

# A non-photochemical route to synthesize simple benzo[1,2-*b*:4,3-*b'*]dithiophenes: FeCl<sub>3</sub>-mediated cyclization of dithienyl ethenes†

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**The FeCl<sub>3</sub>-mediated cyclization of  $\alpha,\alpha'$ -disubstituted *Z*-alkenes **1** is reported as a general and non-photochemical route to synthesize 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 on the scope and limitations of this methodology is also reported.**

Thiophene-containing fused, aromatic compounds represent an interesting class of  $\pi$ -conjugated systems in functional organic materials.<sup>1</sup> Among them, five isomeric tricyclic  $\beta$ -fused benzo-dithiophenes have stimulated a lot of interest thanks to their use as monomers or co-monomers for the synthesis of conductive materials used in electronic devices.<sup>2</sup> 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 repeating units of mono- and polydisperse oligomers in the field of materials science,<sup>3</sup> and, more recently, as  $\pi$ -spacers in push-pull organic chromophores for photovoltaic applications.<sup>4</sup> Moreover, BDT represents a key intermediate in the synthesis of inherently chiral helical systems such as tetrathia[7]helicenes (7-TH),<sup>5</sup> which are an extremely attractive class of conjugated molecules, with unique physicochemical properties provided by their helix-like structure.<sup>6</sup> On the basis of the above considerations, BDT can be identified as a key starting molecule that, through a judicious functionalization of the  $\alpha$ -positions of the thiophene rings, can allow access to more complex and interesting systems.<sup>3,4,7</sup> Despite all these potential advantages, convenient synthetic methodologies to prepare

BDT are still scarce,<sup>8</sup> and normally involve the oxidative photochemical cyclization of dithienyl ethenes as the key step.<sup>9</sup> However, this reaction requires specific photochemical equipment and highly dilute 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<sup>5a,b,10</sup> and push-pull chromophores,<sup>4b</sup> we faced this synthetic problem and we focused our attention on the FeCl<sub>3</sub>-mediated oxidative intramolecular cyclization of dithienyl ethenes *via* C–C bond formation between the  $\beta$ -positions of thiophene rings. In fact, iron(III) chloride is an economical and commercially available salt that has found widespread application as a Lewis acid<sup>11</sup> but also as a mild and selective oxidising agent, and is therefore particularly useful for C–C coupling reactions involving arenes and heteroarenes.<sup>12</sup> In this way, complex polycyclic aromatic compounds, containing the BDT framework as part of an *ortho*-condensed aromatic system, have been prepared.<sup>13</sup> In contrast, no synthesis of the simple tricyclic BDT scaffold has so far been reported using the FeCl<sub>3</sub> mediated oxidative coupling.

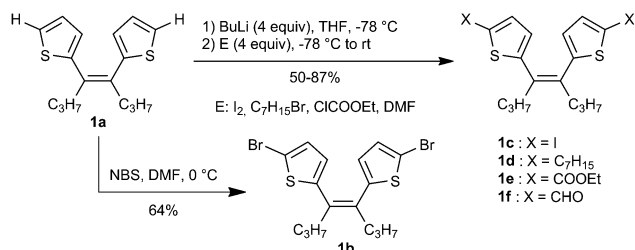
Herein, we report the first results of our investigations on the FeCl<sub>3</sub>-mediated oxidative intramolecular cyclization of  $\alpha,\alpha'$ -disubstituted (*Z*)-dithienyl ethenes **1** to afford benzodithiophene derivatives **2**.<sup>14</sup> In this study we focused our attention on (*Z*)-dithienyl ethenes **1** bearing two *n*-propyl chains on the double bond, which improve the solubility of the BDT derivatives **2** in organic solvents.<sup>4b</sup> (*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  $\alpha,\alpha'$ -disubstituted (*Z*)-dithienyl ethenes **1b–f**, prepared according to Scheme 1. It is interesting to underline that, under the McMurry reaction conditions, we isolated **1a** as a 9 : 1 mixture of the *Z* and *E* isomers.<sup>15</sup> This is a fundamental stereochemical

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† Electronic supplementary information (ESI) available: Experimental details of **1a–f**, **2a–f**, **3** and **4**. Crystal data for **3**. CCDC 967135. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj01567j

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

prerequisite for the further  $\text{FeCl}_3$ -mediated cyclization, which proceeds only with the *Z* isomer.<sup>13b</sup> Dibromo alkene **1b** was obtained in 64% yield by means of regioselective bromination of **1a** with NBS in DMF at 0 °C, whereas all of other  $\alpha,\alpha'$ -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 an appropriate electrophile (Scheme 1). The oxidative cyclization of **1a–f** was then investigated using  $\text{FeCl}_3$  as an oxidant.

In order to assess the best conditions for the oxidative cyclization of **1a–f** to the corresponding BDT derivatives **2a–f**, preliminary screening has been performed to evaluate the influence of the amount of  $\text{FeCl}_3$  on the cyclization of the  $\alpha,\alpha'$ -dibromo ethene **1b**, used as a model alkene, in  $\text{CH}_2\text{Cl}_2$  at room temperature (Table 1).

In particular, the addition of a stoichiometric amount of  $\text{FeCl}_3$  (2 equiv.)<sup>16</sup> to a solution of **1b** in  $\text{CH}_2\text{Cl}_2$  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  $\text{FeCl}_3$  (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  $\text{FeCl}_3$ –alkene to perform the cyclization is 2 : 1, quite often the use of a higher ratio is necessary to obtain higher reaction yield.<sup>13c,m,17</sup> However, in our case, the use of a much larger excess of  $\text{FeCl}_3$  (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  $\text{FeCl}_3$  (10 mol%) in combination with a stoichiometric amount of *m*-CPBA (1 equiv.)<sup>18</sup> as an oxidant resulted in a significant decrease of the yield, and compound **2b** was isolated in only

Table 1  $\text{FeCl}_3$ -mediated cyclization of **1b**: the effect of the  $\text{FeCl}_3$ –**1b** ratio

Entry <sup>a</sup>	$\text{FeCl}_3$ (equiv.) DCM, r. t., 30 min		Yield of <b>2b</b> (%)
	<b>1b</b>	<b>2b</b>	
1	2	60	
2	4	76	
3	12	72	
4	0.1 <sup>b</sup>	13	
5 <sup>c</sup>	4	60	

<sup>a</sup> Unless otherwise noted, an appropriate amount of  $\text{FeCl}_3$  was added to a solution of **1b** (0.25 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (20 mL), and stirred for 30 minutes under a nitrogen atmosphere. <sup>b</sup> *meta*-Chloroperbenzoic acid (*m*-CPBA, 1 equiv.) was used as an oxidant. <sup>c</sup> A mixture of  $\text{CH}_2\text{Cl}_2$ – $\text{MeNO}_2$  (9/1) was used as solvent.

Table 2  $\text{FeCl}_3$ -mediated intramolecular cyclization of **1a–f**

Entry <sup>a</sup>	Reagent		Products				Isolated yield (%)			
	<b>1</b>	X	<b>2</b>	r.t.	0 °C	40 °C	80 °C <sup>b</sup>			
1	<b>1a</b>	H	<b>2a</b>	— <sup>c</sup>	— <sup>c</sup>					
2	<b>1b</b>	Br	<b>2b</b>	76	79	57	60 <sup>d</sup>			
3	<b>1c</b>	I	<b>2c</b>	10	32	74 <sup>e</sup>	<sup>f</sup>			
4	<b>1d</b>	$\text{C}_7\text{H}_{15}$	<b>2d</b>	— <sup>c</sup>	66	<sup>f</sup>	<sup>f</sup>			
5	<b>1e</b>	COOEt	<b>2e</b>	66	<sup>f</sup>	87	89			
6	<b>1f</b>	CHO	<b>2f</b>	< 10	<sup>f</sup>	< 10	40			

<sup>a</sup> Unless otherwise noted,  $\text{FeCl}_3$  (4 equiv.) was added to a solution of **1** (0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), and stirred for 30 min under nitrogen. <sup>b</sup> Solvent:  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (DCE). <sup>c</sup> The starting alkene decomposed completely after a few minutes. <sup>d</sup> Tribromo derivative **3** was isolated in 10% yield. <sup>e</sup> A solution of **1c** (0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added to a slurry of  $\text{FeCl}_3$  (4 equiv.) in  $\text{CH}_2\text{Cl}_2$  (20 mL) at 40 °C. <sup>f</sup> Not performed.

13% yield (entry 4, Table 1). Although  $\text{FeCl}_3$ -mediated cyclo-dehydrogenations are often carried out employing  $\text{CH}_2\text{Cl}_2$  in combination with nitromethane as co-solvent,<sup>12</sup> in our case the use of a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{MeNO}_2$  as solvent in the reaction of **1b** with 4 equiv. of  $\text{FeCl}_3$  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 amounts. Based on these results, we then ran the cyclization reactions of **1a–f** with 4 equiv. of  $\text{FeCl}_3$  in  $\text{CH}_2\text{Cl}_2$ , evaluating the influence of the temperature on the outcome of these reactions (Table 2).

As expected, when a solution of **1a** in  $\text{CH}_2\text{Cl}_2$  was treated with  $\text{FeCl}_3$  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<sup>13b,c</sup> instead of the required benzodithiophene **2a**. In contrast, 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). In contrast, increasing the temperature (up to 40 or 80 °C) was found to produce **2b** in lower yields, together with tribromo derivative **3** (Fig. 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 (Fig. 1b). The formation of **3** could be rationalized by taking into account that thiophenes brominated in the  $\alpha$ -positions readily undergo debromination and/or rearrangement reactions through heating in the presence of catalytic amounts of strong acids.<sup>19</sup>

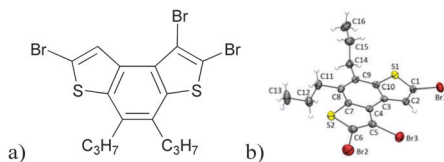
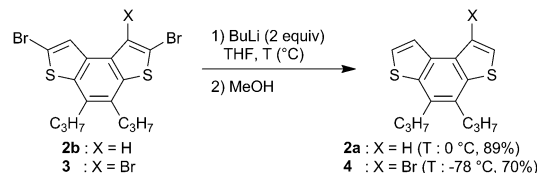


Fig. 1 (a) Chemical structure of **3**. (b) ORTEP view of the crystal structure of **3** (ellipsoids are drawn at their 30% probability level).

These processes, which generally involve the loss of brominating species, could also occur in the  $\text{FeCl}_3$ -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,  $\alpha$ -unsubstituted **BDTs** decompose under these conditions. We found that heating the dibromo **BDT 2b**, in the presence of 4 equiv. of  $\text{FeCl}_3$  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  $\text{HCl}$  arising from  $\text{FeCl}_3$  partially decompose **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.<sup>13b</sup> 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  $\text{FeCl}_3$  (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  $\text{FeCl}_3$  at 40 °C relative to its decomposition. In addition, we found that the substrate **1d**, bearing two alkyl chains in the  $\alpha$ -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  $\alpha$ -positions with the electron-withdrawing groups  $\text{COOEt}$  and  $\text{CHO}$ , 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 unreactive, 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% **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,<sup>13m</sup> and, in this case, the temperature plays a crucial role in promoting the intramolecular cyclization. The synthesis of functionalized benzodithiophene derivatives **2b–f** has important implications for the development of new and



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

more complex molecular architectures. In fact, further modifications exploiting the reactivity of the substituents in the  $\alpha$ -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  $\text{BuLi–MeOH}$  at 0 °C (Scheme 2).

From this reaction we isolated, in 89% yield, unsubstituted **2a**, which as already stated above, cannot be obtained by means of the  $\text{FeCl}_3$ -mediated cyclization of **1a**. More interestingly, the analogous regioselective debromination of the two  $\alpha$ -positions of **3** also occurred using two equivalents of  $\text{BuLi–MeOH}$  at –78 °C, providing the  $\beta$ -bromo substituted **BDT** derivative **4** in 70% yield. The latter compound represents a potential new key intermediate for the synthesis of an interesting class of chiral atropisomeric molecules, from which enantiomerically pure thiahelices could be prepared.<sup>8a</sup> In summary, a non-photochemical methodology for the synthesis of **BDT** scaffolds through the  $\text{FeCl}_3$ -mediated oxidative cyclization of 1,2-dithienyl ethenes **1b–f** has been set up. This work has demonstrated the feasibility of achieving  $\alpha,\alpha'$ -disubstituted **BDT** without the need to be inserted into more complex polyaromatic systems. The presence of two functional groups in the  $\alpha,\alpha'$  positions of alkenes **1b–f** efficiently prevents polymerization under the oxidative conditions of cyclization, and allows further functionalization of the final **BDTs**. For these reasons, we believe that the establishment of this methodology can promote 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 DSSCs. In addition, new investigations aimed at exploring the synthesis of enantiopure thiahelices from 3-bromo **BDT** derivative **4** are currently in progress in our laboratory.

## Experimental

### General procedure for the $\text{FeCl}_3$ -mediated cyclization of alkenes **1b–f**

To a solution of alkenes **1b–f** (0.25 mmol) in dry DCM (20 mL), constantly sparged with nitrogen at an appropriate temperature (0, rt, 40 or 80 °C),  $\text{FeCl}_3$  (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 1 h. 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

- (a) J. Roncali, *Chem. Rev.*, 1997, **97**, 173; (b) T. A. Skotheim and J. R. Reynolds, in *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization (Handbook of Conducting Polymers)*, ed. T. A. Skotheim and J. R. Reynolds, CRC Press LLC., Boca Raton, FL, 3rd edn, 2007; (c) J. Roncali, *Acc. Chem. Res.*, 2009, **42**, 1719.
- (a) R. Rieger, D. Beckmann, A. Mavrinskiy, M. Kastler and K. Müllen, *Chem. Mater.*, 2010, **22**, 5314; (b) L. Huo and J. Hou, *Polym. Chem.*, 2011, **2**, 2453; (c) P. Sista, M. C. Biewer and M. C. Stefan, *Macromol. Rapid Commun.*, 2012, **33**, 9.
- Y. Nishide, H. Osuga, M. Saito, T. Aiba, Y. Inagaki, Y. Doge and K. Tanaka, *J. Org. Chem.*, 2007, **72**, 9141.
- (a) P. Gao, H. N. Tsao, M. Grätzel and M. K. Nazeeruddin, *Org. Lett.*, 2012, **14**, 4330; (b) E. Longhi, A. Bossi, G. Di Carlo, S. Maiorana, F. De Angelis, P. Salvatori, A. Petrozza, M. Binda, V. Rofati, P. R. Mussini, C. Baldoli and E. Licandro, *Eur. J. Org. Chem.*, 2013, 84.
- (a) E. Licandro, C. Rigamonti, M. T. Ticozzelli, M. Monteforte, C. Baldoli, C. Giannini and S. Maiorana, *Synthesis*, 2006, 3670; (b) C. Rigamonti, M. T. Ticozzelli, A. Bossi, E. Licandro, C. Giannini and S. Maiorana, *Heterocycles*, 2008, **76**, 1439; (c) D. Waghay, W. Nulens and W. Dehaen, *Org. Lett.*, 2011, **13**, 5516; (d) D. Waghay and W. Dehaen, *Org. Lett.*, 2013, **15**, 2910.
- (a) S. K. Collins and M. P. Vachon, *Org. Biomol. Chem.*, 2006, **4**, 2518; (b) A. Bossi, E. Licandro, S. Maiorana, C. Rigamonti, S. Righetto, G. R. Stephenson, M. Spassova, E. Botek and B. Champagne, *J. Phys. Chem. C*, 2008, **112**, 7900; (c) Y. Shen and C.-F. Chen, *Chem. Rev.*, 2012, **112**, 1463.
- M. H. Garcia, P. Florindo, M. F. M. Piedade, M. T. Duarte, M. P. Robalo, J. Heck, C. Wittenburg, J. Holtmann and E. Licandro, *J. Organomet. Chem.*, 2008, **693**, 2987.
- Recently, non-photochemical syntheses of three specific BDT derivatives have been reported: (a) A. Rajca, M. Pink, S. Xiao, M. Miyasaka, S. Rajca, K. Das and K. Plessel, *J. Org. Chem.*, 2009, **74**, 7504; (b) M. Shimozu, I. Nagao, Y. Tomioka and T. Hiyama, *Angew. Chem., Int. Ed.*, 2008, **47**, 8096; (c) Y. Xia, P. Qu, Z. Liu, R. Ge, Q. Xiao, Y. Zhang and J. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 2543. In addition, some of us have very recently reported the synthesis of BDT scaffolds by Ullmann/ring closing metathesis and Ullmann/bis-hydrazone coupling reactions: *Synlett*, 2014, **25**, 701.
- M. B. Goldfinger, K. B. Crawford and T. M. Swager, *J. Am. Chem. Soc.*, 1997, **119**, 4578.
- (a) A. Bossi, S. Maiorana, C. Graiff, A. Tiripicchio and E. Licandro, *Eur. J. Org. Chem.*, 2007, 4499; (b) C. Kim, T. J. Marks, A. Facchetti, M. Schiavo, A. Bossi, S. Maiorana, E. Licandro, F. Todeskato, S. Toffanin, M. Muccini, C. Graiff and A. Tiripicchio, *Org. Electron.*, 2009, **10**, 1511; (c) L. M. Ming, F. Rose-Munch, E. Rose, J. C. Daran, A. Bossi, E. Licandro and P. R. Mussini, *Organometallics*, 2012, **31**, 92.
- C. Bolm, J. Legros, J. Le Pailh and L. Zani, *Chem. Rev.*, 2004, **104**, 6217.
- For recent reviews, see: (a) A. A. O. Sarhan and C. Bolm, *Chem. Soc. Rev.*, 2009, **38**, 2730; (b) Y. Cao, X.-Y. Wang, J.-Y. Wang and J. Pei, *Synlett*, 2014, **25**, 313.
- (a) J. Larsen and K. Bechgaard, *J. Org. Chem.*, 1996, **61**, 1151; (b) J. D. Tovar, A. Rose and T. M. Swager, *J. Am. Chem. Soc.*, 2002, **124**, 7762; (c) J. Pei, W. Y. Zhang, J. Mao and X. H. Zhou, *Tetrahedron Lett.*, 2006, **47**, 1551; (d) W. J. Liu, Y. Zhou, Y. Ma, Y. Cao, J. Wang and J. Pei, *Org. Lett.*, 2007, **9**, 4187; (e) Y. Zhou, W. Y. Liu, Y. Ma, H. Wang, L. Qi, Y. Cao, J. Wang and J. Pei, *J. Am. Chem. Soc.*, 2007, **129**, 12386; (f) J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei and D. F. Perepichka, *Chem. Mater.*, 2008, **20**, 2484; (g) Q. Yan, Y. Zhou, B.-B. Ni, Y. Ma, J. Wang, J. Pei and Y. Cao, *J. Org. Chem.*, 2008, **73**, 5328; (h) J. Luo, B. Zhao, J. Shao, K. A. Lim, H. S. O. Chan and C. Chi, *J. Mater. Chem.*, 2009, **19**, 8327; (i) J. Luo, B. Zhao, H. S. O. Chan and C. Chi, *J. Mater. Chem.*, 2010, **20**, 1932; (j) Q. Ye, J. Chang, K. W. Huang and C. Chi, *Org. Lett.*, 2011, **13**, 5960; (k) F. He, W. Wang, W. Chen, T. Xu, S. B. Darling, J. Strzalka, Y. Liu and L. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 3284; (l) L. Zöphel, V. Enkelmann, R. Rieger and K. Müllen, *Org. Lett.*, 2011, **13**, 4506; (m) Q. Ye, J. Chang, K.-H. Huang, G. Dai, J. Zhang, Z.-K. Chen, J. Wu and C. Chi, *Org. Lett.*, 2012, **14**, 2786; (n) J. Wang, H. Xu, B. Li, X.-P. Cao and H.-L. Zhang, *Tetrahedron*, 2012, **68**, 1192; (o) W. Geng, H. Wang, Z. Wang, S. Zhang, W.-X. Zhang and Z. Xi, *Tetrahedron*, 2012, **68**, 5283.
- This preliminary study has been the object of a patent published by some of the authors: S. Maiorana, E. Licandro, E. Longhi, S. Cauteruccio, A. Abboto, C. Baldoli and F. De Angelis, *PCT Int. Appl.*, WO2012107488, 2012.
- The *E* isomer was obtained as the only compound in different reaction conditions. H. Huang, Z. Chen, R. P. Ortiz, C. Newman, H. Usta, S. Lou, J. Youn, Y.-Y. Noh, K.-J. Baeg, L. X. Chen, A. Facchetti and T. Marks, *J. Am. Chem. Soc.*, 2012, **134**, 10966.
- The radical mechanism *via* the one-electron transfer, which is generally proposed for the intramolecular oxidative coupling reactions in the presence of FeCl<sub>3</sub>, requires two equivalents of FeCl<sub>3</sub> to form a C–C bond. See, for example, ref. 13b.
- F. A. Arroyave, C. A. Richard and J. R. Reynolds, *Org. Lett.*, 2012, **14**, 6138.
- K. Wang, M. Lu, A. Yu, X. Zhu and Q. Wang, *J. Org. Chem.*, 2009, **74**, 935.
- R. M. Kellogg, A. P. Schaap, E. T. Harper and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 2902.