Electronic Supplementary Information

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

Masahito Yoshida, Takayuki Doi, Sungmin Kang, Junji Watanabe and Takashi Takahashi

\(^{a}\)Department of Applied Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8552, Japan. Fax: (+81) 3 5734 2884; Tel: (+81) 3 5734-2120. E-mail: ttak@apc.titech.ac.jp

\(^{b}\)Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3 Aza-aoba, Aramaki, Aoba-ku, Sendai, 980-8578, Japan

\(^{c}\)Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8552, Japan.

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\(^{1}\)H NMR spectra of 1(2,2)–1(8,8): S11–S26
General: NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for $^1$H, 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 $^1$H) 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 Accutag™-100 Combinatorial Chemistry System using IRORI MicroKans™ 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 P2O5. 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$_2$Cl$_2$ (264 mL, 5.0 mL/mmol) was added dropwised DHP (7.2 mL, 77.6 mmol) at 0 $^\circ$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. $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{11}$H$_{13}$O$_3$: C, 48.37%; H, 4.80%.

4-(2-Methoxyethoxymethyloxy)iodobenzene (B): To a solution of 4-iodophenol (25.0 g, 113 mmol) and DIEA (32.0 mL, 181 mmol) in CH$_2$Cl$_2$ (170 mL, 1.5 mL/mmol) was added dropwise MEMCl (17.0 mL, 147.7 mmol) at 0 $^\circ$C under argon. After being stirred at 35 $^\circ$C for 5 h, the mixture was quenched with saturated aqueous NH$_4$Cl at 0 $^\circ$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-methoxyethoxymethyloxy)iodobenzene B.
(29.7 g, 96.6 mmol, 85%) as a colorless oil. $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-(Tetrahydropyranoyloxy)iodobenzene (C):** To a solution of 4-iodophenol (25.0 g, 113 mmol) and PPTS (1.42 g, 5.63 mmol) in CH$_2$Cl$_2$ (170 mL, 1.5 mL/mmol) was added dropwise DHP (13.4 mL, 147 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 recrystalized from hexane to afford 4-(tetrahydropyranyloxy)iodobenzene (C) (32.1 g, 105.6 mmol, 93%) as a white powder. $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{11}$H$_{13}$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$_2$CO$_3$ (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. $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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. $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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. $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 159.1, 138.1, 116.9, 82.5, 68.2, 31.6, 29.2, 25.7, 22.7, 14.1. FT-IR (KBr) 2958, 1587, 1486, 1391, 1244, 1174, 999, 819, 631, 506 cm$^{-1}$.

**4-Octyloxyiodobenzene (D4, E4):** yield: 96% as a colorless oil. $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 $\mu$L, 1.73 mmol) in dry CH$_2$Cl$_2$ (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 CH₂Cl₂ (7.0 mL x 3) under argon, and then added a solution of TFOH (103 μL, 1.16 mmol) in dry CH₂Cl₂ (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 CH₂Cl₂ (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 CH₂Cl₂ (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 CH₂Cl₂ (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 NEt₃ 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), Et₂O (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-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 polymer-supported dibenzoate.

To a suspension of the polymer-supported dibenzoate 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 resins were washed with CHCl₃ (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 CHCl₃ to afford 4-bromoresorcinol dibenzoate (8) (5.7 mg, 0.014 mmol, 96%) as a white solid. ¹H NMR (400 MHz, CDCl₃) 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, c), 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). ¹³C NMR (100 MHz, CDCl₃) 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 MicroKans™ with a radiofrequency tag and was used for 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 MicroKans™) was dipped MicroKans™ 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 MicroKans™ 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-methoxyethoxymethoxy)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 MicroKans™ 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 MicroKans™) at room temperature. After being shaken at the same temperature for 24 h, the mixture was filtered. The MicroKans™ 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-methoxyethoxymethoxy)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 MicroKans™) was dipped MicroKans™ 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 MicroKans™ 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-methoxyethoxymethoxy)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 MicroKans™ 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 MicroKans™) at room temperature. After being shaken at the same temperature for 4.0 h, the mixture was filtered. The MicroKans™ 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-methoxyethoxymethoxy)benzoate (12). FT-IR (resin) 2930, 1735, 1603, 1493, 1453, 1240, 1142, 1073, 850, 759, 696, 546 cm⁻¹.
Polymer-supported 3-(4-(4-octyloxybenzoyl oxy)benzoyloxy)phenyl 4-(2-methoxyethoxymethyloxy)benzoate (13): To a mixture of D4 (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 MicroKans™) was dipped MicroKans™ 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 MicroKans™ 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-octyloxybenzoyl oxy)benzoyloxy)phenyl 4-(2-methoxyethoxymethyloxy)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 MicroKans™ containing 13 in a 20 mL vial was added 20% TFA/CH2Cl2 (1.5 mL/1 unit of MicroKans™) at room temperature. After being shaken at the same temperature for 3 h, the mixture was filtered. The MicroKans™ 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 MicroKans™ containing 13 was added 20% TFA/CH2Cl2 (1.5 mL/1 unit of MicroKans™), and shaken at room temperature. After being shaken at the same temperature for 12 h, the mixture was filtered. The MicroKans™ was washed with CH2Cl2 (5.0 mL x 3), Et2O (5.0 mL x 3) to afford polymer-supported phenol.

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), NEt₃ (0.3 M), DMAP (0.1 M) and Pd(PPh₃)₄ (0.025 M) in DMF (1.5 mL/1 unit of MicroKans™) was dipped MicroKans™ 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 MicroKans™ 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 MicroKans™ in a 20 mL vial was added a solution of Br₂ (50 μL/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 MicroKans™ was filtered and washed three times with CHCl₃. The filtrate was concentrated under reduced pressure. The residue was purified by short-pad column chromatography and GPC eluted with CHCl₃.

Procedure for the 3rd Pd-catalyzed carbynylation 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 Pd(PPh₃)₄ (0.025 M, 0.15 mmol, 173 mg) were added a solution of D1–D4 (0.2M), NEt₃ (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 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 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/CH₂Cl₂ (25 mL, 1.5 mL/ 1 unit of MicroKans™) at room temperature. After being shaken at the same temperature for 3 h, the mixture was filtered. The Microkans were washed consecutively with dry CH₂Cl₂ (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 tube 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 μL) 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 μL/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), 1.50-1.56 (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).
yield: 65%, $^1$H 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), 1.72 (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).

$^1$H 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), 1.72 (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).

$^1$H 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), 1.72 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.07 (q, $J = 6.28$ Hz, 2H), 1.47 (t, $J = 6.77$ Hz, 3H), 1.00 (t, $J = 7.25$ Hz, 3H).

$^1$H 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), 1.72 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.07 (q, $J = 6.28$ Hz, 2H), 1.47 (t, $J = 6.77$ Hz, 3H), 1.00 (t, $J = 7.25$ Hz, 3H).

$^1$H 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), 1.72 (dd, $J = 2.42, 9.18$ Hz, 1H), 6.99 (d, $J = 9.18$ Hz, 4H), 4.07 (q, $J = 6.28$ Hz, 2H), 1.47 (t, $J = 6.77$ Hz, 3H), 1.30-1.37 (m, 8H), 0.89 (t, $J = 7.25$ Hz, 3H).
1 (8, 2): yield: 73%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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), 1.47 (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%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, 16H), 0.92 (t, $J = 7.25$ Hz, 3H), 0.89 (t, $J = 7.25$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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), 4.18-1.90 (m, 4H), 1.30-1.55 (m, 20H), 0.89 (t, $J = 7.25$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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 C$_{50}$H$_{53}$BrO$_{10}$ C, 67.18%; H, 5.98%.
Supplementary Material (ESI) for Chemical Communications
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