

Electronic Supplementary Information for: Magnesium-catalyzed hydrosilylation of α,β -unsaturated esters

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General Procedures. 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, toluene, pentane, diethyl ether, and tetrahydrofuran were dried and deoxygenated using an IT PureSolv system. THF-*d*₈, methylene chloride-*d*₂, and benzene-*d*₆ were heated to reflux over Na/K alloy and vacuum-transferred. To^MMgMe,¹ B(C₆F₅)₃,² and PhSiH₃³ were synthesized according to literature procedures. PhMeSiH₂ and BnMe₂SiH were prepared by reaction of the chlorosilane with LiAlH₄. Vinyltrimethylsilane, diphenylsilane, and triethylsilane were purchased from Gelest and purified by distillation under a dry argon atmosphere prior to use. Methyl methacrylate, benzyl methacrylate, and isobutyl methacrylate were purchased from Alfa Aesar and degassed by three freeze-pump-thaw cycles prior to use. 5,6-Dihydro-2*H*-pyran-2-one was purchased from Acros and degassed by three freeze-pump-thaw cycles prior to use. ¹H, ¹³C{¹H}, and ¹¹B NMR spectra were collected on a Bruker AVII 600 spectrometer, a Bruker DRX-400 spectrometer, or a MR-400 spectrometer. ²⁹Si INEPT and ¹H-²⁹Si HMBC spectra were collected on a Bruker AVII 600 spectrometer. ¹⁵N chemical shifts were determined by ¹H-¹⁵N HMBC experiments on a Bruker AVII 600 spectrometer with a Bruker Z-gradient inverse TXI ¹H/¹³C/¹⁵N 5mm cryoprobe; ¹⁵N chemical shifts were originally

referenced to an external liquid NH₃ standard and recalculated to the CH₃NO₂ chemical shift scale by adding -381.9 ppm. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility. X-ray diffraction data was collected on a Bruker APEX II diffractometer.

To^MMgHB(C₆F₅)₃ (1). A solution of To^MMgMe (0.134 g, 0.32 mmol) dissolved in benzene was added in a dropwise fashion into a benzene solution containing PhSiH₃ (0.069 g, 0.64 mmol) and B(C₆F₅)₃ (0.162 g, 0.32 mmol). A white precipitate formed as the reaction mixture stirred for 30 min. The precipitate settled after centrifugation, and the supernatant was decanted. The white solid was washed with pentane (3 × 5 mL) and dried under vacuum, providing analytically pure To^MMgHB(C₆F₅)₃ (0.286 g, 0.31 mmol, 97.6%). Once isolated, To^MMgHB(C₆F₅)₃ is soluble in benzene or toluene, and X-ray quality single crystals were grown from a concentrated toluene solution at -30 °C. ¹H NMR (600 MHz, benzene-*d*₆): δ 0.82 (s, 18 H, CNCMe₂CH₂O), 2.72 (br q, ¹J_{BH} = 68 Hz, 1 H, MgHB(C₆F₅)₃), 3.30 (s, 6 H, CNCMe₂CH₂O), 7.38 (m, ³J_{HH} = 7.2 Hz, 1 H, *para*-C₆H₅), 7.56 (m, ³J_{HH} = 7.6 Hz, 2 H, *meta*-C₆H₅), 8.25 (d, ³J_{HH} = 7.2 Hz, 2 H, *ortho*-C₆H₅). ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 27.35 (CNCMe₂CH₂O, overlapping with THF-*d*₈), 66.13 (CNCMe₂CH₂O, overlapping with THF-*d*₈), 79.28 (CNCMe₂CH₂O), 130.24 (*para*-C₆H₅), 133.26 (*meta*-C₆H₅), 134.79 (C₆F₅), 135.74 (C₆F₅), 136.81 (C₆F₅), 137.49 (*ortho*-C₆H₅), 138.41 (C₆F₅), 142 (br, *ipso*-C₆H₅), 147.78 (C₆F₅), 149.35 (C₆F₅), 191 (CNCMe₂CH₂O). ¹¹B NMR (192 MHz, benzene-*d*₆): δ -18.2 (To^M), -21.1 (d, ¹J_{HB} = 69 Hz, MgHB(C₆F₅)₃). ¹⁹F NMR (544 MHz, benzene-*d*₆): δ -134.2 (*ortho*-C₆F₅), -156.5 (*para*-C₆F₅), -161.4 (*meta*-C₆F₅). ¹⁵N NMR (60 MHz, benzene-*d*₆): δ -162. IR (KBr, cm⁻¹): ν 2976 (s), 2937 (s), 2372 (w br, BH), 1642 (m), 1579 (s), 1511 (s), 1459 (s br), 1373 (m), 1271 (m), 1199 (m), 1180 (m), 1161 (m), 1087 (s), 965

(s br), 843 (w), 804 (w), 735 (w), 705 (w). Anal. Calcd. for $C_{39}H_{30}B_2F_{15}MgN_3O_3$: C, 50.94; H, 3.29; N, 4.57. Found C, 51.38; H, 3.41; N, 4.31. Mp: 166-167 °C.

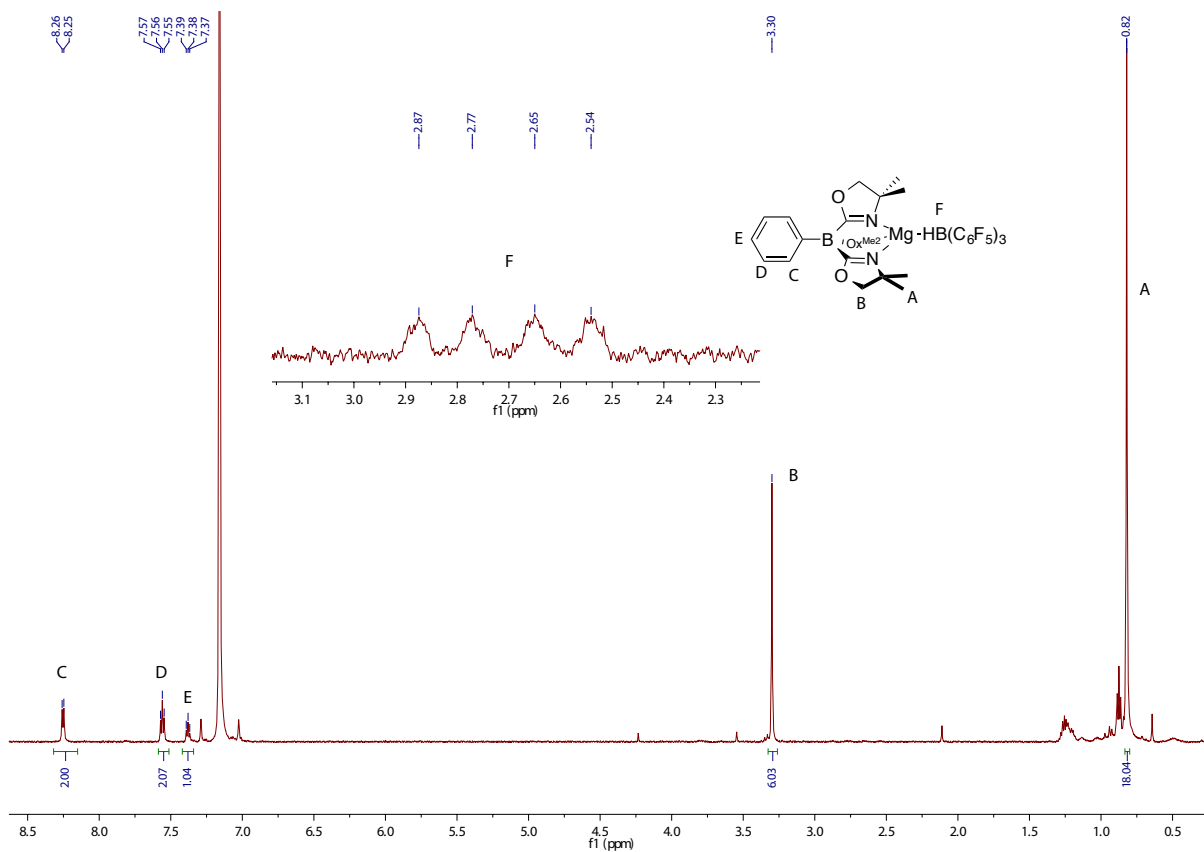


Figure S1. ^1H NMR spectrum (600 MHz, $\text{benzene-}d_6$) of $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$.

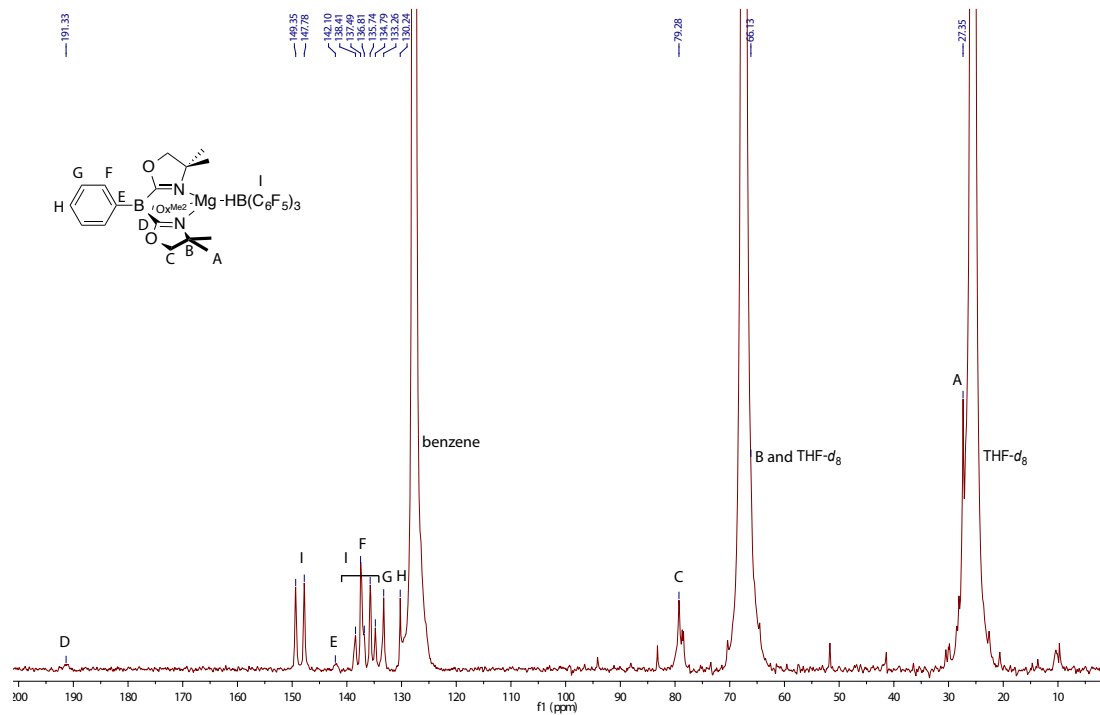


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (150 MHz, THF-d_8) of $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$.

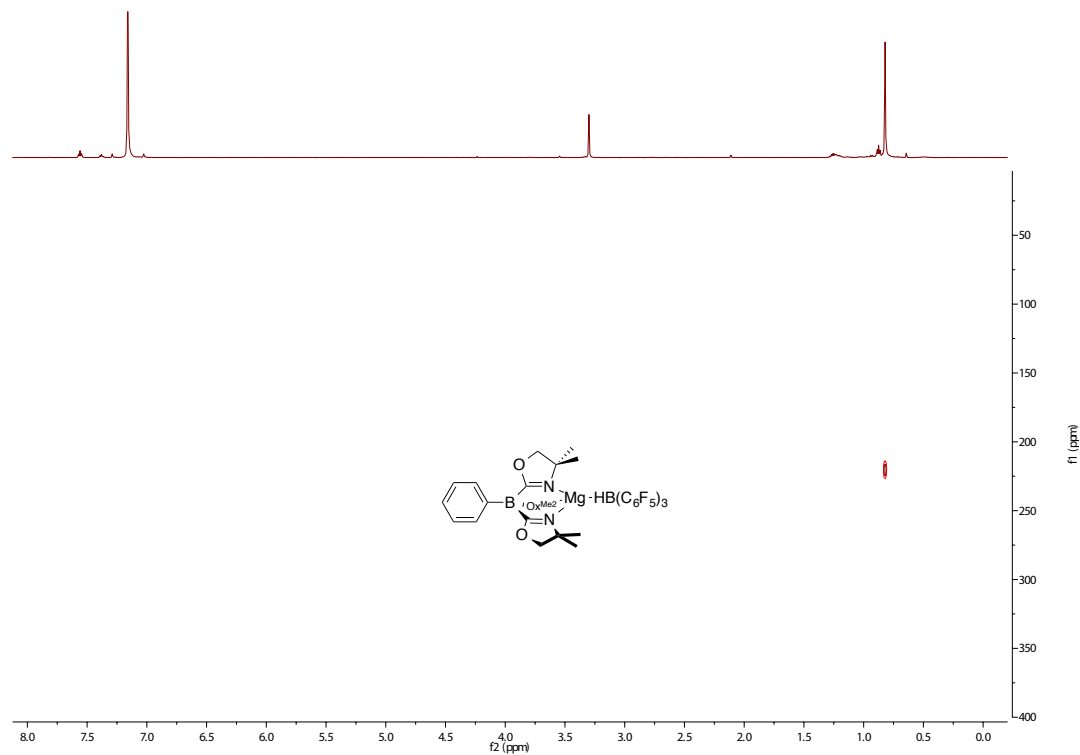


Figure S3. $^1\text{H}-^{15}\text{N}$ HMBC experiment (60 MHz, benzene-d_6) of $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$.

To^MMgMeB(C₆F₅)₃ (2). A pentane solution of B(C₆F₅)₃ (0.031 g, 0.059 mmol) was added to a concentrated solution of To^MMgMe (0.025 g, 0.059 mmol) in benzene. The reaction mixture was stirred for 15 min. and then allowed to stand for 30 min. as a white precipitate formed. The solvent was decanted, and the residue washed with pentane (3 × 5 mL) and then dried under vacuum to provide To^MMgMeB(C₆F₅)₃ (0.046 g, 0.049 mmol, 83.2%). When generated in situ, To^MMgMeB(C₆F₅)₃ is soluble in benzene-*d*₆ and CD₂Cl₂ and NMR spectra can be obtained, with the exception of ¹³C NMR spectral data due to the rate of conversion from To^MMgMeB(C₆F₅)₃ to To^MMgC₆F₅ being too fast. However, once solvent is removed and To^MMgMeB(C₆F₅)₃ isolated, it becomes insoluble in benzene and methylene chloride and only partially redissolves in THF-*d*₈. Though benzene, methylene chloride, and THF solvents were attempted, ¹³C NMR spectral data could not be obtained due to the low solubility of To^MMgMeB(C₆F₅)₃ and its spontaneous conversion to To^MMgC₆F₅. ¹H NMR (600 MHz, benzene-*d*₆): δ 0.79 (s, 18 H, CNCMe₂CH₂O), 1.27 (br s, 3 H, MgMeB(C₆F₅)₃), 3.23 (s, 6 H, CNCMe₂CH₂O), 7.35 (br, 1 H, *para*-C₆H₅), 7.51 (br, 2 H, *meta*-C₆H₅), 8.09 (br, 2 H, *ortho*-C₆H₅). ¹¹B NMR (192 MHz, benzene-*d*₆): δ -15.5 (MeB(C₆F₅)₃), -18.5 (To^M). ¹⁹F NMR (544 MHz, benzene-*d*₆): δ -134.8 (*ortho*-C₆F₅), -159.1 (*para*-C₆F₅), -163.4 (*meta*-C₆F₅). ¹⁵N NMR (60 MHz, benzene-*d*₆): δ -162.2. IR (KBr, cm⁻¹): ν 3037 (w), 2973 (s), 2935 (m), 1636 (m), 1541 (s), 1508 (s), 1458 (s), 1437 (s), 1374 (m), 1267 (m), 1202 (m), 1088 (s), 965 (s), 842 (w), 803 (w), 738 (w), 683 (w). Anal. Calcd. for C₄₀H₃₂B₂F₁₅MgN₃O₃: C, 51.46; H, 3.45; N, 4.50. Found C, 51.09; H, 3.20; N, 4.01. Mp: 205-207 °C (dec.).

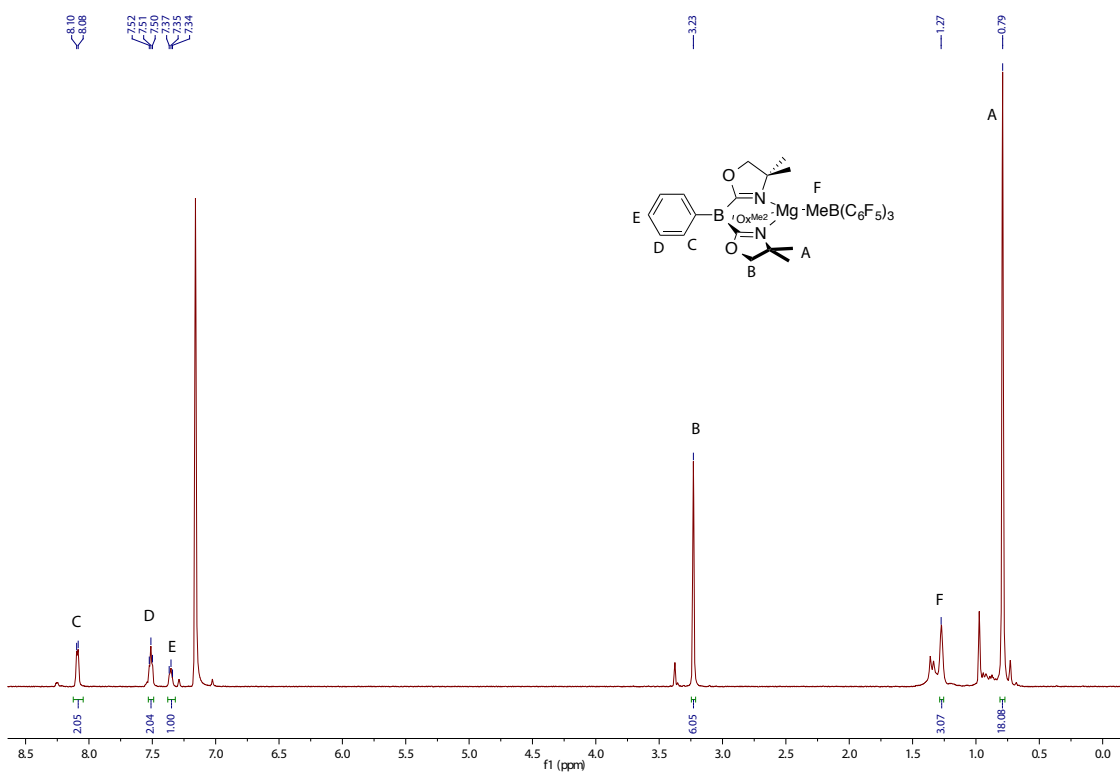


Figure S4. ^1H NMR spectrum (600 MHz, benzene- d_6) of $\text{To}^{\text{M}}\text{MgMeB}(\text{C}_6\text{F}_5)_3$.

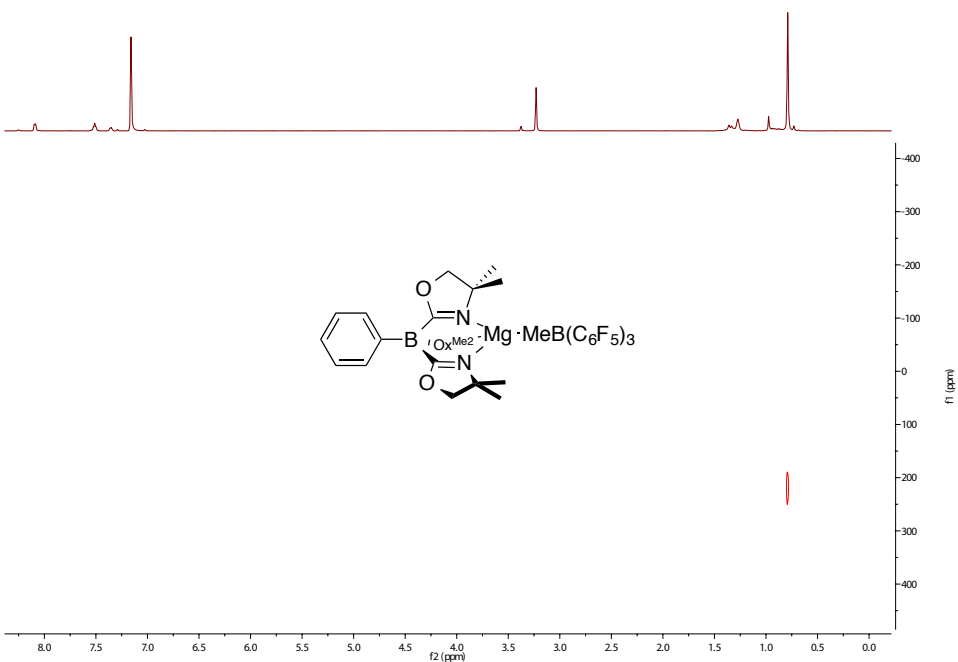


Figure S5. ^1H - ^{15}N HMBC experiment (60 MHz, benzene- d_6) on $\text{To}^{\text{M}}\text{MgMeB}(\text{C}_6\text{F}_5)_3$.

To^MMgC₆F₅. B(C₆F₅)₃ (0.024 g, 0.047 mmol) and 1 equiv. of To^MMgMe (0.020 g, 0.047 mmol) were dissolved in methylene chloride, and the reaction mixture was stirred for 24 h, and then filtered. Solvent was removed under reduced pressure. The white solid was washed with pentane (3 × 5 mL) to afford To^MMgC₆F₅ (0.012 g, 0.021 mmol, 44.4%). ¹H NMR (600 MHz, benzene-*d*₆): δ 0.97 (s, 18 H, CNCMe₂CH₂O), 3.38 (s, 6 H, CNCMe₂CH₂O), 7.38 (m, ³J_{HH} = 7.2 Hz, 1 H, *para*-C₆H₅), 7.55 (m, ³J_{HH} = 7.6 Hz, 2 H, *meta*-C₆H₅), 8.25 (d, ³J_{HH} = 7.2 Hz, 2 H, *ortho*-C₆H₅). ¹³C {¹H} NMR (150 MHz, benzene-*d*₆): δ 28.08 (CNCMe₂CH₂O), 65.91 (CNCMe₂CH₂O), 80.81 (CNCMe₂CH₂O), *para*-C₆H₅ and *meta*-C₆H₅ overlapping with benzene-*d*₆, 136.41 (*ortho*-C₆H₅), C₆F₅ too low intensity to be observed, 148.29 (br, *ipso*-C₆H₅), 193.08 (br, CNCMe₂CH₂O). ¹¹B NMR (192 MHz, benzene-*d*₆): δ -18.3. ¹⁹F NMR (376 MHz, benzene-*d*₆): δ -110.5 (2 F, *ortho*-C₆F₅), -155.8 (1 F, *para*-C₆F₅), -160.7 (2 F, *meta*-C₆F₅). ¹⁵N NMR (60 MHz, benzene-*d*₆): δ -157.7. IR (KBr, cm⁻¹): ν 2965 (s), 2926 (s), 2884 (m), 2853 (m), 1594 (s, CN), 1510 (m), 1463 (s), 1366 (m), 1350 (w), 1268 (s), 1197 (m), 1152 (m), 1117 (w), 1086 (m), 967 (s), 892 (w), 839 (w), 810 (m), 746 (w), 703 (m). Anal. Calcd. for C₂₇H₂₉BF₅MgN₃O₃: C, 56.53; H, 5.10; N, 7.33. Found C, 57.01; H, 5.58; N, 6.89. Mp: 195-197 °C.

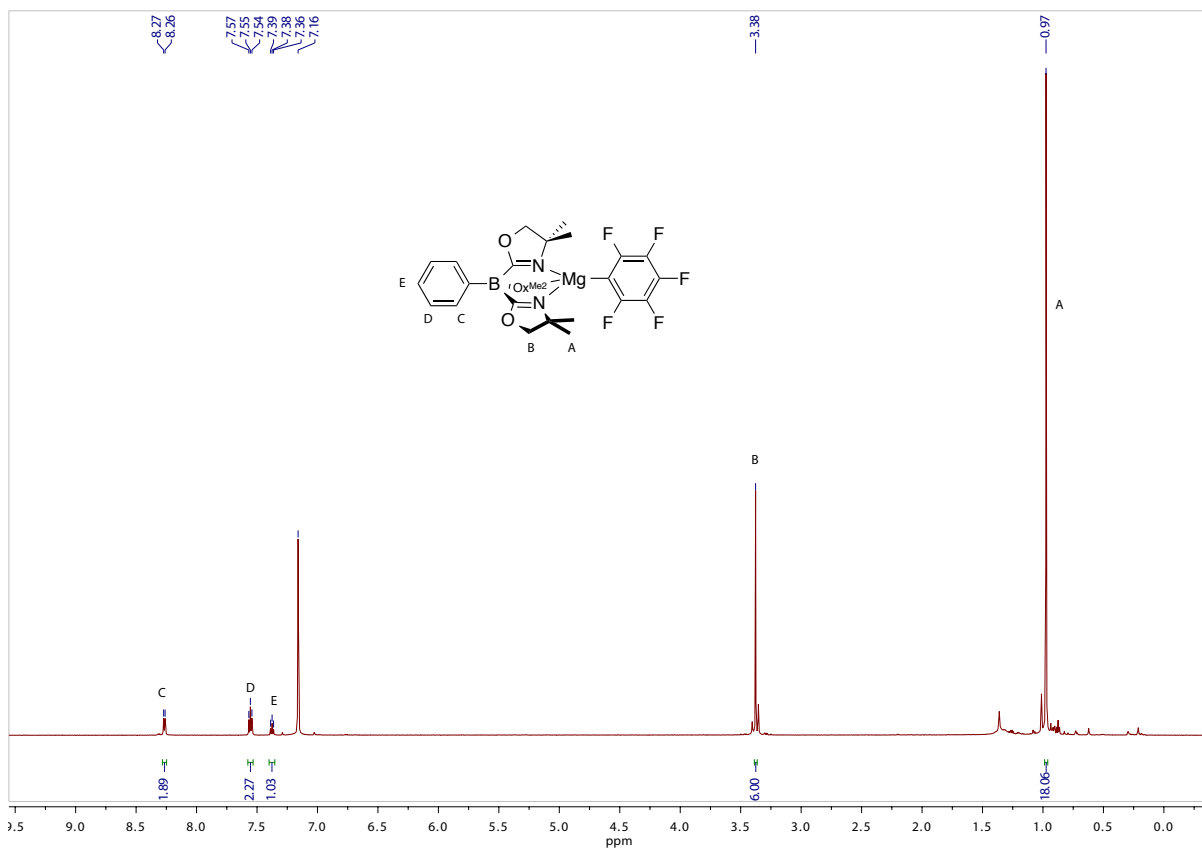


Figure S6. ^1H NMR spectrum (600 MHz, benzene- d_6) of $\text{To}^{\text{Mg}}\text{C}_6\text{F}_5$.

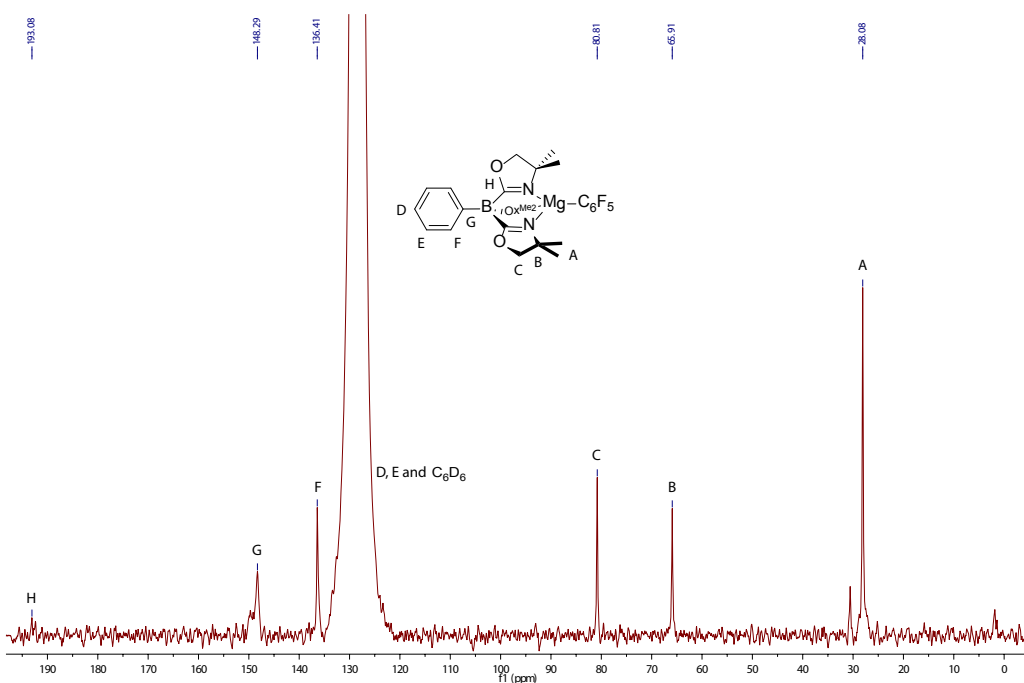


Figure S7. ^{13}C NMR spectrum (150 MHz, benzene- d_6) of $\text{To}^{\text{Mg}}\text{C}_6\text{F}_5$.

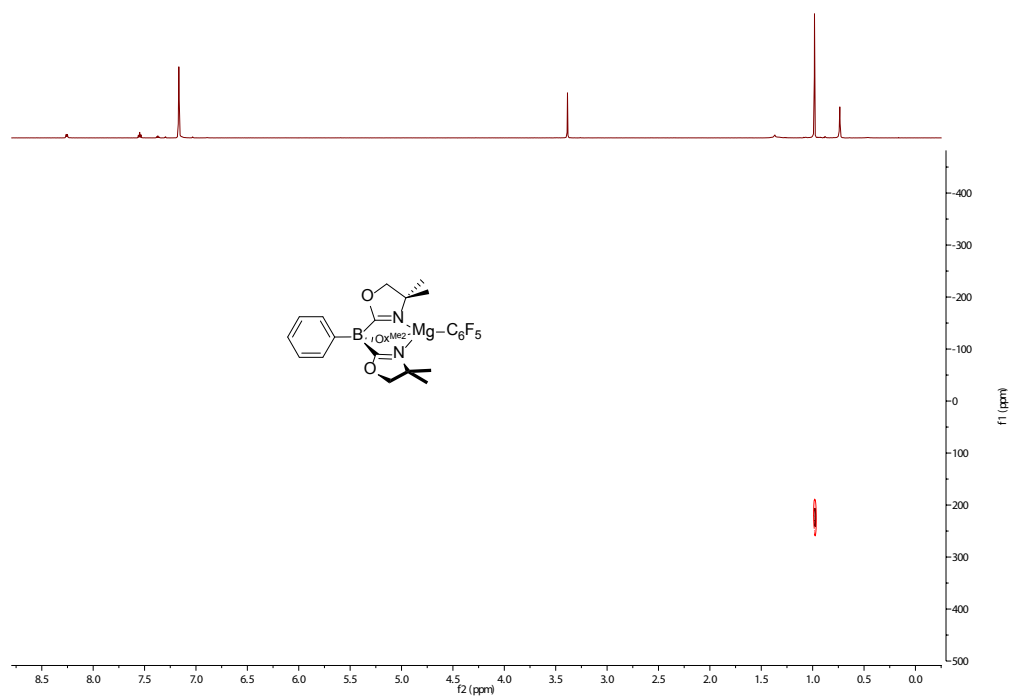


Figure S8. ^1H - ^{15}N NMR HMBC experiment (60 MHz, benzene- d_6) on $\text{To}^{\text{M}}\text{MgC}_6\text{F}_5$.

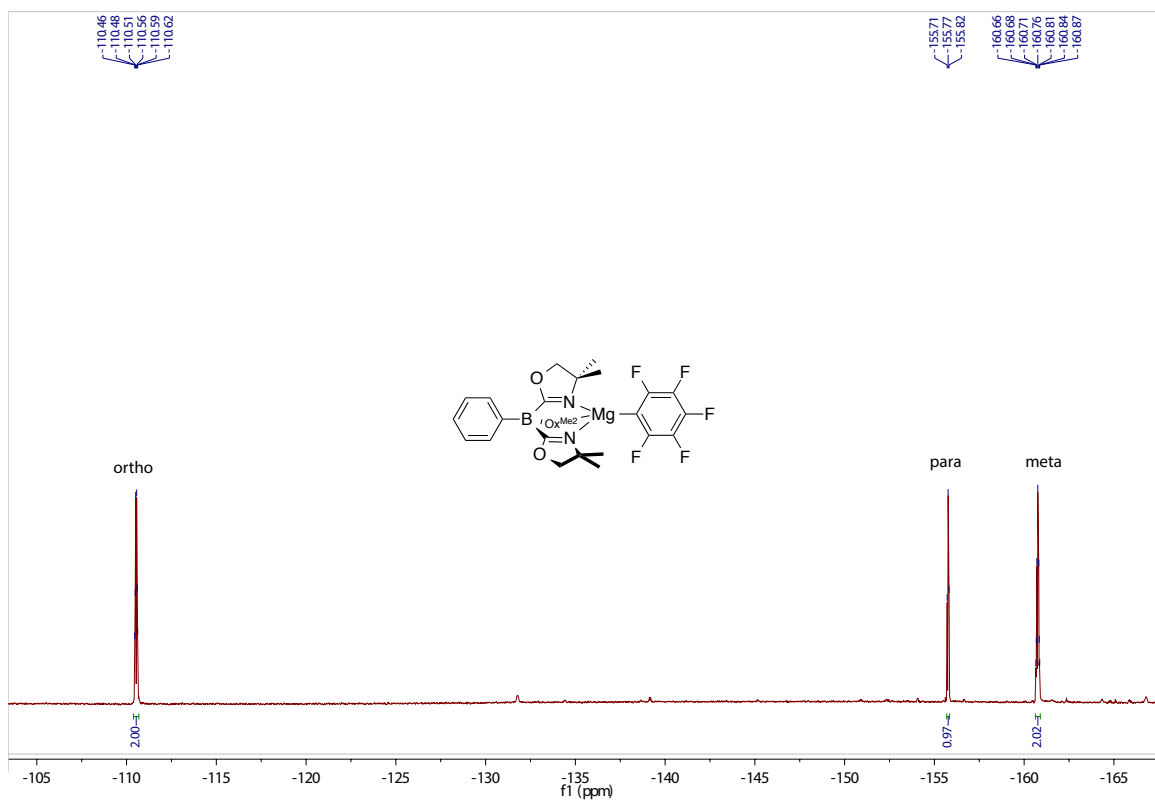


Figure S9. ^{19}F NMR spectrum of $\text{To}^{\text{M}}\text{MgC}_6\text{F}_5$.

[To^MMg][B(C₆F₅)₄]. To^MMgMe (0.026 g, 0.062 mmol) and [Ph₃C][B(C₆F₅)₄] (0.057 g, 0.062 mmol) were dissolved in benzene (10 mL) and stirred for 30 min. to obtain a white precipitate, which was then isolated by decantation of the top liquid. Washing with benzene (3×5 mL) followed by drying under vacuum provided [To^MMg][B(C₆F₅)₄] (0.064 g, 0.059 mmol, 94.9%). Solution-phase characterization is given in THF-*d*₈ of the THF-*d*₈ adduct. ¹H NMR (600 MHz, THF-*d*₈): δ 1.28 (s, 18 H, CNCMe₂CH₂O), 3.90 (s, 6 H, CNCMe₂CH₂O), 7.01 (br, 1 H, *para*-C₆H₅), 7.07 (br, 2 H, *meta*-C₆H₅), 7.64 (br, 2 H, *ortho*-C₆H₅). ¹³C {¹H} NMR (150 MHz, THF-*d*₈): δ 28.61 (CNCMe₂CH₂O), 66.37 (CNCMe₂CH₂O), 80.49 (CNCMe₂CH₂O), 125.33 (*para*-C₆H₅), 126.56 (*meta*-C₆H₅), 134.5 (br, *ipso*-C₆H₅), 136.00 (*ortho*-C₆H₅), 136.38 (C₆F₅), 138.02 (C₆F₅), 138.41 (C₆F₅), 140.02 (C₆F₅), 148.43 (C₆F₅), 150.07 (C₆F₅), 191 (br, CNCMe₂CH₂O). ¹¹B NMR (192 MHz, THF-*d*₈): δ -18.4, -20.2 (B(C₆F₅)₄). ¹⁹F NMR (544 MHz, THF-*d*₈): δ -134.6 (*ortho*-C₆F₅), -166.7 (*para*-C₆F₅), -170.3 (*meta*-C₆F₅). ¹⁵N NMR (THF-*d*₈, 60 MHz): δ -156. IR (KBr, cm⁻¹): ν 2981 (s), 1645 (m), 1559 (w), 1515 (s), 1464 (s), 1374 (w), 1277 (m), 1089 (s), 980 (s), 862 (s), 775 (m), 756 (m), 684 (m), 661 (m). Anal. Calcd. for C₄₅H₂₉B₂F₂₀MgN₃O₃: C, 49.79; H, 2.69; N, 3.87. Found C, 50.20; H, 2.49; N, 4.01. Mp: 86-88 °C.

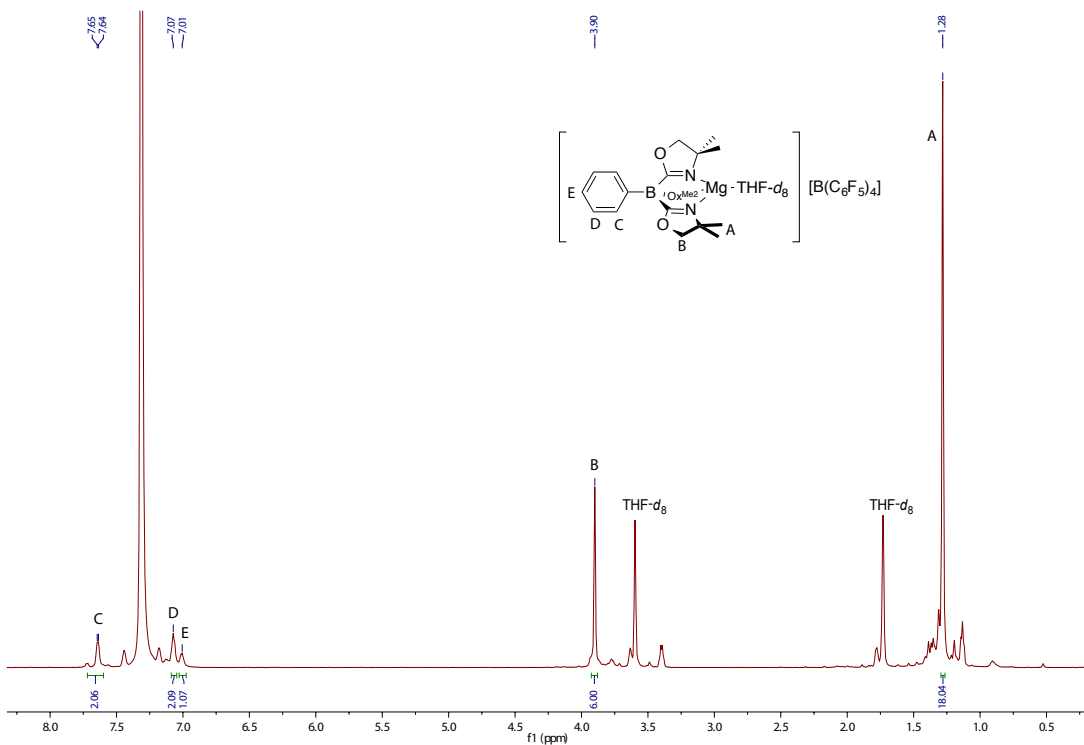


Figure S10. ^1H NMR spectrum (600 MHz, $\text{THF-}d_8$) of $[\text{To}^{\text{M}}\text{Mg}][\text{B}(\text{C}_6\text{F}_5)_4]$.

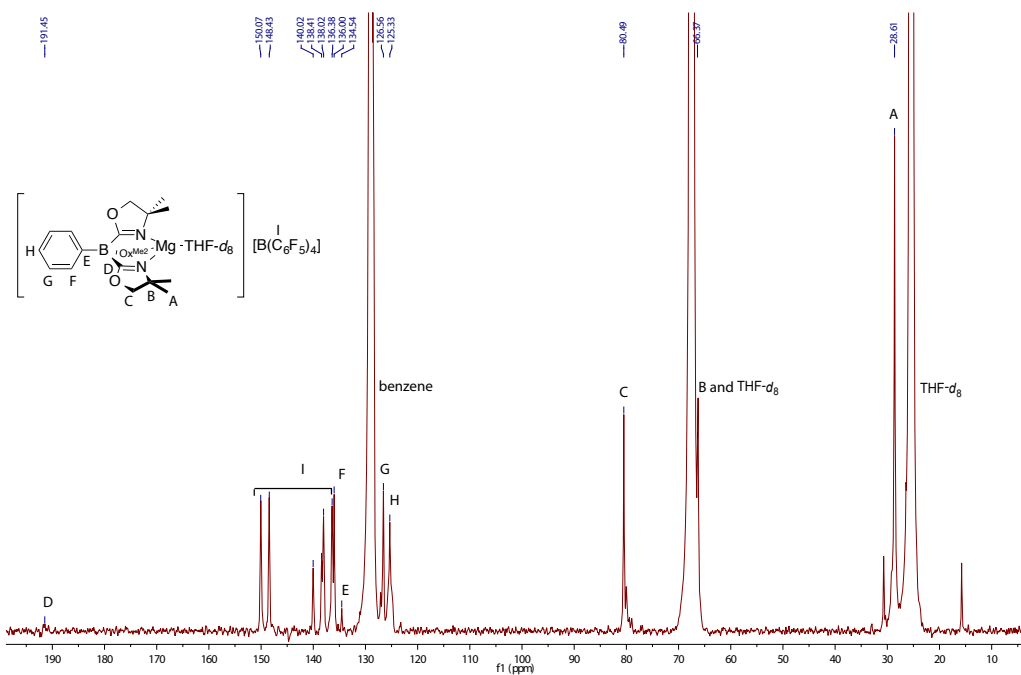


Figure S11. ^{13}C NMR spectrum (150 MHz, $\text{THF-}d_8$) of $[\text{To}^{\text{M}}\text{Mg}][\text{B}(\text{C}_6\text{F}_5)_4]$.

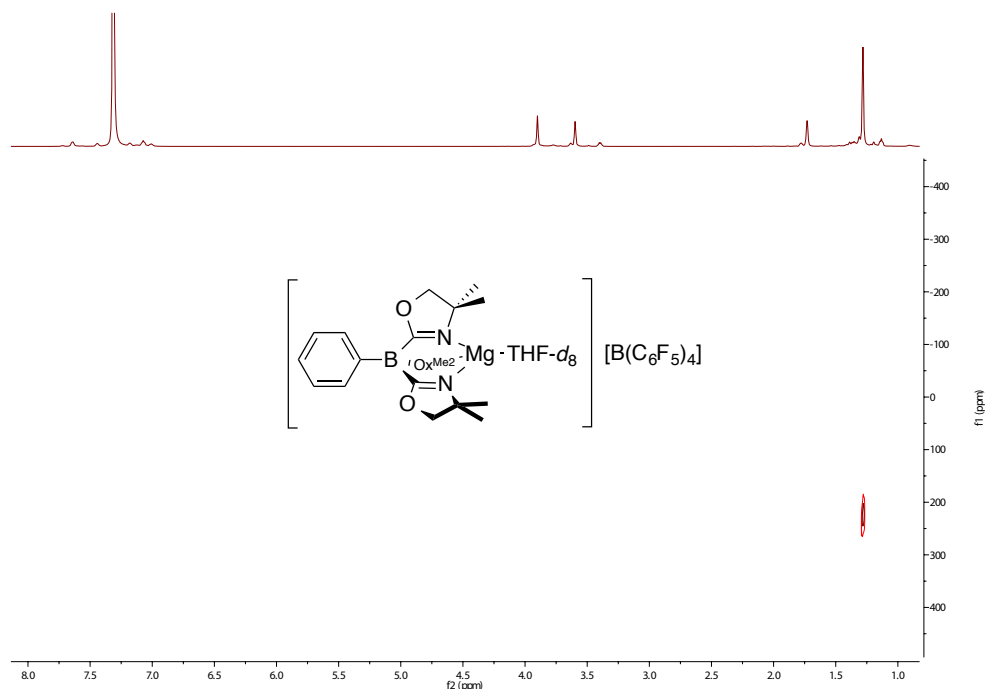


Figure S12. ^1H - ^{15}N NMR experiment (60 MHz, $\text{THF-}d_8$) on $[\text{To}^{\text{M}}\text{Mg}][\text{B}(\text{C}_6\text{F}_5)_4]$.

$\text{BnMe}_2\text{SiO}(\text{MeO})\text{C}=\text{CMe}_2$. Crystallized $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$ (0.011 g, 0.012 mmol), methyl methacrylate (0.117 g, 1.17 mmol), and BnMe_2SiH (0.176 g, 1.17 mmol) were stirred in benzene for 30 min. at room temperature. Evaporation of the volatile materials under reduced pressure afforded a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to afford a colorless liquid (0.290 g, 1.16 mmol, 99.0%). ^1H NMR (600 MHz, benzene- d_6): δ 0.15 (s, 6 H, SiMe_2), 1.61 (s, 3 H, $\text{C}=\text{CMe}_2$), 1.71 (s, 3 H, $\text{C}=\text{CMe}_2$), 2.23 (s, 2 H, PhCH_2Si), 3.29 (s, 3 H, OMe), 7.02 (m, 3 H, C_6H_5), 7.13 (m, 2 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, benzene- d_6): δ -1.44 (SiMe_2), 16.84 ($\text{C}=\text{CMe}_2$), 17.49 ($\text{C}=\text{CMe}_2$), 27.30 (PhCH_2Si), 57.01 (OMe), 91.41 ($\text{C}=\text{CMe}_2$), 125.14 (C_6H_5), 128.98 (C_6H_5), 129.20 (C_6H_5), 139.10 (*ipso*- C_6H_5), 150.64 ($\text{C}=\text{CMe}_2$). ^{29}Si (119 MHz, benzene- d_6) δ 15.7. IR (KBr, cm^{-1}): ν 3062 (w), 3027 (m), 2964 (s), 2919 (s), 2859 (s), 1706 (s), 1601 (m), 1494 (m), 1453 (m), 1410

(m), 1256 (s), 1203 (s), 1176 (s), 1058 (w), 1027 (s), 944 (s), 905 (w), 862 (s), 763 (s), 699 (s), 664 (w), 611 (w). Anal. Calcd. for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found C, 67.63; H, 8.73.

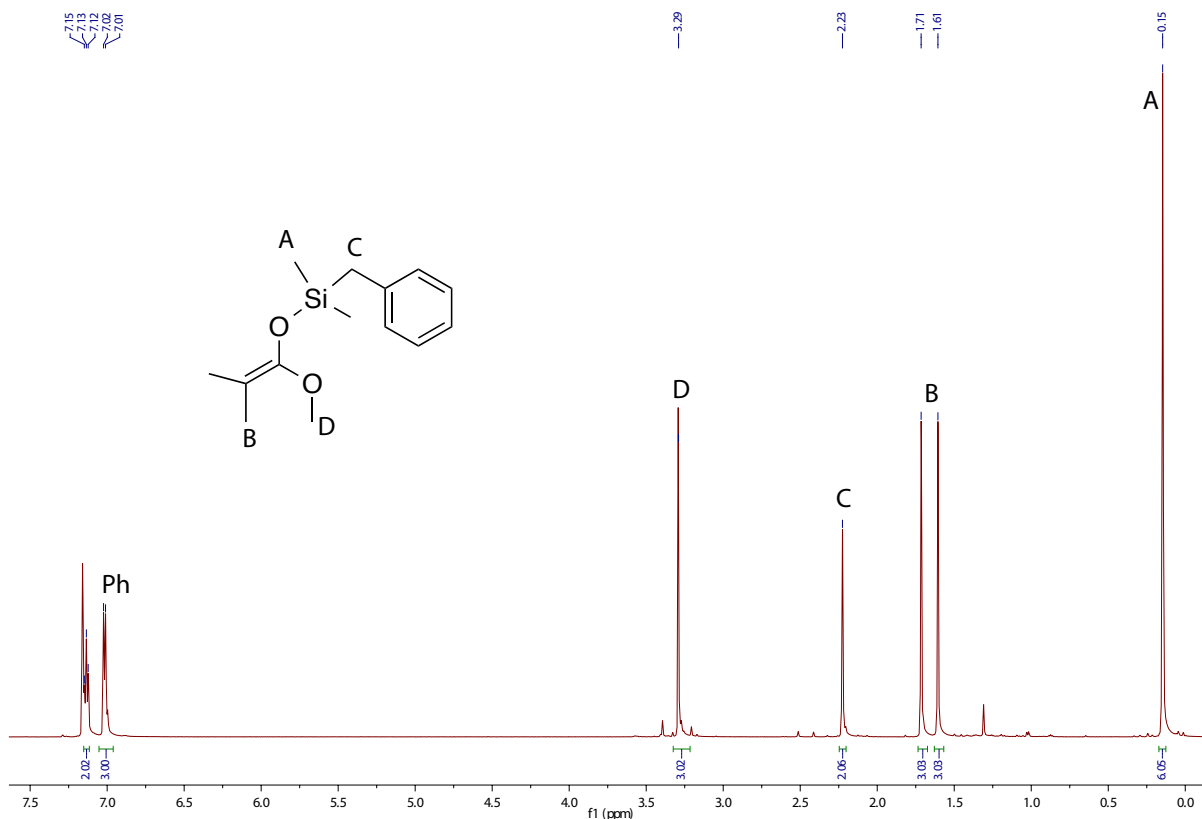


Figure S13. 1H NMR spectrum (600 MHz, benzene- d_6) of $BnMe_2SiO(MeO)C=CMe_2$.

$(H_2C=CH)Me_2SiO(MeO)C=CMe_2$. Crystallized $To^MgHB(C_6F_5)_3$ (0.011 g, 0.012 mmol), methyl methacrylate (0.117 g, 1.17 mmol), and $(CH_2=CH)Me_2SiH$ (0.101 g, 1.17 mmol) were stirred in benzene for 30 min. at room temperature. The volatile materials were removed under reduced pressure, leaving behind a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to afford a colorless liquid (0.201 g, 1.08 mmol, 92.1%). 1H NMR (400 MHz, benzene- d_6): δ 0.26 (s, 6 H, Me_2Si), 1.67 (s, 3 H, $C=CMe_2$), 1.73 (s, 3 H, $C=CMe_2$), 3.34 (s, 3 H, OMe), 5.77 (dd, 1 H, $^3J_{HH} = 21$ Hz, $^2J_{HH} = 3.6$ Hz,

$H_2C=CHSi$), 5.91 (dd, 1 H, $^3J_{HH} = 15$ Hz, $^2J_{HH} = 3.6$ Hz, $H_2C=CHSi$), 6.22 (dd, 1 H, $^3J_{HH} = 15$ Hz, $^2J_{HH} = 16$ Hz, $H_2C=CHSi$). $^{13}C\{^1H\}$ NMR (150 MHz, benzene- d_6): δ -1.20 (Me_2Si), 16.84 ($C=CMe_2$), 17.57 ($C=CMe_2$), 56.90 (OMe), 91.01 ($C=CMe_2$), 133.61 ($H_2C=CHSi$), 137.10 ($H_2C=CHSi$), 150.59 ($C=CMe_2$). ^{29}Si (119 MHz, benzene- d_6) δ 17.5. IR (KBr, cm^{-1}): ν 3055 (m), 2972 (s), 1716 (s), 1605 (w), 1567 (w), 1414 (m), 1266 (s), 1166 (s), 1029 (m), 955 (m), 900 (w), 836 (s), 790 (s), 744 (w), 717 (w), 690 (m), 662 (m). Anal. Calcd. for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found C, 58.50; H, 9.62.

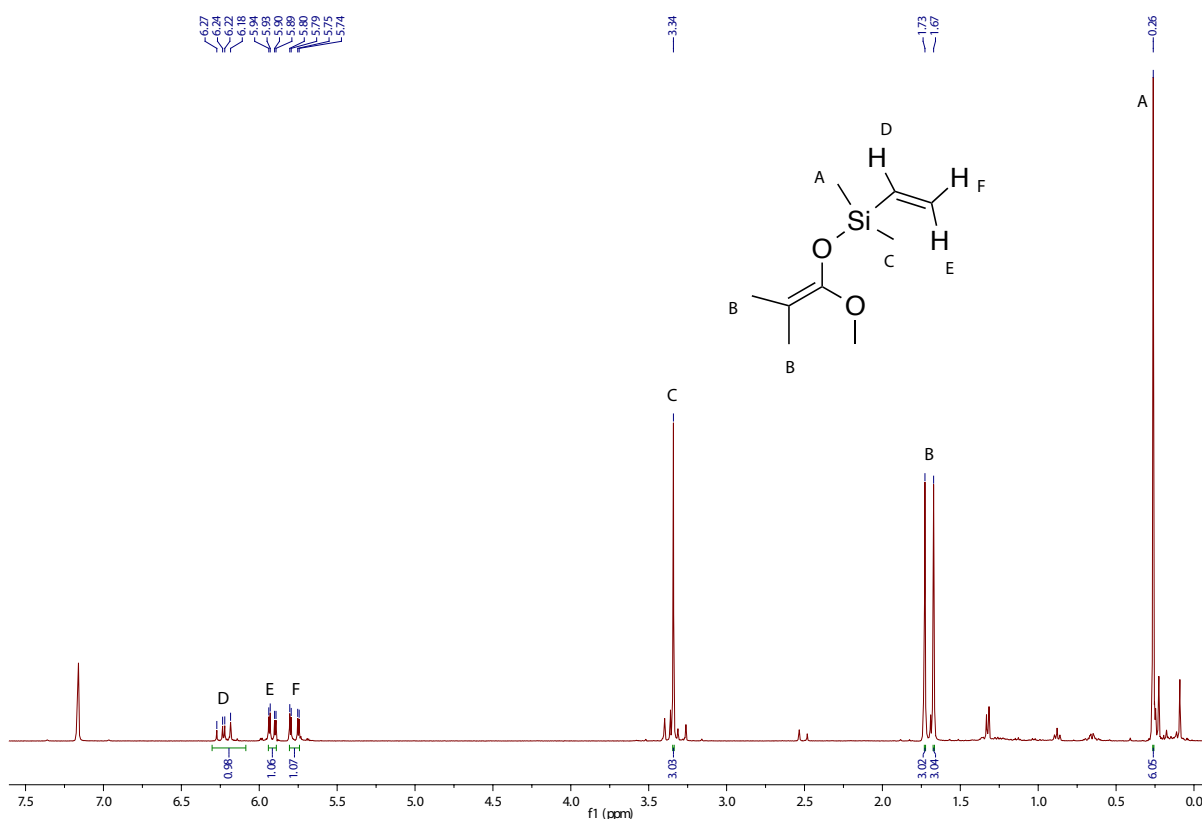


Figure S14. 1H NMR spectrum (400 MHz, benzene- d_6) of $(H_2C=CH)Me_2SiO(MeO)C=CMe_2$.

$Ph_2HSiO(MeO)C=CMe_2$. Crystallized $To^MgHB(C_6F_5)_3$ (0.011 g, 0.012 mmol), methyl methacrylate (0.117 g, 1.17 mmol), and Ph_2SiH_2 (0.216 g, 1.17 mmol) were stirred in benzene for 30 min. at room temperature. Benzene was removed under reduced pressure, leaving behind a

colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to afford a colorless liquid (0.331 g, 1.13 mmol, 96.3%). ^1H NMR (400 MHz, benzene- d_6): δ 1.64 (s, 3 H, $\text{C}=\text{CMe}_2$), 1.69 (s, 3 H, $\text{C}=\text{CMe}_2$), 3.29 (s, 3 H, OMe), 5.84 (s, 1 H, SiH), 7.17 (m, 6 H, C_6H_5), 7.74 (m, 4 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, benzene- d_6): δ 16.79 ($\text{C}=\text{CMe}_2$), 17.42 ($\text{C}=\text{CMe}_2$), 57.92 (OMe), 91.74 ($\text{C}=\text{CMe}_2$), 130.47 (C_6H_5), 131.12 (C_6H_5), 134.16 (*ipso*- C_6H_5), 135.49 (C_6H_5), 136.39 (C_6H_5), 150.93 ($\text{C}=\text{CMe}_2$). ^{29}Si (119 MHz, benzene- d_6) δ -14.5 (d, $^1J_{\text{SiH}} = 201$ Hz). IR (KBr, cm^{-1}): ν 3094 (m), 2931 (s), 2158 (s), 1716 (s), 1661 (w), 1598 (m), 1566 (w), 1548 (w), 1528 (w), 1437 (s), 1263 (m), 1169 (br s), 1029 (m), 949 (m), 858 (s), 738 (s), 701 (s), 671 (w). Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Si}$: C, 71.79; H, 7.09. Found C, 71.61; H, 7.32.

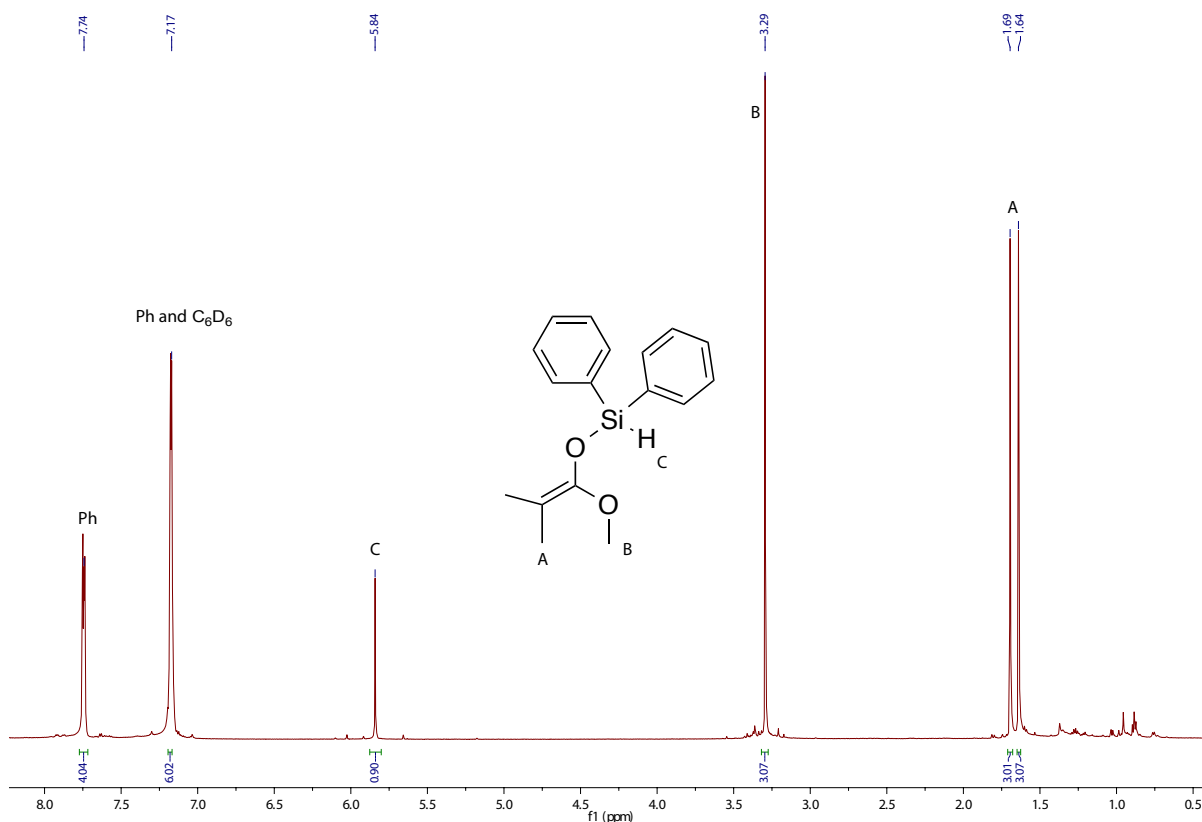


Figure S15. ^1H NMR spectrum (400 MHz, benzene- d_6) of $\text{Ph}_2\text{HSiO}(\text{MeO})\text{C}=\text{CMe}_2$.

PhMeHSiO(MeO)C=CMe₂. Crystallized To^MMgHB(C₆F₅)₃ (0.0428 g, 0.047 mmol), methyl methacrylate (0.467 g, 4.66 mmol), and PhMeSiH₂ (0.570 g, 4.66 mmol) were stirred in benzene for 7 h at 60 °C. The volatile materials were evaporated under reduced pressure to give a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure. Repeated Kugelrohr distillation (3×) under dynamic vacuum at 170 °C provided a colorless liquid (1.01 g, 4.54 mmol, 97.1%). ¹H NMR (600 MHz, benzene-*d*₆): δ 0.44 (d, 3 H, ³J_{HH} = 2.8 Hz, SiMe), 1.66 (s, 3 H, C=CMe₂), 1.67 (s, 3 H, C=CMe₂), 3.30 (s, 3 H, OMe), 5.36 (q, 1 H, ³J_{HH} = 2.8 Hz, SiH), 7.18 (m, 3 H, C₆H₅), 7.64 (m, 2 H, C₆H₅). ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ -2.31 (SiMe), 16.78 (C=CMe₂), 17.36 (C=CMe₂), 57.41 (OMe), 91.31 (C=CMe₂), 128.63 (C₆H₅), 130.92 (C₆H₅), 134.61 (C₆H₅), 135.73 (*ipso*-C₆H₅), 150.75 (C=CMe₂). ²⁹Si (119 MHz, benzene-*d*₆) δ -3.8 (d, ¹J_{SiH} = 216 Hz). IR (KBr, cm⁻¹): ν 3062 (m), 2897 (s), 2809 (m), 2076 (s, ν_{SiH}), 1740 (s), 1589 (w), 1451 (m), 1369 (w), 1257 (s), 1178 (s), 863 (s), 802 (w), 775 (m), 741 (m), 705 (m). Anal. Calcd. for C₁₂H₁₈O₂Si: C, 64.82; H, 8.16. Found C, 64.85; H, 7.79.

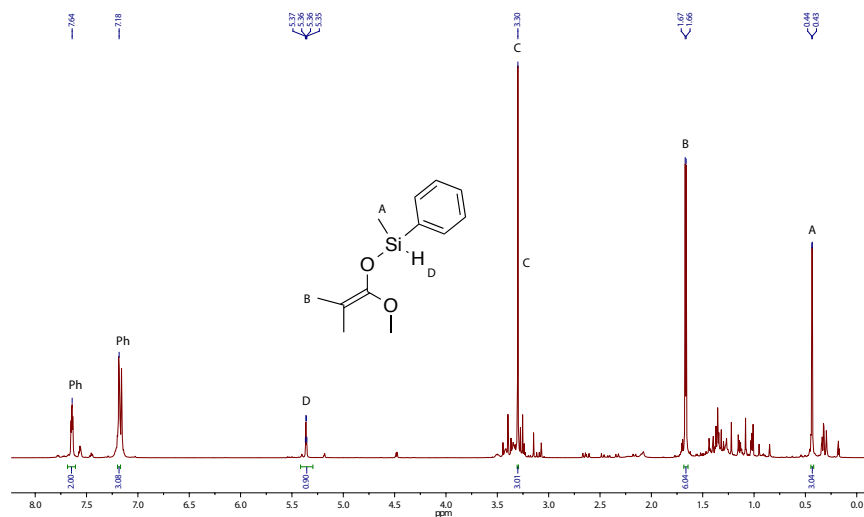


Figure S16. ¹H NMR spectrum (600 MHz, benzene-*d*₆) of PhMeHSiO(MeO)C=CMe₂, obtained from hydrosilylation catalyzed by **1**.

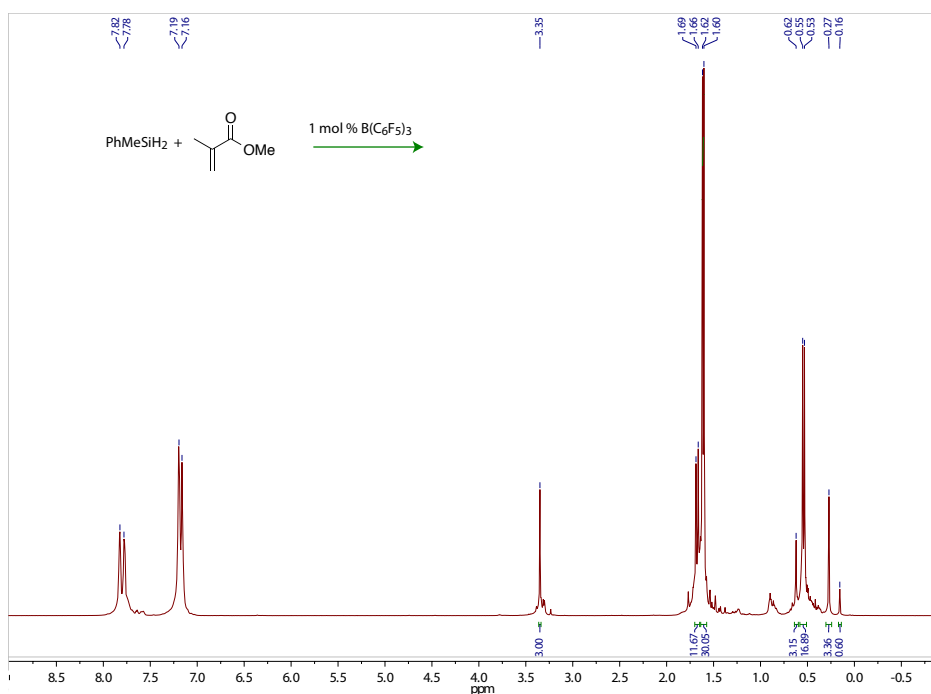


Figure S17. ¹H NMR spectrum of the reaction of PhMeSiH₂ and methyl methacrylate, catalyzed by 1 mol % B(C₆F₅)₃, which gives a mixture of bis-addition products and ester reductive cleavage products, distinct from the reactions catalyzed by To^MMgHB(C₆F₅)₃ (Figure S16). See Figure S23 for authentic PhMeSi{OC(OMe)=CMe₂}₂ from the selective To^MMgHB(C₆F₅)₃ catalyzed addition.

PhMeHSiO(Me₂CHCH₂O)C=CMe₂. Crystallized To^MMgHB(C₆F₅)₃ (0.027 g, 0.029 mmol), isobutyl methacrylate (0.167 g, 1.17 mmol), and PhMeSiH₂ (0.149 g, 1.17 mmol) were stirred in benzene for 8 h at room temperature. The solvent was evaporated under reduced pressure, leaving behind a colorless gel. The product was extracted with pentane, and the extracts were evaporated to dryness under reduced pressure to provide a colorless liquid (0.126 g, 0.476 mmol, 40.5%). ¹H NMR (600 MHz, benzene-*d*₆): δ 0.46 (d, 3 H, ³J_{HH} = 3.0 Hz, SiMe), 0.85 (d, 3 H, ³J_{HH} = 6.6 Hz, Me₂CHCH₂O), 0.86 (d, 3 H, ³J_{HH} = 6.6 Hz, Me₂CHCH₂O), 1.69 (s, 3 H, C=CMe₂), 1.72 (s, 3 H, C=CMe₂), 1.81 (m, 1 H, Me₂CHCH₂O), 3.49 (d, 2 H, ³J_{HH} = 6.6 Hz, Me₂CHCH₂O), 5.39 (q, 1 H, ³J_{HH} = 3.0 Hz, SiH), 7.18 (m, 3 H, C₆H₅), 7.66 (m, 2 H, C₆H₅). ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ -2.26 (SiMe), 16.96 (C=CMe₂), 17.50 (C=CMe₂), 19.75 (OCH₂CHMe₂), 29.20 (Me₂CHCH₂O), 76.78 (Me₂CHCH₂O), 91.51 (C=CMe₂), 128.62 (C₆H₅), 130.92 (C₆H₅), 134.62 (C₆H₅), 135.52 (*ipso*-C₆H₅), 149.96 (C=CMe₂). ²⁹Si (119 MHz, benzene-*d*₆) δ -3.9 (d, ¹J_{SiH} = 222 Hz). IR (KBr, cm⁻¹): ν 2962 (s), 2926 (s), 2876 (s), 2141 (s), 1708 (s), 1470 (m), 1429 (m), 1393 (w), 1257 (s), 1166 (s), 1122 (s), 1024 (m), 969 (w), 868 (s), 732 (w), 700 (m), 611 (m). Anal. Calcd. for C₁₅H₂₄O₂Si: C, 68.13; H, 9.15. Found C, 68.06; H, 8.69.

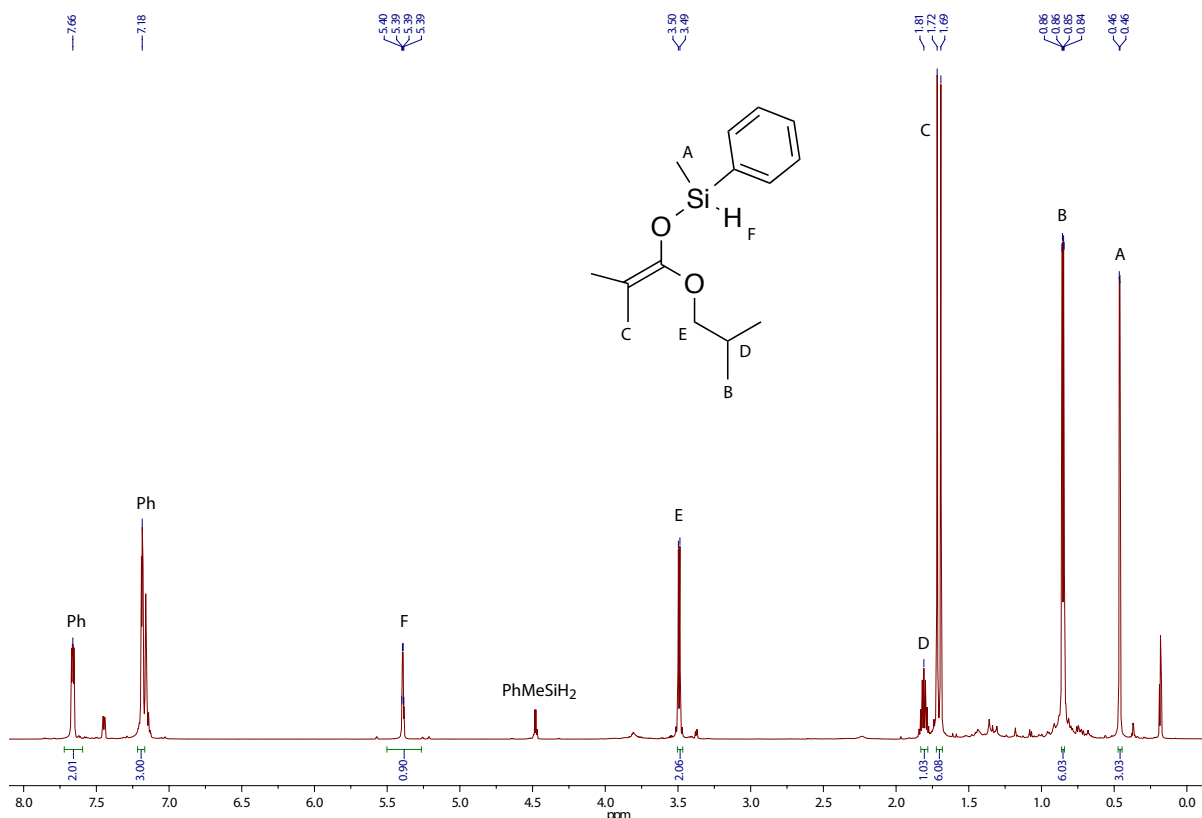


Figure S18. ^1H NMR spectrum (600 MHz, benzene- d_6) of $(\text{PhMeHSiO})(\text{Me}_2\text{CHCH}_2\text{O})\text{C}=\text{CMe}_2$.

$\text{PhMeHSiO}(\text{PhCH}_2\text{O})\text{C}=\text{CMe}_2$. Crystallized $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$ (0.027 g, 0.029 mmol), benzyl methacrylate (0.207 g, 1.17 mmol), and PhMeSiH_2 (0.149 g, 1.17 mmol) were stirred in benzene for 4 h at room temperature. The volatile materials were evaporated under reduced pressure to give a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to provide a colorless liquid (0.348 g, 1.16 mmol, 99.2%). ^1H NMR (600 MHz, benzene- d_6): δ 0.45 (d, 3 H, $^3J_{\text{HH}} = 3.0$ Hz, SiMe), 1.62 (s, 3 H, $\text{C}=\text{CMe}_2$), 1.66 (s, 3 H, $\text{C}=\text{CMe}_2$), 4.70 (s, 2 H, PhCH_2O), 5.40 (q, 1 H, $^3J_{\text{HH}} = 3.0$ Hz, SiH), 7.08 (t, 1 H, $^3J_{\text{HH}} = 7.2$ Hz, $\text{OCH}_2\text{C}_6\text{H}_5$), 7.13 (t, 2 H, $^3J_{\text{HH}} = 7.2$ Hz, $\text{OCH}_2\text{C}_6\text{H}_5$), 7.17 (m, 3 H, SiC_6H_5), 7.25 (d, 2 H, $^3J_{\text{HH}} = 7.2$ Hz, $\text{OCH}_2\text{C}_6\text{H}_5$), 7.66 (m, 2 H, SiC_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, benzene- d_6): δ -2.37 (SiMe), 17.01 ($\text{C}=\text{CMe}_2$), 17.44 ($\text{C}=\text{CMe}_2$), 71.96 (OCH_2Ph), 92.83 ($\text{C}=\text{CMe}_2$), 128.35

(OCH₂C₆H₅), 128.66 (SiC₆H₅), 128.81 (OCH₂C₆H₅), 128.84 (OCH₂C₆H₅), 130.97 (SiC₆H₅), 134.61 (SiC₆H₅), 135.66 (*ipso*-SiC₆H₅), 149.22 (C=CMe₂). ²⁹Si (119 MHz, benzene-*d*₆) δ -3.5 (d, ¹J_{SiH} = 216 Hz). IR (KBr, cm⁻¹): ν 3070 (m), 3032 (m), 2982 (m), 2915 (s), 2859 (m), 2146 (s), 1707 (s), 1591 (w), 1498 (w), 1455 (m), 1429 (m), 1384 (w), 1256 (s), 1161 (s), 1122 (s), 1008 (m), 964 (m), 866 (s), 734 (s), 698 (s). Anal. Calcd. for C₁₈H₂₂O₂Si: C, 72.44; H, 7.43. Found C, 71.98; H, 7.49.

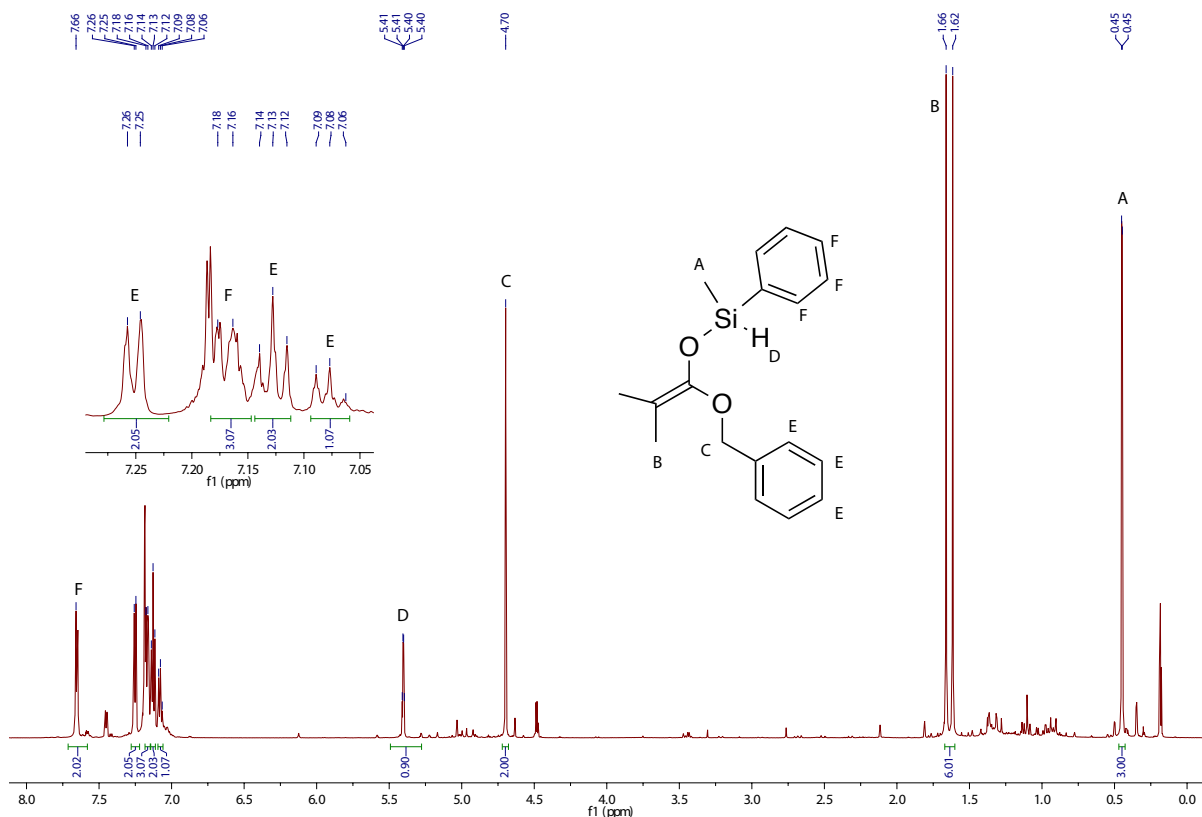


Figure S19. ¹H NMR spectrum (600 MHz, benzene-*d*₆) of PhMeHSiO(PhCH₂O)C=CMe₂.

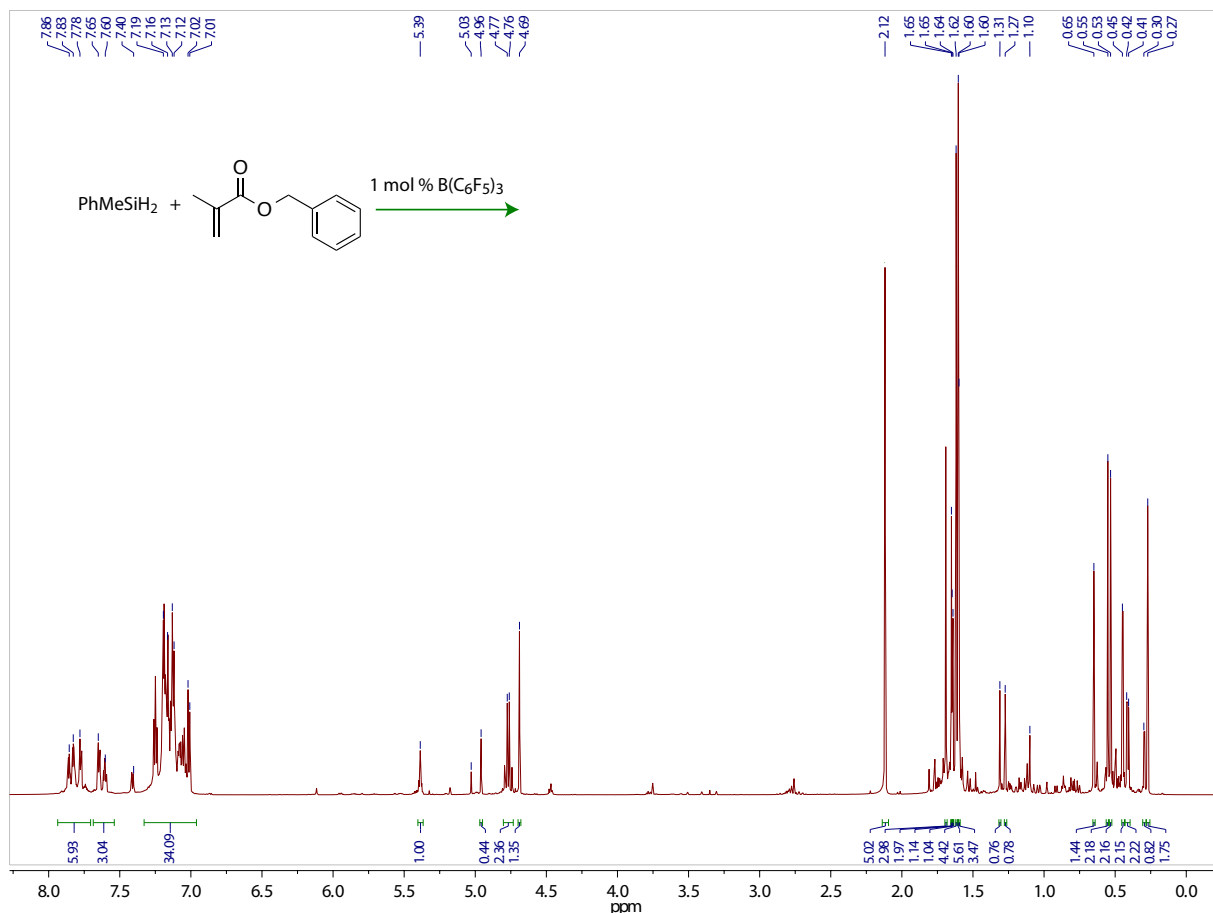


Figure S20. ¹H NMR spectrum of the reaction of PhMeSiH₂ and benzyl methacrylate, catalyzed by 1 mol % B(C₆F₅)₃. The silyl ketene acetyl is formed as one of a few products.

3,4-dihydro-6-(phenylmethylsiloxy)-2*H*-pyran. Crystallized To^MMgHB(C₆F₅)₃ (0.030 g, 0.033 mmol), 5,6-dihydro-2*H*-pyran-2-one (0.032 g, 0.33 mmol), and PhMeSiH₂ (0.042 g, 0.33 mmol) were stirred in benzene for 5 h at room temperature. Evaporation of the volatile materials provided a yellow gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to afford a pale yellow liquid (0.059 g, 0.26 mmol, 80.3%). ¹H NMR (600 MHz, benzene-*d*₆): δ 0.46 (d, 3 H, ³J_{HH} = 3.0 Hz, SiMe), 1.32 (pent, 2 H, ³J_{HH} = 4.8 Hz, OCH₂CH₂CH₂CH=C–OSiHMePh), 1.80 (m, 2 H, OCH₂CH₂CH₂CH=C–OSiHMePh), 3.68 (t, 2 H, ³J_{HH} = 4.8 Hz, OCH₂CH₂CH₂CH=C–OSiHMePh), 4.10 (t, 1 H, ³J_{HH} = 3.6 Hz, OCH₂CH₂CH₂CH=C–OSiHMePh), 5.46 (q, 1 H, ³J_{HH} = 3.0 Hz, SiH), 7.18 (m, 3 H, C₆H₅), 7.66

(m, 2 H, C₆H₅). ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ -1.91 (SiMe), 19.64 (OCH₂CH₂CH₂CH=C–OSiHMePh), 22.24 (OCH₂CH₂CH₂CH=C–OSiHMePh), 67.69 (OCH₂CH₂CH₂CH=C–OSiHMePh), 74.57 (OCH₂CH₂CH₂CH=C–OSiHMePh), 127.85 (C₆H₅), 130.08 (C₆H₅), 133.89 (C₆H₅), 138.21 (*ipso*-C₆H₅), 155.62 (OCH₂CH₂CH₂CH=C–OSiHMePh). ²⁹Si (119 MHz, benzene-*d*₆) δ -5.1 (d, ¹J_{SiH} = 218 Hz). IR (KBr, cm⁻¹): ν 3070 (w), 3050 (w), 2957 (s), 2926 (s), 2854 (m), 2131 (s), 1738 (s), 1637 (w), 1592 (m), 1460 (m), 1429 (s), 1386 (w), 1255 (m), 1121 (s), 1079 (s), 879 (s), 846 (s), 796 (w), 725 (s), 700 (s). Anal. Calcd. for C₁₂H₁₆O₂Si: C, 65.41; H, 7.32. Found C, 65.73; H, 6.98.

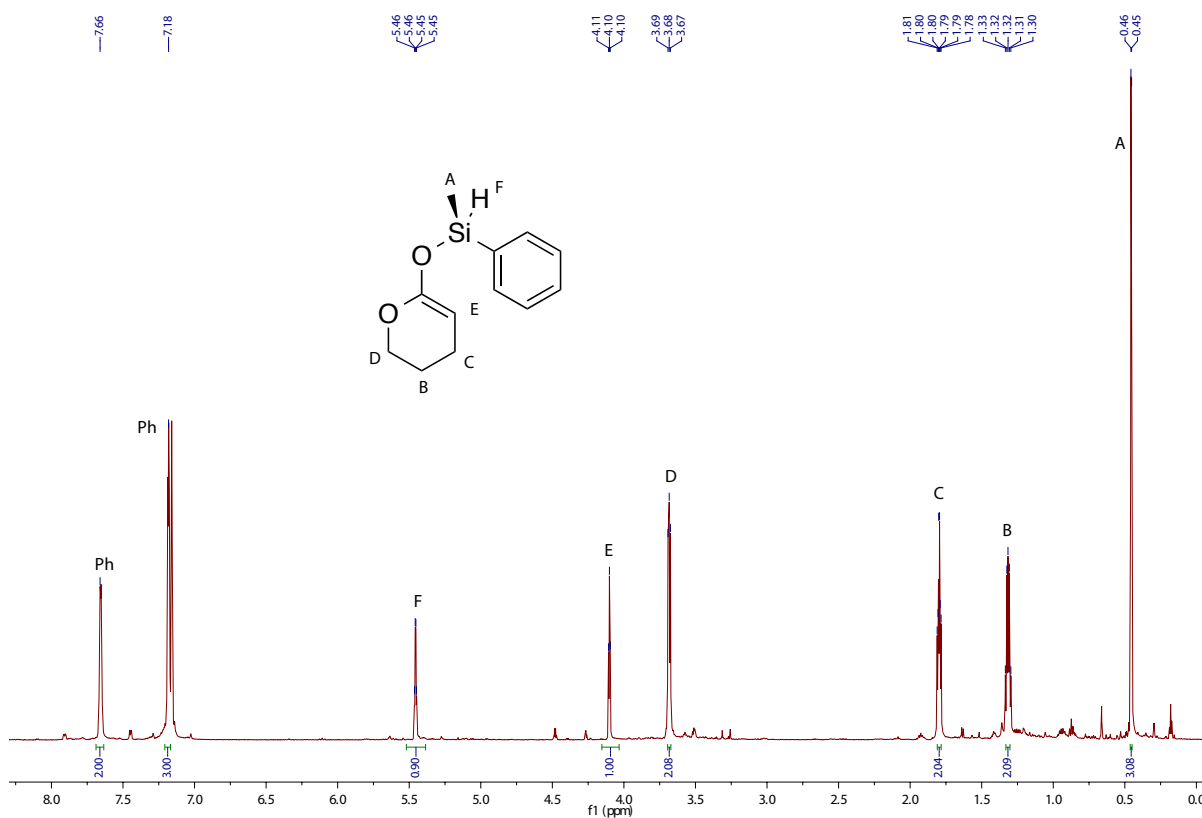


Figure S21. ¹H NMR spectrum (600 MHz, benzene-*d*₆) of 3,4-dihydro-6-(phenylmethylsiloxy)-2H-pyran.

3,4-dihydro-6-(benzyl dimethylsiloxy)-2H-pyran. Crystallized $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$ (0.015 g, 0.015 mmol), 5,6-dihydro-2H-pyran-2-one (0.160 g, 1.65 mmol), and BnMe_2SiH (0.245 g, 1.65 mmol) were stirred in benzene for 30 min. at 35 °C. Benzene was removed under reduced pressure, leaving behind a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to afford a colorless liquid (0.335 g, 1.35 mmol, 82.9%). ^1H NMR (600 MHz, benzene- d_6): δ 0.18 (s, 6 H, SiMe_2), 1.39 (pent, 2 H, $^3J_{\text{HH}} = 4.8$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 1.86 (m, 2 H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 2.27 (s, 2 H, SiCH_2Ph), 3.72 (t, 2 H, $^3J_{\text{HH}} = 4.8$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 4.02 (t, 1 H, $^3J_{\text{HH}} = 3.6$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 7.01 (t, 1 H, $^3J_{\text{HH}} = 7.2$ Hz, C_6H_5), 7.06 (d, 2 H, $^3J_{\text{HH}} = 7.2$ Hz, C_6H_5), 7.14 (t, 2 H, $^3J_{\text{HH}} = 7.2$ Hz, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, benzene- d_6): δ -1.31 (SiMe_2), 20.57 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 23.04 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 27.43 (PhCH_2Si), 67.53 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 74.67 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$), 125.10 (C_6H_5), 128.97 (C_6H_5), 129.23 (C_6H_5), 139.25 (*ipso*- C_6H_5), 155.50 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{OSiMe}_2\text{Bn}$). ^{29}Si (119 MHz, benzene- d_6) δ 15.6. IR (KBr, cm^{-1}): ν 3081 (w), 3059 (w), 3025(w), 2957 (s), 1733 (s), 1600 (w), 1493 (m), 1452 (m), 1403 (m), 1253 (s), 1208 (s), 1157 (s), 1077 (s), 1057 (s), 907 (m), 838 (s), 762 (s), 700 (s), 619 (w). Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Si}$: C, 67.70; H, 8.12. Found C, 67.77; H, 8.15.

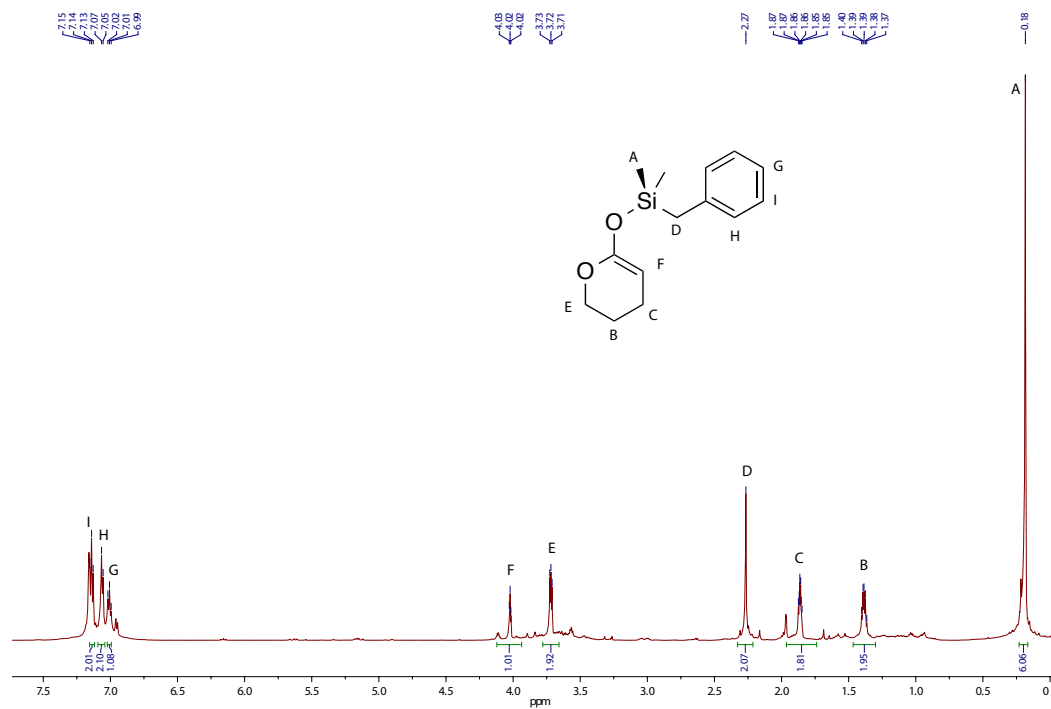


Figure S22. ^1H NMR spectrum (600 MHz, benzene- d_6) of 3,4-dihydro-6-(benzyltrimethylsilyloxy)-2H-pyran.

$\text{PhMeSi}\{\text{O}(\text{MeO})\text{C}=\text{CMe}_2\}_2$.⁴ Crystallized $\text{To}^{\text{M}}\text{MgHB}(\text{C}_6\text{F}_5)_3$ (0.05 g, 0.054 mmol), methyl methacrylate (0.226 g, 2.18 mmol), and PhMeSiH_2 (0.150 g, 1.09 mmol) were stirred in benzene for 12 h at 80 °C. The volatile materials were evaporated under reduced pressure to give a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure. Kugelrohr distillation under dynamic vacuum at 180 °C provided a colorless liquid (0.113 g, 0.351 mmol, 32.2%). ^1H NMR (600 MHz, benzene- d_6): δ 0.63 (s, 3 H, SiMe), 1.67 (s, 6 H, $\text{C}=\text{CMe}_2$), 1.69 (s, 6 H, $\text{C}=\text{CMe}_2$), 3.35 (s, 6 H, OMe), 7.19 (m, 3 H, C_6H_5), 7.83 (m, 2 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, benzene- d_6): δ -3.15 (SiMe), 16.83 ($\text{C}=\text{CMe}_2$), 17.45 ($\text{C}=\text{CMe}_2$), 57.59 (OMe), 92.19 ($\text{C}=\text{CMe}_2$), 128.46 (C_6H_5), 131.04 (C_6H_5), 134.53 (C_6H_5), 134.72 (*ipso*- C_6H_5), 150.00 ($\text{C}=\text{CMe}_2$). ^{29}Si (119 MHz, benzene- d_6) δ -20.2. IR (KBr, cm^{-1}): ν 2966 (m), 2925 (s), 2859 (m), 1709 (s), 1593 (w), 1457 (m), 1384 (w), 1261 (s), 1205 (m), 1161

(s), 1125 (m), 1095 (w), 1027 (m), 949 (m), 873 (m), 855 (m), 794 (m), 737 (w), 700 (w). Anal. Calcd. for C₁₇H₂₆O₄Si: C, 63.32; H, 8.13. Found C, 62.85; H, 8.43.

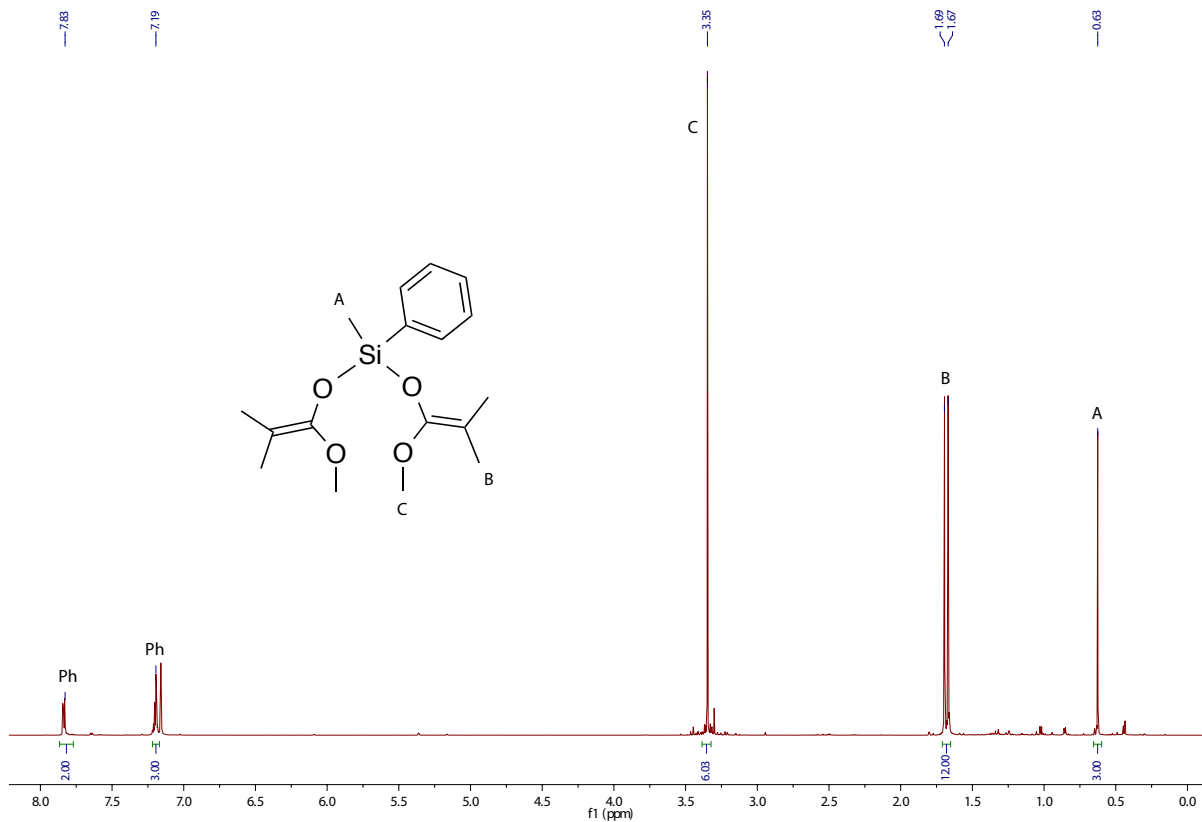


Figure S23. ¹H NMR spectrum (600 MHz, benzene-*d*₆) of PhMeSi{O(MeO)C=CMe₂}₂.

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