# Paper

# Selective Metalation of 1,3-Dithiole-2-thiones: An Effective Preparation of New Symmetrically and Nonsymmetrically Tetraarylated Tetrathiafulvalenes

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**Abstract** We report an efficient preparation of fully functionalized tetrathiafulvalene derivatives (TTF) with an extended  $\pi$ -system via a selective magnesiation of 1,3-dithiole-2-thiones (DTT) using 2,2,6,6-te-tramethylpiperidin-1-ylmagnesium chloride–lithium chloride (TMPMg-Cl-LiCl); subsequent reaction with various electrophiles, such as halides, acid chlorides, allyl bromides, and aryl iodides, smoothly led to new mono- and difunctionalized 1,3-dithiole-2-thione derivatives. A triethyl phosphite mediated cross-coupling of the disubstituted 1,3-dithiole-2-thione derivatives with their oxygen analogues gave access to new symmetrically and nonsymmetrically tetraarylated tetrathiafulvalenes of interest as organic materials.

Key words metalation, organomagnesium reagents, palladium, cross-coupling, organic materials

The functionalization of heterocycles is an important synthetic task since many of these ring systems have interesting biological or electronic properties.<sup>1</sup> The directed metalation of heterocycles is one of the most general methods for achieving broad heterocyclic functionalization.<sup>2</sup> Recently, we have developed a range of 2,2,6,6-tetramethylpiperidin-1-yl (TMP) bases of magnesium and zinc, such as TMPMgCl·LiCl (1),<sup>3</sup> TMPZnCl·LiCl,<sup>4</sup> and (TMP)<sub>2</sub>Zn·2MgCl<sub>2</sub>· 2LiCl.<sup>5</sup> These bases metalate a range of polyfunctionalized aromatics and heterocycles under mild conditions. The large steric hindrance of the 2,2,6,6-tetramethylpiperidin-1-yl moiety ensures a monomeric structure for this base<sup>6</sup> and the extra equivalent of lithium chloride is responsible for the high solubility of these bases in tetrahydrofuran (1.2 M). The metalation of sulfur-containing heterocycles can be achieved with lithium bases.<sup>7</sup> However, the presence of additional sensitive functionalities or the nature of the S-heterocycle may lead to side reactions, such as ring fragmentation. This is the case for 1,3-dithiole-2-thione (**2**; DTT) which produces intermediates of type **3** after metalation. In the next step, the reaction of **3** with an electrophile (E-X) affords substituted heterocycles of type **4**. However, the presence of a leaving group in  $\beta$ -position to the carbonmetal bond may lead to ring fragmentation and, therefore, to the decomposition of intermediate **3** (Scheme 1). This behavior can be expected when the carbon-metal bond is very ionic (Met = Li).<sup>8</sup>



**Scheme 1** Metalation of 1,3-dithiole-2-thione (**2**; DTT) leading to the metalated intermediate of type **3** and quenching with an electrophile (E-X)

Herein, we report a convenient sequential difunctionalization of 1,3-dithiole-2-thione (2) using 2,2,6,6-tetramethchloride-lithium ylpiperdin-1-ylmagnesium chloride (TMPMgCl·LiCl, 1).<sup>3</sup> The quenching of the magnesiated 1,3dithiole-2-thione intermediate with a first electrophile (E1-X) leads to monosubstituted heterocycles of type 4. A second magnesiation can be achieved using the same base and similar reaction conditions and quenching with a second electrophile (E<sup>2</sup>-X) provides disubstituted 1,3-dithiole-2thione derivatives of type 5. To demonstrate the potential of this methodology, the new disubstituted 1,3-dithiole-2-thiones 5 were subjected to triethyl phosphite mediated crosscoupling<sup>9</sup> with their oxygen analogues **6** giving access to a range of new fully functionalized tetrathiafulvalene (TTF)

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derivatives of type **7** that belong to an important class of organic materials<sup>10</sup> due to their electrical and optical properties (Scheme 2).



**Scheme 2** Preparation of mono- and disubstituted 1,3-dithiole-2-thione derivatives of type **4** and **5** by metalation of **2** followed by a triethyl phosphite mediated cross-coupling leading to fully functionalized tetrathiafulvalene derivatives of type **7** 

After extensive optimization, we found that TMPMgCl-LiCl (1: 1.1 equiv. THF. -78 °C. 0.5 h) leads to complete magnesiation of 1,3-dithiole-2-thione (2). Quenching of the metalated species 3 with iodine or 1,2-dibromotetrachloroethane produced the corresponding halogenated products 4a,b in 79-84% isolated yield (Table 1, entries 1 and 2). Thiolation with S-methyl methanethiosulfonate furnished the methyl thioether 4c in 75% yield (entry 3). Various carbon electrophiles reacted readily. Thus, the acylation with 3-chlorobenzoyl chloride, after domino-transmetalation<sup>11</sup> with zinc chloride and copper(I) cvanide-di(lithium chloride) (CuCN-2LiCl),12 provides ketone 4d in 62% yield (entry 4). Copper-mediated allylation with ethyl (2-bromomethyl)acrylate<sup>13</sup> led to the allylated 1,3-dithiole-2-thione **4e** in 50% yield (entry 5). Magnesiated 1,3-dithiole-2-thione 2 undergoes a range of Negishi cross-coupling reactions<sup>14</sup> with arvl iodides as the electrophile in the presence of *N*-methylpyrrolidin-2-one as а polar co-solvent; tetrakis(triphenylphosphine)palladium(0) (10 mol%) was the best catalyst in a tetrahydrofuran-N-methylpyrrolidin-2-one mixture (2:1) (25 °C, 1–18 h). Interestingly, electronwithdrawing and electron-donating groups could be attached to the electron-rich 1,3-dithiole-2-thione-core affording the corresponding arylated 1,3-dithiole-2-thione derivatives **4f**-**n** in 60–94% yield (entries 6–14).

A second magnesiation was achieved by treating various monosubstituted 1,3-dithiole-2-thiones of type **4** with TMPMgCl·LiCl (**1**; 1.1 equiv, THF, -78 °C, 0.5 h). After quenching the reaction with the same type of electrophile as shown in Table 1, it was possible to prepare 4,5-disubstituted 1,3-dithiole-2-thiones **5a**-**i** in 70–94% yield (Table 2). Also in this case, the Negishi cross-couplings were best performed with tetrakis(triphenylphosphine)palladium(0) (10 mol%) as the catalyst in a mixture of tetrahydrofuran-*N*-methylpyrrolidin-2-one (2:1).

 Table 1
 Preparation of Monofunctionalized 1,3-Dithiole-2-thione Derivatives of Type 4 by Magnesiation of 1,3-dithiole-2-thione (2) with

 TMPMgCl-LiCl (1)
 TMPMgCl-LiCl (1)



<sup>a</sup> Isolated yield of analytically pure product.

<sup>b</sup> ZnCl<sub>2</sub> solution was added.

<sup>c</sup> CuCN-2LiCl solution was added

<sup>d</sup> Cross-coupling conditions: ZnCl<sub>2</sub> transmetalation, 10 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>,

THF–NMP (2:1).

Various 4,5-disubstituted 1,3-dithiole-2-thiones of type **5** could be converted into the corresponding oxygen analogues of type **6** by treatment with mercury(II) acetate (3.0 equiv) in a mixture of chloroform and acetic acid (4:1)

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 Table 2
 Preparation of Disubstituted 1,3-Dithiole-2-thione Derivatives of Type 5 by Magnesiation of Monosubstituted 1,3-dithiole-2-thione Derivatives of Type 4 with TMPMgCl-LiCl (1)



<sup>a</sup> Isolated yield of analytically pure product.

 $^{\rm b}$  Cross-coupling conditions:  $ZnCl_2$  transmetalation, 10 mol% Pd(PPh\_3)\_4, THF–NMP (2:1).

(25 °C, 1–2 h).<sup>8f</sup> Thus, the monobromo-oxygen analogue **6a**, as well as the diarylated compounds **6b–d** were obtained in 75–92% yield (Scheme 3).

Both symmetrical and nonsymmetrical tetrathiafulvalenes **7** were prepared via a triethyl phosphite mediated cross-coupling (110 °C, 1.5–3 h).<sup>9b</sup> In the first case, the functionalized 1,3-dithiole-2-ones **6c** and **6d** furnished the corresponding tetraarylated tetrathiafulvalene derivatives **7a** and **7b** (54–63% yield) after treatment with triethyl phosphite. On the other hand, the nonsymmetrically substituted tetrathiafulvalene derivatives **7c** and **7d** were prepared by cross-coupling of **5i** with **6b** and **5f** with **6d**, re-



Scheme 3 Preparation of oxygen analogues 6a-d

spectively (53–67% yield; Scheme 4). These new fully functionalized tetrathiafulvalene derivatives are of interest for material science due to their extended  $\pi$ -system.

In summary, we have developed a novel synthesis allowing the preparation of tailor-made fully substituted tetrathiafulvalene derivatives via a selective functionalization of the 1,3-dithiole-2-thione precursor. 1,3-Dithiole-2thione (**2**) can easily be magnesiated using TMPMgCl·LiCl leading to new mono- and disubstituted 1,3-dithiole-2-thione derivatives. Due to the gentle reaction conditions various functional groups are tolerated. Subsequent triethyl phosphite mediated cross-coupling with their oxygen analogues leads to new symmetrically and nonsymmetrically tetraarylated tetrathiafulvalene derivatives that are potentially useful substrates for materials science.

All air- and moisture-sensitive reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under N2 and stored over molecular sieves. Reactions were monitored by gas chromatography (GC and GC-MS) or TLC. TLC was performed using silica gel (Merck 60, F-254) covered aluminum plates and visualized by UV detection. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by <sup>1</sup>H NMR (25 °C) and capillary GC. Purification by column chromatography was performed using silica gel (0.040-0.063 mm, 230-400 mesh ASTM) from Merck. 2,2,6,6-Tetramethylpiperidine (TMPH) was distilled prior to use. CuCN, ZnCl<sub>2</sub>, and LiCl were obtained from Merck. 1,3-Dithiole-2-thione (2; DTT) was prepared according to the literature.<sup>15</sup> All reagents were obtained from commercial sources.

IR spectra were recorded on a Perkin Elmer Spectrum BX-59343 spectrophotometer. Samples were measured neat (ATR, Smiths Detection DuraSample IR II Diamond ATR). NMR spectra were recorded on Bruker AXR 300, VXR 400 S and Bruker AMX 600 instruments. HRMS



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and LR-MS were recorded on a Finnigan MAT 95Q instrument using electron ionization (El). Gas chromatography was performed with machines of type Hewlett-Packard 6890 or 5890 series II, using a column of type HP 5 (Hewlett-Packard, 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm; film thickness: 0.25 µm).

# Copper(I) Cyanide-Di(lithium chloride) (CuCN·2LiCl) Solution

A 1.0 M CuCN-2LiCl in THF solution was prepared by drying CuCN (7.17 g, 80 mmol) and LiCl (6.77 g, 160 mmol) in a Schlenk flask under high vacuum at 140 °C for 5 h. After cooling, anhyd THF (80 mL) was added and stirring was continued until all salts were dissolved (24 h).

#### **Zinc Chloride Solution**

A 1.0 M ZnCl<sub>2</sub> in THF solution was prepared by drying ZnCl<sub>2</sub> (136.3 g, 100 mmol) in a Schlenk flask under vacuum at 140  $^{\circ}$ C for 5 h. After cooling, anhyd THF (100 mL) was added and stirring was continued until all salts were dissolved (12 h).

# 2,2,6,6-Tetramethylpiperidin-1-ylmagnesium Chloride-Lithium Chloride (TMPMgCl-LiCl, 1)

In a dry and argon flushed Schlenk flask 2,2,6,6-tetramethylpiperidine (14.8 g, 105 mmol) was added to 1.40 M *i*-PrMgCl·LiCl in THF (71.4 mL, 100 mmol) at 25 °C and the mixture was stirred for 24 h at 25 °C. The freshly prepared TMPMgCl·LiCl was titrated prior to use at 0 °C with benzoic acid using 4-(phenylazo)diphenylamine as indicator.

# Magnesiation of 1,3-Dithiole-2-thione (2) with 2,2,6,6-Tetramethylpiperidin-1-ylmagnesium Chloride–Lithium Chloride (1); General Procedure 1 (GP1)

A dry and argon flushed Schlenk flask was charged with a solution of DTT (**2**; 1.0 equiv) in anhyd THF (0.5 M). 1 M TMPMgCl·LiCl in THF (**1**; 1.1 equiv) was added dropwise at -78 °C and the mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with I<sub>2</sub> in anhyd THF.

#### Magnesiation of 4-Functionalized 1,3-Dithiole-2-thione Derivatives 4 with 2,2,6,6-Tetramethylpiperidin-1-ylmagnesium Chloride–Lithium Chloride (1); General Procedure 2 (GP2)

A dry and argon flushed Schlenk flask was charged with a solution the corresponding 4-functionalized DTT derivative **4** (1.0 equiv) in anhyd THF (0.10–0.50 M). 1 M TMPMgCl-LiCl in THF (**1**; 1.1 equiv) was added dropwise at –78 °C and the mixture was stirred at this temperature for 0.5 h. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with iodine in anhyd THF.

# 1,3-Dithiol-2-one Derivatives 6; General Procedure 3 (GP3)

According to the literature procedure,<sup>8f</sup> the corresponding DTT derivative **5** (1.0 equiv) was dissolved in CHCl<sub>3</sub> (0.05 M) and AcOH (0.16 M). Hg(OAc)<sub>2</sub> (3.0 equiv) was added portionwise at 25 °C and the mixture was stirred at this temperature for the indicated time. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq NH<sub>4</sub>Cl solution.

# Tetrathiafulvalene Derivatives 7; General Procedure (GP4)

According to the literature procedure,<sup>9b</sup> the corresponding DTT derivative **5** (1.0 equiv) was dissolved in freshly distilled  $P(OEt)_3$  (0.1 M). The corresponding oxygen analogue **6** (1.2 equiv) was added at 25 °C

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and the mixture was stirred at 110 °C for the indicated time. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with sat. aq  $NH_4Cl$  solution.

# 4-Iodo-1,3-dithiole-2-thione (4a)<sup>16</sup>

According to GP1, DTT (**2**; 1.07 g, 8.0 mmol) was dissolved in anhyd THF (16 mL). TMPMgCl·LiCl (**1**; 7.93 mL, 8.8 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of I<sub>2</sub> (2.44 g, 9.6 mmol) in anhyd THF (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, it was then quenched with sat. aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (50 mL) and extracted with Et<sub>2</sub>O (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–Et<sub>2</sub>O, 95:5) yielding **4a** (1.65 g, 79%) as a brownish solid; mp 106–109 °C.

IR: 3066, 1045, 1015, 885, 758, 645 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.21 (s, 1 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 215.1, 133.8, 69.9.

MS (70 eV, El): *m*/*z* (%) = 260 (62) [M<sup>+</sup>], 184 (13), 135 (11), 133 (100), 127 (22), 89 (26), 88 (11), 76 (45).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>3</sub>HIS<sub>3</sub>: 259.8285; found: 259.8275.

#### 4-Bromo-1,3-dithiole-2-thione (4b)8f

According to GP1, DTT (**2**; 67.1 mg, 0.5 mmol) was dissolved in anhyd THF (1 mL). TMPMgCl·LiCl (**1**; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (195 mg, 0.6 mmol) in anhyd THF (1 mL) at -78 °C. The mixture was allowed to warm up to 25 °C over 12 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with Et<sub>2</sub>O (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–Et<sub>2</sub>O, 95:5) yielding **4b** (90 mg, 84%) as a yellow solid; mp 62–64 °C.

IR: 3071, 1182, 1047, 1012, 904, 881, 765 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.01 (s, 1 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 211.8, 127.4, 106.2.

MS (70 eV, El): *m*/*z* (%) = 214 (66), 212 (63) [M<sup>+</sup>], 57 (86), 57 (100), 55 (58), 45 (50).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>3</sub>HBrS<sub>3</sub>: 211.8424; found: 211.8429.

#### 4-(Methylthio)-1,3-dithiole-2-thione (4c)17

According to GP1, DTT (**2**; 1.07 g, 8.0 mmol) was dissolved in anhyd THF (16 mL). TMPMgCl·LiCl (**1**; 7.93 mL, 8.8 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of *S*-methyl methanethiosulfonate (1.21 g, 0.99 mL, 9.6 mmol) in anhyd THF (16 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with Et<sub>2</sub>O (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–Et<sub>2</sub>O, 95:5) yielding **4c** (1.08 g, 75%) as a brownish solid; mp 73–75 °C.

IR: 3058, 1191, 1056, 1044, 1028, 737 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.91 (s, 1 H), 2.51 (s, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 213.5, 138.5, 127.2, 19.8.

MS (70 eV, EI): m/z (%) = 182 (13), 180 (100) [M<sup>+</sup>], 104 (27), 103 (44), 89 (42), 76 (23), 57 (10), 45 (26).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>4</sub>H<sub>4</sub>S<sub>4</sub>: 179.9196; found: 179.9193.

#### (3-Chlorophenyl)(2-thioxo-1,3-dithiol-4-yl)methanone (4d)

According to GP1, DTT (**2**; 67.1 mg, 0.5 mmol) was dissolved in anhyd THF (1 mL). TMPMgCl·LiCl (**1**; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. A CuCN·2LiCl solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred at -40 °C for 15 min, before 3-chlorobenzoyl chloride (105 mg, 0.08 mL, 0.6 mmol) was added. The mixture was stirred at 25 °C for 12 h, it was then quenched with aq NH<sub>4</sub>Cl/NH<sub>3</sub> solution (8:1, 5 mL) and extracted with Et<sub>2</sub>O (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–Et<sub>2</sub>O, 9:1) yielding **4d** (84 mg, 62%) as a brown oil.

IR: 3061, 1628, 1511, 1266, 1075, 727 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.80–7.72 (m, 2 H), 7.71–7.59 (m, 1 H), 7.49 (t, J = 7.9 Hz, 1 H), 7.11 (s, 1 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl\_3):  $\delta$  = 210.6, 182.5, 145.3, 139.6, 137.2, 135.3, 133.4, 130.3, 128.8, 126.9.

MS (70 eV, El): *m/z* (%) = 274 (26), 272 (58) [M<sup>+</sup>], 196 (21), 141 (30), 139 (100), 111 (53), 75 (29).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>10</sub>H<sub>5</sub>OClS<sub>3</sub>: 271.9191; found: 271.9190.

# Ethyl 2-[(2-Thioxo-1,3-dithiol-4-yl)methyl]acrylate (4e)

According to GP1, DTT (**2**; 134 mg, 1.0 mmol) was dissolved in anhyd THF (2 mL). TMPMgCl·LiCl (**1**; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. A CuCN·2LiCl solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred at -40 °C for 15 min, before ethyl 2-(bromometh-yl)acrylate<sup>13</sup> (214 mg, 0.17 mL, 1.2 mmol) was added. The mixture was stirred at -40 °C for 4 h, it was then quenched with aq NH<sub>4</sub>Cl/NH<sub>3</sub> solution (8:1, 5 mL) and extracted with Et<sub>2</sub>O (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:1) yielding **4e** as a yellow oil (124 mg, 50%).

IR: 2978, 1706, 1630, 1184, 1138, 1101, 1051, 1022 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.76 (s, 1 H), 6.36 (s, 1 H), 5.75 (s, 1 H), 4.24 (q, J = 7.2 Hz, 2 H), 3.60 (s, 2 H), 1.32 (t, J = 7.2 Hz, 3 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl\_3):  $\delta$  = 213.5, 165.6, 144.2, 136.5, 128.1, 124.3, 61.4, 33.5, 14.1.

 $\begin{array}{l} \mathsf{MS} \ (70 \ \mathrm{eV}, \mathrm{El}): \ m/z \ (\%) = 246 \ (100) \ [\mathsf{M}^+], \ 172 \ (23), \ 170 \ (23), \ 142 \ (41), \\ 141 \ (40), \ 127 \ (19), \ 97 \ (15, \ 97 \ (76), \ 85 \ (22), \ 85 \ (12), \ 83 \ (17), \ 71 \ (31), \\ 71 \ (14), \ 70 \ (13), \ 69 \ (24), \ 57 \ (50), \ 56 \ (14), \ 55 \ (31), \ 53 \ (19), \ 45 \ (15), \ 45 \ (37), \ 44 \ (33), \ 43 \ (33), \ 43 \ (15), \ 40 \ (28). \end{array}$ 

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>S<sub>3</sub>: 245.9843; found: 245.9844.

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# Ethyl 4-(2-Thioxo-1,3-dithiol-4-yl)benzoate (4f)

According to GP1, DTT (**2**; 134 mg, 1.0 mmol) was dissolved in anhyd THF (2 mL). TMPMgCl·LiCl (**1**; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the mixture was added to a solution of ethyl 4-iodobenzoate (221 mg, 0.13 mL, 0.8 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.10 mmol) in anhyd NMP (1 mL) at 25 °C. The mixture was stirred at 25 °C for 1 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 1:1) yielding **4f** (191 mg, 84%) as a yellow solid; mp 136–138 °C.

IR: 1709, 1272, 1062, 1053, 754 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 8.10 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.3 Hz, 2 H), 7.28–7.22 (m, 1 H), 4.41 (q, *J* = 7.0 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl\_3):  $\delta$  = 211.6, 165.5, 144.8, 134.8, 131.3, 130.6, 126.3, 123.7, 61.4, 14.3.

MS (70 eV, El): *m*/*z* (%) = 283 (13), 282 (100) [M<sup>+</sup>], 237 (10), 178 (18), 161 (56), 89 (20).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>S<sub>3</sub>: 281.9843; found: 281.9836.

#### 4-(2-Thioxo-1,3-dithiol-4-yl)benzonitrile (4g)18

According to GP1, DTT (**2**; 1.34 g, 10.0 mmol) was dissolved in anhyd THF (20 mL). TMPMgCl·LiCl (**1**; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (1.83 g, 8.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.15 g, 1.0 mmol) in anhyd NMP (10 mL) at 25 °C. The mixture was stirred at 25 °C for 18 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 1:2) yielding **4g** (1.77 g, 94%) as a yellow solid; mp 196–199 °C.

IR: 3037, 2228, 1412, 1063, 783 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.74 (d, *J* = 8.3 Hz, 2 H), 7.53 (d, *J* = 8.3 Hz, 2 H), 7.28 (s, 1 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 210.9, 143.4, 134.9, 133.2, 127.0, 124.8, 117.9, 113.2.

MS (70 eV, EI): *m/z* (%) = 237 (16), 236 (18) [M + H<sup>+</sup>], 160 (12), 159 (100), 146 (11), 115 (12), 76 (22).

HRMS (El): m/z~[M +  $H^{\star}]$  calcd for  $C_{10}H_6NS_3$ : 235.9662; found: 235.9644.

#### 4-(4-Chlorophenyl)-1,3-dithiole-2-thione (4h)19

According to GP1, DTT (**2**; 269 mg, 2.0 mmol) was dissolved in anhyd THF (4 mL). TMPMgCl·LiCl (**1**; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 1-chloro-4-iodobenzene (382 mg, 1.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.2 mmol) in anhyd NMP (2 mL) at 25 °C. The mixture was stirred at 25 °C for 3 h, it was then quenched

with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **4h** (263 mg, 67%) as a yellow solid; mp 91–98 °C.

IR: 3022, 1486, 1402, 1079, 1069, 818, 761 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46–7.30 (m, 4 H), 7.11 (s, 1 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 211.7, 144.7, 135.7, 129.6, 129.5, 127.7, 122.3.

MS (70 eV, EI): m/z (%) = 245 (49), 245 (14), 244 (100) [M<sup>+</sup>], 170 (40), 155 (13), 136 (16), 89 (31), 75 (10).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>9</sub>H<sub>5</sub>ClS<sub>3</sub>: 243.9242; found: 243.9239.

# 4-[4-(Trifluoromethyl)phenyl]-1,3-dithiole-2-thione (4i)

According to GP1, DTT (**2**; 269 mg, 2.0 mmol) was dissolved in anhyd THF (4 mL). TMPMgCl·LiCl (**1**; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added at -78 °C and the mixture was added to a solution of 1-iodo-4-(trifluoromethyl)benzene (435 mg, 1.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.2 mmol) in anhyd NMP (2 mL) at 25 °C. The mixture was stirred at 25 °C for 14 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **4i** (287 mg, 66%) as a yellow solid; mp 122–123 °C.

IR: 1321, 1124, 1112, 1053, 832 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.71 (d, *J* = 8.2 Hz, 2 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 7.24 (s, 1 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 211.4, 144.1, 134.2, 131.5 (q, *J* = 32.8 Hz), 126.8, 126.4 (q, *J* = 3.9 Hz), 123.9, 123.6 (q, *J* = 272.4 Hz).

MS (70 eV, El): m/z (%) = 280 (10), 279 (13), 278 (100) [M<sup>+</sup>], 152 (15). HRMS (El): m/z [M<sup>+</sup>] calcd for C<sub>10</sub>H<sub>5</sub>F<sub>3</sub>S<sub>3</sub>: 277.9505; found: 277.9497.

#### 4-(p-Tolyl)-1,3-dithiole-2-thione (4j)<sup>19</sup>

According to GP1, DTT (**2**; 269 mg, 2.0 mmol) was dissolved in anhyd THF (4 mL). TMPMgCl·LiCl (**1**; 1.98 mL, 2.2 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A Zn-Cl<sub>2</sub> solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodotoluene (349 mg, 1.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.2 mmol) in anhyd NMP (2 mL) at 25 °C. The mixture was stirred at 25 °C for 3 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **4j** (284 mg, 79%) as a yellow solid; mp 91–98 °C.

IR: 1500, 1060, 1033, 762, 752 cm<sup>-1</sup>.

 $^1\text{H}$  NMR (300 MHz, CDCl\_3):  $\delta$  = 7.36–7.28 (m, 2 H), 7.28–7.19 (m, 2 H), 7.06 (s, 1 H), 2.40 (s, 3 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 212.4, 146.5, 140.0, 130.0, 128.3, 126.3, 121.0, 21.3.

MS (70 eV, El): *m/z* (%) = 225 (14), 224 (100) [M<sup>+</sup>], 178 (10), 149 (17), 148 (51), 147 (37), 115 (11), 91 (13), 69 (12), 43 (10).

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HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>10</sub>H<sub>8</sub>S<sub>3</sub>: 223.9788; found: 223.9766.

#### 4-(4-Nitrophenyl)-1,3-dithiole-2-thione (4k)18

According to GP1, DTT (**2**; 1.34 g, 10.0 mmol) was dissolved in anhyd THF (20 mL). TMPMgCl·LiCl (**1**; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-4-nitrobenzene (1.99 g, 8.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.15 g, 1.0 mmol) in anhyd NMP (10 mL) at 25 °C. The mixture was stirred at 25 °C for 14 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 1:1) yielding **4k** (1.57 g, 77%) as a brownish solid; mp 209–211 °C.

IR: 2923, 1503, 1340, 1080, 1062, 742, 688 cm<sup>-1</sup>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.32 (d, J = 8.8 Hz, 2 H), 7.60 (d, J = 8.8 Hz, 2 H), 7.33 (s, 1 H).

 $^{13}\text{C}$  NMR (151 MHz, CDCl\_3):  $\delta$  = 210.7, 148.0, 142.9, 136.6, 127.2, 125.4, 124.8.

MS (70 eV, El): *m*/*z* (%) = 257 (15), 256 (13), 255 (100) [M<sup>+</sup>], 149 (24), 133 (19), 121 (12), 89 (53), 63 (15).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>9</sub>H<sub>5</sub>O<sub>2</sub>NS<sub>3</sub>: 254.9482; found: 254.9479.

#### 4-(4-Methoxyphenyl)-1,3-dithiole-2-thione (41)<sup>19</sup>

According to GP1, DTT (**2**; 1.34 g, 10.0 mmol) was dissolved in anhyd THF (20 mL). TMPMgCl·LiCl (**1**; 9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodoanisole (1.87 g, 8.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.15 g, 1.0 mmol) in anhyd NMP (10 mL) at 25 °C. The mixture was stirred at 25 °C for 14 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **4l** (1.34 g, 70%) as a yellow solid; mp 104–107 °C.

IR: 1602, 1498, 1260, 1026, 770 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.35 (d, *J* = 8.7 Hz, 2 H), 7.00–6.90 (m, 3 H), 3.85 (s, 3 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 212.3, 160.7, 146.2, 127.9, 123.7, 120.0, 114.7, 55.4.

MS (70 eV, El): *m*/*z* (%) = 242 (13), 241 (12), 240 (100) [M<sup>+</sup>], 164 (40), 149 (70), 121 (18).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>10</sub>H<sub>8</sub>OS<sub>3</sub>: 239.9737; found: 239.9724.

#### 4-(3-Nitrophenyl)-1,3-dithiole-2-thione (4m)19

According to GP1, DTT (**2**; 134 mg, 1.0 mmol) was dissolved in anhyd THF (2 mL). TMPMgCl·LiCl (**1**; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-3-nitrobenzene (199 mg, 0.8 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.10 mmol) in anhyd NMP (1 mL)

at 25 °C. The mixture was stirred at 25 °C for 3 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 3:2) yielding **4m** (122 mg, 60%) as a yellow solid; mp 183–186 °C.

IR: 1515, 1346, 1081, 735, 719, 680 cm<sup>-1</sup>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.35–8.30 (m, 1 H), 8.28 (d, *J* = 8.2 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.69–7.62 (m, 1 H), 7.30 (s, 1 H).

 $^{13}\text{C}$  NMR (151 MHz, CDCl\_3):  $\delta$  = 210.8, 148.8, 142.7, 132.5, 132.1, 130.6, 124.5, 124.1, 121.2.

MS (70 eV, El): *m*/*z* (%) = 257 (11), 255 (100) [M<sup>+</sup>], 225 (19), 166 (11), 149 (12), 89 (31), 76 (12), 43 (23).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>9</sub>H<sub>5</sub>O<sub>2</sub>NS<sub>3</sub>: 254.9482; found: 254.9472.

#### 4-(3-Methoxyphenyl)-1,3-dithiole-2-thione (4n)

According to GP1, DTT (**2**; 134 mg, 1.0 mmol) was dissolved in anhyd THF (2 mL). TMPMgCl·LiCl (**1**; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (1.2 mL, 1.2 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 3-iodoanisole (187 mg, 0.8 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.10 mmol) in anhyd NMP (1 mL) at 25 °C. The mixture was stirred at 25 °C for 18 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 3:1) yielding **4n** (181 mg, 94%) as a yellow solid; mp 94–98 °C.

IR: 1575, 1165, 1054, 1034, 853, 757 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.34 (t, J = 7.9 Hz, 1 H), 7.14–7.07 (m, 1 H), 7.04–6.89 (m, 3 H), 3.85 (s, 3 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl\_3):  $\delta$  = 212.1, 160.1, 146.0, 132.1, 130.4, 122.1, 118.9, 115.0, 112.3, 55.4.

MS (70 eV, El): *m*/*z* (%) = 242 (14), 241 (14), 240 (100) [M<sup>+</sup>], 164 (52), 135 (10), 134 (16), 121 (21), 77 (11).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>10</sub>H<sub>8</sub>OS<sub>3</sub>: 239.9737; found: 239.9735.

#### 4,5-Dibromo-1,3-dithiole-2-thione (5a)8f

According to GP2, 4-bromo-1,3-dithiole-2-thione (**4b**; 1.66 g, 7.80 mmol) was dissolved in anhyd THF (31 mL). TMPMgCl·LiCl (**1**; 7.73 mL, 8.58 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (3.04 g, 9.36 mmol) in anhyd THF (15 mL) at -78 °C. The mixture was allowed to warm up to 25 °C over 12 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with Et<sub>2</sub>O (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane) yielding **5a** (2.07 g, 91%) as a yellow solid; mp 96–98 °C.

IR: 2921, 1077, 978, 876, 867 cm<sup>-1</sup>.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 208.7, 107.2.

 $\begin{array}{l} \mathsf{MS} \ (70 \ \mathrm{eV}, \mathrm{El}); \ m/z \ (\%) = 294 \ (63), 292 \ (100), 290 \ (45) \ [\mathrm{M}^+], 218 \ (19), \\ 216 \ (46), 214 \ (19), 213 \ (28), 211 \ (22), 169 \ (11), 167 \ (10), 137 \ (58), \\ 135 \ (58), 125 \ (29), 123 \ (26), 88 \ (26), 82 \ (17), 80 \ (18), 79 \ (11), 76 \ (22), \\ 60 \ (11), 57 \ (12), 56 \ (13), 44 \ (20), 44 \ (15), 43 \ (12). \end{array}$ 

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HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>3</sub>Br<sub>2</sub>S<sub>3</sub>: 289.7529; found: 289.7518.

#### 4-Bromo-5-iodo-1,3-dithiole-2-thione (5b)

According to GP2, 4-bromo-1,3-dithiole-2-thione (**4b**; 107 mg, 0.50 mmol) was dissolved in anhyd THF (1 mL). TMPMgCl·LiCl (**1**; 0.50 mL, 0.55 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of I<sub>2</sub> (152 mg, 0.60 mmol) in anhyd THF (1 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, it was then quenched with sat. aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (5 mL) and extracted with Et<sub>2</sub>O (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane) yielding **5b** (186 mg, 70%) as a yellow solid; mp 126–130 °C.

IR: 1483, 1071, 1047, 1018, 878 cm<sup>-1</sup>.

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 213.1, 112.8, 76.1.

MS (70 eV, El): *m*/*z* (%) = 342 (12), 340 (100), 338 (90) [M<sup>+</sup>], 264 (16), 262 (15), 213 (58).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>3</sub>BrIS<sub>3</sub>: 337.7390; found: 337.7383.

# 4-Bromo-5-(tert-butyldimethylsilyl)-1,3-dithiole-2-thione (5c)

According to GP2, 4-bromo-1,3-dithiole-2-thione (**4b**; 1.06 g, 5.0 mmol) was dissolved in anhyd THF (10 mL). TMPMgCl-LiCl (**1**; 4.95 mL, 5.50 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of TBDMSOTf (1.59 g, 6.0 mmol) in anhyd THF (10 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with Et<sub>2</sub>O (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane) yielding **5c** (1.55 g, 94%) as a yellow solid; mp 50–51 °C.

IR: 2924, 2853, 1074, 955, 835, 804, 774, 674 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 1.01 (s, 9 H), 0.41 (s, 6 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 215.4, 143.7, 110.6, 26.6, 18.5, -4.1.

$$\begin{split} \mathsf{MS} \; (70 \; \mathrm{eV}, \, \mathrm{EI}) \colon m/z \; (\%) &= 328 \; (86), \; 326 \; (74) \; [\mathrm{M}^+], \; 272 \; (100), \; 270 \; (91), \\ 195 \; (55), \; 193 \; (53), \; 149 \; (45), \; 115 \; (45), \; 73 \; (46), \; 71 \; (64), \; 57 \; (58). \end{split}$$

HRMS (EI): m/z [M<sup>+</sup>] calcd for C<sub>9</sub>H<sub>15</sub>BrS<sub>3</sub>Si (325.9289): found: 325.9272.

#### 4,5-Bis(methylthio)-1,3-dithiole-2-thione (5d)<sup>20</sup>

According to GP2, 4-(methylthio)-1,3-dithiole-2-thione (**4c**; 1.04 g, 5.8 mmol) was dissolved in anhyd THF (23 mL). TMPMgCl·LiCl (**1**; 5.75 mL, 6.39 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of *S*-methyl methanethiosulfonate (879 mg, 0.72 mL, 6.98 mmol) in anhyd THF (14 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with Et<sub>2</sub>O (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–Et<sub>2</sub>O, 95:5) yielding **5d** (1.13 g, 86%) as a green-brownish solid; mp 88–96 °C.

IR: 1666, 1417, 1054, 1028, 965, 737 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.50 (s, 6 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 210.8, 135.9, 19.2.

 $\begin{array}{l} \mathsf{MS} \ (70 \ \mathrm{eV}, \mathrm{EI}): \ m/z \ (\%) = 228 \ (29), \ 226 \ (100) \ [\mathrm{M}^+], \ 207 \ (20), \ 150 \ (28), \\ 135 \ (51), \ 103 \ (33), \ 91 \ (55), \ 88 \ (52), \ 76 \ (43), \ 73 \ (16), \ 61 \ (19), \ 48 \ (15), \\ 47 \ (17), \ 45 \ (35), \ 44 \ (10), \ 43 \ (26). \end{array}$ 

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>5</sub>H<sub>6</sub>S<sub>5</sub>: 225.9073; found: 225.9049.

# 4-Iodo-5-(4-methoxyphenyl)-1,3-dithiole-2-thione (5e)

According to GP2, 4-(4-methoxyphenyl)-1,3-dithiole-2-thione (**4**]; 240 mg, 1.0 mmol) was dissolved in anhyd THF (10 mL). TMPMgCl·Li-Cl (**1**; 0.99 mL, 1.1 mmol, 1.11 M in THF) was added dropwise at – 78 °C and the mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of  $I_2$  (305 mg, 1.2 mmol) in anhyd THF (1 mL) at –78 °C. The mixture was stirred at this temperature for 1 h, it was then quenched with sat. aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (5 mL) and extracted with Et<sub>2</sub>O (3 × 10 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **5e** (353 mg, 96%) as a yellow solid; mp 169–174 °C (decomp.).

IR: 1605, 1491, 1255, 1028, 829 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42 (d, *J* = 8.6 Hz, 2 H), 6.99 (d, *J* = 8.3 Hz, 2 H), 3.87 (s, 3 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 214.6, 160.9, 146.4, 130.5, 123.5, 114.4, 68.5, 55.4.

MS (70 eV, El): *m*/*z* (%) = 368 (8), 367 (8), 366 (53) [M<sup>+</sup>], 164 (11), 163 (100), 119 (9), 94 (9), 93 (8), 76 (5).

HRMS (EI): m/z [M<sup>+</sup>] calcd for C<sub>10</sub>H<sub>7</sub>OIS<sub>3</sub>: 365.8704; found: 365.8702.

# 4,4'-(2-Thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile (5f)

According to GP2, 4-(2-thioxo-1,3-dithiol-4-yl)benzonitrile (**4g**; 1.18 g, 5.0 mmol) was dissolved in anhyd THF (50 mL). TMPMgCl·LiCl (**1**; 4.95 mL, 5.5 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (6.0 mL, 6.0 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodobenzonitrile (916 mg, 4.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (578 mg, 0.5 mmol) in anhyd NMP (15 mL) at 25 °C. The mixture was stirred at 25 °C for 5 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:2) yielding **4f** (1.12 g, 83%) as a yellow solid; mp 184–189 °C (decomp.).

IR: 2226, 1037, 838, 810, 690, 554 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.63 (d, *J* = 8.3 Hz, 4 H), 7.31 (d, *J* = 8.3 Hz, 4 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 208.3, 138.5, 134.1, 133.0, 129.8, 117.5, 113.7.

MS (70 eV, EI): *m/z* (%) = 351 (19), 338 (14), 337 (18), 336 (79) [M<sup>+</sup>], 324 (12), 320 (100), 266 (20), 246 (26).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>17</sub>H<sub>8</sub>N<sub>2</sub>S<sub>3</sub>: 335.9850; found: 335.9845.

# 4,5-Bis(4-chlorophenyl)-1,3-dithiole-2-thione (5g)

According to GP2, 4-(4-chlorophenyl)-1,3-dithiole-2-thione (**4h**; 1.50 g, 6.13 mmol) was dissolved in anhyd THF (60 mL). TMPMgCl·LiCl (**1**; 6.07 mL, 6.74 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5. A ZnCl<sub>2</sub> solution (7.36 mL, 7.36 mmol, 1.0 M in THF) was added at -78 °C and the

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mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 1-chloro-4-iodobenzene (1.17 g, 4.90 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (708 mg, 0.6 mmol) in anhyd NMP (30 mL) at 25 °C. The mixture was stirred at 25 °C for 12 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc ( $3 \times 100$  mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 3:1) yielding **5g** (1.62 g, 93%) as a yellow solid; mp 155–158 °C.

IR: 1479, 1398, 1066, 1052, 798 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34–7.27 (m, 4 H), 7.18–7.11 (m, 4 H).

 $^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.7, 138.3, 135.7, 130.4, 129.4, 128.5.

 $\begin{array}{l} MS \ (70 \ eV, \ EI): \ m/z \ (\%) = 358 \ (18), \ 357 \ (13), \ 356 \ (61), \ 355 \ (20), \ 354 \\ (79) \ [M^+], \ 281 \ (10), \ 278 \ (100), \ 246 \ (21), \ 208 \ (29), \ 201 \ (12), \ 199 \ (37), \\ 176 \ (17), \ 163 \ (12), \ 155 \ (12), \ 139 \ (13). \end{array}$ 

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>15</sub>H<sub>8</sub>Cl<sub>2</sub>S<sub>3</sub>: 353.9165; found: 353.9161.

#### 4,5-Bis[4-(trifluoromethyl)phenyl]-1,3-dithiole-2-thione (5h)

According to GP2, 4-[4-(trifluoromethyl)phenyl]-1,3-dithiole-2-thione (**4i**; 1.39 g, 4.99 mmol) was dissolved in anhyd THF (40 mL). TMP-MgCl-LiCl (**1**; 4.95 mL, 5.49 mmol, 1.11 M in THF) was added dropwise at –78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (5.98 mL, 5.98 mmol, 1.0 M in THF) was added at –78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 1-iodo-4-(trifluoromethyl)benzene (1.09 g, 3.99 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (576 mg, 0.5 mmol) in anhyd NMP (20 mL) at 25 °C. The mixture was stirred at 25 °C for 14 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 3:1) yielding **5h** (1.50 g, 89%) as a yellow solid; mp 162–166 °C.

IR: 1615, 1316, 1122, 1112, 1065, 1016 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.60 (d, *J* = 8.2 Hz, 4 H), 7.34 (d, *J* = 8.0 Hz, 4 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 209.2, 138.6, 133.4, 131.6 (q, *J* = 33.1 Hz), 129.6, 126.3 (q, *J* = 3.9 Hz), 123.5 (q, *J* = 272.8 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -63.0.

MS (70 eV, El): m/z (%) = 424 (16), 423 (22), 422 (100) [M<sup>+</sup>], 345 (16), 345 (100), 313 (13), 233 (35), 189 (13), 76 (16).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>17</sub>H<sub>8</sub>F<sub>6</sub>S<sub>3</sub>: 421.9692; found: 421.9687.

#### 4,5-Di-p-tolyl-1,3-dithiole-2-thione (5i)

According to GP2, 4-(*p*-tolyl)-1,3-dithiole-2-thione (**4j**; 1.09 g, 4.88 mmol) was dissolved in anhyd THF (40 mL). TMPMgCl·LiCl (**1**; 4.84 mL, 5.37 mmol, 1.11 M in THF) was added dropwise at -78 °C and the mixture was stirred for 0.5 h. A ZnCl<sub>2</sub> solution (5.86 mL, 5.86 mmol, 1.0 M in THF) was added at -78 °C and the mixture was stirred for 15 min. The freshly prepared zinc reagent was added to a solution of 4-iodotoluene (851 mg, 3.90 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (564 mg, 0.49 mmol) in anhyd NMP (20 mL) at 25 °C. The mixture was stirred at 25 °C for 12 h, it was then quenched with sat. aq NH<sub>4</sub>Cl solution (50 mL) and extracted with EtOAc (3 × 100 mL), and the combined extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **5i** (1.09 g, 89%) as a yellow solid; mp 155–158 °C.

IR: 1064, 1047, 1024, 818, 799 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.10 (s, 8 H), 2.34 (s, 6 H).

 $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 211.0, 139.4, 139.1, 129.6, 129.0, 127.5, 21.3.

MS (70 eV, EI): *m/z* (%) = 316 (15), 315 (20), 314 (99) [M<sup>+</sup>], 239 (18), 238 (100), 237 (18), 221 (10), 179 (15), 178 (14).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>17</sub>H<sub>14</sub>S<sub>3</sub>: 314.0258; found: 314.0254.

#### 4-Bromo-1,3-dithiol-2-one (6a)8f

According to GP3, Hg(OAc)<sub>2</sub> (1.91 g, 6.0 mmol) was added portionwise to a solution of 4-bromo-1,3-dithiole-2-thione (**4b**; 426 mg, 2.0 mmol) in CHCl<sub>3</sub> (40 mL) and AcOH (12.5 mL) at 25 °C. The mixture was stirred at this temperature for 1.5 h and the precipitate was then filtered through Celite. The resulting solution was washed with sat. aq Na<sub>2</sub>CO<sub>3</sub> (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–Et<sub>2</sub>O, 95:5) yielding **6a** (337 mg, 86%) as a colorless solid; mp 60–65 °C.

IR: 2928, 1643, 956, 836, 804, 775 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ):  $\delta = 6.83$  (s, 1 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.4, 117.0, 99.5.

 $\begin{array}{l} \mathsf{MS} \ (70 \ \text{eV}, \ \text{El}): \ m/z \ (\%) = 198 \ (4), \ 196 \ (4) \ [\mathsf{M}^+], \ 170 \ (5), \ 168 \ (5), \ 111 \\ (4), \ 97 \ (5), \ 89 \ (10), \ 88 \ (6), \ 84 \ (6), \ 83 \ (5), \ 73 \ (7), \ 71 \ (6), \ 70 \ (16), \ 69 \ (7), \\ 61 \ (19), \ 57 \ (8), \ 55 \ (7), \ 45 \ (17), \ 45 \ (4), \ 43 \ (5), \ 43 \ (100), \ 42 \ (6), \ 41 \ (5). \end{array}$ 

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>3</sub>HOBrS<sub>2</sub>: 195.8652; found: 195.8647.

#### 4,4'-(2-Oxo-1,3-dithiole-4,5-diyl)dibenzonitrile (6b)

According to GP3, Hg(OAc)<sub>2</sub> (1.91 g, 6.0 mmol) was added portionwise to a solution of 4,4'-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile (**5f**; 673 mg, 2.0 mmol) in CHCl<sub>3</sub> (40 mL) and AcOH (12.5 mL) at 25 °C. The mixture was stirred at this temperature for 2 h and the precipitate was then filtered through Celite. The resulting solution was washed with sat. aq Na<sub>2</sub>CO<sub>3</sub> (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:2) yielding **6b** (480 mg, 75%) as a yellow solid; mp 210–214 °C.

IR: 2223, 1656, 840, 830, 554 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.60 (d, J = 8.3 Hz, 4 H), 7.31 (d, J = 8.6 Hz, 4 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 188.0, 135.5, 132.8, 130.1, 128.8, 117.7, 113.2.

MS (70 eV, EI): *m*/*z* (%) = 322 (11), 321 (24), 320 (100) [M<sup>+</sup>], 293 (17), 292 (74), 291 (13), 260 (31), 229 (12), 228 (66), 215 (15), 207 (10), 147 (10), 146 (94), 102 (17).

HRMS (EI): m/z [M<sup>+</sup>] calcd for C<sub>17</sub>H<sub>8</sub>ON<sub>2</sub>S<sub>2</sub>: 320.0078; found: 320.0072.

#### 4,5-Bis(4-chlorophenyl)-1,3-dithiol-2-one (6c)

According to GP3,  $Hg(OAc)_2$  (1.91 g, 6.0 mmol) was added portionwise to a solution of 4,5-bis(4-chlorophenyl)-1,3-dithiole-2-thione (**5g**; 711 mg, 2.0 mmol) in CHCl<sub>3</sub> (40 mL) and AcOH (12.5 mL) at 25 °C. The mixture was stirred at this temperature for 1 h and the precipitate was then filtered through Celite. The resulting solution was washed with sat. aq Na<sub>2</sub>CO<sub>3</sub> (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and after filtration, the sol-

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vents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **6c** (624 mg, 92%) as a yellow solid; mp 141–146 °C.

IR: 1648, 1587, 1482, 1090, 827 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.31–7.23 (m, 4 H), 7.19–7.09 (m, 4 H).

 $^{13}\text{C}$  NMR (101 MHz, CDCl\_3):  $\delta$  = 189.5, 135.1, 130.7, 129.8, 129.2, 128.0.

MS (70 eV, EI): m/z (%) = 340 (64), 338 (83) [M<sup>+</sup>], 310 (23), 278 (20), 248 (62), 246 (100), 241 (23), 176 (35), 157 (44), 111 (21).

HRMS (EI): m/z [M<sup>+</sup>] calcd for C<sub>15</sub>H<sub>8</sub>OCl<sub>2</sub>S<sub>2</sub>: 337.9394; found: 337.9388.

# 4,5-Bis[4-(trifluoromethyl)phenyl]-1,3-dithiol-2-one (6d)

According to GP3, Hg(OAc)<sub>2</sub> (1.91 g, 6.0 mmol) was added portionwise to a solution of 4,5-bis[4-(trifluoromethyl)phenyl]-1,3-dithiole-2-thione (**5h**; 845 mg, 2.0 mmol) in CHCl<sub>3</sub> (40 mL) and AcOH (12.5 mL) at 25 °C. The mixture was stirred at this temperature for 1 h and the precipitate was then filtered through Celite. The resulting solution was washed with sat. aq Na<sub>2</sub>CO<sub>3</sub> (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and after filtration, the solvents were evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, isohexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1) yielding **6d** (736 mg, 91%) as a yellowish solid; mp 123–125 °C.

IR: 1660, 1320, 1123, 1112, 1065, 838 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57 (d, *J* = 8.2 Hz, 4 H), 7.34 (d, *J* = 8.2 Hz, 4 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 188.9, 134.8, 131.2 (q, *J* = 32.8 Hz), 129.9, 128.6, 126.0 (q, *J* = 3.5 Hz), 123.5 (q, *J* = 272.4 Hz).

<sup>19</sup>F NMR (376 MHz,  $CDCl_3$ ):  $\delta = -63.0$ .

MS (70 eV, El): m/z (%) = 407 (15), 406 (68) [M<sup>+</sup>], 387 (10), 378 (31), 346 (19), 314 (45), 190 (11), 189 (100), 145 (13), 139 (12).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>17</sub>H<sub>8</sub>OF<sub>6</sub>S<sub>2</sub>: 405.9921; found: 405.9917.

#### 4,4',5,5'-Tetrakis(4-chlorophenyl)tetrathiafulvalene (7a)

According to GP4, 4,5-bis(4-chlorophenyl)-1,3-dithiol-2-one (**6c**; 170 mg, 0.5 mmol) was dissolved in freshly distilled  $P(OEt)_3$  (5 mL) and the mixture was stirred at 110 °C for 3 h. After cooling to 25 °C, the crude product was purified by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 9:1) yielding **7a** (87 mg, 54%) as a red solid; mp 260–262 °C.

IR: 1488, 1481, 1089, 1013, 838, 797 cm<sup>-1</sup>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.24 (d, J = 8.2 Hz, 8 H), 7.14 (d, J = 8.5 Hz, 8 H).

 $^{13}\text{C}$  NMR (151 MHz, CDCl\_3):  $\delta$  = 134.6, 130.7, 130.3, 129.1, 128.5, 108.4.

 $\begin{array}{l} \mathsf{MS} \ (70 \ \mathrm{eV}, \ \mathrm{EI}): \ m/z \ (\%) = 650 \ (19), \ 649 \ (21), \ 648 \ (60), \ 647 \ (34), \ 646 \\ (100), \ 645 \ (23), \ 644 \ (62) \ [\mathsf{M}^+], \ 493 \ (11), \ 491 \ (24), \ 489 \ (22), \ 324 \ (11), \\ 323 \ (15), \ 322 \ (10), \ 278 \ (14), \ 248 \ (53), \ 247 \ (13), \ 246 \ (83), \ 176 \ (31). \end{array}$ 

HRMS (EI): m/z [M<sup>+</sup>] calcd for C<sub>30</sub>H<sub>16</sub>Cl<sub>4</sub>S<sub>4</sub>: 643.8889; found: 643.8885.

# 4,4',5,5'-Tetrakis[4-(trifluoromethyl)phenyl]tetrathiafulvalene (7b)<sup>21</sup>

According to GP4, 4,5-bis(4-(trifluoromethyl)phenyl)-1,3-dithiol-2one (**6d**; 235 mg, 0.6 mmol) was dissolved in freshly distilled  $P(OEt)_3$ (5 mL) and the mixture was stirred at 110 °C for 3 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography (silica gel, isohexane–EtOAc, 98:2) yielding **7b** (127 mg, 63%) as a red solid; mp 230–233 °C.

IR: 2923, 1320, 1121, 1106, 1066, 842 cm<sup>-1</sup>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57–7.49 (m, 8 H), 7.38–7.29 (m, 8 H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ = 135.6, 130.8 (q, *J* = 32.8 Hz), 129.4, 126.1, 125.9 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.4 Hz), 108.7.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -62.9.

MS (70 eV, El): *m/z* (%) = 781 (11), 780 (24) [M<sup>+</sup>], 535 (10), 454 (13), 391 (10), 378 (22), 344 (100), 314 (11), 313 (53), 294 (10), 233 (10), 189 (55).

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>34</sub>H<sub>16</sub>F<sub>12</sub>S<sub>4</sub>: 779.9943; found: 779.9945.

#### 4,4'-(4',5'-Di-*p*-tolyltetrathiafulvalene-4,5-diyl)dibenzonitrile (7c)

According to GP4, 4,5-di-*p*-tolyl-1,3-dithiole-2-thione (**5i**; 314 mg, 1.0 mmol) was dissolved in freshly distilled  $P(OEt)_3$  (10 mL). 4,4'-(2-Oxo-1,3-dithiole-4,5-diyl)dibenzonitrile (**6b**; 384 mg, 1.2 mmol) was added at 25 °C and the mixture was stirred at 110 °C for 2 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:1) yielding **7c** (393 mg, 67%) as a brown solid; mp 263–265 °C.

IR: 2225, 849, 838, 813, 802, 778 cm<sup>-1</sup>.

 $^{13}\text{C}$  NMR (101 MHz, CDCl\_3):  $\delta$  = 138.5, 136.7, 132.6, 130.0, 129.7, 129.5, 129.3, 128.9, 128.4, 118.0, 112.5, 104.2, 21.3.

 $\begin{array}{l} \mathsf{MS} \ (70 \ \mathrm{eV}, \mathrm{El}); \ m/z \ (\%) = 588 \ (28), \ 587 \ (41), \ 586 \ (100) \ [\mathsf{M}^+], \ 451 \ (16), \\ \mathsf{440} \ (11), \ 420 \ (19), \ 419 \ (65), \ 397 \ (19), \ 293 \ (12), \ 260 \ (24), \ 238 \ (19), \\ \mathsf{229} \ (13), \ 228 \ (65), \ 215 \ (11), \ 206 \ (51), \ 205 \ (17), \ 191 \ (10), \ 189 \ (12), \\ \mathsf{146} \ (27), \ 135 \ (15), \ \mathsf{44} \ (10). \end{array}$ 

HRMS (EI): *m*/*z* [M<sup>+</sup>] calcd for C<sub>34</sub>H<sub>22</sub>N<sub>2</sub>S<sub>4</sub>: 586.0666; found: 586.0664.

#### 4,4'-{4',5'-Bis[4-(trifluoromethyl)phenyl]tetrathiafulvalene-4,5diyl}dibenzonitrile (7d)

According to GP4, 4,4'-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile (**5f**; 122 mg, 0.36 mmol) was dissolved in freshly distilled  $P(OEt)_3$  (4 mL). 4,5-Bis[4-(trifluoromethyl)phenyl]-1,3-dithiol-2-one (**6d**; 177 mg, 0.44 mmol) was added at 25 °C and the mixture was stirred at 110 °C for 1.5 h. After cooling to 25 °C, the crude product was purified twice by flash column chromatography (silica gel, isohexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:1) yielding **7d** (132 mg, 53%) as a dark red solid; mp 241.2–246.6 °C.

IR: 2227, 1321, 1125, 1111, 1067, 846 cm<sup>-1</sup>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.61–7.51 (m, 8 H), 7.37–7.26 (m, 8 H).

 $^{13}\text{C}$  NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  = 136.3, 135.4, 132.7, 130.9 (q, J = 32.8 Hz), 129.9, 129.7, 129.4, 125.9 (q, J = 3.6 Hz), 123.6 (q, J = 272.4 Hz), 117.9, 112.8, 110.0, 107.4.

<sup>19</sup>F NMR (376 MHz,  $CDCl_3$ ):  $\delta = -62.9$ .

MS (70 eV, El): *m*/*z* (%) = 696 (27), 695 (38), 694 (100) [M<sup>+</sup>], 505 (11), 347 (17), 314 (39), 228 (32).

HRMS (EI): m/z [M<sup>+</sup>] calcd for  $C_{34}H_{16}N_2F_6S_4$ : 694.0101; found: 694.0095.

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# **Supporting Information**

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560728.

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