



## Oxidative Dimerization of Diethyl 3-Thienylmalonate by High Valent Metal Salts. Synthesis of Benzo[1,2-b:4,5-b']dithiophene Derivatives

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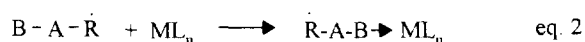
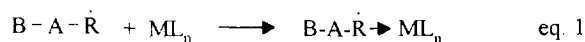
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**Abstract:** The oxidation of diethyl 3-thienylmalonate (**1**) by metal oxidants ( $\text{Fe}(\text{ClO}_4)_3$ ,  $\text{Mn}(\text{OAc})_3$ ,  $\text{MnO}_2$  and  $\text{CuO}$ ) in various solvents at 60 °C affords dimerization products arising from side-chain and nuclear coupling of the intermediate delocalized malonyl radicals **6**. Metal to sulphur binding is suggested to play a role in controlling the distribution of dimers **2** - **5**. The higher thermodynamic stability of unsymmetric dimer **3**, along with its oxidative intramolecular 1,6-cyclization to **4**, allows to develop a new simple synthesis of benzo[1,2-b:4,5-b']dithiophene derivatives **15-18**.

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### INTRODUCTION

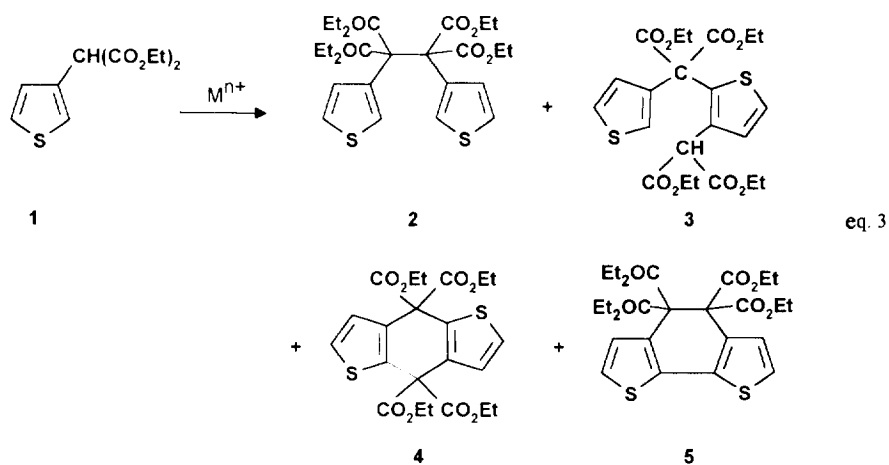
The oxidation of carbonyl compounds by high valent metal salts or complexes has attracted considerable attention in the last years due to their interesting role in organic synthesis.<sup>1</sup> Mechanistic studies<sup>2</sup> have shown that electrophilic  $\alpha$ -carbonylalkyl radicals are key intermediate in these processes. They present an high reactivity and reversibility towards addition to unsaturated substrates substituted by both electron-releasing and electron-withdrawing groups and an inefficient oxidation by metal ions or complexes, making possible a rational design of complex transformations of polyfunctionalised substrates by the use of mild reaction conditions. However, the high concentrations of metal salts used in these stoichiometric redox processes can influence the reactivity of radicals through the formation of complexes between the basic atoms of the paramagnetic species (both on the radical centre (R in eq. 1) or in a remote position (B in eq. 2)) and the metal complex ( $\text{ML}_n$ ).



The relative position of the radical centre and the basic atom(s) can influence the reactivity of the paramagnetic complex by modifying the steric and electronic properties of the intermediate. Higher influence is expected when the bond formed in the complex is close to the radical centre. The phenomenon has been poorly

investigated and in model reactions of addition of malonyl radicals to olefins it was concluded that the complexation has negligible kinetic effect.<sup>3</sup> However, recent studies on Lewis acid mediated radical reactions have suggested a crucial role of metal ions in controlling the regio and stereochemistry of the addition to unsaturated substrates.<sup>4</sup> Because complexation is commonly a fast and reversible process, the product distribution will depend on the relative equilibrium constants and on the difference in reactivity and selectivity of the free and complexed radical. The pattern can be further complicated in the presence of reversible processes of radical addition to unsaturated substrates where metals can determine also the fate of the radical adduct. Recently, cobalt complexes of  $\beta$ -dicarbonyl radicals were identified by e.s.r.<sup>5</sup> in trifluoroacetic acid and their chemistry spectroscopically investigated.

In the attempt to better define the role of metal complexation on radical reactivity, we start an investigation on the influence of metal salts in the coupling at low temperature of mesomeric allyl radical substituted on one side by an heteroatom. The model was chosen because the analysis of the distribution of head to head, tail to tail and head to tail coupling product would provide a fine tune of the involvement of the metal on the basis of the irreversibility of the process and would provide unexplored synthetic possibilities. In this paper we report the results of the oxidative coupling of diethyl 3-thienylmalonate (**1**) to compounds **2** - **5** by representative metal salts in different solvents (eq. 3). Dimers are been previously reported<sup>6</sup> in the oxidation of carbonyl compounds by high valent metal salts in the absence of efficient radical trapping agents, in heterogeneous medium or in the presence of radical stabilising substituents, but cross coupling involving the aromatic nucleus are rare and generally involve bulky substituents at the benzylic position. Table 1 summarises the results obtained in our study.



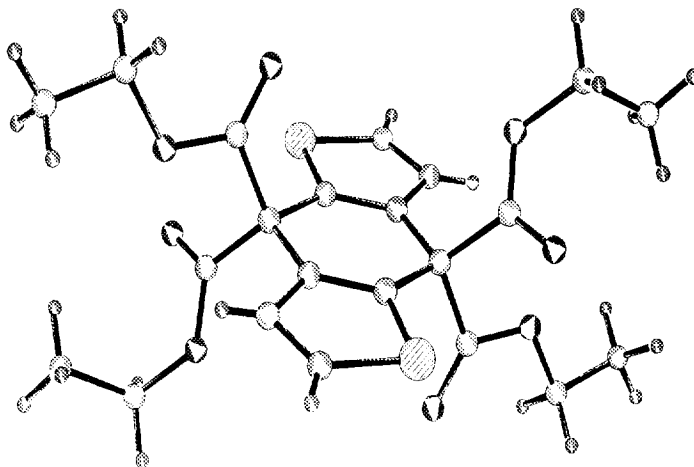
**Table 1.** Products distribution in the oxidation of diethyl 3-thienylmalonate (**1**) by metal oxidants in different solvents.

Entry	----- Reaction conditions <sup>a)</sup> -----				- Products (yield %) -				R 2/(3 + 4 + 5)
	Metal	Solvent	T (°C)	Time (h)	2	3	4	5	
1	FEP <sup>b)</sup>	MeOH/Py	20	6	22	2	50	16	0.32
2	FEP <sup>b)</sup>	MeOH	20	3	22	3	48	16	0.32
3	FEP <sup>b)</sup>	MeOH	60	2	20	-	45	17	0.32
4	Mn(OAc) <sub>3</sub>	AcOH	70	3	41	24	26	-	0.82
5	Mn(OAc) <sub>3</sub>	Me <sub>2</sub> CO	70	4	32	46	3	-	0.65
6	Mn(OAc) <sub>3</sub>	EtOH	70	12	19	28	1	-	0.66
7	MnO <sub>2</sub>	DMF	70	2	39	56	-	-	0.70
8	MnO <sub>2</sub>	C <sub>10</sub> H <sub>18</sub> <sup>c)</sup>	60	4	37	34	8	-	0.88
9	CuO	MeCN	80	24	29	39	-	-	0.74
10	CuO	C <sub>10</sub> H <sub>18</sub> <sup>c)</sup>	80	24	38	47	-	-	0.81

a) [1] = [Metal]/2 = [additive] = 0.10 M. b) FEP = Fe(H<sub>2</sub>O)<sub>6</sub>(ClO<sub>4</sub>)<sub>3</sub>. c) Decahydronaphthalene.

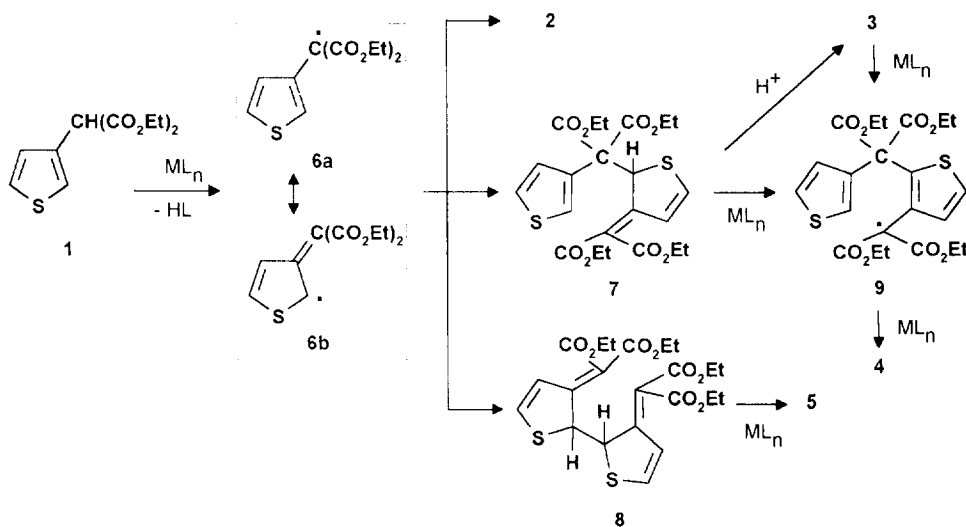
Selective formation of a single product is never observed, but head to head dimer **2** and head to tail dimer **3** (scheme I) are exclusively formed under heterogeneous conditions by using MnO<sub>2</sub> in DMF, CuO in MeCN or decahydronaphthalene, and with Mn(OAc)<sub>3</sub> in ethanol. In all other conditions of Table 1, the reaction mixture contains the cyclic product **4** of four electron oxidation. The head to tail structure of **4** with a nearly planar 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene ring was unambiguously proved by X-ray diffraction analysis (Figure 1)<sup>7</sup>. The tail to tail 4,5-dihydrobenzo[1,2-*b*:3,4-*b'*]dithiophene product **5** is isolated only in experiments with Fe(H<sub>2</sub>O)<sub>6</sub>(ClO<sub>4</sub>)<sub>3</sub> (FEP) in methanol and the structure assigned on the basis of <sup>1</sup>H- and <sup>13</sup>C-NMR. Sequences in the formation of these compounds involving malonyl radicals **6** and **9** are shown in Scheme 1. The coupling process cannot be ensured in the absence of metals by thermal decomposition of azobisisobutyronitrile (AIBN) or dibenzoyl peroxide.

Product **4** arises from a 1,6-intramolecular homolytic aromatic substitution of the malonyl radical **9** of the head to tail dimer (Scheme 1). In parallel experiments compound **3** was in fact selectively oxidised to **4** by Mn(OAc)<sub>3</sub> in AcOH at 60 °C, but no reaction was observed with FEP in MeOH or with MnO<sub>2</sub> in DMF or C<sub>10</sub>H<sub>18</sub>. These results indicate that the formation of **4** in the oxidation of **1** by MnO<sub>2</sub> and FEP does not involve **3** as intermediate, but presumably occurs via the unstable dimer **7**, more easily oxidised than **3**. Compound **7** should be a significant strong acid and tautomerization to **3** is expected under both metal and acid catalysis.



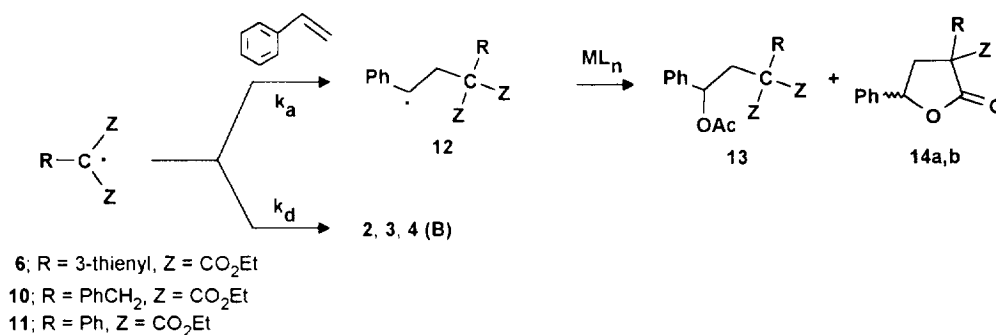
**Figure 1.** Structure of **7** ( $C_{22}H_{24}O_8S_2$ ), determined by single-crystal X-ray diffraction.

In our opinion metal malonate complexes are formed more efficiently by deprotonation of **7** than of **3** and reprotonation at the carbon of the malonate ligand competes with the electron-transfer within the complex to give malonyl radicals **9**, irreversibly trapped by the pendent thiophene ring. All attempt to isolate or synthesise **4** by alternative approaches failed.



**Scheme 1**

The structure of dimer **3** and the absence of any positional isomers excludes the involvement of radical **6** in processes of homolytic aromatic substitution. In fact, the intermolecular addition of malonyl radicals to furans and thiophenes occurs at the less substituted  $\alpha$ -position<sup>8</sup>. Moreover, trapping experiments of oxidation of **1** and **3** by  $\text{Mn}(\text{OAc})_3$  with thiophene as solvent<sup>9</sup> were unsuccessful. This indicates that the intermolecular addition to the heteroaromatic ring is a slow process for radical **6** and does not compete with the coupling, whereas the intramolecular nature of the cyclization step of radical **9**, along with favourable stereoelectronic factors owing the gem-disubstitution, fastens the addition to the thiophene ring to the extent that sufficient stationary concentration of **9** for dimerization cannot be attained. On the other hand, trapping experiments with 1 M styrene in the oxidation of **1** by  $\text{Mn}(\text{OAc})_3$  afford the expected addition products (A = mixture of benzylic acetate **13** and isomeric lactones **14**, arising from the oxidation of the benzyl radical adduct **12**) along with the same mixture of dimerization products (B = **2**, **3**, **4**) obtained in the absence of styrene (scheme 2). The ratio A/B (table 2) is linearly dependent on the styrene concentration, indicating that radical **6** cleanly partitions between coupling and addition to the alkene. From these data a value of about  $\sim 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$  can be estimated for the rate constant of addition of radical **6** to styrene based on a dimerization rate constant of  $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  and a stationary concentration for malonyl radicals in the range  $10^{-6}$ - $10^{-7}$  M. The rate is about five and one order of magnitude lower than the one of addition of benzyl- (**10**) and phenylmalonyl radicals (**11**) to styrene<sup>10</sup>, respectively (table 2). Moreover, radical **6** appears to be more easily oxidised than alkyl or phenyl substituted malonyl radicals because more powerful oxidant metal salts (i.e.  $\text{Ce}(\text{NH}_3)_6(\text{NO}_3)_4$  in MeOH,  $\text{Pb}_3\text{O}_4$ , in AcOH, and FEP in MeCN) convert **1** mainly to products of benzylic or nuclear oxygenation. This is in accord with the radical stabilising and electron-releasing effect of the thio group, due to a favourable interaction of doubly occupied nonbonding molecular orbital of the sulphur with the radical centre,<sup>11</sup> in the tautomer **6b** of malonyl radical **6a**. An stabilization effect of *ca.* 12-28  $\text{kJ mol}^{-1}$  for thiomethyl group in carbon radicals has been reported<sup>12,13</sup> and similar values are expected for vinylogous thioallyl radical **6**.



Scheme 2

**Table 2.** Products distribution in the oxidation of diethyl 3-thienylmalonate (**1**), diethyl phenylmalonate and diethyl benzylmalonate by  $\text{Mn}(\text{OAc})_3$  in the presence of styrene ( $\text{AcOH}$ ,  $60\text{ }^\circ\text{C}$ ).

R	[Styrene] M	A % 13+ 14	B % 2 + 3 + 4	$k_a/k_d$	$k_a$ $\text{l mol}^{-1}\text{s}^{-1}$
PhCH <sub>2</sub>	0.2	100	-	> 1000	$8 \times 10^6$ <sup>(7)</sup>
Ph	0.011	42	16	$64.0 \pm 4$	$\sim 10^3$
Ph	0.052	65	13		
Ph	0.10	72	9		
Ph	0.18	79	6		
3-thienyl	0.10	16	73	$2.7 \pm 0.2$	$\sim 10^2$
3-thienyl	0.21	32	59	-	
3-thienyl	0.34	43	50	-	
3-thienyl	0.51	53	38	-	

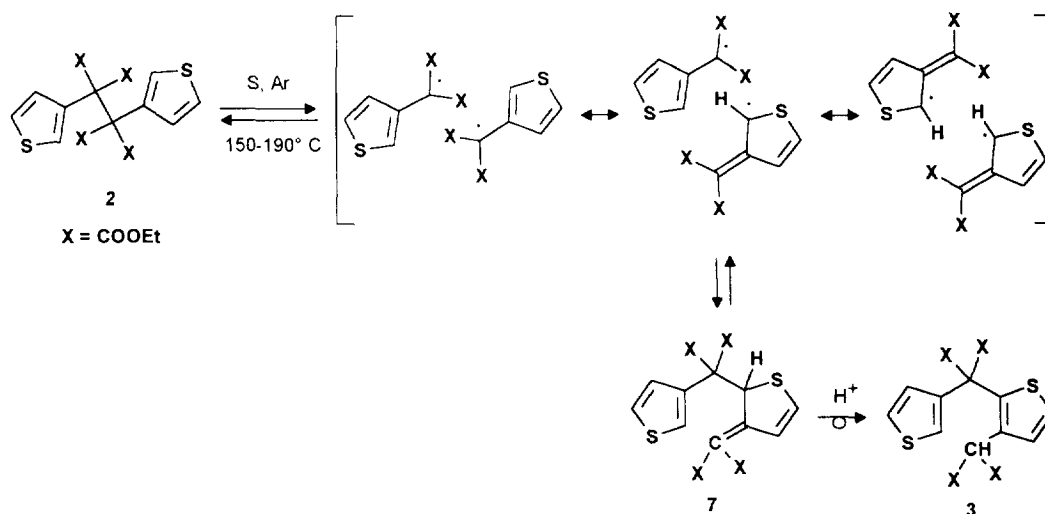
The formation of the 4,5-dihydrobenzo[2,1-b:3,4-b']dithiophene derivative **5** can similarly be interpreted as arising from the further oxidation of the tail to tail dimer **8**. Compound **5** was detected only in the oxidation of **1** by FEP in AN, in yield low but linearly dependent on the FEP concentration, as indicated in table 3. Also in this case the absence of substitution products at the less hindered position 5 of **1** excludes both a mechanism of homolytic aromatic substitution by radical **6** or by **1** cation radical. The latter possibility must be considered because FEP is an efficient oxidant of aromatic rings through outer-sphere electron-transfer mechanism.

**Table 3.** Products distribution in the oxidation of diethyl 3-thienylmalonate (**1**) by FEP ( $\text{MeOH}$ ,  $60\text{ }^\circ\text{C}$ ).

[FEP] M	--- Product yield (%) ----				R
	2	3	4	5	
0,051	30	4	47	10	0,49
0.10	22	3	48	16	0.32
0.26	15	3	46	25	0.20
0.35	13	2	42	28	0,18

All these results taken together are consistent with the idea that dimerization of mesomeric radical **6** occurs in all conditions of table 1 to give the three possible types of dimers **2**, **7** and **8**. The remarkable change of the ratio  $R = 2/(3 + 4 + 5)$  in the narrow range of temperatures investigated appears to be more related to the metal salt used than to other variables of the system (i.e. solvent, temperature, etc.). Because the C-C

dissociation bond energies in compounds **2**, **7** and **8** must be very similar on the basis of previous work on ethoxycarbonyldiphenylmethyl radical dimers<sup>14</sup> and allyl radicals are not kinetically stabilized (i.e. the rate constants of their recombination is in the typical range of the diffusion-controlled reactions<sup>15</sup>), a nearly constant dimer distribution is expected in all media, provided that dimer formation is irreversible at the temperature investigated. We therefore suggest that different paramagnetic species coordinated to the metal are the responsible of the dimer distribution. The binding of radicals to metal ions, affecting the spin distribution on the carbon atoms of radical **6** and the steric access to the radical centre, induces different reactivity at the mesomeric positions and opens new reaction channels. With the model substrate here studied, iron(III) ions show the most relevant effects with an increase of both head to tail and tail to tail dimers and further preference for these last at high metal concentration, suggesting an increased importance of the limit form **6b** through coordination of the thiophene sulphur to the metal. In the more general context of oxidative and reductive stoichiometric redox-radical processes involving metal ions<sup>1c</sup>, paramagnetic species are expected to deviate significantly from the behaviour observed in free-radical reactions without metals when strongly coordinating substituents are present both on radicals and interacting substrates.



Scheme 3

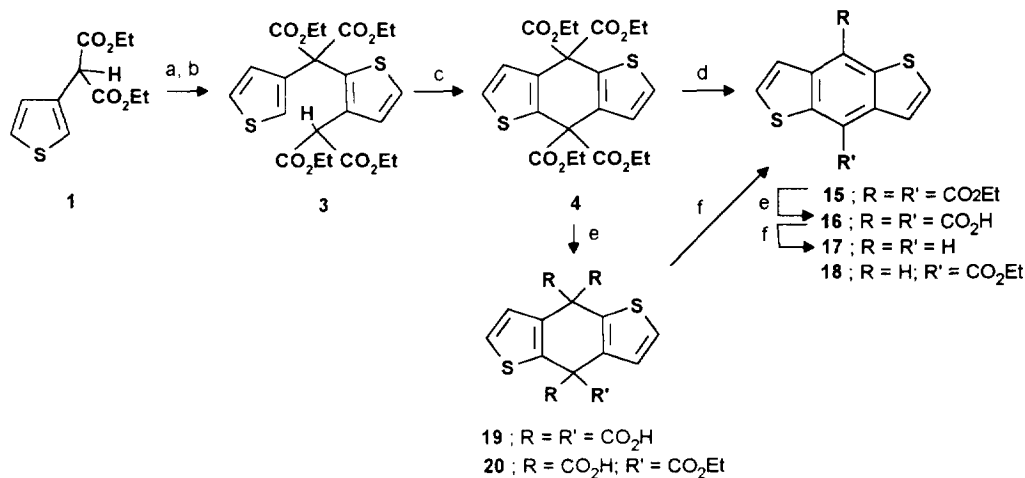
In order to test the irreversibility of the formation of dimer **2**, its thermal decomposition was investigated in different solvents. Selective rearrangement to **3** was observed, but only above 130 °C, indicating that **2** is less thermodynamically stable than **3** but that the interconversion is practically negligible at 60 °C. The rearrangement was found clean first order until 90% conversion and the corresponding kinetic parameters were deduced by product analyses at different temperatures (table 4). The enthalpic parameter obtained are in line

with the one reported for  $\alpha$ -cyano- $\alpha$ -methyltiobenzyl radicals<sup>12</sup> and the small negative entropy has a parallel in the thermal rearrangement of tiomethylsubstituted methylenecyclobutanes for which a biradical mechanism was proposed<sup>16</sup>. The sequence of Scheme 3 can explain the selective rearrangement.

**Table 4.** Rates and activation parameters in the thermolysis of diethyl 3-thienylmalonate (**1**) in decahydronaphthalene.

T (°C)	k (10 <sup>-4</sup> s <sup>-1</sup> )	$\Delta G^{\ddagger}_{300} \pm \sigma$ Kcal/mol	$\Delta H^{\ddagger} \pm \sigma$ Kcal/mol	$\Delta S^{\ddagger} \pm \sigma$ (u.e.)
144	1.31 $\pm$ 0,002	25.0 $\pm$ 1,4	27,9 $\pm$ 1.1	-9.7 $\pm$ 2.3
163	8.43 $\pm$ 0,05			
187	30.95 $\pm$ 0,07			
200	81.07 $\pm$ 0,12			

From the synthetic point of view, the results of this study provide an useful and simple approach to derivatives of the benzo[1,2-b:4,5-b']dithiophene. In fact, the dihydro derivative **4** can be obtained directly in moderate yield by oxidation of **1** with FEP (40-42% isolated yield) or, better (overall yield from **1**: 84 %), by a more complex procedure which involve the oxidation of **1** by MnO<sub>2</sub> in decahydronaphthalene, filtration of the oxide and thermal rearrangement of the crude mixture, then further oxidation of the resulting concentrated residue by Mn(OAc)<sub>3</sub> in acetic acid (scheme 4)



<sup>a</sup> (a) MnO<sub>2</sub>, C<sub>10</sub>H<sub>18</sub>. (b) C<sub>10</sub>H<sub>18</sub> reflux, 2 h (91%). (c) Mn(OAc)<sub>3</sub>, AcOH, 60°C, 12 h (92%). (d) NaI, DMF/O<sub>2</sub>, reflux (88%). (e) KOH, dioxane, HCl. (f) Cu<sub>2</sub>O, quinoline, reflux, 5 h.

**Scheme 4**



Upon NaI catalysed decarboxylation in DMF, under atmosphere containing controlled amount of oxygen, compound **4** is efficiently converted to **15**, whereas the parent benzo[1,2-*b*:4,5-*b'*]dithiophene derivative **17** can be obtained by thermal decarboxylation of the acid **16** with Cu in quinoline (Scheme 4). Alternatively, compounds **15-18** can be obtained by hydrolysis of **4** through analogous decarboxylation with Cu in quinoline of the acid derivatives **19** and **20**. Derivatives **15-18** are useful monomers for oxidative polymerisation or polycondensation<sup>17</sup>. By a similar approach, the benzo[1,2-*b*:3,4-*b'*]dithiophene **21** and the corresponding 4,5-dicarboxylic acid derivative **22** were obtained from **5**.

The interest for fused bithienyls and the simple synthetic approach here presented stimulates further studies to understand the factors affecting the metal assisted coupling of 3-thienylalkyl radicals.

## EXPERIMENTAL

### General methods

Melting points were obtained on a Büchi 535 capillary melting point apparatus. Boiling points were determined in a Büchi GKR-50 short-path distillation apparatus. UV-VIS spectra were recorded on a Jasco UVIDEK-510 spectrophotometer. IR spectra were made on a Perkin-Elmer 467 spectrophotometer. Mass spectra (MS) were determined on a Hitachi RMU-6 or on a VG Micromax ZAB spectrometer at 70 eV. GC-MS analyses were obtained on a Finnigan TSQ-70 GC-MS spectrometer equipped with a J&W DB-5 coated fused silica capillary column (30m x 0.25 mm i.d., film 0.25 µm) or on a Hewell-Packard 5892 GC-MS, composed of a HP-5890 Series II gaschromatograph, equipped with a HP-5 coated silica capillary column (30m x 0.25 mm i.d., film 0.25 µm), and a HP-5972 mass detector with helium as carrier gas. The temperature program was: 70° x 1', 20°'-150°, 150° x 5', 15°' - 280°, 280° x 20'. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded (unless otherwise indicated) in CDCl<sub>3</sub> on Bruker AM 400 and Bruker AT 250 spectrometers; the data are in ppm relative to tetramethylsilane. Gas chromatographic analyses were performed on a DANI 6500 HR capillary gas chromatograph equipped with a PTV injector, a J&W DB-5 coated fused silica capillary column (30m x 0,25 mm i.d., film 0,25 µm), FID detector and H<sub>2</sub> as carrier gas, or on a HP-5890 Series II gas chromatograph equipped with a pressure control, a J&W DB-5 capillary column, a FID detector and H<sub>2</sub> as carrier gas (temperature program: 70° x 1', 20°'-150°, 150° x 5', 15°' - 280°, 280° x 20'). Quantitative GC analyses were performed by the internal standard (biphenyl) method by using the Chromstar Software from Bruker. HPLC analyses were performed on a Bruker LC 21-51 instrument equipped with a Merck Si 60 (5 µm, 25 x 0.4 cm i.d.) column and a UV detector (254 nm) using a mixture hexane-AcOEt 9:1 (1.5 mL/min). Quantitative HPLC analyses were performed by the internal standard (diethyl *o*-phthalate) method. Preparative separations were carried out on Silica gel 60 (230-400 mesh, Merck) using the flash chromatography technique. Elemental Analysis were performed by Redox Laboratory (Milan).

## Materials

All the inorganic compounds are commercial products (purity  $\geq 98\%$ ).  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  (Merck) was tested by iodometric titration,  $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$  (FEP) (Carlo Erba) and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  (Carlo Erba) by  $\text{TiCl}_3$ .  $\text{MnO}_2$ ,  $\text{CuO}$ ,  $\text{Pb}_3\text{O}_4$  (Carlo Erba) were used as received. All organic compounds and solvents were purchased from Aldrich (purity  $\geq 95\%$ ) and, if necessary, were purified by crystallization or distillation. Benzo[1,2-b:4,5-b']dithiophene (XX) (m.p.  $196\text{--}7^\circ\text{C}$ , lit.<sup>18</sup>  $197.5\text{--}198$ ) and benzo[2,1-b:3,4-b']dithiophene (XX) (mp  $44^\circ\text{C}$ , lit.<sup>16</sup> mp  $44\text{--}45$ ) were synthesised as described.

**Diethyl 3-thienylmalonate (1).** In a one-necked flask 3-thienylmalonic acid (19.32 g) and EtOH (96 g) were mixed at  $20^\circ\text{C}$  with magnetic stirring. After few minutes a solution of methanesulphonic acid (3.87 g) in EtOH (96 g) was added. The resulting solution was run with magnetic stirring at  $20^\circ\text{C}$  for 3 days. Then, the solvent was evaporated at  $40^\circ\text{C}$  and 30 mmHg. Water (50 mL) was added to the residue and 10 %  $\text{NaHCO}_3$  solution was added until pH = 7. The aqueous phase was extracted with AcOEt (3 x 15 mL), the layers separated and the combined extracts washed with water, dried and evaporated. Flash chromatography of the residue (eluent hexane/AcOEt 8:2) affords **1** (22.4 g, 89 %), bp  $91^\circ\text{C}/0.05$  mmHg, lit.<sup>19</sup> bp  $151\text{--}152^\circ\text{C}/2$  mmHg; MS: 242 ( $\text{M}^+$ , 30), 171 (6), 170 (26), 169 (76), 142 (18), 141 (39), 124 (51), 113 (56), 97 (100), 96 (35), 85 (49);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.18 (6H, t), 4.22 (4H, q), 4.76 (1H, s), 7.18 (1 H, dd), 7.32 (1 H, dd), 7.37 (1 H, dd). Ethyl 3-thienylacetate (8%) was also formed.

## General procedures for oxidation of diethyl 3-thienylmalonate

**a) with  $\text{MnO}_2$ .** In a two-necked flask under nitrogen,  $\text{MnO}_2$  (3.6 g) was added to the appropriate solvent (52 mL) under stirring at  $20^\circ\text{C}$ . The reaction mixture was heated at  $60\text{--}70^\circ\text{C}$  and a solution of **1** (5 g) in the same solvent (52 mL) was added after 10 min. The reaction was run for 4-12 h (table 1). The hot mixture was filtered on celite, the solvent evaporated at  $35^\circ\text{C}$  under vacuum and the residue taken up with  $\text{CH}_2\text{Cl}_2$ . Products **2**, **3** and **4** were isolated by flash chromatography (eluent hexane/AcOEt 85:15).

**b)  $\text{Fe}(\text{ClO}_4)_3$ .** In a two-necked flask under  $\text{N}_2$  a solution (70 ml, 0.24 M) of FEP in methanol was prepared at  $0^\circ\text{C}$  and a solution (13 mL, 0.64 M) of **1** in methanol was added under magnetic stirring. The resulting solution, warmed at  $20^\circ\text{C}$ , darkens after few minutes. The reaction was run for 3-4 h with magnetic stirring. Then, the solvent was evaporated under vacuum at  $0\text{--}5^\circ\text{C}$ . Water (40 mL) was added, the aqueous phase extracted with ethyl ether (3x15 mL) and the organic phase dried and concentrated. Compound **5** was separated from the reaction mixture after heating in decahydronaphthalene for 4 h at  $180^\circ\text{C}$ . Flash chromatography (eluent toluene/AcOEt 9:1) of the resulting reaction residue allows to isolate pure **3**, **4** and **5**, in sequence.

In experiment with pyridine, the base (0.66 g, 8.4 mmol) was added to FEP before **1**, and the reaction run for 6 h at  $20^\circ\text{C}$ . Then the solvent was evaporated under vacuum at  $0^\circ\text{C}$ , the residue taken up with 10% HCl

solution (40 mL) and diethyl ether (15 mL), the aqueous phase extracted with diethyl ether (3x15 mL) and organic phase dried and concentrated. In parallel experiments the reaction mixture was quantitatively analysed by HPLC by direct injection after dilution in methanol (1:10).

**c) Mn(OAc)<sub>3</sub>.** In a two-necked flask Mn(OAc)<sub>3</sub> (4.4 g) was added under N<sub>2</sub> to the solvent (43 mL) and the slurry was stirred and heated at 60-70 °C. Then a solution of **1** in the same solvent (40 mL, 0.2 M) was added. The reaction was run for 4 h under vigorous stirring. Then, the mixture was filtered and the resulting solution evaporated under vacuum (T ≤ 40 °C). The residue was taken up with CH<sub>2</sub>Cl<sub>2</sub> and the reaction products were separated by flash chromatography (eluent hexane/AcOEt 85:15).

**Tetraethyl 1,2-Bis-(3'-thienyl)ethane-1,1,2,2-tetracarboxylate (2):** mp 59-61°C (from cyclohexane); MS: 482 (M<sup>+</sup>, 38), 409 (100), 391 (15), 364 (20), 335 (7), 318 (10), 291 (31), 263 (24), 245 (249), 235 (17), 217 (43), 191 (38), 147 (14), 111 (43), 84 (40); <sup>1</sup>H NMR δ: 1.18 (12 H, t), 4.19 (8 H, q), 6.42 (2 H, d broad, J= 5.0 Hz), 6.8 (2 H, s broad), 6.98 (2 H, dd, J<sub>1</sub>= 5.0 and 1,2). Anal Calcd for C<sub>22</sub>H<sub>26</sub>O<sub>8</sub>S<sub>2</sub>: C 54.76, H 5.43, S 13.29; found: C 54.9, H 5.5, S 13.4.

**Diethyl 3-thienyl-[2-(3-diethoxycarbonylmethyl)thienyl]propandioate (3):** mp 52-53 °C (from pentane); MS: 482 (M<sup>+</sup>, 28), 409 (100), 364 (26), 291 (30), 263 (23), 245 (20), 217 (37), 191 (37), 111 (40); <sup>1</sup>H NMR δ: 1.10 (6 H, t), 1.22 (6 H, t), 4.6 (1H, s), 4.2 (8 H, q), 7.09 (1H, dd, J = 5,0 and 1.8 Hz), 7.15 (1H, d, J = 5,1 Hz), 7.23 (1H, dd, J = 5,0 and 3.5 Hz), 7.33 (1H, d, J = 5,1), 7.39 (1H, dd, J = 3,5 and 1.8 Hz). Anal Calcd for C<sub>22</sub>H<sub>26</sub>O<sub>8</sub>S<sub>2</sub>: C 54.76, H 5.43, S 13.29; found: C 54.6, H 5.6, S 13.2.

**Tetraethyl 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,4,8,8-tetracarboxylate (4):** mp 103-104 °C (from isopropyl ether /AcOEt); MS: 480 (M<sup>+</sup>, 13), 436 (10), 407 (39), 363 (42), 335 (52), 317 (31), 289 (100), 278 (23), 261 (37), 233 (27), 217 (16), 105 (16); <sup>1</sup>H NMR δ: 1.25 (12 H, t), 4.25 (8H, q), 7.28 (2 H, d, J= 5.0 Hz), 7.37 (2 H, d, J= 5.0 Hz); <sup>13</sup>C NMR δ: 13.89 (q), 59.49 (s), 62.58 (t), 125.95 (d), 127.33 (d), 132.03 (s), 133.57 (s), 168.25 (C=O). UV: λ<sub>max</sub> (CHCl<sub>3</sub>): 244 nm (ε = 11173). Anal Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>8</sub>S<sub>2</sub>: C 54.99, H 5.03, S 13.34; found: C, 55.1; H, 5.11; S, 13.2.

**Tetraethyl 4,5-dihydrobenzo[2,1-*b*:3,4-*b'*]dithiophene-4,4,5,5-tetracarboxylate (5):** mp 119-120 °C (from diethyl ether); MS: 480 (M<sup>+</sup>, 23), 363 (10), 290 (19), 289 (84), 262 (20), 261 (100), 217 (28), 189 (12), 177 (11); <sup>1</sup>H NMR δ: 1.15 (12 H, t), 4.13 (8 H, q), 7.09 (2 H, d, J = 5.0 Hz), 7.38 (2 H, d, J = 5.0 Hz). <sup>13</sup>C NMR δ: 13.63 (q), 62.02 (t), 63.5 (s), 122.11 (d), 127.83 (d), 131.28 (s), 132.08 (s), 168.07 (C=O). Anal Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>8</sub>S<sub>2</sub>: C 54.99, H 5.03, S 13.34; found: C 55.1, H 5.2, S 13.4.

**Oxidation of 1 by radical initiators.** A solution of **1** (1.60 g) in benzene or decahydronaphthalene (66 mL), made under N<sub>2</sub> and stirring, was heated at 70-110 °C and AIBN or dibenzoyl peroxide ([In]/[1] = 1 or 2) was added. After a time of 10 half-live of the initiator at the temperature chosen, the mixture was cooled and analysed by HPLC. No dimerization product was detected.

**Thermal rearrangement of 2.** A solution of **2** (1.00 g) in decahydronaphthalene (11 mL) was made under N<sub>2</sub> in a flash equipped with a rubber septum. The solution was heated in a thermostatic bath at the desired temperature and samples (0.1 mL) were withdrawn by syringe at regular intervals. The decay of **2** and formation of **3** was monitored by HPLC. Mass balance higher than 97% was observed until 90% conversion and first order kinetic was deduced from a plot of ln[**2**] vs. time. The mean of the results in two independent experiments for each temperature, along with the deduced kinetic parameters, are collected in Table 4.

**Oxidation of 1 by Mn(III) in the presence of styrene.** A stock solution of Mn(OAc)<sub>3</sub> (1.13 g) in acetic acid (50 mL) was made under N<sub>2</sub> and magnetic stirring at 60 °C. Then, styrene, warmed at 60 °C under N<sub>2</sub>, (in the amount reported in table 3) was added once and the reaction was run for 24 h. Then the mixture was cooled at 20 °C and worked-up as indicated before for the Mn(OAc)<sub>3</sub> reactions. The products distribution was determined by GC. In a parallel experiment on 10 time scale, the reaction products were isolated by column chromatography with hexane-AcOEt (9:1). **Diethyl 2-acetoxy-2-(3-thienyl)propanedioate (13)** bp 120-2 °C (0.1 mmHg), MS: 300 (M<sup>+</sup>, <1%), 258 (2), 227 (1), 212 (2), 187 (3), 186 (12), 185 (39), 112 (10), 111 (100), coincident with an authentic sample prepared by acetylation of the corresponding 2-hydroxy derivative. **2-Ethoxycarbonyl-2-(3-thienyl)-4-phenylbutyrolactone (14)**. (First eluted, **14a**): Oil, MS: 316 (M<sup>+</sup>, 11), 272 (50), 244 (15), 227 (100), 199 (38), 197 (26), 165 (15), 159 (28), 137 (23), 115 (34), 109 (82), 77 (23); <sup>1</sup>H NMR δ: 1.27 (3H, t, J = 7.5 Hz), 2.6 (1H, dd, J = 12.5 Hz and 10 Hz), 3.56 (1H, dd, J = 12.5 and 5 Hz), 4.3 (2H, q, J = 7.5 Hz), 5.55 (1H, dd, J = 10 Hz and 5 Hz), 7.2-7.6 (8H, m). Anal Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S: C 64.54, H 5.10, S 10.13; found: C 64.5, H 5.0, S 10.1. (Second eluted, **14b**): Oil, MS: 316 (M<sup>+</sup>, 6), 272 (61), 244 (12), 227 (100), 199 (45), 197 (16), 159 (38), 137 (20), 115 (30), 109 (71), 77 (25); <sup>1</sup>H NMR δ: 1.25 (3H, t, J = 7.5 Hz), 3.08 (1H, dd, J = 13 Hz and 7 Hz), 3.17 (1H, dd, J = 13 and 10 Hz), 4.18 (2H, q, J = 7.5 Hz), 5.37 (1H, dd, J = 7 and 10 Hz), 7.2-7.6 (8H, m). Anal Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S: C 64.54, H 5.10, S 10.13; found: C 64.4, H 5.2, S 10.2.

**Diethyl 4,8-benzo[1,2-b:-4,5-b']dithiophenedicarboxylate (15).** In a one-necked flask compound **4** (7.8 g) and DMF (78 mL) were mixed. The resulting solution was stirred and heated at 120 °C and, after 10 min, **4** was completely dissolved. A mixture of 2 % oxygen in nitrogen was fluxed in the flask (3 mL/min), LiI (1.1 g) was added and the solution heated to reflux for 22 h. Then, the solution was cooled to 60 °C and the solvent was evaporated. Water (20 mL) was added to the residue and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL). The organic layers were combined, dried and concentrated. Flash chromatography of the residue (5.2 g) (eluent hexane/AcOEt 9:1) allows to isolate **15** (4.5 g, 83 %). mp 172-173 °C (ethanol); MS m/e: 334 (M<sup>+</sup>, 100), 306 (17), 289 (16), 278 (28), 261 (24), 233 (20), 144 (10); <sup>1</sup>H NMR δ: 1.58 (6 H, t, J = 7.5 Hz), 4.63 (4 H, q, J = 7.5 Hz), 7.72 (2 H, d, J = 5 Hz), 8.3 (2 H, d, J = 5 Hz); <sup>13</sup>C NMR δ: 125.52 (s), 130.20 (d), 132.43 (d), 138.34

(s), 139.99 (s), 177.14 (C=O); UV:  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 366 nm ( $\epsilon$  = 10100), 225 (81.000); IR  $\nu_{\text{max}}$  cm<sup>-1</sup>: (KBr): 1685, 1220, 1135, 740. Anal Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: C 57.47, H 4.22, S 19.17; found: C 57.5, H 4.4, S 19.2.

**4,8-benzo[1,2-*b*:4,5-*b'*]dithiophenedicarboxylic acid (16). Method A.** In a one-necked flask a solution of **15** (1.22 g) in dioxane (15 mL) was stirred and heated at 80 °C for 10 min. A solution of KOH (0.62 g) in dioxane (5 mL) was added and the mixture refluxed for 2h. A light-yellow precipitate formed. The mixture was cooled, acidified with 10 % HCl until pH = 2. The yellow precipitate was stirred and heated at 85 °C for 2 h. After cooling, filtration and washing with water, **16** was obtained as light-yellow crystals (0.88 g, 87 %). mp 225-7; MS: 278 (M<sup>+</sup>, 100), 261 (27), 233 (28), 233 (28), 177 (14), 145 (16), 93 (13), 73 (91); <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$ : 7.72 (2 H, d, J = 4.7 Hz), 7.90 (2 H, d, J = 4.7 Hz); <sup>13</sup>C NMR (D<sub>2</sub>O, KOD)  $\delta$ : 125.52 (s), 130.0 (d), 132.3 (d), 138.4 (s), 139.99 (s), 177.14 (C=O); Anal Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C 51.79, H 2.17, S 23.04; found: C 51.9, H 2.4, S 22.9.

**Method B.** In a two-necked flask a solution of **4** (10 g) in dioxane (100 mL) was heated for 10 min at 80 °C, then KOH (1.66 g) was added. The reaction mixture was refluxed under magnetic stirring for 5 h. After 20 min a light-yellow precipitate was formed. The solution was cooled to 50 °C and 10 % HCl was added until pH = 2. The heterogeneous mixture was then heated at 100 °C for 1 h in oxygen atmosphere. After cooling, water (15 mL) was added and the mixture filtered. Compound **16** (4.5 g, 95 % purity by HPLC, 78 %) was obtained as yellow solid.

**Benzo[1,2-*b*:4,5-*b'*]dithiophene (17).** In a two-necked flask **16** (1 g) was added to quinoline (3.75 mL) and the mixture was heated at 70 °C for 15 min. Then, Cu(I) oxide (0.33 g) was added. The magnetically stirred mixture was heated at 210 °C for 4 h. After cooling, the reaction mixture was quenched with 20 % HCl (10 mL). The aqueous phase was extracted with diethyl ether (2x10 mL) and the organic phase dried and evaporated. The crude product was purified by flash chromatography with hexane-AcOEt (8:2). **17** (0.58 g, 85 %). mp 196-197 °C (lit<sup>17</sup> 197,5-198); MS m/e: 190 (M<sup>+</sup>, 100), 158 (6), 146 (8), 145 (18), 102 (5), 95 (10); <sup>1</sup>H NMR  $\delta$ : 7,38 (2H, d, J= 5 Hz), 7,5 (2 H, d, J= 5 Hz), 8,325 (2 H, s); <sup>13</sup>C NMR  $\delta$ : 117,19 (d), 123,33 (d), 127,56 (d), 137,53 (s), 137,95 (s); UV:  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 260 nm ( $\epsilon$  = 56849,51).

**4,5-benzo[1,2-*b*:3,4-*b'*]dithiophenedicarboxylic acid (21).** Prepared in 85% yield following the above reported method B from compound **5**. dp 211-213 °C. MS: 278 (M<sup>+</sup>, 31), 260 (100), 233 (11), 232 (31), 145 (35), 93 (19), 73 (30); <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$ : 7.81 2 H, d, J = 5.1 Hz), 7.98 (2 H, d, J = 5.1 Hz); Anal Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C 51.79, H 2.17, S 23.04; found: C 51.6, H 2.3, S 23.0. Decarboxylation of **21** by the procedure described for **17** allows to obtain 4,5-benzo[1,2-*b*:3,4-*b'*]dithiophene **22** in 73 % yield (mp 44°C, lit.<sup>16</sup> 44-45°C).

**4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene-4,4,8,8-tetracarboxylic acid (19):** Solid KOH (11.6 g, 20.7 mmol) was added to an homogeneous solution of **4** (10 g, 2.08 mmol) and dioxane (100 mL) and the mixture was vigorously stirred at 40°C for 2 h, then refluxed under nitrogen with magnetic stirring for 5 h. The solvent was distilled off, and the residue was taken up with water at 5 °C (50 mL) and 15 % HCl (50 mL). The precipitate was filtered, washed with water, acetone and dried under vacuum at 10°C for 24 h. The white solid (**19**) (6.8 g) decomposes on heating at 100 °C. <sup>1</sup>H NMR (D<sub>2</sub>O, KOH) δ: 7.28 (2 H, d, J= 5.0 Hz), 7.37 (2 H, d, J= 5.0 Hz), 11.2 (broad); <sup>13</sup>C NMR (D<sub>2</sub>O, KOH) δ: 59.5 (s), 126.1 (d), 128.2 (d), 131.2 (s), 133.6 (s), 175.5 (C=O). When the hydrolysis was carried out by the same procedure by using 5.2 g of KOH, the final solid (8.1 g) was dissolved in acetone (200 ml) at 30 °C, filtered and concentrated to 40 ml. Analytical data for the white solid obtained (4.1 g) are consistent with the structure **20** of the monoethyl ester of **19**. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: 7.28 (2 H, d, J= 5.0 Hz), 7.37 (2 H, d, J= 5.0 Hz), 11.2 (broad); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: 59.5 (s), 126.1 (d), 128.2 (d), 131.2 (s), 133.6 (s), 175.5 (C=O).

**Ethyl 4-benzo[1,2-b:4,5-b']dithiophenecarboxylic acid (18).** The acid **20** (1g) was dissolved in quinoline (8 mL), Cu<sub>2</sub>O (0.3 g) was added and the mixture heated at reflux for 5 h. The cold reaction mixture was slowly poured in 10 % HCl solution (25 ml) and diethyl ether under stirring. Normal work-up and flash chromatography of the residue allows to isolate **18** (0.33 g, 50 %). mp 123-4 °C (from cyclohexane); MS: 262 (M<sup>+</sup>, 97), 236 (10), 235 (14), 234 (100), 219 (7), 218 (11), 217 (74), 189 (75), 145 (72), 94 (15), 93 (12); <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: 1.52 (3 H, t, J= 5,5 Hz), 4,7 (2 H, q, J= 5,5 Hz), 7,52 (1 H, d, J= 5 Hz, **6**), 7,77 (1 H, d, J= 5Hz, **2**), 7,9 (1 H, d, J= 5,5 Hz, **7**), 8,3 (1 H, d, J= 5 Hz, **3**), 8,72 (1 H, s, **8**). Anal Calcd for C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>: C 59.52, H 3.84, S 24.44; found: C 59.4, H 4.0, S 24.3.

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