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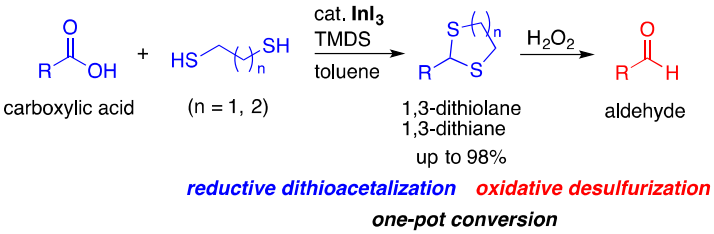
Indium-Catalyzed Reductive Dithioacetalization of Carboxylic Acids with Dithiols: Scope, Limitations, and Application to Oxidative Desulfurization

Kota Nishino, Kohei Minato, Takahiro Miyazaki, Yohei Ogiwara, and Norio Sakai*

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science (RIKADAI), Noda, Chiba 278–8510, Japan

E–mail: sakachem@rs.noda.tus.ac.jp



Abstract

In this study an InI_3-TMDS (1,1,3,3-tetramethyldisiloxane) reducing system effectively catalyzed the reductive dithioacetalization of a variety of aromatic and aliphatic carboxylic acids with 1,2-ethanedithiol or 1,3-propanedithiol leading to the one-pot preparation of either 1,3-dithiolane derivatives or a 1,3-dithiane derivative. Also, the intact indium catalyst continuously catalyzed the subsequent oxidative desulfurization of an in-situ formed 1,3-dithiolane derivative, which led to the preparation of the corresponding aldehydes.

Introduction

Dithioacetals have been utilized as a protecting group for carbonyl compounds, such as aldehydes and ketones, and as a masked acyl anion equivalent in synthetic conversions.[1] Both general and classic methods of dithioacetals have been widely achieved via a main group metal catalyst- or a transition metal catalyst-promoted condensation of carbonyl compounds with thiols or dithiols.[2,3,4] Also,

dithioacetalization has been in continuous development via either a metal catalyst-free system using HCl gas,[5a] PTSA,[5b] SO_2,[5c] $SOCl_2$-SiO_2,[5d] $HClO_4$-SiO_2,[5e] I_2,[5f] NBS,[5g] glycerol,[5h] or by a solid-phase synthesis.[5i] Most of the carbonyl compounds employed in these reactions have been limited to aldehydes and ketones, and no extensive study has been focused on the dithioacetalization of a carboxylic acid in the presence of a thiol. To convert a carboxylic acid to a dithioacetal, it is necessary to add a reducing agent to the reaction system. Carboxylic acids generally tolerates to a typical reducing reagent due to the formation of a carboxylate anion after deprotonation. Hence, the development of a simple and practical procedure for the reductive dithioacetalization of a carboxylic acid has been highly desired.

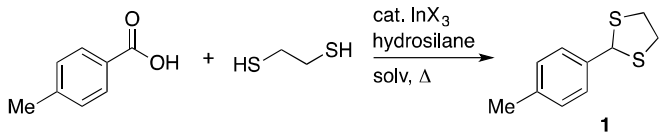
Thus far, the only example has been reported by Kim and co-workers wherein a direct dithioacetalization of carboxylic acids via the treatment with either thexylphenylthioborane or 1,3,2-dithiaborinane-dimethyl sulfide in the presence of $SnCl_2$ was developed. That procedure, however, used a borane as a reducing agent, which required the in-situ formation of an activated borane intermediate and a stoichiometric amount of $SnCl_2$ to complete the desired dithioacetalization.[6] On the other hand, we found an interesting result, in which a reducing system composed of an indium(III) catalyst with TMDS as a reducing agent efficiently catalyzed the condensation of carboxylic acids with 1,2-ethanedithiol leading to the direct preparation of 1,3-dithiolane (dithioacetal) derivatives.[7,8] However, in the previous work, only three examples of 1,3-dithiolane derivatives could be prepared. The details are unclear concerning the reactivity of carboxylic acids with a variety of functional groups. Thus, we report herein the full details of a series of direct dithioacetalizations of carboxylic acids, involving re-examinations of the reaction conditions, the scope and limitations of carboxylic acids, and functional group tolerance. Also, we disclose an interesting application, wherein a one-pot conversion

from an aromatic carboxylic acid into an aromatic aldehyde was achieved via a procedure that combined the previously mentioned reducing catalytic system with a subsequent oxidation step.

Results and discussion

On the basis of our previous work,[7] when dithioacetalization of *p*-toluic acid with 1,2-ethanedithiol was re-examined with 5 mol % of InI_3, which has a stronger Lewis acidity than $InBr_3$ (83%), under same conditions involving TMDS (*Si-H*: 6 equiv) and 1,2-dichloroethane, the desired protection was completed within 20 h to produce 1,3-dithiolane **1** in an 82% yield (entries 1 and 2 in Table 1). To establish milder conditions for the dithioacetalization, the same reaction was conducted at 60 ˚C. However, contrary to our expectation, a decrease in the product yield was observed (entry 3). In contrast, a reaction with chloroform at 60 ˚C showed a high solvent effect (entry 4). Interestingly, when the dithioacetalization was carried out in toluene, a remarkable increase in the reaction rate was observed, and a series of the dithioacetalization was completed within 2 h to isolate 80% of thioacetal **1** after a common column purification (entry 5). The effect of a hydrosilane was then investigated. Consequently, with the exception of $PhMe_2SiH$, other hydrosilanes, such as $PhSiH_3$, Ph_2MeSiH, Et_3SiH, and $(EtO)_3SiH$, were ineffective for the dithioacetalization, which led to a decrease in the yield of **1** (entries 6-10). Also, the use of 4 equiv (per a carboxylic acid) of TMDS showed a similar effect and produced **1** in a relatively excellent yield (entry 11). On the other hand, when an equivalent of TMDS was decreased to 2 equiv, the progress of the protection was remarkably hindered, leading to a rather low yield of **1** (entry 12). Finally, the results shown in entry 11 were regarded as optimal conditions for the dithioacetalization of a carboxylic acid.

TABLE 1. Examinations of the reaction conditions[a]



1

entry	InX_3	hydrosilane (*Si*-H)	solvent	temp (˚C)	time (h)	yield (%)[b]
1	$InBr_3$	TMDS (6)	1,2-DCE[c]	80	20	(83)
2	InI_3	TMDS (6)	1,2-DCE	80	20	82
3	InI_3	TMDS (6)	1,2-DCE	60	20	52
4	InI_3	TMDS (6)	$CHCl_3$	60	20	89
5	InI_3	TMDS (6)	toluene	60	2	92 (80)
6	InI_3	$PhSiH_3$ (6)	toluene	60	2	53
7	InI_3	$PhMe_2SiH$ (6)	toluene	60	2	76
8	InI_3	Ph_2MeSiH (6)	toluene	60	2	23
9	InI_3	Et_3SiH (6)	toluene	60	2	35
10	InI_3	$(EtO)_3SiH$ (6)	toluene	60	2	35
11	**InI_3**	**TMDS (4)**	**toluene**	**60**	**2**	**87**
12	InI_3	TMDS (2)	toluene	60	2	26

[a] Standard conditions: *p*-toluic acid (0.5 mmol), 1,2-ethanedithiol (0.6 mmol), an indium compound (0.025 mmol), a hydrosilane (*Si*-H: 1-3 mmol) and solvent (2 mL).

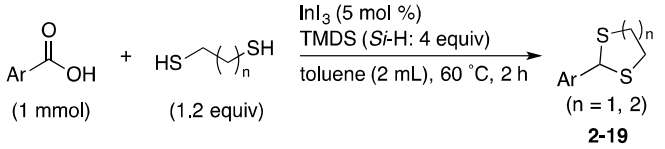
[b] GC (Isolated) yield.

[c] 1,2-DCE = 1,2-dichloroethane.

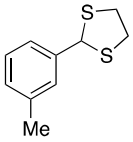
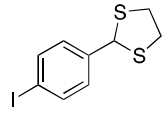
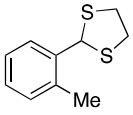
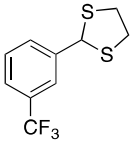
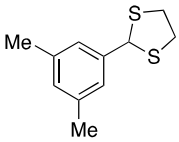
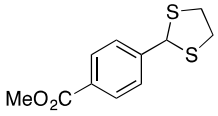
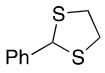
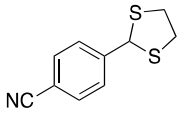
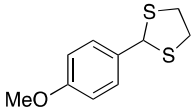
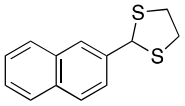
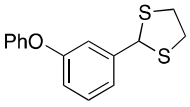
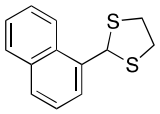
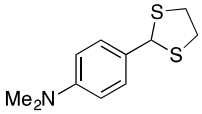
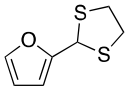
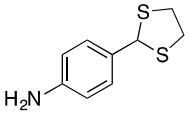
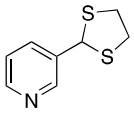
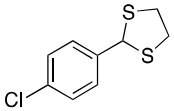
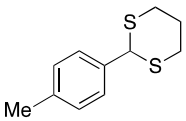
Then, to extend the generality of the present dithioacetalization, the examinations were conducted with a variety of aromatic aldehydes under the optimal conditions, and the results are summarized in Table 2. Carboxylic acids either with a methyl group or without a substituent were converted to the corresponding 1,3-dithiolane derivatives **2**-**5** in relatively good yields (entries 1-4). Also, carboxylic acids with an oxygen-containing substituent, such as methoxy and phenoxy groups, produced 1,3-dithiolane derivatives **6** and **7** in practical yields (entries 5 and 6). In the cases with an *ortho*-methyl

and a *para*-methoxy group, no formation of by-products was observed. In contrast, the substrates with a nitrogen-containing group, such as an *N,N*-dimethyl amino group or an unsubstituted amino group, led to a considerable decrease in the yields of each 1,3-dithiolane derivative (entries 7 and 8). On the other hand, when benzoic acid derivatives with a moderate electron-deficient group, such as a halogen and a trifluoromethyl group, were used under the optimal conditions, the corresponding 1,3-dithiolane derivatives **10**-**12** were obtained in good yields (entries 9-11). For a carboxylic acid derived from a benzoic acid ester, the reducing system similarly worked on the ester C=O double bond to produce a mixture of 1,3-dithiolane **13** and bis(1,3-dithiolanyl)benzene derivative **13'** (entry 12). However, when an aromatic carboxylic acid with a strong electron-deficient group, such as a cyano group, was employed, the expected 1,3-dithiolnae was obtained in a rather low yield (entry 13), and the most starting materials remained with no formation of a reduction product from the cyano group. Regardless of the substituted position, when naphthoic acids were treated under these reducing conditions, the corresponding dithioacetalization effectively proceeded to yield 1,3-dithiolanes **15** and **16** in 67 and 59% yields (entries 14 and 15). Gratifyingly, dithioacetalization was applied to an electron-rich heterocyclic compound, which finally afforded the furan ring-substituted 1,3-dithiolane **17** in a moderate yield (entry 16). Unfortunately, a carboxylic acid with a pyridine ring involved a more basic nitrogen atom did not undertake the expected dithioacetalization, which led to the formation of a complicated mixture (entry 17). Generally, it seems that the basic functional groups containing a nitrogen or an oxygen atom would coordinate to the indium catalyst, which led to the decrease in the catalytic activity (entries 5, 7, 8, 13, 16 and 17). When *p*-toluic acid was also reacted with 1,3-propanedithiol under the same conditions, 2-(4-methylphenyl)-1,3-dithiane (**19**) was obtained in a high yield (entry 18).

TABLE 2. Substrate scope of aromatic carboxylic acids[a]



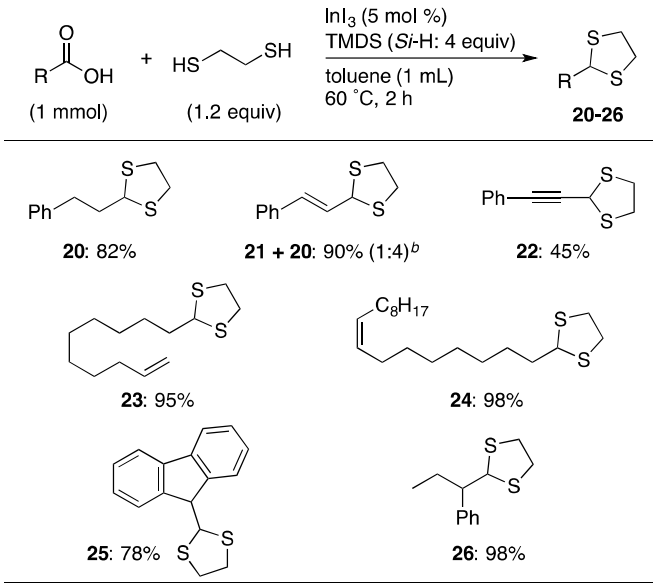
2-19

entry	product	yield (%)[a]		entry	product	yield (%)[a]	
1		**2**	68	10		**11**	63
2		**3**	46	11		**12**	85
3		**4**	90	12		**13 + 13'**	33 + 22
4		**5**	78	13		**14**	9
5		**6**	49	14		**15**	67[d]
6		**7**	77	15		**16**	59[d]
7		**8**	35[b]	16		**17**	43[e]
8		**9**	CM[c]	17		**18**	CM[c,f]
9		**10**	65	18		**19**	77

[a] Isolated yield. [b] InI_3 (10mol %), 120 ˚C (bath temperature). [c] A complex mixture. [d] 80 ˚C (bath temperature). [e] InI_3 (10 mol %). [f] 120 ˚C (bath temperature).

Next, we attempted the dithioacetalization of various aliphatic carboxylic acids (Table 3). For example, dithioacetalization of 3-phenylpropionic acid proceeded cleanly to produce the corresponding dithioacetal **20** in an 82% yield. Also, a conjugate carboxylic acid afforded a good yield of a mixture (1 : 4) of the desired 1,3-dithiolane **21** and an over-reduced 1,3-dithiolane **20** with a reduced double bond. When the carboxylic acid with an alkyne moiety was treated under the optimal conditions, the corresponding dithiolane **22** was produced in a 45% yield. Interestingly, the dithioacetalization of fatty acids, such as 10-undecenoic acid and oleic acid, efficiently produced 1,3-dithiolanes **23** and **24** in excellent yields. Both terminal and internal alkene moieties were tolerated to the reducing system, and the *cis*-geometry of oleic acid has remained the same stereochemistry. Moreover, the reductive dithioacetalization of bulky carboxylic acids with a branched carbon next to the carbonyl moiety, such as 9-fluorenecarboxylic acid and 2-phenylbutylic acid yielded the expected 1,3-dithiolanes **25** and **26** in good yields.

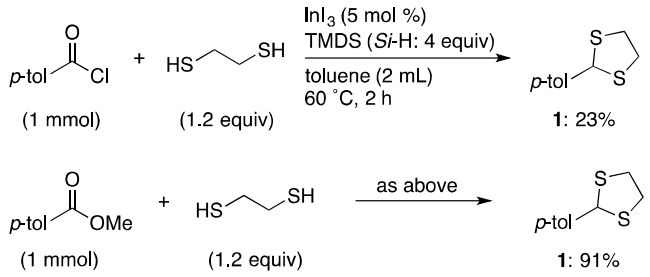
TABLE 3. Substrate scope of aliphatic carboxylic acids[a]



[a] Isolated yield. [b] Determined by NMR.

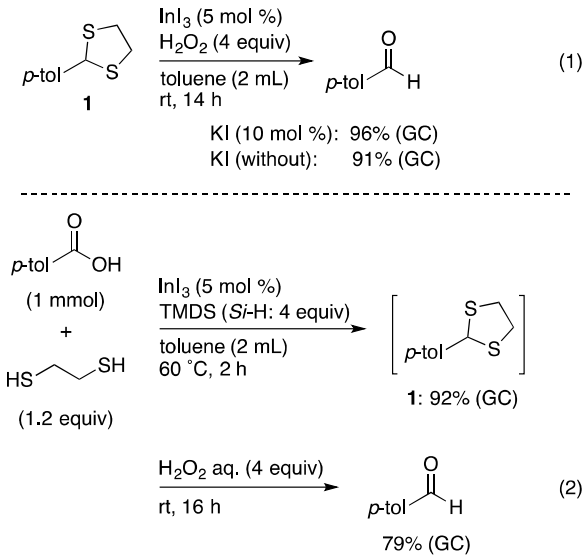
Using the optimal conditions (Scheme 1), we also examined the dithioacetalization of other carbonyl compounds, such as an acyl chloride and an ester, with identical oxidation numbers for the central carbon as well as a carboxylic acid. For example, when the reaction was carried out with an acyl chloride, the corresponding dithioacetal was obtained in a relatively low yield. On the other hand, dithioacetalization of an ester under the same conditions proceeded cleanly to form 1,3-dithiolane **1** in a high yield as shown in entry 11, Table 1.

SCHEME 1. Applications to dithioacetalization of other carbonyl compounds



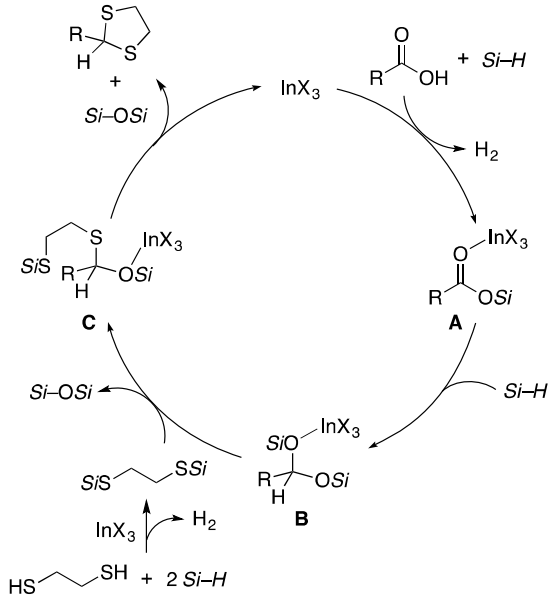
To test the utility of this procedure, a one-pot conversion of aromatic carboxylic acids into aromatic aldehydes was attempted (Scheme 2). On the basis of previous reports on the desulfurization of a dithioacetal with the combination of a promoter as a metal catalyst and an economical and readily-available oxidizing agent, H_2O_2 (hydrogen peroxide),[1f,9] the oxidative desulfurization of 1,3-dithiolane **1** as a model reaction was examined. Consequently, the oxidizing system involving InI_3 (10 mol %), KI (10 mol %) and H_2O_2 aqueous solution (4 equiv), efficiently undertook the expected desulfurization of **1** to yield the corresponding aldehyde, *p*-tolualdehyde in a good yield (eq 1 in Scheme 2). Moreover, it was proved that the oxidative conversion even occurred without the addition of KI. Hence, when the one-pot conversion of *p*-toluic acid into *p*-tolualdehyde was practically carried out using only the further addition of H_2O_2 after the first step, the effective desulfurization smoothly took place to give the desired aldehyde in a 79% yield (eq 2 in Scheme 2). It was implied that the indium catalyst remained intact after the first reduction step, and promoted the second oxidation step.[10]

SCHEME 2. Conversion to an aldehyde via oxidative desulfurization of 1,3-dithiolane **1**



Scheme 3 shows a plausible reaction path for the dithioacetalization of carboxylic acids. Initially, silyl ester **A** was formed through the reaction between a starting carboxylic acid and a hydrosilane involving the generation of hydrogen gas.[7] Then, silyl ester **A**, which was activated by an indium catalyst, was reduced again by another molecule of a hydrosilane to produce the corresponding silyl acetal **B**. The silyl acetal was subsequently substituted by one side of an in-situ generated thiosilane moiety of a dithiol to form *O,S*-acetal intermediate **C**.[11,12] After that, the other side of the thiosilane in intermediate **C** undertook intramolecular cyclization, which finally led to the production of the desired dithioacetal.

SCHEME 3. Plausible reaction pathway for the dithioacetalization of carboxylic acids



Conclusions

We have demonstrated that unlike conventional dithioacetalization of carbonyl compounds, such as aldehydes and ketones, the present reducing system composed of a toluene solution of InI_3 and TMDS achieved the direct and effective conversion of aromatic and aliphatic carboxylic acids with a variety of functional groups into the corresponding 1,3-dithiolanes and 1,3-dithiane. Also, we described how this reducing system could be applied to the similar conversion of an acyl chloride and an ester. Moreover, the indium catalyst that remained intact to successfully catalyze the subsequent oxidative desulfurization of the formed 1,3-dithiolanes, leading to the production of the corresponding aldehydes.

Experimental Section

General methods. All reactions were carried out under a N_2 atmosphere, unless otherwise noted. Toluene was freshly distilled from a Na-benzophenone solution. All indium compounds, aromatic carboxylic acids, aliphatic carboxylic acids and dithiols are commercially available and were used without further purification. Hydrosilanes were also used without further purification. Column chromatography was also performed using silica gel. ^{1}H NMR spectra were measured at 500 MHz using tetramethylsilane as an internal standard (0.00 ppm). ^{13}C NMR spectra were measured at 125 MHz using the center peak of chloroform (77.0 ppm).

General procedure for the synthesis of 1,3-dithiolanes: To a freshly distilled toluene solution (1.0 mL) in a screw-capped test tube under a N_2 atmosphere were successively added a magnetic stirrer bar, an aromatic or aliphatic carboxylic acid (0.5 mmol), 1,2-ethanedithiol (0.60 mmol, 54 mg), InI_3 (0.025 mmol, 23 mg), and TMDS (1.0 mmol, 1.3 x 10^2 μL). The test tube was sealed with a cap that contained a PTFE septum and was heated to 60 °C for 2 h. After the reaction, the resultant mixture was quenched with a saturated NaOH aqueous solution (3 mL). The aqueous layer was extracted with ethyl acetate (3 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and then evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (hexane as an eluent,) to give the corresponding 1,3-dithiolane, and, if necessary, further purified by a Preparative HPLC (chloroform as an eluent).

General procedure for the one-pot conversion of a carboxylic acid to an aldehyde: To a freshly distilled toluene solution (2.0 mL) in a screw-capped test tube under a N_2 atmosphere were successively added a magnetic stirrer bar, *p*-toluic acid (1.0 mmol, 136 mg), 1,2-ethanedithiol (1.20 mmol, 108 mg),

InI_3 (0.05 mmol, 46 mg), and TMDS (2.0 mmol, 2.6 x 10^2 μL). The test tube was sealed with a cap that contained a PTFE septum, and was heated to 60 °C for 2 h. After 2 h, H_2O_2 (30% aqueous solution, 4 mmol, 0.5 mL) was added and stirred at room temperature for 16 h. After the reaction, the resultant mixture was quenched using a saturated $Na_2S_2O_3$ aqueous solution (3 mL). The mixture was filtered and extracted with ethyl acetate (3 mL x 3). The combined organic phase was determined the quantity of *p*-tolualdehyde by gas chromatography.

2- (*p*-Tolyl)-1,3-dithiolane (1).[12] 80% yield (78 mg); a white solid; mp 58-59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.32-3.38 (m, 2H), 3.47-3.54 (m, 2H), 5.63 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 40.2, 56.1, 127.8, 129.2, 137.1, 137.9; MS (EI): 196 (M^+); HRMS (FAB-Magnetic Sector): Calcd for $C_{10}H_{12}S_2$: 196.0381, Found: 196.0378.

2-(*m*-Tolyl)-1,3-dithiolane (2).[13] 68% yield (133 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.32-3.37 (m. 2H), 3.47-3.52 (m, 2H), 5.61 (s, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 40.2, 56.2, 125.0, 128.3, 128.5, 128.8, 138.1, 140.1; MS (EI): 196 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{10}H_{12}S_2$: 196.0381, Found: 196.0378.

2-(*o*-Tolyl)-1,3-dithiolane (3). 46% yield (90 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.32-3.38 (m, 2H), 3.46-3.52 (m, 2H), 5.87 (s, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.14-7.17 (m, 1H), 7.19-7.22 (m, 1H), 7.79 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.7, 39.7, 52.8, 126.4, 127.6, 127.7, 130.3, 135.7, 137.9; MS (EI): 196 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{10}H_{12}S_2$: 196.0381, Found: 196.0377.

2-(3,5-Dimethylphenyl)-1,3-ditholane (4). 90% yield (189 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 6H), 3.28-3.34 (m, 2H), 3.45-3.51 (m, 2H), 5.58 (s, 1H), 6.88 (s, 1H), 7.12-7.13 (m,

2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 40.1, 56.2, 125.6, 129.7, 137.9, 139.9; MS (EI): 210 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{14}S_2$: 210.0537, Found: 210.0533.

2-Phenyl-1,3-dithiolane (5).[12] 78% yield (142 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.32-3.36 (m, 2H), 3.45-3.51 (m, 2H), 5.63 (s, 1H), 7.23-7.32 (m, 3H), 7.50-7.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 56.2, 127.9, 128.0, 128.4, 140.2; MS (EI): 182 (M^+); HRMS (EI-Quadrupole): Calcd for $C_9H_{10}S_2$: 182.0224, Found: 182.0220.

2-(4-Methoxyphenyl)-1,3-dithiolane (6).[12] 49% yield (104 mg); a white solid; mp 60-61 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33-3.36 (m, 2H), 3.49-3.53 (m, 2H), 3.80 (s, 3H), 5.64 (s, 1H), 6.84 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 55.3, 56.0, 113.8, 129.1, 131.7, 159.3; MS (EI): 212 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{10}H_{12}OS_2$: 212.0330, Found: 212.0337.

2-(3-Phenoxyphenyl)-1,3-dithiolane (7). 77% yield (211 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31-3.36 (m, 2H), 3.44-3.49 (m, 2H), 5.59 (s, 1H), 6.87-6.89 (m, 1H), 7.01 (d, J = 7.5 Hz, 2H), 7.11 (t, J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.25-7.28 (m, 2H), 7.34 (td, J = 8.0, 1.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 55.7, 118.1, 118.4, 118.9, 122.6, 123.3, 129.7, 142.7, 156.9, 157.2; MS (EI): 274 (M^+),; HRMS (EI-Quadrupole): Calcd for $C_{15}H_{14}OS_2$: 274.0486, Found: 274.0481.

2-(4-*N*,*N*-Dimethylaminophenyl)-1,3-dithiolane (8).[12] 29% yield (65 mg); a white solid; mp 105-106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.94 (s, 6H), 3.31-3.36 (m, 2H), 3.47-3.52 (m, 2H), 5.65 (s, 1H), 6.66 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.1, 40.5, 56.6, 112.3, 126.6, 128.8, 150.4; MS (EI): 225 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{15}NS_2$: 225.0646, Found: 225.0647.

2-(4-Chlorophenyl)-1,3-dithiolane (10).[12] 65% yield (140 mg) ; a white solid; mp 58-59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30-3.37 (m, 2H), 3.44-3.50 (m, 2H), 5.58 (s, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.45

(d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 55.4, 128.5, 129.3, 133.6, 139.0; MS (EI): 216 (M^+), 218 (M^++2); HRMS (EI-Quadrupole): Calcd for $C_9H_9S_2Cl$: 215.9834, Found: 215.9826.

2-(4-Iodophenyl)-1,3-dithiolane (11). 63% yield (194 mg); a white solid; mp 92-93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.32-3.38 (m, 2H), 3.45-3.51 (m, 2H), 5.55 (s, 1H), 7.26 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 55.6, 93.4, 129.8, 137.5, 140.3; MS (EI): 308 (M^+); HRMS (EI-Quadrupole): Calcd for $C_9H_9S_2I$: 307.9191, Found: 307.9189.

2-(3-Trifluoromethylphenyl)-1,3-dithiolane (12). 85% yield (213 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35-3.41 (m, 2H), 3.48-3.55(m, 2H), 5.65 (s, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 14H), 7.70 (d, J = 7.5 Hz, 1H), 7.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 55.5, 123.9 (q, $J_{C\text{-}F}$ = 271.2 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.75 Hz) (overlap x 2), 128.9, 130.8 (q, $J_{C\text{-}F}$ = 32.5 Hz), 131.4 (d, $J_{C\text{-}F}$ = 1.3 Hz), 141.9; MS (EI): 250 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{10}H_9S_2F_3$: 250.0098, Found: 250.0087.

2-(4-(Methoxycarbonyl)phenyl)-1,3-dithiolane (13).[14] 33% yield (87 mg: **13**/**13'** = 3:2); a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.34-3.41 (m, 2 H), 3.48-3.53 (m, 2 H), 3.91 (s, 3 H), 5.64 (s, 1 H), 7.58 (d, J = 8.0 Hz, 2 H), 7.98 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 55.1, 55.5, 127.9, 129.7, 129.8, 146.0, 166.6; MS (EI): 240 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{12}O_2S_2$: 240.0279, Found: 240.0280.

Bis(1,3-dithiolanyl)benzene (13').[12] 33% yield (87 mg: **13**/**13'** = 3:2); a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.34-3.41 (m, 4 H), 3.48-3.53 (m, 4 H), 5.62 (s, 2 H), 7.46 (s, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 55.8, 128.1, 140.2; MS (EI): 286 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{12}H_{14}S_4$: 285.9979, Found: 285.9987.

2-(4-Cyanophenyl)-1,3-dithiolane (14). 9% yield (21 mg); a white solid; mp 53-55 °C; ^{1}H NMR (500

MHz, $CDCl_3$) δ 3.38-3.42 (m, 2H), 3.47-3.52 (m, 2H), 5.61 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.62 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.4, 55.2, 111.6, 118.6, 128.7, 132.3, 146.5; MS (EI): 207 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{10}H_9NS_2$: 207.0176, Found: 207.0182.

2-(2-Naphtyl)-1,3-dithiolane (15).[15] 67% yield (155 mg); a white solid; mp 140-142 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.38-3.44 (m, 2H), 3.53-3.59 (m, 2H), 5.82 (s, 1H), 7.45-7.49 (m, 2H), 7.69 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.79-7.83 (m, 3H), 7.89 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.4, 56.5, 125.9, 126.2, 126.3, 126.5, 127.6, 127.9, 128.6, 132.9, 133.1, 137.6; MS (EI): 232 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{13}H_{12}S_2$: 232.0381, Found: 232.0383.

2-(1-Naphtyl)-1,3-dithiolane (16). 59% yield (137 mg); a colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 3.35-3.40 (m, 2 H), 3.42-3.48 (m, 2H), 6.41 (s, 1H), 7.42-7.45 (m, 1H), 7.49-7.46 (m, 1H), 7.54 (td, *J* = 8.5, 1.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.6, 52.7, 123.2, 124.7, 125.3, 125.7, 126.2, 128.5, 128.8, 131.0, 133.8, 135.5; MS (EI): 232 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{13}H_{12}S_2$: 232.0381, Found: 232.0389.

2-(2-Furyl)-1,3-dithiolane (17).[12] 43% yield (74 mg); a colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 3.28-3.34 (m, 2H), 3.40-3.46 (m, 2H), 5.63 (s, 1H), 6.27-6.30 (m, 2H), 7.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.1, 47.4, 107.0, 110.3, 142.6, 154.2; MS (EI): 172 (M^+); HRMS (EI-Quadrupole): Calcd for $C_7H_8OS_2$: 172.0017, Found: 172.0018.

2-(*p*-Tolyl)-1,3-dithiane (19).[16] 77% yield (162 mg); a white solid; mp 82-83 °C ;^1H NMR (500 MHz, $CDCl_3$) δ 1.88-1.96 (m, 1H), 2.15-2.17 (m, 1H), 2.33 (s, 3H), 2.88-2.92 (m, 2H), 5.14 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 25.1, 32.1, 51.2, 127.6, 129.4, 136.1, 138.3; MS (EI): 210 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{14}S_2$: 210.0537,

Found: 210.0539.

2-(2-Phenylethyl)-1,3-dithiolane (20).[13] 82% yield (172 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11-2.15 (m, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 3.18-3.29 (m, 4H), 4.44 (t, *J* = 7.0 Hz, 1H), 7.19-7.20 (m, 3H), 7.27-7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.2, 38.4, 41.1, 52.8, 126.0, 128.4, 128.5, 140.8; MS (EI): 210 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{14}S_2$: 210.0537, Found: 210.0545.

2-(2-Phenylethylene)-1,3-dithiolane (21).[12] 90% yield (170 mg, **20**/**21** = 1:4); a colorless oil; ^{1}H NMR (**20**+**21**, 500 MHz, $CDCl_3$) δ 2.10 -2.14 (m, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 3.16-3.20 (m, 2H), 3.21-3.25 (m. 2H), 3.26-3.32 (m, 2H), 3.34-3.37 (m, 2H), 4.43 (t, *J* = 7.0 Hz, 1H), 5.22 (d, *J* = 9 Hz, 1H), 6.21 (dd, *J* = 9, 16 Hz, 1H), 6.50 (d, *J* = 16 Hz, 1H), 7.18-7.21 (m, 12H), 7.22-7.24 (m, 2H); ^{13}C NMR (**20**+**21**,125 MHz, $CDCl_3$) δ 35.2, 38.3, 40.0, 41.0, 52.7, 54.4, 126.0, 126.3, 126.6, 127.8, 128.36, 128.44, 128.5, 129.0, 130.1, 136.0, 140.8; MS (EI): 208 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{12}S_2$: 208.0380, Found: 208.0388.

2-(2-Phenylethynyl)-1,3-dithiolane (22). 45% yield (93 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35-3.40 (m, 2H), 3.49-3.54 (m, 2H), 5.37 (s, 1H), 7.28-7.30 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.4, 40.3, 84.2, 88.0, 122.5, 128.1, 128.4, 131.6; MS (EI): 206 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{11}H_{10}S_2$: 206.0224, Found: 206.0233.

2-(9-Decenyl)-1,3-dithiolane (23).[12] 95% yield (231 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (m, 8H), 1.37-1.43 (m, 4H), 1.79-1.84 (m, 2H), 2.01-2.06 (m, 2H), 3.16-3.27 (m, 4H), 4.46 (td, *J* = 7.0, 2.5 Hz, 1H), 4.91-4.94 (m, 1H), 4.97-5.01 (m, 1H), 5.76-5.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 29.0, 29.1, 29.24, 29.27, 29.31, 33.7, 38.3, 39.3, 53.7, 114.1, 139.1; MS (EI): 244 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{13}H_{24}S_2$: 244.1319, Found: 244.1299.

2-(9*Z*-Octadecenyl)-1,3-dithiolane (24). 98% yield (335 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.27-1.29 (m, 20H), 1.40-1.46 (m, 2H), 1.79-1.84 (m, 2H), 1.99-2.03 (m, 4H), 3.17-3.27 (m, 4H), 4.47 (t, *J* = 7.0 Hz, 1H), 5.33-5.36 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 27.16, 27.21, 29.16, 29.18 (overlap x 2), 29.32, 29.34, 29.5 (overlap x 2), 29.7, 29.8, 31.9, 38.3, 39.3, 53.8, 129.8, 130.0; MS (EI): 342(M^+); HRMS (EI-Quadrupole): Calcd for $C_{20}H_{38}S_2$: 342.2415, Found: 342.2418.

9-Fluorenyl-1,3-dithiolane (25). 78% yield (211 mg); a white solid; mp 80-81 °C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03-3.11 (m, 4H), 4.33 (d, *J* = 4.5 Hz, 1H), 5.33 (d, *J* = 4.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.0 Hz, 2H), 7.40 (td, *J* = 7.5, 1.0 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.1, 52.3, 56.9, 119.7, 125.4, 126.8, 127.9, 141.8, 144.5; MS (EI): 270 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{16}H_{14}S_2$: 270.0537, Found: 270.0529.

2-(1-Phenylpropyl)-1,3-dithiolane (26). 98% yield (220 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (t, *J* = 7.0 Hz, 3H), 1.69-1.75 (m, 1H), 1.98-2.04 (m, 1H), 2.72 (ddd, *J* = 12.0, 8.5, 4.0 Hz, 1H), 3.03-3.18 (m, 4H), 4.79 (d, *J* = 8.5 Hz, 1H), 7.21-7.25 (m, 3H), 7.29-7.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0, 28.5, 38.4, 38.5, 55.6, 59.9, 126.8, 128.1, 128.4, 142.3; MS (EI): 224 (M^+); HRMS (EI-Quadrupole): Calcd for $C_{12}H_{16}S_2$: 224.0694, Found: 224.0687.

Supporting Information

Copies of the ^{1}H and ^{13}C NMR spectra of the chlorinated products produced by this method. This material is available free of charge via the Internet at http://pubs.acs.org.

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