Supporting Information

**Benzidine rearrangement reactions of polyether tethered
cyclic diaryl hydrazides**

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Materials and Methods. Reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents used were dried and purified before use in a Grubbs column, except for methanol and DMF, which were used as received. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Infrared spectra were recorded on a Jasco Model FT/IR-480 Plus spectrometer. Proton and carbon-13 NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts are reported relative to chloroform ($\delta = 7.26$) or TMS ($\delta = 0.00$) for ^1H NMR and chloroform ($\delta = 77.0$) for ^{13}C NMR. High resolution mass spectra were measured by using FAB method at the Korean Basic Research Center, Seoul, Korea.

General procedure for the synthesis of **8a-c**

8a. To a round bottomed flask were charged 5.6 g (9.7 mmol) of tetra(ethylene glycol) di-*p*-tosylate, 5.3 g (2.5 equiv) of 3-bromo phenol, 5.4 g (4.0 equiv) of K_2CO_3 , and DMF (30 mL) under Ar atmosphere. After 12 h at 80 °C, the reaction was quenched with H_2O , and extracted with diethyl ether. The organic solution was dried over anhydrous MgSO_4 , filtered, concentrated under reduced pressure. The residue was purified by column chromatography to give 5.2 g of **8a** (98% yield); ^1H NMR(400 MHz, CDCl_3) δ 7.05 - 7.14 (m, 6H), 6.84 (dd, $J = 2.57, 1.1$ Hz, 1H), 6.82 (dd, $J = 2.57, 1.1$ Hz, 1H), 4.08 (t, $J = 4.4$ Hz, 4H), 3.83 (t, $J = 4.3$ Hz, 4H), 3.66 – 3.72 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 131.1, 124.5, 123.3, 118.5, 114.2, 71.5, 71.3, 70.2, 68.3.

8b. 98% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.05 – 7.13 (m, 6H), 6.82 – 6.85 (m, 2H), 4.08 (t, $J = 4.4$ Hz, 4H), 3.82 (t, $J = 5.1$ Hz, 4H), 3.65 – 3.69 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 131.1, 124.5, 123.3, 118.5, 114.2, 71.4, 71.2, 71.1, 70.1, 68.2.

8c. 93% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.04 – 7.12 (m, 6H), 6.81 – 6.84 (m, 2H), 4.06 (t, $J = 4.4$ Hz, 4H), 3.08 (t, $J = 5.1$ Hz, 4H), 3.63 – 3.69 (m, 16H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 130.9, 124.3, 123.1, 118.3, 114.0, 71.2, 71.1, 71.0, 70.9, 69.9, 68.1.

General procedure for the synthesis of **9a-c**

9a. To a sealed tube were charged 123 mg (0.93 mmol) of *t*-butyl carbazate, 1.53 g (3.0 equiv) of **8a**, 684 mg (1.5 equiv) of Cs_2CO_3 , 267 mg (1.0 equiv) of CuI , 252 mg (1.0 equiv) of 1,10-phenanthroline, and DMF (14 mL) under Ar atmosphere. After 24 h at 80 °C, the reaction was quenched with H_2O and extracted with diethyl ether. The organic solution was dried over anhydrous MgSO_4 , filtered, concentrated under reduced pressure. The residue was purified by column chromatography to give 318 mg of **9a** (57% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, $J = 8.1$ Hz, 1H), 7.05 – 7.13 (m, 5H), 6.84 (ddd, $J = 8.1, 2.2, 1.5$ Hz, 1H), 6.67

(ddd, $J = 8.1, 2.2, 1.1$ Hz, 1H), 4.41 (s, 2H), 4.07 – 4.12 (m, 4H), 3.82 – 3.85 (m, 4H), 3.67 – 3.73 (m, 8H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 159.4, 155.7, 144.9, 131.2, 129.4, 124.6, 123.4, 118.6, 116.6, 114.3, 111.6, 110.6, 82.5, 71.6, 71.5, 71.4, 70.4, 70.2, 68.3, 68.1, 28.9.

9b. 53% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, $J = 8.1$ Hz, 1H), 7.07 – 7.14 (m, 5H), 6.84 (ddd, $J = 8.1, 2.2, 1.1$ Hz, 1H), 6.67 (ddd, $J = 8.1, 2.2, 1.1$ Hz, 1H), 4.04 (s, 2H), 4.10 – 4.13 (m, 4H), 3.83 – 3.85 (m, 4H), 3.66 – 3.72 (m, 12H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 159.3, 155.7, 144.9, 131.2, 130.1, 129.4, 124.6, 123.4, 118.6, 116.6, 115.2, 114.3, 111.6, 110.6, 82.5, 71.5, 71.4, 71.3, 70.4, 70.2, 68.3, 68.1, 29.0.

9c. 55% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, $J = 8.1$ Hz, 1H), 7.07 – 7.12 (m, 5H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.67 (d, $J = 8.4$ Hz, 1H), 4.43 (bs, 2H), 4.08 – 4.12 (m, 4H), 3.82 – 3.86 (m, 4H), 3.65 – 3.72 (m, 16H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 159.3, 155.6, 144.8, 131.1, 129.3, 124.5, 123.3, 118.6, 116.5, 114.3, 111.5, 110.6, 82.4, 71.5, 71.4, 71.2, 71.1, 70.3, 70.2, 68.3, 68.1, 28.9.

General procedure for the synthesis of 10a-c

10a. To a round bottomed flask were charged 466 mg (0.84 mmol) of **9a**, 820 mg (3.0 equiv) of Cs_2CO_3 , 19 mg (10 mol%) of $\text{Pd}(\text{OAc})_2$, 24 mg (10 mol%) of $\text{P}(t\text{-Bu})_3$, and 17 mL of anhydrous toluene under Ar atmosphere. After 12 h at 110 °C, the reaction mixture was cooled to rt and filtered through a plug of silica gel. The filtrate was concentrated in vacuo and chromatographed to give 183 mg of **10a** (46% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.08 – 7.23 (m, 4H), 6.66 (td, $J = 9.2, 1.1$ Hz, 1H), 6.46 (t, $J = 2.2$ Hz, 2H), 6.40 (dd, $J = 8.1, 2.2$ Hz, 2H), 4.15 (t, $J = 4.8$ Hz, 2H), 4.07 (t, $J = 4.8$ Hz, 2H), 3.77 – 3.83 (m, 4H), 3.62 – 3.69 (m, 8H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 159.5, 154.5, 150.3, 144.5, 130.4, 129.7, 115.6, 111.2, 110.9, 107.3, 107.0, 100.5, 83.0, 71.4, 71.1, 69.9, 68.3, 67.9, 30.3, 28.8.

10b. 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.09 – 7.24 (m, 4H), 6.67 – 6.70 (td, $J = 7.0, 2.6$ Hz, 1H), 6.39 – 6.46 (m, 4H), 4.11 (t, $J = 4.4$ Hz, 2H), 4.05 (t, $J = 4.4$ Hz, 2H), 3.78 – 3.83 (m, 4H), 3.62 – 3.70 (m, 12H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8, 159.7, 154.5, 150.3, 144.6, 130.5, 129.7, 115.1, 111.4, 109.3, 107.7, 107.2, 100.0, 83.0, 71.7, 71.6, 71.5, 71.4, 71.3, 71.2, 70.1, 68.4, 68.1, 28.8.

10c. 48% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 6.23$, 1H), 7.19 (t, $J = 8.1$ Hz, 2H), 7.11 (t, $J = 8.1$ Hz, 1H), 6.68 (dd, $J = 8.1, 1.8$ Hz, 1H), 6.39 – 6.46 (m, 4H), 4.11 (t, $J = 4.4$ Hz, 2H), 4.05 (t, $J = 4.8$ Hz, 2H), 3.79 – 3.83 (m, 4H), 3.60 – 3.68 (m, 16H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 159.7, 154.4, 150.2, 144.6, 130.5, 129.6, 114.8, 111.4, 108.9, 107.7, 106.9, 100.3, 82.9, 71.5, 71.4, 71.3, 70.3, 68.3, 68.2, 28.7.

General procedure for the synthesis of 12a-c

12a. To a round bottomed flask were charged 100 mg (0.21 mmol) of **10a**, 2 mL of ethanol, and 5 drops of conc. HCl at rt. The reaction was refluxed for 2 h, cooled to 0 °C, neutralized with solid NaHCO₃, filtered, and concentrated under reduced pressure. To this residue were added 2 mL of MeCN, 0.08 mL (5.0 equiv) of acetyl chloride, 94 mg (5.0 equiv) of NaOAc at rt. After 12 h at rt, the reaction was quenched with H₂O and extracted with methylene chloride. The organic solution was dried over anhydrous MgSO₄, filtered, concentrated under reduced pressure. The residue was purified by column chromatography to give 44 mg of **12a** (46% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (s, 2H), 7.37 (s, 2H), 7.06 (d, *J* = 9.1 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 4.16 – 4.20 (m, 2H), 3.96 – 3.99 (m, 2H), 3.55 – 3.80 (m, 12H), 2.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 157.4, 139.0, 132.0, 124.7, 112.5, 105.2, 71.5, 71.4, 70.1, 68.6, 25.2; FT-IR (CH₂Cl₂) 3317, 3189, 2927, 1657, 1600, 1530, 1491, 1415, 1370, 1313 cm⁻¹; HRMS calcd for C₂₄H₃₀N₂NaO₇ (M + Na⁺): 481.1951, found 481.1953.

12b. 45% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 2H), 7.40 (s, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 4.10 – 4.13 (m, 2H), 3.98 – 4.01 (m, 2H), 3.55 – 3.68 (m, 16H), 2.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.9, 157.6, 138.9, 132.0, 124.9, 112.3, 105.5, 71.5, 71.4, 71.3, 70.4, 69.2, 25.4; FT-IR (CH₂Cl₂) 3430, 3298, 2920, 1658, 1591, 1531, 1419, 1366, 1307 cm⁻¹; HRMS calcd for C₂₆H₃₄N₂NaO₈ (M + Na⁺): 525.2213, found 525.2214.

12c. 47% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (s, 2H), 7.46 (s, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.34 – 4.46 (m, 2H), 3.79 – 3.84 (m, 4H), 3.32 – 3.70 (m, 14H), 1.99 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 160.0, 137.1, 132.1, 122.8, 114.4, 112.0, 72.0, 71.6, 71.5, 71.1, 70.6, 68.3, 24.7; FT-IR (CH₂Cl₂) 3406, 3266, 2870, 1670, 1607, 1575, 1530, 1466, 1421, 1371, 1300 cm⁻¹; HRMS calcd for C₂₈H₃₉N₂O₉ (M + 1): 547.2656, found 569.2663.