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Symmetrical Bisquinolones via Metal-Catalyzed Cross-Coupling and Homocoupling Reactions

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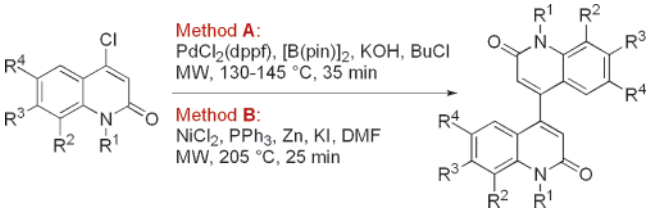
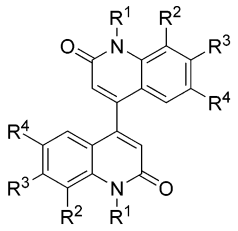


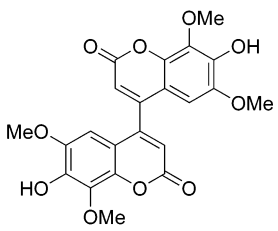
Functionalized 4,4′-bisquinolones can be efficiently synthesized by microwave-assisted palladium(0)-catalyzed one-pot borylation/Suzuki cross-coupling reactions or via nickel(0)-mediated homocouplings of 4-chloroquinolin-2(1*H*)-one precursors. Both methods are also applicable to other types of symmetrical biaryls.

Substituted biaryls play an important role in organic chemistry.[1,2] Many natural products, pharmaceuticals, herbicides, and fine chemicals contain symmetrical or unsymmetrical biaryl units. In addition, biaryls are applied as chiral ligands in catalysis, as liquid crystals or organic conductors.[1] Bis-heterocycles are also well-known in the literature and often display similarly interesting biological and physical properties.[2−5] Important structural motifs are, for example, bipyridines,[3] bithiophenes,[4] and bipyrroles.[5]

In the context of our ongoing interest in the chemistry of functionalized quinolin-2(1*H*)-ones (carbostyrils),[6] we became interested in the generation of the corresponding 4,4′-bisquinolones of type **1**. This novel class of bis-heterocycles are of interest both as aza-analogues of biscoumarin natural products (e.g., 4,4′-biisofraxidin)[7] and because of their anticipated fluorescent properties as push−pull carbostyrils ($R^3 = R^4 =$ OMe).[8]



1; R^1 = Me, Ph; R^2 = H, alkyl
$R^3 = R^4$ = H, OMe



4,4′-biisofraxidin

Here we report two different methods for the synthesis of bisquinolones of type **1** that are based either on Pd(0)-catalyzed one-pot borylation/Suzuki cross-couplings or on Ni(0)-mediated homocouplings (Ullmann reaction) of 4-chloroquinolin-2(1*H*)-one precursors. Both methods rapidly deliver bisquinolones in good to excellent yields employing controlled microwave irradiation (MW) and are applicable not only toward the preparation of the desired symmetrical bisquinolones but also as general methods for a symmetrical biaryl synthesis.

Several recently developed protocols for the preparation of symmetrical biaryls from arylhalides via cross-coupling chemistry involve the use of bis(pinacolato)diboron as a reagent.[9−11] In these Pd(0)-catalyzed one-pot transformations, arylboronic esters are formed as intermediates, which are not isolated, and undergo subsequent Suzuki coupling to directly form the desired biaryls.[9−11] The preferred catalyst for this transformation is $PdCl_2$(dppf) (dppf = diphenylphosphinoferrocene).[9,11]

As a starting point for the synthesis of bisquinolones **1**, we investigated the one-pot borylation/Suzuki cross-coupling of readily available 4-chloro-1-methylquinolin-2(1*H*)-one **2a**[6] as a model substrate (Table 1). All initial optimization studies were performed on a 0.25 mmol scale using automated sequential microwave processing to allow for shorter reaction times and higher yields.[10−12] An extensive optimization of the reaction parameters included the amount of bis(pinacolato)diboron reagent, the type and the concentration of the Pd catalyst, and the required base, solvent, reaction time, and temperature.

An initial attempt to adapt the previously reported protocols where aryl iodides,[9] bromides,[9,11] triflates,[9] and reactive 2-chloroazaheterocycles[10] have been employed as precursors quickly demonstrated that the use of the suggested K_2CO_3 or KF base was not successful. Under the published reaction conditions,[9−11] only trace amounts of the desired bisquinolone product **1a** were obtained from the chloro precursor **2a**, regardless of the catalyst, solvent system, and the reaction temperature. Gratifyingly, we discovered that the use of the much stronger base KOH (4.5

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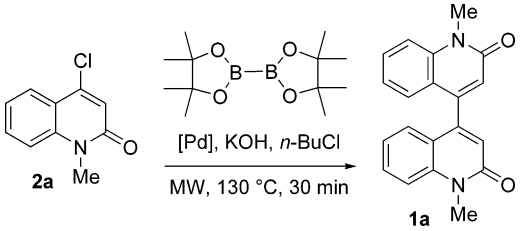
TABLE 1. Catalyst/Ligand Screening for the Pd(0)-Catalyzed Bisquinolone Synthesis[a]



entry	catalyst (mol %)	additive (mol %)	product distribution[b] (%)
1	$PdCl_2$(dppf) (5)	dppf (7)	22/**61**/17
2	$PdCl_2$(dppf) (10)		3/**89**/8
3	$PdCl_2$(dppf) (10)	dppf (7)	0/**97**/3[c]
4	$Pd(OAc)_2$ (5)	dppf (10)	0/**92**/8
5	$Pd(PPh_3)_4$ (8)		1/**91**/8
6	palladacycle[d] (2.5)	dppf (10)	0/**63**/37
7	$Pd_2(dba)_3$ (2.5)		0/**60**/40
8	$Pd_2(dba)_3$ (2.5)	dppf (7)	0/**84**/16
9	$Pd_2(dba)_3$ (2.5)	*t*-Bu_3PHBF_4 (5)	0/**86**/14
10	$Pd_2(dba)_3$ (2.5)	PCy_3 (5)	0/**88**/12

[a] Reaction conditions: 0.25 mmol chloroarene **2a**, 4.5 equiv KOH, 0.7 equiv bis(pinacolato)diboron, 1.5 mL *n*-BuCl, sealed-vessel, single-mode, microwave irradiation at 130 °C for 30 min. See Supporting Information for further details. [b] Product distribution refers to relative peak area (%) ratios of crude HPLC−UV (215 nm) traces: starting material/**product**/dehalogenated product. [c] Product isolation by flash chromatography provided an 85% yield of bisquinolone **1a**. [d] Herrmann's palladacycle.

equiv) in conjunction with $PdCl_2$(dppf) as catalyst (10 mol %) provided excellent conversions (>90%), depending on the solvent system used (dioxane, 115 °C, 30 min).[13]

When several of the commonly used solvents for this type of transformation were screened, such as DMSO, DMF, or toluene, we noticed that, while the starting material was consumed, the major reaction product with these solvents was the dehalogenated product, 1-methylquinolin-2(1*H*)-one. Suitable solvents for the one-pot borylation/Suzuki cross-coupling that minimized dehalogenation (<10%) included dioxane, CH_2Cl_2, and 1,2-dichloroethane. The best solvent identified in our studies, however, was 1-chlorobutane. Under optimized reaction conditions (see Table 1, entry 3), full conversion to the bisquinolone **1a** was achieved within a 25 min reaction time, with only 3% of the dehalogenated product formed. It should be noted that reducing the amount of KOH to, for example, 2.0 equiv also led to an increased formation of the dehalogenated product.

Substantial efforts were made to identify the optimum catalyst, reaction temperature, and time for this reaction (Table 1). After considerable experimentation, it was found that a 130 °C reaction temperature allowed the one-pot bisquinolone coupling to proceed within less than half an hour. Whereas lower reaction temperatures resulted in longer reaction times, higher temperatures produced more side and decomposition products. Among the many catalysts tested, $PdCl_2$(dppf) proved to be optimal. However, a 10 mol % loading of the catalyst was required to achieve acceptable conversions. In fact, best results were obtained upon the addition of a further amount of 7 mol % of the free dppf ligand to slow catalyst decomposition.[9] Many other Pd catalyst/ligand systems proved significantly less

(13) The effect of stronger bases such as KOH probably lies in their stronger nucleophilicity. For a detailed description of the reaction mechanism in these biaryl formations and the role of the base, see ref 9.

TABLE 2. Effect of Iodide Additives on Ni(0)-Mediated Homocouplings of 4-Chloroquinolones[a]

entry	iodide additive (equiv)	product distribution[b] (%)
1	NaI (1.8)	0/**88**/12
2	KI (1.8)	1/**95**/4[c]
3		21/**76**/3
4	KI (1.0)	19/**78**/3
5	KI (1.6)	11/**85**/4

[a] Reaction conditions: 0.25 mmol chloroarene **2a**, 1.3 equiv $NiCl_2$, 1.3 equiv Zn dust, 4.0 equiv PPh_3, iodide additive, 1.5 mL dry DMF, sealed-vessel, single-mode, microwave irradiation at 205 °C for 25 min. See Supporting Information for further details. [b] Product distribution refers to relative peak area (%) ratios of crude HPLC−UV (215 nm) traces: starting material/**product**/dehalogenated product. [c] Product isolation by flash chromatography provided a 90% yield of bisquinolone **1a**.

efficient, leading to a higher percentage of the dehalogenated product, although the use of $Pd(OAc)_2$/dppf or $Pd(PPh_3)_4$ furnished product yields that were also high (Table 1).

Importantly, the conversions determined by the HPLC monitoring of the crude reaction mixtures (Table 1) nicely matched isolated product yields. From the experiment described in entry 3, for example, an 85% yield of bisquinolone **1a** was obtained after flash chromatography. Our optimized one-pot borylation/Suzuki cross-coupling conditions were applicable to a series of 4-chloroquinolin-2(1*H*)-one substrates, allowing the preparation of various functionalized symmetrical bisquinolones (cf. Table 3).

The high costs of the required bis(pinacolato)diboron reagent and the Pd catalyst in the above-mentioned cross-coupling protocols prompted us to explore an alternative homocoupling method such as the Ullmann reaction,[2] which would not require the use of an additional cross-coupling partner. Among the many different available protocols for successful bi(hetero)aryl synthesis via homocoupling methods,[2−5] we were particularly attracted by Ni-mediated reductive homocouplings, where the active Ni(0) complex is prepared directly from an inexpensive Ni(II) salt and a reducing reagent such as Zn dust in the presence of triphenylphosphine.[2,14]

As with the cross-coupling protocol, a careful optimization of the reaction conditions with respect to the solvent, molar ratios (reagents and additives), time, and temperature was performed for the homocoupling of chloroquinolone **2a** (Table 2). Initial experiments indicated that the general procedures for aryl halide homocouplings[2,14,15] involving dry DMF as the solvent, $NiCl_2$ as the metal source, PPh_3 as the ligand, and Zn dust as the reducing reagent were also applicable to bisquinolone

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synthesis under microwave irradiation conditions. Acceptable product yields of the homocoupled bisquinolone **1a** were obtained within 25 min at about a 205 °C reaction temperature; the only observed byproduct being again the dehalogenated quinolone. As a result of the unreactive nature of the aryl chloride precursor, it was necessary to use Ni in stoichiometric amounts (1.3 equiv). Lowering the amount of Ni led to incomplete conversions. Similarly, we found that the presence of 1.3 equiv of Zn proved optimal for this transformation, with both lower and higher amounts of Zn resulting in more dehalogenated product. Ligands such as PPh_3 are essential in Ni-mediated homocoupling reactions to stabilize the in situ generated Ni(0) catalyst and aryl Ni species during the reaction sequence.[15] In the present case, 4.0 equiv of PPh_3 provided optimum product yields.

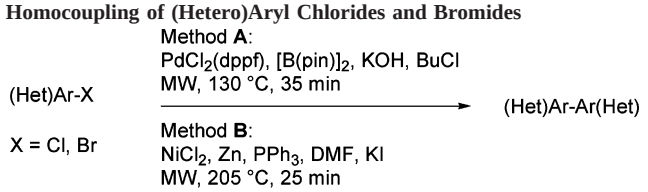
Nevertheless, by applying the above-mentioned reagent mixtures, it proved difficult to achieve high conversions in the desired short time frames. It is well-known that halide ions, especially iodide, enhance the reaction rate of Ni-catalyzed homocoupling reactions.[2,15] The iodide ion is believed to function as a bridging ion between Ni and Zn in the electron-transfer process and/or as a donor ligand for the highly coordinately unsaturated Ni(0) complex.[15] The screening of several iodide sources in our model reaction finally resulted in the use of 1.8 equiv of KI as an additive (Table 2, entry 2). Under these optimized conditions, the formation of the dehalogenated byproduct could be kept to a minimum (ca. 4%), allowing the desired bisquinolone homocoupling product **1a** to be isolated in 90% yield after flash chromatography.

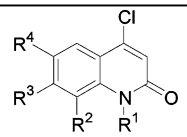
Having two different optimized protocols for the efficient generation of symmetrical bisquinolones from readily available 4-chloroquinolin-2(1*H*)-one substrates at hand, we next proceeded to investigate the scope of these coupling procedures for (i) the preparation of a variety of functionalized bisquinolones and (ii) the use of these methods as general high-speed symmetrical biaryl coupling methods. Gratifyingly, both methods provided moderate to excellent isolated product yields for all the quinolone systems, **2a**−**f**, tested (Table 3). For the electron-rich mono- or disubstituted methoxy analogues **2d**−**f**, somewhat higher reaction temperatures (145 °C) were applied in the cross-coupling protocol (Method A) to achieve good yields.[16] The required 4-chloroquinolone precursors were readily available from the known 4-hydroxyquinolones by microwave-assisted chlorination using $POCl_3$ as the chlorinating reagent (for details, see Supporting Information).[6] For the examples displayed in Table 3, the Pd-catalyzed cross-coupling method (Method A) proved to be somewhat more reliable, furnishing higher isolated product yields (68−85%) as compared to those of the Ni-mediated homocoupling method (Method B, 39−90%). A clear disadvantage of the Ni method additionally lies in the required extensive purification process, removing large quantities of the PPh_3 ligand by flash chromatography.

We next attempted to synthesize 4,4′-biscoumarin starting from 4-chlorocoumarin using both coupling methods. Biscoumarins are of interest because of their physiological properties and their presence as important structural units in a variety of biologically active natural products (i.e., 4,4′-biisofraxidin).[7] The generation of biscoumarins via cross-coupling chemistry to our knowledge has not been reported in the literature.[16,17] By changing to a toluene/Cs_2CO_3 solvent/base system in the Pd-catalyzed one-pot borylation/Suzuki cross-coupling (Method A), we achieved the preparation of 4,4′-biscoumarin in a moderate 67% yield. The standard reaction conditions employing KOH as base furnished only very small amounts of the desired product, presumably a result of the hydrolysis/destruction of the sensitive coumarin heterocycle. When our base-free Ni(0)-mediated homocoupling protocol was used, a near quantitative 98% yield of 4,4′-biscoumarin was obtained.[17,18]

While both our protocols were optimized for the rather specific and comparatively unreactive 4-chloroquinolin-2(1*H*)-one precursors **2a**−**f**, we were interested to see if these procedures could also be used as general high-speed biaryl

TABLE 3. Synthesis of Biaryls via Microwave-Assisted Cross- and Homocoupling of (Hetero)Aryl Chlorides and Bromides



Substrate	yield (%)[a]	
	Method A[b]	Method B[c]
		
2a; R^1 = Me, R^2 = R^3 = R^4 = H	85	90
2b; R^1-R^2 = $(CH_2)_3$, R^3 = R^4 = H	68	68
2c; R^1 = Ph, R^2 = R^3 = R^4 = H	83[d]	39
2d; R^1 = Me, R^2 = R^3 = H, R^4 = OMe	83[e]	70
2e; R^1 = Me, R^2 = R^4 = H, R^3 = OMe	70[e]	74
2f; R^1 = Me, R^2 = H, R^3 = R^4 = OMe	82[e]	41
4-chlorocoumarin	67[f]	98
3-bromoquinoline	91[e]	94
2-bromothiophene	89	65
1-bromonaphthalene	91[e]	65

[a] Isolated yields of pure product. For further details see Supporting Information. [b] Reaction conditions: 0.30 mmol substrate, 10 mol % $PdCl_2$(dppf), 7 mol % dppf, 0.7 equiv bis(pinacolato)diboron, 4.5 equiv KOH, 2.0 mL *n*-BuCl, sealed-vessel, single-mode, microwave irradiation at 130 °C for 35 min. [c] Reaction conditions: 0.25 mmol substrate, 1.3 equiv $NiCl_2$, 4.0 equiv PPh_3, 1.3 equiv Zn, 1.8 equiv KI, 1.5 mL DMF, sealed-vessel, single-mode, microwave irradiation at 205 °C for 25 min. [d] Reaction conditions: 10 mol % $Pd(OAc)_2$, 20 mol % dppf, 1.5 mL dioxane. [e] Reaction temperature: 145 °C. [f] Reaction conditions: 6 mol % $Pd(PPh_3)_4$, 2.5 equiv $CsCO_3$, 1.5 mL toluene.

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(18) For Ni-catalyzed homocouplings of 4-sulfonyloxy-substituted coumarins, see: Lei, J.-G.; Xu, M.-H.; Lin, G.-Q. *Synlett* **2004**, 2364.

coupling methods. Gratifyingly, we were pleased to find that both microwave-assisted coupling methods were also applicable to the more commonly used hetero(aryl) bromide substrates, such as 3-bromoquinoline, 2-bromothiophene, and 1-bromonaphthalene (Table 3). Without any further optimization, good to excellent yields of the corresponding bis(hetero)aryls were obtained. Again, the Pd-catalyzed one-pot borylation/Suzuki cross-coupling conditions generally provided somewhat higher product yields (ca. 90%) compared with those of the Ni-mediated Ullmann homocoupling procedure.

In summary, we have developed two generally applicable high-speed methods for the preparation of symmetrical (hetero)-biaryls using either Pd(0)-catalyzed cross-coupling or Ni(0)-mediated homocoupling principles. The procedures are particularly valuable for the preparation of novel types of bisquinolones, which are presently under investigation as fluorescent probes in our laboratories. Results from these studies will be published elsewhere. We are currently investigating alternative catalytic cross- and homocoupling protocols to access unsymmetrical bisquinolones.

Experimental Section

General Procedure for the One-Pot Borylation/Suzuki Cross-Coupling of Haloarenes (Method A, Table 3). A mixture containing 0.30 mmol of the corresponding haloarene (Table 3), 24.5 mg (0.03 mmol, 10 mol %) of $PdCl_2$(dppf), 11.6 mg (0.021 mmol, 7 mol %) of dppf, 53.3 mg (0.21 mmol, 0.7 equiv) of bis-(pinacolato)diboron, and 75.7 mg (1.35 mmol, 4.5 equiv) of finely crushed KOH powder (analytical grade) was suspended in 2.0 mL of anhydrous 1-chlorobutane under an argon atmosphere in a 5 mL microwave vial (Pyrex) equipped with a magnetic stirring bar. The vial was sealed, stirred for 4 min at room temperature, and then heated for 35 min at 130 °C (see Table 3 for deviations). Thereafter, the solvent was removed under reduced pressure. The product was directly isolated by gradient dry flash chromatography, using appropriate solvents. For yields, see Table 3.

General Procedure for the Homocoupling of Haloarenes (Method B, Table 3). A mixture containing 0.25 mmol of the corresponding haloarene (Table 3), 42.1 mg (0.325 mmol, 1.3 equiv) of anhydrous $NiCl_2$, 262.3 mg (1 mmol, 4.0 equiv) of PPh_3, 21.2 mg (0.324 mmol, 1.3 equiv) of Zn powder (<60 μm particle size), and 74.7 mg (0.45 mmol, 1.8 equiv) of KI was suspended in 1.5 mL anhydrous DMF under an argon atmosphere in a 5 mL microwave vial (Pyrex) equipped with a magnetic stirring bar. The vial was sealed, stirred for 4 min at room temperature, and then heated for 25 min at 205 °C. Thereafter, the solvent was removed under reduced pressure. The product was isolated by gradient dry flash chromatography using appropriate solvents. For yields, see Table 3.

4,4′-Bis-(1-methylquinolin-2(1*H*)-one), 1a. Mp 283−284 °C (acetonitrile). IR (KBr) ν_{max} 1648 cm^{-1}; ^1H NMR (360 MHz, DMSO-d_6) δ 3.71 (s, 6H), 6.67 (s, 2H), 7.11−7.17 (m, 4H), 7.64−7.67 (m, 4H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 29.8, 115.8, 119.6, 121.6, 122.7, 127.3, 131.8, 140.2, 146.1, 160.9; MS (positive APCI, *m*/*z*) 317 [25, (M + 1)], 316 (100, M). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.95; H, 4.98; N, 8.78.

7,7′-Bis-(2,3-dihydro-1*H*,5*H*-pyrido[3,2,1-ij]quinolin-5-one), 1b. Mp 270 °C dec (acetonitrile); IR (KBr) ν_{max} 1637 cm^{-1}; ^1H NMR (360 MHz, DMSO-d_6) δ 2.02−2.13 (m, 4H), 2.99 (t, J = 5.7 Hz, 4H), 4.13 (t, J = 5.7 Hz, 4H), 6.62 (s, 2H), 6.96 (d, J = 7.6 Hz, 2H), 7.02 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 7.0 Hz, 2H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 20.6, 27.8, 42.6, 119.7, 121.4, 121.9, 125.3, 125.4, 130.5, 136.8, 146.4, 161.2; MS (positive APCI, *m*/*z*) 368 (100, M).

4,4′-Bis-(1-phenylquinolin-2(1*H*)-one), 1c. Mp > 400 °C dec (CCl_4); IR (KBr) ν_{max} 1661 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.81 (d, J = 8.4 Hz, 2H), 6.91 (s, 2H), 7.14 (t, J = 7.6 Hz, 2H), 7.38−7.45 (m, 8H), 7.60 (t, J = 7.4 Hz, 2H), 7.68 (t, J = 7.6 Hz, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 116.6, 119.4, 122.4, 122.6, 127.0, 128.9, 129.2, 130.4, 130.9, 137.4, 141.2, 147.0, 161.5; MS (positive APCI, *m*/*z*) 441 [25, (M + 1)], 440 (100, M).

4,4′-Bis-(6-methoxy-1-methylquinolin-2(1*H*)-one), 1d. Mp 256−258 °C (ethanol); IR (KBr) ν_{max} 1648 cm^{-1}; ^1H NMR (360 MHz, DMSO-d_6) δ 3.58 (s, 6H), 3.69 (s, 6H), 6.57 (d, J = 2.8 Hz, 2H), 6.66 (s, 2H), 7.34 (dd, J = 9.3 and 2.8 Hz, 2H), 7.62 (d, J = 9.3 Hz, 2H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 29.8, 55.8, 110.0, 115.9, 119.4, 120.4, 122.5, 134.7, 145.5, 154.8, 161.1; MS (positive APCI, *m*/*z*) 377 [25, (M + 1)], 376 (100, M).

4,4′-Bis-(7-methoxy-1-methylquinolin-2(1*H*)-one), 1e. Mp 232−234 °C (ethanol); IR (KBr) ν_{max} 1658 cm^{-1}; ^1H NMR (360 MHz, DMSO-d_6) δ 3.67 (s, 6H), 3.89 (s, 6H), 6.45 (s, 2H), 6.76 (d, J = 8.7 Hz, 2H), 7.04−7.07 (m, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 29.8, 56.2, 99.7, 110.8, 113.5, 117.9, 128.8, 142.0, 146.3, 161.5, 162.3; MS (positive APCI, *m*/*z*) 377 [25, (M + 1)], 376 (100, M). Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.23; H, 5.26; N, 7.37.

4,4′-Bis-(6,7-dimethoxy-1-methylquinolin-2(1*H*)-one), 1f. Mp 276−277 °C dec (ethanol); IR (KBr) ν_{max} 1642 cm^{-1}; ^1H NMR (360 MHz, DMSO-d_6) δ 3.45 (s, 6H), 3.74 (s, 6H), 3.96 (s, 6H), 6.46 (s, 2H), 6.57 (s, 2H), 7.09 (s, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 30.0, 56.2, 56.4, 97.6, 108.2, 112.7, 119.1, 136.1, 145.2, 145.8, 152.8, 162.0; MS (positive APCI, *m*/*z*) 437 [50, (M + 1)], 436 (100, M).

4,4′-Bis-(2*H*-chromen-2-one). Mp 215−216 °C (acetonitrile; lit.[19] 215 °C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.50 (s, 2H), 7.22−7.24 (m, 4H), 7.47 (d, J = 8.4 Hz, 2H), 7.60−7.65 (m, 2H). MS (positive APCI, *m*/*z*) 291 [95, (M + 1)], 290 (45, M), 252 [100, (M − 38)], 236 (M − 54).

3,3′-Bisquinoline. Mp 269−271 °C (ethanol; lit.[20] 271 °C); ^1H NMR (360 MHz, $CDCl_3$) δ 7.70 (t, J = 7.25 Hz, 2H), 7.85 (t, J = 7.42 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.29 (d, J = 8.4 Hz, 2H), 8.57 (s, 2H), 9.33 (s, 2H). MS (positive APCI, *m*/*z*) 257 [20, (M + 1)], 256 (100, M).

2,2′-Bisthiophene. Mp 30−32 °C (diethyl ether; lit.[21] 32−34 °C); ^1H NMR (360 MHz, $CDCl_3$) δ 7.02 (dd, J = 3.70 and 4.95 Hz, 2H), 7.19−7.24 (m, 4H). MS (positive APCI, *m*/*z*) 166 (100, M).

1,1′-Bisnaphthalene. Mp 158−159 °C (acetone; lit.[22,23] 158.8−159 °C); ^1H NMR (360 MHz, $CDCl_3$) δ 7.29−7.32 (m, 2H), 7.40 (d, J = 8.40 Hz, 2H), 7.47−7.52 (m, 4H), 7.59−7.63 (m, 2H), 7.96 (dd, J = 3.00 and 8.10 Hz, 4H).

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Supporting Information Available: Materials and methods, experimental procedures, and ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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