Supplementary Information

Metal-free molecular iodine-catalyzed direct sulfonation of pyrazolones with sodium sulfinates leading to sulfonated pyrazoles at room temperature

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1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were freshly distilled and dried according to standard procedures. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ on a Bruker Avance III 500 spectrometer with TMS as internal standard (500 MHz $^1$H, 125 MHz $^{13}$C) at room temperature, the chemical shifts ($\delta$) were expressed in ppm and $J$ values were given in Hz. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m or brs). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. FT-IR spectrum was performed using a Thermo Fisher Nicolet IS5. Column chromatography was performed on silica gel (200 - 300 mesh).
2. General procedure for molecular iodine-catalyzed sulfonylation of pyrazolones with sodium sulfinates leading to sulfonated pyrazoles

\[
\begin{align*}
&\text{R}^1\text{N} - \text{R}^2 \quad + \quad \text{R}^2\text{SO}_2\text{Na} \\
&\text{I}_2 (2 \text{ mol\%}) \\
&\text{DME, rt, 2-4h} \\
&\text{HO} - \text{O} - \text{S} - \text{R}^3
\end{align*}
\]

1,2-Dimethoxyethane (2 mL) was added to a mixture of pyrazolone 1 (0.25 mmol), sodium sulfinates 2 (0.5 mmol), I\(_2\) (2 mol%), and TBHP (70% in water, 0.25 mmol) in a 25 mL round-bottomed flask at room temperature. The reaction vessel was allowed to stir at room temperature for 2-4h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of dichloromethane and methanol as eluent to give the desired products.

3. Preliminary mechanistic studies

3.1 The model reaction was performed in the presence of TEMPO

\[
\begin{align*}
&\text{Ph-N} - \text{Ph} \\
&\text{Ph} - \text{SO}_2\text{Na} \\
&\text{I}_2 (2 \text{ mol\%}) \\
&\text{DME, rt, 2h (TEMPO 2 equiv)} \\
&\text{Ph-N} - \text{O} - \text{S} - \text{Ph} (92\%)
\end{align*}
\]

TEMPO (0.5 mmol) was added to a mixture of pyrazolone 1a (0.25 mmol, 43.5 mg), sodium sulfinate 2a (0.5 mmol, 82 mg), I\(_2\) (2 mol%), TBHP (70% in water, 0.25 mmol) and 1,2-dimethoxyethane (2 mL) in a 25 mL round-bottomed flask at room temperature. The reaction vessel was allowed to stir at room temperature for 2h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of dichloromethane and methanol as eluent to give the desired product 3aa in 92% yield.

3.2 The model reaction was performed in the presence of BHT
BHT (0.5 mmol, 110.2 mg) was added to a mixture of pyrazolone 1a (0.25 mmol, 43.5 mg), sodium sulfinate 2a (0.5 mmol, 82 mg), I\(_2\) (2 mol%) and 1,2-dimethoxyethane (2 mL) in a 25 mL round-bottomed flack at room temperature under air. The reaction vessel was allowed to stir at room temperature for 2h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of dichloromethane and methanol as eluent to give the desired product 3aa in 94% yield.

3.3 The reaction of pyrazolone 1a and sodium sulfinate 2a in the presence of I\(_2\) (1 equiv)

1,2-Dimethoxyethane (2 mL) was added to a mixture of pyrazolone 1 (0.25 mmol), sodium sulfinites 2 (0.5 mmol), and I\(_2\) (0.25 mmol) in a 25 mL round-bottomed flack at room temperature. The reaction vessel was allowed to stir at room temperature for 2h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of dichloromethane and methanol as eluent to give the desired product 3aa in 84% yield.

3.4 The reaction of pyrazolone 1a and sulfonyl iodide 4b

1,2-Dimethoxyethane (2 mL) was added to a mixture of pyrazolone 1a (43.5 mg, 0.25 mmol), sodium sulfinic acid 2 (0.5 mmol), I\(_2\) (0.25 mmol) and 1,2-dimethoxyethane (2 mL) in a 25 mL round-bottomed flack at room temperature. The reaction vessel was allowed to stir at room temperature for 2h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of dichloromethane and methanol as eluent to give the desired product 3ab in 84% yield.
0.25 mmol), sulfonyl iodide 4b (141mg, 0.5 mmol) and DME (2 mL) in a 25 mL round-bottomed flack at room temperature under air. The reaction vessel was allowed to stir at room temperature for 2h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of dichloromethane and methanol as eluent to give the desired product 3ab in 60% yield.

5. Characterization data of products 3aa-3la

![3aa](attachment:image)

3-methyl-1-phenyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3aa was obtained in 96% yield according to the general procedure (2h). Yellow solid, mp: 210.2-212.1 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 8.00 (d, $J = 9.5$ Hz, 2H), 7.84 (d, $J = 9.7$ Hz, 2H), 7.50 (t, $J = 9.2$ Hz, 1H), 7.42 (t, $J = 7.3$ Hz, 2H), 7.30 (t, $J = 9.6$ Hz, 2H), 7.12 (t, $J = 9.1$ Hz, 1H), 2.21 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 160.9, 147.0, 144.4, 138.7, 132.1, 128.7, 128.3, 125.8, 124.8, 121.0, 96.3, 12.7. IR (KBr): OH 3429cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{14}$N$_2$O$_3$SNa (M + Na)$^+$ 337.0623, found 337.0616.

![3ab](attachment:image)

3-methyl-1-phenyl-4-tosyl-1H-pyrazol-5-ol, Compound 3ab was obtained in 96% yield according to the general procedure (3h). Yellow solid, mp: 191.7-192.1 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 7.87 (d, $J = 8.3$ Hz, 2H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.30 (t, $J = 6.3$ Hz, 2H), 7.23 (d, $J = 6.2$ Hz, 2H), 7.13 (t, $J = 6.8$ Hz, 1H), 2.37 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 161.6, 146.9, 143.0, 141.7, 139.2, 129.1, 128.2, 125.8, 124.4, 120.8, 95.5, 20.1, 12.7. IR (KBr): OH 3421cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{16}$N$_2$O$_3$SNa (M + Na)$^+$ 351.0779, found 351.0781.
4-(4-methoxyphenylsulfonyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol, Compound 3ac was obtained in 85% yield according to the general procedure (2h). Yellow solid, mp: 191.5-192.8 °C. ¹H NMR (CD₃OD, 500 MHz, ppm): δ 7.92 (d, J = 8.9 Hz, 2H), 7.85 (d, J = 7.7 Hz, 2H), 7.31 (brs, 2H), 7.14 (brs, 1H), 6.90 (brs, 2H), 3.81 (s, 3H), 2.17 (s, 3H); ¹³C NMR (CD₃OD, 125 MHz, ppm): 162.8, 161.4, 146.8, 139.1, 136.2, 128.2, 128.0, 124.5, 120.8, 113.7, 95.9, 54.8, 12.7. IR (KBr): OH 3438 cm⁻¹; HRMS (ESI) calcd for C₁₇H₁₆N₂O₄S (M + Na)⁺ 367.0728, found 367.0732.

4-(4-fluorophenylsulfonyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol, Compound 3ad was obtained in 60% yield according to the general procedure (4h). Yellow solid, mp: 220.0-221.7 °C. ¹H NMR (CD₃OD, 500 MHz, ppm): δ 8.05-8.02 (m, 2H), 7.85 (d, J = 7.9 Hz, 2H), 7.30 (brs, 2H), 7.13 (brs, 3H), 2.19 (s, 3H); ¹³C NMR (CD₃OD, 125 MHz, ppm): 164.8 (d, J = 252.2Hz), 161.8, 150.4, 146.8, 141.0, 139.2, 128.6 (d, J = 7.0 Hz), 128.1, 124.4, 120.8, 115.5 (d, J = 22.1 Hz), 95.0, 12.8. IR (KBr): OH 3421 cm⁻¹; HRMS (ESI) calcd for C₁₆H₁₃FN₂O₃SNa (M + Na)⁺ 355.0529, found 355.0531.

4-(4-bromophenylsulfonyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol, Compound 3ae was obtained in 90% yield according to the general procedure (4h). White solid, mp: 209.1-210.6 °C. ¹H NMR (CD₃OD, 500 MHz, ppm): δ 7.88 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 7.9 Hz, 2H), 7.57 (brs, 2H), 7.32 (brs, 2H), 7.14 (brs, 1H), 2.20 (s, 3H); ¹³C NMR (CD₃OD, 125 MHz, ppm): 161.7, 146.7, 143.8, 138.9, 131.8, 128.2, 127.5, 126.6, 124.6, 120.8, 94.6, 12.9. IR (KBr): OH 3420 cm⁻¹; HRMS (ESI) calcd for
N-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-ylsulfonyl)phenyl)acetamide, Compound 3af was obtained in 89% yield according to the general procedure (3h). Yellow solid, 262.1-263.1 °C. ¹H NMR (CD₃OD, 500 MHz, ppm): δ 7.91 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 6.0 Hz, 2H), 7.63 (d, J = 6.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.13 (t, J = 6.9 Hz, 1H), 2.22 (s, 3H), 2.14 (s, 3H); ¹³C NMR (CD₃OD, 125 MHz, ppm): 170.6, 161.5, 147.0, 142.3, 139.3, 139.1, 128.2, 126.8, 124.6, 120.9, 119.0, 96.2, 22.7, 12.9. IR(KBr): OH 3425 cm⁻¹; HRMS (ESI) calcd for C₁₈H₁₇N₃O₄SNa (M + Na)⁺ 394.0837, found 394.0832.

3-methyl-4-(naphthalen-2-ylsulfonyl)-1-phenyl-1H-pyrazol-5-ol, Compound 3ag was obtained in 88% yield (78.2 mg) according to the general procedure (4h). White solid, mp: 221.2-222.8 °C. ¹H NMR (CD₃OD, 500 MHz, ppm): δ 8.54 (s, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.78 (brs, 3H), 7.54 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 6.6 Hz, 1H), 7.27 (brs, 2H), 7.09 (brs, 1H), 2.22 (s, 3H); ¹³C NMR (CD₃OD, 125 MHz, ppm): 162.0, 146.8, 141.3, 139.2, 134.6, 132.0, 128.8, 128.2, 127.4, 127.0, 126.3, 124.4, 121.6, 120.7, 95.1, 12.9. IR(KBr): OH 3394 cm⁻¹; HRMS (ESI) calcd for C₂₀H₁₆N₂O₃SNa (M + Na)⁺ 387.0779, found 387.0774.

3-methyl-1-phenyl-4-(pyridin-3-ylsulfonyl)-1H-pyrazol-5-ol, Compound 3ah was obtained in 87% yield according to the general procedure (4h). Yellow solid, mp: 231.7-232.7 °C. ¹H NMR (CD₂OD, 500 MHz, ppm): δ 9.11 (d, J = 2.0 Hz, 1H), 8.68 (s, 1H), 8.38 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.47 (brs, 1H), 7.30 (t, J =
7.0 Hz, 2H), 7.13 (t, J = 6.8 Hz, 1H), 2.22 (s, 3H); 13C NMR (CD3OD, 125 MHz, ppm): 162.0, 152.0, 146.8, 146.0, 141.7, 139.1, 134.2, 128.1, 124.5, 124.0, 120.8, 94.4, 12.9. IR(KBr): OH 3429 cm⁻¹; HRMS (ESI) calcd for C15H13N2O3SNa (M + Na)⁺ 338.0575, found 338.0577.

3-methyl-1-phenyl-4-(thiophen-3-ylsulfonyl)-1H-pyrazol-5-ol, Compound 3ai was obtained in 66% yield according to the general procedure (4h). Yellow solid, mp: 210.7-212.6 °C. 1H NMR (CD3OD, 500 MHz, ppm): δ 7.83 (d, J = 8.1 Hz, 2H), 7.72 (dd, J₁ = 3.7 Hz, J₂ = 1.1 Hz, 1H), 7.68 (brs, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.02 (brs, 1H), 2.26 (s, 3H); 13C NMR (CD3OD, 125 MHz, ppm): 161.1, 146.9, 146.5, 139.0, 131.2, 130.5, 128.2, 127.0, 124.6, 120.9, 96.6, 12.8. IR(KBr): OH 3360 cm⁻¹; HRMS (ESI) calcd for C14H12N2O3SNa (M + Na)⁺ 343.0187, found 343.0189.

(5-methyl-4-(methylsulfonyl)-2-phenyl-1H-pyrazol-3(2H)-one, Compound 3aj was obtained in 78% yield according to the general procedure (2h). White solid, mp: 241.3-242.9 °C. 1H NMR (CD3OD, 500 MHz, ppm): δ 7.81 (d, J = 7.9 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 3.10 (s, 3H), 2.31 (s, 3H); 13C NMR (CD3OD, 125 MHz, ppm): 161.4, 146.8, 139.0, 128.2, 124.8, 121.1, 95.3, 44.2, 20.9, 12.6. IR(KBr): OH 3437 cm⁻¹; HRMS (ESI) calcd for C11H12N2O3S2Na (M + Na)⁺ 275.0466, found 275.0460.

1-(4-methoxyphenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3ba was obtained in 65% yield according to the general procedure (4h). White solid,
mp: 206.7-270.6 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 7.91 (d, $J = 8.9$ Hz, 2H), 7.85 (d, $J = 7.7$ Hz, 2H), 7.31 (brs, 2H), 7.13 (brs, 1H), 6.90 (brs, 2H), 3.81 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 162.8, 161.4, 146.8, 139.1, 136.2, 128.2, 128.0, 124.5, 120.8, 113.7, 95.9, 54.8, 12.7. IR(KBr): OH 3455 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{16}$N$_2$O$_4$SNa (M + Na)$^+$ 367.0728, found 367.0731.

(3ca)

3-methyl-4-(phenylsulfonyl)-1-p-tolyl-1H-pyrazol-5-ol, Compound 3ca was obtained in 98% yield according to the general procedure (2h). Yellow solid, mp: 222.1-222.7 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 8.00 (d, $J = 7.5$ Hz, 2H), 7.68 (d, $J = 8.1$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 6.6$ Hz, 2H), 7.11 (d, $J = 6.6$ Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 161.5, 146.6, 144.6, 136.7, 134.3, 132.0, 128.7, 128.6, 125.7, 121.0, 95.0, 19.6, 12.8. IR(KBr): OH 3421 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{16}$N$_2$O$_3$SNa (M + Na)$^+$ 351.0779, found 351.0783.

(3cb)

3-methyl-1-p-tolyl-4-tosyl-1H-pyrazol-5-ol, Compound 3cb was obtained in 98% yield according to the general procedure (2h). White solid, mp: 229.7-230.8 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 7.86 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 7.4$ Hz, 2H), 7.22 (brs, 2H), 7.12 (d, $J = 7.6$ Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 161.4, 146.9, 143.3, 141.0, 136.6, 134.3, 129.1, 128.7, 125.9, 121.1, 95.0, 20.1, 19.6, 12.7. IR(KBr): OH 3438 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{18}$N$_2$O$_3$SNa (M + Na)$^+$ 365.0936, found 365.0937.

(3da)

1-(3,4-dimethylphenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound
3da was obtained in 82% yield according to the general procedure (2h). Yellow solid, mp: 211.7-212.8 °C. 1H NMR (CD$_3$OD, 500 MHz, ppm): δ 8.01 (d, J = 7.7 Hz, 2H), 7.55 (brs, 2H), 7.46 (brs, 3H), 7.07 (d, J = 7.9 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 6H); 13C NMR (CD$_3$OD, 125 MHz, ppm): 161.0, 146.5, 144.4, 136.5, 136.4, 133.3, 132.1, 129.3, 128.6, 125.9, 122.4, 118.8, 96.1, 18.6, 17.9, 12.6. IR(KBr): OH 3418 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{18}$N$_2$O$_3$SNa (M + H)$^+$ 365.0936, found 365.0939.

![3ea](image1)

1-(4-fluorophenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3ea was obtained in 91% yield according to the general procedure (2h). White solid, mp: 201.7-202.5 °C. 1H NMR (CD$_3$OD, 500 MHz, ppm): δ 8.00 (d, J = 7.8 Hz, 2H), 7.85-7.82 (dd, J$_1$ = 8.5 Hz, J$_2$ = 5.0 Hz, 2H), 7.54 (t, J = 5.5 Hz, 1H), 7.47 (t, J = 6.4 Hz, 2H), 7.00 (brs, 2H), 2.18 (s, 3H); 13C NMR (CD$_3$OD, 125 MHz, ppm): 161.9, 159.8 (d, J = 244.3 Hz), 146.9, 145.0, 135.7, 132.1, 128.6, 125.7, 122.5 (d, J = 7.6 Hz), 114.7 (d J = 22.5 Hz), 94.9, 12.8. IR(KBr): OH 3412 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{13}$FN$_2$O$_3$SNa (M + Na)$^+$ 355.0529, found 355.0533.

![3fa](image2)

1-(4-chlorophenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3fa was obtained in 95% yield according to the general procedure (4h). Yellow solid, mp: 241.9-242.7 °C. 1H NMR (CD$_3$OD, 500 MHz, ppm): δ 8.00 (d, J = 7.7 Hz, 2H), 7.89 (d, J = 8.9 Hz, 2H), 7.53 (t, J = 6.7 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.22 (d, J = 7.4 Hz, 2H), 2.17 (s, 3H); 13C NMR (CD$_3$OD, 125 MHz, ppm): 161.9, 147.2, 144.6, 138.0, 132.1, 129.1, 128.6, 128.1, 125.7, 121.5, 95.1, 12.8. IR(KBr): OH 3429 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{13}$ClN$_2$O$_3$SNa (M + Na)$^+$ 371.0233, found 371.0237.
1-(4-chlorophenyl)-3-methyl-4-tosyl-1H-pyrazol-5-ol, Compound 3fb was obtained in 98% yield according to the general procedure (2h). Yellow solid, mp: 219.7-220.6 °C. \( ^1 \)H NMR (CD\(_3\)OD, 500 MHz, ppm): \( \delta \) 7.87 (d, \( J = 2.5 \) Hz, 2H), 7.85 (d, \( J = 2.4 \) Hz, 2H), 7.22 (d, \( J = 6.6 \) Hz, 4H), 2.37 (s, 3H), 2.16 (s, 3H); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz, ppm): 161.8, 147.3, 143.0, 141.7, 138.0, 129.3, 129.1, 128.1, 125.8, 121.6, 95.4, 20.1, 12.8. IR(KBr): OH 3428 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{15}\)ClN\(_2\)O\(_3\)SNa (M + Na\(^+\)) 385.0390, found 385.0395.

1-(3-chlorophenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3ga was obtained in 95% yield according to the general procedure (2h). Yellow solid, mp: 232.1-233.2 °C. \(^1\)H NMR (CD\(_3\)OD, 500 MHz, ppm): \( \delta \) 8.02 (s, 1H), 7.99 (d, \( J = 7.7 \) Hz, 2H), 7.87 (d, \( J = 8.2 \) Hz, 1H), 7.53 (brs, 1H), 7.43 (brs, 2H), 7.24 (brs, 1H), 7.09 (brs, 1H), 2.18 (s, 3H); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz, ppm): 162.2, 147.5, 144.5, 140.5, 133.7, 132.1, 129.4, 128.6, 125.7, 123.7, 119.8, 118.0, 95.2, 12.9. IR(KBr): OH 3438 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{13}\)ClN\(_2\)O\(_3\)SNa (M + Na\(^+\)) 371.0233, found 371.0234.

1-(2-chlorophenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3ha was obtained in 93% yield according to the general procedure (2h). Yellow solid, mp: 221.7-222.9 °C. \(^1\)H NMR (CD\(_3\)OD, 500 MHz, ppm): \( \delta \) 7.99 (d, \( J = 7.4 \) Hz, 2H), 7.57 (t, \( J = 7.4 \) Hz, 1H), 7.52-7.48 (m, 3H), 7.40-7.32 (m, 3H), 2.17 (s, 3H); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz, ppm): 162.2, 147.0, 144.7, 136.1, 132.6, 132.0, 130.3, 129.8, 129.3, 128.6, 127.1, 125.6, 94.1, 12.9. IR(KBr): OH 3429 cm\(^{-1}\); HRMS (ESI) calcd for
C_{16}H_{13}ClN_{2}O_{3}SNa (M + Na)^+ 371.0233, found 371.0235.

1-(2-chlorophenyl)-3-methyl-4-tosyl-1H-pyrazol-5-ol, Compound 3hb was obtained in 92% yield according to the general procedure (2h). Yellow solid, mp: 211.7-212.9 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 7.86 (d, $J = 8.2$ Hz, 2H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.38-7.32 (m, 3H), 7.28 (d, $J = 7.4$ Hz, 2H), 2.41 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 162.1, 147.0, 143.0, 141.6, 136.1, 132.6, 130.2, 129.7, 129.3, 129.1, 127.0, 125.8, 94.4, 20.1, 12.8. IR(KBr): OH 3428 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{15}$ClN$_{2}$O$_{3}$SNa (M + Na)$^+$ 385.0390, found 385.0395.

1-(4-bromophenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3ia was obtained in 90% yield according to the general procedure (4h). Yellow solid, mp: 229.2-230.7 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 7.99 (d, $J = 7.8$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 2H), 7.54 (brs, 1H), 7.45 (brs, 2H), 7.38 (brs, 2H), 2.16 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 162.0, 147.3, 144.5, 138.5, 132.1, 131.1, 128.6, 125.7, 121.8, 116.8, 95.0, 12.8. IR(KBr): OH 3429 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{13}$BrN$_{2}$O$_{3}$SNa (M + Na)$^+$ 414.9728, found 414.9731.

3-methyl-4-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5-ol, Compound 3ja was obtained in 74% yield according to the general procedure (4h). White solid, mp: 209.6-210.7 °C. $^1$H NMR (CD$_3$OD, 500 MHz, ppm): $\delta$ 8.16 (d, $J = 8.6$ Hz, 2H), 8.01 (d, $J = 7.7$ Hz, 2H), 7.54-7.46 (m, 5H), 2.18 (s, 3H); $^{13}$C NMR (CD$_3$OD, 125 MHz, ppm): 162.6, 147.9, 144.6, 142.4, 132.1 (d, $J = 4.3$ Hz), 128.6, 127.6, 125.7, 125.2 (d, $J = 13.9$ Hz), 124.4 (d, $J = 278.7$ Hz), 119.3, 95.2, 12.9.
IR(KBr): OH 3429 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}H_{13}F_3N_2O_3SNa (M + Na)^+\) 405.0497, found 405.0499.

1,3-dimethyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol, Compound 3ka was obtained in 60% yield according to the general procedure (2h). White solid, mp: 250.3-251.7 \(^{\circ}\)C. \(^1\)H NMR (CD\(_3\)OD, 500 MHz, ppm): \(\delta\) 7.95 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 6.7 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 3.36 (s, 3H), 2.13 (s, 3H); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz, ppm): 160.2, 145.3, 132.0, 129.2, 128.6, 125.6, 96.4, 30.2, 12.4. IR(KBr): OH 3534 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{11}H_{12}N_2O_3SNa (M + Na)^+\) 275.0466, found 275.0469.

1-phenyl-4-(phenylsulfonyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol, Compound 3la was obtained in 44% yield according to the general procedure (4h). Yellow solid, mp: 232.2-233.2 \(^{\circ}\)C. \(^1\)H NMR (CD\(_3\)OD, 500 MHz, ppm): \(\delta\) 7.83 (d, J = 7.9 Hz, 2H), 7.73 (d, J = 7.9 Hz, 2H), 7.51-7.49 (m, 3H), 7.38 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz, ppm): 161.8, 143.8, 139.0, 130.2, 128.7, 128.3, 125.5, 125.2, 121.9 (d, J = 265.3 Hz), 121.3, 121.1 (d, J = 267.8 Hz), 99.9. IR(KBr): OH 3395 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}H_{11}F_3N_2O_3SNa (M + Na)^+\) 391.0340, found 391.0346.
6. Copies of NMR spectra for compounds 3aa–3la

3aa
3ca
3ab