KIO₃ 促进的直接合成硫化或磺酰化吡唑啉酮及其抗菌活性董道青^{†,a} 陈文静^{†,a} 陈德茂^a 李丽霞^a 李光辉^a
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摘要 建立了由 KIO₃ 促进的合成硫化或磺酰化的吡唑啉酮的简便有效的方法. 以中等至高产率获得各种所需产物. 该方法可在比较温和的反应条件下进行, 无需任何金属. 对照实验表明, 该反应的机理与先前的 KIO₃ 催化反应不同. 其中一些产物对苹果腐烂菌和灰霉病菌有很高的抑制活性.

关键词 C—S 键, 磺酰化, 硫化, 吡唑啉酮, 碘试剂, 抑菌活性

Direct Synthesis of Sulfonated or Sulfenylated Pyrazolones Mediated by KIO₃ and Their Anti-microbial ActivityDong, Daoqing^{†,a} Chen, Wenjing^{†,a} Chen, Demao^a Li, Lixia^a Li, Guanghui^a
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Abstract A facile and efficient method for the synthesis of sulfonated or sulfenylated pyrazolones catalyzed by KIO₃ was established. A variety of desired products were obtained in moderate to high yields. This methodology could be conducted under mild reaction conditions without requiring any metal. Control experiments showed that the mechanism of this reaction was different from previous KIO₃-catalyzed reactions. Some of these desired products showed high inhibitory activity against *V. mali* and *B. cinerea*.

Keywords C—S bond; sulfonylation; sulfenylation; pyrazolones; iodine reagents; anti-microbial activity

1 Introduction

Pyrazole and its derivatives are important heterocycles and prominent chemical entities which have been found in diverse pharmacological and biologically-active compounds.^[1] Accordingly, more and more efforts have been devoted to the development of a synthetic methodology for the chemical derivatization on the pyrazole nucleus. In particular, the syntheses of sulfenylated or sulfonated pyrazoles have received much attention in organic

chemistry because of their usefulness as herbicidal agents,^[2] antioxidants,^[3] agrochemicals, and materials.^[4] Previous method for the synthesis of sulfonated pyrazoles suffer from the extra steps needed for the preparation of active precursors.^[5] For example, in 2017, Wang and his coworkers^[6] developed a convenient molecular iodine-catalyzed direct sulfonylation of pyrazolones at room temperature (Figure 1b). Shermolovich *et al.*^[7a] had earlier described a protocol for the oxidation of preformed pyrazolones by employing stoichiometric amounts of *m*-

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chloroperoxybenzoic acid (*m*-CPBA) or H₂O₂ (Figure 1a). Our group^[7b] also realized the sulfonylation of pyrazolones using water as solvent (Figure 1c). In 2014, Lu *et al.*^[8] reported sulphenylation of pyrazolones with aryl sulphonylhydrazides catalyzed by I₂. A tetrabutylammonium iodide (TBAI)-HBr system which mediated the reaction between pyrazolones and benzenesulfonyl chlorides was realized by Yan's group.^[9] In 2016, Wang's group^[10] found that NaOH was good promoter for sulphenylation of pyrazolones. In 2017, Wang *et al.*^[11] obtained the sulphenylated pyrazoles via a radical pathway promoted by dimethyl sulfoxide (DMSO). Nevertheless, it is still of interest to develop simple and efficient methods for the synthesis of sulphenylated or sulfonated pyrazoles.

Figure 1 Synthesis of sulfonated pyrazoles.

Compared with other metal catalysts, iodine reagent has the merits of low cost, ready availability, non-toxicity *etc.* At present, various reactions such as sulfonylation,^[12] cyclization,^[13] oxidation *etc.*,^[14] have been successfully realized in the presence of iodine reagents.^[15] With our on-going interest in iodine reagent-catalyzed reactions and C—H bond activation,^[16] herein the KIO₃ mediated reaction for the synthesis of sulfonated or sulphenylated pyrazoles was present.

2 Results and discussion

Initially, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**A1**) and sodium benzenesulfinate (**B1**) were chosen as model substrate for optimization of the reaction condition. When the model reaction was conducted in DMSO, the product was generated in 35% yield (Table 1, Entry 1). Other solvents such as 1,2-dimethoxyethane, tetrahydrofuran (THF), ethylene glycol also gave low yields (Table 1, Entries 2, 4, 5). The desired product could be achieved in higher yield (62%) when ethanol was the solvent (Table 1, Entry 3). However, only trace amount of product was detected when reaction was carried out in CH₃CN, CHCl₃, 1,2-dichloroethane, 1,4-dioxane, toluene (Table 1, Entries

6~10). To our delight, higher yield of product (86%) was obtained when the reaction temperature was changed to 120 °C (Table 1, Entry 11). If the reaction temperature was further elevated to 130 °C, however, no improvement on the yield of product was observed (Table 1, Entry 12). Furthermore, reducing the amounts of catalyst lead to a decreased yield of product (Table 1, Entry 13). When no KIO₃ was added or KCl was used as catalyst, the reaction did not proceed (Table 1, Entries 14, 15). The desired product could be obtained in 83% yield when the reaction was conducted under N₂ atmosphere (Table 1, Entry 16).

Table 1 Optimization of the conditions^a

Entry	Catalyst (equiv.)	Solvent	T/°C	Yield/%
1	KIO ₃ (0.30)	DMSO	100	35
2	KIO ₃ (0.30)	1,2-Dimethoxyethane	100	40
3	KIO ₃ (0.30)	EtOH	100	62
4	KIO ₃ (0.30)	THF	100	24
5	KIO ₃ (0.30)	Ethylene glycol	100	48
6	KIO ₃ (0.30)	CH ₃ CN	100	Trace
7	KIO ₃ (0.30)	CHCl ₃	100	Trace
8	KIO ₃ (0.30)	1,2-Dichloroethane	100	Trace
9	KIO ₃ (0.30)	1,4-Dioxane	100	Trace
10	KIO ₃ (0.30)	Toluene	100	Trace
11	KIO ₃ (0.30)	EtOH	120	86
12	KIO ₃ (0.30)	EtOH	130	86
13	KIO ₃ (0.20)	EtOH	120	78
14 ^b	—	EtOH	120	NR
15	KCl	EtOH	120	NR
16 ^c	KIO ₃ (0.30)	EtOH	120	83

^a reaction conditions: **A1** (0.25 mmol, 1.0 equiv.), **B1** (1.3 equiv.), KIO₃, solvent (1 mL), 8 h. ^b KIO₃ was not added. ^c Under N₂.

With the optimized reaction conditions in hand, the scope of the reaction was examined and it was found that a variety of substrates were applicable to this transformation. As shown in Table 2, pyrazolones which have electron-donating or electron-withdrawing groups on the aryl rings such as 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5(4*H*)-one, 1-(4-chlorophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one and 1-(2-chlorophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one were suitable for this reaction and the desired products were obtained in moderate to high yields (**C1**~**C8**). For the substituted sodium sulfonates, different groups were also well-tolerated in this transformation (**C9**~**C13**). As it is well-known, F is an important substituent in organic synthesis. It is noteworthy that when sodium 4-fluorobenzenesulfinate

Table 2 Sulfonylation of pyrazolones with sodium sulfinates

Reaction conditions: pyrazolones (0.25 mmol, 1.0 equiv.), sodium sulfite (1.3 equiv.), KIO₃ (0.30 equiv.), EtOH (1 mL), 120 °C, 8 h.

was tested, the desired products were obtained in 73%~82% yields (**C10**, **C11**). To our delight, sodium methanesulphinate also worked smoothly in the reaction, affording the corresponding products in moderate yields (**C14**, **C15**).

In order to further explore KIO₃-catalyzed reactions, the reaction between 4-methylbenzenethiol and 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one was also tested in the presence of KIO₃. When EtOH was used as solvent, the desired product was obtained in 60% yield. After a series of reaction condition screening experiments, the optimized reaction conditions for this reaction were found to be KIO₃ (0.30 equiv.) as catalyst, CHCl₃ as solvent at 100 °C for 8 h.

Having the optimized reaction conditions in hand, the scope of substrates which could be used were next investigated (Table 3). When 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one was tested, the product **E1** was obtained in 90% yield. Other substituents, such as Cl and CH₃ on the phenyl ring of pyrazolones were also tolerated in this system (**E2**, **E3**). It is possible that the steric effect plays an important role on the yields. When substituents are on the 4-position of aryl thiols, the corresponding products were afforded in high yields (**E10**~**E16**). On the other hand, when substituents are on 3-position or 2-position of aryl thiols, relatively lower yields were observed (**E4**~**E9**). Naphthalene-1-thiol was also well

tolerated in this reaction and the desired product was obtained in 80% yields (**E17**). To our disappointment, there was no corresponding product when 1,3-dimethyl-1*H*-pyrazol-5(4*H*)-one was subjected to this transformation (**E18**).

Although the reaction mechanism is not clear at this stage, a control experiment was performed to gain an insight into this transformation. When reactions were carried out in the presence of a radical scavenger such as, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), reactions were obviously inhibited (Scheme 1). This result revealed that a radical pathway might be involved in the transformation. This is different from the previously reported KIO₃-catalyzed reactions.^[15h-15j] In those reported KIO₃-catalyzed reactions, the possibility of a radical pathway was excluded.

With a view to discovering the biological activity of these desired products, several products from Tables 2 and 4 were preliminarily screened for anti-microbial activity. It can be seen from Table 4 that products **C4**, **E2**, **E11**, **E12**, **E14**, **E15** and **E16** exhibited significant inhibitory activity against *Valsa mali*. Compound **C4** showed 78% inhibition of *Botrytis cinerea*. These inhibition values are higher than those reported for Carbendazim.^[17,18] To our disappointment, all the compounds were not very active to *C. gloeosporioides* and the highest inhibition rated was 50.52%.

Table 3 Reaction of pyrazolones with aryl thiols

Reaction conditions: pyrazolones (0.25 mmol, 1.0 equiv.), thiols (1.3 equiv.), KIO₃ (0.30 equiv.), CHCl₃ (1 ml), 100 °C, 8 h

Scheme 1 Control experiments**Table 4** Antifungal activity of synthetic compounds (inhibition rate/%)

Compd.	<i>V. mali</i>	<i>B. cinerea</i>	<i>C. gleosporioides</i>
C4	82.63	78.15	25.81
E2	81.38	58.82	24.26
E12	81.12	66.39	50.52
E14	83.33	56.17	39.69
E16	81.67	34.40	38.92
E15	70.34	38.25	26.29
E11	75.34	52.9	20.73
E3	57.66	56.15	11.11

to high yields in mild reaction condition. Radical was proposed for this reaction mechanism which is different from previous KIO₃-catalyzed C—S bond formation reactions. Further studies into the reaction mechanism and bioactivity are ongoing in our laboratory.

3 Conclusions

In summary, an efficient and facile method for construction of sulfonated or sulfenylated pyrazolones has been successfully developed. Without additional oxidant, a variety of desired products could be obtained in moderate

4 Experimental section

4.1 Instruments and reagents

NMR spectra were recorded on a BRUKER AVANCE III HD 500 MHz spectrometers, operating at 500 MHz for ¹H NMR and at 126 MHz for ¹³C NMR acquisitions. HRMS

spectra were performed on a Orbitrap Fusion Lumos. All major chemicals and solvents were obtained from commercial sources and used without further purification.

4.2 General procedure for the synthesis of C and E

Typical procedure for the synthesis of sulfonylated pyrazolones: A sealable reaction tube equipped with a magnetic stirrer bar was charged with pyrazolone (0.5 mmol), sodium benzenesulfinate (1.3 equiv.), KIO_3 (0.3 equiv.), and EtOH (2 mL). The reaction vessel was sealed and carried out 120 °C under air. After completion (detected by thin-layer chromatography), it was diluted with ethyl acetate, washed with water and brine, dried with Mg_2SO_4 . After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, $V:V=1:3$) to afford the corresponding product.

Typical procedure for the synthesis of sulfenylated pyrazolones: A sealable reaction tube equipped with a magnetic stirrer bar was charged with pyrazolone (0.5 mmol), thiols (1.3 equiv.), KIO_3 (0.3 equiv.), CHCl_3 (2 mL). The reaction vessel was sealed and carried out 100 °C under air. After completion (detected by TLC), it was diluted with ethyl acetate, washed with water and brine, dried with Mg_2SO_4 . After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (methanol/dichloromethane, $V:V=1:10$) to afford the corresponding product.

4.3 Characterization of the compounds

3-Methyl-1-phenyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol (**C1**): 67.6 mg, yield 86%. White solid, m.p. 191~192 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 8.00 (d, $J=8.1$ Hz, 2H), 7.93 (d, $J=6.8$ Hz, 2H), 7.50 (d, $J=7.2$ Hz, 3H), 7.26 (t, $J=7.7$ Hz, 2H), 6.97 (t, $J=7.0$ Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 162.69 (s), 147.05 (s), 146.07 (s), 141.19 (s), 131.65 (s), 129.01 (s), 128.62 (s), 125.71 (s), 122.62 (s), 118.24 (s), 95.28 (s), 15.61 (s); IR (KBr) ν : 1580, 1507, 1456, 1132 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}_2\text{S}$ [$\text{M}-\text{H}$] $^-$ 313.06524; found 313.06485.

3-Methyl-1-phenyl-4-tosyl-1H-pyrazol-5-ol (**C2**): 64.9 mg, yield 79%. Brown solid, m.p. 170~172 °C; ^1H NMR (500 MHz, $\text{CD}_3\text{OD}-d_4$) δ : 7.86 (d, $J=30.2$ Hz, 4H), 7.52~6.85 (m, 5H), 2.37 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 162.32 (s), 145.95 (s), 143.98 (s), 141.89 (s), 140.97 (s), 129.53 (s), 128.68 (s), 125.92 (s), 122.91 (s), 118.52 (s), 95.78 (s), 21.39 (s), 15.38 (s); IR (KBr) ν : 1601, 1568, 1497, 1455, 1128, 740 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2\text{S}$ [$\text{M}-\text{H}$] $^-$ 327.08089; found 327.08047.

4-((4-Chlorophenyl)sulfonyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (**C3**): 66.3 mg, yield 76%. Yellow solid, m.p. 140~142 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.96 (dd, $J=18.7, 8.0$ Hz, 4H), 7.56 (d, $J=7.8$ Hz, 2H), 7.26 (t, $J=7.4$ Hz, 2H), 6.99 (t, $J=7.0$ Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 162.26 (s), 146.02 (s), 145.57 (s), 140.89 (s), 136.52 (s), 129.13 (s), 128.65 (s), 127.78 (s), 122.94 (s), 118.47 (s), 15.46 (s); IR (KBr) ν :

1602, 1591, 1499, 1455, 1130, 728 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2\text{ClS}$ [$\text{M}-\text{H}$] $^-$ 347.02626; found 347.02583.

1-(4-Chlorophenyl)-3-methyl-4-(phenylsulfonyl)-1H-pyrazol-5-ol (**C4**): 67.1 mg, yield 77%. Light pink solid, m.p. 196~198 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 8.07 (d, $J=8.7$ Hz, 2H), 7.94 (d, $J=6.7$ Hz, 2H), 7.51 (d, $J=6.9$ Hz, 3H), 7.32 (d, $J=8.6$ Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 162.89 (s), 147.01 (s), 146.69 (s), 140.02 (s), 131.73 (s), 129.08 (s), 128.53 (s), 126.31 (s), 125.68 (s), 119.60 (s), 95.43 (s), 15.53 (s); IR (KBr) ν : 1603, 1587, 1507, 1446, 1136, 721 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2\text{ClS}$ [$\text{M}-\text{H}$] $^-$ 347.02626; found 347.02587.

1-(4-Chlorophenyl)-4-((4-chlorophenyl)sulfonyl)-3-methyl-1H-pyrazol-5-ol (**C5**): 73.8 mg, yield 77%. Brown solid, m.p. 218~221 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 8.08 (d, $J=8.4$ Hz, 2H), 7.98 (d, $J=8.0$ Hz, 2H), 7.61 (d, $J=7.7$ Hz, 2H), 7.35 (d, $J=8.1$ Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 162.48 (s), 146.60 (s), 145.65 (s), 139.87 (s), 136.46 (s), 129.12 (s), 128.56 (s), 127.75 (s), 126.30 (s), 119.50 (s), 95.40 (s), 15.57 (s); IR (KBr) ν : 1582, 1525, 1132, 761 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}_2\text{S}$ [$\text{M}-\text{H}$] $^-$ 380.98729; found 380.98740.

3-Methyl-4-(phenylsulfonyl)-1-(*p*-tolyl)-1H-pyrazol-5-ol (**C6**): 60.8 mg, yield 74%. Yellow solid, m.p. 194~198 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.99 (d, $J=7.4$ Hz, 2H), 7.78~7.56 (m, 3H), 7.51 (d, $J=8.2$ Hz, 2H), 7.24 (d, $J=8.2$ Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 155.91 (s), 147.50 (s), 144.28 (s), 136.04 (s), 134.88 (s), 133.16 (s), 129.80 (s), 129.59 (s), 126.55 (s), 121.76 (s), 102.35 (s), 20.99 (s), 13.77 (s); IR (KBr) ν : 1592, 1569, 1513, 1445, 1136, 744 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2\text{S}$ [$\text{M}-\text{H}$] $^-$ 327.08089; found 327.08047.

4-((4-Chlorophenyl)sulfonyl)-3-methyl-1-(*p*-tolyl)-1H-pyrazol-5-ol (**C7**): 61.7 mg, yield 68%. Yellow-green solid, m.p. 138~140 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.96 (d, $J=8.5$ Hz, 2H), 7.84 (d, $J=8.3$ Hz, 2H), 7.56 (d, $J=8.5$ Hz, 2H), 7.10 (d, $J=8.3$ Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 161.85 (s), 145.91 (s), 145.57 (s), 138.23 (s), 136.65 (s), 132.19 (s), 129.20 (d, $J=7.2$ Hz), 127.75 (s), 118.92 (s), 95.92 (s), 20.92 (s), 15.27 (s); IR (KBr) ν : 1511, 1456, 1140, 757 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2\text{ClS}$ [$\text{M}-\text{H}$] $^-$ 361.04191; found 361.04156.

1-(2-Chlorophenyl)-3-methyl-4-tosyl-1H-pyrazol-5-ol (**C8**): 68.9 mg, yield 76%. Yellow solid, m.p. 179~183 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.83 (d, $J=6.8$ Hz, 2H), 7.52 (s, 1H), 7.46~7.17 (m, 5H), 2.36 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 161.29 (s), 146.34 (s), 143.75 (s), 142.18 (s), 137.12 (s), 131.56 (s), 130.47 (s), 130.28 (s), 130.16~129.93 (m), 129.47 (d, $J=43.9$ Hz), 127.76 (s), 125.97 (s), 95.54 (s), 21.42 (s), 14.57 (s); IR (KBr) ν : 1596, 1507, 1487, 1130, 747 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2\text{ClS}$ [$\text{M}-\text{H}$] $^-$ 361.04191; found 361.04150.

1-(2-Chlorophenyl)-4-((4-chlorophenyl)sulfonyl)-3-met-

hyl-1*H*-pyrazol-5-ol (**C9**): 77.6 mg, yield 81%. Brown solid, m.p. 135~139 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.91 (d, *J*=8.5 Hz, 2H), 7.55 (d, *J*=8.4 Hz, 2H), 7.47 (d, *J*=7.5 Hz, 1H), 7.37~7.17 (m, 3H), 2.09 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 162.82 (s), 146.40 (s), 145.93 (s), 138.15 (s), 136.19 (s), 131.35 (s), 130.21 (d, *J*=12.7 Hz), 129.07 (s), 128.45 (s), 127.53 (d, *J*=7.9 Hz), 93.15 (s), 15.65 (s); IR (KBr) ν: 1596, 1558, 1507, 1134, 757 cm⁻¹; HRMS calcd for C₁₆H₁₁O₃N₂Cl₂S [M-H]⁻ 380.98729; found 380.98746.

1-(4-Chlorophenyl)-4-((4-fluorophenyl)sulfonyl)-3-methyl-1*H*-pyrazol-5-ol (**C10**): 75.2 mg, yield 82%. White solid, m.p. 180~182 °C (dec.); ¹H NMR (500 MHz, DMSO-*d*₆) δ: 8.06 (d, *J*=8.7 Hz, 2H), 7.98 (dd, *J*=7.9, 5.6 Hz, 2H), 7.32 (dd, *J*=11.1, 9.1 Hz, 4H), 2.17 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 164.96 (s), 162.92 (d, *J*=14.9 Hz), 146.55 (s), 143.52 (s), 140.07 (s), 128.51 (t, *J*=4.5 Hz), 126.13 (s), 119.39 (s), 116.08 (s), 115.91 (s), 95.41 (s), 15.64 (s); IR (KBr) ν: 1588, 1490, 1133, 734 cm⁻¹; HRMS calcd for C₁₆H₁₁O₃ClFS [M-H]⁻ 365.01684; found 365.01691.

4-((4-Fluorophenyl)sulfonyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (**C11**): 60.7 mg, yield 73%. Brown solid, m.p. 110~112 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 8.04 (s, 2H), 7.87 (s, 2H), 7.35 (d, *J*=5.7 Hz, 4H), 7.11 (s, 1H), 2.26 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 165.44 (s), 163.45 (s), 159.96 (s), 146.78 (s), 142.06 (s), 139.41 (s), 129.75~128.81 (m), 124.52 (s), 119.81 (s), 116.47 (s), 116.29 (s), 98.47 (s), 40.46 (s), 40.21 (d, *J*=21.0 Hz), 39.88 (d, *J*=21.0 Hz), 39.54 (d, *J*=21.0 Hz), 39.40~39.21 (m), 14.69 (s); IR (KBr) ν: 1605, 1493, 1455, 1141, 728 cm⁻¹; HRMS calcd for C₁₆H₁₂O₃N₂FS [M-H]⁻ 331.05581; found 331.05527.

3-Methyl-1-(*p*-tolyl)-4-tosyl-1*H*-pyrazol-5-ol (**C12**): 63.3 mg, yield 74%. Brown solid, m.p. 190~192 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.86 (d, *J*=8.1 Hz, 2H), 7.49 (d, *J*=8.1 Hz, 2H), 7.39 (d, *J*=8.0 Hz, 2H), 7.25 (d, *J*=8.2 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ: 160.18 (s), 152.18 (s), 148.33 (s), 146.13 (s), 140.94 (s), 139.53 (s), 134.82 (s), 134.68 (d, *J*=25.2 Hz), 131.42 (s), 126.62 (s), 107.76 (s), 26.21 (s), 25.74 (s), 18.44 (s); IR (KBr) ν: 1590, 1559, 1456, 1130, 741 cm⁻¹; HRMS calcd for C₁₈H₁₇O₃N₂S [M-H]⁻ 341.09654; found 341.09659.

1-(4-Chlorophenyl)-3-methyl-4-tosyl-1*H*-pyrazol-5-ol (**C13**): 68.9 mg, yield 76%. Green solid, m.p. 198~200 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 8.01 (d, *J*=9.0 Hz, 2H), 7.79 (d, *J*=7.8 Hz, 2H), 7.53~7.00 (m, 4H), 2.33 (s, 3H), 2.14 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 162.22 (s), 146.70 (s), 144.29 (s), 141.77 (s), 139.85 (s), 129.47 (s), 128.57 (s), 125.88 (s), 119.59 (s), 96.24 (s), 21.38 (s), 15.52 (s); IR (KBr) ν: 1601, 1586, 1491, 1129, 751 cm⁻¹; HRMS calcd for C₁₇H₁₄O₃N₂ClS [M-H]⁻ 361.04191; found 361.04141.

3-Methyl-4-(methylsulfonyl)-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (**C14**): 41.9 mg, yield 63%. Brown solid, m.p. 138~140 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.90 (d, *J*=4.6

Hz, 2H), 7.10 (d, *J*=7.0 Hz, 2H), 3.02 (s, 3H), 2.27 (s, 3H), 2.17 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 162.15 (s), 145.45 (s), 138.67 (s), 131.85 (s), 129.17 (s), 118.78 (s), 95.64 (s), 44.67 (s), 20.93 (s), 15.08 (s); IR (KBr) ν: 1623, 1508, 1130, 771 cm⁻¹; HRMS calcd for C₁₂H₁₃O₃-N₂S [M-H]⁻: 265.06524; found 265.06552.

3-Methyl-4-(methylsulfonyl)-1-phenyl-1*H*-pyrazol-5-ol (**C15**): 41.6 mg, yield 66%. Yellow solid, m.p. 165~167 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 8.01 (d, *J*=7.8 Hz, 2H), 7.30 (t, *J*=7.5 Hz, 2H), 7.03 (t, *J*=7.1 Hz, 1H), 3.02 (s, 3H), 2.17 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 162.15 (s), 145.89 (s), 140.84 (s), 128.71 (s), 123.20 (s), 118.87 (s), 96.13 (s), 44.55 (s), 15.10 (s); IR (KBr) ν: 1602, 1573, 1506, 1119, 773 cm⁻¹; HRMS calcd for C₁₁H₁₁O₃N₂S [M-H]⁻ 251.04959; found 251.04915.

3-Methyl-1-phenyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (**E1**): 66.7 mg, yield 90%. White solid, m.p. 208~210 °C (dec.) (lit.^[10] 178.8~179.7 °C); ¹H NMR (500 MHz, DMSO-*d*₆) δ: 12.20 (s, 1H), 7.77 (d, *J*=8.0 Hz, 2H), 7.48 (t, *J*=7.7 Hz, 2H), 7.28 (t, *J*=7.3 Hz, 1H), 7.10 (d, *J*=7.9 Hz, 2H), 7.01 (d, *J*=7.9 Hz, 2H), 2.24 (s, 3H), 2.14 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 152.47 (s), 138.68 (s), 135.27 (s), 134.79 (s), 130.14 (s), 129.41 (s), 126.15 (s), 125.79 (s), 121.18 (s), 88.49 (s), 20.89 (s), 12.80 (s); IR (KBr) ν: 1609, 1489, 1079, 761 cm⁻¹; HRMS calcd for C₁₇H₁₅ON₂S [M-H]⁻ 295.09106; found 295.09082.

3-Methyl-1-(*p*-tolyl)-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (**E2**): 71.4 mg, yield 92%. Light yellow solid m.p. 195~197 °C (lit.^[10] 98.9~100.7 °C); ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.63 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.1 Hz, 2H), 7.10 (d, *J*=7.9 Hz, 2H), 7.00 (d, *J*=7.9 Hz, 2H), 2.34 (s, 3H), 2.24 (s, 3H), 2.13 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 152.04 (s), 136.34 (s), 135.40 (d, *J*=17.2 Hz), 134.75 (s), 130.13 (s), 129.81 (s), 125.75 (s), 121.24 (s), 88.07 (s), 20.93 (d, *J*=11.2 Hz), 12.78 (s); IR (KBr) ν: 1616, 1489, 1457, 1074, 777 cm⁻¹; HRMS calcd for C₁₈H₁₇ON₂S [M-H]⁻: 309.10671; found 309.10657.

1-(4-Chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (**E3**): 71.1 mg, yield 86%. White solid m.p. 185~188 °C (dec.) (lit.^[10] 89.7~90.1 °C); ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.82 (d, *J*=8.6 Hz, 2H), 7.52 (d, *J*=8.6 Hz, 2H), 7.08 (d, *J*=7.9 Hz, 2H), 7.01 (d, *J*=7.9 Hz, 2H), 2.23 (s, 3H), 2.14 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 157.41 (s), 152.90 (s), 137.55 (s), 135.10 (s), 134.83 (s), 130.14 (s), 129.38 (s), 125.82 (s), 122.41 (s), 88.72 (s), 20.88 (s), 12.81 (s); IR (KBr) ν: 1606, 1489, 1073, 742 cm⁻¹; HRMS calcd for C₁₇H₁₄O- N₂ClS [M-H]⁻ 329.05208; found 329.05167.

4-((2,5-Dimethylphenyl)thio)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (**E4**): 52.8 mg, yield 68%. White solid, m.p. 207~208 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.78 (d, *J*=7.9 Hz, 2H), 7.49 (t, *J*=7.6 Hz, 2H), 7.35~7.22 (m, 1H), 7.14~7.01 (m, 1H), 6.85 (d, *J*=7.5 Hz, 1H), 6.56 (s, 1H), 2.34 (s, 3H), 2.16 (s, 3H), 2.10 (d, *J*=19.1 Hz, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 157.58 (s), 152.68 (s), 138.70 (s), 137.34 (s), 135.98 (s), 131.09 (s), 130.47 (s), 129.44 (s), 126.14 (s), 125.85 (s), 124.62 (s), 121.13 (s),

87.34 (s), 21.34 (s), 19.35 (s), 12.82 (s); IR (KBr) ν : 1600, 1497, 1457, 1075, 730 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{ON}_2\text{S}$ $[\text{M}+\text{H}]^+$ 311.12126; found 311.12103.

(4-Chlorophenyl)-4-((2,5-dimethylphenyl)thio)-3-methyl-1*H*-pyrazol-5-ol (**E5**): 59.5 mg, yield 69%. White solid, m.p. 192~195 °C (dec.); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.84 (d, $J=7.2$ Hz, 2H), 7.54 (d, $J=7.2$ Hz, 2H), 7.06 (d, $J=6.7$ Hz, 1H), 6.84 (d, $J=6.8$ Hz, 1H), 6.57 (s, 1H), 2.30 (d, $J=26.6$ Hz, 3H), 2.20 (d, $J=44.6$ Hz, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.64 (s), 153.11 (s), 137.60 (s), 137.17 (s), 136.01 (s), 131.10 (s), 130.48 (s), 130.08 (s), 129.42 (s), 125.90 (s), 124.61 (s), 122.40 (s), 87.40 (s), 21.33 (s), 19.34 (s), 12.85 (s); IR (KBr) ν : 1621, 1506, 1457, 1074, 741 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{ON}_2\text{ClS}$ $[\text{M}+\text{H}]^+$ 345.08229; found 345.08187.

3-Methyl-1-phenyl-4-(*m*-tolylthio)-1*H*-pyrazol-5-ol (**E6**): 58.5 mg, yield 79%. White solid, m.p. 173~175 °C (lit.^[10] 179.6~181.0 °C); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.79 (d, $J=7.8$ Hz, 2H), 7.49 (t, $J=7.6$ Hz, 2H), 7.29 (t, $J=7.3$ Hz, 1H), 7.23~7.09 (m, 1H), 6.95 (d, $J=7.5$ Hz, 2H), 6.85 (t, $J=22.9$ Hz, 1H), 2.26 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.62 (s), 152.62 (s), 138.94~138.21 (m), 129.40 (d, $J=6.7$ Hz), 126.23 (d, $J=12.8$ Hz), 125.91 (s), 122.58 (s), 121.20 (s), 88.20 (s), 21.45 (s), 12.78 (s); IR (KBr) ν : 1590, 1506, 1456, 1073, 737 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{ON}_2\text{S}$ $[\text{M}-\text{H}]^-$ 295.09106; found 295.09067.

1-(4-Chlorophenyl)-3-methyl-4-(*m*-tolylthio)-1*H*-pyrazol-5-ol (**E7**): 62.9 mg, yield 76%. White solid, m.p. 166~168 °C (dec.); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.82 (d, $J=7.8$ Hz, 2H), 7.54 (d, $J=7.8$ Hz, 2H), 7.17 (t, $J=7.5$ Hz, 1H), 7.03~6.89 (m, 2H), 6.86 (d, $J=7.7$ Hz, 1H), 2.25 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.68 (s), 153.01 (s), 138.82 (s), 138.54 (s), 137.53 (s), 130.10 (s), 129.38 (s), 126.30 (s), 125.88 (s), 122.49 (d, $J=19.1$ Hz), 88.22 (s), 21.44 (s), 12.82 (s); IR (KBr) ν : 1607, 15070, 1472, 1074, 734 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{O}-\text{N}_2\text{ClS}$ $[\text{M}+\text{H}]^+$ 311.06664; found 311.06627.

3-Methyl-1-(*p*-tolyl)-4-(*m*-tolylthio)-1*H*-pyrazol-5-ol (**E8**): 57.4 mg, yield 74%. White solid, m.p. 186~188 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.63 (d, $J=7.8$ Hz, 2H), 7.29 (d, $J=7.9$ Hz, 2H), 7.17 (t, $J=7.7$ Hz, 1H), 6.94 (d, $J=10.4$ Hz, 2H), 6.85 (d, $J=7.7$ Hz, 1H), 2.34 (s, 3H), 2.27 (d, $J=11.4$ Hz, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.80 (s), 152.26 (s), 138.98 (s), 135.92 (d, $J=130.3$ Hz), 135.32~134.39 (m), 130.15 (s), 129.65 (d, $J=55.3$ Hz), 126.35 (s), 126.09 (d, $J=44.5$ Hz), 122.61 (s), 121.19 (s), 87.63 (s), 21.56 (s), 21.04 (s), 12.90 (s); IR (KBr) ν : 1603, 1575, 1507, 1457, 1069, 777 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{ON}_2\text{S}$ $[\text{M}+\text{H}]^+$ 311.12126; found 311.12105.

4-((2-Methoxyphenyl)thio)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (**E9**): 62.8, 77%. White solid, m.p. 198~202 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.63 (d, $J=7.9$ Hz, 2H), 7.29 (d, $J=7.9$ Hz, 2H), 7.16~7.06 (m, 1H), 7.01 (t, $J=13.7$ Hz, 1H), 6.91~6.81 (m, 1H), 6.63 (d, $J=7.1$ Hz, 1H), 3.88 (s, 3H), 2.31 (d, $J=33.8$ Hz, 3H), 2.18~

1.95 (m, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.26 (s), 155.28 (s), 152.46 (s), 136.35 (s), 135.48 (s), 129.81 (s), 126.97 (s), 126.02 (s), 124.56 (s), 121.75~121.70 (m), 121.43 (d, $J=36.9$ Hz), 111.16 (s), 85.87 (s), 56.09 (s), 20.98 (s), 12.75 (s); IR (KBr) ν : 1575, 1507, 1472, 1063, 730 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$ 327.11618; found 327.11583.

1-(2-Chlorophenyl)-3-methyl-4-(*p*-tolylthio)-1*H*-pyrazol-5-ol (**E10**): 67.8 mg, yield 82%. Light yellow solid, m.p. 188~190 °C (lit.^[10] 98.7~100.1 °C); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.67 (d, $J=7.4$ Hz, 1H), 7.62~7.41 (m, 3H), 7.12 (d, $J=7.8$ Hz, 2H), 7.02 (d, $J=7.7$ Hz, 2H), 2.25 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 158.34 (s), 152.44 (s), 135.77 (d, $J=17.4$ Hz), 134.61 (s), 131.89 (s), 130.98 (s), 130.53 (d, $J=15.7$ Hz), 130.10 (s), 128.39 (s), 125.52 (s), 86.27 (s), 20.89 (s), 12.85 (s); IR (KBr) ν : 1599, 1490, 1449, 1065, 737 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{ON}_2\text{ClS}$ $[\text{M}-\text{H}]^-$ 329.05208; found 329.05170.

1-(4-Chlorophenyl)-4-((4-chlorophenyl)thio)-3-methyl-1*H*-pyrazol-5-ol (**E11**): 72.9 mg, yield 83%. Yellow solid, m.p. 197~199 °C (dec.); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.83 (d, $J=8.1$ Hz, 2H), 7.53 (d, $J=8.1$ Hz, 2H), 7.33 (d, $J=7.8$ Hz, 2H), 7.11 (d, $J=7.8$ Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.73 (s), 152.83 (s), 137.98 (s), 137.48 (s), 130.11 (d, $J=14.8$ Hz), 129.38 (d, $J=2.1$ Hz), 127.07 (s), 122.42 (s), 87.60 (s), 12.76 (s); IR (KBr) ν : 1506, 1472, 1088, 741 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{11}\text{O}-\text{N}_2\text{Cl}_2\text{S}$ $[\text{M}-\text{H}]^-$ 348.99746; found 348.00710.

4-((4-Chlorophenyl)thio)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (**E12**): 65.7 mg, yield 83%. Yellow solid, m.p. 177~180 °C (lit.^[10] 179.1~181.1 °C); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 12.33 (s, 1H), 7.80 (d, $J=7.9$ Hz, 2H), 7.49 (t, $J=7.6$ Hz, 2H), 7.45~7.24 (m, 3H), 7.13 (d, $J=8.2$ Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.34 (s), 152.43 (s), 138.34 (d, $J=58.8$ Hz), 130.05 (s), 129.42 (d, $J=1.4$ Hz), 127.07 (s), 126.26 (s), 121.25 (s), 87.52 (s), 12.75 (s); IR (KBr) ν : 1612, 1496, 1471, 1070, 740 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{ON}_2\text{ClS}$ $[\text{M}-\text{H}]^-$ 315.03643; found 315.03625.

4-((4-Chlorophenyl)thio)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (**E13**): 72.8 mg, yield 88%. Yellow solid, m.p. 183~184 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.64 (d, $J=8.1$ Hz, 2H), 7.34 (d, $J=8.2$ Hz, 2H), 7.28 (d, $J=8.0$ Hz, 2H), 7.11 (d, $J=8.2$ Hz, 2H), 2.34 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 157.05 (s), 152.02 (s), 138.18 (s), 136.22 (s), 135.58 (s), 129.99 (s), 129.81 (s), 129.39 (s), 127.03 (s), 121.30 (s), 87.17 (s), 20.98 (s), 12.72 (s); IR (KBr) ν : 1600, 1509, 1471, 1078, 731 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{ON}_2\text{ClS}$ $[\text{M}-\text{H}]^-$ 329.05208; found 329.05182.

1-(4-Chlorophenyl)-3-methyl-4-(phenylthio)-1*H*-pyrazol-5-ol (**E14**): 68.1 mg, yield 86%. White solid, m.p. 214~217 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 12.43 (s, 1H), 7.81 (d, $J=8.6$ Hz, 2H), 7.54 (d, $J=8.7$ Hz, 2H), 7.28 (t, $J=7.6$ Hz, 2H), 7.11 (dd, $J=21.5, 7.5$ Hz, 3H), 2.13 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 152.97 (s), 138.69 (s), 137.51 (s), 130.18 (s), 129.48 (d, $J=15.3$ Hz), 125.43

(d, $J=8.3$ Hz), 122.49 (s), 87.87 (s), 12.82 (s); IR (KBr) ν : 1616, 1582, 1457, 1072, 736 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{ON}_2$ -CIS $[\text{M}-\text{H}]^-$: 315.03643; found 315.03625.

3-Methyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5-ol (**E15**): 63.5 mg, yield 90%. Light yellow solid, m.p. 187~189 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 12.18 (s, 1H), 7.74 (d, $J=8.1$ Hz, 2H), 7.48 (t, $J=7.9$ Hz, 2H), 7.28 (t, $J=7.6$ Hz, 3H), 7.19~6.88 (m, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 152.51 (s), 138.87 (s), 138.64 (s), 129.49 (d, $J=11.1$ Hz), 126.22 (s), 125.40 (d, $J=6.3$ Hz), 121.24 (s), 12.81 (s); IR (KBr) ν : 1617, 1500, 1457, 1076, 731 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{13}\text{ON}_2\text{S}$ $[\text{M}-\text{H}]^-$ 281.07541; found 281.07501.

3-Methyl-4-(phenylthio)-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (**E16**): 58.5 mg, yield 79%. Light yellow solid, m.p. 190~193 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 12.11 (s, 1H), 7.62 (d, $J=8.2$ Hz, 2H), 7.28 (t, $J=7.5$ Hz, 4H), 7.18~6.80 (m, 3H), 2.33 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 152.12 (s), 138.95 (s), 136.32 (s), 135.52 (s), 129.82 (s), 129.51 (s), 125.37 (d, $J=4.7$ Hz), 121.31 (s), 87.47 (s), 20.99 (s), 12.79 (s); IR (KBr) ν : 1605, 1510, 1077, 735 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{ON}_2\text{S}$ $[\text{M}-\text{H}]^-$ 295.09106; found 295.09055.

3-Methyl-4-(naphthalen-1-ylthio)-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (**E17**): 69.3 mg, yield 80%. White solid, m.p. 193~194 °C; ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 8.33 (d, $J=8.1$ Hz, 1H), 7.96 (d, $J=7.8$ Hz, 1H), 7.66 (ddd, $J=26.4$, 20.4, 10.6 Hz, 5H), 7.52~7.36 (m, 1H), 7.30 (d, $J=7.4$ Hz, 2H), 7.03 (d, $J=6.1$ Hz, 1H), 2.35 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ : 152.36 (s), 136.31 (s), 135.68 (d, $J=20.1$ Hz), 133.91 (s), 130.36 (s), 129.86 (s), 129.02 (s), 126.81 (d, $J=11.0$ Hz), 126.48 (s), 125.58 (s), 123.72 (s), 122.18 (s), 121.35 (s), 21.01 (s), 12.80 (s); IR (KBr) ν : 1623, 1506, 1456, 1069, 732 cm^{-1} ; HRMS calcd for $\text{C}_{21}\text{H}_{17}\text{ON}_2\text{S}$ $[\text{M}-\text{H}]^-$ 345.10671; found 345.10617.

Supporting Information ^1H NMR and ^{13}C NMR spectra copies of all the products. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

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