Supporting Information

endo-Functionalized Cyclic Oligophenylenes: Synthesis and Complexation with a Chiral Phosphoric Acid
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1. General methods

All operations were performed under air unless otherwise noted. NMR spectra for product characterization (\(^1\)H and \(^{13}\)C) were recorded on a Bruker DPX-400 (400 MHz for \(^1\)H and 100 MHz for \(^{13}\)C) spectrometer using CDCl\(_3\) [residual CHCl\(_3\) (7.26 ppm) served as an internal standard in \(^1\)H NMR and CDCl\(_3\) (77.0 ppm) in \(^{13}\)C NMR] and dimethylsulfoxide-\(d_6\) (DMSO-\(d_6\)) [residual DMSO (2.50 ppm) served as an internal standard in \(^1\)H NMR and DMSO-\(d_6\) (39.5 ppm) in \(^{13}\)C NMR] as a solvent. Chemical shifts are expressed in parts per million (ppm). IR spectra were recorded on a JASCO FT/IR-4600 (ATR). High-resolution mass analyses (MALDI\(^+\)) were performed on a JEOL JMS-S3000 SpiralTOF (MALDI TOF) mass spectrometer. GPC purification was performed on a LC-908 (Japan Analytical Industry Co., Ltd.) with JAIGEL 1HH and 2HH as purification columns.

2. Retrosynthetic route of cyclic oligophenylenes 1

![Diagram](image-url)

**Scheme S1.** Retrosynthetic route of cyclic oligophenylenes 1.
3. Spectral data of cyclic oligophenylenes 1
1(OH)

Figure S1. $^1$H NMR spectrum of 1(OH).

Figure S2. $^{13}$C NMR spectrum of 1(OH).
Figure S3. ROEY spectrum of 1(OH).

Figure S4. MALDI-TOF MS spectra of 1(OH).

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Figure S5. $^1$H NMR spectrum of $I$(OH, NH$_2$).

Figure S6. $^{13}$C NMR spectrum of $I$(OH, NH$_2$).
Figure S7. ROESY spectrum of 1(OH, NH₂).

Figure S8. MALDI-TOF MS spectra of 1(OH, NH₂).
Figure S9. $^1$H NMR spectrum of 1(OH, OH).

Figure S10. $^{13}$C NMR spectrum of 1(OH, OH).
Figure S11. ROESY spectrum of 1(OH, OH).

Figure S12. MALDI-TOF MS spectra of 1(OH, OH).
I(NH₂, NH₂)

Figure S13. $^1$H NMR spectrum of I(NH₂, NH₂).

Figure S14. $^{13}$C NMR spectrum of I(NH₂, NH₂).
Figure S15. ROESY spectrum of 1(NH₂, NH₂).

Figure S16. MALDI-TOF MS spectra of 1(NH₂, NH₂).
Figure S17. $^1$H NMR spectra (400 MHz, CDCl$_3$, 303 K) of 1(NH$_2$, NH$_2$), 1(OH, NH$_2$), and 1(OH, OH).

Figure S18. IR spectra of 1(OH, NH$_2$), 1(NH$_2$, NH$_2$), and 1(OH, OH).
4. Temperature dependent NMR study of compound 3a

Temperature-dependent $^1$H NMR study of a CDCl$_3$ solution of compound 3a from 20 ºC to 58 ºC was examined for the study of exchange of atropisomers. From the plot of ln(k/T) vs. 1/T, activation parameters $\Delta H^\dagger = 43$ kJ/mol, $\Delta S^\dagger = -87$ J/K•mol, and activation free energy $\Delta G^\dagger (25^\circ$C) = 69 kJ/mol were obtained.

Figure S20. a) Equilibrium of three atropisomers of 3a. b) Temperature-dependent NMR of compound 3a from 20 ºC to 58 ºC. c) ln(k/T) vs. 1/T plot.
5. Complexation of 1(NH₂, NH₂) with (+)–10

5-1. MALDI-TOF MS of the host–guest complex (+)–10@1(NH₂, NH₂)

The molecular ion peak corresponding to 1:1 host–guest complex (+)–10@1(NH₂, NH₂)+K⁺ was clearly observed.

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**Figure S21.** ROESY spectrum of 3a.

**Figure S22.** MALDI-TOF MS spectra of 1:1 host–guest complex (+)–10@1(NH₂, NH₂).
5.2. Dilution experiments of the host–guest complex (+)-10@1(NH₂, NH₂)

Dilution experiments were performed on a CDCl₃ solution of 1: 1 mixture of (+)-10 and 1(NH₂, NH₂) and ¹H NMR spectra were recorded at 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mM. The dilution date was analyzed and fitted to a 1:1 binding model using NMRDil_HG³¹ and association constant was calculated to 608 M⁻¹.
**Figure S23.** Dilution experiment. $^1$H NMR spectra of a CDCl$_3$ solution of 1: 1 mixture of (+)-10 and 1(NH$_2$, NH$_2$) at various concentrations. Curve fitting of dilution data by NMRDil_HG.

5-3. Molecular modeling of the host–guest complex (+)–10@1(NH$_2$, NH$_2$)

Molecular modeling was performed by molecular mechanics calculations (MMFF; Spartan). It clearly shows that the size of inner space of 1(NH$_2$, NH$_2$) is large enough for the inclusion of one molecule of a large chiral phosphoric acid (+)–10.

![Molecular modeling of (+)–10@1(NH$_2$, NH$_2$).](image)

**Figure S24.** Molecular modeling of (+)–10@1(NH$_2$, NH$_2$). a) Top view in ball and spoke model, b) top view in space filling model, and c) side view in space filling model.

6. Complexation of 1(OH, NH$_2$) with (+)–10

6-1. MALDI-TOF MS of the host–guest complex (+)–10@1(OH, NH$_2$)

The molecular ion peak corresponding to 1:1 host–guest complex (+)–10@1(OH, NH$_2$)+K$^+$ was clearly observed.

![MALDI-TOF MS spectra of 1:1 host–guest complex (+)–10@1(OH, NH$_2$).](image)
6-2. Dilution experiments of the host–guest complex (+)-10@1(OH, NH₂)

Dilution experiments were performed on a CDCl₃ solution of 1: 1 mixture of (+)-10 and 1(OH, NH₂) and ¹H NMR spectra were recorded at 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 mM. The dilution date was analyzed and fitted to a 1:1 binding model using NMRDil_HG and association constant was calculated to 641 M⁻¹.
Figure S26. Dilution experiment. $^1$H NMR spectra of a CDCl$_3$ solution of 1: 1 mixture of (+)-10 and 1(OH, NH$_2$) at various concentrations. Curve fitting of dilution data by NMRDil_HG.

7. X-ray crystallographic analysis of a crystal of 1(OMe)

Single crystals of 1(OMe) for X-ray diffraction analysis, were obtained as follows. At first, macrocycle 1(OMe)[Cl] was prepared by the annulation of 2c and septiphenylene precursor which was prepared by using 8d as a starting material. When borylation of Cl of 1(OMe)[Cl] was examined, 1(OMe) was obtained as a byproduct. Vapor diffusion method using a chloroform solution as a good solvent and acetonitrile as a poor solvent gave colorless thin platelet single crystals of 1(OMe).

![Chemical structures of 8d, 1(OMe)[Cl], and 1(OMe).](image)

The single crystal X-ray diffraction data were collected on a Rigaku R-AXIS II with IP area detector using CuKα ($\lambda = 1.54187$ Å). The crystals employed in this study proved to be weakly diffracting and rapidly suffered solvent loss. The structure was solved by direct methods with SHELXT. Although the molecular structure of macrocycle including four chloroform molecules was obtained, solvent molecules could not be successfully resolved. Consequently, the PLATON/SQUEEZE procedure was applied to handle the heavily disordered solvent molecules in the cavity of the macrocycle. The refinement was performed by full-matrix least squares method of $R^2$ using SHELXL-2016 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located at the calculated positions and refined with riding. One of the propyl groups of the macrocycle was disordered.
**Figure S28.** ORTEP drawing (50% probability ellipsoids) of 1(OMe).

**Figure S29.** Packing structure from $b$-axis.
**Table S1.** Crystal data and structure refinement for 1(OMe)

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| CCDC number                           | 1989979                                    |
| Identification code                   | 191113sk                                   |
| Empirical formula                     | C_{111}H_{126}O                            |
| Formula weight                        | 1476.22                                    |
| Temperature                           | 123 K                                      |
| Wavelength                            | 1.54187 Å                                  |
| Crystal system                        | monoclinic                                 |
| Space group                           | $P2_1/c$                                   |
| Unit cell dimensions                  | $a = 19.7001(4)$ Å, $\alpha = 90^\circ$  |
|                                      | $b = 9.7470(2)$ Å, $\beta = 90.421(6)^\circ$  |
|                                      | $c = 63.1258(13)$ Å, $\gamma = 90^\circ$  |
| Volume                                | 12120.9(4) Å³                             |
| Z                                     | 4                                          |
| Density (calculated)                  | 0.809 Mg/m³                                |
| Absorption coefficient                | 0.342 mm⁻¹                                 |
| F(000)                                | 3200                                       |
| Crystal size                          | 0.25 x 0.25 x 0.03 mm³                     |
| Theta range for data collection       | 3.58 to 58.88°.                            |
| Index ranges                          | -21<=h<=21, -10<=k<=10, -70<=l<=67         |
| Reflections collected                 | 116852                                     |
| Independent reflections               | 17343 [R(int) = 0.1357]                    |
| Completeness to theta = 25.24°        | 99.7 %                                     |
| Absorption correction                 | multi-scan                                 |
| Max. and min. transmission            | 0.990 and 0.639                            |
| Refinement method                     | Full-matrix least-squares on $F^2$        |
| Data / restraints / parameters        | 17343 / 0 / 1045                           |
| Goodness-of-fit on $F^2$              | 0.992                                      |
| Final R indices [I>2sigma(I)]         | $R_1 = 0.1098$, $wR_2 = 0.3065$            |
| R indices (all data)                  | $R_1 = 0.2141$, $wR_2 = 0.3701$           |
| Largest diff. peak and hole           | 1.05 and -0.28 e/Å⁻³                      |
PROBLEM: The value of sine(theta_max)/wavelength is less than 0.575
RESPONSE: The crystals employed in this study is thin and proved to be weakly diffracting and rapidly suffered solvent loss.

PROBLEM: Ratio Observed / Unique Reflections (too) Low .. 39% Check
RESPONSE: The crystals employed in this study is thin and proved to be weakly diffracting and rapidly suffered solvent loss.

PROBLEM: High wR2 Value (i.e. > 0.25) ................... 0.37 Report
RESPONSE: The crystals employed in this study is thin and proved to be weakly diffracting and rapidly suffered solvent loss.

PROBLEM: Large Reported Max. (Positive) Residual Density 1.05 eA$^-3$
RESPONSE: Due to flexibility and possibility of positional disorder of the MeO group.

PROBLEM: Disordered C112 has ADP max/min Ratio ..... 4.3 Note
RESPONSE: Due to disordered side chains.

PROBLEM: NonSolvent Resd 1 C Ueq(max) / Ueq(min) Range 6.2 Ratio
RESPONSE: Due to large amplitude around tert-butyl groups.
PROBLEM: Hirshfeld Test Diff for O1 -- C1 . 11.1 s.u.
RESPONSE: Due to flexibility and possibility of positional disorder of the MeO group.

PROBLEM: Large Hirshfeld Difference C90 -- C93 . 0.26 Ang.
RESPONSE: Due to large amplitude around the tert-butyl group.

PROBLEM: Low MainMol Ueq as Compared to Neighbors of C90 Check
RESPONSE: Due to large amplitude around the tert-butyl group.

8. Synthetic procedures and characterization of new compounds

Under an Ar atmosphere, precursor 3a (21.0 mg, 20.0 µmol), pin-protected 2c (20.0 µmol), Pd(PPh₃)₄ (2.4 mg, 2.0 µmol), Cs₂CO₃ (39 mg, 0.12 mmol), and degassed toluene (16 mL) were added to a flask. The resulting mixture was then refluxed for 1 day (Temperature of oil bath: 120 °C). The reaction mixture was treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. The crude product was purified by GPC to afford the desired product 1(OH) (10.0 mg, 33%). The pin-protected 2c was prepared as follows. Diboronic acid 2c (14.4 mg, 20.0 µmol) was treated with 2 equivalents of pinacol (4.8 mg, 40.0 µmol) in methanol/CHCl₃ and evaporated to afford pin-
protected 2c.

\[ ^1 \text{H NMR (400 MHz, CDCl}_3, \text{ r.t.): } \delta 7.22-7.19 (9H), 7.12 (s, 1H), 7.06 (s, 4H), 7.01 (s, 4H), 6.79 (m, 2H), 6.78 (m, 2H), 6.82 (s, 1H), 2.66 (d, \text{J} = 7.4 \text{ Hz, 2H}), 2.30 (s, 6H), 2.21 (s, 24H), 2.00 (s, 24H), 1.67 (tq, \text{J} = 7.4 \text{ Hz, 6H}) \]

\[ ^13 \text{C NMR (100 MHz, CDCl}_3, \text{ r.t.): } \delta 151.4, 151.2, 148.6, 142.4, 142.2, 142.1, 141.7, 141.5, 140.7, 140.4, 140.2, 139.2, 138.7, 136.6, 135.3, 134.6, 134.2, 131.9, 131.8, 129.7, 128.8, 128.3, 127.4, 127.1, 127.0, 126.8, 125.0, 124.8, 124.3, 124.0, 34.9, 34.9, 31.6, 29.7, 24.7, 21.0, 18.9, 18.1, 14.3 \]

HRMS (MALDI\(^+\)): m/z Calcd. for C\(_{112}\)H\(_{127}\)ClONa: 1545.9468, Found: 1545.9409 \[\text{[M+Na]}^+\]. IR (ATR): 3537, 2960, 2921, 2869, 1739, 1592, 1443, 1393, 1377, 1362, 1259, 1089, 1018, 799, 724 cm\(^{-1}\).

Under an Ar atmosphere, precursor 3a (52.6 mg, 50.0 \( \mu \text{mol} \)), pin-protected 2b (50.0 \( \mu \text{mol} \)), Pd(PPh\(_3\))\(_4\) (17.3 mg, 15.0 \( \mu \text{mol} \)), Cs\(_2\)CO\(_3\) (92.9 mg, 0.30 \( \text{mmol} \)), and degassed toluene (50 mL) were added to a flask. The resulting mixture was then refluxed for 1 day (Temperature of oil bath: 120 \(^\circ\text{C}\)). The reaction mixture was treated with sat. NH\(_4\)Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO\(_4\). The crude product was purified by GPC and washed with Et\(_2\)O to afford the desired product 1(OH, NH\(_2\)) (24.2 mg, 32%). The pin-protected 2b was prepared as follows. Diboronic acid 2b (35.5 mg, 50.0 \( \mu \text{mol} \)) was treated with 2 equivalents of pinacol (11.8 mg, 0.1 \( \text{mmol} \)) in methanol/CHCl\(_3\) and evaporated to afford pin-protected 2b.

\[ ^1 \text{H NMR (400 MHz, CDCl}_3, \text{ r.t.): } \delta 7.26 (4H), 7.23 (m, 2H), 7.23 (s, 2H), 7.22 (s, 4H), 7.16 (t, \text{J} = 1.6 \text{ Hz, 2H}), 7.02 (s, 4H), 6.73 (t, \text{J} = 1.2 \text{ Hz, 4H}), 4.87 (s, 1H), 3.59 (brs, 2H), 2.27 (s, 6H), 2.14 (s, 12H), 2.11 (s, 12H), 2.00 (s, 12H), 1.99 (s, 12H), 1.38 (s, 36H), 1.36 (s, 9H) \]

\[ ^13 \text{C NMR (100 MHz, CDCl}_3, \text{ r.t.): } \delta 151.5, 148.4, 142.5, 142.5, 142.1, 141.6, 141.6, 141.4, 140.6, 140.3, 140.2, 138.7, 138.7, 136.7, 136.5, 134.6, 134.4, 131.7, 131.7, 128.8, 128.2, 127.7, 127.4, 127.3, 127.0, 126.8, 126.1, 124.9, 124.6, 124.0, 123.9, 127.1, 126.4, 119.8, 117.8, 106.0, 34.9, 31.5, 20.9 \]

HRMS (MALDI\(^+\)): m/z Calcd. for C\(_{110}\)H\(_{124}\)ClNO: 1509.9366, Found: 1509.9406 \[\text{[M+H]}^+\]. IR (ATR): 3537, 3473, 3378, 2953, 2867, 1734, 1591, 1447, 1362, 1258, 1241, 1053, 1001, 884, 874, 723 cm\(^{-1}\).
Under an Ar atmosphere, precursor 3a (52.6 mg, 50.0 µmol), pin-proteced 2a (50.0 µmol), Pd(PPh₃)₄ (17.3 mg, 15.0 µmol), Cs₂CO₃ (92.9 mg, 0.30 mmol), and degassed toluene (50 mL) were added to a flask. The resulting mixture was then refluxed for 1 day (Temperature of oil bath: 120 ºC). The reaction mixture was treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. The crude product was purified by GPC to afford the desired product 1(OH, OH) (26.6 mg, 35%). The pin-protected 2a was prepared as follows. Diboronic acid 2a (35.8 mg, 50.0 µmol) was treated with 2 equivalents of pinacol (11.8 mg, 0.1 mmol) in methanol/CHCl₃ and evaporated to afford pin-protected 2a.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 7.22 (s, 4H), 7.18 (s, 4H), 7.01 (s, 8H), 6.77 (s, 4H), 4.82 (s, 2H), 2.29 (s, 12H), 2.11 (s, 24H), 2.00 (s, 24H), 1.38 (s, 36H).

¹³C NMR (100 MHz, CDCl₃, r.t.): δ 151.5, 148.5, 142.4, 142.0, 141.6, 140.2, 136.6, 134.6, 134.3, 131.7, 128.8, 127.4, 126.9, 126.8, 124.9, 124.0, 34.9, 31.5, 21.0, 19.0, 18.0. HRMS (MALDI⁺): m/z Calcd. for C₁₀₈H₁₁₈Cl₂O₄: 1516.85034, Found: 1516.84374 [M⁺]. IR (ATR): 3523, 2952, 2917, 2865, 1670, 1591, 1437, 1375, 1299, 1052, 884, 722, 696 cm⁻¹.

Under an Ar atmosphere, precursor 3b (46.3 mg, 44.3 µmol), pin-protected 2b (44.3 µmol), Pd(PPh₃)₄ (15.4 mg, 13.3 µmol), Cs₂CO₃ (86.6 mg, 266 µmol), and degassed toluene (45 mL) were added to a flask. The resulting mixture was then refluxed for 1 day (Temperature of oil bath: 120 ºC). The reaction mixture
was treated with sat. NH$_4$Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO$_4$. The crude product was purified by GPC to afford the desired product 1(NH$_2$, NH$_2$) (29.5 mg, 44%).

$^1$H NMR (400 MHz, CDCl$_3$, r.t.): $\delta$ 7.26 (4H), 7.25 (s, $J = 1.8$ Hz, 4H), 7.23 (s, 8H), 7.23 (s, 4H), 6.69 (t, $J = 1.4$ Hz, 2H), 3.65 (brs, 1H), 2.14 (s, 24H), 1.99 (s, 24H), 1.38 (s, 36H), 1.36 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$, r.t.): $\delta$ 151.6, 142.5, 141.6, 141.6, 140.2, 138.5, 136.6, 135.9, 132.0, 131.7, 128.2, 127.2, 126.3, 124.6, 123.9, 121.9, 34.9, 34.2, 31.7, 31.5, 21.0, 18.0. $^1$H DOSY (CDCl$_3$, r.t.): 0.83 m$^2$/Gs. HRMS (MALDI$^+$): m/z Calcd. for C$_{112}$H$_{130}$N$_2$: 1503.02285, Found: 1503.01652 [M]$^+$. IR (ATR): 3479, 3385, 2960, 2920, 2865, 2360, 2066, 1769, 1591, 1461, 1393, 1362, 1258, 1090, 1016, 874, 840, 798, 724 cm$^{-1}$.

Under an Ar atmosphere, precursor 3c (331 mg, 0.30 mmol), pin-protected 2c (0.30 mmol), Pd(PPh$_3$)$_4$ (34 mg, 0.03 mmol), Cs$_2$CO$_3$ (585 mg, 1.8 mmol), and degassed toluene (300 mL) were added to a flask. The resulting mixture was then refluxed for 22 h (Temperature of oil bath: 120 ºC). The reaction mixture was treated with sat. NH$_4$Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO$_4$. The crude product was purified by column chromatography ($n$-hexane/toluene = 4:1) and the desired product 1(OMe)[Cl] (103 mg, 23%) was obtained. The pin-protected 2c was prepared as follows. Diboronic acid 2c (216.8 mg, 0.30 mmol) was treated with 2 equivalents of pinacol (70.9 mg, 0.60 mmol) in methanol/CHCl$_3$ and evaporated to afford pin-protected 2c.

$^1$H NMR (400 MHz, CDCl$_3$, r.t.): $\delta$ 7.35 (s, 2H), 7.22 (s, 2H), 7.20 (m, 2H), 7.17 - 7.16 (m, 4H), 7.07 (s, 4H), 6.74 (m, 2H), 6.73 (m, 2H), 2.90 (s, 3H), 2.65 (t, $J = 7.8$ Hz, 4H), 2.14 (s, 12 H), 2.10 (s, 12H), 2.00 (s, 12H), 1.99 (s, 12H), 1.66 (tq, $J = 7.7$ Hz, 7.7 Hz, 4H), 1.39 (s,18H), 1.38 (s,18H), 0.97 (t, $J = 7.4$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, r.t.): $\delta$ 152.7, 150.5, 150.3, 141.4, 141.2, 140.8, 140.7, 140.5, 139.7, 139.3, 139.2, 139.1, 138.1, 137.8, 136.7, 134.8, 134.8, 134.3, 130.7, 130.7, 130.0, 128.8, 128.0, 127.8, 127.3, 127.1, 126.4, 125.9, 123.8, 123.5, 123.4, 122.7, 58.9, 33.9, 33.8, 30.5, 23.7, 19.9, 17.0, 17.0, 13.2. HRMS (MALDI$^+$): m/z Calcd. for C$_{111}$H$_{125}$ClO: 1508.9413, Found: 1508.9481 [M]$^+$. IR (ATR): 2959, 2919, 2867, 1591, 1563, 1456, 1378, 1362, 1241, 1093, 1012, 865, 799, 724 cm$^{-1}$.
Compound 1(OMe)[Cl] (35.4 mg, 23.4 µmol), bis(pinacolato)diboron (17.8 mg, 70.2 µmol), Pd(OAc)$_2$ (2.0 mg, 8.9 µmol), SPhos (4.8 mg, 12 µmol), K$_3$PO$_4$ (9.93 mg, 47 µmol) and degassed 1,4-dioxane (0.3 mL) were added to a pressure tube and the tube was filled with Ar. The resulting mixture was then refluxed for 4 days. The reaction mixture was treated with saturated NH$_4$Cl aq. and the organic materials were extracted with EtOAc. The organic layer was washed with brine, and dried over MgSO$_4$. The filtrate was evaporated and the crude product (1(OMe)[Bpin]/1(OMe)/1(OMe)[Cl] = 4 : 1 : 1.2) was purified by silica gel column chromatography (toluene/n-hexane = 1:4 to 1:1) to afford the desired product 1(OMe)[Bpin] (16.6 mg, 44%). Trace amount of 1(OMe) was also obtained as a byproduct.

Physical data of 1(OMe)[Bpin]

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 (s, 2H), 7.28 (s, 4H), 7.24-7.23 (m, 2H), 7.20 (m, 2H), 7.18-7.15 (m, 6H), 7.07 (s, 4H), 6.75 (m, 2H), 6.74 (m, 2H), 2.99 (s, 3H), 2.65 (t, $J$ = 7.8 Hz, 4H), 2.13 (s, 12H), 2.11 (s, 12H), 2.01 (s, 12H), 1.99 (s, 12H), 1.67 (tq, $J$ = 7.6 Hz, 7.6 Hz, 4H), 1.39 (s, 18H), 1.38 (s, 18H), 1.36 (s, 12H), 0.97 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 157.8, 151.4, 151.3, 142.3, 142.3, 141.7, 141.6, 141.2, 140.8, 140.5, 140.4, 140.1, 139.2, 138.8, 137.1, 136.4, 135.6, 135.5, 135.4, 135.3, 131.8, 131.0, 129.8, 128.3, 127.6, 127.0, 124.8, 124.4, 124.4, 123.9, 83.7, 60.0, 34.9, 34.9, 31.6, 31.6, 29.7, 24.9, 24.7, 21.0, 21.0, 18.0, 18.0, 14.3. The boron-bound carbons were not detected due to quadrupole relaxation. HRMS (MALDI$^+$): m/z Calcd. for C$_{117}$H$_{137}$BO$_3$: 1601.0672, Found: 1601.0649 [M$^+$].

IR (ATR): 2954, 2920, 2868, 2731, 1591, 1438, 1371, 1309, 1240, 1206, 1144, 1011, 968, 873, 857, 724, 694 cm$^{-1}$.

Physical data of 1(OMe)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.40 (s, 1H), 7.38 (s, 1H), 7.29 (s, 4H), 7.27 (t, $J$ = 1.6 Hz, 2H), 7.24-7.22 (m, 3H), 7.20 (t, $J$ = 1.6 Hz, 2H), 7.18-7.17 (m, 4H), 7.07 (s, 4H), 6.75 (t, $J$ = 1.6 Hz, 2H), 6.74 (t, $J$ = 1.6 Hz, 2H), 2.94 (s, 3H), 2.65 (t, $J$ = 7.8 Hz, 4H), 2.15 (s, 12H), 2.11 (s, 12H), 2.01 (s, 12H), 1.99 (s, 12H), 1.66 (tq, $J$ = 7.5 Hz, 7.5 Hz, 4H), 1.39 (s, 18H), 1.38 (s, 18H), 1.36 (s, 12H), 0.97 (t, $J$ = 7.4 Hz, 6H). HRMS (MALDI$^+$): m/z Calcd. for C$_{111}$H$_{126}$ONa: 1497.9701, Found: 1497.9703 [M+Na$^+$]. IR (ATR): 2956, 2920, 2867, 2727, 1715, 1590, 1458, 1361, 1259, 1218, 1090, 1010, 885, 860, 803, 723, 708, 529 cm$^{-1}$.
Under an Ar atmosphere, 3,5-dibromo-1-tert-butylbenzene (4.90 g, 16.8 mmol) was dissolved in THF (100 mL) and then n-BuLi (1.54 M in hexane, 10.9 mL, 16.8 mmol) was added dropwise to the solution at –78 ºC. The mixture was stirred for 30 min at –78 ºC, and then B(OiPr)₃ (11.6 mL, 50.4 mmol) was added, and further stirred at room temperature. After 12 h, 1 N HCl aq. was added and organic materials were extracted with EtOAc, and then combined extract was washed with brine and dried over MgSO₄. After the solvent was removed, the crude product of 3-Bromo-5-tert-butylphenylboronic acid was obtained. Without further purification, 1,8-diaminonaphthalene (2.65 g, 16.8 mmol) and toluene (50 mL) was added to the flask. The mixture was refluxed for 6 h. After solvent was evaporated, the residue was washed with MeOH to afford the desired compound 5 (6.98 g, 98% in 2 steps).

**1H NMR** (400 MHz, CDCl₃, r.t.): δ 7.61 (s, 1H), 7.57 (s, 1H), 7.54 (s, 1H), 7.15 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.44 (d, J = 7.8 Hz, 2H), 5.97 (s, 2H), 1.37 (s, 18H).

**13C NMR** (100 MHz, CDCl₃, r.t.): δ 153.5, 140.8, 136.3, 131.4, 130.4, 127.6, 126.7, 123.0, 119.9, 118.1, 106.2, 35.0, 31.3. The boron-bound carbon was not detected due to quadrupole relaxation. HRMS (MALDI⁺): m/z Calcd. for C₂₀H₂₀BrN₂B: 377.0939, Found: 377.0937 [M⁺]. IR (ATR): 3419, 3407, 3056, 2950, 2902, 2867, 1595, 1506, 1398, 1092, 817, 765, 696 cm⁻¹.

Under an Ar atmosphere, compound 5 (16.30 g, 43.0 mmol), bis(pinacolato)diboron (13.10 g, 51.6 mmol), Pd(dppf)Cl₂•DCM (351 mg, 0.43 mmol), KOAc (12.66 g, 129 mmol), and degassed 1,4-dioxane (150 mL) were added to a flask. The resulting mixture was then refluxed for 1 day. The reaction mixture was treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. After the solvent was evaporated, the residue was washed with MeOH to afford the desired product 6 (17.38 g, 95%).

**1H NMR** (400 MHz, CDCl₃, r.t.): δ 7.95 (m, 1H), 7.91 (s, 1H), 7.75 (m, 1H), 7.14 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 7.2 Hz, 2H), 6.10 (brs, 2H), 1.41 (s, 9H), 1.39 (s, 12H). **13C NMR** (100 MHz, CDCl₃, r.t.): δ 149.9, 141.2, 136.3, 135.2, 133.6, 131.1, 127.6, 119.8, 117.6, 105.9, 83.9, 34.8, 31.5, 24.9. The boron-bound carbon was not detected due to quadrupole relaxation. HRMS (MALDI⁺): m/z Calcd.
for C_{26}H_{32}N_{2}O_{2}B_{2}: 424.2723, Found: 424.2726 [M]^+. IR (ATR): 3405, 3377, 3053, 2976, 1597, 1509, 1369, 1314, 1260, 1135, 821, 768 cm^{-1}.

Under an Ar atmosphere, compound 6 (12.10 g, 28.4 mmol), 2-bromo-5-chloro-\(m\)-xylene (7.52 g, 34.3 mmol), Pd(PPh\(_3\))\(_4\) (392 mg, 0.34 mmol), Ba(OH)\(_2\)•8H\(_2\)O (17.94 g, 56.9 mmol), and degassed 1,4-dioxane (210 mL) were added to a flask. The resulting mixture was then refluxed for 1 day. The reaction mixture was treated with sat. NH\(_4\)Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO\(_4\). After the solvent was evaporated, the residue was washed with MeOH to afford the desired product 7 (11.01 g, 88%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), r.t.): \(\delta\) 7.62 (t, \(J = 1.6\) Hz, 1H), 7.26 (s, 1H), 7.20 (t, \(J = 1.2\) Hz, 1H), 7.14 (s, 2H), 7.14 (t, \(J = 7.8\) Hz, 2H), 7.06 (dd, \(J = 8.0, 1.0\) Hz, 2H), 6.42 (dd, \(J = 7.2, 0.8\) Hz, 2H), 6.01 (s, 2H), 2.03 (s, 6H), 1.40 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), r.t.): \(\delta\) 151.3, 141.0, 140.6, 139.5, 138.0, 136.3, 132.4, 129.0, 128.3, 127.6, 127.1, 126.4, 119.8, 117.8, 106.0, 34.9, 31.5, 20.9. The boron-bound carbon was not detected due to quadrupole relaxation. HRMS (MALDI^+): \(m/z\) Calcd. for C\(_{28}\)H\(_{28}\)N\(_2\)ClB: 437.2070, Found: 437.2071 [M]^+. IR (ATR): 3440, 3432, 3055, 2963, 2868, 1599, 1504, 1404, 1323, 1220, 1096, 879, 758, 583 cm\(^{-1}\).

Under an Ar atmosphere, compound 7 (13.70 g, 31.1 mmol), bis(pinacolato)diboron (9.47 g, 37.3 mmol), Pd(OAc)\(_2\) (279 mg, 1.24 mmol), SPhos (1.02 g, 2.48 mmol), K\(_2\)PO\(_4\) (19.80 g, 93.3 mmol) and degassed 1,4-dioxane (70 mL) were added to a flask. The resulting mixture was then refluxed for 2 days. The reaction mixture was treated with sat. NH\(_4\)Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO\(_4\). After the solvent was evaporated, the residue was purified by column chromatography (CHCl\(_3\)). The resultant solid was washed with \(n\)-hexane to afford the desired product 4 (15.34 g, 93%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), r.t.): \(\delta\) 7.61 (s, 3H), 7.29 (t, \(J = 3.2\) Hz, 1H), 7.22 (s, 1H), 7.14 (t, \(J = 7.8\) Hz,
2H), 7.05 (d, J = 8.0 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 6.03 (brs, 2H), 2.07 (s, 6H), 1.39 (s, 9H), 1.38 (s, 12H). ^13C NMR (100 MHz, CDCl₃, r.t.): δ 151.1, 145.3, 141.1, 140.4, 136.3, 135.5, 133.8, 128.8, 128.1, 127.6, 126.2, 119.8, 117.7, 106.0, 83.8, 34.9, 31.5, 24.8, 20.7. The boron-bound carbon was not detected due to quadrupole relaxation. HRMS (MALDI⁺): m/z Calcd. for C₉₄H₄₀N₂O₂B₂: 528.3349, Found: 528.3354 [M⁺]. IR (ATR): 3438, 3049, 2964, 1600, 1504, 1406, 1362, 1309, 1143, 758 cm⁻¹.

2,6-Dibromo-4-chloro-3,5-dimethylphenol (15.00 g, 47.8 mmol) K₂CO₃ (9.89 g, 71.7 mmol) and acetone (50 mL) were added to a flask. The resulting solution was stirred for 15 min at r.t. and then Mel (4.40 mL, 71.7 mmol) was added slowly. The reaction mixture was heated for 3 h. The precipitate was filtered, washed with water and a small amount of acetone dried at 60 ºC under vacuum to afford the desired product 8a (14.86 g, 95%).

^1H NMR (400 MHz, CDCl₃, r.t.): δ 3.86 (s, 3H), 2.54 (s, 6H). ^13C NMR (100 MHz, CDCl₃, r.t.): δ 152.8, 136.4, 130.8, 118.5, 60.3, 21.9. HRMS (EI⁺): m/z Calcd. for C₉₃H₃₉Br₂ClO: 325.8709, Found: 325.8707 [M⁺]. IR (ATR): 2938, 2849, 1445, 1362, 1315, 1072, 930, 743, 677 cm⁻¹.

Under an Ar atmosphere, compound 8a (1.23 g, 3.75 mmol), compound 4 (4.97 g, 9.36 mmol), Pd₂(dba)₃·CHCl₃ (390.8 mg, 0.378 mmol), t-BuPH·BF₄ (218.5 mg, 0.753 mmol), KOH (1.28 g, 22.8 mmol), and degassed THF (75 mL) and H₂O (3.75 mL) were added to a flask. The reaction mixture was stirred for 15 h at r.t. and then filtered through Celite. The resulting solution was evaporated and treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. The crude product was purified by column chromatography (chloroform/n-hexane = 1:1) and the desired product S1 (2.76 g, 75%) was obtained. Three atropisomers were observed in NMR.

^1H NMR (400 MHz, CDCl₃, r.t.): δ 7.63 (s, 2H), 7.40-7.34 (2H), 7.34-7.28 (2H), 7.18-7.11 (4H), 7.07 (s, 4H), 7.10-7.04 (4H), 6.44 (d, J = 7.1 Hz, 4H), 6.10-6.02 (4H), 3.22 (s, 3H), 2.32 (s, 6H), 2.10 (s, 12H), 1.46-1.40 (18H). ^13C NMR (100 MHz, CDCl₃, r.t.): δ 153.9, 151.0, 141.1, 140.9, 140.6, 136.4, 135.6, 134.9, 134.7, 130.9, 129.4, 128.9, 128.7, 127.6, 126.1, 119.8, 117.7, 106.0, 61.1, 34.9, 31.5, 21.1, 19.1. The boron-
bound carbons were not detected due to quadrupole relaxation. HRMS (MALDI\(^{+}\)): \(m/z\) Calcd. for C\(_{65}\)H\(_{65}\)Cl\(_{4}\)N\(_{4}\)B\(_{2}\)O: 974.5048, Found: 974.5018 [M\(^{+}\)]. IR (ATR): 3440, 3050, 2952, 2865, 1599, 1503, 1404, 1097, 1077, 818, 758, 583 cm\(^{-1}\).

Under an Ar atmosphere, Compound S\(_{1}\) (1.95 g, 2.00 mmol) and DCM (30 mL) were added to a flask. The resulting solution was stirred at 0 °C and BBr\(_{3}\) (1.0 M in DCM, 10.00 mL, 10.0 mmol) was added slowly. The reaction mixture was stirred at 0 °C for 3 h. The resulting solution was treated with water and organic materials were extracted with CHCl\(_{3}\), washed with brine and dried over MgSO\(_{4}\). The solvent was removed under reduced pressure to afford demethylated compound in quantitative. The compound was dissolved in THF (30 mL) and 6 N HCl aq. (3.0 mL) was added and then the reaction mixture was stirred under Ar at r.t. for 2 d. To the mixture was added 1 N HCl aq. and the organic materials were extracted with Et\(_{2}\)O. The organic layer was washed with brine, dried over MgSO\(_{4}\), and filtered. The concentration of the filtrate under reduced pressure gave the product 2a (1.39 g, 97%).

\(^{1}\)H NMR (400 MHz, DMSO-\(d_6\), 343 K): \(\delta\) 7.85 (s, 2H), 7.75 (brs, 4H), 7.45 (s, 2H), 7.24 (s, 2H), 6.99 (s, 4H), 2.16 (s, 6H), 2.03 (s, 12H), 1.35 (s, 18H).\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\), r.t.): \(\delta\) 149.7, 149.6, 140.9, 138.7, 135.5, 135.2, 133.8, 133.2, 131.8, 129.3, 129.2, 129.1, 127.8, 34.4, 31.3, 31.2, 20.7. The boron-bound carbons were not detected due to quadrupole relaxation.

Under an Ar atmosphere, compound 2a (1.79 g, 2.50 mmol), compound 9 (2.39 g, 10 mmol), Cs\(_{2}\)CO\(_{3}\) (1.63 g, 5.00 mmol), Pd(PPh\(_{3}\))\(_{4}\) (72.2 mg, 62.5 µmol), and degassed toluene/MeOH (2:1) (45 mL) were added to a flask. The reaction mixture was refluxed for 1 d. The resulting solution was treated with sat. NH\(_{4}\)Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO\(_{4}\). After removal of the solvent, the crude product was washed with \(n\)-hexane/CHCl\(_{3}\) (3:7) (10 mL) and filtered to remove unreacted 9. The filtrate was purified by column chromatography (\(n\)-hexane/CHCl\(_{3}\) = 4:1) and
the desired product 3a (1.80 g, 68%) was obtained. Three atropisomers were observed in NMR.

\[ ^1H\text{NMR (400 MHz, CDCl}_3, \text{r.t.): } \delta 7.22-7.16 (2H), 7.10-7.06 (2H), 7.06-7.00 (4H), 6.78-6.68 (2H), 5.04-4.92 (1H), 2.48-2.44 (12H), 2.30-2.23 (6H), 2.11-2.10 (12H), 2.06-2.00 (12H), 1.38-1.30 (18H). \]

\[ ^{13}C\text{NMR (100 MHz, CDCl}_3, \text{r.t.): } \delta 151.1, 141.1, 141.0, 140.9, 140.4, 139.1, 138.4, 136.6, 136.4, 129.3, 128.6, 128.3, 127.6, 127.6, 126.7, 126.2, 119.8, 117.8, 106.0, 34.9, 34.1, 31.7, 31.5, 21.1. \]

HRMS (MALDI\(^+\)): \( m/z \) Calcd. for C\(_{30}\)H\(_{71}\)OBr\(_2\)ClNa: 1071.3452, Found: 1071.3450 [M+Na]\(^+\). IR (ATR): 3529, 2951, 2919, 2866, 1592, 1442, 1381, 1300, 1214, 1052, 999, 915, 884, 724, 695 cm\(^{-1}\).

![Chemical Reaction Diagram](image)

Under an Ar atmosphere, isophthalaldehyde (3.41 g, 25.4 mmol), triphenylethylphosphonium bromide (19.83 g, 53.4 mmol), 18-crown-6 (370 mg, 1.40 mmol), K\(_2\)CO\(_3\) (7.38 g, 53.4 mmol), and degassed DCM (130 mL) were added to a flask. The reaction mixture was refluxed for 2 d. The resulting solution was filtered and the precipitate was washed with \( n \)-hexane. The combined filtrate was evaporated under reduced pressure. The resulting solid was washed with \( n \)-hexane and filtered and filtrate was purified by colomun chromatography (\( n \)-hexane) to afford the dialkene compound as \( E,Z \) mixture (3.27 g). The diakene compound, 10% Pd/C (300 mg) and THF (135 mL) were added to a flask. The solution was stirred at r.t. for 12 h under H\(_2\) atmosphere and then filtered and filtrate was evaporated to give the desired compound S2 (3.25 g 79%)

\[ ^1H\text{NMR (400 MHz, CDCl}_3, \text{r.t.): } \delta 7.20-7.16 (m, 1H), 7.00-6.98 (m, 3H), 2.56 (t, J = 7.6 Hz, 4H), 1.64 (tq, J = 7.4 Hz, 7.4 Hz, 4H), 0.94 (t, J = 7.2 Hz, 6H). \]

\[ ^{13}C\text{NMR (100 MHz, CDCl}_3, \text{r.t.): } \delta 142.5, 128.7, 128.0, 125.7, 38.1, 24.6, 13.9. \]

HRMS (El\(^-\)): \( m/z \) Calcd. for C\(_{12}\)H\(_8\): 162.1409, Found: 162.1409 [M]\(^+\). IR (ATR): 3054, 3018, 2957, 2928, 1607, 1588, 1487, 1456, 1444, 1378, 1092, 771, 700 cm\(^{-1}\).

Compound S2 (1.62 g, 10.0 mmol), iodine (2.54 g, 10.0 mmol), H\(_3\)IO\(_6\) (1.48 g, 6.50 mmol) AcOH (10 mL), H\(_2\)O (2 mL), and H\(_2\)SO\(_4\) (0.3 mL) were added to a flask. The reaction mixture was heated at 90 °C for 12 h. The resulting solution was treated with 10% NaHSO\(_3\) aq. and organic materials were extracted with \( n \)-hexane and dried over MgSO\(_4\). After removal of solvent, the crude product was purified by colomun chromatography (\( n \)-hexane) to afford the desired product 8c (3.65 g 88%)

\[ ^1H\text{NMR (400 MHz, CDCl}_3, \text{r.t.): } \delta 8.21 (s, 1H), 7.02 (s, 1H), 2.61 (t, J = 7.8 Hz, 4H), 1.60 (tq, J = 7.7 Hz, 4H). \]
7.7 Hz, 2H), 0.98 (t, J = 7.4 Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), r.t.): \(\delta\) 148.1, 145.2, 129.9, 97.7, 42.1, 23.3, 13.7. HRMS (EI\(^+\)): m/z Calcd. for C\(_{12}\)H\(_{18}\)I\(_2\): 413.9338, Found: 413.9340 [M]\(^+\). IR (ATR): 2954, 2925, 2867, 1449, 1362, 1017, 871, 772 cm\(^{-1}\).

Under an Ar atmosphere, compound 8c (1.66 g, 4.00 mmol), compound 4 (4.67 g, 8.80 mmol), Ba(OH)\(_2\)•8H\(_2\)O (3.79 g, 12.0 mmol), Pd(PPh\(_3\))\(_4\) (231 mg, 0.20 mmol), and degassed 1,4-dioxane (40 mL) were added to a flask. The reaction mixture was refluxed for 1 d and then filtered through Celite. The filtrate was treated with sat. NH\(_4\)Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO\(_4\). The crude product was purified by column chromatography (toluene/n-hexane = 2:3) and desired product S3 (3.14 g, 81%) was obtained.

\(^1\)H NMR (400 MHz, CDCl\(_3\), r.t.): \(\delta\) 7.63 (s, 2H), 7.39 (s, 2H), 7.32 (s, 2H), 7.23 (s, 1H), 7.18 (s, 1H), 7.15 (s, 4H), 7.14 (t, J = 7.7 Hz, 4H), 7.05 (d, J = 7.7 Hz, 4H), 6.43 (d, J = 7.7 Hz, 4H), 6.07 (s, 4H), 2.72 (t, J = 7.5 Hz, 4H), 2.01 (s, 12H), 1.69 (tq, J = 7.5 Hz, 7.5 Hz, 4H), 1.42 (s, 18H), 0.98 (t, J = 7.5 Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), r.t.): \(\delta\) 151.0, 141.2, 140.6, 140.5, 140.4, 139.0, 138.7, 136.4, 135.6, 132.0, 130.2, 129.4, 128.8, 128.5, 127.6, 126.1, 119.8, 117.7, 106.0, 34.9, 34.9, 31.5, 24.8, 21.1, 14.3. The boron-bound carbons were not detected due to quadrupole relaxation. HRMS (MALDI\(^+\)): m/z Calcd. for C\(_{68}\)H\(_{72}\)N\(_4\)B\(_2\): 966.5958, Found: 966.5934 [M]\(^+\). IR (ATR): 3440, 3049, 2954, 2866, 2359, 1600, 1502, 1404, 1374, 1326, 1097, 817, 759 cm\(^{-1}\).

Under an Ar atmosphere, Compound S3 (2.14 g, 2.21 mmol) and THF (30 mL) were added to a flask. 6 N HCl aq. (4.0 mL) was added to the solution and then the reaction mixture was stirred at r.t. for 2 d. To the mixture was added 1 N HCl aq. and the organic materials were extracted with Et\(_2\)O. The organic layer was washed with brine, dried over MgSO\(_4\), and filtered. The concentration of the filtrate under reduced pressure gave the product 2c (1.52 g, 95%).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\), r.t.): \(\delta\) 7.99 (s, 4H), 7.84 (s, 2H), 7.43 (s, 2H), 7.26 (s, 1H), 7.23 (s, 2H), 7.10 (s, 4H), 7.02 (s, 1H), 2.65 (t, J = 7.8 Hz, 4H), 2.02 (s, 12H), 1.58 (tq, J = 7.4 Hz, 7.4 Hz, 4H), 1.33 (s, 18H), 0.88 (t, J = 7.4 Hz, 6H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\), r.t.): \(\delta\) 149.6, 140.6, 139.5, 138.9, 138.7,
138.0, 135.1, 131.8, 130.2, 129.2, 128.0, 127.7, 121.6, 34.5, 34.2, 31.3, 24.1, 20.8, 14.0. The boron-bound carbons were not detected due to quadrupole relaxation.

Under an Ar atmosphere, 2,6-dibromo-4-tert-butylaniline (301 mg, 0.980 mmol), compound 4 (1.14 g, 2.16 mmol), Pd2(dba)3•CHCl3 (67.3 mg, 49.0 µmol), t-BuPHBF4 (28.4 mg, 98.0 µmol), KOH (329 mg, 5.88 mmol), and degassed THF (20 mL) and H2O (1 mL) were added to a flask. The reaction mixture was stirred at r.t. for 1 d and then filtered through Celite. The resulting solution was evaporated and treated with sat. NH4Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO4. The crude product was purified by column chromatography (toluene/n-hexane = 1:5) and desired product S4 (836 mg, 90%) was obtained.

\[^1^H\] NMR (400 MHz, CDCl3, r.t.): \(\delta 7.66\) (2H), 7.42 (t, \(J = 1.6\) Hz, 2H), 7.36 (s, 4H), 7.34 (2H), 7.25 (s, 2H), 7.16 (t, \(J = 7.6\) Hz, 4H), 7.07 (d, \(J = 8.0\) Hz, 4H), 6.44 (d, \(J = 7.2\) Hz, 4H), 6.08 (brs, 4H), 3.99 (brs, 2H), 2.16 (s, 12H), 1.44 (s, 18H), 1.40 (s, 9H). \[^13^C\] NMR (100 MHz, CDCl3, r.t.): \(\delta 151.1, 141.1, 141.0, 141.0, 140.4, 139.1, 138.3, 136.3, 136.4, 129.2, 128.6, 128.3, 127.6, 126.7, 126.2, 119.8, 117.8, 106.0, 34.9, 34.1, 31.7, 31.5, 21.1. The boron-bound carbons were not detected due to quadrupole relaxation. HRMS (MALDI\(^{+}\)): \(m/z\) Caled. for C\(_{66}\)H\(_{90}\)N\(_3\)B\(_2\): 953.5734; Found: 953.5694 [M\(^{+}\)]. IR (ATR): 3441, 3050, 2952, 2865, 1599, 1502, 1404, 1326, 1216, 1166, 1097, 874, 818, 758, 719, 665, 582 cm\(^{-1}\).

Compound S4 (1.56 g, 1.64 mmol) was dissolved in THF (15.5 mL) and 6 N HCl aq. (1.55 mL) was added and then the reaction mixture was stirred under Ar at r.t. for 2 d. To the mixture was added 1 N HCl aq. and the organic materials were extracted with Et2O. The organic layer was washed with brine, dried over MgSO4, and filtered. The concentration of the filtrate under reduced pressure gave the product 2b (1.11 g, 96%).

\[^1^H\] NMR (400 MHz, DMSO-\(d_6\), r.t.): \(\delta 7.98\) (s, 4H), 7.85 (s, 2H), 7.44 (s, 2H), 7.24 (t, \(J = 1.6\) Hz, 2H), 7.22 (s, 4H), 7.05 (s, 2H), 4.14 (brs, 2H), 2.04 (s, 12H), 1.33 (s, 18H), 1.31 (s, 9H). \[^13^C\] NMR (100 MHz, DMSO-
materials were extracted with EtOAc. The resulting solution was evaporated and treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. After removal of the solvent, the crude product was purified by column chromatography (n-hexane/CHCl₃ = 4:1) and desired product 3b (66.3 mg, 74%) was obtained.

1H NMR (400 MHz, CDCl₃, r.t.): δ 7.28 (s, 4H), 7.21 (t, J = 1.6 Hz, 2H), 7.20 (s, 2H), 7.08 (t, J = 1.8 Hz, 2H), 6.75 (t, J = 1.6 Hz, 2H), 3.90 (brs, 2H), 2.47 (s, 12H), 2.15 (s, 12H), 2.04 (s, 12H), 1.35 (s, 27H). 13C NMR (100 MHz, CDCl₃, r.t.): δ 151.7, 141.8, 141.7, 141.2, 141.0, 140.4, 138.8, 138.2, 136.5, 133.7, 133.4, 128.2, 128.1, 127.7, 126.9, 126.6, 124.6, 124.5, 34.8, 34.1, 31.6, 31.5, 21.2, 21.0, 19.1. HRMS (MALDI⁺): m/z Calcd. for C₆₆H₇Br₂N: 1041.44173, Found: 1041.43676 [M⁺]. IR (ATR): 3473, 3375, 2951, 2917, 2865, 1591, 1458, 1361, 1242, 1219, 998, 915, 874, 725, 639 cm⁻¹.

Under an Ar atmosphere, compound 8d (1.33 g, 3.37 mmol), compound 4 (3.93 g, 7.41 mmol), Pd₂(dba)₃ (154 mg, 0.17 mmol), SPhos (277 mg, 0.674 mmol), Ba(OH)₂•8H₂O (3.19 g, 10.11 mmol), and degassed 1,4-dioxane (34 mL) were added to a flask. The reaction mixture was refluxed for 20 h and then filtered through Celite. The resulting solution was evaporated and treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. The crude product was purified by column chromatography (toluene/n-hexane = 1:1) and the desired product S5 (2.24 g, 70%) was obtained. Compound S5 was dissolved in THF (20 mL) and 6 N HCl aq. (2 mL) was added and then the reaction mixture was stirred under Ar at r.t for 2 d. To the mixture was added 1 N HCl aq. and the organic materials were extracted with Et₂O. The organic layer was washed with brine, dried over MgSO₄, and
filtered. The concentration of the filtrate under reduced pressure gave the product 2d quantitatively.

Physical data of S5 ¹H NMR (400 MHz, CDCl₃, r.t.): δ 7.65 (s, 2H), 7.39 (brs, 8H), 7.32 (s, 2H), 7.16 (t, J = 8.0 Hz, 4H), 7.07 (d, J = 8.2 Hz 4H), 6.45 (d, J = 7.2 Hz, 4H), 6.08 (brs, 4H), 3.43 (s, 3H), 2.15 (s, 12H), 1.44 (s, 18H). ¹³C NMR (100 MHz, CDCl₃, r.t.): δ 151.1, 141.6, 141.1, 140.3, 137.8, 137.1, 136.4, 136.1, 129.7, 129.2, 128.9, 128.6, 128.0, 127.6, 126.2, 119.9, 119.6, 117.8, 106.0, 34.9, 31.5, 21.1, 14.1. The boron-bound carbons were not detected due to quadrupole relaxation. HRMS (MALDI⁺): m/z Calcd. for C₆₃H₆₁ClN₄Br₂B₂O: 946.4734, Found: 946.4737 [M⁺]. IR (ATR): 3429, 3040, 2952, 2865, 1599, 1501, 1405, 1374, 1325, 1220, 1097, 1011, 817, 758, 570 cm⁻¹.

![Diagram of chemical reaction](image)

Under an Ar atmosphere, compound 2d (3.25 g, 4.62 mmol), compound 9 (3.70 g, 10.9 mmol), Cs₂CO₃ (3.01 g, 9.24 mmol), Pd(PPh₃)₄ (133.0 mg, 115.5 µmol), and degassed toluene/MeOH (1:1) (60 mL) were added to a flask. The reaction mixture was refluxed for 1 d. The resulting solution was treated with sat. NH₄Cl aq. and the organic materials were extracted with EtOAc, washed with brine, and dried over MgSO₄. After removal of the solvent, the crude product was was purified by column chromatography (n-hexane/CHCl₃ = 4:1) and the desired product 3c (1.87 g, 39%) was obtained.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 7.34 (s, 2H), 7.32 (s, 4H), 7.20 (t, J = 1.7 Hz, 2H), 7.08 (t, J = 1.7 Hz, 2H), 6.74 (t, J = 1.7 Hz, 2H), 3.33 (s, 3H), 2.47 (s, 12H), 2.14 (s, 12H), 2.04 (s, 12H), 1.35 (s, 18H). ¹³C NMR (100 MHz, CDCl₃, r.t.): δ 153.7, 151.7, 141.8, 141.7, 141.7, 140.4, 137.2, 136.2, 135.9, 133.7, 133.4, 129.7, 128.8, 128.2, 128.0, 126.9, 124.6, 124.5, 61.0, 34.8, 31.5, 21.2, 21.0, 19.1. HRMS (MALDI⁺): m/z Calcd. for C₆₃H₆₉OBr₂Cl: 1034.3398, Found: 1034.3361 [M⁺]. IR (ATR): 2951, 2916, 2866, 2730, 1591, 1560, 1458, 1380, 1362, 1239, 1007, 914, 883,856, 724, 692 cm⁻¹.
9. $^1$H NMR and $^{13}$C NMR spectra

$^1$H NMR

Current Data Parameters
NAME 07322025
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Data 20150731
Time 11:01
INSTRUM dpq450
PIRSHID 5 mm QNP 350/29
PULSERQ 3200
TD 6534
SOLVENT CDC13
NS 1
DS 2
SWE 8278.145 Hz
FFRMS 0.126344 Hz
AQ 3.9504263 sec
BD 3276
DM 60.403 usec
DE 4.25 usec
TE 0.92 sec
DS 1.0000000 sec
DF 0.0100000 sec
MCERET 0.0100000 sec
MCEREC 0.0100000 sec

F2 - Processing parameters
SI 3276
SF 400.132670 Hz
WDW DE
SSB 0
LB 0.30 Hz
CB 0
PC 1.00

$^{13}$C NMR

Current Data Parameters
NAME 07322025
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Data 20150731
Time 11:01
INSTRUM dpq450
PIRSHID 5 mm QNP 350/29
PULSERQ 3200
TD 6534
SOLVENT CDC13
NS 1
DS 2
SWE 8278.145 Hz
FFRMS 0.126344 Hz
AQ 3.9504263 sec
BD 3276
DM 60.403 usec
DE 4.25 usec
TE 0.92 sec
DS 1.0000000 sec
DF 0.0100000 sec
MCERET 0.0100000 sec
MCEREC 0.0100000 sec

F2 - Processing parameters
SI 3276
SF 400.132670 Hz
WDW DE
SSB 0
LB 0.30 Hz
CB 0
PC 1.00
$^{1}$H NMR

Current Data Parameters
NAME 90902015
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150908
Time 10.52
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PULPROG zg30
TD 32768
SOLVENT CDC13
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DS 0
SWR 8223.665 Hz
FIDGES 0.250647 Hz
AQ 1.9923444 sec
WG 65341
DM 69.800 usec
DE 6.000 usec
TE 300.2 sec
D1 1.00000000 sec
MDST 0.00000000 sec
MCRWK 0.01500000 sec

---------- CHANNEL f1 ----------
NUC1 1H
P1 7.00 usec
P11 3.00 MB
SF01 400.1324710 MHz

F2 - Processing parameters
SP 16384
BF 400.1300000 MHz
NOM 1M
DSB 0
LB 0.30 Hz
GB 0
PC 1.00

$^{13}$C NMR

Current Data Parameters
NAME 90902015
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150908
Time 10.52
INSTRUM dge400
PROBID 5 mm QNP BR/29
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 8
DS 0
SWR 8223.665 Hz
FIDGES 0.250647 Hz
AQ 1.9923444 sec
WG 65341
DM 69.800 usec
DE 6.000 usec
TE 300.2 sec
D1 1.00000000 sec
MDST 0.00000000 sec
MCRWK 0.01500000 sec

---------- CHANNEL f1 ----------
NUC1 1H
P1 7.00 usec
P11 3.00 MB
SF01 400.1324710 MHz

F2 - Processing parameters
SP 16384
BF 400.1300000 MHz
NOM 1M
DSB 0
LB 0.30 Hz
GB 0
PC 1.00

Comp: 34444021
DATIM 26Jul0216 23:00:31
COMM: W8 120
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ENHOC Z00400
CPBUR 100.63 Hz
CRURO 60.42 Hz
CPBUR 999921.0 Hz
POINT 32768
FREQD 2400 Hz
SCANS 128
ACOTM 1.3631 s
SCREEN PROBID 5 MM PABBO BB-1HD Z-2
GRID 2104445
INSTRUM SPECT
PHIUPPRG Z00400
ORDPROG Z00400
CTEMP 25.05 °C
SLVNT CDCl3
BF 0.25 Hz
RGLA 296
$^{1} \text{H NMR}$

Current Data Parameters
NAME 11132015
EXPER 1
PROCNO 1

F2 - Acquisition Parameters
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Time 16:50
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PULSPROG zg30
TD 65536
SOLVENT CDC13
DS 3
DSW 82.79-1.16 Hz
FIDRES 0.126314 Hz
AQ 3.0584243 sec
BS 46341
DW 60,400 usec
DE 6.00 usec
TE 31.2 K
DI 1,0000000 sec
MCHREST 0.0000000 sec
MCWOK 0.0150000 sec

--- CHANNEL f1 ---
MNUC 1H
F1 10.00 usec
F11 2.00 GB
SFQ 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1360000 MHz
MOW 2M
ZBB 0
LB 0.30 Hz
GB 0
PC 1.00

$^{13} \text{C NMR}$

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10. References

S1) Bisson, A. P.; Carver, F. J.; Eggleston, D. S.; Haltiwanger, R. C.; Hunter, C. A.; Livingstone, D. L.; McCabe, J. F.; Rotger, C.; Rowan, A. E. *J. Am. Chem. Soc.* **2000**, *122*, 8856–8868.

S2) Spartan’14, Wavefunction Inc., Irvine CA (USA).