Supporting Information

Synthesis of Ladder-Type π-Conjugated Heteroacenes via Palladium-Catalyzed Double N-Arylation and Intramolecular O-Arylation

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General Methods. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glove box under argon atmosphere or with the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns. Most of reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). For a silica gel column chromatography, Silica gel 60N (spherical neutral, particle size 63-210 μm, Kanto Kagaku Co., Ltd.) was used. NMR spectra were recorded in deuteriochloroform on a 500 MHz spectrometers (1H 500 MHz; 13C 125 MHz). Chemical shifts are reported in ppm relative to the residual protiated solvent peak (7.26 ppm for CHCl3) for 1H and deuteriochloroform (77.16 ppm) or deutrioacetone (206.26 ppm) for 13C. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on a melting point apparatus. UV-Vis absorption spectra were recorded on a UV-VIS-NIR scanning spectrophotometer. The recycling preparative GPC was performed with a JAI GEL-1H and -2H columns (chloroform as an eluent). High resolution mass spectra are taken with FAB method. X-ray crystallographic analyses were recorded on a CCD diffractometer.
X-ray Crystallography. A suitable crystal was mounted with mineral oil to the glass fiber and transferred to the goniometer of a diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) to $2\theta_{\text{max}} = 55^\circ$. The structures were solved by direct methods with SIR-97¹ and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-97²). The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.
Synthetic Procedures

**SCHEME S1.**

![Chemical structure](image)

**Synthesis of 2'-chlorobiphenyl-2-ol (11).** The crude material was obtained by using 2-bromophenol (173 mg, 1.0 mmol), 2-chlorophenylboronic acid (156 mg, 1.0 mmol), Pd(PPh3)4 (58 mg, 0.050 mmol), and Na2CO3 (212 mg, 2.0 mmol) in toluene (3.0 mL), EtOH (2.0 mL), and H2O (1.0 mL) (80 °C, 1 d) according to the procedure described for the synthesis of compound 14. Purification by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, Rf 0.4) provided 179 mg of the title product as a colorless solid (88% yield): mp 145.1−146.4 °C; 1H NMR (CDCl3) δ 7.56−7.52 (m, 1H), 7.38−7.36 (m, 3H), 7.33 (td, J = 7.7, 1.6 Hz, 1H), 7.16 (dd, J = 7.6, 1.6 Hz, 1H), 7.04−7.00 (m, 2H), 4.83 (s, 1H); 13C NMR (CDCl3) δ 152.7, 135.7, 134.2, 132.2, 130.8, 130.2, 129.9, 129.8, 127.4, 126.0, 120.7, 116.0. HRMS-FAB+ (m/z) calcd for C12H9ClO 204.0342, found 204.0344.

**Synthesis of 2'-(1,1,2,2,3,3,4,4,4-nonafluorobutanesulfonyloxy)-2-chlorobiphenyl (6).** The crude material was obtained by using 11 (43 mg, 0.21 mmol), triethylamine (0.10 mL, 1.1 mmol), and nonafluorobuthanesulfonic anhydride (0.10 mL, 0.32 mmol) in dichloromethane (2.0 mL) (0 °C, 7 h) according to the procedure described for the synthesis of compound 5. Purification by column chromatography (silica gel; 14% AcOEt in hexane as an eluent, Rf 0.3) provided 93 mg of the title product (88% yield): mp 170.1−171.4 °C; 1H NMR (CDCl3) δ 7.64−7.60 (m, 1H), 7.40−7.38 (m, 3H), 7.36 (td, J = 7.7, 1.6 Hz, 1H), 7.16 (dd, J = 7.6, 1.6 Hz, 1H), 7.04−7.00 (m, 2H), 4.83 (s, 1H); 13C NMR (CDCl3) δ 152.7, 135.7, 134.2, 132.2, 130.8, 130.2, 129.9, 129.8, 127.4, 126.0, 120.7, 116.0. HRMS-FAB+ (m/z) calcd for C12H9ClO 204.0342, found 204.0344.
as a colorless solid (91% yield): mp 82.4–83.2 °C; $^1$H NMR (CDCl$_3$) $\delta$ 7.52–7.45 (m, 3H), 7.43–7.40 (m, 2H), 7.39–7.33 (m, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 147.2, 134.6, 133.8, 133.4, 132.5, 132.0, 130.09, 130.07, 129.8, 128.4, 126.8, 121.8, 118.5–109.6 (m, CF$_2$CF$_2$CF$_2$CF$_3$). HRMS-FAB$^+$ ($m$/z) calcd for C$_{16}$H$_8$ClF$_9$O$_3$S 485.9739, found 485.9741.

**SCHEME S2.**

2-Chloro-4-hexynylaniline (22). A flame-dried 100 mL round-bottom flask containing a magnetic stirring bar was charged with 2-chloro-4-iodoaniline (4.0 g, 15.8 mmol), 1-hexyne (2.0 mL, 17.4 mmol), PdCl$_2$(PPh$_3$)$_2$ (554 mg, 0.79 mmol), Cul (31 mg, 0.16 mmol), and triethylamine (30 mL) under argon.
The mixture was stirred at room temperature overnight. The reaction mixture was filtered with a pad of Celite and concentrated. The residue was poured into 5 mL of water, extracted with Et$_2$O (10 mL × 3). The combined organic layers were washed with 2 $M$ aqueous NH$_4$Cl and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated. The crude residue was purified by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, $R_f$ 0.5) to provide 3.1 g of the title product as a colorless oil (96% yield): \[^1\text{H NMR} (\text{CDCl}_3) \delta 7.30 (\text{d, } J = 1.9 \text{ Hz} \ 1\text{H}), 7.10 (\text{dd, } J = 8.3, 1.9 \text{ Hz, } 1\text{H}), 6.64 (\text{d, } J = 8.3 \text{ Hz, } 1\text{H}), 4.11 (\text{brs, } 2\text{H}), 2.37 (\text{t, } J = 7.1 \text{ Hz, } 2\text{H}), 1.59–1.53 (\text{m, } 2\text{H}), 1.49–1.42 (\text{m, } 2\text{H}), 0.94 (\text{t, } J = 7.1 \text{ Hz, } 3\text{H}); \[^{13}\text{C NMR} (\text{CDCl}_3) \delta 142.6, 132.5, 131.1, 118.7, 115.4, 114.6, 88.9, 79.7, 31.0, 22.1, 19.2, 13.8.\]

HRMS-FAB$^+$ (m/z) calcd for C$_{12}$H$_{14}$ClN 207.0815, found 207.0811.

2-(2-Chloro-4-hexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23). A suspension of 22 (340 mg, 6.0 mmol) and palladium (10 wt% on activated carbon; 300 mg) in EtOH (5 mL) was stirred at room temperature under a hydrogen atmosphere (1 atm) for 10 h. The reaction mixture was filtered through a pad of Celite, and then the filtrate was concentrated. After the crude residue was dried under reduced pressure for 1 h, 2-chloro-4-hexylaniline was obtained as colorless oil that was used for next step without further purification.

The crude 2-chloro-4-hexylaniline was dissolved in 3.5 $M$ aqueous HCl (8.8 mL) at 0 °C, and then a solution of sodium nitrite (460 mg, 1.1 mmol) in water (5 mL) was added slowly. After the reaction mixture was stirred for 15 min, a solution of sodium iodide (9.9 g, 66.0 mmol) in water (12 mL) was added. The resulting mixture was stirred for further 15 min and extracted with Et$_2$O (15 mL × 3). The combined
organic layers were washed twice with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. After the residue was dried under reduced pressure for 4 h, 2-chloro-1-iodo-4-hexylbenzene was obtained as a brown oil in almost pure form that was used next step without further purification.

A flame-dried 80 mL Schlenk tube containing a magnetic stirring bar was charged with PdCl₂(dppf) (246 mg, 0.14 mmol), KOAc (824 mg, 8.4 mmol), bis(pinacolate)diboron (1.8 g, 7.2 mmol), and the crude 2-chloro-1-iodo-4-hexylbenzene (ca. 2.8 mmol) under argon. After DMSO (15 mL) was added through the septum via syringe, the mixture was degassed by freeze-pump-thaw cycles. The resulting mixture was stirred at 80 °C for 2 d under argon. The reaction mixture was cooled to ambient temperature, poured into 5 mL of water, and extracted with Et₂O (30 mL × 3). The organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude residue was dried under reduced pressure for 1 h, and used for next step without further purification since 23 was found to decompose under purification conditions [silica gel column chromatography, recycling preparative GPC (CHCl₃ as eluent)]. The ¹H NMR analysis of the crude residue showed that it contained almost only 23 and bis(pinacolate)diboron (23/bis(pinacolate)diboron = 1/0.2). Based on this ratio, the amount of 23 added in the reaction mixture was estimated in the next coupling step. ¹H NMR (CDCl₃) δ 7.58 (d, J = 7.6 Hz, 1H), 7.14 (s, 1H), 7.01 (d, J = 7.6 Hz, 1H), 2.54 (t, J = 7.6 Hz, 2H), 1.55 (quint, J = 7.3 Hz, 2H), 1.33 (s, 12H), 1.28–1.21 (m, 6H, The signal of methyl groups of bis(pinacolate)diboron overlaps in this range.), 0.87 (t, J = 6.6 Hz, 3H).

**2-(2-Chloro-4-cyanophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24).** A solution of sodium
nitrite (560 g, 8 mmol) in water (4 mL) was added slowly to a solution of 4-amino-3-chlorobenzonitrile (508 g, 3 mmol) in 5.4 M aqueous HCl (3.5 mL) at 0 °C with stirring over 30 min. To the resulting mixture was added a solution of sodium iodide (5.5 g, 33 mmol) in water (1.5 mL). The reaction mixture was stirred for further 15 min, and then extracted with CHCl₃ (10 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated. After the crude residue was dried for 4 h under reduced pressure, 3-chloro-4-iodobenzonitrile was obtained as a white solid in almost pure form that was used for next step without further purification.

A flame-dried 80 mL Schlenk tube containing a magnetic stirring bar was charged with PdCl₂(dppf) (114 mg, 0.14 mmol), KOAc (883 mg, 9.0 mmol), bis(pinacolate)diboron (853 mg, 3.4 mmol), and the crude 3-chloro-4-iodobenzonitrile under argon. After DMSO (15 mL) was added through the septum via syringe, the resulting mixture was degassed by freeze-pump-thaw cycles, and stirred at 90 °C for 2 days under argon. The reaction mixture was cooled to ambient temperature, poured into 10 mL of water, and extracted with AcOEt (15 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude residue was purified by column chromatography (silica gel; 33% AcOEt in hexane as an eluent, Rf 0.4) to provide 696 mg of the title product as a colorless solid (88% yield): mp 137.6−143.2°C; ¹H NMR (CDCl₃) δ 7.76 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 1.4 Hz, 1H), 7.50 (dd, J = 8.0, 1.4 Hz, 1H), 1.36 (s, 12H); ¹³C NMR (CDCl₃) δ 140.3, 137.0, 134.8 (C−B), 132.4, 129.2, 117.5, 115.4, 85.0, 24.9. Anal. Calcd for C₁₃H₁₅BClNO₂: C, 59.25; H, 5.74; N, 5.32. Found: C, 59.10; H, 5.69; N, 5.29.
Figure S1. $^1$H NMR spectrum of 11 (CDCl$_3$, 500 MHz).
Figure S2. $^{13}$C NMR spectrum of 11 (CDCl$_3$, 125 MHz).
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Figure S28. $^1$H NMR spectrum of 15a (CDCl$_3$, 500 MHz).

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Figure S29. $^{13}$C NMR spectrum of 15a (CDCl$_3$, 125 MHz).
Figure S30. $^1$H NMR spectrum of 15b (CDCl$_3$, 500 MHz).
Figure S31. $^{13}$C NMR spectrum of 15b (CDCl$_3$, 125 MHz).
Figure S32. $^1$H NMR spectrum of 16a (CDCl$_3$, 500 MHz).

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Figure S38. $^1$H NMR spectrum of 23 (CDCl$_3$, 500 MHz).
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Figure S42. nOe spectrum of 2c (CDCl₃).
**Figure S43.** nOe spectrum of 2c (CDCl$_3$).

**Figure S44.** HMQC spectrum of 2c (CDCl$_3$).
Figure S45. HMBC spectrum of 2c (CDCl₃).
Figure S46. nOe spectrum of 3 (CDCl₃).

Figure S47. ¹H–¹H COSY spectrum of 3 (CDCl₃).
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