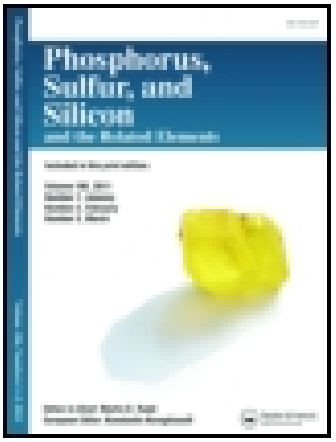

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Structure, and Biological Activities of [5-(Arylthio/Sulfinyl/Sulfonyl)-3-Methyl-1-Phenyl-1H-Pyrazol-4-yl]-Arylmethanones

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SYNTHESIS, STRUCTURE, AND BIOLOGICAL ACTIVITIES OF [5-(ARYLTHIO/SULFINYL/SULFONYL)-3-METHYL-1-PHENYL-1*H*-PYRAZOL-4-YL]-ARYLMETHANONES

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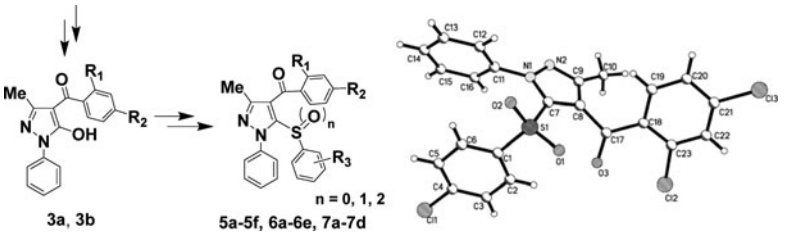
GRAPHICAL ABSTRACT



Abstract *A series of novel N-phenylpyrazolyl aryl methanones derivatives containing the arylthio/sulfinyl/sulfonyl group have been synthesized via multi-step reactions from 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one and characterized by melting point, ^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS. The crystal structure of (5-(4-chlorophenylsulfonyl)-3-methyl-1-phenyl-1H-pyrazol-4-yl)(2,4-dichlorophenyl)methanone containing the arylsulfonyl moiety is reported. The biological activity results showed that some of the title compounds exhibit favorable herbicidal and insecticidal activities.*

Keywords Pyrazole; sulfoxide; sulfone; synthesis; crystal structure; biological activities

INTRODUCTION

Sulfur-containing compounds, such as sulfoethers, sulfoxides, and sulfones play important roles in research areas of organic chemistry, medicinal chemistry, and pesticide chemistry.[1–6] It has been demonstrated that these groups are important pharmacophores of many pesticides, such as Fipronil[7] and KIH-485[8], and are often introduced into some bioactive heterocycles to enhance the possible activities during the pesticide design.

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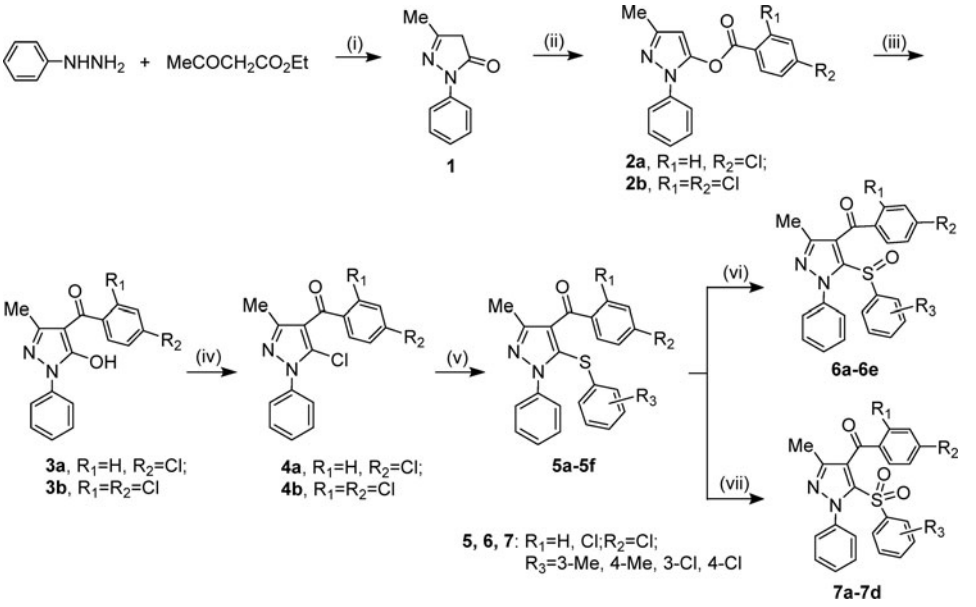
It is known that many pyrazole derivatives possess significant antiinflammatory,[9,10] antibacterial,[11] anti-Alzheimer,[12] antioxidant,[13] and anticancer[14] properties. Also, the herbicidal,[15] insecticidal,[16] and fungicidal[17] activities of some multi-substituted pyrazoles have been reported. Although there are many reports of the modification of substituents on the pyrazole ring, structures containing a 4-arylacyl and 5-arylthio, or 5-arylsulfinyl, or 5-arylsulfonyl on the pyrazole ring have been seldom reported. Thus a series of [5-(4-substituted phenylsulfinyl/sulfonyl)-1,3-dimethyl-1*H*-pyrazol-4-yl]-arylmethanones were synthesized successfully in our recent study,[18] which encouraged us to synthesize some other novel compounds with such modified structures.

In continuation of our research on the synthesis of bioactive heterocyclic compounds, a series of title new pyrazole derivatives were synthesized and structures characterized, also their biological activities were investigated by herbicidal and insecticidal tests in this paper.

RESULTS AND DISCUSSION

Synthesis

The intermediates and the title compounds were synthesized as shown in Scheme 1. Referring to the literature reported by us for the synthesis of (substituted phenyl)(5-hydroxy-1,3-dimethyl-1*H*-pyrazol-4-yl)methanone,[18] intermediate **3** was prepared successfully (yield 72∼85%) *via* a two-step method involving a Scotten-Baumann acylation of pyrazolinone (**1**) with 4-chlorobenzoyl chloride or 2,4-dichlorobenzoyl chloride and then a Fries rearrangement reaction of the product ester catalyzed by K_2CO_3 in dioxane at 80–90°C (1.5 h). Intermediate **3** reacted with $POCl_3$ to easily form intermediate **4**.



Scheme 1 Reagents and conditions: (i) EtOH, reflux, 5 h; (ii) 4-Chlorobenzoyl chloride or 2,4-dichlorobenzoyl chloride, triethylamine, ethylidene chloride, 50∼60°C; (iii) Potassium carbonate, 1,4-dioxane, 80∼90°C, 1.5 h; (iv) phosphorus oxychloride, reflux, 3 h; (v) Substituted thiophenol, NaH, THF, r.t.; (vi) Hydrogen peroxide, AcOH, r.t.; (vii) Hydrogen peroxide, AcOH, 80°C'.

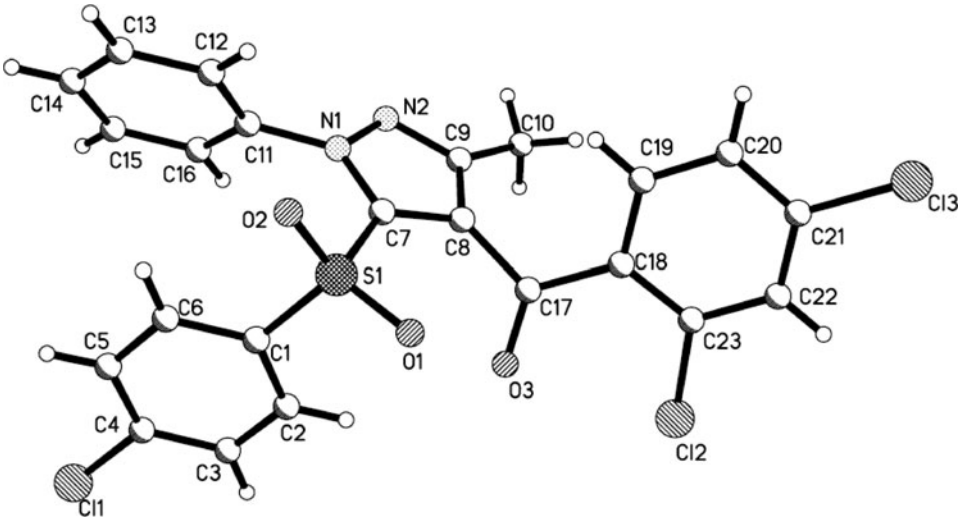


Figure 1 Molecular structure of compound **7d**.

The sulfoether compounds **5** can be synthesized from pyrazole chlorides **4** and substituted thiophenols in THF using NaH as a base at room temperature with yields 51∼87%. In this step, the substrates didn't convert to the sulfoether products completely, which may be due to the weakened reactivity of the Cl atom caused by a p–π conjugative effect of pyrazole ring with Cl atom.[18] The sulfoxide compounds **6** were synthesized from the oxidation of sulfoethers with H_2O_2 in acetic acid for 1–2 h at room temperature, but some amount of substrate sulfoethers existed in the products; sulfone compounds **7** were obtained in the same reaction system at 80°C, and likewise a small amount of substrate sulfoxides also existed in the products. These experimental results indicate that oxidation is not complete under these conditions. According to our similar results reported previously,[18] this probably originated from the electronic effect of the substituents on the structures of these compounds such as the 4-arylacyl, or 5-arylthio, or 5-arylsulfinyl group on the pyrazole ring, and from the existence of steric hindrance because two bulky aryl groups (phenylpyrazole and benzene ring) are located on same sulfur atom.

Spectroscopic Characterization

In the ^{1}H NMR spectra of **5–7**, the CH_3 proton signals in pyrazole ring of sulfoether were observed at δ 2.34–2.49 ppm; sulfoxide were observed at δ 2.24–2.50 ppm and δ 2.20–2.48 ppm as sulfone, respectively. The difference of the chemical shift values of the CH_3 proton signals in pyrazole ring between these three kinds of sulfur-containing derivatives **5**, **6,** and **7** is little. The other peaks observed were the aromatic protons at δ 6.53–7.93 ppm and an additional singlet at δ 2.13–2.23 ppm in compounds **5a**, **5c**, **5d**, **6a**, **6b**, **6d**, **7a,** and **7c,** respectively due to –CH_3 group attached to phenyl ring. In the ^{13}C NMR spectra of **5–7**, the typical carbon resonance at δ 188.2–190.2 ppm was indicative of a carbonyl group. The methyl carbon in pyrazole ring appeared at δ 12.44–14.41 ppm and the aromatic carbon of benzene and pyrazole rings appeared at δ 117.9–156.0 ppm.

Table 1 Crystal structure and data refinement parameters

Compound	7d
Empirical Formula	$C_{23}H_{15}Cl_3N_2O_3S$
Formula Weight	505.78
Crystal System / Space Group	Monoclinic, *P*2(1)/n
a/Å	10.266(2) Å
b/Å	13.960(3) Å
c/Å	15.514(4) Å
α/ °	90°
β/ °	91.073(5) °
γ/ °	90°
V/Å^3	2223.1(9) Å^3
Z	4
D_{calc} (g/cm^3)	1.511 Mg/m^3
μ (mm^{-1})	0.536
Crystal size (mm)	0.16 × 0.10 × 0.10
Color / Shape	Colorless, prism
Temp (K)	294(2)
Theta range for collection	1.96–26.35°
Reflections collected	12613
Independent reflections	4528 [*R*(int) = 0.0725]
Data/restraints/parameters	4528/0/290
Goodness of fit on F^2	0.989
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0477$, w$R2 = 0.0781$
R indices (all data)	$R1 = 0.1363$, w$R2 = 0.0978$
Largest difference peak/hole	0.310 and −0.270 e/A^3

The infrared spectra of compounds **5**–**7** showed the absorption band at 1639∼1676 cm^{-1} for C=O stretching, and 1010∼1103 cm^{-1} for C−S stretching. In the cases of sulfoxide compounds **6**, it showed the strong peak at 1261∼1289 cm^{-1} for S=O stretching, while the characteristic stretching vibration ν (O=S=O) of sulfone compounds **7** appears at 1335∼1362 cm^{-1} and 1163∼1199 cm^{-1} as strong peaks.

In addition, the ESI-FTMS (HRMS) of new compounds **5**, **6,** and **7** showed molecular ion peak of $[M+H]^+$ or $[M+Na]^+$ clearly, and were consistent with those of calculated ones.

Crystal Structure

The structure of compound **7d** was further confirmed by single crystal X-ray diffraction analysis (Figure 1). The crystal structure and data refinement parameters are shown in Table 1. The selected bond lengths and bond angles are shown in Table 2. Selected torsion angles are shown in Table 3.

Compound **7d** belongs to monoclinic system with space group $P2_1/n$. There are three aromatic rings, the average bond lengths and bond angles of each ring are in agreement with the literature data.[19] The C−N and C−C bond lengths of pyrazole ring range between the single and double bonds (1.388(4) ∼ 1.399(4)), and the interior angles of the five-membered ring are 105.5(2) ∼ 111.4(3)°, close to the ideal 108° for pentagon.[20] The bond angles of C1–S1–C7 and C8–C17–C18 is 102.20(14)° and 118.0(3)°, respectively. From the molecular structure, it can be seen that the pyrazole ring (N1, N2, C7, C8, C9) and

Table 2 Selected bond lengths (Å) and angles (°) for the compound **7d**

Bond lengths	Å	Bond angles	(°)
S(1)–O(1)	1.424(2)	C(1)–S(1)–C(7)	102.20(14)
S(1)–O(2)	1.4280(19)	N(2)–N(1)–C(7)	110.9(2)
S(1)–C(1)	1.749(3)	N(2)–N(1)–C(11)	118.3(2)
S(1)–C(7)	1.764(3)	C(7)–N(1)–C(11)	129.8(3)
Cl(1)–C(4)	1.716(4)	C(9)–N(2)–N(1)	105.5(2)
Cl(2)–C(23)	1.727(3)	C(6)–C(1)–S(1)	120.0(3)
Cl(3)–C(21)	1.725(3)	C(2)–C(1)–S(1)	118.9(3)
O(3)–C(17)	1.213(3)	N(1)–C(7)–C(8)	107.2(3)
N(1)–N(2)	1.359(3)	N(1)–C(7)–S(1)	123.9(2)
N(1)–C(7)	1.368(3)	C(8)–C(7)–S(1)	128.9(2)
N(1)–C(11)	1.435(4)	C(7)–C(8)–C(9)	105.1(3)
N(2)–C(9)	1.338(4)	C(7)–C(8)–C(17)	126.9(3)
C(7)–C(8)	1.379(4)	C(9)–C(8)–C(17)	127.1(3)
C(8)–C(9)	1.399(4)	N(2)–C(9)–C(8)	111.4(3)
C(8)–C(17)	1.499(4)	N(2)–C(9)–C(10)	119.8(3)
C(9)–C(10)	1.490(4)	C(8)–C(9)–C(10)	128.8(3)
C(11)–C(12)	1.373(4)	C(16)–C(11)–N(1)	118.3(3)
C(17)–C(18)	1.486(4)	C(12)–C(11)–N(1)	120.8(3)
C(18)–C(23)	1.392(4)	C(18)–C(17)–C(8)	118.0(3)

benzene ring (C11, C12, C13, C14, C15, C16) are not coplanar and have a dihedral angle 63.8°. The X-ray analysis also reveals that in this typical compound **7d**, the torsion angle of C(1)–S(1)–C(7)–C(8) is 108°. This is probably because the existence of two bulky groups (5-arylsulfonyl and 4-aryloyl) leads to the aromatic ring at the 1-position of pyrazole not being coplanar with the pyrazole ring (the steric effect). The crystal structure of this kind of pyrazole sulfone compound has not been reported before, and so will provide useful information for the structural studies of novel pyrazole derivatives.

Biological Activities

From **Table S 1** (Supplemental Materials), we can see that most of the new compounds showed weak herbicidal activity for the inhibition of the rape root growth at 100 μg/mL. However, compounds **5b** and **6e** possessed inhibition rates of 33.6% and 67.0% in rape root test, respectively, and the latter still had 56.1% inhibitory activity at 10 μg/mL, yet

Table 3 Selected torsion angles (°) for the compound **7d**

Torsion angles	(°)	Torsion angles	(°)
C(7)–S(1)–C(1)–C(6)	−102.9(3)	N(2)–N(1)–C(11)–C(16)	63.8(4)
C(7)–S(1)–C(1)–C(2)	74.3(3)	C(7)–N(1)–C(11)–C(16)	−103.8(4)
N(2)–N(1)–C(7)–S(1)	−178.6(2)	N(2)–N(1)–C(11)–C(12)	−116.0(3)
C(11)–N(1)–C(7)–S(1)	−10.3(4)	C(7)–N(1)–C(11)–C(12)	76.4(4)
C(1)–S(1)–C(7)–N(1)	70.9(3)	C(7)–C(8)–C(17)–C(18)	−129.1(3)
C(1)–S(1)–C(7)–C(8)	−108.1(3)	C(9)–C(8)–C(17)–C(18)	63.3(4)
S(1)–C(7)–C(8)–C(17)	9.6(5)	C(8)–C(17)–C(18)–C(23)	−163.8(3)
C(17)–C(8)–C(9)–N(2)	168.7(3)	C(8)–C(17)–C(18)–C(19)	19.7(4)

it was less effective than the control (Chlorsulfuron, 76.0%). For the inhibition of growth of the barnyardgrass stems and leaves, both pyrazole sulfides **6** and pyrazole sulfones **7** showed weak herbicidal activity at 100 μg/mL, while pyrazole sulfoethers **5c** and **5d** held 44.8% and 52.8% inhibition activity in baryardgrass cup test at 100 μg/mL, which are more effective than Chlorsulfuron (29.9%).

From the same table, it was found that most of compounds exhibited apparent larvicidal activity against oriental armyworm with the lethality rate 10∼30% at 200 mg/L, in which the activity difference between sulfides **6** and sulfones **7** is little. Interestingly, sulfoether **5f** exhibited 70% larvicidal activity at 200 mg/L.

EXPERIMENTAL

Melting points were determined using a Taike X-4 apparatus and were uncorrected. Infrared spectra were recorded on a BRUKER EQUINOX 55 spectrophotometer as KBr tablets. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE-300 MHz or a Varian Mercury Vx400MHz instrument using TMS as an internal standard and $CDCl_3$ (or DMSO-d_6) as solvent. HRMS data were obtained on a FTICR-MS instrument (Ionspec 7.0T). Crystallographic data of the compound were collected on a Rigaku MM-07 Saturn 724 CCD diffractometer.

Synthesis of the Intermediate 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one (1)

3-Methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**1**) was synthesized according to Ref.[21]

Synthesis of the Intermediates 3-Methyl-1-phenyl-1*H*-pyrazol-5-yl substituted-benzoate (2)

Intermediates **2** were synthesized according to Ref.[18]

3-Methyl-1-phenyl-1*H*-pyrazol-5-yl 4-chlorobenzoate (2a): white solid, yield 96%, m.p. 88–90°C (Lit.[22] m.p. 95–96°C); **3-methyl-1-phenyl-1*H*-pyrazol-5-yl 2,4-dichlorobenzoate (2b):** white solid, yield 88%, m.p. 113–114°C.

Synthesis of the Intermediates (Substituted-phenyl)(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4- yl)methanone (3)

Intermediates **3** were synthesized according to Ref.[18]

(4-Chlorophenyl)(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methanone (3a): white solid, yield 72%, m.p. 103–105°C (Lit.[23] m.p. 105–107°C); **(2,4-dichlorophenyl)(5-hydroxy-3-methyl-1-phenyl- 1*H*-pyrazol-4-yl)methanone (3b):** white solid, yield 85%, m.p. 151–153°C.

Synthesis of the Intermediate Pyrazole Chloride (4)

Referring to the literature[18] method, intermediates pyrazole chloride (**4**) were successfully synthesized. A mixture of $POCl_3$ (9.25 g, 0.06 mol) and intermediate **3** (0.03 mol) was stirred at reflux condition for 3∼4 h. After cooling, the reaction solution was slowly poured into crushed ice and the mixture was adjusted to pH 7∼8 with 10% sodium

hydroxide solution. The mixture was extracted with ethyl acetate (3 × 25 mL), the organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was recrystallized with a mixed solvent of ethyl acetate and petroleum ether to give intermediate **2**.

5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(4-chlorophenyl)methanone (4a): white solid, yield 88%, m.p. 120–122°C. ^{1}H NMR (400 MHz, DMSO-d_6): 7.85 (d, J = 8.4 Hz, 2H), 7.41–7.75 (m, 7H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): 188.7 (C=O), 151.01 (Pyrazole-C), 138.5 (Ph-C), 137.5 (Ph-C), 136.9 (Ph-C), 131.6 (2C, Ph-C), 129.8 (2C, Ph-C), 129.7 (Ph-C), 129.5 (Pyrazole-C), 129.3 (2C, Ph-C), 126.2 (2C, Ph-C), 117.8 (Pyrazole-C), 14.2 (Pyrazole-**C**H$_3$); **5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(2,4-dichlorophenyl)methanone (4b)**: white solid, yield 82%, m.p. 165–168°C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.02–7.87 (m, 8H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): 187.4 (C=O), 152.6 (Pyrazole-C), 137.9 (Ph-C), 137.2 (Ph-C), 136.7 (Ph-C), 132.0 (Ph-C), 131.3 (Pyrazole-C), 129.9 (Ph-C), 129.7 (Ph-C), 129.2 (3C, Ph-C), 127.5 (Ph-C), 125.5 (2C, Ph-C), 117.7 (Pyrazole-C), 14.7 (Pyrazole-**C**H$_3$).

Synthesis of (5-Arylthio-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-arylmethanones (5a–5f)

To a mixture of NaH (50%, 15 mmol) in THF (10 mL) was added dropwise, a solution of substituted thiophenol (10 mmol) in THF (5 mL) at 0°C. After being stirred at room temperature for 1∼2 h, the mixture was then added dropwise a solution of intermediate **4** (10 mmol) in THF (10 mL). The mixture was further stirred at room temperature for 4∼6 h, then water (25 mL) was added and extracted with ethyl acetate (3 × 15 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by recrystallization with a mixed solvent of ethyl acetate and petroleum ether to give the pyrazole sulfoether (**5a–5f**).

(4-Chlorophenyl)(3-methyl-1-phenyl-5-(*p*-tolylthio)-1*H*-pyrazol-4-yl) methanone (5a): white solid, yield 60%, m.p. 110–112°C; IR (υ, cm^{-1}): 3010 (m, Ph-H), 2920 (m, CH_3), 1644 (vs, C=O), 1590, 1501, 1463 (s, Ar), 1086 (vs, C−S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.68 (d, J = 8.4 Hz, 2H, Ph-H), 7.39–7.45 (m, 7H, Ph-H), 6.85 (d, J = 7.6 Hz, 2H, Ph-H), 6.68 (d, J = 8.0 Hz, 2H, Ph-H), 2.37 (s, 3H, pyrazol-CH_3), 2.20 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 190.3 (C=O), 150.8 (Pyrazole-C), 139.2 (Ph-C), 138.7 (Ph-C), 137.4 (Ph-C), 137.0 (Ph-C), 136.2 (Ph-C), 130.9 (2C, Ph-C), 130.0 (Pyrazole-C), 129.8 (2C, Ph-C), 129.7 (2C, Ph-C), 128.8 (Ph-C), 128.6 (2C, Ph-C), 128.6 (2C, Ph-C), 126.0 (2C, Ph-C), 124.1 (Pyrazole-C), 21.0 (Ph-**C**H$_3$), 13.6 (Pyrazole-**C**H$_3$). ESI-FTMS for $C_{24}H_{19}ClN_2OS$ $[M+H]^+$: Calcd. 419.0979, Found 419.0986.

(4-Chlorophenyl)(5-(4-chlorophenylthio)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl) methanone (5b): white solid, yield 51%, m.p. 143°C; IR (υ, cm^{-1}): 3066 (m, Ph-H), 2964 (m, CH_3), 1650 (vs, C=O), 1594, 1502, 1474, 1457 (s, Ar), 1090 (vs, C−S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.71 (d, J = 8.4 Hz, 2H, Ph-H), 7.41–7.44 (m, 7H, Ph-H), 7.03 (d, J = 8.4 Hz, 2H, Ph-H), 6.74 (d, J = 8.4 Hz, 2H, Ph-H), 2.37 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 190.1 (C=O), 150.8 (Pyrazole-C), 139.4 (Ph-C), 138.5 (Ph-C), 136.8 (Ph-C), 133.3 (Ph-C), 132.2 (Ph-C), 130.9 (2C, Ph-C), 130.5 (2C, Ph-C), 130.5 (Pyrazole-C), 129.2 (2C, Ph-C), 128.9 (2C, Ph-C), 128.8 (2C, Ph-C), 128.8 (Ph-C), 125.9 (2C, Ph-C), 124.6 (Pyrazole-C), 13.7 (Pyrazole-**C**H$_3$). ESI-FTMS for $C_{23}H_{16}Cl_2N_2OS$ $[M+H]^+$: Calcd. 439.0433, Found 439.0425.

(2,4-Dichlorophenyl)(3-methyl-1-phenyl-5-(*m*-tolylthio)-1*H*-pyrazol-4-yl) methanone (5c): white solid, yield 71%, m.p. 99–102°C; IR (υ, cm^{-1}): 3091 (m, Ph-H), 2920 (m, CH_3), 1661 (vs, C=O), 1584, 1508, 1471 (s, Ar), 1103 (vs, C−S); ^{1}H NMR (300 MHz, $CDCl_3$): 7.17–7.68 (m, 12H, Ph-H), 2.34 (s, 3H, pyrazol-CH_3), 2.22 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.0 (C=O), 152.8 (Pyrazole-C), 138.9 (Ph-C), 138.5 (Ph-C), 138.2 (Ph-C), 136.9 (Ph-C), 136.4 (Ph-C), 133.6 (Ph-C), 132.3 (Ph-C), 130.0 (Ph-C), 129.6 (Ph-C), 129.0 (Ph-C), 128.9 (Ph-C), 128.8 (Ph-C), 128.8 (Ph-C), 127.7 (Ph-C), 126.9 (Ph-C), 126.1 (2C, Ph-C), 125.4 (Ph-C), 123.8 (Pyrazole-C), 121.4 (Pyrazole-C), 21.2 (Ph-**C**H_3), 14.4 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{18}Cl_2N_2OS$ $[M+H]^+$: Calcd. 453.0590, Found 453.0592.

(2,4-Dichlorophenyl)(3-methyl-1-phenyl-5-(*p*-tolylthio)-1*H*-pyrazol-4-yl) methanone (5d): white solid, yield 87%, m.p. 82–85°C; IR (υ, cm^{-1}): 3070 (m, Ph-H), 2962 (m, CH_3), 1660 (vs, C=O), 1584, 1505, 1466 (s, Ar), 1052 (vs, C−S); ^{1}H NMR (300 MHz, $CDCl_3$): 7.19–7.28 (m, 6H, Ph-H), 7.08–7.14 (m, 2H, Ph-H), 6.80 (d, J = 8.1 Hz, 2H, Ph-H), 6.53 (d, J = 8.1 Hz, 2H, Ph-H), 2.42 (s, 3H, pyrazol-CH_3), 2.15 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.0 (C=O), 152.7 (Pyrazole-C), 138.5 (Ph-C), 138.3 (Ph-C), 136.6 (Pyrazole-C), 136.5 (Ph-C), 134.0 (Ph-C), 132.2 (Ph-C), 130.0 (Ph-C), 129.7 (Ph-C), 129.0 (Ph-C), 128.9 (2C, Ph-C), 128.8 (2C, Ph-C), 128.2 (2C, Ph-C), 127.0 (Ph-C), 126.9 (Ph-C), 126.0 (2C, Ph-C), 123.9 (Pyrazole-C), 21.2 (Ph-**C**H_3), 14.4 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{18}Cl_2N_2OS$ $[M+H]^+$: Calcd. 453.0590, Found 453.0585.

(5-(3-Chlorophenylthio)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl) (2,4-dichlorophenyl)methanone (5e): white solid, yield 81%, m.p. 98–101°C; IR (υ, cm^{-1}): 3074 (m, Ph-H), 2923 (m, CH_3), 1664 (vs, C=O), 1581, 1504, 1459 (s, Ar), 1071 (vs, C−S); ^{1}H NMR (300 MHz, $CDCl_3$): 7.30–7.39 (m, 6H, Ph-H), 7.20–7.26 (m, 2H, Ph-H), 6.68-6.70 (m, 2H, Ph-H), 6.66 (m, 2H, Ph-H), 2.49 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 188.7 (C=O), 152.8 (Pyrazole-C), 138.3 (Ph-C), 138.1 (Ph-C), 136.7 (Ph-C), 135.7 (Ph-C), 134.8 (Ph-C), 132.3 (Ph-C), 130.0 (Ph-C), 129.9 (Ph-C), 129.8 (Ph-C), 129.5 (Ph-C), 129.1 (Ph-C), 128.9 (2C, Ph-C), 128.0 (Ph-C), 127.1 (Ph-C), 126.3 (Ph-C), 126.0 (2C, Ph-C), 124.0 (Pyrazole-C), 121.4 (Pyrazole-C), 14.3 (Pyrazole-**C**H_3). ESI-FTMS for $C_{23}H_{15}Cl_3N_2OS$ $[M+Na]^+$: Calcd. 494.9863, Found 494.9858.

(5-(4-Chlorophenylthio)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl) (2,4-dichlorophenyl)methanone (5f): white solid, yield 62%, m.p. 105–106°C; IR (υ, cm^{-1}): 3075 (m, Ph-H), 2923 (m, CH_3), 1660 (vs, C=O), 1586, 1503, 1464 (s, Ar), 1087 (vs, C−S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.33–7.38 (m, 4H, Ph-H), 7.18–7.22 (m, 4H, Ph-H), 7.04 (d, J = 8.4 Hz, 2H, Ph-H), 6.67 (d, J = 8.8 Hz, 2H, Ph-H), 2.47 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 188.7 (C = O), 152.7 (Pyrazole-C), 138.3 (Ph-C), 138.2 (Ph-C), 136.7 (Ph-C), 136.1 (Pyrazole-C), 133.1 (Ph-C), 132.3 (Ph-C), 132.2 (Ph-C), 130.0 (Ph-C), 129.8 (Ph-C), 129.7 (2C, Ph-C), 129.1 (2C, Ph-C), 129.0 (2C, Ph-C), 128.9 (Ph-C), 127.1 (Ph-C), 126.0 (2C, Ph-C), 124.0 (Pyrazole-C), 14.3 (Pyrazole-**C**H_3). ESI-FTMS for $C_{23}H_{15}Cl_3N_2OS$ $[M+H]^+$: Calcd. 473.0038, Found 473.0033.

Synthesis of (5-Arylsulfinyl-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-arylmethanones (6a–6e)

To a stirred solution of **5** (2 mmol) in glacial acetic acid (10 mL), solution of H_2O_2 (30%, 4 mmol) was added dropwise. Reaction mixture was then stirred at room temperature

with monitoring by TLC (about 1∼2 h) and poured into H_2O. The mixture was extracted with ethyl acetate (15 mL × 3). The organic layer was combined and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by recrystallization with a mixed solvent of ethyl acetate and petroleum ether to give the product **6**.

(4-Chlorophenyl)(3-methyl-1-phenyl-5-(*m*-tolylsulfinyl)-1*H*-pyrazol-4-yl) methanone (6a): white solid, yield 51%, m.p. 73–75°C; IR (υ, cm^{-1}): 3057 (m, Ph-H), 2922 (m, CH_3), 1649 (vs, C=O), 1589, 1507, 1472 (s, Ar), 1277 (vs, S=O), 1085 (vs, C-S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.65 (d, J = 8.4 Hz, 2H, Ph-H), 7.37-7.46 (m, 7H, Ph-H), 6.95 (t, J = 8.0 Hz, 1H, Ph-H), 6.87 (d, J = 7.6 Hz, 1H, Ph-H), 6.62 (d, J = 8.0 Hz, 1H, Ph-H), 6.54 (s, 1H, Ph-H), 2.39 (s, 3H, pyrazol-CH_3), 2.13 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 190.2 (C=O), 151.0 (Pyrazole-C), 139.1 (Ph-C), 138.9 (Ph-C), 138.7 (Ph-C), 136.9 (Ph-C), 136.0 (Pyrazole-C), 133.2 (Ph-C), 130.8 (2C, Ph-C), 129.9 (Ph-C), 128.9 (Ph-C), 128.8 (2C, Ph-C), 128.7 (2C, Ph-C), 128.6 (Ph-C), 128.0 (Ph-C), 126.4 (Ph-C), 126.0 (2C, Ph-C), 123.9 (Pyrazole-C), 21.2 (Ph-**C**H_3), 13.7 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{19}ClN_2O_2S$ $[M+Na]^+$: Calcd. 457.0748, Found 457.0455.

(4-Chlorophenyl)(3-methyl-1-phenyl-5-(*p*-tolylsulfinyl)-1*H*-pyrazol-4-yl) methanone (6b): white solid, yield 71%, m.p. 198–200°C; IR (υ, cm^{-1}): 3055 (m, Ph-H), 2931 (m, CH_3), 1640 (vs, C=O), 1586, 1502, 1452 (s, Ar), 1261 (vs, S=O), 1085 (vs, C-S); ^{1}H NMR (400 MHz, CDCl3): 7.86 (d, J = 8.4 Hz, 2H, Ph-H), 7.35–7.51 (m, 8H, Ph-H), 6.99–7.04 (m, 3H, Ph-H), 2.28 (s, 3H, pyrazol-CH_3), 2.16 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.1 (C=O), 149.0 (Pyrazole-C), 144.5 (Ph-C), 141.1 (Ph-C), 140.2 (Ph-C), 138.4 (Ph-C), 136.5 (Ph-C), 131.2 (2C, Ph-C), 129.4 (2C, Ph-C), 129.1 (2C, Ph-C), 128.7 (2C, Ph-C), 128.4 (Pyrazole-C), 127.5 (Ph-C), 126.3 (2C, Ph-C), 124.5 (2C, Ph-C), 123.7 (Pyrazole-C), 21.3 (Ph-**C**H_3), 13.3 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{19}ClN_2O_2S$ $[M+H]^+$: Calcd. 435.0929, Found 435.0933.

(4-Chlorophenyl)(5-(3-chlorophenylsulfinyl)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methanone (6c): white solid, yield 73%, m.p. 156–158°C; IR (υ, cm^{-1}): 3085, 3069 (m, Ph-H), 2939 (m, CH_3), 1639 (vs, C=O), 1586, 1574, 1503, 1457 (s, Ar), 1262 (vs, S=O), 1083 (vs, C−S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (d, J = 8.4 Hz, 2H, Ph-H), 7.54 (d, J = 8.4 Hz, 2H, Ph-H), 7.43 (d, J = 7.6 Hz, 1H, Ph-H), 7.36 (t, J = 8.0 Hz, 2H, Ph-H), 7.31 (d, J = 8.0 Hz, 2H, Ph-H), 7.23 (d, J = 8.4 Hz, 1H, Ph-H), 7.16 (t, J = 8.0 Hz, 1H, Ph-H), 7.10 (s, 1H, Ph-H), 7.05 (d, J = 7.2Hz, 1H, Ph-H), 2.29 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 188.8 (C=O), 149.0 (Pyrazole-C), 143.8 (Ph-C), 142.1 (Ph-C), 140.5 (Ph-C), 138.1 (Pyrazole-C), 136.3 (Ph-C), 135.1 (Ph-C), 131.2 (2C, Ph-C), 130.8 (Ph-C), 129.8 (Ph-C), 129.7 (Ph-C), 129.2 (2C, Ph-C), 128.8 (2C, Ph-C), 126.5 (2C, Ph-C), 124.8 (Ph-C), 124.4 (Pyrazole-C), 122.6 (Ph-C), 13.4 (Pyrazole-**C**H_3). ESI-FTMS for $C_{23}H_{16}Cl_2N_2O_2S$ $[M+H]^+$: Calcd. 455.0382, Found 455.0374.

(2,4-Dichlorophenyl)(3-methyl-1-phenyl-5-(*p*-tolylsulfinyl)-1*H*-pyrazol-4-yl) methanone (6d): white solid, yield 88%, m.p. 128–130°C; IR (υ, cm^{-1}): 3057 (m, Ph-H), 2924 (m, CH_3), 1662 (vs, C=O), 1583, 1532, 1504, 1441 (s, Ar), 1280 (vs, S=O), 1063 (vs, C-S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.31–7.38 (m, 6H, Ph-H), 7.14–7.18 (m, 2H, Ph-H), 7.05 (d, J = 8.0 Hz, 2H, Ph-H), 6.87 (d, J = 8.0 Hz, 2H, Ph-H), 2.50 (s, 3H, pyrazol-CH_3), 2.23 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.0 (C=O), 152.6 (Pyrazole-C), 138.5 (Ph-C), 138.3 (Ph-C), 137.1 (Ph-C), 136.5 (Ph-C), 132.3 (Ph-C), 130.2 (Ph-C), 130.0 (Ph-C), 129.7 (Ph-C), 129.7 (Ph-C), 129.5 (Ph-C), 128.8 (Ph-C), 128.7 (Ph-C), 128.7 (Ph-C), 128.1 (Ph-C), 127.7 (Pyrazole-C), 127.0 (Ph-C), 126.1 (2C, Ph-C), 121.4 (Ph-C), 117.9 (Pyrazole-C), 21.0 (Ph-**C**H_3), 14.3 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{18}Cl_2N_2O_2S$ $[M+H]^+$: Calcd. 469.0539, Found 469.0547.

(5-(3-Chlorophenylsulfinyl)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(2,4-dichlorophenyl)methanone (6e): white solid, yield 75%, m.p. 100–102°C; IR (υ, cm^{-1}): 3062 (m, Ph-H), 2930 (m, CH_3), 1657 (vs, C=O), 1587, 1506, 1460 (s, Ar), 1289 (vs, S=O), 1010 (vs, C−S); ^1H NMR (300 MHz, $CDCl_3$): 7.27–7.74 (m, 12H, Ph-H), 2.24 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.0 (C=O), 152.6 (Pyrazole-C), 138.5 (Ph-C), 138.3 (Ph-C), 137.3 (Pyrazole-C), 137.1 (Ph-C), 136.5 (Ph-C), 132.3 (Ph-C), 130.2 (Ph-C), 130.0 (Ph-C), 129.7 (2C, Ph-C), 129.7 (Ph-C), 128.8 (Ph-C), 128.7 (Ph-C), 128.7 (2C, Ph-C), 127.0 (Ph-C), 126.1 (2C, Ph-C), 123.8 (Pyrazole-C), 121.4 (Ph-C), 14.3 (Pyrazole-**C**H_3). ESI-FTMS for $C_{23}H_{16}Cl_3N_2O_2S$ $[M+H]^+$: Calcd. 488.9993, Found 488.9993.

Synthesis of (5-Arylsulfonyl-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-arylmethanones (7a–7d)

The synthetic and purified procedures were similar to those of compound **6**, in addition to a reaction temperature of 80°C.

(4-Chlorophenyl)(3-methyl-1-phenyl-5-(*m*-tolylsulfonyl)-1*H*-pyrazol-4-yl) methanone (7a): white solid, yield 47%, m.p. 143–145°C; IR (υ, cm^{-1}): 3087 (m, Ph-H), 2935 (m, CH_3), 1670 (vs, C=O), 1595, 1549, 1508, 1465 (s, Ar), 1362, 1199 (vs, O=S=O), 1068 (vs, C−S); ^1H NMR (300 MHz, $CDCl_3$): 7.07–7.89 (m, 13H, Ph-H), 2.30 (s, 3H, pyrazol-CH_3), 2.17 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.28 (C=O), 153.73 (Pyrazole-C), 142.37 (Ph-C), 138.85 (Ph-C), 137.15 (Ph-C), 136.92 (Ph-C), 133.08 (Pyrazole-C), 132.54 (Ph-C), 130.57 (2C, Ph-C), 129.86 (Ph-C), 128.78 (Ph-C), 128.65 (2C, Ph-C), 128.48 (2C, Ph-C), 128.24 (Ph-C), 128.03 (Ph-C), 127.13 (Ph-C), 126.34 (2C, Ph-C), 124.68 (Pyrazole-C), 22.13 (Ph-**C**H_3), 13.48 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{19}ClN_2O_3S$ $[M+H]^+$: Calcd. 451.0878, Found 451.0883.

(4-Chlorophenyl)(5-(4-chlorophenylsulfonyl)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methanone (7b): white solid, yield 50%, m.p. 155–157°C; IR (υ, cm^{-1}): 3092 (m, Ph-H), 2934 (m, CH_3), 1669 (vs, C=O), 1583, 1523, 1497, 1476, 1452 (s, Ar), 1343, 1170 (vs, O=S=O), 1089 (vs, C−S); ^1H NMR (400 MHz, $CDCl_3$): 7.93 (d, $J = 8.0$ Hz, 2H, Ph-H), 7.31–7.54 (m, 11H, Ph-H), 2.20 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 189.5 (C=O), 147.1 (Pyrazole-C), 141.0 (Ph-C), 140.7 (Ph-C), 140.1 (Ph-C), 137.8 (Ph-C), 137.8 (Ph-C), 137.6 (Ph-C), 135.9 (Pyrazole-C), 131.2 (2C, Ph-C), 130.2 (Ph-C), 129.8 (2C, Ph-C), 129.3 (Ph-C), 129.3 (2C, Ph-C), 128.9 (2C, Ph-C), 127.5 (2C, Ph-C), 124.3 (Pyrazole-C), 12.4 (Pyrazole−**C**H_3). ESI-FTMS for $C_{23}H_{16}Cl_2N_2O_3S$ $[M+H]^+$: Calcd. 471.0322, Found 471.0331.

(2,4-Dichlorophenyl)(3-methyl-1-phenyl-5-tosyl-1*H*-pyrazol-4-yl)methanone (7c): white solid, yield 48%, m.p. 137–138°C; IR (υ, cm^{-1}): 3081, 3040 (m, Ph-H), 2964 (m, CH_3), 1670 (vs, C=O), 1597, 1584, 1502, 1458 (s, Ar), 1335, 1163 (vs, O=S=O), 1088 (vs, C−S); ^1H NMR (300 MHz, $CDCl_3$): 7.06–7.74 (m, 12H, Ph-H), 2.39 (s, 3H, pyrazol-CH_3), 2.22 (s, 3H, Ph-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 188.4 (C=O), 156.0 (Pyrazole-C), 148.0 (Ph-C), 141.1 (Ph-C), 138.8 (Ph-C), 138.0 (Ph-C), 136.2 (Pyrazole-C), 134.2 (Ph-C), 133.0 (Ph-C), 131.1 (Ph-C), 130.0 (Ph-C), 128.7 (2C, Ph-C), 128.6 (2C, Ph-C), 127.5 (2C, Ph-C), 127.3 (Ph-C), 127.0 (2C, Ph-C), 125.1 (Ph-C), 124.8 (Pyrazole-C), 23.6 (Ph-**C**H_3), 12.53 (Pyrazole-**C**H_3). ESI-FTMS for $C_{24}H_{18}Cl_2N_2O_3S$ $[M+H]^+$: Calcd. 485.0488, Found 485.0493.

(5-(4-Chlorophenylsulfonyl)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(2,4-dichloro phenyl)methanone (7d): white solid, yield 80%, m.p. 116–117°C; IR (υ, cm^{-1}): 3066

(m, Ph-H), 2929 (m, CH_3), 1676 (vs, C=O), 1580, 1546, 1520, 1463 (s, Ar), 1343, 1171 (vs, O=S=O), 1086 (vs, C−S); ^{1}H NMR (400 MHz, $CDCl_3$): 7.36 (m, 6H, Ph-H), 7.22 (d, J = 7.2 Hz, 2H, Ph-H), 7.05 (d, J = 8.8 Hz, 2H, Ph-H), 6.67 (d, J = 8.4 Hz, 2H, Ph-H), 2.48 (s, 3H, pyrazol-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 188.2 (C = O), 148.0 (Pyrazole-C), 141.0 (Ph-C), 140.3 (Pyrazole-C), 139.1 (Ph-C), 137.9 (Ph-C), 137.6 (Ph-C), 135.9 (Ph-C), 134.2 (Ph-C), 133.0 (Ph-C), 131.1 (Ph-C), 130.2 (Ph-C), 130.0 (2C, Ph-C), 129.2 (2C, Ph-C), 128.9 (2C, Ph-C), 127.5 (2C, Ph-C), 127.4 (Ph-C), 125.2 (Pyrazole-C), 12.6 (Pyrazole-**C**H_3). ESI-FTMS for $C_{23}H_{15}Cl_3N_2O_3S$ $[M+Na]^+$: Calcd. 526.9761, Found 526.9753.

Crystal Structure Determination

Compound **7d** was dissolved in a mixed solvent of ethyl acetate and petroleum ether and the resulting solution was allowed to stand in air at room temperature to give single crystal of **7d**. A colorless crystal of **7d** suitable for X-ray diffraction with dimensions of 0.16 mm × 0.10 mm × 0.10 mm was mounted on a Rigaku MM-07 Saturn 724 CCD diffractometer with *Mo-Kα* radiation (λ = 0.71073 Å) for data collection. A total of 12613 reflections were collected in the range of $1.96 < \theta < 26.35$ by using a phi and scan modes at 294(2) K, of which 4528 were independent with $R_{int} = 0.0725$. All calculations were refined anisotropically (SHELXS-97).[24] All hydrogen atoms were located from a difference Fourier map, placed at calculated positions, and included in the refinements in the riding mode with isotropic thermal parameters. A summary of the key crystallgraphic information were given in Table 1.

Herbicidal Activity Tests

Herbicidal activities in vivo of compounds **5**, **6,** and **7** were determined by rape root test (*Brassica campestris*) and barnyardgrass cup test (*Echinochloa crusgalli*) according to the reported method.[25]

Insecticidal Activity Test

Insecticidal activity of compounds against oriental armyworm (*Mythimna separate* Walker) was performed in the greenhouse.[16]

CONCLUSION

A series of novel [5-(arylthio/sulfinyl/sulfonyl)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl]-arylmethanones have been synthesized successfully via multi-step reactions with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one as starting material and characterized by melting point and organic spectroscopy. The crystal structure of (5-(4-chlorophenylsulfonyl)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(2,4-dichlorophenyl)methanone (**7d**) is reported. The biological activity results showed that some of the title compounds exhibit favorable herbicidal and insecticidal activities.

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SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website at http://dx.doi.org/10.1080/10426507.2014.919503

CCDC-999266 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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