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Synthesis and Molecular Structure of Symmetrical 1,8-Diarylnaphthalenes

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The synthesis of substituted 1,8-diarylnaphthalenes is reported. A bis-Suzuki coupling strategy starting from 1,8-dibromonaphthalene provides a useful and general route to the 1,8-diarylnaphthalene scaffold. In this context, N-heterocyclic benzhydrylamine ligands, in combination with $PdCl_2$, were found to form especially efficient catalytic systems. The *syn*/*anti* ratios were determined in solution from their ^1H NMR spectra. Analysis of the molecular structure in the solid state for six new targets focused on deformation of the naphthalene core. The observed lack of planarity occurs as a result of several parameters, such as the nature and number of substituents, the substitution pattern as well as steric congestion and π-stacking between cofacial rings.

Introduction

The 1,8-diarylnaphthalene scaffold is a fascinating example of unusual geometry in organic molecules. Introduction of two aromatic groups into both peri-positions of the naphthalene core causes severe repulsion between the stacked rings. This unique topology is not only due to the nature of the aromatics but also to the presence of additional substituents and their substitution pattern.[1] Generation of steric compression at the rings, which are constrained to face each other, may generate structural deformations such as non-planarity of the almost perpendicular naphthalene skeleton.[2] Since the first synthesis of 1,8-bis(2,2′-dimethyl-1,1′-diphenyl)naphthalene by Clough and Roberts,[3] several groups have described its syntheses and analyses, for example, the *anti*/*syn* isomerization of such motifs.[1a,4] Recently, some appealing applications have taken advantage of the difficult or impossible rotations of the aryl rings along the naphthalene axis. Indeed, 1,8-diacridyl-, 1,8-diquinolyl-, or 1,8-dipyridyl-naphthalenes have been developed as promising candidates for new photoluminescent or chiral sensors and stereodynamic switches.[1a,5] In addition, π-stacking between cofacial aromatics were found to be essential in 1,8-diarylnaphthalene-based nonlinear optic chromophores or abiotic hydrid oligoamides.[6] Blue-transparent frequency-doubling devices incorporating thienyl, oligothienyl, or mixed pyridyl–thienyl branched naphthalenes have also been recently reported.[7] Strong π–π interactions have been characterized in cyclic oligophenylenes containing two 1,8-diarylnaphthalene subunits.[8] Cofacially arranged mono- or polymeric metal sandwich complexes have also attracted interest for their electrical, optical, and magnetic properties.[9] Moreover, the pillared 1,8-diarylnaphthalene motif has been used to elaborate cofacial salen-type ligands and their corresponding Mn complexes.[10] More recently, we described a short route to 6,11-diamino[6]carbohelicenes starting from 1,8-diarylnaphthalene.[11]

Thus, steric and electronic interactions between two cofacial aromatics as well as the substitution pattern are not only essential to the aforementioned applications, but also deeply impact the preparation of 1,8-diarylnaphthalenes. Most of these molecules are obtained through metal-assisted carbon–carbon bond formation. Ni- and Cu- followed by Pd-based catalytic systems have successively been used to transform 1,8-dihalonaphthalenes into the expected 1,8-diarylnaphthalenes (Figure 1).[1–11,12]

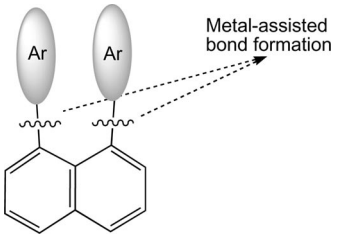

Figure 1. Metal-assisted preparation of 1,8-diarylnaphthalenes.

These cross-coupling reactions, which have been reported to be sensitive to the nature and steric bulk of both partners, often afford mixtures of bis- or monocoupling products. Suzuki- and Stille-type couplings are most commonly employed, with the latter being recently found to be superior for highly congested partners. High yields in the cou-

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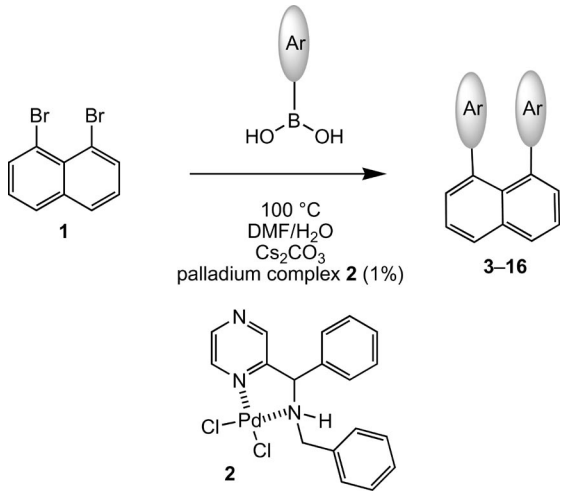
pling may be obtained by using: (i) diiodonaphthalene derivatives; in this case the practicality of the overall process is somewhat hampered by their tedious preparation; (ii) dibromonaphthalenes, which require 5 to 30% catalyst loadings to ensure completion of coupling reactions. In addition, both these procedures suffer from lack of generality.

Further developments and new potential applications of 1,8-diarylnaphthalenes require reliable and convenient preparative methods that (i) allow access to variously substituted targets regardless of the nature and position of the substituents; (ii) take into account the availability of the starting materials; (iii) use easy-to-handle catalyst; (iv) require low catalyst loadings. We first report in this paper the preparation of new 1,8-diarylnaphthalenes from dibromonaphthalene (**1**) through Suzuki type coupling reactions using a phosphane-free catalytic system. The ease of access to the starting material and the wide range of commercially available boronic acids appears to favor this alternative approach. In addition, we recently described the preparation of new nitrogen-based palladium(II) complexes that were found to be stable and highly efficient in the syntheses of biphenyls.[13] In the second part of this paper, we report the results of our investigations into the molecular structure of 1,8-diarylnaphthalenes by means of ^{1}H NMR and X-ray analysis, with particular emphasis on the deformation of the naphthalene core.

Results and Discussion

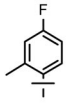
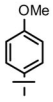
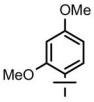
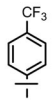
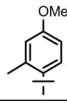
Synthesis

Most of the Pd-catalyzed reactions described in the literature for the synthesis of 1,8-diarylnaphthalene derivatives involve the use of phosphane ligands. However, as described above, those experimental conditions did not give satisfactory results. This prompted us to use a phosphane-free catalytic system (Scheme 1, Table 1).[14] Indeed, 1,8-dibromonaphthalene was coupled to a series of commercially available boronic acids under Suzuki conditions in the presence of cesium carbonate and 1% palladium(II) complex **2**[13] in *N*,*N*-dimethylformamide (DMF)/water (95:5), which led to the corresponding diarylnaphthalenes in good isolated yields. Table 1 summarizes the results obtained under the aforementioned conditions. The coupling reaction proceeded smoothly with most of the tested phenyl boronic acids, even with *ortho*-substituted derivatives. Better yields were observed with boronic acids bearing electron-donating groups (Table 1, entries 2, 3, 5, 7, 9, and 10). Indeed, the presence of the corresponding monocoupling product was only detected when the phenyl boronic acid was substituted with an electron-withdrawing group (Table 1, entries 4, 6, 8, and 13). Nevertheless, the electronic effects alone do not completely explain the observed difference in yields. The steric bulk of the boronic partners may also be responsible for lower yields. However, even with 4-trifluoromethylphenylboronic acid or 3-nitrophenylboronic acid, the bis-coupling products **6** and **8** were isolated with acceptable 60 and 65% yields. Furthermore, when the Suzuki reaction was performed with a very bulky boronic acid, such as naphthylboronic acid, the the bis-coupling product **14** could be obtained in 65% yield. Employing heterocyclic boronic acid derivatives in the reaction appeared to be less versatile. Indeed, the 1,8-di(3-thienyl)naphthalene was isolated in 73% yield, whereas no coupling reaction occurred with pyridinyl boronic acids. This result may be due to a possible decomplexation process that operates with the benzhydrylamine ligand during the catalytic coupling reaction.



Scheme 1. Synthesis of 1,8-diarylnaphthalenes **3**–**16**.

Table 1. Suzuki coupling products.

Entry	Ar HO·B·OH	Ar Ar (%)[a]	Entry	Ar HO·B·OH	Ar Ar (%)[a]
1		**3** (80)	8		**10** (68)
2		**4** (80)	9		**11** (64)
3		**5**(85)	10		**12** (83)
4		**6** (60)	11		**13** (70)
5		**7** (86)	12		**14** (65)
6		**8** (65)	13		**15** (62)
7		**9** (85)	14		**16** (73)

[a] Isolated yield.

Molecular Structures

Since applications in various fields of current research require the positioning of the cofacial rings to be almost perpendicular to the naphthalene axis, deformation of the naphthalene core may hamper further uses. The causes of such deformation ate thus of considerable interest. The deformation of naphthalene planarity may arise from: (i) the distance between the cofacial rings as a result of either π–π or steric repulsive interactions; (ii) the number, nature, and substitution position of additional substituents; (iii) the presence of *syn* and/or *anti* conformers. The influence of these parameters on the deformation of the naphthalene core, which can be determined X-ray and, to a lesser extent, by ^{1}H NMR analysis, has thus been determined and is discussed herein. To this end, the molecular structures of six 1,8-diarylnaphthalenes have been determined by X-ray structure analysis and the degree of naphthalene core deformation is compared.

Structures in Solution

^{1}H NMR analysis may be useful to determine the *anti*/*syn* ratio. However, the ease with which such information can be obtained is strongly dependent on the nature and position of additional probes, such as methyl groups. As shown below, we were able to gain such information for 1,8-naphthalenes **4**, **9**–**12**, and **14**–**15**. In contrast, careful analyses of the ^{1}H NMR spectra for compounds **8** and **13**, did not allow the *anti*/*syn* ratios to be determined even under a range of temperature conditions. The ^{1}H NMR spectroscopic data for 1,8-diarylnaphthalene **4** showed characteristic features, and the observed privileged conformers is noteworthy. As expected, both *syn* (minor, δ = 1.87 ppm for CH_3) and *anti* (major, δ = 1.84 ppm for CH_3) conformers were observed in a 22:78 ratio. The latter combined both "in" and "out" forms as shown in Figure 2.[3]

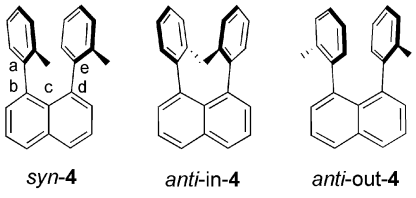


Figure 2. Compound **4**, *syn* and *anti* conformers.

Table 2 summarizes the *anti*/*syn* ratios determined from the ^{1}H NMR spectra, which are in agreement with a thermodynamically favored *anti* conformer in all cases. The *anti*/*syn* ratios were determined by integration of the methyl and methoxy group signals and, when possible, characteristic naphthyl protons. Comparison of the *anti*/*syn* ratios for compounds **4** and **9**–**10** revealed little influence of the *para*-substituent; in these compounds the ratios ranged from 74:26 to 79:21 regardless of the nature of the substituent, indicating that only the *ortho*-methyl group affected the *anti*/*syn* distribution. Interestingly, moving from a *para*- to a *meta*-fluoro-substitution pattern in **10** and **15**, respectively, significantly increased the *anti*/*syn* ratio. The 86:14 ratio observed in the latter case, may be attributed to an increased steric repulsion between the electronically "hard" *meta*-fluorine substituents on each of the cofacial aromatics. Switching from *ortho*-methyl to *ortho*-methoxy groups led to a similar increase in the *anti*/*syn* ratio from 74:26 (**9**) to 90:10 (**11** and **12**). Within this mixture, the *anti* conformer should be favored, in agreement with the ratio determined above.

Table 2. The *anti*/*syn* ratios in solution for compounds **4**, **9**–**12**, and **14**–**15**.

Entry		*anti*/*syn* ratio (T = 20 °C)	Probe	Characteristic ^{1}H NMR shift δ (*anti*)	δ (*syn*)
1	**4**	78:22	CH_3	1.89	1.92
2	**9**	74:26	CH_3	1.79	1.86
3	**10**	79:21	CH_3	1.80	1.85
4	**11**	90:10	OCH_3	3.47	3.79, 3.56
5	**12**	90:10	OCH_3	3.45	3.53
6	**14**	82:18	Ar(H)	6.95	6.75
7	**15**	86:14	CH_3	1.86	1.83

Finally, we succeeded in the determination of the *anti*/*syn* ratio for compound **14**, bearing two cofacial 1-naphthyl units (entry 6). As previously described,[15] in comparison with compound **4** the presence of bulky naphthyl rings did not significantly affect the *anti*/*syn* ratio (entry 6). The 82:18 *anti*/*syn* ratio calculated from the ^{1}H NMR spectra may result from a compromise between an overall increase in the bulk of the cofacial rings and a decrease in the hybridization order from an sp^3-C (methyl in **4**) to an sp^2-C (aromatic in **14**).

Structures in the Solid State

Slow evaporation of solutions of **4**, **6**, **7**, **11**, **13**, and **14** afforded suitable crystals that were subjected to X-ray analysis. Selected data (crystallization space group, the conformer present in the cell unit, bond lengths, and π–π interactions) are gathered in Tables 3 and 4.

Table 3. Space group and conformer observed in the solid state.

Entry		Space group	Conformer
1	**4**	$P2_1/c$	*syn*
2	**7**	$P\bar{1}$	–
3	**14**	*Ibca*	*anti*
4	**11**	$P2_1/c$	*anti*
5	**13**	$P2_1/c$	*syn*
6	**6**	$P2_1/n$	–

Table 4. Bond lengths and π–π interactions.

Entry		Bond lengths [Å] C(a)–C(b)	C(b)–C(c)	C(c)–C(d)	C(d)–C(e)	π–π interaction [Å]
1	**4**	1.507	1.439	1.467	1.511	3.66
2	**7**	1.492	1.441	1.441	1.492	3.52
3	**14**	1.497	1.439	1.439	1.497	3.49
4	**11**	1.500	1.435	1.438	1.500	3.51
5	**13**	1.490	1.440	1.444	1.485	3.46
6	**13**	1.490	1.441	1.441	1.488	3.46
7	**6**	1.489	1.439	1.439	1.490	3.60

Careful examination of the X-ray data revealed a number of features that deserves some comment: (i) compounds **4**, **6**, **7**, **11**, **13**, and **14** do not crystallize in the same space group; compounds **4**, **11**, and **13** crystallize in monoclinic $P2_1/c$ space group, whereas compounds **7** and **14** crystallize in $P\bar{1}$ and Ibca space groups, respectively. (ii) An examination of the cell units and packing revealed the presence of one or more conformers. Unexpectedly, in the case of compound **4**, initial analysis of the X-ray data showed the sole presence of the minor *syn*-**4** conformer, indicating a selective crystallization process (Figure 3). Unfortunately, extensive attempts to obtain suitable crystals of the *anti* conformer failed. In contrast, only the *anti*-in conformer was observed for diarylnaphthalenes **14** and **11**. The crystal structure of **13**, in which the naphthalene bears two cofacial 2-naphthalenyl groups, exhibits two *syn* conformers. (iii) Table 4 summarizes selected bond lengths C(a)–C(b), C(b)–C(c), C(c)–C(d), and C(d)–C(e) (see Figure 2 for atom labels), which may be affected by the steric compression at the cofacial rings. It is worth noting that bond lengths C(a)–C(b) and C(d)–C(e) are almost identical in the same molecule, regardless of the conformation and the nature of the substituents. Symmetrical diarylnaphthalenes **7** and **6** as well as *anti* conformers **14** and **11** exhibit identical C(b)–C(c) and C(c)–C(d) bond lengths, which may be explained by mean of symmetry and homogeneous spreading of both repulsion and steric compression over the naphthalene core. In contrast, a marked difference in bond lengths [C(b)–C(c) (1.439 Å) compared to C(c)–C(d) (1.467 Å)] is observed in *syn*-**4**. In this case, an increase in the steric congestion, combined with the *syn* conformation, may explain the observed slight deformation and dissymmetry of the naphthalene core. The through-space distance between the cofacial rings (π–π interactions) may also reflect steric compression.

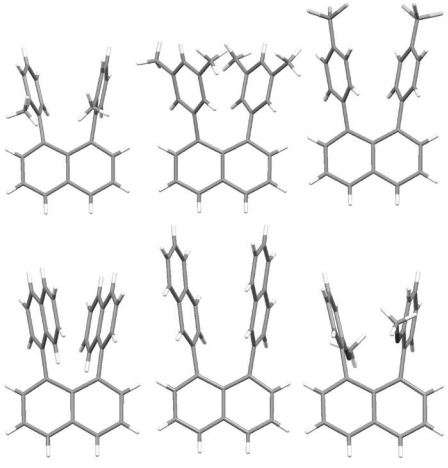


Figure 3. Side view crystal structures of **4** (top left), **7** (top center), **6** (top right), **14** (bottom left), **13** (bottom center), and **11** (bottom right).

Distances ranged from 3.46 to 3.52 Å in diarylnaphthalenes **6**, **7**, *anti*-**11**, **13**, and *anti*-**14**, regardless of the substituent size. Interestingly, no difference was observed between the two *syn* forms isolated for **13**. In addition, the shortest distances were observed for 1- and 2-naphthalenyl substituents in **13** and **14**, in which the planarity of the aromatic cofacial rings, and thus weaker steric congestion, is combined with stronger π–π interactions. A significant increase in the distance between face-to-face rings was observed for compounds **6** and *syn*-**4**. The increase (to 3.60 Å) may be attributed to steric repulsions between the electronically hard fluorine substituents bound to carbon atoms in the CF_3 moieties.[16] Both the *syn* conformation in **4** and the steric crowding imposed by the presence of methyl groups at the same naphthalene side may explain the further increase to 3.66 Å. Based on a recent paper dealing with acenaphtene analogues,[17] a series of selected additional data (interatomic distances, angles, and torsional angles) are gathered in Table 5, for compounds **4**, **6**, **7**, **11**, **13**, and **14**. In accordance with Cross et al.,[17] θ and ϕ values indicate the degree of distortion of the naphthalene unit, whereas τ defines the relative conformation of the *peri*-phenyl ring and the interatomic distances (χ).

Table 5. Selected geometrical parameters.

Entry		θ [°]	ϕ [°]	τ [°]	χ [Å]
1	*syn*-**4**	17.58	2.53	84.50	3.019
			2.24	75.81	
2	**6**	18.09	3.06	115.37	3.000
			3.97	117.74	
3	**7**	20.28	6.26	122.76	3.024
			5.35	122.34	
4	*anti*-**11**	16.12	3.08	107.64	2.940
			3.62	106.86	
5	*anti*-**14**	16.60	3.66	106.90	2.956
			3.66	106.90	
6	*syn*-**13**	16.43	1.68	67.97	2.986
			2.26	65.14	

The observed θ (16.12 to 20.28°) and ϕ (1.68 to 6.26°) values are consistent with an overall increase in the steric bulk and strain in the molecule. Interestingly, these values are somewhat different to those observed in the acenaphtene series, indicating the small influence of the additional ethylene moiety compared with the naphthalene core. Interestingly, the *peri*-aryl rings face each other at angles varying from 56 to 74°. These values, which are larger than the corresponding angles in acenaphtenes, may be attributed to the higher degree of flexibility of the naphthalene core.

Further examination of the X-ray structure revealed a clear deformation of the naphthalene unit, depending on the cofacial substituents (Figure 4). Because the naphthalene plane deviation may be induced by face-to-face aromatics, it can be estimated from the dihedral angles abcd and bcde.

The sums of dihedral angles, which range from 0.4 to 13.4°, are gathered in Table 6. Surprisingly, the presence of two *ortho* methyl groups in *syn*-**4** only slightly influenced the alignment of the naphthalene unit. Almost perfect stacking between both *o*-tolyl substituents is evidenced in the view along the naphthalene axis. An increase in the estimated deviation to 7.3–8.4° was observed for compounds **6**, **11**, and **13**–**14**. Interestingly, the torsion angle does not

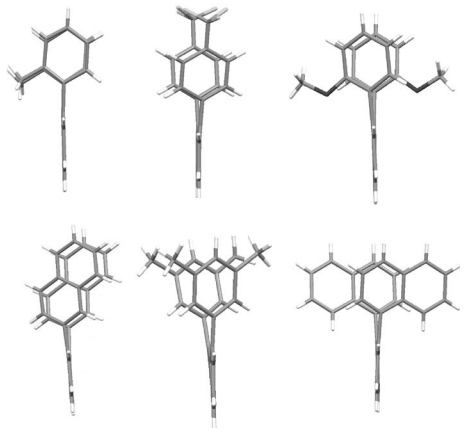


Figure 4. View along the naphthalene axis of **4** (top left), **6** (top center), **11** (top right), **13** (bottom left), **7** (bottom center), and **14** (bottom right).

seem to be dependent on the nature of the conformer, because *syn*-**13**, *anti*-**11**, and **14** display similar deformations. Similarly, *para*-CF_3 (Table 5, entry 2), *ortho*-methoxy (Table 5, entry 4) as well as 1- or 2-naphthyl groups (Table 5, entries 5 and 6) induce a slight deformation of the naphthalene unit. In contrast, a large deformation is observed for compound **7** (Table 5, entry 3). The presence of four methyl groups, all located in *meta* positions of cofacial aromatics, likely generates higher steric compression and maximizes naphthalene torsion.

Table 6. Dihedral angles in naphthalenes.

Entry		Sum of dihedral angles [°] abcd – edcb
1	*syn*-**4**	0.4
2	**6**	8.3
3	**7**	13.4
4	*anti*-**11**	7.3
5	*anti*-**14**	8.4
6	*syn*-**13**	7.7

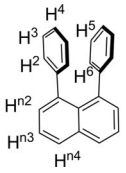
Conclusions

Fourteen 1,8-diarylnaphthalenes bearing various substituents have been synthesized using a reliable and general bis-Suzuki methodology. N-heterocyclic benzhydrylamine-based Pd^{II} complexes were used as highly efficient catalytic systems to afford the target compounds in high yields regardless of the steric bulk of the substituents. The *anti*/*syn* ratios were determined in solution from ^1H NMR spectra and ranged from 74:26 to 90:10, depending on the substitution pattern. Crystal structures have been determined and compared to each other in the context of the naphthalene core deformation. We have found that the steric crowding imposed by the presence of substituents at cofacial rings may significantly affect the alignment of the naphthalene skeleton. The *syn*-**4** conformer displayed an almost perfect stacking between the *o*-tolyl substituents and little deformation, whereas the presence of four methyl substituents in **7** generated the highest steric compression and the largest naphthalene torsion.

Experimental Section

General: Reactions were carried out in round-bottomed flasks equipped with a magnetic stirring bar and capped with a septum. DMF was distilled from CaH_2. TLC analyses were performed on Merck silica gel 60 F254 TLC plates (0.5 mm thickness); PE = petroleum ether. ^1H and ^{13}C NMR spectra were recorded with Bruker 200 and Advance-300 spectrometers and referenced to $CDCl_3$. High-resolution mass spectroscopy (HRMS) data were recorded with an Autospec Ultima (Waters/Micromass) device with a resolution of 5000 RP at 5%. Melting points were measured with a Büchi B-545 apparatus.

General Procedure for the Suzuki Coupling: To a stirred suspension of 1,8-dibromonaphthalene (**1**; 50 mg; 0.17 mmol), boronic acid (0.42 mmol; 2.4 equiv.), and Cs_2CO_3 (285 mg, 0.87 mmol; 5 equiv.) in DMF/H_2O (95:5, 1 mL), was added the palladium complex **2** (0.8 mg; 1 mol-%). The mixture was stirred at 100 °C overnight. Diethyl ether (20 mL) and H_2O (20 mL) were then added and the aqueous phase was extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel to give the substituted 1,8-diarylnaphthalene as a solid. The atom numbering system used in the following data is shown below.



1,8-Diphenylnaphthalene (3): Purified by flash chromatography on silica gel (PE) as a white solid (39 mg, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (dd, J = 8.1, 1.2 Hz, 2 H, H-n4), 7.58 (t, J = 7.0, 1.2 Hz, 2 H, H-n3), 7.44 (dd, J = 7.1, 1.3 Hz, 2 H, H-n2), 7.10–6.9 (m, 10 H, H-2 to H-6) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 140.4, 135.4, 131.0, 129.8, 129.2, 128.5, 127.1, 125.6, 125.1 ppm. Data are in accordance with the literature.[12]

1,8-Di(*o*-tolyl)naphthalene (4): Purified by flash chromatography on silica gel (PE) as a yellow solid (43 mg, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (dd, J = 8.3, 1.0 Hz, 2 H, H-n4), 7.53 (t, J = 7.6 Hz, 2 H, H-n3), 7.21 (dd, J = 7.0, 1.2 Hz, 2 H, H-n2), 7.03 (d, J = 7.6 Hz, 2 H, H-6), 6.95–6.71 (m, J = 21.1, 6.7 Hz, 6 H), 1.92 [s, 2 H, CH_3(*syn*)], 1.89 [s, 4 H, CH_3(*anti*)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 142.00, 139.8, 139.7, 135.5, 135.1, 134.7, 131.4, 130.2, 130.1, 129.9, 128.9, 128.5, 128.4, 128.3, 126.7, 126.1, 125.0, 124.8, 124.4, 124.3, 20.6 ppm. HRMS (EI): calcd. for $C_{24}H_{20}$ $[M]^+$ 308.1565; found 308.1566. Data are in accordance with the literature.[11]

1,8-Bis(4-methoxyphenyl)naphthalene (5): Purified by flash chromatography on silica gel (PE/AcOEt, 95:5) as a white solid (50 mg, 85%); m.p. 147 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, J = 8.2, 1.3 Hz, 2 H, H-n4), 7.53 (t, J = 7.1 Hz, 2 H, H-n3), 7.41 (dd, J = 7.1, 1.4 Hz, 2 H, H-n2), 6.94–6.76 (m, 4 H, H-2 and H-6), 6.56–6.41 (m, 4 H, H-3 and H-5), 3.73 (s, 6 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 140.1, 135.7, 135.4, 130.8,

130.7, 129.6, 128.3, 125.0, 112.7, 55.2 ppm. Data are in accordance with the literature.[10a]

1,8-Bis(4-trifluoromethylphenyl)naphthalene (6): Purified by flash chromatography on silica gel (PE/CH_2Cl_2, 99:1) as a white solid (43 mg, 60%); m.p. 202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.3 Hz, 2 H, H-n4), 7.60 (t, J = 7.6 Hz, 2 H, H-n3), 7.41 (d, J = 7.0 Hz, 2 H, H-n2), 7.23 (d, J = 8.1 Hz, H-3 and H-5), 7.06 (d, J = 8.1 Hz, 4 H, H-2 and H-6) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 138.5, 135.3, 131.1, 130.1, 129.4, 128.9, 128.5, 128.1, 125.7, 125.3, 124.1, 122.1 ppm. HRMS (EI): calcd. for ($C_{24}H_{14}F_6$) $[M]^+$ 416.0999; found 416.1000.

1,8-Bis(3,5-dimethylphenyl)naphthalene (7): Purified by flash chromatography on silica gel (PE) as a white solid (50 mg, 86%); m.p. 139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 8.2, 1.4 Hz, 2 H, H-n4), 7.56 (t, J = 7.5 Hz, 2 H, H-n3), 7.46 (dd, J = 7.0, 1.5 Hz, 2 H, H-n2), 6.66 (s, 4 H, H-2 and H-6), 6.60 (s, 2 H, H-4), 2.17 (s, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.91, 140.74, 136.19, 135.39, 130.50, 129.37, 128.33, 127.50, 127.13, 124.96, 21.09 ppm. HRMS (EI): calcd. for ($C_{26}H_{24}$) $[M]^+$ 336.1878; found 336.1875.

1,8-Bis(3-nitrophenyl)naphthalene (8): Purified by flash chromatography on silica gel (PE/AcOEt, 90:10) as a pale-yellow solid (42 mg, 65%); m.p. 189 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (dd, J = 8.3, 1.1 Hz, 2 H, H-n4), 7.91–7.54 (m, 7 H), 7.46 (dd, J = 7.1, 1.2 Hz, 2 H, H-n2), 7.35–7.13 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.9, 144.3, 136.8, 135.4, 135.1, 135.0, 131.5, 130.1, 128.5, 128.4, 125.6, 125.1, 124.7, 121.1 ppm. HRMS (ESI): calcd. for $C_{22}H_{14}N_2O_4Na$ 393.0851; found 393.0851.

1,8-Bis(2-methyl-4-methoxyphenyl)naphthalene (9): Purified by flash chromatography on silica gel (PE/AcOEt, 95:5) as a white solid (53 mg, 85%); m.p. 124 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.91 (dd, J = 8.3, 1.3 Hz, 2 H, H-n4), 7.49 (dt, J = 8.3, 1.3 Hz, 2 H, H-n3), 7.19 (dd, J = 7.0, 1.3 Hz, 2 H, H-n2), 6.90 [d, J = 8.3 Hz, 1.6 H, H-6 (*anti*)], 6.69 [d, J = 8.1 Hz, 0.4 H, H-6 (*syn*)], 6.39 (dd, J = 8.3, 2.7 Hz, 2 H, H-5), 6.34 [2 × s, 0.4 H, H-3 (*syn*)], 6.29 [2 × s, 1.6 H, H-3 (*anti*)], 3.74 [s, 1.2 H, OCH_3 (*para*, *syn*)], 3.73 [s, 4.8 H, OCH_3 (*para*, *anti*)], 1.86 [s, 1.2 H, CH_3 (*syn*)], 1.79 [s, 4.8 H, CH_3 (*anti*)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 158.0, 157.5, 139.4, 139.3, 136.8, 136.4, 135.3, 134.8, 134.7, 132.2, 130.9, 130.3, 130.1, 128.9, 128.5, 128.4, 124.9, 124.7, 114.3, 114.2, 110.2, 109.8, 56.1, 20.9, 20.8 ppm. Data are in accordance with the literature.[11]

1,8-Bis(2-methyl-4-fluorophenyl)naphthalene (10): Purified by flash chromatography on silica gel (PE) as a yellow solid (41 mg, 68%); m.p. 158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 8.1, 0.8 Hz, 2 H, H-n4), 7.58–7.42 (m, 2 H, H-n3), 7.17 (m, 2 H, H-n2), 6.94 (d, J = 6.0 Hz, 1.6 H), 6.91 (d, J = 6.0 Hz, 0.8 H), 6.74 [d, J = 6.0 Hz, 0.2 H (*syn*)], 6.72 [d, J = 6.0 Hz, 0.2 H (*syn*)], 6.68–6.52 [m, 2 H (*anti*)], 1.85 [s, 1.5 H, CH_3 (*syn*)], 1.80 [s, 4.5 H, CH_3 (*anti*)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.0 (d, J = 245 Hz), 160.0 (d, J = 244 Hz), 138.5, 138.4, 138.3, 138.2, 138.0, 137.9, 137.8, 137.6, 137.4, 135.1, 134.8, 132.7, 132.5, 130.5, 130.4, 130.3, 130.2, 129.5, 129.3, 128.9, 128.8, 125.1, 124.9, 115.3 (d, J = 21 Hz), 115.2 (d, J = 21 Hz), 111.2 (d, J = 21 Hz), 111.1 (d, J = 21 Hz), 20.74, 20.71 ppm. HRMS (EI): calcd. for ($C_{24}H_{18}F_2$) $[M]^+$ 344.1377; found 344.1376.

1,8-Bis(2-methoxyphenyl)naphthalene (11): Purified by flash chromatography on silica gel (PE/AcOEt, 97.5:2.5) as a white solid (38 mg, 64%); m.p. 208 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.92 (dd, J = 8.3, 1.3 Hz, 2 H, H-n4), 7.50 (t, J = 8.1 Hz, 2 H, H-n3), 7.21 (dd, J = 7.0, 1.4 Hz, 2 H, H-n2), 7.08 (dd, J = 7.3, 1.8 Hz, 2 H, H-6), 7.00–6.85 (dt, J = 7.4, 1.0 Hz, 2 H, H-5), 6.73 (dt, J = 7.4, 1.0 Hz, 2 H, H-4), 6.23 (d, J = 8.2 Hz, 2 H, H-3), 3.79 [s, 0.2 H, OCH_3 (*syn*)], 3.56 [s, 0.2 H, OCH_3 (*syn*)], 3.47 [s, 5.6 H, OCH_3 (*anti*)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 137.5, 134.1, 132.4, 131.9, 131.4, 130.9, 130.7, 130.1, 129.9, 128.8, 128.7, 128.2, 127.5, 124.9, 124.6, 119.0, 118.5, 108.9, 108.3, 54.7, 54.1 ppm. HRMS (ESI): calcd. for $C_{24}H_{20}O_2Na$ 393.0851; found 393.0851.

1,8-Bis(2,4-dimethoxyphenyl)naphthalene (12): Purified by flash chromatography on silica gel (PE/AcOEt, 95:5) as a white solid (58 mg, 85%); m.p. 163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (dd, J = 8.3, 1.3 Hz, 2 H, H-n4), 7.54–7.42 (t, J = 7.1 Hz, 2 H, H-n3), 7.31 [dd, J = 7.0, 1.4 Hz, 0.2 H, H-n2 (*syn*)], 7.21 [dd, J = 7.0, 1.4 Hz, 1.8 H, H-n2 (*anti*)], 6.96 [d, J = 8.2 Hz, 1.8 H, H-6 (*anti*)], 6.71 [d, J = 8.1 Hz, 0.2 H, H-6 (*syn*)], 6.32 [dd, J = 8.2, 2.3 Hz, 1.8 H, H-5 (*anti*)], 6.14 [m, 0.4 H, H-3 and H-5 (*syn*)], 5.84 [s, 0.9 H, H-3 (*anti*)], 5.83 [s, 0.9 H, H-3 (*anti*)], 3.77 [s, 5.3 H, OCH_3 (*para*, *anti*)], 3.76 [s, 0.7 H, OCH_3 (*para*, *syn*)], 3.53 [s, 0.7 H, OCH_3 (*ortho*, *syn*)], 3.45 [s, 5.3 H, OCH_3 (*ortho*, *anti*)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 159.3, 156.7, 156.4, 137.2, 136.3, 134.2, 132.6, 131.6, 130.8, 130.1, 129.9, 128.7, 128.6, 125.1, 124.9, 124.6, 124.5, 103.3, 102.8, 97.1, 95.9, 55.3, 55.2, 54.8, 54.3, 54.2 ppm. HRMS (ESI): calcd. for $C_{26}H_{22}O_4Na$ 423.1572; found 423.1567.

1,8-Di(2-naphthyl)naphthalene (13): Purified by flash chromatography on silica gel (PE) as a white solid (46 mg, 70%); m.p. 144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.0 Hz, 2 H, H-n4), 7.72–6.76 (m, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4, 140.1, 135.3, 132.3, 132.1, 131.3, 131.1, 130.9, 130.7, 128.7, 128.3, 128.1, 127.6, 127.2, 126.9, 126.5, 126.2, 125.8, 125.3, 125.1, 124.9 ppm. Data are in accordance with the literature.[14]

1,8-Di(1-naphthyl)naphthalene (14): Purified by flash chromatography on silica gel (PE) as a white solid (43 mg, 65%); m.p. 174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.1 Hz, 2 H), 7.60 (m, 4 H), 7.43–7.19 (m, 8 H), 7.10 (d, J = 8.2 Hz, 2 H), 7.00 (t, J = 7.5 Hz, 1 H), 6.96–6.88 (m, 1.6 H), 6.71 [t, J = 7.5 Hz, 0.4 H (*syn*)], 6.50 (d, J = 7.0 Hz, 2 H), 6.2 (t, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0, 139.2, 138.6, 134.7, 132.5, 132.4, 132.2, 132.1, 131.6, 130.9, 130.8, 128.9, 128.8, 128.3, 127.6, 126.9, 126.8, 126.5, 126.4, 126.2, 125.2, 125.1, 124.9, 124.8, 124.6, 124.5, 123.9, 123.2 ppm. Data are in accordance with the literature.[14]

1,8-Bis(5-fluoro-2-methylphenyl)naphthalene (15): Purified by flash chromatography on silica gel (PE) as a yellow solid (37 mg, 62%); m.p. 98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (dd, J = 8.1, 1.1 Hz, 2 H, H-n4), 7.53 (t, J = 7.5 Hz, 2 H, H-n3), 7.22 (m, 2 H, H-n2), 6.85 (d, J = 6.0 Hz, 0.85 H), 6.83 (d, J = 6.0 Hz, 0.85 H), 6.80 [d, J = 6.0 Hz, 0.15 H (*syn*)], 6.78 [d, J = 6.0 Hz, 0.15 H (*syn*)], 6.67–6.37 (m, 4 H), 1.86 [s, 5.1 H, CH_3 (*anti*)], 1.83 [s, 0.9 H, CH_3 (*syn*)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0 (d, J = 242 Hz), 143.7, 143.6, 143.4, 143.3, 138.2, 138.1, 135.1, 134.8, 131.4, 131.3, 130.2, 130.1, 130.3, 130.3, 130.1, 130.0, 129.8, 129.6, 129.0, 125.1, 125.0, 118.0 (d, J = 21 Hz), 115.2 (d, J = 21 Hz), 113.6 (d, J = 21 Hz), 113.2 (d, J = 21 Hz), 19.6 ppm. HRMS (EI): calcd. for ($C_{24}H_{18}F_2$) $[M]^+$ 344.1377; found 344.1379.

1,8-Di(3-thienyl)naphthalene (16): Purified by flash chromatography on silica gel (PE) as a white solid (37 mg, 73%); m.p. 156 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.93 (dd, J = 7.2, 2.4 Hz, 2 H, H-n4), 7.63–7.41 (m, 4 H, H-n3 and H-n2), 6.90 (m, 4 H), 6.63 (dd, J = 4.7, 0.8 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.6, 135.2, 134.9, 130.7, 129.7, 129.4, 128.7, 125.1, 123.4, 121.9 ppm. HRMS (EI): calcd. for ($C_{18}H_{12}S_2$) $[M]^+$ 292.0380; found 292.3767.

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