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SPECIAL ISSUE ARTICLE

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# New methods for the synthesis of 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole

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**Abstract**

Various alternative methods for the synthesis of 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) starting from commercially available bromothiophene precursors are presented. Crucial steps involve the Cadogan reaction, Ullmann-type C─N couplings, or Buchwald-Hartwig–type aminations to build up the central pyrrole ring of DTP, respectively. The use of ammonia surrogates afforded the fused target heteroacene in overall yields of 33% to 63%, and the corresponding methods are applicable on large scale.

**KEYWORDS**

4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole, ammonia surrogates, Buchwald-Hartwig amination, Cadogan reaction, Ullmann reaction

## 1 | INTRODUCTION

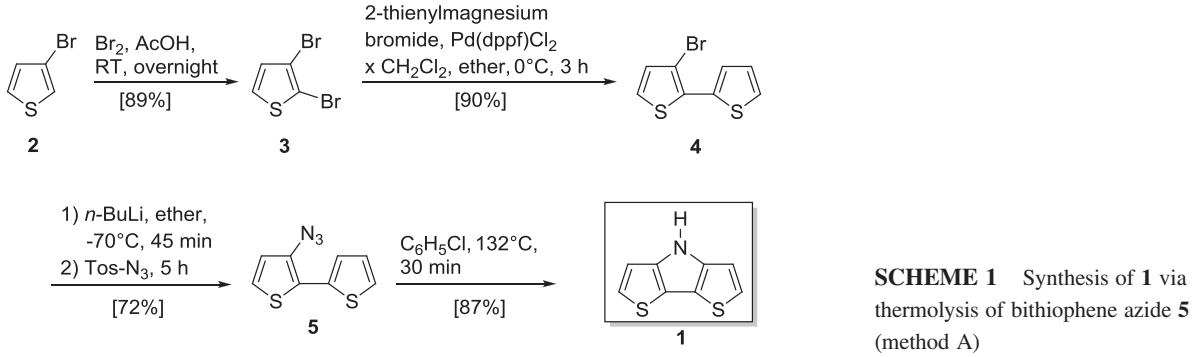
Many conjugated organic oligomers or polymers comprise the electron-rich dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) unit,[1] which for instance functions as the donor part in donor-acceptor–based organic semiconductors for application in organic electronics and in particular organic solar cells.[2–4] The commonly used *N*-alkyl or *N*-aryl DTPs can be effectively synthesized via Pd-catalysed Buchwald-Hartwig amination of bithiophene precursors and respective amines in excellent yields.[5,6] Unfortunately, the scope of this approach is rather limited to the above mentioned alkyl and aryl substituents, and only moderate yields can be achieved for functionalized DTPs bearing acyl,[7] amino,[8,9] or ether residues,[10] respectively. However, it would be highly interesting to have efficient access to functionalized DTPs to either tune electronic or redox properties of DTP-based oligomers[11] or to prepare corresponding functionalized conducting poly(DTP)s.[6,7,10,12–20] The attachment of more complex moieties to the DTP core appears very promising by substituting parent 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole **1** at the nitrogen. A prerequisite concerning this strategy is clearly that precursor **1** can be readily prepared on large scale. Already in 1983, Zanirato et al reported the synthesis of DTP **1** including thermolysis of an azide as the key step (method A, Scheme 1).[21] After bromination of 3-bromothiophene **2** to 2,3-dibromothiophene **3**,[22] Kumada cross-coupling reaction of **3** and 2-thienylmagnesium bromide gives 3-bromo-2,2′-bithiophene **4**.[23] Precursor 3-azido-2,2′-bithiophene **5** is obtained from **4** by bromide azide exchange with tosyl azide,[24] which can be synthesized in quantitative yield.[25] Finally, bithiophene azide **5** is refluxed in chlorobenzene, and presumably, via nitrene intermediate, unsubstituted DTP **1** is afforded.[21] We tried to reproduce the latter reaction, but we could achieve only moderate yields. In particular, it turned out for reactions on larger scale that the formation of several side products accounted for increased and tedious purification efforts. With the aim to have DTP **1** readily available as a precursor in large amounts, we investigated several alternative approaches for the synthesis of **1** starting from commercially available bromothiophenes.

Dedicated to Prof. Waldemar Adam on the occasion of his 80th birthday.

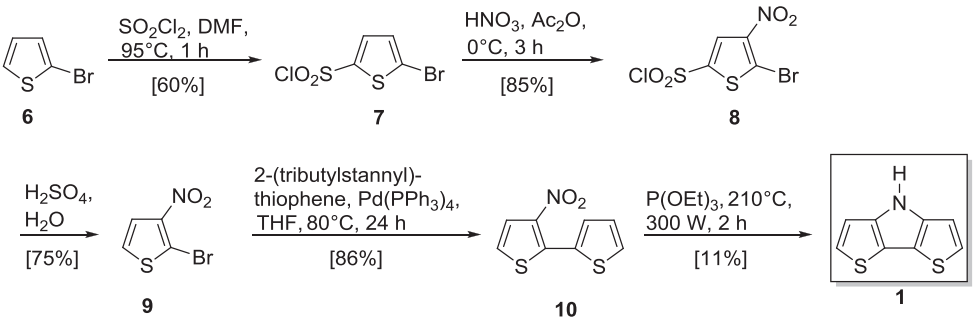
## 2 | RESULTS AND DISCUSSION

In a first approach, the synthesis of target DTP **1** was envisioned by means of a Cadogan reaction as the ring closing step (method B, Scheme 2). This seemed attractive, because, eg, carbazole can be efficiently synthesized from




**SCHEME 1** Synthesis of **1** via thermolysis of bithiophene azide **5** (method A)

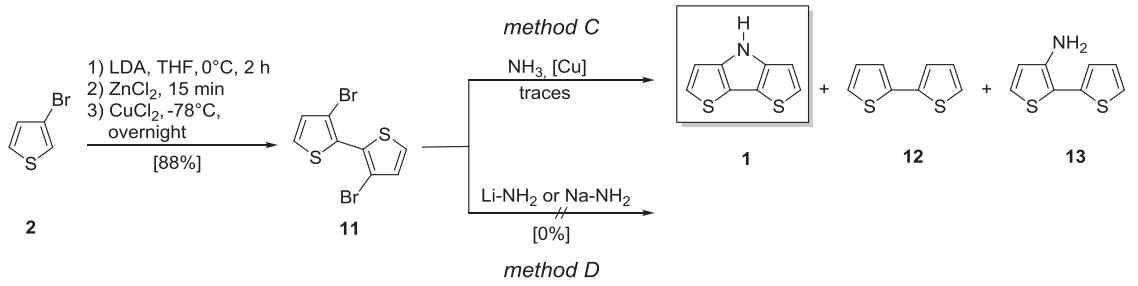



**SCHEME 2** Synthesis of DTP **1** via Cadogan reaction of nitrobithiophene **10** (method B)

2-nitro-1,1′-biphenyl with triethylphosphite as reducing agent.[26–28] For our target molecule, the necessary and analogous precursor 3-nitro-2,2′-bithiophene **10** was obtained in 4 steps starting from 2-bromothiophene **6**. First of all, thionyl chloride was introduced in the free α-position to afford 5-bromothiophene-2-sulfonyl chloride **7**.[29] According to Carpanelli and Leandri, this directing group was required for the selective nitration giving 5-bromo-4-nitrothiophene-2-sulfonyl chloride **8**.[30] Cleavage of the sulfonyl chloride group in **8** with sulphuric acid then yielded 2-bromo-3-nitrothiophene **9**.[30] Finally, a subsequent Pd-catalysed Stille cross-coupling reaction of **9** and 2-(tributylstannyl)thiophene afforded 3-nitro-2,2′-bithiophene **10**, which was then subjected to Cadogan reactions. The reaction mechanism presumably involves a nitrene intermediate, which intramolecularly closes the pyrrole ring in the centre of the forming DTP molecule.[31] We applied various reaction conditions including microwave irradiation (210°C, 300 W) or conventional heating (160°C) and tested several different reducing agents to transform nitrobithiophene **10** to unsubstituted DTP **1** (Table S1). Yet, only very low yields of up to 11% were obtained, while major amounts of an insoluble solid were formed. This indicated either partial decomposition of **1** because of the necessary harsh reaction conditions and/or other follow-up reactions of the assumed reactive nitrene intermediate such as intermolecular couplings or additions. Therefore, we have conducted a series of experiments using mixed nitro-substituted thienylphenylene substrates and found that only arylenes including nitrophenyl moieties led to higher yields in Cadogan reactions, whereas all examples involving nitrothienylene building blocks gave, as in the example described above, only very moderate yields.[32] Hence, to develop a viable synthesis of DTP **1** and to increase the yield other approaches involving milder conditions had to be found.

A very straightforward synthesis of DTP **1** could include an Ullmann-type or Buchwald-Hartwig-type amination of 3,3′-dibromo-2,2′-bithiophene **11** directly with ammonia, because overall only 2 steps would be required and bithiophene **11** can be readily prepared in excellent yields (method C, Scheme 3).[7] In several attempts, we applied ammonia either as an aqueous solution or it was generated in situ from ammonium chloride, whereas reactions were performed under microwave irradiation or conventional heating, respectively (Table S2). Use of Pd catalysts only led to quick dehalogenation of **11**, but no amination product was observed. Because amination reactions of aryl and heteroaryl halides with ammonia are typically performed with copper catalysts,[33–37] we subsequently applied copper(I) iodide together with either *N,N*- dimethylethylenediamine (DMEDA) or *L*-proline as catalytic system. Only in combination with the latter ligand the desired DTP **1** was detectable via gas chromatography-mass spectrometry in trace amounts, yet the predominant reaction products were debrominated 2,2′-bithiophene **12** and mono-coupled 3-amino-2,2′-bithiophene **13**.

Instead of ammonia, we tried lithium or sodium amide as amination reagent in the reaction of dibromobithiophene **11**

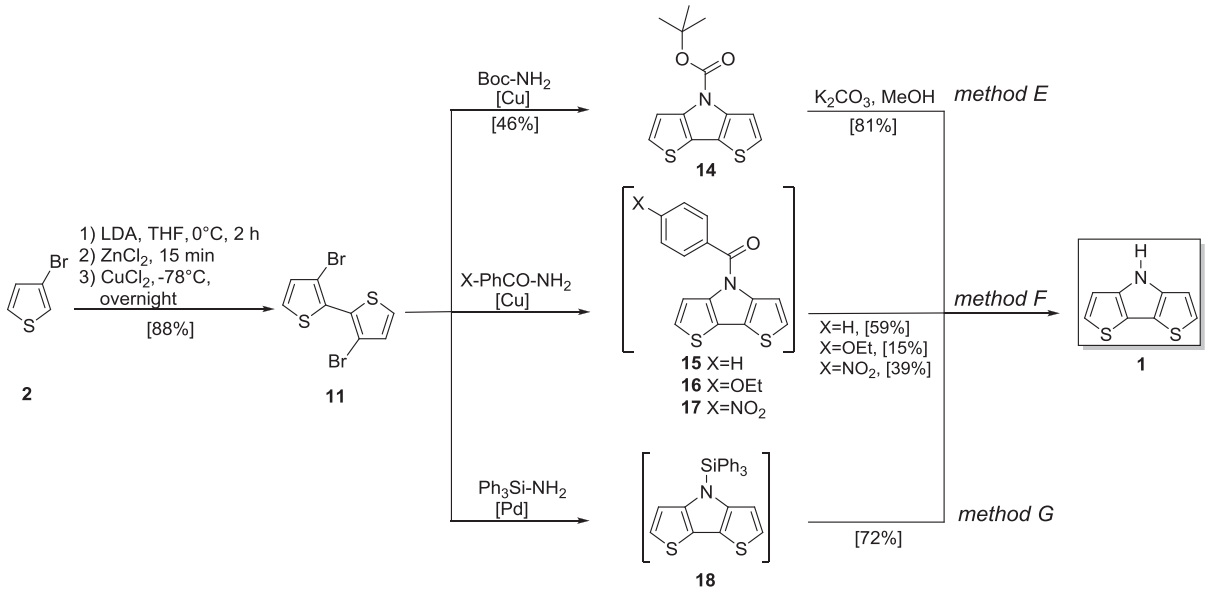



**SCHEME 3** Attempted synthesis of DTP **1** via amination of bithiophene **11** with ammonia (method C) or an amide (method D)

under either Cu(I) or Pd(0) catalysis. In all cases of the various reaction conditions used, no target DTP **1** could be detected and only decomposition or debromination products were identified from the reaction mixtures (method D, Scheme 3; Table S3). However, in the reaction with lithium amide, major amounts of an insoluble solid were obtained. This indicated the occurrence of a coupling reaction and the subsequent decomposition of the formed compound (most likely *N*-lithiated DTP). Consequently, relatively harsh reaction conditions were required to enable the amination in the first place, but the formed product was too unstable under these conditions.

Hence, the direct synthesis of DTP **1** with ammonia or amide salts is not a viable route and alternative strategies involving ammonia surrogates appeared more promising. Previously applied ammonia equivalents for the synthesis of aniline derivatives in a 1-fold C─N coupling were, for instance, benzophenone imine,[38] bis(trimethylsilyl) amide,[39,40] or triphenylsilylamine.[40] To enable the preparation of **1** from **11**, surrogates R─$NH_2$ should bear a protecting group R, which first allows for a 2-fold C─N coupling and then for its cleavage under mild reaction conditions. Thus, in method E, the *tert*-butyloxycarbonyl (Boc) protecting group was chosen and the corresponding Boc-functionalized DTP **14** was synthesized as reported previously from bithiophene **11** and *tert*-butyl carbamate under Cu(I)-catalysis in 46% yield (Scheme 4).[6] With a suspension of potassium carbonate in methanol the deprotection of **14** was accomplished giving DTP **1** in an overall yield of 33% in 3 steps starting from 3-bromothiophene **2**. The rather moderate overall yield was due to the Ullmann-type amination step, where the applied copper catalyst was inhibited by the formed product **14** limiting the conversion of the starting material.[7] A direct in situ cleavage of the protecting group, on the other hand, would reactivate the catalyst and thus should allow for higher conversion of **11**.

In a next approach, we used benzamides as ammonia surrogate and reacted benzamide with dibromobithiophene **11** under Cu(I)-catalysis according to the procedure of Evenson and Rasmussen.[7] In this Ullmann-type reaction with DMEDA as ligand and potassium carbonate as base, expected benzoyl-substituted DTP **15** was formed in 37%




**SCHEME 4** Synthesis of DTP **1** via amination of dibromobithiophene **11** with ammonia surrogates Boc-amide (method E), benzamides (method F), or triphenylsilylamine (method G)

yield, but surprisingly, we already could isolate the unsubstituted DTP **1** in 17% as side product (Scheme 4). This result indicated an in situ hydrolysis of the benzoyl residue in **15** by the formed water, which could enable a 1-pot synthesis of target DTP **1** directly from dibromobithiophene **11** (method F). Nevertheless, we found that isolated benzoyl-substituted DTP **15** was quite stable under identical conditions. Only at elevated temperatures of 110°C and in the presence of CuI activating the benzoyl residue, hydrolysis of **15** to DTP **1** occurred. Thus, we optimized the reaction to an 1-pot procedure, and with increased amount of catalyst and longer reaction times, target DTP **1** was finally isolated in 59% yield, ie, in an overall yield of 52% over 2 steps (Table S4). Moreover, method F could be applied on a multigram scale and full conversion of **11** was achieved. Yet, because of the low reaction rate and harsh conditions, partial decomposition of **1** still limited the yield.

We suspected that substituents at the benzamide precursor could accelerate either the amination reaction or the hydrolysis step leading to shorter reaction times with increased yields of **1**. In this respect, *p*-ethoxybenzamide bearing an electron-donating ether group was subjected to the reaction sequence. However, DTP **1** was obtained in only 11% and 15% after 1 or 2 days of reaction time, respectively, concomitant with large amounts of starting material **11**. In this case, no intermediate benzamide-substituted DTP **16** was observed (Table S5). Another attempt involved the application of a benzamide with an electron-withdrawing nitro group in the *para*-position. After 2 days, *p*-nitrobenzoyl-substituted DTP **17** was isolated in a yield of 9% and target DTP **1** was obtained in 39%, while precursor **11** was completely consumed (Table S5). Hence, substitution in the *para*-position of benzamide did not improve the yield of DTP **1** in method F and benzamide itself gave the best results. Notably, the reaction using thiobenzamide as ammonia equivalent did not afford any product with a palladium or copper catalyst, respectively (Table S6).

In a last approach, we applied triphenylsilylamine as ammonia surrogate in a 2-fold Buchwald-Hartwig amination of dibromobithiophene **11** (method G, Scheme 4). Whereas no reaction was observed using either bidentate 1,1′-bis(diphenylphosphino)ferrocene (dppf) or monodentate triphenylphosphine as ligand, a catalytically active palladium complex was obtained with tri-*tert*-butylphosphine. The conversion of the starting materials already started at ambient temperatures, but after few hours, the reaction did not progress further. Most likely, the catalyst was deactivated by formed silyl side products. Performing the reaction at 80°C overnight then led to the formation of target DTP **1** in 72% yield (Table S7). The *N*-silylated intermediate **18** was not isolable and could only be detected by matrix-assisted laser desorption ionization mass spectrometry. Moreover, the formation of *tert*-butoxytriphenylsilane indicated the cleavage of the silyl residue in situ by the applied base (NaO*t*Bu) or by formed *tert*-butanol, respectively. While the required amine and catalyst in method G were more expensive compared with methods E and F, the much milder reaction conditions with decreased reaction times and temperatures accounted for less decomposition side reactions. Finally, target compound **1** could be efficiently synthesized from dibromobithiophene **11** in a 1-pot approach. In total, DTP **1** was obtained in an excellent overall yield of 63% over 2 steps surpassing all the other methods described in literature or investigated by us (Table 1).

**TABLE 1** Summary of methods A to G for the synthesis of **1**

| Method | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| Number of steps[a] | 5[b] | 5 | 2 | 2 | 3 | 2 | 2 |
| Overall yield, % | 50 | 4 | Traces | 0 | 33 | 52 | 63 |

[a]Starting from 2- or 3-bromothiophene.

[b]Four steps from 3-bromothiophene plus the synthesis of tosyl azide.

## 3 | CONCLUSION

In conclusion, we investigated 6 alternative methods for the synthesis of unsubstituted DTP **1** starting from commercially available bromothiophene precursors. A Cadogan reaction applied in method B afforded the desired product only in low yield. Moreover, the direct amination of 3,3′-dibromo-2,2′-bithiophene **11** with ammonia (method C) or amide salts (method D) was also not a viable synthesis route. However, the corresponding Ullmann-type or Buchwald-Hartwig–type reaction with ammonia surrogates gave DTP **1** in overall yields of 33% to 63%. With Boc-amide, the substituted DTP intermediate **12** had to be isolated (method E), but with benzamides (method F) or triphenylsilylamine (method G), an 1-pot reaction could be developed. Compared to the previously reported method A, which includes a potentially explosive azide, with the latter 2 approaches, the number of steps could be decreased, the reactions were applicable on larger scale, and the highest overall yield of **1** could be achieved in method G. Substitution reactions of the synthesized precursor DTP **1** are currently under work in our laboratories to obtain functionalized DTPs for applications in organic solar cells or secondary batteries, respectively.

## 4 | EXPERIMENTAL SECTION

### 4.1 | Instruments and measurements

Nuclear magnetic resonance (NMR) spectra were recorded on an Avance 400 spectrometer ($^1$H NMR: 400 MHz, $^{13}$C NMR: 101 MHz). Chemical shifts (δ) are reported in parts per million using residual solvent protons ($^1$H NMR:

$\delta_H$ = 7.26 for $CDCl_3$; $\delta_H$ = 5.32 for $CD_2Cl_2$; $^{13}C$ NMR: $\delta_C$ = 77.16 for $CDCl_3$; $\delta_C$ = 53.84 for $CD_2Cl_2$) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), and m (multiplet). Elemental analyses were performed on an Elementar Vario EL. Melting points were determined using a Büchi Melting Point B-545. A microwave reactor (CEM Discover) was used. Thin-layer chromatography was performed on aluminium plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel, Merck Silica 60, particle size 40 to 63 μm. gas chromatography-mass spectrometry (electron ionization, 70 eV) measurements were performed on a Shimadzu GCMS-QP2010 SE. Chemical ionization mass spectra were measured on a Finnigan MAT SSQ-7000.

## 4.2 | Materials

Toluene (VWR), dimethylformamide (Merck), and tetrahydrofuran (Sigma Aldrich) were dried via a MB SPS-800 solvent purifying system (MBraun). 1,4-Dioxane, dimethyl sulfoxide (Merck), methanol, petroleum ether, ethyl acetate, dichloromethane, and triethylamine (VWR) were distilled prior to use. All synthetic steps were performed under an argon atmosphere. An aqueous solution of ammonia (32%) was purchased from VWR. Sodium *tert*-butoxide, triethylphosphite, triphenylphosphine ($PPh_3$), and copper(I) iodide were purchased from Merck. Triphenylphosphite, ammonium chloride, DMEDA, *L*-proline, copper(I) bromide, lithium amide, 12-crown-4, and 4-nitrobenzamide were purchased from Alfa Aesar. 1,2-Bis(diphenylphosphino)ethane (dppe), potassium carbonate, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, tri-*tert*-butylphosphine, $Pd(dba)_2$, $Pd_2(dba)_3$, 15-crown-5, 18-crown-6, 4-ethoxybenzamide, 1,10-phenanthroline (phen), and thiobenzamide were purchased from Sigma Aldrich. 1,1′-Bis(diphenylphosphino)ferrocene (dppf) was purchased from Fluorochem. Sodium amide and benzamide were purchased from Acros Organics.

$Pd(PPh)_4$,[41] 2-(tributylstannyl)thiophene,[42] 5-bromothiophene-2-sulfonyl chloride **7**,[29] 5-bromo-4-nitrothiophene-2-sulfonyl chloride **8**,[30] 2-bromo-3-nitrothiophene **9**,[30] 3,3′-dibromo-2,2′-bithiophene **11**,[7] 4-*tert*-butyloxycarbonyl-4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole **12**,[6] and triphenylsilylamine[43] were synthesized according to literature procedures.

## 4.3 | Synthetic procedures

### 4.3.1 | Synthesis of 3-nitro-2,2′-bithiophene 10

A suspension of tetrakis(triphenylphosphine)palladium(0) (150 mg, 0.13 mmol, 0.05 eq), 2-bromo-3-nitrothiophene **9** (541 mg, 2.60 mmol), and 2-(tributylstannyl)thiophene (970 mg, 2.60 mmol, 1.00 eq) in degassed tetrahydrofuran (100 mL) was heated at 80°C for 24 hours. After removing the solvent under reduced pressure, water was added and the crude product was extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$ and filtrated. After purification via column chromatography (petroleum ether : dichloromethane = 1:1) and recrystallization from petroleum ether, bithiophene **10** was afforded as a yellow crystalline solid (473 mg, 2.24 mmol, 86%). Mp: 44°C to 45°C. $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 7.63 (d, *J* = 5.7 Hz, 1H, H5), 7.51-7.54 (m, 2H, H3′, H5′), 7.20 (d, *J* = 5.7 Hz, 1H, H4), 7.10-7.14 (m, 1H, H4′) ppm. $^{13}C$ NMR ($CDCl_3$, 101 MHz): δ = 142.20, 138.76, 130.97, 130.92, 129.83, 127.67, 125.67, 123.61 ppm. The analytical data were in accordance with the literature.[44]

### 4.3.2 | Synthesis of 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) 1 by method B

A solution of nitrobithiophene **10** (75.0 mg, 0.36 mmol) in triethylphosphite (2.0 mL) was heated in the microwave with 300 W at 210°C for 2 hours. Afterwards, ethyl acetate and aqueous ammonium chloride were added and the solution was stirred for 3 hours. The phases were separated, and the organic phase was washed with water, dried over $MgSO_4$, and filtrated. Residual triethylphosphite was removed via vacuum distillation, and after purification via column chromatography (petroleum ether : dichloromethane = 4:1), DTP **1** was obtained as a white solid (7.0 mg, 0.04 mmol, 11%). Mp: 167°C (dec.). $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 8.32 (s, 1 H, N*H*), 7.15 (d, *J* = 5.3 Hz, 2 H, Th-$H_\alpha$), 7.04 (d, *J* = 5.3 Hz, 2 H, Th-$H_\beta$) ppm. $^{13}C$ NMR ($CD_2Cl_2$, 101 MHz): δ = 143.94, 123.58, 116.58, 112.60 ppm. The analytical data of DTP **1** were in accordance with the literature.[21]

### 4.3.3 | Synthesis of 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) 1 by method E

A suspension of the Boc-substituted DTP **12** (146 mg, 0.52 mmol) and $K_2CO_3$ (217 mg, 1.57 mmol, 3.00 eq) in methanol (10 mL) was stirred at room temperature for 1 day. After purification via column chromatography (petroleum ether : dichloromethane = 3:1), DTP **1** was afforded as a white crystalline solid (75.3 mg, 0.42 mmol, 81%). The analytical data of DTP **1** were in accordance with the data above and with literature.[21]

### 4.3.4 | Synthesis of 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) 1 by method F

A suspension of CuI (1.14 g, 6.00 mmol, 0.20 eq), DMEDA (2.72 mL, 24.0 mmol, 0.80 eq), and $K_2CO_3$ (12.4 g,

90.0 mmol, 3.00 eq) in toluene (60 mL) and water (0.1 mL) was purged with argon. Subsequently, benzamide (4.36 g, 36.0 mmol, 1.20 eq) and 3,3′-dibromo-2,2′-bithiophene **11** (9.72 g, 30.0 mmol) were added and the reaction mixture was heated at 110°C for 2 days. After cooling to room temperature, the crude product was purified via column chromatography (petroleum ether : dichloromethane = 3:1) to yield DTP **1** as a white crystalline solid (3.19 g, 17.8 mmol, 59%). The analytical data of DTP **1** were in accordance with the data above and with literature.[21]

### 4.3.5 | Synthesis of 4-(*p*-nitrobenzoyl)-4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole 15

A suspension of CuI (114 mg, 0.60 mmol, 0.20 eq), DMEDA (0.27 mL, 2.40 mmol, 0.80 eq), $K_2CO_3$ (1.24 g, 9.00 mmol, 3.00 eq), 4-nitrobenzamide (748 mg, 4.50 mmol, 1.50 eq), and 3,3′-dibromo-2,2′-bithiophene **11** (972 mg, 3.00 mmol) in toluene (6 mL) was degassed and heated at 110°C for 2 days. After cooling to room temperature, the suspension was filtered through a plug of celite and the residue was washed with dichloromethane. The raw product was purified via column chromatography (petroleum ether : dichloromethane = 3:1) to give **1** as a white solid (211 mg, 1.18 mmol, 39%) and 4-(*p*-nitrobenzoyl)-4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole **15** as a yellow solid (90.1 mg, 0.27 mmol, 9%). Mp: 140°C (dec.). $^1$H NMR ($CD_2Cl_2$, 400 MHz): δ = 8.43-8.39 (m, 2H, *m*-Ph-*H*), 7.94-7.90 (m, 2H, *o*-Ph-*H*), 7.18 (d, *J* = 5.3 Hz, 2H, Th-$H_\alpha$), 6.81 (s, 2H, Th-$H_\beta$) ppm. $^{13}$C NMR ($CD_2Cl_2$, 101 MHz): δ = 164.97, 150.17, 142.80, 140.53, 130.05, 125.19, 124.45, 122.51, 116.28 ppm. CI-MS: *m/z* (%) = 328 (91) $[M + H]^+$, 178 (16). Elemental analysis: calc. (%) for $C_{15}H_8N_2O_3S_2$: C 54.87, H 2.46, N 8.53, S 19.53; found: C 54.77, H 2.57, N 8.71, S 19.48.

### 4.3.6 | Synthesis of 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) 1 by method G

A suspension of 3,3′-dibromo-2,2′-bithiophene **11** (162 mg, 0.50 mmol), NaO*t*Bu (144 mg, 1.50 mmol, 3.00 eq), $Pd_2(dba)_3$ (22.9 mg, 0.03 mmol, 0.05 eq), tri-*tert*-butylphosphine (20.6 mg, 0.10 mmol, 0.20 eq), and triphenylsilylamine (165 mg, 0.60 mmol, 1.20 eq) in toluene (1.2 mL) was purged with argon and heated at 80°C overnight. After purification via column chromatography (petroleum ether : dichloromethane = 3:1), **1** was afforded as a white crystalline solid (64.2 mg, 0.36 mmol, 72%). The analytical data of DTP **1** were in accordance with the data above and with literature.[21] The side product *tert*-butoxytriphenylsilane was obtained as a white solid and the analytical data were in accordance with the literature.[45]

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