Notes

Aryl Mesylates in Metal-Catalyzed Homocoupling and Cross-Coupling Reactions. 3. A Simple and General Method for the Synthesis of 2,2′-Diaroyl-4,4′-dihydroxybiphenyls

Virgil Percec,* Jin-Young Bae, Mingyang Zhao, and Dale H. Hill

The W. M. Keck Laboratories for Organic Synthesis, Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

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Functionalized symmetrically disubstituted dihydroxybiphenyls such as 2,2′-disubstituted 4,4′-dihydroxybiphenyls are an important class of compounds with various applications in materials and polymer chemistry.[1] A general procedure that can be readily applied to the synthesis of a variety of 2,2′-disubstituted 4,4′-dihydroxybiphenyls has not been developed. In fact, the synthesis of only three of these compounds (i.e., 2,2′-bis(trifluoromethyl)-4,4′-dihydroxybiphenyl,[1a] 2,2′-dimethyl-4,4′-dihydroxybiphenyl,[1b-e] and 2,2′-difluoro-4,4′-dihydroxybiphenyl[1f-g]) has been reported.

2,2′-Bis(trifluoromethyl)-4,4′-dihydroxybiphenyl[1a] and 2,2′-dimethyl-4,4′-dihydroxybiphenyl[1b,c] were synthesized from the corresponding benzidines (2,2′-bis(trifluoromethyl)benzidine and 2,2′-dimethylbenzidine, respectively) by diazotization followed by reaction with water. The application of this method to the preparation of other 2,2′-disubstituted 4,4′-dihydroxybiphenyls is limited by the lack of simple synthetic procedures for other 2,2′-disubstituted benzidines.

2,2′-Dimethyl-4,4′-dihydroxybiphenyl was alternatively synthesized via oxidative coupling of *m*-cresol.[1d] However, this method produces a mixture of two isomers, i.e., 2,2′-dihydroxy-6,6′-dimethylbiphenyl and 2,2′-dihydroxy-4,4′-dimethylbiphenyl. The oxidative coupling of 2-*tert*-butyl-5-methylphenol, followed by transalkylation with benzene, gave a mixture of 3 isomeric dimethylbiphenyldiols including 2,2′-dimethyl-4,4′-dihydroxybiphenyl, which was separated by preparative gas chromatography.[1e] The oxidative coupling method proceeds with lack of regioselectivity. Therefore, yields are reduced and tedious purification procedures are required.

2,2′-Difluoro-4,4′-dihydroxybiphenyl was synthesized from 3-nitro-4-aminoanisole in 15% overall yield by a five-step reaction procedure,[1f,g] which involves preparation of 3-nitro-4-iodoanisole by reaction of KI with the diazonium salt of 3-nitro-4-aminoanisole, Ullmann coupling of the resulting aryl iodide to give 4,4′-dimethoxy-2,2′-dinitrobiphenyl, reduction of nitro groups to amino groups, substitution of amino groups by fluorine atoms via the Schiemann–Balz reaction, and demethylation.

Symmetrical biaryls were traditionally obtained by the Ullmann reaction[2] and more recently by Ni(0)-catalyzed homocoupling of aryl halides,[3] aryl triflates,[4] and other aryl sulfonates including mesylates.[5] Since a large number of substituted phenols, hydroquinones and bisphenols are readily available, aryl sulfonates are particularly important substrates for the synthesis of symmetrical biaryls. The regiospecificity and high yield of the homocoupling of aryl sulfonates allow it to be used in the key reaction step of a general procedure for the synthesis of novel 2,2′-disubstituted 4,4′-dihydroxybiphenyls. This paper reports the use of the Ni(0)-catalyzed homocoupling reaction of aryl mesylates derived from 4-protected 2-substituted hydroquinones as the key reaction step in a novel method for the synthesis of previously unreported 2,2′-dibenzoyl-4,4′-dihydroxybiphenyl (**6a**), 2,2′-bis(*p*-fluorobenzoyl)-4,4′-dihydroxybiphenyl (**6b**), and 2,2′-bis(*p*-*tert*-butylbenzoyl)-4,4′-dihydroxybiphenyl (**6c**). This provides a general method for the preparation of 2,2′-diaroyl-4,4′-dihydroxybiphenyls.

Results and Discussion

The previously unreported **6a-c** were synthesized starting from 1,4-dimethoxybenzene (**1**) according to the sequence of reactions outlined in Scheme 1. In this synthetic procedure, substituted 1,4-dimethoxybenzenes **2a-c** were obtained by aroylation of **1**.[6] Thus 2,5-dimethoxybenzophenone (**2a**), 4′-fluoro-2,5-dimethoxybenzophenone (**2b**), and 4′-*tert*-butyl-2,5-dimethoxybenzophenone (**2c**) were prepared in high yields (85%, 90%, and 84%, respectively) by the Friedel–Crafts reaction of **1** with the corresponding benzoyl chloride derivative in CH_2Cl_2 at 0 °C. The monomethyl ethers **3a-c** were prepared by the regioselective demethylation of the 1-position of **2a-c** with anhydrous aluminum chloride in benzene at 80 °C (yields: 90%, 66%, and 83%, respectively).[6] Alternatively, **3a-c** could be prepared from **1** and the corresponding benzoyl chloride derivatives in a one-pot synthesis according to a modified literature procedure,[6] although the yields were reduced in comparison to the two step synthesis described in Scheme 1. The conversion of **3a-c** to the corresponding mesylates **4a-c** followed by the Ni(0)-catalyzed homocoupling reaction produced biaryls **5a-c** in good yields (65%, 62%, and 45%, respectively). In this case, the electron-withdrawing effect of the benzoyl group derivatives activates the aryl

(1) (a) Rogers, H. G.; Gaudiana, R. A.; Minns, R. A. U. S. Pat. 4,433,132, 1984; *Chem. Abstr.* **1984**, *100*, 175562v. (b) Schmidt, H.-W.; Guo, D. *Makromol. Chem.* **1988**, *189*, 2029. (c) Kern, W.; Gruber, W.; Wirth, H. O. *Makromol. Chem.* **1960**, *37*, 198. (d) Perold, G. W. *J. S. Afr. Chem. Inst.* **1975**, *28*, 292; *Chem. Abstr.* **1976**, *85*, 20739f. (e) Tashiro, M.; Fukata, G.; Yamato, T.; Watanabe, H.; Oe, K.; Tsuge, O. *Org. Prep. Proced. Int.* **1976**, *8*, 249. (f) Vauchier, C.; Vinet, F.; Maiser, N. *Liq. Crys.* **1989**, *5*, 141. (g) Vauchier, C.; Vinet, F. Eur. Pat. 236,215, 1987; *Chem. Abstr.* **1987**, *108*, 104094y.

(2) For example: (a) Fanta, P. E. *Synthesis* **1974**, 9. (b) Kozhevnikov, I. V.; Matveev, K. I. *Russ. Chem. Rev.* **1978**, *47*, 649. (c) Lindley, J. *Tetrahedron* **1984**, *40*, 1433. (d) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327. (e) Hegedus, L. S. *J. Organometal. Chem.* **1988**, *343*, 147. (f) Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989.

(3) (a) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627 and references cited therein. (b) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80 and references cited therein.

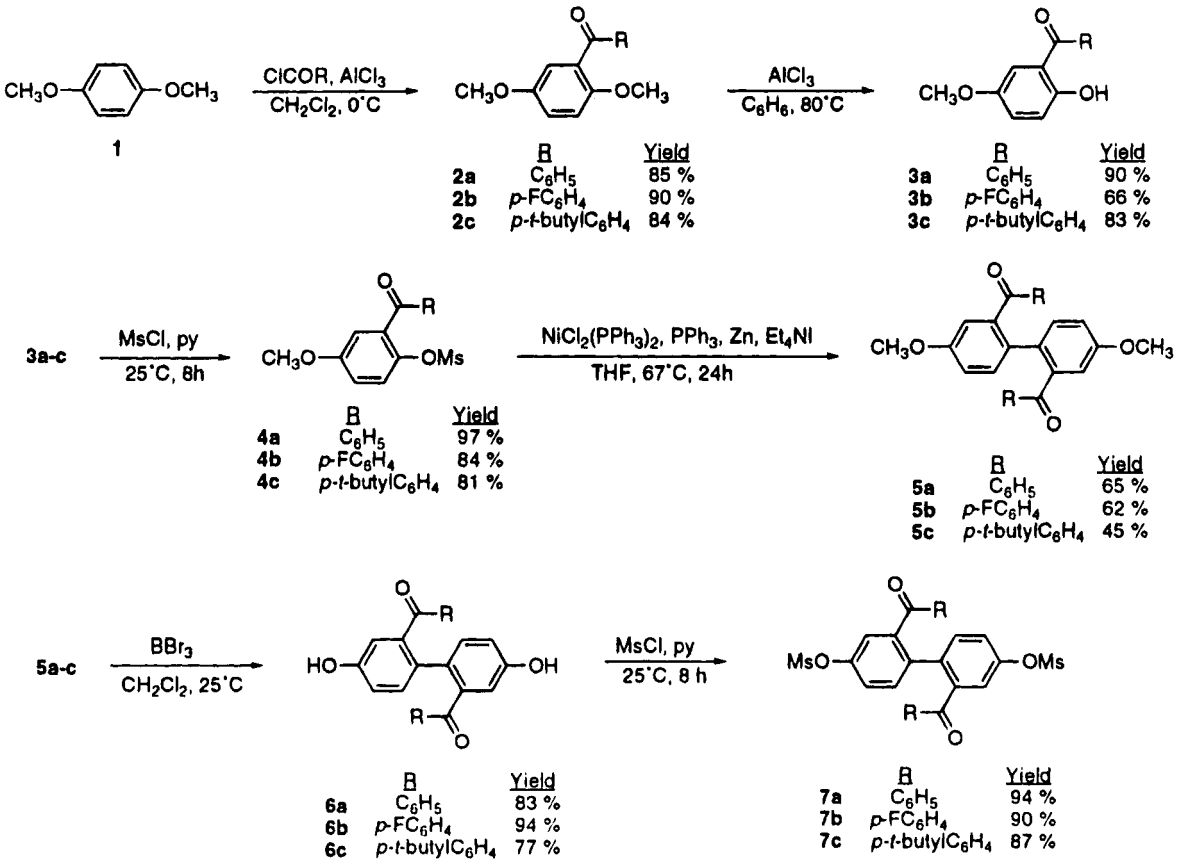
(4) (a) Yamashita, J.; Inoue, Y.; Kondo, T.; Hashimoto, H. *Chem. Lett.* **1986**, 407. (b) Percec, V.; Okita, S.; Weiss, R. *Macromolecules* **1992**, *25*, 1816. (c) Jutand, A.; Mosleh, A. *Synlett* **1993**, 568.

(5) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176.

(6) Bogert, M. T.; Howells, H. P. *J. Am. Chem. Soc.* **1930**, *52*, 837.

0022-3263/95/1960-1066$09.00/0

Scheme 1



mesylate toward oxidative addition, while the size of this ortho substituent sterically hinders the reaction resulting in slower reaction rates. Therefore, it was necessary to stabilize the Ni(0) catalyst against premature degradation with excess PPh_3 (40%). The cleavage of methoxy groups of the compounds **5a-c** by BBr_3 in CH_2Cl_2[7] generated the corresponding bisphenols **6a-c** in good yields. The treatment of **6a-c** with mesyl chloride afforded bismesylates **7a-c**. These bismesylates are not readily oxidized and are easier to purify than the corresponding bisphenols **6a-c**. Thus, they were used for analytical characterization.

Conclusions

Nickel-catalyzed homocoupling of aryl mesylates of 4-protected 2-substituted hydroquinones was utilized in the key step of a reaction scheme which leads to the synthesis of novel and difficult to prepare by alternative methods 2,2′-diaroyl-4,4′-dihydroxybiphenyls: 2,2′-dibenzoyl-4,4′-dihydroxybiphenyl, 2,2′-bis(*p*-fluorobenzoyl)-4,4′-dihydroxybiphenyl, and 2,2′-bis(*p*-*tert*-butylbenzoyl)-4,4′-dihydroxybiphenyl (overall yield: 40%, 29%, and 20%, respectively). The synthetic procedure reported in this paper is of important value since it represents an easy and direct access to a wide variety of 2,2′-disubstituted 4,4′-dihydroxybiphenyls and employs readily available hydroquinone derivatives as starting materials.

Experimental Section

General Methods. General experimental information is identical to that previously reported.[5] All materials were purchased from commercial sources (Aldrich or Fisher) and used without further purification except when noted. Pyridine was dried over CaH_2 and distilled. THF was distilled from sodium–benzophenone ketyl. Zinc dust (325 mesh) was stirred in acetic acid, washed with water, and dried *in vacuo* at 120 °C. $NiCl_2(PPh_3)_2$ was prepared according to a literature procedure.[8]

2,5-Dimethoxybenzophenone (2a). A 500 mL three-neck flask equipped with a mechanical stirrer, addition funnel, and nitrogen inlet was charged with **1** (20.0 g, 0.145 mol) and CH_2Cl_2 (150 mL). The solution was cooled to 0 °C, and $AlCl_3$ (23.0 g, 0.174 mol) was added in several portions. After the solution was stirred for 10 min, benzoyl chloride (22.2 g, 0.158 mol) was added dropwise over 10 min. The solution was stirred at 0 °C for 4 h and poured into 100 mL of ice–water containing 10 mL of concd HCl. The organic phase was separated and washed with 10% NaOH (1 × 100 mL) and H_2O (4 × 100 mL). The solution was dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Recrystallization (hexane/ethyl acetate 1:1) afforded 30.0 g (85%) colorless crystals: mp 51 °C (benzene) (lit.[6] mp 51.2 °C).

4′-Fluoro-2,5-dimethoxybenzophenone (2b) was synthesized by the same procedure as that used for **2a** except that 4-fluorobenzoyl chloride was used instead of benzoyl chloride (90%): white crystals; mp 52 °C (benzene); ^1H NMR δ 7.84 (dd, J = 8.4, 5.5 Hz, 2H), 7.13–6.90 (m, 5H), 3.77 (s, 3H), 3.65 (s, 3H); $^{13}C\{^1H\}$ NMR δ 194.47, 165.64 (d, $^1J_{CF}$ = 254.70 Hz), 153.48, 151.21, 134.00, 132.36 (d, $^3J_{CF}$ = 9.2 Hz), 129.07, 117.34, 115.28 (d, $^2J_{CF}$ = 22.1 Hz), 114.35, 112.95, 56.14, 55.73; EIMS *m*/*e* 260 (M^+, 100), 165 (39), 123 (81), 95 (66); HRMS calcd for $C_{15}H_{13}FO_3$ 260.0849, found 260.0848.

4′-*tert*-Butyl-2,5-dimethoxybenzophenone (2c) was synthesized by the same procedure as that used for **2a** except that 4-*tert*-butylbenzoyl chloride was used instead of benzoyl chloride (84%): white crystals; mp 39–40 °C (benzene); ^1H NMR δ 7.79 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 6.97–6.94 (m, 2H), 6.90 (d, J = 4.6 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 1.34 (s, 9H); $^{13}C\{^1H\}$ NMR δ 195.63, 156.79, 153.35, 151.21, 134.75, 129.88, 125.20, 116.78, 114.24, 113.01, 56.35, 55.76, 35.09, 31.05; EIMS *m*/*e* 298 (M^+, 100), 283 (34), 241 (20), 165 (64), 161 (31), 57 (33);

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(8) (a) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719. (b) Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L. *J. Am. Chem. Soc.* **1961**, *83*, 344.

HRMS calcd for $C_{19}H_{22}O_3$ 298.1569, found 298.1563.

2-Hydroxy-5-methoxybenzophenone (3a). A 250 mL three-neck flask equipped with a reflux condenser, magnetic stirrer, and nitrogen inlet was charged with **2a** (10.2 g, 42 mmol) and 50 mL of benzene. $AlCl_3$ (5.6 g, 42 mmol) was added at 25 °C in several portions to the stirred solution. Stirring was continued at 80 °C for 12 h. The mixture was cooled to 25 °C and poured into 100 mL of ice–water containing 10 mL of concd HCl. The resulting mixture was partitioned between Et_2O (50 mL) and H_2O. The organic phase was washed with H_2O and dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Recrystallization (hexane/ethyl acetate 1:1) afforded 8.6 g (90%) of yellow plates: mp 83.5 °C ($CHCl_3$/hexanes) (lit.[6] mp 84–85.5 °C).

4′-Fluoro-2-hydroxy-5-methoxybenzophenone (3b) was synthesized from **2b** by the same procedure as that used for **3a** (66%): yellow crystals; mp 93 °C (benzene); ^{1}H NMR δ 11.44 (s, 1H), 7.78–7.71 (m, 2H), 7.24–7.00 (m, 5H), 3.72 (s, 3H); ^{13}C{^{1}H} NMR δ 199.45, 164.95 (d, $^1J_{CF}$ = 254.0 Hz), 157.32, 151.43, 134.02, 131.67(d, $^3J_{CF}$ = 8.9 Hz), 123.97, 119.29, 118.53, 116.00, 115.55 (d, $^2J_{CF}$ = 22.1 Hz), 55.86; EIMS *m/e* 246 (M^+, 76), 150 (100), 123 (53), 95 (59); HRMS calcd for $C_{14}H_{11}FO_3$ 246.0692, found 246.0692.

4′-*tert*-Butyl-2-hydroxy-5-methoxybenzophenone (3c) was synthesized from **2c** by the same procedure as that used for **3a** (83%): viscous oil; ^{1}H NMR δ 11.64 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.15–7.13 (m, 2H), 7.00 (d, J = 8.2 Hz, 1H), 3.72 (s, 3H), 1.38 (s, 9H); ^{13}C{^{1}H} NMR δ 200.70, 157.32, 155.75, 151.34, 135.02, 129.24, 125.32, 123.54, 119.05, 118.82, 116.51, 55.90, 35.04, 31.09; EIMS *m/e* 284 (M^+, 62), 269 (13), 227 (44), 150 (100); HRMS calcd for $C_{18}H_{20}O_3$ 284.1412, found 284.1403.

Aryl mesylates were prepared by the reaction of methanesulfonyl chloride with the corresponding phenols in pyridine[9] and purified by column chromatography (silica gel, hexanes/ethyl acetate).

5-Methoxy-2-[(methylsulfonyl)oxy]benzophenone (4a). (97%): colorless oil; ^{1}H NMR δ 7.82 (d, J = 7.4 Hz, 2H), 7.62–7.39 (m, 4H), 7.10–6.99 (m, 2H), 3.82 (s, 3H), 2.93 (s, 3H); ^{13}C{^{1}H} NMR δ 194.00, 157.82, 139.30, 136.75, 133.62, 133.47, 130.09, 128.49, 124.63, 117.40, 115.02, 55.82, 37.58; EIMS *m/e* 306 (M^+, 39), 227 (100), 184 (23), 77 (13); HRMS calcd for $C_{15}H_{14}O_5S$ 306.0562, found 306.0562.

4′-Fluoro-5-methoxy-2-[(methylsulfonyl)oxy]benzophenone (4b) (84%): pale yellow oil; ^{1}H NMR δ 7.87–7.81 (m, 2H), 7.42 (d, J = 8.9 Hz, 1H), 7.20–7.05 (m, 3H), 6.96 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H), 2.97 (s, 3H); ^{13}C{^{1}H} NMR δ 192.30, 166.05 (d, $^1J_{CF}$ = 257.20 Hz), 157.98, 139.23, 133.46, 133.18, 132.89 (d, $^3J_{CF}$ = 9.2 Hz), 124.76, 117.47, 115.80 (d, $^2J_{CF}$ = 22.4 Hz), 115.05, 55.91, 37.69; EIMS *m/e* 324 (M^+, 32), 245 (100), 202 (22); HRMS calcd for $C_{15}H_{13}FO_5S$ 324.0467, found 324.0468.

4′-*tert*-Butyl-5-methoxy-2-[(methylsulfonyl)oxy]benzophenone (4c) (81%): white crystals; mp 88–89 °C (benzene); ^{1}H NMR δ 7.77 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 9.0 Hz, 1H), 7.06 (dd, J = 9.0, 3.0 Hz, 1H), 6.97 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H), 2.96 (s, 3H), 1.35 (s, 9H); ^{13}C{^{1}H} NMR δ 193.49, 157.73, 157.64, 139.38, 134.02, 130.16, 125.69, 125.50, 124.66, 117.06, 114.85, 55.82, 37.59, 35.20, 31.00; EIMS *m/e* 362 (M^+, 31), 324 (11), 283 (6), 245 (34), 227 (100), 57 (83); HRMS calcd for $C_{19}H_{22}O_5S$ 362.1188, found 362.1193.

General Procedure for Homocoupling Reaction of Aryl Mesylates. All reactions were carried out under nitrogen using oven-dried (110 °C) glassware. In a typical reaction a 125 mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (0.10 mmol), PPh_3 (0.40 mmol), Zn powder (1.7 mmol), Et_4NI (1.5 mmol), and a magnetic stirring bar. After the tube was sealed with a rubber septum, the contents were dried at 25 °C under reduced pressure (1×10^{-3} mmHg) for 10 h. Then the tube was filled with N_2 followed by three evacuation-filling cycles. Freshly distilled THF (0.50 mL) was added via a syringe through the rubber septum. The mixture was stirred at room temperature for 5 min, and during this time the color of the mixture gradually changed from green to deep red-brown. Aryl mesylate (1.0 mmol) was dissolved in freshly distilled THF (0.50 mL) and added to the catalyst mixture via a syringe through the rubber septum. The reaction mixture was heated to the reflux temperature and stirred at this temperature for 24 h. Then it was cooled to 25 °C, filtered, diluted with water, extracted with $CHCl_3$, and dried ($MgSO_4$) and the solvent evaporated *in vacuo*. The corresponding biaryl was purified by column chromatography (silica gel, hexanes/ethyl acetate) and then recrystallized from $CHCl_3$/hexanes.

2,2′-Dibenzoyl-4,4′-dimethoxybiphenyl (5a) (65%): white crystals; mp 138–140 °C (benzene); ^{1}H NMR δ 7.76 (d, J = 7.0 Hz, 4H), 7.42–7.39 (m, 2H), 7.32–7.18 (m, 6H), 6.92–6.87 (m, 4H), 3.74 (s, 6H); ^{13}C{^{1}H} NMR δ 197.43, 157.91, 139.41, 137.10, 132.80, 131.75, 130.28, 128.01, 115.51, 114.45, 55.34; EIMS *m/e* 422 (M^+, 5), 317 (100), 151 (25), 105 (32); HRMS calcd for $C_{28}H_{22}O_4$ 422.1518, found 422.1516.

2,2′-Bis(*p*-fluorobenzoyl)-4,4′-dimethoxybiphenyl (5b) (62%): white crystals; mp 144 °C (benzene); ^{1}H NMR δ 7.81–7.74 (m, 4H), 7.17 (d, J = 8.3 Hz, 2H), 7.00–6.84 (m, 8H), 3.76 (s, 6H); ^{13}C{^{1}H} NMR δ 195.86, 165.52 (d, $^1J_{CF}$ = 255.0 Hz), 158.02, 139.06, 133.41, 132.93 (d, $^3J_{CF}$ = 9.5 Hz), 132.73, 131.56, 115.66, 115.16 (d, $^2J_{CF}$ = 21.9 Hz), 114.36, 55.35; EIMS *m/e* 458 (M^+, 9), 335 (100), 123 (15); HRMS calcd for $C_{28}H_{20}F_2O_4$ 458.1329, found 458.1331.

2,2′-Bis(*p*-*tert*-butylbenzoyl)-4,4′-dimethoxybiphenyl (5c) (45%) white crystals; mp 162–164 °C (benzene); ^{1}H NMR δ 7.76 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 7.20 (d, J = 9.0 Hz, 2H), 6.88–6.85 (m, 4H), 3.73 (s, 6H), 1.30 (s, 18H); ^{13}C{^{1}H} NMR δ 197.19, 157.95, 156.45, 139.83, 134.73, 132.83, 131.89, 130.47, 125.07, 115.41, 114.65, 55.42, 35.12, 31.15; EIMS *m/e* 534 (M^+, 5), 519 (1), 373 (100), 343 (10); HRMS calcd for $C_{36}H_{38}O_4$ 534.2770, found 534.2774.

2,2′-Bis(*p*-fluorobenzoyl)-4,4′-dihydroxybiphenyl (6b). A 100 mL three-neck flask equipped with an addition funnel, nitrogen inlet, and magnetic stirrer was charged with 12 mL of CH_2Cl_2 and 12 mL of 1.0 M BBr_3 solution in CH_2Cl_2. The solution was cooled to −70 °C, and a solution of **5b** (1.83g, 4 mmol) in 12 mL CH_2Cl_2 was added dropwise to the stirred solution. The mixture was allowed to warm to 25 °C and stirred for 8 h. Water (10 mL) was added dropwise to the reaction mixture over 10 min. The organic phase was separated, dried ($MgSO_4$), and concentrated. Purification by column chromatography (silica gel, hexanes/ethyl acetate 1:1) gave 1.62 g (94%) of colorless crystals: mp 256–258 °C (benzene); ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ 8.77 (s, 2H), 7.77–7.70 (m, 4H), 7.00–6.76 (m, 10H); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 195.36, 164.83 (d, $^1J_{CF}$ = 252.2 Hz), 155.90, 138.89, 133.46, 132.73 (d, $^3J_{CF}$ = 6.6 Hz), 129.86, 117.32, 115.53, 115.22 (d, $^2J_{CF}$ = 12.9 Hz); EIMS *m/e* 430 (M^+, 2), 307 (100), 123 (28), 95 (12); HRMS calcd for $C_{26}H_{16}F_2O_4$ 430.1016, found 430.1009.

2,2′-Dibenzoyl-4,4′-dihydroxybiphenyl (6a) was prepared from **5a** by the same procedure as that used for **6b** (83% by ^{1}H NMR). Because of the difficulty of separating the product from the reaction mixture, after the usual work-up the crude product was converted to the mesylate and purified by column chromatography (*vide infra*).

2,2′-Bis(*p*-*tert*-butylbenzoyl)-4,4′-dihydroxybiphenyl (6c) was prepared from **5c** by the same procedure as that used for **6b** (77%): white crystals; mp 236–238 °C (benzene); ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ 8.62 (s, 2H), 7.66 (d, J = 8.5 Hz, 4H), 7.25 (d, J = 8.5 Hz, 4H), 7.00 (d, J = 9.1 Hz, 2H), 6.75–6.71 (m, 4H), 1.23 (s, 18H); ^{13}C{^{1}H} NMR ($CDCl_3$/DMSO-d_6) δ 197.45, 156.03, 155.34, 139.56, 134.74, 132.60, 130.70, 130.27, 124.79, 116.98, 116.03, 34.92, 30.99; EIMS *m/e* 506 (M^+, 1), 505 (2), 491 (2), 373 (1), 345 (100), 161 (19); HRMS calcd for $C_{34}H_{34}O_4$ 506.2457, found 506.2465.

Bismesylates of 2,2′-diaroyl-4,4′-dihydroxybiphenyls were prepared by the reaction of methanesulfonyl chloride with the corresponding bisphenols in pyridine[9] and purified by column chromatography (silica gel, hexanes/ethyl acetate).

2,2′-Dibenzoyl-4,4′-bis[(methylsulfonyl)oxy])biphenyl (7a) (94%): white crystals; mp 138–140 °C (benzene); ^{1}H NMR δ 7.65 (d, J = 7.2 Hz, 4H), 7.46–7.38 (m, 6H), 7.31–7.23 (m, 6H), 3.10 (s, 6H); ^{13}C{^{1}H} NMR δ 195.23, 147.71, 139.69, 138.02, 136.25, 133.35, 133.12, 130.22, 128.22, 123.70, 122.93, 37.54; EIMS *m/e* 550 (M^+, 0.1), 471 (12), 445 (100), 105 (75), 77 (37); HRMS calcd for $C_{28}H_{22}O_8S_2$ 550.0756, found 550.0795.

2,2′-Bis(*p*-fluorobenzoyl)-4,4′-bis[(methylsulfonyl)oxy])biphenyl (7b) (90%): white crystals; mp 153–154 °C (benzene); ^{1}H NMR δ 7.68 (dd, J = 8.8, 5.5 Hz, 4H), 7.39 (s, 4H), 7.30 (s, 2H), 6.96 (dd, J = 8.8, 8.6 Hz, 4H), 3.15 (s, 6H); ^{13}C{^{1}H} NMR

(9) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

δ 193.63, 166.53 (d, $^1J_{CF}$ = 255.0 Hz), 147.66, 139.30, 137.87, 133.16, 132.99 (d, $^3J_{CF}$ = 9.8 Hz), 132.55, 123.89, 122.86, 115.44 (d, $^2J_{CF}$ = 21.8 Hz), 37.67; EIMS *m/e* 586 (M^+, 0.1), 507 (4), 463 (97), 305 (21), 123 (100), 95 (31); HRMS calcd for $C_{28}H_{20}F_2O_8S_2$ 586.0567, found 586.0579.

2,2′-Bis(*p*-*tert*-butylbenzoyl)-4,4′-bis[(methylsulfonyl)-oxy]biphenyl (7c) (87%): white crystals; mp 101–103 °C (benzene); ^{1}H NMR δ 7.66 (d, J = 8.4 Hz, 4H), 7.38–7.31 (m, 10 H), 3.12 (s, 6H), 1.29 (s, 18 H); $^{13}C\{^1H\}$ NMR δ 194.85, 157.21, 147.60, 140.02, 138.01, 133.65, 133.10, 130.34, 125.21, 123.40, 122.91, 37.53, 35.09, 30.97; EIMS *m/e* 647 ($M^+ - CH_3$, 1), 583 (1), 501 (100), 423 (23), 161 (13); HRMS calcd for $C_{35}H_{35}O_8S_2$ 647.1773, found 647.1887.

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Supplementary Material Available: ^{1}H NMR, $^{13}C\{^1H\}$ NMR and HRMS spectra of new compounds are listed (45 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead for ordering information.

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