Synlett N. S. Demina et al. Letter

An Effective Route to Dithieno[3,2-*b*:2′,3′-*d*]thiophene-Based Hexaheteroacenes

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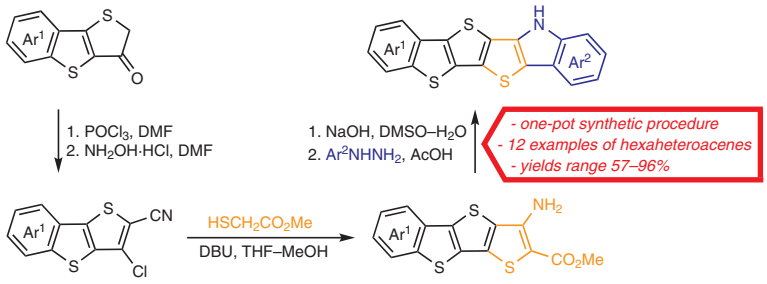

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Abstract A series of 12*H*-[1]benzo[4′′,5′′]thieno[2′′,3′′:4′,5′]thieno[2′,3′:4,5]thieno[3,2-*b*]indoles were efficiently prepared in three steps starting from available benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-ones. These fused ketones were treated with the Vilsmeier reagent and hydroxylamine hydrochloride to give the corresponding 3-chlorobenzo[*b*]thieno[2,3-*d*]thiophene-2-carbonitriles, which then reacted with methyl sulfanylacetate to form methyl 3-aminobenzo[4′,5′]thieno[2′,3′:4,5]thieno[3,2-*b*]thiophene-2-carboxylates, in accordance with the Fiesselmann thiophene synthesis protocol. Finally, the desired N,S-heterohexacenes were obtained by conversion of these fused 3-aminothiophene-2-carboxylates into the corresponding 3-aminothiophene intermediates, which acted as synthetic equivalents of thiophen-3(2*H*)-ones, followed by their acid-promoted reaction with arylhydrazines, in accordance with the Fischer indolization procedure.

Keywords benzothienothienothienoindoles, aminothiophenes, arylhydrazines, Fiesselmann reaction, Fischer indole synthesis

Over the past two decades, many thiophene-based photo- and electroactive compounds have been developed and used to fabricate photonic and electronic devices.[1,2] In this context, because of its rigid planar scaffold and its high degree of π-conjugation, as well as its ability to undergo effective intermolecular S–S interactions, dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT), as well as analogous (het)aryl-linked DTT molecules[3–11] and ring-fused molecules with DTT a core,[12–18] have found widespread application in the design of p-type semiconductors for organic field-effect transistors (OFETs). The DTT subunit has been also used in the construction of light-harvesting materials for organic photovoltaics,[9–27] as well as in electrochromic[28–31] and photochromic materials.[32–34] For instance, two examples of semiconductor materials based on benzo-fused DTT frameworks, **P-BTDT**[12] and **C6-DBTDT**,[17] together with an N,S-heteroheptacene with an indolo-fused DDT framework[18] used in the production of solution-processible OFETs, are shown in Figure 1. Furthermore, we recently described a synthesis of the N,S-heterohexacene 12*H*-[1]benzo[4″,5″]thieno[2″,3″:4′,5′] thieno[2′,3′:4,5]-thieno[3,2-*b*]indole (**BTTTI**; also shown in Figure 1), by using a Fischer indolization reaction as a key transformation,[35] and we demonstrated its promising application as a p-type organic semiconductor.[36]

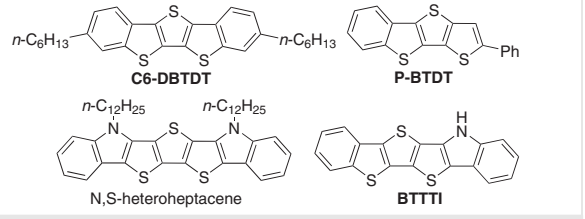

Figure 1 Materials based on ring-annulated DTT frameworks

Nevertheless, the construction of DTT-based molecules and ring-fused molecules containing a DTT core remains challenging. One of the most popular approaches to the DTT fragment is the Stille reaction of 2-unsubstituted 3-bromothiophene substrates with $(Bu_3Sn)_2S$ to form di(3-thienyl) sulfide derivatives, which undergo oxidative cyclization to form a central thiophene ring.[17,18,37–40] However, this approach requires the use of toxic organotin reagents and transition-metal-catalyzed reactions, and it permits the construction of symmetric DTT molecules only.

In regard to the synthesis of asymmetric ring-fused DTT molecules, the benzo[4′,5′]thieno[2′,3′:4,5]thieno[3,2-*b*]thiophene (BTTT) system with a benzo-annulated DTT core can be mentioned. Such BTTT-based compounds are formed by (het)arylation of the simplest BTTT substrate by means of transition-metal-catalyzed reactions.[12,13] Data on other asymmetric DTT-cored heteroacenes are limited to

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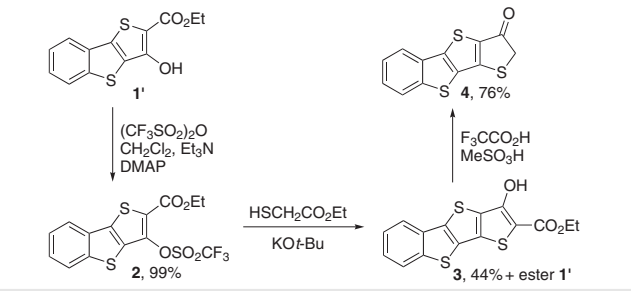
the synthesis of **BTTTI** (Figure 1), reported in our previous study.[35] This molecule was constructed by annulation of the indole part by a Fischer indole synthesis. Compound **BTTTI** was prepared in 51% yield by reaction of the fused thiophen-3(2*H*)-one **4** (Scheme 1) with phenylhydrazine in glacial acetic acid solution. In turn, ketone **4** was synthesized from the 3-hydroxythiophene-2-carboxylate **1′** in the three steps. First, ester **3** was prepared by O-triflation of substrate **1′** followed by reaction of the resulting triflate **2** with ethyl sulfanylacetate in accordance with the Fiesselmann method.[41] Finally, ester **3** was subjected to acid-promoted hydrolysis to afford the desired ketone **4**. However, compound **3** was isolated in a modest yield only due to the partial O-detriflation of substrate **2**, caused by the attack of an S-nucleophile, namely the S-anion of sulfanylacetate, on the sulfur atom of the F_3CSO_2 group, and the formation of ester **1′**. In this context, the synthesis of BTTTI derivatives by this strategy appears to be not entirely successful due to the practical disadvantage in the step of constructing the BTTT derivative **3**.

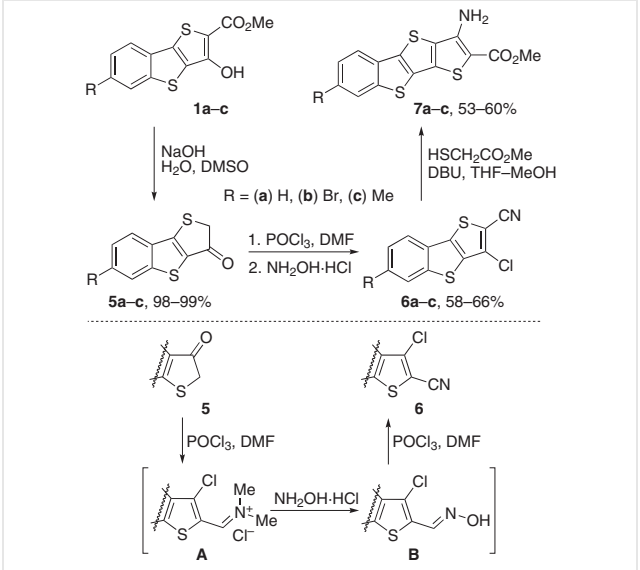


Scheme 1 Previous synthetic route to a BTTT derivative[35]

Because of the high importance of DTT-cored compounds, we wished to develop an alternative synthetic route towards BTTTI heterohexacenes that could provide sustainable access to these compounds.

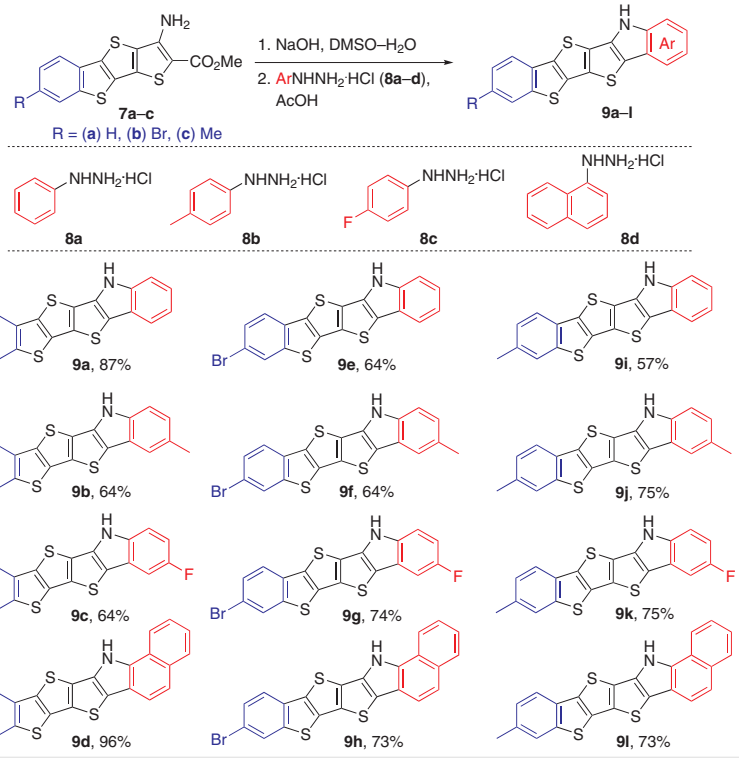
First, we focused on finding appropriate BTTT-cored substrates that can be used for the synthesis of BTTTI heterohexacenes. We recently reported an effective one-pot procedure for the synthesis of thieno[3,2-*b*]indole-containing compounds, including ring-fused structures, by the acid-promoted reaction of arylhydrazines with 2-unsubstituted 3-aminothiophenes generated in situ from 3-aminothiophene-2-carboxylates, which acted as synthetic equivalents of thiophen-3(2*H*)-ones.[42,43] We therefore selected the 3-amino-substituted BTTT molecules **7** as potential substrates for the construction of BTTTIs. Compounds **7a–c** were synthesized from the corresponding benzo[*b*]thieno[2,3-*d*]thiophene-2-carboxylates **1a–c** (Scheme 2). Esters **1a–c** were first saponified by NaOH in aqueous DMSO. Subsequent decarboxylation of the resulting acids gave the fused thiophen-3(2*H*)-ones **5a–c**.[35,44,45] Importantly, this procedure gave ketones **5a–c** in almost quantitative yields, unlike the acid-promoted hydrolysis described earlier.[35]

Thiophen-3(2*H*)-ones **5a–c** were subjected to chloroformylation with $POCl_3$–DMF complex in DMF by a Vilsmeier–Haack–Arnold reaction and the reaction mixtures were then treated with hydroxylamine hydrochloride to convert the initially formed iminium salts **A** into oximes of 3-chlorothiophene-2-carbaldehydes **B**. These were dehydrated in the presence of an excess of the $POCl_3$–DMF complex to form the 3-chlorothiophene-2-carbonitriles **6**.[46] Note that the present protocol for the synthesis of nitriles **6** from ketones **5** is similar to a previously reported one-pot procedure for the preparation of 3-aryl-3-chloroacrylonitriles from acetophenones.[47] Carbonitriles **6** were treated with methyl sulfanylacetate in the presence of DBU to give fused 3-aminothiophene-2-carboxylates **7a–c**[48] with the required BTTT core, according to the Fiesselmann protocol.



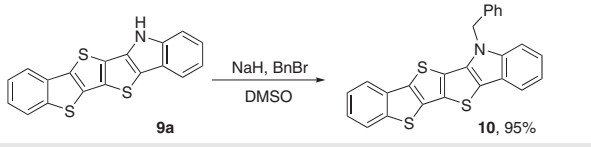
Scheme 2 Proposed approach to BTTT derivatives

Finally, to prepare BTTTI derivatives, esters **7a–c** were saponified by treatment with NaOH in aqueous DMSO (Scheme 3). Saponification of esters **7a–c** could only be performed in DMSO medium due to the poor solubility of these fused compounds in other organic solvents. The reaction mixtures were then neutralized with excess glacial acetic acid to induce decarboxylation of the resulting amino acids to form 3-amino BTTTs. These intermediates, without isolation, were treated with appropriate arylhydrazines hydrochlorides **8** to give the corresponding arylhydrazones of BTTT-cored thiophen-3(2*H*)-ones, which then underwent Fischer indolization to form the desired BTTTI derivatives **9a–l**.[49] The required N,S-heterohexacenes **9a–l** were obtained in overall yields of 57–96% by using this one-pot synthetic procedure. Note that the BTTTI compounds other than **9a** and **9c**, which were moderately soluble in DMSO, showed poor solubilities in most organic solvents.



Scheme 3 Synthesis, substrate scope, and yields of BTTTI derivatives

In addition, compound **9a** was treated with sodium hydride and benzyl bromide to afford the N-benzylated derivative **10**[50] in 95% yield (Scheme 4). The structure of product **10** was confirmed by X-ray diffraction analysis.[51]



Scheme 4 Alkylation of BTTTI derivative **9a**

To sum up, we have developed an effective route to BTTTI heterohexacenes through a Fischer indolization reaction of arylhydrazines with 3-amino-substituted BTTT intermediates, prepared in situ from the corresponding BTTT-cored 3-aminothiophene-2-carboxylates. In turn, the required 3-aminothiophene-2-carboxylates were synthesized in two steps from benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-ones by treatment with Vilsmeier reagent and hydroxylamine hydrochloride to form the corresponding fused 3-chlorothiophene-2-carbonitriles, followed by the reaction of these substrates with methyl sulfanylacetate in the presence of DBU. The N,S-heterohexacene products appear to be promising semiconductor materials for applications in the field of organic electronics. Furthermore, the above-mentioned fused 3-chlorothiophene-2-carbonitriles 3-aminothiophene-2-carboxylates can be considered as useful building blocks for the development of π-extended compounds.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1398-7237.

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(45) **Thiophen-3(2*H*)-ones 5a–c; General Procedure**
All solvents were previously degassed. The appropriate ester **1a–c** (6.0 mmol) was dissolved in DMSO (30 mL), and a solution of NaOH (4.8 g, 120.0 mmol) in H_2O (30.00 mL) was added. The resulting mixture was refluxed at 120 °C for 2 h under an inert atmosphere, then cooled to r.t. and poured into 1.0 M aq HCl (0.20 L). The resulting mixture was boiled with stirring until evolution of CO_2 ceased. The resulting precipitate was collected by filtration, washed with H_2O (2 × 0.10 L), and dried.
6-Methylthieno[3,2-*b*][1]benzothiophen-3(2*H*)-one (5c)
Light-brown solid; yield: 1.59 g (98%); mp 211–212 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.1 Hz, 1 H), 7.66 (s, 1 H), 7.29 (dd, J = 8.1, 1.4 Hz, 1 H), 4.19 (s, 2 H), 2.52 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 191.6, 160.9, 148.0, 140.4, 130.6, 127.1, 124.3, 123.2, 121.3, 44.2, 22.0. Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66. Found: C, 59.90; H, 3.58.
(46) **3-Chlorothiophene-2-carbonitriles 6a–c; General Procedure**
The appropriate thiophen-3(2*H*)-one **5a–c** (5.0 mmol) was dissolved in DMF (50.00 mL) and the solution was cooled 15 °C. $POCl_3$ (10.0 mmol, 0.93 mL) in DMF (20.0 mmol, 1.55 mL) was added dropwise, and the mixture was heated to 60 °C for 3 h while a yellow precipitate of the iminium salt formed. The mixture was cooled to r.t. and a solution of hydroxylamine hydrochloride (10.0 mmol, 0.70 g) in DMF (10.00 mL) was added dropwise. The resulting mixture was stirred for 4 h at r.t., then heated at 60 °C for an additional 1 h. The mixture was diluted with H_2O (50.00 mL), and the residue that formed was collected by filtration, washed with water (2 × 25.00 mL), and dried.
3-Chloro-6-methylthieno[3,2-*b*][1]benzothiophene-2-carbonitrile (6c)
Brown solid; yield: 0.87 g (66%); mp 221–222 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.2 Hz, 1 H), 7.70 (s, 1 H), 7.34–7.28 (m, 1 H), 2.52 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.0, 138.0, 137.6, 135.6, 129.6, 129.4, 127.3, 124.2, 121.4, 112.5, 105.2, 21.8. Anal. Calcd for $C_{12}H_6ClNS_2$: C, 54.65; H, 2.29; N, 5.31. Found: C, 54.57; H, 2.21; N, 5.23.

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(48) **3-Aminothiophene-2-carboxylates 7a-c; General Procedure**
The appropriate nitrile **6a–c** (4.0 mmol) was dissolved in 9:1 THF–MeOH (50.00 mL) under argon. Methyl sulfanylacetate (4.8 mmol, 0.43 mL) and DBU (6.0 mmol, 0.87 mL) were added, and the resultant mixture was refluxed for 15 h, then cooled and diluted with MeOH (40.00 mL). The precipitate that formed was collected by filtration and washed with MeOH (2 × 10.00 mL).
Methyl 3-Amino-7-methylthieno[2′,3′:4,5]thieno[3,2-*b*][1]-benzothiophene-2-carboxylate (7c)
Yellow solid (0.70 g, 53%); mp 270–271 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.99–7.91 (m, 2 H), 7.40–7.33 (m, 1 H), 7.21 (s, 2 H), 3.79 (s, 3 H).^{13}C NMR (126 MHz, DMSO-d_6): δ = 164.2, 148.2, 142.0, 139.1, 135.8, 132.8, 130.5, 130.1, 128.3, 127.0, 124.2, 121.0, 97.6, 51.2, 21.1. Anal. Calcd for $C_{15}H_{11}NO_2S_3$: C, 54.03; H, 3.33; N, 4.20. Found: C, 53.95; H, 3.25; N, 4.12.

(49) **BTTTI derivatives 9a–l; General Procedure**
All solvents were previously degassed. The appropriate compound **7a–c** (1.0 mmol) was dissolved in DMSO (5.00 mL), and a solution of NaOH (20.0 mmol, 0.80 g) in H_2O water (5.00 mL) was added. The mixture was refluxed at 120 °C for 3 h under an inert atmosphere, then cooled to r.t. and diluted with glacial HOAc (10.00 mL). The appropriate hydrazine **8a–d** (1.5 mmol) was added. and the resultant mixture was refluxed at 120 °C for additional 3 h, then cooled again to r.t. The precipitate that formed was collected by filtration, washed successively with H_2O (2 × 10.00 mL) and MeOH (2 × 5.00 mL), and dried. Compounds **9d–i**, and **9k–l** were additionally purified by sublimation under reduced pressure (250 °C, 3 mbar).
3-Fluoro-12*H*-[1]benzothieno[2″,3″:4′,5′]thieno[2′,3′:4,5]-thieno[3,2-*b*]indole (9c)
Light-brown solid (0.23 g, 64%); mp 401–402 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.11 (s, 1 H), 8.12 (d, J = 8.1 Hz, 1 H), 8.07 (d, J = 7.8 Hz, 1 H), 7.69 (dd, J = 9.7, 2.6 Hz, 1 H), 7.58 (dd, J = 8.9, 4.5 Hz, 1 H), 7.55–7.49 (m, 1 H), 7.49–7.42 (m, 1 H), 7.16–7.08 (m, 1 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 156.9 (d, J = 233.1 Hz), 140.6, 136.9, 136.8, 134.8, 132.7, 132.5, 130.4, 125.5, 125.1, 125.0, 124.4, 122.2 (d, J = 11.1 Hz), 120.7, 117.3 (d, J = 4.4 Hz), 113.5 (d, J = 9.9 Hz), 110.7 (d, J = 26.0 Hz), 103.6 (d, J = 25.1 Hz). ^{19}F NMR (471 MHz, DMSO-d_6): δ = 39.24–39.17 (m). Anal. Calcd for $C_{18}H_8FNS_3$: C, 61.17; H, 2.28; N, 3.96. Found: C, 61.20; H, 2.31; N, 3.99.

(50) **12-Benzyl-12*H*-[1]benzothieno[2″,3″:4′,5′]thieno[2′,3′:4,5]-thieno[3,2-*b*]indole (10)**
Compound **9a** (0.5 mmol, 0.17 g) was dissolved in DMSO (2.00 mL) at 100 °C, and a 60% dispersion of NaH in mineral oil (0.8 mmol, 0.03 g) was added. When the evolution of H_2 ceased, BnBr (0.8 mmol, 0.09 mL) was added, and the mixture was stirred at 100 °C for an additional 30 min. The mixture was then cooled to r.t. and diluted with H_2O (5.00 mL). The precipitate that formed was collected by filtration, washed with H_2O (2 ×10.00 mL) and MeOH (2 ×10.00 mL), and dried to give a white product; yield: 0.20 g (95%); mp 284–285 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.84 (m, 1 H), 7.82–7.73 (m, 2 H), 7.47–7.39 (m, 2 H), 7.37–7.33 (m, 1 H), 7.35–7.20 (m, 7 H), 5.64 (s, 2 H).^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.5, 141.0, 137.1, 136.9, 134.9, 133.4, 133.0, 131.3, 129.0, 127.9, 126.8, 125.0, 124.6, 124.5, 124.0, 123.0, 122.9, 120.3, 120.2, 118.8, 118.3, 110.4, 49.2. Anal. Calcd for $C_{25}H_{15}NS_3$: C, 70.56; H, 3.55; N, 3.29. Found: C, 70.59; H, 3.58; N, 3.32.

(51) CCDC 2064036 contains the supplementary crystallographic data for compound **10**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.