

Electronic Supplementary Information

Solid-phase combinatorial synthesis of ester-type banana-shaped molecule by way of sequential palladium-catalyzed carbonylation

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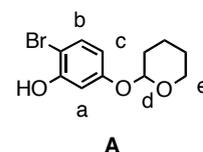
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General: NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for ^1H , 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to chloroform (7.26 ppm for ^1H) or chloroform-*d* (77.1 ppm for ^{13}C) when internal standard is not indicated. Multiplicities are reported by using the following abbreviations: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, br; broad, *J*; coupling constants in Hertz. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important absorption is reported as the IR data given in cm^{-1} . All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by a solution of *p*-anisaldehyde. Merck silica gel was used for column chromatography. KANTO 40-100 mesh silica gel was used for flush column chromatography. High performance liquid chromatography (HPLC) was performed on a Waters 2695 Separation Module using a Senshu Pak Silica-3302-N column with a Waters 2996 Photodiode Array Detector. Gel permeation chromatography (GPC) for qualitative and quantitative analysis were performed on a Japan Analytical Industry Model LC 605 (recycling preparative HPLC), with a Japan Analytical Industry Model RI-5 refractive index detector and a Japan Analytical Industry Model 310 ultra violet detector with polystyrene gel column (JAIGEL-1H, 20 mm x 600 mm), using chloroform as a solvent (3.5 mL/min). ESI-TOF Mass spectra were measured with P. E. Biosystems TK-3500 Biospectrometry Workstation. Elemental analyses were performed on a Perkin-Elmer 2400 II CHNS/O. MicroKan Sorting System was performed on IRORI AccutagTM-100 Combinatorial Chemistry System using IRORI MicroKansTM reactor and Radiofrequency Tag. Dry THF, dry hexane, dry toluene and dry dioxane were distilled from sodium wire contained a catalytic amount of benzophenone. Dry dichloromethane was distilled from P_2O_5 . Dry methanol was distilled from Mg. The optical microscopic textures of the materials were examined using an Olympus BX50 polarizing microscope equipped with a temperature-controlled Mettler Toledo FP82 hot stage.

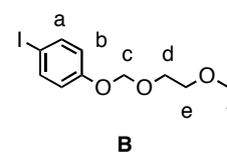
Experimental Section

Preparation of the fragments for Solid-Phase Synthesis

2-Bromo-5-tetrahydropyranyloxyphenol (A): To a solution of 4-bromoresorcinol (10.0 g, 52.9 mmol) and PPTS (665 mg, 2.65 mmol) in CH_2Cl_2 (264 mL, 5.0 mL/mmol) was added dropwise DHP (7.2 mL, 77.6 mmol) at 0 °C under argon. After being stirred at room temperature for 4 h, the mixture was quenched with NEt_3 , and then concentrated in vacuo. The residue was purified by column chromatography on flash silica gel with 20% ethyl acetate in hexane to afford 2-bromo-5-tetrahydropyranyloxyphenol (**A**) (9.00 g, 32.8 mmol, 62%) as a pale yellow powder. ^1H NMR (270 MHz, CDCl_3) δ 7.31 (d, *J* = 8.58 Hz, 1H, b), 6.77 (d, *J* = 2.96 Hz, 1H, a), 6.55 (dd, *J* = 2.96, 8.58 Hz, 1H, c), 5.50 (s, 1H, OH), 5.36 (m, 1H, d), 3.82-3.91 (m, 1H, e), 3.58-3.62 (m, 1H, e), 1.57-1.98 (m, 6H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 158.0, 152.9, 131.9, 110.6, 104.5, 101.6, 96.6, 62.1, 30.2, 25.1, 18.7. FT-IR (solid) 3238, 2956, 1599, 1418, 1298, 1098, 963, 830, 623, 457 cm^{-1} . Elemental Analysis Found: C, 48.37%; H, 4.80%. Calcd for $\text{C}_{11}\text{H}_{13}\text{O}_3$ C, 48.37%; H, 4.80%.

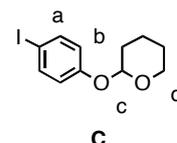


4-(2-Methoxyethoxymethoxy)iodobenzene (B): To a solution of 4-iodophenol (25.0 g, 113 mmol) and DIEA (32.0 mL, 181 mmol) in CH_2Cl_2 (170 mL, 1.5 mL/mmol) was added dropwise MEMCl (17.0 mL, 147.7 mmol) at 0 °C under argon. After being stirred at 35 °C for 5 h, the mixture was quenched with saturated aqueous NH_4Cl at 0 °C. The aqueous layer was extracted twice with ethyl acetate. The combined organic layer was washed with 1 M HCl, saturated aqueous NaHCO_3 , brine and dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography on flash silica gel with 9% ethyl acetate in hexane to afford 4-(2-methoxyethoxymethoxy)iodobenzene (**B**)



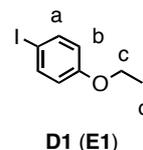
(29.7 g, 96.6 mmol, 85%) as a colorless oil. ^1H NMR (270 MHz, CDCl_3) δ 7.56 (d, $J = 8.91$ Hz, 2H, b), 6.83 (d, $J = 8.91$ Hz, 2H, a), 6.23 (s, 2H, c), 3.78-3.81 (m, 2H, d), 3.53-3.55 (m, 2H, e), 3.37 (s, 3H, f). ^{13}C NMR (67.8 MHz, CDCl_3) δ 157.2, 138.4, 118.7, 93.5, 84.4, 71.6, 67.8, 59.1. FT-IR (KBr) 2924, 2881, 1586, 1485, 1226, 1103, 996, 823, 756, 580 cm^{-1} .

4-(Tetrahydropyranyloxy)iodobenzene (C): To a solution of 4-iodophenol (25.0 g, 113 mmol) and PPTS (1.42 g, 5.63 mmol) in CH_2Cl_2 (170 mL, 1.5 mL/mmol) was added dropwise DHP (13.4 mL, 147 mmol) at 0 $^\circ\text{C}$ under argon. After being stirred at room temperature for 4 h, the mixture was quenched with NEt_3 , and then concentrated in vacuo. The residue was recrystallized from hexane to afford 4-(tetrahydropyranyloxy)iodobenzene (C) (32.1 g, 105.6 mmol, 93%) as a white powder. ^1H NMR (270 MHz, CDCl_3) δ 7.55 (d, $J = 8.90$ Hz, 2H, b), 6.83 (d, $J = 8.90$ Hz, 2H, a), 5.37 (m, 1H, c), 3.86-3.94 (m, 1H, d), 3.81-3.84 (m, 2H, d), 1.52-2.04 (m, 6H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 157.0, 138.3, 119.0, 96.5, 84.0, 62.1, 30.3, 25.2. FT-IR (solid) 2944, 2871, 1584, 1483, 1233, 1113, 1018, 952, 916, 821, 642, 503 cm^{-1} . Elemental Analysis Found: C, 43.14%; H, 4.44%. Calcd for $\text{C}_{11}\text{H}_{13}\text{IO}_2$ C, 43.44%; H, 4.31%.

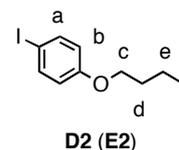


General procedure: Preparation of 4-alkoxyiodobenzene (D, E): To a suspension of 4-iodophenol (10.0 g, 45.5 mmol) and K_2CO_3 (8.7 g, 62.0 mmol) in EtOH (62 mL, 1.5 mL/mmol) was added alkyl bromide (41.3 mmol) at room temperature. After being stirred under reflux for 24 h, the mixture was filtered to remove the solid. The filtrate was concentrated in vacuo and the residue was diluted ether. The organic layer was washed with 1 M NaOH, 3 M HCl, saturated aqueous NaHCO_3 , brine, dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography on flash silica gel to afford 4-alkoxyiodobenzene D, E.

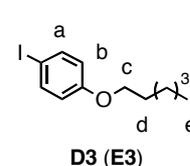
4-Ethoxyiodobenzene (D1, E1): yield: 91% as a colorless oil. ^1H -NMR (270 MHz, CDCl_3) δ 7.54 (d, $J = 9.24$ Hz, 2H, b), 6.67 (d, $J = 9.24$ Hz, 2H, a), 3.99 (q, $J = 6.93$ Hz, 2H, c), 1.40 (t, $J = 6.93$ Hz, 3H, d). ^{13}C -NMR (67.8 MHz, CDCl_3) δ 158.8, 138.2, 116.9, 82.5, 63.6, 14.8. FT-IR (KBr) 2980, 1587, 1486, 1391, 1244, 1175, 999, 818, 631, 506 cm^{-1} .



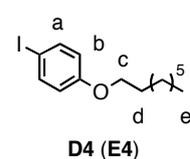
4-Butoxyiodobenzene (D2, E2): yield: 90% as a colorless oil. ^1H -NMR (270 MHz, CDCl_3) δ 7.54 (d, $J = 8.91$ Hz, 2H, b), 6.67 (d, $J = 8.91$ Hz, 2H, a), 3.92 (t, $J = 7.26$ Hz, 2H, c), 1.72-1.78 (m, 2H, d), 1.44-1.55 (m, 2H, e), 0.97 (t, $J = 7.26$ Hz, 3H, f). ^{13}C -NMR (67.8 MHz, CDCl_3) δ 159.0, 138.1, 116.9, 82.5, 67.8, 31.2, 19.2, 13.9. FT-IR (KBr) 2958, 1587, 1486, 1391, 1244, 1174, 999, 819, 631, 506 cm^{-1} .



4-Hexyloxyiodobenzene (D3, E3): yield: 93% as a colorless oil. ^1H -NMR (270 MHz, CDCl_3) δ 7.54 (d, $J = 8.91$ Hz, 2H, b), 6.69 (d, $J = 8.91$ Hz, 2H, a), 3.91 (t, $J = 6.6$ Hz, 2H, c), 1.71-1.81 (m, 2H, d), 1.30-1.54 (m, 6H, alkyl chain), 0.90 (t, $J = 6.6$ Hz, 3H, e). ^{13}C -NMR (67.8 MHz, CDCl_3) δ 159.1, 138.2, 116.9, 82.5, 68.2, 31.6, 29.2, 25.7, 22.7, 14.1. FT-IR (KBr) 2930, 1587, 1486, 1391, 1244, 1174, 999, 819, 631, 505 cm^{-1} .

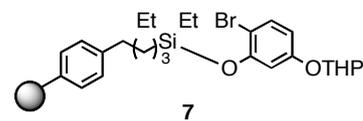


4-Octyloxyiodobenzene (D4, E4): yield: 96% as a colorless oil. ^1H -NMR (270 MHz, CDCl_3) δ 7.54 (d, $J = 8.91$ Hz, 2H, b), 6.67 (d, $J = 8.91$ Hz, 2H, a), 3.91 (t, $J = 6.6$ Hz, 2H, c), 1.73-1.79 (m, 2H, d), 1.30-1.54 (m, 10H, alkyl chain), 0.88 (t, $J = 6.6$ Hz, 3H, e). ^{13}C -NMR (67.8 MHz, CDCl_3) δ 159.1, 138.2, 116.9, 82.5, 68.2, 31.9, 29.4, 29.3, 29.2, 26.1, 22.7, 14.2. FT-IR (KBr) 2926, 1586, 1486, 1390, 1244, 1174, 999, 819, 631, 505 cm^{-1} .



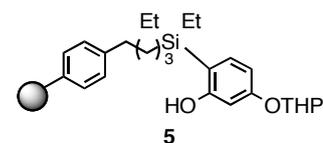
Polymer-supported 2-bromo-5-tetrahydropyranyloxyphenol (7): To 600 mg of PS-DES resin (6) (Argonaut, 0.96 mmol/g loading, 0.58 mmol) in a 20 mL syringe-shaped vessel (Varian Reservoirs) was added a solution of TMSCl (220 μL , 1.73 mmol) in dry CH_2Cl_2 (6.0 mL, 10.0 mL/mmol) at room temperature under argon. After being shaken at

the same temperature for 1 h, the mixture was filtered. The resin was washed with dry CH_2Cl_2 (7.0 mL x 3) under argon, and then added a solution of TfOH (103 μL , 1.16 mmol) in dry CH_2Cl_2 (6.0 mL, 10.0 mL/mmol) at the same temperature. After being shaken at the same temperature for 30 min, the mixture was filtered. The resin was washed with CH_2Cl_2 (7.0 mL x 2) under argon, and then added a solution of 2-bromo-5-tetrahydropyranyloxyphenol (**A**) (317 mg, 1.16 mmol) and 2,6-lutidine (270 μL , 2.32 mmol) in dry CH_2Cl_2 (6.0 mL, 10.0 mL/mmol) at room temperature. After being shaken at the same temperature for 12 h, the mixture was filtered (unreacted substrate was recovered after usual workup). The resin was washed with dry CH_2Cl_2 (5.0 mL x 5) and dried under reduced pressure to afford polymer-supported 2-bromo-5-tetrahydropyranyloxyphenol (**7**). FT-IR (resin) 2910, 1600, 1492, 1452, 1180, 1008, 818, 761, 703, 544 cm^{-1} .



Determination of loading amount of (7): To the suspension of **7** (100 mg) in a 5 mL syringe-shaped vessel was added a solution of CSA (0.1 M solution in MeOH-THF (1:2), 1.5 mL/100 mg) at room temperature. After being shaken vigorously at the same temperature for 1 h, the mixture was quenched with NEt_3 and then filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on flash short-pad silica gel to afford 4-bromoresorcinol as a white solid (9.1 mg, 0.048 mmol). The loading amount of **7** was determined to be 0.5 mmol/g-resin.

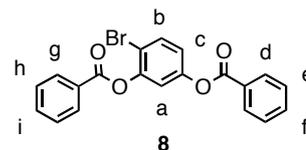
Polymer-supported 3-tetrahydropyranyloxyphenol (5): To a suspension of **7** in dry THF (5.5 mL, 9.5 mL/mmol) was added BuLi (1.59 M in hexane, 1.1 mL, 1.73 mmol) at -78°C under argon. After being shaken at the same temperature for 1.5 h, the mixture was filtered and the resin was washed with dry THF (5.0 mL x 3), MeOH (5.0 mL x 3), Et_2O (5.0 mL x 3), and dried under reduced pressure to afford the polymer-supported 3-tetrahydropyranyloxyphenol (**5**). FT-IR (resin) 3330, 2915, 1601, 1452, 1179, 1070, 1020, 761, 704, 543 cm^{-1} .



4-Bromoresorcinol dibenzoate (8): To a suspension of polymer-supported resorcinol **5** (30 mg) in MeOH-THF (1:2, 4.0 mL) was added CSA (0.1 M, 93 mg, 0.4 mmol) at room temperature. After being shaken at the same temperature for 3 h, the mixture was filtered. The resins were washed with THF- H_2O (3:1) (5.0 mL x 3), MeOH (5.0 mL x 3), Et_2O (5.0 mL x 3) and dried under reduced pressure to afford polymer-supported diphenol.

To a suspension of polymer-supported diphenol in CH_2Cl_2 (4.0 mL) was added BzCl (0.2 M, 92 μL , 0.8 mmol) and DMAP (0.3 M, 147 mg, 1.2 mmol) at room temperature. After being shaken at the same temperature for 6 h, the mixture was filtered. The resins were washed with CH_2Cl_2 (5.0 mL x 3), THF- H_2O (3:1) (5.0 mL x 3), MeOH (5.0 mL x 3), Et_2O (5.0 mL x 3) to afford polymer-supported dibenzoate.

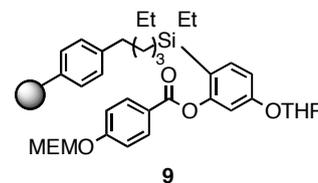
To a suspension of the polymer-supported dibenzoate in dry CH_2Cl_2 (4.0 mL) was added Br_2 (100 μL) at room temperature. After being shaken at the same temperature for 30 min, the mixture was filtered and the resins were washed with CHCl_3 (4.0 mL x 3). The combined filtrate was concentrated in vacuo, and the residue was purified by column chromatography on flash short-pad silica gel and by GPC eluted with CHCl_3 to afford 4-bromoresorcinol dibenzoate (**8**) (5.7 mg, 0.014 mmol, 96%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 7.73$ Hz, 2H, d), 8.18 (d, $J = 7.24$ Hz, 2H, g), 7.69 (d, $J = 8.69$ Hz, 1H, b), 7.65 (t, $J = 7.73$ Hz, 1H, f), 7.64 (t, $J = 7.24$ Hz, 1H, i), 7.52 (t, $J = 7.73$ Hz, 2H, e), 7.50 (t, $J = 7.24$ Hz, 2H, h), 7.31 (d, $J = 2.42$ Hz, 1H, a), 7.12 (dd, $J = 2.42$, 8.69 Hz, 1H, c). ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 163.9, 150.6, 148.8, 134.0, 133.9, 133.5, 130.5, 130.3, 129.0, 128.8, 128.7, 120.9, 118.0, 113.0.



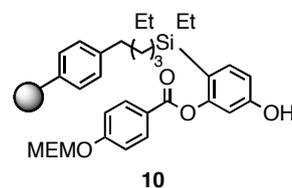
Solid-phase synthesis of **1** utilizing Microkans.

Polymer-supported 3-tetrahydropyranyloxyphenol (**5**) (30 mg) was packed into a MicrokansTM with a radiofrequency tag and was used for the all reactions in the solid-phase synthesis of **1**.

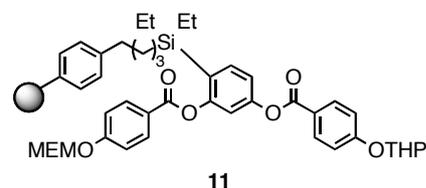
Polymer-supported 3-tetrahydropyranyloxyphenyl 4-(2-methoxyethoxymethyloxy)benzoate (9): To a mixture of **B** (0.2 M), NEt₃ (0.3 M), DMAP (0.1 M) and Pd(PPh₃)₄ (0.025 M) in DMF (1.5 mL/1 unit of MicroKansTM) was dipped MicroKansTM containing 30 mg of **5** under argon. The reaction tube was placed in an autoclave, which was purged with carbon monoxide three times before applying a pressure of 30 atm. After being stirred at 80 °C for 48 h, the mixture was filtered. The MicroKansTM were washed with DMF (5.0 mL x 3), THF-H₂O (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) and dried under reduced pressure to afford polymer-supported 3-tetrahydropyranyloxyphenyl 4-(2-methoxyethoxymethyloxy)benzoate (**9**). FT-IR (resin) 2920, 1737, 1602, 1453, 1235, 1117, 906, 845, 753, 696, 542 cm⁻¹.



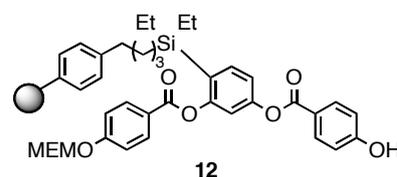
Polymer-supported 3-hydroxyphenyl 4-(2-methoxyethoxymethyloxy)benzoate (10): To the MicroKansTM containing **9** in a 20 mL vial was added a solution of PPTS (0.5 M solution in MeOH-THF (1:2), 1.5mL/1 unit of MicroKansTM) at room temperature. After being shaken at the same temperature for 24 h, the mixture was filtered. The MicroKansTM were washed with THF-H₂O (3:1) (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) and dried under reduced pressure to afford the polymer-supported 3-hydroxyphenyl 4-(2-methoxyethoxymethyloxy)benzoate **10**. FT-IR (resin) 3372, 2912, 1735, 1668, 1602, 1493, 1454, 1235, 1074, 763, 706, 544 cm⁻¹.



Polymer-supported 3-(4-tetrahydropyranyloxybenzoyloxy)phenyl 4-(2-methoxyethoxymethyloxy)benzoate (11): To a mixture of **C** (0.2 M), NEt₃ (0.3 M), DMAP (0.1 M) and Pd(PPh₃)₄ (0.025 M) in DMF (1.5 mL/1 unit of MicroKansTM) was dipped MicroKansTM containing **10** under argon. The reaction tube was placed in an autoclave, which was purged with carbon monoxide three times before applying a pressure of 30 atm. After being stirred at 80 °C for 48 h, the mixture was filtered. The MicroKansTM were washed with DMF (5.0 mL x 3), THF-H₂O (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) and dried under reduced pressure to afford polymer-supported 3-(4-tetrahydropyranyloxybenzoyloxy)phenyl 4-(2-methoxyethoxymethyloxy)benzoate (**11**). FT-IR (resin) 3372, 2912, 1735, 1668, 1602, 1493, 1454, 1235, 1074, 763, 706, 544 cm⁻¹.

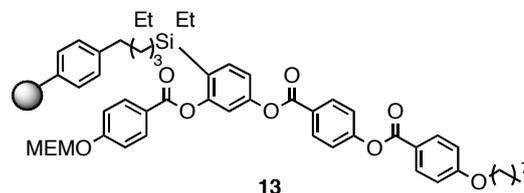


Polymer-supported 3-(4-hydroxybenzoyloxy)phenyl 4-(2-methoxyethoxymethyloxy)benzoate (12): To the MicroKansTM containing **11** in a 20 mL vial was added a solution of CSA (0.1 M solution in MeOH-THF (1:2), 1.5 mL/1 unit of MicroKansTM) at room temperature. After being shaken at the same temperature for 4.0 h, the mixture was filtered. The MicroKansTM were washed with THF (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) and dried under reduced pressure to afford polymer-supported 3-(4-hydroxybenzoyloxy)phenyl 4-(2-methoxyethoxymethyloxy)benzoate (**12**). FT-IR (resin) 2930, 1735, 1603, 1493, 1453, 1240, 1142, 1073, 850, 759, 696, 546 cm⁻¹.



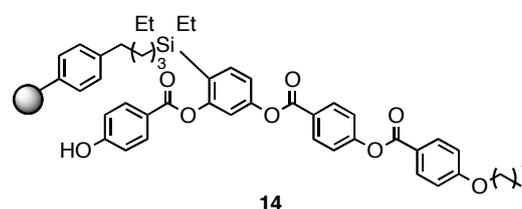
Polymer-supported 3-{4-(4-octyloxybenzoyloxy)benzoyloxy}phenyl 4-(2-methoxyethoxymethyl)benzoate (13):

To a mixture of **D4** (0.2 M), NEt_3 (0.3 M), DMAP (0.1 M) and $\text{Pd}(\text{PPh}_3)_4$ (0.025 M) in DMF (1.5 mL/1 unit of MicroKansTM) was dipped MicroKansTM containing **12** under argon. The reaction tube was placed in an autoclave, which was purged with carbon monoxide three times before applying a pressure of 30 atm. After being stirred at 80 °C for 48 h, the mixture was filtered. The MicroKansTM were washed with DMF (5.0 mL x 3), THF-H₂O (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) and dried under reduced pressure to afford polymer-supported 3-{4-(4-octyloxybenzoyloxy)benzoyloxy}phenyl 4-(2-methoxyethoxymethyl)benzoate (**13**). FT-IR (resin) 2928, 1740, 1603, 1453, 1251, 1164, 1077, 845, 761, 697, 542 cm⁻¹.



Polymer-supported 3-{4-(4-octyloxybenzoyloxy)benzoyloxy}phenyl 4-hydroxybenzoate (14): To the MicroKansTM containing **13** in a 20 mL vial was added 20% TFA/CH₂Cl₂ (1.5 mL/1 unit of MicroKansTM) at room temperature.

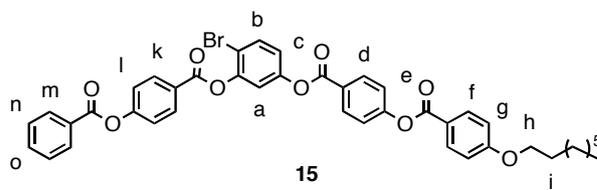
After being shaken at the same temperature for 3 h, the mixture was filtered. The MicroKansTM were washed with dry CH₂Cl₂ (5.0 mL x 5), Et₂O (5.0 mL x 2) and dried under reduced pressure to afford polymer-supported 3-{4-(4-octyloxybenzoyloxy)benzoyloxy}phenyl 4-hydroxybenzoate (**14**). FT-IR (resin) 3423, 3026, 1739, 1602, 1453, 1253, 1163, 1068, 759, 698, 542 cm⁻¹.



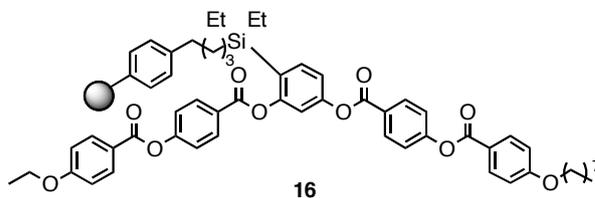
5-{4-(4-Octyloxybenzoyloxy)benzoyloxy}-2-bromophenyl 4-benzoyloxybenzoate (15): To a MicroKansTM containing **13** was added 20% TFA/CH₂Cl₂ (1.5 mL/1 unit of MicroKansTM), and shaken at room temperature. After being shaken at the same temperature for 12 h, the mixture was filtered. The MicroKansTM was washed with CH₂Cl₂ (5.0 mL x 3), Et₂O (5.0 mL x 3) to afford polymer-supported phenol.

To a suspension of the MicroKansTM in CH₂Cl₂ (4.0 mL) was added BzCl (0.2 M, 92 μL, 0.8 mmol) and DMAP (0.3 M, 147 mg, 1.2 mmol) at room temperature. After being shaken at the same temperature for 6 h, the mixture was filtered. The MicroKansTM was washed with CH₂Cl₂ (5.0 mL x 3), THF-H₂O (3:1) (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) to afford polymer-supported benzoate.

To a suspension of the MicroKansTM in dry CH₂Cl₂ (4.0 mL) was added Br₂ (100 μL) at room temperature. After being shaken at the same temperature for 30 min, the mixture was filtered and the resin was washed with CHCl₃. The combined filtrate was concentrated in vacuo, and the residue was purified by column chromatography on flash short-pad silica gel and by GPC eluted with CHCl₃ to afford 5-{4-(4-octyloxybenzoyloxy)benzoyloxy}-2-bromophenyl 4-benzoyloxybenzoate (**16**) (9.6 mg, 0.012 mmol, 84%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.21 Hz, 2H, l), 8.26 (d, *J* = 8.69 Hz, 2H, e), 8.23 (d, *J* = 7.73 Hz, 2H, m), 8.15 (d, *J* = 8.69 Hz, 2H, g), 7.71 (d, *J* = 8.69 Hz, 1H, b), 7.66 (t, *J* = 7.73 Hz, 1H, o), 7.54 (t, *J* = 7.73 Hz, 2H, n), 7.41 (d, *J* = 8.21 Hz, 2H, k), 7.39 (d, *J* = 8.69 Hz, 2H, d), 7.30 (d, *J* = 2.41 Hz, 1H, a), 7.13 (dd, *J* = 2.41, 8.69 Hz, 1H, c), 6.99 (d, *J* = 8.69 Hz, 2H, f), 4.06 (t, *J* = 6.76 Hz, 2H, h), 1.82-1.90 (m, 2H, i), 1.30-1.57 (m, 10H, alkyl chain), 0.89 (t, *J* = 7.25 Hz, 3H, j). ¹³C NMR (67.8 MHz, CDCl₃) δ 164.6, 164.3, 163.9, 163.2, 155.7, 155.5, 150.6, 148.8, 134.0, 133.6, 132.5, 132.2, 131.9, 130.3, 129.0, 128.7, 126.3, 122.3, 122.2, 120.9, 118.0, 114.5, 113.1, 68.4, 31.9, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1.

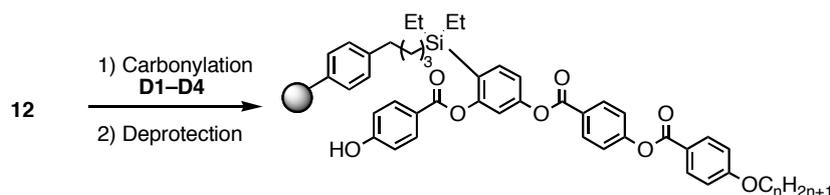


Polymer-supported 3-{4-(4-octyloxybenzoyloxy)benzoyloxy}phenyl 4-(4-ethoxybenzoyloxy)benzoate (16): To a mixture of **E1** (0.2 M), NEt_3 (0.3 M), DMAP (0.1 M) and $\text{Pd}(\text{PPh}_3)_4$ (0.025 M) in DMF (1.5 mL/1 unit of MicroKansTM) was dipped MicroKansTM containing **14** under argon. The reaction tube was placed in an autoclave, which was purged with carbon monoxide three times before applying a pressure of 30 atm. After being stirred at room temperature for 48 h, the mixture was filtered. The MicroKansTM were washed with DMF (5.0 mL x 3), THF-H₂O (5.0 mL x 3), MeOH (5.0 mL x 3), Et₂O (5.0 mL x 3) and dried under reduced pressure to afford the polymer-supported 3-{4-(4-octyloxybenzoyloxy)benzoyloxy}phenyl 4-(4-ethoxybenzoyloxy)benzoate (**16**). FT-IR (resin) 2926, 1740, 1679, 1602, 1452, 1252, 1161, 1064, 1015, 845, 762, 696, 543 cm^{-1} .



General Procedure : Cleavage from Solid-Support: To a MicroKansTM in a 20 mL vial was added a solution of Br_2 (50 μL /1 unit of MicroKansTM) in CH_2Cl_2 (2.0 mL/1 unit of MicroKansTM) at room temperature. After being shaken at the same temperature for 30 min, The MicroKansTM was filtered and washed three times with CHCl_3 . The filtrate was concentrated under reduced pressure. The residue was purified by short-pad column chromatography and GPC eluted with CHCl_3 .

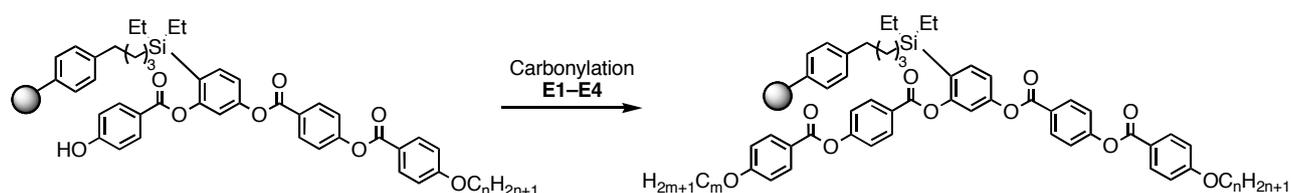
Procedure for the 3rd Pd-catalyzed carbonylation using fragment D1–D4 and removal of the MEM group by a split and pool method utilizing radiofrequency tags



The sixteen Microkans were sorted and distributed into four reaction tubes. To each reaction tubes containing four Microkans and $\text{Pd}(\text{PPh}_3)_4$ (0.025 M, 0.15 mmol, 173 mg) were added a solution of **D1–D4** (0.2M), NEt_3 (0.3 M, 1.8 mmol, 251 μL) and DMAP (0.1 M, 0.6 mmol, 73 mg) in DMF (6.0 mL, 1.5 mL/1 unit of MicroKansTM) at room temperature under argon. The reaction tube was placed in an autoclave, which was purged with carbon monoxide three times before applying a pressure of 30 atm. After being stirred at 80 °C for 48 h, the mixture was filtered. All Microkans were pooled together and were washed with DMF (30 mL x 3), THF-H₂O (30 mL x 3), MeOH (30 mL x 3), Et₂O (30 mL x 3) and dried under reduced pressure.

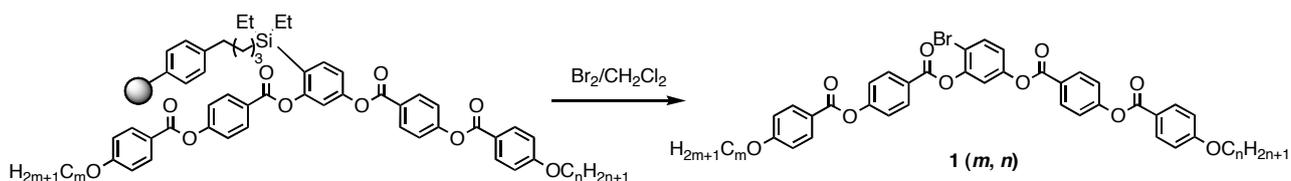
To the sixteen Microkans in a 50 mL vial were added 20% TFA/ CH_2Cl_2 (25 mL, 1.5 mL/ 1 unit of MicroKansTM) at room temperature. After being shaken at the same temperature for 3 h, the mixture was filtered. The Microkans were washed consecutively with dry CH_2Cl_2 (30 mL x 5), Et₂O (30 mL x 3) and dried under reduced pressure.

Procedure for the 4th Pd-catalyzed carbonylation using E1–E4 by a split and pool method utilizing radiofrequency tags



The above sixteen MicroKans were sorted and distributed into four reaction tubes. To each reaction tubes containing four MicroKans and Pd(PPh₃)₄ (0.025 M, 0.15 mmol, 173 mg) were added a solution of **E1–E4** (0.2M), NEt₃ (0.3 M, 1.2 mmol, 168 μ L) and DMAP (0.1 M, 0.6 mmol, 73.5 mg) in DMF (6 mL, 1.5 mL/1 unit of MicroKans™) at room temperature under argon. The reaction tube was placed in an autoclave, which was purged with carbon monoxide three times before applying a pressure of 30 atm. After being stirred at room temperature for 48 h, the mixture was filtered. All MicroKans were pooled together and were washed with DMF (30 mL x 3), THF-H₂O (30 mL x 3), MeOH (30 mL x 3), Et₂O (30 mL x 3) and dried under reduced pressure.

General procedure for cleavage of the 16-member banana-shaped molecules **1 (*m,n*)**



The sixteen MicroKans were sorted by means of radiofrequency signals, and were independently treated with a solution of Br₂ (50 μ L/1 unit of MicroKans) in CH₂Cl₂ (2.0 mL/1 unit of MicroKans) at room temperature. After being shaken at the same temperature for 30 min, the solutions were evaporated by N₂ flash in parallel. The MicroKans were washed three times with CHCl₃, respectively. The cleavage solutions labeled were concentrated in parallel. The residues were purified by column chromatography on flash short-pad silica gel and by GPC eluted with CHCl₃ to afford a 16-member library of banana-shaped molecules **1** in pure form.

1 (2, 2): yield: 82%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.14 (q, *J* = 6.77 Hz, 4H), 1.47 (t, *J* = 6.77 Hz, 6H).

1 (2, 4): yield: 53%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.14 (q, *J* = 6.77 Hz, 2H), 4.07 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 2H), 1.50-1.55 (m, 2H), 1.47 (t, *J* = 6.77 Hz, 3H), 1.00 (t, *J* = 7.25 Hz, 3H).

1 (2, 6): yield: 61%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.14 (q, *J* = 6.77 Hz, 2H), 4.06 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 2H), 1.50-1.56 (m, 2H), 1.47 (t, *J* = 6.77 Hz, 3H), 1.30-1.37 (m, 4H), 0.92 (t, *J* = 7.25 Hz, 3H).

1 (2, 8): yield: 65%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.14 (q, *J* = 6.77 Hz, 2H), 4.05 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 2H), 1.50-1.56 (m, 2H), 1.47 (t, *J* = 6.77 Hz, 3H), 1.30-1.37 (m, 8H), 0.89 (t, *J* = 7.25 Hz, 3H).

1 (4, 2): yield: 49%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.14 (q, *J* = 6.77 Hz, 2H), 4.07 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 2H), 1.50-1.56 (m, 2H), 1.47 (t, *J* = 6.77 Hz, 3H), 1.00 (t, *J* = 7.25 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃), δ 164.4, 163.9, 163.7, 163.3, 155.7, 150.6, 148.9, 133.6, 132.6, 132.2, 132.0, 131.5, 126.4, 126.1, 122.3, 122.2, 121.1, 120.9, 118.0, 114.5, 113.1, 112.1, 68.2, 63.9, 31.2, 19.3, 14.8, 13.9.

1 (4, 4): yield: 90%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.07 (t, *J* = 6.28 Hz, 4H), 1.82-1.90 (m, 4H), 1.50-1.56 (m, 4H), 1.00 (t, *J* = 7.25 Hz, 6H).

1 (4, 6): yield: 50%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.07 (q, *J* = 6.28 Hz, 2H), 4.06 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 8H), 1.00 (t, *J* = 7.25 Hz, 3H), 0.92 (t, *J* = 7.25 Hz, 3H).

1 (4, 8): yield: 61%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.07 (q, *J* = 6.28 Hz, 2H), 4.05 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 12H), 1.00 (t, *J* = 7.25 Hz, 3H), 0.89 (t, *J* = 7.25 Hz, 3H).

1 (6, 2): yield: 67%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.14 (q, *J* = 6.77 Hz, 2H), 4.06 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 2H), 1.50-1.56 (m, 2H), 1.47 (t, *J* = 6.77 Hz, 3H), 1.30-1.36 (m, 4H), 0.92 (t, *J* = 7.25 Hz, 3H).

1 (6, 4): yield: 49%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.07 (t, *J* = 6.28 Hz, 2H), 4.06 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 8H), 1.00 (t, *J* = 7.25 Hz, 3H), 0.92 (t, *J* = 7.25 Hz, 3H).

1 (6, 6): yield: 85%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.06 (t, *J* = 6.28 Hz, 4H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 12H), 0.92 (t, *J* = 7.25 Hz, 6H).

1 (6, 8): yield: 53%, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.70 Hz, 2H), 8.26 (d, *J* = 8.70 Hz, 2H), 8.16 (d, *J* = 9.18 Hz, 2H), 8.15 (d, *J* = 9.18 Hz, 2H), 7.71 (d, *J* = 9.18 Hz, 1H), 7.39 (d, *J* = 8.69 Hz, 2H), 7.38 (d, *J* = 8.69 Hz, 2H), 7.29 (d, *J* = 2.42 Hz, 1H), 7.12 (dd, *J* = 2.42, 9.18 Hz, 1H), 6.99 (d, *J* = 9.18 Hz, 4H), 4.06 (t, *J* = 6.28 Hz, 2H), 4.05 (t, *J* = 6.28 Hz, 2H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 16H), 0.92 (t, *J* = 7.25 Hz, 3H), 0.89 (t, *J* = 7.25 Hz, 3H).

1 (8, 2): yield: 73%, ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.70$ Hz, 2H), 8.26 (d, $J = 8.70$ Hz, 2H), 8.16 (d, $J = 9.18$ Hz, 2H), 8.15 (d, $J = 9.18$ Hz, 2H), 7.71 (d, $J = 9.18$ Hz, 1H), 7.39 (d, $J = 8.69$ Hz, 2H), 7.38 (d, $J = 8.69$ Hz, 2H), 7.29 (d, $J = 2.42$ Hz, 1H), 7.12 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.14 (q, $J = 6.77$ Hz, 2H), 4.05 (t, $J = 6.28$ Hz, 2H), 1.82-1.90 (m, 2H), 1.50-1.56 (m, 2H), 1.47 (t, $J = 6.77$ Hz, 3H), 1.30-1.38 (m, 8H), 0.89 (t, $J = 7.25$ Hz, 3H).

1 (8, 4): yield: 63%, ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.70$ Hz, 2H), 8.26 (d, $J = 8.70$ Hz, 2H), 8.16 (d, $J = 9.18$ Hz, 2H), 8.15 (d, $J = 9.18$ Hz, 2H), 7.71 (d, $J = 9.18$ Hz, 1H), 7.39 (d, $J = 8.69$ Hz, 2H), 7.38 (d, $J = 8.69$ Hz, 2H), 7.29 (d, $J = 2.42$ Hz, 1H), 7.12 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.07 (t, $J = 6.28$ Hz, 2H), 4.05 (t, $J = 6.28$ Hz, 2H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 12H), 1.00 (t, $J = 7.25$ Hz, 3H), 0.89 (t, $J = 7.25$ Hz, 3H).

1 (8, 6): yield: 41%, ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.70$ Hz, 2H), 8.26 (d, $J = 8.70$ Hz, 2H), 8.16 (d, $J = 9.18$ Hz, 2H), 8.15 (d, $J = 9.18$ Hz, 2H), 7.71 (d, $J = 9.18$ Hz, 1H), 7.39 (d, $J = 8.69$ Hz, 2H), 7.38 (d, $J = 8.69$ Hz, 2H), 7.29 (d, $J = 2.42$ Hz, 1H), 7.12 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.06 (t, $J = 6.28$ Hz, 2H), 4.05 (t, $J = 6.28$ Hz, 2H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 16H), 0.92 (t, $J = 7.25$ Hz, 3H), 0.89 (t, $J = 7.25$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 163.9, 163.3, 155.8, 155.7, 150.6, 148.9, 133.6, 132.5, 132.2, 131.9, 126.4, 126.1, 122.3, 121.0, 118.0, 114.5, 113.1, 68.5, 31.9, 31.6, 29.4, 29.3, 29.1, 26.1, 25.7, 22.7, 22.6, 14.2, 14.1.

1 (8, 8): yield: 85%, ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.70$ Hz, 2H), 8.26 (d, $J = 8.70$ Hz, 2H), 8.16 (d, $J = 9.18$ Hz, 2H), 8.15 (d, $J = 9.18$ Hz, 2H), 7.71 (d, $J = 9.18$ Hz, 1H), 7.39 (d, $J = 8.69$ Hz, 2H), 7.38 (d, $J = 8.69$ Hz, 2H), 7.29 (d, $J = 2.42$ Hz, 1H), 7.12 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.05 (t, $J = 6.28$ Hz, 4H), 1.82-1.90 (m, 4H), 1.30-1.55 (m, 20H), 0.89 (t, $J = 7.25$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 163.9, 163.3, 155.8, 155.7, 150.6, 148.8, 133.6, 132.5, 132.2, 131.9, 126.3, 126.1, 122.3, 120.9, 118.0, 114.5, 113.1, 68.5, 31.9, 29.4, 29.3, 29.1, 28.9, 26.1, 25.7, 22.7, 22.7, 14.1. Elemental Analysis Found: C, 66.92%; H, 5.90%. Calcd for $\text{C}_{30}\text{H}_{53}\text{BrO}_{10}$ C, 67.18%; H, 5.98%.

