

Electronic Supplementary Information

Regioselective synthesis of highly functionalized alkenylboronates by Cu-catalyzed borylation of propargylic silylalkynes

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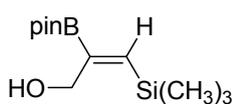
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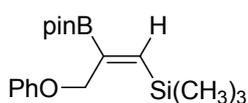
General methods: CuCl, NaO*t*-Bu, bis(pinacolato)diboron and other commercial substrates were purchased and used as received. THF was distilled using sodium benzophenone ketyl as drying agent under nitrogen. Propargylic silylalkynes (**2** and **4**) were prepared by following literature procedures: a) lithiation of propargylic alkyne and subsequent silylation¹ (**2a–2g**, **4a–4c**) b) addition of silylalkyne to ketones or imines² (**4d–4g**). All reactions were performed in oven-dried Schlenk tubes under nitrogen. Flash chromatography was performed on silica gel from Merck (70–230 mesh). GC analysis was performed on a Younglin Acme 6000 series. Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and are recorded in cm⁻¹. All ¹H NMR spectra were obtained on Varian Mercury 300 systems and reported in parts per million (ppm) downfield from tetramethylsilane. ¹³C NMR spectra were reported in ppm. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu, Korea) and Sogang Center for Research Facilities of Sogang university (Seoul, Korea) and reported in the form of *m/z* (intensity relative to base peak = 100).

General procedure for the copper-catalyzed borylation of propargylic silylalkynes: To a Schlenk tube equipped with a stir bar were added CuCl (2.5 mg, 0.025 mmol), NaO*t*-Bu (9.6 mg, 0.10 mmol), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (10.2 mg, 0.03 mmol) and THF (0.50 mL) under nitrogen. After the mixture was stirred at room temperature for 15 min, bis(pinacolato)diboron (153 mg, 0.60 mmol) in THF (0.50 mL) was added. The reaction mixture was stirred for 10 min. Then, internal alkyne (**2** or **4**) (0.50 mmol) was added, followed by MeOH (0.04 mL, 1 mmol). The reaction was washed with THF (0.50 mL), sealed, and stirred until no starting material was detected by TLC and GC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.



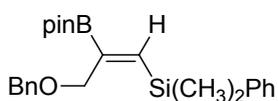
3a

(Z)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)prop-2-en-1-ol (Table 1, entry 1): The title compound was isolated as a yellow oil in 79 % yield (101.0 mg). ¹H NMR: (300 MHz, CDCl₃) δ 6.68 (s, 1H), 4.31 (d, *J* = 6.0 Hz, 2H), 2.39 (t, *J* = 6.0 Hz, 1H), 1.29 (s, 12H), 0.15 (s, 9H); ¹³C NMR: (100 MHz, CDCl₃) δ 149.4, 84.0, 65.4, 25.0, 0.2; IR (neat): 3342, 2943, 2831, 1027, 855 cm⁻¹.



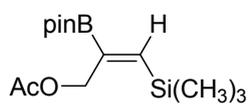
3b

(Z)-Trimethyl(3-phenoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (Table 1, entry 2): The title compound was isolated as a white solid in 64 % yield (107.1 mg). ¹H NMR: (300 MHz, CDCl₃) δ 7.30–7.24 (m, 2H), 6.96–6.90 (m, 3H), 6.86 (s, 1H), 4.65 (s, 2H), 1.26 (s, 12H), 0.16 (s, 9H); ¹³C NMR: (100 MHz, CDCl₃) δ 159.0, 151.8, 129.5, 120.7, 115.0, 83.9, 68.6, 24.9, 0.1; IR (neat): 3335, 2944, 2832, 1027, 852 cm⁻¹; HRMS (ESI) *m/z* calcd C₁₈H₂₉BNaO₃Si [M+Na]⁺ 355.1877, found 355.1875.



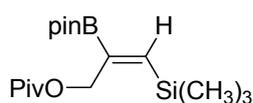
3c

(Z)-3-(Benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)dimethyl(phenyl)silane (Table 1, entry 3): The title compound was isolated as a colorless oil in 72 % yield (125.2 mg). ¹H NMR: (300 MHz, CDCl₃) δ 7.53–7.50 (m, 2H), 7.48–7.27 (m, 8H), 6.81 (s, 1H), 4.30 (s, 2H), 4.09 (d, *J* = 0.9 Hz, 2H), 1.27 (s, 12H), 0.37 (s, 6H); ¹³C NMR: (100 MHz, CDCl₃) δ 147.3, 139.5, 138.7, 133.9, 128.6, 128.2, 127.9, 127.4, 83.8, 72.3, 71.8, 24.9, 0.71; IR (neat): 3332, 2943, 2831, 1450, 1026, 834 cm⁻¹.



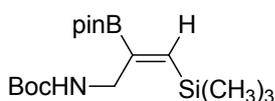
3d

(Z)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl acetate (Table 1, entry 4): The title compound was isolated as a white solid in 85 % yield (127.3 mg). ¹H NMR: (300 MHz, CDCl₃) δ 6.79 (s, 1H), 4.73 (s, 2H), 2.05 (s, 3H), 1.27 (s, 12H), 0.15 (s, 9H); ¹³C NMR: (100 MHz, CDCl₃) δ 171.0, 152.2, 83.9, 65.6, 24.9, 21.3, 0.0; IR (neat): 1737, 1458, 1255, 1147, 1032 cm⁻¹; HRMS (ESI) *m/z* calcd C₁₄H₂₇BNaO₄Si [M+Na]⁺ 321.1669, found 321.1667.



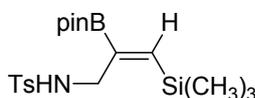
3e

(Z)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl pivalate (Table 1, entry 5): The title compound was isolated as a white solid in 82 % yield (139.4 mg). ^1H NMR: (300 MHz, CDCl_3) δ 6.81 (s, 1H), 4.67 (s, 2H), 1.26 (s, 12H), 1.19 (s, 9H), 0.15 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 178.4, 152.9, 83.8, 65.8, 38.8, 27.3, 24.9, 0.12; IR (neat): 1650, 1481, 1257, 1148, 1039 cm^{-1} ; HRMS (ESI) m/z calcd $\text{C}_{17}\text{H}_{33}\text{BNaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$ 363.2139, found 363.2138.



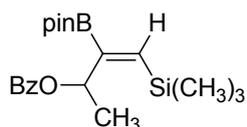
3f

(Z)-Tert-butyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl)carbamate (Table 1, entry 6): The title compound was isolated as a yellow oil in 71 % yield (120.7 mg). ^1H NMR: (300 MHz, CDCl_3) δ 6.66 (s, 1H), 4.92 (brs, 1H), 3.92 (d, $J = 4.5$ Hz, 2H), 1.43 (s, 9H), 1.27 (s, 12H), 0.16 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 155.6, 150.1, 83.9, 77.2, 44.1, 28.6, 24.9, -0.0; IR (neat): 3336, 2944, 2831, 1716, 1144, 1027, 853 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{34}\text{BNO}_4\text{Si}$ 355.2350, found 355.2348.



3g

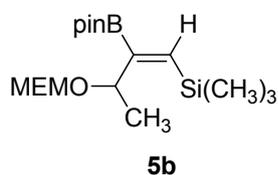
(Z)-4-Methyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl)benzenesulfonamide (Table 1, entry 7): The title compound was isolated as a colorless oil in 60 % yield (101.0 mg). ^1H NMR: (300 MHz, CDCl_3) δ 7.76–7.73 (m, 2H), 7.30–7.26 (m, 3H), 6.65 (s, 1H), 5.21 (t, $J = 6.0$ Hz, 1H), 3.75 (dd, $J_1 = 1.2$ Hz, $J_2 = 6.0$ Hz, 2H), 2.42 (s, 3H), 1.23 (s, 12H), 0.11 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 151.9, 143.3, 137.3, 129.6, 127.5, 84.2, 47.1, 24.9, 21.6, 0.16; IR (neat): 3328, 2943, 2831, 1450, 1111, 1026, 855 cm^{-1} ; HRMS (FAB) m/z calcd for $\text{C}_{19}\text{H}_{33}\text{BNO}_4\text{SSi}$ $[\text{M}+\text{H}]^+$, 410.1993, found 410.1994.



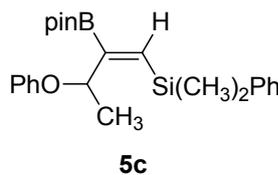
5a

(Z)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)but-3-en-2-yl benzoate (Scheme 2, 5a): The title compound was isolated as a pink oil in 77 % yield (143.8 mg). ^1H NMR: (300 MHz, CDCl_3) δ 8.11–8.08 (m, 2H), 7.52–7.50 (m, 1H), 7.43–7.38 (m, 2H), 6.65 (s, 1H), 5.89 (q, $J = 6.6$ Hz, 1H), 1.51 (d, $J = 6.6$ Hz, 3H), 1.30 (s, 6H), 1.28 (s, 6H), 0.21 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 165.9, 148.7, 132.6, 131.2, 129.8, 128.2, 83.5, 74.4, 25.0, 21.0, 0.2; IR (neat): 3357,

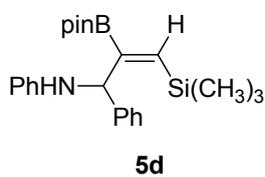
2946, 2832, 1716, 1452, 1274, 1144, 1027, 850 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{31}\text{BO}_4\text{Si}$, 374.2085, found 374.2083.



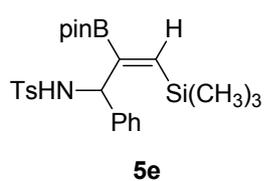
(Z)-8,11,11-Trimethyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5,7-trioxa-11-siladodec-9-ene (Scheme 2, 5b): The title compound was isolated as a colorless oil in 96 % yield (172.4 mg). ^1H NMR: (300 MHz, CDCl_3) δ 6.56 (s, 1H), 4.66 (s, 2H), 4.52 (q, J = 6.6 Hz, 1H), 3.81–3.75 (m, 1H), 3.64–3.59 (m, 1H), 3.58–3.52 (m, 2H), 3.38 (s, 3H), 1.35 (d, J = 6.6 Hz, 3H), 1.26 (s, 12H), 0.15 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 147.9, 92.5, 83.5, 74.7, 72.0, 66.7, 59.1, 24.9, 0.5; IR (neat): 3343, 2943, 2831, 1420, 1387, 1027, 851 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{35}\text{BO}_5\text{Si}$ 358.2347, found 358.2350.



(Z)-Dimethyl(3-phenoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)(phenyl)silane: The title compound was isolated as a colorless oil in 70 % yield (142.9 mg). ^1H NMR: (300 MHz, CDCl_3) δ 7.58–7.53 (m, 2H), 7.36–7.34 (m, 3H), 7.12–7.07 (m, 2H), 6.84–6.79 (m, 1H), 6.68–6.58 (m, 3H), 4.95 (q, J = 6.3 Hz, 1H), 1.35 (d, J = 6.3 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H), 0.46 (s, 3H), 0.43 (s, 3H); ^{13}C NMR: (100 MHz, CDCl_3) δ 158.0, 144.6, 134.9, 134.1, 129.2, 129.2, 128.0, 120.5, 116.6, 83.6, 77.1, 25.0, 24.6, 21.4, 0.83; IR (neat): 3669, 1663, 1596, 1356, 1236, 1107, 1036 cm^{-1} .



(Z)-N-(1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl)aniline: The title compound was isolated as a yellow solid in 82 % yield (167.3 mg). ^1H NMR: (300 MHz, CDCl_3) δ 7.39–7.10 (m, 7H), 6.66–6.59 (m, 3H), 5.36 (d, J = 8.4 Hz, 1H), 4.92 (d, J = 8.4 Hz, 1H), 1.15 (s, 6H), 1.05 (s, 6H), 0.19 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 147.9, 142.7, 129.3, 128.2, 127.4, 126.7, 117.1, 113.6, 83.8, 61.1, 25.0, 24.4, 0.43; IR (neat): 3325, 2944, 2831, 1450, 1115, 1026 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{24}\text{H}_{34}\text{BNO}_2\text{Si}$ 407.2457, found 407.2454.



(Z)-4-Methyl-N-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)allyl)benzenesulfonamide: The title compound was isolated as a white solid in 88 % yield (213.2 mg). ^1H NMR: (300 MHz, CDCl_3) δ 7.71–7.68 (m, 2H), 7.34–7.16 (m, 7H), 6.27 (s, 1H), 6.09 (d, $J = 10.0$ Hz, 1H), 5.41 (d, $J = 10.0$ Hz, 1H), 2.38 (s, 3H), 1.18 (s, 6H), 1.04 (s, 6H), 0.09 (s, 9H); ^{13}C NMR: (100 MHz, CDCl_3) δ 150.7, 142.9, 141.1, 139.0, 129.4, 128.2, 127.3, 127.2, 127.1, 84.1, 60.2, 25.0, 24.2, 21.6, 0.1; IR (neat): 3727, 3664, 2971, 2836, 1369, 1253, 1029 cm^{-1} .

Figure S1 ^1H NMR spectrum of crude mixture of **5f** and **5f'**.

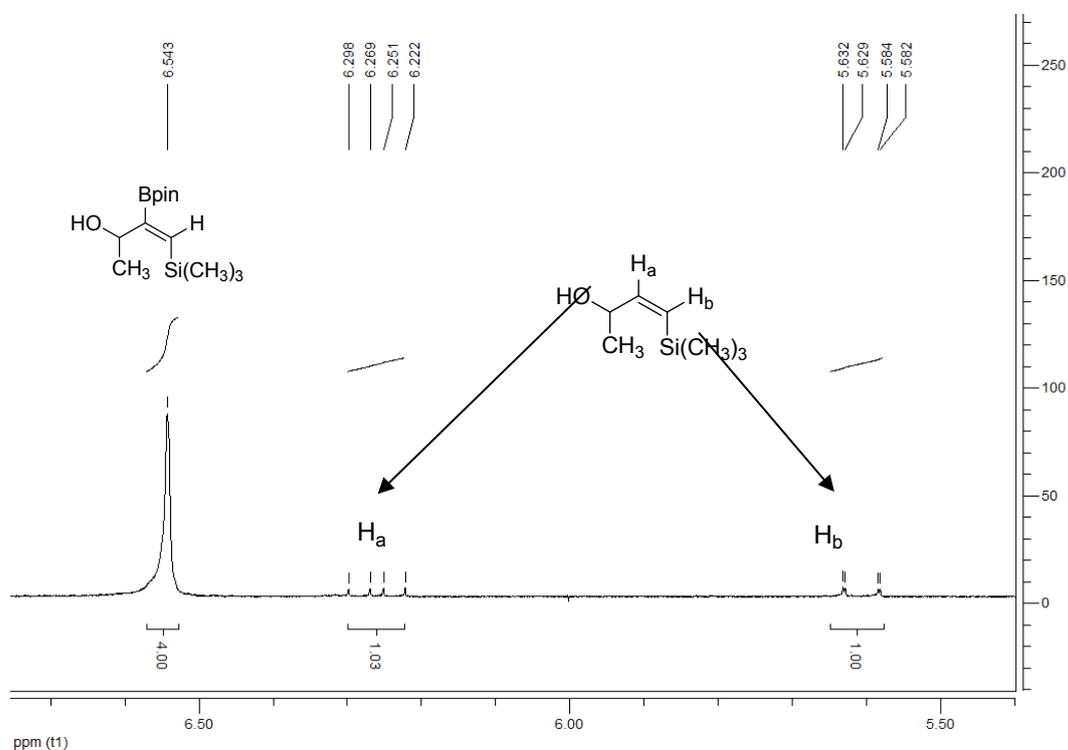


Figure S2 ^1H NMR spectrum of crude mixture of **5g** and **5g'**.

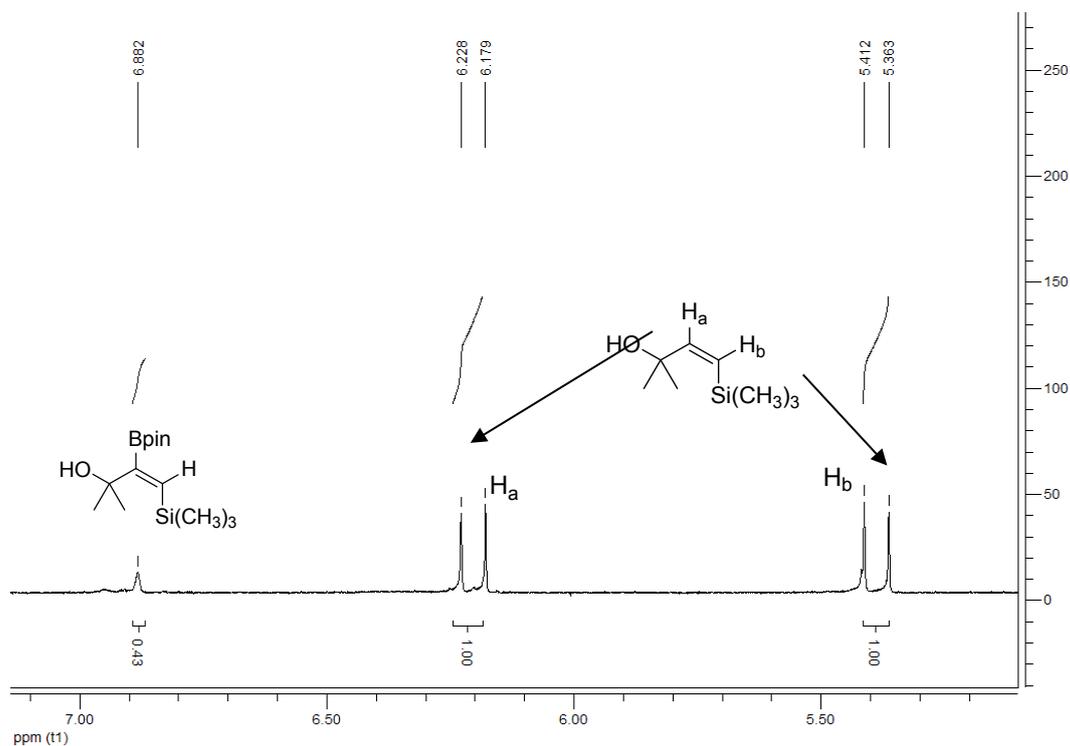
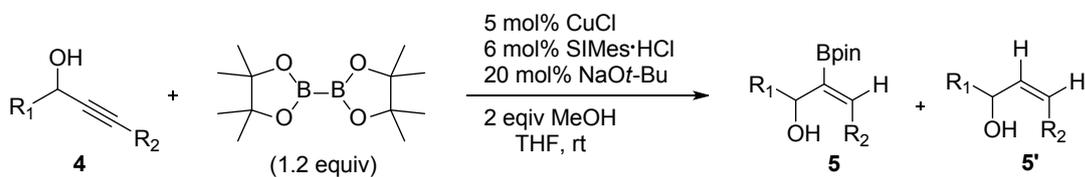


Table S1 Borylation of nonprotected secondary propargylic silylalkynes.



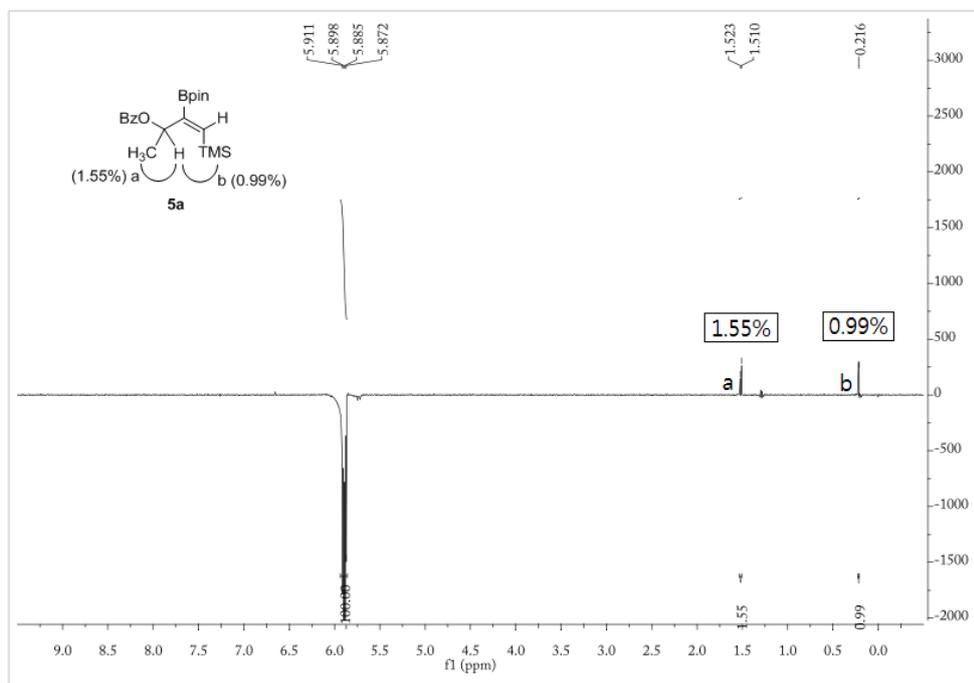
Entry	R ₁	R ₂	Time (h)	Ratio ^a	Conv (%)	Yield (%) ^b
1	Methyl	Me ₃ Si (4f)	6	80 : 20	>99	80
2	Ph	Me ₃ Si (4h)	5	66 : 34	>99	54
3 ^c	<i>t</i> -Butyl	Me ₃ Si (4i)	6	30 : 70	98	26 ^d
4	Ph	PhMe ₂ Si (4j)	6	50 : 50	>99	-

^a Ratio of **5**:**5'**. ^b Isolated yield of **5** and **5'**. ^c 5 mol% CuCl, 5 mol% SiMes·HCl and 10 mol% NaOt-Bu were used.

^d Isolated yield of **5i**.

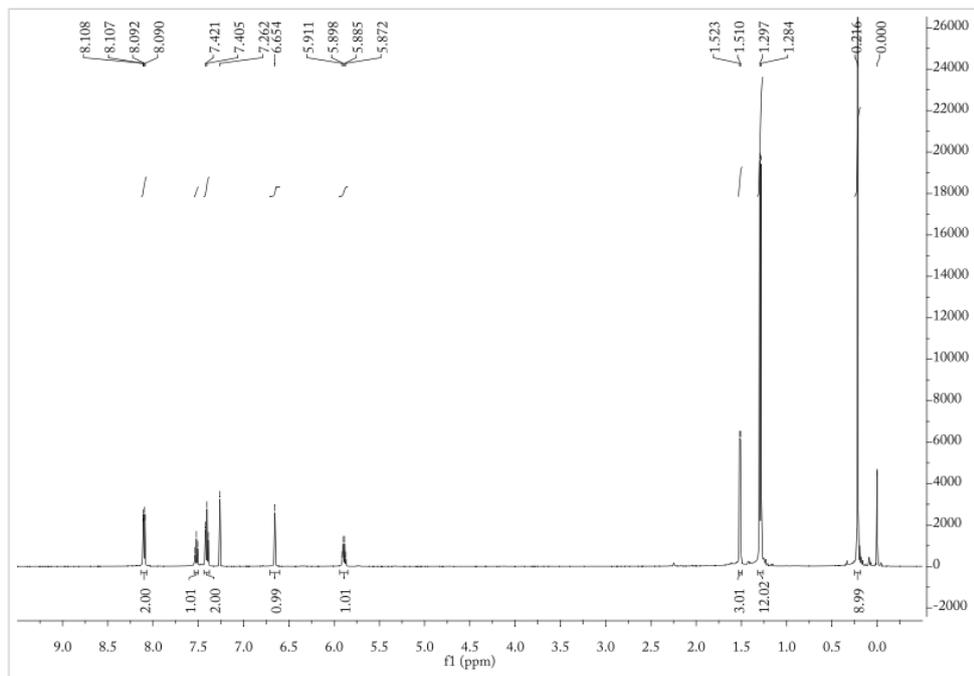
Determination of the (*Z*)-stereochemistry of the addition products: (1) NOE

Figure S3 NOE spectrum of **5a**



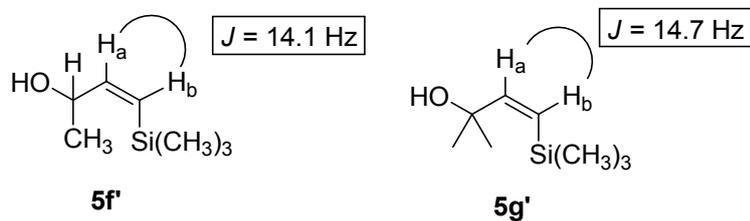
Irradiation of the allylic H's at 5.90 ppm resulted in a 1.55% enhancement of the methyl H's signal at 1.52 ppm, 0.99% enhancement of the TMS H's signal at 0.216 ppm.

Figure S4 ¹H NMR spectrum of **5a**



(2) Coupling constants of **5f'** and **5g'**

^1H NMR analysis of **5f'** and **5g'** (Fig S1 and S2) showed the typical cis coupling of the alkenyl H's.



References

- 1 N. J. Fitzmaurice, W. R. Jackson and P. Perlmutter, *J. Organomet. Chem.*, 1985, **285**, 375–381.
- 2 (a) C. Fischer and E. M. Carreira, *Org. Lett.*, 2001, **3**, 4319–4321; (b) A. Labonne, L. Zani, L. Hintermann and C. Bolm, *J. Org. Chem.*, 2007, **72**, 5704–5709; (c) D. Li, T. Tanaka, H. Ohmiya and M. Sawamura, *Org. Lett.*, 2010, **12**, 3344–3347.