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# New Protocol for the Synthesis of S-thioesters from Benzylic, Allylic and Tertiary Alcohols with Thioacetic Acid

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**Abstract:** A new one-pot solvent-less reaction to convert benzylic, allylic, ferrocenyl or tertiary alcohols into S-thioesters, bench-stable and less odorous precursors of the corresponding thiols, which is based on reactions in neat thioacetic acid in the presence of tetrafluoroboric acid, is presented. Reaction monitoring by NMR and GC of the benzyl alcohol conversion indicated the intermediate formation of benzyl acetate and benzyl thionoacetate ( $\text{PhCH}_2\text{OC}(\text{S})\text{CH}_3$ ) prior to the slower conversion to the final S-benzyl thioacetate product. Increasing the  $\text{HBF}_4$  concentration enhanced the reaction rate, giving good to excellent yield (up to 99%) for a large scope of alcohols. Control experiments, with support of DFT calculations, have revealed a thermodynamically favorable, though requiring  $\text{HBF}_4$ -activation, disproportionation of  $\text{CH}_3\text{C}(\text{O})\text{SH}$  to  $\text{CH}_3\text{C}(\text{O})\text{OH}$  and  $\text{CH}_3\text{C}(\text{S})\text{SH}$ , the latter immediately decomposing to  $\text{H}_2\text{S}$  and  $(\text{MeC})_4\text{S}_6$  but also generating the hitherto unreported  $[\text{MeC}(\text{O})\text{C}(\text{Me})\text{S}]_2(\mu\text{-S})_2$ . Kinetic investigations demonstrated that the rate of benzyl alcohol conversion is second-order in  $[\text{PhCH}_2\text{OH}]$  and second order in  $[\text{HBF}_4]$ , while the rate of conversion of the benzyl acetate intermediate to S-benzyl thioacetate is second order in  $[\text{PhCOOMe}]$  and fourth order in  $[\text{HBF}_4]$ . The DFT calculations rationalize the need to two alcohol molecules and two protons to generate the reactive benzyl cation.

## Introduction

Alkyl thiols are usually considered as malodorous analogues of alcohols. They are essential to life as the thiol function is found in various biological molecules (e.g. cysteine, glutathione, coenzyme A) and in numerous materials and consumer products such as plastics, flavors and fragrances, agricultural chemicals or animal food.<sup>[1]</sup> Thiols are also attracting increasing interest in coordination chemistry, because of their utility for the installation of thioether donor functions. Compared to oxygen or nitrogen, sulfur in thioether ligands is a softer donor, which is a useful property for the design of polydentate ligands. Indeed, careful choice of the donating atoms allows to better tune the ligand

electronic and steric properties, which are fundamental levers to optimize the catalytic activity and selectivity.<sup>[2]</sup>

Many different strategies, using various precursors, have been adopted to synthesize thiols.<sup>[1b, c]</sup> Among them, those using alcohols appear particularly attractive because of the wide commercial availability and low cost of these precursors. According to the literature, alcohols are most efficiently converted to thiols by nucleophilic attack of the electrophilically activated alcohol carbon atom by a sulphur reagent (thioacetic acid, thioester, thiourea, or dithiocarbamate salts).<sup>[1, 3]</sup> The alcohol electrophilic activation involves either conversion of the OH function into a better leaving group (e.g. tosylation, halogenation or the Mitsunobu reaction), or water elimination in the presence of a strong acid, giving rise to a carbocation. The latter strategy is limited to tertiary and benzylic alcohols. Another efficient strategy involves the Lawesson reagent, which allows a one-pot thiolation of secondary or tertiary alcohols.<sup>[1, 4]</sup> However, none of these methods seems universal and a careful screening of the method and reaction conditions is usually necessary to reach the expected yield and purity for the targeted thiol compound. In addition, certain alcohol substrates do not give satisfactory results with any of the above methods. Indeed, we have experienced this difficulty during the synthesis of ferrocene-based phosphine-thioether chiral ligands bearing a phenol function, aiming at silica grafting and subsequent application in heterogenized enantioselective catalysis (Scheme S1).

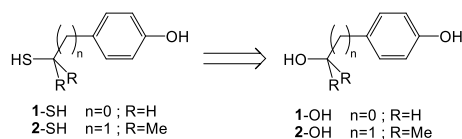
We herein report a new methodology for the conversion of alcohols into the corresponding thiols in a thioester-protected form, which appears generally applicable to tertiary, benzylic, allylic and ferrocenyl substrates. The reaction conditions optimization was explored through a kinetic study, which revealed an unsuspected acid-catalyzed disproportionation of thioacetic acid. This reaction has been thoroughly investigated and has led to the isolation and full characterization of sulfur-based decomposition products, one of which had not been previously described. Finally, the synthesis of two previously unreported thiol-phenols by this new methodology is also described.

## Results and Discussion

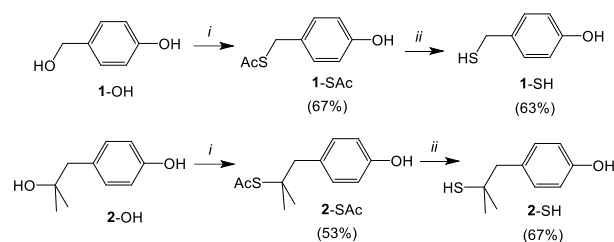
## (a) Exploratory conversions of alcohols to thioesters

The investigation started with the attempted conversion of alcohols **1-OH** and **2-OH** to the corresponding thiols **1-SH** and **2-SH** (Scheme 1). These are simpler model substrates of our target ligands of Scheme S1. Compound **1-OH** is commercially available, whereas **2-OH** has apparently not been previously reported. It was prepared in good yields by methylation of the commercially available ketone with MeMgBr, and has been fully characterized by multinuclear NMR, mass spectroscopy and single-crystal X-ray diffraction (Figure S1). All attempts to introduce the thiol function (using either potassium thioacetate, thioacetic acid or a polymer-supported hydrosulfide reagent)<sup>[5]</sup> after alcohol activation via tosylation or trifluoroacetylation,<sup>[6]</sup> or via the Mitsunobu reaction,<sup>[7]</sup> were unsuccessful. Another attempted strategy consisted of the protection of the phenol function with a *tert*-butyldimethylsilyl group (TBDMS = SiMe<sub>2</sub>tBu), in view of the conversion of the alcohol to the corresponding chloride and further conversion of the C-Cl bond into a C-SH bond by the established one-pot successive additions of magnesium in dry THF, S<sub>8</sub> and H<sub>2</sub>O.<sup>[8]</sup> However, the chlorination by addition of HCl, SOCl<sub>2</sub> or by Ph<sub>2</sub>CCl<sub>2</sub> (catalyzed by FeCl<sub>3</sub>)<sup>[9]</sup> gave a low yield and a complex product mixture for both substrates.

Since **1-OH** and **2-OH** are respectively benzylic and tertiary alcohols, we also explored the addition of an acid to promote carbocation formation, or at least OH activation, facilitating C-S bond formation. An attempt using BF<sub>3</sub>·OEt<sub>2</sub>, followed by addition of thioacetic acid (AcSH) or the corresponding potassium salt (KSAc), were unsuccessful.<sup>[10]</sup> We then investigated the efficiency of a stronger acid, such as tetrafluoroboric acid (HBF<sub>4</sub> in diethyl ether), which was previously used in our laboratory for the formation of a carbocation intermediate involved in the synthesis of functionalized ferrocenyl phosphine ligands.<sup>[11]</sup> This approach was equally unsuccessful when using AcSH in stoichiometric amounts (no reaction was observed). However, convinced about the ability of HBF<sub>4</sub> to generate the carbocation intermediate, the reaction was carried out again using AcSH as solvent, in order to maximize its addition rate and limit the side reactions, given the possible competitive action of other nucleophiles, present in the reaction mixture, for the highly reactive formed carbocation. Under these conditions and with 0.15 equivalents of HBF<sub>4</sub>, both expected S-thioesters **1-SAc** and **2-SAc** could finally be obtained in isolated yields of 67% and 53%, respectively, after 30 minutes (Scheme 2). Subsequent treatment with a methanolic solution of NaOMe led to **1-SH** and **2-SH** with 63% and 67% yield, respectively.



**Scheme 1.** Retrosynthesis of thiol-phenol intermediates from the corresponding alcohol-phenols.

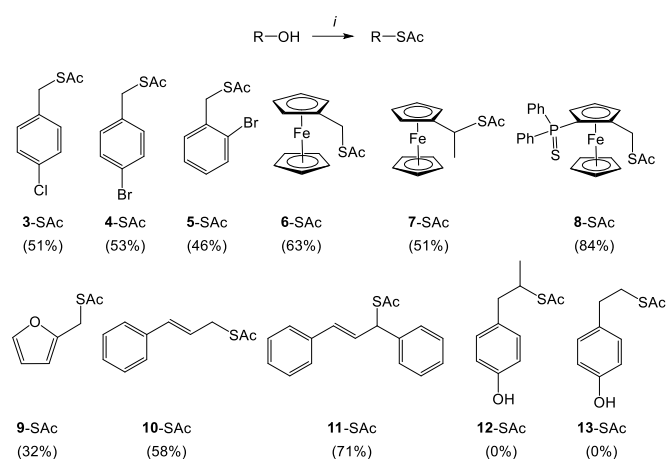


**Scheme 2.** Synthesis of thiol-phenols **1-SH** and **2-SH** from the corresponding alcohols **1-OH** and **2-OH** (isolated yields after purification by column chromatography); *i*: HBF<sub>4</sub> (0.15 mol eq.), AcSH, 30 min; *ii*: NaOMe (2 mol eq.), MeOH, 90 min.

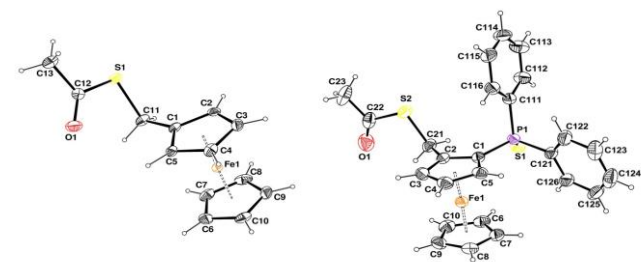
## (b) Reaction scope

In order to assess the robustness of the method, the same protocol was applied to a few other substrates, mainly tertiary, allylic, ferrocenyl and benzylic alcohols. In most cases, the expected S-thioester compound (**R-SAc**), was isolated with moderate to good yield (Scheme 3). Compounds **1-SAc**, **2-SAc**, **6-SAc**, **7-SAc**, **8-SAc** and **15-SAc** are reported here for the first time, whereas all other thioacetates have been previously described but have been more fully characterized in the present investigation (see SI). The C=O function presents a characteristic signal around 195 ppm in the <sup>13</sup>C NMR spectrum.

The collective results of Scheme 3 point to a classical S<sub>N</sub>1 mechanism, since greater yields were obtained for those systems that enable stabilization of the carbocation intermediate. Indeed, no reaction was observed for primary (**13**) and secondary (**12**) alcohols, whereas a moderately good yield (53%) was obtained for a tertiary alcohol (**2-OH**, Scheme 2). Increased delocalization (**10** and **11**) is also beneficial for carbocation stabilization, as is the presence of π-donor *o/p* substituents on the benzylic alcohol aromatic ring (**1** and **3-6**). Computational studies<sup>[12]</sup> and single-crystal X-ray diffraction<sup>[13]</sup> demonstrated that α-ferrocenyl carbocations are stabilized by the interaction with the iron atom, rationalizing the higher yield obtained for the ferrocenyls alcohols (**6**, **7** and **8**). The lower yield of **7-SAc** may result from the steric hindrance around the carbon atom, complicating the nucleophilic attack at the carbocation. Compounds **6-SAc** and **8-SAc** were characterized by X-Ray diffraction (Figure 1). Finally, the low yield obtained for methyl furanol (**9**) may be a consequence of the oxygen electron withdrawing action, decreasing the π-stabilization of the intermediate carbocation, although the presence of impurities in the starting material may also have affected the performance. Moreover, such compounds are known to easily polymerize in acidic media.<sup>[14]</sup> All these assumptions must be taken with caution, as they are only based on a comparison of the isolated yields.



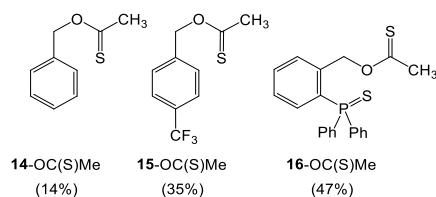
**Scheme 3.** Scope of the thioester (R-SAc) synthesis from alcohols (R-OH) and thioacetic acid; *i*. Conditions- 0.15 molar equivalents of HBF<sub>4</sub> in AcSH, room temperature, 30 min (1 h for **3**, **4** and **5**). Yields were determined on isolated products after extraction and purification by column chromatography.



**Figure 1.** Molecular views of compounds **6**-SAc (left) and **8**-SAc (right) with the atom labelling scheme. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small sphere of arbitrary radii.

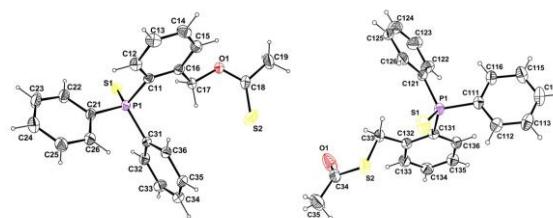
### (c) Thiono- vs. thioester

A surprisingly different and initially puzzling result was obtained for another three different benzylic systems (**14**, **15** and **16**, Figure 2). Instead of the S-thioesters (R-SAc), the isolated products were the O-alkyl thioesters (or thionoesters,<sup>[15]</sup> R-OC(S)Me), suggesting a more complex reaction mechanism. Such structures are clearly proven by their <sup>13</sup>C NMR spectra, because the quaternary C=S group gives a characteristic signal around 219 ppm, a higher chemical shift than the corresponding C=O of the thioester group (around 195 ppm). Compounds **15**-OC(S)Me and **16**-OC(S)Me have not been previously described.



**Figure 2.** Various alcohol transformation into the corresponding thionoesters. Conditions: 0.15 molar equivalents of HBF<sub>4</sub> in AcSH, room temperature, 30 min. Yield were determined after extraction and column chromatography purification.

The S-thioester **16**-SAc, which is also reported for the first time here, could be accessed *via* the Mitsunobu reaction. Full characterization of both **16**-SAc and **16**-OC(S)Me by NMR, mass spectroscopy and single-crystal X-ray diffraction (Figure 3) confirmed the assignment of the <sup>13</sup>C NMR resonance observed around 220 ppm for the C=S moiety of **16**-OC(S)Me, obtained from the **16**-OH/HBF<sub>4</sub>/AcSH reaction.



**Figure 3.** Molecular views of compound **16**-OC(S)Me (left) and **16**-SAc (right) with the atom labelling scheme. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small sphere of arbitrary radii.

### (d) Effect of the HBF<sub>4</sub> amount

Facing difficulties in the rationalization of the results reported in Figure 2, a closer look was taken at the reaction with benzyl alcohol (**14**-OH), always using AcSH as reaction medium. In the absence of HBF<sub>4</sub>, no reaction was observed, confirming the essential catalytic role of this additive. The <sup>1</sup>H NMR spectrum of the final reaction mixture resulting in the preparation of **14**-OC(S)Me (with 0.15 equivalents of HBF<sub>4</sub>) showed the presence of residual **14**-OH in addition to the product resonances. However, two additional compounds were also observed and identified, after chromatographic separation, as the target thioester **14**-SAc and the ester, **14**-OAc. Although the presence of **14**-SAc was anticipated, the observation of the acetate constituted a second surprise. The <sup>1</sup>H and <sup>13</sup>C NMR investigation of the thioacetic acid reagent did not reveal any significant amounts of acetic acid.

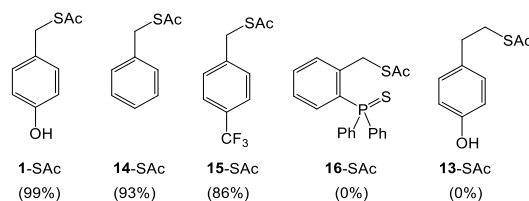
A kinetic investigation was then undertaken at different substrate/HBF<sub>4</sub> ratios, using gas chromatography for quantitative analysis. Even though <sup>1</sup>H NMR would allow determining the relative amounts of each compound (the CH<sub>2</sub> resonances of alcohol, ester, thioester and thionoester, at 4.63, 5.15, 5.50 and 4.14 ppm, respectively, can be well-distinguished), gas chromatography allowed faster sample preparation (no need for solvent removal prior to analysis) and higher sensitivity. The **14**-OC(S)Me, **14**-SAc and **14**-OAc standards were synthesized and purified for calibration purposes. The time evolution of all compounds is shown in Figure 5. In the presence of 0.15 equivalents of HBF<sub>4</sub>, the alcohol conversion was already 40% after only 10 minutes and reached 90 % after 3 hours. Interestingly, the ester is the major final product (around 70%), followed by **14**-OC(S)Me (10%) and the target thioester **14**-SAc in the smallest amount (4 %). Increasing the HBF<sub>4</sub> amount to 0.5 equivalents enhanced dramatically the conversion rate as more than 90% of the alcohol was consumed in less than 10 minutes and 99% in 40 min. Under these conditions, the expected **14**-SAc became the major product after 3 hours (56 %). However, the ester species **14**-OAc remained the kinetically favored product during the initial phase of the reaction (maximum amount of ca. 60 % after 20 min) and persisted even after 3 h (ca. 42%). The thionoester **14**-OC(S)Me is clearly also an intermediate,

increasing up to nearly 21% after 10 min, then dropping to 1 % at 40 min before disappearing completely.

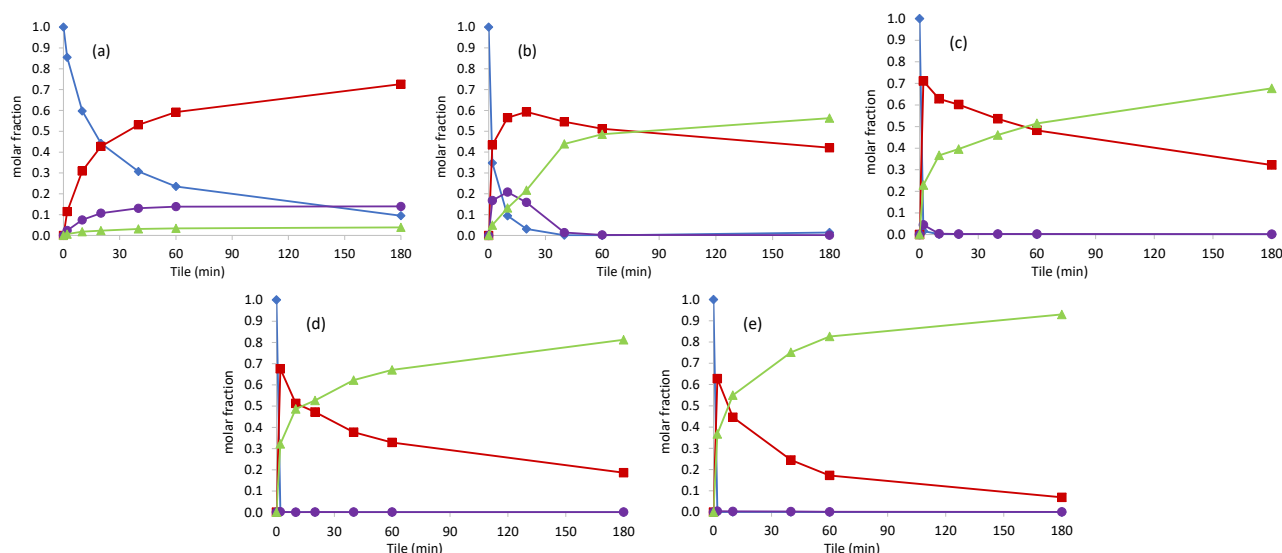
With greater amounts of  $\text{HBF}_4$  (1, 1.5 and 2 equivalents), the reaction rate further increased, the alcohol conversion reaching more than 98 % in less than 2 minutes with 1 equivalent, while no residual alcohol could be detected at the first sampling with 1.5 and 2 equivalents. Gas evolution was observed after the tetrafluoroboric acid addition, without any increase of the solution temperature, more evidently for the runs with greater  $\text{HBF}_4$  amount, whereas this phenomenon was not noticed for the two above experiments with 0.15 and 0.5 equivalents of  $\text{HBF}_4$  per  $\text{PhCH}_2\text{OH}$ . Simultaneously to the gas evolution, the formation of a yellow precipitated was noticed (see below for further details on this product). The thionoester intermediate could be observed only during the first 10 minutes when using 1 equivalent of  $\text{HBF}_4$ , but did not exceed 4 % and was not observed at all in the presence of 1.5 and 2 equivalents of  $\text{HBF}_4$ . In all these runs, the ester remained the major species initially, then progressively converting into the thioester product to reach a 68, 81 or 93% yield after 3 hours in the presence of 1, 1.5 or 2 equivalents of  $\text{HBF}_4$ , respectively.

The reaction conditions of the last experiment (2 equivalents of  $\text{HBF}_4$ ) were then applied to the conversions of alcohols **14**-OH,

**15**-OH and **16**-OH (Figure 4). Under these conditions, **14**-SAc and **15**-SAc were obtained in 93 % and 86 % isolated yields, respectively, with total alcohol conversion. For **16**-OH, however, the NMR analysis indicated the presence of the ester **16**-OAc (nearly 85 %) and ca. 15 % of residual alcohol. This lower conversion may be explained by steric hindrance or intramolecular electronic interaction between the two ortho functional groups. No alcohol conversion and no thioester formation were observed, even under these conditions, for the primary alcohol **13**-OH.



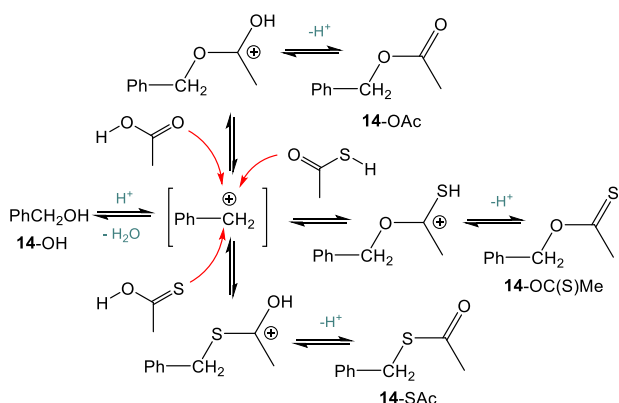
**Figure 4.** Transformation of various alcohols into the corresponding thioesters in the presence of 2 equivalents of  $\text{HBF}_4$  in  $\text{AcSH}$ . Yields were determined by integration of the  $^1\text{H}$  NMR resonances of the crude reaction mixture.



**Figure 5.** Time evolution of alcohol ( $\blacklozenge$ ), ester ( $\blacksquare$ ), thionoester ( $\bullet$ ) and thioester ( $\blacktriangle$ ) in the reaction of  $\text{PhCH}_2\text{OH}$  with 0.15 (a), 0.5 (b), 1.0 (c), 1.5 (d) and 2.0 (e) equivalents of  $\text{HBF}_4$  per  $\text{PhCH}_2\text{OH}$  in  $\text{CH}_3\text{C}(\text{O})\text{SH}$  (the  $\text{PhCH}_2\text{OH}/\text{MeCOSHS}$  ratio was approximately 0.06 in all samples).

**(e) Mechanistic investigations**

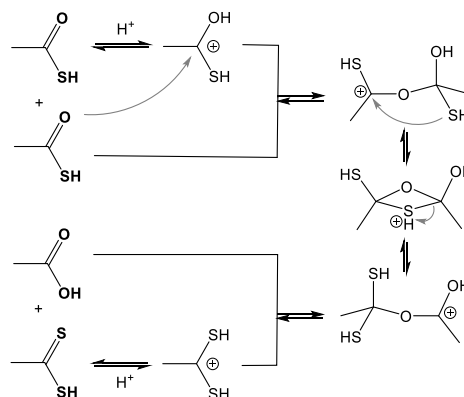
The reaction monitorings detailed in the previous section (Figure 5) clearly indicate a complex reaction scheme with faster generation of the ester (**14-OAc**) and thioester (**14-OC(S)Me**) as intermediates and final generation of the targeted thioester (**14-SAc**) product. A reasonable mechanistic hypothesis is to invoke the generation of the benzyl cation as a common intermediate, followed by the nucleophilic attack by acetic, thioacetic MeC(O)SH and thioacetic acid MeC(S)OH, as shown in Scheme 4. Since the most nucleophilic center is the doubly bonded heteroatom (O or S) in the (thio)carbonyl group, the thioester is generated by thioacetic acid and the thiooester by thioacetic acid. The observed product evolution indicates that the generation of both the acetate and the thioacetate are reversible processes, eventually leading to the irreversible formation of the thioacetate. Both the initial alcohol consumption and the isomerizations appear to be accelerated by greater concentrations of HBF<sub>4</sub>. To confirm the influence of the acid concentration, **14-OAc** was dissolved in thioacetic acid at room temperature, but no reaction was observed over 3 hours. However, full conversion to **14-SAc** occurred over the same time span in the presence of 2 eq. of HBF<sub>4</sub>. The same test was also carried out with the isolated **14-OC(S)Me**: no reaction occurred after dissolution in thioacetic acid. However, the subsequent addition of either acetic acid (more slowly) or HBF<sub>4</sub> to the solution induced its quantitative conversion to **14-SAc**, establishing an acid-catalyzed pathway for this isomerization.



**Scheme 4.** Proposed mechanism of benzyl alcohol thioesterification.

The thioacetic acid needed to yield the final product may be present at equilibrium with thioacetic acid and the equilibration is likely to be fast (see DFT section below). In addition, the final product is obtained only slowly, consistent with the action of a reagent at a very small concentration. The acetate product, on the other hand, forms very rapidly in massive amounts, especially in the presence of a large HBF<sub>4</sub> excess, while the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the thioacetic acid reagent show the presence of only trace amounts of acetic acid, at best (see below). Thus, it seems that acetic acid is produced *in situ* from CH<sub>3</sub>C(O)SH under the conditions of the reaction, namely in the presence of HBF<sub>4</sub>. This appears possible *via* a disproportionation, two molecules of thioacetic acid being converted into one of acetic acid and one of dithioacetic acid, under the catalytic action of the strong HBF<sub>4</sub> acid. We note that dithioacetic acid, CH<sub>3</sub>C(S)SH, is reported as an unstable compound, contrary to the corresponding dithioacetate

esters.<sup>[16]</sup> This transformation may be envisaged by the mechanism shown in Scheme 5.



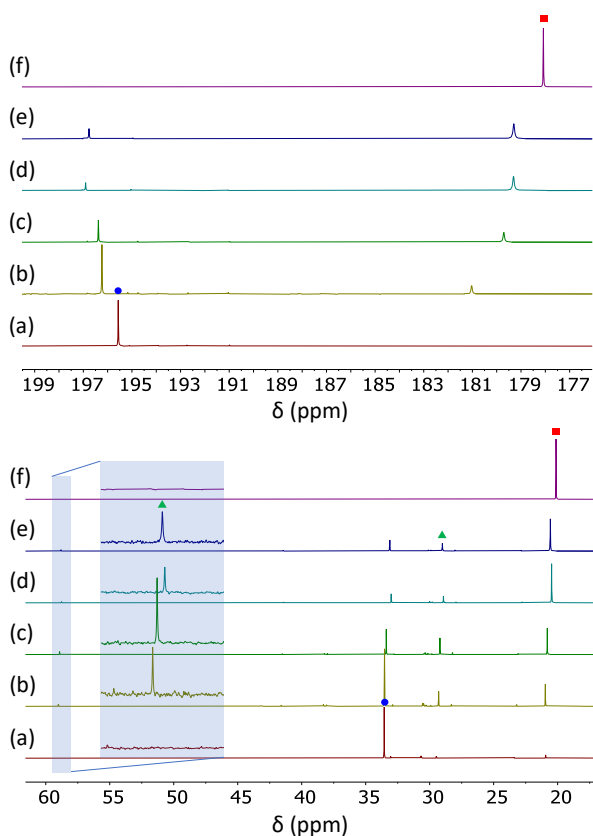
**Scheme 5.** Proposed mechanism for thioacetic acid disproportionation.

**Reaction of HBF<sub>4</sub> with thioacetic acid**

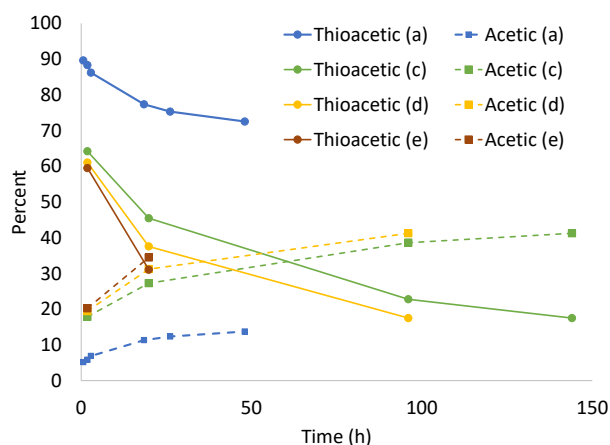
In order to learn more about this hypothesis, various thioacetic acid samples were treated with different amounts of HBF<sub>4</sub> under conditions reproducing the experiments in Figure 5 (same acid concentrations), though without **14-OH**, and monitored by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}v NMR. During these experiment, gas evolution and the formation of a yellow precipitate were noted, like during the reactions run in the presence of **14-OH** (Figure 5), more conspicuously under the conditions of Figure 5e (2 eq. HBF<sub>4</sub>) and not at all under those of Figure 5a (0.15 eq. HBF<sub>4</sub>). The most useful information was obtained from the <sup>13</sup>C{<sup>1</sup>H} spectra. A representative series (conditions equivalent to those of Figure 5c) is shown in Figure 6. The corresponding series of <sup>1</sup>H NMR spectra is shown in the SI (Figure S2).

The carbonyl resonance region (Figure 6, top) clearly shows the absence of a significant amount of CH<sub>3</sub>C(O)OH in the AcSH sample (a) and its rapid and continuous generation after the HBF<sub>4</sub> addition (b-e). The resonances shift as the reaction progresses, probably because of changes in the H-bonding equilibria. There are no other resonances in this region, indicating that the dithioacetic acid generated by the disproportionation reaction decomposes rapidly [<sup>13</sup>C NMR peaks of dithioacetic acid in C<sub>6</sub>D<sub>6</sub> have been reported at δ 43.46 (CH<sub>3</sub>) and 237.15 (C(=S)SH)].<sup>[17]</sup> The Me resonance region (Figure 6, bottom) confirms the gradual conversion of CH<sub>3</sub>C(O)SH into CH<sub>3</sub>C(O)OH, and also revealed the resonances of other products, the most notable ones being two resonances observed at δ 29.3-28.9 and 59.0-59.8 (slightly drifting as the reaction progresses), marked with green triangles (see below for an assignment of these resonances). The amount of converted thioacetic acid was already 36% after only 1.8 hours and increased to 92.5% after 144 h, as shown by integration of the <sup>1</sup>H resonances (Figure S2). The time evolutions of the acetic and thioacetic acid fractions, calculated from the <sup>1</sup>H NMR integrations, as a function of the amount of added HBF<sub>4</sub> are shown in Figure 7. From these results, it can be clearly concluded that the thioacetic acid conversion is faster in the presence of greater amounts of HBF<sub>4</sub> and that it is extensive. However, no simple rate law for the concentration decay could be derived. A possible reason is a variation of the HBF<sub>4</sub> concentration during the MeC(S)SH decomposition (*vide infra*).





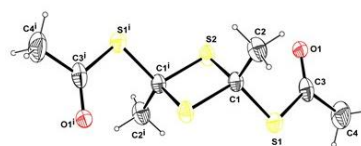
**Figure 6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR monitoring of the reaction of  $\text{CH}_3\text{C}(\text{O})\text{SH}$  in the presence of  $\text{HBF}_4\cdot\text{OEt}_2$  (0.068 equiv, corresponding to the concentration of the experiment in Figure 5c) at room temperature: (a)  $\text{CH}_3\text{C}(\text{O})\text{SH}$ ; (b-e)  $\text{CH}_3\text{C}(\text{O})\text{SH} + \text{HBF}_4\cdot\text{OEt}_2$  recorded after 1.8, 19.8, 96 and 144 h after mixing. (f)  $\text{CH}_3\text{C}(\text{O})\text{OH}$ . The spectra were locked internally on  $\text{D}_2\text{O}$ , introduced in the tube as a sealed capillary. The top and bottom frames show the expanded regions of the carbonyl and methyl nuclei, respectively. Additional visible peaks were only those of  $\text{Et}_2\text{O}$  ( $\delta$  14.3 for  $\text{CH}_3$ , 68.6-67.3, shifting with time, for  $\text{CH}_2$ ) in spectra (b-e). The resonances marked with a blue circle belong to  $\text{CH}_3\text{C}(\text{O})\text{SH}$ ; those marked with a red square to  $\text{CH}_3\text{COOH}$ , and those marked with a green triangle to  $(\text{MeC})_4\text{S}_6$ .



**Figure 7.** Evolutions of the  $\text{CH}_3\text{COSH}$  and  $\text{CH}_3\text{COOH}$  fractions with time in the presence of different  $\text{HBF}_4\cdot\text{OEt}_2$  amounts. The fractions are derived from integration of the  $^1\text{H}$  NMR resonances, with the assumption that the reaction affords equivalent amounts of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{CSSH}$ . The labels (a), (c), (d) and (e) correspond to the conditions used for the experiments shown in Figure 5 (without **14-OH**).

The next question is the fate of the dithioacetic acid presumably produced by the disproportionation and whether its decomposition could account for the observed generation of a gas and a precipitate. In the literature,  $\text{MeC}(\text{S})\text{SH}$  was described as an air sensitive reddish-yellow oil<sup>[16]</sup> and found to readily eliminate  $\text{H}_2\text{S}$ .<sup>[16-17, 19]</sup> Additional experiments were carried out by head-space GC-MS. After degassing (by Ar bubbling) to eliminate any trace of dissolved gaseous compounds and subsequent thermal equilibration in a head-space analytical vial, the gas phase analysis by GC-MS showed the presence of argon ( $M^+ = 40$ ) and  $\text{CH}_3\text{C}(\text{O})\text{SH}$  ( $M^+ = 76$ ) as major components, plus barely detectable traces of acetic acid ( $M^+ = 60$ ). After addition of  $\text{HBF}_4\cdot\text{OEt}_2$  at a concentration corresponding to that of Figure 5e, the solution turned bright yellow and gas evolution was observed. A new head-space GC-MS analysis showed the same three peaks as above, but the peak at  $M^+ = 60$  for acetic acid had now a much greater relative intensity. Two additional peaks were now quite evident at  $M^+ = 74$ , corresponding to  $\text{Et}_2\text{O}$  from the tetrafluoroboric acid diethyl ether complex, and at  $M^+ = 34$ , attributed to  $\text{H}_2\text{S}$ . Finally, the mass spectra of two additional small GC signals are consistent with the formation of  $\text{CH}_3\text{C}(\text{O})\text{OEt}$  and  $\text{CH}_3\text{C}(\text{O})\text{SEt}$ , presumably originating from substitution reactions with diethyl ether. This experiment thus provides further evidence in favor of the disproportionation of  $\text{CH}_3\text{C}(\text{O})\text{SH}$ , with the  $\text{CH}_3\text{C}(\text{S})\text{SH}$  product decomposing to release  $\text{H}_2\text{S}$ . The absence of any dithioacetate product in the reaction mixture indicates that the  $\text{CH}_3\text{C}(\text{S})\text{SH}$  nucleophilicity towards the benzyl cation is insufficient to compete with its decomposition rate.

The precipitate generated during the above decomposition reaction could be recrystallized from  $\text{Et}_2\text{O}$  to afford two different types of suitable crystals for X-ray diffraction analyses. For one of these compounds, the unit cell parameters matched those reported for 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathiaadamantane<sup>[20]</sup> (**17**), henceforth abbreviated as hexathiaadamantane, hence a data set was not collected for this specimen. The second compound was identified as *trans*-2,4-dimethyl-2,4-(*S*-thioacetato)-1,3-dithietane (abbreviated as dithietane, **18**), see Figure 8.

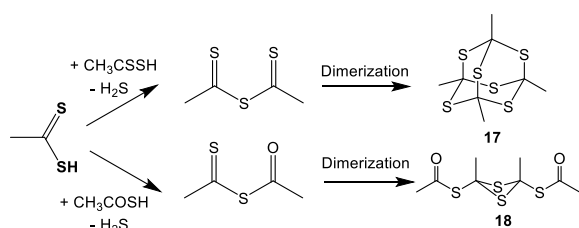


**Figure 8.** Molecular view of 2,4-dimethyl-1,3-dithietane-2,4-diyl diethanethioate, **18**, with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small sphere of arbitrary radii. Symmetry transformations used to generate equivalent atoms: (i)  $-x+1, -y+1, -z+1$ .

The already known hexathiaadamantane compound **17** was previously produced from  $\text{CH}_3\text{C}(\text{S})\text{SH}$  (generated *in situ* from the acidolysis of piperidinium dithioacetate) in the presence of dicyclohexylcarbodiimide, which traps  $\text{H}_2\text{S}$  to afford the corresponding urea,<sup>[16b]</sup> but was also obtained from the  $\text{ZnCl}_2$ -catalyzed decomposition of  $\text{CH}_3\text{C}(\text{O})\text{SH}$ , hinting an acid-catalyzed disproportionation.<sup>[21]</sup> The dithietane product **18**, on the other hand, does not appear to be previously reported, but analogues with the methyl group replaced by  $\text{CH}_{(3-n)}\text{Cl}_n$ , obtained from  $\text{CH}_{(3-n)}\text{Cl}_n\text{C}(\text{O})\text{SH}$  in the presence of  $\text{AlCl}_3$ , have been described.<sup>[22]</sup>

The  $^{13}\text{C}\{^1\text{H}\}$  NMR analysis of the crystalline sample in  $\text{CDCl}_3$  reveals the same two signals at  $\delta$  29.3 et 58.5 observed during the reaction monitoring (Figure 6), which are attributed to the hexathiaadamantane compound (previously reported<sup>[21b]</sup> at  $\delta$  29.5 and 58.5 in  $\text{CDCl}_3$ ). The spectrum also exhibits resonances at  $\delta$  14.6 and 19.7, attributable to  $\text{Et}_2\text{O}$  (confirmed by spiking), but no additional resonances attributable to the dithietane product, suggesting that this by-product is formed in very minor, undetectable amounts.

The formation of the hexathiaadamantane molecule can be envisaged by condensation of two  $\text{MeC}(\text{S})\text{SH}$  molecules to give rise, after release of  $\text{H}_2\text{S}$ , to  $\text{MeC}(\text{S})\text{SC}(\text{S})\text{Me}$ , a sulfur equivalent of an anhydride, which then dimerizes to the hexathiaadamantane (Scheme 6). The dithietane product, on the other hand, can form by an equivalent condensation, with  $\text{H}_2\text{S}$  elimination, of one  $\text{CH}_3\text{C}(\text{S})\text{SH}$  and one thioacetic acid molecule, followed by dimerization. The different structure of the two products, having the same stoichiometry ( $\text{C}_4\text{Me}_4\text{S}_4\text{E}_2$ ;  $\text{E} = \text{O}, \text{S}$ ), is easily rationalized on the basis of the different aptitude of the O and S atoms to form a  $\text{C}=\text{E}$   $\pi$  bond.



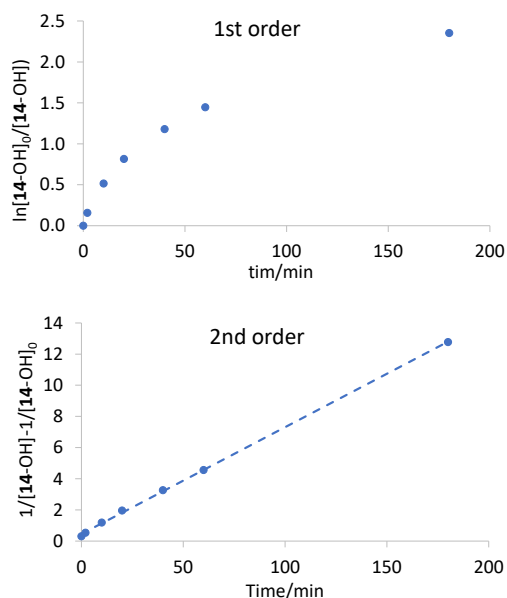
**Scheme 6.** Formation of the hexathiaadamantane and dithietane products by decomposition of dithioacetic acid.

#### Kinetic analyses

The decay of the **14-OH** concentration (Figure 5) and its dependence on the acid catalyst concentration can be analyzed in a straightforward manner. The **[14-OH]** decay for the slower reaction with 0.15 equiv of  $\text{HBF}_4$  catalyst, given the sufficient number of data points, could be analyzed accurately (Figure 9) and clearly fits a second-order decay, yielding a value of  $(1.15 \pm 0.01) \cdot 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$  for the pseudo-second order rate coefficient,  $k_{\text{obs}}$ . The data for the faster reaction with 0.5 equiv. of  $\text{HBF}_4$  equally fit a second order decay for the first two data points (the concentrations are too small for the subsequent point to be reliable, see Figure S66), yielding  $k_{\text{obs}} = 1.6 \cdot 10^{-2} \text{ s}^{-1} \text{ M}^{-1}$ . The other two reactions with 1 and 2 equiv. of  $\text{HBF}_4$  are too fast to be exploitable, since the first measurement after 2 min already shows an alcohol conversion of about 98%. The  $\ln/\ln$  plot of the  $k_{\text{obs}}$  values vs. the  $\text{HBF}_4$  initial concentration (Figure S67) yields a slope greater than 2, strongly indicating that the rate dependence on  $[\text{HBF}_4]$  is also second-order.

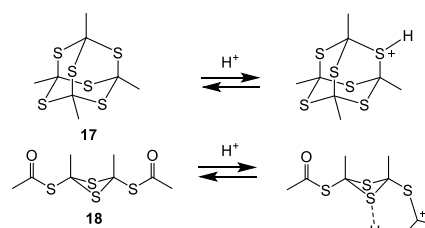
Another rather straightforward analysis could be carried out for the decay of the ester concentration, **[14-OAc]** and for the corresponding formation of **[14-SAc]**, limited to the three experiments with the highest concentrations of  $\text{HBF}_4$  (1.0, 1.5 and 2 equivalents, Figure 5c-e), for which these two compounds are the only remaining ones after the first few minutes. This transformation also clearly follows a second order rate law in the concentration of the ester intermediate (see Figure S68). The pseudo-second order  $k_{\text{obs}}$  values for these experiments are sharply dependent on the acid concentration and the  $\ln/\ln$  plot

suggests a reaction order of four (Figure S69). It appears logical that, if the alcohol conversion to the ester is second order in  $\text{HBF}_4$ , as suggested above, the reverse reaction is also second order in  $\text{HBF}_4$ . The slower transformation of **[14-OH]**, produced as an intermediate from **[14-OAc]**, to the **[14-SAc]** final product is then presumably also second order in  $\text{HBF}_4$ , rendering the overall conversion of **[14-OAc]** to **[14-SAc]** fourth order in  $\text{HBF}_4$ .



**Figure 9.** Analyses of the **[14-OH]** decay for the experiment of Figure 5a (0.15 equiv of  $\text{HBF}_4$ ).

A global analysis of the entire kinetic data on the basis of the kinetic model of Scheme 4 could not be carried out, because the time evolution of the acetic acid and thioacetic acid concentrations (Figure 7) cannot be analytically described. According to the mechanistic interpretation of Scheme 5, the disproportionation should have a first-order dependence on  $\text{HBF}_4$  and a second-order dependence on thioacetic acid (assuming the generation of the carbocation intermediate as a rapid pre-equilibrium). However, the data indicate a more complex evolution, with a clear slow down at high conversions. Indeed, a substantial amount of  $\text{CH}_3\text{C}(\text{O})\text{OH}$  is generated within the first measurement, as shown in the analysis of the data according to the second-order rate law (Figure S70). Although the data recorder under the conditions of Figure 5c do appear to follow a second-order decay, the intercept is far from the origin. A likely explanation of this slowdown is that the  $\text{HBF}_4$  concentration is decreased by partial consumption by the dithioacetic acid decomposition products and two possibilities are illustrated in Scheme 7.

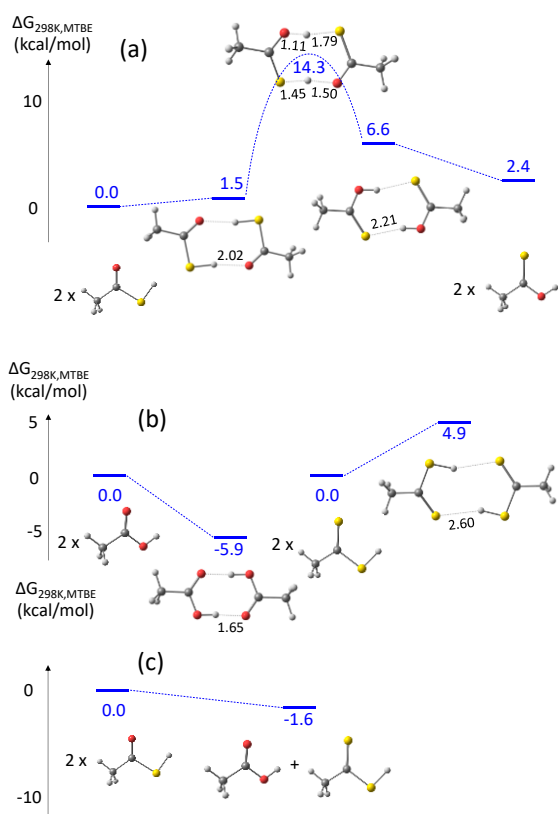




**Scheme 7.** Possible action of the dithioacetic acid decomposition products as Brønsted bases to buffer the  $\text{HBF}_4$  acidity.

### DFT calculations

The calculations were carried out using a polarizable continuum in thioacetic acid ( $\epsilon = 13.0$ ) to simulate the effect of solvation (see the Experimental Section for additional computational details). A first investigation probed the thermodynamics of the thioacetic acid isomerization to thionoacetic acid and of its disproportionation to the 1:1 mixture of acetic acid and dithioacetic acid. Figure 10a shows that the thioacetic acid monomer is more stable than the H-bonded dimer and also more stable than its thionoacetic acid isomer by 2.4 kcal mol<sup>-1</sup>, in agreement with the absence of observable isomerization. The thionoacetic acid isomer also prefers a non-H-bonded mononuclear form. The isomerization takes place via a double proton exchange from the H-bonded dimer, which a Gibbs energy barrier of 14.3 kcal mol<sup>-1</sup>, which is compatible with a very fast process ( $k = 2.1 \cdot 10^2 \text{ s}^{-1}$  at 298 K, according to the Eyring equation).

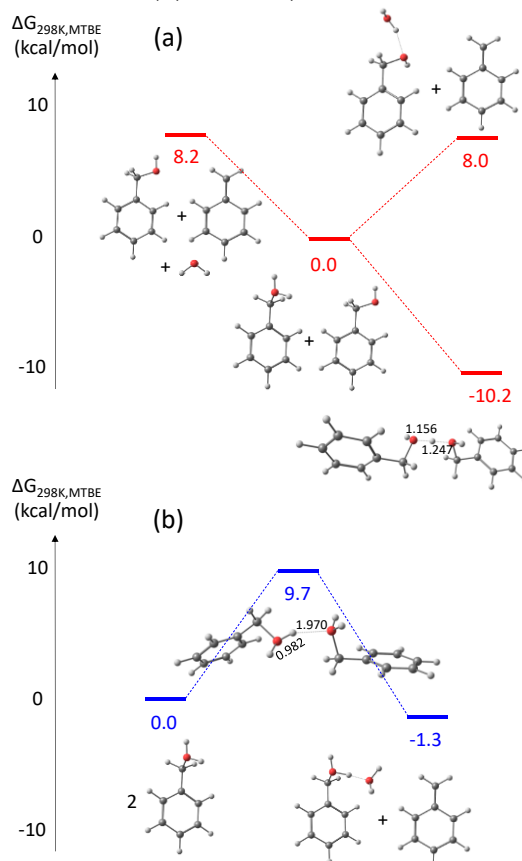


**Figure 10.** Computed Gibbs energy changes for the isomerization of thioacetic to thionoacetic acid (a), for the dimerization of acetic and dithioacetic acids (b) and for the disproportionation of thioacetic to acetic and dithioacetic acids (c). The blue figures are the Gibbs energies and the black figures are the H-bond distances in Å.

The dimerization thermodynamics for acetic and dithioacetic acids is shown in Figure 10b. The H-bonded dimer of acetic acid is favored, whereas that of dithioacetic acid is not and the penalty is greater than for the thioacetic and thionoacetic acids. These results are in line with the relative strength of the H bonds in the order  $\text{O-H}\cdots\text{O} > \text{S-H}\cdots\text{O} > \text{O-H}\cdots\text{S} > \text{S-H}\cdots\text{S}$ . Only acetic acid has

sufficient enthalpic stabilization provided by the H-bonds to compensate for the entropic penalty. Note that the different strength of these H-bonds rationalizes quite well the drift observed for all <sup>1</sup>H NMR resonances, particularly that of the O-H proton, during the disproportionation process (Figure S2). The atom redistribution to convert two  $\text{CH}_3\text{C}(\text{O})\text{SH}$  molecules into one of  $\text{CH}_3\text{C}(\text{O})\text{OH}$  and one of  $\text{CH}_3\text{C}(\text{S})\text{SH}$  is predicted as exoergic, as shown in Figure 10c. When considering, in addition, the favored dimerization of acetic acid, the  $\Delta_r G^\circ$  associated to the disproportionation of four moles of  $\text{CH}_3\text{COSH}$  to yield two of  $\text{CH}_3\text{C}(\text{S})\text{SH}$  and one of  $(\text{CH}_3\text{COOH})_2$  is calculated as -9.1 Kcal. This result is perfectly in line with the observed spontaneous disproportionation in the presence of the  $\text{HBF}_4$  catalyst. The commercially available thioacetic acid is thus a thermodynamically unstable compound, but has a long bench life because its atom redistribution has a high activation barrier and does not occur in the absence of acid catalysts.

Subsequent calculations have explored the generation of the benzyl cation by protonation of benzyl alcohol and water elimination (first step in Scheme 4). Water elimination from  $\mathbf{14-OH}_2^+$  to yield  $\mathbf{14}^+ + \text{H}_2\text{O}$  was calculated to cost +8.2 kcal mol<sup>-1</sup> (Figure 11a). The assistance by a second benzyl alcohol molecule (from  $\mathbf{14-OH}_2^+ + \mathbf{14-OH}$  to  $\mathbf{14}^+ + \mathbf{14-OH}\cdots\text{OH}_2$ ) was then considered in view of the kinetic evidence of a second order dependence in alcohol (previous section). Indeed, the formation of the alcohol-water H bond makes the dehydration process slightly more favorable (+8.0 kcal mol<sup>-1</sup>). However, the combination of  $\mathbf{14-OH}_2^+ + \mathbf{14-OH}$  generates an even more stable adduct,  $\mathbf{14-OH}_2^+\cdots\text{O}(\text{H})-\mathbf{14}$ , at -10.2 kcal mol<sup>-1</sup>. Thus, the formation of  $\mathbf{14}^+$  is actually even more difficult (+18.0 kcal mol<sup>-1</sup> from the  $\mathbf{14-OH}_2^+\cdots\text{O}(\text{H})-\mathbf{14}$  adduct).



**Figure 11.** Computed Gibbs energy changes for the interaction between two molecules of benzyl alcohol with (a) one H<sup>+</sup>; (b) two H<sup>+</sup>. The blue and red figures are the Gibbs energies and the black figures are selected bond distances in Å.

Since the kinetic investigation suggested a second order dependence also in the acid concentration, the effect of a second protonation was then explored. From two alcohol molecules and two protons, two **14-OH<sub>2</sub><sup>+</sup>** ions are generated. Formation of an H-bonded dicationic adduct by dimerization of this cation, yielding [**14-OH<sub>2</sub><sup>+</sup>...O<sup>+</sup>(H)<sub>2</sub>-14**], is endoergic by +9.7 kcal mol<sup>-1</sup> (Figure 11b). On the other hand, dehydration of one protonated alcohol by the second one, to yield the bare benzyl cation **14<sup>+</sup>** plus **14-OH<sub>2</sub><sup>+</sup>...OH<sub>2</sub>**, is actually favorable with a Gibbs energy change of -1.3 kcal mol<sup>-1</sup>. Thus, the calculations rationalize quite well the need for two alcohol molecules and two protons for the formation of the intermediate benzyl cation.

## Conclusion

The investigation reported here unveils a new and practical one-pot solvent-less reaction to convert benzylic, allylic, ferrocenyl and tertiary alcohols into the corresponding thioesters. This procedure also represents a convenient protocol for the on-demand conversion of alcohols into thiols. The reaction takes place in thioacetic acid under the catalytic action of tetrafluoroboric acid. The observation and even isolation of the acetate and/or thionoacetate for certain substrates and under specific conditions has revealed the occurrence of an acid-catalyzed disproportionation of thioacetic acid to acetic acid and dithioacetic acids, with DFT calculation confirming that this is a thermodynamically favourable process. The unstable dithioacetic acid was shown to rapidly decompose with release of H<sub>2</sub>S to generate (MeC)<sub>4</sub>S<sub>6</sub> and, in the thioacetic acid medium, the hitherto unreported {(MeCOS)CMe}<sub>2</sub>(μ-S)<sub>2</sub>. The detailed reaction monitoring using benzyl alcohol as a model substrate has demonstrated that both acetate and thionoacetate are intermediate and subsequently convert to the desired thioacetate quantitatively in thioacetic acid solution under acid catalysis. These intermediates, especially the acetate, accumulate in greater fractions when using a smaller amount of HBF<sub>4</sub>. Increasing the HBF<sub>4</sub> concentration enhanced the reaction rate, giving good to excellent yield (up to 99%) for a large scope of alcohols.

## Experimental Section

**General Considerations.** All manipulations were carried out under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. Solvents for syntheses were dried and degassed by standard methods before use. 1D- and 2D-NMR spectra were recorded with a Bruker Avance 400 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts (δ) are given in ppm downfield from the TMS reference, the residual peak of the deuterated solvent being used for calibration. Peaks are labelled as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). MS spectra were recorded on a Waters Xevo G2 Q TOF instrument. The head-space GC-MS analyses were carried out on a Thermo Scientific trace 1300 GC with a TG-5SiIMS column (30 m x 0.25 mm x 0.25 μm) and a TSQ 8000 Evo MS-MS detector. Commercially available chemicals were purchased from Acros, Aldrich, Alfa Aesar, or Fluka and used as received.

**Syntheses of the alcoholic substrates.** Compounds 1-OH, (3-7)-OH, (9-11)-OH and (13-15)-OH are commercially available and have been used as received. Compound 8-OH was synthesized from racemic 2-(diphenylthiophosphino)-dimethylaminomethylferrocene by a two-step procedure as described in the literature.<sup>[23]</sup> 12-OH synthesis was adapted from a published procedure.<sup>[24]</sup>

**Synthesis of 4-(2-hydroxy-2-methylpropyl)phenol (2-OH).** A solution of MeMgBr (3 M in Et<sub>2</sub>O, 8.56 mL, 25 mmol) was added dropwise to a solution of commercially available 1-(4-hydroxyphenyl)propan-2-one (1.5 g, 10 mmol) in dry THF (80 mL). The reaction mixture was stirred for 22 h at room temperature and then 0.2 additional equivalents of MeMgBr (1.69 mL, 5 mmol) were added and stirring was continued for 2 h. The mixture was then treated with a saturated NH<sub>4</sub>Cl aqueous solution (40 mL). After extraction with Et<sub>2</sub>O (3 x 20 mL), the combined organic layer was washed with a saturated solution of NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to provide the crude materials as a viscous oil. The compound was purified by precipitation with pentane from a concentrated THF solution (4 mL) to give the desired product in a 97% yield (1.6 g). <sup>1</sup>H NMR (400 MHz, 298 K, acetone-d<sub>6</sub>) δ (ppm): 8.11 (s, 1H, Ar-OH), 7.07 (d, J = 8.5 Hz, 2H, 2 CH<sup>Ar</sup>), 6.75 (d, J = 8.6 Hz, 2H, 2 CH<sup>Ar</sup>), 3.22 (s, 1H, CMe<sub>2</sub>OH), 2.66 (s, 2H, CH<sub>2</sub>), 1.14 (s, 6H, 2 CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 298 K, acetone-d<sub>6</sub>) δ (ppm): 155.72 (s, quat. Ar), 131.34 (s, 2 CH<sup>Ar</sup>), 129.59 (s, quat. Ar), 114.51 (s, 2 CH<sup>Ar</sup>), 69.90 (s, CMe<sub>2</sub>), 48.95 (s, CH<sub>2</sub>), 28.60 (s, CH<sub>3</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>10</sub>H<sub>15</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) 167.1072. Found: 167.1062.

**Synthesis of methyl-2-(diphenylthiophosphino)benzoate.** This synthesis was adapted from a published procedure.<sup>[25]</sup> In a 250-mL round bottom Schlenk flask under argon were introduced Cs<sub>2</sub>CO<sub>3</sub> (1.90 g, 5.9 mmol, 1.25 equiv.), CuI (72.4 mg, 0.08 equiv.) and dry toluene (50 mL). The flask was sealed with a rubber septum and then methyl-2-bromobenzoate (1 g, 4.7 mmol, 1 equiv.) and Ph<sub>2</sub>PH (0.72 g, 3.8 mmol, 0.8 equiv.) were consecutively injected into the suspension. After replacing the rubber septum with a reflux condenser, the reaction mixture was refluxed at 110 °C for 24 h. The mixture was then cooled to room temperature. The insoluble residues were eliminated by filtration through a Celite bed. The filtrate was concentrated under reduced pressure and the residue was redissolved in degassed dichloromethane (150 mL). Solid sulfur (3-4 eq) was then added and the mixture was stirred for 2-3 h under argon. After solvent evaporation, the yellow crude material was purified by silica gel column chromatography (eluent: 10/90 Et<sub>2</sub>O/pentane) to obtain pure methyl-2-(diphenylthiophosphino)benzoate as a white crystalline solid (yield: 1.19 g, 73%). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.90-7.83 (m, 1H, CH<sup>Ar</sup>), 7.83-7.73 (m, 4H, CH<sup>Ar</sup>), 7.61-7.40 (m, 8H, CH<sup>Ar</sup>), 7.31-7.23 (m, 1H, CH<sup>Ar</sup>), 3.44 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 168.03 (d, J<sub>CP</sub> = 3.4 Hz, C=O), 136.33 (d, J<sub>CP</sub> = 7.7 Hz, quat. Ar-C=O), 134.01 (d, J<sub>CP</sub> = 10.5 Hz, CH<sup>Ar</sup>), 133.39 (d, J<sub>CP</sub> = 87.4 Hz, quat. Ph-P), 133.29 (d, J<sub>CP</sub> = 91.7 Hz, quat. Ar-P), 132.03 (d, J<sub>CP</sub> = 10.7 Hz, CH<sup>Ph</sup>), 131.46 (d, J<sub>CP</sub> = 2.8 Hz, CH<sup>Ar</sup>), 131.45 (d, J<sub>CP</sub> = 3.0 Hz, CH<sup>Ph</sup>), 131.09 (d, J<sub>CP</sub> = 8.8 Hz, CH<sup>Ar</sup>), 130.50 (d, J<sub>CP</sub> = 11.8 Hz, CH<sup>Ar</sup>), 128.41 (d, J<sub>CP</sub> = 12.8 Hz, CH<sup>Ph</sup>), 52.03 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 46.16 (s, P(S)Ph<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>PS [(M+H)<sup>+</sup>] 383.0765. Found: 353.0758.

**Synthesis of 2-(diphenylthiophosphino)benzyl alcohol (16-OH).** (Scheme S2). This synthesis was adapted from a published procedure.<sup>[26]</sup> A 1 M solution of LiAlH<sub>4</sub> in THF (1 mL, 1 mmol) was added dropwise into a solution of methyl-2-(diphenylthiophosphino)benzoate (100 mg, 0.28 mmol) in dry THF (7 mL) with steady magnetic stirring at 0 °C. The reaction mixture was then slowly allowed to warm to room temperature and stirring was continued with TLC monitoring to determine the benzoate substrate consumption. After 2 h, the reaction mixture was quenched at 0 °C with 2 M HCl and filtered by a Teflon filter-cannula. The filtrate was then dried under vacuum and the residue was extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: 20/80

EtOAc/*n*-hexane) to afford 2-(diphenylthiophosphino)benzyl alcohol as a white solid (0.11 g, 70%). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.80-7.70 (4H, m, CH<sup>A</sup>), 7.65-7.45 (8H, m, CH<sup>A</sup>), 7.22 (1H, m, CH<sup>A</sup>), 6.88 (1H, m, CH<sup>A</sup>), 4.64 (2H, s, CH<sub>2</sub>), 4.03 (1H, br s, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 145.0 (d, J<sub>PC</sub> = 9.3 Hz, quat. Ar-CH<sub>2</sub>), 132.9 (d, J<sub>PC</sub> = 11.2 Hz, CH<sup>A</sup>), 132.66 (d, J<sub>PC</sub> = 4.5 Hz, CH<sup>A</sup>), 132.64 (d, J<sub>PC</sub> = 8.5 Hz, CH<sup>A</sup>), 132.3 (d, J<sub>PC</sub> = 10.7 Hz, CH<sup>Ph</sup>), 132.13 (d, J<sub>PC</sub> = 83.5 Hz, quat. Ar-P), 132.05 (d, J<sub>PC</sub> = 85.0 Hz, quat. Ph-P), 128.8 (d, J<sub>PC</sub> = 12.8 Hz, CH<sup>Ph</sup>), 131.98 (s, CH<sup>Ph</sup>), 127.4 (d, J<sub>PC</sub> = 12.3 Hz, CH<sup>A</sup>), 63.1 (d, J<sub>PC</sub> = 6.2 Hz, CH<sub>2</sub>). <sup>31</sup>P NMR (162 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 41.65 (s, P(S)Ph<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>S ([M+H]<sup>+</sup>) 325.0816. Found: 325.0813.

**General procedure for conversion of alcohols to thio- or thionoesters with thioacetic acid.** To 1 equivalent of the desired amount of alcohol dissolved in thioacetic acid at room temperature were added 0.15 to 2 eq. of HBF<sub>4</sub> (54% w/w solution in Et<sub>2</sub>O). After the desired time (30 min to 3 h) the excess thioacetic acid was removed under reduced pressure and the crude products were chromatographed on a silica gel column.

**S-4-Hydroxybenzyl thioacetate (1-SAc).** Compound 1-OH (300 mg, 2.42 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.05 mL, 0.36 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 50/50 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane. Yield 69% (303 mg) of pale-yellow oil. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.16 (d, J = 8.7 Hz, 2H, CH<sup>A</sup>), 6.80 (d, J = 8.7 Hz, 2H, CH<sup>A</sup>), 6.72 – 6.16 (br s, 1H, OH), 4.09 (s, 2H, CH<sub>2</sub>), 2.37 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 197.38 (s, C=O), 155.12 (s, quat. Ar), 130.20 (s, CH<sup>A</sup>), 129.15 (s, quat. Ar), 115.65 (s, CH<sup>A</sup>), 33.20 (s, CH<sub>2</sub>), 30.41 (s, CH<sub>3</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>S ([M+H]<sup>+</sup>) 183.0480. Found: 183.0487.

**S-1-(4-Hydroxyphenyl)-2-methylpropan-2-yl thioacetate (2-SAc).** Compound 2-OH (300 mg, 1.81 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.037 mL, 0.27 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: CH<sub>2</sub>Cl<sub>2</sub>. Yield 53% (215 mg) of pale-yellow oil. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.05 (d, J = 8.6 Hz, 2H, CH<sup>A</sup>), 6.78 (d, J = 8.6 Hz, 2H, CH<sup>A</sup>), 4.85 (s, 1H, OH), 3.04 (s, 2H, CH<sub>2</sub>), 2.29 (s, 3H, C(O)CH<sub>3</sub>), 1.43 (s, 6H, CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 196.77 (s, C=O), 149.45 (s, quat. Ar), 134.91 (s, quat. Ar), 131.68 (s, CH<sup>A</sup>), 120.88 (s, CH<sup>A</sup>), 51.57 (s, CH<sub>2</sub>), 45.90 (s, quat CCH<sub>3</sub>), 31.49 (s, C(O)CH<sub>3</sub>), 27.22 (s, CCH<sub>3</sub>).

**S-4-Chlorobenzyl thioacetate (3-SAc).** Compound 3-OH (300 mg, 2.11 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.043 mL, 0.32 mmol, 0.15 eq.), reaction time 1 h. Eluent for the chromatographic separation: 0-20% gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 51% (215 mg) of a pale-yellow oil. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.25 (m, 2H, CH<sup>A</sup>), 7.18 (d, 2H, J = 8.4 Hz, CH<sup>A</sup>), 4.09 (s, 2H, CH<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 194.8 (s, CO), 136.3 (s, quat. Ar), 133.1 (s, quat. Ar), 130.1 (s, CH<sup>A</sup>), 128.7 (s, CH<sup>A</sup>), 32.7 (s, CH<sub>3</sub>), 30.3 (s, CH<sub>2</sub>). These data agree with the previously published ones.<sup>[27]</sup>

**S-4-Bromobenzyl thioacetate (4-SAc).** Compound 4-OH (300 mg, 1.61 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.032 mL, 0.24 mmol, 0.15 eq.), reaction time 1 h. Eluent for the chromatographic separation: 0-20% gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 53% (208 mg) of a pale-yellow oil. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.43 (d, 2H, J = 8.4 Hz, CH<sup>A</sup>), 7.18 (d, 2H, J = 8.4 Hz, CH<sup>A</sup>), 4.07 (s, 2H, CH<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 194.8 (s, CO), 136.8 (s, quat. Ar), 131.7 (s, CH<sup>A</sup>), 130.5 (s, CH<sup>A</sup>), 121.2 (s, quat. Ar), 32.8 (s, CH<sub>3</sub>), 31.6 (s, CH<sub>2</sub>). These data agree with the previously published ones.<sup>[28]</sup>

**S-2-Bromobenzyl thioacetate (5-SAc).** Compound 5-OH (300 mg, 1.61 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.032 mL, 0.24 mmol, 0.15 eq.), reaction time 1 h. Eluent for the chromatographic separation: 0-20% gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 46% (181 mg) of a pale-yellow oil. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.56 (m, 1H, CH<sup>A</sup>), 7.47 (m, 1H, CH<sup>A</sup>), 7.27 (m, 1H, CH<sup>A</sup>), 7.13 (m, 1H, CH<sup>A</sup>), 4.26 (s, 2H, CH<sub>2</sub>), 2.36

(s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 194.9 (s, CO), 137.1 (s, quat. Ar), 137.1 (s, CH<sup>A</sup>), 132.8 (s, CH<sup>A</sup>), 131.2 (s, CH<sup>A</sup>), 129.7 (s, CH<sup>A</sup>), 127.6 (s, CH<sup>A</sup>), 124.5 (s, quat. Ar), 34.0 (s, CH<sub>3</sub>), 30.3 (s, CH<sub>2</sub>). These data agree with the previously published ones.<sup>[29]</sup>

**S-Ferrocenylmethyl thioacetate (6-SAc).** Compound 6-OH (300 mg, 1.39 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.028 mL, 0.21 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20% gradient of Et<sub>2</sub>O in *n*-hexane. Yield 63% (239 mg) of a yellow-orange solid. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 4.19 (t, J = 1.8 Hz, 2H, subst Cp), 4.18 (s, 5H, Cp), 4.13 (t, J = 1.8 Hz, 2H, subst Cp), 3.94 (s, 2H, CH<sub>2</sub>), 2.34 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 195.51 (s, CO), 84.07 (s, quat. Cp), 68.80 (s, Cp), 68.62 (s, subst Cp), 68.12 (s, subst Cp), 30.36 (s, CH<sub>2</sub>), 29.38 (s, CH<sub>3</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>13</sub>H<sub>14</sub>FeOS ([M]<sup>+</sup>) 274.0115 Found: 274.0102.

**S-*rac*-1-Ferrocenylethyl thioacetate (7-SAc).** Compound 7-OH (300 mg, 1.30 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.026 mL, 0.20 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20% gradient of Et<sub>2</sub>O in *n*-hexane. Yield 51% (191 mg) of a yellow-orange crystalline solid. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 4.58 (q, J = 7.0 Hz, 1H, CHCH<sub>3</sub>), 4.36 – 3.95 (m, 9H, ferrocenyl CH), 2.33 (s, 3H, SCOC<sub>2</sub>H<sub>5</sub>), 1.69 (d, J = 7.0 Hz, 3H, -CHCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 195.64 (s, CO), 90.11 (s, quat. Cp), 68.77 (s, Cp), 68.00 (s, subst Cp), 67.75 (s, subst Cp), 67.71 (s, subst Cp), 66.20 (s, subst Cp), 38.78 (s, CH), 30.43 (s, COCH<sub>3</sub>), 21.53 (s, CHCH<sub>3</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>14</sub>H<sub>16</sub>FeOS ([M]<sup>+</sup>) 288.0271 Found: 288.0257.

**S-*rac*-(2-Thiodiphenylphosphino)ferrocenylmethyl thioacetate (8-SAc).** Compound 8-OH (300 mg, 0.69 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.014 mL, 0.10 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20% gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 84% (285 mg) or an orange crystalline solid. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.86-7.79 (2H, m, PPh<sub>2</sub>), 7.67-7.60 (2H, m, PPh<sub>2</sub>), 7.60-7.38 (6H, m, PPh<sub>2</sub>), 4.63 (1H, m, subst Cp), 4.53 (1H, d, J = 14.1 Hz, AB system, CH<sub>2</sub>Cp), 4.36 (5H, s, Cp), 4.34 (1H, d, J = 14.0 Hz, AB system, CH<sub>2</sub>Cp), 4.30 (1H, m, subst Cp), 3.76 (1H, m, subst Cp), 2.20 (s, 3H, s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 195.64 (s, CO), 134.52 (d, J<sub>PC</sub> = 86.7 Hz, quat. Ph), 133.28 (d, J<sub>PC</sub> = 86.5 Hz, quat. Ph), 132.11 (d, J<sub>PC</sub> = 8.4 Hz, Ph), 132.03 (d, J<sub>PC</sub> = 10.7 Hz, Ph), 131.33 (d, J<sub>PC</sub> = 3.0 Hz, 2C para Ph), 128.24 (d, J<sub>PC</sub> = 12.4 Hz, Ph), 128.06 (d, J<sub>PC</sub> = 12.3 Hz, Ph), 89.09 (d, J<sub>PC</sub> = 12.2 Hz, quat. Cp), 74.43 (d, J<sub>PC</sub> = 12.3 Hz, subst. Cp), 74.17 (d, J<sub>PC</sub> = 94.6 Hz, quat. Cp), 73.98 (d, J<sub>PC</sub> = 9.2 Hz, subst. Cp), 70.94 (s, Cp), 69.36 (d, J<sub>PC</sub> = 10.1 Hz, subst. Cp), 30.23 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 41.23 (s, P(S)Ph<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>25</sub>H<sub>24</sub>FeOPS<sub>2</sub> [M+H]<sup>+</sup> 491.0322 Found 491.0344.

**S-(Furan-2-yl)methyl thioacetate (9-SAc).** Compound 9-OH (300 mg, 3.05 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.063 mL, 0.46 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20% gradient of Et<sub>2</sub>O in pentane. Yield 32% (152 mg) of a colorless oil. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.34 (d, J = 2.8 Hz, 1H, =CHO), 6.35 – 6.28 (m, 1H, CH), 6.23 (d, J = 3.2 Hz, 1H, CH=C-), 4.17 (s, 2H, CH<sub>2</sub>), 2.37 (s, 3H, SCOC<sub>2</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 194.53 (s, CO), 150.43 (s, furanyl C), 142.21 (s, furanyl CH-O), 110.60 (s, furanyl CH), 107.86 (s, furanyl CH), 30.34 (s, CH<sub>2</sub>), 25.87 (s, CH<sub>3</sub>). These data agree with the previously published ones.<sup>[30]</sup>

**S-Cinnamyl thioacetate (10-SAc).** Compound 10-OH (300 mg, 2.24 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.046 mL, 0.34 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20% gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 58% (249 mg) of a colorless oil. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.41 – 7.29 (m, 4H, CH<sup>Ph</sup>), 7.29 – 7.21 (m, 1H, CH<sup>Ph</sup>), 6.60 (d, J = 15.6 Hz, 1H, Ph-CH=), 6.20 (dt, J = 15.7, 7.4 Hz, 1H, =CH-), 3.74 (dd, J = 7.4, 1.3 Hz, 2H, -CH<sub>2</sub>-S), 2.38 (s, 3H, -SCOC<sub>2</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 195.20 (s, CO), 136.59 (s, quat. Ph), 133.12 (s, CH<sup>Ph</sup>), 128.56 (s, CH<sup>Ph</sup>), 127.71 (s, Ph-

CH=), 126.38 (s, CH<sup>Ph</sup>), 124.42 (s, =CH-), 31.78 (s, CH<sub>3</sub>), 30.53 (s, CH<sub>2</sub>). These data agree with the previously published ones.<sup>[31]</sup>

**S-E-1,3-Diphenylallyl thioacetate (11-SAc).** Compound 11-OH (300 mg, 1.43 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.030 mL, 0.21 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20% gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 71 % (271 mg) of a pale-yellow oil. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.54 – 7.16 (m, 10H, CH<sup>Ph</sup>), 6.65 (d, *J* = 16.3 Hz, 1H, Ph-CH=), 6.50 (dd, *J* = 15.7, 7.4 Hz, 1H, =CH-), 5.54 (d, *J* = 8.3 Hz, 1H, CHS), 2.39 (s, 3H, SCOC<sub>2</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 193.96 (s, CO), 140.01 (s, quat Ph), 136.57 (s, quat Ph), 131.90 (s, CH<sup>Ph</sup>), 128.80 (s, CH<sup>Ph</sup>), 128.59 (s, CH<sup>Ph</sup>), 128.49 (s, Ph-CH=), 128.10 (s, CH<sup>Ph</sup>), 127.82 (s, =CH-), 127.61 (s, CH<sup>Ph</sup>), 126.60 (s, CH<sup>Ph</sup>), 50.21 (s, CHS), 30.53 (s, CH<sub>3</sub>). These data agree with the previously published ones.<sup>[32]</sup>

**O-benzyl thioacetate (14-OC(S)Me).** Compound 14-OH (300 mg, 2.78 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.057 mL, 0.42 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: pentane. Yield 14 % (64 mg) of a pale-yellow oil. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.50 – 7.35 (m, 5H, CH<sup>Ph</sup>), 5.50 (s, 2H, CH<sub>2</sub>), 2.67 (s, 3H, -SCOC<sub>2</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 219.63 (s, C=S), 135.05 (s, quat Ph), 128.66 (s, CH<sup>Ph</sup>), 128.59 (s, CH<sup>Ph</sup>), 128.53 (s, CH<sup>Ph</sup>), 74.19 (s, CH<sub>2</sub>), 34.52 (s, CH<sub>3</sub>). These data agree with the previously published ones.<sup>[33]</sup>

**S-benzyl thioacetate (14-SAc).** Compound 14-OH (300 mg, 2.78 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.76 mL, 5.55 mmol, 2 eq.), reaction time 30 min. Eluent for the chromatographic separation: pentane. Yield 63 % (290 mg) of a pale-yellow oil. A 93 % yield was determined by GC for an equivalent reaction run for 3 h. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.56 – 7.01 (m, 5H, CH<sup>Ph</sup>), 4.16 (s, 2H, CH<sub>2</sub>), 2.38 (s, 3H, -SCOC<sub>2</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 195.1 (s, C=O), 137.61 (s, quat. Ph), 128.82 (s, CH<sup>Ph</sup>), 128.64 (s, CH<sup>Ph</sup>), 127.28 (s, CH<sup>Ph</sup>), 33.47 (s, CH<sub>2</sub>), 30.3 (s, CH<sub>3</sub>). These data agree with the previously published ones.<sup>[34]</sup>

**O-(4-Trifluoromethyl)benzyl thioacetate (15-OC(S)Me).** Compound 15-OH (300 mg, 1.70 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.035 mL, 0.26 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20 % gradient of Et<sub>2</sub>O in pentane. Yield 35 % (139 mg) of a pale-yellow oil. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.67 (d, 2H, *J* = 8.1 Hz, CH<sup>Ar</sup>), 7.53 (d, 2H, *J* = 8.0 Hz, CH<sup>Ar</sup>), 5.55 (s, 2H, CH<sub>2</sub>), 2.67 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 219.3 (s, C=S), 139.04 (s, quat Ph), 130.6 (q, *J*<sub>FC</sub> = 32.6 Hz, CH<sup>Ar</sup>), 128.4 (s, quat Ph), 125.6 (q, *J*<sub>FC</sub> = 3.8 Hz, CH<sup>Ar</sup>), 124.0 (q, *J*<sub>FC</sub> = 272.2 Hz, CF<sub>3</sub>), 72.8 (s, CH<sub>3</sub>), 34.3 (s, CH<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>10</sub>H<sub>10</sub>OF<sub>3</sub>S[M+H]<sup>+</sup> 235.0404. Found 235.0398.

**S-(4-Trifluoromethyl)benzyl thioacetate (15-SAc).** Compound 15-OH (300 mg, 1.70 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.23 mL, 3.4 mmol, 2 eq.), reaction time 3 h. The product was characterized from the crude materials without any purification by <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR (a yield of 86 % was determined by integration of the <sup>1</sup>H NMR resonances). The data agree with the previously published ones.<sup>[35]</sup>

**O-(2-(Thiodiphenylphosphino)benzyl thioacetate (16-OC(S)Me).** Compound 16-OH (300 mg, 0.93 mmol), MeC(O)SH (3 mL), HBF<sub>4</sub>.Et<sub>2</sub>O (0.019 mL, 0.14 mmol, 0.15 eq.), reaction time 30 min. Eluent for the chromatographic separation: 0-20 % gradient of CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane. Yield 47 % (166 mg) of a white solid. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.85-7.75 (4H, m, CH<sup>Ph</sup>), 7.60-7.45 (8H, m, 6H CH<sup>Ph</sup> + 2H CH<sup>Ar</sup>), 7.29 (1H, m, CH<sup>Ar</sup>), 7.06 (1H, dd, *J*<sub>HH</sub> = 7.7 Hz, *J*<sub>HP</sub> = 14.7 Hz, CH<sup>Ar</sup>), 5.77 (2H, s, CH<sub>2</sub>), 2.37 (3H, s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 218.61 (s, C=S), 139.09 (d, *J*<sub>PC</sub> = 8.4 Hz, quat. Ar), 132.99 (d, *J*<sub>PC</sub> = 10.8 Hz, CH<sup>Ar</sup>), 132.43 (d, *J*<sub>PC</sub> = 10.7 Hz, CH<sup>Ph</sup>), 132.30 (d, *J*<sub>PC</sub> = 84.3 Hz, quat. Ar), 132.01 (d, *J*<sub>PC</sub> = 84.7 Hz, quat Ph), 131.91 (d, *J*<sub>PC</sub> = 2.7 Hz, CH<sup>Ar</sup>), 131.83 (d, *J*<sub>PC</sub> = 3.1 Hz, CH<sup>Ph</sup>), 130.77 (d, *J*<sub>PC</sub> = 9.8 Hz, CH<sup>Ar</sup>),

128.67 (d, *J*<sub>PC</sub> = 12.6 Hz, CH<sup>Ph</sup>), 127.89 (d, *J*<sub>PC</sub> = 12.2 Hz, CH<sup>Ar</sup>), 71.58 (d, *J*<sub>PC</sub> = 5.9 Hz, CH<sub>2</sub>), 33.94 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 41.46 (s, PPh<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>25</sub>H<sub>24</sub>FeOPS<sub>2</sub> [M+H]<sup>+</sup> 383.0693 Found 383.0702.

**Synthesis of S-2-(thiodiphenylphosphino)benzyl thioacetate (16-SAc) under Mitsunobu conditions.** (Scheme S2). This new compound was synthesized by adaptation of a reported procedure.<sup>[36]</sup> A mixture of PPh<sub>3</sub> (2.14 g, 8.14 mmol) and a diethylazodicarboxylate solution (3.7 mL, 8.14 mmol, 40% in toluene) in 50 mL dry THF was prepared and stirred at 0°C under argon for 40 min. To the resulting dark orange solution, a THF solution (50 mL) of 16-OH (1.2 g, 3.7 mmol) and CH<sub>3</sub>C(O)SH (574 μL, 8.14 mmol) was added dropwise at room temperature. After solvent evaporation, the crude orange oil was purified by column chromatography on silica gel using hexane-dichloromethane (1:1) as eluent to yield 0.80 g (yield-63%) of pure 16-SAc as an off white crystalline solid. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.84-7.74 (4H, m, CH<sup>Ph</sup>), 7.59-7.44 (8H; m, 2H CH<sup>Ar</sup> + 6H CH<sup>Ph</sup>), 7.16 (1H, br t, *J* = 7.5 Hz, CH<sup>Ar</sup>), 7.06 (1H, dd, *J*<sub>HH</sub> = 7.8 Hz, *J*<sub>HP</sub> = 14.6 Hz, CH<sup>Ar</sup>), 4.45 (2H, s, CH<sub>2</sub>), 2.29 (3H, s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 195.76 (s, CO), 142.90 (d, *J*<sub>PC</sub> = 8.5 Hz, quat. Ar), 132.55 (d, *J*<sub>PC</sub> = 9.2 Hz, CH<sup>Ar</sup>), 132.50 (d, *J*<sub>PC</sub> = 11.5 Hz, CH<sup>Ar</sup>), 132.42 (d, *J*<sub>PC</sub> = 11.0 Hz, CH<sup>Ph</sup>), 132.35 (d, *J*<sub>PC</sub> = 3.8 Hz, CH<sup>Ar</sup>), 132.15 (d, *J*<sub>PC</sub> = 85.1 Hz, quat Ph), 131.84 (d, *J*<sub>PC</sub> = 3.1 Hz, CH<sup>Ph</sup>), 131.84 (d, *J*<sub>PC</sub> = 84.0 Hz, quat. Ar), 128.73 (d, *J*<sub>PC</sub> = 12.5 Hz, CH<sup>Ph</sup>), 126.84 (d, *J*<sub>PC</sub> = 12.2 Hz, CH<sup>Ar</sup>), 31.43 (d, *J*<sub>PC</sub> = 6.5 Hz, CH<sub>2</sub>), 30.08 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 41.77 (s, P(S)Ph<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>21</sub>H<sub>20</sub>OPS<sub>2</sub> ([M+H]<sup>+</sup>) 383.0693. Found: 383.0701.

**Synthesis of 2-(thiodiphenylphosphino)benzyl acetate (16-OAc).** In a round-bottom flask (25 ml) equipped with a magnetic stirrer, a solution of 16-OH (0.32 g, 1 mmol) in Ac<sub>2</sub>O (1 ml) was prepared. A drop of concentrated sulfuric acid was then added and the reaction mixture was stirred at room temperature with TLC monitoring. After completion (4 h), the mixture was directly passed through a short silica gel column, using a 1:1 hexane-ethyl acetate mixture as eluent to remove the catalyst. The eluate was evaporated under reduced pressure and the remaining residue was purified by silica gel chromatography (eluent: 1:1 hexane-ethyl acetate) to afford the pure product (yield 0.35 g, 99%) as a white solid. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.85-7.75 (m, 4H, CH<sup>Ar</sup>), 7.62-7.45 (m, 8H, CH<sup>Ar</sup>), 7.31-7.22 (m, 1H, CH<sup>Ar</sup>), 7.02 (dd, *J*<sub>HH</sub> = 7.8 Hz, *J*<sub>HP</sub> = 14.8 Hz, 1H, CH<sup>Ar</sup>), 5.42 (s, 2H, CH<sub>2</sub>), 1.89 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (125 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 170.29 (s, C=O), 140.20 (d, *J*<sub>CP</sub> = 8.4 Hz, quat. Ar), 132.95 (d, *J*<sub>CP</sub> = 10.8 Hz, CH<sup>Ar</sup>), 132.39 (d, *J*<sub>CP</sub> = 10.7 Hz, CH<sup>Ar</sup>), 132.23 (d, *J*<sub>CP</sub> = 84.1 Hz, quat. Ph), 131.91 (d, *J*<sub>CP</sub> = 2.7 Hz, CH<sup>Ar</sup>), 131.77 (d, *J*<sub>CP</sub> = 2.9 Hz, CH<sup>Ar</sup>), 131.72 (d, *J*<sub>CP</sub> = 82.4 Hz, quat. Ar), 130.21 (d, *J*<sub>CP</sub> = 9.9 Hz, CH<sup>Ar</sup>), 128.63 (d, *J*<sub>CP</sub> = 12.6 Hz, CH<sup>Ar</sup>), 127.54 (d, *J*<sub>CP</sub> = 12.2 Hz, CH<sup>Ar</sup>), 69.90 (d, *J*<sub>CP</sub> = 5.8 Hz, CH<sub>2</sub>), 20.65 (s, CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 41.58 (s, P(S)Ph<sub>2</sub>).

**Synthesis of (4-hydroxyphenyl)methanethiol (1-SH).** Compound 1-SAc (100 mg, 0.55 mmol) and sodium methoxide (60 mg, 1.1 mmol) were dissolved in degassed MeOH (2 mL) and stirred at room temperature for 1.5 h. The mixture was first neutralized with a saturated solution of NH<sub>4</sub>Cl (10 mL) and then HCl (5 %) was added until the pH dropped to 5, followed by extraction with Et<sub>2</sub>O (3 x 10 mL). The combined organic layers were washed with a saturated solution of NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude product was purified by column chromatography on silica gel (eluent: 0-20 % gradient of EtOAc in DCM) to provide 1-SH as a pale-yellow oil (yield 48 mg, 63 %). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.18 (d, *J* = 8.5 Hz, 2H, 2 CH<sup>Ar</sup>), 6.78 (d, *J* = 8.5 Hz, 2H, 2 CH<sup>Ar</sup>), 4.36 – 6.07 (br s, 1H, OH). 3.69 (d, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 1.76 (t, *J* = 7.3 Hz, 1H, SH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 154.54 (s, quat. C<sup>Ar</sup>), 133.35 (s, quat. C<sup>Ar</sup>), 129.37 (s, 2 CH<sup>Ar</sup>), 115.55 (s, 2 CH<sup>Ar</sup>), 28.38 (s, CH<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>7</sub>H<sub>9</sub>OS ([M+H]<sup>+</sup>) 141.0374. Found: 141.0380.

**Synthesis of 2-methyl-2-(4-hydroxyphenyl)propanethiol (2-SH).** Compound 2-SAc (100 mg, 0.55 mmol) and sodium methoxide (60 mg, 1.1

mmol) were dissolved in degassed MeOH (2 mL) and stirred at room temperature. After 6 h, the mixture was neutralized successively with a saturated solution of NH<sub>4</sub>Cl (10 mL) and HCl (5 %) until pH = 5, and extracted with Et<sub>2</sub>O (3 x 10 mL). The combine organic layers were washed with a saturated aqueous solution of NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>) to provide **2-SH** as a pale-yellow oil. Yield 67 % (48 mg). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 7.13 (d, *J* = 8.3 Hz, 2H, 2 CH<sup>A</sup>), 6.83 (d, *J* = 8.3 Hz, 2H, 2 CH<sup>A</sup>), 5.90 (s, 1H, Ar-OH), 2.85 (s, 2H, CH<sub>2</sub>), 1.76 (s, 1H, CMe<sub>2</sub>SH), 1.40 (s, 6H, 2xCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, CDCl<sub>3</sub>) δ (ppm): 154.16 (s, quat Ar), 132.00 (s, 2 CH<sup>A</sup>), 130.26 (s, quat Ar), 114.88 (s, 2 CH<sup>A</sup>), 51.53 (s, CH<sub>2</sub>), 45.20 (s, CMe<sub>2</sub>), 32.34 (s, 2xCH<sub>3</sub>). HRMS (DCI-CH<sub>4</sub>): calculated for C<sub>10</sub>H<sub>15</sub>OS ([M+H]<sup>+</sup>) 183.0844. Found: 183.0832.

**X-ray structure solution and refinement.** A single crystal of each compound was mounted under inert perfluoropolyether at the tip of glass fiber and cooled in the cryostream of either a Rigaku-Oxford Diffraction XCALIBUR Eos Gemini Ultra for **2-OH**, **16-OC(S)Me**, **16-SAc** and **6-SAc** or a Bruker APEXII diffractometer for **8-SAc**. Compound **18** was mounted on the XCALIBUR instrument at room temperature. The structures were solved by using the integrate space-group and crystal structure determination SHELXT<sup>[37]</sup> software and refined by least-squares procedures on F<sup>2</sup> using SHELXL-2014.<sup>[38]</sup> All H atoms attached to carbon atoms were introduced at idealized positions and treated with the riding model. The H atoms attached to the oxygen atoms were localized by difference Fourier syntheses and their coordinates and U<sub>iso</sub> were refined using restraints. In compound **2-OH**, there is one and a half molecule per asymmetric unit, with the half-molecule being statistically distributed around an inversion center. This statistical disorder was refined using the PART -1 instruction within SHELXL. Despite the treatment of the disorder, the refinement residuals remained high, but any attempt to decrease the symmetry and to release the disorder failed. The drawing of the molecules was realised with the help of ORTEP32.<sup>[39]</sup> Crystal data and refinement parameters are shown in Table S1. Deposition Number(s) 2286862 (for **2-OH**), 2286863 (for **6-SAc**), 2286864 (for **8-SAc**), 2286865 (for **16-OC(S)Me**), 2286866 (for **16-SAc**) and 2286866 (for **18**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

**Computational details.** The computational work was carried out using the Gaussian16 suite of programs.<sup>[40]</sup> The geometry optimizations were performed without any symmetry constraint using the B3LYP functional and the 6-311G(d,p) basis functions for all atoms. The effects of dispersion forces (Grimme's D3 empirical method<sup>[41]</sup>) and solvation in thioacetic acid ( $\epsilon = 13.0$ ) by SMD<sup>[42]</sup> were included during the optimization. The ZPVE, PV, and TS corrections at 298 K were obtained with Gaussian16 from the solution of the nuclear equation using the standard ideal gas and harmonic approximations at T = 298.15 K, which also verified the nature of all optimized geometries as local minima or first-order saddle points. A correction of 1.95 kcal/mol was applied to all G values to change the standard state from the gas phase (1 atm) to solution (1 M).<sup>[43]</sup>

## Conflict of interest

The authors declare no conflict of interest.

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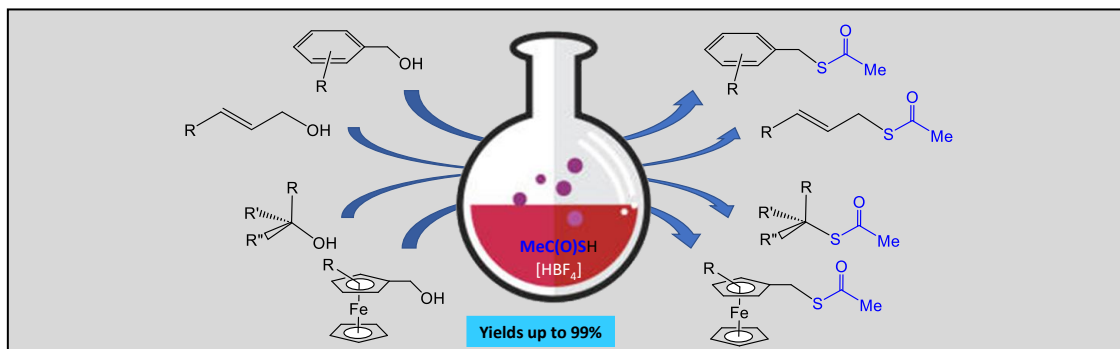
**Keywords:** Alcohol • Thioesterification • Thiol • Mechanism • Kinetics

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