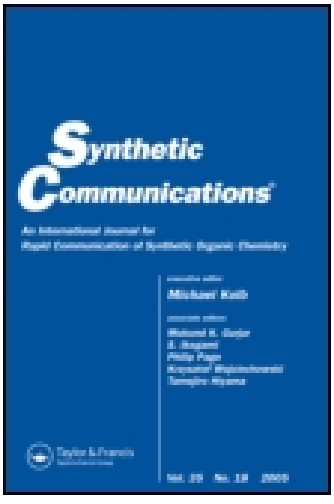

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Facile and Efficient Synthesis of Substituted 1,4-Dithiafulvalenes from β-Dicarbonyl Compounds

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Facile and Efficient Synthesis of Substituted 1,4-Dithiafulvalenes from β-Dicarbonyl Compounds

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Abstract: A facile and efficient synthetic route to substituted 1,4-dithiafulvalenes has been developed. The precursors **2** may be easily prepared from the reactions of β-dicarbonyl compounds **1** with CS_2 and 1,2,3-tribromopropane under mild conditions. The elimination of HBr of **2** in basic media furnishes corresponding acetyl substituted 1,4-dithiafulvalenes **3** in 85–93% yields. The aldol condensation reaction of **2** with various arylaldehydes affords alkenoyl substituted 1,4-dithiofulvalenes **4** in high to excellent yields.

Keywords: aldol condensation, β-dicarbonyl compounds, 1,4-dithiafulvalene derivatives, rearrangement of a double bond, synthesis

Over the past few decades, the utility of α-oxo ketene-(*S*,*S*)-acetals as versatile intermediates in organic synthesis has been recognized, and a few review papers have been presented by Dieter,[1] Hunjappa,[2] Kolb,[3] and Yokoyama,[4] respectively, on their preparation, structure, and synthetic applications. During the course of our studies on the chemistry of α-oxo ketene-(*S*,*S*)-acetals,[5] the easily available and structurally flexible α-alkenoyl ketene-(*S,S*)-acetals[6] have proved to be potent as five-carbon 1,5-bielectrophilic synthons in [5 + 1] annulation reactions.[7] As part of the research on

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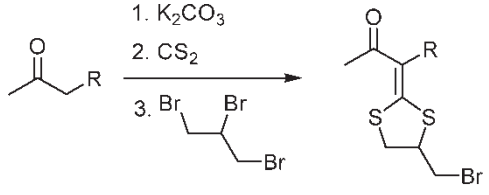
the functionalized ketene-(*S*,*S*)-acetals, we developed dithiafulvalene (DTF) and tetrathiafulvalene (TTF) derivatives through convenient synthetic routes, with the consideration that DTF, TTF, and their derivatives, as strong electron donors,[8] exhibit unusual and fascinating optoelectronic properties and have found wide applications in the field of molecular conductors, small band gap molecular semiconductors, and nonlinear optics.[9] In this context, we have successfully synthesized a heteroatom-substituted expanded 1,3-dithiolan[5]radialene with the structural feature of 25-membered carbocycle peripherally bearing five dihydrodithiafulvalene rings.[10] More recently, novel acetylene-spaced TTFs were designed and synthesized starting from α-acetyl ketene-(*S,S*)-acetals.[11] Generally, 1,4-dithiafulvalene derivatives were synthesized via Knoevenagel-type reaction of dithiolium salt with active methylene compounds[12] or the reaction of dithiocarboxylates with propargyl bromide under basic conditions.[13] However, these methods suffer from harsh reaction conditions, complex procedures, and/or low yields. In this article, we describe a facile and efficient method for the preparation of 1,4-dithiafulvalene derivatives of types **3** and **4**.

In the initial experiments, after treatment of pentane-2,4-dione **1a** (R = $COCH_3$) with CS_2 (1.1 equiv) in the presence of K_2CO_3 (2.2 equiv) in DMF for 1 h under ice bath, 1,2,3-tribromopropane was added to the reaction mixture dropwise and stirred overnight at room temperature. A white solid was obtained after pouring the reaction mixture into a large amount of ice water. The only product was characterized as 3-(4-bromomethyl-[1,3]dithiolan-2-ylidene)-pentane-2,4-dione **2a**, with an excellent yield of 91%, on the basis of its spectra and analytical data (Scheme 1 and Table 1, entry 1). In the following work, other α-dicarbonyl compounds such as **1b** (R = 4-Cl-PhNHCO), **1c** (R = $COOCH_3$), **1d** (R = CN), and **1e** (R = PhCO) were subjected to the reaction sequence under the identical conditions. As a result, the corresponding α-acetyl ketene-(*S,S*)-acetals **2b–e** were obtained in 80–85% yields (Table 1, entries 2–4). It was observed from the ^1H and ^{13}C NMR spectra that each compound of **2b–e** consists of two regio-isomers, due to the introduction of the two different electron-withdrawing groups.



1a-e **2a-e**

Scheme 1.

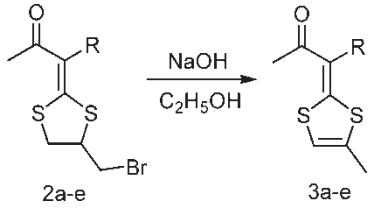
Table 1. Preparation of the precursors **2a–e** to substituted 1,4-dithiafulvalenes

Entry	Substrates	R	Time (h)	Products	Yields (%)[a]
1	**1a**	$COCH_3$	4.0	**2a**	91
2	**1b**	4-Cl-PhNHCO	4.0	**2b**	83
3	**1c**	$COOCH_3$	4.0	**2c**	85
4	**1d**	CN	4.0	**2d**	80
5	**1e**	COPh	4.0	**2e**	81

[a]Isolated yields.

With the readily available precursors **2** at hand, we turned to study the synthesis of 1,4-dithiafulvalene derivatives. The reaction of **2a** and NaOH was first investigated in EtOH at room temperature (Scheme 2). The corresponding 1,4-dithiafulvalene derivative, 2-acetyl-methylene-1,3-dithiole **(3a)**, was produced with an excellent yield of 95% (Table 2, entry 1). The formation of **3a** is supposed to be via the elimination of the hydrobromide under basic conditions to form the double bond, followed by the rearrangement of the double bond.[13,14] In a similar way, acetyl substituted 1,4-dithiafulvalenes **3b–d** were successfully obtained in good to excellent yields of 85–93% (Table 2, entries 2–4). The Same as that of **2b–e**, two regioisomers exist in each product of **3b–e**.

In a further extension of the research, the aldol condensation reactions of **2a** with selected arylaldehydes in the presence of NaOH were performed according to the known procedure (Scheme 3).[7] As a result, a series of alkenoyl substituted 1,4-dithiafulvalenes **4aa–ah**, were achieved in excellent yields (85–93%) and short reaction times (2.0–3.0 h). Some of the results are summarized in Table 3. The rearrangement of the double bond was also observed during the condensation reactions, same as the reactions described previously. Obviously, the present protocol provides a straightforward and general pathway to introduce acetyl or alkenoyl functional groups into the 2-methylene-1,3-dithioles. Also it provides a convenient way to further modify the resulting substituted 1,4-dithiafulvalenes, for example, to construct tetrathiafulvalene derivatives.[10,11,15]

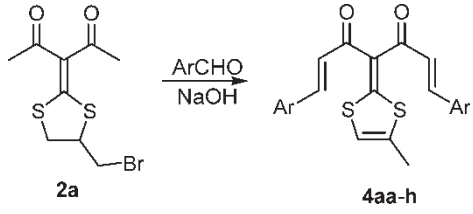


Scheme 2.

Table 2. Preparation of the 2-acetyl-methylene-1,3-dithiole **3a**–**e**

Entry	Substrates	R	Time (h)	Products	Yields (%)[a]
1	**2a**	CH_3CO	1.0	**3a**	95
2	**2b**	4-Cl-PhNHCO	3.0	**3b**	93
3	**2c**	CH_3OCO	1.0	**3c**	92
4	**2d**	CN	2.0	**3d**	85
5	**2e**	PhCO	2.5	**3e**	86

[a]Isolated yields.



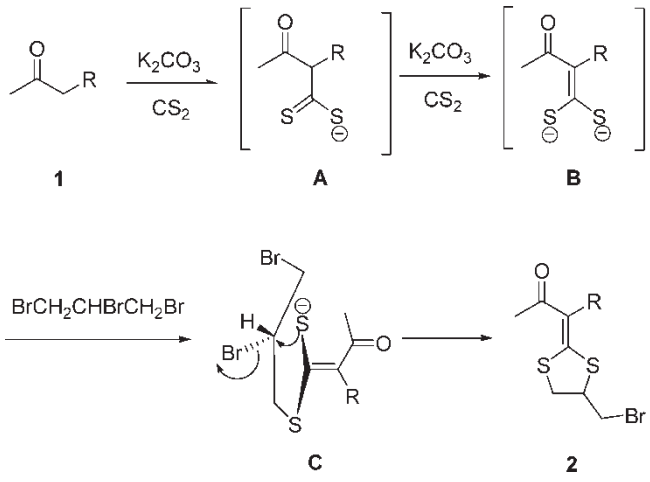
Scheme 3.

On the basis of these results, a possible mechanism for the formation of the precursors **2** is proposed as depicted in Scheme 4. In the presence of potassium carbonate, compound **1** reacted with CS_2 to give dithiolate **B**. Then, one of the sulfur anions of **B** attacks at the side primary carbon atom of 1,2,3-tribromopropane to afford intermediate **C**. Finally, the intramolecular attack to the secondary carbon atom from the other sulfur anion leads to the formation of the corresponding bromomethyl substituted 1,3-dithiolanes **2**.

In summary, we have demonstrated here a facile and efficient synthetic method for a wide range of 1,4-dithiafulvalene derivatives (i.e., acetyl substituted 1,4-dithiofulvalenes **3** and alkenoyl substituted 1,4-dithiafulvalenes **4**)

Table 3. Preparation of the 2-(α,α'-dialkenoyl) methylene-1,3-dithioles **4aa**–**ah**

Entry	Ar	Time (h)	Products **4a**	Yields (%)[a]
1	C_6H_5	2.0	**4aa**	91
2	4-ClC_6H_4	3.0	**4ab**	93
3	4-FC_6H_4	2.5	**4ac**	93
4	4-$CH_3C_6H_4$	2.0	**4ad**	90
5	4-$CH_3OC_6H_4$	2.0	**4ae**	90
6	4-$NO_2C_6H_4$	2.5	**4af**	93
7	2-Furanyl	2.5	**4ag**	85
8	2-Pyridyl	3.0	**4ah**	86



Scheme 4. Proposed mechanism for the formation of precursors **2.**

in high yields under mild conditions, from easily available substrates and cheap reagents. Indeed, the present protocols provide straightforward and effective pathways to construct substituted 1,4-dithiafulvalenes of types **3** and **4** in concise steps. Further work on the synthetic applications of the corresponding substituted 1,4-dithiofulvalenes is under way.

EXPERIMENTAL

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25°C on Varian 500 MHz and 125 MHz instruments, respectively, and TMS was the internal standard. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400–4000 cm^{-1}. Mass spectra were recorded on Agilient 1100 LCMsD mass spectrometer. C, H, N, elemental analyses were conducted with Bio-Rad Co's elemental analytical instrument.

General Procedure for the Preparation of 2 (with 2a as an Example)

To a solution of pentane-2,4-dione (10.1 mL, 100 mmol) and anhydrous K_2CO_3 (30.1 g, 220 mmol) in DMF (150 mL), CS_2 (6.7 mL, 110 mmol) was added at room temperature. After 30 min, 1,2,3-tribromopropane was added in one portion to the reaction mixture under an ice bath and stirred

overnight at room temperature. A white solid was obtained after pouring the reaction mixture into ice water (800 mL). The only product was characterized as 2a with an excellent yield of 91%.

Data

3-(4-Bromomethyl-1,3-dithiolan-2-ylidene)-pentane-2,4-dione (**2a**)

White solid; mp 92–94°C. IR (KBr): 2926, 1619, 1439, 1402, 1269, 1261, 885 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.43$ (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.46–3.50 (m, 2H), 3.57–3.62 (m, 1H), 3.66–3.69 (m, 1H), 4.02 ppm (m, 1H). Anal. calcd. for $C_9H_{11}BrO_2S_2$: C, 36.62; H, 3.76. Found: C, 36.91; H, 3.71.

2-(4-Bromomethyl-1,3-dithiolan-2-ylidene)-*N*-(4-chlorophenyl)-3-oxobutanamide (**2b**)

Yellow solid; mp 137–139°C. IR (KBr): 3302, 2358, 1642, 1618, 1511, 1442, 1245, 818 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.48$ (s, 3H, CH_3), 3.56–3.62 (m, 2H), 3.64–3.66 (m, 1H), 3.76–3.79 (m, 1H), 4.07 ppm (m, 1H). Anal. calcd. for $C_{14}H_{13}BrClNO_2S_2$: C, 41.34; H, 3.22; N, 3.44. Found: C, 41.51; H, 3.09; N, 3.50.

Ethyl 2-(4-(Bromomethyl)-1,3-dithiolan-2-ylidene)-3-oxobutanoate (**2c**)

White solid; mp 77–79°C. IR (KBr): 2984, 1684, 1634, 1437, 1416, 1247, 1025 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): $\delta = 1.39$ (t, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.49 (m, 2H), 3.60 (m, 2H), 4.02 (m, 1H), 4.34 (m, 2H). Anal. calcd. for $C_{10}H_{13}BrO_3S_2$: C, 36.93; H, 4.03. Found: C, 36.91; H, 4.08.

2-(4-(Bromomethyl)-1,3-dithiolan-2-ylidene)-3-oxobutanenitrile (**2d**)

White solid; mp 121–123°C. IR (KBr): 3413, 2199, 1654, 1441, 1270, 609 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.46$ (s, 3H, CH_3), 3.55–3.58 (m, 2H), 3.68–3.71 (m, 1H), 3.90–3.92 (m, 1H), 4.25 ppm (m, 1H). Anal. calcd. for $C_8H_8BrNOS_2$: C, 34.54; H, 2.90; N, 5.03. Found: C, 34.81; H, 2.88; N, 5.21.

2-(4-(Bromomethyl)-1,3-dithiolan-2-ylidene)-1-phenylbutane-1,3-dione (**2e**)

White solid; mp 70–72°C. IR (KBr): 3059, 2959, 2862, 1650, 1446, 1277, 1234, 813 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.00$

(s, 3H, CH_3), 3.41 (m, 2H), 3.62 (m, 2H), 4.06 ppm (m, 1H), 7.51 (m, 2H), 7.59 (t, 1H), 7.79 (m, 2H). Anal. calcd. for $C_{14}H_{13}BrO_2S_2$: C, 47.06; H, 3.67. Found: C, 47.23; H, 3.62.

General Procedure for the Preparation of 3 (with 3a as an Example)

To a solution of **2a** (295 mg, 1.0 mmol) in EtOH (10.0 mL), NaOH (40 mg, 1.0 mmol) was added in one portion. The reaction mixture was stirred at rt for 1 h. After the starting material **2a** was consumed as monitored by TLC, the resulting mixture was then poured onto ice water (250 mL). The precipitated solid was collected by filtration, washed with water (3 × 30 mL), and dried in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether–diethyl ether = 10:1) to give **3a** as a yellow solid.

Data

3-(4-Methyl-1,3-dithiol-2-ylidene)pentane-2,4-dione (**3a**)

Yellow solid; mp 84–86°C. IR (KBr): 3439, 2993, 1567, 1449, 1366, 1314, 1224, 1022, 970 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): δ 2.45 (s, 6H), 2.63 (s, 3H), 6.93 ppm (s, 1H). MS (EI) calcd. m/z 214.0, found 215.1 $[(M + 1)]^+$. Anal. calcd. for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70. Found: C, 50.52; H, 4.76.

N-(4-chlorophenyl)-2-(4-methyl-1,3-dithiol-2-ylidene)-3-oxobutanamide (**3b**)

Yellow solid; mp 188–190°C. IR (KBr): 3284, 1647, 1594, 1492, 1399, 1313, 1247, 1092, 829 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): δ 2.33 (s, 3H), 2.49 (s, 3H), 6.63 (s, 1H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 9.45 ppm (s, 1H). Anal. calcd. for $C_{14}H_{12}ClNO_2S_2$: C, 51.61; H, 3.71; N, 4.30. Found: C, 51.28; H, 3.77; N, 4.23.

Ethyl 2-(4-Methyl-1,3-dithiol-2-ylidene)-3-oxobutanoate (**3c**)

White solid; mp 75–77°C. IR (KBr): 3052, 2980, 2929, 1662, 1589, 1423, 1373, 1345, 1259, 1095, 1031 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K, TMS): δ 1.40–1.43 (m, 3H), 2.40 (s, 3H), 2.58 (s, 3H), 4.33-4.41 (m, 2H), 6.80 ppm (q, 1H). MS (EI) calcd. m/z 244.1, found 267.3 $[(M + 23)]^+$. Anal. calcd. for $C_{10}H_{12}O_3S_2$: C, 49.16; H, 4.95. Found: C, 49.43; H, 4.82.

2-(4-Methyl-1,3-dithiol-2-ylidene)-3-oxobutanenitrile (**3d**)

Yellow solid; mp 130–132°C. IR (KBr): 3742, 3046, 2359, 2197, 1622, 1406, 1301 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): δ 2.42 (s, 3H), 2.46

(s, 3H), 6.76 ppm (s, 1H). MS (EI) calcd. m/z 197.0, found 220.1 $[(M + 23)]^+$. Anal. calcd. for $C_8H_7NOS_2$: C, 48.71; H, 3.58; N, 7.10. Found: C, 48.69; H, 3.53; N, 6.92.

2-(4-Methyl-1,3-dithiol-2-ylidene)-1-phenylbutane-1,3-dione (**3e**)

Yellow solid; mp 112–114°C. IR (KBr): 3062, 1598, 1583, 1560, 1446, 1360 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): δ1.92 (s, 3H), 2.45 (s, 3H), 6.86 (s, 1H), 7.62–7.63 (m, 2H), 7.44–7.47 ppm (m, 3H). Anal. calcd. for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38. Found: C, 61.02; H, 4.23.

General Procedure for the Preparation of 4aa–ah (with 4aa as an Example)

To a solution of **2a** (295 mg, 1.0 mmol) and benzaldehyde (222.6 mg, 2.1 mmol) in EtOH (10.0 mL) at 0°C, NaOH (200 mg, 5.0 mmol) was added in one portion. The reaction mixture was stirred at 0°C for 10 min, followed by stirring at 25°C for 0.5 h. After the starting material **2a** was consumed as indicated by TLC, the resulting mixture was then poured onto ice water (250 mL) under stirring. The precipitated solid was collected by filtration, washed with water (3 × 30 mL), and dried in vacuo to afford the product **2a** as a yellow solid.

Data

4-(4-Methyl-1,3-dithiol-2-ylidene)-1,7-diphenylhepta-1,6-diene-3,5-dione (**4aa**)

Yellow solid; mp 197–199°C. IR (KBr): 1628, 1572, 1539, 1543, 1370, 1304, 1169 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 293 K, TMS): δ 2.49 (s, 3H), 6.96 (s, 1H), 7.33 (d, $J = 8.0$ Hz, 4H), 7.38 (d, $J = 16.0$ Hz, 1H), 7.52 (m, 5H), 7.77 (d, $J = 16.0$ Hz, 2H). MS (EI) calcd. m/z 390.1, found 391.4 $[(M + 1)]^+$. Anal. calcd. for $C_{23}H_{18}OS_2$: C, 70.74; H, 4.65. Found: C, 70.78; H, 4.62.

1,7-Bis(4-chlorophenyl)-4-(4-methyl-1,3-dithiol-2-ylidene)hepta-1,6-diene-3,5-dione (**4ab**)

Yellow solid; mp 191–193°C. IR (KBr): 1740, 1628, 1560, 1491, 1455, 1370, 1224, 1093 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.49$ (s, 3H), 6.96 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 4H), 7.29 (d, $J = 16.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 4H), 7.69 (d, $J = 16.0$ Hz, 2H). Anal. calcd. for $C_{23}H_{16}Cl_2OS_2$: C, 60.13; H, 3.51. Found: C, 60.28; H, 3.48.

1,7-Bis(4-fluorophenyl)-4-(4-methyl-1,3-dithiol-2-ylidene)hepta-1,6-diene-3,5-dione (**4ac**)

Yellow solid; mp 185–187°C. IR (KBr): 3068, 1629, 1576, 1544, 1508, 1451, 1418, 1230 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.48$ (s, 3H), 6.94 (s, 1H), 6.98 (m, 4H), 7.23 (d, $J = 16.0$ Hz, 2H), 7.50 (m, 4H), 7.68 (d, $J = 16.0$ Hz, 2H).

4-(4-Methyl-1,3-dithiol-2-ylidene)-1,7-dip-tolylhepta-1,6-diene-3,5-dione (**4ad**)

Yellow solid; mp 189–191°C. IR (KBr): 3070, 1630, 1595, 1517, 1441, 1412, 1341, 1224 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.35$ (s, 6H, 2 × Me), 2.46 (s, 3H), 6.90 (s, 1H), 7.12 (d, $J = 8.0$ Hz, 4H), 7.29 (d, $J = 16.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 4H), 7.75 (d, $J = 16.0$ Hz, 2H). MS (EI) calcd. m/z 418.1, found 419.2 $[(M + 1)]^+$. Anal. calcd. for $C_{25}H_{22}O_2S_2$: C, 71.74; H, 5.30. Found: C, 71.91; H, 5.24.

1,7-Bis(4-methoxyphenyl)-4-(4-methyl-1,3-dithiol-2-ylidene)hepta-1,6-diene-3,5-dione (**4ae**)

Yellow solid; mp 187–189°C. IR (KBr): 3058, 2928, 2837, 1624, 1604, 1567, 1511, 1449, 1366, 1255 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.46$ (s, 3H), 3.82 (s, 6H, 2 × OMe), 6.84 (d, $J = 8.0$ Hz, 4H), 6.89 (s, 1H), 7.22 (d, $J = 16.0$ Hz, 2H), 7.48–7.49 (d, $J = 6.0$ Hz, 4H), 7.73 (d, $J = 16.0$ Hz, 2H). Anal. calcd. for $C_{25}H_{22}O_4S_2$: C, 66.64; H, 4.92. Found: C, 66.81; H, 4.88.

4-(4-Methyl-1,3-dithiol-2-ylidene)-1,7-bis(4-nitrophenyl)hepta-1,6-diene-3,5-dione (**4af**)

Yellow solid; mp 189–191°C. IR (KBr): 3070, 1630, 1595, 1517, 1441, 1412, 1341, 1224 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.53$ (s, 3H), 7.05 (s, 1H), 7.37–7.40 (m, 2H), 7.63–7.65 (m, 4H), 7.75–7.78 (m, 2H), 8.17–8.19 (m, 4H).

1,7-Di(furan-2-yl)-4-(4-methyl-1,3-dithiol-2-ylidene)hepta-1,6-diene-3,5-dione (**4ag**)

Yellow solid; mp 179–181°C. IR (KBr): 3399, 2170, 1678, 1628, 1549, 1448, 1364, 1289 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.45$ (s, 3H), 6.45 (m, 2H), 6.64 (m, 2H), 6.89 (s, 1H), 7.18 (d, $J = 16.0$ Hz, 2H), 7.42 (m, 2H), 7.50 (d, $J = 16.0$ Hz, 2H). MS (EI) calcd. m/z 370.1, found 371.3 $[(M + 1)]^+$. Anal. calcd. for $C_{19}H_{14}O_4S_2$: C, 61.60; H, 3.81. Found: C, 61.35; H, 3.78.

4-(4-Methyl-1,3-dithiol-2-ylidene)-1,7-di(pyridin-2-yl)hepta-1,6-diene-3,5-dione (**4ah**)

Yellow solid; mp 182–184°C. IR (KBr): 3400, 3024, 1633, 1575, 1538, 1462, 1364, 1293, 1227 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 293 K, TMS): $\delta = 2.50$ (s, 3H), 6.98 (s, 1H), 7.20 (m, 2H), 7.50 (m, 2H), 7.62 (m, 2H), 7.70 (d, $J = 16.0$ Hz, 2H), 7.70 (d, $J = 16.0$ Hz, 2H), 8.52 (m, 2H). MS (EI) calcd. m/z 392.1, found 393.4 $[(M + 1)]^+$. Anal. calcd. for $C_{21}H_{16}N_2O_2S_2$: C, 64.26; H, 4.11; N, 7.14. Found: C, 64.54; H, 4.05; N, 7.09.

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