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Article

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Controllable monobromination of perylene ring system: synthesis of bay-functionalized perylene dyes

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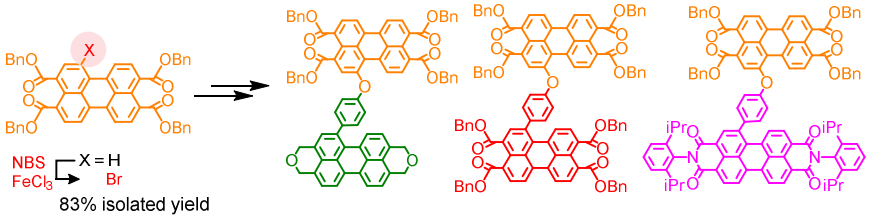
Supporting Information Placeholder



ABSTRACT: Practical synthesis of bay-monofunctionalized perylene dyes has been developed based on controllable NBS bromination of tetrabenzyl perylene-3,4,9,10-tetracarboxylate. The ability to perform the convenient and high-yielding synthesis highlights the potential utility of our multifunctional approach to access diverse range of new perylene systems.

INTRODUCTION

Perylene, a highly fluorescent polycyclic aromatic hydrocarbon molecule, is particularly important in materials chemistry and holds great promise for potential applications in the fields of organic photoelectric and photoluminescence devices.[1] In this context, molecular engineering of perylene dyes has been the subject of intense research interest and considerable efforts have been devoted to the development of efficient synthetic methods for accessing new structures, with particular attention given to the versatile perylene diimide (PDI) systems in recent decades.[2] The conventional preparative approaches typically rely on the procedure developed by BASF AG, which includes bromination of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCA) introducing bromine atoms at the so-called bay-positions, upon exposure to bromine in fuming sulfuric acid at high temperature.[3] The general requirement of the harsh conditions and considerably long reaction times inevitably causes loss of reaction controllability to afford an inseparable mixture of regioisomeric dibromides.[4] This imposes inherent limitations on versatility toward synthesis of custom-designed perylene materials, especially monosubstituted ones.[5] A strategy with PDI substrates can be conceived to obtain the relevant monobrominated products in substantial yields.[6] At the same time, perylene tetraesters (PTEs) are expected to be alternative substrates that would offer a potential advantage with regard to enhanced solubility in many solvent systems, making them useful for further chemical functionalization.[7] With this background, it is highly desirable to develop efficient methods enabling practical synthesis of the monobrominated PTE, which represents a key challenge for synthetic-materials chemists.[8] In this contribution, we disclose our striking findings on efficient synthesis of bay-monofunctionalized perylene dyes via precisely controlled NBS bromination of PTE and further applications for construction of three new perylene-perylene linked dyad systems.

Scheme 1. Synthesis of bay-monofunctionalized perylenes.

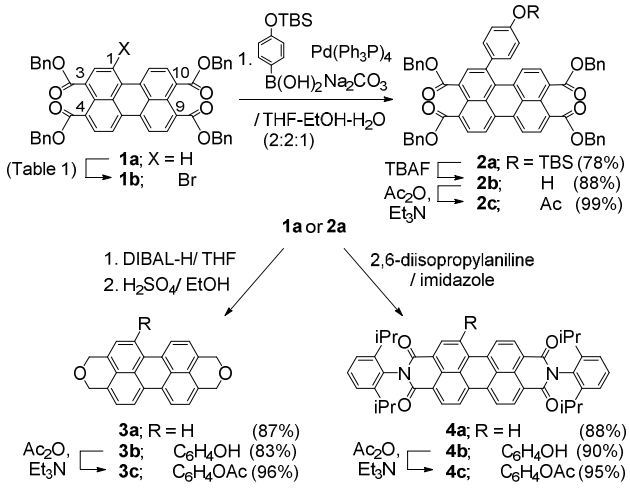


TABLE 1. NBS bromination of 1a to 1b[a]

entry	NBS (eq)	additive (eq)	solvent	T (°C)	t (h)	yield of **1b**[b] (%)	yield of **1b′** (%)	recovery of **1a** (%)
1	1.0	H_2SO_4 (1.0)	MeCN	70	16	50	19[b]	30[b]
2	1.0	$FeCl_3$ (1.0)	MeCN	70	2	68	10[c]	9[c]
3	1.0	$AlCl_3$ (1.0)	MeCN	70	2	23	trace	60[c]
4	1.0	$ZnCl_2$ (1.0)	MeCN	70	2	trace	ND[d]	91[b]
5	1.0	$FeCl_3$ (0.5)	MeCN	70	2	68	14[c]	11[c]
6	1.0	$FeCl_3$ (0.2)	MeCN	70	2	80	9[c]	11[c]
7	1.0	$FeCl_3$ (0.1)	MeCN	70	2	71	10[c]	9[c]
8	1.2	$FeCl_3$ (0.2)	MeCN	70	2	77	21[c]	ND[d]
9	1.1	$FeCl_3$ (0.2)	MeCN	70	2	83	11[c]	4[c]
10	1.1	$FeCl_3$ (0.2)	MeCN	60	3	72	11[c]	6[c]
11	1.1	$FeCl_3$ (0.2)	MeCN	80	2	68	8[c]	8[c]
12	1.1	$FeCl_3$ (0.2)	$CHCl_3$	70	2	38	trace	57[b]
13	1.1	$FeCl_3$ (0.2)	DCE	70	2	71	19[c]	3[c]
14[e]	1.1	$FeCl_3$ (0.2)	MeCN	70	2	77	14[c]	ND[d]

[a]Reactions were carried out with a substrate concentration of 0.1 M. [b]Isolated yields. [c]Yields estimated from ^{1}H NMR of crude reaction mixtures. [d]Not detected. [e]The reaction was conducted on a gram scale quantity.

RESULTS AND DISCUSSION

As a starting PTE substrate for this study, we chose to utilize tetrabenzyl perylene-3,4,9,10-tetracarboxylate **1a** due to its high solubility in common organic solvents and easy availability of bulk quantities from PTCA (Scheme 1).[9] On designing well-regulated experimental conditions to achieve strict stoichiometric control for bromination on this substrate, *N*-bromosuccinimide (NBS) was envisaged as a viable bromine atom source. Our first attempt was thus made to explore the feasibility of clean and efficient transformation of **1a** to monobrominated derivative **1b** by using an equimolar quantity of NBS and various acidic additives. The results are summarized in Table 1. When the reaction was carried out with 1.0 equiv of sulfuric acid in MeCN on heating at 70 °C, slow and incomplete conversion of **1a** took place over 16 h to afford a chromatographically separable mixture of **1b** and dibrominated regioisomers **1b′** in 50 and 19% yields, respectively, with a 30% recovery of the starting material (Table 1, entry 1).[10] We next used $FeCl_3$ with the aim of improving the reaction efficiency.[11] Strikingly, under comparable conditions, this reagent was shown to considerably facilitate the product formation to reach completion in only 2 h, resulting in a much higher yield (68%) of **1b**, with the residual traces of **1b′** and unreacted starting material (Table 1, entry 2). Following this line, attempts were also made with other Lewis acids such as $AlCl_3$ and $ZnCl_2$, but gave only poor results (Table 1, entries 3 and 4). Among the acidic compounds surveyed, $FeCl_3$ proved to be the reagent of choice for further investigations.

We then turned to optimizing the reaction conditions to find the best compromise between chemical reactivity and product selectivity. To address this issue, conducting the reaction at lower loadings of $FeCl_3$ was investigated, since it was expected that milder conditions would suppress the side reactions to lead to better product selectivity. Consistent with this expectation, the reaction performed at reagent loading of 0.2 equiv afforded a marked increase of the product yield to 80%, while little improvement was obtained at either 0.5 or 0.1 equiv (Table 1, entries 5-7). Then, we next proceeded to seek the best reaction conditions by varying stoichiometry of NBS, solvent, and temperature. After extensive experimentation, we found that 1.1 equiv of NBS gave the highest yield (83%) and changes of solvent and temperature have no positive effect (Table 1, entries 8-13), thereby identifying the optimal conditions as given in entry 9.[12]

To our delight, we found that the established protocol is amenable to gram-scale operations, retaining almost the same level of the selectivity and efficiency of the reaction with that of the smaller-scale runs to deliver a gram quantity (1.2 g, 77%) of **1b** (Table 1, entry 14). Moreover, this method is applicable to the synthesis of dibrominated perylene derivative **1b′**.[13] In this case, high chemical yield was obtained when 6.0 equiv of NBS was added in two equal portions over 11 h to the reaction mixture, resulting in 90% yield of **1b′** as a 3:1 mixture of 1,7- and 1,6-regioisomers, respectively.[14] Other halogenation reagents, such as NCS and NIS, did not work analogously under the reaction conditions, exhibiting less efficient and poorly reactive nature to result in a modest yield of the monochlorinated product **1c** (43%) for the chlorination and a substantial recovery of unreacted starting material for the iodination, respectively.

With the key intermediate **1b** in hand, we undertook further derivatization into related perylene derivatives. Our synthetic effort was initially made to introduce a free phenolic functionality that will allow for easy covalent attachment of the perylene dye units to any electrophilic substrates. Accordingly, **1b** underwent Suzuki-Miyaura cross-coupling reaction successfully with TBS-protected aryl boronate, readily available in two steps from *p*-bromophenol, to afford 1-arylated perylene derivative **2a** in a yield of 78% (Scheme 1).[15] The TBS protective group of this product was readily removed by treatment with tetrabutylammonium fluoride (TBAF) in THF to form the phenolic derivative **2b** as a mostly insoluble material in high yield (88%). The insolubility problem of this com-

pound could be alleviated by converting to its acetate ester **2c** (yield: 99%).

Our work was next focused on the utility of the resulting products in further synthesis. To realize this synthetic plan, we investigated chemical transformation of **2a** to decarbonylated variants of this motif. Prior to this experiment, we conducted a model reaction with the unsubstituted analogue **1a**. Subjection of this substrate to a DIBAL-H reduction led to complete conversion to the corresponding tetrol without generating any byproducts. Unfortunately, we encountered a problem of extreme insolubility associated with this compound.[9] This drawback was overcome by replacement of the four hydroxy groups present around the rim of the perylene core by less polar ether moieties. The conversion of these functional groups was performed by refluxing an ethanol solution of the tetrol with catalytic amount of sulfuric acid, which allowed for the formation of **3a** in 87% yield over two steps. Analogously, the above method could be applied to **2a** to generate **3b** in 83% yield, where the TBS protective group was completely removed after exposure to the acidic media. Despite the substantial advances made by following the above sequence of reactions, the product still exhibited poor solubility characteristics unsuitable for spectroscopic studies, as was experienced with **2b**. To this end, the solubility of this molecule was increased by acetylation of the phenolic hydroxyl group, which imparted sufficient solubility to make the resulting compound **3c** more tractable.

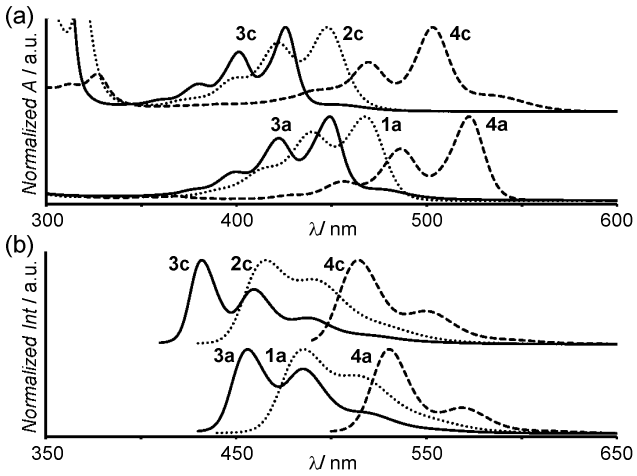
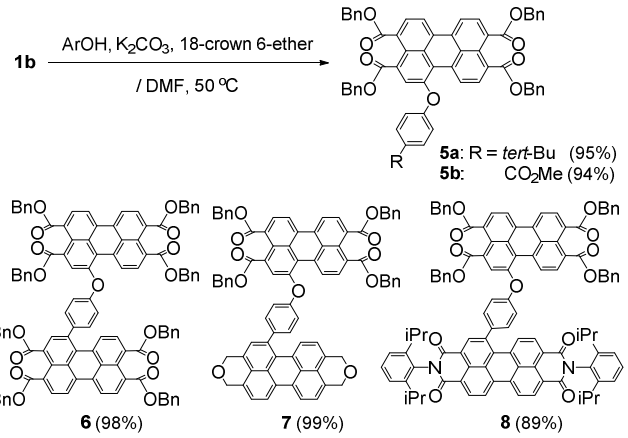


Figure 1. (a) Normalized absorption and (b) fluorescence emission spectra of **3c** (solid, λ_{ex} 400 nm), **2c** (dotted, λ_{ex} 420 nm), **4c** (dashed, λ_{ex} 470 nm)) and unsubstituted ones **3a** (solid, λ_{ex} 400 nm), **1a** (dotted, λ_{ex} 420 nm), and **4a** (dashed, λ_{ex} 470 nm) in MeCN at *c* 10 μM and 1.0 μM, respectively.

In another example of the chemical derivatization, our attention was directed toward straightforward access to the diimide derivatives, which represent a particularly important class of perylene derivatives in the realm of materials science. This was achieved by conducting the imidization reaction under high temperature conditions in melted imidazole.[16] In addition to the preceding success with the model substrate **1a**, giving rise to the diimide **4a** via condensation with 2,6-diisopropylaniline in 88% yield, the 1-arylated analogue **2a** underwent the rapid imidization and deprotection of the TBS ether at 180 °C to furnish a 90% yield of **4b** within 30 min (Scheme 1). The phenolic group of this compound was also acetylated to obtain the more soluble equivalent **4c**.

Having developed the practical procedures to synthesize the three chromophoric types of perylene dyes, we attempted to investigate their spectroscopic properties. Figure 1 presents the steady-state absorption and fluorescence emission spectra of MeCN solutions of **2c-4c**, showing distinct differences in the spectral maxima shifted progressively to longer wavelength as the effective π-conjugation of perylene system extends.[17] Here, it should be noted that, in every case, the aryl-substituted perylene dye exhibited remarkable blue-shift of almost 20 nm in both the absorption and fluorescence bands relative to the unsubstituted counterpart.[18] This probably reflects considerable in-plane distortion of the perylene π-systems caused by steric repulsion from the aryl moieties,[19] as confirmed by X-ray crystallographic analysis of **4c** (Figure S1).[20] These stimulating findings prompted us to develop new types of dyad systems constructed with a couple of different perylene subunits. Thus, we envisaged that the strategy of using the reaction of phenoxide anions with **1b** will be suitable for our next objective.

Scheme 2. Etherification between 1b and phenols.



In a preliminary study on the reaction with **1b**, we examined use of 4-*tert*-butyl and 4-methoxycarbonylphenol as the phenoxide sources.[21] In both cases, we observed excellent reactivity when the reactions were carried out in DMF in the presence of potassium carbonate and 18-crown 6-ether. Under these conditions, **1b** underwent smooth reactions upon heating at 50 °C to give the aryloxy-substituted perylene derivatives **5a** and **5b** with excellent isolated yields of 95 and 94%, respectively (Scheme 2). Interestingly, these compounds, essentially free from the distortion of the perylene π-systems, were found to display red-shifted profiles relative to **2c** with absorption and emission maxima at about 470 and 510 nm, respectively, matching rather closely with those of **1a** (Figure S2).[22] By comparing the spectroscopic properties, it is apparent that the oxygen-substituted systems should possess different electronic excited state characteristics from that of the aryl-substituted perylene one, suggesting that covalent coupling of these dye modules may produce complementary donor-acceptor systems. This consideration motivated us to exploit the above approach to construct a new class of perylene-perylene linked dyad systems. Under the identical reaction conditions, the phenol-substituted perylene **2b** underwent

smooth etherification with **1b** to afford the desired dyad **6** with a satisfactorily high yield of 98%. Given this success, we explored the reactions with the other phenolic perylenes **3b** and **4b**. These compounds were also shown to react with **1b** to produce two additional dyads **7** and **8** in 99 and 89% isolated yields, respectively.

The absorption spectra of the perylene dyads **6-8** measured in various organic solvents exhibited broad and featureless bands instead of the linear superposition features of the component chromophores, indicative of aggregated structures formed in situ (Figure S3). Furthermore, the fluorescence spectra obtained upon excitation of the respective energy donors showed that the individual perylene fluorophores incorporated in these dyad systems are drastically less emissive and substantially quenched, especially in the polar solvent MeCN (Figure S4 and Table S1). The above observations can be rationalized by assuming the donor and acceptor elements of respective dyads undergo appreciable electronic interactions to form charge-transfer (CT) complexes, thereby causing non-radiative deactivation that is likely to occur in high polarity solvents.[23]

CONCLUSION

In conclusion, we have developed the efficient approaches to the bay-monofunctionalized perylene dyes via the controllable bromination of the readily available perylene substrate.[24] The derivatization of the key bromide into the aryl-substituted perylene dyes led to the finding of remarkable blue-shifting in the absorption and emission maxima, which originates from in-plane distortion of the perylene π-systems. The etherification on the bromide was applied to synthesize three new types of perylene-perylene linked dyads that displayed the ability to form CT complexes. This observation raises an attractive prospect to make a significant contribution to the future development of organic photovoltaic materials.[25] Finally, it should be emphasized that our present strategies provide innovative ways to overcome the given synthetic difficulty in preparing the monofunctionalized perylene systems hitherto overlooked by synthetic-materials chemists.

EXPERIMENTAL SECTION

General

All solvents and reagents were of reagent grade quality from Wako Pure Chemicals and Tokyo Chemical Industry (TCI) used without further purification. Melting points were measured with a Yanaco MP-S3 micro melting point apparatus. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra operating at the frequencies of 300 and 75 MHz, respectively, were recorded on a JEOL JNM-AL300 spectrometer in chloroform-*d* ($CDCl_3$) or dimethyl sulfoxide-d_6 (DMSO-d_6). Chemical shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in hertz (Hz). Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. UV-vis and fluorescence spectra were recorded on a JASCO V-630 spectrophotometer and a JASCO FP-6200 spectrofluorometer, respectively. Elemental analyses were performed by JSL Model JM 10 instruments. High resolution laser desorption ionization (LDI) or matrix assisted laser desorption ionization (MALDI) mass spectra were measured on a Shimadzu AXIMA Resonance mass spectrometer using α-cyano-4-hydroxycinnamic acid (α-CHCA) matrix as a cationization agent. High resolution electrospray ionization (ESI) mass spectra were measured on a Waters Xevo Q-TOF UPLC-MS system. Tetrabenzyl perylene-3,4,9,10-tetracarboxylate was prepared according to the literature procedure.[9]

*Synthesis and characterization of **1b** (representative example given in entry 9 of Table 1)*

Under nitrogen atmosphere, *N*-bromosuccinimide (NBS; 1.1 equiv, 0.215 g, 1.21 mmol) and ferric chloride ($FeCl_3$; 0.20 equiv, 35.7 mg, 0.220 mmol) was added to a suspension of **1a** (0.868 g, 1.10 mmol) in anhydrous MeCN (11 mL) with vigorous stirring at room temperature. The temperature of the mixture was raised to 70 °C and kept for 2 h. The mixture was cooled to room temperature, poured into water (10 mL), and then extracted with DCM (50 mL). The extract was washed with brine (30 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo to leave an orange oily residue. The residue was purified by column chromatography (silica gel, toluene/AcOEt = 1/0 to 100/1 to 50/1) to yield **1b** (0.790 g, 0.913 mmol, 83%) as a viscous orange oil. R_f = 0.50 (silica gel, $CHCl_3/CH_3OH$ = 60/1); IR (NaCl) 3032 (C–H), 2954 (C–H), 1718 (C=O), 1587 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.57 (d, 1H, *J* = 7.8 Hz, 1H), 8.17 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.58-7.48 (m, 8H), 7.48-7.33 (m, 12H), 5.38 (s, 4H), 5.37 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.3, 168.2, 168.1, 167.1, 137.6, 135.9, 135.8, 135.6, 132.3, 132.1, 132.0, 131.4, 130.7, 130.5, 130.3, 130.2, 129.9, 129.8, 129.5, 129.4, 129.3, 128.89, 128.85, 128.76, 128.69, 128.60, 128.0, 127.3, 127.1, 122.7, 121.7, 118.6, 67.6, 67.3, 67.2. Anal. Calcd for $C_{52}H_{35}BrO_8$: C, 71.98; H, 4.07; N, 0.00. Found: 71.97; H, 4.07; N, 0.00. HRMS (ESI+) *m/z* calcd for $C_{52}H_{35}BrO_8Na$ $[MNa]^+$: 889.1408, found 889.1396.

*Synthesis and characterization of **1b′***

Under nitrogen atmosphere, NBS (3.0 equiv, 69.1 mg, 0.381 mmol) and $FeCl_3$ (0.20 equiv, 4.3 mg, 0.026 mmol) was added to a suspension of **1a** (1.0 equiv, 0.102 g, 0.130 mmol) in anhydrous MeCN (1.3 mL) with vigorous stirring at room temperature. The temperature of the mixture was raised to 70 °C and kept for 3 h. After cooling down to room temperature, was added the same amount of NBS (3.0 equiv, 69.1 mg, 0.381 mmol) to the reaction mixture. The temperature of the mixture was again raised to 70 °C and kept for another 8 h. The mixture was cooled to room temperature, poured into water (20 mL), and then extracted with DCM (20 mL). The extract was washed with water (20 mL) and brine (20 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo to leave a reddish orange oily residue. The residue was purified by column chromatography (silica gel, toluene/AcOEt = 1/0 to 100/1 to 50/1) to yield a 3:1 regioisomeric mixture of 1,7- and 1,6-dibromides **1b′** (0.110 g, 0.117 mmol, 90%) as a bright orange solid. R_f = 0.73 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 83-85 °C; IR (NaCl) 3060 (C–H), 3032 (C–H), 2956 (C–H), 1717 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.96 (d, *J* = 7.2 Hz, 2H, for 1,6-regioisomer), 8.93 (d, *J* = 7.9 Hz, 2H, for 1,7-regioisomer), 8.33 (s, 2H, for 1,6-regioisomer), 8.31 (s, 2H, for 1,7-regioisomer), 8.12 (d, *J* = 7.9 Hz, 2H, 1,7- and 1,6-regioisomers), 7.5-7.3 (m, 20H, 1,7- and 1,6-regioisomers), 5.33 (s, 4H, for 1,6-regioisomer), 5.32 (s, 4H, for 1,7-regioisomer), 5.31 (s, 4H, for 1,7-regioisomer), 5.29 (s, 4H, for 1,6-regioisomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.3,

168.0, 167.2, 166.9, 137.3, 137.2, 135.8, 135.7, 135.5, 135.4, 132.4, 132.1, 132.0, 131.5, 131.2, 130.6, 130.3, 130.2, 129.8, 129.6, 129.5, 128.95, 128.93, 128.92, 128.90, 128.84, 128.81, 128.78, 128.76, 128.72, 128.66, 127.9, 127.4, 126.8, 120.0, 119.1, 67.8, 67.7, 67.52, 67.47. Anal. Calcd for $C_{52}H_{34}Br_2O_8$: C, 65.98; H, 3.62; N, 0.00. Found: C, 65.60; H, 3.54; N, 0.00. HRMS (MALDI+) *m/z* calcd for $C_{52}H_{34}Br_2O_8Na$ $[MNa]^+$: 969.0498, found 969.0477.

*Synthesis and characterization of **1c***

This compound was synthesized by following a procedure analogously to that described for **1b** with the exception that *N*-chlorosuccinimide (NCS) was used instead of NBS as a halogenation reagent. Under the given conditions employing **1a** (100 mg, 0.127 mmol), NCS (1.1 equiv, 18.7 mg, 0.140 mmol), and $FeCl_3$ (0.20 equiv, 4.1 mg, 0.0254 mmol), the reaction reached essentially completion in 30 h to give a pale orange solid of **1c** with an isolated yield of 43% (44.6 mg, 0.0542 mmol) after column chromatography (silica gel, toluene/AcOEt = 1/0 to 100/1), along with a significant amount (~35%) of the unreacted starting material. R_f = 0.50 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 122-123 °C; IR (KBr) 3060 (C–H), 3032 (C–H), 2959 (C–H), 2925 (C–H), 1717 (C=O), 1587 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 8.78 (d, J = 8.1 Hz, 1H), 8.01 (s, 1H), 7.95-7.92 (m, 4H), 7.90 (d, J = 8.1 Hz, 1H), 7.49-7.31 (m, 20H), 5.32 (s, 4H), 5.31 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.4, 168.25, 168.18, 167.3, 135.9, 135.8, 135.6, 134.6, 132.7, 132.4, 131.1, 131.0, 130.5, 130.0, 129.6, 128.93, 128.91, 128.88, 128.81, 128.76, 128.72, 128.70, 128.67, 128.63, 128.3, 127.5, 127.3, 122.9, 121.9, 67.6, 67.4, 67.32, 67.29. Anal. Calcd for $C_{52}H_{35}ClO_8$: C, 75.86; H, 4.29; N, 0.00. Found: 75.58; H, 4.41; N, 0.00. HRMS (ESI+) *m/z* calcd for $C_{52}H_{35}O_8NaCl$ $[MNa]^+$: 845.1918, found 845.1910.

*Synthesis and characterization of **2a***

To an argon-purged solution of **1b** (0.554 g, 0.640 mmol) and 4-(*tert*-butyldimethylsilyloxy)phenyl boronic acid (1.5 equiv, 0.327 g, 0.960 mol) in a mixture of toluene/EtOH (2/1, 6.4 mL) was added sodium carbonate (Na_2CO_3, 6.4 mL, 19.0 mmol, 3.0 M aqueous solution) with vigorous stirring at room temperature. The temperature of the mixture was raised to 80 °C and then tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, 0.15 equiv, 0.111 g, 0.0960 mmol) was added. The reaction mixture was heated at this temperature for 4 h, quenched with water (20 mL), and extracted with DCM (50 mL). The organic extract was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to leave an orange residue. The residue was purified by column chromatography (silica gel, toluene/AcOEt = 1/0 to 100/1 to 50/1) to yield **2a** (0.496 g, 0.499 mmol, 78%) as a viscous orange oil. R_f = 0.60 (silica gel, $CHCl_3/CH_3OH$ = 60/1); IR (NaCl) 3066 (C–H), 3032 (C–H), 2955 (C–H), 2930 (C–H), 2886 (C–H), 2858 (C–H), 1716 (C=O), 1604 (C=C), 1586 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.99 (s, 1H), 7.94-7.84 (m, 4H), 7.51-7.27 (m, 22H), 7.13 (d, J = 9.6 Hz, 2H), 6.80 (d, J = 9.6 Hz, 2H), 5.33 (s, 4H), 5.30 (s, 2H), 5.27 (s, 2H), 0.99 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.7, 168.6, 168.4, 168.3, 155.9, 139.4, 136.0, 135.9, 135.8, 135.2, 133.2, 133.1, 131.1, 130.5, 130.4, 130.3, 130.1, 129.7, 129.4, 129.2, 128.9, 128.8, 128.7, 128.65, 128.57 128.5, 128.4, 127.5, 122.5, 121.8, 121.4, 67.3, 67.2, 25.8, 18.4, -4.3. Anal. Calcd for $C_{64}H_{54}O_9Si$: C, 77.24; H, 5.47; N, 0.00. Found: C, 77.23; H, 5.47; N, 0.00. HRMS (ESI+) calcd for $C_{64}H_{54}O_9NaSi$ $[MNa]^+$: 1017.3435. Found: 1017.3426.

*Synthesis and characterization of **2b***

To a solution of **2a** (0.319 g, 0.320 mmol) in THF (1.6 mL) was added tetra-*n*-butylammonium fluoride (TBAF, 1.5 equiv, 0.48 mL, 0.480 mmol, 1.0 M THF solution) with vigorous stirring at room temperature. The reaction mixture was stirred for additional 2 h, quenched with water (30 mL), extracted with DCM (50 mL). The organic extract was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to leave an orange residue. The residue was purified by recrystallization from $CHCl_3$/hexane to yield **2b** (0.496 g, 0.499 mmol, 88%) as an orange solid. R_f = 0.40 (silica gel, $CHCl_3/CH_3OH$ = 30/1); dp 150 °C; IR (KBr) 3339 (O–H), 3088 (C–H), 3060 (C–H), 3030 (C–H), 2945 (C–H), 1705 (C=O), 1681 (C=O), 1608 (C=C), 1586 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 8.12 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.47-7.28 (m, 20H), 7.17 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.52 (s, 1H), 5.31 (s, 4H), 5.29 (s, 2H), 5.25 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.8, 168.7, 168.6, 168.5, 156.1, 139.4, 136.0, 135.9, 135.8, 135.5, 133.2, 133.62, 133.55, 133.4, 131.3, 130.7, 130.6, 130.5, 130.4, 129.89, 129.85, 129.7, 129.4, 129.1, 129.0, 128.95, 128.89, 128.86, 128.76, 128.74, 128.6, 127.8, 122.6, 121.5, 117.2, 67.4, 67.3. Anal. Calcd for $C_{58}H_{40}O_9$: C, 79.08; H, 4.58; N, 0.00. Found: 78.89; H, 4.69; N, 0.00. HRMS (ESI+) calcd for $C_{58}H_{40}O_9Na$ $[MNa]^+$: 903.2570. Found: 903.2545.

*Synthesis and characterization of **2c***

To a solution of **2b** (65.7 mg, 0.0845 mmol) in DCM (1.6 mL) was successively added acetic anhydride (Ac_2O, 2.0 equiv, 17.4 mg, 16.9 mmol) and pyridine (1.0 equiv, 6.7 mg, 0.085 mmol) with vigorous stirring at room temperature. The reaction mixture was stirred at this temperature for 15 h, quenched with saturated sodium bicarbonate solution (20 mL), extracted with DCM (40 mL). The organic extract was washed with saturated sodium bicarbonate solution (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to leave an orange solid residue. This residue was purified by column chromatography (silica gel, toluene/AcOEt = 1/0 to 100/1 to 50/1) to yield **2c** (78.0 mg, 0.0844 mmol, 99%) as an orange solid. R_f = 0.33 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 95-96 °C; IR (NaCl) 3066 (C–H), 3020 (C–H), 2955 (C–H), 2890 (C–H), 1762 (C=O), 1715 (C=O), 1603 (C=C), 1587 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.98-7.96 (m, 3H), 7.93 (d, J = 6.3 Hz, 1H), 7.87 (d, J = 6.3 Hz, 1H), 7.48-7.28 (m, 25H), 7.08 (d, J = 8.7 Hz, 1H), 5.32 (s, 4H), 5.29 (s, 2H), 5.26 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 169.5, 168.6, 168.5, 168.4, 168.2, 150.6, 140.4, 138.5, 136.0, 135.9, 135.8, 135.2, 133.3, 133.1, 132.7, 131.4, 130.6, 130.4, 130.1, 129.9, 129.6, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 127.8, 123.2, 122.6, 121.5, 67.4, 67.3, 67.2, 21.3. Anal. Calcd for $C_{60}H_{42}O_{10}$: C, 78.08; H, 4.59; N, 0.00. Found: C, 77.95; H, 4.77; N, 0.00. HRMS (ESI+) calcd for $C_{60}H_{42}O_{10}Na$ $[MNa]^+$: 945.2676. Found: 945.2689.

*Synthesis and characterization of **3a***

A solution of DIBAL-H (1.0 M solution in hexane, 2.6 mL, 2.6 mmol) was added to a solution of **1a** (147 mg, 0.186 mmol) in DCM (3.7 mL) with vigorous stirring at -78 °C. The reaction mixture was stirred for 30 min at this temperature.

Then, the temperature of the mixture was raised to room temperature and kept for 67 h. The mixture was cooled to 0 °C, quenched by successive addition of ethanol (25 mL) and 10% aqueous H_2SO_4 (20 mL). This mixture was further acidified by addition of conc. H_2SO_4 (10 drops), heated with vigorous stirring under reflux for 5 h, and cooled to room temperature. The resulting mixture was quenched with water (20 mL) to obtain a yellowish precipitate, which was collected by vacuum filtration and washed with water (20 mL) to yield **3a** (54.6 mg, 0.162 mmol, 87%) as a pale brownish solid. This compound is only marginally soluble enough in either $CDCl_3$ or DMSO-d_6 for ^{1}H NMR measurement. Due to the limited solubility, the ^{13}C NMR spectra of this compound have not been determined. R_f = 0.67 (silica gel, $CHCl_3/CH_3OH$ = 50/1); dp 224 °C; IR (NaCl) 3033 (C–H), 3016 (C–H), 2941 (C–H), 2889 (C–H), 2817 (C–H), 1717 (C=C), 1590 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.11 (d, J = 7.6 Hz, 4H), 7.19 (d, J = 7.6 Hz, 4H), 5.06 (s, 8H). HRMS (LDI+) calcd for $C_{24}H_{16}O_2$ $[M]^+$: 336.1150. Found: 336.1127.

*Synthesis and characterization of **3b***

This compound was synthesized by following a procedure similar to that described for **3a** with the exception that **2a** (70.1 mg, 0.0705 mmol) was used instead of **1a** as a substrate. Under the given conditions, the reaction reached essentially completion in 51 h to give **3b** with an isolated yield of 83% (25.1mg, 0.0585 mmol) as a pale brownish solid. R_f = 0.40 (silica gel, $CHCl_3/CH_3OH$ = 30/1); dp 235 °C; IR (KBr) 3493 (O–H), 2945 (C–H), 2825 (C–H), 1607 (C=C), 1582 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 9.60 (s, 1H), 8.28 (d, J = 7.8 Hz, 1H), 8.26 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.13 (s, 1H), 6.86 (d, J = 8.6 Hz, 2H), 6.82 (s, 1H), 5.01 (s, 2H), 5.00 (s, 2H), 4.97 (s, 2H), 4.88 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 157.0, 137.6, 135.0, 132.3, 132.2, 131.61, 131.59, 129.74, 129.66, 129.3, 129.1, 128.8, 128.6, 127.2, 126.8, 126.7, 126.4, 121.3, 120.5, 120.2, 119.6, 116.8, 68.2, 68.0. Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.09; H, 4.70; N, 0.00. Found: C, 83.72; H, 4.90; N, 0.00. HRMS (ESI+) calcd for $C_{30}H_{20}O_3$ $[M]^+$: 428.1412. Found: 428.1409.

*Synthesis and characterization of **3c***

This compound was synthesized by following a procedure similar to that described for **2c** with the exception that **3b** (61.2 mg, 0.144 mmol) was used instead of **2b** as a substrate. Under the given conditions, the reaction reached essentially completion in 7 h to obtain **3c** with an isolated yield of 96% (65.0 mg, 0.138 mmol) after purification by recrystallization from $CHCl_3$/hexane as a pale brownish solid. R_f = 0.33 (silica gel, $CHCl_3/CH_3OH$ = 60/1); dp 193 °C; IR (KBr) 3029 (C–H), 2952 (C–H), 2842 (C–H), 1751 (C=O), 1603 (C=C), 1578 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.10 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.7 Hz, 2H), 7.28-7.14 (m, 5H), 7.08 (brs, 1H), 6.73 (d, J = 7.8 Hz, 1H), 5.07 (s, 2H), 5.04 (s, 2H), 5.03 (s, 2H), 4.93 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 169.8, 150.3, 142.8, 136.9, 132.3, 132.0, 131.7, 130.3, 130.2, 129.6, 129.5, 128.2, 127.7, 127.3, 126.3, 123.1, 121.4, 121.2, 120.5, 120.4, 119.5, 69.53, 69.50, 69.33, 69.30, 21.3. Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.69; H, 4.71; N, 0.00. Found: C, 81.35; H, 4.96; N, 0.00. HRMS (ESI+) calcd for $C_{32}H_{22}O_4$ $[M]^+$: 470.1518. Found: 470.1507.

*Synthesis and characterization of **4a***

Under nitrogen atmosphere, a mixture of **1a** (0.142 g, 0.180 mmol), 2,6-diisopropylaniline (10 equiv, 0.339 mL, 1.80 mmol), and imidazole (40 equiv, 0.490 g, 7.21 mmol) was heated at 180 °C with vigorous stirring to produce the melt of the mixture. The mixture was stirred at this temperature for 30 min, cooled to room temperature, quenched with water (10 mL), and then extracted with DCM (20 mL). The extract was washed with water (10 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to leave a dark purple oily residue. The residue was purified by column chromatography (silica gel, DCM/hexane = 1/1 to 2/1 to 1/0) to yield **4a** (0.112 g, 0.158 mol, 88%) as a dark purple solid. The identity of this product was confirmed by measurement of the ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.81 (d, J = 8.0 Hz, 4H), 8.75 (d, J = 8.0 Hz, 4H), 7.51 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 7.7 Hz, 4H), 2.76 (sept, J = 6.8 Hz, 4H, C*H*), 1.19 (d, J = 6.8 Hz, 24H).

*Synthesis and characterization of **4b***

Under nitrogen atmosphere, a mixture of **2b** (0.371 g, 0.373 mmol), 2,6-diisopropylaniline (0.661 g, 3.73 mmol), and imidazole (1.03 g, 14.9 mmol) was heated at 180 °C with vigorous stirring to produce the melt of the mixture. The mixture was stirred at this temperature for 30 min, cooled to room temperature, quenched with water (20 mL), and then extracted with DCM (50 mL). The extract was washed with brine (20 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo to leave a reddish-brown oily residue. The residue was purified by column chromatography (silica gel, toluene/AcOEt = 20/1 to 10/1 to 5/1) to yield **4b** (0.270 g, 0.336 mmol, 90%) as a dark purple solid. This compound is only marginally soluble enough in $CDCl_3$ for ^{1}H NMR measurement. Due to the limited solubility, the ^{13}C NMR spectra of this compound have not been determined. We could not obtain the melting point for this material since no melting occurred until 300 °C, which is the limit of the apparatus. R_f = 0.40 (silica gel, $CHCl_3/CH_3OH$ = 30/1); IR (KBr) 3404 (O–H), 2961 (C–H), 2926 (C–H), 2869 (C–H), 1705 (C=O), 1669 (C=O), 1590 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.79 (d, J = 8.0 Hz, 1H), 8.79 (d, J = 8.0 Hz, 1H), 8.72 (d, J = 8.1 Hz, 1H), 8.71 (d, J = 8.2 Hz, 1H), 8.68 (s, 1H), 8.28 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 8.2 Hz, 1H), 7.55-7.45 (m, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 7.7 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.00 (s, J = 8.6 Hz, 2H), 5.79 (s, 1H), 2.78 (sept, J = 6.8 Hz, 2H), 2.74 (sept, J = 6.8 Hz, 2H), 1.22-1.14 (m, 24H). HRMS (ESI+) calcd for $C_{54}H_{47}N_2O_5$ $[MH]^+$: 803.3485. Found: 803.3475.

*Synthesis and characterization of **4c***

This compound was synthesized by following a procedure similar to that described for **2c** with the exception that **4b** (46.3 mg, 0.0577 mmol) was used instead of **2b** as a substrate. Under the given conditions, the reaction reached essentially completion in 7 h to obtain **4c** with an isolated yield of 95% (46.3 mg, 0.0548 mmol) after purification by recrystallization from $CHCl_3$/hexane as a dark purple solid. R_f = 0.33 (silica gel, $CHCl_3/CH_3OH$ = 60/1); dp 264 °C; IR (KBr) 2962 (C–H), 2928 (C–H), 2871 (C–H), 1772 (C=O), 1705 (C=O), 1670 (C=O), 1591 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.82 (d, J = 8.1 Hz, 1H), 8.79 (d, J = 8.1 Hz, 1H), 8.75 (d, J = 8.1 Hz, 2H), 8.72 (d, J = 8.1 Hz, 2H), 8.69 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.55-7.45 (m, 2H), 7.39-7.30 (m, 5H), 2.75 (sept, J = 6.3 Hz,

4H), 2.37 (s, 3H), 1.22-1.14 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 169.4, 163.9, 163.7, 163.6, 151.4, 145.92, 145.90, 141.3, 140.1, 136.8, 135.6, 135.4, 135.2, 133.4, 132.1, 131.9, 131.0, 130.7, 130.5, 130.1, 130.0, 129.4, 128.8, 128.7, 128.2, 127.3, 124.42, 124.39, 124.2, 124.0, 123.6, 123.4, 123.3, 122.7, 29.4, 29.3, 24.2, 24.1, 21.3. Anal. Calcd for $C_{56}H_{48}N_2O_6$: C, 79.60; H, 5.73; N, 3.32. Found: C, 79.53; H, 5.79; N, 3.62. HRMS (MALDI+) calcd for $C_{56}H_{49}N_2O_6$ $[MH]^+$: 845.3591. Found: 845.3636.

*Synthesis and characterization of **5a***

To a solution of **1b** (97.3 mg, 0.112 mmol) in DMF (1.2 mL) was added 4-*tert*-butylphenol (2.9 equiv, 49.2 mg, 0.328 mmol), potassium carbonate (K_2CO_3, 2.4 equiv, 37.8 mg, 0.274 mmol), and 18-crown 6-ether (2.4 equiv, 72.1 mg, 0.273 mmol) with vigorous stirring at room temperature. The temperature was raised to 50 °C and kept for 18 h. The reaction mixture was cooled to room temperature, and then quenched with water (10 mL) to obtain a brownish precipitate, which was collected by vacuum filtration. The crude solid was dissolved in minimum of toluene, and the residue was purified by column chromatography (silica gel, toluene/AcOEt = 1/0, 100/1, 50/1, and 30/1) to give, after reprecipitation from $CHCl_3$ and hexane, **5a** (99.7 mg, 0.106 mmol, 95%) as a dark yellow solid. R_f = 0.50 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 85-86 °C; IR (KBr) 3060 (C–H), 3036 (C–H), 2962 (C–H), 1718 (C=O), 1589 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.93 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.2, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.0, 1H), 7.95 (d, J = 8.0, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.71 (s, 1H), 7.47-7.26 (m, 22H), 6.94 (d, J = 8.8, 2H), 5.31 (s, 2H), 5.28 (s, 4H), 5.23 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.6, 168.51, 168.47, 167.7, 153.3, 147.4, 136.01, 135.96, 135.71, 135.2, 133.3, 133.2, 131.8, 131.3, 131.2, 131.1, 130.3, 129.9, 129.8, 129.6, 129.5, 129.4, 128.83, 128.78, 128.75, 128.67, 128.59, 128.50, 128.47, 127.3, 127.1, 125.6, 122.54, 122.50, 121.3, 118.6, 67.24, 67.20, 67.14, 67.08, 34.5, 31.6. Anal. Calcd for $C_{62}H_{48}O_9$: C, 79.47; H, 5.16; N, 0.00. Found: C, 79.46; H, 5.16; N, 0.00. HRMS (ESI+) calcd for $C_{62}H_{48}O_9Na$ $[MNa]^+$: 959.3174. Found: 959.3196.

*Synthesis and characterization of **5b***

This compound was synthesized by following a procedure similar to that described for **5a** with the exception that 4-methoxycarbonylphenol was used instead of 4-*tert*-butylphenol as a reagent. Under the given conditions employing **1b** (81.2 mg, 0.0937 mmol) and 4-methoxycarbonylphenol (3.7 equiv, 53.0 mg, 0.348 mmol), the reaction reached essentially completion in 5 h to obtain **5b** with an isolated yield of 94% (83.1 mg, 0.0886 mmol) after reprecipitation from chloroform and hexane as a dark yellow solid. R_f = 0.40 (silica gel, $CHCl_3/CH_3OH$ = 50/1); mp 175-176 °C; IR (KBr) 3064 (C–H), 3040 (C–H), 2951 (C–H), 1719 (C=O), 1589 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.82 (d, J = 8.3 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.69 (s, 1H), 7.49-7.29 (m, 21H), 6.99 (d, J = 8.4 Hz, 2H), 5.30 (s, 2H), 5.29 (s, 2H), 5.28 (s, 2H), 5.26 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.5, 168.4, 168.3, 167.5, 166.6, 159.6, 151.2, 135.91, 135.86, 135.6, 133.3, 132.8, 132.3, 131.6, 131.04, 131.01, 130.4, 130.10, 130.06, 129.9, 129.8, 129.3, 128.88, 128.85, 128.80, 128.77, 128.74, 128.67, 128.61, 128.59, 127.11, 126.4, 126.3, 125.9, 123.7, 122.7, 121.6, 117.8, 67.5, 67.3, 67.2, 52.3. Anal. Calcd for $C_{60}H_{42}O_{11}$: C, 76.75; H, 4.51; N, 0.00. Found: C, 76.60; H, 4.70; N, 0.00. HRMS (ESI+) calcd for $C_{60}H_{42}O_{11}Na$ $[MNa]^+$: 961.2625. Found: 961.2622.

*Synthesis and characterization of **6***

This compound was synthesized by following a procedure similar to that described for **5a** with the exception that **2b** was used instead of 4-*tert*-butylphenol as a phenolic reagent. Under the given conditions employing **2b** (41.8 mg, 0.0475 mmol) and **1b** (1.5 equiv, 62.6 mg, 0.0723 mmol), the reaction reached essentially completion in 5 h to obtain **6** with an isolated yield of 98% (77.4 mg, 0.0464 mmol) after reprecipitation from chloroform and hexane as a brownish solid. R_f = 0.50 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 138-139 °C; IR (KBr) 3064 (C–H), 3032 (C–H), 2963 (C–H), 2905 (C–H), 2849 (C–H), 1717 (C=O), 1586 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.87 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 8.2, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.99-7.92 (m, 5H), 7.89 (d, J = 7.5, 1H), 7.87 (d, J = 7.8, 1H), 7.80 (d, J = 8.2, 1H), 7.67 (s, 1H), 7.50-7.15 (m, 44H), 6.97 (d, J = 8.1, 2H), 5.323 (s, 2H), 5.316 (s, 4H), 5.310 (s, 2H), 5.30 (s, 2H), 5.27 (s, 2H), 5.25 (s, 2H), 5.23 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.62, 168.58, 168.45, 168.38, 168.2, 167.5, 155.2, 152.8, 139.0, 138.3, 136.0, 135.91, 135.89, 135.8, 135.6, 135.3, 131.37, 131.34, 131.28, 131.0, 130.50, 130.45, 130.3, 129.98, 129.97, 129.87, 129.76, 129.65, 129.52, 129.46, 129.17, 129.10, 128.94, 128.83, 128.74, 128.67, 128.56, 128.47, 128.40, 127.7, 127.3, 125.6, 125.1, 122.6, 122.5, 122.3, 121.5, 121.4, 120.84, 120.81, 67.36, 67.30, 67.24, 67.17. Anal. Calcd for $C_{110}H_{74}O_{17}$: C, 79.22; H, 4.47; N, 0.00. Found: C, 79.05; H, 4.63; N, 0.00. HRMS (ESI+) calcd for $C_{110}H_{74}O_{17}Na$ $[MNa]^+$: 1689.4824. Found: 1689.4803.

*Synthesis and characterization of **7***

This compound was synthesized by following a procedure similar to that described for **5a** with the exception that **3b** was used instead of 4-*tert*-butylphenol as a phenolic reagent. Under the given conditions employing **3b** (44.2 mg, 0.103 mmol) and **1b** (1.1 equiv, 98.3 mg, 0.113 mmol), the reaction reached essentially completion in 5 h to obtain **7** with an isolated yield of 99% (124 mg, 0.102 mmol) after reprecipitation from chloroform and hexane as a brownish solid. R_f = 0.33 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 155-157 °C; IR (KBr) 3064 (C–H), 3029 (C–H), 2945 (C–H), 2877 (C–H), 2814 (C–H), 1717 (C=O), 1587 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.97 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 8.2, 1H), 8.05 (d, J = 8.2 Hz, 1H), 8.00-7.90 (m, 5H), 7.81 (s, 1H), 7.50-7.40 (m, 6H), 7.40-7.25 (m, 16H), 7.18 (d, J = 7.8, 1H), 7.11 (d, J = 7.7, 1H), 7.06 (d, J = 7.7, 1H), 7.02 (d, J = 8.7, 2H), 6.96 (s, 1H), 6.66 (d, J = 7.8, 1H), 5.32 (s, 2H), 5.31 (s, 2H), 5.30 (s, 2H), 5.28 (s, 2H), 5.01 (s, 2H), 4.92 (s, 4H), 4.86 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.6, 168.5, 167.6, 154.8, 152.8, 141.3, 136.6, 136.0, 135.93, 153.86, 135.6, 133.2, 133.0, 132.1, 131.8, 131.6, 131.5, 131.4, 131.3, 131.1, 130.6, 130.3, 130.0, 129.9, 129.8, 129.6, 129.53, 129.46, 129.40, 129.3, 128.9, 128.8, 128.73, 128.67, 128.60, 128.4, 128.1, 128.0, 127.5, 127.2, 127.1, 126.2, 125.8, 125.6, 122.7, 122.6, 121.4, 121.2, 121.0, 120.5, 120.3, 120.2, 119.4, 69.41, 69.36, 69.24, 69.17, 67.3, 67.2. Anal. Calcd for $C_{82}H_{54}O_{11}$: C, 81.04; H, 4.48; N, 0.00. Found: C, 80.84; H, 4.57; N, 0.00. HRMS (ESI+) calcd for $C_{82}H_{54}O_{11}Na$ $[MNa]^+$: 1237.3564. Found: 1237.3567.

*Synthesis and characterization of **8***

This compound was synthesized by following a procedure similar to that described for **5a** with the exception that **4b** was used instead of 4-*tert*-butylphenol as a phenolic reagent. Under the given conditions employing **4b** (10.8 mg, 0.0135 mmol) and **1b** (1.5 equiv, 18.0 mg, 0.0208 mmol), the reaction reached essentially completion in 5 h to obtain **8** with an isolated yield of 89% (19.0 mg, 0.0120 mmol) after reprecipitation from chloroform and hexane as a dark purple solid. R_f = 0.33 (silica gel, $CHCl_3/CH_3OH$ = 60/1); mp 240-241 °C; IR (KBr) 3064 (C–H), 3032 (C–H), 2961 (C–H), 2925 (C–H), 2865 (C–H), 1704 (C=O), 1666 (C=O), 1590 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.10 (d, J = 8.2 Hz, 1H), 8.81 (d, J = 8.0 Hz, 1H), 8.79 (d, J = 8.0 Hz, 1H), 8.72 (d, J = 8.2 Hz, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.65 (s, 1H), 8.34-8.19 (m, 3H), 8.10-8.04 (m, 4H), 7.85 (s, 1H), 7.60-7.18 (m, 30H), 5.31 (s, 2H), 5.30 (s, 2H), 5.29 (s, 2H), 5.28 (s, 2H), 2.78 (sept, J = 6.8 Hz, 2H), 2.75 (sept, J = 6.8 Hz, 2H), 1.36-1.13 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.6, 168.5, 168.4, 167.6, 163.96, 163.93, 163.64, 163.59, 156.2, 152.4, 146.00, 145.99, 141.2, 138.6, 136.0, 135.9, 135.6, 135.4, 135.2, 133.5, 133.1, 131.7, 131.5, 131.2, 130.98, 130.88, 130.80, 130.5, 130.3, 130.0, 129.9, 129.6, 129.4, 128.9, 128.84, 128.83, 128.82, 128.78, 128.70, 128.68, 128.64, 128.56, 126.1, 124.41, 124.37, 124.15, 123.6, 123.4, 123.1, 122.74, 122.70, 121.1, 67.51, 67.34, 67.29, 67.22, 29.4, 29.3, 24.1. HRMS (MALDI+) calcd for $C_{106}H_{80}N_2O_{13}Na$ $[MNa]^+$: 1611.5558. Found: 1611.5509.

*X-Ray structure determination for **4c***

The measurement for X-ray crystallographic analysis was made on a Bruker Smart APexII ULTRA CCD area detector with monochromated Cu Kα radiation (λ 1.54178 Å). The structure was solved by direct methods with SHELXL-97 and refined with SHELXL-2014/7.

*Crystal data for **4c*** (CCDC 1566175): $C_{56}H_{48}N_2O_6 \bullet 2CHCl_3$, M = 1083.70, monoclinic, space group C1 c1 (#39), dark purple block, a = 12.6869 (3), b = 37.5546 (12) Å, c = 11.2665 (3), α = 90, β = 104.367 (2), γ = 90°, V = 5200.1 (3) $Å^3$, T = 173 K, Z = 4, D_{calcd} = 1.384 g/cm^3, μ = 3.450 mm^{-1}; in the final least-squares refinement cycles on F^2, the model converged at R_1 = 0.0947 ($I > 2\sigma$ (I)), wR_2 = 0.2709, and GOF = 1.323 for 7508 reflections and 741 parameters (θ_{min} = 3.78 °, θ_{max} = 68.21 °).

ASSOCIATED CONTENT

Supporting Information

Figures S1-S5 (including X-ray crystallographic structure for **4c**), Table S1 (including fluorescence quantum yields for **6**-**8**), experimental details for structural assignment of regioisomeric products **1b′**, copies of ^1H and ^{13}C NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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