

A facile and efficient one-pot three-step protocol for synthesis of 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile

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Abstract

A facile and efficient one-pot three-step approach to the synthesis of substituted 1*H*-pyrazolo[4,3-*d*]pyrimidin-7(6*H*)-ones **4** from ethyl 3-cyano-1-(*p*-tolyl)-4-((triphenylphosphoranylidene)amino)-1*H*-pyrazole-5-carboxylate **1** has been developed. In this method, treatment of phosphazene **1** with arylisocyanates and followed by nucleophilic addition with phenols/alcohols in the presence of a catalytic amount of K₂CO₃/R²ONa in THF at room temperature gave the corresponding 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile **4** in satisfactory to good yields.

Keywords: Nitrogen heterocycle, 1*H*-pyrazolo[4,3-*d*]pyrimidin-7(6*H*)-one, domino reaction, aza-Wittig reaction

Introduction

The study of heterocyclic compounds inclines to complicated structural fused heterocyclic, bis-heterocyclic, multi-heterocyclic compounds, especially nitrogen heterocyclic compounds such as nicotinamide analog, pyrazole, pyridine, pyrrole, thiazole, triazole, pyridazine and fused heterocyclic compounds.¹ Pyrazole derivative as an active branch of heterocyclic compounds has attracted wide attention. Besides, Pyrimidine moiety has been widely employed in the design of biologically active agents, and compounds containing a fused pyrimidine possessing structural similarities with purines exhibit versatile bioactivities and have been widely used as potential pharmaceuticals such as selective and orally bioavailable mGluR1 antagonists,² selective

inhibitors of PDE5^{3,4} antiviral,^{5,6} antimicrobial,^{7,8} anticancer,⁹ anti-inflammatory,¹⁰ and xanthine oxidase inhibitors.¹¹

According to the structure-activity relationship (SAR) of those drugs,⁴ the construction of fused heterocyclic pyrazolo[4,3-*d*]pyrimidin-7-one is most common, and 3-carbonitrile of 3-carbonitrile-5-methyl-7-substituted pyrazolo[1,5-*a*]pyridine compound is favor of abirritative and hypnotic activities. For example, 3-carbonitrile is probably necessary to maintain drug effect in the structure of zaleplon.¹²

There are limited known methods for the synthesis of pyrazolo[4, 3-*d*]pyrimidin-7-ones. The first and most widely applicable method¹³ is the cyclization of 4-substituted amido-1*H*-pyrazole-3-carboxamide with potassium bis(trimethylsilyl)amide. The second approach¹⁴ to them involved in displacement of a chloro group in 5-amino-4,6-dichloropyrimidine with 4-chloroaniline, followed by acylation of the resulting diamino derivative with 2-chlorobenzoyl chloride, gave a intermediate, which underwent a three-step, two-pot procedure that involved cyclocondensation, hydrolysis, and N-alkylation. The third procedure¹⁵ was completed by Tin(II) chloride reduction of 4-azido-1*H*-pyrazole-5-carboxamide proceeded cleanly to afford the 4-aminopyrazole, which was cyclized as before with formic acid to give substituted 1*H*-pyrazolo[4,3-*d*]pyrimidin-7(6*H*)-ones. However, these reported methods suffer from drawbacks such as unavailable key intermediate and tedious synthetic route. Moreover, 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile **4** are not easily accessible by routes described as above.

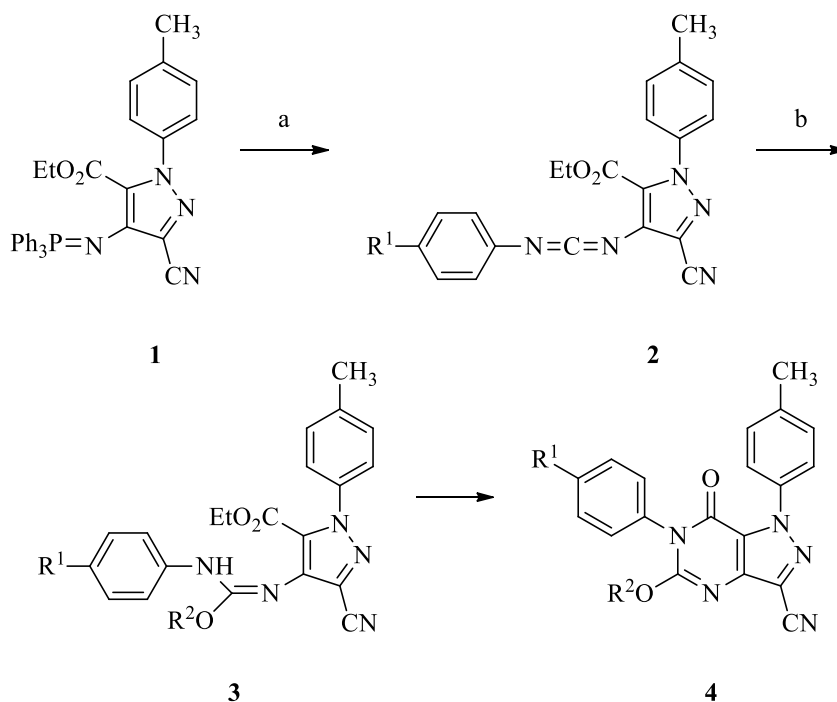
Over the past two decades, the aza-Wittig-mediated annulation strategy has been widely used for the synthesis of nitrogen-containing heterocyclic compounds.¹⁶ This method, which is called Eguchi aza-Wittig protocol,¹⁷ is known as tandem aza-Wittig heterocumulene-mediated annelation, and is recently classified as reaction.¹⁸ Although annelation of ring systems with quinazolinones by means of an aza-Wittig reaction has been developed,¹⁹ synthesis of pyrazolo[4,3-*d*]pyrimidin-7-ones by means of tandem aza-Wittig reactions of iminophosphorane with aryl isocyanates and nucleophiles has received less attention. In connection with our ongoing studies on fused nitrogen-containing heterocyclic construction synthesis and drug discovery project, we have focused on the synthesis of quinazolinones and other fused heterocyclic pyrimidinones. Previously, we reported an efficient approach to the synthesis of a new series of 6-aryl-3-cyano-5-alkylamino-1-*p*-tolyl-1*H*-pyrazolo[4,3-*d*]pyrimidin-7(6*H*)-ones²⁰ via iminophosphorane-mediated annulation involving in reactions of iminophosphorane with aromatic isocyanates, followed by nucleophilic addition with primary amines and secondary amines, respectively. Herein, we further employ this facile and efficient one-pot three-step process, via aza-Wittig/intermolecular nucleophilic addition/intramolecular cyclization, for the preparation of 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitriles **4**. The syntheses as depicted in Scheme 1 rely on the following reactions: (a) reaction of aza ylide with isocyanate to give a carbodiimide, (b) addition of phenol /alcohol to the carbodiimide to generate a carbamimidate, and (c) lactamization of the latter with neighboring ethyl ester group to deliver fused pyrimidinones. Although all the three steps are

frequently utilized for building a pyrimidinone nucleus, the reactions carried out in a one-pot operation leading to complex molecules are still attractive. This three-step synthesis in a one-pot process have economical and environmental advantages over the step by step synthesis in the procedure, isolation and purification steps, time, costs, and waste production.

Results and Discussion

The starting compound, that is iminophosphorane **1**, was prepared by Staudinger reaction reported in our previous papers.²⁰ Our strategy to 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile is proceeded by a one-pot three step protocol commenced with iminophosphorane **1** in hand. Iminophosphorane **1** was first treated with aromatic isocyanates to form carbodiimides **2** by aza-Wittig reaction. The reaction proceeded smoothly in mild conditions (0-5 °C) and was completed in 12 h. The carbodiimides **2** without isolating were then conveniently converted to 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile **4a-l** with various phenols in the presence of K₂CO₃. Specifically, a nucleophilic addition of phenols to the carbodiimide cumulenenic system gave the highly reactive carbamimidate intermediates **3**, which in turn underwent intramolecular hetero-conjugate addition annulation to produce the 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile **4a-l**. In the presence of K₂CO₃, the annulation could be accomplished smoothly to provide the title compounds **4a-m**. Whereas, switching the nucleophilic phenols to alcohols, the needed base catalyst would be changed from K₂CO₃ to R²ONa. In the presence of the selected catalyst, all the titled compound **4** were obtained in satisfactory to good yields (67-93%, see Table 1).

It is notable that slight differences in yields of producing the title compounds **4a-l** were observed when different phenols were used for the nucleophiles. Switching the phenyl group from an electronic withdrawing group (4-Br-phenyl, 4-Cl-phenyl and 2, 4-diCl-phenyl) to an electronic donating group (4-OCH₃ phenyl and 4-CH₃ phenyl) resulted in yield from 67% to 93% for compounds **4** in several cases.



Reagents and conditions: a. $p\text{-R}^1\text{C}_6\text{H}_4\text{NCO}$, THF, $0\text{-}5^\circ\text{C}$, 12 h; b. R^2OH , K_2CO_3 or R^2ONa THF, r.t., 6-12 h. Yield 67-93%.

Scheme 1. Synthesis of 6-aryl-3-cyano-5-phenoxy/alkoxy-1-*p*-tolyl-1*H*-pyrazolo [4,3-*d*]pyrimidin-7(6*H*)-ones **4**.

Encouraged by the aforementioned results and with the suitable reactions in hand, we next examined the feasibility of the protocol employing ethanol for example as nucleophiles in the annulation. Unfortunately, the one-pot reaction gave a complex mixture which mainly containing intermediate **3**. However, when the reaction carried out in the presence of catalytic EtONa, it took place smoothly and the 5-alkoxy-6-aryl-7-oxo-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile **4m** were obtained in satisfactory yields. The final yields are very low when alcohols containing more than three carbon atoms were used as nucleophiles in the annulation.

It is worth noting that the facile cyclization catalysts are K_2CO_3 and R^2ONa , when phenols and alcohols are used, respectively. This can be rationalized in term of the more acidic NHOR^2 in the intermediate **3** when R^2 is alkyl.

Table 1. Preparation of 6-aryl-3-cyano-5-aryloxy/alkoxy-1-*p*-tolyl-1*H*-pyrazolo[4,3-*d*]-pyrimidin-7(6*H*)-ones **4**^a

Entry	R ¹	R ²	Time(h)	Yield (%) ^b
4a	H	4-MeC ₆ H ₄	8	93
4b	H	4- <i>t</i> -BuC ₆ H ₄	12	75
4c	H	4-MeOC ₆ H ₄	8	88
4d	H	4-ClC ₆ H ₄	8	75
4e	H	2,4-diClC ₆ H ₃	12	67
4f	H	4-BrC ₆ H ₄	8	83
4g	F	Ph	12	91
4h	F	4-MeC ₆ H ₄	8	84
4i	F	4- <i>t</i> -BuC ₆ H ₄	12	78
4j	F	2-naphthyl	12	87
4k	F	4-ClC ₆ H ₄	8	77
4l	F	4-BrC ₆ H ₄	8	82
4m	H	Et	8	73

^aThe reactions were carried out according to general experimental procedure.

^bIsolated yields are based on iminophosphorane **1**.

Structural elucidation of compounds **4** was accomplished from the analytical and IR, ¹H NMR and GC-MS spectral data. The mass spectra showed the expected molecular ion peaks or M[±]1 and M[±]2 peaks, and the IR spectra showed a strong bands at 1719-1736 cm⁻¹, attributed to the C=O groups, and a CN absorption at 2236-2341 cm⁻¹, while in the ¹H NMR spectra, the aromatic protons are found, as multiplets, at δ=7.89-7.69 ppm. For example, the ¹H NMR spectra of the compound **4a** show the signal of aromatic C–H at δ=7.57-7.00 ppm as multiplet and –CH₃ at δ=2.37 ppm and δ=2.39 ppm as a singlet. The IR spectra of **4a** exhibit a strong stretching resonance peak at 1720 cm⁻¹ which indicates the presence of a C=O bond, and medium strong sharp peak at 2239 cm⁻¹ belonging to CN stretching resonance. The MS spectra of **4a** show M⁺ at m/z 433 with 100% abundance.

Conclusions

In conclusion, we have established one-pot three step protocol for synthesis of 6-aryl-7-oxo-5-aryoxy/alkoxy-1-(*p*-tolyl)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile **4** by an iminophosphorane-mediated annulation involving in a tandem aza-Wittig reaction of iminophosphorane **1** with aromatic isocyanates followed by intermolecular nucleophilic reaction with phenols/alcohols. Its advantages, such as convenient one-pot three-step synthetic procedures, satisfactory to good yields, and availability of a broad range of phenols or alcohols,

make this protocol attractive.

Experimental Section

General. ^1H NMR were recorded in CDCl_3 on a Varian Mercury Plus 400 (400 MHz) spectrometer and resonance are given in ppm (δ) relative to TMS. Mass spectra were obtained on a Finnigan trace MS spectrometer. Melting points were recorded on X-4 electrothermal melting point apparatus and were uncorrected. Elemental analyses were determined on a 2400 Perkin-Elmer elemental analysis instrument.

General procedure for synthesis of the carbodiimide (**2**)

To a solution of iminophosphorane **5** (1.59 g, 3.0 mmol) in anhydrous THF (10 mL) was added rapidly aryl isocyanate (3.0 mmol) at room temperature. The reaction mixture was left unstirred for 6-12 h at 0-5 $^\circ\text{C}$ to generate carbodiimides **2**, which were used directly for next step without further purification.

Synthesis of the title compounds (4). To the reaction mixture of **2** (3.0 mmol), was added phenol or alcohol (3.1 mmol) and a catalytic amount of K_2CO_3 or R^2ONa at room temperature. The reaction mixture was allowed to stir for 6-12 h, filtered, condensed and the crude residue was recrystallized with EtOH and CH_2Cl_2 to give **4** in 67-93 % yields

7-Oxo-6-phenyl-1-(*p*-tolyl)-5-(*p*-tolylloxy)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4a**).** White solids, mp 272-273 $^\circ\text{C}$; IR (KBr): 2239(CN), 1720(C=O), 1599, 1575, 1431, 1262 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.00(m, 13H), Ar-H, 2.39(s, 3H, CH_3 -Ar), 2.37(s, 3H, CH_3 -Ar) ppm; MS m/z (%), 433 (100, M^+), 315 (62), 261 (12), 143 (12), 117 (28), 91 (45), 77 (82), 65 (34); Anal.calcd for $\text{C}_{26}\text{H}_{19}\text{N}_5\text{O}_2$: C,72.04; H,4.42; N,16.16. Found: C, 72.22; H, 4.41; N, 16.14.

5-(4-*tert*-Butylphenoxy)-7-oxo-6-phenyl-1-*p*-tolyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4b**).** White solids, mp 283-284 $^\circ\text{C}$; IR (KBr): 2238(CN), 1727(C=O), 1607, 1599, 1575, 1433, 1264 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.58-7.05(m, 13H, Ar-H), 2.39(s, 3H, CH_3 -Ar), 1.34(s, 9H, CMe_3) ppm; MS m/z (%), 475(100, M^+), 460(99), 341(86), 300(89), 230(13), 116(29), 91(45), 77(43), 65(12); Anal.calcd for $\text{C}_{29}\text{H}_{25}\text{N}_5\text{O}_2$: C,73.25; H,5.30; N,14.73 found: C,73.41; H,5.28; N,14.62.

5-(4-Methoxyphenoxy)-7-oxo-6-phenyl-1-*p*-tolyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4c**).** White solids, mp 247-248 $^\circ\text{C}$ IR (KBr): 2241(CN), 1724(C=O), 1600, 1578, 1465, 1297 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.57-6.89 (m, 13H, Ar-H), 3.83(s, 3H, CH_3O -Ar), 2.39 (s, 3H, CH_3 -Ar) ppm; MS m/z (%), 449(94, M^+), 330(100), 277(13), 260(4), 123(39), 117(17), 91(74), 77(99.9), 65(29); Anal.calcd for $\text{C}_{26}\text{H}_{19}\text{N}_5\text{O}_3$: C,69.48; H,4.26; N,15.58 found: C,69.52; H,4.23; N,15.43.

5-(4-Chlorophenoxy)-7-oxo-6-phenyl-1-*p*-tolyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4d). White solids, mp 295-296 °C; IR (KBr): 2237(CN), 1722(C=O), 1606, 1574, 1487, 1267 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.09 (m, 13H, Ar-H), 2.40(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 455(11, M⁺+2), 454(21, M⁺), 453(66, M⁺-1), 402(73), 359(100), 334(75), 299(93), 119(70), 91(84), 77(66), 65(18); Anal. calcd for C₂₅H₁₆ClN₅O₂: C,66.16; H,3.55; N,15.43 found: C,66.32; H,3.53; N,15.28.

5-(2,4-Dichlorophenoxy)-7-oxo-6-phenyl-1-*p*-tolyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4e). White solids, mp 240-242 °C; IR (KBr):2236(CN), 1726(C=O), 1599, 1575, 1439, 1264 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.18(m, 12H, Ar-H), 2.40(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 490(12, M⁺+2), 489(19, M⁺+1), 488(17, M⁺), 455(44), 452(100), 334(33), 143(6), 117(11), 91(11), 77(13); Anal. calcd for C₂₅H₁₅N₅O₂Cl₂: C,61.49; H,3.10; N,14.34 found: C,61.52; H,3.08; N,14.20.

5-(4-Bromophenoxy)-7-oxo-6-phenyl-1-*p*-tolyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4f). White solids, mp 306-307 °C; IR (KBr): 2239(CN), 1720(C=O), 1599, 1575,1431, 1262 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.03(m, 13H, Ar-H), 2.40(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 498(78, M⁺), 497(99, M⁺-1), 419(12), 380(26), 299(100), 119(7), 91(7), 77(11), 65(3); Anal. calcd for C₂₅H₁₆BrN₅O₂: C,60.25; H,3.24; N,14.05 found: C,60.35; H,3.22; N,14.13.

6-(4-Fluorophenyl)-7-oxo-5-phenoxy-1-*p*-tolyl--6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4g). White solids, mp 193-194 °C; IR (KBr): 2237(CN), 1719(C=O), 1607, 1574, 1489, 1264 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.13(m, 13H, Ar-H), 2.40(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 437(71, M⁺), 345(14), 300(100), 285(34), 247(31), 143(16), 117(26), 91(92), 77(59), 65(69); Anal. calcd for C₂₅H₁₆FN₅O₂: C,68.64;H,3.69; N,16.01 found: C,68.73; H,3.66; N,16.11.

6-(4-Fluorophenyl)-7-oxo-1-*p*-tolyl-5-(*p*-tolyl-oxo)-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4h). White solids, mp 252-254°C; IR (KBr): 2239(CN), 1720(C=O), 1599, 1575, 1431, 1262 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.57-7.00(m, 12H, Ar-H), 2.39(s, 3H, CH₃-Ar), 2.37(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 451(4, M⁺), 433(100), 315(45), 261(13), 143(2), 116(3), 91(10), 77(14), 65(6); Anal. calcd for C₂₆H₁₈FN₅O₂: C,69.17; H,4.02; N,15.51 found: C,69.57; H,4.06; N,15.39.

5-(4-*tert*-Butylphenoxy)-6-(4-fluorophenyl)-7-oxo-1-*p*-tolyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4i). White solids, mp 312-313 °C; IR (KBr): 2238(CN), 1723(C=O), 1605,1594, 1578, 1433, 1269 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.05(m, 12H, Ar-H), 2.40(s, 3H, CH₃-Ar), 1.34(s, 9H, CMe₃) ppm; MS *m/z* (%), 495(100, M⁺+2), 494(39, M⁺+1), 493 (13, M⁺), 341(48), 300(89), 297(12), 116(17), 91(27), 77(9), 65(6); Anal. calcd for C₂₉H₂₄FN₅O₂: C,70.58; H,4.90; N,14.19 found: C,70.43; H,4.88; N,14.12.

6-(4-Fluorophenyl)-5-(naphthalen-1-yloxy)-7-oxo-1-*p*-tolyl--6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidine-3-carbonitrile (4j). White solids, mp 232-234 °C; IR (KBr): 2236(CN), 1736(C=O), 1606, 1587, 1577, 1465, 1275 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.90-7.25(m, 15H, Ar-H),2.41(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 489(9, M⁺), 487(56, M⁺-2), 350(100),

297(22), 143(28), 117(10), 91(86), 77(8), 65(20); Anal. calcd for C₂₉H₁₈FN₅O₂: C,71.45; H,3.72; N,14.37 found: C,71.22; H,3.78; N,14.41.

5-(4-Chlorophenoxy)-6-(4-fluorophenyl)-7-oxo-1-p-tolyl-6,7-dihydro-1H-pyrazolo[4,3-d]pyrimidine-3-carbonitrile (4k). Yellow solids, mp 231-233 °C; IR (KBr): 2237(CN), 1727(C=O), 1608, 1578, 1487, 1271 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.55-7.09(m, 12H, Ar-H), 2.41(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 473(11, M⁺+2), 471(29, M⁺), 402(27), 359(52), 334(39), 299(75), 91(100), 77(8), 65(25); Anal. calcd for C₂₅H₁₅ClFN₅O₂: C,63.63; H,3.20; N,14.84 found: C,63.74; H,3.33; N,14.68.

5-(4-Bromophenoxy)-6-(4-fluorophenyl)-7-oxo-1-p-tolyl-6,7-dihydro-1H-pyrazolo[4,3-d]pyrimidine-3-carbonitrile (4l). White solids, mp 248-249°C; IR (KBr): 2238(CN), 1721(C=O), 1594, 1562,1430, 1261 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.03(m, 12H, Ar-H), 2.40(s, 3H, CH₃-Ar) ppm; MS *m/z* (%), 517(20, M⁺+2), 516(20, M⁺+1), 514(40, M⁺-1), 298(100), 90(23); Anal. calcd for C₂₅H₁₅BrFN₅O₂: C,58.16; H,2.93; N, 13.56 found: C,58.22; H,2.90; N,13.49.

5-Ethoxy-7-oxo-6-phenyl-1-p-tolyl-6,7-dihydro-1H-pyrazolo[4,3-d]pyrimidine-3-carbonitrile (4m). Yellow solids, mp 231-232 °C; IR (KBr): 2235(CN), 1722(C=O), 1583, 1545, 1432, 1261 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.99-7.26(m, 9H, Ar-H), 4.32(q, 2H, *J*=7.6Hz, OCH₂CH₃), 2.55(s, 3H, CH₃-Ar), 1.15(t, 3H, *J*=7.6Hz, OCH₂CH₃) ppm; MS *m/z* (%) : 369(22, M⁺-2), 307(53), 305(100), 224(7), 197(14), 117(27), 91(58), 77(8); Anal. calcd for C₂₁H₁₇N₅O₂: C,67.91; H,4.61; N,18.86 found: C,68.95; H,4.10; N,18.81.

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