Silicon Grignard Reagents as Nucleophiles in Transition-Metal-Catalyzed Allylic Substitution

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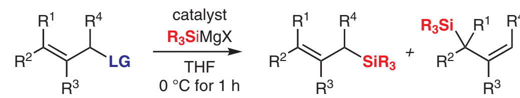

several transition-metal catalysts
broad range of leaving groups
various silicon Grignard reagents

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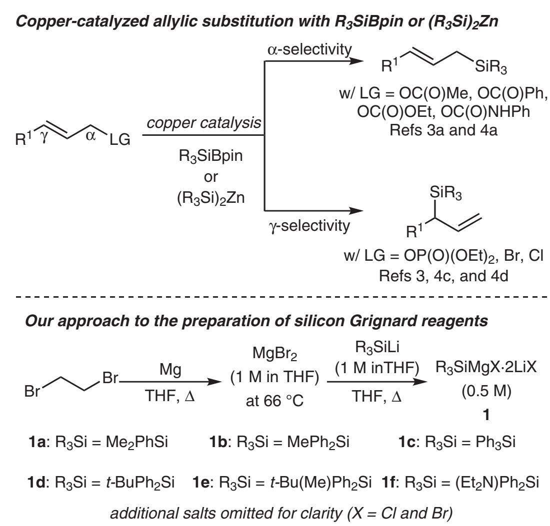
Abstract A broad range of transition-metal catalysts is shown to promote allylic substitution reactions of allylic electrophiles with silicon Grignard reagents. The procedure was further elaborated for CuI as catalyst. The regioselectively is independent of the leaving group for primary allylic precursors, favoring α over γ. The stereochemical course of this allylic transposition was probed with a cyclic system, and *anti*-diastereoselectivity was obtained.

Key words allylic substitution, copper, Grignard reagents, silicon

Allylic silanes are an often-used class of silicon reagents and continue to be widely applied in synthesis.[1] Several methods are available that provide reliable access to these compounds.[2–6] One established methodology is by transition-metal-catalyzed allylic substitution of allylic precursors with silicon (pro)nucleophiles such as Si–Si[2] and Si–B[3] compounds as well as zinc[4] reagents. Examples with copper complexes as catalysts pertinent to the present study are summarized in Scheme 1 (top). The reverse approach, that is, the nucleophilic displacement at silicon electrophiles with carbon nucleophilic, is far less general.[5]

We recently developed a robust method for the preparation of bench-stable solutions of silicon Grignard reagents **1** (Scheme 1, bottom).[7] These had essentially been not available previously,[8] and we decided to assess their suitability as silicon nucleophiles in allylic substitution reactions, particularly with emphasis on the influence of the leaving group on the regioselectivity. Herein, we describe the application of silicon Grignard reagents to allylic substitution reactions catalyzed by manganese, iron, cobalt, nickel, copper, and palladium salts.

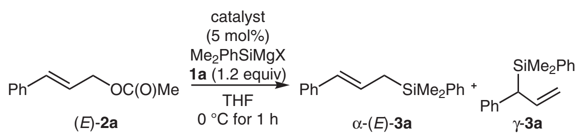


Scheme 1 Copper-catalyzed allylic substitution with silicon (pro)nucleophiles (top; LG: leaving group) and preparation of silicon Grignard reagents (bottom)

We started our investigation by exploring the coupling reaction of commercially available *E*-cinnamyl acetate [(*E*)-**2a**] and $Me_2PhSiMgX$ **1a** (Table 1). At the beginning, several first-row metal salts were employed as catalysts (5 mol%) without additional ligands (Table 1, entries 1–6). Any of these catalysts enabled the reaction, affording the linear allylic silane α-(*E*)-**3a** in near-quantitative yields using $NiBr_2$·glyme, CuI, and CuCN; however, $MnBr_2$, $FeCl_3$, and $CoCl_2$ furnished the desired product in somewhat lower yields. Also, (*E*)-**2a** underwent silylation in the presence of $PdCl_2$ (entry 7). In all these reactions, the thermodynamically favored α-regioisomer was formed with high α/γ ratio. The yield remained high when 2 mol% of CuI were employed. A blank experiment without catalyst gave no conversion (entry 8).

With the ligand-free, copper-catalyzed procedure in hand, we probed the effect of various leaving groups [(*E*)-**2a–i** → α-(*E*)-**3a** and γ-**3a**, Table 2]. Next to model substrate (*E*)-**2a**, *E*-cinnamyl alcohols activated as carboxylate [as in (*E*)-**2b**], carbonates [as in (*E*)-**2c** and (*E*)-**2d**], carbamate [as in (*E*)-**2e**], and phosphate [as in (*E*)-**2f**] participated well in

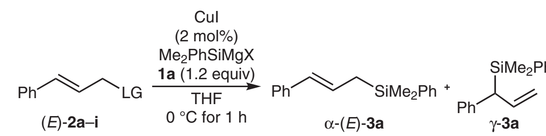
Table 1 Selected Examples of the Catalyst Screening[a]



Entry	Catalyst	*E*/*Z* of α-**3a**[b]	α/γ[b]	Yield (%)[b] of **3a**
1	$MnBr_2$	99:1	96:4	67
2	$FeCl_3$	99:1	98:2	79
3	$CoCl_2$	99:1	99:1	81
4	$NiBr_2$·glyme	99:1	98:2	94
5	CuI	99:1	99:1	95 (95)[c]
6	CuCN	99:1	99:1	95
7	$PdCl_2$	97:3	95:5	80
8	none	–	–	trace

[a] Reactions performed on a 0.50 mmol scale.
[b] Yield is for the mixture of isomers and was determined by GLC analysis with tetracosane as an internal standard.
[c] With CuI (2 mol%).

Table 2 Investigation of Leaving Groups[a]



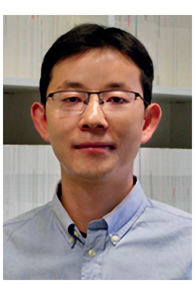
Entry	LG	Substrate	*E*/*Z* of α-**3a**[b]	α/γ[b]	Yield of **3a** (%)[b]
1	OC(O)Me	(*E*)-**2a**	99:1	99:1	95
2	OC(O)Ph	(*E*)-**2b**	97:3	99:1	85
3	OC(O)OMe	(*E*)-**2c**	99:1	96:4	94
4	OC(O)OEt	(*E*)-**2d**	99:1	97:3	92
5	OC(O)NHPh	(*E*)-**2e**	99:1	99:1	88
6	$OP(O)(OEt)_2$	(*E*)-**2f**	95:5	94:6	87
7	Cl	(*E*)-**2g**	96:4	91:9	91
8	Br	(*E*)-**2h**	97:3	96:4	93
9	OH	(*E*)-**2i**	–	–	trace

[a] Reactions performed on a 0.50 mmol scale.
[b] Yield is for the mixture of isomers and was determined by GLC analysis with tetracosane as an internal standard.

this silylation (Table 2, entries 1–6); yields were generally high and α/γ ratios and *E*/*Z* selectivities were good. Cinnamyl halides (*E*)-**2g** and (*E*)-**2h** were also included into the survey (entries 7 and 8), again leading to high yields but to slightly diminished regioselectivities. This outcome, that is α-selectivity for all tested leaving groups, stands in stark contrast to earlier findings in copper-catalyzed allylic substitution with Si–B compounds[3] and silicon zinc reagents[4] (see Scheme 1, top). As expected, the allylic substitution did not occur with free cinnamyl alcohol [(*E*)-**2i**] (entry 9).

This allylic substitution was then applied to a variety of primary allylic precursors using $Me_2PhSiMgX$ **1a** (Scheme 2). In accordance with the previous observations (Tables 1 and 2), isomerically pure geranyl acetate (*E*)-**4a** and neryl acetate (*Z*)-**4a** reacted cleanly to produce allylic silanes α-(*E*)-**8a** and α-(*Z*)-**8a**, respectively, with exclusive preservation of the double bond geometry and excellent α/γ selectivity. Allylic bromide (*E*)-**5h** underwent silylation equally well, however, with reduced regio- and diastereoselectivi-

Biographical Sketches



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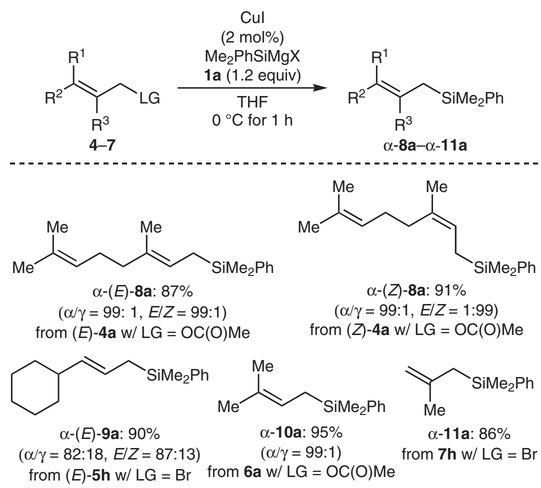
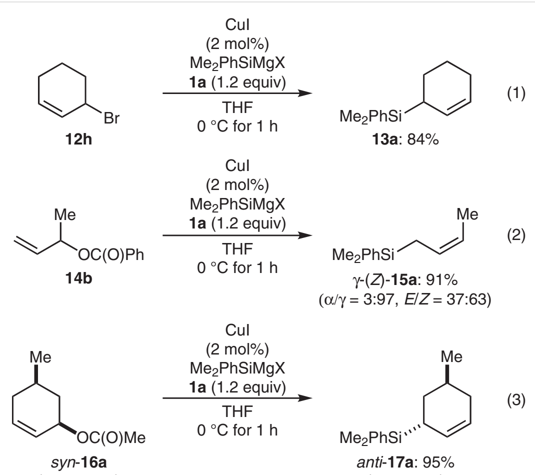
ties. As expected, simple primary allylic electrophiles such as **6a** and **7h** were converted into corresponding silylated products in good yields.



Scheme 2 Copper-catalyzed allylic substitution of primary allylic precursors with silicon Grignard reagents. Yields are for the mixture of isomers, and regiochemical and diasteromeric ratios were confirmed by ^{1}H NMR analysis.

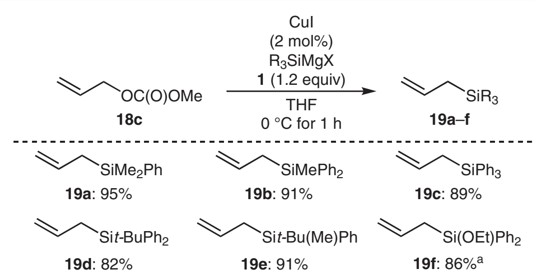
Unlike primary allylic sources that engage in an S_N pathway with high regiocontrol, the regiochemical situation is different for secondary substrates. Cyclic **13a** was obtained in high yield starting from the secondary bromide **12h** (Scheme 3, eq 1). Acyclic **14b** was transformed into γ-(*Z*)-**15a** with excellent γ-selectivity, corresponding to an S_N' mechanism (Scheme 3, eq 2). Interestingly, the *Z*-isomer



Scheme 3 Copper-catalyzed allylic substitution of secondary allylic precursors with silicon Grignard reagents. Yields are for the mixture of isomers, and regiochemical and diasteromeric ratios were confirmed by ^{1}H NMR analysis.

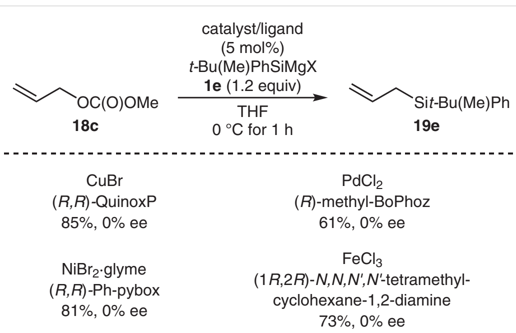
was formed predominantly, which is different from literature precedence.[4a,9] To further distinguish between *anti*-S_N' and *syn*-S_N' mechanisms, cyclic allylic carboxylate *syn*-**16a** was synthesized and subjected to the standard condition (Scheme 3, eq 3).[10] Indeed, *syn*-**16a** was converted into ***anti*-17a** with complete inversion of the stereochemical information. This result is consistent with related copper-promoted allylic substitutions.[3f,4a,11]

Continuing with allyl methyl carbonate (**18c**), different silicon Grignard reagents **1** were subjected to the standard setup (Scheme 4). Similar to $Me_2PhSiMgX$ **1a**, yields are generally excellent for regularly used $MePh_2Si$ (from **1b**) and Ph_3Si (from **1c**) as well as more hindered *t*-$BuPh_2Si$ (from **1d**) and *t*-Bu(Me)PhSi (from **1e**). The same result was obtained with heteroatom-substituted silicon nucleophile **1f**, containing Tamao's silicon anion.[12]



Scheme 4 Copper-catalyzed allylic substitution of allylic precursor **18c** with silicon Grignard reagents. Yields are for the mixture of isomers, and ratios were determined by ^{1}H NMR analysis. [a] $EtOH/NH_4Cl$ added after reaction.

Considering the challenges associated with the construction of silicon-stereogenic silanes,[13] we attempted an enantioselective version of this allylic substitution in the presence of chiral ligands (Scheme 5). The reaction of racemic *t*-Bu(Me)PhSiMgX **1e** and allylic precursor **18c** was chosen as a model reaction. Several catalytic systems were tested but neither led to the asymmetric induction at the silicon atom.



Scheme 5 Attempted enantioselective allylic substitution of allylic carbonate **18c** with *t*-Bu(Me)PhSiMgX (**1e**)

To summarize, we have disclosed here a practical method for the synthesis of allylic silanes from readily accessible allylic precursors and easy-to-handle silicon Grignard reagents. Several metal salts can promote this transformation in moderate to excellent yields without the need of added ligand. The leaving-group scope is broad, comprising the usual oxygen leaving groups as well as halides.

All reactions were performed in flame-dried glassware using conventional Schlenk techniques under a static pressure of N_2, unless otherwise stated. Liquids and solutions were transferred with syringes. CuI (anhyd CuI, 99%, ABCR), other metal salts, and chiral ligands were purchased from commercial suppliers and used as received. Allylic precursors **2a**, **2g**, **2h**, **2i**, (*E*)-**4a**, (*Z*)-**4a**, **6a**, **7h**, **12h**, and **18c** are commercially available. Compounds **2b**,[4c] **2c**,[4c] **2e**,[4c] **2f**,[4c] (*E*)-**5h**,[4c] **14b**,[14] and *syn*-**16a**[10] were synthesized according to the reported procedure, and all spectroscopic data matched those reported. THF was dried over Na or K/benzophenone and distilled prior to use. Technical grade solvents for extraction or chromatography (cyclohexane, CH_2Cl_2, EtOAc, and *n*-pentane) were distilled prior to use. Analytical TLC was performed on silica gel 60 F254 glass plates from Merck. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from Grace using the indicated solvents. ^1H, ^{13}C, and ^{29}Si DEPT NMR spectra were recorded in $CDCl_3$ on Bruker AV400 and AV500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 for ^1H NMR and $CDCl_3$: δ = 77.0 for ^{13}C NMR). ^{29}Si is referenced in compliance with the unified scale for NMR chemical shifts as recommended by the IUPAC stating the chemical shift relative to $BF_3{\cdot}Et_2O$, CCl_3F and Me_4Si.[15] Data are reported as follows: chemical shift, multiplicity (standard abbreviations), coupling constant (Hz), and integration. Gas liquid chromatography (GLC) was performed on a Varian 430-GC gas chromatograph equipped with a Varian FactorFour Capillary column (30 m × 0.25 mm, 0.25 μm film thickness). Enantiomeric excesses were determined by analytical high-performance liquid chromatography (HPLC) analysis on an Agilent Technologies 1290 Infinity instrument with a chiral stationary phase using Daicel Chiralcel OJ-RH, ($MeCN/H_2O$ mixtures as solvent). Melting points were determined using a Leica Galen III melting point apparatus. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

Preparation of R_3SiMgX 1; General Procedure 1 (GP 1)

At 0 °C, the required chlorosilane (24.0 mmol, 1.0 equiv) was added to a flame-dried Schlenk flask charged with activated Li chunks (666 mg, 96.0 mmol, 4.0 equiv) suspended in THF (20 mL), and the resulting suspension was stirred at this temperature overnight under N_2 atmosphere to give R_3SiLi. The concentration of R_3SiLi (~1.0 M in THF, approximately 80–90% conversion) was determined by titration against diphenylacetic acid (Kofron's method).[16] A flame-dried two-necked round-bottomed flask charged with a magnetic stir bar and equipped with a water condenser is connected to a Schlenk line and purged with N_2. The flask was charged with Mg turnings (292 mg, 12.0 mmol, 1.2 equiv) followed by the addition of THF (10 mL) and was then heated to 66 °C. 1,2-Dibromoethane (1.88 g, 10.0 mmol, 1.0 equiv) was quickly added via syringe, and the reaction mixture was heated at reflux for 3 h at high water-flow rate to afford $MgBr_2$ (1.0 M in THF at 66 °C). Then, the corresponding R_3SiLi solution (10 mmol, 1.0 equiv) was subsequently added dropwise to the $MgBr_2$ solution over 10 min at this temperature. $R_3SiMgX{\cdot}2LiX$ solution formed was cooled to r.t. The concentration of $R_3SiMgX{\cdot}2LiX$ (~0.5 M in THF, full conversion) was determined by titration against I_2 (Knochel's method).[17] The homogeneous $R_3SiMgX{\cdot}2LiX$ solution could be stored in a Schlenk flask purged with N_2 at 2–8 °C in a fridge.

The color of the $R_3SiMgX{\cdot}2LiX$ solution depends on the substitution at the silicon atom: $Me_2PhSiMgX{\cdot}2LiX$ **1a** (purple), $MePh_2SiMgX{\cdot}2LiX$ **1b** (light purple), $Ph_3SiMgX{\cdot}2LiX$ **1c** (brown), *t*-$BuPh_2SiMgX{\cdot}2LiX$ **1d** (light green), *t*-Bu(Me)PhSiMgX·2LiX **1e** (light purple), $(Et_2N)Ph_2SiMgBr{\cdot}2LiX$ **1f** (gray).

Copper-Catalyzed Allylic Substitution with R_3SiMgX 1; General Procedure 2 (GP 2)

A flame-dried Schlenk flask equipped with a stir bar was charged with CuI (1.9 mg, 0.010 mmol, 2.0 mol%). The flask was evacuated and backfilled with N_2 (3 ×) followed by the addition of THF (1 mL). After stirring for 10 min at r.t., the indicated allylic precursor (0.50 mmol, 1.0 equiv) was added, and the solution was brought to 0 °C. Then, the corresponding R_3SiMgX **1** (0.60 mmol, 1.2 equiv) was added over 1 min. After 1 h, the reaction was quenched with sat. aq NH_4Cl (5 mL). CH_2Cl_2 (20 mL) was added for extraction, and the CH_2Cl_2 layer was washed with brine (20 mL) and H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and the solvents were evaporated under reduced pressure. Purification of the residue by flash column chromatography on silica gel with indicated solvent as eluent afforded the silylated product.

(*E*)-Cinnamyldimethyl(phenyl)silane [α-(*E*)-3a]

Prepared from (*E*)-cinnamyl acetate [(*E*)-**2a**; 88 mg, 0.50 mmol] according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded α-(*E*)-**3a** as a colorless oil; yield: 120 mg (95%, contaminated with 1,1,2,2-tetramethyl-1,2-diphenyldisilane); R_f = 0.60 (*n*-pentane).

^1H NMR (500 MHz, $CDCl_3$): δ = 0.31 (s, 6 H), 1.90 (d, *J* = 6.5 Hz, 2 H), 6.16–6.26 (m, 2 H), 7.12–7.17 (m, 1 H), 7.24–7.26 (m, 4 H), 7.35–7.38 (m, 3 H), 7.49–7.55 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.3, 23.0, 125.6, 126.3, 127.1, 127.8, 128.4, 128.9, 129.1, 133.6, 138.4, 138.5.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –4.1.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{20}Si$: 252.1334; found: 252.1332.

The spectroscopic data are in accordance with those reported.[4c]

(*E*)-Geranyldimethyl(phenyl)silane [α-(*E*)-8a]

Prepared from (*E*)-geranyl acetate [(*E*)-**4a**; 98 mg, 0.50 mmol] according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded α-(*E*)-**8a** as a colorless oil; yield: 119 mg (87%); R_f = 0.65 (*n*-pentane).

^1H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 6 H), 1.50 (s, 3 H), 1.61 (s, 3 H), 1.64 (d, *J* = 8.6 Hz, 2 H), 1.69 (s, 3 H), 1.97–2.02 (m, 2 H), 2.03–2.10 (m, 2 H), 5.09 (tt, *J* = 6.7, 1.4 Hz, 1 H), 5.17 (tq, *J* = 8.6, 1.4 Hz, 1 H), 7.31–7.38 (m, 3 H), 7.49–7.55 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.3, 15.8, 17.67, 17.69, 25.7, 26.9, 40.0, 119.6, 124.6, 127.7, 128.8, 131.2, 133.1, 133.6, 139.3.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –3.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{28}Si$: 272.1955; found: 272.1952.

The spectroscopic data are in accordance with those reported.[4a]

(*Z*)-Neryldimethyl(phenyl)silane [α-(*Z*)-8a]

Prepared from (*Z*)-neryl acetate [(*Z*)-**4a**; 98 mg, 0.50 mmol] according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded α-(*Z*)-**8a** as a colorless oil; yield: 124 mg (91%); R_f = 0.65 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 6 H), 1.60 (s, 3 H), 1.65 (d, *J* = 8.6 Hz, 2 H), 1.69 (s, 6 H), 1.94–2.02 (m, 4 H), 5.07–5.13 (m, 1 H), 5.17 (t, *J* = 8.6 Hz, 1 H), 7.33–7.38 (m, 3 H), 7.49–7.54 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.2, 17.3, 17.6, 23.4, 25.7, 26.4, 31.7, 119.7, 124.6, 127.7, 128.8, 131.4, 133.6, 133.9, 139.3.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –4.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{28}Si$: 272.1955; found: 272.1952.

The spectroscopic data are in accordance with those reported.[4a]

(3-Cyclohexylallyl)dimethyl(phenyl)silane (9a)

Prepared from (*E*)-(3-bromoprop-1-en-1-yl)cyclohexane [(*E*)-**5h**; 102 mg, 0.50 mmol] according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **9a** as a colorless oil; yield: 116 mg (90%, mixture of all isomers). The ratio of different isomers was confirmed by ^{1}H NMR analysis.

α-(*E*)-9a

R_f = 0.70 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 6 H), 1.03–1.25 (m, 5 H), 1.61–1.71 (m, 8 H), 5.19–5.25 (m, 1 H), 5.29–5.38 (m, 1 H), 7.33–7.37 (m, 3 H), 7.49–7.54 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.4, 21.6, 26.1, 26.2, 33.5, 41.0, 122.7, 127.6, 128.8, 133.7, 136.0, 139.1.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –4.7.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{26}Si$: 258.1798; found: 258.1786.

Prenyldimethy(phenyl)silane (α-10a)

Prepared from prenyl acetate (**6a**; 64 mg, 0.50 mmol) according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded α-**10a** as a colorless oil; yield: 97 mg (95%); R_f = 0.70 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 6 H), 1.50 (s, 3 H), 1.63 (d, *J* = 8.6 Hz, 2 H), 1.69 (s, 3 H), 5.16 (tt, *J* = 8.6, 1.4 Hz, 1 H), 7.31–7.38 (m, 3 H), 7.49–7.55 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.2, 17.6, 17.7, 25.7, 119.3, 127.6, 128.8, 129.5, 133.6, 139.3.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –3.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{20}Si$: 204.1329; found: 204.1329.

The spectroscopic data are in accordance with those reported.[9]

Dimethyl(2-methylallyl)(phenyl)silane (α-11a)

Prepared from 3-bromo-2-methylpropene (**7h**; 68 mg, 0.50 mmol) according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded α-**11a** as a colorless oil; yield: 82 mg (86%); R_f = 0.70 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.32 (s, 6 H), 1.62 (s, 3 H), 1.78 (s, 2 H), 4.47–4.50 (m, 1 H), 4.59–4.62 (m, 1 H), 7.32–7.39 (m, 3 H), 7.50–7.57 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –2.9, 25.2, 25.7, 108.8, 127.7, 128.9, 133.6, 139.1, 143.3.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –5.0.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{18}Si$: 190.1172; found: 190.1164.

The spectroscopic data are in accordance with those reported.[18]

Dimethyl(cyclohex-2-en-1-yl)(phenyl)silane (13a)

Prepared from 3-bromocyclohexene (**12h**; 81 mg, 0.50 mmol) according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **13a** as a colorless oil; yield: 91 mg (84%); R_f = 0.75 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.28 (s, 3 H), 0.29 (s, 3 H), 1.43–1.53 (m, 2 H), 1.63–1.70 (m, 1 H), 1.74–1.82 (m, 2 H), 1.88–2.03 (m, 2 H), 5.60–5.69 (m, 2 H), 7.31–7.39 (m, 3 H), 7.50–7.56 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.8 ($SiCH_3$), –4.6 ($SiCH_3$), 22.5, 23.8, 25.0, 25.6, 125.9, 127.5, 127.7, 128.9, 133.9, 138.3.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –2.5.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{20}Si$: 216.1334; found: 216.1327.

The spectroscopic data are in accordance with those reported.[9]

Dimethyl(but-2-en-1-yl)(phenyl)silane (15a)

Prepared from but-3-en-2-yl benzoate (**14b**; 88 mg, 0.50 mmol) according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **15a** as a colorless oil; yield: 87 mg (91%, mixture of all isomers). The ratio of different isomers was confirmed by ^{1}H NMR analysis; R_f = 0.70 (*n*-pentane).

γ-(*Z*)-15a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 6 H), 1.51 (d, *J* = 6.0 Hz, 3 H), 1.73 (d, *J* = 8.6 Hz, 2 H), 5.34–5.43 (m, 2 H), 7.33–7.38 (m, 3 H), 7.46–7.57 (m, 2 H).

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –3.8.

γ-(*E*)-15a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29 (s, 6 H), 1.61–1.68 (m, 5 H), 5.25–5.46 (m, 2 H), 7.33–7.38 (m, 3 H), 7.46–7.57 (m, 2 H).

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –4.6.

The spectroscopic data are in accordance with those reported.[9]

***anti*-Dimethyl(5-methylcyclohex-2-en-1-yl)(phenyl)silane (*anti*-17a)**

Prepared from *syn*-5-methylcyclohex-2-en-1-yl acetate (*syn*-**16a**; 77 mg, 0.50 mmol) according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded *anti*-**17a** as a colorless oil; yield: 109 mg (95%, mixture of all isomers). The ratio of different isomers was confirmed by ^{1}H NMR analysis; R_f = 0.50 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29 (s, 3 H), 0.30 (s, 3 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 1.41–1.48 (m, 1 H), 1.58–1.72 (m, 3 H), 1.82–1.87 (m, 1 H), 2.01–2.07 (m, 1 H), 5.55–5.59 (m, 1 H), 5.61–5.65 (m, 1 H), 7.33–7.37 (m, 3 H), 7.49–7.54 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.13 ($SiCH_3$), –4.08 ($SiCH_3$), 21.2, 24.9, 26.2, 31.2, 33.0, 124.3, 127.2, 127.7, 128.9, 133.9, 138.5.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –2.6.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{22}Si$: 230.1491; found: 230.1492.

The spectroscopic data are in accordance with those reported.[3f]

Allyldimethyl(phenyl)silane (19a)

Prepared from allyl methyl carbonate (**18c**; 58 mg, 0.50 mmol) according to GP 2 with $Me_2PhSiMgX$ **1a** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **19a** as a colorless oil; yield: 84 mg (95%); R_f = 0.65 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29 (s, 6 H), 1.76 (d, *J* = 8.6 Hz, 2 H), 4.82–4.92 (m, 2 H), 5.73–5.83 (m, 1 H), 7.33–7.39 (m, 3 H), 7.49–7.55 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.5, 23.7, 113.4, 127.7, 129.0, 133.6, 134.6, 138.7.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –4.7.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{16}Si$: 176.1021; found: 176.1018.

The spectroscopic data are in accordance with those reported.[18]

Allyl(methyl)diphenylsilane (19b)

Prepared from allyl methyl carbonate (**18c**; 58 mg, 0.50 mmol) according to GP 2 with $MePh_2SiMgX$ **1b** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **19b** as a colorless oil; yield: 108 mg (91%); R_f = 0.55 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.56 (s, 3 H), 2.08 (d, *J* = 8.6 Hz, 2 H), 4.85–4.95 (m, 2 H), 5.75–5.85 (m, 1 H), 7.33–7.40 (m, 6 H), 7.51–7.56 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.8, 22.1, 114.2, 127.8, 129.2, 134.1, 134.5, 136.6.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –9.6.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{18}Si$: 238.1178; found: 238.1172.

The spectroscopic data are in accordance with those reported.[19]

Allyltriphenylsilane (19c)

Prepared from allyl methyl carbonate (**18c**; 58 mg, 0.50 mmol) according to GP 2 with Ph_3SiMgX **1c** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **19c** as a white solid; yield: 134 mg (89%); mp 90.0–90.8 °C; R_f = 0.35 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (d, *J* = 7.8 Hz, 2 H), 4.87–4.98 (m, 2 H), 5.81–5.92 (m, 1 H), 7.33–7.44 (m, 9 H), 7.50–7.55 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 115.1, 127.8, 129.5, 133.8, 134.6, 135.7.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –13.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{20}Si$: 300.1334; found: 300.1330.

The spectroscopic data are in accordance with those reported.[19]

Allyl(*tert*-butyl)diphenylsilane (19d)

Prepared from allyl methyl carbonate (**18c**; 58 mg, 0.50 mmol) according to GP 2 with *t*-$BuPh_2SiMgX$ **1d** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **19d** as a colorless oil; yield: 115 mg (82%); R_f = 0.65 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 9 H), 2.08 (dt, *J* = 8.6, 1.4 Hz, 2 H), 4.78–4.82 (m, 1 H), 4.88–4.93 (m, 1 H), 5.71–5.82 (m, 1 H), 7.33–7.41 (m, 6 H), 7.59–7.64 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.5, 18.8, 27.9, 114.5, 127.5, 129.1, 134.4, 134.7, 136.0.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –5.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{24}Si$: 280.1642; found: 280.1636.

The spectroscopic data are in accordance with those reported.[20]

Allyl(*tert*-butyl)(methyl)(phenyl)silane (19e)

Prepared from allyl methyl carbonate (**18c**; 58 mg, 0.50 mmol) according to GP 2 with *t*-Bu(Me)PhSiMgX **1e** at 0 °C. Purification by flash column chromatography on silica gel using *n*-pentane afforded **19e** as a colorless oil; yield: 99 mg (91%); R_f = 0.65 (*n*-pentane).

HPLC-analysis: OJ-RH (Dacial), $MeCN/H_2O$ = 65:35, 0.2 mL/min, λ = 210 nm, t_R = 47.9, 51.1 min.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.28 (s, 3 H), 0.90 (s, 9 H), 1.81–1.87 (m, 1 H), 1.93–1.99 (m, 1 H), 4.78–4.82 (m, 1 H), 4.86–4.92 (m, 1 H), 5.71–5.82 (m, 1 H), 7.31–7.44 (m, 3 H), 7.48–7.55 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –8.6, 17.4, 18.7, 26.8, 113.6, 127.5, 128.9, 134.7, 135.0, 136.0.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = 1.5.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{22}Si$: 218.1485; found: 218.1482.

Allyl(ethoxy)diphenylsilane (19f)

Prepared from allyl methyl carbonate (**18c**; 58 mg, 0.50 mmol) according to GP 2 with $(Et_2N)Ph_2SiMgX$ **1f** at 0 °C. Afterwards, anhyd EtOH (1 mL) and NH_4Cl (55 mg, 2.0 mmol) was added, and the reaction mixture was stirred overnight. Purification by flash column chromatography on silica gel using *n*-pentane afforded **19f** as a colorless oil; yield: 115 mg (86%); R_f = 0.30 (*n*-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.1 Hz, 3 H), 2.18 (dt, *J* = 7.8, 1.4 Hz, 2 H), 3.81 (q, *J* = 7.1 Hz, 2 H), 4.88–4.98 (m, 2 H), 5.80–5.90 (m, 1 H), 7.35–7.44 (m, 6 H), 7.59–7.64 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.4, 21.9, 59.5, 115.0, 127.8, 129.9, 133.1, 134.70, 134.73.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –8.6.

HRMS (EI): *m*/*z* $[M - C_3H_5]^+$ calcd for $C_{14}H_{15}OSi$: 227.0887; found: 227.0889.

The spectroscopic data are in accordance with those reported.[21]

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