Supplementary Information

Dynamic or undynamic chirality generated by helical arrangement of a shape-persistent ring and rod doubly bridged in a molecule

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Fig. S1a $^1$H NMR spectra (400 MHz) of 1a/b, 2a/b, 3a/b and 4a/b, measured in chloroform-$d$ at room temperature.
Fig. S1b (a)-(c) Partial $^1$H NMR spectra (400 MHz) of (a) 2a, 2b, 5 and 8, (b) 3a, 3b, 6 and 8, and (c) 4a, 4b, 7 and 9. (d) Partial $^{13}$C NMR spectra (100 MHz) of 4a, 4b, 7 and 9. All spectra were measured in chloroform-$d$ at room temperature.
**Fig. S2** Partial 2D ROESY spectra (600 MHz) of (a) 1a, (b) 2a and (c) 3a. All spectra were measured in chloroform-$d$ at room temperature.

**Fig. S3** UV spectra of (a) 3a, 3b, 6 and 8, and (b) 4a, 4b, 7 and 9. Black solid line: threaded form a, black dashed line: unthreaded form b, orange solid line: ring, and green dashed line: rod. All spectra were measured in dichloromethane at room temperature.
Fig. S4 CD spectra of (a) (−)-3a (solid line, first fraction) and (+)-3b (dashed line, second fraction), measured at 293 K; (b) CD spectra of 4b ([4b] = 1.17 × 10⁻⁴ M) in the presence of (R,R)-10 (1, 2, 4, 6, 8, and 10 equiv. blue lines) or (S,S)-10 (2, 4, and 8 equiv. red lines), measured at 263 K. All spectra were measured in dichloromethane. Chemical structures of chiral ditopic guests (S,S)-10 and (R,R)-10.

Fig. S5 UV spectra of (a) 2b and (b) 4b in the presence of (R,R)-10 [0 (2b or 4b only, black line)-10 equiv. (blue lines)], measured in dichloromethane at room temperature, titration curves and binding constants, obtained by a curve-fitting method, based on a change in absorbance (ΔAbs = Abs_{complex} − Abs_{0}) upon complexation.

Assume 1:2 complexation (K₁ = K₂). Doubled concentration (= [terephthalamide unit]) was used for calculation.
Fig. S6 The most energy-minimized structures for models 1'-4' (NMe): (a) 1a' (rel. 0 kJ mol\(^{-1}\)), (b) 1b' (+4.40 kJ mol\(^{-1}\)), (c) 2a' (rel. 0 kJ mol\(^{-1}\)), (d) 2b' (+11.3 kJ mol\(^{-1}\)), (e) 3a' (+9.40 kJ mol\(^{-1}\)), (f) 3b' (rel. 0 kJ mol\(^{-1}\)), (g) 4a' (+14.3 kJ mol\(^{-1}\)) and (h) 4b' (rel. 0 kJ mol\(^{-1}\)), obtained by conformational searches using MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50 000 steps). No conformation with any local helical form (m- or p-helicity) in the terephthalamide unit was found for 1' (101 conformers found within 30 kJ mol\(^{-1}\)), 2' (47) or 4' (14). However, for 3' (50) a local helical form in the terephthalamide unit was found at a higher energy level (+23.8 kJ mol\(^{-1}\) relative to the most energy-minimized conformer (f)).

Table S1 Chemical shifts (\(\delta/\text{ppm}\)) for central phenylene protons (H\(^c\)) of rod and interior protons (H\(^H\)) of PAMs, measured in chloroform-d at room temperature.

<table>
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<th>central phenylene protons</th>
<th>interior protons</th>
<th></th>
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<tr>
<td>[6]PAM in 1a</td>
<td>8.07 (4H)</td>
<td>7.88 (2H)</td>
<td>7.74 (1H)</td>
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<tr>
<td>[6]PAM in 2a</td>
<td>8.05 (4H)</td>
<td>7.82 (2H+2H)</td>
<td>7.67 (2H)</td>
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<td>8.21 (2H)</td>
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<tr>
<td>[4]PAM in 4a</td>
<td>–</td>
<td>9.07 (2H)</td>
<td>8.60 (2H)</td>
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<tr>
<td>[5]PAM (6)</td>
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<td>7.96 (2H+2H)</td>
<td>7.80 (2H)</td>
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<td>[4]PAM (7)</td>
<td>8.06 (2H)</td>
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<td>7.90 (2H)</td>
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<tr>
<td>rod (8)</td>
<td>7.50 (4H)</td>
<td></td>
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<tr>
<td>[6]PAM</td>
<td>7.5-7.6(^\circ)</td>
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<td>[5]PAM</td>
<td>7.97(^\circ)</td>
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<tr>
<td>[4]PAM</td>
<td>8.05(^\circ)</td>
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*alkylated analogs, from ref 1.
\(^1\)parent hydrocarbon (C\(_4\)H\(_8\)), from ref 2.
\(^2\)parent hydrocarbon (C\(_7\)H\(_8\)), from ref 3.
**Experimental**

Scheme S1. Synthesis of (+)-1a/1b and (+)-3a/3b. Reagents and yields: (a) 1-bromobutane, NaH, THF (78%); (b) di-n-butyl dicarbonate (Boc₂O), 4-dimethylaminopyridine (DMAP), Et₃N, THF (99%); (c) n-BuLi, 1,2-diiodoethane, diethyl ether (96%); (d) trimethylsilylacetylene (TMSA), PdCl₂(PPh₃)₂, CuI, Et₃N, THF (96%); (e) triisopropylsilylacetylene (TIPSA), Pd(PPh₃)₄, CuI, iPr₂NH, THF (97%); (f) i) K₂CO₃, MeOH, THF (94% for 16'); ii) 23', Pd(PPh₃)₄, Cu, tPr₂NH, THF (95%); (g) i) K₂CO₃, MeOH, THF (93% for 17'); ii) 15, Pd(PPh₃)₄, Cu, tPr₂NH, THF (80%); (h) trifluoroacetic acid (TFA), CH₂Cl₂ (97%); (i) i) TFA, CH₂Cl₂ (88% for 8'), ii) terephthaloyl chloride, 8', Et₃N, toluene, THF (43%); (j) i) K₂CO₃, MeOH, THF (96% for 20'); ii) 24'/25', Pd(PPh₃)₄, CuI, Et₃N, THF (66% for 21, 72% for 22); (k) i) tetra-n-butylammonium fluoride (TBAF), THF (95% for 21', 97% for 22'); ii) Pd(PPh₃)₄, CuI, Et₃N, THF (45% for (+)-1a/1b, 78% for (+)-3a/3b).
Preparation of 13

To an ice-cooled solution of 11 (27.3 g, 109 mmol) in THF (120 mL) were added NaH (60% dispersion in oil, 8.70 g, 218 mmol) and 1-bromobutane (11.7 mL, 109 mmol), the mixture was stirred at room temperature for 5 h. After addition of water, the mixture was diluted with ethyl acetate, and which was separated. The organic layer was washed with brine, dried over magnesium sulfate, and then purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 12 (25.9 g) as a reddish yellow oil in 78% yield. 12: 1H NMR δH (400 MHz; CDCl₃; Me₂Si)/ppm 6.92 (1H, t, J = 1.6 Hz), 6.63 (2H, d, J = 1.6 Hz), 3.74 (1H, brt), 3.07 (1H, dd, J = 5.6, 6.8 Hz), 3.05 (1H, dd, J = 5.6, 6.8 Hz), 1.62-1.55 (2H, m), 1.46-1.37 (2H, m), 0.96 (3H, t, J = 7.2 Hz).

To a refluxed solution of 12 (9.21 g, 30.0 mmol), DMAP (76 mg, 0.35 mmol) and Et₂N (8.4 mL, 60 mmol) in THF (100 mL) was added Boc₂O (13.8 mL, 60 mmol), and the mixture was further refluxed for 20 h. After removal of the solvent by evaporation, the residue was purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 13 (12.1 g) as a white solid in 99% yield. An analytical sample was obtained as colorless crystals by recrystallization from methanol. 13: mp 54.0-54.5 °C; elemental analyses Found: C, 44.14; H, 5.15; N, 3.48%. Calc. for C₁₅H₂₁BrINO₂: C, 44.25; H, 5.20; N, 3.44%; IR (KBr) νmax/cm⁻¹ 3111, 3074, 3010, 2979, 2959, 2931, 2899, 2876, 2858, 1711, 1584, 1552; ¹H NMR δH (400 MHz; CDCl₃; Me₂Si)/ppm 7.48 (1H, t, J = 2.0 Hz), 7.31 (2H, d, J = 2.0 Hz), 3.59 (2H, t, J = 7.6 Hz), 1.56-1.46 (2H, m), 1.45 (9H, s), 1.35-1.26 (2H, m), 0.91 (3H, t, J = 7.6 Hz); ¹³C NMR δC (100 MHz; CDCl₃)/ppm 153.9, 144.9, 131.2, 128.7, 122.2, 81.0, 49.6, 30.5, 28.2, 19.8, 13.7; FD-LRMS m/z 405.0 (M⁺, 54%), 406.0 ([M+1]⁺, 10), 407.0 ([M+2]⁺, 100), 408.0 ([M+3]⁺, 18), 409.0 ([M+4]⁺, 52), 410.0 ([M+5]⁺, 9).

Preparation of 14

To a solution of 13 (15.0 g, 37.0 mmol) in diethyl ether (370 mL) was added "BuLi (1.6 M in hexane, 23.7 mL, 38.8 mmol) at -87 °C under an argon atmosphere, and the mixture was stirred at that temperature for 3 min. To the mixture was added a solution of 1,2-diiodoethane (12.5 g, 44.3 mmol) in diethyl ether (60 mL), and the mixture was further stirred for 20 min. After addition of water, the organic layer was separated, dried over magnesium sulfate, and then purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 14 (16.1 g) as a white solid in 96% yield. An analytical sample was obtained as colorless crystals by recrystallization from methanol. 14: mp 71.0-72.0 °C; elemental analyses Found: C, 39.57; H, 4.68; N, 3.11%. Calc. for C₁₅H₂₁BrINO₂: C, 39.67; H, 4.66; N, 3.08%; IR (KBr) νmax/cm⁻¹ 3096, 3068, 3010, 2977, 2959, 2931, 2899, 2876, 2857, 1711, 1578, 1545; ¹H NMR δH (400 MHz; CDCl₃; Me₂Si)/ppm 7.67 (1H, t, J = 1.6 Hz), 7.50 (1H, t, J = 1.6 Hz), 7.34 (1H, t, J = 1.6 Hz), 3.58 (2H, t, J = 7.6 Hz), 1.55-1.45 (2H, m), 1.45 (9H, s), 1.35-1.25 (2H, m), 0.91 (3H, t, J = 7.6 Hz); ¹³C NMR δC (100 MHz; CDCl₃)/ppm 153.8, 144.7, 136.8, 134.5, 129.4, 122.2, 93.3, 80.9, 49.6, 30.5, 28.2, 19.8, 13.7; FD-LRMS m/z 452.9 (M⁺, 100%), 453.9 ([M+1]⁺, 17), 454.9 ([M+2]⁺, 98), 455.9 ([M+3]⁺, 16).
Preparation of 15  
To a solution of 14 (5.85 g, 12.9 mmol), PdCl₂(PPh₃)₂ (96 mg, 0.14 mmol) and CuI (25 mg, 0.13 mmol) in THF (65 mL) and Et₃N (65 mL) was added TMSA (2.0 mL, 14 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at that temperature for 7 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 15 (5.26 g) as a pale yellow oil in 96% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). 15: elemental analyses Found: C, 56.41; H, 7.16; N, 3.29%. Calc. for C₂₀H₃₀BrNO₂Si: C, 56.59; H, 7.12; N, 3.30%; IR (KBr) νmax/cm⁻¹ 3070, 2961, 2932, 2873, 2160, 1707, 1591, 1559; ¹H NMR δ(Hz; CDCl₃) ppm 7.44 (1H, br.dd), 7.31 (1H, br.t), 7.22 (1H, br.t), 3.59 (2H, t, J = 7.6 Hz), 1.53-1.46 (2H, m), 1.44 (9H, s), 1.34-1.25 (2H, m), 0.90 (3H, t, J = 7.6 Hz), 0.24 (9H, s); ¹³C NMR δ(CDCl₃) ppm 154.1, 143.7, 132.0, 130.6, 128.8, 125.1, 121.5, 102.8, 96.1, 80.6, 49.6, 30.5, 28.3, 19.8, 13.7, -0.2; FD-LRMS m/z 423.1 (M⁺, 96%), 424.1 ([M+1]⁺, 28), 425.1 ([M+2]⁺, 100), 426.1 ([M+3]⁺, 27), 427.1 ([M+4]⁺, 7).

Preparation of 16  
To a solution of 15 (676 mg, 1.59 mmol) and TIPSA (0.72 mL, 3.2 mmol) in THF (8 mL) and Pr₂NH (8 mL) were added Pd(PPh₃)₄ (55 mg, 0.048 mmol) and CuI (18 mg, 0.095 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 78-79 °C for 40 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane), followed by GPC (chloroform) to give 16 (813 mg) as a pale yellow oil in 97% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). 16: elemental analyses Found: C, 70.56; H, 9.98; N, 2.59%. Calc. for C₂₁H₃₂NO₂Si₂: C, 70.80; H, 9.77; N, 2.66%; IR (KBr) νmax/cm⁻¹ 3066, 2960, 2943, 2894, 2865, 2153, 1707, 1582; ¹H NMR δ(Hz; CDCl₃) ppm 7.40 (1H, br.s), 1.25-1.12 (2H, m), 0.90 (3H, t, J = 1.6 Hz), 7.25-7.20 (2H, br.m), 3.59 (2H, t, J = 7.6 Hz), 1.54-1.46 (2H, m), 1.43 (9H, s), 1.34-1.25 (2H, m), 1.12 (2H, s), 0.86 (3H, t, J = 7.6 Hz), 0.24 (9H, s); ¹³C NMR δ(CDCl₃) ppm 154.2, 142.6, 132.9, 130.7, 130.4, 124.2, 123.8, 105.6, 103.6, 95.1, 91.6, 80.4, 49.5, 30.5, 28.3, 19.9, 18.6, 13.7, 11.2, -0.2; FD-LRMS m/z 525.3 (M⁺, 100%), 526.3 ([M+1]⁺, 45), 527.3 ([M+2]⁺, 16), 528.3 ([M+3]⁺, 4).

Preparation of 17  
To a solution of 16 (10.5 g, 20.0 mmol) in THF (100 mL) and MeOH (100 mL) was added K₂CO₃ (2.76 g, 20.0 mmol) at room temperature, and the mixture was stirred at that temperature for 15 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 16' (8.51 g) as a white solid in 94% yield. 16': ¹H
NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.43 (1H, $t$, $J = 1.6$ Hz), 7.30-7.22 (2H, br.m), 3.60 (2H, $t$, $J = 7.6$ Hz), 3.08 (1H, $s$), 1.54-1.47 (2H, $m$), 1.44 (9H, $s$), 1.35-1.25 (2H, $m$), 1.13 (21H, br.m), 0.90 (3H, $t$, $J = 7.2$ Hz).

To a solution of 23 (8.73 g, contained 1-bromo-3-(2-trimethylsilyl)ethylbenzene in a ratio of 5:1), Pd(PPh$_3$)$_4$ (563 mg, 0.487 mmol) and Cul (187 mg, 0.982 mmol) in THF (65 mL) and Pr$_2$NH (80 mL) was added a solution of 16 (7.33 g, 16.2 mmol) in THF (15 mL) via a syringe pump over 2 h at 43-45 °C under an argon atmosphere, and the mixture was stirred at that temperature for 20 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (dichloromethane/hexane) to give 17 (9.59 g) as a colorless oil in 95% yield. An analytical sample was obtained as a colorless oil by further purification through GPC (chloroform). 17: elemental analyses Found: C, 74.77; H, 9.06; N, 2.21%. Calc. for C$_{39}$H$_{38}$NO$_2$Si$_2$: C, 74.82; H, 8.86; N, 2.24%; IR (KBr) $\nu$max/cm$^{-1}$ 3063, 2959, 2943, 2894, 2865, 2157, 1706, 1595, 1582; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.65-7.64 (1H, br.m), 7.46 (1H, $t$, $J = 1.6$ Hz), 7.46 (1H, $dt$, $J = 1.6$, 8.0 Hz), 7.43 (1H, $dt$, $J = 1.6$, 8.0 Hz), 7.31-7.24 (3H, br.m), 3.62 (2H, $t$, $J = 7.6$ Hz), 1.57-1.49 (2H, $m$), 1.45 (9H, $s$), 1.36-1.27 (2H, $m$), 1.14 (21H, $s$), 0.91 (3H, $t$, $J = 7.2$ Hz), 0.25 (9H, $s$); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm 154.3, 142.7, 135.1, 132.6, 131.8, 131.5, 130.5, 130.2, 128.4, 124.4, 123.6, 123.5, 123.1, 105.6, 104.0, 95.1, 91.8, 89.1, 88.6, 80.5, 49.6, 30.5, 28.3, 19.9, 18.6, 13.8, 11.3, −0.1; FD-LRMS $m/z$ 625.4 (M$^+$, 100%), 626.4 ([M+1]$^+$, 54), 627.4 ([M+2]$^+$, 22), 628.4 ([M+3]$^+$, 6).

Preparation of 18

To a solution of 17 (3.19 g, 5.10 mmol) in THF (27 mL) and MeOH (27 mL) was added K$_2$CO$_3$ (687 mg, 4.98 mmol) at room temperature, and the mixture was stirred at that temperature for 25 min. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO$_2$ (dichloromethane/hexane) to give 17' (2.62 g) as a white solid in 93% yield. 17': $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.66 (1H, $t$, $J = 1.6$ Hz), 7.49 (1H, $dt$, $J = 1.6$, 8.0 Hz), 7.48 (1H, $t$, $J = 1.6$ Hz), 7.45 (1H, $dt$, $J = 1.6$, 8.0 Hz), 7.33-7.26 (3H, $m$), 3.62 (2H, $t$, $J = 7.6$ Hz), 3.10 (1H, $s$), 1.57-1.49 (2H, $m$), 1.45 (9H, $s$), 1.37-1.27 (2H, $m$), 1.14 (21H, $s$), 0.90 (3H, $t$, $J = 7.2$ Hz).

To a solution of 15 (739 mg, 1.74 mmol), Pd(PPh$_3$)$_4$ (40 mg, 0.035 mmol) and Cul (13 mg, 0.068 mmol) in Pr$_2$NH (6 mL) and THF (4.5 mL) was added a solution of 17 (633 mg, 1.14 mmol) in THF (1.8 mL) via a syringe pump over 1 h at 80 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 1.5 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (dichloromethane/hexane), followed by GPC (chloroform) to give 18 (817 mg) as a pale yellow amorphous solid in 80% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). 18: mp 65.0-66.0 °C; elemental analyses Found: C, 74.89; H, 8.61; N, 3.01%. Calc. for C$_{56}$H$_{76}$N$_2$O$_4$Si$_2$: C, 74.95; H, 8.54; N, 3.12%; IR (KBr) $\nu$max/cm$^{-1}$
3064, 2960, 2941, 2864, 2158, 1705, 1596, 1582; 1H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 7.69 (1H, br.t), 7.51-7.47 (4H, m), 7.36-7.33 (1H, m), 7.31 (2H, br.t), 7.29-7.25 (2H, br.m), 3.63 (2H, t, J = 7.6 Hz), 3.61 (2H, t, J = 7.6 Hz), 1.55-1.48 (4H, m), 1.45 (9H, s), 1.45 (9H, s), 1.36-1.28 (4H, m), 1.14 (21H, s), 0.92 (3H, t, J = 7.6 Hz), 0.91 (3H, t, J = 7.6 Hz), 0.26 (9H, s); 13C NMR δ(100 MHz; CDCl₃)/ppm 154.3, 142.8, 134.7, 132.6, 131.5, 130.5 (br.m), 130.2, 128.6, 124.4, 124.0, 123.7, 123.6, 123.3, 105.6, 103.5, 91.4, 89.1, 89.1, 88.8, 88.7, 80.5, 80.5, 49.6, 49.6, 30.6, 28.3, 19.9, 18.6, 13.8, 11.3, –0.1; FD-LRMS m/z 796.5 ([M–(BOC)]⁺, 22%), 797.5 ([M+1–(BOC)]⁺, 15), 798.5 ([M+2–(BOC)], 7), 896.6 (M⁺, 100), 897.6 ([M+1]⁺, 72), 898.6 ([M+2]⁺, 34), 899.6 ([M+3]⁺, 12), 900.6 ([M+4]⁺, 3).

Preparation of 19
To a solution of 18 (3.16 g, 3.52 mmol) in CH₂Cl₂ (230 mL) was added TFA (23 mL) at room temperature. The mixture was stirred at room temperature for 1 h, neutralized with satd. aq. NaHCO₃, and separated. The organic layer was dried over magnesium sulfate, concentrated, and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 19 (2.39 g) as a white amorphous solid in 97% yield. 19: 1H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 7.67 (1H, br.dd), 7.47-7.43 (2H, m), 7.31 (1H, t, J = 7.6 Hz), 7.00-6.99 (2H, m), 6.72-6.68 (2H, br.m), 6.68-6.66 (2H, m), 3.65 (2H, br.s), 3.11 (2H, t, J = 7.2 Hz), 3.10 (2H, t, J = 7.2 Hz), 1.64-1.56 (4H, m), 1.48-1.38 (4H, m), 1.13 (21H, s), 0.97 (3H, t, J = 7.2 Hz), 0.96 (3H, t, J = 7.2 Hz).

Preparation of 20
To a solution of 8 (554 mg, 0.892 mmol) in CH₂Cl₂ (60 mL) was added TFA (5.9 mL) at room temperature. The mixture was stirred at room temperature for 1 h, diluted with dichloromethane, neutralized with aq. 1M NaOH, and separated. The organic layer was dried over magnesium sulfate, passed through a Celite/SiO₂ pad, and then concentrated. The residue was suspended in dichloromethane/hexane, and then collected by filtration to give 8⁺ (331 mg) as a pale yellow solid in 88% yield. 8⁺: 1H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 7.43 (4H, s), 7.34 (4H, d, J = 8.8 Hz), 6.54 (4H, d, J = 8.8 Hz), 3.82 (2H, br.s), 3.14 (4H, t, J = 7.2 Hz), 1.65-1.58 (4H, m), 1.48-1.39 (4H, m), 0.97 (6H, t, J = 7.6 Hz).

To a solution of terephthaloyl chloride (507 mg, 2.50 mmol) in toluene (70 mL) was added a solution of 19 (858 mg, 1.23 mmol) in toluene (7 mL) containing Et₃N (0.4 mL) at 56 °C over a period of 1.5 h. The reaction mixture was further stirred for 30 min at that temperature, and then passed through a Celite pad to remove a solid. The filtrate was immediately subjected to the following reaction [acid chloride preparation].

Each solution of 8⁺ (482 mg, 1.15 mmol) in THF (70 mL) and as-prepared acid chloride in toluene (70 mL) was simultaneously added via addition funnels over 20 min to refluxed THF (210
mL) containing Et$_3$N (0.4 mL), and the mixture was further stirred for 2 h at that temperature. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, which was washed with satd. aq. NaHCO$_3$, dried over magnesium sulfate, and then passed through a Celite/Ai$_2$O$_3$ pad. The filtrate was concentrated, and then purified by column chromatography on Al$_2$O$_3$/SiO$_2$ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give 20 (680 mg) as a white solid in 43% yield. An analytical sample was obtained as a white solid by HPLC with a standard normal-phase column (ethyl acetate/dichloromethane; YMC-Pack SIL, SIL-06, YMC Co., Ltd.). 20: mp 181.5-182.0 °C; elemental analyses Found: C, 79.34; H, 7.15; N, 3.93%. Calc: for C$_{92}$H$_{96}$Na$_4$O$_{32}$(EtOH): C, 79.28; H, 7.22; N, 3.93%; IR (KBr) $\nu_{max}$/cm$^{-1}$ 3062, 3041, 2956, 2931, 2862, 2215, 2152, 1655, 1560, 1596, 1579, 1518; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm$^{11}$ 7.56 (3H, br.s), 7.49 (2H, br.d), 7.42 (4H, br.d), 7.34 (1H, t, $J$ = 7.6 Hz), 7.25-7.20 (2H, br.m), 7.10 (8H, br.s), 6.82 (2H, br.d), 6.80 (2H, br.d), 6.71-6.62 (2H, m), 4.41-3.39 (8H, br.m), 1.70-1.46 (8H, br.m), 1.43-1.26 (8H, m), 1.16-1.12 (21H, m), 0.95-0.88 (12H, m), 0.28 (9H, s); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$; 313 K)/ppm 169.8, 169.6, 168.6, 143.5, 143.5, 143.3, 137.6, 137.3, 136.7 (br.m), 133.3, 133.1 (br.m), 132.7, 132.4, 132.3, 131.5, 128.8 (br.), 128.7, 128.7, 128.5, 127.7, 127.5, 127.1, 127.1, 124.4, 124.4, 124.3, 124.0, 123.2 (br.m), 123.1, 123.0, 121.2, 121.1, 105.2, 103.3, 96.6, 93.4, 90.8 (br.m), 89.9, 89.7, 88.3, 88.3, 49.8, 49.7, 49.6, 29.8, 29.7, 29.7, 20.1, 20.1, 18.6, 13.7, 11.3, -0.2; FD-LRMS $m/z$ 1376.6 ($M^+; 88\%$), 1377.7 ([M+1]$^+$, 100), 1378.7 ([M+2]$^+$, 65), 1379.7 ([M+3]$^+$, 31), 1380.7 ([M+4]$^+$, 11), 1381.7 ([M+5]$^+$, 4).

Preparation of 21 ($n = 6$)

To a solution of 20 (525 mg, 0.381 mmol) in THF (7 mL) and MeOH (7 mL) was added K$_2$CO$_3$ (104 mg, 0.754 mmol) at room temperature, and the mixture was stirred at that temperature for 15 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane) to give 20' (479 mg) as a white solid in 96% yield. 20': $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm$^{11}$ 7.60 (3H, br.m), 7.50 (2H, dd, $J$ = 1.2, 7.6 Hz), 7.42 (2H, d, $J$ = 8.4 Hz), 7.39 (2H, d, $J$ = 8.8 Hz), 7.34 (1H, br.d), 7.29-7.26 (2H, br.m), 7.12 (2H, d, $J$ = 8.4 Hz), 7.10 (4H, s), 7.09 (2H, d, $J$ = 8.8 Hz), 6.83 (2H, d, $J$ = 8.4 Hz), 6.80 (2H, d, $J$ = 8.0 Hz), 6.70 (1H, t, $J$ = 1.6 Hz), 6.66 (1H, br.s), 4.40-3.34 (8H, br.m), 3.21 (1H, s), 1.70-1.45 (8H, br.m), 1.41-1.28 (8H, m), 1.16-1.11 (21H, m), 0.95-0.88 (12H, m).

To a solution of 24 (486 mg, 0.917 mmol), Pd(PPh$_3$)$_4$ (9 mg, 0.008 mmol) and Cul (3 mg, 0.02 mmol) in Et$_3$N (22 mL) was added a solution of 20' (287 mg, 0.220 mmol) in THF (3 mL) via a syringe pump over 3 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After dilution with ethyl acetate, the organic phase was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column...
chromatography on SiO2 (dichloromethane/hexane), followed by GPC (chloroform) to give 21 (249 mg) as a pale yellow solid in 66% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). 21: mp 164-165 °C; elemental analyses Found: C, 77.51; H, 5.97; N, 3.19%. Calc. for C111H88InN4O3Si (EtOH): C, 77.38; H, 6.03; N, 3.19%; IR (KBr) νmax/cm⁻¹ 3059, 3039, 2955, 2929, 2861, 2214, 2150, 1655, 1650, 1596, 1579, 1517; ¹H NMR δ(400 MHz; CDCl₃; MeSi; 313 K)/ppm 1.79 (1H, t, J = 1.6 Hz), 7.73 (1H, br.t), 7.69 (1H, br.d), 7.67 (1H, br.ddd), 7.64 (1H, br.t), 7.55-7.46 (8H, m), 7.40 (2H, d, J = 8.4 Hz), 7.39 (2H, d, J = 8.4 Hz), 7.41-7.25 (6H, m), 7.12 (4H, s), 7.09 (4H, s), 7.07 (1H, t, J = 8.0 Hz), 6.83 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.4 Hz), 6.76 (1H, dd, J = 1.6, 2.0 Hz), 6.67 (1H, br.t), 4.68-3.21 (8H, br.m), 1.68-1.47 (8H, br.m), 1.41-1.28 (8H, m), 1.14-1.10 (21H, m), 0.94 (3H, t, J = 7.2 Hz), 0.93 (3H, t, J = 7.2 Hz), 0.90 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 7.2 Hz); ¹³C NMR δ(100 MHz; CDCl₃; 313 K)/ppm 169.8, 169.7, 168.7, 168.6, 143.7, 143.7, 143.3, 143.3, 140.2, 137.6 (br), 137.5, 137.3 (br.m), 136.6 (br.m), 134.7, 134.6, 133.0 (br.m), 132.7, 132.4, 132.4, 132.1, 132.1, 131.6, 131.5, 130.7, 129.8, 128.9 (br.), 128.8, 128.7, 128.6, 128.5, 127.7, 127.5, 127.3, 127.1, 125.1, 124.6, 124.4, 124.3, 123.9, 123.8, 123.3, 123.3, 123.1, 123.0, 122.8, 121.2, 121.1, 105.2, 93.6, 93.4, 90.8 (br.m), 90.2, 90.1, 89.9, 89.9, 89.7, 89.5, 88.9, 88.4, 88.3, 49.9, 49.9, 49.7, 49.7, 29.8, 29.8, 20.1, 20.1, 18.6, 13.8, 13.7, 13.7, 11.3; FD-LRMS m/z 1706.7 (M⁺, 77%), 1707.7 ([M+1]⁺, 100), 1708.7 ([M+2]⁺, 69), 1709.7 ([M+3]⁺, 33), 1710.7 ([M+4]⁺, 13), 1711.7 ([M+5]⁺, 5).

Preparation of 22 (n = 5)

To a solution of 25 (1.10 g, 2.56 mmol), Pd(PPh₃)₄ (24 mg, 0.021 mmol) and CuI (11 mg, 0.058 mmol) in Et₂N (61 mL) was added a solution of 20' (840 mg, 0.643 mmol) in THF (7 mL) via a syringe pump over 3 h at 50 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After dilution with ethyl acetate, the organic layer was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO2 (dichloromethane/hexane), followed by GPC (chloroform) to give 22 (743 mg) as a pale yellow amorphous solid in 72% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). 22: mp 169-170 °C; elemental analyses Found: C, 75.98; H, 6.07; N, 3.39%. Calc. for C₆₀H₄₈In₄O₈Si (EtOH): C, 76.25; H, 6.16; N, 3.39%; IR (KBr) νmax/cm⁻¹ 3059, 3041, 2955, 2930, 2862, 2214, 2150, 1651, 1595, 1580, 1517; ¹H NMR δ(400 MHz; CDCl₃; MeSi; 313 K)/ppm 7.89 (1H, t, J = 1.6 Hz), 7.72 (1H, br.t), 7.67 (1H, dd, J = 1.2, 2.0, 8.0 Hz), 7.64 (1H, br.t), 7.55-7.47 (6H, m), 7.40 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.4 Hz), 7.40-7.25 (5H, m), 7.12 (4H, s), 7.10 (4H, s), 7.07 (1H, t, J = 8.0 Hz), 6.82 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.4 Hz), 6.76 (1H, dd, J = 1.6, 2.0 Hz), 6.67 (1H, br.s), 4.42-3.34 (8H, br.m), 1.67-1.49 (8H, br.m), 1.41-1.28 (8H, m), 1.15-1.11 (21H, m), 0.94 (3H, t, J = 7.2 Hz), 0.93 (3H, t, J = 7.2 Hz), 0.90 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 7.6 Hz); ¹³C NMR δ(100 MHz; CDCl₃; 323 K)/ppm 169.8, 169.6, 168.7, 168.6, 143.8, 143.6, 143.4, 143.4, 140.3, 137.6, 137.6, 137.4, 136.9 (br.m),

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136.7 (br,m), 134.6, 133.0 (br,m), 132.7, 132.4, 132.4, 132.1, 132.0, 131.6 (br,m), 130.7, 129.8, 129.0, 128.8, 128.7, 128.5, 127.7, 127.5, 127.3, 127.1, 125.0, 124.6, 124.5, 124.4, 123.9, 123.6, 123.3, 123.2, 123.1, 122.9, 121.3, 121.2, 105.3, 93.6, 93.4, 90.9 (br), 90.9 (br), 90.2, 90.1, 89.9, 89.9, 89.8, 89.5, 88.7, 88.4, 88.4 (br), 88.3, 49.9, 49.9, 49.7, 49.7, 29.8, 29.8 (br), 20.1, 20.1, 20.1, 18.6, 13.7, 13.7 (br,m), 11.4; FD-LRMS m/z 1607.6 (M+, 82%), 1670.7 ([M+1]+, 100), 1608.7 ([M+2]+, 67), 1609.7 ([M+3]+, 31), 1610.7 ([M+4]+, 12), 1611.7 ([M+5]+, 4).

Preparation of (±)-1a and 1b

To a solution of 21 (205 mg, 0.120 mmol) in THF (4 mL) was added TBAF (1 M in THF, 0.13 mL, 0.13 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 21' (176 mg) as a white solid in 95% yield. 21*: 1H NMR ¹H NMR δ (400 MHz; CDCl₃; Me₄Si)/ppm 7.89 (1H, t, J = 1.6 Hz), 7.75 (1H, br.t), 7.70 (1H, br.d), 7.68-7.66 (2H, m), 7.61 (1H, br.t), 7.56-7.47 (7H, m), 7.43-7.28 (10H, m), 7.13 (4H, s), 7.10 (4H, br.d), 7.08 (1H, t, J = 7.6 Hz), 6.83 (4H, br.d), 6.76 (1H, t, J = 1.2 Hz), 6.70 (1H, br.t), 4.43-3.37 (8H, br.m), 3.20 (1H, s), 1.58 (8H, br.s), 1.42-1.26 (8H, m), 0.94 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.6 Hz), 0.88 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 7.2 Hz).

To a solution of Pd(PPh₃)₄ (65 mg, 0.056 mmol) and Cul (11 mg, 0.058 mmol) in Et₃N (14 mL) was added a solution of 21' (145 mg, 0.0934 mmol) in THF (7 mL) via a syringe pump over 9 h at 75 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a purified mixture of (±)-1a and 1b (60 mg, (±)-1a:1b = 1:1.2) as a white solid in 45% yield. (−)-1a, 1b and (+)-1a were isolated in this order by HPLC separation with a chiral stationary column (5:95 ethanol/chloroform; CHIRALPAK IF, DAICEL Co.). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

(+)-1a: mp 264-265 °C (dec); [α]D²⁸ = +411 (c = 0.445 gdl⁻¹ in chloroform); IR (KBr) νmax/cm⁻¹ 3060, 3039, 2955, 2929, 2870, 2861, 2214, 1656, 1650, 1595, 1579, 1518; ¹H NMR δ (400 MHz; CDCl₃; Me₄Si)/ppm 8.07 (4H, s), 7.88 (2H, br.d), 7.74 (1H, br.d), 7.66 (3H, br.t), 7.62 (2H, dd, J = 1.6, 8.0 Hz), 7.55 (2H, dt, J = 1.6, 8.0 Hz), 7.55-7.50 (4H, m), 7.46 (1H, br.dd), 7.41-7.35 (9H, m), 7.16 (4H, br.d), 7.11 (4H, br.d), 6.79 (4H, d, J = 8.0 Hz), 6.66 (2H, dd, J = 1.2, 2.0 Hz), 4.25-4.11 (4H, m), 3.66-3.54 (4H, m), 1.75-1.62 (2H, m), 1.61-1.48 (6H, m), 1.49-1.22 (8H, m), 0.96 (6H, t, J = 7.2 Hz), 0.85

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(6H, t, J = 7.2 Hz); 13C NMR δ(C(100 MHz; CDCl3)/ppm 169.3, 169.2, 143.8, 143.1, 137.4, 136.6, 135.1, 134.6, 134.4, 133.3, 132.4, 132.1, 131.9, 131.9, 131.7, 131.5, 131.3, 129.0, 128.8, 128.7, 128.4, 128.2, 127.4, 124.4, 123.9, 123.7, 123.6, 123.3, 123.1, 122.8, 120.9, 91.5, 90.3, 89.9, 89.4, 89.2, 89.1, 88.9, 88.7, 50.2, 49.5, 29.7, 29.7, 20.2, 20.1, 13.8, 13.7; FD-LRMS m/z 1422.5 (M+, 89%), 1423.5 ([M+1]+, 100), 1424.5 ([M+2]+, 66), 1425.5 ([M+3]+, 29), 1426.5 ([M+4]+, 10), 1427.5 ([M+5]+, 3); FD-HRMS Found: 1422.60403; Calc. for C102H79N4O4: 1422.60230; UV λmax(CH2Cl2)/nm (log e) 333 (sh. 4.72), 305 (5.36), 289 (5.45); CD 348 (+24.5), 340 (+20.7), 321 (+100.3), 312 (+10.3), 306 (+97.2), 283 (−34.6), 271 (−0.1).

(−)-1a: mp 264-265 °C (dec); [α]D20 = −400 (c = 0.217 g/dL−1 in chloroform); FD-LRMS m/z 1422.6 (M+, 87%), 1423.6 ([M+1]+, 100), 1424.6 ([M+2]+, 62), 1425.6 ([M+3]+, 27), 1426.6 ([M+4]+, 10), 1427.6 ([M+5]+, 4); FD-HRMS Found: 1422.60220; Calc. for C102H79N4O4: 1422.60230; CD λ(CH2Cl2)/nm (Δε) 348 (−24.2), 340 (−20.2), 321 (−97.3), 312 (−8.9), 306 (−93.7), 283 (+39.2), 271 (+2.2).

1b: mp 239.0-239.5 °C (dec); IR (KBr) νmax/cm−1 3060, 3039, 2955, 2929, 2870, 2860, 2213, 1656, 1650, 1595, 1580, 1518; 1H NMR δ(400 MHz; CDCl3; MeSi)/ppm 7.76 (2H, br.ddd), 7.74 (1H, br.d), 7.60 (2H, t, J = 1.6 Hz), 7.57-7.48 (8H, m), 7.42-7.31 (5H, m), 7.40 (4H, s), 7.33 (4H, d, J = 8.4 Hz), 7.24 (2H, dd, J = 1.6, 2.0 Hz), 7.18 (4H, d, J = 8.4 Hz), 7.15 (4H, d, J = 8.4 Hz), 6.80 (4H, d, J = 8.4 Hz), 6.75 (2H, dd, J = 1.6, 2.0 Hz), 4.18-4.07 (4H, br.m), 3.75-3.52 (4H, br.m), 1.70-1.39 (8H, br.m), 1.41-1.25 (8H, m), 0.91 (6H, t, J = 7.2 Hz), 0.88 (6H, t, J = 7.2 Hz); 13C NMR δ(100 MHz; CDCl3)/ppm 169.8, 168.5, 143.6, 143.2, 137.5, 136.4, 136.2, 135.3, 135.3, 133.4, 132.4, 131.9, 131.7, 131.5, 131.3, 130.8, 128.9, 128.8, 128.7, 128.6, 128.4, 127.5, 127.2, 124.6, 123.8, 123.6, 123.3, 123.0, 122.7, 121.3, 90.3, 90.1, 89.9, 89.8, 89.5, 89.0, 88.4, 87.9, 49.9, 49.8, 29.7, 29.7, 20.1, 13.8, 13.7; FD-LRMS m/z 1422.5 (M+, 87%), 1423.5 ([M+1]+, 100), 1424.5 ([M+2]+, 60), 1425.5 ([M+3]+, 24), 1426.5 ([M+4]+, 9), 1427.5 ([M+5]+, 3); FD-HRMS Found: 1422.60199; Calc. for C102H79N4O4: 1422.60230; UV λmax(CH2Cl2)/nm (log e) 362 (sh. 4.56), 337 (sh. 4.66), 303 (sh. 5.25), 287 (5.36).

Preparation of (−)-3a and 3b

To a solution of 22 (413 mg, 0.257 mmol) in THF (9 mL) was added TBAF (1 M in THF, 0.28 mL, 0.28 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO2 (ethyl acetate/dichloromethane) to give 22′ (363 mg) as a white solid in 97% yield. 22′: 1H NMR δ(400 MHz; CDCl3; MeSi)/ppm11 7.89 (1H, t, J = 1.6 Hz), 7.73 (1H, br.t), 7.68 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.66 (1H, br.t), 7.61 (1H, br.t), 7.56-7.47 (5H, m), 7.41 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.4 Hz), 7.40-7.28 (5H, m), 7.13 (4H, s), 7.11 (4H, br.d), 7.08 (1H, t, J = 8.0 Hz), 6.83 (4H, br.d), 6.75 (1H, br.t), 6.70 (1H, br.t), 4.37-3.46 (8H, br.m), 3.21 (1H, s), 1.58 (8H, br.s), 1.42-1.28 (8H, m), 0.94 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.6 Hz), 0.90 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J
= 7.2 Hz).

To a solution of Pd(PPh₃)₄ (240 mg, 0.208 mmol) and CuI (42 mg, 0.22 mmol) in Et₂N (52 mL) was added a solution of 22’ (504 mg, 0.347 mmol) in THF (27 mL) via a syringe pump over 35 h at 75 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 0.5 M aq. HCl and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a purified mixture of (+)-3a and 3b (358 mg, (+)-3a: 3b = 1:5.5) as a yellow solid in 78% yield. (-)-3a was first isolated by HPLC with a chiral stationary column (5:95 ethanol/chloroform; CHIRALPAK IF, DAICEL Co.), and 3b and (+)-3a were eluted in this order and collected as a mixture. Next, 3b and (+)-3a were partly separated by repeated HPLC with a standard normal-phase column (8:92 tetrahydrofuran/dichloromethane). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

(-)-3a: mp 263-266 °C (dec); [α]D°20 = -315 (c = 0.221 gdl⁻¹ in chloroform); IR (KBr) νmax/cm⁻¹ 3060, 3040, 2954, 2929, 2869, 2860, 2208, 1655, 1650, 1591, 1578, 1518; 1H NMR δH(400 MHz; CDCl₃; Me₄Si)/ppm 8.21 (2H, t, J = 1.6 Hz), 8.11 (4H, s), 8.07 (1H, t, J = 1.6 Hz), 7.67 (2H, t, J = 1.6 Hz), 7.57-7.43 (7H, m), 7.41 (2H, t, J = 8.0 Hz), 7.27 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 7.17 (2H, t, J = 1.6 Hz), 7.06 (4H, d, J = 8.4 Hz), 6.84 (2H, t, J = 1.6 Hz), 6.80 (4H, br.d), 4.04-3.93 (4H, m), 3.79-3.64 (4H, m), 1.63-1.45 (8H, m), 1.39-1.27 (8H, m), 0.91 (6H, t, J = 7.2 Hz), 0.87 (6H, t, J = 7.2 Hz), 13C NMR δ (100 MHz; CDCl₃)/ppm 169.4, 169.3, 143.8, 143.1, 137.7, 137.1, 136.6, 136.3, 132.2, 132.0, 131.0, 130.9, 130.2, 130.2, 129.2, 129.0, 128.7, 128.3, 127.6, 124.2, 124.2, 123.6, 123.4, 123.3, 123.2, 120.9, 93.9, 90.8, 90.3, 90.2, 89.9, 89.3, 89.3, 50.6, 49.2, 29.8, 29.5, 20.1, 20.1, 13.8, 13.7; FD-LRMS m/z 1322.6 (M⁺, 95%), 1323.6 ([M+1]⁺, 100), 1324.6 ([M+2]⁺, 58), 1325.6 ([M+3]⁺, 23), 1326.6 ([M+4]⁺, 8); FD-HRMS Found: 1322.57117, Calc. for Cu₄H₇₂Na₄O₄: 1322.57100; UV λmax(CH₂Cl₂)/nm (log e) 356 (sh. 4.56), 337 (4.71), 305 (5.23), 289 (5.33); CD [α(CH₂Cl₂)/nm (Δε) 356 (-41.5), 332 (-58.1), 310 (+12.4), 307 (+4.2), 286 (+86.2), 266 (-35.1).

(+)-3a: [α]D°20 = +316 (c = 0.217 gdl⁻¹ in chloroform); FD-LRMS m/z 1322.5 (M⁺, 95%), 1323.5 ([M+1]⁺, 100), 1324.5 ([M+2]⁺, 56), 1325.5 ([M+3]⁺, 21), 1326.5 ([M+4]⁺, 7), 1327.5 ([M+5]⁺, 2); FD-HRMS Found: 1322.56948, Calc. for Cu₄H₇₂Na₄O₄: 1322.57100; CD [α(CH₂Cl₂)/nm (Δε) 356 (+41.8), 332 (+58.3), 310 (-11.1), 307 (-2.6), 286 (-81.2), 266 (+34.9).

3b: mp 246.5-247.0 °C (dec); IR (KBr) νmax/cm⁻¹ 3062, 3040, 2957, 2929, 2870, 2861, 2213, 1655, 1649, 1592, 1580, 1518; 1H NMR δH(400 MHz; CDCl₃; Me₄Si)/ppm 7.88 (2H, br.dt), 7.81 (2H, t, J = 1.6 Hz), 7.75 (1H, br.dt), 7.57-7.51 (5H, m), 7.51-7.39 (4H, m), 7.47 (4H, s), 7.34 (4H, d, J = 8.4 Hz), 7.27 (2H, dd, J = 1.6, 2.0 Hz), 7.19 (4H, d, J = 8.4 Hz), 7.13 (4H, d, J = 8.0 Hz), 6.83 (4H, d, J = 8.4 Hz), 6.63 (2H, dd, J = 1.6, 2.0 Hz), 4.14 (2H, br.s), 4.07 (2H, br.s), 3.63 (4H, br.s), 1.70-1.41 (8H, br.m), 1.39-1.28 (8H, m), 0.89 (6H, t, J = 7.2 Hz), 0.89 (6H, t, J = 7.2 Hz); 13C NMR δ (100 MHz;
CDCl₃/ppm 169.3, 169.3, 144.0, 142.9, 137.9, 137.6, 136.5, 132.3, 131.8, 130.7, 130.2, 130.0, 129.7, 129.0, 129.0, 128.4, 128.2, 127.6, 127.0, 124.4, 123.9, 123.6, 123.3, 123.2, 123.1, 121.3, 91.3, 91.0, 90.5, 89.8, 89.7, 89.4, 89.1, 50.5, 49.3, 29.8, 29.7, 20.1, 13.8; FD-LRMS m/z 1322.6 (M⁺, 95%), 1323.6 ([M+1]⁺, 100), 1324.6 ([M+2]⁺, 56), 1325.6 ([M+3]⁺, 21), 1326.6 ([M+4]⁺, 7); FD-HRMS Found: 1322.57095, Calc. for C₉₄H₇₄N₄O₄: 1322.57100; UV λmax(CH₂Cl₂)/nm (log ε) 355 (sh. 4.53), 336 (4.69), 304 (sh. 5.16), 287 (5.29).
Scheme S2. Synthesis of 2a/2b. Reagents and yields: (a) TMSA, Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, Et\textsubscript{3}N (100%); (b) i) K\textsubscript{2}CO\textsubscript{3}, MeOH, THF (93% for 26'); ii) 1,3-diiodobenzene, Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, Et\textsubscript{3}N (63%); (c) 33\textsuperscript{8}, Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, iPr\textsubscript{2}NH, THF (98%); (d) i) K\textsubscript{2}CO\textsubscript{3}, MeOH, THF (96% for 28'); ii) 23, Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, iPr\textsubscript{2}NH, THF (89%); (e) i) K\textsubscript{2}CO\textsubscript{3}, MeOH, THF (93% for 29'); ii) 27, Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, iPr\textsubscript{2}NH, THF (69%); (f) i) TFA, CH\textsubscript{2}Cl\textsubscript{2} (91% for 30'); ii) methyl 4-(chloroformyl)benzoate, Et\textsubscript{3}N, toluene (92%); (g) i) LiOH, H\textsubscript{2}O, MeOH, THF (97% for 31'); ii) SOCl\textsubscript{2}, BnEt\textsubscript{3}NCl, CH\textsubscript{2}Cl\textsubscript{2}; iii) 8', Et\textsubscript{3}N, THF, toluene (51%); (h) i) TBAF, THF (94% for 32'); ii) Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, Et\textsubscript{3}N, THF (30%).

Preparation of 26

To a solution of 13 (2.06 g, 5.06 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (176 mg, 0.152 mmol) and CuI (60 mg, 0.32 mmol) in Et\textsubscript{3}N (50 mL) was added TMSA (2.86 mL, 20.2 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 52 °C for 8 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO\textsubscript{2} (dichloromethane/hexane) to give 26 (2.22 g) as a light-brown oil in 100% yield. An analytical sample
was obtained as a colorless oil by further purification through GPC (chloroform). 26: elemental analyses Found: C, 67.89; H, 8.96; N, 3.17%. Calc. for C_{25}H_{30}NO_2Si: C, 67.97; H, 8.90; N, 3.17%. IR (neat) \( \nu_{\text{max}}/\text{cm}^{-1} \) 3067, 2961, 2932, 2900, 2874, 2863, 2155, 1707, 1581; \(^1\)H NMR \( \delta_{1}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_2\text{Si})/\text{ppm} \) 7.42 (1H, t, \( J = 1.2 \) Hz), 7.23 (2H, br.d), 3.58 (2H, t, \( J = 7.6 \) Hz), 1.52-1.44 (2H, m), 1.43 (9H, s), 1.33-1.24 (2H, m), 0.89 (3H, t, \( J = 7.2 \) Hz), 0.24 (18H, s); \(^{13}\)C NMR \( \delta_{3}(100 \text{ MHz}; \text{CDCl}_3)/\text{ppm} \) 154.2, 142.6, 133.0, 130.6, 123.8, 103.5, 95.1, 80.4, 49.5, 30.5, 28.3, 19.9, 13.7, –0.2; FD-LRMS \( m/z \) 441.3 (M\(^+\), 100%), 442.3 ([M+1]\(^+\), 41), 443.3 ([M+2]\(^+\), 16), 444.3 ([M+3]\(^+\), 4).

Preparation of 27

To a solution of 26 (2.01 g, 4.55 mmol) in THF (23 mL) and MeOH (23 mL) was added K₂CO₃ (1.26 g, 9.09 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 26\(^{'}\) (1.25 g) as a white solid in 93% yield. 26\(^{'}\): \(^1\)H NMR \( \delta_{1}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_2\text{Si})/\text{ppm} \) 7.44 (1H, t, \( J = 1.2 \) Hz), 7.31 (2H, br.d), 3.60 (2H, d, \( J = 7.6 \) Hz), 3.09 (2H, s), 1.55-1.45 (2H, m), 1.44 (9H, s), 1.34-1.25 (2H, m), 0.90 (3H, t, \( J = 7.6 \) Hz).

To a solution of 26\(^{'}\) (1.25 g, 4.21 mmol) and 1,3-diiodobenzene (5.56 g, 16.8 mmol) in Et₃N (90 mL) were added Pd(PPh₃)₄ (486 mg, 0.421 mmol) and Cul (162 mg, 0.851 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 °C for 18 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 27 (1.85 g) as a yellow oil in 63% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). 27: mp 74-75 °C; elemental analyses Found: C, 53.11; H, 4.07; N, 2.01%. Calc. for C_{35}H_{30}I₂NO₂: C, 53.09; H, 4.17; N, 2.00%. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \) 3052, 2955, 2927, 2870, 2860, 2211, 1702, 1586, 1546; \(^1\)H NMR \( \delta_{1}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_2\text{Si})/\text{ppm} \) 7.90 (2H, t, \( J = 1.2 \) Hz), 7.69 (2H, ddd, \( J = 1.2, 2.0, 8.0 \) Hz), 7.51 (1H, t, \( J = 1.6 \) Hz), 7.49 (2H, br.ddd), 7.34 (2H, br.d), 7.09 (2H, t, \( J = 8.0 \) Hz), 3.64 (2H, t, \( J = 7.6 \) Hz), 1.58-1.50 (2H, m), 1.46 (9H, s), 1.37-1.28 (2H, m), 0.92 (3H, t, \( J = 7.6 \) Hz); \(^{13}\)C NMR \( \delta_{3}(100 \text{ MHz}; \text{CDCl}_3)/\text{ppm} \) 154.2, 142.9, 140.1, 137.5, 132.0, 130.7, 130.2, 129.8, 124.8, 123.6, 93.7, 89.2, 88.4, 80.5, 49.5, 30.5, 28.3, 19.8, 13.8; FD-LRMS \( m/z \) 701.0 (M\(^+\), 100%), 702.0 ([M+1]\(^+\), 36), 703.0 ([M+2]\(^+\), 7).

Preparation of 28

To a solution of 15 (3.00 g, 7.08 mmol) and 33 (5.19 g, 18.4 mmol) in THF (35 mL) and \(^3\)Pr₂NH (35 mL) were added Pd(PPh₃)₄ (245 mg, 0.212 mmol) and Cul (84 mg, 0.44 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 80 °C for 16 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 28 (4.32 g) as a pale yellow oil in 98% yield. An analytical sample was obtained as a colorless oil by further purification through GPC.
elemental analyses Found: C, 74.79; H, 9.11; N, 2.19%. Calc. for C$_{30}$H$_{53}$NO$_2$Si$_2$: C, 74.82; H, 8.86; N, 2.24%. IR (KBr) $\nu$ max/cm$^{-1}$ 3063, 2959, 2942, 2892, 2864, 1517, 1706, 1595, 1582 (too highly viscous to be applied to a plate of NaCl); $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.63 (1H, br.d.), 7.48 (1H, $J$ = 1.6 Hz), 7.45 (1H, br.d.), 7.43 (1H, d, $J$ = 1.6 Hz), 7.31-7.26 (3H, br.m), 3.61 (2H, $t$, $J$ = 7.6 Hz), 1.55-1.47 (2H, m), 1.44 (9H, s), 1.35-1.26 (2H, m), 1.14 (21H, s), 0.91 (3H, t, $J$ = 7.6 Hz), 0.25 (9H, s); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm 154.3, 142.8, 135.1, 132.6, 131.9, 131.3, 130.4, 128.3, 124.0, 123.9, 123.7, 123.0, 106.0, 103.6, 95.3, 91.5, 89.2, 88.6, 80.4, 49.5, 30.5, 28.3, 19.9, 18.6, 13.8, 11.3, −0.1; FD-LRMS $m/z$ 625.4 (M$^+$, 100%), 626.4 ([M+1]$^+$, 56), 627.4 ([M+2]$^+$, 23), 628.4 ([M+3]$^+$, 6).

Preparation of 29

To a solution of 28 (4.02 g, 6.43 mmol) in THF (16 mL) and MeOH (16 mL) was added K$_2$CO$_3$ (890 mg, 6.45 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (dichloromethane/hexane) to give 28' (3.43 g) as a pale yellow oil in 96% yield. 28': $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.64 (1H, br.d.), 7.48 (1H, $t$, $J$ = 1.6 Hz), 7.47-7.43 (2H, m), 7.35 (1H, br.m), 7.31-7.27 (2H, m), 3.62 (2H, $t$, $J$ = 7.6 Hz), 3.10 (1H, s), 1.56-1.48 (2H, m), 1.47 (9H, s), 1.36-1.27 (2H, m), 1.14 (21H, s), 0.91 (3H, t, $J$ = 7.6 Hz).

To a solution of 23 (3.35 g, contained 1-bromo-3-(2-trimethylsilyl)ethynylbenzene in a ratio of 5:1), Pd(PPh$_3$)$_2$ (215 mg, 0.186 mmol) and Cul (71 mg, 0.37 mmol) in Pr$_2$NH (31 mL) and THF (25 mL) was added a solution of 28' (3.43 g, 6.20 mmol) in THF (6 mL) via a syringe pump over 1.5 h at 50 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (dichloromethane/hexane) to give 29 (3.99 g) as a pale yellow amorphous solid in 89% yield. An analytical sample was obtained as a pale yellow oil due to residual hexane, which was indicated by a result of the elemental analyses, by further purification through HPLC. 29: elemental analyses Found: C, 77.79; H, 8.55; N, 1.81%. Calc. for C$_{27}$H$_{51}$NO$_2$Si: C, 77.74; H, 8.19; N, 1.93%; IR (KBr) $\nu$ max/cm$^{-1}$ 3062, 2959, 2941, 2891, 2864, 2158, 1704, 1595, 1582; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.65 (2H, br.d.), 7.52 (1H, $t$, $J$ = 1.6 Hz), 7.48-7.42 (4H, m), 7.34-7.27 (4H, m), 3.64 (2H, $t$, $J$ = 7.6 Hz), 1.58-1.50 (2H, m), 1.46 (9H, s), 1.37-1.28 (2H, m), 1.14 (21H, s), 0.92 (3H, t, $J$ = 7.2 Hz), 0.26 (9H, s); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm 154.3, 142.9, 135.1, 132.1, 132.0, 131.8, 131.5, 131.3, 130.2, 128.4, 123.9, 123.9, 123.5, 123.1, 123.0, 106.0, 104.0, 95.1, 91.5, 89.3, 89.3, 88.6, 88.6, 80.5, 49.6, 30.6, 28.3, 19.9, 18.6, 13.8, 11.3, −0.1; FD-LRMS $m/z$ 725.4 (M$^+$, 100%), 726.4 ([M+1]$^+$, 64), 727.4 ([M+2]$^+$, 28), 728.4 ([M+3]$^+$, 9), 729.4 ([M+4]$^+$, 2).
Preparation of 30

To a solution of 29 (2.36 g, 3.25 mmol) in THF (12 mL) and MeOH (8 mL) was added K<sub>2</sub>CO<sub>3</sub> (448 mg, 3.25 mmol) at room temperature, and the mixture was stirred at that temperature for 10 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO<sub>2</sub> (dichloromethane/hexane) to give 29' (1.97 g) as a pale yellow oil in 93% yield. 29': 1 H NMR δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)/ppm 7.67-7.66 (2H, br.m), 7.54 (1H, t, J = 1.2 Hz), 7.50 (1H, dt, J = 1.2, 7.6 Hz), 7.48-7.44 (3H, m), 7.37-7.28 (4H, br.m), 3.64 (2H, t, J = 7.6 Hz), 3.10 (1H, s), 1.58-1.51 (2H, m), 1.46 (9H, s), 1.38-1.28 (2H, m), 1.14 (21H, s), 0.92 (3H, t, J = 7.6 Hz).

To a solution of 27 (6.92 g, 9.86 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (348 mg, 0.301 mmol) and Cul (116 mg, 0.609 mmol) in Pr<sub>2</sub>NH (30 mL) and THF (24 mL) was added a solution of 29' (1.97 g, 3.01 mmol) in THF (6 mL) via a syringe pump over 1.5 h at 50 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO<sub>2</sub> (dichloromethane/hexane) to give 30 (2.59 g) as a white amorphous solid in 69% yield. An analytical sample was obtained as a white solid by further purification with HPLC (dichloromethane/hexane), followed by GPC (chloroform). 30: mp 74-75 °C; elemental analyses Found: C, 73.36; H, 6.46; N, 2.26%. Calc. for C<sub>75</sub>H<sub>76</sub>N<sub>2</sub>O<sub>3</sub>Si: C, 73.39; H, 6.49; N, 2.28%; IR (KBr) ν<sub>max</sub>/cm<sup>-1</sup> 3061, 2957, 2939, 2929, 2862, 2821, 1715, 1056; 1 H NMR δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)/ppm 7.90 (1H, t, J = 1.6 Hz), 7.72 (2H, br.t), 7.68 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.66 (1H, br.dtt), 7.55-7.44 (9H, m), 7.38-7.32 (6H, m), 7.30 (1H, br.t), 7.09 (1H, t, J = 7.6 Hz), 3.65 (2H, t, J = 7.2 Hz), 3.65 (2H, t, J = 7.6 Hz), 1.59-1.51 (4H, m), 1.46 (18H, br.s), 1.38-1.29 (4H, m), 1.14 (21H, s), 0.93 (6H, t, J = 7.2 Hz); 13C NMR δ<sub>C</sub> (100 MHz; CDCl<sub>3</sub>)/ppm 154.3, 154.3, 143.0, 142.9, 140.2, 137.5, 135.1, 134.6, 132.1, 132.1, 132.0, 131.6, 131.6, 131.5 (br), 131.3, 130.7, 130.3, 130.2 (br), 129.9, 128.6, 128.4, 124.9, 123.9, 123.8, 123.7, 123.4, 123.3, 123.2, 123.0, 106.0, 93.7, 91.5, 89.4, 89.3, 89.2, 89.1, 89.1, 88.7, 88.7, 88.6, 88.4, 80.6, 80.5, 49.6, 30.6, 28.3, 19.9, 18.6, 13.8, 11.3; FD-LRMS m/z 1026.4 ([M−(BOC)]<sup>+</sup>, 55%), 1027.4 ([M+1−(BOC)]<sup>+</sup>, 42), 1028.4 ([M+2−(BOC)]<sup>+</sup>, 19), 1029.4 ([M+3−(BOC)]<sup>+</sup>, 6), 1030.4 ([M+4−(BOC)]<sup>+</sup>, 2), 1070.3 ([M−(TIPS)]<sup>+</sup>, 3), 1071.3 ([M+1−(TIPS)]<sup>+</sup>, 15), 1072.3 ([M+2−(TIPS)]<sup>+</sup>, 11), 1073.3 ([M+3−(TIPS)]<sup>+</sup>, 5), 1074.3 ([M+4−(TIPS)]<sup>+</sup>, 2), 1126.4 ([M−(BOC)]<sup>+</sup>, 96), 1127.4 ([M+1−(BOC)]<sup>+</sup>, 100), 1128.4 ([M+2−(BOC)]<sup>+</sup>, 54), 1129.4 ([M+3−(BOC)]<sup>+</sup>, 20), 1130.4 ([M+4]<sup>+</sup>, 6), 1226.5 (M<sup>+</sup>, 30), 1227.5 ([M+1]<sup>+</sup>, 26), 1228.5 ([M+2]<sup>+</sup>, 13), 1229.5 ([M+3]<sup>+</sup>, 5), 1230.5 ([M+4]<sup>+</sup>, 1).

Preparation of 31

To a solution of 30 (1.54 g, 1.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (82 mL) was added TFA (8.2 mL) at room temperature. The mixture was stirred at room temperature for 30 min, neutralized with 1M aq. NaOH, and separated. The organic layer was dried over magnesium sulfate, passed through a Celite/SiO<sub>2</sub> pad,
and then concentrated. The residue was purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 30' (1.17 g) as a white amorphous solid in 91% yield. 30': 1H NMR δ (400 MHz; CDCl₃) ppm 7.89 (1H, t, J = 1.6 Hz), 7.71 (2H, t, J = 1.6 Hz), 7.68-7.64 (2H, m), 7.50-7.42 (7H, m), 7.37-7.26 (3H, m), 7.08 (1H, t, J = 7.6 Hz), 7.06 (1H, t, J = 1.2 Hz), 7.05 (1H, t, J = 1.2 Hz), 6.75-6.71 (4H, m), 3.72 (2H, br.s), 3.15 (2H, br.t), 3.14 (2H, br.t), 1.67-1.59 (4H, m), 1.50-1.40 (4H, m), 1.13 (21H, s), 0.98 (6H, t, J = 7.6 Hz).

To a solution of 30' (1.17 g, 1.14 mmol) in toluene (20 mL) containing Et₃N (0.8 mL) were added two portions of methyl 4-(chloroformyl)benzoate (477+238 mg, 2.40+1.20 mmol) at room temperature, and the reaction mixture was stirred at 80 °C for each 1.5 h. The mixture was diluted with dichloromethane, and which was washed with satd. aq. NaHCO₃, dried over magnesium sulfate, and then passed through a Celite/AI₂O₃ pad. The filtrate was concentrated and purified by column chromatography on Al₂O₃/SiO₂ (ethyl acetate/dichloromethane) to give 31 (1.42 g) as a white amorphous solid in 92% yield. An analytical sample was obtained as a white solid by further purification through GPC (chloroform). 31: mp 104-105 °C; elemental analyses Found: C, 73.69; H, 5.52; N, 2.07%. Calc. for C₈₃H₃₂N₆O₇Si: C, 73.76; H, 5.59; N, 2.07%; IR (KBr) v max/cm⁻¹ 3059, 2940, 2861, 2214, 1754, 1625, 1595, 1580; ¹H NMR δ (400 MHz; CDCl₃; Me₄Si)/ppm 7.91 (4H, d, J = 8.4 Hz), 7.87 (1H, t, J = 1.6 Hz), 7.71-7.67 (3H, m), 7.63 (1H, br.d), 7.53-7.35 (15H, m), 7.30 (1H, br.d), 7.16 (4H, br.d), 7.09 (1H, br.t), 3.93 (4H, t, J = 7.6 Hz), 3.88 (3H, s), 3.87 (3H, s), 1.68-1.60 (4H, m), 1.44-1.35 (4H, m), 1.13 (21H, s), 0.95 (6H, t, J = 7.6 Hz); ¹³C NMR δ (100 MHz; CDCl₃)/ppm 169.2, 166.3, 143.4, 140.2, 140.0, 140.0, 137.8, 135.0, 134.6, 132.2, 131.9, 131.8, 131.5 (br.m), 131.3, 131.0 (br.m), 130.7, 130.7, 130.6, 130.6, 129.9, 129.3, 128.6, 128.5, 128.4, 124.7, 124.6, 124.5, 124.4, 124.0, 123.4, 123.4, 122.8, 122.8, 122.5, 105.8, 93.7, 91.7, 90.3, 90.2, 90.1, 89.3, 89.1, 88.9, 87.9, 87.9, 87.7, 52.2, 50.2, 29.7, 20.1, 18.6, 13.8, 11.2; FD-LRMS m/z 1307.4 ([M–(Pr)]⁺, 63%), 1308.4 ([M+1–(Pr)]⁺, 58), 1309.4 ([M+2–(Pr)]⁺, 30), 1310.4 ([M+3–(Pr)]⁺, 12), 1311.4 ([M+4–(Pr)]⁺, 4), 1350.4 (M⁺, 99), 1351.4 ([M+1]⁺, 100), 1352.4 ([M+2]⁺, 56), 1353.4 ([M+3]⁺, 22), 1354.4 ([M+4]⁺, 7).

Preparation of 32

To a solution of 31 (1.42 g, 1.05 mmol) in THF (22 mL) and MeOH (7 mL) was added a solution of LiOH·H₂O (224 mg, 5.25 mmol) in water (7 mL) at room temperature, and the resulting suspension was stirred at 40-50 °C for 2 h and turned transparent. The reaction mixture was acidified with 1M aq. HCl, and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, and concentrated to give carboxylic acid 31'
(1.35 g) as an off-white amorphous solid in 97% yield.

To a refluxed solution of \textit{31}' (627 mg, 0.474 mmol) in CH$_2$Cl$_2$ (15 mL) containing a catalytic amount of benzyltriethylammonium chloride was added SOCl$_2$ (0.20 mL, 2.8 mmol), and the mixture was refluxed for 1.5 h, and concentrated to give acid chloride \textit{31}'', which was dissolved in THF, and immediately subjected to the following reaction.

To a solution of \textit{8} (191 mg, 0.454 mmol) and Et$_3$N (0.64 mL, 4.6 mmol) in toluene (56 mL) and THF (30 mL) was added a solution of \textit{31}'' in THF (30 mL) at 92 °C, and the mixture was stirred at 95 °C for 1 h. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with 1M aq. NaOH, dried over magnesium sulfate, passed through a Celite/Al$_2$O$_3$ pad, and then concentrated. The crude product was purified by column chromatography on SiO$_2$/Al$_2$O$_3$ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give \textit{32} (398 mg) as a white solid in 51% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). \textit{32}: mp 165-166 °C; elemental analyses Found: C, 77.62; H, 5.73; N, 3.28%. Calc. for C$_{11}$H$_{30}$In$_2$O$_3$Si: (EtOH)$_{3/2}$: C, 77.71; H, 5.94; N, 3.24%; IR (KBr) $\nu_{\text{max}}$/cm$^{-1}$: 3059, 2955, 2929, 2861, 2213, 1615, 1595, 1581, 1517; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm: 7.91 (1H, t, $J$ = 1.6 Hz), 7.71-7.59 (10H, br.m), 7.54-7.47 (7H, m), 7.40-7.28 (7H, m), 7.13 (8H, br.s), 7.11-7.05 (3H, m), 6.98 (2H, br.m), 6.82 (2H, d, $J$ = 8.4 Hz), 6.82 (2H, d, $J$ = 8.4 Hz), 3.87 (8H, t, $J$ = 7.6 Hz), 1.64-1.50 (8H, m), 1.41-1.27 (8H, m), 1.13 (21H, s), 0.93 (6H, t, $J$ = 7.2 Hz), 0.87 (6H, t, $J$ = 7.2 Hz); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm: 169.1, 169.0, 169.0, 143.6, 143.6, 143.2, 140.1, 137.8, 136.9, 136.6, 135.0, 134.7, 134.7, 133.4, 133.4, 132.3, 131.9, 131.7, 131.7, 131.5, 131.4, 131.3, 130.8, 130.7 (br.m), 130.5, 130.4, 130.0, 128.8, 128.7, 128.5, 128.4, 128.1, 127.3, 124.5, 124.3, 124.1, 123.5, 123.4, 123.2, 123.1, 122.9, 122.9, 122.6, 121.0, 105.8, 93.8, 92.0, 91.1, 91.0, 90.2, 90.1, 90.0, 89.8, 89.3, 89.2, 89.1, 88.8, 88.4, 88.4, 88.1, 50.0, 49.8, 29.6, 20.1, 20.1, 18.6, 13.8, 13.7, 11.2; FD-LRMS $m/z$: 1706.6 (M$^+$, 80%), 1707.6 ([M+1]$^+$, 100), 1708.6 ([M+2]$^+$, 71), 1709.6 ([M+3]$^+$, 35), 1710.6 ([M+4]$^+$, 14), 1711.6 ([M+5]$^+$, 5).

Preparation of \textit{2a} and \textit{2b}

To a solution of \textit{32} (341 mg, 0.200 mmol) in THF (8 mL) was added TBAF (1 M in THF, 0.22 mL, 0.22 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. After removal of the solvent by evaporation, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give \textit{32}' (291 mg) as a white solid in 94% yield. \textit{32}': $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm: 7.93 (1H, t, $J$ = 1.6 Hz), 7.72-7.59 (10H, br.m), 7.55-7.49 (7H, m), 7.41-7.32 (7H, m), 7.14 (8H, br.s), 7.09 (3H,
br.t), 7.00 (2H, br.t), 6.84 (4H, d, J = 8.8 Hz), 3.88 (8H, br.t), 3.11 (1H, s), 1.64-1.50 (8H, m), 1.42-1.27 (8H, m), 0.93 (6H, t, J = 7.2 Hz), 0.88 (6H, t, J = 7.6 Hz).

To a solution of Pd(PPh₃)₄ (130 mg, 0.113 mmol) and Cul (22 mg, 0.12 mmol) in Et₃N (28 mL) was added a solution of 32’ (291 mg, 0.188 mmol) in THF (13 mL) via a syringe pump over 20 h at 73-75 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a mixture containing 2a and 2b (81 mg, 2a:2b = 1.8:1) as a pale yellow solid in 30% yield. 2b and 2a were isolated in this order by HPLC separation (1:9 tetrahydrofuran/chloroform). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

2a: mp >300 °C; IR (KBr) νmax/cm⁻¹ 3057, 2955, 2928, 2870, 2862, 2216, 1647, 1595, 1580, 1518; ¹H NMR δ(Hz)/ppm (400 MHz; CDCl₃; Me₄Si)/ppm 8.05 (4H, s), 7.82 (4H, br.d), 7.67 (2H, t, J = 1.2 Hz), 7.60 (4H, dt, J = 1.6, 7.6 Hz), 7.56 (4H, dt, J = 1.6, 7.6 Hz), 7.43 (4H, br.t), 7.37 (4H, d, J = 8.8 Hz), 7.15 (4H, d, J = 8.8 Hz), 7.12 (4H, d, J = 8.8 Hz), 7.01 (4H, d, J = 1.2 Hz), 6.78 (4H, d, J = 8.8 Hz), 3.87 (4H, t, J = 7.6 Hz), 3.84 (4H, t, J = 7.6 Hz), 1.65-1.24 (8H, m), 0.94 (6H, t, J = 7.2 Hz), 0.84 (6H, t, J = 7.2 Hz); ¹³C NMR δ(C)/ppm (100 MHz; CDCl₃)/ppm 169.5, 169.4, 143.6, 143.2, 137.3, 136.7, 134.8, 133.7, 132.4, 132.0, 131.9, 131.5, 130.6, 128.9, 128.3, 128.1, 127.4, 124.1, 123.7, 123.5, 123.0, 120.9, 91.7, 90.1, 89.5, 89.3, 88.6, 49.9, 49.6, 29.7, 29.2, 20.1, 13.8, 13.7; FD-LRMS m/z 1422.6 (M⁺, 89%), 1423.6 ([M+1]⁺, 100), 1424.6 ([M+2]⁺, 61), 1425.6 ([M+3]⁺, 25), 1426.6 ([M+4]⁺, 9), 1427.6 ([M+5]⁺, 3); FD-HRMS Found: 1422.60434, Calc. for C₁₉₂H₇₈N₄O₄: 1422.60230; UV λmax(CH₂Cl₂)/nm (log ε) 359 (sh. 4.64), 337 (4.72), 306 (5.34), 289 (5.43).

2b: mp >253 °C (dec); IR (KBr) νmax/cm⁻¹ 3061, 3039, 2955, 2928, 2870, 2860, 2212, 1655, 1650, 1595, 1574, 1516; ¹H NMR δ(Hz)/ppm (400 MHz; CDCl₃; Me₄Si)/ppm 7.77 (4H, br.d), 7.60-7.53 (8H, m), 7.55 (4H, s), 7.47 (2H, t, J = 1.6 Hz), 7.44 (4H, br.d), 7.28 (4H, d, J = 8.4 Hz), 7.22 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 7.01 (4H, d, J = 1.2 Hz), 6.82 (4H, d, J = 8.4 Hz), 3.88 (4H, t, J = 7.6 Hz), 3.82 (4H, t, J = 7.6 Hz), 1.62-1.45 (8H, m), 1.40-1.25 (8H, m), 0.91 (6H, t, J = 7.2 Hz), 0.86 (6H, t, J = 7.2 Hz); ¹³C NMR δ(C)/ppm (100 MHz; CDCl₃)/ppm 169.4, 169.2, 143.6, 143.2, 137.3, 136.7, 135.6, 133.0, 132.5, 131.9, 131.5, 131.2, 130.4, 128.9, 128.4, 128.3, 127.2, 124.2, 123.5, 123.3, 123.1, 121.2, 90.9, 90.0, 89.9, 89.4, 88.4, 50.1, 49.8, 29.6, 20.1, 20.1, 13.8, 13.8; FD-LRMS m/z 1422.6 (M⁺, 90%), 1423.6 ([M+1]⁺, 100), 1424.6 ([M+2]⁺, 64), 1425.6 ([M+3]⁺, 27), 1426.6 ([M+4]⁺, 9), 1427.6 ([M+5]⁺, 3); FD-HRMS Found: 1422.60445, Calc. for C₁₉₂H₇₈N₄O₄: 1422.60230; UV λmax(CH₂Cl₂)/nm (log ε) 359 (sh. 4.64), 337 (4.72), 304 (5.29), 288 (5.39).
Scheme S3. Synthesis of 4a/4b. Reagents and yields: (a) TMSA, PdCl₂(PPh₃)₂, CuI, Et₃N (99%); (b) i) K₂CO₃, MeOH, THF (93% for 35'); ii) CuCl, N,N,N',N'-tetramethylethylenediamine (TMEDA), acetone (71%); (c) i) LiOH, H₂O, MeOH, THF (65% for 36'); ii) SOCl₂, BnEt₃NCl, CH₂Cl₂; iii) 19, Et₃N, THF, toluene (67%); (d) i) K₂CO₃, MeOH, THF (97% for 37'); ii) 1,3-diiodobenzene, Pd(PPh₃)₄, CuI, Et₃N, THF (82%); (e) i) TBAF, THF (91% for 38'); ii) Pd(PPh₃)₄, CuI, Et₃N, THF (5%).

Preparation of 35

To a suspended solution of 34 (3.19 g, 7.29 mmol), PdCl₂(PPh₃)₂ (76 mg, 0.11 mmol) and CuI (34 mg, 0.18 mmol) in Et₃N (60 mL) was added TMSA (1.1 mL, 7.8 mmol) at room temperature under an argon atmosphere, and the reaction mixture was stirred at the temperature for 21 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane) to give 35 (2.94 g) as a pale yellow oil in 99% yield.

To a solution of 35 (2.94 g, 7.23 mmol) in THF (35 mL) and MeOH (35 mL) was added K₂CO₃ (974 mg, 7.06 mmol), and the mixture was stirred at room temperature for 25 min, and then diluted with ethyl acetate. The diluted solution was washed with water and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane) to give 35' (2.26 g) as a white solid in 93% yield. An analytical sample was obtained as a white solid by precipitation in ethyl acetate. 35': mp 123-124 °C; elemental analyses Found: C, 75.19; H, 6.17; N, 4.19%. Calc. for C₂₁H₂₁NO₃: C, 75.20; H, 6.31; N, 4.18%; IR (KBr) νmax/cm⁻¹ 3285, 3060, 2951, 2872,
2106, 1721, 1637, 1598, 1504; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 7.85 (2H, d, $J = 8.4$ Hz),
7.33 (2H, d, $J = 8.4$ Hz), 7.32 (2H, d, $J = 8.4$ Hz), 6.96 (2H, d, $J = 8.4$ Hz), 3.92 (2H, t, $J = 7.6$ Hz),
3.88 (3H, s), 3.07 (1H, s), 1.63-1.56 (2H, m), 1.41-1.32 (2H, m), 0.92 (3H, t, $J = 7.2$ Hz); $^{13}$C
NMR $\delta$(100 MHz; CDCl$_3$)/ppm 169.2, 166.3, 143.3, 140.4, 133.0, 130.9, 129.1, 128.5, 127.6, 120.7,
82.5, 78.2, 52.2, 50.0, 29.8, 20.1, 13.8; FD-LRMS m/z 335.2 (M$^+$, 100%), 336.2 ([M+1]$^+$, 23), 337.2
([M+2]$^+$, 3).

Preparation of 36

To an ice-cooled solution of CuCl (242 mg, 2.44 mmol) and TMEDA (1.22 mL, 8.15 mmol)
in acetone (87 mL) was added a solution of 35$^+$ (3.58 g, 10.7 mmol) in acetone (44 mL) under an
oxygen atmosphere, and the mixture was stirred at room temperature for 10 days. After removal of the
solvent by evaporation, the residue was dissolved in dichloromethane, and which was washed with 0.5
M aq. HCl, dried over magnesium sulfate, and concentrated. The resulting solid was separated by
column chromatography on SiO$_2$ (ethyl acetate/dichloromethane) to give 36 as a white solid and
unreacted 35$^+$ (895 mg, recov. 25%), which underwent a repeated procedure similar to the above (CuCl,
TMEDA, acetone, dichloromethane). Combined solids were washed with methanol to give 36 (2.54
g) as a white solid in 71% yield. An analytical sample was obtained as a white solid by further
purification through GPC (chloroform). 36: mp 151-152 ºC; elemental analyses Found: C, 75.01; H,
5.95; N, 4.14%. Calc. for C$_{35}$H$_{30}$N$_2$O$_6$ (EtOH)$_2$·Cu·Cl·TMEDA: C, 75.03; H, 6.15; N, 4.12%; IR
(KBr) $\nu_{max}$/cm$^{-1}$
3059, 2951, 2934, 2873, 2857, 2152, 1725, 1640, 1594, 1504; $^1$H NMR $\delta$(400 MHz; CDCl$_3$;
Me$_4$Si)/ppm 7.85 (4H, d, $J = 8.4$ Hz), 7.35 (4H, d, $J = 8.4$ Hz), 7.33 (4H, d, $J = 8.4$ Hz), 6.97 (4H, d,
$J = 8.4$ Hz), 3.92 (4H, t, $J = 7.6$ Hz), 3.88 (6H, s), 1.63-1.56 (4H, m), 1.41-1.32 (4H, m), 0.92 (6H, t,
$J = 7.2$ Hz); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm 169.2, 166.2, 143.8, 140.2, 133.4, 131.0, 129.2,
128.5, 127.6, 120.0, 80.9, 74.6, 52.2, 50.1, 29.8, 20.1, 13.8; FD-LRMS m/z 668.3 (M$^+$, 100%), 669.3
([M+1]$^+$, 47), 670.3 ([M+2]$^+$, 13), 671.3 ([M+3]$^+$, 3).

Preparation of 37

To a suspension of 36 (2.04 g, 3.06 mmol) in THF (64 mL) and
MeOH (20 mL) was added a solution of LiOH·H$_2$O (643 mg, 15.3 mmol) in
water (20 mL) at room temperature, and the mixture was stirred at 45-48 ºC
for 3 h and turned transparent. The reaction mixture was acidified with 1M aq.
HCl, and extracted with ethyl acetate. The organic layer was dried over
magnesium sulfate, and concentrated. The resulting solid was washed in
refluxed methanol, and collected by filtration to give carboxylic acid 36$^+$ (1.27
g) as a reddish-white solid in 65% yield.

To a refluxed solution of 36$^+$ (1.16 g, 1.81 mmol) in CH$_2$Cl$_2$ (0.12 L) containing a catalytic
amount of benzyltriethylammonium chloride was added SOCl$_2$ (1.1 mL, 15 mmol), and the mixture
was refluxed for 2 h, and concentrated to give acid chloride 36'' as a yellow solid, which was dissolved in THF, and immediately subjected to the following reaction.

To a solution of 19 (1.20 g, 1.73 mmol) and Et$_3$N (2.5 mL, 18 mmol) in toluene (190 mL) and THF (100 mL) was added a solution of 36'' in THF (100 mL) at 99-100 °C, and the mixture was stirred at 99-100 °C for 1 h. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, and which was washed with satd. aq. NaHCO$_3$, passed through a Celite/Al$_2$O$_3$ pad, and then concentrated. The crude product was purified by column chromatography on SiO$_2$/Al$_2$O$_3$ (ethyl acetate/dichloromethane) to give 37 (1.50 g) as a pale-yellowish-white solid in 67% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). 37: mp 161-162 °C; elemental analyses Found: C, 78.59; H, 7.09; N, 4.24%. Calc. for C$_{36}$H$_{32}$N$_2$O$_3$Si$_2$: C, 78.41; H, 7.33; N, 4.16%; IR (KBr) $\nu_{max}$/cm$^{-1}$ 3062, 2956, 2932, 2863, 2213, 1654, 1596, 1580; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 8.05 (1H, br.s), 7.61 (1H, t, $J$ = 1.6 Hz), 7.55 (1H, t, $J$ = 1.6 Hz), 7.53-7.49 (2H, br.m), 7.43-7.36 (5H, m), 7.12-7.07 (1H, br.m), 7.10 (4H, br.s), 7.10 (4H, br.s), 7.02 (1H, t, $J$ = 1.6 Hz), 6.91 (1H, t, $J$ = 1.6 Hz), 6.85 (1H, t, $J$ = 1.6 Hz), 6.79 (2H, d, $J$ = 8.4 Hz), 6.78 (2H, d, $J$ = 8.4 Hz), 3.86 (8H, br.s), 1.64-1.48 (8H, m), 1.42-1.26 (8H, m), 1.18-1.15 (21H, m), 0.94 (3H, t, $J$ = 7.2 Hz), 0.93 (3H, $J$ = 7.6 Hz), 0.87 (6H, t, $J$ = 7.2 Hz), 0.30 (9H, s); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm 169.3, 169.0, 168.9, 144.0, 144.0, 143.4, 143.4, 137.0, 136.8 (br.), 136.7, 136.6, 134.5, 134.2, 133.2, 131.4 (br.m), 130.9, 130.6, 130.5, 130.2, 128.7, 128.3, 128.1, 127.9, 127.1, 127.1, 124.6, 124.5, 123.9, 123.9, 123.1, 123.0, 119.5, 119.4, 104.9, 102.9, 96.6, 93.2, 90.2, 88.6, 88.6, 81.4, 74.8, 74.6, 49.8, 49.7 (br.), 49.6, 29.6 (br.), 29.5, 29.5, 20.0, 20.0, 20.0, 18.6, 13.7, 13.7, 11.2, –0.3; FD-LRMS m/z 1300.7 (M$^+$, 94%), 1301.7 ([M+1]$^+$, 100), 1302.7 ([M+2]$^+$, 62), 1303.7 ([M+3]$^+$, 28), 1304.7 ([M+4]$^+$, 10), 1305.7 ([M+5]$^+$, 3).

Preparation of 38

To a solution of 37 (616 mg, 0.473 mmol) in THF (4.4 mL) and MeOH (4.4 mL) was added K$_2$CO$_3$ (148 mg, 1.07 mmol) at room temperature, and the mixture was stirred at that temperature for 16 min. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (ethyl acetate/dichloromethane) to give 37' (562 mg) as a white solid in 97% yield. 37': $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_4$Si)/ppm 8.07 (1H, br.s), 7.59 (1H, t, $J$ = 1.6 Hz), 7.56 (1H, br.t), 7.53-7.50 (2H, m), 7.43-7.36 (5H, m), 7.12-7.02 (10H, br.m), 6.92 (1H, br.t), 6.89 (1H, br.t), 6.80 (2H, d, $J$ = 8.4 Hz), 6.78 (2H, d, $J$ = 8.4 Hz), 3.96-3.75 (8H, br.m), 3.20 (1H, s), 1.64-1.46 (8H, m), 1.43-1.26 (8H, m), 1.19-1.15 (21H, m), 0.94 (3H, t, $J$ = 7.2 Hz), 0.94 (3H, t, $J$ = 7.6 Hz), 0.87 (6H, t, $J$ = 7.2 Hz).
To a solution of 1,3-diiodobenzene (2.23 g, 6.75 mmol), Pd(PPh₃)₄ (292 mg, 0.253 mmol) and CuI (96 mg, 0.50 mmol) in Et₃N (44 mL) was added a solution of 37 (2.08 g, 1.69 mmol) in THF (7.4 mL) via a syringe pump over 2 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO₂ pad, the filtrate was concentrated, and then purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give 38 (1.99 g) as a pale-yellowish white amorphous solid in 82% yield. An analytical sample was obtained as a white solid by further purification with HPLC (ethyl acetate/dichloromethane). 38: mp 169-170 °C; elemental analyses Found: C, 74.23; H, 6.05; N, 3.86%. Calc. for C₉₉H₄₀N₂O₂Si (EtOH): C, 73.96; H, 6.34; N, 3.79%; IR (KBr) νmax/cm⁻¹ 3056, 2955, 2928, 2861, 2212, 2148, 1652, 1595, 1576; ¹H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 8.08 (1H, br.s), 7.95 (1H, t, J = 1.6 Hz), 7.73 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.60 (2H, br.t), 7.56-7.51 (3H, m), 7.43 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.8 Hz), 7.39 (1H, br.t), 7.18 (1H, brs), 7.15-7.10 (9H, m), 7.02 (1H, br.t), 6.92 (1H, t, J = 1.6 Hz), 6.88 (1H, t, J = 1.6 Hz), 6.80 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.8 Hz), 4.13-3.60 (8H, br.m), 1.65-1.48 (8H, m), 1.43-1.24 (8H, m), 1.19-1.15 (21H, m), 0.95 (3H, t, J = 7.6 Hz), 0.94 (3H, t, J = 7.6 Hz), 0.87 (3H, t, J = 7.2 Hz), 0.86 (3H, t, J = 7.6 Hz); ¹³C NMR δ(100 MHz; CDCl₃)/ppm 169.3, 169.0, 169.0, 144.1, 144.0, 143.6, 143.4, 140.2, 137.8, 137.0, 136.8, 136.7, 136.6, 134.4, 133.6, 133.2, 133.2, 131.5 (br.m), 131.0, 130.7, 130.7, 130.3, 130.2, 129.9, 128.7, 128.3, 128.1, 127.9, 127.1, 127.1, 124.7, 124.4, 124.2, 124.1, 123.9, 123.1, 123.0, 119.5, 119.4, 104.9, 93.7, 93.3, 90.3, 90.1, 89.3, 88.7, 88.6, 88.6, 81.5, 81.4, 74.7, 49.9, 49.7, 49.7, 29.6, 29.6, 20.1, 20.1, 20.0, 20.0, 18.6, 13.8, 13.7, 13.7, 11.2; FD-MS m/z 1430.5 (M⁺, 94%), 1431.5 ([M+1]⁺, 100), 1432.5 ([M+2]⁺, 57), 1433.5 ([M+3]⁺, 23), 1434.5 ([M+4]⁺, 8), 1435.5 ([M+5]⁺, 2).

Preparation of 4a and 4b

To a solution of 38 (1.84 g, 1.28 mmol) in THF (34 mL) was added TBAF (1 M in THF, 1.40 mL, 1.40 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent by evaporation, the residue was dissolved in ethyl acetate, and which was washed with 0.5 M aq. HCl, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give 38' (1.49 g) as a white solid in 91% yield. 38': ¹H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 8.12 (1H, br.s), 7.95 (1H, t, J = 1.6 Hz), 7.73 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.62 (1H, t, J = 1.2 Hz), 7.59 (1H, t, J = 1.2 Hz), 7.56-7.53 (3H, br.m), 7.45-7.38 (5H, m), 7.19 (1H, br.t), 7.15-7.08 (10H, m), 6.97 (1H, t, J = 1.6 Hz), 6.92 (1H, t, J = 1.6 Hz), 6.82 (2H, d, J = 8.8 Hz), 6.28 (2H, d, J = 8.8 Hz), 3.93-3.84 (8H, br.m), 3.25 (1H, s), 1.66-1.47 (8H, m), 1.43-1.26 (8H, m), 0.95 (3H, t, J = 7.6 Hz), 0.94 (3H, t, J = 7.2 Hz), 0.87 (3H, t, J = 7.2 Hz), 0.86 (3H, t, J = 7.6 Hz).
To a solution of Pd(PPh₃)₄ (275 mg, 0.238 mmol) and Cul (48 mg, 0.25 mmol) in Et₂N (60 mL) was added a solution of 38’ (506 mg, 0.397 mmol) in THF (30 mL) via a syringe pump over 43 h at 80 °C under an argon atmosphere. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO₂ (ethyl acetate/dichloromethane), followed by GPC (chloroform) to give a mixture of 4a and 4b (25 mg, 4a:4b = 1.6:1) as a white solid in 5% yield. 4b and 4a were isolated in this order by HPLC separation (1:9 tetrahydrofuran/chloroform). Each analytical sample was obtained as a white solid by reprecipitation with ethyl acetate/hexane.

4a: mp 242-243 °C; IR (KBr) νmax/cm⁻¹ 3064, 2952, 2930, 2868, 2860, 2194, 2147, 1649, 1599, 1587; ¹H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 9.07 (2H, br.m), 8.60 (2H, t, J = 1.6 Hz), 7.46-7.40 (6H, m), 7.16 (4H, d, J = 8.4 Hz), 7.14 (4H, d, J = 8.4 Hz), 7.01 (4H, d, J = 8.4 Hz), 6.92 (4H, d, J = 1.6 Hz), 6.69 (4H, d, J = 8.4 Hz), 3.82 (4H, t, J = 7.6 Hz), 3.76 (4H, t, J = 7.6 Hz), 1.60-1.43 (8H, m), 1.41-1.22 (8H, m), 0.92 (6H, t, J = 7.2 Hz), 0.83 (6H, t, J = 7.2 Hz); ¹³C NMR δ(100 MHz; CDCl₃)/ppm 169.7, 169.7, 144.4, 143.5, 142.2, 140.9, 137.4, 137.0, 132.8, 129.1, 128.8, 128.8, 128.0, 128.0, 127.9, 124.4, 123.6, 118.9, 93.2, 91.1, 87.5, 78.2, 50.1, 49.0, 29.8, 29.6, 20.1, 20.1, 13.8, 13.7; FD-LRMS m/z 1146.5 (M⁺, 100%), 1147.5 ([M+1]⁺, 90), 1148.5 ([M+2]⁺, 43), 1149.5 ([M+3]⁺, 14), 1150.5 ([M+4]⁺, 4); FD-HRMS Found: 1146.50948, Calc. for C₈₀H₇₀N₄O₄: 1146.50840; UV λmax(CH₂Cl₂)/nm (log ε) 354 (4.58), 331 (4.61), 305 (sh. 5.01), 289 (5.14).

4b: mp 218-219 °C (dec); IR (KBr) νmax/cm⁻¹ 3061, 3040, 2955, 2930, 2870, 2861, 2205, 1656, 1650, 1590, 1567, 1502; ¹H NMR δ(400 MHz; CDCl₃; Me₄Si)/ppm 8.06 (2H, br.d, d), 7.75 (2H, t, J = 1.6 Hz), 7.41 (6H, d, J = 1.2 Hz), 7.37 (4H, d, J = 8.8 Hz), 7.20 (4H, d, J = 8.4 Hz), 7.15 (4H, d, J = 8.4 Hz), 6.84 (4H, d, J = 1.6 Hz), 6.83 (4H, d, J = 8.8 Hz), 3.88 (4H, t, J = 7.2 Hz), 3.84 (4H, t, J = 7.6 Hz), 1.59-1.46 (8H, m), 1.38-1.27 (8H, m), 0.89 (6H, t, J = 7.2 Hz), 0.87 (6H, t, J = 7.2 Hz); ¹³C NMR δ(100 MHz; CDCl₃)/ppm 169.2, 169.2, 144.3, 144.1, 142.1, 138.8, 137.1, 136.9, 133.3, 129.2, 128.5, 128.4, 128.3, 127.3, 127.2, 124.5, 123.5, 119.8, 93.5, 91.5, 83.1, 75.0, 50.1, 49.9, 29.7, 20.1, 20.1, 13.8, 13.7; FD-LRMS m/z 1146.5 (M⁺, 100%), 1147.5 ([M+1]⁺, 91), 1148.5 ([M+2]⁺, 42), 1149.5 ([M+3]⁺, 14), 1150.5 ([M+4]⁺, 4); FD-HRMS Found: 1146.50891, Calc. for C₈₀H₇₀N₄O₄: 1146.50840; UV λmax(CH₂Cl₂)/nm (log ε) 353 (sh. 4.35), 331 (sh. 4.50), 306 (sh. 5.06), 289 (5.21).
Scheme S4. Synthesis of PAMs 5-7 and rods 8-9. Reagents and yields: (a) i) \( \text{K}_2\text{CO}_3, \text{MeOH, THF (100\% for 18')} \); ii) \( 24/25/1,3\)-diiodobenzene, \( \text{Pd(PPh}_3)_4, \text{CuI, Et}_3\text{N, THF (79\% for 39, 69\% for 40, 78\% for 41)} \); (b) i) TBAF, THF (98\% for 39', 96\% for 40', 91\% for 41'); ii) \( \text{Pd(PPh}_3)_4, \text{CuI, Et}_3\text{N, THF (66\% for 5, 55\% for 6, 5\% for 7)} \); (c) \( 43', \text{Pd(PPh}_3)_4, \text{CuI, TBAF, Et}_3\text{N, THF (98\%)} \); (d) TMSA, \( \text{PdCl}_2(\text{PPh}_3)_2, \text{CuI, Et}_3\text{N (99\%)} \); (e) i) \( \text{K}_2\text{CO}_3, \text{MeOH, THF (93\% for 44')} \); ii) \( \text{CuCl, TMEDA, acetone (39\%)} \).

Preparation of 39

To a solution of 18 (2.82 g, 3.14 mmol) in THF (17 mL) and MeOH (17 mL) was added \( \text{K}_2\text{CO}_3 \) (442 mg, 3.20 mmol) at room temperature, and the mixture was stirred at that temperature for 16 min. After removal of the solvents by evaporation, the residue was purified by column chromatography on SiO\(_2\) (dichloromethane/hexane) to give 18' (2.59 g) as a white amorphous solid in 100\% yield. 18': \(^1\text{H NMR \( \delta_\text{H}(400 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si})/ppm \)}} 7.70-7.69 (1H, m), 7.51-7.48 (4H, m), 7.37-7.33 (2H, m), 7.32-7.29 (2H, br.m), 7.27 (1H, br.t), 3.62 (4H, t, \( J = 7.6 \text{ Hz} \)), 3.11 (1H, s), 1.57-1.49 (4H, m), 1.45 (18H, s), 1.37-1.27 (4H, m), 1.14 (21H, s), 0.92 (3H, t, \( J = 7.2 \text{ Hz} \)), 0.91 (3H, t, \( J = 7.2 \text{ Hz} \)).

To a solution of 24 (904 mg, 1.71 mmol), \( \text{Pd(PPh}_3)_4 \) (18 mg, 0.016 mmol) and Cul (6 mg, 0.03 mmol) in Et\(_3\)N (40 mL) was added a solution of 18' (356 mg, 0.431 mmol) in THF (4 mL) via a
Preparation of 40

To a solution of 25 (726 mg, 1.69 mmol), Pd[(PPh)$_3$]$_4$ (17 mg, 0.015 mmol) and Cul (6 mg, 0.03 mmol) in Et$_3$N (40 mL) was added a solution of 18' (348 mg, 0.422 mmol) in THF (4 mL) via a syringe pump over 3 h at 50-53 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO$_2$ pad, the filtrate was concentrated and purified by column chromatography on SiO$_2$ (dichloromethane/hexane), followed by GPC (chloroform) to give 39 (417 mg) as a white amorphous solid in 79% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform). 39: mp 74-76 °C; elemental analyses Found: C, 73.27; H, 6.56; N, 2.24%. Calc. for C$_{73}$H$_{79}$N$_2$O$_{3}$Si: C, 73.39; H, 6.49; N, 2.28%. IR (KBr) $\nu_{\text{max}}$/cm$^{-1}$ 3061, 2958, 2939, 2929, 2862, 2215, 2152, 1720, 1699, 1596, 1582; $^1$H NMR $\delta$(400 MHz; CDCl$_3$; Me$_2$Si)/ppm 7.90 (1H, t, $J = 1.6$ Hz), 7.74-7.70 (3H, m), 7.68 (1H, ddd, $J = 1.2$, 2.0, 8.0 Hz), 7.55 (1H, t, $J = 1.6$ Hz), 7.52-7.48 (8H, m), 7.38-7.26 (7H, m), 7.09 (1H, t, $J = 8.0$ Hz), 3.65 (2H, t, $J = 7.6$ Hz), 3.62 (2H, t, $J = 7.6$ Hz), 3.16-1.50 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.39-1.27 (4H, m), 1.14 (21H, br.s), 0.93 (3H, t, $J = 7.2$ Hz), 0.92 (3H, t, $J = 7.2$ Hz); $^{13}$C NMR $\delta$(100 MHz; CDCl$_3$)/ppm 154.3, 154.3, 143.0, 142.8, 140.2, 137.4, 134.7, 134.7 (br.m), 132.6, 132.1, 131.6, 131.6 (br.), 131.5, 131.5, 130.7, 130.5, 130.3, 130.3, 130.2, 129.9, 128.6, 125.0, 124.4, 123.9, 123.6, 123.4, 123.3, 123.3, 123.2, 105.6, 93.7, 91.9, 89.7, 89.3, 89.3, 89.1, 89.1, 88.8, 88.7, 88.3, 80.5, 49.6, 30.6, 30.6, 28.3, 28.3, 19.9, 19.9, 18.6, 13.8, 13.8, 11.3; FD-LRMS m/z 1026.5 ([M−(BOC)$_2$]+, 4%), 1027.5 ([M+1−(BOC)$_2$]+, 4), 1070.4 ([M−(TIPS)]$^+$, 5), 1071.4 ([M+1−(TIPS)]$^+$, 5), 1126.5 ([M−(BOC)$_3$]$^+$, 26), 1127.5 ([M+1−(BOC)$_3$]$^+$, 22), 1128.5 ([M+2−(BOC)$_3$]$^+$, 11), 1129.5 ([M+3−(BOC)$_3$]$^+$, 3), 1226.5 (M+, 100), 1227.5 ([M+1]$^+$, 89), 1228.5 ([M+2]$^+$, 44), 1229.5 ([M+3]$^+$, 15), 1230.5 ([M+4]$^+$, 4).

S31
Preparation of 41

To a solution of 1,3-diiodobenzene (768 mg, 2.33 mmol), Pd(PPh₃)₄ (67 mg, 0.058 mmol) and Cul (22 mg, 0.12 mmol) in Et₃N (54 mL) was added a solution of 18' (469 mg, 0.568 mmol) in THF (5.5 mL) via a syringe pump over 3.5 h at 60 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of a solid by filtration through a Celite/SiO₂ pad, the filtrate was concentrated and purified by column chromatography on SiO₂ (dichloromethane/hexane) to give 41 (458 mg) as a white amorphous solid in 78% yield. An analytical sample was obtained as a white amorphous solid by further purification through GPC (chloroform).

41: mp 52-54 °C; elemental analyses: Found: C, 69.01; H, 6.95; N, 2.71%. Calc. for C₉₉H₇₁N₂O₄Si: C, 68.99; H, 6.97; N, 2.73%. IR (KBr) νmax/cm⁻¹: 3061, 2958, 2940, 2930, 2863, 2215, 2153, 1703, 1582; ¹H NMR δ (400 MHz; CDCl₃; Me₄Si)/ppm: 7.90 (1H, t, J = 1.6 Hz), 7.71-7.70 (1H, br.m), 7.69 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.53 (1H, t, J = 1.6 Hz), 7.51-7.48 (4H, m), 7.38-7.26 (5H, m), 7.10 (1H, t, J = 8.0 Hz), 3.65 (2H, t, J = 8.0 Hz), 3.63 (2H, t, J = 7.6 Hz), 1.59-1.50 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.38-1.28 (4H, m), 1.14 (21H, br.s), 0.93 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz); ¹³C NMR δ (100 MHz; CDCl₃)/ppm: 154.3, 143.0, 142.8, 140.2, 137.5, 134.7, 132.6, 132.1, 131.6, 131.6, 130.7, 130.5, 130.4, 130.2, 129.9, 128.6, 124.9, 124.4, 123.9, 123.7, 123.6, 123.3, 123.2, 105.6, 93.7, 91.9, 89.3, 89.3, 89.1, 88.8, 88.7, 88.4, 80.6, 80.5, 49.6, 30.6, 30.6, 28.3, 28.3, 19.9, 19.9, 18.6, 13.8, 11.3; FD-LRMS m/z: 926.3 ([M–(BOC)]⁺, 29%), 927.3 ([M+(1–(BOC)]⁺, 20), 928.3 ([M+(2–(BOC)]⁺, 8), 929.3 ([M+(3–(BOC)]⁺, 2), 1026.4 (M⁺, 100), 1027.4 ([M+(1)]⁺, 72), 1028.4 ([M+(2)]⁺, 30), 1029.4 ([M+(3)]⁺, 10), 1030.4 ([M+(4)]⁺, 3).

Preparation of 5 ([6]PAM)

To a solution of 39 (425 mg, 0.346 mmol) in THF (10 mL) was added TBAF (1 M in THF, 0.37 mL, 0.37 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.1 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO₂ (dichloromethane/hexane), followed by GPC (chloroform) to give 39' (364 mg) as a white amorphous solid in 98% yield. 39': ¹H NMR δ (400 MHz; CDCl₃; Me₄Si)/ppm: 7.89 (1H, t, J = 1.6 Hz), 7.73-7.70 (3H, m), 7.66 (1H, ddd, J = 1.2, 2.0, 8.0 Hz), 7.56 (1H, t, J = 1.6 Hz), 7.53-7.45 (8H, m), 7.41-7.29 (7H, m), 7.07 (1H, t, J = 8.0 Hz).
Followed by GPC (chloroform) to give 39 mg as a white amorphous solid in 96% yield. An analytical sample was obtained as a white solid by repeating column chromatography on SiO₂ (dichloromethane/hexane), followed by suspension in methanol. 5: mp 209-210 °C (dec); elemental analyses Found: C, 83.79; H, 6.30; N, 2.90%. Calc. for C₆H₅N₂O₃: C, 84.05; H, 6.20; N, 2.97%; IR (KBr) νmax/cm⁻¹ 3060, 2959, 2928, 2871, 2861, 2215, 1702, 1596, 1581; ¹H NMR δ(400 MHz; CDCl₃); Me₄Si/ppm 7.77-7.73 (4H, m), 7.58 (2H, t, J = 1.2 Hz), 7.54-7.49 (8H, m), 7.40-7.33 (8H, m), 3.66 (4H, t, J = 7.6 Hz), 1.60-1.52 (4H, m), 1.47 (18H, s), 1.34-1.30 (4H, m), 0.93 (6H, t, J = 7.6 Hz); ¹³C NMR δ(100 MHz; CDCl₃)/ppm 154.3, 142.9, 135.2, 135.1, 135.1, 132.6, 131.3, 131.3, 131.2, 131.2, 129.9, 128.6, 128.5, 123.9, 123.8, 123.4, 123.3, 123.3, 123.2, 89.4, 89.3, 89.2, 89.1, 88.8, 80.5, 49.6, 30.6, 28.3, 19.9, 13.8; FD-LRMS m/z 842.4 ([M–(BOC)]⁺, 13%), 843.4 ([M+1–(BOC)]⁺, 10), 844.4 ([M+2–(BOC)]⁺, 3), 942.5 (M⁺, 100), 943.5 ([M+1]⁺, 73), 944.5 ([M+2]⁺, 28), 945.5 ([M+3]⁺, 7); UV λmax(CH₂Cl₂)/nm (log ε) 305 (5.27), 287 (5.39), 272 (sh. 5.15).

Preparation of 6 ([5]PAM)

To a solution of 40 (236 mg, 0.209 mmol) in THF (6 mL) was added TBAF (1 M in THF, 0.20 mL, 0.20 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.1 M aq. HCl and brine, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO₂ (dichloromethane/hexane), followed by GPC (chloroform) to give 40 mg as a white amorphous solid in 96% yield. 40: ¹H NMR δ(400 MHz; CDCl₃); Me₄Si/ppm 7.90 (1H, t, J = 1.6 Hz), 7.72-7.70 (2H, m), 7.68 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.55 (1H, t, J = 1.6 Hz), 7.53-7.48 (6H, m), 7.38-7.33 (5H, m), 7.31 (1H, br t), 7.09 (1H, t, J = 8.0 Hz), 3.65 (2H, t, J = 7.6 Hz), 3.63 (2H, t, J = 7.6 Hz), 3.11 (1H, s), 1.63-1.45 (4H, m), 1.47 (9H, s), 1.45 (9H, s), 1.39-1.27 (4H, m), 0.93 (3H, t, J = 7.2 Hz), 0.91 (3H, t, J = 7.2 Hz).

To a solution of Pd(PPh₃)₄ (144 mg, 0.125 mmol) and Cul (26 mg, 0.14 mmol) in Et₃N (31 mL) was added a solution of 40 mg (213 mg, 0.219 mmol) in THF (18 mL) via a syringe pump over 22 h at 75 °C under an argon atmosphere. After removal of a solid by filtration, the filtrate was concentrated and then purified by column chromatography on SiO₂ (dichloromethane/hexane), followed by GPC (chloroform) to give 6 (102 mg) as a white solid in 55% yield. An analytical sample
was obtained as a white solid by further purification through GPC (chloroform), followed by suspension in methanol. 6: mp 221.0-221.5 °C (dec); elemental analyses Found: C, 82.61; H, 6.53; N, 3.25%. Calc. for C58H58N3O12: C, 82.63; H, 6.46; N, 3.32%; IR (KBr) νmax/cm⁻¹ 3060, 2966, 2929, 2872, 2864, 2214, 1708, 1592, 1582; ¹H NMR δ(400 MHz; CDCl₃; MeSi)/ppm 7.97-7.95 (3H, m), 7.80 (2H, t, J = 1.6 Hz), 7.49-7.45 (6H, m), 7.39-7.32 (7H, m), 3.66 (4H, t, J = 7.6 Hz), 1.59-1.52 (4H, m), 1.47 (18H, s), 1.38-1.29 (4H, m), 0.93 (6H, t, J = 7.6 Hz); ¹³C NMR δ(100 MHz; CDCl₃)/ppm 154.3, 143.1, 137.8, 137.8, 135.2, 130.1, 130.0, 128.8, 128.7, 128.7, 123.9, 123.9, 123.5, 123.4, 123.3, 90.0, 89.9, 89.8, 89.4, 89.3, 80.6, 49.6, 30.6, 28.3, 19.9, 13.8; FD-LRMS m/z 742.4 ([M−(BOC)]⁺, 14%), 743.4 ([M+1−(BOC)]⁺, 8), 744.4 ([M+2−(BOC)]⁺, 3), 842.5 (M⁺, 100), 843.5 ([M+1]⁺, 68), 844.5 ([M+2]⁺, 24), 845.5 ([M+3]⁺, 5); UV λmax(CH₂Cl₂)/nm (log ε) 304 (5.20), 287 (5.33), 272 (sh. 5.06).

Preparation of 7 ([4]PAM)

To a solution of 41 (412 mg, 0.401 mmol) in THF (11 mL) was added TBAF (1 M in THF, 0.43 mL, 0.43 mmol) at room temperature, and the mixture was stirred at that temperature for 20 min. After removal of the solvent, the residue was dissolved in ethyl acetate, and which was washed with 0.1 M aq. HCl, dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO₂ (dichloromethane/hexane), followed by GPC (chloroform) to give 41' (316 mg) as a white amorphous solid in 91% yield. 41': ¹H NMR δ(400 MHz; CDCl₃; MeSi)/ppm 7.90 (1H, t, J = 1.6 Hz), 7.72 (1H, brt), 7.67 (1H, ddd, J = 1.2, 1.6, 8.0 Hz), 7.54-7.47 (5H, m), 7.37-7.31 (5H, m), 7.08 (1H, t, J = 8.0 Hz), 3.67-3.61 (4H, m), 3.12 (1H, s), 1.59-1.49 (4H, m), 1.47 (9H, s), 1.46 (9H, s), 1.38-1.27 (4H, m), 0.93 (3H, t, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz).

To a solution of Pd(PPh₃)₄ (252 mg, 0.218 mmol) and Cul (42 mg, 0.22 mmol) in Et₃N (54 mL) was added a solution of 41' (316 mg, 0.363 mmol) in THF (27 mL) via a syringe pump over 36 h at 75-80 °C under argon atmosphere. After removal of a solid by filtration, the filtrate was concentrated and then purified by column chromatography on SiO₂ (dichloromethane/hexane), followed by GPC (chloroform) to give 7 (14 mg) as a white solid in 5% yield. An analytical sample was obtained as a white solid by further purification with HPLC (dichloromethane), followed by suspension in ethyl acetate/methanol. 7: mp 210-211 °C (dec); elemental analyses Found: C, 78.02; H, 6.99; N, 3.39%. Calc. for C₅₀H₅₀N₄O₂: C, 78.04; H, 7.03; N, 3.37%; IR (KBr) νmax/cm⁻¹ 3056, 2962, 2929, 2872, 2203, 1708, 1590; ¹H NMR δ(400 MHz; CDCl₃; MeSi)/ppm 8.06-8.05 (2H, m), 7.90 (2H, t, J = 1.6 Hz), 7.38-7.36 (6H, m), 7.22 (4H, br.d), 3.64 (4H, t, J = 7.6 Hz), 1.58-1.51 (4H, m), 1.46 (18H, s), 1.38-1.28 (4H, m), 0.92 (6H, t, J = 7.6 Hz); ¹³C NMR δ(100 MHz; CDCl₃)/ppm 154.3, 143.4, 141.9, 139.2, 129.0, 128.2, 127.1, 124.0, 123.6, 92.4, 91.8, 80.6, 49.7, 30.6, 28.3, 19.9, 13.8; FD-LRMS m/z 742.3 (M⁺, 100), 743.4 ([M+1]⁺, 60), 744.4 ([M+2]⁺, 18), 745.4 ([M+3]⁺, 4); UV
\[ \lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm} \text{ (log } e) \ 305 \ (4.97), \ 288 \ (5.15), \ 273 \ (4.91). \]

**Preparation of 8**

To a solution of 42 (472 mg, 1.74 mmol), 43 (1.45 g, 3.86 mmol), Pd(PPh\(_3\))\(_4\) (58 mg, 0.050 mmol) and Cul (21 mg, 0.11 mmol) in Et\(_2\)N (52 mL) and THF (10 mL) was added TBAF (1 M in THF, 0.60 mL, 0.60 mmol) at 43 °C, and the mixture was stirred at that temperature for 2 h. After removal of a solid by filtration through a Celite/SiO\(_2\) pad, the filtrate was concentrated, and then purified by column chromatography on SiO\(_2\) (dichloromethane/hexane) to give 8 (1.06 g) as a yellow solid in 98% yield. An analytical sample was obtained as colorless crystals by further purification through GPC (chboroform), followed by recrystallization from methanol. 8: mp 101.5-102.0 °C; elemental analyses Found: C, 77.23; H, 7.84; N, 4.44%. Calc. for C\(_{49}\)H\(_{52}\)N\(_2\)O\(_2\): C, 77.39; H, 7.79; N, 4.51%; IR (KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\) 3041, 2954, 2929, 2872, 2103, 1915, 1683, 1602, 1506; \(^1\)H NMR \(\delta_{(400 \text{ MHz; CDCl}_3)}\) ppm 154.3, 143.1, 132.5, 126.7, 119.3, 83.3, 80.3, 77.1, 49.5, 30.6, 28.3, 19.9, 13.7; FD-LRMS \(m/z\) 620.4 (M\(^+\), 100%), 621.4 ([M+1]\(^+\), 45), 622.4 ([M+2]\(^+\), 12); UV \(\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm} \text{ (log } e) \ 350 \ (4.67), \ 331 \ (4.82).

**Preparation of 44**

To a solution of 43 (5.16 g, 13.8 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (136 mg, 0.194 mmol) and Cul (65 mg, 0.34 mmol) in Et\(_2\)N (100 mL) was added TMSA (2.0 mL, 14 mmol) at room temperature under an argon atmosphere, and the reaction mixture was stirred at the temperature for 22 h. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO\(_2\) (dichloromethane/hexane) to give 44 (4.69 g) as a white solid in 99% yield. To a solution of 44 (4.69 g, 13.6 mmol) in THF (66 mL) and MeOH (66 mL) was added K\(_2\)CO\(_3\) (1.87 g, 13.6 mmol), and the mixture was stirred at room temperature for 40 min, and then diluted with ethyl acetate. The diluted solution was washed with water and brine, dried over magnesium sulfate, and then purified by column chromatography on SiO\(_2\) (dichloromethane/hexane) to give 44' (3.44 g) as a white solid in 93% yield. An analytical sample of 44' was obtained as colorless crystals by recrystallization from dichloromethane/hexane. 44': mp 71-72 °C; elemental analyses Found: C, 74.66; H, 8.66; N, 4.97%. Calc. for C\(_{13}\)H\(_{23}\)NO\(_2\): C, 74.69; H, 8.48; N, 5.12%; IR (KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\) 3241, 2954, 2929, 2872, 2103, 1915, 1683, 1602, 1506; \(^1\)H NMR \(\delta_{(400 \text{ MHz; CDCl}_3)}\) ppm 154.3, 143.1, 132.5, 126.6, 123.0, 120.1, 90.9, 89.0, 80.2, 49.5, 30.5, 28.2, 19.8, 13.7; FD-LRMS \(m/z\) 273.2 (M\(^+\), 100%), 274.2 ([M+1]\(^+\), 20).
Preparation of 9

To an ice-cooled solution of CuCl (46 mg, 0.46 mmol) and TMEDA (0.22 mL, 1.5 mmol) in acetone (15 mL) was added a solution of 44' (487 mg, 1.78 mmol) in acetone (8 mL) under an oxygen atmosphere, and the mixture was stirred at room temperature for 8 days. After removal of the solvent by evaporation, the residue was dissolved in dichloromethane, and which was washed with diluted aq. HCl, dried over magnesium sulfate, and concentrated. The resulting solid was separated by column chromatography on SiO₂ (dichloromethane/hexane) to give 9 (236 mg) as a white solid in 49% yield and 44' (194 mg, recov. 40%). An analytical sample was obtained as colourless crystals by recrystallization from methanol. 9: mp 97.5-98.0 °C; elemental analyses Found: C, 75.05; H, 8.15; N, 5.13%. Calc. for C₃₄H₄₄N₂O₄: C, 74.97; H, 8.14; N, 5.14%; IR (KBr) νmax/cm⁻¹ 3070, 3042, 2963, 2929, 2871, 2148, 1698, 1597, 1504; ¹H NMR δ(H(400 MHz; CDCl₃; Me₄Si)/ppm 7.48 (4H, d, J = 8.4 Hz), 7.18 (4H, d, J = 8.4 Hz), 3.63 (4H, t, J = 7.6 Hz), 1.56-1.48 (4H, m), 1.44 (18H, s), 1.35-1.26 (4H, m), 0.90 (6H, t, J = 7.6 Hz); ¹³C NMR δ(C(100 MHz; CDCl₃)/ppm 154.2, 143.5, 132.9, 126.6, 118.8, 81.3, 80.5, 73.9, 49.5, 30.6, 28.3, 19.9, 13.8; FD-LRMS m/z 544.3 (M⁺, 100%), 545.4 ([M+1]⁺, 39), 546.4 ([M+2]⁺, 8); UV λmax(CH₂Cl₂)/nm (log ε) 344 (4.48), 324 (4.61), 306 (4.54), 288 (sh. 4.42), 275 (sh. 4.35), 261 (sh. 4.24).
**1H and 13C NMR spectra of new compounds**

1H (400 MHz) and 13C (100 MHz) NMR spectra of 1a (second fraction), measured in chloroform-d at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 1b, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 2a, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 2b, containing residual solvents, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 3a (first fraction), measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 3b, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 4a, containing residual solvents, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 4b, containing residual solvents, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 5, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 6, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 7, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 8, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 9, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 13, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 14, measured in chloroform-<i>d</i> at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 15, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 16, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 17, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 18, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 20, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 21, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 22, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 26, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 27, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 28, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 29, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 30, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 31, measured in chloroform-<i>d</i> at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 32, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 36, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 37, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 38, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 39, measured in chloroform-<i>d</i> at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 40, measured in chloroform-$d$ at room temperature.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 41, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectra of new compounds (unprotected)

$^1$H NMR spectrum (400 MHz) of 8', measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of 12, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of 16', measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of 17', measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of $18'$, measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of $19$, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of 20', measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of 21', containing residual solvents, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of $22'$, measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of $26'$, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of 28', measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of 29', measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of 30', measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of 32', measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of $35'$, measured in chloroform-$d$ at room temperature.

$^{13}$C NMR spectrum (100 MHz) of $35'$, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of $37'$, containing residual solvents, measured in chloroform-\textit{d} at room temperature.
$^1$H NMR spectrum (400 MHz) of 38', measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of 39', measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of $40'$, measured in chloroform-$d$ at room temperature.

$^1$H NMR spectrum (400 MHz) of $41'$, measured in chloroform-$d$ at room temperature.
$^1$H NMR spectrum (400 MHz) of 44', measured in chloroform-$d$ at room temperature.

$^{13}$C NMR spectrum (100 MHz) of 44', measured in chloroform-$d$ at room temperature.
References and note


11. The central phenylene protons (4H) of 1,4-bis(phenylethynyl)benzene in 20/20', 21/21' and 22/22' were not assigned due to broadening.