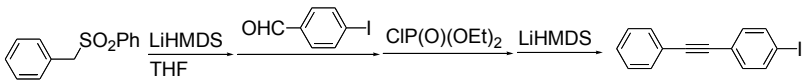
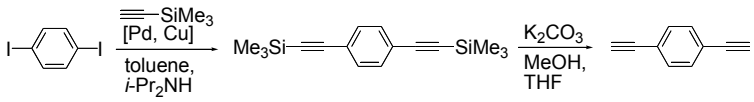
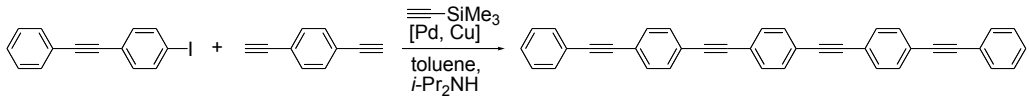
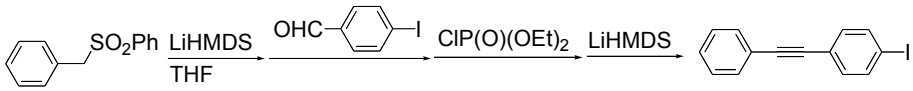
**Preparation of 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene (BPPB)**



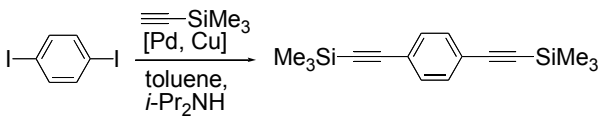




**1-Iodo-4-(phenylethynyl)benzene:**[S1] To a THF solution (40 mL) of benzyl phenyl sulfone (1.02 g, 4.4 mmol) was added lithium hexamethyldisilazide (LiHMDS) (1.0M in THF, 4.4 mL, 4.4 mmol) at -78 °C, and the mixture was stirred for 0.5 h. A THF solution (8.0 mL) of 4-iodobenzaldehyde (928 mg, 4.0 mmol) was added, and the mixture was stirred for 1 h. At –78 °C, $ClP(O)(OEt)_2$ (0.63 mL, 4.4 mmol) was added, and then the mixture was stirred at rt for 1 h. LiHMDS (1.0M in THF, 16.0 mL, 16.0 mmol) was added at -78 °C, and the mixture was stirred at rt for 12 h. After usual workup with AcOEt and water, the organic layer was evaporated. The residue was subjected to column chromatography on silica gel (hexane) to afford 1-iodo-4-(phenylethynyl)benzene in a pure form (1.14 g, 94 %).

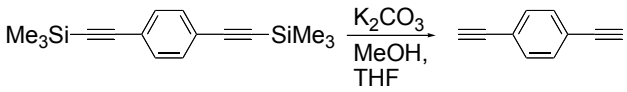
$^1$H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, $J$ = 6.0 Hz, 2H), 7.33-7.35 (m, 3H), 7.50-7.53 (m, 2H), 7.68 (d, $J$ = 8.4 Hz, 2H).




**1,4-Bis(trimethylsilylethynyl)benzene:**[S2] To a solution of 1,4-diiodobenzene (990.0 mg, 3.0 mmol), $Pd(PPh_3)_4$ (346.6 mg, 0.30 mmol) and CuI (57.1 mg, 0.30 mmol) in toluene (25 mL) and diisopropylamine (6 mL) was added (trimethylsilyl)acetylene (1.04 mL, 7.5

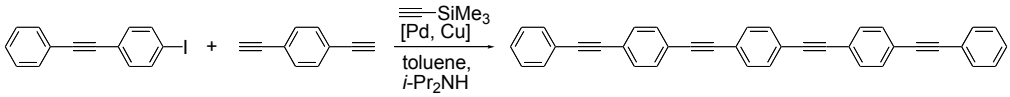
mmol), and the mixture was heated at 50 °C for 24 h. After filtration, the filtrate was poured into aqueous $NH_4Cl$. After usual workup with AcOEt and water, the organic layer was evaporated. The residue was subjected to column chromatography on silica gel (hexane/$CH_2Cl_2$ = 8/1) to afford 1,4-bis(trimethylsilylethynyl)benzene in a pure form (754 mg, 93 %).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 18H), 7.38(s, 4H).




**1,4-Diethynylbenzene:**[S2] To a solution of 1,4-bis(trimethylsilylethynyl)benzene (730.4 mg, 2.7 mmol) in THF (15 mL) and MeOH (15 mL) was added $K_2CO_3$ (3.73 g, 27.0 mmol), and the mixture was stirred at rt for 1 h. After usual workup with AcOEt and water, the organic layer was evaporated. The residue was subjected to column chromatography on silica gel (hexane/$CH_2Cl_2$ = 8/1) to afford the desired product (313 mg, 92 %).

$^1$H NMR (500 MHz, $CDCl_3$): δ 3.17 (s, 2H), 7.44 (s, 4H).




**1,4-bis(4-(phenylethynyl)phenylethynyl)benzene (BPPB):**[S3] A 50 mL flask was charged with 1-iodo-4-(phenylethynyl)benzene (346 mg, 1.14 mmol), 1,4-diethynylbenzene (65 mg, 0.52 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol), and CuI (11 mg, 0.06 mmol), diisopropylamine (3 mL) and toluene (20 mL), and the mixture was heated at 65 °C for 12 h. The mixture was poured into aqueous $NH_4Cl$, and the resultant precipitate was collected by filtration. The crude product was washed with water, AcOEt and $CH_2Cl_2$. After having been dried, 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene was obtained as pale yellow powder (212 mg, 86 %).

Mp >300 °C (decomp); MALDI-MS: calcd for 478.17; found 478.18. Anal. Calcd for $C_{38}H_{22}$: C 95.37; H 4.63. Found: C 95.13; H 4.36.

S1 A. Orita, H. Taniguchi, J. Otera, *Chem. Asian J.* **2006**, *1*, 430; b) A. Orita, K. Miyamoto, M. Nakashima, F. Ye, J. Otera, *Adv. Synth. Catal*. **2004**, *346*, 767.

S2 C-F. Lo, L. Luo, E. W-G. Diau, I-Jy Chang, C-Y. Lin, *Chem. Commun*. **2006**, 1430.

S3 $SnCl_2$-catalyzed synthesis of 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene (BPPB) has been reported. S. Misumi *Bull. Chem. Soc. Jpn* **1961**, *34*, 1827.

Luminance-current density characteristics of OLED devices (I), (II), (III), (IV), (V) and (VI)