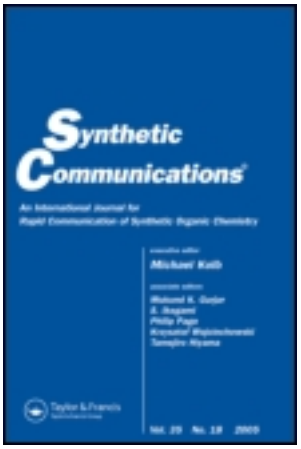

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Silica-Gel Supported Sulfamic Acid (SA/SiO_2) as an Efficient and Reusable Catalyst for Conversion of Ketones into Oxathioacetals and Dithioacetals

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Accepted author version posted online: 13 Feb 2012.Version of record first published: 08 Nov 2012.

To cite this article: Tadashi Aoyama , Toshihiko Suzuki , Takashi Nagaoka , Toshio Takido & Mitsuo Kodomari (2013): Silica-Gel Supported Sulfamic Acid (SA/SiO_2) as an Efficient and Reusable Catalyst for Conversion of Ketones into Oxathioacetals and Dithioacetals, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 43:4, 553-566

To link to this article: http://dx.doi.org/10.1080/00397911.2011.604458

Synthetic Communications®, 43: 553–566, 2013

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.604458

SILICA-GEL SUPPORTED SULFAMIC ACID (SA/SiO_2) AS AN EFFICIENT AND REUSABLE CATALYST FOR CONVERSION OF KETONES INTO OXATHIOACETALS AND DITHIOACETALS

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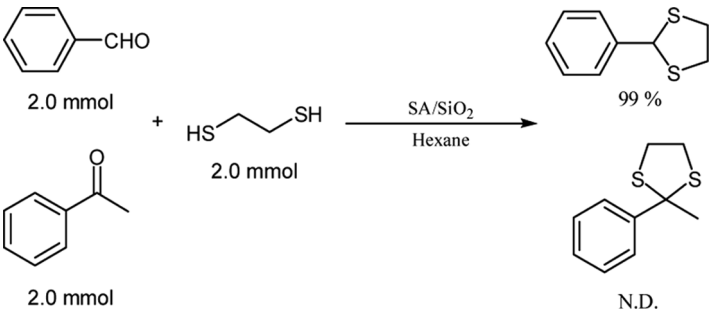
GRAPHICAL ABSTRACT



Abstract *A simple and efficient method for the conversion of carbonyl compounds to oxathioacetals and dithioacetals using SA/SiO_2 as an acid catalyst has been achieved. SA/SiO_2 is easily recovered from the reaction mixture and can be reused at least 15 times without loss of catalytic activity.*

Keywords Acetal; protective group; sulfamic acid; supported reagent

INTRODUCTION

For environmental reasons, it is highly desirable to replace homogeneous catalysts for organic synthesis with heterogeneous catalysts. Solid acid catalysts have many

Received June 13, 2011.
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advantages such as easy handling, decrease of corrosion, and environmentally safe disposal. Many solid acids, therefore, have been developed. Among them, the development of reusable inorganic solid-supported acid catalysts has attracted much attention.

Sulfamic acid [H_2NSO_3H (SA)] is a nonhygroscopic, nonvolatile, odorless, and stable white crystalline solid that is inexpensive and readily commercially available. Granular SA has been used as a heterogeneous catalyst in many organic preparations including protection of carbonyls,[1] alcohols,[2] and amines;[3] esterification;[4] C-C bond formation;[5] and synthesis of heterocycles.[6] In many cases, products are isolated from the reaction mixture by filtration, extraction, and washing. In some cases, SA is recovered and reused after the reaction.

There are many advantages in a reaction using inorganic solid-supported catalysts. The catalysts are easily separated from the reaction mixture by filtration, and some of the catalysts recovered can be applied to subsequent reactions. Recently, Niknam and coworkers developed silica-bonded *N*-propyl sulfamic acid (SBNPSA) and reported efficient formylation and acetylation of alcohols and amines.[7] Although SBNPSA is an efficient catalyst, toxic reagents are needed, and solvents and long reaction times are required for the preparation of it. In continuation of our studies on the application of inorganic solid-supported reagents to organic transformations, we have developed inorganic solid-supported SA, which is easily prepared and reusable.

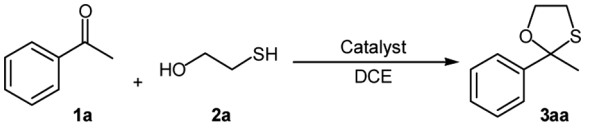
The protection of carbonyl groups plays an important role in organic, medicinal, and drug design chemistry and multistep synthesis of many natural products.[8] Many methods for conversion of carbonyl compounds into oxathioacetals and dithioacetals using silica-gel-supported reagents such as $SOCl_2/SiO_2$,[9] $CoBr_2/SiO_2$,[10] $ZrCl_4/SiO_2$,[11] $TaCl_5/SiO_2$,[12] $Cu(OTf)_2/SiO_2$,[13] $H_3PW_{12}O_{40}/SiO_2$,[14] and $AlCl_3/SiO_2$[15] have been reported.

Therefore, the efficient conversion of carbonyl compounds into oxathioacetals and dithioacetals using SA/SiO_2 shows the effectiveness of SA/SiO_2 as an acid catalyst, and comparison of SA/SiO_2 with the other acid catalysts reported can be easily made. In this article we describe the conversion of carbonyl compounds to oxathioacetals and dithioacetals using SA/SiO_2 as an acid catalyst. Initially the reaction of benzaldehyde with 2-mercapto ethanol using SA/SiO_2 was carried out in 1,2-dichloroethane at room temperature. This reaction easily proceeded, and benzaldehyde was converted quantitatively into the corresponding thioacetal in a minute. We employed the reaction of acetophenone with 2-mercapto ethanol using SA/SiO_2 to determine optimum reaction conditions.

The effectiveness of several inorganic solid-supported SA systems for the reaction was tested. The results obtained are summarized in Table 1. Both finely ground SA and SiO_2 were ineffective in promoting the reaction. SA/SiO_2, however, gave **3aa** in good yield at room temperature within 2 h. The other solid supports such as neutral, acidic, and basic alumina and molecular sieves (4Å) did not activate SA. The activity of SA/SiO_2 is significantly affected by the method of preparation of SA/SiO_2. When the reaction was carried out using SA/SiO_2 prepared by Sadaphal's method,[16] **3aa** was not obtained.

The reaction was carried out in various solvents such as 1,2-dichloroethane, benzene, chlorobenzene, toluene, cyclohexane, and hexane to determine the most effective solvent (Table 2). Hexane was the most effective among the solvents tested.

Table 1. Comparison of effectiveness of solid supports for SA[a]



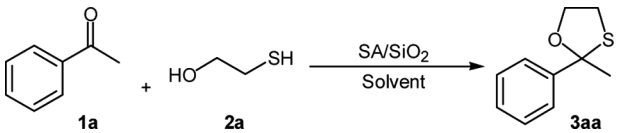
Entry	Catalyst	Yield of **3aa** (%)[b]
1	None	0
2	SA	0
3	SiO_2	0
4	SA/SiO_2	69
5	SA/n-Al_2O_3	0
6	SA/a-Al_2O_3	0
7	SA/b-Al_2O_3	0
8	SA/MS4A	0
9[c]	SA/SiO_2	0

[a]A mixture of **1a** (2.0 mmol), **2a** (2.4 mmol), and catalyst (1.5 mmol) was stirred in 1,2-dichloroethane (DCE) at room temperature for 2 h.
[b]Isolated yield.
[c]SA/SiO_2 was prepared by literature methods.[16]

When this reaction was carried out in hexane at 40 °C for 1 h, **3aa** was formed in 81% yield.

The effect of loading ratio of SA/SiO_2, amount of SA/SiO_2, and molar ratio of **2a** to **1a** on the reaction of **1a** with **2a** was investigated (Table 3). When the reaction was carried out at 40 °C for 1 h in the presence of 75 mol% of SA/SiO_2, which was prepared in various loading ratios, 4.0 mmol/g SA/SiO_2 was most effective (entries 1–6). The yield of **3aa** decreased according to the increase of loading ratio

Table 2. Synthesis of **3aa** using SA/SiO_2 in various solvents[a]



Entry	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	1,2-Dichloroethane	rt	2	69
2	Benzene	rt	2	63
3	Chlorobenzene	rt	2	68
4	Toluene	rt	2	78
5	Cyclohexane	rt	2	85
6	*n*-Hexane	rt	2	87
7	*n*-Hexane	40	1	81

[a]In all reactions **1a** (2.0 mmol), **2a** (2.4 mmol), SA/SiO_2 (3.0 mmol/g, 0.5 g), and solvent (5 mL) were used.
[b]Yields were determined by GLC.

Table 3. Determination of optimum reaction conditions[a]

1a 2a 3aa

Entry	Loading ratio (mmol/g)	Amount (g)	Catalyst (mol%)	Time (h)	**2a**/**1a** (mol/mol)	Yield of **3aa** (%)[b]
1	1.5	1.00	75	1	1.2	68
2	3.0	0.50	75	1	1.2	81
3	4.0	0.37	75	1	1.2	89
4	5.0	0.30	75	1	1.2	85
5	7.0	0.22	75	1	1.2	73
6	10.0	0.15	75	1	1.2	56
7	4.0	0.10	20	6	1.2	74
8	4.0	0.20	40	5	1.2	80
9	4.0	0.30	60	1	1.2	89
10	4.0	0.40	80	1	1.2	89
11	4.0	0.50	100	1	1.2	89
12	4.0	0.3	60	1	1.0	74
13	4.0	0.3	60	1	1.1	85
14	4.0	0.3	60	1	1.5	88

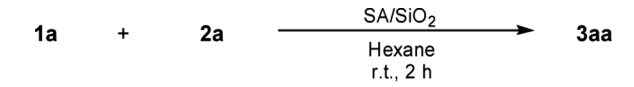
[a]A mixture of **1a, 2a**, and SA/SiO_2 was stirred in hexane at 40 °C.
[b]Yields were determined by GLC.

of SA/SiO_2. For instance, the 10.0 mmol/g SA/SiO_2 gave **3aa** in 56% yield. The results of the reactions using 4.0 mmol/g SA/SiO_2 show that at least 60 mol% of SA against **1a** is needed to afford **3aa** in good yield (entries 3 and 7–11). Finally, we determined the optimum molar ratio of **1a** to **2a**. The reaction using equivalent moles of **1a** and **2a** afforded **3aa** in 74% yield. Yield of **3aa** increased according to increasing amount of **2a** but a larger excess amount of **2a** was not required to obtain **3aa** in good yield (entries 12–14). From these results, we decided that subsequent reactions were carried out as follows: A mixture of **1a** (2.0 mmol), **2a** (2.4 mmol), and SA/SiO_2 (4.0 mmol/g, 0.3 g) in hexane was stirred at room temperature for 2 h.

We checked the reusability of SA/SiO_2 in advance of reactions using a series of various ketones. The results obtained are summarized in Table 4. SA/SiO_2 was recovered from the reaction mixture by filtration, regenerated with drying in vacuo at 160 °C for 1 h, and used for the next reaction. SA/SiO_2 could be reused at least 15 times without loss of activity. The yield of **3aa** in the 15th reaction was less than that of the first reaction. The recovered amount of SA/SiO_2 decreased step by step with each treatment. In the 15th reaction, 0.23 g of SA/SiO_2 was used. When reaction was carried out using fresh SA/SiO_2 (0.20 g), **3aa** gave in 76% yield (entry 1).

To date, several homogeneous, solid, and supported acid catalysts have been used for this reaction. To show the superiority of SA/SiO_2 as catalyst, the efficiency of SA/SiO_2 was compared with efficiency of other catalysts in the conversion of acetophenone with 2-mercapto ethanol into **3aa** obtained by other workers. These results are indicated in Table 5. Although a large amount of SA/SiO_2 is required

Table 4. Recycling of SA/SiO_2 for the synthesis of **3aa**



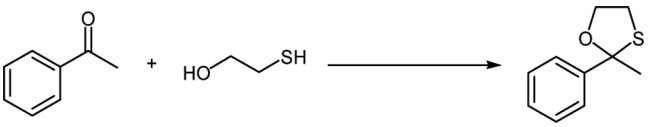
Entry	Catalyst[a]	Amount (g)	Yield (%)[b]
1	SA/SiO_2	0.20	76
2	SA/SiO_2	0.30	89
3	SA/SiO_2 (1)	0.30	88
4	SA/SiO_2 (2)	0.29	87
5	SA/SiO_2 (3)	0.29	87
6	SA/SiO_2 (4)	0.28	86
7	SA/SiO_2 (8)	0.27	87
8	SA/SiO_2 (11)	0.25	85
9	SA/SiO_2 (14)	0.23	79

[a]Parenthetic numbers indicate the number of reuses of SA/SiO_2.
[b]Isolated yield.

to complete the reaction, SA/SiO_2 has some advantages, including mild reaction conditions, good yield, simplicity in operation, and reusability.

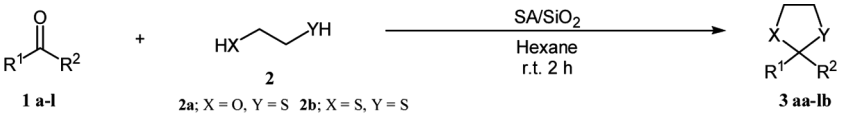
A series of carbonyl compounds was used for acetalization with 2-mercaptho ethanol (**2a**) and ethane-1,2-dithiol (**2b**) in the presence of SA/SiO_2 (Table 6). All of the carbonyls were converted into the corresponding acetals in good to excellent yields. 4-Nitroacetophenone (**1b**) was the most inactive among the acetophenone derivatives and gave **3ba** and **3bb** in 48% and 59% yield. Responsible for the poor yields of **3ba** and **3bb** is the fact that **1b** is slightly soluble in hexane. When the reaction of **1b** with **2a** and **2b** was carried out in hexane at reflux, **3ba** and **3bb** were obtained in 99% yields within 1 h (entry 2). Reactions of 4-methoxyacetophenone

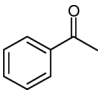
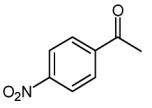
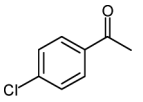
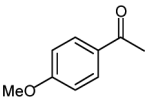
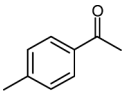
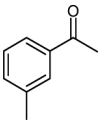
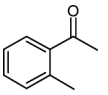
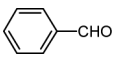
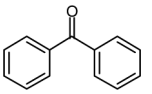
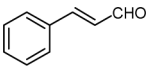
Table 5. Comparison between reported acid catalysts and SA/SiO_2



Catalyst	x/mol (%)	Time	Yield (%)	Ref.
$Sn(HPO_4)\ H_2O$	5	110 min	10	17
$H_3PW_{12}O_{40}/SiO_2$	6	24 h	50	14
$Fe(CF_3CO_2)_3$	5	190 min	82	18
$Fe(CF_3SO_3)_3$	5	3 h	81	18
$ZrCl_4$	10	14 h	88	19
$HClO_4$	10	1.5 h	60	20
$Yb(Otf)_3$	5	5 h	82	21
$TaCl_5/SiO_2$	2.5	1 h	93	12
SA/SiO_2	60	2 h	89	This work

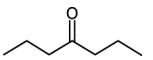
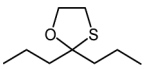
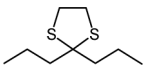
Table 6. Preparation of oxathioacetals and dithioacetals[a]



Entry	1	Substrate	Using **2a** Product	Yield (%)[b]	Using **2b** Product	Yield (%)[b]
1	**1a**		**3aa**	89	**3ab**	93
2	**1b**		**3ba**	48 (98)[c]	**3ab**	59 (99)[c]
3	**1c**		**3ca**	90	**3cb**	82
4	**1d**		**3da**	58 (69)[d]	**3db**	74 (99)[e]
5	**1e**		**3ea**	81	**3eb**	76
6	**1f**		**3fa**	85	**3fb**	78
7	**1g**		**3ga**	70	**3gb**	42
8	**1h**		**3ha**	81	**3hb**	99
9	**1i**		**3ia**	35 (67)[d]	**3ib**	44 (99)[d]
10	**1j**		**3ja**	63	**3jb**	99
11	**1k**		**3ka**	91	**3kb**	98

(*Continued*)

Table 6. Continued

Entry	1	Substrate	Using **2a** Product	Using **2a** Yield (%)[b]	Using **2b** Product	Using **2b** Yield (%)[b]
12	**1l**		 **3la**	99	 **3lb**	99

[a]A mixture of **1a** (2.0 mmol), **2a** (2.4 mmol), and SA/SiO_2 (4.0 mmol/g, 0.3 g) was stirred in hexane (5 mL) at room temperature for 2 h.
[b]Isolated yield.
[c]Reaction was carried out using 20 mL of hexane at reflux for 1 h.
[d]Reaction was carried out at reflux for 2 h.
[e]Reaction was carried out at 40 °C for 12 h.

(**1d**) with **2a** and **2b** needed a high temperature and a long reaction time to obtain **3da** and **3db** in good to excellent yields (Entry 4). Compound **3da** was obtained in 69% yield when the reaction was carried out at reflux for 2 h. Compound **3db** was also obtained in 99% yield at 40 °C for 12 h. Benzaldehyde (**1h**) reacted with **2a** to give the corresponding acetal **3ha** in 81% yield and 8% yield of benzaldehyde bis(2 -hydroxyethly)dithioacetal (**3′ha**) as a by-product. Structure of **3′ha** was determined by comparison with reported spectra of ^{1}H and ^{13}C NMR.[22] The reactivity of benzophenone (**1i**) was poor, and in the reaction with **2a** and **2b** at room temperature the yields of **3ia** and **3ib** were low (entry 9). However, the same reactions were carried out at reflux to form **3ia** and **3ib** in 67% and 99% yields.

The reaction was further explored using acetophenone with various diols and dithiols (Table 7). The reaction of **1a** with **2a, 2b**, and 1,3-dimercaptho propane (**2c**) gave the desired products **3aa–ac** in excellent yields (entries 1–3). Compound **3ac** was obtained in 92% yield in 1 h. In the reaction of **1a** with ethylene glycol (**2d**) the desired product **3ad** could not be isolated. When this reaction was carried out under reflux for 35 h, **3ad** gave 7%. The reaction with butane-2,3-diol (**2e**) gave **3ae** in 25% yield (entries 4 and 5). When the reaction with **2e** was carried out in hexane under reflux for 1.5 h, **3ae** was isolated in 89% yield. 2,2-Dimethyl propane-1,3-diol (**2f**) gave the corresponding acetal **3af** in moderate yield.

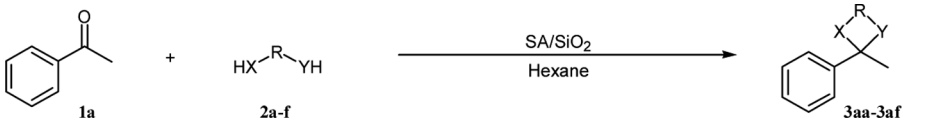
When a mixture of equimolar amounts of benzaldehyde and acetophenone was allowed to react with ethane-1,2-dithiol in the presence of SA/SiO_2 in hexane, only 2-phenyl-1,3-dithiolane was yielded (Scheme 1). Benzaldehyde was more reactive than acetopenone.

In conclusion we have developed a simple and efficient method for the conversion of carbonyl compounds into oxathioacetals and dithioacetals using SA/SiO_2 as an acid catalyst, which affords mild reaction conditions, good yields, simplicity in operation, and utilization of inexpensive and reusable catalyst.

EXPERIMENTAL

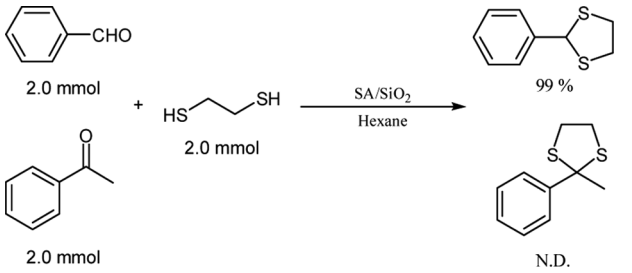
Melting points were determined on a Yanako Micro melting-point apparatus. Elemental analysis were performed on a Yanako CHN recorder MT-5. NMR

Table 7. Reaction of **1a** with diols and dithiols[a]



Entry	2	Product	Yield (%)[b]
1	**2a**	**3aa**	89
2	**2b**	**3ab**	93 (81)[c]
3	**2c**	**3ac**	95 (92)[c]
4	**2d**	**3ad**	Trace
5	**2e**	**3ae**	25 (89)[d]
6	**2f**	**3af**	59

[a]A mixture of **1a** (2.0 mmol), **2a** (2.4 mmol), and SA/SiO_2 (4.0 mmol/g, 0.3 g) was stirred in hexane (5 mL) at room temperature for 2 h.
[b]Isolated yield.
[c]Reaction was running for 1 h.
[d]Reaction was carried out hexane (10 mL) at reflux for 1.5 h.



Scheme 1. Chemoselective protection using SA/SiO_2.

spectra were recorded on a Jeol JNM-GX400 spectrometer or a Jeol JNM-ECX400. Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^{1}H NMR and $CDCl_3$ ($\delta = 77.0$) was used for ^{13}C NMR. Mass analysis were performed on a Agilent G1969 LC/MDS TOF. Infrared (IR) spectra were recorded on a Thermo Electron Nicolet 380 spectrometer.

Preparation of silica-gel-supported SA: silica-gel [Wakogel C-200 (Wako Pure Chemical Ind. Ltd.), 2.33 g] was added to a solution of SA (10 mmol, 1.48 g) in distilled water, and the mixture was stirred at room temperature for 0.5 h. The water was removed by rotary evaporation under reduced pressure, and the resulting reagent was dried in vacuo (10 mmHg) at 160 °C for 2 h.

General Procedure for Synthesis of Oxathio- and Dithioacetals

A mixture of **1** (2.0 mmol), **2** (2.4 mmol), and SA/SiO_2 (1.2 mmol) in hexane (5 mL) was stirred at room temperature for 2 h, and then the supported reagent was removed by filtration. The filtrate was concentrated and dried in vacuo to obtain **3**.

Regeneration of used SA/SiO_2:SA/SiO_2 was recovered by filtration from the reaction mixture, put in a 50-mL round-bottom flask, and dried in vacuo at 160 °C for 1 h.

2-Methyl-2-phenyl-1,3-oxathiolane (3aa)

IR (neat): 2975, 1491, 1446, 1371, 1268, 1217, 1132, 1099, 1066, 763, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.92$ (3H, s), 3.04–3.12 (1H, m), 3.19–3.26 (1H, m), 3.99–4.07(1H, m), 4.32–4.39 (1H, m), 7.20–7.54 (5H, m). ^{13}C NMR ($CDCl_3$): $\delta = 32.3$, 34.4, 70.6, 95.5, 124.8, 127.2, 128.1, 146.7. HRMS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_{10}H_{13}OS$: 181.0687; found: 181.0686.

2-Methyl-2-phenyl-1,3-dithiolane (3ab)[23]

IR (neat): 3056, 2966, 2922, 1489, 1442, 1373, 1276, 1064, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.14$ (3H, s), 3.30–3.49 (4H, m), 7.17–7.24 (1H, m), 7.25–7.35 (2H, m), 7.71–7.77 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 33.8$, 40.2, 68.5, 126.7, 127.0, 127.9, 145.8. HRMS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_{10}H_{13}S_2$: 197.0458; found: 197.0452.

2-Methyl-2-(4-nitrophenyl)-1,3-oxathiolane (3ba)

White solid. Mp 50–51 °C IR (neat): 2988, 2946, 1603, 1511, 1349, 1213, 1110, 1090, 1069, 851, 756, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.92$ (3H, s), 3.07–3.11 (1H, m), 3.25–3.30 (1H, m), 4.01–4.07 (1H, m), 4.36–4.41 (1H, m), 7.62–7.67 (2H, m), 8.16–8.21 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 32.0$, 34.7, 71.2, 94.5, 123.6, 125.9, 154.2. HRMS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_{10}H_{12}NO_3S$: 226.0537; found: 226.0533.

2-Methyl-2-(4-nitrophenyl)-1,3-dithiolane (3bb)

Yellow solid. Mp 56 °C. IR (neat): 2976, 2937, 1591, 1513, 1484, 1353, 1114, 1075, 858, 695 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.16$ (3H, s), 3.31–3.41 (2H, m), 3.48–3.56 (2H, m), 7.91–7.95 (2H, m), 8.14–8.18 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 33.2$, 40.6, 67.7, 123.2, 127.9, 146.7, 153.8. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{10}H_{12}NO_2S_2$: 242.0309; found: 242.0299.

2-(4-Chlorophenyl)-2-methyl-1,3-oxathiolane (3ca)

IR (neat): 2975, 2939, 2876, 1488, 1397, 1267, 1133, 1093, 1068, 1047, 1013, 832, 800 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.88$ (3H, s), 3.04–3.10 (1H, m), 3.20–3.26 (1H, m), 3.97–4.03 (1H, m), 4.31–4.35 (1H, m), 7.26–7.31 (2H, m), 7.40–7.44 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 32.2$, 34.5, 70.7, 95.0, 126.4, 128.2, 132.9, 145.4. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{10}H_{12}OSCl$: 215.0297; found: 215.0291.

2-(4-Chlorophenyl)-2-methyl-1,3-dithiolane (3cb)

IR (neat): 2966, 2923, 1489, 1446, 1397, 1373, 1277, 1094, 1012, 832 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.12$ (3H, s), 3.30–3.39 (2H, m), 3.42–3.48 (2H, m), 7.26 (2H, dd, $J = 8.7$, 2.5 Hz), 7.69 (2H, dd, $J = 8.7$, 2.5 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 33.5$, 40.4, 67.9, 128.0, 128.3, 132.8, 144.6. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{10}H_{12}S_2Cl$: 231.0068; found: 231.0065.

2-(4-Methoxyphenyl)-2-methyl-1,3-oxathiolane (3da)

IR (neat): 2972, 2875, 2835, 1609, 1210, 1463, 1302, 1249, 2276, 1132, 1034 833 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.89$ (3H, s), 3.02–3.10 (1H, m), 3.15–3.24 (1H, m), 3.78 (3H, s), 3.96–4.04 (1H, m), 4.27–4.34 (1H, m), 6.81–6.86 (2H, m), 7.39–7.45 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 32.2$, 34.3, 55.1, 70.4, 95.4, 113.3, 126.2, 138.7, 158.6. HR-MS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}O_2S$: 211.0792; found: 211.0790.

2-(4-Methoxy-phenyl)-2-methyl-1,3-dithiolane (3db)

IR (neat): 2960, 2923, 2834, 1607, 1508, 1463, 1297, 1251, 1180, 1033, 833, 735 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.14$ (3H, s), 3.34–3.50 (4H, m), 3.79 (3H, s), 6.83 (2H, dd, $J = 9.2$, 2.8 Hz), 7.67 (2H, dd, $J = 9.2$, 2.8 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 33.9$, 40.4, 55.2, 68.1, 113.2, 128.1, 137.7, 158.5. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}OS_2$: 227.0564; found: 227.0558.

2-Methyl-2-*p*-tolyl-1,3-oxathiolane (3ea)

IR (neat): 2974, 2924, 2875, 1510, 1441, 1370, 1267, 1133, 1093, 1069, 1047, 818 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.90$ (3H, s), 2.33 (3H, s), 3.03–3.10 (1H, m), 3.18–3.24 (1H, m), 3.98–4.05 (1H, m), 4.31–4.35 (1H, m), 7.13 (1H, d, $J = 8.0$ Hz), 7.38 (1H, d, $J = 8.0$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 21.0$, 32.3, 34.4, 70.6, 95.6, 124.8,

128.8, 136.9, 143.8. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}OS$: 195.0843; found: 195.0837.

2-Methyl-2-*p*-tolyl-1,3-dithiolane (3eb)

IR (neat): 3022, 2965, 2921, 1682, 1508, 1444, 1372, 1275, 1186, 1072, 1018, 820, 732 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.14$ (3H, s), 2.32 (3H, s), 3.32–3.48 (4H, m), 7.11 (1H, dd, $J = 8.2$, 2.0 Hz), 7.63 (1H, dd, $J = 8.2$, 2.0 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 20.9$, 33.8, 40.3, 68.4, 126.6, 128.6, 136.7, 142.8. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}S_2$: 211.0615; found: 211.0611.

2-Methyl-2-*m*-tolyl-1,3-oxathiolane (3fa)

IR (neat): 2974, 1606, 1486, 1444, 1370, 1270, 1131, 1047, 788, 705 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.90$ (3H, s), 2.35 (3H, s), 3.05–3.10 (1H, m), 3.18–3.25 (1H, m), 4.00–4.06 (1H, m), 4.32–4.37 (1H, m), 7.05 (1H, d, $J = 7.6$ Hz), 7.20 (1H, t, $J = 7.6$ Hz), 7.27–7.30 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 21.5$, 32.4, 34.5, 70.7, 95.6, 121.9, 125.5, 128.0, 128.1, 137.8, 146.72. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}OS$: 195.0843; found: 195.0849.

2-Methyl-2-*m*-tolyl-1,3-dithiolane (3fb)

IR (neat): 2966, 2922, 1684, 1487, 1446, 1373, 1276, 1172, 1065, 790, 722 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.14$ (3H, s), 2.36 (3H, s), 3.34–3.50 (4H, m), 7.04 (1H, d, $J = 7.6$ Hz), 7.20 (1H, t, $J = 7.6$ Hz), 7.53–7.56 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 21.5$, 34.1, 40.2, 68.5, 123.7, 127.4, 127.8, 127.89, 137.6, 145.7. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}S_2$: 211.0615; found: 211.0622.

2-Methyl-2-*o*-tolyl-1,3-oxathiolane (3ga)

IR (neat): 2975, 2930, 2874, 1485, 1443, 1269, 1136, 1115, 1047, 759 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.93$ (3H, s), 2.50 (3H, s), 3.00–3.07 (1H, m), 3.16–3.22 (1H, m), 3.96–4.02 (1H, m), 4.35–4.42 (1H, m), 7.14–7.19 (3H, m), 7.55–7.60 (1H, m). ^{13}C NMR ($CDCl_3$): $\delta = 21.4$, 31.2, 34.1, 70.2, 95.5, 124.1, 125.7, 127.2, 132.2, 134.3, 144.1. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}OS$: 195.0843; found: 195.0842.

2-Methyl-2-*o*-tolyl-1,3-dithiolane (3gb)

IR (neat): 3057, 2968, 2922, 1684, 1480, 1452, 1371, 1278, 1058, 765, 729 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.18$ (3H, s), 2.66 (3H, s), 3.28–3.25 (2H, m), 3.39–3.46 (2H, m), 7.11–7.19 (3H, m), 7.90–7.92 (1H, dd, $J = 6.9$, 1.8 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 22.6$, 33.3, 39.7, 69.4, 125.5, 126.7, 127.4, 132.8, 136.2, 142.5. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{15}S_2$: 211.0615; found: 211.0613.

2-Phenyl-1,3-oxathiolane (3ha)

IR (neat): 2920, 2851, 1455, 1232, 1065, 680 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.14$–3.30 (2H, m), 3.90–3.97 (1H, m), 4.49–4.54 (1H, m), 6.04 (1H, s), 7.27–7.37 (3H, m) 7.44–7.48 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 34.0$, 71.9, 87.0, 126.6, 128.4, 128.6, 139.2. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_9H_{11}OS$: 167.0530; found: 167.0531.

2-Phenyl-1,3-dithiolane (3hb)

IR (neat): 1663, 1492, 1445, 1057, 750, 696 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.32$–3.41 (2H, m), 3.48–3.55 (2H, m), 5.64 (1H, s), 7.22–7.34 (3H, m), 7.51–7.55 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 40.2$, 56.2, 127.9, 128.0, 128.5, 140.3. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_9H_{11}S_2$: 183.0302; found: 183.0308.

2,2-Diphenyl-1,3-oxathiolane (3ia)

White solid. Mp 45–46 °C. IR (neat): 3028, 2942, 1487, 1447, 1235, 1056, 751, 705, 696 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.25$ (2H, t, $J = 6.3$ Hz), 4.22 (2H, t, $J = 6.3$ Hz), 7.22–7.33 (6H, m), 7.49–7.53(4H, m). ^{13}C NMR ($CDCl_3$): $\delta = 34.7$, 70.2, 99.5, 126.7, 127.6, 128.0, 144.4. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{15}H_{15}OS$: 243.0843; found: 243.0841.

2,2-Diphenyl-1,3-dithiolane (3ib)

White solid. Mp 107 °C. IR (neat): 1483, 1442, 1237, 1078, 757, 701 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.41$ (4H, s), 7.19–7.32 (6H, m), 7.58–7.63 (4H, m). ^{13}C NMR ($CDCl_3$): $\delta = 40.1$, 76.8, 127.1, 127.9, 128.1, 144.5. HR-MS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{15}H_{15}S_2$: 259.0615; found: 259.0615.

2-Styryl-1,3-oxathiolane (3ja)

IR (neat): 3026, 2939, 2971, 1714, 1496, 1449, 1269, 1204, 1165, 1058, 966, 759, 693 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.09$–3.20 (2H, m), 3.88–3.94 (1H, m), 4.38–4.43 (1H, m), 5.69 (1H, d, $J = 7.3$ Hz), 6.27 (1H, dd, $J = 15.8$, 7.3 Hz), 6.65 (1H, d, $J = 15.8$ Hz), 7.21–7.43 (5H, m). ^{13}C NMR ($CDCl_3$): $\delta = 33.7$, 71.7, 86.3, 126.8, 127.1, 128.1, 128.6, 132.2, 135.9. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{13}OS$: 193.0687; found: 193.0690.

2-Styryl-1,3-dithiolane (3jb)

White solid. Mp 61–62 °C. IR (neat): 1498, 1448, 969, 762, 731, 688 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.25$–3.31 (2H, m), 3.33–3.40 (2H, m), 5.23 (1H, d, $J = 9.2$ Hz), 6.21 (1H, dd, $J = 15.6$, 9.2 Hz), 6.50 (1H, d, $J = 15.6$ Hz), 7.20–7.39 (5H, m). ^{13}C NMR ($CDCl_3$): $\delta = 39.6$, 54.5, 126.6, 127.8, 128.5, 129.0, 130.2, 136.1. HRMS (TOF-CI): m/z $[M+H]^+$ calcd. for $C_{11}H_{13}S_2$: 209.0458; found: 209.0460.

1-Oxa-4-thia-spiro[4,5]decane (3ka)

IR (neat): 2936, 2858, 1448, 1082 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 1.22–1.57$ (4H, m), 1.73–1.91 (6H, m), 3.03 (2H, t, $J = 6.0$ Hz), 4.17 (2H, t, $J = 6.0$ Hz). ^{13}C NMR ($CDCl_3$) $\delta = 24.9, 25.1, 32.9, 40.0, 69.5, 96.6$. HRMS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_8H_{15}OS$: 159.0843; found 159.0844.

1,4-Dithia-spiro[4,5]decane (3kb)

IR (neat): 1447, 1423, 1276, 963, 895, 852 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.37–1.46$ (2H, m), 1.63 (4H, quint, $J = 5.8$ Hz), 2.00 (4H, $J = 5.8$ Hz), 3.28 (4H, s). ^{13}C NMR ($CDCl_3$): $\delta = 24.9, 26.1, 38.3, 42.8, 68.8$. HR-MS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_8H_{15}S_2$: 175.0615; found: 175.0613.

2,2-Dipropyl-1,3-oxathiolane (3la)

IR (neat): 1464, 1378, 1265, 1075 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.93$ (6H, t, $J = 7.3$ Hz), 1.31–1.52 (4H, m), 1.69–1.87 (4H, m), 3.00 (2H, t, $J = 5.7$ Hz), 4.13 (2H, t, $J = 5.7$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 14.3, 18.4, 33.7, 43.2, 70.5, 98.7$. HRMS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_9H_{19}OS$: 175.1156; found: 175.1162.

2,2-Dipropyl-1,3-dithiolane (3lb)

IR (neat): 1463, 1276, 1139, 974, 853, 767 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.93$ (6H, t, $J = 7.3$ Hz), 1.42–1.54 (4H, m), 1.86–1.91 (4H, m), 3.26 (4H, s). ^{13}C NMR ($CDCl_3$): $\delta = 14.2, 20.2, 39.4, 45.8, 71.5$. HR-MS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_9H_{19}S_2$: 191.0928; found: 191.0924.

2-Methyl-2-phenyl-1,3-dithiane (3ac)

IR (neat): 3055, 2904, 2828, 1487, 1442, 1422, 1277, 1065, 765, 701 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.80$ (3H, s), 1.90–2.00 (2H, m), 2.68–2.80 (4H, m), 7.23–7.29 (1H, m), 7.35–7.42 (2H, m), 7.93–7.98 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 24.6, 28.0, 32.7, 54.0, 127.0, 127.7, 128.5, 143.7$. HR-MS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_{11}H_{15}S_2$: 211.0615; found: 211.0617.

2-Methyl-2-phenyl-1,3-dioxolane (3ad)

White solid. ^1H NMR ($CDCl_3$): $\delta = 1.66$ (3H, s), 3.73–3.83 (2H, m), 3.99–4.09 (2H, m), 7.29–7.36 (3H, m), 7.46–7.51 (2H, m). ^{13}C NMR ($CDCl_3$): $\delta = 27.6, 64.4, 108.8, 125.2, 127.8, 128.2, 143.3$. HR-MS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_{10}H_{13}O_2$: 165.0915; found: 165.0916.

2,5,5-Trimethyl-2-phenyl-1,3-dioxane (3af)

IR (neat): 2954, 2864, 1472, 1445, 1371, 1252, 1214, 1183, 1129, 1083 1039, 1015, 874, 764, 704 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.57$ (3H, s), 1.27 (3H, s), 1.54

(3H, s), 3.33 (2H, d, $J = 11.0$ Hz), 3.39 (2H, d, $J = 11.0$ Hz), 7.26–7.46 (5H, m). ^{13}C NMR ($CDCl_3$): $\delta = 21.8$, 22.8, 29.8, 32.0, 71.6, 100.1, 126.7, 127.5, 128.5, 140.8. HRMS (TOF-CI): m/z $[M + H]^+$ calcd. for $C_{13}H_{19}O_2$: 207.1385; found: 207.1381.

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