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Synthesis and herbicidal activity of novel pyrazolo[3,4-*d*]pyrimidin-4-one derivatives containing aryloxyphenoxypropionate moieties

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Abstract—The 6-(4-alkoxycarbonylalkoxy)phenoxy-3-alkylthio(alkylsulfonyl)-1-phenyl-5-(substituted phenyl)pyrazolo[3,4-*d*]pyrimidin-4-ones **6** and **7** have been synthesized via the tandem aza-Wittig and annulation reactions of the corresponding iminophosphoranes **4**, aromatic isocyanates, and substituted phenols **2** in 52–98% yields. Their structures were clearly verified by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis or X-ray diffraction crystallography). And the results of preliminary bioassay indicated that these title compounds possess potential herbicidal activity against the root of rape and barnyard grass.

The derivatives of fused pyrimidinones have been the focus of great interest over many years due to the fact that many compounds containing a fused pyrimidinone ring play an important role in the biochemistry of the living cell.[1] Pyrazolo[3,4-*d*]pyrimidin-4-one derivatives also have extremely rich biological activities because of their structural similarity with purines,[2] they exhibit excellent antibacterial, antiphlogistic, and antitumor activities,[3] and they are employed in the treatment of erectile dysfunction in male animals.[4] In previous reports, various synthetic procedures have been devised for the conversion of *o*-aminonitriles and *o*-aminoesters bearing pyrazole ring to pyrazolopyrimindinone derivatives.[5] However, 3-substituted-6-(4-alkoxycarb-onylalkoxy)phenoxy pyrazolo[3,4-*d*]pyrimidin-4-ones are not easily accessible by these existing methods.

Aryloxyphenoxypropionate (APP) derivatives are a very important class of herbicides in the international market.[6] In recent years, heterocycles were introduced to the structures of APP, which lead to the development of a new series of highly efficient herbicides, such as whip, fenthiaprop-ethyl, quizalofop-ethyl, and heloxyfop-methyl.[7] Furthermore, some heteroaryloxo-phenoxy carbonates are of good fungicidal activity and anti-cancer activity.[8]

Aza-Wittig reactions of iminophosphoranes have received increasing attention in view of their utility in the synthesis of nitrogen-containing heterocyclic compounds.[9] Recently, aza-Wittig reactions of isocyanates were used to synthesize carbodiimides, which, in turn, were able to undergo a plethora of cyclization reactions, leading to the preparation of thienodipyrimidinones,[10] quinazolines,[11] imidazolinones,[12] pteridinones,[13] and fused pyrimidines.[14] As the continuing work of our search for new herbicidal active heterocycles,[15] we designed the structures which contain both pyrazolo-[3,4-*d*]pyrimidin-4-one and aryloxyphenoxypropionate (APP) moieties based on biochemical reasoning, and developed a new annulation process (Scheme 1), which proceeded smoothly via a tandem aza-Wittig and cyclization reaction to afford the novel title compounds 6-(4-alkoxycarbonylalkoxy)phenoxy-3-alkylthio(alkylsulfonyl)-1-phenyl-5-(substituted phenyl)pyrazolo[3,4-*d*]pyrimidin-4-ones **6** and **7**, in order to obtain better herbicidal activity.

The iminophosphorane **4**, which was prepared from 3-alkylthio-5-amino-4-ethoxycarbonyl-1-phenylpyrazole **3**, reacted with aromatic isocyanate to afford carbodiimide **5**. Then reaction of 2-(4-hydroxyphenoxy)-carboxylate **2** with **5** provides intermediate guanidine **8**. In the presence of catalytic amount of potassium carbonate,

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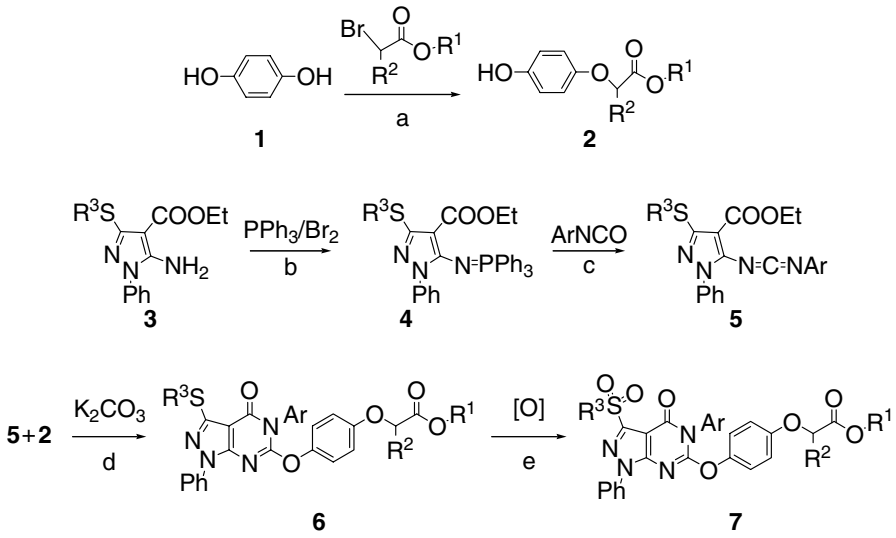
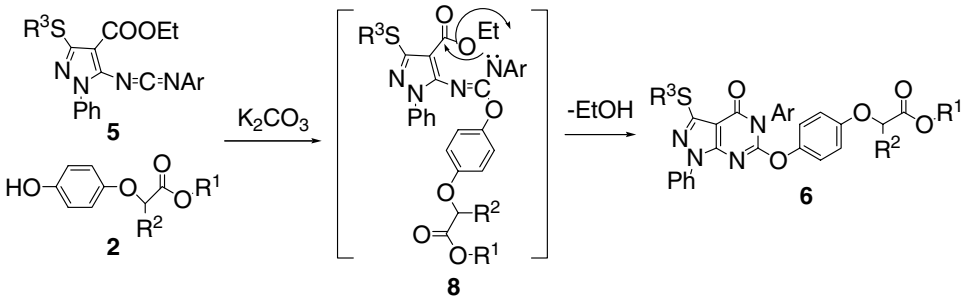


Scheme 1. Synthesis of the title compounds **6** and **7**. Reagents and conditions: (a) R^1ONa, R^1OH, 0–35 °C, 6 h, yields 57–66%; (b) Et_3N, CH_2Cl_2, 0 °C for 30 min then 25 °C for 26 h, yields 84%; (c) CH_2Cl_2, rt, 2–5 h; (d) K_2CO_3, CH_3CN, reflux, 5 h, yields 52–84%; (e) $Na_2WO_4{\cdot}H_2O$, AcOH, 30% H_2O_2, 50 °C, 5 h, yields 75–98%.



Scheme 2. The cyclization of carbodiimide **5** to synthesize the title compounds **6**.

the reaction took place to give **6** in moderate to good yields after recrystallization. This process can be rationalized in Scheme 2.

In this reaction, a variety of substituents can be tolerated in Ar group, such as electron-withdrawing groups (F, Cl) or electron-donating group (Me). R^1, R^2, and R^3 also could be various alkyl groups. Satisfactory yields of **6** were obtained when polar solvent acetonitrile was used;[16] furthermore, compounds **6** could be oxidized by hydrogen peroxide (H_2O_2) using sodium wolframate (Na_2WO_4) as catalyst to give the corresponding compounds **7** at about 40 °C. The results are listed in Table 1.

Table 1. Yields of compounds **6** and **7**

Compounds	R =	R^3	R^2	R^1	Yields of **6** (%)	Yields of **7** (%)
6a, **7a**	H	Me	Me	Me	80	75
6b, **7b**	*o*-Cl	Me	Me	Me	73	78
6c, **7c**	*m*-Me	Me	Me	Me	80	91
6d, **7d**	*o*-F	Me	Me	Me	65	85
6e, **7e**	H	Me	Me	Et	84	98
6f, **7f**	*o*-Cl	Me	Me	Et	71	83
6g, **7g**	*m*-Me	Me	Me	Et	78	86
6h, **7h**	*m*-Me	Me	H	Et	82	77
6i, **7i**	*m*-Me	Bn	Me	Et	52	90
6j, **7j**	*m*-Me	Bn	H	Et	66	82
6k, **7k**	H	Me	Me	*n*-Pr	82	78
6l, **7l**	*o*-Cl	Me	Me	*n*-Pr	72	95
6m, **7m**	*m*-Me	Me	Me	*n*-Pr	74	77

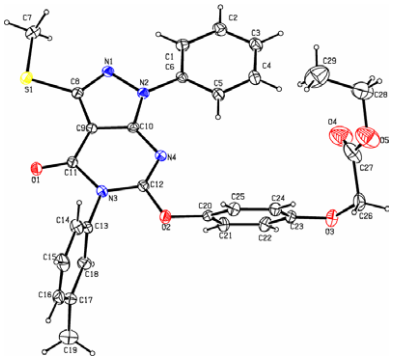


Figure 1. View and atom labeling of **6h**.

Table 2. The herbicidal activity of compounds **6** and **7**

Compound	Relative inhibition (root%/stalk%)			
	Rape (100 mg/L)	Rape (10 mg/L)	Barnyard grass (100 mg/L)	Barnyard grass (10 mg/L)
6a	96.1/76.9	40.2/20.5	93.5/68.9	63.0/44.8
6b	84.3/56.4	27.5/7.7	97.8/68.9	63.0/62.1
6c	52.2/17.8	3.3/6.7	66.7/−7.3	35.5/−5.3
6d	27.2/0.0	19.6/6.7	62.2/0.0	51.1/−31.6
6e	86.1/46.2	57.4/12.9	88.5/32.3	57.7/12.9
6f	93.1/63.5	61.4/26.9	92.3/35.5	75.0/−25.8
6g	97.0/63.5	46.5/9.6	88.5/0.0	59.6/−12.9
6h	100/100	60.4/25.0	98.1/77.4	59.6/−6.5
6i	32.2/10.6	24.4/−2.1	61.9/−6.4	33.3/−6.4
6j	64.1/24.0	20.6/20.0	75.5/−10.5	66.7/5.3
6k	44.4/14.9	21.1/−2.1	71.4/35.5	57.1/25.8
6l	36.7/8.5	5.5/10.6	64.3/25.8	53.4/25.8
6m	35.5/4.3	30.0/31.9	57.1/35.5	30.9/41.9
7a	80.4/48.9	25.0/13.3	93.3/31.6	66.7/5.3
7b	21.7/4.4	14.1/2.2	46.7/15.8	42.2/−5.3
7c	72.8/26.7	19.6/13.3	86.7/15.8	44.4/−15.8
7d	28.0/0.0	16.3/0.0	53.3/−21.0	33.3/10.5
7e	89.2/58.9	42.2/15.4	89.1/34.5	50.0/31.0
7f	81.4/48.7	29.4/5.1	89.1/47.9	63.0/37.9
7g	98.0/74.4	51.0/17.9	95.6/51.7	54.3/3.4
7h	94.1/71.8	50.0/28.2	95.6/37.9	58.7/−3.4
7i	34.8/6.7	9.8/6.7	72.5/16.7	50.0/13.3
7j	51.1/6.7	21.7/15.5	62.2/0.0	35.5/−5.3
7k	27.2/6.7	3.3/2.2	62.5/13.3	32.5/13.3
7l	67.4/42.2	17.4/−17.8	80.0/23.3	50.0/16.7
7m	63.0/31.1	14.1/13.3	80.0/20.0	35.0/13.3
2,4-D	99.0/91.2	98.1/91.2	97.5/33.3	97.5/30.8

The structures of compounds **6** and **7** were deduced from their spectra data (IR, ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis).[17] Compound **6h** was recrystallized by slow evaporation from CH_2Cl_2, and its single crystal was analyzed by X-ray diffraction crystallography.[18] The corresponding structure is shown in Figure 1. X-ray structure analysis further confirmed the proposed structure and showed that ring atoms in pyrazolo[3,4-*d*]pyrimidin-4-one moiety are essentially planar. The bond lengths of C(8)=N(1), C(9)=C(10), and C(12)=N(4) are 1.313(5), 1.371(5), and 1.283(4) Å, respectively, which are longer than the lengths of the typical C=N (1.28 Å) and C=C (1.34 Å), while the single bond lengths of C(10)–N(2), C(8)–C(9), C(9)–C(11), C(12)–N(3), and C(10)–N(4), are 1.345(5), 1.409(5), 1.432(5), 1.375(4), and 1.377(4) Å, respectively, which are significantly shorter than the lengths of typical C(sp^2)–N (1.426 Å) and C–C (1.53 Å). These results show some degree of delocalization in **6h**.

The herbicidal activity of all compounds **6** and **7** against *brassica napus* (rape) and *echinochloa crus-galli* (barnyard grass) has been investigated at the dosage of 100 and 10 mg/L using the reported procedure,[19] compared with distilled water and 2,4-dichlorophenoxyl acetic acid (2,4-D), a commercially available herbicide in the market. The results of preliminary bioassay showed that some of them exhibit good herbicidal activities (the inhibition rates are listed in Table 2). For example, **6a**, **6f**, **6h**, **7g**, and **7h** showed more than 90% inhibitory rate to root of rape and barnyard grass at 100 mg/L. It is also interesting to note that ethyl ester showed higher herbicidal activity than the corresponding methyl ester and *n*-propyl ester in general, the reason may be the hydrolysis of the products.[20] The investigations on *R* and *S* isomers of products are going on further.

In summary, we have developed a novel synthesis of 6-(4-alkoxycarbonylalkoxy)phenoxy-3-alkylthio(alkylsulfonyl)-1-phenyl-5-(substituted phenyl)pyrazolo[3,4-*d*]pyrimidin-4-one derivatives via tandem aza-Wittig and annulation reactions smoothly in moderate to good yields. The structure of the title compounds has both the skeletons of pyrazolo[3,4-*d*]pyrimidin-4-one and aryloxyphenoxypropionate (APP). The herbicidal tests showed that these title compounds possess herbicidal activity and could be further used as potential herbicides.

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General procedure for the preparation of 6-(4-alkoxycarbonylalkoxy)phenoxy-3-alkylthio-1-phenyl-5-(substituted phenyl)pyrazolo[3,4-d]pyrimidin-4-ones (**6a**–**6m**). To a solution of iminophosphorane **4** (2 mmol) in dry dichloromethane (25 mL), aromatic isocyanate (2 mmol) was added under nitrogen at room temperature. After the reaction mixture was stirred for 2–5 h, the solvent was removed off under reduced pressure, then 25 mL anhydrous accetonitrile, 2.0 mmol 2-(4-hydroxyphenoxy)-carboxylate **2**, and 0.05 g anhydrous potassium carbonate were added to the mixture. Stirring for another 5 h at refluxing and filtering, the solution was condensed under reduced pressure, the residue was recrystallized with ethanol to give pure 6-(4-alkoxycarbonylalkoxy)phenoxy-3-alkylthio-1-phenyl-5-(substituted phenyl)pyrazolo[3,4-*d*]pyrimidin-4-ones **6a**–**6m**.

6-[4-(1-Methoxycarbonylethoxy)]phenoxy-3-methylthio-1,5-diphenylpyrazolo[3,4-d]pyrimidin-4-one (**6a**). White crystals, mp 238–240 °C; yield, 80%; IR (KBr) υ (cm^{-1}): 2990, 2926, 1753, 1704, 1604, 1574, 1547, 1516, 1500, 1347, 1204, 1136, 895, 769, 688; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 7.6 Hz, Ph), 7.26–7.52 (m, 7H, Ph), 7.20 (t, 1H, J = 8.0 Hz, Ar), 7.08 (dd, 2H, J = 2.0 and 7.2 Hz, OC_6H_4O), 6.90 (dd, 2H, J = 2.0 and 8.0 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.8 Hz, OCHC=O), 3.75 (s, 3H, OCH_3), 2.67 (s, 3H, SCH_3), 1.65 (d, 3H, J = 6.8 Hz, CH_3CHO); EI-MS (70 eV, *m*/*z*): 528 (M^+-1), 530 (M^++2); Elemental Anal. Calcd for $C_{28}H_{24}N_4O_5S$: C, 63.62; H, 4.58; N, 10.60. Found: C, 63.49; H, 4.67; N, 10.42.

5-(2-Chlorophenyl)-6-[4-(1-methoxycarbonylethoxy)]phenoxy-3-methylthio-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6b**). White crystals, mp 182–183 °C; yield, 73%; IR (KBr) υ (cm^{-1}): 2989, 2955, 1754, 1718, 1591, 1573, 1545, 1352, 1190, 1099, 896, 824, 762, 689; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ph), 7.18–7.71 (m, 8H, Ar), 7.11 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.8 Hz, OCHC=O), 3.76 (s, 3H, OCH_3), 2.68 (s, 3H, SCH_3), 1.65 (d, 3H, J = 6.4 Hz, CH_3CHO); EI-MS (70 eV, *m*/*z*): 562 (M^+-1), 563 (M^+); Elemental Anal. Calcd for $C_{28}H_{23}ClN_4O_5S$: C, 57.93; H, 4.12; N, 9.95. Found: C, 60.00; H, 4.01; N, 10.12.

6-[4-(1-Methoxycarbonylethoxy)]phenoxy-5-(3-methylphenyl)-3-methylthio-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6c**). White crystals, mp 239–241 °C; yield, 80%; IR

(KBr) υ (cm^{-1}): 2989, 2927, 1753, 1701, 1602, 1573, 1548, 1501, 1349, 1195, 1135, 830, 755, 686; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ar), 7.17–7.42 (m, 7H, Ar), 7.08 (d, 2H, J = 9.2 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.4 Hz, OCHC=O), 3.76 (s, 3H, OCH_3), 2.68 (s, 3H, SCH_3), 2.43 (s, 3H, *m*-$CH_3C_6H_4$), 1.65 (d, 3H, J = 6.4 Hz, CH_3CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 18.7, 21.5, 52.5, 73.3, 102.4, 116.0, 120.3, 122.8, 125.4, 126.1, 129.0, 129.4, 130.2, 134.4, 138.8, 139.7, 146.0, 147.5, 151.3, 155.7, 156.4, 157.7, 172.5; EI-MS (70 eV, *m*/*z*): 542 (M^+); Elemental Anal. Calcd for $C_{29}H_{26}N_4O_5S$: C, 64.19; H, 4.83; N, 10.33. Found: C, 64.35; H, 5.01; N, 10.22.

6-[4-(1-Methoxycarbonylethoxy)]phenoxy-5-(2-fluorophenyl)-3-methylthio-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6d**). White crystals, mp 205–206 °C; yield, 65%; IR (KBr) υ (cm^{-1}): 2991, 2951, 1748, 1709, 1601, 1576, 1546, 1501, 1350, 1201, 1136, 896, 829, 756, 680; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, 2H, J = 8.4 Hz, Ar), 7.20–7.44 (m, 7H, Ar), 7.07 (dd, 2H, J = 2.0 and 8.8 Hz, OC_6H_4O), 6.90 (dd, 2H, J = 2.0 and 7.2 Hz, OC_6H_4O), 4.78 (q, 1H, J = 7.2 Hz, OCHC=O), 3.76 (s, 3H, OCH_3), 2.68 (s, 3H, SCH_3), 1.65 (d, 3H, J = 6.8 Hz, CH_3CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 18.6, 52.5, 73.2, 102.1, 116.0, 116.6, 116.8, 120.4, 122.2, 122.7, 124.8, 126.2, 128.9, 130.6, 131.2, 131.3, 138.7, 145.9, 147.5, 151.3, 155.7, 156.0, 156.6, 156.8, 159.1, 172.4; EI-MS (70 eV, *m*/*z*): 546 (M^+-1), 547 (M^+); Elemental Anal. Calcd for $C_{28}H_{23}FN_4O_5S$: C, 61.53; H, 4.24; N, 10.25. Found: C, 61.24; H, 4.36; N, 10.38.

6-[4-(1-Ethoxycarbonylethoxy)]phenoxy-3-methylthio-1,5-diphenylpyrazolo[3,4-d]pyrimidin-4-one (**6e**). White crystals, mp 213–214 °C, yield, 84%; IR (KBr) υ (cm^{-1}): 2991, 2924, 1743, 1703, 1604, 1573, 1548, 1501, 1348, 1192, 1135, 1093, 896, 830, 688; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ph), 7.54 (d, 2H, J = 7.6 Hz, Ph), 7.49 (d, 1H, J = 7.2 Hz, Ph), 7.31–7.37 (m, 4H, Ph), 7.20 (t, 1H, J = 7.2 Hz, Ph), 7.07 (d, 2H, J = 9.2 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.74 (q, 1H, J = 6.8 Hz, OCH), 4.21 (q, 2H, J = 7.2 Hz, OCH_2), 2.67 (s, 3H, SCH_3), 1.64 (d, 3H, J = 6.8 Hz, CH_3CH), 1.23 (t, 3H, J = 6.4 Hz, CH_2CH_3); EI-MS (70 eV, *m*/*z*): 542 (M^+), 543 (M^++1); Elemental Anal. Calcd for $C_{29}H_{26}N_4O_5S$: C, 64.19; H, 4.83; N, 10.33. Found: C, 64.35; H, 4.67; N, 10.54.

5-(2-Chlorophenyl)-6-[4-(1-ethoxycarbonylethoxy)phenoxy-3-methylthio-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6f**). White crystals, mp 192–194 °C, yield, 71%; IR (KBr) υ (cm^{-1}): 2985, 2932, 1747, 1714, 1594, 1575, 1551, 1503, 1350, 1205, 1188, 1130, 895, 825, 778, 759; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.4 Hz, Ar), 7.59 (d, 1H, J = 2.8 Hz, Ar), 7.46 (d, 3H, J = 3.2 Hz, Ar), 7.33 (t, 2H, J = 7.8 Hz, Ar), 7.20 (t, 1H, J = 7.2 Hz, Ar), 7.10 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.91 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.75 (q, 1H, J = 6.8 Hz, OCH), 4.21 (q, 2H, J = 7.2 Hz, OCH_2), 2.68 (s, 3H, SCH_3), 1.65 (d, 3H, J = 6.8 Hz, CH_3CH), 1.24 (t, 3H, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 14.3, 18.6, 61.5, 73.3, 102.2, 115.9, 120.4, 122.7, 126.2, 128.0, 128.9, 130.5, 130.8, 132.5, 138.7, 145.8, 147.6, 151.4, 155.8, 156.0, 156.7, 171.9; EI-MS (70 eV, *m*/*z*): 576 (M^+), 578 (M^++2); Elemental Anal. Calcd for $C_{29}H_{25}ClN_4O_5S$: C, 60.36; H, 4.37; N, 9.71. Found: C, 60.57; H, 4.20; N, 9.69.

6-[4-(1-Ethoxycarbonylethoxy)]phenoxy-5-(3-methylphenyl)-3-methylthio-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6g**). White crystals, mp 223–225 °C; yield, 78%; IR (KBr) υ (cm^{-1}): 2989, 2924, 1744, 1701, 1601, 1573, 1549, 1501, 1349, 1194, 1134, 1093, 831, 779, 755; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ar), 7.42 (t, 1H, J = 7.6 Hz, Ar), 7.15–7.35 (m, 6H, Ar), 7.08 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.74 (q, 1H, J = 7.2 Hz, CHC=O), 4.21 (q, 2H, J = 7.6 Hz, OCH_2), 2.67 (s, 3H, SCH_3), 2.43 (s, 3H, *m*-CH_3Ph), 1.65 (d, 3H, J = 8.4 Hz, $CHCH_3$), 1.23 (t, 3H, J = 7.2 Hz, CH_2CH_3); EI-MS (70 eV, *m*/*z*): 556 (M^+), 557(M^++1); Elemental Anal. Calcd for $C_{30}H_{28}N_4O_5S$: C, 64.73; H, 5.07; N, 10.0. Found: C, 64.87; H, 4.82; N, 10.04.

6-(4-Ethoxycarbonylmethoxy)phenoxy-5-(3-methylphenyl)-3-methylthio-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6h**). White crystals, mp 202–204 °C; yield, 82%; IR (KBr) υ (cm^{-1}): 2974, 2930, 1751, 1701, 1603, 1573, 1549, 1502, 1349, 1186, 1077, 911, 830, 779, 684; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ar), 7.43 (t, 1H, J = 7.8 Hz, Ar), 7.15–7.34 (m, 6H, Ar), 7.10 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.94 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.64 (s, 2H, J = 7.2 Hz, OCH_2C=O), 4.28 (q, 2H, J = 7.2 Hz, OCH_2), 2.67 (s, 3H, SCH_3), 1.30 (t, 3H, J = 7.2 Hz, OCH_2CH_3); EI-MS (70 eV, *m*/*z*): 542 (M^+), 543 (M^++1); Elemental Anal. Calcd for $C_{29}H_{26}N_4O_5S$: C, 64.19; H, 4.83; N, 10.33. Found: C, 64.32; H, 4.64; N, 10.37.

3-Benzylsulfanyl-6-[4-(1-ethoxycarbonylethoxy)]phenoxy-5-(3-methylphenyl)-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6i**). White crystals, mp 117–120 °C; yield, 52%; IR (KBr) υ (cm^{-1}): 2986, 2921, 1728, 1705, 1598, 1572, 1555, 1502, 1271, 1197, 1089, 1047, 911, 828, 762, 698; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.8 Hz, Ar), 7.08–7.49 (m, 12H, Ar), 7.05 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.74 (q, 1H, J = 7.2 Hz, OCHC=O), 4.49 (s, 2H, PhCH_2), 4.21 (q, 2H, J = 6.8 Hz, OCH_2), 2.43 (s, 3H, PhCH_3), 1.65 (d, 3H, J = 6.8 Hz, $CHCH_3$), 1.24 (t, 3H, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 18.6, 21.5, 35.2, 61.5, 73.2, 102.6, 115.9, 120.3, 122.7, 125.4, 126.1, 127.3, 128.5, 128.9, 129.0, 129.3, 130.1, 134.3, 137.7, 138.7, 139.6, 145.9, 146.2, 151.2, 155.7, 156.4, 157.5, 171.9; EI-MS (70 eV, *m*/*z*): 633 (M^+), 634 (M^++1); Elemental Anal. Calcd for $C_{36}H_{32}N_4O_5S$: C, 68.34; H, 5.10; N, 8.85. Found: C, 68.32; H, 4.94; N, 8.77.

3-Benzylsulfanyl-6-(4-ethoxycarbonylmethoxy)phenoxy-5-(3-methylphenyl)-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**6j**). White crystals, mp 130–131 °C; yield, 66%; IR (KBr) υ (cm^{-1}): 2980, 2919, 1759, 1701, 1598, 1572, 1544, 1503, 1193, 1085, 778, 690; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 2H, J = 7.6 Hz, Ar), 7.07–7.49 (m, 12H, Ar), 7.08 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.63 (3, 2H, OCH_2C=O), 4.50 (s, 2H, PhCH_2), 4.28 (q, 2H, J = 7.2 Hz, OCH_2), 2.43 (s, 3H, PhCH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 21.6, 60.5, 61.7, 65.9, 101.5, 115.5, 121.7, 122.6, 125.2, 126.8, 128.0, 128.8, 128.9, 129.0, 129.1, 129.7, 130.7, 131.5, 133.9, 137.6, 140.1, 145.8, 146.5, 151.9, 156.2, 156.6, 157.0, 168.6; EI-MS (70 eV, *m*/*z*): 618 (M^+-1), 619(M^+); Elemental Anal. Calcd for $C_{35}H_{30}N_4O_5S$: C, 67.94; H, 4.89; N, 9.06. Found: C, 68.02; H, 4.94; N, 8.98.

3-Methylthio-1,5-diphenyl-6-[4-(1-propoxycarbonylethoxy)]phenoxy pyrazolo[3,4-d]pyrimidin-4-one (**6k**). White crystals, mp 195–197 °C; yield, 82%; IR (KBr) υ (cm^{-1}): 2974, 2919, 1746, 1701, 1604, 1573, 1548, 1500, 1347, 1191, 1134, 895, 757, 687; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ar), 7.20–7.57 (m, 8H, Ph), 7.08 (dd, 2H, J = 7.2 and 2.0 Hz, OC_6H_4O), 6.90 (dd, 2H, J = 7.2 and 2.0 Hz, OC_6H_4O), 4.75 (q, 1H, J = 7.2 Hz, CHC=O), 4.11 (m, 2H, OCH_2Et), 2.68 (s, 3H, SCH_3), 1.60–1.66 (m, 5H, CH_3CHO and $CH_2CH_2CH_3$), 0.87 (t, 3H, J = 7.2 Hz, CH_3); EI-MS (70 eV, *m*/*z*): 557 (M^+); Elemental Anal. Calcd for $C_{30}H_{28}N_4O_5S$: C, 64.73; H, 5.07; N, 10.07. Found: C, 64.92; H, 5.16; N, 9.96.

5-(2-Chlorophenyl)-3-methylthio-1-phenyl-6-[4-(1-propoxycarbonylethoxy)]phenoxypyrazolo[3,4-d]pyrimidin-4-one (**6l**). White crystals, mp 168–170 °C; yield, 72%; IR (KBr) υ (cm^{-1}): 2974, 1751, 1716, 1594, 1574, 1503, 1399, 1351, 1191, 896, 758; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 7.6 Hz, Ar), 7.20–7.61 (m, 7H, Ar), 7.10 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (dd, 2H, J = 9.2 Hz, OC_6H_4O), 4.76 (q, 1H, J = 6.8 Hz, CHC═O), 4.12 (t, 2H, J = 6.8 Hz, O*CH*$_2$Et), 2.69 (s, 3H, SCH_3), 1.61–1.66 (m, 5H, *CH*$_3$CHO and CH_2*CH*$_2$$CH_3$), 0.88 (t, 3H, J = 7.6 Hz, CH_3); EI-MS (70 eV, *m/z*): 590 (M^+-1), 591 (M^+); Elemental Anal. Calcd for $C_{30}H_{27}ClN_4O_5S$: C, 60.69; H, 4.60; N, 9.48. Found: C, 60.48; H, 4.53; N, 9.57.

5-(2-Methylphenyl)-3-methylthio-1-phenyl-6-[4-(1-propoxycarbonylethoxy)]phenoxypyrazolo[3,4-d]pyrimidin-4-one (**6m**). White crystals, mp 187–188 °C; yield, 74%; IR (KBr) υ (cm^{-1}): 2971, 2919, 1749, 1701, 1602, 1572, 1550, 1500, 1349, 1192, 1132, 779, 684; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.4 Hz, Ar), 7.15–7.44 (m, 7H, Ar), 7.08 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.76 (q, 1H, J = 6.8 Hz, CHC═O), 4.11 (t, 2H, J = 6.8 Hz, O*CH*$_2$Et), 2.67 (s, 3H, SCH_3), 2.43 (s, 3H, *m*-CH_3Ph), 1.60–1.66 (m, 5H, *CH*$_3$CHO and CH_2*CH*$_2$$CH_3$), 0.87 (t, 3H, J = 7.4 Hz, CH_3); EI-MS (70 eV, *m/z*): 570 (M^+-1), 571 (M^+); Elemental Anal. Calcd for $C_{31}H_{30}N_4O_5S$: C, 65.25; H, 5.30; N, 9.82. Found: C, 65.46; H, 5.41; N, 10.01.

General procedure for the preparation of 6-(4-alkoxy carbonylalkoxy)phenoxy-3-alkylsulfonyl-1-phenyl-5-(substituted phenyl)pyrazolo[3,4-d]pyrimidin-4-ones (**7a**–**7m**). To a 25 mL flask, 1.5 mmol **6** and 15 ml acetic acid were added at room temperature, and 0.002 g (0.06 mmol) $Na_2WO_4{\cdot}H_2O$ was added with stirring. Then the reaction mixture was heated to 40 °C with vigorous stirring. Under this condition, 0.51 g (4.5 mmol) of 30% H_2O_2 was added dropped slowly, when addition is complete, the mixture was heated to 50 °C and stirred for another 5 h. The reaction mixture was chilled to room temperature and dumped to a solution that was dispensed by 0.25 g Na_2SO_3 and 20 mL water. A great deal white solid was precipitated with stirring, after filtering, pure compounds **7** were obtained after recrystallization with ethanol.

6-[4-(1-Methoxycarbonylethoxy)]phenoxy-3-methylsulfonyl-1,5-diphenylpyrazolo[3,4-d]pyrimidin-4-one (**7a**). White crystals, mp 256–258 °C; yield, 75%; IR (KBr) υ (cm^{-1}): 2999, 2917, 1753, 1731, 1596, 1573, 1551, 1499, 1329, 1191, 1134, 1088, 901, 762, 690; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.4 Hz, Ph), 7.53–7.58 (m, 3H, Ph), 7.31–7.40 (m, 5H, Ph), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.8 Hz, OCHC═O), 3.75 (s, 3H, OCH_3), 3.51 (s, 3H, $S(O_2)CH_3$), 1.65 (d, 3H, J = 7.2 Hz, *CH*$_3$CHO); EI-MS (70 eV, *m/z*): 560 (M^+), 561 (M^++1); Elemental Anal. Calcd for $C_{28}H_{24}N_4O_7S$: C, 59.99; H, 4.32; N, 9.99. Found: C, 59.89; H, 4.45; N, 10.12.

5-(2-Chlorophenyl)-6-[4-(1-methoxycarbonylethoxy)]phenoxy-3-methylsulfonyl-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7b**). White crystals, mp 153–158 °C; yield, 78%; IR (KBr) υ (cm^{-1}): 3000, 2951, 1715, 1593, 1575, 1544, 1504, 1323, 1199, 1141, 1092, 903, 829, 764, 691; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 7.6 Hz, Ph), 7.27–7.50 (m, 7H, Ar), 7.09 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.8 Hz, OCHC═O), 3.76 (s, 3H, OCH_3), 3.51 (s, 3H, $S(O_2)CH_3$), 1.65 (d, 3H, J = 6.8 Hz, *CH*$_3$CHO); EI-MS (70 eV, *m/z*): 594 (M^+), 595 (M^++1); Elemental Anal. Calcd for $C_{28}H_{23}ClN_4O_7S$: C, 56.52; H, 3.90; N, 9.42. Found: C, 56.50; H, 4.01; N, 9.32.

6-[4-(1-Methoxycarbonylethoxy)]phenoxy-5-(3-methylphenyl)-3-methylsulfonyl-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7c**). White crystals, mp 227–228 °C; yield, 91%; IR (KBr) υ (cm^{-1}): 3012, 2928, 1753, 1723, 1598, 1574, 1545, 1501, 1324, 1202, 1140, 1096, 774, 696; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.4 Hz, Ar), 7.46 (t, 2H, J = 7.6 Hz, Ar), 7.27–7.40 (m, 3H, Ar), 7.18 (d, 2H, J = 8.0 Hz, Ar), 7.06 (d, 2H, J = 9.2 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.8 Hz, OCHC═O), 3.76 (s, 3H, OCH_3), 3.51 (s, 3H, $S(O_2)CH_3$), 2.47 (s, 3H, *m*-$CH_3C_6H_4$), 1.65 (d, 3H, J = 6.8 Hz, *CH*$_3$CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 21.5, 42.7, 52.5, 73.2, 101.0, 116.0, 121.7, 122.6, 125.2, 128.0, 128.8, 129.2, 129.7, 130.6, 133.9, 137.7, 140.0, 145.7, 147.6, 151.9, 155.9, 156.5, 157.1, 172.4; EI-MS (70 eV, *m/z*): 574 (M^+), 576 (M^++2); Elemental Anal. Calcd for $C_{29}H_{26}N_4O_7S$: C, 60.62; H, 4.56; N, 9.75. Found: C, 60.52; H, 4.77; N, 9.89.

5-(2-Fluorophenyl)-6-[4-(1-methoxycarbonylethoxy)]phenoxy-3-methylsulfonyl-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7d**). White crystals, mp 209–210 °C; yield, 85%; IR (KBr) υ (cm^{-1}): 2999, 2954, 1755, 1727, 1601, 1574, 1546, 1502, 1327, 1197, 1135, 1093, 901, 828, 758, 692; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 7.6 Hz, Ar), 7.30–7.40 (m, 7H, Ar), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.77 (q, 1H, J = 6.8 Hz, OCHC═O), 3.75 (s, 3H, OCH_3), 3.51 (s, 3H, $S(O_2)CH_3$), 2.44 (s, 3H, *m*-*CH*$_3$Ph), 1.65 (d, 3H, J = 6.8 Hz, *CH*$_3$CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6, 21.4, 42.6, 52.5, 73.1, 101.0, 116.0, 121.6, 122.5, 127.9, 129.1, 130.5, 131.2, 137.6, 139.8, 145.7, 147.4, 151.8, 155.8, 156.5, 157.2, 172.3; EI-MS (70 eV, *m/z*): 574 (M^+-4), 575 (M^+-3); Elemental Anal. Calcd for $C_{28}H_{23}FN_4O_7S$: C, 58.13; H, 4.01; N, 9.68. Found: C, 58.24; H, 4.11; N, 9.79.

6-[4-(1-Ethoxycarbonylethoxy)]phenoxy-3-methylsulfonyl-1,5-diphenylpyrazolo[3,4-d]pyrimidin-4-one (**7e**). White crystals, mp 228–229 °C, yield, 98%; IR (KBr) υ (cm^{-1}): 2987, 2926, 1744, 1726, 1603, 1575, 1546, 1500, 1328, 1192, 1136, 1097, 904, 776, 699; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.0 Hz, Ph), 7.53–7.59 (m, 3H, Ph), 7.31–7.40 (m, 5H, Ph), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.74 (q, 1H, J = 6.8 Hz, OCH), 4.21 (q, 2H, J = 7.2 Hz, OCH_2), 3.51 (s, 3H, $S(O_2)CH_3$), 1.64 (d, 3H, J = 6.8 Hz, *CH*$_3$CH), 1.23 (t, 3H, J = 7.2 Hz, CH_2*CH*$_3$); EI-MS (70 eV, *m/z*): 574 (M^+), 575 (M^++1); Elemental Anal. Calcd for $C_{29}H_{26}N_4O_7S$: C, 60.62; H, 4.56; N, 9.75. Found: C, 60.53; H, 4.67; N, 9.54.

5-(2-Chlorophenyl)-6-[4-(1-ethoxycarbonylethoxy)phenoxy-3-methylsulfonyl-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7f**). White crystals, mp 123–125 °C, yield, 83%; IR (KBr) υ (cm^{-1}): 2988, 2924, 1747, 1719, 1594, 1575, 1545, 1501, 1321, 1196, 1144, 1098, 903, 828, 766, 670; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.0 Hz, Ar), 7.29–7.63 (m, 7H, Ar), 7.09 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.91 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.75 (q, 1H, J = 7.2 Hz, OCH), 4.21 (q, 2H, J = 7.2 Hz, OCH_2), 3.51 (s, 3H, $S(O_2)CH_3$), 1.65 (d, 3H, J = 7.2 Hz, *CH*$_3$CH), 1.24 (t, 3H, J = 7.2 Hz, CH_2*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 18.6, 42.6, 61.5, 73.2, 100.7, 116.0, 121.7, 122.5, 128.0, 128.3, 129.1, 130.4, 130.6, 131.2, 131.9, 132.3, 137.5, 145.5, 147.6, 152.0, 155.4, 156.0, 156.7, 171.8; EI-MS (70 eV, *m/z*): 608 (M^+), 609 (M^++2); Elemental Anal. Calcd for $C_{29}H_{25}ClN_4O_7S$: C, 57.19; H, 4.14; N, 9.20. Found: C, 57.31; H, 4.20; N, 9.09.

6-[4-(1-Ethoxycarbonylethoxy)]phenoxy-5-(3-methylphenyl)-3-methylsulfonyl-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7g**). White crystals, mp 215–216 °C; yield, 86%; IR (KBr) υ (cm^{-1}): 2986, 2930, 1744, 1720, 1600, 1573, 1553, 1501, 1320, 1196, 1135, 1094, 917, 759, 690; ^1H NMR

($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.0 Hz, Ar), 7.46 (t, 1H, J = 7.6 Hz, Ar), 7.29–7.40 (m, 5H, Ar), 7.18 (d, 1H, J = 8.0 Hz, Ar), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.74 (q, 1H, J = 7.2 Hz, CHC=O), 4.21 (q, 2H, J = 7.6 Hz, OCH_2), 3.51 (s, 3H, $S(O_2)CH_3$), 2.45 (s, 3H, *m-*CH_3Ph), 1.65 (d, 3H, J = 8.4 Hz, CHCH_3), 1.23 (t, 3H, J = 7.2 Hz, CH_2CH_3); EI-MS (70 eV, *m/z*): 588 (M^+), 589(M^++1); Elemental Anal. Calcd for $C_{30}H_{28}N_4O_7S$: C, 61.21; H, 4.79; N, 9.52. Found: C, 61.33; H, 4.82; N, 9.76.

6-(4-Ethoxycarbonylmethoxy)phenoxy-5-(3-methylphenyl)-3-methylsulfonyl-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7h**). White crystals, mp 234–235 °C; yield, 77%; IR (KBr) υ (cm^{-1}): 2976, 2924, 1748, 1709, 1601, 1574, 1502, 1446, 1320, 1188, 1144, 1075, 917, 833, 782, 687; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.0 Hz, Ar), 7.44 (t, 1H, J = 7.8 Hz, Ar), 7.31–7.37 (m, 4H, Ar), 7.18–7.20 (m, 2H, Ar), 7.08 (d, 2H, J = 9.2 Hz, OC_6H_4O), 6.94 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.64 (s, 2H, J = 7.2 Hz, OCH_2C=O), 4.28 (q, 2H, J = 7.2 Hz, OCH_2), 3.51 (s, 3H, $S(O_2)CH_3$), 1.30 (t, 3H, J = 7.2 Hz, OCH_2CH_3); EI-MS (70 eV, *m/z*): 574 (M^+), 575 (M^++1); Elemental Anal. Calcd for $C_{29}H_{26}N_4O_7S$: C, 60.62; H, 4.56; N, 9.75. Found: C, 60.53; H, 4.48; N, 9.87.

3-Benzylsulfonyl-6-[4-(1-ethoxycarbonylethoxy)]phenoxy-5-(3-methylphenyl)-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7i**). White crystals, mp 208–210 °C; yield, 90%; IR (KBr) υ (cm^{-1}): 2984, 2930, 1721, 1599, 1574, 1502, 1197, 1095, 1047, 918, 781, 688; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, 2H, J = 8.2 Hz, Ar), 7.21–7.51 (m, 12H, Ar), 7.08 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 5.00 (s, 2H, Ph$CH_2S(O_2)$), 4.74 (q, 1H, J = 6.8 Hz, OCHC=O), 4.21 (q, 2H, J = 6.8 Hz, OCH_2), 2.47 (s, 3H, PhCH_3), 1.66 (d, 3H, J = 6.4 Hz, CHCH_3), 1.23 (t, 3H, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 18.6, 21.6, 60.5, 61.5, 73.2, 101.4, 116.0, 121.7, 122.5, 125.2, 126.8, 127.9, 128.8, 128.9, 129.0, 129.1, 129.7, 130.6, 131.5, 133.9, 137.6, 140.1, 145.7, 146.4, 156.0, 156.6, 157.1, 171.9; EI-MS (70 eV, *m/z*): 665 (M^+), 666 (M^++1); Elemental Anal. Calcd for $C_{36}H_{32}N_4O_7S$: C, 65.05; H, 4.85; N, 8.43. Found: C, 65.14; H, 4.92; N, 8.57.

3-Benzylsulfonyll-6-(4-ethoxycarbonylmethoxy)phenoxy-5-(3-methylphenyl)-1-phenylpyrazolo[3,4-d]pyrimidin-4-one (**7j**). White crystals, mp 230–231 °C; yield, 82%; IR (KBr) υ (cm^{-1}): 2952, 2913, 1762, 1705, 1598, 1574, 1549, 1504, 1197, 1084, 1045, 699; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, 2H, J = 6.8 Hz, Ar), 7.21–7.42 (m, 12H, Ar), 7.10 (d, 2H, J = 9.2 Hz, OC_6H_4O), 6.94 (d, 2H, J = 8.8 Hz, OC_6H_4O), 5.00 (s, 2H, PhCH_2 $S(O_2)$), 4.64 (3, 2H, OCH_2C=O), 4.28 (q, 2H, J = 7.2 Hz, OCH_2), 2.48 (s, 3H, PhCH_3), 1.30 (t, 3H, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 21.5, 35.3, 61.6, 66.0, 102.6, 115.4, 120.3, 120.9, 122.3, 122.7, 125.4, 126.2, 127.3, 128.5, 128.9, 129.4, 130.2, 134.3, 137.7, 138.7, 139.7, 146.1, 146.2, 151.2, 156.0, 156.4, 157.6, 168.7; EI-MS (70 eV, *m/z*): 649 (M^+-1), 650(M^+); Elemental Anal. Calcd for $C_{35}H_{30}N_4O_7S$: C, 64.60; H, 4.65; N, 8.61. Found: C, 64.75; H, 4.81; N, 8.68.

3-Methylsulfonyl-1,5-diphenyl-6-[4-(1-propoxycarbonylethoxy)]phenoxy pyrazolo[3,4-d]pyrimidin-4-one (**7k**). White crystals, mp 198–199 °C; yield, 78%; IR (KBr) υ (cm^{-1}): 2969, 2923, 1751, 1719, 1605, 1577, 1560, 1501, 1196, 1147, 1093, 1032, 900, 765, 571; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, 2H, J = 8.0 Hz, Ar), 7.26–7.58 (m, 8H, Ph), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 8.8 Hz, OC_6H_4O), 4.74 (q, 1H, J = 6.8 Hz, CHC=O), 4.11 (m, 2H, OCH_2Et), 3.51 (s, 3H, $S(O_2)CH_3$), 1.57–1.66 (m, 5H, CH_3CHO and $CH_2CH_2CH_3$), 0.87 (t, 3H, J = 7.6 Hz, CH_3); EI-MS (70 eV, *m/z*): 589 (M^+); Elemental Anal. Calcd for $C_{30}H_{28}N_4O_7S$: C, 61.21; H, 4.79; N, 9.52. Found: C, 61.18; H, 4.83; N, 9.44.

5-(2-Chlorophenyl)-3-methylsulfonyl-1-phenyl-6-[4-(1-propoxycarbonylethoxy)]phenoxypyrazolo[3,4-d]pyrimidin-4-one (**7l**). White crystals, mp 148–150 °C; yield, 95%; IR (KBr) υ (cm^{-1}): 2971, 1718, 1594, 1575, 1545, 1501, 1196, 1142, 1095, 903, 765; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 2H, J = 8.0 Hz, Ar), 7.26–7.63 (m, 8H, Ar), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (dd, 2H, J = 9.2 Hz, OC_6H_4O), 4.75 (q, 1H, J = 6.8 Hz, CHC=O), 4.11 (t, 2H, J = 7.2 Hz, OCH_2Et), 3.51 (s, 3H, S $(O_2)CH_3$), 1.57–1.66 (m, 5H, CH_3CHO and $CH_2CH_2CH_3$), 0.87 (t, 3H, J = 7.6 Hz, CH_3); EI-MS (70 eV, *m/z*): 624 (M^+); Elemental Anal. Calcd for $C_{30}H_{27}ClN_7O_5S$: C, 57.83; H, 4.37; N, 8.99. Found: C, 57.91; H, 4.43; N, 8.97.

5-(3-Methylphenyl)-3-methysulfonyl-1-phenyl-6-[4-(1-propoxycarbonylethoxy)]phenoxypyrazolo[3,4-d]pyrimidin-4-one (**7m**). White crystals, mp 179–181 °C; yield, 77%; IR (KBr) υ (cm^{-1}): 2969, 2923, 1751, 1717, 1601, 1577, 1553, 1502, 1199, 1147, 1093, 1046, 769, 573; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, 2H, J = 8.0 Hz, Ar), 7.17–7.48 (m, 8H, Ar), 7.06 (d, 2H, J = 8.8 Hz, OC_6H_4O), 6.90 (d, 2H, J = 9.2 Hz, OC_6H_4O), 4.75 (q, 1H, J = 6.8 Hz, CHC=O), 4.11 (t, 2H, J = 7.6 Hz, OCH_2Et), 3.51 (s, 3H, $S(O_2)CH_3$), 2.48 (s, 3H, *m-*CH_3Ph), 1.57–1.66 (m, 5H, CH_3CHO and $CH_2CH_2CH_3$), 0.87 (t, 3H, J = 7.4 Hz, CH_3); EI-MS (70 eV, *m/z*): 602 (M^+-1), 603 (M^+); Elemental Anal. Calcd for $C_{31}H_{30}N_4O_7S$: C, 61.78; H, 5.02; N, 9.30. Found: C, 61.85; H, 5.14; N, 9.29.

18. Single crystal X-ray diffraction data for **6h** at 292 K on a Bruker Smart Apex Area CCD equipped with Mo Ka radiation (λ = 0.71073 Å). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-606703. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk).
19. (a) Yang, G.-F.; Xu, L.; Lu, A.-H. *Heteroat. Chem.* **2001**, *12*, 491; (b) Yang, F.-L.; Liu, Z.-J.; Huang, X.-B.; Ding, M.-W. *Heterocycl. Chem.* **2004**, *41*, 77; Herbicidal testing of the newly synthesized compounds **6** and **7** was carried out in a plant growth room. Temperature 23 ± 1 °C, RH 60 ± 5%, light intensity 10 Klux, and photoperiod 8 h/day. Twenty seeds of each one of weed species including rape and barnyard grass were chosen for testing. Seedlings were grown in the test plate of 9 cm diameter containing two pieces of filter paper and 9 mL solution of the tested compound (100 and 10 mg/L, respectively). Distilled water was used as comparison compound. The herbicidal activity was assessed as the inhibition rate in comparison with the distilled water. The herbicidal rating score based on visual observation. Range from 0% to 100%, 0% means no effect, 100% means complete killing.
20. Bewick, D. W. *Pestic. Sci.* **1986**, *17*, 349.