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Variation of the C_1 Component in the Silicon-Induced Domino Synthesis of Cyclopentanes

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Abstract

The reaction of mono- or bissilylated thioanisole derivatives **2b-e** with 3,4-epoxybutyl tosylate (**3**) affords the cyclopentanols **6a-c**. Migratory aptitudes of two different silyl groups in the Brook 1,4-rearrangement is examined starting from **2d, e** giving the order $SiMe_2Ph > SiMe_3 > SiMePh_2$. The relative configuration of the resulting 1,3-functionalized cyclopentanes is established by NOE experiments after derivatization of the alcohol to the corresponding pivalates **7a-c**.

Keywords: Carbanion; Oxiranes; Rearrangements; Silicon and compounds

Recently, we have reported the one-pot synthesis of 1,3-difunctionalized cyclopentanes by a silicon-induced domino reaction [1,2]. This reaction proceeds via 1,4-shift of the silyl group from carbon to oxygen [3] after nucleophilic attack of a silyl-substituted thioacetal anion on an epoxyhomoallyl tosylate, followed by intramolecular displacement of the tosylate group (Scheme 1, Route B) [4]. Remarkably, the approach is not limited to a migrating $SiMe_3$ group, but the bulky $SiMe_2{}^tBu$ group migrates too [5,6,7,8], but then oxetane formation becomes a competing process (Scheme 1, Route A).

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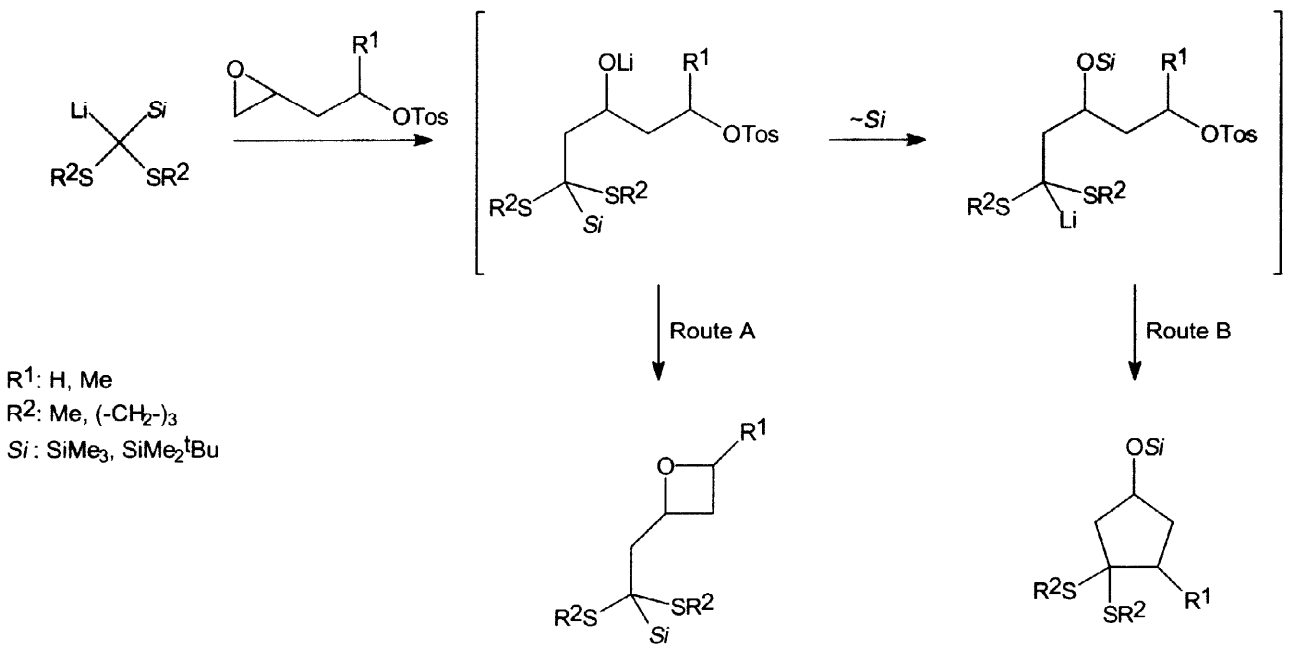
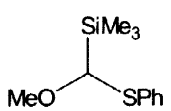


Scheme 1

Here we wish to report on the extension of this reaction by using the C_1 bis-anion equivalents **1, 2a-f** which should allow higher flexibility in subsequent transformations [9]. Furthermore, the modifications should provide information on the relative migratory aptitudes of different silyl groups in the cyclization reaction.



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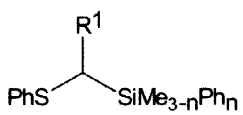
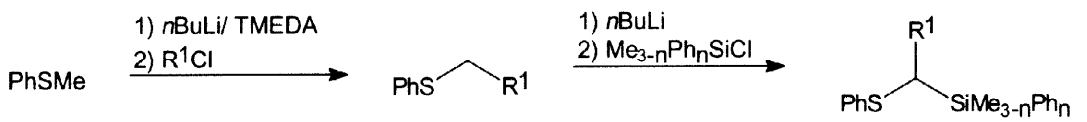


2a-f

2a: R^1 = H, n = 0
b: R^1 = $SiMe_3$, n = 0
c: R^1 = $SiMe_2Ph$, n = 1
d: R^1 = $SiMe_3$, n = 1
e: R^1 = $SiMe_3$, n = 2
f: R^1 = $SiMe_3$, n = 3

The C_1 building blocks **1** and **2a,b** have been reported before [10,11,12]. The C_1 components **2c-f** were synthesized by deprotonation and subsequent silylation of thioanisole using the procedure of Seebach (Scheme 2) [12].

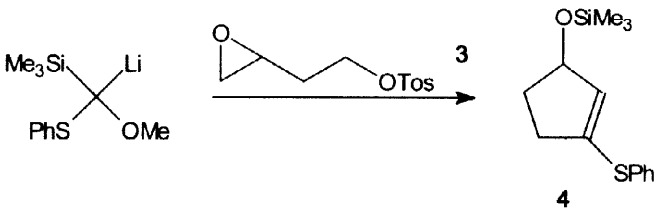


R^1 = $SiMe_3$, 84%
R^1 = $SiMe_2Ph$, 67%

2c: 77%
d: 71%
e: 59%
f: 56%

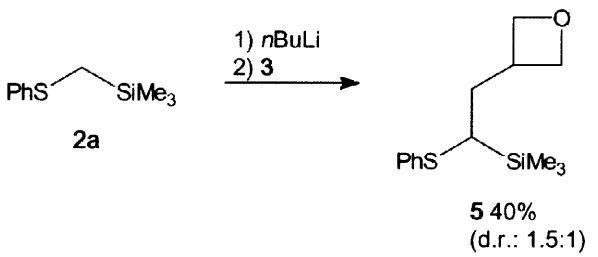
Scheme 2

Reaction of the lithiated O,S-acetal **1** with 3,4-epoxybutyl tosylate (**3**) gave vinyl sulfide **4** in only 14% yield. This indicates that the desired domino reaction does occur, but only in low yields and with elimination of methoxide after the cyclization step (Scheme 3).



Scheme 3

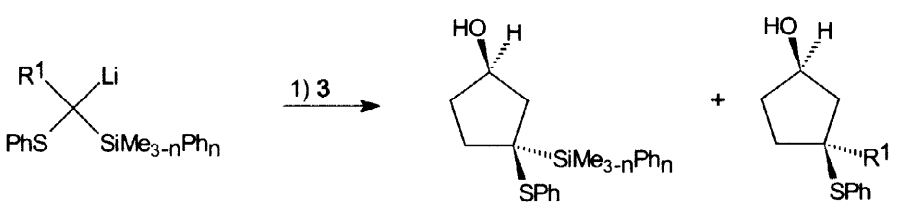
Use of **2a** as C_1 component yielded the oxetane **5** as a mixture of diastereomers (Scheme 4).



Scheme 4

No cyclopentane could be isolated [13]. Insufficient stabilization of the carbanion after 1,4-carbon-oxygen shift seems to be the reason for this failure leading to the alternative oxetane formation (cf. Scheme 1, Route A).

The introduction of a second silyl group into **2a** should favour cyclopentane formation because of its additional stabilizing effect on the carbanion after 1,4-migration. Indeed, reaction of lithiated **2b** with **3** led to the 1,3-difunctionalized cyclopentane, which was isolated as cyclopentanol **6a** after purification by column chromatography (SiO_2) in good yield (Table1, entry 1).



6a: R^1, $SiMe_{3-n}Ph_n$ = $SiMe_3$
b: R^1, $SiMe_{3-n}Ph_n$ = $SiMe_2Ph$
c: R^1, $SiMe_{3-n}Ph_n$ = $SiMePh_2$

Scheme 5

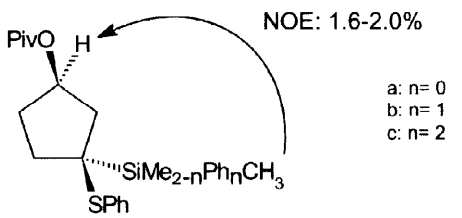
Table 1.
Cyclopentane Formation by Silicon-Induced Domino Reaction and Diastereomer Ratios (d.r.)[a]

Entry	C_1 Component	~R^1 (d.r.)	~$SiMe_{3-n}Ph_n$ (d.r.)
1	**2b**	**6a** 76% (>20:1)[b]	---
2	**2c**	**6b** 62% (8.1:1)	---
3	**2d**	**6b** 35% (6.1:1)	**6a** 40% (>20:1)[b]
4	**2e**	**6c** 28% (10.3:1)	**6a** 16% (>20:1)[b]
5	**2f**	---	---

a) Diastereomer ratios were determined by gas chromatography after derivatization to the corresponding pivalate **7a-c**.
b) No other diastereomer could be detected in the 200 MHz ^{1}H NMR spectrum.

As judged by the yields of products **6a** vs. **6b** from **2d**, the $SiMe_2Ph$ group migrates a little better than the the $SiMe_3$ group (Table 1, entry 3). Obviously, the phenyl ring has a stabilizing effect on the migrating group and this electronic effect compensates steric hindrance. If a second methyl group on silicon is replaced by a phenyl ring as in **2e** the overall yield of **6** decreases, indicating that approach of **2e** on **3** is sterically hindered. Interestingly, **6c** resulting from migration of the $SiMe_3$ group is the main product, and not **6a**. This implies that the bulkiness of $SiMePh_2$ overrules the favourable electronic effect (Table 1, entry 4). Starting from **2f**, no cyclization product could be observed (Table 1, entry 5). Steric hindrance of the initial epoxide ring opening seems to be the reason for this failure.

The relative configuration of the major diastereomer was determined by NOE experiments after derivatization of the alcohol to the corresponding pivalate **7a-c** (62-92%). A 1,3-*trans*-arrangement of pivalate and silyl group was confirmed in each case.



7a-c

Experimental Section

The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX-200 (200 MHz) as dilute solutions in $CDCl_3$ with TMS as internal standard. Chemical shift values are given in parts per million (ppm). NOE measurements were carried out on a Bruker ARX-400 (400 MHz). The infrared spectra were recorded using a Bruker Vektor 22 spectrometer as neat films or as KBr-pellet. Elemental analyses were determined by the Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. High resolution mass spectrum was measured by the Hans-Knöll-Institut für Naturstoff-Forschung, Jena. Column chromatography was carried out using Merck silica gel 6 (70-230 mesh). Silylated thioanisoles **1, 2a,b** [6] and the epoxide **3** [1] are described in the literature.

General procedure for the preparation of silylated thioanisols 2d-f: A solution of **2a** in dry THF (1 ml/mmol) was cooled to -78°C, one equiv. of n-BuLi (1.6 M in hexane) was added dropwise and the mixture was stirred at 0 °C for 2 h. At -78 °C the appropriate silane (1.1 equiv.) was added to this solution.The solution was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was hydrolyzed with diethyl ether/saturated NH_4Cl solution (1:1). The aqueous phase was separated and extracted twice with diethyl ether. The combined organic extracts were dried and the solvent evaporated. The crude product was purified by column chromatography (PE).

Phenyldimethylsilyl(phenylthio)(trimethylsilyl)methane (2d): Preparation from 10.86 g (55.3 mmol) of **2a** gave 12.93 g (71%) as a colourless oil. ^{1}H NMR: δ, -0.02 (*s*, 9H, Si*Me*$_3$), 0.38 and 0.45 (each *s*, 3H, Si*Me*$_2$Ph), 1.73 (*s*, 1H, C*H*), 7.05-7.68 (*m*, 10H, SiMe$_2$*Ph*, S*Ph*); ^{13}C NMR: δ, -2.2, -1.8 (Si*Me*$_2$Ph), -0.4 (Si*Me*$_3$), 18.7 (*C*H), 125.0, 127.6, 127.9, 128.5, 129.1, 133.9, 138.7, 140.0 (S*Ph*, SiMe$_2$*Ph*); IR: 3070, 3019, 2955, 2897, 1582, 1478, 1438, 1427, 1250, 1114, 1086, 1024, 995, 839, 782, 734, 669 cm^{-1}; $C_{18}H_{26}SSi_2$ (330.62): calcd. C 65.39, H 7.93, S 9.70; found C 64.99, H 8.06, S, 9.71.

Diphenylmethylsilyl(phenylthio)(trimethylsilyl)methane (2e): Preparation from 12.62 g (64.2 mmol) of **2a** gave 14.92 g (59%) as a colourless oil. ^{1}H NMR: δ, 0.01 (*s*, 9H, Si*Me*$_3$), 0.79 (*s*, 3H, Si*Me*Ph$_2$), 2.21 (*s*, 1H, C*H*), 7.05-7.72 (*m*, 15H, SiMe*Ph*$_2$, S*Ph*); ^{13}C NMR: δ, -3.4 (Si*Me*$_3$), -0.3 (Si*Me*Ph$_2$), 17.2 (*C*H), 125.6, 127.5, 127.7, 128.1, 128.4, 129.2, 129.3, 134.7, 134.8, 136.4, 136.8, 139.6 (S*Ph*, SiMe*Ph*$_2$); IR: 3069, 3050, 3018, 2955, 2896, 1582, 1478, 1427, 1250, 989, 838, 790, 735, 698 cm^{-1}; $C_{23}H_{28}SSi_2$ (392.69): calcd. C 70.34, H 7.19, S 8.16; found C 70.33, H 7.12, S 7.95.

Phenylthio(trimethylsilyl)(triphenylsilyl)methane (2f): Preparation from 12.4 g (63.2 mmol) of **2a** gave 16.06 g (56%) as colourless solid (Fp: 64 °C). ^{1}H NMR: δ, 0.00 (*s*, 9H, Si*Me*$_3$), 2.61 (*s*, 1H, C*H*), 7.12-7.89 (*m*, 20H, Si*Ph*$_3$, S*Ph*); ^{13}C NMR: δ, 0.3 (Si*Me*$_3$), 16.0 (*C*H), 125.1, 127.6, 127.9, 128.5, 129.5, 130.1, 134.7, 134.9, 135.1, 135.4, 136.1, 139.7 (Si*Ph*$_3$, S*Ph*); IR: 3070, 3050, 3014, 2954, 2926, 2854, 1726, 1632, 1582, 1479, 1428, 1249, 1188, 1167, 1109, 1024, 998, 854, 795, 738, 699 cm^{-1}; $C_{28}H_{30}SSi_2$ (454.75): calcd. C 73.95, H 6.65, S 7.05; found C 73.96, H 6.83, S 7.03.

Bis(phenyldimethylsilyl)(phenylthio)methane (2c): A solution of 8.82 g (71 mmol) of thioanisol in dry THF (1 ml/mmol) was cooled to -78 °C and one equiv. of *n*Buli (1.6M in hexane) and one equiv. of TMEDA were added. The solution was stirred at 0 °C for 2 h. At -78 °C 1.1 equiv. of chlorophenyldimethylsilane was added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After aqueous workup the resulting phenyldimethylsilyl phenylthiomethane was deprotonated and silylated again, repeating the general procedure described above. Column chromatography gave 15.11 g (54%) of **2c** as a colourless solid (Fp: 34 °C). ^{1}H NMR: δ, -0.01 (*s*, 12H, Si*Me*$_2$Ph), 1.66 (*s*, 1H, C*H*), 6.81-7.32 (*m*, 15H, SiMe$_2$*Ph*, S*Ph*); ^{13}C NMR: δ, -2.2 (Si*Me*$_2$Ph), 19.1 (*C*H), 125.2, 127.6, 128.4, 128.5, 129.1, 133.9, 138.5, 139.7 (S*Ph*, SiMe$_2$*Ph*); IR: 3069, 3050, 2956, 1582, 1478, 1427, 1250, 1113, 991, 836, 733, 699 cm^{-1}; $C_{23}H_{28}SSi_2$ (392.69): calcd. C 70.34, H 7.19, S 8.16; found C 70.15, H 7.22, S 8.12.

General procedure for the preparation of compounds 4,5 and 6a-c by the silicon-induced domino reaction: To a solution of 1.2 equiv. of silylated thioanisol **1, 2a-f** in dry THF (4 ml/mmol) 1.1 equiv. of *n*-BuLi (1.6 M in hexane) was added at -78 °C. The solution was stirred at 0 °C for 2 h and cooled again to -78 °C. One equiv. of **3** in dry THF (4 ml/mmol) was added dropwise and the reaction mixture was allowed to warm to 0 °C and stirred for 12 h. The mixture was hydrolyzed with diethyl ether/ saturated NH_4Cl solution (1:1), the aqueous phase was extracted twice with diethyl ether, the combined organic layers were dried and the solvent evaporated. The crude products were purified by column chromatography (PE/EE 20:1→10:1).

1-Phenylthio-3-(trimethylsilyloxy)cyclopent-1-ene (4): 1.21 g (5 mmol) of **3** gave 187 mg (14%) as yellow oil. ^{1}H NMR: δ, 0.03 (*s*, 9H, Si*Me*$_3$), 1.84-2.00 and 2.84-3.13 (each *m*, 2H, C*H*$_2$), 5.08 (*dt*, *J*= 4.6, 7.4 Hz , 1H, *3-H*), 6.56 (*d*, *J*= 7.4Hz, 1H, *2-H*), 6.90-7.35 (m, 5H, S*Ph*); ^{13}C NMR: δ, -0.8 (Si*Me*$_3$), 29.6, 36.5 (*C-4, C-5*), 69.2 (*C-3*), 129.0, 129.1, 129.5 (S*Ph*), 135.6, 137.2 (*C-1*, S*Ph*), 153.6 (*C-2*); IR: 3420, 3060, 2940, 1710, 1580, 1480, 1440, 1250, 1020, 840, 740, 690 cm^{-1}; no elemental analysis could be obtained because of its decomposition character.

2-(2-Phenylthioethyl-2-trimethylsilyl)oxetane (5): 1.21 g (5 mmol) of **3** gave 538 mg (40%) of two diastereomers (1.5:1*) as colourless oil. ^{1}H NMR: δ, -0.05 (*s*, 9H*, Si*Me*$_3$), -0.02 (*s*, 9H, Si*Me*$_3$), 1.64 [*ddd*, *J*= 4.4, 11.4, 14.4 Hz, 1H, PhS(SiMe$_3$)CHC*H*$_2$], 1.84-2.20 and 2.21-2.50 (each *m*, 9H), 4.20-4.48 (*m*, 4H, *4-H*, 4-H*), 4.74-4.90 (*m*, 2H, *2-H*, 2-H*), 6.92-7.25 (*m*, 10H, S*Ph**, S*Ph*); ^{13}C NMR: δ, -2.8*, -2.4 (Si*Me*$_3$), 27.6, 27.7* (*C-3*), 29.1, 29.5* (PhS(SiMe$_3$)*C*H), 39.9, 40.7* (PhS(SiMe$_3$)CH*C*H$_2$), 67.7*, 67.8 (*C-4*), 80.5*, 80.9 (*C-2*), 125.5, 125.7, 127.3, 128.6, 128.7, 129.0, 138.0, 138.6 (S*Ph*, S*Ph**); IR: 2950, 2880, 1580, 1480, 1250, 980, 840, 740, 690 cm^{-1}; $C_{14}H_{22}OSSi$ (266.45): calcd. C 63.10, H 8.32, S 12.03; found C 62.69, H 8.08, S 11.89.

3-Phenylthio-3-(trimethylsilyl)cyclopentanol (6a): 242 mg (1 mmol) of **3** and **2b** as C_1 component gave 201 mg (76%) as a colourless oil. ^{1}H NMR: δ, 0.00 (*s*, 9H, Si*Me*$_3$), 1.63-2.11 (*m*, 6H, C*H*$_2$), 2.31 (*br s*, 1H, O*H*), 4.21 (*qui*, *J*= 4.4 Hz, 1H, *1-H*), 7.20-7.65 (*m*, 5H, S*Ph*); ^{13}C NMR: δ, -3.0 (Si*Me*$_3$), 33.3, 35.9 (*C-4, C-5*), 43.7 (*C-2*), 44.3 (*C-3*), 74.9 (*C-1*), 128.7, 128.9, 133.1, 137.1 (S*Ph*); IR: 3380, 2960, 1440, 1250, 1070, 840, 750, 690 cm^{-1}; $C_{14}H_{22}OSSi$ (266.45): calcd. C 63.10 H 8.32 S 12.03; found C 62.67, H 8.34, S 11.92.

3-Phenyldimethylsilyl-3-(phenylthio)cyclopentanol (6b): 1.21 g (5 mmol) of **3** and **2c** as C_1 component gave 1.02 g (62%) as a colourless oil. ^{1}H NMR: δ, 0.12, 0.18 (each *s*, 3H, Si*Me*$_2$Ph); 1.33-1.48 (*m*, 2H), 1.62-2.06 (*m*, 5H), 3.76-3.89 (*m*, 1H, *1-H*), 6.99-7.47 (*m*, 10H, S*Ph*, SiMe$_2$*Ph*); ^{13}C NMR: δ, -4.6, -4.5 (Si*Me*$_2$Ph), 33.6, 35.7 (*C-4, C-5*), 44.2 (*C-2*), 44.5 (*C-3*), 74.7 (*C-1*), 127.7, 128.7, 128.9, 129.3, 132.8, 134.5, 136.6, 137.0 (S*Ph*, SiMe$_2$*Ph*); IR: 3396, 3069, 2956, 2861, 1473, 1427, 1409, 1250, 1069, 1111, 1026, 831, 818, 774, 749, 737, 702 cm^{-1}; $C_{19}H_{24}OSSi$ (328.52): EI-HRMS: m/z = 328.1326 (Δ = -0.9 mmu).

3-Diphenylmethylsilyl-3-(phenylthio)cyclopentanol (6c): 1.21 g (5 mmol) of **3** and **2e** as C_1 component gave as second major fraction 537 mg (28%) as a colourless oil. ^{1}H NMR: δ, 0.53 (*s*, 3H, Si*Me*Ph$_2$), 1.57-1.71 (*m*, 1H, C*H*$_2$), 2.01 (*br s*, 1H, O*H*), 2.14-2.52 (*m*, 5H, C*H*$_2$), 3.98-4.12 (*m*, 1H, *1-H*), 7.13-7-76 (*m*, 15H, S*Ph*, SiMe*Ph*$_2$); ^{13}C NMR: δ, -5.2 (Si*Me*Ph$_2$), 34.4, 35.5 (*C-4, C-5*), 44.0 (*C-3*), 44.8 (*C-2*), 74.6 (*C-1*), 127.7, 127.8, 128.5, 129.0, 129.3, 129.4, 132.3, 134.9, 135.1, 135.4, 135.5, 137.4 (S*Ph*, SiMe*Ph*$_2$); IR: 3386, 3070, 3049, 2956, 2860, 1473, 1427, 1254, 1109, 1069, 1025, 789, 738, 726, 699 cm^{-1}; $C_{24}H_{26}OSSi$ (390.58): calcd. C 73.80 H 6.71 S 8.21; found C 73.82, H 6.91, S 8.14.

General procedure for the pivaloylation of the alcohols 6a-c: One equiv. of the appropiate alcohol was dissolved in pyridine (2 ml/mmol) and the solution was cooled to -10 °C. 1.2 equiv. of pivaloyl chloride were added dropwise, the reaction mixture was allowed to warm to room temperature and stirred overnight. Pyridine was evaporated under reduced pressure using toluene as co-solvent. The resulting solid was dissolved in dichloromethane and was washed with saturated $NaHCO_3$ solution, water and brine. After drying, the solvent was evaporated and the obtained crude product was purified by column chromatography (PE/EE 20:1).

3-Pivaloyloxy-1-(phenylthio)-1-(trimethylsilyl)cyclopentane (7a): 828 mg (3.1 mmol) of **6a** gave 924 mg (85%) as a colourless oil. ^{1}H NMR: δ, -0.03 (*s*, 9H, Si*Me*$_3$), 1.05 (*s*, 9H, *CMe*$_3$), 1.43-1.64 (*m*, 1H, C*H*$_2$), 1.75-2.02 (*m*, 4H, C*H*$_2$), 2.36 (*dd*, *J*= 7.6, 15.0 Hz, 1H, *2-H*), 4.90 (*m*, 1H, *3-H*); ^{13}C NMR: δ, -3.0 (Si*Me*$_3$), 27.0 (C*Me*$_3$), 31.8, 33.5 (*C-4, C-5*), 38.5 (*C*Me$_3$), 40.9 (*C-2*), 43.0 (*C-1*), 76.0 (*C-3*), 128.5, 128.6, 133.3, 137.2 (S*Ph*), 178.4 (*C*=O); IR: 2960, 2905, 2871, 1725, 1479, 1439, 1284, 1250, 1160, 1035, 841, 750, 694 cm^{-1}; $C_{19}H_{30}O_2SSi$ (350.56): calcd. C 65.09, H 8.63 S 9.15; found C 65.04, H 8.68, S 9.25.

3-Pivaloyloxy-1-(phenyldimethylsilyl)-1-(phenylthio)cyclopentane (7b): 562 mg (1.7 mmol) of **6b** gave 614 mg (87%) of a colourless oil as two diastereomers (8.1:1*). ^{1}H NMR: δ, 0.28, 0.29, 0.31*, 0.32* (each *s*, 3H, Si*Me*$_2$Ph), 0.99*, 1.02 (each *s*, 9H, C*Me*$_3$), 1.33-1.65 (*m*, 2H, 2H*, C*H*$_2$), 1.77-2.01 (*m*, 3H, 3H*, C*H*$_2$), 2.33 (*dd*, *J*= 6.8, 15.2 Hz, 1H, *2-H**), 2.42 (*dd*, *J*= 7.6, 15.2Hz, 1H, *2-H*), 4.58-4.73 (*m*, 1H, *3-H*), 4.86-4.99 (*m*, 1H, *3-H**); ^{13}C NMR (only one diastereomer could be detected): δ, -4.6 (Si*Me*$_2$Ph), 27.0 (C*Me*$_3$), 31.6, 33.9 (*C-4, C-5*), 38.0 (*C*Me$_3$), 41.2 (*C-2*), 43.4 (*C-1*), 75.9 (*C-3*), 127.8, 128.5, 128.6, 129.4, 133.1, 134.6, 136.6, 137.1 (S*Ph*, SiMe$_2$*Ph*), 178.4 (*C*=O); IR: 3070, 2968, 2870, 1723, 1479, 1438, 1428, 1284, 1250, 1160, 1111, 832, 816, 775, 750, 737, 702 cm^{-1}; $C_{24}H_{32}O_2SSi$ (412.62): calcd. C 69.86, H 7.82, S 7.77; found C 70.00, H 7.93, S 7.75.

3-Pivaloyloxy-1-(diphenylmethylsilyl)-1-(phenylthio)cyclopentane (7c): 80 mg (0.2 mmol) of **6c** gave 60 mg (62%) of a colourless oil as two diastereomers (10.3:1*). ^{1}H NMR: δ, 0.49, 0.56* (each *s*, 3H, Si*Me*Ph$_2$), 0.93*, 1.04 (each *s*, 9H, C*Me*$_3$), 1.35-1.66 (*m*, 2H, 2H*, C*H*$_2$), 1.93-2.10 (*m*, 3H, 3H*, C*H*$_2$), 2.49 (*dd*, *J*= 7.6, 15.6 Hz, 1H, *2-H**), 2.62 (*dd*, *J*= 8.0, 15.6 Hz, 1H, *2-H*), 4.55-4.70 (*m*, 1H, *3-H*), 4.89-5.02 (*m*, 1H, *3-H**); ^{13}C NMR (only one diastereomer could be detected): δ, -5.2 (Si*Me*Ph$_2$), 26.9 (C*Me*$_3$), 31.4, 34.6 (*C-4, C-5*), 38.4 (*C*Me$_3$), 41.9 (*C-2*), 43.0 (*C-1*), 76.0 (*C-3*), 127.7, 128.4, 128.7, 129.4, 132.7, 134.9,135.1, 135.4, 135.5, 137.5 (S*Ph*, SiMe*Ph*$_2$), 178.3 (*C*=O); IR: 3070, 2968, 2870, 1723, 1585, 1477, 1429, 1396,

1367, 1285, 1256, 1159, 1108, 1033, 982, 789, 737, 699 cm^{-1}; $C_{29}H_{34}O_2SSi$ (474.69): calcd. C 73.37, H 7.22, S 6.75; found C 73.66, H 7.51, S 6.74.

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