

Electronic supplementary information

Mild partial deoxygenation of esters catalyzed by an oxazoline-coordinated rhodium silylene

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EXPERIMENTAL DETAILS

General Considerations. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, pentane, methylene chloride, and diethyl ether were dried and deoxygenated using an IT PureSolv system. Chloroform was heated to reflux over CaH_2 , and then distilled before use. Bromobenzene and bromobenzene- d_5 were degassed under vacuum and stored with activated molecular sieves. Benzene- d_6 was stirred over Na/K alloy and then vacuum transferred. Compound **1** was synthesized according to the previously published work.¹ Tris(perfluorophenyl)borane was synthesized from boron trichloride and bromopentafluorobenzene.² Phenylsilane was synthesized by reduction of trichlorophenylsilane with LiAlH_4 . Benzyldimethylsilane was purchased from Gelest and stored over 4 Å molecular sieves in the glovebox. Ethyl acetate was purchased from Fisher Scientific, distilled over K_2CO_3 , and stored over 4 Å molecular sieves in the glovebox. Commercial esters, amides, ketones and aldehydes were degassed and stored in the glovebox. Liquid samples were stored over 4 Å molecular sieves.

^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{11}B NMR spectra were collected on a Varian MR 400 MHz spectrometer or an Avance II 600 MHz NMR spectrometer. ^{15}N NMR chemical shifts were determined by ^1H - ^{15}N HMBC experiments on an Avance II 600 MHz NMR spectrometer or a Bruker Avance II 700 MHz spectrometer with a Bruker Z-gradient inverse TXI $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ 5 mm cryoprobe. ^{15}N chemical shifts were originally referenced to an external liquid NH_3 standard and

recalculated to the CH₃NO₂ chemical shift scale by adding -381.9 ppm. ²⁹Si NMR chemical shift was determined by ¹H-²⁹Si HMBC experiment on an Avance II 600 MHz NMR spectrometer. Infrared spectra were recorded on a Bruker Vertex spectrometer. Mass spectrometry data for the catalyst were acquired on an Agilent 6540 QTOF accurate mass spectrometer equipped with 1200 series U-HPLC system and ESI ion source. Mass spectrometry data of the isolated organic substances were acquired from an Agilent Technologies 7890A GC system coupled with 5975C inert MSD with Triple-Axis detector. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S in Iowa State Chemical Instrumentation Facility.



Tris(perfluorophenyl)borane (0.0895 g, 0.175 mmol) and {PhB(Ox^{Me2})₂Im^{Mes}}RhH(SiH₂Ph)CO (0.124 g, 0.175 mmol) were mixed in benzene (5 mL). Dark brown oily precipitate formed in a few minutes, and the solution was then stirred at room temperature for another 3 h. The top layer, a transparent brown solution, was decanted, and the oil was then washed with benzene (2 × 5 mL) and pentane (5 mL), and dried under vacuum to give the product as black solid (0.184 g, 0.151 mmol, 86.3%). ¹H NMR (bromobenzene-*d*₅, 400 MHz): δ 7.65 (d, ³J_{HH} = 6.8 Hz, 2 H, *o*-BC₆H₅), 7.43 (m, 4 H, C₆H₅), 7.14 (m, 2 H, C₆H₅), 6.81 (d, ³J_{HH} = 6.8 Hz, 2 H, *o*-SiC₆H₅), 6.72 (s, 1 H, *m*-C₆H₂Me₃), 6.64 (s, 1 H, *m*-C₆H₂Me₃), 6.34 (d, ³J_{HH} = 2.0 Hz, 1 H, 4,5H-N₂C₃H₂Mes), 6.25 (d, ³J_{HH} = 2.0 Hz, 1 H, 4,5H-N₂C₃H₂Mes), 5.15 (vt, *J* = 4.0 Hz, ¹J_{SiH} = 234.0 Hz, 1 H, SiH), 3.89 (m, 3 H, CNCMe₂CH₂O), 3.80 (d, ²J_{HH} = 9.6 Hz, 1 H, CNCMe₂CH₂O), 2.06 (s, 3 H, *p*-C₆H₂Me₃), 1.68 (s, 3 H, *o*-C₆H₂Me₃), 1.10 (s, 3 H, CNCMe₂CH₂O), 1.07 (s, 3 H, CNCMe₂CH₂O), 1.04 (s, 3 H, CNCMe₂CH₂O), 0.76 (s, 3 H, *o*-C₆H₂Me₃), 0.68 (s, 3 H, CNCMe₂CH₂O), -12.92 (dd, ¹J_{RhH} = 20.0 Hz, ³J_{HH} = 4.0 Hz, 1 H, RhH). ¹³C{¹H} NMR (bromobenzene-*d*₅, 150 MHz): δ 186.33 (d, ¹J_{RhC} = 51 Hz, 2C-N₂C₃H₂Mes), 169.23 (d, ¹J_{RhC} = 37.5 Hz, CO), 148 (br, C₆F₅), 147 (br, C₆F₅), 138.06 (*p*-C₆H₂Me₃), 137.6 (br, *ipso*-C₆H₅), 136.4 (br, C₆F₅), 136.0 (br, *ipso*-C₆H₅), 135 (br, C₆F₅), 133.89 (*o*-BC₆H₅), 133.76 (*ipso*-C₆H₂Me₃), 133.38 (*o*-SiC₆H₅), 132.91 (*o*-C₆H₂Me₃), 131.73 (*o*-C₆H₂Me₃), 128.36 (2 *m*-C₆H₂Me₃, overlapped with C₆D₅Br), 127.03 (C₆H₅), 126.85 (C₆H₅), 126.68 (C₆H₅), 126.52 (C₆H₅), 125.18 (4,5C-N₂C₃H₂Mes, overlapped with C₆D₅Br), 122.92 (4,5C-N₂C₃H₂Mes), 80.68 (CNCMe₂CH₂O), 78.95 (CNCMe₂CH₂O), 68.39 (CNCMe₂CH₂O), 66.94 (CNCMe₂CH₂O), 26.98 (CNCMe₂CH₂O), 26.43 (CNCMe₂CH₂O), 25.04 (CNCMe₂CH₂O), 23.21 (CNCMe₂CH₂O),

19.63 (*p*-C₆H₂Me₃), 18.26 (*o*-C₆H₂Me₃), 15.12 (*o*-C₆H₂Me₃). ¹¹B NMR (bromobenzene-*d*₅, 192 MHz): δ -7.9 (PhB(Ox^{Me2})(Ox^{Me2}SiHPh)Im^{Mes}), -25 (br, HB(C₆F₅)₃). ¹⁵N{¹H} NMR (bromobenzene-*d*₅, 61 MHz): δ -167.7 (CN(Rh)CMe₂CH₂O), -180.7 (N₂C₃H₂Mes), -183.1 (N₂C₃H₂Mes), -199.5 (CN(SiHPh)CMe₂CH₂O). ¹⁹F NMR (bromobenzene-*d*₅, 545 MHz): δ -132.08 (*o*-C₆F₅), -162.79 (*p*-C₆F₅), -165.72 (*m*-C₆F₅). ²⁹Si NMR (bromobenzene-*d*₅, 119 MHz): δ 6.5 (¹J_{RhSi} = 42 Hz). IR (KBr, cm⁻¹): 3398 w, 2972 w, 2928 w, 2859 w, 2386 w, 2162 w, 2076 s, 2016 m, 2000 br, 1652 m, 1639 m, 1560 m, 1508 s, 1464 s, 1373 m, 1301 m, 1274 m, 1209 m, 1184 m, 1162 m, 1110 s, 1075 s, 968 s, 852 m, 827 m, 750 w, 738 w, 705 w, 681 w, 639 w, 567 w. EIMS (positive ion mode): 707.2 M⁺, 679.2 M⁺-CO, 629.2 M⁺-C₇H₆O, 601.2 M⁺-SiC₇H₆O, 471.3 M⁺-RhSiC₇H₇O. EIMS (negative ion mode): 512.9 HB(C₆F₅)₃⁻. Anal. Calcd for C₅₃H₄₂B₂F₁₅N₄O₃RhSi: C, 52.16; H, 3.47; N, 4.59. Found: C, 51.45; H, 3.20; N, 4.55. Mp, 89-91 °C.

Figure S1. A ¹H NMR spectrum of **2** acquired in bromobenzene-*d*₅. The acquisition window extended from -40 to 14 ppm, and no signals were detected in the region not shown.

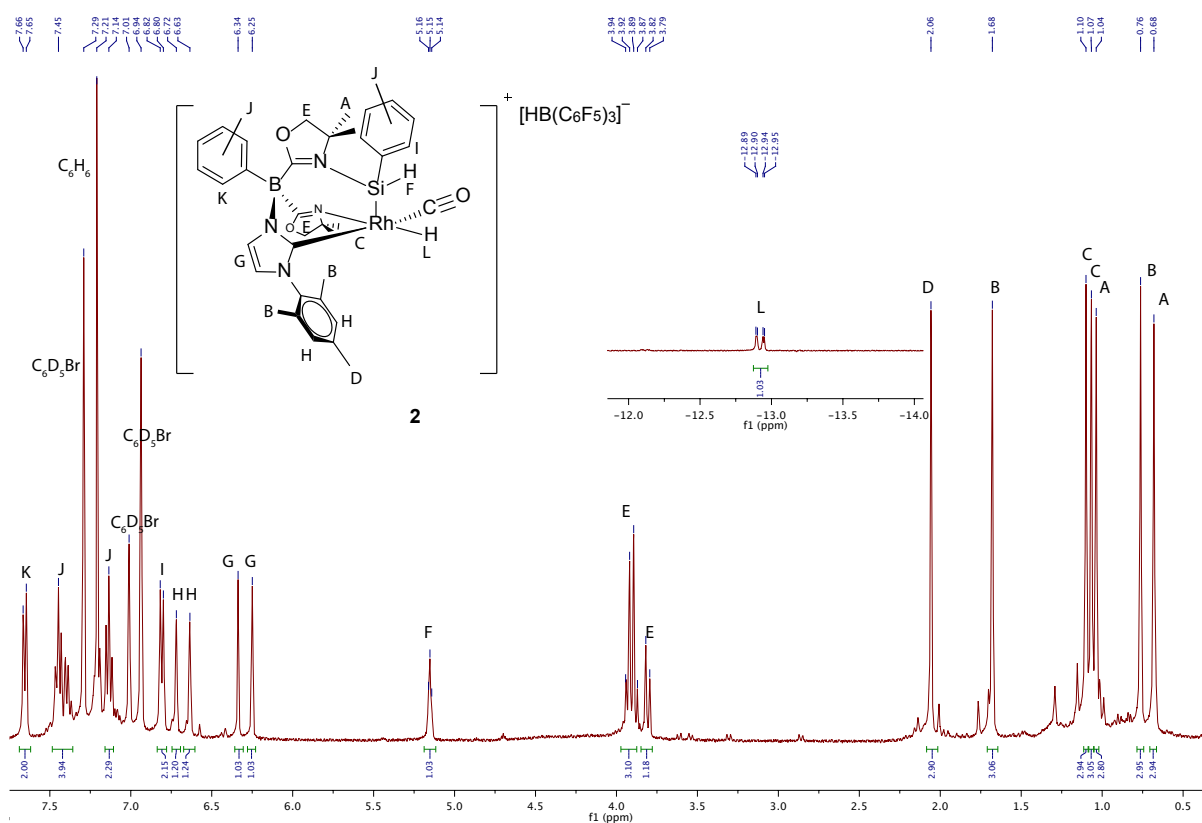


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** acquired in bromobenzene- d_5 .

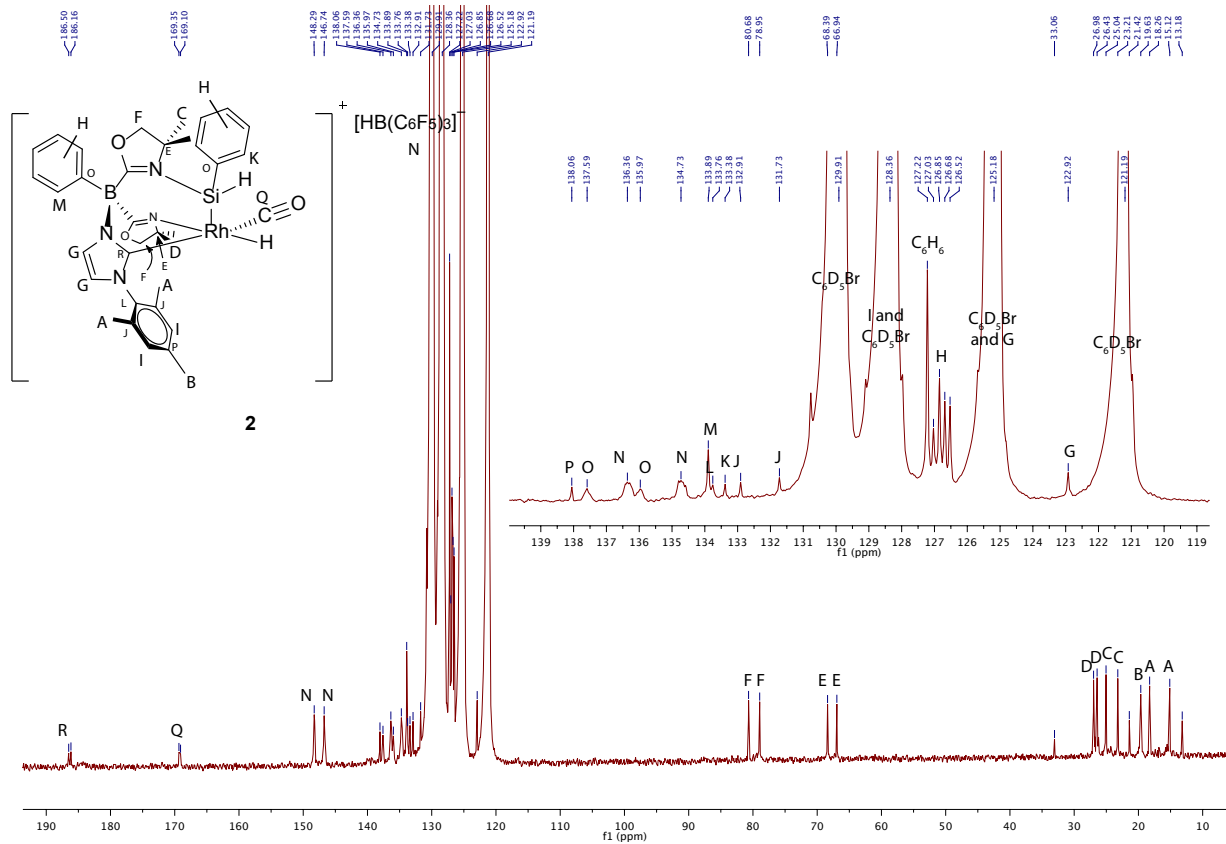


Figure S3. ^1H - ^{15}N HMBC spectrum of **2** acquired in bromobenzene- d_5 on a Bruker Avance 700 spectrometer using a Bruker Z-gradient inverse TXI $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ 5 mm cryoprobe. Inset: a ^1H - ^{15}N HMBC experiment acquired on a Bruker Avance 600 spectrometer with an inverse BB probe. The F1 axis is the ^{15}N dimension, and F2 is the ^1H dimension. The spectrum is machine-calibrated to NH_3 as the standard, and the reported chemical shift values are adjusted to the nitromethane scale. Crosspeaks at ~ 203 ppm from minor contaminants in the above spectrum appeared at longer acquisition times required to observed N-Si-H correlations, and result from more efficient polarization transfer from oxazoline methyl groups to N than the two-bond correlation through silicon.

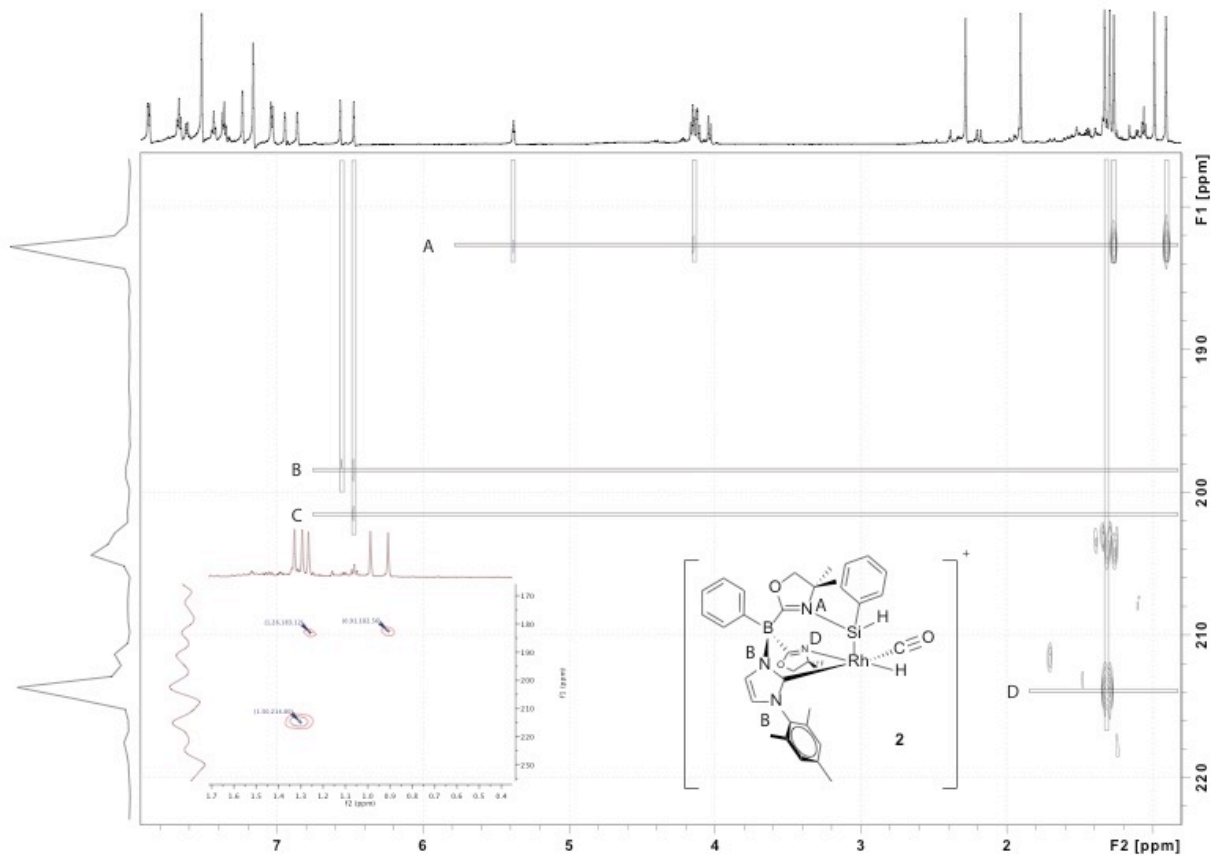


Figure S4. A ^1H - ^{29}Si HSQC experiment on **2** acquired in bromobenzene- d_5 with tetrakis(trimethylsilyl)silane as an internal standard.

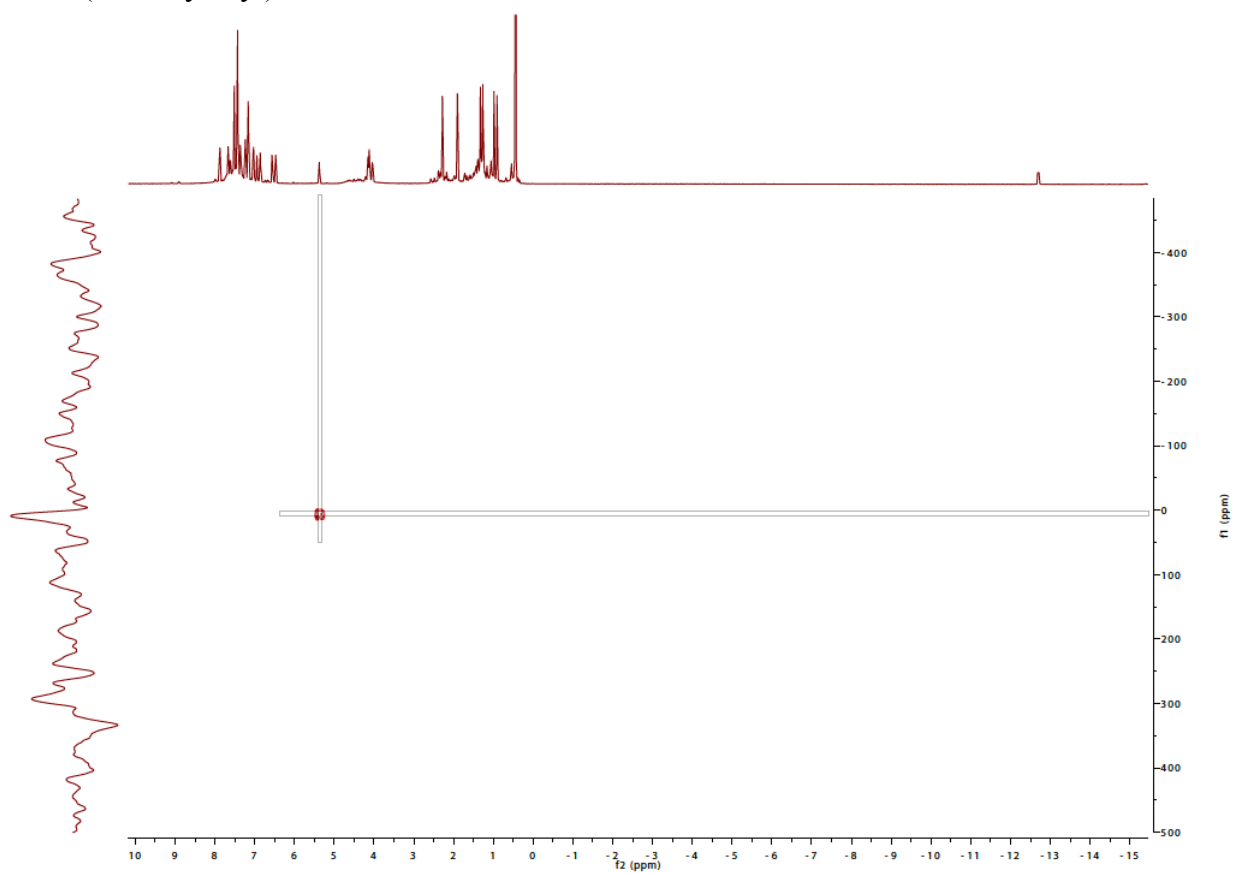
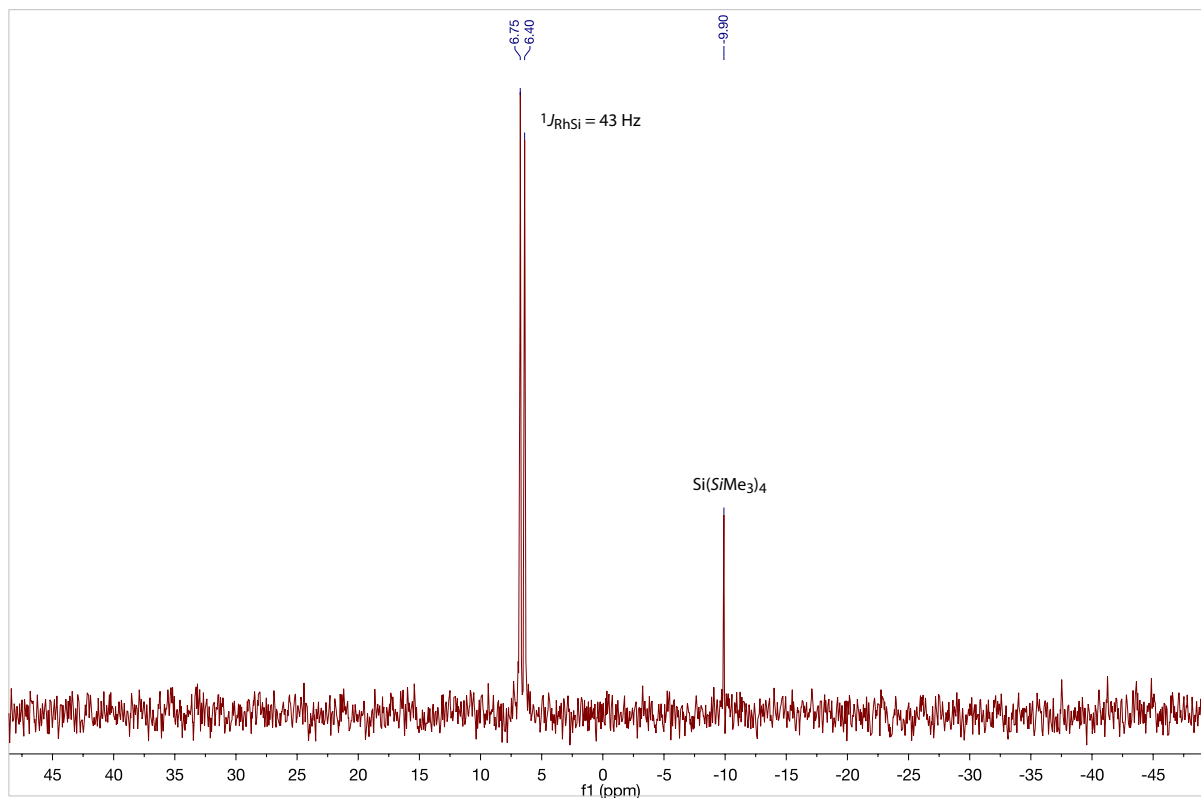


Figure S5. $^{29}\text{Si}\{^1\text{H}\}$ INEPT spectrum showing the $^1J_{\text{RhSi}}$ coupling. The upfield signal is from tetrakis(trimethylsilyl)silane, added as an internal standard.



The $^1\text{H} \rightarrow ^{29}\text{Si}$ cross-polarization magic angle spinning (CPMAS) and ^1H MAS spectra of **2** were acquired on a 600 MHz Varian spectrometer equipped with a 1.6-mm FastMASTM T3 probe. The rotor was packed in a glove box to provide protection from air and moisture contamination and was spun using dry nitrogen gas. The experimental parameters are given in figure captions, where ν_R is the MAS rate, $\nu_{\text{RF}}(\text{X})$ is the magnitude of the RF magnetic field applied to X spins, τ_{CP} is the cross-polarization time, τ_{RD} is the recycle delay, and NS is the number of scans.

Figure S6. The $^1\text{H} \rightarrow ^{29}\text{Si}$ CPMAS spectrum of **2** acquired using the following experimental parameters: $\nu_R = 20$ kHz, $\nu_{\text{RF}}(\text{H}) = 100$ kHz during the excitation pulse, $\nu_{\text{RF}}(\text{H}) = 50$ kHz during CP, $\nu_{\text{RF}}(\text{H}) = 80$ kHz during TPPM heteronuclear decoupling, $\nu_{\text{RF}}(\text{Si}) = 70$ kHz during CP, $\tau_{\text{CP}} = 1$ ms, $\tau_{\text{RD}} = 3$ s, and NS = 8000.

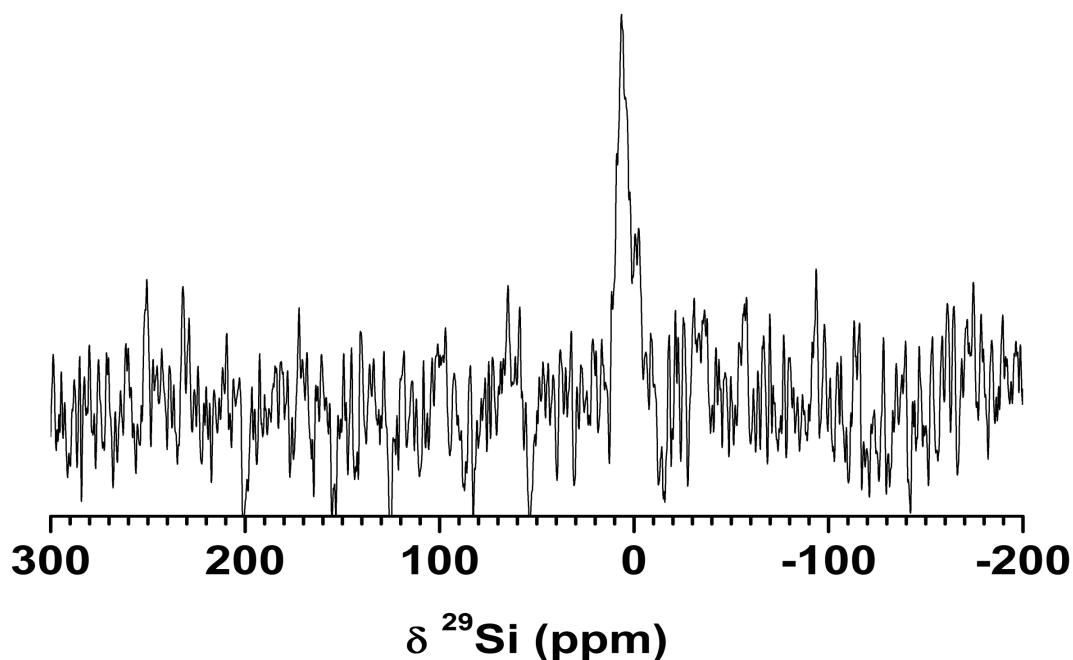


Figure S7. The ^1H MAS spectrum of **2** acquired using the following experimental parameters: $\nu_R = 20$ kHz, $\nu_{\text{RF}}(\text{H}) = 100$ kHz, $\tau_{\text{RD}} = 3$ s, and $\text{NS} = 4$.

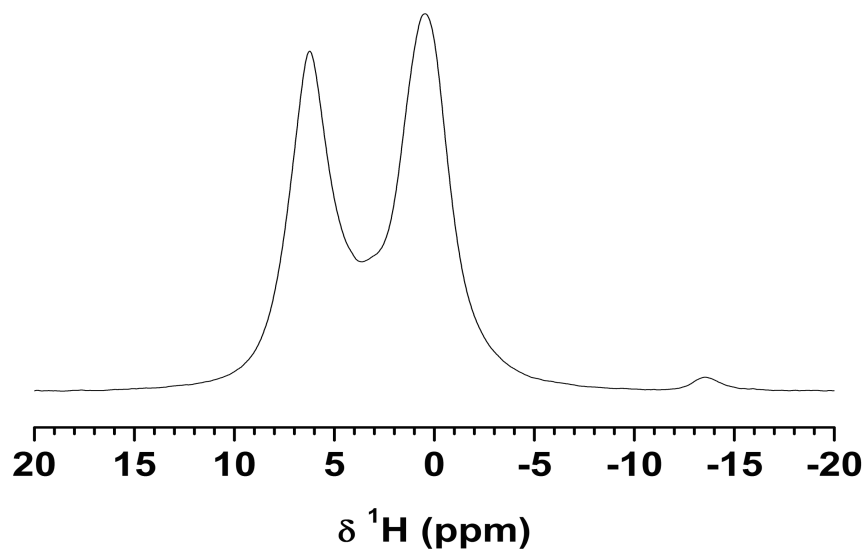


Figure S8. ^{19}F NMR spectrum of **2** acquired in bromobenzene- d_5 .

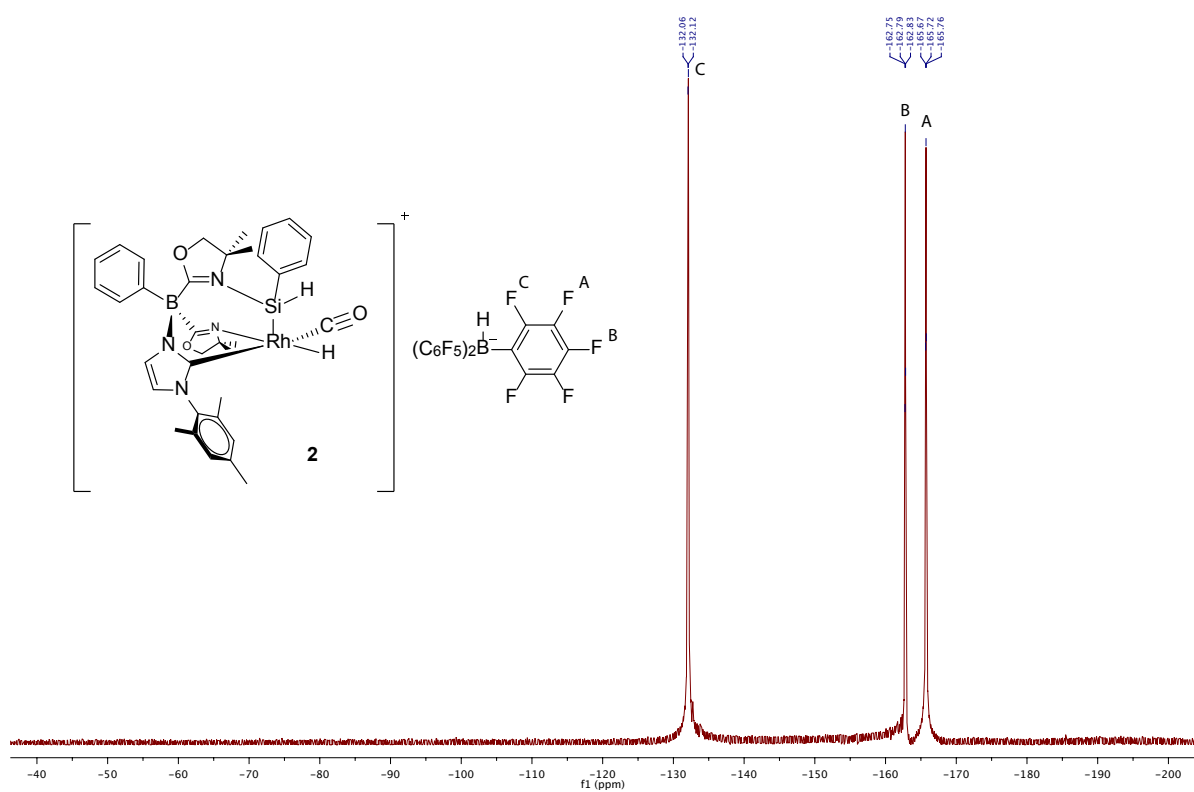


Figure S9. ^{11}B NMR spectrum of **2** acquired in bromobenzene- d_5 .

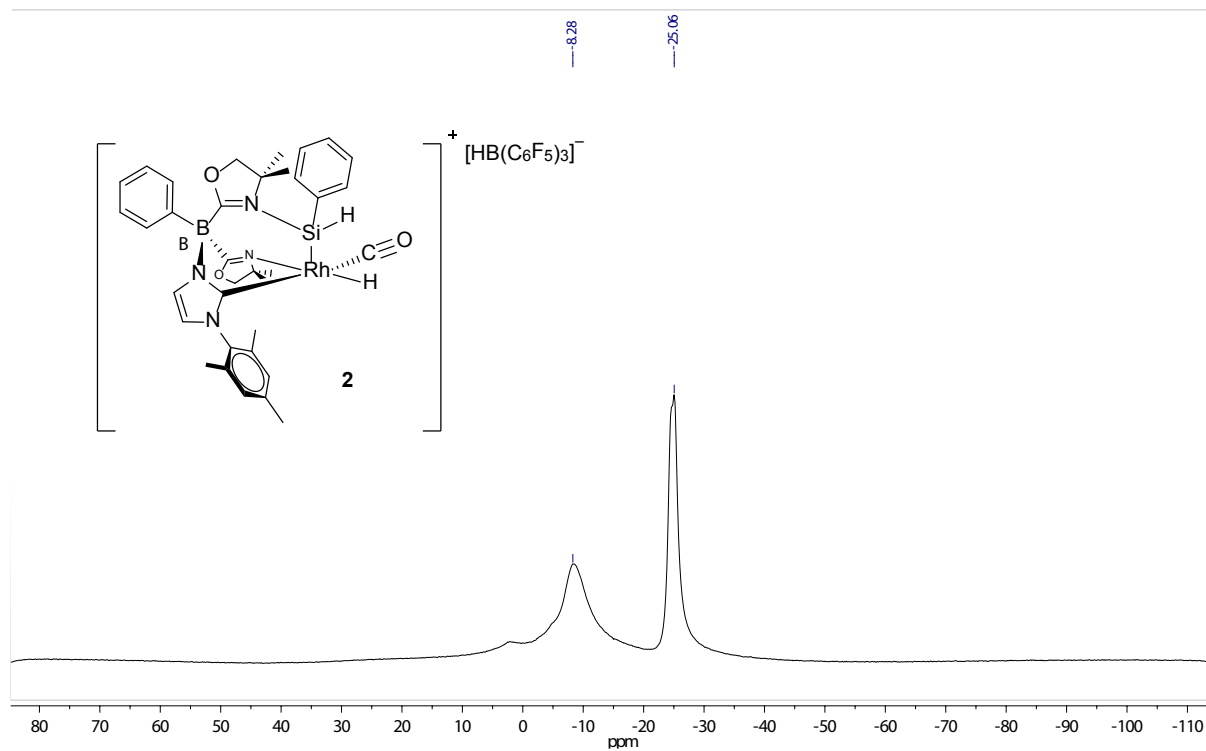


Figure S10. High resolution mass spectrum of **2** acquired in bromobenzene and positive ion mode.

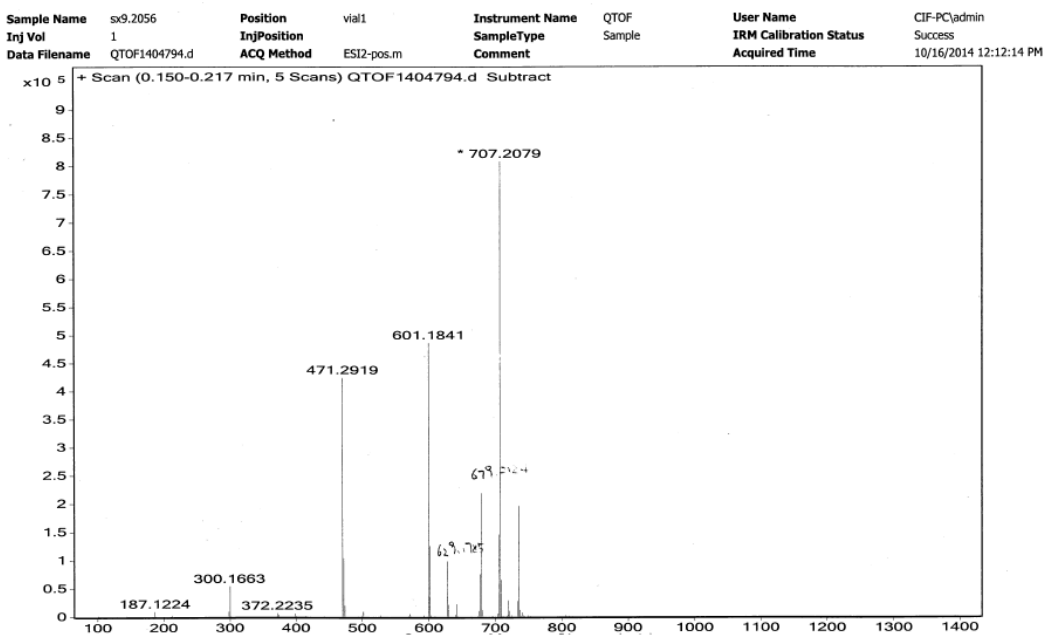
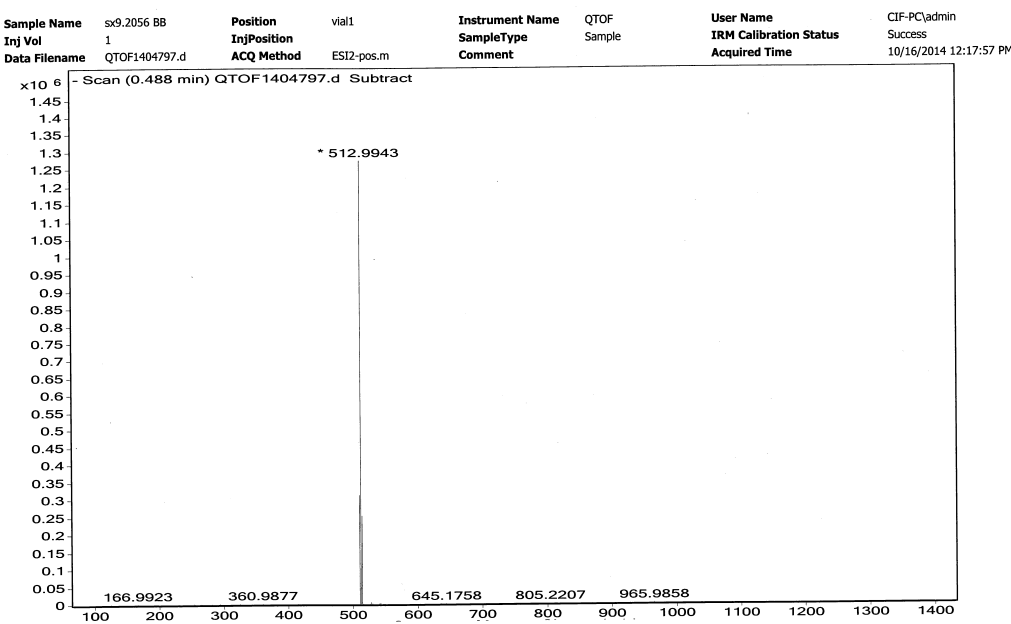


Figure S11. High resolution mass spectrum of **2** acquired in bromobenzene and negative ion mode.



Description of Catalytic Experiments.

exo-2-Methoxybicyclo[2.2.1]heptane. A methylene chloride solution of **2** (0.0150 g, 0.0123 mmol, 10 mL) was added to a mixture of *exo*-2-norbornylformate (1.60 mL, 12.0 mmol) and phenylsilane (3.10 mL, 25.1 mmol). The solution was stirred at room temperature for 24 h and then filtered through a short plug of celite (5 mL). The celite was washed with methylene chloride (2 × 5 mL), the clear and colorless filtrates were combined, and the mixture was purified by distillation. The product was distilled at 167 °C (760 mmHg) as a colorless liquid (0.740 g, 5.86 mmol, 48.8%). The experimental ¹H and ¹³C{¹H} NMR spectra matched those reported in the literature.³ ¹H NMR (chloroform-*d*, 600 MHz): δ 3.27 (s, 3 H, OMe), 3.25 (m, 1 H, 2H-C₇H₉), 2.34 (m, 1 H, 4H-C₇H₉), 2.24 (m, 1 H, 1H-C₇H₉), 1.56 (m, 2 H, 6,7H-C₇H₉), 1.50 (d, 1 H, 3H-C₇H₉), 1.43 (m, 1 H, 5H-C₇H₉), 1.35 (m, 1 H, 7H-C₇H₉), 1.09 (m, 1 H, 3H-C₇H₉), 1.05 (m, 1 H, 5H-C₇H₉), 0.98 (m, 1 H, 6H-C₇H₉). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 84.39 (2C-C₆H₉), 56.01 (OMe), 40.06 (4C-C₇H₉), 39.49 (7C-C₇H₉), 35.30 (1C-C₇H₉), 34.90 (3C-C₇H₉), 28.67 (5C-C₇H₉), 24.77 (6C-C₇H₉). EIMS: C₈H₁₄O m/z 126 (M⁺).

Diethyl ether. A chloroform-*d* solution of **2** (0.0002 g, 0.000164 mmol, 0.5 mL) was added to a mixture of ethyl acetate (16.0 μL, 0.164 mmol), phenylsilane (40.5 μL, 0.328 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The reaction's progress was monitored with ¹H NMR spectroscopy, and all of the ethyl acetate was consumed after 0.5 h to give the product in 70.0% yield. The NMR spectra matched those acquired using an authentic sample of diethyl ether. ¹H NMR (chloroform-*d*, 600 MHz): δ 3.51 (q, ³J_{HH} = 7.2 Hz, 4 H, CH₂CH₃), 1.24 (t, ³J_{HH} = 7.2 Hz, 6 H, CH₂CH₃).

1-Bromo-6-ethoxyhexane. A chloroform solution of **2** (0.0150 g, 0.0123 mmol) was added to ethyl 6-bromohexanoate (0.218 mL, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was heated to 80 °C for 72 h and filtered through a short plug of celite (5 mL). The celite was extracted with chloroform (2 × 3 mL), the colorless filtrates were combined, and the mixture was separated by distillation. The product was distilled at 101 °C (10 mmHg) as a colorless liquid (0.193 g, 0.923 mmol, 75.0%). The experimental spectra matched the literature report.⁴ ¹H NMR (chloroform-*d*, 600 MHz): δ 3.48 (q, ³J_{HH} = 6.6 Hz, 2 H, OCH₂CH₃), 3.42 (m, 4 H, BrCH₂(CH₂)₄CH₂OEt), 1.88 (m, 2 H, BrCH₂CH₂(CH₂)₄OEt), 1.57 (m, 2 H, Br(CH₂)₄CH₂CH₂OEt), 1.47 (m, 2 H, Br(CH₂)₃CH₂(CH₂)₂OEt), 1.39 (m, 2 H,

Br(CH₂)₂CH₂(CH₂)₃OEt), 1.21 (t, ³J_{HH} = 6.6 Hz, 3 H, OCH₂CH₃). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 70.63 (Br(CH₂)₅CH₂OEt), 66.27 (OCH₂CH₃), 34.05 (BrCH₂(CH₂)₅OEt), 32.90 (BrCH₂CH₂(CH₂)₄OEt), 29.78 (Br(CH₂)₄CH₂CH₂OEt), 28.18 (Br(CH₂)₃CH₂(CH₂)₂OEt), 25.59 (Br(CH₂)₂CH₂(CH₂)₃OEt), 15.38 (OCH₂CH₃). EIMS: C₁₈H₁₇BrO m/z 209 (M⁺).

2-(2-Ethoxyethyl)thiophene. A 3 mL chloroform solution of **2** (0.0150 g, 0.0123 mmol) was added to ethyl 2-thiopheneacetate (0.184 mL, 1.23 mmol) and phenylsilane (3.10 mL, 25.1 mmol). The reaction mixture was heated to 80 °C for 24 h and filtered through a short plug of celite (5 mL). The celite was extracted with chloroform (2 × 3 mL), the colorless filtrates were combined, and the mixture was separated by distillation. The product distilled at 69 °C (10 mmHg) as a colorless liquid (0.0958 g, 0.613 mmol, 49.8%). The spectra of the isolated material matched the literature report.⁵ ¹H NMR (chloroform-*d*, 600 MHz): δ 7.15 (d, ³J_{HH} = 4.8 Hz, 1 H, 5H-C₄H₃S), 6.94 (t, ³J_{HH} = 4.2 Hz, 1 H, 4H-C₄H₃S), 6.86 (d, ³J_{HH} = 3.0 Hz, 1 H, ³J_{HH} = 3.0 Hz, 3H-C₄H₃S), 3.68 (t, ³J_{HH} = 7.2 Hz, 2 H, CH₂CH₂OEt), 3.54 (q, ³J_{HH} = 7.2 Hz, 2 H, OCH₂CH₃), 3.11 (t, ³J_{HH} = 7.2 Hz, 2 H, CH₂CH₂OEt), 1.24 (t, ³J_{HH} = 7.2 Hz, 3 H, OCH₂CH₃). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 141.52 (2C-C₄H₃S), 126.78 (3C-C₄H₃S), 125.15 (4C-C₄H₃S), 123.70 (5C-C₄H₃S), 71.31 (CH₂CH₂OEt), 66.44 (OCH₂CH₃), 30.67 (CH₂CH₂OEt), 15.32 (OCH₂CH₃). EIMS: C₁₈H₁₂OS m/z 156 (M⁺).

(Z)-1-Methoxyoctadec-9-ene. Compound **2** (0.0150 g, 0.0123 mmol) dissolved in chloroform (3 mL) was added to methyl oleate (0.417 mL, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was heated to 60 °C for 72 h and filtered through a short plug of celite (5 mL). The celite was extracted with chloroform (3 mL × 2), the colorless filtrates were combined, and the mixture was separated by distillation. The product distilled at 200 °C (0.1 mmHg) as a colorless liquid (0.215 g, 0.761 mmol, 61.9%) to give a substance with NMR spectroscopic properties that matched the literature report.⁶ ¹H NMR (chloroform-*d*, 600 MHz): δ 5.36 (m, 2 H, CH=CH), 3.37 (t, ³J_{HH} = 6.6 Hz, 2 H, CH₂OMe), 3.34 (s, 3 H, OMe), 2.03 (m, 4 H, CH₂CH=CHCH₂), 1.57 (m, 2 H, CH₂CH₂OMe), 1.3 (br, 22 H, CH₃(CH₂)₆CH₂CH=CHCH₂(CH₂)₅CH₂CH₂OMe), 0.89 (t, ³J_{HH} = 6.6 Hz, 3 H, CH₃(CH₂)₇CH=CH(CH₂)₈OMe). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 130.08 (*cis*-CH=CH), 130.00 (*cis*-CH=CH), 73.13 (CH₂OMe), 58.69 (OMe), 32.07 (CH₃CH₂CH₂), 29.93-29.33 (CH₃CH₂CH₂(CH₂)₄CH₂CH=CHCH₂(CH₂)₆CH₂OMe), 27.37 (CH₂CH=CHCH₂), 26.30

(CH₂CH=CHCH₂), 22.84 (CH₃CH₂(CH₂)₆CH=CH(CH₂)₈OMe), 14.27
(CH₃(CH₂)₇CH=CH(CH₂)₈OMe). EIMS: C₁₉H₃₈O m/z 283 (M⁺).

(E)-5-Methoxypent-2-ene. A chloroform-*d* solution of **2** (0.0010 g, 0.000819 mmol) was added to methyl *trans*-3-pentenoate (10.0 μL, 0.0815 mmol), phenylsilane (20.2 μL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The solution was heated to 80 °C, and the conversion of ester to ether was monitored with ¹H NMR spectroscopy. The ester was completely consumed after 24 h to give the product in 64.9% yield.⁷ ¹H NMR (chloroform-*d*, 600 MHz): δ 5.48-5.53 (m, 2 H, CH=CH), 3.42 (t, ³J_{HH} = 10.2 Hz, 2 H, CH₂OMe), 3.37 (s, 3 H, OMe), 2.31 (m, 2 H, CH₂CH₂OMe), 1.69 (m, 3 H, CH₃CH=CH).

Tetrahydrofuran. A methylene chloride solution (3 mL) of **2** (0.0150 g, 0.0123 mmol) was added to γ-butyrolactone (0.100 mL, 1.30 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The resulting mixture was stirred at room temperature for 8 h and filtered through a short plug of celite (5 mL). The product was distilled at 65 °C (760 mmHg) to give a sample of THF (0.0520 g, 0.721 mmol, 55.4%) that matched authentic samples of tetrahydrofuran by ¹H and ¹³C{¹H} NMR spectroscopy. ¹H NMR (chloroform-*d*, 600 MHz): δ 3.7 (br, 4 H, 2,5H-C₄H₈O), 1.8 (br, 4 H, 3,4H-C₄H₈O). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 68.08 (2,5C-C₄H₈O), 25.73 (3,4C-C₄H₈O). EIMS: C₄H₈O m/z 72 (M⁺).

1,1,1-Trifluoro-2-(2,2,2-trifluoroethoxy)ethane. A chloroform-*d* solution (0.5 mL) of **2** (0.0010 g, 0.000819 mmol) was added to trifluoroacetic anhydride (5.7 μL, 0.041 mmol), phenylsilane (20.2 μL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The reaction progress was monitored using ¹H NMR spectroscopy which indicated the anhydride was consumed after 6 h and provides the ether in 50.1% yield.⁸ ¹H NMR (chloroform-*d*, 600 MHz): δ 3.84 (q, ³J_{HF} = 8.0 Hz, CH₂). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 124.10 (q, J_{CF} = 277.5 Hz, CH₂CF₃), 63.51 (q, J_{CF} = 36.0 Hz, CH₂CF₃). ¹⁹F NMR (chloroform-*d*, 376 MHz): δ -76.36 (t, ³J_{HF} = 8.6 Hz, CF₃).

Trimethylamine. A chloroform-*d* solution (0.5 mL) of **2** (0.0010 g, 0.000819 mmol) was added to *N,N*-dimethylformamide (6.3 μL, 0.0814 mmol), phenylsilane (20.2 μL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The solution was heated to 80 °C, and the progress was monitored through ¹H NMR. All amide was consumed after 3 h to give 85.4% yield of

NMe₃. The spectra matched the literature report.⁹ ¹H NMR (chloroform-*d*, 600 MHz): δ 2.24 (s, Me). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 47.84 (Me).

***N,N*-Dimethylbenzylammonium chloride.** A chloroform solution (3 mL) of **2** (0.0150 g, 0.0123 mmol) was added to *N,N*-dimethylbenzamide (0.183 g, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was heated to 80 °C for 24 h and filtered through a short plug of celite (5 mL). The celite was washed with diethyl ether (2 × 3 mL), the extracts were combined, and a diethyl ether solution of hydrochloric acid (2.0 M, 5 mL) was added. The solvent was evaporated from the slightly cloudy solution, and the residual white solid was washed with diethyl ether (3 × 5 mL) and dried under vacuum to give the product as a white solid (0.168 g, 0.979 mmol, 79.6%). The NMR spectra of this material matched the literature report.¹⁰ ¹H NMR (chloroform-*d*, 600 MHz): δ 12.8 (br, 1 H, NH), 7.6 (br, 2 H, C₆H₅), 7.5 (br, 3 H, C₆H₅), 4.17 (s, 2 H, CH₂Ph), 2.75 (s, 6 H, Me). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 131.20 (C₆H₅), 130.41 (C₆H₅), 129.59 (C₆H₅), 128.51 (C₆H₅), 61.39 (CH₂Ph), 42.29 (Me). EIMS: C₉H₁₄N m/z 135 (M⁺-Cl). For *N,N*-dimethyl-1-phenylmethanamine, a chloroform-*d* solution (0.5 mL) of **2** (0.0010 g, 0.000819 mmol) was added to *N,N*-dimethylbenzamide (0.0122 g, 0.0818 mmol), phenylsilane (20.2 μL, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The solution was heated to 80 °C, and the reaction progress was monitored using ¹H NMR spectroscopy which indicated the amide was consumed after 24 h (86.3%). ¹H NMR (chloroform-*d*, 600 MHz): δ 7.31-7.20 (m, 5 H, C₆H₅), 3.37 (s, 2 H, CH₂), 2.20 (s, 6 H, Me).

Ethylbenzene. A methylene chloride solution (3 mL) of **2** (0.0150 g, 0.0123 mmol) was added to a mixture of acetophenone (0.140 mL, 1.20 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was stirred at room temperature for 7 h and filtered through a short plug of celite (5 mL), which was extracted with methylene chloride (2 × 3 mL). The colorless filtrates were combined, and the mixture was separated by distillation. The product was distilled at 132 °C (760 mmHg) as a colorless liquid (0.0739 g, 0.696 mmol, 58.0%). The spectra matched those acquired from an authentic sample of ethylbenzene. ¹H NMR (chloroform-*d*, 600 MHz): δ 7.34 (m, 2 H, C₆H₅), 7.23 (m, 3 H, C₆H₅), 2.70 (m, 2 H, CH₂CH₃), 1.30 (m, 3 H, CH₂CH₃). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 144.38 (*ipso*-C₆H₅), 128.44 (*m*-C₆H₅), 127.99 (*o*-C₆H₅), 125.72 (*p*-C₆H₅), 29.03 (CH₂CH₃), 15.76 (CH₂CH₃). EIMS: C₈H₁₀ m/z 106 (M⁺).

2-Ethyl-1,3-dimethoxybenzene. A methylene chloride solution (3 mL) of **2** (0.0150 g, 0.0123 mmol) was added to a mixture of 2',6'-dimethoxyacetophenone (0.220 g, 1.22 mmol) and phenylsilane (3.10 mL, 25.1 mmol). The reaction mixture was stirred at room temperature for 24 h and then was filtered through a short plug of celite (5 mL). The celite was extracted with methylene chloride (2 × 3 mL), the colorless filtrates were combined, and the product was isolated through column chromatography (ethyl acetate:hexane = 1:9, $R_f = 0.85$) as a white solid (0.112 g, 0.674 mmol, 55.2%). The NMR spectra of the isolated material matched the literature report.¹¹ ¹H NMR (chloroform-*d*, 600 MHz): δ 7.13 (t, $^3J_{\text{HH}} = 8.4$ Hz, 1 H, 5H-C₆H₃), 6.56 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2 H, 4,6H-C₆H₃), 3.83 (s, 6 H, OMe), 2.68 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, CH₂CH₃), 1.10 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H, CH₂CH₃). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 158.27 (1,3C-C₆H₃), 126.55 (5C-C₆H₃), 121.07 (2C-C₆H₃), 103.91 (4,6-C₆H₃), 55.88 (OMe), 16.43 (CH₂CH₃), 13.93 (CH₂CH₃). EIMS: C₁₀H₁₄O₂ *m/z* 166 (M⁺).

1,3,5-Trimethoxy-2-methylbenzene. A methylene chloride solution of cationic rhodium complex **1** (0.0150 g, 0.0123 mmol, 3 mL) was added to 2,4,6-trimethoxybenzaldehyde (0.241 g, 1.23 mmol) and phenylsilane (0.310 mL, 2.51 mmol). The solution was stirred at room temperature for 7 h and filtered through a short plug of celite (5 mL). The celite was washed with methylene chloride (2 × 3 mL), the colorless filtrates were combined, and the mixture was purified by distillation. The product was distilled at 74 °C (0.1 mmHg) as a colorless liquid (0.107 g, 0.587 mmol, 47.8%). The spectra matched the literature report.¹² ¹H NMR (chloroform-*d*, 600 MHz): δ 6.15 (s, 2 H, C₆H₂), 3.82 (s, 9 H, OMe), 2.03 (s, 3 H, Me). ¹³C{¹H} NMR (chloroform-*d*, 150 MHz): δ 159.07 (5C-C₆H₂), 158.95 (1,3C-C₆H₂), 106.94 (2C-C₆H₂), 90.68 (4,6C-C₆H₂), 55.86 (1,3-OMe), 55.52 (5-OMe), 7.80 (Me). EIMS: C₁₀H₁₄O₃ *m/z* 182 (M⁺).

1,3-Dimethoxy-2-methylbenzene. A chloroform-*d* solution (0.5 mL) of **2** (0.0010 g, 0.000819 mmol) was added to 2,6-dimethoxybenzaldehyde (0.0136 g, 0.0818 mmol), phenylsilane (20.2 μ L, 0.163 mmol), and Si(SiMe₃)₄ (0.314 M) as an internal standard. The progress was monitored through ¹H NMR, and all aldehyde was consumed after 4 h to give the hydrocarbon in 77% yield. The products spectra matched the literature report.¹¹ ¹H NMR (chloroform-*d*, 600 MHz): δ 7.15 (t, $^3J_{\text{HH}} = 8.4$ Hz, 1 H, 5H-C₆H₃), 6.57 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2 H, 4,6H-C₆H₃), 3.85 (s, 6 H, OMe), 2.14 (s, 3 H, Me). ¹³C NMR (chloroform-*d*, 150 MHz): δ 158.53 (1,3C-C₆H₃), 128.41

(5C-C₆H₃), 114.67 (2C-C₆H₃), 103.67 (4,6C-C₆H₃), 55.86 (OMe), 8.27 (Me). EIMS: C₉H₁₂O₂ m/z 152 (M⁺).

Computational Details. Structure optimizations were performed in TURBOMOLE¹³ using B3LYP¹⁴ density functional theory. The Stuttgart 1997 relativistic small core basis set plus effective core potential (ECP)¹⁵ was used for Rh, and the 6-311G(d,p) basis set¹⁶ was used for all other atoms. NMR calculations were performed in NWChem¹⁷ using the gauge independent atomic orbital method.¹⁸ The same level of theory and basis sets were used as for the structure optimizations except an all electron basis, ATZP¹⁹ was used for Rh. NMR results for both the ATZP and Stuttgart (with ECP) basis sets are reported below.

Table S1. Comparison of calculated and experimental NMR chemical shifts, with ATZP basis set on Rh.

Complex	Nuclei	shielding	shift (ppm)	expt (ppm)	difference
1-A	Si	326.56	13.92	-21	-34.92
	H (Si)	26.89	5.11	4.23	-0.88
	H (Si)	26.47	5.52	4.68	-0.84
	H (Rh)	39.04	-7.04	-13.36	-6.32
	N (tr Si)	5.55	-150.78	-161	-10.22
	N (tr H)	14.96	-160.18	-172	-11.82
	C (CO)	-33.50	217.64	194.53	-23.11
C (carbene)	-16.60	200.74	178.39	-22.35	
2-A	Si	-30.01	370.48	6.5	-363.98
	H (Si)	23.93	8.07	5.15	-2.92
	H (Rh)	38.21	-6.21	-12.92	-6.71
	N (tr Si)	21.98	-167.21		
	N (tr H)	21.13	-166.35		
	C (CO)	-27.07	211.21	186.33	-24.88
	C (carbene)	-10.10	194.25	169.23	-25.02
2-B	Si	267.52	72.96	6.5	-66.46
	H (Si)	25.98	6.02	5.15	-0.87
	H (Rh)	38.43	-6.43	-12.92	-6.49
	N (bond Si)	46.21	-191.43	-199	-7.57
	N (bond Rh)	7.39	-152.61	-167	-14.39
	C (CO)	-22.87	207.01	186.33	-20.68
	C (carbene)	-6.39	190.53	169.23	-21.30

Table S2. Comparison of calculated and experimental NMR chemical shifts, with Stuttgart basis set and ECP on Rh.

Complex	Nuclei	shielding	shift (ppm)	expt (ppm)	difference
1-A	Si	331.82	8.65	-21	-29.65
	H (Si)	26.77	5.22	4.23	-0.99
	H (Si)	26.69	5.31	4.68	-0.63
	H (Rh)	40.47	-8.47	-13.36	-4.89
	N (tr Si)	5.35	-150.57	-161	-10.43
	N (tr H)	13.43	-158.65	-172	-13.35
	C (CO)	-29.75	213.89	194.53	-19.36
	C (carbene)	-20.67	204.81	178.39	-26.42
2-A	Si	-18.85	359.32	6.5	-352.82
	H (Si)	23.93	8.07	5.15	-2.92
	H (Rh)	38.42	-6.42	-12.92	-6.50
	N (tr Si)	20.05	-165.28		
	N (tr H)	20.88	-166.10		
	C (CO)	-30.28	214.43	186.33	-28.10
	C (carbene)	-9.18	193.32	169.23	-24.09
	2-B	Si	261.20	79.28	6.5
H (Si)		26.62	5.38	5.15	-0.23
H (Rh)		41.65	-9.65	-12.92	-3.27
N (bond Si)		48.30	-193.52	-199	-5.48
N (bond Rh)		6.70	-151.92	-167	-15.08
C (CO)		-26.68	210.82	186.33	-24.49
C (carbene)		-7.05	191.19	169.23	-21.96

Table S3. Reference compounds and shieldings used in calculated NMR shifts.

Compound	Nuclei	shielding (ppm)
tetramethylsilane	Si	340.48
	C	184.14
	H	32.00
nitromethane	N	-145.23

Table S4. Coordinates (Å) for optimized geometry of {PhB(Ox^{Me2})₂Im^{Mes}}RhH(SiH₂Ph)CO (**1-A**).

87 atoms

Rh	8.035129	21.048910	4.018572
H	6.519867	21.327832	4.197061
Si	7.296003	19.381528	2.494723
H	7.564135	19.704933	1.065240
H	8.097154	18.130712	2.713460
B	10.298787	23.452857	3.590013
C	11.140802	19.134141	2.065680
H	10.144750	18.759678	1.829318
H	11.851573	18.308654	1.955030
H	11.399487	19.910388	1.340627
C	11.194506	19.690523	3.497677
C	10.903271	18.598890	4.526515
H	10.862988	19.013951	5.536540
H	11.692433	17.840591	4.500749
H	9.957058	18.100001	4.313249
C	12.545631	20.386570	3.768639
H	12.881288	20.265131	4.803558
H	13.342235	20.083315	3.088946
C	10.931180	21.945104	3.565764
C	6.817045	23.119592	7.058541
H	6.410673	23.883854	6.392070
H	6.572098	23.394405	8.089451
H	6.323655	22.172296	6.832126
C	8.331879	22.996032	6.883697
C	8.905762	21.905426	7.802069
H	8.451633	20.935286	7.600878
H	8.710509	22.156012	8.849615
H	9.986909	21.815596	7.667126
C	9.058096	24.344324	7.111786
H	8.376099	25.199383	7.084193
H	9.647039	24.378504	8.028780
C	9.602749	23.532603	5.075841
C	8.830681	24.471385	1.651007
H	9.533210	25.267554	1.482289
C	7.631045	24.223954	1.078277
H	7.079027	24.749572	0.318569
C	5.849921	22.532376	1.296701
C	5.720725	21.846260	0.080139
C	6.886371	21.645477	-0.858648
H	6.719960	20.772234	-1.492443
H	7.825733	21.505181	-0.324771
H	7.008353	22.512776	-1.517551

C	4.452138	21.385713	-0.281244
H	4.344094	20.835813	-1.211310
C	3.329376	21.610292	0.513226
C	1.981452	21.051752	0.128809
H	1.168663	21.698691	0.468695
H	1.833922	20.067203	0.585595
H	1.891992	20.931114	-0.953515
C	3.489323	22.348577	1.687484
H	2.620598	22.562838	2.302595
C	4.733220	22.829192	2.095358
C	4.851371	23.679899	3.335790
H	5.461572	23.191466	4.098324
H	3.864349	23.877372	3.758079
H	5.325060	24.640989	3.113014
C	8.030842	22.595706	2.596707
C	11.351280	24.614047	3.182917
C	11.359799	25.893597	3.764377
H	10.689975	26.109948	4.585996
C	12.219827	26.900361	3.322825
H	12.198600	27.873723	3.803216
C	13.101819	26.661365	2.273013
H	13.772631	27.441819	1.928829
C	13.113194	25.404400	1.671096
H	13.795417	25.199897	0.851807
C	12.252989	24.405789	2.121825
H	12.292924	23.436416	1.637699
C	7.829487	19.688430	5.324748
C	5.494339	18.764373	2.577456
C	5.067110	17.842281	1.605412
H	5.746836	17.543270	0.812023
C	3.787501	17.293220	1.634127
H	3.486447	16.581292	0.872159
C	2.896059	17.654324	2.644708
H	1.900575	17.223565	2.674751
C	3.295532	18.568392	3.616109
H	2.609371	18.855841	4.406400
C	4.578775	19.115925	3.578054
H	4.866421	19.832069	4.340086
N	10.252597	20.851047	3.612064
N	8.693887	22.709316	5.464583
N	9.067124	23.469682	2.578212
N	7.138593	23.063109	1.666953
O	12.276633	21.791755	3.552637
O	9.965534	24.465846	5.989079
O	7.611882	18.881107	6.106389

Energy: -6803.357051 hartree (ATZP basis on Rh)

Table S5. Coordinates (Å) for Optimized geometry of [$\{\text{PhB}(\text{Ox}^{\text{Me}_2})_2\text{Im}^{\text{Mes}}\}\text{RhH}(\text{SiHPh})\text{CO}]^+$ (2-A).

86 atoms

Rh	7.995679	21.192349	4.053982
H	6.545793	21.591063	4.464559
Si	6.832424	20.011493	2.488178
H	7.408982	19.519996	1.209316
C	10.338046	23.502179	3.622782
C	10.731747	19.205606	1.762994
H	9.696284	18.882475	1.639112
H	11.379059	18.354620	1.532132
H	10.933980	19.996536	1.036175
C	10.988807	19.697176	3.194948
C	10.761695	18.575255	4.207515
H	10.853187	18.942320	5.232343
H	11.506027	17.786644	4.064206
H	9.778586	18.116337	4.083138
C	12.403928	20.304206	3.333911
H	12.865914	20.085758	4.300157
H	13.085954	20.023941	2.531903
C	10.880150	21.964189	3.427363
C	7.044570	23.730702	6.887942
H	7.115534	24.636693	6.280679
H	6.742041	24.017565	7.899190
H	6.262824	23.093820	6.468225
C	8.386556	22.985881	6.924570
C	8.306790	21.760336	7.834556
H	7.445813	21.135757	7.591539
H	8.189882	22.078463	8.874613
H	9.214995	21.156727	7.767417
C	9.545008	23.919342	7.345854
H	9.219815	24.831294	7.845292
H	10.294034	23.411891	7.958899
C	9.736333	23.462815	5.146590
C	8.800567	24.599773	1.732742
H	9.493988	25.403914	1.559122
C	7.614340	24.316309	1.141179
H	7.069846	24.815206	0.358167
C	5.954641	22.453306	1.332745
C	5.998017	21.714517	0.125503
C	7.251243	21.608210	-0.708818
H	7.243801	20.690181	-1.298742
H	8.161861	21.629789	-0.109878
H	7.306311	22.447038	-1.410515
C	4.805732	21.145568	-0.337053

H	4.828948	20.570481	-1.256904
C	3.594666	21.324815	0.326822
C	2.322819	20.701647	-0.185647
H	2.018088	19.870065	0.458157
H	2.443965	20.315039	-1.198614
H	1.503906	21.425546	-0.190327
C	3.578664	22.113339	1.487465
H	2.633668	22.291591	1.990225
C	4.726976	22.704699	1.997179
C	4.657327	23.629935	3.183004
H	5.302901	23.293910	3.997450
H	3.635331	23.699571	3.556702
H	4.988794	24.636728	2.911221
C	8.021429	22.756301	2.711286
C	11.377309	24.674934	3.256475
C	11.331745	25.936922	3.876285
H	10.644331	26.110075	4.694519
C	12.162687	26.983582	3.478113
H	12.103753	27.940348	3.986291
C	13.068122	26.802796	2.435981
H	13.718803	27.613675	2.127309
C	13.130751	25.566822	1.796744
H	13.832605	25.410445	0.984266
C	12.297447	24.526038	2.201986
H	12.379470	23.574944	1.689320
C	7.869457	19.719342	5.315292
C	5.269848	19.061494	2.747612
C	4.902585	18.075492	1.808591
H	5.502329	17.926638	0.916805
C	3.780532	17.279244	2.015292
H	3.515337	16.516675	1.291996
C	3.000220	17.462475	3.156921
H	2.126785	16.840782	3.319246
C	3.341208	18.439621	4.094211
H	2.732521	18.576320	4.980648
C	4.466404	19.230040	3.892974
H	4.726329	19.982841	4.629354
N	10.139227	20.904235	3.470196
N	8.805585	22.648227	5.523375
N	9.041242	23.626677	2.689583
N	7.135749	23.158152	1.753120
O	12.192626	21.737684	3.264636
O	10.184443	24.294372	6.097147
O	7.718932	18.847860	6.028721

Energy: -6802.554917 hartree (ATZP basis on Rh)

Table S6. Coordinates (Å) for optimized geometry of [$\{\kappa^3\text{-N,Si,C-PhB}(\text{Ox}^{\text{Me}_2})(\text{Ox}^{\text{Me}_2}\text{SiHPh})\text{Im}^{\text{Mes}}\}\text{Rh}(\text{H})\text{CO}]^+$ (**2-B**).

86 atoms

Rh	6.865600	21.644470	3.970221
H	5.874576	21.115943	2.878378
Si	8.097435	20.114547	2.786408
H	8.054880	20.271180	1.314714
C	9.960720	23.124209	3.474714
C	11.137707	19.022945	1.434233
H	10.224508	18.574895	1.038050
H	11.953309	18.313940	1.268295
H	11.351556	19.932464	0.867457
C	11.006194	19.313197	2.934987
C	10.804519	18.026468	3.736224
H	10.545901	18.238730	4.775386
H	11.749677	17.474636	3.732914
H	10.043817	17.380062	3.307071
C	12.224646	20.068417	3.485350
H	12.464994	19.797608	4.515441
H	13.114520	19.980752	2.863640
C	10.520077	21.558817	3.329994
C	6.794584	23.362193	7.302627
H	6.662607	24.336143	6.825644
H	6.769468	23.505989	8.386509
H	5.945336	22.727780	7.036291
C	8.117134	22.720026	6.879260
C	8.290459	21.328231	7.503803
H	7.479630	20.656190	7.221609
H	8.289082	21.407291	8.594531
H	9.238394	20.877745	7.197408
C	9.332296	23.619810	7.202447
H	9.051450	24.654284	7.415183
H	9.964807	23.241797	8.004345
C	9.347941	23.130197	4.998487
C	8.868665	24.285718	1.374000
H	9.771648	24.816779	1.133415
C	7.647043	24.326210	0.788148
H	7.278695	24.900030	-0.044621
C	5.420094	23.285431	1.221613
C	5.040764	22.522353	0.107438
C	6.052193	21.877377	-0.809927
H	5.575651	21.110329	-1.422229
H	6.870785	21.413778	-0.256377
H	6.497275	22.609224	-1.492130
C	3.675602	22.381802	-0.151322

H	3.367218	21.785926	-1.004555
C	2.702545	22.983379	0.647921
C	1.235717	22.842801	0.323906
H	0.625227	22.838229	1.229618
H	1.034981	21.922411	-0.228102
H	0.894916	23.679063	-0.296103
C	3.124928	23.749237	1.737061
H	2.383292	24.234616	2.363738
C	4.475283	23.920381	2.042962
C	4.880343	24.771036	3.223526
H	5.192284	24.158119	4.077186
C	4.042150	25.385245	3.555490
H	5.713725	25.435441	2.982682
C	7.538012	22.914437	2.528253
C	11.129044	24.216785	3.220393
C	11.098994	25.463860	3.867704
H	10.353212	25.659700	4.628548
C	12.011206	26.474444	3.568599
H	11.958440	27.420415	4.096802
C	12.988183	26.271745	2.597926
H	13.702331	27.053824	2.365521
C	13.035731	25.051956	1.927384
H	13.787671	24.880003	1.164562
C	12.119447	24.048237	2.235801
H	12.187845	23.115295	1.686930
C	5.903940	20.422083	5.144743
C	7.650629	18.322225	3.115907
C	7.294154	17.533157	2.008842
H	7.330311	17.952318	1.008139
C	6.886099	16.209199	2.171625
H	6.615621	15.616970	1.304737
C	6.821926	15.653041	3.446240
H	6.502288	14.625241	3.575521
C	7.162530	16.423779	4.559182
H	7.107796	15.994409	5.553248
C	7.567010	17.743839	4.393965
H	7.830953	18.321751	5.273808
N	9.923860	20.391452	3.132011
N	8.216778	22.631007	5.381636
N	8.791893	23.409929	2.448392
N	6.827071	23.465135	1.502928
O	11.823883	21.458675	3.491042
O	10.116084	23.623875	5.979451
O	5.201635	19.748790	5.732744

Energy: -6802.582444 hartree (ATZP basis on Rh)

Figure S12. ^1H NMR spectrum of benzyl(1-ethoxyethoxy)dimethylsilane from the hydrosilylation reaction of ethyl acetate and benzyldimethylsilane catalyzed by **2**.

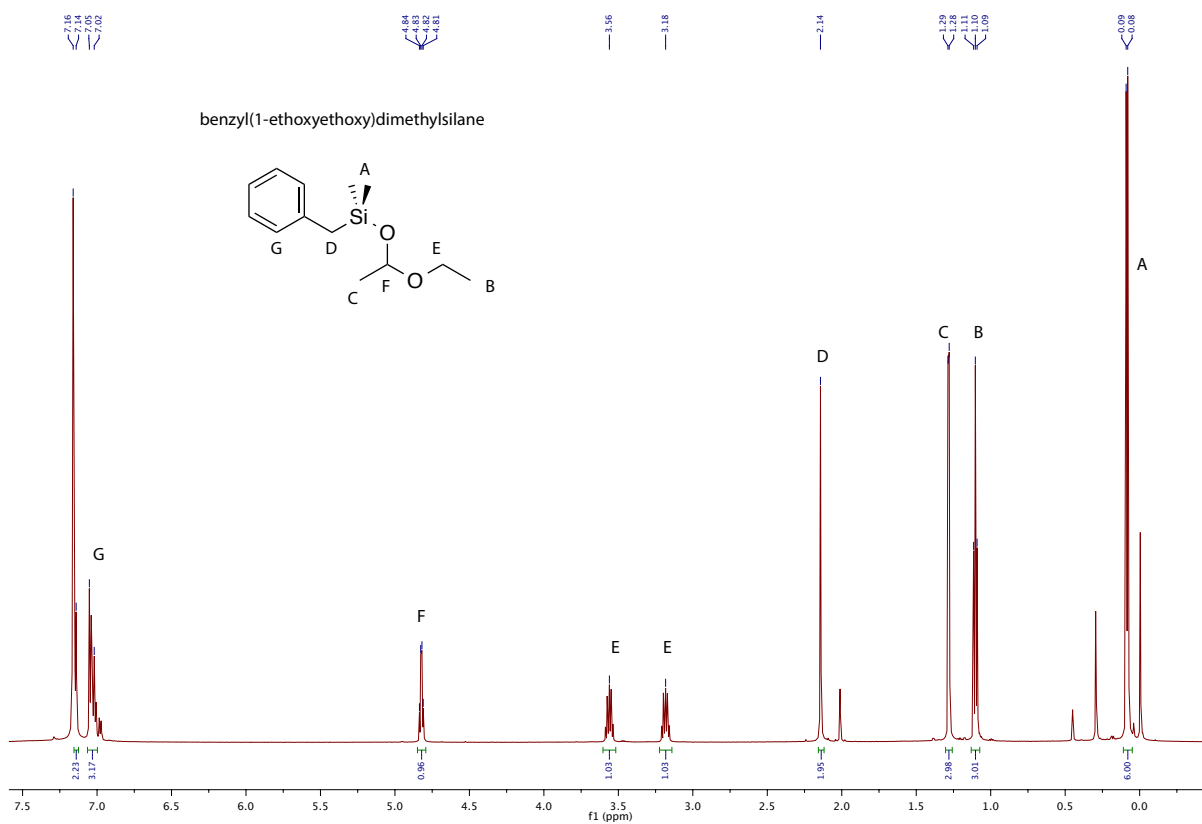


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of benzyl(1-ethoxyethoxy)dimethylsilane from the hydrosilylation reaction of ethyl acetate and benzyldimethylsilane catalyzed by **2**.

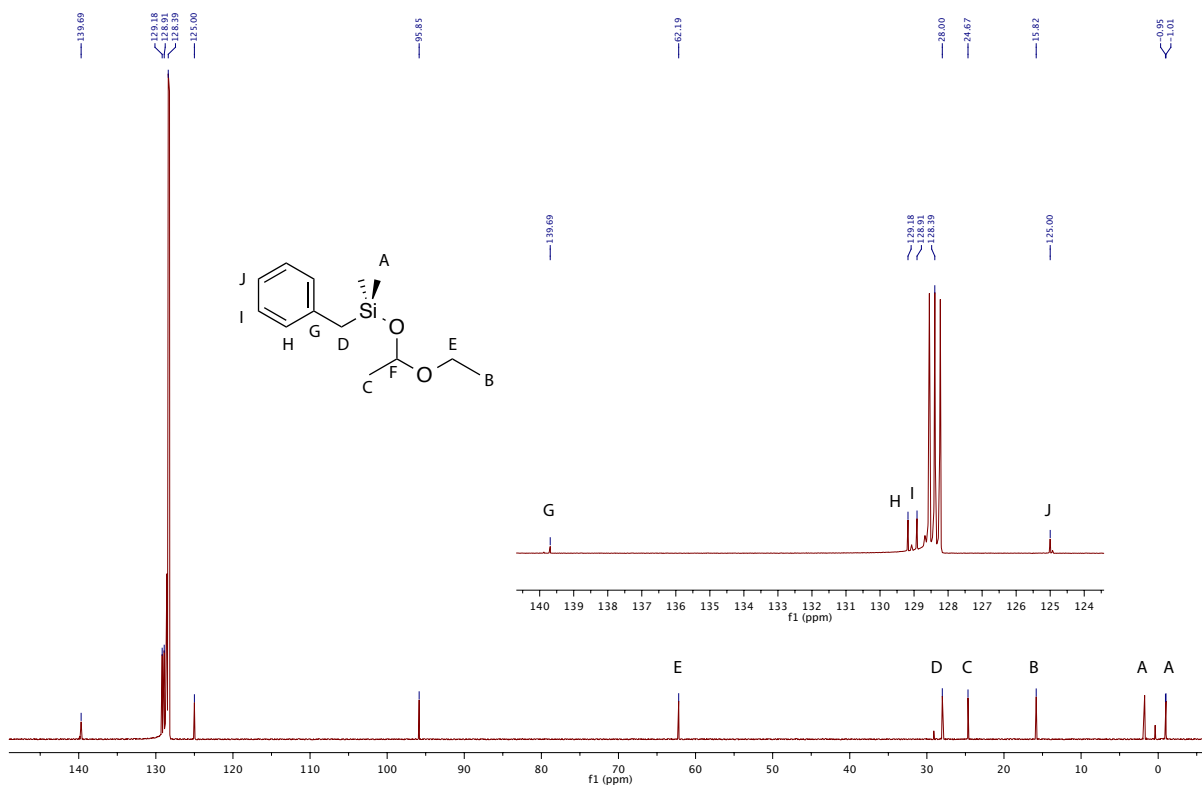


Figure S14. Gas chromatogram of benzyl(1-ethoxyethoxy)dimethylsilane from the hydrosilylation reaction of ethyl acetate and benzyldimethylsilane catalyzed by **2**. Retention time: 8.24 min. Fragmentation: 238.1 (M^+), 193.1 ($M^+ - OCH_2CH_3$), 147.1 ($M^+ - OCH(CH_3)OCH_2CH_3$).

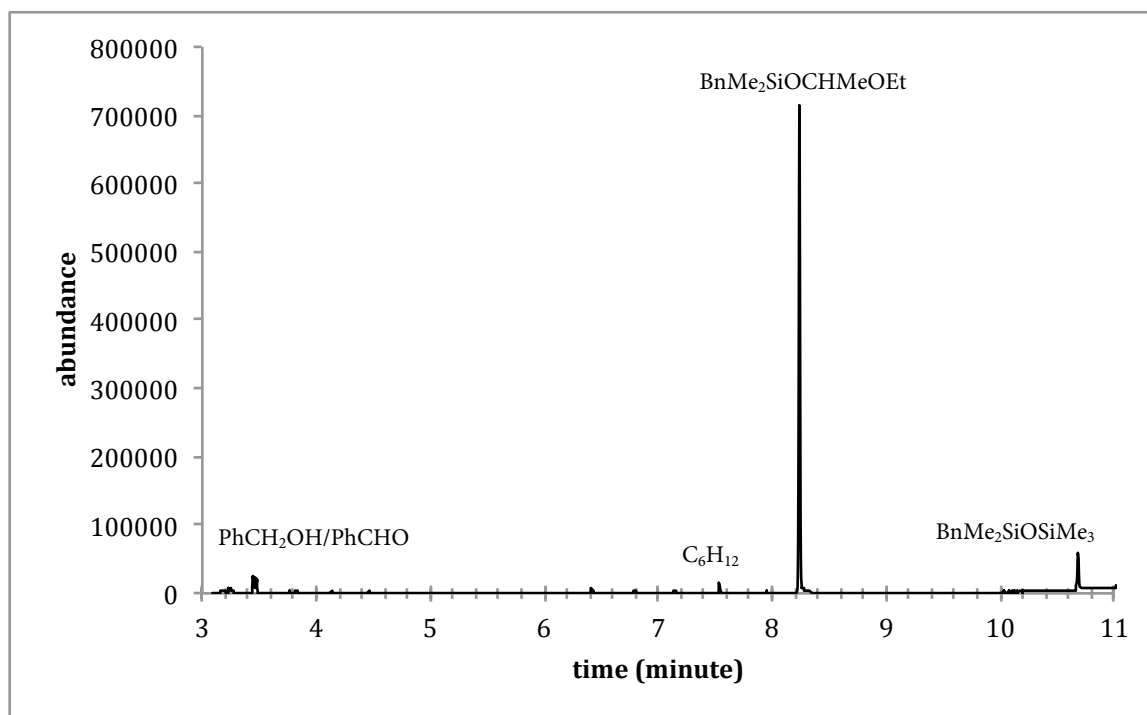


Figure S15. ^1H NMR spectrum of hexadecyl methyl ether from the deoxygenation reaction of methyl palmitate with phenylsilane catalyzed by **2**.

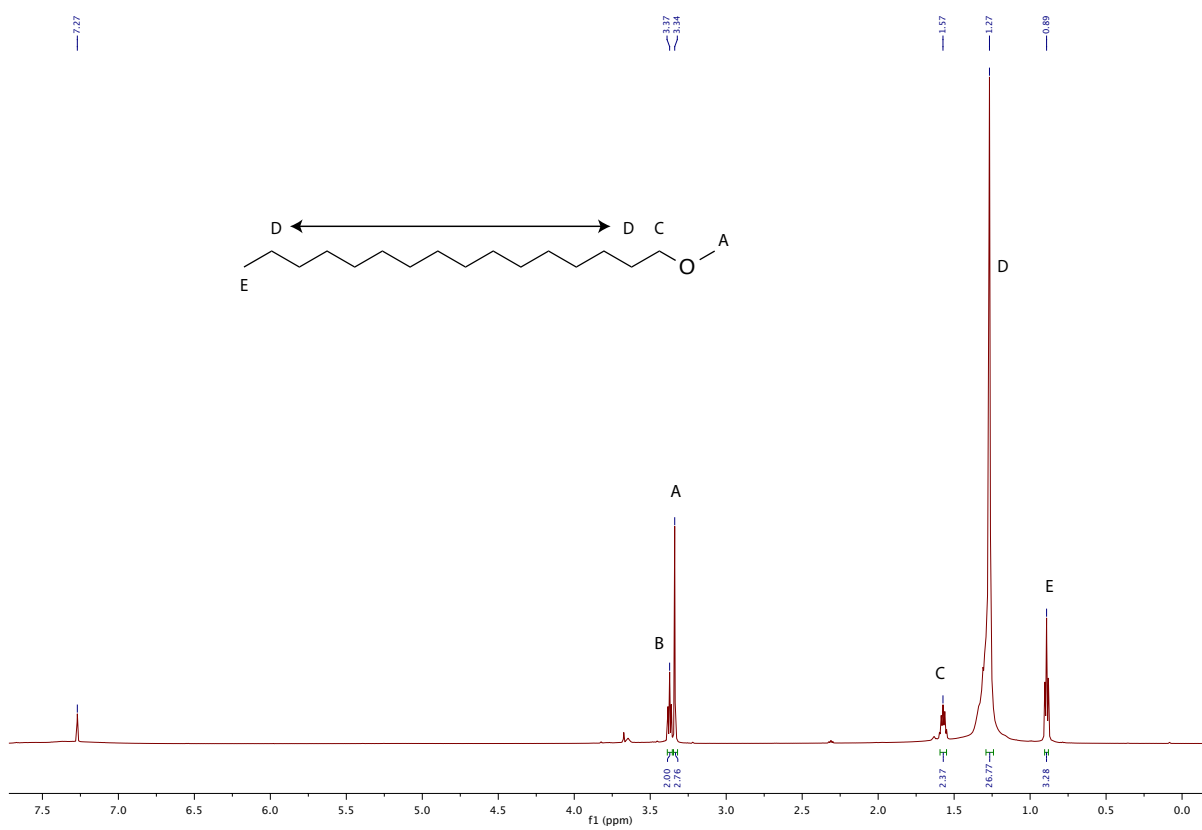


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of hexadecyl methyl ether from the deoxygenation reaction of methyl palmitate with phenylsilane catalyzed by **2**.

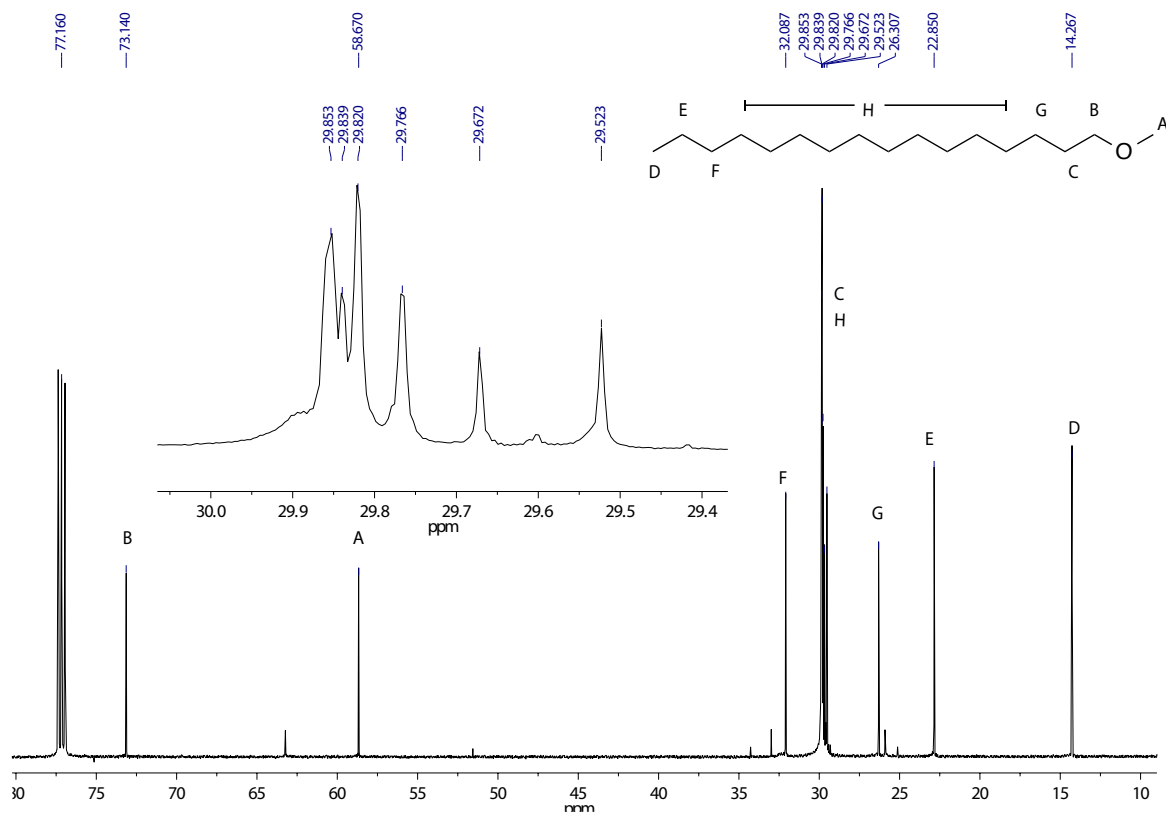


Figure S17. Gas chromatogram of hexadecyl methyl ether from the deoxygenation reaction of methyl palmitate with phenylsilane catalyzed by **2**. Retention time: 9.58 min. Fragmentation: 255.2 (M^+), 224.2 ($M^+ - OCH_3$).

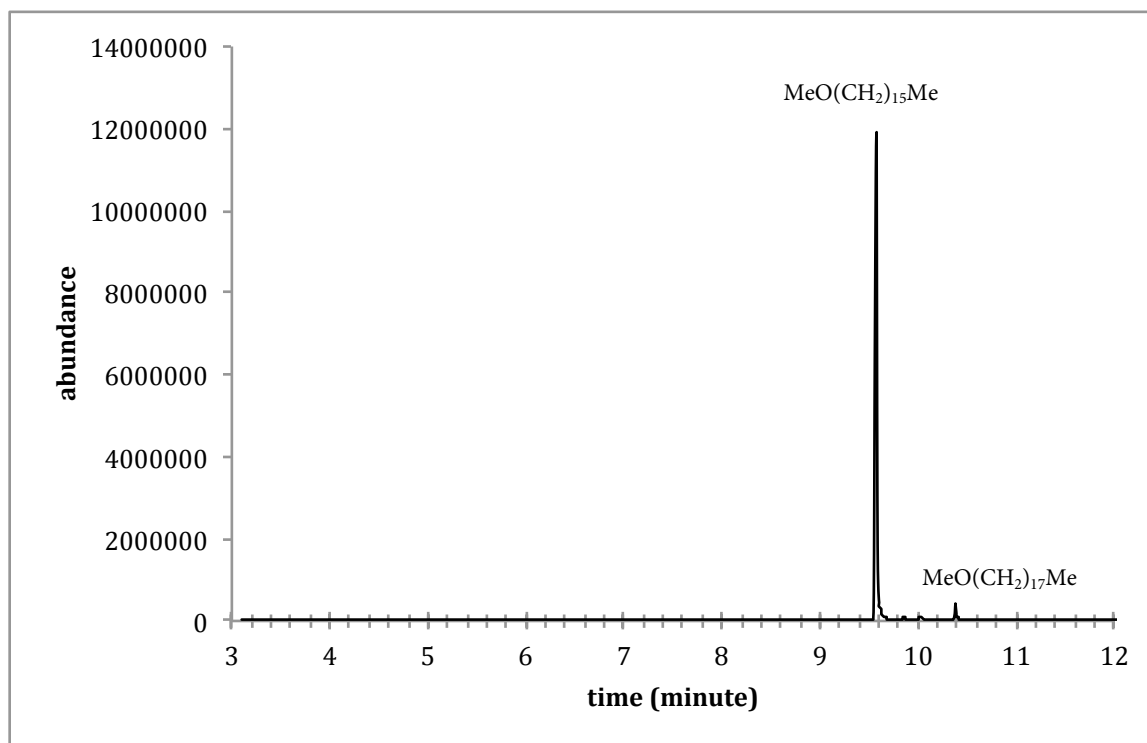


Figure S18. ^1H NMR spectrum of *exo*-2-methoxybicyclo[2.2.1]heptane from the deoxygenation reaction of *exo*-2-norbornylformate with phenylsilane catalyzed by **2**.

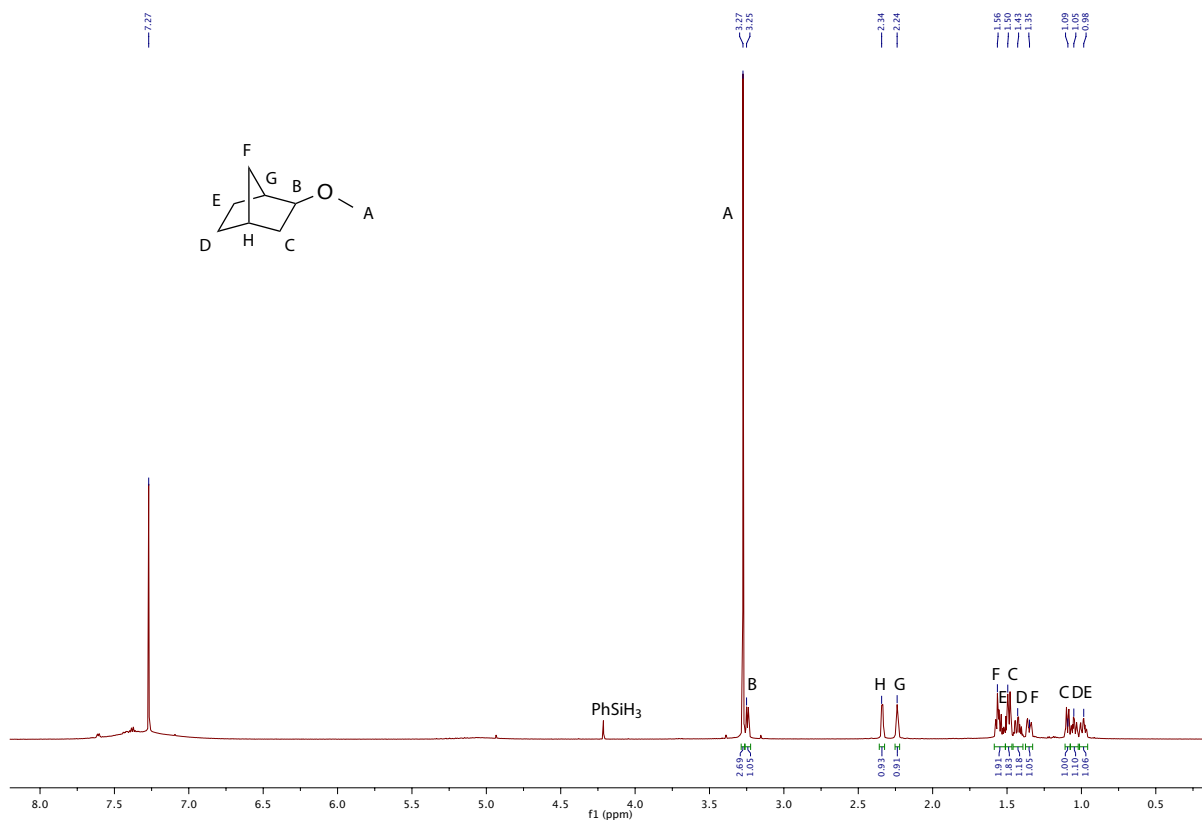


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *exo*-2-methoxybicyclo[2.2.1]heptane from the deoxygenation reaction of *exo*-2-norbornylformate with phenylsilane catalyzed by **2**.

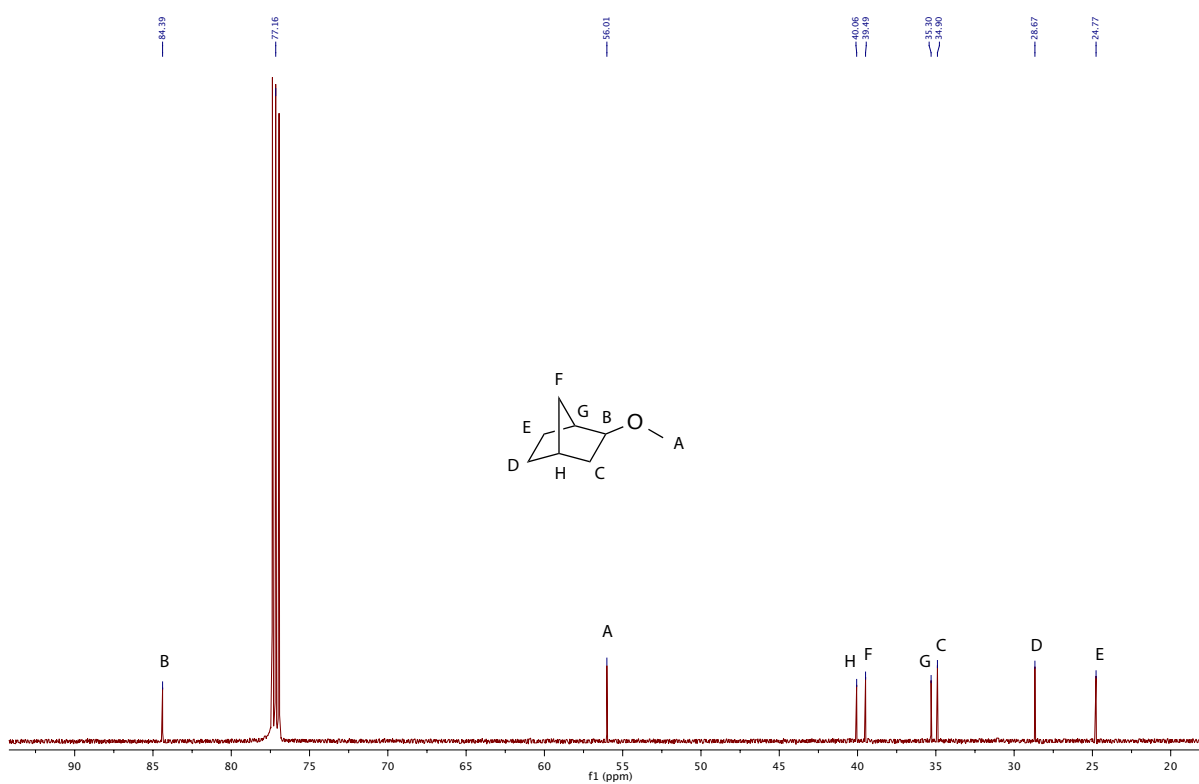


Figure S20. GC chromatograph of *exo*-2-methoxybicyclo[2.2.1]heptane from the deoxygenation reaction of *exo*-2-norbornylformate with phenylsilane catalyzed by **2**. Retention time: 3.46 min. Fragmentation: 126.1 (M^+), 111.1 ($M^+ - CH_3$), 97.0 ($M^+ - OCH_3$).

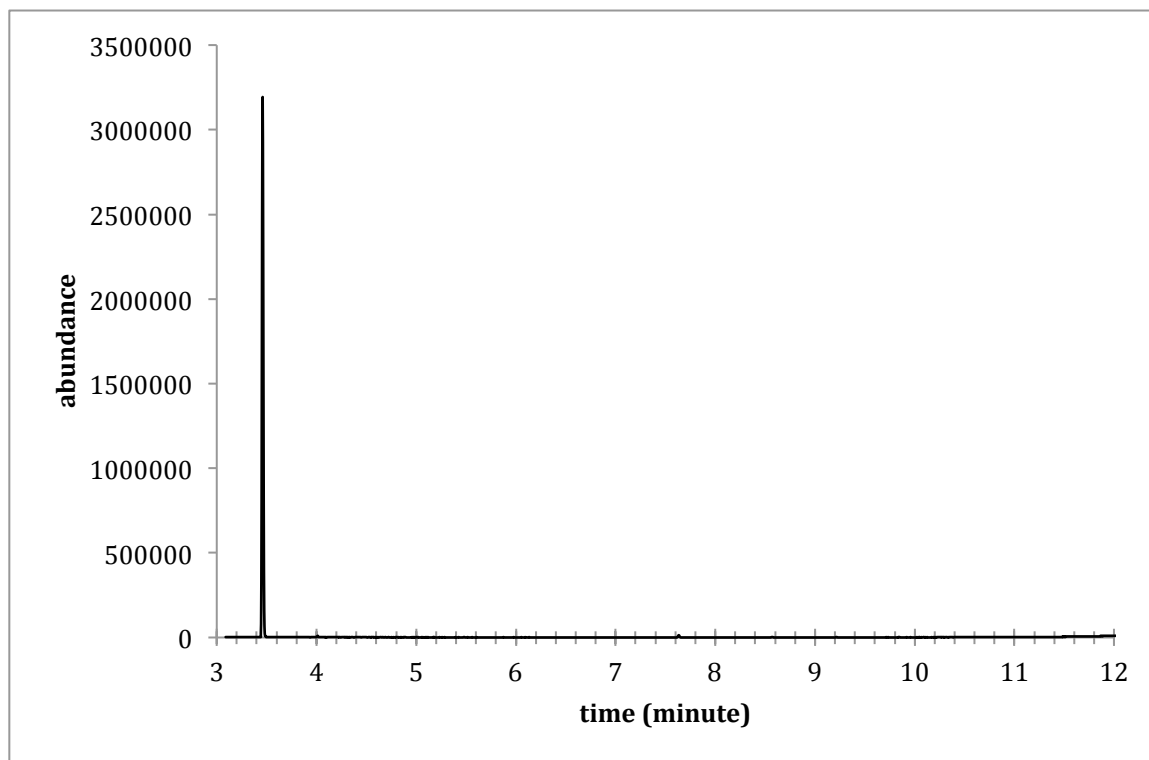


Figure S21. ^1H NMR spectrum of 1-bromo-6-ethoxyhexane from the deoxygenation reaction of ethyl 6-bromohexanoate with phenylsilane catalyzed by **2**. The product was purified by distillation, and GC analysis (Figure S22) confirms the isolated materials is a single product.

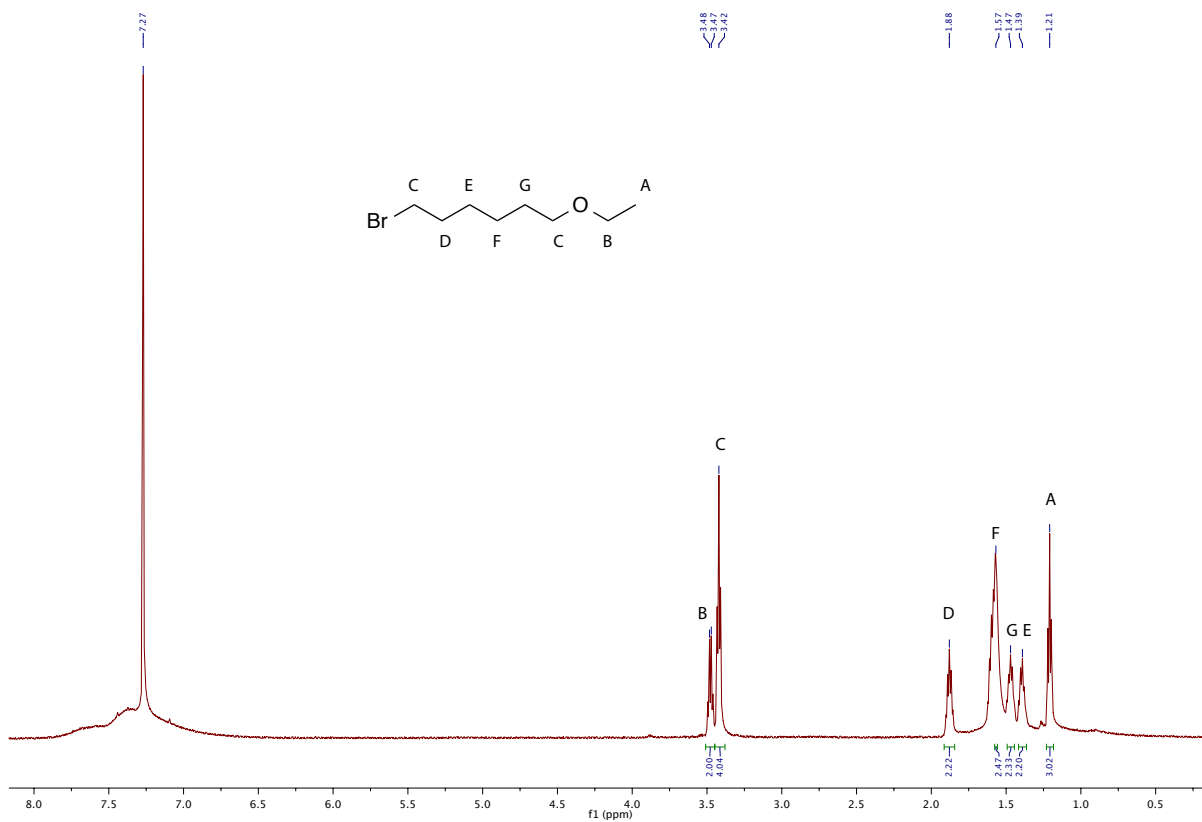


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-bromo-6-ethoxyhexane from the deoxygenation reaction of ethyl 6-bromohexanoate with phenylsilane catalyzed by **2**.

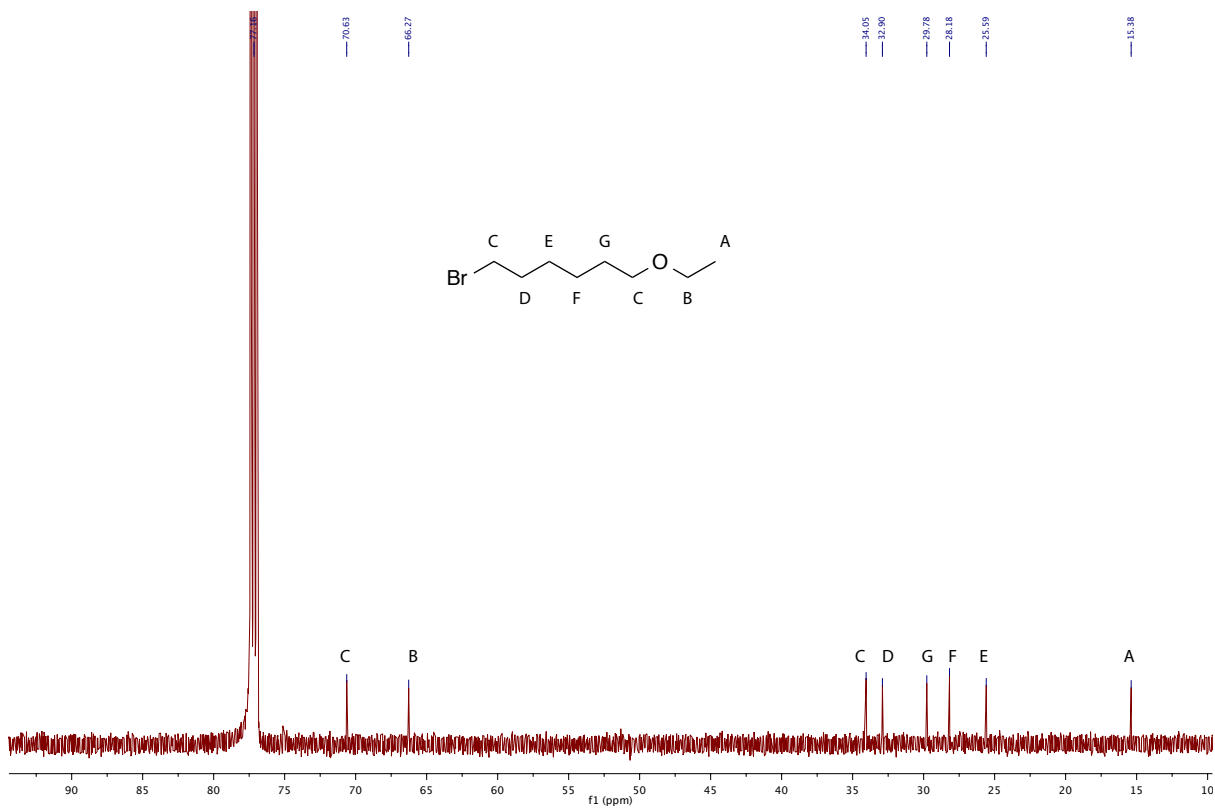


Figure S23. Gas chromatogram of 1-bromo-6-ethoxyhexane from the deoxygenation reaction of ethyl 6-bromohexanoate with phenylsilane catalyzed by **2**. Retention time: 6.12 min. Fragmentation: 209.1 (M^+), 164.0 ($M^+ - OCH_2CH_3$), 83.1 ($M^+ - OCH_2CH_3 - Br$).

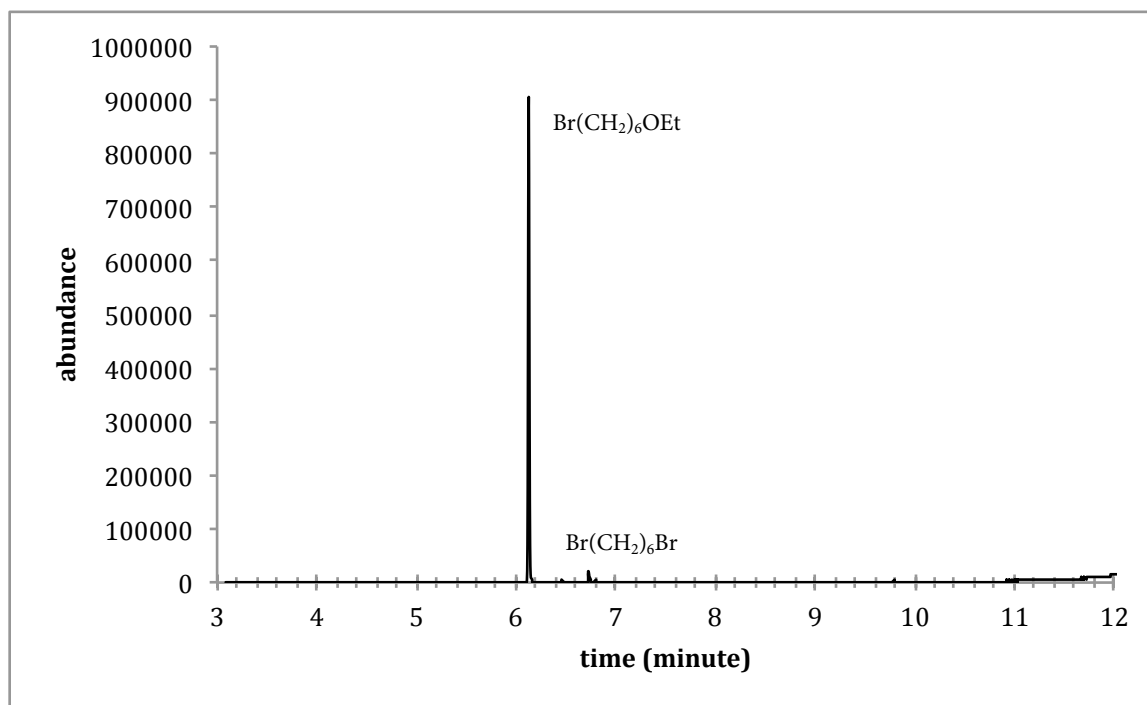


Figure S24. ^1H NMR spectrum of 2-(2-ethoxyethyl)thiophene from the deoxygenation reaction of ethyl 2-thiopheneacetate with phenylsilane catalyzed by **2**.

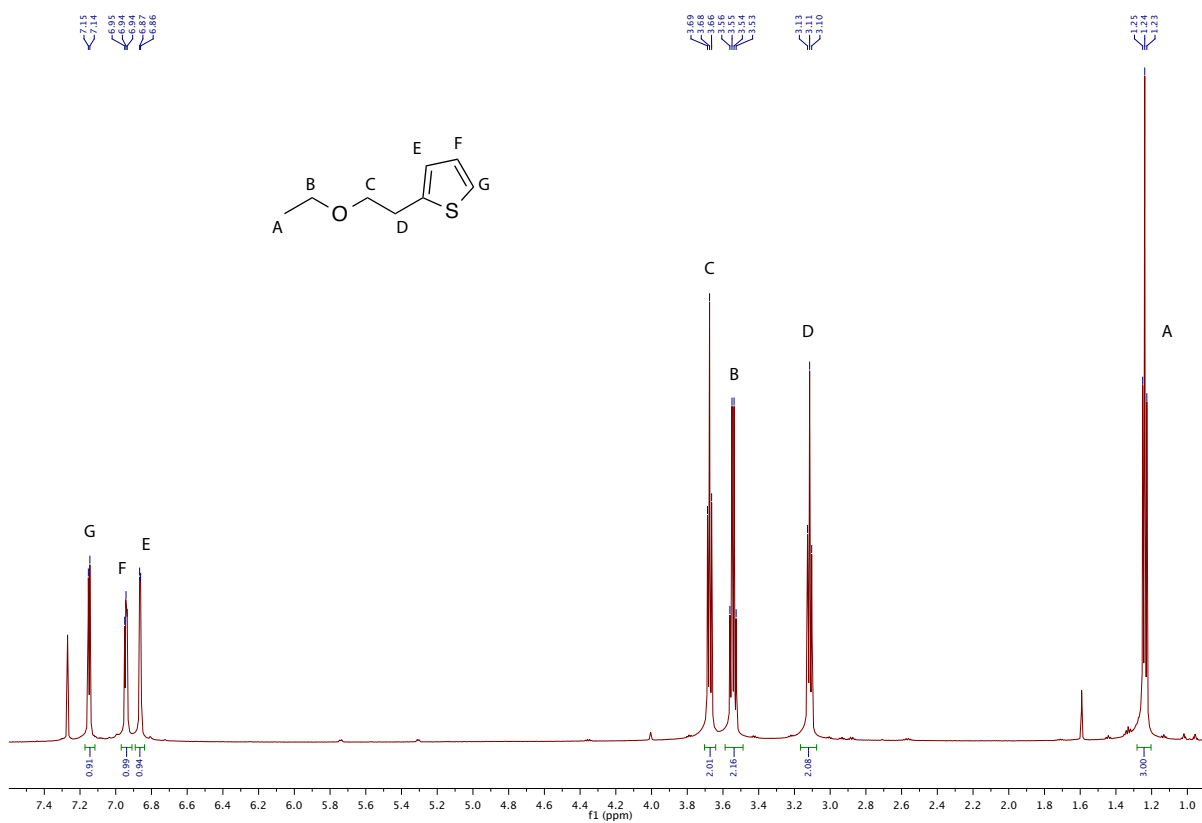


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-(2-ethoxyethyl)thiophene from the deoxygenation reaction of ethyl 2-thiopheneacetate with phenylsilane catalyzed by **2**.

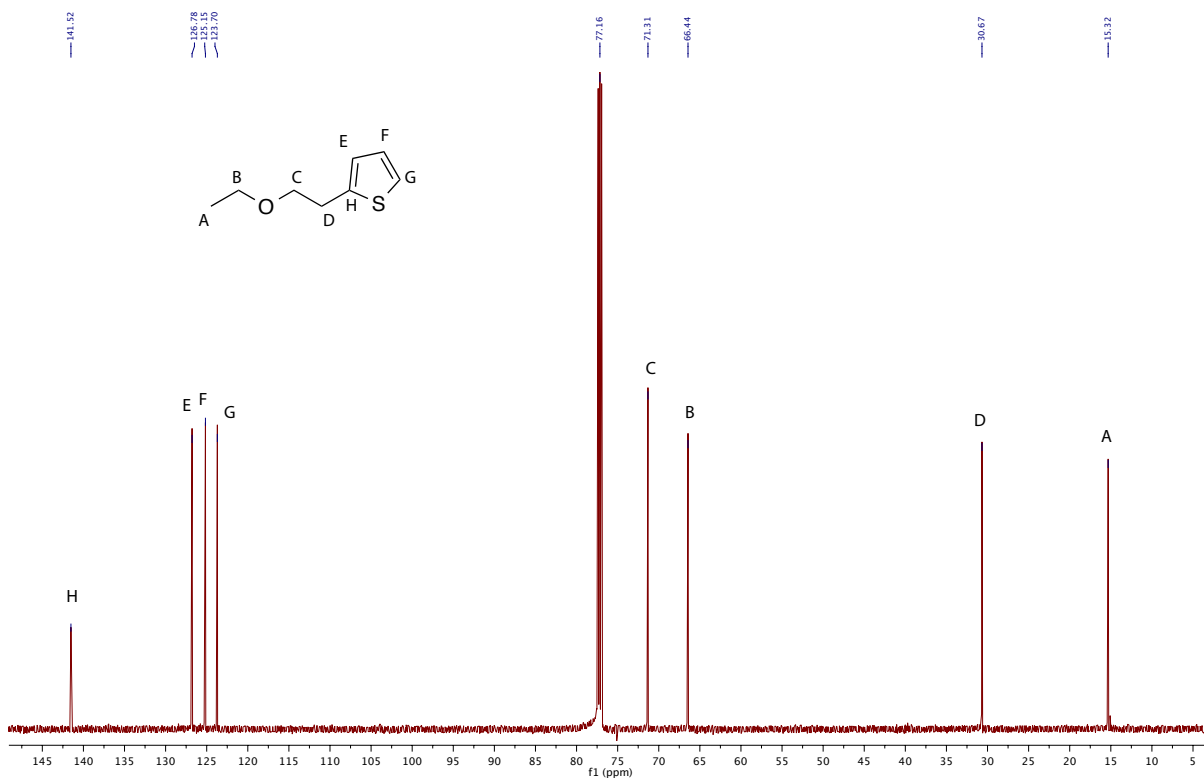


Figure S26. Gas chromatogram of 2-(2-ethoxyethyl)thiophene from the deoxygenation reaction of ethyl 2-thiopheneacetate with phenylsilane catalyzed by **2**. Retention time: 5.43 min. Fragmentation: 156.1 (M^+), 59.0 ($M^+ - CH_2C_4H_3S$).

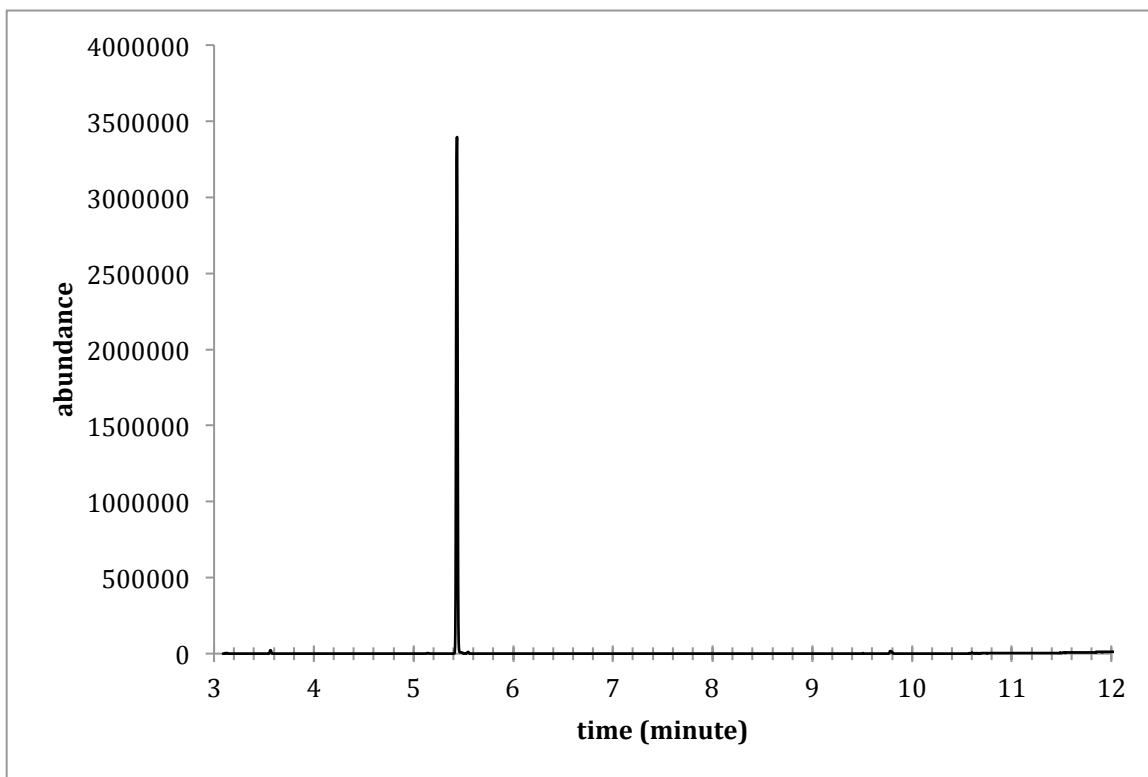


Figure S27. ^1H NMR spectrum of (*Z*)-1-methoxyoctadec-9-ene from the deoxygenation reaction of methyl oleate with phenylsilane catalyzed by **2**.

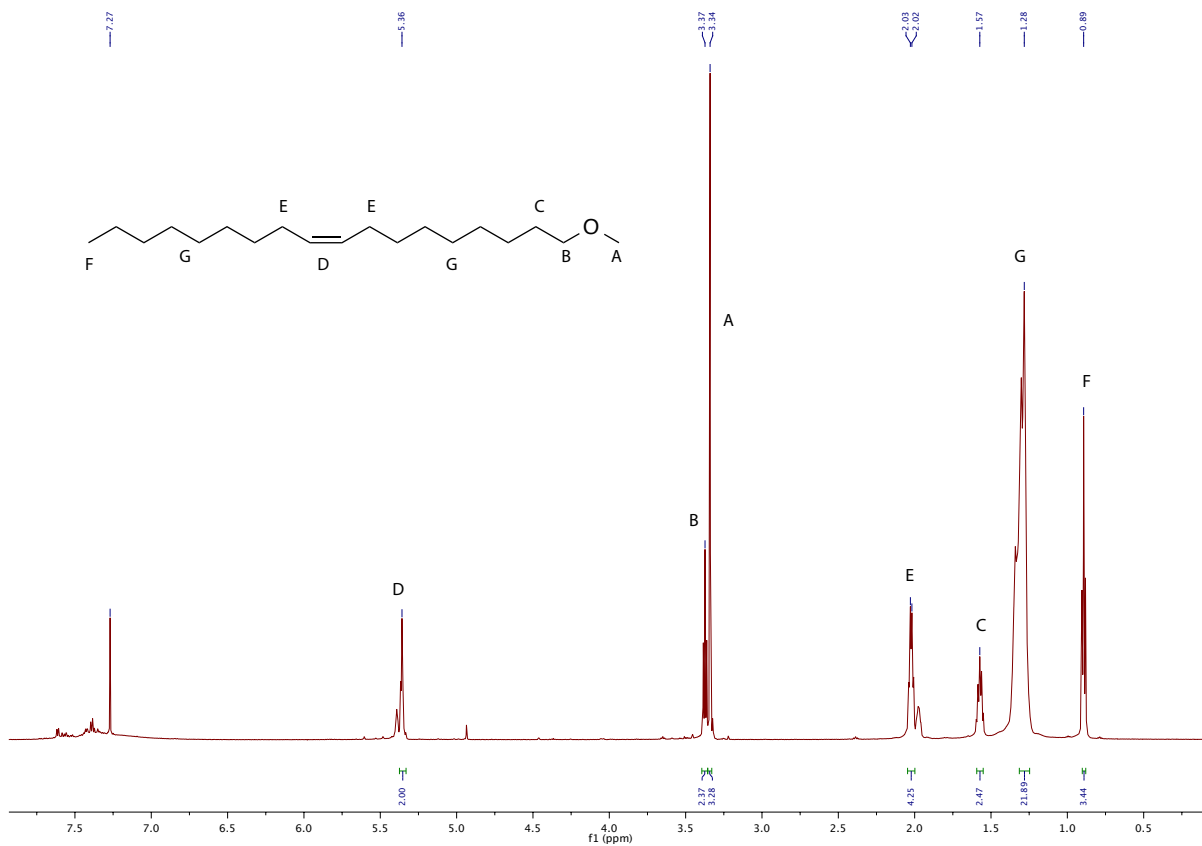


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*Z*)-1-methoxyoctadec-9-ene from the deoxygenation reaction of methyl oleate with phenylsilane catalyzed by **2**.

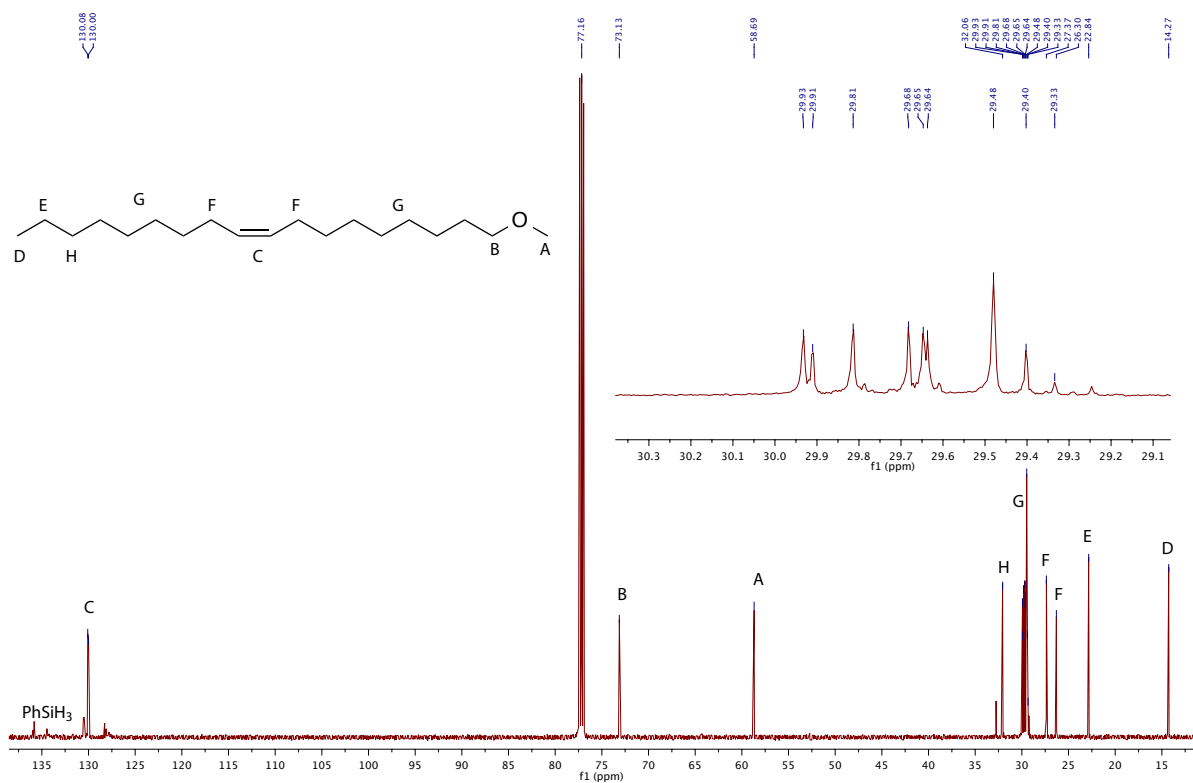


Figure S29. GC chromatograph of (*Z*)-1-methoxyoctadec-9-ene from the deoxygenation reaction of methyl oleate with phenylsilane catalyzed by **2**. Retention time: 10.32 min. Fragmentation: 282.3 (M^+), 251.3 ($M^+ - OCH_3$).

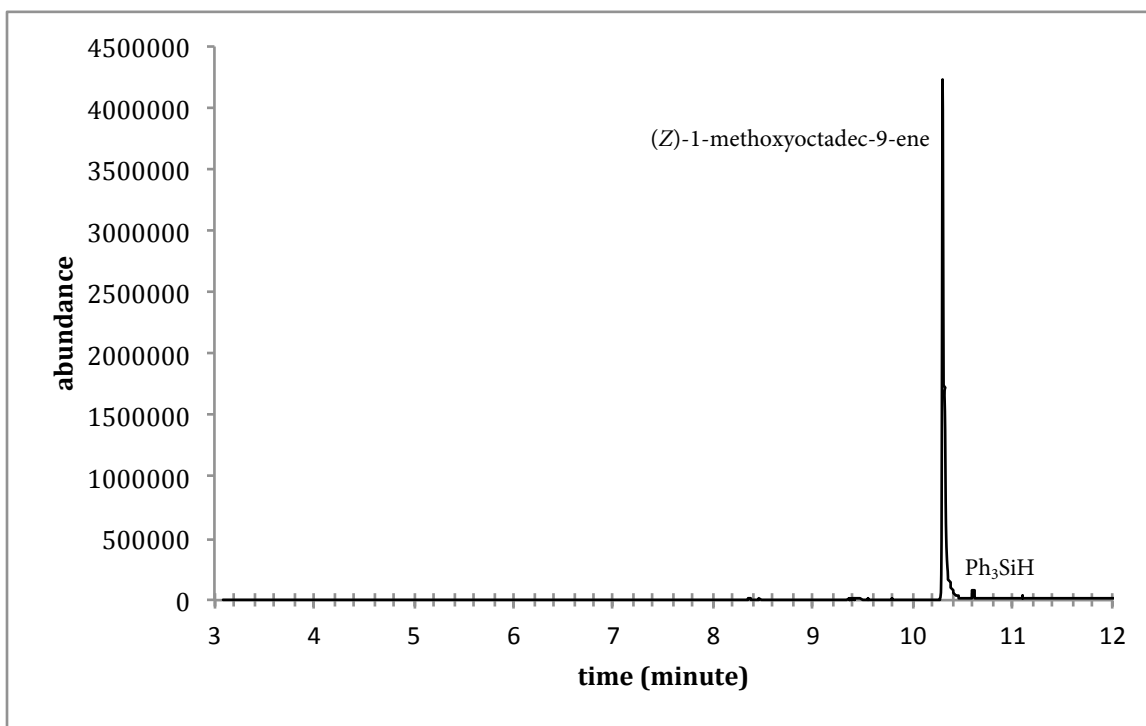


Figure S30. ^1H NMR spectrum of 2-ethyl-1,3-dimethoxybenzene from the deoxygenation reaction of 2',6'-dimethoxyacetophenone with phenylsilane catalyzed by **2**.

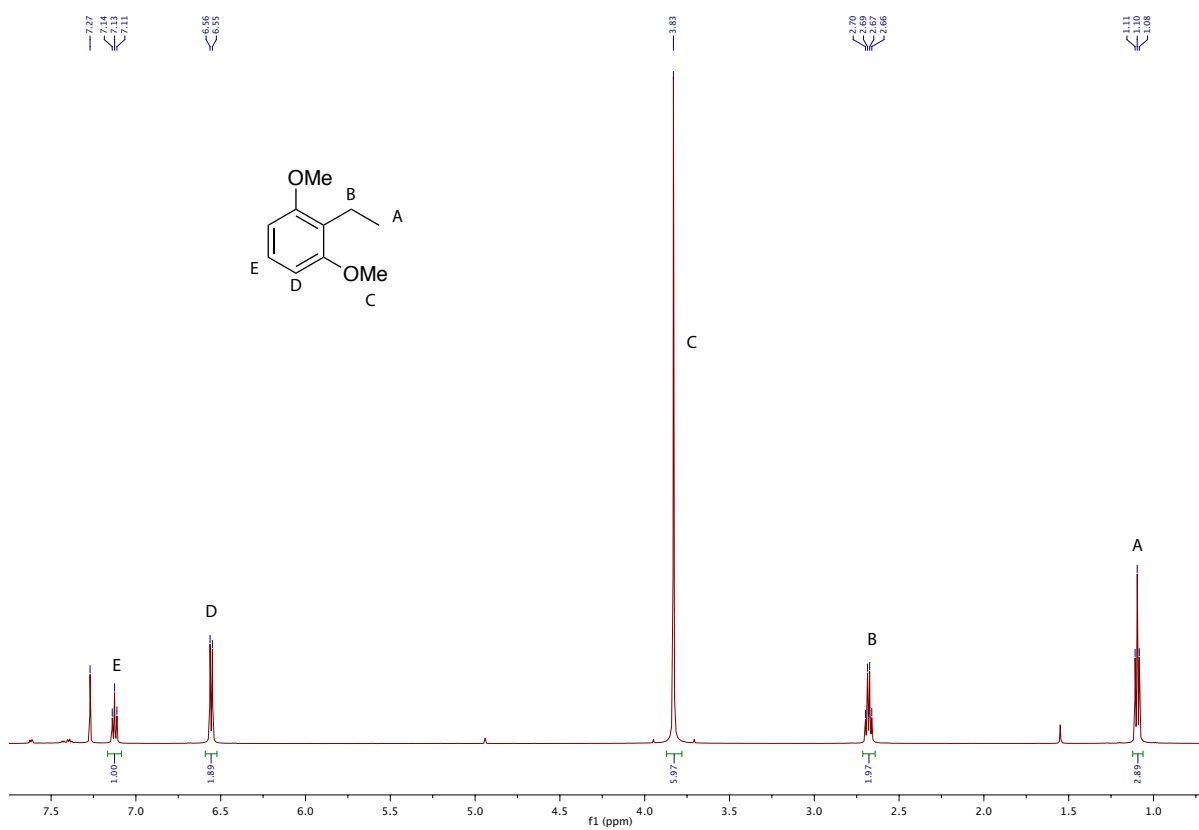


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-ethyl-1,3-dimethoxybenzene from the deoxygenation reaction of 2',6'-dimethoxyacetophenone with phenylsilane catalyzed by **2**.

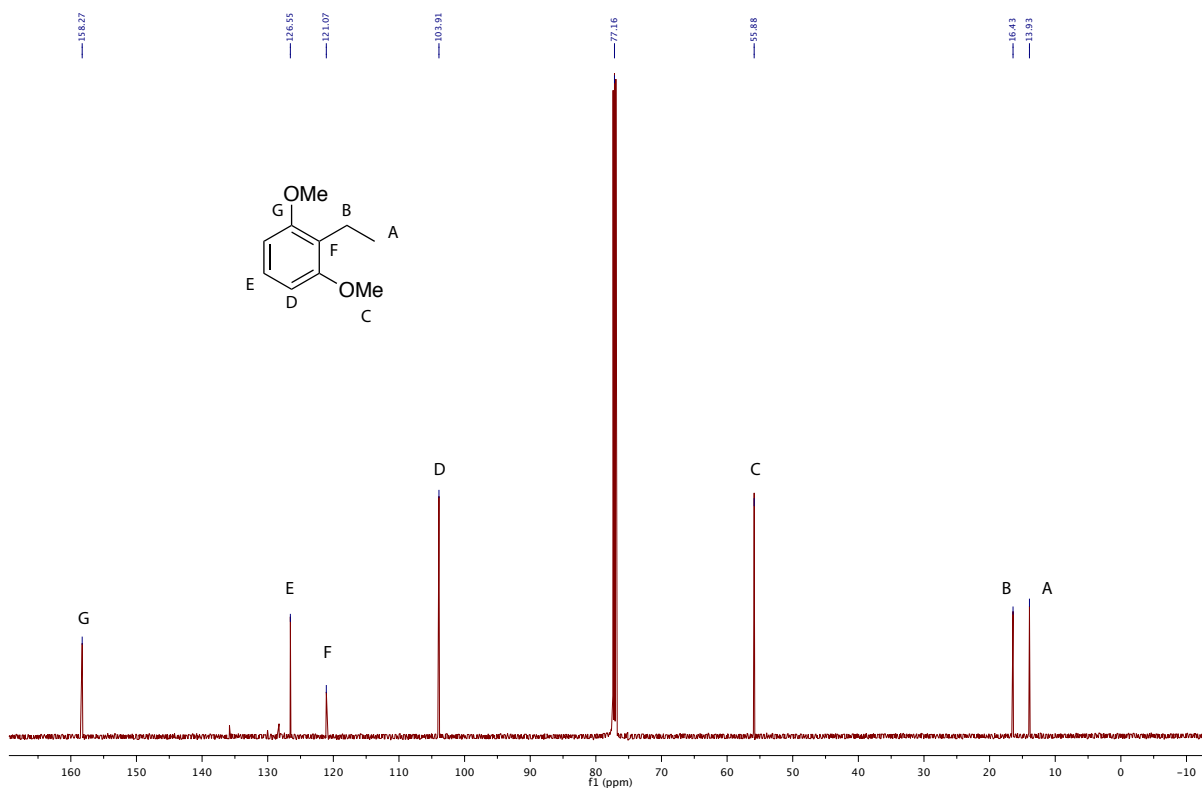


Figure S32. Gas chromatogram of 2-ethyl-1,3-dimethoxybenzene from the deoxygenation reaction of 2',6'-dimethoxyacetophenone with phenylsilane catalyzed by **2**. Retention time: 6.66 min. Fragmentation: 166.1 (M^+), 151.1 ($M^+ - CH_3$), 91.1 ($M^+ - CH_3 - OCH_3 - OCH_3$).

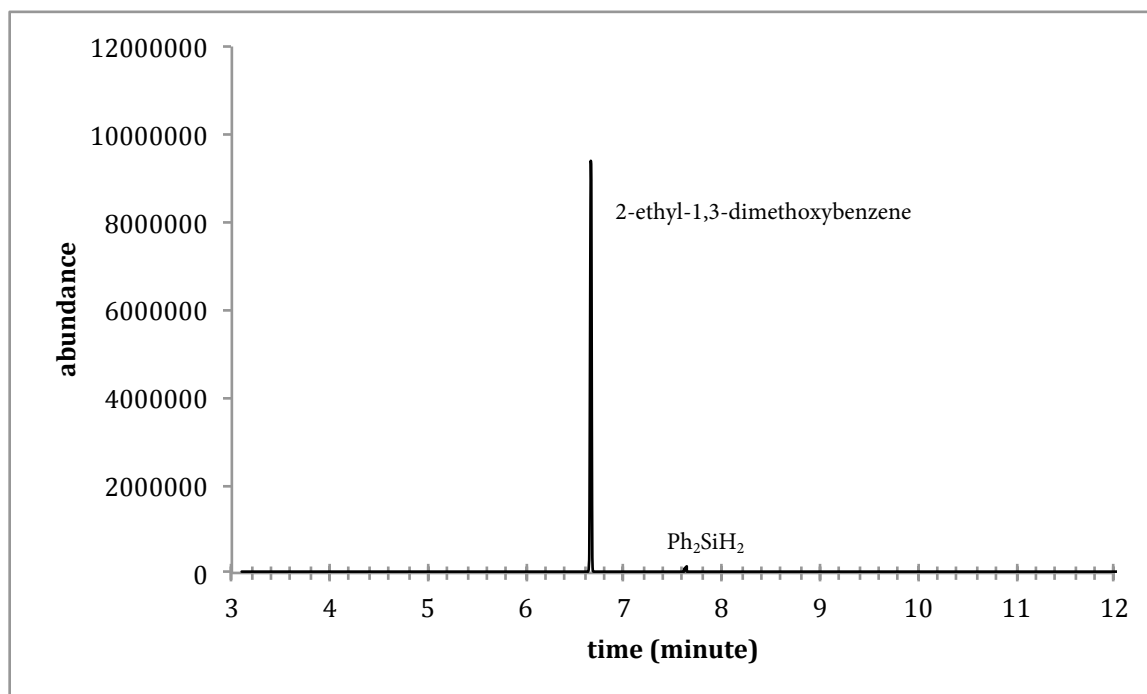


Figure S33. ^1H NMR spectrum of 1,3,5-trimethoxy-2-methylbenzene from the deoxygenation reaction of 2,4,6-trimethoxybenzaldehyde with phenylsilane catalyzed by **2**. The product is isolated by distillation and its purity is confirmed by GC (see Figure S34 below).

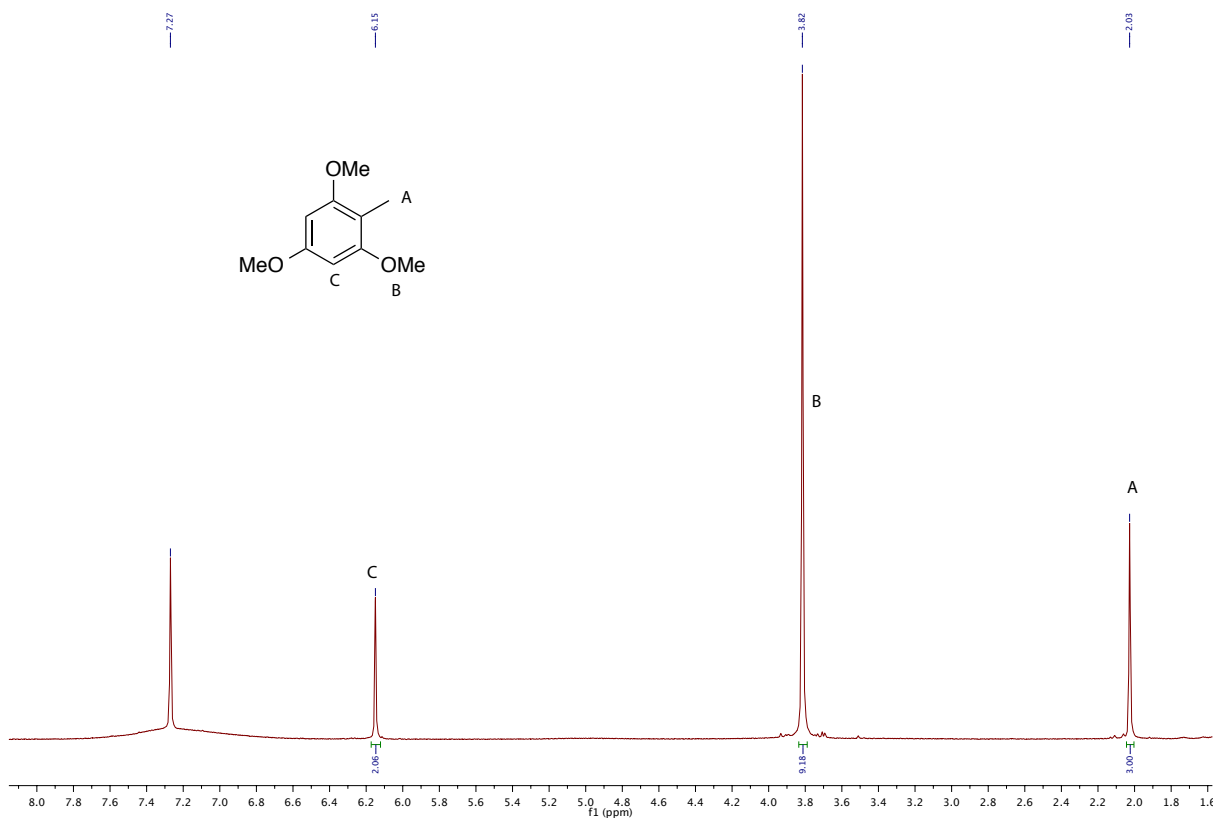


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,3,5-trimethoxy-2-methylbenzene from the deoxygenation reaction of 2,4,6-trimethoxybenzaldehyde with phenylsilane catalyzed by **2**.

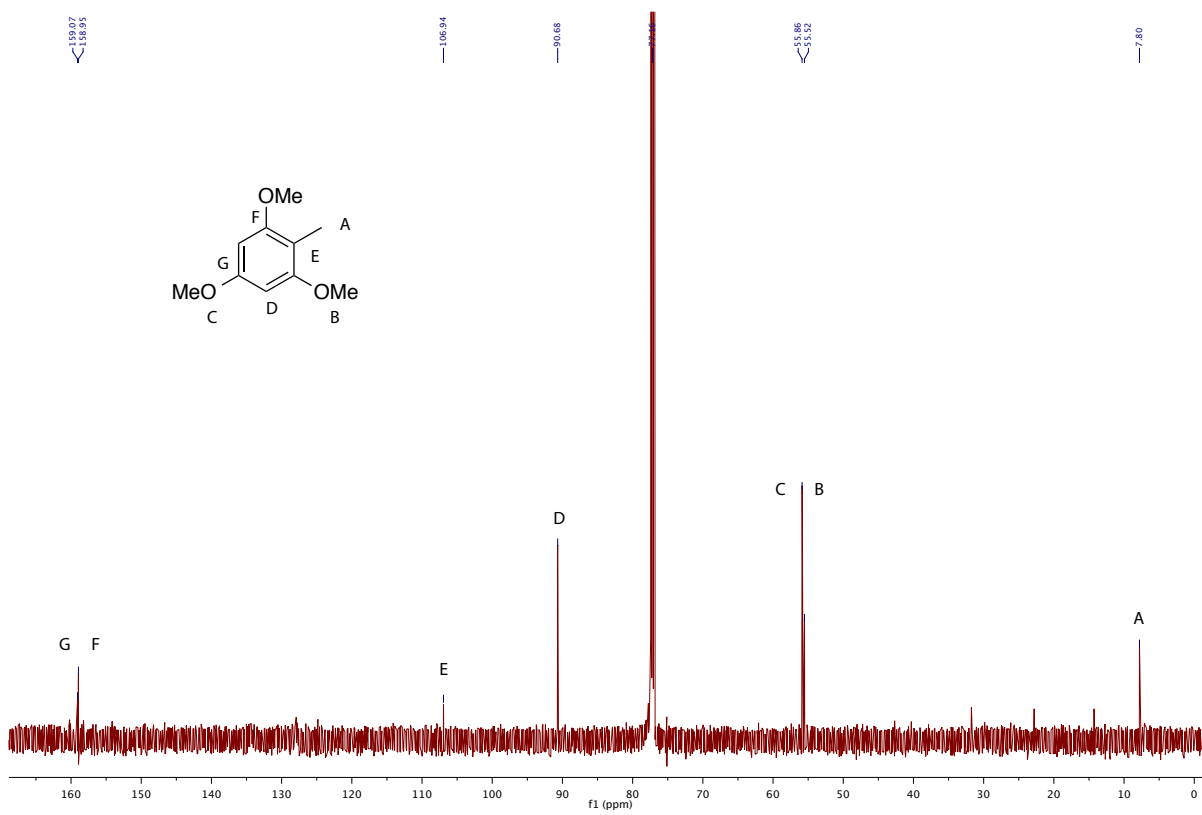
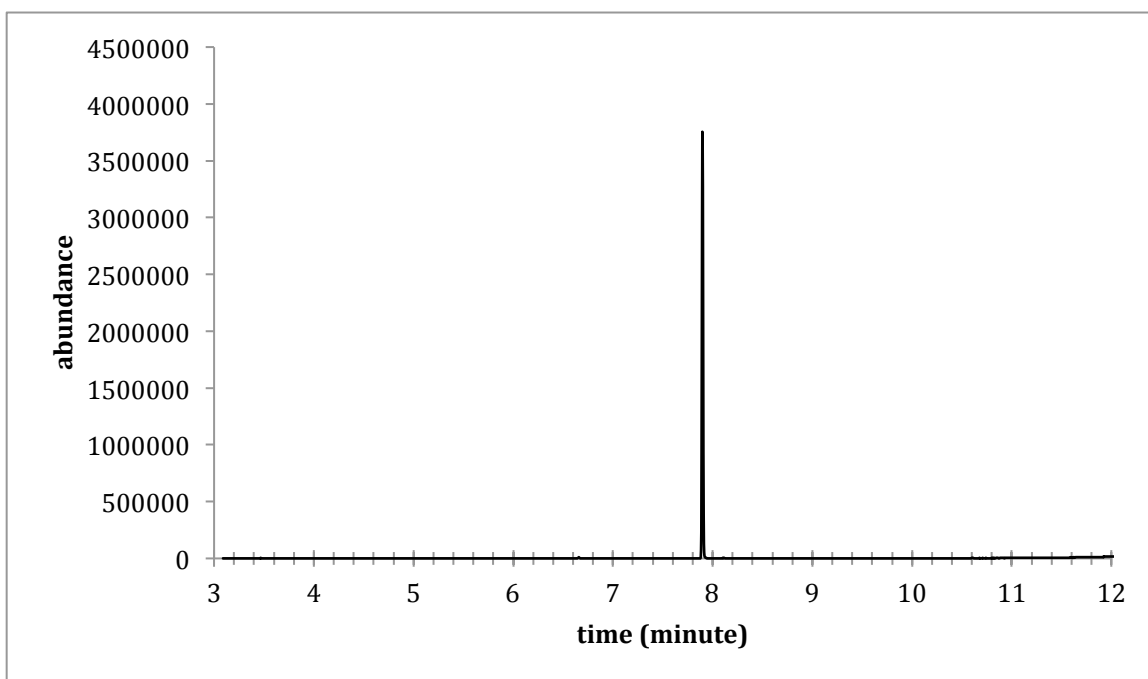


Figure S35. GC chromatograph of 1,3,5-trimethoxy-2-methylbenzene from the deoxygenation reaction of 2,4,6-trimethoxybenzaldehyde with phenylsilane catalyzed by **2**. Retention time: 7.90 min. Fragmentation: 182.1 (M^+), 167.1 ($M^+ - CH_3$), 151.1 ($M^+ - OCH_3$).



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