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Sequential Cu-Catalyzed Amidation-Base-Mediated Camps Cyclization: A Two-Step Synthesis of 2-Aryl-4-quinolones from *o*-Halophenones

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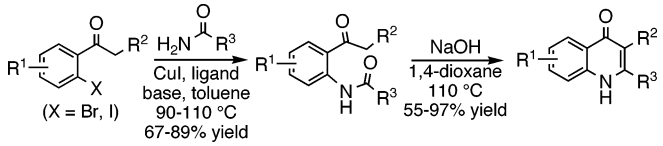


A direct two-step method for the preparation of 2-aryl- and 2-vinyl-4-quinolones that utilizes a copper-catalyzed amidation of *o*-halophenones followed by a base-promoted Camps cyclization of the resulting *N*-(*2*-ketoaryl)amides is described. With CuI, a diamine ligand, and base as the catalyst system, the amidation reactions proceed in good yields for a range of aryl, heteroaryl, and vinyl amides. The subsequent Camps cyclization efficiently provides the desired 4-quinolones with the conditions that are described.

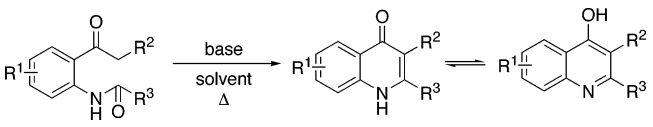
Introduction

The metal-catalyzed formation of aromatic C−N bonds has become increasingly important in organic synthesis over the past decade.[1] Recently, several efficient methods have been developed in which a sequential metal-catalyzed C−N bond-forming/cyclization process yields a nitrogen-containing heterocycle. Benzimidazoles,[2] pyrazoles,[3] pyrroles,[3,4] indoles,[5] 2-naphthyridinones, and 2-quinolones[6] have been synthesized via such sequences.

Nitrogen-containing heterocycles are present in a variety of biologically active compounds that can be used in a wide range of therapeutic areas.[7] Specifically, 4-quinolone derivatives[8] exhibit antibacterial activity, and several quinolones, such as oxolinic acid and ciprofloxacin, have emerged as potent antibiotics.[7] More recently certain 2-aryl-4-quinolones and compounds containing these structures have been studied as potential treatments for a range of diseases[9] as they exhibit antimitotic,[10] antiplatelet,[9b] and antiviral[9f,g,i] activities and have positive cardiac effects.[9a]

Multiple methods have been reported for the synthesis of 2-aryl-4-quinolones.[8a] Classical approaches such as the Conrad−Limpach and Niementowski reactions[11] generally focus on the condensation of amines and carboxyl derivatives followed by cyclization to produce the desired quinolones. Often the substrate scope of these reactions is limited by the necessity to employ harsh cyclization conditions, including temperatures of 250 °C or strong acids such as polyphosphoric acid or Eaton's reagent. Less traditional syntheses of these compounds[12] make use of transition metals, including palladium-catalyzed carbonylation,[13] titanium-mediated reductive coupling,[14] and ruthenium-catalyzed reduction reactions.[15] The base-promoted cyclization of *N*-(ketoaryl)amides (the Camps cyclization)[16] has seen widespread utilization for the synthesis of quinolones (Scheme 1).[9c,f,i,10b−f,17]

SCHEME 1. Camps Quinolone Synthesis



Known methods for the syntheses of the Camps precursors, the *N*-(ketoaryl)amides, comprise condensations of *o*-aminoaceto-

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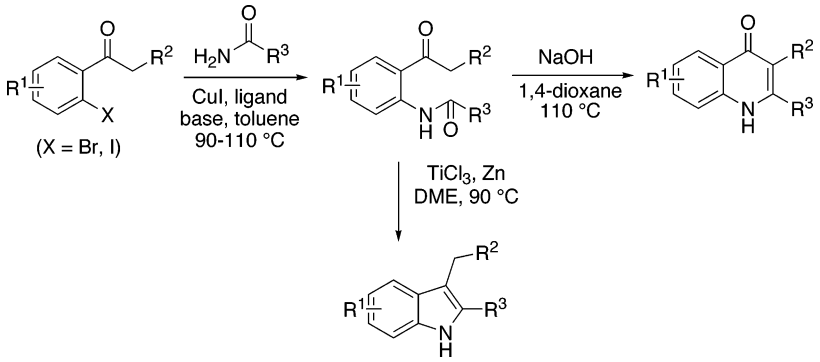
SCHEME 2. Preparation of 2-Substituted-4-quinolones and 2- and 3-Substituted-indoles from 2-Halophenones



phenones and carboxylic acids[9c] or acid chlorides,[10b−e,18] Friedel−Crafts acylations of anilides (which often result in a complex mixture of products),[9i,10f,17c] or synthesis and subsequent opening of a benzoxazinone with the dianion of an *N*-substituted acetamide.[16b,17a]

Herein we report a simple sequence that employs a copper-catalyzed amidation reaction of 2-halophenones with aryl, heteroaryl, and vinyl amides for a means to access *N*-(ketoaryl)-amides and their subsequent Camps cyclizations to 2-aryl- or 2-vinyl-4-quinolones (Scheme 2). We also demonstrate the ability of these same amidation products to undergo McMurry titanium-mediated coupling reactions to form indoles as developed by Fürstner.[14,18,19]

Results and Discussion

On the basis of the Cu(I)-catalyzed amidation of aryl halides in the presence of 1,2-diamine ligands developed in our group,[20] we focused on the application of this methodology to aryl halides with *o*-substituted ketones. As a test case, 2-bromoacetophenone was allowed to react with benzamide by using 10 mol % CuI,

(8) It is known that 4-quinolones have two tautomeric forms and can be drawn as either the 4-hydroxyquinolines in the enol-form or as 4-quinolones in the keto-form (Scheme 1). Both forms are important in understanding the characterization data and the chemical reactivity of such compounds. However, it is believed that in the solid state, as well as in many solvents, these compounds exist primarily in the keto-form. Therefore, for the purposes of this publication, we will refer to and draw the products as 4-quinolones. For discussions on the tautomerization of hydroxyquinolines see: (a) Reitsema, R. H. *Chem. Rev.* **1948**, *43*, 43−68. (b) Katritzky, A. R.; Lagowski, J. M. Prototropic Tautomerism of Heteroaromatic Compounds: II. Six-Membered Rings. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press, Inc.: New York, 1963; Vol. 1, pp 339−437. (c) Mphahlele, M. J.; El-Nahas, A. M. *J. Mol. Struct*. **2004**, *688*, 129−136.

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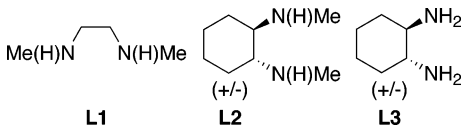
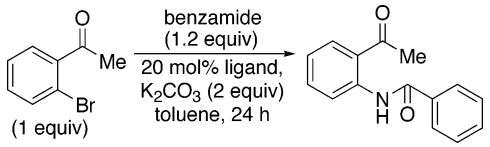


FIGURE 1. Diamine ligands for Cu-catalyzed amidation reactions of aryl halides.

TABLE 1. Ligand Screening for Cu-Catalyzed Amidation with Benzamide



entry	ligand	CuI (mol %)	temp (°C)	mol sieves (5 Å)	GC conversion[a] (%)	GC yield[a] (%)
1	**L1**	10	110	no	98	78
2	**L2**	10	110	no	100	54
3	**L3**	10	110	no	100	75
4	**L1**	10	90	yes	100	94
5	**L1**	0	90	yes	3	0
6	none	0	90	yes	2	0
7	none	10	90	yes	76	66

[a] GC yields and conversions are the average of two or more runs.

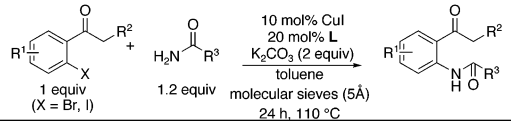
20 mol % ligand, and 2 equiv of K_2CO_3 in toluene at 110 °C for 24 h. In a preliminary screen employing ligands **L1**−**L3** (Figure 1), the reaction with **L1** proceeded in the highest yield (Table 1, entry 1). We observed that 2-hydroxyacetophenone was generated from the reaction of 2-bromoacetophenone with traces of water, presumably introduced into the reaction mixture by moisture in the base. The formation of this byproduct could be suppressed and the yield of the desired product improved by the use of activated molecular sieves or by a reduction in the reaction temperature to 90 °C (Table 1, entry 4).

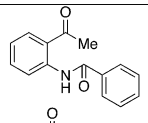
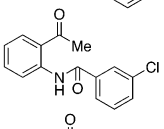
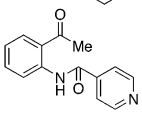
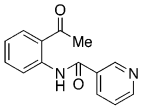
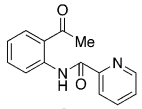
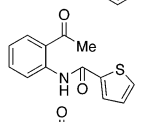
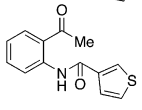
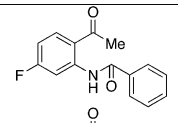
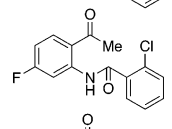
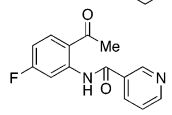
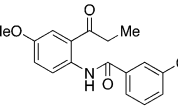
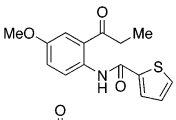
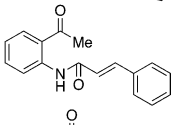
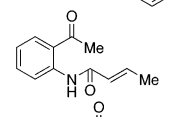
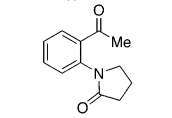
In a series of control experiments, we found that the reaction did not proceed in the absence of CuI indicating that the amidation reaction does not follow a simple nucleophilic aromatic substitution mechanism (Table 1, entries 5 and 6).[21] The reaction did, however, yield product in the absence of ligand (Table 1, entry 7). As reported previously in the Cu-catalyzed synthesis of biaryl ethers, certain electron-withdrawing groups in the ortho position of the aryl halide have the ability to coordinate to copper and hasten the Ullmann-type reaction.[22] Presumably, in this amidation reaction the accelerating *o*-acetyl group had the ability to promote the coupling without the diamine ligand present. Nevertheless, the diamine ligand did enhance the rate of the amidation reaction as the ligand-free reaction did not reach completion after 24 h.

With these reaction conditions in hand, the versatility of the Cu-catalyzed amidation reaction of 2-bromophenones and 2-iodophenones was explored (Table 2). The substrate scope of the coupling reaction encompassed 2-halophenones bearing both electron-withdrawing (**8**−**10**) and electron-donating groups (**11** and **12**). As demonstrated by the use of 2-halopropiophenones, the amidation reaction also tolerated larger ketone substituents than the methyl group (**11** and **12**). The couplings proceeded with heterocyclic amides, including 2-, 3-, and 4-pyridyl amides as well as 2- and 3-thiophenecarboxamides (**3**−**7**, **10**, and **12**). Both aryl and alkyl vinyl amides could be cross-coupled (**13** and **14**), and though the cyclic secondary amide pyrrolidinone reacted in good yield (**15**), acyclic secondary amides were not effective coupling partners.

Though most reactions were conducted with the use of the 2-bromophenones, the low reactivity of picolinamide (**5**), 2-chlorobenzamide (**9**), and crotonamide (**14**) as nucleophiles prompted us to employ the more active 2-iodophenones as substrates for these couplings.[23,24] However, even with the use of the 2-iodophenone, the yields for the syntheses of **9** and **14** were still only moderate. The synthesis of **9** from the 2-iodo-

TABLE 2. Cu-Catalyzed Amidation of 2-Halophenones



X	product		yield (%)[a]
Br		(**1**)	86[b]
Br		(**2**)	83
Br		(**3**)	80[c]
Br		(**4**)	86
I		(**5**)	71[d]
Br		(**6**)	81[c]
Br		(**7**)	82
Br		(**8**)	78
I		(**9**)	67[e,f]
Br		(**10**)	77
Br		(**11**)	72
Br		(**12**)	72
Br		(**13**)	77[g]
I		(**14**)	68[f]
Br		(**15**)	89[h]

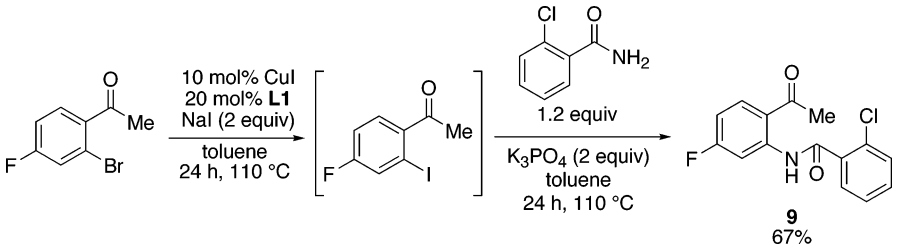
[a] Isolated yields are the average of two or more runs. [b] Heated to 90 °C. [c] Without molecular sieves. [d] Heated for 42 h with K_3PO_4. [e] Aryl iodide generated in situ from aryl bromide. [f] With 2 equiv of K_3PO_4. [g] With 20 mol % of **L2**. [h] With 5 mol % of CuI, 10 mol % of **L1**.

(20) (a) Klapars, A.; Antilla, J. C.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc*. **2001**, *123*, 7727−7729. (b) Klapars, A.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7421−7428. (c) Streiter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4120−4121.

(21) References indicating catalyst-free amination reactions: (a) Beller, M.; Breindl, C.; Riermeier, T. H.; Tillack, A. *J. Org. Chem.* **2001**, *66*, 1403−1412. (b) Shi, L.; Wang, M.; Fan, C.-A.; Zhang, F.-M.; Tu, Y.-Q. *Org. Lett.* **2003**, *5*, 3515−3517. (c) De Lange, B.; Lambers-Verstappen, M. H.; Schmieder-van de Vondervoort, L.; Sereinig, N.; de Rijk, R.; de Vries, A. H. M.; de Vries, J. G. *Synlett* **2006**, *18*, 3105−3109.

(22) (a) Lindley, J. *Tetrahedron* **1984**, *40*, 1433−1456. (b) Nicolaou, K. C.; Boddy, C. N. C.; Natarajan, S.; Yue, T.-Y.; Li, H.; Bräse, Ramanjulu, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 3421−3422. (c) Cai, Q.; Zou, B.; Ma, D. *Angew. Chem., Int. Ed*. **2006**, *45*, 1276−1279.

SCHEME 3. Synthesis of 9 via in Situ Formation of 2-Iodo-4-fluoroacetophenone Followed by Cu-Catalyzed Amidation Reaction



phenone could be accomplished in a one-pot procedure from the corresponding aryl bromide by using a Cu-catalyzed halide exchange reaction[25] followed by the Cu-catalyzed amidation reaction (Scheme 3).

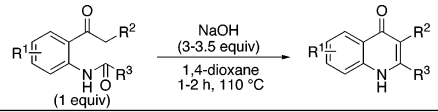
Having developed a successful method for the synthesis of *N*-(2-ketoaryl)amides, we focused on the base-catalyzed Camps cyclization to yield 2-substituted-4-quinolones. The optimal reaction conditions for the cyclization of *N*-(2-ketoaryl)amide **6** to 4-quinolone **21** were found to involve the use of 3−3.5 equiv of NaOH in dioxane at 110 °C. The conditions proved to be generally applicable to a wide range of *N*-(2-ketoaryl)amides providing the appropriate 2-substituted-4-quinolones in good to excellent yields (Table 3). The cyclization method was also effective for the syntheses of more highly substituted quinolones **26** and **27**. Notably, when submitted to the reaction conditions, the pyrrolidinone-coupled substrate **15** provided a more complex tricyclic pyrrolo-quinolone ring system (**29**).

The workup of the 4-quinolone compounds was particularly facile as, with the exception of **29**, all the compounds shown in Table 3 could be isolated in pure form without the need to employ column chromatography; after initial concentration of the organic reaction mixture, the resulting residue was dissolved in water, and the desired products precipitated upon neutralization.

Compound **14** has the ability to cyclize to either 2-vinyl-4-quinolone (**30**) or 4-methyl-3-vinyl-2-quinolone (**31**) depending on the nature of the base utilized (Scheme 4). With NaOH, deprotonation occurred at the α position of the ketone followed by the intramolecular aldol condensation. However, the use of a weaker base (Cs_2CO_3) afforded **31** as the major product via γ-deprotonation of the amide. In both cases, traces of the other isomer were produced, which could be readily separated by column chromatography on silica gel. Similarly, as Camps observed,[16a] substrates with accessible protons at the α position of the amide yield a mixture of 4- and 2-quinolones rendering this method unsuitable for use with alkyl amides for the selective preparation of 2-alkyl-4-quinolones.[26] Unfortunately, the base-dependent selectivity observed for the synthesis of **30** and **31** was not seen for alkyl amides.

Finally, the Cu-catalyzed amidation products in Table 2 were submitted to Fürstner's "instant" $TiCl_3$/Zn powder conditions[14] for the McMurry Ti-promoted coupling reaction to prepare 2- and 3-substituted-indoles (Table 4). The yield was low when the obtained indole contained alkyl substituents in both the 2- and 3-positions (**37**).

TABLE 3. Base-Catalyzed Camps Cyclization to 2-Substituted-4-quinolones



starting material	product	yield (%)[a]	starting material	product	yield (%)[a]
(1)	(16)	94	(8)	(23)	90
(2)	(17)	97	(9)	(24)	72
(3)	(18)	90	(10)	(25)	92
(4)	(19)	89	(11)	(26)	88
(5)	(20)	88	(12)	(27)	86
(6)	(21)	97	(13)	(28)	82[b]
(7)	(22)	92	(15)	(29)	94

[a] Isolated yields are the average of two or more runs. [b] Heated to 90 °C.

In conclusion, we have demonstrated a new two-step synthesis of 2-aryl- and 2-vinyl-4-quinolones. The Cu-catalyzed amidation reaction of 2-halophenones offers access to *N*-(*2*-ketoaryl)amides that readily undergo base-promoted Camps cyclization to provide the desired 4-quinolones. We have also shown the accessibility of 2- and 3-substituted-indoles from the *N*-(2-ketoaryl)amides via Ti-mediated reductive coupling. These sequential methods have potential for application in the synthesis of substituted nitrogen-containing heterocycles.

Experimental Section

General Procedure for the Amidation of *o*-Halophenones. An oven-dried resealable test tube with a Teflon stir bar was charged

(23) Aryl iodides were found to be better starting materials for the more difficult Cu-catalyzed amidation reactions of 2-halophenones with alkyl amides, which are not discussed in this publication due to their problematic reactivity in the Camps cyclization.

(24) K_3PO_4 was employed for reactions with 2-iodophenones due to the superiority of K_3PO_4 for the facilitation of Cu-catalyzed amidation with aryl iodides reported in our earlier work (ref 20b).

(25) (a) Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844−14845. (b) Antilla, J. C.; Baskin, J. M.; Barder, T. E.; Buchwald, S. L. *J. Org. Chem.* **2004**, *69*, 5578−5587.

(26) For example, *N*-(2-acetylphenyl)-*n*-hexanamide (**32**) cyclized to afford 25% of 4-methyl-3-*n*-butyl-2-quinolone (**33**) and 49% of 2-*n*-pentyl-4-quinolone (**34**).

SCHEME 4. Base-Promoted Cyclizations to Synthesize 30 and 31

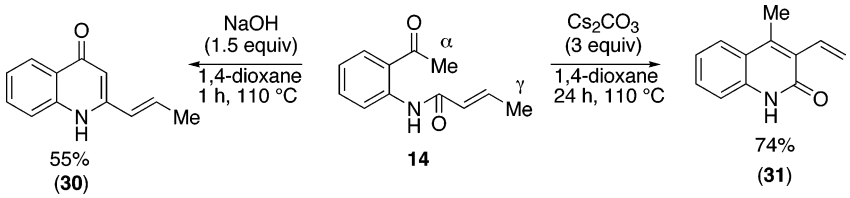
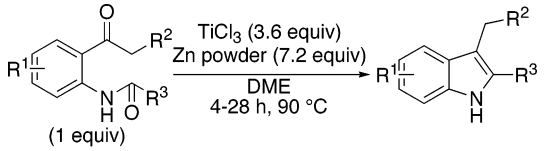
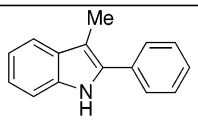
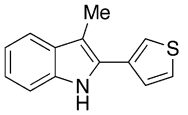
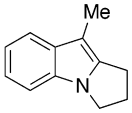


TABLE 4. Ti-Mediated Coupling for the Preparation of Substituted Indoles



starting material	product		yield (%)[a]
(**1**)		(**35**)	67
(**7**)		(**36**)	71
(**15**)		(**37**)	35

[a] Isolated yields are the average of two or more runs.

with amide (1.2 equiv, 0.60 mmol), CuI (10 mol %, 0.05 mmol), base (2 equiv, 1 mmol), and approximately 200 mg of activated 5 Å molecular sieves. The test tube was sealed with a rubber septum and evacuated and refilled with Argon three times through a syringe needle. Under argon, *o*-halophenone (1.0 equiv, 0.50 mmol), *N*,*N*′-dimethylethylenediamine (**L1**) (20 mol %, 0.1 mmol), and toluene (1 mL) were each added via syringe. The rubber septum was then removed and quickly replaced with a Teflon screw-cap. The test tube was then placed in a preheated oil bath at 110 °C. The reaction was heated with stirring for 24 h and then cooled to room temperature. The reaction mixture was partitioned between EtOAc and water and the organic layer was separated. The aqueous layer was extracted with EtOAc and the organic layers were combined, dried over magnesium sulfate, filtered, and concentrated in vacuo to remove solvent. The product was purified by column chromatography on silica gel with EtOAc and hexane.

Representative Example of the General Procedure for the Amidation of *o*-Halophenones: *N*-(2-Acetylphenyl)-3-chlorobenzamide (2). Following the General Procedure above, 3-chlorobenzamide (93 mg, 0.60 mmol) was coupled with 2-bromoacetophenone (67 μL, 0.50 mmol), using CuI (9.5 mg, 0.050 mmol), **L1** (10.5 μL, 0.985 mmol), K_2CO_3 (140 mg, 1.0 mmol), and 200 mg of activated 5 Å molecular sieves in anhydrous toluene (1 mL). **2** was purified by column chromatography with use of a hexane−EtOAc 98:2 to 90:10 gradient, and 112 mg (82% yield) of a white solid was obtained. Mp 137−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.75 (s, 1H), 8.95 (d, J = 8.5 Hz, 1H), 8.07 (s, 1H), 7.98 (dd, J = 8.0, 1.4 Hz, 1H), 7.94 (ddd, J = 7.7, 1.7, 1.1 Hz, 1H), 7.65 (m, 1H), 7.55 (ddd, J = 8.0, 2.0, 1.1 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.20 (m, 1H), 2.74 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 203.5, 164.7, 141.2, 136.7, 135.5, 135.1, 132.1, 132.0, 130.2, 128.2, 125.3, 122.9, 122.0, 120.8, 28.7. IR (neat, cm^{-1}) 3185, 3068, 2920, 1684, 1644, 1608, 1584, 1523, 1452, 1359, 1315, 1258, 1170, 1076, 965, 904, 851, 798, 755, 739, 721, 611. Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42. Found: C, 65.69; H, 4.22.

General Procedure for the Base-Promoted Cyclization to 2-Aryl-4-Quinolones. A resealable oven-dried test tube with a Teflon stir bar was charged with *N*-(ketoaryl)amide (1 equiv) obtained in step one and crushed NaOH (3−3.5 equiv). Anhydrous 1,4-dioxane was added via syringe such that the concentration of the reaction mixture was 0.1 M. The test tube was then sealed with a Teflon screw-cap and the reaction was placed in a preheated oil bath at 110 °C. The reaction mixture was stirred for 1−2 h and then removed from the oil bath and allowed to cool to room temperature. The reaction mixture was then dissolved in ethanol and transferred to a round-bottom flask in which it was concentrated in vacuo to remove solvent. Next, a small amount of water and a large amount of hexane were added to the flask and the flask was sonicated for approximately 2 min. The biphasic mixture was neutralized to pH ∼7 with 1 M HCl and saturated $NaHCO_3$ solutions. Solid precipitated out of the water layer and the heterogeneous mixture was filtered through a Buchner funnel. The solid powder was rinsed with copious amounts of hexane and minimal water. The solid was collected and transferred to a vial with ethanol and concentrated in vacuo to remove residual solvent. In some cases, the hexane rinses during filtration did not completely wash away the alkyl residue and the ^{1}H NMR showed contamination. Further purification involved a more extensive hexane wash in which hexane was added to the vial containing the compound and the mixture was sonicated. The solid was allowed to settle, and then the hexane was carefully removed via pipet. Hexane was added and removed twice more before the product was dried in vacuo.

Representative Example of the General Procedure for the Base-Promoted Cyclization to 2-Aryl-4-quinolones: 2-(3′-Chlorophenyl)-4-quinolone (17). Following the General Procedure above, **2** (107 mg, 0.39 mmol) was cyclized with NaOH (47 mg, 1.2 mmol) in 1,4-dioxane (3.9 mL). The reaction was heated for 1 h at 110 °C. After workup and filtration, 96 mg (96% yield) of a cream-colored solid was obtained. Mp >260 °C. ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$) δ 8.26 (m, 1H), 7.76 (m, 1H), 7.67 (m, 3H), 7.50 (m, 2H), 7.40 (m, 1H), 6.55 (s, 1H). ^{13}C NMR (500 MHz, $CD_3OD/CDCl_3$) δ 180.4, 151.4, 141.6, 137.0, 135.9, 133.5, 131.5, 131.4, 128.3, 126.7, 125.8, 125.6, 125.3, 119.5, 108.7. IR (neat, cm^{-1}) 2193, 1604, 1572, 1558, 1503, 1445, 1350, 841, 769, 757, 705.

General Procedure for the McMurry-Type Coupling To Form Indoles.[14] In a glovebox, $TiCl_3$ (1.8 mmol, 3.6 equiv) and Zn powder (3.6 mmol, 7.2 equiv) were weighed into an oven-dried Schlenk tube with a Teflon-coated stir bar. The Schlenk tube was capped with a rubber septum and removed from the glovebox. Outside of the glovebox, the Schlenk tube was evacuated and refilled with Argon twice. While still under a stream of Argon, the rubber septum was removed and the *N*-(ketoaryl)amide (0.5 mmol, 1 equiv) was added quickly to the Schlenk tube. The Schlenk tube was recapped with the septum and evacuated and refilled with Argon three more times. Anhydrous DME was added via syringe and the rubber septum was replaced with a Teflon Schlenk cap. The reaction was placed in a preheated oil bath at 90 °C, and the reaction was heated with stirring for 4−28 h, monitored by TLC. The reaction mixture was allowed to cool to room temperature and filtered through a pad of silica gel with copious amounts of EtOAc. The filtrate was concentrated in vacuo, and the crude material was

purified via silica gel column chromatography with use of a hexane−EtOAc 100:0 to 92:8 gradient.

Representative Example of the General Procedure for the McMurry-Type Coupling To Form Indoles: 3-Methyl-2-(3′-thiophenyl)indole (36). Following the General Procedure above, **7** (122.7 mg, 0.50 mmol) underwent an intramolecular coupling with use of $TiCl_3$ (280 mg, 1.8 mmol) and Zn powder (235 mg, 3.6 mmol) in DME (6.0 mL). The reaction was heated for 16 h at 90 °C. After filtration and column chromatography, 75 mg (70% yield) of a beige solid was obtained. Mp 92−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, br, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.34 (dd, J = 4.6, 3.4 Hz, 1H), 7.24 (m, 3H), 7.13 (m, 3H), 2.39 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 135.7, 134.2, 130.0, 130.0, 126.7, 126.3, 122.4, 121.3, 119.7, 119.0, 110.8, 108.6, 9.87. IR (neat, cm^{-1}) 3417, 3100, 3056, 2916, 2862, 1461, 1350, 1332, 1291, 1240, 1206, 1153, 1118, 1090, 1025, 1007, 865, 781, 741, 683, 619. Anal. Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20. Found: C, 73.33; H, 5.30.

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Supporting Information Available: Experimental data for Compounds **1**−**37** and 2-bromo-5-methoxypropiophenone and ^{1}H NMR and ^{13}C NMR spectra for unknown compounds and compounds with inadequate elemental analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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