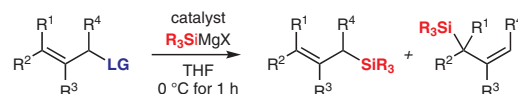


Silicon Grignard Reagents as Nucleophiles in Transition-Metal-Catalyzed Allylic Substitution

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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 regioselectivity 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.

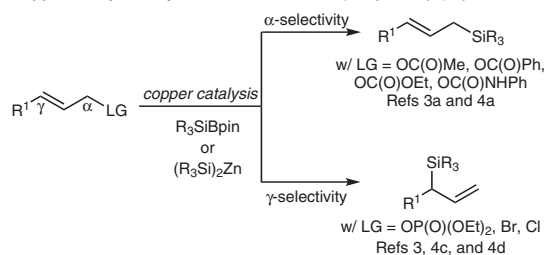
Key words allylic substitution, copper, Grignard reagents, silicon

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–Si² and Si–B³ compounds as well as zinc⁴ 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

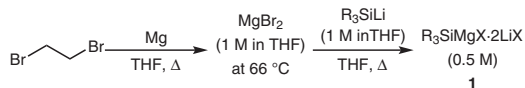
We recently developed a robust method for the preparation of bench-stable solutions of silicon Grignard reagents **1** (Scheme 1, bottom).⁷ These had essentially been not available previously,⁸ and we decided to assess their suitability as silicon nucleophiles in allylic substitution reactions, particularly 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.

We started our investigation by exploring the coupling reaction of commercially available *E*-cinnamyl acetate [(*E*)-**2a**] and Me₂PhSiMgX **1a** (Table 1). At the beginning, several first-row metal salts were employed as catalysts (5 mol%)

Copper-catalyzed allylic substitution with R₃SiBpin or (R₃Si)₂Zn



Our approach to the preparation of silicon Grignard reagents



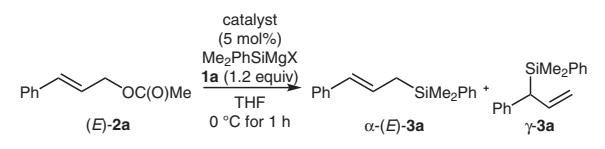
1a: R₃Si = Me₂PhSi **1b:** R₃Si = MePh₂Si **1c:** R₃Si = Ph₃Si
1d: R₃Si = *t*-BuPh₂Si **1e:** R₃Si = *t*-Bu(Me)Ph₂Si **1f:** R₃Si = (Et₂N)Ph₂Si

additional salts omitted for clarity (X = Cl and Br)

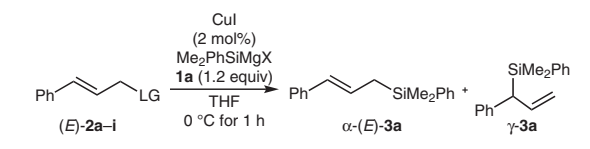
Scheme 1 Copper-catalyzed allylic substitution with silicon (pro)nucleophiles (top); LG: leaving group) and preparation of silicon Grignard reagents (bottom)

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 NiBr₂·glyme, CuI, and CuCN; however, MnBr₂, FeCl₃, and CoCl₂ furnished the desired product in somewhat lower yields. Also, (*E*)-**2a** underwent silylation in the presence of PdCl₂ (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** \rightarrow 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	<i>E/Z</i> 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


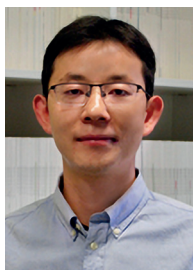
Entry	LG	Substrate	<i>E/Z</i> of α - 3a ^b	α/γ ^b	Yield of 3a (%) ^b
1	OC(O)Me	(<i>E</i>)- 2a	99:1	99:1	95
2	OC(O)Ph	(<i>E</i>)- 2b	97:3	99:1	85
3	OC(O)OMe	(<i>E</i>)- 2c	99:1	96:4	94
4	OC(O)OEt	(<i>E</i>)- 2d	99:1	97:3	92
5	OC(O)NHPh	(<i>E</i>)- 2e	99:1	99:1	88
6	OP(O)(OEt) ₂	(<i>E</i>)- 2f	95:5	94:6	87
7	Cl	(<i>E</i>)- 2g	96:4	91:9	91
8	Br	(<i>E</i>)- 2h	97:3	96:4	93
9	OH	(<i>E</i>)- 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 compounds³ and silicon zinc reagents⁴ (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 Me₂PhSiMgX **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



Weichao Xue (born in 1989 in Pingdingshan/China) studied Chemistry at Henan University (2008–2012) and Shanghai University (2012–2015). He obtained his bachelor's degree with Feng Shi (Kaifeng, 2012) and master's degree with Hegui

Gong (Shanghai, 2015). He then moved to Berlin to pursue doctoral research funded by the China Scholarship Council (2015–2019). Currently, he is a Ph.D. candidate in the group of Martin Oestreich at the Technische Universität Berlin. He is

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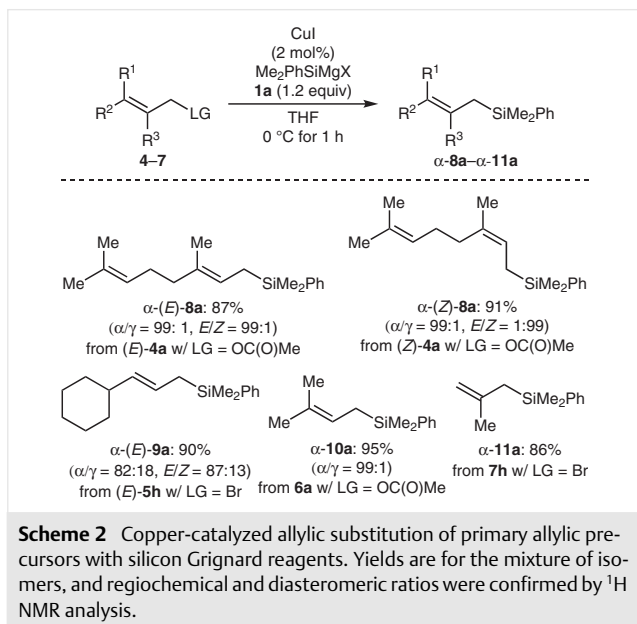


Martin Oestreich (born in 1971 in Pforzheim/Germany) is Professor of Organic Chemistry at the Technische Universität Berlin. He received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe

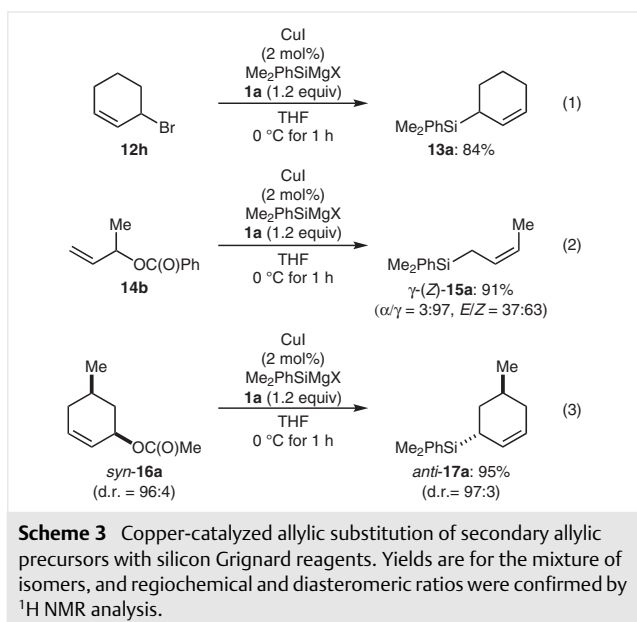
(Münster, 1999). After a two-year postdoctoral stint with Larry E. Overman (Irvine, 1999–2001), he completed his habilitation with Reinhard Brückner (Freiburg, 2001–2005) and was appointed as Professor of Organic Chemistry at the West-

fälische Wilhelms-Universität Münster (2006–2011). He also held visiting positions at Cardiff University in Wales (2005), The Australian National University in Canberra (2010), and Kyoto University (2018).

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

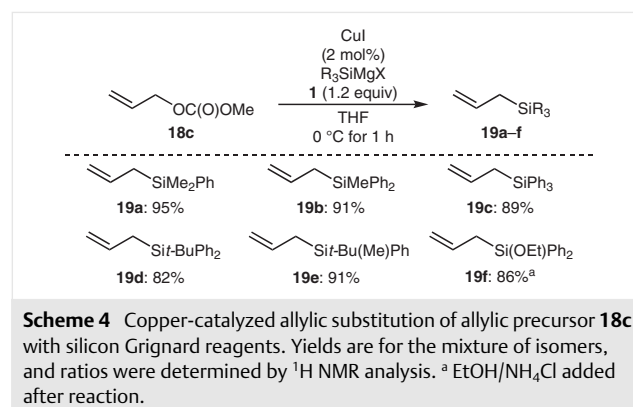


Unlike primary allylic sources that engage in an S_N pathway with high regiocontrol, the regiochemical situation is different for secondary substrates. Cyclic **13a** was obtained in high yield starting from the secondary bromide **12h** (Scheme 3, eq 1). Acyclic **14b** was transformed into γ-(Z)-**15a**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

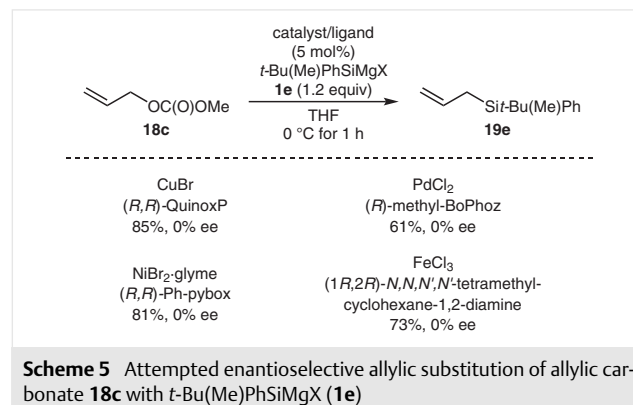


was formed predominantly, which is different from literature precedence.^{4a,9} To further distinguish between *anti*-S_N' and *syn*-S_N' mechanisms, cyclic allylic carboxylate *syn*-**16a** was synthesized and subjected to the standard condition (Scheme 3, eq 3).¹⁰ Indeed, *syn*-**16a** was converted 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 Me₂PhSiMgX **1a**, yields are generally excellent for regularly used MePh₂Si (from **1b**) and Ph₃Si (from **1c**) as well as more hindered *t*-BuPh₂Si (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



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.



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 N₂, 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, CH₂Cl₂, 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, ¹³C, and ²⁹Si DEPT NMR spectra were recorded in CDCl₃ 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 (CHCl₃: δ = 7.26 for ¹H NMR and CDCl₃: δ = 77.0 for ¹³C NMR). ²⁹Si is referenced in compliance with the unified scale for NMR chemical shifts as recommended by the IUPAC stating the chemical shift relative to BF₃·Et₂O, CCl₃F and Me₄Si.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/H₂O 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 R₃SiMgX **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 N₂ atmosphere to give R₃SiLi. The concentration of R₃SiLi (~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 N₂. 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 MgBr₂ (1.0 M in THF at 66 °C). Then, the corresponding R₃SiLi solution (10 mmol, 1.0 equiv) was subsequently added dropwise to the MgBr₂ solution

over 10 min at this temperature. R₃SiMgX·2LiX solution formed was cooled to r.t. The concentration of R₃SiMgX·2LiX (~0.5 M in THF, full conversion) was determined by titration against I₂ (Knochel's method).¹⁷ The homogeneous R₃SiMgX·2LiX solution could be stored in a Schlenk flask purged with N₂ at 2–8 °C in a fridge.

The color of the R₃SiMgX·2LiX solution depends on the substitution at the silicon atom: Me₂PhSiMgX·2LiX **1a** (purple), MePh₂SiMgX·2LiX **1b** (light purple), Ph₃SiMgX·2LiX **1c** (brown), *t*-BuPh₂SiMgX·2LiX **1d** (light green), *t*-Bu(Me)PhSiMgX·2LiX **1e** (light purple), (Et₂N)Ph₂SiMgBr·2LiX **1f** (gray).

Copper-Catalyzed Allylic Substitution with R₃SiMgX **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 N₂ (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 R₃SiMgX **1** (0.60 mmol, 1.2 equiv) was added over 1 min. After 1 h, the reaction was quenched with sat. aq NH₄Cl (5 mL). CH₂Cl₂ (20 mL) was added for extraction, and the CH₂Cl₂ layer was washed with brine (20 mL) and H₂O (20 mL). The aqueous phase was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic phases were dried (anhyd Na₂SO₄), 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*)-Cinnamyl dimethyl(phenyl)silane [α-(*E*)-**3a**]

Prepared from (*E*)-cinnamyl acetate [(*E*)-**2a**; 88 mg, 0.50 mmol] according to GP 2 with Me₂PhSiMgX **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, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): 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.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –4.1.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₇H₂₀Si: 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 Me₂PhSiMgX **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, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): 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.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –3.8.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₈H₂₈Si: 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 Me₂PhSiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): 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.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –4.2.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₈H₂₈Si: 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 Me₂PhSiMgX **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 ¹H NMR analysis.

 α -(E)-9a

R_f = 0.70 (*n*-pentane).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): 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.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –4.7.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₇H₂₆Si: 258.1798; found: 258.1786.

Prenyldimethyl(phenyl)silane (α -10a)

Prepared from prenyl acetate (**6a**; 64 mg, 0.50 mmol) according to GP 2 with Me₂PhSiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –3.2, 17.6, 17.7, 25.7, 119.3, 127.6, 128.8, 129.5, 133.6, 139.3.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –3.8.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₃H₂₀Si: 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 Me₂PhSiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –2.9, 25.2, 25.7, 108.8, 127.7, 128.9, 133.6, 139.1, 143.3.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –5.0.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₂H₁₈Si: 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 Me₂PhSiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –4.8 (SiCH₃), –4.6 (SiCH₃), 22.5, 23.8, 25.0, 25.6, 125.9, 127.5, 127.7, 128.9, 133.9, 138.3.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –2.5.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₂₀Si: 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 Me₂PhSiMgX **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 ¹H NMR analysis; *R_f* = 0.70 (*n*-pentane).

 γ -(Z)-15a

¹H NMR (500 MHz, CDCl₃): 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).

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –3.8.

 γ -(E)-15a

¹H NMR (500 MHz, CDCl₃): 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).

²⁹Si DEPT NMR (99 MHz, CDCl₃): 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 Me₂PhSiMgX **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 ¹H NMR analysis; *R_f* = 0.50 (*n*-pentane).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –4.13 (SiCH₃), –4.08 (SiCH₃), 21.2, 24.9, 26.2, 31.2, 33.0, 124.3, 127.2, 127.7, 128.9, 133.9, 138.5.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –2.6.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₅H₂₂Si: 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 Me₂PhSiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –3.5, 23.7, 113.4, 127.7, 129.0, 133.6, 134.6, 138.7.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –4.7.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₁H₁₆Si: 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 MePh₂SiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –4.8, 22.1, 114.2, 127.8, 129.2, 134.1, 134.5, 136.6.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –9.6.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₆H₁₈Si: 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 Ph₃SiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = 21.8, 115.1, 127.8, 129.5, 133.8, 134.6, 135.7.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –13.8.

HRMS (EI): *m/z* [M]⁺ calcd for C₂₁H₂₀Si: 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*-BuPh₂SiMgX **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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = 18.5, 18.8, 27.9, 114.5, 127.5, 129.1, 134.4, 134.7, 136.0.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –5.2.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₉H₂₄Si: 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 (Dacal), MeCN/H₂O = 65:35, 0.2 mL/min, λ = 210 nm, *t*_R = 47.9, 51.1 min.

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = –8.6, 17.4, 18.7, 26.8, 113.6, 127.5, 128.9, 134.7, 135.0, 136.0.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = 1.5.

HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₂₂Si: 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 (Et₂N)Ph₂SiMgX **1f** at 0 °C. Afterwards, anhyd EtOH (1 mL) and NH₄Cl (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).

¹H NMR (500 MHz, CDCl₃): 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).

¹³C NMR (125 MHz, CDCl₃): δ = 18.4, 21.9, 59.5, 115.0, 127.8, 129.9, 133.1, 134.70, 134.73.

²⁹Si DEPT NMR (99 MHz, CDCl₃): δ = –8.6.

HRMS (EI): *m/z* [M – C₃H₅]⁺ calcd for C₁₄H₁₅OSi: 227.0887; found: 227.0889.

The spectroscopic data are in accordance with those reported.²¹

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