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Regioselective Annulation of Unsymmetrical 1,2-Phenylenebis(diaryl/diheteroarylmethanol): A Facile Synthesis of Anthracene, Tetracene, and Naphtho[*b*]thiophene Analogues

Ramakrishnan Sivasakthikumaran,[a] Settu Muhammad Rafiq,[a] Elumalai Sankar,[a] J. Arul Clement,[a] and Arasambattu K. Mohanakrishnan*[a]

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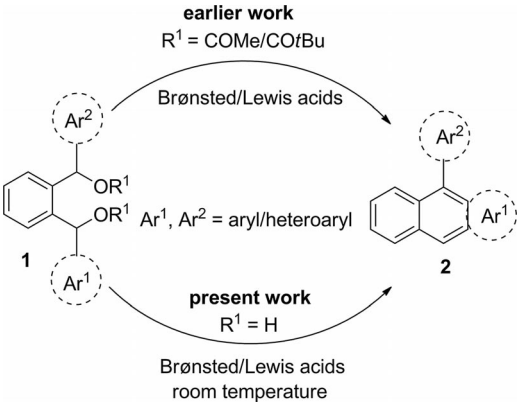
A systematic study on the regioselective cyclization of benzene- and naphthalene-based unsymmetrical diols with HBr (33 %) in acetic acid at room temperature led to the formation of annulation products. By using this method, synthesis of a wide variety of anthracene, tetracene and naphtho[*b*]thiophene analogues was achieved in good to excellent yields. By employing HBr (33 %) in acetic acid as a catalyst for regioselective cyclization of unsymmetrical diols was very facile and devoid of commonly encountered dihydroisobenzofuran formation.

Introduction

π-Conjugated organic compounds with fused ring systems have received significant interest over recent decades as versatile and high-performance active components in a variety of optical devices.[1] Organic π-conjugated molecules show promising applications in the area of optoelectronic devices that include organic light-emitting diodes (OLEDs), photovoltaic cells, and organic field-effect transistors (OFETs).[2] In particular, anthracene analogues are utilized as functional materials in optoelectronic devices.[3] Anthracene and its derivatives have wide applications in OLEDs,[4] dye-sensitized solar cells,[5] OFETs,[6] sensors,[7] biology,[8] and so on. In this regard, scope for the synthesis of anthracene analogues is enormous. Anthracene analogues have been prepared by Friedel–Crafts reaction,[9] Elbs reaction,[10] aromatic cyclodehydration,[11] flash vacuum pyrolysis,[12] Lewis acid induced cyclization of diarylmethanes,[13] and transition metal mediated homologation.[14]

In recent years, the Lewis acid/Brønsted acid mediated domino reaction has been successfully applied for the synthesis of a wide variety of π-conjugated heterocycles.[15] Shu et al. reported[16] the synthesis of substituted anthracenes by gold-catalyzed intramolecular cyclization of orthoalkynyl-diarylmethanes. Matsuo and co-workers achieved[17] the synthesis of anthracenes from diarylmethanes through a Bradsher-type reaction that involved formylation of the aryl unit followed by Lewis acid catalyzed Friedel–Crafts intramolecular cyclization reaction. Yu and Lu reported[18] the synthesis of anthracenes and tosylamino fluorene derivatives that involved $BF_3{\cdot}OEt_2$-catalyzed intramolecular aza-Friedel–Crafts reaction of respective benzylic and biphenylcarbaldehydes. An easy route to anthracenes was achieved by $In(OTf)_3$-catalyzed cyclodehydration reaction of 2-benzbenzaldehydes.[19] The Brønsted acid catalyzed synthesis of substituted anthracenes was realized by Bodzioch et al.[20] In 2007, Liu and co-workers reported the synthesis of 9-arylanthracenes and heteroacenes through triflic acid mediated annulation reaction of symmetrical diacetates.[21] We recently reported[22] the regiospecific synthesis of annulated arenes and heteroarenes by $ZnBr_2$-mediated domino reaction of unsymmetrical dipivalates. It has been observed that 1,2-phenylenebis(diphenylmethanol) upon reaction with Brønsted acids leads to the formation of 9-phenylanthracene as well as 1,3-diphenyldihydroisobenzofuran.[21] This observation, coupled with our recent failure of $ZnBr_2$-mediated annulation reaction of carbazole and tri-



Scheme 1. Synthesis of annulated arenes and heteroarenes.

[a] Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600025, Tamil Nadu, India
E-mail: mohan_67@hotmail.com
mohanakrishnan@unom.ac.in
www.unom.ac.in

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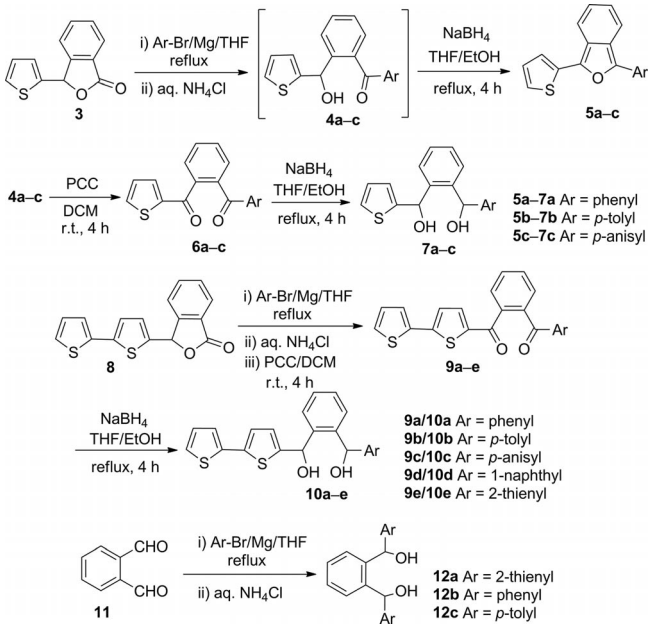
phenylamine tethered dipivalate systems,[22] prompted us to undertake a systematic study on the cyclization of 1,2-phenylenebis(diarylmethanols). In continuation of our studies on the synthesis of π-conjugated heterocycles,[23] we describe herein our results on the synthesis of anthracene and naptho[*b*]thiophene derivatives **2** that involve Lewis acid/Brønsted acid mediated regioselective cyclization reactions of unsymmetrical 1,2-phenylenebis(diaryl/diheteroarylmethanols) **1** (Scheme 1).

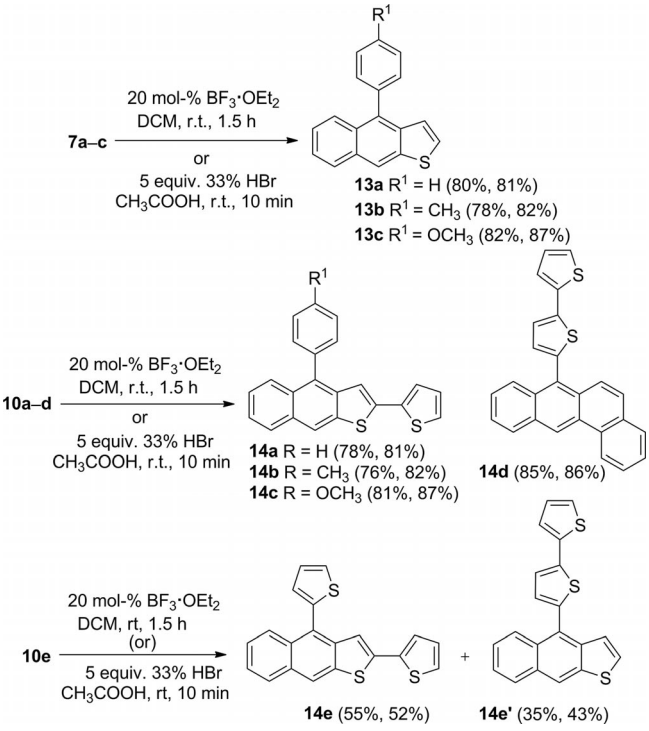
Results and Discussion

The preparation of required diarylmethine diols **7a**–**7c** were initiated from 2-thiophenylisobenzofuranone (**3**).[24] Reaction of 2-thiophenyl-substituted lactone **3** with aryl Grignard reagents followed by an aqueous NH_4Cl workup furnished keto alcohols **4a**–**4c**. Surprisingly, our attempt to reduce keto alcohols **4a**–**4c** by using $NaBH_4$ in tetrahydrofuran (THF)/EtOH at reflux temperatures led to the formation of benzo[*c*]furans **5a**–**5c**[24] through a facile borohydride-induced cyclodehydration reaction. However, a slightly longer route that involved oxidation of keto alcohols **4a**–**4c** with pyridinium chlorochromate (PCC) followed by $NaBH_4$ reduction afforded required benzylic diols **7a**–**7e** as thick liquids (Scheme 2). By using a similar protocol, 2,2′-bithiophenyl lactone **8** upon reaction with aryl Grignard reagents followed by PCC oxidation furnished required diketones **9a**–**9e**. As expected, diketones **9a**–**9e** upon $NaBH_4$ reduction led to respective benzylic diols **10a**–**10e**. By systematic study of annulation reactions of diols, representative symmetrical diols **12a**–**12c** were prepared through heteroaryl/aryl Grignard addition of phthaldehyde **11** (Scheme 2).



Scheme 2. Preparation of unsymmetrical and symmetrical 1,2-phenylenebis(diarylmethanols) **7a**–**7c**, **10a**–**10e**, and **12a**–**12c**.

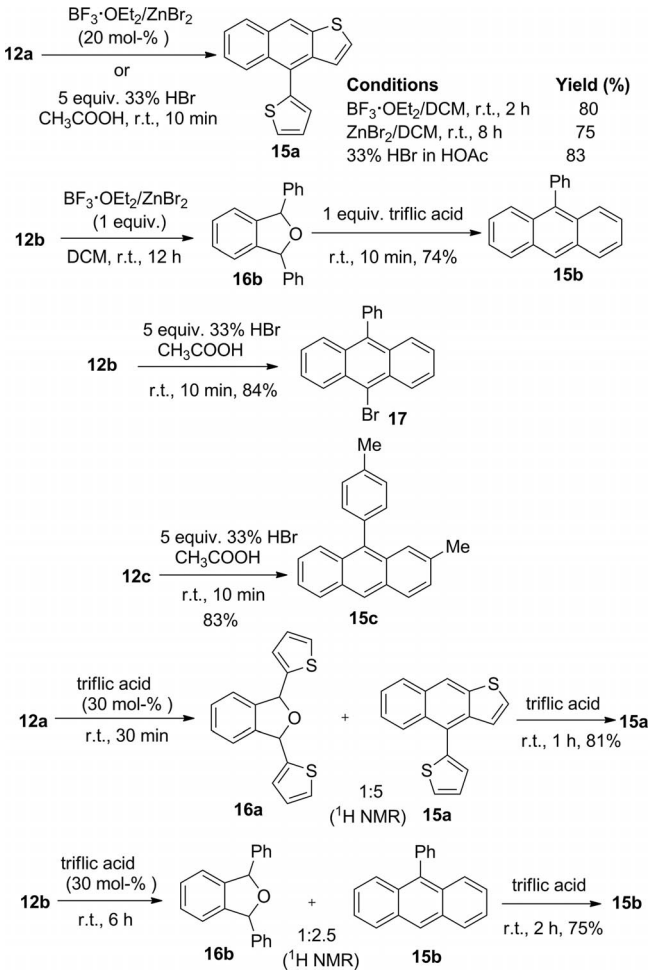
Having prepared the required diols, the subsequent intramolecular cyclization reaction was planned with a suitable Brønsted/Lewis acid, which will overcome the commonly encountered phthalan formation.[25] Moreover, successful annulation reaction of unsymmetrical and symmetrical diarylmethanols will eliminate the unnecessary acetoylation/pivaloylation step.[21,22] As expected, unsymmetrical 1,2-phenylenebis(diarylmethanols) **7a**–**7c** upon reaction with $BF_3{\cdot}OEt_2$ (20 mol-%)/HBr (33%, 5 equiv.) in acetic acid at room temperature led to the formation of naphtho[*b*]thiophenes **13a**–**13c** as the exclusive products (Scheme 3).



Scheme 3. Annulation reaction of unsymmetrical 1,2-phenylenebis(diarylmethanols) **7a**–**7c** and **10a**–**10e**.

Under identical conditions, unsymmetrical diols **10a**–**10c** furnished respective naphtho[*b*]thiophenes **14a**–**14c** in 78–87% yields. Surprisingly, cyclization of diol **10d** with either HBr (33%) in acetic acid or $BF_3{\cdot}OEt_2$ in CH_2Cl_2 furnished benzoanthracene **14d** as the exclusive product. HBr (33%) in acetic acid/$BF_3{\cdot}OEt_2$-mediated cyclization reaction of diheteroaryl diol **10e** led to the isolation of isomeric naphtho[*b*]thiophenes **14e** and **14e′**. The yields of the annulation products obtained with $BF_3{\cdot}OEt_2$ and HBr (33%) in acetic acid were comparable with only a slightly favoring of the latter. Having achieved the facile annulation of diols **7a**–**7c** and **10a**–**10e**, a similar type of cyclization reaction was planned with symmetrical diols **12a**–**12c**. Heteroaryl symmetrical diol **12a** upon reaction with $BF_3{\cdot}OEt_2/ZnBr_2$/HBr (33%) in acetic acid furnished the naphtho[*b*]thiophene **15a** as the sole product in 75–83% yields (Scheme 4). The similar reaction of diphenyl symmetric diol **12b** with $BF_3{\cdot}OEt_2/ZnBr_2$ in CH_2Cl_2 at room temperature led to the formation of 1,3-diphenyl-1,3-dihydroisobenzofuran **16b**.[21] Dihydroisobenzofuran **16b** upon further reaction with triflic acid

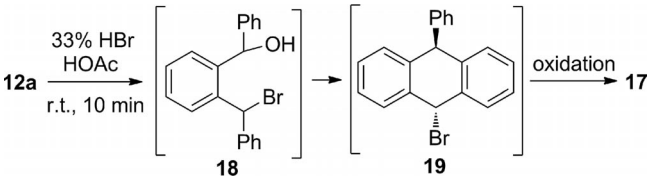
(1 equiv.) in CH_2Cl_2 at room temperature led to the formation of 9-phenylanthracene **15b**. To our surprise, diol **12b** upon reaction with HBr (33%) in acetic acid furnished 9-bromo-10-phenylanthracene **17** as the exclusive product in 84% yield. However, under identical conditions, symmetrical diol **12c** led to anthracene **15c**. Reaction of symmetrical diol **12a/12b** with triflic acid (30 mol-%) afforded mixture of 1,3-disubstituted-1,3-dihydroisobenzofuran **16a/16b** and annulation product **15a/15b** (confirmed by ^{1}H NMR spectroscopy). Further reaction of the mixture of dihydroisobenzofuran **16a/16b** and annulation product **15a/15b** with an additional equivalent of triflic acid ensured the smooth transformation (confirmed by ^{1}H NMR spectroscopy) of dihydroisobenzofuran **16a/16b** into respective annulation product **15a/15b** (Scheme 4).



Scheme 4. Annulation of symmetrical 1,2-phenylenebis(diarylmethanols) **12a/12b**.

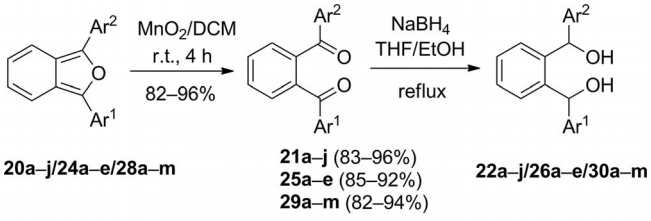
Even though Liu and co-workers observed that reaction of diol **12b** with triflic acid (10 mol-%) in CH_2Cl_2 at room temperature for 1 min led to dihydroisobenzofuran **16b** as the exclusive product,[21] it has now been confirmed that either an increase in the equivalent of triflic acid or reaction time drastically enhanced the yield of 9-phenylanthracene **15b** at the expense of dihydroisobenzofuran **16b**.

The regioselective formation of naphtho[*b*]thiophenes **13a**–**13c** and **14a**–**14c** can be visualized through the intermediacy of diarylmethyl carbocations followed by intramolecular cyclization at the thiophene 3-position and subsequent aromatization through dehydration. In the case of **10d**, exclusive intramolecular cyclization at the naphthalene 2-position led to anthracene **14d**. The formation of isomeric naphtho[*b*]thiophenes **14e** and **14e′** clearly confirms the competing intermolecular cyclization of the resulting carbocations at the 3-positions of thiophene as well as 2,2′-bithiophene. As mentioned above, the formation of annulation product **15a** can be proposed from respective diol **12a** through a cyclization-dehydration protocol. Obviously, when diol **12b** was treated with $BF_3{\cdot}OEt_2/ZnBr_2$, the resulting diarylmethine carbocation reacted with the OH group instead of the less-nucleophilic phenyl unit to produce dihydroisobenzofuran **16b**. However, formation of 9-bromo-10-phenylanthracene **17** can be conceived only through the formation of benzylic bromide **18**[26] followed by intramolecular cyclization and subsequent oxidative aromatization of dihydroanthracene **19** (Scheme 5).



Scheme 5. Mechanistic rational for 9-bromoanthracene **17**.

After achieving the facile annulation of benzylic diols **7a**–**7c**, **10a**–**10d**, and **12a**–**12c** in the presence of HBr (33%) in acetic acid, the preparation of various types of unsymmetrical bis(diaryl/diheteroarylmethanols) was envisaged to



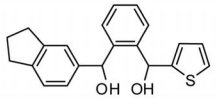
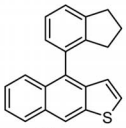
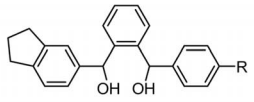
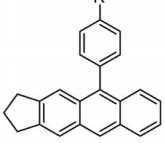
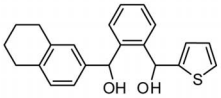
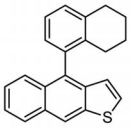
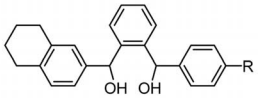
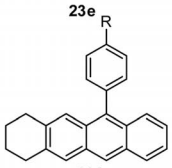
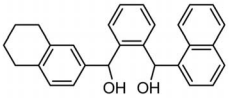
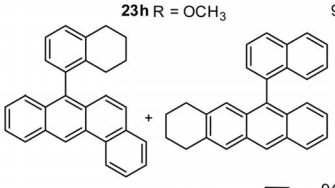
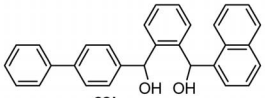
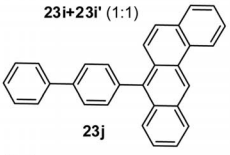
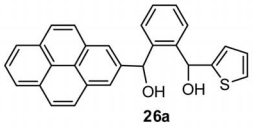
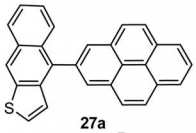
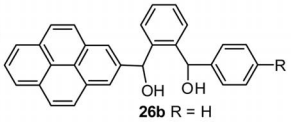
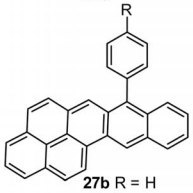
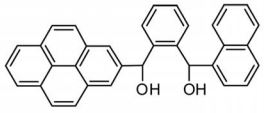
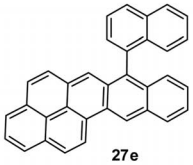
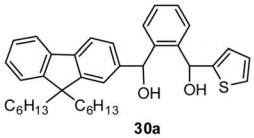
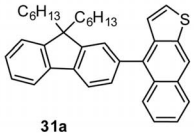
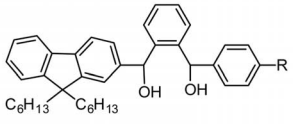
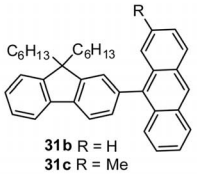
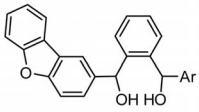
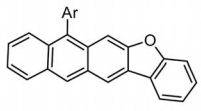
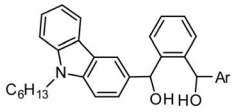
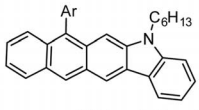
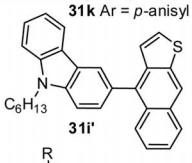
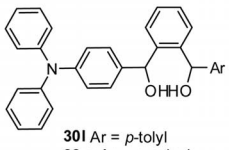
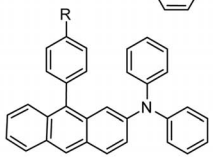
20–22a–d Ar^1 = 2,3-dihydroinden-5-yl
Ar^2 = 2-thiophenyl, phenyl, *p*-tolyl, *p*-anisyl
20–22e–i Ar^1 = 5,6,7,8-tetrahydronaphthalen-2-yl
Ar^2 = 2-thiophenyl, phenyl, *p*-tolyl, *p*-anisyl,1-naphthyl
20–22j Ar^1 = 4-biphenyl; Ar^2 = 1-naphthyl
24–26a–e Ar^1 = 2-pyrenyl
Ar^2 = 2-thiophenyl, phenyl, *p*-tolyl, *p*-anisyl, 1-naphthyl
28–30a–d Ar^1 = 9,9-dihexylfluoren-2-yl
Ar^2 = 2-thiophenyl, phenyl, *p*-tolyl, *p*-anisyl
28–30e–h Ar^1 = dibenzofuran-3-yl
Ar^2 = 2-thiophenyl, *p*-tolyl, *p*-anisyl, 1-naphthyl
28–30i–k Ar^1 = 9-hexylcarbazol-3-yl
Ar^2 = 2-thiophenyl, *p*-tolyl, *p*-anisyl
28–30l, m Ar^1 = 4-(diphenylamino)phenyl
Ar^2 = *p*-tolyl, *p*-anisyl

Scheme 6. Preparation of 1,2-phenylenebis(diaryl/heteroaryl)methanols **22a**–**22j**, **26a**–**26e**, and **30a**–**30m**.

study their efficacy towards the synthesis of annulated arenes. Accordingly, known 1,3-diarylbenzo[*c*]furans **20a**–**20j**, **24a**–**24e**, and **28a**–**28m**[24] could be oxidatively cleaved with active MnO_2[27] to furnish diketones **21a**–**21j**, **25a**–**25e**, and **29a**–**29m**, respectively. These diketones upon $NaBH_4$ reduction afforded required diols **22a**–**22j**, **26a**–**26e,** and **30a**–**30m** as shown in Scheme 6. Crude diols **22a**–**22j**, **26a**–**26e**, and **30a**–**30m** used in the annulation reaction without further characterization.

As expected, unsymmetrical aryl/heteroarylmethine diols **22a**–**22j**, **26a**–**26e**, and **30a**–**30m** upon interaction with HBr (33%, 5 equiv.) in acetic acid at room temperature for

Table 1. Synthesis of anthracenes and naphtho[*b*]thiophenes.

Entry	Substrate	Product[a]	Yield[b]
1	 **22a**	 **23a**	84
2	 **22b-d**	 **23b** R = H **23c** R = Me **23d** R = OMe	81 92 94
3	 **22e**	 **23e**	84
4	 **22f-h**	 **23f** R = H **23g** R = CH_3 **23h** R = OCH_3	83 89 90
5	 **22i**	 **23i+23i'** (1:1)	94[c]
6	 **22j**	 **23j**	87
7	 **26a**	 **27a**	83
8	 **26b** R = H **26c** R = Me **26d** R = OMe	 **27b** R = H **27c** R = Me **27d** R = OMe	61 80 92
9	 **26e**	 **27e**	92
10	 **30a**	 **31a**	89
11	 **30b** R = H **30c** R = Me **30d** R = OMe	 **31b** R = H **31c** R = Me **31d** R = OMe	83 73 71
12	 **30e** Ar = 2-thienyl **30f** Ar = *p*-tolyl **30g** Ar = *p*-anisyl **30h** Ar = 1-naphthyl	 **31e** Ar = 2-thienyl **31f** Ar = *p*-tolyl **31g** Ar = *p*-anisyl **31h** Ar = 1-naphthyl	83 82 89 81
13	 **30i** Ar = 2-thienyl **30j** Ar = *p*-tolyl **30k** Ar = *p*-anisyl	 **31i** Ar = 2-thienyl **31j** Ar = *p*-tolyl **31k** Ar = *p*-anisyl	45 78 78
		 **31i'**	36
14	 **30l** Ar = *p*-tolyl **30m** Ar = *p*-anisyl	 **31l** R = Me **31m** R = OMe	73 68

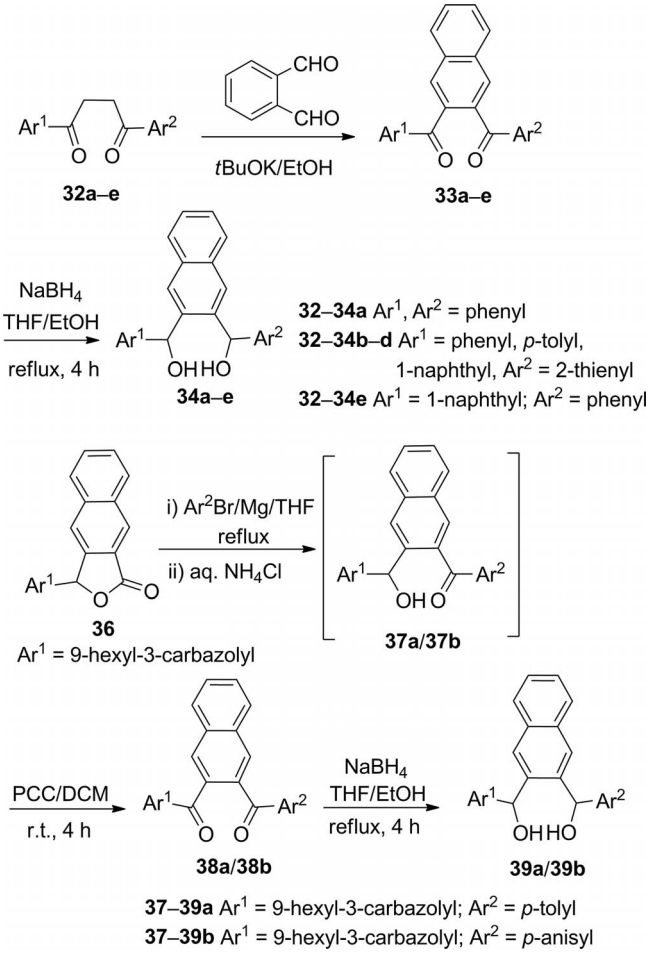
[a] Unsymmetrical diol (1 equiv.) and HBr (33%) in AcOH (5 equiv.) at room temperature for 10 min. [b] Yield after column chromatography. [c] Yield based on ^{1}H NMR spectroscopy.

10 min followed by workup and purification by column chromatography furnished various anthracene and naphtho[*b*]thiophene analogues. The structures of annulated arenes and heteroarenes obtained along with their yields are shown in Table 1.

The reaction of diol **22a** with HBr (33%) in acetic acid at room temperature afforded 4-arylnaphtho[*b*]thiophene **23a** in 84% yield (Table 1, Entry 1). Similarly, the reaction of diols **22b**–**22d** with HBr (33%) in acetic acid furnished 5-aryl-cyclopenta[*b*]anthracenes **23b**–**23d** in 81–94% yields (Table 1, Entry 2). Unsymmetrical diol **22e** treated with HBr (33%) in acetic acid gave naphtho[*b*]thiophene **23e** in 84% yield (Table 1, Entry 3). Similar set of diols **22f**–**22h** underwent facile annulation in the presence of HBr (33%) in acetic acid to afford respective annulated arenes **23f**–**23h** in 83–90% yields (Table 1, Entry 4). Unsymmetrical diol **22i** furnished an inseparable 1:1 mixture (based on ^{1}H NMR spectroscopy) of anthracenes **23i** and **23i′** (Table 1, Entry 5). However, biphenyl- and naphthalene-based diol **22j** was regioselectively annulated to give 7-(biphenyl-4-yl)-tetraphene **23j** in 87% yield (Table 1, Entry 6). Reaction of pyrene-tethered unsymmetrical diol **26a** with HBr (33%) in acetic acid underwent facile cyclization at the thiophene portion to afford 4-pyrenylnaphtho[*b*]thiophene **27a** in 81% yield (Table 1, Entry 7). Nevertheless, similar annulation of diols **26b**/**26c** that contain pyrene and phenyl/*p*-tolyl units led to the formation of separable mixture of respective annulated arenes **27b**/**27c** and **27b′**/**27c′** as major and minor products, respectively (Table 1, Entry 8). In the case of unsymmetrical diol **26d**, the electron-releasing nature of the 4-methoxyphenyl group has effectively facilitated the cyclization at the pyrene portion to give annulated arene **27d** as the exclusive product in 91% yield (Table 1, Entry 8). To our delight, reaction of unsymmetrical diol **26e** with HBr (33%) in acetic acid also produced tetracene **27e** as the sole product (Table 1, Entry 9).

Next, reaction of 9,9′-dihexylfluorenediol **30a**, which bears a thiophenyl unit, with HBr (33%) in acetic acid furnished the fluorenyl-naphtho[*b*]thiophene **31a** in 89% yield (Table 1, Entry 10). In the case of 9,9′-dihexylfluorenediols **30b**–**30d**, which bear aryl units, the HBr (33%)-mediated cyclization reaction led to the formation of respective fluorenyl-anthracenes **31b**–**31d** in good yields (Table 1, Entry 11). The annulation reactions of dibenzofurandiols **30e**–**30h**, which bear aryl/heteroaryl units, underwent regioselective cyclization reaction at the dibenzofuranyl portion to furnish pentacene derivatives **31e**–**31h** in 81–91% yields (Table 1, Entry 12). *N*-Hexylcarbazole-tethered diol **30i**, which bears a thiophene unit, underwent facile annulation to afford naphth-annelated carbazole **31i** and naphtho[*b*]-thiophene **31i′** in 45 and 36% yields, respectively (Table 1, Entry 13). To our delight, *N*-hexylcarbazolediol **30j**/**30k**, which bears an aryl unit, led to the formation of naphtho-[*b*]carbazole **31j** and **31k** as the exclusive products. Similarly, interaction of triphenylamine tethered diol **30l**/**30m** with HBr (33%) in acetic acid led to the isolation of 2-[(diphenylamino)phenyl]-9-arylanthracene **31l**/**31m** in 73 and 68% yields, respectively. It should be noted that our earlier attempts to prepare heterocycles of type **31i**–**31m**, which involves Lewis/Brønsted acid mediated cyclization reaction of *N*-hexylcarbazole/triphenylamine-tethered dipivalate, was found to be unsuccessful.[22] Thus, the regioselective formation of annulated products **23a**–**23j**, **27a**–**27e**, and **31a**–**31m** clearly established that the diols can be used as suitable starting materials for annulation reactions instead of the corresponding acetates/pivalates.[21,22]

Towards further generalizing the above-mentioned annulation reaction, the preparation of naphthalene-2,3-diols was initiated. The condensation of 1,4-diarylbutane-1,4-dione **32a**–**32e**[28] with phthalaldehyde followed by $NaBH_4$ reduction of resulting 2,3-diaroylnaphthalenes **33a**–**33e** furnished naphthalene diols **34a**–**34e**. Next, known *N*-hexylcarbazole naphthalide **36**[29] upon reaction with aryl Grignard reagent followed by an aqueous NH_4Cl workup furnished keto alcohol **37a/37b**. Oxidation of these keto alcohols with PCC followed by $NaBH_4$ reduction led to naphthalene diol **39a/39b** (Scheme 7).



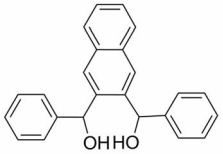
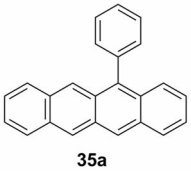
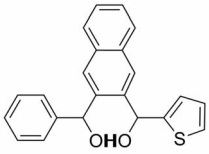
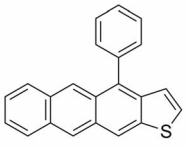
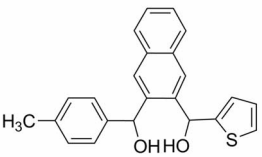
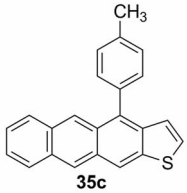
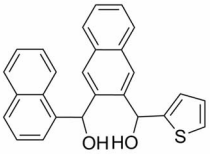
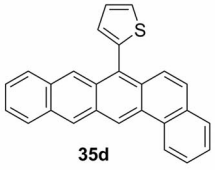
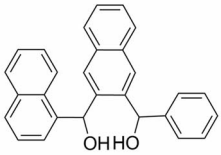
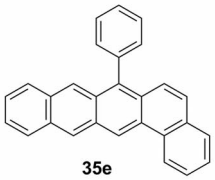
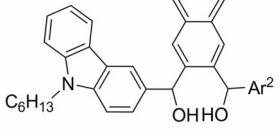
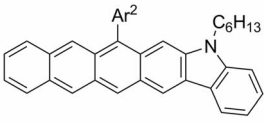
Scheme 7. Preparation of naphthalene-2,3-diylbis(arylmethanols).

As expected, cyclization reaction of naphthalene diols **34a**–**34e** with HBr (33%) in acetic acid furnished annulated compounds **35a**–**35e** in 68–87% yields, Table 2. In the case of symmetrical diol **34a**, cyclization led to the formation of 5-phenyltetracene **35a** in 71% yield (Table 2, Entry 1).

Reaction of aryl- and thiophene-based unsymmetrical naphthalene diol **34b/34c** with HBr (33%) in acetic acid underwent regioselective annulation at the thiophene unit to furnish anthra[*b*]thiophene **35b/35c**. However, under identical conditions, the cyclization of 1-naphthyl-based diols **34d** and **34e** gave benzotetracene **35d** and **35e**, respectively, as exclusive products in 85 and 87% yields, respectively. Reaction of *N*-hexylcarbazole-based naphthalene diols **39a/39b** with HBr (33%) in acetic acid failed to produce expected hexacene **40a/40b**. It should be noted that addition of HBr (33%) in acetic acid to a solution of diols **39a/39b** in acetic acid gave an intense red color. However, even cautious workup followed by purification with column chromatography failed to give the expected product possibly as a result of the unstable nature of hexacene **40a/40b**.

In summary, we have accomplished a facile synthesis of anthracene and naptho[*b*]thiophene analogues that involves HBr in acetic acid mediated regioselective cyclization reaction of unsymmetrical diols. The regioselective cyclization methodology was also found to be applicable for naphthalene diols. Even though, dihydroisobenzofuran was isolated during the Brønsted acid-mediated cyclization of 1,2-diphenylbenzenediol,[21,25] we did not observed any such dihydroisobenzofuran formation during HBr in acetic acid mediated cyclization of a wide variety of the benzene- and naphthalene-based diols. Our present study clearly demonstrated that an inexpensive HBr in acetic acid system can be used as an effective Brønsted acid catalyst for regioselective cyclization of a wide variety of unsymmetrical diols. Moreover, the regioselective formation of annulated arenes and heteroarenes from the diols successfully eliminates the unnecessary preparation of corresponding acetates/pivalates.[21,22] The wide variety of anthracenes, tetracenes, pentacenes, and annulated thiophene derivatives reported herein may find application in OLEDs.[30]

Table 2. Synthesis of anthracenes and naphtho[*b*]thiophenes **35a**–**35e**.

Entry	Substrate	Product[a]	Yield[b]
1	 **34a**	 **35a**	71
2	 **34b**	 **35b**	68
3	 **34c**	 **35c**	74
4	 **34d**	 **35d**	87
5	 **34e**	 **35e**	87
6	 **39a** Ar^2 = *p*-tolyl **39b** Ar^2 = *p*-anisyl	 **40a** Ar^2 = *p*-tolyl 0 **40b** Ar^2 = *p*-anisyl 0	

[a] Unsymmetrical diol (1 equiv.) and HBr (33%) in AcOH (5 equiv.) at room temperature for 10 min. [b] Yield after column chromatography.

Experimental Section

General Methods: Solvents were dried by means of standard procedures. All the experiments were carried out under a nitrogen atmosphere unless otherwise stated. The progress of all reactions was monitored by TLC with a hexanes/ethyl acetate mixture as eluent. Column chromatography was carried out with silica gel (230–400 mesh, Merck) and by eluting with solvents of increasing polarity. ^{1}H NMR, ^{13}C NMR, and DEPT-135 spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard with a 300 MHz spectrometer at room temperature. HRMS spectra were recorded with a MAT 95 XL model instrument under EI mode.

2-Benzoylphenyl(thiophen-2-yl)methanone (6a): Ring opening of 3-(thiophen-2-yl)isobenzofuran-1(3*H*)-one **3**[24] (2.0 g, 9.25 mmol) with freshly prepared phenylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench and workup gave the keto alcohol. The crude keto alcohol (2.1 g, 7.14 mmol) was dissolved in dry CH_2Cl_2 (40 mL), PCC (2.3 g, 10.71 mmol) was added and stirred for 4 h. The reaction mixture was then filtered through a Celite pad and washed with CH_2Cl_2 (2× 10 mL). The combined filtrate was concentrated under reduced pressure. Purification of the residue by column chromatography (silica gel; hexane/ethyl acetate, 95:5) led to the isolation of diketone **6a** (0.88 g, 84%) as a brown solid, m.p. 133–135 °C (Lit.[22] 132.5–133.3 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.61 (m, 3 H), 7.57–7.54 (m, 4 H), 7.46–7.40 (m, 2 H), 7.29 (t, J = 7.6 Hz, 2 H), 7.99 (t, J = 4.5 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 188.3, 144.2, 139.8, 139.6, 137.2, 135.0, 134.9, 133.1, 130.5, 130.5, 129.9, 129.8, 129.1, 128.3, 128.2 ppm.

2-(4-Methylbenzoyl)phenyl(thiophen-2-yl)methanone (6b): Ring opening of lactone **3**[24] (2.0 g, 9.25 mmol) with freshly prepared *p*-tolylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench gave the keto alcohol. Oxidation of the crude keto alcohol (2.2 g, 7.14 mmol) with PCC (2.3 g, 10.71 mmol) by following a procedure similar to that for **6a** furnished diketone **6b** (0.94 g, 89%) as a colorless solid, m.p. 124–126 °C. (Lit.[22] 126–128 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.70 (m, 1 H), 7.64–7.59 (m, 6

H), 7.46 (m, 1 H), 7.17 (d, J = 8.1 Hz, 2 H), 7.06–7.03 (m, 1 H), 2.36 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.2, 188.4, 144.1, 144.0, 139.8, 139.7, 135.0, 134.8, 134.7, 130.5, 130.3, 130.0, 129.6, 129.1, 128.0, 21.7 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 135.0, 134.8, 130.5, 130.3, 130.0, 129.6, 128.0, 21.7 ppm (only eight signals appeared instead of ten).

2-(4-Methoxylbenzoyl)phenyl(thiophen-2-yl)methanone (6c): Ring opening of lactone **3**[24] (2.0 g, 9.25 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench gave the keto alcohol. Oxidation of the crude keto alcohol (1.9, g 5.86 mmol) with PCC (1.89 g, 8.79 mmol) by following a procedure similar to that for **6a** furnished diketone **6c** (0.48 g, 91%) as a colorless solid, m.p. 130–132 °C (Lit.[22] 131–132 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.61 (m, 3 H), 7.56–7.52 (m, 4 H), 7.40–7.39 (m, 1 H), 6.99–6.97 (m, 1 H), 6.77 (d, J = 8.7 Hz, 2 H), 3.76 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 195.3, 188.4, 163.6, 144.2, 140.0, 139.5, 135.1, 134.8, 132.3, 130.5, 130.2, 130.1, 129.4, 129.0, 128.0, 113.6, 55.5 ppm.

2,2′-Bithiophen-5-yl(2-benzoylphenyl)methanone (9a): Ring opening of 3-(2,2′-bithiophen-5-yl)isobenzofuran-1(3*H*)-one **8**[31] (2.0 g, 6.71 mmol) with freshly prepared phenylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench and workup gave the keto alcohol. The crude keto alcohol (2.4 g, 6.38 mmol) was dissolved in dry CH_2Cl_2 (40 mL) and PCC (2.07 g, 9.60 mmol) was added and stirred for 4 h. The reaction mixture was then filtered through a Celite pad and washed with CH_2Cl_2 (2 × 10 mL). The combined filtrate was concentrated under reduced pressure. Purification of the residue by column chromatography (silica gel; hexane/ethyl acetate, 95:5) gave diketone **9a** (2.0 g, 91%) as a pale brown solid, m.p. 156–158 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.70 (m, 3 H), 7.64–7.63 (m, 2 H), 7.57–7.50 (m, 1 H), 7.41–7.35 (m, 3 H), 7.33–7.31 (m, 1 H), 7.29–7.26 (m, 1 H), 7.12–7.10 (m, 2 H), 7.06–7.03 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 187.8, 146.9, 142.1, 139.6, 137.2, 136.2, 135.9, 133.1, 130.5, 129.8, 129.7, 129.0, 128.5, 128.3, 127.8, 126.8, 126.7, 125.9, 124.1 ppm. $C_{22}H_{14}O_2S_2$ (374.47): calcd. C 70.56, H 3.77, S 17.13; found C 70.42, H 3.61, S 17.32.

2,2′-Bithiophen-5-yl[2-(4-methylbenzoyl)phenyl]methanone (9b): Ring opening of lactone **8**[31] with freshly prepared *p*-tolylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench gave the keto alcohol. Oxidation of the crude keto alcohol (2.0, 4.22 mmol) with PCC (1.60 g, 3.62 mmol) by following a procedure similar to that for **9a** furnished diketone **9b** (0.45 g, 90%) as a pale yellow solid, m.p. 140–142 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.64 (m, 1 H), 7.56–7.50 (m, 5 H), 7.30–7.18 (m, 3 H), 7.1 (d, J = 8.1 Hz, 2 H), 7.03 (d, J = 3.9 Hz, 1 H), 6.98–6.94 (m, 1 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.2, 187.9, 146.7, 144.0, 142.1, 139.8, 139.4, 136.2, 135.9, 134.7, 130.4, 130.3, 130.0, 129.6, 129.0, 128.9, 128.2, 126.6, 125.8, 124.1, 21.7 ppm. $C_{23}H_{16}O_2S_2$ (388.50): calcd. C 71.11, H 4.15, S 16.51; found C 71.05, H 4.09, S 16.57.

2,2′-Bithiophen-5-yl[2-(4-methoxybenzoyl)phenyl]methanone (9c): Ring opening of lactone **8**[31] (2.0 g, 6.71 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench gave the keto alcohol. Oxidation of the crude keto alcohol (2.5, g 6.16 mmol) with PCC (1.99 g, 9.23 mmol) by following a procedure similar to that for **9a** furnished diketone **9c** (2.10 g, 88%) as a pale green solid, m.p. 120–122 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.4 Hz, 3 H), 7.61–7.55 (m, 3 H), 7.35–7.27 (m, 3 H), 7.10–7.09 (m, 1 H), 7.04–7.03 (m, 1 H), 6.85 (d, J = 8.4 Hz, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 195.2, 188.0, 163.6, 146.8, 142.1, 140.0, 139.3, 136.3, 136.0, 132.3, 130.5, 130.2, 129.5, 128.9, 128.3, 126.7, 125.8, 124.1, 113.7, 55.5 ppm. $C_{23}H_{16}O_3S_2$ (404.50): calcd. C 68.29, H 3.99, S 15.85; found C 68.48, H 3.71, S 15.99.

2,2′-Bithiophen-5-yl[2-(1-naphthoyl)phenyl]methanone (9d): Ring opening of lactone **8**[31] (2.0 g, 6.71 mmol) with freshly prepared 1-naphthylmagnesium bromide followed aqueous NH_4Cl (10 mL) quench gave the keto alcohol. Oxidation of the crude keto alcohol (2.45 g, 5.75 mmol) with PCC (1.86 g, 8.63 mmol) by following a procedure similar to that for **9a** furnished diketone **9d** (2.09 g, 90%) as a pale yellow solid. The crude diketone was used directly in the next step without any further characterization.

2,2′-Bithiophen-5-yl[2-(thiophen-2-ylcarbonyl)phenyl]methanone (9e): Ring opening of lactone **8**[31] (2.0 g, 6.7 mmol) with freshly prepared 2-thienylmagnesium bromide followed by an aqueous NH_4Cl (10 mL) quench gave the keto alcohol. Oxidation of the crude keto alcohol (2.0, 5.34 mmol) with PCC (1.72 g, 21.55 mmol) by following a procedure similar to that for **9a** furnished diketone **9e** (1.77 g. 87%) as a brown solid, m.p. 145–147 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 2 H), 7.60–7.55 (m, 3 H), 7.40 (d, J = 3.9 Hz, 1 H), 7.28–7.22 (m, 3 H), 7.05–6.99 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 188.3, 187.8, 147.0, 144.1, 142.0, 139.3, 139.1, 136.2, 136.1, 135.2, 135.0, 130.7, 130.6, 129.2, 129.1, 128.3, 128.0, 126.7, 125.9, 124.2 ppm. $C_{20}H_{12}O_2S_3$ (380.49): calcd. C 63.13, H 3.18, S 25.28; found C 63.26, H 3.13, S 25.35.

Annulation of {2-[Hydroxy(phenyl)methyl]phenyl}(thiophen-2-yl)-methanol (7a) with $BF_3{\cdot}OEt_2$: To a solution of diketone **6a** (1 g, 3.4 mmol) in THF/ethanol (20 mL; 1:3) sodium borohydride (0.64 g, 16.8 mmol) was added in portions and heated at reflux for 4 h. The reaction mixture was then poured into water (100 mL), extracted with ethyl acetate (2 × 20 mL) and dried (Na_2SO_4). The removal of solvent gave crude diol **7a**. Crude diol **7a** (0.30 g, 1 mmol) was dissolved in dry CH_2Cl_2 (15 mL), a catalytic amount of $BF_3{\cdot}OEt_2$ (0.025 g, 0.2 mmol) was added and stirred for 1.5 h under a nitrogen atmosphere. The reaction mixture was then poured into water (40 mL), extracted with CH_2Cl_2 (2 × 10 mL) and dried (Na_2SO_4). The removal of solvent in vacuo followed by column chromatographic purification (silica gel; hexane) afforded compound **13a** (0.21 g, 80%) as a pale yellow solid, m.p. 82–83 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 8.02 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.60–7.44 (m, 9 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.3, 139.1, 138.3, 133.3, 131.6, 130.1, 128.9, 128.9, 128.6, 128.2, 125.4, 125.3, 124.8, 123.9, 121.6 ppm (only fifteen signals appeared instead of sixteen). DEPT-135 (75.4 MHz, $CDCl_3$): δ = 130.1, 128.9, 128.9, 128.6, 128.2, 125.4, 125.3, 124.8, 123.9, 121.6 ppm.

Annulation of {2-[Hydroxyl(phenyl)methyl]phenyl}(thiophen-2-yl)-methanol (7a) with 33% HBr in AcOH: To a solution of crude diol 7**a** (0.3 g, 1 mmol) in acetic acid (15 mL), HBr (33%, 1.24 g, 15.2 mmol) in acetic acid was added and stirred for 10 min. The reaction mixture was then poured into water (80 mL), extracted with CH_2Cl_2 (2 × 20 mL), and dried (Na_2SO_4). The removal of solvent in vacuo followed by column chromatographic purification (silica gel; hexane) afforded compound **13a** (0.22 g, 81%).

Annulation of {2-[Hydroxy(*p*-tolyl)methyl]phenyl}(thiophen-2-yl)-methanol (7b) with $BF_3{\cdot}OEt_2$: Reduction of diketone **6b** (1 g, 3.26 mmol) with sodium borohydride (0.6 g, 16.32 mmol) followed by workup led to diol **7b**. Crude diol **7b** (0.34 g, 1.1 mmol) upon annulation with $BF_3{\cdot}OEt_2$ (0.030 g, 0.22 mmol) by adopting a procedure similar to that for **7a** afforded compound **13b** (0.24 g, 78%) as a pale yellow solid, m.p. 110–111 °C (Lit.[22] 107–109 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.36 (s, 1 H, ArH), 7.90 (d, J =

8.1 Hz, 1 H, ArH), 8.1 (d, *J* = 10.2 Hz, 1 H, ArH), 7.46–7.31 (m, 7 H, ArH), 7.11 (d, *J* = 7.8 Hz, 1 H, ArH), 2.47 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.1, 137.8, 137.2, 135.8, 135.4, 131.2, 130.6, 129.2, 129.1, 127.6, 127.5, 126.5, 125.1, 124.9, 123.7, 120.3, 21.4 ppm.

Annulation of {2-[Hydroxyl(*p*-tolyl)methyl]phenyl}(thiophen-2-yl)-methanol (7b) with 33% HBr in AcOH: Crude diol **7b** (0.17 g, 0.55 mmol) upon annulation with HBr (33%, 0.67 g, 8.27 mmol) in acetic acid by adopting a procedure similar to that for **7a** afforded **13b** (0.12 g, 82%).

Annulation of {2-[Hydroxy(4-methoxyphenyl)methyl]phenyl}(thiophen-2-yl)methanol (7c) with $BF_3{\cdot}OEt_2$: Reduction of diketone **6c** (1.4 g, 4.34 mmol) with sodium borohydride (0.8 g, 21.72 mmol) followed by workup led to diol **7c**. Crude diol **7c** (0.4 g, 1.22 mmol) upon annulation with $BF_3{\cdot}OEt_2$ (0.04 g, 0.03 mmol) in dry CH_2Cl_2 by adopting a procedure similar to that for **7a** afforded compound **13c** (0.29 g, 82%) as a pale yellow solid, m.p. 151–153 °C (Lit.[22] 152–153 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, ArH), 7.92 (d, *J* = 8.1 Hz, 1 H, ArH), 7.82 (d, *J* = 8.4 Hz, 1 H, ArH), 7.50–7.33 (m, 5 H, ArH), 7.14–1.06 (m, 3 H, ArH), 3.91 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.09, 138.2, 137.7, 134.2, 131.8, 131.2, 131.0, 129.4, 127.5, 127.4, 126.5, 125.1, 124.9, 123.7, 120.2, 113.9, 55.4 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 135.1, 134.8, 132.2, 130.5, 129.4, 129.0, 128.0, 113.6, 55.5 ppm (only nine signals appeared instead of ten).

Annulation of {2-[Hydroxyl(4-methoxyphenyl)methyl]phenyl} (thiophen-2-yl)methanol (7c) with 33% HBr in AcOH: Crude diol **7c** (0.2 g, 0.61 mmol) upon annulation with HBr (33%, 0.74 g, 9.2 mmol) in acetic acid by adopting a procedure similar to that for **7a** afforded **13c** (0.155 g, 87%).

4-Phenyl-2-(thiophen-2-yl)naphtho[2,3-*b*]thiophene (14a): Reduction of diketone **9a** (0.92 g, 2.37 mmol) with sodium borohydride (0.45 g, 11.8 mmol) followed by workup led to diol **10a**. Crude diol **10a** (0.63 g, 1.67 mmol) was dissolved in acetic acid (15 mL) and HBr (33%, 0.67 g, 8.27 mmol) in acetic acid was added and stirred for 10 min. The reaction mixture was then poured into water (80 mL), extracted with CH_2Cl_2 (2 × 20 mL), and dried (Na_2SO_4). The removal of solvent in vacuo followed by column chromatographic purification (silica gel; hexane/ethyl acetate, 99:1) afforded compound **14a** (0.46 g, 81%) as a pale yellow solid, m.p. 166–168 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.90 (d, *J* = 8.1 Hz, 1 H), 7.74 (d, *J* = 9.3 Hz, 1 H), 7.60–7.55 (m, 2 H), 7.50–7.43 (m, 4 H), 7.37–7.33 (m, 1 H), 7.29–7.26 (m, 2 H), 7.14 (s, 1 H), 7.04–7.02 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.8, 138.7, 138.0, 137.4, 137.3, 134.2, 131.4, 130.0, 129.6, 128.5, 128.0, 127.7, 126.3, 126.0, 125.7, 125.2, 125.1, 123.8, 120.0, 119.0 ppm. HRMS (EI): calcd. for $C_{22}H_{14}S_2$ [M^+] 342.0537; found 342.0500.

Annulation of 2,2′-Bithiophen-5-yl{2-[hydroxy(phenyl)methyl]phenyl}methanol (10a) with $BF_3.OEt_2$: Crude diol **10a** (0.29 g, 0.77 mmol) upon annulation with $BF_3{\cdot}OEt_2$ (0.02 g, 0.15 mmol) in dry CH_2Cl_2 by adopting a procedure similar to that for **7a** afforded **14a** (0.20 g, 78%).

2-(Thiophen-2-yl)-4-*p*-tolylnaphtho[2,3-*b*]thiophene (14b): Reduction of diketone **9b** (0.75 g, 1.94 mmol) with sodium borohydride (0.29 g, 7.77 mmol) followed by workup led to diol **10b**. Crude diol **10b** (0.63 g, 1.67 mmol) upon annulation with HBr (33%, 0.65 g, 8.03 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **14b** (0.57 g, 82%) as a pale yellow solid, m.p. 190–192 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.43 (d, *J* = 9 Hz, 1 H), 7.39–7.17 (m, 8 H), 7.09 (s, 1 H), 6.95 (t, *J* = 4.3 Hz, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.8, 137.7, 137.4, 137.3, 137.2, 135.6, 134.2, 131.4, 130.6, 129.7, 129.2, 127.9, 127.4, 126.4, 125.9, 125.6, 125.1, 125.0, 119.7, 119.1, 21.4 ppm. $C_{23}H_{16}S_2$ (356.50): calcd. C 77.49, H 4.52, S 17.99; found C 77.61, H 4.38, S 17.81.

Annulation of 2,2′-Bithiophen-5-yl{2-[hydroxy(*p*-tolyl)methyl]-phenyl}methanol (10b) with $BF_3{\cdot}OEt_2$: Crude diol **7c** (0.62 g, 1.58 mmol) upon annulation with $BF_3{\cdot}OEt_2$ (0.04 g, 0.31 mmol) in dry CH_2Cl_2 by adopting a procedure similar to that for **7a** afforded **14b** (0.42 g, 76%).

4-(4-Methoxyphenyl)-2-(thiophen-2-yl)naphtho[2,3-*b*]thiophene (14c): Reduction of diketone **9c** (0.60 g, 1.49 mmol) with sodium borohydride (0.25 g, 6.58 mmol) followed by workup led to diol **10c**. Crude diol **10c** (0.67 g, 1.64 mmol) upon annulation with HBr (33%, 0.66 g, 8.15 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **14c** (0.53 g, 87%) as a pale green solid, m.p. 188–190 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.21 (s, 1 H), 7.98 (d, *J* = 8.1 Hz, 1 H), 7.80–7.75 (m, 1 H), 7.53–7.50 (m, 3 H), 7.43 (t, *J* = 7.8 Hz, 1 H), 7.32–7.28 (m, 3 H), 7.13 (d, *J* = 8.1 Hz, 1 H), 7.06–7.03 (m, 1 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.1, 139.1, 137.8, 137.3, 131.8, 131.5, 131.2, 130.9, 130.0, 127.9, 127.5, 126.4, 125.9, 125.7, 125.1, 125.0, 120.9, 119.7, 114.3, 114.0, 55.4 ppm. HRMS (EI): calcd for $C_{23}H_{16}OS_2$ [M^+] 372.0643; found 372.0640.

Annulation of 2,2′-Bithiophen-5-yl{2-[hydroxy(4-methoxyphenyl)-methyl]phenyl}methanol (10c) with $BF_3{\cdot}OEt_2$: Crude diol **7c** (0.64 g, 1.54 mmol) upon annulation with $BF_3{\cdot}OEt_2$ (0.04 g, 0.30 mmol) in dry CH_2Cl_2 by adopting a procedure similar to that for **7a** afforded **14c** (0.48 g, 87%).

5-(Tetraphen-7-yl)-2,2′-bithiophene (14d): Reduction of diketone **9d** (0.60 g, 1.42 mmol) with sodium borohydride (0.26 g, 6.84 mmol) followed by workup led to diol **10d**. Crude diol **10d** (0.60 g, 1.40 mmol) upon annulation with HBr (33%, 0.50 g, 21.0 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **14d** (0.47 g, 86%) as a pale green solid, m.p. 150–152 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.27 (s, 1 H), 8.86 (d, *J* = 8.1 Hz, 1 H), 8.14 (d, *J* = 7.8 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 7.83–7.79 (m, 2 H), 7.72–7.67 (m, 1 H), 7.63–7.48 (m, 4 H), 7.38–7.36 (m, 1 H), 7.26–7.24 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.8, 138.2, 137.4, 132.3, 131.6, 131.4, 130.6, 130.4, 130.3, 128.7, 128.6, 128.5, 127.9, 127.7, 127.3, 127.1, 126.4, 126.3, 125.7, 125.2, 124.5, 123.8, 123.5, 123.4, 123.1 ppm. HRMS (EI): calcd. for $C_{26}H_{16}S_2$ [M^+] 392.0693; found 392.0679.

Annulation of 2,2′-Bithiophen-5-yl{2-[hydroxy(naphthalen-1-yl)-methyl]phenyl}methanol (10d) with $BF_3{\cdot}OEt_2$: Crude diol **7d** (0.6 g, 1.40 mmol) upon annulation with $BF_3{\cdot}OEt_2$ (0.04 g, 0.28 mmol) in dry CH_2Cl_2 by adopting a procedure similar to that for **7a** afforded **14d** (0.23 g, 85%).

Preparation of Naphtho[*b*]thiophenes 14e and 14e′: Reduction of diketone **9e** (0.61 g, 1.60 mmol) with sodium borohydride (0.30 g, 7.89 mmol) followed by workup led to diol **10e**. Crude diol **10e** (0.59 g, 1.54 mmol) upon annulation with HBr (33%, 0.62 g, 22.99 mmol) in acetic acid by adopting a procedure similar to that for **14a** followed by column chromatographic purification (silica gel; hexane/ethyl acetate, 99:1) led to the isolation of products **14e** and **14e′**.

2,4-Di(thiophen-2-yl)naphtho[2,3-*b*]thiophene (14e): Pale green solid, 0.28 g (52%), m.p. 140–142 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 8.12 (d, *J* = 8.1 Hz, 1 H), 7.94 (d, *J* = 8.1 Hz, 1 H), 7.52–7.45 (m, 3 H), 7.42–7.40 (m, 1 H), 7.31 (d, *J* = 3.6 Hz, 1 H),

7.26–7.24 (m, 2 H), 7.11 (d, J = 3.6 Hz, 1 H), 7.04 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.4, 138.5, 138.0, 137.7, 137.3, 131.0, 130.3, 129.6, 128.5, 127.9, 127.6, 126.1, 125.8, 125.6, 125.4, 124.5, 123.8, 123.7, 121.8 ppm. HRMS (EI): calcd. for $C_{20}H_{12}S_3$ [M^+] 348.0101; found 348.0100.

4-(2,2′-Bithiophen-5-yl)naphtho[2,3-*b*]thiophene (14e′): Pale green solid, 0.24 g (43%), m.p. 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (s, 1 H), 8.21–8.13 (m, 1 H), 8.03–7.97 (m, 1 H), 7.52–7.45 (m, 4 H), 7.35 (d, J = 3.6 Hz, 1 H), 7.28–7.25 (m, 3 H), 7.08–7.05 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.1, 138.8, 138.3, 138.0, 137.2, 131.5, 130.0, 129.5, 128.9, 128.6, 127.9, 125.9, 125.0, 124.6, 124.0, 123.9, 123.8, 122.7, 122.1, 119.1 ppm. $C_{20}H_{12}S_3$ (348.49): calcd. C 68.93, H 3.47, S 27.60; found C 68.84, H 3.59, S 27.48.

Annulation of 2,2′-Bithiophen-5-yl{2-[hydroxy(thiophen-2-yl)-methyl]phenyl}methanol (10e) with BF_3·OEt_2: Crude diol **7e** (0.6 g, 1.56 mmol) upon annulation with BF_3·OEt_2 (0.04 g, 0.3 mmol) in dry CH_2Cl_2 by adopting a procedure similar to that for **7a** afforded **14e** (0.30 g, 55%) and **14e′** (0.14 g, 35%).

Annulation of 1,2-Phenylenebis(thiophen-2-ylmethanol) (12a) with BF_3·OEt_2: To a solution of 1,2-phenylenebis(thiophen-2-ylmethanol) (**12a**; 0.25 g, 0.84 mmol) in dry CH_2Cl_2 (10 mL), a catalytic amount of BF_3·OEt_2 (0.021 g, 0.16 mmol) was added and allowed to stir for 2 h followed by workup in a procedure similar to that for **7a** afforded **15a**[21] as a sticky liquid (0.17 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 8.02–7.98 (m, 2 H), 7.56 (dd, J = 4.8, 1.2 Hz, 1 H), 7.48–7.40 (m, 3 H), 7.24–7.33 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.4, 139.3, 138.3, 131.6, 130.2, 129.0, 128.8, 128.7, 127.6, 126.9, 125.9, 125.8, 125.2, 125.1, 123.9, 122.7 ppm.

Annulation of 1,2-Phenylenebis(thiophen-2-ylmethanol) (12a) with $ZnBr_2$: A solution of 1,2-phenylenebis(thiophen-2-ylmethanol) (**12a**; 0.25 g, 0.84 mmol) in dry CH_2Cl_2 (10 mL) a catalytic amount of $ZnBr_2$ (0.038 g, 0.16 mmol) was added and allowed to stir for 8 h followed by workup as mentioned above furnished **15a** (0.16 g, 75%).

Annulation of 1,2-Phenylenebis(thiophen-2-ylmethanol) (12a) with 33% HBr in acetic acid: Diol **12a** (0.5 g, 1.67 mmol) upon annulation with HBr (33%, 2.16 g, 26.1 mmol) in acetic acid by adopting a procedure similar to that for **7a** afforded **15a** as a thick liquid (0.37 g, 83%).

Annulation of 1,2-Phenylenebis(phenylmethanol) (12b) with BF_3·OEt_2: To a solution of 1,2-phenylenebis(thiophen-2-ylmethanol) (**12a**; 0.25 g, 0.85 mmol) in dry CH_2Cl_2 (10 mL), BF_3·OEt_2 (0.1 g, 0.85 mmol) was added and allowed to stir for 12 h followed by workup in a procedure similar to that for **7a** afforded dihydroisobenzofuran **16b**[21] (0.19 g, 82%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.44 (m), 7.10–7.13 (m), 7.00–7.03 (m), 6.44 (s), 6.20 (s) ppm (mixture of diastereomers). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 142.5, 142.1, 141.7, 141.2, 128.6, 128.5, 128.2, 128.0, 127.9, 127.8, 126.9, 122.3, 122.1, 85.9, 85.5 ppm (mixture of diastereomers).

Annulation of 1,2-Phenylenebis(phenylmethanol) (12b) with $ZnBr_2$: To a solution of 1,2-phenylenebis(thiophen-2-ylmethanol) (**12a**; 0.25 g, 0.85 mmol) in dry CH_2Cl_2 (10 mL), $ZnBr_2$ (0.19 g, 0.85 mmol) was added and allowed to stir for 12 h followed by workup with the above mentioned procedure afforded dihydroisobenzofuran **16b**[21] (0.195 g, 84%).

Annulation of 1,3-Diphenyl-1,3-dihydroisobenzofuran (16b) with Triflic Acid: To a solution of 1,3-diphenyl-1,3-dihydroisobenzofuran (**16b**; 0.49 g, 1.7 mmol) in dry CH_2Cl_2 (15 mL), CF_3SO_3H (0.26 g, 1.73 mmol) was added and allowed to stir for 12 h followed by workup with a procedure similar to that for **7a** afforded 9-phenylanthracene **15b** (0.32 g, 74%) as a yellow solid, m.p. 153–155 °C (Lit.[19] 155–157 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 8.03 (d, J = 8.4 Hz, 2 H), 7.66 (d, J = 8.4 Hz, 2 H), 7.52–7.60 (m, 3 H), 7.41–7.47 (m, 4 H), 7.31–7.36 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.7, 136.9, 131.3, 131.2, 130.1, 128.3, 128.3, 127.4, 126.5, 125.3, 125.1 ppm (only eleven signals observed instead of twelve).

Annulation of 1,2-Phenylenebis(phenylmethanol) (12b) with 33% HBr in Acetic Acid: Diol **12b** (0.2 g, 0.68 mmol) upon annulation with HBr (33%, 2.03 g, 25.09 mmol) in acetic acid by adopting a procedure similar to that for **7a** afforded **17**[32] (0.22 g, 84%) as a yellow solid, m.p. 132–134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, J = 9 Hz, 2 H), 7.55 (d, J = 9 Hz, 2 H), 7.56–7.43 (m, 4 H), 7.30–7.23 (m, 5 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.4, 137.8, 131.2, 131.1, 130.2, 128.5, 127.9, 127.8, 127.4, 127.0, 125.6, 122.8 ppm.

2-Methyl-9-*p*-tolylanthracene (15c): Diol **12b** (0.5 g, 1.58 mmol) upon annulation with HBr (33%, 1.92 g, 23.73 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded **15c**[21] (0.36 g, 81%) as a sticky liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.3 (s, 1 H), 7.88 (d, J = 8.1 Hz, 1 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.34–7.16 (m, 8 H), 2.41 (s, 3 H), 2.29 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 136.9, 136.1, 135.9, 134.9, 131.2, 130.9, 130.6, 130.1, 129.5, 129.1, 128.4, 128.3, 128.0, 127.9, 126.2, 125.2, 125.0, 124.7, 22.3, 21.5 ppm.

Annulation of 1,2-Phenylenebis(thiophen-2-ylmethanol) (12a) with Triflic Acid: A solution of 1,2-phenylenebis(thiophen-2-ylmethanol) (**12a**; 0.25 g, 0.84 mmol) in dry CH_2Cl_2 (10 mL), CF_3SO_3H (0.056 g, 0.37 mmol) was added and allowed to stir at room temperature for 30 min. Subsequent aqueous $NaHCO_3$ quench followed by usual workup afforded a 1:5 mixture (based on ^{1}H NMR spectroscopy) of 1,3-di(thiophen-2-yl)-1,3-dihydroisobenzofuran (**16a)** and 4-(thiophen-2-yl)naphtho[2,3-*b*]thiophene (**15a)** as a thick liquid. The mixture of dihydroisobenzofuran **16a** and naphtho[2,3-*b*]thiophene **15a** upon further reaction with CF_3SO_3H (0.18 g, 1.2 mmol) in CH_2Cl_2 (10 mL) for 1 h followed by workup and column chromatographic purification afforded 4-(thiophen-2-yl)naphtho[2,3-*b*]thiophene (**15a**; 0.16 g, 81%).

Annulation of 1,2-Phenylenebis(phenylmethanol) (12b) with Triflic Acid: A solution of 1,2-phenylenebis(phenylmethanol) (**12b**; 0.49 g, 1.7 mmol) in dry CH_2Cl_2 (10 mL), CF_3SO_3H (0.076 g, 0.50 mmol) was added and allowed to stir at room temperature for 6 h. Subsequent aqueous $NaHCO_3$ quench followed by usual workup afforded a 1:2.5 mixture (based on ^{1}H NMR spectroscopy) of 1,3-diphenyl-1,3-dihydroisobenzofuran (**16b)** and 9-phenylanthracene (**15b)** as a yellow liquid. The mixture of dihydroisobenzofuran **16b** and phenylanthracene **15b** upon further reaction with CF_3SO_3H (0.23 g, 1.52 mmol) in CH_2Cl_2 (10 mL) for 2 h followed by workup and column chromatographic purification afforded 9-phenylanthracene (**15b**; 0.26 g, 75%).

(2,3-Dihydro-1*H*-inden-5-yl)[2-(thiophen-2-ylcarbonyl)phenyl]methanone (21a): Ring opening of 3-(2,3-dihydro-1*H*-inden-5-yl)isobenzofuran-1(3*H*)-one (2.0 g, 8.0 mmol) with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20a** as a fluorescent bright yellow solid. To a stirred solution of benzo[*c*]furan **20a** (0.74 g, 2.34 mmol) in CH_2Cl_2 (20 mL), MnO_2 (0.61 g, 7.12 mmol) was added and stirred for 4 h. The reaction mixture was then filtered through a Celite pad and washed with CH_2Cl_2 (2× 10 mL). The combined filtrate was con-

centrated under reduced pressure and crystallization from methanol furnished **21a** (0.67 g, 86%) as a brown solid, m.p. 132–134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.71 (m, 1 H), 7.64–7.60 (m, 4 H), 7.57 (d, J = 6.3 Hz, 1 H), 7.51–7.48 (m, 2 H), 7.20 (d, J = 7.5 Hz, 1 H), 2.93–2.83 (m, 4 H), 2.11–2.01 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 188.3, 150.4, 144.6, 144.2, 140.2, 139.7, 135.6, 134.9, 134.6, 130.4, 130.2, 129.6, 129.0, 128.6, 128.0, 125.8, 124.1, 33.0, 32.5, 25.3 ppm. $C_{21}H_{16}O_2S$ (332.42): calcd. C 75.88, H 4.85, S 9.65; found C 75.67, H 4.90, S 9.81.

4-(2,3-Dihydro-1*H*-inden-4-yl)naphtho[2,3-*b*]thiophene (23a): Reduction of diketone **21a** (0.60 g, 1.81 mmol) with sodium borohydride (0.34 g, 8.95 mmol) followed by workup led to diol **22a**. Crude diol **22a** (0.54 g, 1.62 mmol) upon annulation with HBr (33%, 0.65 g, 8.22 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded **23a** (0.39 g, 84%) as a pale yellow solid, m.p. 190–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1 H), 7.97 (d, J = 8.1 Hz, 1 H), 7.80–7.76 (m, 2 H), 7.62–7.58 (m, 2 H), 7.43–7.37 (m, 2 H), 7.34–7.28 (m, 1 H), 7.16–7.15 (m, 1 H), 3.09–2.96 (m, 4 H), 2.16–2.06 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.4, 143.3, 139.7, 131.9, 131.5, 131.2, 130.7, 129.2, 128.2, 127.6, 127.2, 127.1, 126.4, 125.3, 124.7, 121.8, 120.1, 32.9, 32.5, 29.2 ppm. HRMS (EI): calcd. for $C_{21}H_{16}S$ [M^+] 300.0973; found 300.0970.

(2-Benzoylphenyl)(2,3-dihydro-1*H*-inden-5-yl)methanone (21b): Ring opening of 3-(2,3-dihydro-1*H*-inden-5-yl)isobenzofuran-1(3*H*)-one (2.0 g, 8.0 mmol) with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20b** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20b** (1.5 g, 4.84 mmol) with MnO_2 (1.2 g, 13.80 mmol) by following a procedure similar to that for **20a** afforded diketone **21b** (1.33 g, 84%) as a yellow solid, m.p. 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.69 (m, 2 H), 7.63–7.55 (m, 5 H), 7.53–7.48 (m, 2 H), 7.36 (t, J = 7.5 Hz, 2 H), 7.19 (d, J = 7.8 Hz, 1 H), 2.93–2.83 (m, 4 H), 2.11–2.01 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 150.3, 144.6, 140.6, 139.9, 137.3, 135.7, 132.9, 130.0, 129.8, 129.6, 128.8, 128.6, 128.3, 127.2, 125.7, 124.1, 33.0, 32.5, 25.3 ppm. $C_{23}H_{18}O_2$ (326.39): calcd. C 84.64, H 5.56; found C 84.48, H 5.74.

9-(2,3-Dihydro-1*H*-inden-4-yl)anthracene (23b): Reduction of diketone **21b** (1.0 g, 3.07 mmol) with sodium borohydride (0.58 g, 15.26 mmol) followed by workup led to diol **22b**. Crude diol **22b** (1.1 g, 3.33 mmol) upon annulation with HBr (33%, 1.34 g, 16.55 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded **23b** (0.79 g, 81%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 8.02 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 8.7 Hz, 2 H), 7.46–7.42 (m, 3 H), 7.35–7.30 (m, 2 H), 7.27 (s, 1 H), 7.17 (d, J = 7.5 Hz, 2 H), 3.10–2.99 (m, 4 H), 2.25–2.15 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.3, 143.4, 137.8, 136.4, 131.4, 129.1, 128.3, 127.2, 127.1, 126.2, 125.1, 125.0, 124.2, 33.0, 32.9, 25.6 ppm. HRMS (EI): calcd. for $C_{23}H_{18}$ [M^+] 294.1409; found 294.1400.

(2,3-Dihydro-1*H*-inden-5-yl)[2-(4-methylbenzoyl)phenyl]methanone (21c): Ring opening of 3-(2,3-dihydro-1*H*-inden-5-yl)isobenzofuran-1(3*H*)-one (2.0 g, 8.0 mmol) with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20c** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20c** (0.75 g, 2.31 mmol) with MnO_2 (0.60 g, 6.90 mmol) by following a procedure similar to that for **20a** afforded diketone **21c** (0.35 g, 94%) as a pale yellow solid, m.p. 108–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.56 (m, 7 H), 7.49 (d, J = 7.5 Hz, 1 H), 7.18 (t, J = 7.4 Hz, 3 H), 2.93–2.83 (m, 4 H), 2.37 (s, 3 H), 2.11–2.04 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.7, 196.3, 150.2, 144.5, 143.8, 140.5, 140.2, 135.8, 134.8, 130.1, 129.5, 129.4, 129.0, 128.6, 125.7, 124.1, 33.0, 32.5, 25.3, 21.7 ppm. $C_{24}H_{20}O_2$ (340.42): calcd. C 84.68, H 5.92; found C 84.51, H 6.04.

5-*p*-Tolyl-2,3-dihydro-1*H*-cyclopenta[*b*]anthracene (23c): Reduction of diketone **21c** (0.68 g, 2.0 mmol) with sodium borohydride (0.38 g, 10 mmol) followed by workup led to diol **22c**. Crude diol **22c** (0.79 g, 2.33 mmol) upon annulation with HBr (33%, 0.95 g, 11.73 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **23c** (0.66 g, 92%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 7.83 (s, 1 H), 7.62 (d, J = 8.7 Hz, 1 H), 7.47 (s, 1 H), 7.41–7.37 (m, 3 H), 7.32–7.28 (m, 3 H), 2.95 (t, J = 7.1 Hz, 2 H), 2.53 (s, 3 H), 2.15–2.05 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.7, 143.2, 137.0, 136.5, 136.4, 131.6, 131.5, 131.4, 131.2, 130.5, 130.2, 129.3, 128.4, 127.0, 125.9, 124.8, 124.7, 120.6, 33.0, 32.7, 26.5, 21.6 ppm. $C_{24}H_{20}$ (308.42): calcd. C 93.46, H 6.54; found C 93.32, H 6.62.

(2,3-Dihydro-1*H*-inden-5-yl)[2-(4-methoxybenzoyl)phenyl]methanone (21d): Ring opening of 3-(2,3-dihydro-1*H*-inden-5-yl)isobenzofuran-1(3*H*)-one with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20d** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20d** (0.67 g, 1.97 mmol) with MnO_2 (0.51 g, 5.91 mmol) by following a procedure similar to that for **20a** afforded diketone **21d** (0.65 g, 94%) as a colorless solid, m.p. 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.60 (m, 2 H), 7.53–7.48 (m, 5 H), 7.41 (d, J = 7.8 Hz, 1 H), 7.12 (d, J = 7.2 Hz, 1 H), 6.79–6.76 (m, 2 H), 3.77 (s, 3 H), 2.86–2.76 (m, 4 H), 2.05–1.95 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.7, 195.3, 163.5, 150.2, 144.5, 140.4, 140.3, 135.7, 132.2, 130.0, 130.3, 129.9, 129.5, 129.3, 128.6, 125.7, 124.1, 113.5, 55.5, 33.0, 32.5, 25.3 ppm. $C_{24}H_{20}O_3$ (356.42): calcd. C 80.88, H 5.66; found C 80.62, H 5.79.

5-(4-Methoxyphenyl)-2,3-dihydro-1*H*-cyclopenta[*b*]anthracene (23d): Reduction of diketone **21d** (0.65 g, 1.82 mmol) with sodium borohydride (0.34 g, 8.94 mmol) followed by workup led to diol **22d**. Crude diol **22d** (0.67 g, 1.86 mmol) upon annulation with HBr (33%, 0.75 g, 9.26 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **23d** (0.70 g, 94%) as a pale yellow solid, m.p. 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.79 (s, 1 H), 7.63 (d, J = 8.7 Hz, 1 H), 7.48 (s, 1 H), 7.40–7.37 (m, 4 H), 7.09 (d, J = 8.7 Hz, 2 H), 3.91 (s, 3 H), 3.04 (t, J = 7.2 Hz, 2 H), 2.93 (t, J = 7.2 Hz, 2 H), 2.13–2.05 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.9, 143.6, 143.1, 135.9, 132.4, 131.5, 131.4, 131.0, 130.5, 130.2, 128.2, 126.8, 125.7, 124.7, 124.5, 121.9, 120.4, 113.9, 55.4, 32.9, 32.5, 26.3 ppm. HRMS (EI): calcd. for $C_{24}H_{20}O$ [M^+] 324.1514; found 324.1510.

(5,6,7,8-Tetrahydronaphthalen-2-yl)[2-(thiophen-2-ylcarbonyl)phenyl]methanone (21e): Ring opening of 3-(5,6,7,8-tetrahydronaphthalen-2-yl)isobenzofuran-1(3*H*)-one with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20e** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20e** (1.14 g, 3.45 mmol) with MnO_2 (0.90 g, 1.35 mmol) by following a procedure similar to that for **20a** afforded diketone **21e** (0.96 g, 81%) as a brown solid, m.p. 90–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.71 (m, 1 H), 7.65–7.59 (m, 4 H), 7.48–7.47 (m, 1 H), 7.42 (d, J = 8.1 Hz, 1 H), 7.08–7.04 (m, 2 H), 2.77–2.69 (m, 4 H), 1.78–1.76 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.5, 188.4, 144.2, 143.3, 140.0, 139.7, 137.3, 134.9, 134.6, 130.8, 130.4, 130.2, 129.7, 129.1, 129.0, 128.0, 127.0, 29.7, 29.2, 22.9, 22.8 ppm. $C_{22}H_{18}O_2S$ (346.44): calcd. C 76.27, H 5.24, S 9.26; found C 76.46, H 5.06, S 9.43.

4-(5,6,7,8-Tetrahydronaphthalen-1-yl)naphtho[2,3-*b*]thiophene (23e): Reduction of diketone **21e** (1.0 g, 2.98 mmol) with sodium borohydride (0.55 g, 14.47 mmol) followed by workup led to diol **22e**. Crude diol **22e** (0.92 g) upon annulation with HBr (33%, 1.07 g, 39.5 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded **23e** (0.82 g, 84%) as a pale yellow solid, m.p. 174–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, J = 9.0 Hz, 1 H), 8.28 (s, 1 H), 7.76 (d, J = 8.1 Hz, 1 H), 7.61–7.59 (m, 1 H), 7.52–7.50 (m, 2 H), 7.39–7.36 (m, 1 H), 7.34–7.28 (m, 2 H), 7.16–7.14 (m, 1 H), 3.09–3.06 (m, 2 H), 2.92–2.89 (m, 2 H), 1.89–1.84 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.9, 138.5, 137.4, 132.1, 129.7, 129.5, 129.3, 128.1, 127.7, 127.1, 127.0, 126.8, 126.4, 126.0, 125.4, 125.1, 123.1, 30.1, 29.9, 23.2, 23.1 ppm. HRMS (EI): calcd. for $C_{22}H_{18}S$ [M^+] 314.1129; found 314.1120.

(2-Benzoylphenyl)(5,6,7,8-tetrahydronaphthalen-2-yl)methanone (21f): Ring opening of 3-(5,6,7,8-tetrahydronaphthalen-2-yl)isobenzofuran-1(3*H*)-one with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20f** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20f** (0.92 g, 2.84 mmol) with MnO_2 (0.74 g, 8.51 mmol) by following a procedure similar to that for **20a** afforded diketone **21f** (0.83 g, 86%) as a yellow solid, m.p. 70–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 2 H), 7.59–7.55 (m, 4 H), 7.47–7.40 (m, 3 H), 7.34 (t, J = 7.7 Hz, 2 H), 7.02 (d, J = 8.4 Hz, 1 H), 2.73–2.67 (m, 4 H), 1.74–1.72 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 196.5, 143.2, 140.5, 139.9, 137.3, 134.7, 132.9, 130.7, 130.4, 130.1, 129.8, 129.6, 129.5, 129.1, 128.3, 127.0, 29.7, 29.3, 22.9, 22.8 ppm. $C_{24}H_{20}O_2$ (340.42): calcd. C 84.68, H 5.92; found C 84.57, H 6.11.

9-(5,6,7,8-Tetrahydronaphthalen-1-yl)anthracene (23f): Reduction of diketone **21f** (0.35 g, 1.03 mmol) with sodium borohydride (0.19 g, 5.0 mmol) followed by workup led to diol **22f**. Crude diol **22f** (0.36 g, 1.05 mmol) upon annulation with HBr (33%, 0.42 g, 5.19 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **23f** (0.27 g, 83%) as a pale yellow solid, m.p. 82–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 8.03 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.7 Hz, 2 H), 7.48–7.45 (m, 1 H), 7.42 (s, 1 H), 7.39–7.37 (m, 1 H), 7.35–7.32 (m, 1 H), 7.31–7.26 (m, 1 H), 7.13 (s, 2 H), 2.94–2.90 (m, 2 H), 2.90–2.85 (m, 2 H), 1.92–1.90 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 137.5, 137.1, 136.2, 135.7, 133.3, 131.8, 131.4, 130.3, 129.0, 128.4, 128.3, 128.2, 127.8, 127.6, 127.1, 126.2, 125.1, 124.6, 29.5, 29.3, 23.4, 23.3 ppm. HRMS (EI): calcd. for $C_{24}H_{20}$ [M^+] 308.1565; found 308.1560.

[2-(4-Methylbenzoyl)phenyl](5,6,7,8-tetrahydronaphthalen-2-yl)methanone (21g): Ring opening of 3-(5,6,7,8-tetrahydronaphthalen-2-yl)isobenzofuran-1(3*H*)-one with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20g** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20g** (1.13 g, 2.70 mmol) with MnO_2 (0.86 g, 9.89 mmol) by following a procedure similar to that for **20a** afforded diketone **21g** (1.05 g, 89%) as a yellow solid, m.p. 68–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.59 (m, 6 H), 7.41 (d, J = 6.3 Hz, 2 H), 7.17 (d, J = 8.1 Hz, 2 H), 7.04 (d, J = 8.1 Hz, 1 H), 2.77–2.70 (m, 4 H), 2.38 (s, 3 H), 1.78–1.76 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 196.3, 165.2, 143.8, 143.2, 140.4, 140.2, 137.3, 134.8, 134.7, 130.7, 130.1, 130.0, 129.6, 129.6, 129.5, 129.1, 129.0, 127.0, 29.7, 29.3, 22.9, 22.8, 21.7 ppm. $C_{25}H_{22}O_2$ (354.45): calcd. C 84.72, H 6.26; found C 84.91, H 6.07.

6-*p*-Tolyl-1,2,3,4-tetrahydrotetracene (23g): Reduction of diketone **21g** (0.74 g, 2.09 mmol) with sodium borohydride (0.40 g, 10.58 mmol) followed by workup led to diol **22g**. Crude diol **22g** (0.70 g, 1.97 mmol) upon annulation with HBr (33%, 0.79 g, 9.76 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **23g** (0.56 g, 89%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (s, 1 H), 7.95 (d, J = 8.1 Hz, 1 H), 7.77 (d, J = 7.8 Hz, 1 H), 7.46 (d, J = 9.0 Hz, 1 H), 7.38–7.36 (m, 2 H), 7.29–7.26 (m, 3 H), 7.23–7.22 (m, 1 H), 7.12 (d, J = 8.7 Hz, 1 H), 2.92–2.87 (m, 2 H), 2.50 (s, 3 H), 2.33 (t, J = 6 Hz, 2 H), 1.70–1.65 (m, 2 H), 1.53–1.48 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1, 136.5, 136.1, 135.1, 133.5, 132.4, 131.7, 131.3, 131.2, 130.4, 129.1, 128.4, 128.3, 127.8, 127.1, 125.1, 124.6, 31.8, 31.3, 24.1, 22.3, 21.5 ppm. HRMS (EI): calcd. for $C_{25}H_{22}$ [M^+] 322.1722; found 322.1720.

[2-(4-Methoxybenzoyl)phenyl](5,6,7,8-tetrahydronaphthalen-2-yl)methanone (21h): Ring opening of 3-(5,6,7,8-tetrahydronaphthalen-2-yl)isobenzofuran-1(3*H*)-one (2.0 g, 7.58 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20h** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20h** (1.0 g, 2.70 mmol) with MnO_2 (0.71 g, 8.17 mmol) by following a procedure similar to that for **20a** afforded diketone **21h** (0.92 g, 88%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.69 (m, 1 H), 7.68–7.67 (m, 1 H), 7.60–7.57 (m, 4 H), 7.41 (d, J = 6.3 Hz, 2 H), 7.04 (d, J = 8.4 Hz, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 3.84 (s, 3 H), 2.77–2.70 (m, 4 H), 1.78–1.76 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.6, 195.3, 163.5, 143.2, 140.4, 140.2, 137.2, 134.7, 132.2, 130.7, 130.4, 130.0, 129.9, 129.5, 129.3, 129.1, 127.1, 113.6, 55.5, 29.7, 29.3, 22.9, 22.8 ppm. $C_{25}H_{22}O_3$ (370.45): calcd. C 81.06, H 5.99; found C 81.35, H 5.78.

6-(4-Methoxyphenyl)-1,2,3,4-tetrahydrotetracene (23h): Reduction of diketone **21h** (0.85 g, 2.30 mmol) with sodium borohydride (0.45 g, 11.84 mmol) followed by workup led to diol **22h**. Crude diol **22h** (0.80 g, 2.15 mmol) upon annulation with HBr (33%, 0.87 g, 10.75 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **23h** (0.65 g, 90%) as a pale yellow solid, m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 1 H), 7.95 (d, J = 8.4 Hz, 1 H), 7.71 (s, 1 H), 7.63 (d, J = 8.7 Hz, 1 H), 7.38–7.23 (m, 5 H), 7.10 (d, J = 8.7 Hz, 2 H), 3.93 (s, 3 H), 3.01–2.97 (m, 2 H), 2.87–2.83 (m, 2 H), 1.84–1.82 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1, 136.5, 136.1, 135.1, 133.5, 132.4, 131.3, 131.1, 130.7, 130.2, 128.3, 126.8, 126.4, 125.2, 124.9, 124.7, 124.5, 113.8, 55.4, 30.3, 29.9, 23.4 ppm. HRMS (EI): calcd. for $C_{25}H_{22}O$ [M^+] 338.1671; found 338.1650.

[2-(1-Naphthoyl)phenyl](5,6,7,8-tetrahydronaphthalen-2-yl)methanone (21i): Ring opening of 3-(5,6,7,8-tetrahydronaphthalen-2-yl)isobenzofuran-1(3*H*)-one (2.0 g, 7.58 mmol) with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20i** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20i** (1.95 g, 5.21 mmol) with MnO_2 (1.35 g, 15.53 mmol) by following a procedure similar to that for **20a** afforded diketone **21i** (0.65 g, 90%) as a pale yellow solid, m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.4 Hz, 1 H), 7.93 (d, J = 8.1 Hz, 1 H), 7.80 (d, J = 8.1 Hz, 1 H), 7.73 (d, J = 6.9 Hz, 1 H), 7.69–7.57 (m, 4 H), 7.50 (d, J = 7.2 Hz, 1 H), 7.46–7.43 (m, 1 H), 7.40–7.36 (m, 1 H), 7.19 (t, J = 8.1 Hz, 1 H), 6.88 (d, J = 8.1 Hz, 1 H), 2.66–2.55 (m, 4 H), 1.72–1.59 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 197.4, 196.9, 143.2, 141.2, 140.4, 137.3, 135.3, 135.1, 133.6, 132.9, 131.5, 130.8, 130.7, 130.6, 130.1, 130.0, 129.1, 129.0, 128.0, 127.3, 126.6, 126.4, 125.8, 124.0, 29.6, 29.1, 22.8, 22.7 ppm. $C_{28}H_{22}O_2$ (390.48): calcd. C 86.13, H 5.68; found C 86.41, H 5.51.

Preparation of Compounds 23i and 23i′: Reduction of diketone **21i** (0.75 g, 1.92 mmol) with sodium borohydride (0.36 g, 9.47 mmol)

followed by workup led to diol **22i**. Crude diol **22i** (0.67 g, 1.71 mmol) upon annulation with HBr (33%, 0.69 g, 8.52 mmol) in acetic acid by adopting a procedure similar to that for **14a** furnished an inseparable mixture of compounds **23i** and **23i′** (0.57 g, 94%) as a colorless solid, m.p. 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.22 (s, 1 H), 8.87 (d, J = 8.1 Hz, 1 H), 8.42 (s, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 8.04–7.97 (m, 3 H), 7.80–7.73 (m, 3 H), 7.69–7.64 (m, 2 H), 7.61–7.56 (m, 2 H), 7.52–7.41 (m, 4 H), 7.38–7.33 (m, 1 H), 7.29–7.24 (m, 2 H), 7.17–7.09 (m, 6 H), 2.99–2.96 (m, 2 H), 2.94–2.93 (m, 2 H), 2.86–2.84 (m, 2 H), 2.70–2.67 (m, 2 H), 1.92–1.91 (m, 4 H), 1.82–1.75 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 137.2, 136.3, 136.2, 133.6, 131.8, 131.1, 130.6, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 126.4, 126.2, 126.0, 125.9, 125.7, 125.6, 125.5, 124.9, 124.8, 124.6, 123.1, 121.3, 30.1, 29.9, 29.5, 29.4, 23.4, 23.4, 23.3, 23.2 ppm. $C_{28}H_{22}$ (358.48): calcd. C 93.81, H 6.19; found C 93.96, H 6.04.

[2-(1-Naphthoyl)phenyl](biphenyl-4-yl)methanone (21j): Ring opening of 3-(biphenyl-4-yl)isobenzofuran-1(3*H*)-one with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **20j** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **20j** (07 g, 1.77 mmol) with MnO_2 (0.46 g, 5.28 mmol) by following a procedure similar to that for **20a** afforded diketone **21j** (0.60 g, 82%) as a pale yellow solid, m.p. 70–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.4 Hz, 1 H), 7.96–7.92 (m, 1 H), 7.81 (d, J = 8.1 Hz, 1 H), 7.74 (d, J = 7.8 Hz, 1 H), 7.68–7.66 (m, 1 H), 7.62 (d, J = 8.1 Hz, 3 H), 7.58–7.50 (m, 4 H), 7.47–7.42 (m, 5 H), 7.40–7.34 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 197.5, 196.6, 145.8, 141.0, 140.5, 139.9, 136.2, 133.6, 131.6, 130.9, 130.7, 130.2, 130.0, 129.0, 128.9, 128.2, 128.1, 127.7, 127.6, 127.5, 127.3, 127.2, 127.0, 126.5, 125.6, 124.0 ppm. $C_{30}H_{20}O_2$ (412.49): calcd. C 87.36, H 4.89; found C 87.58, H 5.08.

7-(Biphenyl-4-yl)tetraphene (23j): Reduction of diketone **21j** (0.42 g, 1.02 mmol) with sodium borohydride (0.20 g, 5.26 mmol) followed by workup led to diol **22j**. Crude diol **22j** (0.36 g, 0.87 mmol) upon annulation with HBr (33%, 0.35 g, 4.32 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **23j** (0.29 g, 87%) as a pale yellow solid, m.p. 218–220 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.28 (s, 1 H), 8.91 (d, J = 8.4 Hz, 1 H), 8.19 (d, J = 8.1 Hz, 1 H), 7.83 (m, 3 H), 7.79–7.74 (m, 1 H), 7.71–7.60 (m, 3 H), 7.57–7.51 (m, 6 H), 7.48–7.42 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.9, 140.3, 138.0, 137.2, 131.7, 131.6, 131.5, 131.0, 130.5, 128.9, 128.7, 128.6, 128.5, 127.5, 127.2, 127.1, 127.0, 126.7, 125.8, 125.6, 125.5, 123.1, 121.7 ppm. $C_{30}H_{20}$ (380.49): calcd. C 94.70, H 5.30; found C 94.86, H 5.17.

Pyren-2-yl[2-(thiophen-2-ylcarbonyl)phenyl]methanone (25a): Ring opening of 3-(pyren-2-yl)isobenzofuran-1(3*H*)-one (2.0 g, 5.99 mmol) with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **24a** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **24a** (0.51 g, 1.28 mmol) with MnO_2 (0.33 g, 3.79 mmol) by following a procedure similar to that for **20a** afforded diketone **25a** (0.46 g, 88%) as a yellow solid, m.p. 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, J = 9.3 Hz, 1 H), 8.14–8.12 (m, 2 H), 8.04 (t, J = 9.2 Hz, 2 H), 7.97–7.91 (m, 4 H), 7.64–7.58 (m, 3 H), 7.53–7.50 (m, 1 H), 7.38–7.35 (m, 2 H), 6.92–6.89 (m,1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 198.0, 188.7, 144.4, 140.9, 140.7, 134.8, 134.6, 134.0, 131.7, 131.3, 131.1, 130.9, 130.6, 130.5, 130.3, 129.7, 129.4, 128.9, 128.6, 127.9, 127.2, 126.4, 126.3, 126.2, 124.7, 124.6, 124.1, 123.5 ppm. $C_{28}H_{16}O_2S$ (416.49): calcd. C 80.75, H 3.87, S 7.70; found C 80.69, H 3.73, S 7.95.

4-(Pyren-2-yl)naphtho[2,3-*b*]thiophene (27a): Reduction of crude diketone **25a** (0.32 g, 0.77 mmol) with sodium borohydride (0.15 g, 3.95 mmol) followed by workup gave diol **26a**. Crude diol **26a** (0.31 g, 0.73 mmol) upon annulation with HBr (33%, 0.30 g, 3.69 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **27a** (0.23 g, 83%) as a yellow solid, m.p. 220–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.36 (d, J = 7.8 Hz, 1 H), 8.26 (d, J = 7.8 Hz, 1 H), 8.25 (s, 2 H), 8.18–8.13 (m, 1 H), 8.09–8.01 (m, 3 H), 7.81 (d, J = 9.3 Hz, 1 H), 7.54–7.49 (m, 3 H), 7.35 (d, J = 6.0 Hz, 1 H), 7.30–7.7.25 (m, 1 H), 6.78 (d, J = 6 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.3, 137.8, 133.9, 132.8, 131.5, 131.2, 131.1, 130.3, 130.2, 128.9, 128.1, 127.8, 127.7, 127.5, 126.8, 126.2, 125.7, 125.4, 125.3, 125.2, 125.0, 124.9, 124.7, 123.7, 121.0 ppm. HRMS (EI): calcd. for $C_{28}H_{16}S$ [M$^+$] 384.0973; found 384.0970.

(2-Benzoylphenyl)(pyren-2-yl)methanone (25b): Ring opening of 3-(pyren-2-yl)isobenzofuran-1(3*H*)-one (1.5 g, 4.49 mmol) with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **24b** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **24b** (0.45 g, 1.15 mmol) with MnO_2 (0.30 g, 3.45 mmol) by following a procedure similar to that for **20a** afforded diketone **25b** (0.42 g, 91%) as a yellow solid, m.p. 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (d, J = 9.3 Hz, 1 H), 8.23 (t, J = 6.0 Hz, 2 H), 8.06 (d, J = 9 Hz, 1 H), 8.09–8.02 (m, 5 H), 7.70–7.56 (m, 6 H), 7.48 (t, J = 7.42 Hz, 1 H), 7.27 (t, J = 6.1 Hz, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 198.0, 197.0, 141.2, 141.1, 137.3, 133.9, 133.0, 131.7, 131.3, 131.0, 130.6, 130.5, 130.0, 129.7, 129.5, 129.4, 129.1, 128.7, 128.3, 127.1, 126.4, 126.3, 126.2, 124.8, 124.7, 124.1, 123.5 ppm. $C_{30}H_{18}O_2$ (410.47): calcd. C 87.78, H 4.42; found C 87.59, H 4.61.

Annulation of Diol 26b: Reduction of diketone **25b** (0.30 g, 0.71 mmol) with sodium borohydride (0.13 g, 3.42 mmol) followed by workup gave diol **26b**. The annulation of crude diol **26b** (0.30 g, 0.72 mmol) with HBr (33%, 0.29 g, 3.63 mmol) in acetic acid by adopting a procedure similar to that for **14a** followed by column chromatographic purification (silica gel; hexane/ethyl acetate, 99:1) furnished products **27b** and **27b′**.

7-Phenylnaphtho[2,1,8-*qra*]tetracene (27b): Orange solid, 0.16 g (61%), m.p. 244–246 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.64 (s, 1 H), 9.25 (d, J = 9.3 Hz, 1 H), 8.32 (t, J = 9.6 Hz, 2 H), 8.17 (s, 2 H), 7.93–7.85 (m, 2 H), 7.79 (d, J = 8.7 Hz, 1 H), 7.64–7.63 (m, 5 H), 7.61–7.56 (m, 3 H), 7.54–7.47 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.0, 137.4, 131.7, 131.6, 128.9, 128.8,127.8, 127.6, 127.5, 126.6, 126.3, 125.8, 125.6, 125.2, 124.7, 123.8, 122.5, 121.9 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 131.6, 128.9, 128.8, 127.8, 127.6, 127.5, 126.6, 126.3, 125.8, 125.6, 125.2, 124.7, 123.8, 122.5, 121.9 ppm (only fifteen signals appeared instead of sixteen). HRMS (EI): calcd. for $C_{30}H_{18}$ [M$^+$] 378.1409; found 378.1400.

2-(Anthracen-9-yl)pyrene (27b′): Pale yellow solid, 0.08 g (30%), m.p. 228–230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 1 H), 8.36 (d, J = 7.5 Hz, 1 H), 8.25–8.19 (m, 3 H), 8.11 (t, J = 7.7 Hz, 3 H), 8.03–7.97 (m, 2 H), 7.77 (d, J = 9.3 Hz, 1 H), 7.45 (t, J = 7.4 Hz, 2 H), 7.36–7.30 (m, 3 H), 7.26–7.17 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 135.6, 133.9, 131.5, 131.3, 131.1, 130.8, 129.4, 128.5, 127.8, 127.7, 127, 127.0, 126.1, 125.7, 125.6, 125.3, 125.2, 124.7 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 129.4, 128.5, 127.8, 127.7, 127.5, 127.0, 126.1, 125.6, 125.3, 124.7 ppm. HRMS (EI): calcd. for $C_{30}H_{18}$ [M$^+$] 378.1409; found 378.1404.

[2-(4-Methylbenzoyl)phenyl](pyren-2-yl)methanone (25c): Ring opening of 3-(pyren-2-yl)isobenzofuran-1(3*H*)-one (1.0 g, 2.99 mmol) with freshly prepared *p*-tolylmagnesium bromide fol-

lowed by acidic workup gave benzo[*c*]furan **24c** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **24c** (0.74 g, 1.81 mmol) with MnO_2 (0.57 g, 5.41 mmol) by following a procedure similar to that for **20a** afforded diketone **25c** (0.72 g, 94%) as a yellow solid, m.p. 136–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, J = 9.3 Hz, 1 H), 8.22–8.11 (m, 3 H), 8.06–8.0 (m, 5 H), 7.68 (t, J = 7.1 Hz, 2 H), 7.64–7.57 (m, 2 H), 7.48 (d, J = 8.1 Hz, 2 H), 6.99 (d, J = 8.1 Hz, 2 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 198.0, 196.7, 143.9, 141.4, 141.0, 134.9, 133.9, 131.9, 131.3, 131.0, 130.9, 130.6, 130.4, 130.0, 129.6, 129.5, 129.1, 129.0, 128.7, 127.2, 126.4, 126.2, 126.1, 124.8, 124.7, 124.1, 123.5, 21.6 ppm. $C_{31}H_{20}O_2$ (424.50): calcd. C 87.71, H 4.75; found C 87.82, H 4.69.

Annulation of Diol 26c: Reduction of diketone **25c** (0.65 g, 1.51 mmol) with sodium borohydride (0.29 g, 7.66 mmol) followed by workup led to diol **26c**. The annulation of crude diol **26c** (0.69 g, 1.60 mmol) with HBr (33%, 0.65 g, 24.22 mmol) in acetic acid by adopting a procedure similar to that for **14a** followed by column chromatographic purification (silica gel; hexane/ethyl acetate, 99:1) afforded annulated compounds **27c** and **27c′**.

7-*p*-Tolylnaphtho[2,1,8-*qra*]tetracene (27c): Orange solid, 0.51 g (80%), m.p. 180–190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.61 (s, 1 H), 9.21 (d, J = 9.3 Hz, 1 H), 8.29 (t, J = 9.0 Hz, 2 H), 8.20 (s, 1 H), 8.16–8.13 (m, 1 H), 7.91–7.81 (m, 3 H), 7.65 (s, 1 H), 7.57 (t, J = 7.3 Hz, 1 H), 7.48–7.41 (m, 5 H), 2.59 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 137.7, 137.2, 136.1, 131.9, 131.8, 131.5, 131.0, 130.2, 129.9, 129.2, 128.9, 128.8, 128.7, 127.7, 127.6, 127.5, 126.9, 126.8, 126.3, 125.8, 125.5, 125.2, 124.6, 124.0, 123.8, 122.5, 121.8, 21.5 ppm. HRMS (EI): calcd. for $C_{31}H_{20}$ [M^+] 392.1565; found 392.1560.

2-(2-Methylanthracen-9-yl)pyrene (27c′): Yellow solid, 0.07 g (11%), m.p. 178–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 8.29 (d, J = 7.8 Hz, 1 H), 8.17–8.11 (m, 3 H), 8.02 (d, J = 6.0 Hz, 2 H), 7.96–7.89 (m, 3 H), 7.69 (d, J = 9.3 Hz, 1 H), 7.37–7.33 (m, 1 H), 7.31–7.21 (m, 3 H), 7.09 (d, J = 6.9 Hz, 1 H), 7.06 (s, 1 H), 2.13 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 135.4, 134.3, 134.2, 131.6, 131.5, 131.2, 131.1, 131.0, 130.8, 130.2, 129.5, 128.5, 128.4, 128.2, 127.7, 127.6, 127.5, 126.9, 126.8, 126.1, 125.9, 125.5, 125.2, 125.1, 125.1, 125.0, 124.9, 124.8, 124.7, 22.1 ppm. HRMS (EI): calcd. for $C_{31}H_{20}$ [M^+] 392.1565; found 392.1560.

[2-(4-Methoxybenzoyl)phenyl](pyren-2-yl)methanone (25d): Ring opening of 3-(pyren-2-yl)isobenzofuran-1(3*H*)-one (2.0 g, 5.99 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **24d** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **24d** (0.7 g, 1.65 mmol) with MnO_2 (0.43 g, 4.95 mmol) by following a procedure similar to that for **20a** afforded diketone **25d** (0.67 g, 92%) as a yellow solid, m.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, J = 9.3 Hz, 1 H), 8.20–8.16 (m, 2 H), 8.12 (d, J = 9.0 Hz, 1 H), 8.04–7.98 (m, 5 H), 7.71 (d, J = 7.5 Hz, 1 H), 7.63 (d, J = 6.3 Hz, 1 H), 7.51 (d, J = 8.7 Hz, 2 H), 6.63 (d, J = 8.7 Hz, 2 H), 3.68 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 198.1, 195.6, 163.4, 141.4, 140.9, 133.9, 131.9, 131.8, 131.3, 131.0, 130.8, 129.9, 129.6, 129.3, 129.2, 128.9, 128.8, 127.2, 126.4, 126.3, 126.1, 124.8, 124.6, 124.1, 123.6, 114.5, 113.6, 109.8, 55.4 ppm. $C_{31}H_{20}O_3$ (440.50): calcd. C 84.53, H 4.58; found C 84.71, H 4.39.

7-(4-Methoxyphenyl)naphtho[2,1,8-*qra*]tetracene (27d): Reduction of diketone **25d** (0.37 g, 0.84 mmol) with sodium borohydride (0.16 g, 4.21 mmol) followed by workup led to diol **26d**. Crude diol **26d** (0.42 g, 0.95 mmol) upon annulation with HBr (33%, 0.38 g, 14.34 mmol) in acetic acid by following a procedure similar to that for **14a** furnished **27d** 0.67 g (92%) as an orange solid, m.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.54 (s, 1 H), 9.16 (d, J = 9.0 Hz, 1 H), 8.23 (t, J = 10.2 Hz, 2 H), 8.14 (s, 1 H), 8.08 (d, J = 7.2 Hz, 1 H), 7.85–7.75 (m, 3 H), 7.59 (s, 2 H), 7.50 (t, J = 6.9 Hz, 1 H), 7.39 (t, J = 8.1 Hz, 3 H), 7.13 (t, J = 9.9 Hz, 2 H), 3.92 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.1, 136.3, 131.6, 130.8, 130.7, 130.2, 129.9, 129.3, 128.8, 127.8, 127.7, 126.6, 126.4, 125.8, 125.6, 125.2, 124.7, 124.4, 124.1, 123.6, 122.9, 122.6, 121.4, 120.7, 112.9, 54.4 ppm. HRMS (EI): calcd. for $C_{31}H_{20}O$ [M^+] 408.1514; found 408.1510.

[2-(1-Naphthoyl)phenyl](pyren-2-yl)methanone (25e): Ring opening of 3-(pyren-2-yl)isobenzofuran-1(3*H*)-one (1.5 g, 5.99 mmol) with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **24e** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **24e** (0.45 g, 1.01 mmol) with MnO_2 (0.26 g, 2.99 mmol) by following a procedure similar to that for **20a** afforded diketone **25e** (0.41 g, 90%) as a pale yellow solid, m.p. 163–165 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (d, J = 9.3 Hz, 1 H), 8.16 (d, J = 7.5 Hz, 1 H), 8.11–8.06 (m, 2 H), 8.03–7.94 (m, 3 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.83–7.64 (m, 7 H), 7.47 (d, J = 6.9 Hz, 1 H), 7.33 (t, J = 8.6 Hz, 2 H), 6.72 (t, J = 7.4 Hz, 1 H), 6.63 (t, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 197.8, 197.7, 141.8, 141.7, 135.4, 134.2, 133.6, 133.3, 131.7, 131.2, 131.1, 130.8, 130.5, 130.4, 130.3, 130.2, 129.8, 129.6, 129.2, 127.5, 127.0, 126.8, 126.2, 126.1, 126.0, 125.7, 125.0, 124.8, 124.2, 123.9, 123.7, 123.4 ppm. $C_{34}H_{20}O_2$ (460.53): calcd. C 88.67, H 4.38; found C 88.56, H 4.52.

7-(Naphthalen-1-yl)naphtho[2,1,8-*qra*]tetracene (27e): Reduction of diketone **25e** (0.34 g, 0.76 mmol) with sodium borohydride (0.14 g, 3.68 mmol) followed by workup gave diol **26e**. Crude diol **26e** (0.31 g, 0.73 mmol) upon annulation with HBr (33%, 0.29 g, 3.58 mmol) by adopting a procedure similar to that for **14a** afforded compound **27e** (0.28 g, 92%) as a yellow solid, m.p. 202–204 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.40 (s, 1 H), 8.97 (d, J = 8.1 Hz, 1 H), 8.38 (d, J = 7.8 Hz, 1 H), 8.26–8.17 (m, 4 H), 8.10 (d, J = 7.5 Hz, 1 H), 8.06–7.98 (m, 2 H), 7.80–7.70 (m, 3 H), 7.62 (d, J = 7.2 Hz, 1 H), 7.56–7.52 (m, 1 H), 7.35 (d, J = 9.3 Hz, 3 H), 7.30–7.23 (m, 1 H), 7.17 (d, J = 9.3 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 135.8, 134.1, 131.9, 131.7, 131.5, 131.1, 130.8, 130.6, 129.9, 129.4, 128.7, 128.6, 128.3, 127.8, 127.7, 127.5, 127.3, 127.1, 126.9, 126.2, 126.0, 125.7, 125.6, 125.3, 125.2, 125.0, 124.8, 124.7, 123.2, 122.1 ppm. HRMS (EI): calcd. for $C_{34}H_{20}O$ [M^+] 428.1565; found 428.1560.

9,9-Dihexyl-9*H*-fluoren-3-yl[2-(2-thienyl)phenyl]methanone (29a): Ring opening of 3-(9,9-dihexyl-9*H*-fluoren-2-yl)isobenzofuran-1(3*H*)-one[33] with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28a** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **28a** (0.6 g, 1.15 mmol) with MnO_2 (0.3 g, 3.46 mmol) by following a procedure similar to that for **20a** afforded diketone **29a** (0.53 g, 86%) as a thick yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.51 (m, 9 H, ArH), 7.38 (dd, J_1 = 1.2, J_2 = 3.9 Hz, 1 H, ArH), 7.28–7.26 (broad s, 3 H, ArH), 6.98–6.95 (m, 1 H, ArH), 1.88–1.83 (m, 4 H, CH_2), 1.05–0.95 (m, 12 H, CH_2), 0.71–0.47 (m, 10 H, CH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.5, 188.4, 152.1, 150.8, 146.1, 144.3, 139.7, 139.81, 139.6, 135.8, 135.1, 134.7, 130.5, 130.4, 130.0, 129.9, 129.0, 128.5, 127.9, 127.0, 123.9, 123.1, 120.8, 119.2, 55.2, 40.1, 31.5, 29.6, 23.7, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 135.1, 134.7, 130.6, 130.5, 130.0, 129.9, 129.0, 128.5, 127.9, 127.0, 123.9, 123.1, 120.8, 119.2, 40.1, 31.5, 29.6, 23.7, 22.6, 14.0 ppm. $C_{37}H_{40}O_2S$ (548.78): calcd. C 80.98, H 7.35, S 5.84; found C 81.26, H 7.48, S 5.71.

4-(9,9-Dihexyl-9*H*-fluoren-2-yl)naphtho[2,3-*b*]thiophene (31a): Reduction of diketone **29a** (0.42 g, 0.76 mmol) with sodium borohydride (0.12 g, 3.1 mmol) followed by workup led to diol **30a**. Crude diol **30a** (0.43 g, 0.77 mmol) upon annulation with HBr (33%, 0.38 g, 14.34 mmol) in acetic acid by following a procedure similar to that for **14a** afforded compound **31a** (0.35 g, 89%) as a green solid, m.p. 154–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 7.97 (d, J = 8.4 Hz, 1 H), 7.87 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 7.5 Hz, 1 H), 7.51–7.44 (m, 3 H), 7.42–7.34 (m, 5 H), 7.16 (d, J = 5.4 Hz, 1 H), 1.99 (t, J = 7.8 Hz, 4 H, CH_2), 1.14–1.08 (m, 12 H, CH_2), 0.79–0.74 (m, 10 H, CH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.0, 150.9, 140.9, 140.6, 138.1, 137.8, 137.4, 135.1, 131.3, 129.3, 127.6, 127.5, 127.2, 126.9, 126.5, 125.5, 125.1, 124.9, 123.7, 122.9, 120.4, 119.8, 119.6, 55.3, 40.4, 31.5, 29.7, 23.9, 22.5, 14.1 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 129.3, 127.6 127.5, 127.2, 126.9, 126.5, 125.5, 125.1, 124.9, 123.7, 122.9, 120.4, 119.8, 119.6, 40.4, 31.5, 29.7, 23.9, 22.5, 14.1 ppm. $C_{37}H_{40}S$ (516.78): calcd. C 85.99, H 7.80, S 6.20; found C 85.86, H 7.71, S 6.31.

(9,9-Dihexyl-9*H*-fluoren-3-yl)[2-(benzoyl)phenyl]methanone (29b): Ring opening of 3-(9,9-dihexyl-9*H*-fluoren-2-yl)isobenzofuran-1(3*H*)-one[33] with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28b** as a thick orange liquid. Oxidation of benzo[*c*]furan **28b** (0.9 g, 1.71 mmol) with MnO_2 (0.44 g, 5.13 mmol) by following a procedure similar to that for **20a** afforded diketone **29b** (0.79 g, 85%) as a thick orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.62 (m, 3 H), 7.58–7.55 (m, 3 H), 7.39–7.32 (m, 2 H), 7.26–7.10 (m, 6 H), 1.87–1.82 (m, 4 H, CH_2), 1.04–0.99 (m, 12 H, CH_2), 0.70–0.44 (m, 10 H, CH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.8, 196.5, 152.1, 150.9, 146.1, 140.3, 140.2, 139.7, 137.3, 135.7, 132.9, 130.4, 130.2, 130.1, 129.9, 129.8, 129.5, 128.8, 128.5, 128.3, 127.2, 127.0, 124.0, 123.1, 120.8, 119.2, 55.3, 40.1, 31.5, 29.7, 23.8, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 133.0, 130.4, 130.2, 130.1, 129.9, 129.8, 129.5, 128.5, 128.3, 127.0, 124.0, 123.1, 120.8, 119.2, 40.1, 31.5, 29.7, 23.8, 22.6, 14.0 ppm. $C_{40}H_{44}O_2$ (556.79): calcd. C 86.29, H 7.97; found C 86.35, H 7.88.

9-(9,9-Dihexyl-9*H*-fluoren-2-yl)anthracene (31b): Reduction of diketone **29b** (0.6 g, 1.1 mmol) with sodium borohydride (0.17 g, 4.45 mmol) followed by workup led to diol **30b**. Crude diol **30b** (0.61 g, 1.1 mmol) upon annulation with HBr (33%, 0.45 g, 5.55 mmol) in acetic acid by following a procedure similar to that for **14a** afforded compound **31b** (0.47 g, 83%) as a green solid, m.p. 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.08 (d, J = 8.4 Hz, 2 H), 7.93 (d, J = 7.5 Hz, 1 H), 7.83 (d, J = 7.2 Hz, 1 H), 7.78 (d, J = 8.7 Hz, 2 H), 7.51–7.33 (m, 9 H), 1.99 (t, J = 7.8 Hz, 4 H, CH_2), 1.14–1.08 (m, 12 H, CH_2), 0.79–0.74 (m, 10 H, CH_2 & CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.0, 150.9, 141.0, 140.5, 137.7, 137.4, 131.5, 130.4, 129.8, 128.4, 127.2, 126.9, 126.9, 126.5, 126.0, 125.3, 125.1, 122.9, 119.8, 119.6, 55.3, 40.5, 31.6, 29.7, 23.9, 22.5, 14.1 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 129.8, 128.4, 127.2, 126.9, 126.5, 126.0, 125.3, 125.1, 122.9, 119.8, 119.6, 40.5, 31.6, 29.7, 23.9, 22.5, 14.1 ppm.

(9,9-Dihexyl-9*H*-fluoren-3-yl)[2-(4-methylbenzoyl)phenyl]methanone (29c): Ring opening of 3-(9,9-dihexyl-9*H*-fluoren-2-yl)isobenzofuran-1(3*H*)-one[33] with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28c** as a thick orange liquid. Oxidation of benzo[*c*]furan **28c** (1.1 g, 2.03 mmol) with MnO_2 (3.51 g, 7.91 mmol) by following a procedure similar to that for **20a** afforded diketone **29c** (0.92 g, 82%) as a thick orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.53 (m, 10 H), 7.28–7.25 (m, 3 H), 7.06 (d, J = 7.5 Hz, 2 H), 2.27 (s, 3 H), 1.87–1.82 (m, 4 H), 1.04–0.95 (m, 12 H), 0.70–0.44 (m, 10 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.5, 196.3, 152.1, 150.8, 146.0, 143.8, 140.4, 140.2, 139.8, 135.8, 134.8, 130.3, 130.1, 129.7, 129.4, 129.0, 128.4, 127.0, 124.0, 123.1, 120.7, 119.2, 55.2, 40.1, 31.5, 29.6, 23.7, 22.6, 21.6, 14.0 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 130.3, 130.1, 130.0, 129.7, 129.4, 129.0, 128.4, 127.0, 124.0, 123.1, 120.7, 119.2, 40.1, 31.5, 29.6, 23.7, 22.6, 21.6, 14.0 ppm. $C_{40}H_{44}O_2$ (556.79): calcd. C 86.29, H 7.97; found C 86.35, H 7.88.

9-(9,9-Dihexyl-9*H*-fluoren-2-yl)-2-methylanthracene (31c): Reduction of diketone **29c** (0.75 g, 1.94 mmol) with sodium borohydride (0.29 g, 7.77 mmol) followed by workup led to diol **30c**. Crude diol **30c** (0.63 g, 1.12) upon annulation with HBr (33%, 0.45 g, 5.62 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded anthracene **31c** (0.46 g, 73%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.10 (d, J = 8.4 Hz, 1 H), 8.05–7.98 (m, 2 H), 7.90 (d, J = 6.6 Hz, 1 H), 7.82 (d, J = 8.7 Hz, 1 H), 7.58 (s, 1 H), 7.54–7.43 (m, 6 H), 7.48–7.38 (m, 2 H), 2.47 (s, 3 H), 2.12–2.04 (m, 3 H), 1.25–1.17 (m, 11 H), 0.88–0.82 (m, 10 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.0, 150.8, 141.1, 140.5, 137.7, 136.6, 135.0, 131.0, 130.7, 130.6, 130.1, 129.9, 128.5, 128.3, 128.0, 127.2, 127.0, 126.9, 126.3, 126.1, 125.3, 125.2, 124.8, 122.9, 119.8, 119.7, 55.29, 40.6, 31.78, 31.6, 29.9, 29.7, 27.0, 24.0, 23.9, 22.8, 22.7, 22.6, 22.3, 14.1 ppm. HRMS (EI): calcd. for $C_{40}H_{44}$ [M^+] 524.3443; found 524.3439.

(9,9-Dihexyl-9*H*-fluoren-3-yl)[2-(4-benzoyl)4-methoxyphenyl]methanone (29d): Ring opening of 3-(9,9-dihexyl-9*H*-fluoren-2-yl)isobenzofuran-1(3*H*)-one[33] (2.0 g, 4.29 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28d** as a fluorescent yellow solid. Oxidative cleavage of benzo[*c*]furan **28d** (1 g, 1.78 mmol) with MnO_2 (0.46 g, 5.35 mmol) by adopting a procedure similar to that for **20a** furnished diketone **29d** as a thick liquid (0.85 g, 83%). The crude diketone was used in the next step without further characterization.

9-(9,9-Dihexyl-9*H*-fluoren-2-yl)-2-methoxyanthracene (31d): Reduction of crude diketone **29d** (0.62 g, 1.08 mmol) with sodium borohydride (0.20 g, 5.41 mmol) followed by workup gave diol **30d**. Crude diol **30d** (0.59 g, 1.02 mmol) upon annulation with HBr (33%, 0.41 g, 5.12 mmol) in acetic acid by adopting a procedure similar to that for **14a** furnished compound **31d** (0.39 g, 71%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 7.98 (d, J = 8.1 Hz, 1 H), 7.91–7.86 (m, 2 H), 7.65 (d, J = 7.5 Hz, 2 H), 7.39 (d, J = 7.8 Hz, 2 H), 7.30–7.28 (m, 4 H), 7.12 (d, J = 7.5 Hz, 2 H), 3.97 (s, 3 H), 2.07–1.89 (m, 4 H), 1.26–1.22 (m, 4 H), 1.04–1.00 (m, 12 H), 0.72–0.67 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.0, 151.1, 148.4, 140.3, 140.2, 139.8, 132.5, 131.7, 131.3, 131.2, 128.2, 128.1, 127.0, 126.9, 126.8, 126.7, 126.2, 125.0, 124.8, 123.1, 122.9, 121.1, 120.7, 119.6, 113.9, 55.4, 54.4, 41.7, 31.5, 29.8, 24.0, 22.6, 14.0 ppm. HRMS (EI): calcd. for $C_{40}H_{44}O$ [M^+] 540.3392; found 540.3390.

[2-(Dibenzo[*b*,*d*]furan-2-carbonyl)phenyl](thiophen-2-yl)methanone (29e): Ring opening of 3-(dibenzo[*b*,*d*]furan-2-yl)isobenzofuran-1(3*H*)-one[34] with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28e** as an orange solid. Oxidation of the benzo[*c*]furan **28e** (0.72 g, 1.96 mmol) with MnO_2 (0.51 g, 5.9 mmol) by following a procedure similar to that for **20a** afforded diketone **29e** (0.66 g, 89%) as a thick red liquid. The crude diketone was used in the next step without further characterization.

7-(Thiophen-2-yl)anthra[2,3-*d*]benzo[*b*]furan (31e): Reduction of diketone **29e** (0.55 g, 1.44 mmol) with sodium borohydride (0.27 g, 7.2 mmol) followed by workup led to diol **30e**. Crude diol **30e** (0.54 g, 1.41) upon annulation with HBr (33%, 0.54 g, 6.62 mmol)

in acetic acid by adopting a procedure similar to that for **14a** afforded compound **31e** (0.42 g, 83%) as a yellow solid, m.p. 222–224 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 8.54 (s, 1 H), 8.05 (t, J = 6.9 Hz, 2 H), 7.85 (s, 2 H), 7.63 (d, J = 5.1 Hz, 1 H), 7.49–7.48 (m, 2 H), 7.47–7.40 (m, 2 H), 7.37–7.32 (m, 2 H) 7.23–7.22 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.8, 155.2, 139.2, 131.9, 131.8, 130.2, 129.4, 129.0, 128.7, 128.5, 128.3, 128.0, 127.3, 126.8, 126.3, 126.0, 124.7, 123.6, 122.8, 121.6, 119.2, 111.5, 104.7 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 129.4, 129.0, 128.5, 128.3, 127.3, 126.8, 126.3, 126.0, 124.7, 122.8, 121.6, 119.2, 111.5, 104.7 ppm. HRMS (EI): m/z. calcd. for $C_{24}H_{14}OS$ [M^+] 350.0765; found 350.0760.

[2-(Dibenzo[*b*,*d*]furan-2-carbonyl)phenyl](*p*-tolyl)methanone (29f): Ring opening of 3-(dibenzo[*b*,*d*]furan-2-yl)isobenzofuran-1(3*H*)-one[34] (2 g, 6.67 mmol) with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28f** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **28f** (1.84 g, 4.92 mmol) with MnO_2 (1.28 g, 14.75 mmol) by following a procedure similar to that for **20a** afforded diketone **29f** (1.72 g, 89%) as a colorless solid, m.p. 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 7.92–7.84 (m, 2 H), 7.65–7.59 (m, 6 H), 7.56–7.46 (m, 3 H), 7.38–7.33 (m, 1 H), 7.16 (d, J = 7.8 Hz, 2 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.3, 196.1, 158.9, 156.9, 144.0, 140.4, 140.2, 134.7, 132.6, 130.3, 130.2, 130.1, 129.7, 129.6, 129.1, 127.9, 124.5, 123.7, 123.3, 123.2, 121.1, 111.9, 111.5, 21.7 ppm. $C_{27}H_{18}O_3$ (390.44): calcd. C 83.06, H 4.65; found C 83.21, H 4.49.

7-*p*-Tolylanthra[2,3-*b*]benzo[*d*]furan (31f): Reduction of diketone **29f** (0.77 g, 1.97 mmol) with sodium borohydride (0.38 g, 7.77 mmol) followed by workup led to diol **30f**. Crude diol **30f** (0.51 g, 1.29 mmol) upon annulation with HBr (33%, 0.52 g, 6.43 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **31f** (0.38 g, 82%) as a yellow solid, m.p. 212–214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.54 (s, 1 H), 8.05 (d, J = 7.5 Hz, 2 H), 7.72–7.69 (m, 2 H), 7.46–7.40 (m, 5 H), 7.36–7.31 (m, 4 H), 2.54 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.2, 154.8, 137.2, 136.5, 136.0, 131.2, 130.4, 130.2, 129.3, 128.9, 128.3, 126.9, 126.6, 126.1, 125.3, 124.6, 123.7, 122.8, 121.6, 119.2, 111.4, 104.9, 21.4 ppm. $C_{27}H_{18}O$ (358.44): calcd. C 90.47, H 5.06; found C 90.61, H 4.97.

[2-(Dibenzo[*b*,*d*]furan-2-carbonyl)phenyl](4-methoxyphenyl) methanone (29g): Ring opening of 3-(dibenzo[*b*,*d*]furan-2-yl)isobenzofuran-1(3*H*)-one[34] (2 g, 6.67 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28g** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **28g** (2.0 g, 5.12 mmol) with MnO_2 (1.33 g, 15.38 mmol) by following a procedure similar to that for **20a** afforded diketone **29g** (1.90 g, 91%) as a colorless solid, m.p. 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 7.92–7.90 (m, 1 H), 7.87–7.83 (m, 1 H), 7.71–7.65 (m, 6 H), 7.58 (d, J = 8.4 Hz, 1 H), 7.53–7.49 (m, 2 H), 7.38–7.33 (m, 1 H), 6.83 (d, J = 9.0 Hz, 2 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.3, 195.4, 163.6, 128.9, 156.9, 140.4, 140.3, 133.3, 132.6, 132.3, 130.2, 129.6, 129.5, 129.4, 127.9, 124.4, 123.7, 123.3, 123.2, 121.1, 120.3, 113.6, 111.9, 111.5, 55.5 ppm. $C_{27}H_{18}O_4$ (406.44): calcd. C 79.79, H 4.46; found C 79.58, H 4.63.

7-(4-Methoxyphenyl)anthra[2,3-*b*]benzo[*d*]furan (31g): Reduction of diketone **29g** (1.0 g, 2.46 mmol) with sodium borohydride (0.47 g, 12.37 mmol) followed by workup led to diol **30g**. Crude diol **30g** (1.0 g, 2.45 mmol) upon annulation with HBr (33%, 0.97 g, 12.2 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded **31g** (0.81 g, 89%) as a yellow solid, m.p. 200–202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.54 (s, 1 H), 8.05 (d, J = 7.5 Hz, 2 H), 7.72 (d, J = 8.1 Hz, 2 H), 7.52–7.46 (m, 3 H), 7.40–7.31 (m, 4 H), 7.14 (d, J = 8.7 Hz, 2 H), 3.95 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 159.1, 158.2, 154.8, 136.2, 132.4, 131.1, 130.6, 130.4, 128.9, 128.3, 126.9, 126.6, 126.1, 125.4, 124.6, 123.7, 122.8, 121.6, 119.2, 114.1, 111.4, 104.8, 55.4 ppm. $C_{27}H_{18}O_2$ (374.44): calcd. C 86.61, H 4.85; found C 86.77, H 4.64.

[2-(1-Naphthoyl)phenyl](dibenzo[*b*,*d*]furan-2-yl)methanone (29h): Ring opening of 3-(dibenzo[*b*,*d*]furan-2-yl)isobenzofuran-1(3*H*)-one[34] (2 g, 6.67 mmol) with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28h** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **28h** (1.0 g, 2.33 mmol) with MnO_2 (0.6 g, 6.9 mmol) by following a procedure similar to that for **20a** afforded diketone **29h** (0.90 g, 88%) as a thick yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (d, J = 9.3 Hz, 1 H), 8.16 (d, J = 7.5 Hz, 1 H), 8.11–8.06 (m, 2 H), 8.03–7.94 (m, 3 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.83–7.64 (m, 7 H), 7.47 (d, J = 6.9 Hz, 1 H), 7.33 (t, J = 8.6 Hz, 2 H), 6.72 (t, J = 7.4 Hz, 1 H), 6.63 (t, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 197.8, 197.7, 141.8, 135.4, 134.2, 133.6, 133.3, 131.2, 131.1, 130.8, 130.5, 130.4, 130.3, 130.2, 129.8, 129.6, 129.2, 127.5, 127.0, 126.8, 126.2, 126.1, 126.0, 125.7, 125.0, 124.8, 124.2, 123.9, 123.7, 123.4 ppm. $C_{30}H_{18}O_3$ (426.47): calcd. C 84.49, H 4.25; found C 84.38, H 4.16.

7-(Naphthalen-1-yl)anthra[2,3-*d*]benzo[*b*]furan (31h): Reduction of diketone **29h** (0.9 g, 2.11 mmol) with sodium borohydride (0.40 g, 10.56 mmol) followed by workup led to diol **30h**. Crude diol **30h** (0.6 g, 1.39 mmol) upon annulation with HBr (33%, 0.11 g, 1.35 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **31h** (0.44 g, 81%) as a yellow solid, m.p. 198–200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.28 (s, 1 H), 8.90 (d, J = 7.8 Hz, 1 H), 8.18 (d, J = 8.1 Hz, 1 H), 8.01 (s, 1 H), 7.90 (d, J = 7.5 Hz, 1 H), 7.78 (t, J = 6.3 Hz, 2 H), 7.69 (d, J = 7.8 Hz, 3 H), 7.67–7.63 (m, 6 H), 7.60–7.45 (m, 1 H), 7.43–7.31 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 156.8, 155.7, 137.3, 133.5, 132.5, 131.6, 131.4, 130.5, 130.3, 129.4, 129.2, 128.7, 128.6, 127.5, 127.2, 127.0, 126.8, 126.6, 125.9, 125.7, 125.6, 124.6, 124.1, 123.4, 123.1, 122.9, 121.8, 120.9, 111.9, 111.6 ppm. HRMS (EI): calcd. for $C_{30}H_{18}O$ [M^+] 394.1358; found 394.1356.

(9-Hexyl-9*H*-carbazol-3-yl)[2-(2-thienoyl)phenyl]methanone (29i): Interaction of 3-(*N*-hexylcarbazol-3-yl)isobenzofuran-1(3*H*)-one[34] with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28i** as a thick orange liquid. Oxidation of benzo[*c*]furan **28i** (0.83 g, 1.85 mmol) with MnO_2 (0.48 g, 5.54 mmol) by following a procedure similar to that for **20a** afforded diketone **29i** (0.75 g, 85%) as a thick yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H), 7.87–7.84 (m, 1 H), 7.77 (d, J = 8.7 Hz, 1 H), 7.62–7.60 (m, 1 H), 7.58–7.53 (m, 1 H), 7.48–7.43 (m, 2 H), 7.38 (t, J = 6.6 Hz, 2 H), 7.33–7.27 (m, 1 H), 7.25–7.21 (m, 1 H), 7.18–7.14 (m, 1 H), 7.1–7.05 (m, 1 H) 4.08 (t, J = 6.9 Hz, 2 H, NCH_2), 1.67–1.66 (m, 2 H, CH_2), 1.13 (s, 6 H, CH_2), 0.71 (t, J = 3.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.1, 188.6, 144.2, 143.3, 141.1, 140.7, 139.8, 135.0, 134.6, 130.5, 130.0, 129.8, 129.1, 128.5, 128.1, 128.0, 126.5, 123.8, 123.1, 122.5, 120.8, 120.0, 109.3, 108.4, 43.3, 31.6, 28.9, 27.0, 22.6, 14.1 ppm. $C_{30}H_{27}NO_2S$ (465.61): calcd. C 77.39, H 5.84, N 3.01, S 6.89; found C 77.43, H 5.72, N 2.93, S 6.78.

Annulation of Diol 30i: Reduction of diketone **29i** (0.7 g, 1.49 mmol) with sodium borohydride (0.28 g, 7.46 mmol) followed by workup led to diol **30i**. Crude diol **30i** (0.71 g, 1.51 mmol) upon annulation with HBr (33%, 0.61 g, 7.56 mmol) in acetic acid fol-

lowed by workup and purification by column chromatography (silica gel; hexane) led to the isolation of naphtho[*b*]carbazole **31i** (0.29 g, 45%). Further elution of the column (silica gel; hexane/ethyl acetate, 99:1) afforded naphtho[*b*]thiophene **31i′** (0.23 g, 36%) as a yellow solid.

5-Hexyl-7-(thiophen-2-yl)-5*H*-naphtho[2,3-*b*]carbazole (31i): M.p. 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 8.2 (s, 1 H), 8.05 (d, J = 7.8 Hz, 1 H), 7.97 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 8.7 Hz, 1 H), 7.55 (s, 2 H), 7.52–7.44 (m, 3 H), 7.38–7.34 (m, 2 H), 7.24–7.16 (m, 2 H), 4.38 (t, J = 7.2 Hz, 2 H, -CH_2), 2.0–1.92 (m, 2 H, -CH_2), 1.68–1.64 (m, 2 H, -CH_2), 1.5–1.36 (m, 4 H, -CH_2), 0.90 (t, J = 6.6 Hz, 3 H, -CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.9, 140.2, 140.1, 138.2, 134.2, 131.7, 129.6, 129.5, 129.0, 128.4, 127.6, 125.9, 125.6, 125.1, 124.7, 123.9, 123.2, 122.9, 122.0, 121.1, 120.5, 119.0, 108.9, 108.5, 43.4, 31.6, 29.0, 27.0, 22.6, 14.0 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 128.4, 127.5, 127.3, 126.9, 125.9, 125.1, 124.8, 124.1, 122.5, 120.5, 120.1, 119.0, 108.9, 108.5, 43.4, 31.7, 29.1, 27.1, 22.6, 14.1 ppm.

9-Hexyl-3-(naphtho[2,3-*b*]thiophen-4-yl)-9*H*-carbazole (31i′): M.p. 124–128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (s, 1 H), 8.30 (s, 1 H), 8.05 (t, J = 8.7 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.66–7.56 (m, 2 H),7.52–7.45 (m, 5 H), 7.37 (t, J = 7.5 Hz, 1 H), 7.23–7.20 (m, 1 H), 4.38 (m, J = 7.5 Hz, 2 H, CH_2), 2.02–1.92 (m, 2 H, CH_2), 1.52–1.44 (m, 2 H, CH_2), 1.37–1.36 (m, 4 H, CH_2), 0.90 (t, J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.9, 140.2, 138.2, 134.2, 131.7, 129.6, 129.5, 129.0, 128.4, 127.6, 125.9, 125.6, 125.1, 123.9, 123.2, 122.0, 121.1, 120.5, 119.0, 108.9, 108.8, 43.4, 31.6, 29.1, 27.1, 22.6, 14.0 ppm.

(9-Hexyl-9*H*-carbazol-3-yl)[2-(4-methylbenzoyl)phenyl]methanone (29j): Interaction of 3-(*N*-hexylcarbazol-3-yl)isobenzofuran-1(3*H*)-one[34] (1 g, 2.61 mmol) with *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28j** as a thick orange liquid (0.69 g, 58%). Oxidation of benzo[*c*]furan **28j** (0.5 g, 1.02 mmol) with MnO_2 (0.26 g, 3.08 mmol) by following a procedure similar to that for **20a** afforded diketone **29j** (0.42 g, 80%) as a thick yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H), 7.94 (d, J = 7.8 Hz, 1 H), 7.79 (d, J = 8.7 Hz, 1 H), 7.63–7.52 (m, 6 H), 7.37 (d, J = 7.5 Hz, 1 H), 7.31 (d, J = 8.1 Hz, 1 H), 7.23 (d, J = 8.7 Hz, 1 H), 7.15 (t, J = 7.4 Hz, 1 H), 7.03 (d, J = 8.1 Hz, 2 H), 4.18 (t, J = 7.2 Hz, 2 H), 2.24 (s, 3 H), 1.78–1.71 (m, 2 H), 1.22–1.20 (m, 6 H), 0.77 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 195.5, 195.2, 142.7, 142.2, 140.1, 139.9, 139.2, 133.8, 129.1, 128.9, 128.8, 128.6, 128.4, 127.9, 127.6, 127.1, 125.3, 122.7, 122.1, 121.5, 119.7, 118.9, 108.2, 107.2, 42.3, 30.5, 27.8, 25.9, 22.5, 21.7, 14.0 ppm. $C_{33}H_{31}NO_2$ (473.61): calcd. C 83.69, H 6.60, N 2.96; found C 83.58, H 6.51, N 2.85.

5-Hexyl-7-*p*-tolyl-5*H*-naphtho[2,3-*b*]carbazole (31j): Reduction of diketone **29j** (0.82 g, 1.68 mmol) with sodium borohydride (0.39 g, 10.26 mmol) followed by workup led to diol **30j**. Crude diol **30j** (0.70 g, 1.45 mmol) upon annulation with HBr (33%, 0.59 g, 7.29 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded carbazole **31j** (0.50 g, 78%) as a yellow solid, m.p. 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 1 H), 8.64 (s, 1 H), 8.16 (d, J = 7.5 Hz, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 7.62 (d, J = 8.7 Hz, 1 H), 7.35–7.33 (m, 6 H), 7.25–7.15 (m, 4 H), 4.05–4.01 (m, 2 H), 2.45 (s, 3 H), 1.72–1.68 (m, 2 H), 1.20–1.17 (m, 6 H), 0.79–0.77 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.2, 141.0, 136.8, 136.7, 134.7, 131.4, 130.2, 129.8, 129.3, 129.2, 128.4, 127.8, 127.4, 126.9, 126.5, 126.4, 124.8, 123.5, 122.6, 121.3, 118.7, 108.0, 100.7, 42.8, 31.4, 28.0, 26.9, 22.5, 21.5, 14.0 ppm. HRMS (EI): calcd. for $C_{33}H_{31}N$ [M^+] 441.2457; found 441.2450.

(9-Hexyl-9*H*-carbazol-3-yl)[2-(4-methoxybenzoyl)phenyl]methanone (29k): Interaction of 3-(*N*-hexylcarbazol-3-yl)isobenzofuran-1(3*H*)-one[34] (2.0 g, 5.18 mmol) with *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28k** as a thick orange liquid. Oxidation of benzo[*c*]furan **28k** (1.80 g, 11.11 mmol) with MnO_2 (1.02 g, 7.91 mmol) by following a procedure similar to that for **20a** afforded diketone **29k** (1.50 g, 81%) as a thick yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 8.02 (d, J = 7.8 Hz, 1 H), 7.90–7.86 (m, 1 H), 7.70–7.67 (m, 3 H), 7.62–7.58 (m, 3 H), 7.47–7.44 (m, 1 H), 7.40 (d, J = 8.4 Hz, 1 H), 7.31 (d, J = 8.7 Hz, 1 H), 7.26–7.21 (m, 1 H), 6.81–6.80 (m, 2 H), 4.26 (t, J = 7.2 Hz, 2 H, -NCH_2), 3.77 (s, 3 H), 1.84–1.82 (m, 2 H), 1.31–1.26 (m, 6 H), 0.85 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.3, 195.6, 163.5, 143.3, 141.1, 140.9, 132.3, 130.4, 129.9, 129.8, 129.6, 129.3, 128.6, 128.2, 128.1, 126.4, 123.8, 123.2, 122.5, 120.8, 119.9, 113.5, 109.2, 108.3, 55.4, 43.3, 31.5, 28.9, 26.9, 22.5, 14.0 ppm. $C_{33}H_{31}NO_3$ (489.61): calcd. C 80.95, H 6.38, N 2.86; found C 80.87, H 6.31, N 2.72.

5-Hexyl-7-(4-methoxyphenyl)-5*H*-naphtho[2,3-*b*]carbazole (31k): Reduction of diketone **29k** (0.90 g, 1.89 mmol) with sodium borohydride (0.36 g, 9.47 mmol) followed by workup led to diol **30k**. Crude diol **30k** (0.72 g, 1.46 mmol) upon annulation with HBr (33%, 0.59 g, 22.12 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **31k** (0.53 g, 78%) as a yellow solid, m.p. 163–165 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.75 (s, 1 H), 8.71 (s, 1 H), 8.23 (d, J = 7.5 Hz, 1 H), 8.06 (d, J = 8.4 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.52 (t, J = 7.5 Hz, 1 H), 7.45–7.39 (m, 4 H), 7.36–7.26 (m, 4 H), 7.20–7.15 (m, 2 H), 4.14–4.09 (m, 2 H), 3.99 (s, 3 H), 1.80–1.75 (m, 2 H), 1.30–1.25 (m, 6 H), 0.90–0.82 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.9, 144.2, 141.0, 134.4, 132.5, 131.9, 130.5, 130.0, 129.3, 128.4, 127.8, 127.4, 126.9, 126.5, 126.4, 124.8, 123.5, 122.6, 121.3, 118.7, 114.0, 108.0, 100.6, 55.4, 42.9, 31.4, 28.1, 26.9, 22.5, 14.0 ppm. HRMS (EI): calcd. for $C_{33}H_{31}NO$ [M^+] 457.2406; found 457.2400.

{2-[4-(Diphenylamino)benzoyl]phenyl}(*p*-tolyl)methanone (29l): Ring opening of 3-[4-(diphenylamino)phenyl]isobenzofuran-1(3*H*)-one[34] (2 g, 5.30 mmol) with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28l** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **28l** (1.5 g, 3.32 mmol) with MnO_2 (0.87 g, 10.0 mmol) by following a procedure similar to that for **20a** afforded diketone **29l** (1.38 g, 92%) as a colorless solid, m.p. 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.60 (m, 3 H), 7.55–7.52 (m, 5 H), 7.32–7.25 (m, 4 H), 7.18 (d, J = 7.8 Hz, 2 H), 7.13–7.11 (m, 6 H), 6.88 (d, J = 8.7 Hz), 2.39 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.5, 195.0, 152.1, 146.4, 143.8, 140.6, 140.1, 134.8, 131.6, 130.1, 130.0, 129.8, 129.7, 129.6, 129.4, 129.3, 129.2, 129.0, 126.0, 124.7, 119.4, 21.7 ppm. $C_{33}H_{25}NO_2$ (467.57): calcd. C 84.77, H 5.39, N 3.00; found C 84.98, H 5.22, N 3.19.

***N*,*N*-Diphenyl-9-*p*-tolylanthracen-2-amine (31l):** Reduction of diketone **29l** (1.0 g, 2.14 mmol) with sodium borohydride (0.40 g, 10.52 mmol) followed by workup gave diol **29l**. Crude diol **29l** (1.1 g, 2.33 mmol) upon annulation with HBr (33%, 0.94 g, 11.61 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **31l** (0.74 g, 73%) as a pale green solid, m.p. 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 7.93 (d, J = 8.7 Hz, 1 H), 7.75 (d, J = 8.4 Hz, 1 H), 7.53 (s, 1 H), 7.44–7.35 (m, 3 H), 7.32–7.22 (m, 6 H), 7.06 (t, J = 7.2 Hz, 2 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 147.9, 147.0, 135.8, 134.9, 132.6, 132.1, 131.0, 130.6, 130.1, 129.0, 128.4, 128.3, 128.0, 126.8, 126.2, 125.2, 125.0, 124.7, 123.1, 123.0, 22.4 ppm. HRMS (EI): calcd. for $C_{33}H_{25}N$ [M^+] 435.1987; found 435.1987.

{2-[4-(Diphenylamino)benzoyl]phenyl}(4-methoxyphenyl)methanone (29m): Ring opening of 3-[4-(diphenylamino)phenyl]isobenzofuran-1(3*H*)-one[34] (2 g, 5.83 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **28m** as a fluorescent bright yellow solid. Oxidation of benzo[*c*]furan **28m** (0.2 g, 0.42 mmol) with MnO_2 (0.11 g, 1.26 mmol) by following a procedure similar to that for **20a** afforded diketone **29m** (0.19 g, 93%) as a colorless solid, m.p. 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.7 Hz, 2 H), 7.53–7.44 (m, 6 H), 7.25–7.18 (m, 4 H), 7.05–7.03 (m, 6 H), 6.82–6.78 (m, 4 H), 3.77 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 195.5, 195.0, 163.5, 152.1, 146.4, 140.4, 140.2, 132.3, 131.6, 130.3, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 129.0, 124.7, 119.4, 113.6, 55.5 ppm. $C_{33}H_{25}NO_3$ (483.57): calcd. C 81.97, H 5.21, N 2.90; found C 81.84, H 5.09, N 2.99.

9-(4-Methoxyphenyl)-*N*,*N*-diphenylanthracen-2-amine (31m): Reduction of diketone **29m** (0.20 g, 0.41 mmol) with sodium borohydride (0.07 g, 18.42 mmol) followed by workup gave diol **30m**. Crude diol **30m** (0.22 g, 0.45 mmol) upon annulation with HBr (33%, 0.18 g, 2.22 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **31m** (0.14 g, 68%) as a pale green solid, m.p. 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (s, 1 H), 7.88 (d, J = 8.7 Hz, 1 H), 7.80 (d, J = 9.0 Hz, 1 H), 7.60 (d, J = 8.4 Hz, 1 H), 7.38 (d, J = 9.0 Hz, 1 H), 7.25–7.24 (m, 1 H), 7.16–7.09 (m, 8 H), 7.01–6.99 (m, 3 H), 6.99–6.81 (m, 2 H), 2.91 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.7, 146.3, 133.8, 131.2, 131.0, 130.3, 129.8, 129.7, 129.4, 128.3, 128.2, 128.1, 127.7, 127.4, 126.7, 125.5, 125.4, 125.0, 124.3, 123.5, 123.4, 122.4, 121.9, 116.7, 113.1, 112.6, 54.3 ppm. $C_{33}H_{25}NO$ (451.57): calcd. C 87.77, H 5.58, N 3.10; found C 87.65, H 5.69, N 3.01.

Naphthalene-2,3-bis(phenylmethanone) (33a): 1,4-Diphenylbutane-1,4-dione **32a** (1.0 g, 4.20 mmol) and phthalaldehyde (0.56 g, 4.18 mmol) were dissolved in hot ethanol (25 mL). To this, *t*BuOK (1.13 g, 10 mmol) was slowly added and the reaction mixture was stirred for 3 h at room temperature. The solid obtained was filtered and washed with methanol (10 mL) to afford diketone **33a** (1.01 g, 72%) as a colorless solid, m.p. 156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (s, 2 H), 7.94–7.90 (m, 2 H), 7.80 (d, J = 7.5 Hz, 4 H), 7.65–7.62 (m, 2 H), 7.53 (t, J = 7.2 Hz, 2 H), 7.40 (t, J = 7.5 Hz, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.3, 137.4, 137.0, 133.0, 132.9, 130.8, 129.9, 128.8, 128.7, 128.4 ppm.

5-Phenyltetracene (35a): Reduction of crude diketone **33a** (0.5 g, 1.49 mmol) with sodium borohydride (0.22 g, 5.95 mmol) followed by workup gave diol **34a**. Crude diol **34a** (0.4 g, 0.45 mmol) upon annulation with HBr (33%, 0.21 g, 1.43 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **35a**[35] (0.25 g, 71%) as a pale green solid, m.p. 177–178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71 (s, 1 H), 8.68 (s, 1 H), 8.29 (s, 1 H), 8.03–7.96 (m, 2 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.67–7.59 (m, 4 H), 7.51 (d, J = 6.3 Hz, 2 H), 7.41–7.36 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.0, 136.9, 131.5, 131.4, 131.2, 131.1, 130.0, 129.7, 129.4, 128.8, 128.5, 127.9, 127.6, 126.9, 126.7, 126.4, 125.6, 125.3, 125.1, 125.0, 124.8 ppm.

3-Benzoylnaphthalen-2-yl(thiophen-2-yl)methanone (33b): Condensation of 1-phenyl-4-(thiophen-2-yl)butane-1,4-dione **32b** (1.0 g, 4.10 mmol) with phthalaldehyde (0.55 g, 4.10 mmol) and *t*BuOK (1.14 g, 10.24 mmol) by adopting a procedure similar to that for **32a** furnished diketone **33b** (1.01 g, 72%) as a colorless solid, m.p. 154–155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = (s, 1 H), 7.97–7.92 (m, 2 H), 7.86–7.83 (m, 2 H), 7.68–7.56 (m, 5 H), 7.44–7.41 (m, 2 H), 7.12–7.10 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.3, 188.1, 144.1, 137.4, 136.8, 136.5, 136.3, 135.3, 134.9, 134.7, 134.5, 133.1, 130.9, 130.2, 130.1, 129.9, 128.8, 128.7, 128.4, 128.1 ppm.

4-Phenylanthra[2,3-*b*]thiophene (35b): Reduction of diketone **33b** (0.5 g, 1.46 mmol) with sodium borohydride (0.21 g, 5.84 mmol) followed by workup gave diol **34b**. Crude diol **34b** (0.4 g, 0.45 mmol) upon annulation with HBr (33%, 0.21 g, 1.43 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **35b** (0.24 g, 68%) as a yellow solid, m.p. 177–178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 8.52 (s, 1 H), 8.42 (s, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 8.1 Hz, 1 H), 7.65–7.56 (m, 5 H), 7.43–7.35 (m, 3 H), 7.11 (d, J = 5.7 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.0, 137.9, 137.5, 134.1, 131.1, 130.9, 130.2, 129.8, 128.6, 128.5, 128.3, 128.2, 127.9, 127.7, 125.4, 125.3, 125.2, 124.9, 123.5, 120.4 ppm. $C_{22}H_{14}S$ (310.41): calcd. C 85.12, H 4.55, S 10.33; found C 84.93, H 4.68.

[3-(4-Methylbenzoyl)naphthalen-2-yl](thiophen-2-yl)methanone (33c): Condensation of 1-(thiophen-2-yl)-4-*p*-tolylbutane-1,4-dione **32c** (1.1 g, 4.26 mmol) with phthalaldehyde (0.57 g, 4.25 mmol) and *t*BuOK (1.19 g, 10.60 mmol) by adopting a procedure similar to that for **32a** furnished diketone **33c** (1.25 g, 83%) as a colorless solid, m.p. 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 8.08 (s, 1 H), 7.97–7.95 (m, 2 H), 7.73–7.60 (m, 6 H), 7.25–7.20 (m, 2 H), 7.12–7.10 (m, 1 H), 2.4 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.0, 188.1, 144.2, 143.9, 136.9, 136.8, 134.9, 134.6, 133.1,133.0, 130.7, 130.2, 130.1, 129.1, 128.8, 128.6, 128.0, 21.7 ppm. $C_{23}H_{16}O_2S$ (356.44): calcd. C 77.50, H 4.52, S 9.00; found C 77.37, H 4.61, S 8.87.

4-*p*-Tolylanthra[2,3-*b*]thiophene (35c): Reduction of diketone **33c** (0.8 g, 2.24 mmol) with sodium borohydride (0.42 g, 11.05 mmol) followed by workup gave diol **34c**. Crude diol **34c** (0.8 g, 2.22 mmol) upon annulation with HBr (33%, 0.89 g, 10.99 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **35c** (0.51 g, 74%) as a yellow solid, m.p. 132–134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55–854 (m, 2 H), 8.42 (s, 1 H), 8.0 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.4 Hz, 1 H), 7.47–7.38 (m, 5 H), 7.36–7.35 (m, 2 H), 7.11 (d, J = 5.7 Hz, 1 H), 2.54 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.0, 137.6, 135.9, 134.2, 131.1, 131.0, 130.7, 129.9, 129.2, 128.6, 128.5, 128.0, 127.8, 125.4, 125.3, 124.9, 124.8, 123.7, 120.1, 21.4 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 130.7, 129.2, 128.6, 128.0, 127.8, 125.4, 125.3, 124.8, 123.7, 120.1, 21.4 ppm. HRMS (EI): calcd. for $C_{23}H_{16}S$ [M^+] 324.0973; found 324.0970.

[3-(1-Naphthoyl)naphthalen-2-yl](thiophen-2-yl)methanone (33d): Condensation of 1-(naphthalen-1-yl)-4-(thiophen-2-yl)butane-1,4-dione (**32d**) (1.1 g, 3.74 mmol) with phthalaldehyde (0.50 g, 3.73 mmol) and *t*BuOK (1.04 g, 9.26 mmol) by adopting a procedure similar to that for **32a** furnished compound **33d** (1.23 g, 84%) as a colorless solid, m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 8.16 (d, J = 8.1 Hz, 2 H), 7.99–7.93 (m, 3 H), 7.88–7.80 (m, 3 H), 7.68–7.54 (m, 5 H), 7.51–7.46 (m, 1 H), 7.10–7.09 (m, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.2, 188.0, 144.2, 137.0, 136.9, 135.6, 134.9, 134.8, 134.6, 133.1, 133.0, 132.3, 130.9, 129.6, 128.9, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 126.7, 125.3 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 134.9, 134.7, 132.3, 130.9, 130.2, 129.6, 128.9, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 126.7, 125.2 ppm (only fifteen signals appeared instead of sixteen). $C_{26}H_{16}O_2S$ (392.47): calcd. C 79.57, H 4.11, S 8.17; found C 79.43, H 3.93, S 8.31.

2-(Benzo[*a*]tetracen-7-yl)thiophene (35d): Reduction of crude diketone **33d** (0.96 g, 2.44 mmol) with sodium borohydride (0.46 g, 12.10 mmol) followed by workup gave diol **34d**. Crude diol **34d** (1.0 g, 3.12 mmol) upon annulation with HBr (33%, 1.22 g,

15.07 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **35d** (0.47 g, 87%) as a yellow solid, m.p. 196–198 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 1 H), 8.56 (s, 1 H), 8.46 (s, 1 H), 8.02 (d, J = 8.1 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 1 H), 7.71–7.64 (m, 4 H), 7.49–7.39 (m, 5 H), 7.27–7.21 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.3, 134.0, 132.3, 131.8, 131.5, 131.4, 130.9, 129.7, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 127.8, 127.7, 127.6, 127.4, 127.0, 126.0, 125.8, 125.7, 125.2 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 129.1, 129.0, 128.7, 128.5, 128.2, 128.1, 127.7, 127.6, 127.4, 127.0, 126.0, 125.8, 125.7, 125.2 (only fourteen signals appeared instead of sixteen) ppm. HRMS (EI): calcd. for $C_{26}H_{16}S$ [M^+] 360.0973; found 360.0970.

[3-(1-Naphthoyl)naphthalen-2-yl](phenyl)methanone (33e): Condensation of 1-(naphthalen-1-yl)-4-phenylbutane-1,4-dione (**32e**) (0.59 g, 2.0 mmol) with phthalaldehyde (0.27 g, 2.01 mmol) and *t*BuOK (0.57 g, 5.07 mmol) by adopting a procedure similar to that for **32a** furnished compound **33e** as a colorless solid (0.48 g, 81%) as a yellow solid, m.p. 166–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (s, 1 H), 8.15 (d, J = 8.1 Hz, 2 H), 7.97–7.91 (m, 3 H), 7.87–7.79 (m, 5 H), 7.68–7.65 (m, 2 H), 7.60–7.47 (m, 3 H), 7.38 (t, J = 7.8 Hz, 2 H) 2.54 (s, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.3, 137.5, 137.3, 137.1, 136.2, 135.5, 134.9, 133.1, 132.9, 132.3, 132.2, 130.9, 130.8, 130.0, 129.6, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 126.7, 125.3 ppm. $C_{28}H_{18}O_2$ (386.45): calcd. C 87.02, H 4.69; found C 86.88, H 4.92.

7-Phenylbenzo[*a*]tetracene (35e): Reduction of crude diketone **33e** (0.42 g, 1.16 mmol) with sodium borohydride (0.22 g, 5.78 mmol) followed by workup gave diol **34e**. Crude diol **34e** (1.0 g, 3.12 mmol) upon annulation with HBr (33%, 0.5 g, 1.36 mmol) in acetic acid by adopting a procedure similar to that for **14a** afforded compound **35e** (0.43 g, 89%) as a yellow solid, m.p. 200–202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1 H), 8.46 (s, 1 H), 8.12 (s, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.65–7.53 (m, 5 H), 7.40–7.28 (m, 7 H), 6.97 (t, d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 142.5, 137.3, 133.9, 131.5, 131.4, 131.3, 130.8, 130.0, 129.7, 129.1, 129.0, 128.5, 128.3, 127.8, 127.6, 127.5, 126.7, 126.6, 126.4, 125.6, 125.0 ppm. DEPT-135 (75.4 MHz, $CDCl_3$): δ = 130.8, 129.7, 129.1, 129.0, 128.5, 128.3, 127.8, 127.6, 127.5, 126.6, 126.4, 125.7, 125.6, 125.0 ppm (only fourteen signals appeared instead of sixteen). HRMS (EI): calcd. for $C_{28}H_{18}$ [M^+] 354.1409; found 354.1400.

9-Hexyl-9*H*-carbazol-3-yl[3-(4-methylbenzoyl)naphthalen-2-yl]methanone (38a): Ring opening of 3-(9-hexyl-9*H*-carbazol-3-yl)-3,3a-dihydronaphtho[2,3-*c*]furan-1(9a*H*)-one[29] (**36**) (2.0 g, 4.61 mmol) with freshly prepared *p*-tolylmagnesium bromide followed by an aqueous NH_4Cl quench gave keto alcohol **37a**. Keto alcohol **37a** (1.0 g, 1.90 mmol) upon oxidation with PCC (0.9 g, 2.85 mmol) by following a procedure similar to that for **6a** furnished diketone **38a** (0.78 g, 79%) as a colorless solid, m.p. 82–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (s, 1 H), 8.15 (s, 1 H), 8.10 (s, 1 H), 8.01–7.98 (m, 2 H), 7.92–7.90 (m, 1 H), 7.72 (d, J = 7.8 Hz, 2 H), 7.62–7.59 (m, 2 H), 7.45–7.32 (m, 4 H), 7.23–7.21 (m, 1 H), 7.18–7.14 (m, 2 H), 4.27–4.22 (m, 2 H), 2.33 (s, 3 H), 1.83–1.81 (m, 2 H), 1.30–1.26 (m, 6 H), 0.87–0.84 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.2, 196.0, 143.6, 143.3, 141.2, 138.2, 137.6, 135.1, 133.1, 132.9, 130.5, 130.2, 129.7, 129.0, 128.9, 128.8, 128.6, 128.4, 128.3, 128.2, 126.6, 126.4, 123.9, 123.2, 122.6, 120.8, 119.9, 108.4, 43.3, 31.6, 28.9, 26.9, 22.5, 21.7, 14.0 ppm. $C_{37}H_{33}NO_2$ (523.67): calcd. C 84.86, H 6.35, N 2.67; found C 84.71, H 6.17, N 2.81.

Attempted Annulation of Diol 39a: Reduction of diketone **38a** (0.60 g, 1.17 mmol) with sodium borohydride (0.22 g, 5.78 mmol) followed by workup gave diol **39a**. To a solution of crude diol **39a** (0.40 g, 0.89 mmol) in acetic acid (15 mL), HBr (33%, 0.36 g, 4.44 mmol) in acetic acid was added and stirred for 10 min (an intense red coloration was observed). The usual workup followed by column chromatography did not afford any detectable product.

9-Hexyl-9*H*-carbazol-3-yl[3-(4-methoxybenzoyl)naphthalen-2-yl]-methanone (38b): Ring opening of 3-(9-hexyl-9*H*-carbazol-3-yl)-3,3a-dihydronaphtho[2,3-*c*]furan-1(9a*H*)-one[29] **36** (2.0 g, 4.61 mmol) with freshly prepared *p*-anisylmagnesium bromide followed by basic workup gave keto alcohol **37b**. Oxidation of crude keto alcohol **37b** (1.0 g, 1.84 mmol) with PCC (0.59 g, 8.35 mmol) by following a procedure similar to that for **6a** furnished the diketone **38b** (0.73 g, 74%) as a thick brown liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.13 (s, 1 H), 8.06 (s, 1 H), 8.0–7.96 (m, 2 H), 7.87–7.86 (m, 2 H), 7.81–7.78 (m, 2 H), 7.57–7.54 (m, 2 H), 7.57–7.32 (m, 3 H), 7.17 (t, J = 6.9 Hz, 1 H), 6.80 (d, J = 8.7 Hz, 2 H), 4.21–4.17 (m, 2 H), 3.70 (s, 3 H), 1.81–1.77 (m, 2 H), 1.27–1.26 (m, 6 H), 0.85–0.83 (m, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 196.1, 195.3, 163.5, 143.3, 141.2, 138.2, 137.8, 133.0, 132.9, 132.8, 132.4, 130.6, 130.4, 130.1, 129.5, 129.0, 128.8, 128.4, 128.3, 126.4, 123.9, 123.2, 122.6, 120.8, 119.9, 113.6, 113.5, 108.4, 55.4, 43.3, 31.6, 28.9, 26.9, 22.6, 14.1 ppm. $C_{37}H_{33}NO_3$ (539.67): calcd. C 82.35, H 6.16, N 2.60; found C 82.41, H 6.02, N 2.48.

Attempted Annulation of Diol 39b: Reduction of diketone **38b** (0.65 g, 1.23 mmol) with sodium borohydride (0.23 g, 6.05 mmol) followed by workup gave diol **39b**. To a solution of crude diol **39a** (0.40 g, 0.75 mmol) in acetic acid (15 mL), HBr (33%, 0.31 g, 3.71 mmol) in acetic acid was added and stirred for 10 min (an intense red coloration was observed). The usual workup followed by column chromatography did not afford any detectable product.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H NMR, ^{13}C NMR, and DEPT-135 spectra (only selected cases) of final compounds.

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