

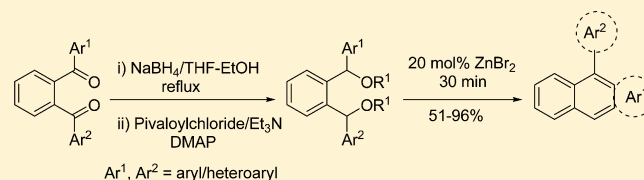
Synthesis of Annulated Arenes and Heteroarenes Involving Lewis Acid-Mediated Regioselective Annulation of Unsymmetrical 1,2-(Diaryl/diheteroarylmethine)dipivalates

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S Supporting Information

ABSTRACT: A ZnBr_2 -mediated regioselective annulation of unsymmetrical 1,2-diarylmethinedipivalates in DCM at room temperature led to the formation of annulated arenes and heteroarenes. The annulation of the dipivalate proceeds through the intermediacy of benzylic carbocations followed by intramolecular cyclization and subsequent aromatization to give the annulated products. The annulation methodology is highly efficient for the syntheses of anthracene as well as naphtho[*b*]thiophene analogues.



INTRODUCTION

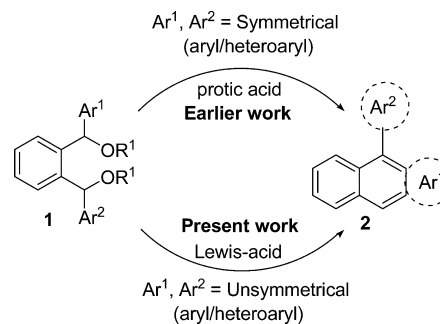
Traditionally, the Friedel–Crafts alkylation has been labeled as synthetically problematic, since controlling the reaction to the monoalkylation stage was thought to be difficult.¹ However, the Friedel–Crafts alkylation/cyclization using mild Lewis acid has been gaining momentum.² Apart from the first report of Beller and co-workers³ on Lewis acid-mediated arylation of benzylic acetates, a plethora of controlled Friedel–Crafts alkylation employing mild Lewis acids have been achieved.⁴ Recently, the Lewis acid-mediated domino reaction has been successfully applied for the synthesis of wide variety of π -conjugated heterocycles.⁵

Anthracene and its derivatives, the most important class of polycyclic aromatic compounds,⁶ have been prepared via Friedel–Crafts reaction,¹ flash vacuum pyrolysis,⁷ cyclodehydration,⁸ Lewis acid-induced cyclization of diarylmethanes,⁹ transition metal-mediated homologation¹⁰ and so on. Among the polyaromatic compounds, anthracene and its derivatives are regarded as an important class of functional material for optoelectronic device fabrication.¹¹ In recent times, the anthracene derivatives have been widely explored in OLEDs,¹² molecular switches¹³ and other optical applications.¹⁴ Because of its low electronic band gap and strong blue fluorescence, they have been extensively used as fluorescent chromophores in the construction of chemosensors for many applications.¹⁵ It has been confirmed that the incorporation of anthracene units as pendant groups led to the formation of films with excellent optical quality.¹⁶ Hence, there is plenty of demand for the synthesis of anthracene analogues with good solubility to further explore their optoelectronic device applications.

Recently, Liu and co-workers achieved the synthesis of 9-arylanthracenes¹⁷ and indenes¹⁸ involving either Bronsted acid or Lewis acid-catalyzed cyclization of symmetrical aryldiacetates. Very recently, an efficient synthesis of anthracene derivatives is realized via interaction of phthalaldehyde with

arenes under super electrophilic conditions.¹⁹ Kuninobu and co-workers achieved the synthesis of anthracenes and naphtho[*b*]thiophenes through indium triflate-mediated cycloaromatization reaction.²⁰ In further continuation of our interest on synthesis of π -conjugated heterocycles involving Lewis-acids,²¹ we report herein our detailed study on synthesis of anthracene and naphtho[*b*]thiophene analogues involving regioselective annulation of unsymmetrical diarylmethine dipivalates **1** (Scheme 1).

Scheme 1. Synthesis of Annulated Arenes and Heteroarenes



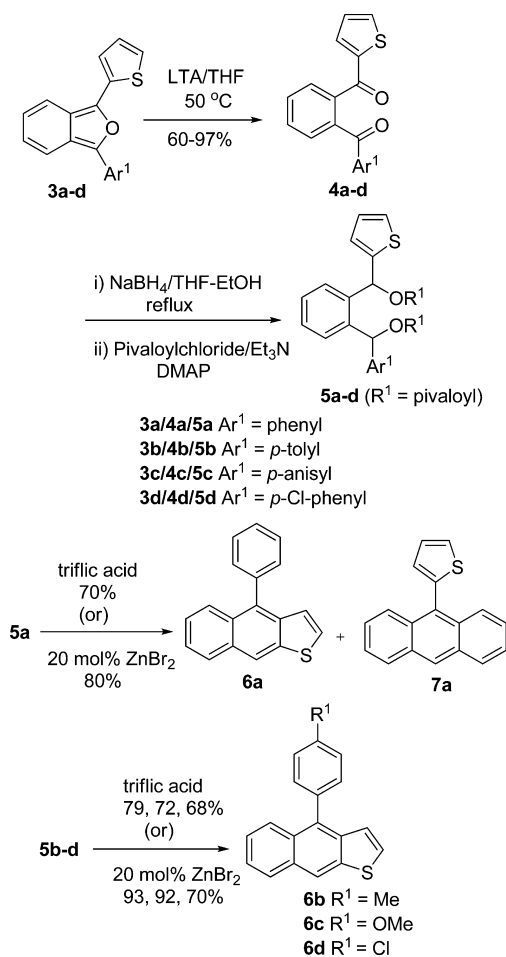
RESULTS AND DISCUSSION

The required diarylmethine dipivalates **5a–d** were conveniently prepared from 1,3-disubstituted isobenzofuran (IBF) derivatives **3a–d**.²² Lead tetraacetate (LTA)-mediated oxidative cleavage²³ of **3a–d** led to the diketones **4a–d**, which upon NaBH_4 reduction followed by subsequent pivaloylation furnished benzylic dipivalates **5a–d** as thick liquids (Scheme 2). The interaction of pivalate ester **5a** with triflic acid/ ZnBr_2 as

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Scheme 2. Annulation of Benzylic Dipivalates 5a–d



catalyst in DCM at room temperature for 30 min led to the formation of naphtho[*b*]thiophene **6a** and anthracene **7a** as an inseparable mixture (1:1, confirmed by ¹H NMR). Under identical conditions, to our delight, the reaction of pivalate esters **5b–d** with triflic acid/ZnBr₂ as catalyst led to the formation of naphtho[*b*]thiophenes **6b–d** as exclusive products.

Next, as a representative case, the annulation of **5b** was performed using 20 mol % of different Lewis acids/Bronsted acids, and the results obtained are presented in Table 1. The

Table 1. Effect of Catalyst (20 mol %) on Annulation of **5b**

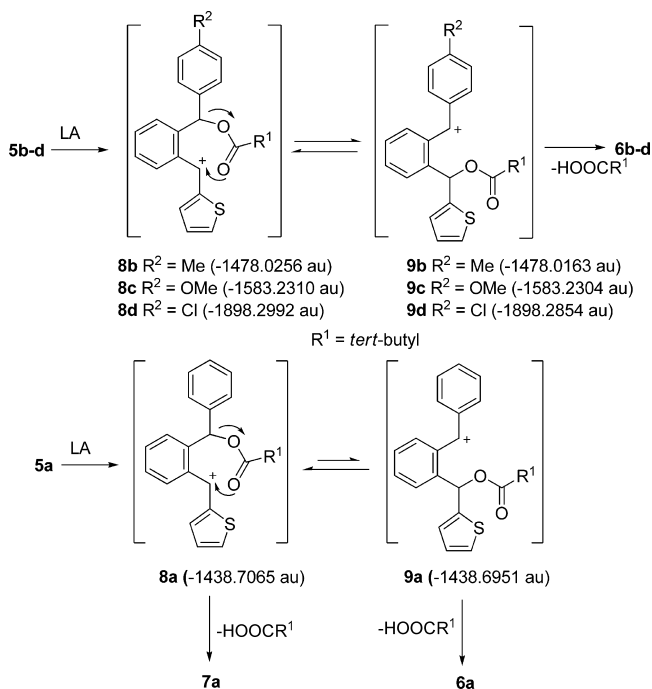
entry	catalyst	condition (min)	yield ^a
1	ZnBr ₂	30	93
2	FeCl ₃	60	78
3	BF ₃ ·OEt ₂	30	81
4	CF ₃ SO ₃ H	30	80
6	Me ₃ SO ₃ H	45	78
7	CF ₃ CO ₂ H	45	79

^aIsolated yields of **6b**.

reaction was found to be successful with Lewis acids as well as Bronsted acids. The maximum yield for naphtho[*b*]thiophene **6b** could be obtained using 20 mol % of ZnBr₂. It is noteworthy to mention that as reported in the case of symmetrical benzylic diacetates,¹⁷ we have not observed any dihydrofuran formation

during the interaction of unsymmetrical dipivalates **5b–d** with Lewis acids as well as Bronsted acids.

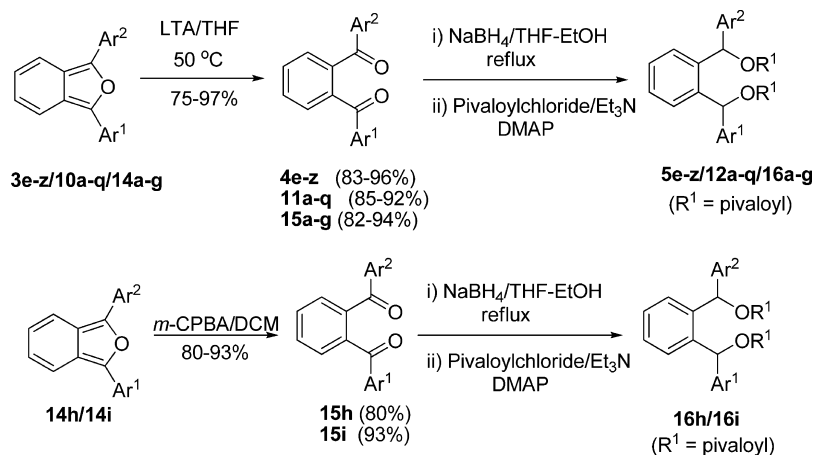
To rationalize the regioselective formation of annulated heterocycles **6b–d**, stabilization energies of benzylic carbocations **8a–e** and **9a–e** were calculated using Gaussian 09 program (package: B3LYP/6-31G* basis set). From the calculated values (Scheme 3), it is clear that the carbocation

Scheme 3. Mechanistic Rational for Benzo[*b*]thiophenes 6a–d

formation is more favored at 2-thienylmethyl position compared to the benzyl, *p*-tolylmethyl, *p*-anisylmethyl and *p*-chlorophenylmethyl positions. In the case of dipivalate **5b–d**, the highly stabilized thiophenylmethyl carbocations **8b–d** upon isomerization led to the formation of respective arylmethyl carbocations **9b–d**. The comparatively less stable benzylic carbocations **9b–d** underwent Friedel–Crafts type intramolecular cyclization at 3-position of thiophene followed by elimination of pivalic acid to produce naphtho[*b*]thiophenes **6b–d**. The formation of a mixture of naphtho[*b*]thiophene **6a** and anthracene **7a** upon reaction of dipivalate **5a** with Lewis acid can be visualized through the Friedel–Crafts type intramolecular cyclization of carbocations of **9a** and **8a**, respectively. Among the carbocations **8a–d**, the thiophenylmethyl carbocation **8a** being highly reactive (–1438.7065 au) underwent intramolecular cyclization to afford the anthracene **7a**. However, the similar kind of cyclization was not observed with relatively more stable thiophenylmethyl carbocations **8b–d**.

Having achieved a facile regioselective annulation of benzylic dipivalate **5b–d** in the presence of ZnBr₂, the preparation of various types of unsymmetrical dipivalates was planned to study their efficacy toward the synthesis of annulated arenes. Known 1,3-diarylbenzo[*c*]furans **3e–z**, **10a–q** and **14a–g**²² could be smoothly converted into the respective dipivalates **5e–z**, **12a–q** and **16a–g** using the similar sequence of reactions mentioned in Scheme 2. The additional dipivalate **16h/16i** was prepared through *m*-CPBA-mediated oxidative cleavage of 1,3-

Scheme 4. Preparation of Unsymmetrical Benzylic Dipivalates



diarylbenzo[*c*]furan **14h/14i** followed by reduction and subsequent pivaloylation (Scheme 4).

As expected the unsymmetrical aryl/heteroarylmethine dipivalates **5e–z**, **12a–q** and **16a–g** upon interaction with 20 mol % of ZnBr_2 in DCM at room temperature for 30 min furnished annulated products. The various types of annulated arenes and heteroarenes obtained along with their yields are described in Table 2. The reaction of dipivalates **5e–h** with 20 mol % of ZnBr_2 furnished respective 4-arylnaphtho[*b*]thiophenes **6e–h** in 65–92% yields (entry 1). The moderate yield of naphtho[*b*]thiophene **6e** obtained from *o*-tolyl tethered dipivalate **5e** may be due to the steric crowding encountered during intramolecular cyclization. The annulation of dipivalate **5i** containing a 2-methoxy-1-naphthyl unit gave naphtho[*b*]thiophene **6i** in 90% yield (entry 2). In the case of dipivalate **5j/5k** tethered with 1-naphthyl/2-methyl-1-naphthyl group, the ZnBr_2 -mediated annulation led to the formation of benz-annulated anthracene **6j**, **6k** (entry 3). However, the similar reaction of dipivalate **5l/5m** afforded the corresponding naphtho[*b*]thiophene **6l/6m** (entries 4, 5). As expected, the unsymmetrical dipivalates **5n–w** upon interaction with ZnBr_2 led to the isolation of arylanthracenes **6n–w** in excellent yields (entries 6, 7). The nature of arylanthracenes **6n–w** produced is determined by the preferential formation of benzylic carbocations followed by subsequent intramolecular cyclization and aromatization. Obviously, the regioselective formation of the benzylic carbocations is governed by the inductive effect of the substituents present in the aryl unit.

The 2-methoxy-1-naphthyl and aryl based unsymmetrical dipivalates **5x–z** afforded 2-methoxy-1-naphthylanthracenes **6x–z** in 88–95% yields as colorless solid (entry 8). In the case of 1-naphthyl and aryl based unsymmetrical dipivalates **12a–g**, the reaction led to the formation of benz-annulated anthracenes **13a–g** (entries 9, 10). The dipivalate **12h** containing 2-methoxy-1-naphthyl and 1-naphthyl rings furnished the respective benz-annulated anthracene **13h** in 86% yield (entry 11). However, the ZnBr_2 -mediated annulation of unsymmetrical dipivalate **12i** lacking a methoxy group at naphthalene portion led to the formation of an inseparable mixture of benz-annulated anthracenes **13i** and **13i'** (entry 12). The 9,9-dihexylfluorenyl unsymmetrical dipivalate **12j/12k** underwent smooth annulation at benzene portion to furnish the respective fluorenyl anthracene **13j/13k** (entry 13).

The interaction of 3-benzo[*b*]thiophenyl dipivalates **12l–q** with 20 mol % of ZnBr_2 led to the formation of corresponding

annulated heterocycles **13l–q** in 70–78% yields (entries 14–17). The annulation of 3-benzo[*b*]thiophenyl dipivalates **12l–o** afforded benz-annulated dibenzothiophene analogues **13l–o**. However, in the case of 2-methyl-3-benzo[*b*]thiophenyl dipivalate **12p/12q**, a similar type of annulation is not possible at the benzo[*b*]thiophene framework and hence led to the formation of benzo[*b*]thiophenyl anthracene **13p/naphtho[*b*]thiophene 13q** (entries 16, 17). Always, the yields of heterocycles obtained with the benzo[*b*]thiophenyl dipivalates **12l–q** were relatively less compared to either thiophene/arene tethered dipivalates **5a–z/12a–k**.

The unsymmetrical dibenzo[*b*]thiophenyl dipivalates **16a–f** upon reaction with 20 mol % ZnBr_2 furnished naphth-annulated dibenzothiophenes **17a–f** in 51–87% yields (entries 18–20). The low yield of dibenzothiophene **17e** isolated is due to the competing annulation at naphthalene portion. The annulation reaction with dibenzo[*b*]furan dipivalate **16g** led to the isolation of naphth-annulated dibenzofuran **17g** and naphtho[*b*]thiophene **17g'** in 48 and 23% yields, respectively. Finally, the ZnBr_2 -mediated annulation of carbazole/triphenylamine tethered dipivalate **16h/16i** was found to be unsuccessful. The usual work up followed by column chromatographic separation did not afford any characterizable product.

As representative case, the structures of annulated heterocycles **6m**, **13o** and **17a** were confirmed by single crystal X-ray analyses.²⁴

In summary, we have developed a simple and versatile annulation protocol for the synthesis of anthracene and naphtho[*b*]thiophene analogues involving ZnBr_2 -mediated regioselective annulation of unsymmetrical dipivalates. The annulation methodology could be successfully performed with variety of unsymmetrical dipivalates under very mild conditions. On the basis of theoretical calculation of stabilization values of the benzylic carbocations, a reasonable mechanism for the formation of annulated heterocycles was proposed. The attractive feature of this methodology is that a large number of π -conjugated arenes as well as heteroarenes are easily accessible. The anthracene as well as annulated thiophene derivatives reported herein may find application in OLEDs.²⁵

EXPERIMENTAL SECTION

General Methods. All melting points were uncorrected. Dry THF was prepared by refluxing with sodium. Dry DCM was prepared by refluxing with P_2O_5 . The progression of reaction was monitored by

Table 2. ZnBr₂-Mediated Intramolecular Cyclization of Unsymmetrical Dipivalates

entry	dipivalates	Anthracenes/naphtho[b]thiophenes	Yield ^a	entry	dipivalates	Anthracenes/naphtho[b]thiophenes	Yield ^a	
1	5e Ar ¹ = 2-thienyl Ar ² = <i>o</i> -tolyl			8	5x Ar ¹ = phenyl Ar ² = 2(OMe)-1-naphthyl			
	5f Ar ¹ = 2-thienyl Ar ² = <i>o</i> -xylenyl	6e-h			5y Ar ¹ = <i>o</i> -tolyl Ar ² = 2(OMe)-1-naphthyl			
	5g Ar ¹ = 2-thienyl Ar ² = <i>m</i> -xylenyl	6e R ¹ = Me, R ² , R ³ = H	65		5z Ar ¹ = <i>p</i> -tolyl Ar ² = 2(OMe)-1-naphthyl		6x R ¹ , R ² = H, R ³ = OMe	95
	5h Ar ¹ = 2-thienyl Ar ² = veratryl	6f R ¹ = H, R ² , R ³ = Me	93			6y R ¹ = Me, R ² = H, R ³ = OMe	89	
		6g R ¹ , R ³ = Me, R ² = H	82			6z R ¹ = H, R ² = Me, R ³ = OMe	88	
	6h R ¹ = H, R ² , R ³ = OMe	92						
2	5i Ar ¹ = 2-thienyl Ar ² = 2-methoxy-1-naphthyl			9	12a Ar ¹ = 1-naphthyl Ar ² = phenyl			
		6i	90		12b Ar ¹ = 1-naphthyl Ar ² = <i>p</i> -tolyl			
3	5j Ar ¹ = 2-thienyl Ar ² = 1-naphthyl				12c Ar ¹ = 1-naphthyl Ar ² = <i>m</i> -xylenyl		13a R ¹ , R ² , R ³ = H	88
	5k Ar ¹ = 2-thienyl Ar ² = 4-Me-1-naphthyl	6j R ¹ = H	81		12d Ar ¹ = 1-naphthyl Ar ² = veratryl		13b R ¹ = Me, R ² , R ³ = H	91
		6k R ¹ = Me	92			13c R ¹ , R ³ = Me, R ² = H	81	
4	5l Ar ¹ = 2-thienyl Ar ² = <i>p,p'</i> -biphenyl			10	12e Ar ¹ = 4-(Me)-1-naphthyl Ar ² = phenyl			
		6l (R ¹ = phenyl)	93		12f Ar ¹ = 4-(Me)-1-naphthyl Ar ² = <i>p</i> -tolyl		13e R ¹ = H	96
5	5m Ar ¹ = 2(5,5'-dithienyl) Ar ² = <i>p</i> -tolyl				12g Ar ¹ = 4-(Me)-1-naphthyl Ar ² = <i>p</i> -anisyl		13f R ¹ = Me	82
		6m	81			13g R ¹ = OMe	91	
6	5n Ar ¹ = phenyl Ar ² = <i>p</i> -tolyl			11	12h Ar ¹ = 1-naphthyl Ar ² = 2-(OMe)-1-naphthyl			
	5o Ar ¹ = phenyl Ar ² = <i>p</i> -anisyl				13h R ¹ = H	86		
	5p Ar ¹ = <i>p</i> -anisyl Ar ² = <i>p</i> -tolyl			12	12i Ar ¹ = 1-naphthyl Ar ² = 4-(Me)-1-naphthyl			
	5q Ar ¹ = phenyl Ar ² = <i>o</i> -xylenyl	6n R ¹ , R ² = H, R ³ = Me	89		13i + 13i'			
	5r Ar ¹ = <i>p</i> -tolyl Ar ² = <i>o</i> -xylenyl	6o R ¹ , R ² = H, R ³ = OMe	94		13i R ¹ = H, R ² = Me	85		
	5s Ar ¹ = <i>p</i> -tolyl Ar ² = veratryl	6p R ¹ = Me, R ² = H, R ³ = OMe	86		13i' R ¹ = Me, R ² = H			
	5t Ar ¹ = <i>p</i> -anisyl Ar ² = <i>o</i> -xylenyl	6q R ¹ = H, R ² , R ³ = Me	86					
	5u Ar ¹ = phenyl Ar ² = <i>p</i> -tolyl	6r R ¹ , R ² , R ³ = Me	92					
	5v Ar ¹ = phenyl Ar ² = <i>p</i> -tolyl	6s R ¹ = Me, R ² , R ³ = OMe	96					
	5v Ar ¹ = phenyl Ar ² = <i>p,p'</i> -biphenyl	6t R ¹ = OMe, R ² , R ³ = Me	88					
		6u R ¹ = phenyl, R ² = H, R ³ = Me	95					
	6v R ¹ , R ² = H, R ³ = phenyl	94						
7	5w Ar ¹ = <i>o</i> -tolyl Ar ² = <i>p</i> -tolyl			13	12j Ar ¹ = phenyl Ar ² = 9,9-dihexyl-2-fluorenyl			
		6w	91		12k Ar ¹ = <i>p</i> -tolyl Ar ² = 9,9-dihexyl-2-fluorenyl		13j R ¹ = H	71
					13k R ¹ = Me	73		

Table 2. continued

entry	dipivalates	Anthracenes/naphtho[<i>b</i>]thiophenes	Yield ^a	entry	dipivalates	Anthracenes/naphtho[<i>b</i>]thiophenes	Yield ^a
14	12l Ar ¹ = 3-benzo[<i>b</i>]thienyl Ar ² = phenyl		71 78 70	19	16e Ar ¹ = 1-naphthyl Ar ² = 3-dibenzothiophenyl		51
	12m Ar ¹ = 3-benzo[<i>b</i>]thienyl Ar ² = <i>p</i> -tolyl						
	12n Ar ¹ = 3-benzo[<i>b</i>]thienyl Ar ² = <i>p</i> -anisyl						
	13l R ¹ = H 13m R ¹ = Me 13n R ¹ = OMe						
15	12o Ar ¹ = 3-benzo[<i>b</i>]thienyl Ar ² = 2-thienyl	13o	72	20	16f Ar ¹ = 2-thienyl Ar ² = 3-dibenzothiophenyl	17f	82
16	12p Ar ¹ = 2(Me)-3-benzo[<i>b</i>]thienyl Ar ² = <i>p</i> -tolyl	13p	78	21	16g Ar ¹ = 5-hexyl-2-thienyl Ar ² = 3-dibenzofuranyl	17g	48
17	12q Ar ¹ = 2(Me)-3-benzo[<i>b</i>]thienyl Ar ² = 2-thienyl	13q	77			17g'	23
18	16a Ar ¹ = phenyl Ar ² = 3-dibenzothiophenyl		72 79 76 87	22	16h Ar ¹ = <i>p</i> -tolyl Ar ² = 1-hexyl-3-carbazolyl	17h	0 ^b
	16b Ar ¹ = <i>p</i> -tolyl Ar ² = 3-dibenzothiophenyl						
	16c Ar ¹ = <i>p</i> -anisyl Ar ² = 3-dibenzothiophenyl						
	16d Ar ¹ = <i>o</i> -tolyl Ar ² = 3-dibenzothiophenyl						
	17a R ¹ , R ² = H 17b R ¹ = H, R ² = Me 17c R ¹ = H, R ² = OMe 17d R ¹ = Me, R ² = H						
23	16i Ar ¹ = <i>p</i> -anisyl Ar ² = 4-(diphenylamino)phenyl	17i	0 ^b				

^aIsolated yield after column chromatographic purification. ^bNo characterizable product could be isolated.

TLC using a mixture of hexane/ethyl acetate as an eluent. Column chromatography was carried out on silica gel (230–400 mesh, Merck) by using increasing polarity. ¹H, ¹³C and DEPT 135 spectra were recorded in CDCl₃ using TMS as an internal standard on a 300 MHz spectrometer at room temperature. Chemical shift values were quoted in parts per million (ppm), and coupling constants (*J*) were quoted in hertz (Hz). High-resolution mass spectra (HRMS) were recorded using EI and ES-TOF mass spectrometers.

Preparation of 2-Benzoylphenyl(thiophene-2-yl)methanone (4a). To a stirred solution of benzo[*c*]furan **3a**²² (1.0 g, 3.62 mmol) in dry THF (20 mL), lead tetraacetate (LTA) (1.60 g, 3.62 mmol) was added and then stirred at 50 °C for half an hour. The reaction mixture was then poured into water (200 mL) and extracted with ethyl acetate (2 × 20 mL), washed with brine solution and dried (Na₂SO₄). Removal of solvent in vacuo followed by crystallization from methanol furnished **4a** as a brown solid (0.88 g, 84%): mp 134–135 °C (132.5–133.3 °C);²⁶ ¹H NMR (300 MHz, CDCl₃) δ 7.68–7.61 (m, 3H), 7.57–7.54 (m, 4H), 7.46–7.40 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.00–6.97 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.6, 188.3, 144.2, 139.8, 139.6, 137.2, 135.0, 134.9, 133.1, 130.5 (2C), 129.9, 129.8, 129.1, 128.3, 128.2.

Preparation of (2-(4-Methylbenzoyl)phenyl(thiophene-2-yl)methanone (4b). Ring-opening of 3-(thiophen-2-yl)isobenzofuran-1(3*H*)-one²⁷ with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3b** as a fluorescent bright yellow solid. Oxidative cleavage of the benzo[*c*]furan **3b**²² (1 g, 3.44 mmol) using LTA (1.52 g, 3.42 mmol) in dry THF (20 mL)

following the procedure similar to that of **4a** furnished **4b** as a colorless solid (0.94 g, 89%): mp 126–128 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.74–7.70 (m, 1H), 7.64–7.59 (m, 6H), 7.45–7.46 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.06–7.03 (m, 1H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 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; DEPT 135 (75 MHz, CDCl₃) δ 135.0, 134.8, 130.5, 130.3, 130.0, 129.6, 128.0, 21.7. Anal. Calcd for C₁₉H₁₄O₂S: C, 74.48; H, 4.61; S, 10.47. Found: C, 74.22; H, 4.41; S, 10.35.

Preparation of (2-(4-Methoxybenzoyl)phenyl(thiophene-2-yl)methanone (4c). Ring-opening of 3-(thiophen-2-yl)-isobenzofuran-1(3*H*)-one²⁷ with freshly prepared *p*-anisyl magnesium bromide followed by acidic workup gave benzo[*c*]furan **3c** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3c** (0.5 g, 1.63 mmol) with LTA (0.72 g, 1.62 mmol) using the procedure similar to that of **4a** furnished **4c** as a colorless solid (0.48 g, 91%): mp 131–132 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.65–7.61 (m, 3H), 7.56–7.52 (m, 4H), 7.40–7.39 (m, 1H), 6.99–6.97 (m, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 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; DEPT 135 (75 MHz, CDCl₃) δ 135.1, 134.8, 132.2, 130.5, 129.4, 129.0, 128.0, 113.6, 55.5. Anal. Calcd for C₁₉H₁₄O₃S: C, 70.79; H, 4.38; S, 9.95. Found: C, 70.58; H, 4.23; S, 9.71.

Preparation of Annulated Compounds (6a) and (7a). To a solution of diketone **4a** (0.8 g, 2.73 mmol) in THF–ethanol (20 mL; 1:3), sodium borohydride (0.52 g, 13.69 mmol) was added in portions

and refluxed for 4 h. The reaction mixture was then poured into water (200 mL), extracted with ethyl acetate (2 × 20 mL) and dried (Na₂SO₄). The removal of solvent gave crude diol (0.81 g, 2.73 mmol), which was dissolved in dry DCM (20 mL). To this, pivaloyl chloride (1.62 g, 13.51 mmol), triethylamine (5.46 g, 54.05 mmol), and a catalytic amount of DMAP (10 mg) were added. The reaction mixture was refluxed under nitrogen atmosphere for half an hour, and then hexane (20 mL) was added to the reaction mixture. The triethylamine hydrochloride salt formed was filtered off. The filtrate was concentrated, and the crude product was purified using column chromatography (silica gel; hexane–ethyl acetate 98:2). Pivaloyl ester **5a** (0.99 g, 2.13 mmol) was then dissolved in dry DCM (20 mL), a catalytic amount of ZnBr₂ (0.02 g, 0.13 mmol) was added, and stirred for 20 min under nitrogen atmosphere. Removal of solvent followed by column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of an inseparable 1:1 mixture (based on ¹H NMR integration of singlet proton at δ 8.50 and 8.39) of **6a** and **7a** as a colorless solid (0.7 g, 80%): mp 100–102 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.50 (s, 1H), 8.39 (s, 1H), 8.03–8.00 (d, J = 8.3 Hz, 2H), 8.01–7.96 (m, 1H), 7.93–7.78 (m, 2H), 7.60–7.36 (m, 13H), 7.18–7.16 (m, 1H), 7.00–7.09 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 138.9, 138.8, 138.0, 137.7, 134.4, 131.8, 131.2, 131.1, 130.7, 129.4, 129.1, 128.7, 128.4, 128.3, 127.9, 127.6, 127.5 (2C), 127.1, 126.7, 126.6, 126.4, 125.9, 125.2, 125.1, 124.9, 123.6, 120.4; HRMS (EI) Calcd for C₁₈H₁₂S [M⁺] 260.0660, found 260.0658.

Preparation of 4-*p*-Tolylnaphtho[2,3-*b*]thiophene (6b). Reduction of diketone **4b** (0.94 g, 3.07 mmol) in THF–ethanol (20 mL; 1:3) using sodium borohydride (0.58 g, 15.35 mmol) following the procedure similar to that of **6a** gave diol. The crude diol (0.92 g, 2.96 mmol) upon pivaloylation using pivaloyl chloride (1.78 g, 14.83 mmol) and triethylamine (6.0 g, 59.35 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) furnished dipivalate **5b**. Dipivalate **5b** (1.30 g, 2.71 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6b** as a pale yellow solid (0.75 g, 93%): mp 107–109 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.36 (s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 10.2 Hz, 1H), 7.46–7.31 (m, 7H), 7.11 (d, J = 7.8 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 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; DEPT 135 (75 MHz, CDCl₃) δ 130.6, 129.1, 127.6, 127.5, 126.5, 125.1, 124.9, 123.7, 120.3, 21.4. Anal. Calcd for C₁₉H₁₄S: C, 83.17; H, 5.14; S, 11.69. Found: C, 82.81; H, 5.21; S, 11.52.

Preparation of 4-(4-Methoxyphenyl)naphtho[2,3-*b*]thiophene (6c). Reduction of diketone **4c** (0.55 g, 1.70 mmol) in THF–ethanol (20 mL; 1:3) using sodium borohydride (0.32 g, 8.42 mmol) following the procedure similar to that of **6a** gave diol. The crude diol (0.53 g, 1.62 mmol) upon pivaloylation using pivaloyl chloride (0.98 g, 8.12 mmol) and triethylamine (3.29 g, 32.51 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) furnished dipivalate **5c** (0.72 g, 1.45 mmol). Dipivalate **5c** upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6c** as a pale yellow solid (0.43 g, 92%): mp 152–153 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.37 (s, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.50–7.33 (m, 5H), 7.14–1.06 (m, 3H), 3.91 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.1, 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; DEPT 135 (75 MHz, CDCl₃) δ 131.8, 127.6, 127.5, 126.5, 125.1, 124.9, 123.7, 120.2, 113.8, 55.4. Anal. Calcd for C₁₉H₁₄OS: C, 78.59; H, 4.86; S, 11.04. Found: C, 78.27; H, 4.71; S, 11.16.

Preparation of 2-(4-Chlorobenzoyl)phenyl(thiophene-2-yl)methanone (4d). Ring-opening of 3-(4-chlorophenyl)isobenzofuran-1(3*H*)-one with freshly prepared 2-thienyl magnesium bromide followed by acidic workup gave benzo[*c*]furan **3d** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3d** (0.7 g, 2.25 mmol) with LTA (0.99 g, 2.23 mmol) using the procedure similar to that of **4a** furnished **4d** as a brown solid (0.53 g, 72%): mp 124–126 °C; ¹H

NMR (300 MHz, CDCl₃) δ 7.69–7.67 (m, 1H), 7.60–7.51 (m, 6H), 7.42 (d, J = 3.6 Hz, 1H), 7.27 (d, J = 3.6 Hz, 2H), 7.02–7.0 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 194.2, 186.8, 142.7, 138.4, 138.2, 134.4, 133.9, 133.8, 129.9, 129.5, 128.3, 128.1, 127.5, 126.9; HRMS (ES-TOF) Calcd for C₁₈H₁₁³⁵ClO₂S [MNa⁺] 349.0060, found 349.0099; HRMS (ES-TOF) Calcd for C₁₈H₁₁³⁷ClO₂S [MNa⁺] 351.0030, found 351.0029.

Preparation of 4-(4-Chlorophenyl)naphtho[2,3-*b*]thiophene (6d). Reduction of diketone **4d** (0.60 g, 1.84 mmol) in THF–ethanol (20 mL; 1:3) using sodium borohydride (0.35 g, 9.19 mmol) following the procedure similar to that of **6a** gave diol. The crude diol (0.50 g, 1.53 mmol) upon pivaloylation using pivaloyl chloride (0.92 g, 7.62 mmol) and triethylamine (3.09 g, 30.53 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) furnished dipivalate **5d** (0.65 g, 1.37 mmol). Dipivalate **5d** upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:2) gave compound **6d** as a colorless solid (0.28 g, 70%): mp 120–122 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.35 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.48–7.41 (m, 2H), 7.37–7.31 (m, 5H), 7.02–7.0 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 137.9, 137.8, 137.3, 133.6, 132.9, 132.5, 131.1, 129.0, 128.7, 128.1, 127.6, 126.0, 125.2, 123.2, 120.8; DEPT 135 (75 MHz, CDCl₃) δ 132.1, 128.7, 128.1, 127.6, 126.0, 125.2, 123.2, 120.8; HRMS (EI) Calcd for C₁₈H₁₁ClS [M⁺] 294.0270, found 294.0284.

2-(2-Methylbenzoyl)phenyl(thiophene-2-yl)methanone (4e). Ring-opening of 3-(thiophen-2-yl)isobenzofuran-1(3*H*)-one²⁷ with freshly prepared *o*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3e** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3e** (1.0 g, 3.44 mmol) using LTA (1.52 g, 3.44 mmol) adopting the procedure similar to that of **4a** furnished diketone **4e** as a brown solid (0.92 g, 88%): mp 98–100 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.63–7.58 (m, 5H), 7.41–7.39 (m, 1H), 7.32–7.27 (m, 2H), 7.17 (d, J = 7.5 Hz, 1H), 7.11–7.03 (m, 2H), 2.33 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 198.0, 188.8, 144.4, 140.3, 140.0, 139.0, 137.3, 134.8, 134.7, 131.5, 131.3, 131.2, 130.7, 130.5, 130.3, 128.5, 128.0, 125.1, 20.5. Anal. Calcd for C₁₉H₁₄O₂S: C, 74.48; H, 4.61; S, 10.47. Found: C, 74.72; H, 4.25; S, 10.24.

4-*o*-Tolylnaphtho[2,3-*b*]thiophene (6e). Reduction of diketone **4e** (0.92 g, 3.0 mmol) using sodium borohydride (0.57 g, 15.03 mmol) followed by workup led to diol. Dipivaloylation of the diol (0.90 g, 2.90 mmol) using pivaloyl chloride (1.75 g, 14.51 mmol) and triethylamine (5.87 g, 58.06 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5e**. Dipivalate **5e** (1.20 g, 2.51 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6e** as a brown solid (0.47 g, 65%): mp 98–100 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.40 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.6–7.2 (m, 4H), 6.92–6.90 (m, 1H), 1.92 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 138.2, 137.9, 137.7, 137.3, 133.8, 131.1, 130.7, 130.1, 129.1, 129.6, 127.7, 127.6, 126.6, 125.8, 125.1, 125.0, 123.4, 120.3; DEPT 90 (75 MHz, CDCl₃) δ 130.7, 130.1, 127.9, 127.7, 127.6, 126.2, 125.8, 125.1, 125.0, 123.4, 120.3. Anal. Calcd for C₁₉H₁₄S: C, 83.17; H, 5.14; S, 11.69. Found: C, 82.93; H, 5.21; S, 11.76.

2-(3,4-Dimethylbenzoyl)phenyl(thiophene-2-yl)methanone (4f). Ring-opening of 3-(3,4-dimethylphenyl)isobenzofuran-1(3*H*)-one with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3f** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3f** (0.78 g, 2.56 mmol) using LTA (1.13 g, 2.56 mmol) following the procedure similar to that of **4a** furnished diketone **4f** as a pale yellow solid (0.69 g, 85%): mp 126–128 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.74–7.71 (m, 1H), 7.64–7.60 (m, 4H), 7.49–7.42 (m, 3H), 7.12 (d, J = 7.8 Hz, 1H), 7.08–7.05 (m, 1H), 2.28 (s, 3H), 2.22 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.4, 188.4, 144.2, 142.7, 140.0, 136.8, 135.0, 134.9, 134.6, 130.9, 130.4, 130.2, 129.7, 129.6, 129.0, 127.9, 127.8, 20.0, 19.6. Anal. Calcd for C₂₀H₁₆O₂S: C, 74.97; H, 5.03; S, 10.01. Found: C, 74.76; H, 5.40; S, 10.21.

4-(3,4-Dimethylphenyl)naphtho[2,3-*b*]thiophene (6f). Reduction of diketone **4f** (0.74 g, 2.43 mmol) using sodium borohydride (0.46 g, 12.17 mmol) followed by workup led to diol. Dipivaloylation of the diol (0.74 g, 2.40 mmol) using pivaloyl chloride (1.44 g, 11.94 mmol) and triethylamine (4.86 g, 48.02 mmol) in the presence of catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5f**. Dipivalate **5f** (0.99 g, 2.07 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of **6f** as a pale yellow solid (0.80 g, 93%): mp 118–120 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.36 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.80–7.75 (m, 2H), 7.59–7.56 (m, 2H), 7.42–7.23 (m, 2H), 7.15–7.14 (m, 1H), 2.44 (s, 3H), 2.36 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 139.4, 136.3, 135.5, 131.5, 130.9, 130.7, 129.2, 128.2, 127.3, 127.1, 126.6, 126.5, 125.3, 124.7, 20.8, 20.2; DEPT 135 (75 MHz, CDCl₃) δ 129.2, 128.2, 127.1, 126.6, 126.5, 125.4, 125.3, 124.7, 20.8, 20.2; HRMS (EI) Calcd for C₂₀H₁₆S [M⁺] 288.0973, found 288.0978.

(2-(2,4-Dimethylbenzoyl)phenyl)(thiophene-2-yl)methanone (4g). Ring-opening of 3-(2,4-dimethylphenyl)-isobenzofuran-1(3*H*)-one with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3g** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3g** (1.76 g, 5.78 mmol) using LTA (2.56 g, 5.78 mmol) adopting the procedure similar to that of **4a** furnished diketone **4g** as a brown solid (1.69 g, 91%): mp 98–100 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.63–7.54 (m, 5H), 7.40–7.39 (m, 1H), 7.21–7.18 (m, 1H), 7.05–7.02 (m, 1H), 6.99 (s, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 197.9, 188.8, 144.4, 142.2, 140.4, 140.1, 139.4, 134.9, 134.6, 134.5, 132.2, 131.4, 130.9, 130.3, 130.2, 128.5, 128.0, 125.8, 21.4, 20.5; DEPT 135 (75 MHz, CDCl₃) δ 134.9, 134.7, 132.2, 131.4, 130.9, 130.3, 130.2, 128.5, 128.0, 125.8, 21.4, 20.5. Anal. Calcd for C₂₀H₁₆O₂S: C, 74.97; H, 5.03; S, 10.01. Found: C, 74.84; H, 5.03; S, 10.17.

4-(2,4-Dimethylphenyl)naphtho[2,3-*b*]thiophene (6g). Reduction of diketone **4g** (1.50 g, 4.68 mmol) using sodium borohydride (0.94 g, 24.73 mmol) followed by workup led to diol. Dipivaloylation of the diol (1.41 g, 4.57 mmol) using pivaloyl chloride (2.79 g, 22.39 mmol) and triethylamine (9.26 g, 91.51 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5g**. Dipivalate **5g** (1.70 g, 3.57 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6g** as a thick light brown liquid (1.35 g, 82%): ¹H NMR (300 MHz, CDCl₃) δ 8.32 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.39–7.32 (m, 1H), 7.31–7.27 (m, 2H), 7.18–7.12 (m, 2H), 6.90–6.89 (m, 1H), 2.41 (s, 3H), 1.86 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 138.2, 137.8, 137.6, 137.1, 135.4, 134.0, 131.2, 131.0, 130.7, 129.4, 127.7, 126.7, 126.5, 125.2, 125.1, 123.7, 120.3, 21.4, 19.9; DEPT 90 (75 MHz, CDCl₃) δ 131.0, 130.7, 129.4, 128.8, 127.7, 127.2, 126.7, 126.5, 125.9, 125.2, 125.1, 124.4, 123.7, 120.3. Anal. Calcd for C₂₀H₁₆S: C, 83.29; H, 5.59; S, 11.12. Found: C, 82.97; H, 5.41; S, 11.24.

(2-(3,4-Dimethoxybenzoyl)phenyl)(thiophene-2-yl)methanone (4h). Ring-opening of 3-(3,4-dimethoxyphenyl)-isobenzofuran-1(3*H*)-one²⁸ with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3h** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3h** (0.52 g, 1.54 mmol) using LTA (0.62 g, 1.54 mmol) following the procedure similar to that of **4a** furnished diketone **4h** as a brown solid (0.48 g, 89%): mp 128–130 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.75–7.72 (m, 1H), 7.65–7.60 (m, 4H), 7.47–7.46 (m, 1H), 7.33–7.32 (m, 1H), 7.24–7.21 (m, 1H), 7.08–7.05 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 3.94 (s, 3H), 3.77 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 195.3, 188.4, 153.4, 149.0, 144.2, 139.9, 135.0, 134.8, 130.6, 130.4, 130.2, 129.5, 129.0, 128.0, 125.6, 111.1, 109.7, 56.0, 55.9; DEPT 135 (75 MHz, CDCl₃) δ 135.0, 134.8, 130.6, 130.2, 129.5, 129.0, 128.0, 125.6, 111.1, 109.7, 56.0, 55.9. Anal. Calcd for C₂₀H₁₆O₄S: C, 68.16; H, 4.58; S, 9.10. Found: C, 67.84; H, 4.35; S, 8.94.

4-(3,4-Dimethoxyphenyl)naphtho[2,3-*b*]thiophene (6h). Reduction of diketone **4h** (0.46 g, 1.30 mmol) using sodium borohydride (0.24 g, 6.31 mmol) followed by workup led to diol. Dipivaloylation of the diol (0.43 g, 1.20 mmol) using pivaloyl chloride (0.72 g, 34.98 mmol) and triethylamine (2.44 g, 24.11 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5h**. Dipivalate **5h** (0.65 g, 1.24 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate 99:1) led to the isolation of product **6h** as a thick liquid (0.35 g, 92%): ¹H NMR (300 MHz, CDCl₃) δ 8.38 (s, 1H), 7.95–7.7.81 (m, 2H), 7.48–7.39 (m, 3H), 7.16–7.00 (m, 4H), 3.99 (s, 3H), 3.86 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 148.8, 148.5, 138.2, 137.7, 134.3, 131.4, 131.1, 129.4, 127.6, 126.4, 125.1, 125.0, 123.7, 123.0, 120.3, 113.9, 111.1, 56.0; DEPT 135 (75 MHz, CDCl₃) δ 127.5, 126.5, 125.1, 125.0, 123.7, 123.0, 113.9, 111.1, 56.0. Anal. Calcd for C₂₀H₁₆O₂S: C, 74.97; H, 5.03; S, 10.01. Found: C, 75.23; H, 5.18; S, 9.89.

(2-(2-Methoxy-1-naphthoyl)phenyl)(thiophene-2-yl)methanone (4i). Ring-opening of 3-(2-methoxy-1-naphthyl)-isobenzofuran-1(3*H*)-one²⁸ with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3i** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3i** (1.25 g, 3.51 mmol) using LTA (1.55 g, 3.51 mmol) adopting the procedure similar to that of **4a** furnished diketone **4i** as a pale yellow solid (1.21 g, 93%): mp 162–164 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, *J* = 9 Hz, 1H), 7.74 (d, *J* = 6.9 Hz, 1H), 7.65–7.58 (m, 3H), 7.54–7.43 (m, 3H), 7.35–7.29 (m, 3H), 7.20 (d, *J* = 9 Hz, 1H), 6.99–6.96 (m, 1H), 3.74 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.3, 190.0, 155.4, 144.9, 140.5, 138.3, 134.4, 134.2, 132.6, 132.3, 132.0, 131.1, 129.9, 128.7, 128.0, 127.9, 127.8, 127.7, 124.2, 124.1, 121.8, 56.4. Anal. Calcd for C₂₃H₁₆O₃S: C, 74.17; H, 4.33; S, 8.61. Found: C, 74.01; H, 4.35; S, 8.91.

4-(2-Methoxynaphthalen-1-yl)naphtho[2,3-*b*]thiophene (6i). Reduction of diketone **4i** (1.09 g, 2.93 mmol) using sodium borohydride (0.55 g, 14.47 mmol) followed by workup led to diol. Dipivaloylation of the diol (1.0 g, 2.65 mmol) using pivaloyl chloride (1.60 g, 13.29 mmol) and triethylamine (5.38 g, 53.19 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5i**. Dipivalate **5i** (1.30 g, 2.38 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6i** as a colorless solid (1.06 g, 90%): mp 208–210 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.46 (s, 1H), 8.03–7.96 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.48–7.40 (m, 3H), 7.32–7.21 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.73–6.71 (m, 1H), 3.67 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 155.1, 139.1, 137.8, 134.0, 131.3, 130.1, 130.0, 129.1, 128.8, 128.1, 127.9, 127.7, 126.7, 126.4, 125.5, 125.1, 125.0, 123.7, 121.2, 120.7, 113.9, 56.8; DEPT 135 (75 MHz, CDCl₃) δ 130.0, 127.9, 127.8, 127.7, 126.7, 126.4, 125.5, 125.1, 125.0, 123.7, 120.7, 113.9, 56.8; HRMS (EI) Calcd for C₂₃H₁₆O₃S 340.0922, found 340.0920.

2-(Tetraphene-7-yl)thiophene (6j). Oxidation of benzo[*c*]furan **3j** (1.5 g, 4.6 mmol) with LTA (2.04 g, 4.6 mmol) using the procedure similar to that of **4a** furnished diketone **4j** as a colorless solid. Reduction of the crude diketone **4j** (1.56 g, 4.56 mmol) using sodium borohydride (0.87 g, 22.89 mmol) followed by workup gave diol (1.39 g, 3.75 mmol). The dipivaloylation of the diol using pivaloyl chloride (2.42 g, 20.06 mmol) and triethylamine (8.13 g, 80.3 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5j**. Dipivalate **5j** (1.58 g, 3.07 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6j** as a colorless solid (1.01 g, 81%): mp 150–152 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.30 (s, 1H), 8.88 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.83 (t, *J* = 6.9 Hz, 3H), 7.73–7.47 (m, 5H), 7.46–7.31 (m, 1H), 7.2–7.18 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 139.2, 132.4, 131.6, 131.3, 130.6, 130.3, 129.4, 129.3, 128.6, 127.5, 127.3, 127.2, 127.1, 126.7, 126.5, 126.2, 125.7, 125.3, 123.1, 122.9. Anal. Calcd for

$C_{22}H_{14}S$: C, 85.12; H, 4.55; S, 10.33. Found: C, 85.31; H, 4.40; S, 10.27.

(2-(4-Methyl-1-naphthoyl)phenyl)(thiophen-2-yl)methanone (4k). Ring-opening of 3-(4-methyl-1-naphthyl)isobenzofuran-1(3H)-one with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[c]furan **3k** as a fluorescent yellow solid. Oxidative cleavage of the benzo[c]furan **3k** (1.1 g, 3.23 mmol) using LTA (1.43 g, 3.23 mmol) following the procedure similar to that of **4a** furnished diketone **4k** as a dark brown solid (0.95 g, 83%): mp 154–156 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.62–7.60 (m, 1H), 7.55–7.30 (m, 8H), 7.13–7.10 (m, 1H), 6.92–6.89 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 188.8, 144.5, 140.7, 140.6, 134.8, 134.6, 133.5, 132.7, 131.3, 131.2, 131.0, 130.7, 128.6, 128.0, 127.4, 126.4, 126.3, 124.9, 124.1, 20.1; DEPT 135 (75 MHz, $CDCl_3$) δ 134.8, 134.7, 131.3, 131.1, 130.7, 128.6, 128.0, 127.4, 126.3, 124.9, 124.1, 20.1. Anal. Calcd for $C_{23}H_{16}O_2S$: C, 77.50; H, 4.52; S, 9.0. Found: C, 77.31; H, 4.63; S, 8.79.

2-(5-Methyl-tetraphen-7-yl)thiophene (6k). Reduction of diketone **4k** (1.27 g, 3.56 mmol) using sodium borohydride (0.54 g, 14.21 mmol) followed by workup led to diol. Dipivaloylation of the diol (1.13 g, 3.13 mmol) using pivaloyl chloride (1.89 g, 15.67 mmol) and triethylamine (6.35 g, 62.75 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5k**. Dipivalate **5k** (1.39 g, 2.63 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6k** as a pale yellow solid (0.93 g, 92%): mp 190–192 °C; 1H NMR (300 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.79 (d, $J = 7.2$ Hz, 1H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.90 (d, $J = 6.9$ Hz, 1H), 7.71 (d, $J = 8.1$ Hz, 1H), 7.61–7.09 (m, 8H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 133.1, 132.5, 132.0, 130.6, 129.4, 128.6, 128.2, 128.1, 127.3, 127.2, 126.8, 126.6, 126.3, 126.1, 125.3, 124.8, 124.6, 123.3, 122.7, 20.6; DEPT 135 (75 MHz, $CDCl_3$) δ 129.3, 128.5, 127.3, 127.2, 126.7, 126.6, 126.3, 125.3, 124.7, 124.6, 123.3, 122.7, 20.6. Anal. Calcd for $C_{23}H_{16}O_2S$: C, 85.15; H, 4.97; S, 9.88. Found: C, 84.89; H, 5.14; S, 9.72.

Biphenyl-4-yl(2-(thiophen-2-carbonyl)phenyl)methanone (4l). Ring-opening of 3-(biphenyl-4-yl)isobenzofuran-1(3H)-one with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[c]furan **3l** as a fluorescent yellow solid. Oxidative cleavage of the benzo[c]furan **3l** (1.51 g, 4.17 mmol) using LTA (1.84 g, 4.17 mmol) adopting the procedure similar to that of **4a** furnished diketone **4l** as a colorless solid (1.35 g, 85%): mp 150–152 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.72–7.66 (m, 3H), 7.56–7.55 (m, 3H), 7.52–7.49 (m, 3H), 7.43–4.41 (m, 1H), 7.39–7.27 (m, 2H), 7.00–6.97 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 188.3, 145.8, 144.1, 139.9, 139.8, 139.7, 135.9, 135.0, 134.9, 130.6, 130.4, 129.6, 129.2, 128.9, 128.2, 128.0, 127.3, 127.0. Anal. Calcd for $C_{24}H_{16}O_2S$: C, 78.24; H, 4.38; S, 8.70. Found: C, 77.98; H, 4.52; S, 8.93.

2-(2-Phenylanthracen-9-yl)thiophene (6l). Reduction of diketone **4l** (0.42 g, 1.11 mmol) using sodium borohydride (0.21 g, 5.58 mmol) followed by workup led to diol. Dipivaloylation of the diol (0.40 g, 1.05 mmol) using pivaloyl chloride (0.63 g, 5.22 mmol) and triethylamine (2.13 g, 21.04 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5l**. Dipivalate **5l** (0.66 g, 1.20 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6l** as a colorless solid (0.33 g, 93%): mp 206–208 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.99 (d, $J = 8.7$ Hz, 1H), 7.69–7.62 (m, 4H), 7.47–7.27 (m, 8H), 7.13–7.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 140.3, 138.0, 137.8, 134.0, 131.2, 130.5, 129.1, 128.9, 127.7, 127.6, 127.5, 127.2, 127.1, 126.4, 125.2, 125.0, 123.6, 120.5; DEPT 135 (75 MHz, $CDCl_3$) δ 131.2, 130.5, 128.9, 127.7, 127.6, 127.5, 127.2, 127.1, 126.4, 125.2, 125.0, 123.6, 120.5. Anal. Calcd for $C_{24}H_{16}S$: C, 85.68; H, 4.79; S, 9.53; Found: C, 85.39; H, 4.61; S, 9.75.

Preparation of 1-(5-(Thiophen-2-yl)thiophen-2-yl)-3-*p*-tolylisobenzofuran (3m). Ring-opening of 3-(2,2'-bithiophen-5-yl)-

isobenzofuran-1(3H)-one²⁹ (1.0 g, 3.36 mmol) with freshly prepared *p*-tolylmagnesium bromide [prepared from 4-bromotoluene (1.14 g, 6.66 mmol) and Mg (0.20 g, 8.20 mmol)] followed by acidic workup gave benzo[c]furan **3m**³⁰ as a fluorescent thick orange liquid (0.64 g, 52%): 1H NMR (300 MHz, $CDCl_3$) δ 7.75–7.72 (m, 3H), 7.66–7.63 (m, 1H), 7.29 (d, $J = 3.9$ Hz, 1H), 7.22–7.11 (m, 5H), 6.98–6.94 (m, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 139.4, 137.3, 137.0, 135.6, 132.4, 129.7, 128.6, 128.0, 125.3, 125.3, 124.7, 124.5, 124.3, 123.5, 122.5, 121.9, 121.6, 120.3, 119.9, 21.4; DEPT 135 (75 MHz, $CDCl_3$) δ 129.7, 128.0, 125.3, 124.7, 124.5, 124.3, 123.5, 122.5, 120.3, 119.9, 21.4.

(2,2'-Bithiophen-5-yl)(2-(4-methylbenzoyl)phenyl)methanone (4m). Oxidation of benzo[c]furan **3m** (0.5 g, 1.34 mmol) using LTA (0.59 g, 1.34 mmol) following the procedure similar to that of **4a** furnished diketone **4m**³⁰ as a pale yellow solid (0.45 g, 88%): mp 140–142 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.67–7.64 (m, 1H), 7.56–7.50 (m, 5H), 7.30–7.18 (m, 3H), 7.1 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 3.9$ Hz, 1H), 6.98–6.94 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (75 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, 126.6, 125.8, 124.1, 21.7; DEPT 135 (75 MHz, $CDCl_3$) δ 135.9, 130.4, 130.3, 130.0, 129.6, 129.0, 128.9, 128.2, 126.6, 125.8, 124.1, 21.7.

2-(Thiophene-2-yl)-4-*p*-tolylthiophene (6m). Reduction of diketone **4m** (0.75 g, 1.94 mmol) using sodium borohydride (0.29 g, 7.77 mmol) followed by workup led to diol. Dipivaloylation of the diol (0.78 g, 2.0 mmol) using pivaloyl chloride (1.59 g, 10.26 mmol) and triethylamine (1.23 g, 41.05 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5m**. Dipivalate **5m** (0.94 g, 1.68 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6m** as a pale yellow solid (0.57 g, 81%): mp 190–192 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 7.39–7.17 (m, 8H), 7.09 (s, 1H), 6.95 (t, $J = 4.3$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (75 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; HRMS (EI) Calcd for $C_{23}H_{16}S_2$ 356.0693, found 356.0693.

(2-Benzoylphenyl)(*p*-tolyl)methanone (4n). Ring-opening of 3-(4-methylphenyl)isobenzofuran-1(3H)-one³¹ with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[c]furan **3n** as a fluorescent bright yellow solid. Oxidation of the benzo[c]furan **3n** (2.18 g, 7.67 mmol) using LTA (3.32 g, 7.66 mmol) adopting the procedure similar to that of **4a** furnished diketone **4n**²⁶ as a pale yellow solid (2.01 g, 87%): mp 146–147 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, $J = 7.8$ Hz, 2H), 7.61–7.60 (m, 6H), 7.53–7.48 (m, 1H), 7.39–7.34 (m, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 196.3, 143.9, 140.3, 139.9, 137.2, 134.7, 133.0, 130.3, 130.1, 130.0, 129.8, 129.6, 129.5, 129.0, 128.3, 21.7; DEPT 135 (75 MHz, $CDCl_3$) δ 133.0, 130.3, 130.2, 130.0, 129.6, 129.5, 129.1, 128.3, 21.7.

9-*p*-Tolylanthracene (6n). Reduction of diketone **4n** (1.0 g, 3.33 mmol) using sodium borohydride (0.63 g, 16.57 mmol) followed by workup led to diol. Dipivaloylation of the diol (1.0 g, 3.28 mmol) using pivaloyl chloride (1.98 g, 16.44 mmol) and triethylamine (6.65 g, 65.78 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5n**. Dipivalate **5n** (1.30 g, 2.75 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6n** as a pale yellow solid (0.86 g, 89%): mp 108–110 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.03 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.7$ Hz, 2H), 7.45–7.30 (m, 8H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 137.1, 135.7, 131.4, 131.1, 130.3, 129.1, 128.3, 127.0, 126.4, 125.2, 125.0, 21.4; DEPT 135 (75 MHz, $CDCl_3$) δ 131.1, 129.0, 128.3, 127.0, 126.3, 125.2, 125.0. Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.58; H, 5.96.

(2-Benzoylphenyl)(4-methoxyphenyl)methanone (4o). Ring-opening of 3-(phenyl)isobenzofuran-1(3H)-one with freshly prepared

p-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3o** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3o** (2.41 g, 8.03 mmol) using LTA (3.56 g, 8.03 mmol) following the procedure similar to that of **4a** furnished diketone **4o** as a pale yellow solid (2.22 g, 87%): mp 120–121 °C (118.6–119.1 °C); ¹H NMR (300 MHz, CDCl₃) δ 7.72–7.67 (m, 4H), 7.64–7.62 (m, 4H), 7.55–7.50 (m, 1H), 7.41–7.36 (m, 2H), 6.86–6.85 (m, 2H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.7, 195.3, 163.6, 140.4, 139.8, 137.3, 133.0, 132.2, 130.3, 130.2, 130.0, 129.8, 129.6, 129.3, 128.3, 113.6, 55.5.

9-(4-Methoxyphenyl)anthracene (6o). Reduction of diketone **4o** (1.62 g, 4.18 mmol) using sodium borohydride (0.97 g, 25.52 mmol) followed by workup led to diol. Dipivaloylation of the diol (1.60 g, 5.0 mmol) using pivaloyl chloride (3.01 g, 25 mmol) and triethylamine (10.11 g, 100.0 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5o**. Dipivalate **5o** (1.91 g, 3.91 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6o** as a pale yellow solid (1.33 g, 94%): mp 148–150 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.4 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.45–7.30 (m, 6H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.06, 136.9, 132.2, 131.5, 130.9, 130.6, 128.4, 127.0, 126.4, 125.3, 125.1, 55.4; DEPT 135 (75 MHz, CDCl₃) δ 132.3, 128.3, 126.9, 126.4, 125.2, 125.1, 113.8, 55.4. Anal. Calcd for C₂₁H₁₆O: C, 88.70; H, 5.67. Found: C, 88.49; H, 5.75.

(2-(4-Methoxybenzoyl)phenyl(*p*-tolyl)methanone (4p). Ring-opening of 3-(4-methylphenyl)isobenzofuran-1(3*H*)-one³¹ with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3p** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3p** (3 g, 9.55 mmol) using LTA (4.23 g, 9.54 mmol) following the procedure similar to that of **4a** gave diketone **4p**²⁶ as a colorless solid (2.8 g, 88%): mp 165–167 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.68 (d, *J* = 9 Hz, 2H), 7.61–7.58 (m, 6H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.4, 195.3, 163.5, 143.8, 140.3, 140.0, 134.8, 132.2, 130.3, 130.1, 130.0, 129.9, 129.5, 129.3, 129.0, 113.6, 55.5, 21.7; DEPT 135 (75 MHz, CDCl₃) δ 132.3, 130.1, 130.0, 130.0, 129.5, 129.3, 129.0, 113.6, 55.3, 21.7.

9-(4-Methoxyphenyl)-2-methylanthracene (6p). Reduction of diketone **4p** (1.6 g, 4.84 mmol) using sodium borohydride (0.92 g, 24.21 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.44 g, 4.31 mmol) using pivaloyl chloride (1.59 g, 13.18 mmol) and triethylamine (5.35 g, 52.8 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5p**. Dipivalate **5p** (1.78 g, 3.54 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) led to the isolation of product **6p** as a colorless solid (1.1 g, 86%): mp 136–138 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.40 (s, 1H), 8.01–7.90 (m, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.42–7.26 (m, 7H), 7.12–7.09 (m, 2H), 3.96 (s, 3H), 2.40 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 158.9, 135.8, 134.9, 132.3, 131.0, 130.9, 130.7, 130.1, 129.2, 128.3, 128.2, 127.9, 126.8, 126.3, 126.1, 125.1, 125.0, 124.6, 113.8, 55.3, 22.3; HRMS (EI) Calcd for C₂₂H₁₈O [M⁺] 298.1358, found 298.1354.

(2-Benzoylphenyl)(3,4-dimethylphenyl)methanone (4q). Ring-opening of 3-(3,4-dimethylphenyl)isobenzofuran-1(3*H*)-one with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3q** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3q** (1.04 g, 3.48 mmol) using LTA (1.54 g, 3.47 mmol) following the procedure similar to that of **4a** furnished diketone **4q**^{32a} as a colorless solid (0.98 g, 90%): mp 132–134 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.84 (d, *J* = 7.2 Hz, 2H), 7.62–7.58 (m, 4H), 7.53–7.48 (m, 2H), 7.44–7.34 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 1H), 2.27 (s, 3H), 2.21 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.6, 196.5, 142.7, 140.4, 139.9, 137.3, 136.8, 135.0, 132.9, 130.9, 130.3, 130.1, 129.8, 129.6, 129.6, 128.3, 127.8, 20.0, 19.7.

9-(3,4-Dimethylphenyl)anthracene (6q). Reduction of diketone **4q** (0.83 g, 2.64 mmol) using sodium borohydride (0.50 g, 13.15

mmol) followed by workup gave diol. Dipivaloylation of the diol (0.79 g, 2.48 mmol) using pivaloyl chloride (1.49 g, 12.35 mmol) and triethylamine (5.02 g, 49.60 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5q**. Dipivalate **5q** (0.98 g, 2.01 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6q** as a colorless solid (0.62 g, 86%): mp 166–168 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.41 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.80 (s, 1H), 7.70–7.59 (m, 4H), 7.51–7.44 (m, 4H), 7.38–7.33 (m, 1H), 2.51 (s, 3H), 2.40 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.2, 135.7, 135.6, 135.3, 131.3, 131.1, 130.9, 129.9, 129.6, 128.4, 127.9, 127.3, 127.2, 126.8, 125.6, 125.3, 124.8, 124.6, 20.7, 20.3. DEPT 135 (75 MHz, CDCl₃) δ 131.3, 128.4, 128.3, 127.3, 126.8, 125.3, 124.8, 124.6, 20.7, 20.3. Anal. Calcd for C₂₂H₁₈: C, 93.57; H, 6.43. Found: C, 93.34; H, 6.31.

(2-(3,4-Dimethylbenzoyl)phenyl(*p*-tolyl)methanone (4r). Ring-opening of 3-(3,4-dimethylphenyl)isobenzofuran-1(3*H*)-one with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup afforded benzo[*c*]furan **3r** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3r** (1.44 g, 4.60 mmol) using LTA (2.04 g, 4.6 mmol) following the procedure similar to that of **4a** gave diketone **4r** as a pale yellow solid (1.42 g, 94%): mp 168–170 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.60–7.58 (m, 6H), 7.48 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.17–7.10 (m, 3H), 2.68 (s, 3H), 2.37 (s, 3H), 2.21 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.5, 196.3, 143.8, 142.6, 140.3, 140.2, 136.7, 135.1, 134.8, 130.9, 130.1, 130.0, 129.6, 129.6, 129.0, 127.8, 21.7, 20.0, 19.6. Anal. Calcd for C₂₃H₂₀O₂: C, 84.12; H, 6.14. Found: C, 83.96; H, 6.31.

9-(3,4-Dimethylphenyl)-2-methylanthracene (6r). Reduction of diketone **4r** (1.46 g, 4.45 mmol) using sodium borohydride (0.84 g, 22.16 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.29 g, 3.88 mmol) using pivaloyl chloride (2.34 g, 19.40 mmol) and triethylamine (7.86 g, 77.67 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5r**. Dipivalate **5r** (1.48 g, 2.96 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6r** as a colorless solid (1.06 g, 92%): mp 100–102 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.31 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.49 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.41–7.24 (m, 7H), 2.51 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 136.9, 136.0, 135.8, 135.5, 135.3, 131.3, 131.2, 131.1, 130.9, 129.7, 129.1, 128.6, 128.2, 127.2, 126.9, 125.6, 125.0, 124.7, 124.5, 21.4, 20.7, 20.2; DEPT 135 (75 MHz, CDCl₃) δ 131.1, 129.1, 128.3, 127.2, 126.9, 125.6, 125.0, 124.7, 124.5, 21.4, 20.7, 20.2; HRMS (EI) Calcd for C₂₃H₂₀ [M⁺] 296.1565, found 296.1560.

(2-(3,4-Dimethoxybenzoyl)phenyl(*p*-tolyl)methanone (4s). Ring-opening of 3-(3,4-dimethoxyphenyl)isobenzofuran-1(3*H*)-one²⁸ with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3s** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3s** (2.56 g, 7.44 mmol) using LTA (3.3 g, 7.44 mmol) following the procedure similar to that of **4a** furnished diketone **4s** as a colorless solid (2.4 g, 90%): mp 162–164 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.60–7.55 (m, 6H), 7.28–7.27 (m, 1H), 7.22–7.15 (m, 3H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.3, 195.4, 153.4, 149.0, 143.8, 140.2, 139.9, 134.8, 130.5, 130.3, 130.1, 129.5, 129.3, 129.0, 125.6, 111.1, 109.7, 56.1, 55.9, 21.7. Anal. Calcd for C₂₃H₂₀O₄: C, 76.65; H, 5.59. Found: C, 76.80; H, 5.45.

9-(3,4-Dimethoxyphenyl)-2-methylanthracene (6s). Reduction of diketone **4s** (0.56 g, 1.55 mmol) using sodium borohydride (0.29 g, 7.63 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.51 g, 1.40 mmol) using pivaloyl chloride (0.84 g, 6.96 mmol) and triethylamine (2.83 g, 27.96 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5s**. Dipivalate **5s** (0.76 g, 1.42 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and silica gel column chromatographic purification (hexane–ethyl acetate, 99:1) gave compound **6s** as a colorless solid (0.43 g,

96%): mp 173–175 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.24 (s, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.39–7.35 (m, 3H), 7.31–7.24 (m, 3H), 7.20 (s, 1H), 6.87 (s, 1H), 4.02 (s, 3H), 3.75 (s, 3H), 2.50 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 149.8, 149.7, 137.0, 136.0, 135.0, 131.0, 130.7, 129.5, 129.2, 127.8, 127.1, 126.5, 124.5, 124.3, 124.0, 105.0, 104.0, 55.9, 55.6, 21.4; DEPT 135 (75 MHz, CDCl_3) δ 131.0, 129.2, 127.8, 126.5, 124.5, 124.3, 124.0, 105.0, 104.0, 56.0, 55.6, 21.4; HRMS (EI) Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2$ [M^+] 328.1463, found 328.1462.

(2-(3,4-Dimethylbenzoyl)phenyl(4-methoxyphenyl)methanone (4t). Ring-opening of 3-(3,4-dimethylphenyl)isobenzofuran-1(3H)-one with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3t** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3t** (1.44 g, 4.39 mmol) using LTA (1.94 g, 4.39 mmol) following the procedure similar to that of **4a** afforded diketone **4t**³⁰ as a colorless solid (1.44 g, 96%): mp 132–134 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.72–7.69 (m, 3H), 7.59–7.50 (m, 5H), 7.45–7.43 (m, 2H), 7.12 (d, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 8.7$ Hz, 2H), 3.84 (s, 3H), 2.28 (s, 3H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.6, 195.3, 163.5, 142.6, 140.3, 140.2, 136.7, 135.1, 132.2, 130.9, 130.3, 130.0, 129.9, 129.5, 129.3, 127.8, 113.6, 55.5, 20.0, 19.6; DEPT 135 (75 MHz, CDCl_3) δ 132.2, 130.9, 130.0, 129.9, 129.5, 129.3, 127.8, 113.6, 55.5, 20.0, 19.7.

9-(3,4-Dimethylphenyl)-2-methoxyanthracene (6t). Reduction of diketone **4s** (0.41 g, 1.19 mmol) using sodium borohydride (0.18 g, 4.76 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.41 g, 1.17 mmol) using pivaloyl chloride (0.71 g, 5.95 mmol) and triethylamine (2.41 g, 23.83 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5t**. Dipivalate **5t** (0.69 g, 1.34 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and silica gel column chromatographic purification (hexane–ethyl acetate, 99:1) gave compound **6t** as a colorless solid (0.33 g, 88%): mp 158–160 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.18 (s, 1H), 7.86–7.81 (m, 1H), 7.62 (s, 1H), 7.86 (t, $J = 8.7$ Hz, 1H), 7.32–7.14 (m, 5H), 7.01–6.95 (m, 2H), 3.80 (s, 3H), 2.31 (s, 3H), 2.20 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 158.9, 135.5, 135.2, 132.3, 131.2, 131.1, 130.9, 130.2, 129.9, 128.3, 127.2, 126.8, 125.6, 125.0, 124.7, 124.5, 113.8, 55.3, 20.7, 20.2; DEPT 135 (75 MHz, CDCl_3) δ 132.3, 128.2, 127.2, 126.8, 125.6, 125.0, 124.7, 124.5, 113.8, 55.3, 20.7, 20.2. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}$: C, 88.43; H, 6.45. Found: C, 88.27; H, 6.41.

Biphenyl-4-yl(4-methoxybenzoyl)phenyl)methanone (4u). Ring-opening of 3-(biphenyl-4-yl)isobenzofuran-1(3H)-one with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3u** as a fluorescent yellow solid. Oxidative ring cleavage of the benzo[*c*]furan **3u** (1.5 g, 4.15 mmol) using LTA (1.84 g, 4.15 mmol) adopting the procedure similar to that of **4a** furnished diketone **4u**^{32b} as a colorless solid (1.50 g, 96%): mp 163–165 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.70 (d, $J = 8.4$ Hz, 1H), 7.56–7.49 (m, 10H), 7.38–7.27 (m, 3H), 7.16–7.08 (m, 2H), 2.29 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.3, 145.7, 143.9, 140.2, 140.1, 139.9, 136.0, 135.0, 130.4, 130.3, 130.1, 129.7, 129.5, 129.1, 128.9, 128.2, 127.3, 127.0, 21.7; DEPT 135 (75 MHz, CDCl_3) δ 130.4, 130.3, 130.1, 129.7, 129.5, 129.1, 128.9, 128.2, 127.3, 127.0, 21.7.

2-Phenyl-9-*p*-tolylanthracene (6u). Reduction of diketone **4u** (1.10 g, 2.91 mmol) using sodium borohydride (0.44 g, 11.67 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.0 g, 2.62 mmol) using pivaloyl chloride (1.58 g, 13.10 mmol) and triethylamine (5.31 g, 52.47 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5u**. Dipivalate **5u** (1.28 g, 2.33 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and silica gel column chromatographic purification (hexane–ethyl acetate, 99:1) gave compound **6u** as a pale yellow solid (0.86 g, 95%): mp 197–198 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.50 (s, 1H), 8.07 (d, $J = 8.1$ Hz, 1H), 8.0 (d, $J = 7.8$ Hz, 1H), 7.87–7.81 (m, 4H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.59–7.28 (m, 8H), 2.47 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 140.9, 140.0, 128.0, 135.6, 135.1, 131.7, 130.9, 130.4, 130.0, 128.9, 128.4, 128.2, 128.0, 127.4, 127.1, 127.0, 126.7, 126.4, 125.3, 124.9, 124.7, 22.2; DEPT 135 (75 MHz, CDCl_3) δ 131.7, 128.9, 128.4, 128.2,

128.0, 127.4, 127.1, 127.0, 126.7, 126.4, 125.4, 124.9, 124.7, 22.3. Anal. Calcd for $\text{C}_{27}\text{H}_{20}$: C, 94.15; H, 5.85. Found: C, 94.37; H, 5.78.

(2-Benzoylphenyl)(biphenyl-4-yl)methanone (4v). Ring-opening of 3-(biphenyl-4-yl)isobenzofuran-1(3H)-one with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3v** as a fluorescent yellow solid. Oxidative cleavage of the benzo[*c*]furan **3v** (1.43 g, 4.12 mmol) using LTA (1.82 g, 4.12 mmol) adopting the procedure similar to that of **4a** furnished diketone **4v** as a pale yellow solid (1.27 g, 85%): mp 152–154 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.70 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 7.2$ Hz, 2H), 7.56–7.55 (m, 3H), 7.53–5.0 (m, 4H), 7.44–7.39 (m, 2H), 7.36–7.27 (m, 5H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 196.6, 196.2, 145.7, 140.2, 139.9, 139.0, 137.2, 135.9, 133.0, 130.4, 130.3, 130.0, 129.8, 129.6, 128.9, 128.8, 128.4, 128.2, 127.3, 127.2, 127.0; DEPT 135 (75 MHz, CDCl_3) δ 130.4, 130.3, 130.1, 129.7, 129.5, 129.1, 128.9, 128.2, 127.3, 127.0. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{O}_2$: C, 86.16; H, 5.01. Found: C, 85.87; H, 5.29.

9-(Biphenyl-4-yl)anthracene (6v). Reduction of diketone **4v** (0.90 g, 2.47 mmol) using sodium borohydride (0.47 g, 12.39 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.86 g, 2.34 mmol) using pivaloyl chloride (1.41 g, 11.69 mmol) and triethylamine (4.74 g, 46.86 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5v**. Dipivalate **5v** (1.04 g, 1.94 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6v** as a colorless solid (0.72 g, 94%): mp 212–213 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.42 (s, 1H), 7.96 (d, $J = 8.1$ Hz, 2H), 7.74–7.66 (m, 6H), 7.45–7.26 (m, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 140.8, 140.2, 137.7, 136.6, 131.7, 131.4, 130.2, 128.9, 127.4, 127.3, 127.0, 126.8, 126.6, 125.4, 125.1; DEPT 135 (75 MHz, CDCl_3) δ 131.7, 128.9, 128.4, 127.4, 127.3, 127.0, 126.8, 126.6, 125.4, 125.1. Anal. Calcd for $\text{C}_{26}\text{H}_{18}$: C, 94.51; H, 5.49. Found: C, 94.62; H, 5.26.

(2-(2-Methylbenzoyl)phenyl)(*p*-tolyl)methanone (4w). Ring-opening of 3-(4-methylphenyl)isobenzofuran-1(3H)-one²⁸ with freshly prepared *o*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3w** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **3w** (2.36 g, 7.91 mmol) using LTA (3.51 g, 7.91 mmol) following the procedure similar to that of **4a** afforded diketone **4w**²⁶ as a colorless solid (2.12 g, 86%): mp 86–88 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.45–7.43 (m, 2H), 7.36–7.25 (m, 6H), 7.14–7.13 (m, 2H), 7.06–7.03 (m, 2H), 2.39 (s, 6H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 190.1, 146.9, 142.7, 138.3, 136.5, 136.4, 136.3, 131.1, 130.3, 128.3, 128.0, 126.7, 125.9, 125.2, 124.2, 19.7.

1-Methyl-10-*p*-tolylanthracene (6w). Reduction of diketone **4w** (1.0 g, 3.18 mmol) using sodium borohydride (0.60 g, 15.92 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.99 g, 3.11 mmol) using pivaloyl chloride (1.87 g, 15.58 mmol) and triethylamine (6.30 g, 62.26 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5w**. Dipivalate **5w** (1.22 g, 2.51 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6w** as a colorless solid (0.80 g, 91%): mp 142–143 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.6 (s, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.7$ Hz, 1H), 7.55 (d, $J = 8.7$ Hz, 1H), 7.46–7.18 (m, 8H), 2.8 (s, 3H), 2.5 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 137.7, 137.0, 136.1, 134.1, 131.2, 131.0, 130.5, 130.1, 129.0, 128.7, 126.9, 125.6, 125.5, 125.3, 125.1, 125.0, 122.9, 21.4, 20.1; DEPT 135 (75 MHz, CDCl_3) δ 131.2, 129.0, 128.8, 126.9, 125.6, 125.5, 125.3, 125.1, 125.0, 122.9, 21.4, 20.1; HRMS (EI) Calcd for $\text{C}_{22}\text{H}_{18}$ [M^+] 282.1408, found 282.1405.

(2-Benzoylphenyl)(2-methoxynaphthalen-1-yl)methanone (4x). Ring-opening of 3-(2-methoxy-1-naphthyl)isobenzofuran-1(3H)-one with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3x** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3x** (1.54 g, 4.23 mmol) using LTA (1.87 g, 4.23 mmol) adopting the procedure similar to that of **4a** furnished diketone **4x**^{32c} as a pale yellow solid (1.21 g, 88%): mp 164–166 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.87 (d, $J = 9$ Hz, 1H), 7.77–

7.75 (m, 2H), 7.64–7.59 (m, 1H), 7.55–7.52 (m, 2H), 7.47–7.42 (m, 3H), 7.37–7.28 (m, 5H), 7.19 (d, $J = 9$ Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.3, 195.7, 154.3, 140.7, 137.3, 136.6, 132.1, 131.9, 131.5, 131.2, 128.8, 128.5, 128.0, 127.4, 127.2, 126.9, 123.4, 123.3, 121.0, 112.1, 55.6.

9-(2-Methoxynaphthalen-1-yl)anthracene (6x). Reduction of diketone **4x** (1.6 g, 4.87 mmol) using sodium borohydride (0.92 g, 24.39 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.67 g, 5.03 mmol) using pivaloyl chloride (3.03 g, 25.12 mmol) and triethylamine (10.1 g, 99.8 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5x**. Dipivalate **5x** (1.90 g, 3.80 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6x** as a pale yellow solid (1.58 g, 95%): mp 222–224 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.55 (s, 1H), 8.07 (d, $J = 7.8$ Hz, 3H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.50 (d, $J = 9$ Hz, 1H), 7.44–7.36 (m, 5H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 8.7$ Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 155.4, 134.6, 131.6, 131.5, 131.0, 129.9, 129.2, 128.6, 127.9, 126.8, 126.6, 125.5, 125.1, 123.7, 121.1, 114.0, 56.8; DEPT 135 (75 MHz, CDCl_3) δ 129.0, 128.6, 127.9, 126.8, 126.6, 125.6, 125.5, 125.1, 123.7, 114.0, 56.8; HRMS (EI) Calcd for $\text{C}_{25}\text{H}_{18}\text{O}$ [M^+] 334.1358, found 334.1354.

(2-(2-Methoxy-1-naphthoyl)phenyl)(o-tolyl)methanone (4y). Ring-opening of 3-(2-methoxy-1-naphthyl)isobenzofuran-1(3H)-one with freshly prepared *o*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3y** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3y** (2.69 g, 7.39 mmol) using LTA (3.27 g, 7.39 mmol) following the procedure similar to that of **4a** furnished diketone **4y** as a colorless solid (2.49 g, 89%): mp 136–138 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.80 (d, $J = 9$ Hz, 1H), 7.68–7.65 (m, 1H), 7.58–7.53 (m, 1H), 7.49–7.46 (m, 1H), 7.41–7.34 (m, 2H), 7.28–7.24 (m, 1H), 7.23–7.20 (m, 2H), 7.17–7.16 (m, 1H), 7.14–7.11 (m, 3H), 7.05–7.01 (m, 1H), 3.62 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.5, 196.7, 155.1, 142.7, 138.6, 135.1, 133.9, 133.4, 132.3, 131.8, 131.2, 130.9, 129.1, 128.2, 128.0, 127.9, 127.6, 126.9, 126.4, 124.0, 123.9, 123.4, 112.9, 56.4, 21.3; DEPT 135 (75 MHz, CDCl_3) δ 132.3, 131.2, 130.9, 129.1, 128.2, 128.0, 127.9, 127.6, 126.9, 126.4, 124.1, 123.9, 123.4, 112.8, 56.4, 21.3. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_3$: C, 82.08; H, 5.30. Found: C, 82.35; H, 5.24.

10-(2-Methoxynaphthalen-1-yl)-1-methylanthracene (6y). Reduction of diketone **4y** (1.7 g, 4.47 mmol) using sodium borohydride (0.68 g, 17.89 mmol) followed by workup afforded diol. Dipivaloylation of the diol (1.65 g, 4.29 mmol) using pivaloyl chloride (2.59 g, 21.47 mmol) and triethylamine (8.69 g, 85.87 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5y** as a thick colorless liquid. Dipivalate **5y** (1.92 g, 3.47 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6y** as a colorless solid (1.32 g, 89%): mp 236–238 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.62 (s, 1H), 8.05–7.97 (m, 2H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 7.35 (t, $J = 7.3$ Hz, 1H), 7.29–6.99 (m, 8H), 6.71 (d, $J = 8.4$ Hz, 1H), 3.51 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 155.3, 134.6, 134.4, 132.0, 131.4, 131.2, 131.1, 130.7, 129.8, 129.1, 128.9, 127.8, 126.6, 126.4, 125.6, 125.5, 125.4, 125.2, 125.1, 123.6, 123.2, 121.5, 114.0, 20.0; DEPT 90 (75 MHz, CDCl_3) δ 129.8, 128.9, 127.8, 126.6, 126.4, 125.6, 125.5, 125.4, 125.2, 125.1, 123.6, 123.2, 113.9. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}$: C, 89.62; H, 5.79. Found: C, 89.31; H, 5.63.

(2-(2-Methoxy-1-naphthoyl)phenyl)(*p*-tolyl)methanone (4z). Ring-opening of 3-(2-methoxy-1-naphthyl)isobenzofuran-1(3H)-one with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **3z** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **3z** (1 g, 2.74 mmol) using LTA (1.2 g, 2.7 mmol) adopting the procedure similar to that of **4a** furnished diketone **4z** as a colorless solid (0.98 g, 96%): mp 138–140 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.80 (d, $J = 9.0$ Hz, 1H), 7.67–7.64 (m, 1H), 7.56–7.54 (m, 3H), 7.51–7.46 (m, 2H), 7.38–7.33 (m, 2H), 7.25–7.22 (m, 2H),

7.17–7.11 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 3.68 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.7, 196.4, 155.1, 143.6, 141.5, 138.1, 134.9, 132.6, 132.3, 131.9, 131.1, 129.5, 129.4, 128.9, 128.7, 128.1, 127.9, 127.6, 124.1, 124.0, 121.8, 112.8, 56.4, 21.7. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_3$: C, 82.08; H, 5.30. Found: C, 82.35; H, 5.36.

9-(2-Methoxynaphthalen-1-yl)-2-methylanthracene (6z). Reduction of diketone **4z** (0.85 g, 2.23 mmol) using sodium borohydride (0.42 g, 11.05 mmol) followed by workup afforded diol. Dipivaloylation of the diol (0.71 g, 1.84 mmol) using pivaloyl chloride (1.12 g, 9.28 mmol) and triethylamine (3.74 g, 36.96 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **5z** as a thick liquid. Dipivalate **5z** (0.92 g, 1.66 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **6z** as a pale yellow solid (0.56 g, 88%): mp 184–186 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.49 (s, 1H), 8.06–8.01 (m, 2H), 7.69 (d, $J = 8.9$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.51–7.47 (m, 1H), 7.40–7.34 (m, 1H), 7.32–7.23 (m, 3H), 7.20–7.15 (m, 1H), 7.11–7.06 (m, 2H), 6.82–6.80 (m, 1H), 3.63 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 155.4, 135.1, 134.6, 131.3, 131.2, 130.4, 130.3, 129.8, 129.2, 128.6, 128.5, 128.1, 127.9, 126.8, 126.6, 126.5, 125.7, 125.3, 125.0, 124.7, 124.6, 123.7, 56.8, 22.2; DEPT 135 (75 MHz, CDCl_3) δ 129.8, 128.6, 128.4, 128.1, 127.9, 126.6, 126.5, 126.5, 125.7, 125.3, 125.0, 124.7, 123.7, 123.7, 56.8, 22.2. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}$: C, 89.62; H, 5.79. Found: C, 89.39; H, 5.85.

(2-(1-Naphthoyl)phenyl)(phenyl)methanone (11a). Ring-opening of 3-(phenyl)isobenzofuran-1(3H)-one with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10a** as a fluorescent bright yellow solid. Oxidative cleavage of the benzo[*c*]furan **10a** (1 g, 3.44 mmol) using LTA (1.52 g, 3.42 mmol) following the procedure similar to that of **4a** furnished diketone **11a**²⁶ as a pale yellow solid (0.86 g, 85%): mp 128–130 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.33–8.30 (m, 1H), 7.96 (d, $J = 8.1$ Hz, 1H), 7.86–7.83 (m, 1H), 7.83–7.64 (m, 5H), 7.61–7.57 (m, 3H), 7.51–7.42 (m, 3H), 7.37–7.28 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.5, 197.0, 141.1, 140.5, 137.3, 135.2, 133.6, 133.1, 132.8, 131.4, 131.0, 130.8, 130.5, 129.5, 129.0, 128.3, 128.1, 127.8, 126.5, 125.8, 124.0.

7-Phenyltetraphene (13a). Reduction of diketone **11a** (1.0 g, 2.93 mmol) using sodium borohydride (0.56 g, 14.88 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.02 g, 3.0 mmol) using pivaloyl chloride (1.80 g, 15.0 mmol) and triethylamine (6.07 g, 60.0 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12a** as a thick liquid. Dipivalate **12a** (1.26 g, 2.48 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13a** as a yellow solid (0.80 g, 88%): mp 184–186 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.20 (s, 1H), 8.86 (d, $J = 7.8$ Hz, 1H), 8.14 (d, $J = 8.1$ Hz, 1H), 7.70–7.50 (m, 7H), 7.47–7.45 (m, 2H), 7.43–4.40 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.0, 137.6, 131.6, 131.5, 131.2, 130.9, 130.5, 128.7, 128.6, 1128.5, 128.4, 127.5, 127.1, 127.0, 126.9, 126.7, 125.8, 125.6, 125.5, 123.1, 121.6; DEPT 90 (75 MHz, CDCl_3) δ 128.6, 128.5, 128.4, 127.5, 127.2, 126.9, 126.8, 126.7, 125.8, 125.6, 125.5. Anal. Calcd for $\text{C}_{24}\text{H}_{16}$: C, 94.70; H, 5.30. Found: C, 94.29; H, 5.26.

(2-(1-Naphthoyl)phenyl)(*p*-tolyl)methanone (11b). Ring-opening of 3-(4-methylphenyl)isobenzofuran-1(3H)-one²⁸ with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10b** as a fluorescent bright yellow solid. Oxidation of the benzo[*c*]furan **10b** (0.75 g, 2.24 mmol) using LTA (0.99 g, 2.23 mmol) adopting the procedure similar to that of **4a** furnished diketone **11b** as a pale yellow solid (0.65 g, 85%): mp 139–140 °C (139.7–140.4 °C);²⁶ ^1H NMR (300 MHz, CDCl_3) δ 8.34 (d, $J = 8.4$ Hz, 1H), 7.99–7.94 (m, 2H), 7.84 (d, $J = 8.7$ Hz, 1H), 7.73–7.28 (m, 9H), 7.08 (d, $J = 7.8$ Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.5, 196.7, 143.9, 141.2, 140.5, 135.3, 134.9, 133.6, 132.9, 131.5, 130.9, 130.8, 130.5, 130.1, 129.6, 129.0, 128.1, 127.5, 126.4, 125.8, 125.8, 124.0, 21.6.

7-p-Tolyltetraphene (13b). Reduction of diketone **11b** (0.95 g, 2.79 mmol) using sodium borohydride (0.53 g, 13.94 mmol) followed by workup afforded diol. Dipivaloylation of the diol (0.78 g, 2.26 mmol) using pivaloyl chloride (1.36 g, 11.27 mmol) and triethylamine (4.58 g, 45.20 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12b** as a thick liquid. Dipivalate **12b** (1.03 g, 2.01 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13b** as a colorless solid (0.63 g, 91%): mp 114–116 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.24 (s, 1H), 8.88 (d, $J = 8.1$ Hz, 1H), 8.15 (d, $J = 8.1$ Hz, 1H), 7.81–7.30 (m, 12H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.7, 137.1, 135.9, 131.6, 131.5, 131.1, 131, 130.5, 129.1, 128.8, 128.6, 128.5, 127.1, 126.9, 126.8, 126.7, 125.7, 125.6, 125.5, 123.1, 121.4, 21.4; DEPT 135 (75 MHz, CDCl_3) δ 131.1, 129.1, 128.6, 128.5, 127.1, 126.9, 126.8, 126.7, 125.7, 125.6, 125.4, 123.1, 123.1, 21.4; HRMS (EI) Calcd for $\text{C}_{25}\text{H}_{18}$ [M^+] 318.1409, found 318.1409.

(2-(1-Naphthoyl)phenyl)(2,4-dimethylphenyl)methanone (11c). Ring-opening of 3-(2,4-dimethylphenyl)isobenzofuran-1(3H)-one with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10c** as a fluorescent yellow solid. Oxidative cleavage of the benzo[*c*]furan **7c** (2.43 g, 6.98 mmol) using LTA (3.1 g, 6.99 mmol) adopting the procedure similar to that of **4a** furnished diketone **11c** as a pale yellow solid (2.26 g, 89%): mp 88–90 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.22 (d, $J = 8.4$ Hz, 1H), 7.91–7.79 (m, 3H), 7.62–7.60 (m, 4H), 7.50–7.31 (m, 3H), 7.13 (d, $J = 7.8$ Hz, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.70 (s, 1H), 2.33 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 198.0, 197.9, 142.2, 141.6, 141.1, 139.9, 135.4, 133.8, 133.0, 132.5, 131.6, 131.1, 130.9, 130.6, 130.2, 129.7, 128.0, 127.5, 126.5, 126.30, 125.7, 124.0, 21.3, 20.4; DEPT 135 (75 MHz, CDCl_3) δ 133.0, 132.5, 131.7, 131.1, 131.0, 130.2, 129.7, 128.0, 127.5, 126.5, 126.0, 125.7, 124.0, 21.3, 20.4. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2$: C, 85.69; H, 5.53. Found: C, 85.38; H, 5.32.

7-(2,4-Dimethylphenyl)tetraphene (13c). Reduction of diketone **11c** (1.69 g, 4.18 mmol) using sodium borohydride (0.88 g, 21.0 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.69 g, 4.59 mmol) using pivaloyl chloride (2.76 g, 22.88 mmol) and triethylamine (9.29 g, 91.80 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12c** as a thick liquid. Dipivalate **12c** (1.86 g, 3.47 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13c** as a colorless solid (1.25 g, 81%): mp 97–98 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.24 (s, 1H), 8.89 (d, $J = 8.1$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 7.5$ Hz, 1H), 7.68–7.59 (m, 2H), 7.55–7.47 (m, 3H), 7.42–7.35 (m, 2H), 7.26–7.14 (m, 3H), 2.49 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.6, 137.4, 137.0, 135.2, 131.7, 131.6, 131.0, 130.8, 128.7, 128.6, 128.5, 127.1, 126.9, 126.8, 126.6, 126.4, 125.89, 125.5, 125.4, 123.0, 121.3, 21.3, 19.7; DEPT 135 (75 MHz, CDCl_3) δ 131.0, 130.8, 128.7, 128.5, 127.1, 127.0, 126.9, 126.6, 126.5, 125.8, 125.5, 125.4, 123.1, 121.3, 21.3, 19.7; HRMS (EI) Calcd for $\text{C}_{26}\text{H}_{20}$ [M^+] 332.1565, found 332.1568.

(2-(1-Naphthoyl)phenyl)(3,4-dimethoxyphenyl)methanone (11d). Ring-opening of 3-(3,4-dimethoxyphenyl)isobenzofuran-1(3H)-one²⁸ with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup afforded benzo[*c*]furan **10d** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **10d** (2.6 g, 6.84 mmol) using LTA (3.03 g, 6.83 mmol) adopting the procedure similar to that of **4a** furnished diketone **11d** as a brown solid (2.35, 87%): mp 122–124 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.19 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.81–7.73 (m, 2H), 7.66–7.57 (m, 3H), 7.48–7.35 (m, 4H), 7.06–7.03 (m, 1H), 6.97 (s, 1H), 6.67 (d, $J = 8.4$ Hz, 1H), 3.86 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.6, 195.6, 153.2, 149.0, 141.0, 140.5, 135.3, 133.5, 132.9, 131.5, 131.0, 130.8, 130.4, 130.1, 128.9, 127.9, 127.5, 126.5, 125.8, 125.5, 125.3, 124.0, 110.0, 109.7, 56.0, 55.7; HRMS (EI) Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_4$ [M^+] 396.1362, found 396.1355.

7-(3,4-Dimethoxyphenyl)tetraphene (13d). Reduction of diketone **11d** (1 g, 2.52 mmol) using sodium borohydride (0.47 g, 12.62 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.01 g, 2.52 mmol) using pivaloyl chloride (1.52 g, 12.62 mmol) and triethylamine (5.11 g, 50.5 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12d** as a thick liquid. Dipivalate **12d** (1.22 g, 2.14 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13d** as a colorless solid (0.78 g, 85%): mp 168–170 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.25 (s, 1H), 8.89 (d, $J = 8.1$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 7.83–7.47 (m, 8H), 7.11–6.96 (m, 3H), 4.03 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.9, 148.4, 137.4, 131.6, 131.5, 131.4, 131.2, 130.5, 129.0, 128.6, 128.5, 127.2, 126.9, 126.8, 126.7, 125.7, 125.6, 125.5, 123.5, 123.1, 121.5, 114.4, 111.1, 56; DEPT 135 (75 MHz, CDCl_3) δ 128.6, 128.5, 127.2, 126.9, 126.8, 125.8, 125.5, 123.5, 121.5, 114.3, 111.1, 56.0; HRMS (EI) Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2$ [M^+] 364.1463, found 364.1466.

(2-Benzoylphenyl)(4-methylnaphthalen-1-yl)methanone (11e). Ring-opening of 3-(4-methyl-1-naphthyl)isobenzofuran-1(3H)-one with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10e** as a fluorescent yellow solid. Oxidative cleavage of the benzo[*c*]furan **10e** (1.53 g, 4.58 mmol) using LTA (2.03 g, 4.58 mmol) following the procedure similar to that of **4a** furnished diketone **11e** as a thick pale yellow liquid (1.53 g, 87%): ^1H NMR (300 MHz, CDCl_3) δ 8.27 (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.60–7.45 (m, 7H), 7.40–7.31 (m, 3H), 7.22–7.12 (m, 3H), 2.61 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.4, 197.1, 141.0, 140.9, 140.1, 137.4, 133.6, 133.0, 132.7, 131.2, 131.0, 130.8, 130.0, 129.5, 129.0, 128.3, 127.4, 126.4, 124.9, 124.1, 20.1. Anal. Calcd for $\text{C}_{25}\text{H}_{18}\text{O}_2$: C, 85.69; H, 5.18. Found: C, 85.34; H, 5.41.

5-Methyl-7-phenyltetraphene (13e). Reduction of diketone **11e** (1.12 g, 3.2 mmol) using sodium borohydride (0.48 g, 12.63 mmol) followed by workup afforded diol. Dipivaloylation of the diol (1.06 g, 2.99 mmol) using pivaloyl chloride (1.80 g, 14.92 mmol) and triethylamine (6.05 g, 59.78 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12e** as a thick liquid. Dipivalate **12e** (1.28 g, 2.45 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13e** as a colorless solid (0.91 g, 96%): mp 169–171 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.26 (s, 1H), 8.96 (d, $J = 7.8$ Hz, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 8.02 (d, $J = 7.8$ Hz, 1H), 7.77–7.25 (m, 11H), 2.6 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.1, 136.4, 132.3, 131.9, 131.2, 131.1, 131.0, 130.6, 128.6, 128.4, 128.3, 127.4, 127.1, 126.6, 126.5, 125.6, 125.1, 124.9, 124.7, 123.3, 121.4, 20.5; DEPT 135 (75 MHz, CDCl_3) δ 131.2, 128.6, 128.4, 127.4, 126.6, 126.5, 125.6, 125.2, 125.1, 124.7, 123.3, 121.4, 20.5. Anal. Calcd for $\text{C}_{25}\text{H}_{18}$: C, 94.30; H, 5.70. Found: C, 94.01; H, 5.64.

5-Methyl-7-p-tolyltetraphene (13f). Ring-opening of 3-(4-methyl-1-naphthyl)isobenzofuran-1(3H)-one with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10f** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **10f** (0.63 g, 1.82 mmol) with LTA (0.80 g, 1.82 mmol) using the procedure similar to that of **4a** furnished diketone **11f** as a thick liquid (0.56 g, 85%). Reduction of the diketone **11f** (0.40 g, 1.10 mmol) using sodium borohydride (0.17 g, 4.47 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.37 g, 1.01 mmol) using pivaloyl chloride (0.69 g, 5.04 mmol) and triethylamine (2.04 g, 20.16 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12f** as a thick liquid. Dipivalate **12f** (0.54 g, 1.01 mmol) upon interaction with ZnBr_2 (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13f** as a colorless solid (0.27 g, 82%): mp 178–180 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.25 (s, 1H), 8.97 (d, $J = 7.8$ Hz, 1H), 8.18 (d, $J = 8.1$ Hz, 1H), 8.03 (d, $J = 7.5$ Hz, 1H), 7.78–7.68 (m, 3H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.47–7.37 (m, 6H), 2.62 (s, 3H), 2.6 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.0, 136.5, 136.0, 132.2, 132.0,

131.2, 130.6, 129.1, 128.7, 128.6, 128.3, 127.1, 126.7, 126.6, 125.5, 125.1, 125.0, 124.7, 123.4, 121.3, 21.4, 20.5; DEPT 135 (75 MHz, CDCl₃) δ 131.2, 129.1, 128.6, 127.1, 126.7, 126.6, 125.5, 125.1, 125.0, 124.7, 123.4, 121.3, 21.4, 20.5. Anal. Calcd for C₂₆H₂₀: C, 93.94; H, 6.06. Found: C, 93.62; H, 5.98.

(2-(4-Methoxybenzoyl)phenyl)(4-methylnaphthalen-1-yl)methanone (11g). Ring-opening of 3-(4-methyl-1-naphthyl)-isobenzofuran-1(3H)-one with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10g** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **10g** (1.99 g, 5.42 mmol) using LTA (2.40 g, 5.42 mmol) adopting the procedure similar to that of **4a** furnished diketone **11g** as a thick liquid (1.82 g, 88%): ¹H NMR (300 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.59–7.51 (m, 1H), 7.48–7.42 (m, 5H), 7.35–7.32 (m, 2H), 7.13–7.10 (m, 1H), 6.87–6.84 (m, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 3.68 (s, 3H), 2.60 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 197.5, 195.7, 163.4, 141.2, 140.7, 140.1, 133.7, 132.7, 131.8, 131.2, 131.0, 130.9, 130.6, 129.9, 128.8, 127.7, 127.2, 126.4, 126.3, 124.9, 124.0, 114.2, 113.5, 55.4, 20.1. Anal. Calcd for C₂₆H₂₀O₃: C, 82.08; H, 5.30. Found: C, 82.34; H, 5.11.

7-(4-Methoxyphenyl)-5-methyltetraphene (13g). Reduction of diketone **11g** (1.68 g, 4.38 mmol) using sodium borohydride (0.66 g, 17.36 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.58 g, 4.08 mmol) using pivaloyl chloride (2.46 g, 20.40 mmol) and triethylamine (8.56 g, 81.62 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12g** as a thick liquid. Dipivalate **12g** (1.92 g, 3.45 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13g** as a colorless solid (1.30 g, 91%): mp 181–183 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.13 (s, 1H), 8.85 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.65–7.55 (m, 3H), 7.45–7.25 (m, 5H), 7.17–7.04 (m, 2H), 3.88 (s, 3H), 2.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 158.9, 136.2, 132.3, 132.2, 132.0, 131.4, 131.1, 130.6, 128.9, 128.6, 128.3, 127.1, 126.6, 125.5, 125.1, 125.0, 124.6, 123.3, 121.2, 113.8, 55.3, 20.5; HRMS (EI) Calcd for C₂₆H₂₀O [M⁺] 348.1514, found 348.1518.

(2-(1-Naphthoyl)phenyl)(2-methoxynaphthalen-1-yl)methanone (11h). Ring-opening of 3-(2-methoxy-1-naphthyl)-isobenzofuran-1(3H)-one with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup afforded benzo[*c*]furan **10h** as a fluorescent bright yellow solid. Oxidative cleavage of the benzo[*c*]furan **10h** (2.31 g, 5.76 mmol) using LTA (2.55 g, 5.75 mmol) following the procedure similar to that of **4a** gave diketone **11h**^{32d} as a colorless solid (2.13 g, 89%): mp 226–228 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.06 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.81–7.76 (m, 2H), 7.66–7.65 (m, 3H), 7.63–7.60 (m, 1H), 7.53–7.44 (m, 4H), 7.35–7.32 (m, 2H), 7.22–7.19 (m, 2H), 7.17–7.13 (m, 1H), 3.67 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 199.5, 196.7, 155.1, 142.7, 138.6, 135.1, 133.9, 133.4, 132.3, 131.8, 131.4, 131.2, 130.9, 129.9, 129.1, 128.7, 128.2, 128.0, 127.9, 127.6, 126.9, 126.4, 124.0, 123.9, 123.4, 121.9, 112.9, 56.4; DEPT 135 (75 MHz, CDCl₃) δ 133.3, 132.4, 132.3, 131.2, 130.9, 129.9, 129.1, 128.2, 128.0, 127.9, 127.6, 126.9, 126.4, 124.1, 123.9, 123.4, 112.8, 56.4.

7-(2-Methoxynaphthalen-1-yl)tetraphene (13h). Reduction of diketone **11h** (1.0 g, 2.39 mmol) using sodium borohydride (0.45 g, 11.99 mmol) followed by workup afforded diol. Dipivaloylation of the diol (1.0 g, 2.38 mmol) using pivaloyl chloride (1.43 g, 11.87 mmol) and triethylamine (4.80 g, 47.50 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12h** as a thick liquid. Dipivalate **12h** (1.29 g, 2.19 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13h** as a colorless solid (0.78 g, 86%): mp 202–204 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.33 (s, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.77–7.16 (m, 1H), 7.69–7.66 (m, 1H), 7.58–7.55 (m, 1H), 7.54–7.49 (m, 2H), 7.40–7.33 (m, 2H), 7.32–7.27 (m, 2H), 7.23–7.20 (m, 1H), 7.13–7.08 (m, 1H), 6.85 (d, *J*

= 8.4 Hz, 1H), 3.63 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 155.4, 134.6, 132.0, 131.8, 131.5, 130.9, 129.9, 129.8, 129.2, 128.8, 128.5, 127.9, 127.1, 127.0, 126.8, 126.7, 126.4, 125.9, 125.6, 123.8, 123.1, 121.8, 121.3, 114.0, 56.8; DEPT 135 (75 MHz, CDCl₃) δ 130.0, 128.9, 128.5, 127.9, 127.1, 127.0, 126.9, 126.7, 126.4, 125.9, 125.6, 123.8, 123.0, 121.9, 114.0, 56.8; HRMS (EI) Calcd for C₂₉H₂₀O [M⁺] 384.1514, found 384.1520.

(2-(1-Naphthoyl)phenyl)(4-methylnaphthalen-1-yl)methanone (11i). Ring-opening of 3-(4-methyl-1-naphthyl)-isobenzofuran-1(3H)-one with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup furnished benzo[*c*]furan **10i** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **10i** (1.99 g, 5.16 mmol) using LTA (2.29 g, 5.16 mmol) adopting the procedure similar to that of **4a** afforded diketone **11i** as a thick liquid (1.76 g, 85%): ¹H NMR (300 MHz, CDCl₃) δ 8.42 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.73–7.49 (m, 7H), 7.39–7.32 (m, 1H), 7.29–7.08 (m, 7H), 2.51 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 197.8, 197.7, 141.7, 141.5, 140.4, 135.4, 133.8, 133.7, 133.2, 132.8, 131.3, 131.1, 131.0, 130.9, 130.7, 130.2, 130.1, 127.9, 127.4, 127.4, 126.2, 126.0, 125.5, 124.7, 123.8, 123.7, 20.1. DEPT 135 (75 MHz, CDCl₃) δ 133.2, 131.3, 131.1, 131.0, 130.9, 130.2, 127.9, 127.4, 127.4, 126.2, 126.1, 126.0, 125.5, 124.7, 123.8, 20.1; HRMS (EI) Calcd for C₂₉H₂₀O₂ [M⁺] 400.1463, found 400.1466.

Preparation of Annulated Compounds (13i) and (13i'). Reduction of diketone **11i** (1.35 g, 3.36 mmol) using sodium borohydride (0.51 g, 13.42 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.28 g, 3.16 mmol) using pivaloyl chloride (1.90 g, 15.75 mmol) and triethylamine (6.39 g, 63.14 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12i** as a thick liquid. Dipivalate **12i** (1.41 g, 2.46 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave an inseparable 1:1 mixture of compound **13i** and **13i'** as colorless solid (0.99 g, 85%): mp 148–150 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.33 (s, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.20–8.13 (m, 2H), 8.06–7.94 (m, 1H), 7.77–7.69 (m, 3H), 7.67–7.64 (m, 1H), 7.53–7.51 (m, 3H), 7.43–7.39 (m, 3H), 7.35–7.22 (m, 4H), 7.18–7.07 (m, 3H), 2.87 (s, 3H), 2.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 133.6, 132.8, 132.7, 131.8, 131.7, 131.6, 130.6, 129.7, 129.6, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 127.2, 127.0, 126.9, 126.9, 126.7, 126.6, 126.4, 126.3, 125.9, 125.8, 125.6, 125.5, 125.2, 125.0, 124.8, 124.4, 123.4, 123.1, 121.8, 20.4, 19.7; HRMS (EI) Calcd for C₂₉H₂₀ [M⁺] 368.1565, found 368.1567.

9-(9,9-Dihexyl-9H-fluoren-2-yl)anthracene (13j). Ring-opening of 3-(9,9-dihexyl-9H-fluoren-2-yl)isobenzofuran-1(3H)-one^{33a} with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10j** as a fluorescent yellow solid. Oxidative cleavage of the benzo[*c*]furan **10j** (1 g, 1.84 mmol) using LTA (0.81 g, 1.84 mmol) adopting the procedure similar to that of **4a** furnished diketone **11j** as a thick liquid (0.87 g, 85%). Reduction of the diketone **11j** (0.62 g, 1.11 mmol) using sodium borohydride (0.21 g, 5.57 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.65 g, 1.16 mmol) using pivaloyl chloride (0.69 g, 13.18 mmol) and triethylamine (2.34 g, 23.21 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12j** as a thick liquid. Dipivalate **12j** (0.79 g, 1.08 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13j** as a pale yellow solid (0.43 g, 71%): mp 148–150 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.43 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.75–7.72 (m, 1H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.41–7.36 (m, 2H), 7.33–7.28 (m, 5H), 7.23–7.17 (m, 1H), 1.94–1.87 (m, 4H), 1.06–1.01 (m, 12H), 0.71–0.66 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 151.0, 150.8, 141.0, 140.5, 137.7, 137.4, 131.4, 130.4, 129.8, 128.4, 127.2, 126.9, 126.4, 126.0, 125.3, 125.1, 122.9, 119.8, 119.6, 55.2, 40.4, 31.5, 29.7, 23.9, 22.5, 14.0; DEPT 135 (75 MHz, CDCl₃) δ 129.8, 128.4, 127.2, 126.9, 126.4, 126.0, 125.3, 125.1, 122.9, 119.8, 119.6, 40.4, 31.5,

29.7, 23.9, 22.5, 14.0; HRMS (EI) Calcd for $C_{39}H_{42} [M^+]$ 510.3287, found 510.3273.

(9,9-Dihexyl-9H-fluoren-3-yl)(2-(4-methylbenzoyl)phenyl)methanone (11k). Ring-opening of 3-(9,9-dihexyl-9H-fluoren-2-yl)isobenzofuran-1(3H)-one^{33a} with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10k** (1 g, 1.79 mmol) using LTA (0.79 g, 1.79 mmol) following the procedure similar to that of **4a** furnished diketone **11k**³⁰ as a thick orange liquid (0.90 g, 88%): ¹H NMR (300 MHz, CDCl₃) δ 7.64–7.53 (m, 10H), 7.28–7.25 (m, 3H), 7.06 (d, *J* = 7.5 Hz, 2H), 2.27 (s, 3H), 1.87–1.82 (m, 4H), 1.04–0.95 (m, 12H), 0.70–0.44 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 196.5, 196.3, 152.1, 150.8, 146.0, 143.8, 140.43, 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; DEPT 135 (75 MHz, CDCl₃) 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.

9-(9,9-Dihexyl-9H-fluoren-2-yl)-2-methylanthracene (13k). Reduction of diketone **11k** (0.66 g, 1.15 mmol) using sodium borohydride (0.21 g, 5.76 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.68 g, 1.07 mmol) using pivaloyl chloride (0.71 g, 5.90 mmol) and triethylamine (2.38 g, 23.31 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12k** as a thick liquid. Dipivalate **12k** (0.84 g, 1.12 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13k** as a thick red liquid (0.46 g, 73%): ¹H NMR (300 MHz, CDCl₃) δ 8.53 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.05–7.98 (m, 2H), 7.90 (d, *J* = 6.6 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.58 (s, 1H), 7.54–7.43 (m, 6H), 7.48–7.38 (m, 2H), 2.47 (s, 3H), 2.12–2.04 (m, 3H), 1.25–1.17 (m, 11H), 0.88–0.82 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) 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; DEPT 135 (75 MHz, CDCl₃) δ 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, 40.6, 31.7, 31.6, 29.9, 29.7, 27.0, 24.1, 23.9, 22.7, 22.6, 22.3, 14.2; HRMS (EI) Calcd for $C_{40}H_{44} [M^+]$ 524.3443, found 524.3439.

Benzo[*b*]thiophen-3-yl(2-benzoylphenyl)methanone (11l). Ring-opening of 3-(benzo[*b*]thiophen-3-yl)isobenzofuran-1(3H)-one^{33b} with freshly prepared phenylmagnesium bromide followed by acidic workup afforded benzo[*c*]furan **10l** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **10l** (1.31 g, 4.01 mmol) using LTA (1.78 g, 4.01 mmol) adopting the procedure similar to that of **4a** furnished diketone **11l** as a pale yellow solid (1.16 g, 85%): mp 139–140 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.29–8.26 (m, 1H), 7.79 (s, 1H), 7.73–7.70 (m, 1H), 7.68–7.61 (m, 1H), 7.56–7.55 (m, 4H), 7.53 (s, 1H), 7.33–7.27 (m, 3H), 7.22–7.17 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 196.6, 190.2, 141.0, 139.9, 139.8, 139.6, 137.3, 136.6, 133.1, 130.7, 130.6, 129.9, 129.7, 129.6, 129.4, 128.4, 128.3, 125.6, 125.2, 122.0. Anal. Calcd for $C_{22}H_{14}O_2S$: C, 77.17; H, 4.12; S, 9.36. Found: C, 76.98; H, 4.39; S, 9.27.

6-Phenylbenzo[*b*]naphtho[2,3-*d*]thiophene (13l). Reduction of diketone **11l** (0.73 g, 2.13 mmol) using sodium borohydride (0.32 g, 8.42 mmol) followed by workup afforded diol. Dipivaloylation of the diol (0.72 g, 2.08 mmol) using pivaloyl chloride (1.25 g, 10.36 mmol) and triethylamine (4.21 g, 41.61 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12l** as a thick liquid. Dipivalate **12l** (0.94 g, 1.82 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13l** as a colorless solid (0.50 g, 78%): mp 162–164 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.67 (s, 1H), 8.33–8.30 (m, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.82–7.75 (m, 2H), 7.66–7.55 (m, 5H), 7.51–7.45 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.5, 139.0, 135.6, 134.6, 133.2, 131.5, 131.0, 128.9, 128.6, 128.2, 127.7, 126.0, 125.3, 125.1, 125.0, 124.5, 122.7, 122.0, 119.6;

DEPT 135 (75 MHz, CDCl₃) δ 130.1, 128.9, 128.7, 128.2, 127.7, 126.0, 125.1, 125.0, 124.5, 122.6, 122.0, 119.6. Anal. Calcd for $C_{22}H_{14}S$: C, 85.12; H, 4.55; S, 10.33. Found: C, 84.97; H, 4.63; S, 10.12.

Benzo[*b*]thiophen-3-yl(2-(4-methylbenzoyl)phenyl)methanone (11m). Ring-opening of 3-(benzo[*b*]thiophen-3-yl)isobenzofuran-1(3H)-one^{33b} with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10m** as a fluorescent yellow solid. Oxidative ring-opening of the benzo[*c*]furan **10m** (1.48 g, 4.35 mmol) using LTA (1.92 g, 4.33 mmol) adopting the procedure similar to that of **4a** furnished diketone **11m** as a thick pale yellow liquid (1.30 g, 85%): ¹H NMR (300 MHz, CDCl₃) δ 8.25–8.22 (m, 1H), 7.74 (s, 1H), 7.70–7.62 (m, 2H), 7.53–7.50 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.28–7.24 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 2.18 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.3, 190.6, 143.8, 140.8, 140.0, 139.7, 139.3, 136.5, 135.8, 134.7, 130.6, 130.4, 129.5 (2C), 129.3, 128.8, 125.4, 125.3, 125.0, 121.9, 21.5; HRMS (EI) Calcd for $C_{23}H_{16}O_2S [M^+]$ 356.0871, found 356.0870.

6-*p*-Tolylbenzo[*b*]naphtho[2,3-*d*]thiophene (13m). Reduction of diketone **11m** (0.85 g, 2.38 mmol) using sodium borohydride (0.49 g, 12.89 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.77 g, 2.31 mmol) using pivaloyl chloride (1.39 g, 11.52 mmol) and triethylamine (4.69 g, 45.20 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12m** as a thick liquid. Dipivalate **12m** (0.98 g, 1.96 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13m** as a pale green solid (0.53 g, 78%): mp 118–120 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.65 (s, 1H), 8.32–8.29 (m, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.80–7.77 (m, 1H), 7.58–7.44 (m, 8H), 2.56 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.6, 138.7, 138.0, 136.0, 135.7, 134.6, 133.2, 131.6, 131.1, 129.9, 129.7, 128.7, 127.6, 125.9, 125.1, 125.0, 124.5, 122.7, 122.0, 119.5, 21.5; DEPT 135 (75 MHz, CDCl₃) δ 129.9, 129.7, 128.7, 125.9, 125.1, 125.0, 124.5, 122.7, 122.0, 119.5, 21.5. Anal. Calcd for $C_{23}H_{16}S$: C, 85.15; H, 4.97; S, 9.88. Found: C, 84.85; H, 4.88; S, 9.98.

Benzo[*b*]thiophen-3-yl(2-(4-methoxybenzoyl)phenyl)methanone (11n). Ring-opening of 3-(benzo[*b*]thiophen-3-yl)isobenzofuran-1(3H)-one^{33b} with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup afforded benzo[*c*]furan **10n** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **10n** (1.32 g, 4.02 mmol) using LTA (1.78 g, 4.2 mmol) following the procedure similar to that of **4a** furnished diketone **11n** as a colorless solid (1.08 g, 92%): mp 118–120 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.28–8.25 (m, 1H), 7.77 (s, 1H), 7.74–7.71 (m, 1H), 7.69–7.66 (m, 1H), 7.56–7.55 (m, 3H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.30–7.27 (m, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 3.70 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 195.4, 190.8, 163.5, 140.8, 140.3, 139.8, 139.5, 136.7, 135.9, 131.9, 130.7, 130.5, 130.3, 129.4, 129.3, 125.5, 125.4, 125.1, 122.0, 113.5, 55.4. Anal. Calcd for $C_{23}H_{16}O_3S$: C, 74.17; H, 4.33; S, 8.61. Found: C, 73.96; H, 4.62; S 8.60.

6-(4-Methoxyphenyl)benzo[*b*]naphtho[2,3-*d*]thiophene (13n). Reduction of diketone **11n** (0.90 g, 2.61 mmol) using sodium borohydride (0.61 g, 16.14 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.72 g, 2.31 mmol) using pivaloyl chloride (1.24 g, 10.28 mmol) and triethylamine (4.18 g, 41.3 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12n** as a thick liquid. Dipivalate **12n** (0.95 g, 3.16 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13n** as a pale green solid (0.45 g, 70%): mp 187–188 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.64 (s, 1H), 8.32–8.29 (m, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.79–7.76 (m, 1H), 7.55–7.46 (m, 6H), 7.16 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 140.5, 138.9, 135.7, 134.5, 132.9, 131.6, 131.2, 131.2, 131.1, 128.7, 127.6, 125.9, 125.1, 125.0, 124.5, 122.7, 122.0, 119.4, 114.3, 55.4; DEPT 135 (75 MHz, CDCl₃) δ 131.2, 128.7, 127.6, 125.9,

125.0, 124.5, 122.7, 122.0, 119.4, 114.3, 55.4; HRMS (EI) Calcd for $C_{23}H_{16}OS [M^+]$ 340.0922, found 340.0923.

6-(Thiophen-2-yl)benzo[*b*]naphtho[2,3-*d*]thiophene (13o). Ring-opening of 3-(benzo[*b*]thiophen-3-yl)isobenzofuran-1(3*H*)-one^{33b} with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10o** as a fluorescent yellow solid. Oxidative cleavage of the benzo[*c*]furan **10o** (0.84 g, 2.51 mmol) using LTA (1.11 g, 2.51 mmol) adopting the procedure similar to that of **4a** furnished diketone **11o** as a colorless solid (0.77 g, 88%). Reduction of the diketone **11o** (0.38 g, 1.08 mmol) using sodium borohydride (0.16 g, 4.21 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.34 g, 0.96 mmol) using pivaloyl chloride (0.57 g, 4.72 mmol) and triethylamine (1.94 g, 19.17 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12o** as a thick liquid. Dipivalate **12o** (0.51 g, 0.97 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13o** as a pale green solid (0.21 g, 72%): mp 158–160 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.28–8.04 (m, 3H), 7.80–7.33 (m, 8H); ¹³C NMR (75 MHz, $CDCl_3$) δ 140.8, 140.3, 138.9, 135.4, 134.5, 132.0, 131.3, 128.7, 127.7, 127.5, 126.9, 126.4, 125.6, 125.1, 124.9, 124.6, 122.6, 122.0, 120.5; DEPT 135 (75 MHz, $CDCl_3$) δ 128.7, 128.6, 127.8, 127.5, 126.9, 126.4, 125.1, 124.9, 124.6, 122.7, 122.0, 120.6. Anal. Calcd for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82; S, 20.27. Found: C, 75.72; H, 3.96; S, 20.38.

2-Methylbenzo[*b*]thiophen-3-yl(2-(4-methylbenzoyl)phenyl)methanone (11p). Ring-opening of 3-(2-methylbenzo[*b*]thiophen-3-yl)isobenzofuran-1(3*H*)-one^{33b} with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10p** as a fluorescent orange solid. Oxidation of the benzo[*c*]furan **10p** (1.8 g, 4.94 mmol) using LTA (2.19 g, 3.42 mmol) following the procedure similar to that of **4a** furnished the diketone **11p** as a pale yellow solid (1.71 g, 91%): mp 94–96 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 7.71–7.68 (m, 1H), 7.64–7.59 (m, 2H), 7.57–7.55 (m, 2H), 7.46–7.42 (m, 3H), 7.25–7.19 (m, 1H), 7.17–7.11 (m, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 196.1, 192.2, 150.1, 144.0, 141.1, 140.5, 138.7, 137.3, 134.7, 132.4, 131.4, 130.5, 129.4, 129.2, 129.0, 124.6, 124.3, 123.5, 121.2, 21.6, 15.9; HRMS (EI) Calcd for $C_{24}H_{18}O_2S [M^+]$ 370.1028, found 370.1021.

2-Methyl-3-(2-methylanthracen-9-yl)benzo[*b*]thiophene (13p). Reduction of diketone **11p** (1.8 g, 4.73 mmol) using sodium borohydride (0.9 g, 23.0 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.57 g, 4.08 mmol) using pivaloyl chloride (2.46 g, 20.40 mmol) and triethylamine (8.27 g, 81.72 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12p** as a thick liquid. Dipivalate **12p** (1.89 g, 3.42 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13p** as a pale brown solid (1.14 g, 78%): mp 168–169 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.49–7.46 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.30–7.24 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 2.34 (s, 3H), 2.18 (s, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 141.6, 138.5, 138.4, 136.0, 131.4, 131.2, 131.1, 131.0, 130.3, 129.0, 128.6, 127.1, 126.3, 126.0, 125.0, 124.4, 124.3, 124.0, 123.1, 122.1, 22.3, 14.6; DEPT 135 (75 MHz, $CDCl_3$) δ 129.0, 127.0, 128.3, 127.1, 126.3, 126.0, 125.0, 124.9, 124.4, 124.3, 124.0, 123.0, 122.1, 122.3, 14.6. Anal. Calcd for $C_{24}H_{18}S$: C, 85.17; H, 5.36; S, 9.47. Found: C, 85.34; H, 5.24; S, 9.61.

2-Methylbenzo[*b*]thiophen-3-yl(2-(thiophen-2-carbonyl)phenyl)methanone (11q). Ring-opening of 3-(2-methylbenzo[*b*]thiophen-3-yl)isobenzofuran-1(3*H*)-one^{33b} with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **10q** as a fluorescent orange solid. Oxidative cleavage of the benzo[*c*]furan **10q** (1.1 g, 3.17 mmol) using LTA (1.38 g, 3.11 mmol) adopting the procedure similar to that of **4a** furnished diketone **11q** as a thick liquid (1.06 g, 92%): ¹H NMR (300 MHz, $CDCl_3$) δ 7.70–7.60 (m, 5H), 7.54–7.48 (m, 2H), 7.34–7.33 (m, 1H), 7.26–7.15 (m,

2H), 7.01–6.98 (m, 1H), 2.34 (s, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 192.3, 188.1, 150.6, 144.2, 141.2, 139.8, 138.7, 137.4, 134.9, 134.7, 132.3, 131.3, 130.8, 129.2, 128.9, 128.0, 124.8, 124.3, 123.4, 121.3, 15.9. Anal. Calcd for $C_{21}H_{14}O_2S_2$: C, 69.59; H, 3.89; S, 17.69. Found: C, 69.38; H, 4.02; S, 17.92.

4-(2-Methylbenzo[*b*]thiophen-3-yl)naphtho[2,3-*b*]thiophene (13q). Reduction of diketone **11q** (0.89 g, 2.45 mmol) using sodium borohydride (0.47 g, 12.36 mmol) followed by workup afforded diol. Dipivaloylation of the diol (0.84 g, 2.29 mmol) using pivaloyl chloride (1.38 g, 11.44 mmol) and triethylamine (4.64 g, 45.85 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **12q** as a thick liquid. Dipivalate **12q** (1.06 g, 1.98 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **13q** as a pale yellow solid (0.58 g, 77%): mp 170–172 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.39–7.37 (m, 1H), 7.35–7.26 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.94–6.90 (m, 2H), 2.25 (s, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 140.9, 139.1, 138.4, 138.3, 137.9, 131.3, 130.5, 129.9, 128.3, 127.8, 127.0, 126.2, 125.3, 124.2, 123.9, 123.5, 122.9, 122.0, 121.1, 14.7; DEPT 90 (75 MHz, $CDCl_3$) δ 128.3, 127.8, 126.2, 125.3, 124.2, 123.9, 123.5, 122.9, 122.0, 121.1; HRMS (EI) Calcd for $C_{21}H_{14}S_2 [M^+]$ 330.0537, found 330.0537.

(2-Benzoylphenyl)(dibenzo[*b,d*]thiophen-2-yl)methanone (15a). Ring-opening of 3-(dibenzo[*b,d*]thiophen-2-yl)isobenzofuran-1(3*H*)-one^{33c} with freshly prepared phenylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14a** as a thick yellow liquid. Oxidation of the benzo[*c*]furan **14a** (2.64 g, 7.02 mmol) using LTA (3.11 g, 7.02 mmol) adopting the procedure similar to that of **4a** led to the isolation of diketone **15a** as a pale yellow solid (1.4 g, 81%): mp 138–140 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 8.12–8.11 (m, 1H), 8.14–8.08 (m, 1H), 7.88–7.80 (m, 3H), 7.75–7.62 (m, 6H), 7.53–7.46 (m, 3H), 7.40–7.31 (m, 2H); ¹³C NMR (75 MHz, $CDCl_3$) δ 196.6, 196.3, 144.7, 140.3, 140.0, 139.7, 137.2, 135.5, 135.1, 133.8, 133.0, 130.5, 130.3, 129.9, 129.6, 128.3, 127.8, 127.4, 124.9, 123.3, 122.9, 122.6, 122.0; HRMS (EI) Calcd for $C_{26}H_{16}O_2S [M^+]$ 392.0871, found 392.0866.

7-Phenylanthra[2,3-*d*]benzo[*b*]thiophene (17a). Reduction of diketone **15a** (1.11 g, 2.83 mmol) using sodium borohydride (0.53 g, 13.94 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.12 g, 2.82 mmol) using pivaloyl chloride (1.70 g, 14.14 mmol) and triethylamine (5.72 g, 56.56 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16a** as a thick liquid. Dipivalate **16a** (1.28 g, 2.26 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 99:1) gave compound **17a** as a yellow solid (0.83 g, 72%): mp 190–192 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.60 (s, 1H), 8.19–8.16 (m, 1H), 8.01–7.96 (m, 2H), 7.67–7.65 (m, 1H), 7.60–7.52 (m, 5H), 7.40–7.28 (m, 6H); ¹³C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.8, 137.7, 135.6, 135.1, 134.9, 131.4, 130.9, 129.6, 129.1, 128.6, 128.3, 128.2, 127.6, 127.2, 126.8, 125.5, 124.9, 124.7, 122.8, 122.1, 120.1, 119.2; DEPT 135 (75 MHz, $CDCl_3$) δ 131.4, 128.6, 128.3, 128.2, 127.6, 126.8, 125.5, 124.9, 124.7, 122.8, 122.1, 120.1, 119.2; HRMS (EI) Calcd for $C_{26}H_{16}S [M^+]$ 360.0973, found 360.0974.

Dibenzo[*b,d*]thiophen-2-yl(2-(4-methylbenzoyl)phenyl)methanone (15b). Ring-opening of 3-(dibenzo[*b,d*]thiophen-2-yl)isobenzofuran-1(3*H*)-one^{33c} with freshly prepared *p*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14b** as a thick yellow liquid. Oxidative cleavage of the benzo[*c*]furan **14b** (0.65 g, 1.66 mmol) using LTA (0.73 g, 1.64 mmol) following the procedure similar to that of **4a** led to the isolation of diketone **15b** as a pale yellow solid (0.60 g, 90%): mp 144–146 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.05–8.02 (m, 1H), 7.75–7.72 (m, 2H), 7.63–7.52 (m, 7H), 7.42–7.39 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.27 (s, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 196.4, 196.3, 144.6, 144.0, 140.3, 140.2, 139.6, 135.5, 135.1, 134.7, 133.8, 130.3, 130.0, 129.7,

129.6, 129.0, 127.8, 127.4, 124.8, 123.3, 122.9, 122.5, 122.0, 21.7; HRMS (EI) Calcd for $C_{27}H_{18}O_2S$ [M^+] 406.1028, found 406.1025.

7-*p*-Tolylanthra[2,3-*d*]benzo[*b*]thiophene (17b). Reduction of diketone **15b** (0.71 g, 1.74 mmol) using sodium borohydride (0.33 g, 8.68 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.62 g, 1.51 mmol) using pivaloyl chloride (0.91 g, 7.55 mmol) and triethylamine (3.05 g, 30.14 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16b** as a thick liquid. Dipivalate **16b** (0.89 g, 1.53 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 98:2) gave compound **17b** as a yellow solid (0.44 g, 79%): mp 218–220 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.60 (s, 1H), 8.16 (d, $J = 7.8$ Hz, 1H), 8.05 (s, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.40–7.38 (m, 5H), 7.32–7.30 (m, 3H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 137.6, 137.3, 135.0, 134.9, 131.3, 130.9, 130.3, 129.8, 129.3, 129.1, 128.4, 128.1, 127.0, 126.9, 125.4, 124.8, 124.6, 122.8, 122.1, 120.1, 119.2, 21.5; DEPT 135 (75 MHz, $CDCl_3$) δ 131.3, 129.3, 128.4, 127.0, 126.9, 125.4, 124.8, 124.6, 122.8, 122.1, 120.1, 119.2, 21.5; HRMS (EI) Calcd for $C_{27}H_{18}S$ 374.1129, found 374.1128.

7-(4-Methoxyphenyl)anthra[2,3-*d*]benzo[*b*]thiophene (17c). Ring-opening of 3-(dibenzo[*b,d*]thiophen-2-yl)isobenzofuran-1(3*H*)-one^{33c} with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14c** as a fluorescent yellow solid. Oxidation of the benzo[*c*]furan **14c** (1.50 g, 3.69 mmol) using LTA (1.63 g, 3.69 mmol) adopting the procedure similar to that of **4a** led to the isolation of diketone **15c** as a colorless solid (1.38 g, 89%). Reduction of the diketone **15c** (1.20 g, 2.84 mmol) using sodium borohydride (0.54 g, 14.21 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.10 g, 2.58 mmol) using pivaloyl chloride (1.55 g, 12.85 mmol) and triethylamine (5.20 g, 51.38 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16c** as a thick liquid. Dipivalate **16c** (1.28 g, 2.15 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 97:3) gave compound **17c** as a yellow solid (0.7 g, 70%): mp 172–174 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.70 (s, 1H), 8.31–8.28 (m, 1H), 8.12–8.07 (m, 2H), 7.79–7.73 (m, 2H), 7.51–7.38 (m, 6H), 7.20–7.17 (m, 2H), 4.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 140.4, 137.6, 135.4, 135.1, 134.9, 132.5, 131.0, 130.8, 130.6, 13.0, 129.2, 128.3, 128.1, 127.0, 126.9, 125.4, 124.8, 124.8, 124.6, 122.8, 122.1, 120.1, 119.2, 114.0, 55.4; DEPT 135 (75 MHz, $CDCl_3$) δ 132.5, 128.3, 128.1, 127.0, 126.9, 125.4, 124.8, 124.6, 122.8, 122.1, 120.1, 119.2, 114.0, 55.4; HRMS (EI) Calcd for $C_{27}H_{18}OS$ [M^+] 390.1078, found 390.1081.

Dibenzo[*b,d*]thiophen-2-yl(2-(2-methylbenzoyl)phenyl)methanone (15d). Ring-opening of 3-(dibenzo[*b,d*]thiophen-2-yl)isobenzofuran-1(3*H*)-one^{33c} with freshly prepared *o*-tolylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14d** as a thick yellow liquid. Oxidative cleavage of the benzo[*c*]furan **14d** (1.13 g, 2.89 mmol) using LTA (1.28 g, 2.89 mmol) following the procedure similar to that of **4a** led to the isolation of diketone **15d** as a pale yellow solid (0.96 g, 82%): mp 164–166 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.02–7.91 (m, 1H), 7.73–7.64 (m, 3H), 7.51–7.47 (m, 4H), 7.35–7.30 (m, 2H), 7.22–7.11 (m, 2H), 7.02–6.98 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 196.8, 144.7, 141.0, 140.1, 139.7, 138.9, 137.3, 135.5, 135.1, 133.9, 131.5, 131.4, 131.3, 130.7, 130.5, 130.1, 129.0, 127.6, 127.4, 125.2, 124.9, 123.0, 122.9, 122.6, 121.9, 20.4; DEPT 135 (75 MHz, $CDCl_3$) δ 131.4, 131.4, 131.3, 130.7, 130.5, 130.1, 129.0, 127.6, 127.4, 125.2, 124.9, 124.7, 123.0, 122.9, 122.6, 121.9, 20.4. Anal. Calcd for $C_{27}H_{18}O_2S$: C, 79.78; H, 4.46; S, 7.89. Found: C, 79.53; H, 4.61; S, 7.84.

7-*o*-Tolylanthra[2,3-*d*]benzo[*b*]thiophene (17d). Reduction of diketone **15d** (0.74 g, 1.82 mmol) using sodium borohydride (0.28 g, 7.36 mmol) followed by workup afforded diol. Dipivaloylation of the diol (0.72 g, 1.75 mmol) using pivaloyl chloride (1.05 g, 8.77 mmol) and triethylamine (3.55 g, 35.09 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation

of dipivalate **16d** as a thick liquid. Dipivalate **16d** (0.97 g, 1.67 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 98:2) gave compound **17d** as a yellow solid (0.57 g, 87%): mp 218–220 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.70 (s, 1H), 8.29–8.26 (m, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.97 (s, 1H), 7.79 (d, $J = 6.3$ Hz, 1H), 7.60–7.28 (m, 9H), 3.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 138.1, 137.9, 137.7, 135.1, 134.9, 134.8, 131.3, 130.9, 130.1, 129.9, 129.2, 129.1, 128.4, 128.0, 127.9, 126.9, 126.4, 125.9, 125.5, 124.8, 124.5, 122.7, 122.0, 120.3, 118.7, 14.7; DEPT 135 (75 MHz, $CDCl_3$) δ 131.4, 130.2, 128.5, 128.0, 127.0, 126.5, 126.0, 125.6, 124.9, 124.6, 122.8, 122.1, 120.3, 118.8, 19.8; HRMS (EI) Calcd for $C_{27}H_{18}S$ [M^+] 374.1129, found 374.1124.

(2-(1-Naphthoyl)phenyl)dibenzo[*b,d*]thiophen-2-yl)methanone (15e). Ring-opening of 3-(dibenzo[*b,d*]thiophen-2-yl)isobenzofuran-1(3*H*)-one^{33c} with freshly prepared 1-naphthylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14e** as a thick yellow liquid. Oxidative cleavage of the benzo[*c*]furan **14e** (2.13 g, 5.0 mmol) using LTA (2.21 g, 5.0 mmol) adopting the procedure similar to that of **4a** led to the isolation of diketone **15e**³⁰ as a colorless solid (1.92 g, 87%): mp 88 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, $J = 1.2$ Hz, 1H), 8.08–8.05 (m, 1H), 8.01–7.98 (m, 1H), 7.89–7.87 (d, $J = 8.4$ Hz, 1H), 7.85–7.78 (m, 3H), 7.70–7.61 (m, 5H), 7.58–7.53 (m, 2H), 7.47–7.43 (m, 2H), 7.37–7.32 (m, 1H), 7.22–7.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.3, 196.6, 144.7, 140.9, 140.5, 139.4, 135.4, 135.1, 134.9, 134.1, 133.3, 132.9, 131.6, 130.8, 130.6, 130.4, 129.1, 127.9, 127.3, 127.2, 127.1, 126.0, 125.1, 124.7, 123.9, 122.7, 122.5, 122.4, 121.8; DEPT 135 (75 MHz, $CDCl_3$) δ 133.0, 131.7, 130.9, 130.7, 130.5, 129.2, 128.0, 127.4, 127.3, 127.2, 126.3, 125.2, 124.8, 123.9, 122.8, 122.6, 122.5, 121.9.

7-(Naphthalen-1-yl)anthra[2,3-*d*]benzo[*b*]thiophene (17e). Reduction of diketone **15e** (1.11 g, 2.51 mmol) using sodium borohydride (0.53 g, 12.63 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.15 g, 2.57 mmol) using pivaloyl chloride (1.55 g, 12.85 mmol) and triethylamine (5.21 g, 51.57 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16e** as a thick liquid. Dipivalate **16e** (1.30 g, 2.11 mmol) upon interaction with $ZnBr_2$ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 98:2) gave compound **17e** as a yellow solid (0.53 g, 51%): mp 184–186 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.74 (s, 1H), 8.22 (s, 1H), 8.08–8.02 (m, 2H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.73 (s, 1H), 7.65 (d, $J = 6.9$ Hz, 2H), 7.50 (d, $J = 6.9$ Hz, 1H), 7.44–7.35 (m, 4H), 7.18–7.09 (m, 3H), 7.02–6.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 137.9, 134.8, 133.8, 133.5, 131.0, 130.4, 129.3, 129.2, 128.4, 128.3, 128.2, 127.5, 127.0, 126.9, 126.7, 126.5, 126.4, 126.1, 125.7, 125.6, 125.0, 124.6, 122.8, 122.1, 121.8, 120.2, 119.3; HRMS (EI) Calcd for $C_{30}H_{18}S$ [M^+] 410.1129, found 410.1123.

Dibenzo[*b,d*]thiophen-2-yl(2-(thiophen-2-carbonyl)phenyl)methanone (15f). Ring-opening of 3-(dibenzo[*b,d*]thiophen-2-yl)isobenzofuran-1(3*H*)-one^{33c} with freshly prepared 2-thienylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14f** as a thick yellow liquid. Oxidative cleavage of the benzo[*c*]furan **14f** (2.10 g, 5.49 mmol) using LTA (2.43 g, 5.49 mmol) following the procedure similar to that of **4a** afforded diketone **15f**⁵⁰ as a pale yellow solid (1.75 g, 92%): mp 110–112 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.91–7.90 (m, 2H), 7.85–7.82 (m, 3H), 7.70–7.65 (m, 3H), 7.58–7.47 (m, 3H), 7.39–7.34 (m, 1H), 7.23–7.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 188.2, 144.7, 144.0, 139.9, 139.8, 139.6, 135.4, 135.1, 135.0, 134.8, 133.7, 130.6, 130.4, 129.7, 129.2, 128.0, 127.8, 127.7, 127.4, 125.8, 124.8, 122.6, 122.0; DEPT 135 (75 MHz, $CDCl_3$) δ 135.0, 134.9, 130.6, 130.4, 129.7, 129.2, 128.0, 127.7, 127.4, 124.8, 123.3, 122.8, 122.6, 122.0.

7-(Thiophen-2-yl)anthra[2,3-*d*]benzo[*b*]thiophene (17f). Reduction of diketone **15f** (1.12 g, 2.81 mmol) using sodium borohydride (0.53 g, 13.94 mmol) followed by workup afforded diol. Dipivaloylation of the diol (1.12 g, 2.82 mmol) using pivaloyl

chloride (1.67 g, 13.84 mmol) and triethylamine (5.63 g, 55.68 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16f** as a thick liquid. Dipivalate **16f** (1.32 g, 2.34 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 98:2) gave compound **17f** as a yellow solid (0.83 g, 82%): mp 219–220 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.79 (s, 1H), 8.74 (s, 1H), 8.29–8.26 (m, 1H), 8.24 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.78–7.75 (m, 1H), 7.66–7.65 (m, 1H), 7.49–7.41 (m, 4H), 7.37–7.34 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 140.4, 139.0, 135.3, 134.8, 131.9, 131.1, 130.7, 129.6, 129.0, 128.6, 128.3, 127.3, 126.9, 126.5, 125.7, 125.0, 124.7, 122.8, 122.1, 120.0, 118.9; DEPT 135 (75 MHz, CDCl₃) δ 129.6, 128.6, 128.2, 127.3, 126.6, 126.0, 125.0, 124.7, 122.9, 122.1, 120.0, 119; HRMS (EI) Calcd for C₂₄H₁₄S₂ [M⁺] 366.0537, found 366.0533.

(2-(Dibenzo[*b,d*]furan-2-carbonyl)phenyl)(5-hexylthiophen-2-yl)methanone (15g). Ring-opening of 3-(dibenzo[*b,d*]furan-2-yl)isobenzofuran-1(3*H*)-one^{33c} (1.8 g, 6.00 mmol) with freshly prepared 5-hexyl-2-thienylmagnesium bromide [prepared from 5-hexyl-2-bromo thiophene (2.22 g, 9 mmol) and Mg (0.328 g, 13.48 mmol)] followed by acidic workup gave benzo[*c*]furan **14g** as a thick orange solid (1.52 g, 56%). The crude benzo[*c*]furan **14g** (1.0 g, 2.14 mmol) upon reaction with LTA (0.95 g, 2.14 mmol) in DCM adopting the procedure similar to that of **4a** led to the isolation of diketone **15g**³⁰ as a thick red liquid (0.92 g, 89%): ¹H NMR (300 MHz, CDCl₃) δ 8.33 (s, 1H), 7.91–7.89 (m, 1H), 7.87–7.84 (m, 1H), 7.79–7.76 (m, 1H), 7.68–7.63 (m, 3H), 7.59–7.56 (m, 1H), 7.53–7.51 (m, 1H), 7.50–7.46 (m, 1H), 7.37–7.32 (m, 2H), 6.75–6.74 (m, 1H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.63–1.55 (m, 2H), 1.27–1.25 (m, 6H), 0.86 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.1, 187.9, 158.9, 157.5, 156.8, 141.5, 140.0, 139.8, 135.7, 132.6, 130.5, 130.3, 129.5, 129.1, 127.9, 125.6, 124.4, 123.7, 123.3, 123.2, 121.1, 111.9, 111.5, 31.4, 31.2, 30.7, 28.7, 22.5, 14.1.

Annulation of Dipivaloyl Ester (16g). Reduction of diketone **15g** (1.08 g, 2.22 mmol) using sodium borohydride (0.42 g, 11.11 mmol) followed by workup gave diol. Dipivaloylation of the diol (1.10 g, 2.26 mmol) using pivaloyl chloride (1.36 g, 11.31 mmol) and triethylamine (4.58 g, 45.26 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16g** as a thick liquid. Dipivalate **16g** (1.32 g, 2.01 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification (silica gel; hexane–ethyl acetate, 98:2) gave compounds **17g** and **17g'**.

7-(5-Hexylthiophen-2-yl)anthra[2,3-*d*]benzo[*b*]furan (17g). Dark brown solid; 0.48 g (48%): mp 90–92 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.67 (s, 1H), 8.53 (s, 1H), 8.09–7.97 (m, 4H), 7.53–7.44 (m, 5H), 7.05–7.02 (m, 2H), 3.03–2.98 (m, 2H), 1.89–1.84 (m, 2H), 1.60–1.42 (m, 6H), 1.01–0.90 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 158.2, 155.1, 147.4, 136.3, 131.9, 131.7, 129.0, 128.9, 128.7, 128.2, 126.7, 126.4, 126.2, 125.8, 124.6, 124.0, 123.6, 122.8, 121.6, 119.1, 111.4, 104.8, 31.7, 31.6, 30.3, 29.0, 22.6; DEPT 135 (75 MHz, CDCl₃) δ 130.4, 129.0, 128.9, 128.2, 126.4, 125.8, 125.0, 124.6, 124.0, 122.8, 121.6, 119.1, 1, 111.4, 104.8, 31.8, 31.7, 30.4, 29.0, 22.7, 14.1. Anal. Calcd for C₃₀H₂₆OS: C, 82.91; H, 6.03; S, 7.38. Found: C, 82.68; H, 6.17; S, 7.45.

3-(2-Hexylnaphtho[2,3-*b*]thiophen-4-yl)dibenzo[*b,d*]benzo-*b*]furan (17g'). Thick pale green liquid; 0.23 g (23%): ¹H NMR (300 MHz, CDCl₃) δ 8.18 (s, 1H), 7.93 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.45–7.19 (m, 5H), 6.65 (s, 1H), 2.73–2.68 (m, 2H), 1.63–1.56 (m, 2H), 1.26–1.16 (m, 6H), 0.76–0.72 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 156.7, 155.6, 148.5, 139.2, 138.0, 133.8, 132.7, 130.7, 129.8, 127.5, 127.4, 126.2, 124.9, 124.7, 124.5, 124.2, 122.9, 122.8, 120.8, 120.1, 119.7, 111.8, 111.6, 31.5, 31.4, 31.0, 30.7, 28.9, 22.5, 14.0; DEPT 135 (75 MHz, CDCl₃) δ 129.8, 127.5, 127.4, 126.2, 124.9, 124.7, 122.9, 122.7, 120.8, 120.1, 119.7, 111.8, 111.6, 31.5, 31.4, 30.7, 28.9, 22.5, 14.0. Anal. Calcd for C₃₀H₂₆OS: C, 82.91; H, 6.03; S, 7.38. Found: C, 82.74; H, 6.18; S, 7.49.

(9-Hexyl-9*H*-carbazol-3-yl)(2-(4-methylbenzyl)phenyl)methanone (15h). Interaction of 3-(*N*-hexylcarbazol-3-yl)-isobenzofuran-1(3*H*)-one^{33c} (1 g, 2.61 mmol) with *p*-tolylmagnesium bromide [prepared from 4-bromotoluene (0.67 g, 4.11 mmol) and Mg (0.15 g, 6.16 mmol)] followed by acidic workup gave benzo[*c*]furan **14h** as a thick orange liquid (0.69 g, 58%). To a solution of crude benzo[*c*]furan **14h** (0.50 g, 1.09 mmol) in DCM (15 mL), *m*-CPBA (0.37 g, 1.64 mmol) was added, and the reaction mixture was stirred at room temperature for 5 min. It was then poured into saturated sodium bicarbonate solution, extracted with DCM (3 × 30 mL). The combined organic extract was washed with water (2 × 30 mL) and dried (Na₂SO₄). Removal of solvent followed by column chromatographic purification (silica gel, hexane–ethyl acetate, 95:5) afforded diketone **15h**³⁰ as a thick yellow liquid (0.42 g, 80%): ¹H NMR (300 MHz, CDCl₃) δ 8.38 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.63–7.52 (m, 6H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 4.18 (t, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.78–1.71 (m, 2H), 1.22–1.20 (m, 6H), 0.77 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 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, 21.5, 20.6, 12.9; DEPT 135 (75 MHz, CDCl₃) δ 130.1, 130.0, 129.9, 129.6, 129.5, 128.9, 128.1, 126.4, 123.7, 120.7, 119.9, 109.2, 108.3, 43.3, 31.5, 28.8, 26.9, 22.5, 21.7, 14.0.

Attempted Preparation of 5-Hexyl-7-*p*-tolyl-5*H*-naphtho[2,3-*b*]carbazole (17h). Reduction of diketone **15h** (0.42 g, 0.94 mmol) using sodium borohydride (0.18 g, 4.74 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.40 g, 0.83 mmol) using pivaloyl chloride (0.56, 13.27 mmol) and triethylamine (1.90 g, 18.82 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16h** as a thick liquid. Dipivalate **16h** (0.61 g, 0.94 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification did not afford any characterizable product.

(2-(4-(Diphenylamino)benzoyl)phenyl)(4-methoxyphenyl)methanone (15i). Ring-opening of 3-(4-(diphenylamino)phenyl)-isobenzofuran-1(3*H*)-one^{33c} with freshly prepared *p*-anisylmagnesium bromide followed by acidic workup gave benzo[*c*]furan **14i** as an orange solid. The benzo[*c*]furan **14i** (0.50 g, 1.07 mmol) upon oxidative ring-opening reaction with *m*-CPBA (0.36 g, 1.61 mmol) using the above-mentioned procedure led to the isolation of diketone **15i**³⁰ as a pale yellow solid (0.43 g, 93%): mp 144–145 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.53–7.44 (m, 6H), 7.25–7.18 (m, 4H), 7.05–7.03 (m, 6H), 6.82–6.78 (m, 4H), 3.77 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) 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.

Attempted Preparation of 10-(4-Methoxyphenyl)-*N,N*-diphenylanthracen-2-amine (17i). Reduction of diketone **15i** (0.43 g, 0.89 mmol) using sodium borohydride (0.16 g, 4.45 mmol) followed by workup gave diol. Dipivaloylation of the diol (0.41 g, 0.84 mmol) using pivaloyl chloride (0.51 g, 13.4 mmol) and triethylamine (1.70 g, 35.09 mmol) in the presence of a catalytic amount of DMAP (10 mg) in dry DCM (20 mL) led to the isolation of dipivalate **16i** as a thick liquid. Dipivalate **16i** (0.62 g, 0.94 mmol) upon interaction with ZnBr₂ (0.02 g, 0.13 mmol) followed by removal of solvent and column chromatographic purification did not afford any characterizable product.

■ ASSOCIATED CONTENT

📄 Supporting Information

Copies of ¹H, ¹³C NMR, DEPT 135, HRMS spectra (most of the cases) and X-ray data (**6m**, **13o** and **17a**) of annulated heterocycles. Copies of ¹H, ¹³C NMR and HRMS (**4d**, **11d**, **11i**, **11m**, **11p**, **15a** and **15b**) spectra of 1,2-diaroylbenzenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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