Lewis Acid Mediated Addition of Silyl Ketene Acetals to Sulfinimines

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Recent years showed that homochiral β-amino acids play an important role in the synthesis of numerous biologically active compounds,[1] and the synthetic methods leading to derivatives of β-amino acids are of great significance.[1a,b,d] One approach to the synthesis of β-amino acids is the addition of silyl ketene acetals to imines usually catalyzed by Lewis acids.[2] Few examples of an enantioselective version of this reaction are known. [3] The most versatile methods use imines with a removable group on the nitrogen atom, such as benzyl or silyl. In this paper, preparation of optically active β-amino esters by reaction of homochiral sulfinimines with ketene silyl acetals in the presence of Lewis acids is described. A new, camphor-derived chiral auxiliary has been used in these reactions. Because the behavior of sulfinimines in an acidic environment has not been studied before, it was of great interest to recognize their stability and reactivity in the presence of Lewis acids.

Sulfinimines are known as very good amine precursors. Reactions studied to date are the addition of organometallic reagents[4] including enolates[4d,f,g,i] and phosphites,[4c] reduction,[5] and addition of a cyanide group.[6] The main advantage of their use is that after creation of new stereogenic center, the homochiral sulfinyl auxiliary can be easily removed by acid treatment and recycled without loss of optical purity.

N-Benzylidene *p*-tolylsulfinamide **1,** easily available in an optically pure form,[7] was chosen as a model compound for this study. Ketene silyl acetals **2** reacted with **1** only in the presence of Lewis acids, providing *N*-*p*-toluenesulfinyl-β-amino esters **3** and **4** (Scheme 1).

The yield and diastereoisomeric excess (de) of the product strongly depends on the Lewis acid used (Table 1). The most effective appeared to be TMSOTf and BF_3·Et_2O. However, the latter gave poorer results at low temperatures compared to TMSOTf. Mild Lewis acids such as $Yb(OTf)_3$ or $Zn(OTf)_2$ were ineffective, and usually the conversion of the substrate was very slow. In the case of stronger Lewis acids such as $TiCl_4$ or $SnCl_4$ the substrate was consumed quickly but the yield of expected product was very low. It was necessary to use at least 1 mol equiv of the Lewis acid, but the excess did not improve the yield. The preferred solvent was dichloromethane. In one case where acetonitrile was used as solvent, the stereoselectivity was reversed (entry 12). Attempts to use enol silyl ethers as nucleophiles were unsuccessful. When trimethylsilyl ethers of enols derived from acetophenone or 1-acetylcyclohexene were used, only traces of expected products were detected.

The presence of strong Lewis acids in the reaction mixture may lead to racemization at sulfur atom of sulfinimine. Possibility of such a process in sulfinimine **1** was checked by removal of *p*-toluenesulfinyl auxiliary from nonpurified mixture **3c** + **4c** with TFA in MeOH and inspection of the ee of the resulting β-amino ester. In the case of using TMSOTf, the sample of sulfinamide (de 83%) afforded after acid treatment β-amino ester with 75% ee. A similar result was observed for BF_3·Et_2O. The de of sulfinamide **3c** was 77% (Table 1, entry 6), but the ee of the β-amino ester was only 63%. A possible explanation is that a small part of the minor diastereoisomer of sulfinamide **4c** hydrolyzed during aqueous workup (exact amount of missing β-amino ester was actually detected in reaction mixture) or partial racemization at the sulfur atom occurred in sulfinimine **1**.

The stereoselectivity of this reaction is dependent upon the ketene substitution. Silyl ketene acetal **2b** derived from phenyl acetate gave with (*S*)-(+) sulfinimine **1** predominantly diastereoisomer (3*S*,S_S)-**4b** with 59% de (entry 2). Ketene **2c** under the same reaction conditions (entry 4) formed sulfinamide (3*S*,S_S)-**3c** as a main diastereoisomer with 85% de. Although the absolute configuration at newly formed stereogenic center is the same (*S*), the steric course of these two reactions must be different. Interestingly, lithium enolate of methyl acetate reacts with (*S*)-(+)-**1** to give sulfinamide with (3*R*,S_S) configuration and 80% de.[8] Under the same conditions (THF, −70 °C), the lithium enolate of methyl isobutyrate gives (3*R*,S_S)-**4c** as the major diastereoisomer with 51% de (see Experimental Section). Both methods, i.e., metal enolate addition and silyl ketene addition, seem to be complementary.

In the course of our work on new homochiral organosulfur auxiliaries it was found that reaction of sulfinate

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Scheme 1

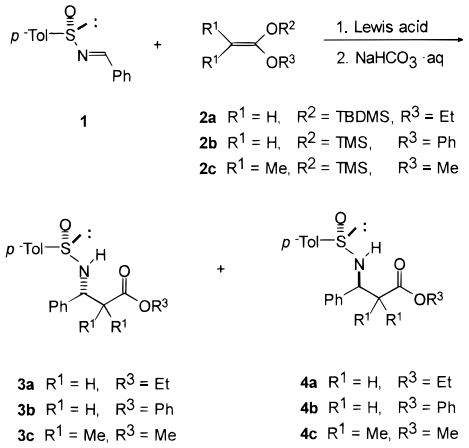
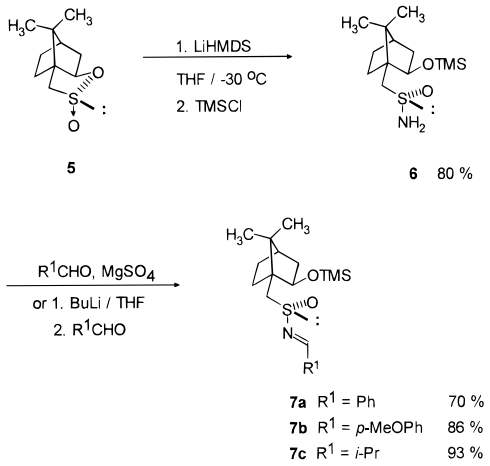


Table 1. Effect of Lewis Acid on Addition of Silyl Ketene Acetals to Sulfinimine 1[a]

entry	ketene acetal	temp, °C	Lewis acid	yield **3** + **4**, %	de,%[b](config)[c]
1	**2a**	−70	TMSOTf[d]	68	50
2	**2b**	−70	TMSOTf[d]	80	59 (3*S*,S_S)
3	**2c**	20	TMSOTf	40	71 (3*SR*,$S_S R_S$)
4	**2c**	−70	TMSOTf	79	85 (3*S*,S_S)
5	**2c**	−70	TMSOTf[d]	75	91 (3*SR*,$S_S R_S$)
6	**2c**	20	BF_3·Et_2O	56	77 (3*S*,S_S)
7	**2c**	−70	BF_3·Et_2O	9	34 (3*SR*,$S_S R_S$)
8	**2c**	20	BF_3·Et_2O	35	42 (3*SR*,$S_S R_S$)
9	**2c**	20	Et_2AlCl[e]	28	47 (3*SR*,$S_S R_S$)
10	**2c**	20	$EtAlCl_2$[e]	39	60 (3*SR*,$S_S R_S$)
11	**2c**	20	$Yb(OTf)_3$[f]	19	61 (3*SR*,$S_S R_S$)
12	**2c**	20	$Yb(OTf)_3$[f]	17	26 (3*RS*,$S_S R_S$)

[a] Reaction solvent was CH_2Cl_2 except for entries 8 and 12 which was CH_3CN. Reaction time was 16 h except for entries 1, 2 which was 6 h and entries 4, 5 which was 2 h. [b] Calculated from ^1H NMR spectra of crude reaction mixture. [c]Configuration of the major diastereoisomer was determined by conversion of enantiomerically enriched sulfinamide (TFA, MeOH) to known *β*-amino esters **9b**[3f] and **9d**[8] (R^1 = Ph, R^2 = H, R^3 = Me). [d] TMSOTf was added 30 min prior to addition of **2**. [e] 1 M solution in hexane. [f] 0.5 equiv.

Scheme 2

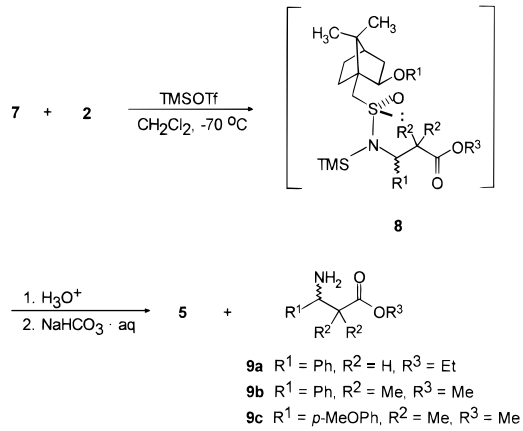


5[9] with lithium hexamethyldisilazide in THF at −30 °C followed by TMSCl quenching afforded primary sulfinamide **6** in 80% yield (Scheme 2). The stereochemistry of this reaction was assumed to be the same as the reaction of sulfinate **5** with Grignard reagents[9b] and on this basis was made the assignment at sulfur atom. 2-Hydroxy derivative of sulfinamide **6** can be isolated by quenching the reaction mixture with aq NH_4Cl (see Supporting Information). However, the use of TMS derivative **6** was more convenient due to its better solubility. It also turned out that **6** is stable enough toward hydrolysis and can be stored for a long time without decomposition. Condensation of sulfinamide **6** with aromatic aldehydes was performed in boiling toluene or by reaction of its anion generated by *n*-butyllithium in THF at −40 °C. In both cases optically pure sulfinimines were obtained as confirmed by NMR. The yield of product **7a** was higher using *n*-butyllithium (70%) than carrying out the reaction in boiling toluene (41%). Aliphatic aldehydes can be conveniently condensed with **6** in dichloromethane in the presence of $MgSO_4$. The reactions of ketene silyl acetals **2** with sulfinimines **7** (Table 2) were successful only when TMSOTf was used as the Lewis acid. Aromatic sulfinimines **7a** and **7b** gave expected *β*-amino esters **9** in good yields as opposed to aliphatic sulfinimine **7c** which gave only traces of the product. Sulfinamide **8** was not isolated, as most of the product, even after basic workup, was already hydrolyzed to *β*-amino ester **9** and sulfinate **5** (Scheme 3). The enantiomeric excess of **9b** was 81% as determined by ^1H NMR using *tert*-butylphenylphosphinothioic acid[10] as a chiral solvating agent. This value is comparable with those obtained using *p*-tolylsulfinyl derivative **1** and ketene silyl acetal **2c** (Table 1, entry 4). With ketene **2a**, ee is even higher using sulfinimine **7a**. The main advantage of using 10-isobornylsulfinate **5** is that removal of sulfinyl auxiliary is easy (no necessary to use TFA) and quantitative. Epimerization at the sulfur atom and side reactions were not detected as opposed to *p*-toluenesulfinyl derivative.[8] The optical purity of sulfinate **5** and sulfinimines **7** can be easily checked by ^1H NMR due to the presence of several stereogenic centers.

Table 2. TMSOTf-Mediated Addition of Silyl Ketene Acetals to 10-Isobornylsulfinimines

entry	substrate	product	yield, %	ee, % (config)
1	**2a** + **7a**	**9a**	63	81 (*S*)
2	**2c** + **7a**	**9b**	74	81 (*S*)
3	**2c** + **7b**	**9c**	79	40

Scheme 3



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The results presented here show a rather low reactivity of sulfinimines with derivatives of enol silyl ethers. This may be due to weak activation of the C=N bond by the sulfinyl group (compared to *N*-sulfonylimines[11]) or a different interaction with Lewis acids than observed in simple imines. The latter hypothesis seems to be reasonable in light of the high dependence of the above-mentioned reaction on the Lewis acid used. Unfortunately, very little is known about the site of protonation of sulfinimines. ^{1}H NMR spectra of sulfinimine **1** with BF_3·Et_2O or TMSOTf recorded at room temperature do not exhibit any changes in chemical shifts. This aspect of the chemistry of sulfinimines is now under investigation.

Experimental Section

All reactions were performed under an argon atmosphere. Anhydrous solvents were obtained as follows: THF was distilled from sodium benzophenone ketyl, dichloromethane was distilled from CaH_2, acetonitrile was distilled from P_2O_5. Boron trifluoride etherate and diisopropylamine were distilled from CaH_2. Ketene silyl acetals were prepared by known procedures.[12] Melting points were uncorrected. NMR spectra were recorded at 200 and 500 MHz (^{1}H NMR).

General Procedure for Preparation of *N*-*p*-Toluenesulfinyl-*β*-amino Acid Esters. *N*-benzylidene-*p*-tolyl-sulfinamide **1** (160 mg, 0.66 mmol) and ketene silyl acetal **2** (1 mmol) were dissolved in dry CH_2Cl_2 (4 cm^3) under argon and cooled to −70 °C. Lewis acid (0.8 mmol) was added slowly, and the reaction mixture was kept for the time and temperatures indicated in Table 1. The reaction mixture was quenched with saturated solution of $NaHCO_3$ and extracted with dichloromethane. Organic extracts were dried and evaporated. Chromatography on silica gel (CH_2Cl_2 and MeOH, 50:1) gave mixture of diastereoisomers.

Methyl *N*-(*p*-tolylsulfinyl)-3-amino-2,2-dimethyl-3-phenylpropanoate (3c and 4c). IR (KBr): 3177 (NH), 1729 (C=O), 1089, 1057 (SO) cm^{-1} (3*S*,*S*$_S$)−**(3c)**. ^{1}H NMR ($CDCl_3$, ref TMS): δ 1.07 (s, 3H), 1.28 (s, 3H), 2.29 (s, 3H), 3.69 (s, 3H), 4.36 (d, J = 7.6 Hz, 1H), 5.56 (d, J = 7.6 Hz, 1H), 6.85−7.15 (m, 9H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 21.1, 21.4, 24.7, 47.0, 51.9, 62.6, 125.7, 127.0, 127.5, 127.8, 128.8, 139.5, 140.7, 140.8, 176.7. (3*R*,*S*$_S$)−**(4c)**: ^{1}H NMR ($CDCl_3$, ref TMS): δ 1.13 (s, 3H), 1.17 (s, 3H), 2.41 (s, 3H), 3.66 (s, 3H), 4.54 (d, J = 5.6 Hz, 1H), 5.12 (d, J = 5.6 Hz, 1H), 7.3 (m, 7H), 7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 21.0, 21.3, 24.1, 47.0, 52.1, 64.5, 125.3, 127.8, 127.9, 128.7, 129.4, 138.5, 141.2, 142.3, 176.5. HR LSIMS calcd for $C_{19}H_{24}NO_3S$ $(M + H)^+$: 346.1477, found: 346.1460. Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05; S, 9.28. Found: C, 65.95; H, 6.89; N, 4.09; S, 9.12.

Phenyl *N*-(*p*-Tolylsulfinyl)-3-amino-3-phenylpropanoate (3b and 4b). IR (KBr): 3291 (NH), 1754 (C=O), 1090, 1023 (SO) cm^{-1}, (3*S*,*S*$_S$)−**(4b)**. ^{1}H NMR ($CDCl_3$, ref TMS): δ 2.26 (s, 3H), 3.14 and 3.20 (ABX, J = 17.5, 6.5 Hz, 2H), 4.81 (ddd, J = 6.5, 6.5, 7.0 Hz, 1H), 5.09 (d, J = 7.0 Hz, 1H), 6.82 (m, 2H), 7.1−7.5 (m, 12H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 21.1, 42.5, 53.3, 121.2, 125.7, 125.7, 126.5, 127.5, 128.4, 129.1, 129.2, 140.5, 140.7, 141,0, 150.0, 169.1. (3*R*,*S*$_S$)−**(3b)**. ^{1}H NMR ($CDCl_3$, ref TMS): δ 2.30 (s, 3H), 3.0 (d, J = 6.0 Hz, 2H), 4.95 (m, 2H), 6.79 (m, 2H), 7.0−7.5 (m, 12H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 21.1, 42.2, 54.6, 121.1, 125.2, 125.7, 127.1, 127.9, 128.6, 129.1, 129.3, 140.1, 141.2, 141.8, 150.0, 169.0. Anal. Calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69; S, 8.45. Found: C, 69.45; H, 5.58; N, 3.64; S, 8.30.

Addition of Lithium Enolate of Methyl Isobutyrate to Sulfinimine 1. To the solution of LDA prepared by addition of *n*-butyllithium (1.6 M in hexane, 1.05 mL, 1.7 mmol) to the solution of diisopropylamine (172 mg, 1.7 mmol) in THF (5 mL) was added dropwise at −20 °C methyl isobutyrate (174 mg, 1.7 mmol). The reaction mixture was stirred for 1 h at −20 °C. The solution was cooled to −70 °C, and sulfinimine (*S*)-(+)-**1** (324 mg, 1.3 mmol) in THF (1.5 mL) was added slowly. Stirring was continued for 4 h, and a saturated solution of NH_4Cl was added at −70 °C. The reaction mixture was extracted three times with dichloromethane (2 mL), and the organic extracts were dried ($MgSO_4$). Filtration and evaporation gave pure sulfinamides **3c** and **4c** (410 mg, 89%). The de of the (3*R*,*S*$_S$) diastereoisomer was 51%, as determined by ^{1}H NMR.

(1*S*, 2*R*, 4*R*, *S*$_S$)-7,7-Dimethyl-2-(trimethylsilyloxy)bicyclo-[2.2.1]heptane-1-methanesulfinamide (6). To a solution of lithium hexamethyldisilazide, prepared from HMDS (34 mmol, 5.40 g) and *n*-butyllithium (1.6 M in hexane, 34 mmol, 21 mL) in THF (80 mL) at −30 °C, was added a solution of sulfinate **5** (17 mmol, 3.37 g) in THF (18 mL). The mixture was stirred at −30 °C for 3 h. Trimethylsilyl chloride (50 mmol, 5.46 g) was added dropwise, and the solution was stirred for next 2 h at −30 °C. The cooling bath was removed, and the mixture was left overnight at room temperature. A saturated solution of NH_4Cl was added, and the reaction mixture was extracted three times with CH_2Cl_2. The organic extract was dried and evaporated to give 3.9 g (80%) of waxy solid which was pure enough for next steps. Analytically pure sample was obtained by crystallization from hexane. Yield 1.46 g (first crop) and 0.48 g from second crop (40%). Mp 146−148 °C; $[\alpha]^{22}_D$ = −116.6 (c = 0.98, $CHCl_3$); IR (KBr): 3269 (NH), 1047 (SO) cm^{-1}. ^{1}H NMR ($CDCl_3$, ref 7.26 ppm): δ 0.01 (s, 9H), 0.77 (s, 3H), 0.95 (s, 3H), 1.0 (m, 1H), 1.3 (m, 1H), 1.4 (m, 5H), 2.50, 3.18 (AB, J = 12.7 Hz, 2H), 3.87 (dd, J = 3.6, 7.1 Hz, 1H), 4.40 (br, 2H), ^{13}C NMR ($CDCl_3$ ref 77 ppm): δ 0.2, 19.9, 20.4, 27.2, 30.1, 41.8, 44.6, 48.5, 50.0, 57.5, 76.7. MS: 289 (M^+), 225 (M^+ − $SONH_2$). Anal. Calcd for $C_{13}H_{27}NO_2SSi$: C, 53.93; H, 9.40; N, 4.84. Found: C, 53.98; H, 9.59; N, 4.66.

Typical Procedure for the Synthesis of 10-Isobornyl Sulfinimines. (1*S*,2*R*,4*R*,*S*$_S$)-7,7-Dimethyl-*N*-(phenylmethylene)-2-(trimethylsilyloxy)bicyclo[2.2.1]heptane-1-methanesulfinamide (7a). To a stirred solution of sulfinamide **6** (1.264 g, 4.4 mmol) in THF (18 mL) was added a solution of *n*-butyllithium (1.6 M in hexane, 3.0 mL, 4.8 mmol) at −40 °C, and the resulting white slurry was stirred for 1 h. The solution of benzaldehyde (0.56 g, 5.3 mmol) in THF (1.5 mL) was added at −20 °C, and the reaction mixture was stirred for 4 h, warmed to room temperature, and left to stand overnight. Saturated solution of NH_4Cl was added, and the reaction mixture was extracted three times with dichloromethane (15 mL). Combined organic layers were dried, filtered, and evaporated. Purification by chromatography on silica gel (CH_2Cl_2 and hexane 1:1 and then CH_2Cl_2) afforded 1.16 g (70%) of a colorless oil. $[\alpha]^{22}_D$ = −59.1 (c = 1.82, CH_2Cl_2), IR (CH_2Cl_2) 1575, 1608 (C=N), 1089 (SO) cm^{-1}. ^{1}H NMR ($CDCl_3$, ref 7.26 ppm): δ 0.12 (s, 9H), 0.82 (s, 3H), 1.07 (s, 3H), 1.1 (m, 1H), 1.5−1.9 (m, 6H), 2.26; 3.61 (AB, J = 12.9 Hz, 2H), 4.10 (dd, J = 3.9, 6.6 Hz, 1H), 7.5 (m, 3H), 7.85 (m, 2H), 8.62 (s, 1H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ = 0.3, 20.1, 20.5, 27.4, 30.7, 42.1, 44.8, 48.8, 50.3, 57.3, 77.0, 128.8, 129.3, 132.2, 134.0, 160.9. HRMS: calcd for $C_{20}H_{31}NO_2SSi$ $(M)^+$: 377.1845; found: 377.1846. Calcd for $C_{19}H_{28}NO_2SSi$ $(M - CH_3)^+$: 362.1610; found: 362.1608.

(1*S*,2*R*, 4*R*,*S*$_S$)-7,7-Dimethyl-*N*-(4-methoxyphenylmethylene)-2-(trimethylsilyloxy)bicyclo[2.2.1]heptane-1-methanesulfinamide (7b). Crude product was purified by crystallization from hexane. Yield 1.764 g (86%). Mp 112−113 °C; $[\alpha]^{22}_D$ = −59.5 (c = 1.12, $CHCl_3$). IR (KBr): 1599 (C=N), 1093 (SO) cm^{-1}. ^{1}H NMR ($CDCl_3$, ref 7.26 ppm): δ 0.12 (s, 9H), 0.81 (s, 3H), 1.07 (s, 3H), 1.1 (m, 1H), 1.5−1.9 (m, 6H), 2.24 and 3.57 (AB, J = 12.8 Hz, 2H), 3.87 (s, 3H), 4.09 (dd, J = 4.0, 6.8 Hz, 1H), 7.0 (m, 2H), 7.8 (m, 2H), 8.54 (s, 1H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 0.3, 20.2, 20.5, 27.4, 30.7, 42.1, 44.9, 48.8, 50.3, 55.4, 57.5, 77.1, 114.2, 127.2, 131.2, 160.0, 162.9. Anal. Calcd for $C_{21}H_{33}NO_3SSi$: C, 61.88; H, 8.16; N, 3.44. Found: C, 61.95; H, 8.24; N, 3.29.

(1*S*,2*R*, 4*R*,*S*$_S$)-7,7-Dimethyl-*N*-(2-methylpropylidene)-2-(trimethylsilyloxy)bicyclo[2.2.1]heptane-1-methanesulfinamide (7c). To a solution of sulfinamide **6** (0.482 mg, 1.7 mmol) in dichloromethane (7.5 mL) were added anhydrous magnesium sulfate (ca. 200 mg) and a few crystals of pyridinium *p*-toluenesulfonate. Freshly distilled isobutyraldehyde (0.6 g, 8.3

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mmol) was added, and the resulting slurry was gently shaken for 3 days at room temperature. Filtration and evaporation of volatiles gave pure sulfinimine **7c** as a colorless oil. Chromatography on silica gel (dichloromethane) afforded 0.531 g (93%) of analytically pure product. $[\alpha]^{22}_D = +8.4$ ($c = 1.03$, $CHCl_3$). IR (neat) 1621 (C═N), 1090 (SO) cm^{-1}, ^1H NMR ($CDCl_3$, ref 7.26 ppm): δ 0.09 (s, 9H), 0.80 (s, 3H), 1.05 (s, 3H), 1.16 (d, $J = 6.8$ Hz, 6H), 1.47 (m, 1H), 1.74 (m, 6H), 2.08 (d, $J = 12.9$ Hz, 1H), 2.69 (m, 1H), 3.45 (d, $J = 12.9$ Hz, 1H), 4.04 (dd, $J = 3.9$, 6.7 Hz, 1H), 7.96 (d, $J = 4.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 0.2, 18.9, 20.1, 20.5, 27.4, 30.8, 34.6, 42.1, 44.9, 48.8, 50.3, 57.2, 77.0, 171.6. HRMS: calcd for $C_{17}H_{33}NO_2SSi$ $(M)^+$: 343.2001; found: 343.2024.

General Procedure for Preparation of *β*-Amino Esters 9. To the solution of sulfinimine **7b** (152 mg, 0.37 mmol) in dichloromethane (3.5 mL) cooled to −70 °C, was added dropwise TMSOTf (118 mg, 0.53 mmol). The mixture was stirred for 15 min at −70 °C and ketene silyl acetal **2** (105 mg, 0.60 mmol) was added, dropwise. The solution was kept for 6 h at −70 °C. Water (1 mL) was added and the cooling bath was removed. After the reaction mixture was stirred 30 min at room temperature, saturated $NaHCO_3$ solution (3 mL) was added and stirring was continued for next 30 min. The mixture was extracted three times with CH_2Cl_2, and the combined organic layers were dried, filtered, and evaporated. The residue was chromatographed on a short pad of silica gel eluting CH_2Cl_2 until removal of all quantity of sulfinate **5** and then eluting with CH_2Cl_2 and MeOH, 5:1. Yield 70 mg (79%).

Methyl 3-Amino-2,2-dimethyl-3-(4-methoxyphenyl)propanoate (9c). Oil. IR (neat): 1728 (C═O). ^1H NMR ($CDCl_3$, ref $CHCl_3$, 7.26 ppm): δ 1.07 (s, 3H), 1.14 (s, 3H), 1.61 (br 2H), 3.69 (s, 3H), 3.80 (s, 3H), 4.20 (s, 1H), 6.84 (m, 2H), 7.20 (m, 2H), ^{13}C NMR ($CDCl_3$, ref 77 ppm): δ 19.4, 23.5, 47.8, 51.7, 55.1, 61.2, 113.1, 129.0, 133.9, 158.7, 177.8. Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.47; H, 8.01; N, 5.93.

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Supporting Information Available: Determination of configuration for compounds **3b**, **4b, 3c**, **4c** and ^{13}C NMR spectra of sulfinimines **7a** and **7c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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