Supporting Information

Chemoselective Silylzincation Reaction to Functionalized Terminal Alkynes Using Dianion-type Zincate (SiBNOL-Zn-ate): Regio-controlled Synthesis of Vinylsilanes

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General Methods. Proton (400MHz) NMR spectra were measured on a JEOL Caliber-GX400 NMR spectrometer with TMS as an internal reference in $CDCl_3$ as the solvent. Chemical shifts are shown in ppm. Coupling constants are given in hertz. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-O1SG-2 sprecrtometer. All experiments were done under Ar atmosphere. Flash column chromatography was carried out on silica gel (silica gel 60 (40-63 μm), Merck).

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification (distillation or recrystalization). ^{t}BuLi in n-pentane and ^{t}BuMgCl in THF were obtained from Kanto Chemical Co. Ltd. The concentrations ^{t}BuLi were determined by titration prior to use.[1]

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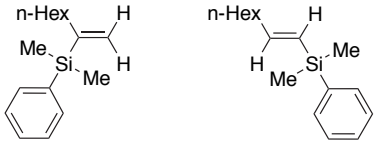
Silylzincation of SiBNOL-Zn-ate to 1-octyne (1a); Typical Procedure



7a **7a'**

To a mixture of 2,2′-biphenol (186.2 mg, 1.0 mmol) in 5 mL of dry THF and 2.2 mL of $ZnCl_2$ (0.5M solution in THF, 1.1 mmol), 3.3 mL of ^{t}BuMgCl (1.0 M solution in THF, 3.3 mmol) and 1.34 mL of dimethylphenylsilyllithium (0.82 M solution in THF, 1.1 mmol) were added at –78°C. The solution was stirred at 0°C for 30 minutes. After that, 1-octyne (110.2 mg, 1.0 mmol) was added dropwise to the solution at -78°C. The mixture was stirred at room temperature for 12 hours. Dropping sat. NH_4Cl quenched the reaction, and the mixture was extracted with Et_2O, dried over $MgSO_4$, and evaporated under reduced pressure. Then it was purified by silica-gel chromatography (eluent; n-hexane) and 246.5 mg of a mixture of 2-Dimethylphenylsilyl-1-octene (**7a**) and *(E)*-1-Dimethylphenylsilyl-1-octene (**7a'**) was obtained as colorless oil (100% yield).

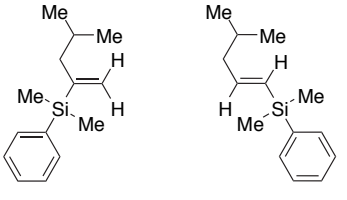
400 MHz ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm):[2] 2- Dimethylphenylsilyl-1-octene (**7a**): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.67 (1H, dt, *J* = 2.8, 2 Hz), 5.38 (1H, d, *J* = 2.8 Hz), 2.1 (2H, m), 1.2-1.42 (8H, m), 0.88 (3H, t, *J* = 7 Hz), 0.36 (6H, s).

(E)-1-Dimethylphenylsilyl-1-octene (**7a'**): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.12 (1H, dt, *J* = 18, 6 Hz), 5.75 (1H, dt, *J* = 18, 1.5 Hz), 2.1 (2H, tdd, *J* = 7, 6, 1.5 Hz), 1.2-1.42 (8H, m), 0.88 (3H, t, *J* = 7 Hz), 0.3 (6H, s).

MS *m*/*z*: 246 (M^+). HRMS Calcd for $C_{16}H_{26}Si$:246.1802. Found:246.1789.

Experimental Details of Table 2

(Entry 1)



7b **7b'**

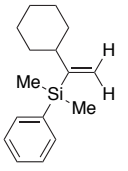
7b: Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.64 (1H, d, *J* = 3.2 Hz), 5.43 (1H, d, *J* = 3.2 Hz), 2.0 (2H, d, *J* = 7.2 Hz), 1.6 (1H, m), 0.80 (6H, d, *J* = 6.4 Hz), 0.35 (6H, s).

7b': Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.12 (1H, dt, *J* = 18.4, 7.2 Hz), 5.7 (1H, dt, *J* = 18.4, 1.6 Hz), 2.0 (2H, dd, *J* = 7.2, 1.6 Hz), 1.6 (1H, m), 0.88 (6H, d, *J* = 6.8 Hz), 0.32 (6H, s).

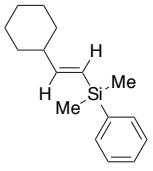
MS *m*/*z*: 218 (M^+). HRMS Calcd for $C_{14}H_{22}Si$:218.1491. Found:218.1472.

(Entry 2)[3]

7c : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.71 (1H, td, *J* = 2.8, 1.6 Hz), 5.40 (1H, td, *J* = 2.8, 1.2 Hz), 2.0 (1H, m), 1.55-1.73 (4H, m), 1.06-1.25 (6H, m), 0.37 (6H, s).



7c



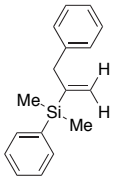
7c'

7c' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.09 (1H, dd, *J* = 18.8, 6.0 Hz), 5.66-5.72 (1H, dd, *J* = 18.8, 1.2 Hz), 2.0 (1H, m), 1.55-1.73 (4H, m), 1.06-1.25 (6H, m), 0.31 (6H, s).

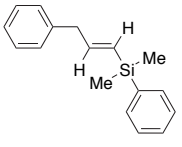
MS *m*/*z*: 244 (M^+). HRMS Calcd for $C_{16}H_{24}Si$:244.1647. Found:244.1650.

(Entry 3)

7d : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 7.03-7.30 (5H, m), 5.55 (1H, dt, *J* = 2.8, 1.2 Hz), 5.48 (1H, dt, *J* = 2.8, 1.2 Hz), 3.41 (2H, d, *J* = 1.2 Hz), 0.25 (6H, s).



7d



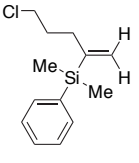
7d'

7d' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 7.03-7.30 (5H, m), 6.2 (1H, dt, *J* = 18.4, 6 Hz), 5.82 (1H, dt, *J* = 18.4, 1.6 Hz), 3.45 (2H, dd, *J* = 6.0, 1.6 Hz), 0.32 (6H, s).

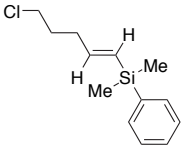
MS *m*/*z*: 252 (M^+). HRMS Calcd for $C_{17}H_{20}Si$:252.1334. Found:252.1321.

(Entry 4)

7e : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.68 (1H, d, *J* = 1.6 Hz), 5.43 (1H, d, *J* = 1.6 Hz), 3.40 (2H, t, *J* = 6.8 Hz), 2.13 (2H, t, *J* = 7.6 Hz), 1.65 (2H, m, 8.0 Hz), 1.45 (2H, m, 8.0 Hz), 0.37 (6H, s).



7e



7e'

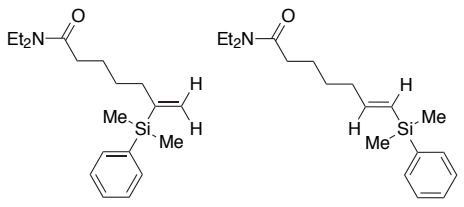
7e' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.12 (1H, dt, *J* = 18.4, 6.4 Hz), 5.7 (1H, d, *J* = 18 Hz), 3.50 (2H, t, *J* = 6.8 Hz), 2.20 (2H, t, *J* = 7.2 Hz), 1.75 (2H, m, 7.2 Hz), 1.55 (2H, m, 8.0 Hz), 0.32 (6H, s).

MS *m*/*z*: 223 (M^+-Me). HRMS Calcd for $C_{12}H_{16}{}^{35}ClSi$:223.0710. Found:223.0674.

(Entry 5)

7f : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m),

5.68 (1H, dt, *J* = 2.8, 1.6 Hz), 5.4 (1H, d, *J* = 2.8 Hz), 3.20-3.39 (4H, dq, *J* = 26.8, 6.8 Hz), 2.17 (2H, t, *J* = 7.6 Hz), 2.13 (2H, t, *J* = 7.6 Hz), 1.59 (2H, m), 1.39 (2H, m), 1.07-1.17 (6H, dt, *J* = 26.8, 6.8 Hz), 0.35 (6H, s)



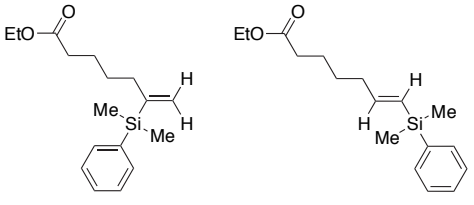
7f **7f'**

7f' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.10 (1H, dt, *J* = 18.8, 6 Hz), 5.73-5.79 (1H, dt, *J* = 18.8, 1.6 Hz), 3.20-3.39 (4H, dq, *J* = 26.8, 6.8 Hz), 2.29 (2H, t, *J* = 7.6 Hz), 2.1 (2H, t, *J* = 7.6 Hz), 1.66 (2H, m), 1.46 (2H, m), 1.07-1.17 (6H, dt, *J* = 26.8, 6.8 Hz), 0.31 (6H, s).

MS *m*/*z*: 317 (M^+). HRMS Calcd for $C_{19}H_{31}NOSi$:317.2175. Found:317.2168.

(Entry 6)

7g : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.77 (1H, td, *J* = 2.8, 1.6 Hz), 5.40 (1H, td, *J* = 2.8, 1.2 Hz), 4.09 (2H, q, *J* = 6.8 Hz), 2.2 (2H, t, *J* = 8.0 Hz), 2.1 (2H, tdd, *J* = 8.0, 1.6, 1.2 Hz), 1.55 (2H, m), 1.36 (2H, m), 1.25 (3H, t, *J* = 6.8 Hz), 0.36 (6H, s).



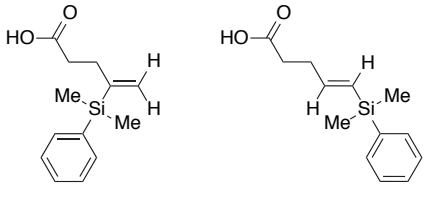
7g **7g'**

7g' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.08 (1H, dt, *J* = 18.8, 6.0 Hz), 5.73-5.79 (1H, dt, *J* = 18.8, 1.6 Hz), 4.09 (2H, q, *J* = 7.2 Hz), 2.29 (2H, t, *J* = 8.0 Hz), 2.1 (2H,m), 1.55 (2H, m), 1.36 (2H, m), 1.25 (3H, t, *J* = 7.2 Hz), 0.31 (6H, s).

MS *m*/*z*: 290 (M^+). HRMS Calcd for $C_{17}H_{26}O_2Si$:290.1702. Found:290.1707.

(Entry 7)

7h : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.65 (1H, d, *J* = 1.2 Hz), 5.42 (1H, d, *J* = 1.2 Hz), 2.32-2.44 (4H, m), 0.35 (6H, s).



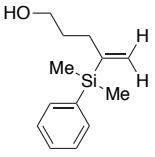
7h **7h'**

7h' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.2 (1H, dt, *J* = 18.8, 5.2 Hz), 5.9 (1H, dt, *J* = 18.8, 1.6 Hz), 2.32-2.44 (4H, m), 0.30 (6H, s).

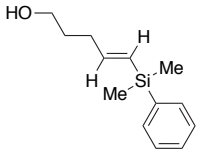
MS *m*/*z*: 234 (M^+). HRMS Calcd for $C_{13}H_{18}O_2Si$:234.1075. Found:234.1025.

(Entry 8)[4]

7i : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.7 (1H, dt, *J* = 2.4, 1.6 Hz), 5.4 (1H, dt, *J* = 2.4, 1.6 Hz), 3.5 (2H, t, *J* = 8.0 Hz), 2.15 (2H, m), 1.58 (2H, m), 0.37 (6H, s).



7i



7i'

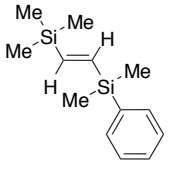
7i' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.1 (1H, dt, *J* = 18.4, 6.4 Hz), 5.7 (1H, dt, *J* = 18.4, 6.4 Hz), 3.60 (2H, t, *J* = 6.4 Hz), 2.2 (2H, m), 1.67 (2H, m), 0.31 (6H, s).

MS *m*/*z*: 220 (M^+), 205 (M^+-Me). HRMS Calcd for $C_{12}H_{17}OSi$:205.1049. Found:205.1050.

(Entry 9)[5]

7j' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.70 (2H, s), 0.32 (6H, s), 0.06 (9H, s).

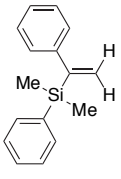
MS *m*/*z*: 234 (M^+), HRMS Calcd for $C_{13}H_{22}Si_2$:234.1260. Found:234.1242.



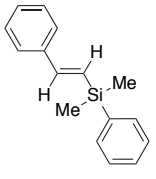
7j'

(Entry 10)[6]

7k : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.21-7.45 (5H, m), 7.31-7.34 (3H, m), 5.98 (1H, d, *J* = 1.2 Hz), 5.68 (1H, d, *J* = 1.2 Hz), 0.39 (6H, s).



7k



7k'

7k' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.21-7.45 (5H, m), 7.31-7.34 (3H, m), 6.95 (1H, d, *J* = 18.4 Hz), 6.60 (1H, d, *J* = 18.4 Hz), 0.42 (6H, s).

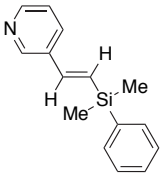
MS *m*/*z*: 238 (M^+). HRMS Calcd for $C_{12}H_{16}{}^{35}ClSi$:238.1177. Found:238.1178.

(Entry 11)

Purified by SiO_2 column chromatography using hexane: ethylacetate (6 : 1) as an eluent.

7l' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 8.55 (1H, s), 8.45 (1H, d, *J* = 4 Hz), 7.74 (1H, dt, *J* = 8.0, 2.4 Hz), 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 7.2 (1H, dt, *J* = 8.0 Hz), 6.9 (1H, d, *J* = 18.4 Hz), 6.6 (1H, d, *J* = 18.4 Hz), 0.45 (6H, s).

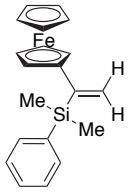
MS *m*/*z*: 239 (M^+). HRMS Calcd for $C_{15}H_{17}NSi$: 239.1130. Found: 239.1130.



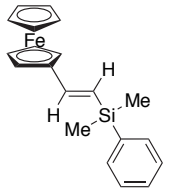
7l'

(Entry 12)

7m : Red oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.18 (1H, d, *J* = 2.4 Hz), 5.4 (1H, d, *J* = 2.4 Hz), 4.23 (2H, m), 4.11 (2H, m), 3.91 (5H, s), 0.47 (6H, s).



7m



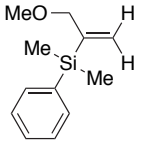
7m'

7m' : Red oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.7 (1H, d, *J* = 18.8 Hz), 6.1 (1H, d, *J* = 18.8 Hz), 4.37 (2H, m), 4.2 (2H, m), 4.06 (5H, s), 0.38 (6H, s).

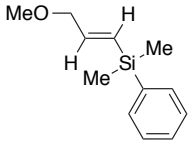
MS *m*/*z*: 346 (M^+). HRMS Calcd for $C_{20}H_{22}FeSi$: 346.0840. Found: 346.0832.

(Entry 13)[7]

7h : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.88 (1H, dt, *J* = 2.8, 2 Hz), 5.48 (1H, d, *J* = 2.8 Hz), 3.98 (2H, d, *J* = 2 Hz), 3.25 (3H, s), 0.79 (6H, s).



7n



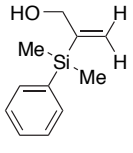
7n'

7h' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.1 (1H, dt, *J* = 18, 4.4 Hz), 6.0 (1H, d, *J* = 18Hz), 3.97 (2H, t, *J* = 4.4 Hz), 3.35 (3H, s), 0.35 (6H, s).

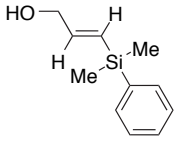
MS *m*/*z*: 206 (M^+), 191 (M^+-Me). HRMS Calcd for $C_{11}H_{15}OSi$: 191.0892. Found: 191.0874.

(Entry 14)[5]

7o : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.88 (1H, dt, *J* = 2.0, 1.6 Hz), 5.47 (1H, dt, *J* = 2.0, 1.6 Hz), 4.2 (2H, t, *J* = 1.6 Hz), 0.39 (6H, s).



7o



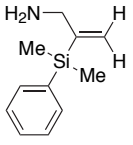
7o'

7o' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.2 (1H, dt, *J* = 19.2, 4 Hz), 6.0 (1H, dt, *J* = 19.2, 1.6 Hz), 4.15 (2H, t, *J* = 1.6 Hz), 0.35 (6H, s).

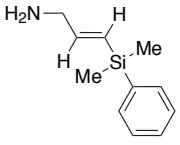
MS 177 (M^+-Me). HRMS Calcd for $C_{10}H_{13}OSi$: 177.0736. Found: 177.0701.

(Entry 15)

7p : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.80 (1H, d, *J* = 2.4 Hz), 5.45 (1H, d, *J* = 2.4 Hz), 3.2 (2H, s), 2.0 (2H, br), 0.36 (6H, s).



7p



7p'

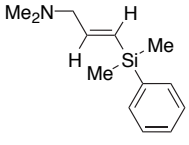
7p' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.2 (1H, dt, *J* = 18.8, 5.2 Hz), 5.9 (1H, dt, *J* = 18.8, 1.6 Hz), 3.35 (2H, dd, *J* = 5.2, 1.6 Hz), 2.0 (2H, br), 0.29 (6H, s).

MS *m*/*z*: 219 (M^+). HRMS Calcd for $C_{13}H_{21}NSi$: 219.1442. Found: 219.1438.

(Entry 16)

7q' : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.1 (1H, dt, *J* = 18.8, 5.6 Hz), 5.9 (1H, dt, *J* = 18.8, 1.2 Hz), 3.35 (2H, dd, *J* = 5.6, 1.2 Hz), 2.2 (6H, s), 0.34 (6H, s).

MS *m*/*z*: 191 (M^+). HRMS Calcd for $C_{11}H_{17}NSi$: 191.1130. Found: 191.1096.



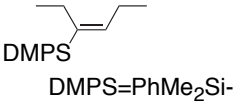
7q'

Experimental Details of Scheme 1

Internal alkyne[8]

8 : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.77 (1H, t, *J* = 7.2 Hz), 2.1 (4H, m), 1.0 (3H, t, *J* = 7.6 Hz), 0.8 (3H, t, *J* = 7.6 Hz), 0.32 (6H, s).

MS *m*/*z*: 218 (M^+). HRMS Calcd for $C_{14}H_{22}Si$: 218.1491. Found: 219.1480.



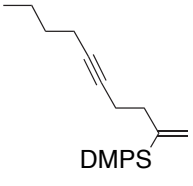
DMPS=PhMe$_2$Si-

8

Terminal-internal mixed diyne

9 : Colorless oil. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.1 (1H, dt, *J* = 18.4, 2.4 Hz), 5.8 (1H, d, *J* = 18.4 Hz), 2.1-2.3 (6H, m), 1.34-1.45 (4H, m), 0.89 (3H, t, *J* = 7.2 Hz), 0.32 (6H, s).

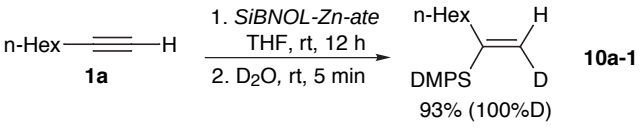
MS *m*/*z*: 270 (M^+). HRMS Calcd for $C_{18}H_{26}Si$: 270.1804. Found: 270.1801.



9

Electrophilic Trapping of the Intermediate (2a) Generated In Situ by Silylzincation of 1-Octyne (1a) Using SiBNOL-Zn-ate

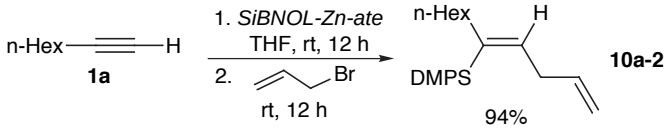
Trapping with Deuterium-oxide[ii]



The vinylzinc species (**2a**) was quenched with 1 mL of deuterium-oxide and the mixture was extracted with Et_2O, dried over $MgSO_4$, and evaporated under reduced pressure. Then it was purified by silica-gel chromatography (eluent; n-hexane) and 245.0 mg of a regio-mixture (93:7) of the vinylsilane was obtained as colorless oil (99% yield). **10a-1** : ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 5.67 (1H, t, *J* = 2 Hz), 2.1 (2H, td, *J* = 7.2, 1.2 Hz), 1.2-1.42 (8H, m), 0.88 (3H, t, *J* = 7.2 Hz), 0.36 (6H, s).

MS *m*/*z*: 247 (M^+). HRMS Calcd for $C_{15}H_{25}DSi$: 247.1866. Found: 247.1851.

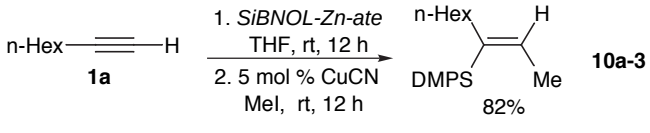
Coupling with 3-Bromo-propene



3-Bromo-propene (145.2 mg, 1.2 mmol) was added to the vinylzinc species (**2a**) at –78°C and the mixture was stirred at room temperature for 12 hours. The mixture was extracted with Et_2O, dried over $MgSO_4$, and evaporated under reduced pressure. Then it was purified by silica-gel chromatography (eluent; n-hexane) and 283.4 mg of a regio-mixture (94:6) of the vinylsilane was obtained as colorless oil (99% yield). **10a-2** : ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.04 (1H, tt, *J* = 7.2, 2 Hz), 5.6 (1H, m), 4.8 (2H, m), 2.6 (2H, t, *J* = 7.2 Hz), 2.1 (2H, m), 1.2-1.42 (8H, m), 0.88 (3H, t, *J* = 7.2 Hz), 0.38 (6H, s).

MS *m*/*z*: 286 (M^+), 271 (M^+-Me). HRMS. Calcd for $C_{19}H_{15}Si$: 271.0943. Found: 271.0952.

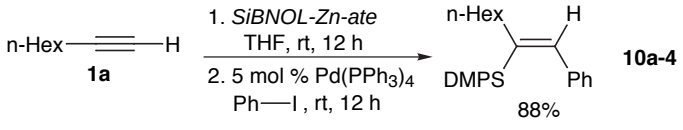
Coupling with Iodomethane



To a mixture of CuCN (4.5 mg, 0.05 mmol) in 5 mL of dry THF and iodomethane (212.9 mg, 1.5 mmol), the vinylzinc species (**2a**) was added dropwise at –78°C. The mixture

was stirred at room temperature for 12 hours. The mixture was extracted with Et_2O, dried over $MgSO_4$, and evaporated under reduced pressure. Then it was purified by silica-gel chromatography (eluent; n-hexane) and 234.4 mg of a regio-mixture (91:9) of the vinylsilane was obtained as colorless oil (90% yield). **10a-3** : ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.31-7.34 (3H, m), 6.15 (1H, q, *J* = 6.8 Hz), 2.1 (2H, m), 2.1 (3H, d, *J* = 6.8 Hz), 1.2-1.42 (8H, m), 0.88 (3H, t, *J* = 7 Hz), 0.87 (6H, s).
MS *m*/*z*: 260 (M^+). HRMS Calcd for $C_{17}H_{28}Si$: 260.1959. Found: 260.1928.

Coupling with Iodo-benzene



To the vinylzinc species (**2a**), $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) in 10 mL of dry THF and iodo-benzene (244.9 mg, 1.2 mmol) were added at –78°C. The mixture was stirred at room temperature for 12 hours. The mixture was extracted with Et_2O, dried over $MgSO_4$, and evaporated under reduced pressure. Then it was purified by silica-gel chromatography (eluent; n-hexane) and 306.3 mg of a regio-mixture (93:7) of the vinylsilane was obtained as colorless oil (95% yield). **10a-4** : ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.49-7.53 (2H, m), 7.49-7.53 (2H, m), 7.31-7.34 (4H, m), 7.08-7.18 (5H, m), 2.27 (2H, td, *J* = 6.4, 1.2 Hz), 1.2-1.42 (8H, m), 0.88 (3H, t, *J* = 7 Hz), 0.17 (6H, s).
MS *m*/*z*: 322 (M^+). HRMS Calcd for $C_{22}H_{30}Si$: 322.2115. Found: 322.2112.

NMR Spectroscopic Analyses of Organometallic Species.

^{1}H, ^{13}C, and ^{7}Li NMR spectra were obtained on a JEOL ECA-500 spectrometer, operating at 500.160, 125.765 and 194.381 MHz, respectively. All samples were run in THF solution at -100 °C. The capillary tube contained THF-d_8 used as the ^{13}C chemical shift reference and lock solvent. ^{1}H NMR spectra were referenced to a solvent signal (3.58 ppm). ^{13}C NMR spectra were referenced to a THF-d_8 signal (67.4 ppm). ^{7}Li NMR spectra were referenced to external 0.5 M LiBr in THF-d_8 at the temperature at which each sample was run (0.0 ppm). Complete ^{1}H and ^{13}C NMR chemical shift assignments were made on the basis of decoupled 1D NMR and DEPT experiments.

^{t}Bu$_4$ZnLi$_2$ (a model highly crowded zincate)

^{t}Bu$_2$Zn were prepared by using a modification of the literature method:[9] A solution of ^{t}BuLi in pentane (1.32 M, 22.5 ml, 30 mmol) and zinc chloride in THF (0.5 M, 30 ml, 15 mmol) was stirred at 0°C for 30 minutes. The solution was distilled (34-35°C/ 9 mmHg) to give ^{t}Bu$_2$Zn (no lithium ion was detected by ^{7}Li NMR).

Table. ^{1}H, ^{13}C, and ^{7}Li NMR Spectroscopic Data for ^{t}BuLi, ^{t}Bu$_2$Zn, and ^{t}Bu$_4$ZnLi$_2$ at -100°C

	^{1}H (δ, ppm)	^{13}C (δ, ppm)	^{7}Li (δ, ppm)
^{t}BuLi	0.74 (0.74)[a]	17.0 (17.1)[a], 40.6 (40.4)[a]	0.82 (0.26)[a]
^{t}Bu$_2$Zn	0.85	22.7 (28.43)[b], 34.4 (31.03)[b]	-
^{t}Bu$_4$ZnLi$_2$	0.69	24.2, 36.7	-0.32

[a] Reported data for ^{t}BuLi in THF-d_8; ref.10. [b] Reported NMR data for ^{t}Bu$_2$Zn in benzene-d_6; ref.11.

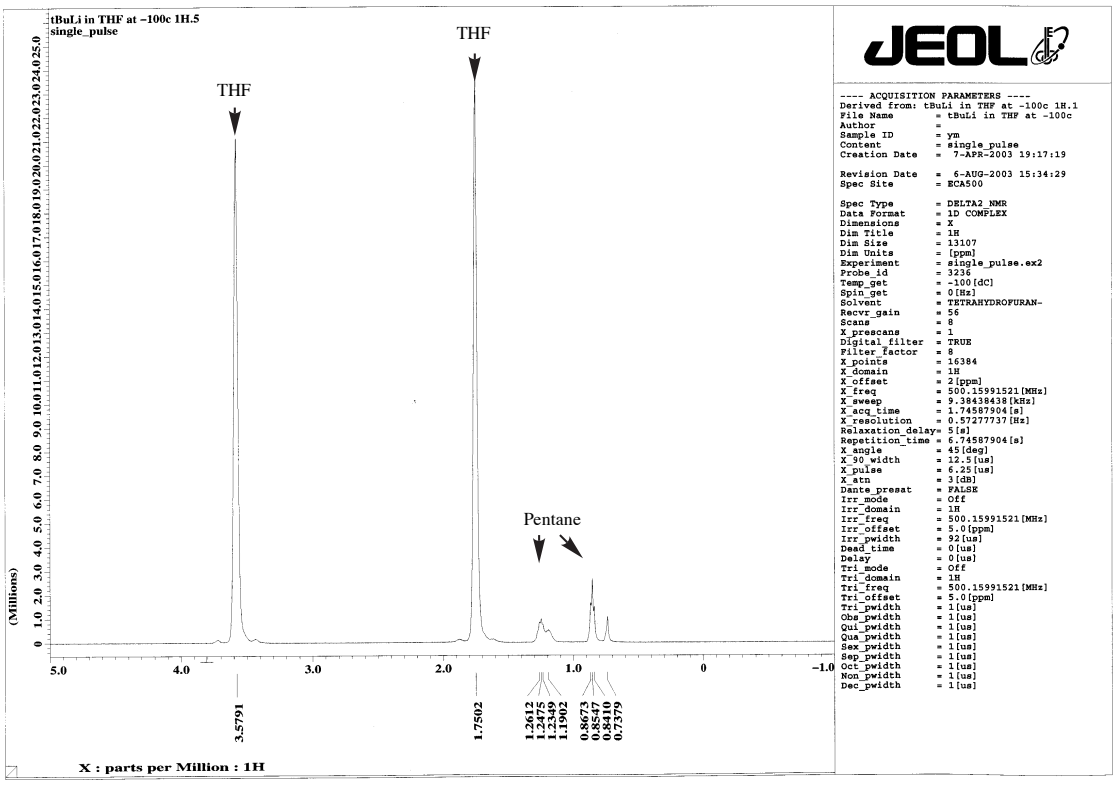


Figure S-1. ^{1}H NMR Spectrum of ^{t}BuLi in THF at -100°C

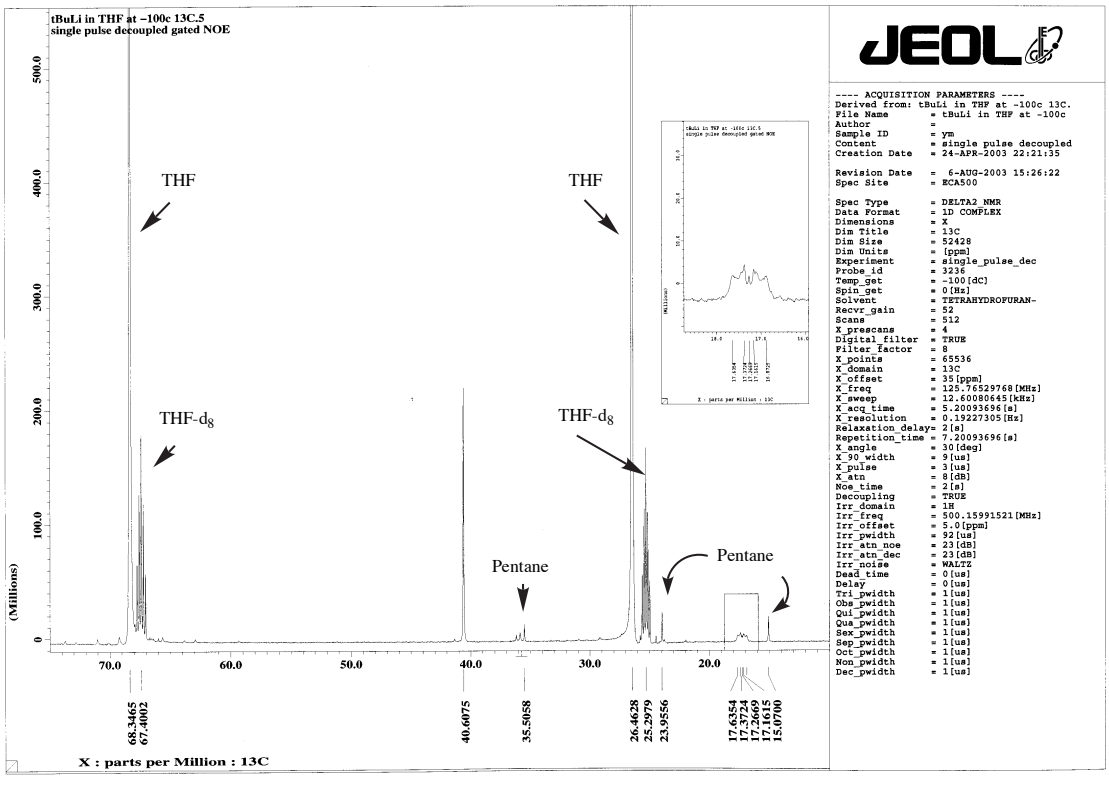


Figure S-2. ^{13}C NMR Spectrum of ^{t}BuLi in THF at -100°C

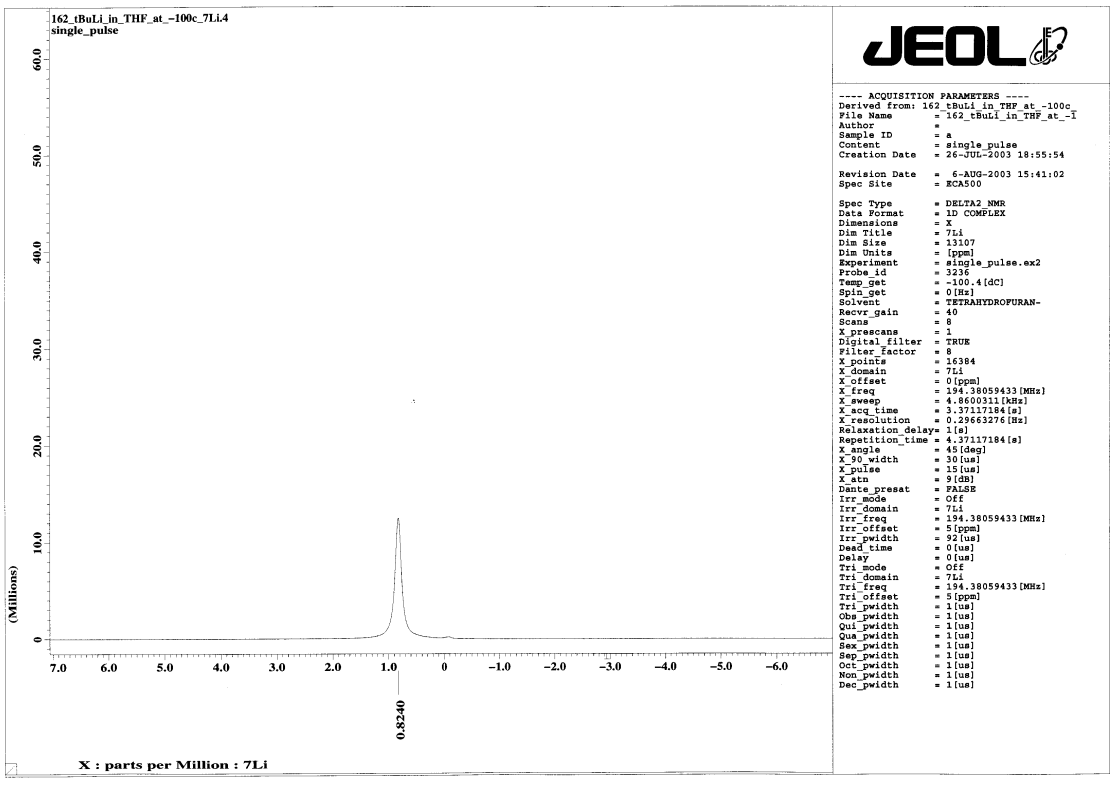


Figure S-3. ^{7}Li NMR Spectrum of ^{t}BuLi in THF at -100°C

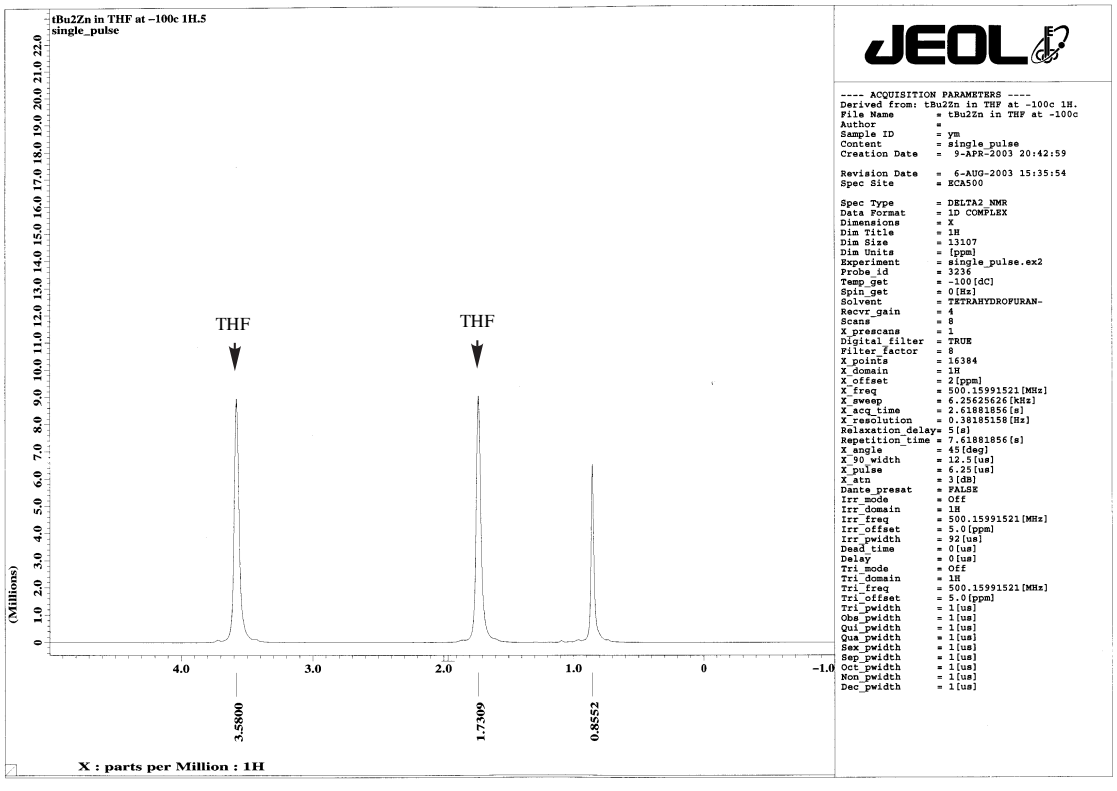


Figure S-4. ^{1}H NMR Spectrum of $^{t}Bu_2Zn$ in THF at -100°C

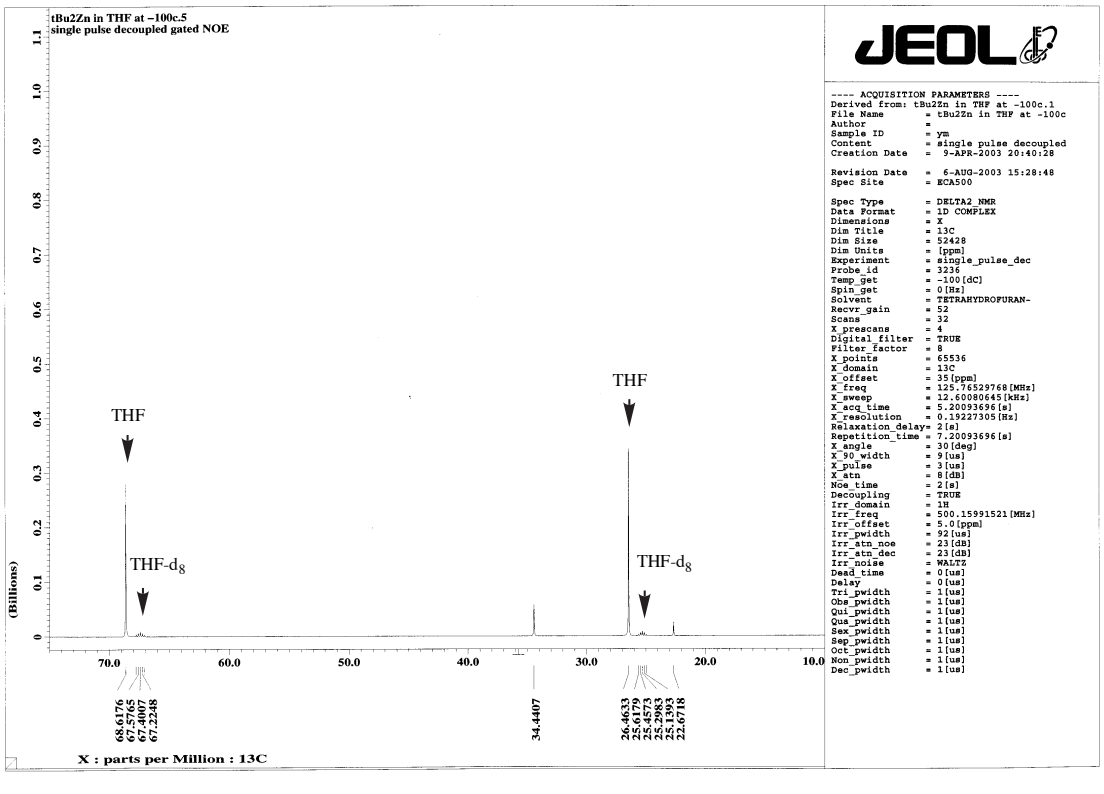


Figure S-5. ^{13}C NMR Spectrum of $^{t}Bu_2Zn$ in THF at -100°C

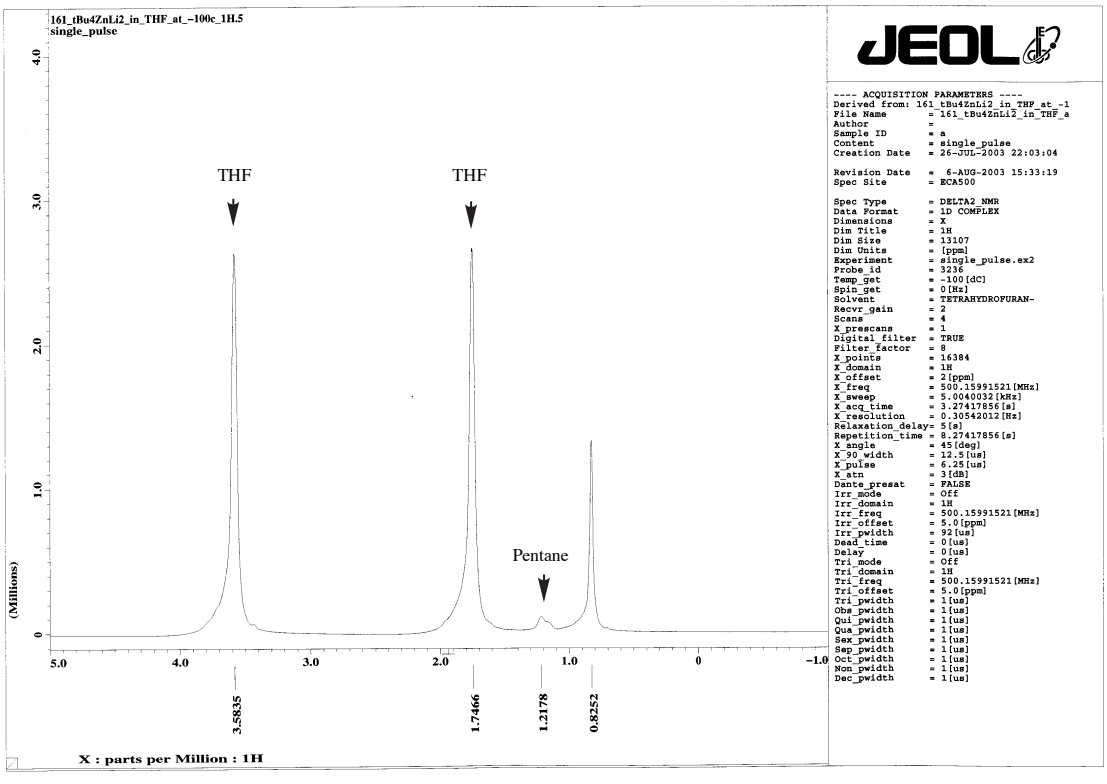


Figure S-6. ^{1}H NMR Spectrum of $^{t}Bu_4ZnLi_2$ in THF at -100°C

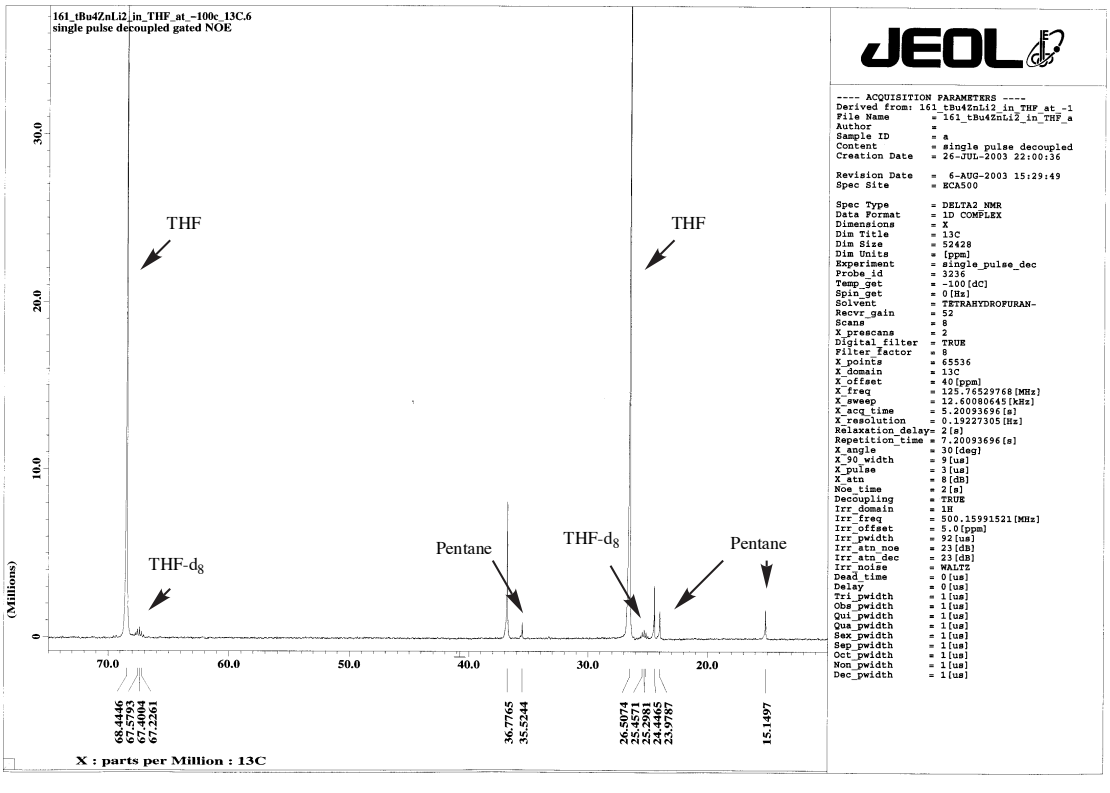


Figure S-7. ^{13}C NMR Spectrum of $^{t}Bu_4ZnLi_2$ in THF at -100°C

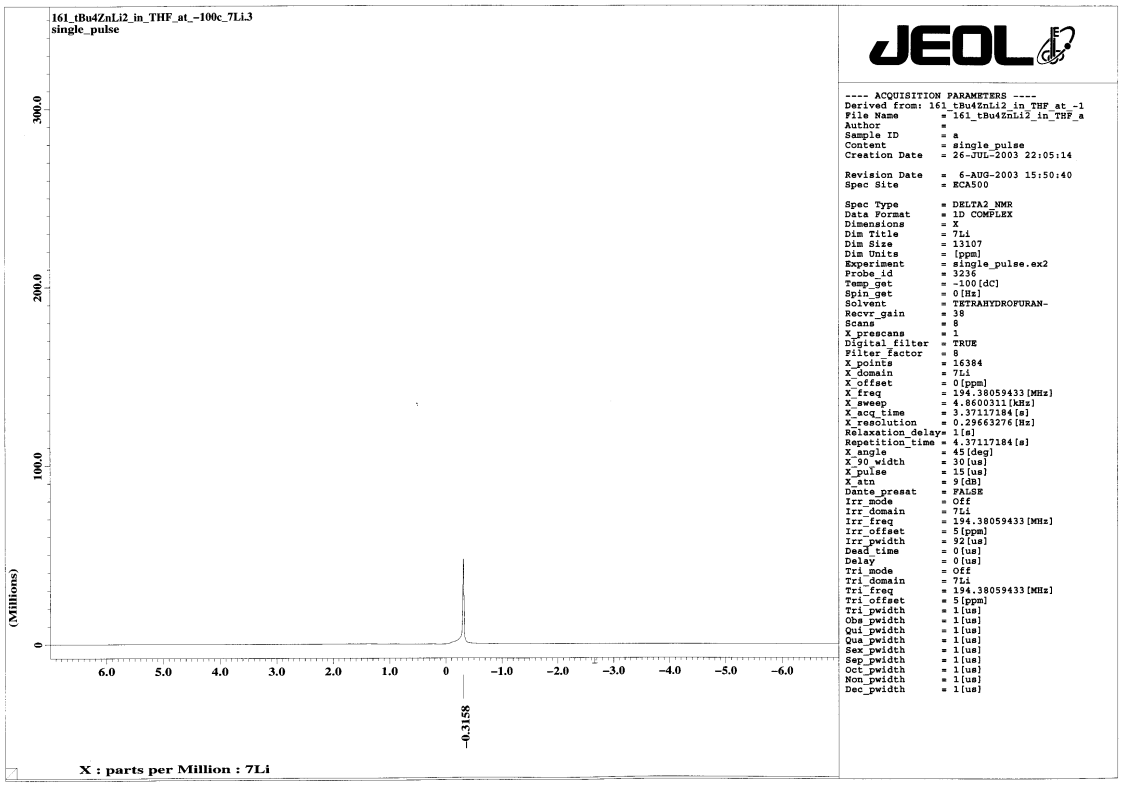


Figure S-8. ^{7}Li NMR Spectrum of $^{t}Bu_4ZnLi_2$ in THF at -100°C

$(Me_2PhSi)_4ZnLi_2$ (the most crowded zincate in this study; Table 1 entry 3)

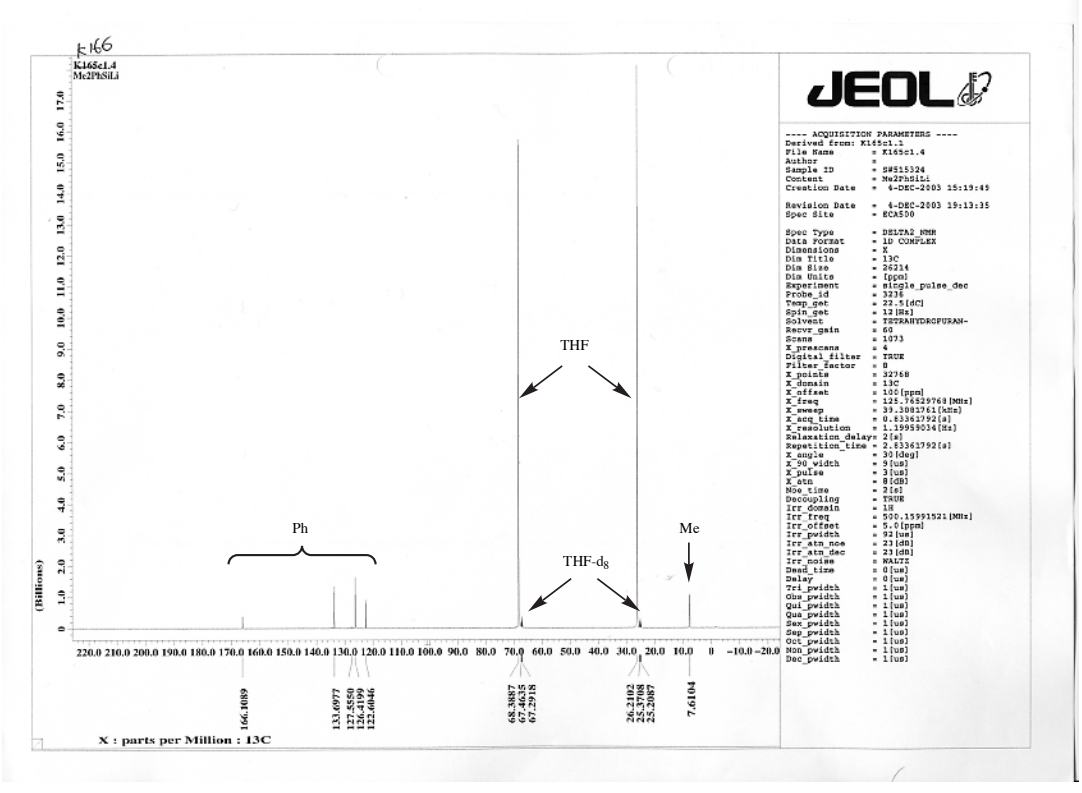


Figure S-9. ^{13}C NMR Spectrum of $Me_2PhSiLi$ in THF at -100°C

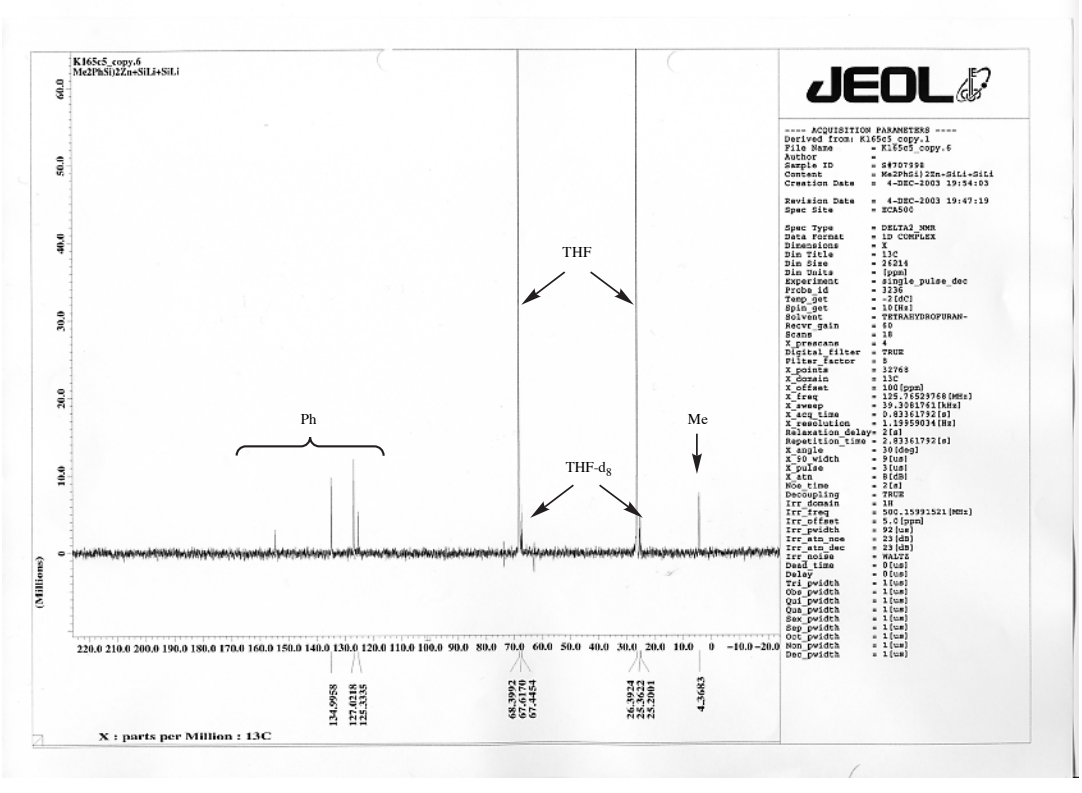


Figure S-10. ^{13}C NMR Spectrum of $(Me_2PhSi)_4ZnLi_2$ in THF at -100°C

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