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Synthesis and characterization of benzo[*c*]thiophene analogs tethered with dibenzo-heterocycles as potential OLEDs

Natarajan Senthil Kumar, J. Arul Clement, Arasambattu K. Mohanakrishnan *

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India

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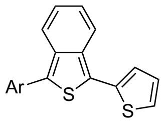
ABSTRACT

Synthesis of mixed heterocyclic system containing benzo[*c*]thiophene, dibenzo-heterocycles, and thiophene unit is described.

1. Introduction

Electronic properties of the linear conjugated oligomers acquired growing importance in many areas of modern chemistry. In particular, π-conjugated thiophene oligomers possess interesting electronic and optical properties and they have been investigated as Organic Field Effect Transistors (OFETs)[1] and Organic Light-Emitting Diodes (OLEDs).[2] Carbazole analogs due to their unique optical and chemical properties are often used as functional building blocks in the construction of organic materials for opto-electronic devices.[3] Triarylamine-substituted carbazole based dendrimer containing oligothiophene core has been explored in Organic Solar Cells (OSCs) as well as OLEDs.[4] Promarak and co-workers recently reported the synthesis of *N*-carbazole end-capped oligothiophene-fluorenes as promising hole-transporting and light-emitting layers in OLED devices. The incorporation of *N*-carbazole units at the terminal ends improved its morphology and electrochemical properties.[5] Thus, the carbazole analogs due to their intense luminescence[6] have been widely used in OLEDs as blue emitters,[7] white emitters,[8] green emitters,[9] and red emitters.[10]

Over the years, benzo[*c*]thiophene analogs **1** (Fig. 1) are explored as components in OLEDs[11] as well as photovoltaics.[12] Very recently, Swager and co-workers compared the effectiveness of isobenzofuran over isothionaphthene as red-shifting component in donor–acceptor type dyes.[13] In further continuation of our work on benzo[*c*]thiophenes,[14] we report here our results on the synthesis of benzo[*c*]thiophene containing dibenzo-heterocycles.



1 Ar = aryl/heteroaryl

Figure 1.

2. Results and discussion

Friedel–Crafts phthaloylation of dibenzo-heterocycles **2a**–**f** in the presence of anhydrous $AlCl_3$ in dry DCM at room temperature for 4 h followed by workup afforded crude keto acids **4a**–**f**. Selective reduction of the ketone carbonyl function of acids **4a**–**f** using $NaBH_4$ in THF/EtOH (2:5) at reflux for 10 h followed by workup and acid catalyzed cyclization furnished the required lactones **5a**–**f** in 38–45% yields. Ring opening of the lactones **5a**–**f** using freshly prepared 2-thienyl/arylmagnesium bromides **6a**–**f** followed by quenching with aq NH_4Cl led to the isolation of keto alcohols.

The DCM solution of keto alcohol on thionation using 0.5 equiv / of Lawesson's reagent followed by workup and column chromatographic purification afforded the respective benzo[*c*]thiophene

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* Corresponding author. Tel.: +91 44 22202813; fax: +91 44 22300488.
E-mail address: mohan_67@hotmail.com (A.K. Mohanakrishnan).

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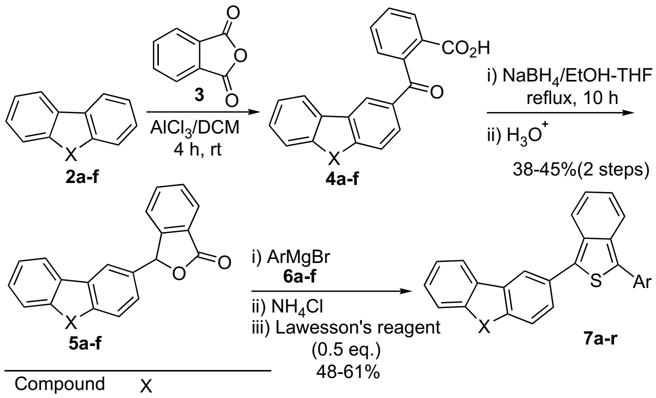


Compound	X
2a/4a/5a	N-*n*-C_6H_{13}
2b/4b/5b	N-(*n*-2-ethyllhexyl)
2c/4c/5c	N-phenyl
2d/4d/5d	N-*p*-anisyl
2e/4e/5e	O
2f/4f/5f	S

Scheme 1.

analogs **7a**–**r** in 48–61% yields (Scheme 1). Complete details such as type of the lactones, Grignards employed, and the respective benzo[*c*]thiophene analogs obtained along with their yields are presented in Table 1. Ring opening of the 9-alkyl and 9-arylcarbazolyl lactones **5a**/**b**, **5c**, and **5d** with 2-thienyl/aryl Grignards **6a**–**f** followed by subsequent thionation gave the respective 1-(carbazolyl)-3-(thienyl/aryl)benzo[*c*]thiophenes **7a**–**n** in 48–61% yields (Table 1, entries 1–4). Similarly, the ring opening of dibenzofuranyl lactone **5e** using thienyl-2-magnesium bromides **6b**/**6c** followed by thionation furnished 1-(dibenzofuranyl)-3-(2/5-hexylthienyl)benzo[*c*]thiophenes **7o**/**7p** in 51% and 55% yields (Table 1, entry 5).

Reaction of dibenzothiophenyl lactone **5f** with 3-hexyl-2-thienylmagnesium bromide/5-hexyl-2-thienylmagnesium bromide gave 1-dibenzothiophenyl-3-thienylbenzo[*c*]thiophenes **7q**/**7r** in 60% and 57% yields, respectively (Table 1, entry 6). All these benzo[*c*]thiophenes **7a**–**r** were found to be highly soluble in common organic solvents.

Following the similar procedure as mentioned above, triphenylamine incorporated benzo[*c*]thiophene analogs **11a**–**c** are smoothly prepared in 55–60% yields (Scheme 2).

Some selected dibenzo-heterocycles tethered benzo[*c*]thiophenes **7b**, **7g**, **7j**, **7o**, and **7q** are converted into the corresponding dimers **12a**–**e** in moderate yields (47–61%) using anhydrous $FeCl_3$ in dry DCM (Scheme 3). However, all attempts to dimerize triphenylamine based benzo[*c*]thiophene **11a** or **11b** were complicated due to the poor solubility of the resulting dimerization products.

3. Photophysical and electrochemical studies

The UV–vis spectra of monomeric benzo[*c*]thiophenes exhibited a strong absorption in the region of 445–465 nm due to the π–π^* electronic transition of the conjugated backbone system. The dimerization of monomeric benzo[*c*]thiophenes red shifted the λ_{max} values in the range of 35–60 nm. The exact absorption λ_{max} values of these compounds are given in Table 2. The qualitative emission data of selected dibenzo-heterocycles incorporated benzo[*c*]thiophenes were recorded in DCM solution and the emission values are also presented. The HOMO and LUMO energy levels of benzo[*c*]thiophenes were calculated from the absorption and the onset oxidation potential. The E_g, HOMO, and LUMO values obtained for the representative benzo[*c*]thiphenes are presented in Table 2. The monomeric benzo[*c*]thiophene analogs showed E_g values in the range of 2.7–2.8 eV. The dimerization of benzo[*c*]thiophenes reduced the E_g values around ~0.3 eV. In general, dimerization only slightly reduced and enhanced the HOMO energy levels (~5.2 eV to ~5.0 eV) and LUMO energy levels (~2.4 eV to ~2.5 eV), respectively (Table 2).

4. Conclusions

In summary, the synthesis of benzo[*c*]thiophene analogs incorporating dibenzo-heterocycle as well as triphenylamine units was achieved in reasonable yields. The highly soluble nature of these benz-annelated thiophenes may make them suitable for transistor applications through spin-coating techniques. The higher-lying HOMO energy levels of these dibenzo-heterocycles incorporated benzo[*c*]thiophenes (~5.1 to 5.2 eV) may find them as suitable candidates for application as hole-transporting materials in double-layer OLEDs.

5. Experimental

5.1. General

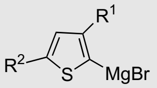
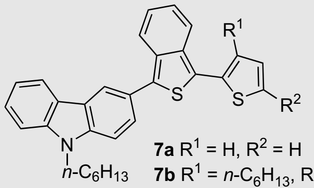
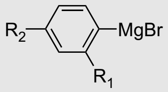
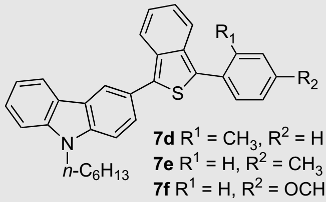
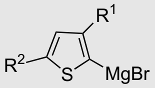
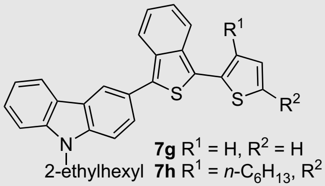
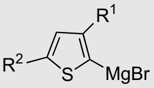
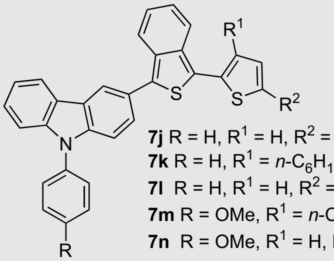
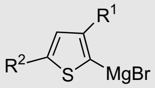
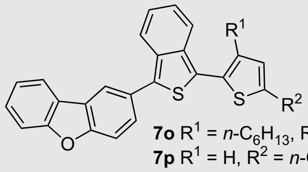
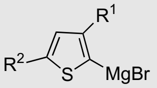
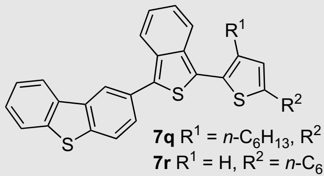
All melting points are uncorrected. IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Bruker-300 spectrometer. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. Elemental analyses were carried out on a Perkin–Elmer series II 2400 (IIT Madras) instrument. All UV–vis spectra were recorded in CH_2Cl_2 solution. The emission spectra were recorded on Perkin–Elmer LS-45 spectrophotometer. The cyclic voltammogram of 10^{-3} M solution of benzo[*c*]thiophenes was carried out on a CHI 600C electrochemical analyzer. All the measurements were carried out under oxygen free condition using three electrode cells in which glassy carbon electrode was working electrode, saturated Ag/AgCl electrode was reference electrode, and platinum wire was used as an auxiliary electrode. Tetrabutylammoniumhexafluoro phosphate ($TBAPF_6$) was used as supporting electrolyte and its concentration was 10^{-1} M.

5.2. A representative procedure for the preparation of lactone 5a from dibenzo-heterocycle 2a (procedure A)

*5.2.1. 3-(9-Hexyl-9H-carbazol-3-yl)isobenzofuran-1(3H)-one (**5a**)*

To a stirred suspension of phthalic anhydride (7.07 g, 47.81 mmol) in dry DCM (150 mL), powdered anhydrous $AlCl_3$ (7.96 g, 59.76 mmol) was added in two portions to get yellow solution, which was cooled to 0 °C. *N*-Hexyl carbazole **2a** (10 g, 39.84 mmol) in DCM (20 mL) was added dropwise to the above solution at 0 °C and stirred for 4 h at room temperature. The reaction mixture was quenched with ice water containing HCl and extracted with DCM (2×30 mL). Evaporation of solvent gave crude keto acid, which was dissolved in THF/EtOH (2:5). To this solution, $NaBH_4$ (7.57 g, 199.2 mmol) was added in portions and refluxed for 10 h. The reaction mixture was poured into water and concd HCl was added dropwise under stirring (pH=1–2). It was then extracted with EtOAc and dried (Na_2SO_4). Solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (10% EA/Hexane) to give the title compound **5a** [6.1 g, 40% (two steps)] as a thick yellow liquid. [Found: C, 81.6; H, 6.4; N, 3.5. $C_{26}H_{25}NO_2$ requires: C, 81.43; H, 6.57; N, 3.65%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2851, 1759, 1595, 1500, 745 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.03–7.97 (3H, m, ArH), 7.64–7.48 (2H, m, ArH), 7.46–7.43 (1H, m, ArH), 7.40–7.31 (3H, m, ArH), 7.27–7.18 (2H, m, ArH), 6.58 (1H, s, CH), 4.23 (2H, t, *J* 7.2 Hz, NCH_2), 1.84–1.71 (2H, m, CH_2), 1.42–1.25 (6H, m, CH_2), 0.90–0.82 (3H, m, CH_3); δ_C

Table 1
Synthesis of benzo[*c*]thiophene analogs containing dibenzo-heterocycles

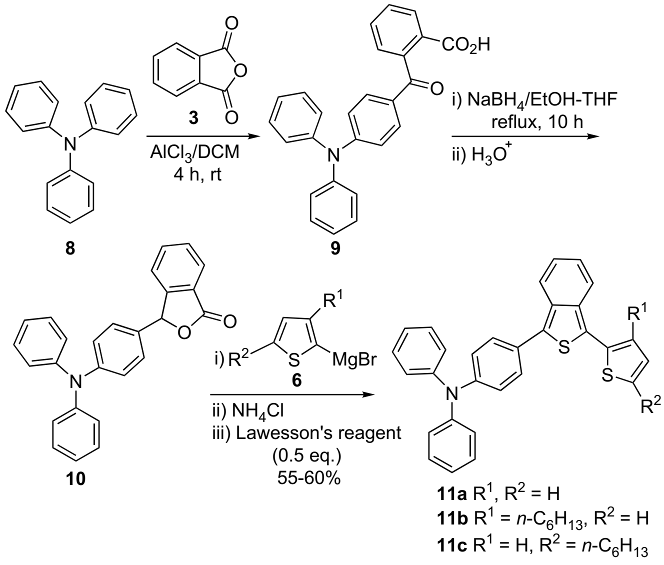
Entry	Lactones	ArMgBr	Products	Yield (%)[a] mp
1	**5a**	 **6a** $R^1 = H, R^2 = H$ **6b** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **6c** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	 **7a** $R^1 = H, R^2 = H$ **7b** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **7c** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	52 (Orange liquid) 48 (Orange liquid) 53 (Orange liquid)
2	**5a**	 **6d** $R^1 = CH_3, R^2 = H$ **6e** $R^1 = H, R^2 = CH_3$ **6f** $R^1 = H, R^2 = OCH_3$	 **7d** $R^1 = CH_3, R^2 = H$ **7e** $R^1 = H, R^2 = CH_3$ **7f** $R^1 = H, R^2 = OCH_3$	55 (Orange liquid) 48 (Orange liquid) 57 (Orange liquid)
3	**5b**	 **6a** $R^1 = H, R^2 = H$ **6b** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **6c** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	 **7g** $R^1 = H, R^2 = H$ **7h** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **7i** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	57 (Orange liquid) 61 (Orange liquid) 50 (Orange liquid)
4	**5c**/**5d**	 **6a** $R^1 = H, R^2 = H$ **6b** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **6c** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	 **7j** $R = H, R^1 = H, R^2 = H$ **7k** $R = H, R^1 = n\text{-}C_6H_{13}, R^2 = H$ **7l** $R = H, R^1 = H, R^2 = n\text{-}C_6H_{13}$ **7m** $R = OMe, R^1 = n\text{-}C_6H_{13}, R^2 = H$ **7n** $R = OMe, R^1 = H, R^2 = n\text{-}C_6H_{13}$	55 (114 °C) 57 (62 °C) 51 (Orange liquid) 61 (Orange liquid) 49 (Orange liquid)
5	**5e**	 **6b** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **6c** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	 **7o** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **7p** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	51 (115 °C) 55 (Orange liquid)
6	**5f**	 **6b** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **6c** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	 **7q** $R^1 = n\text{-}C_6H_{13}, R^2 = H$ **7r** $R^1 = H, R^2 = n\text{-}C_6H_{13}$	60 (107 °C) 57 (Orange liquid)

[a] Isolated yield of products after column chromatography.

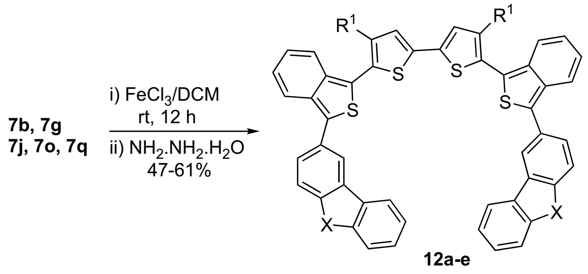
(75.6 MHz, $CDCl_3$) 170.8, 150.3, 140.9, 134.2, 129.2, 126.4, 126.1, 126.0, 125.5, 124.9, 123.2, 123.0, 122.5, 120.5, 119.8, 119.2, 109.2, 109.0, 84.0, 43.2, 31.6, 28.9, 26.9, 22.5, 14.0; *m*/*z* (EI) 383 (100, M^+).

*5.2.2. 3-(9-(2-Ethylhexyl)-9H-carbazol-3-yl)isobenzofuran-1(3H)-one (**5b**)*

Following the above-mentioned procedure (A), lactone **5b** (6.03 g, 41%) was obtained using *N*-(2-ethylhexyl carbazole) **2b**



Scheme 2.



Compound	X	R^1	Yield
12a	N-*n*-C_6H_{13}	*n*-C_6H_{13}	61%
12b	N-*n*-2-Ethylhexyl	H	50%
12c	N-Ph	H	47%
12d	O	*n*-C_6H_{13}	52%
12e	S	n-C_6H_{13}	55%

Scheme 3.

Table 2
Summary of the physical properties of selected benzo[*c*]thiophenes

Compound	λ_{max}[a] (nm)	λ_{emiss}[b] (nm)	E_g[c] (eV)	E_{ox}^{onset} (eV)	HOMO[d] (eV)	LUMO[e] (eV)
7a	455	550	2.72	0.70	5.14	2.42
7b	450	540	2.75	0.69	5.13	2.38
7g	465	544	2.67	0.71	5.15	2.48
7h	458	550	2.71	0.68	5.12	2.41
7j	445	530	2.78	0.70	5.14	2.36
7l	458	545	2.71	0.73	5.17	2.46
7o	445	530	2.78	0.70	5.14	2.36
7q	458	545	2.71	0.73	5.17	2.46
11a	457	545	2.71	0.65	5.09	2.38
11b	445	535	2.78	0.72	5.16	2.38
11c	440	540	2.82	0.71	5.15	2.33
12a	497	615	2.49	0.57	5.01	2.52
12b	492	597	2.52	0.55	4.99	2.47
12c	498	605	2.49	0.58	5.02	2.53
12d	505	650	2.45	0.55	4.99	2.54
12e	510	645	2.43	0.57	5.01	2.58

[a] Measured in dilute dichloromethane solution.
[b] Excited at absorption maxima.
[c] Estimated from the absorption (E_g=1240/λ_{max}).
[d] Calculated using the empirical equation: HOMO=(4.44+E_{ox}^{onset}).
[e] Calculated from LUMO=HOMO−E_g.

(10 g, 35.84 mmol), phthalic anhydride (6.36 g, 43.00 mmol), $AlCl_3$ (7.16 g, 53.75 mmol), and $NaBH_4$ (6.81 g, 179.2 mmol) as a thick yellow liquid. [Found: C, 82.0; H, 7.3; N, 3.2. $C_{28}H_{29}NO_2$ requires: C, 81.72; H, 7.10; N, 3.40%.] R_f (10% EA/Hexane) 0.65; ν_{max} (KBr) 2822, 1759, 1596, 1500, 762 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.04–7.97 (3H, m, ArH), 7.66–7.60 (2H, m, ArH), 7.57–7.52 (1H, m, ArH), 7.48–7.43 (1H, m, ArH), 7.39–7.35 (1H, m, ArH), 7.33 (1H, s, ArH), 7.27–7.18 (2H, m, ArH), 6.59 (1H, s, CH), 4.13–4.10 (2H, m, NCH_2), 2.03 (1H, m, CH), 1.42–1.21 (7H, m, CH_2CH_3), 0.91–0.82 (7H, m, CH_2CH_3); δ_C (75.6 MHz, $CDCl_3$) 170.8, 150.3, 140.4, 134.3, 129.2, 126.4, 126.1, 126.0, 125.5, 124.9, 123.2, 123.0, 122.4, 120.4, 119.8, 119.2, 109.5, 109.3, 84.0, 47.5, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.9; *m*/*z* (EI) 411 (13, M^+).

5.2.3. *3-(9-Phenyl-9H-carbazol-3-yl)isobenzofuran-1(3H)-one (**5c**)*

Following the above-mentioned procedure (A), lactone **5c** (6.93 g, 45%) was obtained using *N*-phenyl carbazole **2c** (10 g, 41.15 mmol), phthalic anhydride (7.30 g, 49.38 mmol), $AlCl_3$ (8.22 g, 61.72 mmol), and $NaBH_4$ (7.82 g, 205.76 mmol) as a colorless solid; mp 87 °C. [Found: C, 83.0; H, 4.8; N, 3.5. $C_{26}H_{17}NO_2$ requires: C, 83.18; H, 4.56; N, 3.73%.] R_f (10% EA/Hexane) 0.55; ν_{max} (KBr) 1761, 1600, 1501, 753 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.09–7.98 (3H, m, ArH), 7.64–7.41 (7H, m, ArH), 7.40–7.20 (6H, m, ArH), 6.60 (1H, s, CH); δ_C (75.6 MHz, $CDCl_3$) 170.8, 150.3, 141.5, 141.4, 137.3, 134.3, 130.0, 129.3, 127.8, 127.7, 127.1, 126.5, 125.9, 125.6, 125.1, 123.6, 123.1, 122.9, 120.5, 120.3, 119.6, 110.3, 110.0, 83.8; *m*/*z* (EI) 375 (13, M^+).

5.2.4. *3-(9-(4-Methoxyphenyl)-9H-carbazol-3-yl)isobenzofuran-1(3H)-one (**5d**)*

Following the above-mentioned procedure (A), lactone **5d** (6.22 g, 42%) was obtained using *N*-(*p*-anisyl)carbazole **2d** (10 g, 36.49 mmol), phthalic anhydride (6.48 g, 43.79 mmol), $AlCl_3$ (7.29 g, 54.74 mmol), and $NaBH_4$ (6.93 g, 182.48 mmol) as a colorless solid; mp 95 °C. [Found: C, 80.2; H, 4.5; N, 3.3. $C_{27}H_{19}NO_3$ requires: C, 79.98; H, 4.72; N, 3.45%.] R_f (10% EA/Hexane) 0.51; ν_{max} (KBr) 2811, 1759, 1605, 1500, 755, 685 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.04–8.01 (3H, m, ArH), 7.61–7.54 (2H, m, ArH), 7.36–7.25 (8H, m, ArH), 7.08 (2H, s, ArH), 6.59 (1H, s, CH), 3.87 (3H, s, OCH_3); δ_c (75.6 MHz, $CDCl_3$) 170.8, 159.1, 150.3, 141.9, 141.8, 134.3, 129.83, 129.3, 128.5, 127.5, 126.4, 126.0, 125.6, 125.1, 123.4, 123.1, 122.7, 120.4, 120.1, 119.6, 115.2, 110.3, 110.0, 83.9, 55.6; *m*/*z* (EI) 405 (13, M^+).

5.2.5. *3-(Dibenzofuran-3-yl)isobenzofuran-1(3H)-one (**5e**)*

Following the above-mentioned procedure (A), lactone **5e** (7.14 g, 40%) was obtained using dibenzofuran **2e** (10 g, 59.52 mmol), phthalic anhydride (10.57 g, 71.43 mmol), $AlCl_3$ (11.89 g, 89.28 mmol), and $NaBH_4$ (11.3 g, 297.61 mmol) as a colorless solid; mp 171 °C. [Found: C, 80.2; H, 3.8; $C_{20}H_{12}O_3$ requires: C, 79.99; H, 4.03%.] R_f (10% EA/Hexane) 0.60; ν_{max} (KBr) 1755, 1585, 1500, 741 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.99 (1H, t, *J* 7.5 Hz, ArH), 7.92–7.83 (2H, m, ArH), 7.66–7.61 (1H, m, ArH), 7.58–7.52 (3H, m, ArH), 7.44 (1H, t, *J* 7.5 Hz, ArH), 7.34–7.25 (3H, m, ArH), 6.55 (1H, s, CH); δ_C (75.6 MHz, $CDCl_3$) 170.6, 156.7, 156.5, 149.9, 134.5, 131.0, 129.5, 127.7, 126.2, 125.7, 124.9, 123.6, 123.0, 123.0, 120.9, 119.7, 112.2, 111.8, 83.0; *m*/*z* (EI) 300 (100, M^+).

5.2.6. *3-(Dibenzothiophen-3-yl)isobenzofuran-1(3H)-one (**5f**)*

Following the above-mentioned procedure (A), lactone **5f** (6.52 g, 38%) was obtained using dibenzothiophene **2f** (10 g, 54.34 mmol), phthalic anhydride (9.65 g, 65.22 mmol), $AlCl_3$ (10.86 g, 81.52 mmol), and $NaBH_4$ (10.3 g, 271.74 mmol) as a colorless solid; mp 90 °C. [Found: C, 75.7; H, 3.7; S, 10.4. $C_{20}H_{12}O_2S$ requires: C, 75.93; H, 3.82; S, 10.14%.] R_f (10% EA/Hexane) 0.65; ν_{max} (KBr) 1759, 1595, 1500, 741 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.09–8.04 (2H, m, ArH), 7.99 (1H, t, *J* 7.5 Hz, ArH), 7.82–7.80 (2H, m, ArH), 7.65–7.52 (2H, m, ArH), 7.45–7.42 (2H, m, ArH), 7.34–7.26 (2H, m, ArH), 6.55 (1H, s, CH);

δ_C (75.6 MHz, $CDCl_3$) 170.6, 149.8, 140.5, 139.9, 136.0, 134.9, 134.5, 132.8, 129.5, 127.2, 125.7, 125.6, 125.3, 124.6, 123.4, 123.0, 122.9, 121.8, 120.3, 82.9; *m*/*z* (EI) 316 (45, M^+).

5.3. A representative procedure for the preparation of benzo[*c*]thiophene (7a) from lactone (5a) (procedure B)

*5.3.1. 9-Hexyl-3-(1-(thiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**7a**)*

To a solution of lactone **5a** (2 g, 5.22 mmol) in anhydrous THF (25 mL) was added 2-thienylmagnesium bromide [prepared from 2-bromothiophene (1.02 g, 6.26 mmol) and magnesium turnings (0.16 g, 6.88 mmol)] at 0 °C under N_2. The reaction mixture was slowly raised to room temperature and stirred for 4 h. It was then quenched with aq NH_4Cl solution, extracted with DCM (2×20 mL), and dried (Na_2SO_4). The DCM solution was then stirred with Lawesson's reagent (1.06 g, 2.61 mmol) at room temperature for 4 h. Solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (100% Hexane) to give the title compound **7a** (1.26 g, 52%) as an orange liquid. [Found: C, 77.1; H, 5.7; N, 3.2; S, 14.0. $C_{30}H_{27}NS_2$ requires: C, 77.38; H, 5.84; N, 3.01; S, 13.77%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2822, 1596, 1500, 762 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.34 (1H, s, ArH), 8.12 (1H, d, *J* 7.5 Hz, ArH), 7.97 (1H, d, *J* 8.7 Hz, ArH), 7.87 (1H, d, *J* 8.7 Hz, ArH), 7.72 (1H, d, *J* 8.4 Hz, ArH), 7.70–7.37 (3H, m, ArH), 7.34–7.30 (2H, m, ArH), 7.23 (1H, t, *J* 6.9 Hz, ArH), 7.14–7.06 (3H, m, ArH), 4.26 (2H, t, *J* 7.05 Hz, NCH_2), 1.90–1.81 (2H, m, CH_2), 1.38–1.25 (6H, m, CH_2), 0.88–0.84 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 141.0, 140.1, 136.5, 135.8, 135.4, 135.0, 127.9, 127.3, 126.1, 125.7, 125.1, 124.9, 124.6, 124.6, 124.0, 123.6, 122.8, 121.7, 121.4, 121.2, 120.6, 119.2, 109.3, 109.0, 43.3, 31.7, 29.1, 27.1, 22.6, 14.1; *m*/*z* (EI) 465 (13, M^+).

*5.3.2. 9-Hexyl-3-(1-(3-hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**7b**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7b** (1.38 g, 48%) was obtained using lactone **5a** (2 g, 5.22 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.55 g, 6.27 mmol) and Mg (0.16 g, 6.90 mmol)], and Lawesson's reagent (1.06 g, 2.61 mmol) as a thick orange liquid. [Found: C, 78.4; H, 7.3; N, 2.8; S, 11.4. $C_{36}H_{39}NS_2$ requires: C, 78.64; H, 7.15; N, 2.55; S, 11.66%.] R_f (100% Hexane) 0.72; δ_H (300 MHz, $CDCl_3$) 8.37 (1H, s, ArH), 8.13 (1H, d, *J* 7.8 Hz, ArH), 7.91–7.87 (1H, m, ArH), 7.76 (1H, d, *J* 10.2 Hz, ArH), 7.61–7.60 (1H, m, ArH), 7.48–7.34 (4H, m, ArH), 7.24 (1H, d, *J* 7.35 Hz, ArH), 7.08–7.05 (3H, m, ArH), 4.29 (2H, t, *J* 7.2 Hz, NCH_2), 2.68 (2H, d, *J* 7.8 Hz, CH_2), 1.94–1.85 (2H, m, CH_2), 1.63–1.58 (2H, m, CH_2), 1.41–1.21 (12H, m, CH_2), 0.88–0.79 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.2, 141.0, 140.1, 137.9, 137.1, 134.2, 129.3, 128.6, 127.4, 126.1, 125.7, 124.8, 124.0, 123.8, 123.7, 123.6, 122.8, 121.7, 121.3, 121.2, 120.6, 119.2, 109.2, 109.0, 43.3, 31.7, 30.9, 29.2, 29.1, 29.0, 27.0, 22.6, 14.1, 14.0; *m*/*z* (EI) 549 (45, M^+).

*5.3.3. 9-Hexyl-3-(1-(5-hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**7c**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7c** (1.52 g, 53%) was obtained using lactone **5a** (2 g, 5.22 mmol), 5-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.55 g, 6.27 mmol) and Mg (0.16 g, 6.90 mmol)], and Lawesson's reagent (1.06 g, 2.61 mmol) as a thick orange liquid. [Found: C, 78.4; H, 7.3; N, 2.8; S, 11.4. $C_{36}H_{39}NS_2$ requires: C, 78.64; H, 7.15; N, 2.55; S, 11.66%.] R_f (100% Hexane) 0.72; δ_H (300 MHz, $CDCl_3$) 8.34 (1H, s, ArH), 8.13 (1H, d, *J* 7.5 Hz, ArH), 7.97 (1H, d, *J* 8.4 Hz, ArH), 7.86 (1H, d, *J* 8.7 Hz, ArH), 7.74 (1H, d, *J* 8.4 Hz, ArH), 7.51–7.40 (3H, m, ArH), 7.23–7.22 (1H, m, ArH), 7.17–7.04 (3H, m, ArH), 6.80 (1H, t, *J* 3.3 Hz, ArH), 4.30 (2H, t, *J* 6.9 Hz, NCH_2), 2.85 (2H, t, *J* 7.5 Hz, CH_2), 1.91–1.83 (2H, m, CH_2), 1.76–1.69 (2H, m, CH_2), 1.39–1.25 (12H, m, CH_2), 0.93–0.85 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 146.0, 141.0, 140.0, 135.0, 134.9, 133.8, 127.3, 126.5, 126.1, 124.8, 124.7, 124.6, 124.3, 123.9, 123.5, 122.8, 121.6, 121.5, 121.2, 120.6, 119.2, 109.2, 109.0, 43.3, 31.6, 30.3, 29.0, 28.9, 27.0, 22.6, 22.6, 14.1, 14.0; *m*/*z* (EI) 549 (27, M^+).

*5.3.4. 9-Hexyl-3-(1-o-tolylbenzo[c]thiophen-3-yl)-9H-carbazole (**7d**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7d** (1.36 g, 55%) was obtained using lactone **5a** (2 g, 5.22 mmol), *o*-tolylmagnesium bromide [prepared from 2-bromotoluene (1.07 g, 6.26 mmol) and Mg (0.16 g, 6.88 mmol)], and Lawesson's reagent (1.06 g, 2.61 mmol) as a thick orange liquid. [Found: C, 83.5; H, 6.8; N, 2.8; S, 6.5. $C_{33}H_{31}NS$ requires: C, 83.68; H, 6.60; N, 2.96; S, 6.77%.] R_f (100% Hexane) 0.72; δ_H (300 MHz, $CDCl_3$) 8.39 (1H, s, ArH), 8.12 (1H, d, *J* 7.5 Hz, ArH), 7.90 (1H, d, *J* 8.4 Hz, ArH), 7.76 (1H, d, *J* 8.4 Hz, ArH), 7.46–7.44 (3H, m, ArH), 7.39–7.27 (6H, m, ArH), 7.02 (2H, t, *J* 8.4 Hz, ArH), 4.26 (2H, t, *J* 6.9 Hz, NCH_2), 2.33 (3H, s, CH_3), 1.85 (2H, q, *J* 6.4 Hz, CH_2), 1.40–1.29 (6H, m, CH_2), 0.85 (3H, t, *J* 5.8 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 141.0, 140.0, 139.0, 138.1, 136.7, 135.8, 134.0, 133.2, 132.3, 131.7, 130.9, 130.6, 128.3, 127.4, 126.1, 125.8, 125.1, 123.7, 122.9, 121.6, 121.4, 121.2, 120.7, 119.2, 109.2, 109.0, 43.3, 31.7, 29.1, 27.1, 22.7, 20.8, 14.0; *m*/*z* (EI) 473 (23, M^+).

*5.3.5. 9-Hexyl-3-(1-p-tolylbenzo[c]thiophen-3-yl)-9H-carbazole (**7e**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7e** (1.18 g, 48%) was obtained using lactone **5a** (2 g, 5.22 mmol), *p*-tolylmagnesium bromide [prepared from 4-bromotoluene (1.07 g, 6.26 mmol) and Mg (0.16 g, 6.88 mmol)], and Lawesson's reagent (1.06 g, 2.61 mmol) as a thick orange liquid. [Found: C, 83.4; H, 6.7; N, 2.8; S, 6.6. $C_{33}H_{31}NS$ requires: C, 83.68; H, 6.60; N, 2.96; S, 6.77%.] R_f (100% Hexane) 0.72; δ_H (300 MHz, $CDCl_3$) 8.37 (1H, s, ArH), 8.14 (1H, d, *J* 7.8 Hz, ArH), 7.91–7.84 (2H, m, ArH), 7.78–7.75 (1H, m, ArH), 7.61 (1H, d, *J* 7.8 Hz, ArH), 7.49–7.43 (3H, m, ArH), 7.40–7.20 (5H, m, ArH), 7.09–7.05 (1H, m, ArH), 4.31 (2H, t, *J* 7.2 Hz, NCH_2), 2.42 (3H, s, CH_3), 1.91–1.87 (2H, m, CH_2), 1.41–1.25 (6H, m, CH_2), 0.87 (3H, t, *J* 6.9 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 141.0, 140.0, 137.1, 135.4, 135.0, 134.9, 133.2, 131.8, 129.8, 129.1, 127.4, 126.8, 126.1, 125.0, 124.0, 123.8, 123.5, 122.8, 121.6, 121.2, 120.6, 119.1, 109.2, 109.0, 43.3, 37.6, 29.1, 27.0, 22.6, 21.3, 14.1; *m*/*z* (EI) 473 (35, M^+).

*5.3.6. 9-Hexyl-3-(1-(4-methoxyphenyl)benzo[c]thiophen-3-yl)-9H-carbazole (**7f**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7f** (1.45 g, 57%) was obtained using lactone **5a** (2 g, 4.86 mmol), *p*-anisylmagnesium bromide [prepared from 4-bromoanisole (1.17 g, 6.26 mmol) and Mg (0.16 g, 6.88 mmol)], and Lawesson's reagent (1.06 g, 2.61 mmol) as a thick orange liquid. [Found: C, 80.7; H, 6.6; N, 2.7; S, 6.8. $C_{33}H_{31}NOS$ requires: C, 80.94; H, 6.38; N, 2.86; S, 6.55%.] R_f (100% Hexane) 0.69; δ_H (300 MHz, $CDCl_3$) 8.37 (1H, s, ArH), 8.14 (1H, d, *J* 7.5 Hz, ArH), 7.81–7.75 (2H, m, ArH), 7.91–7.88 (1H, m, ArH), 7.50–7.43 (3H, m, ArH), 7.25 (1H, t, *J* 6.9 Hz, ArH), 7.08–7.02 (3H, m, ArH), 6.94 (1H, d, *J* 8.7 Hz, ArH), 4.31 (2H, t, *J* 7.05 Hz, NCH_2), 3.87 (3H, s, OCH_3), 1.92–1.89 (2H, m, CH_2), 1.42–1.25 (6H, m, CH_2), 0.88 (3H, t, *J* 6.9 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 159.1, 158.7, 141.0, 139.9, 134.9, 133.5, 133.0, 130.4, 127.7, 127.4, 126.0, 125.0, 123.9, 123.7, 123.5, 122.8, 121.5, 121.1, 120.6, 119.1, 114.5, 114.2, 109.2, 108.9, 55.4, 43.3, 31.6, 29.0, 27.0, 22.6, 14.0; *m*/*z* (EI) 489 (13, M^+).

*5.3.7. 9-(2-Ethylhexyl)-3-(1-(thiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**7g**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7g** (1.37 g, 57%) was obtained using lactone **5b** (2 g, 4.86 mmol), 2-thienylmagnesium bromide [prepared from 2-bromothiophene (0.95 g, 5.84 mmol) and Mg (0.15 g, 6.41 mmol)], and

Lawesson's reagent (0.98 g, 2.43 mmol) as a thick orange liquid. [Found: C, 77.6; H, 6.1; N, 2.6; S, 13.2. $C_{32}H_{31}NS_2$ requires: C, 77.85; H, 6.33; N, 2.84; S, 12.99%.] R_f (100% Hexane) 0.75; δ_H (300 MHz, $CDCl_3$) 8.24 (1H, s, ArH), 8.02 (1H, d, *J* 7.8 Hz, ArH), 7.87 (1H, d, *J* 8.7 Hz, ArH), 7.77 (1H, d, *J* 8.4 Hz, ArH), 7.63–7.60 (1H, m, ArH), 7.39–7.21 (5H, m, ArH), 7.16–7.08 (1H, m, ArH), 7.04–6.94 (3H, m, ArH), 4.05–4.02 (2H, m, NCH_2), 1.99–1.96 (1H, m, CH), 1.32–1.15 (7H, m, CH_2CH_3), 0.84–0.75 (7H, m, CH_2CH_3); δ_C (75.6 MHz, $CDCl_3$) 141.5, 140.6, 136.5, 135.8, 135.4, 135.0, 127.9, 127.3, 126.1, 125.7, 125.1, 125.0, 124.6, 124.5, 124.0, 123.5, 122.8, 121.7, 121.4, 121.1, 120.6, 119.2, 109.5, 109.3, 47.6, 39.5, 31.1, 28.9, 24.5, 23.2, 14.1, 11.0; *m*/*z* (EI) 493 (100, M^+).

*5.3.8. 9-(2-Ethylhexyl)-3-(1-(3-hexylthiophen-2-yl)benzo[c]-thiophen-3-yl)-9H-carbazole (**7h**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7h** (1.71 g, 61%) was obtained using lactone **5b** (2 g, 4.86 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.44 g, 5.84 mmol) and Mg (0.5 g, 6.41 mmol)], and Lawesson's reagent (0.98 g, 2.43 mmol) as a thick orange liquid. [Found: C, 77.8; H, 7.3; N, 2.2; S, 11.3. $C_{38}H_{43}NS_2$ requires: C, 78.98; H, 7.50; N, 2.42; S, 11.10%.] R_f (100% Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.49–8.48 (1H, m, ArH), 8.24 (1H, d, *J* 7.8 Hz, ArH), 8.02–7.99 (1H, m, ArH), 7.88–7.85 (1H, m, ArH), 7.73–7.70 (1H, m, ArH), 7.60–7.44 (4H, m, ArH), 7.37–7.31 (1H, m, ArH), 7.20–7.15 (3H, m, ArH), 4.30–4.24 (2H, m, NCH_2), 2.78 (2H, d, *J* 7.5 Hz, CH_2), 2.23–2.18 (1H, m, CH), 1.74–1.67 (2H, m, CH_2), 1.52–1.33 (13H, m, CH_2CH_3), 1.05–0.98 (10H, m, CH_2CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.2, 141.5, 140.6, 137.9, 137.1, 134.2, 129.3, 128.6, 127.4, 126.1, 125.7, 124.8, 124.1, 123.8, 123.7, 123.5, 122.8, 121.7, 121.4, 121.2, 120.6, 119.2, 109.5, 109.3, 47.6, 39.6, 31.7, 31.1, 31.0, 29.8, 29.2, 29.2, 28.9, 24.5, 23.2, 22.7, 14.2, 11.0; *m*/*z* (EI) 577 (25, M^+).

*5.3.9. 9-(2-Ethylhexyl)-3-(1-(5-hexylthiophen-2-yl)benzo[c]-thiophen-3-yl)-9H-carbazole (**7i**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7i** (1.40 g, 50%) was obtained using lactone **5b** (2 g, 4.86 mmol), 5-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.44 g, 5.84 mmol) and Mg (0.5 g, 6.41 mmol)], and Lawesson's reagent (0.98 g, 2.43 mmol) as a thick orange liquid. [Found: C, 78.8; H, 7.3; N, 2.6; S, 11.3. $C_{38}H_{43}NS_2$ requires: C, 78.98; H, 7.50; N, 2.42; S, 11.10%.] R_f (100% Hexane) 0.75; δ_H (300 MHz, $CDCl_3$) 8.41–8.40 (1H, m, ArH), 8.07 (1H, d, *J* 8.1 Hz, ArH), 8.03–8.01 (1H, m, ArH), 7.95–7.92 (1H, m, ArH), 7.81–7.78 (1H, m, ArH), 7.57–7.45 (3H, m, ArH), 7.33–7.28 (1H, m, ArH), 7.18–7.10 (3H, m, ArH), 6.86 (1H, d, *J* 3.6 Hz, ArH), 4.24–4.21 (2H, m, NCH_2), 2.92 (2H, d, *J* 7.5 Hz, CH_2), 2.22–2.14 (2H, m, CH_2), 1.80 (2H, q, *J* 7.5 Hz, CH_2), 1.47–1.40 (12H, m, CH_2), 1.04–0.92 (10H, m, CH_2CH_3); δ_C (75.6 MHz, $CDCl_3$) 146.0, 141.5, 140.5, 135.0, 134.9, 133.8, 127.3, 126.5, 126.1, 124.8, 124.8, 124.7, 124.3, 123.9, 123.5, 122.8, 121.6, 121.1, 120.5, 119.1, 109.5, 109.3, 47.6, 39.5, 31.7, 31.1, 30.9, 30.3, 29.8, 28.9, 24.5, 23.1, 22.6, 14.1, 14.0, 11.1; *m*/*z* (EI) 577 (13, M^+).

*5.3.10. 3-(1-(Thiophen-2-yl)benzo[c]thiophen-3-yl)-9-phenyl-9H-carbazole (**7j**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7j** (1.33 g, 55%) was obtained using lactone **5c** (2 g, 5.33 mmol), 2-thienylmagnesium bromide [prepared from 2-bromothiophene (1.04 g, 6.4 mmol) and Mg (0.17 g, 7.02 mmol)], and Lawesson's reagent (1.08 g, 2.66 mmol) as an orange solid; mp 80 °C. [Found: C, 79.0; H, 4.3; N, 2.8; S, 13.8. $C_{30}H_{19}NS_2$ requires: C, 78.74; H, 4.18; N, 3.06; S, 14.01%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 1600, 1505, 761 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.40–8.39 (1H, m, ArH), 8.18 (1H, d, *J* 7.8 Hz, ArH), 8.00 (1H, d, *J* 8.4 Hz, ArH), 7.88 (1H, d, *J* 8.4 Hz, ArH), 7.71–7.58 (6H, m, ArH), 7.53–7.48 (2H, m, ArH), 7.46–7.42 (2H, m, ArH), 7.37–7.30 (2H, m, ArH), 7.16–7.09 (3H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 141.5, 140.5, 137.5, 136.3, 135.4, 135.3, 135.1, 130.1, 130.0, 127.8, 127.7, 127.6, 127.1, 126.5, 125.8, 125.2, 125.1, 124.6, 124.1, 124.0, 123.2, 121.5, 121.4, 121.1, 120.6, 120.3, 110.4, 110.1; *m*/*z* (EI) 457 (41, M^+).

*5.3.11. 3-(1-(3-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-9-phenyl-9H-carbazole (**7k**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7k** (1.47 g, 52%) was obtained using lactone **5c** (2 g, 5.33 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.58 g, 6.4 mmol) and Mg (0.17 g, 7.02 mmol)], and Lawesson's reagent (1.08 g, 2.66 mmol) as an orange solid; mp 62 °C. [Found: C, 79.5; H, 6.0; N, 2.8; S, 11.6. $C_{36}H_{31}NS_2$ requires: C, 79.81; H, 5.77; N, 2.59; S, 11.84%.] R_f (100% Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.41 (1H, d, *J* 6.3 Hz, ArH), 8.16 (1H, t, *J* 8.1 Hz, ArH), 7.90–7.85 (1H, m, ArH), 7.72–7.69 (1H, m, ArH), 7.60–7.55 (5H, m, ArH), 7.51–7.36 (4H, m, ArH), 7.34–7.27 (2H, m, ArH), 7.09–7.02 (3H, m, ArH), 2.71–2.63 (2H, m, CH_2), 1.63–1.56 (2H, m, CH_2), 1.21–1.19 (6H, m, CH_2), 0.81–0.77 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.2, 141.4, 140.5, 137.9, 137.5, 136.7, 134.3, 130.0, 129.3, 128.5, 127.7, 127.1, 127.0, 126.5, 126.0, 125.7, 124.1, 124.0, 123.9, 123.3, 121.7, 121.2, 121.1, 120.6, 120.3, 110.4, 110.1, 31.7, 30.9, 29.2, 29.1, 22.6, 14.1; *m*/*z* (EI) 541 (100, M^+).

*5.3.12. 3-(1-(5-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-9-phenyl-9H-carbazole (**7l**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7l** (1.47 g, 51%)was obtained using lactone **5c** (2 g, 5.33 mmol), 5-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.58 g, 6.4 mmol) and Mg (0.17 g, 7.02 mmol)], and Lawesson's reagent (1.08 g, 2.66 mmol) as a thick orange liquid. [Found: C, 79.6; H, 6.1; N, 2.8; S, 11.6. $C_{36}H_{31}NS_2$ requires: C, 79.81; H, 5.77; N, 2.59; S, 11.84%.] R_f (100% Hexane) 0.72; ν_{max} (KBr) 2851, 1597, 1500, 765 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.43–8.42 (1H, m, ArH), 8.19 (1H, d, *J* 7.5 Hz, ArH), 7.91–7.88 (1H, m, ArH), 7.74–7.65 (1H, m, ArH), 7.64–7.59 (5H, m, ArH), 7.52–7.46 (4H, m, ArH), 7.43 (1H, d, *J* 3.9 Hz, ArH), 7.36–7.30 (2H, m, ArH), 7.10–7.06 (2H, m, ArH), 2.69 (2H, t, *J* 7.65 Hz, CH_2), 1.64–1.59 (2H, m, CH_2), 1.29–1.22 (6H, m, CH_2), 0.84–0.80 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.2, 141.4, 140.5, 137.9, 137.5, 136.7, 134.3, 130.0, 129.3, 128.5, 127.7, 127.1, 127.0, 126.5, 126.0, 125.7, 124.1, 124.0, 123.9, 123.3, 121.7, 121.2, 121.1, 120.6, 120.3, 110.4, 110.1, 31.7, 30.9, 29.2, 29.1, 22.6, 14.1; *m*/*z* (EI) 541 (51, M^+).

*5.3.13. 3-(1-(3-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-9-(4-methoxyphenyl)-9H-carbazole (**7m**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7m** (1.20 g, 61%) was obtained using lactone **5d** (2 g, 4.94 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.46 g, 5.92 mmol) and Mg (0.16 g, 6.48 mmol)], and Lawesson's reagent (1.00 g, 2.47 mmol) as a thick orange liquid. [Found: C, 77.5; H, 6.0; N, 2.7; S, 11.4. $C_{37}H_{33}NOS_2$ requires: C, 77.72; H, 5.82; N, 2.45; S, 11.22%.] R_f (100% Hexane) 0.65; δ_H (300 MHz, $CDCl_3$) 8.23–8.22 (1H, m, ArH), 8.00 (1H, d, *J* 7.5 Hz, ArH), 7.87–7.84 (1H, m, ArH), 7.87–7.59 (4H, m, ArH), 7.52–7.49 (1H, m, ArH), 7.37–7.34 (4H, m, ArH), 7.15–7.12 (2H, m, ArH), 6.77–6.74 (3H, m, ArH), 3.76 (3H, s, OCH_3), 2.70 (2H, t, *J* 7.8 Hz, CH_2), 1.28–1.23 (8H, m, CH_2), 0.85–0.81 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.4, 140.0, 138.8, 137.9, 136.4, 135.3, 134.6, 130.6, 130.3, 129.3, 128.1, 127.1, 125.9, 125.2, 124.8, 124.5, 124.2, 123.3, 123.2, 123.0, 122.1, 121.8, 121.7, 120.8, 120.6, 119.7, 117.1, 116.4, 55.5, 31.6, 30.9, 29.1, 29.0, 22.6, 14.1; *m*/*z* (EI) 571 (53, M^+).

*5.3.14. 3-(1-(5-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-9-(4-methoxyphenyl)-9H-carbazole (**7n**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7n** (1.38 g, 49%) was obtained using lactone **5d** (2 g, 4.94 mmol), 5-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.46 g, 5.92 mmol) and Mg (0.16 g, 6.48 mmol)], and Lawesson's reagent (1.00 g, 2.47 mmol) as a thick orange liquid. [Found: C, 77.5; H, 6.0; N, 2.7; S, 11.5. $C_{37}H_{33}NOS_2$ requires: C, 77.72; H, 5.82; N, 2.45; S, 11.22%.] R_f (100% Hexane) 0.65; δ_H (300 MHz, $CDCl_3$) 8.22–8.20 (1H, m, ArH), 8.01 (1H, d, *J* 7.8 Hz, ArH), 7.85–7.79 (1H, m, ArH), 7.87–7.57 (4H, m, ArH), 7.52–7.49 (1H, m, ArH), 7.37–7.34 (4H, m, ArH), 7.15–7.12 (2H, m, ArH), 6.77–6.74 (3H, m, ArH), 3.77 (3H, s, OCH_3), 2.75 (2H, t, *J* 7.65 Hz, CH_2), 1.28–1.23 (8H, m, CH_2), 0.85–0.79 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.4, 141.9, 141.7, 139.8, 138.9, 138.1, 137.9, 136.7, 135.7, 135.0, 134.6, 133.8, 132.9, 132.1, 131.1, 129.8, 128.1, 127.9, 125.5, 125.1, 124.7, 123.7, 123.1, 120.6, 120.4, 120.3, 120.2, 55.4, 31.4, 30.6, 29.6, 23.8, 22.5, 14.0; *m/z* (EI) 571 (15, M$^+$).

*5.3.15. 3-(1-(3-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)dibenzofuran (**7o**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7o** (1.58 g, 51%) was obtained using lactone **5e** (2 g, 6.66 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.98 g, 8.00 mmol) and Mg (0.21 g, 8.82 mmol)], and Lawesson's reagent (1.35 g, 3.33 mmol) as an orange solid; mp 115 °C. [Found C, 77.0; H, 5.5; S, 13.5. $C_{30}H_{26}OS_2$ requires: C, 77.21; H, 5.62; S, 13.74%.] R_f (100% Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.30 (1H, s, ArH), 7.93–7.88 (2H, m, ArH), 7.78 (1H, d, *J* 8.1 Hz, ArH), 7.67 (1H, d, *J* 8.1 Hz, ArH), 7.56–7.48 (2H, m, ArH), 7.42–7.37 (1H, m, ArH), 7.28 (1H, t, *J* 7.35 Hz, ArH), 7.20 (1H, d, *J* 5.1 Hz, ArH), 6.98–6.89 (3H, m, ArH), 2.95 (t, *J* 7.8 Hz, 2H, CH_2), 1.71 (q, *J* 7.65 Hz, 2H, CH_2), 1.39 (2H, q, *J* 6.9 Hz, CH_2), 1.27–1.18 (4H, m, CH_2), 0.78–0.73 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 156.7, 155.2, 143.7, 140.5, 139.3, 130.3, 127.5, 127.0, 126.7, 125.4, 125.0, 124.7, 124.2, 124.1, 123.9, 122.9, 120.9, 120.8, 120.5, 119.7, 116.5, 112.2, 111.8, 31.9, 31.0, 30.1, 29.6, 22.7, 14.1; *m/z* (EI) 466 (25, M$^+$).

*5.3.16. 3-(1-(5-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)dibenzofuran (**7p**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7p** (1.71 g, 55%) was obtained using lactone **5e** (2 g, 6.66 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.98 g, 8.00 mmol) and Mg (0.21 g, 8.82 mmol)], and Lawesson's reagent (1.35 g, 3.33 mmol) as a thick orange liquid. [Found: C, 77.1; H, 5.4; S, 13.5. $C_{30}H_{26}OS_2$ requires: C, 77.21; H, 5.62; S, 13.74%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2835, 1605, 1510, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.40 (1H, s, ArH), 7.93–7.28 (9H, m, ArH), 7.05–6.85 (3H, m, ArH), 2.92–2.90 (2H, m, CH_2), 1.78–1.28 (8H, m, CH_2), 0.93–0.91 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 156.7, 155.2, 145.2, 143.0, 140.4, 131.2, 129.6, 127.5, 125.4, 125.0, 124.9, 124.7, 124.3, 124.1, 122.9, 122.0, 121.3, 121.1, 120.9, 120.2, 119.9, 116.6, 112.2, 111.8, 31.6, 31.6, 30.2, 28.8, 22.6, 14.1; *m/z* (EI) 466 (45, M$^+$).

*5.3.17. 3-(1-(3-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)dibenzothiophene (**7q**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7q** (1.83 g, 60%) was obtained using lactone **5f** (2 g, 6.33 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.87 g, 7.59 mmol) and Mg (0.20 g, 8.33 mmol)], and Lawesson's reagent (1.28 g, 3.16 mmol) as an orange solid; mp 117 °C. [Found: C, 74.4; H, 5.7; S, 19.7. $C_{30}H_{26}S_3$ requires: C, 74.64; H, 5.43; S, 19.93%.] R_f (100% Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.47 (1H, s, ArH), 8.26–8.23 (1H, m, ArH), 8.00–7.90 (3H, m, ArH), 7.81 (1H, d, *J* 8.4 Hz, ArH), 7.68–7.65 (1H, m, ArH), 7.53–7.51 (2H, m, ArH), 7.44 (1H, d, *J* 5.4 Hz, ArH), 7.17–7.12 (3H, m, ArH), 2.73 (2H, t, *J* 7.8 Hz, CH_2), 1.69–1.64 (2H, m, CH_2), 1.34–1.27 (6H, m, CH_2), 0.89–0.84 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.4, 140.0, 138.8, 138.0, 136.4, 135.3, 135.1, 134.6, 130.6, 129.3, 128.1, 128.0, 127.1, 125.9, 125.2, 124.6, 124.4, 124.1, 123.3, 123.0, 122.1, 121.8, 120.8, 31.6, 30.9, 29.1, 29.0, 22.6, 14.1; *m/z* (EI) 482 (15, M$^+$).

*5.3.18. 3-(1-(5-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)dibenzothiophene (**7r**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **7r** (1.74 g, 57%) was obtained using lactone **5f** (2 g, 6.33 mmol), 5-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.87 g, 7.59 mmol) and Mg (0.20 g, 8.33 mmol)], and Lawesson's reagent (1.28 g, 3.16 mmol) as a thick orange liquid. [Found: C, 74.8; H, 5.2; S, 19.7. $C_{30}H_{26}S_3$ requires: C, 74.64; H, 5.43; S, 19.93%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2871, 1610, 1500, 775 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.46 (1H, s, ArH), 8.29–8.25 (1H, m, ArH), 8.00–7.90 (3H, m, ArH), 7.78 (1H, d, *J* 8.2 Hz, ArH), 7.68–7.65 (1H, m, ArH), 7.53–7.51 (2H, m, ArH), 7.44 (1H, d, *J* 5.4 Hz, ArH), 7.17–7.12 (3H, m, ArH), 2.76 (2H, t, *J* 7.65 Hz, CH_2), 1.71–1.65 (2H, m, CH_2), 1.34–1.27 (6H, m, CH_2), 0.87–0.81 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.5, 140.0, 138.8, 138.0, 136.4, 135.3, 135.2, 134.6, 130.6, 129.3, 128.2, 128.1, 127.1, 126.0, 125.2, 124.6, 124.5, 124.2, 123.4, 123.0, 122.1, 121.8, 120.8, 31.7, 30.9, 29.2, 29.1, 22.6, 14.1; *m/z* (EI) 482 (22, M$^+$).

*5.3.19. 3-(4-(Diphenylamino)phenyl)isobenzofuran-1(3H)-one (**10**)*

Following the above-mentioned procedure (A), lactone **10** (6.46 g, 42%) was obtained using triphenylamine **8** (10 g, 40.81 mmol), phthalic anhydride (7.25 g, 48.97 mmol), $AlCl_3$ (8.15 g, 61.22 mmol), and $NaBH_4$ (7.74 g, 204.00 mmol) as colorless solid; mp 96 °C. [Found: C, 82.5; H, 5.3; N, 3.5. $C_{26}H_{19}NO_2$ requires: C, 82.74; H, 5.07; N, 3.71%.] R_f (10% EA/Hexane) 0.61; ν_{max} (KBr) 1759, 1600, 1505, 755 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.95 (1H, t, *J* 7.5 Hz, ArH), 7.68 (1H, t, *J* 7.2 Hz, ArH), 7.56 (1H, t, *J* 7.5 Hz, ArH), 7.38 (1H, t, *J* 7.5 Hz, ArH), 7.27–7.20 (4H, m, ArH), 7.09–7.00 (10H, m, ArH), 6.36 (1H, s, CH); δ_C (75.6 MHz, $CDCl_3$) 170.5, 149.6, 149.0, 147.9, 147.3, 134.3, 129.4, 129.3, 129.2, 128.4, 125.6, 124.9, 124.2, 123.5, 123.1, 122.9, 122.7, 82.8; *m/z* (EI) 377 (11, M$^+$).

*5.3.20. N-Phenyl-N-(4-(1-(thiophen-2-yl)benzo[c]thiophen-3-yl)phenyl)benzenamine (**11a**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **11a** (1.33 g, 55%) was obtained using lactone **10** (2 g, 5.30 mmol), 2-thienylmagnesium bromide [prepared from 2-bromothiophene (1.04 g, 6.36 mmol) and Mg (0.17 g, 7.02 mmol)], and Lawesson's reagent (1.07 g, 2.65 mmol) as orange solid; mp 140 °C. [Found: C, 78.6; H, 4.8; N, 2.9; S, 14.2. $C_{30}H_{21}NS_2$ requires: C, 78.39; H, 4.61; N, 3.05; S, 13.95%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 1601, 1500, 765 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.01 (1H, d, *J* 8.1 Hz, ArH), 7.87 (1H, d, *J* 8.1 Hz, ArH), 7.57 (2H, d, *J* 7.8 Hz, ArH), 7.38–7.32 (6H, m, ArH), 7.24–7.12 (11H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 147.5, 136.2, 135.4, 134.9, 134.1, 129.9, 129.4, 127.9, 127.7, 125.9, 125.2, 124.8, 124.6, 124.1, 123.5, 123.4, 121.5; *m/z* (EI) 459 (13, M$^+$).

*5.3.21. 4-(1-(3-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)benzenamine (**11b**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **11b** (1.73 g, 60%) was obtained using lactone **10** (2 g, 5.30 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.57 g, 6.36 mmol) and Mg (0.17 g, 7.00 mmol)], and Lawesson's reagent (1.08 g, 2.66 mmol) as a thick orange liquid. [Found: C, 79.7; H, 6.3; N, 2.3; S, 11.6. $C_{36}H_{33}NS_2$ requires: C, 79.51; H, 6.12; N, 2.58; S, 11.79%.] R_f (100% Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 7.88–7.85 (1H, m, ArH), 7.63–7.56 (3H, m, ArH), 7.40 (1H, d, *J* 5.1 Hz, ArH), 7.36–7.28 (4H, m, ArH), 7.23–7.19 (6H, m, ArH), 7.12–7.07 (5H, m, ArH), 2.69 (2H, t, *J* 7.8 Hz, CH_2), 1.65–1.60 (2H, m, CH_2), 1.33–1.24 (6H, m, CH_2), 0.89–0.82 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 147.5, 147.4, 142.3, 137.9, 135.4, 134.1, 129.9, 129.4, 129.3, 128.3, 127.9, 125.7, 124.8, 124.0, 123.9, 123.5, 123.3, 121.7, 121.1, 31.6, 30.9, 29.1, 29.0, 22.6, 14.0; *m*/*z* (EI) 543 (33, M^+).

*5.3.22. 4-(1-(5-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)benzenamine (**11c**)*

Following the above-mentioned procedure (B), benzo[*c*]thiophene **11c** (1.64 g, 57%) was obtained using lactone **10** (2 g, 5.30 mmol), 5-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.57 g, 6.36 mmol) and Mg (0.17 g, 7.00 mmol)], and Lawesson's reagent (1.08 g, 2.66 mmol) as a thick orange liquid. [Found: C, 79.7; H, 6.4; N, 2.3; S, 11.5. $C_{36}H_{33}NS_2$ requires: C, 79.51; H, 6.12; N, 2.58; S, 11.79%.] R_f (100% Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.03–8.00 (1H, m, ArH), 7.87–7.84 (1H, m, ArH), 7.57 (2H, d, *J* 8.4 Hz, ArH), 7.38–7.32 (4H, m, ArH), 7.25–7.20 (7H, m, ArH), 7.16–7.09 (4H, m, ArH), 6.86 (1H, d, *J* 3.6 Hz, ArH), 2.91 (2H, t, *J* 7.65 Hz, CH_2), 1.83–1.78 (2H, m, CH_2), 1.51–1.31 (6H, m, CH_2), 1.00–0.90 (3H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 147.5, 147.3, 146.2, 135.1, 134.9, 133.6, 133.3, 129.9, 129.4, 127.9, 126.8, 125.0, 124.8, 124.8, 124.3, 124.1, 123.6, 123.3, 121.7, 121.4, 31.7, 30.3, 28.9, 22.7, 14.2; *m*/*z* (EI) 543 (55, M^+).

5.4. A representative procedure for the preparation of compound 12a (procedure C)

*5.4.1. 9-Hexyl-3-(1-(3-hexyl-5-(4-hexyl-5-(1-(9-hexyl-9H-carbazol-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**12a**)*

To a stirred solution of **7b** (0.5 g, 0.91 mmol) in dry DCM (20 mL) was added $FeCl_3$ (0.29 g, 1.82 mmol) under N_2 atmosphere. The reaction mixture was stirred for 12 h at room temperature and quenched with dilute solution of $N_2H_4 \cdot H_2O$. Then, it was filtered through Celite, extracted with DCM, and dried (Na_2SO_4). Solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (100% Hexane) to give the title compound **12a** (0.30 g, 61%) as a red solid; mp 80 °C. [Found C, 78.6; H, 7.3; N, 2.7; S, 11.5. $C_{72}H_{76}N_2S_4$ requires: C, 78.78; H, 6.98; N, 2.55; S, 11.68%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2911, 1600, 1510, 771 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.30 (2H, s, ArH), 8.05 (2H, d, *J* 7.8 Hz, ArH), 7.83–7.80 (2H, m, ArH), 7.67 (4H, t, *J* 8.4 Hz, ArH), 7.40–7.31 (6H, m, ArH), 7.18–7.00 (8H, m, ArH), 4.21 (4H, t, *J* 6.6 Hz, NCH_2), 2.62 (4H, t, *J* 7.5 Hz, CH_2), 1.82–1.78 (4H, m, CH_2), 1.62–1.53 (4H, m, CH_2), 1.35–1.15 (24H, m, CH_2), 0.80–0.74 (12H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.9, 141.0, 140.1, 137.8, 137.4, 137.0, 134.3, 127.8, 127.4, 126.1, 125.9, 124.7, 124.2, 123.9, 123.6, 123.4, 122.8, 121.8, 121.34, 121.2, 120.6, 119.2, 109.3, 109.0, 43.3, 31.7, 31.6, 30.9, 29.4, 29.2, 29.1, 27.1, 22.6, 22.5, 14.1, 14.0; *m*/*z* (EI) 1096 (13, M^+).

*5.4.2. 9-(2-Ethylhexyl)-3-(1-(5-(5-(1-(9-(2-ethylhexyl)-9H-carbazol-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**12b**)*

Following the above-mentioned procedure (C), compound **12b** (0.25 g, 50%) was obtained using compound **7g** (0.5 g, 1.01 mmol) and $FeCl_3$ (0.33 g, 2.02 mmol) as a black solid; mp 112 °C. [Found: C, 77.8; H, 6.5; N, 3.0; S, 12.9. $C_{64}H_{60}N_2S_4$ requires: C, 78.00; H, 6.14; N, 2.84; S, 13.02%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2875, 1596, 1505, 775 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.35 (2H, s, ArH), 8.14 (2H, d, *J* 7.8 Hz, ArH), 8.04 (2H, d, *J* 8.7 Hz, ArH), 7.89 (2H, d, *J* 8.7 Hz, ArH), 7.73 (2H, d, *J* 9.3 Hz, ArH), 7.53–7.36 (6H, m, ArH), 7.28–7.07 (10H, m, ArH), 4.21–4.16 (4H, m, NCH_2), 2.16–2.09 (2H, m, CH), 1.42–1.30 (14H, m, CH_2), 0.96–0.86 (14H, m, CH_2CH_3); δ_C (75.6 MHz, $CDCl_3$) 141.5, 140.6, 136.3, 136.0, 135.4, 135.3, 135.1, 127.2, 126.1, 125.6, 125.4, 124.8, 124.5, 124.1, 124.0, 123.5, 122.7, 121.8, 121.5, 121.1, 120.5, 119.2, 109.5, 109.3, 47.6, 39.5, 31.1, 28.9, 24.5, 23.1, 14.1, 10.9; *m*/*z* (EI) 984 (35, M^+).

*5.4.3. 9-Phenyl-3-(1-(5-(5-(1-(9-phenyl-9H-carbazol-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)-9H-carbazole (**12c**)*

Following the above-mentioned procedure (C), compound **12c** (0.23 g, 47%) was obtained using compound **7j** (0.5 g, 1.09 mmol) and $FeCl_3$ (0.35 g, 2.19 mmol) as a red solid; mp 220 °C. [Found: C, 78.7; H, 4.2; N, 2.9; S, 14.3. $C_{60}H_{36}N_2S_4$ requires: C, 78.91; H, 3.97; N, 3.07; S, 14.05%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 1595, 1500, 762 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.37 (2H, s, ArH), 8.15 (2H, d, *J* 7.5 Hz, ArH), 7.96 (2H, d, *J* 8.4 Hz, ArH), 7.85 (2H, d, *J* 8.4 Hz, ArH), 7.63–7.52 (8H, m, ArH), 7.46–7.39 (8H, m, ArH), 7.32–7.26 (6H, m, ArH), 7.13–7.05 (6H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 141.5, 140.5, 137.5, 136.4, 135.5, 135.4, 135.1, 130.0, 127.9, 127.7, 127.6, 127.1, 126.5, 126.0, 125.8, 125.2, 125.1, 124.7, 124.2, 124.1, 123.3, 121.6, 121.5, 121.2, 120.6, 120.4, 110.4, 110.1; *m*/*z* (EI) 912 (33, M^+).

*5.4.4. 3-(1-(3-Hexyl-5-(4-hexyl-5-(1-(dibenzofuran-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)dibenzofuran (**12d**)*

Following the above-mentioned procedure (C), compound **12d** (0.26 g, 52%) was obtained using compound **7o** (0.5 g, 1.07 mmol) and $FeCl_3$ (0.35 g, 2.14 mmol) as a red solid; mp 112 °C. [Found: C, 77.6; H, 5.2; S, 14.0. $C_{60}H_{50}O_2S_4$ requires: C, 77.38; H, 5.41; S, 13.77%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2825, 1595, 1495, 762 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.27 (2H, s, ArH), 8.04 (2H, d, *J* 6.9 Hz, ArH), 7.89–7.64 (10H, m, ArH), 7.56–7.52 (m, 2H, ArH), 7.44–7.42 (2H, m, ArH), 7.19–7.17 (6H, m, ArH), 2.75–2.71 (4H, m, CH_2), 1.70–1.60 (4H, m, CH_2), 1.37–1.27 (12H, m, CH_2), 0.89–0.85 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 156.8, 155.9, 143.1, 137.8, 137.2, 135.5, 134.7, 128.8, 128.7, 127.6, 127.4, 125.9, 125.2, 124.4, 124.3, 124.0, 123.0, 121.8, 121.4, 120.9, 112.2, 111.9, 31.6, 30.8, 29.4, 29.1, 22.6, 14.1; *m*/*z* (EI) 930 (55, M^+).

*5.4.5. 3-(1-(3-Hexyl-5-(4-hexyl-5-(1-(dibenzothiophen-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)dibenzothiophene (**12e**)*

Following the above-mentioned procedure (C), compound **12e** (0.27 g, 55%) was obtained using compound **7q** (0.5 g, 1.04 mmol) and $FeCl_3$ (0.33 g, 2.07 mmol) as a red solid; mp 105 °C. [Found: C, 74.6; H, 5.1; S, 20.2. $C_{60}H_{50}S_6$ requires: C, 74.80; H, 5.23; S, 19.97%.] R_f (100% Hexane) 0.70; ν_{max} (KBr) 2911, 1596, 1505, 765 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.34–8.33 (2H, m, ArH), 8.13–8.10 (2H, m, ArH), 7.87–7.77 (4H, m, ArH), 7.69–7.65 (4H, m, ArH), 7.40–7.37 (6H, m, ArH), 7.13–7.12 (2H, m, ArH), 7.07–7.04 (4H, m, ArH), 2.62 (4H, d, *J* 7.5 Hz, CH_2), 1.58–1.55 (4H, m, CH_2), 1.25–1.16 (12H, m, CH_2), 0.79–0.72 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 143.1, 140.0, 138.9, 137.9, 137.2, 136.4, 135.4, 135.3, 134.7, 130.5, 128.0, 127.4, 127.2, 126.0, 124.8, 124.6, 124.6, 124.4, 123.4, 123.0, 122.1, 121.8, 120.9, 31.6, 30.8, 29.4, 29.1, 22.6, 14.1; *m*/*z* (EI) 962 (22, M^+).

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