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Monothioacetalization of Acetals Catalyzed by Dicyanoketene Acetals

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Abstract: A type of capto-dative olefin, dicyanoketene acetal such as dicyanoketene dimethyl acetal and ethylene acetal is introduced to be a novel type of π-acid catalyst for the monothioacetalization of acetals as well as the corresponding α,β-unsaturated systems. Particularly, the catalytic activity of dicyanoketene ethylene acetal was found to be superior to that of tetracyanoethylene and highly chemoselective in the crossover reaction of a ketone-, aldehyde-acetal, an alcohol THP-, and MOM-ether providing a ketone monothioacetal favorably.

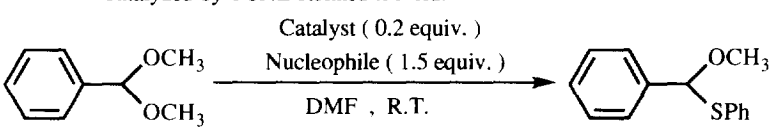
Monothioacetals are useful protected carbonyl compounds[1] and sometimes reactive intermediates[2] in organic synthesis. Especially, α,β-unsaturated monothioacetals are useful intermediates in organic synthesis.[2a] Otera and coworkers showed that α,β-unsaturated monothioacetals serve as a β-vinyl anion and an acyl carbanion equivalent of the corresponding α,β-unsaturated aldehydes.[3] A great deal of activities have been devoted to search for efficient catalysts which are easy to handle, in order to avoid overreaction leading to dithioacetals and to achieve chemoselective monothioacetalization. The most convenient method for preparation of saturated monothioacetals is the transacetalization of acetals using such combination of reagents as RSH/BF_3-Et_2O,[4a] RSH/$MgBr_2$,[4b] Me_2BBr/RSH/*i*-Pr_2NEt,[4c] $Bu_{4-n}Sn(SPh)_n$/BF_3-Et_2O,[4d] or PhSH/Et_3Al.[4e]

As for α,β-unsaturated acetals, the transacetalization with sulfur nucleophiles in the presence of Lewis acids usually affords γ-alkoxyallyl sulfides and gives no α,β-unsaturated monothioacetals.[5, 6] For the synthetic methods of α,β-unsaturated monothioacetals, there are Wittig type olefination of 1-methoxy-2-oxoalkyl phenyl sulfides[3] and S_N2' type substitution reactions of 3-chloro-1-methoxypropene with thiols in the presenece of Hunig's base.[7] In addition, S. Kim and coworkers have recently reported that 3-alkoxy-2-alkenylenesulfonium salts, which are given by the reaction of α,β-unsaturated acetals with dimethyl sulfide in the presence of a stoichiometric amount of trimethylsilyl triflate (TMS-OTf) at -78 °C, undergo nucleophilic substitution reactions with lithium thioalkoxides to yield α,β-unsaturated monothioacetals.[6] However, this method must be carried out at very low temperature (-78 °C), and highly reactive TMS-OTf used as a promoter is cumbersome to use because of moisture sensitivity. Therefore, new efficient catalysts, which can be easily prepared, handled, and used under mild conditions, are expected for the direct transformation of α,β-unsaturated acetals to the corresponding monothioacetals.

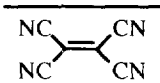
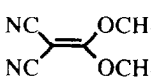
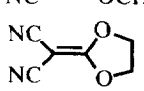
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) which is one of the representative one electron oxidants was reported to catalyze alcoholysis of epoxides,[8a] tetrahydropyranylation of alcohols,[8b] glycosidation of glycals,[8c] and deprotection of acetals,[8d] silyl ethers,[8e] and orthoesters.[8f] In this context, we have recently reported that a catalytic amount of tetracyanoethylene (TCNE), a representative π-acid and one-electron acceptor,[9] accelerates substrate-specific rearrangement,[10a] acetonidation,[10a] and alcoholysis of epoxides[10b] and Mukaiyama aldol reaction of acetals.[10c] During investigation of the reaction mechanism of TCNE-catalyzed alcoholysis of epoxides,[10b] we have envisaged catalytic ability of dicyanoketene dimethylacetal ($(CN)_2C=C(OMe)_2$), which can be formed in methanolysis of TCNE,[11] in the reactions of epoxides and acetals. Recently, we have reported that dicyanoketene acetals, a new type of π-acid which have a capto-dative olefin structure, catalyze monothioacetalization of saturated acetals,[12a] tetrahydropyranylation of alcohols,[12b] and alcoholysis of epoxides[12c] in preliminary communications. We disclose herein a full detail of monothioacetalization of acetals as well as the corresponding α,β-unsaturated systems under mild reaction conditions using a novel type of π-acid catalyst, dicyanoketene acetals such as dicyanoketene dimethyl acetal ($(CN)_2C=C(OMe)_2$) (DCKDMA) and dicyanoketene ethylene acetal ($(CN)_2C=C(OCH_2)_2$) (DCKEA) prepared easily from TCNE.[11]

Treatment of benzaldehyde dimethyl acetal (**1a**) with thiophenol (PhSH) (1.5 equiv) in the presence of a 0.2 equiv. of DCKDMA in DMF at room temperature for 1 day afforded the corresponding monophenylthioacetal (**1b**) in 76% yield. The same product (**1b**) was obtained in good to high yields with DCKEA, another catalyst of this type, using PhSH as well as phenylthiotrimethylsilane (TMS-SPh) as a nucleophile. As shown in Table 1, TCNE worked but not so efficiently as the dicyanoketene acetals.

Table 1. Reactivity of Benzaldehyde Dimethyl Acetal with Sulfur Nucleophiles Catalyzed by TCNE-Related π-Acid.



1a **1b**

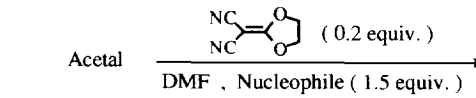
Catalyst		Nucleophile	Time	Yield[a]
	(TCNE)	PhSH	42 h	62 %
		TMS-SPh	42 h	48 %
	(DCKDMA)	PhSH	26 h	76 %
	(DCKEA)	PhSH	44 h	77 %
		TMS-SPh	42 h	90 %

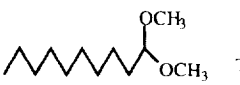
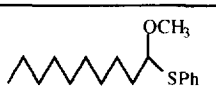
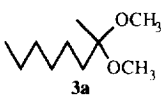
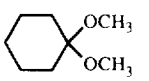
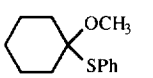
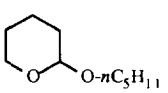
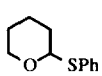
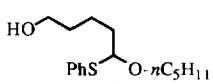
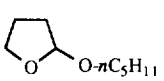
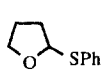
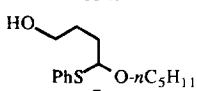
[a] Isolated yields.

Because of ease of preparation and purification, we selected DCKEA as catalyst and screened reactions of several representative acetals. Results are summarized in Table 2. Typical acetals of aldehydes and ketones

underwent smoothly monothioacetalization under the conditions at the ambient temperature to 60 °C for 1/2 to 2 days. Reaction of dimethyl acetals of aliphatic ketones proceeds more rapidly than that of an aliphatic aldehyde (entrys 1-7). DCKEA was a poor catalyst for the reaction of a methoxymethyl (MOM)-ether of *n*-dodecanol with PhSH or TMS-SPh at room temperature, and the starting MOM ether was recovered unchanged. (entrys 8, 9) Tetrahydropyranyl (THP)- and tetrahydrofuranyl (THF)-ethers derived from *n*-pentanol react with PhSH at 60°C to afford 2-phenylthiotetrahydropyran (**6b**) or 2-phenylthiotetrahydrofuran (**7b**) in 89% or 93% yields, respectively. It is known that the cleavage of exocyclic carbon-oxygen bond is the favored process when this type of acetals are treated with common Lewis acids.[4b, d] However, the use of TMS-SPh as a nucleophile mainly afford the ring-opened products (**6c**, **7c**) which are obtained by cleavage of endocyclic carbon-oxygen bond. (entrys 11-14) Guindon's observation by using Me_2BBr[4c] has been an only case reported to give the analogous results.

Table 2. Monothioacetalization of Dimethyl Acetals or Acetal-Type Ethers Catalyzed by Dicyanoketene Ethylene Acetal (DCKEA).

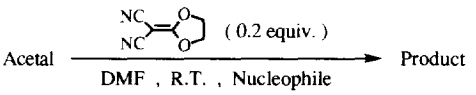


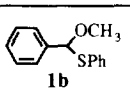
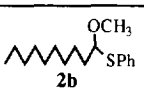
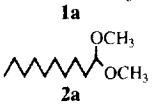
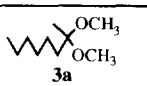
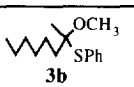
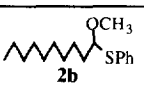
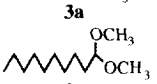
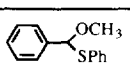
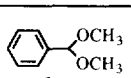
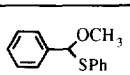
Entry	Acetal	Nucleophile	Temp.	Time	Product (Yield)[a]
1	 **2a**	PhSH	R.T.	44 h	 **2b** no reaction
2		PhSH	60 °C	42 h	80 %
3		TMS-SPh	R.T.	46 h	73 %
4	 **3a**	PhSH	R.T.	44 h	 **3b** 66 %[b]
5		TMS-SPh	R.T.	13 h	93 %
6	 **4a**	PhSH	R.T.	49 h	 **4b** 65 %[b]
7		TMS-SPh	R.T.	18 h	87 %
8	*n*-$C_{12}H_{25}$O-MOM **5a**	PhSH	R.T.	46 h	no reaction
9		TMS-SPh	R.T.	47 h	no reaction
10	 **6a**	PhSH	R.T.	49 h	 **6b** 8 % (S.M. 70 %)
11		PhSH	60 °C	42 h	89 %
12		TMS-SPh	60 °C	6 h	4 %
					 **6c** —
					—
					61 %
13	 **7a**	PhSH	60 °C	24 h	 **7b** 93 %
14		TMS-SPh[c]	60 °C	6 h	11 %
					 **7c** —
					66 %

[a] Isolated yields. [b] A considerable amount of the corresponding carbonyl compound was obtained as by-product.
[c] TMS-SPh (2 equiv.) was used in this reaction.

In order to investigate the chemoselectivity of the catalyst DCKEA, our attention was focused on the crossover reactions between different acetals. As summarized in Table 3, when an equimolar mixture of benzaldehyde dimethyl acetal (**1a**) and *n*-decanal dimethyl acetal (**2a**) was treated with a 1.5 equiv. of PhSH, the monothioacetal (**1b**) of benzaldehyde was obtained in 57% yield with nearly quantitative recovery of *n*-decanal dimethyl acetal (**2a**). (entry 1) No selectivity was observed in the reaction with TMS-SPh. (entry 2) The reaction of dimethyl acetals darived from a saturated ketone (**3a**) with PhSH or TMS-SPh proceed faster than that of saturated aldehydes (**2a**) to afford the monothioacetal of ketone (**3b**) in 43% or 90% yields, respectively. (entry 3, 4) THP- and MOM-ethers, which are acid sensitive functional groups, are intact under the reaction conditions. Only the monothioacetal of benzaldhyde could be obtained in good yields in the precence of THP- or MOM-ethers. (entry 5-8) Furthermore, mildness and high chemoselectivity of DCKEA as a catalyst for monothioacetalization were also demonstrated in the crossover experiments among three type of acetals: an aldehyde acetal (**2a**), a ketone acetal (**3a**), and an alcohol THP-ether (**6a**). (Table 4)

Table 3. Competitve Monothioacetalizations of Various Acetals Catalyzed by Dicyanoketene Ethylene Aceatls (DCKEA).

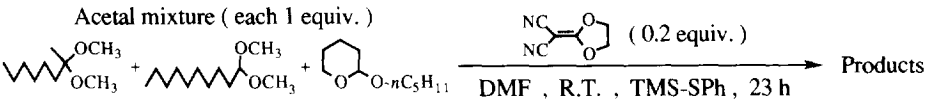


Entry	Acetal	Nucleophile	Time	Product (Yield[a])		Recovered Acetal (Yield[a])	
	 **1a**			 **1b**	 **2b**	**1a**	**2a**
1	 **2a**	PhSH (1.5 equiv.)	26 h	57 %	trace	15 %[b]	94 %
2		TMS-SPh (1.1 equiv.)	47 h	49 %	46 %	40 %	46 %
	 **3a**			 **3b**	 **2b**	**3a**	**2a**
3	 **2a**	PhSH (1.5 equiv.)	48 h	43 %	0 %	0 %[b]	94 %
4		TMS-SPh (1.1 equiv.)	24 h	90 %	10 %	4 %	88 %
	 **1a**			 **1b**	 **6b**	**1a**	**6a**
5	 **6a**	PhSH (1.5 equiv.)	49 h	66 %	0 %	5 %[b]	72 %
6		TMS-SPh (1.1 equiv.)	46 h	85 %	0 %	6 %	65 %
	 **1a**			 **1b**	**1a**	**5a**	
7	n-$C_{12}H_{25}$O-MOM **5a**	PhSH (1.5 equiv.)	49 h	56 %	6 %[b]	97 %	
8		TMS-SPh (1.5 equiv.)	46 h	97 %	trace	97 %	

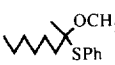
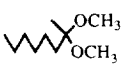
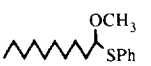
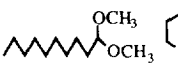
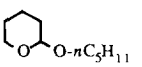
[a] Determined by ^{1}H NMR analysis directly on the crude reaction mixture.

[b] A considerable amount of the corresponding carbonyl compound was obtained as by-product.

Table 4. Competitive Monothioacetalization of a Mixture of Acetals Catalyzed by Dicyanoketene Ethylene Acetal (DCKEA).

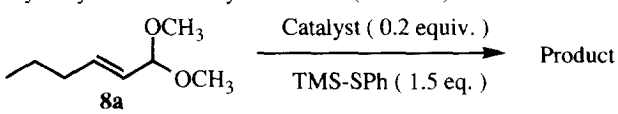


3a **2a** **6a**

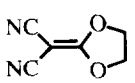
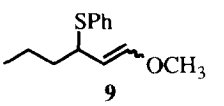
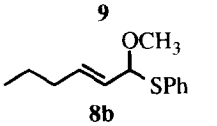
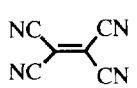
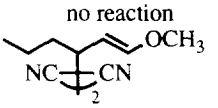
Equiv. of TMS-SPh	Yield[a] (%) of Product and Recovered Starting Material				
					
	3b	**3a**	**2b**	**2a**	**6a**
1.1	80	10	9	86	82
2.1	93	2	52	43	76

[a] Determined by ^{1}H NMR analysis directly on the crude reaction mixture.

Table 5. The Reaction of α,β-Unsaturated Acetal (**8a**) with TMS-SPh Catalyzed by Dicyanoketene Ethylene Acetal (DCKEA).



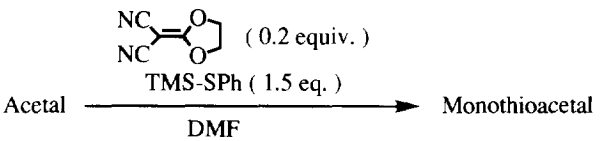
8a

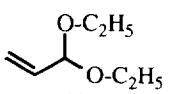
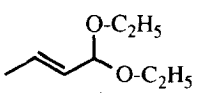
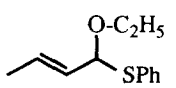
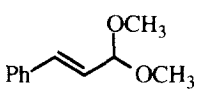
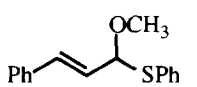
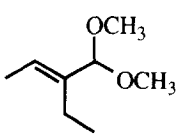
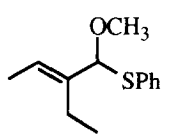
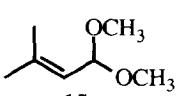
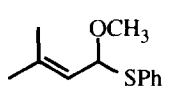
Catalyst	Solvent	Time	Temp.	Product	Yield[a]
 (DCKEA)	ether	24 h	R.T.	no reaction	
	benzene	43 h	R.T.		
	CH_2Cl_2	44 h	R.T.	 **9**	28 %[b]
	CH_3NO_2	42 h	R.T.		36 %[b]
	CH_3CN	38 h	R.T.		70 %
	CH_3CN	13 h	0 °C	 **8b**	30 %[b]
	DMF	13 h	0 °C		77 %
 (TCNE)	CH_3CN	52 h	R.T.	no reaction	
	DMF	13 h	0 °C	 **10**	19 %[b]

[a] Isolated yields. [b] A considerable amount of the starting material was recovered unchanged.

Next, it has been tried to prepare directly α,β-unsaturated monothioacetals from the corresponding acetals. The reaction of (*E*)-2-hexenal dimethyl acetal (**8a**) with TMS-SPh (1.5 equiv) was investigated in the presence of DCKEA (0.2 equiv.) in several solvents, and γ-alkoxyallyl sulfide (**9**) was found to be produced in CH_2Cl_2, CH_3NO_2, and CH_3CN at room temperature in 28 %, 36 %, and 70 % yields, respectively. During the screening of the reaction conditions, formation of (*E*)-1-methoxy-1-phenylthio-2-hexene (**8b**) in 30 % yield was observed at 0 °C in CH_3CN. Finally, **8b** was found to be obtained in 77 % yield at 0 °C in DMF as a reaction solvent. In contrast with DCKEA, TCNE was a poor catalyst for these reaction due to its lability under the present reaction conditions, when most of the starting acetals were recovered and a significant amount of the 1:2-adduct (**10**) of TCNE and **8a** was obtained. (Table 5)

Table 6. Preparation of α,β-Unsaturated Monothioacetal Catalyzed by Dicyanoketene Ethylene Acetal (DCKEA).



Entry	Substrate	Time	Temp.	Product	Yield[a]
1	 **11a**	9 h	R.T.	—	0 %[b]
2	 **12a**	9 h	0 °C	 **12b**	76 %
3	 **13a**	6 h	R.T.	 **13b**	92 %
4	 **14a**	10 h	0 °C	 **14b**	74 %
5	 **15a**	3 h	R.T.	 **15b**	91 %

[a] Isolated yields. [b] A considerable amount of the starting material was recovered unchanged.

As shown in Table 6, various types of α,β-unsaturated acetals reacted smoothly with TMS-SPh in the presence of a catalytic amount of DCKEA at 0 °C or the ambient temperature for 3-10 h to afford the corresponding α,β-unsaturated monothioacetals in good yields, except for the reaction of acrolein diethyl acetal (**11a**). (entry 1)

As described in the preliminary communication,[12a] it should be worth noting that the reduction-potential of DCKEA measured was very low (E_p^{red} <-2.0V vs. SCE in MeCN) compared with those of TCNE (E_p^{red} 0.15V vs. SCE in MeCN)[8d] and DDQ (E_p^{red} 0.59V vs. SCE in MeCN)[8d] and that any charge-transfer (CT) absorption band could not be detected in the UV spectroscopic measurement of the mixture of DCKEA and dimethyl acetal of *n*-decanal (**2a**) in CH_3CN, although the same mixture of TCNE exhibited a CT absorption band. Although mechanisms for the present reaction are still ambiguous only on the basis of the above observations so far, coordination between the π-system of DCKEA and the acetal oxygen is presumed to be one of the factors responsible for the activation of the C-O bond of acetal group.

In conclusion, we have shown that DCKEA is a novel type of catalyst differing from Lewis acids, protic acids, and π-acids such as TCNE, and an efficient catalyst for monothioacetalization of acetals, especially for the direct conversion of α,β-unsaturated acetals into the corresponding monothioacetals.

Acknowledgements

We are grateful to Dr. Magoichi Sako in this University for measurement of the reduction-potentials and differential UV spectra, and helpful discussion on the reaction mechanism.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and were uncorrected. IR absorption spectra were recorded on a JASCO IRA-1 spectometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) and a JEOL JNM-EX-400 (400 MHz) spectrometer with $SiMe_4$ or $CHCl_3$ as an internal standard. Mass spectra (MS) and high-resolution MS (HRMS) were recorded on a JEOL JMS-SX102A spectrometer. UV-visible absorption spectra were recorded on a Shimazu UV-260. Products were purified by column chromatography on silica gel (Merck, Kieselgel 60, 70-230 or 230-400 mesh). The reaction solvents were distilled from appropriate drying agents and stored over Molecular Sieves.

Dimethyl acetals were prepared by transacetalization of the corresponding aldehydes or ketones with trimethyl orthoformate in the presence of *p*-$TsOH\cdot H_2O$,[13] and purified by distillation. DCKDMA and DCKEA were prepared from TCNE according to the reported method.[11]

General Procedure for Monothioacetalization of Acetals Catalyzed by DCKEA: Benzaldehyde dimethyl acetal (**1a**, 50.7mg, 0.333 mmol) and PhSH (55 mg, 0.500 mmol) were added to a solution of DCKEA (9.1 mg, 0.067 mmol) in DMF (1 ml) at room temperature under argon atmosphere, and the mixture was stirred at room temperature for 44 h. The reaction mixture was extracted with ether. The organic extract was washed with water and brine, and dried over anhydrous $MgSO_4$, then the solvent was removed *in vacuo*. The crude product thus obtained was purified by column chromatography on silica gel to give (methoxy(phenylthio)-methyl)benzene (**1b**, 58.9 mg, 77 %) as a colorless oil.

Compounds (**1b**, **3b**, **4b**, **6b**, **7b**, **9**) were identified by comparision of their spectroscopic properties with those described in the literature.[4d] The yields and conditions were shown in Tables. Compound (**6c**) was identified by the derivation to the corresponding acetate. Spectral data for other compounds were presented below.

1-Methoxy-1-phenylthiodecane (**2b**): colorless oil, IR ($CHCl_3$): 1470, 1440, 1130, 1090, 1070, 1020, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.87 (t, *J*=6.8 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.24 (m, 12H), 1.44 (m, 2H, CH-CH_2-C<u>H</u>$_2$), 1.73 (m, 2H, CH-C<u>H</u>$_2$), 3.47 (s, 3H, O-CH_3), 4.62 (t, *J*=6.8 Hz, 1H, CH), 7.27 (m, 3H, ArH), 7.46 (m, 2H, ArH). HRMS (EI) Calcd for $C_{17}H_{28}OS$ (M^+): 280.1861. Found: 280.1857.

5-Pentyloxy-5-phenylthiopentyl acetate (*Acetate of* **6c**): colorless oil, IR ($CHCl_3$): 1730 (C=O), 1430, 1360, 1240, 1080, 1060, 1020, 680 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.90 (t, *J*=7.3 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.32 (m, 4H), 1.58 (m, 6H), 1.78 (m, 2H), 2.03 (s, 3H, Ac), 3.40, 3.90 (each dt, *J*=9.3, 6.8 Hz, 2H, O-CH_2), 4.03 (t, *J*=6.4 Hz, 2H, AcO-C<u>H</u>$_2$), 4.67 (t, *J*=6.8 Hz, 1H, CH), 7.28 (m, 3H, ArH), 7.47 (m, 2H, ArH). Anal. Calcd for $C_{18}H_{28}O_3S$: C, 66.60; H, 8.70. Found: C, 66.39; H, 8.69.

4-Pentyloxy-4-phenylthio-1-butanol (**7c**): colorless oil, IR (neat): 3340 (OH), 1480, 1440, 1060, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.89 (t, *J*=6.8 Hz, 3H, CH_3), 1.33 (m, 4H), 1.55-1.91 (m, 7H), 3.41, 3.92 (each dt, *J*=9.3, 6.8 Hz, 2H, O-CH_2), 3.62 (t, *J*=6.4 Hz, 2H, HO-C<u>H</u>$_2$), 4.71 (t, *J*=6.4 Hz, 1H, CH), 7.27 (m, 3H, ArH), 7.47 (m, 2H, ArH). HRMS (FAB) Calcd for $C_{15}H_{25}O_2S$ [$(M+H)^+$]: 269.1575. Found: 269.1556.

General Procedure for the Preparation of α,β-Unsaturated Monothioacetalization Catalyzed by DCKEA: (*E*)-2-Hexenal dimethyl acetal (**8a**, 51.7 mg, 0.358 mmol) and TMS-SPh (98 mg, 0.537 mmol) were added to a solution of DCKEA (9.8 mg, 0.072 mmol) in DMF (1 ml) at 0 °C under argon atmosphere, and the mixture was stirred at 0 °C for 13 h. The reaction mixture was extracted with AcOEt. The organic extract was washed with saturated $NaHCO_3$aq. and brine, and dried over anhydrous Na_2SO_4, then the solvent was removed *in vacuo*. The crude product thus obtained was purified by frash column chromatography on silica gel to give *(E)-1-methoxy-1-phenylthio-2-hexene* (**8b**) (61.3 mg, 77 %) as a colorless oil. IR (neat): 1440, 1110, 1060, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.82 (t, *J*=7.8 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.31 (m, 2H, C<u>H</u>$_2$-CH_3), 1.96 (m, 2H, =CH-C<u>H</u>$_2$), 3.49 (s, 3H, O-CH_3), 5.12 (d, *J*=5.9 Hz, 1H, O-CH), 5.50 (dd, *J*=15.6, 5.9 Hz, 1H, CH-C<u>H</u>=), 5.66 (m, 1H, CH_2-C<u>H</u>=), 7.26 (m, 3H, ArH), 7.45 (m, 2H, ArH). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 69.99; H, 8.16.

(**10**): colorless prism, m.p. 86 °C. IR ($CHCl_3$): 2250 (CN), 1645 (C=C), 1465, 1170, 1120, 950, 930 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.98 (t, *J*=7.3 Hz, 6H, CH_2-C<u>H</u>$_3$×2), 1.23-1.98 (m, 8H, CH_2-CH_2×2), 2.95 (m, 2H, C<u>H</u>-CH=×2), 3.69 (s, 6H, O-CH_3×2), 4.51 (dd, *J*=12.1, 10.7 Hz, 2H, CH-C<u>H</u>=×2), 6.71 (d, *J*=12.7 Hz, 2H, =CH-O×2). ^{13}C NMR ($CDCl_3$) δ: 13.3 (q), 19.9 (t), 34.4 (t), 48.4 (s), 49.2 (d), 56.1 (q), 95.6 (d), 110.5 (s), 111.4 (s), 153.5 (d). Anal. Calcd for $C_{20}H_{26}O_2N_4$: C, 67.77; H, 7.39; N, 15.81. Found: C, 67.52; H, 7.38; N, 15.67.

(E)-1-Ethoxy-1-phenylthio-2-butene (**12b**): colorless oil, IR (neat): 1480, 1440, 1110, 1090, 1065, 1020, 960, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.23 (t, *J*= 7.1 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.65 (d, *J*= 6.1 Hz, 3H, =CH-C<u>H</u>$_3$), 3.53, 3.89 (each dq, *J*= 9.3, 7.1 Hz, 2H, O-CH_2), 5.19 (d, *J*= 6.1 Hz, 1H, O-CH), 5.49-5.75 (m, 2H, CH=CH), 7.26 (m, 3H, ArH), 7.46 (m, 2H, ArH). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 69.03; H, 7.76.

(E)-1-Methoxy-3-phenyl-1-phenylthio-2-propene (**13b**): colorless oil, IR ($CHCl_3$): 1440, 1110, 1070, 960, 680 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.57 (s, 3H, O-CH_3), 5.31 (dd, *J*=5.9, 1.5 Hz, 1H, O-CH), 6.20 (dd, *J*=16.1, 5.9 Hz, 1H, Ph-CH=C<u>H</u>), 6.50 (dd, *J*=16.1, 1.5 Hz, 1H, Ph-C<u>H</u>), 7.27 (m, 8H, ArH), 7.47 (m, 2H, ArH). HRMS (EI) Calcd for $C_{16}H_{16}OS$ (M^+): 256.0922. Found: 256.0916.

(E)-2-Ethyl-1-methoxy-1-phenylthio-2-butene (**14b**): colorless oil, IR (neat): 1480, 1465, 1440, 1230, 1185, 1130, 1095, 1020, 740, 705, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.06 (t, *J*= 6.6 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.58 (d, *J*= 7.1 Hz, 3H, =CH-C<u>H</u>$_3$), 2.19 (m, 2H, CH_2), 3.42 (s, 3H, O-CH_3), 4.99 (s, 1H, O-CH), 5.42 (q, *J*= 6.8 Hz, 1H, =CH), 7.26 (m, 3H, ArH), 7.40 (m, 2H, ArH). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 70.05; H, 8.18.

1-Methoxy-3-methyl-1-phenylthio-2-butene (**15b**): colorless oil, IR (neat): 1470, 1440, 1125, 1070, 1020, 940, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.67, 1.71 (each s, 6H, CH_3×2), 3.45 (s, 3H, O-CH_3), 5.25 (m, 1H, =CH), 5.39 (d, *J*=8.8 Hz, 1H, O-CH), 7.29 (m, 3H, ArH), 7.47 (m, 2H, ArH). HRMS (EI) Calcd for $C_{11}H_{13}S$ [$(M\text{-}OCH_3)^+$]: 177.0738. Found: 177.0729.

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