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Syntheses of Ladder-Type Oligonaphthalene Derivatives and Their Photophysical and Electrochemical Properties

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Abstract: Ladder-type oligophenylene derivatives are important compounds for light-emitting devices. However, the closely related ladder-type oligonaphthalene derivatives have received little attention due to the lack of synthetic accessibility. We hereby report the syntheses of these novel conjugated systems by means of an intramolecular cationic cyclization protocol. Utilizing a one-pot–multiple-component reaction, the acyclic precursors to these ladder-type oligomers up to pentamer can be synthesized from small fragments in just two or three steps. Photophysical and electrochemical studies revealed that the electron delocalization in these compounds is considerably enhanced relative to that found in the regular unplanarized oligonaphthalene derivatives. However, such an effect is much weaker than that found in fully planar rylene derivatives.

Keywords: chromophores · conjugation · fused-ring systems · oligomers · structure–property relationships

Polynuclear aromatic compounds are fascinating to chemists due to the general curiosity in electronically delocalized systems[1] and their applications in optical and electronic devices.[2] In the syntheses, characterizations, and fabrications of these large conjugated systems, poor solubility is a common problem. To overcome this difficulty, flexible alkyl groups are frequently grafted onto the aromatic rings as solublizing groups. However, the additional substitutions often cause twists along the π-backbone and severely disrupt the conjugation effect.[3]

An ingenious solution to this dilemma was conceived for *para*-oligophenylene-type systems by employing solublizing groups that can also force the backbone to adopt planar geometries (Scheme 1a). In practice, the *para*-phenylene oligomers carrying cyclizable substitutions were first synthesized by Suzuki's coupling. The bridges between phenylene units were then formed by intramolecular Freidel–Craft reactions. The planarized oligophenylene or other conjugated systems thus formed are often referred to as the "ladder-type" oligomers. Since being independently explored by Müllen, Tour, and Swager,[4] this paradigm has been studied by numerous other researchers with a view to constructing ladder-type π-systems. The much exploited oligofluorene materials for light-emitting applications clearly emerged from this concept.[5] A similar idea was also applied to the synthesis of 1,8-double-bridged oligonaphthalene, commonly known as rylene compounds. The synthesis starts with the construction of oligonaphthalene connected at the 1 position by means of palladium-catalyzed cross-coupling reactions. The 8–8′ bridges were subsequently connected by oxidative or reductive cyclization (Scheme 1b).[10]

While the applications of ladder-type oligophenylene flourish, the closely related ladder-type oligonaphthalene (LON) system has been completely overlooked. We attribute this neglect to the lack of synthetic accessibility. One major difficulty for this class of compounds is that the common strategy to synthesize ladder-type oligophenylene can not be adapted to construct LON directly. As shown in Scheme 2, such synthesis would require a scarce 1,2,5,6-substituted naphthalene derivative as the starting material. A more serious problem is the regioselectivity in the cyclization step. As depicted in the scheme, to construct 1,1′-connected oligonaphthalenes, the cyclization step can proceed through either 1,2- or 1,8-selectivity to produce regioisomers with different topologies.

To overcome the synthetic difficulties, we propose a new strategy to synthesize LON derivatives based on the acid-catalyzed intramolecular cyclization of 1- and 2-bisnaphthylphenyl or trisnaphthyl methanol. Such cationic cyclization reactions were first documented in the literature in the

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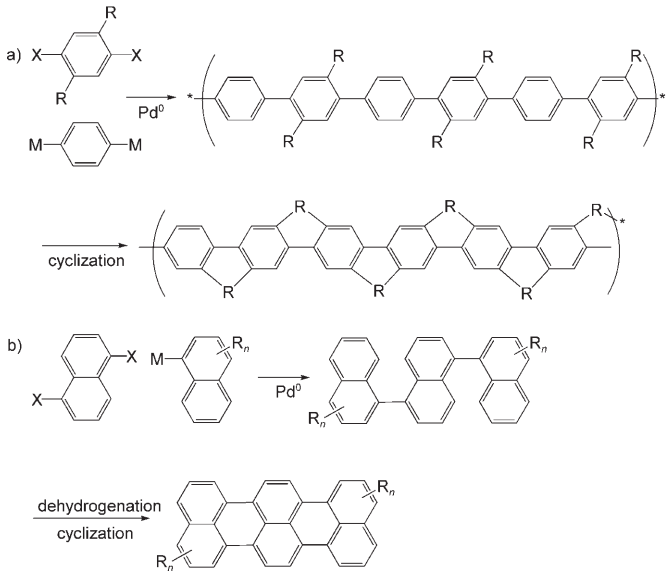
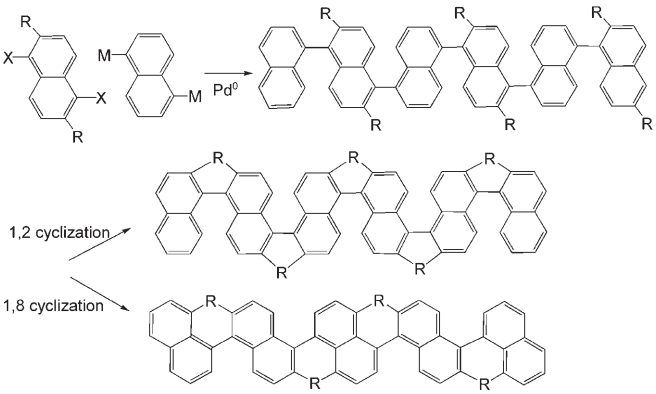


Scheme 1. Established synthetic strategy for ladder-type oligophenylene and rylene derivatives.



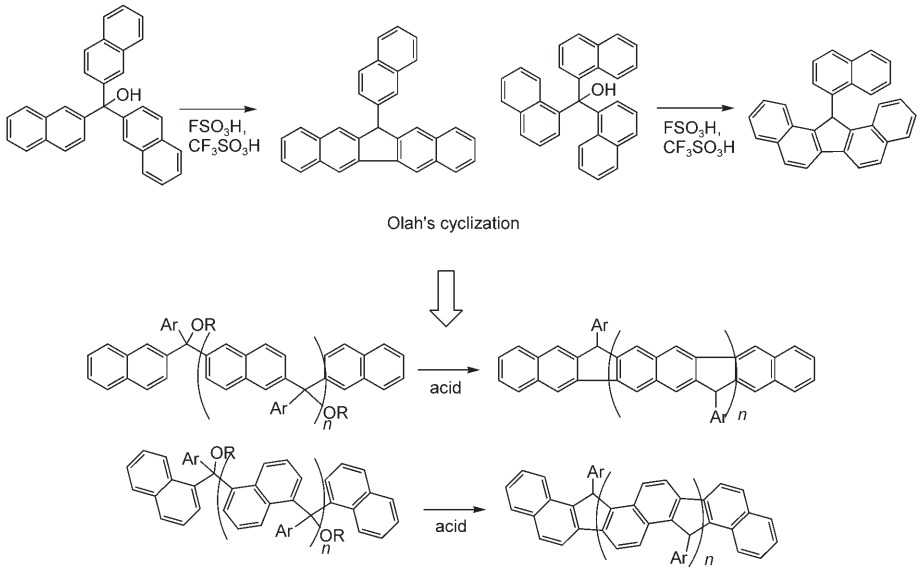
Scheme 2. Difficulties with applying conventional strategy to the synthesis of LONs.

1920s, however, it was not until 1998 that satisfactory spectral characterizations of the cyclization products were reported by Olah et al. (Scheme 3).[6]

This reaction constitutes a formal synthesis of ladder-type binaphthalene, we believe a similar concept can be applied to constructing higher LON derivatives with some fine tuning of the reaction conditions (Scheme 3). Conceptually, this strategy reverses the order of bond constructions in the well-established route to ladder-type oligophenylene in which aryl–aryl bonds were formed before the cyclization of the bridging units. In the present approach, the bridging groups between naphthyl units are formed before the naphthyl–naphthyl bonds are connected by means of cationic cyclization. Here, we report our preliminary success with this strategy and some basic photophysical properties of the LON derivatives thus produced.

Results and Discussion

We first sought to optimize the acid-catalyzed cyclization step in dinaphthylphenyl methanol compounds (synthesized through the addition of 1- or 2-lithionaphthalene to the corresponding benzoic esters) by screening various substitutions on the phenyl rings. Because such a cyclization reaction has to be carried out at multiple sites in one molecule in the syntheses of higher oligomers, it is therefore crucial to seek out a combination of substrate and reaction conditions that ensures the best yield. Otherwise, the multiple cyclization reaction would likely produce very low yield of high oligomers contaminated with inseparable byproducts. Under such adverse circumstances, the precise spectroscopic characterization of the desired LON products would be unfeasible. After screening a number of common acidic conditions (AcOH/HCl at various ratios, dichloroacetic acid, and $BF_3{\cdot}OEt_2$), we found that neat trifluoromethane sulfonic acid can serve as the medium for a wide range of substrates in this cyclization reaction. (For simpler substrates, trifluoroacetic acid can also be used.) As for substrates (Scheme 4), the compounds (**1**, **3**, **5**) carrying electron-withdrawing groups (*N*,*N*′-dibutyl amide, CF_3) on the *para* position of the phenyl groups gave satisfactory yields of corresponding cyclized products **2**, **4**, **6**. In contrast,

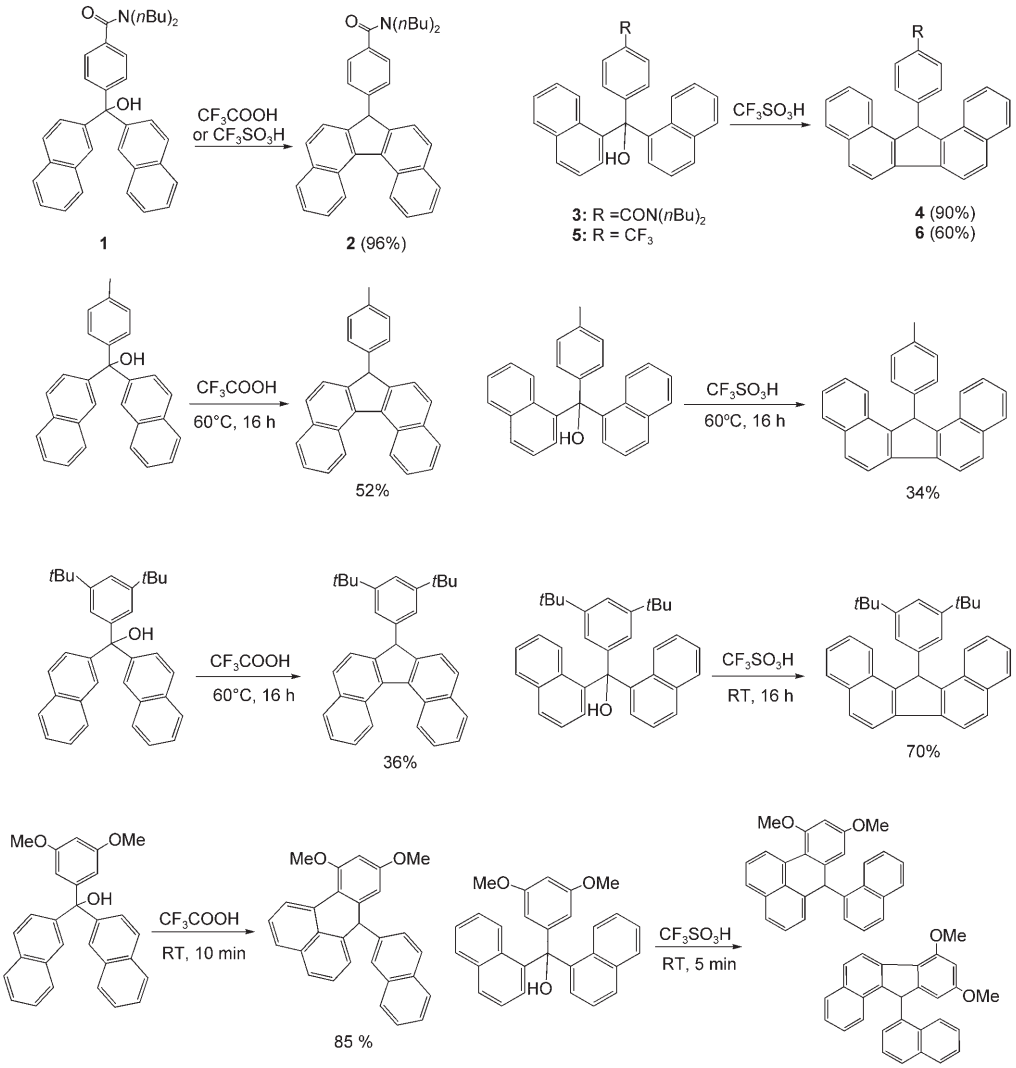


Scheme 3. Utilization of the acid-catalyzed intramolecular trisnaphthyl methanol cyclization reaction in the synthesis of LON derivatives.

when the phenyl ring is substituted with mild electron-donating groups (methyl, *tert*-butyl), the reactions require higher temperature and the yields for cyclization products are much inferior. With strong electron-donating methoxy substitutions, the regioselectivity of cyclization reactions was altered from the desired naphthyl–naphthyl bond formation to the phenyl–naphthyl one. We therefore reckoned that the cyclization reactions with substrates carrying electron-withdrawing substitutions on the phenyl rings are much more amenable to the syntheses of long LON derivatives. Such substrates are, therefore, employed in the subsequent synthesis of higher LON derivatives.

The regioselectivity of the cyclization reaction from compound **1** (and other similar compounds) to produce **2** requires further clarification, as three isomeric products (1,1′-, 1,3′-, and 3,3′-connection) are possible. Fortunately, these products are distinguishable by routine ^{1}H NMR spectroscopy. Based on the number of ^{1}H signals observed in the aromatic region, the unsymmetrical 1,3′-connected structure was immediately ruled out. In addition, the ^{1}H NMR spectrum of all isolable cyclized products from this series contains four sets of doublets ($J \approx 8$ Hz) in the aromatic region, whereas no singlet signal was observed. Such spectral features are consistent with the 1,1′-connected product as shown, rather than of the 3,3′-type product reported by Olah. We therefore concluded that this series of cyclization produces 1,1′-connected products. Such regioselectivity can be reasonably attributed to the larger molecular orbital (MO) coefficients of the intermediate cations at these positions.

With the conditions for synthesizing dimeric LON derivatives optimized, we proceeded to synthesize trimeric LON derivatives (Scheme 5). The cyclization precursors for 1,1′- and 2,2′-connected trimers were synthesized through two-fold addition reactions of 1- or 2-lithionaphthalene to the corresponding diketones **7** and **10**, respectively (synthesized through other two-fold addition reactions of corresponding Grignard reagents to known naphthalene dialdehydes fol-

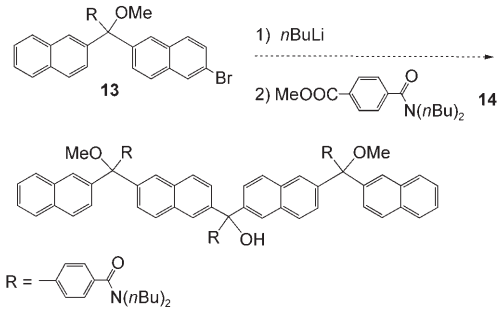


Scheme 4. Model reactions to synthesize dimeric LON derivatives: a) *N*,*N*′-dibutyl-4-iodobenzamide, cyclopentylmagnesium bromide (THF), then PCC (CH_2Cl_2); b) 1- or 2-bromonaphthalene, *n*BuLi (−78 °C, THF); then NaH, MeI (RT, THF).

lowed by pyridinium chlorochromate (PCC) oxidation). *N,N′*-Dibutyl amide substitutions on phenyl groups are introduced to serve two purposes: to facilitate the cyclization reaction and to improve the solubility of ladder-type products. The crude diol products from the double addition reactions were converted to methyl ethers **8** and **11** to aid their purification and characterization. The key double cyclization steps in acidic mediums (CF_3COOH and CF_3SO_3H, respectively) gave the desired LON derivatives **9** and **12** in excellent yields.

To synthesize the cyclization precursors to tetramer LON and higher oligomers, the most straightforward way is to follow Rajca's strategy for the syntheses of polytrityl ethers.[7] With methyl ether as a protecting group for the tertiary alcohol during the lithium–halogen exchange step, the addition of lithiated dinaphthylphenylmethyl methyl ether derivative **13** to amide ester **14** (Scheme 6) should furnish the desired tetranaphthalene cyclization precursor. To our surprise, we did not detect any expected addition products with this intuitive approach. After several futile attempts to optimize the reaction, we noticed the diminution of the methoxy group signal in the ^{1}H NMR of the complex crude mixture from the reaction. This observation indicated that the *n*BuLi and methyl ether underwent some unknown side reaction that is even more facile than the lithium–halogen exchange process at low temperature.

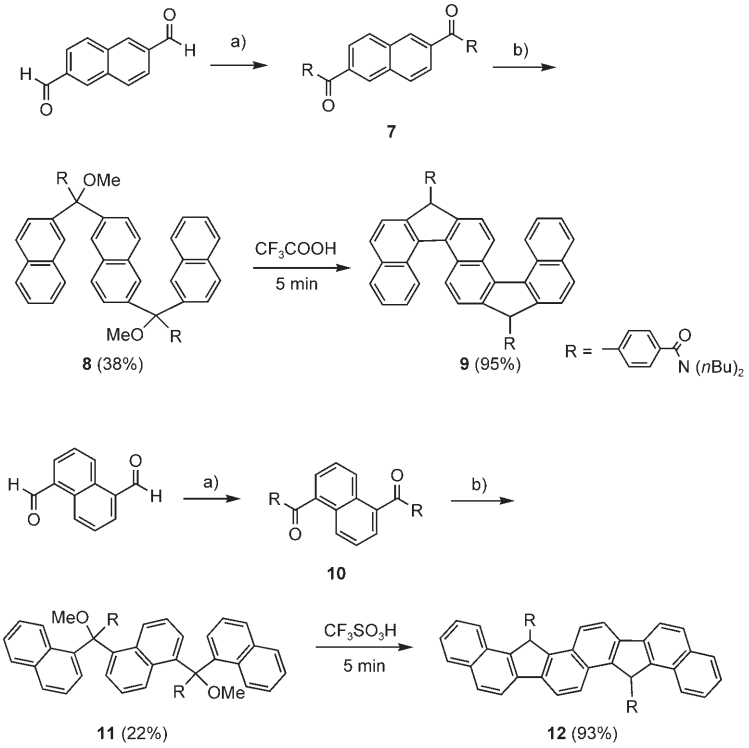
Having identified that the ether functionality might have caused the failure in Scheme 6, it is clear that the proper lithium reagents must be generated in the absence of methyl ethers. To avoid ether-type protecting groups for the tertiary



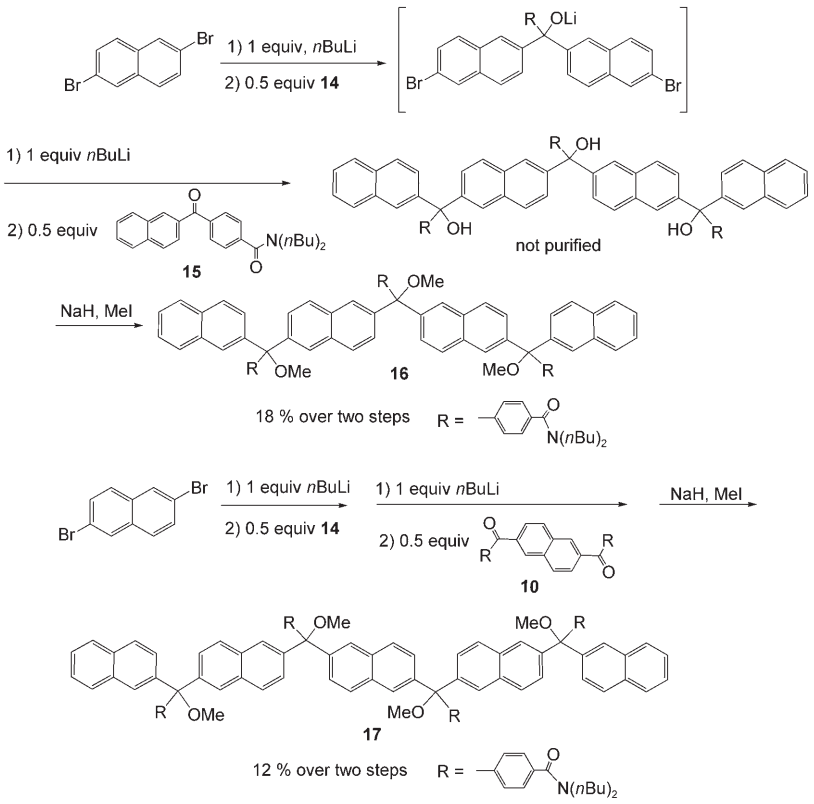
Scheme 6. Failed synthesis of 1,1′-tetramer LON precursor.

alcohol, we perceived the lithium alkoxide intermediate might be viewed as an unconventionally protected alcohol. In practice, the addition of 2-bromo-6-lithionaphthalene to ester **14** first generated an intermediate alkoxide that then underwent double lithium–bromide exchange to furnish the bis-lithium reagent. Two equivalents of **15** were then added to furnish the double addition. The crude product from such a reaction sequence was then treated with NaH and MeI to convert the tertiary alcohols into methyl ethers (Scheme 7). With this two-step strategy, we not only solved the chemoselectivity problem, but also devised a one-pot–five-component reaction for this class of compounds. Though the yield of the tetranaphthalene cyclization precursor **16** from flash chromatography is only 18%, this unoptimized yield should be considered fair bearing in mind that the reaction sequence includes four lithium–bromide exchange reactions, four carbon–carbon bond formation reactions, and four carbon–oxygen bond formation reactions. More importantly, this reaction sequence provided access to our cyclization precursors from simple building blocks in just two convenient steps. The pentanaphthalene cyclization precursor **17** was synthesized accordingly in 12% yield (Scheme 7) by simply switching ester **14** in tetramer synthesis to diketone **10**.

The cyclization steps to achieve tetramer and pentamer LONs are performed in triflic acid (Scheme 8) to give **18** and **19** in 52 and 47% yields, respectively. Notably, compounds **8**, **9**, **11**, **12**, **16**–**19** were all produced as mixtures of stereoisomers. These isomers are neither separable by simple flash chromatography nor clearly differentiable by NMR spectroscopy. Therefore, all the subsequent photophysical and electrochemical measurements are performed on



Scheme 5. Syntheses of trimer LONs.

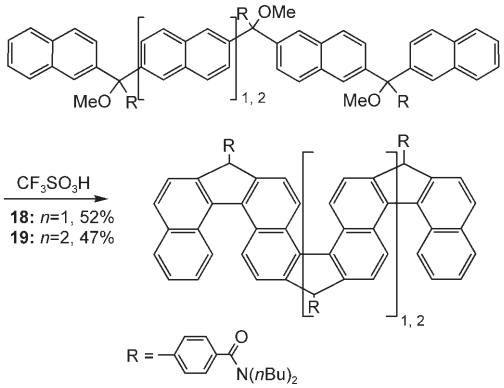


Scheme 7. Synthesis of 1,1′-tetramer and -pentamer LON cyclization precursors.

the supposed mixtures of stereoisomers. Furthermore, due to the spectral similarity among oligomers, the spectral identifications of **9**, **12**, **18**, **19**, and their cyclization precursors **8**, **11**, **16**, **17** are nontrivial tasks. Fortunately, these diastereomeric mixtures are distinguishable by some subtle differences in ^{1}H and ^{13}C NMR (see Supporting Information). By comparing these subtle spectral features, we confirmed that each compound is of good purity without contamination from shorter oligomers. High-resolution mass spectra also showed molecular-ion peaks that are consistent with the proposed structures.

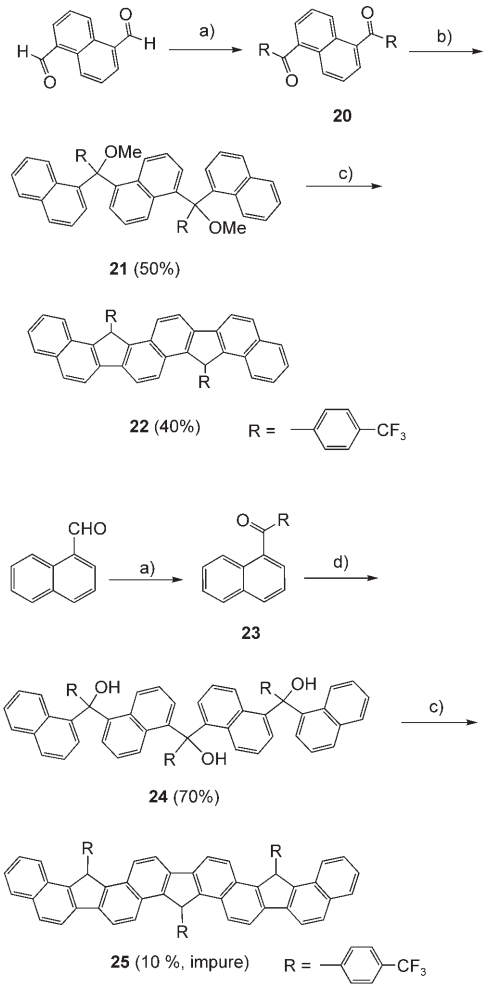
To construct tetrameric 2,2′-connected LON derivatives, the one-pot procedure similar to that for 1,1′-connected compounds was followed, as shown in Scheme 9. A trifluoromethyl group is employed as the electron-withdrawing substitution on the phenyl group instead of the amide used in the 1,1′ system. This modification is necessary because the addition of the lithium reagent to amide groups becomes competitive in the addition step. (The ketones in **20** and **23** are much more hindered than those in **10** and **15**.) Unfortunately, in the synthesis of tetramer LON **25**, the key cyclization step only furnished impure ladder-type products in low yield. Nevertheless, the production of **25** is evident from ^{1}H, ^{13}C NMR and mass spectra.

The photophysical data of LON derivatives are shown in Figure 1 and Table 1. As expected, the absorption and emission spectra of these LON derivatives both show marked bathochromic shifts compared to their unplanarized counterparts (entries 2–5 in Table 1).[8] However, the effect is much smaller than those found in rylene-type compounds (entries 6, 7 in Table 1).[9] Judged by the absorption spectra, the effect of cyclization on spectral shift is more pronounced in the 1,1′-connected compound **2** than in the 2,2′-connected **4** and **6**. It is tempting to attribute the results to the larger MO coefficients of naphthyl units at the 1 position. However, this trend is reversed upon comparing the absorption spectra of dimers **2**, **4**, **6**, with those of trimers **9**, **12**, **22** and higher oligomers. These seemingly conflicting observations suggest that the optical band gap is not influenced solely by simple conjugation lengths. We believe the larger bathochromic shift in the 1,1′-connected series **2**, **9**, **18**, **19** is partly due to structural deformation in individual naphthyl



Scheme 8. Synthesis of 1,1′-tetramer and -pentamer LONs: a) 1-bromo-4-trifluoromethylbenzene, *n*BuLi in THF at −78 °C; then PCC in CH_2Cl_2 at RT; b) 1-bromonapthalene, *n*BuLi in THF at −78 °C; then NaH, MeI in THF at RT; c) CF_3SO_3H; d) 1) 2,6-dibromonaphthalene, 1 equiv *n*BuLi in THF at −78 °C to RT; 2) 1 equiv *n*BuLi in THF at −78 °C, then methyl 4-trifluoromethyl benzoate.

units coerced by a strong 8,8′ hydrogen interaction. This 8,8′ hydrogen interaction also forces the intramolecular twists (estimated 23°) between the naphthyl units and causes the rapid decay of the long-range conjugation effect in these 1,1′ compounds. On the other hand, the red shifts observed in the 2,2′ series (**4**–**12**, **6**–**22**–**25**) are mainly the result of extended conjugation and such interaction apparently persists over a longer range than in the 1,1′ series. Relative to the



Scheme 9. Syntheses of 2,2′-trimer and -tetramer LONs.

fully planar rylene compounds in which the conjugation effect does not show signs of saturation, even for a hexarylene derivative,[10] the diminutions of conjugation effect are rather quick in both series. The quantum yields of these LON derivatives range from 28–83%. The longer oligomers appear to be better emitters. This trend is also seen in the ladder-type oligophenylene series in which the emission quantum efficiency can be enhanced when the rotations around the aryl–aryl bonds are restricted.

The HOMO levels of dimeric and trimeric LON **2**, **4**, **9**, **12** were probed by cyclic voltammetry (Table 1). The result indicates the HOMO levels were raised by 0.16 eV from **2** to **9** and 0.20 eV from **4** to **12**. Because the optical bathochromic shifts in these two pairs of LONs are 0.3 and 0.4 eV, respectively, it can be inferred that the LUMO levels are lowered by 0.14 and 0.20 eV by one ladder-type unit. These observation is consistent with our previous hypothesis that the conjugation effect is stronger in the 2,2′-connected series. It also appears that one additional laddered naphthyl unit exerts roughly equal influences on HOMO and LUMO levels in both series of short oligomers.

Conclusion

We have synthesized two series of isomeric LONs up to pentamers. The naphthyl units are first assembled as oligomeric dinaphthylphenylmethyl methyl ethers. A convenient one-pot–five-component reaction was developed for the syntheses of tetramers and one pentamer. The key aryl–aryl bonds were then constructed through an intramolecular cationic cyclization reaction. These compounds show marked red shifts in both absorption and emission spectra compared to their unplanarized counterparts. Decent fluorescence quantum yields were observed in these systems, as in the ladder-type phenylene. The HOMO and LUMO levels in dimers and trimers were estimated from their cyclic voltammetry (CV) and optical absorption data. This two-step strategy provides simple and efficient access to these new conjugated compounds that can be utilized as light-emitting materials or further elaborated into other interesting systems, such as rylene derivatives. Both research directions are currently being pursued in our group.

Experimental Section

General protocols: All chemicals and reagents were purchased from TCI, Acros, or Lancaster Company and were used without further purification. Reaction solvents THF and ether were distilled from Na/benzophenone. CH_2Cl_2 was distilled from CaH_2.

***N*,*N*-Dibutylterephthalamic acid methyl ester (14)**: A THF solution of terephthaloyl chloride (2.0 g, 9.85 mmol in 40 mL) was mixed with Et_3N (4.40 mL, 29.55 mmol) at 0 °C before dibutyl amine (2.35 mL, 13.79 mmol) was slowly added. The mixture was warmed back to RT and stirred for 1 h. The reaction was cooled to 0 °C again before CH_3OH was added (0.57 mL, 13.79 mmol). The reaction was stirred at RT and was quenched with water after 1.5 h. The THF was removed in vacuo and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated. Pure ester amide (0.86 g, 30%) was obtained by performing flash column chromatography (silica gel; CH_2Cl_2/hexane 1:8 to CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 0.74–1.63 (m, 14H), 3.10–3.48 (m, 4H), 3.91 (s, 3H), 7.39 (d, J = 8.5 Hz, 2H), 8.04 ppm (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 13.47, 13.80, 19.16, 20.17, 29.53, 30.70, 44.42, 48.60, 52.14, 126.36, 129.62, 130.45, 141.63, 166.35, 170.47 ppm; IR (KBr): $\tilde{\nu}$ = 731, 787, 864, 1115, 1277, 1635, 1723, 2873 cm^{-1}; HRMS: m/z: calcd for $C_{17}H_{26}NO_3$: 292.1913 [M+H$^+$]; found: 292.1909.

***N*,*N*-Dibutyl-4-(methoxydinaphthalen-2-yl-methyl)-benzamide (1)**: 1-Bromonaphthalene (0.78 g, 3.76 mmol) was dissolved in THF (13 mL) and the solution was cooled to −78 °C. *n*BuLi (1.6 M in hexane, 2.4 mL, 3.86 mmol) was slowly added at this temperature and the exchange reaction was completed within 1 h. To the lithium reagent solution was added a THF solution of **14** (0.50 g, 1.72 mmol in 5 mL). The reaction was warmed back to RT and stirred for another hour before being quenched with saturated NH_4Cl solution. THF was removed by using a rotary evaporator and the residue was extracted with CH_2Cl_2 several times. The combined organic phase was dried over $MgSO_4$ and concentrated to give the crude alcohol (0.84 g).

This crude intermediate and CH_3I were dissolved in THF (10 mL). NaH powder (60% mixture in mineral oil, 0.1 g, 2.50 mmol) was added in portions and the methylation was completed within 3 h. The remaining NaH was quenched with saturated NH_4Cl solution before the THF was removed. The residue was extracted with CH_2Cl_2 and the combined organic extracts were dried over $MgSO_4$ and concentrated. The remaining viscous material was purified by performing flash column chromatography

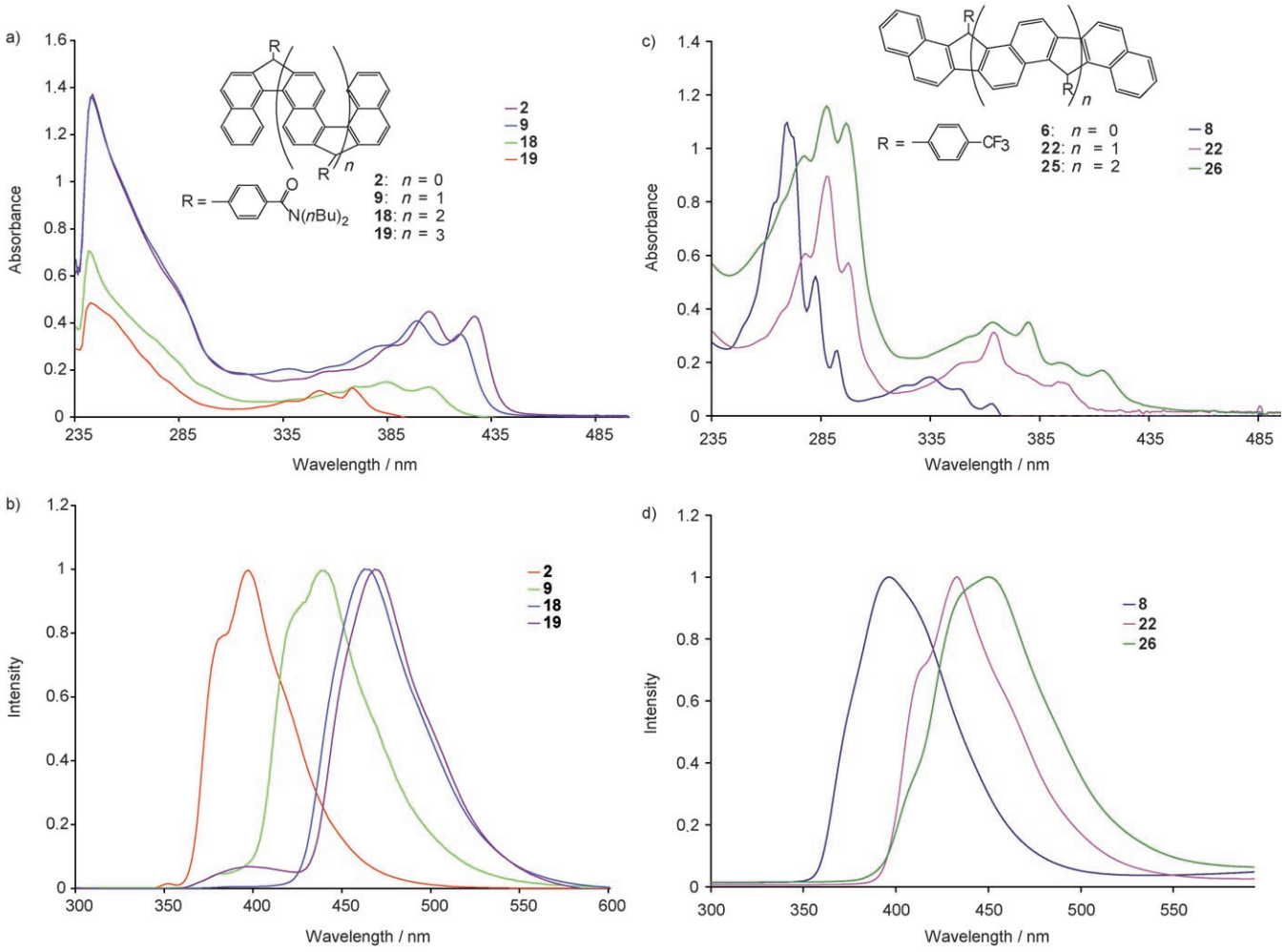


Figure 1. UV/Vis and fluorescence spectra of LON derivatives a, b) **2**, **9**, **18**, **19**, c, d) **8**, **22**, **26**.

(CH_2Cl_2) to give **1** (0.36 g, 40 % over two steps). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.68–1.60 (m, 14 H), 3.16 (s, 3 H), 3.16–3.45 (m, 4 H), 7.31 (d, J = 8 Hz, 2 H), 7.44–7.50 (m, 6 H), 7.56 (d, J = 8 Hz, 2 H), 7.74–7.80 (m, 6 H), 8.00 ppm (d, J = 1.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.41, 13.87, 19.56, 20.23, 29.59, 30.67, 44.43, 48.62, 52.42, 87.22, 126.04, 126.18, 126.97, 127.39, 127.44, 127.55, 128.35, 128.72, 132.41, 132.80, 136.00, 140.70, 144.69, 171.40 ppm; IR (KBr): $\tilde{\nu}$ = 2955, 2867, 1617, 1461, 1432, 811, 749, 476 cm^{-1}; HRMS: m/z: calcd for $C_{37}H_{40}NO_2$: 530.3059 [M+H$^+$]; found: 530.3060.

***N*,*N*-Dibutyl-4-(7*H*-dibenzo[*c*,*g*]fluoren-7-yl)-benzamide (2)**: Under an inert atmosphere, compound **1** (0.20 g, 0.38 mmol) was dissolved in CF_3COOH (2 mL). After 5 min, the cyclization reaction was stopped by adding a deoxygenated $NaHCO_3$ aqueous solution (15 mL). The crude mixture was extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$ and concentrated. Cyclized product **2** (0.18 g, 96 %) was isolated by performing flash column chromatography (silica gel; CH_2Cl_2/hexane 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.73–1.57 (m, 14 H), 3.02–3.44 (m, 4 H), 5.18 (s, 1 H), 7.10 (d, J = 8.0 Hz, 2 H), 7.23–7.25 (m, 2 H), 7.45 (d, J = 8 Hz, 2 H), 7.53–7.60 (m, 4 H), 7.82 (d, J = 8 Hz, 2 H), 7.96 (dd, J = 1.2, 8 Hz, 2 H), 8.77 ppm (d, J = 8 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 13.52, 13.87, 19.65, 20.25, 29.67, 30.72, 44.52, 48.69, 55.53, 122.76, 125.01, 125.20, 126.97, 127.09, 128.28, 128.56, 128.67, 128.83, 134.25, 136.10, 137.77, 141.37, 147.15, 171.44 ppm; IR (KBr): $\tilde{\nu}$ = 2952, 2929, 2863, 1627, 1458, 1432, 1104, 812, 747 cm^{-1}; HRMS: m/z: calcd for $C_{36}H_{36}NO$: 498.2797 [M+H$^+$]; found: 498.2798.

***N*,*N*-Dibutyl-4-(methoxydinaphthalen-1-yl-methyl)-benzamide (3)**: This compound was synthesized by following the same procedure as for its isomeric compounds **1** except that 2-bromonaphthalene was used instead of 1-bromonaphthalene. Yield 42 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.55–1.56 (m, 14 H), 3.05 (br m, 2 H), 3.23 (s, 3 H), 3.40 (br m, 2 H), 7.16–7.26 (m, 8 H), 7.34 (dd, J = 7.7, 7.7 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 7.76–7.80 (m, 4 H), 8.33 ppm (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.25, 13.84, 19.44, 20.17, 29.60, 30.59, 44.51, 48.62, 54.14, 91.30, 124.24, 125.17, 125.76, 128.38, 128.44, 128.54, 129.23, 131.90, 134.64, 135.32, 139.06, 144.82, 171.41 ppm; IR (KBr): $\tilde{\nu}$ = 3049, 2957, 2929, 2868, 1632, 1100, 782, 736 cm^{-1}; HRMS: m/z: calcd for $C_{37}H_{40}NO_2$: 530.3059 [M+H$^+$]; found: 530.3060.

***N*,*N*-Dibutyl-4-(13*H*-dibenzo[*a*,*i*]fluoren-13-yl)-benzamide (4)**: In an inert atmosphere, compound **3** (0.20 g, 0.38 mmol) was dissolved in triflic acid (2 mL). The reaction was quenched with a deoxygenated 1.0 M $NaHCO_3$ solution after 10 min. The mixture was extracted with CH_2Cl_2 and the combined extracts were dried over $MgSO_4$. The solvent was removed in vacuo and pure product **4** (0.17 g, 90 %) was isolated by performing flash chromatography (silica gel; CH_2Cl_2/hexane 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.61–1.55 (m, 14 H), 3.02–3.40 (m, 4 H), 5.67 (s, 1 H), 7.19–7.25 (m, 4 H), 7.27–7.37 (m, 4 H), 7.84–7.86 (m, 4 H), 7.92 (d, J = 8.4 Hz, 2 H), 8.00 ppm (d, J = 8.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 13.42, 13.86, 19.51, 20.21, 29.63, 30.61, 44.58, 48.66, 53.74, 118.33, 123.68, 125.10, 126.48, 127.21, 128.69, 128.93, 129.03, 130.08, 133.29, 135.56, 139.21, 142.90, 144.22, 171.40 ppm; IR (KBr): $\tilde{\nu}$ = 3047,

Table 1. Photophysical and electrochemical properties of LON derivatives.[a]

	Compounds	Abs λ_{max} [nm]	Flu. λ_{max} [nm]	Emission quantum yield [%][b]	Oxidation potential (vs. ferrocene)[c]
1	naphthalene	278	326		
2	[1,1′]binaphthalenyl	295	365		
3	[2,2′]binaphthalenyl[d]	306	373	57	
4	[1,1′;5′,5″]ternaphthalene[e]	299			
5	[2,2′;6′,2″]ternaphthalene[d]	332	388		
6	rylene	440	434		
7	terylene	555	579		
8	**2**	368	396	39	1.13
9	**9**	404	439	28	0.97
10	**18**	420	463	60	
11	**19**	427	468	58	
12	**4**	348	389	41	1.23
13	**6**	348	396	45	
14	**12**	395	426	83	1.03
15	**22**	393	432	74	
16	**25** (impure)	413	450		

[a] All optical measurements for LON derivatives were carried out in chloroform solution ($\approx 10^{-5}$ M) at RT. [b] Quantum yields were determined by using coumarin 6 dye as the standard. [c] CV measurements were carried out in CH_2Cl_2 solution with $TBAPF_6$ as the supporting electrolyte. $Ag/AgNO_3$ electrode was used as the reference electrode. [d] Chromophores were attached to pentose. See ref. [8d]. [e] Dialkyl derivative. See ref. [8e,f].

2952, 2870, 1627, 1461, 1428, 1306, 812, 735 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{36}H_{36}NO$: 498.2797 [$M+H^+$]; found: 498.2798.

Naphthalen-1-yl-(4-trifluoromethylphenyl)-methanone (23): A THF solution of 4-bromobenzotrifluoride (1.5 g, 6.7 mmol in 20 mL) was cooled to −78 °C and to this chilled solution was added *n*BuLi (2.65 mL, 2.5 M in hexane, 6.7 mmol). After the reaction was stirred at low temperature for 1 h, a THF solution of 1-naphthaldehyde (0.95 g, 6.1 mmol in 5 mL) was slowly added to the mixture. The reaction was then warmed back to RT and stirred for 1 h before being quenched with saturated NH_4Cl solution. The THF was removed by using a rotary evaporator and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. The crude alcohol thus obtained (1.7 g) was directly dissolved in CH_2Cl_2 (30 mL) with pyridinium chlorochromate (1.95 g, 9.02 mmol) and stirred at RT for 2 h. The chromium-containing side products were removed by a short column. Pure **23** (1.6 g, 88%) was obtained by performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:2.5). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.50$–7.60 (m, 4H), 7.73 (d. $J = 8.1$ Hz, 1H), 7.93–7.96 (m, 2H), 7.97 (s, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 8.14–8.18 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 124.26$, 125.42, 125.46, 125.48, 125.49, 125.53, 126.69, 127.65, 128.51, 128.53, 130.56, 130.86, 132.10, 133.79, 134.33 (q, $J = 33$ Hz, CF_3), 135.24, 141.32, 196.75 ppm; IR (KBr): $\tilde{\nu} = 3060$, 1664, 1325, 1282, 1250, 1171, 1130, 1066, 781 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{18}H_{12}F_3O$: 301.0840 [$M+H^+$]; found: 301.0837.

4-(Methoxydinaphthalen-1-yl-methyl)-α,α,α-trifluorotoluene (5): A THF solution of 1-bromonaphthalene (0.18 g, 0.87 mmol in 20 mL) was cooled to −78 °C and to this chilled solution was slowly added *n*BuLi (0.35 mL, 2.5 M in hexane, 0.88 mmol). The exchange reaction was allowed to proceed for 1 h at low temperature before a THF solution of **23** (0.23 g, 0.77 mmol in 5 mL) was added. The reaction was warmed back to RT and stirred for another hour before being quenched with saturated NH_4Cl solution. THF was removed by using a rotary evaporator and the residual mixture was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated. The crude alcohol (0.33 g) was dissolved in THF (25 mL) and to this solution was added MeI (0.15 mL, 2.4 mmol) and NaH (0.1 g, 60% dispersed in mineral oil, 2.5 mmol). The reaction was stirred for 16 h at RT before being quenched with saturated NH_4Cl solution. The THF was removed by using a rotary evaporator and the residual mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated. The crude ether product was purified by performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:4) to give pure **5** (0.29 g, 82%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 3.23$ (s, 3H), 7.19–7.29 (m, 6H), 7.35–7.37 (m, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.78–8.82 (m, 4H), 8.30 ppm (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 54.09$, 91.28, 124.37, 124.53, 124.57, 124.61, 125.40, 125.47, 128.22, 128.34, 128.65, 128.91, 129.53, 131.81, 134.75, 138.82, 147.79 ppm; IR (KBr): $\tilde{\nu} = 3048$, 2939, 1507, 1406, 1326, 1166, 1117, 1070, 799, 781 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{29}H_{21}F_3O$: 442.1544 [M^+]; found: 442.1549.

13-(4-Trifluoromethylphenyl)-13*H*-dibenzo[*a*,*i*]fluorine (6): In a round-bottomed flask, compound **5** (0.1 g, 0.22 mmol) was kept in a strict N_2 atmosphere before triflic acid (2 mL) was added. The reaction was stirred at RT for 5 min before being quenched with a deoxygenated 1.0 M $NaHCO_3$ solution. The product was extracted with CH_2Cl_2 and the combined organic phase was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:5) to give pure **6** as a white solid (0.56 g, 60%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 5.69$ (s, 1H), 7.31–7.38 (m, 6H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.79–7.82 (m, 2H), 7.85–7.88 (m, 2H), 7.93 (d, $J = 8.4$ Hz, 2H), 7.99 ppm (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 53.33$, 118.39, 125.22, 125.89 (q), 126.66, 128.97, 129.11, 129.18, 129.92, 133.33, 139.29, 143.93, 146.04 ppm; IR (KBr): $\tilde{\nu} = 3055$, 2922, 1517, 1324, 1164, 1121, 1068, 840, 808 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{28}H_{17}F_3$: 410.1282 [M^+]; found: 410.1273.

***N*,*N*-Dibutyl-4-iodobenzamide**: 4-Iodobenzoic acid (9.0 g, 36.28 mmol) and thionyl chloride (3.96 mL, 54.42 mmol) were dissolved in toluene (80 mL) and the solution was refluxed under a nitrogen atmosphere for 16 h. The volatiles were removed by using a rotary evaporator to give the crude 4-iodobenzoyl chloride. This intermediate was then dissolved in CH_2Cl_2 (40 mL) and to this solution was slowly added dibutyl amine (12.2 mL, 72.66 mmol) at 0 °C. The reaction was warmed back to RT at stirred for 2 h. The reaction solution was washed with water (4×) before being dried over $MgSO_4$ and concentrated. The crude product was then purified by performing flash chromatography (silica gel; CH_2Cl_2/hexane 8:1) to give the amide as a clear liquid (12.6 g, 96%). ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.78$–1.62 (m, 14H), 3.1–3.6 (m, bs, 4H), 7.05–7.08 (d, $J = 8$ Hz, 2H), 7.69–7.72 ppm (d, $J = 8$ Hz, 2H).

Bis-4,4′-(*N*,*N*-dibutylbenzamide)-(2,6-naphthalenediyldicarbonyl) (7): *N*,*N*-Dibutyl-4-iodobenzamide (2.92 g, 8.14 mmol) was dissolved in THF (20 mL) and the solution was cooled to 0 °C in an ice bath. Cyclopentylmagnesium bromide (1.3 M in THF, 6.88 mL, 8.95 mmol) was slowly added and the exchange reaction was stirred for 20 min. Powder of 2,6-naphthyl dialdehyde (0.5 g, 2.71 mmol) was added at this point. The reaction was allowed to proceed at RT for 1 h before quenched with saturated NH_4Cl solution. The volatiles were removed in vacuo and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to give the crude product. Without further purification, the crude diol was dissolved in CH_2Cl_2 and mixed with pyridinium chlorochromate (2.34 g, 10.84 mmol). The oxidation proceeded for 90 min and the reaction mixture was passed through a short silica-gel column to remove chromium side product. The pure product (1.12 g, 64%) was obtained by performing flash column chromatography (silica gel; CH_2Cl_2/diethyl ether 9:1). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.78$–1.65 (m, 28H), 3.18–3.53 (m, 8H), 7.49 (d, $J = 8.0$ Hz, 4H), 7.87 (d, $J = 8.0$ Hz, 4H), 7.97–8.03 (m, 4H), 8.28 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 13.58$, 13.86, 19.69, 20.22, 29.55, 30.76, 44.46, 48.68, 126.50, 126.53, 129.82, 130.12, 131.28, 134.11, 136.57, 137.76, 141.40, 170.41, 195.64 ppm; IR (KBr): $\tilde{\nu} = 2957$, 2935, 2871, 1660, 1632, 1286, 1266, 1113, 867, 734 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{42}H_{51}N_2O_4$: 647.3849 [$M+H^+$]; found: 647.3839.

Compound 8: A solution of 2-bromonaphthalene in THF (0.16 g, 0.77 mmol in 3 mL) was cooled to −78 °C and *n*BuLi (2.5 M in hexane, 0.31 mL, 0.77 mmol) was added slowly. The exchange reaction was stirred at low temperature for 1 h before another THF solution of **7** was added (0.20 g, 0.31 mmol in 4 mL). The reaction was warmed back to RT and

stirred for 1 h. Saturated NH_4Cl solution was added to quench the reaction and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 and the combined organic extracts were dried over $MgSO_4$ before being concentrated to give the crude diol. Without further purification, the crude intermediate was dissolved in THF (10 mL). To this solution was added CH_3I (0.1 mL, 1.62 mmol) and NaH (60% in mineral oil, 0.1 g, 2.50 mmol). After the alkylation reaction proceeded for 16 h, the excess NaH was quenched with saturated NH_4Cl solution and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by performing flash chromatography (silica gel; CH_2Cl_2/diethyl ether 15:1) to give pure **8** (0.11 g, 38%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 0.69–1.58 (m, 28H), 3.15 (s, 6H), 3.15–3.45 (m, 8H), 7.30 (d, J = 8.5 Hz, 4H), 7.31–7.48 (m, 8H), 7.55 (d, J = 8.5 Hz, 4H), 7.70–7.97 (m, 8H), 7.98 ppm (d, J = 9.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.46, 13.90, 19.60, 20.26, 29.67, 30.70, 44.45, 48.66, 52.44, 87.23, 126.08, 126.22, 126.95, 127.22, 127.42, 127.46, 127.61, 128.09, 128.38, 128.77, 131.84, 132.43, 132.81, 136.05, 140.64, 141.31, 144.60, 171.39 ppm; IR (KBr): $\tilde{\nu}$ = 2944, 2868, 1631, 1461, 1432, 1082, 816, 742, 481 cm^{-1}; HRMS: m/z: calcd for $C_{64}H_{71}N_2O_4$: 931.5414 [M+H$^+$]; found: 931.5405.

Compound 9: Under an inert atmosphere, compound **8** (0.10 g, 0.11 mmol) was dissolved in CF_3COOH (1 mL). After stirring for 5 min, the cyclization reaction was quenched with deoxygenated 1.0 M $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2 and the combined organic extracts were dried over $MgSO_4$ and concentrated. Purification was performed by performing flash chromatography (CH_2Cl_2) to give **9** (91 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.75–1.58 (m, 28H), 3.20–3.44 (m, 8H), 5.25 (s, 2H), 7.17 (m, J = 8 Hz, 4H), 7.24–7.29 (m, 4H), 7.45–7.60 (m, 8H), 7.85 (d, J = 8 Hz, 2H), 7.98 (dd, J = 1.2, 8 Hz, 2H), 8.62–8.65 (m, 2H), 8.76 ppm (d, J = 8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 13.55, 13.89, 19.67, 20.27, 29.69, 30.75, 44.54, 48.73, 55.61, 121.33, 121.43, 122.87, 125.33, 126.81, 126.85, 127.06, 127.13, 128.45, 128.59, 128.63, 128.89, 129.95, 134.23, 136.16, 137.84, 137.92, 138.25, 138.36, 141.39, 146.46, 147.38, 147.50, 171.48 ppm; IR (KBr): $\tilde{\nu}$ = 2957, 2927, 2864, 1631, 1465, 1428, 809, 750 cm^{-1}; HRMS: m/z: calcd for $C_{62}H_{63}N_2O_2$: 867.4890 [M+H$^+$]; found: 867.4884.

Bis-4,4′-(*N*,*N*-dibutylbenzamide)-(1,5-naphthalenediyldicarbonyl) (10): Under a nitrogen atmosphere a THF solution *N*,*N*-dibutyl-4-iodobenzamide (2.92 g, 8.14 mmol in 20 mL) was immersed in an ice bath and cyclopentylmagnesium bromide (1.3 M in THF, 6.88 mL, 8.95 mmol) was slowly added. The exchange reaction was stirred for 20 min before powder of compound 1,5-naphthyl dialdehyde (0.5 g, 2.71 mmol) was added. The reaction was stirred at RT for 1 h before being quenched with NH_4Cl solution. The THF and other volatiles were removed in vacuo and the residue was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated to give the crude diol.

The subsequent oxidation was carried out with the unpurified diol in CH_2Cl_2 solution (70 mL) with pyridinium chlorochromate (2.34 g, 10.84 mmol) as the oxidant. The oxidation was accomplished in 2 h and the chromium(III) side products were removed by passing the reaction mixture through a short silica-gel column. Pure compound **10** (1.08 g, 62%) was obtained by performing further flash chromatography (silica gel; CH_2Cl_2/diethyl ether 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.76–1.62 (m, 28H), 3.14–3.50 (m, 8H), 7.43 (d, J = 8.0 Hz, 4H), 7.54 (t, J = 7.9 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 7.88 (d, J = 8.0 Hz, 4H), 8.24 ppm (d, J = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 13.61, 13.90, 19.75, 20.28, 29.60, 30.80, 44.52, 48.71, 125.83, 126.66, 128.29, 128.95, 130.57, 131.16, 136.48, 138.29, 142.18, 170.40, 197.04 ppm; IR (KBr): $\tilde{\nu}$ = 2958, 2928, 2872, 1663, 1635, 1273, 981, 796 cm^{-1}; HRMS: m/z: calcd for $C_{42}H_{51}N_2O_4$: 647.3849 [M+H$^+$]; found: 647.3841.

Compound 11: To a THF solution of 1-bromonapthalene (0.22 g, 1.07 mmol in 3 mL) was slowly added *n*BuLi solution (2.5 M in hexane, 0.43 mL, 1.07 mmol) at −78 °C. The exchange reaction was finished after 1 h. A THF solution of **10** (0.5 g, 1.72 mmol in 5 mL) was slowly added before the reaction was warmed back to RT and stirred for another 1 h. The reaction was quenched with saturated NH_4Cl. The volatiles were removed in vacuo and the residual mixture was extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and concentrated to give the crude diol.

The methylation was carried out as in the synthesis of **8** in THF (10 mL) with NaH and CH_3I (0.1 g, 2.50 mmol and 0.10 mL, 1.61 mmol, respectively). After the established work-up procedure, the desired product (95 mg, 22%) was isolated as a mixture of two diastereomers by performing flash chromatography (silica gel; CH_2Cl_2/diethyl ether 8:1). HRMS: m/z: calcd for $C_{64}H_{71}N_2O_4$: 931.5414 [M+H$^+$]; found: 931.5416. For other spectroscopic data, see Supporting Information.

Compound 12: Under an inert atmosphere, compound **11** was dissolved (0.12 g, 0.13 mmol) in trifilic acid (1 mL) and the cyclization reaction was allowed to proceed for 5 min before the reaction was quenched with deoxygenated 1.0 M $NaHCO_3$ solution. The reaction mixture was extracted with CH_2Cl_2 before the combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. Pure product (0.10 g, 93%) was isolated as a mixture of two diastereomers by performing flash chromatography (CH_2Cl_2). HRMS: m/z: calcd for $C_{62}H_{63}N_2O_2$: 867.4890 [M+H$^+$]; found: 867.4877. For other spectroscopic data, see Supporting Information.

Compound 13: A THF solution of 2,6-dibromonaphthalene (0.53 g, 1.85 mmol in 16 mL) was cooled to −78 °C and to this solution *n*BuLi (1.6 M in hexane, 1.27 mL, 2.03 mmol) was slowly added. After the exchange reaction proceeded for 1 h, a THF solution of **15** (0.72 g. 1.85 mmol in 7 mL) was added dropwise. The reaction was then warmed back to RT and stirred for another 60 min before being quenched with saturated NH_4Cl solution. The volatiles were removed in vacuo and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to give the crude alcohol. Without further purification, the crude mixture was dissolved in THF solution (15 mL) and CH_3I (0.31 mL, 1.62 mmol) and NaH (60% in mineral oil, 0.12 g, 3.00 mmol) were added to fulfil the methylation. After being stirred for 3 h at RT, the reaction was quenched with saturated NH_4Cl solution and the solvent was evaporated in vacuo. The remaining mixture was extracted with CH_2Cl_2 several times and the combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by performing flash column chromatography (CH_2Cl_2) to give **13** (0.53 g, 48%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 0.68–1.60 (m, 14H), 3.15 (s, 3H), 3.15–3.46 (m, 4H), 7.32 (d, J = 8 Hz, 2H), 7.45–7.47 (m, 3H), 7.53 (m, 4H), 7.65 (dd, J = 1.2, 8 Hz, 2H), 7.76–7.81 (m, 3H), 7.94–7.97 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.40, 13.87, 19.56, 20.23, 29.63, 30.66, 44.45, 48.62, 52.43, 87.12, 120.13, 126.13, 126.18, 126.24, 126.29, 126.64, 126.87, 127.10, 127.41, 127.55, 127.66, 127.91, 128.35, 128.76, 129.43, 129.99, 131.25, 131.45, 132.44, 132.78, 133.43, 136.15, 140.26, 141.61, 144.26, 171.33 ppm; IR (KBr): $\tilde{\nu}$ = 2955, 2932, 2868, 1630, 1461, 1428, 1078, 812, 743, 477 cm^{-1}; HRMS: m/z: calcd for $C_{37}H_{39}{}^{79}BrNO_2$: 608.2164 [$M$+H$^+$]; found: 608.2167.

***N*,*N*-Dibutyl-4-(naphthalene-2-carbonyl)-benzamide (15)**: *N*,*N*-Dibutyl-4-iodobenzamide (3.24 g, 9.02 mmol) was dissolved in THF (30 mL) and to this solution was slowly added cyclopentylmagnesium bromide (1.0 M in THF, 10 mL, 10.00 mmol). The exchange reaction was allowed to proceed for 20 min and a THF solution of 2-naphthaldehyde (1.30 g, 8.32 mmol in 30 mL) was added. The reaction was stirred at RT for 1 h before being quenched with saturated NH_4Cl solution. The volatiles were removed in vacuo and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to furnish the crude alcohol that underwent subsequent oxidation without further purification.

The crude alcohol was dissolved in CH_2Cl_2 (50 mL) and to this solution was added pyridinium chlorochromate (3.89 g, 18.04 mmol). The reaction was stirred at RT for 50 min and the mixture was passed through a short silica-gel column to remove chromium side products. Flash column chromatography (silica gel; CH_2Cl_2/hexane 8:1) was performed and yielded **15** (2.40 g, 82%) as an amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.77–1.65 (m, 14H), 3.17–3.52 (m, 4H), 7.48 (d, J = 8 Hz, 2H), 7.53–7.62 (m, 2H), 7.84–7.93 (m, 6H), 8.22 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.63, 13.91, 19.74, 20.28, 29.61, 30.82, 44.50, 48.73, 125.53, 126.42, 126.91, 127.80, 128.44, 128.51, 129.46, 130.11, 132.17, 132.21, 134.41, 135.36, 138.36, 141.08, 170.63, 196.21 ppm; IR (KBr): $\tilde{\nu}$ = 2957, 2931, 2871, 1656, 1631, 1465, 1428, 1292, 783, 753,

477 cm^{-1}; HRMS: *m/z*: calcd for $C_{26}H_{30}NO_2$: 388.2277 [$M+H^+$]; found: 388.2277.

Compound 16: A THF solution of 2,6-dibromonaphthalene (0.59 g, 2.06 mmol in 10 mL) was cooled to −78 °C and to this solution was slowly added *n*BuLi (2.5 M in hexane, 0.88 mL, 2.20 mmol). The exchange reaction was stirred at low temperature for 1 h and a THF solution of **15** (0.31 g, 1.06 mmol in 30 mL) was added. The reaction was then warmed back to RT and stirred for 40 min to furnish the double addition. The reaction vessel was re-cooled to −78 °C and another portion of *n*BuLi was slowly added (2.5 M in hexane, 0.88 mL, 2.20 mmol). The double-exchange reaction was stirred at low temperature for 40 min before a THF solution of **14** (0.80 g, 2.06 mmol in 6 mL) was slowly added. The reaction was warmed back to RT and stirred for 40 min before being quenched with saturated NH_4Cl solution. The volatiles were evaporated by using a rotary evaporator and the residue was extracted with CH_2Cl_2 several times. The combined organic extracts were dried over $MgSO_4$ and concentrated to give the triol crude intermediate. The crude product was dissolved in THF (15 mL) and to this solution were added CH_3I (0.39 mL, 6.18 mmol) and NaH (60% mixture in mineral oil, 0.15 g, 3.75 mmol). The reaction was stirred for 16 h before being worked-up by the same procedure as before. Pure product **16** (0.53 g, 18%) was then isolated by performing flash chromatography (silica gel; CH_2Cl_2/diethyl ether 8:1). ESI-LRMS: calcd for $C_{91}H_{102}N_3O_6$: 1332.78 [$M+H^+$]; found: 1333.35. For additional spectroscopic data, see Supporting Information.

Compound 18: Under an inert atmosphere, compound **16** (48 mg, 0.04 mmol) was dissolved in triflic acid (0.5 mL) at RT. The cyclization reaction was completed in 5 min and quenched with an deoxygenated $NaHCO_3$ aqueous solution. The resulting mixture was extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$ and concentrated. Pure **18** (28 mg, 52%) was obtained as an amorphous solid by performing flash column chromatography (silica gel; CH_2Cl_2/diethyl ether 10:1). HRMS: *m/z*: calcd for $C_{88}H_{89}N_3O_3$: 1235.6904 [M^+]; found: 1235.6923. For additional spectroscopic data, see Supporting Information.

Compound 17: A solution of 2,6-dibromonaphthalene in THF (0.70 g, 2.45 mmol in 20 L) was cooled to −78 °C and to this solution was slowly added *n*BuLi (2.5 M in hexane, 1.02 mL, 2.56 mmol). After the exchange reaction proceeded for 1 h, a THF solution of **14** (0.69 g, 1.07 mmol in 10 mL) was slowly added. The reaction mixture was then warmed back to RT and stirred for 40 min for the completion of the double addition. The reaction flask was then re-cooled to −78 °C and another portion of *n*BuLi (2.5 M in hexane, 0.98 mL, 2.45 mmol) was added. After the double-exchange reaction was completed in 30 min, a THF solution of **13** (0.95 g, 2.45 mmol in 10 mL) was slowly added. The reaction was then warmed back to RT and stirred for 40 min before being quenched with saturated NH_4Cl solution. The solvent was removed in vacuo and the remaining mixture was extracted with CH_2Cl_2 several times. The combined organic extracts were dried over $MgSO_4$ and concentrated to furnish the crude product. To this crude tetrahydroxy mixture was added THF (15 mL), CH_3I (0.54 mL, 8.56 mmol) and NaH (60% in mineral oil, 0.21 g, 5.25 mmol) to carry out the methylation. After stirring for 16 h at RT, the reaction was worked-up as in the previous step. Pure tetramethylether **17** (0.22 g, 12%) was obtained by performing flash column chromatography (silica gel; CH_2Cl_2/diethyl ether 10:1). ESI-LRMS [$M+H^+$] calcd for $C_{118}C_{133}N_4O_8$: 1734.01; found: 1734.60. For additional spectroscopic data, see Supporting Information.

Compound 19: Under an inert atmosphere, compound **17** (78 mg, 0.04 mmol) was dissolved in triflic acid (0.7 mL). The cyclization reaction was stirred at RT for 5 min before being quenched with deoxygenated 1.0 M $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. Purification was carried out by performing flash column chromatography (silica gel; CH_2Cl_2/diethyl ether 5:1) to give **19** as an amorphous solid (30 mg, 47%). HRMS: *m/z*: calcd for $C_{114}H_{117}N_4O_4$: 1605.9075 [$M+H^+$]; found: 1605.9071. For additional spectroscopic data, see Supporting Information.

Bis-4,4′-(α,α,α-trifluorotoluene)-(1,5-naphthalenediyldicarbonyl) (20): A THF solution of 4-bromobenzotrifluoride (1.5 g, 6.7 mmol in 25 mL) was cooled to −78 °C and to this chilled solution was slowly added *n*BuLi (2.65 mL, 2.5 M in hexane, 6.67 mmol). The reaction was kept at low temperature for 1 h before a THF solution of 1,5-diformyl naphthalene (0.55 g, 2.9 mmol in 5 mL) was slowly added. The reaction was then warmed back to RT and stirred for another 60 min before being quenched with saturated NH_4Cl solution. After the THF was removed by using a rotary evaporator, the remaining mixture was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated. The crude diol thus obtained (1.5 g) was mixed with pyridinium chlorochromate (1.7 g, 7.93 mmol) in CH_2Cl_2 (30 mL) and the reaction was stirred at RT for 2 h. The chromium side products were removed by a short silica-gel column and the pure diketone product (1.13 g, 80%) was obtained by performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:1.5). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.57$ (dd, $J = 7.8$, 7.0 Hz, 2H), 7.62 (dd, $J = 7.0$, 1.0 Hz, 2H), 7.74 (d, $J = 8.1$ Hz, 4H), 7.97 (d, $J = 8.1$ Hz, 4H), 8.32 ppm (dd, $J = 7.8$, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 125.62$, 125.65, 125.99, 128.77, 129.25, 130.63, 131.26, 134.71 (q, $J = 33$ Hz, CF_3), 135.95, 140.94, 196.36 ppm; IR (KBr): $\tilde{\nu} = 3048$, 1659, 1322, 1162, 1126, 1064, 857, 795, 772 cm^{-1}; HRMS: *m/z*: calcd for $C_{26}H_{15}F_6O_2$: 473.0976 [$M+H^+$]; found: 473.0975.

Compound 21: A THF solution of 1-bromonaphthalene (0.8 g, 3.88 mmol in 30 mL) was cooled to −78 °C and to this solution was slowly added *n*BuLi (1.55 mL, 2.5 M in hexane, 3.88 mmol). The exchange reaction was stirred at low temperature for 1 h before a THF solution of **20** (0.8 g, 1.70 mmol in 5 mL) was added. The reaction was then warmed back to RT and stirred for 1 h before being quenched with saturated NH_4Cl. THF was removed by using a rotary evaporator and the residue was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $NaSO_4$. The crude diol (1.3 g) was dissolved in THF (30 mL) and to this was added NaH (0.35 g, 60% dispersed in mineral oil, 4.7 mmol) and MeI (0.55 mL, 81 mmol). The reaction was stirred at RT for 16 h before being quenched with saturated NH_4CL solution. THF was again removed by using the rotary evaporator and the residual mixture was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated. The crude **21** was purified by performing flash chromatography (silica gel; CH_2Cl_2/hexane 2:5) to give pure product (0.64 g, 50%). HRMS: *m/z*: calcd for $C_{48}H_{34}F_6O_2$: 756.2463 [M^+]; found: 756.2451. For additional spectroscopic data, see Supporting Information.

Compound 22: In an oxygen-free atmosphere, compound **21** (0.2 g, 0.26 mmol) was dissolved in triflic acid (4 mL) at RT. The reaction was neutralized with deoxygenated 1.0 M $NaHCO_3$ solution (20 mL) after 5 min. The mixture was then extracted with CH_2Cl_2 and the combined organic phase was dried over anhydrous $MgSO_4$ and concentrated. Pure **22** (0.07 g, 40%) was obtained by performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:3). The ^1H NMR spectrum indicates only one isomer present. HRMS: *m/z*: calcd for $C_{46}H_{26}F_6$: 692.1939 [M^+]; found: 692.19380. For additional spectroscopic data, see Supporting Information.

Compound 24: A THF solution of 1,5-dibromonaphthalene (1.05 g, 3.67 mmol in 30 mL) was cooled to −78 °C and to this solution was slowly added *n*BuLi (1.46 mL, 2.5 M in hexane, 3.67 mmol). The reaction was stirred at low temperature for 1 h before a THF solution of **23** (1.00 g, 3.32 mmol in 5 mL) was added. The reaction was warmed back to RT and stirred for 60 min before being cooled to −78 °C again. Another portion of *n*BuLi (1.46 mL, 2.5 M in hexane, 3.67 mmol) was then slowly added and the reaction was stirred for another hour. THF solution of 4-trifluoromethyl benzoyl chloride (0.35 g, 1.68 mmol in 5 mL) was added before the reaction was again warmed back to RT and stirred for 1 h. The reaction was quenched with saturated NH_4Cl and the THF was evaporated by using a rotary evaporator. The residue was then extracted with CH_2Cl_2 and the combined organic phase was dried over anhydrous $NaSO_4$ and concentrated. Purification was carried out by performing flash chromatography to give triol **24** (1.2 g, 70%). HRMS: *m/z*: calcd for $C_{64}H_{41}F_9O_3$: 1028.2912 [M^+]; found: 1028.2902. For additional spectroscopic data, see Supporting Information.

Compound 24′: Compound **24** (0.5 g, 0.48 mmol) was dissolved in THF (30 mL) and to this solution was added MeI (0.28 mL, 4.8 mmol) and NaH (0.19 g, 60% dispersed in mineral oil, 7.9 mmol). The reaction was

stirred at RT for 16 h before being quenched with saturated NH_4Cl solution. The residual mixture was extracted with CH_2Cl_2 and the combined organic phase was dried over anhydrous $MgSO_4$ and concentrated. Pure triether product **24′** (0.44 g, 85%) was obtained by performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:3.5). HRMS: *m*/*z*: calcd for $C_{67}H_{47}F_9O_3$: 1070.3381 [M^+]; found: 1070.3372. For additional spectroscopic data, see Supporting Information.

Compound 25: To deoxygenated triflic acid (25 mL) was slowly added a CH_2Cl_2 solution of **24** (0.5 g, 0.48 mmol in 0.8 mL). After being stirred for 5 min at RT, the reaction was quenched with 1.0 M deoxygenated $NaHCO_3$ solution (40 mL). The mixture was then extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$ and concentrated. By performing flash chromatography (silica gel; CH_2Cl_2/hexane 1:5), the desired product **25** (0.05 g, 10%, impure by NMR) was isolated with some unidentified contaminants. HRMS: *m*/*z*: calcd for $C_{64}H_{35}F_9$: 974.2595 [M^+]; found: 974.2603. For additional spectroscopic data, see Supporting Information.

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