Supporting Information for

p-Toluenesulphonic Acid-Promoted, I_2-Catalysed Sulphenylation of Pyrazolones with Aryl Sulphonyl Hydrazides

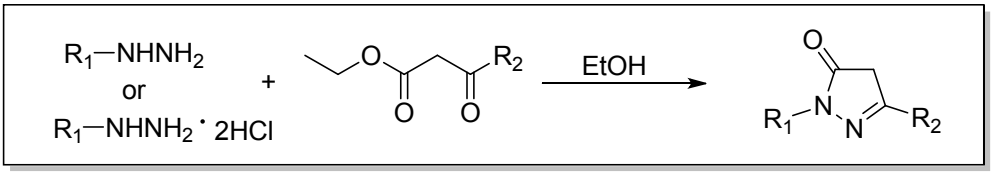
Xia Zhao,*[a] Lipeng Zhang,[a] Tianjiao Li,[a] Guiyan Liu,[a] Haomeng Wang,[a] Kui Lu*[b]

[a] *College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, China*
[b] *College of Biotechnology, Tianjin University of Science & Technology Tianjin 300457, China*
hxxyzhx@mail.tjnu.edu.cn
lukui@tust.edu.cn

1) General

All solvents were distilled prior to use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Brucker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. Mass spectra were obtained on a Bruker SCION 436-GC SQ mass spectrometer or on a Bruker Apex IV FTMS spectrometer.

2) The synthesis and spectral data of pyrazolones[1]



Pyrazolones were prepared by literature procedures

1,3-dimethyl-1H-pyrazol-5(4H)-one **1a** was bought from Adamas-Bepa and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **1f** was bought from Alfa-Aesar.

Method A for **1b**, **1g**

Hydrazine dihydrochloride (10 mmol) and triethyl amine (23 mmol) were mixed in EtOH (10 mL) and the mixture was stired at 0 °C for 10 minutes. Subsequently, the ester (10 mmol) was added to this mixture drop by drop. Then the reaction mixture

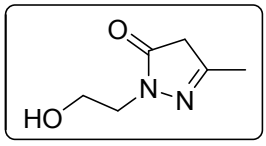
was allowed to room temperature and stired for 12 hours. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic layer was washed with water, and brine, and dried over Na_2SO_4. The organic solvent was evaporated under reduced pressure and the residue was purified on silica gel flash chromatography. And the crude solid was recrystallized from EtOH and collected by filtration to give white crystals.

Method B for **1c**, **1d**, **1e**, **1i**

4-Hydrazinylbenzonitrile dihydrochloride (10 mmol) and triethyl amine (23 mmol) were mixed in EtOH (10 mL) and the mixture was stired at 0 ^{o}C for 10 minutes. Subsequently, the ethyl 3-oxobutanoate (10 mmol) was added to this mixture slowly. Then the reaction mixture was stired at reflux temperature for 12 hours. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic layer was washed with water, and brine, and dried over Na_2SO_4. The organic solvent was evaporated under reduced pressure and the residue was purified by recrystallization (for **1c**, **1e**, **1i**) or silica gel flash chromatography to give white crystals (for **1d**).

Method C for **1h**

The ester (10 mmol) was added slowly to the solution of hydrazine (10 mmol) in ethanol (10 mL). Then the reaction mixture was refluxed for 12 hours. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic layer was washed with water, and brine, and dried over Na_2SO_4. The organic solvent was evaporated under reduced pressure and the residue was purified on silica gel flash chromatography. And the crude solid was recrystallized and collected by filtration to give white crystals.

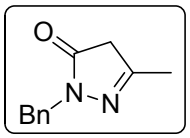


1-(2-hydroxyethyl)-3-methyl-1H-pyrazol-5(4H)-one 1b:[2]

Yield 68 %； Yellow solid;

^{1}H NMR (400 MHz, ^{d6}DMSO) δ 5.10 (s, 1H), 3.76 (t, *J* = 6.4 Hz, 2H), 3.60 (t, *J* = 6.4

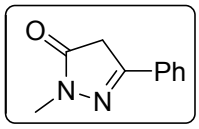
Hz, 2H), 2.00 (s, 3H);



1-benzyl-3-methyl-1H-pyrazol-5(4H)-one 1c:[3]

Yield 35%; White solid;

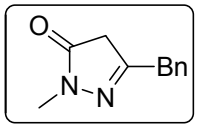
^{1}H NMR (400 MHz, ^{d6}DMSO) δ 10.92 (s, 1H), 7.32-7.29 (m, 2H), 7.25-7.24 (m, 1H), 7.16-7.14 (m, 2H), 5.17 (s, 1H), 4.94 (s, 2H), 2.00 (s, 3H);



1-methyl-3-phenyl-1H-pyrazol-5(4H)-one 1d:[4]

Yield 60%; White solid;

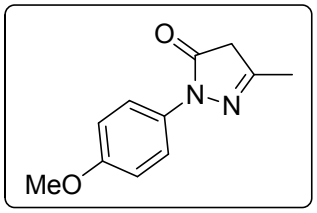
^{1}H NMR (400 MHz, ^{d6}DMSO) δ 11.02 (s, 1H), 7.71-7.69 (m, 2H), 7.37-7.33 (m, 2H), 7.26-7.22 (m, 1H), 5.80 (s, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO) δ 153.7, 148.0, 134.6, 128.9, 127.6, 125.1, 83.7, 33.7;



3-benzyl-1-methyl-1H-pyrazol-5(4H)-one 1e:

Yield 45%; White solid;

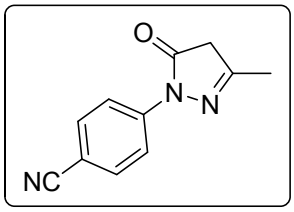
^{1}H NMR (400 MHz, ^{d6}DMSO) δ 10.76 (s, 1H), 7.28-7.14 (m, 5H), 5.09 (s, 1H), 3.68 (s, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO) δ 153.3, 148.9, 140.2, 128.6, 128.2, 125.9, 85.6, 34.8, 32.6; EI-MS (*m/z*, relative intensity): 188 (M^{+}, 62), 117 (100), 115 (43); HRMS (ESI) *m/e* calcd for $C_{11}H_{13}N_2O$ $(M+H)^{+}$ 189.1022, found 189.1017.



1-(4-methoxyphenyl)-3-methyl-1H-pyrazol-5(4H)-one 1g:[1]

Yield 25%; White solid;

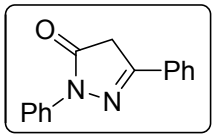
^{1}H NMR (400 MHz, ^{d6}DMSO) δ 11.28 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.33 (s, 1H), 3.76 (s, 3H), 2.10 (s, 3H);



4-(3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile 1h:[5]

Yield 60%; Yellow solid;

^{1}H NMR (400 MHz, ^{d6}DMSO) δ 11.97 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 2.14 (s, 3H); EI-MS (*m/z*, relative intensity): 199 (M^+, 100), 130 (33), 116 (72), 102 (47); HRMS (ESI) *m/e* calcd for $C_{11}H_{10}N_3O$ $(M+H)^+$ 200.0818, found 200.0813.



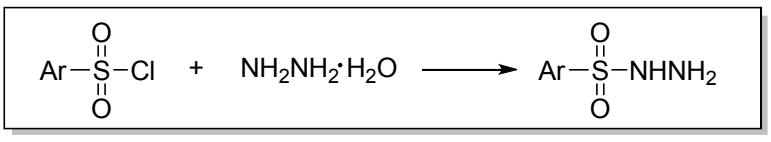
1,3-diphenyl-1H-pyrazol-5(4H)-one 1i:[1]

Yield 32%; White solid;

^{1}H NMR (400 MHz, ^{d6}DMSO) δ 11.82 (s, 1H), 7.86-7.84 (m, 4H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 2H), 7.35-7.27 (m, 2H), 6.04 (s, 1H);

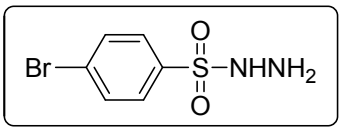
^{13}C NMR (100 MHz, ^{d6}DMSO) δ 153.9, 149.7, 138.9, 133.5, 128.9, 128.6, 127.9, 125.7, 125.2, 121.2, 85.2;

3) The synthesis and spectral data of aryl sulfonyl hydrazides[6]



The hydrazine hydrate (40%) (23 mmol) was added into the solution of aryl sulfonyl chloride (10 mmol) in THF (50 mL) at 0 ^{o}C. Subsequently, the mixture was stired at room temperature for 30 minutes. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic layer was washed with

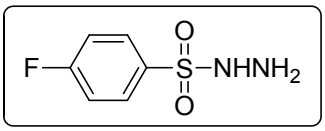
water, and brine, and dried over Na_2SO_4. The organic solvent was evaporated under reduced pressure and the residue was purified on silica gel flash chromatography to give products.



4-bromobenzenesulfonohydrazide 2d:[6]

Yield 93%; White solid;

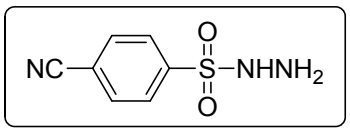
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.8 Hz, 2H), 7.71 (d, *J* = 6.8 Hz, 2H), 5.72 (s, 1H), 3.63 (s, 2H);



4-fluorobenzenesulfonohydrazide 2e:[6]

Yield 76%; White solid;

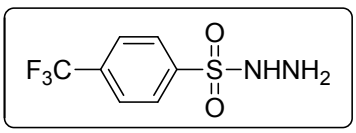
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.26-7.21 (m, 2H), 6.09 (s, 1H), 3.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 255 Hz, 1C) 132.4 (d, *J* = 3.0 Hz, 1C), 131.1 (q, *J* = 9.0 Hz, 1C), 116.6 (d, *J* = 23 Hz, 1C);



4-cyanobenzenesulfonohydrazide 2f:[7]

Yield 84%; White solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 5.78 (s, 1H), 3.68 (s, 2H);

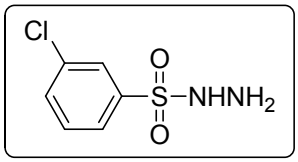


4-(trifluoromethyl)benzenesulfonohydrazide 2g:[8]

Yield 90%; White solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 5.81

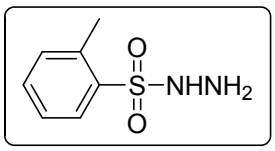
(s, 1H), 3.66 (s, 2H);



3-chlorobenzenesulfonohydrazide 2h:[9]

Yield 92%; White solid;

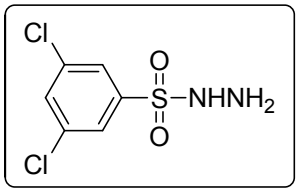
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 6.11 (s, 1H), 3.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.6, 133.7, 130.6, 128.3, 126.3;



2-methylbenzenesulfonohydrazide 2i:[10]

Yield 95%; White solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J_1 = 8.0 Hz, J_1 = 1.2 Hz, 1H), 7.52 (td, J_1 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 7.38-7.35 (m, 2H), 5.60 (s, 1H), 3.27 (s, 2H), 2.66 (s, 3H);



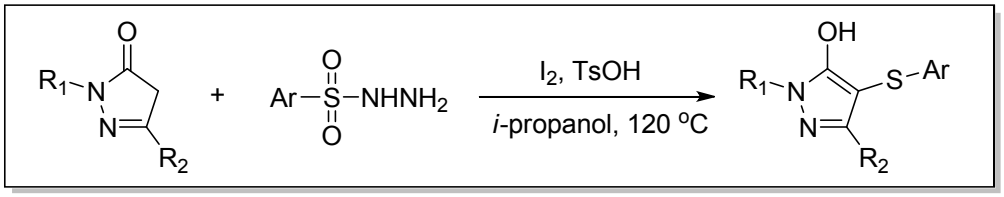
3,5-dichlorobenzenesulfonohydrazide 2j:[7]

Yield 94%; White solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.62 (s, 1H), 5.79 (s, 1H), 3.68 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 136.3, 133.5, 126.5;

4) The synthesis and spectral data of pyrazolone thioethers.

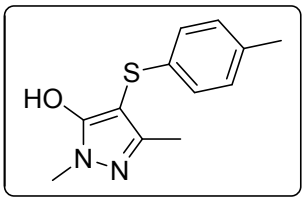


Method A for **3a-p**

Pyrazolones (1.0 mmol), aryl sulfonyl hydrazides (1.2 mmol), I_2 (0.05 mmol), TsOH (0.5 mmol) and *i*-PrOH (1mL) were mixed in a sealed tube. The mixture was stirred at 120 ^{o}C for 1.5 hours. Then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel.

Method B for **4a-m**

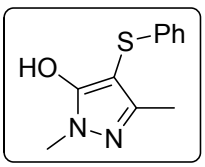
Pyrazolones (1.0 mmol), aryl sulfonyl hydrazides (1.2 mmol), I_2 (0.01 mmol), TsOH (1.0 mmol) and *i*-PrOH (1mL) were mixed in a sealed tube. The mixture was stirred at 120 ^{o}C for 1.5 hours. Then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel.



1,3-dimethyl-4-(p-tolylthio)-1H-pyrazol-5-ol 3a:

Yield 88 %；Yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.48 (s, 3H), 2.22 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 25 ^{o}C) δ 155.9, 149.3, 135.4, 134.0, 129.5, 124.9, 85.2, 33.0, 20.4, 12.1; EI-MS (*m/z*, relative intensity): 234 (M^{+}, 100), 91 (46), 43 (43); HRMS (ESI) *m/e* calcd for $C_{12}H_{15}N_2OS$ $(M+H)^{+}$ 235.0900, found 235.0898.

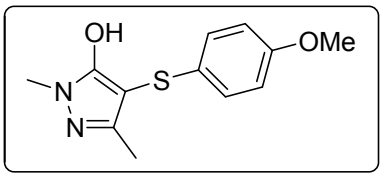


1,3-dimethyl-4-(phenylthio)-1H-pyrazol-5-ol 3b:

Yield 92%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 21 ^{o}C) δ 11.35 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.49 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100

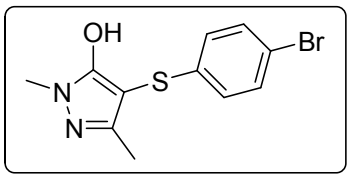
MHz, ^{d6}DMSO, 25 ^{o}C) δ 155.6, 149.4, 139.1, 128.9, 124.7, 124.6, 84.5, 33.1, 12.1; EI-MS (*m/z*, relative intensity): 220 (M^+, 100), 111 (25), 43 (40); HRMS (ESI) *m/e* calcd for $C_{11}H_{13}N_2OS$ $(M+H)^+$ 221.0743, found 221.0738.



4-((4-methoxyphenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3c:

Yield 85%; Pale yellow solid

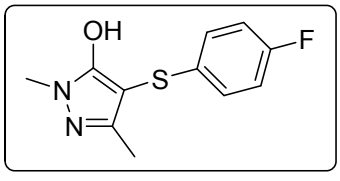
^{1}H NMR (400 MHz, ^{d6}DMSO, 23 ^{o}C) δ 11.34 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 3H), 3.46 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 25 ^{o}C) δ 157.4, 156.2, 149.2, 129.5, 127.3, 114.7, 86.6, 55.2, 33.0, 12.2; HRMS (ESI) *m/e* calcd for $C_{12}H_{15}N_2O_2S$ $(M+H)^+$ 251.0849, found 251.0843.



4-((4-bromophenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3d:

Yield 85%; White solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25^{o}C) δ 11.41 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.49 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.1, 149.1, 138.8, 131.3, 126.6, 117.2, 84.4, 32.8, 11.8; EI-MS (*m/z*, relative intensity): 300 (M^++2, 100), 298 (M^+, 100), 186 (57), 142 (70), 114 (48), 111 (72); HRMS (ESI) *m/e* calcd for $C_{11}H_{12}BrN_2OS$ $(M+H)^+$ 298.9848, found 298.9842.

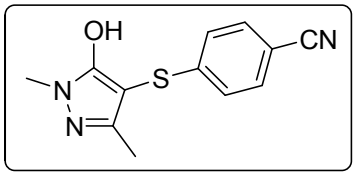


4-((4-fluorophenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3e:

Yield 93%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 11.35 (s, 1H), 7.14-7.01 (m, 2H), 7.04-7.03 (d, 2H), 3.49 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 25 ^{o}C) δ 160.2 (d, *J* =

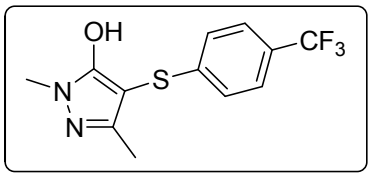
239 Hz, 1C), 156.1, 149.3, 134.6 (d, J = 2.0 Hz, 1C), 126.8 (d, J = 8.0 Hz, 1C), 115.9 (d, J = 22 Hz, 1C), 85.2, 33.0, 12.1; EI-MS (*m/z*, relative intensity): 238(M^+, 100), 142 (30), 111(35); HRMS (ESI) *m/e* calcd for $C_{11}H_{12}FN_2OS$ $(M+H)^+$ 239.0649, found 239.0643.



4-((5-hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)thio)benzonitrile 3f:

Yield 85%; White solid

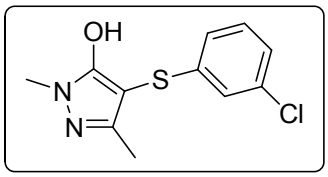
^{1}H NMR (400 MHz, ^{d6}DMSO, 18 ^{o}C) δ 11.73 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 1H), 3.50 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 25 ^{o}C) δ 155.8, 149.3, 146.9, 132.5, 124.8, 119.0, 106.8, 82.4, 33.1, 12.0; EI-MS (*m/z*, relative intensity): 245 (M^+, 100), 212 (28); HRMS (ESI) *m/e* calcd for $C_{12}H_{12}N_3OS$ $(M+H)^+$ 246.0696, found 246.0688.



1,3-dimethyl-4-((4-(trifluoromethyl)phenyl)thio)-1H-pyrazol-5-ol 3g:

Yield 94%; Pale yellow solid

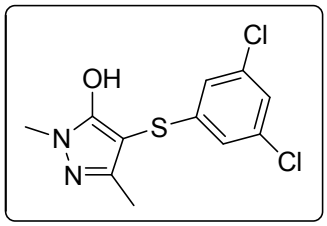
^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 11.32 (s, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 3.54 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.3, 149.3, 145.2, 125.3 (q, J = 4.0 Hz, 1C), 125.2 (q, J = 32 Hz, 1C), 124.7, 124.2 (q, J = 270 Hz, 1C), 83.7, 32.8, 11.7; EI-MS (*m/z*, relative intensity): 288 (M^+, 100); HRMS (ESI) *m/e* calcd for $C_{12}H_{12}F_3N_2OS$ $(M+H)^+$ 289.0617, found 289.0611.



4-((3-chlorophenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3h:

Yield 91%; White solid;

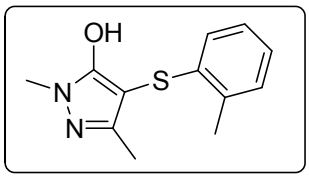
^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 10.76 (s, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.00-6.98 (m, 2H), 3.52 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.2, 149.2, 141.8, 133.6, 130.2, 124.4, 123.8, 123.2, 84.3, 32.8, 11.7; EI-MS (*m/z*, relative intensity): 256 (M^{+}+2, 33), 254 (M^{+}, 100), 111 (42); HRMS (ESI) *m/e* calcd for $C_{11}H_{12}ClN_2OS$ $(M+H)^{+}$ 255.0353, found 255.0348.



4-((3,5-dichlorophenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3i:

Yield 92%; White solid

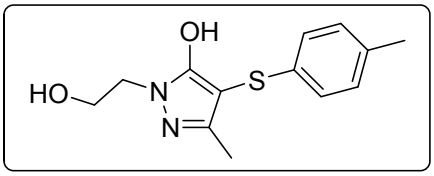
^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 11.59 (s, 1H), 7.32 (s, 1H), 6.97 (s, 2H), 3.50 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.2, 149.0, 144.0, 134.3, 124.1, 122.6, 83.3, 32.8, 11.7; EI-MS (*m/z*, relative intensity): 290 (M^{+}+2, 68), 288 (M^{+}, 100), 255 (30), 111 (60); HRMS (ESI) *m/e* calcd for $C_{11}H_{11}Cl_2N_2OS$ $(M+H)^{+}$ 288.9964, found 288.9957.



1,3-dimethyl-4-(o-tolylthio)-1H-pyrazol-5-ol 3j:

Yield 75%; White solid;

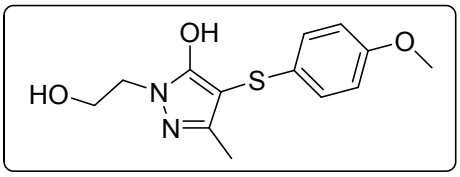
^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 11.23 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.01-6.97 (m, 1H), 6.60 (d, *J* = 6.4 Hz, 1H), 3.51 (s, 3H), 2.33 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.0, 149.3, 137.7, 133.2, 129.6, 126.0, 124.0, 123.7, 84.2, 32.8, 18.9, 11.8; EI-MS (*m/z*, relative intensity): 234 (M^{+}, 100), 123 (48); HRMS (ESI) *m/e* calcd for $C_{12}H_{15}N_2OS$ $(M+H)^{+}$ 235.0900, found 235.0894.



1-(2-hydroxyethyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol 3k:

Yield 85%; Pale yellow solid

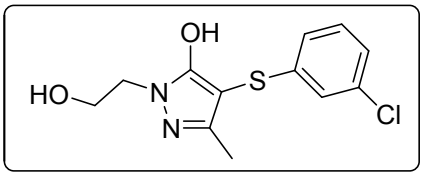
^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 7.05 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.23 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.3, 149.3, 135.4, 133.8, 129.2, 125.1, 85.6, 59.1, 48.1, 20.1, 11.9; EI-MS (*m/z*, relative intensity): 264 (M^{+}, 100), 220 (52), 141 (42), 111 (31), 91 (86), 45 (59), 39 (30); HRMS (ESI) *m/e* calcd for $C_{13}H_{17}N_2O_2S$ $(M+H)^{+}$ 265.1005, found 265.0999.



1-(2-hydroxyethyl)-4-((4-methoxyphenyl)thio)-3-methyl-1H-pyrazol-5-ol 3l:

Yield 92%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 6.98 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.66 (s, 3H), 3.65 (t, *J* = 6.0 Hz, 2H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 26 ^{o}C) δ 157.4, 156.6, 149.4, 129.6, 127.3, 114.7, 86.7, 59.3, 55.2, 48.2, 12.2; HRMS (ESI) *m/e* calcd for $C_{13}H_{17}N_2O_3S$ $(M+H)^{+}$ 281.0954, found 281.0946.

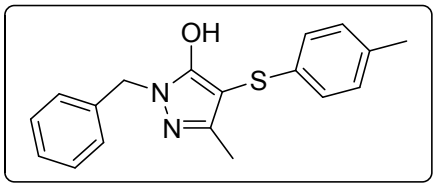


4-((3-chlorophenyl)thio)-1-(2-hydroxyethyl)-3-methyl-1H-pyrazol-5-ol 3m:

Yield 89%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 7.30-7.26 (m, 1H), 7.16-7.14 (m, 1H), 6.99-6.96 (m, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 157.2, 149.5, 141.7, 133.7, 130.2, 124.6, 124.1,

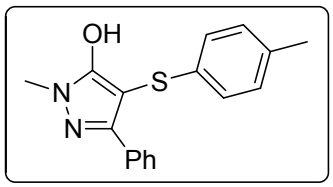
123.4, 85.0, 59.1, 48.2, 11.7; EI-MS (*m/z*, relative intensity): 286 (M^++2, 33), 284 (M^+, 100), 242 (22), 240 (65), 155 (40), 111(48); HRMS (ESI) *m/e* calcd for $C_{12}H_{14}ClN_2O_2S$ $(M+H)^+$ 285.0459, found 285.0453.



1-benzyl-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol 3n:

Yield 46%; White solid

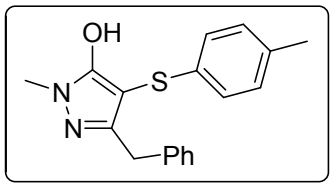
^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 11.40 (s, 1H), 7.31-7.22 (m, 5H), 7.03-6.95 (m, 4H), 5.06 (s, 2H), 2.21 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.4, 150.0, 137.3, 135.3, 133.9, 129.3, 128.2, 127.1, 127.0, 125.1, 86.0, 49.1, 20.1, 11.9; HRMS (ESI) *m/e* calcd for $C_{18}H_{19}N_2OS$ $(M+H)^+$ 311.1213, found 311.1209.



1-methyl-3-phenyl-4-(p-tolylthio)-1H-pyrazol-5-ol 3o:

Yield 76%; White solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 11.36 (s, 1H), 7.86 (d, *J* = 6.4 Hz, 2H), 7.30-7.24 (m, 3H), 7.04-6.97 (m, 4H), 3.68 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 155.9, 149.6, 135.5, 133.9, 133.2, 129.4, 127.8, 127.4, 126.6, 124.9, 84.0, 33.8, 20.1; EI-MS (*m/z*, relative intensity): 296 (M^+, 100), 173 (48), 161 (98), 103 (72); HRMS (ESI) *m/e* calcd for $C_{17}H_{17}N_2OS$ $(M+H)^+$ 297.1056, found 297.1049.

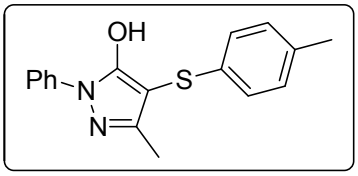


3-benzyl-1-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol 3p:

Yield 79%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25^{o}C) δ 11.35 (s, 1H), 7.18-7.10 (m, 5H), 7.02 (d, *J* =

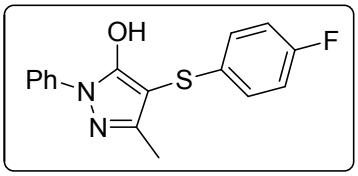
8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.69 (s, 2H), 3.54 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 155.4, 151.7, 138.9, 135.3, 133.8, 129.1, 128.4, 127.8, 125.5, 125.2, 85.4, 33.2, 32.5, 20.1; HRMS (ESI) *m/e* calcd for $C_{18}H_{19}N_2OS$ $(M+H)^+$ 311.1213, found 311.1206.



3-methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-ol 4a:

Yield 84%; White solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 12.14 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 25 ^{o}C) δ 156.7, 152.1, 138.3, 134.9, 134.4, 129.7, 129.0, 125.7, 125.4, 120.8, 87.8, 20.5, 12.4; EI-MS (*m/z*, relative intensity): 296 (M^+, 60), 173 (43), 105 (74), 77 (100); HRMS (ESI) *m/e* calcd for $C_{17}H_{17}N_2OS$ $(M+H)^+$ 297.1056, found 297.1050.



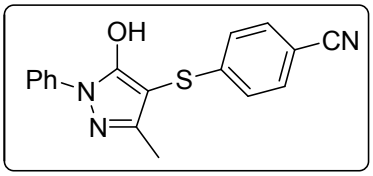
4-((4-fluorophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5-ol 4b:

Yield 57%; White solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 11.92 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.19 (s, 1H), 7.11-7.07 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 160.4 (d, *J* = 241 Hz, 1C), 157.1, 151.9, 138.1, 133.8 (d, *J* = 3.0 Hz, 1C), 128.7, 127.4 (d, *J* = 8.0 Hz, 1C), 125.5, 120.7, 115.7 (d, *J* = 22 Hz, 1C), 88.8, 12.0;

EI-MS (*m/z*, relative intensity): 300 (M^+, 100), 173 (67), 138 (37), 105 (86);

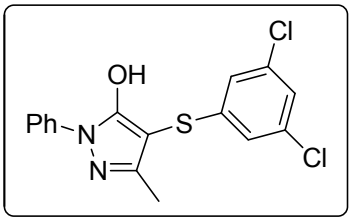
HRMS (ESI) *m/e* calcd for $C_{16}H_{14}FN_2OS$ $(M+H)^+$ 301.0805, found 301.0800.



4-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)thio)benzonitrile 4c:

Yield 79%; White solid

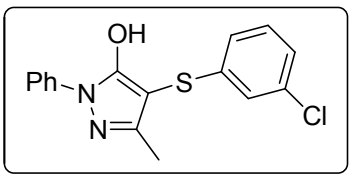
^{1}H NMR (400 MHz, ^{d6}DMSO, 18 ^{o}C) δ 12.48 (s, 1H), 7.74 (t, *J* = 8.0 Hz, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.28-7.22 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 157.0, 151.8, 146.0, 137.9, 132.3, 128.7, 125.7, 125.0, 120.7, 118.6, 107.1, 85.9, 11.9; HRMS (ESI) *m/e* calcd for $C_{17}H_{14}N_3OS$ $(M+H)^+$ 308.0852, found 308.0845.



4-((3,5-dichlorophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5-ol 4d:

Yield 92%; White solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.49-7.45 (m, 2H), 7.29-7.26 (m, 2H), 7.06 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 25 ^{o}C) δ 157.3, 151.9, 143.5, 137.9, 134.7, 129.0, 125.9, 124.6, 122.9, 120.8, 85.8, 12.2; HRMS (ESI) *m/e* calcd for $C_{16}H_{13}Cl_2N_2OS$ $(M+H)^+$ 351.0120, found 351.0110.

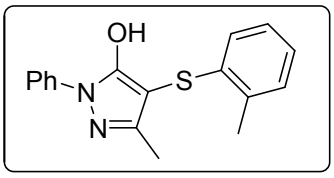


4-((3-chlorophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5-ol 4e:

Yield 82%; White solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 12.30 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.29 (q, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 12 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 23 ^{o}C) δ 156.6, 152.0, 141.2, 138.0, 133.8, 130.7, 129.0, 125.9, 124.9, 124.0, 123.5, 120.8, 86.3, 12.3; HRMS (ESI) *m/e*

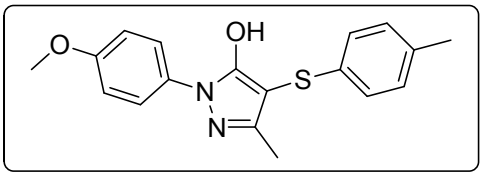
calcd for $C_{16}H_{14}ClN_2OS$ $(M+H)^+$ 317.0510, found 317.0502.



3-methyl-1-phenyl-4-(o-tolylthio)-1H-pyrazol-5-ol 4f:

Yield 45%; White solid

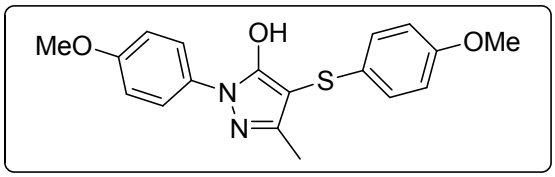
^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 12.12 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.50-7.46 (m, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.12-7.08 (m, 1H), 7.04-7.01 (m, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.9, 151.9, 138.0, 137.0, 133.5, 129.7, 128.6, 126.2, 125.4, 124.3, 123.9, 120.5, 87.1, 19.0, 12.0; EI-MS (*m/z*, relative intensity): 296 (M^+, 88), 204 (26), 173 (54), 123 (38), 105 (100); HRMS (ESI) *m/e* calcd for $C_{17}H_{17}N_2OS$ $(M+H)^+$ 297.1056, found 297.1047.



1-(4-methoxyphenyl)-3-methyl-4-(p-tolylthio)-1H-pyrazol-5-ol 4g:

Yield 83%; White solid

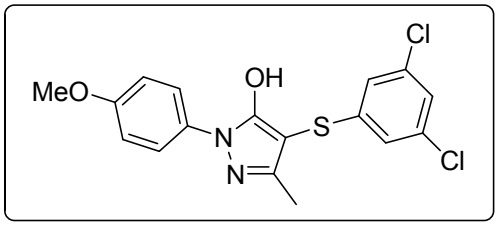
^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 11.86 (s, 1H), 7.60 (d, *J* = 9.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 9.2 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.23 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 157.1, 155.7, 151.0, 134.7, 134.0, 131.4, 129.3, 125.3, 122.6, 113.9, 87.6, 55.1, 20.1, 12.0; HRMS (ESI) *m/e* calcd for $C_{18}H_{19}N_2O_2S$ $(M+H)^+$ 327.1162, found 327.1160.



1-(4-methoxyphenyl)-4-((4-methoxyphenyl)thio)-3-methyl-1H-pyrazol-5-ol 4h:

Yield 70%; Pale yellow solid

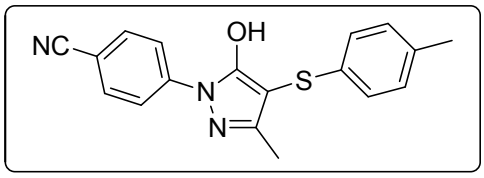
^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 11.67 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 157.5, 157.2, 156.0, 150.9, 131.4, 128.8, 127.7, 122.6, 114.6, 113.9, 89.1, 55.2, 55.0, 12.0; HRMS (ESI) *m/e* calcd for $C_{18}H_{19}N_2O_3S$ $(M+H)^+$ 343.1111, found 343.1108.



4-((3,5-dichlorophenyl)thio)-1-(4-methoxyphenyl)-3-methyl-1H-pyrazol-5-ol 4i:

Yield 71%; White solid

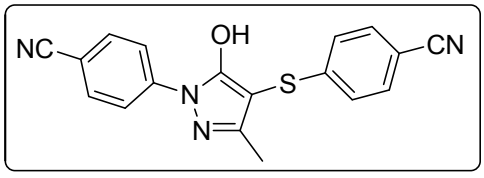
^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 11.67 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.27 (s, 1H), 7.07-7.02 (m, 4H), 3.80 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 157.4, 156.4, 151.0, 143.5, 134.4, 131.0, 124.3, 122.9, 122.8, 113.9, 85.5, 55.2, 11.9; HRMS (ESI) *m/e* calcd for $C_{17}H_{15}Cl_2N_2O_2S$ $(M+H)^+$ 381.0226, found 381.0225.



4-(5-hydroxy-3-methyl-4-(p-tolylthio)-1H-pyrazol-1-yl)benzonitrile 4j:

Yield 61%; Pale yellow solid

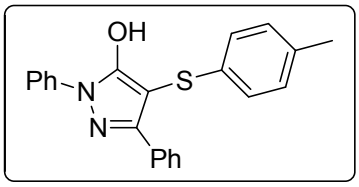
^{1}H NMR (400 MHz, ^{d6}DMSO, 60 ^{o}C) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 2.23 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 157.9, 153.6, 141.4, 134.4, 134.0, 133.0, 129.4, 125.6, 119.6, 118.3, 107.1, 89.7, 20.1, 12.0; HRMS (ESI) *m/e* calcd for $C_{18}H_{16}N_3OS$ $(M+H)^+$ 322.1009, found 322.1002.



4-((1-(4-cyanophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)thio)benzonitrile 4k:

Yield 43%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 158.2, 153.6, 145.4, 141.3, 133.0, 132.3, 125.1, 119.8, 118.5, 118.3, 107.4, 107.2, 86.8, 12.0; HRMS (ESI) *m/e* calcd for $C_{18}H_{13}N_4OS$ $(M+H)^+$ 333.0805, found 333.0796.

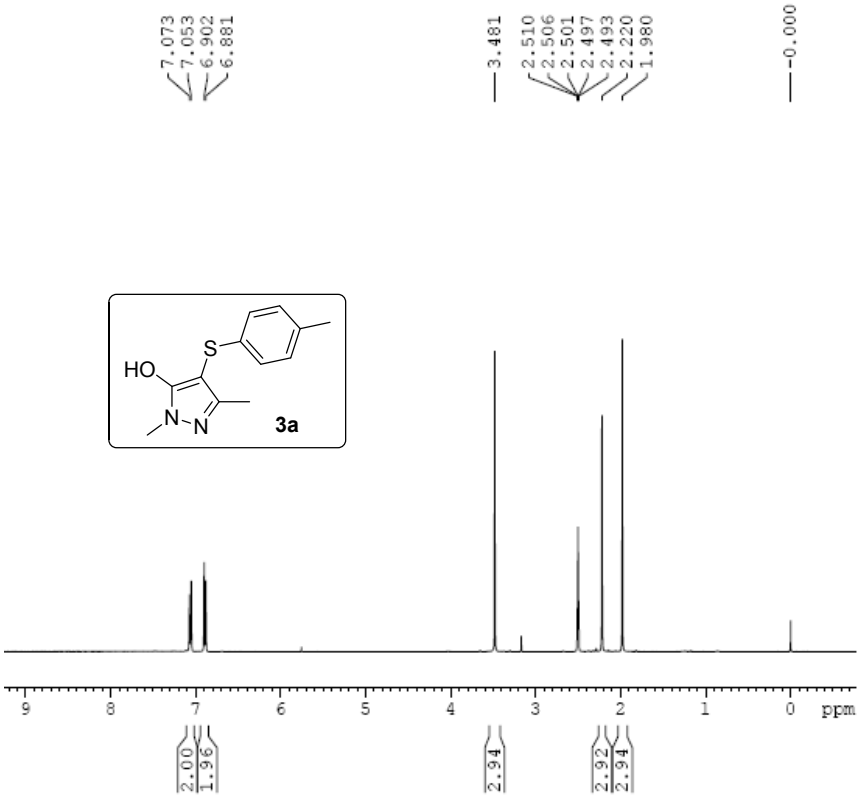


1,3-diphenyl-4-(p-tolylthio)-1H-pyrazol-5-ol 4l:

Yield 61%; Pale yellow solid

^{1}H NMR (400 MHz, ^{d6}DMSO, 25 ^{o}C) δ 12.36 (s, 1H), 7.88-7.84 (m, 4H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.38-7.34 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, ^{d6}DMSO, 60 ^{o}C) δ 156.4, 151.3, 138.3, 134.9, 134.2, 132.6, 129.5, 128.7, 128.0, 127.9, 126.9, 126.1, 125.1, 121.4, 86.4, 20.1; HRMS (ESI) *m/e* calcd for $C_{22}H_{19}N_2OS$ $(M+H)^+$ 359.1213, found 359.1212.

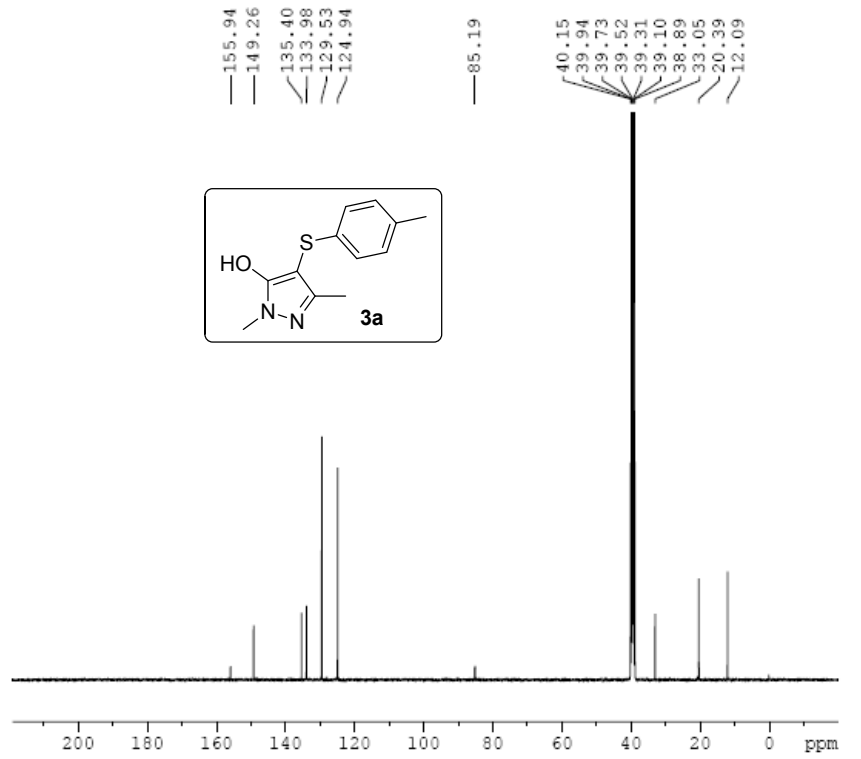
5) The spectrum of unknown pyrazolone and pyrazolone thioethers



BRUKER

```
NAME                 22-H
EXPNO                   1
PROCNO                  1
Date_           20131024
Time                11.09
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                   203
DW              60.800 usec
DE               6.50 usec
TE                298.1 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                13.00 usec
SI                 65536
SF          400.1300030 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```



BRUKER

```
NAME                 22-C
EXPNO                   1
PROCNO                  1
Date_           20131025
Time                13.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                  2400
DS                     4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                 193.28
DW              20.800 usec
DE               6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                  13C
P1                12.00 usec
SI                 32768
SF          100.6128170 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
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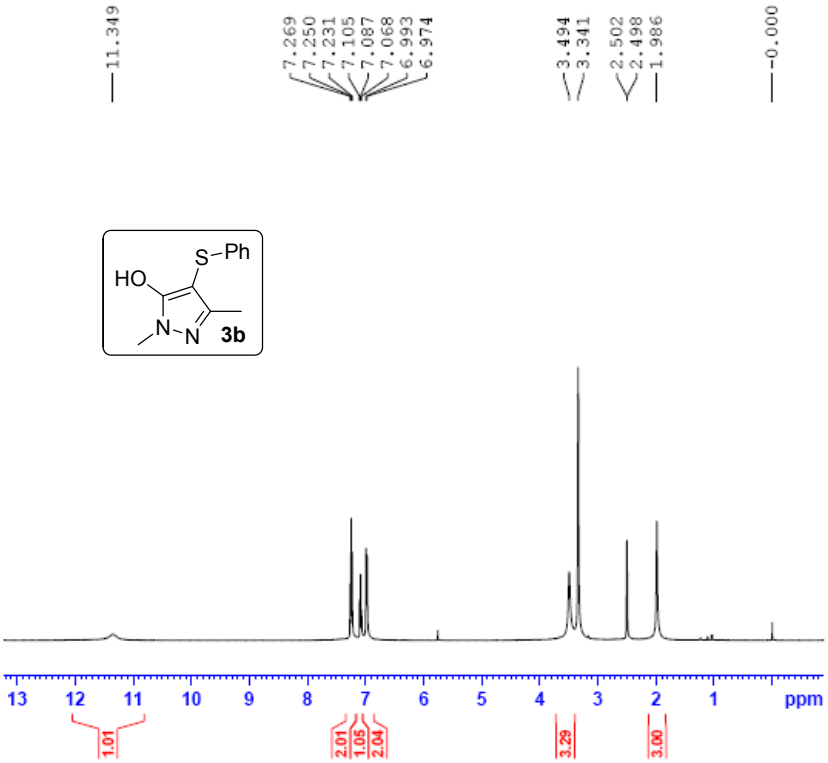

BRUKER

```
NAME                ZLP-70
EXPNO                    1
PROCNO                   1
Date_             20131213
Time                 10.49
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     181
DW                60.800 usec
DE                 6.50 usec
TE                296.8 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
SI                  65536
SF          400.1300026 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
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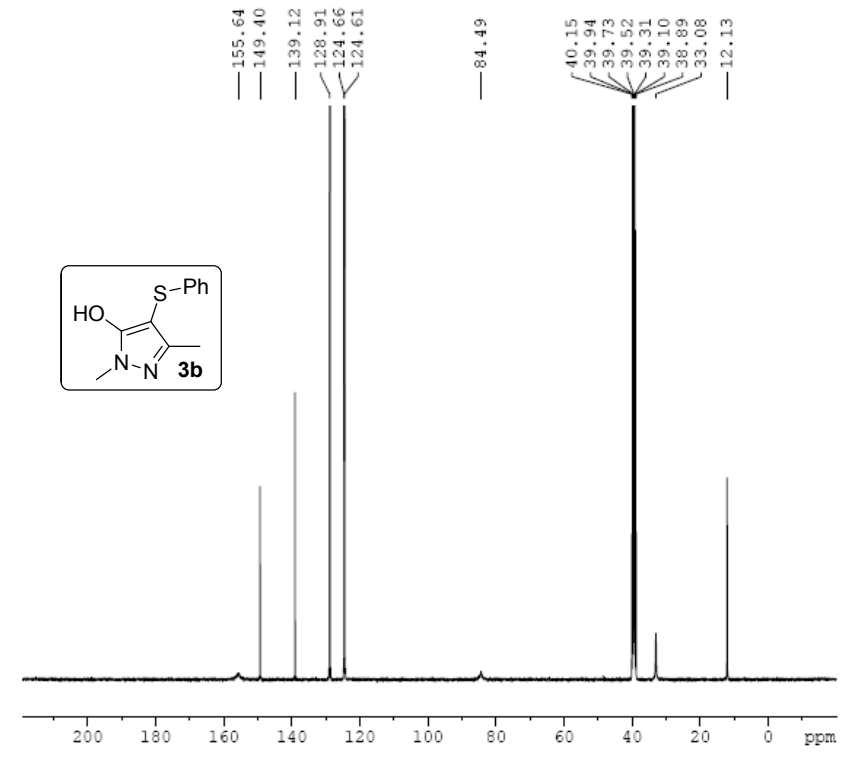
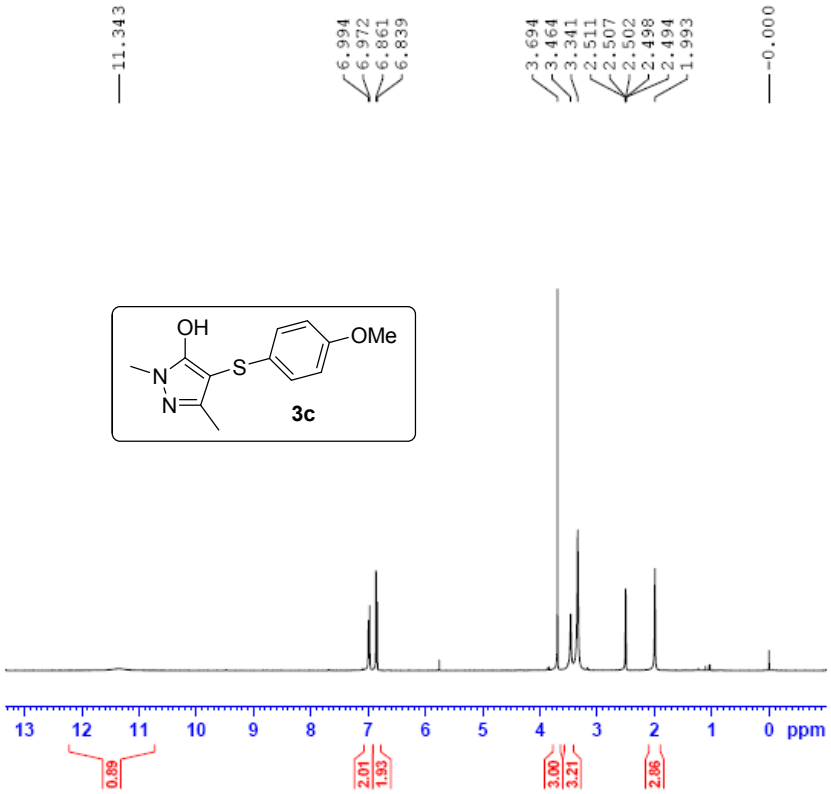


BRUKER

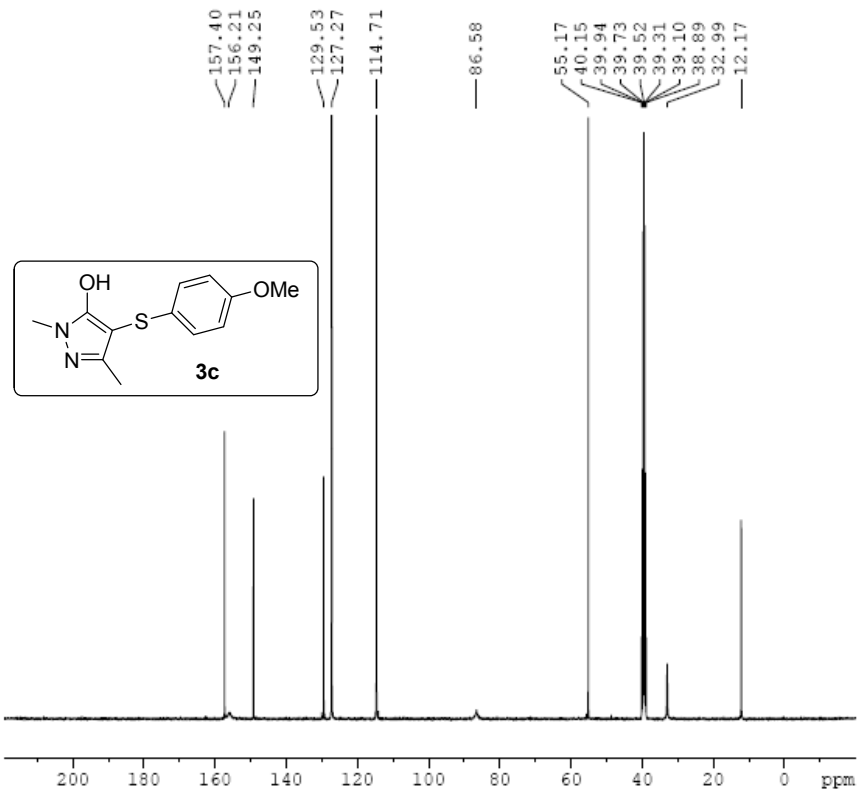
```
NAME          ZLP-70-20140116
EXPNO                    1
PROCNO                   1
Date_             20140116
Time                 19.04
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT              DMSO
NS                    2000
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                  193.28
DW                20.800 usec
DE                 6.50 usec
TE                298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                   13C
P1                 12.00 usec
SI                  32768
SF          100.6128143 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```



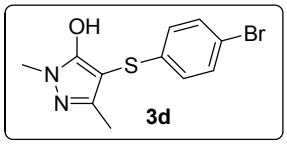

```
NAME                 zlp-73
EXPNO                     1
PROCNO                    1
Date_              20131212
Time                  18.54
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     203
DW                60.800 usec
DE                 6.50 usec
TE                 296.7 K
D1                1.00000000 sec

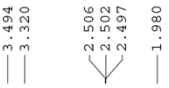
======== CHANNEL f1 ========
NUC1                   1H
P1                  13.00 usec
SI                  65536
SF            400.1300022 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
NAME          ZLP-73-1-20140116
EXPNO                     1
PROCNO                    1
Date_              20140116
Time                  20.05
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                   193.28
DW                20.800 usec
DE                 6.50 usec
TE                 298.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                  12.00 usec
SI                  32768
SF            100.6128095 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



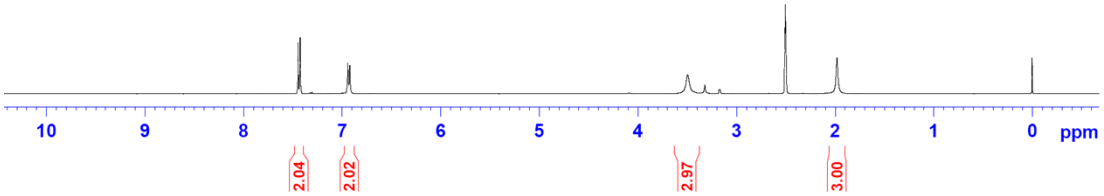


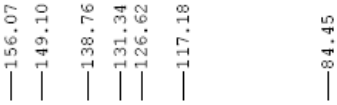

```
Current Data Parameters
NAME      ZLP-88-20140429
EXPNO              1
PROCNO             1

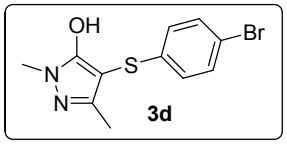
F2 - Acquisition Parameters
Date_          20140429
Time              14.51
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          DMSO
NS                16
DS                 2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG              193.28
DW             62.400 usec
DE              6.50 usec
TE             298.2 K
D1          1.00000000 sec
TD0                1

======== CHANNEL f1 =======
SFO1       400.1324710 MHz
NUC1              1H
P1              14.80 usec
PLW1       12.50000000 W

F2 - Processing parameters
SI             65536
SF        400.1300035 MHz
WDW               EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

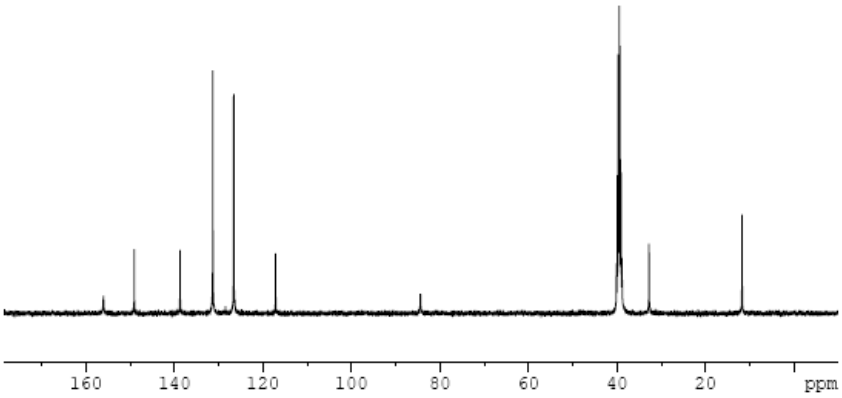


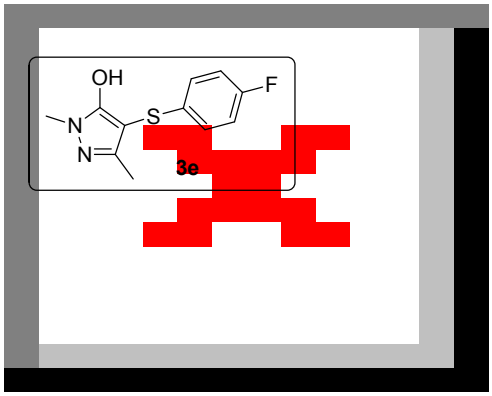


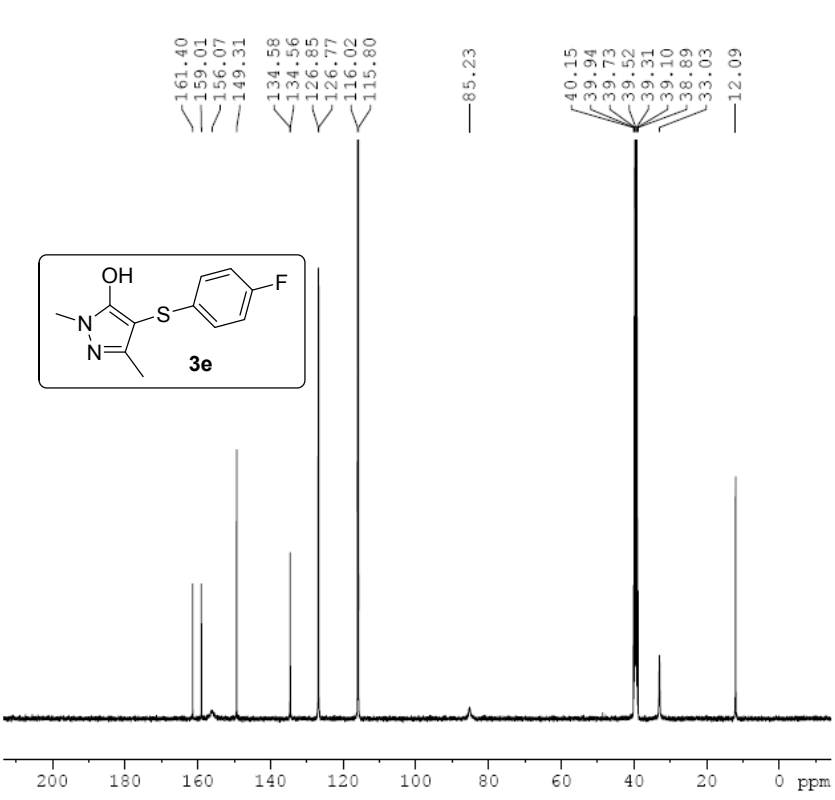



```
NAME          ZLP-88-20140423
EXPNO                       2
PROCNO                      1
Date_              20140423
Time                  20.10
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                   794
DS                     4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.36311988 sec
RG               193.28
DW              20.800 usec
DE               6.50 usec
TE              333.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1       100.6228293 MHz
NUC1              13C
P1              12.00 usec
SI              32768
SF        100.6128405 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

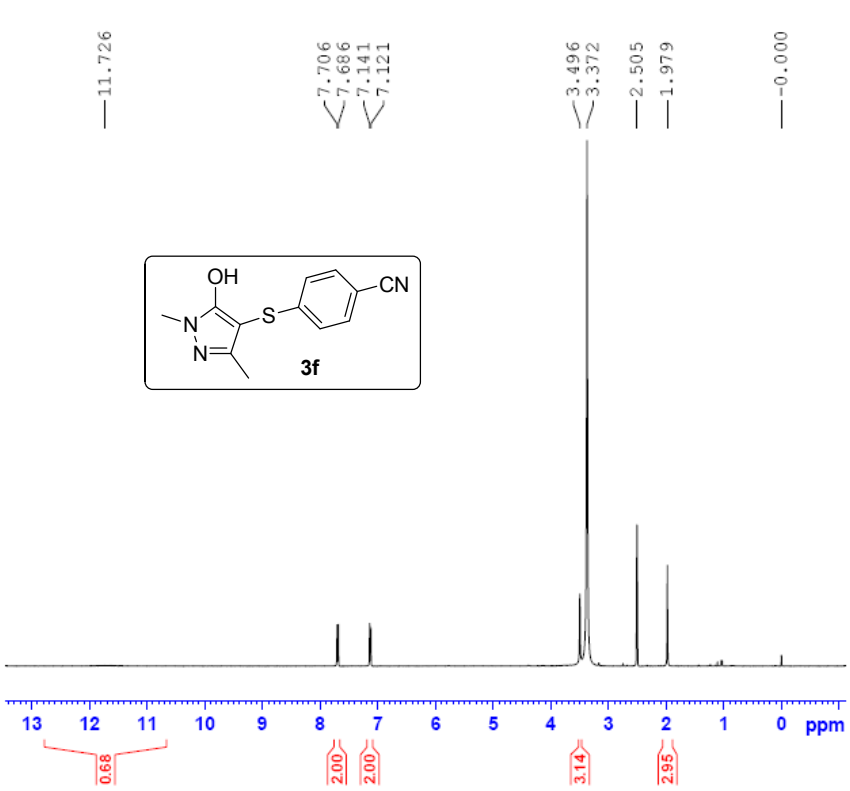






BRUKER

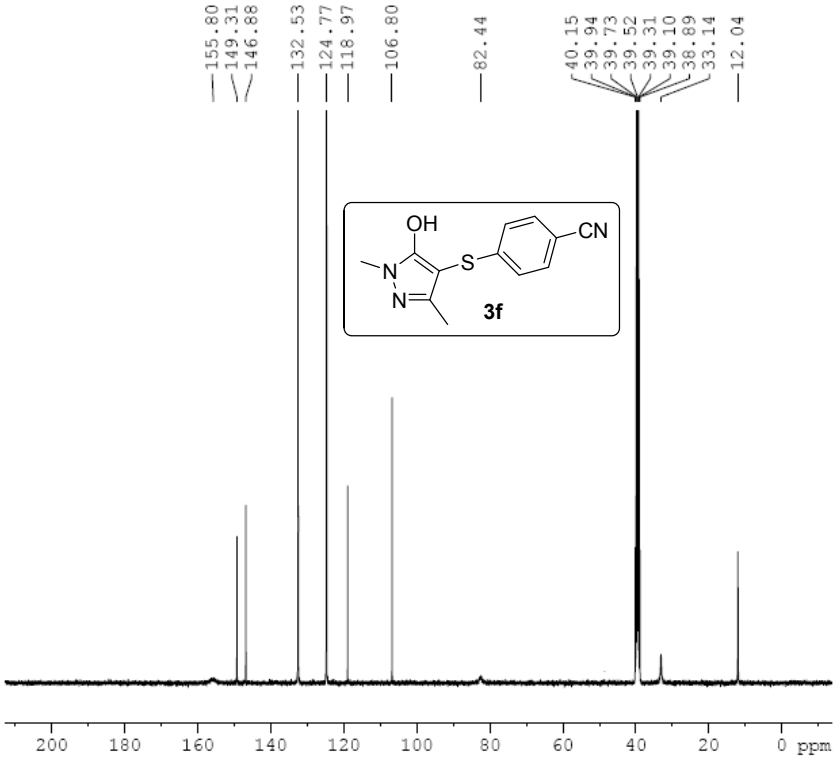
NAME	ZLP-101-1-20140116
EXPNO	1
PROCNO	1
Date_	20140117
Time	4.33
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	193.28
DW	20.800 usec
DE	6.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6128112 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

```
NAME                 94-H
EXPNO                   1
PROCNO                  1
Date_            20131220
Time                10.54
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    203
DW                60.800 usec
DE                 6.50 usec
TE                290.7 K
D1             1.00000000 sec

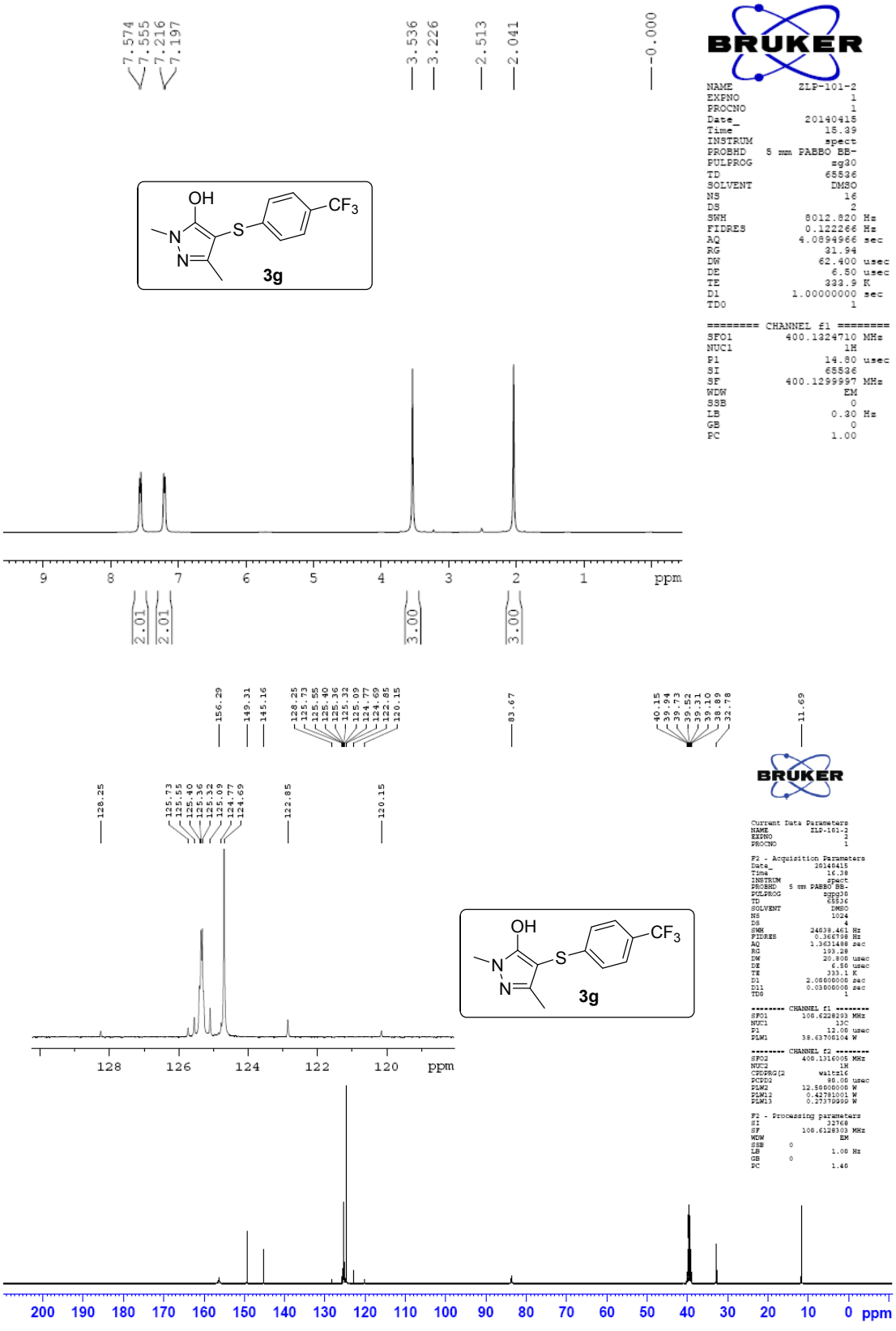
======== CHANNEL f1 ========
NUC1                   1H
P1                  13.00 usec
SI                  65536
SF          400.1300013 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



BRUKER

```
NAME          ZLP-94-20140116
EXPNO                       1
PROCNO                      1
Date_                20140117
Time                     3.32
INSTRUM                 spect
PROBHD       5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1024
DS                        4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                     193.28
DW                     20.800 usec
DE                      6.50 usec
TE                     298.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                      13C
P1                      12.00 usec
SI                        32768
SF               100.6128137 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```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3.226
2.513
2.041
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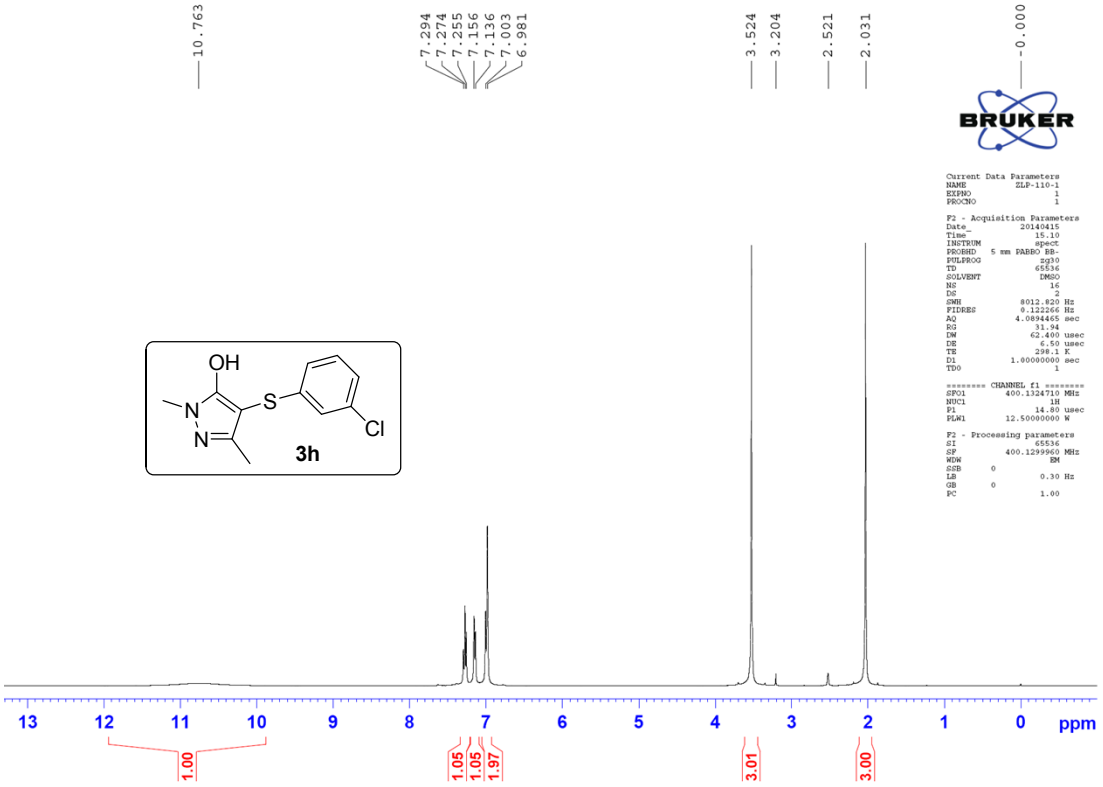
OH
N
N
S
CF3
3g
9
8
7
6
5
4
3
2
1
ppm
2.01
2.01
3.00
3.00
156.29
149.31
145.16
128.25
125.73
125.55
125.40
125.36
125.32
125.09
124.77
124.69
122.85
120.15
83.67
40.15
39.94
39.73
39.52
39.31
39.10
38.89
32.78
11.69
BRUKER
NAME ZLP-101-2
EXPNO 1
PROCNO 1
Date_ 20140415
Time 15.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 21.94
DW 62.400 usec
DE 6.50 usec
TE 333.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.80 usec
SI 65536
SF 400.1299997 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
128
126
124
122
120
ppm
Current Data Parameters
NAME ZLP-101-2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140415
Time 16.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 193.28
DW 20.800 usec
DE 6.50 usec
TE 333.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 12.00 usec
PLW1 38.63700104 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 12.50000000 W
PLW12 0.42781001 W
PLW13 0.27379999 W
F2 - Processing parameters
SI 32768
SF 100.6128303 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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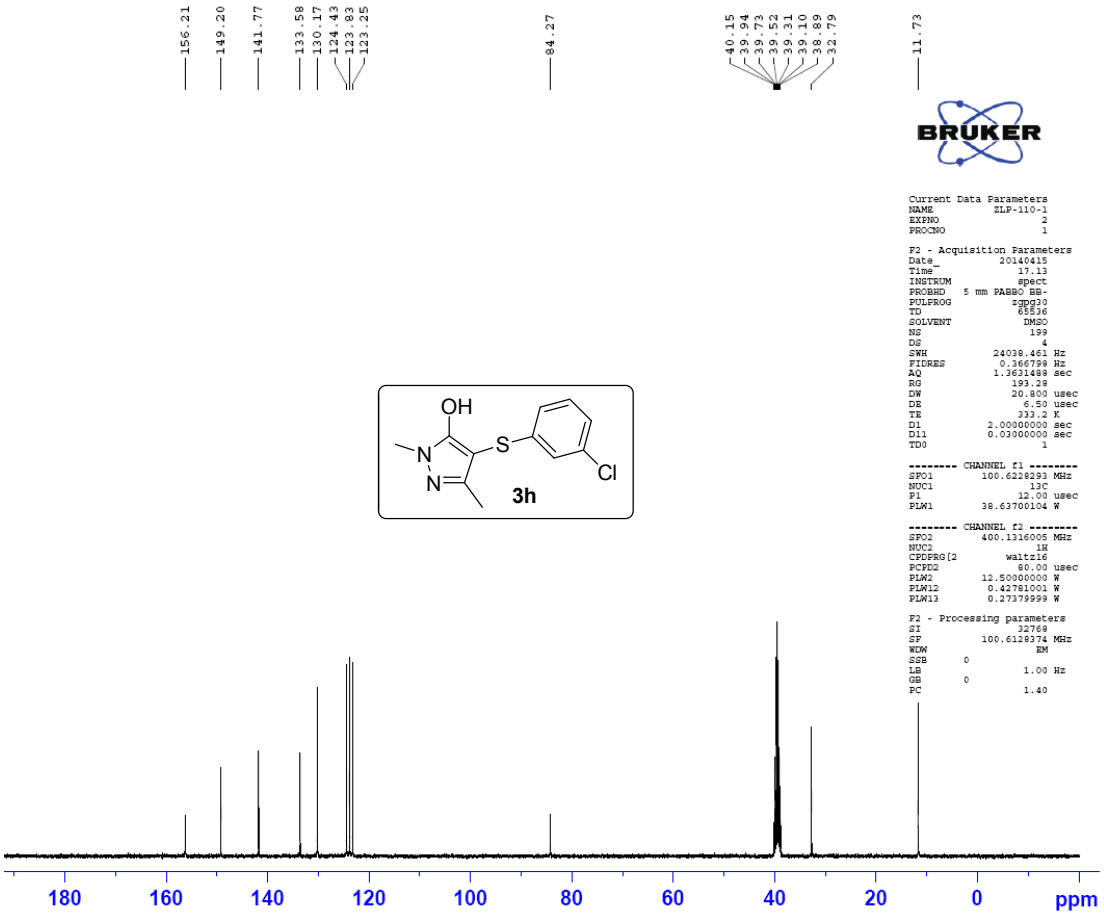
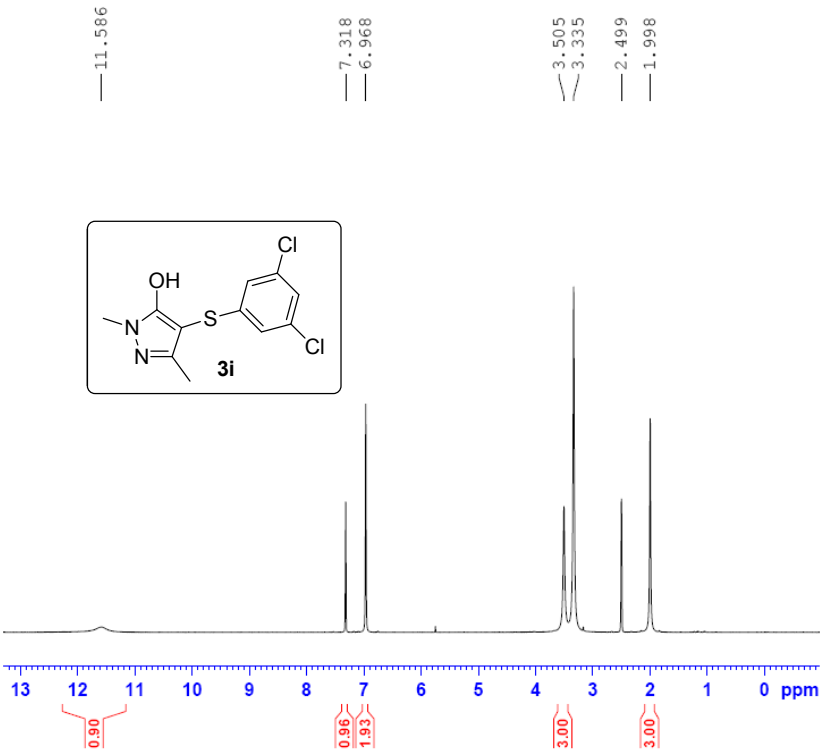
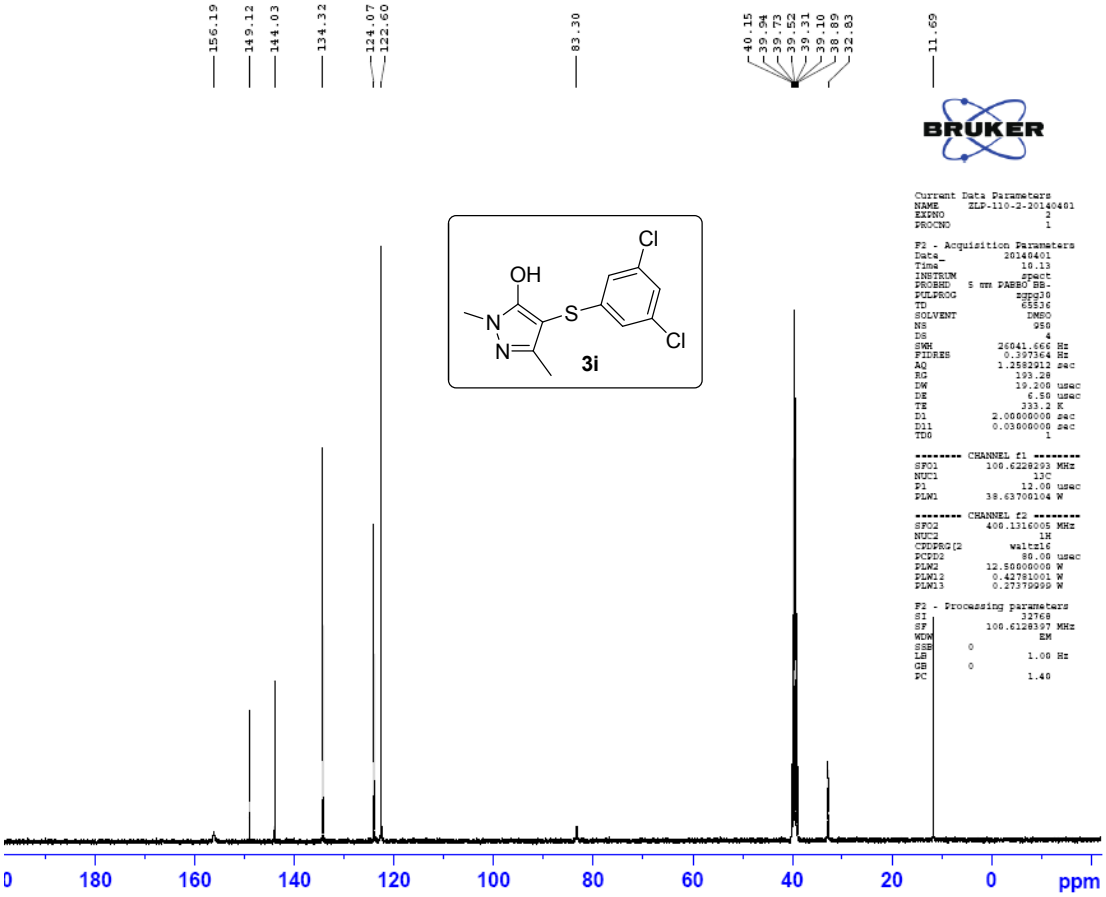
7.156
7.136
7.003
6.981
3.524
3.204
2.521
2.031
0.000
OH
N
N
S
Cl
3h
Current Data Parameters
NAME ELP-110-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140415
Time 15.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 31.94
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.80 usec
PLW1 12.50000000 W
F2 - Processing parameters
SI 65536
SF 400.1299960 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
1.05
1.97
3.01
3.00


156.21
149.20
141.77
133.58
130.17
124.43
123.83
123.25
84.27
40.15
39.94
39.73
39.52
39.31
39.10
38.89
32.79
11.73
OH
N
N
S
Cl
3h
Current Data Parameters
NAME ELP-110-1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140415
Time 17.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 199
DS 4
SWH 24038.461 Hz
FIDRES 0.366799 Hz
AQ 1.3631488 sec
RG 193.29
DW 20.800 usec
DE 6.50 usec
TE 333.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 12.00 usec
PLW1 38.63700104 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 12.50000000 W
PLW12 0.42781001 W
PLW13 0.27379999 W
F2 - Processing parameters
SI 32768
SF 100.6128374 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm




```
NAME                 110-2-H
EXPNO                      1
PROCNO                     1
Date_             20140305
Time                  19.18
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894966 sec
RG                    159.15
DW                    62.400 usec
DE                     6.50 usec
TE                    298.1 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                    14.80 usec
SI                        65536
SF               400.1300040 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



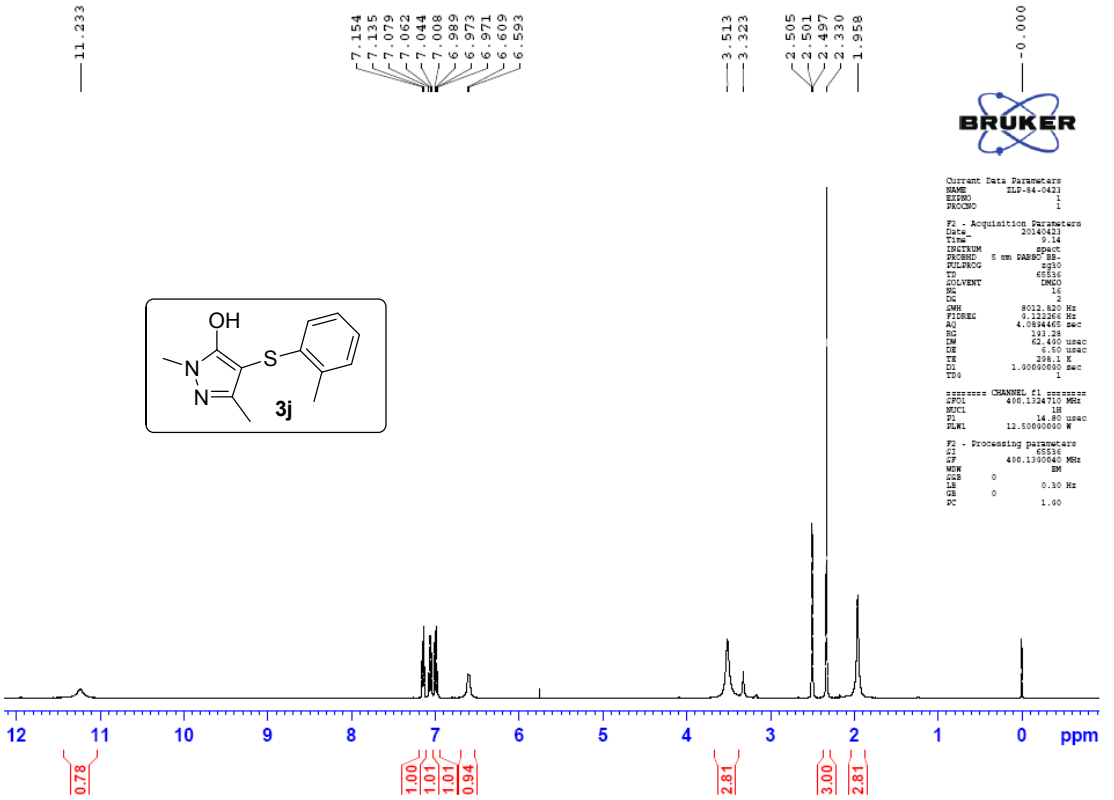

```
Current Data Parameters
NAME      ZLP-110-2-20140401
EXPNO                      2
PROCNO                     1

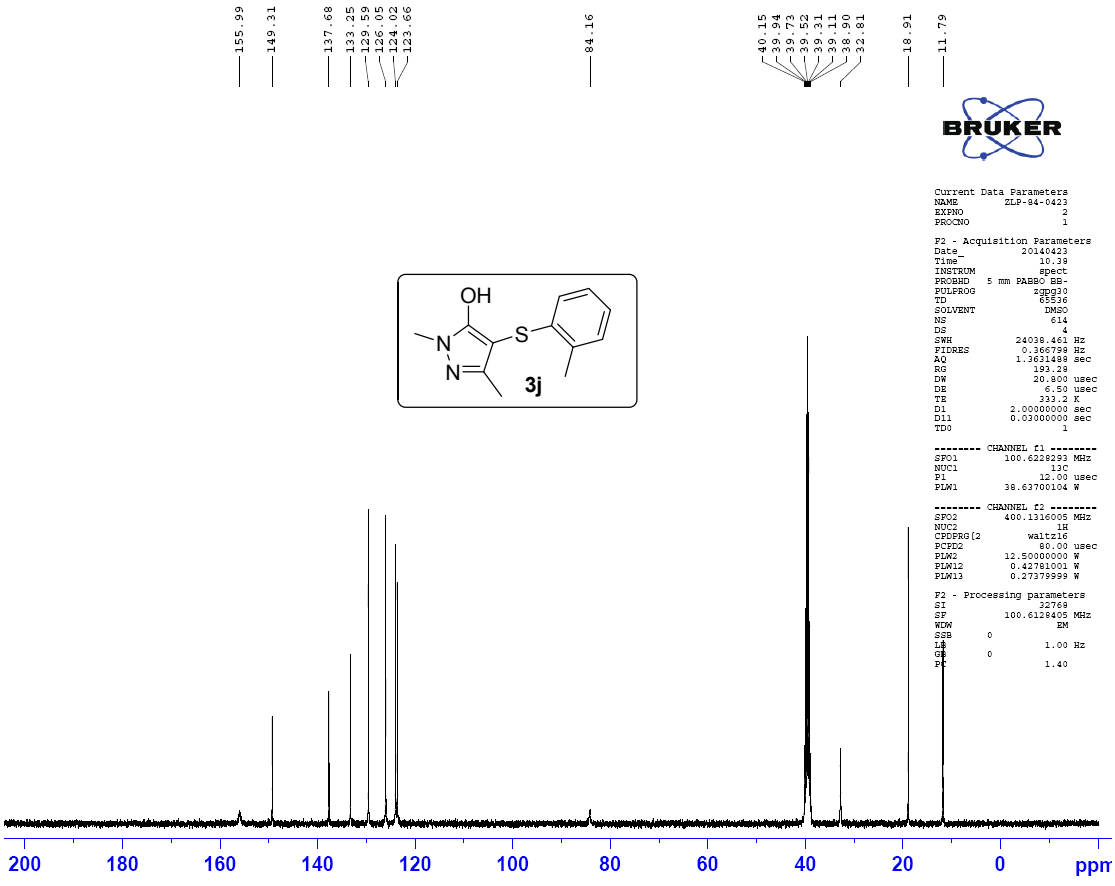
F2 - Acquisition Parameters
Date_             20140401
Time                  10.13
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zgpg30
TD                    65536
SOLVENT                DMSO
NS                       250
DS                         4
SWH              26041.666 Hz
FIDRES            0.397364 Hz
AQ                1.2582912 sec
RG                    193.28
DW                    19.200 usec
DE                     6.50 usec
TE                    333.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

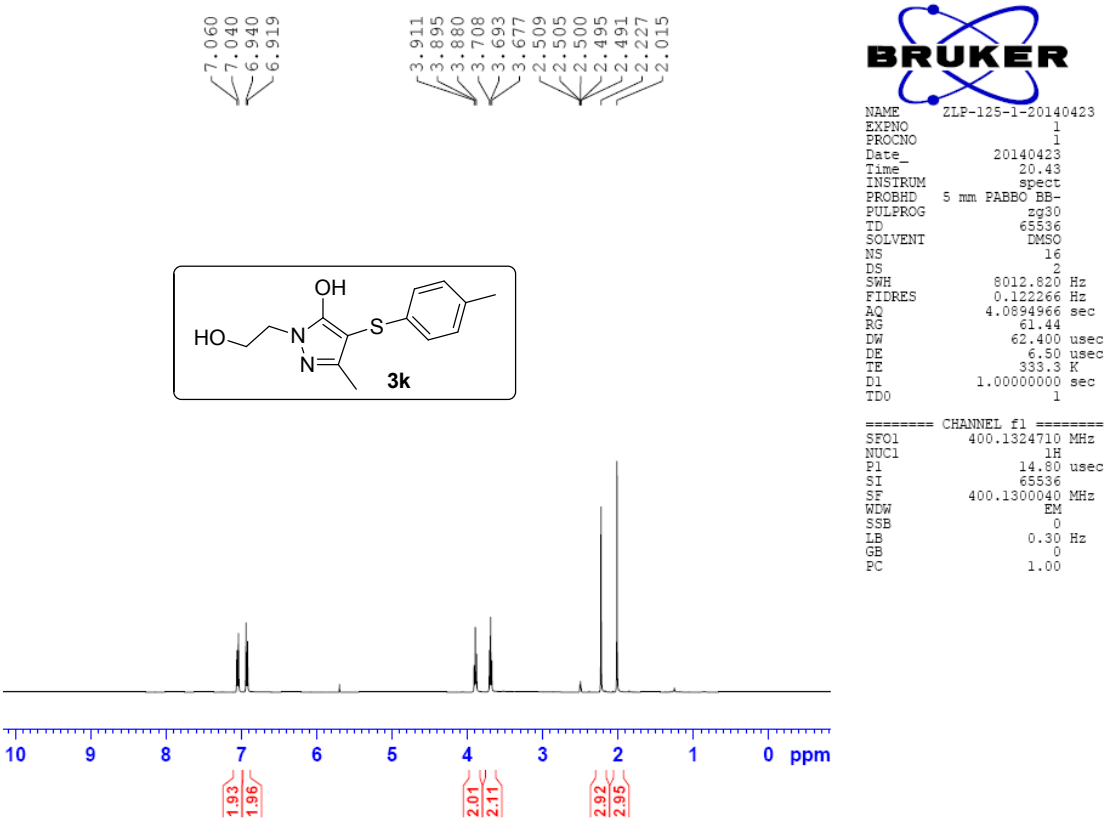
======== CHANNEL f1 ========
SFO1            100.6228293 MHz
NUC1                      13C
P1                    12.00 usec
PLW1             38.63700104 W

======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                 80.00 usec
PLW2             12.50000000 W
PLW12             0.42781001 W
PLW13             0.27379999 W

F2 - Processing parameters
SI                        32768
SF              100.6128397 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40
```


11.233
7.154
7.135
7.079
7.062
7.044
7.008
6.989
6.973
6.971
6.609
6.593
3.513
3.323
2.505
2.501
2.497
2.330
1.958
0.000
OH
N
N
S
3j
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.78
1.00
1.01
1.01
0.94
2.81
3.00
2.81

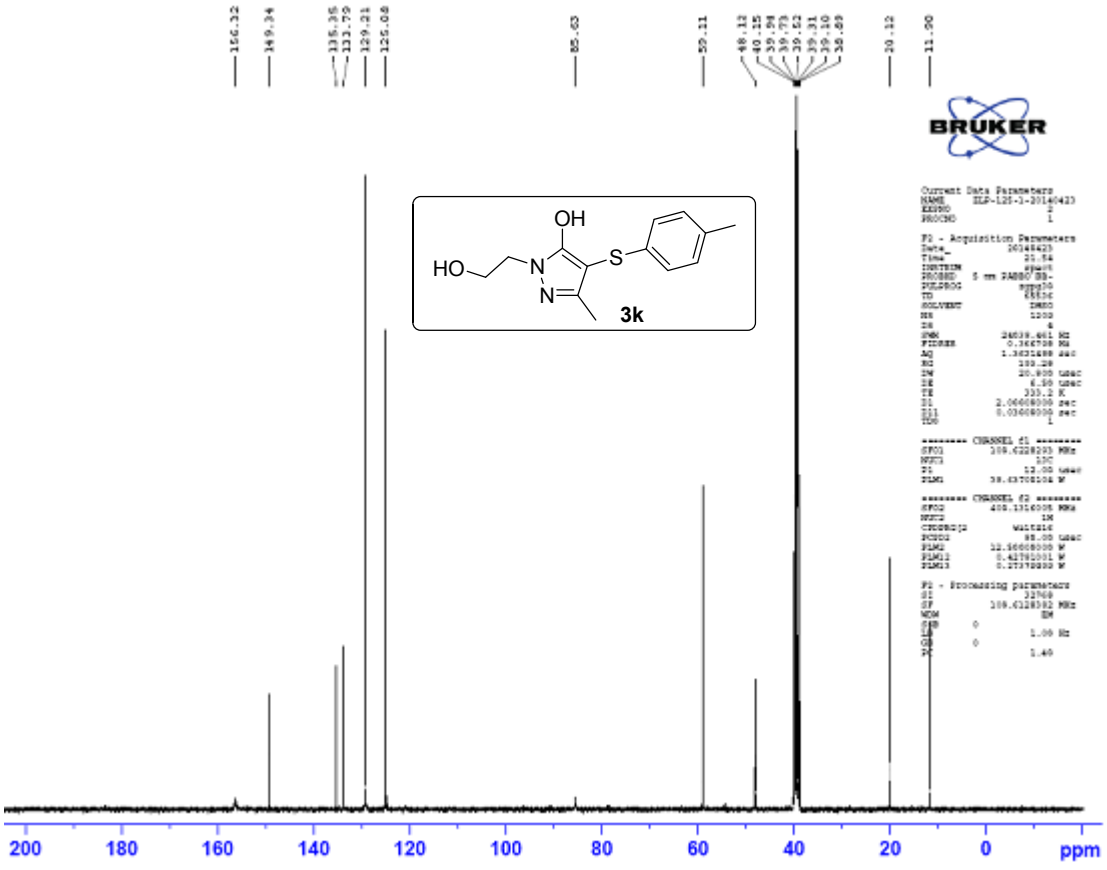

155.99
149.31
137.68
133.25
129.59
126.05
124.02
123.66
84.16
40.15
39.94
39.73
39.52
39.31
39.11
38.90
32.81
18.91
11.79
OH
N
N
S
3j
200
180
160
140
120
100
80
60
40
20
0
ppm



BRUKER

```
NAME          ZLP-125-1-20140423
EXPNO                          1
PROCNO                         1
Date_                   20140423
Time                       20.43
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                           16
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                         61.44
DW                        62.400 usec
DE                         6.50 usec
TE                        333.3 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 400.1324710 MHz
NUC1                          1H
P1                         14.80 usec
SI                        65536
SF                   400.1300040 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



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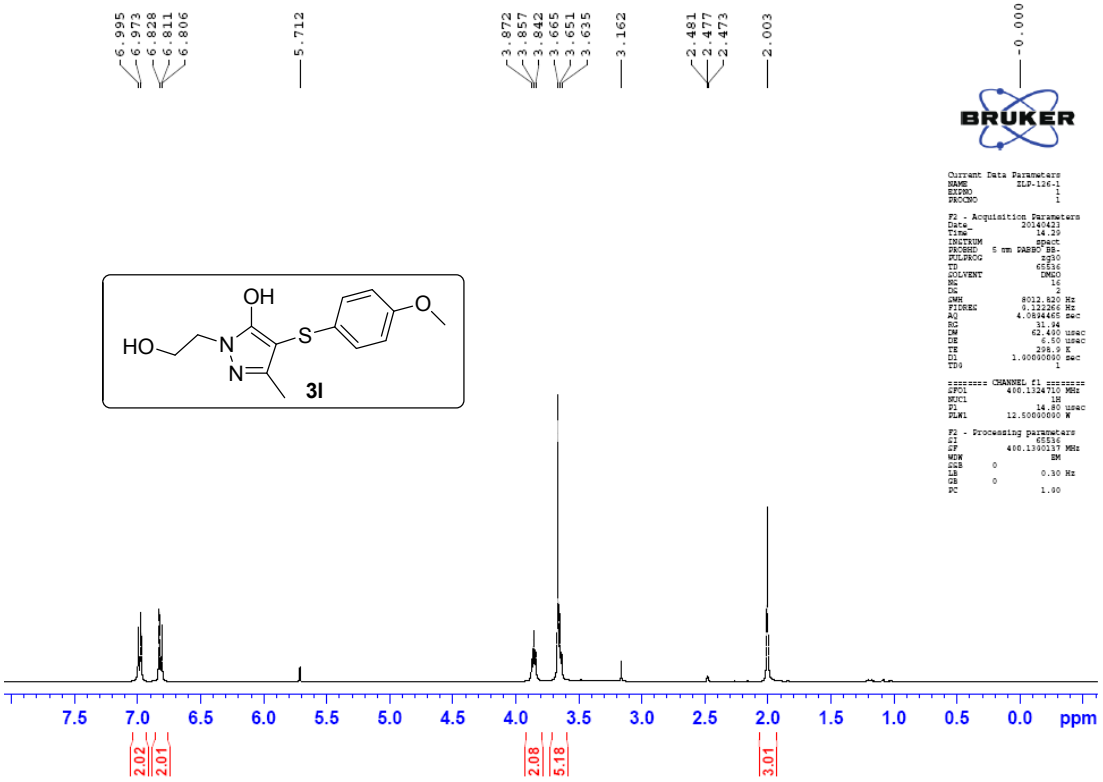
Current Data Parameters
NAME ZLP-125-1-20140423
EXPNO 2
PROCNO 1

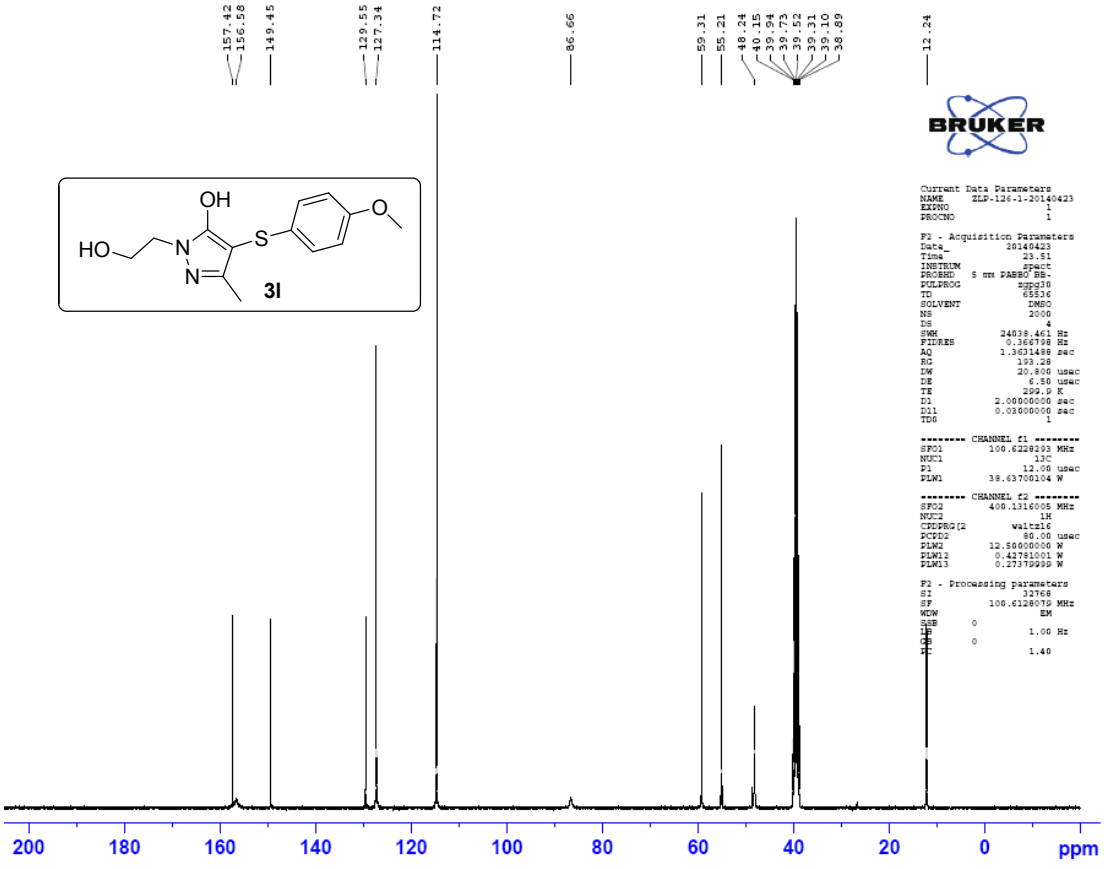
F2 - Acquisition Parameters
Date_ 20140423
Time 25.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1200
DS 4
SWH 24038.461 Hz
FIDRES 0.366708 Hz
AQ 1.3631488 sec
RG 180.28
DW 20.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

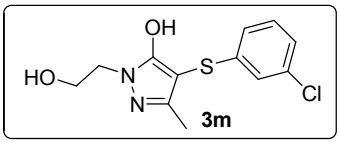
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 13.00 usec
PLW1 38.43700104 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 98.00 usec
PLW2 12.50000000 W
PLW12 0.42792001 W
PLW13 0.27379202 W

F2 - Processing parameters
SI 32768
SF 100.6128382 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

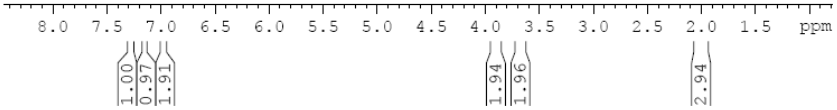

6.995
6.973
6.828
6.811
6.806
5.712
3.872
3.857
3.842
3.665
3.651
3.635
3.162
2.481
2.477
2.473
2.003
0.000
OH
HO
N
N
S
O
3l
BRUKER
Current Data Parameters
NAME ZLP-126-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140423
Time 14.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 31.94
DW 62.400 usec
DE 6.50 usec
TE 298.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.80 usec
PLW1 12.50000000 W
F2 - Processing parameters
SI 65536
SF 400.1300137 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
ppm
2.02
2.01
2.08
5.18
3.01

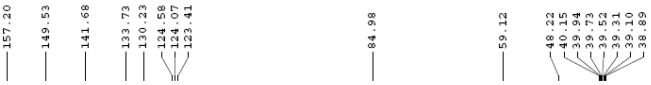

157.42
156.58
149.45
129.55
127.34
114.72
86.66
59.31
55.21
48.24
40.15
39.94
39.73
39.52
39.31
39.10
38.89
12.24
OH
HO
N
N
S
O
3l
BRUKER
Current Data Parameters
NAME ZLP-126-1-20140423
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140423
Time 23.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 193.28
DW 20.800 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 12.00 usec
PLW1 38.63700104 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 12.50000000 W
PLW12 0.42781001 W
PLW13 0.27379999 W
F2 - Processing parameters
SI 32768
SF 100.6128079 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

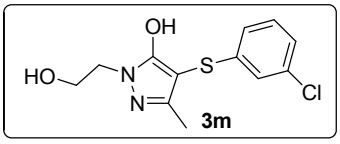



```
NAME          ZLP-126-2-20140415
EXPNO                          1
PROCNO                         1
Date_                   20140416
Time                        2.53
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                           16
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                        193.28
DW                        62.400 usec
DE                         6.50 usec
TE                       298.2 K
D1                  1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                       1H
P1                      14.80 usec
SI                        65536
SF              400.1300032 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```







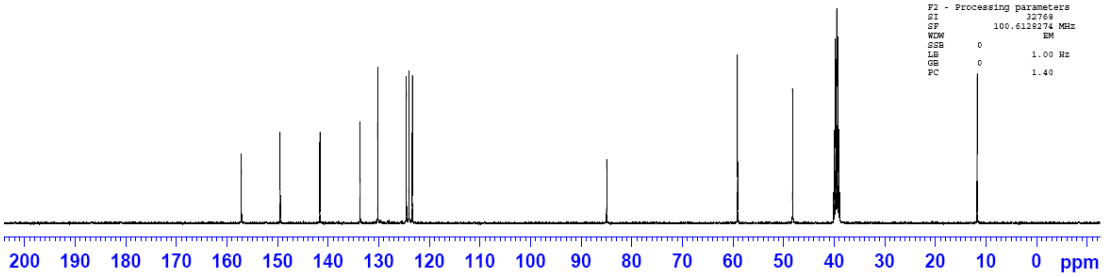

```
Current Data Parameters
NAME      ZLP-126-2-20140416
EXPNO                      2
PROCNO                     1

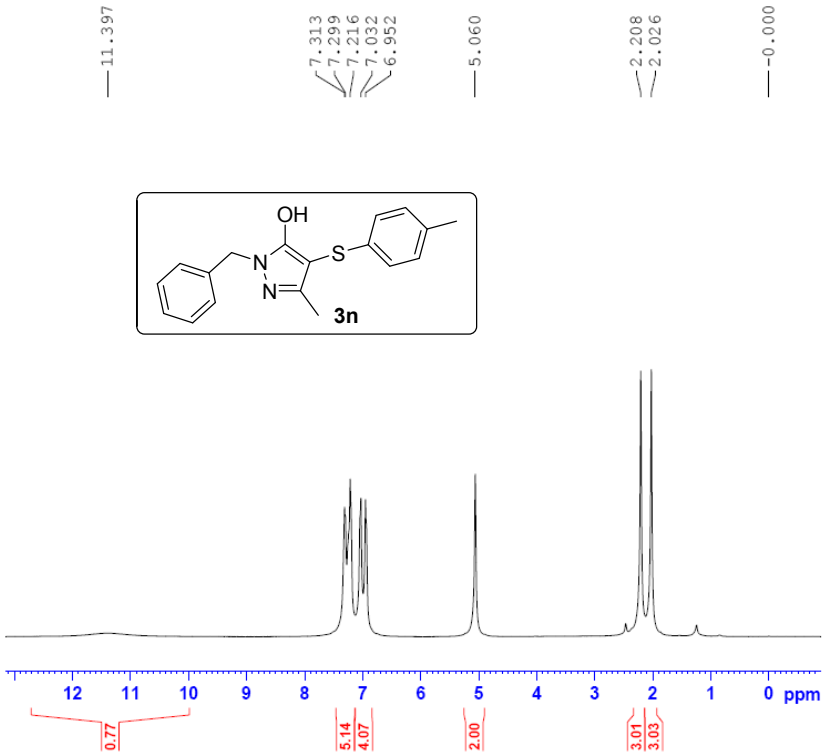
F2 - Acquisition Parameters
Date_               20140416
Time                   10.56
INSTRUM                spect
PROBHD  5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               DMSO
NS                      480
DS                        4
SWH              24038.461 Hz
FIDRES            0.366799 Hz
AQ                1.3631488 sec
RG                   193.28
DW                   20.800 usec
DE                    6.50 usec
TE                   233.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            100.6228293 MHz
NUC1                      13C
P1                      12.00 usec
PLW1            38.63700104 W

======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                  80.00 usec
PLW2            12.50000000 W
PLW12            0.42781001 W
PLW13            0.27379999 W

F2 - Processing parameters
SI                        32768
SF              100.6128274 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

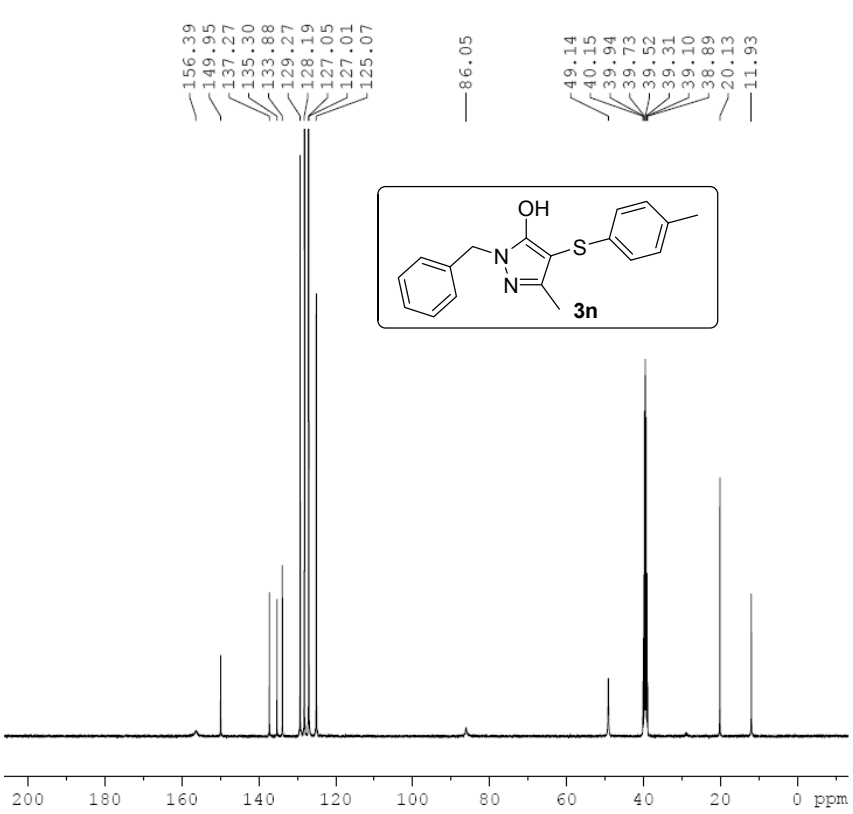




BRUKER

```
NAME          ZLP-151-20140410-2
EXPNO                          1
PROCNO                         1
Date_               20140409
Time                      20.45
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                   DMSO
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                  4.0894966 sec
RG                       31.94
DW                     62.400 usec
DE                      6.50 usec
TE                     333.2 K
D1                  1.00000000 sec
TD0                          1

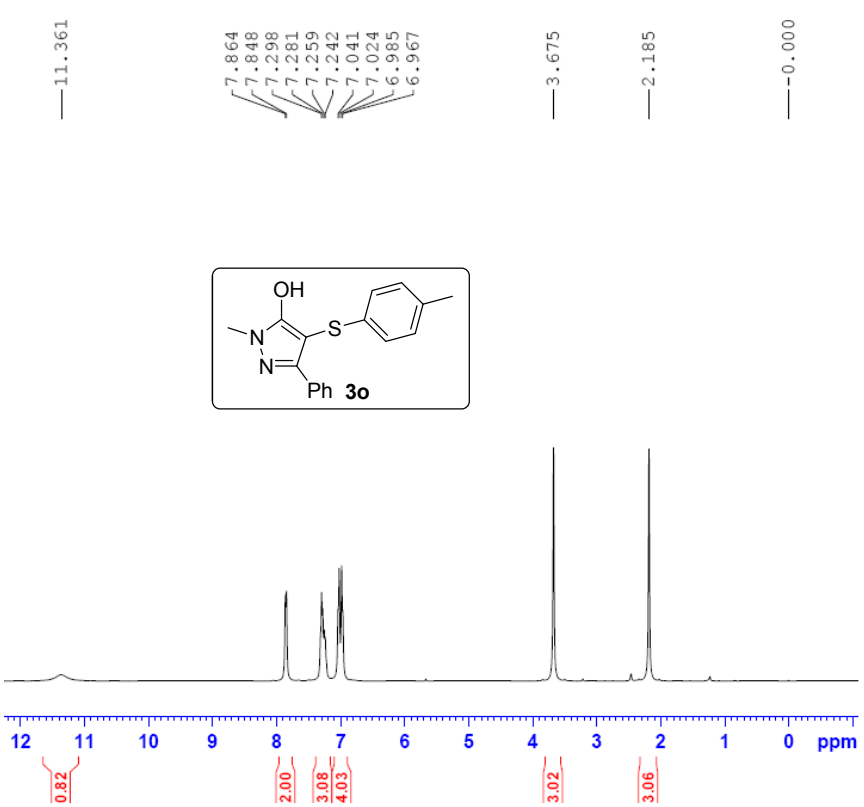
======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                       1H
P1                      14.80 usec
SI                       65536
SF              400.1300193 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



BRUKER

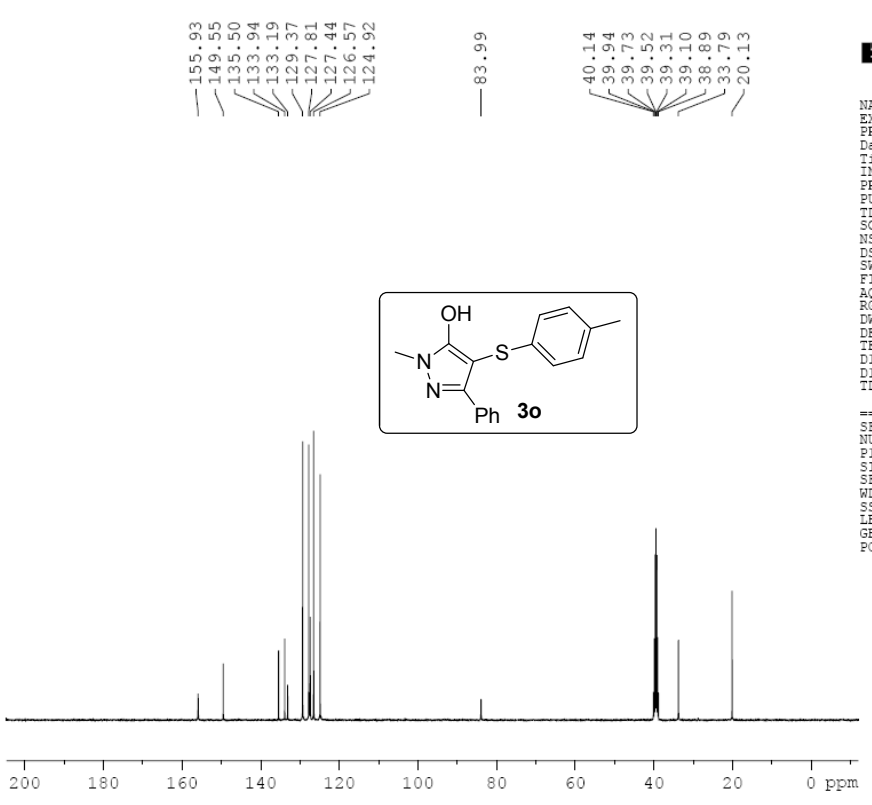
```
NAME          ZLP-151-20140410-2
EXPNO                          2
PROCNO                         1
Date_               20140410
Time                      12.44
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                   DMSO
NS                         1024
DS                            4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                  1.3631988 sec
RG                      193.28
DW                     20.800 usec
DE                      6.50 usec
TE                     333.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            100.6228293 MHz
NUC1                       13C
P1                      12.00 usec
SI                       32768
SF              100.6128389 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



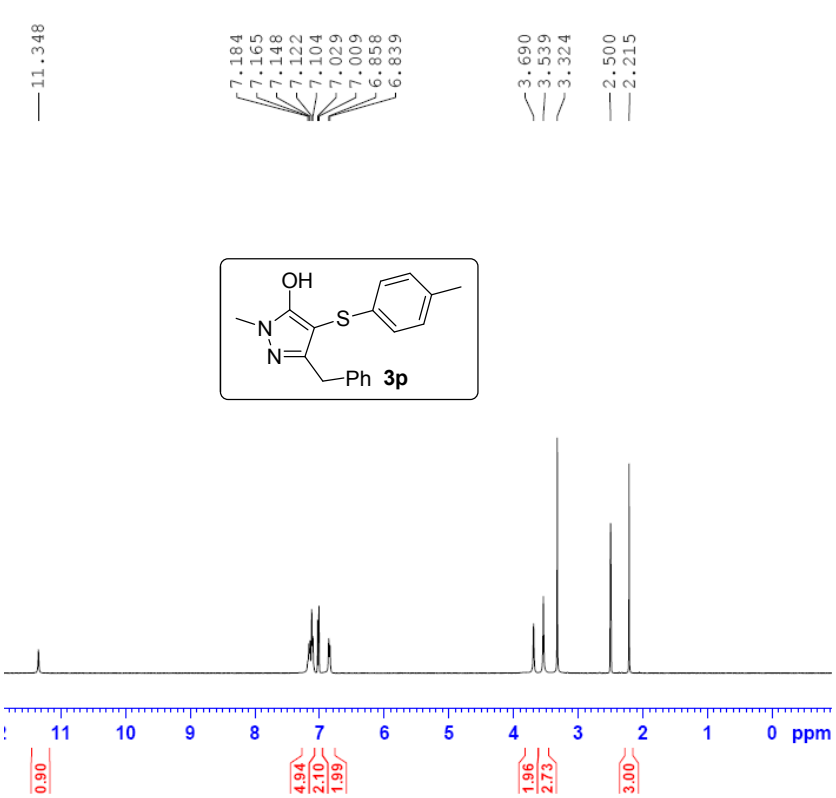

```
NAME                ZLP-154
EXPNO                     1
PROCNO                    1
Date_              20140409
Time                  13.04
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                       31.94
DW                    62.400 usec
DE                     6.50 usec
TE                    333.4 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                    14.80 usec
SI                        65536
SF               400.1300189 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                      1.00
```



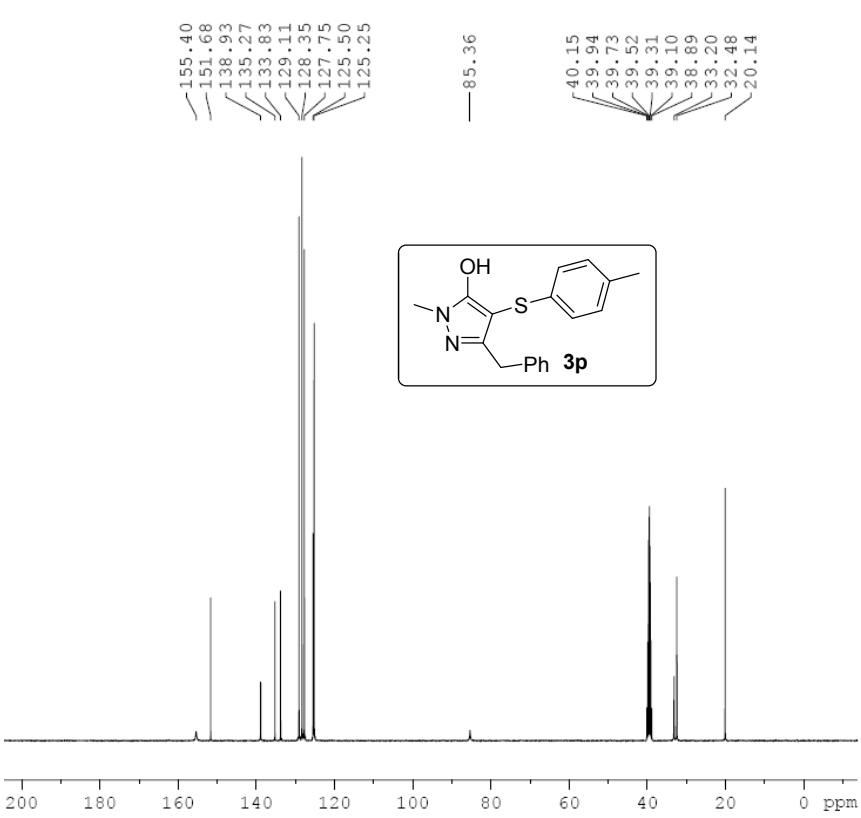

```
NAME                ZLP-154
EXPNO                     2
PROCNO                    1
Date_              20140409
Time                  13.21
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                      285
DS                        4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                      193.28
DW                    20.800 usec
DE                     6.50 usec
TE                    333.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                    12.00 usec
SI                        32768
SF               100.6128377 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40
```



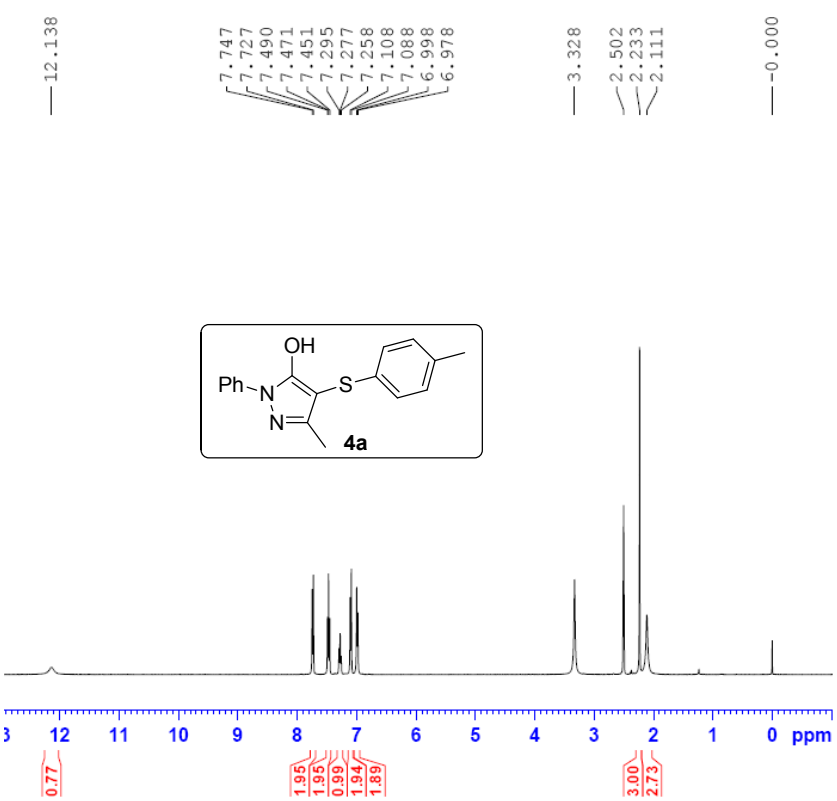

```
NAME                ZLP-164-H
EXPNO                       1
PROCNO                      1
Date_                20140314
Time                    14.37
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                        203
DW                   60.800 usec
DE                    6.50 usec
TE                    298.1 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    13.00 usec
SI                     65536
SF              400.1300028 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00
```




```
NAME                ZLP-164
EXPNO                     2
PROCNO                    1
Date_              20140410
Time                  13.48
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                   193.28
DW                20.800 usec
DE                 6.50 usec
TE                 333.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                    13C
P1                 12.00 usec
SI                     32768
SF           100.6128388 MHz
WDW                       EM
SSB                        0
LB                 1.00 Hz
GB                         0
PC                     1.40
```



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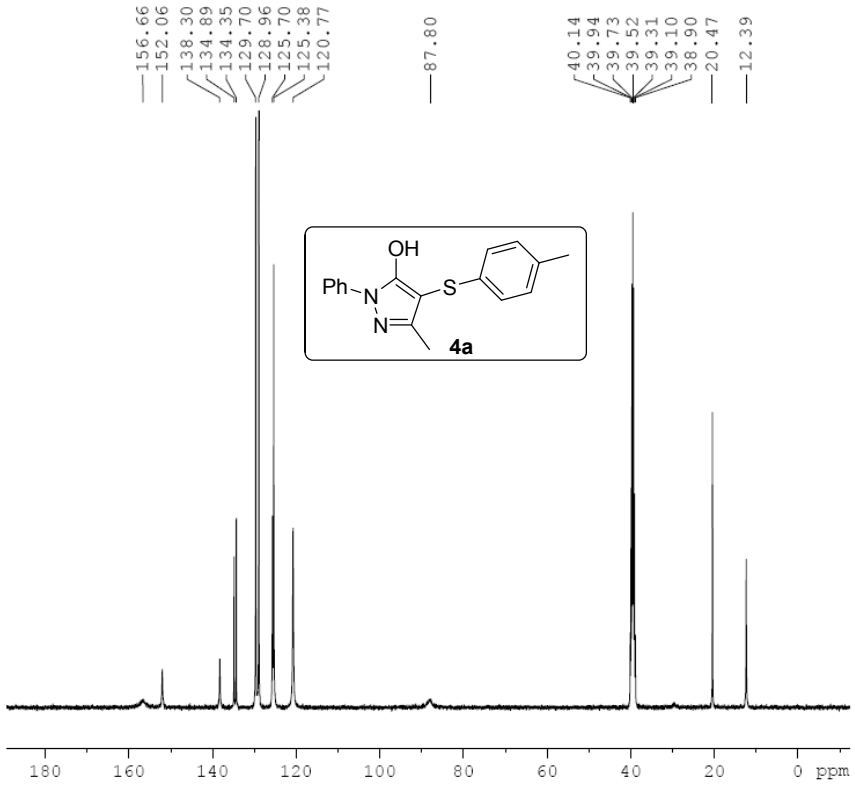
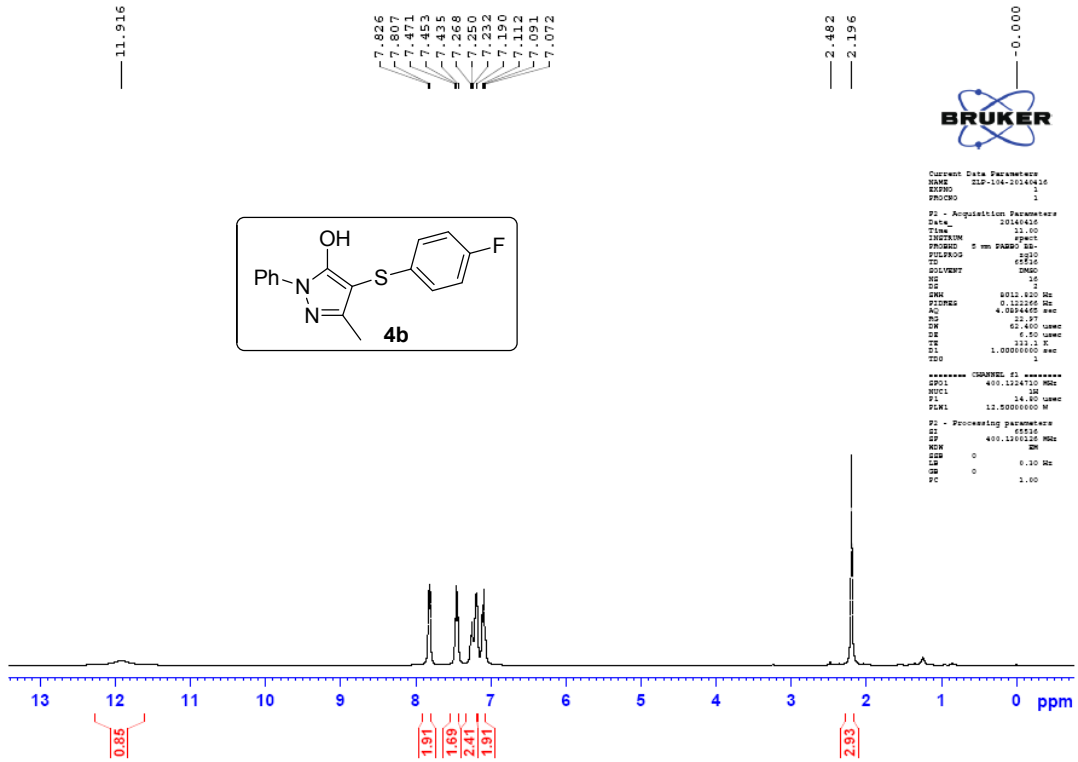
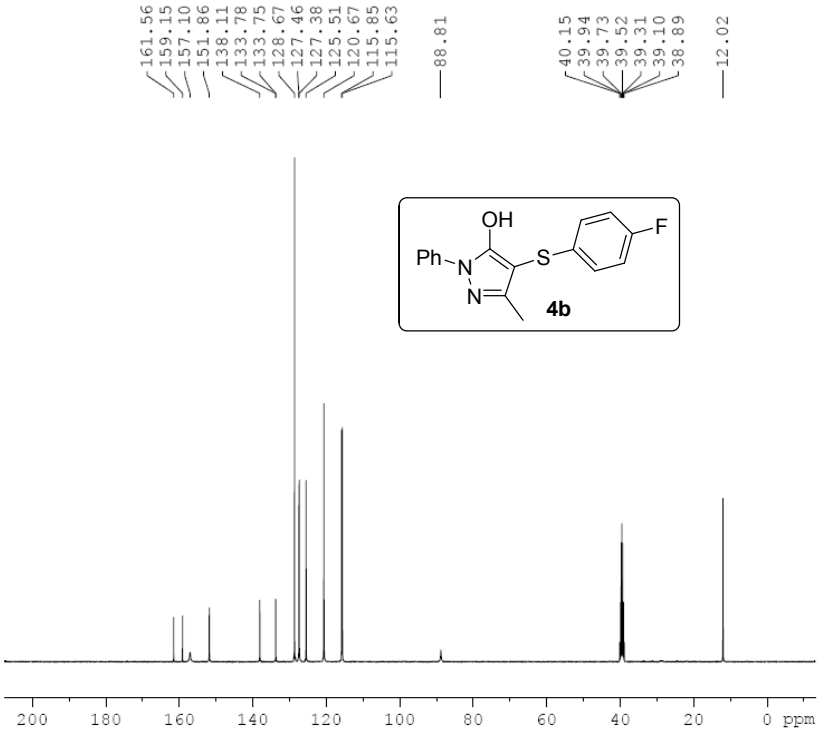
NAME	ZLP-35
EXPNO	1
PROCNO	1
Date_	20131108
Time	16.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	193.28
DW	62.400 usec
DE	6.50 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	14.80 usec
SI	65536
SF	400.1300027 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

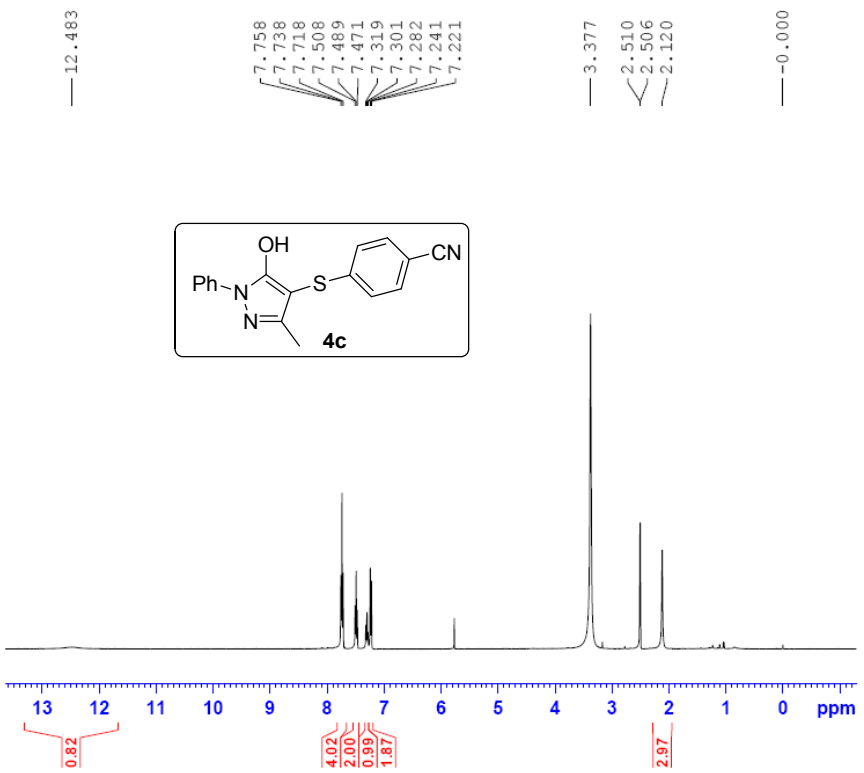
NAME	ZLP-35-1-20140109
EXPNO	1
PROCNO	1
Date_	20140109
Time	17.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	193.28
DW	20.800 usec
DE	6.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6128115 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40





BRUKER

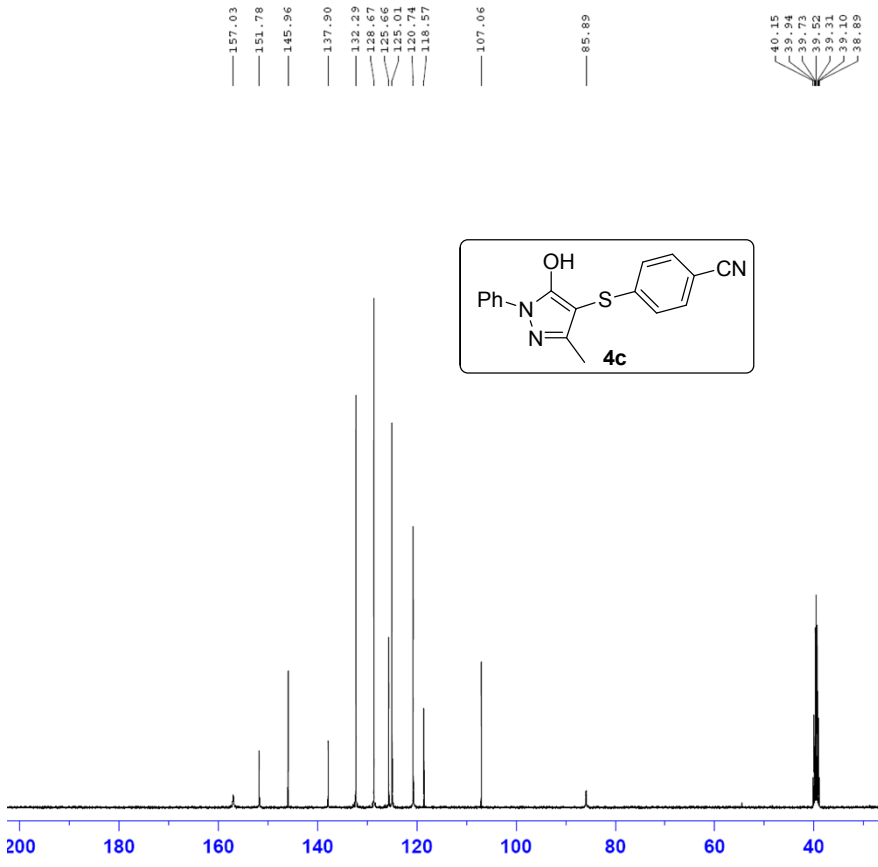
NAME	ZLP-104-20140416
EXPNO	2
PROCNO	1
Date_	20140416
Time	11.46
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	783
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	193.28
DW	20.800 usec
DE	6.50 usec
TE	333.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6128309 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

```
NAME                ZLP-96-H
EXPNO                      1
PROCNO                     1
Date_               20131220
Time                   10.59
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                       181
DW                  60.800 usec
DE                   6.50 usec
TE                   290.9 K
D1                1.00000000 sec

========= CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
SI                     65536
SF              400.1300004 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



BRUKER

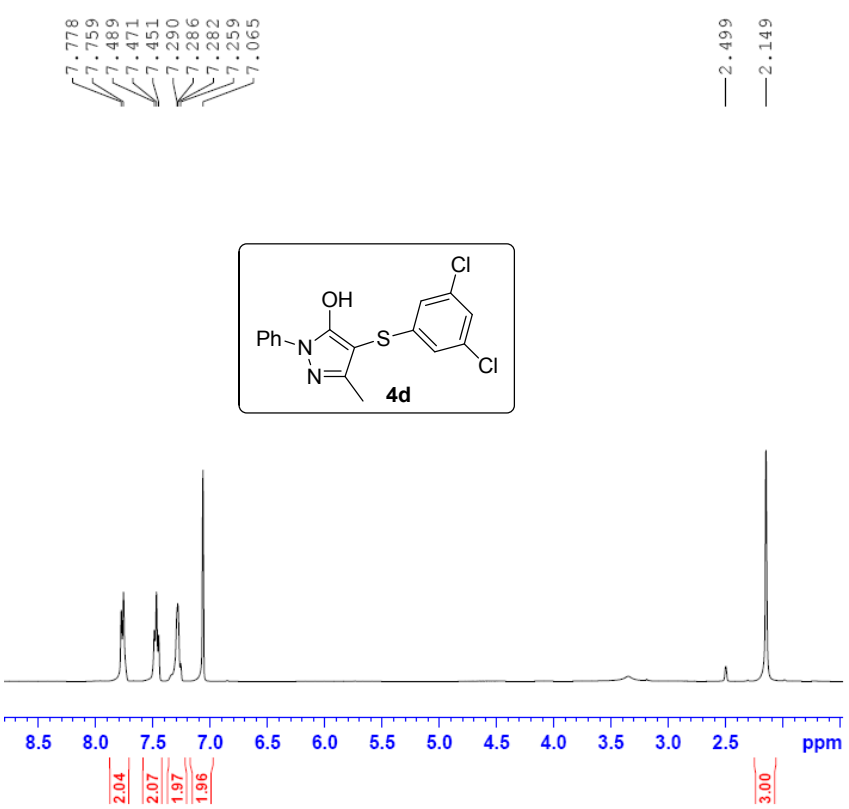
```
Current Data Parameters
NAME      ZLP-96-20140402
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140402
Time                10.02
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                     500
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                   193.28
DW                  20.800 usec
DE                   6.50 usec
TE                   333.2 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                    13C
P1                   12.00 usec
PLW1          38.63700104 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                80.00 usec
PLW2          12.50000000 W
PLW12          0.42781001 W
PLW13          0.27379999 W

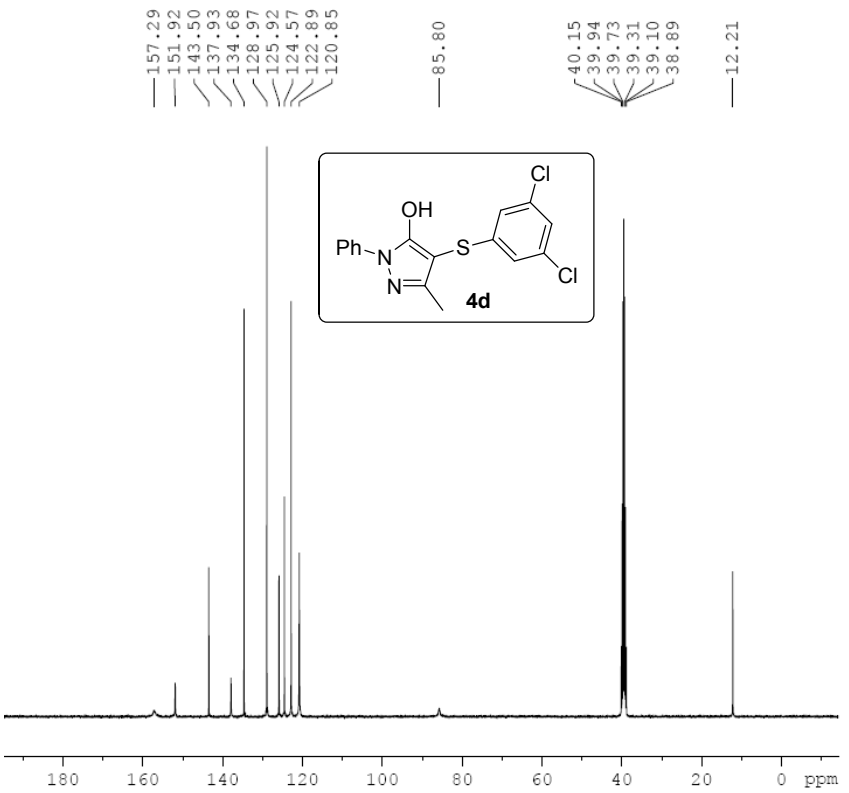
F2 - Processing parameters
SI                      32768
SF            100.6128364 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



BRUKER

```
NAME          ZLP-111-2-20140226
EXPNO                          1
PROCNO                         1
Date_                   20140226
Time                       15.26
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                     zg30
TD                         65536
SOLVENT                     DMSO
NS                            16
DS                             2
SWH                     8012.820 Hz
FIDRES                  0.122266 Hz
AQ                      4.0894966 sec
RG                         61.44
DW                         62.400 usec
DE                          6.50 usec
TE                        298.1 K
D1                      1.00000000 sec
TD0                            1

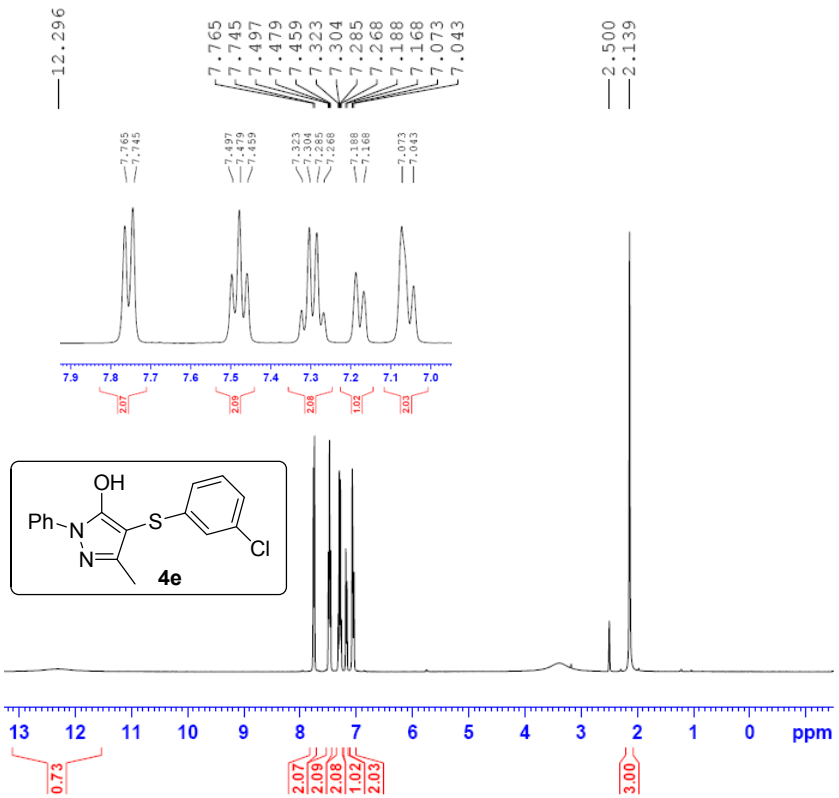
======== CHANNEL f1 ========
SFO1                  400.1324710 MHz
NUC1                          1H
P1                         14.80 usec
SI                         65536
SF                    400.1300042 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



BRUKER

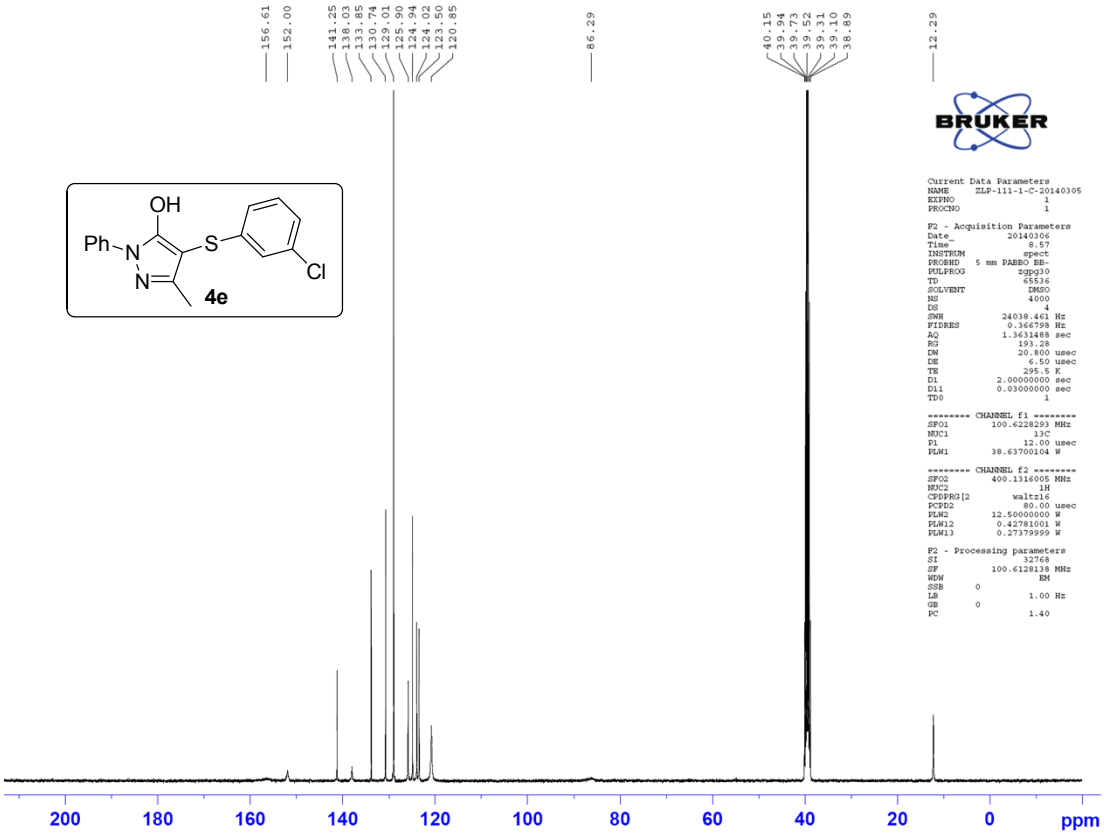
```
NAME          ZLP-111-2-20140117
EXPNO                          1
PROCNO                         1
Date_                   20140117
Time                       16.23
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                   zgpg30
TD                         65536
SOLVENT                     DMSO
NS                           1024
DS                             4
SWH                    24038.461 Hz
FIDRES                  0.366798 Hz
AQ                      1.3631988 sec
RG                        193.28
DW                         20.800 usec
DE                          6.50 usec
TE                        298.1 K
D1                      2.00000000 sec
D11                     0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                  100.6228293 MHz
NUC1                          13C
P1                         12.00 usec
SI                         32768
SF                    100.6128145 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```




```
NAME            ZLP-111-1-H
EXPNO                 1
PROCNO                1
Date_          20140226
Time              15.33
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT           DMSO
NS                  16
DS                   2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894966 sec
RG                77.88
DW              62.400 usec
DE               6.50 usec
TE              298.1 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1               1H
P1              14.80 usec
SI                65536
SF           400.1300038 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```



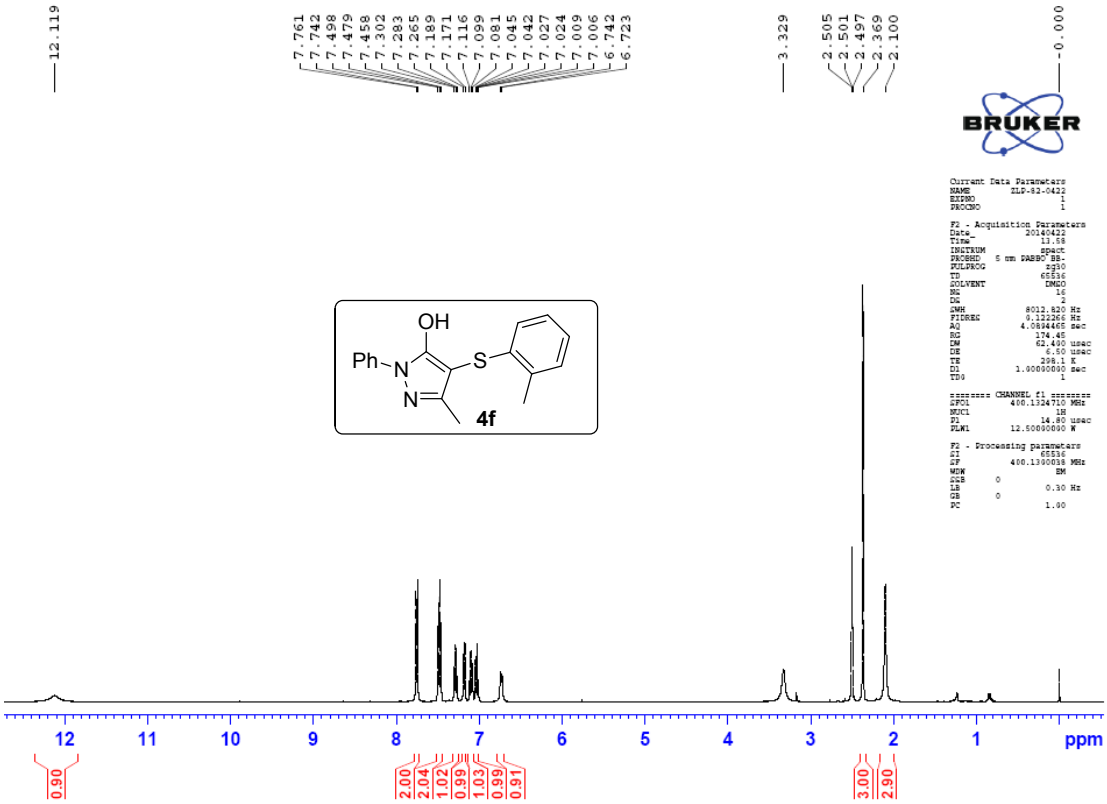

```
Current Data Parameters
NAME      ZLP-111-1-C-20140305
EXPNO                 1
PROCNO                1

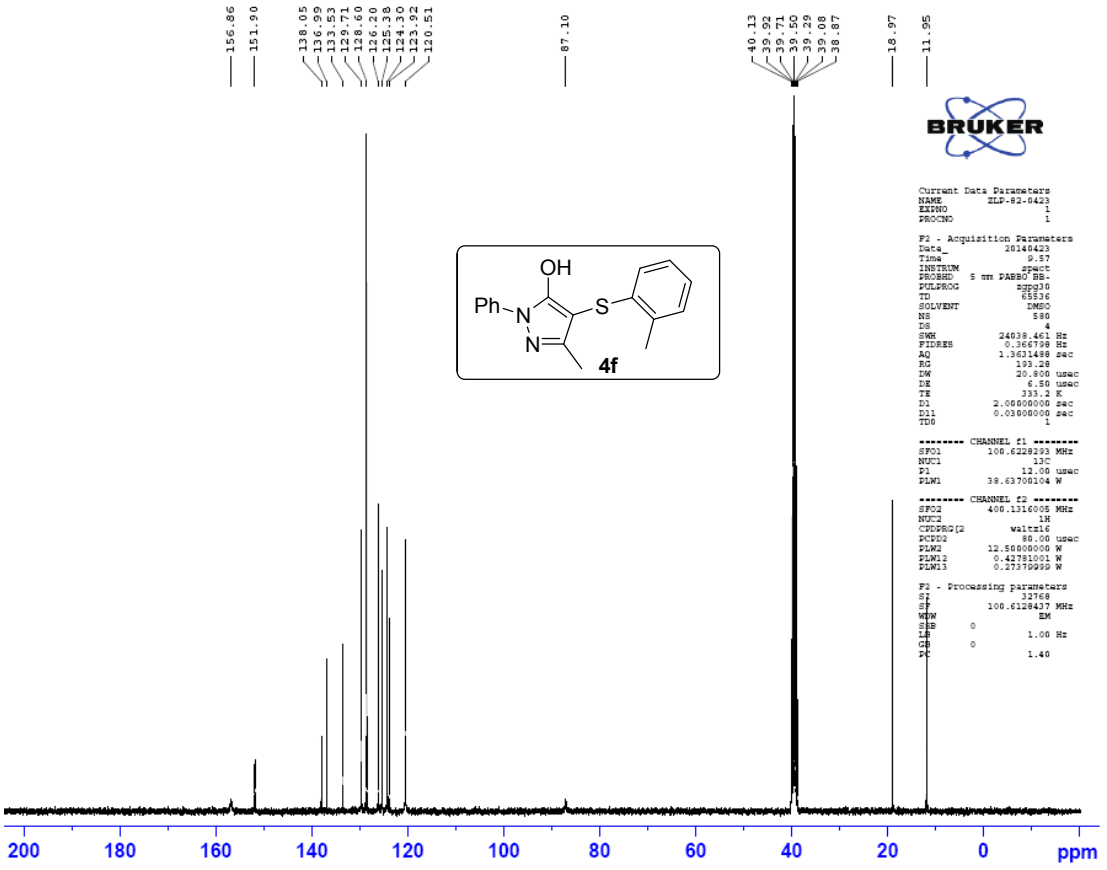
F2 - Acquisition Parameters
Date_          20140306
Time               8.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD               65536
SOLVENT           DMSO
NS                 4000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                193.28
DW              20.800 usec
DE               6.50 usec
TE              295.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1

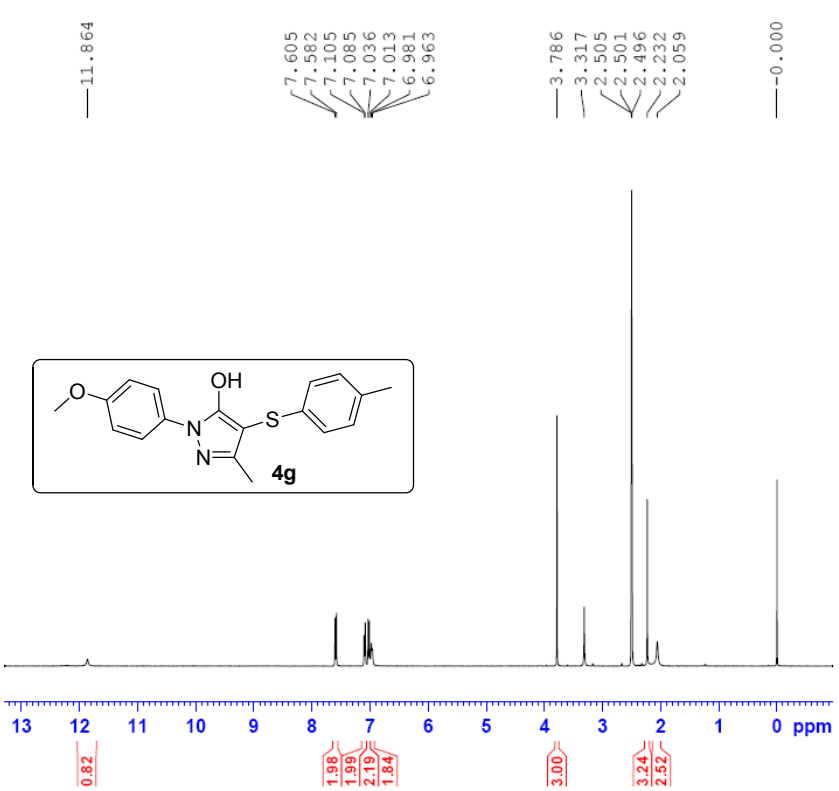
======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1               13C
P1              12.00 usec
PLW1         38.63700104 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2               1H
CPDPRG[2          waltz16
PCPD2           80.00 usec
PLW2         12.50000000 W
PLW12         0.42781001 W
PLW13         0.27379999 W

F2 - Processing parameters
SI                32768
SF           100.6128138 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

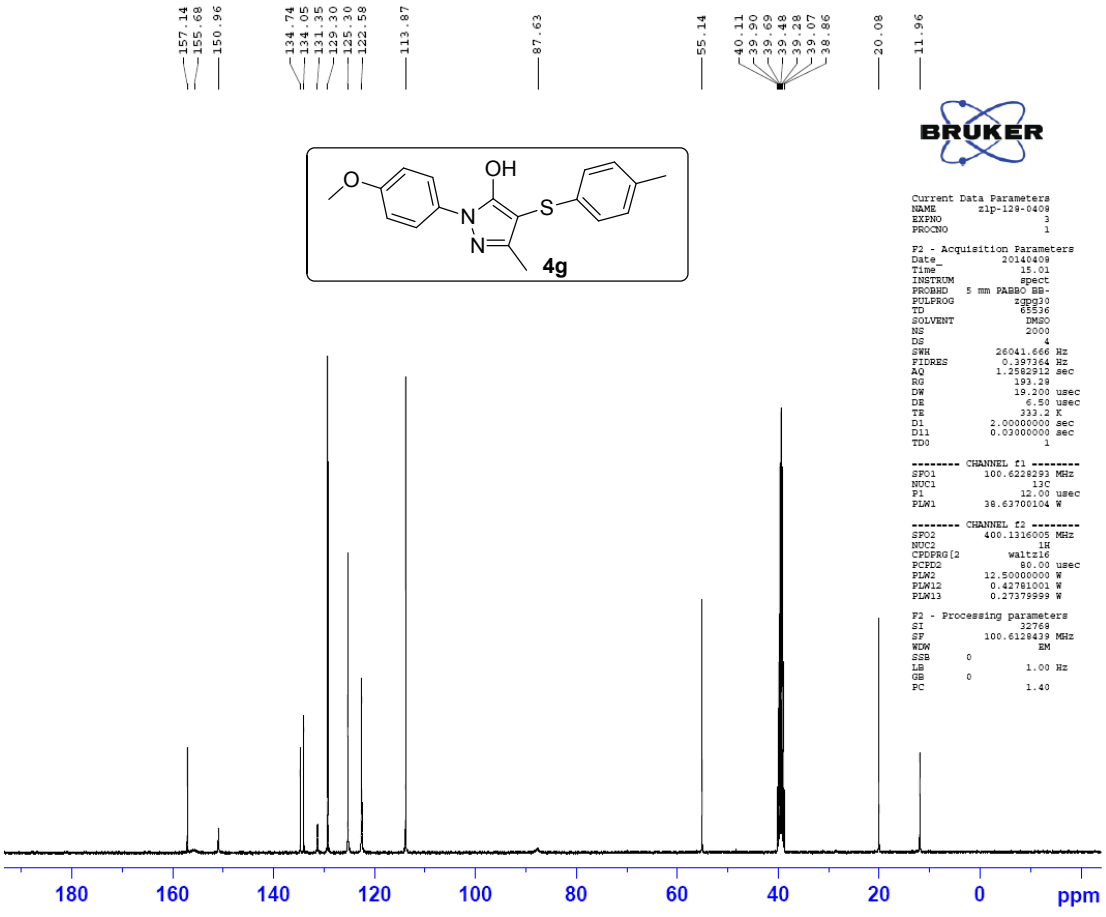

12.119
7.761
7.742
7.498
7.479
7.458
7.302
7.283
7.265
7.189
7.171
7.116
7.099
7.081
7.045
7.042
7.027
7.024
7.009
7.006
6.742
6.723
3.329
2.505
2.501
2.497
2.369
2.100
0.000
BRUKER
OH
Ph
N
N
S
4f
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.90
2.00
2.04
1.02
0.99
1.03
0.99
0.91
3.00
2.90


156.86
151.90
138.05
136.99
133.53
129.71
128.60
126.20
125.38
124.30
123.92
120.51
87.10
40.13
39.92
39.71
39.50
39.29
39.08
38.87
18.97
11.95
BRUKER
OH
Ph
N
N
S
4f
200
180
160
140
120
100
80
60
40
20
0
ppm




```
NAME          ZLP-128-20140403
EXPNO                        1
PROCNO                       1
Date_                 20140403
Time_                    11.28
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                  DMSO
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                     193.28
DW                     62.400 usec
DE                      6.50 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                       1H
P1                      14.80 usec
SI                      65536
SF             400.1300037 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



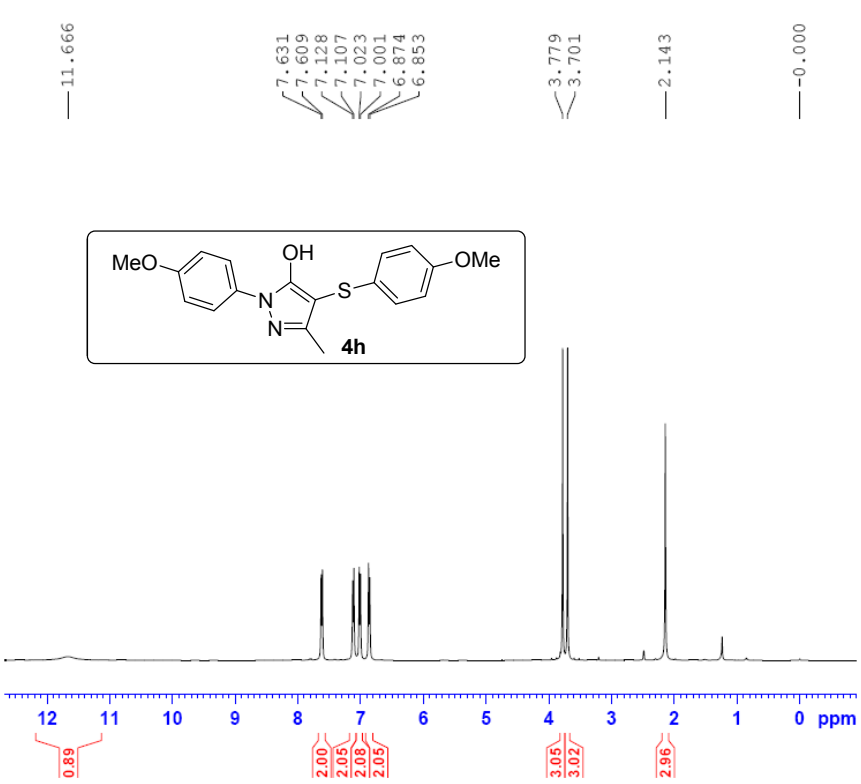

```
Current Data Parameters
NAME          zlp-128-0409
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140409
Time_                 15.01
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    2000
DS                       4
SWH              26041.666 Hz
FIDRES            0.397364 Hz
AQ                1.2582912 sec
RG                   193.28
DW                   19.200 usec
DE                    6.50 usec
TE                   333.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

-------- CHANNEL f1 --------
SFO1            100.6228293 MHz
NUC1                     13C
P1                     12.00 usec
PLW1           38.63700104 W

-------- CHANNEL f2 --------
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                  80.00 usec
PLW2           12.50000000 W
PLW12           0.42781001 W
PLW13           0.27379999 W

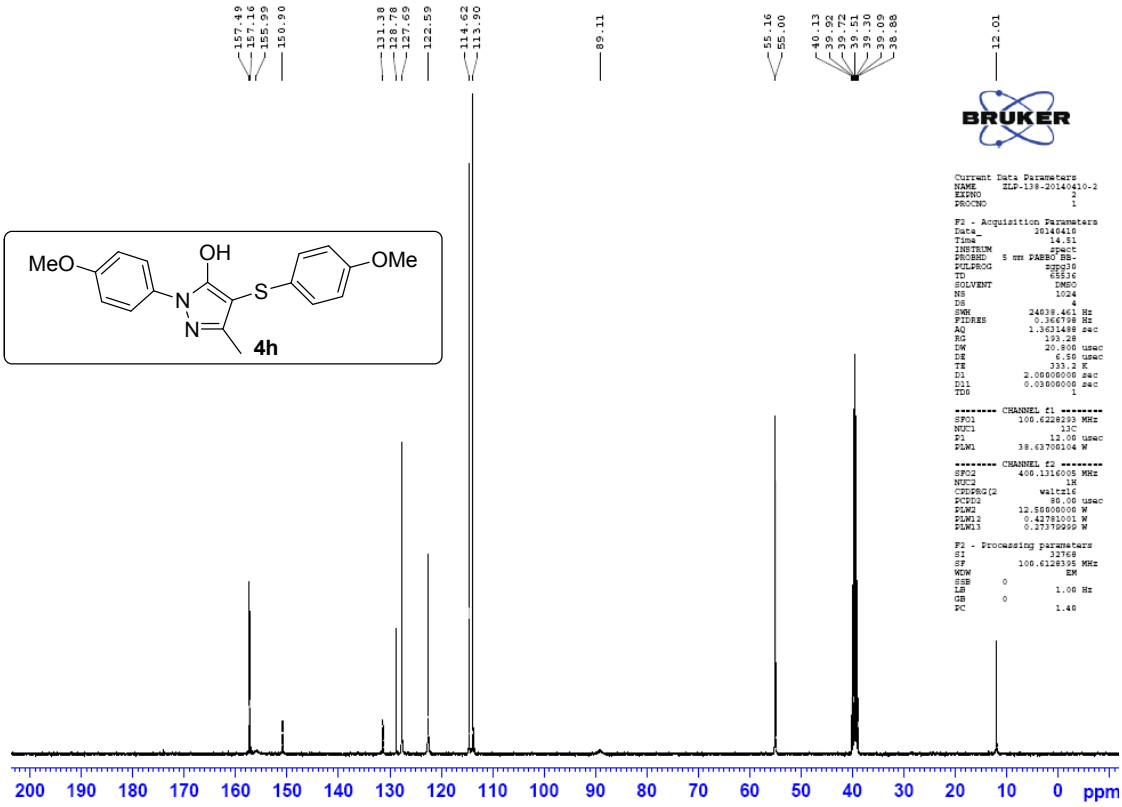
F2 - Processing parameters
SI                       32768
SF              100.6128439 MHz
WDW                        EM
SSB                 0
LB                       1.00 Hz
GB                  0
PC                       1.40
```



BRUKER

```
NAME                ZLP-138
EXPNO                     1
PROCNO                    1
Date_              20140410
Time                  13.51
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                     31.94
DW                    62.400 usec
DE                     6.50 usec
TE                    333.1 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                    14.80 usec
SI                     65536
SF             400.1300102 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
```



BRUKER

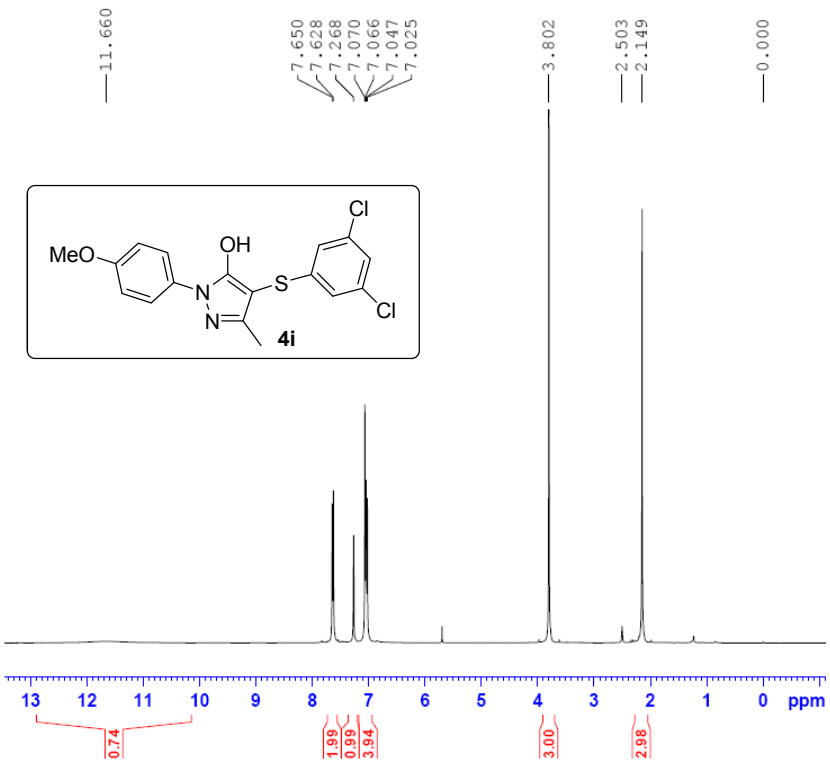
```
Current Data Parameters
NAME      ZLP-138-20140410-2
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140410
Time                  14.51
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                    193.28
DW                   20.800 usec
DE                    6.50 usec
TE                    333.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                      13C
P1                   12.00 usec
PLW1          38.63708104 W

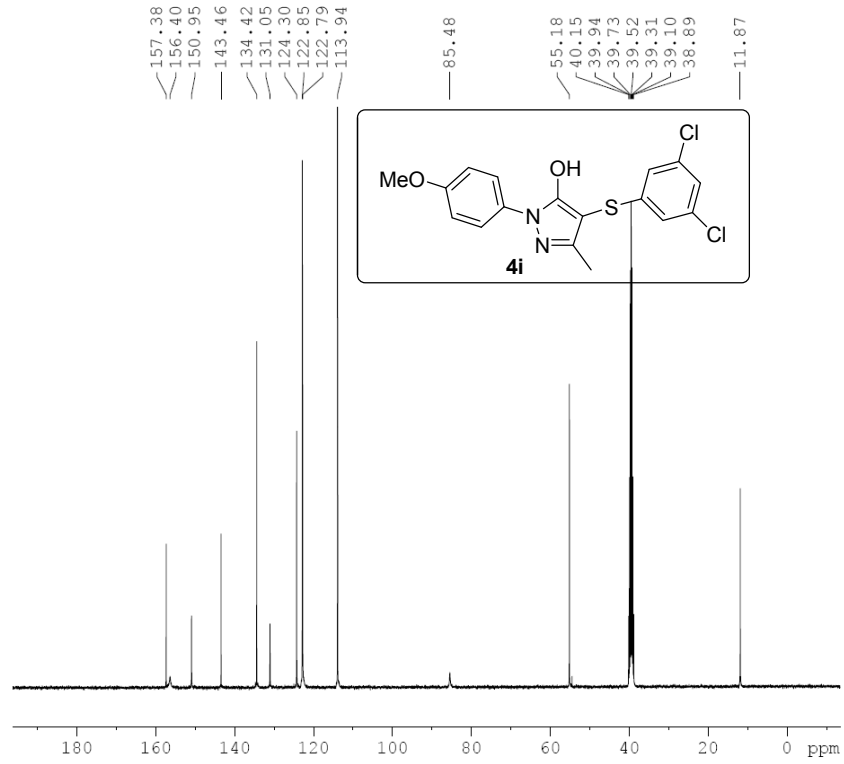
======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                80.00 usec
PLW2          12.50000000 W
PLW12          0.42791001 W
PLW13          0.27379999 W

F2 - Processing parameters
SI                    32768
SF            100.6128395 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```



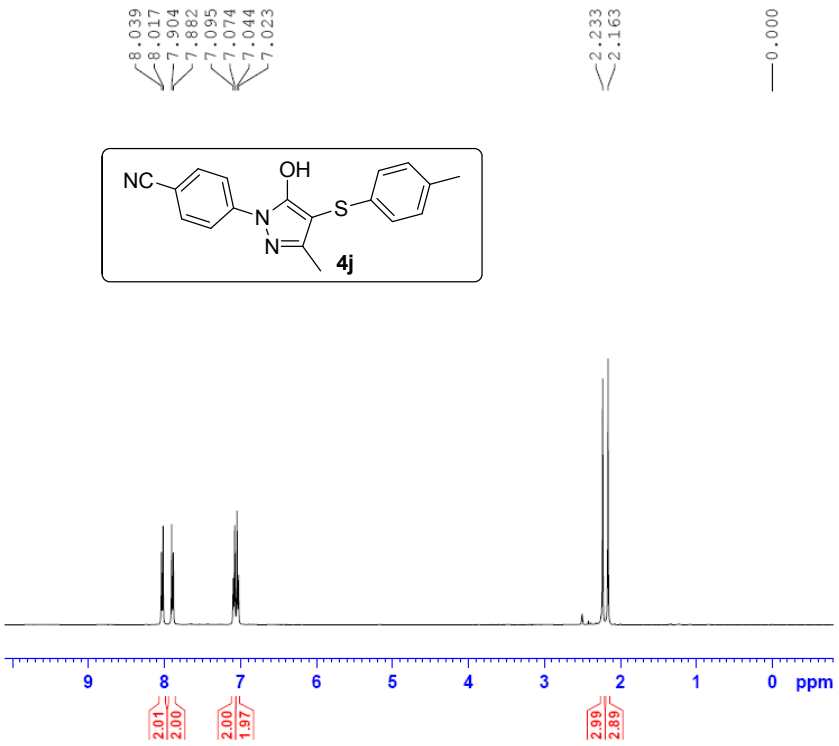

```
NAME            ZLP-131-0321
EXPNO                      5
PROCNO                     1
Date_               20140321
Time                   10.26
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                      51.4
DW                   62.400 usec
DE                    6.50 usec
TE                   333.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      14.80 usec
SI                      65536
SF               400.1300029 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



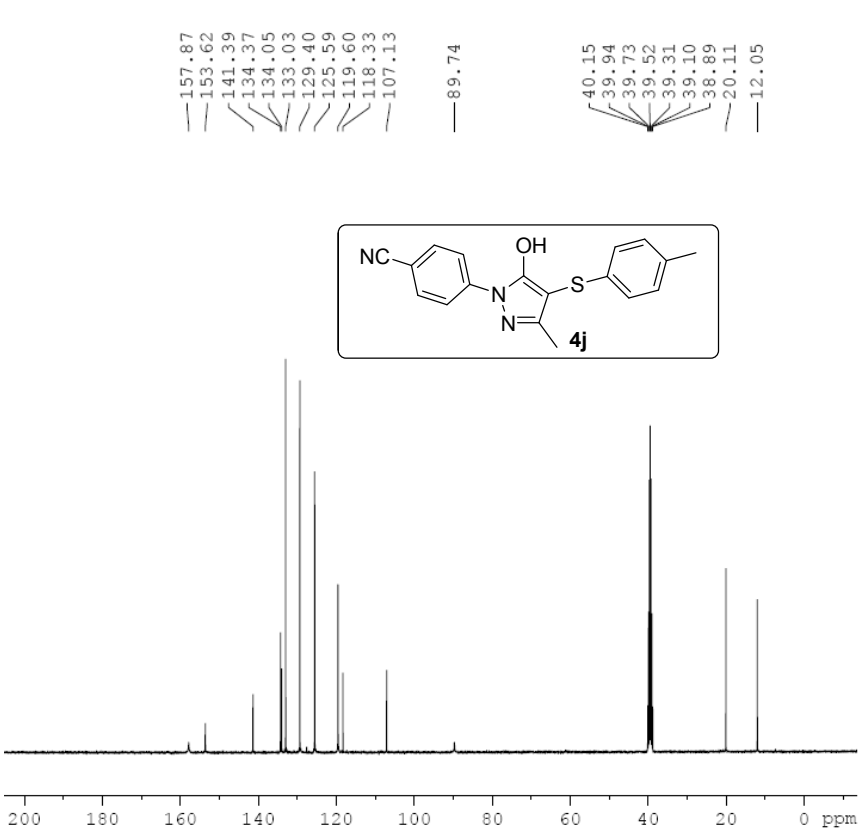

```
NAME            ZLP-131-0321
EXPNO                      4
PROCNO                     1
Date_               20140321
Time                   10.22
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1234
DS                        4
SWH               26041.666 Hz
FIDRES            0.397364 Hz
AQ                1.2583412 sec
RG                    193.28
DW                   19.200 usec
DE                    6.50 usec
TE                   333.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                      12.00 usec
SI                      32768
SF               100.6128392 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



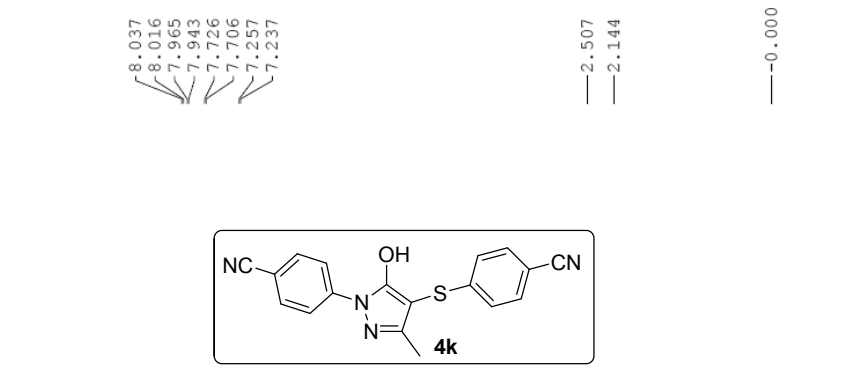

```
NAME                ZLP-133
EXPNO                     1
PROCNO                    1
Date_              20140328
Time                 14.06
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH               8012.820 Hz
FIDRES               0.122266 Hz
AQ                4.0894966 sec
RG                       61.44
DW                    62.400 usec
DE                     6.50 usec
TE                    333.2 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                   14.80 usec
SI                    65536
SF           400.1300025 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
NAME                ZLP-133
EXPNO                     2
PROCNO                    1
Date_              20140328
Time                 14.03
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                       746
DS                         4
SWH              26041.666 Hz
FIDRES               0.397364 Hz
AQ                1.2583412 sec
RG                      193.28
DW                    19.200 usec
DE                     6.50 usec
TE                    333.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                   13C
P1                   12.00 usec
SI                    32768
SF           100.6128406 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```




```
NAME                ZLP-135
EXPNO                     1
PROCNO                    1
Date_              20140305
Time                   3.35
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                      174.45
DW                     62.400 usec
DE                      6.50 usec
TE                     298.1 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      14.80 usec
SI                      65536
SF               400.1300015 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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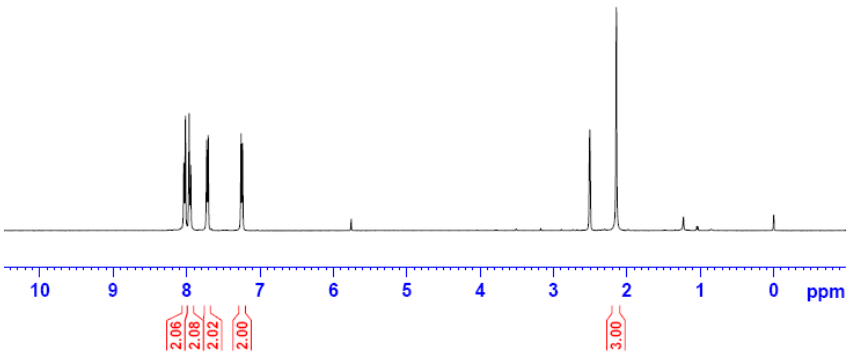

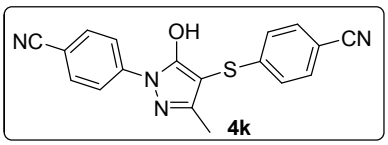


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NAME                ZLP-135
EXPNO                     2
PROCNO                    1
Date_              20140409
Time                  13.46
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                      336
DS                        4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                     193.28
DW                     20.800 usec
DE                      6.50 usec
TE                     333.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                      12.00 usec
SI                      32768
SF               100.6128356 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
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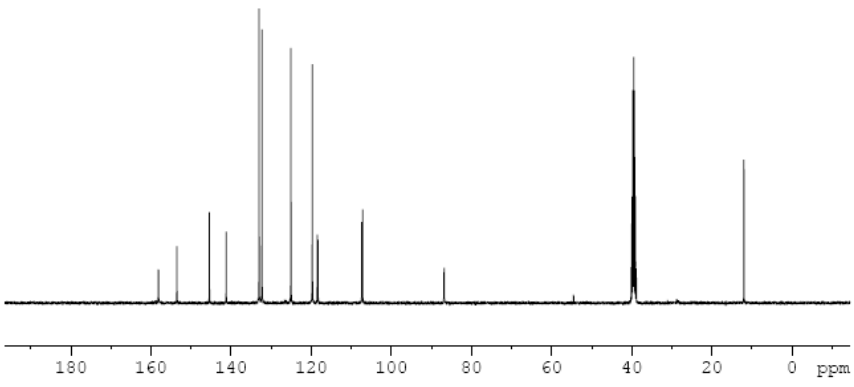
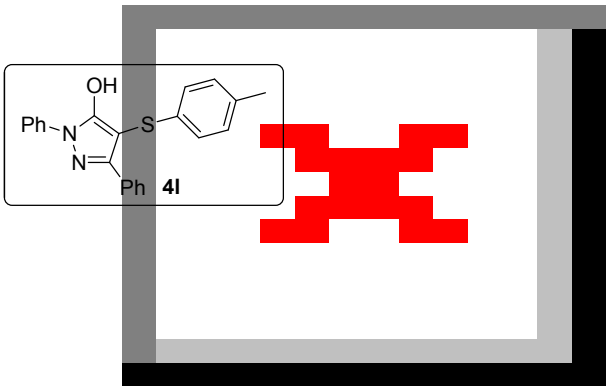
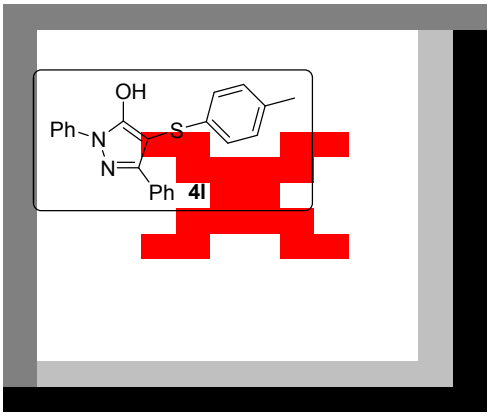
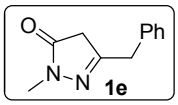



OH
Ph
N
N
S
Ph
4l


OH
Ph
N
N
S
Ph
4l




```
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EXPNO                         1
PROCNO                        1
Date_                  20140412
Time                      16.49
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                           16
DS                            2
SWH                    8012.820
FIDRES                 0.122266
AQ                     4.0894966
RG                         70.34
DW                        62.400
DE                          6.50
TE                         298.1
D1                    1.00000000
TD0                           1

======== CHANNEL f1 ====
SFO1                 400.1324710
NUC1                          1H
P1                         14.80
SI                        65536
SF                   400.1300054
WDW                           EM
SSB                            0
LB                          0.30
GB                             0
PC                          1.00
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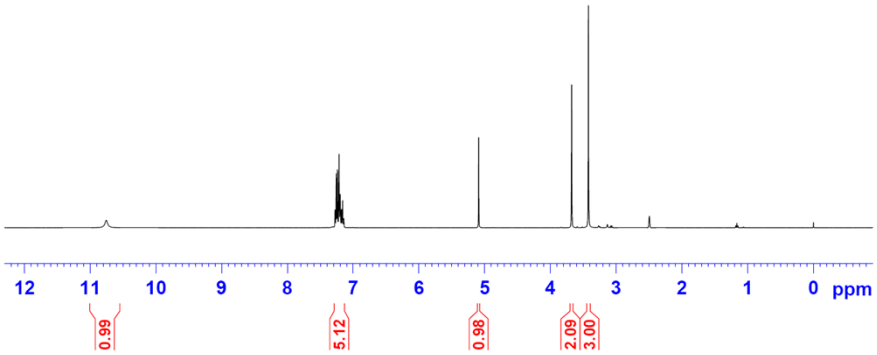

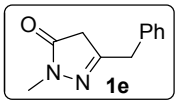


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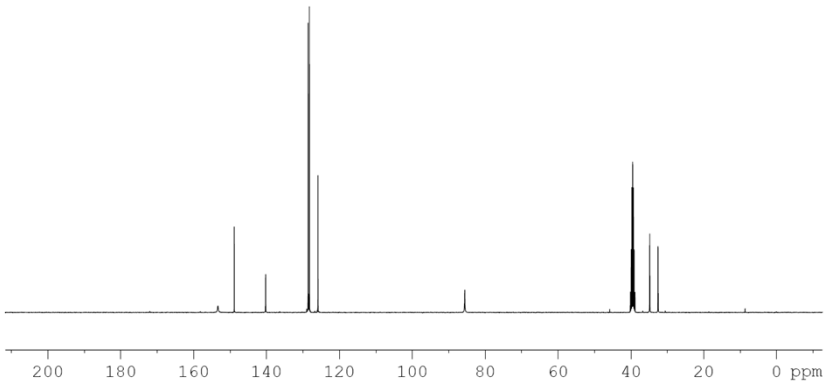
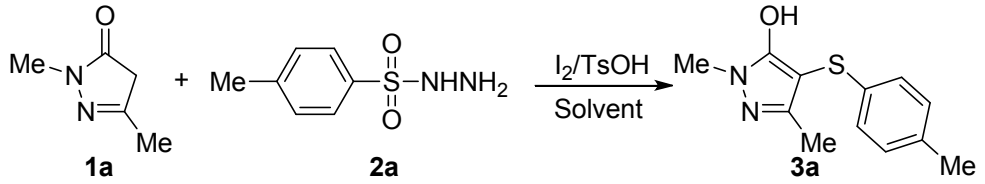
NAME        ZLP-162-20140412
EXPNO                      2
PROCNO                     1
Date_               20140412
Time                   22.42
INSTRUM                spect
PROBHD  5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                DMSO
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                   193.28
DW                  20.800 usec
DE                   6.50 usec
TE                  298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                     13C
P1                   12.00 usec
SI                     32768
SF             100.6128117 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



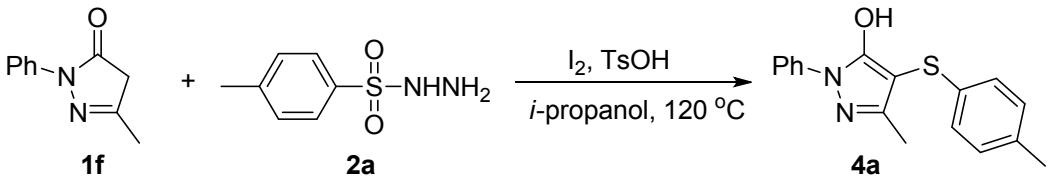
6) Optimization of I_2-catalysed reaction of 1a with 2a[a]



Entry	I_2 (equiv)	TsOH (equiv)	t (h)	T (°C)	Solvent	Yield (%)[b]
1	0.1	0	>72	70	EtOH	*trace*
2	0.1	1	48	70	EtOH	63
3	0.1	1	3	100	EtOH	75
4	0.1	1	1.5	120	EtOH	82
5	0.1	1	1.7	120	*i*-PrOH	87
6	0.1	1	1.5	120	1,4-dioxane	78
7	0.1	1	2	120	toluene	68
8	0.1	1	2	120	DCE	65
9	0.1	0.5	1.5	120	*i*-PrOH	88
10	0.05	0.5	1.5	120	*i*-PrOH	88
11	0.01	0.5	2.5	120	*i*-PrOH	75
12	0.05	0	3	120	*i*-PrOH	83

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), solvent (1 mL).[b] Yield of isolated product after silica gel chromatography

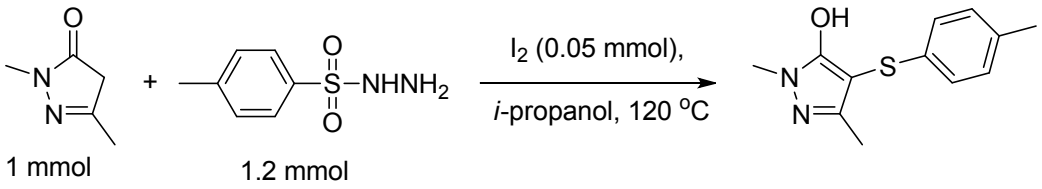
7) Optimization of loadings of I_2 and TsOH in the cross-coupling of 1f with 2a [a]



Entry	I_2 (equiv)	TsOH (equiv)	T (°C)	Yield (%)[b]
1	0.1	1	120	30
2	0.05	1	120	67
3	0.02	1	120	80
4	0.01	1	120	84
5	0.01	0.8	120	67
6	0.01	0	120	20[c]

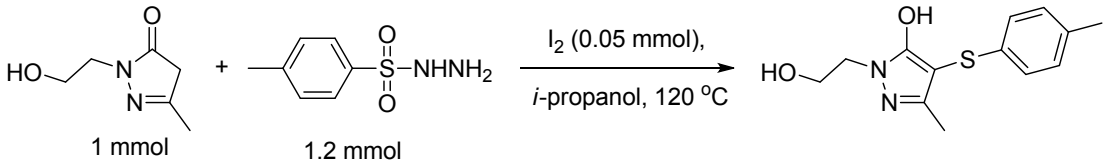
[a]Reaction conditions: **1f** (1.0 mmol), **2a** (1.2 mmol), *i*-PrOH (1 mL), 120 °C, 1.5 h. [b] Yield of isolated product after silica gel chromatography. [c] The reaction time was 12 h.

8) The effects of TsOH on the reaction.



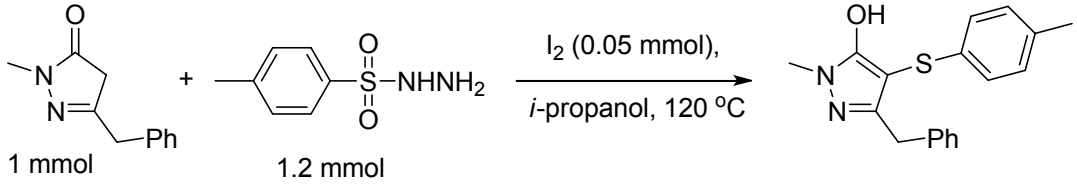
1 mmol 1.2 mmol

TsOH	time (h)	Yield (%)
0.5 mmol	1.5	88
no	3	83



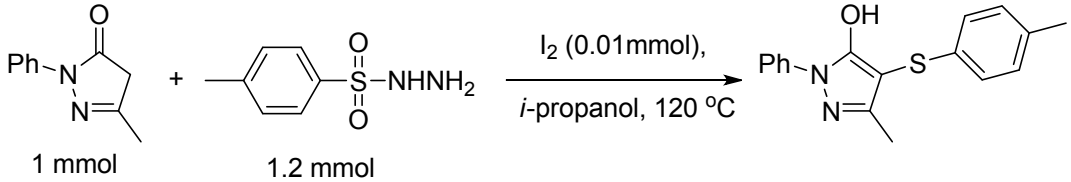
1 mmol 1.2 mmol

TsOH	time (h)	Yield (%)
0.5 mmol	1.5	85
no	No reaction	



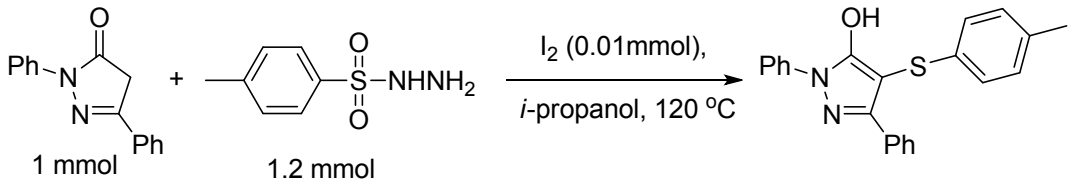
1 mmol 1.2 mmol

TsOH	time (h)	Yield (%)
0.5 mmol	1.5	79
no	3	43



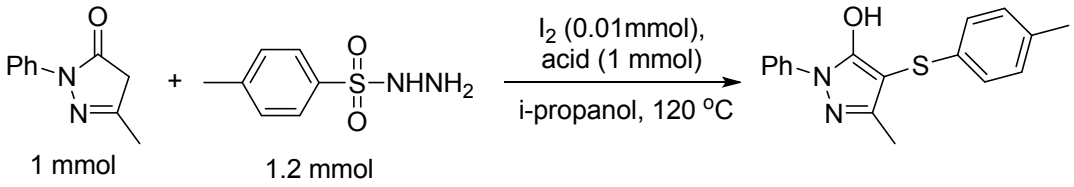
1 mmol 1.2 mmol

TsOH	time (h)	Yield (%)
1 mmol	1.5	84
no	24	20



TsOH	time (h)	Yield (%)
1 mmol	1.5	61
no	24	26

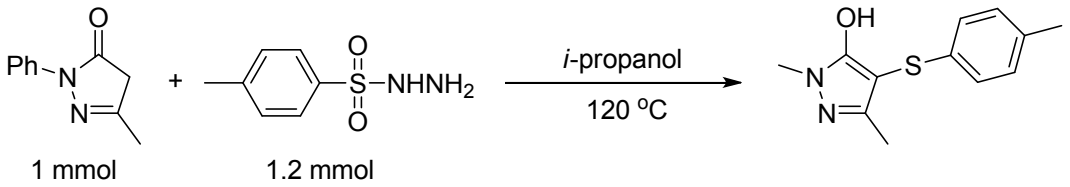
9) The table for the reations of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (1g) with different acids.



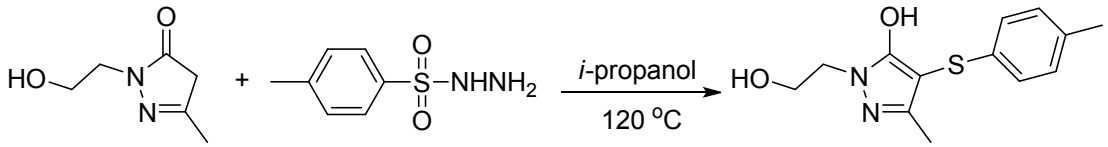
Entry	Acid	Time (h)	Yield (%)[a]
1	TsOH	1.5	84
2	CF_3COOH	3	29
3	CH_3COOH	6	70
4	$BF_3\,Et_2O$	2	76
5	CF_3SO_2H	30	65

[a] Yield of isolated product after chromatography with silica gel.

10) TsOH catalyzed reaction in the absence of I_2.

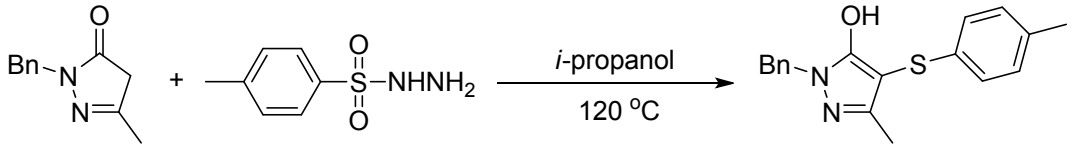


TsOH	Time (h)	Yield (%)
1 mmol	24	12
no	24	0



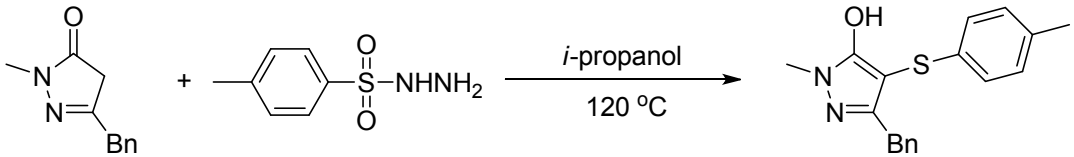
1 mmol 1.2 mmol

TsOH	Time (h)	Yield (%)
0.5 mmol	24	43



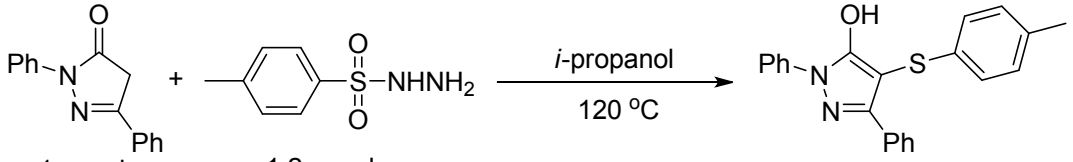
1 mmol 1.2 mmol

TsOH	Time (h)	Yield (%)
0.5 mmol	24	13



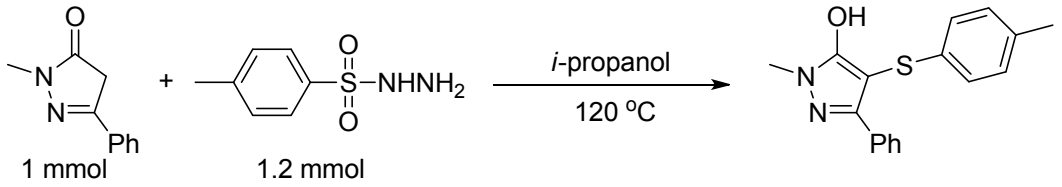
1 mmol 1.2 mmol

TsOH	Time (h)	Yield (%)
0.5 mmol	24	trace



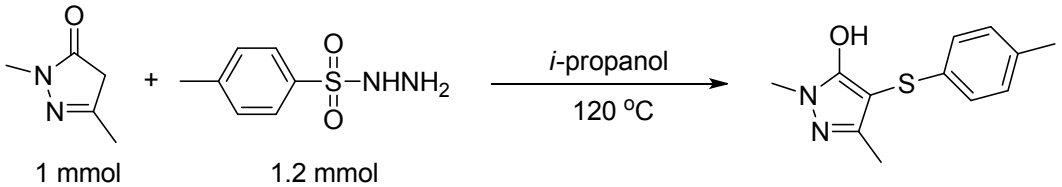
1 mmol 1.2 mmol

TsOH	Time (h)	Yield (%)
1 mmol	24	47



1 mmol 1.2 mmol

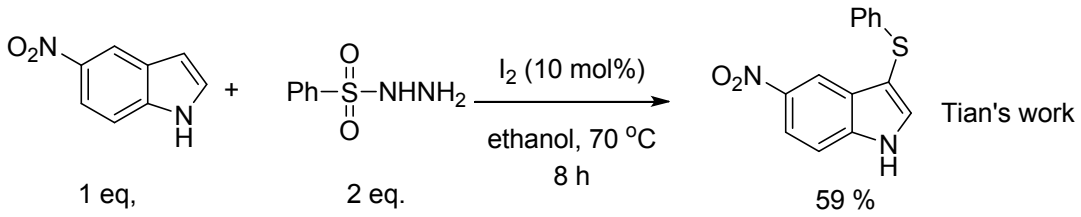
TsOH	Time (h)	Yield (%)
0.5 mmol	24	15



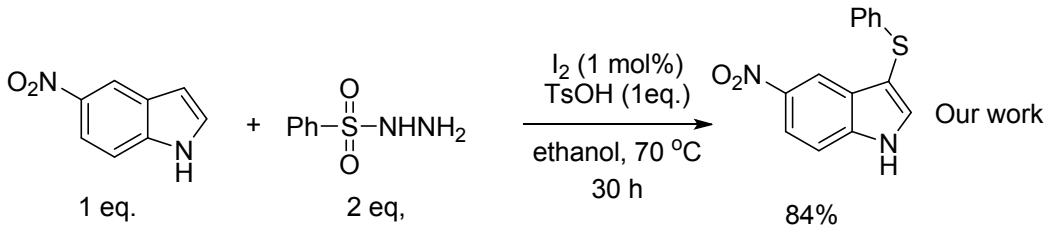
1 mmol 1.2 mmol

TsOH	Time (h)	Yield (%)
0.5 mmol	24	0

11) The effect of TsOH in the catalysis of 5-nitroindole of phenyl sulphonyl hydrazide[11]



1 eq, 2 eq. 59 %



1 eq. 2 eq, 84%

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