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Swift and Efficient Synthesis of 4-Phenylquinazolines: Involvement of *N*-Heterocyclic Carbene in the Key Cyclization Step

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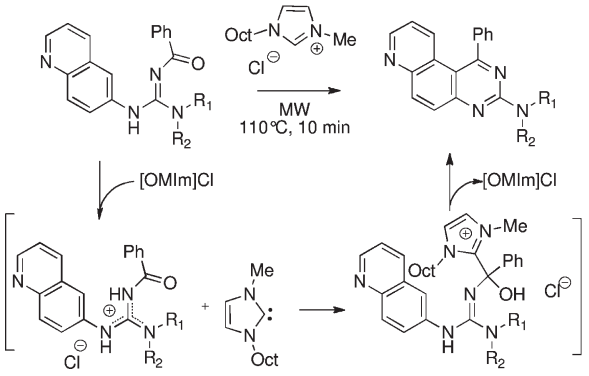
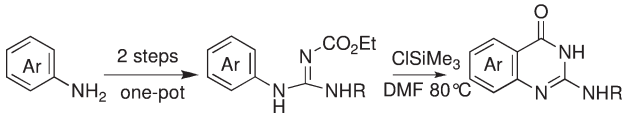


An original route to 2-alkyamino-4-phenylquinazolines in three steps from simple (hetero)aromatic amines is reported here. The key step involves the intramolecular cyclization of benzoyl arylguanidines performed in [OMIm]Cl ionic liquid. The basic (hetero)aromatic guanidines deprotonate the imidazolium-based ionic liquid, thus triggering the cascade process ultimately leading to the intramolecular cyclization. This reaction is the first example of a Friedel−Crafts-type reaction in which an *N*-heterocyclic carbene is involved in the formation of the electrophilic intermediate.

Our group is interested in the design of original nitrogen heterocycles and, among them, quinazoline fused polycycles. Quinazoline derivatives constitute an important class of compounds, from natural or synthetic sources,[1] that exhibit remarkable activities, including anti-inflammatory,[2] antihypertensive[3] antitubercular,[4] antibacterial,[5] antimalarial,[6] and antitumor properties.[7] Quinazolines also display promising activities against neurological disorders.[8] The growing importance of these heterocycles in therapeutics as well as the development of green chemistry encourage the search for environmentally benign synthetic methods for their preparation.[9]

We recently described[10] the synthesis of 2-alkylaminoquinazolin-4-one analogues by Friedel−Crafts cyclization of ethoxycarbonyl-protected guanidino(hetero)cycles in the presence of Lewis acid catalyst (halosilanes/DMF or $AlCl_3$/toluene) (Scheme 1).

SCHEME 1. Synthesis of 2-Alkylaminoquinazolin-4-ones



To increase the scope of this reaction and in an effort to prepare 2-amino-4-phenylquinazolines, we turned our attention to the reactivity of the *N*-benzoyl-protected analogues. We report here a process based on the microwave-assisted cyclization of *N*-alkyl-*N*′-(hetero)arylbenzoylguanidines, emphasizing the essential and unexpected role played by the ionic liquid in the key Friedel−Crafts-type reaction.

To test the ability of the benzoyl arylguanidines to undergo intramolecular Friedel−Crafts reaction, the guanidinoquinoline **2a**, prepared in two steps from 6-aminoquinoline **1**, was treated with $POCl_3$ in a Vilsmeier−Haack-type procedure. The cyclization proceeded well, and the desired quinazolinone **3a** was isolated in reasonable yield (60%). The polycyclic structure of **3a** was confirmed by X-ray crystallography.

To avoid the use of toxic reactants, we then looked for a greener procedure. Combination of Lewis acid and ionic liquids

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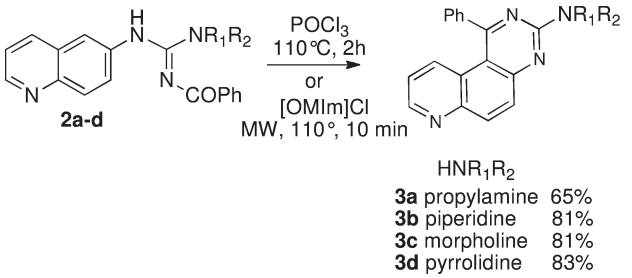
SCHEME 2. Cyclization of Benzoylguanidines 2a−d



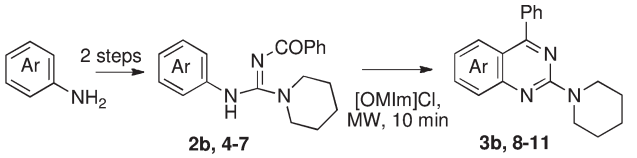
has been reported to achieve Friedel−Crafts reactions.[11] We therefore chose to investigate the reactivity of benzoylguanidines in the imidazolium-based ionic liquid [OMIm]Cl under microwave irradiation. The ionic liquid is commercially available, but it can be easily prepared on a large scale by alkylation of methyl imidazole with octyl chloride.

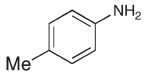
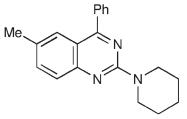
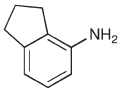
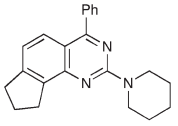
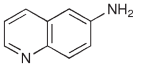
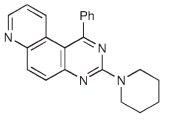
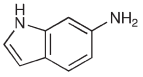
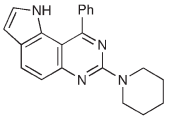
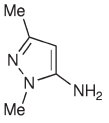
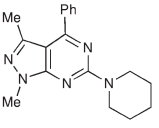
As imidazolium-based ionic liquids are known to be non-innocent solvents, a solution of benzoylguanidines **2a** in [OMIm]Cl was first irradiated (10 min, 110 °C) in the absence of any acid or basic catalyst. To our great satisfaction and surprise, **2a** was quantitatively (as indicated by HPLC analysis) transformed into the desired tricyclic derivatives **3a** (Scheme 2). The reaction also occurred under traditional heating (110 °C), but it required a longer time to completion (1 h compared to 10 min under microwave irradiation). The reaction was then performed with arylbenzoylguanidines containing various amino substituents. The cyclization proceeded well with secondary (propylamine) or tertiary amines (piperidine, morpholine, or pyrrolidine). The lower yield (65%) observed for the propylamine-containing quinazoline **3a** was due to less efficient purification steps. One limitation of the methodology is the access to quinazolines containing aromatic amines at position 2 (NR_1R_2 = ArNH). Indeed, in these cases, the presence of two competing aromatic rings on the guanidine generates a mixture of compounds as the cyclization may occur on the two rings.

To assess its scope, the reaction was performed using benzoylguanidines containing various aromatic and heteroaromatic rings. As shown in Table 1, the cyclization occurred in good to excellent yields on phenyl and both electron-rich and electron-deficient heterocycles. As indicated in lines 3 and 4, the reaction was regioselective.

This unexpected cyclization under relatively mild conditions prompted us to study the mechanism of reaction and, in particular, the possible role of the ionic liquid in the process. When the ionic liquid was replaced by *N*-methylpyrrolidinone as a solvent, no reaction occurred, even at higher temperature (220 °C, 10 min irradiation). Imidazolium-based ionic liquids are prone to form the corresponding highly reactive *N*-heterocyclic carbenes in the presence of strong bases.[12] To check the possible involvement of carbenes in

TABLE 1. Synthesis of 2-Piperidinyl-4-phenylquinazolines



	Starting amine	Guanidines	Quinazoline analogues	Yields (%)
1		**4**	 **8**	79%
2		**5**	 **9**	80%
3		**2b**	 **3b**	81%
4		**6**	 **10**	82%
5		**7**	 **11**	92%

the process, we replaced the 1,3-disubstituted imidazolium [OMIm]Cl with the 1,2,3-trisubstituted analogue [OMMIm]Cl. The reaction was performed using the indan derivative **5** (Table 1, entry 2). The solution of **5** in [OMMIm]Cl was submitted to microwave irradiation (110 °C, up to 30 min), and no reaction was observed, the starting guanidine **5** being recovered. Exchanging the chloride counterion by the less nucleophilic tetrafluoroborate ion in either [OMIm]X or [OMMIm]X ionic liquids does not modify the course of the reaction, indicating that the counterion was not involved in the mechanism.

From these experiments, we therefore propose the mechanism depicted in Scheme 3. The first step involves the [OMIm] H-2 abstraction by the basic arylguanidine, with formation of the corresponding carbene and the acylguanidinium species **I**. Addition of the carbene to the hydroxyimino tautomer (**I′**), assisted by the presence of the positive charge on the guanidine nitrogens, gives the highly electrophilic intermediate **II** that undergoes the Friedel−Crafts-type cyclization. Elimination of imidazolium and water yields the pyrimidine ring.

Other experiments also support this hypothesis. In situ formation of the guanidinium cation, by addition of 1 equiv of hydrochloric acid to the solution of **5** in [OMMIm]Cl, prevents the cyclization step, thus indicating that the presence of the positive charge conjugated to the CO (species **I**/**I′**

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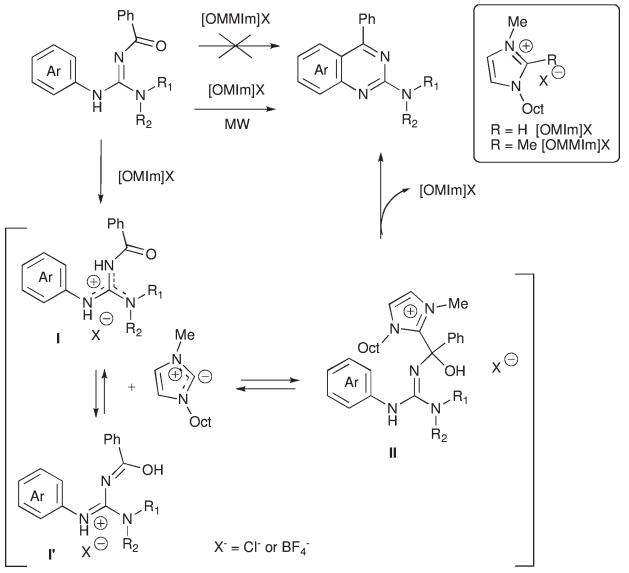
SCHEME 3. Proposed Reaction Pathway



in Scheme 2) is not sufficient to activate the C=O bond toward the aromatic electrophilic substitution. Addition of 1 equiv of hydrochloric acid to the solution of **5** in [OMIm]Cl also inhibits the cyclization process, confirming the crucial role of the guanidine as a base. The acidity of the ionic liquid, [OMIm]Cl, is not sufficient to catalyze the reaction, as the cyclization is not observed when the reaction was performed in the 2-methyl-substituted analogue [OMMIm]Cl, which displays similar acidic properties.[13] Moreover, increasing the acidity of the solvent by addition of HCl has definitely a negative effect as shown above. To evidence a possible catalytic effect, we performed the cyclization reation in dichloroethane using 0.5 equiv of [OMIm]Cl. The cyclization proceeded, but due to higher dilution, we only observed 70% transformation after 1 h of irradiation at 110 °C.

In summary, we have designed an original, efficient, and sustainable route to highly substituted aromatic and heteroaromatic fused 2-alkyamino-4-phenylquinazolines in three steps from simple (hetero)aromatic amines. The key step involves an intramolecular Friedel−Crafts-type cyclization under mild conditions. The reaction is performed in the easily accessible [OMIm]X ionic liquid, which plays the dual roles of an excellent solvent of polar molecules particularly suitable for using microwave technology and a key reagent by generating *N*-heterocyclic carbenes. The cyclization may be performed using traditional heating, but the use of microwave irradiation shortens the reaction time (10 min instead of 1 h).

Unlike what has been reported so far in the literature, there is no need of strongly basic catalyst for the carbene generation. Indeed, the intrinsic basicity of the reacting molecules, (hetero)aromatic guanidines, is sufficient to deprotonate the imidazolium-based ionic liquid, thus initiating the process ultimately leading to the intramolecular cyclization. This methodology is original in two aspects: the reacting molecule itself induces the carbene formation, and therefore triggers the events leading to the final cylization, and second, it is, to the best of our knowledge, the first example of aromatic electrophilic substitution in which a carbene is involved to form the electrophilic reagent.[14]

Experimental Section

Microwave reactions were conducted using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC) equipped with a continuous focused microwave power delivery system with selectable power output from 0 to 300 W. The reaction was performed in glass vessels (capacity 10 mL) sealed with a septum. The temperature of the reaction mixture was monitored using a calibrated infrared temperature control mounted under the reaction vessel. All experiments were conducted under magnetic stirring (rotating magnetic plate located under the microwave cavity and using Teflon-coated magnetic stir bar in the vessel). The typical experiment was irradiated in a sealed tube at 110 °C for 10 min (ramp time 30 s, T_{max} = 110 °C, power max = 200 W).

General Procedure for the Synthesis of Guanidine Derivatives. Benzoyl isothiocyanate (135 μL, 1.2 mmol) was added to a solution of the (hetero)cyclic amine (1 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 1 h. The disappearance of the starting amine was checked by TLC or HPLC analysis. To the solution were successively added Et_3N (416 μL, 3 mmol), amines (2 mmol), and EDCI (229 mg, 1.2 mmol). The resulting mixture was stirred for 6 h at room temperature or 60 °C (depending on the solubility of the intermediate thiourea). The solvent was then evaporated to dryness. The resulting oily residue was then diluted with water. The guanidine was filtered, washed with water, and dried under vacuum at 50 °C . The purity of the guanidine was checked by HPLC analysis and was found to be >95%. The guanidines **2a**−**d** and **4**−**7** were characterized by ^{1}H and ^{13}C NMR and HRMS. The data are given as Supporting Information.

General Procedure for the Synthesis of Quinazoline Derivatives. The protected guanidine (1 mmol) was solubilized in [OMIm]Cl (2 mL), and the solution was stirred at 110 °C during 10 min under microwave irradiation (CEM Discover). The reaction was monitored by HPLC or TLC. When the reaction was completed, the hot solution was poured into water, and aqueous NH_4OH was added dropwise to reach pH 9−10. The solid was filtered and washed several times with water. If necessary, the crude quinazolines were purified by column chromatography (SiO_2) dichloromethane/methanol 99/1).

4-Phenyl-2-propylaminopyrido[3,2-*f*]quinazoline (3a): yield 62%; mp 185−186 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65 (d, 1H, J = 4 Hz), 8.11 (d, 1H, J = 9 Hz), 7.75 (d, 1H, J = 9 Hz), 7.58−7.51 (m, 5H), 7.15 (m, 1H), 3.89 (m, 4H), 1.64−1.58 (m, 6H); HRMS calcd for $C_{20}H_{19}N_4$ (M^+) 315.1604, found 315.1596.

4-Phenyl-2-(piperidin-1-yl)-pyrido[3,2-*f*]quinazoline (3b): yield 81%; mp 181−182 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65−8.64 (m, 1H), 8.11 (d, 1H, J = 9 Hz), 7.75 (d, 1H, J = 9 Hz), 7.58−7.51 (m, 5H), 7.15 (m, 1H), 3.89 (m, 4H), 1.64−1.58 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.3, 157.9, 154.9, 147.9, 146.0, 141.1, 136.4, 132.5, 129.9, 129.5, 129.1, 128.3, 124.9, 120.8, 111.5, 44.2, 25.4, 24.3; HRMS calcd for $C_{22}H_{21}N_4$ (M^+) 341.1760, found 341.1751.

(13) Indeed the characteristic source of reactivity of the imidazolium cation is the high acidity of its C2-H position (pK_a = 21−24), whose abstraction results in a highly stabilized *N*-heterocyclic carbene; see: (a) Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. *J. Am. Chem. Soc.* **2003**, *125*, 5264. (b) Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366. (c) Sowmiah, S.; Srinivasadesikan, V.; Tseng, M.-C.; Chu, Y.-H. *Molecules* **2009**, *14*, 3780.

(14) *N*-Heterocyclic carbene palladium(II) complexes have been used as catalysts for various reactions included Friedel−Crafts-type processes; see: Liu, Z; Shi, M. *Tetrahydron: Asymmetry* **2009**, *20*, 119. Liu, Z.; Zhang, T.; Shi, M. *Organometallics* **2008**, *27*, 2668.

2-Morpholino-4-phenylpyrido[3,2-*f*]quinazoline (3c): yield 81%; mp 181−182 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.69−8.68 (m, 1H), 8.15 (d, 1H, J = 9 Hz), 7.78 (d, 1H, J = 9 Hz), 7.59−7.50 (m, 5H), 7.20−7.15 (m, 1H), 3.87 (t, 4H), 3.70 (t, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.1, 158.7, 155.5, 148.9, 146.9, 141.6, 137.4, 133.4, 130.5, 130.3, 129.8, 129.0, 125.5, 121.7, 112.9, 66.7, 44.6; HRMS calcd for $C_{21}H_{19}N_4O$ (M^+) 343.1553, found 343.1546.

4-Phenyl-2-(pyrrolidin-1-yl)-pyrido[3,2-*f*]quinazoline (3d): yield 81%; mp 205−206 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.70−8.68 (m, 1H), 8.15 (d, 1H, J = 9 Hz), 7.83 (d, 1H, J = 9 Hz), 7.59−7.51 (m, 5H), 7.22−7.19 (m, 1H), 3.66 (m, 4H), 1.99 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.1, 157.7, 155.6, 148.4, 146.0, 141.9, 136.9, 133.5, 130.8, 130.3, 129.9, 129.0, 125.8, 121.7, 112.2, 47.2, 25.7; HRMS calcd for $C_{21}H_{19}N_4$ (M^+) 327.1604, found 327.1595.

6-Methyl-4-phenyl-2-(piperidin-1-yl)quinazoline (8): yield 76%; mp 104−106 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.70−7.74 (m, 2H), 7.50−7.58 (m, 6H), 3.97−4.02 (m, 4H), 2.38 (s, 3H), 1.72−1.77 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 19.3, 25.2; 26.0, 44.4, 117.0, 118.3, 120.4, 122.7, 123.4, 125.2, 127.9, 130.0, 135.3, 145.3, 157.7, 166.3; HRMS calcd for $C_{20}H_{22}N_3$ (M^+) 304.1808, found 304.1797.

4-Phenyl-2-(piperidin-1-yl)cyclopenta[*g*]quinazoline (9): yield 72%; mp 122−123 °C °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.64 (m, 2H), 7.55 (d, 1H, J = 8.4 Hz), 7.43−7.42 (m, 3H), 6.95 (d, 1H, J = 8.4 Hz), 3.91−3.90 (m, 4H), 3.17 (t, 2H), 2.97 (t, 2H), 2.13 (q, 2H), 1.60−1.58 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 158.6, 150.7, 149.5, 138.7, 138.3, 129.9, 129.3, 128.1, 126.0, 118.9, 116.1, 44.9, 34.3, 30.3, 25.9, 25.0, 24.7; HRMS calcd for $C_{22}H_{23}N_3$ (M^+) 330.1964, found 330.1953.

4-Phenyl-2-(piperidin-1-yl)-5*H*-pyrrolo[2,3-*f*]quinazoline (10): yield 73%; mp 175−177 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.96 (s, 1H), 7.92 (d, 1H, J = 8.7 Hz), 7.62 (m, 5H), 7,23 (d, 1H, J = 8.7 Hz), 7.03 (m, 1H), 6.49 (m, 1H), 3.84 (m, 4H), 1.61−1.56 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.6, 157.5, 152.4, 140.4, 130.2, 129.6, 129.5, 128.6, 128.5, 124.2, 123.0, 118.8, 106.3, 103.4, 44.8, 25.8, 24.9; HRMS calcd for $C_{21}H_{21}N_4$ (M^+) 329.1760, found 329.1750.

5,7-Dimethyl-2-(piperidyl-1-yl)pyrazolo[4,3-*e*]pyrimidine (11): yield 92%; mp 105−106 °C ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.72−7.68 (m, 2H), 7.55−7.53 (m, 3H), 3.88−3.76 (m, 4H), 1.64−1.54 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.6, 159.4, 156.4, 140.4, 137.6, 129.9, 128.9, 128.2, 103.9, 44.6, 32.4, 25.3, 24.3, 15.2; HRMS calcd for $C_{18}H_{22}N_5$ (M^+) 308.1869, found 308.1859.

X-ray Crystallography. Crystal data for $C_{20}H_{18}N_4$: M_r, 314.39 g·mol^{-1}; crystal dimensions (mm), 0.30 × 0.26 × 0.10; crystal system, triclinic; space group, P-1; unit cell dimensions and volume, a = 8.770(6) Å, b = 10.038(4) Å, c = 10.810(5) Å, α = 107.39(4)°, β = 102.58(7)°, γ = 108.01(4)°, V = 812(1) Å^3, no. of formula units in the unit cell Z = 2; calculated density r_{calcd}, 1.286 g/cm^3; linear absorption coefficient, m 0.617 mm^{-1}; radiation and wavelength, l Cu Kα = 1.54178 Å; temperature of measurement, 293.0 K, 2 Q_{max} 150°; no. of measured and independent reflections, 3397 and 3215; R_{int}, 0.04; R [$I > 2.0\sigma(I)$] = 0.0649, wR = 0.0775, GoF = 1.98, refined on F; residual electron density, 0.32. The data collection was scaned in ω mode on a Bruker AXS-Enraf-Nonius CAD4 diffractometer.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds, including crystallographic data for compounds **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.