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Lewis-Acid-Mediated Domino Reactions of Bis(diacetoxymethyl)-Substituted Arenes and Heteroarenes

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A one-pot synthesis of annulated heterocycles involving a Lewis-acid-mediated domino reaction of bis(diacetoxymethyl)-substituted arenes and heteroarenes is described. The reaction of the tetraacetates with arenes and heteroarenes leads to the formation of 1,1-bis-arylated diacetates upon elimination followed by electrocyclohetero-arylated intermediate may lead to the formation of bis-arylated 1,1-diacetates, which on cyclization followed by aromatization furnish annulated heterocycles.

Introduction

Highly π-extended aromatic compounds are currently attracting attention as organic semiconductors for various applications including organic light-emitting diodes (OLEDs), photovoltaic cells, and organic field-effect transistors (OFETs).[1] Among such aromatic compounds, higher oligoacenes such as naphthacene[2] and pentacene[3] are essential as an active layer in high-performance OFETs. It is well known that polyacene analogues, especially pentacene, show great electron mobility and can be used as charge carriers.[4] Anthracene and its derivatives are one of the most important classes of polycyclic aromatic compounds.[5] Anthracenes possess efficient photochromic properties and have found applications in data storage and as molecular switches.[6] Substituted anthracenes have been prepared, for example, by Friedel–Crafts reactions,[7] aromatic cyclodehydration,[8] Elbs reactions,[9] Lewis-acid-induced Bradsher-type reactions of diarylmethanes,[10] and homologation mediated by metallacycles.[11]

Recently, Beller and co-workers reported[12] a facile $FeCl_3$-catalyzed arylation of benzylic alcohol, benzylic acetate, and benzyl carboxylates with arenes affording the corresponding biaryls. An easy access to the triarylmethane derivatives has been achieved by the reaction of aromatic aldehydes with arenes in the presence of $FeCl_3$ and acetic anhydride.[13] Kodomari et al. reported[14] a convenient synthesis of 9,10-diarylanthracenes by the reaction of aromatic aldehydes and arenes in the presence of acetyl bromide and $ZnBr_2/SiO_2$. Liu and co-workers[15] achieved the synthesis of 9-arylanthracene as well as naphtho[*b*]thiophenes by trifluoromethanesulfonic acid catalyzed annulation of diacetates. The same group also reported the synthesis of indenyl ketones,[16a] fluorenes, and heterocycle-fused indenes[16b] as well as xanthenes[16c] that involved either Brønsted acid or Lewis acid catalyzed cyclization reactions. An efficient synthesis of the anthracene derivatives has also been realized by Surya Prakash et al. by the reaction of phthalaldehyde with alkylbenzenes under superelectrophilic conditions.[17]

The Lewis-acid-mediated domino reaction has been successfully employed in the synthesis of a wide variety of polycyclic heterocycles.[18] As a continuation of our interest in the synthesis of π-conjugated heterocycles involving Lewis acids,[19] we report herein our results on the annulation of bis(diacetoxymethyl)-substituted arenes and heteroarenes.

Results and Discussion

The reaction of phthalaldehyde (**1**) with electron-rich arenes such as anisole, 1,2-dimethoxybenzene, or 1,3-dimethoxybenzene in the presence of $CH_3COCl(Br)/ZnBr_2$ at room temperature was found to be successful, affording the expected products **3a**–**c** in 45–61% yields, respectively (Scheme 1).

However, the similar reaction of phthalaldehyde (**1**) with *o*- or *p*-xylene in the presence of $CH_3COCl(Br)/ZnBr_2$ failed to produce the expected annulation product. Moreover, this methodology could not be applied to heteroarenes because they are susceptible to acetylation. Hence, an alternative annulation protocol involving the reaction of pre-prepared tetraacetate with arenes catalyzed by a Lewis acid was proposed. Accordingly, the required tetraacetate **4** was pre-

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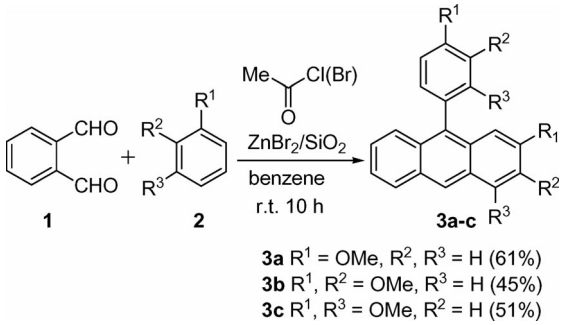
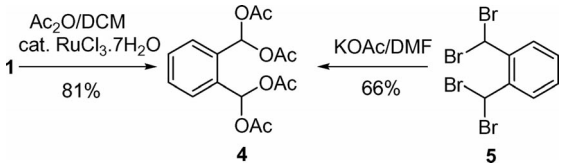


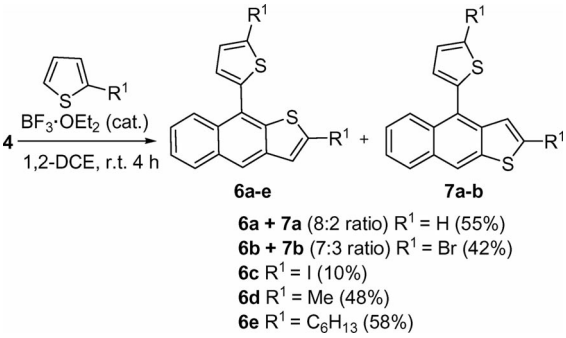
Scheme 1. Domino reactions of phthalaldehyde with arenes.

pared either from the phthalaldehyde (**1**) following the published procedure[20] or from the tetrabromo compound **5**[21] (Scheme 2).



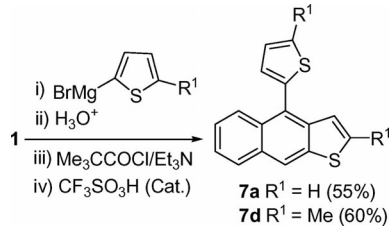
Scheme 2. Preparation of 1,2-bis(diacetoxymethyl)benzene (**4**).

Having prepared tetraacetate **4**, its Lewis-acid-mediated annulation with arenes was planned. However, all our attempts to perform domino reactions of **4** with electron-rich arenes, anisole, veratrole, or xylenes in the presence of a catalytic amount of a Lewis acid such as $FeCl_3$, $ZnBr_2$, or $BF_3{\cdot}OEt_2$ were found to be unsuccessful. However, the reaction of tetraacetate **4** with 2-substituted thiophenes in the presence of 40 mol-% (3 drops) of $BF_3{\cdot}OEt_2$ led to the isolation of a mixture of 9- and 4-substituted naphtho[2,3-*b*]thiophenes **6a**,**b** and **7a**,**b** (Scheme 3). Fortunately, the reaction of **4** with 2-iodothiophene, 2-methylthiophene, or 2-hexylthiophene led to the formation of 9-substituted naphtho[2,3-*b*]thiophenes **6c**–**e** as a single isomer.



Scheme 3. Domino reactions of **4** with 2-substituted thiophenes.

Comparison of the ^1H NMR spectra of the positional isomers **6a**,**b** and **7a**,**b** revealed only a slight difference in their spectral patterns. To verify the structures of positional isomers **6** and **7**, the 4-substituted heterocycles **7a** and **7d** were independently synthesized following the procedure[15] reported by Liu and co-workers (Scheme 4).



Scheme 4. Preparation of naphtho[2,3-*b*]thiophenes **7a** and **7d**.

The structures of heterocycles **7a** and **7d** were characterized by ^1H and ^{13}C NMR spectral analysis. As a representative case, the ^1H NMR spectra (region: 7.7–8.6 ppm) of a mixture (ca. 1:0.3) of **6a** and **7a** and that of pure isomer **7a** are presented in parts a and b of Figure 1. A perfect merging of the ^1H NMR signal of the minor component in the mixture of **6a** and **7a** was confirmed (Figure 1, c) by the addition of pure **7a**.

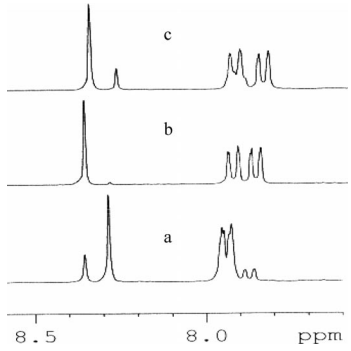


Figure 1. a) ^1H NMR spectrum (region: 7.7–8.6 ppm) of a mixture of **6a** + **7a** (1:0.3) prepared using tetraacetate **4**. b) ^1H NMR spectrum (7.6–8.7 ppm) of **7a** prepared according to ref.[15]. c) ^1H NMR spectrum (7.6–8.7 ppm) of a mixture of **6a** + **7a** after the addition of pure compound **7a**.

Finally, the structure of 9-(5-methylthiophen-2-yl)-naphtho[2,3-*b*]thiophene (**6d**) was confirmed by single-crystal X-ray diffraction analysis (Figure 2).

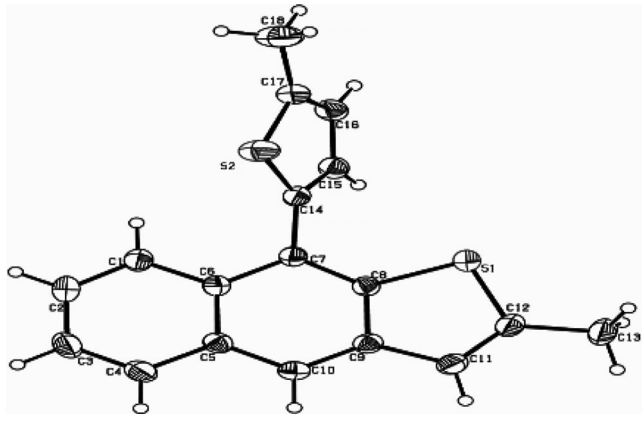
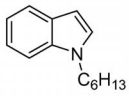
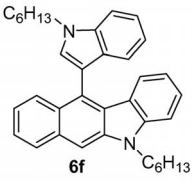
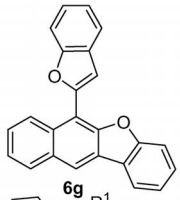
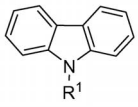
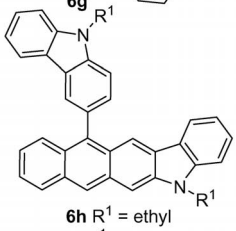
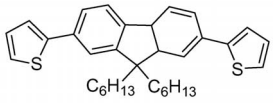
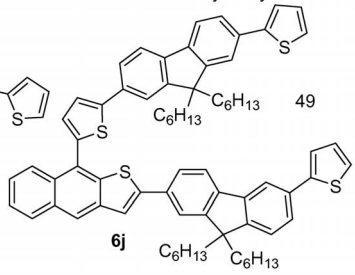


Figure 2. ORTEP diagram of compound **6d**.

As expected, the annulation of tetraacetate **4** was successfully achieved with complex heteroarenes in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ affording the corresponding fused heterocycles **6f**–**j** in 49–58% yields (Table 1).

Table 1. Annulation of tetraacetate **4** with heteroarenes.

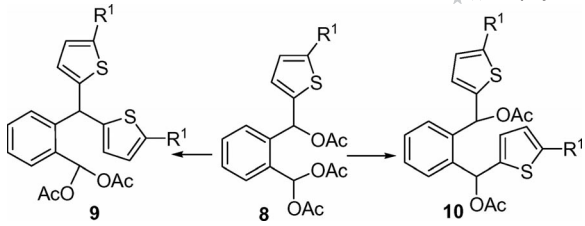
Entry	Ar^1H	Product	Yield (%)[a]
1		 **6f**	55
2		 **6g**	51
3		 **6h** R^1 = ethyl **6i** R^1 = 2-ethyl hexyl	58 52
4		 **6j**	49

[a] Isolated yield after column chromatographic purification.

The domino reaction of **4** with bicyclic heteroarene 1-hexylindole and benzo[*b*]furan led to the isolation of heterocycles **6f** and **6g** in 55 and 51% yields, respectively (entries 1 and 2). Similarly, the annulation of **4** with *N*-alkylcarbazoles also afforded the expected products **6h** and **6i** in 58 and 52% yields (entry 3). The annulation of **4** was also successfully performed with 9,9-dihexyl-2,7-di(thiophen-2-yl)fluorene[22] to furnish mixed heterocycle **6j** in 49% yield (entry 4).

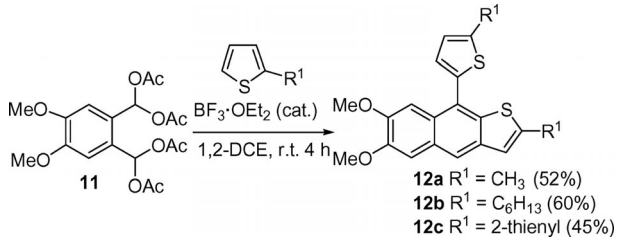
It is clear that the domino reaction of **4** proceeds predominantly through the intermediacy of 1,1-diacetate **9** rather than 1,4-diacetate **10** to form the corresponding annulation products **6** and **7** in major and minor amounts, respectively. Clearly, in the case of 2-methythiophene and other electron-rich heteroarenes only the corresponding 1,1-diacetate was formed, which led to the isolation of heterocycles **6d**–**j**. The nucleophilic character of the heteroaryl unit facilitates the preferential formation of the 1,1-diacetate **9** (Scheme 5).

Next, the methoxy-tethered tetraacetate **11** was prepared from 4,5-dimethoxyphthalaldehyde[23] following the procedure established for phthaldehyde (**1**). As expected, the



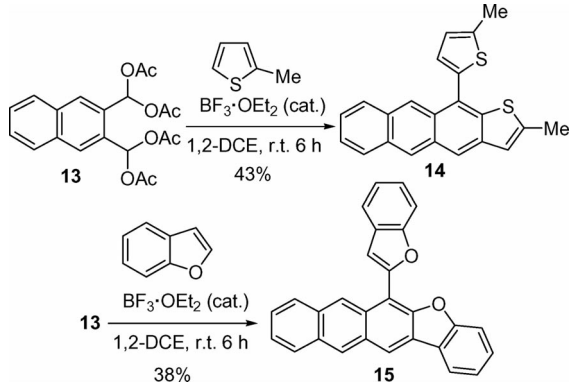
Scheme 5. Formation for isomeric diacetates **9** and **10**.

annulation of tetraacetate **11** with heteroarenes such as 2-methylthiophene, 2-hexylthiophene, and bithiophene in the presence of $BF_3{\cdot}OEt_2$ in 1,2-DCE at room temperature furnished the corresponding heterocycles **12a**–**c** in 45–60% yields (Scheme 6).



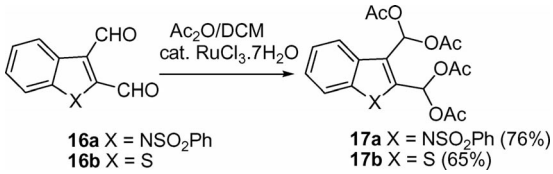
Scheme 6. Domino reactions of tetraacetate **11**.

Having achieved the smooth annulation of tetraacetates **4** and **11**, the tetraacetate **13** was prepared from naphthalene-2,3-dicarbaldehyde.[24] As a representative case, the domino reaction of tetraacetate **13** was successfully carried out with heteroarenes such as 2-methylthiophene and benzofuran to afford heterocycles **14** and **15** in moderate yields (Scheme 7).



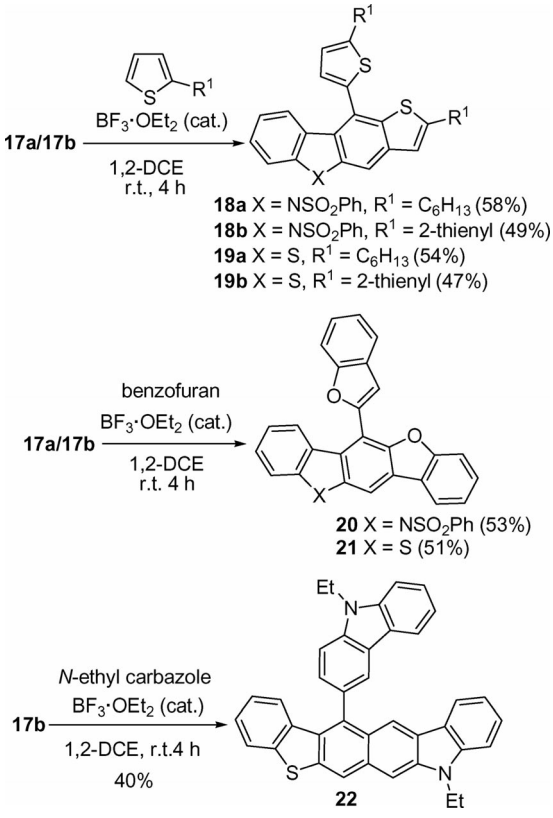
Scheme 7. Domino reactions of tetraacetate **13**.

Towards a further generalization of the observed domino reaction protocol, tetraacetate derivatives of 1-(phenylsulfonyl)indole and benzo[*b*]thiophene were prepared by reaction of the corresponding dialdehydes **16a** and **16b** with acetic anhydride in the presence of a catalytic amount of $RuCl_3{\cdot}7H_2O$ in DCM (Scheme 8).



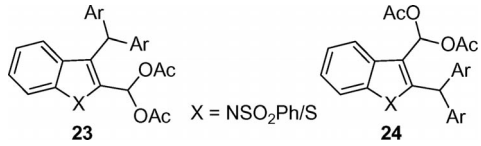
Scheme 8. Preparation of tetraacetates **17a** and **17b**.

As expected, the reactions of the indole-derived tetraacetate **17a** and benzo[*b*]thienyl-derived tetraacetate **17b** with 2-hexylthiophene and bithiophene in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ at room temperature followed by work-up and column chromatographic purification furnished the corresponding annulated carbazoles **18a** and **18b** and benzo[*b*]thiophenes **19a** and **19b** in 47–58% yields. Similarly, the annulation of tetraacetates **17a** and **17b** with benzofuran furnished the expected products **20** and **21** in 53 and 51% yields, respectively. Under identical conditions, the reaction of tetraacetate **17b** with *N*-ethylcarbazole produced the annulated heterocycle **22** in 40% yield (Scheme 9).



Scheme 9. Domino reactions of tetraacetates **17a** and **17b**.

The formation of a single isomer in the reactions of tetraacetates **17a** and **17b** can be visualized through the preferential diarylation at the 3-position leading to the formation of intermediate 1,1-diacetate **23** rather than **24** (Scheme 10). Thus, the preferential formation of bis-heteroarylated 1,1-diacetate in the case of symmetrical as well as unsymmetrical tetraacetates is controlled by the electronic influence of the heteroaryl units.



Scheme 10. Mechanistic visualization of the domino reactions of the tetraacetates **17a** and **17b**.

Conclusions

We have developed a simple and versatile domino reaction protocol for bis(diacetoxymethyl)-substituted arenes and heteroarenes by reaction with heteroarenes in the presence of a Lewis acid. A possible mechanism for the formation of the annulated heterocycles is proposed. Further studies to extend the scope and synthetic utility of the domino reaction for the synthesis of complex heteroacenes are in progress.

Experimental Section

General Methods: All reactions were carried out in oven-dried apparatus using dry solvent under anhydrous conditions unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on silica and the components were visualized by observation with iodine or under UV light. Flash chromatography was performed on silica gel (230–400 mesh). NMR spectra (Bruker 300 MHz) were recorded in $CDCl_3$ solution containing TMS as an internal standard unless otherwise stated. Organic extracts were dried with anhydrous Na_2SO_4. The multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hz. Carbon types were determined from ^{13}C NMR experiments. Elemental analyses were performed with a Perkin–Elmer series II 2400 (IIT Madras) elemental analyzer. Mass spectra were recorded with a JEOL DX 303 HF mass spectrometer.

3a: CH_3COCl (1.74 g, 22.38 mmol), $ZnBr_2$ (1.67 g, 7.46 mmol), anisole (2.41 g, 22.39 mmol), and silica gel (1 g) were added to a solution of phthalaldehyde (**1**; 0.5 g, 3.73 mmol) in dry benzene (30 mL). The reaction mixture was stirred at room temperature for 10 h under N_2. Filtration of the inorganic residue followed by removal of the solvent and subsequent column chromatographic purification (*n*-hexane/ethyl acetate, 96:4) afforded **3a** (0.71 g, 61%) as a colorless solid, m.p. 169 °C (ref.[15] 175–176 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, ArH), 8.01 (d, J = 8.1 Hz, 1 H, ArH), 7.94 (d, J = 9.0 Hz, 1 H, ArH), 7.67 (d, J = 8.7 Hz, 1 H, ArH), 7.42–7.35 (m, 4 H, ArH), 7.19–7.12 (m, 3 H, ArH), 6.91 (s, 1 H, ArH), 3.96 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.9, 157.0, 134.7, 132.3, 131.6, 131.2, 131.1, 130.1, 128.4, 128.1, 126.4 (2 C), 125.4, 124.2, 120.1, 114.1, 102.8, 55.4, 55.1 ppm. MS (EI): *m/z* (%) = 314 (50) $[M]^+$. $C_{22}H_{18}O_2$ (314.13): calcd. C 84.05, H 5.77; found C 84.32, H 5.61.

3b: The reaction of phthalaldehyde (**1**; 0.5 g, 3.73 mmol) with 1,2-dimethoxybenzene (3.08 g, 22.38 mmol) in the presence of $ZnBr_2$ (1.67 g, 7.46 mmol), CH_3COCl (1.74 g, 22.38 mmol), and silica gel (1 g) using the same procedure as that for the synthesis of **3a** afforded compound **3b** (0.62 g, 45%) as a colorless solid, m.p. 194 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 2 H, ArH), 7.92–7.87 (m, 2 H, ArH), 7.40–7.33 (m, 2 H, ArH), 7.16 (s, 1 H, ArH), 6.92–6.83 (m, 3 H, ArH), 4.01 (s, 6 H, OCH_3), 3.85 (s, 6 H, OCH_3) ppm.

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.1, 149.1, 148.0, 146.1, 130.8, 128.6, 127.6, 124.6, 124.5, 124.3, 123.9, 121.5, 120.9, 120.2, 114.6, 111.4, 110.8, 107.8, 104.9, 104.3, 55.9, 55.8 ppm. MS (EI): *m*/*z* (%) = 374 (54) $[M]^+$. $C_{24}H_{22}O_4$ (374.15): calcd. C 76.99, H 5.92; found C 76.72, H 6.14.

3c: The reaction of phthalaldehyde (**1**; 0.5 g, 3.73 mmol) with 1,3-dimethoxybenzene (3.08 g, 22.38 mmol) using the same procedure as that for the synthesis of **3a** afforded compound **3c** (0.71 g, 51%) as a colorless solid, m.p. 156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.78 (s, 1 H, ArH), 8.0 (d, *J* = 8.1 Hz, 1 H, ArH), 7.51 (d, *J* = 8.4 Hz, 1 H, ArH), 7.37–7.27 (m, 2 H, ArH), 7.15 (d, *J* = 7.8 Hz, 1 H, ArH), 6.70–6.67 (m, 2 H, ArH), 6.41 (d, *J* = 4.8 Hz, 2 H, ArH), 4.04 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 160.7, 158.9, 157.4, 156.8, 133.1, 132.1, 131.7, 130.9, 129.7, 129.1, 126.2, 125.6, 123.8, 122.1, 121.2, 120.4, 104.8, 99.2, 97.0, 95.4, 55.8, 55.7, 55.4, 55.1 ppm. MS (EI): *m*/*z* (%) = 374 (45) $[M]^+$. $C_{24}H_{22}O_4$ (374.15): calcd. C 76.99, H 5.92; found C 77.18, H 5.83.

Preparation of Benzene-Derived Tetraacetate 4

From Phthaldehyde (1): $RuCl_3 \cdot 7H_2O$ (0.23 g, 1.11 mmol) was added to a solution of phthaldehyde (**1**; 3 g, 22.38 mmol) and acetic anhydride (13.69 g, 134.32 mmol) in DCM (100 mL) and the mixture was stirred at room temperature for 8 h. It was then diluted with DCM (50 mL) and washed with saturated $NaHCO_3$ solution (3 × 15 mL) followed by brine solution. The organic layer was then dried (Na_2SO_4) and concentrated in vacuo to afford **4** (6.12 g, 81%) as a colorless solid, m.p. 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0 (s, 2 H, ArH), 7.64–7.61 (m, 2 H, ArH), 7.49–7.45 (m, 2 H, ArH), 2.11 (s, 12 H, OAc) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 168.4, 133.7, 130.0, 128.4, 88.3, 20.8 ppm. MS (EI): *m*/*z* (%) = 338 (60) $[M]^+$.

From Tetrabromo Compound 5: KOAc (2.80 g, 28.50 mmol) was added to a solution of tetrabromo compound **5**[21] (2 g, 4.75 mmol) in DMF (20 mL) and the reaction mixture was stirred at room temperature for 24 h. It was then poured into ice–water, extracted with DCM (2 × 15 mL), and dried (Na_2SO_4). Removal of the solvent led to the isolation of **4** (1.06 g, 66%) as a colorless solid, m.p. 132 °C.

6a and 7a: Thiophene (0.37 g, 4.43 mmol) and $BF_3 \cdot OEt_2$ (40 mg) were added to a solution of **4** (0.5 g, 1.47 mmol) in dry DCE (20 mL). The reaction mixture was then stirred at room temperature for 4 h under N_2. Removal of the solvent followed by column chromatographic purification (*n*-hexane/ethyl acetate, 98:2) furnished a mixture of the annulated heterocycles **6a** and **7a** in a 8:2 ratio as a yellow solid (0.20 g, 55%), m.p. 77–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (s, ArH), 8.34 (s, ArH), 8.03–7.92 (m, ArH), 7.94–7.92 (m, ArH), 7.58–7.56 (m, ArH), 7.48–7.43 (m, ArH), 7.33–7.26 (m, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.3, 139.6, 131.1, 138.2, 137.6, 131.4, 131.0, 130.4, 130.1, 128.9, 128.8, 128.6, 128.5, 128.3, 127.5, 127.4, 127.1, 126.7, 126.4, 126.3, 126.2, 125.7, 125.4, 125.3, 125.1, 124.9, 123.8, 123.7, 122.5, 121.6 ppm.

6b and 7b: The reaction of **4** (0.5 g, 1.47 mmol) with 2-bromothiophene (0.72 g, 4.43 mmol) in the presence of $BF_3 \cdot OEt_2$ (40 mg) using the above-mentioned procedure followed by column chromatographic purification (*n*-hexane/ethyl acetate, 98:2) afforded a mixture of the heterocycles **6b** and **7b** as a yellow solid (0.26 g, 42%), m.p. 124–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (s, ArH), 8.20 (s, ArH), 7.98 (d, *J* = 8.4 Hz, ArH), 7.93 (d, *J* = 7.8 Hz, ArH), 7.53–7.43 (m, ArH), 7.31–7.20 (m, ArH), 7.06–7.04 (m, ArH), 6.95–6.93 (m, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 142.3, 140.2, 140.1, 139.3, 138.6, 137.9, 131.5, 130.8, 130.5, 130.4, 130.2, 129.9, 129.2, 129.1, 128.5, 127.5, 126.4, 126.3, 126.2, 126.0, 125.8, 125.7, 125.5, 124.6, 124.3, 123.8, 121.9, 121.1, 118.4, 113.7, 113.1 ppm.

6c: The reaction of **4** (0.5 g, 1.47 mmol) with 2-iodothiophene (0.93 g, 4.43 mmol) in the presence of $BF_3 \cdot OEt_2$ (40 mg) using the above-mentioned procedure followed by column chromatographic purification (*n*-hexane/ethyl acetate, 98:2) led to the isolation of compound **6c** (0.07 g, 10%) as a pale-brown solid, m.p. 171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (s, 1 H, ArH), 7.97 (d, *J* = 8.4 Hz, 1 H, ArH), 7.90 (d, *J* = 8.1 Hz, 1 H, ArH), 7.54–7.40 (m, 4 H, ArH), 6.88 (d, *J* = 3.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.9, 141.7, 140.3, 138.8, 137.3, 133.3, 130.7, 130.6, 130.3, 127.6, 126.1, 126, 125.9, 123.8, 120.5 ppm. MS (EI): *m*/*z* (%) = 518 (37) $[M]^+$. $C_{16}H_8I_2S_2$ (517.82): calcd. C 37.09, H 1.56, S 12.38; found C 37.34, H 1.85, S 12.62.

6d: The reaction of **4** (0.5 g, 1.47 mmol) with 2-methylthiophene (0.43 g, 4.43 mmol) in the presence of $BF_3 \cdot OEt_2$ (40 mg) using the above-mentioned procedure followed by column chromatographic purification (*n*-hexane/ethyl acetate, 98:2) afforded compound **6d** (0.21 g, 48%) as a colorless solid, m.p. 88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (s, 1 H, ArH), 8.04 (d, *J* = 7.8 Hz, 1 H, ArH), 7.94 (d, *J* = 7.5 Hz, 1 H, ArH), 7.44–7.41 (m, 2 H, ArH), 7.08–7.05 (m, 2 H, ArH), 6.90 (s, 1 H, ArH), 2.60 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.3, 141.5, 141.1, 139.2, 136.8, 131.6, 129.6, 128.5, 128.3, 125.5, 125.1, 124.7, 121.2, 120.8, 16.6, 15.4 ppm. MS (EI): *m*/*z* (%) = 294 (51) $[M]^+$. $C_{18}H_{14}S_2$ (294.05): calcd. C 73.43, H 4.79, S 21.78; found C 73.69, H 4.66, S 21.92.

For single-crystal X-ray analysis of **6d**, all calculations were performed by using the SHELXL-97 program.[25] Crystal data of **6d**: $C_{18}H_{14}S_2$, M = 294.41 g mol^{-1}, triclinic crystal system, space group $P\bar{1}$, Z = 2, a = 7.2672(9), b = 9.7350(12), c = 11.3376(14) Å, α = 89.647(7), β = 82.381(7), γ = 68.381(6)°, V = 737.04(12) Å^3, D_X = 1.327 Mg m^{-3}. In total, 13430 independent reflections were collected of which 3634 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to give a final R value of 3.72%.

CCDC-783657 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6e: The reaction of **4** (0.5 g, 1.47 mmol) with 2-hexylthiophene (0.75 g, 4.4 mmol) in the presence of $BF_3 \cdot OEt_2$ (40 mg) using the above-mentioned procedure followed by column chromatographic purification (*n*-hexane/ethyl acetate, 98:2) afforded compound **6e** (0.37 g, 58%) as a thick yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07–8.04 (m, 2 H, ArH), 7.89–7.85 (m, 1 H, ArH), 7.39–7.37 (m, 2 H, ArH), 7.08 (d, *J* = 3.3 Hz, 1 H, ArH), 6.98 (s, 1 H, ArH), 6.87 (d, *J* = 3.6 Hz, 1 H, ArH), 2.88 (t, *J* = 7.6 Hz, 2 H, ArH), 2.80 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.77–1.67 (m, 4 H, CH_2), 1.43–1.26 (m, 12 H, CH_2), 0.91–0.84 (m, 6 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.3, 147.3, 141.2, 139.2, 136.3, 131.7, 129.7, 128.4, 128.3, 125.8, 125.3, 125.2, 124.7, 124.3, 120.9, 120.1, 31.7 (2 C), 31.4, 30.8, 30.4, 29.1, 29.0, 22.7, 22.6, 14.2 ppm. MS (EI): *m*/*z* (%) = 434 (54) $[M]^+$. $C_{28}H_{34}S_2$ (434.21): calcd. C 77.36, H 7.88, S 14.75; found C 77.52, H 7.93, S 14.62.

6f: The reaction of **4** (0.5 g, 1.47 mmol) with 1-hexylindole (0.89 g, 4.43 mmol) in the presence of $BF_3 \cdot OEt_2$ (40 mg) using the above-mentioned procedure led to the isolation of the heterocycle **6f**

(0.40 g, 55%) as a colorless solid, m.p. 154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H, ArH), 8.26 (d, J = 8.1 Hz, 1 H, ArH), 8.07 (d, J = 8.7 Hz, 1 H, ArH), 7.66 (d, J = 8.7 Hz, 1 H, ArH), 7.51–7.46 (m, 2 H, ArH), 7.39–7.33 (m, 1 H, ArH), 7.30–7.22 (m, 5 H, ArH), 7.18 (d, J = 7.8 Hz, 1 H, ArH), 7.01 (t, J = 7.5 Hz, 1 H, ArH), 4.28 (t, J = 7.2 Hz, 2 H, NCH_2), 3.74 (t, J = 6.8 Hz, 2 H, NCH_2), 1.98–1.95 (m, 2 H, CH_2), 1.47–1.33 (m, 10 H, CH_2), 1.04–0.99 (m, 3 H, CH_3), 0.93–0.83 (m, 4 H, CH_2), 0.81–0.71 (m, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.9, 139.2, 136.1, 134.2, 130.1, 128.3, 128.2, 128.1, 127.2, 126.0, 125.6, 124.8, 123.0, 122.5, 122.1, 120.7, 119.7, 118.9, 118.4, 110.9, 110.7, 109.6, 108.8, 100.9, 46.6, 44.3, 31.6, 31.3, 30.6, 28.9, 26.9, 26.5, 22.7, 14.2, 14.1 ppm. MS (EI): m/z (%) = 500 (44) $[M]^+$. $C_{36}H_{40}N_2$ (500.32): calcd. C 86.35, H 8.05, N 5.59; found C 86.13, H 8.14, N 5.72.

6g: The reaction of **4** (0.5 g, 1.47 mmol) with benzo[*b*]furan (0.52 g, 4.43 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) using the above-mentioned procedure led to the isolation of the heterocycle **6g** (0.25 g, 51%) as a colorless solid, m.p. 152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (d, J = 8.7 Hz, 1 H, ArH), 8.46 (s, 1 H, ArH), 8.07 (d, J = 7.8 Hz, 2 H, ArH), 7.78–7.75 (m, 1 H, ArH), 7.67 (d, J = 7.8 Hz, 1 H, ArH), 7.62–7.58 (m, 2 H, ArH), 7.55–7.51 (m, 2 H, ArH), 7.45 (s, 1 H, ArH), 7.41–7.34 (m, 3 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.5, 155.1, 153.1, 150.5, 130.9, 130.6, 128.9, 128.6, 126.7, 125.9, 125.1, 124.6, 124.5, 123.7, 123.1, 123.0, 121.3, 121.2, 120.7, 111.8, 111.5, 109.5, 109.0 ppm. MS (EI): m/z (%) = 334 (52) $[M]^+$. $C_{24}H_{14}O_2$ (334.10): calcd. C 86.21, H 4.22; found C 86.05, H 4.13.

6h: The reaction of **4** (0.5 g, 1.47 mmol) with *N*-ethylcarbazole (0.87 g, 4.43 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) using the above-mentioned procedure led to the isolation of the heterocycle **6h** (0.42 g, 58%) as a pale-yellow solid, m.p. 178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (s, 1 H, ArH), 8.46 (s, 1 H, ArH), 8.25 (s, 1 H, ArH), 8.06–8.02 (m, 2 H, ArH), 7.90 (d, J = 7.5 Hz, 1 H, ArH), 7.79 (s, 1 H, ArH), 7.74 (d, J = 9.0 Hz, 1 H, ArH), 7.62–7.57 (m, 2 H, ArH), 7.49–7.37 (m, 4 H, ArH), 7.24–7.19 (m, 3 H, ArH), 7.04 (d, J = 7.2 Hz, 1 H, ArH), 4.50–4.47 (m, 2 H, CH_2), 4.35–4.33 (m, 2 H, CH_2), 1.59–1.54 (m, 3 H, CH_3), 1.48–1.46 (m, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.6, 140.5, 140.1, 139.5, 138.4, 131.2, 129.8, 129.3, 128.9, 127.8, 127.7, 127.4, 126.9, 125.9, 124.7, 124.3, 123.7, 123.4, 123.2, 123.1, 121.5, 120.7, 119.0, 118.6, 118.2, 108.7, 108.4, 107.6, 101.2, 37.8, 37.6, 14.1, 13.1 ppm. MS (EI): m/z (%) = 488 (50) $[M]^+$. $C_{36}H_{28}N_2$ (488.22): calcd. C 88.49, H 5.78, N 5.73; found C 88.71, H 5.65, N 5.68.

6i: The reaction of **4** (0.5 g, 1.47 mmol) with *N*-(2-ethylhexyl)carbazole (1.23 g, 4.43 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) using the above-mentioned procedure led to the isolation of the heterocycle **6i** (0.50 g, 52%) as a brown solid, m.p. 126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H, ArH), 8.45 (d, J = 6.9 Hz, 1 H, ArH), 8.26 (d, J = 5.7 Hz, 1 H, ArH), 8.10–8.03 (m, 2 H, ArH), 7.91–7.88 (m, 1 H, ArH), 7.80–7.76 (m, 2 H, ArH), 7.61–7.59 (m, 2 H, ArH), 7.50–7.48 (m, 2 H, ArH), 7.43–7.41 (m, 2 H, ArH), 7.29–7.23 (m, 3 H, ArH), 7.09–7.06 (m, 1 H, ArH), 4.34–4.31 (m, 2 H, NCH_2), 4.18–4.16 (m, 2 H, NCH_2), 2.14–2.12 (m, 2 H, CH), 1.52–1.35 (m, 16 H, CH_2), 1.04–0.94 (m, 12 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.6, 141.5, 141.2, 140.5, 138.4, 131.2, 129.8, 129.2, 128.9, 127.7, 127.6, 127.4, 127.3, 126.7, 125.8, 124.7, 124.4, 124.1, 120.5, 118.9, 118.6, 118.1, 109.2, 108.9, 108.2, 101.7, 47.7, 39.7, 38.9, 31.2, 28.9, 26.9, 24.7, 24.6, 23.2, 14.1, 11.1 ppm. MS (EI): m/z (%) = 656 (45) $[M]^+$. $C_{48}H_{52}N_2$ (656.41): calcd. C 87.76, H 7.98, N 4.26; found C 87.53, H 7.84, N 4.41.

6j: The reaction of **4** (0.5 g, 1.47 mmol) with 9,9-dihexyl-2,7-di-(thiophen-2-yl)fluorene[22] (2.21 g, 4.43 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) using the above-mentioned procedure led to the isolation of the heterocycle **6j** (0.79 g, 49%) as a yellow solid, m.p. 140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (s, 1 H, ArH), 8.16–8.15 (m, 1 H, ArH), 7.98–7.96 (m, 1 H, ArH), 7.78–7.62 (m, 10 H, ArH), 7.64–7.59 (m, 5 H, ArH), 7.49–7.46 (m, 3 H, ArH), 7.39–7.32 (m, 3 H, ArH), 7.28–7.27 (m, 1 H, ArH), 7.10–7.07 (m, 1 H, ArH), 2.05–2.04 (m, 8 H, CH_2), 1.07–0.91 (m, 24 H, CH_2), 0.78–0.70 (m, 20 H, CH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.9 (2 C), 151.8, (2 C) 146.8, 146.5, 145.2, 145.1, 141.5, 140.9, 140.6, 140.3 (2 C) 140.0, 139.6, 138.2, 135.9, 133.7, 133.4, 133.3, 133.2, 133.1, 132.8, 131.9, 130.3, 129.9, 128.5, 128.1, 125.8, 125.7, 125.3, 125.1, 124.9, 124.7, 124.6, 123.3, 123.0, 122.9, 122.3, 120.9, 120.4, 120.2, 119.9, 118.8, 55.5, 55.4, 40.5, 40.5, 31.5, 31.5, 29.7, 29.7, 23.8, 22.6, 22.6, 14.1, 14.0 ppm. MS (EI): m/z (%) = 1094 (22) $[M]^+$. $C_{74}H_{78}S_4$ (1094.49): calcd. C 81.12, H 7.18, S 11.71; found C 81.38, H 7.27, S 11.57.

7a: The reaction of phthalaldehyde (**1**; 1.0 g, 7.46 mmol) with freshly prepared 2-thienylmagnesium bromide (3 equiv.) followed by protection of the resulting diol using pivaloyl chloride and subsequent triflic acid catalyzed cyclization following the published procedure[15] gave known compound **7a** (0.95 g, 55%) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (s, 1 H, ArH), 8.01 (d, J = 8.4 Hz, 1 H, ArH), 7.95 (d, J = 8.1 Hz, 1 H, ArH), 7.56–7.40 (m, 4 H, ArH), 7.31–7.22 (m, 3 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.6, 139.1, 137.6, 131.0, 130.5, 128.8, 128.4, 127.6, 127.2, 126.5, 126.4, 126.3, 125.5, 125.3, 123.8, 121.6 ppm.

7d: The reaction of phthalaldehyde (**1**; 1.0 g, 7.46 mmol) with freshly prepared 5-methyl-2-thienylmagnesium bromide followed by protection of the resulting diol using pivaloyl chloride and subsequent triflic acid catalyzed cyclization following the published[15] procedure furnished compound **7d** (1.1 g, 60%) as a colorless fluffy solid, m.p. 99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, ArH), 8.02 (d, J = 9.0 Hz, 1 H, ArH), 7.85 (d, J = 9.6 Hz, 1 H, ArH), 7.45–7.35 (m, 2 H, ArH), 6.98 (s, 1 H, ArH), 6.94 (d, J = 3.3 Hz, 1 H, ArH), 6.87–6.86 (m, 1 H, ArH), 2.59 (s, 3 H, CH_3), 2.54 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 142.8, 140.7, 140.5, 138.2, 137.0, 130.6, 130.5, 128.5, 127.4, 126.2, 125.3, 125.1, 124.8, 121.4, 120.8, 18.7, 15.4 ppm. MS (EI): m/z (%) = 294 (58) $[M]^+$. $C_{18}H_{14}S_2$ (294.05): calcd. C 73.43, H 4.79, S 21.78; found C 73.65, H 4.69, S 21.95.

Tetraacetate 11: The reaction of 4,5-dimethoxybenzene-1,2-dicarbaldehyde[23] (1 g, 5.15 mmol) with acetic anhydride (3.15 g, 30.30 mmol) in the presence of $RuCl_3{\cdot}7H_2O$ (0.05 g, 0.25 mmol) following the procedure similar to that for the synthesis of **4** afforded **10** (1.41 g, 69%) as a pale-yellow solid, m.p. 114 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s, 2 H, ArH), 7.07 (s, 2 H, ArH), 3.90–3.86 (m, 6 H, OCH_3), 2.09–2.04 (m, 12 H, OAc) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 168.4, 149.9, 126.5, 110.9, 88.3, 56.1, 20.81 ppm. MS (EI): m/z (%) = 398 (57) $[M]^+$.

12a: The reaction of **11** (0.5 g, 1.25 mmol) with 2-methylthiophene (0.36 g, 3.76 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **12a** (0.22 g, 52%) as a light-brown solid, m.p. 146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1 H, ArH), 7.27 (s, 1 H, ArH), 7.07–7.08 (m, 1 H, ArH), 7.01–7.0 (m, 1 H, ArH), 6.89 (s, 1 H, ArH), 6.80 (s, 1 H, ArH), 3.91 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 2.52 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.3, 148.9, 141.7, 140.9, 139.8, 137.9, 137.4, 128.2, 127.8, 125.8, 125.6, 123.9, 121.2, 119.2, 106.0, 103.6, 55.8 (2 C), 16.4, 15.5 ppm. MS (EI): m/z (%) = 354 (56) $[M]^+$.

$C_{20}H_{18}O_2S_2$ (354.07): calcd. C 67.76, H 5.12, S 18.09; found C 67.92, H 5.25, S 17.91.

12b: The reaction of **11** (0.5 g, 1.25 mmol) with 2-hexylthiophene (0.63 g, 3.76 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **12b** (0.37 g, 60%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.29 (s, 1 H, ArH), 7.11 (s, 1 H, ArH), 7.05 (d, J = 3.3 Hz, 1 H, ArH), 6.95 (s, 1 H, ArH), 6.83 (d, J = 3.3 Hz, 1 H, ArH), 3.95 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 2.84 (t, J = 7.7 Hz, 2 H, CH_2), 2.78 (t, J = 7.7 Hz, 2 H, CH_2), 1.75–1.61 (m, 4 H, CH_2), 1.37–1.25 (m, 12 H, CH_2), 0.86–0.79 (m, 6 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.2, 148.9, 147.7, 147.1, 139.3, 137.8, 137.0, 127.9, 127.8, 125.8, 124.2 (2 C), 119.9 (2 C), 105.9, 103.6, 55.8, 55.7, 31.6 (2 C), 31.2, 30.8, 30.3, 28.9, 28.8, 22.6 (2 C), 14.1 ppm. MS (EI): m/z (%) = 494 (44) $[M]^+$. $C_{30}H_{38}O_2S_2$ (494.23): calcd. C 72.83, H 7.74, S 12.96; found C 73.02, H 7.81, S 12.79.

12c: The reaction of **11** (0.5 g, 1.25 mmol) with bithiophene (0.62 g, 3.76 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **12c** (0.28 g, 45%) as a colorless solid, m.p. 206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (s, 1 H, ArH), 7.36 (s, 1 H, ArH), 7.29–7.27 (m, 2 H, ArH), 7.22–7.17 (m, 5 H, ArH), 7.12 (s, 1 H, ArH), 6.99–6.96 (m, 2 H, ArH), 3.96 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.9, 149.3, 138.9, 138.7, 138.3, 137.8, 137.7, 137.5, 137.2, 129.2, 128.1, 127.9 (2 C), 126.5, 125.7, 125.4, 124.6, 124.1, 123.9, 123.1, 120.6, 119.1, 106.1, 103.3, 55.9 ppm. MS (EI): m/z (%) = 490 (38) $[M]^+$. $C_{26}H_{18}O_2S_4$ (490.02): calcd. C 63.64, H 3.70, S 26.14; found C 63.88, H 3.59, S 26.02.

Tetraacetate 13: The reaction of naphthalene-1,2-dicarbaldehyde[24] (1 g, 5.43 mmol) with acetic anhydride (3.32 g, 32.60 mmol) in the presence of $RuCl_3{\cdot}7H_2O$ (0.05 g, 0.25 mmol) following the procedure similar to that used for the synthesis of **4** furnished **13** (1.19 g, 65%) as a colorless solid, m.p. 158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 (s, 2 H, ArH), 7.99 (s, 2 H, ArH), 7.60–7.56 (m, 4 H, ArH), 2.22–2.18 (m, 12 H, OAc) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.6, 131.7, 127.4, 126.8, 126.2, 124.5, 93.8, 20.7 ppm. MS (EI): m/z (%) = 338 (50) $[M]^+$.

14: The reaction of **13** (0.3 g, 0.77 mmol) with 2-methylthiophene (0.23 g, 2.31 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **14** (0.11 g, 43%) as a colorless solid, m.p. 178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, ArH), 8.55 (s, 1 H, ArH), 8.28 (s, 1 H, ArH), 8.0–7.97 (m, 1 H, ArH), 7.94–7.92 (m, 1 H, ArH), 7.42–7.38 (m, 2 H, ArH), 7.05–7.04 (m, 1 H, ArH), 6.98–6.96 (m, 2 H, ArH), 2.65 (s, 3 H, CH_3), 2.56 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.1, 139.8, 137.5, 131.5, 131.2, 129.8, 129.5, 128.8, 128.5, 127.7, 127.6, 126.4, 125.8, 125.6, 125.1, 124.8, 123.9, 121.1 ppm. MS (EI): m/z (%) = 344 (59) $[M]^+$. $C_{22}H_{16}S_2$ (344.07): calcd. C 76.70, H 4.68, S 18.62; found C 76.45, H 4.73, S 18.79.

15: The reaction of **13** (0.3 g, 0.77 mmol) with benzo[*b*]furan (0.7 g, 2.31 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **15** (0.11 g, 38%) as a colorless solid, m.p. 205 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (s, 1 H, ArH), 8.61 (s, 1 H, ArH), 8.16 (s, 1 H, ArH), 8.05–7.92 (m, 2 H, ArH), 7.85–7.80 (m, 2 H, ArH), 7.54–7.42 (m, 6 H, ArH), 7.40–7.14 (m, 3 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.2, 149.8, 145.8, 141.5, 139.2, 134.8, 128.5, 127.8, 126.5, 124.7, 123.3 (2 C), 121.4, 120.8, 113.6, 111.1 ppm. MS (EI): m/z (%) = 384 (43) $[M]^+$. $C_{28}H_{16}O_2$ (384.12): calcd. C 87.48, H 4.20; found C 87.25, H 4.03.

Benzo[*b*]thiophene-2,3-dicarbaldehyde (16b): Paraformaldehyde (5.5 g, 183.3 mmol) and 33% HBr in acetic acid (45 mL) were added to a solution of benzo[*b*]thiophene (10 g, 74.63 mmol) in acetic acid (50 mL). The reaction mixture was stirred for 12 h at room temperature. The precipitated solid was filtered, washed with water several times, and dried to yield 2,3-bis(bromomethyl)benzo[*b*]thiophene (19.5 g, 81%) as a colorless solid. Sodium hydrogen carbonate (15.75 g, 187 mmol) was added to a solution of the bis(bromomethyl)benzo[*b*]thiophene (10 g, 31.25 mmol) in acetonitrile (125 mL) and water (10 mL) and the mixture was heated at reflux for 8 h. Then the solvent was completely removed and the sticky residue was extracted with DCM (3 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo to give 2,3-bis(hydroxymethyl)benzo[*b*]thiophene (4.6 g, 76%) as a colorless solid. Active manganese dioxide (13 g) was added to a solution of the diol (3.5 g, 18.04 mmol) in DCE (100 mL) and the mixture was heated at reflux for 8 h. The progress of the reaction was monitored by TLC until the disappearance of the starting material. Then the inorganic solid was filtered off and washed with $CHCl_3$ (3 × 20 mL). Removal of the solvent afforded the dialdehyde **16b** (2.38 g, 69%) as colorless solid, m.p. 108 °C (ref.[27] 112–113 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.84 (s, 1 H, ArH), 10.68 (s, 1 H, ArH), 8.60 (d, J = 8.1 Hz, 1 H, ArH), 7.92–7.90 (m, 1 H, ArH), 7.57–7.54 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 183.32, 182.74, 149.05, 140.47, 135.98, 135.77, 127.75, 126.07, 125.28, 121.94 ppm.

Tetraacetate 17a: The reaction of 1-phenylsulfonylindole-2,3-dicarbaldehyde (**16a**;[26] (1 g, 3.19 mmol) with acetic anhydride (1.96 g, 19.16 mmol) in the presence of $RuCl_3{\cdot}7H_2O$ (0.05 g, 0.25 mmol) following the procedure similar to that used for the synthesis of **4** furnished **17a** (1.25 g, 76%) as a colorless solid, m.p. 138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (s, 1 H, ArH), 8.53 (s, 1 H, ArH), 8.14 (d, J = 8.4 Hz, 1 H, ArH), 8.05 (d, J = 7.8 Hz, 2 H, ArH), 7.93 (d, J = 7.8 Hz, 1 H, ArH), 7.60 (d, J = 7.35 Hz, 1 H, ArH), 7.56–7.46 (m, 2 H, ArH), 7.43–7.38 (m, 1 H, ArH), 7.34–7.29 (m, 1 H, ArH), 2.15 (s, 6 H, OAc), 2.08 (s, 6 H, OAc) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 168.4, 168.2, 138.1, 136.1, 134.3, 132.1, 129.4, 127.2, 126.6, 126.4, 124.1, 122.1, 119.2, 114.8, 84.9, 84.1, 20.8, 20.6 ppm. MS (EI): m/z (%) = 517 (60) $[M]^+$.

Tetraacetate 17b: The reaction of benzo[*b*]thiophene-2,3-dicarbaldehyde (**16b**; 1 g, 5.26 mmol) with acetic anhydride (3.25 g, 31.86 mmol) in the presence of $RuCl_3{\cdot}7H_2O$ (0.05 g, 0.25 mmol) following the procedure similar to that used for the synthesis of **4** furnished **17b** (1.35 g, 65%) as a light-brown solid, m.p. 158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, ArH), δ = 8.21 (s, 1 H, ArH), 8.12 (d, J = 7.5 Hz, 1 H, ArH), 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.44–7.40 (m, 2 H, ArH), 2.22–2.08 (m, 12 H, OAc) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 168.6, 168.2, 139.0, 138.9, 136.7, 128.8, 125.8, 124.9, 124.1, 122.5, 85.0, 20.7 ppm. MS (EI): m/z (%) = 394 (52) $[M]^+$.

18a: The reaction of **17a** (0.5 g, 0.96 mmol) with 2-hexylthiophene (0.48 g, 2.90 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **18a** (0.34 g, 58%) as a colorless solid, m.p. 104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H, ArH), 8.24 (d, J = 8.4 Hz, 1 H, ArH), 7.74 (d, J = 8.7 Hz, 2 H, ArH), 7.35–7.31 (m, 2 H, ArH), 7.24–7.19 (m, 2 H, ArH), 7.09–7.03 (m, 3 H, ArH), 6.89 (d, J = 3.3 Hz, 1 H, ArH), 6.82 (d, J = 3.3 Hz, 1 H, ArH), 2.86–2.77 (m, 4 H, CH_2), 1.70–1.62 (m, 4 H, CH_2), 1.32–1.22 (m, 12 H, CH_2), 0.84–0.80 (m, 6 H, CH_3) ppm. ^{13}C NMR (75.4 MHz,

$CDCl_3$): δ = 149.3, 147.8, 139.3 (2 C), 137.8, 137.1, 135.3, 133.8, 129.1, 127.3, 127.1, 126.6, 126.1, 124.6, 123.8, 123.4, 122.7, 122.3, 121.0, 114.9, 108.4, 31.6, 31.2, 31.1, 30.3, 28.9, 28.8, 22.6, 22.5, 14.1 ppm. MS (EI): *m*/*z* (%) = 613 (45) $[M]^+$. $C_{36}H_{39}NO_2S_3$ (613.21): calcd. C 70.43, H 6.40, N 2.28, S 15.67; found C 70.69, H 6.53, N 2.13, S 15.52.

18b: The reaction of **17a** (0.5 g, 0.96 mmol) with bithiophene (0.48 g, 2.90 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **18b** (0.29 g, 49%) as a colorless solid, m.p. 142 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.73 (s, 1 H, ArH), 8.35 (d, *J* = 8.4 Hz, 1 H, ArH), 7.85 (d, *J* = 7.2 Hz, 2 H, ArH), 7.56 (s, 1 H, ArH), 7.44–7.40 (m, 2 H, ArH), 7.34–7.23 (m, 4 H, ArH), 7.16–7.10 (m, 5 H, ArH), 7.03–6.98 (m, 3 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.5, 139.4, 139.3, 137.7, 137.4, 137.2, 136.9, 136.4, 133.9, 129.2, 128.7, 128.1, 127.9, 127.8, 127.6, 126.6, 125.9, 125.6, 125.4, 124.9, 124.4, 124.2 (2 C), 124.1, 123.8, 122.4, 120.1, 114.9, 109.3 ppm. MS (EI): *m*/*z* (%) = 609 (52) $[M]^+$. $C_{33}H_{19}NO_2S_5$ (609.01): calcd. C 63.03, H 3.14, N 2.30, S 26.29; found C 63.32, H 3.21, N 2.18, S 26.19.

19a: The reaction of **17b** (0.5 g, 1.26 mmol) with 2-hexylthiophene (0.63 g, 3.80 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **19a** (0.34 g, 54%) as a thick liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H, ArH), 8.07–8.04 (m, 1 H, ArH), 7.71–7.69 (m, 1 H, ArH), 7.40–7.35 (m, 3 H, ArH), 7.03 (s, 1 H, ArH), 6.82 (d, *J* = 3.3 Hz, 1 H, ArH), 2.81 (t, *J* = 6.6 Hz, 4 H, CH_2), 1.67 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.25–1.24 (m, 12 H, CH_2), 0.83–0.80 (m, 6 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 147.1, 139.5, 138.9, 138.8, 137.1, 135.9, 135.5, 134.1, 127.6, 126.7, 124.3, 123.7, 122.6, 121.4, 120.7, 114.1, 31.6, 30.9, 30.3, 29.8, 28.9 (2 C), 22.6, 14.1 ppm. MS (EI): *m*/*z* (%) = 490 (47) $[M]^+$. $C_{30}H_{34}S_3$ (490.18): calcd. C 73.42, H 6.98, S 19.60; found C 73.18, H 7.11, S 19.71.

19b: The reaction of **17b** (0.5 g, 1.26 mmol) with bithiophene (0.63 g, 3.80 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **19b** (0.29 g, 47%) as a colorless solid, m.p. 172 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H, ArH), 8.80 (d, *J* = 7.8 Hz, 1 H, ArH), 7.46 (s, 1 H, ArH), 7.40–7.32 (m, 2 H, ArH), 7.28–7.23 (m, 4 H, ArH), 7.21–7.15 (m, 2 H, ArH), 7.08–7.01 (m, 3 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.8, 140.2, 139.5, 138.8, 137.7, 137.6, 137.3, 137.1, 134.6, 131.6, 128.5, 128.1, 127.9, 127.8, 126.7, 125.9, 125.5, 124.9, 124.8, 124.4, 124.3, 124.2, 123.8, 122.6, 118.6, 117.1 ppm. MS (EI): *m*/*z* (%) = 486 (40) $[M]^+$. $C_{26}H_{14}S_5$ (485.97): calcd. C 64.16, H 2.90, S 32.94; found C 64.01, H 3.03, S 33.09.

20: The reaction of **17a** (0.5 g, 0.96 mmol) with benzo[*b*]furan (0.34 g, 2.90 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **20** (0.26 g, 53%) as a colorless solid, m.p. 178 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.06 (s, 1 H, ArH), 8.41 (d, *J* = 8.4 Hz, 1 H, ArH), 8.16 (d, *J* = 7.5 Hz, 1 H, ArH), 7.85 (d, *J* = 8.7 Hz, 2 H, ArH), 7.79–7.76 (m, 1 H, ArH), 7.62–7.53 (m, 3 H, ArH), 7.54–7.46 (m, 4 H, ArH), 7.41–7.36 (m, 2 H, ArH), 7.35–7.29 (m, 3 H, ArH), 7.23–7.20 (m, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.2, 154.8, 151.9, 148.4, 139.7, 137.6, 135.4, 133.9, 129.2, 128.9, 127.9, 127.8, 126.5, 125.9, 124.9, 124.8, 124.3, 124.1, 123.3, 123.2, 122.9, 121.5, 121.1, 115.2, 111.9, 111.6, 108.9, 108.7, 107.8 ppm. MS (EI): *m*/*z* (%) = 513 (59) $[M]^+$. $C_{32}H_{19}NO_4S$ (513.10): calcd. C 74.84, H 3.73, N 2.73, S 6.24; found C 74.65, H 3.63, N 2.80, S 6.37.

21: The reaction of **17b** (0.5 g, 1.26 mmol) with benzo[*b*]furan (0.45 g, 3.80 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **21** (0.25 g, 51%) as a colorless solid, m.p. 150 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, ArH), 8.02 (d, *J* = 7.5 Hz, 1 H, ArH), 7.86–7.80 (m, 2 H, ArH), 7.63–7.61 (m, 1 H, ArH), 7.56–7.50 (m, 1 H, ArH), 7.49 (d, *J* = 6.9 Hz, 1 H, ArH), 7.42–7.34 (m, 4 H, ArH), 7.31–7.25 (m, 2 H, ArH), 7.21–7.16 (m, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 157.2, 155.1, 153.6, 148.8, 140.8, 134.9, 134.8, 133.4, 128.9, 128.0, 126.8, 124.8, 124.6, 124.2, 124.1, 123.4, 123.2, 123.1, 122.7, 121.5, 120.9, 115.4, 111.9, 111.8, 110.6, 108.6 ppm. MS (EI): *m*/*z* (%) = 390 (59) $[M]^+$. $C_{26}H_{14}O_2S$ (390.07): calcd. C 79.98, H 3.61, S 8.21; found C 79.79, H 3.74, S 8.34.

22: The reaction of **17b** (0.5 g, 1.26 mmol) with *N*-ethylcarbazole (0.74 g, 3.80 mmol) in the presence of $BF_3{\cdot}OEt_2$ (40 mg) following the same procedure as that used for the synthesis of **6d** afforded compound **22** (0.28 g, 40%) as a light-yellow solid, m.p. 244 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.24 (s, 1 H, ArH), 8.69 (d, *J* = 7.8 Hz, 1 H, ArH), 8.15 (s, 1 H, ArH), 7.98 (d, *J* = 7.5 Hz, 1 H, ArH), 7.73 (d, *J* = 7.8 Hz, 1 H, ArH), 7.68–7.60 (m, 3 H, ArH), 7.56–7.52 (m, 1 H, ArH), 7.51–7.46 (m, 4 H, ArH), 7.42–7.39 (m, 3 H, ArH), 6.83 (t, *J* = 7.7 Hz, 1 H, ArH), 6.56 (d, *J* = 8.1 Hz, 1 H, ArH), 4.49–4.40 (m, 4 H, CH_2), 1.56–1.51 (m, 6 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.5, 139.7, 138.9, 138.8, 138.2, 137.5, 136.4, 130.3, 130.1, 128.9, 127.6, 127.2, 126.5, 126.1, 126.0, 125.2, 124.0, 123.9, 123.8, 123.6, 122.9, 122.4, 122.0, 121.9, 120.7, 119.9, 119.1, 115.4, 113.5, 109.8, 109.3, 109.2, 108.7, 37.9, 37.7, 14.4, 14.0 ppm. MS (EI): *m*/*z* (%) = 544 (31) $[M]^+$. $C_{38}H_{28}N_2S$ (544.19): calcd. C 83.79, H 5.18, N 5.14, S 5.89; found C 83.95, H 5.09, N 5.06, S 6.01.

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[1] A special issue on organic electronics has recently been published, see: *Chem. Mater.* **2004**, *16*, 4381–4846.
[2] D. J. Gundlach, J. A. Nichols, L. Zhou, T. N. Jackson, *Appl. Phys. Lett.* **2002**, *80*, 2925–2927.
[3] a) Y. Y. Lin, D. J. Gundlach, S. F. Nelson, T. N. Jackson, *IEEE Electron Device Lett.* **1997**, *18*, 606–608; b) T. W. Kelly, L. D. Boardman, T. D. Dunbar, D. V. Muyres, M. J. Pellerite, T. P. Smith, *J. Phys. Chem. B* **2003**, *107*, 5877–5881.
[4] C. D. Dimitrakopoules, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99–117.
[5] a) H.-D. Becker, *Chem. Rev.* **1993**, *93*, 145–172; b) J.-P. Desvergne, F. Fages, H. Bouas-Laurent, P. Marsau, *Pure Appl. Chem.* **1992**, *64*, 1231–1238; c) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, *Pure Appl. Chem.* **1980**, *52*, 2633–2648.
[6] a) H. Bouas-Laurent, J.-P. Desvergne in *Photochromism Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **1990**; b) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.* **2000**, *29*, 43–55.
[7] L. R. C. Barclay, in: *Friedel–Crafts and Related Reactions* (Ed.: G. A. Olah), Interscience, New York, **1964**.
[8] C. K. Bradsher, *Chem. Rev.* **1946**, *38*, 447–499.

[9] L. F. Fieser, *Org. React.* **1942**, *1*, 129–131.
[10] a) T. Yamato, N. Sakaue, N. Shinoda, K. Matsuo, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1193–1200; b) M. Ahmed, J. Ashby, M. Ayad, O. Methcohn, *J. Chem. Soc. Perkin Trans. 1* **1973**, 1099–1103.
[11] a) T. Takahashi, M. Kitamura, B. Shen, K. Nakajima, *J. Am. Chem. Soc.* **2000**, *122*, 12876–12877; b) T. Takahashi, S. Li, W. Huang, F. Kong, K. Nakajima, B. Shen, T. Ohe, K. Kanno, *J. Org. Chem.* **2006**, *71*, 7967–7977.
[12] I. Ioval, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem. Int. Ed.* **2005**, *44*, 3913–3917.
[13] Z. Li, Z. Duan, J. Kang, H. Wang, L. Yu, Y. Wu, *Tetrahedron* **2008**, *64*, 1924–1930.
[14] M. Kodomari, M. Nagamatsu, M. Akaike, T. Aoyama, *Tetrahedron Lett.* **2008**, *49*, 2537–2540.
[15] G. Li, S. Zhou, G. Su, Y. Liu, P. G. Wang, *J. Org. Chem.* **2007**, *72*, 9830–9833.
[16] a) Y. Liu, S. Zhou, G. Li, B. Yan, S. Guo, Y. Zhou, H. Zhang, P. G. Wang, *Adv. Synth. Catal.* **2008**, *350*, 797–801; b) G. Li, E. Wang, H. Chen, H. Li, Y. Liu, P. G. Wang, *Tetrahedron* **2008**, *64*, 9033–9043; c) H. Li, J. Yang, Y. Liu, Y. Li, *J. Org. Chem.* **2009**, *74*, 6797–6801.
[17] G. K. Surya Prakash, C. Panja, A. Shakhmin, E. Shah, T. Mathew, G. A. Olah, *J. Org. Chem.* **2009**, *74*, 8659–8668.
[18] a) M. Rueping, B. J. Nachtsheim, T. Scheidt, *Org. Lett.* **2006**, *8*, 3717–3719; b) K. Mertins, I. Iovel, J. Kischel, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2006**, *348*, 691–695; c) M. Dorbec, J. C. Florent, C. Monneret, M. N. Rager, C. Fosse, E. Bertounesque, *Eur. J. Org. Chem.* **2008**, 1723–1731; d) S. Murarka, C. Zhang, M. D. Konieczynska, D. Seidel, *Org. Lett.* **2009**, *11*, 129–132; e) K. M. McQuaid, J. Z. Long, D. Sames, *Org. Lett.* **2009**, *11*, 2972–2975; f) X. Xu, H. Li, X. Xie, Y. Li, *Org. Lett.* **2010**, *12*, 100–103.
[19] V. Dhayalan, J. A. Clement, R. Jagan, A. K. Mohanakrishnan, *Eur. J. Org. Chem.* **2009**, 531–546.
[20] A. Saini, S. Kumar, J. S. Sandhu, *Synth. Commun.* **2008**, *38*, 106–113.
[21] M. P. Cava, A. A. Deana, K. Muth, *J. Am. Chem. Soc.* **1959**, *81*, 6458–6460.
[22] V. Promarak, A. Pankvuang, S. Ruchirawat, *Tetrahedron Lett.* **2007**, *48*, 1151–1154.
[23] a) F. D. Drop, D. J. Battacharjee, *J. Heterocycl. Chem.* **1980**, *17*, 315–320; b) M. Barfield, R. J. Spear, S. J. Sternhell, *J. Am. Chem. Soc.* **1975**, *97*, 5160–5167; c) G. A. Edwards, W. H. Perkin, F. W. Stoyle, *J. Chem. Soc.* **1925**, 195–199; d) M. Harig, B. Newmann, H.-G. Stammler, D. Kuck, *Eur. J. Org. Chem.* **2004**, 2381–2397.
[24] R. G. Carlson, K. Srinivasachar, R. S. Givens, B. K. Matuszewski, *J. Org. Chem.* **1986**, *51*, 3978–3983.
[25] a) G. M. Sheldrick, *SHELXS97*, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXL97*, University of Göttingen, Göttingen, Germany, **1997**.
[26] A. K. Mohanakrishnan, P. C. Srinivasan, *Synth. Commun.* **1995**, *25*, 2407–2414.
[27] F. Kröhnke, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 380–393.

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