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Supporting Information

DMSO-Promoted Regioselective Synthesis of Sulfenylated pyrazoles via a Radical Pathway

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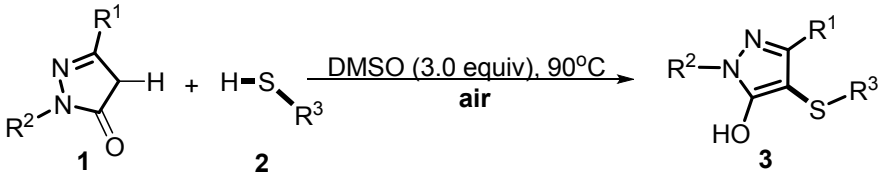
General information

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

General experimental procedures for synthesis of C-4 sulfenylated pyrazoles

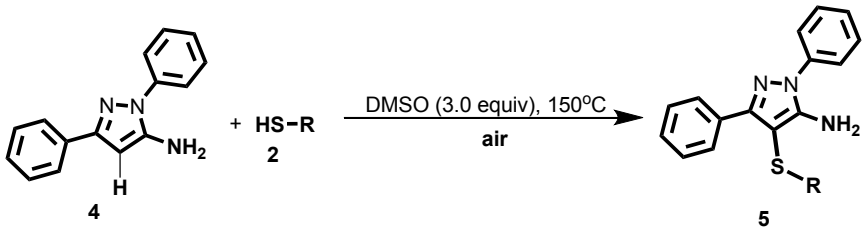
Direct coupling of pyrazolones (1) with thiols (2) leading to C-4 sulfenylated pyrazoles



A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with pyrazolones (**1**) (0.5mmol), thiols (**2**) (0.6 mmol), and DMSO (3 equiv, 1.5 mmol).

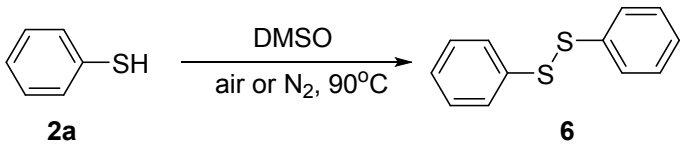
The tube was sealed, and then the mixture was stirred under air atmosphere at 90 °C for 30 h. After completion of the reaction, the resulting solution was cooled down to room temperature, then a small portion of silica gel was added to the resulting solution. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**3**).

Direct coupling of 1,3-diphenyl-1H-pyrazol-5-amine (4) with thiols (2) leading to C-4 sulfenylated pyrazoles



A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with 1,3-diphenyl-1*H*-pyrazol-5-amine (**4**) (0.5mmol), thiols (**2**) (0.6 mmol), and DMSO (3 equiv, 1.5 mmol). The tube was sealed, and then the mixture was stirred under air atmosphere at 150 °C for 30 h. After completion of the reaction, the resulting solution was cooled down to room temperature, then a small portion of silica gel was added to the resulting solution. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**5**).

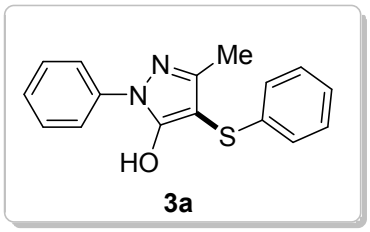
General procedure for synthesis of compounds 6



A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with

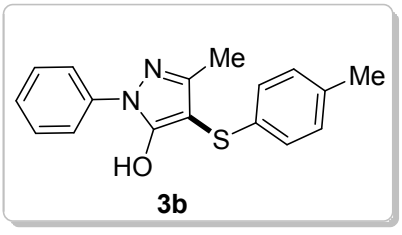
benzenethiol (0.6 mmol), and DMSO (1.5 mmol). The tube was sealed, and then the mixture was stirred under air atmosphere or nitrogen atmosphere at 90 °C for 20 h. After completion of the reaction, the resulting solution was cooled down to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**6**) in 96% and 98% yield, respectively.

Characterization data of products 3a-3aa, 5a-5c, and 6



3a

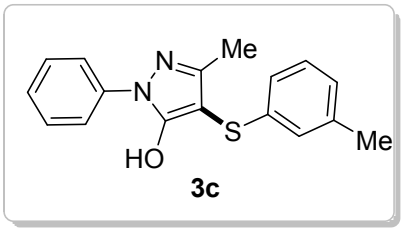
3-methyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5-ol (3a).[1] Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 103 mg, 73% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.24 (s, br, 1H), 7.79 (d, 2H, J = 10.0 Hz), 7.48 (t, 2H, J = 10.0 Hz), 7.28 (t, 3H, J = 10.0 Hz), 7.14-7.08 (m, 3H), 2.16 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.2, 152.5, 138.9, 138.6, 129.5, 129.4, 129.2, 126.2, 125.4, 121.2, 87.8, 12.8. HRMS calc. for $C_{16}H_{14}N_2NaOS$ $[M + Na]^+$ 305.0719, found 305.0721.



3b

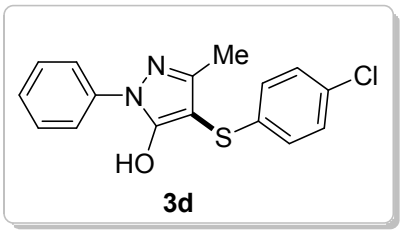
3-methyl-1-phenyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (3b).[2] Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 95 mg, 64% yield. ^{1}H NMR (DMSO-d_6, 500

MHz, ppm) δ 12.20 (s, br, 1H), 7.78 (d, 2H, J = 10.0 Hz), 7.48 (t, 2H, J = 10.0 Hz), 7.28 (t, 1H, J = 10.0 Hz), 7.10 (d, 2H, J = 10.0 Hz), 7.01 (d, 2H, J = 10.0 Hz), 2.23 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 156.7, 152.4, 138.7, 135.3, 134.8, 130.1, 129.3, 126.1, 125.8, 121.2, 87.8, 20.9, 12.8. HRMS calc. for $C_{17}H_{16}N_2NaOS$ $[M + Na]^+$ 319.0876, found 319.0872.



3c

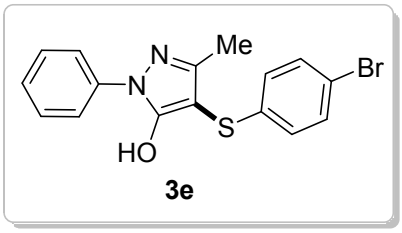
3-methyl-1-phenyl-4-(*m*-tolylthio)-1*H*-pyrazol-5-ol (3c). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 104 mg, 70% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.81 (d, 2H, J = 8.0 Hz), 7.47 (t, 2H, J = 8.0 Hz), 7.27 (t, 1H, J = 7.5 Hz), 7.16 (t, 1H, J = 7.5 Hz), 6.95 (s, 1H), 6.92 (d, 1H, J = 8.0 Hz), 6.87 (d, 1H, J = 8.0 Hz), 2.24 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.6, 152.5, 138.9, 138.8, 138.7, 129.4, 129.3, 126.2, 126.1, 125.8, 122.5, 121.1, 21.5, 12.8. HRMS calc. for $C_{17}H_{16}N_2NaOS$ $[M + Na]^+$ 319.0876, found 319.0872.



3d

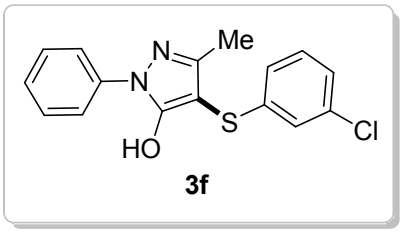
4-(4-chlorophenylthio)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3d).[1] Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 144 mg, 91% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.33 (s, br, 1H), 7.75 (d, 2H, J = 8.0 Hz), 7.48 (dd, 2H, J = 8.0, 8.5 Hz), 7.34 (d, 2H, J = 8.5 Hz), 7.28 (dd, 1H, J = 7.0, 7.5 Hz), 7.11 (d, 2H, J = 8.5 Hz),

2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.6, 152.4, 138.6, 138.1, 130.0, 129.4, 129.3, 127.0, 126.2, 121.2, 87.6, 12.7. HRMS calc. for $C_{16}H_{13}ClN_2NaOS$ $[M + Na]^+$ 339.0329, found 339.0335.



3e

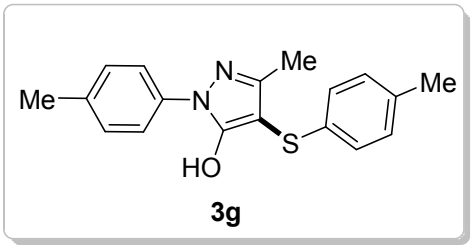
4-(4-bromophenylthio)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3e). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 171 mg, 95% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.34 (s, br, 1H), 7.78 (d, 2H, J = 7.5 Hz), 7.49-7.51 (m, 4H), 7.28 (t, 1H, J = 7.5 Hz), 7.04 (d, 2H, J = 8.5 Hz), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.5, 152.4, 138.7, 132.2, 129.4, 129.2, 127.4, 126.2, 121.2, 118.2, 12.8. HRMS calc. for $C_{16}H_{13}BrN_2NaOS$ $[M + Na]^+$ 382.9824, found 382.9826, 384.9825.



3f

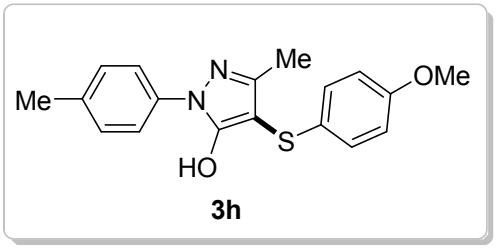
4-(3-chlorophenylthio)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3f). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 145 mg, 92% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.78 (d, 2H, J = 7.5 Hz), 7.48 (dd, 2H, J = 7.5, 8.5 Hz), 7.30-7.26 (m, 2H), 7.16 (d, 1H, J = 8.0 Hz), 7.09-7.06 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.5, 152.5, 141.8, 138.5, 134.3, 131.1, 129.4, 126.3, 125.4, 124.5, 124.0, 121.3, 87.1, 12.7. HRMS calc. for $C_{16}H_{13}ClN_2NaOS$ $[M + Na]^+$ 339.0329,

found 339.0335.



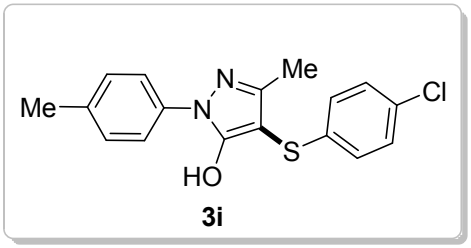
3g

3-methyl-1-*p*-tolyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (3g).[1] Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 99 mg, 64% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.60 (d, 2H, J = 8.0 Hz), 7.27 (d, 2H, J = 7.5 Hz), 7.08 (d, 2H, J = 7.5 Hz), 6.98 (d, 2H, J = 8.0 Hz), 2.32 (s, 3H), 2.22 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.2, 152.1, 136.2, 135.6, 135.2, 134.8, 130.1, 129.8, 125.8, 121.3, 88.5, 20.9, 20.8, 12.7. HRMS calc. for $C_{18}H_{18}N_2NaOS$ [M + Na]$^+$ 333.1032, found 333.1033.



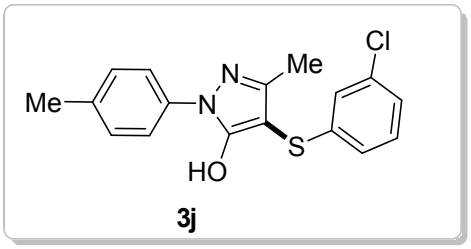
3h

4-(4-methoxyphenylthio)-3-methyl-1-*p*-tolyl-1*H*-pyrazol-5-ol (3h). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 90 mg, 55% yield. δ 7.61 (d, 2H, J = 8.0 Hz), 7.26 (d, 2H, J = 8.0 Hz), 7.01 (d, 2H, J = 9.0 Hz), 6.87 (d, 2H, J = 9.0 Hz), 3.70 (s, 3H), 2.32 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 158.0, 151.9, 138.0, 136.4, 135.3, 129.8, 129.3, 128.2, 121.2, 115.2, 89.5, 55.6, 21.0, 12.8. HRMS calc. for $C_{18}H_{18}N_2NaO_2S$ [M + Na]$^+$ 349.0981, found 349.0980.



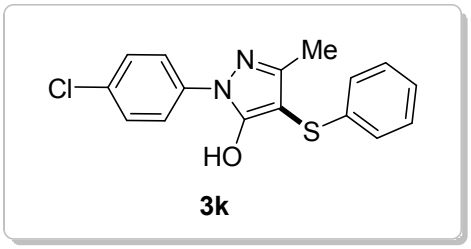
3i

4-(4-chlorophenylthio)-3-methyl-1-*p*-tolyl-1*H*-pyrazol-5-ol (3i).[1] Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 155 mg, 94% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.60 (d, 2H, J = 8.5 Hz), 7.32 (d, 2H, J = 7.0 Hz), 7.27 (d, 2H, J = 8.0 Hz), 7.08 (d, 2H, J = 7.0 Hz), 2.32 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.3, 152.1, 138.1, 136.0, 135.7, 130.0, 129.8, 129.4, 127.1, 121.3, 87.4, 21.0, 12.7. HRMS calc. for $C_{17}H_{15}ClN_2NaOS$ $[M + Na]^+$ 353.0486, found 353.0483.



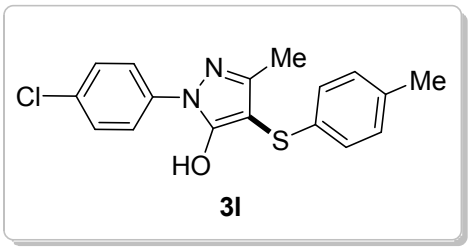
3j

4-(3-chlorophenylthio)-3-methyl-1-*p*-tolyl-1*H*-pyrazol-5-ol (3j). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 119 mg, 72% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.26 (s, br, 1H), 7.63 (d, 2H, J = 8.5 Hz), 7.32-7.27 (m, 3H), 7.17 (d, 1H, J = 8.0 Hz), 7.08-7.05 (m, 2H), 2.33 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.2, 152.0, 141.8, 135.6, 134.3, 131.1, 129.8, 125.3, 124.5, 123.9, 121.3, 86.6, 21.0, 12.7. HRMS calc. for $C_{17}H_{15}ClN_2NaOS$ $[M + Na]^+$ 353.0486, found 353.0483.



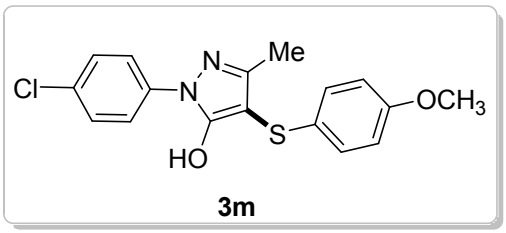
3k

1-(4-chlorophenyl)-3-methyl-4-(phenylthio)-1*H*-pyrazol-5-ol (3k). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 111 mg, 70% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.83 (d, 2H, J = 8.5 Hz), 7.53 (d, 2H, J = 9.0 Hz), 7.27 (dd, 2H, J = 8.0, 7.5 Hz), 7.13-7.09 (m, 3H), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.4, 152.9, 138.7, 137.5, 130.2, 129.5, 129.4, 125.4, 125.3, 122.4, 88.1, 12.8. HRMS calc. for $C_{16}H_{13}ClN_2NaOS$ $[M + Na]^+$ 339.0329, found 339.0335.



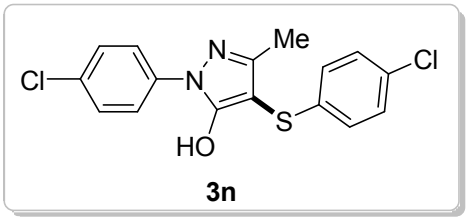
3l

1-(4-chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (3l). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 112 mg, 68% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.39 (s, br, 1H), 7.82 (d, 2H, J = 9.0 Hz), 7.53 (d, 2H, J = 8.5 Hz), 7.09 (d, 2H, J = 9.0 Hz), 7.00 (d, 2H, J = 8.5 Hz), 2.23 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.3, 152.9, 137.6, 135.1, 134.8, 130.1, 129.3, 125.8, 122.4, 88.7, 20.9, 12.8. HRMS calc. for $C_{17}H_{15}ClN_2NaOS$ $[M + Na]^+$ 353.0486, found 353.0483.



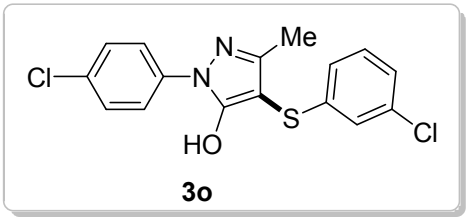
3m

1-(4-chlorophenyl)-4-(4-methoxyphenylthio)-3-methyl-1*H*-pyrazol-5-ol (3m). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 104 mg, 60% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.36 (s, br, 1H), 7.79 (d, 2H, J = 8.0 Hz), 7.53 (d, 2H, J = 7.5 Hz), 7.10 (d, 2H, J = 8.0 Hz), 6.88 (d, 2H, J = 7.5 Hz), 3.70 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 158.1, 152.8, 138.0, 137.5, 130.1, 129.4, 128.9, 128.3, 122.4, 115.3, 89.9, 55.6, 12.8. HRMS calc. for $C_{17}H_{15}ClN_2NaO_2S$ [M + Na]$^+$ 369.0435, found 369.0436.



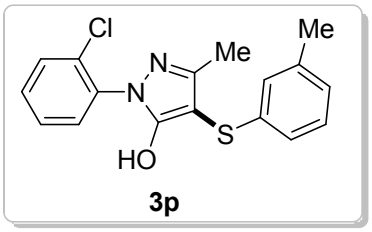
3n

1-(4-chlorophenyl)-4-(4-chlorophenylthio)-3-methyl-1*H*-pyrazol-5-ol (3n). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 161 mg, 92% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.80 (d, 2H, J = 9.0 Hz), 7.52 (d, 2H, J = 9.0 Hz), 7.44 (d, 2H, J = 8.5 Hz), 7.02 (d, 2H, J = 8.5 Hz), 2.13 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.3, 152.8, 138.5, 137.4, 132.3, 130.2, 129.4, 127.4, 122.5, 118.2, 87.5, 12.8. HRMS calc. for $C_{16}H_{12}Cl_2N_2NaOS$ [M + Na]$^+$ 372.9940, found 372.9944.



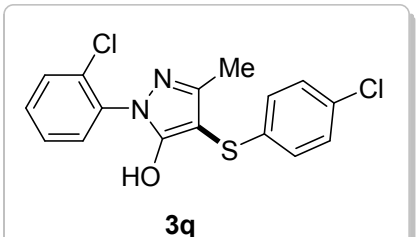
3o

1-(4-chlorophenyl)-4-(3-chlorophenylthio)-3-methyl-1*H*-pyrazol-5-ol (3o). Eluent petroleum ether/ethyl acetate (8:1). Yellow solid, 158 mg, 90% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.82 (d, 2H, J = 8.5 Hz), 7.51 (d, 2H, J = 8.5 Hz), 7.28 (dd, 1H, J = 7.5, 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.09 (s, 1H), 7.05 (d, 1H, J = 8.0 Hz), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.7, 152.9, 141.6, 137.4, 134.3, 131.1, 130.3, 129.4, 125.4, 124.5, 123.9, 122.5, 87.1, 12.7. HRMS calc. for $C_{16}H_{12}Cl_2N_2NaOS$ $[M + Na]^+$ 372.9940, found 372.9944.



3p

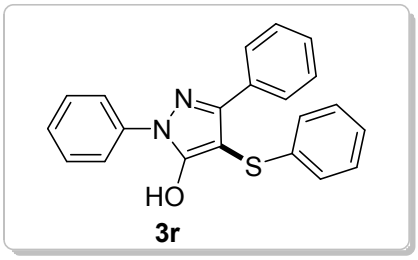
1-(2-chlorophenyl)-3-methyl-4-(*m*-tolylthio)-1*H*-pyrazol-5-ol (3p). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, 124 mg, 75% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 11.93 (s, br, 1H), 7.67 (d, 1H, J = 7.5 Hz), 7.58-7.50 (m, 3H), 7.18 (dd, 1H, J = 7.5, 8.0 Hz), 6.95-6.89 (m, 3H), 2.25 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 156.8, 152.4, 139.0, 138.7, 135.9, 131.9, 130.6, 129.3, 128.4, 126.1, 125.6, 122.3, 85.1, 21.5, 12.9. HRMS calc. for $C_{17}H_{15}ClN_2NaOS$ $[M + Na]^+$ 353.0486, found 353.0483.



3q

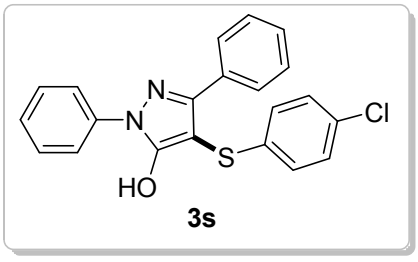
1-(2-chlorophenyl)-4-(4-chlorophenylthio)-3-methyl-1*H*-pyrazol-5-ol (3q). Eluent

petroleum ether/ethyl acetate (10:1). Yellow solid, 168 mg, 96% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.01 (s, br, 1H), 7.67 (d, 1H, J = 8.0 Hz), 7.57-7.48 (m, 5H), 7.05 (d, 2H, J = 8.5 Hz), 2.10 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 156.6, 152.2, 138.9, 132.2, 131.9, 131.2, 130.6, 130.5, 128.4, 127.2, 118.1, 84.4, 12.9. HRMS calc. for $C_{16}H_{12}Cl_2N_2NaOS$ $[M + Na]^+$ 372.9940, found 372.9944.



3r

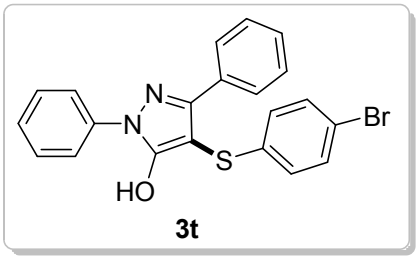
1,3-diphenyl-4-(phenylthio)-1*H*-pyrazol-5-ol (3r).[3] Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 146 mg, 85% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.44 (s, br, 1H), 7.90-7.88 (m, 4H), 7.54 (t, 2H, J = 8.5 Hz), 7.40-7.35 (m, 4H), 7.29 (dd, 2H, J = 8.5, 7.5 Hz), 7.14-7.11 (m, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.1, 151.9, 150.2, 140.6, 139.1, 138.8, 136.8, 129.6, 129.5, 128.7, 127.5, 125.5, 125.2, 115.5, 85.6. HRMS calc. for $C_{21}H_{16}N_2NaOS$ $[M + Na]^+$ 367.0876, found 367.0878.



3s

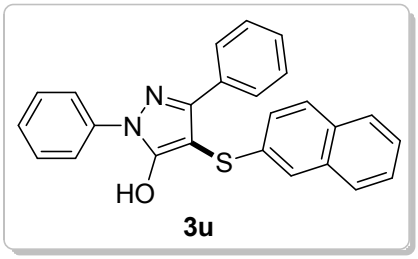
4-(4-chlorophenylthio)-1,3-diphenyl-1*H*-pyrazol-5-ol (3s). Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 179 mg, 95% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.50 (s, br, 1H), 7.92-7.91 (m, 4H), 7.54 (dd, 2H, J = 8.5, 7.5 Hz),

7.41-7.34 (m, 6H), 7.16 (d, 2H, J = 8.5 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.2, 151.9, 138.8, 138.3, 130.1, 129.5, 128.9, 128.8, 127.5, 127.0, 126.9, 122.2, 85.4. HRMS calc. for $C_{21}H_{15}ClN_2NaOS$ $[M + Na]^+$ 401.0486, found 401.0489.



3t

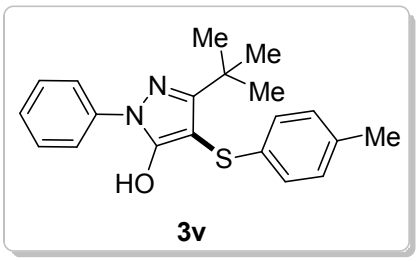
4-(4-bromophenylthio)-1,3-diphenyl-1*H*-pyrazol-5-ol (3t). Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 209 mg, 99% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.89-7.87 (m, 4H), 7.54 (dd, 2H, J = 7.5, 8.5 Hz), 7.47 (d, 2H, J = 8.5), 7.41-7.35 (m, 4H), 7.08 (d, 2H, J = 8.5 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 157.1, 151.9, 138.9, 138.8, 132.4, 129.5, 128.9, 128.8, 127.5, 127.3, 127.1, 122.2, 118.3, 85.2. HRMS calc. for $C_{21}H_{15}BrN_2NaOS$ $[M + Na]^+$ 444.9981, found 444.9988, 446.9985.



3u

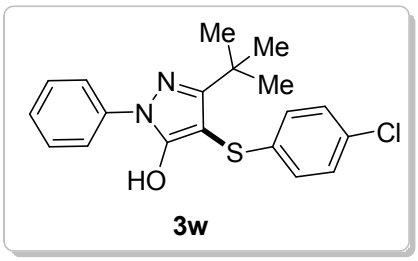
4-(naphthalen-2-ylthio)-1,3-diphenyl-1*H*-pyrazol-5-ol (3u). Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 163 mg, 83% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.39 (s, br, 1H), 7.96-7.93 (m, 4H), 7.85 (t, 2H, J = 9.0), 7.75 (d, 1H, J = 8.5 Hz), 7.61 (s, 1H), 7.56 (dd, 2H, J =7.5, 9.0 Hz), 7.45-7.32 (m, 7H). ^{13}C NMR

(DMSO-d_6, 125 MHz, ppm) δ 157.4, 152.1, 138.9, 136.9, 133.9, 131.5, 129.5, 129.2, 128.9, 128.8, 128.2, 127.6, 127.3, 127.2, 127.0, 125.8, 124.2, 122.5, 122.2, 85.6. HRMS calc. for $C_{25}H_{18}N_2NaOS$ $[M + Na]^+$ 417.1032, found 417.1035.



3v

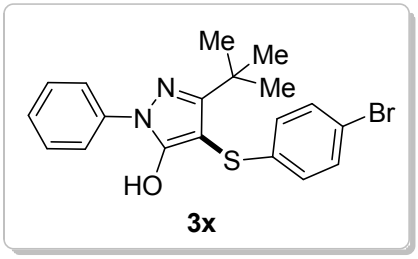
3-*tert*-butyl-1-phenyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (3v). Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 139 mg, 82% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 11.94 (s, br, 1H), 7.82 (d, 2H, J = 7.5 Hz), 7.47 (t, 2H, J = 6.0 Hz), 7.28 (t, 1H, J = 6.0 Hz), 7.08 (d, 2H, J = 7.0 Hz), 6.96 (d, 2H, J = 8.0 Hz), 2.23 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 160.9, 156.9, 139.2, 136.1, 134.3, 129.9, 129.3, 126.2, 125.1, 121.6, 84.7, 34.1, 29.4, 20.8. HRMS calc. for $C_{20}H_{22}N_2NaOS$ $[M + Na\ ]^+$ 361.1345, found 361.1349.



3w

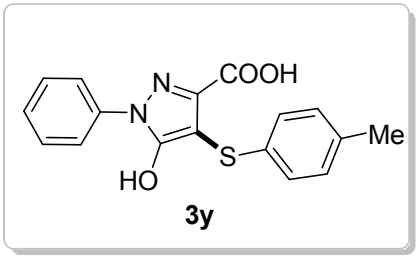
3-*tert*-butyl-4-(4-chlorophenylthio)-1-phenyl-1*H*-pyrazol-5-ol (3w). Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 167 mg, 93% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.03 (s, br, 1H), 7.80 (d, 2H, J = 8.0 Hz), 7.48 (t, 2H, J = 7.5 Hz), 7.33 (d, 2H, J = 8.5 Hz), 7.29 (t, 1H, J = 7.5 Hz), 7.07 (d, 2H, J = 8.5 Hz), 1.31 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 160.9, 157.0, 139.0, 138.8,

129.7, 129.4, 129.3, 126.6, 126.4, 121.7, 83.9, 34.1, 29.4. HRMS calc. for $C_{19}H_{19}ClN_2NaOS$ $[M + Na]^+$ 381.0799, found 381.0785.



3x

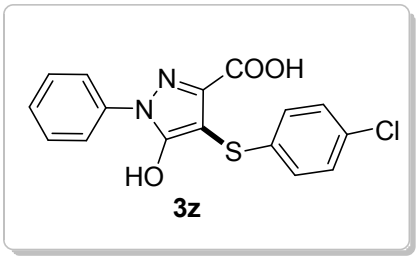
4-(4-bromophenylthio)-3-*tert*-butyl-1-phenyl-1*H*-pyrazol-5-ol (3x). Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, 191 mg, 95% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.05 (s, br, 1H), 7.78 (d, 2H, J = 8.0 Hz), 7.50-7.45 (m, 4H), 7.29 (t, 1H, J = 7.5 Hz), 7.00 (d, 2H, J = 8.5 Hz), 1.31 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 160.9, 157.0, 139.4, 138.9, 132.1, 129.4, 127.0, 126.4, 121.7, 117.8, 83.9, 34.1, 29.4. HRMS calc. for $C_{19}H_{19}BrN_2NaOS$ $[M + Na]^+$ 425.0294, found 425.0295, 427.0292.



3y

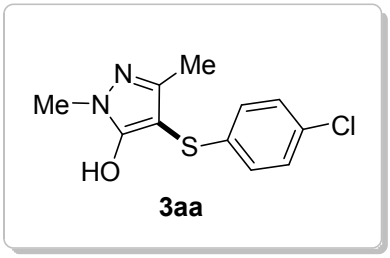
5-hydroxy-1-phenyl-4-(*p*-tolylthio)-1*H*-pyrazole-3-carboxylic acid (3y). Eluent petroleum ether/ethyl acetate (1.5:1). Yellow solid, 117 mg, 72% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.71 (s, br, 2H), 7.76 (d, 2H, J = 7.5 Hz), 7.55 (t, 2H, J = 7.5 Hz), 7.49 (t, 1H, J = 7.5 Hz), 7.09 (d, 2H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.0 Hz), 2.23 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 162.9, 156.3, 144.9, 138.4, 135.4, 134.7, 130.0, 129.6, 127.9, 126.1, 122.9, 89.8, 20.9. HRMS calc. for

$C_{17}H_{14}N_2NaO_3S$ $[M + Na]^+$ 349.0617, found 349.0619.



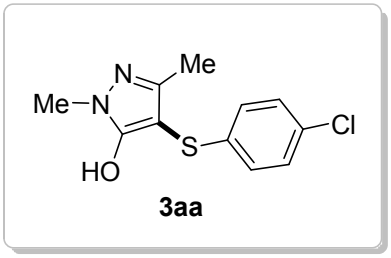
3z

4-(4-chlorophenylthio)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylic acid (3z). Eluent petroleum ether/ethyl acetate (1.5:1). Yellow solid, 131 mg, 76% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 12.87 (s, br, 2H), 7.77 (d, 2H, J = 8.0 Hz), 7.55 (t, 2H, J = 8.0 Hz), 7.41 (t, 1H, J = 7.5 Hz), 7.33 (d, 2H, J = 8.5 Hz), 7.10 (d, 2H, J = 8.5 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 162.8, 156.5, 144.8, 138.4, 138.3, 129.8, 129.6, 129.2, 127.9, 127.4, 123.0, 88.7. HRMS calc. for $C_{16}H_{11}ClN_2NaO_3S$ $[M + Na]^+$ 369.0071, found 369.0072.



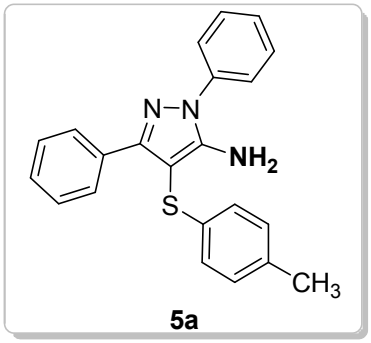
3aa

4-(4-chlorophenylthio)-1,3-dimethyl-1*H*-pyrazol-5-ol (3z). Eluent petroleum ether/ethyl acetate (2:1). Yellow solid, 117 mg, 92% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.29 (d, 2H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.0 Hz), 3.50 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 156.7, 149.7, 138.9, 129.7, 129.3, 126.7, 84.6, 33.5, 12.5. HRMS calc. for $C_{11}H_{11}ClN_2NaOS$ $[M + Na]^+$ 277.0173, found 277.0175.



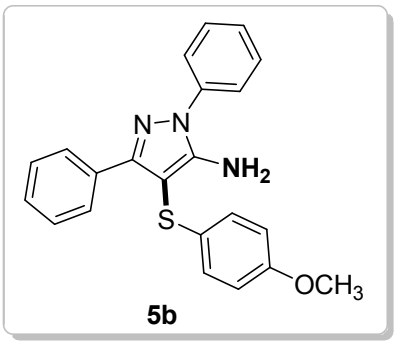
3aa

4-(4-chlorophenylthio)-1,3-dimethyl-1*H*-pyrazol-5-ol (3z). Eluent petroleum ether/ethyl acetate (2:1). Yellow solid, 117 mg, 92% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.29 (d, 2H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.0 Hz), 3.50 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 156.7, 149.7, 138.9, 129.7, 129.3, 126.7, 84.6, 33.5, 12.5. HRMS calc. for $C_{11}H_{11}ClN_2NaOS$ $[M + Na]^+$ 277.0173, found 277.0175.



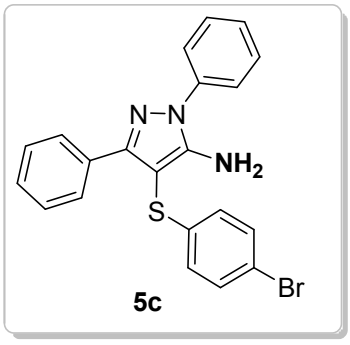
5a

1,3-diphenyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-amine (5a).[4] Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, 104 mg, 58% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.85 (d, 2H, J = 7.2 Hz), 7.52 (d, 2H, J = 7.5 Hz), 7.35 (t, 2H, J = 7.2 Hz), 7.23-7.16 (m, 4H), 6.93 (dd, 4H, J = 8.4 Hz), 4.16 (s, br, 2H), 2.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 152.3, 148.5, 137.6, 133.9, 133.5, 131.6, 128.8, 128.6, 127.2, 127.1, 126.6, 126.5, 124.3, 122.4, 85.8, 19.8. HRMS calc. for $C_{22}H_{20}N_3S$ $[M + H]^+$ 358.1372, found 358.1375.



5b

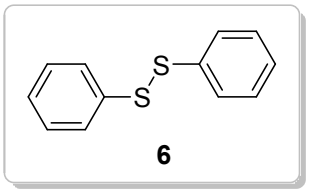
4-(4-methoxyphenylthio)-1,3-diphenyl-1*H*-pyrazol-5-amine (5b).[4] Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, 97 mg, 52% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.98 (d, 2H, J = 7.9 Hz), 7.67 (d, 2H, J = 7.9 Hz), 7.51 (t, 2H, J = 7.6 Hz), 7.38-7.31 (m, 4H), 7.11 (d, 2H, J = 8.9 Hz), 6.8 (d, 2H, J = 8.9 Hz), 4.33 (s, br, 2H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 157.9, 153.2, 149.4, 137.7, 132.7, 129.7, 128.8, 128.3, 128.2, 127.7, 127.6, 127.3, 123.6, 114.9, 87.9, 55.4, . HRMS calc. for $C_{12}H_{20}N_3OS$ $[M + H]^+$ 374.1322, found 374.1328.



5c

4-(4-bromophenylthio)-1,3-diphenyl-1*H*-pyrazol-5-amine (5c).[4] Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, 158 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.91 (d, 2H, J = 9.6 Hz), 7.45 (d, 2H, J = 7.9 Hz), 7.50 (t, 2H, J = 7.7 Hz), 7.38-7.30 (m, 6H), 7.01 (d, 2H, J = 8.5 Hz), 4.31 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.3, 149.6, 138.5, 137.5, 132.4, 132.1, 129.8, 128.5, 128.4, 127.9, 127.5, 126.8, 123.7, 118.8, 85.7. HRMS calc. for $C_{21}H_{20}N_3OS$ $[M + H]^+$ 374.1322,

found 374.1328.



6

1,2-Diphenyldisulfane (6). Eluent petroleum ether/ethyl acetate (50:1). White solid. (petroleum ether/ethyl acetate = 50:1, Rf= 0.8). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.60 (d, 4H, J = 10.0 Hz), 7.34 (dd, 4H, J = 5.0 Hz, J = 10.0 Hz), 7.27 (dd, 2H, J = 5.0 Hz, J = 10.0 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 137.2, 129.2, 127.6, 127.3.

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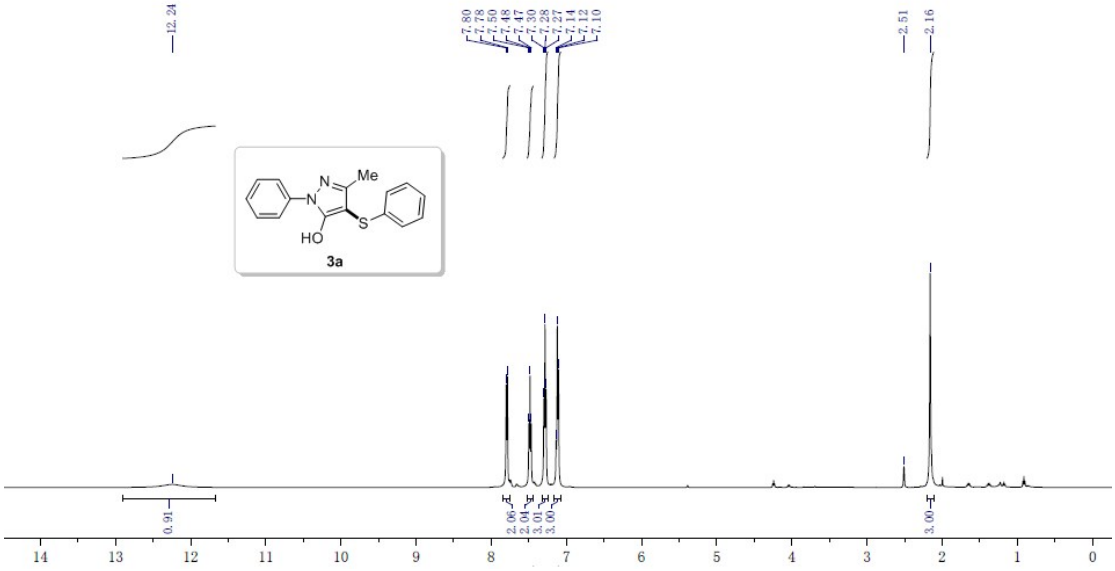
1. V. B. Purohit, S. C. Karad, K. H. Patel, D. K. Raval. *Tetrahedron.* **2016**, *72*, 1114
2. Q. Wu, D.-B. Zhao, X.-R. Qin, J.-B. Lan, J.-S. You. *Chem. Commun*. **2011***, 47,* 9188.
3. D. C. Mohan, S. N. Rao, C. Ravi, S. Adimurthy. *Asian J. Org. Chem.* **2014**, *3*, 609.
4. J. Sun, J.-K. Qiu, Y-L. Zhu, C. Guo, W-J. Hao, B. Jiang, S.-J. Tu. *J. Org. Chem.* **2015**, *80*, 8217.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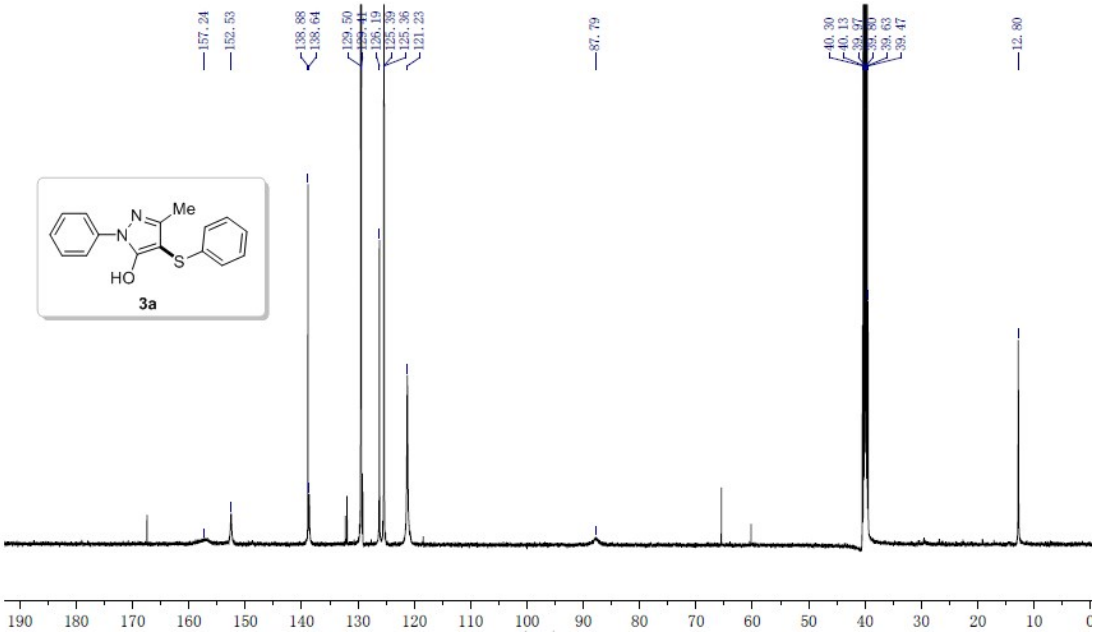
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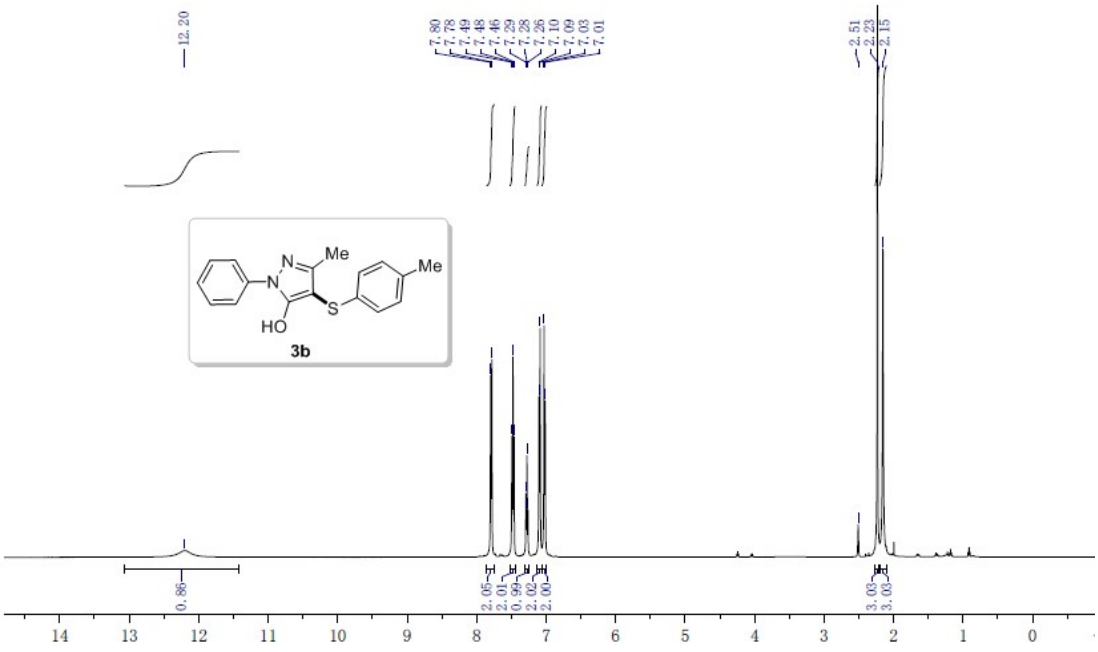
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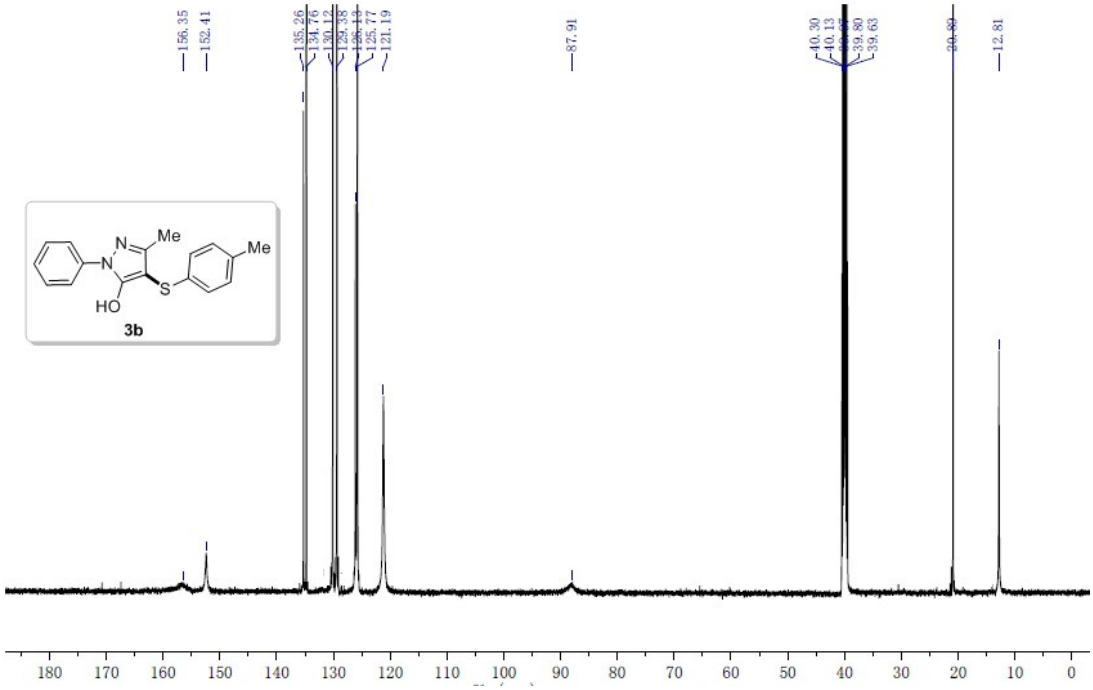
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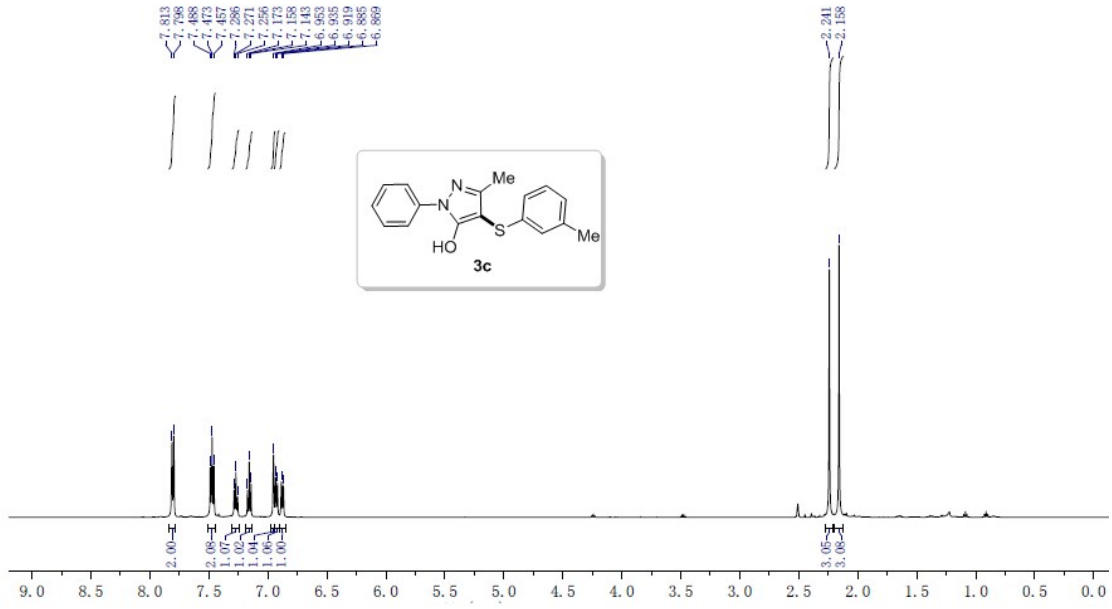
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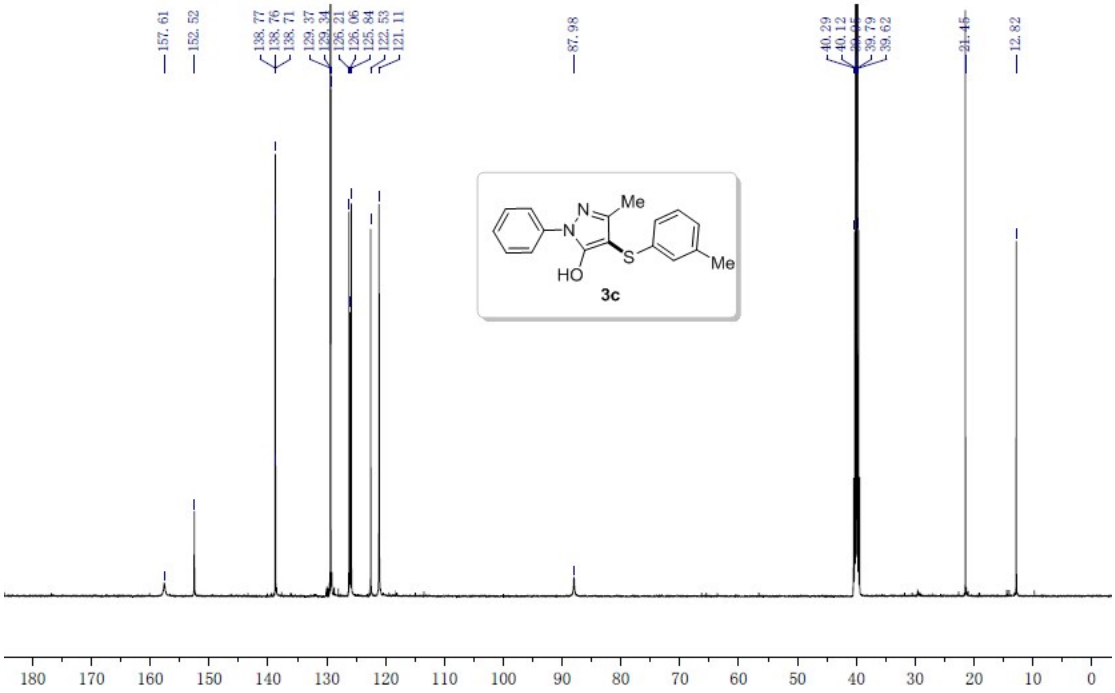
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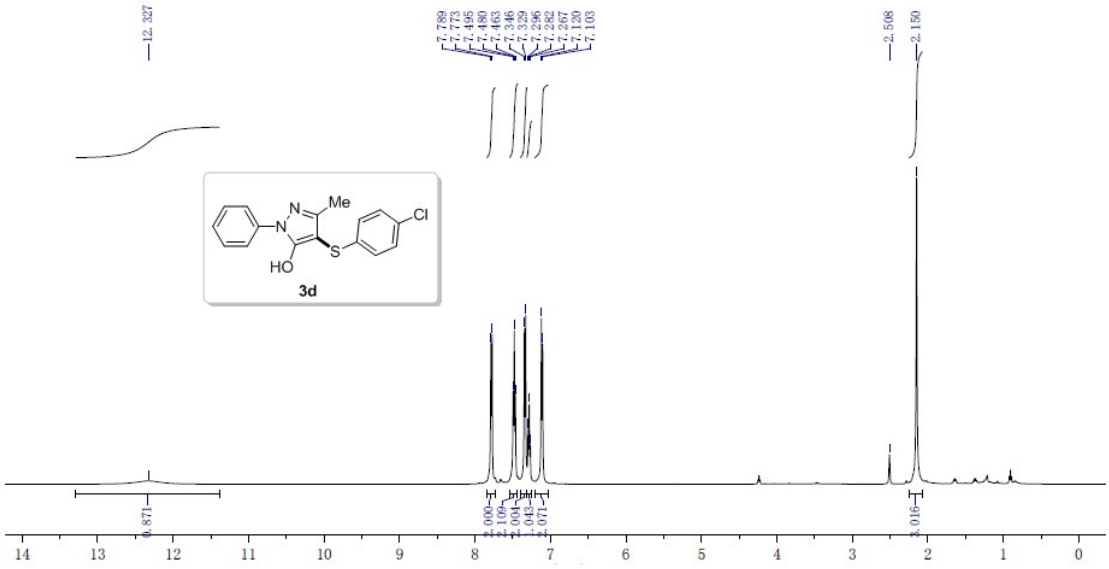
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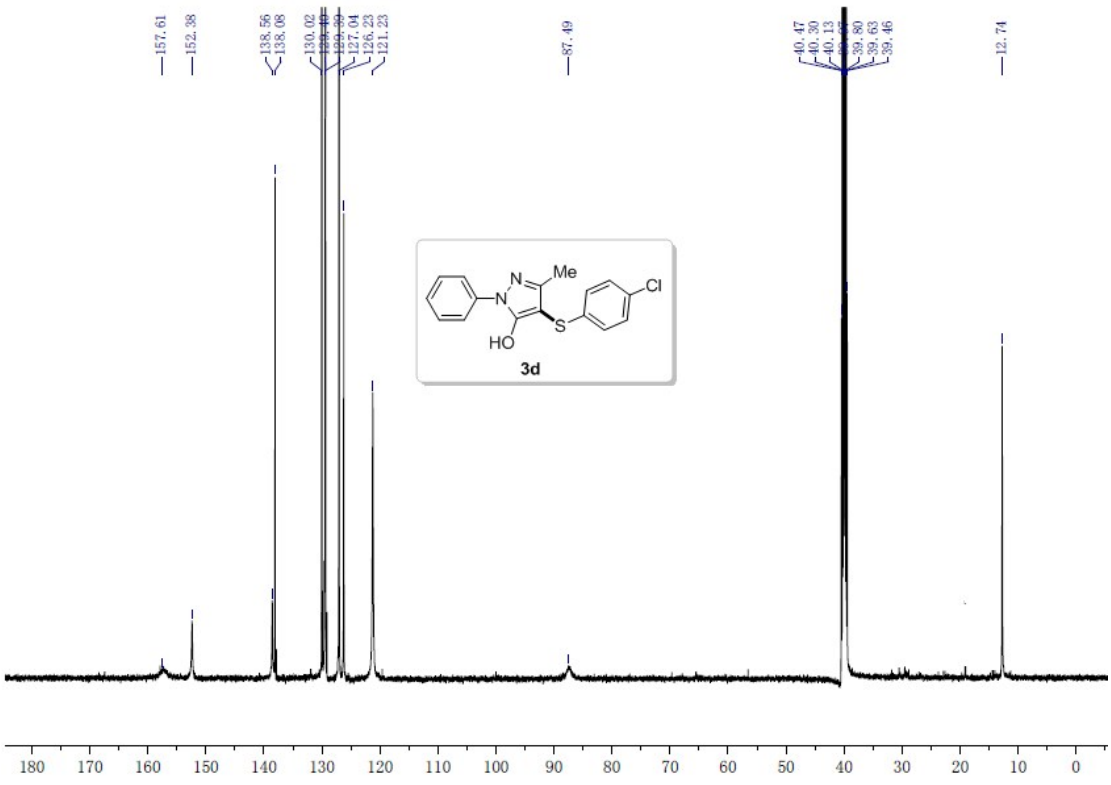
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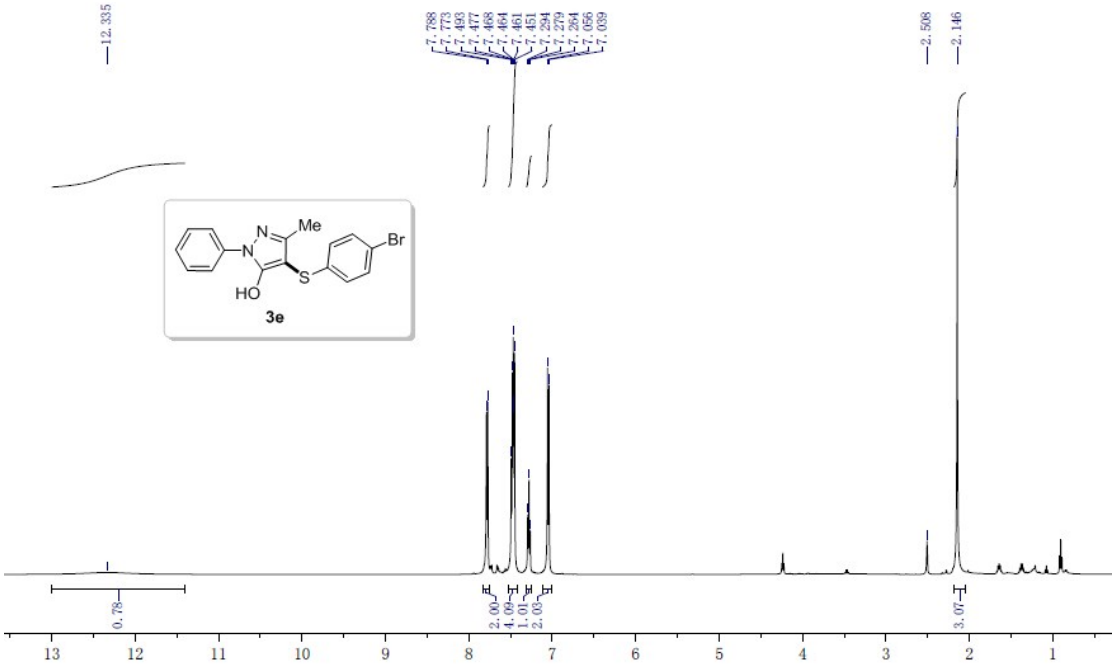
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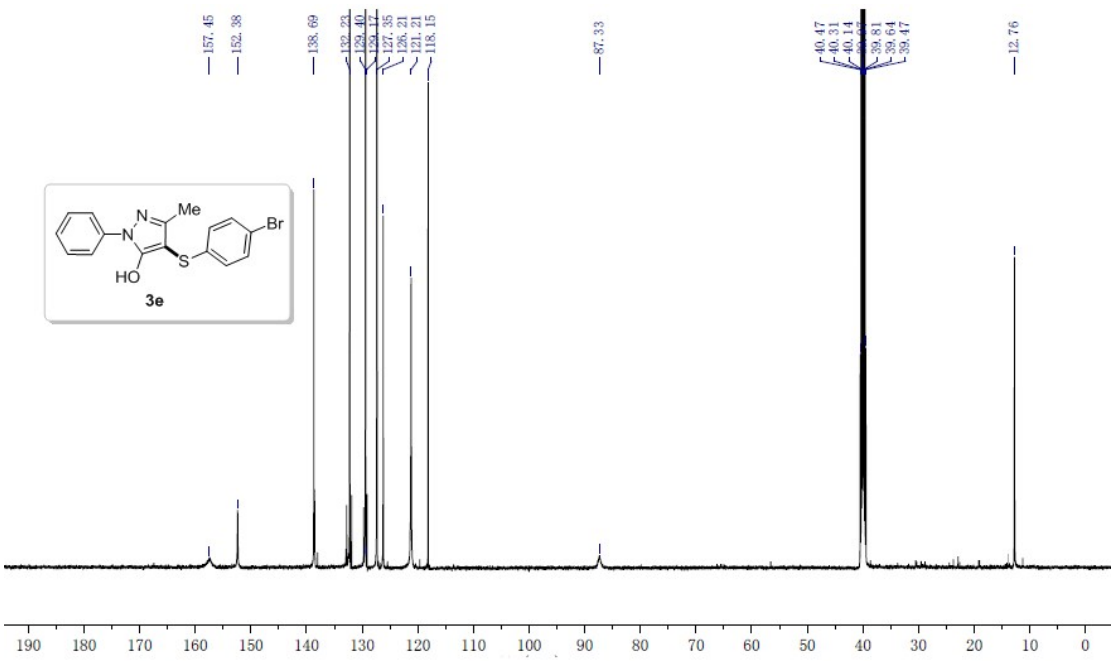
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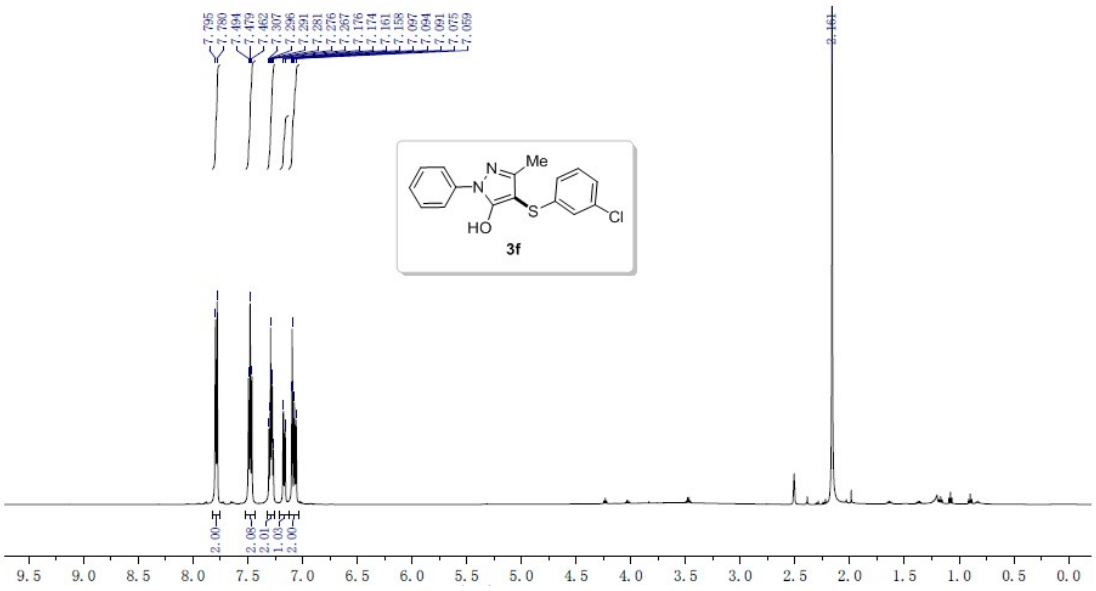
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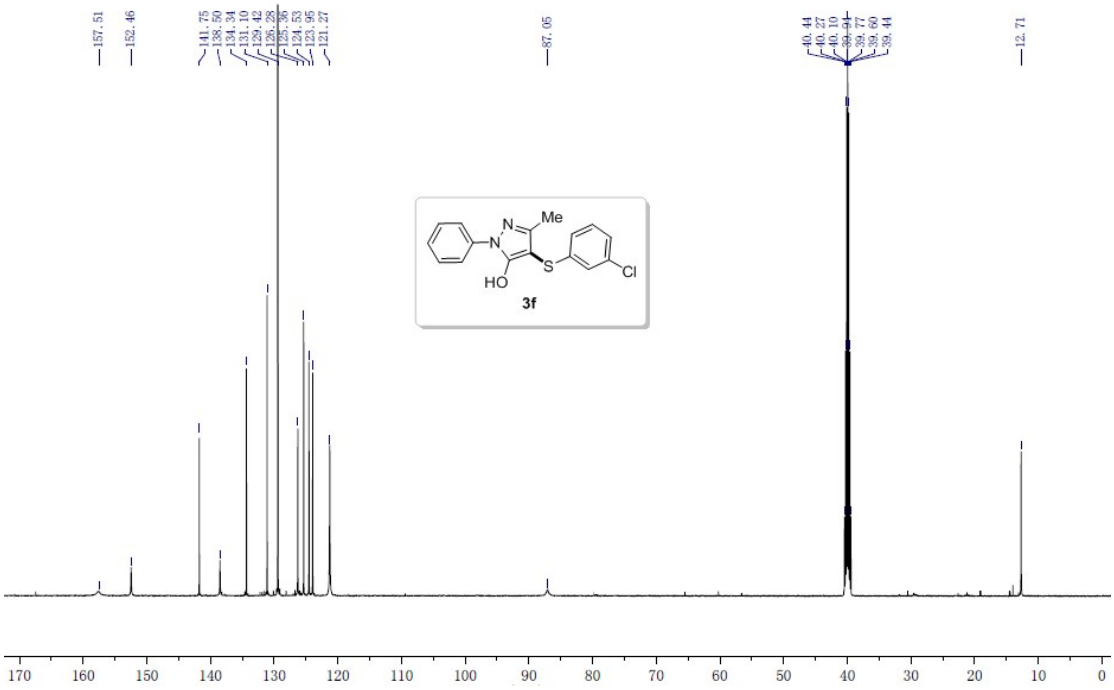
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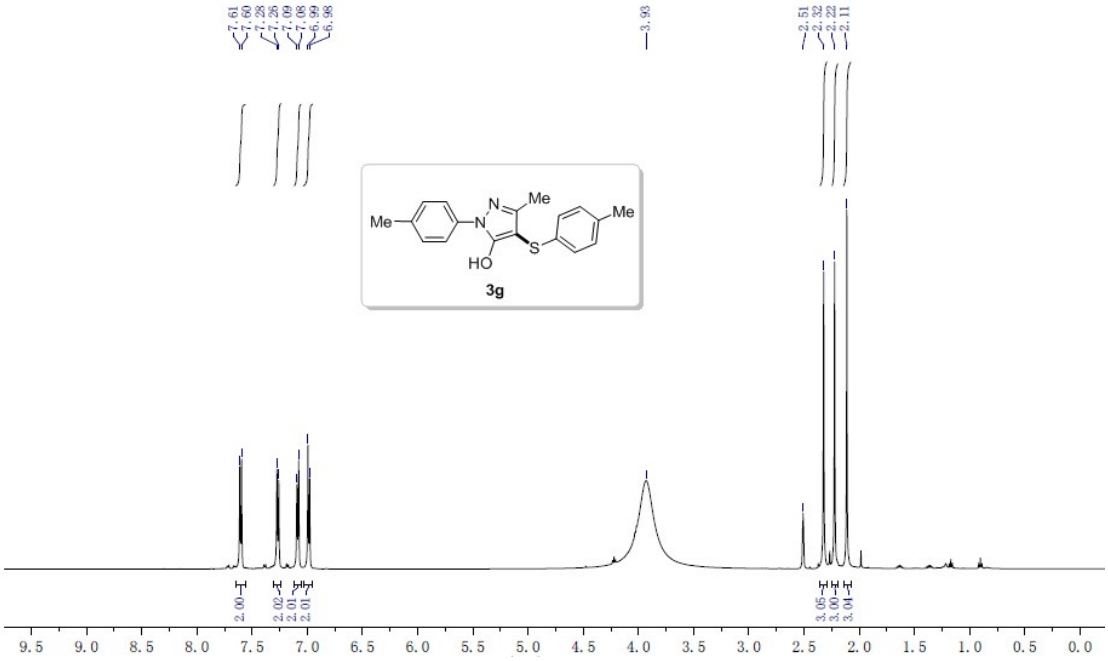
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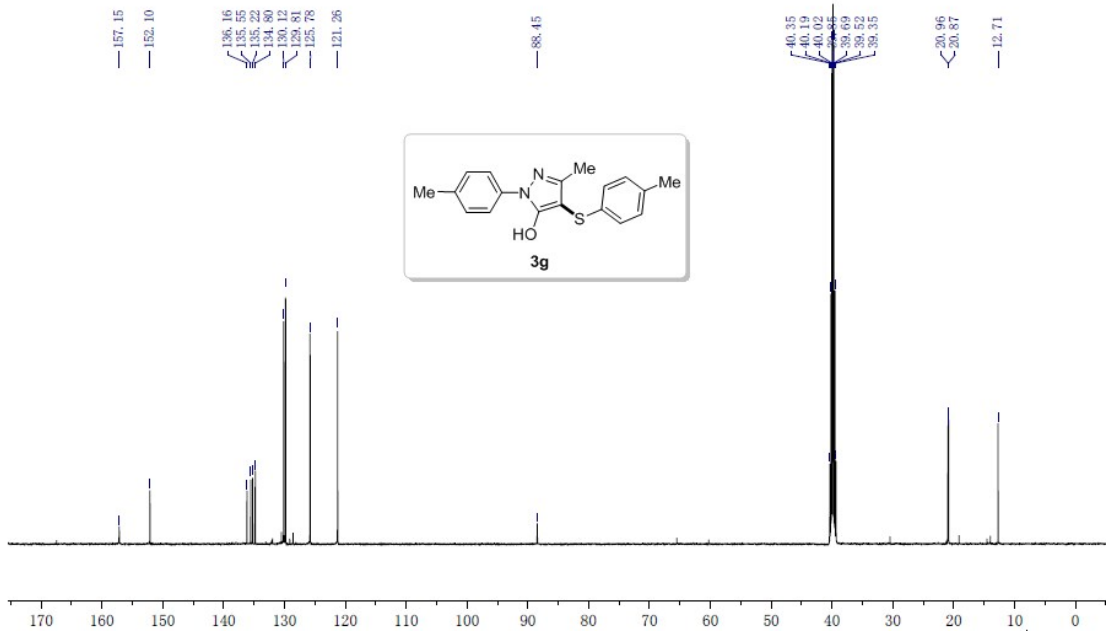
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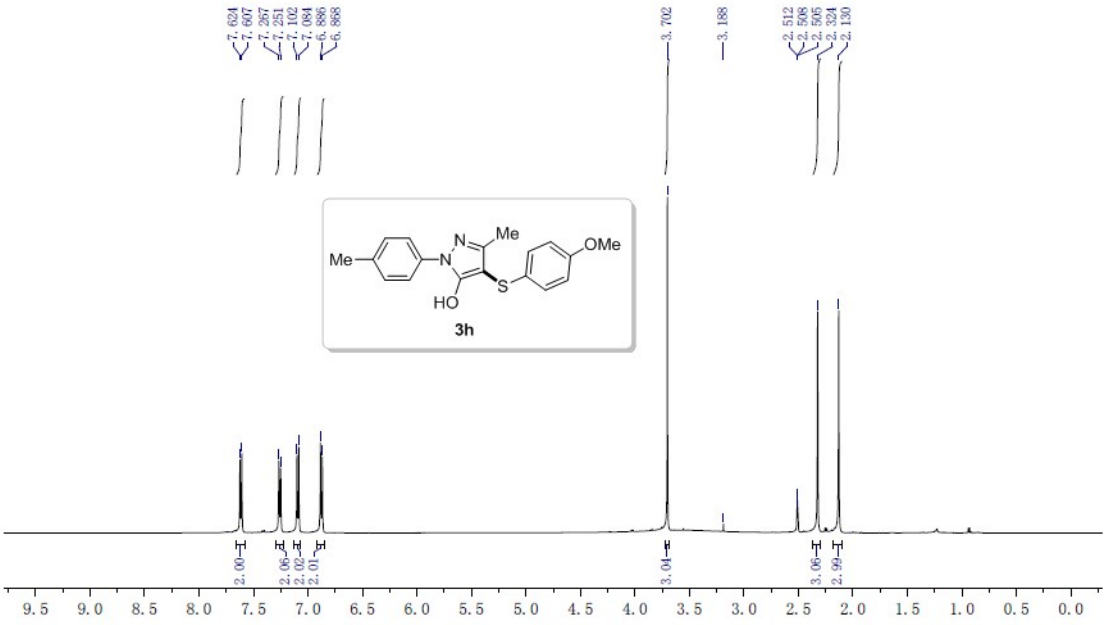
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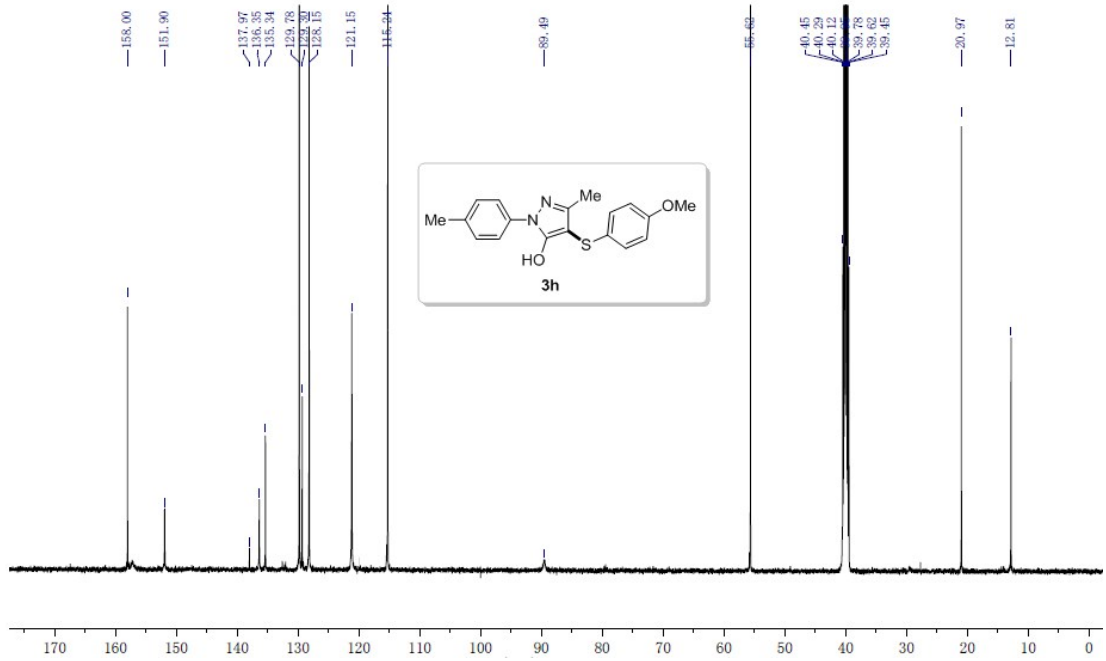
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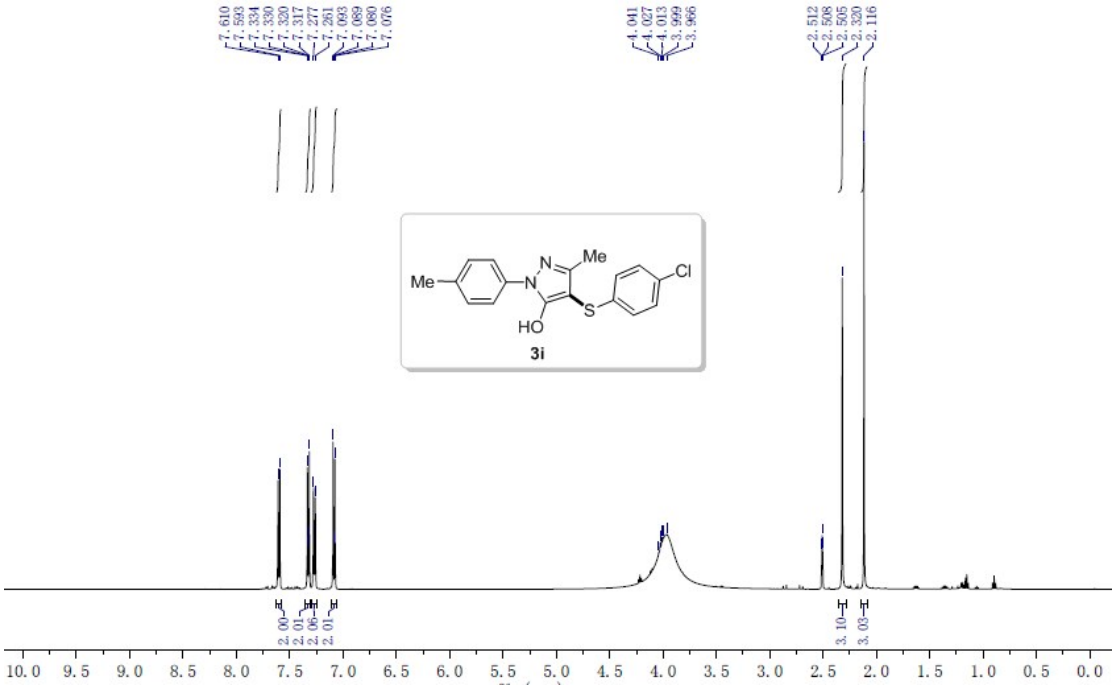
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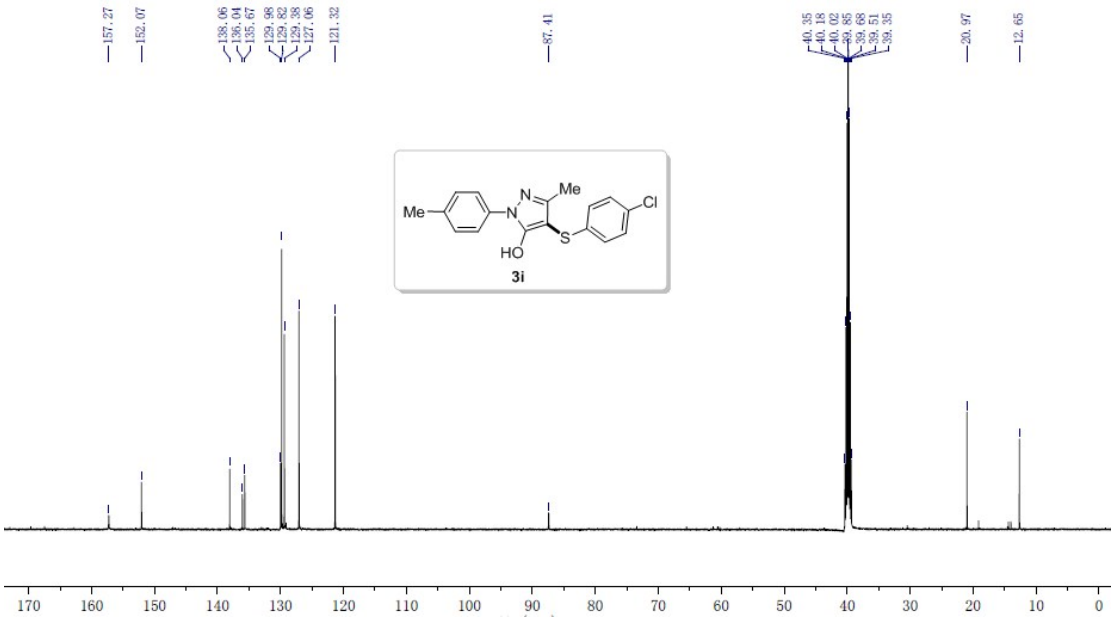
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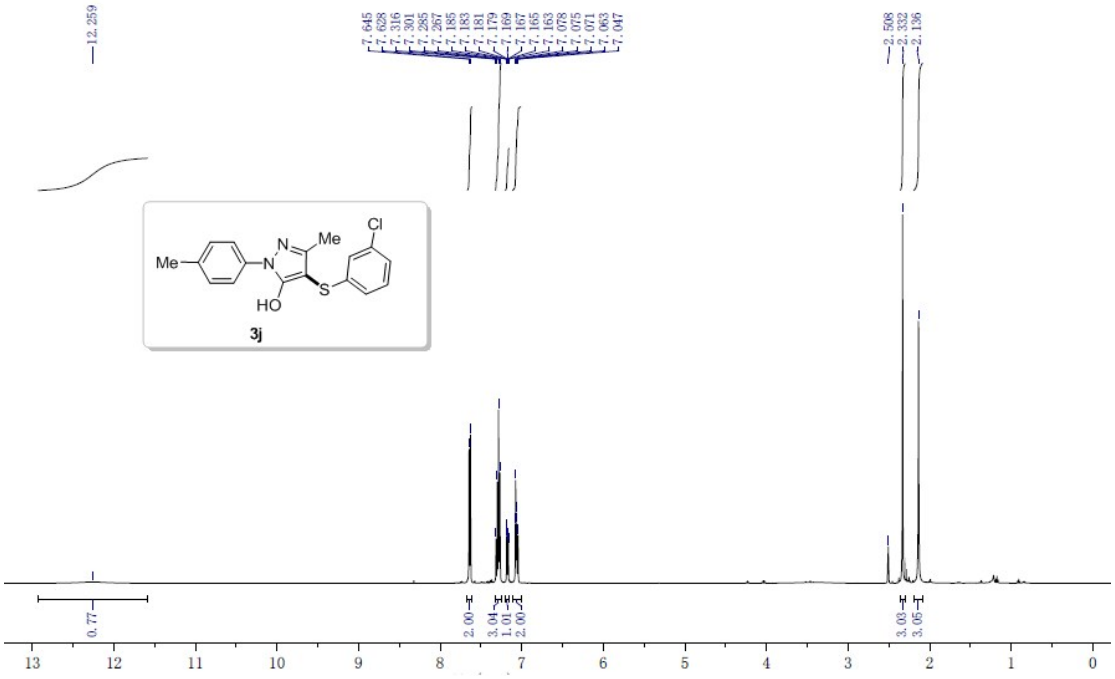
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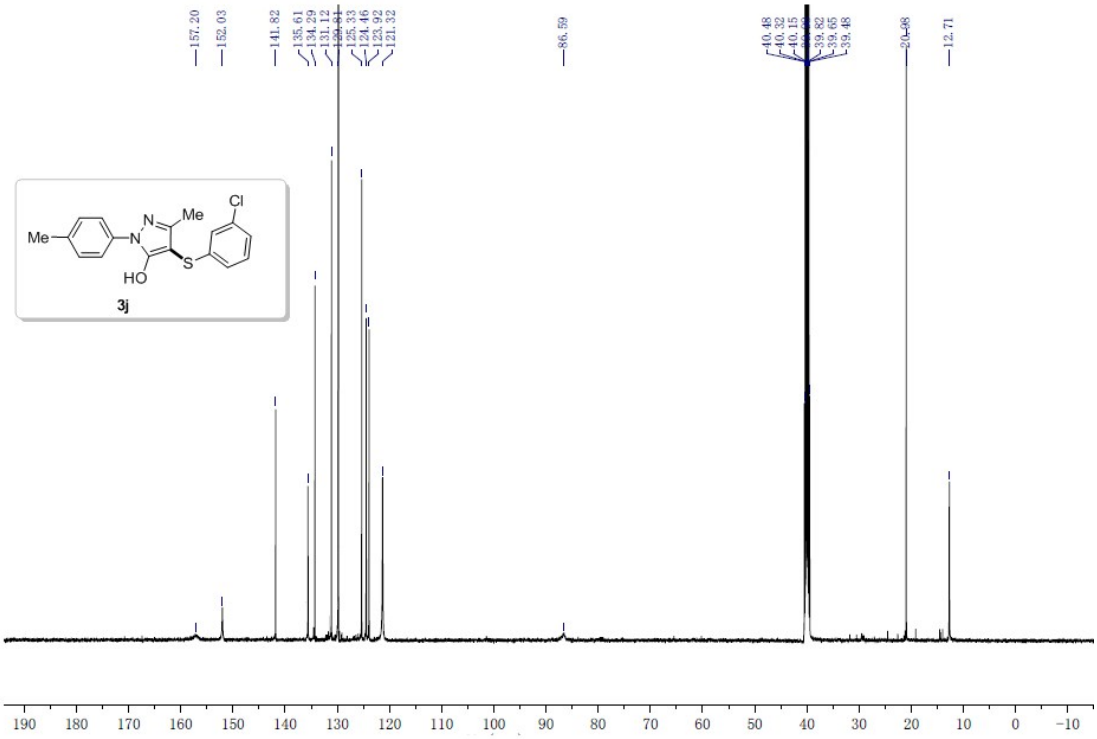
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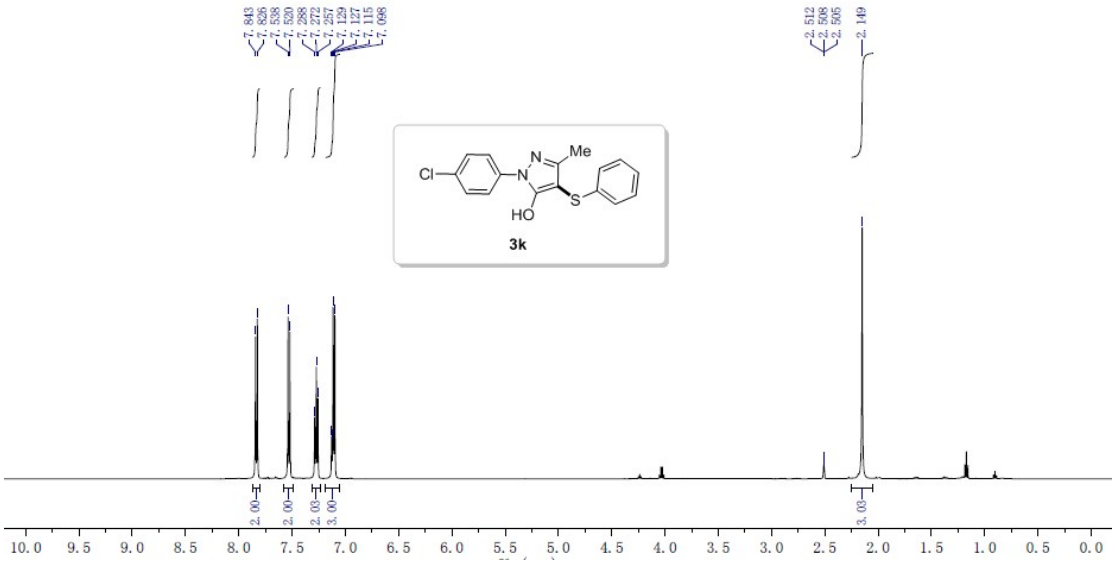
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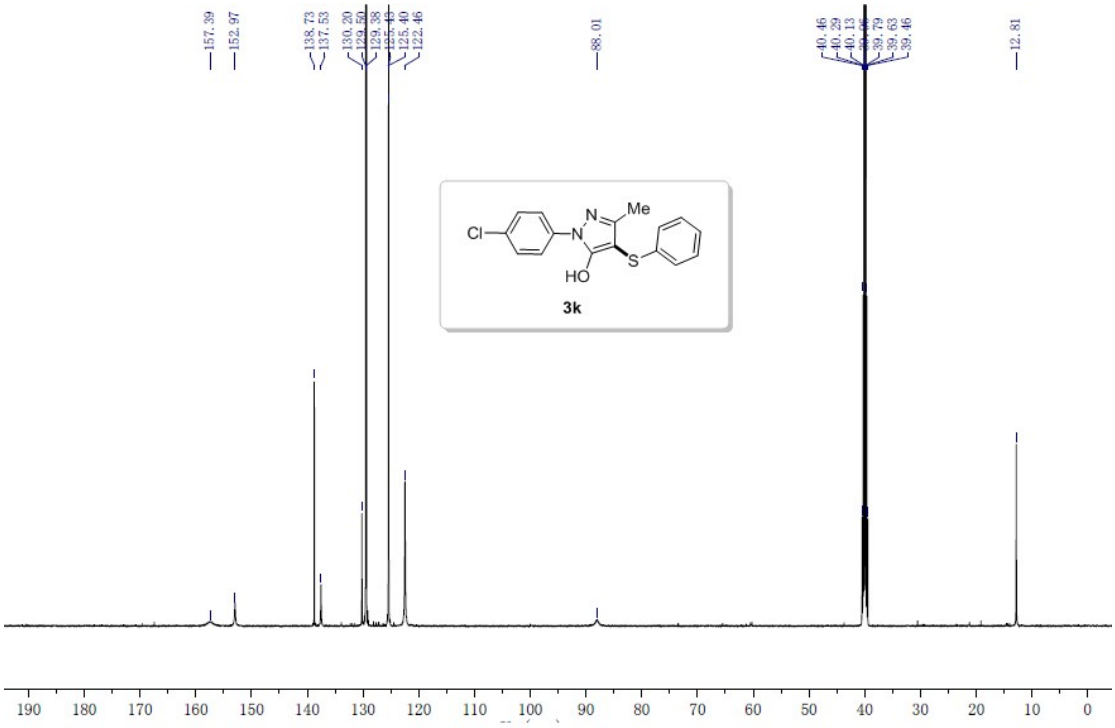
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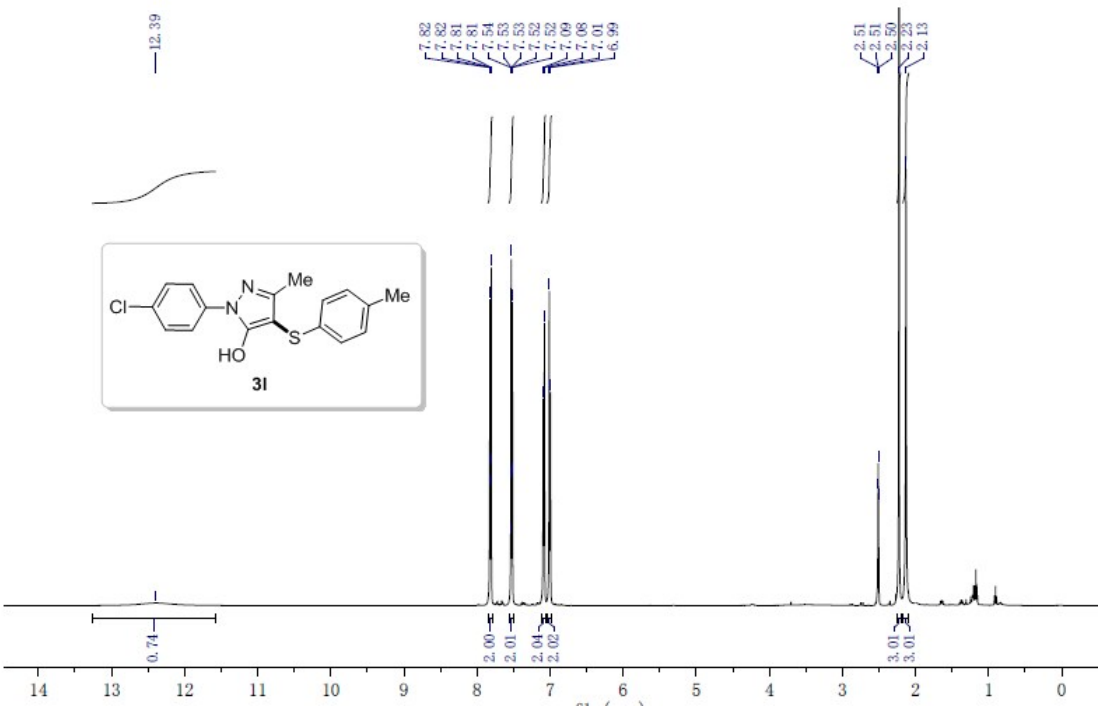
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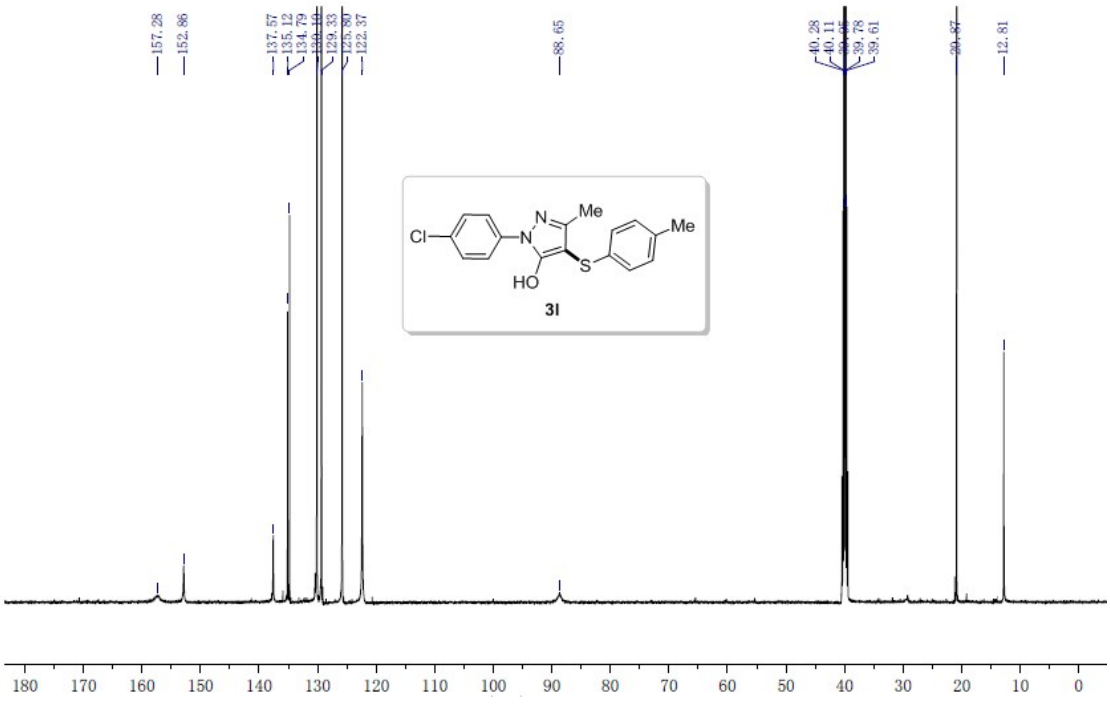
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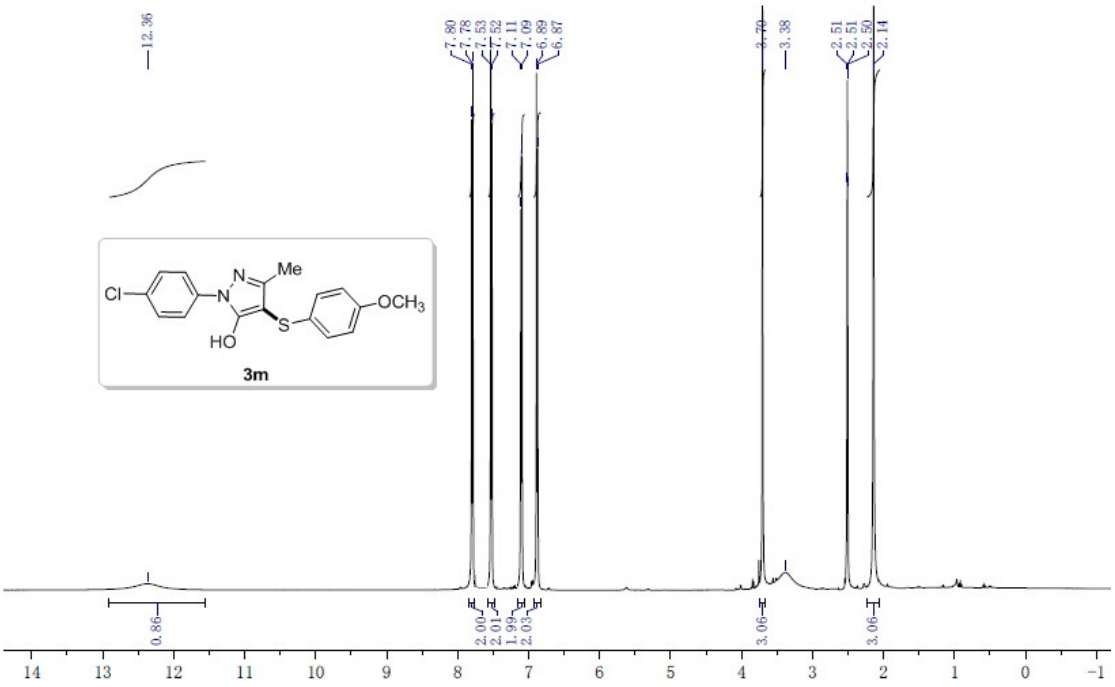
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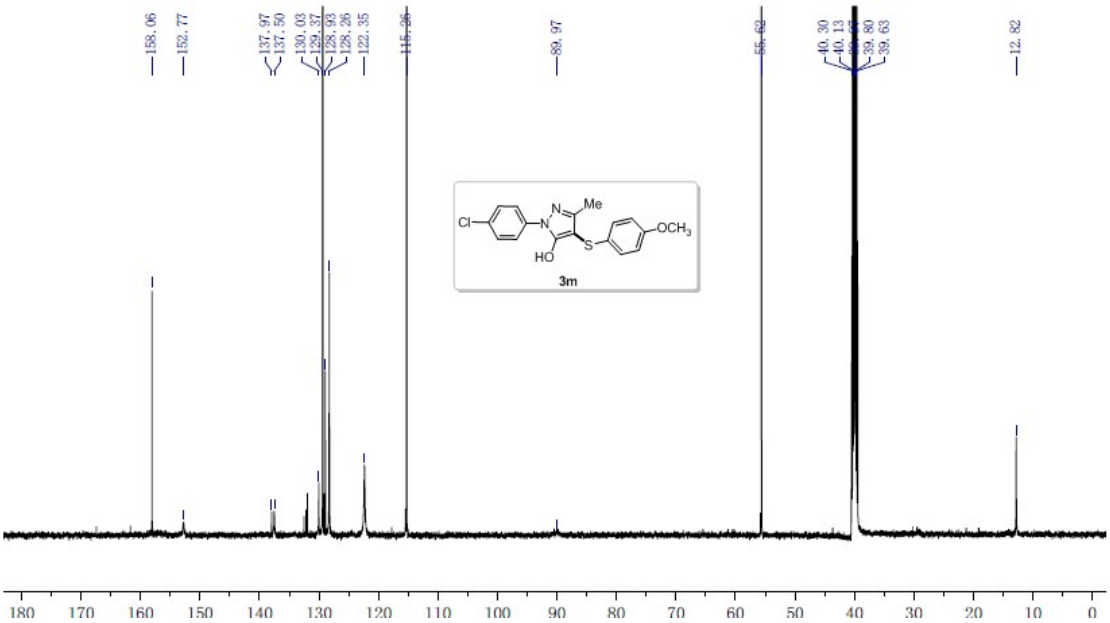
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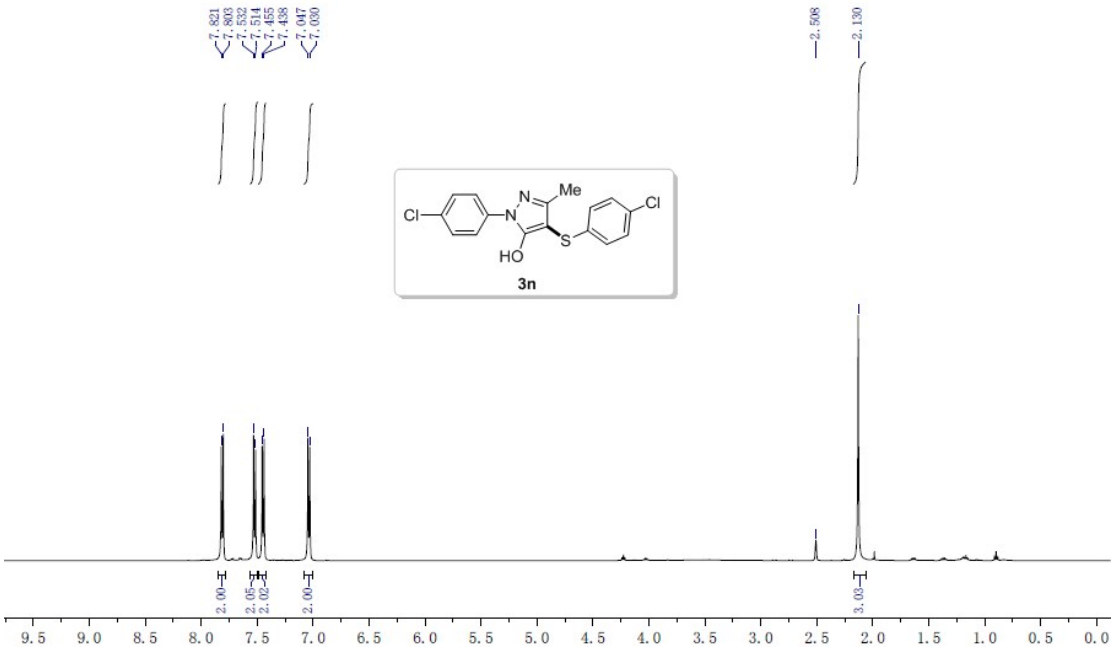
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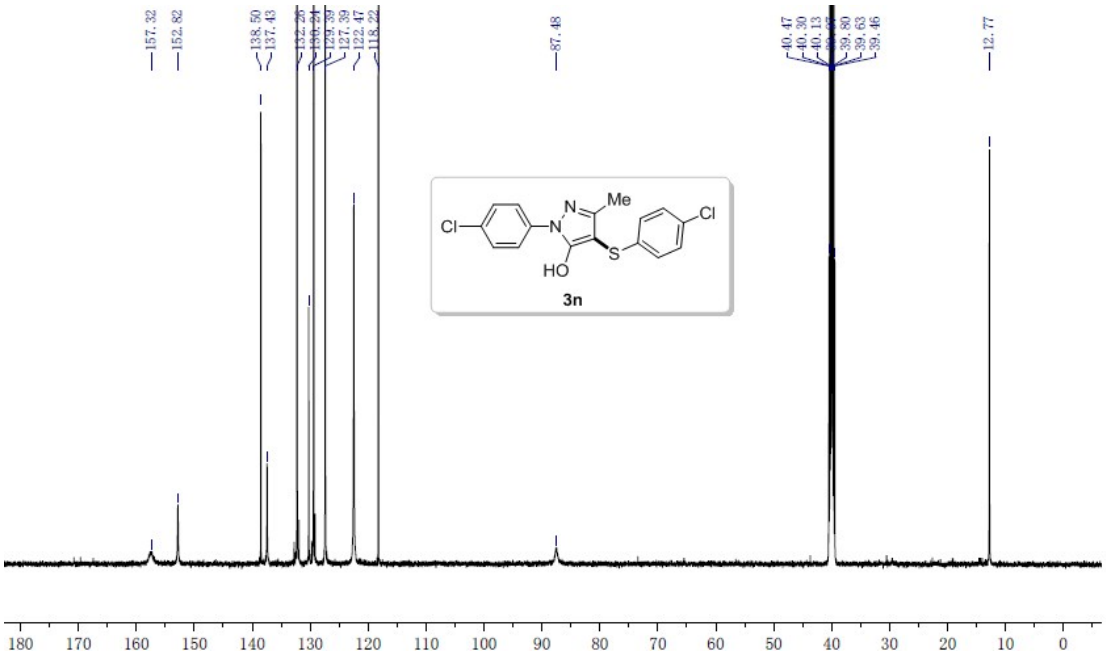
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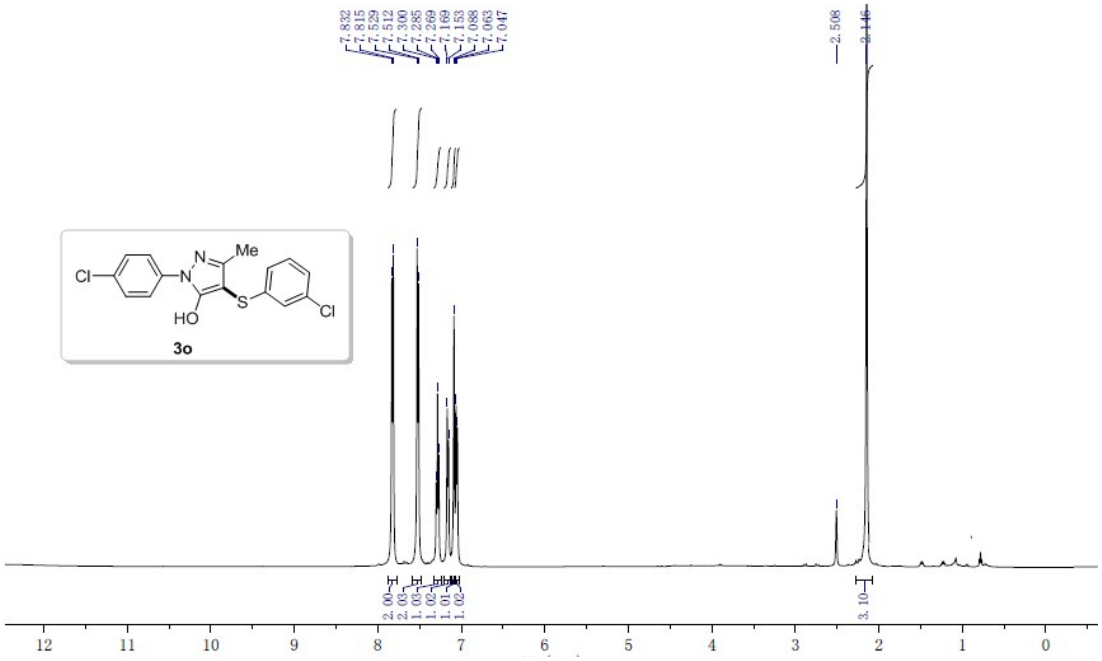
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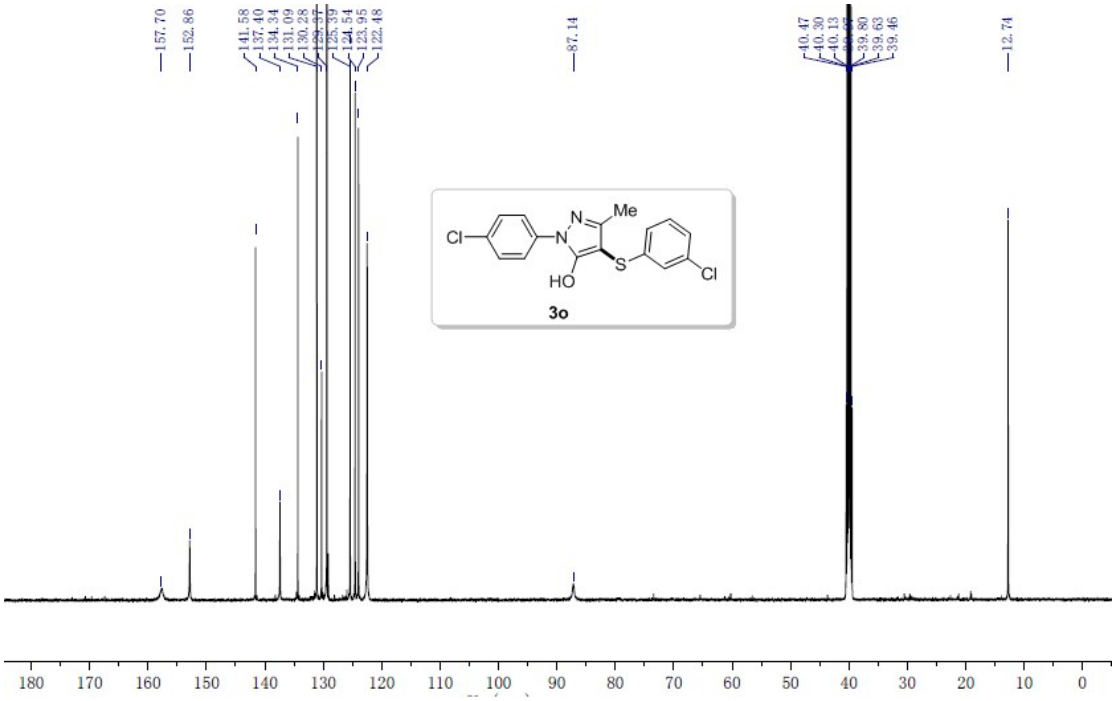
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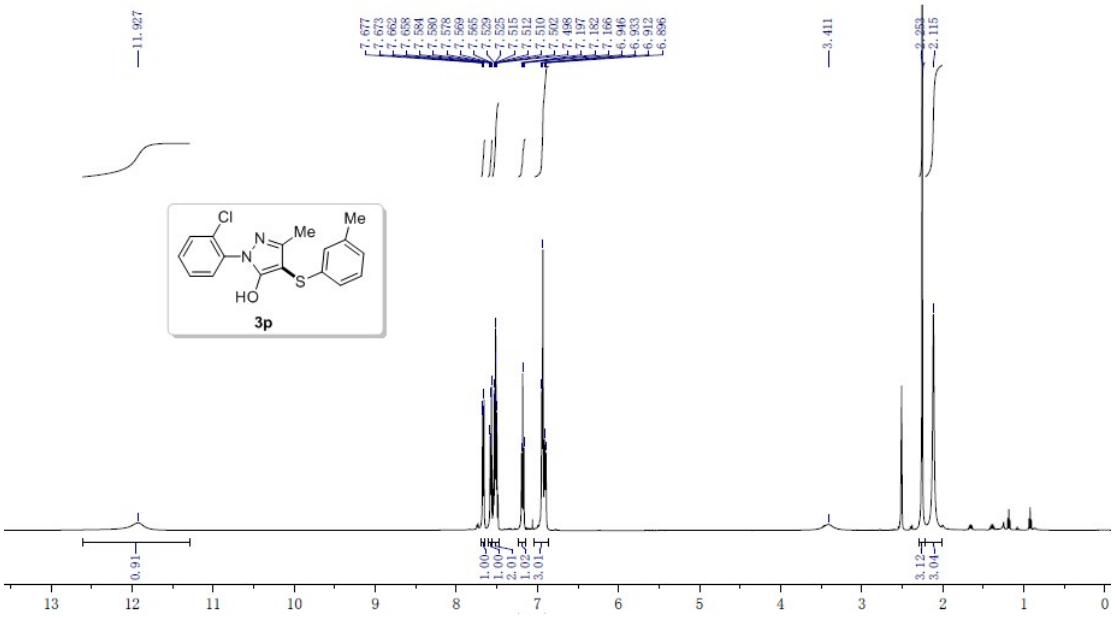
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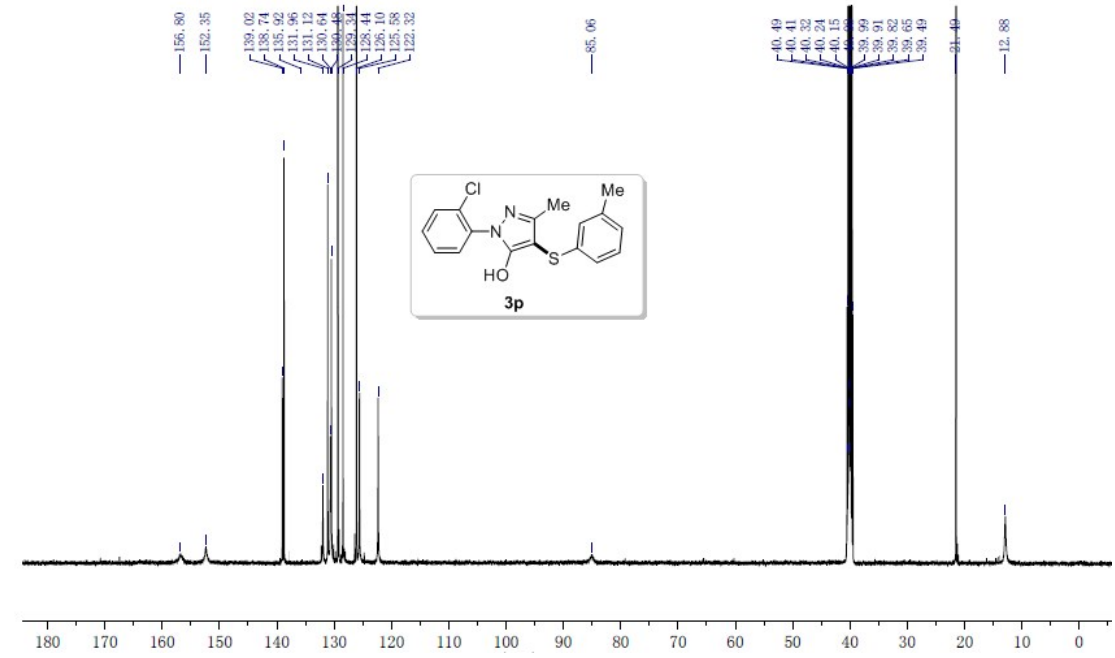
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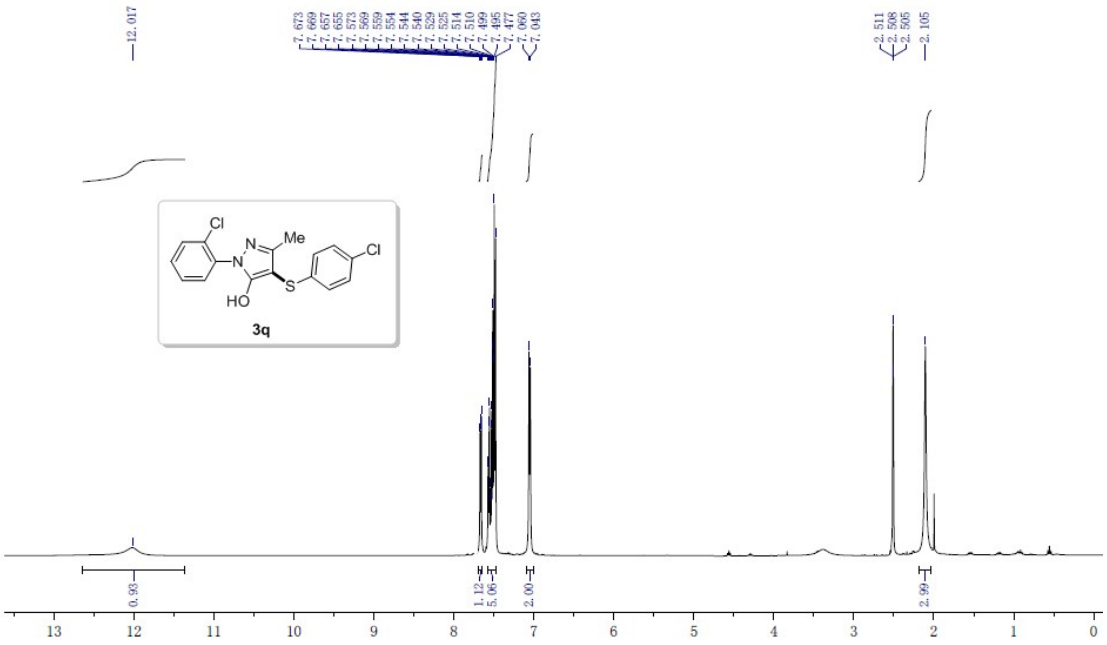
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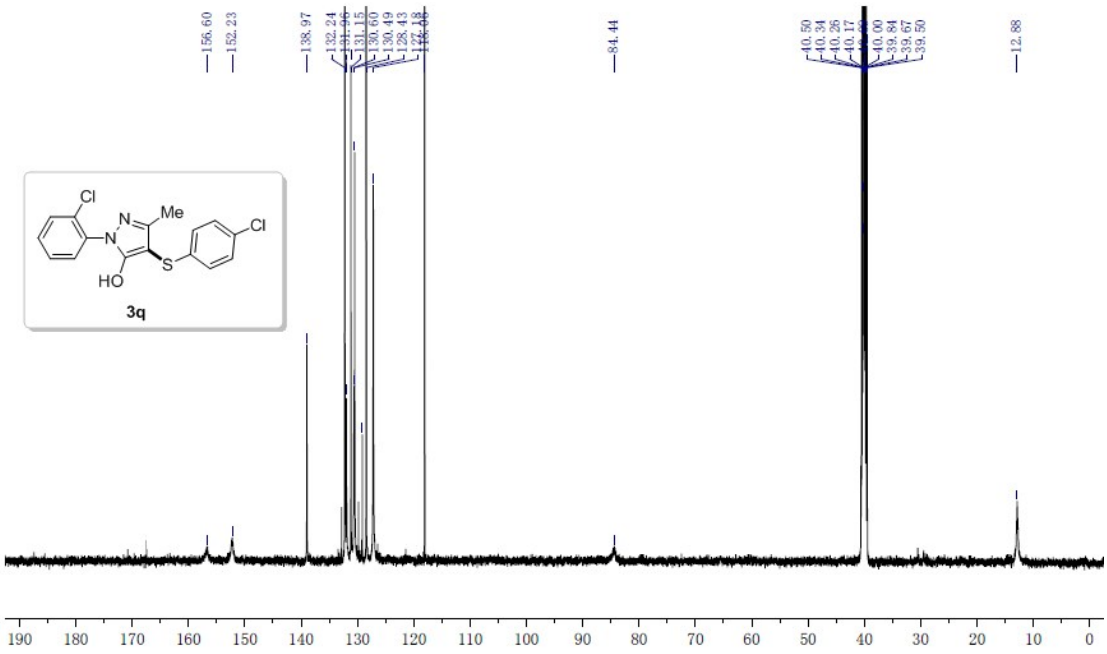
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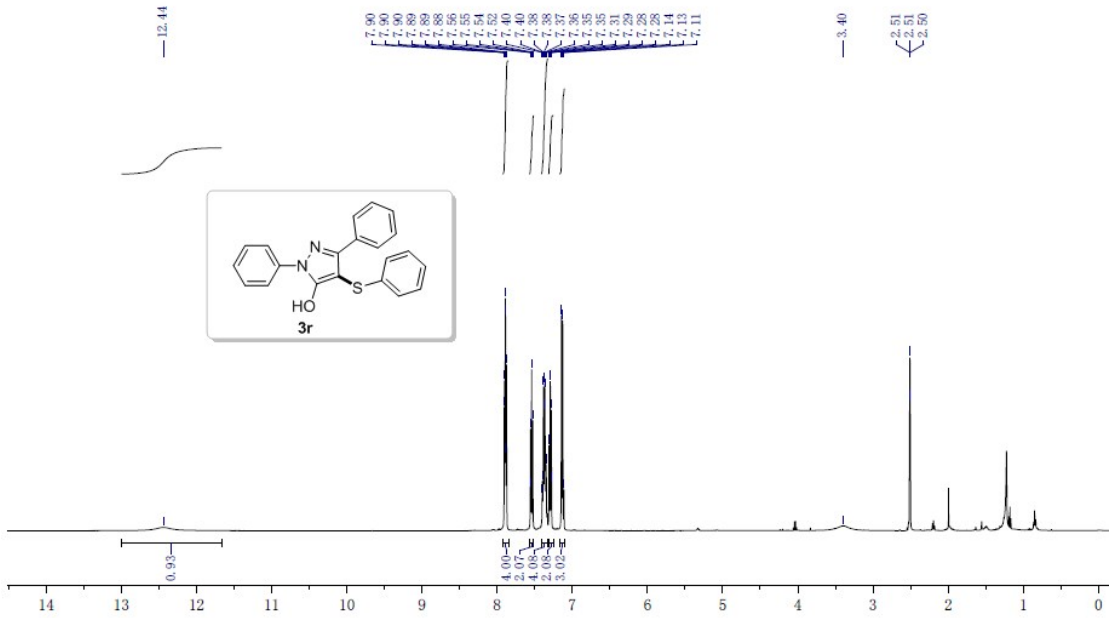
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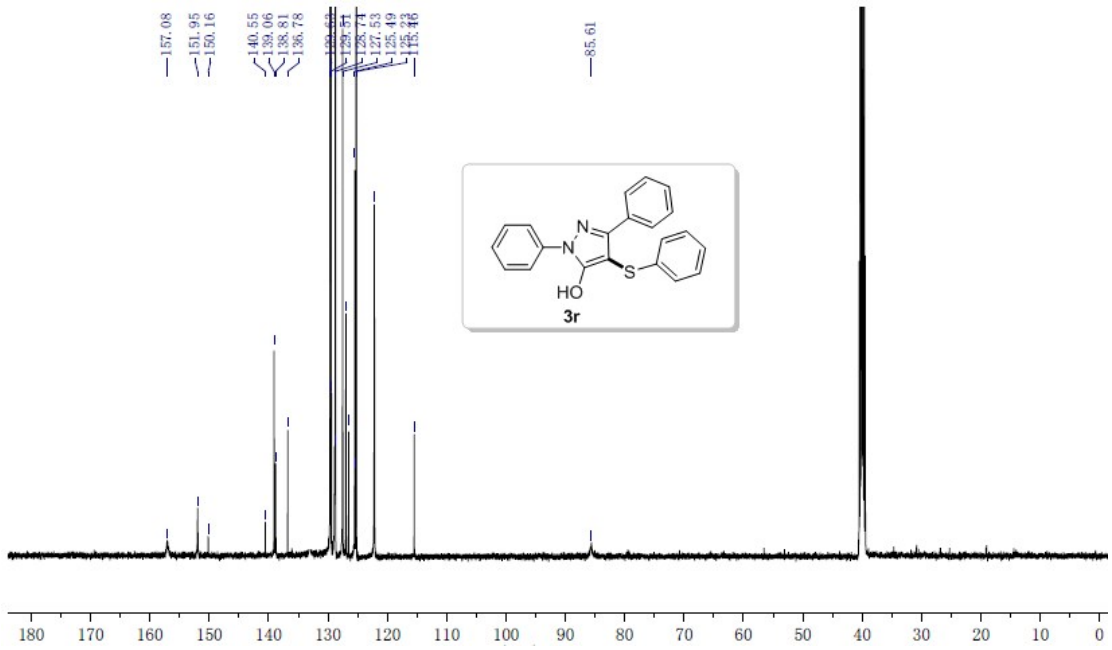
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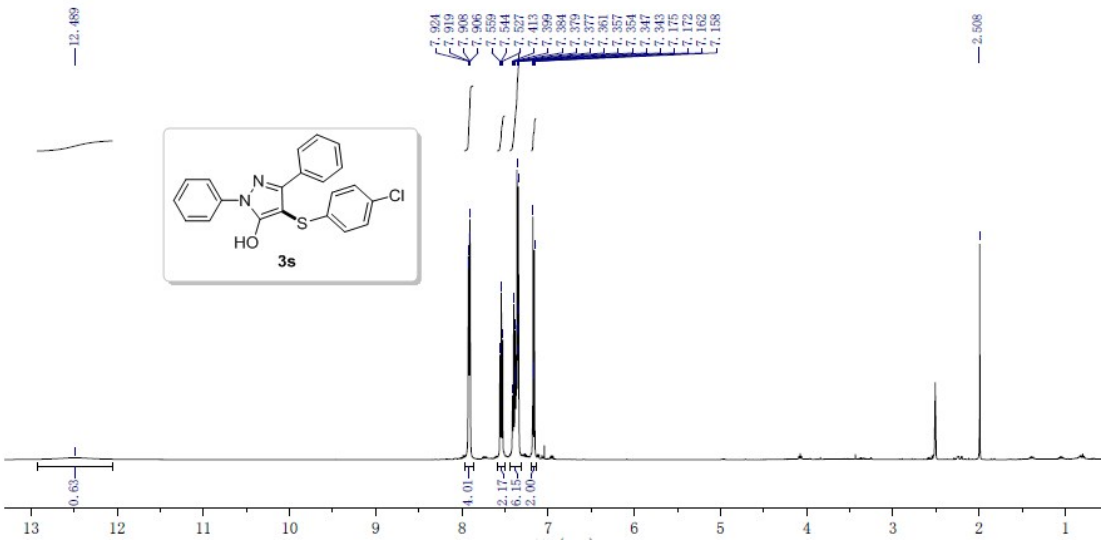
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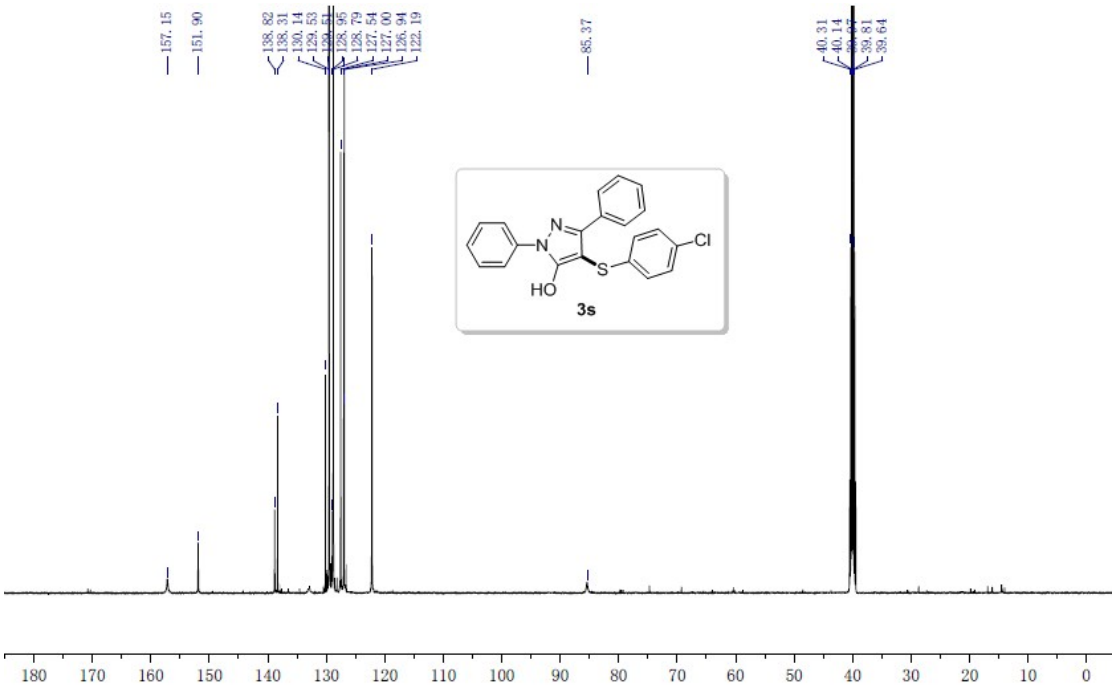
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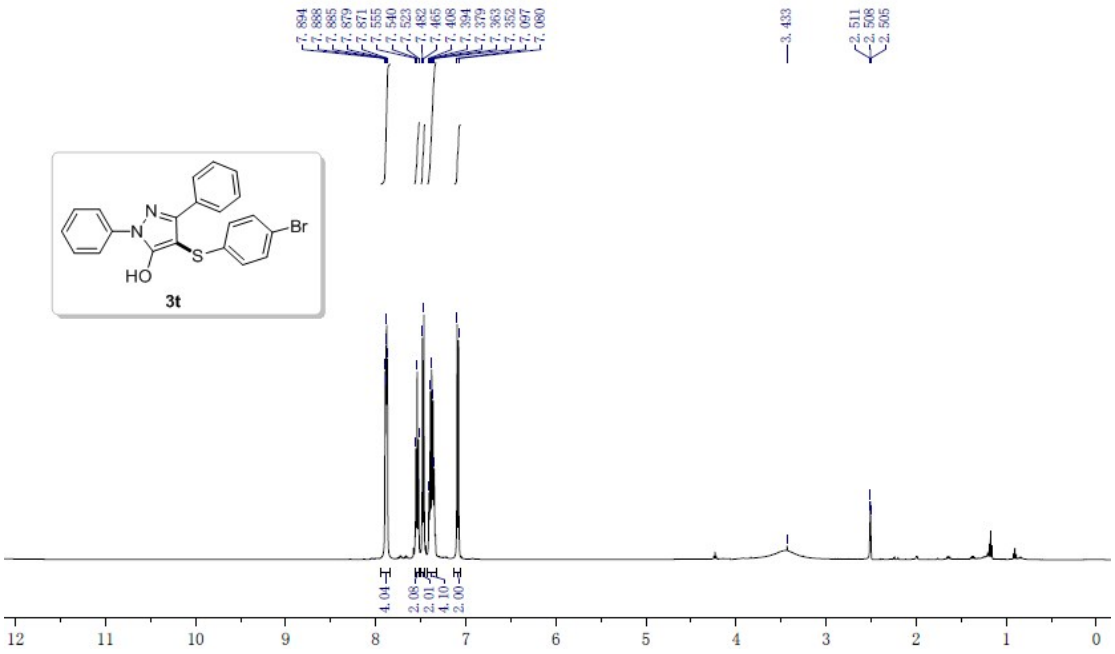
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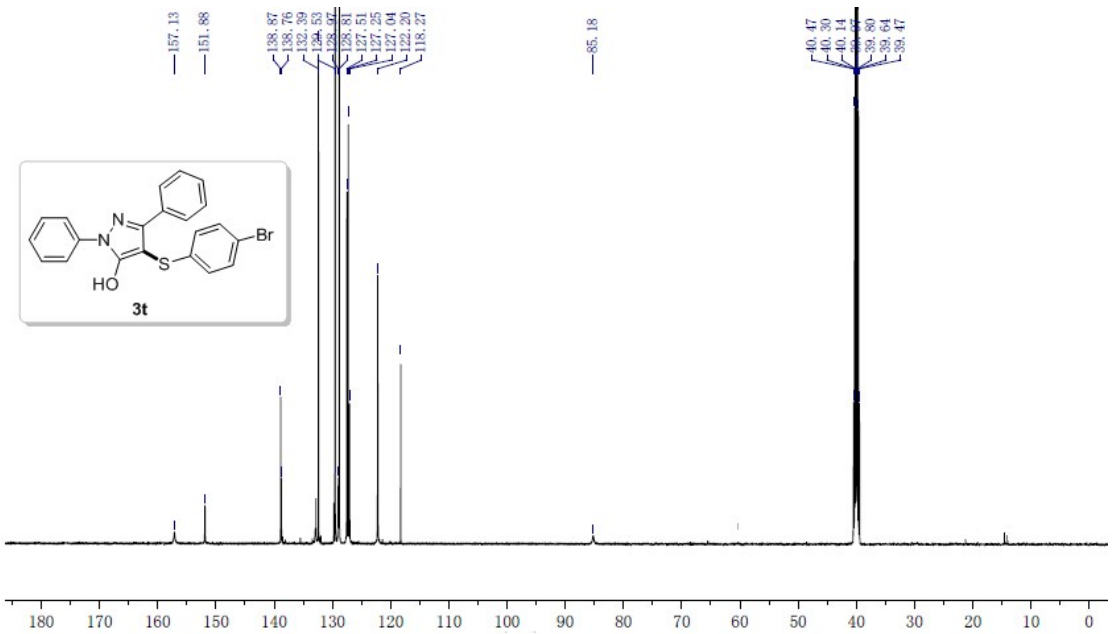
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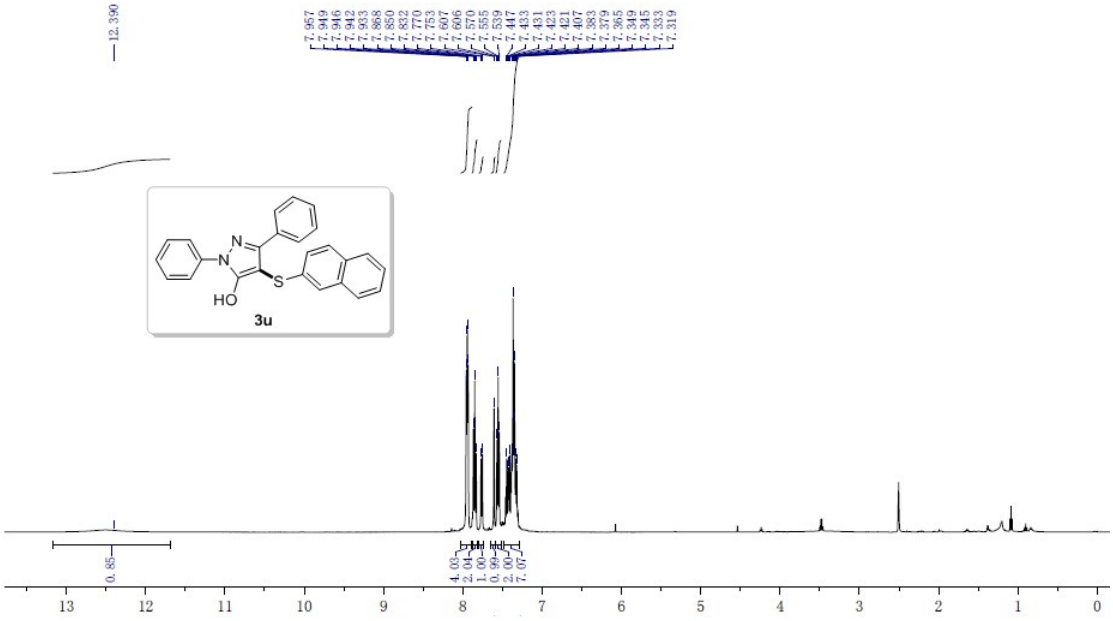
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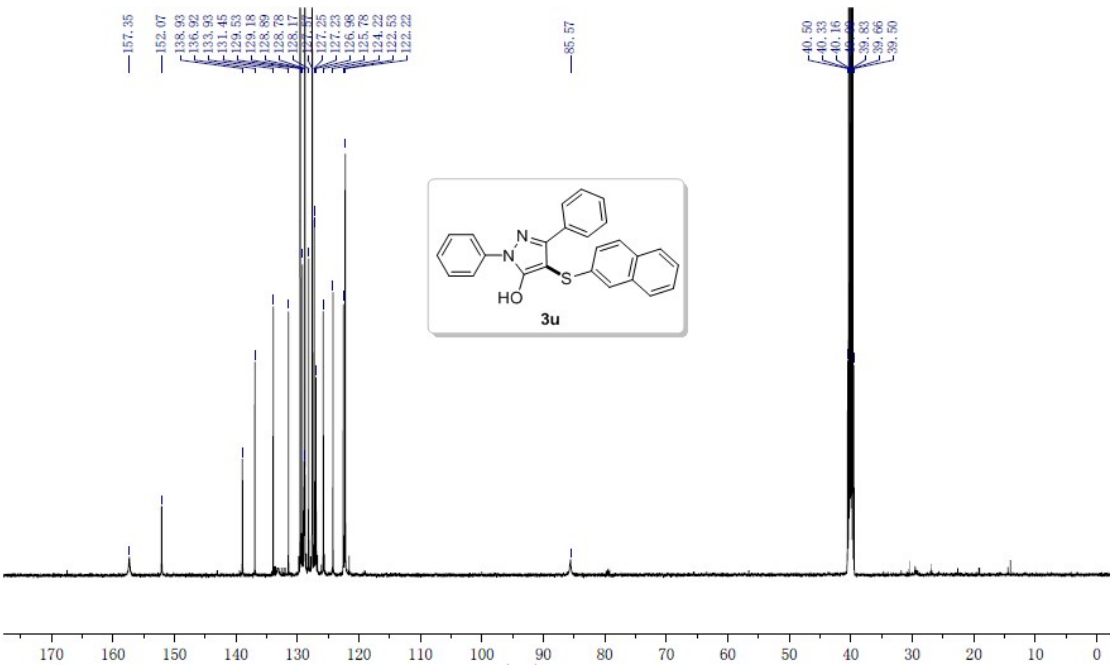
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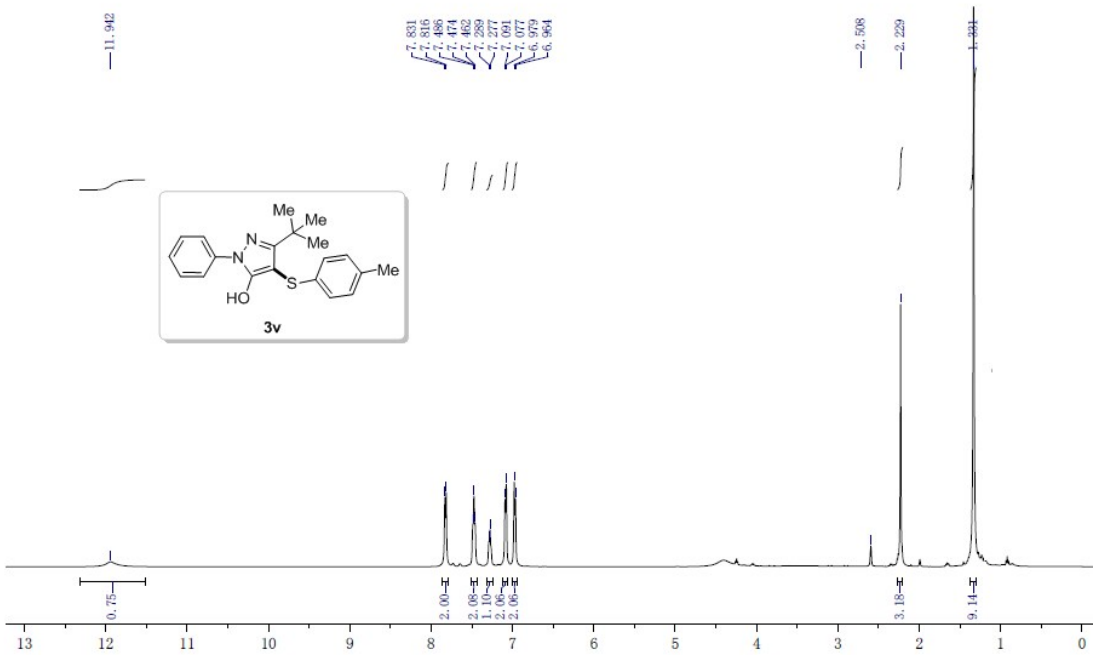
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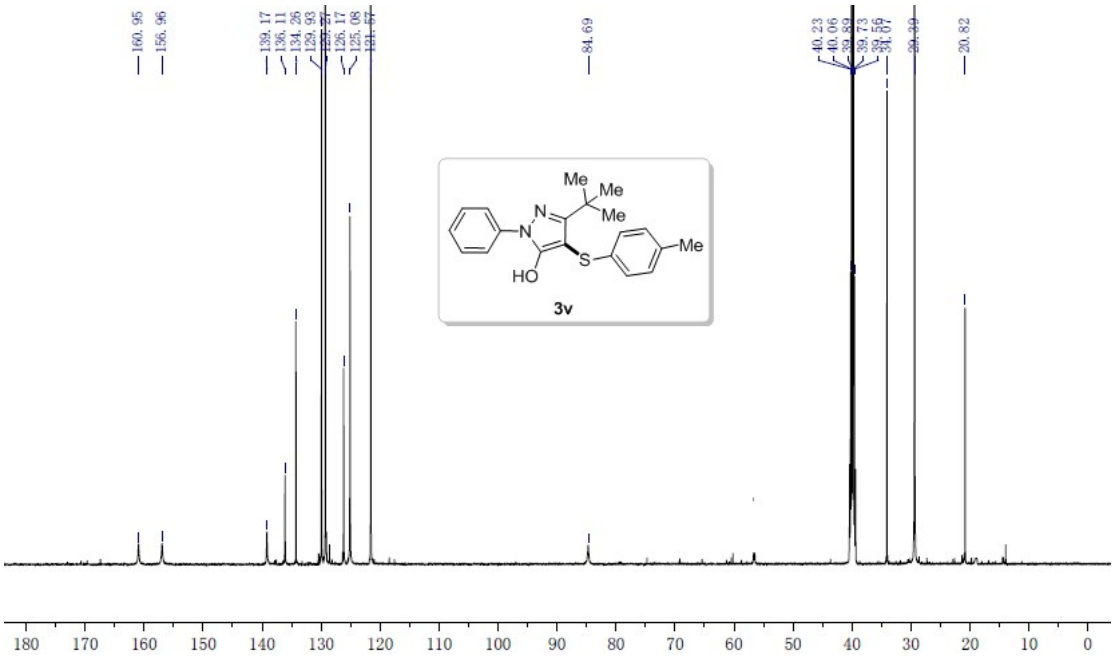
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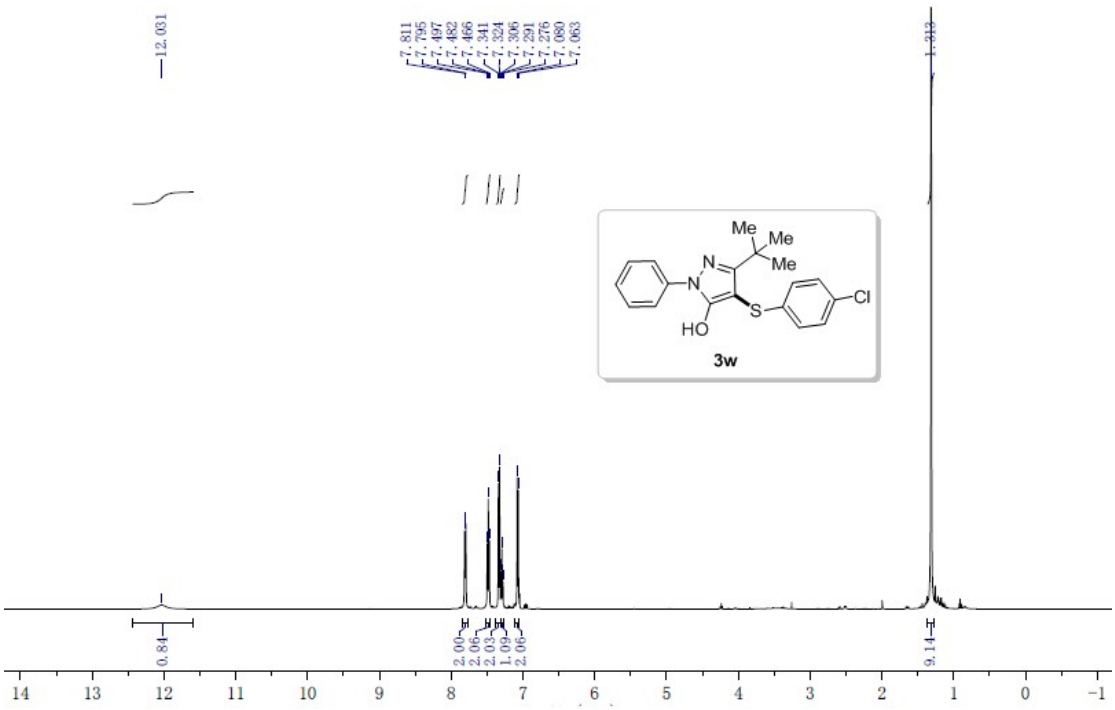
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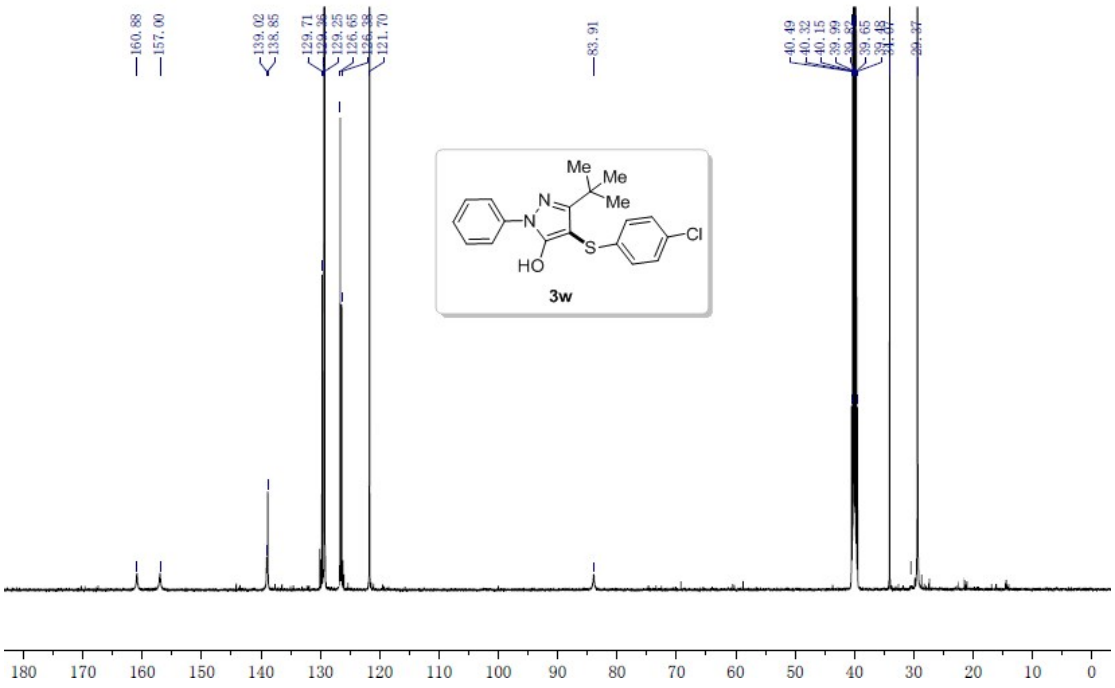
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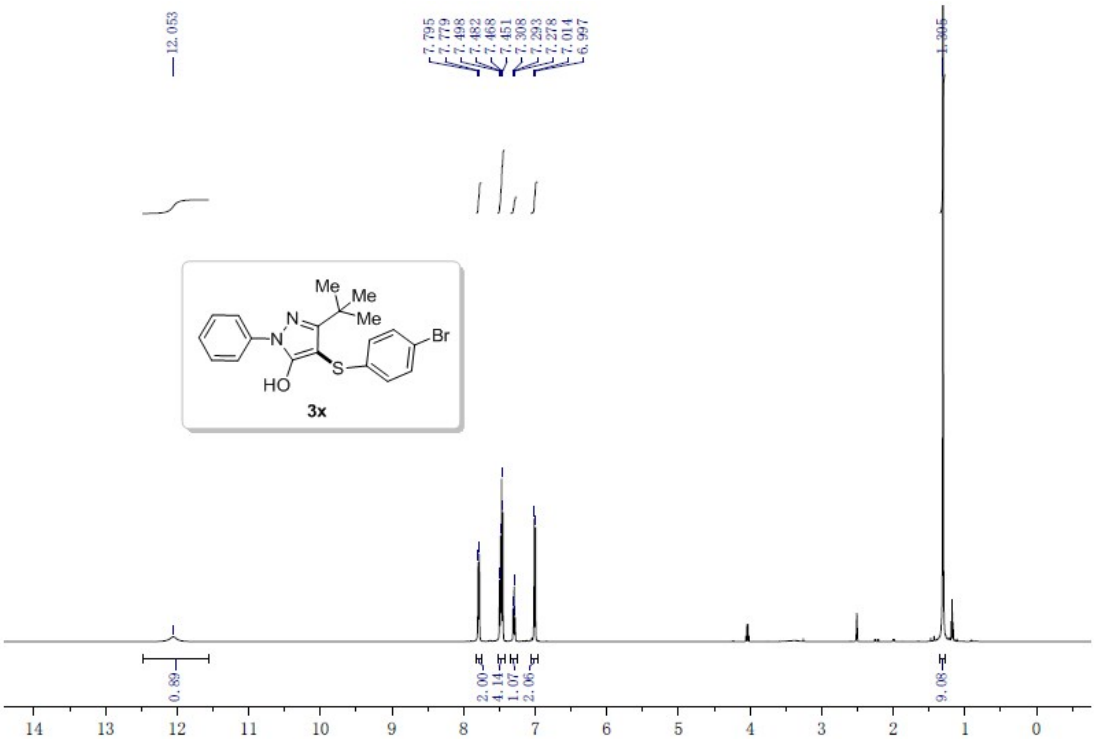
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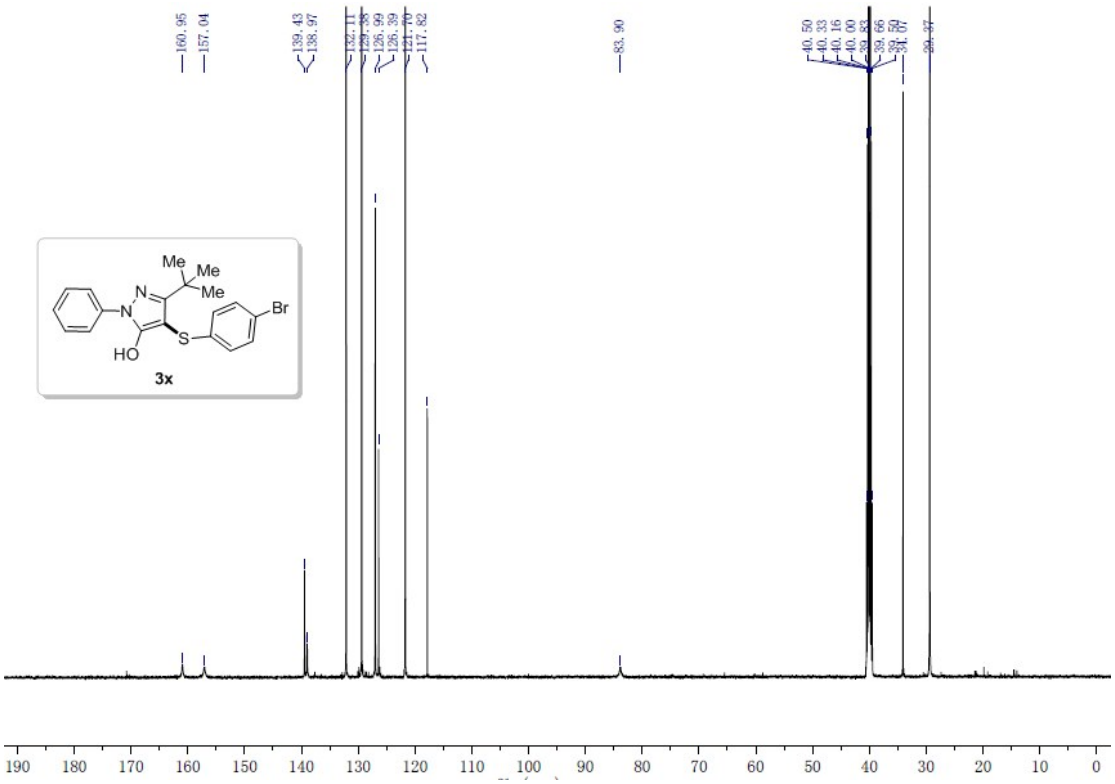
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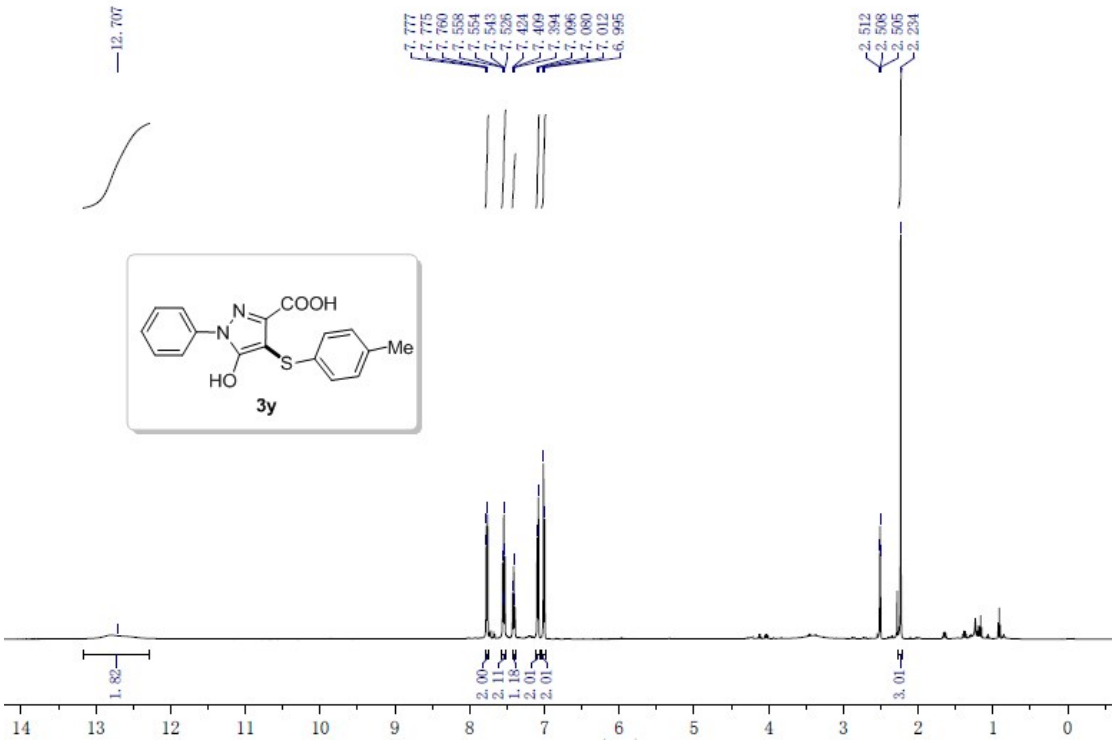
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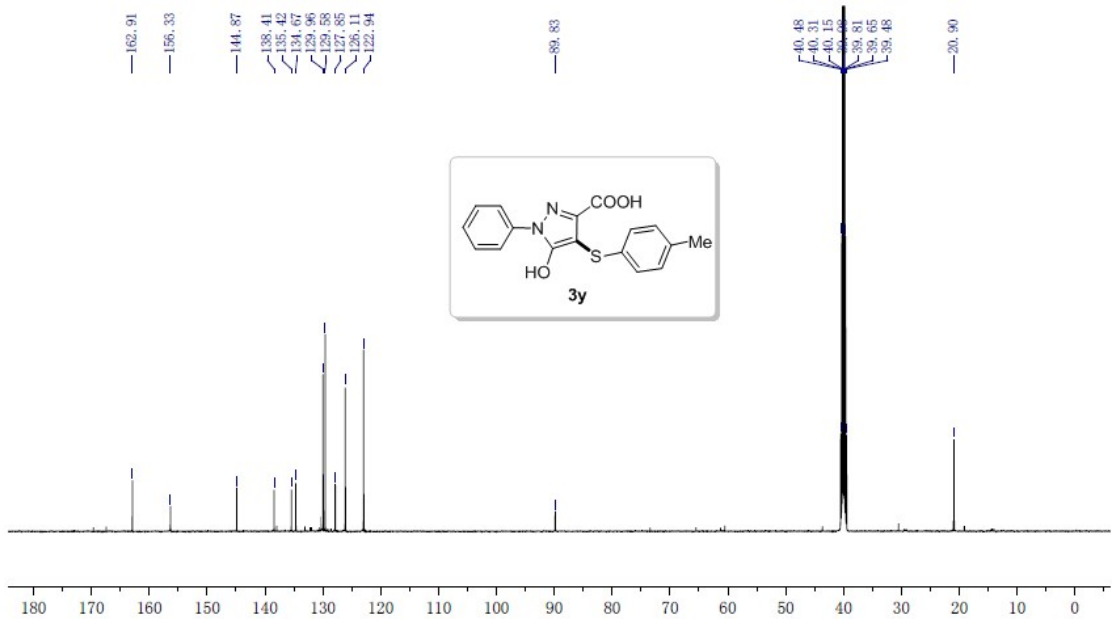
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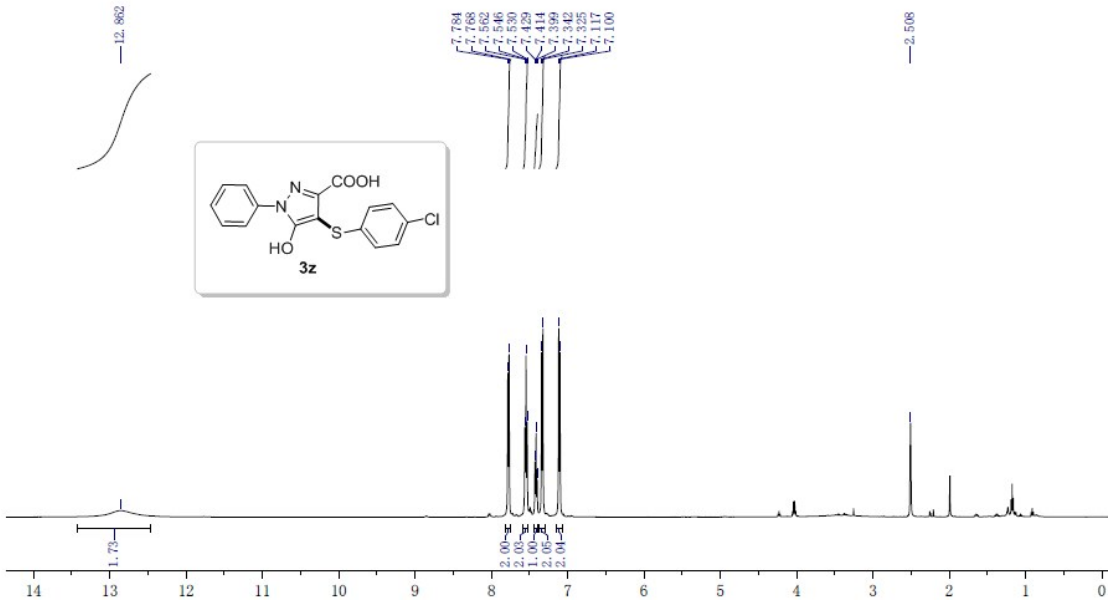
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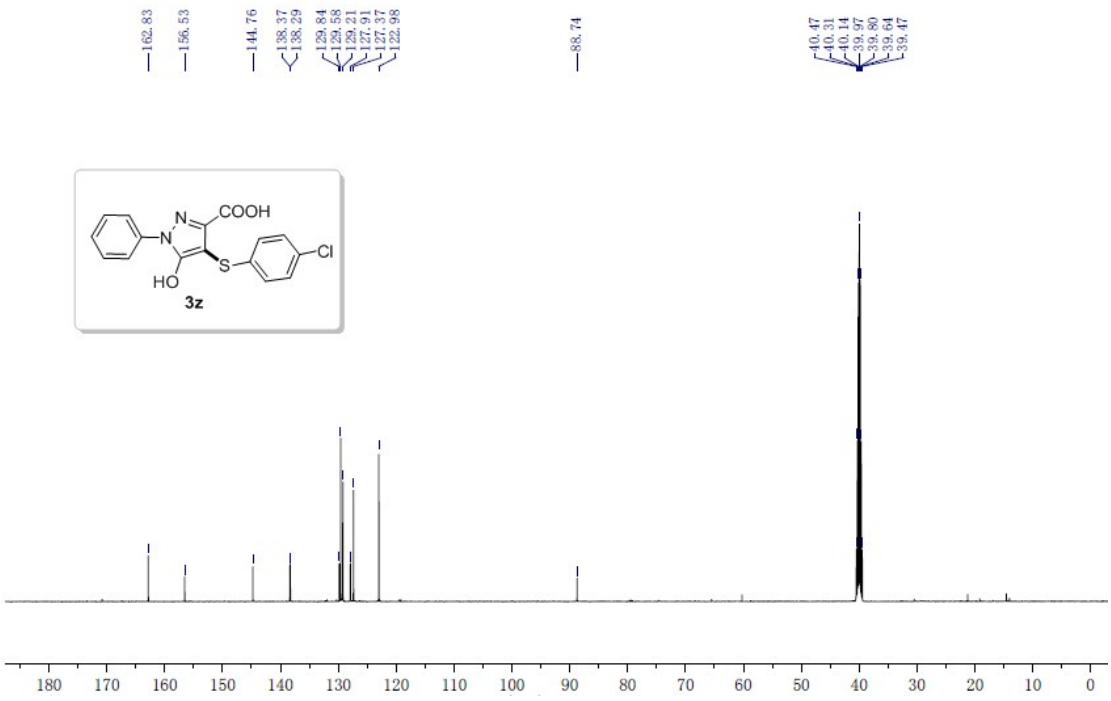
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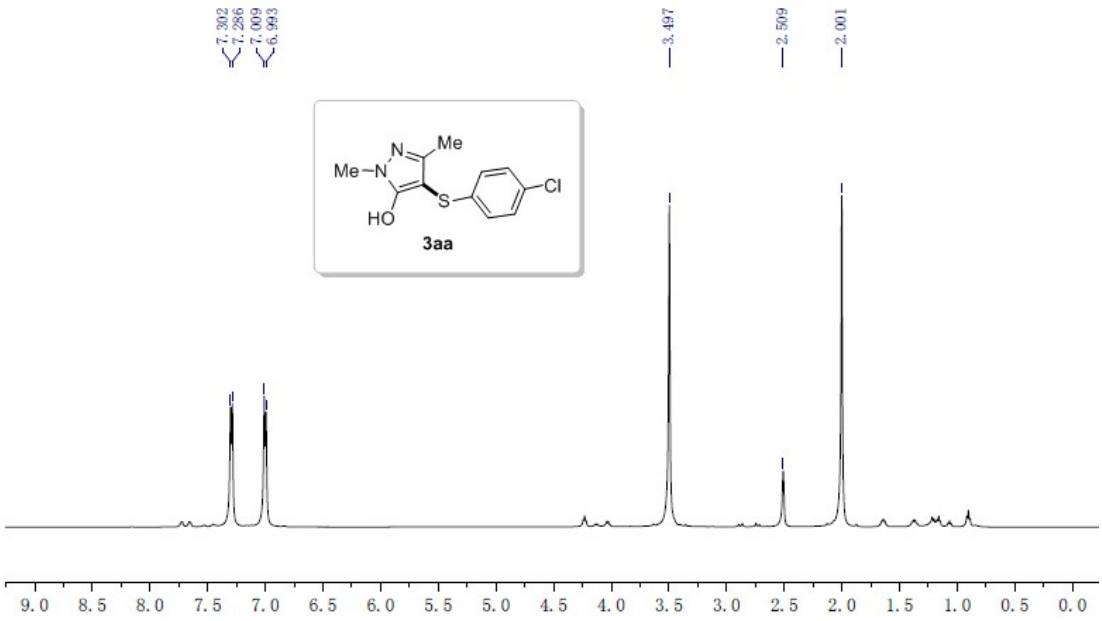
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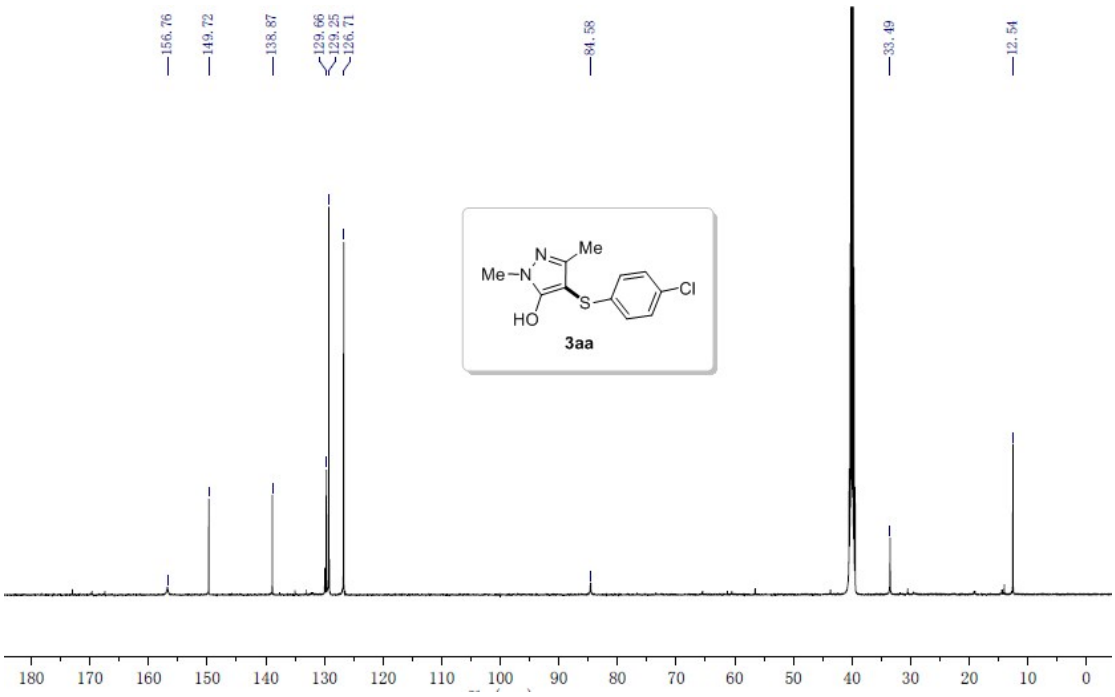
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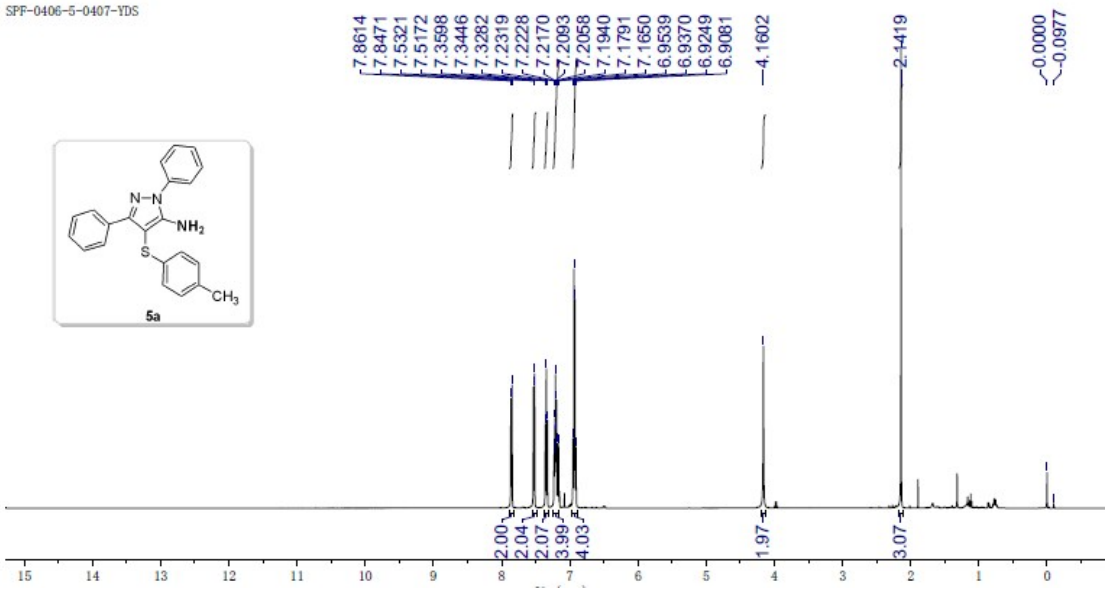
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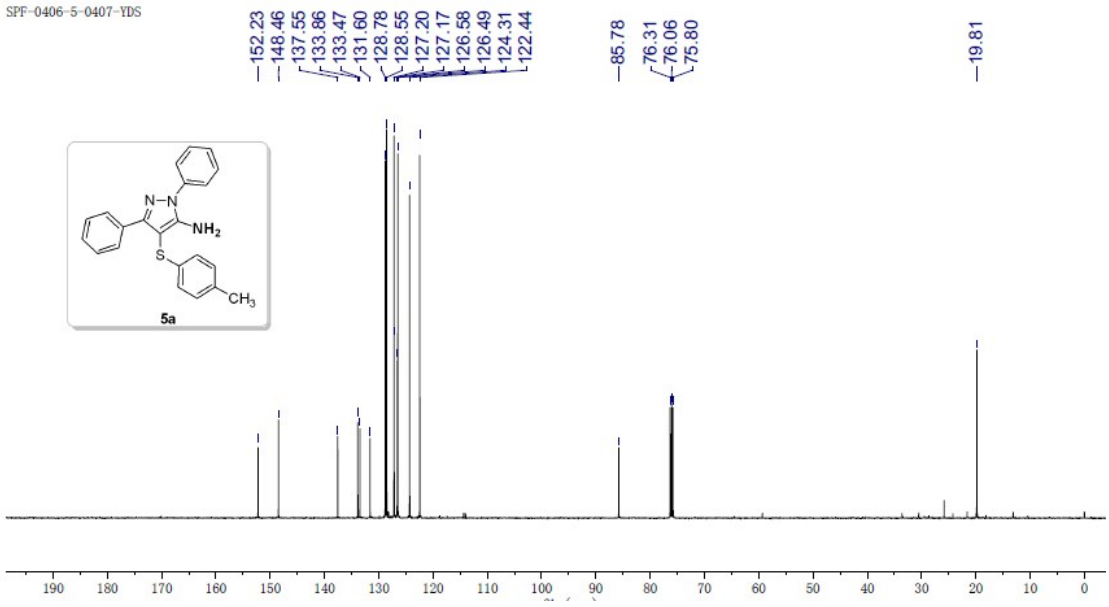
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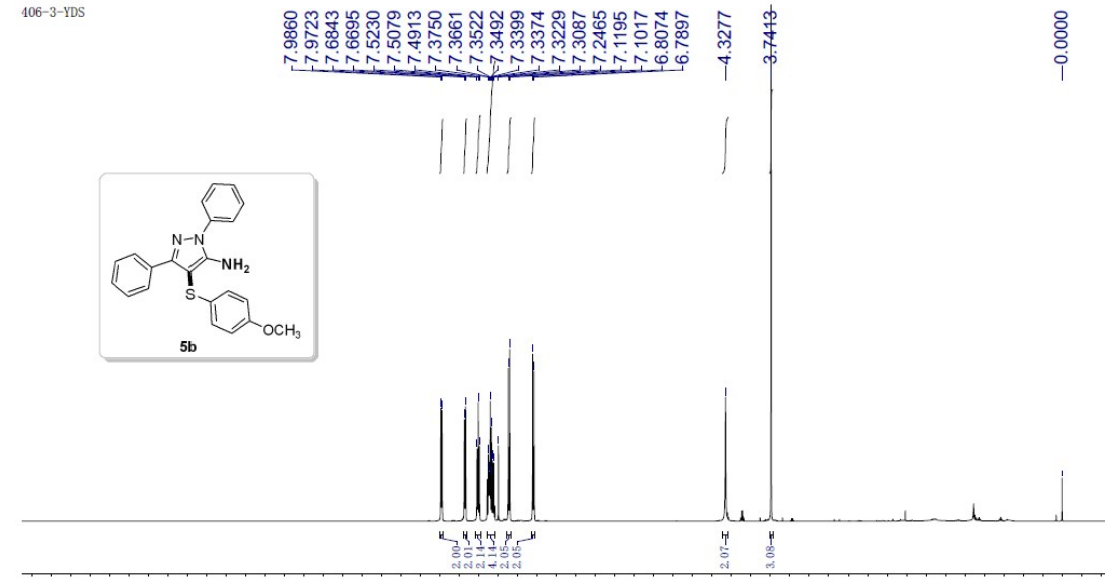
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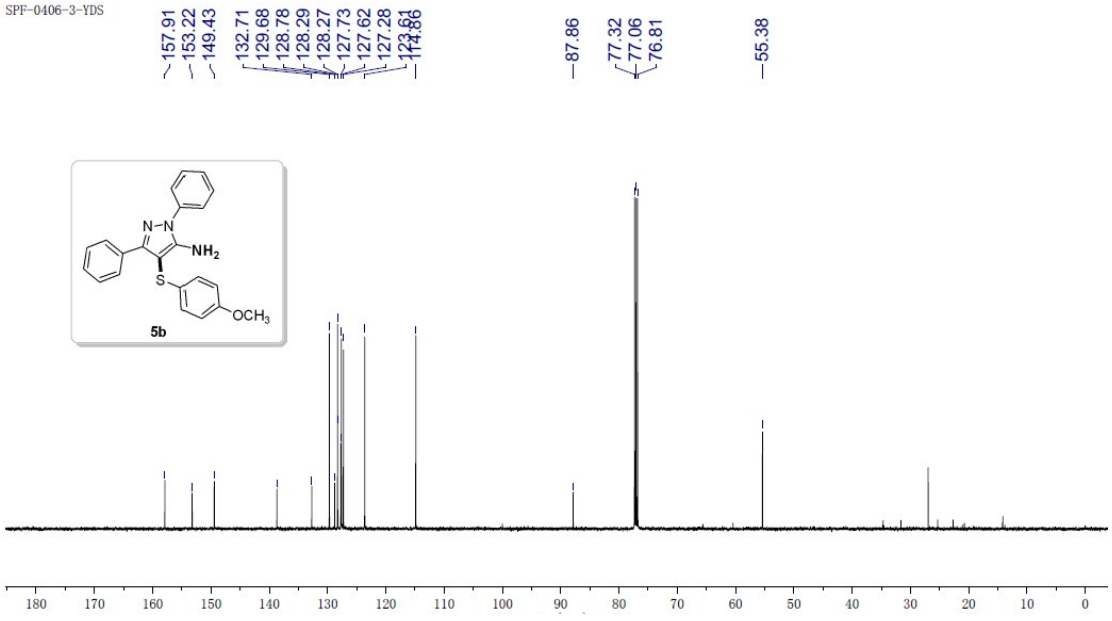
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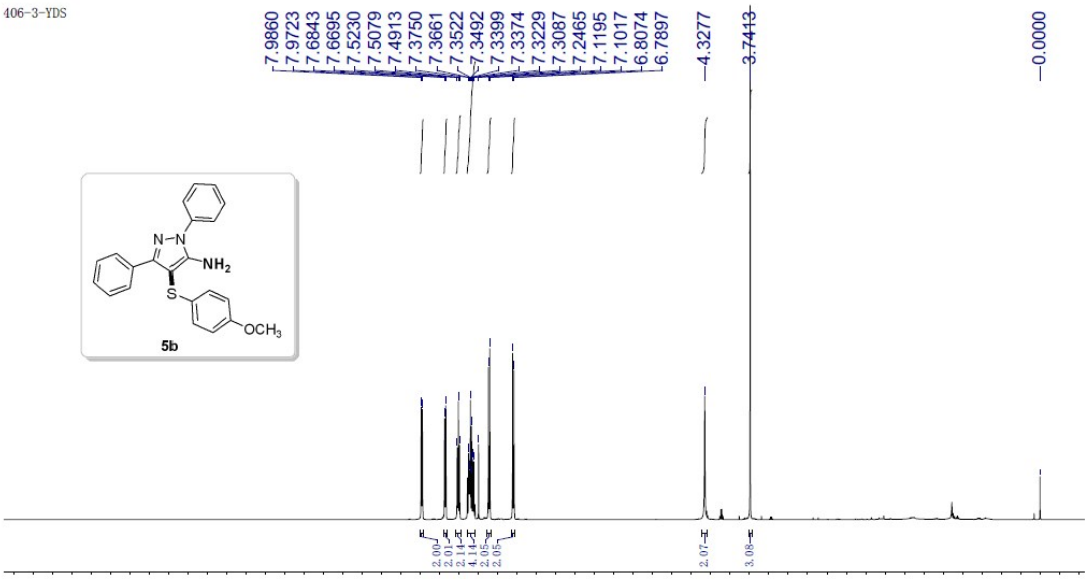
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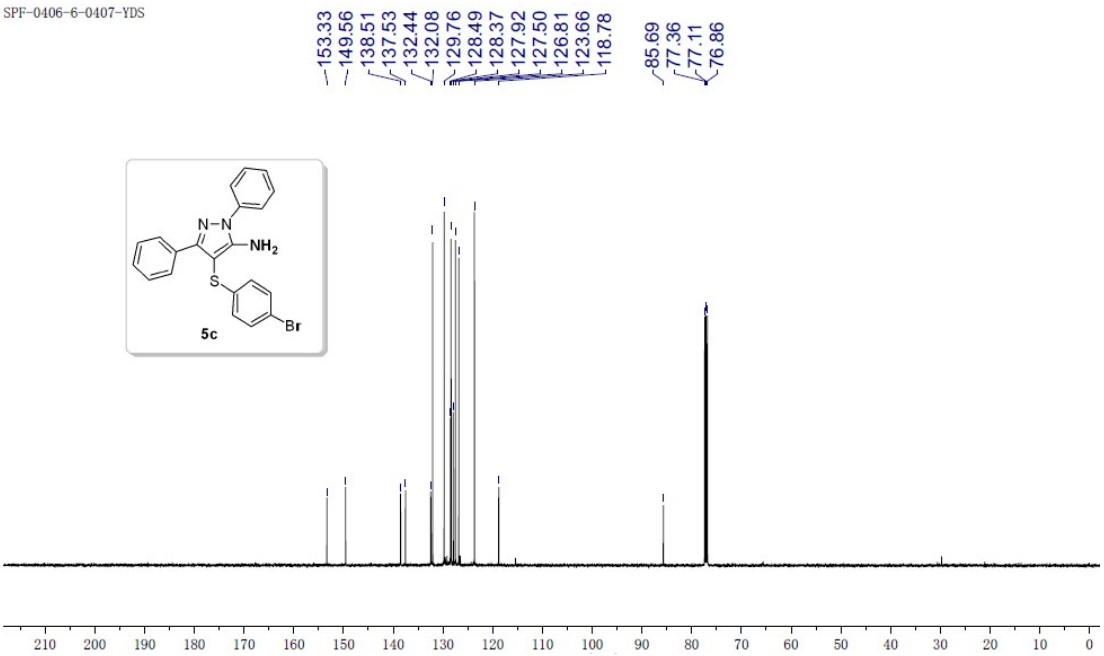
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76.86
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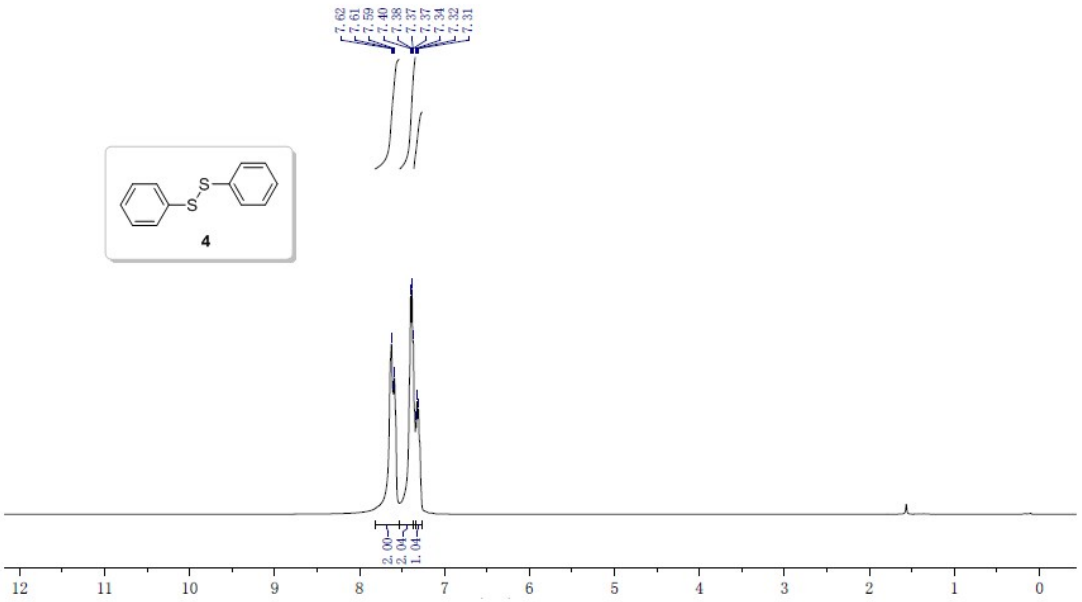
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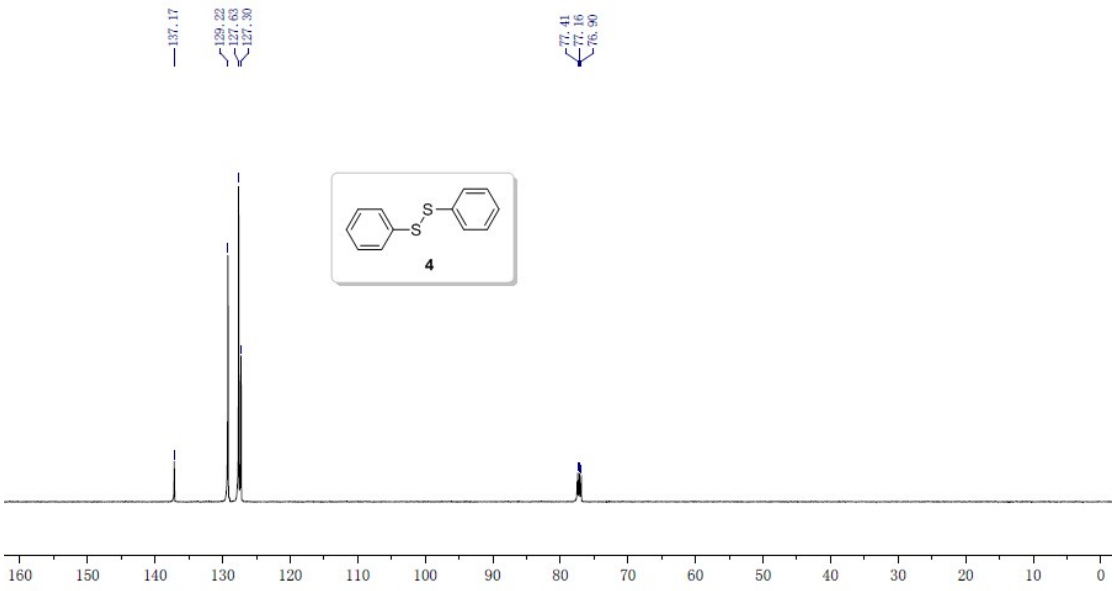
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