Synthesis of BIB

All reagents were purchased commercially and used without further purification. Bruker AVANCE 400 (400 MHz), Varian 1000 FT-IR, EA 3000 CHNS and Büchi SMP-20 instruments were used to measure NMR spectra, infrared spectra, elemental analysis, and melting point, respectively. The following abbreviations are utilized in the analysis of NMR signals: s = singlet, d = doublet, t = triplet and m = multiplet. The numbering of the carbon skeleton of molecular formulae does not comply with IUPAC nomenclature rules.

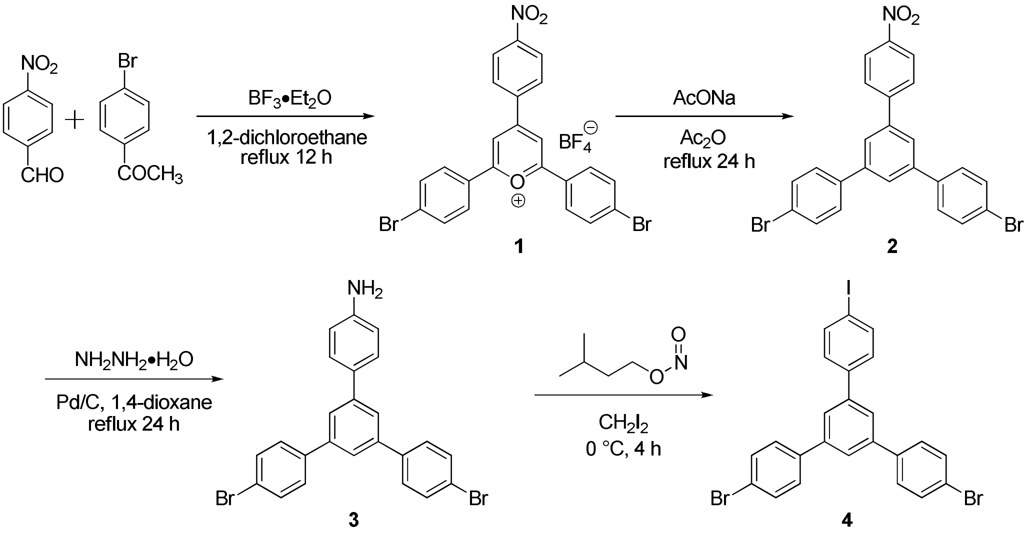

Figure S1. Synthetic route to 1,3-bis(*p*-bromophenyl)-5-(*p*-iodophenyl)benzene (4).

1.1. Experimental section

2,6-Bis(*p*-bromophenyl)-4-(*p*-nitrophenyl)pyrylium tetrafluoroborate (1). Boron trifluoride etherate (44.0 mL, 0.347 mol) in 1,2-dichloroethane (100 mL) was added dropwise to a stirred solution of 4-nitrobenzaldehyde (21.2 g, 0.140 mol) and 4-bromoacetophenone (55.7 g, 0.280 mol) in 1,2-dichloroethane (300 mL) at room temperature under N_2. Thereafter, the reaction mixture was refluxed for 12 h. The resulting solution was concentrated under vacuum and a brown colored precipitate was obtained upon addition of diethylether. The crude precipitate was filtered off and washed with dichloromethane to afford **1** (9.80 mmol, 5.90 g, 7% yield) as residue. MP >250 °C. IR (KBr): $\tilde{\nu}$ 3396, 3102, 2368, 1930, 1795, 1622, 1516, 1450, 1392, 1345, 1279, 1251, 1208, 1166, 1127, 1067, 1003, 954, 900, 839, 784 cm^{-1}. Anal. Calcd for $C_{23}H_{14}BBr_2F_4NO_3 \cdot CH_2Cl_2$: C, 42.15, H, 2.36, N, 2.05. Found: C, 41.89, H, 2.06, N, 2.22.

1-(*p*-Nitrophenyl)-3,5-bis(*p*-bromophenyl)benzene (2). A mixture of pyrylium salt **1** (3.00 g, 5.01 mmol), anhydrous sodium acetate (820 mg, 10.0 mmol) and acetic anhydride (10 mL) was placed in a three-neck round-bottomed flask equipped with a condenser under N_2 atmosphere and refluxed for 24 h. Thereafter, the mixture was kept in the refrigerator (about –30 °C) for overnight. The resulting yellow precipitate was filtered off and recrystallized from ethanol to afford **2** (0.49 mmol, 0.25 g, 5% yield). MP >250 °C. IR (KBr): 3073, 1899, 1783, 1644, 1590, 1511, 1441, 1381, 1340, 1242, 1184, 1109, 1070, 1002, 888, 854, 813, 749 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.54 (d, ^{3}J = 8.8 Hz, 4H, 1-H), 7.63 (d, ^{3}J = 8.8 Hz, 4H, 2-H), 7.75 (d, ^{4}J = 1.6 Hz, 2H, 4-H), 7.77 (t, ^{4}J = 1.6 Hz, 1H, 3-H), 7.82 (d, ^{3}J = 9.0 Hz, 2H, 5-H), 8.34 (d, ^{3}J = 9.0 Hz, 2H, 6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ= 122.5, 124.4, 125.4, 126.3, 128.2, 129.0, 132.3, 139.4, 140.5, 142.0, 147.2, 147.5 ppm. Anal. Calcd for $C_{24}H_{15}Br_2NO_2$: C, 56.61, H, 2.97, N, 2.75. Found: C, 56.54, H, 2.83, N, 2.79.

1-(*p*-Aminophenyl)-3,5-bis(*p*-bromophenyl)benzene (3). Hydrazine hydrate, (80% in water, 2.00 mL, 32.8 mmol) was added dropwise to a stirred and boiling hot mixture of **2** (235 mg, 460 µmol), 1,4-dioxane (10 mL) in presence of a catalytic amount of palladium 10% on activated carbon. After refluxing for 24 h, the mixture was filtered off and concentrated under vacuum. The resulting black residue was washed with water and recrystallized from hexane to afford **3** (164 mg, 342 µmol, 74% yield). MP 176 °C. IR (KBr): 3444, 3361, 3028, 1895, 1775, 1614, 1514, 1490, 1441, 1380, 1346, 1278, 1182, 1071, 1004, 883, 818, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.79 (s, 2H, 7-H), 6.79 (d, ^3J = 8.0 Hz, 2H, 1-H), 7.50 (d, ^3J = 8.0 Hz, 2H, 2-H), 7.53 (d, ^3J = 8.4 Hz, 4H, 6-H), 7.59-7.61 (m, 5H, 4, 5-H), 7.69 (d, ^4J = 1.6 Hz, 2H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 115.5, 121.9, 123.7, 124.6, 128.3, 129.0, 130.9, 132.0, 140.1, 141.3, 142.7, 146.4 ppm. Anal. Calcd for $C_{24}H_{17}Br_2N$: C, 60.15, H, 3.58, N, 2.92. Found: C, 60.28, H, 3.45, N, 2.93.

1-(*p*-Iodophenyl)-3,5-bis(*p*-bromophenyl)benzene (4). Isoamyl nitrite (0.320 mL, 2.38 mmol) was added dropwise into a stirred solution of **3** (380 mg, 793 μmol) in diiodomethane (2 mL) at 0 °C under N_2 atmosphere. After stirring for 4 h at 0 °C, the reaction mixture had assumed a golden color and a yellow solid had deposited around the walls of the flask. A yellow mass was collected after filtration and recrystallized from dichloromethane to afford **4** (254 mg, 430 μmol, 54% yield) as a white solid. MP 228 °C. IR (KBr): 3040, 1898, 1779, 1643, 1591, 1486, 1436, 1375, 1241, 1185, 1068, 1001, 883, 812, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.41 (d, ^3J = 8.6 Hz, 2H, 1-H), 7.53 (d, ^3J = 8.4 Hz, 4H, 6-H), 7.61 (d, ^3J = 8.4 Hz, 4H, 5-H), 7.69 (s, 3H, 3, 4-H), 7.81 (d, ^3J = 8.6 Hz, 2H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ= 92.7, 121.2, 124.0, 124.1, 128.0, 128.2, 131.1, 137.1, 138.7, 139.3, 140.6, 140.6 ppm. Anal. Calcd. for $C_{24}H_{15}Br_2I$: C, 48.85, H, 2.56. Found: C, 48.95, H, 2.56.

1.2. ^{1}H and ^{13}C NMR spectra

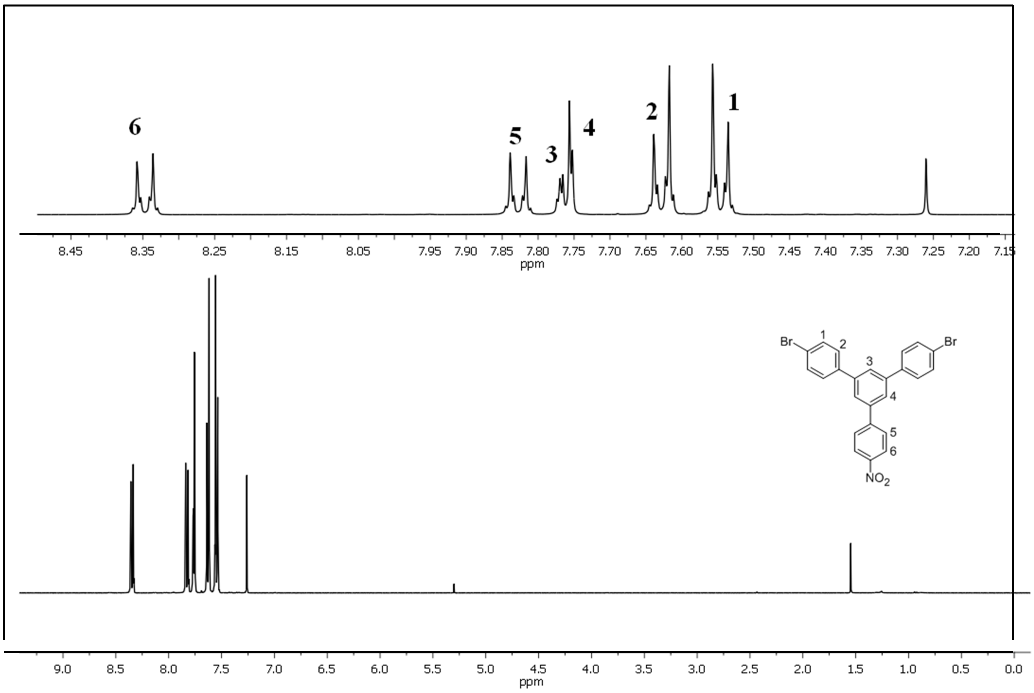

Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

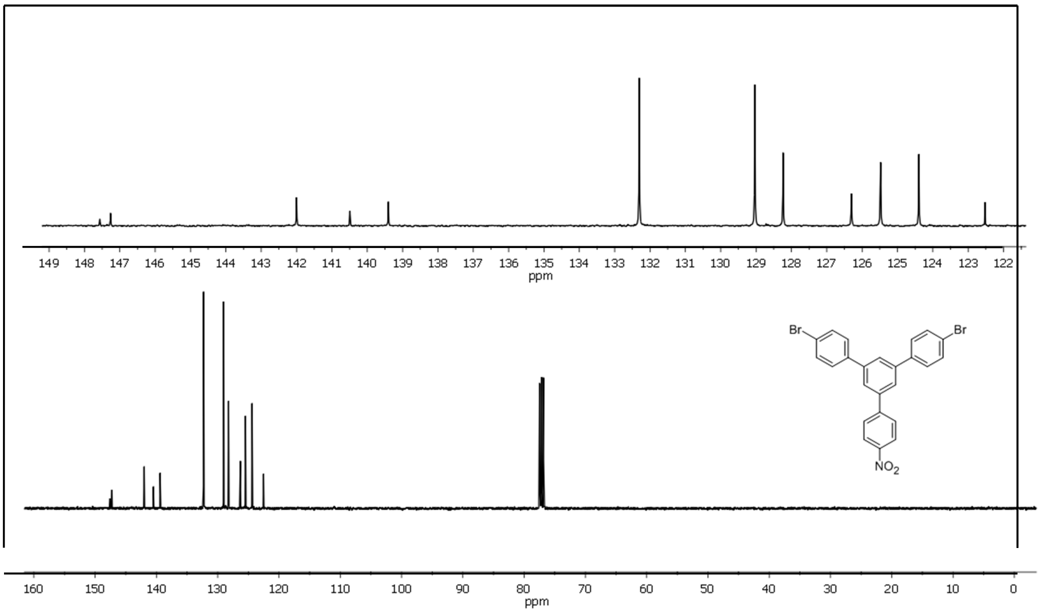

Figure S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2**.

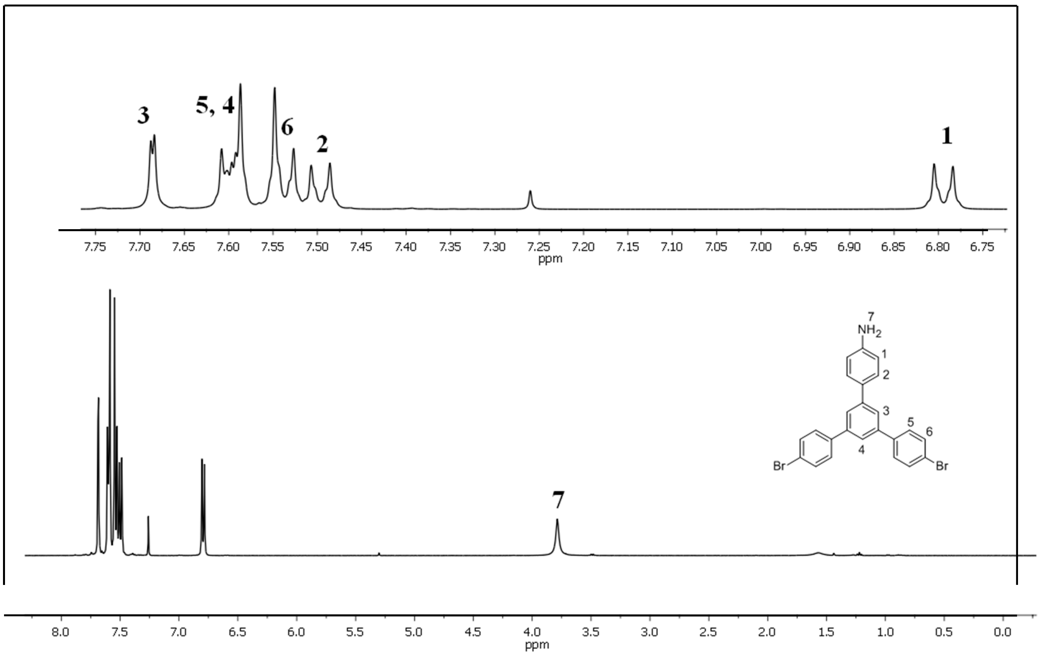

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3**.

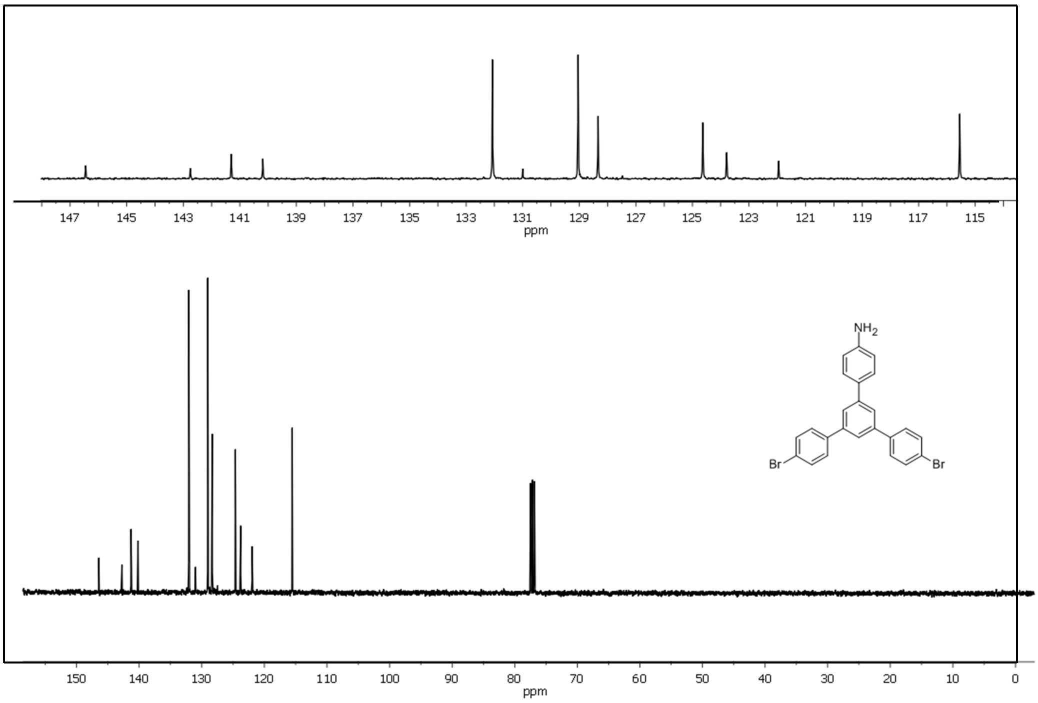

Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**.

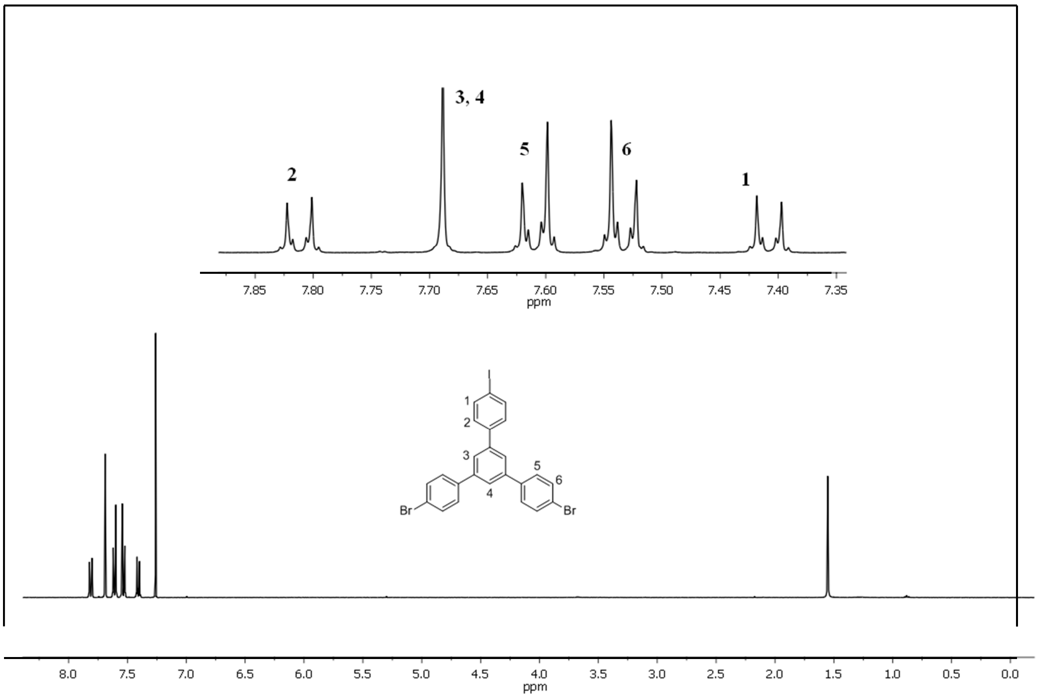

Figure S6. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **4**.

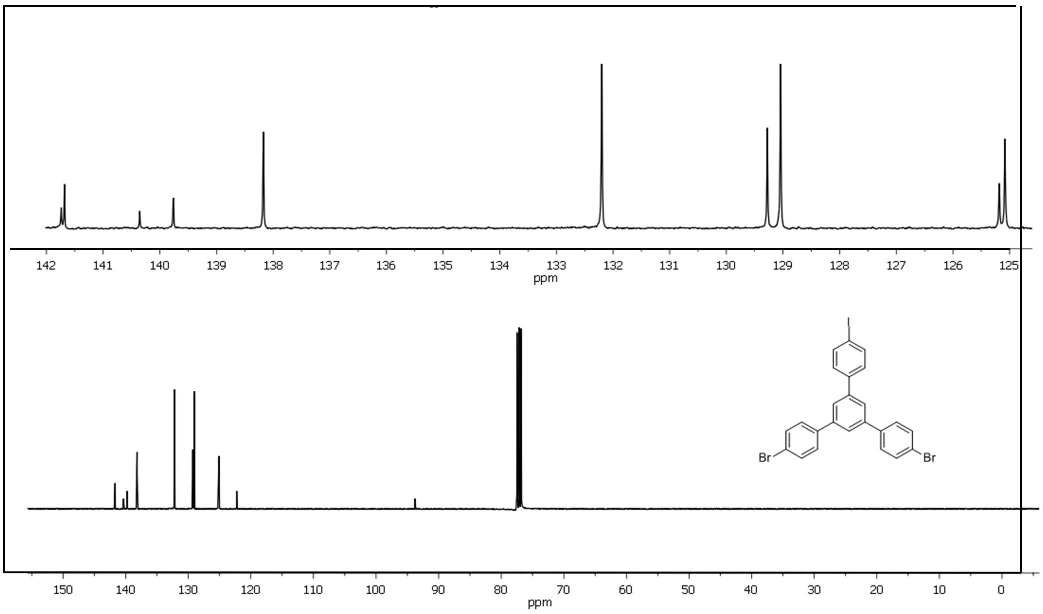

Figure S7. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 298 K) of **4**.