

Supporting Information
For
Synthesis of Differentially-Substituted Hexaethynylbenzenes Based on Tandem
Sonogashira and Negishi Cross-Coupling Reactions

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General. ^1H NMR (400, 300 or 270 MHz) and ^{13}C NMR (100.5, 75.0 or 67.5 MHz) spectra were recorded on a JEOL JNM-AL-400, a Varian Mercury 300 or a JEOL JNM-GSX-270 spectrometer in CDCl_3 or $\text{DMSO}-d_6$ at 30 °C. The chemical shifts of ^1H NMR and ^{13}C NMR signals are quoted relative to internal CHCl_3 ($\delta = 7.26$ and 77.0) or tetramethylsilane. IR spectra were recorded as a KBr disk on a JASCO FTIR-410 spectrometer. Mass spectral analyses were performed on a JEOL JMS-DX303HF or a Shimadzu Kompact MALDI2 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400II analyzer. Melting points were measured with a Ishii Melting Point Apparatus. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm \times 20 mm JAIGEL-1H and 2H GPC columns with CHCl_3 as an eluent.

Hexakis[(trimethylsilyl)ethynyl]benzene (1)¹ and
Pentakis[(trimethylsilyl)ethynyl]benzene (7).^{1b} To a three-necked flask, 552 mg (1.00 mmol) of hexabromobenzene (**5**), 225 mg (0.200 mmol) of $\text{Pd}(\text{PPh}_3)_4$, 7 mL of toluene, and a solution of 10.0 mmol of [(trimethylsilyl)ethynyl]zinc chloride (**6**) in 10 mL of THF prepared by the literature method² were added in this order. The mixture was stirred under a nitrogen atmosphere at 80 °C (oil bath temp.) for 3 days. After 50 mL of 1 N HCl was added, the reaction mixture was extracted with ether (100 mL \times 3). The combined organic layer was washed with brine (50 mL) and dried over MgSO_4 . The solvent was evaporated and the residue was chromatographed on silica gel (eluent: hexane/toluene = 12/1) to give 54 mg (10%) of pentaethynylbenzene **7** followed by 418 mg (64%) of hexaethynylbenzene **1** both as pale yellow solids. **1**: ^1H NMR (270 MHz, CDCl_3 , 30 °C) δ 0.28 (s); ^{13}C NMR (67.5 MHz, CDCl_3 , 30 °C) δ 127.9, 105.2, 101.0, 0.1; MS (FAB) m/z 655 ($\text{M}^+ + \text{H}$). **7**: ^1H NMR (270 MHz, CDCl_3 , 30 °C) δ 7.50 (s, 1H), 0.28 (s, 27H), 0.25 (s, 18H); ^{13}C NMR (67.5 MHz, CDCl_3 , 30 °C) δ 135.1, 128.9, 127.7, 125.5, 105.1, 103.9, 101.9, 101.1, 101.0, 100.9, 0.1, 0.0; MS (FAB) m/z 558 (M^+).

2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-triazine (9).³ To a three-necked flask, 184 mg (1.00 mmol) of trichlorotriazine **8** in 2 mL of THF, 58 mg (0.050 mmol) of Pd(PPh₃)₄, and a solution of 5.00 mmol of **6** in 10 mL of THF were added in this order. The mixture was stirred under a nitrogen atmosphere at 30 °C (oil bath temp.) for 3 h. After 10 mL of 0.1 N HCl was added, the reaction mixture was extracted with ether (20 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated, and the residue was chromatographed on silica gel which was deactivated with 6 % (wt/wt) of water (eluent: hexane/AcOEt = 10/1) to give 295 mg (80%) of triethynyltriazine **9** as a white solid. mp 158–161 °C; ¹H NMR (300 MHz, CDCl₃, 30 °C) δ 0.26 (s); ¹³C NMR (75.0 MHz, CDCl₃, 30 °C) δ 159.7, 102.2, 100.0, -0.8.

1,3,5-Tris[(trimethylsilyl)ethynyl]-2,4,6-tris(phenylethynyl)benzene (2).⁴ To a three-necked flask, 47 mg (0.10 mmol) of 1,3,5-trichloro-2,4,6-tris[(trimethylsilyl)ethynyl]benzene (**12**),⁵ 19 mg (0.016 mmol) of Pd(PPh₃)₄, a solution of 1.03 mmol of (phenylethynyl)zinc chloride (**13**) in 5 mL of THF prepared by the literature method² were added, and the mixture was heated under reflux. After 2 days additional Pd(PPh₃)₄ (0.010 mmol) and a solution of **13** (1.00 mmol) in THF (5 mL) were added and the reaction mixture was heated under reflux for further 2 days. After 300 mL of 1 N HCl was added, the reaction mixture was extracted with ether (50 mL × 3). The combined organic layer was washed with saturated NaHCO₃ solution (100 mL) followed by brine (100 mL) and dried over MgSO₄. The solvent was evaporated and the residue was chromatographed on silica gel (eluent: hexane/toluene = 10/1). The product was purified by preparative HPLC to give 46 mg (69%) of **2** as a pale yellow solid. mp 207–208 °C; ¹H NMR (300 MHz, CDCl₃, 30 °C) δ 7.63–7.61 (m, 6H), 7.40–7.39 (m, 9H), 0.33 (s, 27H); ¹³C NMR (75.0 MHz, CDCl₃, 30 °C) δ 131.9, 128.8, 128.5, 128.3, 127.0, 123.1, 105.2, 101.5, 99.2, 87.0, 0.0; IR (KBr) 2958, 2215, 2155, 1408, 1249, 930, 845, 755 cm⁻¹; MS (FAB) *m/z* 667 (M⁺+H). Anal. Calcd for C₄₅H₄₂Si₃: C, 81.02; H, 6.35. Found: C, 80.67; H, 6.35.

1,3,5-Trichloro-2,4,6-tris(phenylethynyl)benzene (14). To a degassed solution of 1.68 g (3.00 mmol) of 1,3,5-trichloro-2,4,6-triiodobenzene (**11**),⁶ 41 mg (0.036 mmol) of Pd(PPh₃)₄, and 60 mg (0.32 mmol) of CuI in 15 mL of THF was added under a nitrogen atmosphere 130 mg (1.28 mmol) of diisopropylamine followed by 1.32 mL (12.0 mmol) of phenylacetylene, and the mixture was heated under reflux for 2 days. After 200 mL of 1 N HCl was added, the reaction mixture was extracted with ether (100 mL × 3). The combined organic layer was washed with saturated NaHCO₃ solution (50 mL) followed by brine (100 mL), and dried over MgSO₄. The solvent was evaporated and the residue

was chromatographed on silica gel (eluent: hexane/toluene = 10/1). The product was purified by preparative HPLC followed by recrystallization from ether to give 678 mg (47%) of **14** as a white solid. mp 203–204 °C; ¹H NMR (400 MHz, CDCl₃, 30 °C) δ 7.65–7.63 (m, 6H), 7.41–7.40 (m, 9H); ¹³C NMR (100.5 MHz, CDCl₃, 30 °C) δ 137.9, 131.9, 129.3, 128.4, 123.0, 122.2, 100.9, 83.1; IR (KBr) 2220, 1489, 1389, 749, 686 cm⁻¹; MS (FAB) *m/z* 484, 482, 480 (rel. intensity ca. 1:2:2, M⁺). Anal. Calcd for C₃₀H₁₅Cl₃: C, 74.79; H, 3.14. Found: C, 74.38; H, 2.99. This compound was converted to **2** in a manner similar to the preparation of **2** described above using 103 mg (0.214 mmol) of **14**, 49 mg (0.040 mmol) of Pd(PPh₃)₄, and a solution of 1.00 mmol of **6** in 5 mL of THF. The product was purified by recrystallization to give 115 mg (81%) of **2**.

1,3-Dichloro-2,4,5,6-tetrakis(phenylethynyl)benzene (15). This compound was prepared in a manner similar to the preparation of **14** using 561 mg (1.00 mmol) of **11**, 123 mg (0.106 mmol) of Pd(PPh₃)₄, and 22 mg (0.12 mmol) of CuI, 10 mL of THF, 540 mg (5.34 mmol) of diisopropylamine and 521 mg (5.10 mmol) of phenylacetylene. The product was purified by preparative HPLC to give 182 mg (33%) of tetraethynylbenzene **15** as a pale yellow solid. mp 143–145 °C; ¹H NMR (270 MHz, CDCl₃, 30 °C) δ 7.60–7.50 (m, 8H), 7.34–7.18 (m, 12H); ¹³C NMR (67.5 MHz, CDCl₃, 30 °C) δ 137.4, 131.9, 131.8, 129.2, 129.1, 129.0, 128.8, 128.42, 128.37, 124.6, 123.7, 122.7, 122.6, 122.3, 101.5, 100.6, 99.7, 87.1, 84.9, 83.8; IR (KBr) 2923, 2215, 1489, 1385, 1267, 1070, 1022, 756, 689 cm⁻¹; MS (FAB) *m/z* 548, 546 (rel. intensity ca. 4:5, M⁺). Anal. Calcd for C₃₈H₂₀Cl₂: C, 83.37; H, 3.68. Found: C, 83.30; H, 3.35.

1,3-Bis[(trimethylsilyl)ethynyl]-2,4,5,6-tetrakis(phenylethynyl)benzene (3). This compound was prepared in a manner similar to the preparation of hexaethynylbenzene **2** using 103 mg (0.188 mmol) of tetraethynylbenzene **15**, 35 mg (0.030 mmol) of Pd(PPh₃)₄, and a solution of 1.00 mmol of ethynylzinc chloride **6** in 5 mL of THF. The product was purified by preparative HPLC to give 78 mg (62%) of **3** as a pale yellow solid. mp 185–187 °C; ¹H NMR (270 MHz, CDCl₃, 30 °C) δ 7.64–7.60 (m, 8H), 7.40–7.38 (m, 12H), 0.32 (s, 18H); ¹³C NMR (100.5 MHz, CDCl₃, 30 °C) δ 131.83, 131.80, 131.75, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.3, 127.1, 123.2, 123.1, 105.2, 101.5, 99.4, 99.2, 87.23, 87.15, 0.1; IR (KBr) 3053, 2956, 2213, 2150, 1597, 1493, 1442, 1407, 1247, 1068, 1025, 930, 844, 753, 687 cm⁻¹; MS (FAB) *m/z* 670 (M⁺). Anal. Calcd for C₄₈H₃₈Si₂: C, 85.92; H, 5.71. Found: C, 85.80; H, 5.53.

1,4-Dichloro-2,3,5,6-tetraiodobenzene (17). To a 100 mL three-necked flask, 3.64 g (14.3 mmol) of orthoperiodic acid, 30 mL of concentrated sulfuric acid, and 9.78 g (42.9 mmol) of iodine was added. After 30 min 1.49 g (1.10 mmol) of 1,4-dichlorobenzene were added to the flask and the mixture was stirred at ambient temperature for 44 h. The

reaction mixture was poured into ice-cold water followed by an addition of saturated NaHSO_3 solution (500 mL). The precipitate was filtered and the filter was washed with water (100 mL), ethanol (100 mL), ether (50 mL), and cold benzene (50 mL) to give 5.56 g of a crude product. The product was purified by recrystallization from THF to give 5.00 g (76%) of **17** as a yellow solid, which sublimed at 247 °C. ^{13}C NMR (100.5 MHz, $\text{DMSO}-d_6$, 30 °C) δ 139.5, 115.1; IR (KBr) 1649, 1281, 1270, 1253 cm^{-1} ; MS (LD) m/z 652, 650 (rel. intensity ca. 4:5, M^+). Anal. Calcd for $\text{C}_6\text{Cl}_2\text{I}_4$: C, 11.08. Found: C, 11.03.

1,4-Dichloro-2,3,5,6-tetrakis(phenylethynyl)benzene (18). This compound was prepared in a manner similar to the preparation of **14** using 1.95 g (3.00 mmol) of **17**, 58 mg (0.050 mmol) of $\text{Pd}(\text{PPh}_3)_4$, 118 mg (0.620 mmol) of CuI , 25 mL of THF, 152 mg (1.50 mmol) of diisopropylamine, and 1.58 g (15.5 mmol) of phenylacetylene. The product was purified by recrystallization from toluene to give 715 mg (44%) of **18** as a pale yellow solid. mp 224–225 °C; ^1H NMR (270 MHz, CDCl_3 , 30 °C) δ 7.63–7.60 (m, 8H), 7.39–7.37 (m, 12H); ^{13}C NMR (67.5 MHz, CDCl_3 , 30 °C) δ 135.6, 131.8, 129.2, 128.4, 126.1, 122.5, 101.0, 85.5; IR (KBr) 2207, 1493, 1440, 1404, 1269, 1069, 920, 843, 758, 693 cm^{-1} ; MS (FAB) m/z 548, 546 (rel. intensity ca. 2:3, M^+). Anal. Calcd for $\text{C}_{38}\text{H}_{20}\text{Cl}_2$: C, 83.37; H, 3.68. Found: C, 83.48; H, 3.34.

1,4-Bis[(trimethylsilyl)ethynyl]-2,3,5,6-tetrakis(phenylethynyl)benzene (4). This compound was prepared in a manner similar to the preparation of **2** using 274 mg (0.500 mmol) of tetraethynylbenzene **18**, 72 mg (0.062 mmol) of $\text{Pd}(\text{PPh}_3)_4$, and a solution of 2.00 mmol of ethynylzinc chloride **6** in 13 mL of THF. The product obtained after evaporation of the solvent of extraction was washed with hexane (10 mL) and ether (10 mL) to give 234 mg (70%) of **4** as a pale yellow solid. mp 236–237 °C; ^1H NMR (270 MHz, CDCl_3 , 30 °C) δ 7.64–7.61 (m, 8H), 7.39–7.36 (m, 12H), 0.32 (s, 18H); ^{13}C NMR (67.5 MHz, CDCl_3 , 30 °C) δ 131.8, 128.8, 128.3, 128.2, 127.7, 123.1, 101.4, 99.3, 87.2, 0.1; IR (KBr) 2941, 2209, 1493, 1410, 1349, 1249, 931, 846, 755, 687; MS (FAB) m/z 548, 546 (rel. intensity ca. 2:3, M^+). Anal. Calcd for $\text{C}_{48}\text{H}_{38}\text{Si}_2$: C, 85.92; H, 5.71. Found: C, 85.75; H, 5.36.

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