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Harnessing Anionic Rearrangements on the Benzenoid Ring of Quinoline for the Synthesis of 6,6′-Disubstituted 7,7′-Dihydroxy-8,8′-biquinolyls

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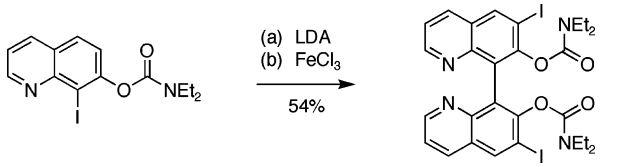

7,7′-Bis(((dimethylamino)carbonyl)oxy)-8,8′-biquinolyl (**5**) was prepared in 71% yield by regioselective directed ortho metalation (DoM) of *N,N*-dimethyl *O*-quinol-7-yl carbamate (**2**) with LDA followed by oxidation with anhydrous ferric chloride. DoM of **5** with excess LDA induced double anionic ortho-Fries rearrangement and gave 6,6′-bis((dimethylamino)carbonyl)-7,7′-dihydroxy-8,8′-biquinolyl (**8**). Treatment of *N,N*-diethyl *O*-(8-iodoquinol-7-yl) carbamate (**16**) with LDA in THF solvent at −78 °C, followed by addition of anhydrous ferric chloride, resulted in an efficient tandem halogen-dance dimerization process which afforded 7,7′-bis(((diethylamino)-carbonyl)oxy)-6,6′-diiodo-8,8′-biquinolyl (**17**) directly in 54% yield.

Directed ortho metalation (DoM) of arenes, and heteroarenes, provides a powerful tool for the assembly of polysubstituted aromatic compounds which may be difficult, or else impossible, to synthesize by other means.[1] The DoM paradigm is most commonly employed for the direct regiocontrolled introduction of external electrophiles; however, in some cases rearrangement pathways are available to the carbanionic intermediates, which may also be usefully exploited to build up substitution patterns of interest. Herein, we describe DoM-induced halogen-dance and anionic ortho-Fries rearrangements of *N,N*-dialkyl *O*-quinol-7-yl carbamates which were harnessed, in combination with ferric chloride mediated oxidative dimerization, to prepare novel 6,6′-disubstituted 7,7′-dihydroxy-8,8′-biquinolyls (vide infra).

In connection with a new research program, we required synthetic entry to symmetric 8,8′-biquinolyl derivatives, such as **1a**−**c**, equipped with metal ion chelating substructure at C6−C7′ and C6′−C7′ (Figure 1).[2] 8,8′-Biquinolyls constitute a little known class of biaryl molecules, and a survey of the literature revealed a paucity of suitable methods for their preparation.[3] Pertinent to our problem, there were no reported examples of 8,8′-biquinolyls which possessed oxygenation at C7 and C7′. The parent member of this unprecedented group, 7,7′-dihydroxy-8,8′-biquinolyl (**6**), is an analogue of the important axially chiral ligand 1,1′-bi-2-naphthol (BINOL)[4] and possesses the semblance of an unusual bipyridyl system. The coordination chemistry of **6** is therefore of interest, as is the question of configurational stability about its potentially chirotopic biaryl bond.[5] Since it was hoped that **6** would constitute a pivotal intermediate en route to compounds **1a**−**c**, we began by synthesizing this intriguing molecule.

Early attempts to prepare **6** directly from 7-hydroxyquinoline, by simple analogy to the one-step oxidative syntheses of BINOL from 2-naphthol,[4b] met with failure.[6] A reductive dimerization approach to **6** was more successful, however, and a suitable 8-haloquinoline derivative[7] for this purpose was available via regioselective DoM of carbamate **2** (Scheme 1).[8] Lithiation of **2** with LDA, followed by addition of the resulting metalate **3** to

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(1) For a review of directed ortho metalation, see: Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.

(2) Homobimetallic complexes of **1a**−**c** are of interest to us as novel platforms for ambifunctional catalysis. For reviews of ambifunctional catalysis, see: (a) Ma, J.-A.; Cahard, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4566. (b) Shibasaki, M.; Kanai, M.; Funabashi, K. *Chem. Commun.* **2002**, 1989. (c) Rowlands, G. J. *Tetrahedron* **2001**, *57*, 1865. (d) Gröger, H. *Chem. Eur. J.* **2001**, *7*, 5246. (e) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed.* **1997**, *36*, 1236.

(3) Only 24 unique examples of 8,8′-biquinolyls were retrieved from a Scifinder Scholar substructure search. For selected examples, see: (a) Kitamura, C.; Yamamoto, S.; Ouchi, M.; Yoneda, A. *J. Chem. Res., Synop.* **2000**, 46. (b) Staab, H. A.; Zirnstein, M. A.; Krieger, C. *Angew. Chem.* **1989**, *101*, 73. (c) Benito, Y.; Canoira, L.; Rodriguez, J. G. *Appl. Organomet. Chem.* **1987**, *1*, 535. (d) Vaughan, L. G. *J. Organomet. Chem.* **1980**, *190*, C56.

(4) For reviews of 1,1′-binaphthyl systems, including 1,1′-bi-2-naphthol (BINOL) derivatives, see: (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (b) Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155.

(5) The peri C−H bonds of BINOL, which are largely responsible for the prodigious configurational stability of its enantiomeric atropisomers, are formally replaced by sp^2-hybridized nitrogen-atom lone pairs in analogous 7,7′-dihydroxy-8,8′-biquinolyls. The precise effect that this heteroatom placement will have on configurational stability of the biaryl is unknown; furthermore, various tautomeric forms are available to **6**, and each may allow for a different racemization pathway. For a recent high-level computation study of racemization pathways in BINOL, see: Meca, L.; Reha, D.; Havlas, Z. *J. Org. Chem.* **2003**, *68*, 5677.

(6) A number of single-electron oxidants, including salts of Cu(II), Fe(III), V(V), and Ce(IV), were evaluated for the direct synthesis of **6** from 7-hydroxyquinoline. The experiments were wholly unsuccessful and typically returned unreacted starting material. Failure of the coupling reactions is perhaps not surprising when given the possibility of interference from the basic quinoline nitrogen atom and the known difficulties associated with oxidizing electron-deficient phenols in the desired manner. Methods evaluated are as follows. CuCl(OH)·TMEDA: (a) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983; $CuCl_2$·$BnNH_2$: (b) Vyskocil, S.; Smrcina, M.; Lorenc, M.; Tislerova, I.; Brooks, R. D.; Kulagowski, J. J.; Langer, V.; Farrugia, L. J.; Kocovsky, P. *J. Org. Chem.* **2001**, *66*, 1359. $FeCl_3$: (c) Ding, K.; Wang, Y.; Zhang, L.; Wu, Y.; Matsuura, T. *Tetrahedron* **1996**, *52*, 1005. $VO(acac)_2$: (d) Hwang, D.-R.; Chen, C.-P.; Uang, B.-J. *Chem. Commun.* **1999**, 1207. $(NH_4)_2Ce(NO_3)_6$: (e) Jiang, P.; Lu, S. *Synth. Commun.* **2001**, *31*, 131.

(7) 8,8′-Biquinolyls have been previously prepared by metal-mediated reductive dimerization of 8-haloquinolines; for example, see ref 3c,d.

(8) Godard, A.; Robin, Y.; Quéguiner, G. *J. Organomet. Chem.* **1987**, *336*, 1.

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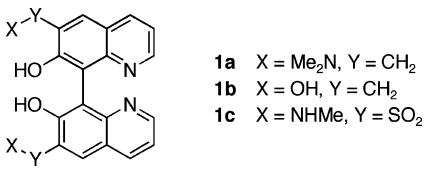
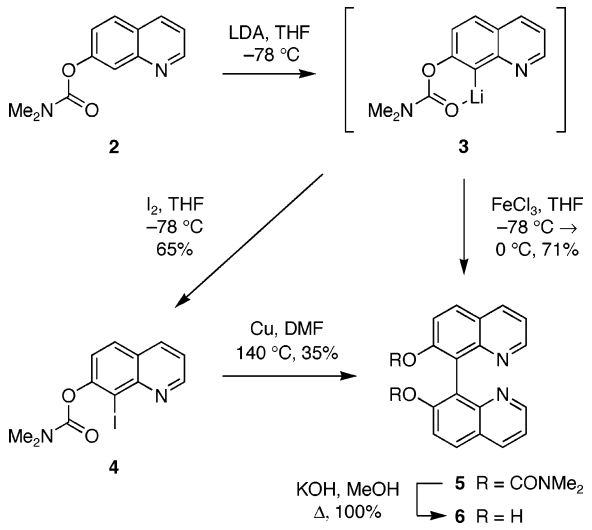


FIGURE 1. 8,8′-Biquinolyls of interest.

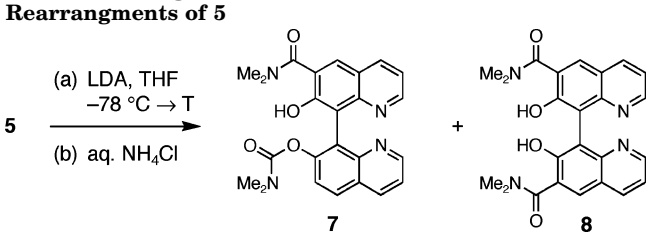
SCHEME 1. Two Syntheses of 7,7'-Dihydroxy-8,8'-biquinolyl (6)



a solution of iodine in THF at −78 °C, gave the 8-iodoquinoline **4** in 65% yield. Ullmann coupling[9] of iodide **4** proceeded in at best a 53% yield, and more typically this problematic transformation gave only a 30−40% yield of biaryl **5**. Basic methanolysis of the carbamate groups of **5** occurred without incident to afford biquinolyl **6** in quantitative yield. An X-ray crystallographic analysis of **6** provided definitive proof of structure and revealed a preferred transoid conformation about the biaryl linkage in the solid state.[10] The synthesis of **6** was subsequently much improved with the discovery that **5** could be prepared directly from **2** in 71% yield by in situ oxidative dimerization of 8-lithioquinoline **3** with anhydrous ferric chloride.[11]

Advancement of **6** toward compounds **1a**−**c** was envisioned by way of aromatic electrophilic substitution at C6 and C6′. In the event, biquinolyl **6** proved resistant to electrophilic attack and could not be chlorosulfonated even after protracted heating in a mixture of thionyl chloride and chlorosulfonic acid (100 °C, 7 days). Double DoM of **5** presented an alternative possibility for elaboration of the biquinolyl nucleus at C6 and C6′, and this option was next investigated. The new strategy took an unexpected course when lithiation of **5** with a large excess of LDA (7 equiv) in THF solvent at −78 °C resulted in a

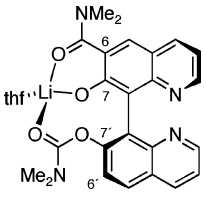
TABLE 1. Single and Double Anionic Ortho-Fries Rearrangments of 5



entry	*T* (°C)	time (h)	yield of **7** (%)	yield of **8** (%)
1	−78	2 h	70	0
2	6	16 h	18	43

rapid anionic ortho-Fries rearrangement[12] and delivered amide **7** in 70% yield (Table 1, entry 1).[13] Intramolecular carbamoyl transfer from **5** was unavoidable and prevented any putative 6-lithioquinoyl species being intercepted by external electrophiles. Nevertheless, the anionic ortho-Fries rearrangement was not without its merits, since the salicyl amide moiety present in **7** could form the basis of metal chelating substructure to suit our needs. Further experimentation revealed that both carbamoyl moieties of **5** could be coaxed into migration if, following addition of LDA, the reaction mixture was warmed to near ambient temperature prior to protonolysis. In this manner, the symmetric bis(salicylamide) **8** was obtained directly from **5** in 43% yield (Table 1, entry 2). Bifurcation of **8** to target compounds **1a**,**b** was readily achieved by reduction of its amide moieties with the appropriate reagent in each case. Thus, trialkylamine **1a** was available in 63% yield by reduction of **8** with lithium aluminum hydride, whereas alcohol **1b** was obtained from the same precursor in 83% yield by treatment with Myers' lithium amidotrihydroborate reagent.[14]

The efficiency of double anionic ortho-Fries rearrangement from **5** was compromised by the inherent sluggishness of the second acyl transfer event, and quantities of **7** invariably accompanied **8** in the crude reaction mixture. Use of HMPA as a reaction cosolvent did not remedy this situation. The recalcitrance of the second rearrangement step was ascribed to the difficulty of further proton removal from the putative alkoxide intermediate **Li-7**.[15]



Li-7

Ring-to-ring coordination of the carbamate group at C7′ by the adjacent lithium cation in **Li-7** (possibly as

(9) Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613.

(10) The angle between the two quinolyl ring planes of racemic **6** (as its dimethanol solvate, **6**·2MeOH) is 104.5°. In contrast, racemic BINOL is only slightly transoid in the solid state (angle between naphthyl ring planes is 91.4°); see: Mori, K.; Masuda, Y.; Kashino, S. *Acta Crystallogr.* **1993**, *C49*, 1224.

(11) For the oxidative dimerization of alkenyl and aryllithiums with $FeCl_3$, see: (a) Li, G.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2003**, *44*, 8705. (b) Broka, C. A. *Tetrahedron Lett.* **1991**, *32*, 859. (c) Wittig, G.; Klar, G. *Liebigs Ann. Chem.* **1967**, *704*, 91.

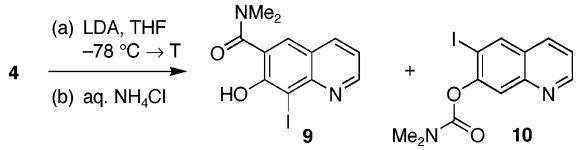
(12) Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1935.

(13) Quéguiner has previously reported examples of anionic ortho-Fries rearrangements on *N*,*N*-dimethyl *O*-quinolyl carbamates; see ref 8.

(14) Myers, A. G.; Yang, B. H.; Chen, H.; McKinstry, L.; Kopecky, D. J.; Gleason, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6496.

(15) A 6,6′-dilithio intermediate was not involved in the formation of **8**, since treatment of **5** with excess LDA in THF at −78 °C (2 h) followed by quenching with CD_3OD gave **7** (70% yield) with no deuterium incorporation at C6′.

TABLE 2. Base-Induced Rearrangements of 4



entry	*T* (°C)	time	yield of **9** (%)	yield of **10** (%)
1	0	24 h	76	0
2	−50	2 h	58	10
3	−78	10 min	36	62

illustrated) would significantly reduce any complex-induced proximity effect (CIPE)[16] at C6′ and make deprotonation of that site exceedingly difficult.[17]

In an effort to improve on the synthesis of **8**, recourse was made to iodide **4** and attention directed at achieving an anionic ortho-Fries rearrangement prior to dehalogenative dimerization. Low-temperature lithiation of 8-iodoquinoline **4** followed by protonolysis of the reaction mixture at 0 °C gave the expected product of carbamoyl transfer, amide **9**, in 76% yield, the structure of which was proved by X-ray crystallography (Table 2, entry 1). Reductive dimerization of **9** was attempted with both Ullmann- and Suzuki-type protocols, but neither method afforded any of the desired product **8**.[18] Fortunately, during the course of these studies we had cause to reexamine the synthesis of **9** from **4** and made a useful discovery. Premature termination of this seemingly simple transformation revealed the operation of a convoluted reaction mechanism capable of furnishing both amide **9** and 6-iodoquinoline **10** (entries 2 and 3). To the best of our knowledge, the conversion of **4** to **10** represents the first example of a halogen-dance reaction[19] on the benzenoid ring of a quinoline derivative.[20,21] A likely explanation for these findings is as follows (Figure 2). Initial metalation of **4** gives the expected 6-lithioquinoline (**11**), which exists in a facile halogen-dance equilibrium with its thermodynamically more stable 8-lithio regioisomer **12**. As the temperature rises, and the reaction is

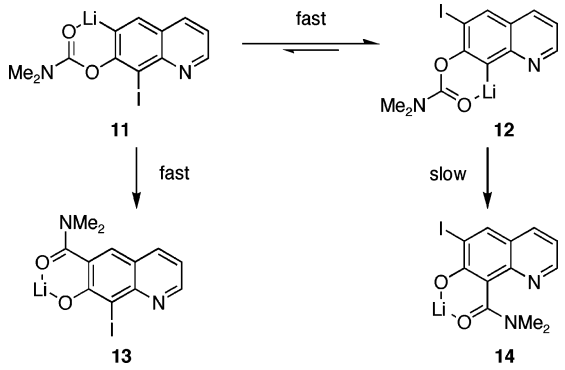
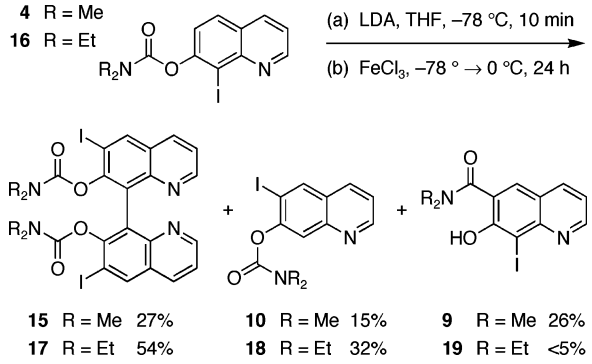


FIGURE 2. Halogen-dance vs anionic ortho-Fries rearrangements.

SCHEME 2. Tandem Halogen-Dance Oxidative Dimerization of 4 and 16



allowed to progress over time, the less stable organolithium **11** may go on to form **13** via an anionic ortho-Fries rearrangement. However, the corresponding rearrangement from **12** is unable to compete kinetically with halogen-dance equilibration and 8-amidoquinoline **14** is not formed.[22] Thus, the transformation of **4** to **9** proceeds in large part indirectly via a halogen-dance "two-step", **11** → **12** → **11**, and then on to **13** (and thence **9**). To lend further credence to the above hypothesis, the 6-iodoquinolyl carbamate **10** was treated with LDA in THF at −78 °C and allowed to warm to 0 °C before protonolysis of the reaction mixture. Amide **9** was produced in 82% yield, an entirely consistent result.

The discovery of halogen-dance behavior was fortuitous and, in combination with organolithium oxidative dimerization, provided a general strategy for the synthesis of 6,6′-disubstituted 7,7′-dihydroxy-8,8′-biquinolyls. Thus, low-temperature lithiation of **4** followed by almost immediate treatment with ferric chloride resulted in a tandem halogen-dance/oxidative coupling reaction to afford 8,8′-biquinolyl **15** directly in 27% yield (Scheme 2). This novel tandem reaction succeeded in creating the pivotal biaryl bond while at the same time activating positions C6 and C6′ of the newly formed 8,8′-biquinolyl nucleus for further elaboration. The formation of biquinolyl **15** was accompanied by the generation of a comparable

(16) For reviews of complex-induced proximity effects in deprotonation reactions, see: (a) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (b) Whisler, M. C.; MacNeil, S.; Snieckus, V.; Beak, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2206.

(17) Attempted double O → C carbamoyl transfer on a biaryl template en route to gymnopusin by Snieckus and co-workers failed to progress beyond the mono acyl transfer stage, possibly due to a similar effect.[16b]

(18) Ullmann coupling experiments from **9** (Cu bronze, DMF, 140 °C) resulted only in significant dehalogenation of the starting material. Application of Hutton's tandem Miyaura borylation/Suzuki coupling sequence to **9** (Pd(dppf)Cl_2, bis(pinacolato)diboron, K_2CO_2, DMSO, 80 °C) returned unreacted starting material, and this process was not pursued further; see: Hutton, C. A.; Skaff, O. *Tetrahedron Lett.* **2003**, *44*, 4895.

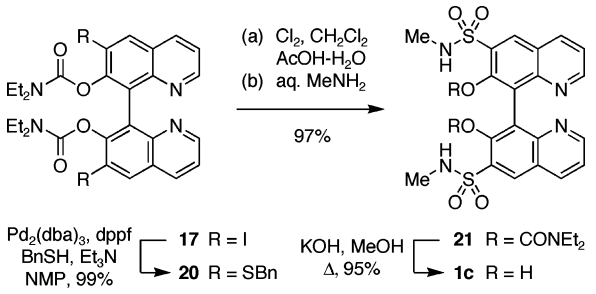
(19) For an introduction to the halogen-dance reaction and discussion of the mechanism, see: Bunnett, J. F. *Acc. Chem. Res.* **1972**, *5*, 139.

(20) For halogen-dance reactions on the heterocyclic ring of quinoline derivatives, see: (a) Arzel, E.; Rocca, P.; Marsais, F.; Godard, A.; Quéguiner, G. *Tetrahedron* **1999**, *55*, 12149. (b) Arzel, E.; Rocca, P.; Marsais, F.; Godard, A.; Quéguiner, G. *Tetrahedron Lett.* **1998**, *39*, 6465.

(21) For selected examples of halogen-dance reactions on heterocycles other than quinoline, see: (a) Sammakia, T.; Stangeland, E. L.; Whitcomb, M. C. *Org. Lett.* **2002**, *4*, 2385. (b) Comins, D. L.; Saha, J. K. *Tetrahedron Lett.* **1995**, *36*, 7995. (c) Bury, P.; Hareau, G.; Kocienski, P.; Dhanak, D. *Tetrahedron* **1994**, *50*, 8793. (d) Fröhlich, H.; Kalt, W. *J. Org. Chem.* **1990**, *55*, 2993. (e) Guildford, A.; Tometzki, M. A.; Turner, R. W. *Synthesis* **1983**, 987.

(22) Conversion of **12** to **14** may conceivably be promoted under high dilution conditions. The anionic ortho-Fries rearrangement is an intramolecular process, whereas the equilibrating halogen-dance reaction is an intermolecular chain reaction almost certainly involving *N*,*N*-dimethyl *O*-(6,8-diiodo-7-quinolyl) carbamate as the propagating intermediate.

SCHEME 3. Synthesis of Bis(sulfonamide) 1c from 17



quantity of the anionic ortho-Fries rearrangement product **9** and 15% of halogen-dance adduct **10**. The unwanted anionic ortho-Fries rearrangement could be largely suppressed by conducting an analogous reaction with diethyl carbamate **16**. In this case, the corresponding biquinolyl product (**17**) was produced in an acceptable 54% yield and only traces of the anionic ortho-Fries rearrangement product **19** were formed (<5%). The structure of **17** was verified by X-ray crystallography.

Biaryl **17** provides a versatile platform for the synthesis of all manner of 6,6′-disubstituted 7,7′-dihydroxy-8,8′-biquinolyls, and its advancement to bis(sulfonamide) **1c** was easily accomplished (Scheme 3). Palladium-catalyzed sulfide formation[23] from **17** with benzyl mercaptan gave the bis(thioether) **20**, which was further converted to bis(sulfonamide) **21** by oxidation with chlorine[24] followed by treatment with methylamine. Finally, basic methanolysis of **21** gave the target molecule **1c** in an overall yield of 91% from **17**.

In summary, oxidative dimerization of *N,N*-dialkyl *O*-(8-lithio-7-quinolyl) carbamates with anhydrous ferric chloride has been demonstrated for the efficient preparation of hitherto unknown 7,7′-dioxygenated 8,8′-biquinolyls. Novel halogen-dance and anionic ortho-Fries rearrangements of lithiated quinolyl carbamates were discovered and exploited to synthesize various 6,6′-disubstituted 7,7′-dihydroxy-8,8′-biquinolyls. We anticipate that the tandem halogen-dance oxidative dimerization reaction reported here for the synthesis of **17** will find further applications in alternative guises for the synthesis of other highly substituted biaryl molecules.

Experimental Section

7,7'-Bis(((diethylamino)carbonyl)oxy)-6,6'-diiodo-8,8'-biquinolyl (17). A solution of *i*-Pr_2NH (0.40 mL, $d = 0.722$, 289 mg, 2.86 mmol) in anhydrous THF (5 mL) at −20 °C under N_2 was treated dropwise with *n*-BuLi (1.75 mL, 1.48 M in hexanes, 2.59 mmol) and stirred for 10 min. The resulting solution of LDA was further cooled to −78 °C and iodide **16** (800 mg, 2.16 mmol) in anhydrous THF (5 mL) added carefully down the cold flask side wall. The brown mixture of lithiated quinoline was stirred for 10 min at −78 °C, and then a chilled suspension of $FeCl_3$ (350 mg, 2.16 mmol) in THF (9 mL) was added (n.b.: the suspension was prepared by drying finely powdered $FeCl_3$ (350 mg) at 120 °C at ca. 0.5 mmHg for 24 h, cooling it, and then adding it rapidly in one portion to stirred anhydrous THF (9 mL) at −78 °C under N_2). The resulting purple mixture was stirred for 24 h while being slowly warmed to 0 °C. After this time, saturated aqueous NH_4Cl (40 mL) was added and the reaction mixture further warmed to room temperature. EtOAc (100 mL) and H_2O (100 mL) were added and the layers shaken and separated. The aqueous phase was extracted (2 × 100 mL, EtOAc), and the combined organic extracts were washed with brine (100 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude residue was purified by column chromatography (with 1−3% MeOH in CH_2Cl_2 as eluent) to yield, in order of elution, the simple halogen-dance adduct **18** (252 mg, 0.68 mmol, 32%) and the desired biquinoyl **17** (427 mg, 0.58 mmol, 54%), both as colorless solids. The anionic-Fries rearrangement product **19** (32 mg, 0.086 mmol, 4%) was obtained by neutralization of the aqueous phase with 3 M aqueous HCl, followed by its partial concentration (to 25%) and extraction with EtOAc. Data for **17**: mp >300 °C; IR (neat) 2973, 1717, 1471, 1402, 1205, 1149, 1061, 879, 792, 616 cm^{-1}; ^1H NMR (500 MHz, d_6-DMSO, $T = 373$ K) δ 8.62 (2H, s), 8.61 (2H, dd, $J = 4.1$, 1.5 Hz), 8.31 (2H, dd, $J = 8.3$, 1.5 Hz), 7.42 (2H, dd, $J = 8.3$, 4.1 Hz), 3.30−2.95 (4H, m), 2.95−2.86 (4H, m), 0.75 (12H, br t, 6.5 Hz) ppm; ^{13}C NMR (125 MHz, d_6-DMSO, $T = 373$ K) δ 150.2 (2C, 0), 149.8 (2C, 1), 148.8 (2C, 0), 146.9 (2C, 0), 137.3 (2C, 1), 133.9 (2C, 1), 127.4 (2C, 0), 126.6 (2C, 0), 120.4 (2C, 1), 91.9 (2C, 0), 40.7 (4C, 2), 12.4 (4C, 3) ppm; MS (ES+) *m/z* 739 $(M + H)^+$; HRMS (ES+) *m/z* 739.0281 (calcd for $C_{28}H_{29}{}^{127}I_2N_4O_4$ 739.0278).

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Supporting Information Available: Text giving all other experimental procedures and characterization data, figures giving ^1H NMR spectra for new compounds, and CIF files for compounds **6**, **9**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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