A New Synthetic Method for Non-symmetric Pillar[5]arenes with Simple Isolation and Improved Yield

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To a 500 mL round bottom flask equipped with a magnetic stir bar was added compound 3a (4.00 g, 21.0 mmol), CH₂Cl₂ (50 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH₄ (800 mg, 21.2 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature and was stirred for another 12 h. The solvent was then removed under reduced pressure. Water (100 mL) was added, followed by extraction with ethyl acetate (20 mL x 4). The organic layer was dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. Column chromatography (silica, 300-400 mesh, dichloromethane/methanol, v/v 100:0-25:1) afforded compound 4a as a white solid (4.00 g, 99%).

M.p. 38.6-40.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.96–6.90 (m, 2H), 6.79 (dd, J₁ = 8.9 Hz, J₂ = 3.1 Hz, 1H), 4.70 (d, J = 2.4 Hz, 2H), 4.68 (s, 2H), 3.78 (s, 3H), 2.51 (t, J = 2.4 Hz, 1H), 2.22 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 154.56, 131.35, 114.85, 113.69, 113.24, 78.84, 75.74, 61.82, 56.99, 55.85. FT-IR (KBr): ν max (cm⁻¹) 3246, 2992, 2916, 2834, 1498, 1457, 1439, 1365, 1301, 1282, 1209, 1163, 1045, 793, 629. HR-MS: m/z calcd for [M + H]⁺, C₁₁H₁₅O₁₃, 193.0865, found 193.0862 (error: 1.5 ppm).
Fig. S1 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 4a.
Fig. S2 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 4a.
MgCl₂ (2.850 g, 30 mmol) and paraformaldehyde (1.500 g, 50 mmol) was added to a 500 mL three-necked round bottom flask fitted with a reflux condenser under an atmosphere of N₂. Anhydrous THF (100 mL) was added with a syringe followed by Et₃N (4.2 mL, 30 mmol). Compound 1b (2.224 g, 10 mmol) was added under nitrogen atmosphere. The reaction mixture was then heated to reflux, during which period the solution turned yellow. The reaction was stirred for another 12 h, and quenched with 1 M aqueous HCl (100 mL). The aqueous phase was extracted with diethyl ether (50 mL x 3), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to afford crude product as a yellow oil. The crude product was directly used in the next step without further purification.

The crude product 5-(n-octylocy)salicylaldehyde was dissolved in anhydrous MeCN (80 mL). Cs₂CO₃ (7.0 g, 21 mmol) was then added. The mixture was heated to 60 °C and stirred for 30 min. 1,2-dibromoethane (10.0 mL, 115 mmol) was added through a syringe and the reaction mixture was heated overnight. The mixture was cooled, filtered and concentrated under reduced pressure. The crude product was then dissolved in ethyl acetate (100 mL) and washed with brine (25 mL x 3). Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 9:1) afforded compound 3b as a pale yellow solid (2.452 g, 69% for two steps).

M.p. 35.6-37.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.51 (s, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.12 (dd, J₁ = 8.5 Hz, J₂ = 2.4 Hz, 1H), 6.92 (d, J = 8.9 Hz, 1H), 4.38 (t, J = 5.8 Hz, 2H), 3.95 (t, J = 6.3 Hz, 2H), 3.68 (t, J = 5.8 Hz, 2H), 1.76 (m, 2H), 1.43 (m, 2H), 1.30 (m, 8H), 0.89 (t, J = 5.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 189.39, 154.92, 153.76, 125.62, 123.80, 114.84, 111.09, 69.08, 68.65, 31.77, 29.29, 29.20, 29.15, 29.02, 25.95, 22.62, 14.08. FT-IR (KBr) νₘₐₓ (cm⁻¹) 3065, 2955, 2917, 2869, 2852, 1682, 1613, 1590, 1495, 1469, 1427, 1406, 1392, 1379, 1314, 1277, 1256, 1217,
1172, 1071, 1046, 1034, 1020, 874, 865, 818, 788, 748, 719, 638, 602. HR-MS: m/z calcd for [M + H]^+, C_{17}H_{25}BrO_3, 357.1060, found 357.1062 (error: 0.6 ppm).

**Fig. S3** ^1^H NMR spectrum (400 MHz, CDCl_3) recorded for compound 3b.
Fig. S4 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, 298 K) recorded for compound 3b.
To a 250 mL round bottom flask equipped with a magnetic stir bar was added compound 3b (2.390 g, 6.7 mmol), CH₂Cl₂ (50 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH₄ (370 mg, 9.8 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature, and was stirred for another 12 h. The solvent was then evaporated under reduced pressure. Water (50 mL) was added, followed by extraction with ethyl acetate (30 mL x 5). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 3:1) afforded compound 4b as a white solid (2.161 g, 90%).

M.p. 39.8-42.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.89 (s, 1H), 6.77 (s, 2H), 4.68 (d, J = 5.0 Hz, 2H), 4.31 (t, J = 5.8 Hz , 2H), 3.91 (t, J = 5.8 Hz , 2H), 3.68 (t, J =5.7 Hz , 2H), 2.45 (t, J = 6.7 Hz , 1H), 1.75 (m, 2H), 1.44 (m, 2H), 1.33 (m, 8H), 0.88 (t, J = 6.5 Hz , 3H). ¹³C NMR (100 MHz, CDCl₃): δ 153.75, 149.83, 130.81, 115.66, 113.87, 112.68, 68.59, 68.34, 62.00, 31.79, 29.99, 29.34, 29.31, 29.22, 26.01, 22.64, 14.09. FT-IR (KBr): v_max (cm⁻¹) 3347, 2947, 2922, 2848, 1610, 1505, 1466, 1455, 1429, 1391, 1367, 1302, 1276, 1220, 1177, 1160, 1077, 1027, 870, 859, 815, 805, 765, 707, 583. HR-MS: m/z calcd for [M + NH₄]⁺, C₁₇H₂₇BrO₃, 376.1482, found 376.1483 (error: 0.3 ppm).
Fig. S5 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 4b.
Fig. S6 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 4b.
MgCl$_2$ (3.65 g, 38.3 mmol), paraformaldehyde (1.92 g, 60 mmol) was added to a 500 mL three-necked round bottom flask fitted with a reflux condenser under an atmosphere of N$_2$. Anhydrous THF (100 mL) was added with a syringe followed by Et$_3$N (5.4 mL, 38.6 mmol). Compound 1b (2.85 g, 12.8 mmol) was added under nitrogen atmosphere. The reaction mixture was then heated to reflux, during which period the solution turned yellow. The reaction was stirred for another 12 h, and quenched with 1 M aqueous HCl (100 mL). The aqueous phase was extracted with diethyl ether (50 mL × 3), dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure to afford crude product as a yellow oil. The crude product was directly used in the next step without further purification.

The crude product 5-(n-octyloxy)salicylaldehyde was dissolved in anhydrous MeCN (100 mL). Cs$_2$CO$_3$ (11.70 g, 36 mmol) was then added. The mixture was heated to 60 ºC and stirred for 30 min. Propargyl bromide (2.0 mL, 18 mmol) was added through a syringe and the reaction mixture was heated overnight. The mixture was cooled, filtered and concentrated under reduced pressure. The crude product was then dissolved in ethyl acetate (100 mL) and washed with brine (25 mL × 3). Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 9:1) afforded compound 3c as a pale yellow solid (2.91 g, 79% for two steps).

M.p. 49.6-51.2 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.44 (s, 1H), 7.34 (d, $J = 3.2$ Hz, 1H), 7.14 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.2$ Hz , 1H), 4.78 (d, $J = 2.4$ Hz, 2H), 3.95 (t, $J = 6.6$ Hz, 2H), 2.55 (t, $J = 2.4$ Hz, 1H), 1.77 (m, 2H), 1.44 (m, 2H), 1.30 (m, 8H), 0.89 (t, $J = 6.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.33, 154.28, 153.96, 126.07, 123.57, 116.01, 115.51, 115.23, 111.09, 77.94, 76.36, 68.59, 57.29, 31.76, 29.29, 29.19, 29.15, 25.95, 22.62, 14.06. FT-IR (KBr): $\nu_{\text{max}}$ (cm$^{-1}$) 3277, 2957, 2941, 2918, 2871, 2853, 2120,
1677, 1614, 1583, 1492, 1458, 1432, 1297, 1244, 1176, 1080, 1021, 946, 890, 814, 794, 760, 672, 657, 617, 525. HR-MS: m/z calcd for [M + H]^+, C_{18}H_{24}O_3, 289.1798, found 289.1797 (error: 0.3 ppm).
Fig. S7 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 3c.
Fig. S8 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 3c.
Fig. S9 NOE spectrum (400 MHz, CDCl$_3$) recorded for compound 3c. H$_a$ (3.95 ppm) was selectively excited. Strong coupling was observed for H$_c$ and H$_b$, while weak or no coupling was observed for H$_d$ and H$_e$. 

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To a 250 mL round bottom flask equipped with a magnetic stir bar was added compound 3c (1.582 g, 5.0 mmol), CH₂Cl₂ (25 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH₄ (126 mg, 3.3 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature and was stirred for another 12 h. The solvent was then evaporated under reduced pressure. Water (50 mL) was added and followed by extraction with ethyl acetate (30 mL x 5). The organic layer was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to afforded compound 4c as a white solid (1.512 g, 95%).

M.p. 54.6-57.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (d, J = 8.2 Hz, 1H), 6.91 (s, 1H), 6.78 (dd, J₁ = 8.8 Hz, J₂ = 3.0Hz, 1H), 4.70 (s, 2H), 4.68 (s, 2H), 3.91 (t, J = 6.6 Hz, 2H), 2.51 (s, 1H), 2.16 (brs, 1H), 1.75 (m, 2H), 1.44 (m, 2H), 1.28 (m, 8H), 0.89 (t, J = 5.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 153.97, 149.20, 131.13, 115.34, 113.76, 113.49, 78.73, 75.54, 68.52, 61.62, 56.81, 31.79, 29.34, 29.31, 29.22, 26.02, 22.63, 14.09. FT-IR (KBr) νmax (cm⁻¹) 3277, 2965, 2952, 2935, 2919, 2869, 2850, 2116, 1619, 1593, 1492, 1476, 1465, 1396, 1375, 1362, 1313, 1284, 1200, 1172, 1127, 1056, 1042, 1026, 1007, 922, 877, 789, 758, 739, 693, 672, 629. HR-MS: m/z calcd for [M + NH₄]⁺, C₁₈H₂₆O₃, 308.2220, found 308.2227 (error: 2.3 ppm).
Fig. S10 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 4c.
Fig. S11 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 4c.
To a 500 mL round bottom flask equipped with a magnetic stir bar, compound 1d (5.00 g, 36.2 mmol) and 1H-imidazole (3.70 g, 54.3 mmol) was dissolved in anhydrous CH₂Cl₂ (150 mL). The solution was cooled to 0 °C in ice water bath. tert-butyldimethylsilyl chloride (6.55 g, 43.4 mmol) was added portion wise into the solution. The reaction was warmed up to room temperature during a time period of 1 h. After the starting material was consumed, the reaction mixture was then filtered through a celite pad, dried over anhydrous Na₂SO₄, and concentrated to afford a yellow oil. The crude 5-((tert-butyldimethylsilyl)oxy)salicylaldehyde was directly used in the next step without further purification.

The crude 5-((tert-butyldimethylsilyl)oxy)salicylaldehyde was dissolved in anhydrous MeCN (150 mL). K₂CO₃ (7.49 g, 54.3 mmol) was then added. The mixture was heated to 60 °C and stirred for 30 min. Propargyl bromide (ca. 9.2 mol/L solution in toluene) (5.9 mL, 54.3 mmol) was added through a syringe and the reaction mixture was heated overnight. After the starting material was consumed, the reaction mixture was cooled to room temperature, filtered and concentrated under reduced pressure. The crude product was then dissolved in ethyl acetate and washed with brine. Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 40:1) afforded the desired product as a yellow oil. The 5-((tert-butyldimethylsilyl)oxy)-2-(propargyloxy)benzaldehyde was directly subjected to deprotection without characterization.

To a 500 mL round bottom flask equipped with a magnetic stir bar, the crude 5-((tert-butyldimethylsilyl)oxy)-2-(propargyloxy)benzaldehyde was added and dissolved in THF (70 mL). The solution was cooled to 0 °C in ice water bath. Tetrabutylammonium fluoride (1 M solution in THF) (30 mL, 30 mmol) was added dropwise into the solution. The reaction mixture was warmed to room temperature and stirred for 12 h. The
reaction mixture was then concentrated under reduced pressure, diluted with ethyl acetate (100 mL), and washed with brine (50 mL x 3). Column chromatography (silica, 200-300 mesh, petroleum ether/ethyl acetate, v/v 3:1) afforded compound 2d as a pale yellow solid (4.21 g, 66% for 3 steps).

M.p. 111.6-112.1 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.42 (s, 1H), 7.33 (d, $J$ = 3.2 Hz, 1H), 7.09 (d, $J$ = 3.4 Hz, 1H), 7.06 (d, $J$ = 4.8 Hz, 1H), 4.96 (s, 1H), 4.78 (s, 2H), 2.54 (t, $J$ = 2.8 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 189.95, 152.98, 152.03, 125.86, 123.29, 116.79, 112.23, 78.98, 78.77, 57.42. FT-IR (KBr): $\nu_{max}$ (cm$^{-1}$) 3396, 3269, 3046, 2937, 2902, 2793, 2116, 1670, 1661, 1609, 1600, 1507, 1457, 1407, 1354, 1310, 1244, 1275, 1228, 1210, 1167, 1107, 1022, 1013, 976, 922, 881, 869, 816, 791, 661, 612, 594, 561, 531, 449. HR-MS: m/z calcd for [M + H]$^+$, C$_{10}$H$_8$O$_3$, 177.0546, found 177.0551 (error: 2.8 ppm).
Fig. S12 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 2d.
Fig. S13 $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$) recorded for compound 2d.
To a 250 mL round bottom flask equipped with a magnetic stir bar, compound 2d (0.704 g, 4.0 mmol) was dissolved in MeCN (80 mL). Cs₂CO₃ (3.906 g, 12.0 mmol) and KI (125 mg) was then added. The mixture was heated to 60 °C and stirred for 30 min. 1,4-Dibromobutane (4.6 mL, 39 mmol) was then added and the mixture was stirred for another 2 h. After the starting material was consumed, the reaction mixture was cooled, filtered, and concentrated under reduced pressure. The crude product was diluted by ethyl acetate (50 mL) and washed with brine (25 mL). Column chromatography (silica, 200-300 mesh, petroleum ether/ethyl acetate, v/v 4:1) afforded compound 3d as a pale yellow crystalline solid (1.146 g, 92%).

M.p. 79.8-81.1 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 10.44 (s, 1H), 7.33 (d, J = 3.1 Hz, 1H), 7.13 (dd, J₁ = 9.0 Hz, J₂ = 3.2 Hz, 1H), 7.07 (d, J = 9.0 Hz, 1H), 4.78 (d, J = 2.4 Hz, 2H), 4.00 (t, J = 6.1 Hz, 2H), 3.48 (t, J = 6.5 Hz, 2H), 2.54 (t, J = 2.4 Hz, 1H), 2.06 (m, 2H), 1.93 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 189.33, 154.45, 153.66, 126.08, 123.55, 115.58, 111.12, 77.88, 76.41, 67.47, 57.31, 33.35, 29.37, 27.79.

FT-IR (KBr): νₘₐₓ (cm⁻¹) 3279, 3100, 2970, 2950, 2915, 2877, 2773, 2120, 1675, 1615, 1584, 1493, 1474, 1456, 1432, 1407, 1393, 1282, 1242, 1210, 1178, 1043, 1020, 1007, 944, 891, 815, 794, 743, 701, 661, 616, 570, 516. HR-MS: m/z calcd for [M + H]⁺, C₁₄H₁₅BrO₃, 311.0277, found 311.0279 (error: 0.6 ppm).
Fig. S14 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 3d.
Fig. S15 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3d.
**Fig. S16** NOE spectrum (400 MHz, CDCl₃) recorded for compound 3c. H₉ (4.00 ppm) was selectively excited. Strong coupling was observed for H₉ and H₆, while weak or no coupling was observed for H₄ and H₅.
To a 250 mL round bottom flask equipped with a magnetic stir bar was added compound 3d (1.478 g, 4.75 mmol), CH₂Cl₂ (30 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH₄ (190 mg, 5.0 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature and was stirred for another 12 hours. The solvent was then evaporated under reduced pressure. Water (20 mL) was added and followed by extraction with ethyl acetate (20 mL x 4). The organic layer was dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 3:1) afforded compound 3d as a white solid (1.447 g, 97%).

M.p. 40.1-42.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (d, J = 9.0 Hz, 1H), 6.90 (d, J = 3.3 Hz, 1H), 6.77 (dd, J₁ = 8.8 Hz, J₂ = 3.1 Hz, 1H), 4.70 (s, 2H), 4.67 (d, J = 5.5 Hz, 2H), 3.96 (t, J = 6.0 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.50 (t, J = 2.4 Hz, 1H), 2.16 (t, J = 6.2 Hz, 1H), 2.05 (m, 2H), 1.92 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 153.62, 149.20, 131.31, 115.09, 113.62, 113.48, 78.81, 75.70, 67.34, 61.09, 56.80, 33.64, 29.44, 27.92. FT-IR (KBr): v max (cm⁻¹) 3347, 3276, 3069, 2941, 2930, 2912, 2896, 2861, 2118, 1595, 1500, 1476, 1451, 1440, 1392, 1379, 1347, 1290, 1277, 1259, 1209, 1135, 1056, 1043, 1023, 991, 969, 921, 877, 831, 797, 770, 747, 677, 645. HR-MS: m/z calcd for [M + Na]⁺, C₁₄H₁₇BrO₃, 335.0253, found 335.0255 (error: 0.6 ppm).
Fig. S17 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 4d.
Fig. S18 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 4d.
Syntheses of Non-symmetric PA[5]s 5a-d.

Compound 5a: 88.3 mg, yield = 16%, eluent: petroleum ether/dichloromethane, v/v 1:2, white solid. M.p. 110.1-114.5 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.91 (s, 5H), 6.87 (s, 5H), 4.56 (s, 10H), 3.79 (s, 10H), 3.75 (s, 15H), 2.46 (s, 5H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 151.34, 148.97, 129.11, 128.33, 115.73, 114.16, 79.39, 74.85, 56.59, 56.02, 29.81. FT-IR (KBr) νₘₐₓ (cm⁻¹): 3454, 3282, 3042, 2859, 2829, 1637, 1500, 1467, 1402, 1375, 1266, 1210, 1042, 933, 881, 857, 779, 740, 708, 651. HR-MS: m/z calcd for [M+H]⁺ 871.3482, found 871.3440 (error: 4.8ppm).

Compound 5b: 147.6 mg, yield = 14%, eluent: petroleum ether/dichloromethane, v/v 2:1, white solid. M.p. 72.6-74.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (s, 5H), 6.80 (s, 5H), 4.17 (t, J = 6.0 Hz, 10H), 3.86 (t, J = 6.3 Hz, 10H), 3.79 (s, 10H), 3.58 (t, J = 5.6 Hz, 10H), 1.83 (m, 10H), 1.54 (m, 10H), 1.30 (m, 40H), 0.86 (t, J = 6.3 Hz, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 150.74, 149.07, 129.08, 128.53, 116.43, 114.80, 69.24, 68.49, 32.01, 30.91, 30.01, 29.76, 29.57, 29.47, 26.54, 22.81, 14.25. FT-IR (KBr) νₘₐₓ (cm⁻¹): 3455, 2929, 2855, 1637, 1499, 1475, 1406, 1278, 1208, 1101, 1069, 1029, 938, 880, 852, 779, 712, 655, 578, 478. HR-MS: calculated for [M+Na]⁺ 1724.5166, found 1724.5470 (error: 18 ppm).

Compound 5c: 114.3 mg, yield = 15%, eluent: petroleum ether/dichloromethane, v/v 2:1, white solid. M.p. 87.6-88.7 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.94 (s, 5H), 6.75 (s, 5H), 4.56 (s, 10H), 3.86 (t, J = 6.1 Hz, 10H), 3.78 (s, 10H), 2.31 (s, 5H), 1.79
(m, 10H), 1.53 (m, 10H), 1.25 (m, 40H), 0.82 (t, J = 5.8 Hz, 15H). $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ 150.51, 148.69, 128.76, 128.16, 115.17, 114.69, 79.63, 74.84, 68.31, 56.49, 31.91, 29.92, 29.70, 29.41, 26.48, 22.75, 14.24. FT-IR (KBr) $\nu_{\text{max}}$ (cm$^{-1}$) 3294, 2929, 2856, 2129, 1610, 1477, 1467, 1458, 1406, 1375, 1307, 1212, 1048, 965, 937, 879, 853, 782, 744, 670, 632. HR-MS: m/z calcd for [M + NH$_4$]$^+$, C$_{90}$H$_{120}$O$_{10}$, 1378.9220, found 1378.9221 (error: 0.1 ppm).

Compound 5d: 117.0 mg, yield = 13%, eluent: petroleum ether/dichloromethane, v/v 1:1, white solid. M.p. 139.2-142.4 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.93 (s, 5H), 6.71 (s, 5H), 4.56 (s, 10H), 3.92 (t, J = 6.1 Hz, 10H), 3.78 (s, 10H), 3.46 (t, J = 6.5 Hz, 10H), 2.26 (s, 5H), 2.08 (m, 10H), 1.93 (m, 10H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.33, 148.90, 128.83, 128.28, 115.47, 114.78, 79.47, 74.94, 67.59, 56.54, 33.92, 29.97, 29.75, 28.59. FT-IR (KBr) $\nu_{\text{max}}$ (cm$^{-1}$) 3287, 3047, 2963, 2866, 2127, 1611, 1499, 1474, 1454, 1439, 1407, 1246, 1208, 1044, 878, 852, 780, 736, 642, 560. HR-MS: m/z calcd for [M + NH$_4$]$^+$, C$_{70}$H$_{75}$O$_{10}$Br$_5$, 1494.1558, found 1494.1582 (error: 1.6 ppm).
Fig. S19 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 5a
Fig. S20 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 5a
Fig. S21. $^{1}H$ NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 5b.
Fig. S22 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 5b.
Fig. S23. $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 5c.
Fig. S24 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 5c.
Fig. S25 $^1$H NMR spectrum (400 MHz, CDCl$_3$) recorded for compound 5d.
Fig. S26 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) recorded for compound 5d.

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Single crystal XRD data

**Fig. S27** Single crystal structure of compound 5d. Color code: C, grey; H, white; O, red; Br, brown. The red circle indicates the two possible bromobutyl chain conformations.