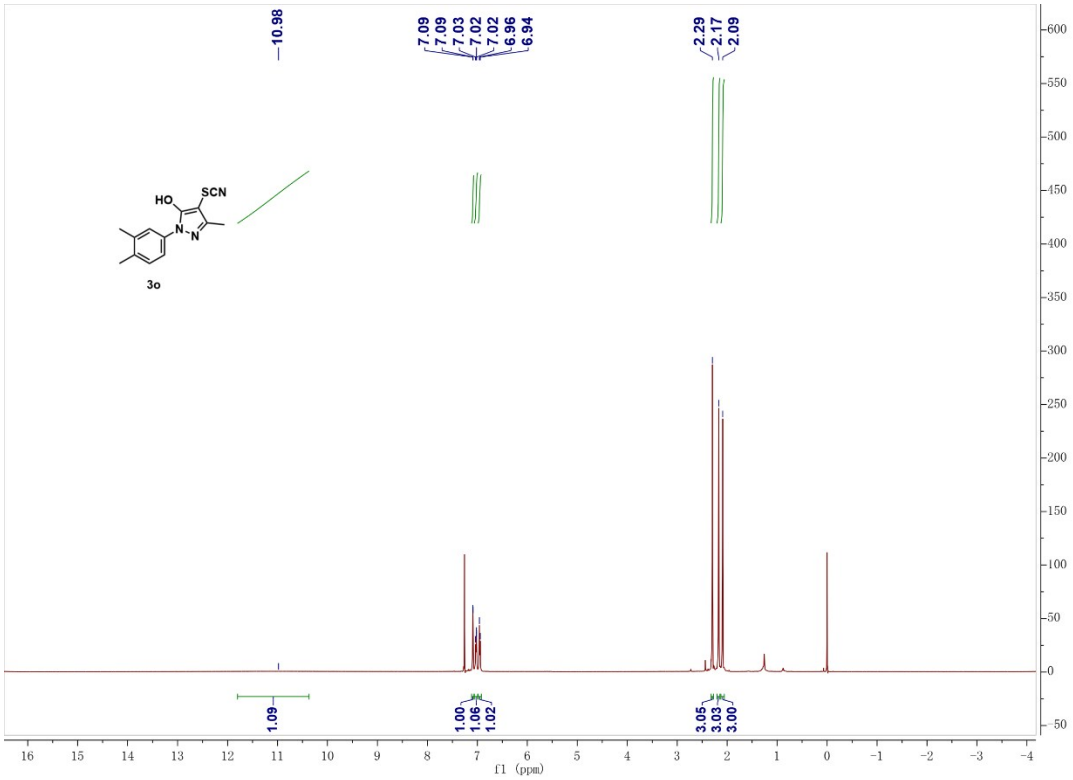
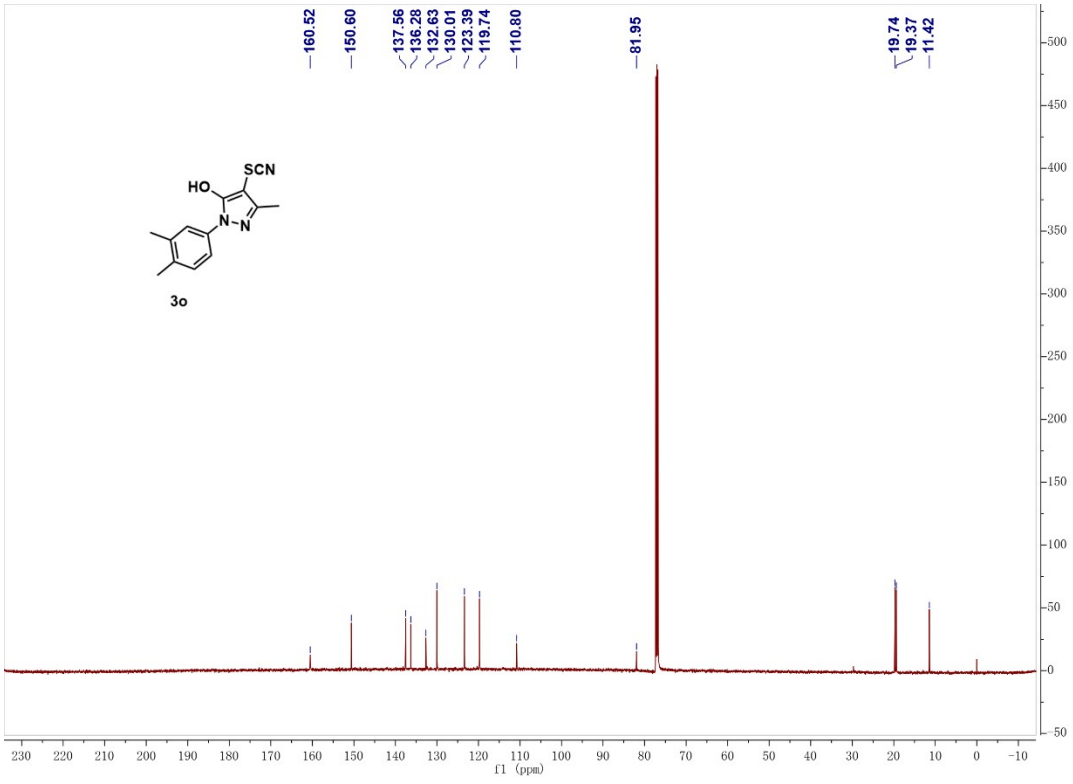
2.33
HO
SCN
N
N
F
3n
2.03
2.00
3.00
f1 (ppm)

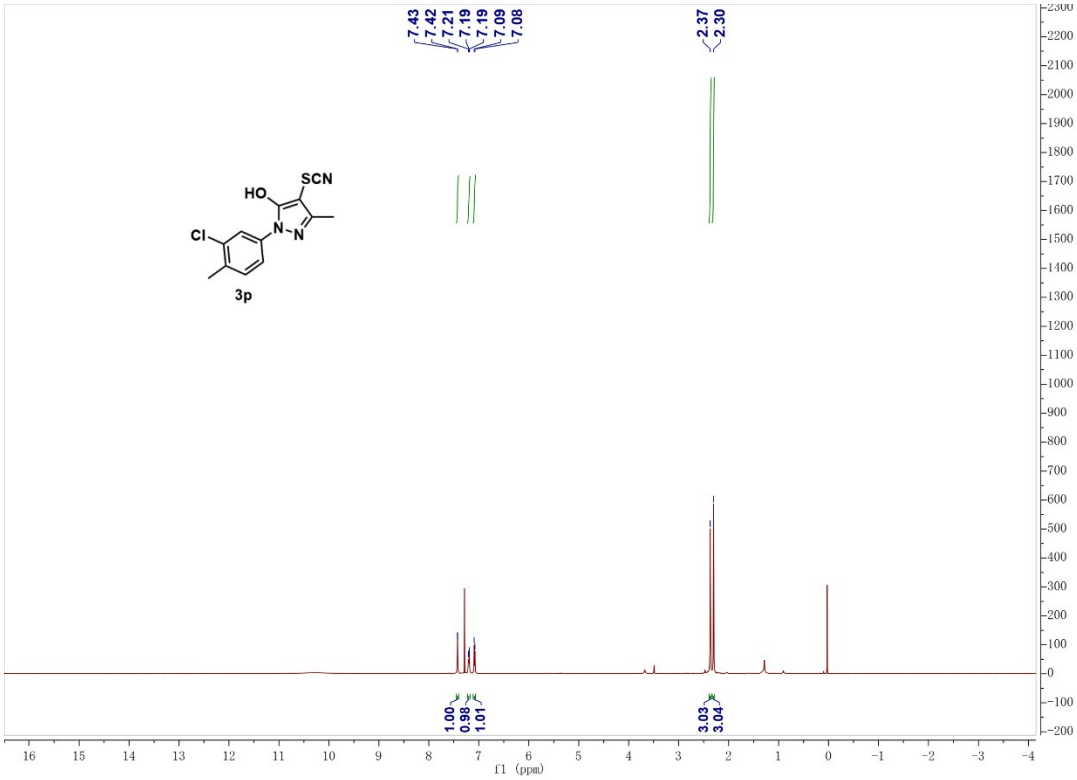


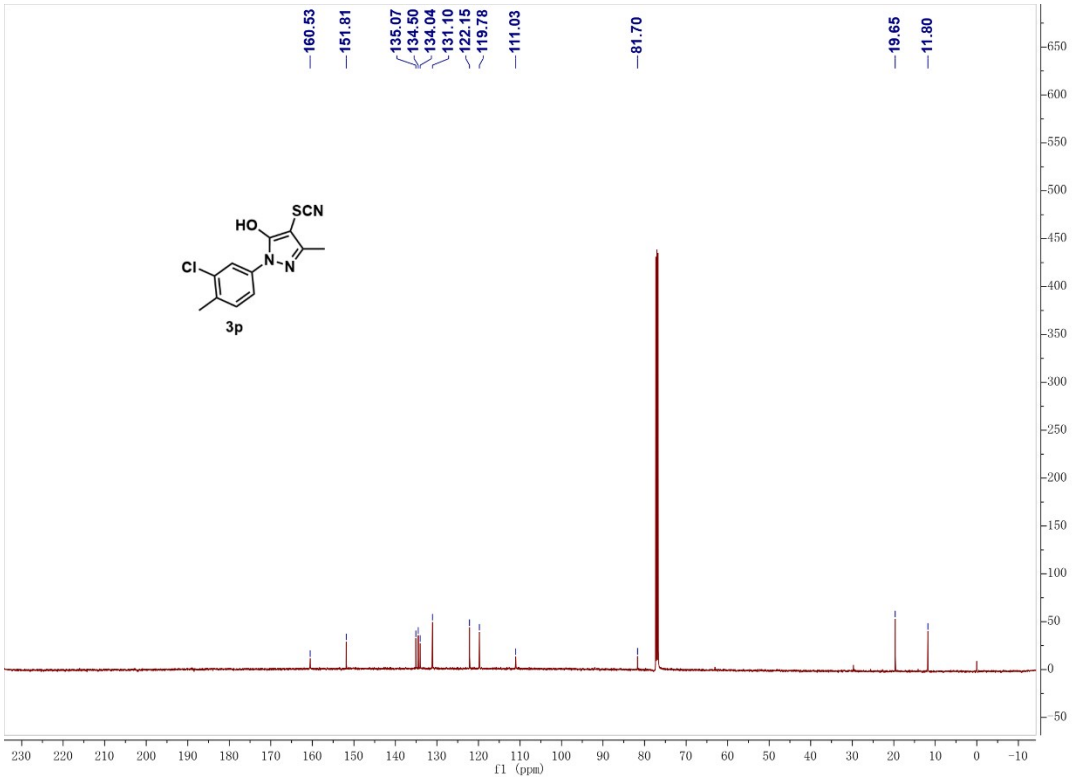
^{19}F NMR spectrum of **3n**:

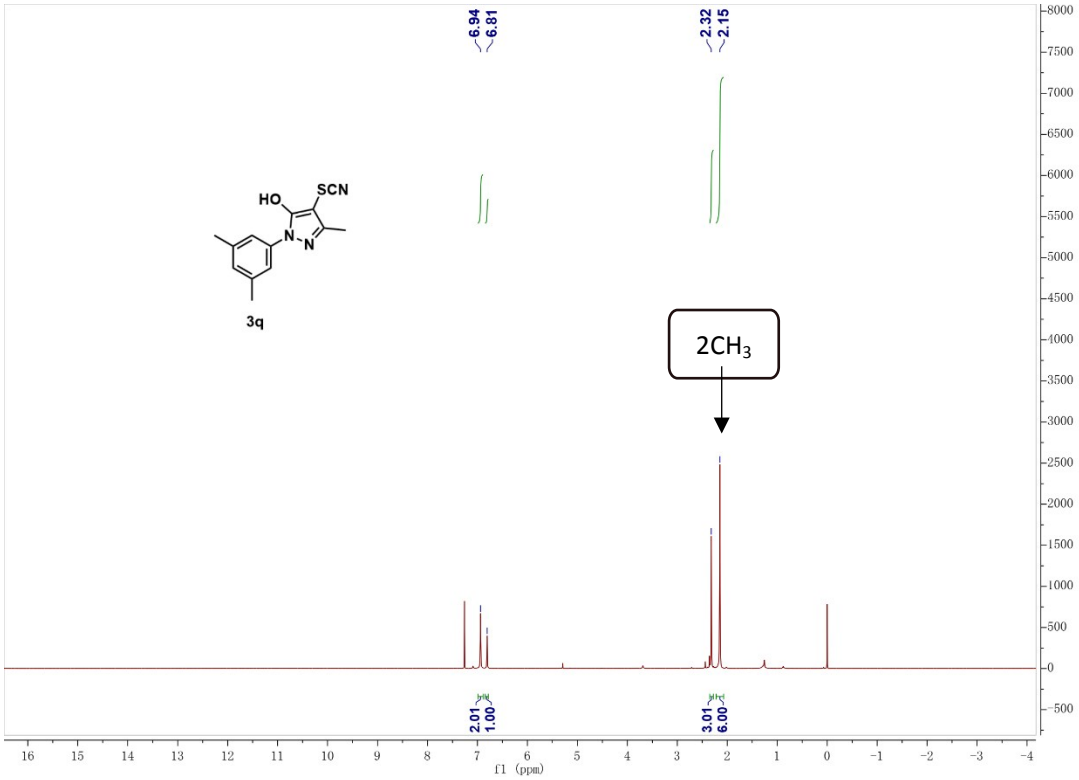


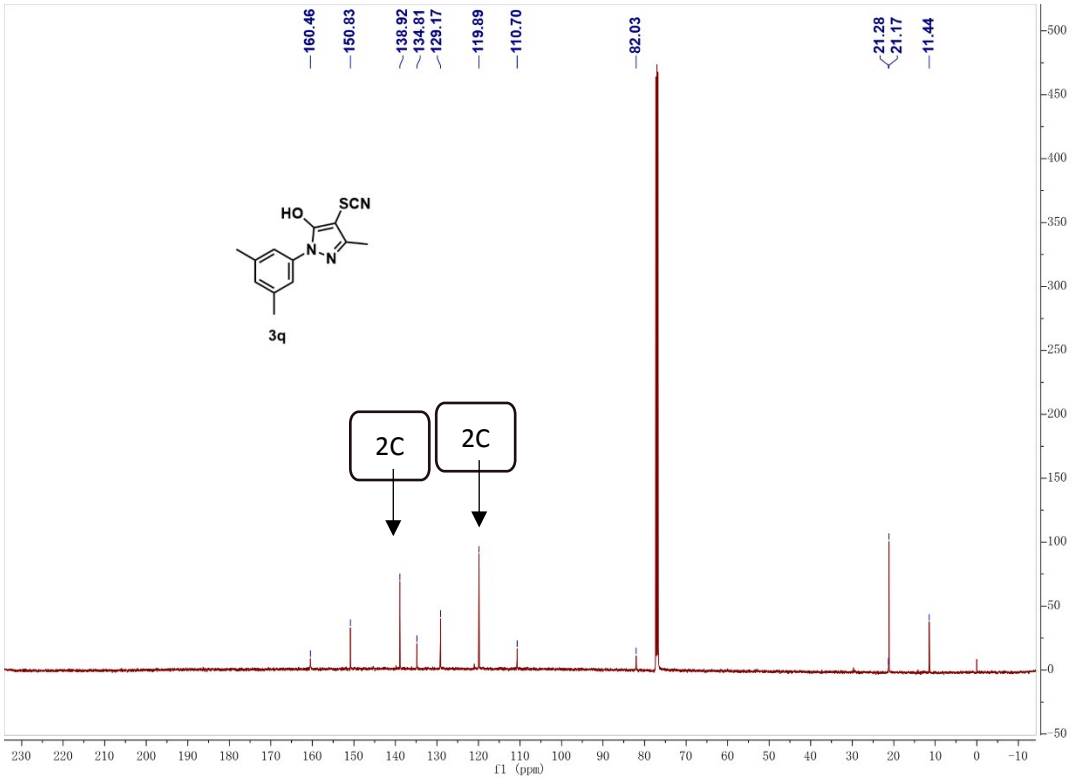

10.98
7.09
7.09
7.03
7.02
7.02
6.96
6.94
2.29
2.17
2.09
HO
SCN
N
N
3o
1.09
1.00
1.06
1.02
3.05
3.03
3.00
f1 (ppm)

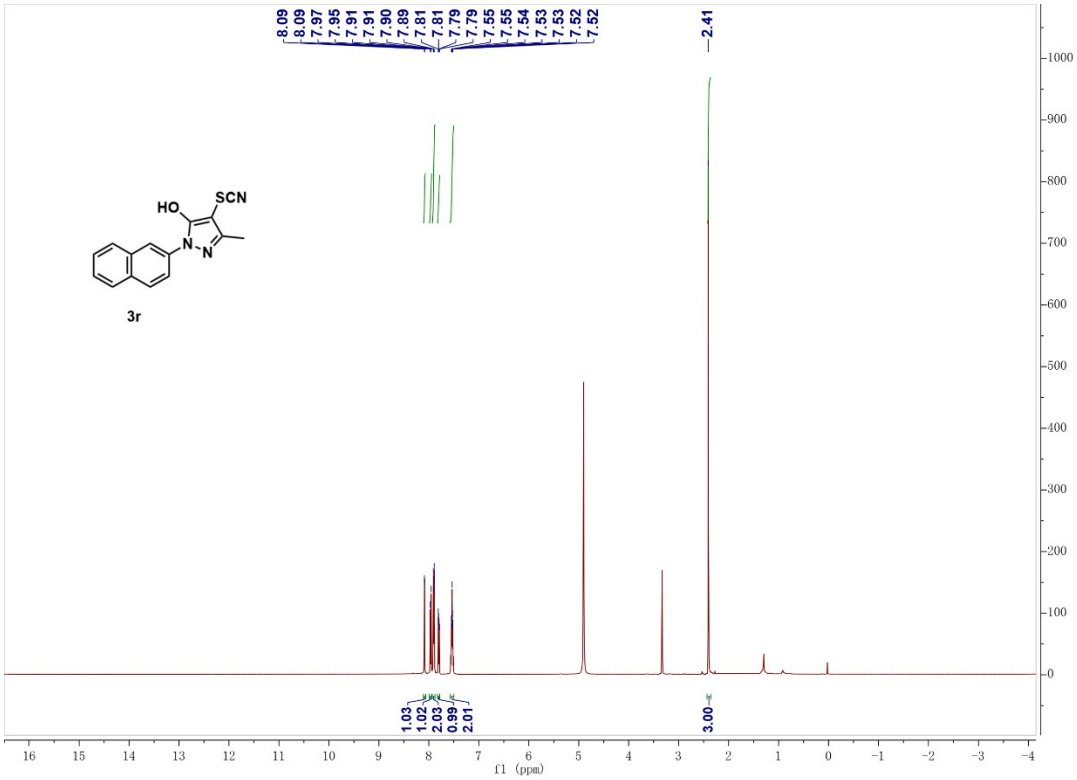

160.52
150.60
137.56
136.28
132.63
130.01
123.39
119.74
110.80
81.95
19.74
19.37
11.42
HO
SCN
N
N
3o
f1 (ppm)

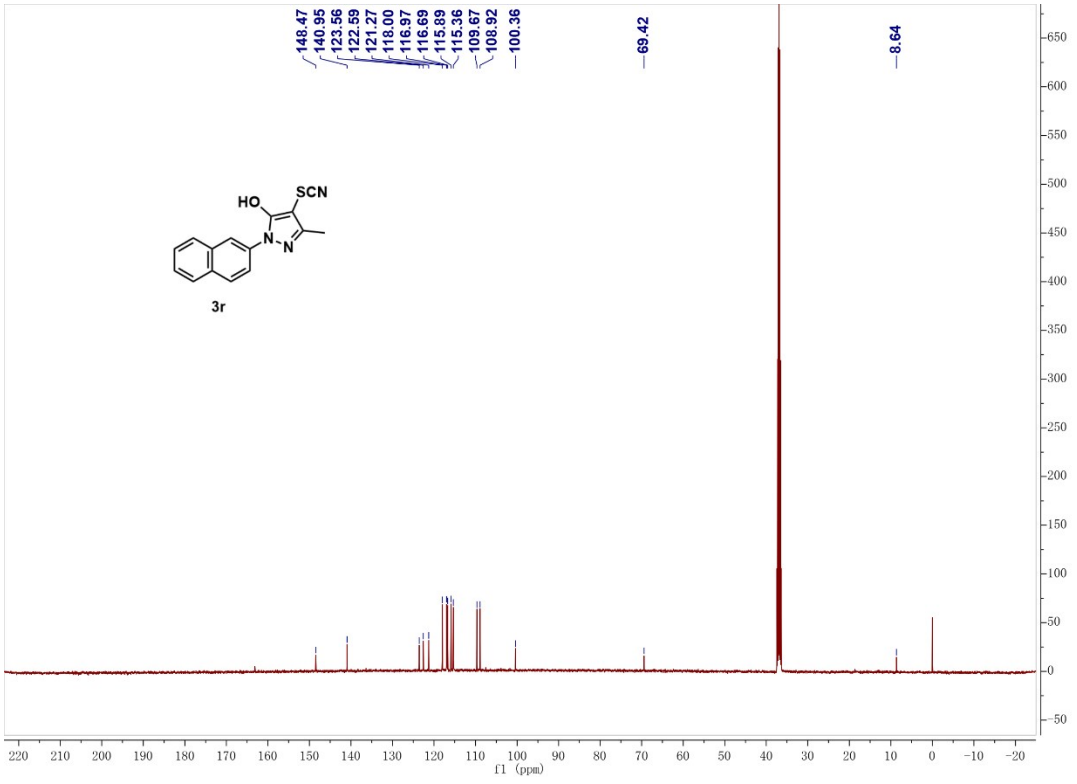

7.43
7.42
7.21
7.19
7.19
7.09
7.08
2.37
2.30
HO
SCN
Cl
N
N
3p
1.00
0.98
1.01
3.03
3.04
f1 (ppm)

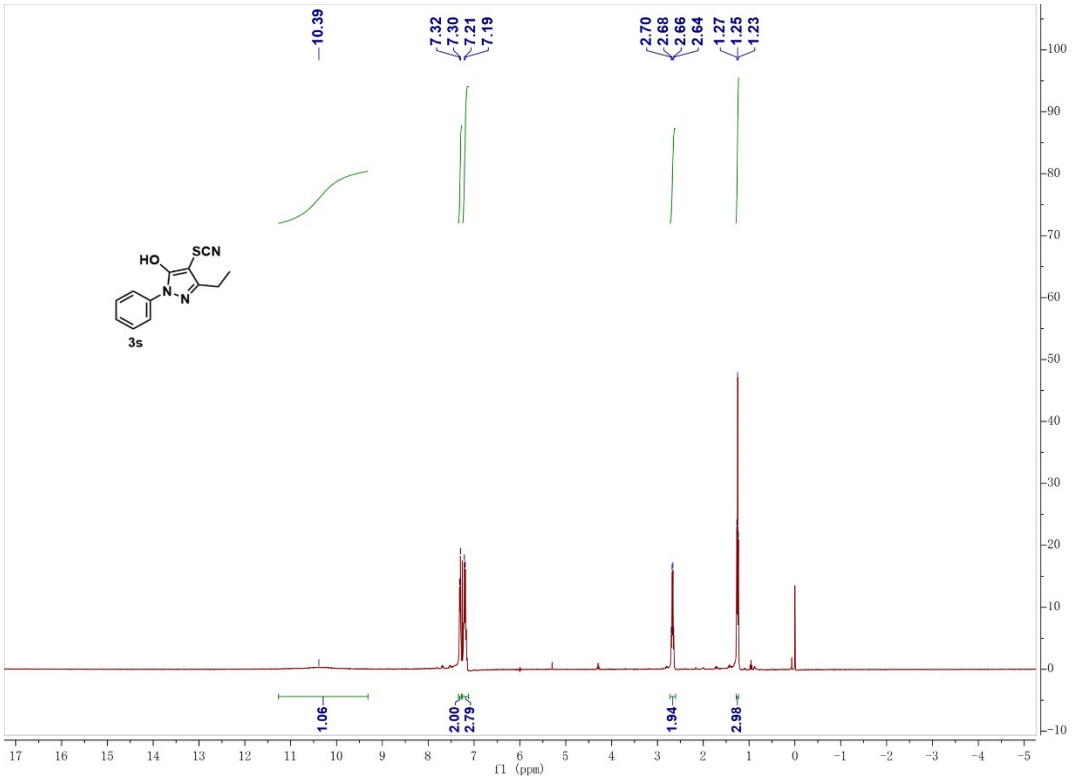

160.53
151.81
135.07
134.50
134.04
131.10
122.15
119.78
111.03
81.70
19.65
11.80
HO
SCN
Cl
N
N
3p
f1 (ppm)

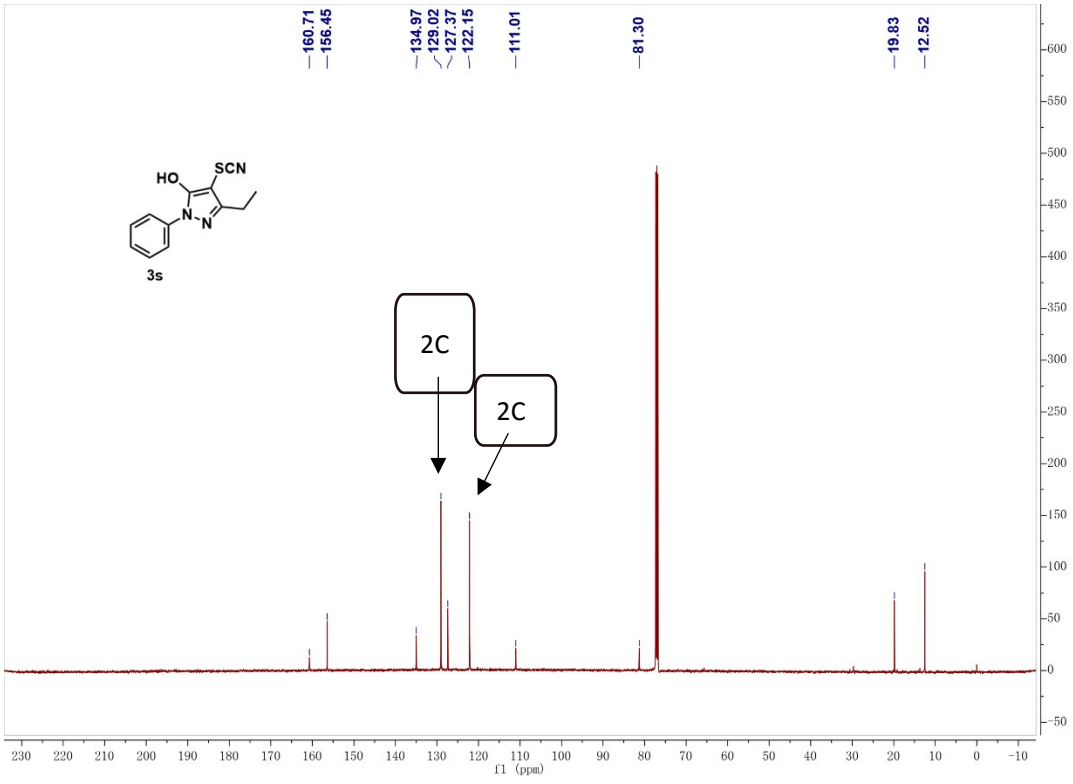

6.94
6.81
2.32
2.15
HO
SCN
N
N
3q
2CH3
2.01
1.00
3.01
6.00
f1 (ppm)

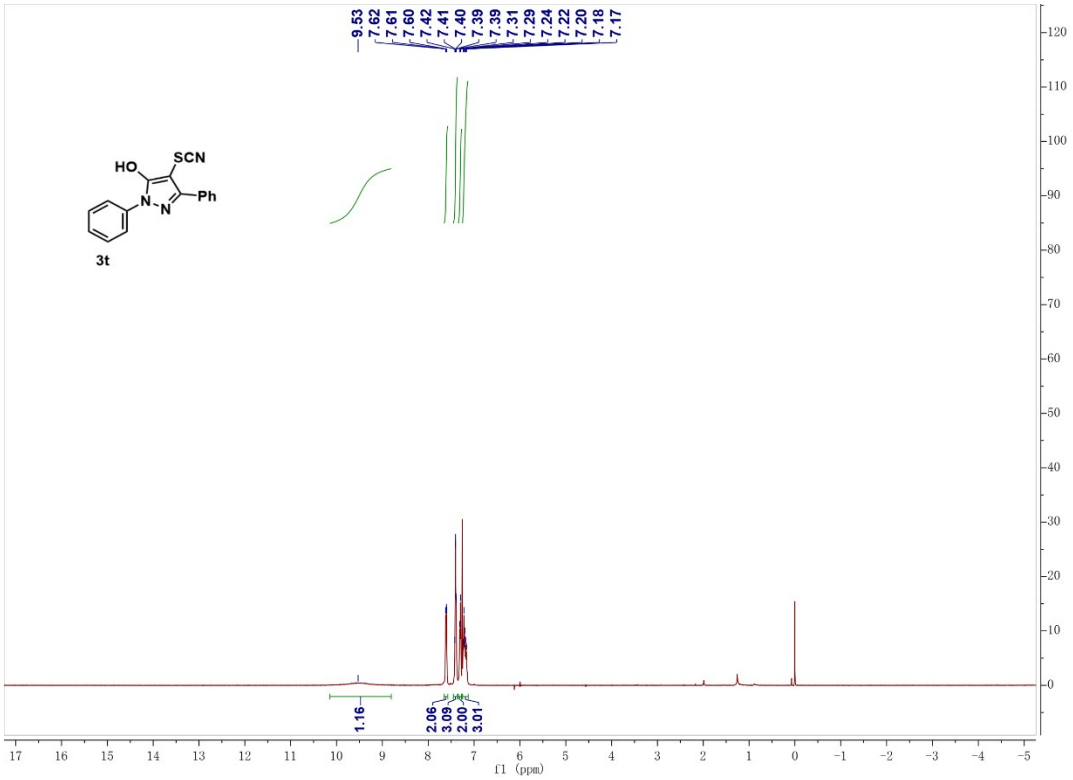

160.46
150.83
138.92
134.81
129.17
119.89
110.70
82.03
21.28
21.17
11.44
HO
SCN
N
N
3q
2C
2C
f1 (ppm)

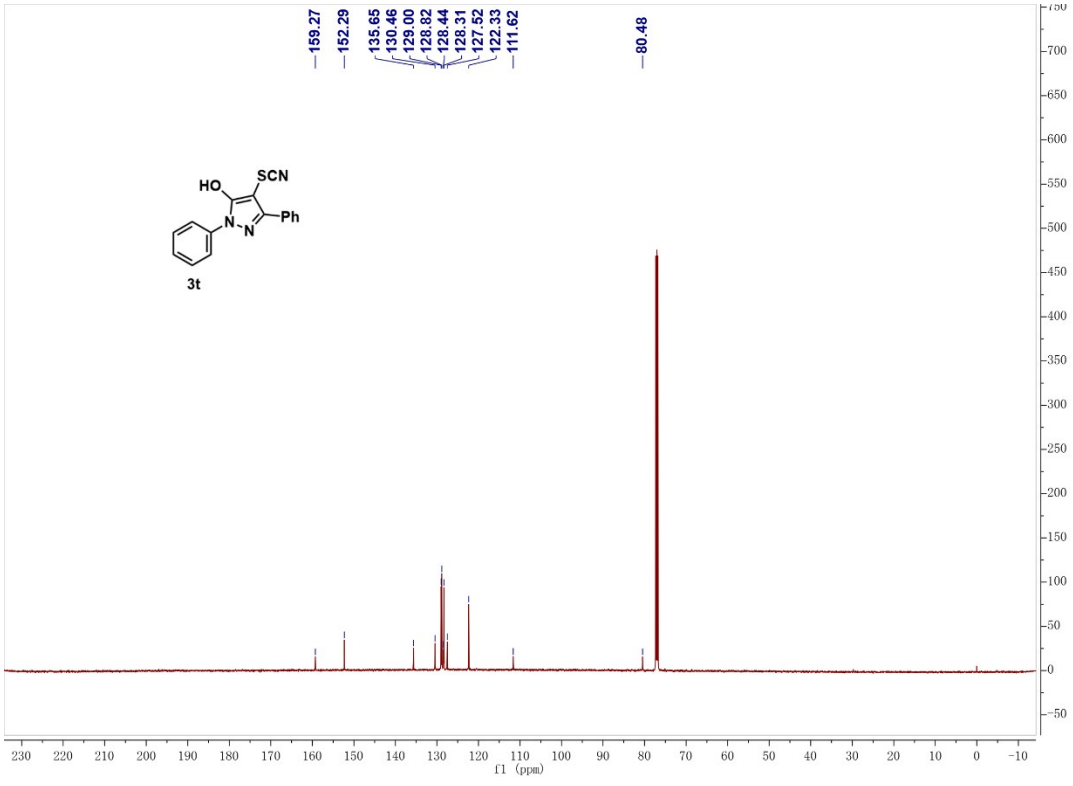

8.09
8.09
7.97
7.95
7.91
7.91
7.90
7.89
7.81
7.81
7.79
7.79
7.55
7.55
7.54
7.53
7.53
7.52
7.52
2.41
HO
SCN
N
N
3r
1.03
1.02
2.03
0.99
2.01
3.00
f1 (ppm)

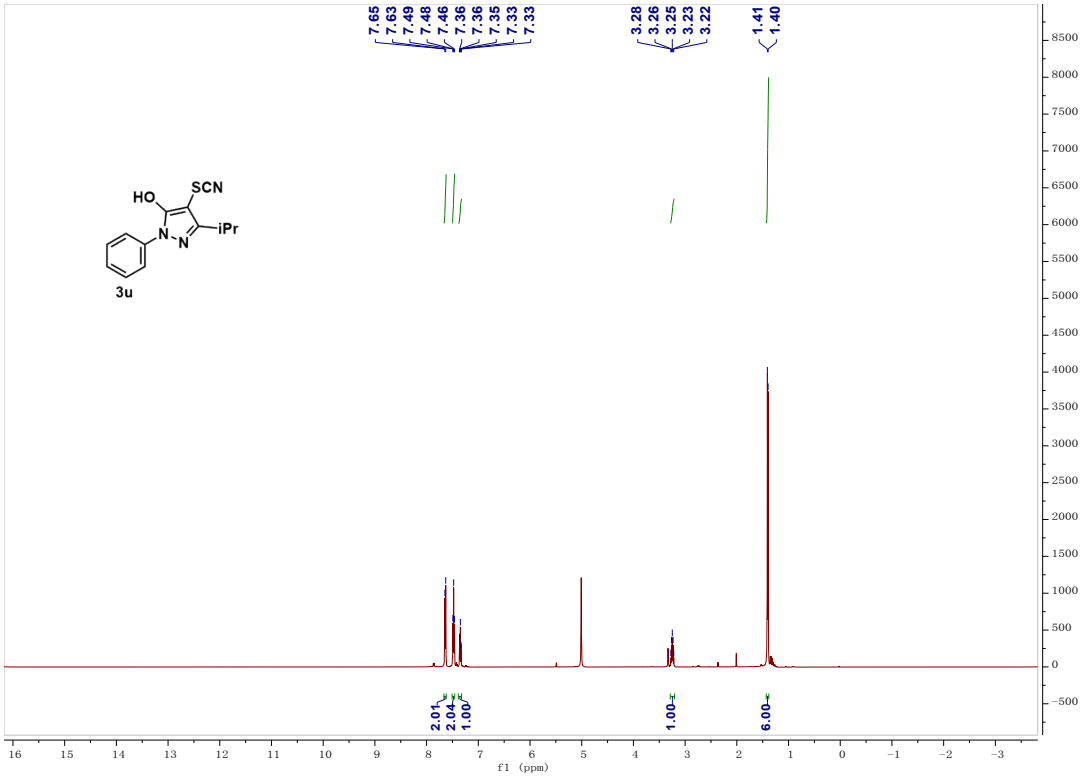

148.47
140.95
123.56
122.59
121.27
118.00
116.97
116.69
115.89
115.36
109.67
108.92
100.36
69.42
8.64
HO
SCN
N
N
3r
f1 (ppm)

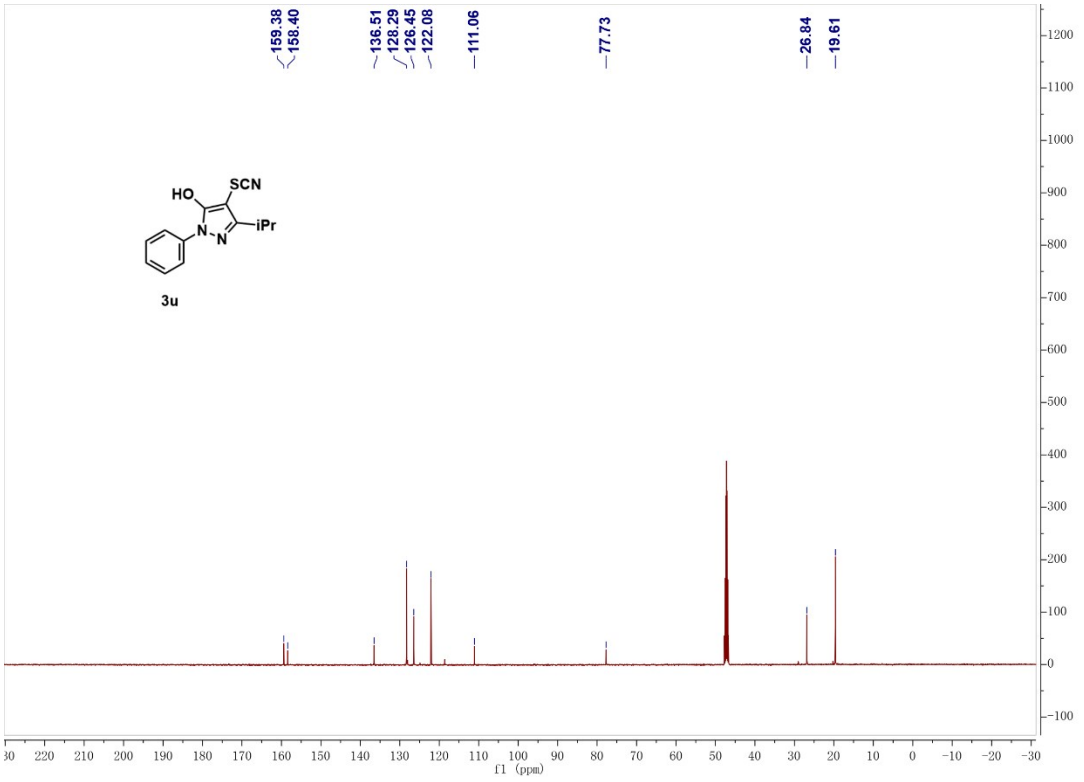

10.39
7.32
7.30
7.21
7.19
2.70
2.68
2.66
2.64
1.27
1.25
1.23
HO
SCN
3s
1.06
2.00
2.79
1.94
2.98
f1 (ppm)


160.71
156.45
134.97
129.02
127.37
122.15
111.01
81.30
19.83
12.52
HO
SCN
3s
2C
2C
f1 (ppm)


9.53
7.62
7.61
7.60
7.42
7.41
7.40
7.39
7.39
7.31
7.29
7.24
7.22
7.20
7.18
7.17
HO
SCN
Ph
N
N
3t
1.16
2.06
3.09
2.00
3.01
f1 (ppm)


159.27
152.29
135.65
130.46
129.00
128.82
128.44
128.31
127.52
122.33
111.62
80.48
HO
SCN
Ph
N
N
3t
f1 (ppm)


7.65
7.63
7.49
7.48
7.46
7.36
7.36
7.35
7.33
7.33
3.28
3.26
3.25
3.23
3.22
1.41
1.40
HO
SCN
iPr
N
N
3u
2.01
2.04
1.00
1.00
6.00
f1 (ppm)


159.38
158.40
136.51
128.29
126.45
122.08
111.06
77.73
26.84
19.61
HO
SCN
iPr
N
N
3u
f1 (ppm)