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Trialkylsilyl Triflates – Practical Diastereoselective Catalysts in Conjugate Addition Reaction of Silyl Ketene Acetals and α,β-Unsaturated Ketones

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Catalytic effect of trimethylsilyl triflate (TMSOTf) or *tert*-butyldimethylsilyl triflate (TBSOTf) in conjugate addition reaction of the respective trialkylsilyl derivatives of thioester enolates (silyl ketene acetals) **2a**–**2e** and α,β-unsaturated ketones **1a**–**1c** has been studied. It was shown that silyl triflates are efficient catalysts with stereochemical profile similar to that of trityl hexachloroantimonate. The use of silyl triflates is particularly advantageous in tandem reactions involving conjugate addition as the first step.

Key words: enones, silyl enol ethers, Mukaiyama-Michael reaction, trialkylsilyl triflates

Lewis acid-promoted conjugate addition of silyl enol ethers to α,β-unsaturated ketones affording 1,5-dicarbonyl compounds was introduced to organic chemistry by Mukaiyama and coworkes [1] as a vinylogous version of the "direct aldol reaction" [2]. Initially, the reaction was carried out using stoichiometric amounts of titanium(IV) chloride alone or in mixtures with titanium(IV) isopropoxide, or with tin(IV) chloride [3–7] as the catalyst (in dichloromethane or other aprotic solvents). It was subsequently recognized that this reaction may be promoted by catalytic amounts of certain Lewis acids, such as $Al(OTf)_3$ [8], $BF_3{\cdot}OEt_2$ [9], Et_2AlCl [10]. Since then several other catalyst or catalytic systems have been successfully applied. These include: HgI_2 [11], $LiClO_4$-Et_2O [12], 10-methylacridinium perchlorate [13], $Bu_2Sn(OTf)_2$ [14], $Ln(OTf)_3$ [15], $LiClO_4$-CH_2Cl_2 [16], $Sc(OTf_3)$ [17], tris(pentafluorophenyl)boron [18], lithium cobalt-bis-dicarbollide [19], aluminum tris(2,6-diphenylphenoxide) [20], $LiAl[OC(Ph)(CF_3)_2]_4$-toluene [21], 2,7-dimethyl-1,8-biphenylenedioxy)bis(dimethylaluminum) [22], bis(pentafluorophenyl)tin [23], lanthanide iodides [24], $Ir[(COD)(PPh_3)_2]OTf$-H_2 [25]. The catalysts generating triphenylmethyl cation such as $TrClO_4$ [26–28], $TrBF_4$ [29], TrOTf [30] and $TrSbCl_6$ [27] proved particularly important. With these catalysts the reaction occurs in a highly diastereoselective manner yielding the adducts in the form of silyl enol ethers which, if required, may be used in successive reactions.

Recently, the interest is focused on catalysts that could potentially be applied in conjunction with chiral ligands to enantioselective transformations [31–33]. In this

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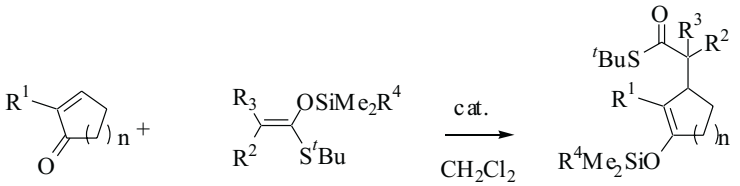
context, the mechanism of the trialkylsilylgroup transfer is of crucial importance. With regard to the direct aldol reaction, in which silyl group transfer also occurs, it has been postulated [34–36] that many of the reported Lewis acid-type catalysts may only be agents for the production (from silyl enol ethers) of R_3SiX species which are the real catalysts. Surprisingly, the effect of silyl triflates or silyl halides as catalysts in the Mukaiyama conjugated addition reaction has been examined only marginally. Otera, Nakai and their coworkers [37] have reported on application of TMSOTf or TBSOTf in a *syn*-diasteroselective addition [38] of silylated ketene acetal to 4-silyl-oxycyclopenenone [14, 39–46].

In order to assess the effect of cationic silicon species and, eventually, to develop useful catalysts, the Mukaiyama-Michael reaction of selected silylated ketene acetals and α,β-unsaturated ketones in the presence of TMSOTf and TBSOTf was studied.

RESULTS AND DISCUSSION

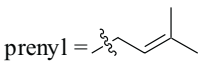
The reaction of cyclic α,β-unsaturated ketones **1a**–**1c** and ketene acetals **2a**–**2e** was scrutinized. Ketene acetals were prepared from the respective *tert*-butylthio esters, using LDA in THF, and the trialkylsilyl chlorides [47,48]. Mixtures of *E* and *Z* isomers [49] were distilled and used without separation of the isomers (*E*:*Z* in the range of 90:10 to over 95:5). It has been shown that in cases where ketene acetals bear the *tert*-butylthio- group and a large silyl group the configuration has a negligible effect on the steric course of the reaction [28].

Scheme 1



1a, R^1=H, n=1
1b, R^1=Me, n=1
1c, R^1=H, n=2

2a, R^2=Me, R^3=H, R^4=Me
2b, R^2=Me, R^3=H, R^4=^{t}Bu
2c, R^2=prenyl, R^3=H, R^4=Me
2d, R^2=prenyl, R^3=H, R^4=^{t}Bu
2e, R^2=Me, R^3=Me, R^4=Me

prenyl = 

3a, R^1=H, R^2=Me, R^3=H, R^4=Me, n=1
3b, R^1=H, R^2=Me, R^3=H, R^4=^{t}Bu, n=1
3c, R^1=H, R^2=prenyl, R^3=H, R^4=Me, n=1
3d, R^1=H, R^2=prenyl, R^3=H, R^4=^{t}Bu, n=1
3e, R^1=H, R^2=Me, R^3=Me, R^4=Me, n=1
3f, R^1=Me, R^2=Me, R^3=H, R^4=Me, n=1
3g, R^1=Me, R^2=Me, R^3=H, R^4=^{t}Bu, n=1
3h, R^1=Me, R^2=prenyl, R^3=H, R^4=Me, n=1
3i, R^1=Me, R^2=prenyl, R^3=H, R^4=^{t}Bu, n=1
3j, R^1=H, R^2=Me, R^3=H, R^4=Me, n=2
3k, R^1=H, R^2=Me, R^3=H, R^4=^{t}Bu, n=2
3l, R^1=H, R^2=prenyl, R^3=H, R^4=Me, n=2
3m, R^1=H, R^2=prenyl, R^3=H, R^4=^{t}Bu, n=2
3n, R^1=H, R^2=Me, R^3=Me, R^4=Me, n=2

Table 1. Results of reaction of α,β-unsaturated ketones **1** with ketene acetals **2** in the presence of catalytic amounts of trialkylsilyl triflates or $TrSbCl_6$, accordingly to Scheme 1.

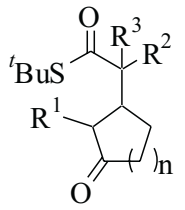
Entry	Enone	Ketene acetal	Adduct	RMe_2SiOTf cat.				$TrSbCl_6$ cat.[a]	
				R	Temp (°C), h	Yield (%)	*l/u*	Yield (%)	*l/u*
1	**1a**	**2a**	**3a**	Me	-78, 1	83	25:75[b]	83	25:75
2	**1a**	**2b**	**3b**	^{t}Bu	-78, 3	75	25:75[b]	66	25:75
3	**1a**	**2c**	**3c**	Me	-78, 2	55[c]	15:85		
4	**1a**	**2d**	**3d**	^{t}Bu	-78, 4	69	10:90		
5	**1a**	**2e**	**3e**	Me	r.t., 4[d]	31[e]			
6	**1b**	**2a**	**3f**	Me	-78, 1	98	>95:5	83	>95:5
7	**1b**	**2b**	**3g**	^{t}Bu	-78, 3	89	>95:5	87	>95:5
8	**1b**	**2c**	**3h**	Me	-78, 3	96	>95:5		
9	**1b**	**2d**	**3i**	^{t}Bu	-78, 5	89	>95:5		
10	**1c**	**2a**	**3j**	Me	-78, 1	98	20:80	95	20:80
11	**1c**	**2b**	**3k**	^{t}Bu	-78, 3	93	30:70	81	30:70
12	**1c**	**2c**	**3l**	Me	-78, 2	100[f]	10:90	92[f]	10:90
13	**1c**	**2d**	**3m**	^{t}Bu	-78, 4	95	10:90	83	10:90
14	**1c**	**2e**	**3n**	Me	r.t., 4[d]	16[e]			

[a]All reactions were carried at –78 °C for 15 min.
[b]Isomer ratios were determined by GC.
[c]The yield refers to ketone **4a**, see the text.
[d]The reaction was quenched before the enone was consumed.
[e]Reaction afforded the respective ketones (**4b** or **4c**).
[f]The product was contaminated with small amounts of thioester

Reaction of cyclopent-2-en-1-one (**1a**) with ketene acetal **2a** (1.1 eq., *E*:*Z ca*. 10:1) in the presence of TMSOTf, 5 mol%, in CH_2Cl_2 at –78°C was completed in 1 h; product **3a** was obtained in 83% yield as a mixture of *unlike* (*u*) and *like* (*l*) isomers in a ratio of 75:25 (by GC) (Table 1, entry 1). The same reagents **1a** and **2a** were allowed to react in the presence of $TrSbCl_6$ [27] (5 mol%). The reaction was completed in few minutes to give the same mixture of products **3a** in a 83% yield (Table 1, entry 1). Mukaiyama *et al*. [27] have reported reaction of **1a** and **2a** (silyl enol ether of *E* configuration) catalyzed by trityl perchlorate ($TrClO_4$) under similar conditions, afforded the corresponding product as a mixture of *u* and *l* diastereomers in a ratio of 66:34. Predominance of the product with *u* configuration in other trityl salt catalyzed reactions of cyclopent-2-en-1-one and ketene acetals has been well documented [27].

As evidenced by direct comparison, the product obtained with the silyl catalyst was of higher purity, devoid of the corresponding ketone and other contaminations generated in the in the presence of the trityl catalyst [50].

Reaction of enone **1a** with the ketene acetal bearing the *tert*-butyldimethylsilyl group **2b** catalyzed with *tert*-butyldimethylsilyl triflate (TBSOTf) afforded **3b** in a 75% yield (after chromatography), consisting of diastereomers in a ratio of 75:25 (Table 1, entry 2). TMSOTf-catalyzed reaction of **1a** and **2c** afforded adduct **3c** contaminated with the thioester derived from hydrolysis of the unreacted **2c**, which could not be removed by chromatography. This crude product was hydrolyzed to afford ketone **4a**, isomer ratio 85:15, (Figure 1) in 55% yield from **1a** (Table 1, entry 3).



4a, R^1=H, R^2=prenyl, R^3=H, n=1
4b, R^1=H, R^2=R^3=Me, n=1
4c, R^1=H, R^2=R^3=Me, n=2

Figure 1.

An analogous reaction of **1a** and **2d** in the presence of TBSOTf gave **3d** in 69% yield (*u*:*l* = 90:10) (entry 4).

Reaction of the sterically more hindered isobutyric ketene acetal **2e** and enone **1a** in the presence of TMSOTf was sluggish. It was quenched after 4 h, before all enone was consumed. Ketone **4b** was obtained in 31% yield. Replacement of TMSOTf with $TrSbCl_6$ did not improve the reaction outcome.

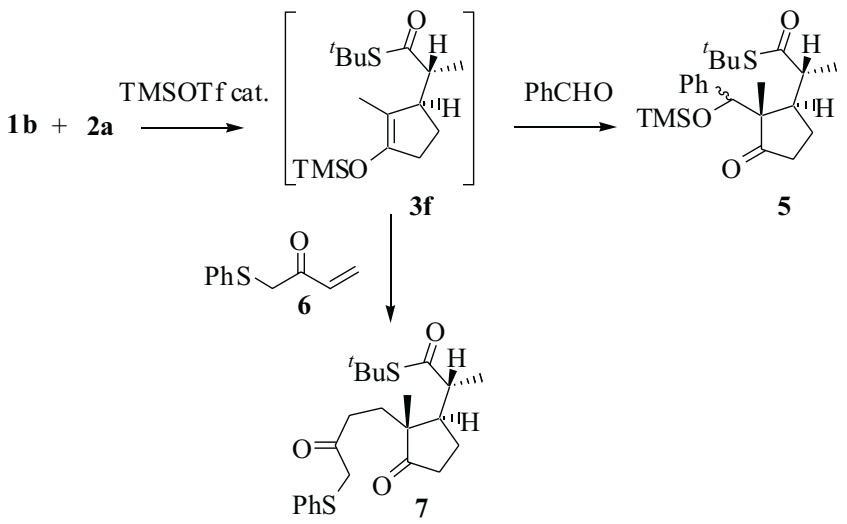
Conjugate addition of silyl enol ethers to 2-methylcyclopent-2-en-1-one (**1b**) catalyzed by $TrSbCl_6$ is relatively well documented owning to its applications to the terpenoid synthesis [27,51,52]. The TMSOTf-catalyzed reaction of **1b** and **2a** gave **3f** in 98% yield, virtually as the pure *l* diastereomer (entry 6). The results obtained on examining the reaction of **1b** with ketene acetals **2b**–**2d** in the presence of the appropriate silyl triflate are summarized in Table 1, entries 7–9.

Reaction of cyclohex-2-en-1-one (**1c**) with ketene acetals **2a**–**2d** in the presence of TMSOTf afforded adducts **3j**–**3m** mixtures of diastereomers with predominance of that with *u* configuration. The results are combined in Table 1 (entries 10–13). Similarly as in previous case, the reaction with sterically hindered ketene acetal **2e** affording **4c** was slow.

The foregoing results prompted us to examine tandem reactions utilizing silyl enol ethers generated in the Mukaiyama-Michael reactions. Thus, enone **1b** was allowed to react with ketene acetal **2a** in the presence of catalytic account of TMSOTf. After the enone was consumed, silyl enol ether **3a** was treated with benzaldehyde [53] without isolation (Scheme 2). Silylated carbinol **5** was obtained in 91% yield as a mixture of diastereoisomers in a ratio of 3:2. Similarly, treatment of **3a** with α,β-unsaturated ketone [54,55] **6** (1.5 mol equivalent) afforded the product of subsequent conjugate addition **7** (70% yield). High purity of the products obtained with these catalysts is noteworthy.

It was of interest to get some insight into silyl group transfer processes in the presence of silyl triflates. First, it was established that *tert*-butyldimethylsilyl enol ether **3g** remains unchanged on treatment with TMSOTf, in CH_2Cl_2, at –78°C for 4 h.

Scheme 2



Then enone **1b** and *tert*-butyldimethylsilyl acetal **2b** were treated with TMSOTf (60 mol%). After the reaction was completed, a mixture of **3f** and **3g** in a ratio of 3:2 was obtained. An increase of the amount of TMSOTf to 100 mol% afforded **3f** and **3g** in a ratio of 7:3. These results indicate that internal silyl group transfer from the ketene acetal to the enone unit, concomitant with C–C bond formation has no significant contribution to the process, if occurs at all.

The mechanistic details of the silyl group transfer in trityl salt catalyzed conjugate addition reaction have not been reviled till now. It has been shown that the counter anions in trityl salts ($TrClO_4$, $TrSbCl_6$, TrOTf) have a little effect on the reaction steric course and the product yield [27]. The present study demonstrate that silicon cationic species act as catalysts in a similar way as trityl salts. These results reiterate the question which of these cationic species, trityl or silyl, is the real catalyst in the Mukaiyama-Michael conjugate addition reaction. In conclusion, it was shown that silyl triflates act as an efficient catalyst of the Mukaiyama-Michael conjugate addition affording the products with yields and diastereoselectivity similar to those obtained with $TrSbCl_6$. Advantage of using silyl triflates consists in high purity of the products, higher efficiency of tandem reactions (which may result from preventing of silyl enol ethers hydrolysis), operational simplicity and availability.

EXPERIMENTAL

General methods: NMR spectra were recorded for $CDCl_3$ solutions, at 200 (^1H) or 50 (^{13}C) MHz with Varian Gemini instrument. Chemical shifts are reported in δ units, downfield from tetramethylsilane. Mass spectra (electron impact, 70 eV) were taken on AMD 604 (AMD Intectra GmbH, Germany). GC analyses were performed using a Shimadzu GC-14A unit equipped with a capillary column Quadrex Q5-30W-0.5F at programmed temperature 120–220°C; 10°C/min.

Reactions were carried out in flame-dried glassware under argon. Methylene chloride was distilled over calcium hydride under argon. Organic extracts were dried over anhydrous Na_2SO_4 and the solvents were removed on a rotary evaporator under reduced pressure. Merck silica gel, 230–400 mesh, was used for column chromatography; crude reaction mixtures were filtered through a column deactivated by passing hexanes containing 2% of triethylamine (2 volumes of the column) and then washing with hexanes (2 volumes of the column); mixtures of products were separated on silica gel deactivated by passing hexanes containing 1% of triethylamine. Trimethylsilyl- and *tert*-butyldimethyl trifluorosulfonates triflates were purchased from Fluka and distilled before use.

General procedure for trialkylsilyl triflate – catalyzed conjugate addition. To a solution of an enone (0.5 mmol) and a silyl triflate (0.05 ml, *ca*. 5 mol%) in CH_2Cl_2 (3 ml), stirred at – 78°C, a ketene acetal (0.6 mmol) was added [56]. The progress of the reaction was monitored by TLC; after consumption of the enone, 2-pyridinemethanol (*ca*. 0.01 ml) was added. The mixture was stirred at – 78°C for 15 min, allowed warm to room temperature and diluted with hexanes (20–25 ml). The whole was filtered through deactivated silica gel (2 ml) and evaporated. Further workup included: For (*tert*-butyldimethylsilyl enol ethers) – the residue was chromatographed on deactivated silica gel [30 ml, using for elution hexanes (100 ml) and then hexane-ethyl acetate, 99:1 (200 ml)]; the main fraction was collected. For (trimethylsilyl enol ethers) – the residue was dried in high vacuum for 8 hours.

General procedure for $TrSbCl_6$ – catalyzed conjugate addition. To a solution of a ketene acetal (0.6 mmol) and $TrSbCl_6$ (12 mg, 5 mol%) in CH_2Cl_2 (3 ml), stirred at –78°C, an enone (0.5 mmol) was added in *ca*. 1–2 min. The mixture was stirred for 15 min and the reaction was quenched with 2-pyridinemethanol (0.01 ml). After 15 min. the mixture was allowed warm to room temperature and then diluted with hexanes (20 ml), and filtered through deactivated silica gel (2 ml). The filtrate was evaporated. The further workup included: For (*tert*-butyldimethylsilyl enol ethers) – the residue was chromatographed on deactivated silica gel [30 ml, using for elution hexanes (100 ml) and then hexane--ethyl acetate, 99:1 (200 ml)]; the main fraction was collected. For (trimethylsilyl enol ethers) – the residue was dried in high vacuum for 8 hours.

(2*R,1′*R**)- and (2*R**,1′*S**)-*S*-(*tert*-Butyl) 2-(3′-trimethylsilyloxycyclopent-2′-en-1′-yl)propanethiolate (3a).** Cyclopent-2-en-1-one (**1a**) (0.042 ml, 0.5 mmol), TMSOTf (0.05 ml, 5 mol%), 1-*tert*-butylthio)-1-(trimethylsilyl)prop-1-ene (**2a**) (*E*:*Z* – 10:1)(131 mg, 0.6 mmol); reaction time: 1 h. Product **3a** was obtained (124 mg, 83% yield) as a mixture of diastereomers *l* (*R**,*R**) and *u* (*R**,*S**) in a ratio of 25:75, respectively, by GC: (retention times: *u* 12.27 min.; *l* 12.33 min). ^{1}H NMR: δ = 0.15 (s, 9H, $SiMe_3$), 1.02 (d, 2.75H, *J* = 6.8 Hz, C(3)-H), 1.04 (d, 0.75H, *J* = 6.8 Hz, C(3)-H), 1.40 (s, 9H, *t*BuS), overlapping 1.35–1.66 (m, 1H), 1.82 –2.41 (m, 4H), 2.75–2.90 (m, 1H), 4.50 (dd, 0.75H, *J* = 1.8, 3.7 Hz, C(2′)-H), 4.56 (dd, 0.25H, *J* = 1.8, 3.7 Hz, C(2′)-H); ^{13}C NMR: *u* isomer: δ = –0.1 (Si-CH_3), 14.5, 25.1, 29.7 (SC-$\underline{C}H_3$), 33.1, 45.8, 47.4, 54.7, 104.3 (2′), 155.5 (C3′), 203.9 (C1); *l* isomer: δ = 103.5, 156.1; MS EI (*m/z*): 300 (M^+, 1), 243 (86), 182 (14), 155 (100), 73 (39), 57 (15); MS EI HR: Calcd. for $C_{15}H_{28}O_2SiS$ (M^+): 300.15793. Found: 300.15671.

In an analogous experiment $TrSbCl_6$ (12 mg, 5 mol%) was used in place of TMSOTf; reaction time 15 min. Product **3a** was obtained (125 mg , 83% yield) as a mixture of *l* and *u* isomers in a ratio of 25:75.

(2*R,1′*R**)- and (2*R**,1′*S**)-*S*-(*tert*-Butyl)-2-[3′-(*tert*-butyldimethylsilyloxy)cyclopent-2′-en-1′yl]propanethioate (3b).** Enone **1a** (0.042 ml, 0.5 mmol), TBSOTf (0.006 ml, 5 mol%), 1-*tert*-butylthio-1-(*tert*-butyldimethylsilyloxy)prop-1-ene (**2b**) (*E*:*Z* > 95:5)(156 mg, 0.6 mmol); reaction time: 3 h. The product **3b** was obtained (128 mg, 75%) as a mixture of *u* and *l* diastereomers in a ratio of 75:25 by GC (retention times: *u* 16.48, min; *l* 16.65 min): ^{1}H NMR: δ = 0.14 (s, 3H, $SiMe_3$), 0.15 (s, 3H, $SiMe_3$), 0.90 (s, 9H, *t*BuSi), 1.06 (d, 2.2H, *J* = 6.8 Hz, C(3)-H), 1.07 (d, 0.8H, *J* = 6.8 Hz, C(3)-H), 1.44 (s, 9H, *t*BuS), overlapping 1.40–1.70 (m, 1H), 2.18–2.44 (m, 3H), 2.78–2.95 (m, 1H), 4.54 (dd, 0.75H, *J* = 1.7, 3.7 Hz, C(2′)-H), 4.60 (dd, 0.25H, *J* = 1.8, 3.8 Hz, C(2′)-H); ^{13}C NMR: *u* isomer: δ = –4.7 (Si-CH_3), –4.6 (Si-CH_3), 14.6, 18.1, 25.2, 25.7 (SiC-$\underline{C}H_3$), 29.8 (SC-$\underline{C}H_3$), 33.1, 45.8, 47.5, 54.8, 104.6 (C2′), 155.9 (C3′), 204.2 (C1); *l* 103.8 (C2′), 155.9 (C3′), 204.0 (C1); MS LSIMS (*m/z*): 343 [$(M+H)^+$, 18], 285 (37), 197 (100), 80 (28); MS LSIMS HR: Calcd. for $C_{18}H_{34}O_2SiS(M^+ + H)$: 343.21271. Found: 343.21172.

In an analogous experiment $TrSbCl_6$ (12 mg, 5 mol%) was used in place of TBSOTf ; reaction time 15 min. Adduct **3b** was obtained (114 mg, 66% yield) as a mixture of isomers *l* and *u* in a ratio of 25:75.

***S*-(*tert*-Butyl)-(2*R**,1′*R**)- and (2*S**,1′*R**)-2-(3′-oxocyclopent-1′-yl)-5-methylhex-4-enethioate (4a).** Enone **1a** (0.042 ml, 0.5 mmol), TMSOTf (0.05 ml, 5 mol%), 1-*tert*-butylthio-5-methyl-1-(trimethylsilyloxy)hex-4-ene (**2c**) (*E*:*Z* > 95:5)(163 mg, 0.6 mmol); reaction time: 2 h. After the usual workup, the product was obtained (130 mg). The NMR spectra of this material showed that it contained *S*-(*tert*-butyl)-(2*R**,1′*R**)- and (2*S**,1′*R**)-5-methyl-2-(3′-trimethylsilyloxycyclopent-2′-en-1′-yl)hex-4-enethioate (**3c**), the thioester derived from the ketene acetal and some other minor contaminations. A part of this crude product (95 mg) was dissolved in a mixture of THF (5 ml) and MeOH (2 ml), and treated with TMSCl (0.05 ml). The mixture was stirred for 2h and the solvent was evaporated in vacuum. The residue was chromatographed on silica gel (15 ml, hexane – ethyl acetate, 98:2 and hexane – ethyl acetate 95:5). The product **4a** was obtained (57 mg which corresponds to 55% yield from enone **1a**): ^{1}H NMR: δ = 1.41 (s, 7.9 H, *t*BuS), 1.43 (s, 1.1 H, *t*BuS), 1.58 (s, 3H, C=CCH_3), 1.67 (s, 3H, C=CCH_3), 1.90–2.46 (m, 8H), 5.00–5.13 (m, 1H, C(4)-H); ^{13}C NMR: major isomer: δ = 17.8, 25.8, 27.8, 29.6 (SC-$\underline{C}H_3$), 38.4, 39.3, 43.1, 48.2, 59.6, 120.2 (C4), 133.7 (C5), 202.4 (C1), 217.8 (C3'); Isomer ratio 15:85, from integration of the signals at δ 1.43 and 1.41 ppm in the ^{1}H NMR spectrum. MS EI (*m/z*): 282 (M^+, 1.5), 226 (20), 193 (15), 165 (27), 164 (52), 145 (10), 144 (42), 143 (12), 111 (12), 109 (18), 83 (44), 69 (100), 57 (51), 41 (44); MS EI HR: Calcd. for $C_{16}H_{26}O_2S$: 282.16535. Found: 282.16606.

***S*-(*tert*-Butyl)-(2*R**,1′*R**)- and (2*S**,1′*R**)-2-[3′-(*tert*-butyldimethylsilyloxy)cyclopent-2′-en-1′-yl]-5-methylhex-4-enethioate (3d).** Enone **1a** (0.042 ml, 0.5 mmol), TBSOTf (0.006 ml, 5 mol%), 1-*tert*-butylthio-5-methyl-1-(*tert*-butyldimethylsilyloxy)hex-4-ene (**2d**) (*E*:*Z* > 95:5) (188 mg, 0.6 mmol); reaction time: 4 h. The product **3d** was obtained (136 mg, 69%): ^{1}H NMR: δ = 0.14 (s, 3H, $SiMe_3$), 0.15 (s, 3H, $SiMe_3$), 0.90 (s, 9H, *t*BuSi), 1.43 (s, 7.8H, *t*BuS), 1.44 (s, 1.2H, *t*BuS), 1.57 (s, 3H, C(6)-H), 1.66 (s, 3H, C(7)-H) overlapping 1.40–1.80 (m, 1H), 1.90–2.50 (m, 7H), 2.76–2.92 (m, 1H), 4.55 (dd, 0.90H, *J* = 1.7, 3.7 Hz, C(2′)-H), 4.65 (dd, 0.10H, *J* = 1.8, 3.7 Hz, C(2′)-H), 5.05–5.15 (m, 1H, C(4)-H); ^{13}C NMR: δ = –4.6 (Si-CH_3), –4.5 (Si-CH_3), 17.3, 18.2, 25.7, 26.1, 29.1, 29.7 (SC-$\underline{C}H_3$), 33.1, 45.1, 47.6, 61.2, 104.5 (C2′), 121.2 (C4), 132.9 (C5), 155.8 (C3′), 203.5 (C1). Isomer ratio 10:90 from integration of the signals at δ 4.65 and 4.55 ppm in the ^{1}H NMR spectrum. MS EI HR: Calcd. for $C_{22}H_{40}O_2SiS$ (M^+): 396.25183. Found: 396.25129.

***S*-(*tert*-Butyl)-(1′*R**)- and (1′*S**)-2-methyl-2-(3′-oxocyclopent-1′-yl)-propanethioate (4b).** Enone **1a** (0.042 ml, 0.5 mmol), TMSOTf (0.01 ml, 10 mol%) 1-(*tert*-butylthio)-2-methyl-1-(trimethylsilyloxy)prop-1-ene (**2e**) (139 mg, 0.6 mmol); reaction time: 4 h (the reaction was quenched before the enone was consumed). Ketone **4b** was obtained (37 mg, 31%): ^{1}H NMR: δ = 1.16 (s, 3H, C(2)-CH_3), 1.19 (s, 3H, C(2)-CH_3), 1.43 (s, 9H, *t*BuS), 1.48–1.78 (m, 2H), 1.90–2.60 (m, 5H); ^{13}C NMR: δ = 22.3, 24.2, 29.7 (SC-$\underline{C}H_3$), 38.8, 40.2, 45.4, 47.5 (S-C), 51.5 (C2), 206.3 (C3′), 218.0 (C1); MS EI (*m/z*): 185 ((M-^{t}Bu)$^+$, 14), 160 (23), 153 (13), 125 (100), 97 (16), 83 (42), 69 (38), 57 (73); MS EI HR: Calcd. for $C_9H_{13}O_2S$ (M-^{t}Bu)$^+$: 185.06363. Found: 185.06329.

***S*-(*tert*-Butyl)-(2*S**,1′*R**)-2-(3′-trimethylsilyloxy-2′-methylcyclopent-2′-en-1′-yl)propanethioate (3f).** Enone **1b** (0.050 ml, 0.5 mmol), TMSOTf (0.005 ml, 5 mol%), ketene acetal **2a** (*E*:*Z* – 10:1) (131 mg, 0.6 mmol); reaction time: 1 h. The product **3f** was obtained (154 mg, 98%): ^{1}H NMR: δ = 0.14 (s, 9H, $SiMe_3$), 0.92 (d, 3H, *J* = 6.8 Hz, C(3)-H), 1.42 (s, 9H, *t*BuS), 1.44 (br s, 3H, C(2′)-CH_3), 1.50–1.90 (m, 2H), 2.12–2.26 (m, 2H), 2.60–2.75 (m, 1H), 2.90–3.00 (m, 1H); ^{13}C NMR: δ = 0.6 (Si-CH_3), 10.3, 10.6, 21.2, 29.9 (SC-$\underline{C}H_3$), 32.9, 47.4, 48.0, 50.5, 113.6 (C2′), 148.4 (C3′), 203.8 (C1); MS EI (*m/z*): 314 (M^+, 2.25), 257 (28), 169 (100), 97 (16), 83 (10), 73 (99), 57 (36); MS EI HR: Calcd. for $C_{16}H_{30}O_2SiS$ (M^+): 314.17358. Found: 314.17258.

In an analogous experiment $TrSbCl_6$ (12 mg, 5 mol%) was used in place of TMSOTf; reaction time 15 min. Adduct **3f** was obtained (130 mg , 83% yield).

***S*-(*tert*-Butyl)-(2*S**,1′*R**)-2-[3′-(*tert*-butyldimethylsilyloxy)-2′-methylcyclopent-2′-en-1′-yl] propanethioate (3g).** Enone **1b** (0.050 ml, 0.5 mmol), TBSOTf (0.006 ml, 5 mol%), ketene acetal **2b** (*E*:*Z* – 95:5) (156 mg, 0.6 mmol); reaction time: 3 h. The product **3g** was obtained (161 mg, 89%): ^{1}H NMR: δ = 0.11 (s, 6H, $SiMe_3$), 0.94 (s, 9H, *t*BuSi) overlapping 0.95 (d, *J* = 6.3 Hz, C(3)-H), 1.45 (s, 9H, *t*BuS)

overlapping 1.48 (br s, 3H, C(3′)-CH_3), 1.52–1.80 (m, 2H), 2.14–2.28 (m, 2H), 2.63–2.77 (m, 1H), 2.92–3.06 (m, 1H); ^{13}C NMR: δ = –4.0 (Si-CH_3), –3.9 (Si-CH_3), 10.3, 10.8, 18.1, 21.3, 25.7 (SiC-$\underline{C}H_3$), 29.9 (SC-$\underline{C}H_3$), 33.0, 47.4, 48.0, 50.5, 113.3 (C2′), 148.7 (C3′), 203.8 (C1); MS EI HR: Calcd. $C_{19}H_{36}O_2SiS$ (M^+): 356.220531. Found: 356.2206.

In an analogous experiment $TrSbCl_6$ (12 mg, 5 mol%) was used in place of TBSOTf ; reaction time 15 min. Adduct **3g** was obtained (156 mg, 87% yield).

***S*-(*tert*-Butyl)-(2*S**,1′*R**)-5-methyl-2-(3′-trimethylsilyloxy-2′-methylcyclopent-2′-en-1′-yl) hex-4-enethioate (3h).** Enone **1b** (0.050 ml, 0.5 mmol), TMSOTf (0.005 ml, 5 mol%), **2c** (*E*:*Z* > 95:5)(163 mg, 0.6 mmol); reaction time: 3 h. The product **3h** was obtained (177 mg, 96%): ^{1}H NMR: δ = 0.15 (s, 9H, $SiMe_3$), 1.41 (s, 9H, *t*BuS), 1.46 (d, 3H, *J* = 0.9 Hz, C(2′)-CH_3), 1.54 (s, 3H, C=CCH_3), 1.62 (s, 3H, C=CCH_3), 1.68–1.94 (m, 3H), 2.14–2.40 (m, 3H), 2.48–2.60 (m, 1H), 2.79–2.94 (m, 1H), 5.06–5.07 (br t, 1H, *J* = 7.3 Hz, C(4)-H); ^{13}C NMR: δ = 0.6 (Si-CH_3), 10.6, 17.7, 22.2, 25.3, 25.8, 29.8 (CS-$\underline{C}H_3$), 32.8, 47.5, 48.0, 57.1, 113.7 (C2′), 121.7 (C4), 132.5 (C5), 148.6 (C3′), 202.9 (C1); MS EI (*m/z*): 368 (M^+, 2), 311 (17), 243 (13), 209 (10), 169 (100), 109 (11), 73 (61), 69 (13), 57 (14), 41 (12); MS EI HR: Calcd. for $C_{20}H_{36}O_2SiS$ (M^+): 368.22053. Found: 368.22026.

***S*-(*tert*-Butyl)-(2*S**,1′*R**)-2-[3′-(*tert*-butyldimethylsilyloxy)-2′-methylcyclopent-2′-en-1′-yl]-5-methylhex-4-enethioate (3i).** Enone **1b** (0.050 ml, 0.5 mmol), TBSOTf (0.006 ml, 5 mol%), **2d** (*E*:*Z* > 95:5) (188 mg, 0.6 mmol); reaction time: 5 h. The product **3i** was obtained (184 mg, 89%): ^{1}H NMR: δ = 0.11 (s, 6H, $SiMe_3$), 0.92 (s, 9H, *t*BuSi), 1.43 (s, 9H, *t*BuS), 1.50 (d, 3H, *J* = 1 Hz, C(2′)-CH_3), 1.56 (s, 3H, C=CCH_3), 1.65 (s, 3H, C=CCH_3), 1.67–1.98 (m, 3H), 2.15–2.42 (m, 3H), 2.51–2.62 (m, 1H), 2.82–2.95 (m, 1H), 5.05 (br t, 1H, *J* =7.3 Hz, C(4)-H); ^{13}C NMR: δ = –4.0 (Si-CH_3), 10.6, 17.7, 18.1, 22.3, 25.4, 25.7 (SiC-$\underline{C}H_3$), 25.8, 29.8 (CS-$\underline{C}H_3$), 32.8, 47.5, 48.0, 57.2, 113.4 (C2′), 121.8 (C4), 132.6 (C5), 148.8 (C3′), 203.1 (C1); MS EI (*m/z*): 410 (M^+, 2.5), 353 (19), 285 (7), 211 (100), 75 (16), 73 (84), 57 (11); MS EI HR: Calcd. for $C_{23}H_{42}O_2SiS$ (M^+): 410.26748. Found: 410.26771.

***S*-(*tert*-Butyl)-(2*R**,1′*R**) and (2*S**,1′*R**)-2-(3′-trimethylsilyloxycyclohex-2′-en-1′-yl)propanethioate (3j).** Enone **1c** (0.050 ml, 0.5 mmol), TMSOTf (0.05 ml, 5 mol%), **2a** (*E*:*Z* > 10:1) (131 mg, 0.6 mmol); reaction time: 1 h. The product **3j** was obtained (154 mg, 98%): ^{1}H NMR: δ = 0.15 (s, 9H, $SiMe_3$), 1.05 (d, 2.3H, *J* = 6.8 Hz, C(3)-H), 1.07 (d, 0.7H, *J* = 6.6 Hz, C(3)-H), 1.43 (s, 9H, *t*BuS) overlapping 1.0–1.80 (m, 4H), 1.86–1.98 (m, 2H), 2.24–2.56 (m, 2H), 4.72 (br.s, 0.8H, C(2′)-H), 4.77–4.81 (m, 0.2H, C(2′)-H); ^{13}C NMR: δ = 0.3 (Si-CH_3), 14.5, 21.7, 25.3, 26.9, 29.8 (SC-$\underline{C}H_3$), 38.4, 47.6, 54.3, 106.5 (C2'), 151.5 (C3'), 204.0 (C1); minor isomer: 105.2. Isomer ratio 20:80 from integration of the signals at δ 4.81–4.77 and 4.72 ppm in the ^{1}HNMR spectrum. MS EI (*m/z*): 314 (M^+, 1), 257 (43), 179 (11), 196 (29), 169 (100), 73 (45), 57 (12); MS EI HR: Calcd. for $C_{16}H_{30}O_2SiS$ (M^+): 314.17358. Found: 314.17365.

In an analogous experiment with $TrSbCl_6$ (12 mg, 5 mol%) as the catalyst the same products **3j** (149 mg, 95% yield) were obtained, isomer ratio 20:80. Reaction time 15 min.

***S*-(*tert*-Butyl)-(2*R**,1′*R**) and (2*S**,1′*R**)-2-[3′-(*tert*-butyldimethylsilyloxy)-cyclohex-2′-en-1′-yl]propanethioate (3k).** Enone **1c** (0.050 ml, 0.5 mmol), TBSOTf (0.006 ml, 5 mol%), ketene acetal **2b** (*E*:*Z* > 95:5) (156 mg, 0.6 mmol); reaction time: 3 h. The product **3k** was obtained (166 mg, 93%): ^{1}H NMR: δ = 0.11 (s, 6H, $SiMe_3$), 0.88 (s, 6.2H, *t*BuSi), 0.89 (s, 2.8H, *t*BuSi), 1.06 (d, 2.1H, *J* = 6.8Hz, C(3)-H), 1.08 (d, 0.9H, *J* = 6.6 Hz, C(3)-H), 1.43 (s, 2.8H, *t*BuS), 1.44 (s, 6.2H, *t*BuS) overlapping 1.00–1.82 (m, 4H), 1.89–2.0 (m, 2H), 2.24–2.56 (m, 2H), 4.73 (br.s, 0.7H, C(2′)-H), 4.78–4.83 (m, 0.3H, C(2′)-H); ^{13}C NMR δ = –4.5, –4.2, 14.6, 18.0, 21.7, 25.4 (SiC-$\underline{C}H_3$), 25.7, 26.9, 29.8 (SC-$\underline{C}H_3$), 38.4, 47.6, 54.3, 106.7 (C2'), 151.7 (C3'), 204.1 (C1); minor isomer: 105.2, 152.1, 203.9. Isomer ratio 30:70 from integration of the signals at δ 4.83–4.78 and 4.73 ppm in the ^{1}HNMR spectrum. MS EI (*m/z*): 356 (M^+, 1), 299 (44), 238 (11), 211 (47), 115 (10), 73 (100), 57 (16); MS EI HR: Calcd. For $C_{19}H_{36}O_2SiS$ (M^+): 356.22053. Found: 356.21901.

In an analogous experiment with $TrSbCl_6$ (12 mg, 5 mol%) as the catalyst the product **3k** (144 mg, 81% yield) was obtained; isomer ratio 30:70; reaction time: 1 h.

***S*-(*tert*-butyl)-(2*R**,1′*R**) and (2*S**,1′*R**)-2-(3′-trimethylsilyloxycyclohex-2′-en-1′-yl)-5-methylhex-4-enethioate (3l).** Enone **1c** (0.050 ml, 0.5 mmol), TMSOTf (0.005 ml, 5 mol%), ketene

acetal **2c** (*E*:*Z* > 95:5) (163 mg, 0.6 mmol); reaction time: 2 h. The product **3l** was obtained 189 mg. GC analysis showed that this product contains 95% of **3l** and 4% of the thioester corresponding to **2c** and some minor contaminations. ^{1}H NMR: δ = 0.15(s, 9H, $SiMe_3$), 1.40 (s, 9H, *t*BuS), 1.54 (s, 3H, C=CCH_3), 1.63 (s, 3H, C=CCH_3) overlapping 1.05–1.80 (m, 4H), 1.87–1.95 (m, 2H), 2.05–3.55 (m, 4H), 4.75 (br.s, 0.9H, C(2′)-H), 4.83–4.88 (m, 0.1H, C(2′)-H), 4.98–5.09 (m, 1H, C(4)-H); ^{13}C NMR: δ = 0.35 ($SiCH_3$), 17.7, 21.8, 25.8, 26.2, 28.5, 29.7 (SC-$\underline{C}H_3$), 29.9, 37.7, 47.7, 60.2, 106.2 (C2′), 121.1 (C4), 132.8 (C5), 151.3 (C3'), 203.1 (C1). Isomer ratio 10:90 from integration of signals at δ 4.83–4.88 and 4.75 ppm in the ^{1}H NMR spectrum. MS EI (*m/z*): 368 (M^+, 2), 311 (28), 279 (11), 250 (16), 243 (14), 209 (18), 169 (100), 109 (13), 73 (86), 69 (25), 57 (23), 41 (23); MS EI HR: Calcd. for $C_{20}H_{36}O_2SiS$ (M^+): 368.22053. Found: 368.22043.

In an analogous experiment with $TrSbCl_6$ (12 mg, 5 mol%) as the catalyst, adduct **3l** was obtained (169 mg, 92%yield) as a mixture of isomers in a ratio of 10:90. Reaction time: 15 min. GC analysis showed that this product contains 95% of **3l** and 4% of the thioester corresponding to **2c** and some minor contaminations.

***S*-(*tert*-Butyl)-(2*R**,1′*R**) and (2*S**,1′*R**)-2-[3′-(*tert*-butyldimethylsilyloxy)cyclohex-2′-en-1′-yl]-5-methylhex-4-enethioate (3m).** Enone **1c** (0.050 ml, 0.5 mmol), TBSOTf (0.006 ml, 5 mol%), ketene acetal **2d** (*E*:*Z* > 95:5) (188 mg, 0.6 mmol); reaction time: 4 h. The product **3m** was obtained (195 mg, 95% yield): ^{1}H NMR: δ = 0.12 (s, 6H, $SiMe_3$), 0.89 (s, 9H, *t*BuSi), 1.43 (s, 8H, *t*BuS), 1.44 (s, 1H, *t*BuS), 1.56 (s, 3H, C=CCH_3), 1.65 (s, 3H, C=CCH_3) overlapping 1.04–1.84 (m, 4H), 1.90–2.02 (m, 2H), 2.10–2.59 (m, 4H), 4.78 (br.s, 0.9H, C(2′)-H), 4.86–4.90 (m, 0.1H, C(2′)-H), 5.02–5.12 (m, 1H, C(4)-H); ^{13}C NMR: δ = –4.6 ($SiCH_3$), –4.2 ($SiCH_3$), 17.7, 18.0, 21.8, 25.7 (SiC-$\underline{C}H_3$), 26.3, 28.5, 29.7 (SC-$\underline{C}H_3$), 29.8, 37.7, 47.7, 60.3, 106.5 (C2'), 121.2 (C4), 132.9 (C5), 151.6 (C3'), 203.3 (C1). Isomer ratio 90:10 from integration of signals at δ4.90–4.86 and 4.78 ppm in the ^{1}H NMR spectrum. MS EI (*m/z*): 410 (M^+, 1), 353 (21), 292 (8), 251 (9), 211 (100), 75 (13), 73 (62), 57 (16); MS EI HR: Calcd. for $C_{23}H_{42}O_2SSi$ (M^+): 410.26748. Found: 410.26671.

In an analogous experiment with $TrSbCl_6$ (12 mg, 5 mol%) as the catalyst, adduct **3m** was obtained (170 mg, 83% yield) as a mixture of isomers in a ratio of 90:10; Reaction time: 1 h.

***S*-(*tert*-Butyl)-2-methyl-2-(3-oxocyclohexyl)propanethioate (3n).** Enone **1c** (0.050 ml, 0.5 mmol), TMSOTf (0.01 ml, 10 mol%) ketene acetal **2e** (139 mg, 0.6 mmol); reaction time: 4 h. The product **4c** was obtained (21 mg, 16%): ^{1}H NMR: δ = 1.13 (s, 3H, C(2)-CH_3), 1.15 (s, 3H, C(2)-CH_3), 1.44 (s, 6H, *t*BuS) overlapping 1.20–1.88 (m, 3H), 2.00–2.44 (m, 3H); ^{13}C NMR: δ = 21.6 (C-$\underline{C}H_3$), 22.4 (C-$\underline{C}H_3$), 25.1, 26.2, 29.8 (SC-CH_3), 41.3, 43.1, 46.3, 47.5, 52.8, 206.6 (C1), 211.1 (C3′); MS EI (*m/z*): 256 (M^+, 0.5), 200 ((M-^{t}Bu)$^+$, 5), 167 (11), 167 (12), 139 (100), 121 (26), 97 (30), 95 (16), 93 (13), 83 (49), 82 (33), 69 (33), 57 (50); MS EI HR: Calcd. for $C_{10}H_{16}O_2S$ ((M-^{t}Bu)$^+$): 200.08710. Found: 200.08696.

***S*-(*tert*-Butyl)-(2*S**,1′*R**,1"*R**)- and (2*S**,1′*R**,1"*S**)-2-{2′-[(*tert*-butyldimethylsilyloxy phenyl) methyl]-2′-methyl-3′-oxocyclopentyl}propanethioate (5).** To a solution of enone **1b** (0.050 ml, 0.5 mmol) and TMSOTf (0.005 ml, ca. 5 mol%) in CH_2Cl_2 (3 ml), stirred at –78°C, a ketene acetal **2a** (*E*:*Z* – 10:1) (131 mg, 0.6 mmol) was added. Stirring was continued for 1 h, and then freshly distilled benzaldehyde (0.050 ml, 0.5 mmol) was added and the mixture was allowed to warm to room temperature in 4 h, and was left aside for 12 h. The solvent was evaporated and the residue was chromatographed on silica gel (30 ml, hexane – ethyl acetate, 98:2). The product **5** was obtained as a mixture of diasteromers (192 mg, 91% yield): ^{1}H NMR: δ = –0.09 (s, 5.6H, $SiMe_3$), 0.01 (s, 3.4H, $SiMe_3$), 0.83 (s, 1.9H, C(2′)-CH_3), 0.92 (s, 1.1H, C(2′)-CH_3), 0.96 (d, 1.9H, *J* = 7.1 Hz, C(3)-H), 1.18 (d, 1.14H, *J* = 7.0 Hz, C(3)-H), 1.46 (s, 5.6H, SC-CH_3), 1.51 (s, 3.4H, SC-CH_3) overlapping 1.22–2.36 (m, 8.6H), 2.64–2.79 (m, 0.4H), 2.91–3.06 (m, 0.3H), 3.16–3.28 (m, 0.6H), 4.67 (s, 0.6H, PhC$\underline{H}$), 4.80 (s, 0.4H, PhC$\underline{H}$), 7.15–7.33 (m, 5H, Arom-H). ^{13}C NMR (selected signals): δ = 29.9 (SC-$\underline{C}H_3$), 78.8 and 79.6 (Ph$\underline{C}$), 204.2 and 204.4 (C1), 220.2 and 221.3 (C3′); Isomer ratio of 40:60 from integration of signals δ 4.80 and 4.67 ppm in the ^{1}H NMR spectrum. MS LSIMS (*m/z*): 443 ((M^++Na), 3), 421 ((M^++H), 5), 405 (4), 387 (5), 331 (27), 275 (59), 179 (100), 105 (15), 91 (10), 75 (12); MS LSIMS HR: Calcd. for $C_{18}H_{35}O_2SiS$ (M^++Na): 443.20522. Found: 443.20560.

***S*-(*tert*-Butyl)-(2*S**,1′*R**,2′*R**)-2-{2′-methyl-3′-oxo-2′-[3"-oxo-3"-(phenylsulfanyl)propyl]cyclopentyl}propanethioate (7).** To a solution of enone **1b** (0.050 ml, 0.5 mmol) and TMSOTf (0.005 ml, *ca*. 5 mol%) in CH_2Cl_2 (3 ml), stirred at –78°C, a ketene acetal **2a** (*E*:*Z* – 10:1) (131 mg, 0.6 mmol) was added. Stirring was continued for 1 h, and then freshly purified by chromatography 1-phenylsulfanyl-but-3-en-2-one [57] (**6**) (134 mg, 0.75 mmol) was added and the mixture was allowed to warm to room temperature in *ca*. 4 h, and was left aside for 12 h. The solvent was evaporated and the residue was chromatographed on deactivated silica gel (30 ml, hexane – ethyl acetate, 9:1). The product **7** was obtained (143 mg, 70% yield): ^{1}H NMR: δ = 0.96 (s, 3H, C(2′)-CH_3), 1.17 (d, 3H, *J* = 6.8 Hz, C(3)-H), 1.39 (s, 9H, S*t*Bu), 1.42–1.60 (m, 2H), 1.82–2.86 (m, 8H), 3.64 (s, 2H, PhSC$\underline{H}_2$), 7.12–7.36 (m, 6H, Arom-H); ^{13}C NMR: δ = 17.3, 18.8, 22.8, 29.3, 29.6 (SC$\underline{C}H_3$), 35.8, 36.7, 43.5, 44.0, 48.3, 49.1, 51.2, 126.7, 129.0, 129.8, 134.8, 203.3, 204.4, 221.5; MS EI (*m/z*): 420 (M^+, 59), 330 (74), 241 (100), 223 (42), 207 (32), 185 (24), 179 (85), 161 (33), 123 (52), 119 (18), 57 (88), 45 (27); MS EI HR: Calcd. for $C_{23}H_{32}O_3S$ (M^+): 420.17929. Found: 420.17892.

Preparation of 3f and 3g from 1b and 2b using TMSOTf as the catalyst. To a solution of **1b** (0.050 ml, 0.5 mmol) and TMSOTf (0.055 ml, 60 mol%) in CH_2Cl_2 (3 ml), stirred at –78°C, ketene acetal **2b** (*E*:*Z* > 95:5) (156 mg, 0.6 mmol) was added. After 2 h the reaction was quenched with pyridine-methanol (0.032 ml). The mixture was allowed to warm to room temperature and then it was diluted with hexanes (20 ml) and filtered through silica gel (4 ml). The filtrate was evaporated and the residue was dried in high vacuum to give a mixture of **3f** and **3g** (171 mg) in a ratio of 3:2 as determined as by integration of methyl group protons at 0.15 and 0.08 ppm in the ^{1}H NMR spectrum of the mixture (96% total yield).

In an analogous experiment with the use **1b** (0.050 ml, 0.5 mmol), **2b** (*E*:*Z*> 95:5) (156 mg, 0.6 mmol) and TMSOTf (0.090 ml, 100 mol%), a mixture of **3f** and **3g** in a ratio of 7:3 was obtained (160 mg, 90%).

Attempted reaction of 3g and TMSOTf. To a solution of **3g** (151 mg, 0.42 mmol) in CH_2Cl_2 (3 ml), stirred at –78°C, TMSOTf (0.076 ml) was added. The mixture was stirred for 3 h and then pyridine-methanol (0.01 ml) was added and the mixture was allowed to warm to room temperature. The mixture was filtered through silica gel (15 ml). Evaporation of the filtrate afforded **3g** (140 mg); no signals corresponding to **3f** could be detected in the ^{1}H NMR spectrum of this product.

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