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Lewis Base Catalyzed 1,3-Dithiane Addition to Carbonyl and Imino Compounds Using 2-Trimethylsilyl-1,3-dithiane

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Lewis base-catalyzed 1,3-dithiane addition to electrophiles such as carbonyl compounds and *N*-substituted aldimines with 2-trimethylsilyl-1,3-dithiane (TMS-dithiane) is described. By the activation of the carbon-silicon bond in the presence of a Lewis base catalyst such as tetrabutylammonium phenoxide (PhON*n*Bu$_4$), a 1,3-dithiane addition reaction proceeded smoothly to afford the corresponding adducts in good to high yields under mild conditions. This synthesis is also applied to the reactions of ketones having α-protons, and of *N*-substituted aldimines.

Keywords: addition · autocatalysis · Lewis bases · silicon · umpolung

Introduction

The Corey-Seebach Umpolung approach based on addition reactions of 1,3-dithiane anions is a very useful tool in synthetic organic chemistry and has widely been applied to the synthesis of natural and unnatural compounds by temporarily reversing the characteristic reactivity of carbonyl groups.[1] For example, α-hydroxy or α-amino dithiane derivatives are widely used for the synthesis of natural products.[2,3] Dithiane anions react with electrophiles such as carbonyl compounds and the dithiane moiety of the thus produced adducts can easily be converted either into the corresponding carbonyl groups under mild oxidation conditions[4] or into saturated alkyl substituents by reduction (Figure 1).[2]

In general, a 1,3-dithiane addition reaction is carried out by using 1,3-dithiane and an equimolar amount of a strong base such as *n*-butyllithium, and the thus formed 2-lithio-1,3-dithiane would be expected to work as a useful nucleophile. Andersen et al. reported an alternative method by using 2-trimethylsilyl-1,3-dithiane (TMS-dithiane) as the 1,3-dithiane equivalent, which was activated by a stoichiometric amount of tetrabutylammonium fluoride (TBAF) to generate the corresponding carbanion.[5] Further, tetrabutylammonium triphenyldifluorosilicate (TBAT) was found to be an alternative of TBAF by DeShong et al. as a mild fluoride source in 1995.[6] On the other hand, Corey et al. reported that various cesium salt mixtures containing cesium fluoride, could be used as heterogeneous desilylating reagents.[7] Most of these reactions are carried out by using an equimolar amount of harmful fluoride reagents, and only a few examples of catalytic activation of TMS-dithiane are shown to have been achieved.[6] Generally, these 1,3-dithiane addition reactions are rather hard to apply to the ketones having α-protons such as acetophenone because of the deprotonation of its methyl group by dithiane anions. Therefore, it is essential to find milder conditions for the addition reaction of 1,3-dithiane to various electrophiles.

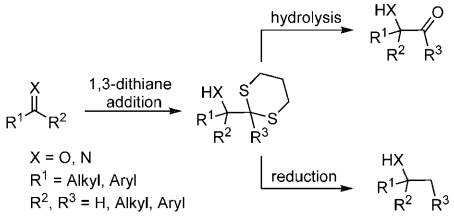

Figure 1. Addition reactions and manipulations of 1,3-dithiane.

In our previous papers, it was shown that the nitrogen- or oxygen-containing anions behaved as effective Lewis base catalysts in the activation of trimethylsilyl (TMS) derivatives.[8] Also, addition reactions with carbonyl and imino

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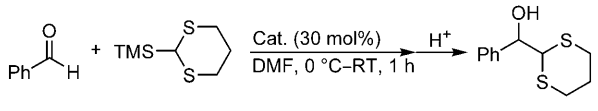
compounds such as Aldol reactions,[9] Michael reactions,[10] Mannich reactions,[11] trifluoromethylation,[12] cyanomethylation[13] and alkynylation[14] were successfully carried out in the presence of Lewis base catalysts. In order to extend the synthetic utility, activation of the carbon-silicon bond of TMS-dithiane with a Lewis base was reported recently.[15] In this paper, we would like to describe the scope and limitation of the convenient method for the 1,3-dithiane addition of various electrophiles with TMS-dithiane under mild conditions promoted by Lewis base catalysts such as PhON*n*-Bu_4.

Results and Discussion

Lewis Base-Catalyzed 1,3-Dithiane Addition to Carbonyl Compounds Using 2-Trimethylsilyl-1,3-dithiane

In order to investigate the effect of Lewis base catalysts, the 1,3-dithiane addition reaction of benzaldehyde **1a** with TMS-dithiane **2a** was studied (Table 1). When acetates that

Table 1. Screening of Lewis base catalysts.



1a **2a** (1.5 equiv) **3a**

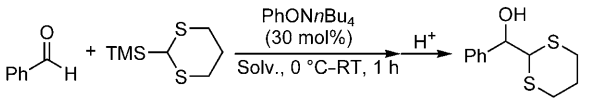
Entry	Catalyst	Yield [%][a]	Entry	Catalyst	Yield [%][a]
1	AcOLi	no reaction	6	PhONa	25
2	AcOK	no reaction	7	PhOK	77
3	AcON*n*Bu_4	no reaction	8	PhON*n*Bu_4	96
4	phthalimide K	no reaction	9	4-MeOPhON*n*-Bu_4	96
5	PhOLi	16	10	4-NO_2PhON*n*Bu_4	no reaction

[a] Yield of isolated product.

have counter cations such as lithium, potassium, or ammonium were used, the reaction did not take place (entries 1–3), nor did nitrogen-containing anions such as potassium phthalimide work (entry 4). On the other hand, the reaction proceeded when a phenoxide anion was employed as a counter anion, though the yield of the desired product **3a** was low. The effect of the counter cations were further examined, and the yield of **3a** increased as the nucleophilicities of the anions increased (entries 5–8), with the ammonium ion giving the best result. This indicated that a suitable choice of the counter cation of phenoxide was crucial for obtaining the adducts in high yield. Further, the substituent effect of the phenoxide anions were examined. Although **3a** was obtained in high yield when the phenoxide anion had an electron-donating group, the reaction did not proceed when an electron-withdrawing group was employed (entries 9 and 10).

Next, the effects of solvents were examined in the presence of a catalytic amount of PhON*n*Bu_4 (Table 2). When

Table 2. Effect of solvents on 1,3-dithiane addition reaction.



1a **2a** (1.5 equiv) **3a**

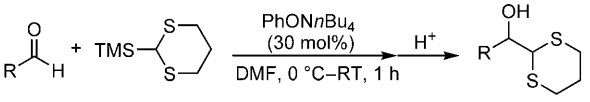
Entry	Solvent	Yield [%][a]	Entry	Solvent	Yield [%][a]
1	CH_2Cl_2	no reaction	5	DMF	96
2	THF	14[b]	6	DMAc	90
3	toluene	20[b]	7	NMP	84
4	MeCN	60	8	DMSO	77[c]

DMAc: Dimethylacetamide [a] Yield of isolated product. [b] The reaction was carried out for 2 h. [c] The reaction was carried out at room temperature.

dichloromethane was used, the reaction did not take place (entry 1). Similarly, no reaction took place in a less polar solvent such as THF or toluene and **3a** was obtained in poor yield and a large amount of **1a** remained unreacted (entries 2 and 3). On the other hand, **3a** was afforded in good to high yields (entries 4–8) when the reaction was carried out in polar solvents such as MeCN, DMF, dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), or DMSO. It was then found that the activation of TMS-dithiane was promoted in polar solvents, and the best result was obtained in DMF.

The reactions of various aldehydes **1b**–**1l** with TMS-dithiane **2a** in the presence of a catalytic amount of PhON*n*Bu_4 were attempted (Table 3). Aromatic aldehydes having electron-donating or -withdrawing groups reacted smoothly with TMS-dithiane to afford **3b**–**3g** in good to high yields (entries 1–6) and the yields obtained from the reactions of the heteroaromatic aldehydes **1h** and **1i** were also good (entries 7 and 8). In the case of the aliphatic aldehydes **1j** and **1k**, the reactions proceeded to give the desired adducts in good yields as well (entries 9 and 10). When an α,β-unsaturated aldehyde **1l** was used, only the 1,2-addition

Table 3. PhON*n*Bu_4 catalyzed dithiane addition of various aldehydes.



1b–l **2a** (1.5 equiv) **3b–l**

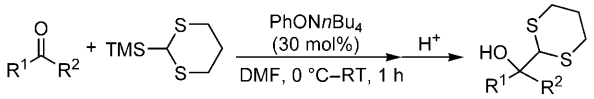
Entry	**1**	R	Product	Yield [%][a]
1	**b**	2-ClC_6H_4	**3b**	95
2	**c**	3-ClC_6H_4	**3c**	94
3	**d**	4-ClC_6H_4	**3d**	83
4	**e**	4-MeC_6H_4	**3e**	97
5	**f**	4-$MeOC_6H_4$	**3f**	92
6	**g**	1-naphthyl	**3g**	81
7	**h**	2-furyl	**3h**	94
8	**i**	3-pyridyl	**3i**	80
9	**j**	*tert*-butyl	**3j**	60
10	**k**	cyclohexyl	**3k**	83
11	**l**	(*E*)-PhCH=CH	**3l**	95

[a] Yield of isolated product.

product **3l** was obtained in high yield (entry 11). Since the dithiane adducts were a mixture of TMS ether and desilylated alcohol, in most cases, a complete desilylation by treating the mixture with 1 N HCl in a short time was necessary.

In order to extend the synthetic utility of this method, the reactions of various electrophilic ketones were investigated (Table 4). As shown in entry 1 where ketones have no pro-

Table 4. PhON*n*Bu$_4$ catalyzed dithiane addition of various ketones.



4a–i **2a** (1.5 equiv) **5a–i**

Entry	**4**	Ketone R^1	R^2	Product	Yield [%][a]
1	**a**	Ph	CF_3	**5a**	93
2	**b**	Ph	CO_2Me	**5b**	88
3	**c**	*(E)*-PhCH=CH	Ph	**5c**	91
4	**d**	*(E)*-PhCH=CH	Me	**5d**	75
5	**e**	Ph	Me	**5e**	60 (90[b])
6	**f**	4-MeOPh	Me	**5f**	75[b]
7	**g**	4-pyridyl	Me	**5g**	70
8	**h**	Ph	*i*Pr	**5h**	74[b]
9	**i**	cyclohexyl	Me	**5i**	63[b]

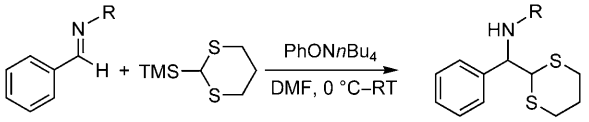
[a] Yield of isolated product. [b] 50 mol% of catalyst and 3 equivalent of TMS-dithiane were used.

tons at the α-position, the reaction proceeded smoothly to afford **5a** in high yields. In the case where an α-keto ester **4b** was employed, the 1,3-dithiane addition took place regioselectively to give the corresponding α-hydroxy ester **5b** in high yield (entry 2). The 1,2-adducts **5c** and **5d** were also obtained in good to high yields when α,β-unsaturated ketones were employed (entries 3 and 4). Importantly, the reactions of the substrates having α-protons such as acetophenone **4e** afforded the desired adduct in moderate yield though the reaction did not proceed to completion (entry 5). When the amounts of **2a** and PhON*n*Bu$_4$ were increased in order to complete the reaction, **5e** was obtained in 90% yield (entry 6). Similarly, various aromatic ketones having α-protons were successfully converted to the correponding tertiary alcohols **5f**–**5h** in good yields (entries 7–9). Also, when cyclohexylmethyl ketone **4i** was employed as the aliphatic substrate, **5i** was obtained in moderate yield (entry 10). These results indicate that the nucleophilic addition reaction takes place prior to deprotonation of the substrates.

Lewis Base-Catalyzed 1,3-Dithiane Addition to *N*-Substituted Aldimines Using 2-Trimethylsilyl-1,3-dithiane

Although catalytic 1,3-dithiane addition reactions of aldimines have yet to be reported, the reactions of *N*-substituted aldimines were also attempted in order to extend the utility of this synthetic method. At first, the effect of substituents on the nitrogen atom of aldimine were examined by using a catalytic amount of PhON*n*Bu$_4$ in DMF (Table 5). When *N*-toluenesulfonylimine **6a** was used, the desired adduct **7a** was obtained in poor yield (entry 1). On the other hand, the yield increased when an equimolar

Table 5. Effect of substituents on the nitrogen of aldimine.



6a–e **2a** (1.5 equiv) **7a–e**

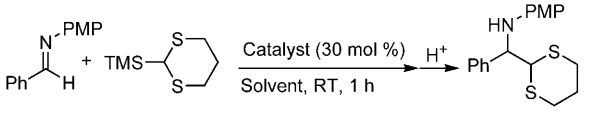
Entry	**6**	R	PhON*n*Bu$_4$ (mol%)	Product	Yield [%][a]
1	**a**	Ts	30	**7a**	24
2	**a**	Ts	100	**7a**	83
3	**b**	Ns	30	**7b**	not detected
4	**c**	Boc	30	**7c**	53
5	**d**	4-MeOPh	30	**7d**	64
6	**e**	Bn	30	**7e**	no reaction

[a] Yield of isolated product.

amount of Lewis base was used (entry 2). These results show that the Lewis base did not work catalytically for this substrate. The desired product **7b** was not detected when *N*-*o*-nitrobenzenesulfonyl aldimine **6b** was used (entry 3), while the reaction proceeded catalytically to afford the corresponding adduct **7c** in moderate yield with *N*-Boc imine **6c** (entry 4). Also, when *N*-*p*-methoxyphenyl (PMP) imine **6d** was used, the reaction proceeded smoothly to give the best result (entry 5). On the other hand, when *N*-benzylimine **6e** was used, the desired products were not detected because **6e** was less reactive (entry 6). Notably, the influence of the reactivities of the imines in this reaction has been found to be highly significant.

Based on the yields obtained, *N*-PMP benzaldimine **6d** was then chosen to optimize the reaction conditions (Table 6). First, the reaction of **6d** with **2a** was examined in the presence of various Lewis bases. The reactivity of the Lewis base showed the same tendancy with the addition to carbonyl compounds (entries 1–4), with PhON*n*Bu$_4$ giving a better result (entry 5). However, some unreacted starting

Table 6. Optimization of reaction conditions.



6d **2a** **7d**

Entry	Catalyst	TMS-dithiane (equiv)	Yield [%][a]
1	AcOLi	2.0	no reaction
2	AcON*n*Bu$_4$	2.0	no reaction
3	PhOLi	2.0	7
4	PhOK	2.0	42
5	PhON*n*Bu$_4$	2.0	64
6	PhON*n*Bu$_4$	3.0	85[b]
7	PhON*n*Bu$_4$	3.0	46[c]

[a] Yield of isolated product. [b] 9% of compound **8** was isolated. [c] 20 mol% of PhON*n*Bu$_4$ was used.

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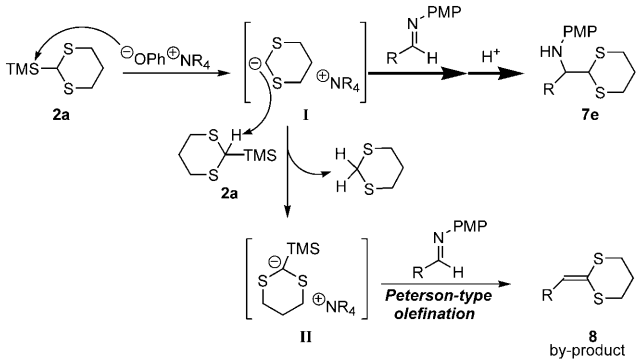
material **6d** was also obtained along with the 1,3-dithiane adduct **7d**. Then, 3.0 equivalents of **2a** was used in order to complete the reaction. Thus, **6d** completely disappeared and gave the desired adduct in high yield (entry 6); however, the yield decreased when the amount of the catalyst was reduced to 20 mol% (entry 7). As shown in entry 6, 9% of olefin **8** was isolated as a by-product even under the optimized conditions. The by-product **8** has been proposed to be formed by the mechanism shown in Scheme 1. Hence, along

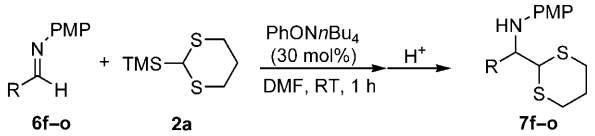


Scheme 1. Mechanism of the by-product generation.

with the addition reaction, deprotonation of the remaining unreacted **2a** took place competitively with the dithiane anion **I** to form anion **II**. The anion **II** successively reacted with the electrophiles to form the olefin **8** (Peterson-type olefination). These side reactions were not observed when more reactive electrophiles such as carbonyl compounds were used.

Reactions of various *N*-PMP aldimines **6f–o** with **2a** were subsequently attempted under the optimized conditions (Table 7). Aromatic aldimines having electron-donating or -withdrawing groups reacted smoothly with **2a** to afford the adducts **7f–m** in moderate to good yields (entries 1–8). Heteroaromatic *N*-PMP aldimines reacted smoothly as well,

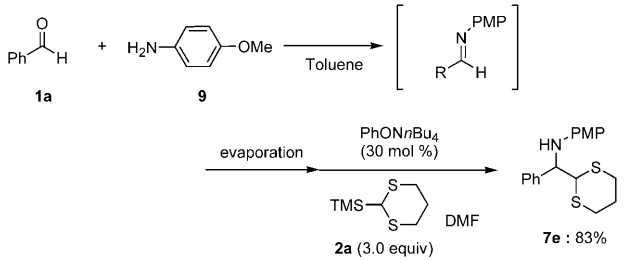
Table 7. PhON*n*Bu$_4$ catalyzed dithiane addition to various aldimines.



Entry	6	R	Product	Yield [%][a]
1	**f**	1-naphthyl	**7f**	74
2	**g**	2-ClC_6H_4	**7g**	70
3	**h**	3-ClC_6H_4	**7h**	87
4	**i**	4-ClC_6H_4	**7i**	92
5	**j**	4-FC_6H_4	**7j**	82
6	**k**	4-BrC_6H_4	**7k**	80
7	**l**	4-$CF_3C_6H_4$	**7l**	78
8	**m**	4-MeOC_6H_4	**7m**	78
9	**n**	2-furyl	**7n**	85
10	**o**	3-pyridyl	**7o**	84

[a] Yield of isolated product.

and afforded the adducts **7n** and **7o** in good yields (entries 9 and 10). In addition, it was found that an α-amino dithiane compound could be directly prepared from benzaldehyde **1a** and *p*-anisidine **9**, and the resulting imine successively treated with **2a** in a one-pot synthesis (Scheme 2).

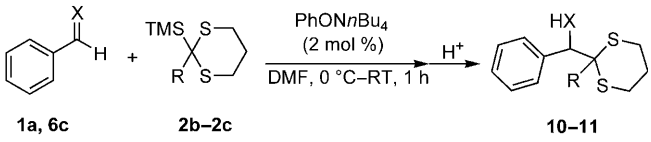


Scheme 2. One-pot synthesis of α-amino dithiane compound from aldehyde.

2-Substituted 1,3-Dithiane Addition to Various Electrophiles

The 2-substituted 1,3-dithiane addition to various electrophiles such as aldehyde, ketone and imine by using **2b** and **2c** having no proton at the 2-position were examined (Table 8) with the expectation that the reactions would pro-

Table 8. Substituted dithiane addition to various electrophiles.



1a : X = O
6c : X = N-Boc

Entry	Electrophiles	X	2	R	Product	Yield [%][a]
1	**1a**	O	**2b**	Ph	**10a**	99
2	**1a**	O	**2b**	Ph	**10a**	97[b]
3	**1a**	O	**2c**	Me	**10b**	95
4	**6c**	*N*-Boc	**2b**	Ph	**11a**	96
5	**6c**	*N*-Boc	**2c**	Me	**11b**	45

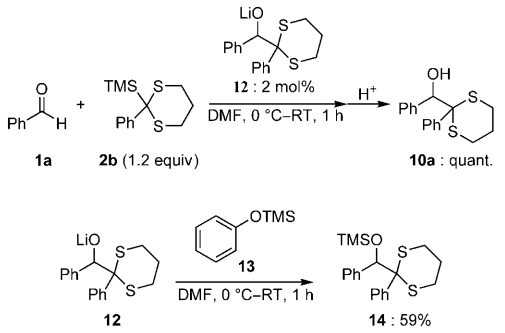
[a] Yield of isolated product. [b] 2 mol% of PhOLi was used.

ceed without the side-reaction mentioned above. As a result, when 2-phenyl-2-TMS-dithiane **2b** was treated with **1a**, the reaction proceeded in the presence of only 2 mol% of the catalyst to afford the corresponding adduct **10a** in excellent yield (entry 1). In addition, it reacted similarly even when PhOLi was used as a catalyst (entry 2). Also, when 2-methyl-2-TMS-dithiane **2c** was employed, the desired product **10b** was obtained in 95% yield (entry 3). Further, these reactions were also observed for *N*-Boc aldimine **6c**, and the corresponding adducts **11a** and **11b** were afforded (entries 4 and 5). Thus, this method is quite useful because the reaction proceeded smoothly in the presence of only 2 mol% of a Lewis base catalyst such as PhON*n*Bu$_4$. Therefore, it is noted that this is quite an effective procedure for

the preparation of 2-substituted-α-hydroxy or α-amino dithiane compounds.

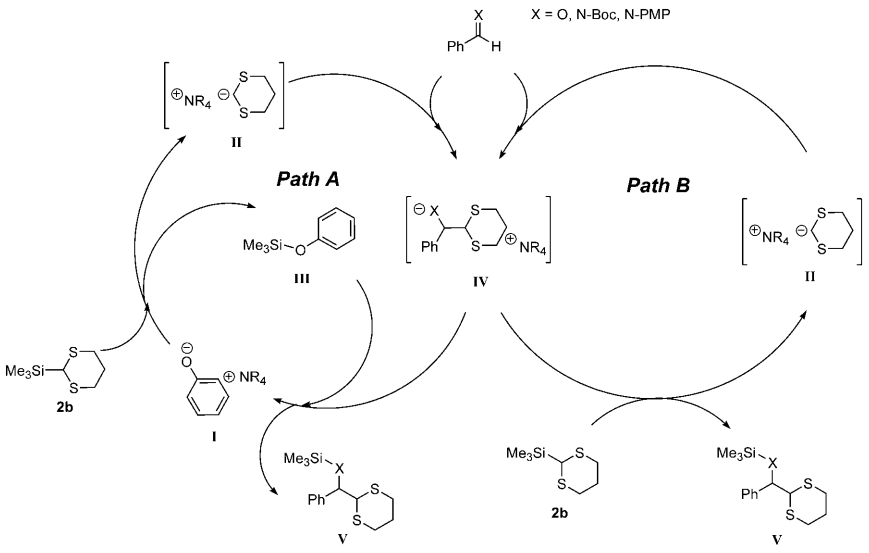
Mechanisms of Lewis Base-catalyzed 1,3-Dithiane Addition

As shown in Scheme 3, the reaction was carried out by using lithiated alkoxide-intermediate **12** as a catalyst in order to study the mechanism of the Lewis base-catalyzed 1,3-dithiane addition reaction.



Scheme 3. Confirmation experiments of the catalytic process.

It was observed that the addition reaction of **2b** to benzaldehyde **1a** in the presence of a catalytic amount of **12** proceeded smoothly to form the corresponding adduct **10a** in a quantitative yield. Thus, it was found that **12** worked as an autocatalyst. Further, the intermediate **12** was silylated with trimethylsilyl phenyl ether **13** to afford the corresponding silyl ether **14** in 59% yield. Thus, it is assumed that the reaction would proceed through either one or both of the catalytic cycles illustrated in Scheme 4. In the first step, the Lewis base catalyst **I** coordinates to the silicon atom of TMS-dithiane **2b** to form the carbanion **II** together with trimethylsilyl phenyl ether **III**. Then, the carbanion will react with the electrophiles to form the alkoxide-intermediate **IV**, which is then silylated by trimethylsilyl phenyl ether **III** to afford the *O*-silyl ether **V** along with the regeneration of **I** (Path A). An alternative pathway for the formation of carbanion **II** by the direct attack of **IV** on **2b** (Path B: autocatalytic process) has also been considered.



Scheme 4. Proposed catalytic cycle of dithiane addition reaction.

Conclusions

An efficient method for the synthesis of α- hydroxy or α-amino dithiane derivatives has been established by using 2-TMS-dithiane and various carbonyl or imino compounds in the presence of Lewis base-catalysts. It is noteworthy that this reaction is applicable to various aromatic ketones having α-protons, and *N*-substituted aldimines. Additionally, the reaction of 2-substituted-2-TMS-1,3-dithianes proceeded effectively in the presence of a small amount of Lewis base catalyst as illustrated in the proposed mechanism. Further studies on the catalytic reactions by using various organosilicon reagents, and a detailed investigation of the mechanisms are now in progress.

Experimental Section

General

All melting points were determined on a Yanagimoto micro melting apparatus (Yanaco MP-S3) and are uncorrected. Infrared (IR) spectra were recorded by using an attenuated total reflection (ATR) method on a SensIR Technologies Travel IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM EX270L (270 MHz) or a Varian Mercury Plus 400 (400 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. ^{13}C NMR spectra were recorded on a JEOL EX270L (68 MHz) or a Varian Mercury Plus 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$; $\delta = 77.0$ ppm). High-resolution mass spectra (HRMS) were recorded on a JMS-700 V (JEOL) or a Q-Tof-2-(micromass) mass spectrometer. Elemental analyses were conducted using a Yanaco MT-5 CHN corder. Analytical TLC was performed on Merck preparative TLC plates (silica gel 60 GF254, 0.25 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. Dry solvents were purchased from Kanto Chemical. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Kokusan Chemical, or Aldrich Chemical. Carboxylic acids were used without further purification. Alcohols and amines were used after purification by distillation.

Typical Experimental Procedure for 1,3-Dithiane Addition of Carbonyl Compounds

To a stirred solution of PhON*n*Bu$_4$[16] (50.3 mg, 0.15 mmol) and benzaldehyde (53.1 mg, 0.50 mmol) in DMF

(1.5 mL), 2-trimethylsilyl-1,3-dithiane (142 μL, 0.75 mmol) was added at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for 1 h and quenched with 1 N HCl (1.0 mL, 1.0 mmol). The mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The crude product was purified by preparative TLC (hexane/EtOAc = 2:1) to give the desired product **3a** (109.2 mg, 96 %) as white crystals.

3a:[17] 1,3-Dithian-2-yl-phenylmethanol: White crystals; m.p. 68–70 °C. IR (ATR): $\tilde{\nu}$ = 3419, 3029, 2896, 2827, 1036, 910, 698 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.31–7.44 (m, 5H), 4.87 (d, J = 7.6 Hz, 1H), 4.08 (d, J = 7.6 Hz, 1H), 3.12 (br, 1H), 2.89–3.01 (m, 2H), 2.67–2.78 (m, 2H), 1.85–2.10 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.0, 128.1, 128.0, 126.6, 74.6, 52.7, 28.2, 27.6, 25.3 ppm.

3b: 1,3-Dithian-2-yl-2-chlorophenylmethanol: White crystals; m.p. 75–78 °C; IR (ATR): $\tilde{\nu}$ = 3397, 2953, 2890, 1436, 1421, 1081, 1029, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.64–7.55 (m, 1H), 7.37–7.19 (m, 3H), 5.43 (d, J = 6.8 Hz, 1H), 4.14 (d, J = 6.8 Hz, 1H), 3.25 (br, 1H), 3.12–2.94 (m, 2H), 2.82–2.63 (m, 2H), 2.12–1.94 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 137.9, 133.1, 129.2, 129.1, 128.0, 126.8, 71.0, 51.3, 28.6, 27.3, 25.3 ppm; elemental analysis: calcd (%) for $C_{11}H_{13}OClS_2$: C 50.66, H 5.02; found: C 50.50, H 4.99.

3c: 1,3-Dithian-2-yl-3-chlorophenylmethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3396, 2892, 1421, 1080, 1030, 758, 696 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 7.29 (d, J = 6.8 Hz, 3H), 4.89 (d, J = 8.1 Hz, 1H), 3.99 (d, J = 8.1 Hz, 1H), 3.10 (br, 1H), 2.99–2.90 (m, 2H), 2.78–2.66 (m, 2H), 2.09–1.99 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 142.1, 134.0, 129.3, 128.3, 126.8, 125.0, 73.9, 52.4, 28.0, 27.4, 25.2 ppm; HRMS (EI+): m/z calcd for $C_{11}H_{13}OClS_2$: 260.0096 $[M]^+$; found 260.0108.

3d: 1,3-Dithian-2-yl-4-chlorophenylmethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3417, 2899, 2361, 1490, 1419, 1013, 824 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.33 (s, 4H), 4.87 (d, J = 7.6 Hz, 1H), 3.99 (d, J = 7.6 Hz, 1H), 3.25 (br, 1H), 2.96–2.87 (m, 2H), 2.76–2.67 (m, 2H), 2.04–1.98 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.5, 133.9, 128.2, 128.1, 73.9, 52.6, 28.1, 27.5, 25.3 ppm; HRMS (EI+): m/z calcd for $C_{11}H_{13}OClS_2$: 260.0096 $[M]^+$; found: 260.0097.

3e: 1,3-Dithian-2-yl-4-methylphenylmethanol: White crystals; m.p. 77–80 °C; IR (ATR): $\tilde{\nu}$ = 3407, 2893, 1511, 1417, 1015, 810, 731 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.23 (dd, J = 34.3, 7.8 Hz, 4H), 4.87 (d, J = 7.6 Hz, 1H), 4.08 (d, J = 7.6 Hz, 1H), 2.96–2.86 (m, 3H), 2.77–2.66 (m, 2H), 2.34 (s, 3H), 2.06–2.01 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.0, 137.0, 128.9, 126.5, 74.6, 53.0, 28.4, 27.8, 25.5, 21.3 ppm; elemental analysis: calcd (%) for $C_{12}H_{16}OS_2$: C 59.96, H 6.71; found: C 59.90, H 6.89.

3f:[18] 1,3-Dithian-2-yl-4-methoxyphenylmethanol: White crystals; m.p. 84–87 °C; IR (ATR): $\tilde{\nu}$ = 3425, 2889, 1608, 1512, 1246, 1029, 1012, 819, 796 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.83 (d, J = 7.7 Hz, 1H), 4.06 (d, J = 7.7 Hz, 1H), 3.79 (s, 3H), 3.01 (br, 1H), 2.98–2.85 (m, 2H), 2.76–2.66 (m, 2H), 2.12–1.91 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 159.3, 132.1, 127.8, 113.5, 74.3, 55.2, 53.0, 28.3, 27.7, 25.4 ppm.

3g: 1,3-Dithian-2-yl-1-naphthylmethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3418, 2897, 1420, 1243, 1041, 792, 775 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 8.09–8.06 (m, 1H), 7.87–7.67 (m, 3H), 7.53–7.43 (m, 3H), 5.65 (d, J = 5.9 Hz, 1H), 4.50 (d, J = 5.9 Hz, 1H), 3.06 (br, 1H), 2.91–2.73 (m, 2H), 2.70–2.59 (m, 2H), 2.06–1.82 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 135.4, 133.6, 130.4, 128.9, 128.6, 126.0, 125.4, 124.9, 124.6, 122.8, 72.7, 52.9, 29.4, 28.5, 25.5 ppm; HRMS (EI+): m/z calcd for $C_{15}H_{16}OS_2$: 276.0643 $[M]^+$; found: 276.0640.

3h: 1,3-Dithian-2-yl-2-furylmethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3415, 2900, 2362, 1421, 1276, 1146, 1008, 921, 738 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.41–7.40 (m, 1H), 6.42–6.35 (m, 2H), 4.95 (dd, J = 7.9, 4.0 Hz, 1H), 4.25 (d, J = 7.9 Hz, 1H), 3.23 (d, J = 4.0 Hz, 1H), 2.97–2.85 (m, 2H), 2.76–2.65 (m, 2H), 2.12–1.90 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.1, 142.0, 110.1, 108.4, 68.5, 49.4, 27.7, 27.1, 25.2 ppm; HRMS (EI+): m/z calcd for $C_9H_{12}O_2S_2$: 216.0279 $[M]^+$; found: 216.0287.

3i:[19] 1,3-Dithian-2-yl-3-pyridylmethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 2939, 2362, 1422, 1054, 1032, 1020, 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 8.55 (d, J = 2.1 Hz, 1H), 8.45 (dd, J = 4.8, 1.6 Hz, 1H), 7.82–7.78 (m, 1H), 7.30–7.26 (m, 1H), 4.95 (d, J = 7.2 Hz, 1H), 4.67 (br, 1H), 4.06 (d, J = 7.2 Hz, 1H), 2.99–2.68 (m, 4H), 2.12–1.90 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 148.8, 148.2, 136.4, 134.5, 123.1, 72.5, 52.7, 28.3, 27.8, 25.3 ppm.

3j:[17] 1,3-Dithian-2-yl-*tert*-butylmethanol: White crystals; m.p. 47–50 °C; IR (ATR): $\tilde{\nu}$ = 3397, 2953, 2898, 2349, 1364, 1080, 1014, 894, 789 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 4.31 (d, J = 3.0 Hz, 1H), 3.49 (br, 1H), 3.02–2.77 (m, 4H), 2.43 (br, 1H), 2.12–1.82 (m, 2H), 1.02 ppm (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 81.6, 50.1, 36.2, 30.2, 29.2, 26.6, 25.5 ppm.

3k: 1,3-Dithian-2-yl-cyclohexylmethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3449, 2920, 2850, 2361, 1448, 1421, 1085, 1067 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 4.10 (d, J = 6.1 Hz, 1H), 3.60 (br, 1H), 2.98–2.72 (m, 4H), 2.38 (br, 1H), 2.14–1.65 (m, 8H), 1.37–1.03 ppm (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 76.3, 50.3, 39.7, 30.0, 28.9, 28.2, 26.7, 26.3, 26.2, 25.8, 25.7 ppm; HRMS (EI+): m/z calcd for $C_{11}H_{20}OS_2$: 232.0956 $[M]^+$; found: 232.0963.

3l:[18] (2*E*)-1-(1,3-Dithian-2-yl)-3-phenylprop-2-en-1-ol: White crystals; m.p. 67–70 °C; IR (ATR): $\tilde{\nu}$ = 3441, 2881, 2362, 1419, 1006, 966, 753, 693 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.41–7.20 (m, 5H), 6.75–6.29 (m, 2H), 4.60–4.42 (m, 1H), 4.02 (d, J = 6.8 Hz, 1H), 2.98–2.70 (m, 5H), 2.13–1.96 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 136.1, 132.5, 128.3, 127.8, 127.7, 126.5, 73.3, 52.0, 28.3, 28.0, 25.5 ppm.

5a: 1-(1,3-Dithian-2-yl)-1-[4-(trifluoromethyl)phenyl]ethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3467, 2898, 1346, 1157, 1149, 1052, 1028, 693, 671 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.68–7.65 (m, 2H), 7.43–7.36 (m, 3H), 4.85 (s, 1H), 3.63 (s, 1H), 2.99–2.69 (m, 4H), 2.05–1.92 (m, 1H), 1.89–1.73 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 135.1, 128.9, 128.0, 126.0 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1 Hz), 124.4 (q, $J_{C\text{-}F}$ = 288 Hz), 79.1 (q, $J_{C\text{-}C\text{-}F}$ = 29 Hz), 53.3, 30.2, 29.6, 24.6 ppm; elemental analysis: calcd (%) for $C_{12}H_{13}OF_3S_2$: C 48.96, H 4.45; found: C 49.24, H 4.41.

5b: Methyl 1,3-dithian-2-yl(hydroxy)phenylacetate: White crystals; m.p. 113–115 °C; IR (ATR): $\tilde{\nu}$ = 3650, 2968, 2357, 1721, 1237, 1105, 1055, 1033, 1014, 692 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.67–7.64 (m, 2H), 7.40–7.30 (m, 3H), 4.57 (s, 1H), 4.13 (s, 1H), 3.83 (s, 3H), 3.32–3.11 (m, 2H), 2.79–2.53 (m, 2H), 2.04–1.93 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 173.5, 138.9, 128.2, 128.1, 125.8, 85.0, 53.9, 50.4, 28.4, 28.1, 25.1 ppm; elemental analysis: calcd (%) for $C_{13}H_{16}O_3S_2$: C 54.90, H 5.67; found: C 54.52, H 5.63.

5c: (2*E*)-1-(1,3-dithian-2-yl)-1,3-diphenylprop-2-en-1-ol: White crystals; m.p. 138–141 °C; IR (ATR): $\tilde{\nu}$ = 3514, 2931, 2898, 2362, 1491, 1445, 1068, 967, 743, 692, 671 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.59–7.55 (m, 2H), 7.44–7.22 (m, 8H), 6.81 (d, J = 32.5 Hz, 1H), 6.75 (d, J = 32.5 Hz, 1H), 4.65 (s, 1H), 3.10 (s, 1H), 2.88–2.73 (m, 4H), 2.09–1.99 (m, 1H), 1.91–1.75 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 142.6, 136.2, 131.9, 130.1, 128.4, 128.1, 127.6, 126.7, 125.9, 78.6, 59.2, 30.4, 30.1, 25.4 ppm; elemental analysis: calcd (%) for $C_{19}H_{20}OS_2$: C 69.47, H 6.14; found: C 69.58, H 6.23.

5d: (3*E*)-2-(1,3-dithian-2-yl)-4-phenylbut-3-en-2-ol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3680, 2971, 2362, 1055, 1033, 1013, 968, 748, 693 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.43–7.19 (m, 5H), 6.77 (d, J = 16.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.22 (s, 1H), 2.97–2.72 (m, 5H), 2.12–2.01 (m, 1H), 1.96–1.73 (m, 1H), 1.55 ppm (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 136.4, 132.9, 128.8, 128.4, 127.5, 126.5, 75.3, 59.2, 30.4, 30.0, 26.3, 25.5 ppm; HRMS (EI+): m/z calcd for $C_{14}H_{18}OS_2$: 266.0799 $[M]^+$; found: 266.0800.

5e:[18] 1-(1,3-Dithian-2-yl)-1-phenylethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3449, 2898, 2361, 1716, 1058, 909, 790, 766, 699 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 2H), 7.38–7.30 (m, 3H), 4.43 (s, 1H), 3.06–2.71 (m, 5H), 2.07–1.94 (m, 1H), 1.92–1.70 ppm (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 144.3, 127.9, 127.3, 125.2, 76.4, 60.0, 30.4, 30.2, 27.3, 25.4 ppm.

5f: 1-(1,3-Dithian-2-yl)-1-(4-methoxyphenyl)ethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3466, 2936, 2833, 2362, 1610, 1510, 1245, 1176, 1032, 832 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.7 Hz, 2H), 6.88 (d, J =

8.7 Hz, 2H), 4.41 (s, 1H), 3.80 (s, 3H), 2.85–2.78 (m, 5H), 2.07–1.99 (m, 1H), 1.85–1.73 ppm (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 158.6, 136.4, 126.5, 113.2, 76.1, 60.3, 55.1, 30.5, 30.3, 27.2, 25.4 ppm; HRMS (EI+): *m/z* calcd for $C_{13}H_{18}O_2S_2$: 270.0748 $[M]^+$; found: 270.0749.

5g: 1-(1,3-Dithian-2-yl)-1-pyridin-4-ylethanol: White crystals; m.p. 135–137 °C; IR (ATR): $\tilde{\nu}$ = 3680, 2971, 2362, 1412, 1055, 1033, 1009 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 5.8 Hz, 2H), 7.45 (d, *J* = 5.8 Hz, 2H), 4.40 (s, 1H), 2.88–2.79 (m, 4H), 2.08–2.01 (m, 1H), 1.90–1.72 ppm (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 153.9, 149.2, 120.7, 75.9, 59.1, 30.4, 30.2, 27.2 ppm, 25.6; HRMS (EI+): *m/z* calcd for $C_{11}H_{15}ONS_2$: 241.0595 $[M]^+$; found: 241.0587.

5h: 1-(1,3-Dithian-2-yl)-3-methyl-1-phenylbutan-1-ol: White crystals; m.p. 66–68 °C; IR (ATR): $\tilde{\nu}$ = 2968, 2362, 1274, 1055, 1032, 1005, 909, 766, 701 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.51–7.25 (m, 5H), 4.66 (s, 1H), 3.07–2.64 (m, 5H), 2.63–2.34 (m, 1H), 2.05–1.99 (m, 1H), 1.88–1.68 (m, 1H), 0.97 (d, *J* = 8.1 Hz, 3H), 0.80 ppm (d, *J* = 8.1 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 141.1, 127.3, 127.1, 126.2, 80.3, 58.6, 34.4, 31.0, 30.3, 29.9, 25.6, 17.4, 16.5 ppm; HRMS (EI+): *m/z* calcd for $C_{14}H_{20}OS_2$: 268.0956 $[M]^+$; found: 268.0955.

5i: 1-Cyclohexyl-1-(1,3-dithian-2-yl)ethanol: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 2924, 2849, 2362, 1453, 1421, 1375, 1339, 1056, 1033, 1013 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.31 (s, 1H), 3.00–2.81 (m, 4H), 2.15–2.03 (m, 1H), 2.00 (s, 1H), 1.92–1.65 (m, 7H), 1.30–1.02 ppm (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 76.4, 59.2, 44.6, 31.0, 30.9, 27.4, 26.6, 26.5, 26.4, 26.1, 21.6 ppm; HRMS (EI+): *m/z* calcd for $C_{12}H_{22}OS_2$: 246.1112 $[M]^+$; found: 246.1111.

*Typical Experimental Procedure for 1,3-Dithiane Addition of N-*PMP Aldimines.

To a stirred solution of PhON*n*Bu$_4$ (30.2 mg, 0.09 mmol) in DMF (1.5 mL), a combined solution of 2-trimethylsilyl-1,3-dithiane (170 μL, 0.9 mmol) and *N-p*-methoxyphenyl benzaldimine (63.4 mg, 0.3 mmol) in DMF (1.5 mL) was added slowly at room temperature. The reaction mixture was stirred for 1 h and quenched with 1 N HCl (1.0 mL, 1.0 mmol). The mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The crude product was purified by preparative TLC (hexane/EtOAc = 4:1, hexane/CH_2Cl_2 = 1:1) to give the desired product (84.1 mg, 85 %) as white crystals.

7a: *N*-[1,3-Dithian-2-yl(phenyl)methyl]-4-methylbenzenesulfonamide: White crystals; m.p. 145–147 °C; IR (ATR): $\tilde{\nu}$ = 3327, 2899, 2361, 1326, 1158, 704, 664 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.2 Hz, 2H), 7.26–7.11 (m, 7H), 5.57 (d, *J* = 5.4 Hz, 1H), 4.61 (t, *J* = 5.9 Hz, 1H), 4.12 (d, *J* = 6.5 Hz, 1H), 2.85–2.60 (m, 4H), 2.36 (s, 3H), 2.07–1.95 (m, 1H), 1.89–1.74 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 143.1, 137.1, 136.7, 129.2, 128.1, 128.0, 127.4, 127.2, 60.4, 51.9, 29.2, 28.9, 25.2, 21.6 ppm; elemental analysis: calcd (%) for $C_{18}H_{21}NO_2S_3$: C 56.96, H 5.58, N 3.69; found: C 56.79, H 5.37, N 3.56.

7c: *t*-Butyl [1,3-dithian-2-yl(phenyl)methyl]carbamate: White crystals; m.p. 185–188 °C; IR (ATR): $\tilde{\nu}$ = 3383, 2361, 1678, 1501, 1166, 704 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.33 (s, 5H), 5.42 (br, 1H), 5.05 (br, 1H), 4.37 (d, *J* = 5.6 Hz, 1H), 2.86–2.76 (m, 4H), 2.09–2.04 (m, 1H), 1.89–1.81 (m, 1H), 1.43 ppm (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 154.8, 138.4, 128.1, 127.7, 126.5, 79.8, 57.8, 52.7, 29.9, 29.8, 28.3, 25.4 ppm; HRMS (EI+): *m/z* calcd for $C_{16}H_{23}O_2NS_2$: 325.1170 $[M]^+$; found: 325.1161.

7d: *N*-[1,3-Dithian-2-yl(phenyl)methyl]-4-methoxyaniline: White crystals; m.p. 88–90 °C; IR (ATR): $\tilde{\nu}$ = 3352, 2892, 2830, 2361, 1512, 1232, 1041, 811, 701 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 5H), 6.70–6.64 (m, 2H), 6.49–6.43 (m, 2H), 4.58 (d, *J* = 4.8 Hz, 1H), 4.50 (br, 1H), 4.44 (d, *J* = 4.8 Hz, 1H), 3.66 (s, 3H), 2.93–2.68 (m, 4H), 2.10–2.01 (m, 1H), 1.92–1.80 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.0, 140.9, 139.8, 128.2, 127.7, 127.1, 114.6, 114.5, 62.5, 55.6, 54.5, 30.6, 30.3, 25.7 ppm; elemental analysis: calcd (%) for $C_{18}H_{21}NOS_2$: C 65.22, H 6.39, N 4.23; found: C 64.99, H 6.45, N 4.42.

7f: *N*-[1,3-Dithian-2-yl(naphthalen-1-yl)methyl]-4-methoxyaniline: White crystals; m.p. 149–152 °C; IR (ATR): $\tilde{\nu}$ = 2970, 2867, 2360, 1513, 1251, 1054, 1033, 1014, 796 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.80–7.70 (m, 2H), 7.62–7.49 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 8.9 Hz, 2H), 5.39 (d, *J* = 2.8 Hz, 1H), 4.74 (d, *J* = 4.6 Hz, 1H), 4.65 (br, 1H), 3.63 (s, 3H), 2.99–2.56 (m, 4H), 2.08–2.03 (m, 1H), 1.92–1.77 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 151.9, 140.9, 134.1, 134.0, 130.6, 129.3, 128.2, 126.3, 125.3, 125.2, 125.0, 121.9, 114.5, 114.4, 58.9, 55.6, 53.2, 31.1, 30.6, 25.7 ppm; HRMS (EI+): *m/z* calcd for $C_{22}H_{23}ONS_2$: 381.1121 $[M]^+$; found: 381.1233.

7g: *N*-[(2-Chlorophenyl)(1,3-dithian-2-yl)methyl]-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3385, 2900, 2360, 1510, 1236, 1177, 1033, 908, 817, 752, 728 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 1H), 7.41–7.36 (m, 1H), 7.25–7.16 (m, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 4.1 Hz, 2H), 5.03 (d, *J* = 4.1 Hz, 1H), 4.63 (d, *J* = 8.9 Hz, 1H) , 4.55 (br, 1H), 3.67 (s, 3H), 3.02–2.69 (m, 4H), 2.12–2.04 (m, 1H), 1.95–1.80 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.1, 140.5, 136.7, 132.9, 129.6, 129.1, 128.9, 126.6, 114.6, 114.3, 59.1, 55.6, 51.9, 30.8, 30.3, 25.7 ppm; HRMS (EI+): *m/z* calcd for $C_{18}H_{20}ONClS_2$: 365.0675 $[M]^+$; found: 365.0668.

7h: *N*-[(3-Chlorophenyl)(1,3-dithian-2-yl)methyl]-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3379, 2900, 2360, 1510, 1236, 1179, 1034, 908, 817, 728, 693 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 7.33–7.22 (m, 3H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 8.7 Hz, 2H), 4.53 (d, *J* = 4.9 Hz, 1H), 4.49 (br, 1H), 4.39 (d, *J* = 4.9 Hz, 1H), 3.67 (s, 3H), 2.93–2.67 (m, 4H), 2.10–2.04 (m, 1H), 1.92–1.77 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.2, 142.2, 140.5, 134.2, 129.4, 127.9, 127.1, 125.4, 114.6, 114.5, 62.1, 55.6, 54.1, 30.5, 30.2, 25.6 ppm; HRMS (EI+): *m/z* calcd for $C_{18}H_{20}ONClS_2$: 365.0675 $[M]^+$; found: 365.0674.

7i: *N*-[(4-Chlorophenyl)(1,3-dithian-2-yl)methyl]-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 2939, 2360, 1511, 1483, 1236, 1033, 1013, 817 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 4H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 8.9 Hz, 2H), 4.55 (d, *J* = 4.6 Hz, 1H), 4.53 (br, 1H), 4.40 (d, *J* = 4.6 Hz, 1H), 3.68 (s, 3H), 2.95–2.71 (m, 4H), 2.17–2.04 (m, 1H), 1.93–1.79 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.2, 140.5, 138.4, 133.4, 128.5, 114.7, 114.6, 62.0, 55.7, 54.3, 30.6, 30.3, 25.7 ppm; HRMS (EI+): *m/z* calcd for $C_{18}H_{20}ONClS_2$: 365.0675 $[M]^+$; found: 365.0674.

7j: *N*-[(4-Fluorophenyl)(1,3-dithian-2-yl)methyl]-4-methoxyaniline: White crystals; m.p. 102–104 °C; IR (ATR): $\tilde{\nu}$ = 3382, 2938, 2900, 2360, 1510, 1236, 1178, 1033, 909, 817, 729 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.41–7.36 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.44 (d, *J* = 8.9 Hz, 2H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.49 (br, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 3.68 (s, 3H), 2.94–2.70 (m, 4H), 2.13–2.05 (m, 1H), 1.93–1.79 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 162.0 (d, $J_{C\text{-}F}$ = 246 Hz), 152.2, 140.6, 135.5 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3 Hz), 128.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6 Hz), 115.4, 115.1, 114.6 (d, $J_{C\text{-}C\text{-}F}$ = 9 Hz), 61.9, 55.6, 54.4 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1 Hz), 30.6, 30.3, 25.7 ppm; elemental analysis: calcd (%) for $C_{18}H_{20}ONFS_2$: C 61.86, H 5.77 N 4.01; found: C 61.69, H 5.88, N 4.20.

7k: *N*-[(4-Bromophenyl)(1,3-dithian-2-yl)methyl]-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3381, 2900, 2360, 1510, 1236, 1178, 1034, 908, 817, 727 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 6.43 (d, *J* = 8.1 Hz, 2H), 4.53 (d, *J* = 4.8 Hz, 1H), 4.49 (br, 1H), 4.39 (d, *J* = 4.8 Hz, 1H), 3.67 (s, 3H), 2.90–2.69 (m, 4H), 2.12–2.04 (m, 1H), 1.90–1.82 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.2, 140.5, 138.9, 131.4, 128.8, 121.6, 114.6, 114.5, 62.0, 55.6, 54.1, 30.6, 30.3, 25.6 ppm; HRMS (EI+): *m/z* calcd for $C_{18}H_{20}ONBrS_2$: 409.0170 $[M]^+$; found: 409.0160.

7l: *N*-{1,3-Dithian-2-yl[4-(trifluoromethyl)phenyl]methyl}-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 2940, 2360, 1511, 1322, 1237, 1112, 1064, 1034, 1016, 818, 730 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.61–7.53 (m, 4H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 8.9 Hz, 2H), 4.63 (d, *J* = 4.4 Hz, 1H), 4.53 (br, 1H), 4.43 (d, *J* = 4.4 Hz, 1H), 3.68 (s, 3H), 2.97–2.76 (m, 4H), 2.14–2.04 (m, 1H), 1.95–1.80 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.3, 144.1, 140.4, 129.9 (q, $J_{C\text{-}C\text{-}F}$ = 32 Hz), 127.5, 125.3 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272 Hz), 114.7, 114.6, 62.2, 55.6, 54.0, 30.6, 30.3, 25.6 ppm; HRMS (EI+): *m/z* calcd for $C_{19}H_{20}ONF_3S_2$: 399.0938 $[M]^+$; found: 399.0925.

7m: *N*-[1,3-Dithian-2-yl(4-methoxyphenyl)methyl]-4-methoxyaniline: White crystals; m.p. 93–95 °C; IR (ATR): $\tilde{\nu}$ = 3370, 2965, 2360, 1610, 1511, 1237, 1172, 1053, 1033, 819 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 6.48 (d, J = 8.9 Hz, 2H), 4.56 (d, J = 4.9 Hz, 1H), 4.50 (br, 1H), 4.44 (d, J = 4.6 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 2.95–2.72 (m, 4H), 2.14–2.06 (m, 1H), 1.95–1.80 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 158.9, 152.0, 140.9, 131.6, 128.1, 114.7, 114.5, 113.6, 61.9, 55.6, 55.1, 54.7, 30.6, 30.4, 25.8 ppm; HRMS (EI+): m/z calcd for $C_{19}H_{23}O_2NS_2$: 361.1170 $[M]^+$; found: 361.1183.

7n: *N*-[1,3-Dithian-2-yl(furan-2-yl)methyl]-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3372, 2939, 2360, 1509, 1234, 1033, 1009, 817, 734 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 6.73 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 8.7 Hz, 2H), 6.32–6.30 (m, 2H), 4.71 (d, J = 5.3 Hz, 1H), 4.58 (d, J = 5.3 Hz, 1H), 4.25 (br, 1H), 3.71 (s, 3H), 2.85–2.81 (m, 4H), 2.12–2.04 (m, 1H), 1.94–1.78 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.5, 152.2, 141.9, 140.4, 115.3, 114.5, 110.2, 108.3, 57.3, 55.6, 51.4, 30.1, 30.0, 25.7 ppm; HRMS (EI+): m/z calcd for $C_{16}H_{19}O_2S_2$: 321.0857 $[M]^+$; found: 321.0854.

7o: *N*-[1,3-Dithian-2-yl(pyridin-3-yl)methyl]-4-methoxyaniline: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3373, 2939, 2830, 2361, 1510, 1423, 1235, 1033, 909, 817, 715 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 8.69–8.68 (m, 1H), 8.54–8.52 (m, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.28–7.23 (m, 1H), 6.68 (d, J = 8.9 Hz, 2H), 6.45 (d, J = 8.9 Hz, 2H), 4.64 (d, J = 4.8 Hz, 1H), 4.51 (br, 1H), 4.40 (d, J = 4.8 Hz, 1H), 3.68 (s, 3H), 2.94–2.70 (m, 4H), 2.12–2.04 (m, 1H), 1.94–1.79 ppm (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.4, 149.1, 149.0, 140.2, 135.5, 134.8, 123.1, 114.8, 114.6, 60.3, 55.6, 53.9, 30.4, 30.1, 25.5 ppm; HRMS (EI+): m/z calcd for $C_{17}H_{20}ON_2S_2$: 332.1017 $[M]^+$; found: 332.1003.

8:[20] 2-(Phenylmethylidene)-1,3-dithiane: Pale yellow oil; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.48–7.15 (m, 5H), 6.86 (s, 1H), 3.03–2.87 (m, 4H), 2.25–2.16 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 135.9, 130.4, 128.9, 128.8, 128.0, 126.7, 29.8, 29.2, 24.4 ppm.

Typical Experimental Procedure for Substituted Dithiane Addition Reaction.

To a stirred solution of benzaldehyde (53.1 mg, 0.50 mmol) and 2-phenyl-2-trimethylsilyl-1,3-dithiane (148 mg, 0.60 mmol) in DMF (1.4 mL), a 0.1 M solution of PhONnBu$_4$ (0.01 mmol) in DMF was added at room temperature. Then the reaction mixture was stirred for 1 h and quenched with 1 N HCl (1.0 mL, 1.0 mmol). The mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The crude product was purified by preparative TLC (hexane/EtOAc = 3:1) to give the desired product **10a** (149.3 mg, 99%) as white crystals.

10a: Phenyl-(2-phenyl-1,3-dithian-2-yl)methanol: White crystals; m.p. 127–129 °C; IR (ATR): $\tilde{\nu}$ = 3674, 3650, 2972, 2866, 2357, 1054, 1033, 1016, 704 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.75–7.53 (m, 2H), 7.40–6.96 (m, 6H), 6.90–6.73 (m, 2H), 4.94 (s, 1H) 3.05 (s, 1H), 2.80–2.39 (m, 4H), 1.99–1.72 ppm (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 137.0, 136.9, 130.2, 127.9, 127.8, 127.7, 127.2, 126.7, 80.7, 66.2, 27.1, 26.8, 24.6 ppm; elemental analysis: calcd (%) for $C_{17}H_{18}OS_2$: C 67.51, H 6.00; found: C 67.33, H 6.13.

10b: Phenyl-(2-methyl-1,3-dithian-2-yl)methanol: White crystals; m.p. 86–88 °C; IR (ATR): $\tilde{\nu}$ = 3737, 3451, 2970, 2360, 1055, 1033, 1019, 755, 704 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.48–7.45 (m, 2H), 7.32–7.25 (m, 3H), 5.09 (s, 1H), 3.37–3.01 (m, 3H), 2.73–2.63 (m, 2H), 2.17–2.11 (m, 1H), 1.96–1.82 (m, 1H), 1.30 ppm (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 137.3, 128.3, 127.7, 127.1, 73.6, 53.8, 26.6, 25.9, 24.2, 22.3 ppm; elemental analysis: calcd (%) for $C_{12}H_{16}OS_2$: C 59.96, H 6.21; found: C 59.70, H 6.66.

11a: *tert*-Butyl [(2-phenyl-1,3-dithian-2-yl)(phenyl)methyl]carbamate: White crystals; m.p. 150–152 °C; IR (ATR): $\tilde{\nu}$ = 3651, 3251, 2970, 2350, 1698, 1378, 1363, 1164, 1052, 1033, 1014, 697 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 2H), 7.33–7.25 (m, 3H), 7.16–7.05 (m, 3H), 6.73 (d, J = 7.1 Hz, 2H), 5.75 (d, J = 8.2 Hz, 1H), 5.07 (d, J = 8.2 Hz, 1H), 2.68–2.55 (m, 4H), 1.90–1.86 (m, 2H), 1.42 ppm (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 154.7, 137.9, 136.4, 130.2, 128.3, 128.1, 127.3, 126.8, 79.6, 65.0, 63.9, 28.3, 27.3, 27.1, 24.5 ppm; elemental analysis: calcd (%) for $C_{22}H_{27}O_2NS_2$: C 65.80, H 6.78, N 3.49; found: C 65.75, H 6.78, N 3.51.

11b: *tert*-Butyl [(2-methyl-1,3-dithian-2-yl)(phenyl)methyl]carbamate: White crystals; m.p. 145–147 °C; IR (ATR): $\tilde{\nu}$ = 3739, 2970, 2350, 1687, 1396, 1056, 1033, 1008, 761, 703 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 5H), 5.67 (d, J = 8.1 Hz, 1H), 4.98 (br, 1H), 2.97–2.70 (m, 4H), 1.97–1.88 (m, 2H), 1.56 (s, 3H), 1.40 ppm (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 155.0, 128.5, 127.5, 127.4, 79.6, 61.4, 52.7, 28.3, 26.9, 26.3, 26.1, 24.5 ppm; elemental analysis: calcd (%) for $C_{17}H_{25}O_2NS_2$: C 60.14, H 7.42, N 4.13; found: C 59.72, H 7.15, N 4.20.

14: 2-[Trimethylsiloxy(phenyl)methyl]-2-phenyl-1,3-dithiane: Pale yellow oil; IR (ATR): $\tilde{\nu}$ = 3058, 3028, 2952, 2901, 1249, 1095, 1069, 899, 838, 750, 699 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ = 8.03–8.00 (m, 2H), 7.58–7.36 (m, 6H), 7.15–7.12 (m, 2H), 5.28 (s, 1H), 3.05–2.80 (m, 4H), 2.25–2.09 (m, 2H), 0.28 ppm (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.8, 137.0, 131.5, 128.4, 127.8, 127.3, 126.9, 126.6, 81.8, 65.7, 27.4, 27.0, 25.1, 0.00 ppm; HRMS (EI+): m/z calcd for $C_{20}H_{26}OSiS_2$: 374.1194 $[M]^+$; found: 374.1207.

[1] a) E. J. Corey, D. Seebach, *Angew. Chem.* **1965**, *77*, 1136–1137; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1075–1077; b) E. J. Corey, D. Seebach, *Angew. Chem.* **1965**, *77*, 1136–1137; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1077–1078; c) D. Seebach, R. Freedman, *J. Am. Chem. Soc.* **1967**, *89*, 434–436; d) D. Seebach, E. J. Corey, *J. Org. Chem.* **1975**, *40*, 231–237; e) B. T. Gloebel, D. Seebach, *Synthesis* **1977**, 357–402; f) P. C. B. Page, M. B. Niel, J. C. Prodger, *Tetrahedron* **1989**, *45*, 7643–7677; g) A. B. Smith, C. M. Adams, *Acc. Chem. Res.* **2004**, *37*, 365–377; h) *Comprehensive Organic Functional Group Transformations II*, *Vol. 4* (Eds.: A. R. Katritzky, R. J. K. Taylor), Elsevier, Oxford, **2005**, pp. 271–322.

[2] M. Yus, C. Nájera, F. Foubelo, *Tetrahedron* **2003**, *59*, 6147–6212.

[3] a) Y. L. Chen, R. Leguijt, H. Redlich, *Synthesis* **2006**, *13*, 2242–2250; b) Y. L. Chen, R. Leguijt, H. Redlich, R. Fröhlich, *Synthesis* **2006**, *24*, 4212–4218.

[4] a) *Protective Groups in Organic Synthesis*, 3rd ed. (Eds.: W. Theodora, P. Greene, G. M. Wuts), Wiley-Interscience, Canada, **1991**, p. 336; b) H. Firouzabadi, N. Iranpoor, H. Hazarkhani, B. Karimi, *J. Org. Chem.* **2002**, *67*, 2572–2576; c) N. Iranpoor, H. Firouzabadi, H. R. Shaterian, *Tetrahedron Lett.* **2003**, *44*, 4769–4773; d) K. C. Nicolaou, C. J. N. Mathison, T. Montagnon, *J. Am. Chem. Soc.* **2004**, *126*, 5192–5201; e) B. Karimi, H. Hazarkhani, *Synthesis* **2003**, *16*, 2547–2551.

[5] N. H. Andersen, D. A. Mccrae, D. B. Grotjahn, S. Y. Gabhe, L. J. Theodore, R. M. Ippolito, T. K. Sarkar, *Tetrahedron* **1981**, *37*, 4069–4079.

[6] a) A. S. Pilcher, P. DeShong, *J. Org. Chem.* **1996**, *61*, 6901–6905; b) A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am. Chem. Soc.* **1995**, *126*, 5192–5201.

[7] J. Busch-Petersen, Y. Bo, E. J. Corey, *Tetrahedron Lett.* **1999**, *40*, 5166–5167.

[8] a) H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2002**, 182–183; b) T. Nakagawa, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2003**, *32*, 462–463.

[9] a) H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2002**, 858–859; b) H. Fujisawa, T. Nakagawa, T. Mukaiyama, *Adv. Synth. Catal.* **2004**, *346*, 1241–1246; c) Y. Kawano, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2005**, *34*, 614–615.

[10] a) T. Mukaiyama, T. Nakagawa, H. Fujisawa, *Chem. Lett.* **2003**, *32*, 56–57; b) T. Mukaiyama, T. Tozawa, H. Fujisawa, *Chem. Lett.* **2004**, *33*, 1410–1411.

[11] a) H. Fujisawa, E. Takahashi, T. Nakagawa, T. Mukaiyama, *Chem. Lett.* **2003**, *32*, 1036–1037; b) E. Takahashi, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2004**, *33*, 1426–1427; c) E. Takahashi, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2005**, *34*, 84–85.

[12] a) T. Mukaiyama, Y. Kawano, H. Fujisawa, *Chem. Lett.* **2005**, *34*, 88–89; b) Y. Kawano, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2005**, *34*, 422–423.

[13] Y. Kawano, N. Kaneko, T. Mukaiyama, *Chem. Lett.* **2005**, *34*, 1508–1509.
[14] T. Kitazawa, T. Minowa, T. Mukaiyama, *Chem. Lett.* **2006**, *35*, 1002–1003.
[15] For recent reports relevant to 1,3-dithiane addition reaction, see: M. Michida, T. Mukaiyama, *Chem. Lett.* **2008**, *37*, 26–27.
[16] Preparation of catalyst; M. A. Rahim, Y. Matsui, T. Matsuyama, Y. Kosugi, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2191–2195.
[17] Z. Li, A. G. Kutateladze, *J. Org. Chem.* **2003**, *68*, 8236–8239.
[18] W. A. McHale, A. G. Kutateladze, *J. Org. Chem.* **1998**, *63*, 9924–9931.
[19] C. W. Ong, C. Y. Yu, *Tetrahedron* **2003**, *59*, 9677–9682.
[20] V. K. Aggarwal, R. M. Steele, Ritmaleni, J. K. Barrell, I. Grayson, *J. Org. Chem.* **2003**, *68*, 4087–4090.

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