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Controlled Regioregularity in Oligo(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylenes

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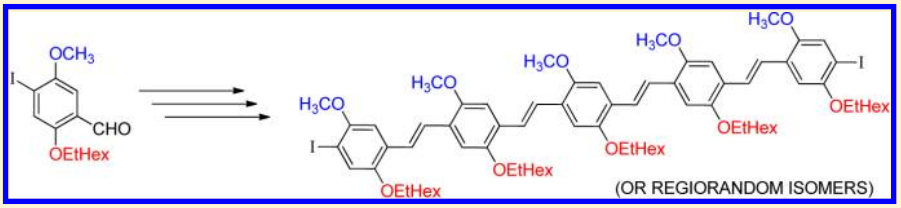
Supporting Information



ABSTRACT: A series of three pentameric derivatives of 2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylenes (**2**–**4**), with varying degrees of side chain regioregularity, was prepared. The oligomerization chemistry was carried out using repetitive Horner–Wadsworth–Emmons (HWE) reactions of precisely substituted aryl rings with four different substituents. The resulting oligomers were characterized by nuclear magnetic resonance spectroscopy (NMR), cyclic voltammetry (CV) and absorption spectroscopy in solution and in thin films. Each of the oligomers gave discrete ^{1}H and ^{13}C NMR spectra. The regioregular pentamer (**2**) displayed the most resolution between signals and suggests those nuclei reside in more unique chemical environments than the regiorandom pentamers (**3** and **4**). The solution phase electronic (CV) and absorption properties of each of the new oligomers were found to be essentially identical. In contrast, the thin film absorption spectra were not equivalent. The more regioregular pentamers (**2** and **3**) possessed a new, red-shifted shoulder structure that suggests the packing order is heavily influenced by side chain regioregularity even at the pentamer level.

INTRODUCTION

The inherent regioregularity[1−3] and composition[4−11] of the solubilizing side chains in conjugated polymers (CPs) has a significant impact on that material's performance in organic electronic devices such as field-effect transistors, light emitting diodes, and organic photovoltaics. Fine tuning of the interplay between the aromatic core backbone and the aliphatic hydrocarbon chains can lead to highly aligned polymeric materials, which are known to facilitate charge transport, by way of $\pi-\pi$ overlap between neighboring polymer chains.[4,12] While solubilizing chains on the polymer backbone are often varied in length and in structure (e.g., straight vs branched), these structural modifications are not always systematic, and the ramifications of the changes are not always known at the molecular level. However, recent advances in single-molecule characterization techniques have provided opportunities to probe how chemical structure can influence the conformations of individual polymer chains.[13−19]

Using single-molecule techniques, we recently investigated the impact of the conjugation length of individual chromophores on their alignment in a single polymer chain.[20] To accomplish this task, we created polychromophore[21−25] polymers composed of alternating conjugated oligomers of bis(2-ethylhexyl)-*p*-phenylene-vinylenes (BEH-PPV) and saturated flexible linkers of tetraethylene glycol.[26] The maximum effective conjugation length was controlled at the synthetic level with the resulting polymers having nearly identical solution absorption and emission spectra to the isolated oligomer counterparts. By varying the number of PPV repeat units from 3 to 5 to 7 at the prepolymerization stage, the spectral properties, as well as the single-polymer chain anisotropies, were systematically controlled.[20] The short PPV oligomer-containing polychromophores were disordered giving isotropic structures, while the longer PPV oligomer-containing polychromophores folded into highly anisotropic nanostructures that are even more ordered than native poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) polymers.[15]

Our recent goal is to probe the effects of chromophore side chain regioregularity on polychromophore anisotropy. While our former polychromophore studies utilized oligo-BEH-PPVs that are symmetrically substituted with ethylhexyloxy side chains (Figure 1, **1**), traditional MEH-PPV[27−29] monomers are nonsymmetric (methoxy and ethylhexyloxy side chains) and typically lead to regiorandom polymeric materials. Although recent progress has led to regioregular MEH-PPV,[30] this polymer has yet to be investigated with single-polymer techniques. Here we demonstrate the discrete chemical synthesis of a series of three MEH-PPV pentamers (Figure 1, **2**–**4**) with varying degrees of side chain regioregularity. We have fully characterized the compounds via NMR spectroscopy and find the more regioregular derivatives contain more

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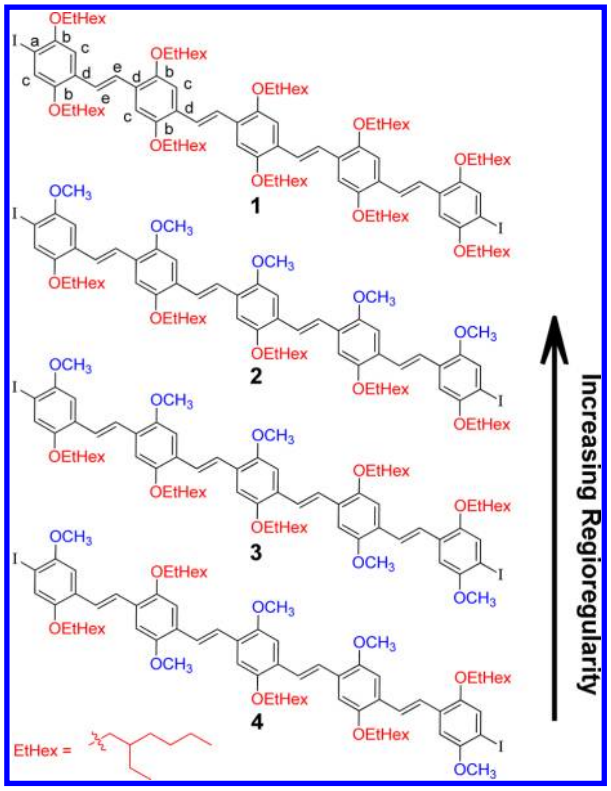


Figure 1. MEH-PPV pentamers (**2**–**4**) of varying regioregularity. BEH-PPV **1** was previously prepared.[26] General ^{13}C NMR assignments provided (see Figure 2).

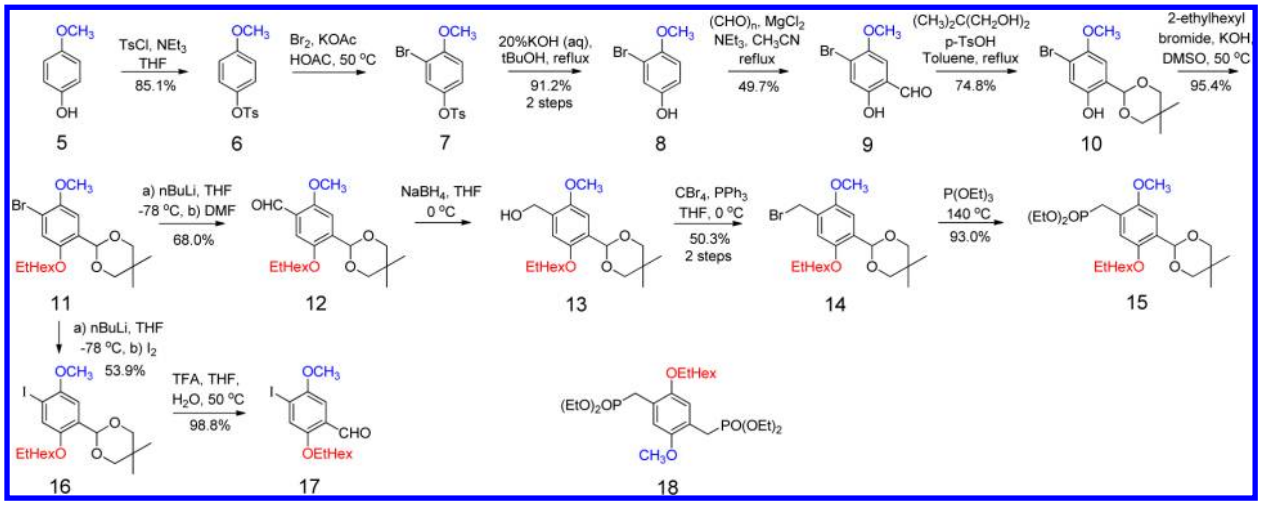
resolved signals. Furthermore, we have investigated the solution and thin film UV–vis properties of each oligomer and demonstrate the more regioregular oligomers adopt more ordered aggregates in the solid state.

RESULTS AND DISCUSSION

Synthesis of Oligomers. Through a series of oligomerization steps using the Horner–Wadsworth–Emmons (HWE) reaction, we have synthesized MEH-PPV oligomers with terminal iodo-functionality. The synthetic methodology for this effort is a direct extension of our previous work;[26] however, the methods to create the well-defined MEH-PPV oligomers are much more demanding owing to the unsymmetrical nature of the side chains. The strategy relies on the ability to add aldehyde and bromo functionality at exact locations around an aryl ring (e.g., bromo *ortho* to methoxy; aldehyde *ortho* to ethylhexyloxy). This specificity requires electronic manipulation of the aryl ring during electrophilic additions.[31] To address this need, the electron rich 4-methoxyphenol (**5**) was tosylated to form **6**, which provides a compound with reduced electron-density *ortho* to the tosyl group (Scheme 1). Bromination of **6** can then selectively proceed *ortho* to the electron rich methoxy group to form **7**. Deprotection of the tosylate group (**8**) provides a system that can undergo formylation *ortho* to the newly formed hydroxyl substituent to give **9**. Protection of the aldehyde (**10**), followed by Williamson ether synthesis with 2-ethylhexyl bromide, creates the desired spatially arranged side chains of **11**. To access a building block capable of repetitive HWE reactions, a series of transformations can convert the aryl bromide **11** into phosphonate ester **15** that maintains a protected aldehyde to be utilized for subsequent transformations. Alternatively, bromide **11** can be converted to an iodide **16** and then iodo-aldehyde **17** for oligomerization chemistries. The orthogonal side chain functionalized derivatives (**29** and **34**) were prepared from 4-ethylhexyloxyphenol through an analogous reaction pathway (Scheme 2).

With the asymmetrically substituted monomers in hand, access to the three pentamers of varying regioregularity was relatively straightforward. For the completely regioregular MEH-PPV example, **17** was used as an initiation point for repetitive HWE couplings and deprotections with **15** to produce dimer (**35**), trimer (**36**), tetramer (**37**), and finally pentamer (**2**) (Scheme 3). It is important to note that after each HWE reaction in this study, the crude mixture was refluxed in toluene with catalytic iodine to ensure all vinyl groups were in the more stable *trans* configuration. Access to the semiregular pentamer **3** was accomplished by branching away from the regioregular synthesis by combining 2 equiv of dimer **35** with diphosphonate ester **18**.[18] The most regiorandom (yet still an atomically defined material) pentamer **4** was accessed by coupling **17** with **29** to create dimer **38** that has equivalent side chains on opposite sides of the ring system. The combination of 2 equiv of **38** with diphosphonate **18** gave pentamer **4**. All coupling reactions proceeded in reasonable

Scheme 1. Route to Asymmetric Oligomer Building Blocks I



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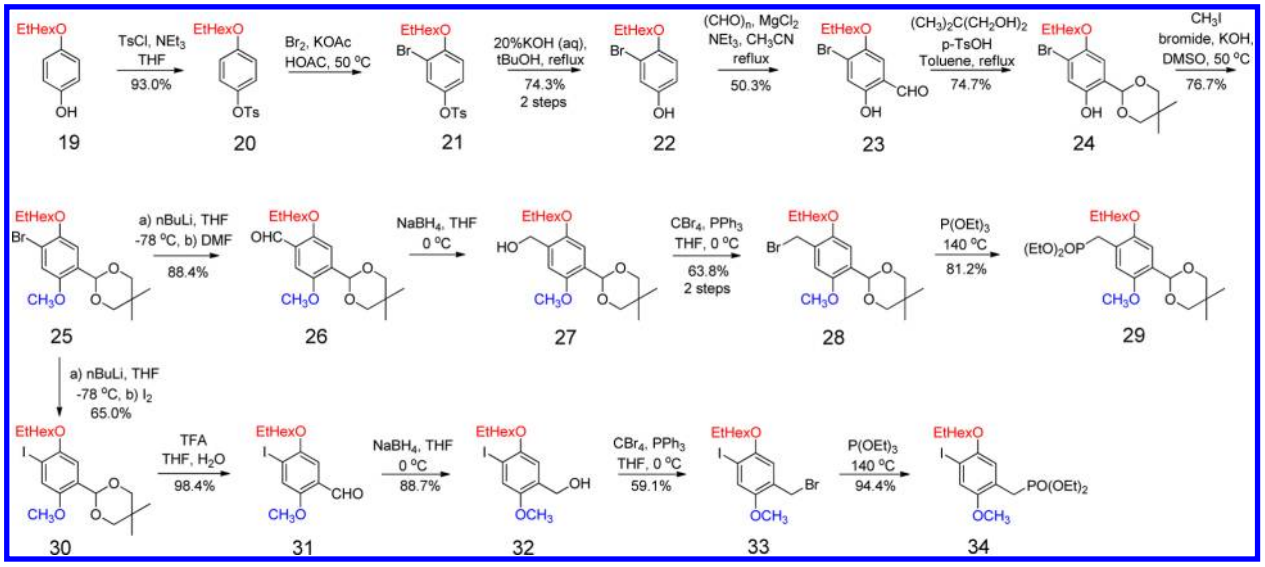
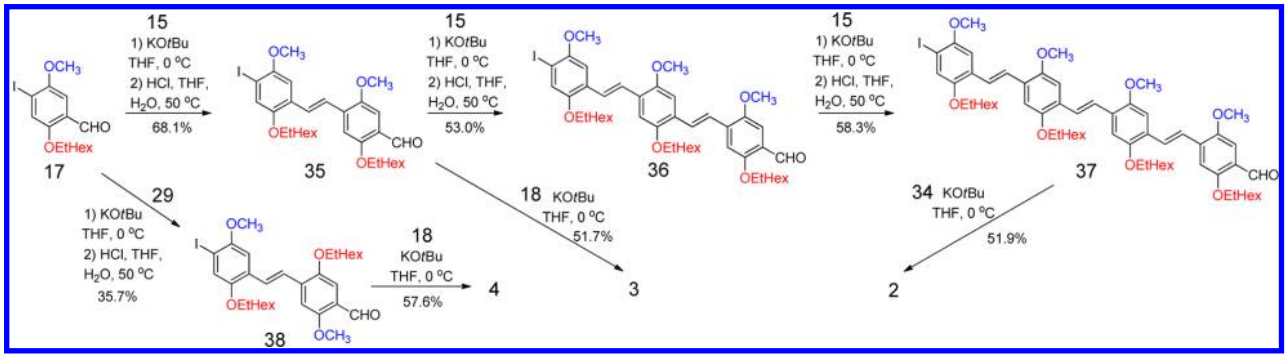
Scheme 2. Route to Asymmetric Oligomer Building Blocks II



Scheme 3. Step-Wise Oligomerization Strategy



yields (36–68%) following iodine reflux and acetal deprotection steps.

Oligomer Characterization. Significant overlap in the aromatic region (especially due to ABq splitting of vinylic protons) of the ^{1}H NMR spectra limits the ability to unambiguously assign specific proton resonances. However, integration of the aryl and vinylic protons clearly demonstrated the desirable quantities in each region. Moreover, a qualitative evaluation of the spectra (Supporting Information) shows the regioregular pentamer **2** provided more chemically resolved signals (8 aryl singlets, with two overlapping, for 10 protons) than the more regiorandom pentamers **3** and **4** (5 aryl singlets for 10 protons). These data suggest the regioregular protons reside in more distinctive chemical environments than the regiorandom protons. The aromatic and vinylic signals were significantly more resolved in the ^{13}C NMR spectra in all cases (Figure 2). Each of the 38 individual aromatic and vinylic carbon atoms gave resolved signals[32] that varied in chemical shift for each derivative. The general assignments for the carbons can be found in Figure 1. Overall, there were five regions where the signals were found. Two of the regions containing 10 resonances each, which are assigned to the aryl carbons bound to oxygen (150.0–152.0 ppm, b) and aryl carbons bound to hydrogen (121.0–123.0 ppm, c). Two other signal regions contain the vinylic carbons (126.0–128.0 ppm, e) and eight aryl carbons bound to the vinyl groups (107.0–111.0 ppm, d). Finally, one region contained the two carbons

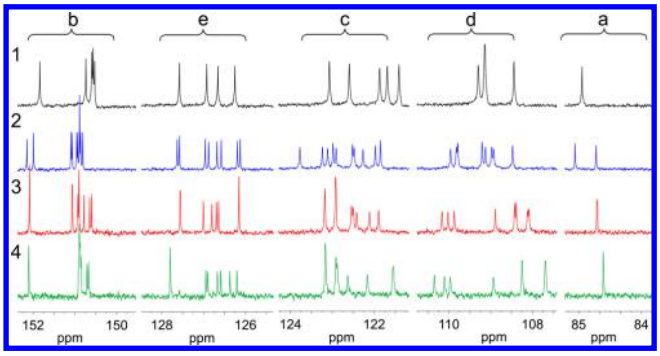


Figure 2. ^{13}C NMR spectra for PPV oligomers **1**–**4**. Each set of signals can be assigned to either a carbon on the aryl rings or vinylic bonds.

bound to iodides (84.0–86.0 ppm, a). Each of the new MEH-PPV oligomers show more complex spectra than the BEH-PPV pentamer **1** (Figure 2, top) that has half the number of the signals owing to the full symmetry of the compound. Comparison of the two regioregular examples shows that the signals are essentially split into two (e.g., vinylic carbons 126.0–128.0 ppm) going from BEH-pentamer **1** to MEH-pentamer **2**.

The electronic and photophysical properties of each of the new oligomers were characterized by cyclic voltammetry and UV–vis spectroscopy. As expected, for a chromophore with the exact same pi-conjugated system, the electrochemistry of each

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oligomer is essentially the same (Figure 3). The oxidation wave onsets were measured to be 0.24, 0.25, and 0.23 V (vs ferrocene

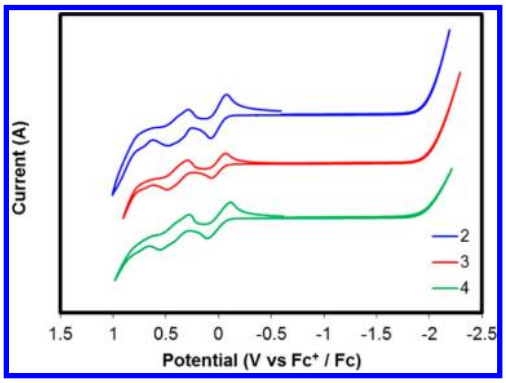

Figure 3. Cyclic voltammograms of **2**, **3**, and **4** in chloroform with 0.1 M tetrabutylammonium hexafluorophosphate, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV/s. Ferrocene added as internal standard and referenced to 0 V.

Table 1. Physical Properties of Pentamers

pentamer	$\lambda_{abs,max,sol}$ (nm)	$\lambda_{abs,max,film}$ (nm)	$\lambda_{onset,film}$ (nm)	$E_{ox,onset}$ (V)[a]	mp (°C)
2	464	458	565	0.24	176
3	464	471	568	0.25	158
4	463	467	540	0.23	106

[a]Potential relative to ferrocenium/ferrocene redox couple.

at 0 V) for **2**, **3**, and **4** respectively (Table 1). No low lying reduction waves are observed. These results confirm the regioregularity of the side chains does not significantly affect the solution phase electrochemistry of these similarly conjugated compounds.

The solution phase UV−vis gives identical absorption spectra for all three pentamers with the λ_{max} ∼ 464 nm (Figure 4).

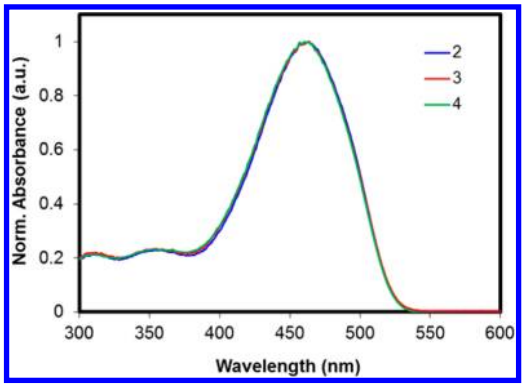

Figure 4. Absorbance of MEH-PPV oligomers **2**, **3**, and **4** in toluene.

Complementary to the electrochemistry, these results demonstrate that pentamers **2**, **3**, and **4** are photochemically equivalent in solution. However, the similarities in their electronic structure diverge when in the solid state. The thin film absorption spectra obtained after spin coating and thermal annealing are not equivalent for the three oligomers (Figure 5). While the spectrum of the regiorandom pentamer **4** broadens in comparison to the solution, the peak shape remains relatively

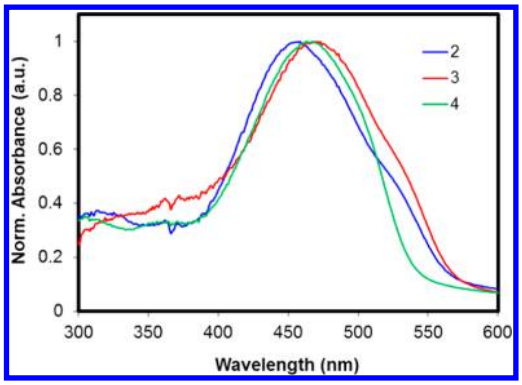

Figure 5. Absorbance of MEH-PPV oligomers **2**, **3**, and **4** in thin film after annealing at 100 °C for 45 min.

constant. However, the two more regioregular pentamers **2** and **3** show different peak shapes and possess a new red-shifted, shoulder structure. The relative definition of the shoulder is greater in **2** than in **3** and appears to be directly related to the regioregularity of the side chains. Similar presence and absence of low-energy shoulders are known in conjugated polymers and often depend on the degree of regioregularity.[33−35] These shoulder structures have been assigned to new $\pi-\pi^*$ transitions that are associated with interchain absorption in materials such as MEH-PPV[36,37] and poly(3-hexylthiophene)[34] with the intensity of the shoulder correlating with the degree of order in the film. The melting points (mp) of each oligomer was also dramatically affected by the substitution pattern with the mp decreasing stepwise going from regioregular **2** to regiorandom **4** (Table 1). Although only preliminary, these results show that even at the MEH-PPVs pentamer level, the role of side chain order is important for creating more ordered materials in the solid state.

In conclusion, we have demonstrated the discrete synthesis and characterization of three MEH-PPV pentamers with a range of side chain regioregularity. We are currently investigating the solid state packing, as well as the single molecule and small-aggregate fluorescence, of these materials in more detail. With these new materials in hand we will also probe the effects of regioregularity on the anisotropies of polychromophore structures.

EXPERIMENTAL SECTION

Unless otherwise noted, all reagents were used as received, and all reactions were carried out under an argon atmosphere. Column chromatography was performed on a chromatographing system with normal phase silica columns. ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz NMR station at room temperature, unless otherwise noted. Cyclic voltammetry was performed on a potentiostat with a 0.1 M tetrabutylammonium hexafluorophosphate solution (Chloroform) using a glassy carbon electrode, platinum counter electrode, and an Ag/AgCl reference electrode.

4-Methoxyphenyl 4-methylbenzenesulfonate (6). In a 500 mL round-bottom flask was added 4-methoxy-phenol **5** (25.0 g, 201.4 mmol), TsCl (38.3 g, 201.4 mmol) in 250 mL of THF. Then, Et_3N (42 mL, 301.5 mmol) was added slowly. The mixture was stirred at room temperature overnight. CH_2Cl_2 (200 mL) was added and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was crystallized using MeOH to give 47.7 g (85.1%) white needle solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.65 (m, 2H), 7.32−7.27 (m, 2H), 6.90−6.84 (m, 2H), 6.79−6.72 (m, 2H), 3.76 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 145.2, 143.1, 132.3,

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129.7, 128.6, 123.3, 114.4, 55.5, 21.7. Proton and Carbon NMR match previous report.[31]

3-Bromo-4-methoxyphenyl 4-methylbenzenesulfonate (7). In a 250 mL round bottle flask was stirred a mixture of **6** (15.5 g, 55.7 mmol), KOAc (12.0 g, 122.5 mmol) in acetic acid (150 mL). Br_2 (10.7 g, 66.8 mmol, 3.5 mL) was then added. The mixture was stirred at 50 °C overnight. After that, more Br_2 (0.12 equiv) was added and allowed to react for another 12 h. The reaction was cooled at room temperature, and $NaHSO_3$ was added until the color of Br_2 disappeared. CH_2Cl_2 (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was pure enough to be used for next reaction without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.67 (m, 2H), 7.35−7.30 (m, 2H), 7.15 (d, J = 2.8 Hz, 1H), 6.93 (dd, J = 9.0, 2.8 Hz, 1H), 6.79−6.75 (m, 1H), 3.86 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 145.6, 142.8, 132.0, 129.8, 128.5, 127.4, 122.3, 111.6, 111.4, 56.5, 21.7.

3-Bromo-4-methoxy-phenol (8). In a 250 mL round bottle flask wad added **7** from last step in tBuOH (40 mL). A solution of 20% aqueous NaOH (40 mL) was added. The mixture was reflux overnight. The reaction mixture was cooled and neutralized with 1 M HCl. CH_2Cl_2 (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−70% CH_2Cl_2 in hexane) to give 10.3 g (91.2%, two steps) white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 2.7 Hz, 1H), 6.81−6.74 (m, 2H), 4.62 (s, 1H), 3.83 (d, J = 2.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 149.8, 120.5, 115.0, 113.2, 112.0, 57.0; LRMS (EI+) 202.0; HRMS (TOF MS EI+) m/z for $C_7H_7O_2Br$ calcd 201.9629, found 201.9627. Proton and Carbon NMR match previous report.[38]

4-Bromo-2-hydroxy-5-methoxy-benzaldehyde (9). In a 250 mL round bottle flask was added $MgCl_2$ (7.24 g, 76.1 mmol) and dry Et_3N (27 mL, 192.6 mmol) into a solution of **8** (10.3 g, 50.3 mmol) in 150 mL of dry CH_3CN. Then paraformaldehyde (10.6 g, 354.9 mmol) was added. The reaction mixture was reflux overnight and cooled down to room temperature. After that, the mixture was poured into 1 M HCl to neutralize. CH_2Cl_2 (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−40% CH_2Cl_2 in hexane) to give 5.82 g (49.7%) bright yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 9.84 (s, 1H), 7.27 (s, 1H), 6.98 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 155.9, 149.6, 123.0, 122.9, 119.3, 113.9, 56.9. Proton and Carbon NMR match previous report.[39]

5-Bromo-2-(5,5-dimethyl-1,3-dioxan-2-yl)-4-methoxy-phenol (10). In a 250 mL round-bottom flask with a dean-stark trap were added **9** (4.25 g, 18.3 mmol), 2,2-dimethylpropane-1,3-diol (7.62 g, 73.2 mmol) and catalytic amount (1%) of p-TsOH (35.2 mg, 0.18 mmol) in toluene (100 mL). The mixture was reflux overnight and then cooled to room temperature. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−40% CH_2Cl_2 in hexane) to give 4.34 g (74.8%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.12 (s, 1H), 6.77 (s, 1H), 5.50 (s, 1H), 3.84−3.79 (m, 5H), 3.69−3.64 (m, 2H), 1.28 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 149.3, 122.0, 121.3, 113.0, 111.2, 102.0, 77.5, 56.9, 30.4, 22.9, 21.8; LRMS (EI+) 316.0; HRMS (TOF MS EI+) m/z for $C_{13}H_{17}O_4Br$ calcd 316.0310, found 316.0309.

2-[4-Bromo-2-((2-ethylhexyl)oxy)-5-methoxy-phenyl]-5,5-dimethyl-1,3-dioxane (11). In a 250 mL round-bottom flask was stirred **10** (9.2 g, 29.0 mmol) in DMSO (100 mL) under argon. After fully deoxygenated, KOH power (4.1 g, 72.5 mmol) was added. Then, 2-ethylhexyl bromide (11.2 g, 58.0 mmol) was added slowly. The mixture was stirred at 50 °C overnight. The reaction mixture was neutralized with 1 M HCl. Diethyl ether (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0−35% CH_2Cl_2 in hexane) to give 11.88 g (95.4%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.08 (s, 1H), 5.68 (s, 1H), 3.88 (s, 3H), 3.81 (d, J = 5.5 Hz, 2H), 3.75 (d, J = 11.0 Hz, 2H), 3.63 (d, J = 11.1 Hz, 2H), 1.76−1.66 (m, 1H), 1.52−1.37 (m, 4H), 1.37−1.23 (m, 7H), 0.96−0.84 (m, 6H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 150.1, 127.0, 117.5, 112.2, 110.8, 96.7, 77.9, 71.7, 56.8, 39.5, 30.7, 30.3, 29.1, 24.0, 23.2, 23.1, 21.8, 14.1, 11.2; LRMS (ES+ + H) 429.2; HRMS (TOF MS ES+) m/z for $C_{21}H_{34}O_4Br$ calcd 429.1640, found 429.1648.

4-(5,5-Dimethyl-1,3-dioxan-2-yl)-5-((2-ethylhexyl)oxy)-2-methoxy-benzaldehyde (12). In a glovebox were added **11** (1.05 g, 2.45 mmol) in THF (50 mL) in a 100 mL two neck round bottle flask. The solution was taken out of glovebox and cooled down to −78 °C under Ar. A solution of n-BuLi (3.18 mmol, 2.0 mL) in hexane was added dropwise and stirred at −78 °C for 1 h. Then DMF (2 mL) was added to the mixture and stirred for another 2 h and temperature was allowed to increase to room temperature. H_2O (20 mL) was added to quench the reaction. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0−60% CH_2Cl_2 in hexane) to give 0.63 g (68%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.32 (s, 1H), 7.31 (s, 1H), 5.72 (s, 1H), 3.93 (s, 3H), 3.88 (d, J = 5.6 Hz, 2H), 3.77 (d, J = 11.2 Hz, 2H), 3.65 (d, J = 11.2 Hz, 2H), 1.77−1.65 (m, 1H), 1.52−1.37 (s, 4H), 1.37−1.29 (m, 7H), 0.96−0.88 (m, 6H), 0.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 156.5, 150.4, 134.5, 125.0, 110.9, 110.1, 96.5, 77.9, 71.3, 56.1, 39.4, 30.7, 30.3, 29.0, 24.1, 23.2, 23.1, 21.8, 14.1, 11.2; LRMS (ES+ + H) 379.2; HRMS (TOF MS ES+) m/z for $C_{22}H_{35}O_5$ calcd 379.2484, found 379.2477.

[4-(5,5-Dimethyl-1,3-dioxan-2-yl)-5-((2-ethylhexyl)oxy)-2-methoxy-phenyl] methanol (13). In a 100 mL two-necked round-bottom flask was stirred **12** (1.30 g, 3.43 mol) in THF (30 mL) at 0 °C for 10 min. $NaBH_4$ (156 mg, 4.12 mmol) was carefully added, and the mixture was stirred overnight. Methanol was added to quench the $NaBH_4$. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated to give colorless oil without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.86 (s, 1H), 5.74 (s, 1H), 4.65 (d, J = 6.5 Hz, 2H), 3.86 (s, 3H), 3.84 (d, J = 5.6 Hz, 2H), 3.75 (d, J = 11.1 Hz, 2H), 3.64 (d, J = 11.0 Hz, 2H), 2.25 (t, J = 6.5 Hz, 1H), 1.75−1.68 (m, 1H), 1.53−1.39 (m, 4H), 1.37−1.28 (m, 7H), 0.96−0.89 (s, 6H), 0.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 150.3, 130.6, 126.4, 112.9, 108.7, 97.0, 77.9, 71.6, 61.6, 55.7, 39.6, 30.7, 30.3, 29.1, 24.0, 23.2, 23.1, 21.9, 14.1, 11.2.

2-[4-Bromomethyl-2-((2-ethylhexyl)oxy)-5-methoxy-phenyl]-5,5-dimethyl-1,3-dioxane (14). In a 100 mL two-necked round-bottom flask was stirred **13** (1.31 g, 3.45 mmol) in THF (50 mL) at 0 °C for 10 min. Carbon tetrabromide (1.48 g, 4.49 mmol) and triphenyl-phosphine (1.18 g, 4.49 mmol) was added, and the mixture was stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 20% CH_2Cl_2 in hexane, R_f = 0.4) to give 0.77 g (50.3%, two steps) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.86 (s, 1H), 5.71 (s, 1H), 4.53 (s, 2H), 3.88 (s, 3H), 3.83 (d, J = 5.6 Hz, 2H), 3.75 (d, J = 11.1 Hz, 2H), 3.63 (d, J = 11.0 Hz, 2H), 1.76−1.68 (s, 1H), 1.53−1.39 (m, 4H), 1.38−1.28 (m, 7H), 0.97−0.88 (m, 6H), 0.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 150.2, 128.4, 127.1, 114.9, 109.9, 96.9, 77.9, 71.6, 56.2, 39.6, 30.7, 30.3, 29.1, 28.9, 24.1, 23.2, 23.1, 21.9, 14.1, 11.2.

Diethyl 4-(5,5-dimethyl-1,3-dioxan-2-yl)-5-((2-ethylhexyl)-oxy)-2-methoxy-benzyl-phosphonate (15). In a 20 mL vial was added **14** (770 mg, 0.96 mmol) and triethyl phosphite (404 mg, 2.44 mmol). The mixture was heated in 140 °C for 2 h and then cooled to room temperature. The residue was directly purified by silica gel chromatography (0 → 33% EtOAc in hexane, R_f = 0.4) to give 810 mg (93%) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.91 (d, J = 2.7 Hz, 1H), 5.71 (s, 1H), 4.05−3.96 (m, 4H), 3.84−3.80 (m, 5H), 3.75 (d, J = 11.2 Hz, 2H), 3.63 (d, J = 10.7 Hz, 2H), 3.21 (d,

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J = 21.9 Hz, 2H), 1.74−1.66 (m, 1H), 1.54−1.37 (m, 4H), 1.36−1.28 (m, 7H), 1.23 (t, J = 7.1 Hz, 6H), 0.95−0.88 (m, 6H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 151.2, 150.1, 150.0, 126.2, 126.2, 121.5, 121.4, 115.6, 115.6, 109.2, 109.2, 97.1, 97.1, 77.9, 71.5, 61.9, 61.8, 56.1, 39.6, 30.7, 30.3, 29.1, 27.2, 25.8, 24.0, 23.2, 23.1, 21.9, 16.4, 16.3, 14.1, 11.2; LRMS (ES+ + H) 501.3; HRMS (TOF MS ES +) m/z for $C_{26}H_{46}O_7P$ calcd 501.2981, found 501.2980.

2-[2-((2-Ethylhexyl)oxy)-4-iodo-5-methoxyphenyl]-5,5-dimethyl-1,3-dioxane (16). In a glovebox were added **11** (1.00 g, 2.33 mmol) in THF (50 mL) in a 100 mL two neck round bottle flask. The solution was taken out of glovebox and cooled down to −78 °C under Ar. A solution of n-BuLi (3.03 mmol, 1.9 mL) in hexane was added dropwise and stirred at −78 °C for 1 h. Then I_2 (0.768 g, 3.03 mmol) of THF solution was added to the mixture and stirred for another 2 h and temperature was allowed to increase to room temperature. H_2O (20 mL) was added to quench the reaction. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0−35% CH_2Cl_2 in hexane) to give 598 mg (53.9%) colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.13 (s, 1H), 5.67 (s, 1H), 3.87 (s, 3H), 3.80 (d, J = 5.5 Hz, 2H), 3.74 (d, J = 11.2 Hz, 2H), 3.63 (d, J = 10.6 Hz, 2H), 1.75−1.66 (m, 1H), 1.53−1.37 (m, 4H), 1.36−1.28 (m, 7H), 0.96−0.88 (m, 6H), 0.79 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 150.9, 128.1, 123.4, 109.4, 96.8, 86.4, 77.8, 71.7, 57.0, 39.5, 30.7, 30.3, 29.1, 24.0, 23.2, 23.1, 21.8, 14.1, 11.2; LRMS (ES+ + H) 477.1; HRMS (TOF MS ES+) m/z for $C_{21}H_{34}O_4I$ calcd 477.1502, found 477.1495.

2-((2-Ethylhexyl)oxy)-4-iodo-5-methoxy-benzaldehyde (17). **16** (1.05 g, 2.20 mmol) was dissolved in a solution of trifluoroacetic acid (2 mL), THF (10 mL) and H_2O (2 mL) in 100 mL round-bottom flask and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 40% CH_2Cl_2 in hexane, R_f = 0.4) to give 850 mg (98.8%) as a bright yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.47 (s, 1H), 7.22 (s, 1H), 3.94−3.89 (m, 2H), 3.87 (s, 3H), 1.81−1.72 (m, 1H), 1.52−1.39 (m, 4H), 1.37−1.28 (m, 4H), 0.98−0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 156.1, 152.5, 125.1, 124.5, 107.7, 96.0, 71.6, 56.9, 39.4, 30.6, 29.0, 23.9, 23.0, 14.1, 11.2; LRMS (ES+ +H) 391.1; HRMS (TOF MS ES+) m/z for $C_{16}H_{24}O_3I$ calcd 391.0770, found 391.0772.

Tetraethyl-2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene-bis(methylene)-bis(phosphonate) (18). In a 20 mL vial was added 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (454 mg, 1.07 mmol) and triethyl phosphite (446 mg, 2.68 mmol). The mixture was heated in 140 °C for 2 h and then cooled to room temperature. The residue was directly purified by silica gel chromatography (0 → 66% EtOAc in hexane) to give 73 mg (82%) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.89 (s, 1H), 4.07−3.95 (m, 8H), 3.82−3.78 (m, 5H), 3.22 (dd, J = 20.5, 7.0 Hz, 4H), 1.74−1.66 (m, 1H), 1.56−1.36 (m, 4H), 1.34−1.28 (m, 4H), 1.23 (td, J = 7.1, 4.4 Hz, 12H), 0.94−0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 150.8, 150.8, 150.7, 150.6, 150.6, 150.6, 150.5, 119.5, 119.4, 119.4, 119.3, 119.3, 119.3, 119.2, 119.2, 114.79, 114.77, 114.74, 114.7, 113.9, 113.90, 113.88, 113.85, 71.1, 61.89, 61.86, 61.83, 61.8, 56.1, 39.6, 30.6, 29.1, 23.9, 23.0, 16.4, 16.3, 16.3, 16.3, 14.0, 11.1; LRMS (ES+ + H) 537.3; HRMS (TOF MS ES+) m/z for $C_{25}H_{47}O_8P_2$ calcd 537.2746, found 537.2743. Proton and Carbon NMR match previous report.[18]

4-((2-Ethylhexyl)oxy)phenol (19). In a 250 mL round-bottom flask was stirred hydro-quinone (8 g, 72.6 mmol) in 100 mL of DMSO under argon. After fully deoxygenated, KOH power (8.2 g, 145.2 mmol) was added. Then, 2-ethylhexyl bromide (14.0 g, 72.6 mmol) was added slowly. The mixture was stirred at 50 °C overnight. The reaction mixture was neutralized with 1 M HCl. Diethyl ether (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−10% EtOAc in hexane) to give 5.73 g (35.5%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81−6.72 (m, 4H), 4.42 (s, 1H), 3.81−3.74 (m, 2H), 1.69 (dt, J = 12.2, 6.1 Hz, 1H), 1.55−1.36 (m, 4H), 1.34−1.27 (m, 4H), 0.95−0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 149.2, 115.9, 115.6, 71.3, 39.4, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1. Proton and Carbon NMR match previous report.[40]

4-((2-Ethylhexyl)oxy)phenyl 4-methylbenzenesulfonate (20). In a 250 mL round-bottom flask was added **19** (8.90 g, 40.03 mmol), TsCl (7.63 g, 40.03 mmol) in 150 mL of THF. Then, Et_3N (8.4 mL, 60.05 mmol) was added slowly. The mixture was stirred at room temperature overnight. CH_2Cl_2 (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0−60% CH_2Cl_2 in hexane) to give 14 g (93%) of colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.66 (m, 2H), 7.32−7.28 (m, 2H), 6.88−6.83 (m, 2H), 6.78−6.73 (m, 2H), 3.79−3.74 (m, 2H), 2.45 (s, 3H), 1.72−1.65 (m, 1H), 1.51−1.36 (m, 4H), 1.35−1.26 (m, 4H), 0.94−0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 145.1, 142.8, 132.4, 129.7, 128.6, 123.2, 115.0, 70.9, 39.3, 30.5, 29.0, 23.8, 23.0, 21.7, 14.1, 11.1; LRMS (ES+ + H) 377.2; HRMS (TOF MS ES+) m/z for $C_{21}H_{29}O_4S$ calcd 377.1787, found 377.1785.

3-Bromo-4-((2-ethyl-hexyl)oxy)phenyl 4-methylbenzenesulfonate (21). In a 250 mL round bottle flask was stirred a mixture of **20** (16.0 g, 42.5 mmol), KOAc (9.2 g, 93.5 mmol) in acetic acid (150 mL). Br_2 (8.2 g, 51.0 mmol, 2.6 mL) was then added. The mixture was stirred at 50 °C overnight. After that, more Br_2 (0.12 equiv) was added and allowed to react for another 12 h. The reaction was cooled at room temperature and $NaHSO_3$ was added until the color of Br_2 disappeared. CH_2Cl_2 (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was pure enough to be used for next reaction without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.67 (m, 2H), 7.35−7.30 (m, 2H), 7.13 (d, J = 2.8 Hz, 1H), 6.89 (dd, J = 8.9, 2.8 Hz, 1H), 6.74 (d, J = 9.0 Hz, 1H), 3.84 (d, J = 5.5 Hz, 2H), 2.46 (s, 3H), 1.75 (dt, J = 12.2, 6.0 Hz, 1H), 1.54−1.39 (m, 4H), 1.35−1.27 (m, 4H), 0.96−0.85 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 145.5, 142.5, 132.0, 129.8, 128.6, 127.2, 122.2, 112.4, 111.9, 71.8, 39.3, 30.4, 29.0, 23.8, 23.0, 21.7, 14.1, 11.2.

3-Bromo-4-((2-ethyl-hexyl)oxy)phenol (22). In a 250 mL round bottle flask was added **21** from last step in tBuOH (60 mL). A solution of 20% aqueous NaOH (60 mL) was added. The mixture was heated at reflux overnight. The reaction mixture was cooled and neutralized with 1 M HCl. CH_2Cl_2 (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−70% CH_2Cl_2 in hexane) to give 9.51 g (74.3%, two steps) colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 2.8 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 2.8 Hz, 1H), 4.44 (s, 1H), 3.83 (d, J = 5.6 Hz, 2H), 1.74 (dt, J = 12.2, 6.1 Hz, 1H), 1.60−1.39 (m, 4H), 1.36−1.28 (m, 4H), 0.96−0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 149.5, 120.5, 115.1, 114.8, 112.8, 72.7, 39.4, 30.4, 29.1, 23.8, 23.1, 14.1, 11.2; LRMS (EI+) 300.1; HRMS (TOF MS EI+) m/z for $C_{14}H_{21}O_2Br$ calcd 300.0725, found 300.0726.

4-Bromo-5-((2-ethylhexyl)oxy)-2-hydroxy-benzaldehyde (23). In a 250 mL round bottle flask was added $MgCl_2$ (4.51 g, 47.4 mmol) and dry Et_3N (16 mL, 120 mmol) into a solution of **22** (9.51 g, 31.6 mmol) in 150 mL of dry CH_3CN. Then paraformaldehyde (6.64 g, 221.2 mmol) was added. The reaction mixture was heated under reflux overnight and cooled down to room temperature. After that, the mixture was poured into 1 M HCl to neutralize. CH_2Cl_2 (150 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−40% CH_2Cl_2 in hexane) to give 5.23 g (50.3%) light yellow oil: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.71 (s, 1H), 9.85 (d, J = 0.6 Hz, 1H), 7.26 (s, 1H), 7.04 (s, 1H), 3.92 (d, J = 5.6 Hz, 2H), 1.79 (dt, J = 12.1, 5.9 Hz, 1H), 1.62−1.44 (m, 4H), 1.39−1.32 (m, 4H), 1.00−0.90 (m,

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6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 155.7, 149.4, 123.7, 122.7, 119.3, 114.9, 72.3, 39.4, 30.5, 29.0, 23.9, 23.0, 14.1, 11.2; LRMS (ES+ + H) 331.1; HRMS (TOF MS ES+) m/z for $C_{15}H_{22}O_3Br$ calcd 329.0752, found 329.0747.

5-Bromo-2-(5,5-dimethyl-1,3-dioxan-2-yl)-4-((2-ethylhexyl)-oxy)-phenol (24). In a 250 mL round-bottom flask with a dean-stark trap were added **23** (5.23 g, 15.9 mmol), 2,2-dimethylpropane-1,3-diol (6.62 g, 63.6 mmol) and catalytic amount (1%) of *p*-TsOH (30.2 mg, 0.16 mmol) in toluene (100 mL). The mixture was reflux overnight and then cooled to room temperature. CH_2Cl_2 (150 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−40% CH_2Cl_2 in hexane) to give 4.93 g (74.7%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.11 (s, 1H), 6.74 (s, 1H), 5.49 (s, 1H), 3.85−3.79 (m, 5H), 3.67 (d, J = 10.6 Hz, 2H), 1.77−1.68 (m, 1H), 1.60−1.39 (m, 4H), 1.37−1.27 (m, 4H), 1.28 (s, 3H), 0.96−0.88 (m, 6H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 149.1, 121.9, 121.2, 113.8, 112.3, 102.1, 77.6, 72.2, 39.5, 30.5, 30.4, 29.1, 23.9, 23.0, 23.0, 21.8, 14.1, 11.2; LRMS (ES+ + H) 415.1.

4-Bromo-2-[5-((2-ethylhexyl)oxy)-2-methoxy-phenyl]-5,5-dimethyl-1,3-dioxane (25). In a 250 mL round-bottom flask was stirred **24** (4.93 g, 11.9 mmol) in 100 mL of DMSO under argon. After fully deoxygenated, KOH power (3.3 g, 59.4 mmol) was added. Then, CH_3I (3.4 g, 23.7 mmol) was added slowly. The mixture was stirred at 40 °C overnight. The reaction mixture was neutralized with 1 M HCl. Diethyl ether (200 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0−30% CH_2Cl_2 in hexane) to give 3.91 g (76.7%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.07 (s, 1H), 5.69 (s, 1H), 3.91 (d, J = 5.5 Hz, 2H), 3.79 (s, 3H), 3.75 (d, J = 11.1 Hz, 2H), 3.67 (d, J = 10.9 Hz, 2H), 1.78−1.70 (m, 1H), 1.58−1.40 (m, 4H), 1.36−1.28 (m, 7H), 0.96−0.87 (m, 6H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 150.1, 126.6, 116.4, 113.0, 111.9, 96.5, 77.8, 72.0, 56.5, 39.5, 30.5, 30.3, 29.1, 23.9, 23.2, 23.1, 21.9, 14.1, 11.2; LRMS (ES+ + H) 431.2; HRMS (TOF MS ES+) m/z for $C_{21}H_{34}O_4Br$ calcd 429.1640, found 429.1637.

4-(5,5-Dimethyl-1,3-dioxan-2-yl)-2-((2-ethylhexyl)oxy)-5-methoxy-benzaldehyde (26). In a glovebox were added **25** (1.05 g, 2.45 mmol) in THF (50 mL) in a 100 mL two neck round bottle flask. The solution was taken out of glovebox and cooled down to −78 °C under Ar. A solution of *n*-BuLi (3.18 mmol, 2.0 mL) in hexane was added dropwise and stirred at −78 °C for 1 h. Then DMF (2 mL) was added to the mixture and stirred for another 2 h and temperature was allowed to increase to room temperature. H_2O (20 mL) was added to quench the reaction. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0−60% CH_2Cl_2 in hexane) to give 0.82 g (88.4%) light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.31 (s, 1H), 5.75 (s, 1H), 4.00 (dd, J = 5.3, 1.2 Hz, 2H), 3.84 (s, 3H), 3.77 (d, J = 11.1 Hz, 2H), 3.69 (d, J = 10.8 Hz, 2H), 1.79−1.71 (m, 1H), 1.52−1.40 (m, 4H), 1.36−1.27 (m, 7H), 0.98−0.86 (m, 6H), 0.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 156.6, 150.4, 134.3, 125.2, 112.0, 109.0, 96.3, 77.9, 71.1, 56.2, 39.5, 30.7, 30.3, 29.1, 24.1, 23.2, 23.0, 21.8, 14.0, 11.2; LRMS (ES+ + H) 379.2; HRMS (TOF MS ES+) m/z for $C_{22}H_{35}O_5$ calcd 379.2484, found 379.2480.

[4-(5,5-Dimethyl-1,3-dioxan-2-yl)-2-((2-ethylhexyl)oxy)-5-methoxy-phenyl]methanol (27). In a 100 mL two-necked round-bottom flask was stirred **26** (1.36 g, 3.59 mol) in THF (30 mL) at 0 °C for 10 min. $NaBH_4$ (204 mg, 5.39 mmol) was carefully added, and the mixture was stirred overnight. Methanol was added to quench the $NaBH_4$. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated to give colorless oil without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.86 (s, 1H), 5.75 (s, 1H), 4.66 (s, 2H), 3.93 (dd, J = 5.3, 1.6 Hz, 2H), 3.80 (s, 3H), 3.76 (d, J = 10.7 Hz, 2H), 3.68 (d, J = 10.7 Hz, 2H), 2.34 (s, 1H), 1.75−1.67 (m, 1H), 1.52−1.38 (m, 4H), 1.35−1.28 (m, 7H), 0.95−0.87 (m, 6H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.3, 130.7, 126.1, 111.8, 109.5, 96.8, 77.9, 70.4, 62.1, 56.5, 39.5, 30.8, 30.3, 29.1, 24.2, 23.2, 23.0, 21.9, 14.1, 11.3.

2-[4-Bromomethyl-5-((2-ethylhexyl)oxy)-2-methoxy-phenyl]-5,5-dimethyl-1,3-dioxane (28). In a 100 mL two-necked round-bottom flask was stirred **27** (1.2 g, 3.15 mmol) in THF (50 mL) at 0 °C for 10 min. Carbon tetrabromide (1.36 g, 4.1 mmol) and triphenylphosphine (1.08 g, 4.1 mmol) was added, and the mixture was stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 20% CH_2Cl_2 in hexane, R_f = 0.4) to give 0.89 g (63.8%, two steps) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.86 (s, 1H), 5.73 (s, 1H), 4.53 (s, 2H), 3.93 (d, J = 5.2 Hz, 2H), 3.80 (a, 3H), 3.78−3.74 (d, J = 11.0 Hz, 3H), 3.67 (d, J = 10.6 Hz, 3H), 1.77−1.70 (m, 1H), 1.59−1.44 (m, 4H), 1.38−1.26 (m, 7H), 0.97−0.87 (m, 6H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 150.0, 128.0, 127.2, 113.8, 110.3, 96.7, 77.9, 70.4, 56.5, 39.6, 30.7, 30.3, 29.2, 28.9, 24.1, 23.2, 23.1, 21.9, 14.1, 11.3.

Diethyl 4-(5,5-dimethyl-1,3-dioxan-2-yl)-2-((2-ethylhexyl)-oxy)-5-methoxy-benzyl-phosphonate (29). In a 20 mL vial was added **28** (893 mg, 2.01 mmol) and triethyl phosphite (469 mg, 2.82 mmol). The mixture was heated in 140 °C for 2 h and then cooled to room temperature. The residue was directly purified by silica gel chromatography (0 → 33% EtOAc in hexane, R_f = 0.4) to give 817 mg (81.2%) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 6.97 (d, J = 2.6 Hz, 1H), 5.73 (s, 1H), 4.00 (m, 4H), 3.89−3.85 (m, 2H), 3.80 (s, 3H), 3.76 (d, J = 11.0 Hz, 2H), 3.68 (d, J = 10.9 Hz, 2H), 3.24 (d, J = 21.8 Hz, 2H), 1.74−1.65 (m, 1H), 1.55−1.39 (m, 4H), 1.36−1.28 (m, 7H), 1.23 (t, J = 7.1 Hz, 6H), 0.95−0.87 (m, 6H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 150.9, 150.0, 145.0, 148.8, 125.8, 125.8, 121.6, 121.5, 114.4, 114.4, 110.0, 110.0, 96.9, 96.8, 77.9, 70.8, 61.9, 61.8, 56.3, 39.7, 30.7, 30.3, 29.2, 26.8, 25.5, 24.0, 23.2, 23.0, 21.9, 16.4, 16.3, 14.1, 11.2; LRMS (ES+ + H) 501.3; HRMS (TOF MS ES+) m/z for $C_{26}H_{46}O_7P$ calcd 501.2981, found 501.2985.

2-[5-((2-Ethylhexyl)oxy)-4-iodo-2-methoxy-phenyl]-5,5-dimethyl-1,3-dioxane (30). In a glovebox were added **25** (1.00 g, 2.33 mmol) in THF (50 mL) in a 100 mL two neck round bottle flask. The solution was taken out of glovebox and cooled down to −78 °C under Ar. A solution of *n*-BuLi (3.03 mmol, 1.9 mL) in hexane was added dropwise and stirred at −78 °C for 1 h. Then I_2 (0.768 g, 3.03 mmol) of THF solution was added to the mixture and stirred for another 2 h and temperature was allowed to increase to room temperature. H_2O (20 mL) was added to quench the reaction. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0−30% CH_2Cl_2 in hexane) to give 722 mg (65%) of light colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.09 (s, 1H), 5.69 (s, 1H), 3.90 (d, J = 5.4 Hz, 2H), 3.78 (s, 3H), 3.75 (d, J = 11.1 Hz, 2H), 3.66 (d, J = 10.8 Hz, 2H), 1.77−1.68 (m, 1H), 1.61−1.46 (m, 4H), 1.38−1.29 (m, 7H), 0.98−0.87 (m, 9H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 150.9, 127.8, 122.4, 110.3, 96.7, 87.1, 77.8, 71.8, 56.6, 39.5, 30.6, 30.3, 29.1, 24.1, 23.2, 23.1, 21.9, 14.2, 11.3; LRMS (ES+ + H) 477.1; HRMS (TOF MS ES+) m/z for $C_{21}H_{34}O_4I$ calcd 477.1502, found 477.1508.

5-((2-Ethylhexyl)oxy)-4-iodo-2-methoxy-benzaldehyde (31). **30** (2.73 g, 5.73 mmol) was dissolved in a solution of trifluoroacetic acid (4 mL), THF (20 mL) and H_2O (4 mL) in 100 mL round-bottom flask and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 40% CH_2Cl_2 in hexane) to give 2.2 g (98.4%) as a bright yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.46 (s, 1H), 7.19 (s, 1H), 3.90−3.85 (m, 5H), 1.79−1.70 (m, 1H), 1.61−1.40 (m, 4H), 1.37−1.28 (m, 4H), 0.96−0.89 (m, 6H); ^{13}C NMR (101 MHz,

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$CDCl_3$) δ 189.1, 156.0, 152.4, 125.0, 123.5, 108.7, 96.6, 72.1, 56.4, 39.3, 30.5, 29.0, 24.0, 23.0, 14.1, 11.2; LRMS (ES+ + H) 391.1; HRMS (TOF MS ES+) m/z for $C_{16}H_{24}O_3I$ calcd 391.0770, found 391.0768. Proton and Carbon NMR match previous report.[41]

[5-((2-Ethylhexyl)oxy)-4-iodo-2-methoxy-phenyl]methanol (32). In a 100 mL two-necked round-bottom flask was stirred **31** (2.20 g, 5.64 mol) in THF (30 mL) at 0 °C for 10 min. $NaBH_4$ (320 mg, 8.46 mmol) was carefully added, and the mixture was stirred overnight. Methanol was added to quench the $NaBH_4$. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated to give colorless oil without further purification (crude mass 1.96 g, 88.7%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.81 (s, 1H), 4.63 (d, J = 6.2 Hz, 2H), 3.85 (d, J = 5.5 Hz, 2H), 3.81 (s, 3H), 2.19 (t, J = 6.4 Hz, 1H), 1.79−1.69 (m, 1H), 1.61−1.41 (m, 4H), 1.37−1.30 (m, 4H), 0.96−0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 151.5, 130.2, 121.3, 112.4, 84.7, 72.2, 61.5, 56.0, 39.5, 30.5, 29.1, 23.9, 23.1, 14.1, 11.2.

1-Bromomethyl-5-((2-ethylhexyl)oxy)-4-iodo-2-methoxy-benzene (33). In a 100 mL two-necked round-bottom flask was stirred **32** (1.90 g, 4.84 mmol) in THF (50 mL) at 0 °C for 10 min. Carbon tetrabromide (2.09 g, 6.30 mmol) and triphenylphosphine (1.65 g, 6.30 mmol) was added, and the mixture was stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 20% CH_2Cl_2 in hexane, R_f = 0.4) to give 1.30 g (59.1%) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 6.78 (s, 1H), 4.50 (s, 4H), 3.85−3.82 (m, 5H), 1.78−1.70 (m, 1H), 1.61−1.42 (m, 4H), 1.37−1.30 (m, 4H), 0.98−0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 151.7, 126.8, 122.4, 113.9, 87.2, 72.1, 56.4, 39.5, 30.5, 29.1, 28.6, 23.9, 23.1, 14.2, 11.3.

Diethyl 5-((2-ethylhexyl)oxy)-4-iodo-2-methoxy-benzyl-phosphonate (34). In a 20 mL vial was added **33** (360 mg, 0.79 mmol) and triethyl phosphite (184 mg, 1.11 mmol). The mixture was heated in 140 °C for 2 h, and then cooled to room temperature. The residue was directly purified by silica gel chromatography (0 → 33% EtOAc in hexane) to give 382 mg (94.4%) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 6.83 (d, J = 2.7 Hz, 1H), 4.08−3.99 (m, 4H), 3.83 (d, J = 5.5 Hz, 2H), 3.78 (s, 3H), 3.18 (d, J = 21.8 Hz, 2H), 1.76−1.69 (m, 1H), 1.57−1.47 (m, 4H), 1.35−1.29 (m, 4H), 1.25 (t, J = 7.1 Hz, 6H), 0.96−0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 152.00, 151.7, 151.7, 121.7, 121.7, 121.3, 121.2, 114.9, 114.8, 84.4, 84.3, 72.0, 62.0, 61.9, 56.3, 39.5, 30.5, 29.0, 27.4, 26.0, 23.9, 23.0, 16.4, 16.3, 14.1, 11.2; LRMS (ES+ + H) 513.1; HRMS (TOF MS ES+) m/z for $C_{20}H_{35}O_5PI$ calcd 513.1267, found 513.1265.

Regioregular Dimer Aldehyde (35). In a 100 mL two-necked round-bottom flask was stirred **15** (379 mg, 0.79 mmol) and **17** (340 mg, 0.87 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (133 mg, 1.2 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was then dissolved in a solution of 12 M HCl (5 mL), THF (15 mL) and H_2O (2 mL) in 100 mL round-bottom flask and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to get crude product. The residue and a catalytic amount of iodine (1 mg, 0.004 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 350 mg (68.1%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.54, 7.49 (ABq, J = 16.8 Hz, 2H), 7.34 (s, 1H), 7.31 (s, 1H), 7.20 (s, 1H), 7.08 (s, 1H), 3.99 (d, J = 5.5 Hz, 2H), 3.93−3.83 (m, 8H), 1.83−1.73 (m, 2H), 1.63−1.41 (m, 8H), 1.40−1.27 (m, 8H), 0.99−0.86 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 156.5, 152.6, 151.8, 151.1, 134.5, 127.1, 126.8, 124.1, 123.5, 123.1, 110.2, 108., 108.7, 86.0, 71.6, 71.2, 57.2, 56.0, 39.7, 39.6, 30.8, 30.7, 29.1, 29.1, 24.2, 24.0, 23.1, 23.0, 14.1, 14.1, 11.3, 11.2; LRMS (ES+ + H) 651.3; HRMS (TOF MS ES+) m/z for $C_{33}H_{48}O_5I$ calcd 651.2547, found 651.2550.

Regioregular Trimer Aldehyde (36). In a 100 mL two-necked round-bottom flask was stirred **15** (297 mg, 0.60 mmol) and **35** (651 mg, 0.54 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (91 mg, 0.8 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was then dissolved in a solution of 12 M HCl (5 mL), THF (15 mL) and H_2O (2 mL) in 100 mL round-bottom flask and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to get crude product. The residue and a catalytic amount of iodine (0.7 mg, 0.003 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 260 mg (53%) as a orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.68−7.41 (m, 4H), 7.35 (s, 1H), 7.30 (s, 1H), 7.23 (s, 1H), 7.17 (s, 1H), 7.16 (s, 1H), 7.10 (s, 1H), 4.02−3.83 (m, 15H), 1.85−1.74 (m, 3H), 1.67−1.43 (m, 12H), 1.41−1.28 (m, 12H), 1.03−0.86 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 156.58, 152.6, 151.6, 151.6, 151.4, 151.0, 135.0, 127.9, 127.7, 127.1, 126.3, 123.9, 123.6, 123.54, 123.47, 122.2, 109.94, 109.89, 109.3, 108.8, 108.5, 84.8, 71.6, 71.2, 57.2, 56.3, 56.0, 39.8, 39.7, 39.6, 30.9, 30.8, 30.7, 29.2, 29.14, 29.12, 24.3, 24.2, 24.0, 23.09, 23.07, 23.02, 14.09, 14.08, 14.06, 11.38, 11.36, 11.2; LRMS (ES+ + H) 911.4; HRMS (TOF MS ES+) m/z for $C_{50}H_{72}O_7I$ calcd 911.4323, found 911.4324.

Regioregular Tetramer Aldehyde (37). In a 100 mL two-necked round-bottom flask was stirred **15** (133 mg, 0.27 mmol) and **36** (220 mg, 0.24 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (40 mg, 0.36 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was then dissolved in a solution of 12 M HCl (5 mL), THF (15 mL) and H_2O (2 mL) in 100 mL round-bottom flask and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to get crude product. The residue and a catalytic amount of iodine (0.3 mg, 0.001 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 165 mg (58.3%) as a red solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.69−7.41 (m, 6H), 7.35 (s, 1H), 7.30 (s, 1H), 7.25 (s, 1H), 7.21−7.17 (m, 3H), 7.16 (s, 1H), 7.11 (s, 1H), 4.04−3.82 (m, 20H), 1.87−1.74 (m, 4H), 1.69−1.43 (m, 16H), 1.43−1.27 (m, 16H), 1.05−0.84 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 156.6, 152.6, 151.7, 151.6, 151.4, 151.3, 151.0, 135.1, 128.2, 128.01 127.2, 127.1, 126.9, 126.1, 124.0, 123.9, 123.7, 123.5, 123.1, 122.8, 122.0, 110.0, 109.9, 109.7, 109.3, 109.0, 108.8, 108.5, 84.6, 71.7, 71.3, 71.2, 57.2, 56.4, 56.4, 56.0, 39.8, 39.7, 39.6, 30.9, 30.8, 30.7, 29.3, 29.14, 29.12, 24.3, 24.2, 24.0, 23.19, 23.06, 23.02, 14.09, 14.06, 11.38, 11.35, 11.2; LRMS (ES+ + H) 1171.6; HRMS (TOF MS ES+) m/z for $C_{67}H_{96}O_9I$ calcd 1171.6099, found 1171.6105.

Regiorandom Dimer Aldehyde (38). In a 100 mL two-necked round-bottom flask was stirred **17** (250 mg, 0.64 mmol) and **29** (353 mg, 0.71 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (86.3 mg, 0.77 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was then dissolved in a solution of 12 M HCl (5 mL), THF (15 mL) and H_2O (2 mL) in 100 mL round-bottom flask and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and

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concentrated. The residue was purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to get crude product. The residue and a catalytic amount of iodine (0.8 mg, 0.003 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 149 mg (35.7%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.55, 7.52 (ABq, J = 16.8 Hz, 2H), 7.33 (s, 1H), 7.32 (s, 1H), 7.21 (s, 1H), 7.08 (s, 1H), 3.96−3.83 (m, 10H), 1.84−1.73 (m, 2H), 1.56−1.40 (m, 8H), 1.37−1.26 (m 8H), 0.99−0.85 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 156.4, 152.6, 151.6, 150.8, 134.5, 127.3, 125.9, 124.0, 123.7, 122.7, 110.2, 108.7, 107.9, 85.8, 71.9, 71.5, 56.8, 55.9, 39.6, 39.6, 30.80, 30.77, 29.11, 29.08, 24.23, 24.20, 23.1, 14.1, 11.3; LRMS (ES+ + H) 651.2; HRMS (TOF MS ES+) m/z for $C_{33}H_{48}O_5I$ calcd 651.2547, found 651.2540.

Regioregular Pentamer PPV (2). In a 100 mL two-necked round-bottom flask was stirred **34** (73 mg, 0.14 mmol) and **37** (152 mg, 0.13 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (22 mg, 0.2 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue and a catalytic amount of iodine (0.2 mg, 0.0007 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 103 mg (51.9%) as a red solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.40 (m, 8H), 7.30 (d, J = 2.1 Hz, 2H), 7.22−7.19 (m, 4H), 7.18 (s, 1H), 7.17 (s, 1H), 7.12 (s, 1H), 7.08 (s, 1H), 4.03−3.81 (m, 25H), 1.88−1.73 (m, 5H), 1.71−1.45 (m, 20H), 1.44−1.29 (m, 20H), 1.06−0.87 (m, 30H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 152.5, 151.69, 151.57, 151.5, 151.43, 151.39, 151.36, 151.31, 128.13, 128.08, 127.5, 127.4, 127.2, 127.1, 126.7, 126.6, 124.3, 123.7, 123.6, 123.5, 123.4, 123.0, 123.0, 122.8, 122.5, 122.4, 110.0, 109.82, 109.79, 109.2, 109.1, 109.0, 108.9, 108.5, 85.1, 84.6, 72.0, 71.7, 71.30, 71.29, 71.2, 57.2, 56.42, 56.36, 39.91, 39.90, 39.7, 39.6, 39.5, 30.9, 30.8, 30.6, 29.24, 29.18, 29.14, 24.34, 24.27, 24.0, 23.14, 23.11, 14.17, 14.15, 14.14, 11.44, 11.42, 11.41, 11.28; LRMS (ES+ + H) 1529.7; HRMS (TOF MS ES+) m/z for $C_{83}H_{119}O_{10}I_2$ calcd 1529.6893, found 1529.6897.

Regiorandom Pentamer PPV (3). In a 100 mL two-necked round-bottom flask was stirred **18** (77.4 mg, 0.14 mmol) and **35** (187.6 mg, 0.28 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (39.3 mg, 0.35 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue and a catalytic amount of iodine (0.2 mg, 0.0007 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 114 mg (51.7%) as a red solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.41 (m, 8H), 7.29 (s, 2H), 7.21 (s, 2H), 7.19 (d, J = 1.2 Hz, 2H), 7.16 (d, J = 1.0 Hz, 2H), 7.11 (s, 2H), 4.01−3.82 (m, 25H), 1.87−1.73 (m, 5H), 1.68−1.44 (m, 20H), 1.42−1.29 (m, 20H), 1.03−0.95 (m, 15H), 0.94−0.87 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 151.56, 151.56, 151.43, 151.40, 151.28, 151.15, 151.10, 128.1, 127.5, 127.3, 127.2, 127.1, 126.7, 123.7, 123.4, 123.0, 123.0, 122.9, 122.6, 110.2, 110.0, 109.9, 108.9, 108.4, 108.4, 108.1, 108.1, 84.67, 84.56, 71.63, 71.59, 71.56, 71.2, 57.2, 56.4, 56.0, 55.9, 39.9, 39.8, 39.7, 30.91, 30.88, 30.8, 29.22, 29.17, 24.30, 24.25, 23.16, 23.15, 23.12, 14.16, 14.15, 11.4; LRMS (ES+ + H) 1529.7; HRMS (TOF MS ES+) m/z for $C_{83}H_{119}O_{10}I_2$ calcd 1529.6893, found 1529.6886.

Regiorandom Pentamer PPV (4). In a 100 mL two-necked round-bottom flask was stirred **18** (65.3 mg, 0.12 mmol) and **38** (158.4 mg, 0.24 mmol) in THF (50 mL) at 0 °C for 10 min *t*-BuOK (34.1 mg, 0.30 mmol) was gradually added and stirred overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue and a catalytic amount of iodine (0.2 mg, 0.0006 mmol) was dissolved in toluene (100 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, R_f = 0.3) to give 107 mg (57.6%) as a red sticky oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.41 (m, 8H), 7.30 (s, 2H), 7.21−7.16 (m, 6H), 7.12 (s, 2H), 4.04−3.82 (m, 25H), 1.87−1.75 (m, 5H), 1.69−1.44 (m, 20H), 1.42−1.28 (m, 20H), 1.03−0.95 (s, 15H), 0.94−0.87 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 151.41, 151.40, 151.37, 151.35, 151.21, 151.17, 128.3, 127.5, 127.4, 127.2, 127.1, 126.9, 126.7, 123.7, 123.41, 123.38, 123.1, 122.7, 122.1, 122.0, 110.4, 110.1, 110.0, 109.0, 108.3, 107.70, 107.68, 84.4, 72.0, 71.8, 71.6, 71.4, 56.8, 56.5, 56.1, 56.0, 39.9, 39.78, 39.76, 39.6, 30.9, 30.8, 29.3, 29.24, 29.20, 29.16, 24.34, 24.30, 24.29, 24.22, 23.2, 23.1, 14.18, 14.15, 14.14, 11.49, 11.46, 11.40, 11.37; LRMS (ES+ + H) 1529.7; HRMS (TOF MS ES+) m/z for $C_{83}H_{119}O_{10}I_2$ calcd 1529.6893, found 1529.6868.

■ ASSOCIATED CONTENT

Supporting Information

Figures containing the expanded aromatic regions of ^{1}H and ^{13}C NMR spectra for compounds **1**−**4**; ^{1}H NMR and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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