Light-Induced Synthesis of π-Extended Tetrathiafulvalenes Incorporating Ferrocenes: An Efficient Route for the Synthesis of Electron-Donor Materials

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Abstract: A new method for the synthesis of π-extended tetrathiafulvalenes was developed. The protocol is based on the exposure of 1,4-dithiafulvenes to sunlight or UV light at ambient temperature. In the resulting chalcogenofulvalenes the 1,3-dithiole ring systems are separated by conjugated spacers. Extended TTF analogues are obtained by insertion of linear π-conjugated spacers (C=C–C=C) of increasing dimensions between the two 1,4-dithiafulvenyl moieties.

Key words: Wittig–Horner reaction, 1,4-dithiafulvenes, ferrocene, oxidative dimerization, sunlight, π-extended tetrathiafulvalenes, organic conductors, electrochemical properties, charge-transfer complex

After the discovery that tetrathiafulvalene (TTF, **1a**) can act as a molecular conductor,[1] modifications of TTF involving the replacement of the four hydrogen atoms at positions 4,5 and 4′,5′ have been extensively studied (Figure 1).[2] With the finding of the metallic behavior of the TTF–TCNQ complex, synthetic approaches towards tetrathiafulvalenes and tetraselenafulvalenes gained significant attention and various electrically (super)conducting salts and charge-transfer (CT) complexes were prepared. Furthermore, the charge-transfer process from tetrathiafulvalene to tetracyanoquinodimethane (TCNQ) between adjacent stacks has been extensively investigated.[3]

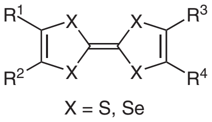
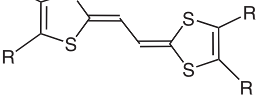


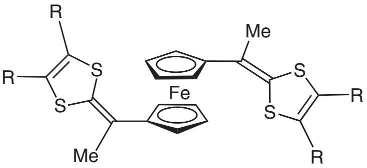
Figure 1 Tetrathiafulvalenes [for **1a** (TTF), X = S and R^1–R^4 = H] and tetraselenafulvalenes (**1b**, X = Se)

Various TTF derivatives can be prepared in a single step in low to moderate yields.[4] The replacement of the central ethylenic linkage (C=C) by larger conjugated spacers $(C=C–C=C)_n$ leads to extended TTFs such as ETTH (**2**) with enhanced intra- and interchain contacts (Figure 2), due to the lowering of their charge density and increased π-interactions.[5] Also from these extended derivatives, conducting salts have been prepared.[6] Studies of their properties revealed that the extended tetrathiafulvalenes are strong electron donors, which exhibit small on-site Coulomb repulsion owing to the extended π-conjugation.[7] Furthermore, vinylogous TTFs with bulky groups at the vinylic positions afforded conductors with uncommon multidimensional structures and, due to the Coulomb repulsion in the dicationic states as a result of the extended π-conjugation, stable dication salts with unusual crystal structures were obtained.[8]

Ueno and co-workers synthesized the first ferrocene-containing tetrathiafulvalene and its vinylogues **3**.[9] Their charge-transfer complexes with TCNQ and DDQ were also described. Since then a few more reports have appeared, which deal with the electrochemical properties and charge-transfer complexes of tetrathiafulvalenes bearing ferrocene moieties.[10]



2 (ETTH)



3 [R = H, Me, $(CH=CH)_2$]

Figure 2 π-Extended tetrathiafulvalenes

Here, we describe an environmentally benign approach towards the synthesis of new electron-donor tetrathiafulvalene vinylogues using 1,4-dithiafulvenes as building blocks.

Starting point for the synthesis of the tetrachalcogenofulvalene derivatives was a Wittig–Horner reaction with dimethyl 1,3-benzodithiol-2-ylphosphonate (**4**), which was prepared following the previously reported method.[11] After deprotonation of **4** with butyllithium at –78 °C in anhydrous tetrahydrofuran under argon, the resulting anion was allowed to react with aldehydes **5a**–**e** to give the corresponding 1,4-dithiafulvenes **6a**–**e** (Scheme 1).[12]

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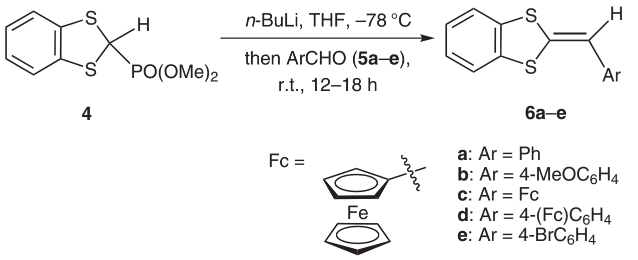


Scheme 1 Synthesis of thiafulvenes **6a–e**

Attempts to synthesize extended TTFs **7** from **6a–e** using either electrochemical oxidation or treatment with hydrogen chloride and/or hydrogen bromide in an organic solvent followed by reduction with zinc to dimerize the intermediately formed radical cation of **6** led to low yields of **7** and decomposition of the 1,4-dithiafulvenes.[11d] Unexpected nitrofulvene **8** was obtained (as yellow crystals) in considerable amounts when the oxidation was tried with a mixture of acetic acid and nitric acid (Figure 3). The molecular ion peak in the mass spectra of **8** ([M – 1], 286) confirmed its structures. Refluxing **6a** in acetic acid in the presence of concentrated sulfuric acid gave no product and only the starting material was recovered.

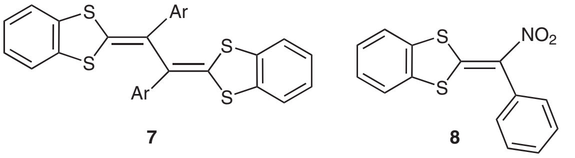
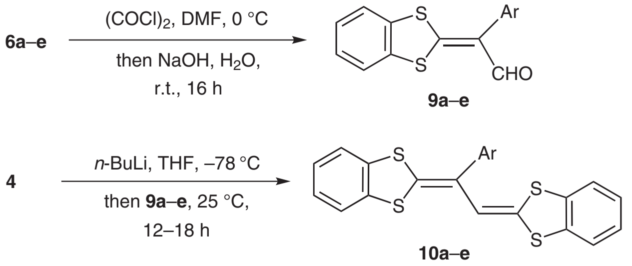


Figure 3 π-Extended tetrathiafulvalenes and nitrofulvene **8**

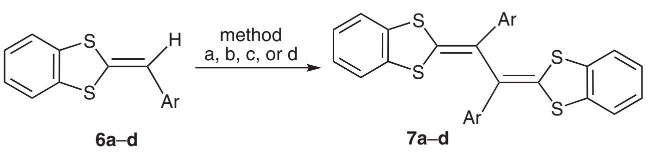
Consequently, the strategy for the preparation of extended tetrathiafulvalenes had to be changed. Formylation of dithiafulvenes **6a–e** according to the reported procedure[13] using oxalyl chloride in anhydrous *N*,*N*-dimethylformamide at 0 °C and subsequent alkaline hydrolysis afforded the corresponding products **9a–e** in high yields. Wittig–Horner-type reactions of **9a–e** with phosphonate ester **4** gave the extended tetrathiafulvalene **10a–e** in excellent yields (Scheme 2).



Scheme 2 Synthesis of extended tetrathiafulvalenes **10a–e**

Upon standing a darkening of the red color of 1,4-dithiafulvene **6c** was noticed and ^1H NMR spectroscopy revealed that the ethylenic CH proton disappeared with time. To our delight, mass spectrometry and ^{13}C NMR spectroscopy showed that **6c** had unexpectedly dimerized to form the extended tetrathiafulvalene **7c**. Encouraged by this result the behavior of the other 1,4-dithiafulvenes was studied (Table 1). As noticed also by Bryce and co-workers,[12] only the ferrocenyl-substituted substrates underwent rapid dimerization, and thus, **7c** (50%) and **7d** (23%) were obtained in conversions of **6c** and **6d**, respectively. Oxidation of **6d** with iodine in dichloromethane[13] followed by the reduction of the resulting dication with sodium thiosulfate ($Na_2S_2O_4$) afforded **7d** in 60% yield. The aryl-substituted dithiafulvenes **6a**, **6b**, and **6e** were more stable. Thus, neither stirring them in chloroform or dichloromethane solutions in a reactor under UV light at room temperature for 4–12 hours nor treating them with hydrogen chloride (as oxidizing agent) in anhydrous diethyl ether[12a] or using the iodine/dichloromethane method[13] led to significant amounts of the corresponding dimers. At best, only traces of **7b** could be identified by mass spectrometry {$[M]^+$ 542 (12%)} upon boiling 1,4-dithiafulvene **6b** in an iodine/dichloromethane mixture.

Table 1 Syntheses of π-Extended Tetrathiafulvalenes **7** by Induced Dimerizations



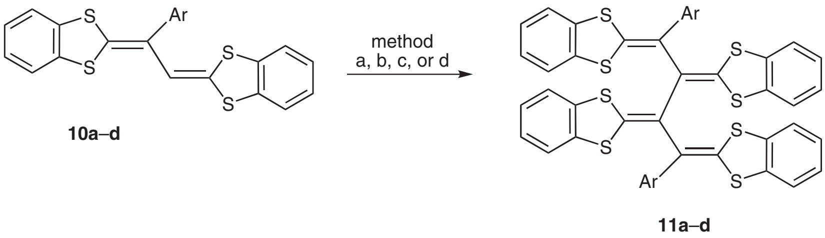
Product	Ar[a]	Yield (%)	Method[b]
7a	Ph	–	a–d
7b	4-MeOC$_6$H$_4$	trace	a, c
7c	Fc	50	a
7d	4-(Fc)C$_6$H$_4$	23/60	a/c
7e	4-BrC$_6$H$_4$	–	a, c

[a] Fc = ferrocenyl.
[b] Method a: sunlight; b: UV light; c: I_2, CH_2Cl_2; d: HCl, Et_2O.

Following the same strategy established for the dimerizations of 1,4-dithiafulvenes **6a–e**, the conversions of tetrathiafulvalenes **10a–e** were attempted. Those compounds possessed highly active CH protons on the conjugated system [>C=C(Ar)–CH=C<], and their dimer formation was expected to lead to chalcogenofulvalenes **11a–e** (Table 2). Confirming this hypothesis, dimers **11b–d** were formed upon exposure to sunlight albeit the yields remained moderate ranging from 37% to 45%. Use of UV light led to substrate decomposition and from the complex product mixtures none of the targeted compounds could be isolated. Oxidative dimerization of **10d** using iodine/dichloromethane gave **11d** in 28% yield.

In conclusion, we prepared various ferrocene-containing π-extended tetrathiafulvalenes by dimerization of thiafulvenes using a simple protocol involving sunlight. The electrochemical properties and conductivity measure-

Table 2 Syntheses of π-Extended Tetrathiafulvalenes **11** by Induced Dimerizations



Product	Ar[a]	Yield (%)	Method[b]
11a	Ph	trace	a–d
11b	4-$MeOC_6H_4$	39	a
11c	Fc	37	a
11d	4-(Fc)C_6H_4	45/0/28/0	a/b/c/d
11e	4-BrC_6H_4	trace	a, c

[a] Fc = ferrocenyl.

[b] Method a: sunlight; b: UV light; c: I_2, CH_2Cl_2; d: HCl, Et_2O.

ments are now being investigated and those results will be published in due course.

All Wittig–Horner reactions were carried out under argon using standard Schlenk techniques. THF was distilled from Na/benzophenone ketyl radical. Hexane, CH_2Cl_2, and $CHCl_3$ for column chromatography were distilled before use. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer (300 MHz and 75 MHz respectively) and on a Varian Inova 400 spectrometer (400 MHz and 100 MHz respectively); TMS was used as an internal standard. Phosphonate ester **4** was prepared according to the method previously reported in literature.[11] Except 4-(ferrocenyl)benzaldehyde, which was synthesized following a previously reported method,[14] all aldehydes were commercially available and used without further purification. The analytical data for compounds **6a** and **6b** were in agreement with those previously reported.[11]

1,4-Dithiafulvenes 6a–e; General Procedure

A sample of the 1,3-benzdithiol-2-ylphosphonate **4** (0.786 g, 3 mmol) was stirred in anhyd THF (50 mL) under a stream of argon at –78 °C. A soln 1.6 M of BuLi (2.3 mL) was added portionwise and the mixture was stirred for 15 min. A soln of the aldehyde **5** (3 mmol) in anhyd THF (50 mL) was added portionwise over 15 min. The temperature of the reaction was raised to r.t., and the mixture was stirred overnight. Then the solvent was removed under vacuum and the residue washed with H_2O and extracted with $CHCl_3$. The extracts were dried ($MgSO_4$) and the crude product was chromatographed (silica gel, $CHCl_3$–hexane, 1:2) to give the corresponding product **6a**–**e** in high yields. The analytical data for compounds **6a** and **6b** were in satisfactory agreement with those reported in the literature.[11d]

2-(Ferrocenylmethylene)-1,3-benzodithiole (6c)

Orange red crystals; yield: 71%; mp 154–155 °C.

IR (KBr): 3091 (m), 2994 (w), 1589 (s), 1448 (s), 1430 (s), 1407 (s), 1292 (m), 1259 (m), 1124 (m), 1101 (m), 1049 (m), 1029 (m), 998 (s), 809 (s), 744 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.24 (m, 1 H_{arom}), 7.17 (m, 1 H_{arom}), 7.08 (m, 2 H_{arom}), 6.16 (s, 1 H, CH=C), 4.42 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.23 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.17 (s, 5 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 137.6, 136.2, 128.3, 126.4, 126.1, 122.3, 121.6 (C_{arom}, CH_{arom}, thiafulvalene-*C*=CH), 112.7 (thiafulvalene-C=*C*H), 83.4 ($C_{ferrocene}$), 69.8, 69.0, 68.1 ($CH_{ferrocene}$).

MS (FAB): *m*/*z* (%) = 350 ([M]$^+$, 90).

Anal. Calcd for $C_{18}H_{14}FeS_2$ (350.2756): C, 61.72; H, 4.03; S, 18.31. Found: C, 61.51; H, 4.22; S, 18.61.

2-[4-(Ferrocenyl)benzylidene]-1,3-benzodithiole (6d)

Orange crystals; yield: 85%; mp (dec).

IR (KBr): 3093 (m), 3050 (w), 2987 (w), 1604 (m), 1575 (s), 1546 (s), 1521 (s), 1448 (s), 1284 (s), 1083 (s), 1033 (s), 1002 (m), 935 (s), 887 (s), 844 (s), 819 (s), 744 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.48 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.26 (d, *J* = 8.5 Hz, 4 H_{arom}), 7.12–7.10 (m, 2 H_{arom}), 6.54 (s, 1 H, CH=C), 4.65 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.32 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.04 (s, 5 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 137.1, 136.5, 134.8, 134.2, 131.3, 127.0, 126.1, 126.0, 125.6, 121.7, 120.9, 114.7, 114.7 (C_{arom}, CH_{arom}, thiafulvalene-*C*=CH), 85.0 ($C_{ferrocene}$), 69.6, 69.0, 66.4 ($CH_{ferrocene}$).

MS (EI): *m*/*z* (%) = 425 ([M – 1], 100), 426 ([M]$^+$, 41).

Anal. Calcd for $C_{24}H_{18}FeS_2$ (426.2756): C, 67.61; H, 4.26. Found: C, 67.49; H, 4.15.

2-(4-Bromobenzylidene)-1,3-benzodithiole (6e)

Colorless crystals (EtOH); yield: 70%; mp 189.5–190 °C.

IR (KBr): 3050 (m), 2982 (w), 2918 (w), 1643 (s), 1549 (s), 1478 (s), 1431 (s), 1387 (s), 1332 (w), 1260 (w), 1187 (m), 1117 (s), 1068 (m), 931 (m), 831 (s), 738 (s), 670 cm^{-1} (m).

^1H NMR ($CDCl_3$): δ = 7.47 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.27–7.18 (m, 4 H_{arom}), 7.13–7.11 (m, 2 H_{arom}), 6.48 (s, 1 H, CH=C).

^{13}C NMR ($CDCl_3$): δ = 135.4, 131.5, 128.4, 126.1, 125.7, 121.7, 121.0, 119.4, 113.2 (C_{arom}, CH_{arom}, thiafulvalene-*C*=CH).

MS (EI): *m*/*z* (%) = 321 ([M]$^+$, 100).

Anal. Calcd for $C_{14}H_9BrS_2$ (321.2553): C, 52.34; H, 2.82. Found: C, 52.06; H, 2.85.

2-[Nitro(phenyl)methylene]-1,3-benzodithiole (8)

To a sample of dithiafulvene **6a** (60 mg, 0.25 mmol) in stirred hot AcOH (10 mL), concd HNO_3 (32 mg, 0.5 mmol) was added, and the mixture kept at ca. 100 °C for 5–10 min. The color turned to orange red and the mixture was stirred for an additional 10 min at r.t. and monitored (TLC). After 10 min no starting material was left in the mixture. H_2O (25 mL) was added, and the yellow precipitate thus formed was collected by filtration and chromatographed (CH_2Cl_2) to give the product as yellow crystals; yield: 35%.

^{1}H NMR ($CDCl_3$): δ = 7.68–7.65 (m, 1 H_{arom}), 7.58–7.50 (m, 4 H_{arom}), 7.45–7.30 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 130.4 (thiafulvalene, >*C*=C), 130.3, 129.6 (C_{arom}), 128.8, 127.2, 127.1, 123.1 (CH_{arom}), 121.9 (>C=*C*NO_2).

MS (EI): *m*/*z* (%) = 286 ([M – 1], 87), 288 ([M + 1], 14), 240 (M – NO_2], 100).

Anal. Calcd for $C_{14}H_9NO_2S_2$ (287.3568): C, 58.52; H, 3.16; N, 4.87. Found: C, 59.06; H, 3.67, N; 4.02.

2-Aryl-2-(1,3-benzodithiol-2-ylidene)acetaldehydes 9a–e; General Procedure

To anhyd DMF (25 mL) under stream of argon at 0 °C was added dropwise oxalyl chloride (0.3 mL, 3.45 mmol) and the mixture stirred for 15 min. After this time, **6** (2.28 mmol) was added and the mixture warmed to 20 °C and stirred overnight. The mixture was quenched with aq 1 M NaOH (75 mL), precipitating a deep yellow to red solid. This product was collected by filtration and washed with H_2O (50 mL). The solid product was dissolved in CH_2Cl_2, washed with H_2O; the organic phase was separated, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, CH_2Cl_2) to afford products **9a**–**e**.

2-(1,3-Benzodithiol-2-ylidene)-2-phenylacetaldehyde (9a)

Yellow crystals (EtOH); yield: 76%; mp 97–98 °C.

IR (KBr): 3058 (s), 2928 (s), 2830 (s), 1695 (s), 1627 (s), 1558 (s), 1499 (s), 1459 (s), 1424 (s), 1382 (s), 1251 (s), 1096 (s), 926 (m), 854 (m), 745 (s), 701 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ = 9.45 (s, 1 H, CHO), 7.61–7.60 (m, 1 H_{arom}), 7.58–7.56 (m, 1 H_{arom}), 7.52–7.38 (m, 5 H_{arom}), 7.33–7.24 (m, 2 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 184.7 (CHO), 159.3, 138.3, 137.4 (*C*=CS_2), 132.4, 129.3, 128.8, 128.4, 126.6, 126.5, 122.9, 122.8, 121.6 (C_{arom}, CH).

MS (EI): *m*/*z* (%) = 269 ([M – 1], 100), 271 ([M + 1], 23).

Anal. Calcd for $C_{15}H_{10}OS_2$ (270.3693): C, 66.63; H, 3.73. Found: C, 66.43; H, 4.09.

2-(1,3-Benzodithiol-2-ylidene)-2-(4-methoxyphenyl)acetaldehyde (9b)

Yellow crystals; yield: 91%; mp 123.5–124.5 °C.

IR (KBr): 3093 (m), 2848 (m), 1635 (s), 1562 (s), 1492 (s), 1452 (s), 1427 (s), 1376 (s), 1265 (s), 1114 (s), 1047 (s), 1002 (s), 831 (s), 802 (s), 736 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ = 9.43 (s, 1 H, CHO), 7.58 (dd, *J* = 3, 8 Hz, 1 H_{arom}), 7.43–7.41 (m, 1 H_{arom}), 7.37–7.34 (m, 2 H_{arom}), 7.32–7.27 (m, 2 H_{arom}), 7.03–7.01 (m, 2 H_{arom}), 3.86 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 184.9 (CHO), 159.6, 158.9, 136.4, 132.4, 130.2 (C_{arom}, *C*=CS_2), 129.7, 126.6, 126.5, 122.8, 122.6, 121.6, 114.7 (C_{arom}), 55.4 (OCH_3).

MS: *m*/*z* (%) = 300 (M^+, 100).

Anal. Calcd for $C_{16}H_{12}O_2S_2$ (300.3953): C, 63.97; H, 4.03. Found: C, 63.38; H, 4.12.

2-(1,3-Benzodithiol-2-ylidene)-2-(ferrocenyl)acetaldehyde (9c)

Red crystals; yield: 71%; mp 147–148 °C.

IR (KBr): 3094 (m), 3010 (s), 2920 (s), 2847 (m), 1632 (s), 1493 (s), 1426 (s), 1378 (s), 1272 (s), 1213 (s), 1164 (w), 1112 (s), 1048 (s), 999 (m), 931 (m), 824 (s), 752 (s), 665 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ = 9.96 (s, 1 H, CHO), 7.58–7.57 (m, 1 H_{arom}), 7.51–7.49 (m, 1 H_{arom}), 7.31–7.28 (m, 2 H_{arom}), 4.55 (t, *J* = 1.5 Hz, 2 $H_{ferrocene}$), 4.36 (t, *J* = 1.5 Hz, 2 $H_{ferrocene}$), 4.21 (s, 5 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 186.3 (CHO), 154.8, 138.5 (*C*=CS_2), 132.9, 126.5, 126.4, 122.6, 121.6, 118.0 (C_{arom}, CH), 84.2 ($C_{ferrocene}$), 69.3, 68.3, 67.6 ($CH_{ferrocene}$).

MS (DIP): *m*/*z* (%) = 378 ([M]$^+$, 100).

Anal. Calcd for $C_{19}H_{14}FeOS_2$ (378.2889): C, 60.33; H, 3.73. Found: C, 60.44; H, 3.89.

2-(1,3-Benzodithiol-2-ylidene)-2-[4-(ferrocenyl)phenyl]acetaldehyde (9d)

Red crystals; yield: 51%; mp 188.5–189 °C.

IR (KBr): 3057 (w), 2925 (m), 2815 (m), 1526 (s), 1458 (s), 1382 (s), 1264 (s), 1101 (s), 937 (m), 819 (s), 738 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ = 9.5 (d, *J* = 3 Hz, 1 H, CHO), 7.61–7.60 (dd, *J* = 3, 5.5 Hz, 1 H_{arom}), 7.55–7.54 (d, *J* = 7.5 Hz, 2 H_{arom}), 7.46–7.45 (d, *J* = 7.5 Hz, 1 H_{arom}), 7.36–7.25 (m, 4 H_{arom}), 4.75 (s, 2 $H_{ferrocene}$), 4.42 (s, 2 $H_{ferrocene}$), 4.14 (s, 5 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 184.8 (CHO), 158.9, 139.7 (*C*=CS_2), 138.4, 134.9, 132.5 (C_{arom}), 128.7, 126.9, 126.7, 126.5, 122.8, 122.8, 121.6 (CH_{arom}), 78.8 ($C_{ferrocene}$), 70.3, 69.9, 67.0 ($CH_{ferrocene}$).

MS (EI): *m*/*z* (%) = 454 ([M]$^+$, 100).

Anal. Calcd for $C_{25}H_{18}FeOS_2$ (454.3848): C, 66.08; H, 3.99. Found: C, 65.23; H, 4.01.

2-(1,3-Benzodithiol-2-ylidene)-2-(4-bromophenyl)acetaldehyde (9e)

Dark yellow crystals; yield: 97%; mp 173–173.5 °C.

IR (KBr): 3055 (m), 2920 (m), 2808 (s), 1694 (s), 1638 (s), 1556 (s), 1495 (s), 1438 (s), 1380 (s), 1268 (s), 1176 (m), 1074 (s), 1008 (m), 934 (m), 869 (s), 816 (s), 741 (s), 670 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ = 9.42 (s, 1 H, CHO), 7.65–7.60 (m, 3 H_{arom}), 7.47–7.44 (m, 1 H_{arom}), 7.36–7.27 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 184.1 (CO), 138.2, 136.2 (*C*=CS_2), 132.5, 130.5, 126.8 (C_{arom}), 126.7, 122.9, 122.4, 121.7.

MS (EI): *m*/*z* (%) = 349 ([M]$^+$, 100).

Anal. Calcd for $C_{15}H_9BrOS_2$ (349.2654): C, 51.58; H, 2.60. Found: C, 51.36; H, 2.70.

π-Extended Tetrathiafulvalenes 10a–e; General Procedure

To a stirred soln of the Wittig–Horner reagent **4** (1.0 mmol) in anhyd THF (50 mL) under argon atmosphere 1.6 M BuLi in hexane was added at –78 °C and the reaction allowed to stir at this temperature for 30 min. A soln of aldehyde **9** (1.0 mmol) in anhyd THF was then added dropwise and the reaction allowed to warm to 20 °C and stirred overnight. The solvent was evaporated under vacuum and the residue was washed with H_2O, extracted with CH_2Cl_2, and the organic phase was separated, washed with H_2O, dried ($MgSO_4$), and evaporated. The solid residue was chromatographed (silica gel, CH_2Cl_2–hexane, 1:3) to give the targeted π-extended tetrathiafulvalenes **10a**–**e**.

2,2′-(1-Phenylethane-1,2-diylidene)bis(1,3-benzodithiole) (10a)

Yellow crystals; yield: 68%; mp 185.5–186 °C.

IR (KBr): 3104 (m), 3051 (w), 2961 (w), 2924 (m), 2842 (w), 1641 (s), 1558 (s), 1505 (s), 1432 (s), 1383 (s), 1320 (s), 1253 (s), 1154 (s), 1112 (s), 1062 (s), 926 (s), 807 (s), 739 (s), 691 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.47–7.35 (m, 4 H_{arom}), 7.23 (m, 1 H_{arom}), 7.22–7.19 (m, 4 H_{arom}), 7.13–6.89 (m, 4 H_{arom}), 6.21 (s, 1 H, CH=C).

^{13}C NMR ($CDCl_3$): δ = 137.6, 137.6 (C2, C2′, *C*=CS_2), 136.4, 136.0, 134.6, 132.7, 131.3, 125.3 (C_{arom}, *C*=CH), 129.9, 129.1, 128.3, 125.7, 125.5, 124.7, 121.5, 121.4, 121.4, 120.8 (CH_{arom}, *C*H=C), 112.5 (CH).

MS (EI): *m*/*z* (%) = 406 ($[M]^+$, 100).

Anal. Calcd for $C_{22}H_{14}S_4$ (406.6066): C, 64.99; H, 3.47. Found: C, 64.64; H, 3.52.

2,2′-[1-(4-Methoxyphenyl)ethane-1,2-diylidene]bis(1,3-benzodithiole) (10b)

Yellow crystals; yield: 89%; mp 187–187.5 °C.

IR (KBr): 3047 (m), 2947 (m), 2828 (m), 1603 (s), 1565 (s), 1513 (s), 1440 (s), 1383 (s), 1320 (s), 1293 (s), 1246 (s), 1171 (s), 1115 (s), 1027 (s), 927 (s), 828 (s), 739 (s), 674 (s), 606 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.33–7.23 (m, 4 H_{arom}), 7.23–7.06 (m, 4 H_{arom}), 7.05–6.96 (m, 4 H_{arom}), 6.23 (s, 1 H, CH=C), 3.90 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 159.65 (C_{arom}–O), 137.9, 136.6, 136.3, 134.7, 131.5, 125.9, 125.7 (C2, C2′, *C*=CS_2, C_{arom}), 125.6, 125.5, 121.6, 121.5, 121.0, 114.6 (CH_{arom}, *C*H=C), 55.5 (OCH_3).

MS (EI): *m*/*z* (%) = 406 (M^+, 100).

Anal. Calcd for $C_{23}H_{16}OS_4$ (436.6325): C, 63.27; H, 3.69. Found: C, 63.20; H, 3.73.

2,2′-[1-(Ferrocenyl)ethane-1,2-diylidene]bis(1,3-benzodithiole) (10c)

Red crystals; yield: 61%; mp 94–95 °C.

IR (KBr): 3056 (s), 2923 (s), 2851 (m), 1642 (s), 1539 (s), 1441 (s), 1383 (s), 1262 (s), 1187 (m), 116 (s), 1031 (s), 997 (s), 814 (s), 738 (s), 675 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.30–7.28 (m, 1 H_{arom}), 7.24–7.20 (m, 2 H_{arom}), 7.15–7.13 (m, 1 H_{arom}), 7.10–7.03 (m, 4 H_{arom}), 6.18 (s, 1 H, CH=C), 4.56 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.27 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.23 (s, 5 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 137.2, 136.8, 136.2, 136.3, 135.5, 128.5, 125.5 (C2, C2′, *C*=CS_2, C_{arom}), 125.5, 125.5, 125.3, 121.7, 121.5, 121.3, 121.2, 119.5, 114.7 (CH_{arom}, *C*H=C), 83.8 ($C_{ferrocene}$), 69.2, 68.3, 67.4 ($CH_{ferrocene}$).

MS (EI): *m*/*z* (%) = 513 ([M – 1], 100), 514 ($[M]^+$, 49).

Anal. Calcd for $C_{26}H_{18}FeS_4$ (514.5261): C, 60.69; H, 3.53. Found: C, 60.46; H, 3.70.

2,2′-{1-[4-(Ferrocenyl)phenyl]ethane-1,2-diylidene}bis(1,3-benzodithiole) (10d)

Orange crystals; yield: 96%; mp (dec).

IR (KBr): 3052 (s), 2926 (m), 2859 (m), 1633 (s), 1566 (s), 1522 (s), 1441 (s), 1383 (s), 1278 (s), 1159 (s), 1113 (s), 1060 (s), 1007 (s), 925 (s), 881 (m), 815 (s), 739 (s), 676 (m), 608 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.57–7.54 (m, 2 H_{arom}), 7.30–7.24 (m, 4 H_{arom}), 7.15–7.10 (m, 4 H_{arom}), 7.09–6.89 (m, 2 H_{arom}), 6.25 (s, 1 H, CH=C), 4.75 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.37 (t, *J* = 2 Hz, 2 $H_{ferrocene}$), 4.04 (s, 5 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 139.5, 137.7, 136.6, 136.1, 134.8, 134.6, 132.5, 130.5, 130.1 (C2, C2′, *C*=CS_2, C_{arom}), 126.3, 125.7, 125.5, 125.4, 124.7, 122.8, 121.5, 121.4, 121.3, 120.8, 112.5 (CH_{arom}, *C*H=C), 84.1 ($C_{ferrocene}$), 70.0, 69.4, 66.4 ($CH_{ferrocene}$).

MS (EI): *m*/*z* (%) = 590 ($[M]^+$, 100).

Anal. Calcd for $C_{32}H_{22}FeS_4$ (590.6221): C, 65.07; H, 3.75. Found: C, 64.97; H, 3.96.

2,2′-[1-(4-Bromophenyl)ethane-1,2-diylidene]bis(1,3-benzodithiole) (10e)

Yellow crystals; yield: 66%; mp 206.5–207.5 °C.

IR (KBr): 3058 (s), 2928 (s), 2804 (m), 1652 (s), 1557 (s), 1507 (s), 1472 (s), 1433 (s), 1387 (s), 1258 (m), 1161 (m), 1116 (s), 1063 (s), 1009 (s), 927 (s), 819 (s), 740 (s), 675 (m), 603 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 7.59–7.55 (m, 2 H_{arom}), 7.29–7.21 (m, 3 H_{arom}), 7.16–6.97 (m, 7 H_{arom}), 6.17 (s, 1 H, CH=C).

^{13}C NMR ($CDCl_3$): δ = 136.5, 136.2, 134.6, 133.3 (C2, C2′, *C*=CS_2, C_{arom}), 132.3, 131.6 (CH_{arom}), 127.7, 125.9, 125.7, 125.6, 125.4, 122.3, 121.6, 120.9, 112.1 (CH_{arom}, *C*H=C).

MS (EI): *m*/*z* (%) = 485 ($[M]^+$, 100).

Anal. Calcd for $C_{22}H_{13}BrS_4$ (485.5026): C, 54.43; H, 2.70. Found: C, 54.14; H, 2.76%

1,2-Diaryl-1,2-bis(1,3-benzodithiol-2-ylidene)ethanes 7c,d and 2,2′,2″,2‴-(1,4-diarylbutane-1,2,3,4-tetraylidene)tetrakis(1,3-benzodithioles) 11b–d; General Procedures

Method a: A sample of the dithiafulvene **6** (0.1 mmol) in $CHCl_3$ (20 mL) was stirred at r.t. under sunlight for 3–18 h. The soln was concentrated under vacuum and the residue was chromatographed (silica gel, hexane–CH_2Cl_2) to give the corresponding π-extended tetrathiafulvalenes (Tables 1 and 2).

Method b: A sample of the dithiafulvene **6** or **10** (0.1 mmol) in CH_2Cl_2 (20 mL) was stirred in a UV reactor at r.t. under UV irradiation for 3–18 h. The soln was concentrated under vacuum and the residue was chromatographed (silica gel, hexane–CH_2Cl_2) to afford the corresponding π-extended tetrathiafulvalenes (Tables 1 and 2).

Method c: To a soln of the dithiafulvene **6a**,**b**,**d**,**e**, **10a**,**d**,**e** (100 mg) in CH_2Cl_2 (20 mL) under a stream of argon, I_2 (3 mmol) was added and the mixture was heated to reflux for 8 h. Then, excess $Na_2S_2O_4$ (0.5 g) was added. The mixture was refluxed overnight and allowed to reach r.t. After filtration of the suspension, the filtrate was washed with H_2O (2 × 50 mL) and dried ($MgSO_4$); the solvent was removed under vacuum and the extended TTFs **7b**,**d** and **11a**,**d**,**e** were purified by column chromatography (silica gel, hexane–CH_2Cl_2).

Method d: To a stirred soln of the dithiafulvene (0.10 mmol) in anhyd Et_2O (25 mL) under argon at r.t. was added anhyd HCl (0.1 mL in anhyd Et_2O) and the mixture was stirred for 24 h. The solvent was evaporated and the residue chromatographed (silica gel, hexane–CH_2Cl_2) to afford the corresponding chalcogenofulvalenes **7** and **11** (Tables 1 and 2).

1,2-Bis(1,3-benzodithiol-2-ylidene)-1,2-bis(ferrocenyl)ethane (7c)

Dark red crystals; yield: 50% (method a); mp (dec).

IR (KBr): 3055 (w), 2968 (w), 2814 (w), 1636 (s), 1534 (s), 1440 (s), 1383 (s), 1253 (s), 1159 (m), 1108 (s), 1043 (m), 999 (m), 924 (s), 821 (s), 734 (s), 676 cm^{-1} (m).

^1H NMR ($CDCl_3$): δ = 7.34 (m, 2 H_{arom}), 7.22–7.20 (m, 2 H_{arom}), 7.13–7.09 (m, 4 H_{arom}), 4.55 (m, 2 $H_{ferrocene}$), 4.45 (m, 2 $H_{ferrocene}$), 4.28 (s, 10 $H_{ferrocene}$), 4.21 (m, 4 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 137.5, 136.4, 130.7, 123.6 (C1, C2, 2 *C*=CS_2, C_{arom}), 125.5, 125.1, 122.5, 121.2 (CH_{arom}), 83.9 ($C_{ferrocene}$), 69.4, 68.0, 67.9, 67.7, 65.9 ($CH_{ferrocene}$).

MS (EI): *m*/*z* (%) = 698 ($[M]^+$, 100).

MS (FAB): *m*/*z* (%) = 698 ($[M]^+$, 100).

Anal. Calcd for $C_{36}H_{26}Fe_2S_4$ (698.5314): C, 61.90; H, 3.75. Found: C, 62.60; H, 4.60%

1,2-Bis(1,3-benzodithiol-2-ylidene)-1,2-bis[4-(ferrocenyl)phenyl)]ethane (7d)

Chromatography (silica gel, hexane–$CHCl_3$, 1:1) gave orange crystals; yield: 23% (method a), 60% (method c).

IR ($CHCl_3$): 3091 (m), 3013 (m), 2924 (m), 2854 (m), 1603 (w), 1571 (m), 1528 (s), 1441 (s), 1383 (m), 1281w (s), 1215 (s), 1107 (s), 1073 (s), 927 (w), 887 (w), 823 (s), 756 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ = 7.49 (m, 8 H_{arom}), 7.24–7.17 (m, 4 H_{arom}), 7.12–7.06 (m, 4 H_{arom}), 4.61 (s, 4 $H_{ferrocene}$), 4.30 (s, 4 $H_{ferrocene}$), 4.05 (s, 10 $H_{ferrocene}$).

^{13}C NMR ($CDCl_3$): δ = 139.6, 138.1, 136.7, 136.3, 126.3 (C1, C2, 2 *C*=CS_2, C_{arom}), 128.3, 126.9, 125.7, 125.5, 121.6, 121.2 (CH_{arom}), 85.3 ($C_{ferrocene}$), 69.7, 69.0, 66.5 ($CH_{ferrocene}$).

MS (FAB): *m*/*z* (%) = 850 ([M]$^+$, 8).

Anal. Calcd for $C_{48}H_{34}Fe_2S_4$ (850.7336): C, 67.77; H, 4.03. Found: C, 66.98; H, 4.12.

2,2′,2″,2‴-[1,4-Bis(4-methoxyphenyl)butane-1,2,3,4-tetraylidene]tetrakis(1,3-benzodithiole) (11b)

Chromatography (silica gel, hexane–CH_2Cl_2, 1:1); yellow crystals; yield: 40% (method a); mp >300 °C.

IR (KBr): 3051 (m), 2923 (m), 2838 (w), 1602 (s), 1566 (m), 1506 (s), 1453 (s), 1385 (s), 1297 (m), 1245 (s), 1175 (s), 1118, 1026 (s), 908 (s), 826 (s), 734 (s), 676 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ = 7.35 (m, 4 H_{arom}), 7.25 (m, 8 H_{arom}), 7.10 (m, 8 H_{arom}), 6.78 (m, 4 H_{arom}), 3.79 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 137.7, 128.7, 125.8, 125.7, 121.8, 121.3, 120.8, 114.4, 114.1 (C1, C2, 2 *C*=CS_2, C_{arom}, CH_{arom}), 55.4 (OCH_3).

MS (EI): *m*/*z* (%) = 870 ([M]$^+$, dec.).

MS (FAB): *m*/*z* (%) = 870 ([M]$^+$, 12).

Anal. Calcd for $C_{46}H_{30}O_2S_8$ (871.2492): C, 63.41; H, 3.47. Found: C, 63.22; H, 3.99.

2,2′,2″,2‴-[1,4-Bis(ferrocenyl)butane-1,2,3,4-tetraylidene]tetrakis(1,3-benzodithiole) (11c)

Chromatography (silica gel, hexane–$CHCl_3$, 2:1); dark red crystals; yield: 37% (method a); mp (dec).

IR ($CHCl_3$): 3021 (m), 2922 (m), 2854 (w), 1542 (m), 1437 (s), 1384 (s), 1262 (w), 1215 (s), 1091 (s), 923 (w), 756 (s), 670 cm^{-1} (s).

^{1}H NMR ($CDCl_3$): δ = 7.61–7.56 (m, 4 H_{arom}), 7.36–7.30 (m, 4 H_{arom}), 7.24 (m, 4 H_{arom}), 7.04 (m, 4 H_{arom}), 4.89 (m, 2 $H_{ferrocene}$), 4.77 (m, 4 $H_{ferrocene}$), 4.50 (t, 2 $H_{ferrocene}$), 4.26 (s, 10 $H_{ferrocene}$).

MS (ESI): *m*/*z* (%) = 1094 ([M + 67], 6), 566 ([M – 461], 100).

Anal. Calcd for $C_{52}H_{34}Fe_2S_8$ (1027.0364): C, 60.81; H, 3.34. Found: C, 60.46; H, 3.52.

2,2′,2″,2‴-{1,4-Bis[4-(ferrocenyl)phenyl]butane-1,2,3,4-tetraylidene}tetrakis(1,3-benzodithiole) (11d)

Chromatography (silica gel, hexane–CH_2Cl_2, 3:1); dark red crystals; yield: 45% (method a), 0% (method b); 28% (method c); mp 164–165 °C.

IR (KBr): 3060 (m), 3011 (s), 2997 (s), 2858 (s), 1670 (s), 1574 (m), 1527 (m), 1444 (s), 1381 (m), 1262 (m), 1215 (s), 1116 (s), 1013 (s), 925 (m), 872 (s), 823 (s), 755 (s), 670 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ = 7.55 (m, 4 H_{arom}), 7.30 (m, 8 H_{arom}), 7.20–6.9 (m, 12 H_{arom}), 4.74 (t, *J* = 3 Hz, 4 $H_{ferrocene}$), 4.39 (t, *J* = 3 Hz, 4 $H_{ferrocene}$), 4.06 (s, 10 $H_{ferrocene}$).

MS (EI): *m*/*z* (%) = 648 ([M – 530], 28), 590 ([M – 589], 100).

Anal. Calcd for $C_{64}H_{42}Fe_2S_8$ (1179.2283): C, 65.19; H, 3.59. Found: C, 65.35; H, 3.27.

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References

(1) (a) Wudl, F.; Smith, G. M.; Hufnagel, E. G. *J. Chem. Soc., Chem. Commun.* **1970**, 1453. (b) Coffen, D. L. *Tetrahedron Lett.* **1970**, *11*, 2633. (c) Sarhan, A. A. O.; Murakami, M.; Izumi, T. *J. Heterocycl. Chem.* **2002**, *39*, 1.

(2) (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209. (b) Schukat, G.; Fänghanel, E. *Sulfur Rep.* **1993**, *14*, 245. (c) Sarhan, A. A. O. *Tetrahedron* **2005**, *61*, 3889.

(3) (a) Narita, M.; Pittman, C. U. Jr. *Synthesis* **1976**, 489; and references cited therein. (b) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (c) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

(4) (a) Coustumer, G.; Moller, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 38. (b) Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1983**, *24*, 3469. (c) Khanous, A.; Gorgues, A.; Jubault, M. *Synth. Met.* **1991**, *41-43*, 2327.

(5) (a) Bryce, M. R.; Fleckenstein, E.; Hünig, S. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1777. (b) Sallè, M.; Belyasmine, A.; Gorgues, A.; Jubault, M.; Soya, N. *Tetrahedron Lett.* **1991**, *32*, 2897. (c) Sugimoto, T.; Awaji, H.; Sugimoto, I.; Misaki, Y.; Kawase, T.; Yoncda, S.; Yoshida, Z. *Chem. Mater.* **1989**, *1*, 535. (d) Hansen, T. K.; Lakshmikantham, M. V.; Cava, U. P.; Becher, J. *J. Chem. Soc., Perkin Trans. 2* **1991**, 2873. (e) Belyasmine, A.; Gorgues, A.; Jubault, M.; Duguay, G. *Synth. Met.* **1991**, *42*, 2323. (f) Sallè, M.; Gorgues, A.; Jubault, M.; Gouriou, Y. *Synth. Met.* **1991**, *42*, 2575. (g) Benahmed, A. S.; Frère, P.; Belyasmine, A.; Malik, K. M. A.; Hursthouse, M. B.; Moore, A. J.; Bryce, M. R.; Jubault, M.; Gorgues, A. *Tetrahedron Lett.* **1993**, *34*, 2131.

(6) (a) Balavoine, G. G. A.; Dosneau, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1991**, *412*, 381. (b) Rinehart, K. L. Jr.; Motz, K. L.; Moon, S. *J. Am. Chem. Soc.* **1957**, *79*, 2749. (c) Gokel, G. W.; Ugi, I. K. *J. Chem. Educ.* **1972**, *49*, 294. (d) Woodward, R. B.; Rosenblum, M.; Whiting, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 3458.

(7) Roncoli, J. *J. Mater. Chem.* **1997**, *7*, 2307.

(8) Yamashita, Y.; Tomura, M. *J. Solid State Chem.* **2002**, *168*, 427.

(9) Ueno, Y.; Sano, H.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1980**, 28.

(10) (a) Togni, A.; Hobi, M.; Rihs, G.; Rist, G.; Albinati, A.; Zanello, P.; Zech, D.; Keller, H. *Organometallics* **1994**, *13*, 1224. (b) Togni, A. In *Ferrocenes*; Togni, A.; Hayashi, T., Eds.; Weinheim: VCH, **1995**, 434. (c) Liu, S.; Perez, I.; Martin, N.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 9092. (d) Sarhan, A.; Murakami, M.; Izumi, T. *Monatsh. Chem.* **2002**, *133*, 1055.

(11) (a) Nakayama, J. *Synthesis* **1975**, 38. (b) Sarhan, A.; Izumi, T. *J. Chem. Res., Synop.* **2002**, 11. (c) Nakayama, J.; Fujiwara, K.; Hoshino, M. *Chem. Lett.* **1975**, 1099. (d) Akiba, K.; Ishikawa, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2674.

(12) (a) Moore, A. J.; Bryce, M. R.; Skabara, P. J.; Batsanov, A. S.; Goldenberg, L. M.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3443. (b) Sarhan, A.; Izumi, T. *Synth. Met.* **2004**, *140*, 95.

(13) Massue, J.; Bellec, N.; Guerro, M.; Bergamini, J.-F.; Hapiot, P.; Lorcy, D. *J. Org. Chem.* **2007**, *72*, 4655.

(14) Misaki, Y.; Matsumura, Y.; Sugimoto, T.; Yoshida, Z.-I. *Tetrahedron Lett.* **1989**, *30*, 5289.