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LETTER

Non-Photochemical Route to Simple Benzo[1,2-*b*:4,3-*b'*]dithiophenes: FeCl₃-Mediated Cyclization of Dithienyl Ethenes

Cite this: DOI: 10.1039/c3nj00000x

Received 00th XXXXX 2013,
Accepted 00th XXXXX 2013

DOI: 10.1039/c3nj00000x

www.rsc.org/njc

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The FeCl₃-mediated cyclization of α,α' -disubstituted *Z*-alkenes **1** is reported as a general and non-photochemical synthesis of benzo[1,2-*b*:4,3-*b'*]dithiophene (**BDT**) derivatives **2**, achievable in good yields starting from cheap and easily available materials. The influence of the temperature and the nature of the substituents in determining the scope and limitations of this methodology are also reported.

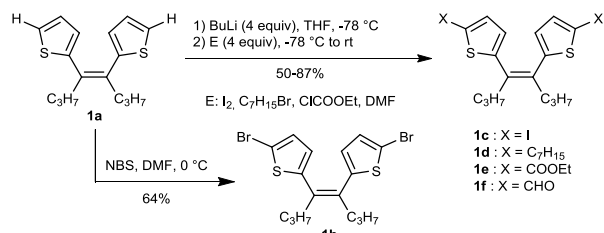
Thiophene-containing fused, aromatic compounds represent an interesting class of π -conjugated systems in functional organic materials.¹ Among them, five isomeric tricyclic β -fused benzodithiophenes have stimulated a lot of interest thanks to their use as monomers or co-monomers for the synthesis of conductive materials in electronic devices.² A role of increasing importance is going to be acquired by one of these isomers, namely benzo[1,2-*b*:4,3-*b'*]dithiophene (**BDT**) and its derivatives, which have been studied as units in mono and polydisperse oligomers in field of the materials science,³ and, more recently, as π -spacers in push-pull organic chromophores for photovoltaic applications.⁴ Moreover, **BDT** represents a key intermediate in the synthesis of inherently chiral helical systems such as tetrathia[7]helicenes (7-TH),⁵ that are an extremely attractive class of conjugated molecules, with unique physicochemical properties provided by their helix-like structure.⁶ On the basis of the above considerations, **BDT** can be identified as a key starting molecule that, through a judicious functionalization of the α -positions of the thiophene rings, can allow access to more complex and interesting systems.^{3,4,7} Despite all these potential advantages, convenient synthetic

methodologies to prepare **BDT** are still scarce,⁸ and normally involve the oxidative photochemical cyclization of dithienyl ethenes as the key step.⁹ However, this reaction requires specific photochemical equipment and highly diluted solutions, takes several hours, and, to a significant extent, can limit the scale-up of the synthesis of **BDT**.

Within this context, and in view of potential wider and industrial applications, a simple, reliable, reproducible and economic synthesis of **BDT** which avoids the use of photochemical pathways is highly desirable. In the course of our research projects in which we use **BDT** as a relevant precursor for the construction of both thiahelicenes^{5a-b,10} and push-pull chromophores,^{4b} we faced this synthetic problem and we focused our attention on the FeCl₃-mediated oxidative intramolecular cyclization of dithienyl ethenes via C-C bond formation between the β -positions of thiophene rings. In fact, iron(III) chloride is an economical and commercially available salt that has found wide-spread application as a Lewis acid¹¹ but also as mild and selective oxidising agent, and is therefore particularly useful in C-C coupling reactions involving arene and heteroarenes.¹² In this way, complex polycyclic aromatic compounds, containing the **BDT** framework as part of an *ortho*-condensed aromatic system have been prepared.¹³ On the contrary, no synthesis of the simple tricyclic **BDT** scaffold has so far been reported using the FeCl₃ mediated oxidative coupling.

Herein, we report the first results of our investigations on the FeCl₃-mediated oxidative intramolecular cyclization of α,α' -disubstituted (*Z*)-dithienyl ethenes **1** to afford benzodithiophene

derivatives **2**.¹⁴ In this study we focused our attention on (*Z*)-dithienyl ethenes **1** bearing two *n*-propyl chains on the double bond, which improve the solubility of the **BDT** derivatives **2** in organic solvents.^{4b} (*Z*)-alkene **1a**, obtained as the major isomer from the corresponding *n*-propyl thienyl ketone by means of a McMurry coupling, was the starting compound for the synthesis of new α,α' -disubstituted (*Z*)-dithienyl ethenes **1b-f**, prepared according to Scheme 1. It is interesting to underline that, in the McMurry reaction conditions used, we isolated **1a** as a 9:1 mixture of the *Z* and *E* isomers.¹⁵ This is a fundamental stereochemical prerequisite for the further FeCl₃-mediated cyclization, which proceeds only with the *Z* isomer.^{13b} Dibromo alkene **1b** was obtained in 64% yield by means of a regioselective bromination of **1a** with NBS in DMF at 0 °C, whereas all of other α,α' -disubstituted (*Z*)-dithienyl ethenes **1c-f** were prepared in 50-87% yield, by deprotonation of the two alpha positions of the thiophene rings of **1a** with BuLi at -78 °C, followed by reaction with the appropriate electrophile (Scheme 1). The oxidative cyclization of **1a-f** was then investigated using FeCl₃ as oxidant.



Scheme 1. Synthesis of (*Z*)-dithienyl ethenes **1b-f**

In order to assess the best conditions for the oxidative cyclization of **1a-f** to the corresponding **BDT** derivatives **2a-f**, a preliminary screening has been performed to evaluate the influence of the amount of FeCl₃ in the cyclization of the α,α' -dibromo ethene **1b**, used as model alkene, in CH₂Cl₂ at room temperature (Table 1).

Table 1. FeCl₃-mediated cyclization of **1b**: effect of FeCl₃/**1b** ratio

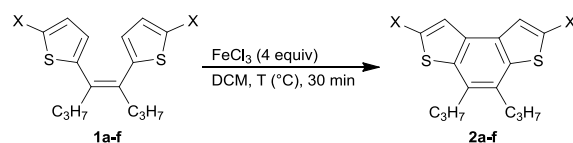
Entry ^a	1b		Yield of 2b (%)
	FeCl ₃ (equiv)	DCM, r. t., 30 min	
1	2		60
2	4		76
3	12		72
4	0.1 ^b		13
5 ^c	4		60

^a Unless otherwise noted, the appropriate amount of FeCl₃ was added to a solution of **1b** (0.25 mmol) in dry CH₂Cl₂ (20 mL), and stirred for 30 minutes under a nitrogen atmosphere. ^b *meta*-Chloroperbenzoic acid (*m*-CPBA, 1 equiv) was used as oxidant. ^c A mixture of CH₂Cl₂/MeNO₂ (9/1) was used as solvent.

In particular, the addition of a stoichiometric amount of FeCl₃ (2 equiv)¹⁶ to a solution of **1b** in CH₂Cl₂ at room temperature, gave the expected product **2b** in 60% yield after 30 minutes (Entry 1, Table 1). The use of twice the stoichiometric amount

of FeCl₃ (4 equiv) resulted in the formation of **2b** in higher yield (76%, Entry 2, Table 1). This result is in accordance with the literature. In fact, even if the stoichiometric ratio of FeCl₃/alkene to perform the cyclization is 2:1, quite often the use of higher ratio is necessary to obtain higher reaction yield.^{13c,m,17} However, in our case, the use of a much larger excess of FeCl₃ (12 equiv) did not result in an improvement of the reaction yield (72%, Entry 3, Table 1). Moreover, an experiment performed with a catalytic amount of FeCl₃ (10 mol %) in combination with a stoichiometric amount of *m*-CPBA (1 equiv)¹⁸ as oxidant resulted in a significant decreasing of the yield, and compound **2b** was isolated in only 13% yield (Entry 4, Table 1). Although FeCl₃-mediated cyclodehydrogenations are often carried out employing CH₂Cl₂ in combination with nitromethane as co-solvent,¹² in our hands the use of a mixture of CH₂Cl₂ and MeNO₂ as solvent in the reaction of **1b** with 4 equiv of FeCl₃ did not improve the efficiency, affording **2b** in lower yield (60%, Entry 5, Table 1). Finally, the same reaction run in acetonitrile as solvent gave a complex mixture in which the expected **2b** was present in low amount. Based on these results, we then ran the cyclization reactions of **1a-f** with 4 equiv of FeCl₃ in CH₂Cl₂, evaluating the influence of the temperature on the outcome of these reactions (Table 2).

Table 2. FeCl₃-mediated intramolecular cyclization of **1a-f**



Entry ^a	Reagent		Products	Isolated yield (%)			
	1	X		2	r.t.	0 °C	40 °C
1	1a	H	2a	- ^c	- ^c		
2	1b	Br	2b	76	79	57	60 ^d
3	1c	I	2c	10	32	74 ^e	^f
4	1d	C ₇ H ₁₅	2d	- ^c	66	^f	^f
5	1e	COOEt	2e	66	^f	87	89
6	1f	CHO	2f	<10	^f	<10	40

^a Unless otherwise noted, FeCl₃ (4 equiv) was added to a solution of **1** (0.25 mmol) in CH₂Cl₂ (20 mL), and stirred for 30 min under nitrogen. ^b Solvent: Cl₂CH₂CH₂Cl₂ (DCE). ^c **1a** decomposed completely after few minutes. ^d Tribromo derivative **3** was isolated in 10% yield. ^e A solution of **1c** (0.25 mmol) in CH₂Cl₂ (5 mL) was added to a slurry of FeCl₃ (4 equiv) in CH₂Cl₂ (20 mL) at 40 °C. ^f Not performed.

As expected, when a solution of **1a** in CH₂Cl₂ was treated with FeCl₃ at room temperature or 0 °C, a complex mixture of polymerization products was obtained after a few minutes (Entry 1, Table 2). In this case, the known higher spin density of the thiophene radical cation at the 2-position favours the formation of polymers^{13b-c} instead of the required benzodithiophene **2a**. On the contrary, when alkenes **1b-f** with substituents on the alpha positions of the thiophenes were used, the polymerization was prevented and the corresponding disubstituted **BDT** derivatives **2b-f** were obtained. As reported in Entry 2 of Table 1, while the cyclization of **1b** at room temperature gave **2b** in 76% yield, a slightly higher yield (79%) of **2b** was obtained at 0 °C (Entry 2, Table 2). On the contrary,

increasing the temperature (up to 40 or 80 °C) was found to produce **2b** in lower yields, together with tribromo derivative **3** (Figure 1a) which, was isolated in 10% yield at 80 °C. The structure of tribromide **3** was confirmed by the X-ray analysis. The ORTEP view of **3** shows that the molecule is essentially planar neglecting the two n-propyl chains, which extend on two opposite sites of the mean plane of the benzodithiophene unit (Figure 1b). The formation of **3** could be rationalized by taking into account that thiophenes brominated in the α -positions readily undergo debromination and/or rearrangement reactions through heating in the presence of catalytic amounts of strong acids.¹⁹

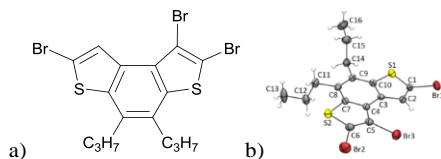
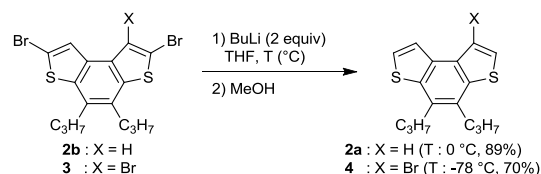


Figure 1. (a) Chemical Structure of **3**. (b) ORTEP view of the crystal structure of **3** (ellipsoids are drawn at their 30% probability level).

These processes, which generally involve the loss of brominating species, could occur also in the FeCl₃-mediated cyclization of **1b** at 80 °C. In fact, the hydrogen chloride generated during the cyclization of **1b** could catalyze the loss, from **2b**, of a “brominating” species, which then could be able to brominate **2b** to furnish the tribromo **BDT 3**. The fate of the resulting debrominated **2b** is not known because, as already stated above, α -unsubstituted **BDTs** decompose under these conditions. We found that heating the dibromo **BDT 2b**, in the presence of 4 equiv of FeCl₃ in DCE at 80 °C, resulted in the formation of **3** in 40% yield after 1 hour, besides the recovery of 5% of **2b**. In this case, it could be that catalytic amounts of HCl arising from FeCl₃ partially decomposes **2b** thus generating the brominating species which affords **3**. In contrast to bromide **1b**, the iodide **1c** gave the cyclized product **2c** in only 10% and 32% yields at room temperature and at 0 °C, respectively (Entry 3, Table 2). Moreover, **2c** decomposed completely and very quickly when the reaction mixture was warmed to 40 °C, with evident loss of iodine, presumably due to the carbon-iodine bond lability.^{13b} We found, however, that the order of addition of the reagents played a crucial role in the cyclization of **1c**. In fact, when a solution of **1c** in DCM was dropped into a slurry of FeCl₃ (4 equiv) in DCM at reflux, **2c** was isolated in 74% yield. This could be the consequence of a faster cyclization of **1c** in the presence of excess of FeCl₃ at 40 °C relative to its decomposition. In addition, we found that the substrate **1d**, bearing two alkyl chains in the α -positions, underwent fast degradation at room temperature, while a lower reaction temperature (0 °C) allowed us to obtain the required product **2d** in 66% yield (Entry 4, Table 2). Different results were obtained with (*Z*)-dithienyl ethenes **1e** and **1f**, substituted in the α -positions with the electron-withdrawing groups COOEt and CHO, respectively. In particular, the oxidative coupling of **1e** efficiently occurred at room temperature, 40 °C and 80 °C, providing **2e** in 66%, 87% and 89% yields, respectively (Entry

5, Table 2). These results indicate that **2e** is stable under these oxidative conditions, and that higher temperatures favour its cyclization. On the other hand, the more electron-poor substrate **1f** remained practically unreacted, affording only traces of **2f**, both at room temperature and 40 °C (Entry 6, Table 2). However, by increasing the temperature from 40 °C to 80 °C, **2f** could be isolated in 40% yield along with 10% of **1f**. Most likely, the presence of the electron-withdrawing formyl substituents on the thiophene rings of **1f** makes it difficult to generate the supposed radical cation intermediate,^{13m} and, in this case, the temperature plays a crucial role to promote the intramolecular cyclization. The synthesis of functionalized benzodithiophene derivatives **2b-f** has important implications for the development of new and more complex molecular architectures. In fact, further modifications exploiting the reactivity of the substituents in the α -positions of the thiophene rings appear just as useful. Among these, the possibility of the debromination of **BDT 2b** was explored by treating it with BuLi/MeOH at 0 °C (Scheme 2).



Scheme 2. Debromination of bromo **BDT** derivatives **2b** and **3**.

From this reaction we isolated, in 89% yield, unsubstituted **2a**, which as already stated above, cannot be obtained by means of the FeCl₃-mediated cyclization of **1a**. More interestingly, the analogous regioselective debromination of the two α -positions of **3** also occurred using two equivalents of BuLi/MeOH at -78 °C, providing the β -bromo substituted **BDT** derivative **4** in 70% yield. This latter compound represents a potential new key intermediate for the synthesis of an interesting class of chiral atropisomeric molecules, from which enantiomerically pure thiahelicenes could be prepared.^{8a} In summary, a non-photochemical methodology for the synthesis of **BDT** scaffolds through the FeCl₃-mediated oxidative cyclization of 1,2-dithienylethenes **1b-f** has been set up. This work has demonstrated the feasibility to achieve α,α' disubstituted **BDT** without the need to be inserted into more complex polyaromatic systems. The presence of two functional groups in the α,α' positions of alkenes **1b-f** efficiently prevents polymerization in the oxidative conditions of the cyclization, and allow further functionalization of the final **BDTs**. For these reasons, we believe that the establishment of this methodology can promote a renewed and increased interest in the [1,2-b:4,3-b'] **BDT** scaffold and consequently the development of new applications, for example in conductive organic polymers and DSSC. In addition, new perspectives for exploring the synthesis of enantiopure thiahelicenes from 3-bromo **BDT** derivative **4** are currently in progress in our laboratory.

Experimental

General Procedure for the FeCl₃-mediated Cyclization of Alkenes **1b-f**

To a solution of the alkene **1b-f** (0.25 mmol) in dry DCM (20 mL), constantly sparged with nitrogen at the proper temperature (0, rt, 40 or 80 °C), FeCl₃ (1 mmol, 4 eq) was added. The resulting mixture was stirred under a nitrogen purge for 30', and then treated with methanol (ca. 50 mL) for 1h. The solvents were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel. The chromatographic fractions containing the required compound were collected and concentrated to give the corresponding **2b-f** as pale yellow solids in 40-89 % yield (Entries 2-6, Table 2).

Notes and references

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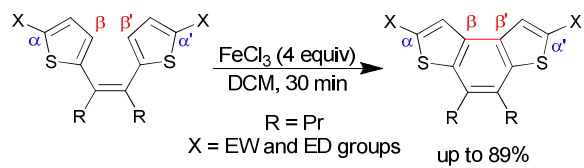
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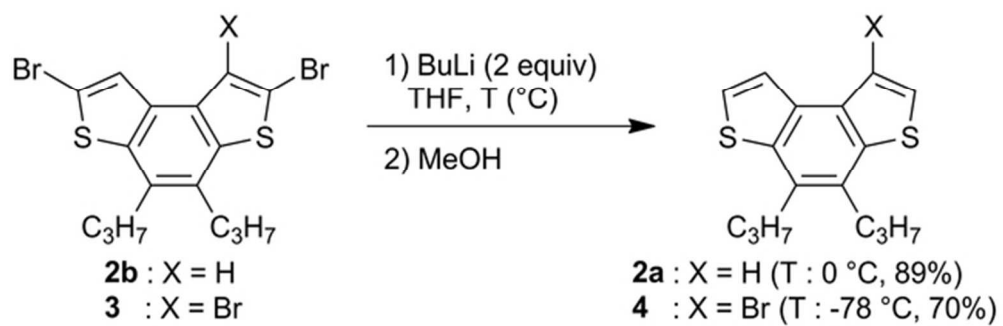
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† Electronic Supplementary Information (ESI) available: Experimental details for **1a-f**, **2a-f**, **3** and **4**. Crystal data and crystallographic information for **3**. See DOI: 10.1039/c000000x/

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The FeCl_3 -mediated cyclization of α,α' -disubstituted *Z*-alkenes as a general and non-photochemical synthesis of benzo[1,2-*b*:4,3-*b'*]dithiophene derivatives.





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