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Supporting Information for

A Concise Synthetic Approach Towards Hydroxytetraphenylenes

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Dedicated to Professors Xi-Yan Lu and Li-Xin Dai
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Experimental Procedures.

General. All solvents and reagents were dried and purified by the usual techniques. Melting point (M.p.) determination was performed using a Shanghai Shenguang SGW XT-4 instrument. IR spectra were recorded on a FT-IR Bio-Rad FTS-185 spectrometer. $^1$H NMR spectra were recorded on a Bruker AM300 (300 MHz) NMR spectrometer at ambient temperature unless otherwise indicated. $^{13}$C NMR spectra were recorded on a Bruker DPX-400 (100.4 MHz) at ambient temperature and were proton decoupled. Chemical shifts are reported in ppm from tetramethylsilane on the scale with the solvent resonance employed as the internal standard. Mass spectras were measured at an ionization voltage of 70 eV.

General Procedure for the Synthesis of Substituted N-pivaloyl-aniline.$^{1a}$ To a solution of substituted aniline (200 mmol), pyridine (32.4 mL, 400 mmol) and 4-dimethylaminopyridine (244 mg, 2 mmol) in dry CH$_2$Cl$_2$ (400 mL) was added pivaloyl chloride (27.0 mL, 220 mmol) dropwise at 0°C. The resulting mixture was stirred for 2 hours at that temperature, and poured into ice-cooled 1 M HCl. The organic layer was separated and the aqueous phase was extracted with CH$_2$Cl$_2$. The combined organic extracts were washed with 1 M HCl and brine, and dried over Na$_2$SO$_4$. Evaporation of solvents, purification of the residue by column chromatography with hexane/AcOEt as the eluent on silica gel and dried in vacuo gave corresponding N-pivaloylaniline.

3-Methoxy-N-pivaloylaniline (14a)$^3$ White solid; 97% yield; m.p. 132.6-133.4 °C (Lit$^{1b}$: 130-131 °C); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.40 (t, $J$ = 2.1 Hz, 1H), 7.36 (s, 1H), 7.20 (t, $J$ = 8.1 Hz, 1H), 6.94 (t, $J$ = 8.1 Hz, 1H), 1.31 (s, 9H); MS (EI): m/z (relative intensity) 207 (M$^+$, 74), 164 (7), 150 (6), 123 (62), 94 (22), 57 (100), 41 (25).

N-Pivaloylaniline (14b)$^2$ White solid; 96% yield; m.p. 140.3-142.0 °C (Lit$^{2b}$: 138-139 °C); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J$ = 7.8 Hz, 2H), 7.42 (s, 1H), 7.31 (d, $J$ = 7.5 Hz, 2H), 1.30 (s, 9H); MS (EI): m/z (relative intensity) 177 (M$^+$, 59), 134 (9), 120 (7), 93(91), 77 (13), 85 (8), 57 (100), 41 (23).

2,5-Dimethoxy-N-pivaloylamine (14c)$^3$ White solid; 99% yield; m.p. 55.0-56.3 °C (Lit$^{3}$: 54 °C); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.17 (s, 1H), 8.16 (s, 1H), 6.77 (d, $J$ = 8.7 Hz, 1H), 6.94 (dd, $J$ = 2.7, 8.7 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 1.31 (s, 9H); MS (EI): m/z (relative intensity) 237 (M$^+$, 41).
2-Methoxy-N-pivaloylaniline (14d) White solid; 97% yield; m.p. 34.5-36.0 °C (Lit\textsuperscript{4b}: 39-41 °C); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \delta 8.40 (d, J = 8.7 Hz, 1H), 8.13 (s, 1H), 7.05-6.92 (m, 2H), 6.86 (d, J = 7.8 Hz, 1H), 3.89 (s, 3H), 1.31 (s, 9H); MS (EI): m/z (relative intensity) 207 (M\textsuperscript{+}, 83), 150 (14), 123 (71), 108 (76), 92 (11), 80 (17), 57 (100), 41 (25).

General Procedure for the Synthesis of Symmetrical Diaminobiphenyls Using a Consecutive Direct \textit{ortho}-Metalation and Oxidative Coupling Sequence.\textsuperscript{1a, 5} To a solution of N-pivaloylamiline (40 mmol) in dry THF (200 mL) was added a 2.5 M hexane solution of \textit{n}-BuLi (40 mL, 100 mmol) dropwise over 15 min at 0 °C. After 4 hours of stirring at 0 °C, the solution was cooled to -78 °C and CuCN (3.58 g, 40 mmol) was added. The mixture was vigorously stirred 30 min at room temperature, and then was cooled to -78 °C again. To the solution of Lipshutz cuprate was added \textit{p}-benzoquinone (10.48 g, 60 mmol), and the mixture was stirred at room temperature overnight. The mixture was filtered through a bed of Celite and the filter residue was washed four times with 200 mL each of THF. The filtrate was evaporate under reduced pressure. Purification of the residue by column chromatography on silica gel with hexane/AcOEt as the eluent gave the corresponding N-pivaloyl protected diaminobiphenyls.

\textbf{N,N'-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(2,2-dimethylpropanamide) (15a)} White solid; 82% yield; m.p. 148.0-149.0 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \delta 7.95 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 8.4 Hz, 2H), 7.18 (s, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.74 (s, 6H), 0.98 (s, 18H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 176.9, 157.2, 137.9, 130.4, 114.8, 112.9, 107.1, 56.1, 39.8, 27.4; MS (EI): m/z (relative intensity) 412 (M\textsuperscript{+}, 41), 355 (40), 328 (8), 311 (25), 271 (55), 227 (19), 85 (10), 57 (100), 41 (17); IR: $\nu_{\text{max}}$(cm\textsuperscript{-1}) 3418, 2954, 2868, 2843, 1686, 1587, 1531, 1512, 1472, 1440, 1289, 1307, 1257, 1179, 1165, 1076, 949, 788; HRMS (M\textsuperscript{+}): Calcd. for C\textsubscript{24}H\textsubscript{32}N\textsubscript{2}O\textsubscript{4} (M\textsuperscript{+}) 412.2362, found (M\textsuperscript{+}) 412.2363; Anal. Calcd. For C\textsubscript{24}H\textsubscript{32}N\textsubscript{2}O\textsubscript{4}: C, 69.83; H, 7.89; N, 6.64; Found: C, 69.88; H, 7.82; N, 6.79.

\textbf{N,N'-(Biphenyl-2,2'-diyl)bis(2,2-dimethylpropanamide) (15b)} White solid; 41% yield; m.p. 135.6-137.8 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \delta 8.31 (d, J = 8.7 Hz, 2H), 7.48-7.43 (m, J = 7.5 Hz,
N,N'-(3,3',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(2,2-dimethylpropanamide) (15c) White solid; 75% yield; m.p. 172.5-173.6 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.22\) (s, 2H), 6.90 (t, \(J = 9.0\) Hz, 2H), 6.81 (t, \(J = 8.7\) Hz, 2H), 3.79 (s, 6H), 3.63 (s, 6H), 1.00 (s, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 177.6, 151.3, 150.2, 126.9, 124.2, 112.2, 110.0, 56.9, 56.4, 39.0, 27.5\); MS (EI): \(m/z\) (relative intensity) 472 (M\(^+\), 20), 415 (13), 388 (7), 331 (27), 266 (14), 248 (16), 85 (7), 57(100), 41(18); IR: \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3340, 2963, 2837, 1668, 1581, 1510, 1475, 1435, 1287, 1265, 1238, 1182, 1142, 1036, 783, 773, 731; HRMS (M\(^+\)): Calcd. for C\(_{26}\)H\(_{36}\)N\(_2\)O\(_6\) (M\(^+\)) 472.2573, found (M\(^+\)) 472.2571; Anal. Calcd. For C\(_{26}\)H\(_{36}\)N\(_2\)O\(_6\): C, 66.27; H, 7.72; N, 5.91; Found: C, 66.08; H, 7.68; N, 5.93.

N,N'-(3,3'-Dimethoxybiphenyl-2,2'-diyl)bis(2,2-dimethylpropanamide) (15d) White solid; 78% yield; m.p. 174.1-175.6 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.34\) (s, 2H), 7.20 (t, \(J = 8.1\) Hz, 2H), 6.90 (d, \(J = 8.1\) Hz, 2H), 6.75 (d, \(J = 7.5\) Hz, 1H), 3.83 (s, 6H), 1.02 (s, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 178.3, 155.7, 139.3, 127.4, 124.7, 121.8, 110.9, 56.3, 39.0, 27.5\); MS (EI): \(m/z\) (relative intensity) 412 (M\(^+\), 12), 355 (15), 328 (8), 271 (24), 227 (13), 212 (9), 85 (9), 57 (100), 41 (32); IR: \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3273, 2960, 2871, 2837, 1668, 1581, 1510, 1475, 1435, 1287, 1265, 1238, 1182, 1142, 1036, 783, 773, 731; HRMS (M\(^+\)): Calcd. for C\(_{24}\)H\(_{32}\)N\(_2\)O\(_4\) (M\(^+\)) 412.2362, found (M\(^+\)) 412.2365; Anal. Calcd. For C\(_{24}\)H\(_{32}\)N\(_2\)O\(_4\): C, 69.64; H, 8.03; N, 6.65; Found: C, 69.88; H, 7.82; N, 6.79.

N,N'-(3,6,6'-Trimethoxybiphenyl-2,2'-diyl)bis(2,2-dimethylpropanamide) (16) To a solution of 14a (8.28 g, 40 mmol) and 14c (9.48 g, 40 mmol) in dry THF (320 mL) was added a 2.5 M hexane solution of n-BuLi (80 mL, 200 mmol) dropwise over 15 min at 0 °C. After 6 hours of stirring at 0 °C, the solution was cooled to -78°C and CuCN (7.16 g, 80 mmol) was added. The
mixture was vigorously stirred 30 min at room temperature, and then was cooled to -78°C again. To the solution of Lipshutz cuprate was added \( p \)-benzoquinone (20.96 g, 120 mmol), and the mixture was stirred at room temperature overnight. The mixture was filtered through a bed of Celite and the filter residue was washed four times with 200 mL each of THF. The filtrate was evaporate under reduced pressure. Purification of the residue by column chromatography on silica gel, gradient elution with hexane/AcOEt (3:1~1:1:3) gave 16 (6.60 g, 14.9 mmol, 37% yield) as a white solid. 

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\): } \delta 7.64-7.61 (m, 2H), 7.30 (t, J = 8.1 Hz, 1H), 6.95 (d, J = 9.3 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 6.79 (s, 1H), 6.74 (d, J = 8.4 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 1.05 (s, 9H), 0.95 (s, 9H); \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\): } \delta 178.4, 176.7, 156.6, 151.4, 150.2, 138.2, 129.1, 126.7, 123.7, 116.7, 116.6, 111.9, 110.4, 106.9, 56.5, 56.4, 56.1, 39.5, 38.9, 27.4, 27.3; \text{MS (El): } m/z (relative intensity) 442 (M\textsuperscript{+}, 11), 385 (8), 358 (3), 301 (13), 227 (5), 85 (16), 57 (100), 41 (22); \text{IR: } \nu_{\text{max}} \text{ (cm}^{-1}) 3304, 3004, 2965, 2933, 2835, 1663, 1589, 1533, 1470, 1427, 1294, 1254, 1181, 1126, 1078, 1026, 790, 780, 718; \text{HRMS (M\textsuperscript{+}): } \text{Calcd. for C}_{25}\text{H}_{34}\text{N}_2\text{O}_5 (M\textsuperscript{+}) 442.2468, \text{found (M\textsuperscript{+}) 442.2465; Anal. Calcd. For C}_{25}\text{H}_{34}\text{N}_2\text{O}_5: } \text{C, 67.72; H, 7.75; N, 6.36; Found: C, 67.85; H, 7.74; N, 6.33. Also, two expected symmetrical homo-coupling products } 15\text{a} (3.80 g, 9.2 mmol, 46% yield) and 15\text{c} (2.84 g, 6.0 mmol, 30% yield) were obtained and the data were identified with that were described above.

**N,N’-(3-Methoxybiphenyl-2,2’-diyl)bis(2,2-dimethylpropanamide) (17)** To a solution of 14b (7.08 g, 40 mmol) and 14d (8.28 g, 40 mmol) in dry THF (320 mL) was added a 2.5 M hexane solution of n-BuLi (80 mL, 200 mmol) dropwise over 15 min at 0°C. After 6 hours of stirring at 0°C, the solution was cooled to -78°C and CuCN (7.16 g, 80 mmol) was added. The mixture was vigorously stirred 30 min at room temperature, and then was cooled to -78°C again. To the solution of Lipshutz cuprate was added \( p \)-benzoquinone (20.96 g, 120 mmol), and the mixture was stirred at room temperature overnight. The mixture was filtered through a bed of Celite and the filter residue was washed four times with 200 mL each of THF. The filtrate was evaporate under reduced pressure. Purification of the residue by column chromatography on silica gel, gradient elution with hexane/AcOEt (1:10~1:5~1:1) gave 17 (4.44 g, 11.6 mmol, 29% yield) as a white solid. 

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\): } \delta 7.88 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.34-7.25 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 7.03 (dd, J = 1.5, 7.5 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H),
6.91 (s, 1H), 6.81 (d, J = 7.8 Hz, 1H), 3.86 (s, 3H), 1.09 (s, 9H), 0.99 (s, 9H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 178.4, 177.4, 155.3, 138.8, 136.2, 132.9, 129.3, 128.3, 128.0, 125.0, 124.5, 122.6, 110.9, 56.2, 39.5, 39.1, 27.6, 27.4; \(\text{MS (EI)}\): \text{m/z (relative intensity)} 382 (M\(^{+}\), 14), 325 (20), 241 (29), 238(9), 197 (22), 182 (16), 57 (100), 41 (19); \(\text{IR}\): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3264, 3007, 2965, 2873, 2838, 1663, 1652, 1583, 1515, 1471, 1445, 1435, 1316, 1266, 1241, 1179, 1128, 1024, 783, 754, 729; \(\text{HRMS (M^+)}\): Calcd. for C\(_{23}\)H\(_{30}\)N\(_2\)O\(_3\) (M\(^{+}\)) 382.2256, found (M\(^{+}\)) 382.2255; Anal. Calcd. For C\(_{23}\)H\(_{30}\)N\(_2\)O\(_3\): C, 72.20; H, 7.86; N, 7.18; Found: C, 72.22; H, 7.91; N, 7.32. Similarly, other two expected symmetrical homo-coupling products 15b (1.67 g, 4.8 mmol, 46% yield) and 15d (3.79 g, 9.2 mmol, 46% yield) were obtained and the data were identified with that were described above.

**General Procedure for the Synthesis of Substituted 2,2’-Diiodobiphenyls.**\(^{16,7}\) N-pivaloyl protected diaminobiphenyl (10 mmol) was dissolved into 1,4-dioxane (10 mL) and conc. HCl (20 mL), and heated to reflux for 6 hours. The dark-brown mixture was added conc. HCl (20 mL) and cooled to -5 °C, then a solution of NaNO\(_2\) (1.73 g, 25 mmol) in water (10 mL) was added dropwise at -5 °C, followed the generated diazonium salt solution was added in a solution of KI (16.6 g, 100 mmol) in water (100 mL) at that temperature. After the addition was completed, the mixture was heated to 80 °C and stirred for 2 hours. The resulting mixture was cooled to room temperature and extracted with CH\(_2\)Cl\(_2\) (3 x 100 mL). The combined extracts were washed with 10% aqueous NaHSO\(_3\) (50 mL) and dried over Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel with hexane/CH\(_2\)Cl\(_2\) as the eluent gave the corresponding substituted 2,2’-diiodobiphenyls.

**2,2’-Diiodo-6,6’-dimethoxybiphenyl (7)** White solid; 60% yield; m.p. 194.8-196.0 °C (Lit\(^7\): 187.5-188.0 °C); \(^{1}\text{H NMR}\) (300 MHz, CDCl\(_3\)): \(\delta\) 7.55 (d, \(J = 8.1\) Hz, 4H), 7.09 (t, \(J = 8.4\) Hz, 4H), 6.96 (d, \(J = 8.4\) Hz, 4H), 3.73 (s, 12H); \(\text{MS (EI)}\): \text{m/z (relative intensity)} 466 (M\(^{+}\), 100), 339 (59), 324 (31, 59), 309 (16), 281 (15), 197 (12), 169 (18), 139 (29).

**2,2’-Diiodobiphenyl (8)** White solid; 14% yield; m.p. 112.3-113.8 °C (Lit\(^8\): 108-109 °C); \(^{1}\text{H NMR}\) (300 MHz, CDCl\(_3\)): \(\delta\) 7.94 (dd, \(J = 0.9, 7.8\) Hz, 2H), 7.42 (td, \(J = 0.9, 7.5\) Hz, 2H), 7.20 (dd, \(J = 1.2, 7.5\) Hz, 2H), 7.09 (td, \(J = 1.5, 7.8\) Hz, 2H); \(\text{MS (EI)}\): \text{m/z (relative intensity)} 406 (M\(^{+}\), 19),
279 (94), 280 (14), 153 (14), 152 (100), 151 (35), 150 (19), 76 (26).

2,2’-Diiodo-3,6,6’-trimethoxybiphenyl (9)  White solid; 75% yield; m.p. 187.6-188.4 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.54 (d, 1H), 7.08 (t, \(J = 8.1\) Hz, 1H), 6.96-6.92 (m, 2H), 6.84 (d, \(J = 8.7\) Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.6, 153.1, 151.9, 137.2, 135.6, 131.2, 130.5, 112.2, 111.3, 110.7, 102.1, 94.6, 57.1, 56.4; MS (EI): \(m/z\) (relative intensity) 496 (M\(^+\), 100), 369 (29), 354 (29), 339 (19), 227 (6), 184 (8), 177 (6), 128 (8); IR: \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3007, 2988, 2939, 2834, 1560, 1481, 1459, 1426, 1251, 1179, 1093, 1075, 1026, 818, 804, 768, 734, 713; HRMS (M\(^+\)): Calcd. for C\(_{15}\)H\(_{14}\)I\(_2\)O\(_3\) (M\(^+\)) 495.9021, found (M\(^+\)) 495.9030.

2,2'-Diiodo-3-methoxybiphenyl (10)  White solid; 38% yield; m.p. 85.4-86.6 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.93 (dd, \(J = 0.4, 8.1\) Hz, 1H), 7.44-7.33 (m, 2H), 7.35 (t, \(J = 8.1\) Hz, 1H), 7.18 (dd, \(J = 1.5, 7.5\) Hz, 1H), 7.08 (td, \(J = 1.5, 7.5\) Hz, 1H), 6.84-6.80 (m, 2H), 3.94 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.5, 151.0, 149.4, 139.1, 130.1, 129.5, 129.3, 128.2, 122.6, 99.8, 92.2, 5.68; MS (EI): \(m/z\) (relative intensity) 436 (M\(^+\), 15), 310 (18), 309 (100), 182 (9), 181 (11), 167 (12), 154 (10), 139 (30); IR: \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3060, 3038, 2939, 2836, 1577, 1561, 1459, 1456, 1432, 1411, 1311, 1265, 1124, 1092, 1048, 1016, 1007, 779, 754, 715, 654; HRMS (M\(^+\)): Calcd. for C\(_{13}\)H\(_{10}\)I\(_2\)O (M\(^+\)) 435.8821, found (M\(^+\)) 435.8824.

2,2'-Diiodo-3,3',6,6'-tetramethoxybiphenyl (11)  White solid; 77% yield; m.p. 199.2-200.8 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 6.95 (d, \(J = 9.0\) Hz, 2H), 6.85 (d, \(J = 9.0\) Hz, 2H), 3.89 (s, 6H), 3.70 (s, 6H); MS (EI): \(m/z\) (relative intensity) 526 (M\(^+\), 100), 399 (72), 384 (27), 369 (30).

2,2'-Diiodo-3,3'-dimethoxybiphenyl (12)  White solid; 37% yield; m.p. 199.2-200.8 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.35 (t, \(J = 7.8\) Hz, 2H), 6.84-6.79 (m, 4H), 3.93 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.4, 151.2, 129.3, 122.6, 109.8, 92.1, 56.8; MS (EI): \(m/z\) (relative intensity) 466 (M\(^+\), 8), 340 (17), 339 (100), 324 (10), 169 (13), 139 (30), 91 (19), 77 (14); IR: \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3014, 2967, 2933, 2835, 1578, 1561, 1458, 1432, 1411, 1279, 1263, 1142, 1020, 779, 714;
HRMS (M⁺): Calcd. for C₁₄H₁₂I₂O₂(M⁺) 465.8927, found (M⁺) 495.8932.

1,8,9,16-Tetramethoxytetraphenylene (18) To a suspension of 2,2’-diodo-6,6’-dimethoxybiphenyl (7) (466 mg, 1 mmol) in Et₂O (30 mL) was added a 2.5 M hexane solution of n-BuLi (1.0 mL, 2.5 mmol) dropwise at -78°C and the reaction mixture was stirred for 2 hours at the same temperature. Then, anhydrous CuCl₂ (403 mg, 3.0 mmol) was added. After stirring for 2 hours at -78°C, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was quenched with NH₃•H₂O (2 M, 30 mL) The organic layer was then separated and the aqueous layer was extracted with CH₂Cl₂ (100 mL × 3). The combined organic extracts were washed with NaHSO₃ (2 M, 30 mL), brine (100 mL × 2) and dried over Na₂SO₄, filtered and concentrated under reduced pressure. Chromatography on silica gel with CH₂Cl₂/hexane 1:2 as the eluent gave 1,8,9,16-tetramethoxytetraphenylene (18) as a white solid (57 mg, 27% yield), m.p. 334.4-340.1 °C (Lit⁹: 283.5-284.5 °C); ¹H NMR (300 MHz, CD₃COCD₃): δ 7.20 (t, J = 7.8 Hz, 4H), 6.86 (d, J = 7.8 Hz, 4H), 6.72 (d, J = 8.1 Hz, 4H), 3.66 (s, 12H); MS (EI): m/z (relative intensity) 424 (M⁺, 100), 469 (10), 242 (7).

1,4,5,8,9,12,13,16-Octamethoxytetraphenylene (19) The experimental procedure is the same as the synthesis of 18 which was described above. White solid; 29% yield; m.p. 356.2-360.4 °C (Lit⁹: >225-226°C); ¹H NMR (300 MHz, CD₃COCD₃): δ 6.76 (s, 8H), 3.62 (s, 24H); MS (EI): m/z (relative intensity) 544 (M⁺, 100), 545 (37), 546 (8), 272 (5), 84 (9), 57 (14), 49 (9), 43 (8).

1,16-Dimethoxytetraphenylene (20) To a suspension of 2,2’-diodo-6,6’-dimethoxybiphenyl (7) (466 mg, 1 mmol) and 2,2’-diodobiphenyl (8) (406 mg, 1 mmol) in Et₂O (60 mL) was added a 2.5 M hexane solution of n-BuLi (2 mL, 5 mmol) dropwise at -78 °C and the reaction mixture was stirred for 2 hours at the same temperature. Then, anhydrous CuCl₂ (807 mg, 6.0 mmol) was added. After stirring for 2 hours at -78 °C, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was quenched with NH₃•H₂O (2 M, 60 mL) The organic layer was then separated and the aqueous layer was extracted with CH₂Cl₂ (100 mL × 3). The combined organic extracts were washed with NaHSO₃ (2 M, 60 mL), brine (100 mL × 2) and dried over Na₂SO₄, filtered and concentrated under reduced pressure. Chromatography on
silica gel with CH$_2$Cl$_2$/hexane 1:4 as the eluent gave 1,8,9,16-tetramethoxytetraphenylene (18) (36 mg, 10%) as a white solid, m.p. 218.2-220.4 °C (Lit$^{10}$: 185-195°C); $^1$H NMR (300 MHz, CD$_2$COCD$_3$): $\delta$ 7.31-7.24 (m, 4H), 7.22-7.16 (m, 4H), 6.87 (dd, $J = 0.9$, 8.7 Hz, 2H), 6.72 (dd, $J = 0.9$, 7.5 Hz, 1H), 3.65 (s, 6H); MS (EI): $m/z$ (relative intensity) 364 (M$^+$, 100), 289 (21), 145 (16), 144 (14), 86 (83), 55 (25), 57 (28).

1,4,5,8,9,16-Hexamethoxytetraphenylene (21) The experimental procedure is the same as the synthesis of 20 which was described above. White solid; 13% yield; m.p. 256.2-258.4 °C; $^1$H NMR (300 MHz, CD$_3$COCD$_3$): $\delta$ 7.18 (t, $J = 9.0$ Hz, 2H), 6.85-6.75 (m, 8H), 3.68 (s, 6H), 3.64 (s, 6H), 3.59 (s, 6H); $^{13}$C NMR (75.3 MHz, CDCl$_3$): $\delta$ 156.6, 151.1, 151.0, 143.1, 128.4, 128.1, 127.9, 126.2, 120.8, 111.4, 111.1, 110.3, 56.8, 56.6, 56.6; MS (EI): $m/z$ (relative intensity) 484 (M$^+$, 100), 469 (10), 242 (7); IR: $\nu_{\text{max}}$ (cm$^{-1}$) 2932, 2831, 1571, 1484, 1431, 1421, 1431, 1251, 1143, 1078, 1029, 798, 786, 737; HRMS (M): Calcd. for C$_{30}$H$_{28}$O$_6$ 484.1886, found 484.1885.

1,4,5,16-Tetramethoxytetraphenylene (22)$^{11}$ and 1,4,5,16-Tetramethoxytetraphenylene (23) To a solution of 2,2,-diiodo-3,6,6'-trimethoxybiphenyl (9) (2.48 g, 5 mmol) and 2,2'-diiodo-3-methoxy biphenyl (10) (2.18 g, 5 mmol) in THF (90 mL) and Et$_2$O (60 mL) was was added a 2.5 M hexane solution of $n$-BuLi (10 mL, 2.5 M in hexane, 25 mmol) dropwise at -78 °C and the reaction mixture was stirred for 4 hours at the same temperature. Then, anhydrous CuCl$_2$ (4.03 g, 15.0 mmol) was added. After stirring for 2 hours at -78 °C, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was quenched with NH$_3$•H$_2$O (2 M, 150 mL) The organic layer was then separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (200 mL × 3). The combined organic extracts were washed with NaHSO$_3$ (2 M, 150 mL), brine (200 mL × 2) and dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Chromatography on silica gel with AcOEt/CH$_2$Cl$_2$/hexane 1:15:30 as the eluent first gave 1,4,5,9-tetramethoxytetraphenylene (23) (418 mg, 20%, $R_f = 0.43$) as a white solid, m.p. 222.5-226.0 °C; $^1$H NMR (300 MHz, CD$_2$COCD$_3$): $\delta$ 7.23-7.05 (m, 6H), 6.93 (d, $J = 8.1$ Hz, 2H), 6.82 (s, 2H), 6.75 ($J = 7.8$ Hz, 2H), 6.67 ($J = 7.8$ Hz, 1H), 3.64 (s, 6H), 3.58 (s, 3H), 3.53 (s, 3H); IR: $\nu_{\text{max}}$ (cm$^{-1}$) 3445, 2931, 2832, 1596, 1576, 1489, 1455, 1429, 1266, 1248, 1122, 1105, 1074, 1019, 800, 758, 748, 732; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.0, 156.2, 151.7, 150.9,
143.9, 141.7, 138.9, 137.0, 129.7, 129.0, 128.7, 128.1, 127.7, 127.1, 126.8, 126.7, 122.9, 121.5, 112.04, 112.01, 111.1, 110.0, 57.4, 56.8, 56.5, 56.3; **MS** (EI): \( m/z \) (relative intensity) 424 (M+, 100), 409 (6), 394 (5), 378 (6), 349 (4), 263(3), 189 (5), 131 (6); **HRMS** (M+): Calcd. for C\(_{28}H_{24}O_4\) (M+) 424.1675, found (M+) 424.1671.

Followed gave the desired product 1,4,5,16-tetramethoxytetraphenylene (22) (234 mg, 11%, \( R_f = 0.36 \)) as a white solid, m.p. 199.3-204.6 °C (Lit\(^{11}\): 204 °C).

**1H NMR** (400 MHz, CD\(_3\)COCD\(_3\)): \( \delta \) 7.70-7.67 (m, 2H), 7.62-7.56 (m, 4H), 7.30 (d, \( J = 8.4 \) Hz, 2H), 7.19 (s, 2H), 7.12 (\( J = 7.2 \) Hz, 2H), 4.10 (s, 2H), 4.01 (s, 2H); **MS** (ESI): \( m/z \) 425 ([M+H]+).

**1,16-Dihydroxytetraphenylene (2)\(^{10}\)** To a suspension of 1,16-dimethoxytetraphenylene (18) (36.4 mg, 0.1 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added a 1.0 M hexane solution of BBr\(_3\) (2 mL, 2 mmol) dropwise at 0 °C. The mixture was stirred overnight at room temperature and a clear brownish red solution was obtained. The reaction mixture was quenched with water (2 mL) at 0 °C, and a white solid precipitated which was dissolved by the addition of ethyl acetate (20 mL). The organic layer was separated and the residual aqueous layer was extracted with ethyl acetate (20 mL \( \times 3 \)). The combined organic phase was washed with NaHCO\(_3\) (2 M, 30 mL), brine (30 mL \( \times 2 \)), dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with AcOEt/hexane 1:3 as the eluent gave 1,16-dihydroxytetraphenylene (2) (33.6 mg, 100% yield) as a white solid. m.p. 200-220 °C (Lit\(^{10}\): 200-220 °C); **1H NMR** (300 MHz, CD\(_3\)COCD\(_3\)): \( \delta \) 7.36-7.22 (m, 6H), 7.11-7.03 (m, 4H), 6.77 (dd, \( J = 1.2, 8.1 \) Hz, 2H), 6.61 (dd, \( J = 1.2, 7.2 \) Hz, 2H); **MS** (EI): \( m/z \) (relative intensity) 336 (M+, 100), 337 (17), 308(16), 307 (16), 289 (21), 145 (13), 144 (11), 40 (14).

**1,8,9,16-Tetrahydroxytetraphenylene (3)\(^{7}\)** The experimental procedure is the same as the synthesis of 2 which was described above. White solid; m.p. >300°C (Lit\(^{7}\): >300 °C); **1H NMR** (300 MHz, CD\(_3\)SOCD\(_3\)): \( \delta \) 8.74 (s, 4H), 6.97 (dd, \( J = 7.5 \), 8.1 Hz, 4H), 6.62 (d, \( J = 8.1 \) Hz, 4H), 6.55 (d, \( J = 7.5 \) Hz, 4H); **MS** (ESI): \( m/z \) 367 ([M-H]+).

**1,4,5,16-Tetrahydroxytetraphenylene (4)\(^{11}\)** White solid; m.p. >300 °C (Lit\(^{11}\): 135 °C [dec.]); **1H NMR** (400 MHz, CD\(_3\)SOCD\(_3\)): \( \delta \) 7.80 (d, \( J = 8.4 \) Hz, 2H), 7.68 (dd, \( J = 8.4 \), 2.6 Hz, 2H), 7.24 (d, \( J = 2.6 \) Hz, 2H), 4.10 (s, 2H), 4.01 (s, 2H); **MS** (EI): \( m/z \) 425 ([M+H]+).
NMR (300 MHz, CD$_3$COCD$_3$): δ 7.27-7.17 (m, 4H), 7.08 (t, $J = 7.8$ Hz, 2H), 6.75 (dd, $J = 1.5$, 7.8 Hz, 2H), 6.64 (s, 2H), 6.60 (dd, $J = 1.5$, 7.5 Hz, 2H); MS (ESI): $m/z$ 367 ([M-H]$^+$).

1,4,5,8,9,16-Hexahydroxytetraphenylene (5)$^{12}$ White solid; m.p. >300 °C (Lit$^{12}$: >300 °C); $^1$H NMR (300 MHz, CD$_3$COCD$_3$): δ 7.03 (t, $J = 7.8$ Hz, 2H), 6.70-6.51 (m, 8H); MS (ESI): $m/z$ 399 ([M-H]$^+$).

1,4,5,8,9,12,13,16-Octahydroxytetraphenylene (6)$^{9}$ White solid; m.p. >300 °C (Lit$^{9}$: >300 °C); $^1$H NMR (300 MHz, CD$_3$COCD$_3$): δ 6.56 (s); MS (ESI): $m/z$ 431 ([M-H]$^+$).
References

$^{1} \text{H NMR Spectrum of 15a}$

$^{13} \text{C NMR Spectrum of 15a}$
$^1$H NMR Spectrum of 15c

$^{13}$C NMR Spectrum of 15c
$^1$H NMR Spectrum of 15d

**File:** up

**Pulse Sequence:** sdpul

**Solute:** odcl3

**Temp.:** 39.0 °C / 296.1 K

**Temperature:** vtop1

**NMR:** 400 MHz

**Water delay:** 2.000 sec

**Pulse:** 45.0 degrees

**Acq. time:** 1.200 sec

**Width 2500.0 Hz 30 repetitions**

**Acq. time:** 1.200 sec

**NMR:** 400 MHz

**Continuously:** on

**NMR:** 400 MHz

**Data:** 2048 points

**Line Broadening:** 2.0 Hz

**PT time:** 25 min, 45 sec

$^{13}$C NMR Spectrum of 15d
1H NMR Spectrum of 16

and carbon

Pulse sequence: edp15
saturation: c6d13
Temp: 296 K / 25.0°C
Operator: c6d13
G3M02-003 "G0M0R" 

Data: Delay 2.400 sec
Pulse 45.0 degrees
Ampl. 1.250 sec
FID 24001.9 Hz
64 repetitions
G3M02 1H, 100.600011 MHz
G3M02 13C, 125.000000 MHz
Power 43 dB
continuously

Data processing
Gain 0.9581 Hz
Total time 91 hr, 51 min, 46 sec

13C NMR Spectrum of 16
$^1$H NMR Spectrum of 17

File: sp
Pulse sequence: apseal
Sweep: 10.0 Hz / 220.1 s
Operator: venom
UNIQCES-003, "491M"  

Pulsed delay 2.200 sec
Pulse 90.0 degrees
Avg. time 1.100 sec
Width 1480.0 Hz
1000 repetitions
concentration C5, 100.498044 MHz
NMR8TURBO 63, 100.498044 MHz
Power 43 dB
continuously on

data: 1414-4421-9
The NMR spectrum of 17

$^{13}$C NMR Spectrum of 17


**S19**

**1H NMR Spectrum of 9**

- **File**: mp
- **Pulse sequence**: zgspip
- **Solvent**: cdcl3
- **Temp**: 298.1 K
- **Operation**: normal

- **Measurements**: 4096.5 sec
- **Pulse 90° degrees**
- **Acq. Time**: 1.210 sec
- **Width**: 2000.0 Hz
- **Repetitions**: 64

** Spectrometer**: GL1, 400.1368 MHz
** Resonance**: 83.4646477 MHz
- **Power**: 43 dB
- **Continuously ev**
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**13C NMR Spectrum of 9**

- **Total time**: 1 hr, 59 min, 40 sec
**1H NMR Spectrum of 10**

**13C NMR Spectrum of 10**

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File: up
Pulse sequence: singp
Solvent: d6o13
Temp: 25.0 °C / 300.1 K
Spin decoupler: normal

Untuned 2.600 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Mech 24555.8 Hz
66 repetitions

Recorded 25.0, 0.00 ppm
Decoupled 25.0, 0.004747 MHz
Power 43 dB
Continuously on

DATA PROCESSING
Line broadening 5.0 Hz
2F alias 0.0001
Total time 91 hr, 95 min, 45 sec
\[ \text{\^{1}H NMR Spectrum of 12} \]

File: HP

Pulse sequence: 90pul
Solenoid: 90p13
Temp.: 298 K / 25.0 Hz
Solvent: voss
VND: 431 "900kHz"

Relax. delay 3.000 sec
Pulse 90.0 degrees
Amp. time 1.000 sec
NMR 2410.3 Hz
128 repetitions
CHROMA 255, 100.64600 MHz
CHROMA II, 125.626471 MHz
Power 110 W
Continuously on

\[ \text{\^{13}C NMR Spectrum of 12} \]
$^{1}H$ NMR Spectrum of 23

$^{13}C$ NMR Spectrum of 23