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# Chlorotrimethylsilane and Sodium Iodide: A Remarkable Metal-Free Association for the Desulfurization of Benzylic Dithioketals under Mild Conditions

Guangkuan Zhao, Ling-Zhi Yuan, Mouad Alami\* and Olivier Provot\*

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**Abstract.** A novel metal-free process allowing the reductive desulfurization of various benzylic dithioketals to afford diarylmethane and benzylester derivatives with good to excellent yields is reported. At room temperature, this mild reduction process requires only the use of TMSCl and NaI in CH<sub>2</sub>Cl<sub>2</sub> and tolerates a large variety of functional groups.

**Keywords:** Desulfurization, Trimethylsilylchloride, Sodium iodide, Thioketal, Reduction

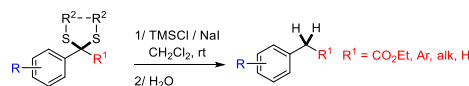
## Introduction

The Mozingo reaction consisting in the reductive desulfurization of dithioketals of ketones into methylene derivatives is an important chemical transformation.<sup>[1]</sup> This process which can be achieved under neutral conditions is preferable to Clemmensen or Wolff-Kishner reduction in particular with contraindicated acidic or basic sensitive substrates. Historically, the first desulfurization of dithioketals was reported in 1944 by Wolfrom and Karabinos, which successfully achieved this transformation using Raney-Ni.<sup>[1i]</sup> Examination of the literature reveals that Raney-Ni is from far the most reported process to achieve this reduction.<sup>[1a,2]</sup> Although effective, this transformation requires the use of Raney-Ni<sup>[3]</sup> in large excess (in the presence or absence of H<sub>2</sub>) and is sometimes accompanied by side-reactions when sensitive-substrates were used such as, debenzoylation,<sup>[1g]</sup> hydrogenolysis of C-halogen bonds,<sup>[4]</sup> reduction of multiple bonds,<sup>[5]</sup> deoxygenation of epoxides<sup>[1b]</sup> and others. As Raney-Ni is highly pyrophoric and difficult to handle in large quantities, a variety of non-pyrophoric nickel-containing reducing agents (NiCRAs) was developed and used in large excess to achieve the desulfurization of dithioketals.<sup>[6]</sup> Due to the toxicity of Ni and Ni-derivatives<sup>[7]</sup> and their use in more than stoichiometric amounts, other metals or metal salts (e.g. Na, Li, Mo, ZnCl<sub>2</sub>, CuCl<sub>2</sub> and TiCl<sub>4</sub>) were reported to desulfurize robust dithioketal substrates devoid of functional groups.<sup>[1a]</sup> Therefore,

there is an urgent need to find a novel metal-free alternative process to desulfurize dithioketals and we assumed that this transformation can be performed under mild conditions using of TMSCl and NaI.

We recently reported that the TMSCl/NaI association, which did not provide TMSI<sup>[8]</sup> in CH<sub>2</sub>Cl<sub>2</sub>, regioselectively reduced at rt a large variety of 1,2-diketones into deoxybenzoins.<sup>[8]</sup> This reducible system having a great functional group tolerance in CH<sub>2</sub>Cl<sub>2</sub> (on the contrary to TMSI), was also extended to selectively reduce various arylalkyl- $\alpha$ -diketones into alkylbenzylketones with high yields.<sup>[9]</sup> Herein, we wish to report the reductive properties of the TMSCl/NaI in CH<sub>2</sub>Cl<sub>2</sub> towards a variety of dithioketals, which were successfully desulfurized in good yields (Figure 1).

**Figure 1.** TMSCl/NaI promoted the reductive desulfurization of dithioketals.

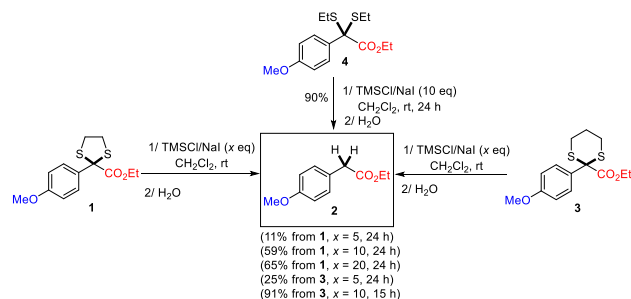


## Results and Discussion

At the beginning of this work, we studied the reactivity of TMSCl/NaI<sup>[10]</sup> in CH<sub>2</sub>Cl<sub>2</sub> at rt with thiolanester **1** (Scheme 1). We were pleasantly surprised to observe that in the presence of 20 equiv of

TMSCl/NaI, the dithiolane function of **1** was totally desulfurized into a methylene moiety to give benzylester **2** in a 65% yield after 24 h of reaction.

**Scheme 1.** TMSCl/NaI promoted the reductive desulfurization of thiolanester **1**, dithianester **3** and *bis*-ethylsulfane **4**.



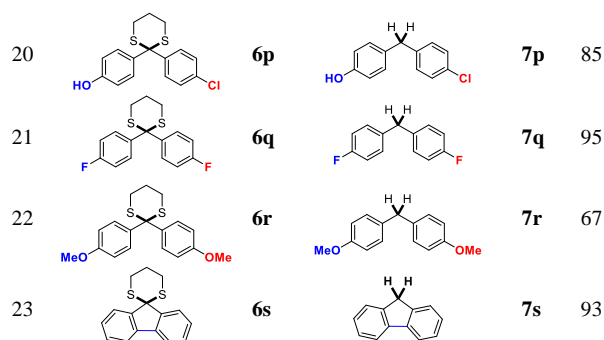
To optimize this welcome result, we tried to reduce the quantity of TMSCl/NaI from 20 to 10 and to 5 equiv. In the presence of 10 equiv of TMSCl/NaI, we observed a slight decline in yield (59% vs 65%) that dramatically decreased to 11% using 5 equiv of this combination. CH<sub>2</sub>Cl<sub>2</sub> was found to be the best solvent for this desulfurization reaction since the use of CH<sub>3</sub>CN, acetone, or toluene resulted in a decrease in the yield (e.g., 51% for CH<sub>3</sub>CN). Next, for structural comparisons, the dithianester **3** and *bis*-ethylsulfane **4** were also desulfurized in the presence of 10 equiv of TMSCl/NaI to give **2** in excellent yields. This result indicated that dithioketal **3** appeared to be more cooperative than thiolanester **1** for the desulfurizing process, which was achieved in a shorter reaction time of 15 h and with a lower quantity of TMSCl/NaI. As we have previously demonstrated in the deoxygenation of diketones,<sup>[8]</sup> replacing TMSCl/NaI combination by TMSI in CH<sub>2</sub>Cl<sub>2</sub> resulted in lower yields. In the presence of 10 equiv of TMSI, dithiane **3**, dithiolanester **1** and *bis*-ethylsulfane **4** were desulfurized in CH<sub>2</sub>Cl<sub>2</sub> to furnish **2** but with modest yields (63%, 40% and 45% respectively), significantly inferior to 91%, 59% and 90% obtained with the TMSCl/NaI system.

Next, we examined whether this unexpected desulfurization reaction was more general and could be extended to various thiolanes other than to  $\alpha$ -thiolanester and  $\alpha$ -dithianester derivatives. To this end, we tested the reductive properties of the TMSCl/NaI system with 2,2-diaryl-1,3-dithiolanes **5** and 2,2-diaryl-1,3-dithianes **6** to obtain the corresponding diarylmethane derivatives<sup>[11]</sup> of type **7**. A series of diarylthiolanes **5** and diaryldithianes **6** having different substituents on their aromatic rings were prepared from diarylketones and ethane-1,2-dithiol and/or propan-1,3-dithiol in the presence of BF<sub>3</sub>·Et<sub>2</sub>O. The results of the desulfurization of substrates **5** and **6** in CH<sub>2</sub>Cl<sub>2</sub> by the TMSCl/NaI system are reported in Table 1.<sup>[12]</sup> In entries 1 and 2, one can observe that the desulfurization process occurred well with 2,2-diphenyl-1,3-dithiolane **5a** and 2,2-diphenyl-1,3-dithiane **6a** in excellent yields of 88% and 90%, respectively. These results indicate that this

desulfurization reaction is not limited to  $\alpha$ -thiolanesters and can be applied to diaryldithioketals.

**Table 1.** Reductive desulfurization of diarylthiolanes **5** and diaryldithianes **6** by the TMSCl/NaI system<sup>a</sup>.

Entry	Thiolanes <b>5</b> or dithianes <b>6</b>	Diarylmethanes <b>7</b>	Yield <sup>b</sup> (%)
1	<b>5a</b>	<b>7a</b>	88
2	<b>6a</b>	<b>7a</b>	90
3	<b>5b</b>	<b>7b</b>	89 <sup>c</sup>
4	<b>6b</b>	<b>7b</b>	90 <sup>d</sup>
5	<b>6c</b>	<b>7c</b>	88
6	<b>6d</b>	<b>7d</b>	93
7	<b>6e</b>	<b>7e</b>	89
8	<b>6f</b>	<b>7f</b>	95
9	<b>6g</b>	<b>7g</b>	90
10	<b>6h</b>	<b>7h</b>	55
11	<b>6i</b>	<b>7i</b>	86
12	<b>5c</b>	<b>7i</b>	85
13	<b>6j</b>	<b>7j</b>	90
14	<b>6k</b>	<b>7k</b>	91
15	<b>6l</b>	<b>7l</b>	92
16	<b>6m</b>	<b>7m</b>	93
17	<b>6n</b>	<b>7n</b>	85
18	<b>6o</b>	<b>7o</b>	95
19	<b>5d</b>	<b>7p</b>	83

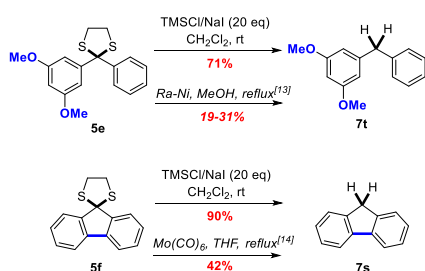


a) Typical reaction conditions: a mixture of dithioketal **5** or **6** (0.5 mmol) and NaI (5-10 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> for 5 min. Then, 5 to 10 mmol of TMSCl were added to the solution, which was stirred until completion (judged by TLC). b) Yield of isolated product. c) Almost no reaction when using 5 equiv of TMSCl/NaI. d) Yield of 40% when using 5 equiv of TMSCl/NaI.

Moreover, as we previously observed with arylalkyl- $\alpha$ -diketones,<sup>[9]</sup> the presence of electron-rich substituent(s) on aromatic ring(s) is not necessary for the reduction process to occur (entries 1 and 2). In entries 3-10, we were pleased to observe that the presence of electron-withdrawing groups (EWGs) as Cl, F, Br, CF<sub>3</sub> on *ortho*, *meta* and *para*-positions did not affect the yield of the desulfurization process and the corresponding diarylmethanes **7b-h** were obtained with excellent yields. As expected, the presence of electron-donating groups (EDGs) on aromatic ring(s) was also allowed as demonstrated with the desulfurization of diaryldithianes **6i-o** (entries 11-18). Similarly, push-pull-, pull-pull- and push-push-diaryldithianes **6p-r** were successfully desulfurized to furnish diarylmethanes **7p-r** with good yields (from 67 to 95%). The results depicted in entries 1-4, 11-12 and 19-20, clearly indicated that thiolanes **5** and dithianes **6** displayed similar reactivity as were desulfurized in 24 h with comparable yields. Moreover, a variety of functional groups (e.g., OMe, halogens, OH, CO<sub>2</sub>Me, NO<sub>2</sub>, aryl) remained unchanged using this mild process.

To show the superiority of this process with respect to other methods using Raney-Ni<sup>[13]</sup> or Mo(CO)<sub>6</sub>,<sup>[14]</sup> dithiolanes **5e** and **5f** were desulfurized by TMSCl/NaI (Scheme 2).

**Scheme 2.** Reductive desulfurization of **5e** and **5f** by TMSCl/NaI.



Comparison of the yields obtained using the TMSCl/NaI association vs Raney-Ni or Mo(CO)<sub>6</sub>

clearly supports that this metal-free process is particularly welcome since the yields of reduced derivatives are largely higher (Scheme 2, **7t**: 71%, **7s**: 90%).

**Table 2.** Reductive desulfurization of arylalkyldithioketals by TMSCl/NaI<sup>a</sup>.

Entry	Arylalkyldithioketals <b>8</b>	Arylalkylmethanes <b>9</b>	Yield <sup>b</sup> (%)
1			<b>9a</b> 78
2			<b>9a</b> 83
3			<b>9b</b> 76
4			<b>9c</b> 85 <sup>c</sup>
5			<b>9d</b> 85
6			<b>9e</b> 88

a) Typical reaction conditions: a mixture of dithioketal **8** (0.5 mmol) and NaI (10 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> for 5 min. Then, 10 mmol of TMSCl were added to the solution, which was stirred for 40 h. b) Yield of isolated product. c) **8d** was stirred for 20 h with 10 equiv of TMSCl/NaI.

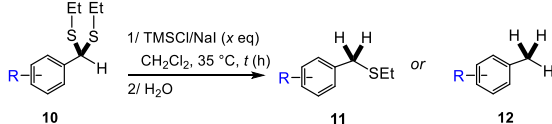
Next, we focused our attention on the desulfurization of a variety of arylalkyldithioketals **8** and the operating conditions optimization was realized with dithiane **8a** and thiolane **8b**, which were totally desulfurized at 35 °C using TMSCl/NaI (20 equiv) in CH<sub>2</sub>Cl<sub>2</sub> to give the expected 1,2,3,4-tetrahydronaphthalene **9a** (78% and 83%, resp.) after 40 h of reaction (Table 2, entries 1 and 2). Using these conditions, thiolanes **8c** and **8d** were well desulfurized to give the reduced derivatives **9b** and **9c** with good yields (entries 3 and 4, 76% and 85%, resp.). As showed in entry 5 the desulfurization process was successfully applied to spiro[thiochromane-4,2'-[1,3]dithiolane] **8e** to afford the reduced derivative **9d** in a good yield of 85%. Finally, the reduction of dithiane **8f** was effective and provided 2-ethylnaphthalene **9e** in a good yield (entry 6, 88%).

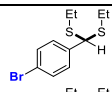
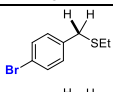
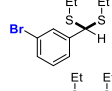
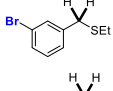

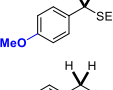
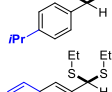
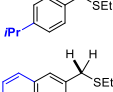
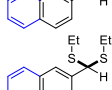
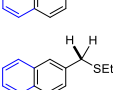
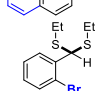
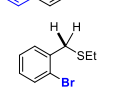
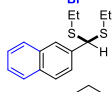
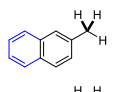
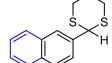
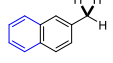
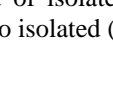
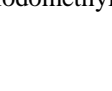
To complete this study, we next examined the reducing properties of dithioketals of type **10**, prepared from aromatic aldehydes (Table 3).

In the presence of TMSCl/NaI, *bis*-ethylsulfanes **10a-e** were partially desulfurized to give the corresponding half-desulfurized derivatives **11a-e** in fair to good yields (Table 3, entries 1-5). By adjusting the quantities of TMSCl/NaI and the reaction time (e.g., 5 equiv, 20 h, entry 6), ethyl(naphthalen-2-ylmethyl)sulfane **10e** was half-desulfurized with a

better yield of 80%. Similarly, using the same reaction conditions, *ortho*-brominated dithioketal **10f** was half-desulfurized to provide **11f** (90%, entry 7). Finally, as hoped, a total desulfurization reaction of *bis*-ethylsulfane **10e** and dithiane **10g** was observed by increasing the charge of TMSCl/NaI to 20 equiv yielding, after 40 h of reaction, the desulfurized 2-methylnaphthalene **12a** in good yields (84% and 75%, respectively, entries 8 and 9). These results indicated that by using a *bis*-ethylsulfane of aldehyde, it is possible to prepare half- and totally-desulfurized products by adjusting carefully the quantity of TMSCl/NaI, the temperature and the reaction time (TLC).

**Table 3.** Desulfurization of 2-aryldithioketals **10** (prepared from aromatic aldehydes) by the TMSCl/NaI combination.



Entry	Dithioketals <b>10</b>	<i>x</i>	<i>t</i> (h)	Reduced products <b>11</b> or <b>12</b>	Yield <sup>a</sup> (%)
1		10a	20 40		<b>11a</b> 92
2		10b	20 40		<b>11b</b> 81
3		10c	10 20		<b>11c</b> 85
4		10d	10 20		<b>11d</b> 82
5		10e	10 20		<b>11e</b> 53 <sup>b</sup>
6		10e	5 20		<b>11e</b> 80
7		10f	5 20		<b>11f</b> 90
8		10e	20 40		<b>12a</b> 84
9		10g	20 40		<b>12a</b> 75

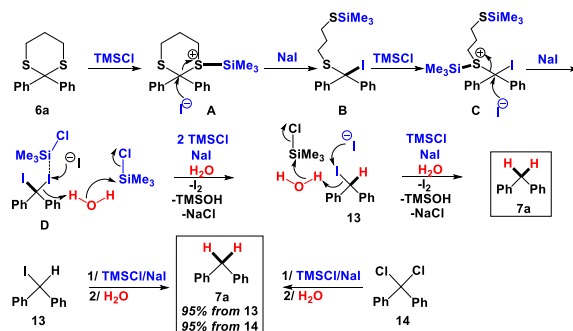
<sup>a</sup>) Yield of isolated product. <sup>b</sup>) 2-(Iodomethyl)naphthalene was also isolated (35%).

Based on the above results obtained with the desulfurization of dithianes, thiolanes and *bis*-ethylsulfanes, we proposed a possible mechanism illustrated in Scheme 3.

First, as we previously demonstrated with the regioselective reduction of benzil derivatives<sup>[8]</sup> and to definitively prove that the TMSCl/NaI combination is the reducing system rather than small amounts of HI formed between TMSCl/NaI and traces of water present in the solvent, several control experiments were achieved. When performing the reduction of dithiane **6j** in CH<sub>2</sub>Cl<sub>2</sub> at rt for 24 h with 0.1, 1 or 2

equiv of aqueous HI (wt 57%), no desulfurization occurred.

**Scheme 3.** A proposed reaction mechanism for the desulfurization of dithiane **6a** by TMSCl/NaI combination.



Moreover, adding a large excess of base (20 equiv.) as Na<sub>2</sub>CO<sub>3</sub> or Et<sub>3</sub>N (to neutralize HI if formed) in CH<sub>2</sub>Cl<sub>2</sub> in the presence of TMSCl/NaI did not inhibit the desulfurization of dithiane **6j** which was transformed into the expected reduced compound **7j** in good yields (90% using Na<sub>2</sub>CO<sub>3</sub> and 60% using Et<sub>3</sub>N).

On the contrary to previous expectations,<sup>[15]</sup> we believe that, in methylene chloride, a sulfur atom of dithioketal **6a** reacted with the silicon of TMSCl to give a possible sulfonium complex **A**. An iodide from NaI<sup>[16]</sup> then added on the benzylic carbon of **A** (or to a benzylic stabilized-carbocation) to give a half-open intermediate **B**. Then, the second sulfur atom of **B** attached on the benzylic carbon reacted with a second equiv of TMSCl to give **C**,<sup>[17]</sup> which added another iodide to provide a very instable diiododiphenylmethane<sup>[18]</sup> derivative **D**. Finally, hydrolysis of **D** in the presence of NaI and TMSCl<sup>[19]</sup> would led to a (iodomethylene)diphenyl derivative **13**<sup>[20]</sup> and furthermore into the desulfurized compound **7a** after the release of two equiv of I<sub>2</sub>. Note that, at the end of the reaction and after hydrolysis, the methylene chloride solution took a brown hue, which was discolored by sodium thiosulphate revealing the presence of I<sub>2</sub>.

To validate the transformation of the highly unstable electrophilic diiododiphenylmethane **D** into **E** and finally into **7a**, by structural analogy,<sup>[18]</sup> we mixed the more stable dichlorodiphenylmethane **14** with 10 equiv of TMSCl/NaI<sup>[21]</sup> for 12 h in CH<sub>2</sub>Cl<sub>2</sub>. Similarly, **13** which was prepared by independent synthesis, was reacted with TMSCl/NaI for 12 h. In both cases, after hydrolysis, diphenylmethane **7a** was obtained with an excellent identical yield of 95% indicating that di- and mono-iodinated derivatives **D** and **13** are possible intermediates in the desulfurizing process.

## Conclusion

In conclusion, we have found a very efficient metal-free process to desulfurize a large variety of dithioketals of ketones and aldehydes bearing electron-donating and electron-withdrawing substituents on aromatic rings. The great advantages

of this novel desulfurizing process compared to other methods which require the use of toxic metals are (i) low costs of non-toxic reagents (TMSCl and NaI) which are easy to handle, (ii) reactions occur at room temperature, (iii) high to excellent yields are obtained, (iv) functional groups on aromatics are well tolerated whatever their position (*o*, *m*, *p*), (v) ease of treatment and purification (hydrolysis followed by chromatography on SiO<sub>2</sub>). We now believe that this novel green-process, which appear to be compatible with environmental requirements would quickly find large scale industrial applications.

## Experimental Section

### General experimental methods

All glasswares were oven-dried at 140 °C and all reactions were conducted under an argon atmosphere. Solvents: cyclohexane, ethyl acetate (EtOAc), for chromatography, were technical grade. All new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR, IR spectroscopy, HRMS. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR and spectra were measured in CDCl<sub>3</sub> with a Bruker Avance 300. <sup>1</sup>H NMR chemical shifts are reported in ppm from an internal standard TMS or of residual chloroform (7.26 ppm). The following abbreviation are used: m (multiplet), s (singlet), brs (broad singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet). <sup>13</sup>C chemical shifts are reported in ppm from the central peak of deuteriochloroform (77.14). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm<sup>-1</sup>). High-resolution mass spectra were recorded on a Bruker Daltonics microTOF-Q instrument. Analytical TLC was performed on Merck precoated silica gel 60 F-254 plates. Merck silica gel 60 (230-400 mesh) was used for column chromatography. The plates were visualized by either UV light (254 nm) or by a phosphomolybdic acid solution in ethanol.

### General procedure for the synthesis of compounds 1, 3, 4, 5, 6, 8, 10.

To a solution of ketone or aldehyde (1 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added the thiol derivative (EtSH (10 mmol), 1,2-ethanedithiol (5 mmol or 1,3-propanedithiol (5 mmol)), followed by 1 mL of boron trifluoride etherate. The solution was stirred at room temperature until disappearance of starting material (judged by TLC). Then, H<sub>2</sub>O (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (30 mL) were added to the solution. The organic layer was separated, washed with H<sub>2</sub>O (2 x 10 mL) and saturated NaCl solution (2 x 10 mL), dried over MgSO<sub>4</sub>, and concentrated under reduced pressure to give a residue which was purified by chromatography on silica gel.

### General procedure for the synthesis of compounds 7, 9, 11, 12a.

A mixture of thioketal (0.5 mmol) and NaI (5 to 10 mmol, see text) was stirred in CH<sub>2</sub>Cl<sub>2</sub> for 5 min. Then, 5 to 10 mmol of TMSCl were added to the solution which was stirred until completion (judged by TLC). The reaction was hydrolyzed for 5 min with H<sub>2</sub>O (5 mL) and the brown mixture was washed with of a saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Organic layers were dried over MgSO<sub>4</sub> and concentrated under reduced pressure to give a residue which was purified by chromatography on silica gel.

### Ethyl 2-(4-methoxyphenyl)-1,3-dithiolane-2-carboxylate (1):

Yellow oil, yield 99%, 281.5 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.56 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.54 – 3.36 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR

(75 MHz, CDCl<sub>3</sub>) δ = 171.4 (Cq), 159.4 (Cq), 131.4 (Cq), 128.4 (2 CH), 113.6 (2 CH), 73.6 (Cq), 62.7 (CH<sub>2</sub>), 55.4 (CH<sub>3</sub>), 40.4 (2 CH<sub>2</sub>), 14.0 (CH<sub>3</sub>). IR (neat): 1729, 1723, 1607, 1580, 1508, 1464, 1441, 1417, 1365, 1298, 1250, 1206, 1177, 1115, 1094, 1027, 955, 838, 795, 749 cm<sup>-1</sup>. HRMS (ESI): *m/z* [2M+Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>32</sub>O<sub>6</sub>NaS<sub>4</sub>: 591.0979; found: 591.0984.

### Ethyl 2-(4-methoxyphenyl)-1,3-dithiane-2-carboxylate (3):

White solid, mp 43.1 – 43.4 °C, yield 99%, 295.4 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.63 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.17 – 3.07 (m, 2H), 2.83 – 2.70 (m, 2H), 2.11 – 1.86 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 170.4 (Cq), 159.5 (Cq), 130.1 (Cq), 129.1 (2 CH), 114.0 (2 CH), 62.6 (CH<sub>2</sub>), 59.4 (Cq), 55.4 (CH<sub>3</sub>), 29.1 (2 CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>). IR (neat): 2903, 1722, 1607, 1509, 1464, 1414, 1365, 1299, 1251, 1209, 1179, 1155, 1116, 1094, 1026, 905, 846, 833, 792, 729 cm<sup>-1</sup>. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub>S<sub>2</sub>: 299.0776 found: 299.0779.

### Ethyl 2,2-bis(ethylthio)-2-(4-methoxyphenyl)acetate (4):

Yellow oil, yield 99%, 311.3 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.47 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.59 – 2.37 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 170.8 (Cq), 159.1 (Cq), 130.5 (Cq), 129.1 (2 CH), 113.5 (2 CH), 68.4 (Cq), 62.5 (CH<sub>2</sub>), 55.3 (CH<sub>3</sub>), 25.1 (2 CH<sub>2</sub>), 14.1 (CH<sub>3</sub>), 13.4 (2 CH<sub>3</sub>). IR (neat): 2930, 1609, 1581, 1509, 1464, 1442, 1366, 1251, 1220, 1176, 1117, 1094, 1029, 976, 908, 839, 792, 754 cm<sup>-1</sup>. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>NaS<sub>2</sub>: 337.0908; found: 337.0904.

### Ethyl 2-(4-methoxyphenyl)acetate (2)<sup>[22]</sup>:

Colorless oil, for yield; see the text. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.20 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.55 (s, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 172.0 (Cq), 158.8 (Cq), 130.4 (2 CH), 126.4 (Cq), 114.1 (2 CH), 60.9 (CH<sub>2</sub>), 55.4 (CH<sub>3</sub>), 40.6 (CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). IR (neat): 2905, 1613, 1595, 1512, 1488, 1440, 1406, 1345, 1239, 1172, 1091, 1015, 912, 843, 816, 803, 767, 718 cm<sup>-1</sup>. HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>15</sub>O<sub>3</sub>: 195.1021; found: 195.1020.

### 2,2-Diphenyl-1,3-dithiolane (5a)<sup>[23]</sup>:

White solid, mp 102.3 – 102.5 °C, yield 99%, 255.8 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.69 – 7.65 (m, 4H), 7.37 – 7.25 (m, 6H), 3.45 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 144.7 (2 Cq), 128.3 (4 CH), 128.0 (4 CH), 127.3 (2 CH), 76.9 (Cq), 40.2 (2 CH). IR (neat): 2924, 1591, 1481, 1442, 1415, 1314, 1275, 1253, 1236, 1078, 1031, 998, 951, 908, 873, 852, 755, 737 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>15</sub>S<sub>2</sub>: 259.0610; found: 259.0616.

### 2,2-Diphenyl-1,3-dithiane (6a)<sup>[24]</sup>:

White solid, mp 110.7 – 110.9 °C, yield 99%, 269.7 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.76 – 7.73 (m, 4H), 7.41 – 7.28 (m, 6H), 2.82 (t, *J* = 5.7 Hz, 4H), 2.08 – 1.99 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 142.6 (2 Cq), 129.4 (4 CH), 128.5 (4 CH), 127.6 (2 CH), 62.8 (Cq), 29.5 (2 CH<sub>2</sub>), 24.6 (CH<sub>2</sub>). IR (neat): 3057, 2904, 1594, 1481, 1443, 1422, 1312, 1276, 1180, 1150, 1080, 1034, 1004, 913, 892, 964, 801, 753, 735, 696 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>17</sub>S<sub>2</sub>: 273.0766; found: 273.0770.

### 2-(4-Chlorophenyl)-2-phenyl-1,3-dithiolane (5b):

White solid, mp 56.2 – 56.4 °C, yield 99%, 290.0 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.67 – 7.61 (m, 4H), 7.41 – 7.22 (m, 5H), 3.48 – 3.40 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 144.0 (Cq), 143.5 (Cq), 133.0 (Cq), 129.7 (2 CH), 128.1 (2 CH), 128.0 (2 CH), 127.9 (2 CH), 127.4 (CH), 76.3 (Cq), 40.3 (2 CH<sub>2</sub>). IR (neat): 2923, 1486, 1443, 1418, 1396, 1276, 1242, 1180, 1158, 1091, 1032, 1012, 955, 870,

830, 801, 784, 752, 735, 712 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub><sup>35</sup>ClS<sub>2</sub>: 293.0220; found: 293.0231.  
**2-(4-Chlorophenyl)-2-phenyl-1,3-dithiane (6b):**

White solid, mp 99.1 – 99.4 °C, yield 99%, 303.8 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.78 – 7.74 (m, 4H), 7.46 – 7.31 (m, 5H), 2.90 – 2.73 (m, 4H), 2.11 – 1.96 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 142.1 (Cq), 141.2 (Cq), 133.3 (Cq), 130.9 (2 CH), 129.1 (2 CH), 128.4 (4 CH), 127.7 (CH), 62.1 (Cq), 29.3 (2 CH<sub>2</sub>), 24.3 (CH<sub>2</sub>). IR (neat): 1568, 1485, 1444, 1423, 1410, 1396, 1345, 1313, 1275, 1244, 1181, 1153, 1121, 1092, 1033, 1013, 969, 908, 892, 868, 850, 811, 783, 757, 737, 708 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub><sup>35</sup>ClS<sub>2</sub>: 307.0376; found: 307.0380.

**2-(4-Fluorophenyl)-2-phenyl-1,3-dithiane (6c):**

White solid, mp 94.9 – 95.2 °C, yield 99%, 287.5 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.68 – 7.52 (m, 4H), 7.30 – 7.16 (m, 3H), 6.93 (t, *J* = 8.7 Hz, 2H), 2.76 – 2.63 (m, 4H), 1.97 – 1.87 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 162.1 (d, *J* = 253.7 Hz, Cq), 142.4 (Cq), 138.5 (d, *J* = 2.0 Hz, Cq), 131.3 (d, *J* = 8.0 Hz, 2 CH), 129.4 (2 CH), 128.6 (2 CH), 127.8 (CH), 115.2 (d, *J* = 21.2 Hz, 2 CH), 62.2 (Cq), 29.5 (2 CH<sub>2</sub>), 24.5 (CH<sub>2</sub>).  
<sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ = -117.4. IR (neat): 2905, 1598, 1501, 1444, 1408, 1276, 1223, 1160, 1100, 1033, 1015, 912, 873, 853, 818, 802, 788, 740 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>F<sub>2</sub>S<sub>2</sub>: 291.0672; found: 291.0672.

**2-(4-Bromophenyl)-2-phenyl-1,3-dithiane (6d):**

White solid, mp 109.6 – 109.9 °C, yield 99%, 347.8 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.73 – 7.64 (m, 4H), 7.53 – 7.49 (m, 2H), 7.41 – 7.28 (m, 3H), 2.87 – 2.74 (m, 4H), 2.06 – 1.98 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 142.2 (Cq), 141.8 (Cq), 131.6 (2 CH), 131.4 (2 CH), 129.2 (2 CH), 128.6 (2 CH), 127.9 (CH), 121.8 (Cq), 62.3 (Cq), 29.4 (2 CH<sub>2</sub>), 24.4 (CH<sub>2</sub>). IR (neat): 2905, 1482, 1391, 1276, 1181, 1075, 1033, 1008, 907, 866, 850, 808, 785, 755, 729, 695, 675 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub><sup>81</sup>BrS<sub>2</sub>: 352.9850; found: 352.9851.

**2-Phenyl-2-(4-(trifluoromethyl)phenyl)-1,3-dithiane (6e):**

White solid, mp 108.3 – 108.6 °C, yield 99%, 337.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.78 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.50 (m, 4H), 7.32 – 7.16 (m, 3H), 2.86 – 2.58 (m, 4H), 1.98 – 1.89 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 146.9 (Cq), 142.0 (Cq), 130.0 (2 CH), 129.6 (Cq), 129.2 (2 CH), 128.7 (2 CH), 128.0 (CH), 125.5 (d, *J* = 3.5 Hz, 2 CH), 124.0 (q, *J* = 270.3 Hz, Cq), 62.3 (Cq), 29.4 (2 CH<sub>2</sub>), 24.4 (CH<sub>2</sub>).  
<sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ = -62.6. IR (neat): 2906, 1615, 1483, 1444, 1408, 1321, 1277, 1245, 1164, 1126, 1111, 1069, 1034, 1018, 918, 873, 856, 819, 792, 746, 736, 697 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>16</sub>F<sub>3</sub>S<sub>2</sub>: 341.0640; found: 341.0650.

**2-(3-Chlorophenyl)-2-phenyl-1,3-dithiane (6f):**

White solid, mp 81.8 – 82.0 °C, yield 99%, 303.8 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.81 (s, 1H), 7.70 – 7.64 (m, 3H), 7.46 – 7.23 (m, 5H), 2.93 – 2.68 (m, 4H), 2.12 – 1.92 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 144.9 (Cq), 142.2 (Cq), 134.5 (Cq), 129.7 (2 CH), 129.2 (2 CH), 128.6 (2 CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 62.2 (Cq), 29.4 (2 CH<sub>2</sub>), 24.4 (CH<sub>2</sub>). IR (neat): 3058, 2951, 2904, 1588, 1566, 1495, 1472, 1444, 1422, 1407, 1276, 1244, 1155, 1080, 1033, 1002, 942, 904, 877, 853, 783, 771, 741, 711 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub><sup>35</sup>ClS<sub>2</sub>: 307.0376; found: 307.0379.

**2-(2-Bromophenyl)-2-phenyl-1,3-dithiane (6g):**

Colorless oil, yield 88%, 309.2 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.29 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.26 – 7.07 (m, 4H), 2.94 – 2.71 (m, 4H), 2.06 – 1.91 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 143.0 (Cq), 140.9 (Cq), 136.4 (CH), 132.6 (CH), 128.9 (CH), 128.3 (2 CH), 127.8 (2 CH), 127.5 (CH), 126.4 (CH), 124.5 (Cq), 70.7 (Cq), 29.8 (2 CH<sub>2</sub>), 24.0 (CH<sub>2</sub>). IR (neat): 2906, 1596, 1562, 1494, 1482, 1454, 1444,

1423, 1278, 1158, 1117, 1023, 901, 861, 757, 740, 695, 676 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub><sup>81</sup>BrS<sub>2</sub>: 352.9850; found: 352.9853.

**2-(4-Nitrophenyl)-2-phenyl-1,3-dithiane (6h):**

Yellow solid, mp 127.4 – 127.7 °C, yield 99%, 314.2 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.18 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.27 (m, 3H), 2.88 – 2.71 (m, 4H), 2.08 – 1.99 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 150.3 (Cq), 147.2 (Cq), 141.5 (Cq), 130.6 (2 CH), 129.1 (2 CH), 128.9 (2 CH), 128.3 (CH), 123.6 (2 CH), 62.1 (Cq), 29.4 (2 CH<sub>2</sub>), 24.2 (CH<sub>2</sub>). IR (neat): 2905, 1602, 1516, 1486, 1444, 1346, 1310, 1277, 1109, 1033, 1014, 916, 861, 841, 799, 756, 738, 703 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>NO<sub>2</sub>S<sub>2</sub>: 318.0617; found: 318.0623.

**2-(4-Methoxyphenyl)-2-phenyl-1,3-dithiane (6i):**

White solid, mp 104.7 – 104.9 °C, yield 99%, 299.4 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.74 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.40 – 7.27 (m, 3H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 2.82 – 2.73 (m, 4H), 2.07 – 1.95 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 158.9 (Cq), 142.8 (Cq), 134.7 (Cq), 130.7 (2 CH), 129.4 (2 CH), 128.5 (2 CH), 127.6 (CH), 113.7 (2 CH), 62.5 (Cq), 55.3 (CH<sub>3</sub>), 29.6 (2 CH<sub>2</sub>), 24.6 (CH<sub>2</sub>). IR (neat): 2951, 2904, 2834, 1605, 1577, 1504, 1482, 1462, 1442, 1410, 1300, 1276, 1250, 1176, 1150, 1115, 1079, 1033, 1004, 915, 893, 869, 850, 817, 788, 741 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>19</sub>OS<sub>2</sub>: 303.0872; found: 303.0874.

**2-(4-Methoxyphenyl)-2-phenyl-1,3-dithiolane (5c):**

White solid, mp 42.4 – 42.5 °C, yield 99%, 285.5 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.53 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.21 – 7.09 (m, 3H), 6.70 (d, *J* = 8.7 Hz, 2H), 3.68 (s, 3H), 3.31 – 3.26 (m, 4H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 158.7 (Cq), 144.8 (Cq), 136.5 (Cq), 129.6 (2 CH), 128.3 (2 CH), 127.9 (2 CH), 127.2 (CH), 113.2 (2 CH), 76.7 (Cq), 55.3 (CH<sub>3</sub>), 40.2 (2 CH<sub>2</sub>). IR (neat): 2927, 2834, 1578, 1504, 1462, 1441, 1413, 1304, 1245, 1177, 1157, 1113, 1078, 1032, 875, 829, 803, 784, 741 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>17</sub>OS<sub>2</sub>: 289.0715; found: 289.0722.

**2-Phenyl-2-(p-tolyl)-1,3-dithiane (6j)<sup>[23]</sup>:**

White solid, mp 110.3 – 110.6 °C, yield 99%, 283.6 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.76 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.29 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.89 – 2.76 (m, 4H), 2.39 (s, 3H), 2.07 – 1.99 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 142.7 (Cq), 139.7 (Cq), 137.4 (Cq), 129.4 (2 CH), 129.3 (2 CH), 129.2 (2 CH), 128.4 (2 CH), 127.5 (CH), 62.7 (Cq), 29.5 (2 CH<sub>2</sub>), 24.6 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>). IR (neat): 2904, 1505, 1480, 1443, 1409, 1310, 1275, 1182, 1151, 1116, 1078, 1034, 1004, 910, 868, 848, 803, 780, 739, 696 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>19</sub>S<sub>2</sub>: 287.0923; found: 287.0931.

**2-([1,1'-Biphenyl]-4-yl)-2-phenyl-1,3-dithiane (6k):**

White solid, mp 148.6 – 148.9 °C, yield 99%, 345.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.80–7.76 (m, 4H), 7.64 – 7.58 (m, 4H), 7.48 – 7.27 (m, 6H), 2.86 – 2.81 (m, 4H), 2.11 – 1.98 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 142.6 (Cq), 141.8 (Cq), 140.5 (Cq), 140.4 (Cq), 129.9 (2 CH), 129.4 (2 CH), 128.9 (2 CH), 128.6 (2 CH), 127.7 (CH), 127.5 (CH), 127.2 (4 CH), 62.7 (Cq), 29.5 (2 CH<sub>2</sub>), 24.6 (CH<sub>2</sub>). IR (neat): 3056, 3028, 2904, 1597, 1483, 1444, 1408, 1276, 1181, 1154, 1118, 1077, 1034, 1006, 909, 871, 854, 820, 796, 760, 729, 696 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>21</sub>S<sub>2</sub>: 349.1079; found: 349.1077.

**2-(4'-((Methylperoxy)l2-methyl)-[1,1'-biphenyl]-4-yl)-2-phenyl-1,3-dithiane (6l):**

Yellow solid, mp 163.9 – 164.7 °C, yield 78%, 317.1 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.02 (d, *J* = 8.1 Hz, 2H), 7.73 – 7.50 (m, 8H), 7.35 – 7.19 (m, 3H), 3.86 (s, 3H), 2.90 – 2.58 (m, 4H), 1.99 – 1.91 (m, 2H).  
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 167.0 (Cq), 144.9 (Cq), 142.8 (Cq), 142.4 (Cq), 139.1 (Cq), 130.2 (2 CH), 130.1 (2 CH), 129.4 (2 CH),

129.1 (Cq), 128.6 (2 CH), 127.8 (CH), 127.3 (2 CH), 127.1 (2 CH), 62.6 (Cq), 52.2 (CH<sub>3</sub>), 29.5 (2 CH<sub>2</sub>), 24.5 (CH<sub>2</sub>). IR (neat): 2950, 2905, 1717, 1609, 1492, 1434, 1395, 1275, 1179, 1112, 1103, 1032, 1005, 967, 908, 850, 817, 794, 769, 729 cm<sup>-1</sup>. HRMS (ESI): m/z [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>O<sub>2</sub>S<sub>2</sub>: 407.1139; found: 407.1135.

#### 2-Phenyl-2-(*m*-tolyl)-1,3-dithiane (6m):

White solid, mp 78.3 – 78.8 °C, yield 99%, 283.6 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.64 (d, *J* = 7.5 Hz, 2H), 7.48 (s, 1H), 7.37 – 7.10 (m, 5H), 7.00 (d, *J* = 7.5 Hz, 1H), 2.89 – 2.57 (m, 4H), 2.27 (s, 3H), 1.97 – 1.88 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 142.7 (Cq), 142.6 (Cq), 138.2 (Cq), 129.9 (CH), 129.5 (2 CH), 128.5 (3 CH), 128.4 (CH), 127.6 (CH), 126.5 (CH), 62.9 (Cq), 29.5 (2 CH<sub>2</sub>), 24.6 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>). IR (neat): 3058, 2949, 2904, 1601, 1483, 1443, 1422, 1409, 1310, 1275, 1245, 1173, 1137, 1096, 1034, 1003, 907, 883, 771, 737, 697 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>19</sub>S<sub>2</sub>: 287.0923; found: 287.0933.

#### 2-Phenyl-2-(*o*-tolyl)-1,3-dithiane (6n):

Yellow oil, yield 95%, 272.1 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.12 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.14 (m, 6H), 3.02 – 2.78 (m, 4H), 2.16 – 1.97 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 143.7 (Cq), 140.4 (Cq), 138.2 (Cq), 133.4 (CH), 130.9 (CH), 128.5 (2 CH), 128.2 (2 CH), 127.7 (CH), 127.6 (CH), 125.2 (CH), 61.4 (Cq), 29.8 (2 CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 23.0 (CH<sub>3</sub>). IR (neat): 3058, 2949, 2904, 1601, 1482, 1443, 1422, 1409, 1310, 1275, 1244, 1173, 1137, 1096, 1033, 1002, 907, 883, 838, 769 735 cm<sup>-1</sup>. HRMS (ESI): m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>19</sub>S<sub>2</sub>: 287.0928; found: 287.0935.

#### 3-(2-Phenyl-1,3-dithian-2-yl)phenol (6o):

White solid, mp 125.4 – 125.8 °C, yield 99%, 285.5 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.70 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.19 (m, 6H), 6.79 (d, *J* = 7.5 Hz, 1H), 4.77 (brs, 1H), 2.94 – 2.69 (m, 4H), 2.07 – 1.99 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 155.7 (Cq), 144.5 (Cq), 142.5 (Cq), 129.8 (CH), 129.3 (2 CH), 128.5 (2 CH), 127.8 (CH), 122.1 (CH), 116.5 (CH), 114.8 (CH), 62.6 (Cq), 29.5 (2 CH<sub>2</sub>), 24.6 (CH<sub>2</sub>). IR (neat): 2905, 1582, 1482, 1443, 1423, 1276, 1221, 1160, 1133, 1082, 1033, 1002, 966, 907, 876, 775, 739, 728, 700 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>17</sub>OS<sub>2</sub>: 289.0715; found: 289.0715.

#### 4-(2-(4-Chlorophenyl)-1,3-dithiolan-2-yl)phenol (5d):

White solid, mp 90.3 – 90.5 °C, yield 99%, 305.7 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.59 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 5.09 (brs, 1H), 3.50 – 3.35 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 154.9 (Cq), 143.6 (Cq), 136.1 (Cq), 133.1 (Cq), 129.8 (4 CH), 128.1 (2 CH), 114.9 (2 CH), 76.1 (Cq), 40.3 (2 CH<sub>2</sub>). IR (neat): 2925, 1721, 1690, 1609, 1589, 1507, 1485, 1436, 1396, 1295, 1275, 1174, 1154, 1119, 1107, 1091, 1012, 957, 908, 825, 770, 730, 699 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub><sup>35</sup>ClOS<sub>2</sub>: 309.0169; found: 309.0176.

#### 4-(2-(4-Chlorophenyl)-1,3-dithian-2-yl)phenol (6p):

white solid, mp 134.7 – 134.9 °C, yield 99%, 319.6 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.67 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.23 (brs, 1H), 2.93 – 2.64 (m, 4H), 2.08 – 1.92 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 155.1 (Cq), 141.3 (Cq), 134.6 (Cq), 133.5 (Cq), 131.1 (2 CH), 130.8 (2 CH), 128.6 (2 CH), 115.4 (2 CH), 61.8 (Cq), 29.5 (2 CH<sub>2</sub>), 24.4 (CH<sub>2</sub>). IR (neat): 2905, 1589, 1505, 1485, 1424, 1395, 1275, 1224, 1174, 1150, 1093, 1013, 908, 873, 853, 818, 786, 731 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub><sup>35</sup>ClOS<sub>2</sub>: 323.0326; found: 323.0334.

#### 2,2-bis(4-Fluorophenyl)-1,3-dithiane (6q):

White solid, mp 53.8 – 54.0 °C, yield 99%, 305.3 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.73 – 7.68 (m, 4H), 7.09 – 7.02 (m, 4H), 2.92 – 2.68 (m, 4H), 2.06 – 1.98 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 162.0 (d, *J* = 246.5 Hz, 2 Cq), 138.3 (d, *J* = 1.6 Hz, 2 Cq), 131.2 (d, *J* = 8.0 Hz, 4 CH),

115.3 (d, *J* = 21.2 Hz, 4 CH), 61.5 (Cq), 29.5 (2 CH<sub>2</sub>), 24.3 (CH<sub>2</sub>). <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>): δ = -114.6. IR (neat): 2906, 1598, 1501, 1424, 1406, 1296, 1276, 1222, 1158, 1101, 1015, 908, 876, 856, 836, 818, 789, 732 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub>S<sub>2</sub>: 309.0578; found: 309.0577.

#### 2,2-bis(4-Methoxyphenyl)-1,3-dithiane (6r):

White solid, mp 96.4 – 96.7 °C, yield 99%, 329.2 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.60 (d, *J* = 8.7 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 4H), 3.81 (s, 6H), 2.93 – 2.63 (m, 4H), 2.03 – 1.95 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 158.9 (2 Cq), 134.9 (2 Cq), 130.7 (4 CH), 113.7 (4 CH), 62.1 (Cq), 55.4 (2 CH<sub>3</sub>), 29.7 (2 CH<sub>2</sub>), 24.7 (CH<sub>2</sub>). IR (neat): 2952, 2904, 2834, 1604, 1577, 1503, 1463, 1440, 1411, 1299, 1249, 1247, 1172, 1152, 1114, 1031, 1004, 909, 872, 852, 818, 791, 777, 731 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>21</sub>O<sub>2</sub>S<sub>2</sub>: 333.0977; found: 333.0971.

#### Spiro[fluorene-9,2'-[1,3]dithiane] (6s):

White solid, mp 183.3 – 183.7 °C, yield 99%, 267.7 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.92 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.29 (m, 4H), 3.42 – 3.22 (m, 4H), 2.41 – 2.33 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 149.7 (2 Cq), 138.1 (2 Cq), 128.8 (2 CH), 128.0 (2 CH), 124.2 (2 CH), 120.4 (2 CH), 52.7 (Cq), 27.8 (2 CH<sub>2</sub>), 24.5 (CH<sub>2</sub>). IR (neat): 2953, 1474, 1447, 1419, 1272, 1233, 1031, 999, 903, 872, 842, 740 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>S<sub>2</sub>: 271.0615; found: 271.0622.

#### 2-(3,5-Dimethoxyphenyl)-2-phenyl-1,3-dithiolane (5e):

White solid, mp 87.5 – 87.8 °C, yield 99%, 315.3 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.52 (d, *J* = 6.9 Hz, 2H), 7.21 – 7.09 (m, 3H), 6.72 (d, *J* = 2.1 Hz, 2H), 6.26 (t, *J* = 2.1 Hz, 1H), 3.66 (s, 6H), 3.31 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 160.4 (2 Cq), 147.3 (Cq), 144.4 (Cq), 128.1 (2 CH), 128.0 (2 CH), 127.3 (CH), 106.9 (2 CH), 99.1 (CH), 77.0 (Cq), 55.4 (2 CH<sub>3</sub>), 40.2 (2 CH<sub>2</sub>). IR (neat): 2999, 2959, 2927, 2834, 1603, 1587, 1455, 1420, 1350, 1327, 1306, 1283, 1245, 1203, 1153, 1105, 1067, 1054, 1032, 995, 972, 930, 834, 803, 771, 714 cm<sup>-1</sup>. HRMS (ESI): m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>S<sub>2</sub>: 319.0826; found: 319.0827.

#### Spiro[fluorene-9,2'-[1,3]dithiolane] (5f):

white solid, mp 126.1 – 126.4 °C, yield 99%, 253.8 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.75 – 7.59 (m, 4H), 7.41 – 7.29 (m, 4H), 3.79 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 150.5 (2 Cq), 138.5 (2 Cq), 128.7 (2 CH), 128.4 (2 CH), 125.2 (2 CH), 119.9 (2 CH), 68.6 (Cq), 42.4 (2 CH<sub>2</sub>). IR (neat): 3061, 2921, 1475, 1447, 1418, 1276, 1236, 1184, 1154, 1098, 1029, 975, 953, 914, 853, 737, 704 cm<sup>-1</sup>. HRMS (APCI): m/z [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>S<sub>2</sub>: 257.0453; found: 257.0454.

#### Diphenylmethane (7a)<sup>[25]</sup>:

Colorless oil, for yield: see the text. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.39 – 7.16 (m, 10H), 4.01 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 141.2 (2 Cq), 129.1 (4 CH), 128.6 (4 CH), 126.2 (2 CH), 42.1 (CH<sub>2</sub>). IR (neat): 2903, 1600, 1494, 1479, 1452, 1396, 1367, 1276, 1175, 1093, 1072, 1030, 1012, 907, 867, 833, 801, 737, 699 cm<sup>-1</sup>.

#### 1-Benzyl-4-chlorobenzene (7b)<sup>[25]</sup>:

Colorless oil, for yield: see the text. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.25 – 7.01 (m, 9H), 3.86 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 140.7 (Cq), 139.7 (Cq), 132.0 (Cq), 130.4 (2 CH), 130.0 (2 CH), 128.7 (4 CH), 126.4 (CH), 41.4 (CH<sub>2</sub>). IR (neat): 2958, 2924, 2853, 1491, 1453, 1433, 1407, 1277, 1260, 1205, 1178, 1092, 1073, 1031, 1015, 910, 845, 791, 747, 714 cm<sup>-1</sup>.

#### 1-Benzyl-4-fluorobenzene (7c)<sup>[26]</sup>:

Colorless oil, Yield 88%, 81.9 mg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.24 – 7.03 (m, 7H), 6.89 (t, *J* = 8.7 Hz, 2H), 3.87 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 161.5 (d, *J* = 242.6 Hz, Cq), 141.1 (Cq), 136.9 (d, *J* = 2.9 Hz, Cq), 130.4 (d, *J* = 7.7 Hz, 2 CH), 128.9 (2 CH),

128.6 (2 CH), 126.3 (CH), 115.3 (d,  $J = 21.1$  Hz, 2 CH), 41.2 (CH<sub>2</sub>). <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>):  $\delta = -119.9$ . IR (neat): 3028, 1603, 1507, 1453, 1221, 1158, 1093, 1015, 841, 800, 776, 725, 697 cm<sup>-1</sup>.

#### 1-Benzyl-4-bromobenzene (7d)<sup>[25]</sup>:

Colorless oil, Yield 93%, 114.9 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.32$  (d,  $J = 8.1$  Hz, 2H), 7.24 – 7.06 (m, 5H), 6.98 (d,  $J = 8.1$  Hz, 2H), 3.85 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 140.6$  (Cq), 140.2 (Cq), 131.6 (2 CH), 130.8 (2 CH), 129.0 (2 CH), 128.7 (2 CH), 126.4 (CH), 120.0 (Cq), 41.4 (CH<sub>2</sub>). IR (neat): 3062, 3026, 1604, 1486, 1453, 1433, 1404, 1261, 1223, 1099, 1072, 1012, 843, 788, 743, 696 cm<sup>-1</sup>.

#### 1-Benzyl-4-(trifluoromethyl)benzene (7e)<sup>[26]</sup>:

Colorless oil, yield 89%, 105.1 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.46$  (d,  $J = 8.1$  Hz, 2H), 7.27 – 7.07 (m, 7H), 3.95 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 145.3$  (Cq), 140.1 (Cq), 129.3 (2 CH), 129.1 (2 CH), 128.8 (2 CH), 126.6 (CH), 126.2 (Cq), 125.5 (d,  $J = 3.5$  Hz, 2 CH), 122.6 (Cq), 41.8 (CH<sub>2</sub>). <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>):  $\delta = -62.361$ . IR (neat): 1619, 1495, 1454, 1417, 1324, 1162, 1123, 1107, 1066, 1018, 854, 800, 769, 733, 698 cm<sup>-1</sup>.

#### 1-Benzyl-3-chlorobenzene (7f)<sup>[26]</sup>:

Colorless oil, yield 95%, 96.3 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.29 - 6.95$  (m, 9H), 3.87 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 143.3$  (Cq), 140.3 (Cq), 134.4 (Cq), 129.8 (CH), 129.1 (CH), 129.0 (2 CH), 128.7 (2 CH), 127.2 (CH), 126.5 (CH), 126.4 (CH), 41.7 (CH<sub>2</sub>). IR (neat): 3062, 3027, 1595, 1494, 1473, 1453, 1431, 1078, 1030, 999, 865, 774, 751, 731, 702 cm<sup>-1</sup>.

#### 1-Benzyl-2-bromobenzene (7g)<sup>[27]</sup>:

Colorless oil, yield 90%, 111.2 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.49$  (d,  $J = 8.1$  Hz, 1H), 7.30 – 6.94 (m, 8H), 4.04 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 140.4$  (Cq), 139.5 (Cq), 132.9 (CH), 131.1 (CH), 129.0 (2 CH), 128.5 (2 CH), 127.9 (CH), 127.5 (CH), 126.3 (CH), 124.9 (Cq), 41.7 (CH<sub>2</sub>). IR (neat): 3061, 3027, 2906, 1603, 1566, 1519, 1494, 1440, 1347, 1276, 1110, 1074, 1026, 860, 841, 800, 746 cm<sup>-1</sup>.

#### 1-Benzyl-4-nitrobenzene (7h)<sup>[26]</sup>:

Colorless oil, yield 55%, 58.6 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 8.07$  (d,  $J = 8.7$  Hz, 2H), 7.31 – 7.07 (m, 7H), 4.01 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 154.3$  (Cq), 149.0 (Cq), 139.3 (Cq), 129.8 (2 CH), 129.1 (2 CH), 128.9 (2 CH), 126.9 (CH), 123.9 (2 CH), 41.9 (CH<sub>2</sub>). IR (neat): 2961, 2927, 2870, 1606, 1595, 1519, 1494, 1453, 1419, 1377, 1347, 1265, 1180, 1154, 1109, 1054, 1017, 971, 917, 859, 845, 781, 743, 703 cm<sup>-1</sup>.

#### 1-Benzyl-4-methoxybenzene (7i)<sup>[25]</sup>:

Colorless oil, for yield: see the text.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.23 - 7.01$  (m, 7H), 6.75 (d,  $J = 8.7$  Hz, 2H), 3.85 (s, 2H), 3.70 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 158.1$  (Cq), 141.7 (Cq), 133.4 (Cq), 130.0 (2 CH), 128.9 (2 CH), 128.5 (2 CH), 126.1 (CH), 114.0 (2 CH), 55.4 (CH<sub>3</sub>), 41.2 (CH<sub>2</sub>). IR (neat): 3027, 2905, 2833, 1611, 1583, 1511, 1493, 1442, 1300, 1276, 1245, 1177, 1075, 1034, 837, 798, 770, 725, 697 cm<sup>-1</sup>.

#### 1-Benzyl-4-methylbenzene (7j)<sup>[25]</sup>:

Colorless oil, yield 90%, 82.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.24 - 6.97$  (m, 9H), 3.86 (s, 2H), 2.23 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 141.5$  (Cq), 138.2 (Cq), 135.6 (Cq), 129.3 (2 CH), 129.0 (2 CH), 128.9 (2 CH), 128.5 (2 CH), 126.1 (CH), 41.6 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>). IR (neat): 3026, 2920, 1603, 1513, 1493, 1453, 1261, 1106, 1073, 1028, 1011, 789, 767, 723, 697 cm<sup>-1</sup>.

#### 4-Benzyl-1,1'-biphenyl (7k)<sup>[28]</sup>:

Colorless oil, yield 91%, 111.2 mg.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.50 - 7.42$  (m, 4H), 7.34 (t,  $J = 7.5$  Hz, 2H), 7.28 – 7.10 (m, 8H), 3.94 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 141.1$  (2 Cq), 140.4 (Cq), 139.2 (Cq), 129.4 (2 CH), 129.1 (2 CH), 128.8 (2 CH), 128.6 (2 CH), 127.3 (2 CH), 127.2 (CH), 127.1 (2 CH), 126.3 (CH), 41.7 (CH<sub>2</sub>). IR (neat): 3056, 3026, 1599, 1487, 1454, 1407, 1073, 1007, 907, 851, 758, 724, 700, 688 cm<sup>-1</sup>.

#### Methyl 4'-benzyl-[1,1'-biphenyl]-4-carboxylate (7l):

White solid, mp 108.5 – 109.0 °C, yield 92%, 139.1 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 8.01$  (d,  $J = 8.4$  Hz, 2H), 7.55 (d,  $J = 8.4$  Hz, 2H), 7.47 (d,  $J = 8.1$  Hz, 2H), 7.29 – 7.10 (m, 7H), 3.95 (s, 2H), 3.85 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 167.1$  (Cq), 145.5 (Cq), 141.4 (Cq), 140.9 (Cq), 137.9 (Cq), 130.2 (2 CH), 129.6 (2 CH), 129.0 (2 CH), 128.8 (Cq), 128.7 (2 CH), 127.5 (2 CH), 127.0 (2 CH), 126.3 (CH), 52.2 (CH<sub>3</sub>), 41.7 (CH<sub>2</sub>). IR (neat): 2950, 1717, 1607, 1494, 1434, 1398, 1274, 1193, 1178, 1111, 1102, 1030, 1005, 966, 909, 848, 801, 769, 728, 698 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>: 303.1385; found: 303.1390.

#### 1-Benzyl-3-methylbenzene (7m)<sup>[25]</sup>:

Colorless oil, yield 93%, 84.8 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.39 - 7.01$  (m, 9H), 3.99 (s, 2H), 2.36 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 141.4$  (Cq), 141.1 (Cq), 138.1 (Cq), 129.8 (CH), 129.0 (2 CH), 128.5 (2 CH), 128.4 (CH), 126.9 (CH), 126.1 (2 CH), 42.0 (CH<sub>2</sub>), 21.5 (CH<sub>3</sub>). IR (neat): 3061, 3026, 2919, 1603, 1493, 1452, 1092, 1073, 1030, 879, 777, 759, 722, 697 cm<sup>-1</sup>.

#### 1-Benzyl-2-methylbenzene (7n)<sup>[25]</sup>:

Colorless oil, yield 85%, 77.5 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.29 - 6.96$  (m, 9H), 3.90 (s, 2H), 2.15 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 140.5$  (Cq), 139.1 (Cq), 136.8 (Cq), 130.4 (CH), 130.1 (CH), 128.9 (2 CH), 128.5 (2 CH), 126.6 (CH), 126.1 (CH), 126.0 (CH), 39.6 (CH<sub>2</sub>), 19.8 (CH<sub>3</sub>). IR (neat): 3060, 3025, 2962, 2921, 1611, 1583, 1491, 1451, 1324, 1273, 1204, 1177, 1142, 1031, 826, 768, 744, 726, 698 cm<sup>-1</sup>.

#### 3-Benzylphenol (7o)<sup>[29]</sup>:

Colorless oil, yield 95%, 87.5 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.23 - 7.04$  (m, 6H), 6.69 (d,  $J = 7.8$  Hz, 1H), 6.63 – 6.51 (m, 2H), 4.79 (br, 1H), 3.84 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 155.7$  (Cq), 143.2 (Cq), 140.9 (Cq), 129.7 (CH), 129.1 (2 CH), 128.6 (2 CH), 126.3 (CH), 121.6 (CH), 116.0 (CH), 113.2 (CH), 41.9 (CH<sub>2</sub>). IR (neat): 3026, 2905, 1616, 1598, 1587, 1492, 1452, 1274, 1153, 1075, 1030, 1000, 954, 881, 865, 782, 766, 726, 699 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  [M-H]<sup>-</sup> calcd for C<sub>13</sub>H<sub>11</sub>O: 183.0810; found: 183.0818.

#### 4-(4-Chlorobenzyl)phenol (7p)<sup>[30]</sup>:

Colorless oil, for yield: see the text.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.17$  (d,  $J = 8.4$  Hz, 2H), 7.01 (d,  $J = 8.4$  Hz, 2H), 6.95 (d,  $J = 8.4$  Hz, 2H), 6.68 (d,  $J = 8.4$  Hz, 2H), 4.64 (br, 1H), 3.80 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 154.1$  (Cq), 140.1 (Cq), 133.0 (Cq), 131.9 (Cq), 130.2 (2 CH), 130.1 (2 CH), 128.6 (2 CH), 115.5 (2 CH), 40.4 (CH<sub>2</sub>). IR (neat): 3023, 2923, 2852, 1614, 1597, 1513, 1489, 1441, 1407, 1373, 1239, 1172, 1092, 1015, 843, 816, 803, 768, 718 cm<sup>-1</sup>. HRMS (APCI):  $m/z$  [M-H]<sup>-</sup> calcd for C<sub>13</sub>H<sub>10</sub><sup>35</sup>ClO: 217.0426; found: 217.0428.

#### bis(4-Fluorophenyl)methane (7q)<sup>[31]</sup>:

Colorless oil, yield 95%, 97.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.15 - 7.09$  (m, 4H), 7.01 – 6.95 (m, 4H), 3.92 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 161.6$  (d,  $J = 242.7$  Hz, 2 Cq), 136.7 (d,  $J = 2.5$  Hz, 2 Cq), 130.3 (d,  $J = 7.8$  Hz, 4 CH), 115.4 (d,  $J = 21.1$  Hz, 4 CH), 40.3 (CH<sub>2</sub>). <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>):  $\delta = -117.168$ . IR (neat): 1603, 1506, 1439, 1222, 1156, 1095, 1015, 855, 819, 767 cm<sup>-1</sup>.

**bis(4-Methoxyphenyl)methane (7r)**<sup>[32]</sup>:

Colorless oil, yield 67%, 76.5 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.11 (d, *J* = 8.4 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 4H), 3.88 (s, 2H), 3.79 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 158.0 (2 Cq), 133.8 (2 Cq), 129.8 (4 CH), 114.0 (4 CH), 55.4 (2 CH<sub>3</sub>), 40.2 (CH<sub>2</sub>). IR (neat): 2954, 2906, 2834, 1611, 1583, 1463, 1439, 1300, 1275, 1243, 1175, 1108, 1035, 852, 808, 762, 747, 701 cm<sup>-1</sup>.

**9H-Fluorene (7s)**<sup>[33]</sup>:

Colorless oil, for yield: see the text.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.81 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.29 (m, 4H), 3.92 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 143.3 (2 Cq), 141.8 (2 Cq), 126.8 (4 CH), 125.1 (2 CH), 120.0 (2 CH), 37.1 (CH<sub>2</sub>). IR (neat): 1478, 1448, 1402, 1189, 954, 907, 733, 696 cm<sup>-1</sup>.

**1-Benzyl-3,5-dimethoxybenzene (7t)**<sup>[25]</sup>:

Colorless oil, yield 71%, 81.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.24 – 7.09 (m, 5H), 6.28 – 6.23 (m, 3H), 3.84 (s, 2H), 3.68 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 161.0 (2 Cq), 143.5 (Cq), 140.8 (Cq), 129.0 (2 CH), 128.6 (2 CH), 126.2 (CH), 107.3 (2 CH), 98.1 (CH), 55.4 (2 CH<sub>3</sub>), 42.31 (CH<sub>2</sub>). IR (neat): 2999, 2959, 2924, 2836, 1609, 1594, 1494, 1467, 1453, 1428, 1348, 1321, 1290, 1252, 1205, 1157, 1097, 1065, 1058, 1031, 993, 948, 923, 863, 851, 820, 797, 757, 735, 705 cm<sup>-1</sup>.

**3,4-Dihydro-2H-spiro[naphthalene-1,2'-[1,3]dithiane] (8a)**<sup>[24]</sup>:

Yellow oil, yield 99%, 234.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.90 (d, *J* = 9 Hz, 1H), 7.14 – 6.94 (m, 3H), 3.11 (td, *J* = 13.8 Hz, *J* = 2.4 Hz, 2H), 2.77 – 2.52 (m, 6H), 2.14 – 2.05 (m, 1H), 1.96 – 1.83 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 137.9 (Cq), 137.7 (Cq), 130.0 (CH), 129.1 (CH), 127.9 (CH), 126.3 (CH), 52.4 (Cq), 36.3 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 28.1 (2 CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 20.3 (CH<sub>2</sub>). IR (neat): 2929, 2834, 1484, 1448, 1419, 1273, 1237, 1156, 1066, 1019, 942, 902, 868, 809, 761, 740, 697, 675 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>17</sub>S<sub>2</sub>: 237.0766; found: 237.0772.

**3,4-Dihydro-2H-spiro[naphthalene-1,2'-[1,3]dithiolane] (8b)**:

White solid, mp 58.3 – 58.5 °C, yield 99%, 220.1 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.96 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.08 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 3.66 – 3.42 (m, 4H), 2.81 (t, *J* = 6.3 Hz, 2H), 2.48 – 2.35 (m, 2H), 2.06 – 1.98 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 139.1 (Cq), 137.4 (Cq), 130.9 (CH), 128.7 (CH), 127.3 (CH), 126.2 (CH), 68.8 (Cq), 43.9 (CH<sub>2</sub>), 41.0 (2 CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>). IR (neat): 3060, 3017, 2919, 2861, 2835, 1482, 1451, 1438, 1418, 1275, 1240, 1155, 1066, 1016, 954, 901, 849, 820, 788, 740 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>15</sub>S<sub>2</sub>: 223.0610; found: 223.0617.

**5-Methoxy-3,4-dihydro-2H-spiro[naphthalene-1,2'-[1,3]dithiolane] (8c)**:

White solid, mp 108.6 – 108.8 °C, yield 99%, 249.9 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.60 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 3.63 – 3.41 (m, 4H), 2.70 (t, *J* = 6.3 Hz, 2H), 2.45 – 2.30 (m, 2H), 2.12 – 1.95 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 156.4 (Cq), 140.4 (Cq), 126.9 (Cq), 126.0 (CH), 122.6 (CH), 108.0 (CH), 68.8 (Cq), 55.4 (CH<sub>3</sub>), 43.3 (CH<sub>2</sub>), 40.9 (2 CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>). IR (neat): 2997, 2936, 2918, 2834, 1681, 1600, 1580, 1464, 1434, 1346, 1311, 1254, 1237, 1175, 1106, 1060, 1025, 974, 906, 878, 852, 804, 786, 760, 730, 701 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>17</sub>OS<sub>2</sub>: 253.0715; found: 253.0715.

**6-Methoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithiolane] (8d)**:

White solid, mp 78.6 – 78.9 °C, yield 99%, 236.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.22 – 6.89 (m, 2H), 6.78 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 3.60 – 3.37

(m, 4H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.69 (t, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 159.4 (Cq), 146.6 (Cq), 134.4 (Cq), 125.2 (CH), 115.3 (CH), 109.0 (CH), 73.4 (Cq), 55.6 (CH<sub>3</sub>), 48.5 (CH<sub>2</sub>), 40.90 (2 CH<sub>2</sub>), 30.1 (CH<sub>2</sub>). IR (neat): 2959, 2919, 2831, 1610, 1583, 1488, 1464, 1421, 1324, 1294, 1271, 1242, 1203, 1177, 1141, 1096, 1082, 1030, 961, 936, 888, 824, 803, 767, 741, 699 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>15</sub>OS<sub>2</sub>: 239.0559; found: 239.0553.

**Spiro[thiochromane-4,2'-[1,3]dithiolane] (8e)**:

White solid, mp 45.4 – 45.5 °C, yield 99%, 238.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.09 – 7.98 (m, 1H), 7.07 – 6.99 (m, 3H), 3.62 – 3.42 (m, 4H), 3.24 – 3.16 (m, 2H), 2.74 – 2.65 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 135.7 (Cq), 133.3 (Cq), 131.5 (CH), 127.7 (CH), 126.5 (CH), 124.3 (CH), 67.7 (Cq), 42.0 (CH<sub>2</sub>), 40.9 (2 CH<sub>2</sub>), 25.8 (CH<sub>2</sub>). IR (neat): 3053, 2917, 1588, 1560, 1463, 1422, 1296, 1277, 1264, 1226, 1158, 1123, 1061, 1038, 1006, 968, 901, 850, 811, 780, 739, 711 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>13</sub>S<sub>3</sub>: 241.0173; found: 241.0168.

**2-Methyl-2-(naphthalen-2-yl)-1,3-dithiane (8f)**:

White solid, mp 90.7 – 90.9 °C, yield 99%, 257.8 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.41 (s, 1H), 8.06 (dd, *J* = 8.7 Hz, *J* = 1.8 Hz, 1H), 7.91 – 7.83 (m, 3H), 7.52 – 7.48 (m, 2H), 2.79 – 2.75 (m, 4H), 2.01 – 1.93 (m, 2H), 1.88 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 141.2 (Cq), 133.4 (Cq), 132.5 (Cq), 128.5 (CH), 128.4 (CH), 127.5 (CH), 127.1 (CH), 126.3 (CH), 126.2 (CH), 125.8 (CH), 54.2 (Cq), 32.8 (CH<sub>3</sub>), 28.2 (2 CH<sub>2</sub>), 24.8 (CH<sub>2</sub>). IR (neat): 3053, 2974, 2912, 2895, 1596, 1501, 1440, 1418, 1366, 1343, 1265, 1244, 1162, 1126, 1063, 1045, 1017, 997, 969, 949, 904, 861, 819, 750, 730, 702 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>17</sub>S<sub>2</sub>: 261.0766; found: 261.0769.

**1,2,3,4-Tetrahydronaphthalene (9a)**<sup>[34]</sup>:

Colorless oil, for yield: see the text.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.68 – 6.88 (m, 4H), 3.10 – 2.90 (m, 4H), 2.12 – 1.95 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 137.1 (2 Cq), 129.2 (2 CH), 125.5 (2 CH), 29.5 (2 CH<sub>2</sub>), 23.35 (2 CH<sub>2</sub>). IR (neat): 3016, 2927, 2858, 2838, 1494, 1452, 1435, 1283, 1111, 1037, 945, 865, 804, 739 cm<sup>-1</sup>.

**5-Methoxy-1,2,3,4-tetrahydronaphthalene (9b)**<sup>[35]</sup>:

Colorless oil, yield 76%, 61.6 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.07 (t, *J* = 7.8 Hz, 1H), 6.72 – 7.63 (m, 2H), 3.81 (s, 3H), 2.78 – 2.62 (m, 4H), 1.89 – 1.66 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 157.5 (Cq), 138.6 (Cq), 126.1 (Cq), 125.8 (CH), 121.5 (CH), 106.9 (CH), 55.4 (CH<sub>3</sub>), 29.8 (CH<sub>2</sub>), 23.2 (CH<sub>2</sub>), 23.0 (2 CH<sub>2</sub>). IR (neat): 2930, 2857, 2836, 2181, 2058, 2020, 1604, 1586, 1468, 1437, 1336, 1309, 1272, 1252, 1170, 1096, 1058, 1000, 959, 880, 856, 826, 764, 710 cm<sup>-1</sup>.

**5-Methoxy-2,3-dihydro-1H-indene (9c)**<sup>[36]</sup>:

Colorless oil, yield 85%, 63.0 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.11 (d, *J* = 8.1 Hz, 1H), 6.80 (s, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.78 (s, 3H), 2.91 – 2.81 (m, 4H), 2.14 – 1.96 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 158.7 (Cq), 145.8 (Cq), 136.3 (Cq), 124.8 (CH), 112.0 (CH), 110.0 (CH), 55.6 (CH<sub>3</sub>), 33.3 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>). IR (neat): 2955, 2935, 2906, 2845, 1608, 1585, 1492, 1465, 1443, 1411, 1329, 1294, 1277, 1255, 1243, 1213, 1194, 1164, 1143, 1097, 1082, 1034, 921, 861, 914, 802, 755, 731 cm<sup>-1</sup>.

**Thiochromane (9d)**<sup>[37]</sup>:

Colorless oil, yield 85%, 63.9 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.20 – 6.88 (m, 4H), 3.03 (t, *J* = 6.0 Hz, 2H), 2.82 (t, *J* = 6.0 Hz, 2H), 2.17 – 2.08 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 134.0 (Cq), 133.0 (Cq), 130.1 (CH), 126.7 (CH), 126.5 (CH), 124.0 (CH), 29.8 (CH<sub>2</sub>), 27.7 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>). IR (neat): 3060, 3006, 2934, 2853, 1587, 1566, 1479, 1438, 1393, 1296, 1268, 1123, 1074, 1049, 932, 836, 781, 744 cm<sup>-1</sup>.

**2-Ethynaphthalene (9e)<sup>[38]</sup>:**

Colorless oil, yield 88%, 68.7 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.89 – 7.72 (m, 3H), 7.64 (s, 1H), 7.50 – 7.32 (m, 3H), 2.83 (q, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 141.9 (Cq), 133.8 (Cq), 132.1 (Cq), 127.9 (CH), 127.7 (CH), 127.5 (CH), 127.2 (CH), 125.9 (CH), 125.7 (CH), 125.1 (CH), 29.2 (CH<sub>2</sub>), 15.6 (CH<sub>3</sub>). IR (neat): 3051, 2965, 2929, 1632, 1601, 1509, 1454, 1380, 1320, 1270, 1125, 1055, 1019, 946, 889, 854, 817, 744 cm<sup>-1</sup>.

**((4-Bromophenyl)methylene)bis(ethylsulfane) (10a)<sup>[39]</sup>:**

Pale brown oil, yield 95%, 276.7 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.87 (s, 1H), 2.65 – 2.46 (m, 4H), 1.22 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 139.8 (Cq), 131.8 (2 CH), 129.5 (2 CH), 121.6 (Cq), 51.9 (CH), 26.4 (2 CH<sub>2</sub>), 14.4 (2 CH<sub>3</sub>). IR (neat): 2969, 2926, 2869, 1587, 1485, 1452, 1400, 1375, 1264, 1184, 1153, 1098, 1072, 1052, 1010, 974, 840, 774, 744 cm<sup>-1</sup>.

**((3-Bromophenyl)methylene)bis(ethylsulfane) (10b)<sup>[39]</sup>:**

Pale brown oil, yield 95%, 276.7 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.70 (s, 1H), 7.51 – 7.47 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 4.96 (s, 1H), 2.74 – 2.58 (m, 4H), 1.32 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 143.0 (Cq), 130.9 (CH), 130.7 (CH), 130.1 (CH), 126.4 (CH), 122.5 (Cq), 51.9 (CH), 26.3 (2 CH<sub>2</sub>), 14.3 (2 CH<sub>3</sub>). IR (neat): 3058, 3029, 2904, 1603, 1494, 1481, 1454, 1442, 1309, 1277, 1245, 1223, 1182, 1078, 1034, 958, 907, 874, 811, 785, 750, 698 cm<sup>-1</sup>.

**((4-Methoxyphenyl)methylene)bis(ethylsulfane) (10c)<sup>[39]</sup>:**

White solid, mp 34.6 – 34.8 °C, yield 95%, 230.3 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.37 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.91 (s, 1H), 3.80 (s, 3H), 2.66 – 2.45 (m, 4H), 1.22 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 159.2 (Cq), 132.6 (Cq), 128.9 (2 CH), 114.0 (2 CH), 55.4 (CH), 52.0 (CH<sub>3</sub>), 26.3 (2 CH<sub>2</sub>), 14.4 (2 CH<sub>3</sub>). IR (neat): 2963, 2927, 2870, 2834, 1609, 1583, 1509, 1465, 1454, 1441, 1420, 1375, 1320, 1302, 1248, 1173, 1151, 1107, 1033, 974, 839, 784, 747, 701 cm<sup>-1</sup>.

**((4-*iso*Propylphenyl)methylene)bis(ethylsulfane) (10d):**

Pale brown oil, yield 95%, 241.7 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.28 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 4.83 (s, 1H), 2.86 – 2.76 (m, 1H), 2.57 – 2.39 (m, 4H), 1.18 – 1.12 (m, 12H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 148.5 (Cq), 137.8 (Cq), 127.6 (2 CH), 126.6 (2 CH), 52.4 (CH), 33.9 (CH), 26.3 (2 CH<sub>2</sub>), 24.0 (2 CH<sub>3</sub>), 14.4 (2 CH<sub>3</sub>). IR (neat): 2960, 2926, 2869, 1658, 1608, 1510, 1452, 1419, 1376, 1339, 1314, 1264, 1215, 1153, 1098, 1054, 1018, 972, 915, 845, 780, 752, 723, 700 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M-H]<sup>-</sup> calcd for C<sub>14</sub>H<sub>21</sub>S<sub>2</sub>: 253.1079; found: 253.1089.

**(Naphthalen-2-ylmethylene)bis(ethylsulfane) (10e)<sup>[39]</sup>:**

Pale brown oil, yield 95%, 249.3 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.97 – 7.85 (m, 4H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.50 (m, 2H), 5.19 (s, 1H), 2.77 – 2.56 (m, 4H), 1.32 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 137.7 (Cq), 133.0 (Cq), 132.9 (Cq), 128.6 (CH), 127.9 (CH), 127.6 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 125.8 (CH), 52.7 (CH), 26.3 (2 CH<sub>2</sub>), 14.3 (2 CH<sub>3</sub>). IR (neat): 3055, 2965, 2926, 2869, 2822, 1693, 1656, 1629, 1599, 1508, 1452, 1442, 1420, 1374, 1360, 1346, 1264, 1170, 1153, 1144, 1120, 1053, 1018, 973, 895, 861, 821, 785, 750, 706 cm<sup>-1</sup>.

**((2-Bromophenyl)methylene)bis(ethylsulfane) (10f)<sup>[39]</sup>:**

Pale brown oil, yield 95%, 276.7 mg.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.77 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 5.47 (s, 1H), 2.70 – 2.48 (m, 4H), 1.25 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 139.8 (Cq), 132.6 (CH), 129.9 (CH), 129.1 (CH), 127.9 (CH), 123.3 (Cq), 50.8 (CH), 26.5 (2 CH<sub>2</sub>), 14.5 (2 CH<sub>3</sub>). IR (neat): 2970, 2964, 2926, 2869, 1586, 1565, 1463, 1439, 1422, 1375, 1264, 1218, 1189, 1156, 1114, 1052, 1021, 971, 866, 843, 787, 741 cm<sup>-1</sup>.

**2-(Naphthalen-2-yl)-1,3-dithiane (10g)<sup>[40]</sup>:**

White solid, mp 120.1 – 120.3 °C, yield 99%, 243.9 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.99 (s, 1H), 7.90 – 7.79 (m, 3H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 5.35 (s, 1H), 3.16 – 2.91 (m, 4H), 2.22 – 1.91 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 136.6 (Cq), 133.4 (Cq), 133.3 (Cq), 128.5 (CH), 128.1 (CH), 127.7 (CH), 126.9 (CH), 126.3 (2 CH), 125.7 (CH), 51.6 (CH), 32.2 (2 CH<sub>2</sub>), 25.2 (CH<sub>2</sub>). IR (neat): 3055, 2953, 2929, 2894, 2824, 1630, 1599, 1506, 1422, 1361, 1276, 1184, 1171, 1125, 1017, 964, 913, 897, 866, 816, 776, 760, 733 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub>S<sub>2</sub>: 247.0610; found: 247.0613.

**(4-Bromobenzyl)ethylsulfane (11a):**

Pale brown oil, yield 92%, 106.3 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.43 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.66 (s, 2H), 2.42 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 137.8 (Cq), 131.7 (2 CH), 130.6 (2 CH), 120.8 (Cq), 35.4 (CH<sub>2</sub>), 25.4 (CH<sub>2</sub>), 14.5 (CH<sub>3</sub>). IR (neat): 2970, 2927, 1660, 1589, 1486, 1451, 1422, 1401, 1375, 1267, 1236, 1204, 1070, 1011, 972, 914, 879, 832, 806, 744 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>12</sub><sup>79</sup>BrS: 230.9838; found: 230.9836.

**(3-Bromobenzyl)ethylsulfane (11b):**

Pale brown oil, yield 81%, 93.6 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.40 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.07 (m, 2H), 3.59 (s, 2H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 141.2 (Cq), 131.9 (CH), 130.1 (CH), 130.0 (CH), 127.5 (CH), 122.6 (Cq), 35.5 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>). IR (neat): 2970, 2926, 2870, 1594, 1567, 1474, 1451, 1427, 1375, 1301, 1265, 1234, 1198, 1166, 1090, 1070, 1052, 997, 970, 910, 890, 868, 848, 785, 766, 749 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>12</sub><sup>79</sup>BrS: 230.9838; found: 230.9828.

**Ethyl(4-methoxybenzyl)sulfane (11c):**

Pale brown oil, yield 85%, 77.5 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.23 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.68 (s, 2H), 2.43 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 158.7 (Cq), 130.7 (Cq), 129.9 (2 CH), 114.0 (2 CH), 55.4 (CH<sub>3</sub>), 35.4 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 14.5 (CH<sub>3</sub>). IR (neat): 2964, 2929, 2908, 2870, 2834, 2057, 1885, 1719, 1641, 1610, 1584, 1511, 1465, 1454, 1441, 1423, 1372, 1341, 1301, 1249, 1234, 1175, 1150, 1103, 1058, 1035, 971, 877, 830, 808, 752, 736 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M]<sup>+</sup> calcd for C<sub>10</sub>H<sub>14</sub>OS: 182.0765; found: 182.0751.

**Ethyl(4-*isopropyl*benzyl)sulfane (11d):**

Pale brown oil, yield 82%, 79.7 mg.  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.16 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.62 (s, 2H), 2.86 – 2.76 (m, 1H), 2.37 (q, *J* = 7.5 Hz, 2H), 1.19 – 1.13 (m, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 147.6 (Cq), 136.0 (Cq), 128.8 (2 CH), 126.6 (2 CH), 35.71 (CH<sub>2</sub>), 33.9 (CH), 25.4 (CH<sub>2</sub>), 24.1 (2 CH<sub>3</sub>), 14.5 (CH<sub>3</sub>). IR (neat): 2960, 2926, 2869, 2349, 2241, 1607, 1517, 1466, 1452, 1423, 1382, 1347, 1266, 1237, 1177, 1109, 1054, 1019, 970, 919, 838, 824, 745, 703 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>18</sub>S: 194.1124; found: 194.1123.

**Ethyl(naphthalen-2-ylmethyl)sulfane (11e):**

Pale brown oil, for yield: see the text.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.89 – 7.76 (m, 3H), 7.71 (s, 1H), 7.53 – 7.43 (m, 3H), 3.89 (s, 2H), 2.45 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 136.1 (Cq), 133.4 (Cq), 132.6 (Cq), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.2 (2 CH), 126.2 (CH), 125.8 (CH), 36.3 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 14.5 (CH<sub>3</sub>). IR (neat): 3054, 2967, 2926, 2869, 2360, 1654, 1599, 1509, 1453, 1421, 1359, 1269, 1231, 1123, 1019, 959, 911, 892, 863, 851, 818, 750 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>14</sub>S: 202.0811; found: 202.0805.

#### (2-Bromobenzyl)(ethyl)sulfane (11f):

Pale brown oil, yield 90%, 104.0 mg.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.58 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 3.87 (s, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 138.2 (Cq), 133.2 (CH), 130.8 (CH), 128.6 (CH), 127.5 (CH), 124.6 (Cq), 36.3 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 14.7 (CH<sub>3</sub>). IR (neat): 3055, 2967, 2925, 2869, 1589, 1567, 1468, 1440, 1419, 1375, 1293, 1266, 1235, 1202, 1159, 1110, 1046, 1025, 969, 944, 819, 762, 734, 719 cm<sup>-1</sup>. HRMS (APCI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>12</sub><sup>79</sup>BrS: 230.9838; found: 230.9829.

#### 2-Methylnaphthalene (12a)<sup>[41]</sup>:

Colorless oil, for yield: see the text.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.86 – 7.74 (m, 3H), 7.64 (s, 1H), 7.50 – 7.40 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 2.55 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 135.5 (Cq), 133.8 (Cq), 131.8 (Cq), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 126.9 (CH), 126.0 (CH), 125.1 (CH), 21.8 (CH<sub>3</sub>). IR (neat): 3052, 3015, 2968, 2917, 2855, 1756, 1632, 1600, 1509, 1454, 1429, 1379, 1273, 1238, 1221, 1174, 1124, 1074, 1038, 962, 948, 889, 852, 812, 766, 740 cm<sup>-1</sup>.

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[10] Other iodides sources as LiI and KI were also evaluated and compared to NaI. If LiI gave comparable results as NaI, no reaction occurred when KI replaced NaI. Note that when we replaced NaI by NaBr, we were unable to observe any desulfurization reaction, demonstrating the crucial role of iodides in these reactions.

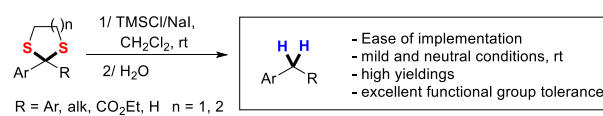
[11] <sup>1</sup>H and <sup>13</sup>C NMR data of derivatives **7** matched perfectly with diarylmethanes previously prepared in our laboratory from a disproportionation reaction of diarylmethylisopropylethers see: N. L'Hermite, A. Giraud, O. Provot, J. F. Peyrat, M. Alami, J. D. Brion, *Tetrahedron* **2006**, 62, 11994–12002.

[12] All desulfurization reactions were optimized with 10 equiv of TMSCl/NaI but depended of the nature of the substrates (see tables for dithioketals, dithiolanes,

- bis*-ethylsulfanes). To avoid too long reaction times for robust substrates, we preferred to increase the quantity of TMSCl/NaI to 20 equiv.
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- [17] Intermediates of type **C** may also exist as highly stable iodonium salts see: H. Volz, W. D. Mayer, *Liebigs Ann. Chem.* **1981**, 1419–1423.
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Chlorotrimethylsilane and Sodium Iodide: A Remarkable Metal-Free Association for the Desulfurization of Benzylic Dithioketals under Mild Conditions

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