Hydrosilylation of Epoxides with a Cationic η^1-Silane Iridium(III) Complex

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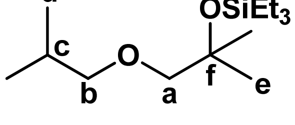
Supporting Information

General considerations. All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Argon and nitrogen were purified by passing through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. THF was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. Pentane, methylene chloride and toluene were passed through columns of activated alumina[1] and degassed by either freeze-pump-thaw methods or by purging with argon. Benzene and acetone was dried with 4 Å molecular sieves and degassed by freeze-pump-thaw methods. Et_3SiH was dried with $LiAlH_4$ or 4 Å molecular sieves and vacuum transferred into a sealed flask. Et_3SiD (97 atom % D) was purchased from Sigma-Aldrich and used without purification for the hydrosilylation reactions. All of the other substrates purchased from Sigma-Aldrich were dried with either K_2CO_3 or 4 Å molecular sieves. CD_2Cl_2 for NMR was dried with CaH_2 or 4 Å molecular sieves and vacuum transferred into a sealed flask. NMR spectra were recorded on Bruker spectrometers (DRX-400, AVANCE-400, AMX-300 and DRX-500). ^1H and ^{13}C NMR spectra were referenced to residual protio solvent peaks. $Ph_3C[B(C_6F_5)_4]$,[2] and (POCOP)Ir(H)$_2$, **3**[3] were prepared according to published procedures.

General Procedure for the Hydrosilylation of Substrates with Et_3SiH in CD_2Cl_2. Et_3SiH (1.5 or 3.0 mmol, 1.5 equiv.) was added to a solution of **1** (6.6 mg, 0.005 mmol) in CD_2Cl_2 (0.3 mL) in a 25-ml Schlenk tube and the contents were well shaken. The solution of substrate (1.0 or 2.0 mmol, 1 equiv.) in CH_2Cl_2 was added to the solution containing **1** and the silane via syringe pump over 2 h at 22 °C. After the complete addition of the substrate, the reaction mixture was allowed to be stirred for further 1 to 2.5 h. Finally, the reaction mixture was subject to NMR spectroscopy. Conversions are quantitative and no starting material remains at the end of the reaction. Some of the desired products are isolated by column chromatography on silica gel using hexane-ethyl acetate (10:1, v/v) as eluent. A small amount of silyl ether is lost on the column, probably due to Si-O bond hydrolysis.

Hydrosilylation of styrene oxide by 1 (Table 1, entry 1). ^1H NMR (C_6D_6): δ 7.27-7.14 (m, 5H); 3.78 (t, J = 7.2 Hz, 2H); 2.83 (t, 2 H, 7.2 Hz); 1.10 (m, 9H, $-OSiEt_3$); 0.68 (m, 6H, $-OSiEt_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.3, 129.2, 128.2, 126.1, 64.1, 39.9, 6.8, 4.6.

Hydrosilylation of 1,2-epoxy-2-methyl propane by 1 (entry 2). ^1H NMR ($CDCl_3$): δ 3.36 (d, J = 6.5 Hz, 2H); 1.75 (d, J = 8.5 Hz, 1 H); 0.88 (d, J = 8.5 Hz, 6H); 1.05 (m, 9H, $-OSiEt_3$); 0.61 (m, 6H, $-OSiEt_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 69.1, 31.0, 18.9, 6.5, 4.4.



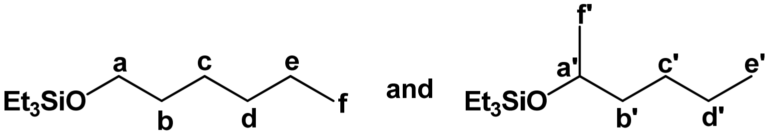
Dimeric isomer as a side product in the reaction in entry 2. ^1H NMR ($CDCl_3$): δ 3.45 (s, 2H^a); 3.17 (d, J = 7 Hz, 2H^b); 1.75 (m, 1H^c); 1.16 (s, 6H); 0.98 (m, 9H, $-OSiEt_3$); 0.90 (d, J = 6.5

Hz, $6H^{d}$); 0.62 (m, 6H, $-OSiEt_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 75.1 (C^{f}), 69.7 (C^{a}), 68.7 (C^{b}), 29.1 (C^{c}), 22.5 (C^{e}), 19.6 (C^{d}), 6.8 ($-OSiEt_3$), 4.4 ($-OSiEt_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 18.5.

Hydrosilylation of 2-methyl-2,3-epoxy butane by 1 (entry 3). ^1H NMR (CD_2Cl_2): δ 3.62 (m, 1H); 1.64 (m, 1H); 1.11 (d, J = 6 Hz, 3H); 1.00 (m, 9H, $-OSiEt_3$); 0.91 (m, 6H), 0.63 (m, 6H, $-OSiEt_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 72.9, 35.4, 20.0, 17.9, 17.7, 6.7, 4.9.

Hydrosilylation of 2,3-dimethyl-2,3-epoxy butane by 1 (entry 4). ^1H NMR (C_6D_6): δ 3.50 (q, J = 6.0 Hz, 1H); 1.11 (m, 12H, overlapped with Et_3SiH); 0.91 (s, 9H); 0.71 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 76.0, 35.4, 25.7, 18.5, 7.0, 5.3.

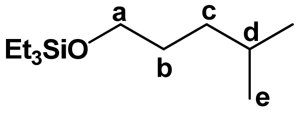
Hydrosilylation of trans-stilbene oxide by 1 (entry 5). ^1H NMR (CD_2Cl_2): δ 7.43-7.32 (m, 10H); 4.34-4.31 (m, 3H, $Et_3SiOC\mathit{H}_2C\mathit{H}Ph_2$); 3.12 (trace, s, 4H, $PhC\mathit{H}_2C\mathit{H}_2Ph$), 1.15-1.05 (m, 9H, $-OSiEt_3$); 0.74-0.71 (m, 6H, $-OSiEt_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 142.8, 128.5, 128.4, 126.4, 66.4 ($-O\mathit{C}H_2CHPh_2$), 54.0 ($-OCH_2\mathit{C}HPh_2$), 38.3 (trace), 6.7, 4.4. $^{29}Si\{^1H\}$ NMR (CD_2Cl_2): δ 19.2, 9.1 (minor, $Et_3SiOSiEt_3$).



Hydrosilylation of 1,2-epoxy hexane by 1 (entry 6). ^1H NMR ($CDCl_3$): δ 3.80 (m, J = 6.0 Hz, $1H^{a'}$); 3.62 (t, J = 6.5 Hz, $2H^{a}$); 1.56-1.32 (m, $14H^{b\text{-}e,b'\text{-}d'}$); 1.16 (d, J = 6 Hz, $3H^{f'}$); 0.99 (m, 18H, $-OSiEt_3$); 0.91 (m, $6H^{f,e'}$); 0.61 (m, 12H, $-OSiEt_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 68.5 ($C^{a'}$), 63.0 (C^{a}), 39.5 ($C^{b'}$), 32.9 (C^{b}), 31.7 (C^{d}), 28.1 ($C^{d'}$), 25.5 (C^{c}), 23.9 ($C^{c'}$), 22.8 (C^{e}), 22.7 ($C^{f'}$), 14.14 ($C^{e'}$), 14.07 (C^{f}), 6.9 ($-OSiEt_3$), 6.8 ($-OSiEt_3$), 4.9 ($-OSiEt_3$), 4.4 ($-OSiEt_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 15.2, 17.2.

Hydrosilylation of methyl-1,2-cyclopentene oxide by 1 (entry 7). ^{1}H NMR ($CDCl_3$): δ 4.06 (m, 0.41H); 3.64 (m, 0.59H); 1.98-1.30 (m, 7H); 1.18-1.07 (m, 12H, overlapped with Et_3SiH); 0.70 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 80.6, 76.2, 42.7, 40.1, 35.2, 34.6, 31.2, 30.9, 22.0, 21.4, 18.2, 14.2, 6.9, 5.1.

Hydrosilylation of tetrahydrofuran by 1 (entry 8). ^{1}H NMR (C_6D_5Cl): δ 3.80 (t, J = 6.0 Hz, 2H); 1.71 (m, 2H); 1.60 (m, 2H); 1.11 (t, *J* = 7.2 Hz, 3H), 1.20 (m, 9H, overlapped with Et_3SiH); 0.80 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 62.5, 35.4, 19.3, 13.9, 6.9, 4.7.



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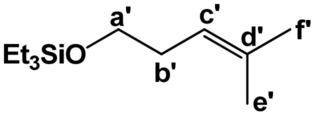
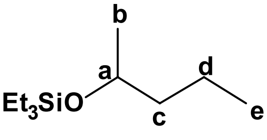
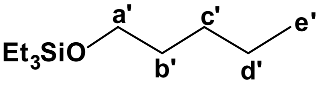


Hydrosilylation of 2,2-dimethyl tetrahydrofuran by 1 (entry 9). ^{1}H NMR (C_6D_5Cl, characteristic signals): δ 5.36 (m, $1H^{c'}$); 3.78 (m, $2H^{a}$ and $2H^{a'}$); 2.43 (m, $2H^{b'}$); 1.86 (s, $3H^{f'}$); 1.77 (s, $3H^{e'}$); 1.72 (m, $2H^{b}$ and $2H^{c}$). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 132.7 and 121.2 ($C^{e'}$ and $C^{f'}$), 63.1 (C^{a}), 62.8 ($C^{a'}$), 35.3 (C^{b}), 32.3 ($C^{b'}$), 31.1 (C^{c}), 28.0 (C^{d}), 25.6 ($C^{f'}$), 17.6 ($C^{e'}$), 22.6 (C^{e}), 6.8 ($-OSiEt_3$), 4.7 ($-OSiEt_3$).



and



Hydrosilylation of 2-methyl tetrahydrofuran by 1 (entry 10). ^{1}H NMR (C_6D_5Cl): δ 4.00 (m, $1H^{a}$); 3.82 (m, small, $2H^{a'}$); 1.75-1.47 (m, $2H^{c}$ and $2H^{d}$); 1.34 (d, *J* = 6 Hz, $3H^{b}$); 1.12 (t, *J* = 7.2 Hz, $3H^{e}$). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 68.3 (C^{a}), 62.9 (small, $C^{a'}$), 42.2 (C^{c}), 33.1 (small, $C^{b'}$), 24.0 (C^{d}), 21.0 (small, $C^{c'}$), 19.1 (C^{b}), 14.3 (C^{e}), 7.0 ($-OSiEt_3$), 5.3 ($-OSiEt_3$).

Hydrosilylation of 1,2-epoxy-2-methyl propane by 1 with $DSiEt_3$ (97 atom % D). ^{1}H NMR (C_6D_6): δ 3.37 (d, *J* = 6.8 Hz, 1H); 1.77 (m, 1 H); 0.95 (d, *J* = 8.5 Hz, 6H); 1.08 (m, 9H, overlapped with Et_3SiH); 0.68 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 69.0 (t), 31.0, 18.9, 6.6, 4.6.

Hydrosilylation of styrene oxide by 1 with $DSiEt_3$ (97 atom % D). ^1H NMR (CD_2Cl_2): δ 7.27-7.14 (m, 5H); 4.04 (t, *J* = 8.0 Hz, 1H); 3.06 (d, 2 H, 7.2 Hz); 1.25 (m, 9H, overlapped with Et_3SiH); 0.80 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 139.6, 129.1, 128.4, 126.2, 63.9 (t), 39.8, 6.8, 4.7.

Hydrosilylation of methyl-1,2-cyclopentene oxide by 1 with $DSiEt_3$ (97 atom % D). ^1H NMR (C_6D_6): δ 4.04, 3.97, 3.70, and 3.62 (m, 1H, small); 1.98-1.50 (m, 7H); 1.15-1.05 (m, 12H, overlapped with Et_3SiH); 0.70 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 80.6, 80.1 (t), 76.2, 75.7 (t), 42.7 (small), 42.6, 40.1 (small), 40.0, 35.2 (small), 35.1, 31.2, 30.9, 22.0, 21.4, 18.1, 14.2, 6.8, 5.1. ^2H NMR (C_6D_6): δ 3.82 (cis, 43%), 3.46 (trans, 57%).

Low temperature reaction of 1, Et_3SiH, and methyl-1,2-cyclopentene oxide, -60 ^oC to -20 ^oC. To the solution of **1** (10.1 mg, 0.0075 mmol) in CD_2Cl_2 in a medium-walled J. Young NMR tube was added 53 equiv. of Et_3SiH (64 μL, 0.4 mmol), and the solution was stirred at 22 ^oC for 10 min. The solution was cooled to -70 ^oC and 27 equiv. of methyl-1,2-cyclopentene oxide was added. After briefly shaking, the NMR tube was quickly placed in the NMR probe pre-cooled to -70 ^oC. The reaction was allowed to warm to -60 ^oC and monitored by NMR spectroscopy. After NMR experiments at -60 ^oC, the reaction temperature was carefully increased up to -20 ^oC over ca. 30 min. The hydrosilylation product, 2-methyl cyclopentyl triethyl silyl ether could be clearly observed by ^{13}C NMR spectroscopy at -20 ^oC (Figure S27).

References

1 (a) P. J. Alaimo, D. W. Peters, J. Arnold and R. G. Bergman, *J. Chem. Educ.,* 2001, **78**, 64. (b) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

2 V. J. Scott, R. Çelenligil-Çetin and O. V. Ozerov, *J. Am. Chem. Soc.*, 2005, **127**, 2852.

3. I. Goettker-Schnetmann, P. White and M. Brookhart, *Organometallics*, 2004, **23**, 1766.

^{1}H and ^{13}C{^{1}H} NMR Spectra of Silyl Ether Products

(* indicates solvent resonance.)

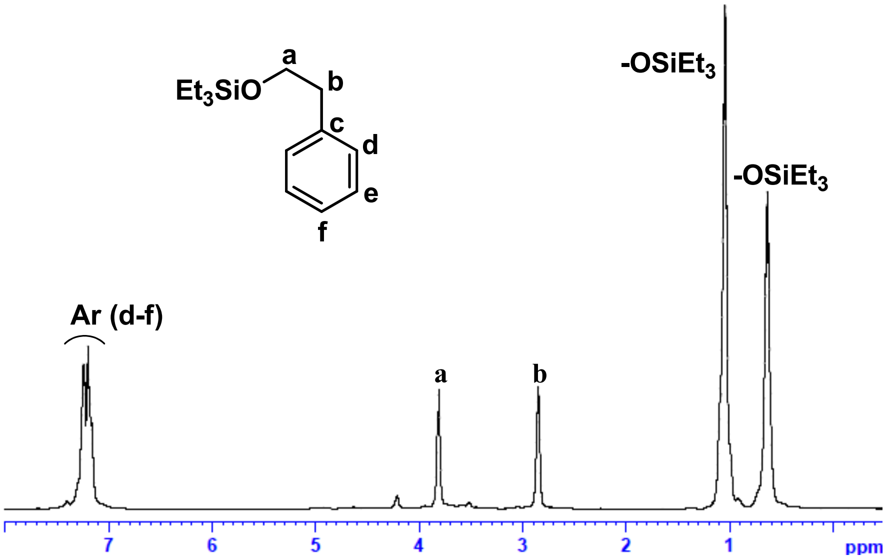


Figure S1. ^{1}H NMR spectrum of the reaction mixture after 1 h at r.t. (entry 1) (C_6D_6).

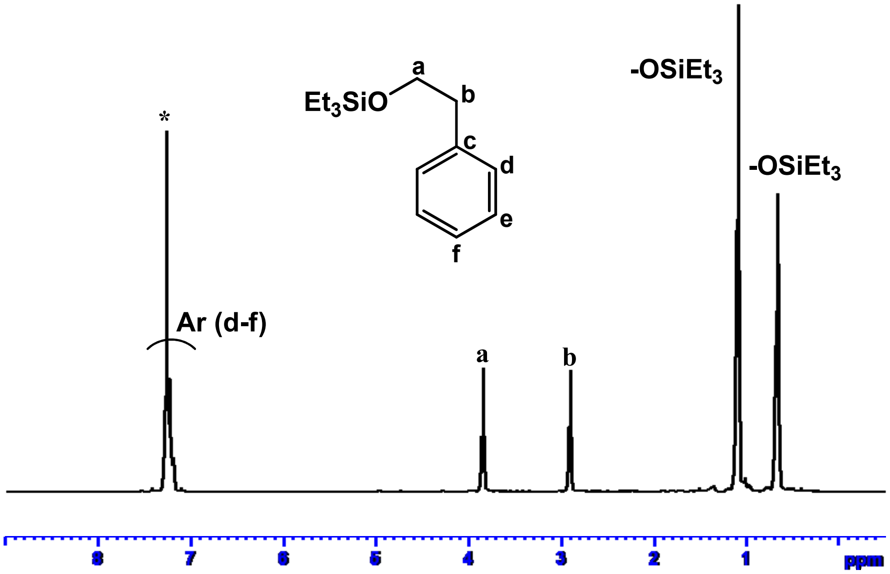


Figure S2. ^{1}H NMR spectrum of the isolated product (entry 1) (C_6D_6).

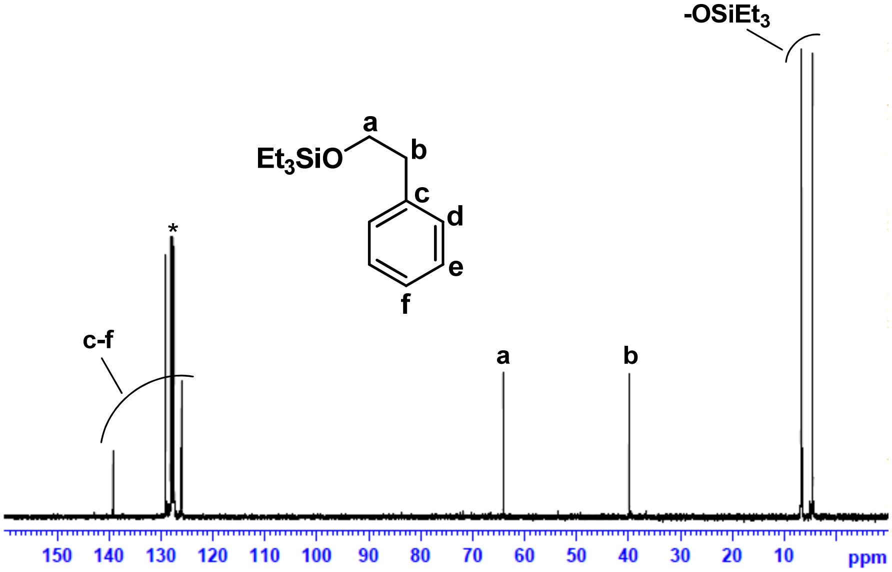


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture after 1 h at r.t. (entry 1) (C_6D_6).

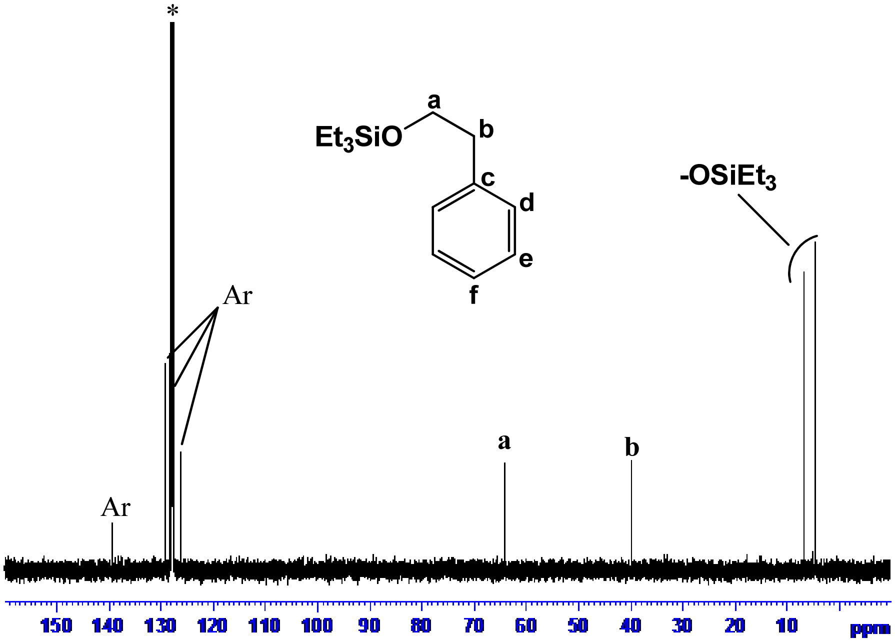


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of the isolated product (entry 1) (C_6D_6).

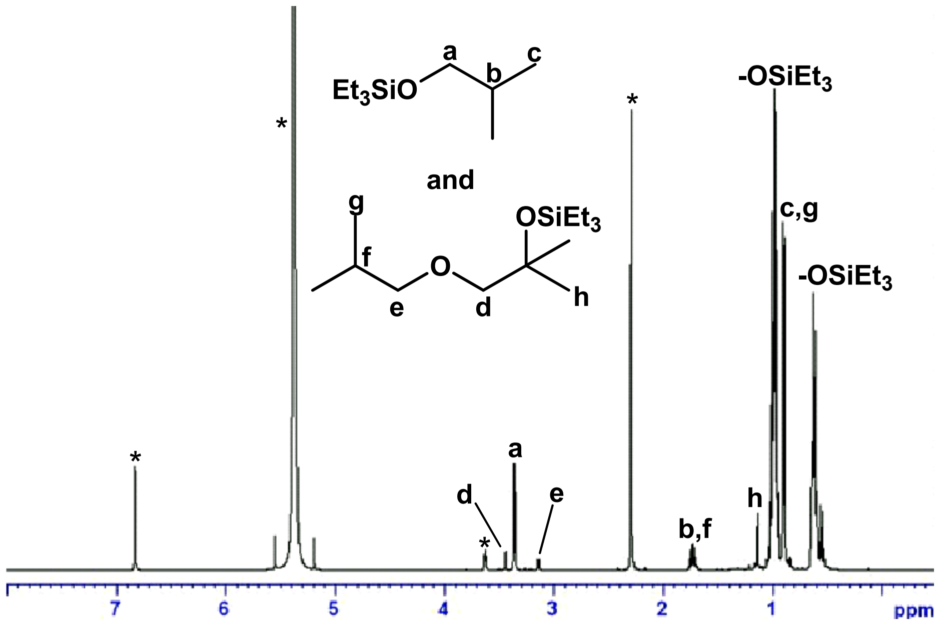


Figure S5. ^{1}H NMR spectrum of the reaction mixture after 1 h at r.t. (entry 2) (CD_2Cl_2).

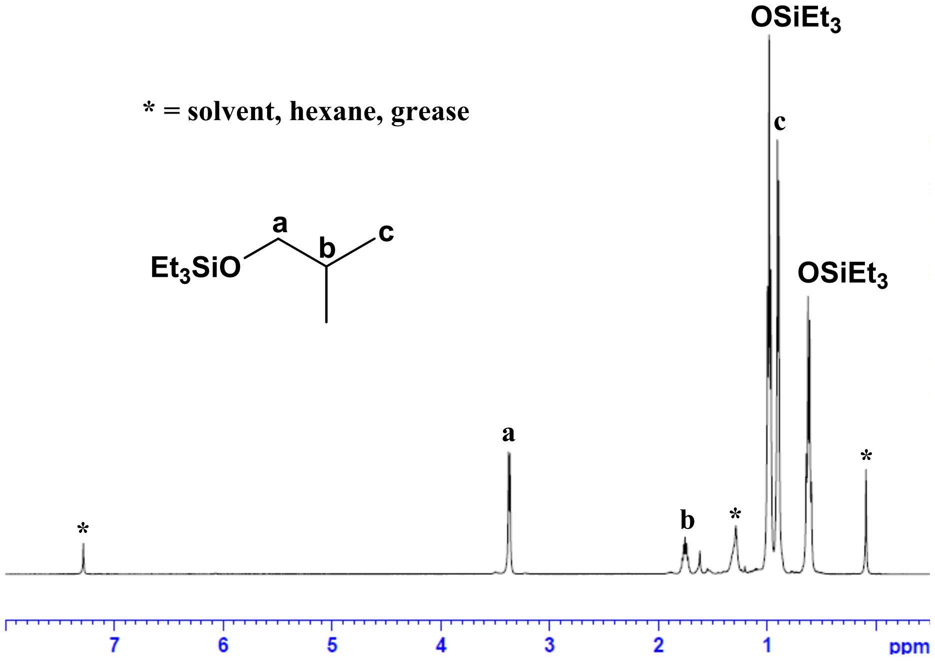


Figure S6. ^{1}H NMR spectrum of the isolated product (entry 2) ($CDCl_3$).

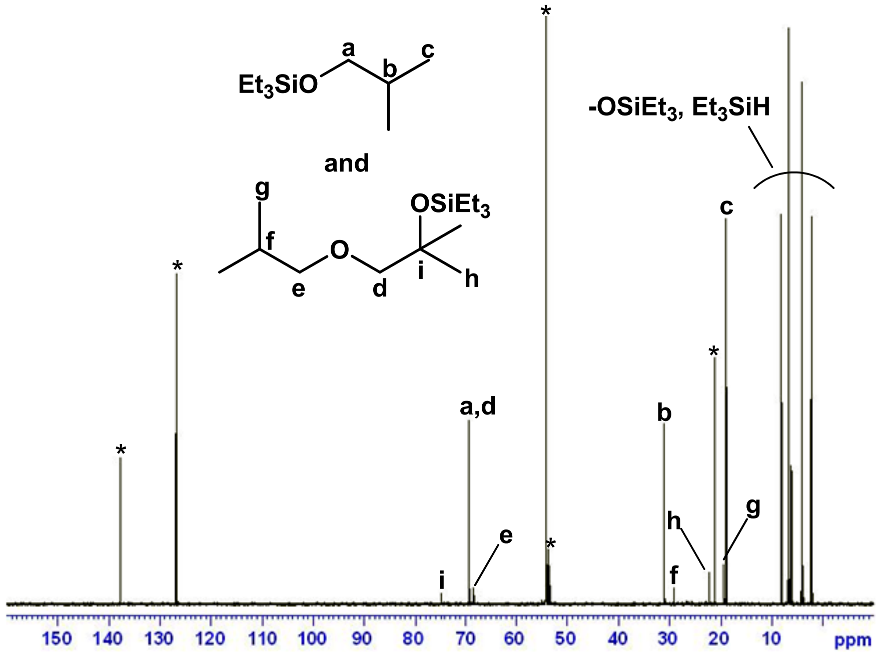


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture after 1 h at r.t. (entry 2) (CD_2Cl_2).

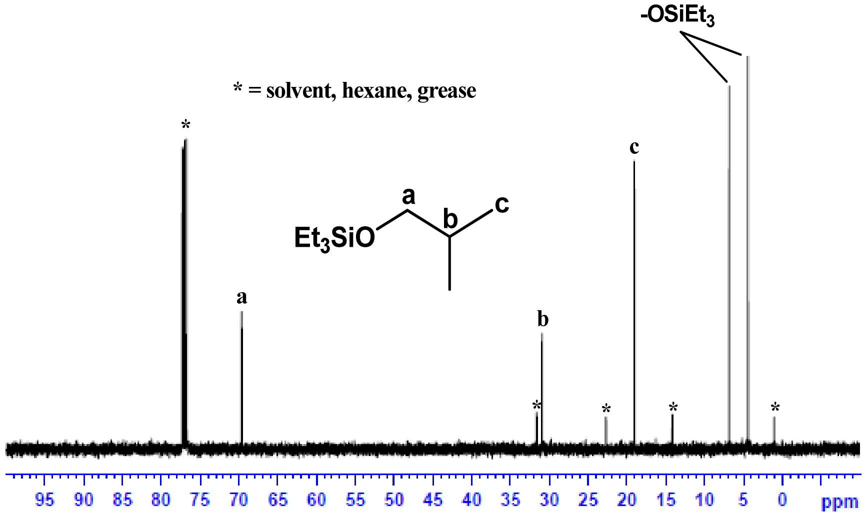


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of the isolated product (entry 2) ($CDCl_3$).

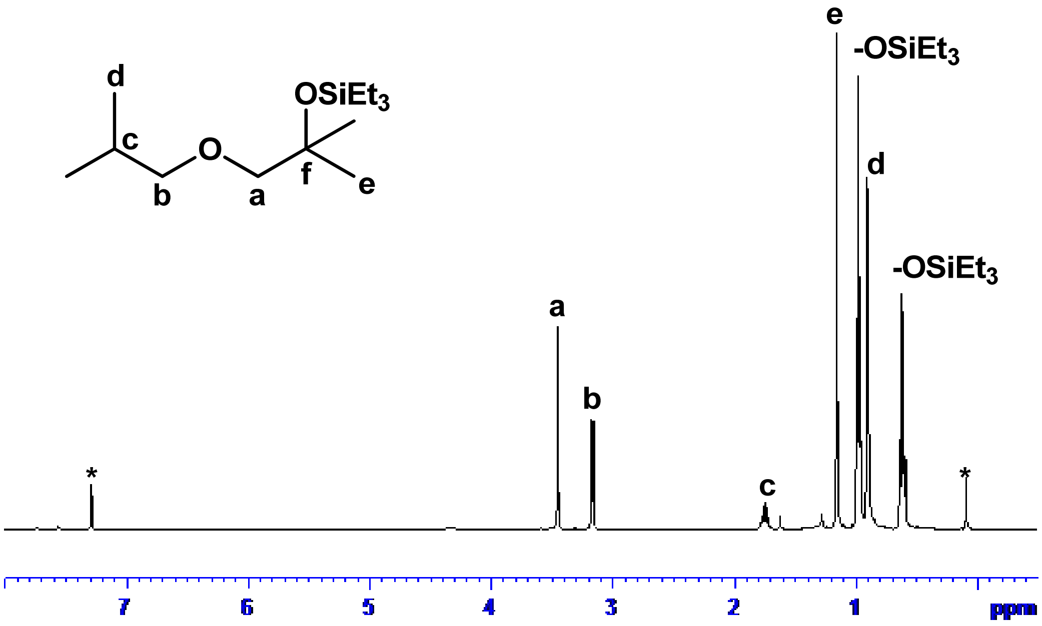


Figure S9. ^{1}H NMR spectrum of the dimeric isomer of 1,2-epoxy-2-methyl propane ($CDCl_3$).

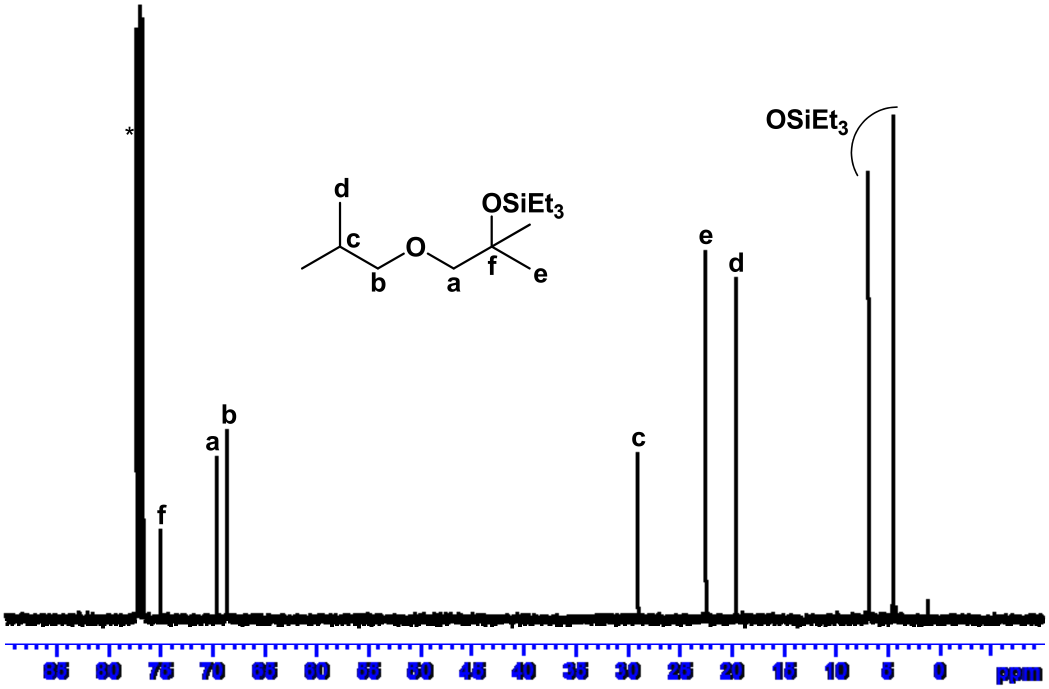


Figure S10. $^{13}C\{^1H\}$ NMR spectrum of the dimeric isomer of 1,2-epoxy-2-methyl propane ($CDCl_3$).

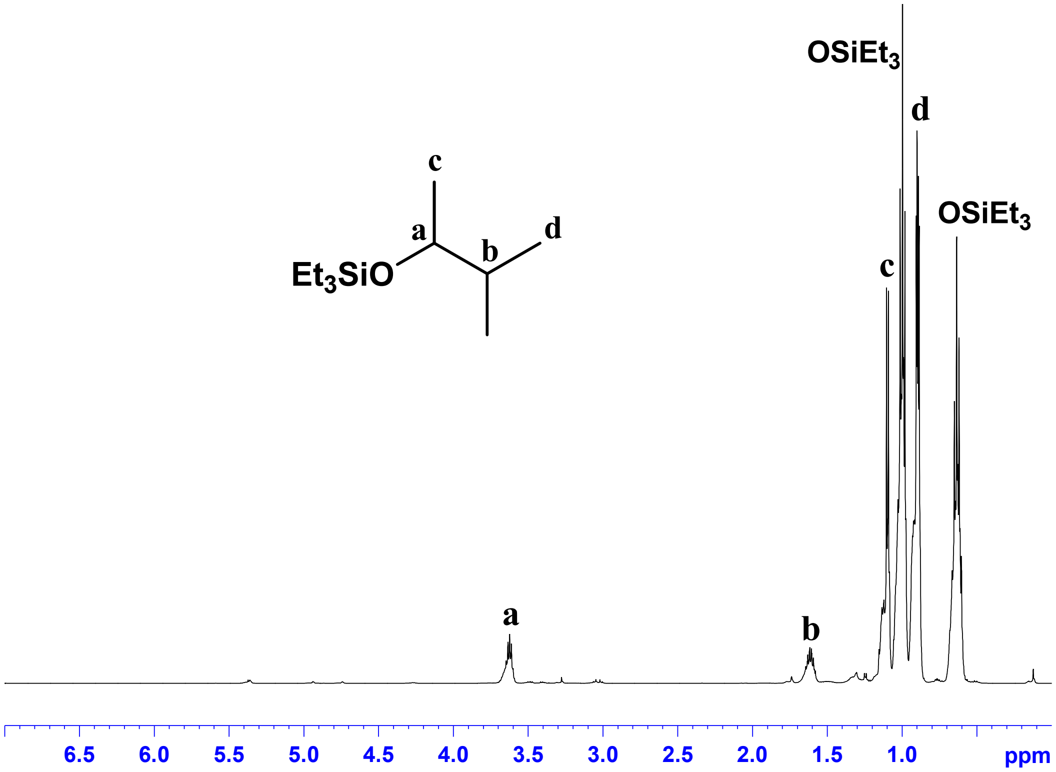


Figure S11. ^{1}H NMR spectrum of the isolated product (entry 3) (CD_2Cl_2).

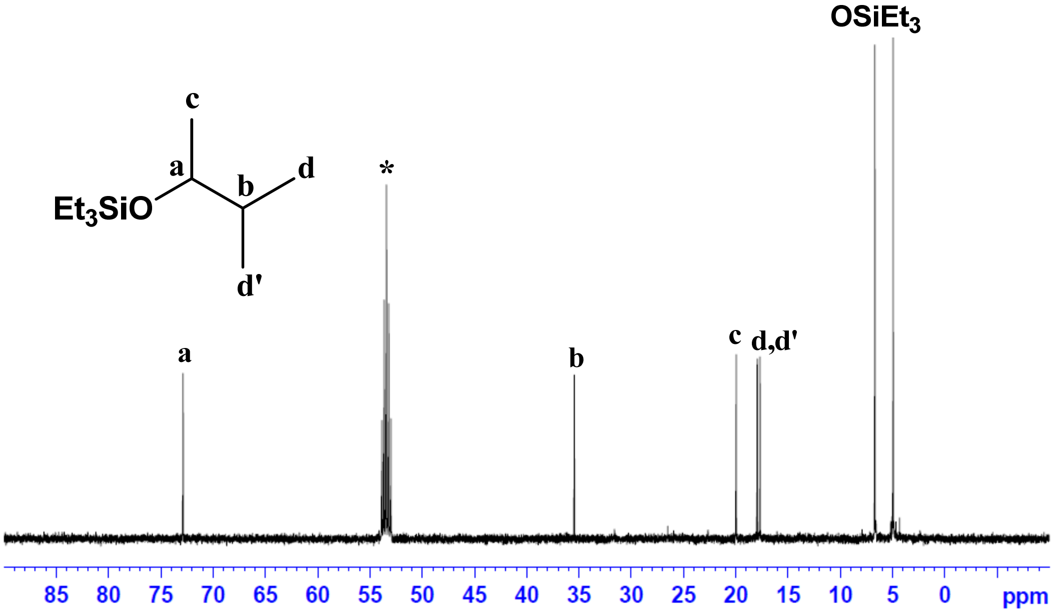


Figure S12. ^{13}C{^{1}H} NMR spectrum of the isolated product (entry 3) (CD_2Cl_2).

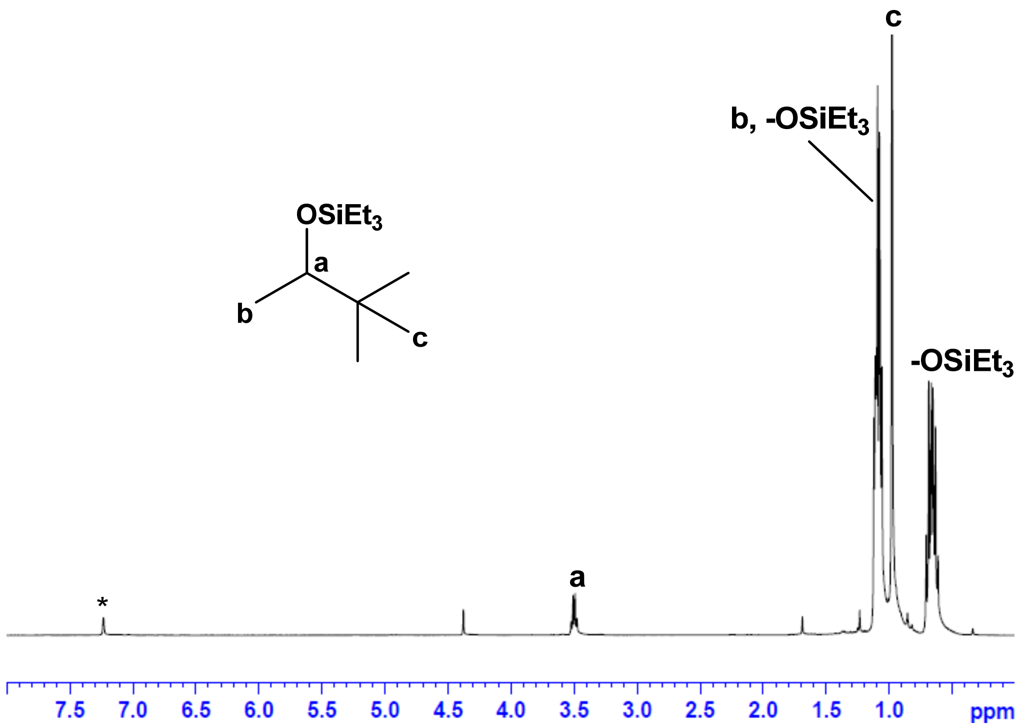


Figure S13. ^{1}H NMR spectrum of the reaction mixture after 1 h at r.t. (entry 4) (C_6D_6).

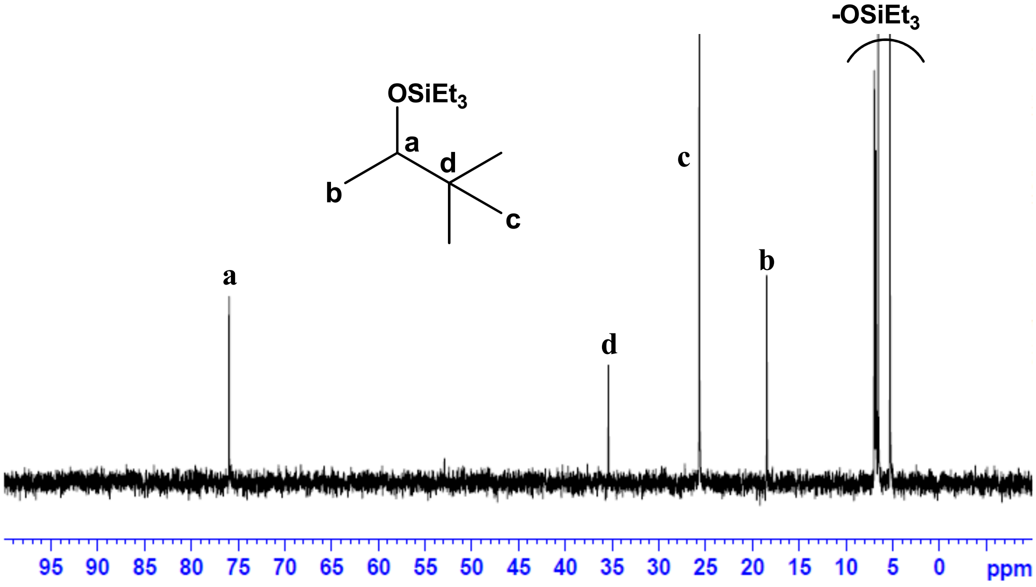


Figure S14. ^{13}C{ ^{1}H} NMR spectrum of the reaction mixture after 1 h at r.t. (entry 4) (C_6D_6).

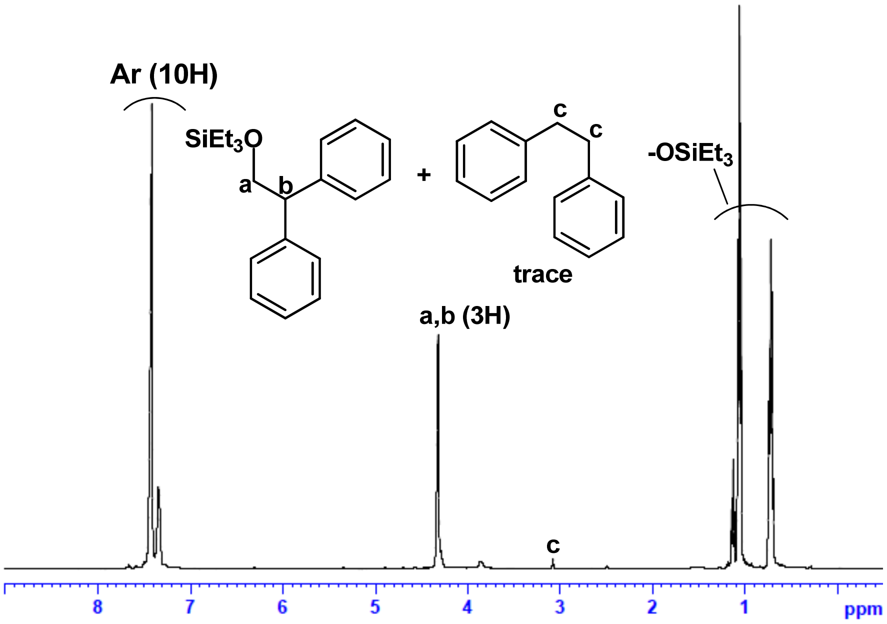


Figure S15. ^{1}H NMR spectrum of the reaction mixture after 1 h at r.t. (entry 5) (CD_2Cl_2).

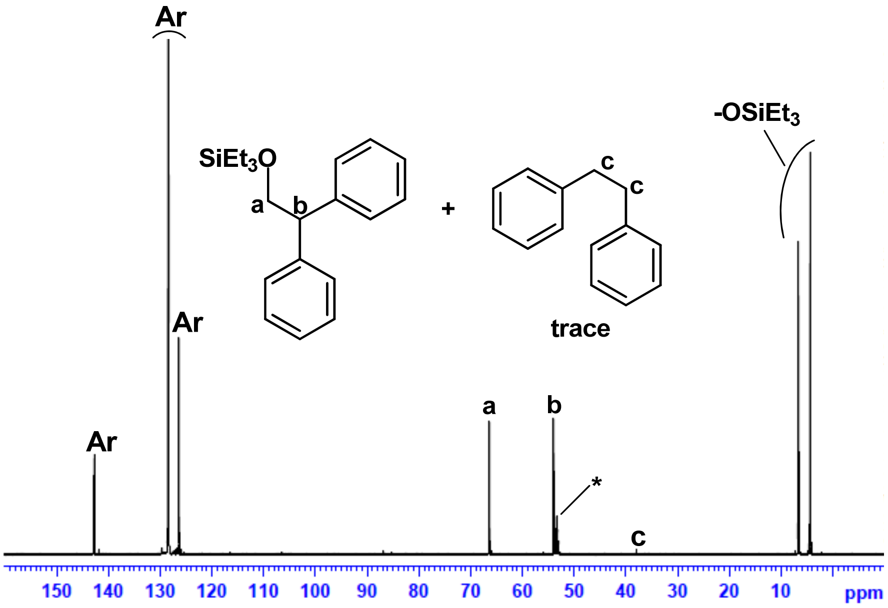


Figure S16. $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture after 1 h at r.t. (entry 5) (CD_2Cl_2).

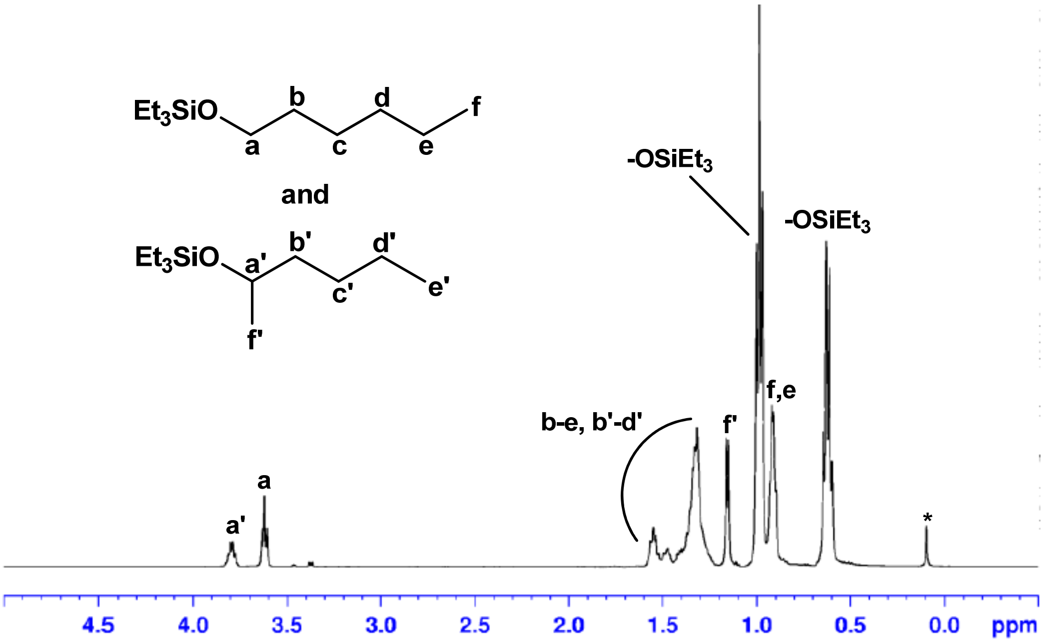


Figure S17. ^{1}H NMR spectrum of the isolated product (entry 6) ($CDCl_3$).

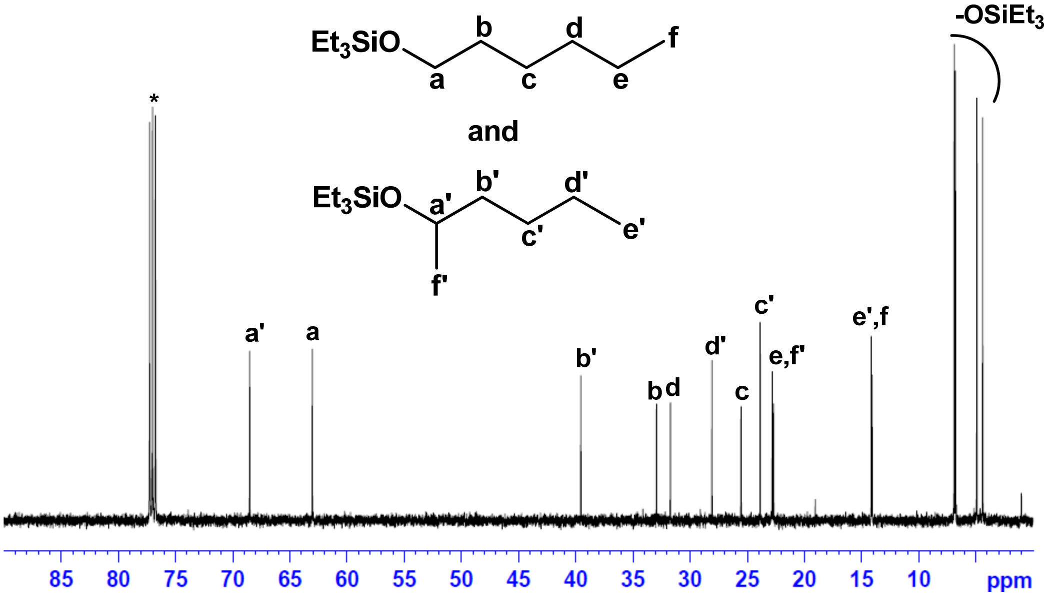


Figure S18. ^{13}C{ ^{1}H} NMR spectrum of the isolated product (entry 6) ($CDCl_3$).

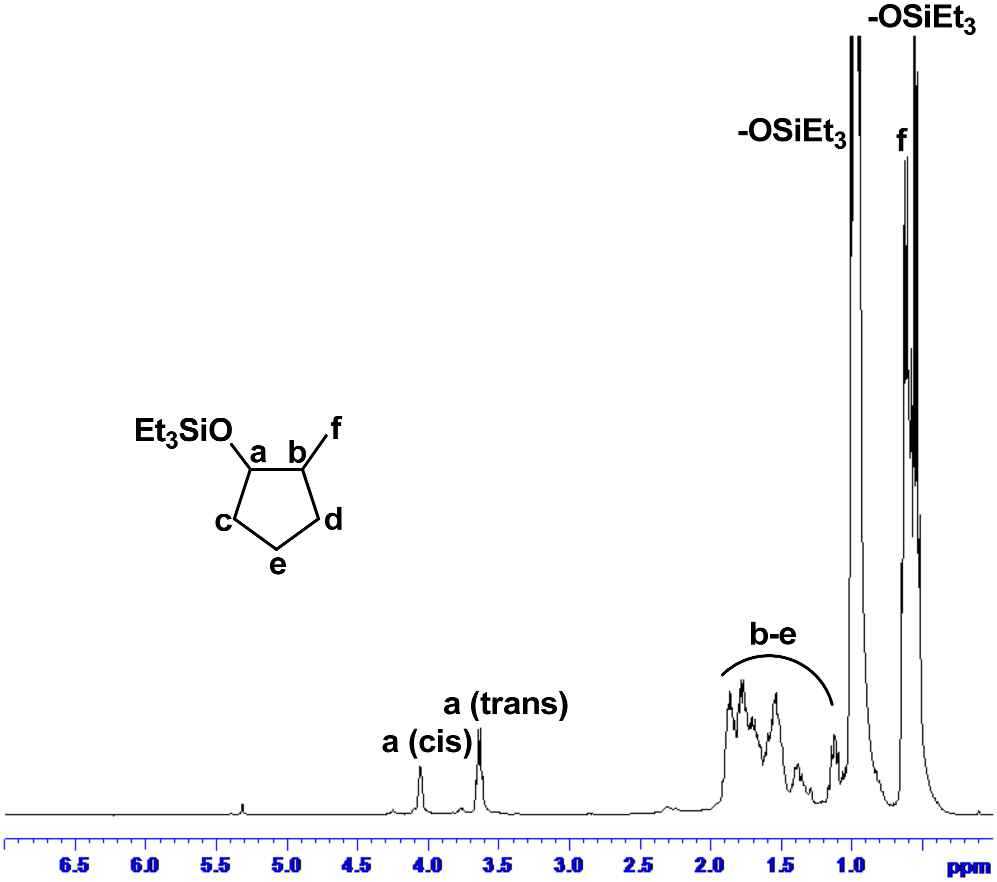


Figure S19. ^{1}H NMR spectrum of the reaction mixture after 1 h at r.t. (entry 7) (CDCl$_3$).

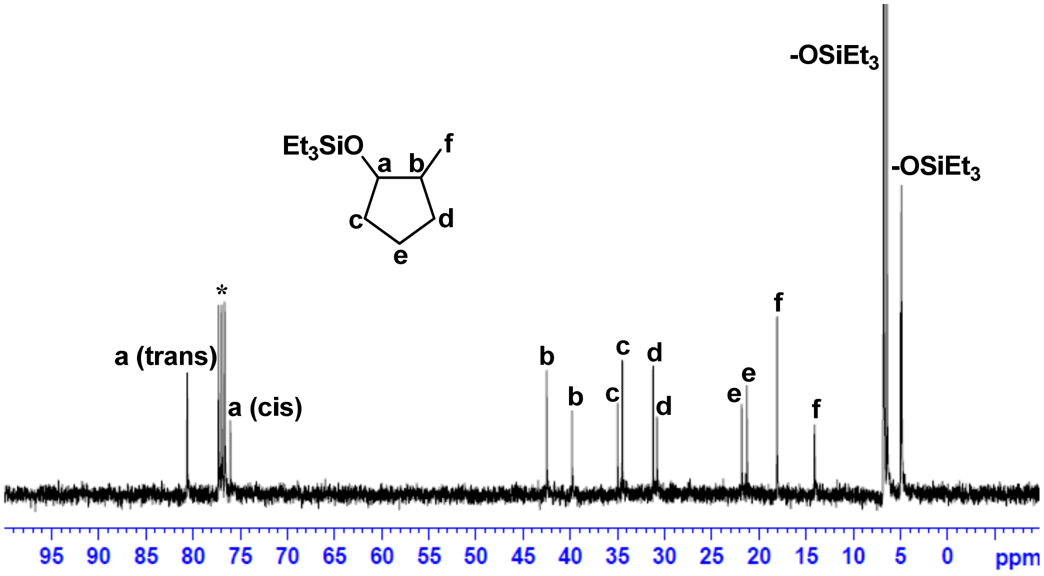


Figure S20. ^{13}C{ ^{1}H} NMR spectrum of the reaction mixture after 1 h at r.t. (entry 7) (CDCl$_3$).

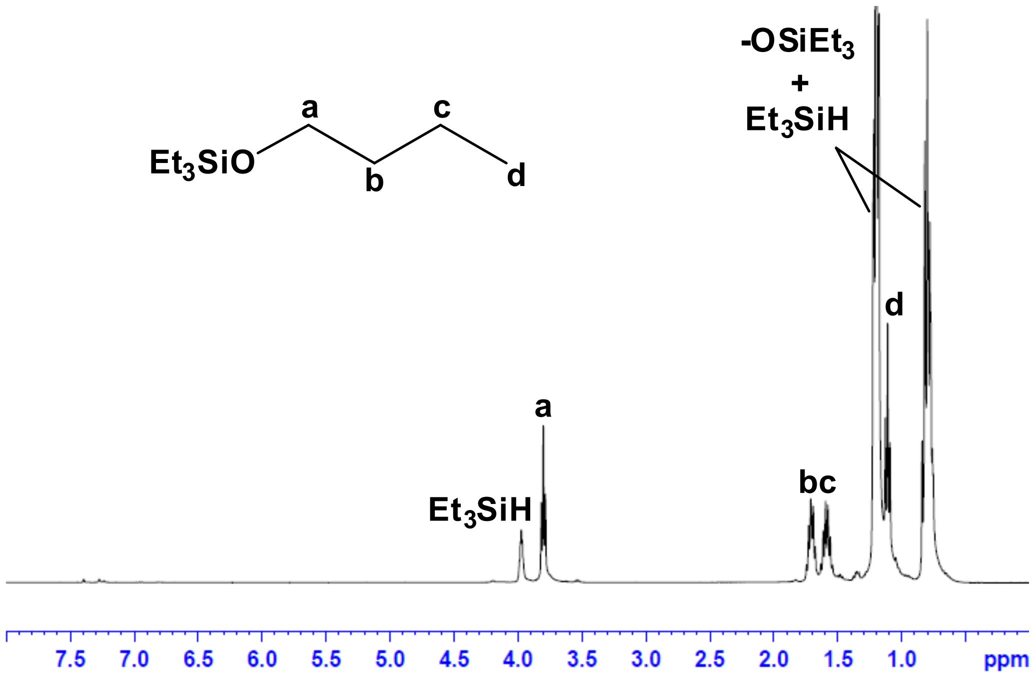


Figure S21. ^{1}H NMR spectrum of the reaction mixture after 1 h at r.t. (entry 8) (C_6D_5Cl).

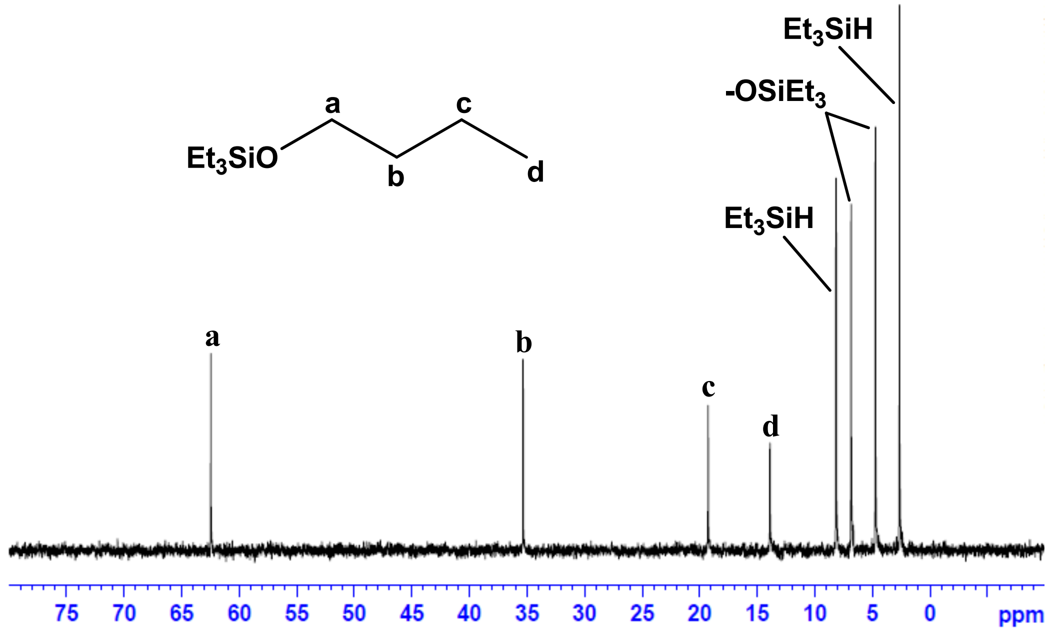


Figure S22. $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture after 1 h at r.t. (entry 8) (C_6D_5Cl).

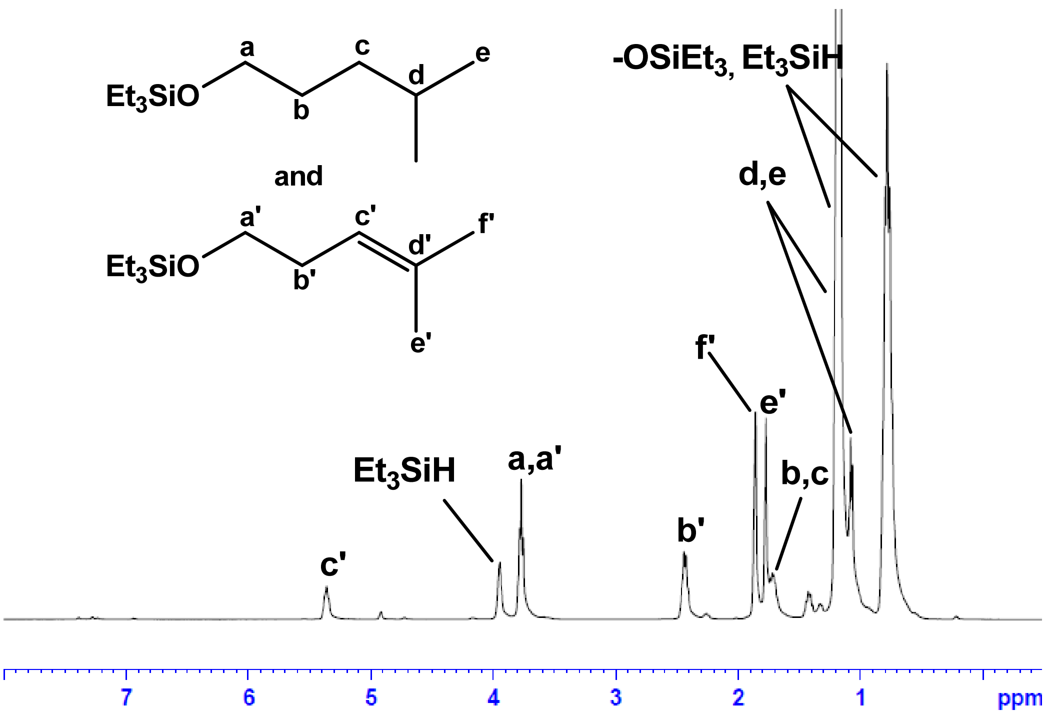


Figure S23. ^{1}H NMR spectrum of the reaction mixture after 2.2 h at r.t. (entry 9) (C_6D_5Cl).

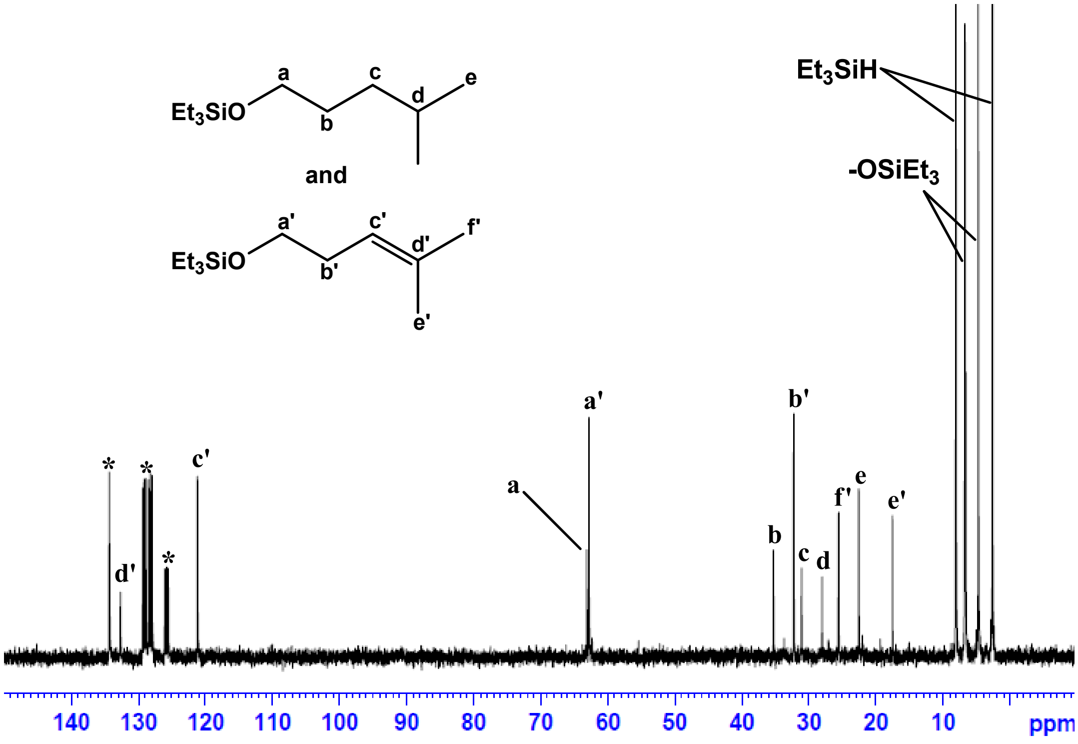


Figure S24. $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture after 2.2 h at r.t. (entry 9) (C_6D_5Cl).

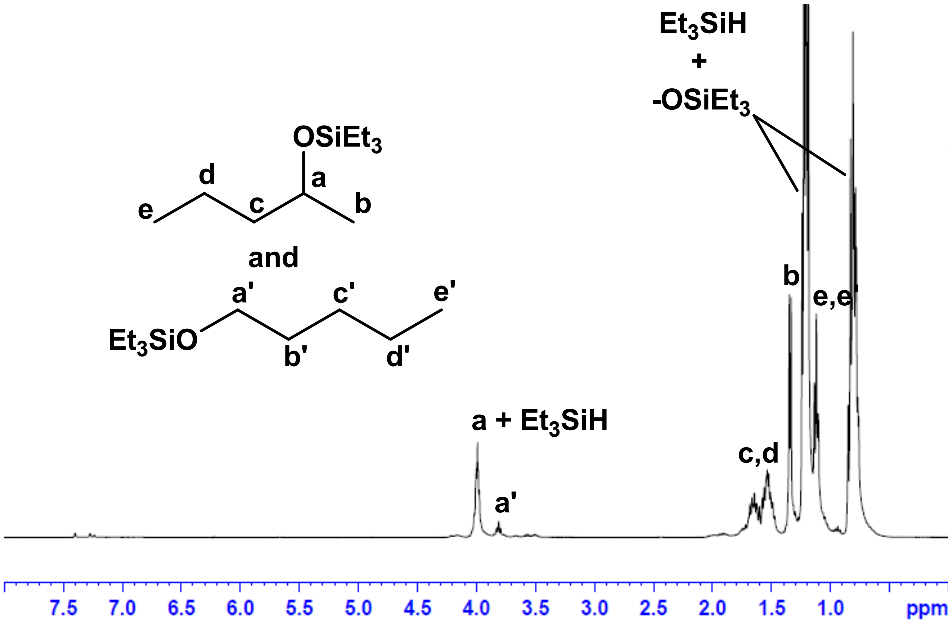


Figure S25. ^{1}H NMR spectrum of the reaction mixture after 2.5 h at r.t. (entry 10) (C_6D_5Cl).

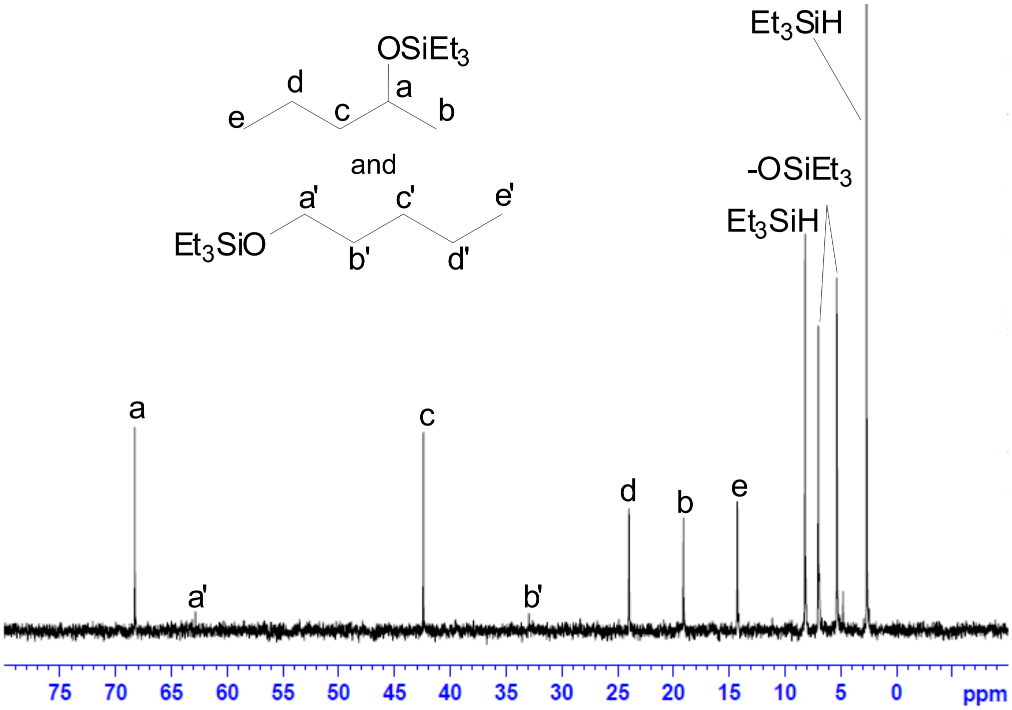


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture after 2.5 h at r.t. (entry 10) (C_6D_5Cl).

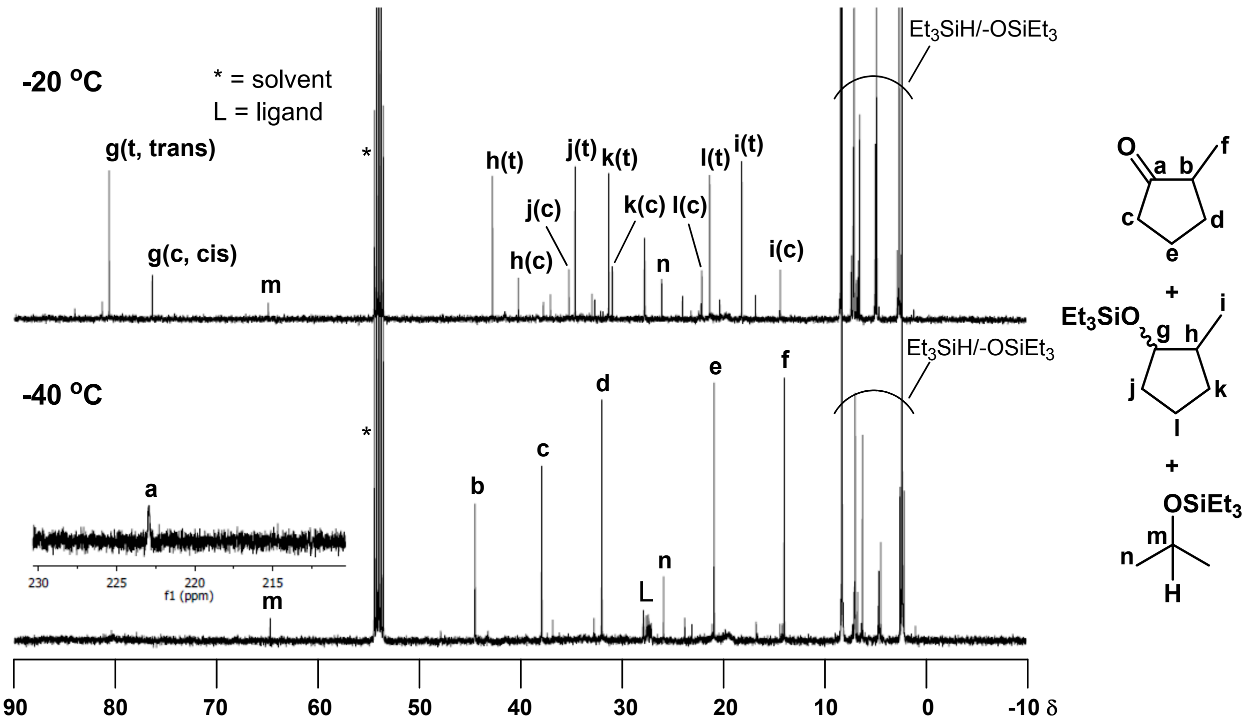


Figure S27. ^{13}C{^{1}H} NMR spectra obtained from the reaction mixture of **1**, Et$_3$SiH, and methyl-1,2-cyclopentene oxide in a ratio of 1:53:27 in CD$_2$Cl$_2$ over -40 to -20 ^{o}C.