

# Synthesis of Annulated Anthracenes, Carbazoles, and Thiophenes Involving Bradsher-Type Cyclodehydration or Cyclization–Reductive-Dehydration Reactions

Settu Muhamad Rafiq,<sup>[a]</sup> Ramakrishnan Sivasakthikumar,<sup>[a]</sup>  
Jayachandran Karunakaran,<sup>[a]</sup> and Arasambattu K. Mohanakrishnan<sup>\*[a]</sup>

**Keywords:** Synthetic methods / Cyclization / Polycycles / Fused-ring systems / Nitrogen heterocycles / Fluorescence

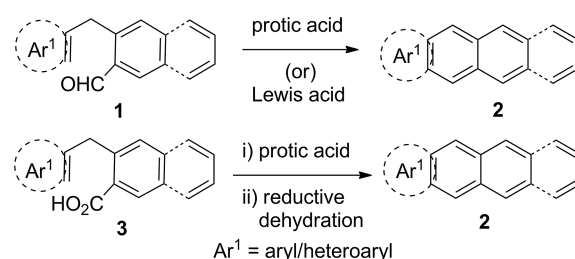
A conventional  $\text{BF}_3 \cdot \text{OEt}_2$ -mediated Bradsher-type cyclodehydration of 2-arylmethyl benzaldehydes in  $\text{CH}_2\text{Cl}_2$  at room temperature gave polycyclic aromatic and heteroaromatic compounds. Alternatively, these compounds could be syn-

thesized in better yields from 2-arylmethylbenzoic acids by triflic-acid-mediated cyclization followed by reductive dehydration.

## Introduction

Over the past two decades, fused polycyclic aromatic compounds have played a starring role in materials chemistry.<sup>[1]</sup> More specifically,  $\pi$ -extended aromatic compounds<sup>[2]</sup> have received significant attention as organic semiconductors for various applications, including organic light-emitting diodes (OLEDs), photovoltaic cells, and organic field-effect transistors (OFETs). Anthracene and its derivatives<sup>[3]</sup> are polycyclic aromatic compounds that have been widely explored as a result of their unique chemical properties and electron-rich structure. The low electronic band gap and strongly blue-fluorescent character of anthracene derivatives make them important materials for optoelectronic devices.<sup>[4]</sup> Thus, anthracene derivatives have been explored for use in OLEDs,<sup>[5]</sup> molecular switches,<sup>[6]</sup> solar cells,<sup>[7]</sup> and also in other optical applications.<sup>[8]</sup> The incorporation of aryl or alkyl units at the 9- and 10-positions of anthracene<sup>[9]</sup> is known to enhance the quantum yield of the compounds, and thus the performance of devices based on these compounds. Similar substitution at the 2- and 6-positions effectively suppresses the crystallization of the compounds, which leads to the formation of stable amorphous films.<sup>[10]</sup> It has been established that the presence of anthracene units as pendant groups leads to the formation of films with good optical quality suitable for device fabrication.<sup>[11]</sup> Recently, a plethora of heteroannulated anthracene analogues have been explored for optical applications.<sup>[12]</sup>

Traditionally, anthracene and its derivatives have been prepared by Friedel–Crafts reaction followed by reductive cyclization and subsequent aromatization.<sup>[13]</sup> The Bradsher reaction, which involves Lewis- or Brønsted-acid-catalysed cyclodehydration of 2-formyl/acetyl diarylmethanes,<sup>[14]</sup> is a prominent strategy for the synthesis of anthracene analogues. This reaction has also been found to be widely applicable for the synthesis of heteroannulated anthracenes as well.<sup>[14]</sup> Recently, different variants of Bradsher reaction have been explored for the synthesis of  $\pi$ -conjugated systems with anthracene and naphthalene frameworks.<sup>[15]</sup> A very recent report by Serevičius and coworkers<sup>[15a]</sup> confirmed that the incorporation of heteroatoms, including O, S, and N, into the anthracene core skeleton results in an increased HOMO level; this is essential for hole injection into the active layer. Thus, there is plenty of scope for the synthesis of anthracene analogues with annulation at the 1- and 2-positions; such compounds may find applications in optoelectronic devices. Hence, as part of our continued interest in the synthesis of  $\pi$ -conjugated heterocycles,<sup>[16]</sup> we report in this paper the results of our detailed study on the synthesis of annulated anthracene analogues **2** involving either Bradsher-type cyclodehydration or cyclization followed reductive dehydration (Scheme 1).



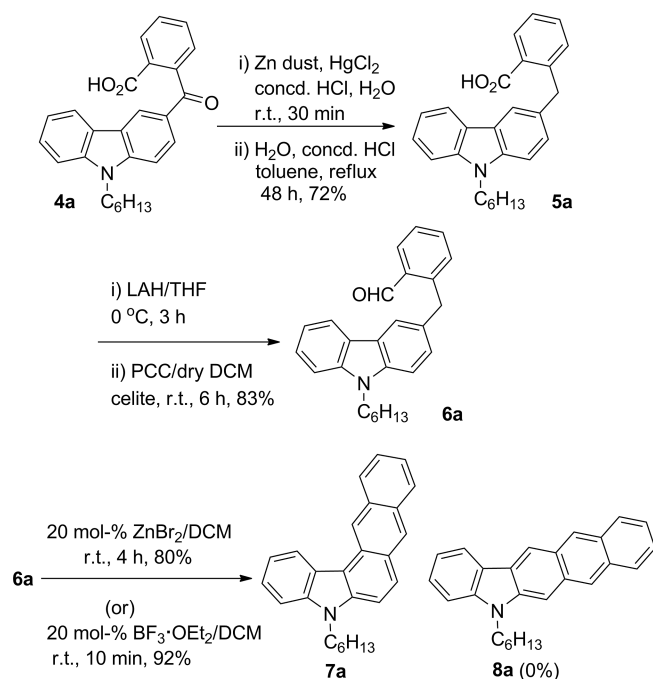
Scheme 1. Synthesis of anthracenes from aldehydes **1** or acids **3**.

[a] Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India  
E-mail: mohan\_67@hotmail.com; mohanakrishnan@unom.ac.in  
www.unom.ac.in

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.201500493>.

## Results and Discussion

As a representative case, 2-[(9-hexyl-carbazol-3-yl)methyl]benzaldehyde (**6a**) was first prepared from the corresponding keto acid (i.e., **4a**).<sup>[17]</sup> The reduction of the ketone group of **4a** under Clemmensen conditions following the published procedure<sup>[17b]</sup> led to benzyl acid **5a**. The benzyl acid was reduced with LiAlH<sub>4</sub>, and the resulting alcohol was oxidized with PCC (pyridinium chlorochromate) to give benzyl aldehyde **6a** as a thick liquid (Scheme 2). Carbazol-3-ylmethyl-substituted benzaldehyde **6a** underwent cyclization upon treatment with ZnBr<sub>2</sub> (20 mol-%) as catalyst in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 4 h. Work-up and purification by column chromatography gave 5-hexyl-naphtho[2,3-*c*]carbazole (**7a**). The <sup>1</sup>H NMR spectrum of the crude product clearly confirmed the exclusive formation of **7a** rather than naphtho[*b*]carbazole **8a**. Aldehyde **6a** also underwent a facile cyclodehydration upon treatment with BF<sub>3</sub>·OEt<sub>2</sub> (20 mol-%) in dry CH<sub>2</sub>Cl<sub>2</sub> at room temperature to give naphtho[2,3-*c*]carbazole **7a** in a slightly better yield. The formation of naphtho[2,3-*c*]carbazole **7a** as the sole product from the cyclodehydration of aldehyde **6a** is consistent with our earlier observations.<sup>[16c]</sup>

Scheme 2. Annulation of carbazol-3-ylmethyl benzaldehyde **6a**.

Next, the cyclodehydration of **6a** was carried out using 20 mol-% of different Lewis acids/Brønsted acids, and the results are presented in Table 1. The reaction was successful with Lewis acids as well as Brønsted acids. Unlike 2-benzylmethyl benzaldehydes, for which cyclodehydration was carried out using In(OTf)<sub>3</sub> (5 mol-%) at elevated temperature,<sup>[15c]</sup> the transformation of **6a** into **7a** reported here could be achieved at room temperature.

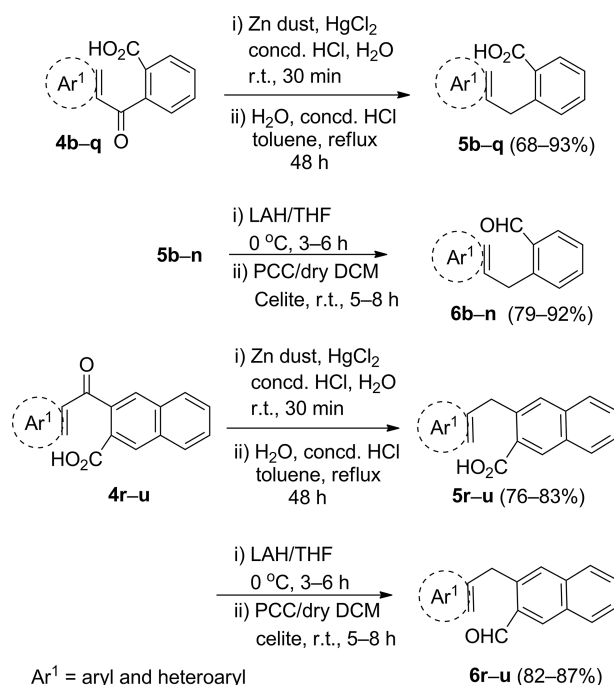
Table 1. Effect of the catalyst (20 mol-%) on the cyclization of **6a**.

Entry	Catalyst	Time	Yield [%] <sup>[a]</sup>
1	ZnBr <sub>2</sub>	4 h	84
2	In(OTf) <sub>3</sub>	3 h	71
3	Sc(OTf) <sub>3</sub>	6 h	67
4	BF <sub>3</sub> ·OEt <sub>2</sub>	10 min	92
5	CF <sub>3</sub> SO <sub>3</sub> H	10 min	83
6	Me <sub>3</sub> SO <sub>3</sub> H	45 min	75
7	CF <sub>3</sub> CO <sub>2</sub> H	12 h	25

[a] Isolated yield of **7a**.

It should be noted that Yu and Xu recently achieved<sup>[15d]</sup> the transformation of 2-benzylmethyl benzaldehydes into 2-substituted anthracenes using a combination of BF<sub>3</sub>·OEt<sub>2</sub> and TsNH<sub>2</sub> in a reaction involving in-situ-generated *N*-tosylbenzaldimines. However, in our case, BF<sub>3</sub>·OEt<sub>2</sub> alone was sufficient for the effective transformation of **6a** into **7a**. TFA (trifluoroacetic acid) was the least efficient of the Brønsted acids tested, giving naphtho[2,3-*c*]carbazole **7a** in poor yield. Thus, of the conditions tested for the cyclodehydration of **6a**, BF<sub>3</sub>·OEt<sub>2</sub> (20 mol-%) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature was found to be the most suitable, giving the product (i.e., **7a**) in the highest yield.

We planned to test the generality of the BF<sub>3</sub>·OEt<sub>2</sub>-mediated cyclodehydration reaction, and so we prepared various 2-arylmethyl benzaldehydes. Known keto acids **4b–4q**<sup>[17a,18a]</sup> and **4r–4u**<sup>[18b]</sup> led, upon Clemmensen reduction,<sup>[17b]</sup> to the formation of the respective 2-benzyl benzoic acids (i.e., **5b–5q**) and 2-naphthyl benzoic acids (i.e., **5r–5u**), respectively. LiAlH<sub>4</sub> reduction followed by PCC oxidation of the benzoic acids (**5b–5n** and **5r–5u**) gave the respective benzaldehydes (i.e., **6b–6n** and **6r–6u**) in good to excellent yields (Scheme 3).

Scheme 3. Preparation of 2-benzyl/naphthyl benzaldehydes **6b–6n** and **6r–6u**.

As expected, benzaldehydes **6b–6n**, as well as naphthaldehydes **6r–6u**, upon interaction with  $\text{BF}_3 \cdot \text{OEt}_2$  (20 mol-%) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 10 min gave the respective annulated products (i.e., **7b–7n** and **7r–7u**) in excellent yields. The structures of annulated arene and heteroarene products are given in Table 2 along with their yields. Bradsher-type cyclodehydration of 2-arylmethylbenzaldehydes **6b–6h** using  $\text{BF}_3 \cdot \text{OEt}_2$  (20 mol-%) in  $\text{CH}_2\text{Cl}_2$  at room temperature gave anthracenes **7b–7h** in excellent yields (Table 2, entries 1–3). Under identical conditions, 2-thiophenylmethyl benzaldehydes **6i–6k** gave annulated thiophene derivatives **7i–7k** (Table 2, entries 4 and 5).

The annulation of diphenylaminomethyl benzaldehyde **6l** led to the formation of 2-diphenylaminoanthracene (**7l**) in 83% yield (Table 2, entry 6). As observed in the case of carbazol-3-ylmethyl benzaldehyde **6a**, cyclodehydration of dibenzoheterocycle-tethered aldehyde **6m** or **6n** in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  gave naphtho[*c*]-fused dibenzoheterocycle **7m** or **7n** as the exclusive product (Table 2, entry 7). Finally, the expected cyclization of naphthyl aldehydes **6r–6u** was also achieved by using  $\text{BF}_3 \cdot \text{OEt}_2$  (20 mol-%) in dry  $\text{CH}_2\text{Cl}_2$  at room temperature to give the corresponding anthra[*b*]-annulated compounds (i.e., **7r–7u**) in 78–91% yields (Table 2, entries 8–11).

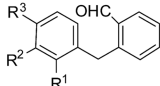
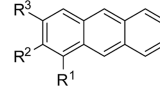
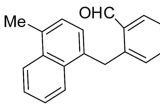
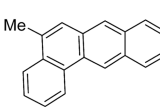
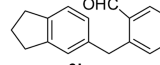
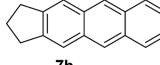
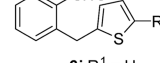
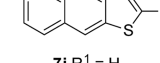
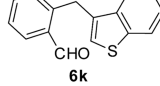
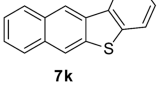
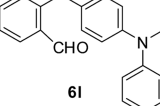
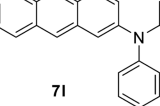
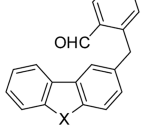
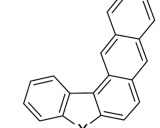
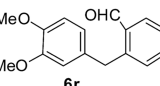
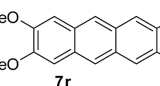
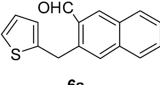
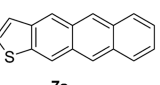
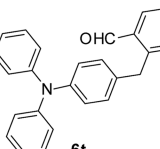
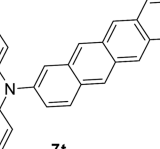
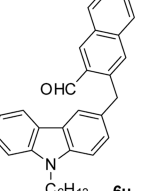
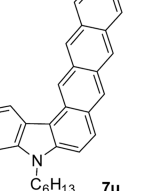
Next, *N*-hexylcarbazole-tethered bis-keto acid **4v** was prepared through Friedel–Crafts phthaloylation of *N*-hexylcarbazole in 1,2-dichloroethane (DCE) at reflux. Subsequent Clemmensen reduction of bis-keto acid **4v** using zinc–mercury amalgam gave bis-benzyl acid **5v** in 66% yield. The benzoic acid **5v** was reduced with  $\text{LiAlH}_4$ , and the resulting alcohol was oxidized using PCC to give benzaldehyde **6v** as a yellow solid. Bradsher-type cyclodehydration of carbazole-(3,6-diyl)bis(methylene) dibenzaldehyde **6v** using  $\text{BF}_3 \cdot \text{OEt}_2$  (40 mol-%) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 10 min followed by work-up and column chromatographic purification gave dinaphtho carbazole **7v** in 78% yield (Scheme 4). The structure of **7v** was confirmed by its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data.

Having achieved the facile synthesis of annulated arenes and heteroarenes involving  $\text{BF}_3 \cdot \text{OEt}_2$ -mediated cyclodehydration of benzaldehydes/naphthaldehydes, we went on to investigate the cyclization followed by reductive dehydration of the corresponding benzoic/naphthoic acids. As a representative case, carbazol-3-ylmethyl benzoic acid **5a** was treated with triflic acid (20 mol-%) in dry  $\text{CH}_2\text{Cl}_2$  at room temperature for 30 min; this was followed by  $\text{NaBH}_4$ -mediated reductive dehydration to give linear naphtho[*b*]carbazole **8a** as the exclusive product (Scheme 5).

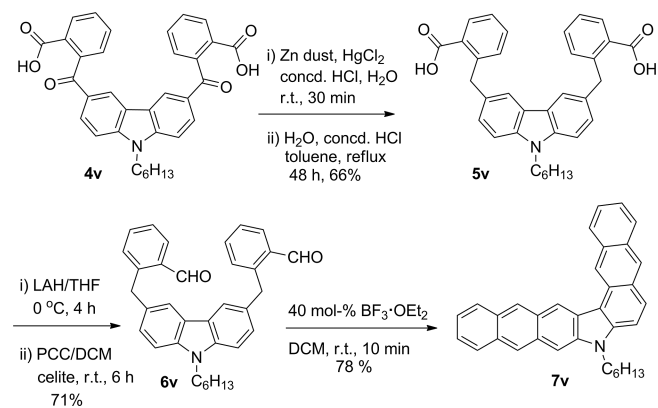
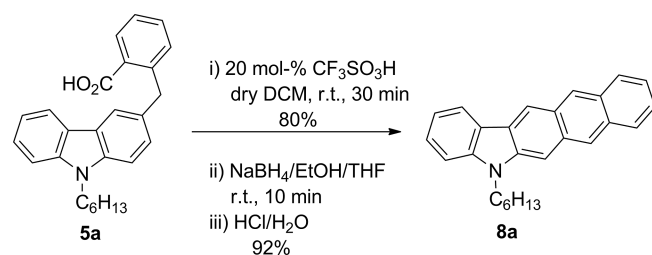
The different types of annulated arenes and heteroarenes obtained from benzoic acids through cyclization followed by reductive dehydration are presented in Table 3.

As expected, benzyl benzoic acids **5b–5q** underwent smooth cyclization in the presence of triflic acid (20 mol-%), and subsequent reductive dehydration using  $\text{NaBH}_4$  gave annulated products **7b–7q** in 75–92% yield. The yields of anthracenes **7b–7h** obtained from benzoic acids **5b–5h** by the cyclization–reductive-dehydration protocol (Table 3, entries 1–3) were almost comparable to those obtained by

Table 2.  $\text{BF}_3 \cdot \text{OEt}_2$ -mediated cyclodehydration of benzaldehydes **6b–6n** and naphthaldehydes **6r–6u**.

Entry	Substrate	Product <sup>[a]</sup>	Yield (%) <sup>[b]</sup>
1	 <b>6b–f</b>	 <b>7b–f</b>	
	<b>6b/7b</b> $\text{R}^1, \text{R}^2 = \text{H}, \text{R}^3 = \text{Me}$ <b>6c/7c</b> $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}, \text{R}^3 = \text{Me}$ <b>6d/7d</b> $\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}, \text{R}^3 = \text{Me}$ <b>6e/7e</b> $\text{R}^1 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^3 = \text{OMe}$ <b>6f/7f</b> $\text{R}^1 = \text{H}, \text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}$		92 88 83 87 91
2	 <b>6g</b>	 <b>7g</b>	89
3	 <b>6h</b>	 <b>7h</b>	92
4	 <b>6i</b> $\text{R}^1 = \text{H}$ <b>6j</b> $\text{R}^1 = 2\text{-thienyl}$	 <b>7i</b> $\text{R}^1 = \text{H}$ <b>7j</b> $\text{R}^1 = 2\text{-thienyl}$	87 91
5	 <b>6k</b>	 <b>7k</b>	85
6	 <b>6l</b>	 <b>7l</b>	83
7	 <b>6m</b> $\text{X} = \text{S}$ <b>6n</b> $\text{X} = \text{O}$	 <b>7m</b> $\text{X} = \text{S}$ <b>7n</b> $\text{X} = \text{O}$	88 93
8	 <b>6r</b>	 <b>7r</b>	91
9	 <b>6s</b>	 <b>7s</b>	86
10	 <b>6t</b>	 <b>7t</b>	78
11	 <b>6u</b>	 <b>7u</b>	87

[a] Benzaldehyde (1 equiv.) and  $\text{BF}_3 \cdot \text{OEt}_2$  (20 mol-%) at room temperature for 10 min. [b] Isolated yield.

Scheme 4. Cyclodehydration of carbazolylmethyl bis-benzaldehyde **6v**.Scheme 5. Annulation of carbazolylmethyl benzoic acid **5a**.

the Bradsher-type cyclization of benzaldehydes **6b–6h** (Table 2, entries 1–3). However, considering the number of steps involved, the benzoic-acid-mediated two-step protocol is synthetically more advantageous than the cyclodehydration procedure based on benzaldehydes. Thiophenylmethyl benzoic acids **5i–5k** underwent the cyclization–reductive-dehydration sequence to give annulated thienyl heterocycles **7i–7k** in 85–92% yield (Table 3, entries 4 and 5). Under identical conditions, diphenylaminomethyl benzoic acid **5l** led to the formation of 2-diphenylaminoanthracene (**7l**) in 88% yield (Table 3, entry 6). Dibenzothiophenylmethyl benzoic acid **5m** underwent triflic-acid-mediated cyclization followed by reductive dehydration to give naphtho[*c*]-fused dibenzothiophene **7m** in 93% yield as the exclusive product (Table 3, entry 7). However, when the same type of synthetic transformation was attempted with dibenzofuranylmethyl benzoic acid **5n**, naphtho[*c*]- and naphtho[*b*]-fused dibenzofuranyl heterocycles **7n** and **8n** were formed in 47 and 28% yields, respectively (Table 3, entry 8).

As expected, triflic-acid-mediated cyclization followed by reductive dehydration of carbazol-3-ylmethyl benzoic acid **5o** gave naphtho[*c*]carbazole **7o** (Table 3, entry 9). Dihexylfluorenylmethyl benzoic acid **5p** and pyrenylmethyl benzoic acid **5q** underwent cyclization followed reductive dehydration to give the corresponding annulated arenes (i.e., **7p** and **7q**) in 82 and 84% yields, respectively.

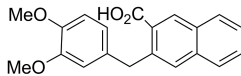
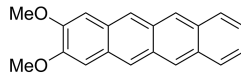
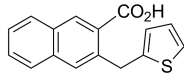
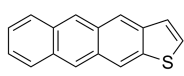
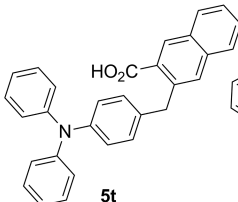
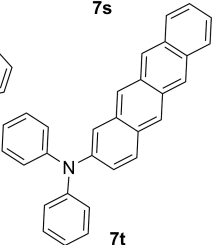
Finally, cyclization of naphthoic acids **5r–5t** using triflic acid (20 mol-%) in dry  $\text{CH}_2\text{Cl}_2$  at room temperature followed by  $\text{NaBH}_4$ -mediated reductive dehydration gave the

Table 3. Cyclization followed by reductive dehydration of benzoic acids **5b–5q**.

Entry	Substrate	Product <sup>[a]</sup>	Yield (%) <sup>[b]</sup>
1			
	<b>5b/7b</b> R <sup>1</sup> , R <sup>2</sup> = H, R <sup>3</sup> = Me		89
	<b>5c/7c</b> R <sup>1</sup> = H, R <sup>2</sup> = Me, R <sup>3</sup> = Me		87
	<b>5d/7d</b> R <sup>1</sup> = Me, R <sup>2</sup> = H, R <sup>3</sup> = Me		85
	<b>5e/7e</b> R <sup>1</sup> = H, R <sup>2</sup> = OMe, R <sup>3</sup> = OMe		91
	<b>5f/7f</b> R <sup>1</sup> = H, R <sup>2</sup> = H, R <sup>3</sup> = Ph		92
2			
	<b>5g</b>	<b>7g</b>	91
3			
	<b>5h</b>	<b>7h</b>	89
4			
	<b>5i</b> R <sup>1</sup> = H	<b>7i</b> R <sup>1</sup> = H	92
	<b>5j</b> R <sup>1</sup> = 2-thienyl	<b>7j</b> R <sup>1</sup> = 2-thienyl	85
5			
	<b>5k</b>	<b>7k</b>	87
6			
	<b>5l</b>	<b>7l</b>	88
7			
	<b>5m</b>	<b>7m</b>	93
8			
	<b>5n</b>	<b>7n</b>	47
		<b>8n</b>	28
9			
	<b>5o</b>	<b>7o</b>	87
10			
	<b>5p</b>	<b>7p</b>	82
11			
	<b>5q</b>	<b>7q</b>	84

[a] Arylmethyl benzoic acid (1 equiv.) and  $\text{CF}_3\text{SO}_3\text{H}$  (20 mol-%) at room temperature for 30 min, followed by  $\text{NaBH}_4$  (5 equiv.) at room temperature for 10 min. [b] Yield after column chromatography.

Table 4. Cyclization followed by reductive dehydration of naphthyl acids **5r–5t**.

Entry	Substrate	Product <sup>[a]</sup>	Yield (%) <sup>[b]</sup>
1			86
2			91
3			88

[a] Benzoic acid (1 equiv.) and  $\text{CF}_3\text{SO}_3\text{H}$  (20 mol-%) at room temperature for 30 min followed by  $\text{NaBH}_4$  (5 equiv.) at room temperature for 10 min. [b] Yield after column chromatography.

corresponding anthra[2,3-*b*]annulated products (i.e., **7r–7t**) in 86–91% yield (Table 4, entries 1–3).

*N*-Hexylcarbazolylmethyl bis-benzoic acid **5v** underwent cyclization with triflic acid (20 mol-%) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 0.5 h; usual work-up and purification by column chromatography led to the isolation of dinaphtho[*c*]fused carbazole **8v** in a low yield of 33% (Scheme 6). Further elution of the column gave a major compound (>40%; possibly **9**) with a complex  $^1\text{H}$  NMR spectrum. When bis-benzoic acid **5v** was subjected to cyclization followed by reductive dehydration, bis-naphtho-annulated carbazoles **7v** and **8v** were isolated in 45 and 31% yields, respectively.

The optical properties of selected anthracene derivatives are presented in Table 5. The UV/Vis absorption spectra of naphtho[*c*]fused dibenzo heterocycles (**7a**, **7m**, **7n**, and **7o**)

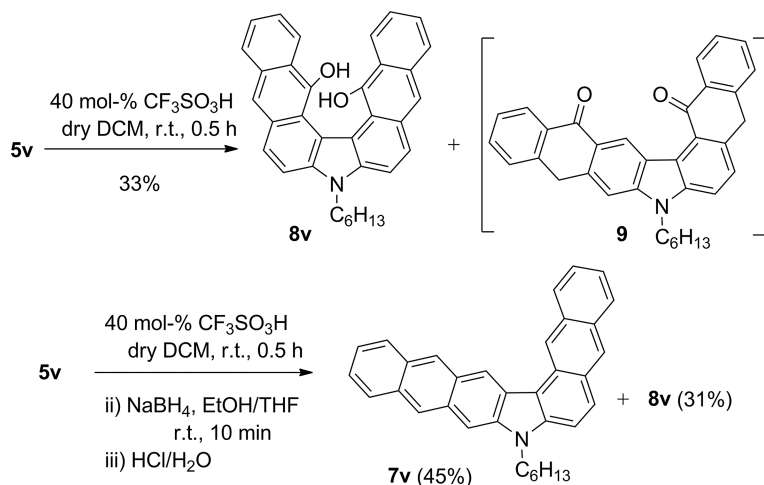
showed  $\lambda_{\text{max}}$  values in the range of 396–476 nm. Among the benzo[*b*]heterocycle-fused anthracenes (**7a**, **7m**, and **7n**), the  $\lambda_{\text{max}}$  value of *N*-hexylindolyl tethered compound **7a** was redshifted by ca. 30 nm. The introduction of bromine atoms at 2- and 7-positions of *N*-hexylindolylanthracene **7a** slightly enhanced its absorption value. The annulation of a benzene ring into 2-diphenylaminoanthracene (**7l** to **7t**) increased its  $\lambda_{\text{max}}$  value by ca. 150 nm. However, similar incorporation of a benzene ring into benzo[*b*]anthracene (**7a** to **7u**) had only a negligible influence on its  $\lambda_{\text{max}}$  value. Conjugation was found to be more favourable in linearly fused anthracenes (**8a** and **8n**) than in their angular counterparts (**7a** and **7n**). Angular type annulation of an additional naphthalene unit onto naphthocarbazole **8a** (to give **7v**) resulted in an increase in  $\lambda_{\text{max}}$  by ca. 51 nm. The UV/Vis absorption spectra of representative anthracenes are given in Figure 1.

Table 5. Photophysical data of selected anthracenes.

Entry	Compound	Absorption <sup>[a]</sup>	Emission <sup>[a,b]</sup>	Stokes shift <sup>[c]</sup>
		$\lambda_{\text{max(abs)}} [\text{nm}]$	$\lambda_{\text{max(em)}} [\text{nm}]$	$[\text{cm}^{-1}]$
1	<b>7a</b>	431	471	1970
2	<b>7l</b>	371	439	4175
3	<b>7m</b>	402	441	2200
4	<b>7n</b>	403	434	1772
5	<b>7o</b>	440	551	4578
6	<b>7s</b>	435	495	2786
7	<b>7t</b>	520	557	1277
8	<b>7u</b>	445	580	5231
9	<b>7v</b>	527	578	1674
10	<b>8a</b>	476	522	1477
11	<b>8n</b>	430	468	1888

[a] Recorded in  $\text{CH}_2\text{Cl}_2$  at 25 °C. [b] Excited at the longest wavelength of the absorption maxima. [c] Stokes shift =  $\lambda_{\text{max(abs)}} - \lambda_{\text{max(em)}} [\text{cm}^{-1}]$ .

The photoluminescence spectra of the anthracene analogues showed emission in the region 434–580 nm. Similar to the absorption spectra, the annulation of benzene rings (**7l** to **7t**, and **7a** to **7u**) also resulted in redshifted luminescence values. Linearly fused anthracenes (**8a** and **8n**) emit

Scheme 6. Annulation of carbazolylmethyl bis-benzoic acid **5v**.

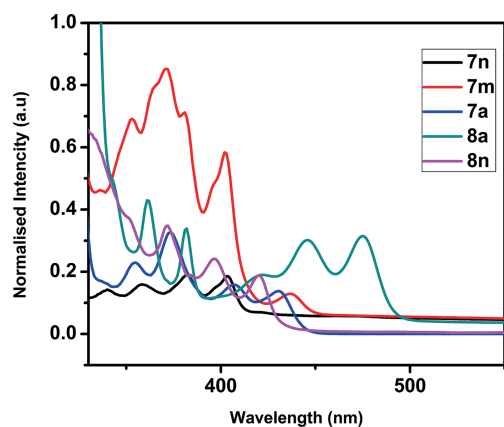


Figure 1. Absorption spectra of anthracenes **7a**, **7m**, **7n**, **8a**, and **8n**.

lower energy light than their angular counterparts (**7a** and **7n**). The emission spectra of representative anthracenes are presented in Figure 2.

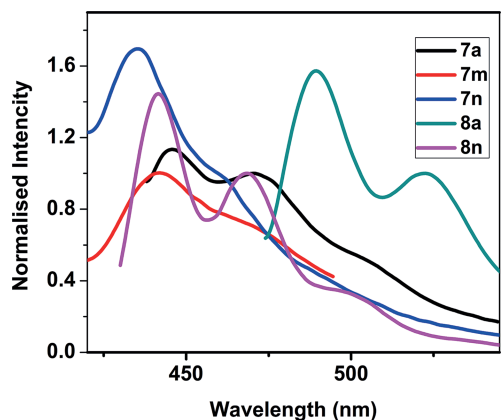


Figure 2. Emission spectra of anthracenes **7a**, **7m**, **7n**, **8a**, and **8n**.

## Conclusions

In summary, a conventional  $\text{BF}_3 \cdot \text{OEt}_2$ -mediated Bradsher-type cyclodehydration of 2-aryl/2-heteroaryl-methyl benzaldehydes led to the formation of annulated anthracenes in very good yields. The cyclodehydration reaction was successfully extended to 2-arylmethyl/2-heteroaryl-methyl naphthaldehydes. Alternatively, the 2-arylmethyl-benzoic acids as well as 2-arylmethylnaphthoic acids underwent triflic-acid-mediated cyclization followed by reductive dehydration to give annulated anthracenes in better yields. Compared to existing methods for the cyclodehydration of 2-arylmethyl benzaldehydes,<sup>[14,15a,15f]</sup> this protocol, which uses  $\text{BF}_3 \cdot \text{OEt}_2$  (20 mol-%), is simple, widely applicable, and also less time consuming. The absorption and emission data of selected anthracene analogues are also presented. The various types of benzo[*b*]heterocycle-fused anthracenes and triphenylamino derivatives reported in this paper may find applications in field-effect transistors, and also in organic solar cells (OSCs).

## Experimental Section

**General Methods:** Experiments were carried out under a nitrogen atmosphere unless otherwise stated. The progress of reactions was monitored by TLC using mixtures of ethyl acetate and hexanes. Column chromatography was carried out on silica gel (230–400 mesh, Merck) with solvents of increasing polarity.  $^1\text{H}$ ,  $^{13}\text{C}$ , and DEPT-135 spectra were recorded in  $\text{CDCl}_3$  and  $[\text{D}_6]\text{DMSO}$  with a Bruker 300 MHz spectrometer, at room temperature using tetramethylsilane as an internal standard. Chemical shift values are quoted in parts per million (ppm) and coupling constants are quoted in Hertz (Hz). Elemental analysis data were recorded with an Elementar Vario Series Analyzer instrument. HRMS data were recorded with a JEOL GC Mate II (EI) instrument. Keto acids **4a–4q** and **4v** were prepared following published procedures<sup>[17,17a,18a]</sup> by Friedel–Crafts phthaloylation of the corresponding arene/heteroarene using  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. Keto acids **4r–4u** were prepared from the corresponding arene/heteroarene following a published procedure<sup>[18b]</sup> in two steps by Friedel–Crafts reaction with ethyl 4-chloro-4-oxobutanoate in the presence of anhydrous  $\text{SnCl}_4$  at room temperature followed by condensation of resulting keto esters with phthalaldehyde.

**2-[(9-Hexyl-9H-carbazol-3-yl)methyl]benzoic Acid (**5a**):** Zinc dust (2.15 g, 39.30 mmol) and mercuric chloride (0.21 g, 0.78 mmol) were added to a mixture of distilled water (5.5 mL) and conc. HCl (0.2 mL). The resulting mixture was stirred for 0.5 h until the solution became homogenous (i.e., amalgamation was complete). The stirring was stopped, and the supernatant liquid was decanted as completely as possible from Zn/Hg amalgam. To this solution, distilled water (2.7 mL), conc. HCl (0.65 mL), toluene (3.6 mL), 1,4-dioxane (3.6 mL) and keto acid **4a** (2.4 g, 5.95 mmol) were added, and the resulting mixture was heated at reflux for 48 h. Conc. HCl (1.8 mL) was added every 6 h to maintain its concentration at a constant level. Then, the reaction mixture was poured into water (100 mL). This mixture was extracted with ethyl acetate ( $2 \times 20$  mL), and the organic phase was dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed in vacuo to give compound **5a** (1.78 g, 77%) as a colourless solid, m.p. 119–121 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.98–7.92 (m, 2 H, ArH), 7.81 (s, 1 H, ArH), 7.37–7.27 (m, 4 H, ArH), 7.20–7.04 (m, 4 H, ArH), 4.54 (s, 2 H,  $\text{CH}_2$ ), 4.13 (t,  $J$  = 7.2 Hz, 2 H,  $\text{CH}_2$ ), 1.75–1.68 (m, 2 H,  $\text{CH}_2$ ), 1.26–1.13 (m, 6 H,  $\text{CH}_2$ ), 0.78–0.73 (m, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.2, 144.7, 140.7, 139.1, 131.0, 129.1, 128.5, 128.3, 127.2, 126.1, 125.8, 125.6, 124.9, 123.0, 122.7, 120.9, 120.6, 118.7, 108.6, 43.2, 39.6, 31.6, 29.0, 27.0, 22.6, 14.1 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 132.9, 131.6, 129.1, 127.2, 126.1, 125.5, 120.8, 120.4, 118.5, 108.6, 43.2, 39.6, 31.6, 29.0, 27.0, 22.6, 14.1 ppm.

**2-[(9-Hexyl-9H-carbazol-3-yl)methyl]benzaldehyde (**6a**):** A solution of 2-(4-methylbenzyl)benzoic acid (**5a**; 1.37 g, 3.53 mmol) in dry THF (10 mL) was slowly added by syringe to a suspension of  $\text{LiAlH}_4$  (0.67 g, 17.63 mmol) in dry THF at 0 °C. The reaction mixture was then stirred at room temperature for 4 h. After this time, it was quenched with methanol (5 drops), followed by NaOH (5% aq.; 6 mL). Then the precipitate was removed by filtration, and the filtrate was dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed in vacuo to give the alcohol as a thick liquid.

The crude [2-(4-methylbenzyl)phenyl]methanol (0.9 g, 2.42 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (15 mL), and PCC (0.73 g, 3.38 mmol) and Celite (1 g) were added. The reaction mixture was stirred at room temperature for 6 h. Then, the reaction mixture was filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by column chromatography (silica gel, 10% EtOAc in

hexane) to give aldehyde **6a** (0.71 g, 83%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.26 (s, 1 H, CHO), 7.98–7.91 (m, 1 H, ArH), 7.80–7.75 (m, 2 H, ArH), 7.43 (t, *J* = 7.4 Hz, 1 H, ArH), 7.36–7.28 (m, 3 H, ArH), 7.26–7.15 (m, 3 H, ArH), 7.09 (t, *J* = 7.2 Hz, 1 H, ArH), 4.53 (s, 2 H, CH<sub>2</sub>), 4.15 (t, *J* = 7.2 Hz, 2 H, CH<sub>2</sub>), 1.74 (t, *J* = 7.2 Hz, 2 H, CH<sub>2</sub>), 1.34–1.19 (m, 6 H, CH<sub>2</sub>, CH<sub>3</sub>), 0.78 (t, *J* = 6.6 Hz, 3 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 192.5, 144.3, 140.8, 139.2, 134.0, 131.6, 130.6, 126.8, 126.7, 125.6, 124.0, 123.1, 122.6, 120.8, 120.4, 120.4, 118.6, 108.8, 108.7, 43.2, 38.0, 31.6, 29.0, 27.0, 22.6, 14.1 ppm.

**5-Hexyl-5H-naphtho[2,3-*c*]carbazole (7a):** BF<sub>3</sub>·OEt<sub>2</sub> (0.03 g, 0.21 mmol) was added to a solution of aldehyde **6a** (0.4 g, 1.1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The reaction mixture was stirred for 10 min at room temperature under a nitrogen atmosphere. The solvent was removed in vacuo, and the residue was purified by column chromatography (1% EtOAc in hexane) to give **7a** (0.35 g, 92%) as a pale green solid, m.p. 104–106 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.22 (s, 1 H, ArH), 8.74 (d, *J* = 7.2 Hz, 1 H, ArH), 8.51 (s, 1 H, ArH), 8.15 (d, *J* = 8.4 Hz, 1 H, ArH), 8.05–7.95 (m, 2 H, ArH), 7.62 (d, *J* = 9.3 Hz, 1 H, ArH), 7.57–7.50 (m, 2 H, ArH), 7.49–7.44 (m, 3 H, ArH), 4.38 (t, *J* = 6.9 Hz, 2 H, CH<sub>2</sub>), 1.88 (t, *J* = 6.8 Hz, 2 H, CH<sub>2</sub>), 1.30–1.25 (m, 6 H, CH<sub>2</sub>), 0.87–0.82 (m, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 138.8, 137.3, 132.5, 130.0, 128.7, 128.3, 128.0, 127.9, 127.9, 125.7, 124.3, 124.0, 123.5, 121.8, 120.7, 120.1, 113.2, 112.4, 110.0, 43.2, 31.6, 29.8, 27.0, 22.6, 14.1 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): δ = 128.3, 128.0, 128.0, 127.9, 125.7, 124.3, 123.5, 121.8, 120.7, 120.1, 112.4, 109.6, 43.2, 31.6, 29.8, 27.0, 22.6, 14.1 ppm. HRMS (EI): calcd. for C<sub>26</sub>H<sub>25</sub>N [M]<sup>+</sup> 351.1987; found 351.1980.

**2-(4-Methylbenzyl)benzoic Acid (5b):** Zinc dust (4.3 g, 65.75 mmol) and mercuric chloride (0.43 g, 1.58 mmol) were added to a mixture of distilled water (5.5 mL) and conc. HCl (0.2 mL). The mixture was stirred until it became homogeneous ca. 0.5 h). To this solution, distilled water (2.7 mL), conc. HCl (0.65 mL), toluene (3.6 mL), 1,4-dioxane (3.6 mL), and keto acid **4b** (2.4 g, 9.99 mmol) were added. The reaction mixture was heated at reflux for 48 h, and conc. HCl (1.8 mL) was added every 6 h. Usual work-up following a procedure similar to that described for **5a** gave benzyl acid **5b** (1.72 g, 75%) as a colourless solid, m.p. 112–114 °C (ref.<sup>[19]</sup> 111–112 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.89 (d, *J* = 7.8 Hz, 1 H, ArH), 7.28 (t, *J* = 7.3 Hz, 1 H, ArH), 7.12 (t, *J* = 7.5 Hz, 1 H, ArH), 7.04 (d, *J* = 7.5 Hz, 1 H, ArH), 6.91–6.88 (m, 4 H, ArH), 4.25 (s, 2 H, CH<sub>2</sub>), 2.15 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 173.5, 143.9, 137.7, 135.5, 133.0, 131.7, 129.1, 129.0, 128.5, 128.3, 126.3, 39.2, 21.1 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): δ = 133.0, 131.7, 129.1, 129.0, 128.3, 126.3, 39.2, 21.1 ppm.

**2-(3,4-Dimethylbenzyl)benzoic Acid (5c):** Keto acid **4c** (2.0 g, 7.86 mmol), upon reduction using zinc dust (3.39 g, 51.84 mmol) and mercuric chloride (0.33 g, 1.21 mmol) following a procedure similar to that described for **5a** gave benzyl acid **5c** (1.73 g, 92%) as a colourless solid, m.p. 108–110 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.05 (d, *J* = 7.8 Hz, 1 H, ArH), 7.97–7.65 (m, 1 H, ArH), 7.63–7.53 (m, 1 H, ArH), 7.45–7.43 (m, 1 H, ArH), 7.33–7.23 (m, 1 H, ArH), 7.20–6.95 (m, 2 H, ArH), 4.39 (s, 2 H, CH<sub>2</sub>), 2.20 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 172.9, 150.0, 143.9, 138.1, 134.3, 133.0, 131.7, 130.5, 129.6, 128.2, 126.5, 126.2, 123.0, 39.1, 19.8 ppm.

**2-(2,4-Dimethylbenzyl)benzoic Acid (5d):** Keto acid **4d** (2 g, 7.87 mmol), upon reduction using zinc dust (3.39 g, 51.84 mmol) and mercuric chloride (0.34 g, 1.24 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5d** (1.66 g, 88%) as a colourless solid, m.p. 74 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ

= 8.01 (d, *J* = 7.8 Hz, 1 H, ArH), 7.32 (t, *J* = 7.5 Hz, 1 H, ArH), 7.21 (t, *J* = 7.5 Hz, 1 H, ArH), 6.92–6.83 (m, 3 H, ArH), 6.74 (d, *J* = 7.5 Hz, 1 H, ArH), 4.31 (s, 2 H, CH<sub>2</sub>), 2.22 (s, 3 H, CH<sub>3</sub>), 2.11 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 173.2, 143.4, 136.8, 135.8, 135.5, 133.0, 131.6, 131.0, 130.6, 129.6, 128.4, 126.6, 126.0, 36.9, 20.9, 19.5 ppm.

**2-(3,4-Dimethoxybenzyl)benzoic Acid (5e):** Keto acid **4e** (2 g, 6.99 mmol), upon reduction using zinc dust (3.01 g, 46.03 mmol) and mercuric chloride (0.30 g, 1.10 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5e** (1.57 g, 83%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.99–7.96 (m, 1 H, ArH), 7.59–7.49 (m, 1 H, ArH), 7.42–7.36 (m, 1 H, ArH), 7.26–7.23 (m, 1 H, ArH), 7.15–7.12 (m, 1 H, ArH), 6.71 (s, 1 H, ArH), 6.62–6.58 (m, 1 H, ArH), 4.31 (s, 2 H, CH<sub>2</sub>), 3.74 (s, 3 H, OCH<sub>3</sub>), 3.73 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 172.9, 148.7, 147.2, 143.7, 133.2, 132.9, 131.5, 131.4, 126.2, 121.0, 120.1, 112.5, 111.1, 55.8, 55.7, 39.1 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): δ = 131.9, 130.5, 125.3, 120.0, 111.5, 110.1, 108.9, 55.8, 55.7, 39.1 ppm.

**2-(Biphenyl-4-ylmethyl)benzoic Acid (5f):** Keto acid **4f** (3 g, 9.93 mmol), upon reduction using zinc dust (4.37 g, 65.56 mmol) and mercuric chloride (0.43 g, 1.58 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5f** (2.63 g, 88%) as a colourless solid, m.p. 166–168 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.99 (d, *J* = 7.5 Hz, 1 H, ArH), 7.61–7.54 (m, 3 H, ArH), 7.53–7.48 (m, 3 H, ArH), 7.42–7.38 (m, 2 H, ArH), 7.37 (d, *J* = 7.4 Hz, 1 H, ArH), 7.35–7.33 (m, 1 H, ArH), 7.30 (d, *J* = 4.2 Hz, 1 H, ArH), 7.25 (t, *J* = 6.3 Hz, 1 H, CH<sub>2</sub>), 4.50 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 172.4, 143.4, 141.0, 139.9, 139.0, 133.1, 131.9, 131.8, 129.5, 128.9, 128.7, 128.4, 127.7, 127.5, 127.2, 127.1, 127.0, 126.5, 39.3 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): δ = 133.0, 131.8, 131.8, 129.4, 128.9, 128.7, 127.7, 127.5, 127.2, 127.1, 127.0, 126.5, 122.9, 39.3 ppm.

**2-[(4-Methylnaphthalen-1-yl)methyl]benzoic Acid (5g):** Keto acid **4g** (2 g, 6.36 mmol), upon reduction using zinc dust (2.97 g, 45.41 mmol) and mercuric chloride (0.29 g, 1.06 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5g** (1.77 g, 93%) as a colourless solid, m.p. 152–154 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.12 (d, *J* = 7.5 Hz, 1 H, ArH), 8.03 (d, *J* = 8.1 Hz, 1 H, ArH), 7.91 (d, *J* = 7.8 Hz, 1 H, ArH), 7.50–7.43 (m, 2 H, ArH), 7.33–7.23 (m, 3 H, ArH), 7.06 (d, *J* = 7.2 Hz, 1 H, ArH), 6.92 (d, *J* = 6.9 Hz, 1 H, ArH), 4.88 (s, 2 H, CH<sub>2</sub>), 2.69 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 173.0, 143.5, 134.5, 134.1, 133.1, 132.3, 131.7, 130.9, 129.1, 128.3, 127.2, 126.4, 126.2, 125.9, 125.7, 125.5, 124.8, 36.9, 19.5 ppm.

**2-[(2,3-Dihydro-1H-inden-5-yl)methyl]benzoic Acid (5h):** Keto acid **4h** (2 g, 7.51 mmol), upon reduction using zinc dust (3.24 g, 49.54 mmol) and mercuric chloride (0.32 g, 1.17 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5h** (1.33 g, 71%) as a colourless solid, m.p. 76–78 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.05–8.02 (m, 1 H, ArH), 7.91 (d, *J* = 7.8 Hz, 1 H, ArH), 7.67–7.65 (m, 1 H, ArH), 7.55–7.44 (m, 1 H, ArH), 7.30–7.20 (m, 1 H, ArH), 7.19–7.04 (m, 1 H, ArH), 7.01–6.92 (m, 1 H, ArH), 4.41 (s, 2 H, CH<sub>2</sub>), 2.87–2.80 (m, 4 H, CH<sub>2</sub>), 2.07–1.99 (m, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 172.8, 146.6, 144.4, 143.9, 141.8, 138.5, 134.1, 131.7, 129.1, 127.0, 125.8, 124.2, 122.2, 39.3, 32.8, 32.5, 25.5 ppm.

**2-(Thiophen-2-ylmethyl)benzoic Acid (5i):** Keto acid **4i** (2 g, 8.62 mmol), upon reduction using zinc dust (3.72 g, 56.88 mmol) and mercuric chloride (0.369 g, 1.35 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5i** (1.65 g, 88%) as colourless crystals, m.p. 105–106 °C (ref.<sup>[22]</sup> 105–106 °C). <sup>1</sup>H NMR

(300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.98 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.44–7.36 (m, 1 H, ArH), 7.29–7.20 (m, 2 H, ArH), 7.02–7.0 (m, 1 H, ArH), 6.84–6.71 (m, 1 H, ArH), 6.70 (s, 1 H, ArH), 4.53 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.7, 143.6, 143.1, 133.2, 131.8, 131.3, 128.0, 126.8, 126.7, 125.4, 124.0, 34.1 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): 133.1, 131.8, 131.3, 126.9, 126.5, 125.8, 123.8, 34.1 ppm.

**2-(2,2'-Bithiophen-5-ylmethyl)benzoic Acid (5j):** Keto acid **4j** (2 g, 6.36 mmol), upon reduction using zinc dust (2.74 g, 42.03 mmol) and mercuric chloride (0.27 g, 1.0 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5j** (1.60 g, 84%) as a yellow solid, m.p. 125 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92–7.89 (m, 1 H, ArH), 7.59–7.47 (m, 1 H, ArH), 7.45–7.42 (m, 1 H, ArH), 7.34–7.30 (m, 1 H, ArH), 7.17–7.15 (m, 1 H, ArH), 7.13–7.11 (m, 1 H, ArH), 6.97–6.93 (m, 2 H, ArH), 6.68–6.66 (m, 1 H, ArH), 4.45 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.0, 140.5, 139.0, 136.5, 134.7, 133.4, 131.2, 130.2, 129.2, 127.0, 126.1, 125.1, 123.4, 122.4, 122.2, 33.3 ppm.

**2-(Benzo[*b*]thiophen-3-ylmethyl)benzoic Acid (5k):** Keto acid **4k** (2 g, 7.09 mmol), upon reduction using zinc dust (3.06 g, 46.79 mmol) and mercuric chloride (0.3 g, 1.10 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5k** (1.29 g, 68%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.09 (d,  $J$  = 7.8 Hz, 1 H, ArH), 8.49–8.32 (m, 1 H, ArH), 7.71–7.68 (m, 1 H, ArH), 7.47–7.38 (m, 2 H, ArH), 7.31–7.29 (m, 2 H, ArH), 7.19–6.95 (m, 2 H, ArH), 4.63 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.8, 142.0, 140.4, 135.4, 133.1, 131.8, 131.2, 130.0, 126.6, 124.3, 124.1, 124.0, 123.2, 122.8, 122.0, 36.2 ppm.

**2-[4-(Diphenylamino)benzyl]benzoic Acid (5l):** The reduction of keto acid **4l** (2 g, 5.08 mmol), using zinc dust (2.19 g, 33.49 mmol) and mercuric chloride (0.21 g, 0.07 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5l** (1.71 g, 89%) as a colourless solid, m.p. 176–178 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.39 (t,  $J$  = 7.4 Hz, 1 H, ArH), 7.24–7.16 (m, 2 H, ArH), 7.09 (t,  $J$  = 7.8 Hz, 4 H, ArH), 6.95 (d,  $J$  = 8.4 Hz, 6 H, ArH), 6.90–6.82 (m, 4 H, ArH), 4.31 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 173.2, 147.9, 145.8, 143.7, 135.3, 133.0, 131.8, 131.7, 130.0, 129.2, 128.6, 128.3, 126.4, 124.4, 124.0, 122.5, 39.1 ppm.

**2-(Dibenzo[*b,d*]thiophen-2-ylmethyl)benzoic Acid (5m):** The reduction of keto acid **4m** (3 g, 9.03 mmol), using zinc dust (3.88 g, 59.63 mmol) and mercuric chloride (0.38 g, 1.39 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5m** (2.04 g, 71%) as a colourless solid, m.p. 118–120 °C (ref.<sup>[23]</sup> 118–120 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.86–7.95 (m, 3 H, ArH), 7.74 (s, 1 H, ArH), 7.66 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.50 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.34–7.31 (m, 1 H, ArH), 7.25–7.11 (m, 2 H, ArH), 7.07–7.0 (m, 2 H, ArH), 4.40 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 173.5, 143.2, 139.8, 137.1, 135.7, 135.5, 132.7, 131.5, 131.4, 128.3, 126.6, 126.3, 124.2, 122.9, 122.8, 122.6, 122.1, 121.6, 39.5 ppm.

**2-(Dibenzo[*b,d*]furan-2-ylmethyl)benzoic Acid (5n):** The reduction of keto acid **4n** (3 g, 9.48 mmol), using zinc dust (4.09 g, 62.6 mmol) and mercuric chloride (0.4 g, 1.47 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5n** (2.15 g, 75%) as a colourless solid, m.p. 146–148 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.95 (d,  $J$  = 7.2 Hz, 1 H, Ar), 7.77–7.70 (m, 1 H, ArH), 7.58 (s, 1 H, ArH), 7.45–7.22 (m, 4 H, ArH), 7.19–7.08 (m, 4 H, ArH), 4.45 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 173.5, 156.5, 154.9, 144.0, 135.3, 133.2, 131.9, 131.7, 128.5, 127.1, 126.5, 124.3, 124.3, 122.7, 122.6, 121.0, 120.7, 111.7, 111.4,

39.6 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 133.2, 131.9, 131.7, 128.5, 127.1, 126.5, 122.6, 121.0, 120.7, 111.7, 111.4, 39.6 ppm.

**2-[2,7-Dibromo-9-hexyl-9H-carbazol-3-yl]methylbenzoic Acid (5o):** Keto acid **4o** (2 g, 3.57 mmol), upon reduction using zinc dust (1.54 g, 23.55 mmol) and mercuric chloride (0.153 g, 0.56 mmol) following a procedure similar to that described for **4a**, gave benzyl acid **5o** (1.44 g, 74%) as a colourless solid, m.p. 110–112 °C. The crude product was used as such in the next step without any further characterization.

**2-[9,9-Dihexyl-9H-fluoren-2-yl]methylbenzoic Acid (5p):** Keto acid **4p** (2 g, 4.14 mmol), upon reduction using zinc dust (1.79 g, 27.37 mmol) and mercuric chloride (0.178 g, 0.65 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5p** (1.32 g, 67%) as a colourless solid, m.p. 132–134 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.09 (d,  $J$  = 7.5 Hz, 1 H, ArH), 7.61 (t,  $J$  = 8.7 Hz, 2 H, ArH), 7.42 (t,  $J$  = 7.2 Hz, 1 H, ArH), 7.27–7.29 (m, 4 H, ArH), 7.12–7.17 (m, 3 H, ArH), 4.55 (s, 2 H, CH<sub>2</sub>), 1.92 (s, 4 H, CH<sub>2</sub>), 1.01 (s, 12 H, CH<sub>2</sub>), 0.71–0.73 (m, 6 H, CH<sub>3</sub>), 0.61 (s, 4 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 173.5, 151.1, 150.8, 144.4, 141.1, 139.4, 139.3, 133.0, 131.7, 131.2, 128.4, 128.0, 126.7, 126.2, 124.0, 122.8, 119.6, 119.5, 54.9, 40.4, 31.5, 29.7, 23.8, 22.6, 14.1 ppm. C<sub>33</sub>H<sub>40</sub>O<sub>2</sub> (468.68): calcd. C 84.57, H 8.60; found C 84.31, H 8.43.

**2-(Pyren-2-ylmethyl)benzoic Acid (5q):** Keto acid **4q** (2 g, 5.88 mmol), upon reduction using zinc dust (2.51 g, 38.8 mmol) and mercuric chloride (0.251 g, 0.92 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5q** (1.57 g, 79%) as a colourless solid, m.p. 156–158 °C. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 8.19 (d,  $J$  = 9.3 Hz, 1 H, ArH), 8.16–8.04 (m, 3 H, ArH), 8.01–7.92 (m, 5 H, ArH), 7.71 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.23 (t,  $J$  = 3.9 Hz, 2 H, ArH), 6.87 (t,  $J$  = 4.1 Hz, 1 H, ArH), 5.13 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 169.4, 142.0, 134.8, 131.6, 131.1, 130.7, 130.6, 130.6, 129.7, 129.0, 127.9, 127.3, 127.2, 126.6, 126.0, 125.8, 124.8, 124.7, 124.7, 124.5, 123.7, 40.4, 40.2, 39.9, 39.6, 39.3, 36.7 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): 136.5, 135.7, 135.5, 132.8, 132.3, 132.2, 131.5, 130.9, 130.8, 129.8, 129.7, 129.6, 128.6, 41.7 ppm. C<sub>24</sub>H<sub>16</sub>O<sub>2</sub> (336.39): calcd. C 85.69, H 4.79; found C 85.37, H 4.95.

**3-(3,4-Dimethoxybenzyl)-2-naphthoic Acid (5r):** Keto acid **4r** (2 g, 5.95 mmol), upon reduction using zinc dust (2.56 g, 39.28 mmol) and mercuric chloride (0.25 g, 0.92 mmol) following a procedure similar to that described for **5a**, gave naphthyl acid **5r** (1.49 g, 78%) as a brown solid, m.p. 154–156 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.6 (s, 1 H, ArH), 7.84 (s, 1 H, ArH), 7.69 (s, 1 H, ArH), 7.51–7.44 (m, 3 H, ArH), 6.71–6.63 (m, 3 H, ArH), 4.43 (s, 2 H, CH<sub>2</sub>), 3.76 (s, 6 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.8, 148.8, 147.3, 138.8, 135.4, 133.6, 133.4, 131.1, 130.0, 128.9, 128.7, 127.3, 126.3, 126.4, 121.2, 112.7, 111.2, 55.9, 55.8, 39.6 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): 133.6, 130.0, 128.9, 128.7, 127.3, 126.3, 121.2, 112.7, 111.2, 55.9, 55.8, 39.6 ppm.

**2-(Thiophen-2-ylmethyl)-1-naphthoic Acid (5s):** Keto acid (2.0 g, 7.09 mmol), upon reduction using zinc dust (3.07 g, 46.80 mmol), mercuric chloride (0.30 g, 1.12 mmol) following a procedure similar to that described for **5a**, gave **5s** (1.54 g, 76%) as a yellow solid, m.p. 168–170 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.62 (s, 1 H, ArH), 7.84 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.25 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.60 (s, 1 H, ArH), 7.53–7.41 (m, 2 H, ArH), 7.02 (d,  $J$  = 5.1 Hz, 1 H, ArH), 6.85–6.82 (m, 1 H, ArH), 6.75–6.74 (m, 1 H, ArH), 4.74 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.6, 144.0, 138.1, 135.5, 133.9, 131.3, 130.0, 129.0, 128.8, 127.4, 126.7, 126.5, 126.1, 125.5, 123.9, 34.5 ppm. DEPT-135 (75.4 MHz,



CDCl<sub>3</sub>): 133.9, 129.9, 129.0, 128.8, 127.4, 126.8, 126.5, 125.5, 123.9, 34.5 ppm.

**3-[4-(Diphenylamino)benzyl]-2-naphthoic Acid (5t):** Keto acid **4t** (3 g, 6.77 mmol), upon reduction using zinc dust (2.9 g, 44.69 mmol) and mercuric chloride (0.29 g, 0.106 mmol) following a procedure similar to that described for **5a**, gave benzyl acid **5t** (2.23 g, 83%) as a colourless solid, m.p. 196–188 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.64 (s, 1 H, ArH), 7.90 (d, *J* = 7.8 Hz, 1 H, ArH), 7.79 (d, *J* = 7.8 Hz, 1 H, ArH), 7.68 (s, 1 H, ArH), 7.58 (t, *J* = 7.2 Hz, 1 H, ArH), 7.49 (t, *J* = 7.2 Hz, 1 H, ArH), 7.14–7.24 (m, 5 H, ArH), 7.02–7.08 (m, 5 H, ArH), 6.89–6.99 (m, 4 H, ArH), 4.52 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 172.9, 147.9, 145.8, 138.6, 135.4, 135.4, 133.6, 131.2, 130.3, 129.9, 129.3, 129.1, 128.9, 128.7, 127.3, 126.9, 126.4, 124.3, 123.9, 122.4, 39.4 ppm. C<sub>30</sub>H<sub>23</sub>NO<sub>2</sub> (429.52): calcd. C 83.89, H 5.40, N 3.26; found C 83.73, H 4.95, N 3.41.

**3-(9-Hexyl-9H-carbazol-4-yl)methyl-2-naphthoic Acid (5u):** Reduction of keto acid **4u** (2 g, 4.45 mmol), using zinc dust (1.92 g, 29.36 mmol) and mercuric chloride (0.19 g, 0.69 mmol) following a procedure similar to that described for **4a**, gave benzyl acid **5u** (1.53 g, 79%) as a colourless solid, m.p. 119–121 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.63 (s, 1 H, ArH), 8.01 (d, *J* = 7.5 Hz, 1 H, ArH), 7.94 (s, 1 H, ArH), 7.9 (d, *J* = 7.8 Hz, 1 H, ArH), 7.71 (d, *J* = 7.8 Hz, 1 H, ArH), 7.62 (s, 1 H, ArH), 7.55–7.47 (m, 2 H, ArH), 7.45–7.29 (m, 4 H, ArH), 7.14–7.09 (m, 1 H, ArH), 4.74 (s, 2 H, CH<sub>2</sub>), 4.23 (t, *J* = 7.2 Hz, 2 H, CH<sub>2</sub>), 1.86–1.81 (m, 2 H, CH<sub>2</sub>), 1.36–1.25 (m, 6 H, CH<sub>2</sub>), 0.84 (t, *J* = 6.6 Hz, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 173.1, 140.7, 139.7, 139.2, 135.4, 133.5, 131.1, 131.0, 130.1, 129.9, 129.5, 127.4, 127.3, 127.0, 126.2, 125.4, 123.0, 122.8, 121.0, 120.4, 118.5, 108.6, 43.1, 40.0, 31.6, 29.0, 27.0, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>): δ = 133.5, 130.1, 129.9, 129.5, 127.4, 127.3, 126.2, 125.4, 121.0, 120.4, 118.5, 108.6, 43.1, 40.0, 31.6, 29.0, 27.0, 22.6, 14.0 ppm. C<sub>30</sub>H<sub>29</sub>NO<sub>2</sub> (435.56): calcd. C 82.73, H 6.71, N 3.22; found C 83.01, H 6.64, N 3.45.

**2-(4-Methylbenzyl)benzaldehyde (6b):** Reduction of 2-(4-methylbenzyl)benzoic acid (**5b**; 0.8 g, 3.53 mmol) using LiAlH<sub>4</sub> (0.67 g, 17.63 mmol), followed by oxidation of the crude 2-(4-methylbenzyl)phenylmethanol (0.48 g, 2.26 mmol) using PCC (0.73 g, 3.38 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6b** (0.39 g, 87%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.16 (s, 1 H, CHO), 7.75 (d, *J* = 7.5 Hz, 1 H, ArH), 7.41 (t, *J* = 7.2 Hz, 1 H, ArH), 7.30 (t, *J* = 7.3 Hz, 1 H, ArH), 7.16 (d, *J* = 7.8 Hz, 1 H, ArH), 6.96 (q, *J* = 7.8 Hz, 4 H, ArH), 4.30 (s, 2 H, CH<sub>2</sub>), 2.20 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 192.5, 143.4, 137.3, 135.8, 134.0, 133.9, 131.9, 131.6, 130.2, 129.3, 128.7, 127.0, 37.6, 21.0 ppm.

**2-(3,4-Dimethylbenzyl)benzaldehyde (6c):** Reduction of 2-(3,4-dimethylbenzyl)benzoic acid (**5c**; 1.0 g, 4.16 mmol) using LiAlH<sub>4</sub> (0.79 g, 20.78 mmol), followed by oxidation of the crude 2-(3,4-dimethylbenzyl)benzyl alcohol (0.52 g, 2.32 mmol) using PCC (0.74 g, 3.43 mmol), following a procedure similar to that described for **6a** gave aldehyde **6c** (0.33 g, 81%) as a thick liquid. The crude product was used as such in the next step without any further characterization.

**2-(2,4-Dimethylbenzyl)benzaldehyde (6d):** Reduction of 2-(2,4-dimethylbenzyl)benzoic acid (**5d**; 1 g, 4.16 mmol) using LiAlH<sub>4</sub> (0.79 g, 20.78 mmol), followed by oxidation of the crude [2-(2,4-dimethylbenzyl)phenyl]methanol (0.79 g, 3.52 mmol) using PCC (1.14 g, 5.28 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6d** (0.68 g, 87%) as a colourless solid, m.p. 80 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.14 (s, 1 H, CHO), 7.79–

7.76 (m, 1 H, ArH), 7.38–7.30 (m, 2 H, ArH), 6.97–6.93 (m, 2 H, ArH), 6.83 (d, *J* = 7.8 Hz, 1 H, ArH), 6.66 (d, *J* = 7.5 Hz, 1 H, ArH), 4.28 (s, 2 H, CH<sub>2</sub>), 2.21 (s, 3 H, CH<sub>3</sub>), 2.13 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 192.7, 143.0, 136.2, 136.1, 135.2, 134.0, 133.9, 132.2, 131.1, 130.8, 129.6, 129.4, 126.8, 126.7, 126.1, 35.3, 21.0, 19.6 ppm.

**2-(3,4-Dimethoxybenzyl)benzaldehyde (6e):** Reduction of 3,4-dimethoxybenzylbenzoic acid (**5e**; 1 g, 3.67 mmol) using LiAlH<sub>4</sub> (0.69 g, 18.10 mmol), followed by oxidation of the crude [2-(3,4-dimethoxybenzyl)phenyl]methanol (0.65 g, 2.51 mmol) using PCC (0.81 g, 3.77 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6e** (0.59 g, 90%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.26 (s, 1 H, CHO), 7.85 (d, *J* = 7.5 Hz, 1 H, ArH), 7.52 (t, *J* = 7.2 Hz, 1 H, ArH), 7.41 (d, *J* = 7.5 Hz, 1 H, ArH), 7.25 (d, *J* = 7.2 Hz, 1 H, ArH), 6.77 (d, *J* = 8.1 Hz, 1 H, ArH), 6.70 (s, 1 H, ArH), 6.64 (d, *J* = 8.1 Hz, 1 H, ArH), 4.39 (s, 2 H, CH<sub>2</sub>), 3.84 (s, 3 H, OCH<sub>3</sub>), 3.81 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 192.5, 149.0, 147.5, 143.3, 133.9, 133.8, 132.9, 132.1, 131.4, 127.0, 120.8, 112.1, 111.2, 55.9, 55.8, 37.6 ppm.

**2-(Biphenyl-4-ylmethyl)benzaldehyde (6f):** Reduction of 2-(biphenyl-4-ylmethyl)benzoic acid (**5f**; 1.1 g, 3.90 mmol) using LiAlH<sub>4</sub> (0.74 g, 19.47 mmol), followed by oxidation of the crude [2-(biphenyl-4-ylmethyl)phenyl]methanol (0.65 g, 2.37 mmol) using PCC (0.76 g, 3.52 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6f** (0.84 g, 79%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.26 (s, 1 H, ArH), 7.87 (d, *J* = 7.5 Hz, 1 H, ArH), 7.56–7.29 (m, 8 H, ArH), 7.22–7.16 (m, 4 H, ArH), 4.48 (s, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 192.5, 142.9, 140.9, 139.5, 139.3, 134.0, 132.4, 131.8, 130.4, 130.0, 129.2, 128.8, 127.4, 127.1, 126.6, 126.1, 37.8 ppm.

**2-[(4-Methylnaphthalen-1-yl)methyl]benzaldehyde (6g):** Reduction of 2-[(4-methylnaphthalen-1-yl)methyl]benzoic acid (**5g**; 1 g, 3.59 mmol) using LiAlH<sub>4</sub> (0.68 g, 17.89 mmol), followed by oxidation of the crude {2-[(4-methylnaphthalen-1-yl)methyl]phenyl}methanol (0.65 g, 2.58 mmol) using PCC (0.8 g, 3.71 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6g** (0.52 g, 81%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.28 (s, 1 H, CHO), 8.05 (d, *J* = 8.1 Hz, 1 H, ArH), 7.96–7.90 (m, 2 H, ArH), 7.54–7.40 (m, 4 H, ArH), 7.25–7.20 (m, 1 H, ArH), 7.04–6.94 (m, 2 H, ArH), 4.87 (s, 2 H, CH<sub>2</sub>), 2.69 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 192.7, 143.0, 134.1, 134.0, 133.4, 133.0, 132.2, 132.0, 131.1, 126.9, 126.8, 126.4, 125.9, 125.6, 125.0, 124.4, 35.2, 19.5 ppm.

**2-[(2,3-Dihydro-1H-inden-5-yl)methyl]benzaldehyde (6h):** Reduction of 2-[(2,3-dihydro-1H-inden-5-yl)methyl]benzoic acid (**5h**; 1 g, 3.96 mmol) using LiAlH<sub>4</sub> (0.75 g, 19.93 mmol), followed by oxidation of the crude 2-[(4-methylnaphthalen-1-yl)methyl]phenyl methanol (0.61 g, 2.58 mmol) using PCC (0.83 g, 3.86 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6h** (0.51 g, 92%) as a thick liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.02 (s, 1 H, CHO), 7.92 (d, *J* = 7.5 Hz, 2 H, ArH), 7.66–7.68 (m, 2 H, ArH), 7.51–7.57 (m, 2 H, ArH), 7.27–7.49 (m, 4 H, ArH), 5.32 (s, 2 H, CH<sub>2</sub>), 2.86–2.98 (m, 4 H, CH<sub>2</sub>), 2.06–2.16 (m, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 190.6, 151.3, 146.5, 145.0, 134.0, 129.6, 129.0, 128.9, 128.8, 125.8, 124.5, 122.1, 32.5, 25.3 ppm.

**2-(Thiophen-2-ylmethyl)benzaldehyde (6i):** Reduction of 2-(thiophen-2-ylmethyl)benzoic acid (**5i**; 1 g, 4.58 mmol) using LiAlH<sub>4</sub> (0.87 g, 22.93 mmol), followed by oxidation of the crude [2-(thiophen-2-ylmethyl)phenyl]methanol (0.5 g, 2.45 mmol) using PCC (0.79 g, 3.67 mmol), following a procedure similar to that described

for **6a**, gave aldehyde **6i** (0.45 g, 91%) as a thick liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.11 (s, 1 H, CHO), 7.72 (d,  $J$  = 7.5 Hz, 1 H, ArH), 7.41 (t,  $J$  = 6.9 Hz, 1 H, ArH), 7.30 (t,  $J$  = 7.2 Hz, 1 H, ArH), 7.21 (d,  $J$  = 7.5 Hz, 1 H, ArH), 7.01 (t,  $J$  = 5.1 Hz, 1 H, ArH), 6.78–6.75 (m, 1 H, ArH), 6.63–6.22 (m, 1 H, ArH), 4.09 (s, 2 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.4, 143.1, 142.3, 134.1, 133.6, 132.6, 131.2, 127.4, 126.9, 125.8, 125.5, 124.2, 32.5 ppm. DEPT 135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.4, 134.1, 132.6, 131.2, 127.4, 126.9, 125.5, 124.2, 32.5 ppm.

**2-(2,2'-Bithiophen-5-ylmethyl)benzaldehyde (6j)**: Reduction of 2-(2,2'-bithiophen-5-ylmethyl)benzoic acid (**5j**; 1 g, 3.44 mmol) using  $\text{LiAlH}_4$  (0.70 g, 17.20 mmol), followed by oxidation of the crude [2-(2,2'-bithiophen-5-ylmethyl)phenyl]methanol (0.2 g, 0.72 mmol) using PCC (0.25 g, 1.15 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6j** (0.16 g, 83%) as a thick liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.24 (s, 1 H, CHO), 7.87–7.86 (m, 1 H, ArH), 7.56–7.53 (m, 1 H, ArH), 7.48–7.45 (m, 1 H, ArH), 7.39–7.36 (m, 1 H, ArH), 7.34–7.30 (m, 1 H, ArH), 7.18–7.14 (m, 1 H, ArH), 7.07–7.05 (m, 1 H, ArH), 6.97–6.94 (m, 2 H, ArH), 4.58 (s, 2 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.5, 142.4, 141.9, 137.5, 136.2, 134.1, 133.6, 133.1, 131.2, 127.7, 127.5, 126.2, 124.0, 123.4, 123.2, 32.8 ppm.

**2-(Benzo[*b*]thiophen-2-ylmethyl)benzaldehyde (6k)**: Reduction of 2-(benzo[*b*]thiophen-3-ylmethyl)benzoic acid (**5k**; 1.50 g) using  $\text{LiAlH}_4$  (1.06 g, 27.89 mmol), followed by oxidation of the crude 2-(benzo[*b*]thiophen-3-ylmethyl)phenylmethanol (0.98 g, 3.85 mmol) using PCC (0.76 g, 1.62 mmol), following a procedure similar to that described for **6a**, gave known aldehyde **6k** (0.85 g, 87%) as a thick liquid. The crude product was used as such in the next step without any further characterization.

**2-[4-(*N,N*-Diphenylamino)benzyl]benzaldehyde (6l)**: Reduction of 2-(benzo[*b*]thiophen-3-ylmethyl)benzoic acid (**5l**; 1.60 g, 4.21 mmol) using  $\text{LiAlH}_4$  (0.80 g, 21.05 mmol), followed by oxidation of the crude 2-[4-(diphenylamino)benzyl]phenylmethanol (0.77 g, 2.11 mmol) using PCC (0.68 g, 3.15 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6l** (0.63 g, 83%) as a thick liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.31 (s, 1 H, CHO), 7.91 (d,  $J$  = 7.5 Hz, 1 H, ArH), 7.67 (d,  $J$  = 6.6 Hz, 1 H, ArH), 7.66–7.55 (m, 1 H, ArH), 7.36–7.35 (m, 1 H, ArH), 7.33–7.32 (m, 2 H, ArH), 7.27–7.20 (m, 4 H, ArH), 7.13–7.08 (m, 4 H, ArH), 7.03–7.01 (m, 4 H, ArH), 4.43 (s, 2 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.4, 147.8, 146.1, 143.2, 134.6, 134.0, 131.9, 131.8, 131.7, 130.0, 129.5, 129.4, 129.2, 127.0, 126.4, 124.9, 124.3, 124.1, 122.6, 37.4 ppm.

**2-(Dibenzo[*b,d*]thiophen-2-ylmethyl)benzaldehyde (6m)**: Reduction of 2-(dibenzo[*b,d*]thiophen-2-ylmethyl)benzoic acid (**5m**; 0.70 g, 2.19 mmol) using  $\text{LiAlH}_4$  (0.41 g, 10.78 mmol), followed by oxidation of the crude 2-(dibenzo[*b,d*]thiophen-2-ylmethyl)methanol (0.5 g, 1.63 mmol) using PCC (0.53 g, 2.24 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6m** (0.41 g, 83%) as a thick liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.30 (s, 1 H, CHO), 8.15–8.12 (m, 1 H, ArH), 8.06–7.91 (m, 1 H, ArH), 7.88–7.82 (m, 3 H, ArH), 7.79–7.72 (m, 2 H, ArH), 7.58–7.41 (m, 3 H, ArH), 7.40–7.24 (m, 1 H, ArH), 4.62 (s, 2 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.6, 143.0, 139.8, 137.4, 136.7, 135.9, 134.0, 132.7, 131.6, 130.7, 128.9, 127.9, 127.1, 126.7, 125.0, 124.3, 123.0, 121.8, 121.6, 38.1 ppm.

**2-(Dibenzo[*b,d*]furan-2-ylmethyl)benzaldehyde (6n)**: Reduction of 2-(dibenzo[*b,d*]thiophen-2-ylmethyl)benzoic acid (**5n**; 0.72 g, 2.38 mmol) using  $\text{LiAlH}_4$  (0.51 g, 11.84 mmol), followed by oxidation of the crude 2-(dibenzo[*b,d*]thiophen-2-ylmethyl)methanol (0.49 g, 1.72 mmol) using PCC (0.55 g, 2.55 mmol), following a

procedure similar to that described for **6a**, gave aldehyde **6n** (0.60 g, 84%) as a brown oil. The crude product was used as such in the next step without any further characterization.

**3-(3,4-Dimethoxybenzyl)-2-naphthaldehyde (6r)**: Reduction of 3-(3,4-dimethoxybenzyl)-2-naphthoic acid (**5r**; 0.9 g, 2.79 mmol) using  $\text{LiAlH}_4$  (0.76 g, 20.0 mmol), followed by oxidation of the crude 2-(dibenzo[*b,d*]thiophen-2-ylmethyl)methanol (0.7 g, 1.72 mmol) using PCC (0.73 g, 3.40 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6r** (0.60 g, 87%) as a brown solid, m.p. 132–134 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.19 (s, 1 H, CHO), 8.27 (s, 1 H, ArH), 7.88 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.71 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.52 (t,  $J$  = 6.9 Hz, 2 H, ArH), 7.47 (t,  $J$  = 6.9 Hz, 1 H, ArH), 6.71–6.68 (m, 2 H, ArH), 6.62 (s, 1 H, ArH), 4.43 (s, 2 H,  $\text{CH}_2$ ), 3.76 (s, 3 H,  $\text{OCH}_3$ ), 3.72 (s, 3 H,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.8, 143.9, 147.4, 138.0, 136.5, 135.7, 133.0, 132.6, 131.4, 130.1, 129.3, 129.2, 127.5, 126.6, 121.0, 112.4, 111.2, 55.9, 55.8, 38.3 ppm.

**2-(Thiophen-3-ylmethyl)-1-naphthaldehyde (6s)**: Reduction of 2-(thiophen-2-ylmethyl)-1-naphthoic acid (**5s**; 1.0 g, 3.74 mmol) using  $\text{LiAlH}_4$  (0.71 g, 18.64 mmol), followed by oxidation of the crude [2-(thiophen-3-ylmethyl)naphthalen-1-yl]methanol (0.66 g, 2.61 mmol) using PCC (0.73 g, 3.94 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6s** (0.53 g, 82%) as a colourless solid, m.p. 78–80 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.26 (s, 1 H, CHO), 8.33 (s, 1 H, ArH), 7.95 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.80 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.70 (s, 1 H, ArH), 7.61 (t,  $J$  = 7.1 Hz, 1 H, ArH), 7.53 (d,  $J$  = 7.5 Hz, 1 H, ArH), 7.13 (d,  $J$  = 5.1 Hz, 1 H, ArH), 6.92–6.89 (m, 1 H, ArH), 6.80 (broad s, 1 H, ArH), 4.74 (s, 2 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.6, 143.5, 137.2, 137.1, 135.7, 132.3, 131.6, 130.0, 129.4, 129.2, 127.6, 126.9, 126.8, 125.5, 124.1, 33.1 ppm.

**3-[4-(Diphenylamino)benzyl]-2-naphthaldehyde (6t)**: Reduction of 2-(benzo[*b*]thiophen-3-ylmethyl)benzoic acid (**5t**; 0.8 g, 1.86 mmol) using  $\text{LiAlH}_4$  (0.35 g, 9.32 mmol), followed by oxidation of the crude {3-[4-(diphenylamino)benzyl]naphthalen-2-yl}methanol (0.6 g, 1.44 mmol) using PCC (0.71 g, 3.29 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6t** (0.63 g, 83%) as a thick liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.23 (s, 1 H, CHO), 8.30 (s, 1 H, ArH), 7.89 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.75 (d,  $J$  = 8.4 Hz, 1 H, ArH), 7.60 (s, 1 H, ArH), 7.54–7.52 (m, 1 H, ArH), 7.43 (t,  $J$  = 7.5 Hz, 1 H, ArH), 7.17–7.09 (m, 4 H, ArH), 7.02–6.96 (m, 6 H, ArH), 6.92–6.87 (m, 4 H, ArH), 4.45 (s, 2 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.6, 147.9, 146.0, 137.8, 136.1, 135.8, 134.9, 132.6, 131.5, 130.3, 129.7, 129.3, 129.2, 127.5, 126.6, 124.3, 124.0, 122.5, 118.8, 116.8, 38.0 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.7, 136.1, 130.3, 129.7, 129.3, 129.2, 127.5, 126.6, 124.3, 124.0, 122.5, 38.0 ppm.

**3-[(9-Hexyl-9*H*-carbazol-4-yl)methyl]-2-naphthaldehyde (6u)**: Reduction of 3-[(9-hexyl-9*H*-carbazol-4-yl)methyl]-2-naphthoic acid (**5u**; 0.72 g, 1.65 mmol) using  $\text{LiAlH}_4$  (0.32 g, 8.27 mmol), followed by oxidation of the crude benzyl alcohol using PCC (0.33 g, 1.53 mmol), following a procedure similar to that described for **6a**, gave aldehyde **6u** (0.33 g, 83%) as a thick liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.26 (s, 1 H, CHO), 8.28 (s, 1 H, ArH), 7.93–7.86 (m, 2 H, ArH), 7.8 (s, 1 H, ArH), 7.69 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.58 (s, 1 H, ArH), 7.52–7.40 (m, 2 H, ArH), 7.27–7.37 (m, 2 H, ArH), 7.15–7.20 (m, 2 H, ArH), 7.08 (t,  $J$  = 7.2 Hz, 1 H, ArH), 4.67 (s, 2 H,  $\text{CH}_2$ ), 4.16 (t,  $J$  = 7.2 Hz, 2 H,  $\text{CH}_2$ ), 1.73–1.78 (m, 2 H,  $\text{CH}_2$ ), 1.18–1.34 (m, 6 H,  $\text{CH}_2$ ), 0.77 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.7, 140.7, 139.2, 138.9, 135.8, 135.8, 132.7, 131.4, 130.7, 130.1, 129.2, 129.1, 127.5, 126.9, 126.4, 125.5, 123.0, 122.6, 120.6, 120.4, 118.5, 108.7, 108.6,

43.1, 38.7, 31.5, 28.9, 26.9, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 192.7, 135.8, 130.1, 129.2, 128.5, 127.6, 126.9, 126.5, 125.5, 120.6, 120.4, 118.5, 108.7, 108.6, 43.1, 38.7, 31.5, 28.9, 26.9, 22.6, 14.0 ppm.

**2-Methylantracene (7b):** Cyclodehydration of 2-(4-methylbenzyl)-benzaldehyde (**6b**; 0.35 g, 1.66 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.05 g, 0.33 mmol) following a procedure similar to that described for **7a** gave known 2-methylantracene (**7b**; 0.29 g, 92%) as a colourless solid, m.p. 204–206 °C (ref.<sup>[15c]</sup> 205–206 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.52 (s, 1 H, ArH), 8.03–7.94 (m, 2 H, ArH), 7.30 (t,  $J$  = 7.5 Hz, 2 H, ArH), 7.20–7.17 (m, 1 H, ArH), 7.02–6.99 (m, 1 H, ArH), 6.97–6.90 (m, 1 H, ArH), 6.76 (s, 1 H, ArH), 2.06 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 135.5, 132.3, 131.9, 131.8, 131.1, 130.3, 128.5, 128.4, 128.3, 126.9, 126.8, 125.7, 125.0, 124.9, 22.2 ppm.

**2,3-Dimethylantracene (7c):** Cyclodehydration of 2-(3,4-dimethylbenzyl)benzaldehyde (**6c**; 0.30 g, 1.33 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.04 g, 0.26 mmol) following a procedure similar to that described for **7a** gave 2,3-dimethylantracene (**7c**; 0.24 g, 88%) as a colourless solid, m.p. 246–248 °C (ref.<sup>[16f]</sup> 248 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.28 (s, 2 H, ArH), 7.97–7.94 (m, 2 H, ArH), 7.75 (s, 2 H, ArH), 7.42–7.40 (m, 2 H, ArH), 2.47 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 135.6, 131.4, 131.2, 128.1, 126.9, 124.8, 120.4 ppm. DEPT 135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.1, 126.9, 124.8, 20.4 ppm.

**1,3-Dimethylantracene (7d):** Cyclodehydration of 2-(2,4-dimethylbenzyl)benzaldehyde (**6d**; 0.5 g, 2.23 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.06 g, 0.4 mmol) following a procedure similar to that described for **7a** gave 1,3-dimethylantracene (**7d**; 0.38 g, 83%) as a colourless solid, m.p. 76–78 °C (ref.<sup>[16f]</sup> 78 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.46 (s, 1 H, ArH), 8.28 (s, 1 H, ArH), 8.01–7.93 (m, 2 H, ArH), 7.59 (s, 1 H, ArH), 7.46–7.42 (m, 2 H, ArH), 7.14 (s, 1 H, ArH), 2.76 (s, 3 H, CH<sub>3</sub>), 2.48 (s, 3 H, ArH) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.7, 134.1, 132.4, 131.7, 131.2, 130.1, 128.7, 128.6, 127.9, 125.8, 125.3, 124.9, 122.6, 22.0, 19.7 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.6, 128.6, 127.9, 125.8, 124.9, 122.6, 22.0, 19.7 ppm.

**2,3-Dimethoxyanthracene (7e):** Cyclodehydration of 2-(3,4-dimethoxybenzyl)benzaldehyde (**6e**; 0.35 g, 1.36 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.04 g, 0.27 mmol) following a procedure similar to that described for **7a** gave 2,3-dimethoxyanthracene (**7e**; 0.28 g, 87%) as a colourless solid, m.p. 200–202 °C (ref.<sup>[16a]</sup> 200–202 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21 (s, 2 H, ArH), 7.94–7.91 (m, 2 H, ArH), 7.41–7.38 (m, 2 H, ArH), 7.18 (s, 2 H, ArH), 4.04 (s, 6 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.1, 130.8, 128.6, 127.6, 124.6, 124.0, 104.8, 55.9 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 127.6, 124.6, 124.0, 104.8, 55.9 ppm.

**2-Phenylantracene (7f):** Cyclodehydration of 2-(biphenyl-4-ylmethyl)benzaldehyde (**6f**; 0.5 g, 1.90 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.05 g, 0.38 mmol) following a procedure similar to that described for **7a** gave known 2-phenylantracene (**7f**; 0.42 g, 91%) as a colourless solid, m.p. 202–204 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.48 (s, 1 H, ArH), 8.44 (s, 1 H, ArH), 8.20 (s, 1 H, ArH), 8.10–8.01 (m, 3 H, ArH), 7.77 (s, 3 H, ArH), 7.51–7.40 (m, 4 H, ArH), 7.30–7.25 (m, 1 H, ArH) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.1, 137.9, 132.1, 131.9, 130.9, 128.9, 128.8, 128.2, 128.2, 127.4, 127.4, 126.6, 126.0, 125.7, 125.5, 125.4 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.9, 128.7, 128.3, 127.4, 127.1, 127.0, 126.6, 126.0, 125.7, 125.6, 125.4 ppm.

**5-Methyltetrathene (7g):** Cyclodehydration of 2-[(4-methylnaphthalen-1-yl)methyl]benzaldehyde (**6g**; 0.2 g, 0.76 mmol) using

BF<sub>3</sub>·OEt<sub>2</sub> (0.02 g, 0.15 mmol) following a procedure similar to that described for **7a** gave 1,3-dimethylantracene (**7g**; 0.17 g, 89%) as a colourless solid, m.p. 156–158 °C (ref.<sup>[21]</sup> 155.9–156.9 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.13 (s, 1 H, ArH), 8.87 (d,  $J$  = 8.1 Hz, 1 H, ArH), 8.26 (s, 1 H, ArH), 8.12–8.09 (m, 1 H, ArH), 8.02 (d,  $J$  = 8.0 Hz, 2 H, ArH), 7.70–7.64 (m, 3 H, ArH), 7.54–7.51 (m, 2 H, ArH), 2.72 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.5, 132.4, 132.1, 131.6, 130.7, 130.7, 128.5, 127.6, 127.1, 126.8, 126.6, 125.7, 125.7, 125.3, 124.8, 123.2, 121.4, 20.3 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.5, 127.6, 127.1, 126.8, 126.6, 125.7, 125.3, 124.8, 123.2, 121.4, 20.3 ppm.

**2,3-Dihydro-1H-cyclopenta[*b*]anthracene (7h):** Cyclodehydration of crude 2-[(4-methylnaphthalen-1-yl)methyl]benzaldehyde (**6h**; 0.30 g, 1.27 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.04 g, 0.25 mmol) following a procedure similar to that described for **7a** gave anthracene **7h** (0.27 g, 92%) as a white crystalline solid, m.p. 226–228 °C (ref.<sup>[20]</sup> 228–230 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31 (s, 2 H, ArH), 7.97–7.94 (m, 2 H, ArH), 7.80 (s, 2 H, ArH), 7.42–7.38 (m, 2 H, ArH), 3.09 (t,  $J$  = 7.1 Hz, 4 H, CH<sub>2</sub>), 2.20–2.11 (m, 2 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.6, 131.7, 131.3, 128.0, 125.3, 124.8, 121.6, 32.6, 26.3 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.0, 125.3, 124.8, 121.6, 32.6, 26.3 ppm.

**Naphtho[2,3-*b*]thiophene (7i):** Cyclodehydration of 2-(thiophen-2-ylmethyl)benzaldehyde (**6i**; 0.3 g, 1.48 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.04 g, 0.29 mmol) following a procedure similar to that described for **7a** gave **7i** (0.24 g, 87%) as a colourless solid, m.p. 192–194 °C (ref.<sup>[15c]</sup> 192–193 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.35 (s, 1 H, ArH), 8.3 (s, 1 H, ArH), 7.87–7.96 (m, 2 H, ArH), 7.38–7.48 (m, 3 H, ArH), 7.39 (d,  $J$  = 5.7 Hz, 1 H, ArH) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.9, 138.2, 131.0, 130.9, 128.3, 128.2, 127.3, 125.3, 124.9, 123.5, 121.8, 120.7 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.3, 128.2, 127.3, 125.3, 124.9, 123.5, 121.8, 120.7 ppm.

**2-(Thiophen-2-yl)naphtho[2,3-*b*]thiophene (7j):** Cyclodehydration of 2-(2,2'-bithiophen-5-ylmethyl)benzaldehyde (**6j**; 0.2 g, 0.7 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.02 g, 0.14 mmol) following a procedure similar to that described for **7a** gave **7j** (0.17 g, 91%) as a colourless solid, m.p. 258–260 °C (ref.<sup>[16c]</sup> 258–260 °C). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 8.51 (s, 1 H, ArH), 8.38 (s, 1 H, ArH), 8.05–7.96 (m, 2 H, ArH), 7.77 (s, 1 H, ArH), 7.70 (d,  $J$  = 7.8 Hz, 1 H, ArH), 7.54–7.49 (m, 3 H, ArH), 7.20 (t,  $J$  = 7.4 Hz, 1 H, ArH) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.6, 136.8, 136.3, 131.0, 130.8, 128.6, 128.1, 127.5, 127.2, 126.3, 125.5, 125.3, 121.6, 120.4, 119.1 ppm. DEPT 135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.6, 128.1, 127.5, 127.2, 126.3, 125.5, 125.3, 121.6, 120.4, 119.1 ppm.

**Benzo[*b*]naphtho[2,3-*d*]thiophene (7k):** Cyclodehydration of aldehyde **6k** (0.49 g, 1.94 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.06 g, 0.38 mmol) following a procedure similar to that described for **7a** gave **7k** (0.39 g, 85%) as a pale green solid, m.p. 146–148 °C (ref.<sup>[16c]</sup> 146–147 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.58 (s, 1 H, ArH), 8.24 (s, 1 H, ArH), 8.21–8.23 (m, 1 H, ArH), 7.99–8.02 (m, 1 H, ArH), 7.87–7.90 (m, 1 H, ArH), 7.77–7.81 (m, 1 H, ArH), 7.42–7.53 (m, 4 H, ArH) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.2, 137.7, 135.5, 132.6, 130.8, 128.4, 127.7, 127.1, 126.0, 125.2, 124.5, 122.7, 122.0, 120.6, 120.0 ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.4, 127.7, 127.1, 126.0, 125.2, 124.5, 122.7, 122.0, 120.6, 120.0 ppm.

***N,N*-Diphenylantracene-1-amine (7l):** Cyclodehydration of aldehyde **6l** (0.4 g, 1.1 mmol) using BF<sub>3</sub>·OEt<sub>2</sub> (0.03 g, 0.22 mmol) following a procedure similar to that described for **7a** gave **7l** (0.31 g, 83%) as a pale green solid, m.p. 156 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31 (s, 1 H, ArH), 8.11 (s, 1 H, ArH), 7.96–7.93 (m, 1 H, ArH), 7.87 (d,  $J$  = 9.0 Hz, 2 H, ArH), 7.49 (s, 1 H, ArH), 7.40 (t,  $J$  =

6.9 Hz, 1 H, ArH), 7.32–7.30 (m, 3 H, ArH), 7.27–7.26 (m, 2 H, ArH), 7.22–7.19 (m, 3 H, ArH), 7.16–7.10 (m, 1 H, ArH), 7.09–7.05 (m, 3 H, ArH) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.6, 144.9, 132.6, 132.2, 131.0, 129.2, 129.1, 129.1, 128.9, 128.2, 127.8, 126.0, 125.5, 124.8, 124.7, 124.7, 124.5, 124.4, 124.0, 123.2, 118.4 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 129.4, 129.2, 129.2, 129.1, 128.2, 127.8, 126.0, 125.5, 124.8, 124.7, 124.5, 124.4, 123.9, 123.2, 118.4 ppm. HRMS (EI): calcd. for  $\text{C}_{26}\text{H}_{19}\text{N}$  [ $\text{M}$ ] $^+$  345.1517; found 345.1510.

**Anthra[1,2-*d*]benzo[*b*]thiophene (7m):** Cyclodehydration of 2-(di-benzo[*b,d*]thiophen-2-ylmethyl)benzaldehyde (**6m**; 0.3 g, 0.99 mmol) using  $\text{BF}_3\cdot\text{OEt}_2$  (0.03 g, 0.20 mmol) following a procedure similar to that described for **7a** gave **7m** (0.25 g, 88%) as a pale green solid, m.p. 168 °C (ref.<sup>[23]</sup> 228–230 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.40 (s, 1 H, ArH), 8.95 (d,  $J$  = 8.4 Hz, 1 H, ArH), 8.47 (s, 1 H, ArH), 8.11 (d,  $J$  = 8.1 Hz, 1 H, ArH), 7.99–7.90 (m, 3 H, ArH), 7.75 (d,  $J$  = 9.0 Hz, 1 H, ArH), 7.60 (t,  $J$  = 7.7 Hz, 1 H, ArH), 7.53–7.42 (m, 3 H, ArH) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.7, 138.5, 137.1, 132.3, 130.7, 130.6, 128.9, 128.5, 128.4, 128.2, 128.0, 127.9, 126.1, 125.5, 125.1, 125.0, 124.5, 123.3, 121.7, 120.9 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.5, 128.4, 128.0, 126.1, 125.6, 125.1, 125.0, 124.5, 123.3, 121.7, 121.0 ppm. HRMS (EI): calcd. for  $\text{C}_{20}\text{H}_{12}\text{S}$  [ $\text{M}$ ] $^+$  284.0660; found 284.0654.

**Anthra[1,2-*d*]benzo[*b*]furan (7n):** Cyclodehydration of 2-(di-benzo[*b,d*]furan-2-ylmethyl)benzaldehyde (**6n**; 0.35 g, 1.23 mmol) using  $\text{BF}_3\cdot\text{OEt}_2$  (0.04 g, 0.25 mmol) following a procedure similar to that described for **7a** gave **7n** (0.31 g, 93%) as a pale green solid, m.p. 152–154 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.03 (s, 1 H, ArH), 8.53–8.48 (m, 2 H, ArH), 8.10 (d,  $J$  = 8.1 Hz, 1 H, ArH), 8.02 (s, 1 H, ArH), 8.0 (s, 1 H, ArH), 7.63–7.65 (m, 2 H, ArH), 7.52–7.46 (m, 4 H, ArH) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.7, 154.1, 132.3, 130.5, 129.5, 129.4, 128.4, 128.2, 128.0, 127.4, 126.2, 125.5, 125.3, 125.1, 123.4, 121.8, 121.6, 116.2, 113.9, 112.0 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 129.4, 128.4, 128.2, 128.0, 126.2, 125.6, 125.1, 123.4, 121.7, 121.6, 113.9, 112.0 ppm. HRMS (EI): calcd. for  $\text{C}_{20}\text{H}_{12}\text{O}$  [ $\text{M}$ ] $^+$  268.0888; found 268.0880.

**2,3-Dimethoxytetraphene (7r):** Cyclodehydration of naphthaldehyde **6r** (0.2 g, 0.65 mmol) using  $\text{BF}_3\cdot\text{OEt}_2$  (0.2 g, 0.13 mmol) following a procedure similar to that described for **7a** gave **7r** (0.17 g, 91%) as a colourless solid, m.p. 278–280 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.48 (s, 1 H, ArH), 8.35 (s, 1 H, ArH), 7.91–7.89 (m, 1 H, ArH), 7.31–7.29 (m, 1 H, ArH), 7.09 (s, 1 H, ArH), 3.99 (s, 3 H,  $\text{OCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.1, 135.7, 133.7, 132.9, 130.1, 129.6, 128.3, 109.1, 60.6 ppm. DEPT 135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 132.9, 130.1, 129.6, 128.3, 109.0, 60.6 ppm. HRMS (EI): calcd. for  $\text{C}_{20}\text{H}_{16}\text{O}_2$  [ $\text{M}$ ] $^+$  288.1150; found 288.1150.

**Anthra[2,3-*b*]thiophene (7s):** Cyclodehydration of 2-(thiophen-3-ylmethyl)-1-naphthaldehyde (**6s**; 0.2 g, 0.79 mmol) using  $\text{BF}_3\cdot\text{OEt}_2$  (0.02 g, 0.16 mmol) following a procedure similar to that described for **7a** gave known anthra[2,3-*b*]thiophene (**7s**; 0.16 g, 86%) as a yellow solid, m.p. > 330 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_6$ -acetone):  $\delta$  = 7.87 (s, 1 H, ArH), 7.85 (s, 1 H, ArH), 7.80 (s, 1 H, ArH), 7.79 (s, 1 H, ArH), 7.24–7.21 (m, 2 H, ArH), 6.88 (d,  $J$  = 5.7 Hz, 1 H, ArH), 6.67 (d,  $J$  = 5.7 Hz, 1 H, ArH), 6.62–6.59 (m, 2 H, ArH) ppm. Due to poor solubility, a  $^{13}\text{C}$  NMR spectrum was not recorded.

***N,N*-Diphenyltetracen-2-amine (7t):** Cyclodehydration of aldehyde **6t** (0.28 g, 0.67 mmol) using  $\text{BF}_3\cdot\text{OEt}_2$  (0.02 g, 0.13 mmol) following a procedure similar to that described for **7a** gave **7t** (0.21 g, 78%) as a pale green solid, m.p. 256–258 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.59 (s, 1 H, ArH), 8.55 (s, 1 H, ArH), 8.50 (s, 1 H,

ArH), 8.31 (s, 1 H, ArH), 8.0–7.93 (m, 2 H, ArH), 7.87 (d,  $J$  = 9.3 Hz, 1 H, ArH), 7.45 (s, 1 H, ArH), 7.39–7.29 (m, 5 H, ArH), 7.24–7.18 (m, 5 H, ArH), 7.19–7.05 (m, 3 H, ArH) ppm. Due to poor solubility, a  $^{13}\text{C}$  NMR spectrum was not recorded. HRMS (EI): calcd. for  $\text{C}_{30}\text{H}_{21}\text{N}$  [ $\text{M}$ ] $^+$  395.1674; found 395.1670.

**5-Hexyl-5*H*-anthra[2,3-*c*]carbazole (7u):** Cyclodehydration of aldehyde **6u** (0.25 g, 0.59 mmol) using  $\text{BF}_3\cdot\text{OEt}_2$  (0.02 g, 0.11 mmol) following a procedure similar to that described for **7a** gave **7u** (0.21 g, 87%) as a pale green solid, m.p. 236–238 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.39 (s, 1 H, ArH), 8.79 (s, 2 H, ArH), 8.74 (s, 1 H, ArH), 8.67 (s, 1 H, ArH), 8.07–7.96 (m, 3 H, ArH), 7.63–7.58 (m, 2 H, ArH), 7.52–7.46 (m, 2 H, ArH), 7.43–7.4 (m, 2 H, ArH), 4.44 (t,  $J$  = 7.2 Hz, 2 H,  $\text{NCH}_2$ ), 1.98–1.88 (m, 2 H,  $\text{CH}_2$ ), 1.42–1.25 (m, 6 H,  $\text{CH}_2$ ), 0.86 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 138.5, 136.9, 131.7, 130.9, 130.7, 129.3, 128.5, 128.3, 128.2, 128.1, 128.0, 126.4, 125.5, 125.1, 124.5, 124.1, 123.2, 121.6, 120.2, 120.1, 112.9, 112.4, 109.6, 43.2, 31.5, 29.8, 26.9, 22.5, 13.9 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.3, 128.3, 128.2, 128.0, 126.4, 125.6, 125.1, 124.6, 123.3, 121.6, 120.3, 120.1, 112.9, 109.6, 43.2, 31.5, 29.8, 26.9, 22.5, 14.0 ppm. HRMS (EI): calcd. for  $\text{C}_{30}\text{H}_{27}\text{N}$  [ $\text{M}$ ] $^+$  401.2143; found 401.2140.

**2,2'-(9-Hexyl-9*H*-carbazole-3,6-yl)bis(methylene)dibenzoic Acid (5v):** Zinc dust (3.16 g, 48.31 mmol) and mercuric chloride (0.48 g, 1.76 mmol) were added to a mixture of distilled water (5.5 mL) and conc. HCl (0.2 mL). The resulting mixture was stirred for 0.5 h, until it became homogeneous. To this solution, distilled water (5.4 mL), conc. HCl (1.3 mL), toluene (7.2 mL), 1,4-dioxane (7.2 mL), and keto acid **4v** (2 g, 3.6 mmol) were added. The reaction mixture was then heated at reflux for 40 h, and conc. HCl (1.8 mL) was added every 6 h. Usual work-up following a procedure similar to that described for **5a** gave benzyl acid **5v** (1.28 g, 66%) as a colourless solid, m.p. 144–146 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  and  $[\text{D}_6]$ DMSO):  $\delta$  = 7.86 (d,  $J$  = 7.5 Hz, 2 H, ArH), 7.80 (s, 2 H, ArH), 7.35–7.40 (m, 2 H, ArH), 7.21–7.26 (m, 8 H, ArH), 4.53 (s, 4 H,  $\text{CH}_2$ ), 4.20 (t,  $J$  = 6.6 Hz, 2 H,  $\text{CH}_2$ ), 1.74–1.79 (m, 2 H,  $\text{CH}_2$ ), 1.22–1.26 (m, 6 H,  $\text{CH}_2$ ), 0.8–0.85 (m, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 174.4, 147.9, 143.9, 136.4, 136.1, 136.1, 135.6, 131.8, 130.7, 127.2, 125.3, 113.3, 47.8, 44.0, 36.2, 33.7, 31.6, 27.2, 18.8 ppm.  $\text{C}_{30}\text{H}_{33}\text{NO}_4$  (471.60): calcd. C 78.69, H 6.40, N 2.70; found C 78.93, H 6.58, N 2.85.

**2,2'-(9-Hexyl-9*H*-carbazole-3,6-diyl)bis(methylene)dibenzaldehyde (6v):** A solution of benzyl acid **5v** (0.43 g, 0.86 mmol) in dry THF (10 mL) was slowly added by syringe to a suspension of  $\text{LiAlH}_4$  (0.33 g, 8.6 mmol) in dry THF at 0 °C. After the addition of benzylic acid **5v** was complete, the reaction mixture was stirred at room temperature for 4 h. Usual work-up following a procedure similar to that described for **5a** gave the alcohol as a thick liquid.

The crude alcohol (0.4 g, 0.81 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (15 mL), and then PCC (0.52 g, 2.4 mmol) and Celite (1 g) were added. The reaction mixture was stirred at room temperature for 6 h. Work-up of the reaction mixture following the procedure described for **6a** gave dialdehyde **6v** (0.28 g, 71%) as a yellow solid, m.p. 134–136 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.28 (s, 1 H, CHO), 10.06 (s, 1 H, CHO), 8.50 (s, 1 H, ArH), 7.99 (d,  $J$  = 7.2 Hz, 1 H, ArH), 7.88 (t,  $J$  = 8.1 Hz, 1 H, ArH), 7.80–7.72 (m, 2 H, ArH), 7.64–7.61 (m, 1 H, ArH), 7.58–7.56 (m, 1 H, ArH), 7.54–7.51 (m, 2 H, ArH), 7.45–7.44 (m, 2 H, ArH), 7.30–7.41 (m, 2 H, ArH), 7.23–7.26 (m, 3 H, ArH), 4.60 (s, 4 H,  $\text{CH}_2$ ), 4.23 (t,  $J$  = 7.1 Hz, 2 H,  $\text{CH}_2$ ), 1.83–1.79 (m, 2 H,  $\text{CH}_2$ ), 1.26 (s, 6 H,  $\text{CH}_2$ ), 0.84 (s, 3 H,  $\text{CH}_2$ ,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.5, 190.7, 143.8, 143.6, 143.0, 139.9, 135.2, 134.0, 133.8, 133.3, 132.3, 131.6, 130.1, 129.1, 128.8, 128.5, 128.2, 127.8, 127.0, 123.9,

123.3, 122.6, 120.8, 109.4, 108.5, 43.5, 38.0, 31.5, 28.9, 26.8, 22.5, 14.0 ppm.  $C_{34}H_{33}NO_2$  (487.64): calcd. C 83.74, H 6.82, N 2.87; found C 83.89, H 7.03, N 3.11.

**8-Hexyl-8H-dinaphtho[2,3-b:2',3'-g]carbazole (7v):** Aldehyde **6v** (0.3 g, 0.63 mmol) was dissolved in dry  $CH_2Cl_2$  (10 mL), and  $BF_3 \cdot OEt_2$  (0.04 g, 0.25 mmol) was added. Then the reaction mixture was stirred for 10 min at room temperature. The solvent was removed in vacuo, and the residue was purified by column chromatography (1% EtOAc in hexane) to give dinaphthocarbazole **6v** (0.22 g, 78%) as a red solid, m.p. 284–286 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 9.30 (s, 1 H, ArH), 9.29 (s, 1 H, ArH), 8.82 (s, 1 H, ArH), 8.57 (s, 1 H, ArH), 8.52 (s, 1 H, ArH), 8.22 (d,  $J$  = 8.4 Hz, 1 H, ArH), 8.10–7.93 (m, 5 H, ArH), 7.61 (d,  $J$  = 9 Hz, 1 H, ArH), 7.40 (t,  $J$  = 9 Hz, 1 H, ArH), 7.39–7.36 (m, 3 H, ArH), 4.41 (t,  $J$  = 7.2 Hz, 2 H, ArH), 1.94–1.91 (m, 2 H,  $CH_2$ ), 1.44–1.41 (m, 2 H,  $CH_2$ ), 1.29–1.23 (m, 4 H,  $CH_2$ ), 0.81 (t,  $J$  = 6.6 Hz, 3 H,  $CH_3$ ) ppm.  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  = 142.0, 139.8, 132.9, 131.1, 129.8, 129.5, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.7, 127.5, 127.2, 126.7, 126.0, 124.7, 124.3, 123.9, 123.8, 120.3, 119.6, 112.0, 111.8, 102.7, 43.2, 31.6, 29.1, 27.0, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz,  $CDCl_3$ ):  $\delta$  = 130.5, 128.3, 128.3, 128.2, 128.0, 127.7, 127.5, 126.7, 126.0, 124.7, 124.3, 123.9, 120.3, 119.6, 111.8, 102.7, 43.2, 31.6, 29.1, 27.0, 22.6, 14.0 ppm. HRMS (EI): calcd. for  $C_{34}H_{29}N$  [M] $^+$  451.2300; found 451.2247.

**5-Hexyl-5H-naphtho[2,3-b]carbazole (8a):** Carbazolymethyl acid **5a** (0.38 g, 1 mmol) was dissolved in dry  $CH_2Cl_2$  (20 mL), and triflic acid (0.030 g, 0.2 mmol) was added. The reaction mixture was stirred at room temperature for 0.5 h, then it was poured into water. The mixture was extracted with  $CH_2Cl_2$  ( $3 \times 15$  mL). The combined organic extracts were washed with water ( $2 \times 30$  mL), and dried ( $Na_2SO_4$ ). The solvent was removed in vacuo to give the cyclic ketone.

The crude cyclic ketone (0.35 g, 0.95 mmol) was dissolved in THF/EtOH (1:2; 30 mL).  $NaBH_4$  (0.18 g, 4.75 mmol) was added, and the resulting mixture was stirred at room temperature for 10 min. The reaction mixture was then poured into water (40 mL) and conc. HCl was added dropwise to adjust the pH to 1–2. The mixture was then extracted with EtOAc ( $2 \times 20$  mL), and the extracts were dried ( $Na_2SO_4$ ). The solvent was removed in vacuo, and the residue was purified by column chromatography (1% EtOAc/hexane) to give compound **8a** (0.32 g, 92%) as a yellow solid, m.p. 122–124 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 8.73 (s, 1 H, ArH), 8.66 (s, 1 H, ArH), 8.54 (s, 1 H, ArH), 8.23 (d,  $J$  = 7.5 Hz, 1 H, ArH), 8.02 (t,  $J$  = 8.9 Hz, 2 H, ArH), 7.78 (s, 1 H, ArH), 7.54 (t,  $J$  = 7.7 Hz, 1 H, ArH), 7.44 (t,  $J$  = 6.4 Hz, 2 H, ArH), 7.35 (t,  $J$  = 7.4 Hz, 1 H, ArH), 7.24–7.22 (m, 1 H, ArH), 4.32 (t,  $J$  = 7.4 Hz, 2 H,  $CH_2$ ), 1.95 (t,  $J$  = 6.8 Hz, 2 H,  $CH_2$ ), 1.51–1.38 (m, 2 H,  $CH_2$ ), 1.36–1.25 (m, 4 H,  $CH_2$ ), 0.88 (t,  $J$  = 6.9 Hz, 3 H,  $CH_3$ ) ppm.  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  = 144.2, 141.0, 138.0, 131.4, 129.6, 128.2, 127.9, 127.6, 127.0, 126.7, 124.9, 124.1, 123.8, 122.8, 121.2, 118.8, 118.6, 108.0, 101.2, 43.3, 31.7, 28.3, 27.1, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz,  $CDCl_3$ ):  $\delta$  = 128.2, 127.9, 127.6, 126.7, 125.0, 124.1, 123.8, 121.2, 118.8, 118.6, 108.0, 101.2, 43.3, 31.7, 28.3, 27.1, 22.6, 14.1 ppm.

**2-Methylanthracene (7b):** The cyclization of 2-(4-methylbenzyl)-benzoic acid (**5a**; 0.23 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.2 g, 0.96 mmol) using  $NaBH_4$  (0.18 g, 4.80 mmol), following a procedure similar to that described for **8a**, gave **7b** (0.17 g, 89%) as a colourless solid, m.p. 204–206 °C. The  $^1H$  NMR spectroscopic data of **7b** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**2,3-Dimethylanthracene (7c):** Cyclization of benzyl acid **5c** (0.24 g, 1 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.20 g, 0.92 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7c** (0.17 g, 87%) as a colourless solid, m.p. 247–248 °C. The  $^1H$  NMR spectroscopic data of **7c** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**1,3-Dimethylanthracene (7d):** Cyclization of benzyl acid **5d** (0.24 g, 1 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.21 g, 0.93 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7d** (0.18 g, 85%) as a colourless solid, m.p. 78–80 °C. The  $^1H$  NMR spectroscopic data of **7d** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**2,3-Dimethoxyanthracene (7e):** Cyclization of benzyl acid **5e** (0.27 g, 1 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.24 g, 0.96 mmol) using  $NaBH_4$  (0.16 g, 4.21 mmol), following a procedure similar to that described for **8a**, gave **7e** (0.22 g, 91%) as a colourless solid, m.p. 200–202 °C. The  $^1H$  NMR spectroscopic data of **7e** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**2-Phenylanthracene (7f):** Cyclization of benzyl acid **5f** (0.29 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.26 g, 0.95 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7f** (0.26 g, 92%) as a colourless solid, m.p. 202–204 °C. The  $^1H$  NMR spectroscopic data of **7f** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**5-Methyltetraphene (7g):** Cyclization of benzyl acid **5g** (0.29 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of cyclic ketone (0.25 g, 0.92 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7g** (0.24 g, 91%) as a colourless solid, m.p. 156–158 °C. The  $^1H$  NMR spectroscopic data of **7g** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**2,3-Dihydro-1H-cyclopenta[b]anthracene (7h):** Cyclization of benzyl acid **5h** (0.25 g, 0.99 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.21 g, 0.91 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7h** (0.20 g, 89%) as a colourless solid, m.p. 226–228 °C. The  $^1H$  NMR spectroscopic data of **7h** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**Naphtho[2,3-b]thiophene (7i):** Cyclization of benzyl acid **5i** (0.22 g, 1.02 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.19 g, 0.95 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7i** (0.17 g, 92%) as a colourless solid, m.p. 194–196 °C. The  $^1H$  NMR spectroscopic data of **7i** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**2-(Thiophen-2-yl)naphtho[2,3-b]thiophene (7j):** Cyclization of benzyl acid **5j** (0.3 g, 1 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.26 g, 0.93 mmol) using  $NaBH_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7j** (0.23 g, 85%) as a

colourless solid, m.p. 256–258 °C. The  $^1\text{H}$  NMR spectroscopic data of **7j** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**Benzo[*b*]naphtho[2,3-*d*]thiophene (7k):** Cyclization of benzyl acid **5k** (0.27 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.24 g, 0.95 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7k** (0.20 g, 87%) as a pale green solid, m.p. 146–148 °C. The  $^1\text{H}$  NMR spectroscopic data of **7k** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

***N,N*-Diphenylanthracen-1-amine (7l):** Cyclization of benzyl acid **5k** (0.38 g, 1 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.35 g, 0.97 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.85 mmol), following a procedure similar to that described for **8a**, gave **7l** (0.31 g, 88%) as a green solid, m.p. 156–158 °C. The  $^1\text{H}$  NMR spectroscopic data of **7l** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**Anthra[1,2-*d*]benzo[*b*]thiophene (7m):** Cyclization of benzyl acid **5m** (0.32 g, 1.02 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.29 g, 0.97 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.85 mmol), following a procedure similar to that described for **8a**, gave **7m** (0.29 g, 93%) as a pale green solid, m.p. 228–230 °C. The  $^1\text{H}$  NMR spectroscopic data of **7m** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**Anthra[1,2-*d*]benzo[*b*]furan (7n) and Anthra[2,3-*d*]benzo[*b*]furan (8n):** Cyclization of benzyl acid **5n** (0.3 g, 0.99 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.27 g, 0.95 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave a mixture of compounds. Usual column chromatographic purification (hexane) gave anthra[1,2-*d*]benzo[*b*]furan (**7n**; 0.13 g, 47%) as a pale green solid. Further elution of the column (1% EtOAc in hexane) gave anthra[2,3-*d*]benzo[*b*]furan (**8n**; 0.08 g, 28%) as a yellow solid, m.p. 326–328 °C. (ref.<sup>[15a]</sup> 325–327 °C);  $^1\text{H}$  NMR (300 MHz, DMSO):  $\delta$  = 8.89 (s, 1 H, ArH), 8.82 (s, 1 H, ArH), 8.73 (s, 1 H, ArH), 8.32 (d,  $J$  = 7.2 Hz, 1 H, ArH), 8.27 (s, 1 H, ArH), 8.16–8.01 (m, 2 H, ArH), 7.73–7.7 (m, 1 H, ArH), 7.65–7.62 (m, 1 H, ArH), 7.55–7.5 (m, 3 H, ArH) ppm. Due to poor solubility, a  $^{13}\text{C}$  NMR spectrum was not recorded.

**3,7-Dibromo-5-hexyl-5*H*-naphtho[2,3-*c*]carbazole (7o):** Cyclization of benzyl acid **5o** (0.55 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.50 g, 0.95 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7o** (0.45 g, 87%) as a yellow solid, m.p. 168 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.89 (s, 1 H, ArH), 8.83 (s, 1 H, ArH), 8.37 (d,  $J$  = 8.4 Hz, 1 H, ArH), 8.07 (d,  $J$  = 7.8 Hz, 2 H, ArH), 7.83 (s, 1 H, ArH), 7.59–7.44 (m, 4 H, ArH), 4.15 (t,  $J$  = 7.2 Hz, 2 H,  $\text{NCH}_2$ ), 1.81 (t,  $J$  = 6.6 Hz, 2 H,  $\text{CH}_2$ ), 1.42 (s, 6 H,  $\text{CH}_2$ ), 0.89 (d,  $J$  = 6.9 Hz, 3 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.5, 136.7, 132.6, 130.0, 128.7, 128.1, 128.0, 127.5, 126.6, 126.4, 125.0, 123.4, 122.7, 122.2, 122.1, 121.0, 117.6, 116.2, 112.9, 112.6, 43.3, 31.5, 29.6, 26.8, 22.5, 14.0 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.7, 128.0, 127.5, 126.6, 125.0, 123.4, 122.8, 122.1, 121.0, 117.6, 116.2, 112.6, 43.3, 31.5, 29.6, 26.8, 22.5, 14.0 ppm.

**13,13-Dihexyl-13*H*-indeno[1,2-*b*]anthracene (7p):** Cyclization of benzyl acid **5p** (0.47 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic

ketone (0.49 g, 0.99 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7p** (0.36 g, 82%) as a green powder.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.37 (s, 1 H, ArH), 8.33 (s, 1 H, ArH), 8.15 (s, 1 H, ArH), 7.90–7.80 (m, 3 H, ArH), 7.77 (s, 1 H, ArH), 7.35–7.27 (m, 5 H, ArH), 2.0–1.93 (m, 4 H,  $\text{CH}_2$ ), 1.0–0.93 (m, 12 H,  $\text{CH}_2$ ), 0.65–0.61 (m, 10 H,  $\text{CH}_2$  and  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.1, 148.8, 140.3, 140.2, 131.8, 131.5, 128.3, 128.0, 128.0, 127.0, 126.2, 126.0, 125.0, 123.2, 120.8, 120.5, 117.2, 54.5, 41.7, 31.5, 29.7, 23.9, 22.7, 13.9 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.3, 128.0, 128.0, 127.0, 126.2, 126.0, 125.0, 123.2, 120.8, 120.5, 117.2, 54.5, 41.7, 31.5, 29.7, 23.9, 22.7, 13.9 ppm. HRMS (EI): calcd. for  $\text{C}_{33}\text{H}_{38}$   $[\text{M}]^+$  434.2974; found 434.2970.

**Naphtho[2,1,8-*gr*]tetracene (7q):** Cyclization of benzyl acid **5q** (0.33 g, 1.02 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.30 g, 0.96 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.80 mmol), following a procedure similar to that described for **8a**, gave **7q** (0.25 g, 84%) as a yellow solid, m.p. 222–224 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.52 (s, 1 H, ArH), 9.17 (d,  $J$  = 9.2 Hz, 1 H, ArH), 8.76 (s, 1 H, ArH), 8.46 (s, 1 H, ArH), 8.28 (d,  $J$  = 9.2 Hz, 1 H, ArH), 8.21 (d,  $J$  = 6.4 Hz, 1 H, ArH), 8.13–8.11 (m, 2 H, ArH), 7.91–7.80 (m, 3 H, ArH), 7.71 (d,  $J$  = 9.2 Hz, 1 H, ArH), 7.55–7.53 (m, 2 H, ArH) ppm.  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 131.8, 131.7, 131.5, 131.4, 130.5, 130.2, 130.0, 128.6, 128.4, 128.0, 127.8, 127.6, 127.5, 127.2, 126.9, 126.2, 125.9, 125.7, 125.5, 125.4, 125.0, 124.7, 124.1, 122.3, 121.8 ppm. DEPT-135 (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.6, 128.4, 128.0, 127.8, 127.5, 126.9, 126.2, 125.9, 125.7, 125.5, 125.0, 124.7, 122.3, 121.8 ppm.

**2,3-Dimethoxytetracene (7r):** Cyclization of benzyl acid **5o** (0.32 g, 0.99 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.29 g, 0.96 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7r** (0.25 g, 86%) as a yellow solid, m.p. 276–278 °C. The  $^1\text{H}$  NMR spectroscopic data of **7r** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**Anthra[2,3-*b*]thiophene (7s):** Cyclization of benzyl acid **5o** (0.27 g, 1.02 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.24 g, 0.96 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7s** (0.21 g, 91%) as a yellow solid, m.p. > 330 °C. The  $^1\text{H}$  NMR spectroscopic data of **7s** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

***N,N*-Diphenyltetracene-2-amine (7t):** Cyclization of benzyl acid **5o** (0.43 g, 1.01 mmol) using triflic acid (0.030 g, 0.2 mmol), followed by reductive dehydration of the crude cyclic ketone (0.38 g, 0.93 mmol) using  $\text{NaBH}_4$  (0.18 g, 4.75 mmol), following a procedure similar to that described for **8a**, gave **7t** (0.31 g, 88%) as a green solid, m.p. 252–253 °C. The  $^1\text{H}$  NMR spectroscopic data of **7t** was identical to that of the compound obtained earlier using Bradhser-type cyclization.

**8-Hexyl-8*H*-dinaphtho[2,3-*b*:2',3'-*g*]carbazole (7v):** Cyclization of benzyl acid **5q** (0.5 g, 0.99 mmol) using triflic acid (0.060 g, 0.4 mmol), followed by  $\text{NaBH}_4$  (0.36 g, 9.5 mmol) reduction of resulting cyclic ketone and diol (0.45 g, 0.93 mmol), following a procedure similar to that described for **8a**, led to the isolation (1% EtOAc in hexane) of 8-hexyl-8*H*-dinaphtho[2,3-*b*:2',3'-*g*]carbazole (**7v**; 0.20 g, 45%) as a red solid. Further elution (5% EtOAc in hexane) of the column gave diol **8v** (0.14 g, 31%) as a yellow solid, m.p. 188–190 °C. Data for **8v**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  =

9.06 (d,  $J = 9$  Hz, 2 H, ArH), 8.10 (s, 2 H, ArH), 7.97 (d,  $J = 8.4$  Hz, 2 H, ArH), 7.68–7.63 (m, 4 H, ArH), 7.49 (t,  $J = 7.5$  Hz, 2 H, ArH), 7.41 (d,  $J = 9$  Hz, 2 H, ArH), 4.23 (t,  $J = 6.9$  Hz, 2 H, ArH), 1.89–1.82 (m, 2 H, CH<sub>2</sub>), 1.37–1.25 (m, 6 H, CH<sub>2</sub>), 0.84 (t,  $J = 6.6$  Hz, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta = 147.7, 134.1, 131.7, 128.6, 128.5, 125.4, 125.3, 124.4, 128.3, 128.2, 128.0, 127.7, 127.5, 127.2, 126.7, 126.0, 124.7, 124.3, 124.3, 122.8, 122.2, 116.3, 115.4, 112.1, 43.4, 31.5, 30.5, 26.8, 22.5, 14.0$  ppm. DEPT-135 (75.4 MHz, CDCl<sub>3</sub>):  $\delta = 128.5, 125.4, 125.3, 124.4, 122.7, 122.2, 112.1, 43.4, 31.5, 30.5, 26.8, 22.5, 14.0$  ppm. HRMS (EI): calcd. for C<sub>34</sub>H<sub>29</sub>NO<sub>2</sub> [M]<sup>+</sup> 483.2198; found 483.2140.

**Supporting Information** (see footnote on the first page of this article): Copies of <sup>1</sup>H, <sup>13</sup>C, and DEPT-135 NMR (only selected cases) spectra of starting materials (representative) and final compounds.

## Acknowledgments

S. M. R. thanks Department of Science and Technology (DST), New Delhi for a DST-INSPIRE fellowship. R. S. and J. K. thank University Grants Committee (UGC) and Council of Scientific and Industrial Research (CSIR), New Delhi, respectively, for fellowships. The authors thank DST-FIST for the use of the high-resolution NMR spectroscopy facility.

- [1] a) C.-H. Lin, K.-H. Lin, B. Pal, L.-D. Tsou, *Chem. Commun.* **2009**, 803–805; b) J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483; *Angew. Chem.* **2008**, *120*, 460–492; c) Q. Miao, X. Chi, S. Xiao, R. Zeis, M. Lefenfeld, T. Siegrist, M. L. Steigerwald, C. J. Nuckolls, *J. Am. Chem. Soc.* **2006**, *128*, 1340–1345; d) M. M. Ling, Z. Bao, *Chem. Mater.* **2004**, *16*, 4824–4840; e) S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2003**, *5*, 4245–4248; f) H. E. Katz, Z. Bao, S. L. Gilat, *Acc. Chem. Res.* **2001**, *34*, 359–369.
- [2] Special Issue on Organic Electronics: *Chem. Mater.* **2004**, *16*, 4381–4846.
- [3] a) C. Shu, C.-B. Chen, W.-X. Chen, L.-W. Ye, *Org. Lett.* **2013**, *15*, 5542–5545; b) Y. Takaguchi, T. Tajima, K. Ohta, J. Motoyoshiya, H. Aoyama, T. Wakahara, T. Akasaka, M. Fujit-suka, O. Ito, *Angew. Chem. Int. Ed.* **2002**, *41*, 817–819; *Angew. Chem.* **2002**, *114*, 845–847; c) T. Yasukawa, T. Satoh, M. Mi-ura, M. Nomura, *J. Am. Chem. Soc.* **2002**, *124*, 12680–12681; d) T. Takahashi, Y. Li, P. Stepnicka, M. Kitamura, Y. Liu, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **2002**, *124*, 576–582; e) H.-D. Becker, *Chem. Rev.* **1993**, *93*, 145–172; f) J.-P. Desvergne, F. Fages, H. Bouas-Laurent, P. Marsau, *Pure Appl. Chem.* **1992**, *64*, 1231–1238; g) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, *Pure Appl. Chem.* **1980**, *52*, 2633–2648.
- [4] a) J. R. Jadhav, C. H. Bae, H.-S. Kim, *Tetrahedron Lett.* **2011**, *52*, 1623–1627; b) K. Ghosh, I. Saha, *Tetrahedron Lett.* **2010**, *51*, 4995–4999; c) S. Kumar, P. Singh, S. Kaur, *Tetrahedron* **2007**, *63*, 11724–11732; d) G. Kaur, H. Fang, X. Gao, H. Li, B. Wang, *Tetrahedron* **2006**, *62*, 2583–2589; e) A. Caballero, R. Tormos, A. Espinosa, M. D. Velasco, A. Tarraga, M. A. Miranda, P. Molina, *Org. Lett.* **2004**, *6*, 4599–4602; f) D. E. Stack, A. L. Hill, C. B. Diffendaffer, N. M. Burns, *Org. Lett.* **2002**, *4*, 4487–4490; g) H. Miyaji, P. Anzenbacher Jr., J. L. Sessler, E. R. Bleasdale, P. A. Gale, *Chem. Commun.* **1999**, 1723–1724.
- [5] a) Y.-H. Chen, S.-L. Lin, Y.-C. Chang, Y.-C. Chen, J.-T. Lin, R.-H. Lee, W. J. Kuo, R. J. Jeng, *Org. Electron.* **2012**, *13*, 43–52; b) A. Thangthong, D. Meunmart, N. Prachumrak, S. Jung-suttiwong, T. Keawin, T. Sudyoasuk, V. Promarak, *Tetrahe-dron* **2012**, *68*, 1853–1861; c) M. Zhu, T. Ye, C.-G. Li, X. Cao, C. Zhong, D. Ma, J. Qin, C. Yang, *J. Phys. Chem. C* **2011**, *115*, 17965–17972; d) J. Wang, W. Wan, H. Jiang, Y. Gao, X. Jiang, H. Lin, W. Zhao, J. Hao, *Org. Lett.* **2010**, *12*, 3874–3877; e) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, D. F. Huang, T. J. Chow, *J. Am. Chem. Soc.* **2008**, *130*, 17320–17333; f) Y. Matsubara, A. Kimura, Y. Yamaguchi, Z.-i. Yoshida, *Org. Lett.* **2008**, *10*, 5541–5544; g) J. Shi, C. W. Tang, *Appl. Phys. Lett.* **2002**, *80*, 3201–3203; see also ref.<sup>[3b]</sup>
- [6] a) K. Nikitin, C. Bothe, H. Müller-Bunz, Y. Ortin, M. J. McGlinchey, *Organometallics* **2012**, *31*, 6183–6198; b) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.* **2000**, *29*, 43–55; c) H. Bouas-Laurent, J.-P. Desvergne, in: *Photochromism Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, The Netherlands, **1990**, chapter 27, p. 919.
- [7] a) H. U. Kim, J.-H. Kim, H. Kang, A. C. Grimsdale, B. J. Kim, S. C. Yoon, D.-H. Hwang, *ACS Appl. Mater. Interfaces* **2014**, *6*, 20776–20785; b) C. Liu, W. Xu, X. Guan, H.-L. Yip, X. Gong, F. Huang, Y. Cao, *Macromolecules* **2014**, *47*, 8585–8593; c) C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt, L. Sun, *J. Phys. Chem. C* **2010**, *114*, 9101–9110; d) L. Valentini, D. Bagnis, A. Marrocchi, M. Seri, A. Taticchi, J. M. Kenny, *Chem. Mater.* **2008**, *20*, 32–34.
- [8] a) A. Thangthong, D. Meunmart, N. Prachumrak, S. Jung-suttiwong, T. Keawin, T. Sudyoasuk, V. Promarak, *Tetrahedron* **2012**, *68*, 1853–1861; b) M. Takahashi, A. Yamamoto, T. In-uzuka, T. Sengoku, H. Yoda, *Tetrahedron* **2011**, *67*, 9484–9490.
- [9] a) J. V. Morris, M. A. Mahaney, J. R. Huber, *J. Phys. Chem.* **1976**, *80*, 969–974; b) M. T. Lee, H. H. Chen, C. H. Liao, C. H. Tsai, C. H. Chen, *Appl. Phys. Lett.* **2004**, *85*, 3301–3303; c) K. R. Wee, W. S. Han, J. E. Kim, A. L. Kim, S. Kwon, S. O. Kang, *J. Mater. Chem.* **2011**, *21*, 1115–1123; d) C. H. Wu, C. H. Chien, F. M. Hsu, P. I. Shih, C. F. Shu, *J. Mater. Chem.* **2009**, *19*, 1464–1470.
- [10] a) B. Balaganesan, W. J. Shen, C. H. Chen, *Tetrahedron Lett.* **2003**, *44*, 5747–5750; b) J. K. Bin, J. I. Hong, *Org. Electron.* **2011**, *12*, 802–808; c) W. J. Jo, K. H. Kim, D. Y. Shin, S. J. Oh, J. H. Son, Y. H. Kim, *Synth. Met.* **2009**, *159*, 1359–1364.
- [11] T. J. Boyd, Y. Geerts, J.-K. Lee, D. E. Fogg, G. G. Lavoie, R. R. Schrock, M. F. Rubner, *Macromolecules* **1997**, *30*, 3553–3559.
- [12] a) M. Mamada, H. Katagiri, M. Mizukami, K. Honda, T. Min-amiki, R. Teraoka, T. Uemura, S. Tokito, *ACS Appl. Mater. Interfaces* **2013**, *5*, 9670–9677; b) L. Chen, S. R. Puniredd, Y.-Z. Tan, M. Baumgarten, U. Zschieschang, V. Enkelmann, W. Pisula, X. Feng, H. Klauk, K. Müllen, *J. Am. Chem. Soc.* **2012**, *134*, 17869–17872; c) J.-Y. Balandier, F. Quist, N. Sebaihi, C. Niebel, B. Tylleman, P. Boudard, S. Bouzakraoui, V. Lemaury, J. Cornil, R. Lazzaroni, Y. H. Geerts, S. Stas, *Tetrahedron* **2011**, *67*, 7156–7161; d) M. M. Payne, S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2004**, *6*, 3325–3328; e) J. Zhang, Z. C. Smith, S. W. Thomas III, *J. Org. Chem.* **2014**, *79*, 10081–10093; f) J. E. Anthony, S. Subramanian, S. R. Parkin, S. K. Park, T. N. Jackson, *J. Mater. Chem.* **2009**, *19*, 7984–7989.
- [13] a) K. L. Platt, F. Oesch, *J. Org. Chem.* **1981**, *46*, 2601–2603; b) R. G. Harvey, C. Leyba, M. Konieczny, P. P. Fu, K. B. Sukumar-an, *J. Org. Chem.* **1978**, *43*, 3423–3425; c) I. Agranat, Y.-S. Shih, *J. Chem. Educ.* **1976**, *53*, 488–493.
- [14] C. K. Bradsher, *Chem. Rev.* **1987**, *87*, 1277–1297.
- [15] a) T. Serevičius, P. Adomėnas, O. Adomėnienė, R. Rimkus, V. Jankauskas, A. Gruodis, K. Kazlauskas, S. Juršėnas, *Dyes Pigm.* **2013**, *98*, 304–315; b) M. Mamada, T. Minamiki, H. Katagiri, S. Tokito, *Org. Lett.* **2012**, *14*, 4062–4065; c) Y. Kuni-nobu, T. Tatsuzaki, T. Matsuki, K. Takai, *J. Org. Chem.* **2011**, *76*, 7005–7009; d) X. Yu, X. Lu, *Adv. Synth. Catal.* **2011**, *353*, 569–574; e) K. Okamoto, T. Kawamura, M. Sone, K. Ogino, *Liq. Cryst.* **2007**, *34*, 1001–1007; f) G. K. Surya Prakash, C. Panja, A. Shakhmin, E. Shah, T. Mathew, G. A. Olah, *J. Org. Chem.* **2009**, *74*, 8659–8668; g) M. Kodomari, M. Nagamatsu, M. Akaike, T. Aoyama, *Tetrahedron Lett.* **2008**, *49*, 2537–2540.
- [16] a) S. M. Rafiq, R. Sivasakthikumar, A. K. Mohanakrishnan, *Org. Lett.* **2014**, *16*, 2720–2723; b) R. Sivasakthikumar, M. Nandakumar, A. K. Mohanakrishnan, *J. Org. Chem.* **2012**, *77*, 9053–9071; c) R. Sureshbabu, V. Saravanan, V. Dhayalan, A. K. Mohanakrishnan, *Eur. J. Org. Chem.* **2011**, 922–935; d)

- J. A. Clement, R. Sivasakthikumar, A. K. Mohanakrishnan, S. Sundaramoorthy, D. Velmurugan, *Eur. J. Org. Chem.* **2011**, 569–577; e) V. Dhayalan, R. Sureshbabu, A. K. Mohanakrishnan, *Indian J. Chem. B* **2011**, 50, 843–857; f) V. Dhayalan, J. A. Clement, R. Jagan, A. K. Mohanakrishnan, *Eur. J. Org. Chem.* **2009**, 4, 531–546.
- [17] a) N. Senthil Kumar, J. A. Clement, A. K. Mohanakrishnan, *Tetrahedron* **2009**, 65, 822–830; b) N. O. Mahmoodi, M. Salehpour, *J. Heterocycl. Chem.* **2003**, 40, 875–877.
- [18] a) N. Senthil Kumar, A. K. Mohanakrishnan, *Tetrahedron* **2010**, 66, 5660–5670; b) J. A. Clement, A. K. Mohanakrishnan, *Tetrahedron* **2010**, 66, 2340–2350.
- [19] N. O. Mahmoodi, M. Salehpour, *J. Heterocycl. Chem.* **2010**, 40, 875–878.
- [20] M. S. Newman, R. Gaertner, *J. Am. Chem. Soc.* **1950**, 72, 264–273.
- [21] J. L. Hallman, R. A. Bartach, *J. Org. Chem.* **1991**, 56, 6243–6245.
- [22] M. L. Tedjamulia, Y. Tominaga, R. N. Castle, *J. Heterocycl. Chem.* **1983**, 20, 1143–1148.
- [23] M. L. Tedjamulia, Y. Tominaga, R. N. Castle, M. L. Lee, *J. Heterocycl. Chem.* **1983**, 20, 861–866.

Received: April 14, 2015  
Published Online: July 2, 2015