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In situ generated HClO for the conversion of thiols and disulfides into thiosulfonates

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Dedicated to Prof. Józef Drabowicz for his 75th birthday

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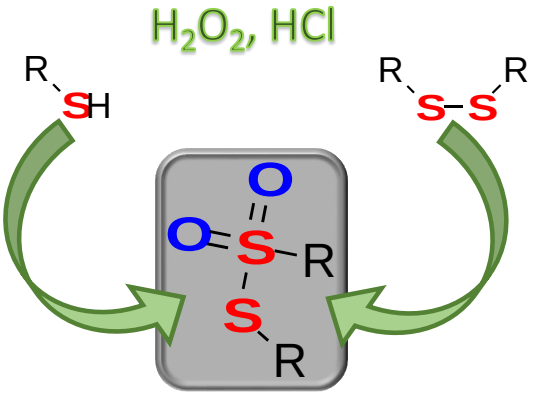
Abstract

A new, practical method for the oxidative conversion of disulfides into thiosulfonates is reported. It is based on the use of hydrogen peroxide as a green oxidant and HCl as a source of the actual catalyst, in acetonitrile as solvent at room temperature. Both disulfides and thiols are efficient substrates in this chemistry that permitted the preparation of a small library of symmetrical thiosulfonates in good yields.



Keywords: Thiosulfonates, thiols, disulfides, hydrogen peroxide, metal-free oxidation

Introduction

Thiosulfonates, the S-esters of thiosulfonic acids, are interesting organosulfur compounds displaying remarkable pharmacological properties and having synthetic applications. In particular, when introduced into organic scaffolds, such functional groups equip the molecule with the ability to block the normal metabolism of pathogenic microorganisms. The chemical mechanism behind such behavior is the ability of thiosulfonates to trigger the sulfonation of thiol groups of various enzymes, that leads to their inhibition (Figure 1).[1] Several antifungal,[2] antiviral[3-5] and anticancer compounds[6] having such a functional group have been reported.[7]

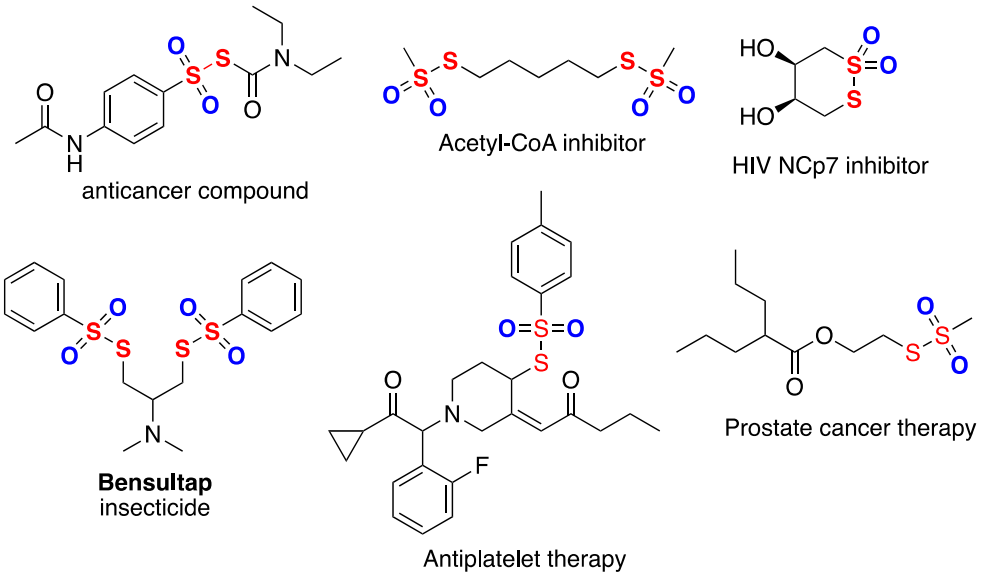


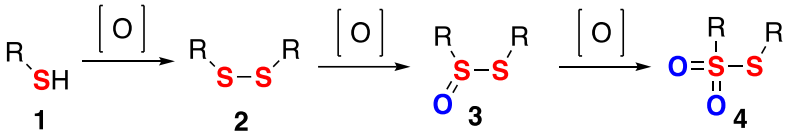
Figure 1. Biologically active compounds bearing the thiosulfonate functionality

From a synthetic perspective, thiosulfonates are particularly useful due to their ability to work as either nucleophiles or electrophiles depending on the reaction conditions. In addition, they are generally more reactive than disulfides, due to the higher polarization of the S-S bond, but, at the same time, they are easier to handle than the highly reactive sulfenyl halides. The synthetic versatility of such compounds is evident in that they can transfer either the sulfenyl as well as the sulfonyl groups to the reaction partners and also the S-S bond has the propensity to break under electrochemical and photocatalytic conditions generating sulfur centered radicals.[8]

There are several methods for the preparation of thiosulfonates, all of them were very recently and comprehensively reviewed highlighting also the parameters associated with each synthetic procedure that make them address the green chemistry prescriptions.[8]

The most practical method to synthesize thiosulfonates is the direct oxidation of disulfides or thiols (Scheme 1) with *m*-chloroperbenzoic acid[9-11] or hydrogen peroxide under acidic conditions,[12] which represent the most employed reagents to perform such transformations. Among several oxidative protocols that have been reported, in the most recent, Back developed a bioinspired selenium catalyzed protocol capable of converting disulfides into the corresponding thiosulfonates in high yields,[13] while Kirihara *et al.* used selectfluor to perform the same transformation.[14,15] In 2010, Chen and coworkers reported the use of trichloroisocyanuric acid as oxidant under mechanochemical conditions.[16] Microwave heating was also implemented for the synthesis of such compounds, as demonstrated by Luu in 2015.[17] Oxone in combination with KBr proved to be a valid alternative as shown by Natarajan *et al.*[18] Finally, molecular oxygen can be used

under photoredox catalysis conditions,[19] and very recently, also an electrochemical approach has been reported to perform such chemistry allowing formation of unsymmetrical thiosulfonates.[20]



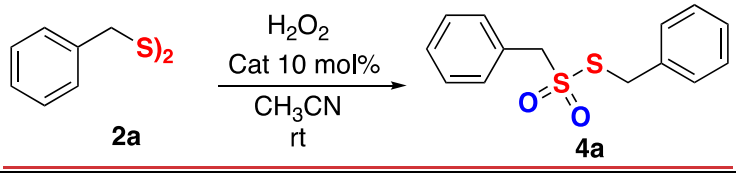
Scheme 1. Stepwise oxidation of thiols to thiosulfonates.

In the context of our ongoing interest in developing green and sustainable chemistry-oriented procedures [21-27] and hydrogen peroxide mediated transformations,[28-30] we here report a practical procedure to synthesize thiosulfonates **4** starting from thiols **1** or disulfides **2** using an halogenide- assisted oxidation with H_2O_2.

Results and Discussion

Acetonitrile was selected as the most suitable solvent to convert the model substrate, dibenzyldisulfide **2a**, into the corresponding thiosulfonate derivative **4a** in the presence of a catalytic amount of copper salts, which were selected as it is known that they are useful in oxidative transformations.[31] Different combinations of catalysts, amounts of catalysts and amounts of hydrogen peroxide were tested monitoring the reactions at different times. The most relevant results are collected in Table 1.

Table 1. Catalysts screening.



Entry	Catalyst	H_2O_2 equiv.	time (h)	Conv%[a]	4a[b]
1		3	31	53	45%
2	$CuCl_2 \bullet 2H_2O$	5	13	100	60%
3		11	13	100	0
4		3	8	95	37%
6	CuCl	3	24	100	45%
7		5	13	100	6%
8		11	13	100	0
9	None	3	71	-	-

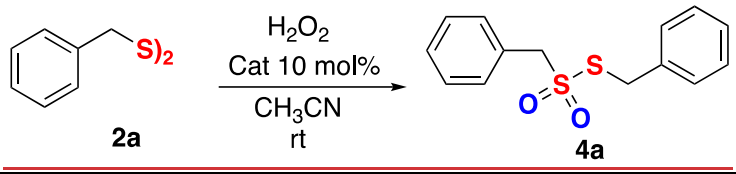
[a]Calculated by ^{1}H NMR analysis of the crude reaction mixture, based on the consumption of **2a**, [b]yield calculated by ^{1}H NMR.

While cuprous nitrite and iodide proved to be ineffective, even after a reaction time of 72 hours (not shown), both copper chlorides (I) and (II) showed an appreciable catalytic capability. In particular, CuCl is able to almost completely convert the starting material in the presence of three equivalents of oxidant after eight

hours (Table 1, entry 4). Unfortunately, the reaction is not selective, since, beside the target compound **4a**, several other overoxidized products were detected in the crude reaction mixture. Cupric chloride, is a weaker catalyst, indeed, to reach a conversion of 53%, 31 hours were needed, but this helped the selectivity, indeed the desired thiosulfonate **4a** was the main reaction product (entry 1). Increasing the reaction time, as well as the amount of hydrogen peroxide did not improve the outcome of the reaction.

In order to understand if the catalytic activity is exerted by the metal or its counter-anion, experiments using catalytic amounts of NaCl or KCl were performed (Table 2).

Table 2. Evaluation of alkaline metal chlorides.



2a **4a**

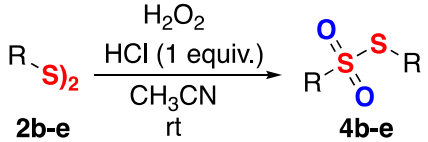
Entry	Catalyst	H_2O_2 equiv.	time (h)	Conv%[c]	4a[d]
1	NaCl	3	55	100	78%
2	KCl	3	45	100	94%
3	HCl[a,b]	3	8	100	93%[e]
4	HCl[a,b]	4	8	100	94%

[a]stoichiometric amounts were used, [b]a stoichiometric amount of 37% (w/w) aqueous hydrochloric acid was used, [c]calculated by ^{1}H NMR of the crude reaction mixture on the consumption of **2a**, [d]yield calculated by ^{1}H NMR, [e]isolated yield.

Using these alkaline metals chlorides the reaction reached completion in a time ranging from 55 h to 45 h and the formation of overoxidized products is almost completely abolished, thus the thiosulfonate **4a** was formed as the main reaction product (Table 2, entries 1 and 2). Comparative reactions were carried out replacing the metal catalysts with stoichiometric amounts of HCl. The reactions in the presence of hydrochloric acid are faster if compared to those catalyzed by alkaline metals chlorides, and if compared to those catalyzed by the copper salts, they are more efficient as lower amounts of oxidant are needed to make the reaction complete. Thiosulfonate **4a** was the only compound obtained from the reaction and only traces of side products, removed after a fast and easy chromatographic purification, were observed.

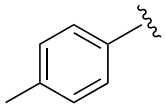
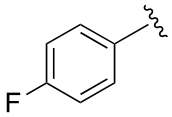
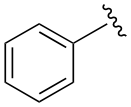
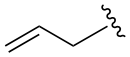
With the best conditions in hansd, the scope of the reaction was briefly explored starting from a small library of aromatic and aliphatic disulfides and aromatic thiols (Tables 3 and 4).

Table 3. Scope of the reaction: disulfides.



2b-e **4b-e**

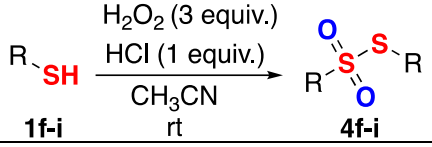
Entry	R	H_2O_2 equiv.	time (h)	Yield of 4

1	 **b**	3	9	95%
2	 **c**	3	8	91%
3	 **d**	3	42	50%
4	 **e**	3	4	34%
		4	16	51%

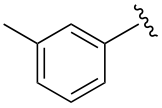
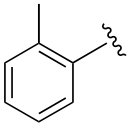
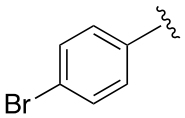
The presence of an electron-donating or -withdrawing group in the phenyl ring did not influence the outcome of the reaction, indeed *p*-tolyldisulfide **2b** and **2c** *p*-fluorophenyl disulfide were straightforwardly converted into the corresponding thiosulfonates in excellent yields, in reaction times ranging from 8 to 9 hours. Diphenyldisulfide **2d** was converted into the target compound after 42 h in fair yield. The aliphatic diallyldisulfide **2e** showed a reduced reactivity when subjected to the oxidation protocol using either three or four equivalents of hydrogen peroxide, yielding S-allyl prop-2-ene-1-sulfonothioate **4e** in fair yields (entry 4) which were slightly improved by prolonging the reaction times to 16 hours.

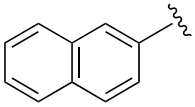
The flexibility of the proposed protocol was tested by using thiols as starting materials. From a stoichiometric standpoint, three equivalents of hydrogen peroxide were enough for both the formation of the disulfide link as well as for the oxidation to thiosulfonate (Table 4).

Table 4. Scope of the reaction: thiols.



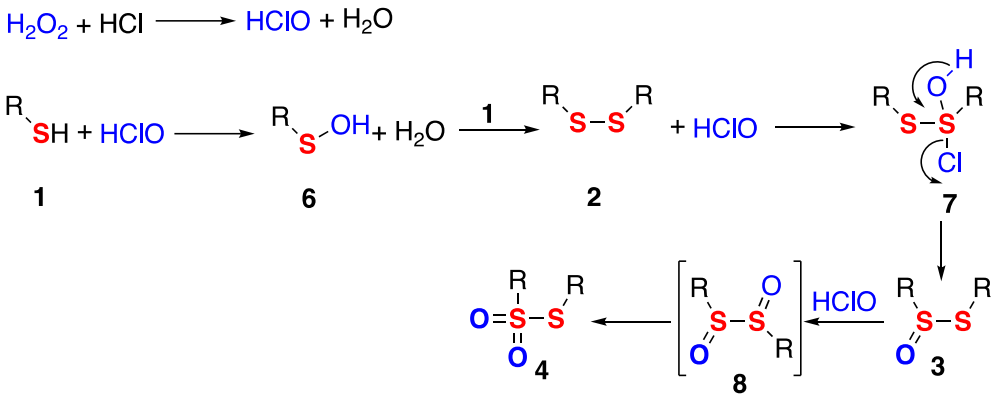
1f-i **4f-i**

Entry	R	time (h)	Yield of 4
1	 **f**	24	94%
2	 **g**	24	84%
3	 **h**	22	54%

4	 **i**	65	74%

Meta-methylphenyl thiol **1f** gave the corresponding thiosulfonate in excellent yield (entry 1) after 24 hours of reaction time. The use of its *ortho* regioisomer **1g** gave a very similar result. (entry 2). Compound **1h** was converted into the thiosulfonate **4h** in lower yield (entry 3). In this specific case the formation of *p*-Br-benzensulfonic acid as an overoxidation and undesired product was observed. The naphthyl derivative **4i** was prepared in good yield but a longer reaction time was required (entry 4).

Based on literature evidence,[32,33] a reaction mechanism can be suggested (Scheme 2). Initially, the oxidation of HCl into hypochlorous acid takes place. Then, HClO reacts with the thiol leading to disulfides that in turn are converted into **7**. Intermediate **7** decomposes to the elusive thiosulfinate **3** which is in turn further oxidized to the target thiosulfonate **4** via the intermediate gem disulfoxide **8**.



Scheme 2. Plausible reaction mechanism.

Conclusions

In the present paper a novel process for the synthesis of thiosulfonates has been developed, including screening of copper and alkali metal chlorides as catalysts. While the reactions catalyzed by copper chloride were unselective, the use of alkali metal chlorides, such as NaCl and KCl, avoided the formation of over-oxidation products, thus obtaining the target thiosulfonates. The use of stoichiometric amounts of HCl shortened the reaction time while maintaining the same chemoselectivity and this allowed the preparation of a small library of thiosulfonates potentially useful for other purposes. This also sugests that in the reaction catalyzed by copper and alkali metal chlorides, it is reasonable to suppose that they act as precursors of HCl and thus of HClO.

Experimental Section

General. Reactions were conducted in round bottom flasks and were stirred with Teflon-coated magnetic stirring bars. Solvents and reagents were used as received unless otherwise noted. The starting materials are commercially available. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 precoated aluminum foil sheets and visualized by UV irradiation or by iodine staining. Sigma Aldrich silica gel (230-400 mesh) was used for flash chromatography and silica gel Kieselgel 60 (70–230 mesh) was used for column chromatography. NMR measurements were conducted at 25 °C on a Bruker Avance 400 spectrometer operating at 400 MHz for ^{1}H, 100.62 MHz for ^{13}C and 376 MHz for ^{19}F experiments. ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) and they are relative to TMS 0.0 ppm and the residual solvent peak of $CDCl_3$ at δ 7.26 and δ 77.00 in ^{1}H and ^{13}C NMR, respectively. ^{19}F spectra were referenced to $CFCl_3$ resonating at 0 ppm. Data are reported as follows: chemical shift (multiplicity, number of hydrogens, coupling constants where applicable, and assignment where possible). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (double of triplet), tt (triplet of triplet), m (multiplet), br s (broad signal). Coupling constant (*J*) are quoted in Hertz (Hz) to the nearest 0.1 Hz. Melting points were measured using a Kofler hot-stage-microscope Thermovar (Reichert, Vienna, Austria) and are reported as uncorrected data.

General procedure for the preparation of thiosulfonates 4a-i. Disulfide or thiol was poured in a round bottom flask and dissolved in acetonitrile in the amount required to prepare 0.1 M solution. To this solution, a stoichiometric amount of 37% (w/w) hydrochloric acid and hydrogen peroxide 30% (3 or 4 molar equivalents) were added. The mixture was stirred at rt until the disappearance of the starting material was revealed by TLC. The reaction was quenched with $NaHSO_2$ 10%, extracted with EtOAc (CH_2Cl_2 only in the case of **4e**), the combined organic layers were washed with brine, dried with Na_2SO_4, filtered and the filtrate evaporated in vacuo. The crude reaction mixture was purified by column chromatography eluting as indicated above.

***S*-Benzyl phenylmethanesulfonothioate (4a).** Compound **4a** was obtained starting from dibenzyldisulfide (100 mg, 0.4 mmol) as white solid in 93% yield (104 mg, 0.37 mmol) after chromatographic purification eluting with PE/EtOAc 99:1 (Rf = 0.4), m.p. 107-110 °C (106 °C [34]). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50-7.25 (m, 10H, ArH), 4.22 (s, 2H, C*H*$_2$SO$_2$), 4.05 (s, 2H, CH_2) ppm; **^{13}C NMR** (100.62 MHz, $CDCl_3$)**:** δ 135.0, 131.6, 129.6, 129. 5, 129.2, 128.9, 128.5, 127.8, 69.2, 41.1 ppm. Spectral data are in agreement with those reported in the literature.[35]

***S*-(*p*-Tolyl) 4-methylbenzenesulfonothioate (4b).** Compound **4b** was obtained starting from di(*p*-tolyl)disulfide (100 mg, 0.4 mmol) as a white solid in 95% yield (105 mg, 0.38 mmol) after chromatographic purification eluting with PE/EtOAc 95:5 (Rf = 0.5), m.p. 75-78 °C (69-70 °C).[16] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48-7.40 (m, 2H), 7.28-7.11 (m, 6H), 2.42 (s, 3H), 2.38 (s, 3H) ppm. **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ 144.8, 142.3, 140.5, 136.7, 130.4, 129.6, 127.7, 124.7, 21.9, 21.8 ppm. Spectral data are in agreement with those reported in the literature.[16]

***S*-(4-Fluorophenyl) 4-fluorobenzenesulfonothioate (4c).** Compound **4c** was obtained starting from di(*p*-fluorophenyl)disulfide (100 mg, 0.4 mmol) as a colorless oil in 91% yield (104 mg, 0.36 mmol) without further purifications. (PE/EtOAc 95:5, Rf = 0.5). **^{1} H NMR** (400MHz, $CDCl_3$): δ 7.60-7.54 (m, 2H), 7.39-7.31 (m, 2H), 7.17-7.01 (m, 4H) ppm; **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ 166.7 (d, J_{HF} = 74.5 Hz), 163.9 (d, J_{HF} = 72.0 Hz), 139.0 (d, J_{HF} 9.16 Hz), 138.9 (d, J_{HF} 3.12Hz), 130.6 (d, J_{HF} 9.7Hz), 117.1 (d, J_{HF} 3.28Hz), 116.4 (d, J_{HF} 22.13Hz).; **^{19}F NMR** (376 MHz, $CDCl_3$): δ - 102.9, - 107.2 ppm. Spectral data are in agreement with those reported in the literature.[16]

***S*-Phenyl benzenesulfonothioate (4d).** Compound **4d** was obtained starting from diphenyldisulfide (100 mg, 0.46 mmol) as a colorless oil in 50% yield (58 mg, 0.23 mmol) after chromatographic purification eluting with PE/EtOAc 99:1 (Rf = 0.4). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61-7.53(m, 3H), 7.50-7.38 (m, 3H), 7.36- 7.29 (m, 4H)

ppm; **^{13}CNMR** (100.62 MHz, $CDCl_3$)**:** δ 143.0, 136.8, 133.9, 131.7, 129. 7, 129.0, 127.9, 127.7 ppm. Spectral data are in agreement with those reported in the literature.[16]

***S*-allyl prop-2-ene-1-sulfonothioate (4e).** Compound **4e** was obtained starting from diallyldisulfide (100 mg, 0.7 mmol) using 4 molar equivalents of H_2O_2 as a yellow oil in 51% yield (62 mg, 0.35 mmol) after chromatographic purification eluting with PE/EtOAc 99:1 (Rf = 0.3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.01- 5.83(m, 2H), 5.61-5.45 (m, 2H), 5.36 (d, *J* = 17 Hz, 1H); 5.26 (d, *J* =10 Hz, 1H) 3.99 (d, *J*= 7.3 Hz, 2H), 3.79 (d, *J*= 7.2 Hz, 2H) ppm; **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ 131.9, 126.2, 124.6, 120.3, 67.4, 39.6 ppm. Spectral data are in agreement with those reported in the literature.[36]

***S*–(*m*-Tolyl) 3-methylbenzenesulfonothioate (4f).** Compound **4f** was obtained starting from *m*-methylthiophenol (25 mg, 0.2 mmol) as a colorless oil in 94% (26 mg, 0.09 mmol). (PE/EtOAc 97:3, Rf = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.25 (m, 6H), 7.22-7.16 (m, 2H), 2.40 (s, 3H), 2.35 (s, 3H) ppm; **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ 142.9, 139.6, 139.2, 137.4, 134.5, 133.8, 132.4, 129.3, 128.7, 128.2, 127.8, 124.9, 21.3, 21.3 ppm. Spectral data are in agreement with those reported in the literature.[16]

***S*-(*o*-Tolyl) 2-methylbenzenesulfonothiote (4g).** Compound **4g** was obtained starting from *o*-methylthiophenol (100 mg, 0.8 mmol) as a colorless oil in 84% yield (93 mg, 0.4 mmol) after chromatographic purification eluting with PE/EtOAc 99:1 (Rf = 0.4). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.50-7.43 (m, 1H), 7.39 (d, *J* = 8Hz, 1H), 7.35-7.29 (m, 2H), 7,27-7.16 (m, 2H), 7.15-7.05 (m, 2H), 2.72 (s, 3H), 2.17 (s, 3H) ppm. **^{13}CNMR** (100.62 MHz, $CDCl_3$): δ 144.3, 141.1, 138.6, 137.9, 134.0, 133.1, 132.0, 131.0, 130.2, 127.1, 127.0, 126.1, 20.7, 20.6 ppm. Spectral data are in agreement with those reported in the literature.[37]

***S*-(4-Bromophenyl) 4-bromobenzenesulfonothioate (4h).** Compound **4h** was obtained starting from *p*-bromothiophenol (104 mg, 0.55 mmol) as a white solid in 54% yield (61 mg, 0.15 mmol) after chromatographic purification eluting with PE/EtOAc 90:10 (Rf = 0.5), m.p.152-158 °C (150-152 °C).[16] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64-7.58 (m, 2H), 7.55-7.49 (m, 2H), 7.48-7.42 (m, 2H), 7.28-7.22 (m, 2H) ppm. **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ 142.0, 138.0, 133.1, 132.5, 129.4, 129.1, 127.2, 126.7 ppm. Spectral data are in agreement with those reported in the literature.[16]

***S*-(Naphthalen-2-yl)naphthalene-2-sulfonothioate (4i).** Compound **41** was obtained starting from naphthalene-2-thiol (100 mg, 0.6 mmol) as white solid in 74% yield (78 mg, 0.22 mmol) after chromatographic purification eluting with PE/EtOAc 99:1 (Rf = 0.4), m.p. 99-103 °C (100-102 °C)[38]; **^{1} H NMR** (400MHz, $CDCl_3$): δ 7.96-7.93 (m, 1H), 7.92-7.87 (m, 2H), 7.86-7.82 (m, 2H), 7.74 (d, *J*= 8.5 Hz, 1H), 7.69-7.61 (m, 4H), 7.60-7.46 (m, 3H), 7.38-7.32 (dd, *J*= 1.5 and 8.5 Hz, 1H) ppm. **^{13}C NMR** (100.62 MHz, $CDCl_3$): δ 139.8, 137.9, 135.3, 134.3, 133.4, 132.0, 131.8, 129.6, 129.6, 129.5, 129.3, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127,1, 125.3, 122.6 ppm. Spectral data are in agreement with those reported in the literature.[38]

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Supplementary Material

Copies of the ^{1}H, ^{13}C, ^{19}F NMR spectra are available in the supplementary material file associated with this manuscript.

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