Synthesis of 1-Functionalized Silylcyclopropanes Via Cyclization of 3-Silylalk-4-enols

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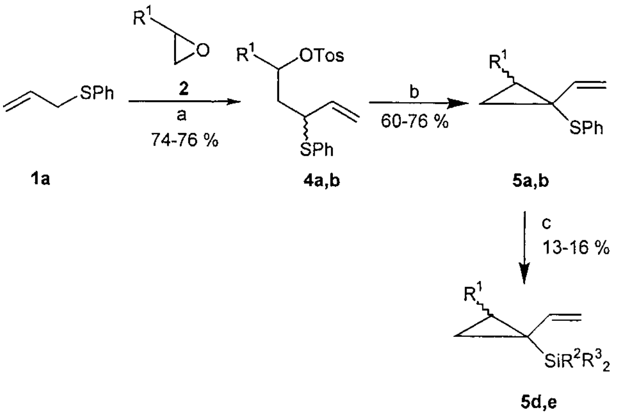
Abstract: Tosylation of 3-silylalk-4-en-1-ols 3, as obtained via ring opening of epoxides **2** by silyl-substituted allyl anions **1**, yields 4-alkenyl tosylates **4**. Anion generation by deprotonation gives vinylcyclopropanes **5**. 1-Silylcyclopropane-1-carboxylic acids **7** were prepared in two steps by ozonization of **5**.

Key words: 1-silylcyclopropane-1-carboxylic acids, 3-silylalk-4-en-1-ols, 4-alkenyl tosylates, epoxide ring opening, vinylcyclopropanes

Functionalized trimethylsilyl-substituted cyclopropanes have emerged as useful synthetic building blocks.[1] They are usually obtained by Simmons–Smith cyclopropanation of silyl-substituted olefins[2] or sulfur–silicon exchange of sulfur-substituted cyclopropanes.[3] The latter approach seems attractive also for the synthesis of the so far unknown 1-silyl-1-vinylcyclopropanes, promising intermediates for the synthesis of, for example, cyclopropane-derived amino acids.[4] The required precursors 1-(phenylthio)-1-vinylcylopropanes **5a,b** are accessible by cyclization of tosylated 3-(phenylthio)alk-4-en-1-ols **4a,b**, the ring-opening products of epoxides **2** by phenylthio-stabilized allyl anions.[5] In fact, reductive lithiation of **5a,b** using the aromatic radical anions lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[6] or lithium 1-(dimethylamino)naphthalenide (LDMAN)[7] and treatment of the resulting 1-lithio-1-vinylcyclopropanes with trialkylchlorosilanes gave the desired 1-silyl-1-vinylcyclopropanes, but gave **5d** in only 13% yield from the reaction of **5b** with LDBB/chlorotrimethylsilane and gave **5e** in 16% yield from the reaction of **5a** with LDMAN/chlorodimethylphenylsilane (Scheme 1).

As an alternative for the synthesis of silylcyclopropanes, cyclization of tosylated 3-silylalk-4-en-1-ols may be envisaged. Compounds of type **4** had been obtained previously by tosylation of alcohols obtained by ring opening of epoxides **2** by silyl-substituted allyl anions **1b–e**.[8] However, they had failed to give anions with the usual alkyllithium bases.[5, 8] We have now found that the particularly efficient Schlosser[9] reagent (BuLi/potassium *tert*-butoxide) allows deprotonation leading to immediate intramolecular displacement of tosylate to give 1-silyl-1-vinylcyclopropanes **5d–j** in good to very good yields. Products **5d,e** and **5g–j** were isolated as mixtures of two diastereomers, which can be distinguished by NMR spectroscopy. **5f** was a pure diastereomer. Only **4c** failed to undergo the reaction (Scheme 2).



Compound	R^1	R^2	R^3
2a, 4a, 5a	Me	—	—
2b, 4b, 5b	$BnOCH_2$	—	—
5d	$BnOCH_2$	Me	Me
5e	Me	Ph	Me

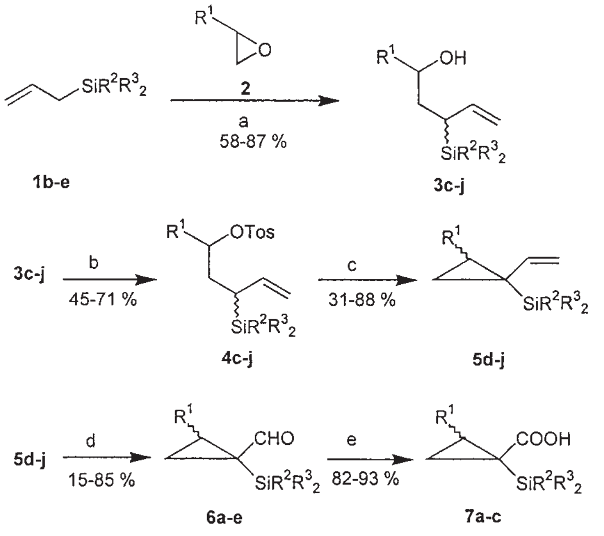
a: (i) BuLi, THF, –78 °C, 4 h; (ii) **2**, –78 °C to r.t. b: BuLi, THF, –78 °C, 3 h. c: (i) LDMAN (for **5a**) or LDBB (for **5b**), THF, –78 °C, 2 h; (ii) $ClSiR^2R^3_2$.

Scheme 1

Ozonization of the vinyl group and subsequent reductive ozonide cleavage by sodium borohydride, dimethyl sulfide or zinc/HOAc gave carbaldehydes **6** in good yields. Products **6** were oxidized by potassium permanganate under phase-transfer conditions to provide cyclopropanecarboxylic acids **7**. This approach gave better yields of carboxylic acids **7** than direct oxidative workup of the ozonization mixture (see Scheme 2).

In the present work racemic epoxides were used, but optically active starting materials would provide straightforward access to non-racemic silylcyclopropane building blocks.

All experiments were performed under dry N_2. THF was distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from CaH_2. Column chromatography was carried out on Merck silica gel (70–230 mesh). Petroleum ether (PE) with the boiling range 60–70 °C was always used in the separations. Analytical TLC was performed on Merck silica gel 60 PF_{254} plates (visualization with UV light or 4-methoxybenzaldehyde spray reagent). Mps are uncorrected. IR spectra were recorded on a Pye-Unicam SP 3-200 spectrometer and on a Bruker Vektor 22 instrument. NMR spectra were obtained on Bruker ARX 400 or DPX 200 spectrometers; coupling constants, *J*, are given in Hz. Assignments of ^{13}C NMR signals were supported by broadband decoupled DEPT.



Compound	R^1	R^2	R^3
1b	—	Me	Me
1c	—	Ph	Me
1d	—	Me	Ph
1e	—	Ph	Ph
3c, 4c	Me	Me	Me
3d, 4d, 5d	$BnOCH_2$	Me	Me
3e, 4e, 5e, 6b, 7a	Me	Ph	Me
3f, 4f, 5f, 6d	$BnOCH_2$	Ph	Me
3g, 4g, 5g, 6c, 7b	Me	Me	Ph
3h, 4h, 5h	$BnOCH_2$	Me	Ph
3i, 4i, 5i, 6a, 7c	Me	Ph	Ph
3j, 4j, 5j, 6e	$BnOCH_2$	Ph	Ph

a: (i) BuLi, (for **1d**, **1e**), or *s*-BuLi, TMEDA (for **1b**, **1c**), THF, –78 °C, 4 h; (ii) **2**, –78 °C, 4 h. b: Et_3N, 4-DMAP, TosCl, CH_2Cl_2, –20 °C, 48 h. c: BuLi, *t*-BuOK, THF, –78 °C, 3 h. d: O_3, MeOH, –78 °C, $NaBH_4$ (for **6b**, **6c**, **6e**) or Zn, HOAc (for **6d**), –78 °C, to r.t. e: $KMnO_4$, H_2O, CH_2Cl_2, PTC (methyltrioctylammonium chloride), r.t.

Scheme 2

Oxirane **2a** is commercially available, (benzyloxymethyl)oxirane (**2b**) was prepared from epichlorohydrin by conventional methods.[10] Silylalkenols 3 were prepared according to a general procedure.[5] Products **3c,g,i**[8] and **3f,h**[11] have been reported before. Products **3d,e,j** were obtained as a mixture of diastereomers (ratio α,α^* 1.1:1, 1.3:1, 1.5:1, respectively). Separation of α,α^*-isomers and minor γ-isomers[5, 8] (ratio α,γ5:1, 5:1, 4.5:1) was not achieved by chromatography; for spectroscopic data see Tables 1, 2. Alkenols **3a,b** were generated only in situ.

For the tosylation of **3c–j** to give **4c–j**, a protocol given previously was used.[5] Instead of pyridine, CH_2Cl_2 (1 mL/mmol) and Et_3N (1.3 equiv) was used. Separation of α- and γ-isomers was achieved at this stage by chromatography. Products **4c–h** and **4j** were obtained as a mixture of diastereomers (ratio α,α^* 1.4:1, 3:1, 1.1:1, 1.3:1, 1.7, 2.9:1 and 1.5:1 for **4j**), **4i** was a pure diastereomer; for spectroscopic data see Tables 1, 2.

The synthesis of sulfur-substituted precursors **4a**, **5a** has been reported previously.[5] Compounds **4b, 5b** were obtained analogously as a mixture of diastereomers (for **4b** ratio 1.25:1, for **5b** ratio 1.9:1). For spectroscopic data see Tables 1, 2 (for **4b**) and Tables 3, 4 (for **5b**).

Desulfurization; General Procedure:

The preparation of lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[12] and lithium 1-(dimethylamino)naphthalenide (LDMAN)[13] is described in the literature. A solution of **5a,b** (1 mmol) in THF (5 mL) was treated with LDBB (for **5b**) or LDMAN (for **5a**) (3 mmol) for 2 h at –78 °C. Then a solution of a trialkylchlorosilane (4 mmol) in THF (10 mL) was added. The mixture was allowed to warm to r.t. overnight. Then hydrolysis was carried out with a mixture of sat. aq NH_4Cl and Et_2O (50 mL). The organic layer was washed with sat. brine (2×), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (PE) to give **5d** (13%) and **5e** (16%), respectively, as single diastereomers; for spectroscopic data see Tables 3, 4.

Preparation of Vinylcyclopropanes 5 from Tosylates 4 Using Butyllithium/Potassium *tert*-Butoxide; General Procedure:

t-BuOK (3 equiv) in anhyd THF (5 mL/mmol) was mixed with 1.6 M BuLi in hexane (3.3 equiv) at –95 °C. The solution was stirred for 15 min and transferred via transfer syringe into a solution of tosylate **4** in THF (5 mL/mmol) at –95 °C. The mixture was allowed to warm to –78 °C, and consumption of the tosylate was followed by TLC (PE/Et_2O 5:1). After the completion of the reaction, the solution was poured into sat. aq NH_4Cl/pentane/Et_2O (1:1:1). The organic layer was washed with sat. brine (2×), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography (PE). Products **5d,e** and **5g–j** were obtained as a mixture of diastereomers (ratio 1.6:1, 2.6:1, 2.5:1, 3:1, 4:1 and 2:1, respectively). The minor isomer was not obtained free of the major isomer. **5f** was a pure diastereomer for which *trans*-orientation of the silyl and R^1 substituents is assumed; for spectroscopic data see Tables 3, 4.

Ozonization of 5e–g,i,j; General Procedure:

A stirred solution of **5** in MeOH (10 mL/mmol) was treated with ozone at –78 °C. After complete consumption of the starting material, $NaBH_4$ (1.5 equiv) (for **6b,c,e**) or DMS (1.5 equiv) (for **6a**) or Zn/HOAc (1.5 equiv) (for **6d**) was added at the same temperature. The mixture was allowed to warm to r.t. and stirred overnight. The solution was poured into a two-phase system of H_2O and Et_2O. The organic layer was separated, washed with sat. brine (2×), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography (PE/EtOAc). Products **6a–c** and **6e** were obtained as a mixture of diastereomers (ratio 1.8:1, 1.9:1, 1.7:1 and 1.8:1 for **6e**); **6d** was a pure diastereomer. For spectroscopic data of **6a** (mp 127–129 °C) and **6b–e** see Tables 3, 4.

Oxidation of Carbaldehydes 6; General Procedure:

To a solution of **6** (1 mmol) in H_2O (1.5 mL)/CH_2Cl_2 (2.5 mL) and methyltrioctylammonium chloride (3 drops) was added $KMnO_4$ (316.1 mg, 2 mmol). The mixture was stirred overnight at r.t. and then treated with sodium bisulfite solution, followed by 2 N H_2SO_4 (5 mL). The organic layer was separated, dried (Na_2SO_4), and concentrated in vacuo. Purification of the crude product was achieved by recrystallization. Products **7a–c** were obtained as a mixture of diastereomers (ratio 1.2:1, 1.2:1, 1.3:1, respectively). For spectro-

Table 1. IR and ^{1}H NMR Spectroscopic Data* of **3**, **4**

Product	IR (neat) ν (cm^{-1})	^{1}H NMR (400 MHz, CDCl$_3$/TMS) δ, J (Hz)[a]
3d[c]	3430, 2920, 1615, 1490, 1450, 1360, 1245, 1090, 850, 820, 740	0.005*, 0.015 (s, 9H, SiCH$_3$), 1.40–1.59, 1.88 (m, 3H, CH$_2$, CHSi, α, α*), 3.34, 3.54 (dd, J = 7.6, 9.6 and 3.9, 9.6, 1H, BnOCH$_2$), 3.49*, 3.53* (dd, J = 7.6, 9.4 and 3.6, 9.4, 1H, BnOCH$_2$), 3.88 (m, 1H, CHOH), 4.52*, 4.56, 4.58*, 4.62 (d, J = 12.0, 12.0*, 1H, PhCH$_2$), 4.82, 4.88* (dd, J = 1.6, 17.0, 1.6*, 17.0*, 1H, CH=CH_2), 4.89, 4.92* (dd, J = 1.6, 10.4, 1.6*, 10.4*, 1H, CH=CH_2), 5.60*, 5.68 (dd, J = 10.4*, 17.0*, 10.4, 17.0, 1H, CH=CH$_2$), 7.33–7.39 (m, 5H, ArH)
3e[b]	3346, 3070, 2964, 2924, 1624, 1590, 1427, 1249, 1114, 896, 841, 731	0.27, 0.32* (s, 6H, SiCH$_3$), 1.00 (d, J = 6.0, 3H, CH$_3$), 1.08–1.24, 1.45 (m, 3H, CH$_2$, CHSi), 3.80 (m, 1H, CHOH), 4.85, 4.88* (dd, J = 1.6, 17.0, 1.6*, 17.0*, 1H, CH=CH_2), 4.93*, 4.95 (dd, J = 1.6*, 10.4*, 1.6, 10.4, 1H, CH=CH_2), 5.68*, 5.72 (dd, J = 10.4*, 17.0*, 10.4, 17.0, 1H, CH=CH$_2$), 7.30–7.40, 7.45–7.53 (m, 5H, ArH)
3j[c]	3450, 3068, 2923, 2860, 1625, 1428, 1110, 998, 903, 739, 679	1.23–1.42, 1.56 (m, 3H, CH$_2$, CHSi), 3.36–3.55 (m, 2H, BnOCH$_2$), 3.92 (m, 1H, CHOH), 4.49* (s, 2H, PhCH$_2$), 4.56, 4.59 (d, J = 12.0, 1H, PhCH$_2$), 4.89, 4.90* (dd, J = 1.6, 17.0, 1.6*, 17.0*, 1H, CH=CH_2), 4.94*, 4.98 (dd, J = 1.6*, 10.4*, 1.6, 10.4, 1H, CH=CH_2), 5.67*, 5.74 (dd, J = 10.4*, 17.0*, 10.4, 17.0, 1H, CH=CH$_2$), 7.28–7.41, 7.48–7.59 (m, 20H, ArH)
4b[d]	3062, 2921, 2863, 1634, 1598, 1364, 1189, 1176, 1097, 917, 815	1.69, 2.01 (m, 2H, CH_2CHSPh), 2.38, 2.42* (s, 3H, CH$_3$), 3.54–3.90 (m, 3H, BnOCH$_2$, CHSPh), 4.39–4.61 (m, 3H, PhCH$_2$, CHOTos), 4.74*, 4.78 (dd, J = 1.6*, 17.0*, 1.6, 16.0, 1H, CH=CH_2), 4.90*, 4.96 (dd, J = 1.6*, 10.4*, 1.6, 10.2, 1H, CH=CH_2), 5.58–5.70 (m, 1H, CH=CH$_2$), 7.21–7.36, 7.76–7.81 (m, 14H, ArH)
4c[d]	3080, 2940, 2890, 1640, 1610, 1370, 1250, 1180, 840	–0.10*, –0.09 (s, 9H, SiCH$_3$), 1.17*, 1.27 (d, J = 6.2*, 6.0, 3H, CH$_3$), 1.45–1.58 (m, 2H, CH$_2$), 1.72 (m, 1H, CHSi), 2.36, 2.41* (s, 3H, CH$_3$), 4.61 (m, 1H, CHOTos), 4.55*, 4.72 (d, J = 17.2*, 17.2, 1H, CH=CH_2), 4.80*, 4.84 (d, J = 10.6*, 10.4, 1H, CH=CH_2), 5.40, 5.48* (dt, J = 10.4, 17.2, 10.6*, 17.2*, 1H, CH=CH$_2$), 7.32–7.78 (m, 4H, ArH)
4d[b]	3050, 2970, 2930, 1630, 1580, 1370, 1250, 1180, 1080, 900, 840	–0.02, 0.06* (s, 9H, SiCH$_3$), 1.40, 1.52* (m, 2H, CH_2CHSi), 1.74, 1.83* (m, 1H, CHSi), 2.45, 2.52* (s, 3H, CH$_3$), 3.56, 3.58* (m, 2H, BnOCH$_2$), 4.50, 4.53* (s, 2H, PhCH$_2$), 4.72, 4.76* (m, 1H, CHOTos), 4.88 (dd, J = 1.6, 10.4, 1H, CH=CH_2), 4.93 (dd, J = 1.6, 17.4, 1H, CH=CH_2), 5.52 (ddd, J = 1.6, 10.4, 17.4, 1H, CH=CH$_2$)
4e[d]	2957, 1625, 1599, 1358, 1250, 1189, 1177, 1097, 913, 814, 733, 701	0.09, 0.17* (s, 6H, SiCH$_3$), 1.00, 1.03* (d, J = 6.2, 6.0*, 3H, CH$_3$), 1.32 (m, 1H, CHSi), 1.49–1.60 (m, 2H, CH$_2$), 2.30, 2.32* (s, 3H, CH$_3$), 4.40, 4.48* (m, 1H, CHOTos), 4.59, 5.54* (dd, J = 1.2, 17.2, 1.2*, 18.6*, 1H, CH=CH_2), 4.71*, 4.74 (dd, J = 1.2*, 10.6*, 1.2, 10.4, 1H, CH=CH_2), 5.23, 5.28* (ddd, J = 1.2, 10.4, 17.2, 1.2*, 10.6*, 18.6*, 1H, CH=CH$_2$), 7.12–7.35, 7.57–7.68 (m, 5H, ArH)
4f[b]	3060, 3020, 2950, 1630, 1600, 1360, 1250, 1190, 1170, 920, 810, 730	0.23*, 0.24 (s, 6H, SiCH$_3$), 1.23 (m, 1H, CHSi), 1.61–1.82 (m, 2H, CH$_2$), 2.41*, 2.43 (s, 3H, CH$_3$), 3.48, 3.51 (dd, J = 3.4, 9.4 and 7.6, 9.4, 1H, BnOCH$_2$), 4.31*, 4.38, 4.43, 4.44* (d, J = 12.0, 12.0*, 1H, PhCH$_2$), 4.66 (dd, J = 1.2, 17.6, 1H, CH=CH_2), 4.71 (m, 1H, CHOTos), 4.89 (dd, J = 1.2, 10.4, 1H, CH=CH_2), 5.40 (ddd, J = 1.2, 10.4, 17.6, 1H, CH=CH$_2$), 7.2–7.5, 7.7–7.9 (m, 14H, ArH)
4g[b]	3080, 2940, 2885, 1630, 1600, 1360, 1250, 1180, 880	0.38*, 0.41 (s, 3H, SiCH$_3$), 1.11, 1.16* (d, J = 6.0, 6.2*, 3H, CH$_3$), 1.19 (m, 1H, CHSi), 1.72 (m, 2H, CH$_2$), 2.35, 2.36* (s, 3H, CH$_3$), 4.51 (m, 1H, CHOTos), 4.66 (dd, J = 1.4, 17.6, 1H, CH=CH_2), 4.80 (dd, J = 1.4, 10.4, 1H, CH=CH_2), 5.23 (dd, J = 10.4, 17.6, 1H, CH=CH$_2$), 7.21–7.79 (m, 14H, ArH)
4h[d]	3069, 2957, 2868, 1625, 1599, 1355, 1251, 1189, 907, 815	0.52, 0.64* (s, 3H, SiCH$_3$), 1.27, 1.73 (m, 1H, CH$_2$), 2.13 (m, 1H, CHSi), 2.43*, 2.45 (s, 3H, CH$_3$), 3.54, 3.58 (m, 1H, BnOCH$_2$), 4.41, 4.51 (d, J = 12.0, 1H, PhCH$_2$), 4.70 (m, 1H, CHOTos), 4.75 (d, J = 17.2, 1H, CH=CH_2), 4.93 (d, J = 10.4, 1H, CH=CH_2), 5.50 (dt, J = 10.4, 17.2, 1H, CH=CH$_2$), 7.31–7.56, 7.73–7.82 (m, 19H, ArH)
4i[b]	3080, 2940, 2885, 1630, 1600, 1360, 1180, 920, 880, 750	1.17 (d, J = 6.4, 3H, CH$_3$), 1.77 (m, 2H, CH$_2$), 2.30 (m, 1H, CHSi), 2.34 (s, 3H, CH$_3$), 4.52 (m, 1H, CHOTos), 4.69 (d, J = 17.6, 1H, CH=CH_2), 4.84 (d, J = 10.4, 1H, CH=CH_2), 5.41 (dt, J = 10.4, 17.6, 1H, CH=CH$_2$), 7.1–7.4 (m, 19H, ArH)
4j[b]	3068, 2924, 2865, 1625, 1598, 1362, 1176, 1110, 916, 740, 700	1.21, 1.72 (m, 1H, CH$_2$), 2.19 (m, 1H, CHSi), 2.36*, 2.37 (s, 3H, CH$_3$), 3.45, 3.48 (m, 1H, BnOCH$_2$), 4.39, 4.50 (d, J = 12.0, 1H, PhCH$_2$), 4.58* (s, 2H, PhCH$_2$), 4.68 (m, 1H, CHOTos), 4.70 (d, J = 16.8, 1H, CH=CH_2), 4.90 (d, J = 10.2, 1H, CH=CH_2), 5.48 (dt, J = 10.2, 16.8, 1H, CH=CH$_2$), 7.16–7.56, 7.64–7.73 (m, 24H, ArH)

* Starred δ values designate signals of the minor diastereomer.

[a] For methyl silylated compounds the signal of residual CHCl$_3$ in CDCl$_3$ was used as internal standard (δ = 7.26).

[b] Satisfactory elemental analyses: C ± 0.23, H ± 0.31, S ± 0.34.

[c] Elemental analyses of the corresponding tosylates are satisfactory.

[d] Elemental analyses of the corresponding vinylcyclopropanes are satisfactory.

Table 2. ^{13}C NMR Spectroscopic Data* of **3**, **4**

Product	^{13}C NMR (101 MHz, CDCl$_3$/TMS; for methyl silylated compounds, CDCl$_3$ at δ = 77.00) δ
3d	–3.7, –1.4* (SiCH$_3$), 30.0*, 31.6 (CHSi), 31.5*, 31.8 (CH$_2$), 68.6*, 70.2 (CHOH), 70.5*, 72.8, 73.1*, 74.7 (PhCH$_2$OCH$_2$), 112.0*, 112.5 (CH=*C*H$_2$), 127.5, 128.2, 128.9, 133.8, 134.0 (ArCH), 137.6, 137.7 (ArC), 139.2, 139.4* (*C*H=CH$_2$)
3e	–4.3, –2.5* (SiCH$_3$), 22.4*, 23.5 (CH$_3$), 30.5, 31.4* (CHSi), 37.6, 38.1* (CH$_2$), 66.1, 67.7* (CHOH), 112.9*, 113.2 (CH=*C*H$_2$), 127.7, 127.8, 129.0, 133.8, 134.0, 134.1 (ArCH), 137.3 (ArC), 139.2, 139.8* (*C*H=CH$_2$)
3j	27.7, 29.3* (CHSi), 32.5*, 32.8 (CH$_2$), 68.3*, 70.3 (CHOH), 72.8*, 73.3*, 74.4, 74.9 (PhCH$_2$OCH$_2$), 115.0, 115.4* (CH=*C*H$_2$), 127.7, 127.8, 128.4, 128.5, 129.4, 129.5, 133.4, 133.8, 135.9, 136.1 (ArCH), 137.9, 138.0 (ArC), 138.1, 138.6* (*C*H=CH$_2$)
4b	21.6 (CH$_3$), 35.6, 36.0* (CH$_2$), 47.2, 47.7* (CHSPh), 70.6, 70.8*, 73.2, 73.3* (PhCH$_2$OCH$_2$), 79.0, 79.2* (CHOTos), 115.9*, 117.3 (CH=*C*H$_2$), 127.3, 127.4, 127.6, 127.8, 128.3, 128.6, 128.7, 129.7, 132.7, 133.3 (ArCH), 133.6, 133.9, 134.2 (ArC), 137.5*, 137.7 (*C*H=CH$_2$), 144.6 (CSO)
4c	–3.7, –3.6* (SiCH$_3$), 19.0, 20.7*, 21.5*, 21.8 (CH$_3$), 30.2*, 30.9 (CHSi), 34.8, 35.6* (CH$_2$), 80.0*, 80.1 (CHOTos), 112.7*, 112.8 (CH=*C*H$_2$), 127.7, 127.8, 129.6, 129.7 (ArCH), 134.5, 134.7* (ArC), 137.8, 138.4* (*C*H=CH$_2$), 144.3*, 144.4 (CSO)
4d	–3.8, –3.6* (SiCH$_3$), 21.5*, 21.6 (CH$_3$), 29.8, 31.1* (CH$_2$), 30.6*, 31.2 (CHSi), 70.3, 71.3*, 73.0, 73.1* (PhCH$_2$OCH$_2$), 81.1*, 81.6 (CHOTos), 112.9 (CH=*C*H$_2$), 126.9, 127.5, 127.7, 128.2, 129.5, 129.6, 130.1 (ArCH), 137.6, 138.2 (ArC), 137.9 (*C*H=CH$_2$), 146.8 (CSO)
4e	–5.8*, –4.9 (SiCH$_3$), 19.0, 21.6, 21.8* (CH$_3$), 30.6 (CHSi), 35.3, 35.6* (CH$_2$), 80.0 (CHOTos), 113.5 (CH=*C*H$_2$), 127.7, 129.2, 129.7, 133.9, 137.7 (ArCH), 133.8, 134.4, 136.5 (ArC), 137.4*, 137.9 (*C*H=CH$_2$), 144.4, 146.9* (CSO)
4f	–2.4, –1.9* (SiCH$_3$), 21.6 (CH$_3$), 29.3 (CHSi), 30.4 (CH$_2$), 65.8*, 68.8*, 71.3, 73.1 (PhCH$_2$OCH$_2$), 80.9, 81.5* (CHOTos), 113.6 (CH=*C*H$_2$), 127.6, 127.7, 127.8, 128.3, 129.1, 129.2, 129.5, 134.5, 137.6, 137.7 (ArCH), 133.8, 134.0, 136.8 (ArC), 137.8 (*C*H=CH$_2$), 144.3 (CSO)
4g	–2.3, –2.0* (SiCH$_3$), 19.1, 21.6, 21.9* (CH$_3$), 27.9*, 29.0 (CHSi), 34.9, 35.6* (CH$_2$), 79.8 (CHOTos), 114.2*, 114.3 (CH=*C*H$_2$), 127.7, 127.9, 129.3, 129.4, 129.5, 129.7, 134.7, 134.8 (ArCH), 134.4, 137.4 (ArC), 136.9 (*C*H=CH$_2$), 144.3 (CSO)
4h	–6.2, –3.8* (SiCH$_3$), 21.6 (CH$_3$), 28.7, 29.6* (CHSi), 30.3*, 31.7 (CH$_2$), 65.8*, 68.9, 70.6*, 73.2 (PhCH$_2$OCH$_2$), 81.1*, 81.4 (CHOTos), 114.4 (CH=*C*H$_2$), 127.6, 127.7, 127.8, 128.3, 129.2, 129.4, 129.5, 129.6, 134.1, 134.4 (ArCH), 134.8*, 134.9 (ArC), 137.1, 137.7* (*C*H=CH$_2$), 144.4, 149.0* (CSO)
4i	19.0, 21.4 (CH$_3$), 28.3 (CHSi), 35.2 (CH$_2$), 79.4 (CHOTos), 115.3 (CH=*C*H$_2$), 127.5, 127.6, 129.4, 135.8 (ArCH), 132.7, 134.1 (ArC), 136.5 (*C*H=CH$_2$), 144.1 (CSO)
4j	21.6 (CH$_3$), 28.0 (CHSi), 30.0, 31.8* (CH$_2$), 65.8*, 69.0, 70.8*, 73.3 (PhCH$_2$OCH$_2$), 81.0*, 81.3 (CHOTos), 114.8*, 115.6 (CH=*C*H$_2$), 127.7, 127.8, 128.4, 129.5, 129.6, 133.0, 134.1 (ArCH), 134.8*, 134.9 (ArC), 137.1, 137.7* (*C*H=CH$_2$), 144.4, 149.0* (CSO)

* Starred δ values designate signals of the minor diastereomer.

Table 3. IR and ^{1}H NMR Spectroscopic Data* of **5**, **6**, **7**

Product	IR (neat or KBr) ν (cm^{-1})	^{1}H NMR (400 MHz, CDCl$_3$/TMS) δ, J (Hz)[a]
5b[b]	3061, 3029, 2857, 1633, 1584, 1454, 1439, 1094, 1027, 911, 738	1.03*, 1.17 (dd, J = 5.4*, 6.6*, 5.4, 6.0, 1H, CH$_2$), 1.39 (dd, J = 5.4, 9.0, 1H, CH$_2$), 1.76*, 1.91 (m, 1H, CH), 3.41 (dd, J = 8.8, 10.6, 1H, BnOCH$_2$), 3.71 (m, 1H and 2H*, BnOCH$_2$), 4.48* (s, 2H, PhCH$_2$), 4.50, 4.56 (d, J = 12.0, 1H, PhCH$_2$), 5.03*, 5.15 (dd, J = 1.0*, 10.4*, 1.4, 10.4, 1H, CH=C*H*$_2$), 5.30*, 5.32 (dd, J = 1.0*, 16.6*, 1.4, 16.6, 1H, CH=C*H*$_2$), 5.67*, 5.85 (dd, J = 10.4*, 16.6*, 10.4, 16.6, 1H, C*H*=CH$_2$), 7.10–7.42 (m, 10H, ArH)
5d[b]	3065, 2994, 2956, 2854, 1624, 1249, 1098, 906, 838, 749, 698	–0.04*, 0.00 (s, 9H, SiCH$_3$), 0.56*, 0.60 (dd, J = 4.0, 4.4*, 1H, CH$_2$), 0.77, 0.91* (dd, J = 4.0, 8.2, 4.4*, 7.6*, 1H, CH$_2$), 1.25 (m, 1H, CH), 3.36, 3.44 (dd, J = 7.4, 10.2 and 6.6, 10.2, 1H, BnOCH$_2$), 4.45*, 4.53* (d, J = 12.0*, 1H, PhCH$_2$), 4.53 (s, 2H, PhCH$_2$), 4.87, 4.94* (dd, J = 1.8, 16.6, 2.0*, 17.0*, 1H, CH=C*H*$_2$), 4.91, 5.04* (dd, J = 1.8, 10.2, 2.0*, 10.2*, 1H, CH=C*H*$_2$), 5.94*, 5.98 (dd, J = 10.2*, 17.0*, 10.2, 16.6, 1H, C*H*=CH$_2$), 7.28–7.43 (m, 5H, ArH)
5e[b]	3069, 3051, 2995, 2956, 1623, 1428, 1250, 1112, 993, 831, 700	0.25, 0.27* (s, 6H, SiCH$_3$), 0.84 (m, 2H, CH$_2$), 0.92 (m, 1H, CH), 1.02, 1.04* (d, J = 6.0, 3H, CH$_3$), 4.76*, 4.85 (dd, J = 1.6*, 17.2*, 1.6, 16.4, 1H, CH=C*H*$_2$), 4.79*, 4.98 (dd, J = 1.6*, 10.4*, 1.6, 11.0, 1H, CH=C*H*$_2$), 5.84*, 5.90 (dd, J = 10.4*, 17.2*, 11.0, 16.4, 1H, C*H*=CH$_2$), 7.22–7.34, 7.42–7.55 (m, 5H, ArH)

Product	IR (neat or KBr) ν (cm^{-1})	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, J (Hz)[a]
5f[b]	3070, 2950, 2860, 1625, 1590, 1455, 1425, 1250, 1100, 990, 835	0.29 (s, 6H, $SiCH_3$), 0.61, 0.76 (m, 1H, CH_2), 1.24 (m, 1H, CH), 3.51, 3.52 (dd, J = 6.2, 10.2 and 8.0, 10.2, 1H, $BnOCH_2$), 4.44, 4.51 (d, J = 12.0, 1H, $PhCH_2$), 4.94 (dd, J = 1.6, 17.2, 1H, $CH=C\mathit{H}_2$), 5.03 (dd, J = 1.6, 10.2, 1H, $CH=C\mathit{H}_2$), 5.93 (dd, J = 10.2, 17.2, 1H, $C\mathit{H}=CH_2$), 7.33–7.58 (m, 10H, ArH)
5g[b]	3068, 2954, 2873, 1623, 1590, 1428, 1252, 1111, 992, 905, 839	0.46*, 0.52 (s, 3H, $SiCH_3$), 0.62, 0.93* (dd, J = 4.0, 8.8, 4.0*, 8.8*, 1H, CH_2), 0.68*, 1.06 (dd, J = 4.0*, 7.6*, 4.0, 7.6, 1H, CH_2), 0.79 (m, 1H, CH), 0.91, 0.99* (d, J = 6.0, 6.0*, 3H, CH_3), 4.74*, 4.99 (dd, J = 1.8*, 10.2*, 1.4, 10.2, 1H, $CH=C\mathit{H}_2$), 4.78, 4.89* (dd, J = 1.4, 17.2, 1.8*, 17.2*, 1H, $CH=C\mathit{H}_2$), 5.83*, 5.90 (dd, J = 10.2*, 17.2*, 10.2, 17.2, 1H, $C\mathit{H}=CH_2$), 7.23–7.54 (m, 10H, ArH)
5h[b]	3060, 2960, 2860, 1615, 1590, 1425, 1245, 1100, 990, 890, 730	0.43*, 0.47 (s, 3H, $SiCH_3$), 0.60*, 0.61 (dd, J = 4.8*, 4.8, 1H, CH_2), 0.82 (dd, J = 4.8, 8.0, 1H, CH_2), 0.88 (m, 1H, CH), 3.01, 3.09* (dd, J = 7.6, 10.2, 7.6*, 10.2*, 1H, $BnOCH_2$), 3.29, 3.52* (dd, J = 5.6, 10.2, 5.6*, 10.2*, 1H, $BnOCH_2$), 4.18* (s, 2H, $PhCH_2$), 4.36, 4.44 (d, J = 12.0, 1H, $PhCH_2$), 4.79*, 4.99 (dd, J = 1.2*, 10.0*, 1.6, 10.6, 1H, $CH=C\mathit{H}_2$), 4.84*, 4.91 (dd, J = 1.2*, 17.2*, 1.6, 17.0, 1H, $CH=C\mathit{H}_2$), 5.92*, 5.94 (dd, J = 10.0*, 17.2*, 10.6, 17.0, 1H, $C\mathit{H}=CH_2$), 7.31–7.62 (m, 15H, ArH)
5i[b]	3030, 2990, 2920, 1610, 1590, 1420, 1240, 1100, 1020, 890, 830, 730	0.86 (m, 1H, CH_2), 1.10*, 1.12 (d, J = 6.0*, 6.2, 3H, CH_3), 1.15–1.23 (m, 2H, CH_2, CH), 4.81, 5.12* (dd, J = 1.0, 10.2, 1.6*, 10.4*, 1H, $CH=C\mathit{H}_2$), 4.85, 5.03* (dd, J = 1.0, 17.2, 1.6*, 17.6*, 1H, $CH=C\mathit{H}_2$), 6.02*, 6.07 (dd, J = 10.4*, 17.6*, 10.2, 17.2, 1H, $C\mathit{H}=CH_2$), 7.31–7.78 (m, 15 H, ArH)
5j[b]	3068, 3049, 2998, 2855, 1623, 1428, 1250, 1109, 997, 741	0.80*, 1.34* (m, 1H, CH_2), 0.94, 1.20 (dd, J = 4.4, 5.8 and 4.4, 8.6, 1H, CH_2), 1.44 (m, 1H, CH), 2.76, 3.28* (dd, J = 8.0, 10.2, 9.2*, 10.2*, 1H, $BnOCH_2$), 2.98, 3.54* (dd, J = 7.2, 10.2, 5.4*, 10.2*, 1H, $BnOCH_2$), 3.97, 4.03, 4.33*, 4.43* (d, J = 12.0, 12.0*, 1H, $PhCH_2$), 4.75*, 5.00 (dd, J = 1.2*, 10.6*, 1.2, 10.4, 1H, $CH=C\mathit{H}_2$), 4.82*, 4.97 (dd, J = 1.2*, 17.4*, 1.2, 17.2, 1H, $CH=C\mathit{H}_2$), 5.96*, 6.06 (dd, J = 10.4, 17.2, 10.6*, 17.4*, 1H, $C\mathit{H}=CH_2$), 7.05–7.33, 7.51–7.62 (m, 20H, ArH)
6a[b]	(KBr) 3070, 3050, 2928, 1689, 1485, 1429, 1258, 1189, 1110, 926, 742	0.93, 0.95* (d, J = 6.0, 6.0*, 3H, CH_3), 1.14, 1.60 (m, 2H, CH_2), 1.79 (m, 1H, CH), 7.31–7.45, 7.52–7.66 (m, 15H, ArH), 9.24, 9.62* (s, 1H, CHO)
6b[c]	3070, 2999, 2955, 1717, 1429, 1250, 1112, 834, 819, 776	0.33, 0.37* (s, 6H, $SiCH_3$), 0.67, 0.92 (m, 2H, CH_2), 1.02, 1.17* (d, J = 6.2, 6.0*, 3H, CH_3), 1.28–1.44 (m, 1H, CH), 7.22–7.30, 7.42–7.51 (m, 5H, ArH), 8.58, 9.21* (s, 1H, CHO)
6c[b]	3069, 2998, 2957, 1696, 1428, 1254, 1112, 1040, 927, 858, 793, 700	0.66*, 0.70 (s, 3H, $SiCH_3$), 1.02, 1.12* (d, J = 6.0, 6.0*, 3H, CH_3), 1.30, 1.45 (m, 2H, CH_2), 1.62 (m, 1H, CH), 7.33–7.43, 7.48–7.57 (m, 10H, ArH), 8.93, 9.44* (s, 1H, CHO)
6d[d]	3090, 2980, 2860, 1690, 1270, 1120, 840, 820	0.33, 0.36 (s, each 3H, $SiCH_3$), 1.06, 1.44 (dd, J = 4.8, 7.6 and 4.8, 6.0, 2H, CH_2), 1.66 (m, 1H, CH), 3.38, 3.71 (dd, J = 8.0, 10.6 and 6.2, 10.6, 1H, $BnOCH_2$), 4.36, 4.44 (d, J = 12.0, 1H, $PhCH_2$), 7.17–7.35, 7.48–7.55 (m, 10H, ArH), 9.31 (s, 1H, CHO)
6e[d]	3069, 2927, 1705, 1485, 1428, 1261, 1114, 856	0.75, 1.09 (m, 2H, CH_2), 1.33–1.51 (m, 1H, CH), 3.08, 3.24* (m, 1H, $BnOCH_2$), 3.12*, 3.36 (dd, J = 5.4*, 10.2*, 7.2, 10.2, 1H, $BnOCH_2$), 3.97*, 4.05* (d, J = 12.0*, 1H, $PhCH_2$), 4.01 (s, 2H, $PhCH_2$), 7.08–7.36, 7.51–7.65 (m, 20H, ArH), 9.12, 9.63* (s, 1H, CHO)
7a[b]	(KBr) 3071, 2958, 2931, 1681, 1407, 1252, 1112, 820, 775, 702	0.37, 0.45* (s, 6H, $SiCH_3$), 0.81–0.89 (m, 2H, CH_2), 1.09*, 1.18 (d, J =6.2*, 6.0, 3H, CH_3), 1.52, 1.59 (m, 1H, CH), 7.33–7.41, 7.49–7.63 (m, 5H, ArH), 10.8 (bs, 1H, COOH)
7b[b]	(KBr) 3070, 2927, 2856, 1675, 1429, 1254, 1112, 1035, 873, 794	0.68*, 0.70 (s, 3H, $SiCH_3$), 1.09*, 1.18 (d, J = 6.0*, 6.0, 3H, CH_3), 1.23–1.28 (m, 2H, CH_2), 1.55 (m, 1H, CH), 7.21–7.33, 7.45–7.53 (m, 10H, ArH), 9.42 (bs, 1H, COOH)
7c[c]	(KBr) 3070, 2927, 2857, 1672, 1428, 1289, 1259, 1189, 1110, 870	0.85–0.93 (m, 3H, CH_3), 1.55–1.59 (m, 2H, CH_2), 1.75–1.77 (m, 1H, CH), 7.33–7.35, 7.62–7.65 (m, 15H, ArH), 9.52 (bs, 1H, COOH)

* Starred δ values designate signals of the minor diastereomer.

[a] For methyl silylated compounds the signal of residual $CHCl_3$ in $CDCl_3$ was used as internal standard (δ = 7.26).

[b] Satisfactory elemental analyses: C ± 0.29, H ± 0.39, S ± 0.02 (Exceptions, **5b**: H + 0.49; **5d**: C – 3.49, **5h**: H + 1.04).

[c] HRMS values: ± 0.0000 were obtained.

[d] Unstable substances (decomposition).

Table 4. ^{13}C NMR Spectroscopic Data* of **5**, **6**, **7**

Product	^{13}C NMR (101 MHz, CDCl$_3$/TMS; for methyl silylated compounds, CDCl$_3$ at $\delta = 77.00$) δ
5b	19.5, 21.0* (CH$_2$), 28.5*, 29.2 (CH), 30.9, 32.0* (CSPh), 69.4, 70.4*, 72.2, 72.9* (PhCH$_2$OCH$_2$), 113.9*, 116.8 (CH=*C*H$_2$), 125.0, 125.2, 127.3, 127.5, 127.6, 127.8, 128.3, 128.5, 128.6 (ArCH), 136.0, 141.0* (*C*H=CH$_2$), 136.6, 136.7*, 138.3 (ArC)
5d	–3.5*, –1.1 (SiCH$_3$), 12.6*, 15.0 (CH$_2$), 17.6 (*C*SiCH$_3$), 19.7*, 25.5 (CH), 70.9*, 71.4, 72.5 (PhCH$_2$OCH$_2$), 113.4, 116.6* (CH=*C*H$_2$), 127.4, 127.5, 127.6, 127.9, 128.3 (ArCH), 138.1, 138.4* (*C*H=CH$_2$), 143.0 (ArC)
5e	–4.6*, –2.4 (SiCH$_3$), 13.9, 14.7* (CH$_3$), 15.3*, 16.5 (CH), 16.6*, 17.0 (*C*SiCH$_3$), 17.9 (CH$_2$), 112.8, 116.8* (CH=*C*H$_2$), 127.6, 127.7, 127.8, 128.7, 128.9, 129.0 (ArCH), 133.8, 134.2, (ArC), 138.7, 139.2* (*C*H=CH$_2$)
5f	–4.8, –4.7 (SiCH$_3$), 17.0 (*C*SiCH$_3$), 19.9 (CH), 22.6 (CH$_2$), 70.7, 72.5 (PhCH$_2$OCH$_2$), 117.2 (CH=*C*H$_2$), 126.5, 127.5, 127.6, 127.8, 128.2 (ArCH), 137.4, 137.8 (ArC), 138.7 (*C*H=CH$_2$)
5g	–5.4*, –2.3 (SiCH$_3$), 13.7, 13.8* (CH$_3$), 16.0 (*C*SiCH$_3$), 18.5 (CH$_2$), 20.9 (CH), 112.7, 117.3* (CH=*C*H$_2$), 126.6, 126.7, 127.7, 129.0, 134.8, 135.2, 135.3 (ArCH), 136.9*, 137.1 (ArC), 138.4*, 144.0 (*C*H=CH$_2$)
5h	–5.6, –3.3* (SiCH$_3$), 15.4*, 15.7 (*C*SiCH$_3$), 20.2, 20.8* (CH), 26.1 (CH$_2$), 70.5, 72.4*, 72.8, 73.2* (PhCH$_2$OCH$_2$), 113.9*, 117.6 (CH=*C*H$_2$), 126.2, 127.4, 127.7, 128.4, 129.2 (ArCH), 134.5, 135.3 (ArC), 137.7, 138.8* (*C*H=CH$_2$)
5i	14.7 (CH$_3$), 16.1 (CSiPh$_3$), 19.0 (CH$_2$), 22.9 (CH), 112.1 (CH=*C*H$_2$), 127.7, 129.2, 129.4, 129.8, 134.2, 136.3, 136.5 (ArCH), 135.1 (ArC), 144.8 (*C*H=CH$_2$)
5j	14.5*, 15.4 (CSiPh$_3$), 21.1 (CH), 28.2 (CH$_2$), 70.7, 72.4 (PhCH$_2$OCH$_2$), 113.1 (CH=*C*H$_2$), 127.3, 127.7, 128.2, 128.3, 129.4 (ArCH), 133.7, 134.6, 136.6 (ArC), 143.6 (*C*H=CH$_2$)
6a	13.4*, 15.4 (CH$_3$), 18.4*, 20.7 (CH$_2$), 23.2*, 24.8 (CH), 24.4*, 24.9 (CSiPh$_3$), 128.0, 129.7, 129.8, 136.0, 136.2 (ArCH), 133.0*, 133.9 (ArC), 203.3, 203.4* (CHO)
6b	–1.9, –1.8* (SiCH$_3$), 14.0*, 14.9 (CH$_3$), 17.2*, 17.5 (*C*SiCH$_3$), 18.8, 19.2* (CH$_2$), 21.4, 21.5* (CH), 127.6, 127.8, 128.8, 129.1, 134.1, 134.3 (ArCH), 139.3, 139.5* (ArC), 203.6, 204.5* (CHO)
6c	–4.8*, –2.4 (SiCH$_3$), 13.7*, 15.2 (CH$_3$), 18.6*, 19.5 (CH$_2$), 22.0*, 22.6 (CH), 24.9*, 25.4 (*C*SiCH$_3$), 127.9, 129.4, 129.5, 135.0, 135.1 (ArCH), 135.8, 135.9* (ArC), 203.3, 203.9* (CHO)
6d	–4.1 (SiCH$_3$), 15.1 (CH$_2$), 25.3 (*C*SiCH$_3$), 26.3 (CH), 68.5, 72.7 (PhCH$_2$OCH$_2$), 127.5, 127.6, 127.8, 128.3, 129.4, 134.2 (ArCH), 136.1, 138.0 (ArC), 202.7 (CHO)
6e	15.2, 16.8* (CH), 23.5 (CSiPh$_3$), 29.1, 29.7* (CH$_2$), 65.8*, 69.1, 71.6*, 72.5 (PhCH$_2$OCH$_2$), 127.7, 127.9, 128.0, 128.3, 129.8, 135.0, 135.1 (ArCH), 136.2, 136.3* (ArC), 202.7 (CHO)
7a	–1.4, –1.2* (SiCH$_3$), 13.4, 15.7* (CH$_3$), 17.3*, 17.9 (*C*SiCH$_3$), 17.8, 19.8* (CH$_2$), 20.2, 25.4* (CH), 127.6, 128.9, 129.2, 134.2, 134.4 (ArCH), 136.8, 138.4* (ArC), 180.4, 182.7* (COOH)
7b	–4.2*, –1.9 (SiCH$_3$), 14.0, 15.6* (CH$_3$), 18.6*, 19.5 (CH$_2$), 22.2*, 22.6 (CH), 25.2*, 26.2 (*C*SiCH$_3$), 127.5, 127.6, 127.7, 129.0, 135.0, 135.2 (ArCH), 136.6, 136.9* (ArC), 179.5*, 181.6 (COOH)
7c	14.5, 16.3* (CH$_3$), 22.3*, 22.6 (CH$_2$), 25.6*, 26.2 (CH), 26.0*, 26.6 (CSiPh$_3$), 128.1, 129.6, 136.7 (ArCH), 135.4 (ArC), 180.88 (COOH)

* Starred δ values designate signals of the minor diastereomer.

scopic data of 7a (mp 132–134 °C), **7b** (mp 135–137 °C), and **7c** (mp 192–194 °C) see Tables 3, 4.

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