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# An expedient and efficient chemoselective protection of carbonyl compounds and transthioacetalization of *O*,*O*- and *S*,*O*-acetals catalyzed by $HBF_4$-$SiO_2$

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**Abstract**

Trace amount of solid-supported fluoroboric acid ($HBF_4$-$SiO_2$) was found to be an effective catalyst for chemoselective and highly efficient protection of carbonyl compounds and transthioacetalization of *O*,*O*- and *S*,*O*-acetals under solvent-free conditions. Moreover, the catalyst can be recycled for number of times without significant loss of activity.


*Keywords:* Aldehydes; Ketones; *O*,*O*- and *S*,*O*-acetals; $HBF_4$-$SiO_2$; Chemoselective

## 1. Introduction

The development of mild, efficient and selective methods for the protection and deprotection of functional groups continues to be an important tool in the synthetic chemistry of polyfunctional molecules [1]. Protection of carbonyl groups is often required during the synthesis of many biologically important compounds [2]. Among the various carbonyl protecting groups, thioacetals and oxathioacetals are important owing to their stability under both mildly acidic and basic conditions [2,3]. In addition, the use of 1,3-oxathiolanes as chiral auxiliaries for the enantioselective synthesis of α-hydroxy acids and glycols clearly exemplified the importance of these protecting groups in organic synthesis [4]. The existing methods employ HCl [5a], $HClO_4$ [5b], refluxing with TsOH [5c], TMSOTf [5d], $Bu_4NBr_3$ [5e], *i*-$Pr_3SiOTf$ [5f], $SOCl_2$-$SiO_2$ [5g], sulfated zirconia [5h], CAN [5i], $I_2$ [5j], LiBr [5k], as catalyst or stoichiometric reagents. Most recently, some methods employing $NiCl_2$ [6a], montimorillonite K-10 [6b], $LiBF_4$ [6c], $MoO_2(acac)_2$ [6d], $ScCl_3$ [6e], $Y(OTf)_3$ [6f], $In(OTf)_3$ [7g], $Sc(OTf)_3$ [6h], [bmim]$BF_4$ [6i], Amberlyst-15 [6j], and $FeF_3$ [6k] have been reported. However, many of these methods have some disadvantages such as use of relatively large [6a,c–g] or stoichiometric amount of catalyst [6b], expensive reagents [6d–f], and cannot be reused as they destroyed in the work-up procedure [6a,c]. Alternatively, transthioacetalization of acetals also has gained attention as the method of choice for the preparation of dithioacetals. Though, there is quite a plethora of procedures available for condensation of carbonyl compounds with thiols, dithiols or mercaptoethanols, only a few methods have been developed for transthioacetalization of *O*,*O*- and *S*,*O*-acetals. The existing methods employ $MgBr_2$ [7a], $TeCl_4$ [7b], $WCl_6$ [7c], $ZrCl_4$ [7d], $SOCl_2$-$SiO_2$ [7e], trichloroisocyanuric acid [7f], $I_2$ [7g], $InCl_3$ [7h] in methylene chloride and other organic solvents. But, many of these reported methods require expensive [7d,h], stoichiometric [7a,b,e], and hazardous [7f] reagents. Thus, an improved alternative procedure free from aforesaid disadvantages for the protection of carbonyl compounds and transthioacetalization of *O*,*O*- and *S*,*O*-acetals is highly appreciated.

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis have posed serious problems to the environment. Therefore, the possibility of performing chemical processes in the absence of solvent (solvent-free conditions) has been receiving more attention [8,9]. Solid-supported reagents [10] have recently attracted much attention due to their low toxicity, high

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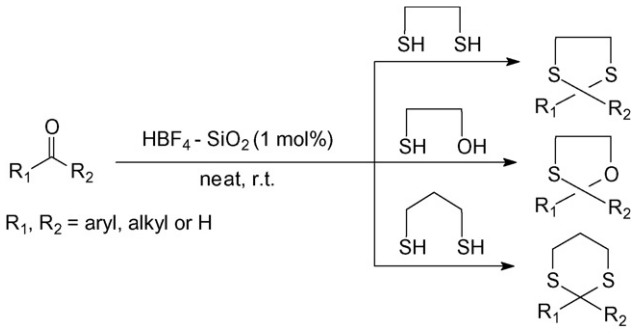


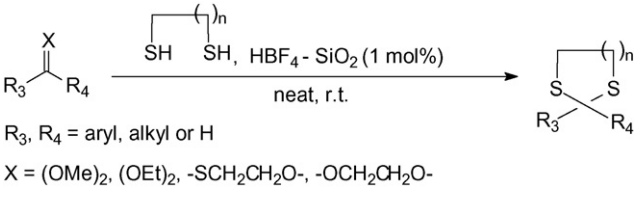

Scheme 1.

catalytic activity, moisture and air tolerance, ease of separation, recyclability and low price. This fact has prompted us to initiate an investigation to explore the catalytic activity of solid-supported fluoroboric acid ($HBF_4$-$SiO_2$) for useful organic transformations under solvent-free conditions. In this paper, we wish to report a mild and highly chemoselective procedure for the protection of carbonyl compounds and transthioacetalization of *O*,*O*- and *S*,*O*-acetals using trace amount of $HBF_4$-$SiO_2$ (1 mol%) under solvent-free conditions at room temperature.

## 2. Results and discussion

The catalyst was prepared by following literature procedure [11]. The reaction of aldehydes with 1,2-ethanedithiol or 1,3-propanedithiol and 2-mercaptothanol in the presence of 1 mol% of $HBF_4$-$SiO_2$ under solvent-free conditions at room temperature afforded the corresponding thioacetals and oxathioacetals respectively in excellent yields (Scheme 1). Similarly, several types of *O*,*O*- and *S*,*O*-acetals are efficiently and rapidly converted to the corresponding thioacetals at room temperature using 1 mol% of $HBF_4$-$SiO_2$ under solvent-free conditions (Scheme 2).

Initially a systematic study was carried out for catalytic evaluation of $HBF_4$-$SiO_2$ for thioacetalization of benzaldehyde under various conditions (Table 1). The reaction is slow in the absence of catalyst (Table 1, entry 1). The reaction is best carried out at room temperature under neat conditions (Table 1, entry 2). However, inferior results are obtained with $CH_2Cl_2$, THF, $CH_3CN$ and $CHCl_3$ (Table 1, entries 3–6). Next, we optimized the quantity of catalyst at room temperature under solvent-free conditions for this reaction (Table 1, entries 7–10). It was observed that, the use of just 1 mol% is sufficient to push the reaction forward. Larger amounts of catalyst did not improve the results (Table 1, entries 9 and 10). Similar types of results are obtained in the transthioacetalization of dimethyl acetal of benzaldehyde.




Scheme 2.

Table 1
Thioacetalization of benzaldehyde under various conditions

| Entry | Solvent | Amount of catalyst (mol%) | Time | Yield[a] (%) |
|---|---|---|---|---|
| 1 | Neat | – | 72 h | 10 |
| 2 | Neat | 1 | 5 min | 97 |
| 3 | $CH_2C1_2$ | 1 | 30 min | 65 |
| 4 | THF | 1 | 30 min | 67 |
| 5 | $CH_3CN$ | 1 | 30 min | 78 |
| 6 | $CHC1_3$ | 1 | 30 min | 70 |
| 7 | Neat | 0.3 | 5 min | 74 |
| 8 | Neat | 0.7 | 5 min | 80 |
| 9 | Neat | 2 | 5 min | 97 |
| 10 | Neat | 3 | 5 min | 97 |

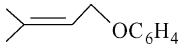
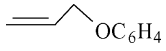
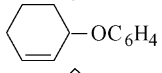
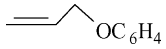
[a] Isolated yields.

Structurally diverse aldehydes undergo protection reaction with 1,2-ethanedithiol or 1,3-propanedithiol and 2-mercaptoethanol in the presence of 1 mol% of $HBF_4$-$SiO_2$ at room temperature to give the corresponding thioacetals and oxathioacetals, respectively, in good to excellent yields (Table 2). The rate of reactions was found to be very fast and in most cases acetal formation was completed in 5–40 min. The results shown in Table 2 clearly indicate the scope and generality of this protocol with respect to variety of aldehydes. The reaction conditions were compatible with wide range of substrates bearing methyl, chloro, *N*,*N*-dimethyl, nitro, fluoro, and cyano group (Table 2, entries b–k). Acid sensitive substrate like furfural and thiophene-2-carboxaldehyde (Table 2, entries m and n) are also protected in excellent yields without any difficulty. It is noteworthy that the conversion can be achieved in the presence of other protecting groups such as –OMe, $–OCH_2Ph$, –OPh, OEt, $–OCH_2O–$, allyl, TBS and TBDPS ethers (Table 2, entries r–dd). The present method is also highly effective to protect aliphatic aldehydes as thioacetals and oxathioacetals (Table 2, entries ee–ff). It is important to mention that thioacetal of naphthaldehyde was obtained from naphthaledehyde (Table 2, entry gg) by using 1 mol% of $HBF_4$-$SiO_2$ in 90% yield in 25 min, which provides much better yield than the procedure reported recently [6e]. Remarkably, cyclic, heterocyclic and aliphatic ketones (Table 2, entries hh–ll) can also be protected as thioketals and oxathioketals in good yields, although the time required for the completion of reaction of aliphatic ketones was found to be longer compared to aldehydes.

Excellent chemoselectivity was observed for conjugated aldehydes (Table 2, entries o–q) without any competitive conjugate addition [12]. Also, when compared to reported methods [6a–g], enhanced reaction rates and improved yields with conjugated aldehydes are obtained by the present catalytic system.

Furthermore, open chain as well as cyclic *O*,*O*- and *S*,*O*-acetals derived from aliphatic, aromatic, α,β-unsaturated, and heterocyclic aldehydes underwent clean transthioacetalization with a variety of dithiols by this procedure to furnish the corresponding *S*,*S*-acetals in high yields (Table 3, entries 1–15). A variety of functional groups such as Me, Cl, OMe, OBn, OTBS, $NO_2$ and OH are found to be quite stable under the present reaction conditions. Dialkyl acetals of cyclic and open chain aliphatic

Table 2
Synthesis of various thioacetals and oxathioacetals using $HBF_4$-$SiO_2$

| Entry | $R_1$ | $R_2$ | Thiol | Product | Time (min) | Yield[a,b] (%) | Refefence |
|---|---|---|---|---|---|---|---|
| a | $C_6H_5$ | H | $HS(CH_2)_2SH$ | 2a | 5 | 97 | [5g] |
| b | 4-$MeC_6H_4$ | H | $HS(CH_2)_2SH$ | 2b | 8 | 96 | [5g] |
| c | 4-$ClC_6H_4$ | H | $HS(CH_2)_2SH$ | 2c | 7 | 97 | [5g] |
| d | 4-$NMe_2C_6H_4$ | H | $HS(CH_2)_2SH$ | 2d | 25 | 73 | [5g] |
| e | 4-$NO_2C_6H_4$ | H | $HS(CH_2)_2SH$ | 2e | 15 | 80 | – |
| f | 4-$FC_6H_4$ | H | $HS(CH_2)_2SH$ | 2f | 7 | 90 | [5l] |
| g | 4-$NO_2C_6H_4$ | H | $HS(CH_2)_2OH$ | 2g | 25 | 78 | [5j] |
| h | 4-$MeC_6H_4$ | H | $HS(CH_2)_2OH$ | 2h | 20 | 95 | [6e] |
| i | 4-$CNC_6H_4$ | H | $HS(CH_2)_2OH$ | 2i | 10 | 90 | [5j] |
| j | 4-$ClC_6H_4$ | H | $HS(CH_2)_3SH$ | 2j | 10 | 96 | [5k] |
| k | 4-$MeC_6H_4$ | H | $HS(CH_2)_3SH$ | 2k | 15 | 95 | [5k] |
| 1 | $C_6H_5$ | H | $HS(CH_2)_2OH$ | 21 | 8 | 94 | [5j] |
| m | Furfuryl | H | $HS(CH_2)_2SH$ | 2m | 10 | 85 | [5h] |
| n | 2-thienyl | H | $HS(CH_2)OH$ | 2n | 15 | 82 | [5j] |
| o | $C_6H_5CH{=}CH$ | H | $HS(CH_2)_2SH$ | 2o | 15 | 95 | [5g] |
| P | $C_6H_5CH{=}CH$ | H | $HS(CH_2)_2OH$ | 2p | 20 | 91 | – |
| q | $C_6H_5CH{=}CH$ | H | $HS(CH_2)_3SH$ | 2q | 20 | 92 | [5k] |
| r | 4-$OMeC_6H_4$ | H | $HS(CH_2)_2SH$ | 2r | 10 | 94 | [5g] |
| s | 3,4-$(OMe)_2C_6H_3$ | H | $HS(CH_2)_2SH$ | 2s | 15 | 95 | [5i] |
| t | 3-OMe, 4-$OCH_2PhC_6H_3$ | H | $HS(CH_2)_2SH$ | 2t | 25 | 90 | [5i] |
| u |  | H | $HS(CH_2)_2SH$ | 2u | 15 | 91 | – |
| v |  | H | $HS(CH_2)_2SH$ | 2v | 15 | 90 | – |
| w | 3,4-$(–OCH_2O–)C_6H_3$ | H | $HS(CH_2)_2OH$ | 2w | 25 | 85 | [5j] |
| x | 4-$OPhC_6H_4$ | H | $HS(CH_2)_2OH$ | 2x | 30 | 89 | – |
| y | 4-$OEtC_6H_4$ | H | $HS(CH_2)_2OH$ | 2y | 20 | 92 | [5j] |
| z |  | H | $HS(CH_2)_2OH$ | 2z | 25 | 89 | – |
| aa |  | H | $HS(CH_2)_2OH$ | 2aa | 20 | 88 | – |
| bb | 4-$TBSOC_6H_4$ | H | $HS(CH_2)_2OH$ | 2bb | 25 | 84 | – |
| cc | 3-OMe, 4-$TBDPSOC_6H_3$ | H | $HS(CH_2)_2OH$ | 2cc | 30 | 85 | – |
| dd | 4-$OMeC_6H_4$ | H | $HS(CH_2)_3SH$ | 2dd | 15 | 93 | [5k] |
| ee | $CH_3(CH_2)_4$ | H | $HS(CH_2)_2SH$ | 2ee | 5 | 96 | [5i] |
| ff | $CH_3(CH_2)_4$ | H | $HS(CH_2)_2OH$ | 2ff | 8 | 90 | [5j] |
| gg | 1-naphthyl | H | $HS(CH_2)_3SH$ | 2gg | 25 | 90 | [5k] |
| hh | cyclohexyl | H | $HS(CH_2)_2SH$ | 2hh | 30 | 89 | [5h] |
| ii | cyclopentyl | H | $HS(CH_2)_2SH$ | 2ii | 30 | 90 | [5h] |
| jj | Pr | Pr | $HS(CH_2)_2OH$ | 2jj | 40 | 80 | – |
| kk | 2-thienyl | Me | $HS(CH_2)_2SH$ | 2kk | 15 | 70 | – |
| ll | Furfuryl | Me | $HS(CH_2)_2SH$ | 2ll | 15 | 71 | – |

[a] Yields of pure isolated products.
[b] Products are characterized by $^1H$ NMR, Mass and elemental analysis and comparison with authentic samples.

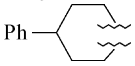
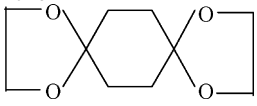
ketones as well as aromatic ketones were efficiently thioacetalized at room temperature giving the corresponding dithioacetals in high yields (Table 3, entries 16–18). In general, the reactions are very fast, clean and just 1 mol% of $HBF_4$-$SiO_2$ is sufficient to push the reaction efficiently. Compared to reported methods for transthioacetalization [7a–h], the present method is convincingly superior with respect to reaction time, yield, amount of catalyst, and solvent-free conditions employed.

In order to compare the effectiveness of $HBF_4$-$SiO_2$ over aqueous $HBF_4$ we chose to carry out the oxathioacetalization of acid sensitive substrate. Thus, while using 1 mol% of $HBF_4$-$SiO_2$ the oxathioacetalization of cinnamaldehyde with 1.1 equiv. of 1,2-mercaptoethanol afforded 91% yield of corresponding oxathioacetal in 20 min at room temperature under solvent-free conditions. However, when the corresponding reaction, carried out under similar conditions in the presence of 1 mol% aqueous $HBF_4$ afforded 25% yield of the corresponding oxathioacetal. This result revealed that $HBF_4$-$SiO_2$ is better suited for protection of acid sensitive substrates compared to aqueous $HBF_4$. The high activity of $HBF_4$-$SiO_2$ may be attributed to larger surface area and better selectivity.

While comparing the effect of recently reported catalysts in the thioacetalization and oxathioacetalization of benzaldehyde, we found that $HBF_4$-$SiO_2$ is more effective than recently reported catalysts in terms of the amount of catalyst, yields and reaction times (Table 4).

The advantage of the use of heterogeneous catalyst for this transformation is the ease of catalyst/substrate separation. In our process, when the catalytic reaction was completed, $HBF_4$-$SiO_2$ could be recovered conveniently from the reaction mixture

Table 3
Transthioacetalization of *O*,*O*- and *S*,*O*- acetals using $HBF_4$-$SiO_2$

| Entry | $R_3$ | $R_4$ | X | n | Time (min.) | Yield[a,b] (%) |
|---|---|---|---|---|---|---|
| 1 | $CH_3(CH_2)_8$ | H | $(OMe)_2$ | 1 | 7 | 96 |
| 2 | $C_6H_5$ | H | $(OMe)_2$ | 1 | 7 | 97 |
| 3 | $C_6H_5$ | H | $(OMe)_2$ | 2 | 8 | 94 |
| 4 | $C_6H_5$ | H | $(OEt)_2$ | 2 | 10 | 93 |
| 5 | 4-$MeC_6H_4$ | H | $O(CH_2)_3O$ | 2 | 10 | 96 |
| 6 | 4-$ClC_6H_4$ | H | $O(CH_2)_3O$ | 2 | 10 | 98 |
| 7 | 4-$OMeC_6H_4$ | H | $S(CH_2)_2O$ | 2 | 8 | 91 |
| 8 | 4-$MeC_6H_4$ | H | $S(CH_2)_3O$ | 2 | 10 | 96 |
| 9 | 4-$OHC_6H_4$ | H | $O(CH_2)_2O$ | 2 | 15 | 90 |
| 10 | 4-$OBnC_6H_4$ | H | $O(CH_2)_2O$ | 2 | 10 | 92 |
| 11 | 4-$OTBSC_6H_4$ | H | $S(CH_2)_2O$ | 1 | 10 | 93 |
| 12 | PhCH=CH | H | $S(CH_2)_2O$ | 2 | 15 | 95 |
| 13 | PhCH=CH | H | $(OEt)_2$ | 2 | 14 | 96 |
| 14 | 4-$ClC_6H_5$ | H | $(OEt)_2$ | 2 | 10 | 97 |
| 15 | 4-$NO_2C_6H_4$ | H | $S(CH_2)_2O$ | 2 | 15 | 97 |
| 16 | $C_4H_3S$ | H | $S(CH_2)_2O$ | 1 | 15 | 91 |
| 17 |  | H | $(OEt)_2$ | 2 | 20 | 90 |
| 18 | $PhCH_2CH_2$ | Me | $(OEt)_2$ | 2 | 25 | 90 |
| 19 | $C_6H_5$ | Me | $(OMe)_2$ | 1 | 40 | 89 |
| 20 |  | | – | 1 | 35 | 90 |

[a] Products have been characterized by $^1H$ NMR, Mass, elemental analysis and comparison with authentic samples.
[b] Isolated yields.

Table 4
Comparison of catalytic efficiencies of $HBF_4$-$SiO_2$ with recently reported catalysts taking benzaldehyde (1 mmol) as an example

| Catalyst | Catalyst load (mol%) | Time min/(h) | Yield (%) | Ref. |
|---|---|---|---|---|
| $NiCl_2$ | 10 | [2.75] | 96[a] | [6a] |
| MontmorilloniteK-10 | 200 mg | 30 | 86[b] | [6b] |
| $LiBF_4$ | 10 | [1] | 100[a] | [6c] |
| $MoO_2(acac)_2$ | 10 | [1.5]/[4] | 95[a]/86[b] | [6d] |
| $ScCl_3$ | 5 | [2] | 86[a] | [6e] |
| $Y(OTf)_3$ | 5 | 90/110 | 92[a]/79[b] | [6f] |
| $ln(OTf)_3$ | 5 | [1] | 82[b] | [6g] |
| [bmim]$BF_4$ | 2 mL | [2.5] | 92[b] | [6i] |
| Amberlyst-15 | 500 mg | [21] | 93[a] | [6j] |
| $FeF_3$ | 5 | 10/5 | 92[a]/95[b] | [6k] |
| $HBF_4$-$SiO_2$ | 1 | 5/8 | 97[a]/94[b] | – |

[a] Yields refer to pure isolated products of thioacetals.
[b] Yields refer to pure isolated products of oxathioacetals.

through filtration and subsequent washing with ethyl acetate. Then, efforts were made to examine the reusability of $HBF_4$-$SiO_2$ by using benzaldehyde as a model substrate and the results are described in typical experimental procedure for thioacetalization reaction.

## 3. Conclusion

In summary, we have developed a simple and efficient method for chemoselective protection of carbonyl compounds and transthioacetalization of acetals using catalytic amount of $HBF_4$-$SiO_2$ under solvent-free conditions where the catalyst can be recovered and reused. Further, the present protocol allows the protection of carbonyl compounds and transthioacetalization of *O*,*O*- and *S*,*O*-acetals in the presence of other protecting groups. Other important features of the present method are: requirement of very low amount of catalyst, non-aqueous work-up, high yields, cost-effective, highly efficient, convenient and mild reaction conditions.

## 4. Experimental

All chemicals were of analytical grade. $^1H$ NMR spectra were recorded on AC 300 F spectrometer (300 MHz). Mass spectra were recorded with a Bruker ion trap spectrometer. CHN analyses were recorded on a Vario EL analyzer. Most of the products are known and were determined using comparison of their physical and spectral data with those reported in the literature.

### 4.1. Preparation of catalyst

$HBF_4$ (1.65 g, as a 40% aqueous solution) was added to the suspension of silica gel (13.35 g, 230–400 mesh) in diethyl ether (40 mL). The mixture was concentrated and the residue dried under vaccum at 100 °C for 72 h to afford $HBF_4$-$SiO_2$ (0.5 mmol $g^{-1}$) as a free flowing powder.

### 4.2. Typical experimental procedure for thioacetalization:

A mixture of benzaldehyde (5 mmol) and ethanedithiol (5.5 mmol) was stirred at room temperature in the presence of a

catalytic amount of $HBF_4$-$SiO_2$ (50 mg, 0.025 mmol, 1 mol%) for an appropriate time (Table 2). After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was allowed to settle down. The supernatant ethyl acetate was decanted off, the catalyst was washed with ethyl acetate (5 mL) and the combined ethyl acetate layer concentrated under reduced pressure to afford crude product which was purified by recrystallization from hexane to afford pure 2-phenyl-1,3-dithioacetal (97%).

The recovered catalyst was activated by heating at 80 °C under vacuum for 2 h and reused for thioacetalization of fresh lot of benzaldehyde (5 mmol) affording 94% yield of 2-phenyl-1,3-dithioacetal after 10 min. The recovered catalyst, after activation, was reused for two more consecutive thioacetalization reactions of benzaldehyde (5 mmol) affording 91, 87% yields, respectively, in 15 and 20 min.

### 4.3. General procedure for transthioacetalization:

A mixture of acetal (5 mmol) and dithiol (5.5 mmol) was stirred at room temperature in the presence of a catalytic amount of $HBF_4$-$SiO_2$ (50 mg, 0.025 mmol, 1 mol%) for an appropriate time (Table 3). After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was allowed to settle down. The supernatant ethyl acetate was decanted off, the catalyst was washed with ethyl acetate (5 mL) and the combined ethyl acetate layer concentrated under reduced pressure to afford crude product, which was purified by recrystallization from hexane to afford pure product.

Spectral data of some of compounds are given below

#### 4.3.1. 2e

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 8.20$ (d, $J = 8.8$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 5.64 (s, 1H), 3.52–3.42 (m, 2H), 3.40–3.35 (m, 2H); MS: $m/z = 228$ $(M+H)^+$; Anal. Calcd. For $C_9H_9NO_2S_2$: C, 47.56; H, 3.99; N, 6.16; Found C, 47.54; H, 4.00; N, 6.15.

#### 4.3.2. 2i

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$ (d, $J = 8.8$ Hz, 2H), 7.25 (d, $J = 8.8$ Hz, 2H), 5.70 (s, 1H), 4.30–4.21 (m, 2H), 3.55–3.48 (m, 2H); MS: $m/z = 192$ $(M+H)^+$; Anal. Calcd. For $C_{10}H_9NOS$: C, 62.80; H, 4.74; N, 7.32; Found C, 62.75; H, 4.70; N, 7.33.

#### 4.3.3. 2p

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.35 (m, 5H), 6.65 (d, $J = 16.2$ Hz, 1H), 6.30 (dd, $J = 16.2$ Hz and 8.4 Hz, 1H), 5.60 (d, $J = 8.4$ Hz, 1H), 4.40–4.30 (m, 2H), 3.50–3.44 (m, 2H); MS: $m/z = 193$ $(M+H)^+$; Anal. Calcd. For $C_{11}H_{12}OS$: C, 68.71; H, 6.29; Found C, 68.62; H, 6.25.

#### 4.3.4. 2u

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.43$ (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.4$ Hz, 2H), 5.63 (s, 1H), 5.50 (m, 1H), 4.50 (dd, $J = 10.5$ Hz and 2.0 Hz, 2H), 3.62–3.56 (m, 2H), 3.42–3.38 (m, 2H), 1.80 (s, 3H), 1.75 (s, 3H); MS: $m/z = 268$ $(M+H)^+$; Anal. Calcd. For $C_{14}H_{18}OS_2$: C, 63.11; H, 6.80; Found C, 63.08; H, 6.76.

#### 4.3.5. 2v

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$ (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.01–5.90 (m, 1H), 5.55 (m, 1H), 5.35–5.20 (m, 2H), 4.50–4.45 (m, 2H), 3.52–3.44 (m, 2H), 3.30–3.25 (m, 2H); MS: $m/z = 240$ $(M+H)^+$.

#### 4.3.6. 2x

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 8.2$–7.6 (m, 5H), 7.70 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 5.85 (s, 1H), 4.20–4.15 (m, 2H), 3.95–3.90 (m, 2H); MS: $m/z = 259$ $(M+H)^+$; Anal. Calcd. For $C_{15}H_{14}O_2S$: C, 69.73; H, 5.46; Found C, 69.68; H, 5.43.

#### 4.3.7. 2z

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$ (d, $J = 8.6$ Hz, 2H), 6.75 (d, $J = 8.6$ Hz, 2H), 6.00–5.90 (m, 3H), 4.90–4.75 (m, 1H), 4.60–4.54 (m, 1H), 3.98–3.90 (m, 1H), 3.40–3.25 (m, 2H), 2.12–1.90 (m, 6H); MS: $m/z = 263$ $(M+H)^+$; Anal. Calcd. For $C_{15}H_{18}O_2S$: C, 68.67; H, 6.91; Found C, 68.62; H, 6.87.

#### 4.3.8. 2aa

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.45$ (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.15–6.10 (m, 1H), 5.95 (s, 1H), 5.45 (d, $J = 16.5$ Hz, 1H), 5.30 (d, $J = 9.8$ Hz, 1H), 4.55 (m, 3H), 3.90–3.85 (m, 1H), 3.35–3.20 (m, 2H); MS: $m/z = 223$ $(M+H)^+$; Anal. Calcd. For $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; Found C, 64.75; H, 6.31.

#### 4.3.9. 2bb

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$ (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 5.95 (s, 1H), 4.55 (m, 1H), 3.95 (m, 1H), 3.30 (m, 1H), 3.20 (m, 1H), 0.98 (s, 9H), 0.25 (s, 6H); MS: $m/z = 297$ $(M+H)^+$; Anal. Calcd. For $C_{15}H_{24}O_2SSi$: C, 60.76; H, 8.16; Found C, 60.61; H, 8.12.

#### 4.3.10. 2cc

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.75$–7.65 (m, 4H), 7.42–7.32 (m, 6H), 6.92 (d, $J = 2.6$ Hz, 1H), 6.75 (dd, $J = 8.6$, 2.6 Hz, 1H), 6.60 (d, $J = 8.6$ Hz, 1H), 5.86 (s, 1H), 4.43 (m, 1H), 3.89 (m, 1H), 3.61 (m, 3H), 3.20 (m, 2H), 1.23 (s, 9H).

#### 4.3.11. 2jj

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.10$ (t, $J = 5.6$ Hz, 2H), 2.85 (t, $J = 5.6$ Hz, 2H), 1.90–1.65 (m, 4H), 1.54–1.34 (m, 4H), 0.96 (t, $J = 7.2$ Hz, 6H); MS: $m/z = 175$ $(M+1)^+$; Anal. Calcd. For $C_9H_{18}OS$: C, 62.02; H, 10.41; Found C, 62.27; H, 10.34.

#### 4.3.12. 2kk

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.19$ (d, $J = 4.6$ Hz, 1H), 7.12 (d, $J = 2.6$ Hz, 1H), 6.90–6.85 (dd, $J = 4.2$, 3.9 Hz, 1H), 3.50 (s, 4H), 2.20 (s, 3H); MS: $m/z = 203$ $(M+1)^+$; Anal. Calcd. For $C_8H_{10}OS_3$: C, 47.48; H, 4.98; Found C, 47.51; H, 4.95.

*4.3.13. 2ll*

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$ (s, 1H), 6.25–6.30 (m, 2H), 3.50 (s, 4H), 2.20 (s, 3H); MS: $m/z = 187$ $(M+1)^+$; Anal. Calcd. For $C_8H_{10}OS_2$: C, 51.58; H, 5.41; Found C, 51.57; H, 5.43.

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