Supporting Information for

*p*-Toluenesulphonic Acid-Promoted, I₂-Catalysed Sulphenylation of Pyrazolones with Aryl Sulphonyl Hydrazides

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1) General

All solvents were distilled prior to use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H and ¹³C 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 a Bruker Apex IV FTMS spectrometer.

2) The synthesis and spectral data of pyrazolones

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 stirred 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 Na₂SO₄. 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 stirred at 0 °C for 10 minutes. Subsequently, the ethyl 3-oxobutanoate (10 mmol) was added to this mixture slowly. Then the reaction mixture was stirred 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 Na₂SO₄. 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 Na₂SO₄. 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.

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\text{1-(2-hydroxyethyl)-3-methyl-1H-pyrazol-5(4H)-one 1b:}^2
\]

Yield 68 %; Yellow solid;

\[
{^1}H \text{ NMR (400 MHz, } d^6\text{DMSO)} \delta 5.10 \,(s, \, 1H), \, 3.76 \,(t, \, J = 6.4 \text{ Hz, } 2H ), \, 3.60 \,(t, \, J = 6.4
\]
1-benzyl-3-methyl-1H-pyrazol-5(4H)-one 1c:\textsuperscript{3}

Yield 35%; White solid;

$^1$H NMR (400 MHz, $d_6$DMSO) $\delta$ 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:\textsuperscript{4}

Yield 60%; White solid;

$^1$H NMR (400 MHz, $d_6$DMSO) $\delta$ 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);

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

Yield 45%; White solid;

$^1$H NMR (400 MHz, $d_6$DMSO) $\delta$ 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, $d_6$DMSO) $\delta$ 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$_2$O (M+H)$^+$ 189.1022, found 189.1017.

1-(4-methoxyphenyl)-3-methyl-1H-pyrazol-5(4H)-one 1g:\textsuperscript{1}
Yield 25%; White solid;

\[^{1}\text{H} \text{ NMR (400 MHz, } d^6\text{DMSO)} \delta 11.28 (s, 1H), 7.70 (d, J = 8.8 \text{ Hz, 2H}), 6.98 (d, J = 8.8 \text{ Hz, 2H}), 5.33 (s, 1H), 3.76 (s, 3H), 2.10 (s, 3H);\]

\[
\text{4-(3-methyl-5-oxo-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile 1h}^{5}
\]

Yield 60%; Yellow solid;

\[^{1}\text{H} \text{ NMR (400 MHz, } d^6\text{DMSO)} \delta 11.97 (s, 1H), 7.98 (d, J = 8.4 \text{ Hz, 2H}), 7.88 (d, J = 8.4 \text{ Hz, 2H}), 5.41 (s, 1H), 2.14 (s, 3H); \text{EIM-MS (m/z, relative intensity)}: 199 (M^+, 100), 130 (33), 116 (72), 102 (47); \text{HRMS (ESI) m/e calcd for C}_{11}\text{H}_{10}\text{N}_3\text{O (M+H)}^+ 200.0818, \text{found 200.0813.}\]

\[
\text{1,3-diphenyl-1H-pyrazol-5(4H)-one 1i}^{1}
\]

Yield 32%; White solid;

\[^{1}\text{H} \text{ NMR (400 MHz, } d^6\text{DMSO)} \delta 11.82 (s, 1H), 7.86-7.84 (m, 4H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 2H), 7.35-7.27 (m, 2H), 6.04 (s, 1H);\]

\[^{13}\text{C} \text{ NMR (100 MHz, } d^6\text{DMSO)} \delta 153.9, 149.7, 138.9, 133.5, 128.9, 128.6, 127.9, 125.7, 125.2, 121.2, 85.2;\]

3) The synthesis and spectral data of aryl sulfonyl hydrazides\(^6\)

\[
\text{The hydrazine hydrate (40%) (23 mmol) was added into the solution of aryl sulfonyl chloride (10 mmol) in THF (50 mL) at 0 °C. Subsequently, the mixture was stired at room temperature for 30 minutes. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic layer was washed with...}
\]
water, and brine, and dried over Na$_2$SO$_4$. 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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.

\[
\begin{align*}
\text{Ar}^1\text{N} & + \text{SO} \rightarrow \text{I}_2, \text{TsOH} \rightarrow \text{Ar}^1\text{N} \quad \text{R}_1^1\text{N} \quad \text{OH} \quad \text{S} \quad \text{Ar}
\end{align*}
\]
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 °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 °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, $^{d_6}$DMSO, 25 °C) $\delta$ 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, $^{d_6}$DMSO, 25 °C) $\delta$ 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$_2$OS (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, $^{d_6}$DMSO, 21 °C) $\delta$ 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, \( ^{1}H \) NMR, \( ^{13}C \) NMR, EI-MS, HRMS)

4-((4-methoxyphenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3c:
Yield 85%; Pale yellow solid

\( ^{1}H \) NMR (400 MHz, \( ^{6}DMSO \), 23 °C) \( \delta \) 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); 13C NMR (100 MHz, \( ^{6}DMSO \), 25 °C) \( \delta \) 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\(_{11}\)H\(_{13}\)N\(_{2}\)OS \((\text{M}+\text{H})^+\) 221.0743, found 221.0738.

4-((4-bromophenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3d:
Yield 85%; White solid

\( ^{1}H \) NMR (400 MHz, \( ^{6}DMSO \), 25°C) \( \delta \) 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); 13C NMR (100 MHz, \( ^{6}DMSO \), 60 °C) \( \delta \) 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\(_{2}\)OS \((\text{M}+\text{H})^+\) 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, \( ^{6}DMSO \), 25 °C) \( \delta \) 11.35 (s, 1H), 7.14-7.01 (m, 2H), 7.04-7.03 (d, 2H), 3.49 (s, 3H), 2.00 (s, 3H); 13C NMR (100 MHz, \( ^{6}DMSO \), 25 °C) \( \delta \) 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 C₁₁H₁₄FN₂OS (M+H)⁺ 239.0649, found 239.0643.

![Image of 4-((5-hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)thio)benzonitrile 3f](image)

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

Yield 85%; White solid

\(^1\)H NMR (400 MHz, \( \text{d}^6\text{DMSO}, 18 \degree \text{C}\)) \( \delta \) 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, \( \text{d}^6\text{DMSO}, 25 \degree \text{C}\)) \( \delta \) 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 C₁₂H₁₂N₂OS (M+H)⁺ 246.0696, found 246.0688.

![Image of 1,3-dimethyl-4-((4-(trifluoromethyl)phenyl)thio)-1H-pyrazol-5-ol 3g](image)

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

Yield 94%; Pale yellow solid

\(^1\)H NMR (400 MHz, \( \text{d}^6\text{DMSO}, 60 \degree \text{C}\)) \( \delta \) 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, \( \text{d}^6\text{DMSO}, 60 \degree \text{C}\)) \( \delta \) 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 C₁₂H₁₂F₃N₂OS (M+H)⁺ 289.0617, found 289.0611.

![Image of 4-((3-chlorophenyl)thio)-1,3-dimethyl-1H-pyrazol-5-ol 3h](image)

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

Yield 91%; White solid;
$^1$H NMR (400 MHz, $^{d_6}$DMSO, 25 °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, $^{d_6}$DMSO, 60 °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$_2$OS (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, $^{d_6}$DMSO, 25 °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, $^{d_6}$DMSO, 60 °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$_2$N$_2$OS (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, $^{d_6}$DMSO, 25 °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, $^{d_6}$DMSO, 60 °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$_2$OS (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, $^{6}{D}$MSO, 60 °C) $\delta$ 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, $^{6}{D}$MSO, 60 °C) $\delta$ 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$_2$O$_2$S (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, $^{6}{D}$MSO, 25 °C) $\delta$ 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, $^{6}{D}$MSO, 26 °C) $\delta$ 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$_2$O$_3$S (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, $^{6}{D}$MSO, 25 °C) $\delta$ 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, $^{6}{D}$MSO, 60 °C) $\delta$ 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_{2}O_{2}S (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, d^6^DMSO, 60 °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, d^6^DMSO, 60 °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_{2}OS (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, d^6^DMSO, 60 °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, d^6^DMSO, 60 °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_{19}N_{2}OS (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, d^6^DMSO, 25°C) δ 11.35 (s, 1H), 7.18-7.10 (m, 5H), 7.02 (d, J =
3-methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-ol 4a:

Yield 84%; White solid

$^1$H NMR (400 MHz, $^{d6}$DMSO, 25 °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 °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$_2$OS (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 °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 °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$_2$OS (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, $d^6$DMSO, 18 °C) $\delta$ 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, $d^6$DMSO, 60 °C) $\delta$ 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$_3$OS (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, $d^6$DMSO, 25 °C) $\delta$ 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, $d^6$DMSO, 25 °C) $\delta$ 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$_2$N$_2$OS (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, $d^6$DMSO, 25 °C) $\delta$ 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, $d^6$DMSO, 23 °C) $\delta$ 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$_2$OS (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, $d_6$DMSO, 25 °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, $d_6$DMSO, 60 °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; El-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$_2$OS (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, $d_6$DMSO, 25 °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, $d_6$DMSO, 60 °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$_2$O$_2$S (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, $d^6$DMSO, 60 °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, $d^6$DMSO, 60 °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) $m/e$ calcld for C$_{18}$H$_{19}$N$_2$O$_3$S (M+H)$^+$ 343.1111, found 343.1108.

![Structure of 4-((3,5-dichlorophenyl)thio)-1-(4-methoxyphenyl)-3-methyl-1H-pyrazol-5-ol 4i](image)

4-((3,5-dichlorophenyl)thio)-1-(4-methoxyphenyl)-3-methyl-1H-pyrazol-5-ol 4i:
Yield 71%; White solid

$^1$H NMR (400 MHz, $d^6$DMSO, 60 °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, $d^6$DMSO, 60 °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) $m/e$ calcld for C$_{17}$H$_{15}$Cl$_2$N$_2$O$_2$S (M+H)$^+$ 381.0226, found 381.0225.

![Structure of 4-(5-hydroxy-3-methyl-4-(p-tolylthio)-1H-pyrazol-1-yl)benzonitrile 4j](image)

4-(5-hydroxy-3-methyl-4-(p-tolylthio)-1H-pyrazol-1-yl)benzonitrile 4j:
Yield 61%; Pale yellow solid

$^1$H NMR (400 MHz, $d^6$DMSO, 60 °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, $d^6$DMSO, 60 °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) $m/e$ calcld for C$_{18}$H$_{15}$N$_3$O$_3$S (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
H NMR (400 MHz, d6DMSO, 25 °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); C NMR (100 MHz, d6DMSO, 60 °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 C18H13N4OS (M+H)+ 333.0805, found 333.0796.

1,3-diphenyl-4-(p-tolylthio)-1H-pyrazol-5-ol 4l:
Yield 61%; Pale yellow solid
H NMR (400 MHz, d6DMSO, 25 °C) δ 12.36 (s, 1H), 7.88-7.84 (m, 4H), 7.10 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H); C NMR (100 MHz, d6DMSO, 60 °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 C22H19N2OS (M+H)+ 359.1213, found 359.1212.
5) The spectrum of unknown pyrazolone and pyrazolone thioethers
6) Optimization of I₂-catalysed reaction of 1a with 2a

![Reaction scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>I₂ (equiv)</th>
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<th>t (h)</th>
<th>T (°C)</th>
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*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 I₂ and TsOH in the cross-coupling of 1f with 2a

![Reaction scheme](image)

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<th>Entry</th>
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<th>Yield (%)b</th>
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*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. *e* The reaction time was 12 h.
8) The effects of TsOH on the reaction.

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

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a Yield of isolated product after chromatography with silica gel.

10) TsOH catalyzed reaction in the absence of I₂.

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<tbody>
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11) The effect of TsOH in the catalysis of 5-nitroindole of phenyl sulphonyl hydrazide

References: