Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Piers' Borane-Mediated Hydrosilylation of Epoxides and Cyclic Ethers

Jianbo Zhang,[‡,†] Sehoon Park,*[,‡,†] and Sukbok Chang*[,‡,†]

[†]*Department of Chemistry, Korea Advanced Institute of Science & Technology (KAIST),*
Daejeon 305-701, South Korea

[‡]*Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS),*
Daejeon 305-701, South Korea

*Email: sehoonp@kaist.ac.kr; sbchang@kaist.ac.kr

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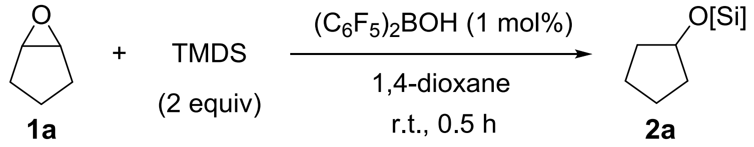
I. General Considerations

Unless otherwise stated, all reactions were carried out under argon atmosphere. 1,4-dioxane-d_8, CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, Inc. and used without additional purification. All other solvents used in this study were freshly distilled before use. All commercial reagents were directly used as received from chemical sources. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) or treatment with phosphomolybdic acid or potassium permanganate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent system. ^1H NMR was recorded on Agilent Technologies DD2 (600 MHz) or Bruker AVHD-400 (400 MHz). ^1H chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak (1,4-dioxane in 1,4-dioxane-d_8: 3.53 ppm; mesitylene in 1,4-dioxane-d_8: 6.74 and 2.22 ppm; CH_2Cl_2 in CD_2Cl_2: 5.32 ppm; mesitylene in CD_2Cl_2: 6.81 and 2.29 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublet, m = multiplet. Coupling constants, J, were reported in hertz unit (Hz). $^{13}C\{^1H\}$ NMR was recorded on Agilent Technologies DD2 (151 MHz) or Bruker AVHD-400 (101 MHz) and was fully decoupled by broad band proton decoupling. ^{13}C chemical shifts were reported in ppm referenced to the center of a quintet at 66.8 ppm of 1,4-dioxane-d_8 or 53.8 ppm of CD_2Cl_2. $^{19}F\{^1H\}$ NMR was recorded on Agilent Technologies DD2 (564 MHz) or Bruker AVHD-400 (376 MHz). ^{19}F chemical shifts were reported in ppm referenced to external α,α,α-trifluorotoluene at -63.72 ppm. $^{11}B\{^1H\}$ NMR was recorded on Agilent Technologies DD2 (192 MHz). ^{11}B chemical shifts were reported in ppm referenced to external BF_3–OEt_2 at 0 ppm. Infrared (IR) spectra were recorded on Bruker Alpha ATR FT-IR Spectrometer. Frequencies were given in wave numbers (cm^{-1}) and only selected peaks were reported. High resolution mass spectra were obtained by using EI method from Korea Basic Science Institute (Daegu) or ESI from KAIST Research Analysis Center (Daejeon). $(C_6F_5)_2BOH$[S1], TMDS-d_2[S2], *p*-nitrostyrene oxide[S3a], and methyl 4-(oxiran-2-yl)benzoate[S3b] were synthesized according to literature.

※*The initially formed crude products possess several siloxane moieties of [Si] (-O[Si]), for which slightly differed ^{13}C shifts for a specific carbon of the crude products were often observed in the NMR spectra.*

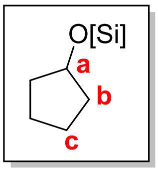
II. $(C_6F_5)_2BH$-Catalysed Hydrosilylation of Cyclopentene Oxide 1a [Eq. (2)]



General procedure for hydrosilylation of epoxides:

In an Ar-filled glove box, Piers' borane precusor $(C_6F_5)_2BOH$ (1.45 mg, 1 mol%) was dissolved in 1,4-dioxane-d_8 (0.4 mL) in a NMR tube, into which TMDS (141.4 μL, 0.8 mmol) was subsequently treated. After shaking for 10 min at room temperature (*in situ* generation of Piers' borane), cyclopentene oxide **1a** (34.9 μL, 0.4 mmol) was added into the catalyst solution. After 0.5 h, the reaction mixture was subjected to ^1H NMR analysis to determine the crude NMR yield of **2a** on the basis of an internal standard material (mesitylene, 14.0 μL, 0.1 mmol).

Cyclopentyl silyl ether [Eq. (2), **2a**]



Crude yield: 85%; **^1H NMR** (600 MHz, 1,4-dioxane-d_8): δ 4.403 – 4.314 (m, 1H), 1.746 – 1.653 (m, 4H), 1.601 – 1.541 (m, 2H), 1.527 – 1.476 (m, 2H); **$^{13}C\{^1H\}$ NMR** (151 MHz, 1,4-dioxane-d_8): δ 74.7 (C^a), 74.6 (C^a), 36.3(9) (C^b), 36.3(8) (C^b), 23.9 (C^c).

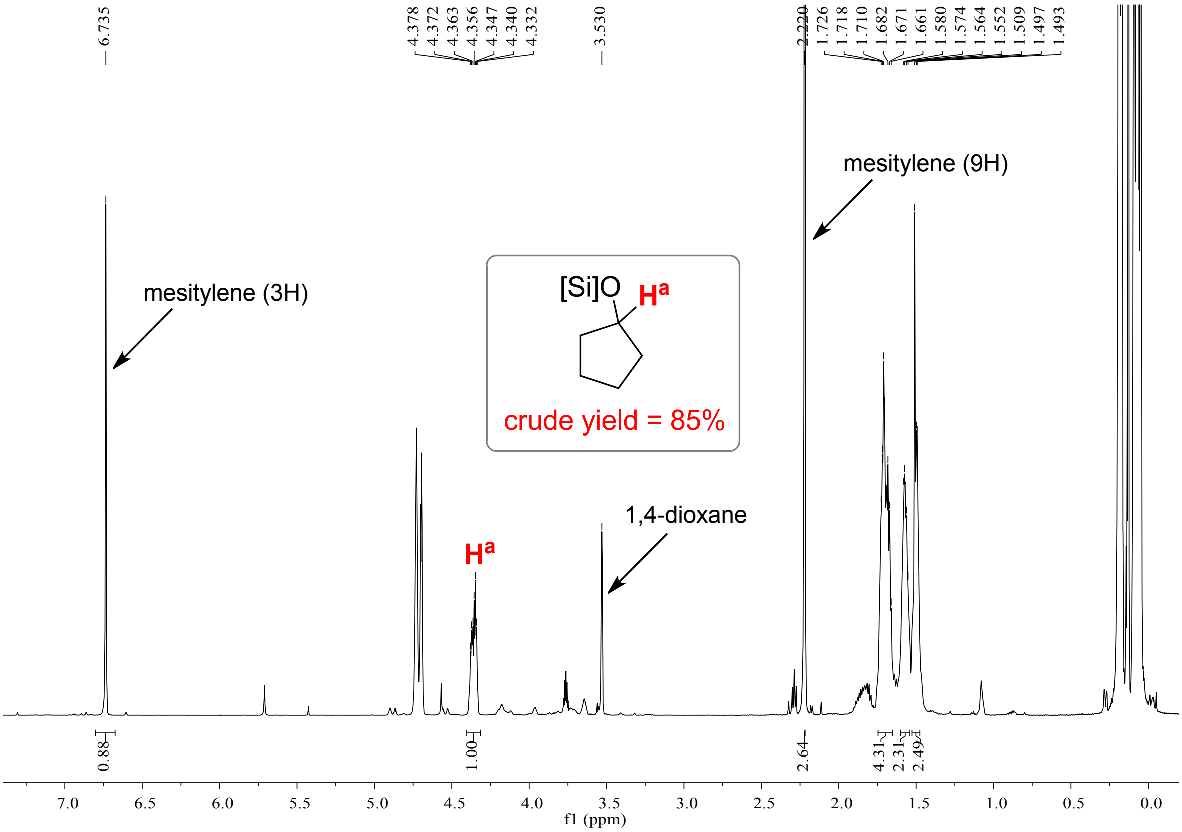


Figure S1. ^1H NMR spectrum of the crude reaction mixture in the hydrosilylation of **1a**

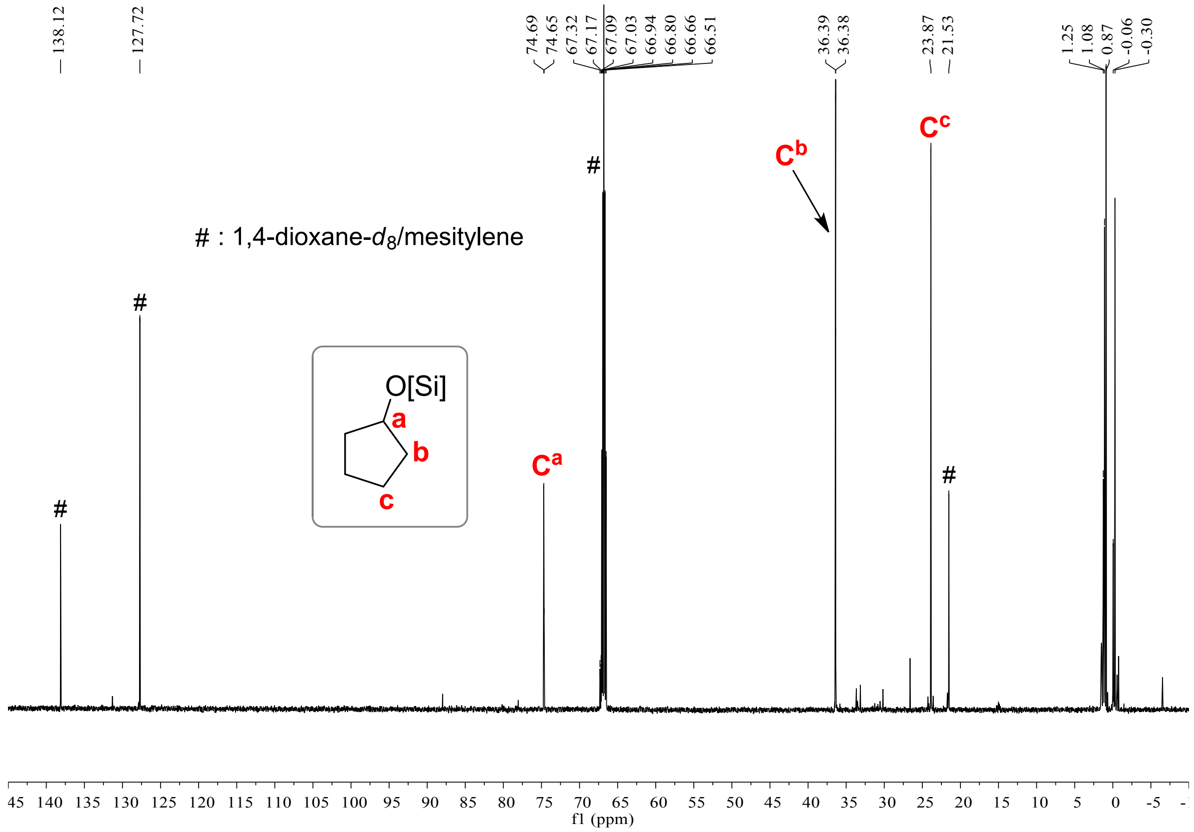


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of the crude reaction mixture in the hydrosilylation of **1a**

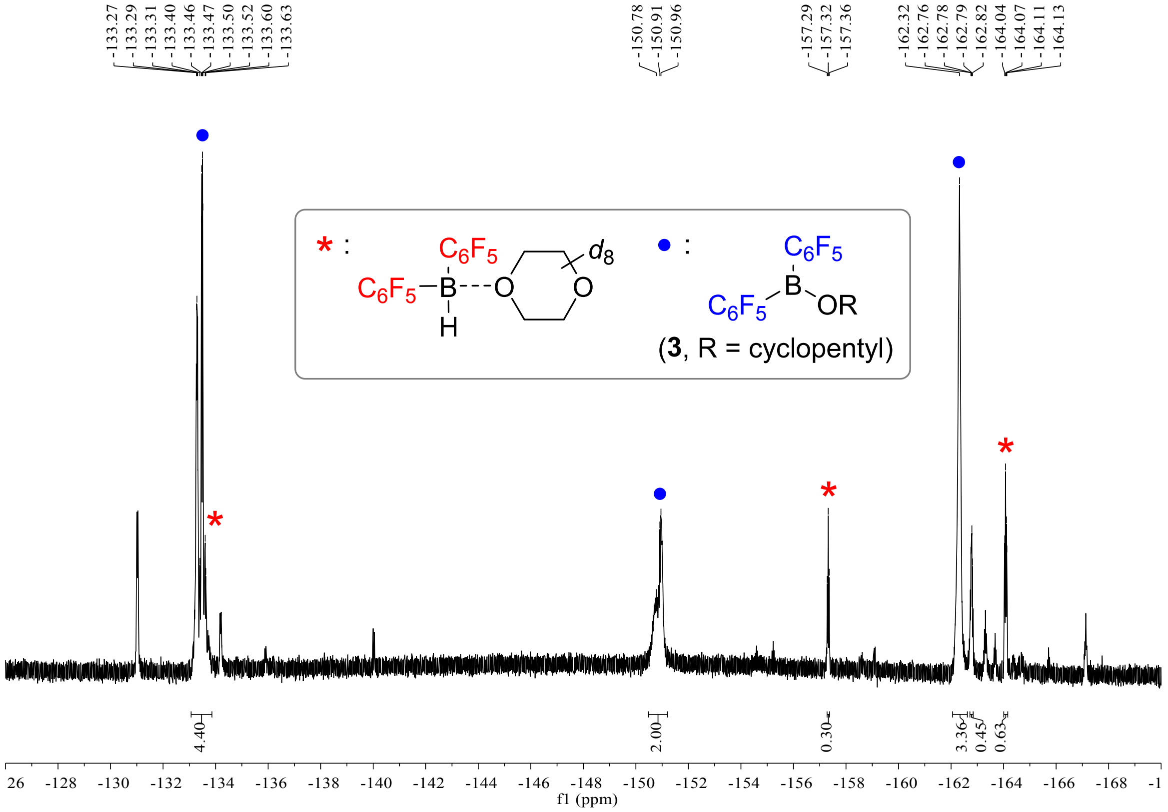
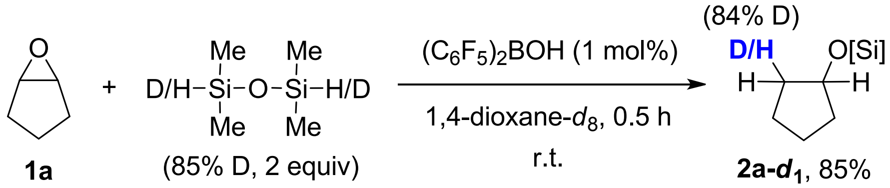


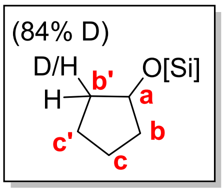
Figure S3. $^{19}F\{^1H\}$ NMR spectrum of the crude reaction mixture in the hydrosilylation of **1a**

III. Mechanistic Experiments (Scheme 2)

III-1. Deuterium labeling experiment (Scheme 2a)



Cyclopentyl-2-d_1 silyl ether (2a-d_1)



As shown above, TMDS-d_2 (85% D) (109.1 mg, 0.8 mmol, 2 equiv) was employed as a reductant instead of TMDS.

Crude yield: 85% (84% D); **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8) δ 4.398 – 4.316 (m, 1H), 1.754 – 1.648 (m, 3.16H), 1.598 – 1.535 (m, 2H), 1.519 – 1.458 (m, 2H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8) δ 74.7 (C^a), 74.6(3) (C^a), 74.6(0) (C^a), 36.4 (C^b), 36.0 (t, J = 19.5 Hz, C$^{b'}$, CHD), 23.9 (C^c), 23.8 (C$^{c'}$).

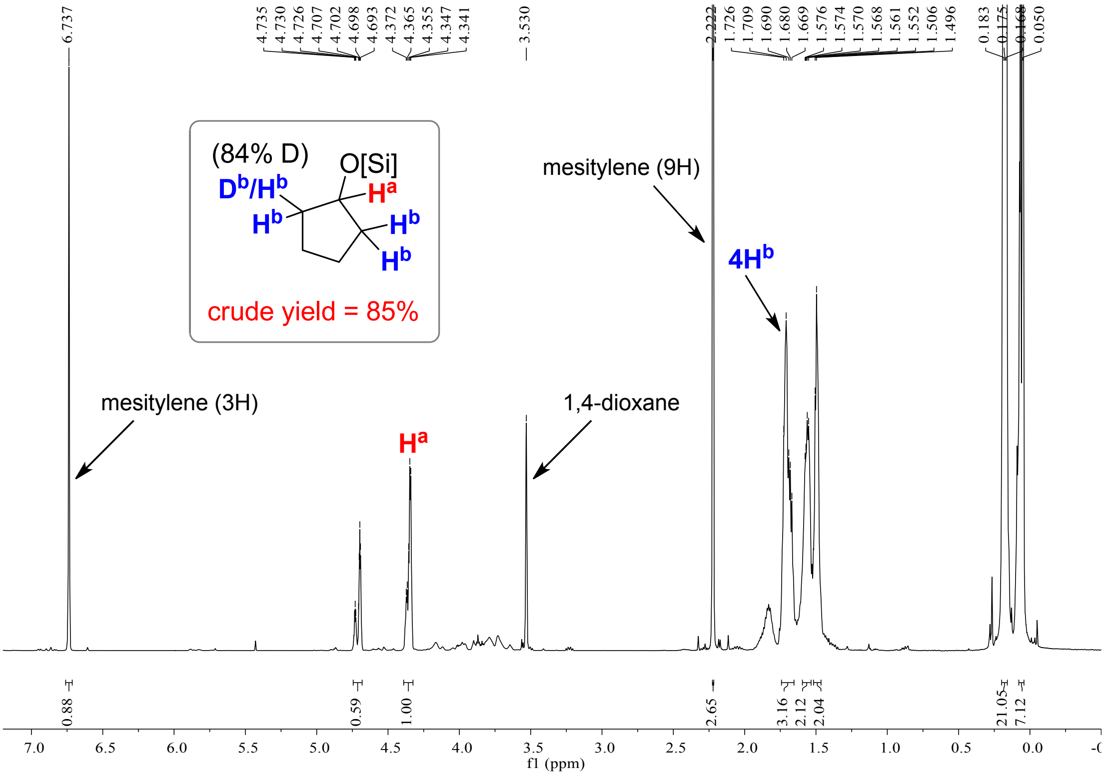


Figure S4. ^{1}H NMR spectrum of the reaction mixture in the hydrosilylation of **1a** with TMDS-d_2

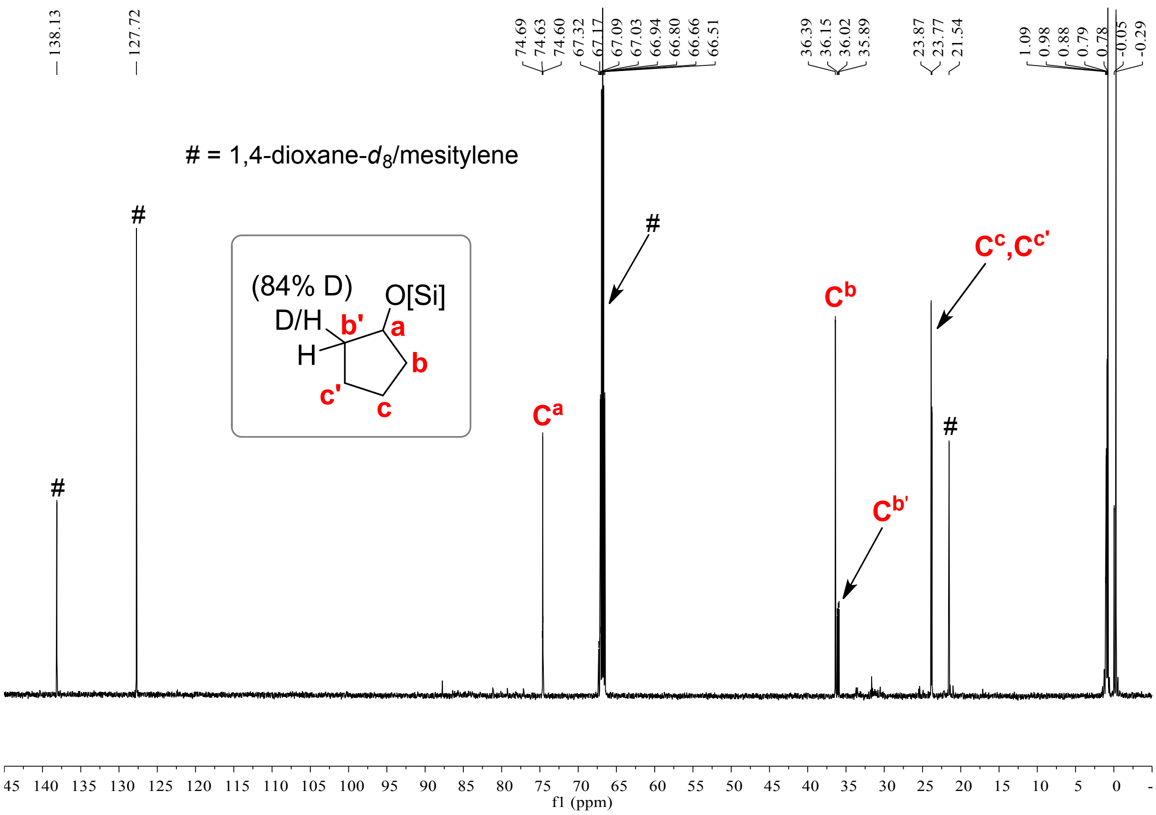
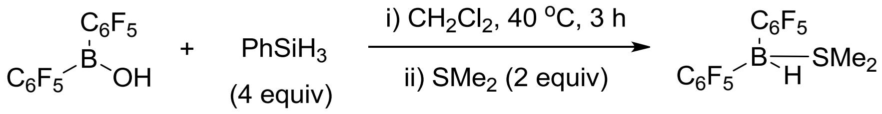


Figure S5. $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture in the hydrosilylation of **1a** with TMDS-d_2

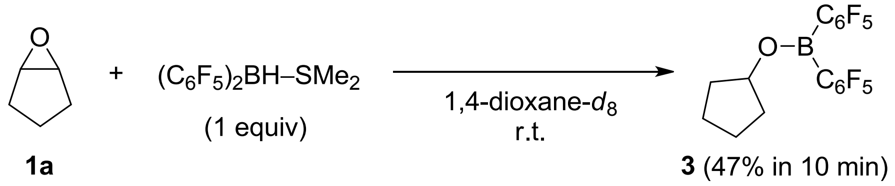
III-2. Stoichiometric reaction of 1a and the Piers' borane–SMe$_2$ adduct (Scheme 2b)

i) Synthesis of $(C_6F_5)_2BH{-}SMe_2$



An oven-dried schlenk flask was charged with $(C_6F_5)_2BOH$ (181.0 mg, 0.5 mmol) in CH_2Cl_2 (3 mL) under Ar atmosphere, into which $PhSiH_3$ (246.8 μL, 2.0 mmol, 4 equiv) was added. *Caution: a large amount of hydrogen generated!* After stirring at room temperature for 10 min, the reaction mixture was stirred for 3 h at 40 °C. The resulting mixture was then cooled down to room temperature, into which SMe_2 (73.4 μL, 1.00 mmol, 2 equiv) was added. After 0.5 h, the crude solution was concentrated under reduced pressure and the residue was subjected for recrystallization to obtain the desired adduct [CH_2Cl_2 (0.5 mL)/n-hexane (3 mL) at -35 °C]. The precipitate was filtered and washed with cold n-hexane (2 mL) to give white needle-like crystals (150.6 mg, 74%). **^{1}H NMR** (400 MHz, C_6D_6) δ 3.593 (br s, 1H), 1.096 (s, 6H); **$^{19}F\{^1H\}$ NMR** (376 MHz, C_6D_6) δ -131.6 (m, 4F, *o*-F), -156.0 (t, *J* = 20.6 Hz, 2F, *p*-F), -163.0 (m, 4F, *m*-F). Analytical data agree with the previous report.[S4]

*ii) Stoichiometric reaction of **1a** and $(C_6F_5)_2BH–SMe_2$*



To a solution of $(C_6F_5)_2BH–SMe_2$ (40.8 mg, 0.1 mmol) in 1,4-dioxane-d_8 (0.4 mL) in an oven-dried NMR tube was added cyclopentene oxide **1a** (8.7 µL, 0.1 mmol, 1 equiv) at room temperature under Ar atmosphere. After 10 min, the resulting mixture was subjected to ^{1}H NMR analysis to determine the crude NMR yield of **3** on the basis of an internal standard material (mesitylene, 14.0 µL, 0.1 mmol).

*Crude NMR data of **3***:

Crude yield: 47%; **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8) δ 4.820 (br s, 1H), 1.899 – 1.793 (m, 4H), 1.668 – 1.602 (m, 2H), 1.592 – 1.506 (m, 2H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8) δ 84.3 (C^a), 35.8 (C^b), 24.1 (C^c); **^{19}F{^{1}H} NMR** (564 MHz, 1,4-dioxane-d_8) δ -133.7 (m, 4F, *o*-F), -151.3 (br s, 2F, *p*-F), -162.6 (br s, 4F, *m*-F); **^{11}B{^{1}H} NMR** (192 MHz, 1,4-dioxane-d_8) δ 39.4.

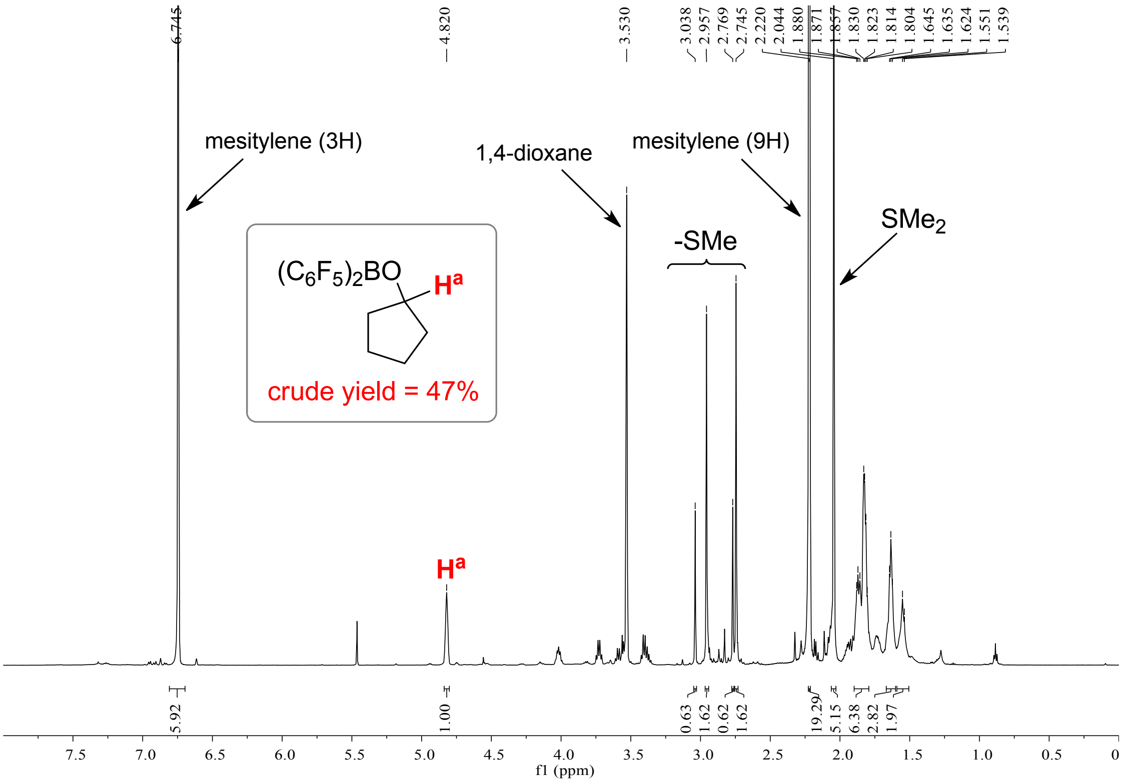


Figure S6. ^{1}H NMR spectrum of the crude mixture in the reaction of **1a** with $(C_6F_5)_2BH–SMe_2$ in 10 min

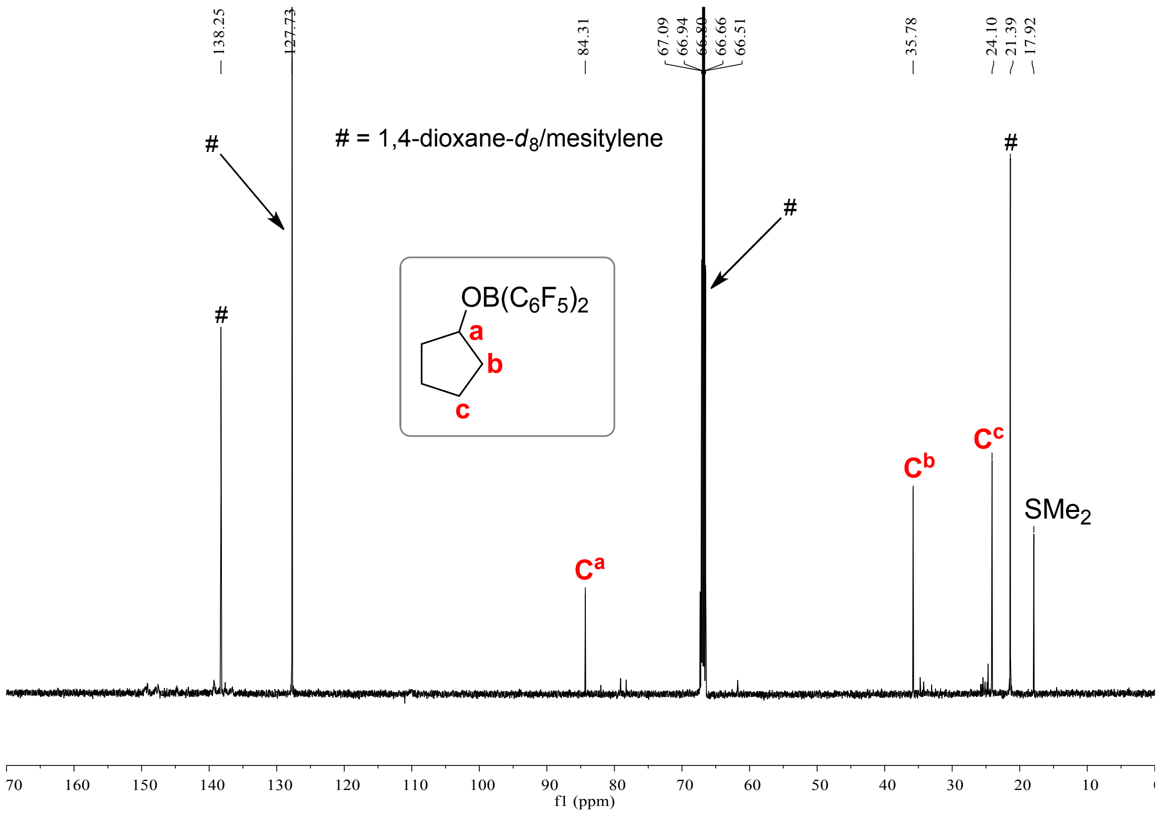


Figure S7. $^{13}C\{^1H\}$ NMR spectrum of the crude mixture in the reaction of **1a** with $(C_6F_5)_2BH–SMe_2$ in 10 min

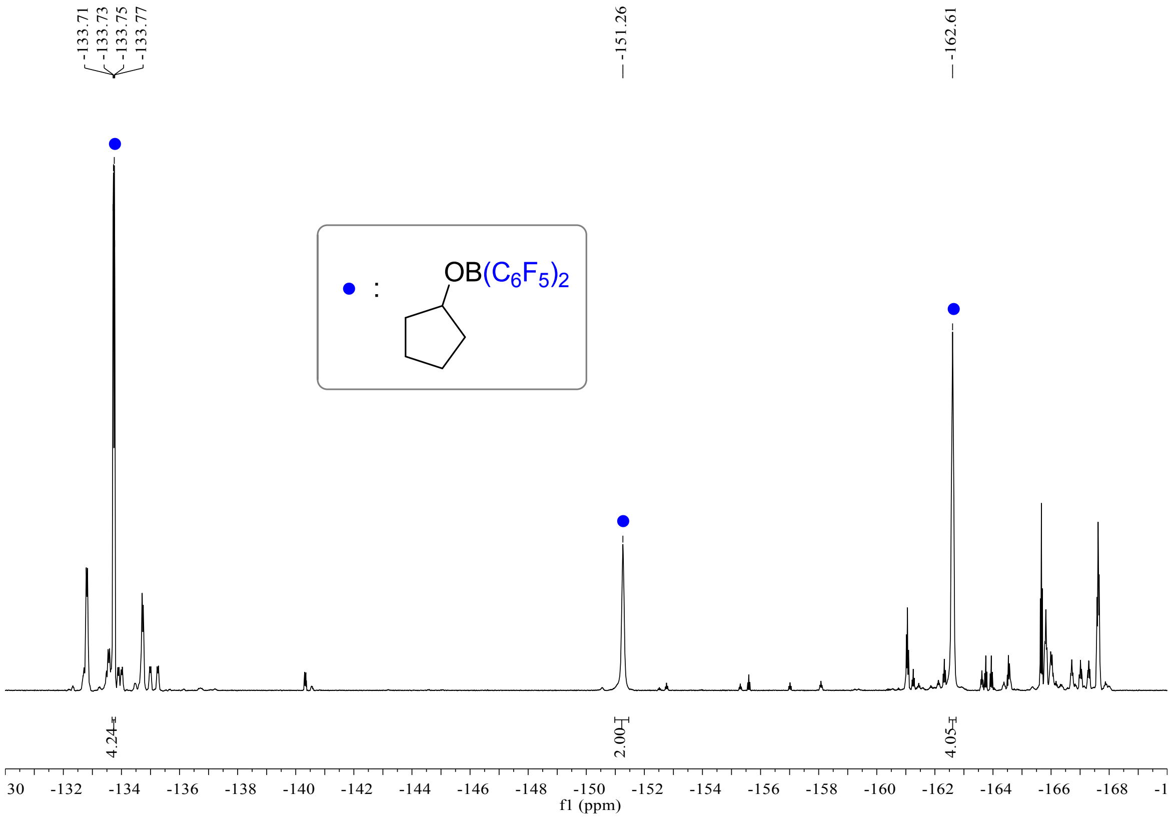
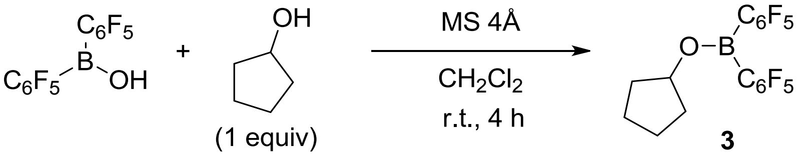


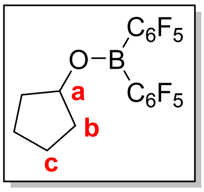
Figure S8. $^{19}F\{^1H\}$ NMR spectrum of the crude mixture in the reaction of **1a** with $(C_6F_5)_2BH–SMe_2$ in 10 min

III-3. Reaction of 3 with TMDS (Scheme 2c)

i) Synthesis of $(C_6F_5)_2BO(C_5H_9)$ 3

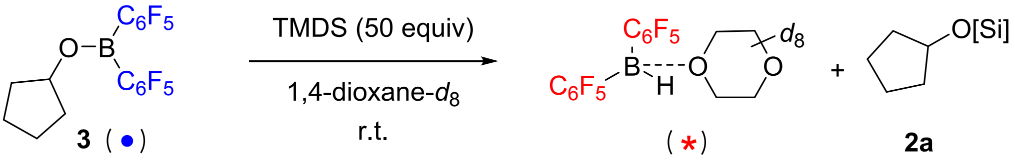


To a suspension of $(C_6F_5)_2BOH$ (181.0 mg, 0.5 mmol) and freshly activated MS 4Å (180 mg) in CH_2Cl_2 (4.0 mL) was added cyclopentanol (43.1 mg, 0.5 mmol, 1 equiv). The mixture was then stirred at room temperature for 4 h, and filtered to remove molecular sieves. Finally, all volatiles were removed under reduced pressure to give the corresponding borinic ester **3**.[S5]



Yellow oil, 193.4 mg, isolated yield: 90%; **^{1}H NMR** (600 MHz, C_6D_6) δ 4.496 (br s, 1H), 1.776 – 1.694 (m, 4H), 1.496 – 1.425 (m, 2H), 1.398 – 1.341 (m, 2H); **$^{13}C\{^1H\}$ NMR** (101 MHz, C_6D_6; selected data) δ 83.5 (C^a), 35.3 (C^b), 23.6 (C^c); **$^{19}F\{^1H\}$ NMR** (564 MHz, C_6D_6) δ -132.8 (br s, 4F, *o*-F), -149.5 (br s, 2F, *p*-F), -161.1 (br s, 4F, *m*-F); **$^{11}B\{^1H\}$ NMR** (192 MHz, C_6D_6) δ 39.0; **HRMS** (EI): Calculated for $C_{17}H_9F_{10}OB$ $[M]^+$: 430.0587, Found: 430.0586.

*ii) Reacion of **3** with TMDS*



In an Ar-filled glove box, TMDS (234.3 µL, 1.3257 mmol, 50 equiv) was added to a solution of **3** (11.4 mg, 0.02651 mmol) in 1,4-dioxane-d_8 (0.4 mL) in an oven-dried NMR tube. Then, the reaction progress was monitored by NMR spectroscopy at room temperature to determine the crude NMR yields of a dioxane adduct of Piers' borane and **2a** on the basis of internal standard materials (mesitylene, 14.0 µL, 0.1 mmol and $PhCF_3$, 12.3 µL, 0.1 mmol).

Table S1. Generation of a dioxane adduct of Piers' borane from **3**

entry	time (h)	conv. of **3** (%)[a]	yield of **2a** (%)[a]	yield of adduct (%)[b]
1	0.5	8	8	10
2	1	15	14	18
3	16	-	80	89

[a]Determined by ^{1}H NMR; [b]Determined by ^{19}F{^{1}H} NMR.

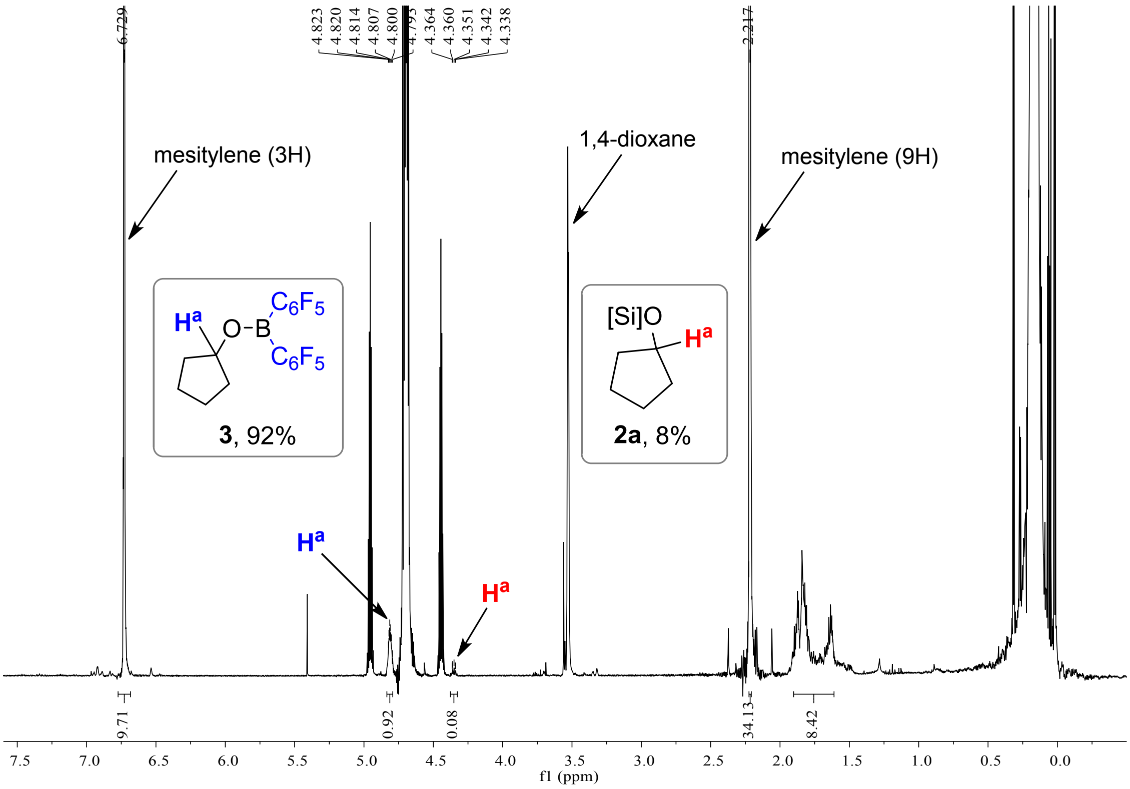


Figure S9. ^{1}H NMR spectrum of the crude mixture in the reaction of **3** with excess TMDS in 0.5 h

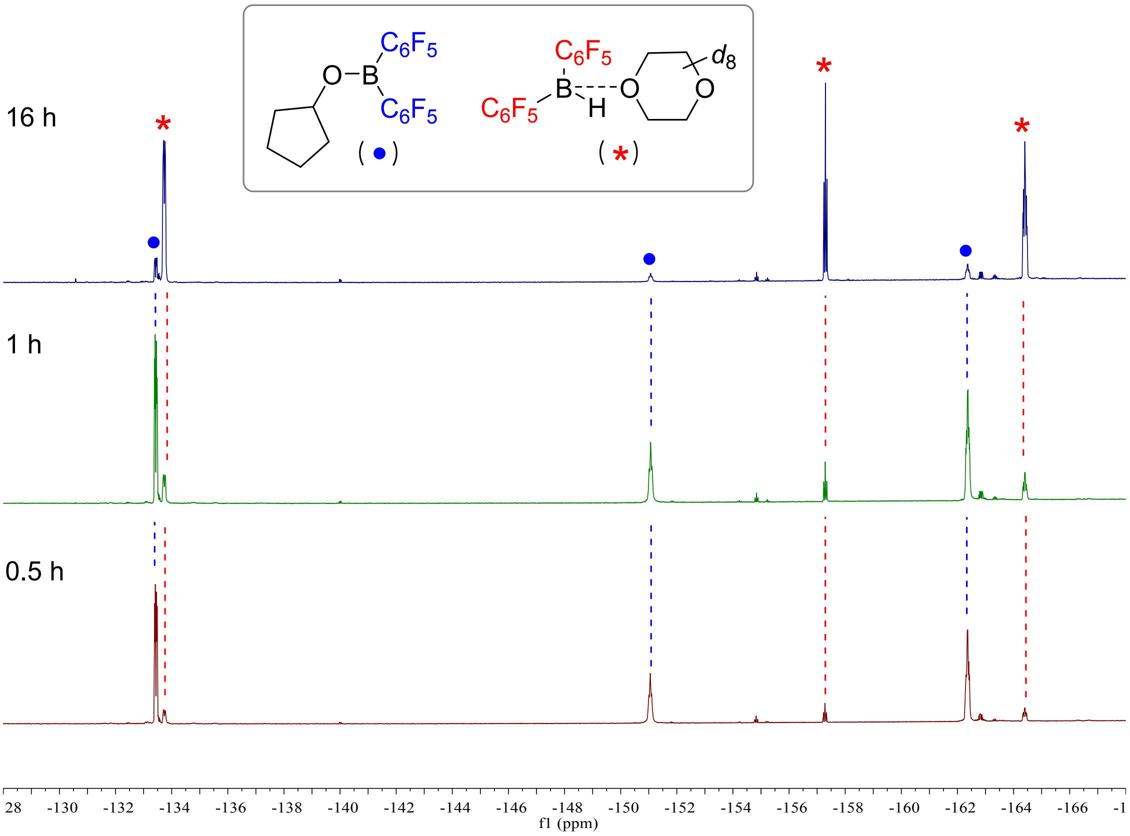
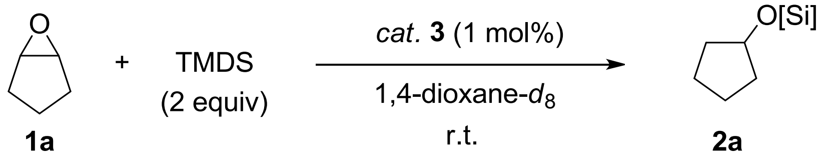


Figure S10. $^{19}F\{^1H\}$ NMR spectra of the crude mixture in the reaction of **3** with excess TMDS over time

III-4. Catalytic hydrosilylation mediated by 3 (Scheme 2d)



To a solution of **1a** (34.9 μL, 0.4 mmol) and TMDS (141.4 μL, 0.8 mmol, 2 equiv) in 1,4-dioxane-d_8 (0.4 mL) was added borinic ester **3** (1.72 mg, 1 mol%). After 10 min at room temperature, the reaction mixture was subjected to ^1H NMR analysis to determine the crude NMR yield on the basis of an internal standard material (mesitylene, 14.0 μL, 0.1 mmol). [crude yield: 79%]

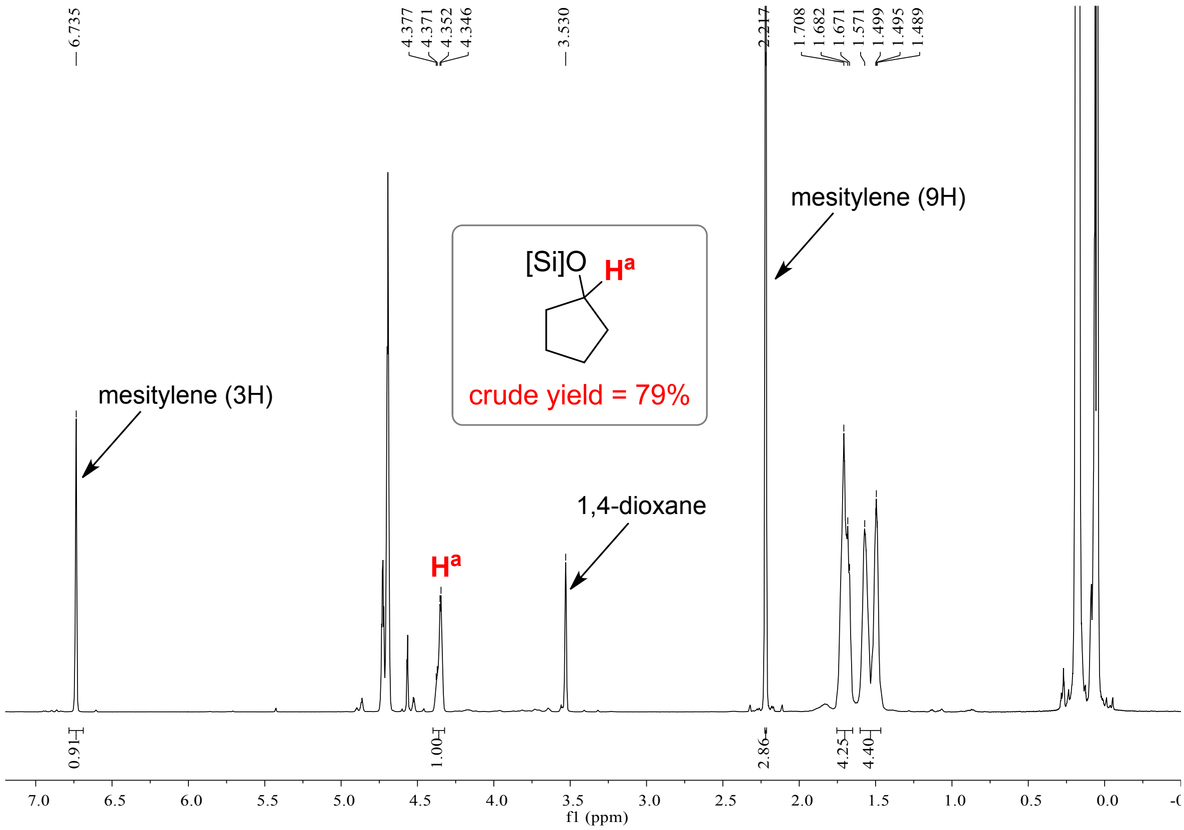
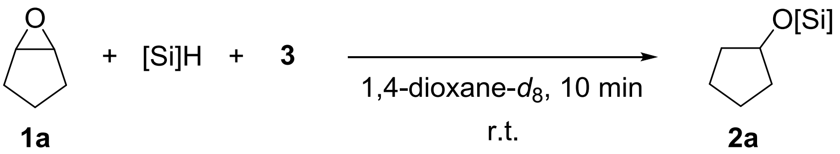


Figure S11. ^{1}H NMR spectrum of the crude mixture in the **3**-catalysed hydrosilylation of **1a** in 10 min

III-5. Stoichiometric reaction of 1a, [Si]H, and 3 (1:1:1) (Scheme 2e)



To a solution of **1a** (8.4 mg, 0.1 mmol) and silane (0.1 mmol) in 1,4-dioxane-d_8 (0.4 mL) was added borinic ester **3** (43.0 mg, 0.1 mmol). After 10 min at room temperature, the reaction mixture was subjected to NMR analysis to determine crude yields of **2a** and **3** (internal standard material: mesitylene, 14.0 µL, 0.1 mmol).

i) TMDS (13.4 mg, 0.1 mmol), 10 min, ***2a*** *(87%):*

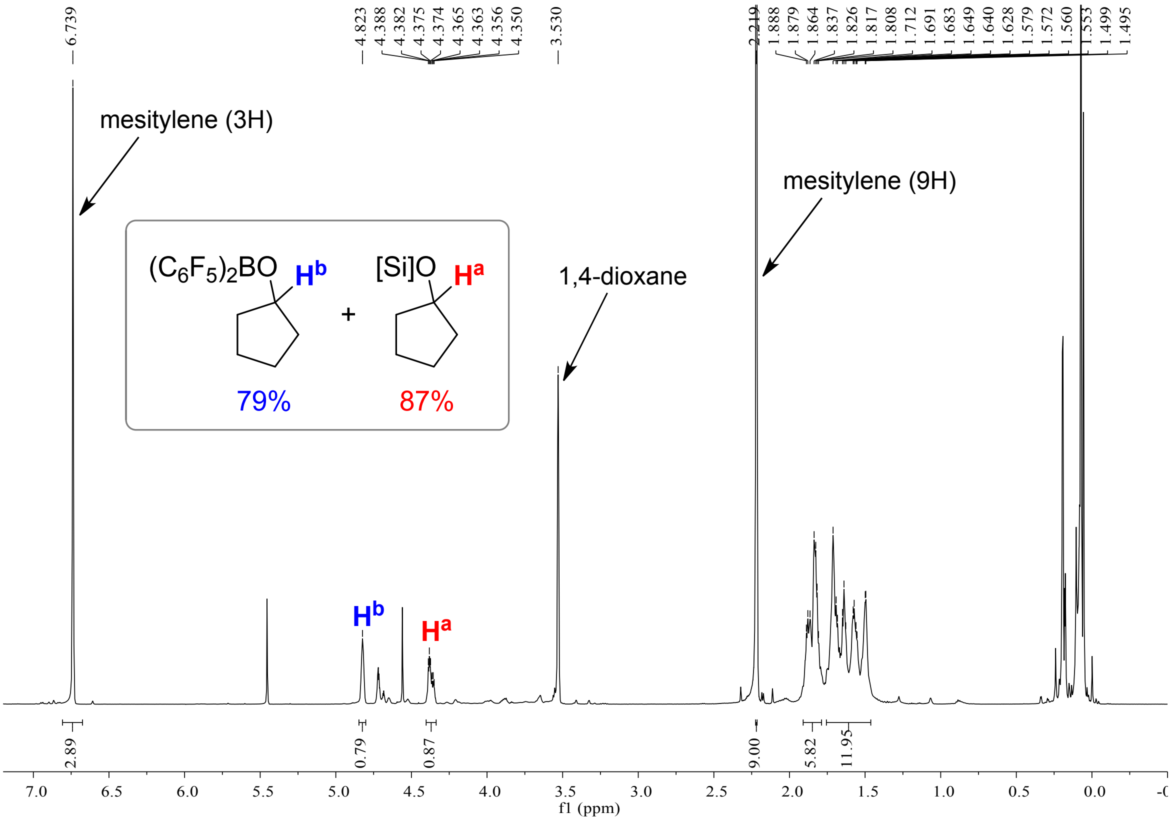


Figure S12. ^{1}H NMR spectrum of the crude mixture in the reaction of **1a**, TMDS, and **3** (1:1:1)

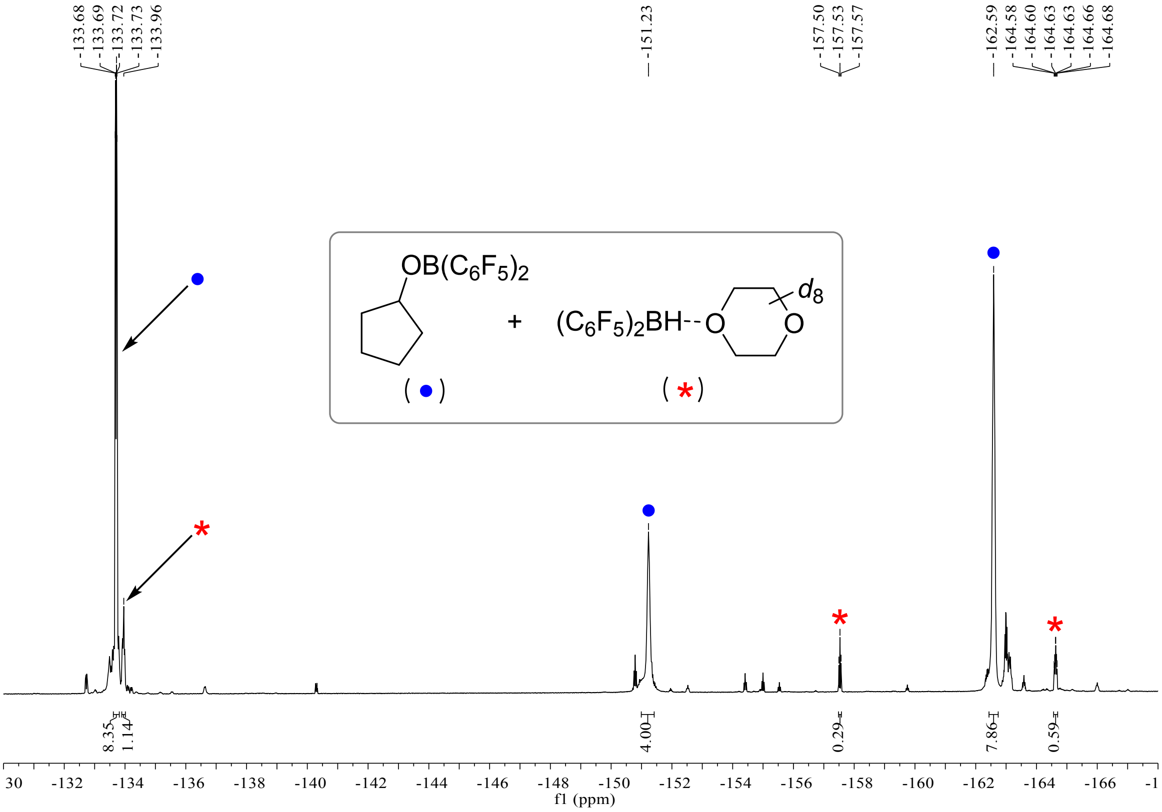


Figure S13. ^{19}F{^{1}H} NMR spectrum of the crude mixture in the reaction of **1a**, TMDS, and **3** (1:1:1) *ii) Me$_2$PhSiH (13.6 mg, 0.1 mmol), 10 min, **2a** (46%):*

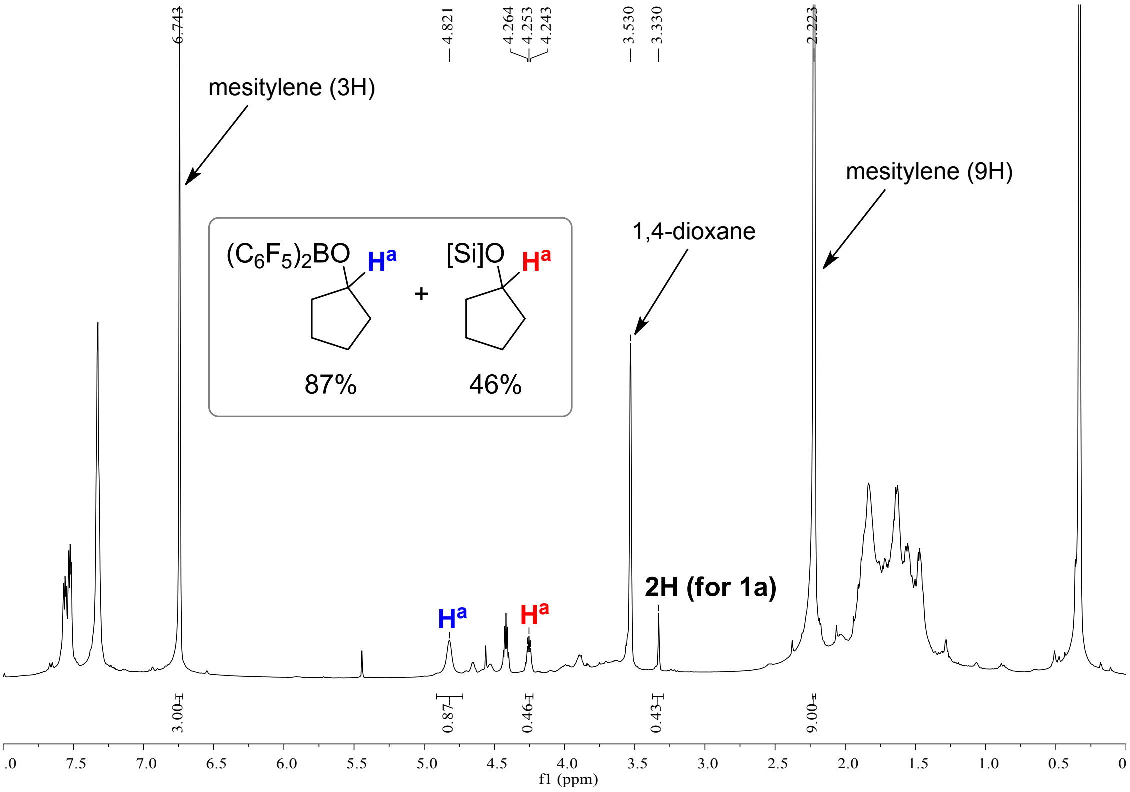


Figure S14. ^{1}H NMR spectrum of the crude mixture in the reaction of **1a**, Me$_2$PhSiH, and **3** (1:1:1)

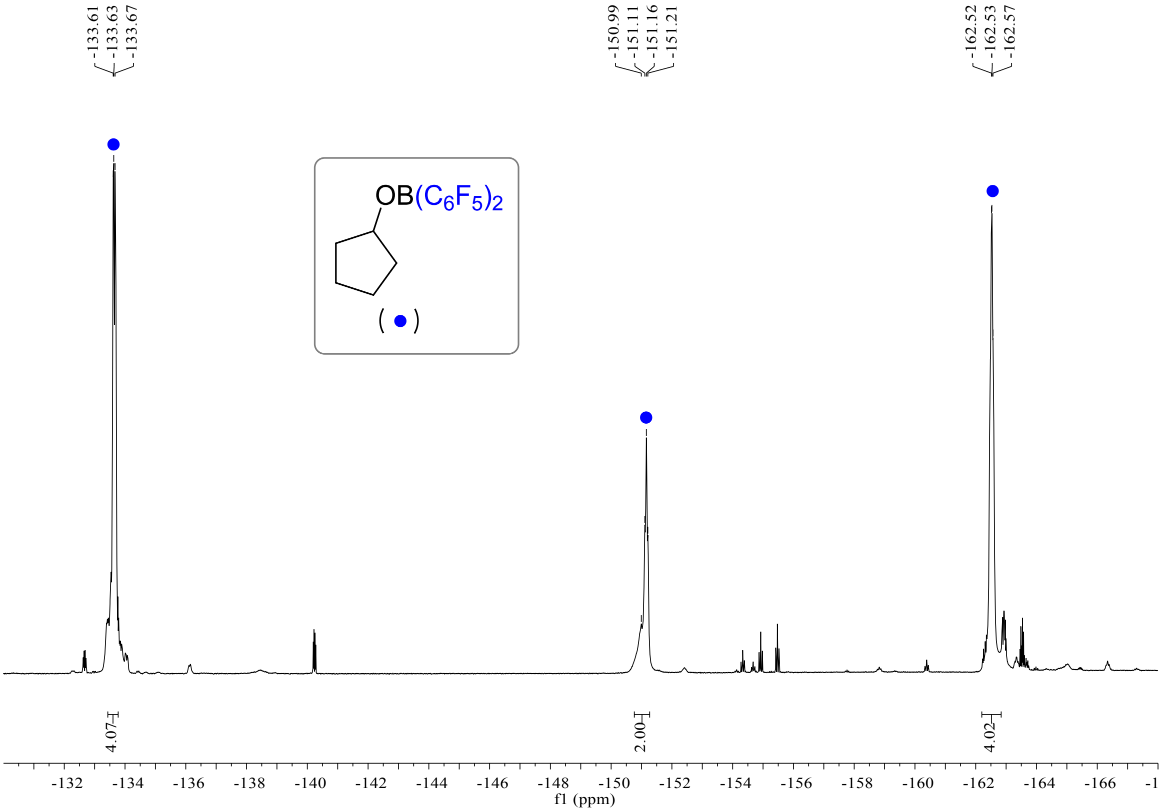
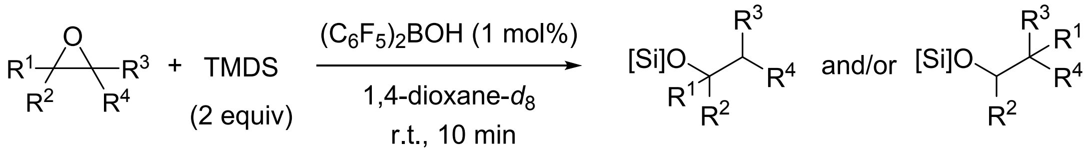


Figure S15. ^{19}F{^{1}H} NMR spectrum of the crude mixture in the reaction of **1a**, Me$_2$PhSiH, and **3** (1:1:1)

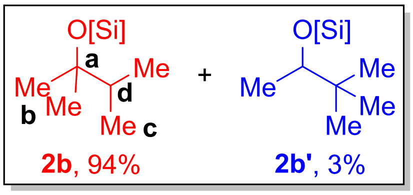
IV. Comparative Experiments: Piers' borane *vs.* B(C_6F_5)$_3$ (Scheme 4a)

IV-1. (C_6F_5)$_2$BH-catalysed hydrosilylation of epoxides



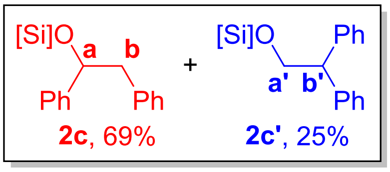
The catalytic procedure for this hydrosilylation reaction is the same as described in **part II**.

2,3-Dimethylbutan-2-yl silyl ether and 3,3-dimethylbutan-2-yl silyl ether (2b and 2b')



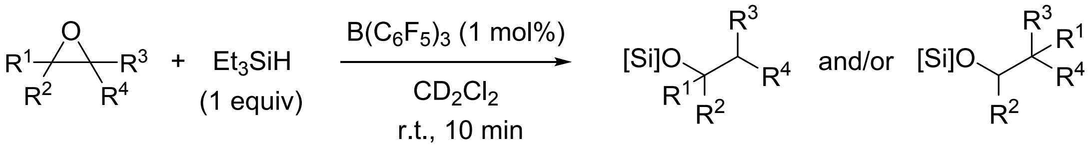
Crude yield: 97% (**2b**:**2b'** = >20:1); **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8; selected data of **2b**): δ 1.669 – 1.600 (m, 1H), 1.222 – 1.176 (m, 6H), 0.980 – 0.855 (m, 6H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8; selected data of **2b**): δ 77.5 (C^a), 77.4 (C^a), 40.4 (C^d), 27.4 (C^b), 18.3 (C^c), 18.2 (C^c).

1,2-Diphenylethan-2-yl silyl ether and 1,1-diphenylethan-2-yl silyl ether (2c and 2c')



Crude yield: 94% (**2c**:**2c'** = 2.8:1); **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8): δ 7.321 – 7.070 (m, 10H), 4.942 (dd, J = 7.9, 5.1 Hz, 0.74H), 4.216 – 4.164 (m, 0.78H), 2.980 – 2.874 (m, 1.48H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8): δ 145.7 (C), 143.6 (C), 139.8 (C), 130.8 (2CH), 129.4 (2CH), 129.1(2) (2CH), 129.1(1) (2CH), 128.8(8) (2CH), 128.8(3) (2CH), 128.8(1) (2CH), 128.7(8) (2CH), 127.9(6) (2CH), 127.8(9) (2CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 126.9(6) (CH), 126.9(2) (CH), 77.0 (C^a), 76.8 (C^a), 66.5 ($C^{a'}$), 54.4 ($C^{b'}$), 48.0 (C^b).

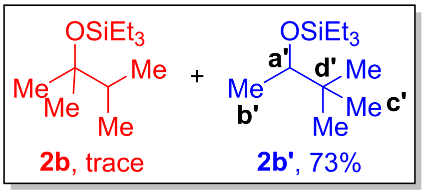
IV-2. B(C_6F_5)$_3$-catalysed hydrosilylation of epoxides



In an Ar-filled glove box, B(C_6F_5)$_3$ (2.0 mg, 1 mol%) was dissolved in CD_2Cl_2 (0.4 mL) in a NMR tube, into which Et_3SiH (63.9 μL, 0.4 mmol) was subsequently treated and the solution was shaken briefly. Then, epoxides

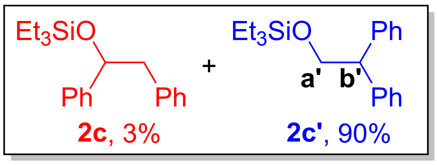
(0.4 mmol) were added into the above solution. After 10 min, the reaction mixture was subjected to ^{1}H NMR analysis to determine the crude NMR yield on the basis of an internal standard material (mesitylene, 14.0 µL, 0.1 mmol).

2,3-Dimethylbutan-2-yl triethylsilyl ether and 3,3-dimethylbutan-2-yl triethylsilyl ether (2b and 2b’)



Crude yield: 73% (**2b**:**2b’** = 1:>99); **^{1}H NMR** (600 MHz, CD_2Cl_2; selected data of **2b‘**): δ 3.518 (q, *J* = 6.4 Hz, 1H), 1.090 (d, *J* = 6.0 Hz, 3H), 0.887 (s, 9H); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2; selected data of **2b‘**): δ 76.5 ($C^{a'}$), 36.0 ($C^{d'}$), 26.2 ($C^{b'}$), 19.0 ($C^{c'}$).

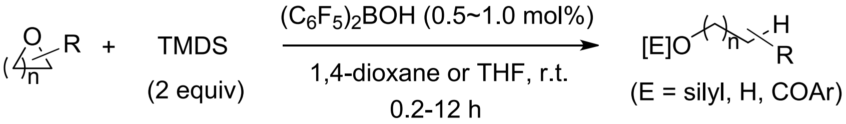
1,2-Diphenylethan-2-yl triethylsilyl ether and 1,1-diphenylethan-2-yl triethylsilyl ether (2c and 2c’)



Crude yield: 93% (**2c**:**2c’** = 1:>20); **^{1}H NMR** (600 MHz, CD_2Cl_2; selected data of **2c’**): δ 7.433 – 7.386 (m, 8H), 7.337 – 7.298 (m, 2H), 4.322 – 4.275 (m, 3H), 1.044 (t, *J* = 8.0 Hz, 9H), 0.702 (q, *J* = 7.9 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2; selected data of **2c’**): δ 143.2 (2C), 129.0 (4CH), 128.8 (4CH), 126.8 (2CH), 66.8 ($C^{a'}$), 54.4 ($C^{b'}$).

V. Substrate Scope of the Piers’ Borane-Catalysed Hydrosilylation (Scheme 5)

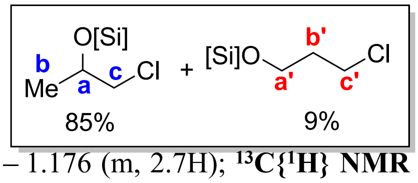
i) Hydrosilylation of epoxides:



The catalytic procedure for this hydrosilylation reaction is the same as described in **part II**.

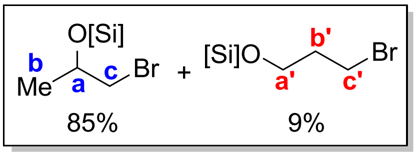
Hydrolysis of alkyl silyl ethers: The resulting reaction mixture was concentrated under reduced pressure and hydrolyzed with saturated K_2CO_3 in MeOH (2 mL). Further purification by column chromatography on silica gel gave the corresponding alcohols.

1-Chloropropane-2-silyl ether and 3-chloropropyl silyl ether



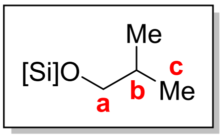
Crude yield: 94% (9:1); **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8) δ 4.134 – 4.046 (m, 0.9H), 3.814 – 3.758 (m, 0.2H), 3.659 – 3.614 (m, 0.2H), 3.487 – 3.433 (m, 0.9H), 3.421 – 3.369 (m, 0.9H), 1.961 – 1.902 (m, 0.2H), 1.290 – 1.176 (m, 2.7H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8) δ 69.4 (C^{a}), 69.3 (C^{a}), 59.2 ($C^{a'}$), 50.4(3) (C^{c}), 50.4(0) (C^{c}), 42.1 ($C^{c'}$), 36.0 ($C^{b'}$), 21.7(8) (C^{b}), 21.7(6) (C^{b}).

1-Bromopropane-2-silyl ether and 3-bromopropyl silyl ether



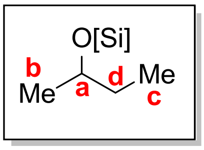
Crude yield: 94% (9:1); **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8) δ 4.145 – 4.061 (m, 0.9H), 3.793 – 3.744 (m, 0.2H), 3.511 – 3.472 (m, 0.2H), 3.375 – 3.266 (m, 1.8H), 2.033 – 1.983 (m, 0.2H), 1.312 – 1.213 (m, 2.7H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8) δ 69.0(4) (C^a), 69.0(2) (C^a), 60.3 ($C^{a'}$), 39.4(2) (C^c), 39.3(8) (C^c), 36.2 ($C^{c'}$), 30.8 ($C^{b'}$), 22.6 (C^b), 22.5 (C^b).

Isobutyl silyl ether



Crude yield: 90% (internal standard material: CH_2Br_2, 7.0 µL, 0.1 mmol); **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8): δ 3.417 – 3.373 (m, 2H), 1.746 – 1.683 (m, 1H), 0.868 (d, J = 6.7 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8): δ 69.4 (C^a), 31.4 (C^b), 19.4(0) (C^c), 19.3(8) (C^c).

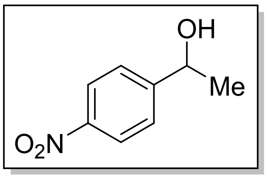
sec-Butyl silyl ether



Crude yield: 94%; **^{1}H NMR** (600 MHz, 1,4-dioxane-d_8): δ 3.880 – 3.788 (m, 1H), 1.485 – 1.372 (m, 2H), 1.161 – 1.107 (m, 3H), 0.875 (t, J = 7.5 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8): δ 69.3(3) (C^a), 69.2(6) (C^a), 32.0 (C^d), 22.8 (C^b), 9.6 (C^c).

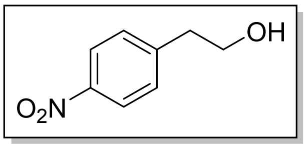
1-(4-Nitrophenyl)ethanol and 2-(4-nitrophenyl)ethanol [Crude yield: 97% (1:8), in THF]

1-(4-Nitrophenyl)ethanol[S6]



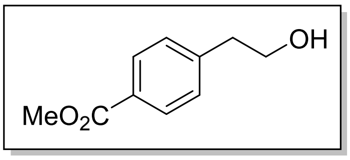
Yellow solid: 4.8 mg, isolated yield: 7%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.208 (d, J = 9.0 Hz, 2H), 7.546 (d, J = 8.4 Hz, 2H), 5.026 (q, J = 6.4 Hz, 1H), 1.985 (br s, 1H), 1.522 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.2 (C), 147.4 (C), 126.3 (2CH), 123.9 (2CH), 69.7 (CH), 25.7 (CH_3).

2-(4-Nitrophenyl)ethanol[S6]



Yellow solid: 40.3 mg, isolated yield: 60%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.142 (d, J = 8.4 Hz, 2H), 7.392 (d, J = 8.4 Hz, 2H), 3.907 (t, J = 6.6 Hz, 2H), 2.962 (t, J = 6.3 Hz, 2H), 1.774 (br s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.9 (C), 146.8 (C), 130.0 (2CH), 123.8 (2CH), 63.0 (CH_2), 39.0 (CH_2).

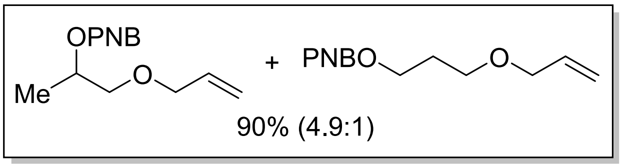
Methyl 4-(2-hydroxyethyl)benzoate[S7]



Crude yield: 65%, in THF; Colorless oil: 33.5 mg, isolated yield: 46%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.970 (d, J = 7.8 Hz, 2 H), 7.294 (d, J = 8.4 Hz, 2 H), 3.902 – 3.863 (m, 5 H), 2.914 (t, J = 6.6 Hz, 2 H), 1.657 (br s, 1 H); **^{13}C{^{1}H} NMR**

(150 MHz, $CDCl_3$) δ 167.2 (C=O), 144.3 (C), 130.0 (2CH), 129.2 (2CH), 128.5 (C), 63.4 (CH_2), 52.2 (CH_3), 39.3 (CH_2).

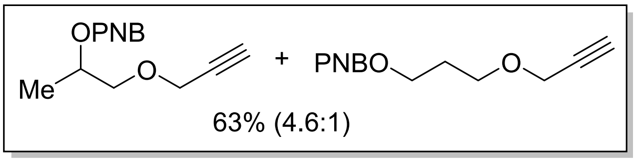
1-Allyloxypropan-2-yl 4-nitrobenzoate and 3-allyloxypropyl 4-nitrobenzoate (PNB = 4-nitrobenzoyl)



Crude yield: 95% (4:1); The crude alcohols were further protected according to literature.[S8]

Yellow oil: 95.3 mg, isolated yield: 90% (4.9:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.264 (d, J = 7.8 Hz, 2H), 8.200 (d, J = 7.8 Hz, 2H), 5.935 – 5.817 (m, 1H), 5.383 – 5.329 (m, 0.83H), 5.260 (d, J = 17.4 Hz, 1H), 5.168 (d, J = 10.2 Hz, 1H), 4.476 (t, J = 6.0 Hz, 0.34H), 4.073 – 3.968 (m, 2H), 3.657 – 3.572 (m, 2H), 2.092 – 2.048 (m, 0.34H), 1.383 (d, J = 6.0 Hz, 2.49H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.8 (C=O), 164.4 (C=O), 150.7 (C), 136.2 (C), 135.9 (C), 134.8 (CH_2=), 134.6 (CH_2=), 130.9(4) (2CH), 130.8(8) (2CH), 123.7(2) (2CH), 123.6(6) (2CH), 117.4 (CH=), 117.2 (CH=), 72.5 (CH_2), 72.4 (CH_2), 72.2 (CH_2), 71.6 (CH), 66.8 (CH_2), 63.5 (CH_2), 29.3 (CH_2), 16.9 (CH_3); **IR** (cm^{-1}): 2982, 2862, 1720, 1606, 1524, 1347, 1269, 1100, 926, 838, 718; **HRMS** (ESI): Calculated for $C_{13}H_{15}NO_5Na$ $[M+Na]^+$: 288.0848, found: 288.0850.

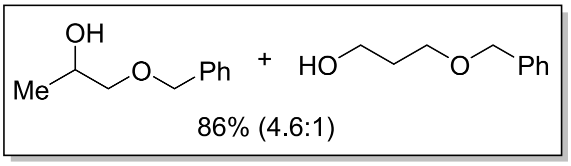
1-Propargyloxypropan-2-yl 4-nitrobenzoate and 3-propargyloxypropyl 4-nitrobenzoate (PNB = 4-nitrobenzoyl)



Crude yield: 99% (4:1); The crude alcohols were further protected according to literature.[S8]

Yellow oil: 66.0 mg, isolated yield: 63% (4.6:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.266 (d, J = 8.4 Hz, 2H), 8.205 (d, J = 8.4 Hz, 2H), 5.404 – 5.330 (m, 0.82H), 4.473 (t, J = 6.3 Hz, 0.36H), 4.204 (s, 1.64H), 4.155 (s, 0.36H), 3.720 (d, J = 5.4 Hz, 1.64H), 3.680 (t, J = 6.0 Hz, 0.36H), 2.441 (s, 0.82H), 2.411 (s, 0.18H), 2.108 – 2.061 (m, 0.36H), 1.394 (d, J = 6.0 Hz, 2.46H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.8 (C=O), 164.4 (C=O), 150.7 (C), 136.1 (C), 135.9 (C), 131.0 (2CH), 130.9 (2CH), 123.7(3) (2CH), 123.6(7) (2CH), 79.8 (C≡), 79.5 (C≡), 75.1 (HC≡), 74.7 (HC≡), 72.0 (CH_2), 71.3 (CH), 66.5 (CH_2), 63.3 (CH_2), 58.6 (CH_2), 58.4 (CH_2), 29.1 (CH_2), 16.8 (CH_3); **IR** (cm^{-1}): 3288, 2983, 2869, 1719, 1607, 1524, 1347, 1270, 1096, 838, 718, 644; **HRMS** (ESI): Calculated for $C_{13}H_{13}NO_5Na$ $[M+Na]^+$: 286.0691, found: 286.0707.

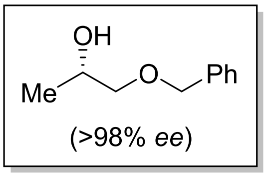
1-Benzyloxy-2-propanol and 3-benzyloxypropanol[S9a]



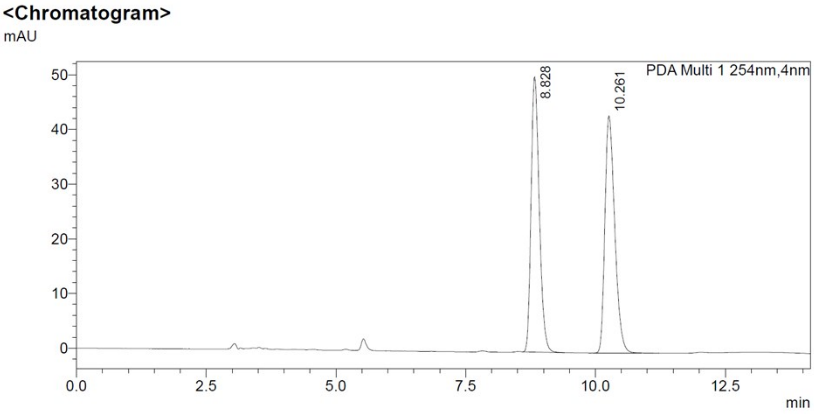
Crude yield: 99% (4:1); Colorless oil: 57.4 mg, isolated yield: 86% (4.6:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.385 –

7.265 (m, 5H), 4.554 (s, 1.64H), 4.519 (s, 0.36H), 4.021 – 3.971 (m, 0.82H), 3.775 – 3.744 (m, 0.36H), 3.647 (t, J = 5.7 Hz, 0.36H), 3.458 (dd, J = 9.6, 3.0 Hz, 0.82H), 3.295 (t, J = 8.7 Hz, 0.82H), 2.724 (br s, 0.82H), 2.605 (br s, 0.18H), 1.879 – 1.837 (m, 0.36H), 1.149 (d, J = 6.0 Hz, 2.46H); **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$) δ 138.2 (C), 138.0 (C), 128.5 (2CH), 127.8(2) (2CH), 127.8(0) (2CH), 127.7(4) (2CH), 127.7(0) (2CH), 75.9 (CH$_2$), 73.4 (CH$_2$), 73.3 (CH$_2$), 69.1 (CH$_2$), 66.5 (CH), 61.5 (CH$_2$), 32.2 (CH$_2$), 18.8 (CH$_3$).

(*S*)-1-Benzyloxy-2-propanol



From (*S*)-(+)-2-[(benzyloxy)methyl]oxirane (98% *ee*). Colorless oil: 45.2 mg, isolated yield: 67% (>98% *ee*); **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.405 – 7.273 (m, 5H), 4.560 (s, 2H), 4.031 – 3.976 (m, 1H), 3.471 (dd, J = 9.4, 3.0 Hz, 1H), 3.310 – 3.273 (m, 1H), 2.385 (br s, 1H), 1.152 (d, J = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$) δ 138.1 (C), 128.6 (2CH), 127.9 (CH), 127.8 (2CH), 76.0 (CH$_2$), 73.4 (CH$_2$), 66.6 (CH), 18.8 (CH$_3$). The *ee* value was determined by chiral HPLC analyses [column: Daicel Chiralcel OD-H (4.6 mm x 250 mm), eluent: hexane/*i*-PrOH = 95/5, flow rate: 1 mL/min, temperature: 32 °C, detector: 254 nm].[S9b]

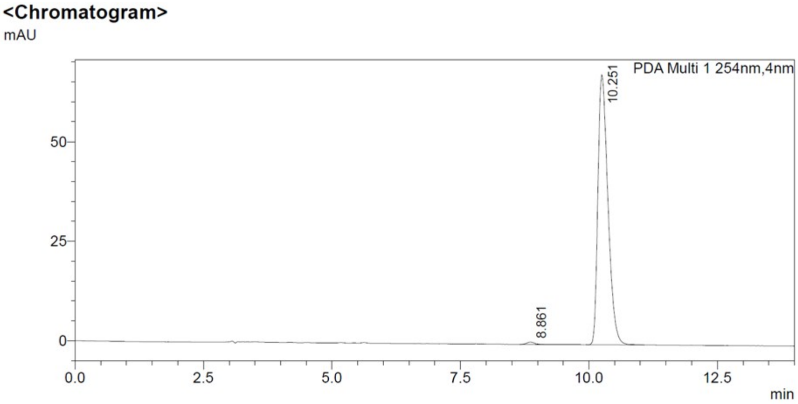


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.828	551776	50329	49.158
2	10.261	570685	43364	50.842
Total		1122462	93693	100.000

Figure S16. Chromatogram of (±)-1-benzyloxy-2-propanol



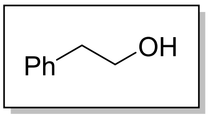
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.861	5840	552	0.632
2	10.251	918520	67773	99.368
Total		924360	68325	100.000

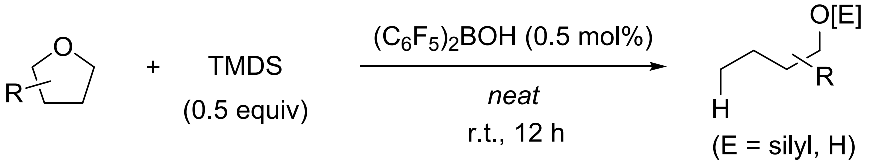
Figure S17. Chromatogram of (*S*)-1-benzyloxy-2-propanol

2-Phenylethanol



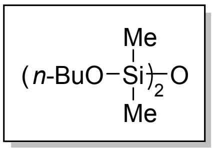
[*Gram-scale reaction*: *cat.* $(C_6F_5)_2BOH$ (36.2 mg, 0.5 mol%), styrene oxide (2.3 mL, 20 mmol) and TMDS (7.07 mL, 40 mmol) in THF (20 mL) at room temperature for 12 h] The reaction mixture was concentrated, hydrolyzed with K_2CO_3 saturated MeOH solution (30 mL) and further purified by column chromatography on silica gel to give a colorless oil 1.74 g (71%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.324 (t, *J* = 7.8 Hz, 2H), 7.257 – 7.215 (m, 3H), 3.856 (t, *J* = 6.6 Hz, 2H), 2.872 (t, *J* = 6.6 Hz, 2H), 1.624 (br s, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 138.6 (C), 129.1 (2CH), 128.7 (2CH), 126.6 (CH), 63.8 (CH_2), 39.3 (CH_2). Spectroscopic data were well matched with those provided by Sigma Aldrich (2-phenylethanol, CAS: 60-12-8).

ii) Hydrosilylation of cyclic ethers:



In an Ar-filled glove box, $(C_6F_5)_2BOH$ (1.45 mg, 0.5 mol%) was dissolved in THF derivatives as a substrate (0.8 mmol) in a NMR tube, into which TMDS (70.7 μL, 0.4 mmol) was subsequently treated, and the mixture was allowed to react at room temperature for 12 h. The reaction mixture was then analyzed by ^{1}H NMR in $CDCl_3$ containing an internal standard material (mesitylene, 14.0 μL, 0.1 mmol).

1,3-Dibutoxy-1,1,3,3-tetramethyldisiloxane[S10]

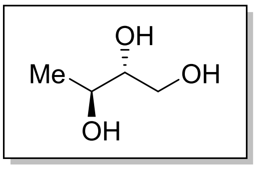


$(n\text{-BuO}-\text{SiMe}_2)_2\text{O}$

[*Gram-scale reaction*: *cat.* $(C_6F_5)_2BOH$ (1.1 mg, 0.01 mol%), THF (2.5 mL, 30.8 mmol) and TMDS (2.72 mL, 15.4 mmol) at room temperature for 3 days] All volatiles were removed under reduced pressure to afford the desired product as a colorless oil 3.85 g

(90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.663 (t, *J* = 6.7 Hz, 4H), 1.533 (quint, *J* = 6.7 Hz, 4H), 1.399 – 1.321 (m, 4H), 0.917 (t, *J* = 7.4 Hz, 6H), 0.104 (s, 12H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 62.2 ($2CH_2$), 34.9 ($2CH_2$), 19.1 ($2CH_2$), 14.0 ($2CH_3$), -0.9 ($4CH_3$).

1-Deoxyerythritol[S11]



Crude yield: 97%; colorless oil: 73.2 mg, isolated yield: 87%; **^{1}H NMR** (600 MHz, D_2O) δ 3.742 (quint, *J* = 6.1 Hz, 1H), 3.687 – 3.638 (m, 1H), 3.560 – 3.472 (m, 2H), 1.129 (d, *J* = 6.5 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, D_2O) δ 77.9 (CH), 70.3 (CH), 65.0 (CH_2), 19.8 (CH_3).

VI. References

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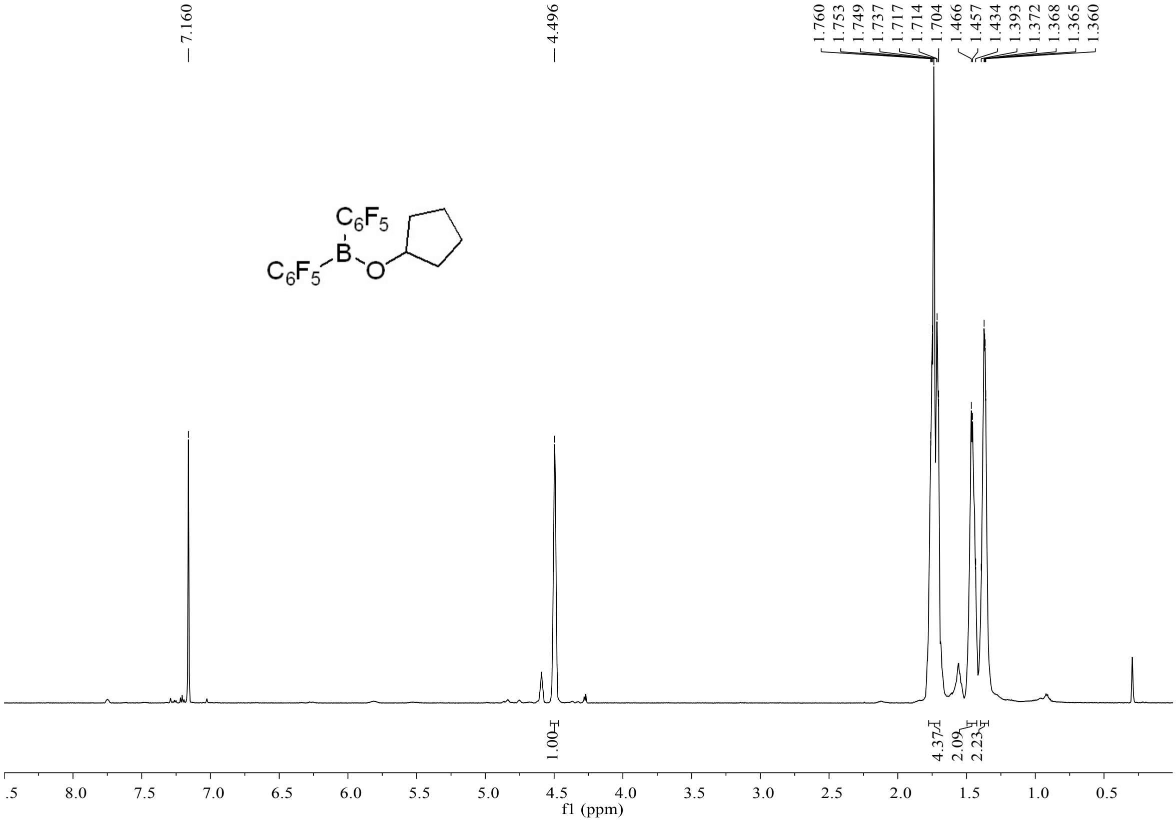
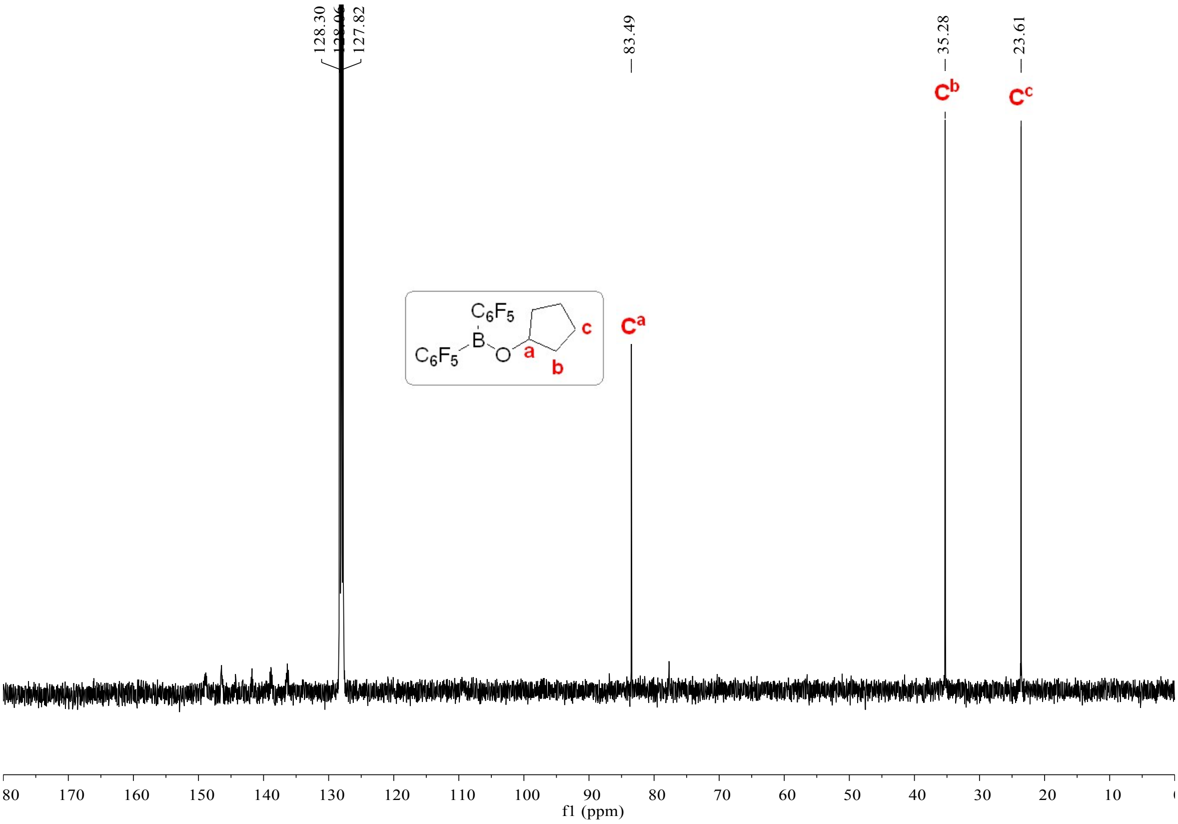
Appendix I

Spectral Copies of ^{1}H, ^{13}C, and ^{19}F NMR of Compounds Obtained in This Study

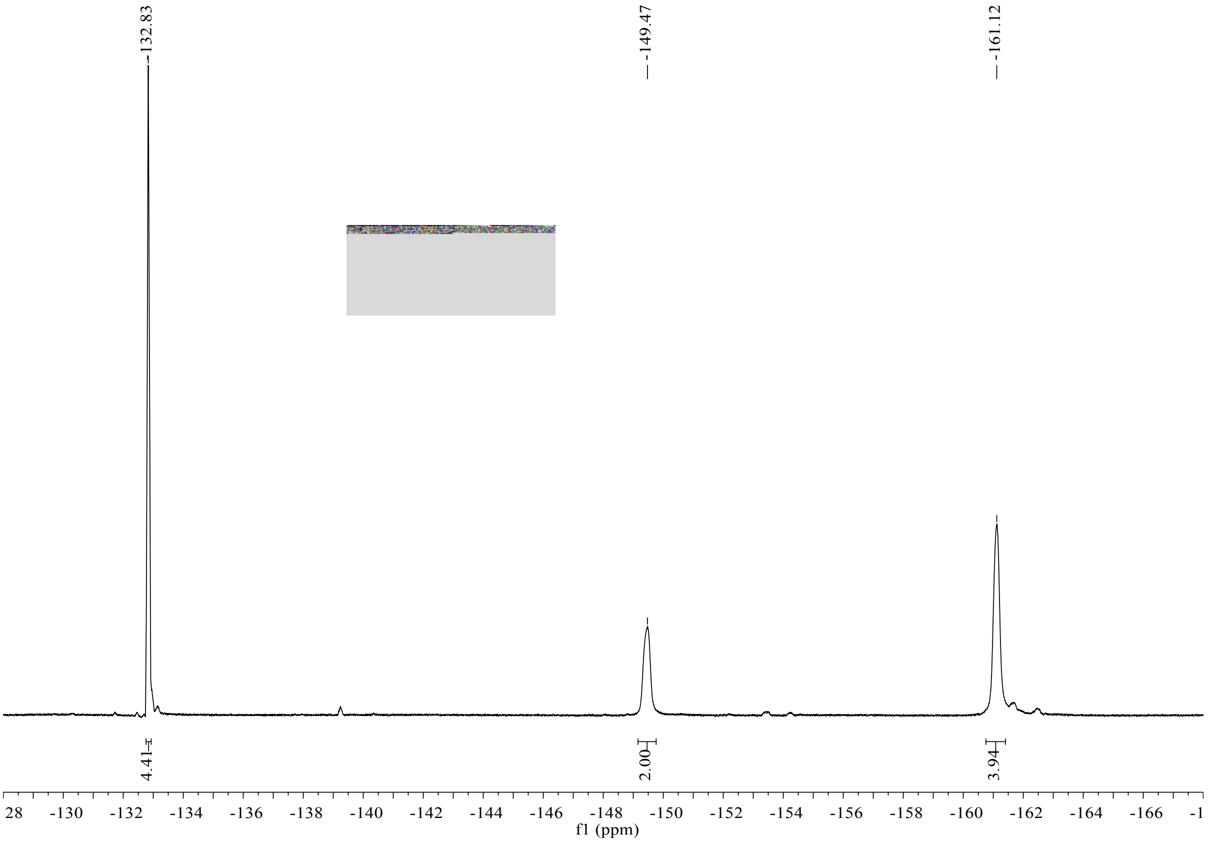
Cyclopentyl bis(perfluorophenyl)borinic ester 3 (Scheme 2)

^{1}H NMR (600 MHz, C_6D_6) & **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6);





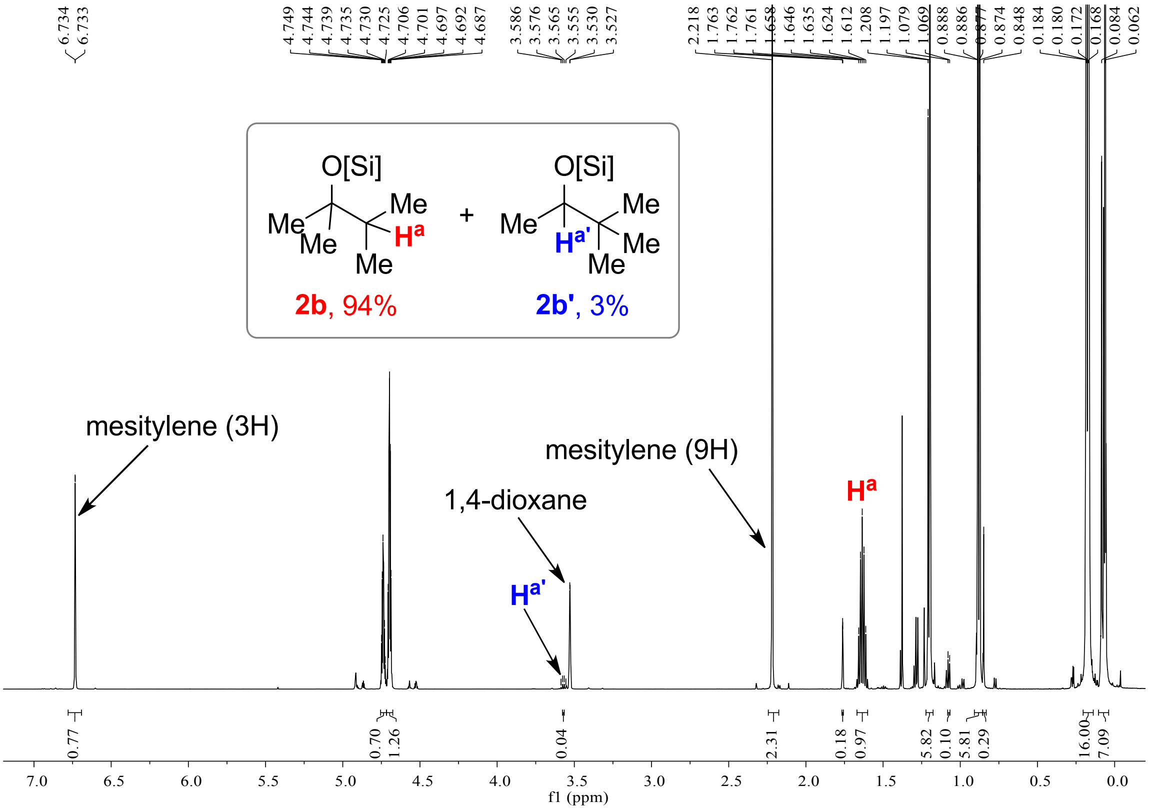
^{19}F{^{1}H} NMR (564 MHz, C_6D_6);



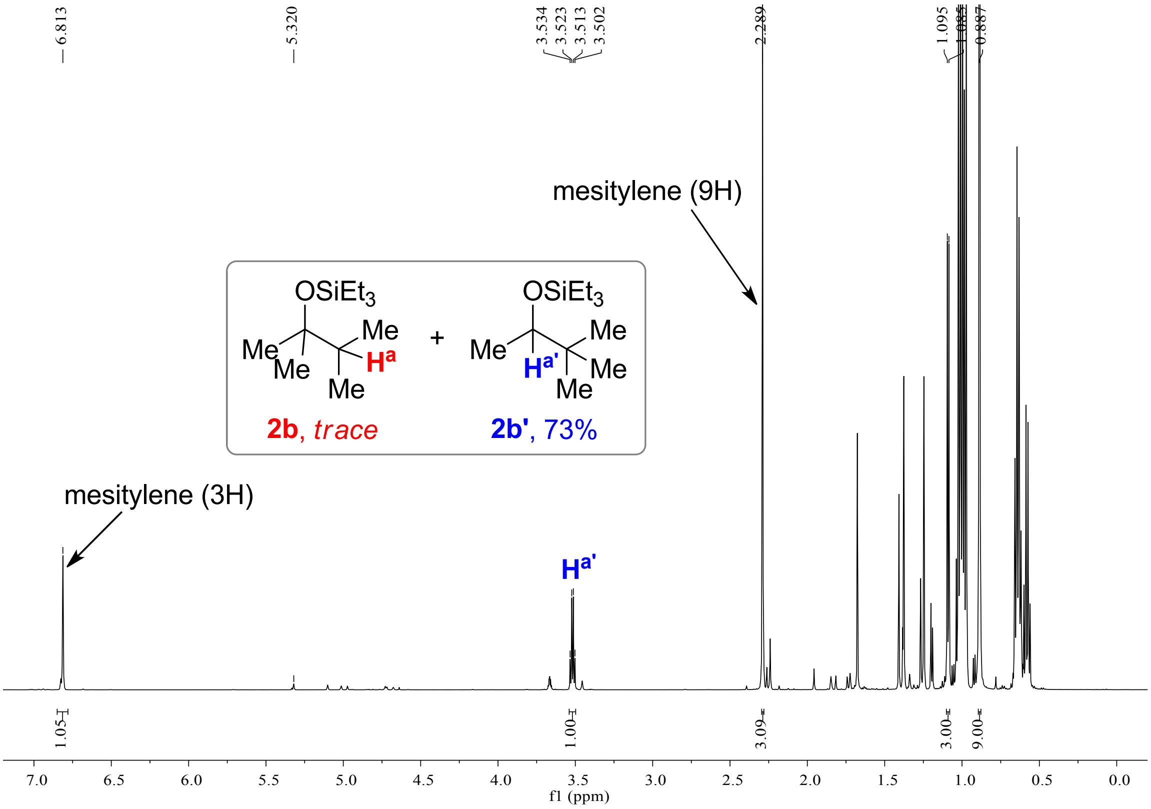
2,3-Dimethyl-2-butyl silyl ether and **3,3-dimethyl-2-butyl silyl ether** (**Scheme 4**, **2b** and **2b'**)

^{1}H NMR (600 MHz), internal standard: mesitylene;

cat. $(C_6F_5)_2BOH$/TMDS in 1,4-dioxane-*d*$_8$, crude yield: 97% (**2b**:**2b'** = >20:1);



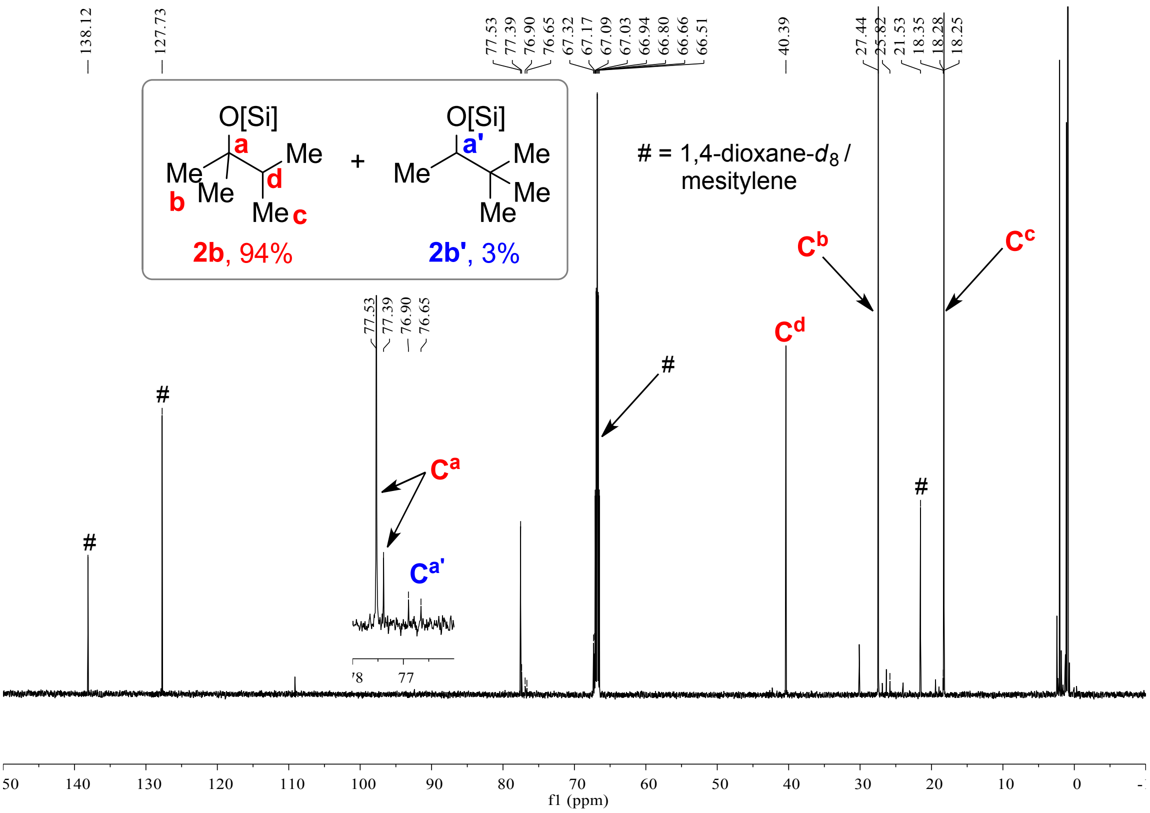
cat. $B(C_6F_5)_3$/Et_3SiH in CD_2Cl_2, crude yield: 73% (**2b**:**2b'** = 1:>99);



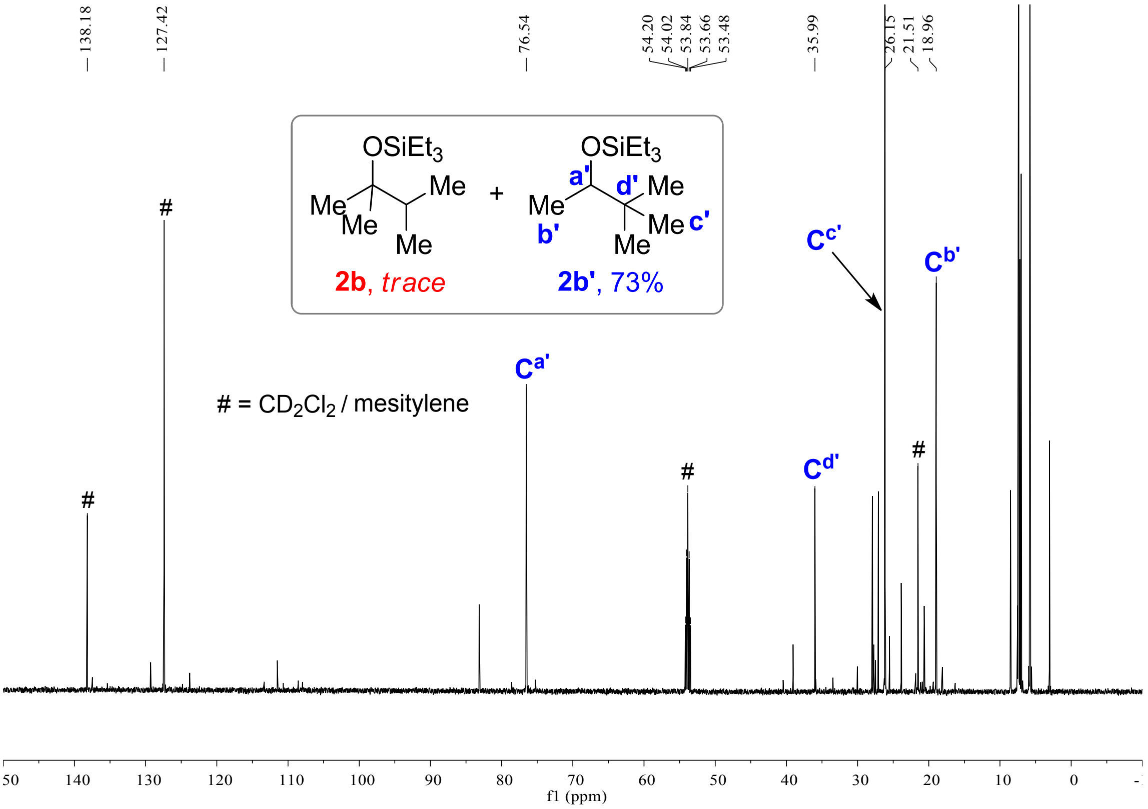
2,3-Dimethyl-2-butyl silyl ether and **3,3-dimethyl-2-butyl silyl ether** (**Scheme 4**, **2b** and **2b'**)

^{13}C{^{1}H} NMR (151 MHz), internal standard: mesitylene;

cat. $(C_6F_5)_2BOH$/TMDS in 1,4-dioxane-d_8;



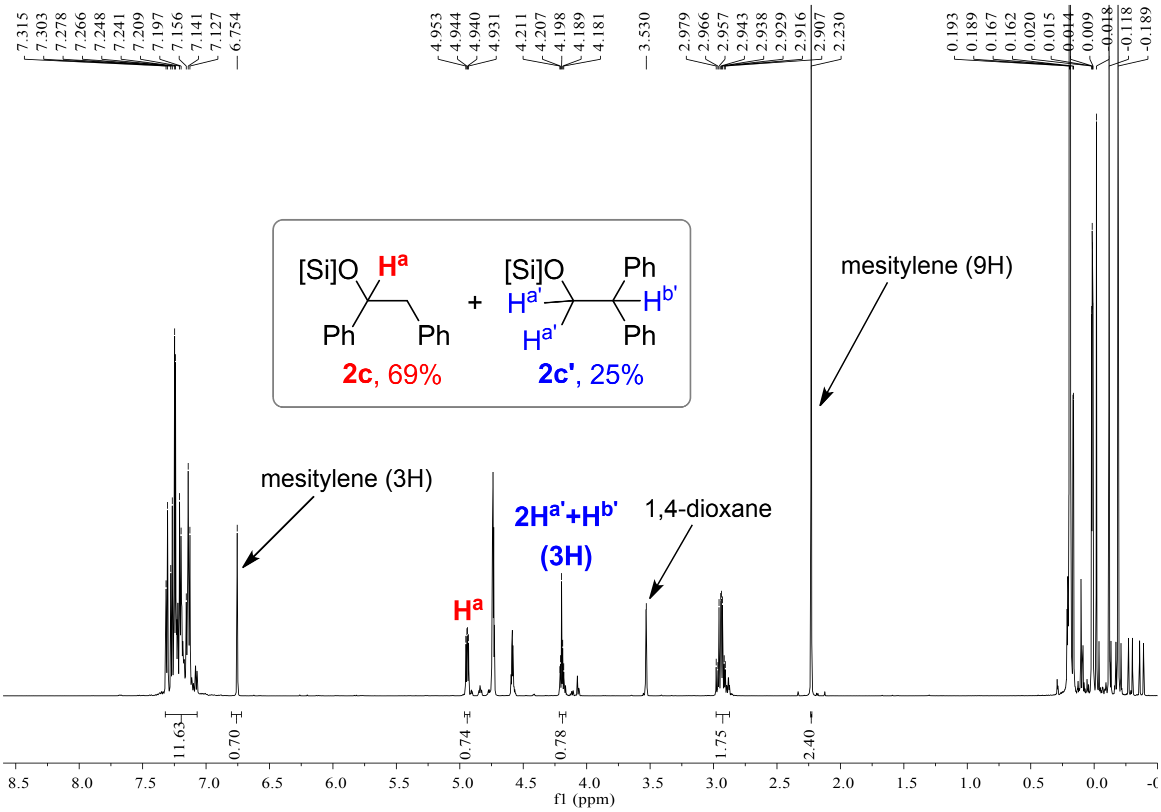
cat. $B(C_6F_5)_3$/Et_3SiH in CD_2Cl_2;



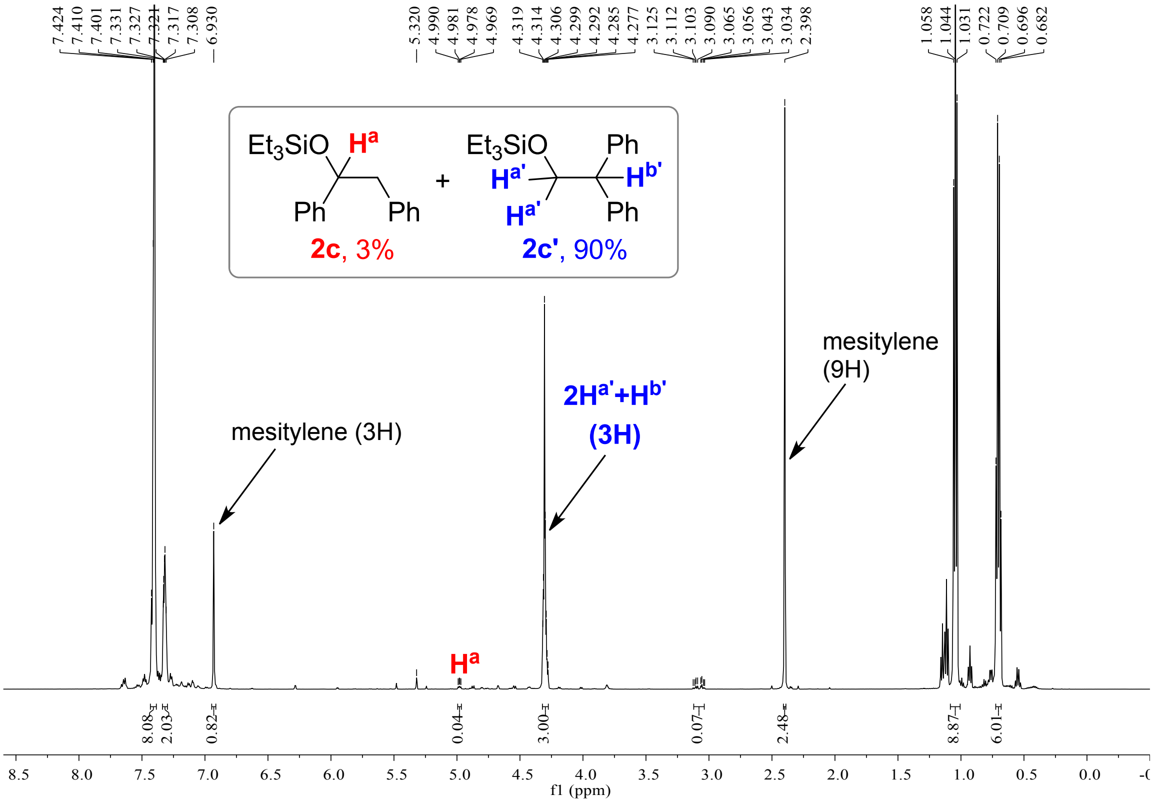
1,2-Diphenylethan-2-yl silyl ether and **1,1-diphenylethan-2-yl silyl ether** (**Scheme 4**, **2c** and **2c'**)

^{1}**H NMR** (600 MHz), internal standard: mesitylene;

cat. $(C_6F_5)_2BOH$/TMDS in 1,4-dioxane-d_8, crude yield: 94% (**2c**:**2c'** = 2.8:1);



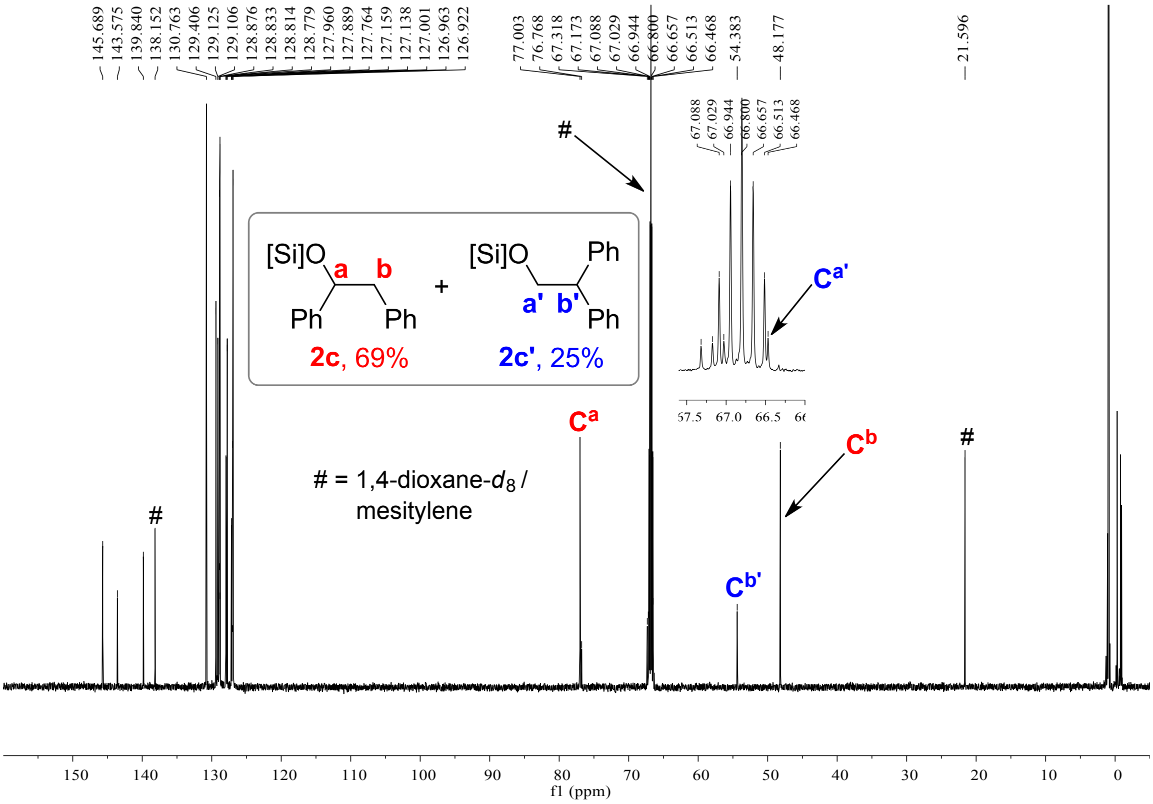
cat. $B(C_6F_5)_3$/Et_3SiH in CD_2Cl_2, crude yield: 93% (**2c**:**2c'** = 1:>20);



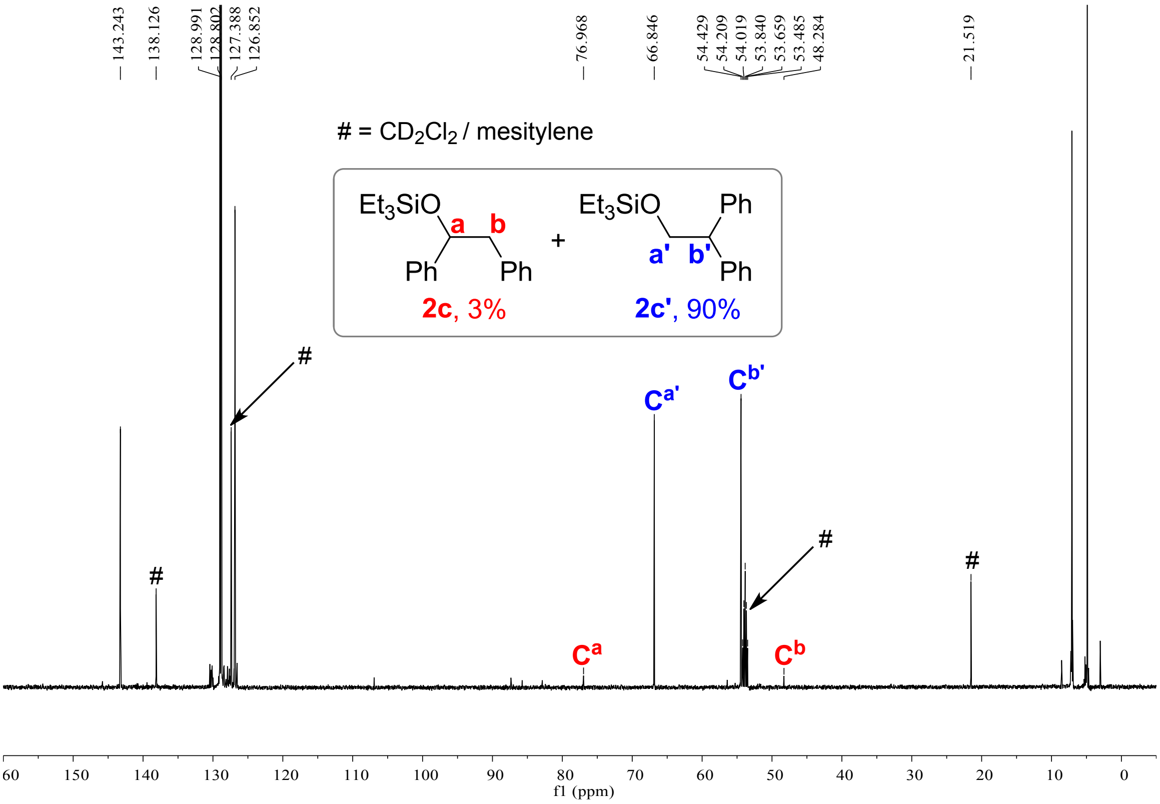
1,2-Diphenylethan-2-yl silyl ether and **1,1-diphenylethan-2-yl silyl ether** (**Scheme 4**, **2c** and **2c'**)

^{13}**C{^{1}H} NMR** (151 MHz), internal standard: mesitylene;

cat. $(C_6F_5)_2BOH$/TMDS in 1,4-dioxane-d_8;



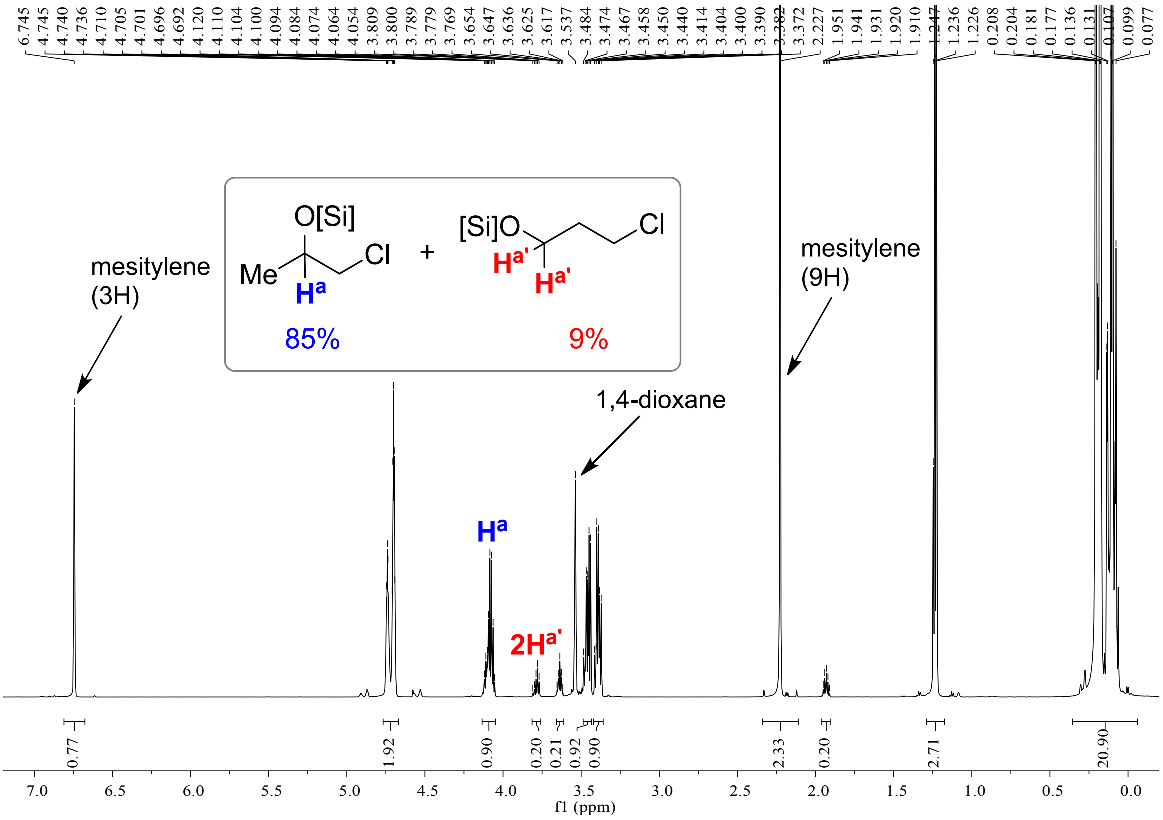
cat. $B(C_6F_5)_3$/Et_3SiH in CD_2Cl_2;

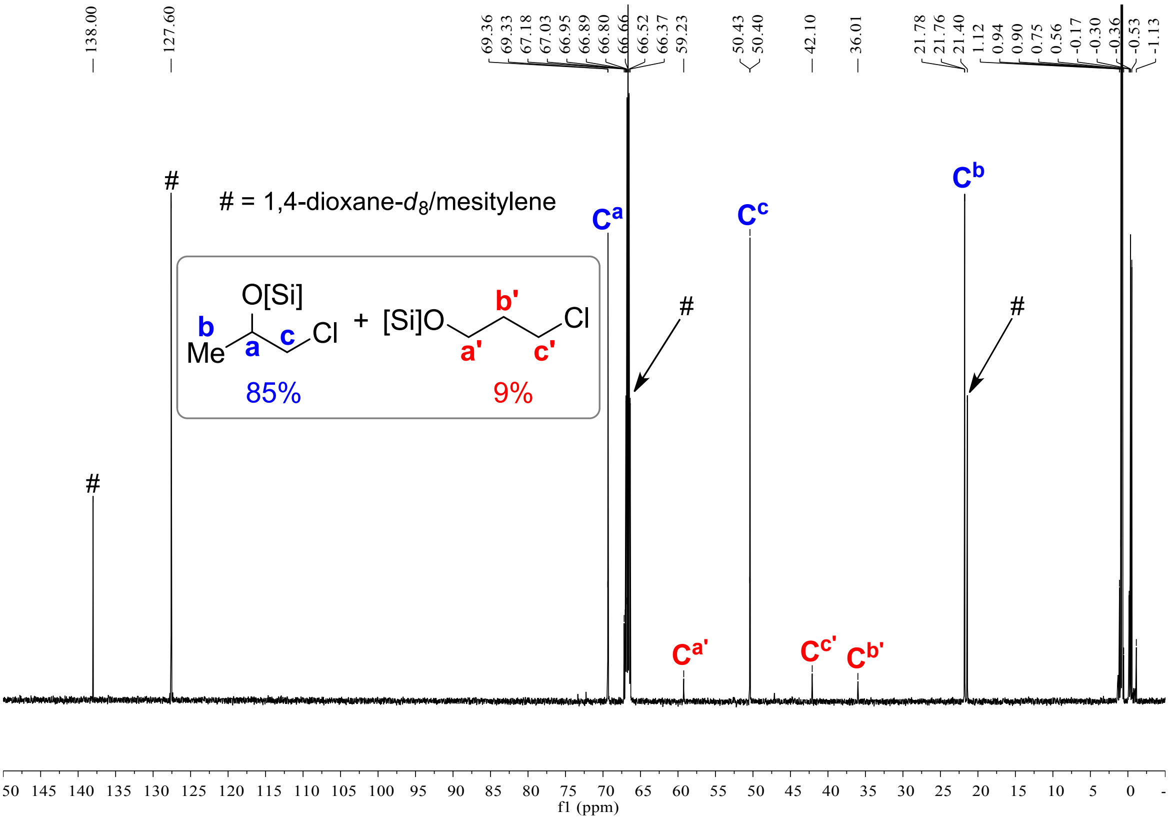


1-Chloro-2-propyl silyl ether and 3-chloropropyl silyl ether (**Scheme 5**)

Crude yield: 94% (9:1), internal standard: mesitylene;

^{1}H NMR (600 MHz, 1,4-dioxane-d_8) & **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8);

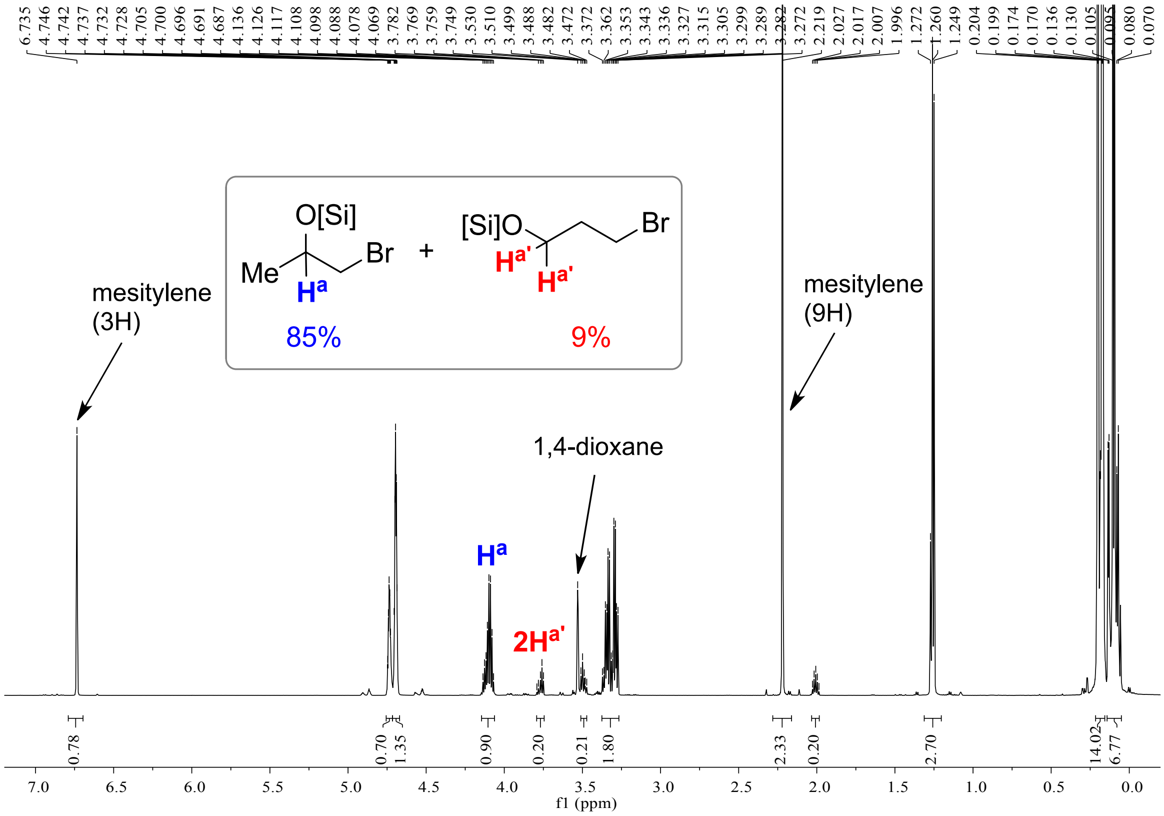


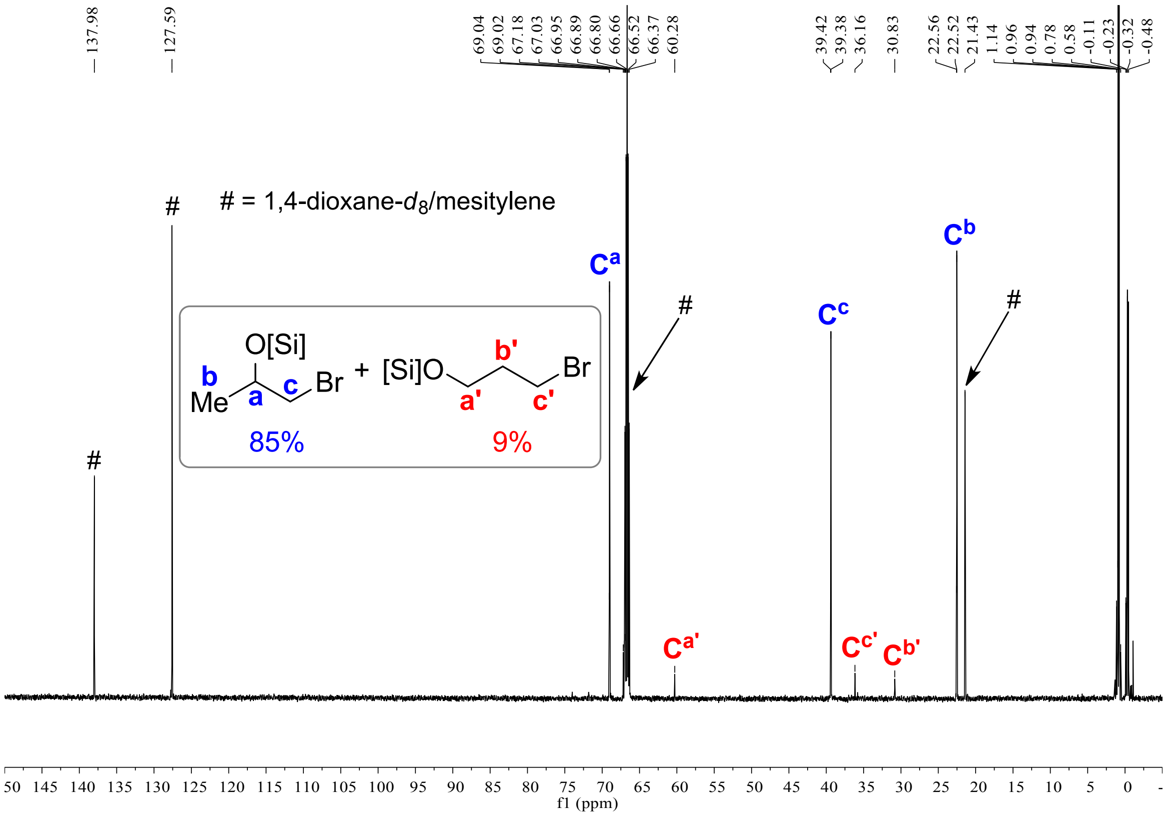


1-Bromo-2-propyl silyl ether and 3-bromopropyl silyl ether (**Scheme 5**)

Crude yield: 94% (9:1), internal standard: mesitylene;

^{1}H NMR (600 MHz, 1,4-dioxane-d_8) & **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8);

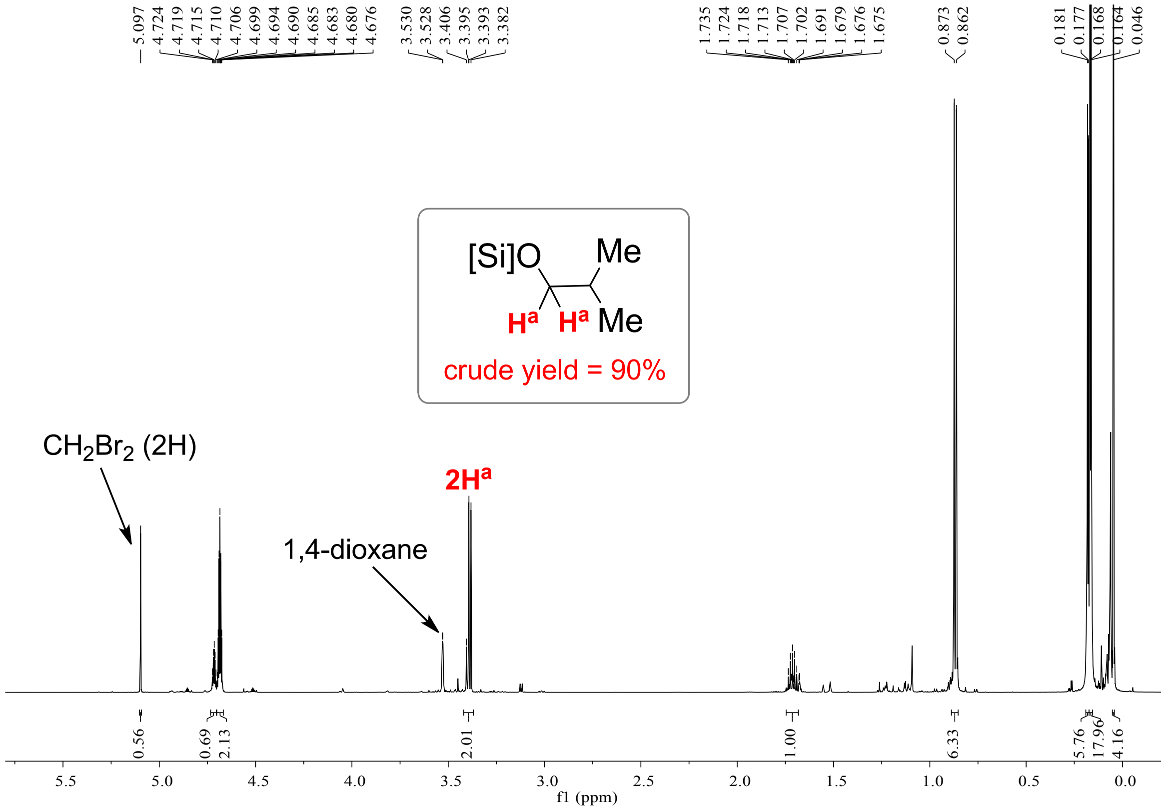


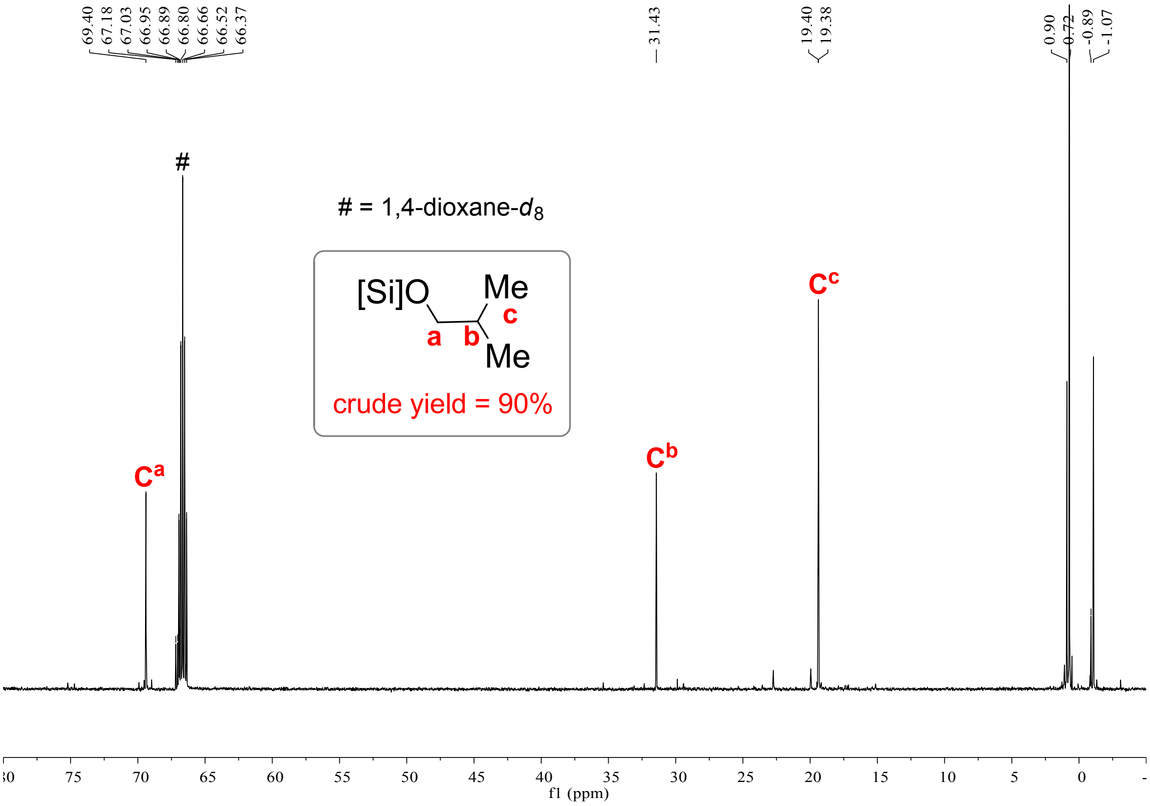


Isobutyl silyl ether (Scheme 5)

Crude yield: 90%, internal standard: CH_2Br_2;

^{1}H NMR (600 MHz, 1,4-dioxane-d_8) & **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8);

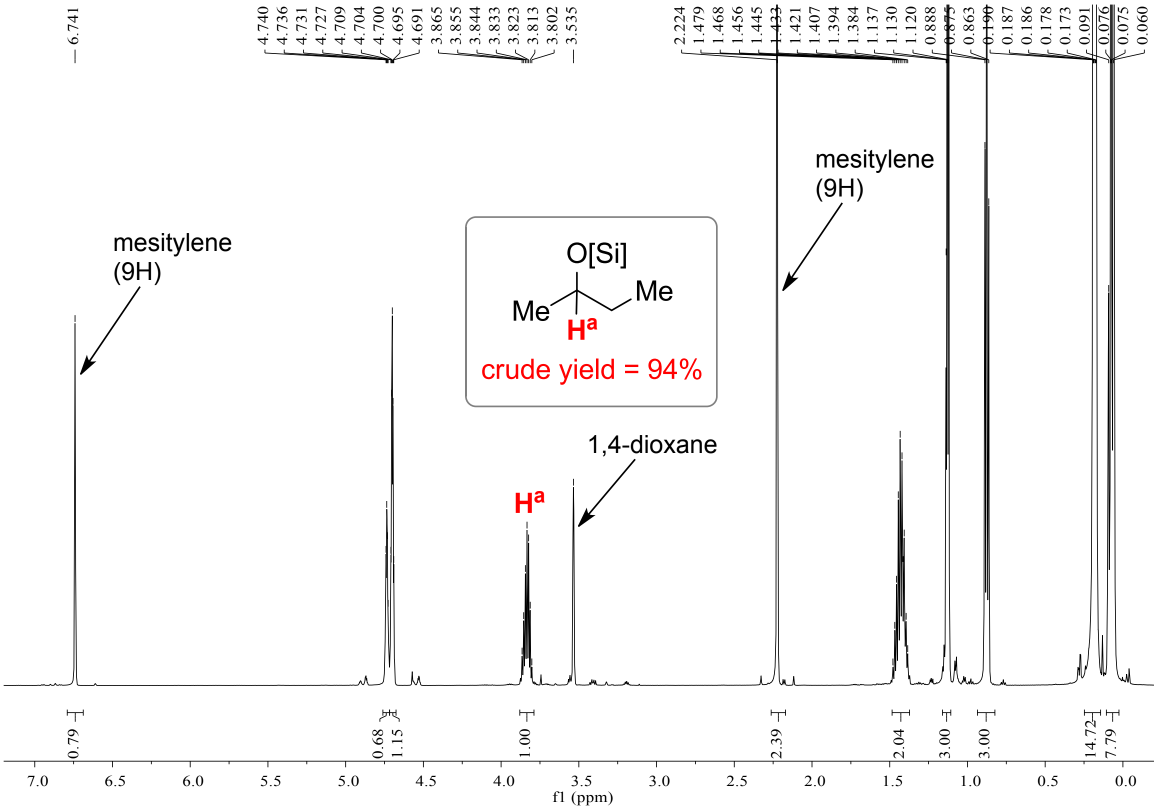


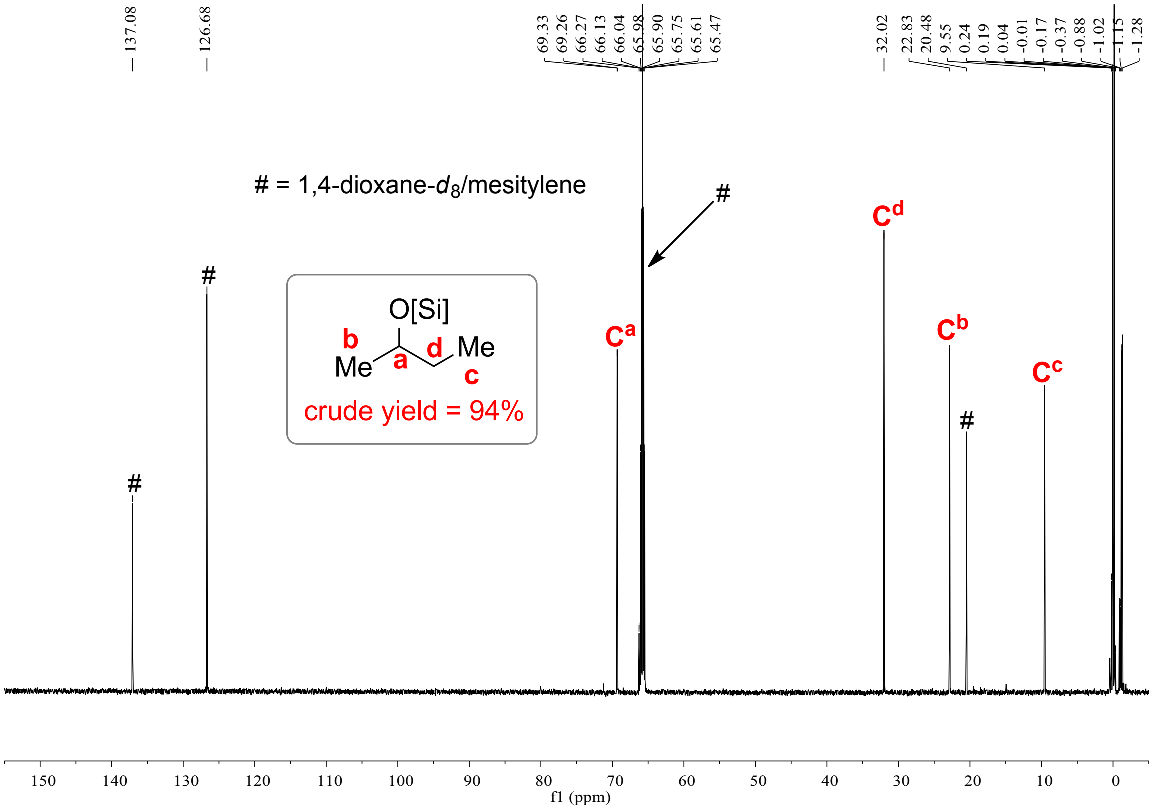


***sec*-Butyl silyl ether** (Scheme 5)

Crude yield: 94%, internal standard: mesitylene;

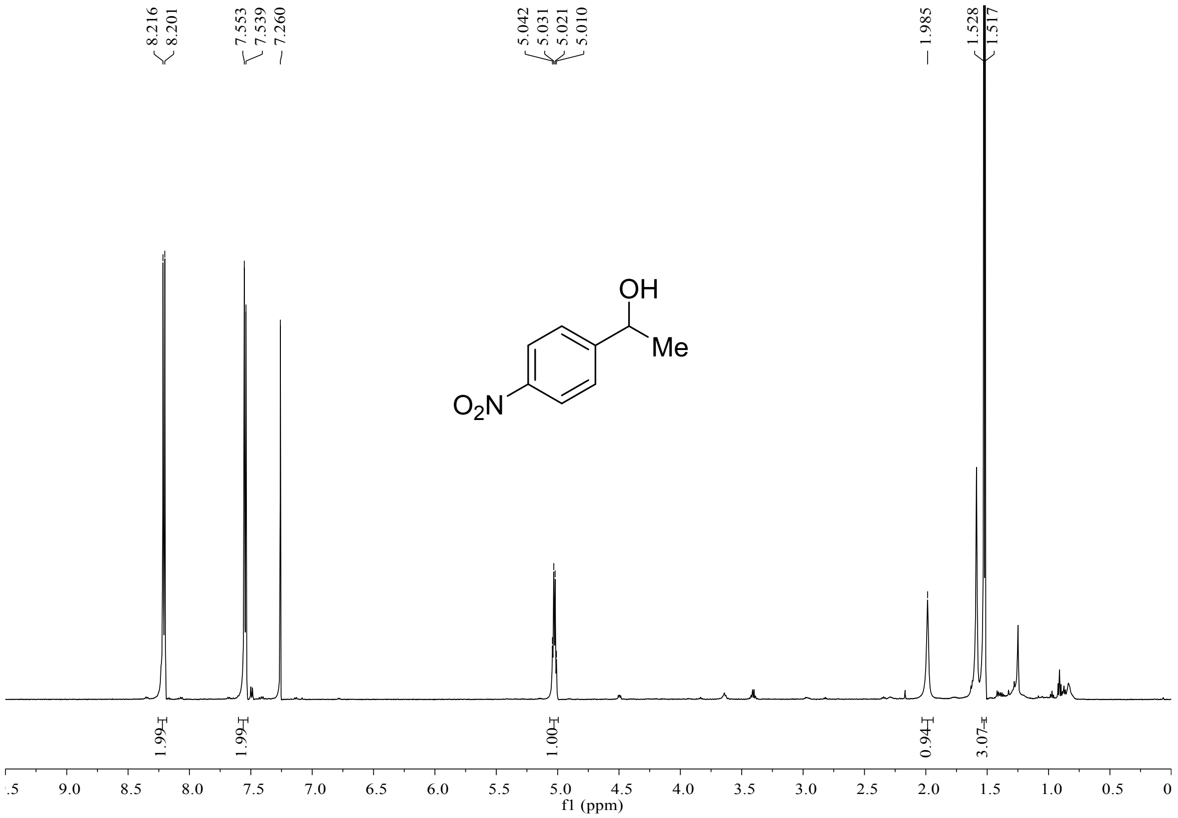
^{1}H NMR (600 MHz, 1,4-dioxane-d_8) & **^{13}C{^{1}H} NMR** (151 MHz, 1,4-dioxane-d_8);

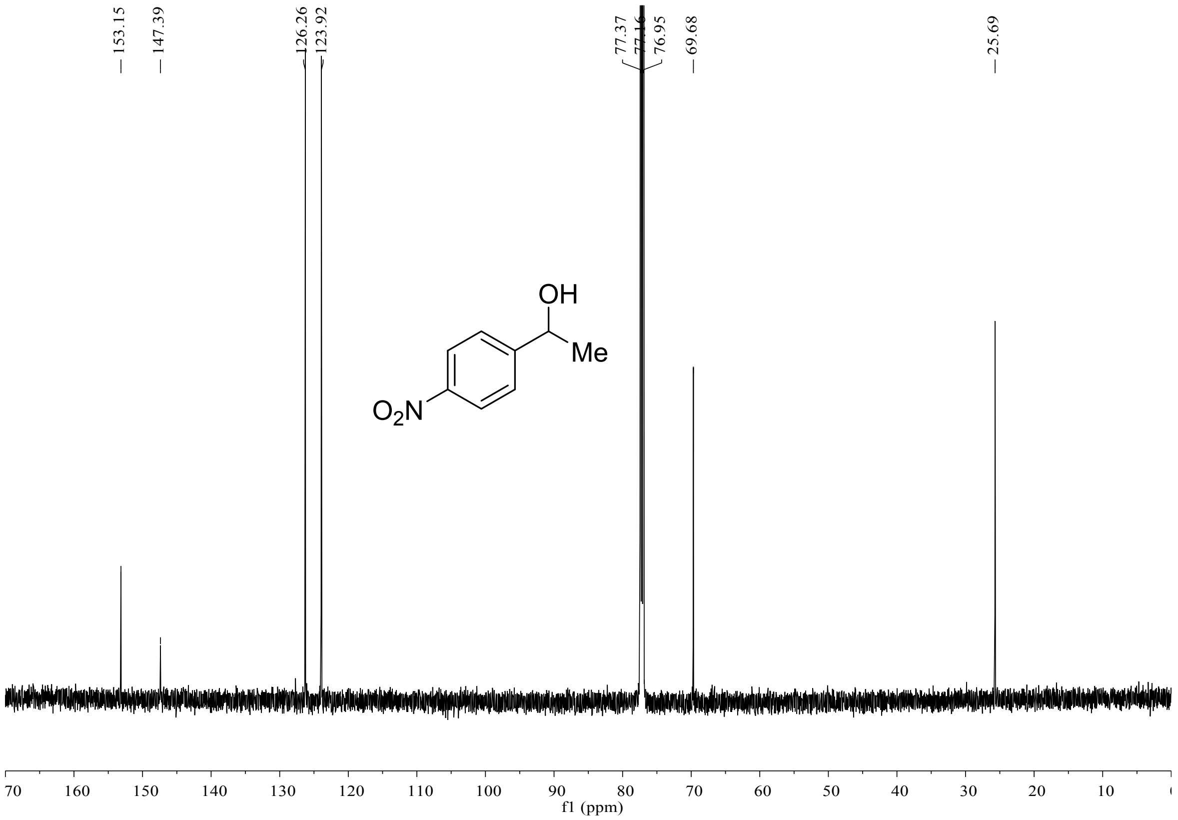




1-(4-Nitrophenyl)ethanol (Scheme 5)

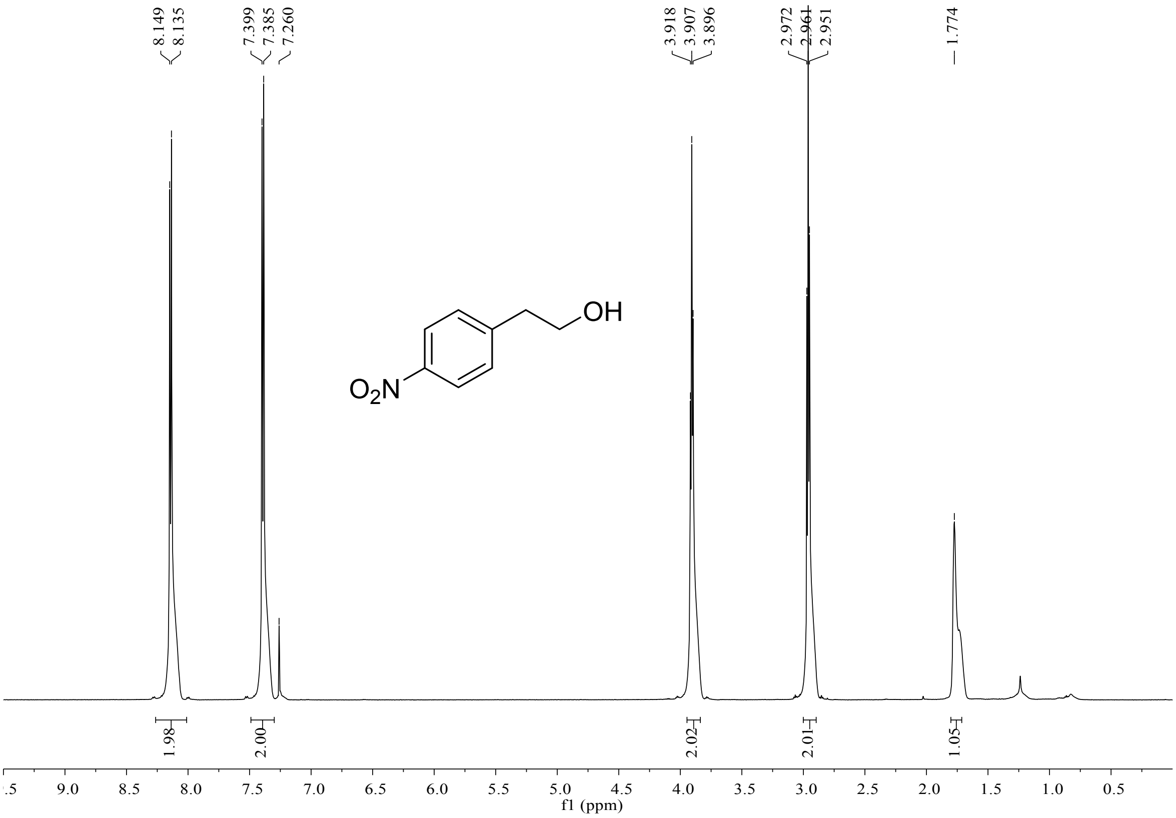
^{1}H NMR (600 MHz, CDCl$_3$) & **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$);

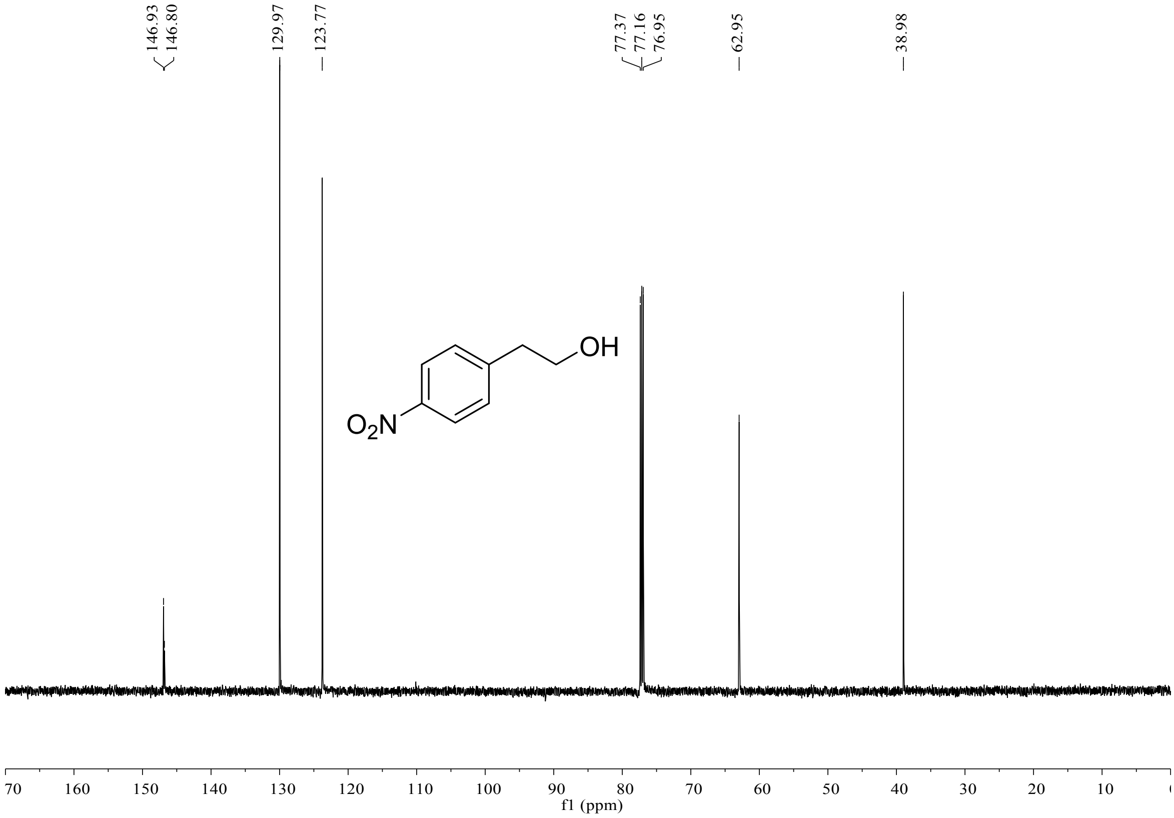




2-(4-Nitrophenyl)ethanol (Scheme 5)

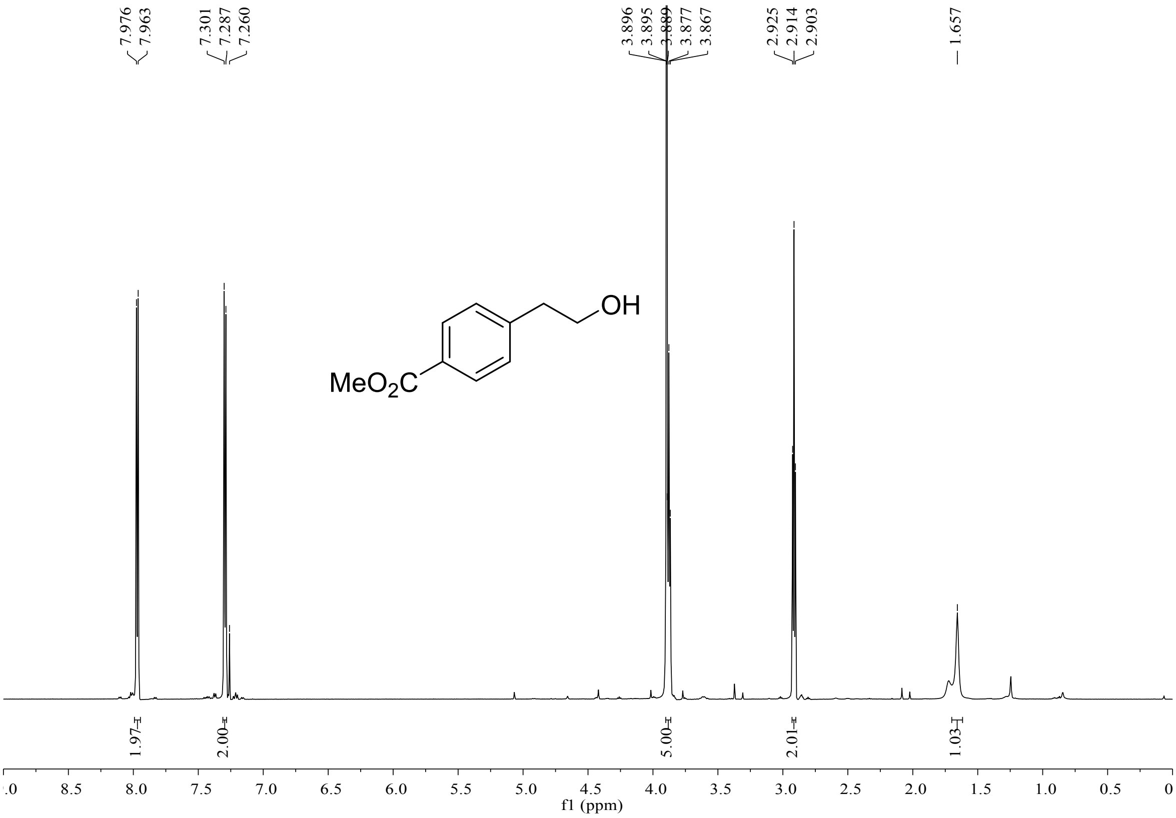
^{1}H NMR (600 MHz, $CDCl_3$) & **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$);

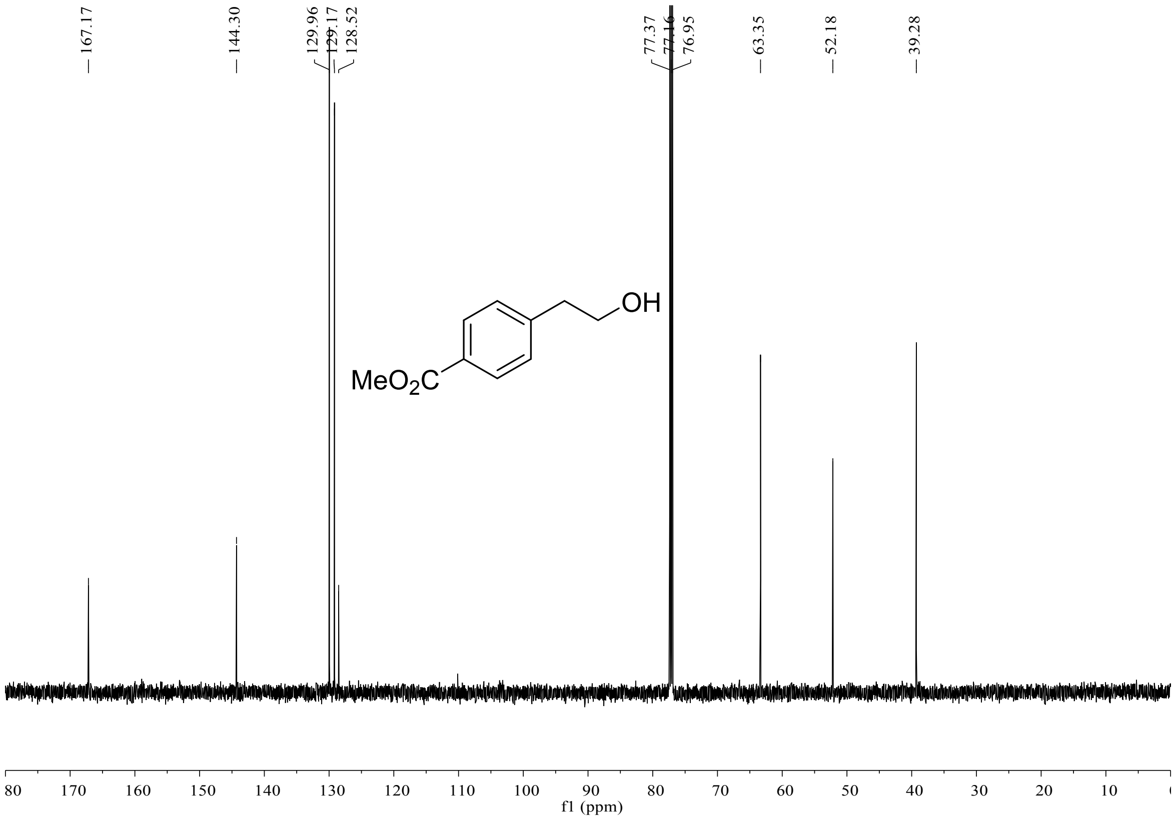




Methyl 4-(2-hydroxyethyl)benzoate (**Scheme 5**)

^{1}H NMR (600 MHz, $CDCl_3$) & **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$);

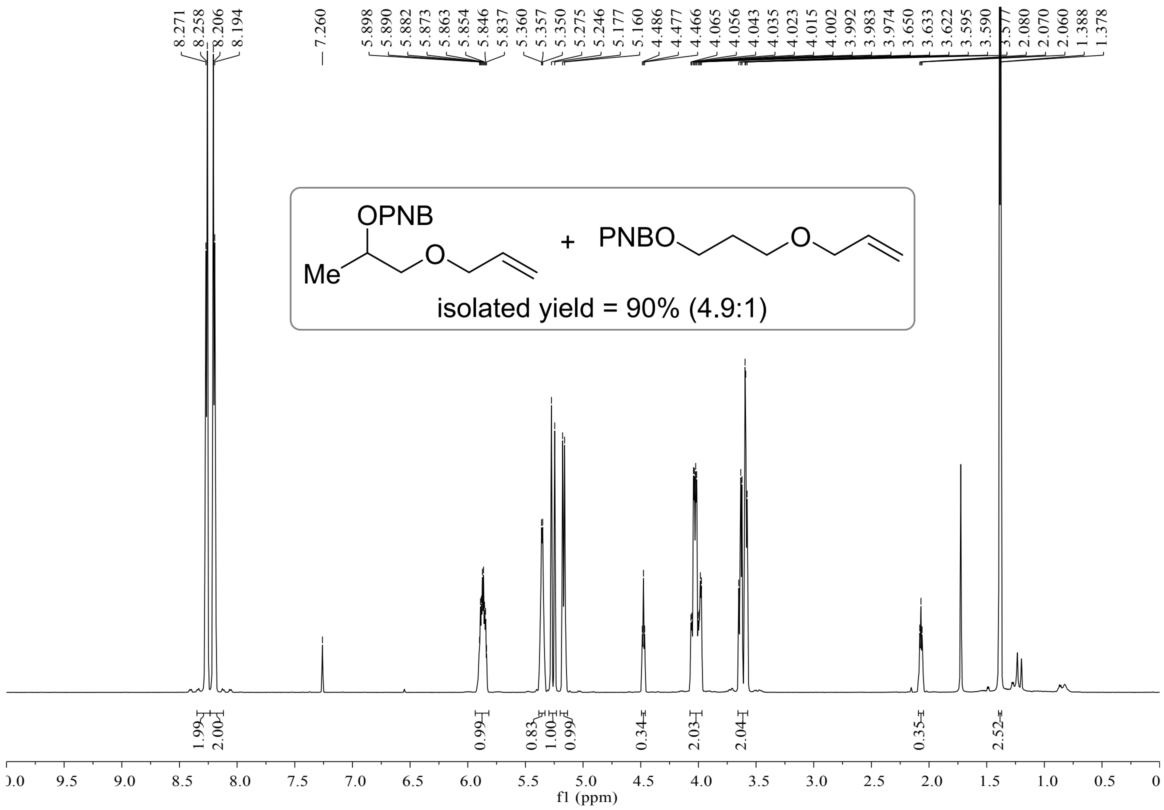


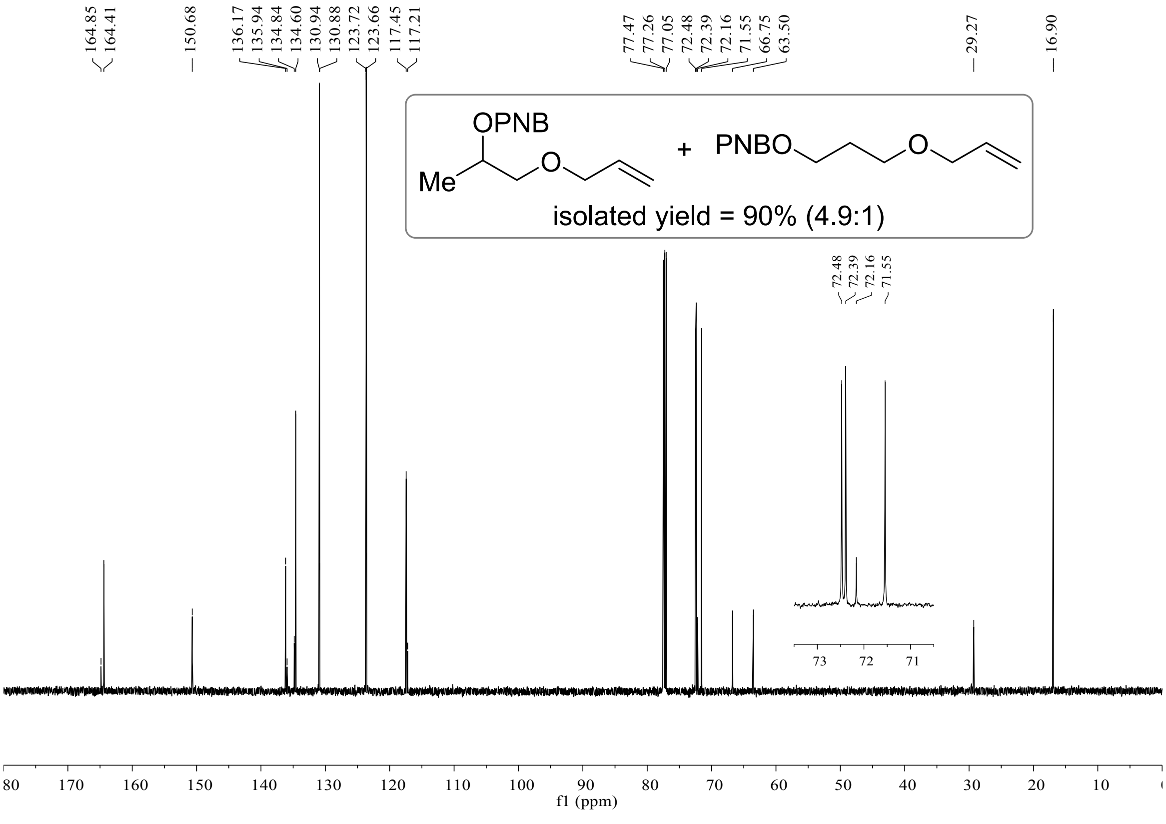


1-Allyloxypropan-2-yl 4-nitrobenzoate and 3-allyloxypropyl 4-nitrobenzoate (**Scheme 5**)

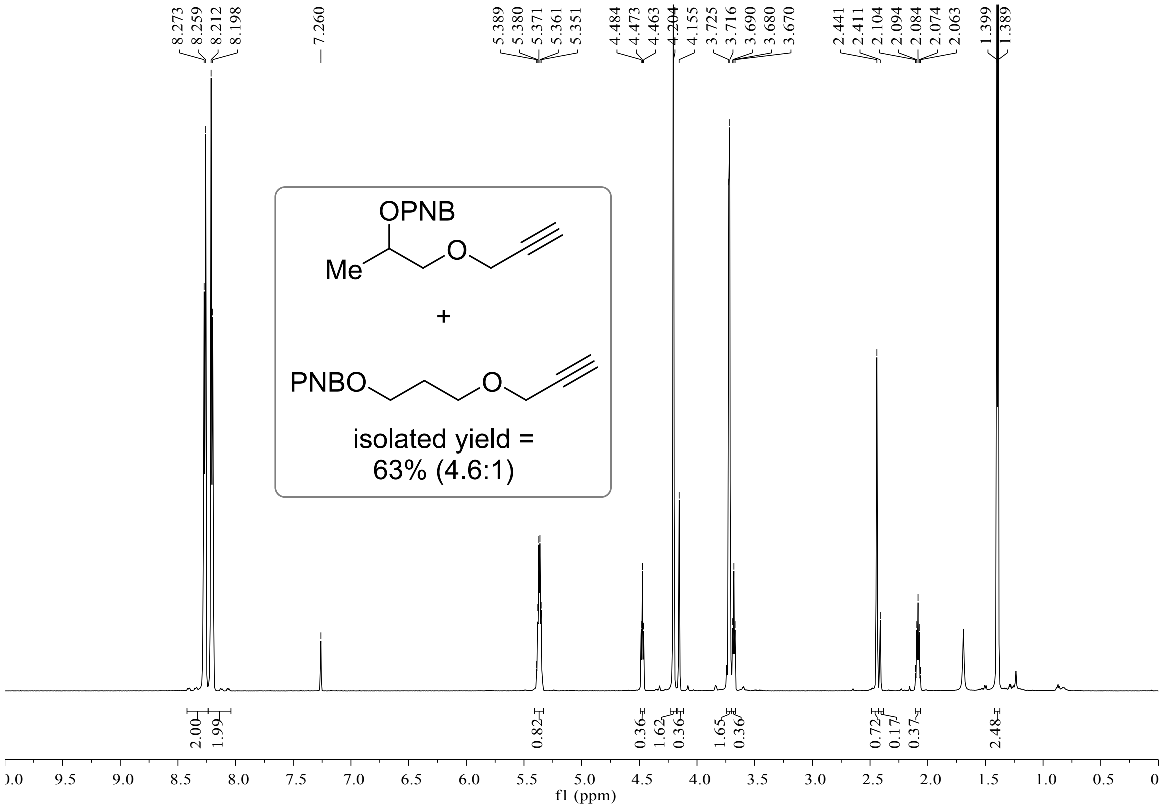
Crude yield: 95% (4:1), isolated yield: 90% (4.9:1);

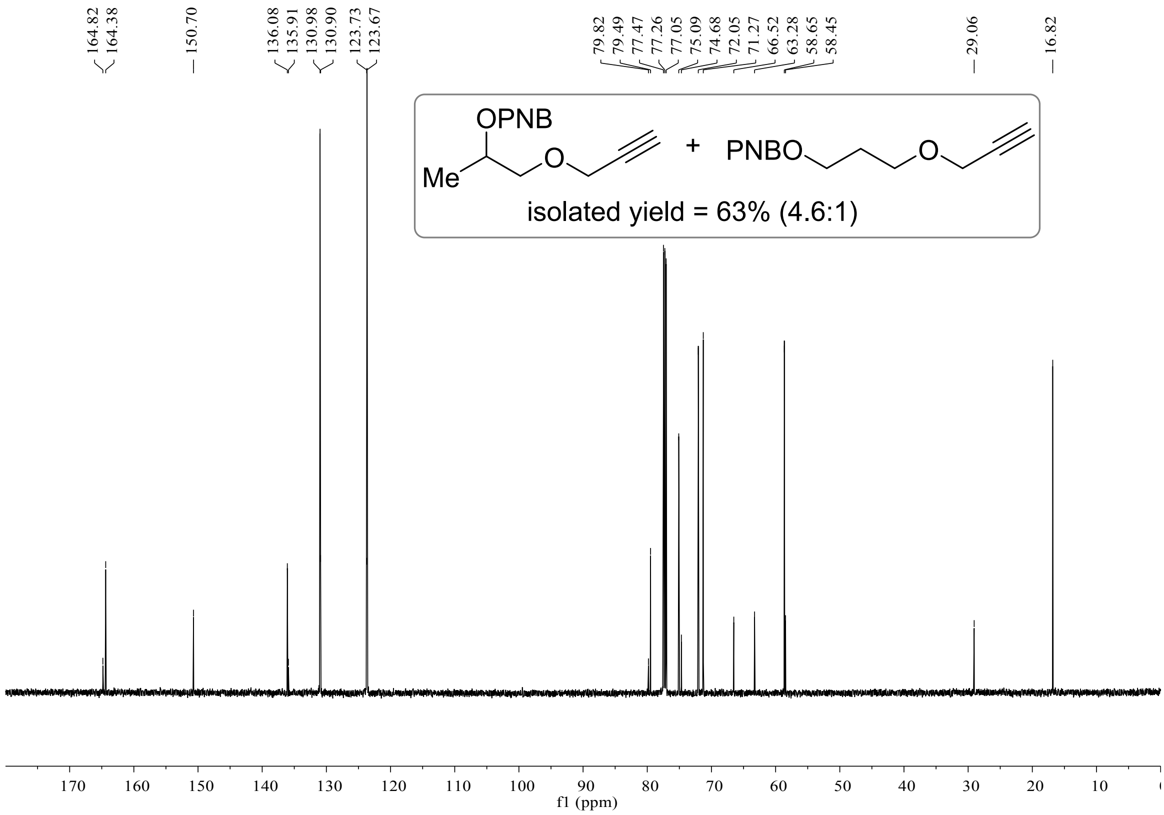
^{1}H NMR (600 MHz, $CDCl_3$) & **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$);





1-Propargyloxypropan-2-yl 4-nitrobenzoate and 3-propargyloxypropyl 4-nitrobenzoate (**Scheme 5**)
Crude yield: 99% (4:1), isolated yield: 63% (4.6:1);
^{1}H NMR (600 MHz, CDCl$_3$) & **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$);

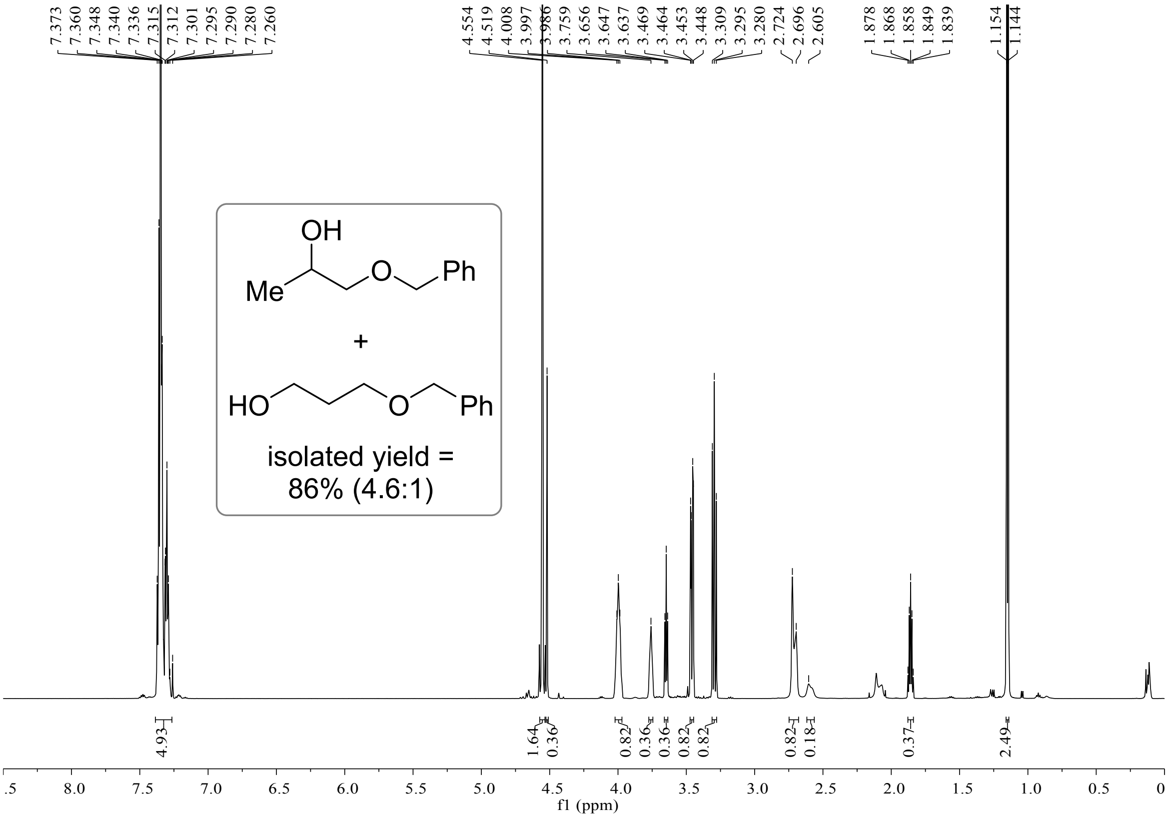


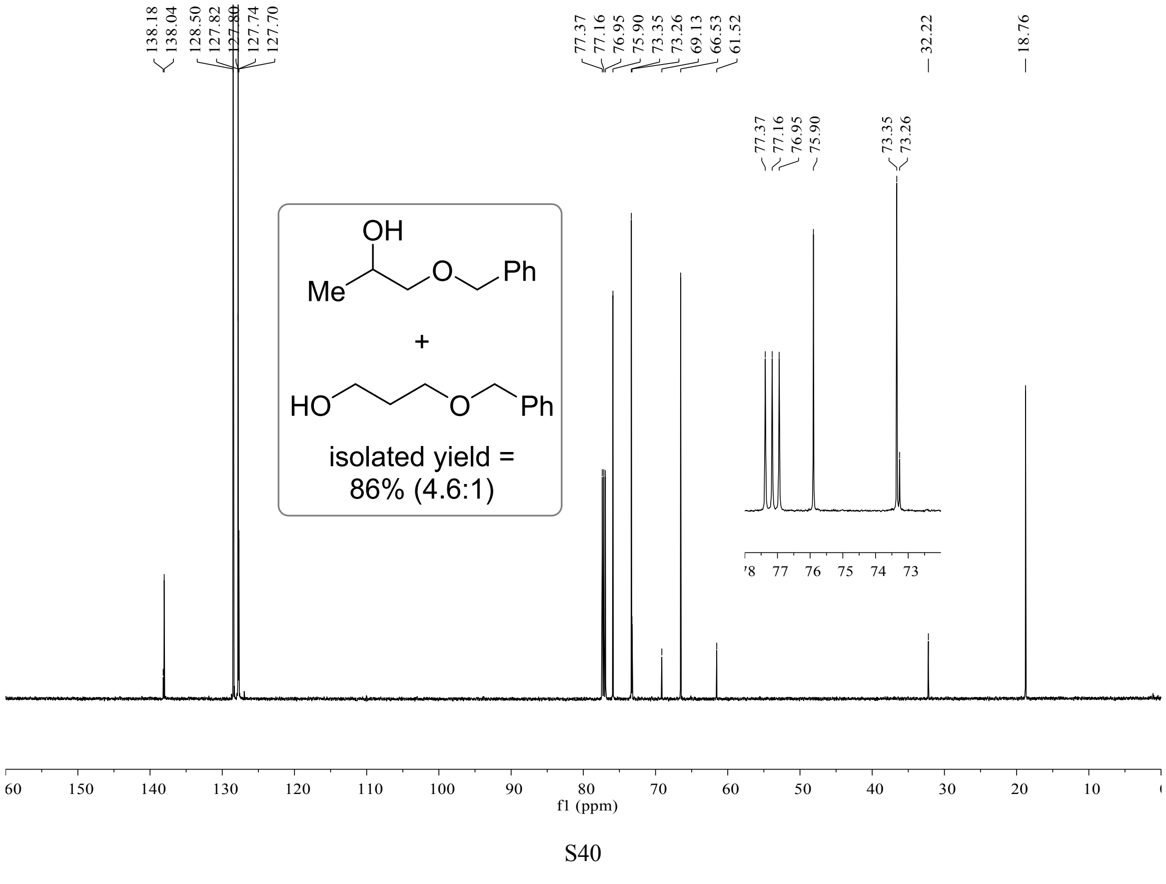


1-Benzyloxy-2-propanol and 3-benzyloxypropanol (**Scheme 5**)

Crude yield: 99% (4:1), isolated yield: 86% (4.6:1);

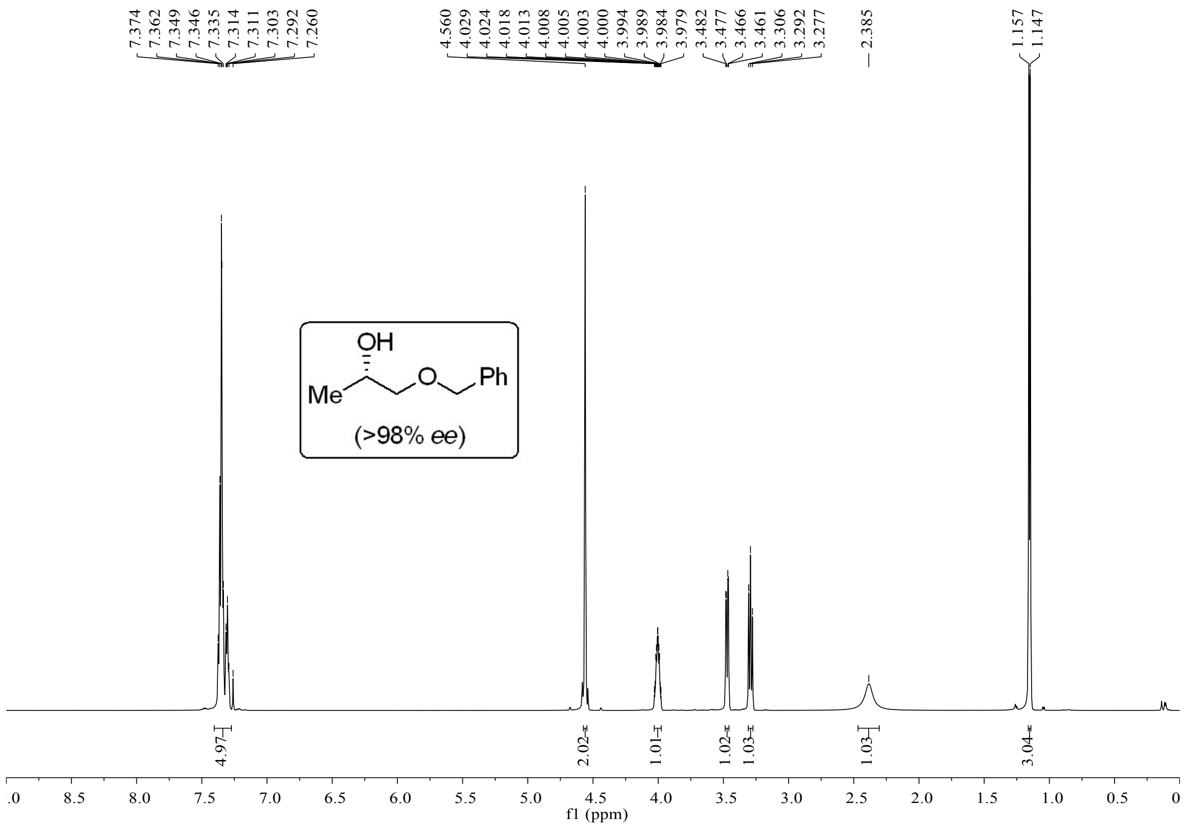
^{1}H NMR (600 MHz, CDCl$_3$) & **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$);

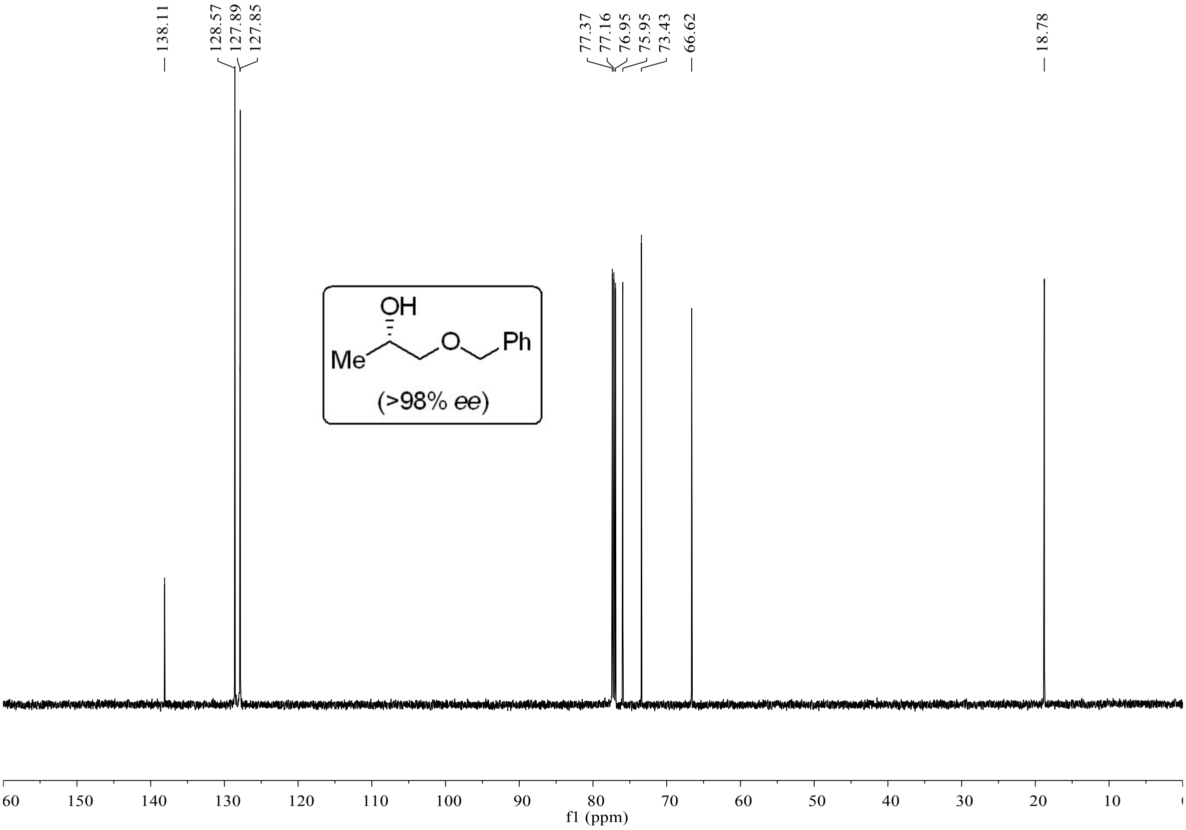




(*S*)-1-Benzyloxy-2-propanol (Scheme 5)

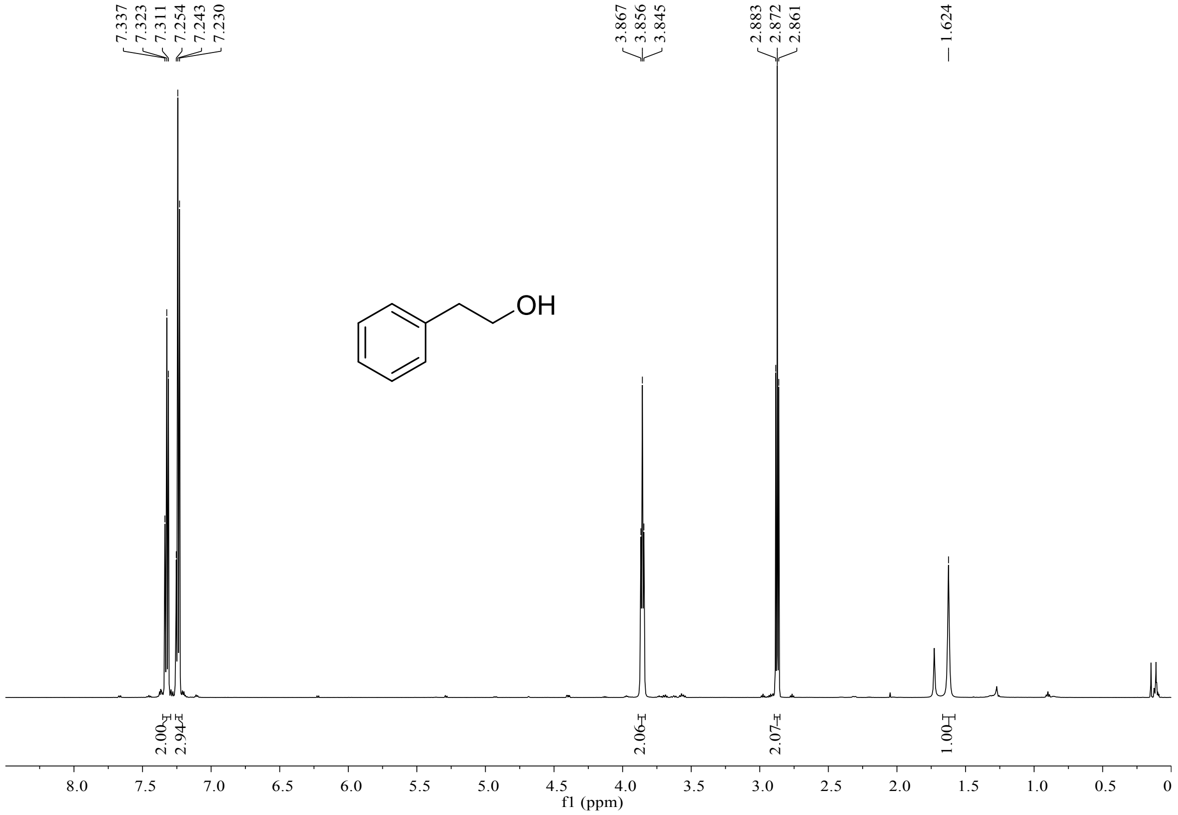
^{1}H NMR (600 MHz, CDCl$_3$) & **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$);

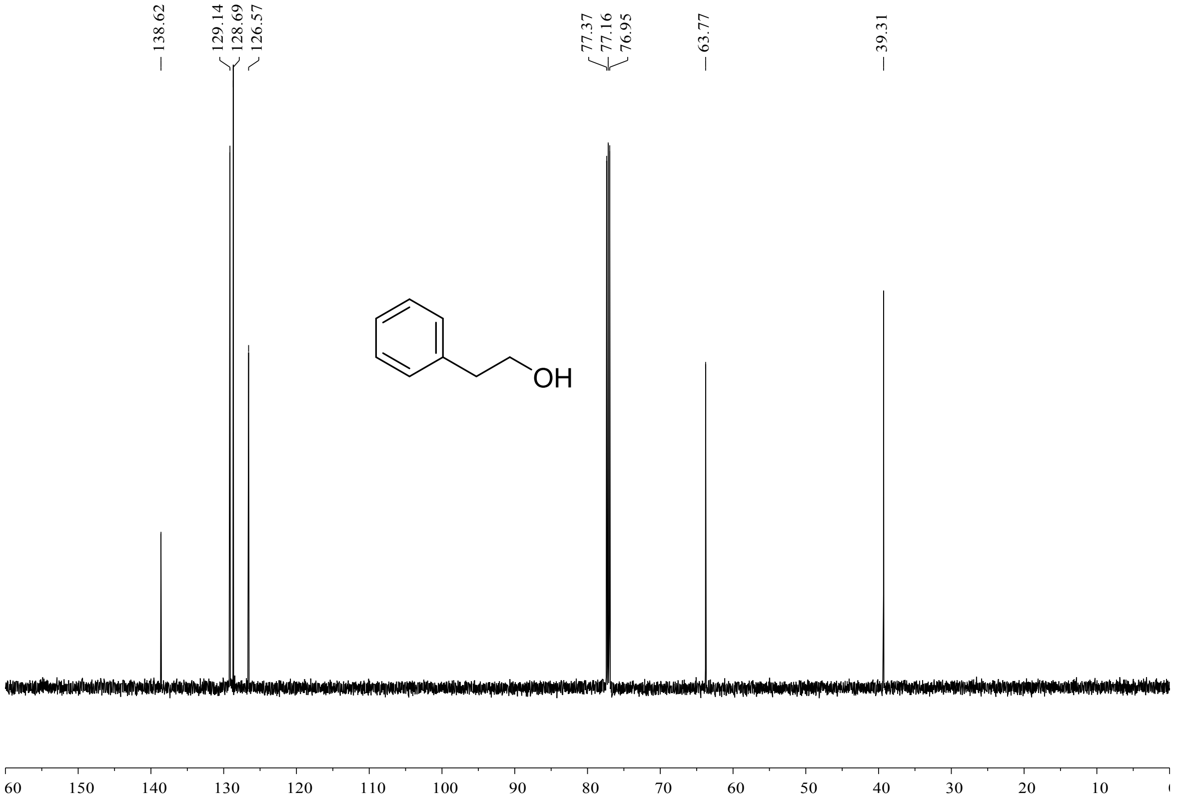




2-Phenylethanol (Scheme 5)

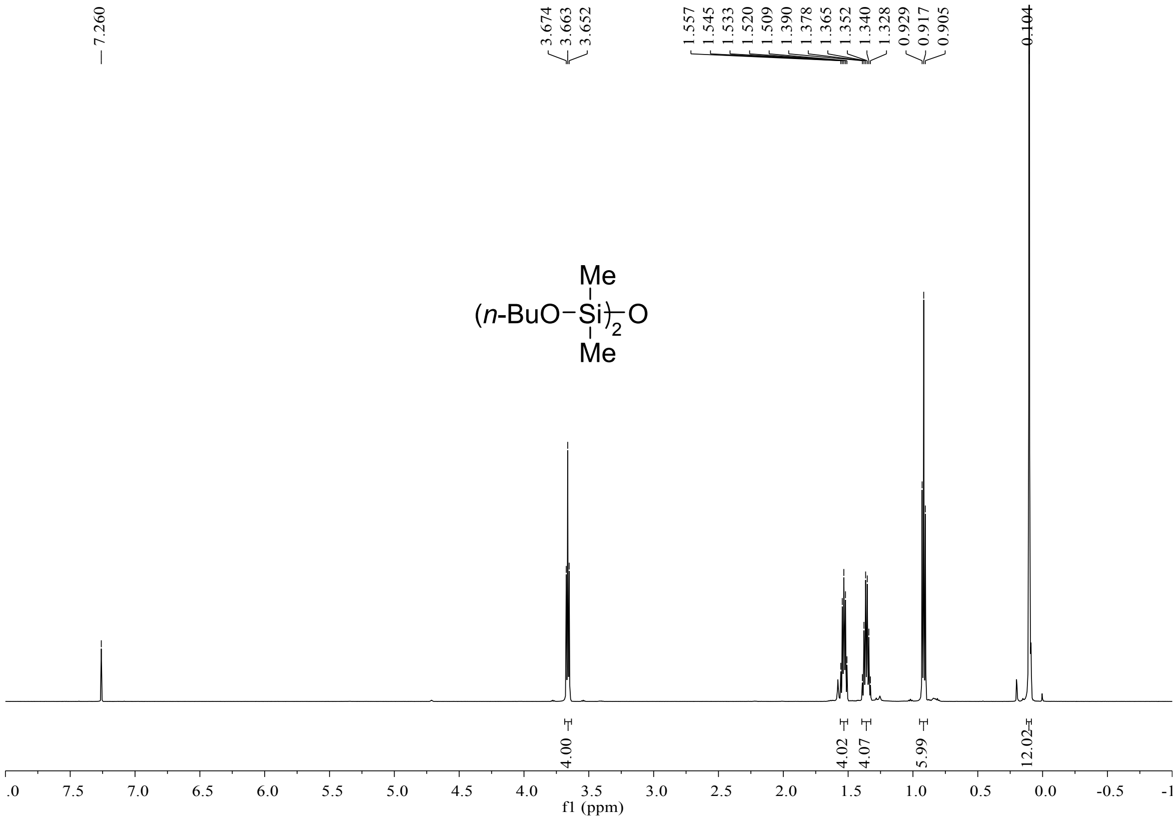
^{1}H NMR (600 MHz, $CDCl_3$) & **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$);

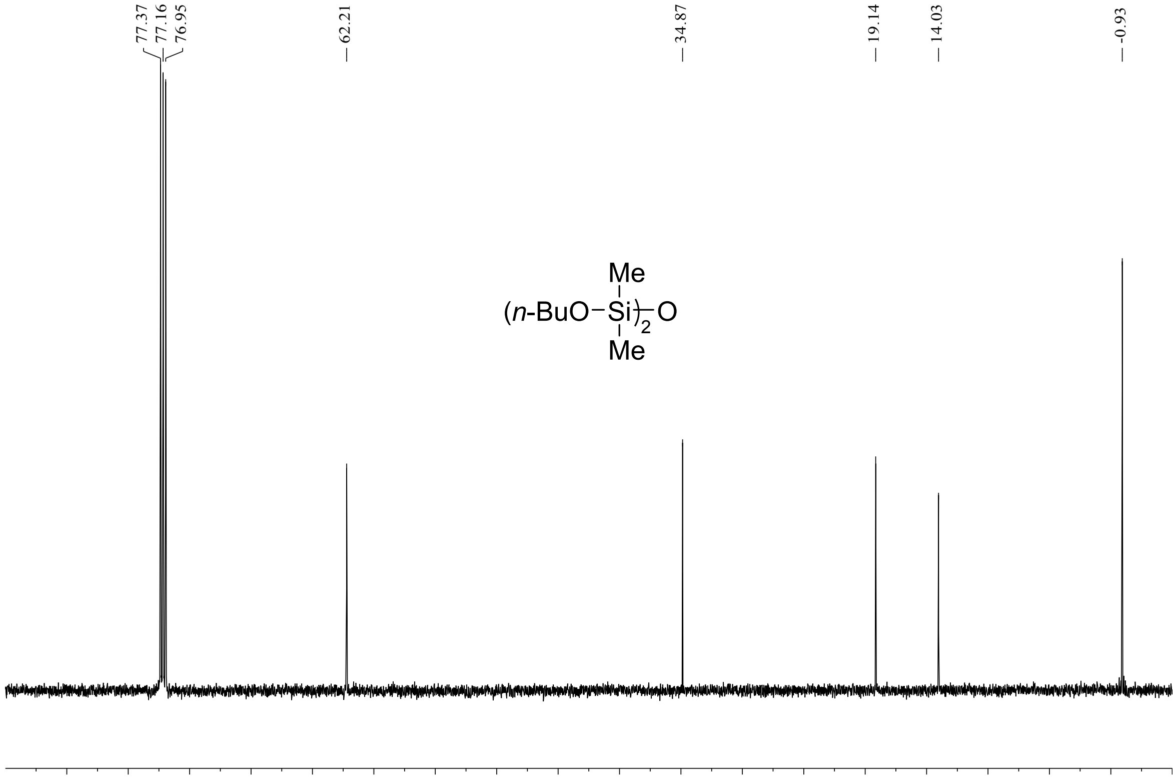




1,3-Dibutoxy-1,1,3,3-tetramethyldisiloxane (Scheme 5)

^{1}H NMR (600 MHz, CDCl$_3$) & **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$);





1-Deoxyerythritol (**Scheme 5**)

^{1}H NMR (600 MHz, D_2O) & **$^{13}C\{^1H\}$ NMR** (151 MHz, D_2O);