An Efficient Synthesis of 3*H*-Pyrrolo[3,2-*d*]pyrimidin-4(5*H*)-one Derivatives via an Iminophosphorane

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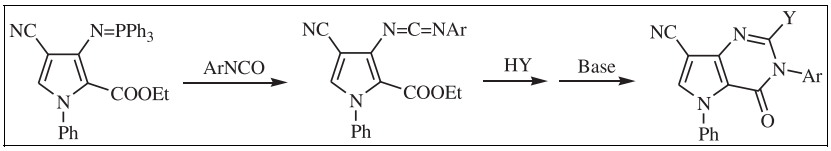

The iminophosphorane (**3**), obtained from reaction of ethyl 3-amino-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (**2**) with triphenylphosphine, hexachloroethane, and triethylamine, reacted with aromatic isocyanates to give carbodiimides (**4**). Further reaction of **4** with various amines, phenols, or ROH to give 2,3,5,7-tetrasubstituted 3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-ones (**6**) in satisfactory yields in the presence of catalytic amount of sodium alkoxide or solid potassium carbonate.

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INTRODUCTION

Pyrrolo[3,2-*d*]pyrimidines (also called 9-deazapurines) have been reported to exhibit widespread biological activities and have been used as potent A_1- and A_2- adenosine receptor antagonists [1], purine nucleoside phosphorylase inhibitors [2–5]. Some derivatives of this ring system have also shown good anticancer activity [6,7]. Many methods have been reported for the synthesis of pyrrolo[3,2-*d*]pyrimidines. One of the generally used approach involved elaboration of a pyrrole ring onto the preformed pyrimidine bearing reactive functionalities at C-4 and C-5 [8–11]; another used strategy involved the formation of a pyrimidine ring onto the 3-amino-pyrrole intermediate [12–14]. Although some 3*H*-pyrrolo [3,2-*d*]pyrimidine-4(5*H*)-ones have been constructed via 3-amino-2-carboxylpyrroles, which seems to be a very useful method, but the synthesis of 2,3,5,7-tetrasubstituted 3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-ones are rarely described.

On the other hand, aza-Wittig reactions have received increased attention because of their utility in the synthesis of nitrogen-containing heterocyclic compounds [15–20]. Recently, we have been interested in the synthesis of fused pyrimidinones via aza-Wittig reaction, with the aim of evaluating their fungicidal activities [21–26]. Herein, we wish to report a new facile and efficient synthesis of 2,3,5,7-tetrasubstituted 3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-ones via aza-Wittig reaction, starting from easily accessible ethyl 3-amino-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate.

RESULTS AND DISCUSSION

The ethyl 3-amino-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (**2**), easily obtained by reaction of compound **1** with ethyl 2-bromoacetate in the basic condition [27], was converted to iminophosphorane (**3**) by treatment with triphenyl phosphine, hexachloroethane, and triethylamine in dry acetonitrile (Scheme 1).

The iminophosphorane (**3**) was allowed to react with aromatic isocyanates to yield carbodiimides (**4**), which were further treated with amines to provide guanidine intermediates (**5**). In the presence of EtONa/EtOH, **5** were easily converted to 2-amino-3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one derivatives (**6**) (Y = NR^1R^2) at RT in satisfactory yields (Scheme 2). The results are listed in Table 1 (entry **6a–6j**). The cyclization reactions were achieved all in moderate to good yields whatever the amine that used was cyclic or acyclic ones. It is noteworthy that the product **6** contain a carbonitrile group, which is very important in design of biologically active heterocycles.

The structure of 3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-ones (**6**) was confirmed by their spectrum data. For example, the IR spectra of **6a** revealed CN and C═O absorption bands at 2214 and 1709 cm^{-1}, respectively. The ^{1}H-NMR spectrum of **6a** shows two triplets at 3.16 and 3.43 ppm because of the NCH_2 and OCH_2, respectively. The signals attributable to the Ar—Hs and 6-H of the pyrrole ring are found at 7.30–7.47 and 7.63 ppm as mutiplet and singlet, respectively. The MS spectrum of **6a** shows molecular ion peak at *m/z* 397 with 53% abundance.

To expand the method of preparation of 3*H*-pyrrolo[3,2-*d*] pyrimidine-4(5*H*)-ones, alcohols and phenols were further used to react with carbodiimides (**4**). When alcohols were added to the solution of carbodiimides (**4**), catalytic amount of RONa was necessary for the reaction to occur to give 2-alkoxy-3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-ones derivatives (**6**) (Y = OR). When carbodiimides (**4**) reacted with phenols, the presence of catalytic amount of potassium carbonate can

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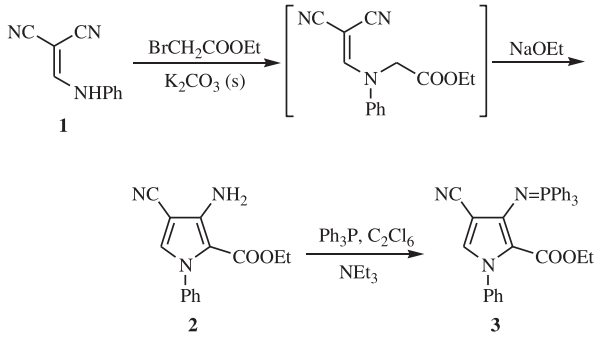
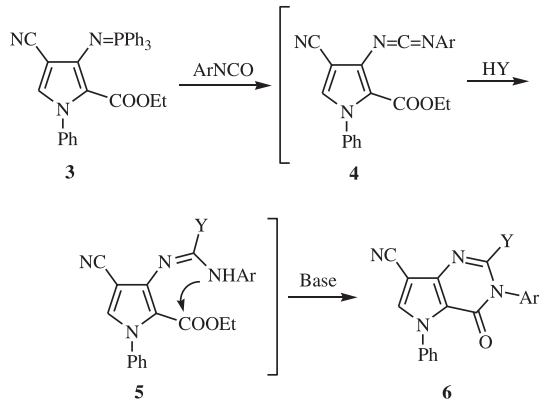
Scheme 1



Scheme 2



make the reaction took place to give **6** (Y = OAr′) directly in good yields. The results are listed in Table 1 (entry **6k–6r**). It is reasonable to assume that both of the reactions of carbodiimides (**4**) with alcohols and phenols take place through an original nucleophilic addition to give the intermediates **5**, which consequently cyclized to produce 3*H*-pyrrolo[3,2-*d*] pyrimidine-4(5*H*)-ones (**6**) under the basic condition.

In conclusion, we have developed an efficient way to prepare various 3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one derivatives via reaction of carbodiimides with a variety of amines, alcohols, and phenols. Because of its mild reaction conditions, good yields, and easily changing substituents, it will serves as a new tool for preparing of many biologically and pharmaceutically active 3*H*-pyrrolo[3,2-*d*]pyrimidine-4 (5*H*)-ones.

EXPERIMENTAL

Melting points were determined using a X-4 model apparatus (Beijing Taike Company, Beijing, People's Republic of China) and were uncalibrated. MS were measured on a Finnigan Trace MS spectrometer (Thermo Company, Palo Alto, CA). NMR spectra were recorded in $CDCl_3$ on a Varian Mercury Plus 400 (400 MHz) spectrometer (Varian Company, Palo Alto, CA), and chemical shifts (δ) were given in parts per million using $(CH_3)_4Si$ as an internal reference (δ = 0). IR were recorded on a PE-983 IR spectrometer (PerkinElmer Company, Waltham, MA) as KBr pellets with absorption in reciprocal centimeter. Elementary analyses were taken on a Vario Elementary III elementary analysis instrument (Elementar Company, Hanau, Germany).

Procedure for the preparation of compound 2. Compound **2** was obtained from the reaction of malononitrile with aniline and ethyl orthoformate in the presence of K_2CO_3, followed by reacting with ethyl 2-bromoacetate according to a literature report. White crystals (yield: 75%); mp: 150–151°C (Lit. [27] mp: 153–154°C).

Ethyl-3-triphenylphosphoranylideneamino-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (3). To a mixture of ethyl 3-amino-4-cyano-1-phenyl-1*H*-pyrrole-2-carboxylate (**2**) (2.04 g, 8 mmol), PPh_3 (3.14 g, 12 mmol), and C_2Cl_6 (2.84 g, 12 mmol) in dry CH_3CN (40 mL) was added dropwise NEt_3 (2.42 g, 24 mmol) at RT. After stirred at 25°C for 4 h, the solvent was removed under reduced pressure, and the residue was recrystallized from EtOH to give iminophosphorane (**3**) as white crystals, 3.91 g (95%), mp 122–123°C; ^{1}H-NMR ($CDCl_3$): δ 0.89 (t, J = 7.2 Hz, 3H, CH_3), 3.82 (q, J = 7.2 Hz, 2H, CH_2), 7.02 (s, 1H, C═C—H), 7.15–7.84 (m, 20H, Ar—H); MS: *m/z* (%) 515 (3, M^+), 501 (48), 458 (29), 430 (100), 388 (55), 374 (99), 360 (61), 345 (65), 320 (45), 264 (47), 251 (47), 180 (38), 125 (27), 77 (47). *Anal*. Calcd for $C_{32}H_{26}N_3O_2P$: C, 74.55; H, 5.08; N, 8.15; Found: C, 74.60; H, 5.11; N, 8.09.

General preparation of 2-amino-3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6a–6j). To a solution of iminophosphorane (**3**) (1.55 g, 3 mmol) in dry methylene dichloride (15 mL), aromatic isocyanate (3 mmol) was added under nitrogen at RT. After the reaction mixture was left to stand for 10–12 h at 0–5°C, the solvent was removed under reduced pressure, and a mixture of ether/petroleum ether (1:2, 20 mL) was added to precipitate triphenylphosphine oxide. After filtration, the solvent was removed to give carbodiimide (**4**), which was used directly without further purification. To the solution of **4** prepared earlier in methylene dichloride (15 mL), amine (3 mmol) was added. After the reaction mixture was allowed to stand for 2–8 h, the solvent was removed, and anhydrous ethanol (10–15 mL) with several drops of EtONa in EtOH was added. The mixture was stirred for 1–4 h at RT. The solution was then concentrated under reduced pressure, and the residual was recrystallized from methylene dichloride/ethanol to give 2-amino-3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one.

***7-Cyano-3,5-diphenyl-2-(4-morpholino)-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6a)**. ^{1}H-NMR ($CDCl_3$): δ 3.16 (t, J = 4.6 Hz, 4H, $2NCH_2$), 3.43 (t, J = 4.6 Hz, 4H, $2OCH_2$), 7.30–7.47 (m, 10H, Ar—H), 7.63 (s, 1H, Ar—H); IR (potassium bromide): 2214 (CN), 1709 (C═O), 1606, 1581, 1563, 1506, 1349, 1247 cm^{-1}; MS: *m/z* (%) 397 (53, M^+), 352 (65), 340 (100), 311 (60), 264 (34), 209 (30), 180 (31), 154 (24), 103 (21), 77 (55).

***7-Cyano-3,5-diphenyl-2-(pyrrolidin-1-yl)-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6b)**. ^{1}H-NMR ($CDCl_3$): δ 1.70–1.74 (m, 4H, $2CH_2$), 3.07 (t, J = 6.4 Hz, 4H, $2NCH_2$), 7.27–7.45 (m, 10H, Ar—H), 7.56 (s, 1H, Ar—H); IR (potassium bromide): 2212 (CN), 1700 (C═O), 1608, 1586, 1564, 1500, 1429, 1230 cm^{-1}; MS: *m/z* (%) 381 (74, M^+), 352 (40), 276 (32), 77 (100).

***7-Cyano-3,5-diphenyl-2-(piperidin-1-yl)-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6c)**. ^{1}H-NMR ($CDCl_3$): δ 1.20–1.43 (m, 6H, $3CH_2$), 3.12 (t, J = 5.6 Hz, 4H, $2NCH_2$), 7.28–7.45 (m, 10H, Ar—H), 7.60 (s, 1H, Ar—H); IR (potassium bromide): 2210 (CN), 1701 (C═O), 1605, 1577, 1569, 1504, 1241 cm^{-1}; MS: *m/z* (%) 395 (82, M^+), 366 (56), 352 (29), 311 (37), 290 (34), 276 (46), 209 (33), 160 (100), 103 (52), 84 (82), 77 (62).

Table 1

Physical and analytical data of compounds **6**.

Compd	Ar	Y	Time hours	mp (°C)	Yield % [a]	Molecular Formula	Analysis % Calcd/found		
							C	H	N
6a	Ph	4-morpholinyl	2	249–250	80	$C_{23}H_{19}N_5O_2$	69.51 69.80	4.82 4.93	17.62 17.51
6b	Ph	1-pyrrolidinyl	2	287–288	85	$C_{23}H_{19}N_5O$	72.42 72.49	5.02 5.16	18.36 18.51
6c	Ph	1-piperidinyl	2	241–242	80	$C_{24}H_{21}N_5O$	72.89 72.99	5.35 5.46	17.71 17.58
6d	Ph	-NEt_2	4	180–181	89	$C_{23}H_{21}N_5O$	72.04 72.14	5.52 5.48	18.26 18.38
6e	Ph	-N(*n*-Pr)$_2$	4	179–180	90	$C_{25}H_{25}N_5O$	72.97 73.14	6.12 6.18	17.02 17.15
6f	Ph	-N(*n*-C_5H_{11})$_2$	4	101–103	80	$C_{29}H_{33}N_5O$	74.49 74.54	7.11 7.08	14.98 15.13
6g	Ph	-N(*n*-C_6H_{13})$_2$	8	84–86	86	$C_{31}H_{37}N_5O$	75.12 75.24	7.52 7.63	14.13 14.32
6h	Ph	-N(*n*-Bu)$_2$	8	117–118	78	$C_{27}H_{29}N_5O$	73.78 73.83	6.65 6.77	15.93 15.86
6i	4-ClC_6H_4	-N(*n*-Pr)$_2$	6	204–205	82	$C_{25}H_{24}ClN_5O$	67.33 67.14	5.42 5.65	15.70 15.92
6j	4-FC_6H_4	-NEt_2	6	171–173	85	$C_{23}H_{20}FN_5O$	68.81 68.68	5.02 4.99	17.45 17.56
6k	Ph	C_6H_5O-	8	264–265	65	$C_{25}H_{16}N_4O_2$	74.25 74.46	3.99 4.13	13.85 13.95
6l	Ph	4-MeC_6H_4O-	5	245–246	67	$C_{26}H_{18}N_4O_2$	74.63 74.69	4.34 4.45	13.39 13.56
6m	Ph	3,4-2Me-C_6H_3O-	3	237–238	75	$C_{27}H_{20}N_4O_2$	74.98 75.17	4.66 4.85	12.95 13.08
6n	4-FC_6H_4	4-$MeOC_6H_4O$-	4	244–245	80	$C_{26}H_{17}FN_4O_3$	69.02 69.28	3.79 3.84	12.38 12.44
6o	4-FC_6H_4	4-ClC_6H_4O-	5	242–243	85	$C_{25}H_{14}ClFN_4O_2$	65.72 65.79	3.09 3.22	12.26 12.35
6p	4-FC_6H_4	2-MeC_6H_4O-	8	288–289	65	$C_{26}H_{17}FN_4O_2$	71.55 71.67	3.93 3.75	12.84 12.94
6q	Ph	*i*-PrO-	3	252–254	75	$C_{22}H_{18}N_4O_2$	71.34 71.29	4.90 4.99	15.13 15.33
6r	4-FC_6H_4	EtO-	1	269–270	65	$C_{21}H_{15}FN_4O_2$	67.37 67.28	4.04 4.16	14.97 14.84

[a]Isolated yields based on iminophosphorane (**3**).

***7-Cyano-2-diethylamino-3,5-diphenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6d)**. ^{1}H-NMR ($CDCl_3$): δ 0.82 (t, *J* = 7.2 Hz, 6H, $2CH_3$), 3.12 (q, *J* = 7.2 Hz, 4H, $2NCH_2$), 7.24–7.45 (m, 10H, Ar—H), 7.61 (s, 1H, Ar—H); IR (potassium bromide): 2218 (CN), 1698 (C═O), 1611, 1589, 1568, 1501, 1239 cm^{-1}; MS: *m/z* (%) 383 (23, M^+), 354 (97), 311 (30), 278 (62), 264 (34), 235 (29), 209 (32), 180 (50), 103 (39), 77 (100).

***7-Cyano-3,5-diphenyl-2-dipropylamino-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6e)**. ^{1}H-NMR ($CDCl_3$): δ 0.73 (t, *J* = 7.2 Hz, 6H, $2CH_3$), 1.22–1.27 (m, 4H, $2CH_2$), 3.00 (t, *J* = 7.2 Hz, 4H, $2NCH_2$), 7.23–7.46 (m, 10H, Ar—H), 7.60 (s, 1H, Ar—H); IR (potassium bromide): 2211 (CN), 1707 (C═O), 1600, 1587, 1565, 1511, 1250 cm^{-1}; MS: *m/z* (%) 411 (100, M^+), 368 (54), 340 (83), 311 (72), 292 (55), 264 (78), 100 (47), 77 (85).

***7-Cyano-2-dipentylamino-3,5-diphenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6f)**. ^{1}H-NMR ($CDCl_3$): δ 0.86 (t, *J* = 7.6 Hz, 6H, $2CH_3$), 1.08–1.26 (m, 12H, $6CH_2$), 3.02 (t, *J* = 7.6 Hz, 4, $2NCH_2$), 7.22–7.45 (m, 10H, Ar—H), 7.59 (s, 1H, Ar—H); IR (potassium bromide): 2215 (CN), 1705 (C═O), 1604, 1587, 1554, 1507, 1420, 1259 cm^{-1}; MS: *m/z* (%) 467 (77, M^+), 424 (37), 410 (56), 396 (99), 354 (78), 340 (100), 326 (85), 311 (90), 264 (57), 251 (54), 180 (29), 103 (26), 91 (30), 77 (70).

***7-Cyano-2-dihexylamino-3,5-diphenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6g)**. ^{1}H-NMR ($CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 6H, $2CH_3$), 1.09–1.28 (m, 16H, $8CH_2$), 3.01 (t, *J* = 7.2 Hz, 4H, $2NCH_2$), 7.22–7.46 (m, 10H, Ar—H), 7.60 (s, 1H, Ar—H); IR (potassium bromide): 2218 (CN), 1704 (C═O), 1618, 1588, 1560, 1511, 1427, 1254 cm^{-1}; MS: *m/z* (%) 495 (61, M^+), 438 (36), 424 (45), 410 (100), 354 (49), 340 (64), 326 (82), 311 (82), 264 (24), 251 (33), 180 (22), 103 (26), 77 (66).

***7-Cyano-2-dibutylamino-3,5-diphenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6h)**. ^{1}H-NMR ($CDCl_3$): δ 0.84 (t, *J* = 7.2 Hz, 6H, $2CH_3$), 1.15–1.20 (m, 8H, $4CH_2$), 3.03 (t, *J* = 7.2 Hz, 4H, $2NCH_2$), 7.22–7.44 (m, 10H, Ar—H), 7.60 (s, 1H, Ar—H); IR

(potassium bromide): 2211 (CN), 1701 (C═O), 1600, 1585, 1559, 1508, 1433, 1234 cm^{-1}; MS: *m/z* (%) 439 (62, M^+), 410 (34), 396 (51), 382 (100), 339 (91), 311(84), 264 (81), 179 (38), 77 (88).

***3-(4-Chlorophenyl)-7-cyano-2-dipropylamino-5-phenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6i).** ^{1}H-NMR ($CDCl_3$): δ 0.76 (t, *J* = 7.2 Hz, 6H, $2CH_3$), 1.27–1.33 (m, 4H, $2CH_2$), 3.00 (t, *J* = 7.2 Hz, 4H, $2NCH_2$), 7.19–7.44 (m, 9H, Ar—H), 7.61 (s, 1H, Ar—H); IR (potassium bromide): 2215 (CN), 1685 (C═O), 1604, 1577, 1567, 1503, 1240 cm^{-1}; MS: *m/z* (%) 445 (40, M^+), 404 (90), 374 (100), 345 (65), 306 (38), 264 (48), 153 (24), 111 (24), 77 (64).

***7-Cyano-2-diethylamino-3-(4-fluorophenyl)-5-phenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6j).** ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 6H, $2CH_3$), 3.11 (q, *J* = 7.2 Hz, 4H, $2NCH_2$), 7.14–7.44 (m, 9H, Ar—H), 7.60 (s, 1, Ar—H); IR (potassium bromide): 2211 (CN), 1701 (C═O), 1598, 1584, 1542, 1505, 1234 cm^{-1}; MS: *m/z* (%) 401 (59, M^+), 371 (100), 329 (53), 278 (42), 264 (39), 153 (19), 121 (25), 103 (20), 95 (25), 77 (50).

General preparation of 2-aryloxy-3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6k–6p). To the solution of carbodiimide (**4**) (3 mmol) prepared earlier in anhydrous acetonitrile (15 mL), phenol (3 mmol) and potassium carbonate (0.2 g, 1.5 mmol) were added. The mixture was stirred at 40–50°C for 3–8 h. After cooling, 30 mL water was added, and stir was continued until all the product was precipitated, then filtered and washed with ethanol; the residual was recrystallized from methylene dichloride/ethanol to give **6k–6p**.

***7-Cyano-3,5-diphenyl-2-phenoxy-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6k).** ^{1}H-NMR ($CDCl_3$): δ 7.51–7.16 (m, 15H, Ar—H), 7.64 (s, 1H, Ar—H); IR (potassium bromide): 2207 (CN), 1700 (C═O), 1601, 1549, 1235, 1221 cm^{-1}; MS: *m/z* (%) 404 (80, M^+), 311 (22), 285 (100), 256 (9), 180 (15), 153 (9), 103 (7), 77 (33).

***7-Cyano-3,5-diphenyl-2-(4-methylphenoxy)-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6l).** ^{1}H-NMR ($CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.02–7.52 (m, 14H, Ar—H), 7.64 (s, 1H, Ar—H); IR (potassium bromide): 2178 (CN), 1702 (C═O), 1594, 1548, 1230 cm^{-1}; MS: *m/z* (%) 418 (16, M^+), 311 (10), 299 (100), 180 (29), 153 (19), 103 (17), 77 (79).

***7-Cyano-2-(3,4-dimethylphenoxy)-3,5-diphenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6m).** ^{1}H-NMR ($CDCl_3$): δ 2.25 (s, 6H, $2CH_3$), 6.89–7.52 (m, 13H, Ar—H), 7.63 (s, 1H, Ar—H); IR (potassium bromide): 2194 (CN), 1705 (C═O), 1603, 1556, 1267, 1209 cm^{-1}; MS: *m/z* (%) 432 (100, M^+), 313 (94), 298 (25), 180 (13), 103 (12), 91 (27), 77 (81).

***7-Cyano-3-(4-fluorophenyl)-2-(4-methoxyphenoxy)-5-phenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6n).** ^{1}H-NMR ($CDCl_3$): δ 3.82 (s, 3H, OCH_3), 6.91–7.44 (m, 13H, Ar—H), 7.64 (s, 1H, Ar—H); IR (potassium bromide): 2187 (CN), 1707 (C═O), 1592, 1534, 1245, 1208 cm^{-1}; MS: *m/z* (%) 452 (74, M^+), 329 (16), 315 (100), 300 (57), 272 (28), 180 (9), 77 (8).

***2-(4-Chlorophenoxy)-7-cyano-3-(4-fluorophenyl)-5-phenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6o).** ^{1}H-NMR ($CDCl_3$): δ 7.11–7.46 (m, 13H, Ar—H), 7.65 (s, 1H, Ar—H); IR (potassium bromide): 2196 (CN), 1701 (C═O), 1589, 1545, 1233, 1211 cm^{-1}; MS: *m/z* (%) 456 (50, M^+), 319 (100), 284 (96), 256 (18), 180 (41), 153 (26), 121 (12), 99 (21), 77 (84).

***7-Cyano-3-(4-fluorophenyl)-2-(2-methylphenoxy)-5-phenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6p).** ^{1}H-NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3), 7.16–7.47 (m, 13H, Ar—H), 7.63 (s, 1H, Ar—H); IR (potassium bromide): 2201 (CN), 1703 (C═O), 1585, 1543, 1229 cm^{-1}; MS: *m/z* (%) 436 (19, M^+), 329 (14), 299 (34), 218 (8), 180 (15), 153 (25), 121 (23), 95 (30), 77 (100).

General preparation of 2-alkoxy-3*H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6q–6r). To the solution of carbodiimide (**4**) (3 mmol) prepared earlier, anhydrous ROH (15 mL) and several drops of RONa were added. The mixture was stirred at RT for 1–3 h. The solution was condensed, and the residual was recrystallized from methylene dichloride/petroleum ether to give **6q–6r**.

***7-Cyano-3,5-diphenyl-2-isopropoxy-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6q).** ^{1}H-NMR ($CDCl_3$): δ 1.26 (d, *J* = 7.6 Hz, 6H, $2CH_3$), 5.45–5.50 (m, 1H, OCH), 7.15–7.47 (m, 10H, Ar—H), 7.63 (s, 1H, Ar—H); IR (potassium bromide): 2209 (CN), 1689 (C═O), 1583, 1547, 1223 cm^{-1}; MS: *m/z* (%) 370 (32, M^+), 328 (100), 236 (50), 209 (89), 181 (33), 154 (53), 77 (34).

***7-Cyano-2-ethoxy-3-(4-fluorophenyl)-5-phenyl-3H*-pyrrolo[3,2-*d*]pyrimidine-4(5*H*)-one (6r).** ^{1}H-NMR ($CDCl_3$): δ 1.28 (t, *J* = 7.2 Hz, 3H, CH_3), 4.51 (q, *J* = 7.2 Hz, 2H, OCH_2), 7.14–7.45 (m, 9H, Ar—H), 7.64 (s, 1H, Ar—H); IR (potassium bromide): 2198 (CN), 1701 (C═O), 1576, 1541, 1210 cm^{-1}; MS: *m/z* (%) 374 (92, M^+), 346 (71), 252 (20), 236 (49), 209 (100), 181 (32), 154 (41), 103 (44), 77 (40).

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