# Comparison of Ullmann/RCM and Ullmann/Bis-hydrazone Coupling Reactions; New Access to Benzodithiophenes for Dye-Sensitized Solar Cell and Thiahelicene Applications

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**Abstract:** The use of CuTC (Liebeskind's catalyst), followed by methylenation and ring-closing metathesis, or bis-hydrazone coupling reactions is described. This approach establishes an alternative non-photochemical synthesis of the strategically important 1,2-*b*:4,3-*b*′ BDT regioisomer, which has previously been underused in applications such as dye-sensitized solar cells and nonlinear optics because of the difficulty of synthesis on a large scale.

**Key words:** benzodithiophene, Liebeskind's catalyst, bis-hydrazone coupling, alkene metathesis, non-photochemical synthesis

The combination of thiophenes and benzene rings in high-performance chromophores has proved to be a powerful strategy[1] because of the lower aromatic resonance energy of thiophene compared to benzene.[2] Linear and fused-ring structures, of which the simplest (examples are shown in Figure 1) are benzothiophenes (BTs), benzodithiophenes (BDTs, e.g. **1**,**2**,**3**) and benzothienobenzothiophenes (BTBTs, e.g. **4**). These have found significant commercial applications in organic field-effect transistors[3] (OFETs), organic light-emitting diodes[4] (OLEDs) and solar cells.[5] In practice, isomers **2** and **3** are by far the most widely studied, and are of growing importance,[6] however, recent papers describing applications in dye-sensitized solar cells (DSCs) point out that the symmetrical isomer **1** is underused.[7] For our own interests in tetrathia[7]helicenes as components in nonlinear optics [8,9] and in novel chelating diphosphine ligands,[10] regioisomer **1** is a well-established key intermediate which, of the available BTDs, has a unique role because its extension (by incorporating additional fused rings) is ideal for helix formation.[11] The most efficient access[12] to tetrathia[7]helicenes employs a photochemical electrocyclic reaction of **5** combined with oxidative rearomatisation as the final step. Currently, this type of photochemical cyclisation is also used for the preparation of regioisomer **1**, but this approach is slow and inconvenient in the unsubstituted series because the *Z*-isomer of the alkene is required for photocyclisation. In most cases, applications have involved substituted examples, which are easier to prepare.[13]

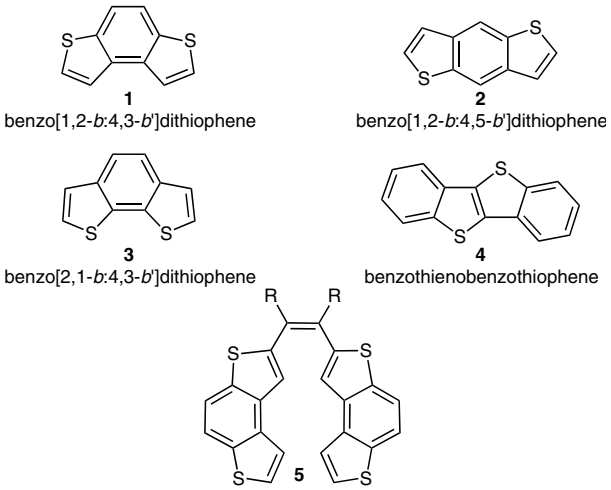


**Figure 1** Structures of thiophene-based cores of high-performance chromophores **1**–**4** and the tetrathia[7]helicene precursor **5**

We describe here chemical syntheses[14] of benzo[1,2-*b*:4,3-*b*′]dithiophenes that will not only make **1** more easily available for tetrathia[7]helicene synthesis, but will also open up opportunities for more rapid development for commercial applications, where previous reliance on photochemical steps cause complications in production chemistry that has held back evaluation of the 1,2-*b*:4,3-*b*′ isomer series.

Development of the two strategies shown in Scheme 1 both required diformyl bithiophene **12a** (Scheme 2), which we approached by using the Liebeskind modification[15] of Ullmann coupling or the mild copper(I) iodide triethylphosphite method of Ziegler.[16] The standard dimerisation method involving (2-formyl-3-thienyl)boronic acid gave the product in only 18% yield[17] and required three steps from 3-bromo-2-formylthiophene (**9**). From **12a**, formation of the bis-hydrazone[18] or dimethylenation should give easy access to precursors for the cyclisation step. The novel intermediate 2,2′-divinyl-3,3′-bithiophene (**6**) was also expected to be important for the formation of BDT by alkene metathesis, which should be an efficient strategy because the corresponding metathesis reaction of 2,2′-divinylbiphenyl to form phenanthrene is known to work well.[19]

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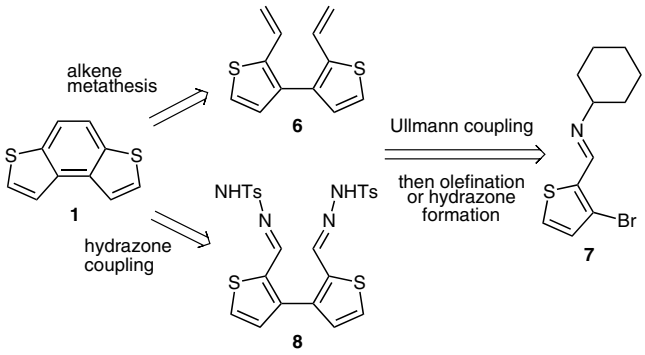
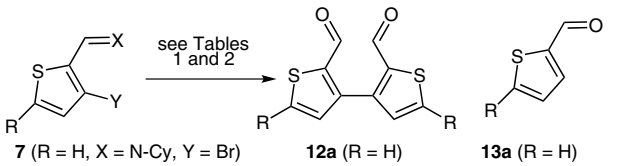



**Scheme 1** Strategies for the non-photochemical preparation of benzo[1,2-*b*:4,3-*b*′]dithiophene **1**




**7** (R = H, X = N-Cy, Y = Br)
**9** (R = H, X = O, Y = Br)
**10** (R = $SiMe_3$, X = N-Cy, Y = I)
**11** (R = $SiMe_3$, X = O, Y = I)

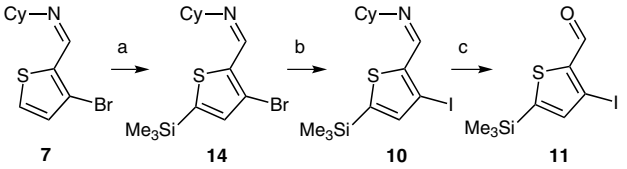
**12a** (R = H)
**12b** (R = $SiMe_3$)

**13a** (R = H)
**13b** (R = $SiMe_3$)

**Scheme 2** Ullmann coupling of 3-bromo- and 3-iodothiophenes

To gain access to the bis-formyl derivatives **12**, we explored coupling chemistry using compounds **7**, **9**, **10**, and **11** (Scheme 2). The *N*-formylpiperidine method could be used to convert 3-bromothiophene into **9**, improving the yield from 72–86%[20] to 97%, which is also an improved yield over more common alternatives that use DMF[21] or *N*-formyl-*N*-methylaniline,[22] or the Vilsmeier–Haack process.[23] The required imine **7** was easily made in quantitative yield by heating **9** to reflux in toluene with cyclohexylamine using a Dean–Stark trap.[24]

Our first attempt at the Ullmann coupling (Scheme 2) of cyclohexylimine **7** with Liebeskind catalyst in *N*-methyl-2-pyrrolidinone (NMP) at room temperature[25] gave a disappointing 25% yield (Table 1, entry 2). To prepare the more reactive 3-iodothiophene analogue (Scheme 3), we first protected the 5-position of **7** with a trimethylsilyl group to give **14**[26] through selective C-5 lithiation, which proceeded in the presence of the 3-bromo substituent by using LDA.[27] This was followed by bromine–lithium exchange and quenching with $I_2$ to form **10**.[28] Unfortunately, the Ullmann coupling was not significantly improved by using iodoimine derivative **10**, and the required product was obtained in only 29% yield (Table 1, entry 3). The silyl-protected aldehyde intermediate **11** was also examined in the Ullmann step (14% yield; Table 1, entry 5). This was compared with the Ziegler method,[16] which was found to perform similarly (15% yield; Table 1, entry 4) with our substrate.[29] The direct palladium-catalyzed coupling[30] of the 3-bromo-2-formylthiophene starting material **9** was also investigated because it would save a step, and this gave the required product in 35% yield (Table 1, entry 1).[31]




**Scheme 3** Preparation of iodothiophenes **10** and **11**. *Reagents and conditions*: (a) LDA, $Me_3SiCl$, THF, $N_2$, 99%; (b) *n*-BuLi, $I_2$, THF, $N_2$, 90%; (c) AcOH, $CH_2Cl_2$, $H_2O$, 88%.

The problem of low yields was initially addressed by using a microwave reactor[32] (using **7** and **10**), and it soon became apparent that careful purification of the CuTC was crucial for obtaining good results (Table 2). Further examination of reaction conditions to control competing dehalogenation allowed **12a** to be obtained in a satisfactory 67% isolated yield (Table 2, entry 8). On a large scale, however, we found that simply heating **7** at 90 °C for 17 hours gave **12a** in 68% isolated yield (e.g., Table 2, entry 9).

The BDT synthesis was completed by a simple Wittig reaction to produce 2,2′-divinyl-3,3′-bithiophene (**6**),[33] followed by a ring-closing metathesis (RCM) step. For the RCM step, we chose to use Iuliano conditions[19] with the 1st generation Grubbs catalyst [$Ru(Pcy_3)_2(CHPh)Cl_2$], which has been reported[19a] to give 100% yield in the preparation of phenanthrene in the case of divinylbiphenyl. Gratifyingly, this does indeed appear to be a very efficient and general RCM method, and in our case we achieved 90% yield of **1** at 5 mol% catalyst loading, which was im-

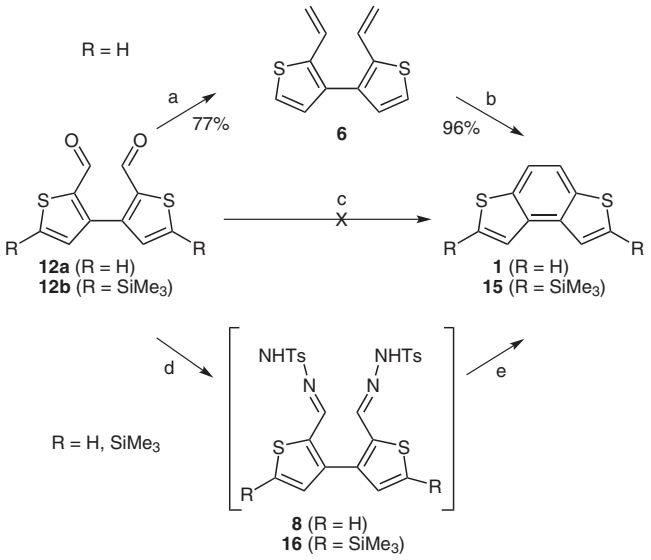
**Table 1** Coupling Reactions to 2,2′-Diformyl-3,3′-bithiophenes **12a** and **12b**

| Entry | Substrate | Catalyst (equiv) | Solvent | Temp (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | **9** | Cu (10) / $Pd(PPh_3)_4$ (0.1) | DMSO | 100 | 15 | 35[a] |
| 2 | **7** | CuTC (2.2) | NMP | r.t. | 60 | 25[b] |
| 3 | **10** | CuTC (3.0) | NMP | r.t. | 60 | 29[b] |
| 4 | **10** | CuI-$P(OEt)_3$ (1.5) | THF | –78 to r.t. | 60 | 15[b] |
| 5 | **11** | CuTC (3.0) | NMP | r.t. | 60 | 14[b] |

[a] Isolated yield.
[b] Based on NMR analysis of the crude bis-aldehyde **12a** or **12b**.

proved to 96% yield by using 10 mol% catalyst (Scheme 4).[34]




**Scheme 4** Cyclisation reactions to form benzo[1,2-*b*:4,3-*b*′]dithiophenes. *Reagents and conditions*: (a) *n*-BuLi, $MePPh_3Br$, THF, $N_2$, 77%; (b) $CH_2Cl_2$, $[Ru(Pcy_3)_2(CHPh)Cl_2]$ (0.1 equiv), r.t., 8 h, Ar, 96%; (c) $TiCl_3(DME)_{1.5}$/Zn(Cu), DME, 5%; (d) tosylhydrazide (2 equiv), THF, **8**: 100%, **16**: 100%; (e) **8**, NaH, $N_2$, THF, 37% or **16**, *n*-BuLi, $N_2$, THF, 32%.

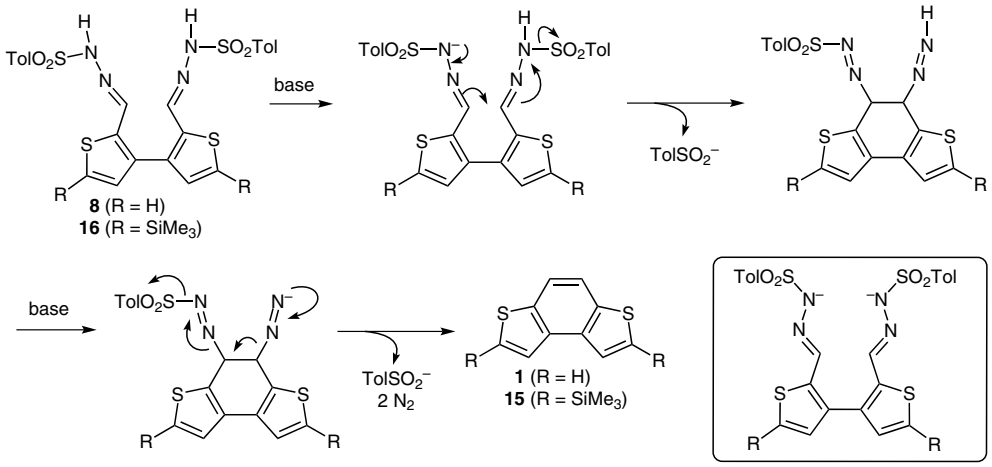
We also examined the formation of a bis-tosylhydrazone in the double condensation reaction of 2,2′-diformyl-3,3′-bithiophene (**12a**).[35] This alternative[18] to the McMurry coupling[36] of aldehydes gives direct access to the benzo[1,2-*b*:4,3-*b*′]dithiophene ring system in 32–37% yield and was successful both for **1** itself[37] and the 2,7-di(trimethylsilyl)-protected derivative **15**,[38] which was obtained from **16** by bis-hydrazone coupling of **12b**.[39] The conditions used to form **1** resemble those for the Bamford–Stevens reaction,[40] but the use of *n*-butyllithium in the preparation of **11** is more typical of a Shapiro reaction.[41] Both the Bamford–Stevens and Shapiro procedures employ arylsulfonylhydrazones and are generally considered to begin by deprotonation of the NH-$SO_2Ar$,[42] and exploit the chemistry of arylsulfinate ($ArSO_2^-$) leaving groups, and the elimination of $N_2$ to provide a powerful driving force. Under aprotic conditions the Bamford–Stevens reaction is believed to proceed by formation of a carbene,[43,44] but with the bis-hydrazones shown in Scheme 4 it seems probable that the initial anion[45] cyclises as shown in Scheme 5 by intramolecular nucleophile addition to the hydrazone and elimination of an arylsulfinate.[46] Subsequent loss of two molecules of $N_2$ and the second arylsulfinate completes the benzo[1,2-*b*:4,3-*b*′]dithiophene ring. The bis-hydrazone coupling reaction is useful, but requires further optimisation, perhaps by the use of more modern bases[47] which have become popular in the Shapiro reaction.

Finally, because the highest yielding route to BDT **1** was achieved by the application of the RCM reaction, we considered the possibility of coupling of 3-bromo-2-vinylthiophene to make 2,2′-divinyl-3,3′-bithiophene (**6**) more directly from **9** in just two steps. Wittig methylenation of **9**, however, proceeded in only 30% yield. It is possible that the ease of dimerisation and polymerisation of the reactive vinyl group in 3-bromo-2-vinylthiophene limits the efficiency of this reaction. Thus, Ullmann coupling prior to Wittig methylenation is the better approach.

**Table 2** Control of Dehalogenation in the Coupling of Halothiophenes

| Entry | Substrate | Conditions | Yield (%) | |
|---|---|---|---|---|
| | | | **12** | **13** |
| 1 | **10** | r.t., 48 h, CuTC (3.5 equiv) | **12b** (20[a]) | **13b** (23[a,c]) |
| 2 | **10** | 60 °C, 60 h, CuTC (3 equiv), $N_2$ | **12b** (29[a]) | **13b** (60[a,c]) |
| 3 | **10** | r.t., 60 h, CuTC (3 equiv), $N_2$ | **12b** (43[b]) | **13b** (37[b]) |
| 4 | **10** | 60 °C, MW, 20 min, CuTC (3 equiv), $N_2$ | **12b** (48[b]) | **13b** (26[b]) |
| 5 | **10** | 90 °C, MW, 15 min, CuTC (3 equiv), Ar | **12b** (51[b]) | **13b** (33[b]) |
| 6 | **10** | 60 °C, MW, 30 min, CuTC (3 equiv), $N_2$ | **12b** (55[b]) | **13b** (21[b]) |
| 7 | **7** | 90 °C, MW, 15 min, CuTC (2.2 equiv), Ar | **12a** (62[b,d]) | **13a** (19[a,b]) |
| 8 | **7** | 90 °C, MW, 25 min, CuTC (2.2 equiv), Ar | **12a** (67[b,e]) | **13a** (17[b]) |
| 9 | **7** | 90 °C, 17 h, CuTC (2.2 equiv), Ar | **12a** (68[f]) | – |

[a] Based on NMR analysis of crude bis-aldehyde.
[b] Based on NMR analysis of crude bis-imine.
[c] Catalyst not pure.
[d] 52% isolated yield.
[e] 55% isolated yield.
[f] Isolated yield.




**Scheme 5** Possible mechanism for the bis-hydrazone cyclisation. The monoanion formed by the first deprotonation step will be in equilibrium with the dianion (see box) when one equivalent of base is used,[38] but with an excess of base[37] the dianion is likely to be formed before loss of the first *p*-toluenesulfinate.[45]

In conclusion, we have shown that benzo[1,2-*b*:4,3-*b*′]dithiophene (**1**) is accessible in 50% overall yield in four steps from 3-bromo-2-formylthiophene by Ullmann coupling of the cyclohexylimine, methylenation, and ring-closing metathesis in a simple reaction sequence that avoids the use of photochemical conditions. The less costly alternative, bis-hydrazone route was found to be less effective than the metathesis route.

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**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(24) **Preparation of *N*-[(3-Bromothiophen-2-yl)methylene]cyclohexylimine (7)**: In a 1-L three-necked round-bottom flask, equipped with a Dean–Stark trap, a solution of 3-bromo-2-formylthiophene **9** (84.15 g, 0.44 mol, 1 equiv) and cyclohexylamine (54.6 g, 0.55 mol, 1.25 equiv) in toluene (700 mL) was heated at reflux under nitrogen for 16 h. The solution was then evaporated to afford an orange oil (120 g, 100%) which was used directly in the next step. IR (ATR): 3075, 2925, 2851, 1623 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 8.44 (s, 1 H), 7.34 (dd, *J* = 5.3, 1.1 Hz, 1 H), 7.00 (d, *J* = 5.2 Hz, 1 H), 3.22 (m, 1 H), 1.51–1.85 (m, 7 H), 1.18–1.41 (m, 3 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 151.0, 136.5, 130.5, 128.4, 113.5, 69.8, 34.1, 25.5, 24.7. HRMS (GC, CI+): *m/z* $[M–H]^-$ calcd for $C_{11}H_{13}BrNS$: 269.9947; found: 269.9947.
(25) **General Procedure**: *N*-[(3-Bromothiophen-2-yl)methylene]cyclohexylimine (**7**; 1 equiv) was dissolved in anhydrous NMP under argon, CuTc (2.2 equiv) was added in several portions (to achieve good mixing), and the reaction mixture was stirred at 90 °C under argon for 17 h. After cooling, the mixture was filtered through a pad of kieselguhr, which was then washed with EtOAc until no more brown colour was released from the filter cake. The filtrate was washed with 15% aqueous ammonia, producing a clear deep-blue aqueous layer. The organic layer was separated and retained, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine to remove as much NMP as possible, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The brown oily residue was dissolved in $CH_2Cl_2$ and 15% aqueous AcOH was added and mixture was at stirred r.t. overnight. The organic layer was separated and retained, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, filtered through a $MgSO_4$/neutral alumina pad, and evaporated under reduced pressure to give a solution of crude product in NMP (despite the washing, the NMP was not removed completely). The

resultant brown oil was taken up in $H_2O$ and shaken until the product precipitated. The mixture was then filtered and the residue was washed with $H_2O$ and dissolved in $CH_2Cl_2$, dried over $MgSO_4$, filtered and evaporated. The solid residue was washed with a mixture of hexanes and EtOAc (8:1 v/v) and dried under vacuum to give [3,3′-bithiophene]-2,2′-dicarboxaldehyde **12a**; for yields, see Table 1 and Table 2.

(26) **Preparation of *N*-{[3-Bromo-5-(trimethylsilyl)thiophen-2-yl]methylene}cyclohexylimine (14)**: A solution of *n*-BuLi (1.6 M in hexanes, 53 mL, 84.5 mmol, 1.15 equiv) was added dropwise to diisopropylamine (12 mL, 8.5 g, 84.5 mmol, 1.15 equiv) in anhydrous THF (600 mL) at 0 °C under nitrogen. After stirring for 45 min at 0 °C, *N*-[(3-bromothiophen-2-yl)methylene]cyclohexylimine (**7**; 20 g, 73.5 mmol, 1 equiv) in anhydrous THF (50 mL) was added dropwise over 10 min. After stirring for a further 45 min at 0 °C under nitrogen, the reaction mixture was cooled to –78 °C and trimethylsilyl chloride (10.7 mL, 9.2 g, 84.5 mmol, 1.15 equiv) was added dropwise. After stirring for 1 h at –78 °C, the reaction mixture was allowed to warm to r.t., sat. aq $NH_4Cl$ (700 mL) was added, and the organic layer was separated and retained. The aqueous layer was extracted with EtOAc (2 × 400 mL) and the combined organic layers were washed with brine (500 mL), filtered through a $MgSO_4$/basic alumina pad, and evaporated to give **14** (25.2 g, 99%) as an orange oil. IR (ATR): 2927, 2853, 1624 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 8.43 (s, 1 H), 7.10 (s, 1 H), 3.22 (m, 1 H), 1.22–1.87 (m, 10 H), 0.31 (s, 9 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 151.0, 144.4, 140.5, 136.5, 114.5, 70.0, 34.1, 25.5, 24.7, –0.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{23}BrNSSi$: 344.0498; found: 344.0503.

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(28) **Preparation of *N*-{[3-Iodo-5-(trimethylsilyl)thiophen-2-yl]methylene}cyclohexylimine (10)**: A solution of *N*-{[3-bromo-5-(trimethylsilyl)thiophen-2-yl]methylene}cyclohexylimine (**14**; 6.94 g, 20.2 mmol, 1 equiv) in anhydrous THF (350 mL) was cooled to –78 °C, under nitrogen. *n*-BuLi (1.6 M in hexanes, 13.9 mL, 22.2 mmol, 1.1 equiv) was added dropwise. The mixture was stirred for 30 min at –78 °C and a solution of iodine (7.7 g, 30.3 mmol, 1.5 equiv) in anhydrous THF (25 mL) was added dropwise until the red iodine colour persisted. After 15 min at –78 °C, the reaction mixture was allowed to warm to r.t., $H_2O$ (350 mL) was added and the mixture was extracted with $CH_2Cl_2$ (3 × 250 mL). The combined organic layers were concentrated to 300 mL, washed with sat. aq sodium sulfite (2 × 300 mL), dried over $MgSO_4$, filtered, and evaporated to give **10** (7.12 g, 90%) as a brown oil, that crystallised upon standing. Mp 59 °C. IR (ATR): 2928, 2851, 1618 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 8.34 (s, 1 H), 7.20 (s, 1 H), 3.24 (br. m, 1 H), 1.85–1.57 (m, 7 H), 1.38–1.23 (m, 3 H), 0.31 (s, 9 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 153.2, 145.4, 143.7, 141.4, 85.1, 69.9, 34.2, 25.5, 24.7, –0.5. HRMS (ESI): *m/z* $[M–H]^-$ calcd for $C_{14}H_{21}NISSi$: 390.0203; found: 390.0203.

(29) **General Procedure**: A solution of *N*-{[3-bromo-5-(trimethylsilyl)thiophen-2-yl]methylene}cyclohexylimine **14** (1 equiv) in anhydrous THF was cooled to –78 °C under nitrogen. *n*-BuLi (1.05 equiv) was added dropwise and the mixture was stirred at –78 °C for 30 min. Then CuI-$P(OEt)_3$ (1.5 equiv) was added in one portion and the mixture was stirred for a further 30 min at –78 °C before a solution of *N*-{[3-iodo-5-(trimethylsilyl)thiophen-2-yl]methylene}cyclohexylimine **10** in anhydrous THF was added dropwise. The reaction mixture was allowed to warm to r.t. and stirred at r.t. for 60 h. The reaction was quenched with $H_2O$ and the reaction mixture was diluted with $CH_2Cl_2$, and 15% aqueous AcOH was added. The mixture was at stirred r.t. overnight, then the organic layer was separated and retained and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, filtered through a $MgSO_4$/neutral alumina pad and evaporated under reduced pressure. Crude material was purified by column chromatography (silica; hexanes–EtOAc, 100:0 to 2:1 v/v) to give 5,5′-bis(trimethylsilyl)-[3,3′-bithiophene]-2,2′-dicarbaldehyde (**12b**); for yields, see Table 1.

(30) Some, S.; Dutta, B.; Ray, J. K. *Tetrahedron Lett.* **2006**, *47*, 1221.

(31) **Preparation of [3,3′-Bithiophene]-2,2′-dicarboxaldehyde (12a)**: Anhydrous DMSO (50 mL) was degassed under nitrogen for 30 min, then 3-bromo-2-formylthiophene (**9**; 1 equiv) was added and nitrogen gas was bubbled through the resulting solution for 10 min. $Pd(PPh_3)_4$ (0.1 equiv) and copper powder (3 equiv) were added and the solution was stirred and heated to 100 °C, under nitrogen for 15 h and then at 120 °C for 8 h. The progress of the reaction was monitored by TLC (hexanes–EtOAc, 3:1 v/v). The solution was cooled to r.t. before adding EtOAc (200 mL) and filtration through a pad of kieselghur. The filtrate was washed with $H_2O$ (2 × 150 mL) and brine (150 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure to give a brown oil that was purified by chromatography (silica; hexanes–EtOAc, 95:5 to 3:1 v/v) to afford **12a** (405 mg, 35%) as a yellow powder.

(32) **General Procedure**: A dried 20-mL microwave vial was flushed with argon. To a solution *N*-[(3-bromothiophen-2-yl)methylene]cyclohexylimine (**7**; 1 equiv) in NMP (15 mL), CuTC (2.2 equiv) was added with stirring. The microwave vial was then sealed, vacuum was applied, and then the vial was filled with argon. The reaction mixture was irradiated (see Table 2), then diluted with EtOAc and 15% aqueous ammonia was added to produce a clear deep-blue aqueous layer. The organic layer was separated and retained and the aqueous layer was extracted with EtOAc. The organic layers were combined and evaporated and the resultant crude product (green oil) was dissolved in $Et_2O$. This solution was washed with brine, dried over $MgSO_4$, filtered, and evaporated to leave a brown oil, which was dissolved in $CH_2Cl_2$ (50 mL), 15% aqueous AcOH (50 mL) was added and mixture was stirred overnight at r.t. The organic layer was separated and retained and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated (first under reduced pressure on a rotary evaporator and then under high vacuum using a vacuum line) to give a brown oil. The oil was purified by column chromatography (silica; hexanes–EtOAc, 100:0 to 2:1 v/v) to afford [3,3′-bithiophene]-2,2′-dicarbaldehyde **12a** as a yellow solid (for yields, see Table 2).

(33) **Preparation of 2,2′-Divinyl-3,3′-bithiophene (6)**: To a suspension of methyltriphenylphosphonium bromide (1.7 g, 4.75 mmol, 2.2 equiv) in distilled THF (50 mL), *n*-BuLi (1.6 M in hexanes, 2.96 mL, 4.75 mmol, 2.2 equiv) was added dropwise at –10 °C under nitrogen. The deep-orange solution was stirred at r.t. for 30 min, then a solution of [3,3′-bithiophene]-2,2′-dicarbaldehyde (**12a**; 460 mg, 2.16 mmol, 1 equiv) in distilled THF (10 mL) was added dropwise. The mixture was stirred at r.t. under nitrogen for 17 h, then the reaction was quenched with sat. aq $NH_4Cl$ (20 mL). The aqueous layer was extracted with $CHCl_3$ (3 × 50 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and evaporated. The crude product was



 

purified by column chromatography (silica; hexanes), to afford **6** (350 mg, 77%) as a viscous oil. The product was kept in the freezer in the dark, and used as soon as possible. IR (ATR): 3103, 3066, 3005, 2957, 2925, 2869, 1800, 1616 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 7.19 (dd, *J* = 5.3, 0.8 Hz, 1 H), 6.94 (d, *J* = 5.3 Hz, 1 H), 6.66 (ddd, *J* =17.3, 11.0, 0.8 Hz, 1 H), 5.58 (d, *J* = 17.3 Hz, 1 H), 5.13 (d, *J* = 11.0 Hz, 1 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 139.1, 134.2, 130.1, 129.2, 123.1, 113.7. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{12}H_{11}S_2$: 219.0299; found: 219.0297.

(34) **Preparation of Benzo[1,2-*b*:4,3-*b*′]dithiophene (1) by RCM**: Under argon, Grubbs' 1st generation catalyst $[Ru(Pcy_3)_2(CHPh)Cl_2]$ (30 mg, 0.1 equiv) was added to a solution of 2,2′-divinyl-3,3′-bithiophene (**6**; 80 mg, 0.36 mmol, 1 equiv) in anhydrous $CH_2Cl_2$ (25 mL). The reaction mixture was stirred at r.t. for 8 h, then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica; hexanes), to afford **1** (67 mg, 96%).

(35) **Preparation of *N*′,*N*″-{[3,3′-Bithiophene]-2,2′-diylbis(methanylylidene)}bis(4-methylbenzenesulfonylhydrazone) (8)**: [3,3′-Bithiophene]-2,2′-dicarbaldehyde **12a** (1.05 g, 4.7 mmol, 1 equiv) and tosylhydrazide (1.75 g, 9.4 mmol, 2 equiv) were dissolved in distilled THF (300 mL) and stirred at r.t. overnight. The reaction mixture was dried over $MgSO_4$, filtered and evaporated to give **8** (2.62 g, 100%) as a bright-yellow-orange solid foam. Mp 129 °C. IR (ATR): 3176, 2958, 2923, 2867, 1645, 1594 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 11.33 (s, 2 H), 7.77 (d, *J* = 0.9 Hz, 2 H), 7.69 (dd, *J* = 5.1, 0.7 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 4 H), 7.40 (dd, *J* = 8.1, 0.6 Hz, 4 H), 7.03 (d, *J* = 5.1 Hz, 2 H), 2.36 (s, 6 H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 143.7, 140.7, 136.4, 136.0, 134.7, 130.3, 129.8, 128.7, 127.2, 21.1. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{23}N_4O_4S_4$: 559.0597; found: 559.0587.

(36) The intramolecular McMurry cyclisation of **12a** was unsuccessful under a variety of conditions [e.g., $TiCl_4$/Zn and $TiCl_3(DME)_{1.5}$/Zn(Cu)], despite its use as an intermolecular coupling reaction to obtain the 1,2-dithiophenylethene starting material for the photochemical route. For typical reaction conditions, see: (a) Yoshida, S.; Fujii, M.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1994**, *59*, 3077. (b) See also ref. 15c.

(37) **Preparation of Benzo[1,2-*b*:4,3-*b*′]dithiophene (1) by Bis-hydrazone Coupling**: [3,3′-Bithiophene]-2,2′-dicarbaldehyde (**12a**; 4 g, 18 mmol, 1 equiv) and tosylhydrazide (6.59 g, 36 mmol, 2 equiv) were dissolved in distilled THF (850 mL), and the mixture was stirred at r.t. overnight, dried over $Na_2SO_4$, and transferred to a 1 L three-necked round-bottom flask that has been flame-dried under nitrogen. The reaction mixture was cooled to 0 °C and NaH (95%; 1.08 g, 45 mmol, 2.5 equiv) was added in portions. The reaction mixture was allowed to warm to r.t. and then heated at reflux for 3 h under nitrogen. After cooling, the solution was concentrated under reduced pressure to 100 mL, and sat. aq $NH_4Cl$ (300 mL) was added. The mixture was extracted with EtOAc (2 × 400 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and evaporated to leave a brown solid (4 g). The crude product was purified by column chromatography (silica; hexanes) to afford **1** (1.21 g, 37%) as colourless crystals.

(38) **Preparation of 2,7-Bis(trimethylsilyl)benzo[1,2-*b*:4,3-*b*′]dithiophene (15) by Bis-hydrazone Coupling**: 5,5′-Bis(trimethylsilyl)-[3,3′-bithiophene]-2,2′-dicarbaldehyde (**12b**; 2.62 g, 7.15 mmol, 1 equiv) and tosylhydrazide (2.66 g, 15.30 mmol, 2 equiv) were dissolved in distilled THF (450 mL) and stirred at r.t. overnight. The THF solution was dried over $Na_2SO_4$, and transferred to a 500-mL three-necked round-bottom flask that had been flame-dried under nitrogen. The reaction mixture was cooled to –78 °C, *n*-BuLi (1.6 M in hexanes, 4.7 mL, 7.5 mmol, 1.05 equiv) was added dropwise and the mixture was stirred for 5 min at –78 °C. The reaction mixture was allowed to warm to r.t., then heated at reflux for 5 h. After cooling, sat. aq $NH_4Cl$ (200 mL) was added and the mixture was extracted with EtOAc (200 mL). The organic layer was concentrated under reduced pressure to 100 mL, diluted with $Et_2O$ (200 mL), washed with brine (2 × 250 mL), dried over $MgSO_4$, filtered, and evaporated to leave a brown solid (5.1 g). Crude material was purified by column chromatography (silica; hexanes) to afford **15** (770 mg, 32%) as colourless crystals. Mp 128 °C. IR (ATR): 3053, 2985, 2959, 2897 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 7.88 (s, 2 H), 7.80 (s, 2 H), 0.44 (s, 18 H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 142.3, 140.4, 135.9, 128.7, 118.4, –0.2. HRMS (ESI): *m*/*z* $[M]^+$ calcd. for $C_{16}H_{22}S_2Si_2$: 334.0696; found: 334.0696.

(39) **Preparation of *N*′,*N*″-{[5,5′-Bis(trimethylsilyl)-(3,3′-bithiophene)-2,2′-diyl]bis(methanylylidene)}bis(4-methylbenzenesulfonylhydrazone) (16)**: Using the method employed for the synthesis of **8** (see ref. 35) 5,5′-bis(trimethylsilyl)-(3,3′-bithiophene)-2,2′-dicarbaldehyde (**12b**; 2 g, 5.45 mmol, 1 equiv) and tosylhydrazide (2.03 g, 10.9 mmol, 2 equiv) were dissolved in distilled THF (250 mL) and the mixture was stirred at r.t. overnight, dried over $MgSO_4$, and evaporated to afford **16** (3.83 g, 100%) as a bright-yellow-orange solid foam. Mp 156 °C. IR (ATR): 3190, 3065, 2955, 2926, 2898, 2856, 1597 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$, 400 MHz): δ = 11.38 (s, 2 H), 7.74 (s, 2 H), 7.67 (d, *J* = 8.2 Hz, 4 H), 7.40 (dd, *J* = 8.2, 0.7 Hz, 4 H), 7.16 (s, 2 H), 2.36 (s, 6 H), 0.30 (s, 18 H). $^{13}C$ NMR (DMSO-$d_6$, 100 MHz): δ = 143.5, 142.5, 140.2, 139.2, 137.3, 137.0, 136.1, 129.7, 127.0, 21.0, –0.5. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{30}H_{39}N_4O_4S_4Si_2$: 703.1387; found: 703.1387.

(40) (a) Bamford, W. R.; Stevens, T. S. M. *J. Chem. Soc.* **1952**, 4735. (b) Chamberlain, A. R.; Bloom, S. H. *Org. React.* **1990**, *39*, 1.

(41) (a) Shapiro, R. H.; Duncan, J. H.; Clopton, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 471. (b) Shapiro, R. H. *Org. React.* **1976**, *23*, 405. (c) Aldington, R. M.; Barrett, A. G. M. *Acc. Chem. Res.* **1983**, *16*, 55.

(42) (a) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147. (b) Miranda, R.; Hernandez, A.; Angeles, E.; Cabrera, A.; Salmon, M.; Joseph-Nathan, P. *Analyst* **1990**, *115*, 1483.

(43) Chamberlin, A. R.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 154.

(44) Carbene intermediates have also been proposed for the Shapiro reaction, see ref. 41c.

(45) A referee has suggested that the dianion (see Scheme 5, box) is the intermediate in the cyclisation reaction, which is entirely reasonable, especially in the sodium hydride procedure (see ref. 37) in which the base was used in excess, but when 1.05 equiv butyllithium is employed (see ref. 38), the second deprotonation is probably effected by the toluenesulfinate anion in a reversible step that is driven, ultimately, by the irreversible loss of nitrogen, and the reaction then probably follows the mechanism drawn in Scheme 5.

(46) Jung tentatively proposes (see ref. 18a) that when the base is sodium hydride, both tosylhydrazones deprotonate and eliminate the tosylsulphinate, before ring closure occurs.

(47) Kerr, W. J.; Morrison, A. J.; Pazicky, M.; Weber, T. *Org. Lett.* **2012**, *14*, 2250.