Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Selective Hydrosilylation of Alkynes and Ketones: Contrasting Reactivity Between Cationic 3-Iminophosphine Palladium and Nickel Complexes

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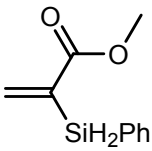
1) General methods and instrumentation: All NMR-scale reactions were set up in a nitrogen-filled glovebox. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories and for air-sensitive usage, dried over calcium hydride and sodium, respectively, freeze-pump-thawed three times, vacuum-transferred, and stored over molecular sieves in a nitrogen-filled glovebox. Precatalysts **1a** and **1b** were synthesized via the previously reported procedure.[1-2] Hydrosilanes for catalytic hydrosilylation reactions were purchased from Gelest, AK Scientific, or Acros, dried neat over calcium hydride and distilled under nitrogen, freeze-pump-thawed, and transferred to the glovebox. All aromatic aldehydes and ketones were supplied from Alfa Aesar, AK Scientific, Sigma-Aldrich, and Acros. Alkynes were purchased from either Sigma-Aldrich or AK Scientific. ^1H and ^{13}C NMR data were obtained either on a 400 MHz Varian VXRS NMR spectrometer at 399.95 MHz for ^1H and 100.56 MHz for ^{13}C NMR spectroscopy or on a 600 MHz Bruker Avance III at 599.9 MHz for ^1H and 150.8 MHz for ^{13}C NMR spectroscopy. High resolution mass spectrometry data were determined by the University of Illinois Mass Spectrometry Laboratory, Urbana, IL, USA.

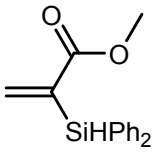
2) Catalytic reactions and isolation of hydrosilylation products: For the hydrosilylation reactions of alkynes, unless otherwise noted, **1a** or **1b** was suspended in $CDCl_3$ or C_6D_6, followed by addition of hydrosilane (1 eq.) and alkyne (1 eq.). In the case of carbonyl hydrosilylation, the carbonyl derivative was added before the hydrosilane. Then, the resulting solution was transferred to an NMR tube, sealed and reaction progress was monitored by acquiring ^1H NMR data frequently. Gram scale reactions were set up in 20 ml vials, sealed with gentle stirring, and reaction completion was monitored by TLC analysis of the reaction mixture. After detection of reaction completion by ^1H NMR spectroscopy (based on diminishing starting material peaks), all volatiles were removed under vacuum, and the crude reaction mixture was extracted with hexanes and passed through a short plug of silica gel to remove inorganics. This mixture was concentrated and purified by flash chromatography (hexanes for vinylsilane products and 90:10 hexanes:ethylacetate for silylether products) as a colorless oily liquid. Isolated yields are calculated based on unsaturated substrate (alkyne or carbonyl derivative). For silylether products, due to partial hydrolysis of the product on silica gel, yields are based on total of

silylether and corresponding alcohol. All vinylsilanes were characterized by ^{1}H and ^{13}C NMR spectroscopy and high resolution mass spectrometry. Silylether products were characterized only by ^{1}H and ^{13}C NMR spectroscopy. Hydrosilylation products **3a**,[3] **3b**,[4] **3d**,[5] **3i**,[5] **3j**,[6] **3k**,[5] **3l**,[7] **3m**,[8] **4a**,[9] **4b**,[10] and **4c**[10] were identified by comparison to previously reported NMR spectral data. Nonetheless, their observed spectra are included below.

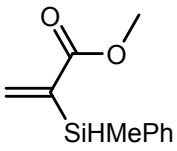
3) Characterization of hydrosilylation products:



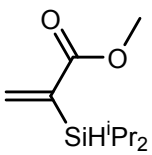
Methyl 2-(phenylsilyl)acrylate (2a): 86% isolated yield (83 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.64-7.61 (m, 2H), 7.44-7.37 (m, 3H), 7.03 (d, ^{2}J=2.0 Hz, 1H), 6.26 (d, ^{2}J=2.0 Hz, 1H), 4.69 (s, 2H), 3.76 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 168.5, 144.6, 137.2, 135.7, 130.5, 130.2, 128.2, 52.1; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{10}H_{11}O_2Si$, 191.0528; found, 191.0530.



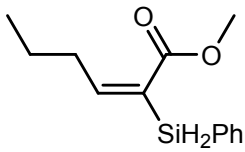
Methyl 2-(diphenylsilyl)acrylate (2b): 91% isolated yield (122 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66-7.63 (m, 4H), 7.47-7.41 (m, 6H), 7.15 (d, ^{2}J=2.8 Hz, 1H), 6.25 (d, ^{2}J=2.8 Hz, 1H), 5.31 (s, 1H), 3.73 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 168.9, 145.0, 138.9, 135.7, 132.4, 130.1, 128.2, 52.0; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{16}H_{15}O_2Si$, 267.0841; found, 267.0841.



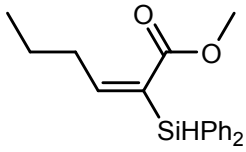
Methyl 2-(methyl(phenyl)silyl)acrylate (2c): 80% isolated yield (83 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.60-7.58 (m, 2H), 7.42-7.37 (m, 3H), 6.96 (d, ^{2}J=2.8 Hz, 1H), 6.16 (d, ^{2}J=2.8 Hz, 1H), 4.72 (q, ^{3}J= 4.0 Hz, 1H), 3.75 (s, 3H), 0.57 (d, ^{3}J=4.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 169.0, 142.9, 140.3, 134.8, 133.5, 129.8, 128.0, 51.9, -5.3; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{11}H_{13}O_2Si$, 205.0685; found, 205.0684.



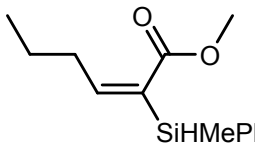
Methyl 2-(diisopropylsilyl)acrylate (2d): 64% isolated yield (64 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 6.92 (d, ^{2}J=3.6 Hz, 1H), 6.17 (d, ^{2}J=3.6 Hz, 1H), 3.75 (s, 3H), 3.65 (t, ^{3}J=3.6 Hz, 1H), 1.20-1.15 (m, 2H), 1.05 (d, ^{3}J=7.2 Hz, 6H), 0.98 (d, ^{3}J=7.2 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 169.6, 143.3, 139.0, 51.8, 18.9, 18.8, 10.7; HRMS (CI) (m/z): $[M+H]^+$ calc for $C_{10}H_{21}O_2Si$, 201.1311; found, 201.1313.



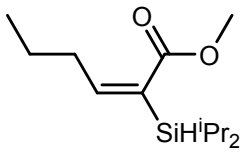
Methyl (E)-2-(phenylsilyl)hex-2-enoate (2e): 93% isolated yield (109 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.62-7.60 (m, 2H), 7.42-7.36 (m, 3H), 6.68 (t, ^{3}J=6.8 Hz, 1H), 4.66 (s, 2H), 3.70 (s, 3H), 2.62 (q, ^{3}J=6.8 Hz, 2H), 1.53-1.47 (m, 2H), 0.95 (t, ^{3}J=7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 168.7, 162.9, 135.6, 131.5, 129.9, 128.1, 127.5, 51.4, 33.9, 22.2, 13.9; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{13}H_{17}O_2Si$, 233.0998; found, 233.0990.



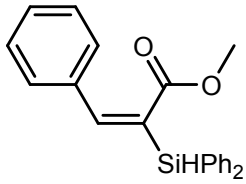
Methyl (E)-2-(diphenylsilyl)hex-2-enoate (2f): (same regio- and stereoisomers from either **1a** or **1b**) 88% isolated yield (137 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.64-7.62 (m, 4H), 7.45-7.39 (m, 6H), 6.60 (t, ^{3}J=7.2 Hz, 1H), 5.23 (s, 1H), 3.63 (s, 3H), 2.62 (q, ^{3}J=7.2 Hz, 2H), 1.55-1.49 (m, 2H), 0.97 (t, ^{3}J=7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 169.3, 161.7, 135.6, 133.1, 129.9, 129.5, 128.0, 51.3, 33.9, 22.3, 13.9; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{19}H_{21}O_2Si$, 309.1311; found, 309.1306.



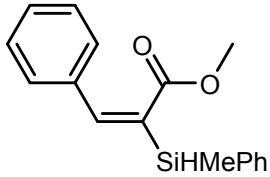
Methyl (E)-2-(methyl(phenyl)silyl)hex-2-enoate (2g): 85% isolated yield (106 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.60-7.57 (m, 2H), 7.41-7.38 (m, 3H), 6.52 (t, ^{3}J= 7.2 Hz, 1H), 4.67 (q, ^{3}J=4.0 Hz, 1H), 3.69 (s, 3H), 2.54 (q, ^{3}J= 7.2 Hz, 2H), 1.49 (sext, ^{3}J=7.2 Hz, 2H), 0.95 (t, ^{3}J=7.2 Hz, 3H), 0.54 (d, ^{3}J=4.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 169.5, 159.2, 134.9, 134.7, 131.0, 129.6, 127.9, 51.2, 33.8, 22.3, 13.9, -5.0; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{14}H_{19}O_2Si$, 247.1154; found, 247.1153.



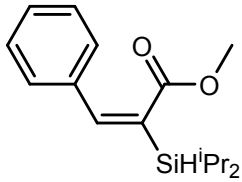
Methyl (E)-2-(diisopropylsilyl)hex-2-enoate (2h): 83% isolated yield (101 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): 6.38 (t, ^{3}J=7.6 Hz, 1H), 3.68 (s, 3H), 3.56 (t, ^{3}J=3.2 Hz, 1H), 2.42 (q, ^{3}J=7.6 Hz, 2H), 1.50-1.41 (m, 2H), 1.13-1.05 (m, 2H), 1.01 (d, ^{3}J=6.8 Hz, 6H), 0.97 (d, ^{3}J=6.8 Hz, 6H), 0.90 (t, ^{3}J=7.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 170.4, 158.1, 129.9, 51.1, 33.8, 22.4, 18.8, 18.7, 13.8, 11.0. HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{13}H_{25}O_2Si$, 241.1624; found, 241.1624.



Methyl (E)-2-(diphenylsilyl)-3-phenylacrylate (2j): 93% isolated yield (160 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.69-7.68 (m, 4H), 7.48-7.45 (m, 2H), 7.43-7.41 (m, 4H), 7.38-7.32 (m, 5H), 7.10 (s, 1H), 5.34 (s, 1H), 3.58 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 171.2, 148.8, 136.2, 135.8, 132.0, 131.7, 130.3, 129.3, 128.7, 128.5, 128.2, 51.8; HRMS (EI) (m/z): $[M]^+$ calc for $C_{22}H_{20}O_2Si$, 344.1233; found, 344.1238.

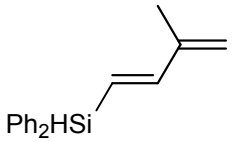


Methyl (E)-2-(methyl(phenyl)silyl)-3-phenylacrylate (2k): 79% isolated yield (112 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66-7.64 (m, 2H), 7.44-7.31 (m, 8H), 7.03 (s, 1H), 4.81 (q, ^{3}J=3.6 Hz, 1H), 3.67 (s, 3H), 2.62 (d, ^{3}J=3.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 171.5, 146.6, 136.3, 134.9, 133.4, 130.8, 130.1, 129.0, 128.53, 128.50, 128.2, 51.8, -5.3; HRMS (EI) (m/z): $[M]^+$ calc for $C_{17}H_{18}O_2Si$, 282.1076; found, 282.1079.

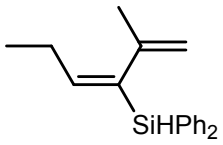


Methyl (E)-2-(diisopropylsilyl)-3-phenylacrylate (2l): 68% isolated yield (94 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.33-7.24 (m, 5H), 7.05 (s, 1H), 3.77-3.75 (m, 1H), 3.69 (s, 3H), 1.24-1.19 (m, 2H), 1.12 (d, ^{3}J=7.6 Hz, 6H), 1.10 (d, ^{3}J=7.6 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 172.3, 158.8,

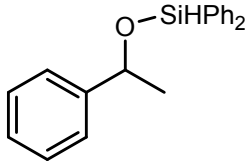
146.4, 136.5, 128.8, 128.5, 128.4, 51.7, 18.61, 18.56, 11.1; HRMS (EI) (m/z): $[M-H]^+$ calc for $C_{16}H_{23}O_2Si$, 275.1467; found, 275.1471.



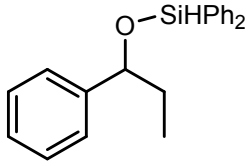
(3-Methylbuta-1,3-dien-1-yl)diphenylsilane (2m): 92% isolated yield (115 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.60-7.58 (m, 4H), 7.43-7.37 (m, 6H), 6.83 (d, ^{4}J=18.8 Hz, 1H), 6.09 (dd, ^{4}J=18.8 Hz, ^{2}J=3.2 Hz, 1H), 5.17 (d, ^{2}J=3.2 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 1.92 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 152.1, 143.3, 135.6, 133.9, 129.8, 128.2, 121.4, 119.0, 18.1; HRMS (EI) (m/z): $[M]^+$ calc for $C_{17}H_{18}Si$, 250.1178; found, 250.1172.



(E)-(2-Methylhexa-1,3-dien-3-yl)diphenylsilane (2n): (same regio- and stereoisomers from either **1a** or **1b**) 81% isolated yield (113 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.60 (dd, ^{3}J=7.8 Hz, ^{4}J=1.4 Hz, 4H), 7.42-7.26 (m, 6H), 5.89 (t, ^{3}J=7.1 Hz, 1H), 5.09 (s, 1H), 4.86 (d, ^{2}J=1.3 Hz, 1H), 4.53 (d, ^{3}J=1.3 Hz, 1H), 2.20 (quint, ^{3}J=7.1 Hz, 2H), 1.71 (s, 3H), 0.99 (t, ^{3}J=7.1 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 147.5, 145.4, 139.2, 135.9, 133.9, 129.7, 128.0, 112.2, 24.5, 23.8, 14.4; HRMS (EI) (m/z): $[M]^+$ calc for $C_{19}H_{22}Si$, 278.1491; found, 278.1491.

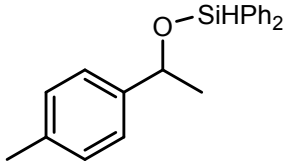


Diphenyl(1-phenylethoxy)silane (3a):[3] 94% isolated yield (143 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.71 (dd, ^{3}J=7.6 Hz, ^{4}J=1.6 Hz, 2H), 7.66 (d, ^{3}J=2.0 Hz, 2H), 7.52-7.36 (m, 11H), 5.51 (s, 1H), 5.09 (q, ^{3}J=6.4 Hz, 1H), 1.60 (d, ^{3}J=6.4 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 145.4, 134.83, 134.79, 134.4, 134.3, 130.5, 130.4, 128.4, 128.13, 128.06, 127.3, 125.7, 72.8, 26.4.

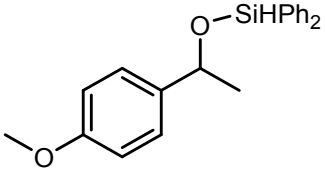


Diphenyl(1-phenylpropoxy)silane (3b):[4] 85% isolated yield (135 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.71-7.62 (m, 4H), 7.51-7.36 (m, 11H), 5.47 (s, 1H), 4.81 (t, ^{3}J=6.0 Hz, 1H), 2.01-1.91 (m, 1H),

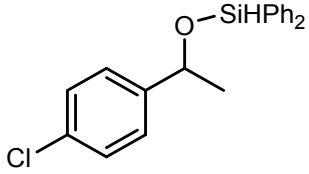
1.91-1.82 (m, 1H), 0.96 (t, ^{3}J=7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 143.9, 135.9, 135.8, 134.9, 134.8, 134.4, 134.2, 130.4, 130.3, 130.0, 129.9, 128.2, 128.1, 128.0, 127.3, 126.4, 78.2, 32.9, 10.1.



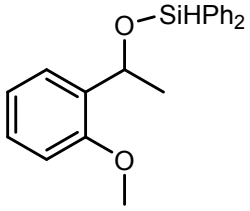
Diphenyl(1-(p-tolyl)ethoxy)silane (3c): 71% isolated yield (113 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.72 (d, ^{3}J=7.6 Hz, 2H), 7.67 (d, ^{3}J=7.2 Hz, 2H), 7.52-7.41 (m, 6H), 7.33 (d, ^{3}J=8.0 Hz, 2H), 7.21 (d, ^{3}J=8.0 Hz, 2H), 5.51 (s, 1H), 5.07 (q, ^{3}J=6.0 Hz, 1H), 2.42 (s, 3H), 1.59 (d, ^{3}J=6.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 142.4, 136.8, 135.9, 134.83, 134.79, 134.4, 130.41, 130.36, 129.0, 128.1, 128.0, 125.6, 72.7, 26.4, 21.4.



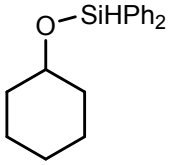
(1-(4-Methoxyphenyl)ethoxy)diphenylsilane (3d):[5] 86% isolated yield (144 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.63 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 2H), 7.57 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 2H), 7.46-7.33 (m, 6H), 7.26 (d, ^{3}J=8.8 Hz, 2H), 6.85 (d, ^{3}J=8.8 Hz, 2H), 5.39 (s, 1H), 4.97 (q, ^{3}J=6.4 Hz, 1H), 3.81 (s, 3H), 1.50 (d, ^{3}J=6.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 158.8, 137.6, 134.84, 134.79, 134.4, 134.3, 130.4, 130.3, 128.1, 128.0, 127.0, 113.7, 72.5, 55.4, 26.3.



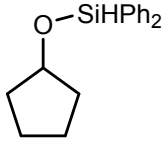
(1-(4-Chlorophenyl)ethoxy)diphenylsilane (3e): 66% isolated yield (112 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.62 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 2H), 7.57 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 2H), 7.46-7.33 (m, 6H), 7.27 (s, 4H), 5.40 (s, 1H), 4.96 (q, ^{3}J=6.4 Hz, 1H), 1.48 (d, ^{3}J=6.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz): 143.9, 134.81, 134.76, 134.1, 133.9, 132.9, 130.6, 130.5, 128.5, 128.2, 128.1, 127.1, 72.2, 26.4.



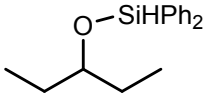
(1-(2-Methoxyphenyl)ethoxy)diphenylsilane (3g): 77% isolated yield (129 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.64 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 2H), 7.59 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 2H), 7.45-7.34 (m, 6H), 7.23 (t, ^{3}J=8.4 Hz, 1H), 6.93-6.90 (m, 2H), 6.79 (dm, ^{3}J=8.4 Hz, 1H), 5.42 (s, 1H), 4.99 (q, ^{3}J=6.4 Hz, 1H), 3.77 (s, 3H), 1.51 (d, ^{3}J=6.4 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 159.7, 147.1, 134.84, 134.82, 134.3, 134.1, 130.5, 130.4, 129.4, 128.14, 128.07, 118.1, 112.8, 111.1, 72.7, 55.3, 26.4.



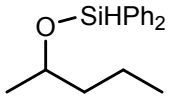
(Cyclohexyloxy)diphenylsilane (3i):[5] 89% isolated yield (126 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.69 (dd, ^{3}J=8.0 Hz, ^{4}J=1.6 Hz, 4H), 7.49-7.41 (m, 6H), 5.53 (s, 1H), 3.90-3.83 (m, 1H), 1.94-1.91 (m, 2H), 1.81-1.76 (m, 2H), 1.56-1.45 (m, 3H), 1.33-1.24 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 134.9, 134.7, 130.3, 128.1, 73.1, 35.4, 25.6, 24.2.



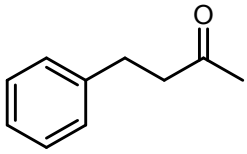
(Cyclopentyloxy)diphenylsilane (3j):[6] 82% isolated yield (110 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.65 (dd, ^{3}J=7.1 Hz, ^{4}J=1.2 Hz, 4H), 7.47-7.39 (m, 6H), 5.46 (s, 1H), 4.44 (quint, ^{3}J=4.6 Hz, 1H), 1.81-1.78 (m, 2H), 1.77-1.71 (m, 4H), 1.57-1.51 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 134.8, 134.7, 130.3, 128.1, 76.7, 35.4, 23.2.



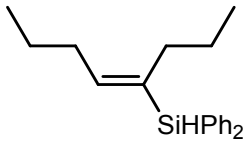
(Pentan-3-yloxy)diphenylsilane (3k):[5] 76% isolated yield (103 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.65 (dd, ^{3}J=7.8 Hz, ^{4}J=1.4 Hz, 4H), 7.44-7.38 (m, 6H), 5.49 (s, 1H), 3.70 (quint, ^{3}J=5.8 Hz, 1H), 1.58-1.53 (m, 4H), 0.90 (t, ^{3}J=7.4 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 134.8, 134.4, 128.2, 128.0, 77.4, 29.2, 10.0.



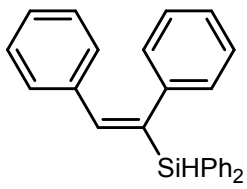
(Pentan-2-yloxy)diphenylsilane (3l):[7] 83% isolated yield (112 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66-7.58 (m, 4H), 7.45-7.35 (m, 6H), 5.46 (s, 1H), 4.01-3.95 (m, 1H), 1.62-1.55 (m, 1H), 1.47-1.32 (m, 3H), 1.21 (d, ^{3}J=6.0 Hz, 3H), 0.87 (t, ^{3}J=7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 134.82, 134.79, 130.3, 128.1, 70.9, 41.6, 23.4, 19.0, 14.2.



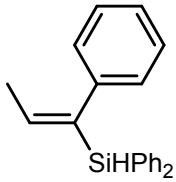
4-Phenylbutan-2-one (3m):[8] 79% isolated yield (58 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.31-7.26 (m, 2H), 7.22-7.18 (m, 3H), 2.91 (t, ^{3}J=7.2 Hz, 2H), 2.77 (t, ^{3}J=7.2 Hz, 2H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 208.1, 134.4, 128.6, 128.4, 126.2, 45.3, 30.2, 29.8.



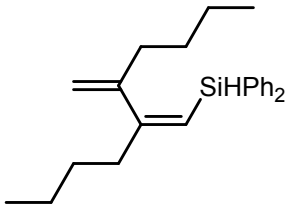
(E)-Oct-4-en-4-yldiphenylsilane (4a):[9] 84% isolated yield (124 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.57 (d, ^{3}J=6.6 Hz, 4H), 7.41-7.36 (m, 6H), 5.92 (t, ^{3}J=7.2 Hz, 1H), 5.09 (s, 1H), 2.22 (t, ^{3}J=7.8 Hz, 2H), 2.18 (q, ^{3}J=7.2 Hz, 2H), 1.45-1.37 (m, 2H), 1.36-1.30 (m, 2H), 0.93 (t, ^{3}J=7.2 Hz, 3H), 0.84 (t, ^{3}J=7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 146.8, 135.8, 134.4, 129.6, 128.3, 128.0, 32.8, 31.0, 23.2, 22.7, 14.4, 14.1; HRMS (EI) (m/z): $[M]^+$ calc for $C_{20}H_{26}Si$, 294.1804; found, 294.1811.



(E)-(1,2-Diphenylvinyl)diphenylsilane (4b):[10] 77% isolated yield (140 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.58 (dd, ^{3}J=7.6 Hz, ^{4}J=1.6 Hz, 4H), 7.45-7.35 (m, 6H), 7.23-7.16 (m, 3H), 7.13-7.10 (m, 3H), 7.04-7.00 (m, 5H), 5.30 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 143.0, 141.7, 140.3, 137.1, 136.0, 133.1, 129.9, 129.8, 128.8, 128.2, 128.14, 128.09, 127.7, 126.3; HRMS (EI) (m/z): $[M]^+$ calc for $C_{26}H_{22}Si$, 362.1491; found, 362.1479.



(E)-Diphenyl(1-phenylprop-1-en-1-yl)silane (4c):[10] 80% isolated yield (120 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.53 (dd, ^{3}J=7.8 Hz, ^{4}J=1.8 Hz, 4H), 7.42-7.39 (m, 2H), 7.36-7.34 (m, 4H), 7.25 (t, ^{3}J=7.8 Hz, 2H), 7.17-7.15 (m, 1H), 7.03 (dd, ^{3}J=7.2 Hz, ^{4}J=1.2 Hz, 2H), 6.31 (q, ^{3}J=6.6 Hz, 1H), 5.21 (s, 1H), 1.74 (d, ^{3}J=6.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 142.2, 141.2, 139.1, 135.9, 133.7, 129.7, 128.6, 128.2, 128.0, 126.0, 16.5; HRMS (EI) (m/z): $[M]^+$ calc for $C_{21}H_{20}Si$, 300.1334; found, 300.1340.



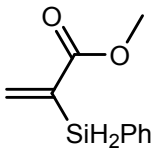
(E)-(2-Butyl-3-methylenehept-1-en-1-yl)diphenylsilane (4e): 86% isolated yield (150 mg, 2,3-di^{n}butyl/2,4-di^{n}butyl isomer : 1/0.27 from crude mixture), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.56-7.54 (dd, ^{3}J=7.6 Hz, ^{4}J=1.6 Hz, 4H), 7.37-7.33 (m, 6H), 5.64 (d, ^{3}J=5.7 Hz, 1H), 5.14 (d, ^{3}J=5.7 Hz, 1H), 4.80 (d, ^{2}J=2.0 Hz, 1H), 4.77 (d, ^{2}J=2.0 Hz, 1H), 2.28 (t, ^{3}J=7.6 Hz, 2H), 2.05 (t, ^{3}J=7.1 Hz, 2H), 1.44-1.24 (m, 8H), 0.92 (t, ^{3}J=7.3 Hz, 3H), 0.86 (t, ^{3}J=6.9 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 166.3, 150.9, 136.3, 135.1, 128.0, 127.9, 118.1, 113.1, 38.8, 34.6, 30.4, 29.6, 22.8, 22.4, 14.11, 14.08; HRMS (EI) (m/z): $[M]^+$ calc for $C_{24}H_{32}Si$, 348.2273; found, 348.2269.

4) Crystallography: A summary of crystal data and collection parameters for the crystal structure of **1b** is provided in Table S1. Detailed descriptions of data collection, as well as data solution, are provided below. A suitable crystal was mounted on a polymer loop using Paratone-N hydrocarbon oil. The crystal was transferred to an Apex2 diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to 150 K using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° ω scans, and the data were integrated by the program SAINT. The final unit cell parameters were determined by a least-squares refinement of the reflections with $I > 2\sigma(I)$. Data analysis using Siemens XPREP and the successful solution and refinement of the structure determined the space group. Equivalent reflections were averaged, and the structure was solved by direct methods using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically. X-ray quality crystals of **1b** were grown from a pentane layered tetrahydrofuran solution at room temperature.

Table S1. Crystallographic data for compound **1b**.

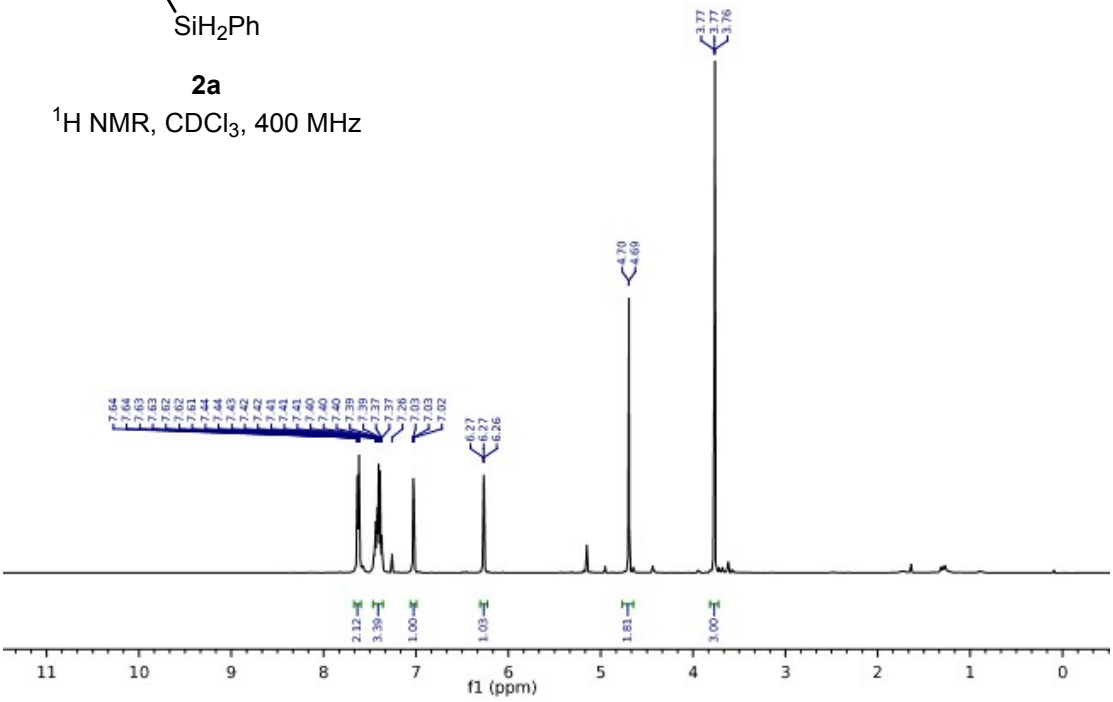
Compound	**1b**
Formula	$C_{26}H_{31}F_3NNiO_3PS$
Formula weight	584.26
Space group	*Pbca*
Crystal system	Orthorhombic
Temperature (K)	150(2)
a (Å)	16.472(2)
b (Å)	17.510(2)
c (Å)	18.549(2)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	5350.2(9)
Z	8
Density$_{calc}$ (g/cm^3)	1.451
Diffractometer	Bruker APEX2
Radiation	Mo-K$_\alpha$ (λ = 0.71073 Å)
Monochromator	Graphite
Detector	CCD detector
Scan type, width	Ω, 0.3°
Scan speed (s)	10
Reflections measured	Hemisphere
2θ range (°)	4.04-60.76
Crystal dimensions (mm)	0.42 x 0.21 x 0.18
Reflections measured	82719
Unique reflections	8069
Observations (I > 2σ(I))	6345
R_{int}	0.0269
Parameters	325
R_{obs}, R_w, R_{all}	0.0325, 0.0925, 0.0467
GoF	1.070

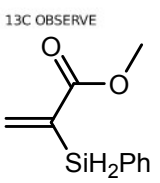
5) NMR spectra of hydrosilylation products:



2a

^{1}H NMR, $CDCl_3$, 400 MHz

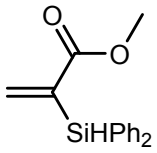




2a

^{13}C NMR, $CDCl_3$, 400 MHz

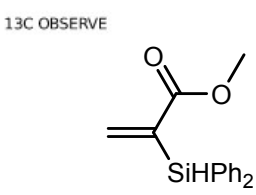
STANDARD 1H OBSERVE



2b

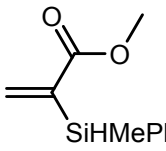
^{1}H NMR, $CDCl_3$, 400 MHz

13C OBSERVE



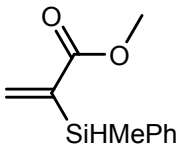
2b

^{13}C NMR, $CDCl_3$, 400 MHz



2c

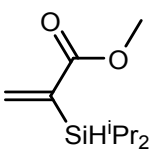
^{1}H NMR, $CDCl_3$, 400 MHz



2c

^{13}C NMR, $CDCl_3$, 400 MHz

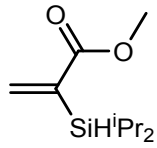
STANDARD 1H OBSERVE



2d

^{1}H NMR, $CDCl_3$, 600 MHz

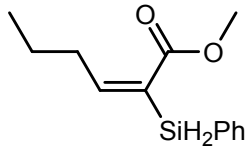
STANDARD CARBON PARAMETERS



2d

^{13}C NMR, $CDCl_3$, 600 MHz

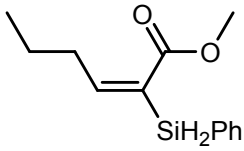
STANDARD 1H OBSERVE



2e

^{1}H NMR, $CDCl_3$, 400 MHz

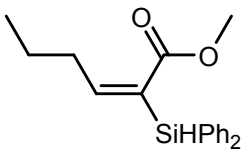
13C OBSERVE



2e

^{13}C NMR, $CDCl_3$, 400 MHz

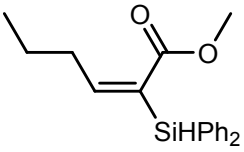
STANDARD 1H OBSERVE



2f

^{1}H NMR, $CDCl_3$, 400 MHz

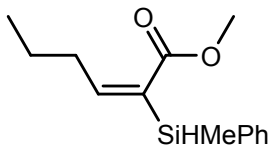
13C OBSERVE



2f

^{13}C NMR, $CDCl_3$, 400 MHz

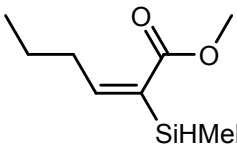
STANDARD 1H OBSERVE



2g

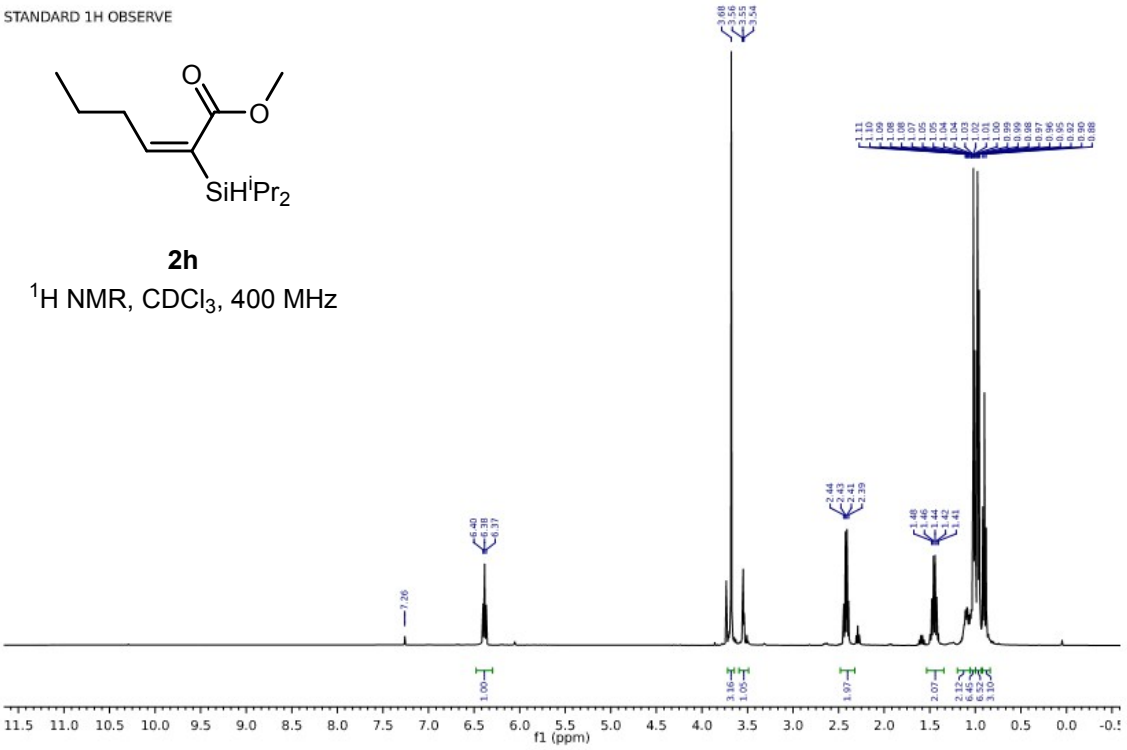
^{1}H NMR, $CDCl_3$, 400 MHz

13C OBSERVE



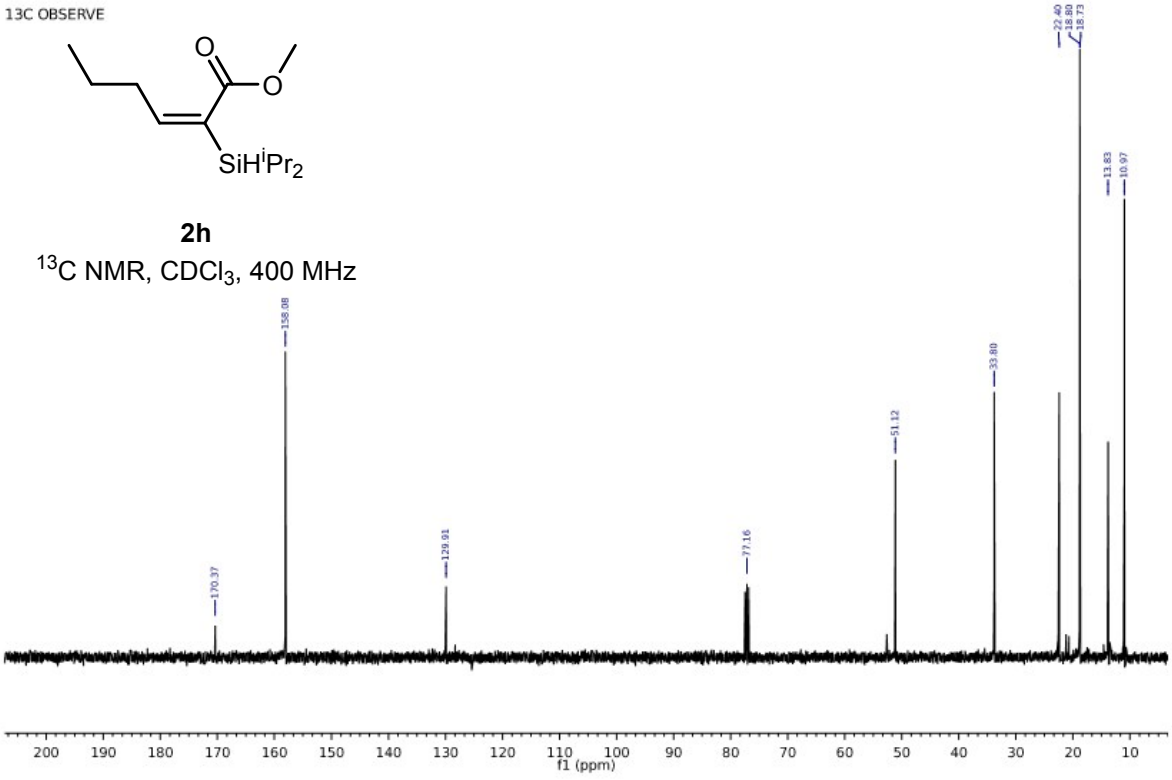
2g

^{13}C NMR, $CDCl_3$, 400 MHz



2h

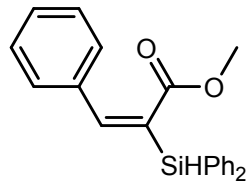
^{1}H NMR, $CDCl_3$, 400 MHz



2h

^{13}C NMR, $CDCl_3$, 400 MHz

STANDARD PROTON PARAMETERS



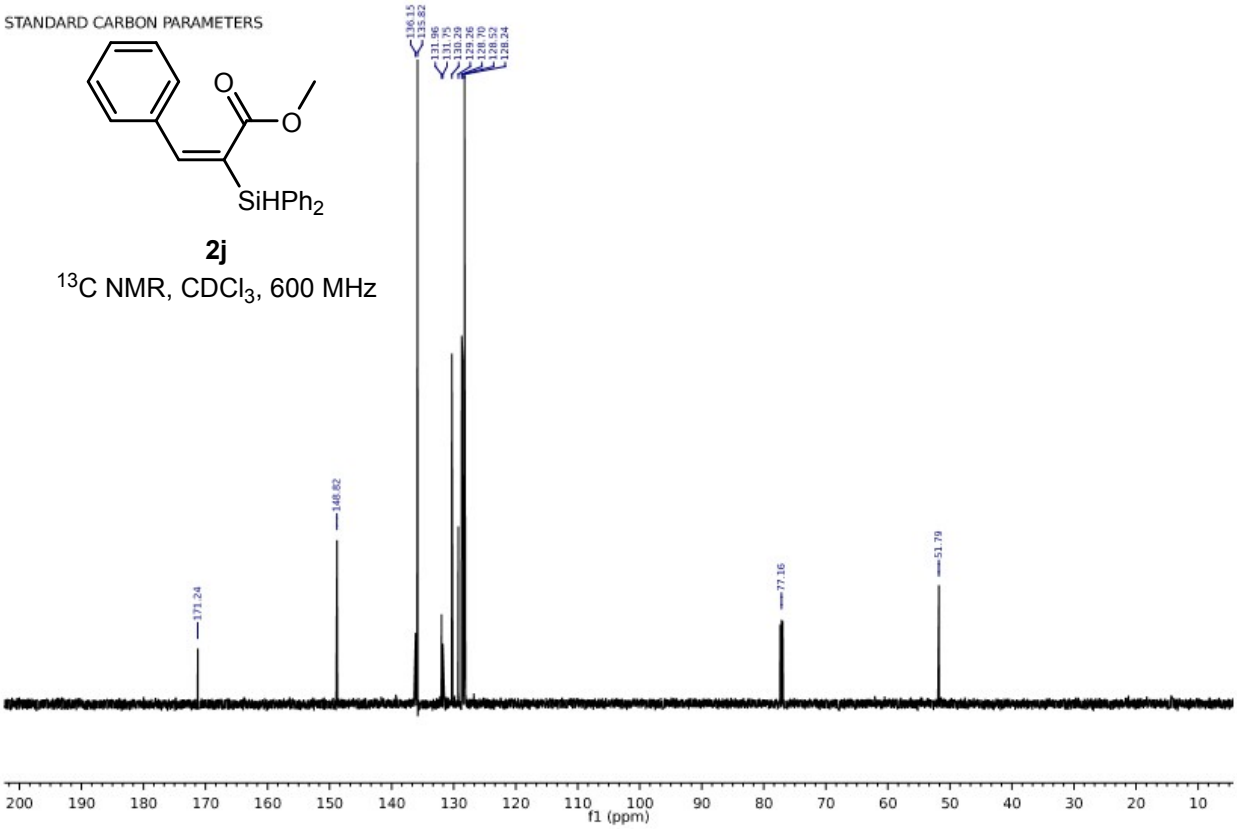
2j

^{1}H NMR, $CDCl_3$, 600 MHz

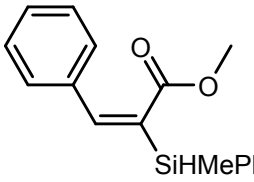
STANDARD CARBON PARAMETERS

2j

^{13}C NMR, $CDCl_3$, 600 MHz



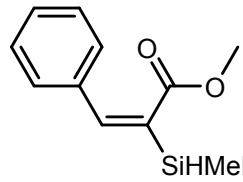
STANDARD 1H OBSERVE



2k

^{1}H NMR, $CDCl_3$, 400 MHz

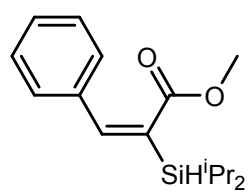
13C OBSERVE



2k

^{13}C NMR, $CDCl_3$, 400 MHz

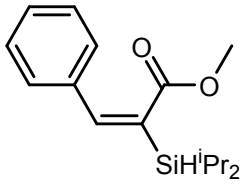
STANDARD PROTON PARAMETERS



2l

^{1}H NMR, $CDCl_3$, 600 MHz

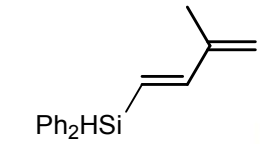
N503.3.fid



2l

^{13}C NMR, $CDCl_3$, 600 MHz

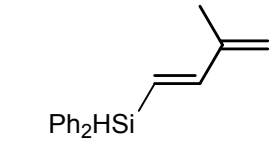
STANDARD 1H OBSERVE



2m

^{1}H NMR, $CDCl_3$, 400 MHz

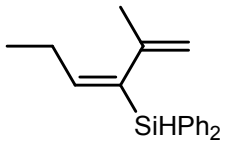
13C OBSERVE



2m

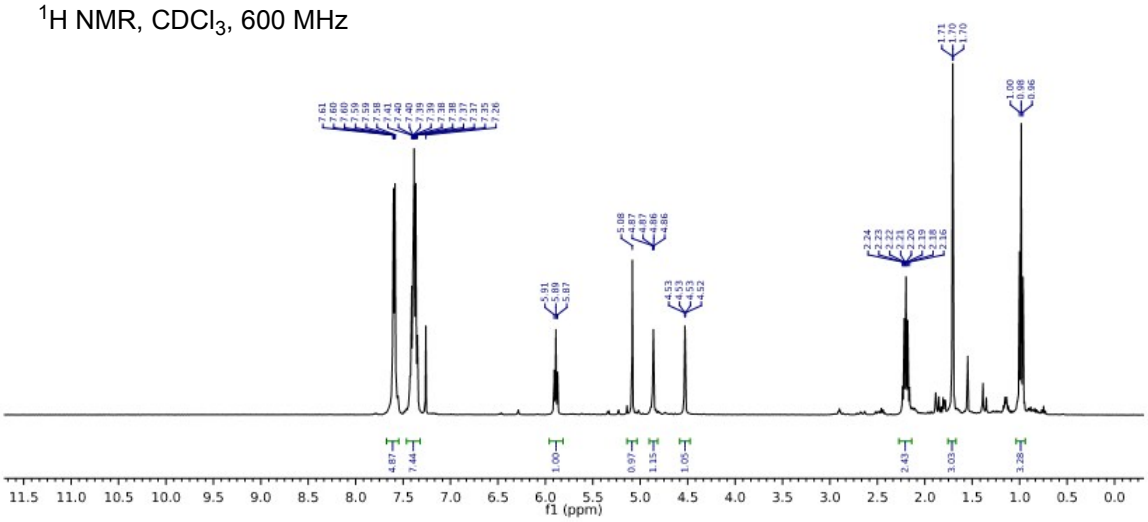
^{13}C NMR, $CDCl_3$, 400 MHz

STANDARD 1H OBSERVE



2n

^{1}H NMR, $CDCl_3$, 600 MHz

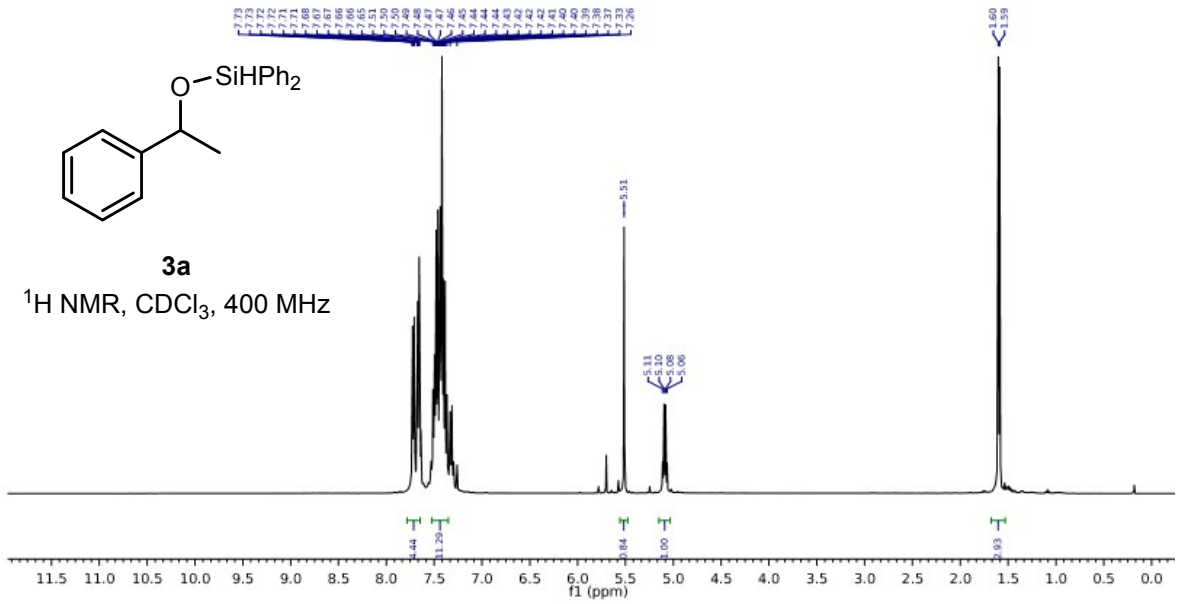


13C OBSERVE

2n

^{13}C NMR, $CDCl_3$, 600 MHz

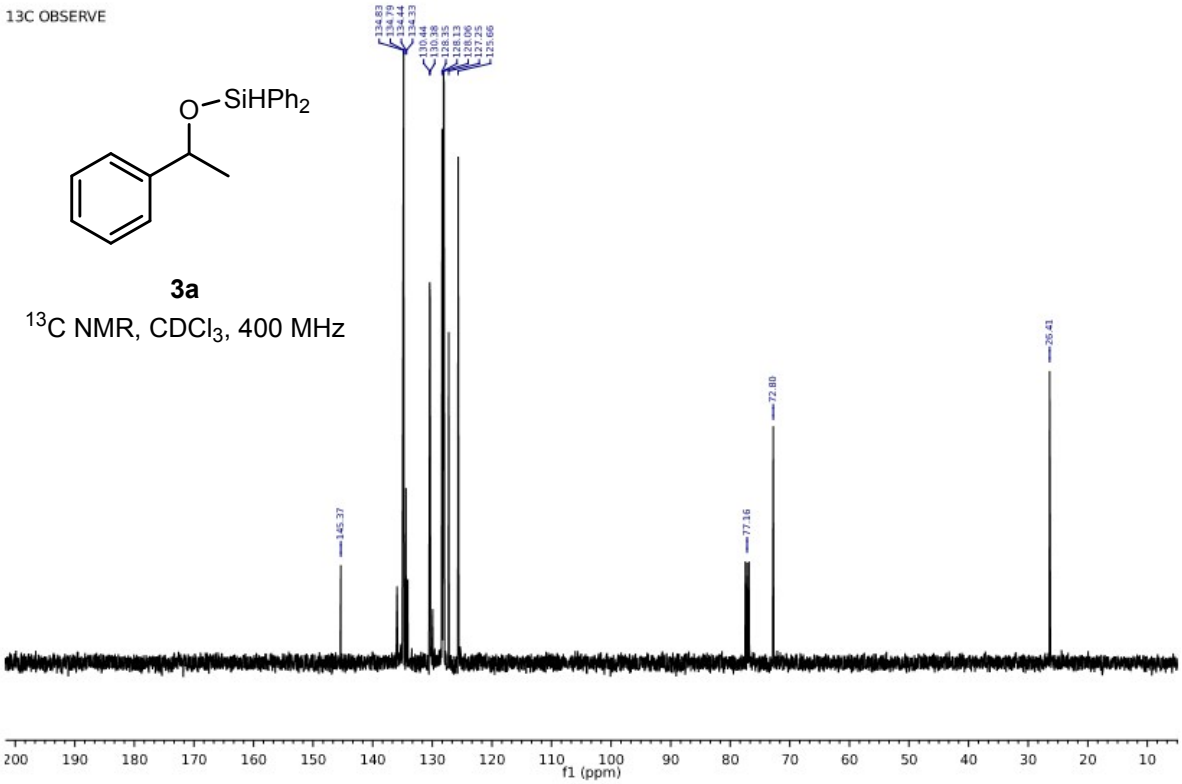
STANDARD 1H OBSERVE



3a

^{1}H NMR, $CDCl_3$, 400 MHz

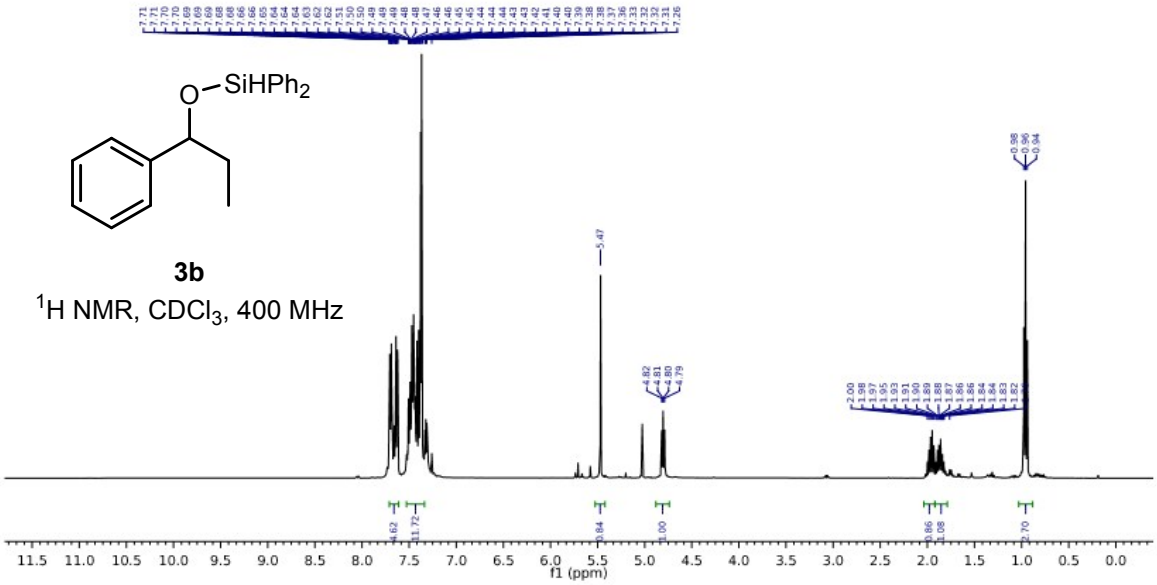
13C OBSERVE



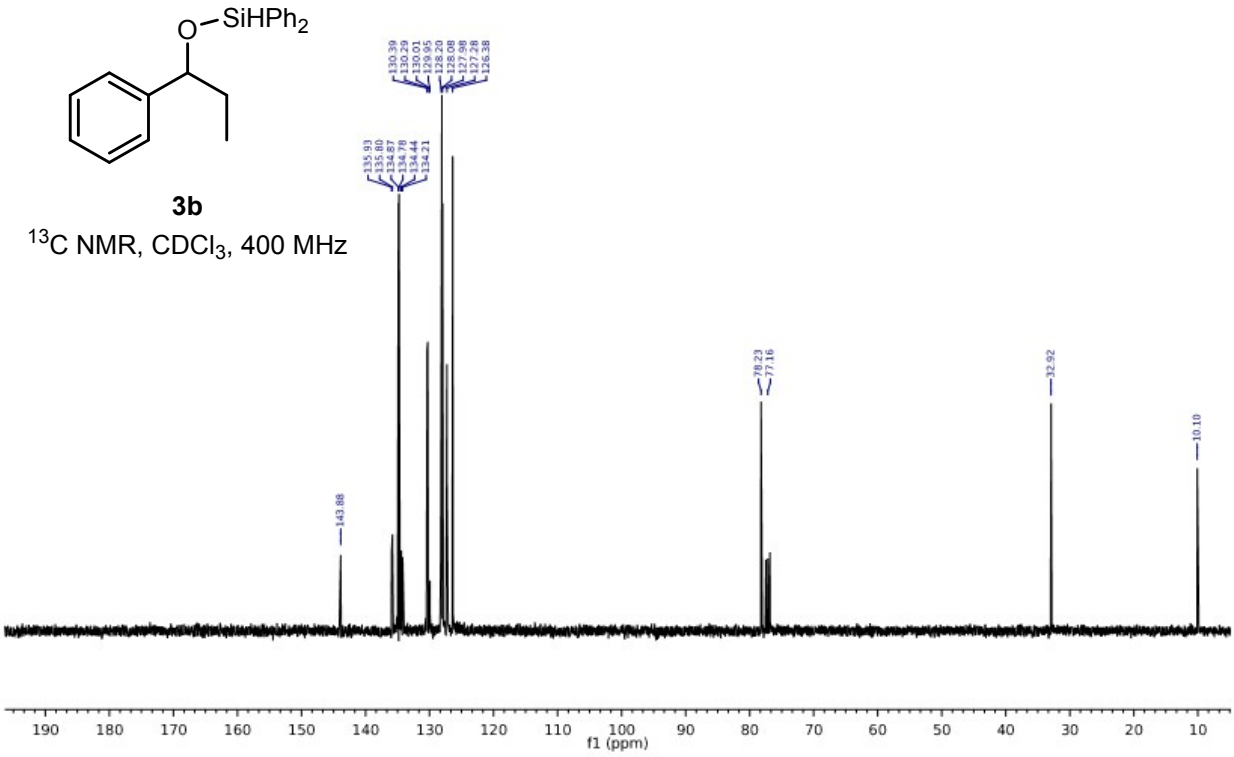
3a

^{13}C NMR, $CDCl_3$, 400 MHz

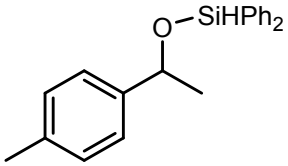
STANDARD 1H OBSERVE



13C OBSERVE



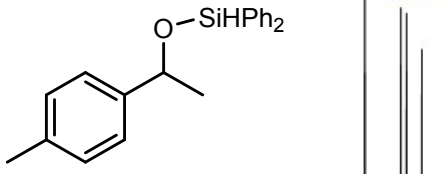
STANDARD 1H OBSERVE



3c

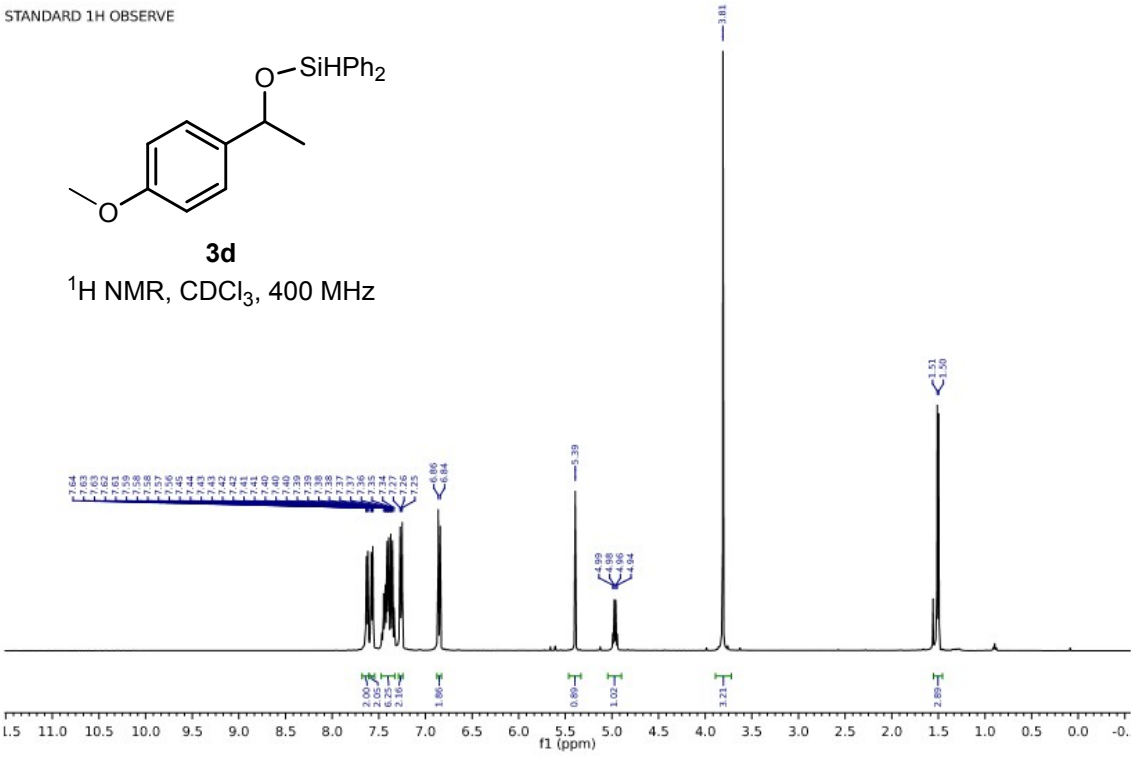
^{1}H NMR, $CDCl_3$, 400 MHz

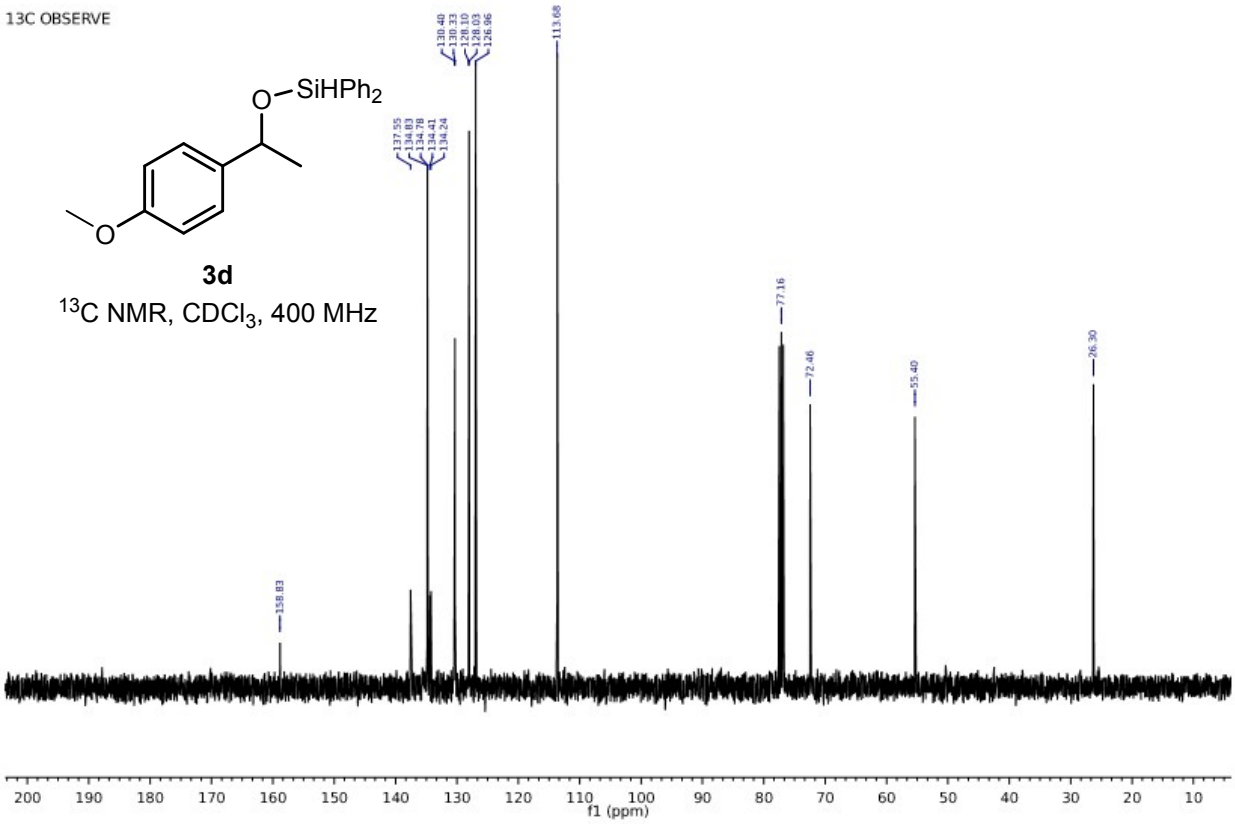
13C OBSERVE

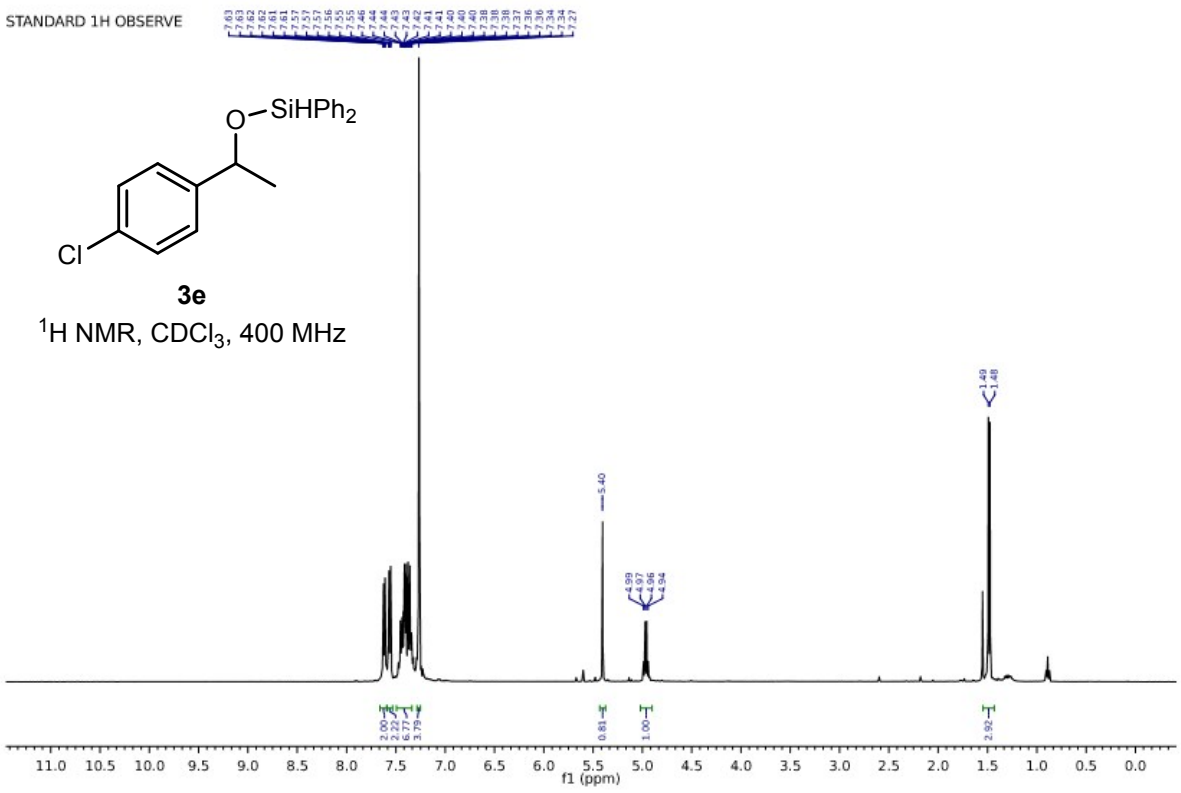


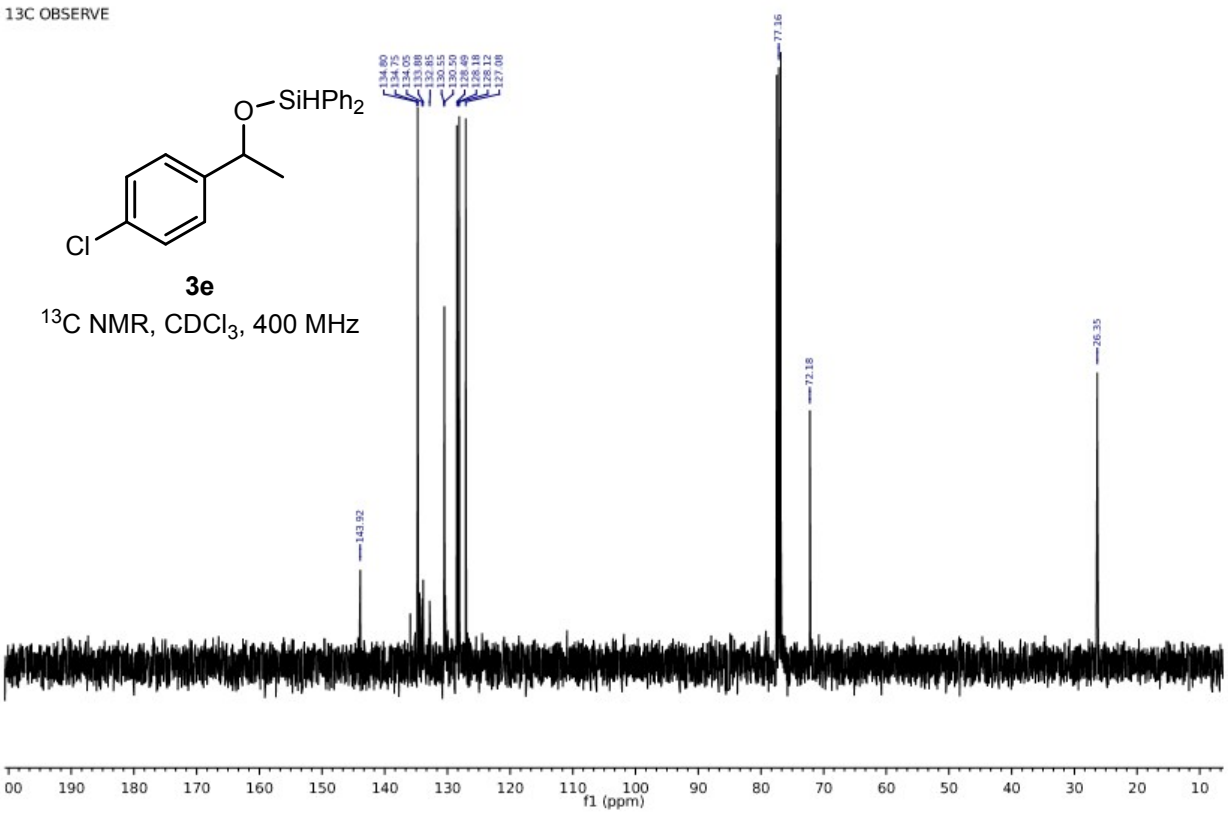
3c

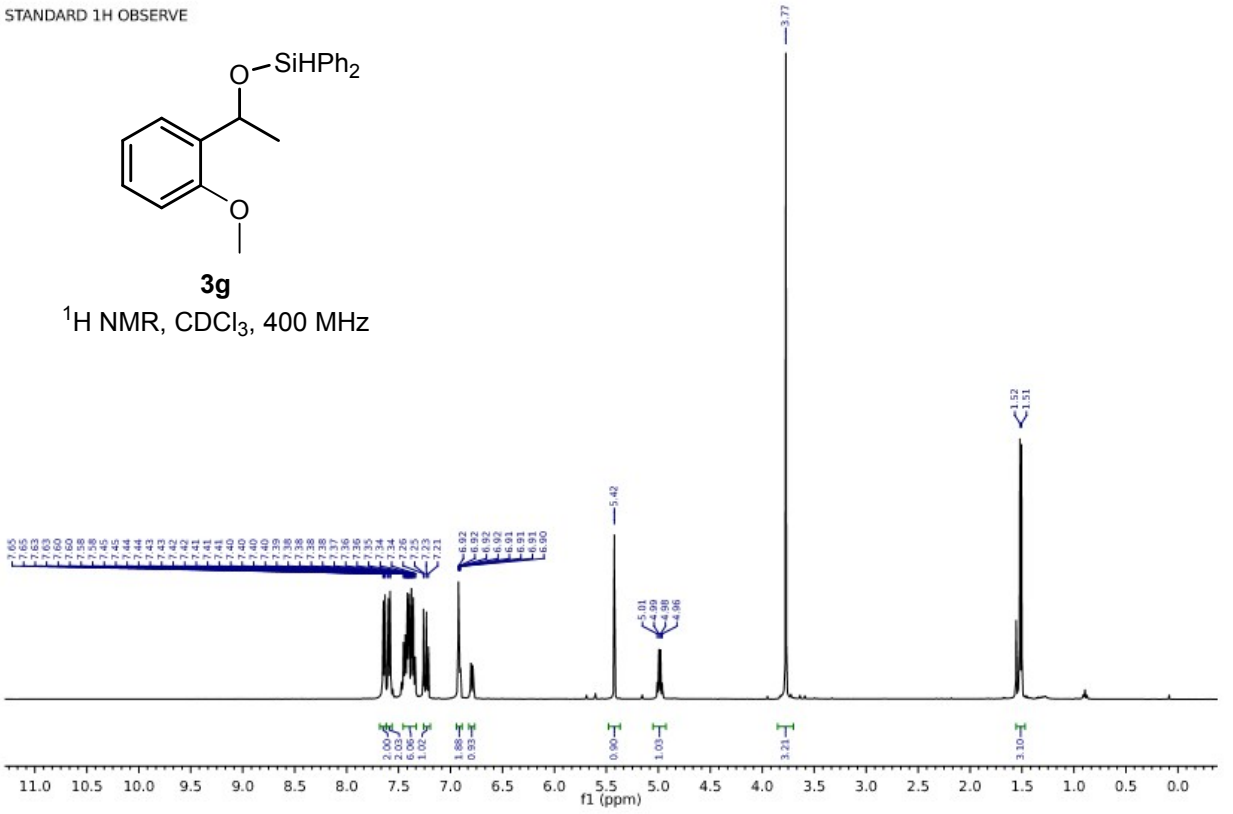
^{13}C NMR, $CDCl_3$, 400 MHz


STANDARD 1H OBSERVE
O
SiHPh2
O
3d
1H NMR, CDCl3, 400 MHz
f1 (ppm)


13C OBSERVE
O
SiHPh2
O
3d
13C NMR, CDCl3, 400 MHz
f1 (ppm)

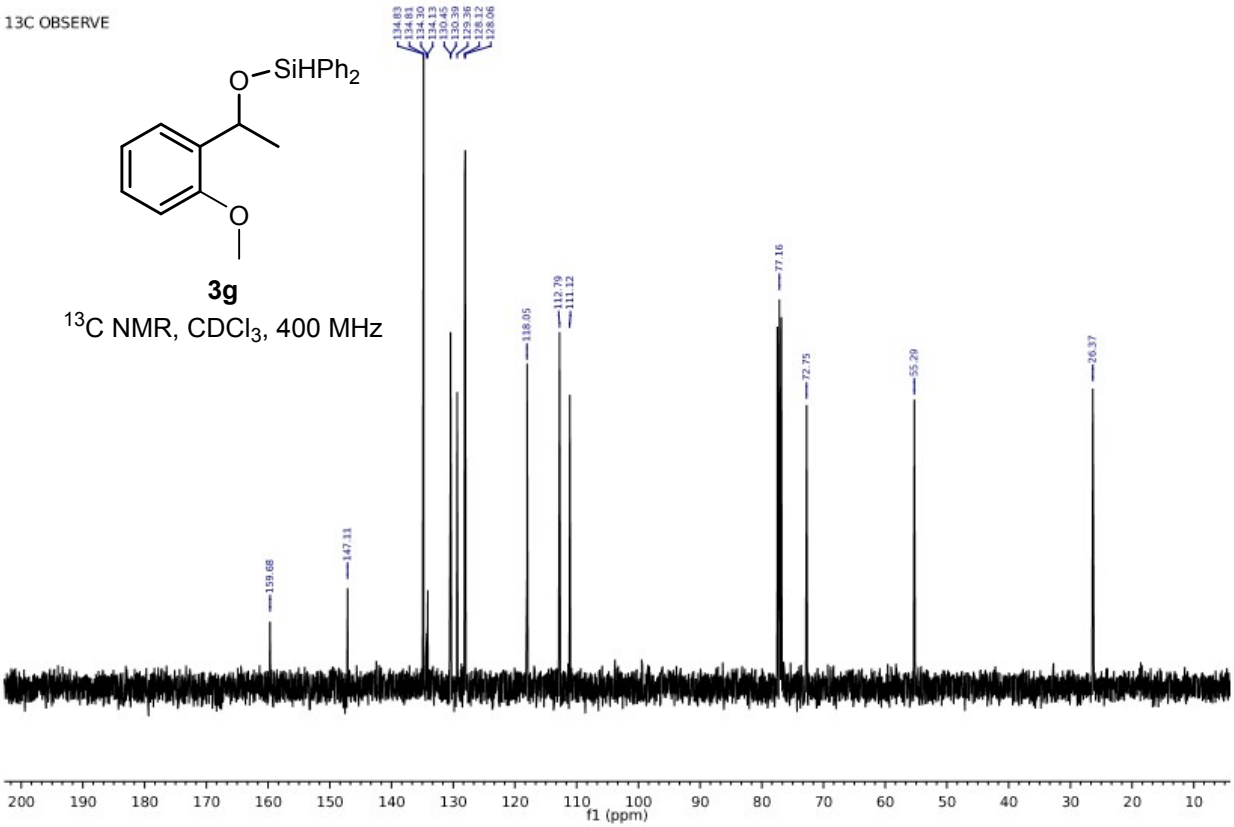

STANDARD 1H OBSERVE
O–SiHPh2
Cl
3e
1H NMR, CDCl3, 400 MHz
f1 (ppm)


13C OBSERVE
O–SiHPh2
Cl
3e
13C NMR, CDCl3, 400 MHz
f1 (ppm)



3g

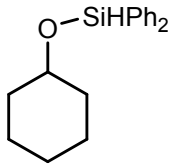
^{1}H NMR, $CDCl_3$, 400 MHz



3g

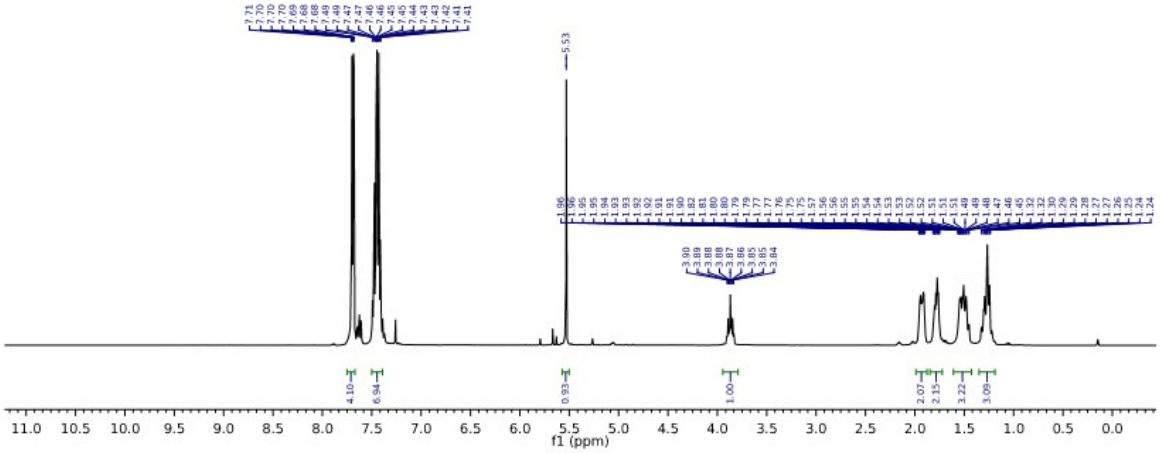
^{13}C NMR, $CDCl_3$, 400 MHz

STANDARD 1H OBSERVE



3i

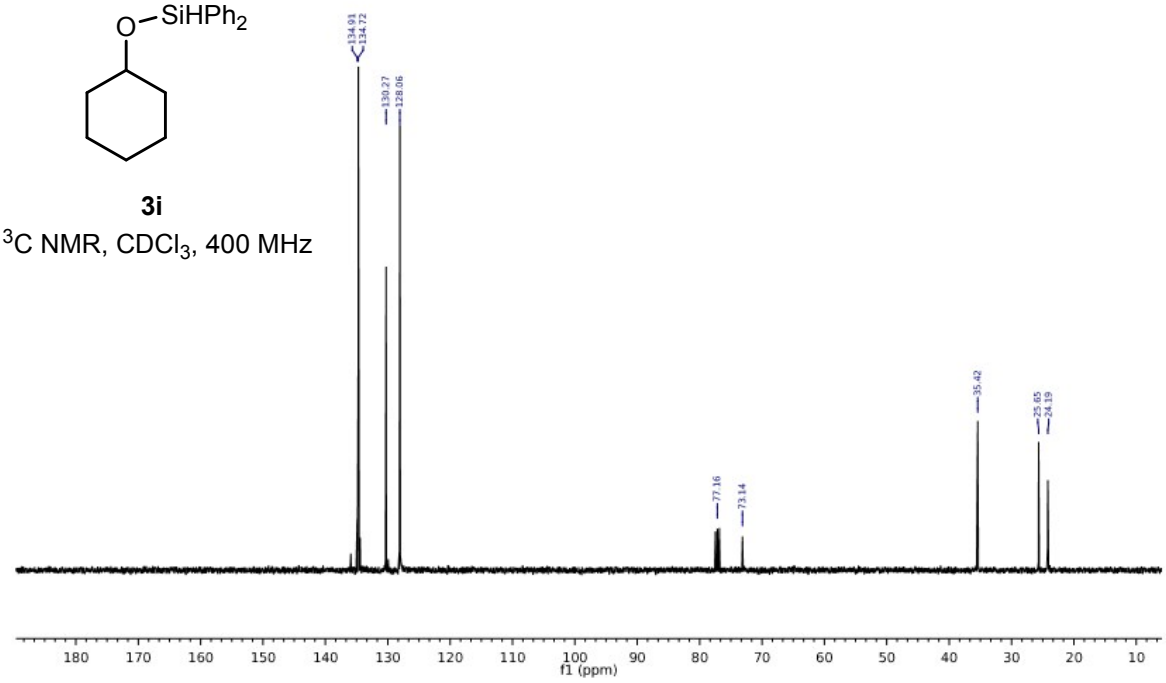
^{1}H NMR, $CDCl_3$, 400 MHz



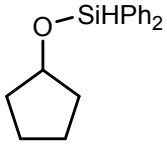
13C OBSERVE

3i

^{13}C NMR, $CDCl_3$, 400 MHz

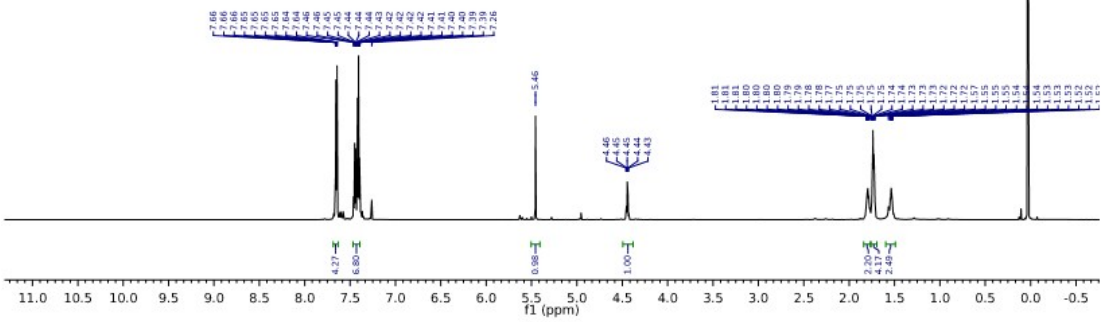


HS3.2.fid

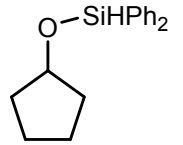


3j

^{1}H NMR, $CDCl_3$, 600 MHz



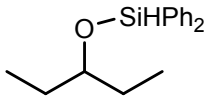
HS3.1.fid



3j

^{13}C NMR, $CDCl_3$, 600 MHz

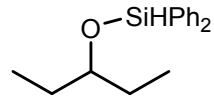
STANDARD 1H OBSERVE



3k

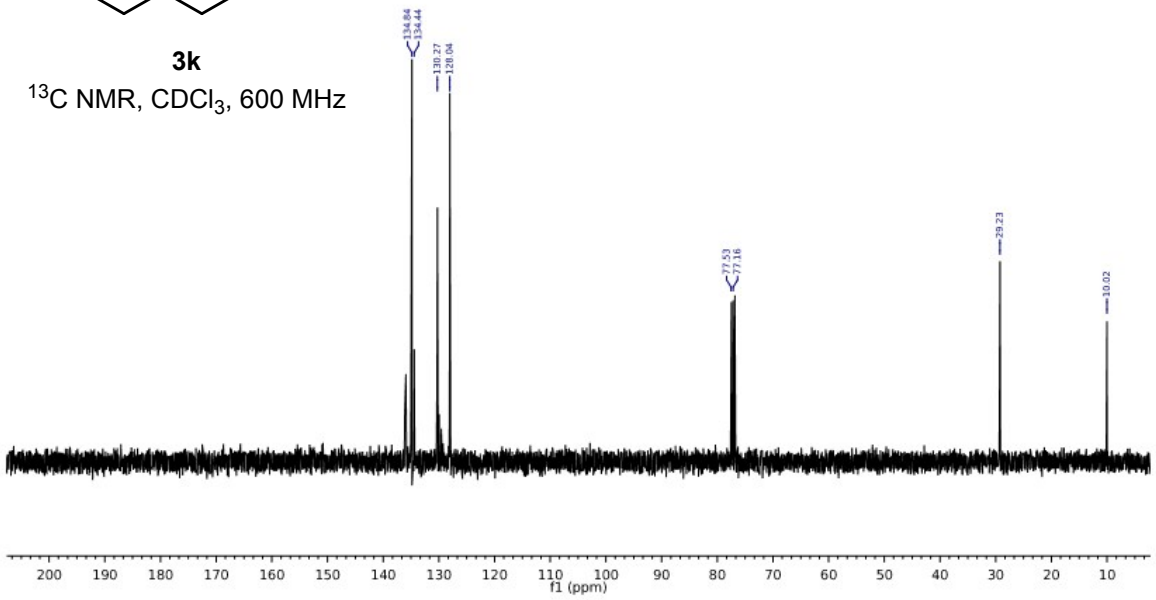
^{1}H NMR, $CDCl_3$, 600 MHz

13C OBSERVE

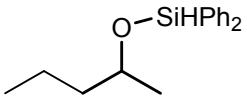


3k

^{13}C NMR, $CDCl_3$, 600 MHz

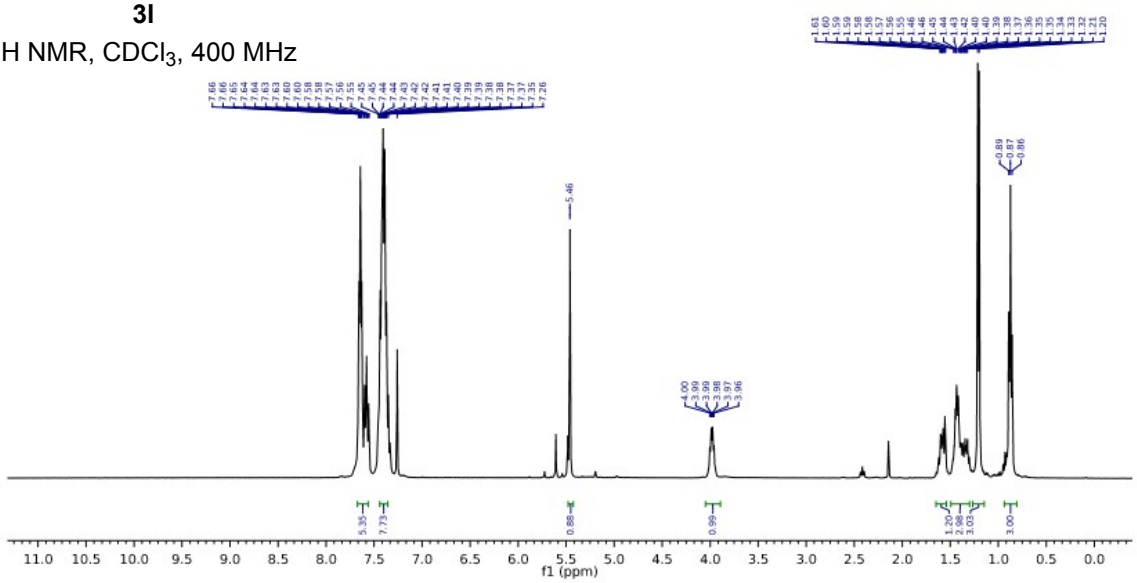


STANDARD 1H OBSERVE

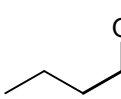


3l

^{1}H NMR, $CDCl_3$, 400 MHz



13C OBSERVE

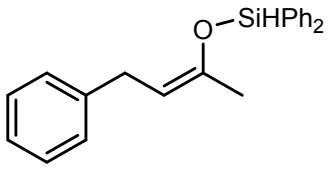


3l

^{13}C NMR, $CDCl_3$, 400 MHz

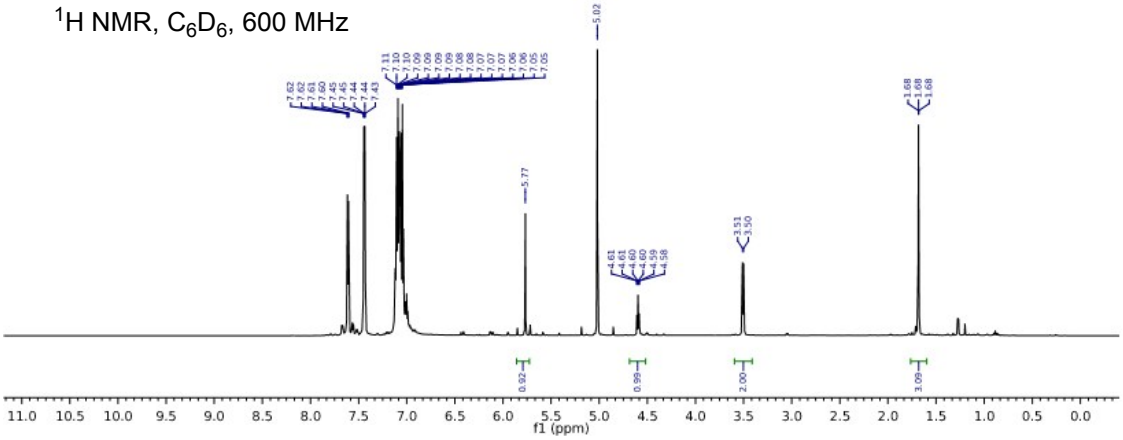
^{1}H NMR spectra of **3m** as crude mixture after reaction completion

STANDARD PROTON PARAMETERS

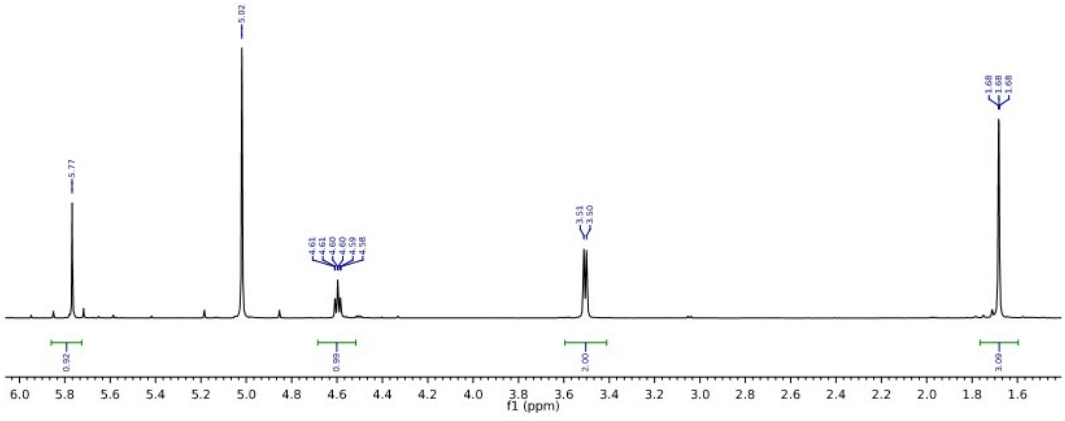


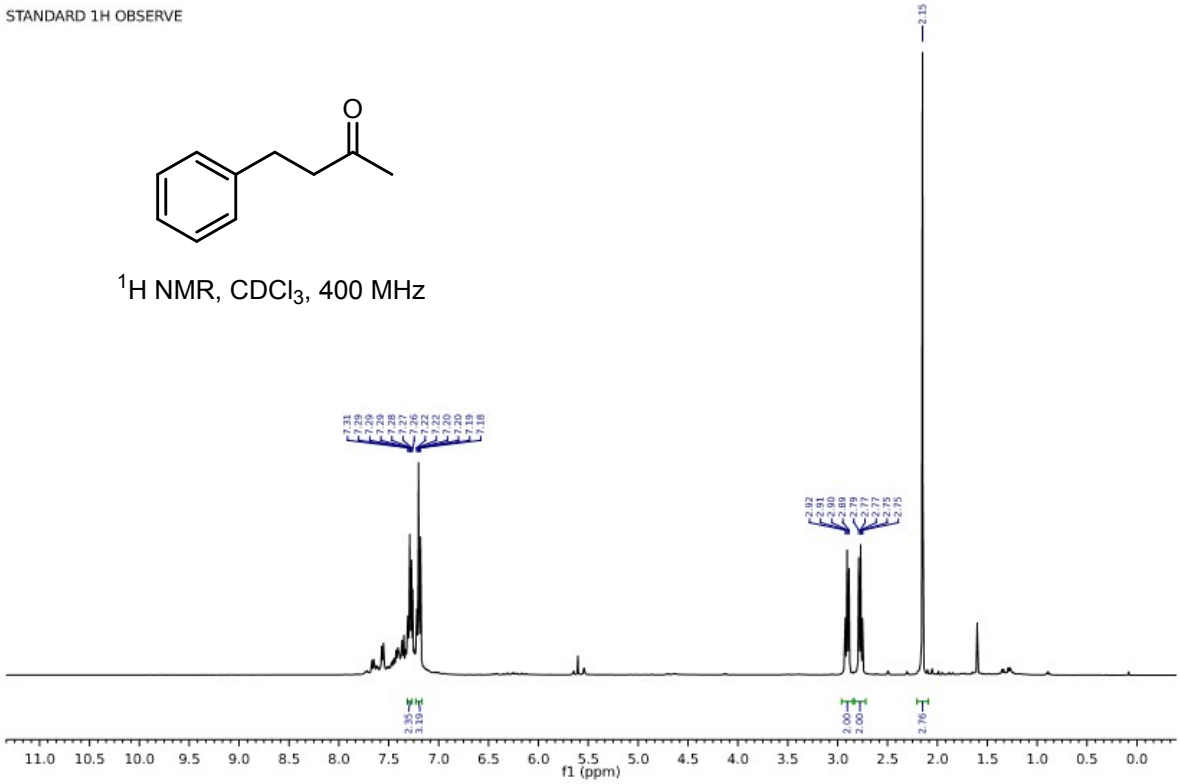
3m

^{1}H NMR, C_6D_6, 600 MHz

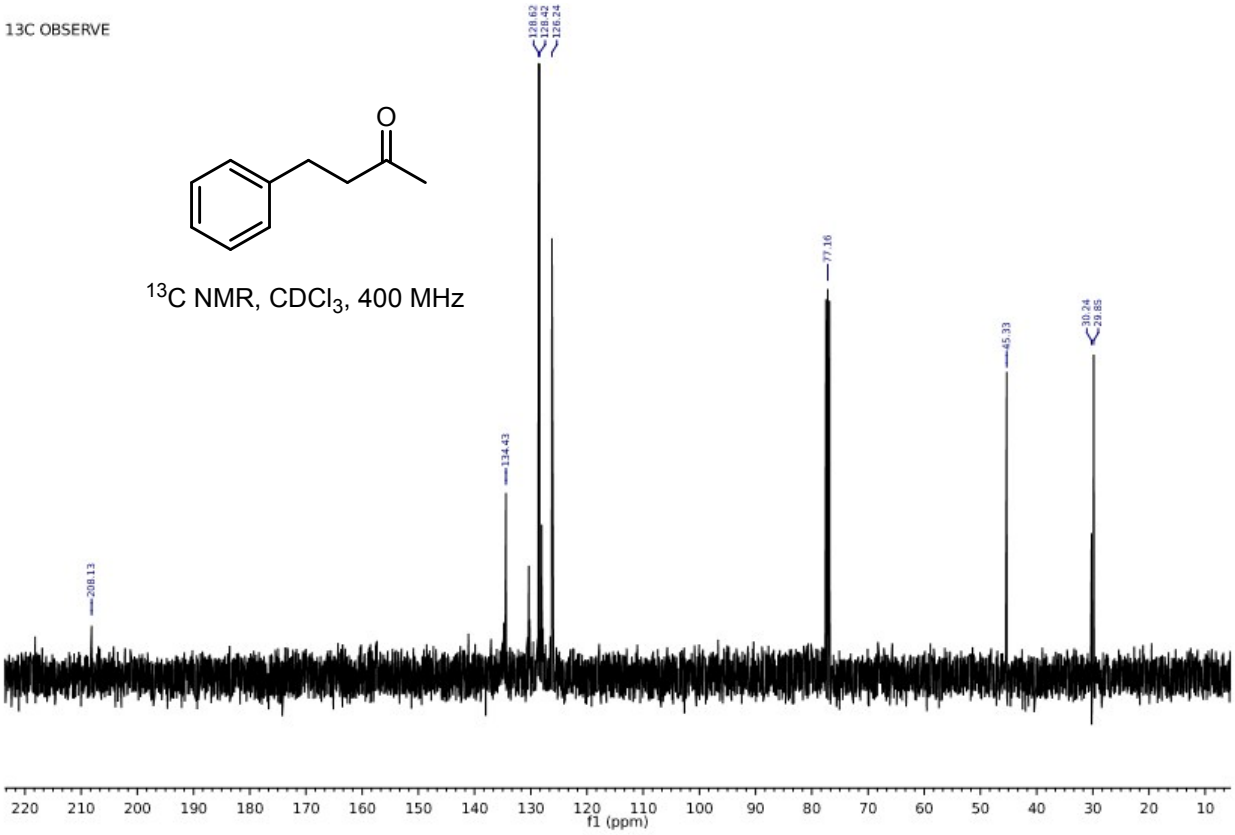


STANDARD PROTON PARAMETERS



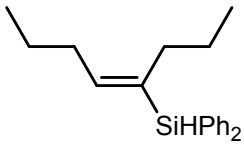


^{1}H NMR, $CDCl_3$, 400 MHz



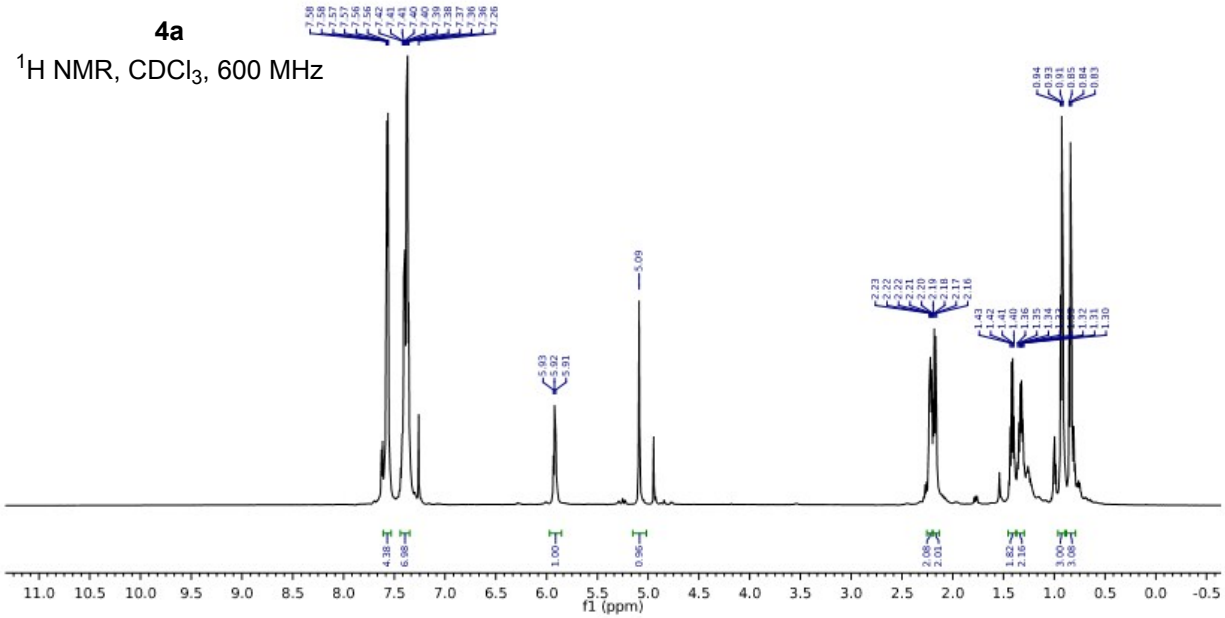
^{13}C NMR, $CDCl_3$, 400 MHz

STANDARD PROTON PARAMETERS

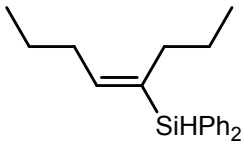


4a

^{1}H NMR, $CDCl_3$, 600 MHz

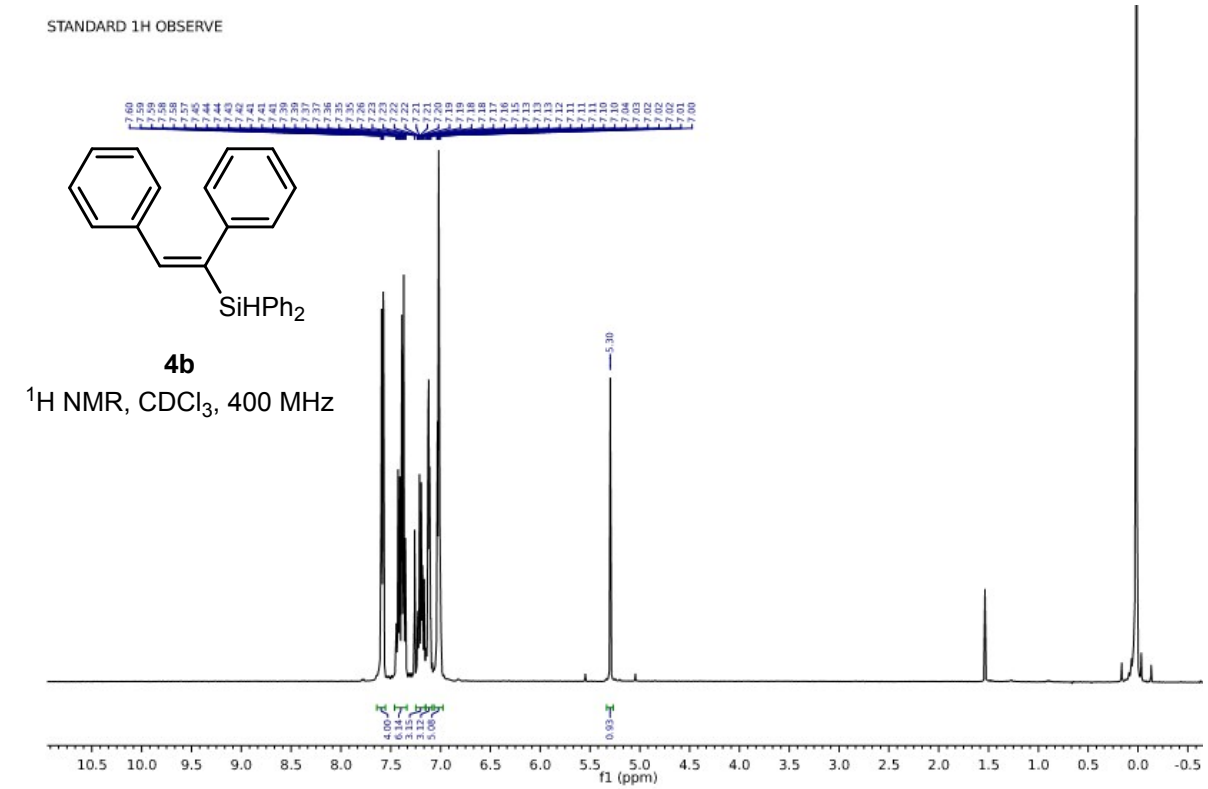


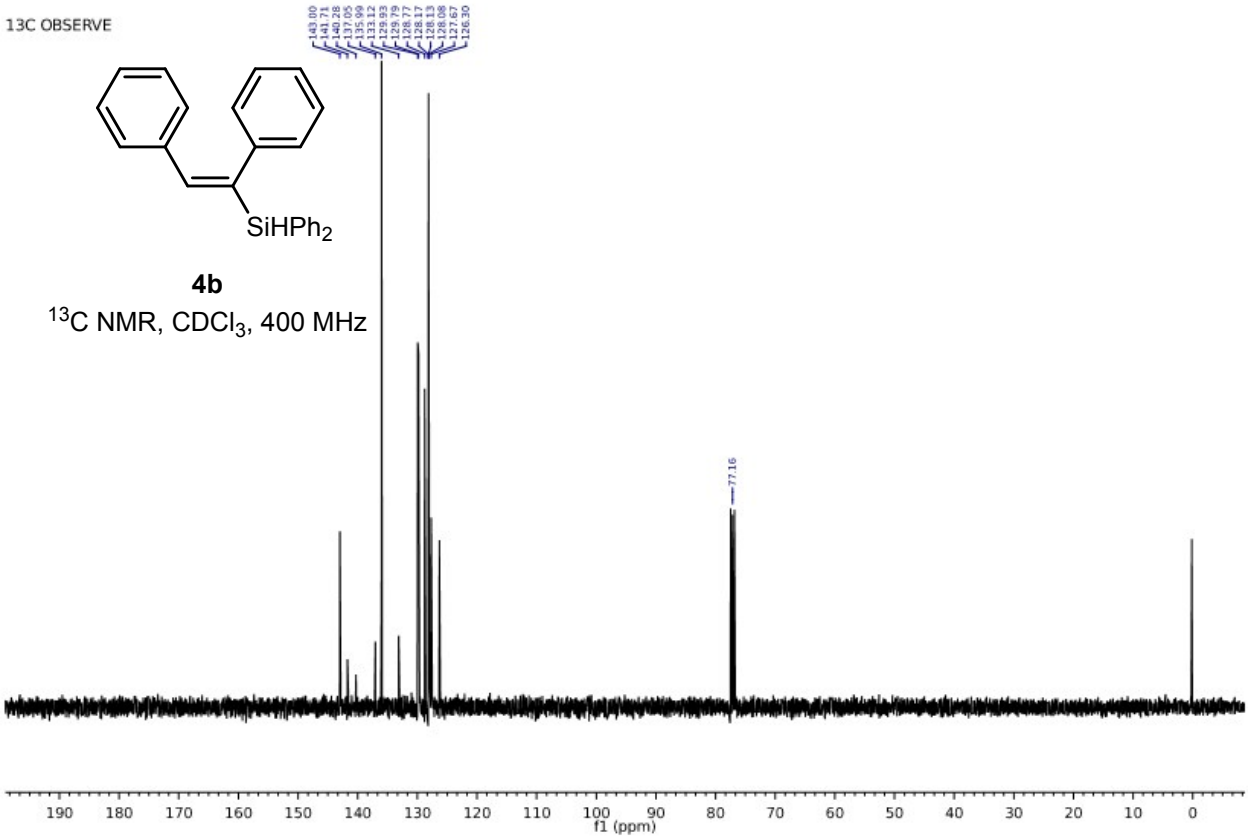
STANDARD CARBON PARAMETERS



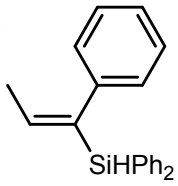
4a

^{1}H NMR, $CDCl_3$, 600 MHz


STANDARD 1H OBSERVE
SiHPh2
4b
1H NMR, CDCl3, 400 MHz
f1 (ppm)

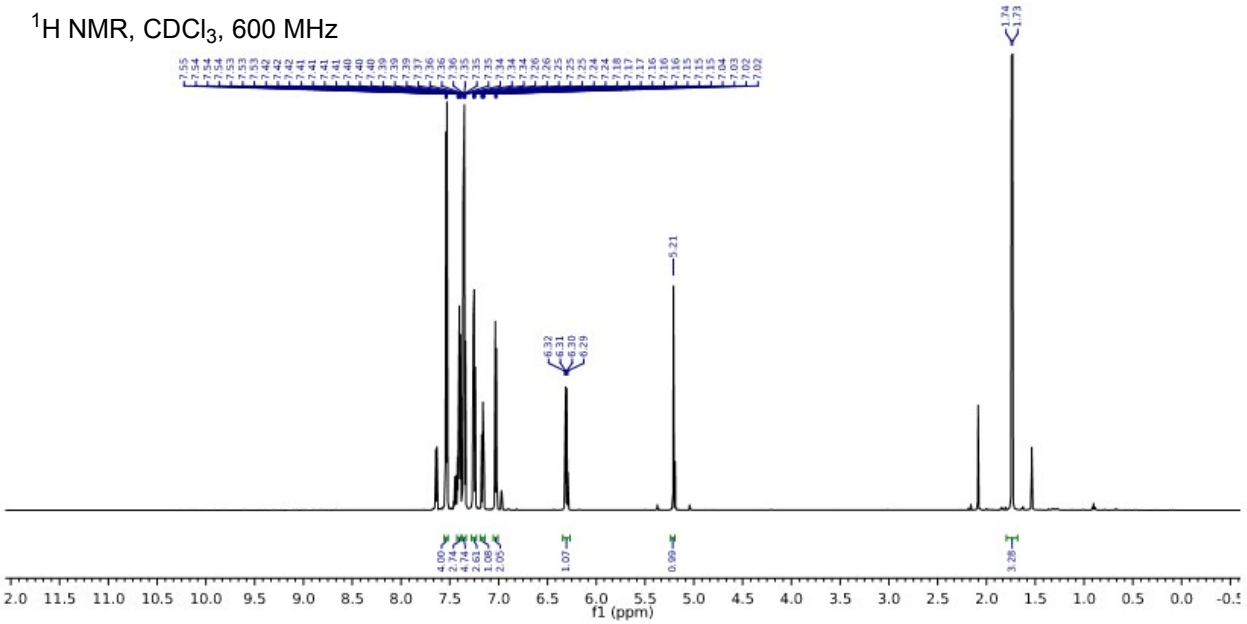

13C OBSERVE
SiHPh2
4b
13C NMR, CDCl3, 400 MHz
f1 (ppm)

N504.1.fid

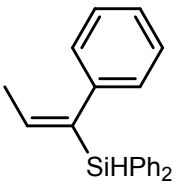


4c

^{1}H NMR, $CDCl_3$, 600 MHz



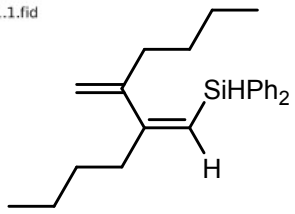
N504.4.fid



4c

^{13}C NMR, $CDCl_3$, 600 MHz

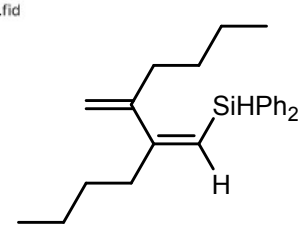
N531.1.fid



4e

^{1}H NMR, $CDCl_3$, 600 MHz

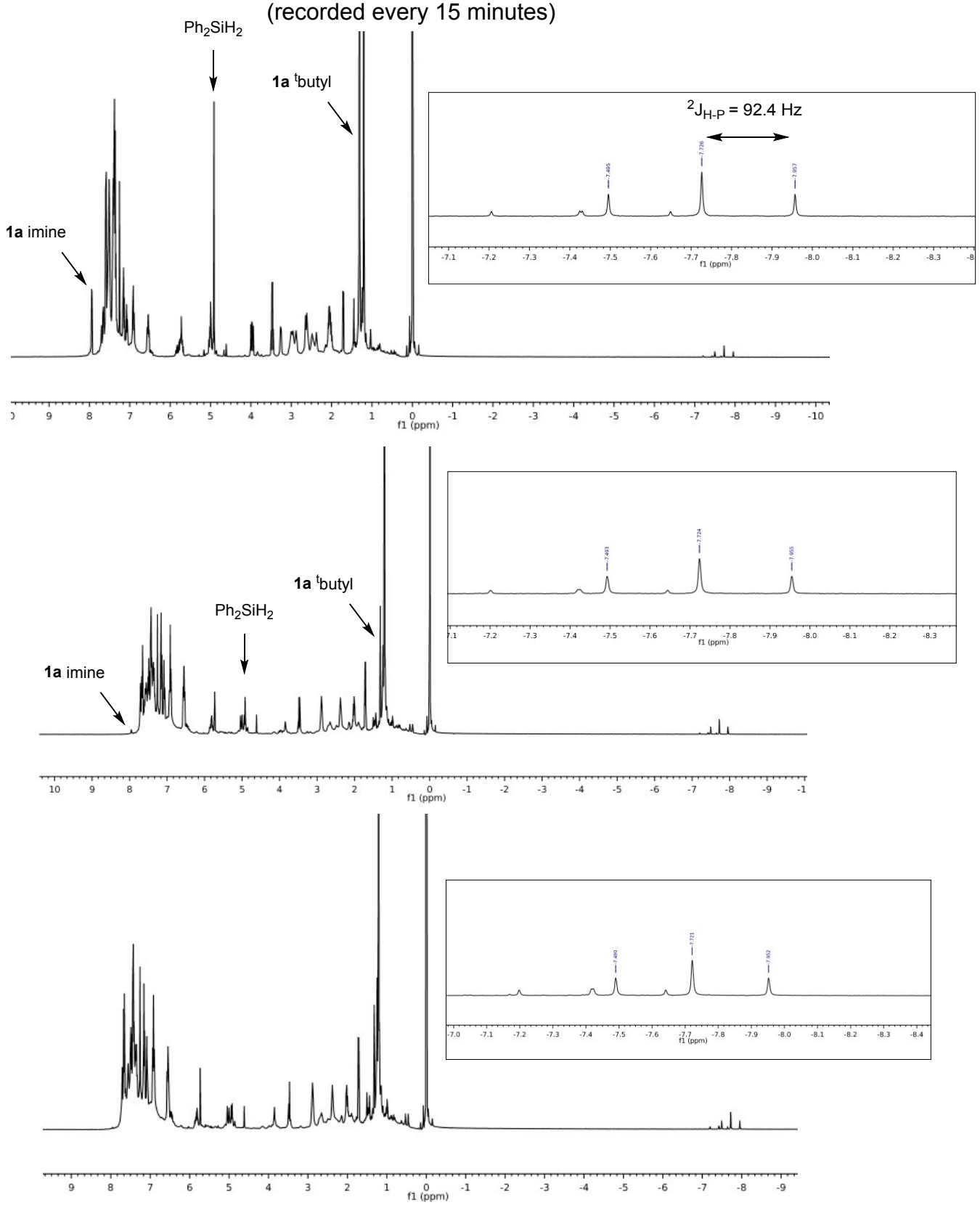
N531.2.fid



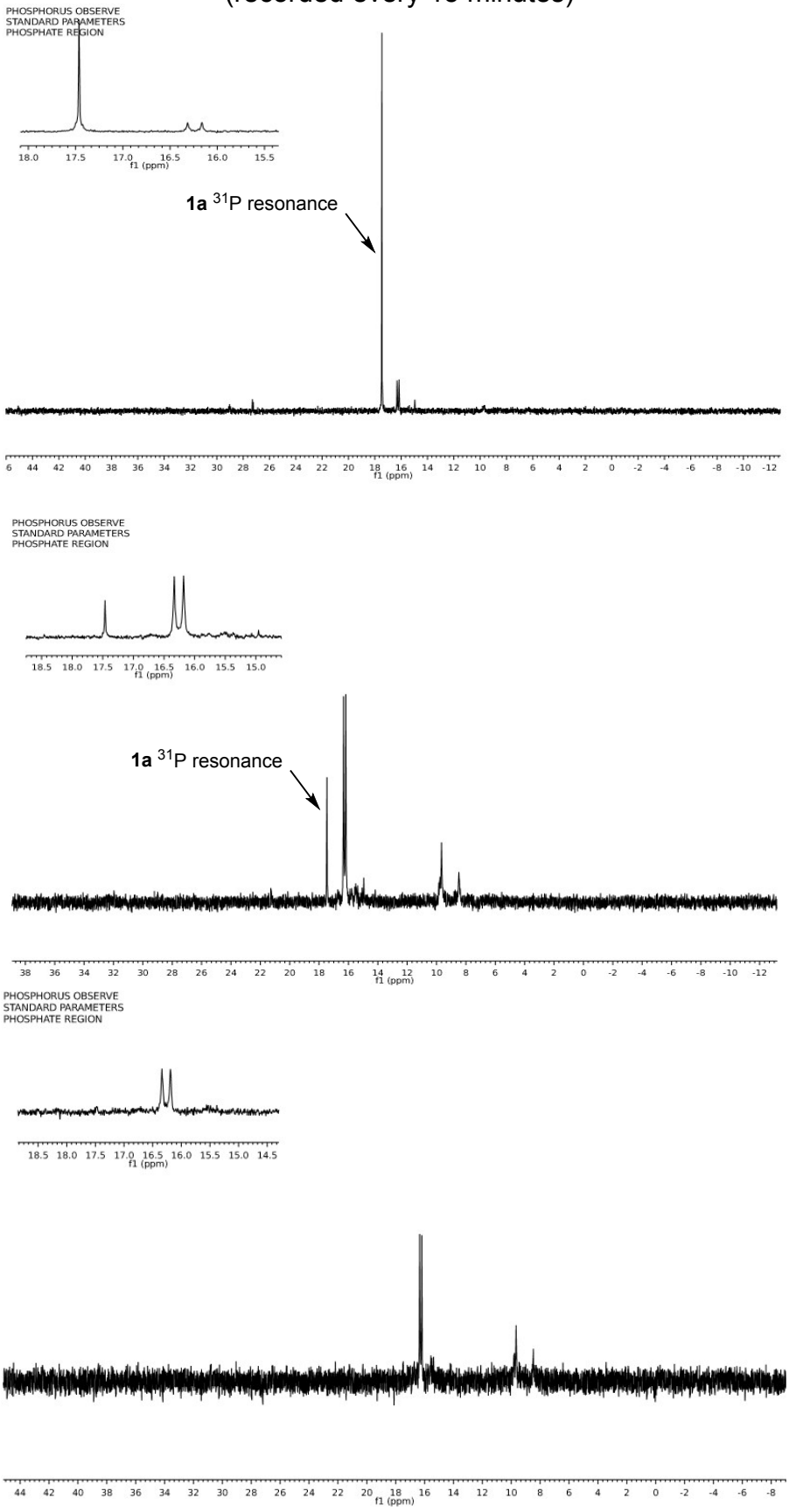
4e

^{13}C NMR, $CDCl_3$, 600 MHz

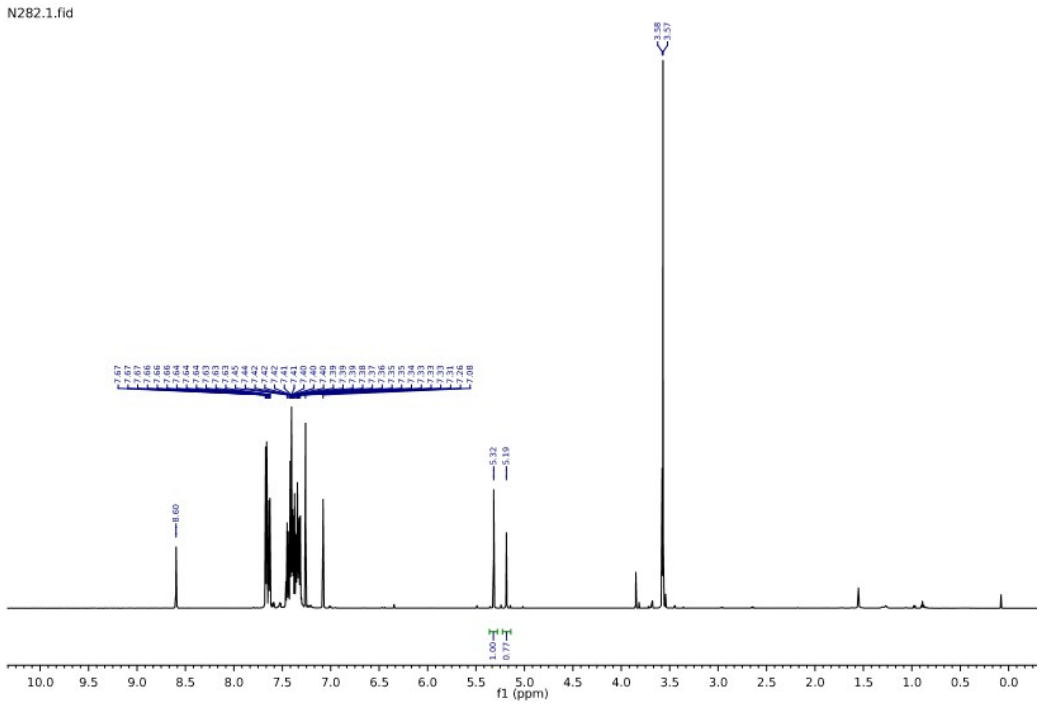
Time-resolved ^{1}H NMR analysis of reaction of **1a** and diphenylsilane (recorded every 15 minutes)



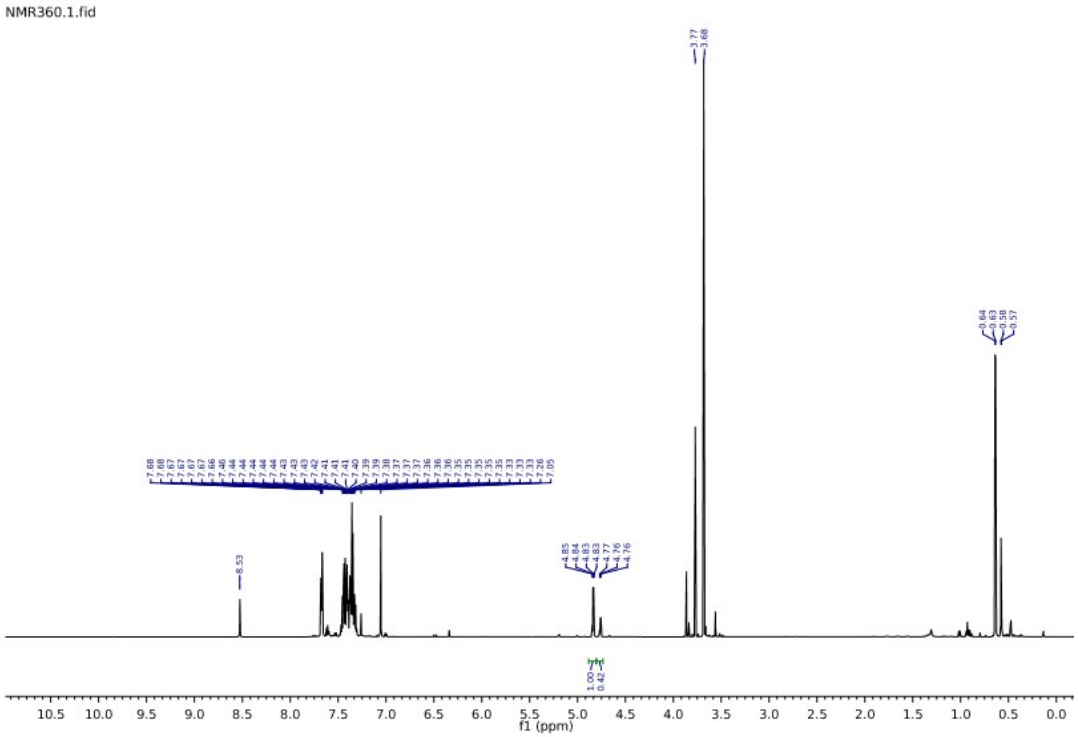
Time-resolved ^{31}P NMR analysis of reaction of **1a** and diphenylsilane (recorded every 15 minutes)



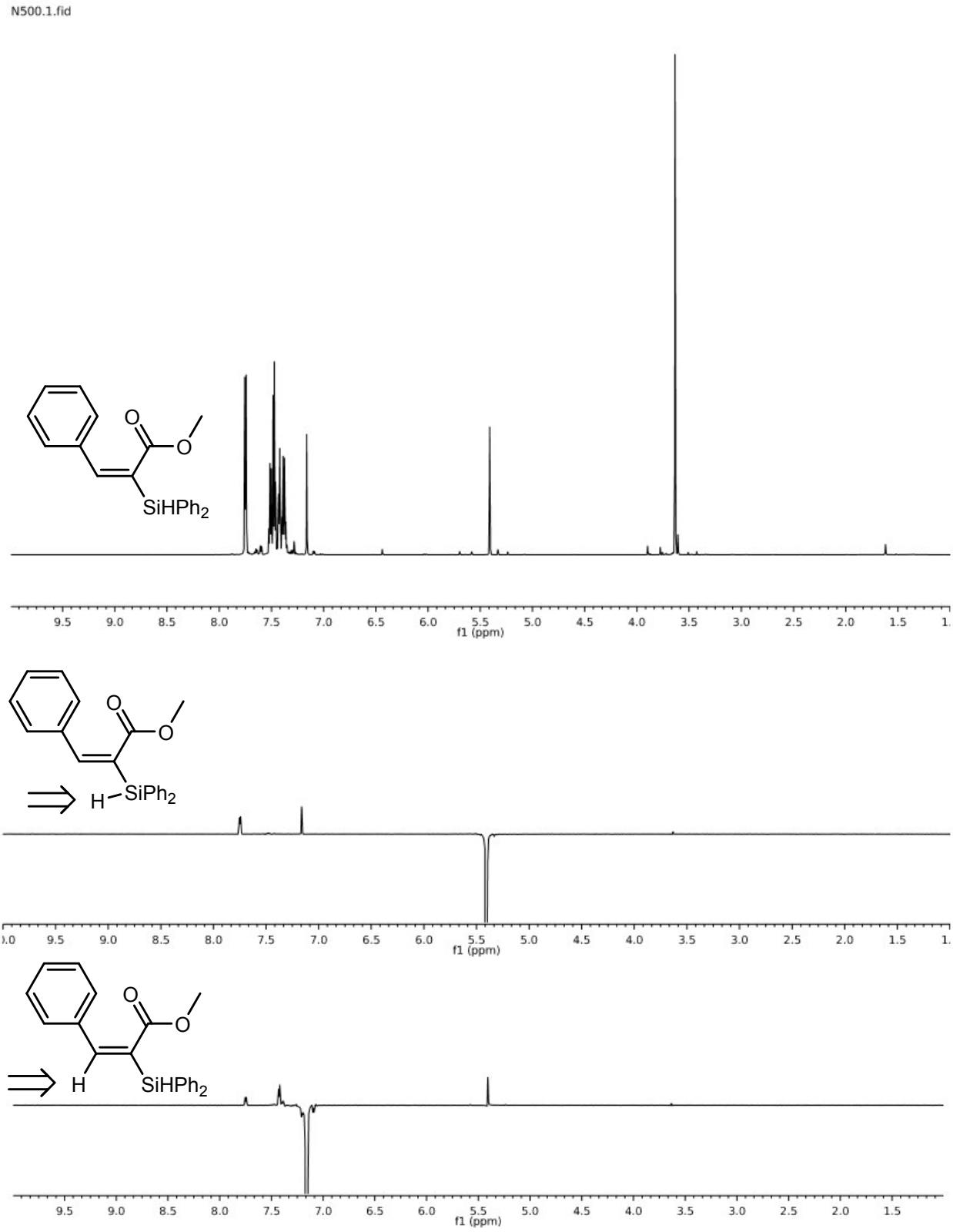
^{1}H NMR spectra of catalytic reaction of methyl phenylpropiolate and diphenylsilane at room temperature (forming mixture of *E* and *Z* isomer)

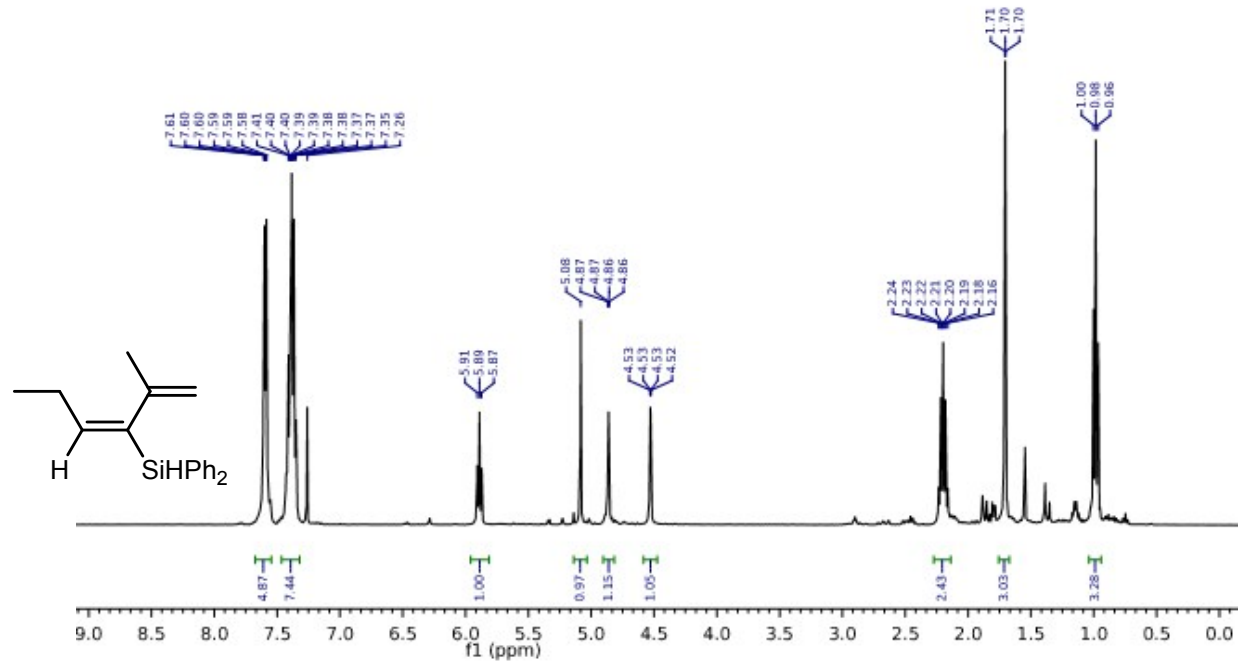


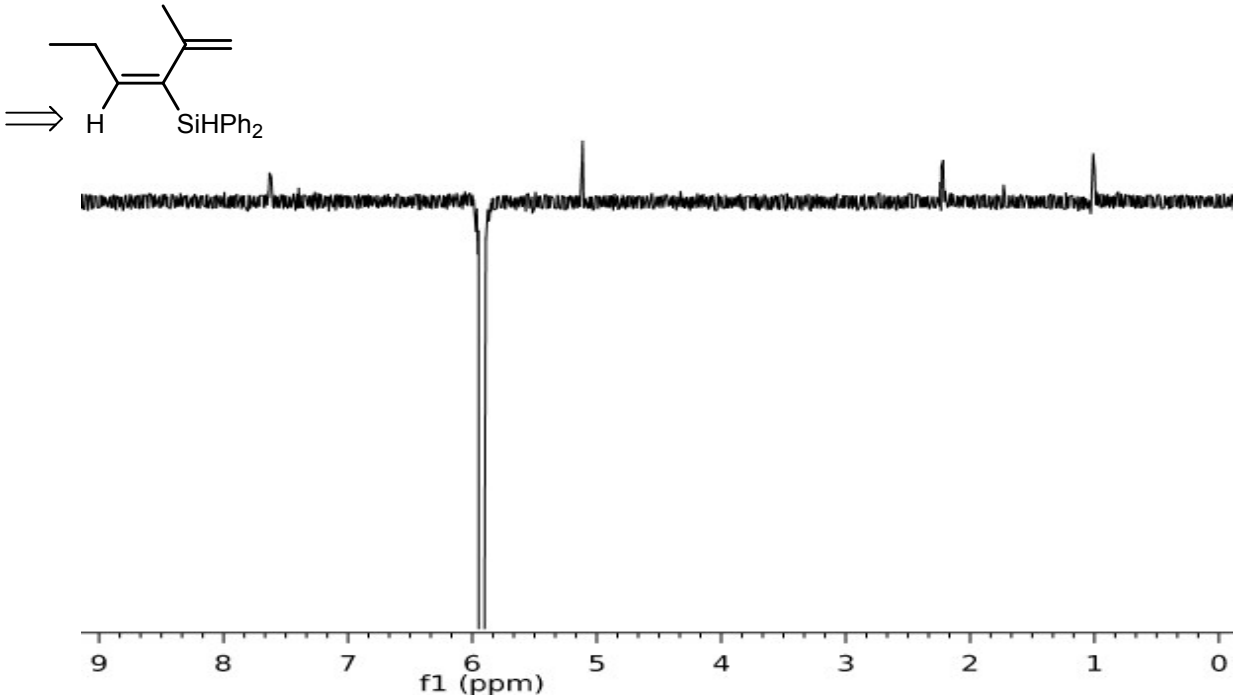
^{1}H NMR spectra of catalytic reaction of methylphenylpropiolate and methylphenylsilane at room temperature (forming mixture of *E* and *Z* isomer)

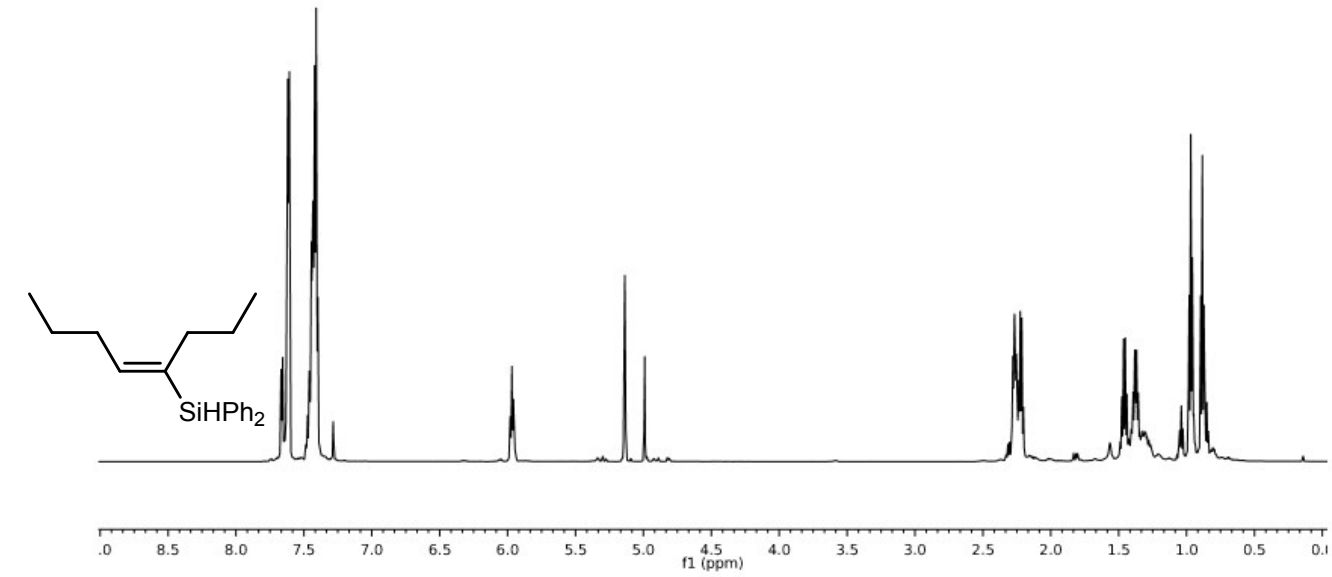


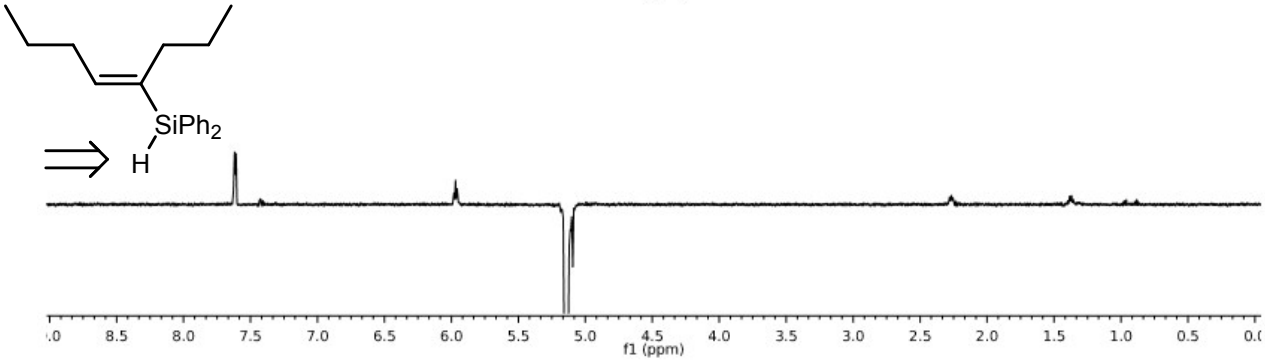
Representative SELNOE experiments to determine between stereoisomers

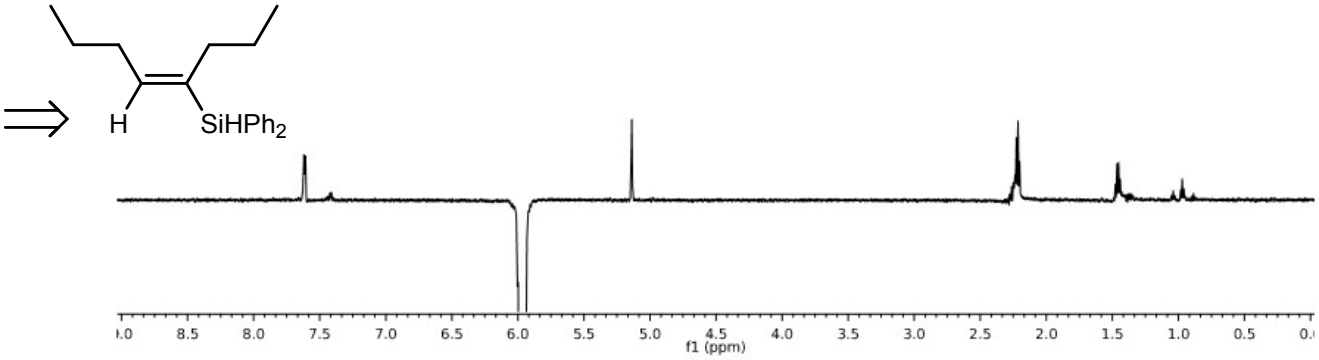



H
SiHPh2
f1 (ppm)


H
SiHPh2
f1 (ppm)


SiHPh2
f1 (ppm)


SiPh2
H
f1 (ppm)


H
SiHPh2
f1 (ppm)

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