

General, Auxiliary-Enabled Photoinduced Pd-Catalyzed Remote Desaturation of Aliphatic Alcohols

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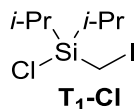
1. General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. ^1H signals are referenced to residual CHCl_3 at 7.26 ppm. ^{13}C signals are referenced to CDCl_3 at 77.0 ppm. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., TCI America, Oakwood Chemical, AK Sci. or Alfa Aesar, or synthesized via known literature procedures. The 34 W Blue LED lamp (Kessil KSH150B LED Grow Light), 23W Philips Household CFL, and Vornado 133 Small Air Circulator fan were purchased from amazon.com. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques.

2. Synthesis of Starting Materials

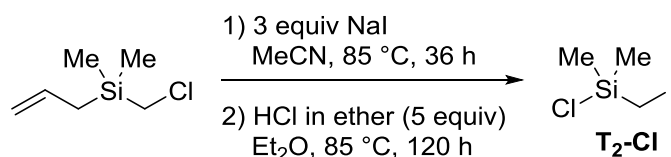
2.1. Synthesis of Si-tethers

Synthesis of **T₁-Cl**:



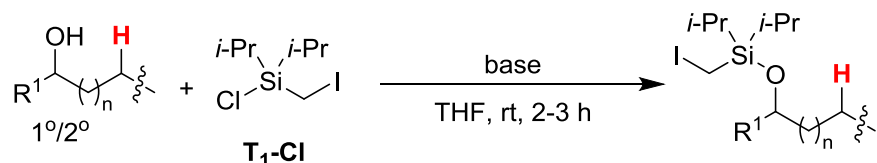
T₁-Cl was prepared according to the published procedure.¹

Synthesis of **T₂-Cl**:



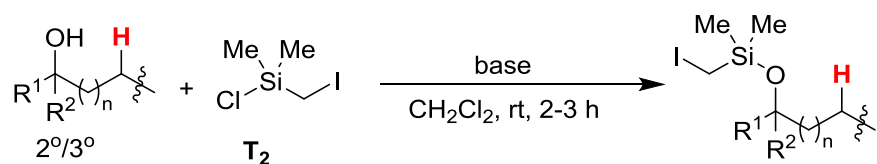
Allyl(chloromethyl)dimethylsilane (5.6 mL, 34 mmol, 1 equiv) in MeCN (10 mL) was added to the solution of sodium iodide (15.4 g, 102 mmol, 3 equiv) in MeCN (20 mL) under Ar atmosphere. The mixture was refluxed for 36 hours. The reaction was cooled to rt, diluted with EtOAc (60 mL), then washed with Na₂S₂O_{3(sat)} solution (30 mL) and water (30 mL), dried over Na₂SO_{4(anh)}, concentrated and purified by flash chromatography (hexanes) to afford 4.8 g (67%) of the Finkelstein reaction product. The product was transferred to a 250 mL Schlenk flask equipped with a reflux condenser and then purged with Ar. The substrate was diluted with dry Et₂O (20 mL). Then, dry HCl (48 mL, 97 mmol, 2M Et₂O) was added at rt under Ar. The mixture was then refluxed at 85 °C for 120 h. After completion, the mixture was cooled down to rt and then filtered with celite under Ar atmosphere. The mixture was then concentrated *in vacuo* to furnish 3.9 g (86%, 95% pure) **T₂-Cl** as a greenish-yellow oil. The substrate was used for the next step without further purification. *Warning: T₂-Cl is highly moisture sensitive!* ¹H NMR (500 MHz, CDCl₃): δ ppm 2.24 (s, 2H), 0.6 (s, 6H). ¹³C NMR (126 MHz, CDCl₃): δ ppm -0.14, 0.99.

2.2 Synthesis of T₁ and T₂ tethered alcohols (1)



Method A: To a stirred mixture of imidazole (410 mg, 4 mmol, 2 equiv) and THF (5 mL), chlorosilane **T₁-Cl** (640 mg, 2.2 mmol, 1.1 equiv) was added at rt under Ar atmosphere. To this mixture, primary alcohol (2 mmol, 1 equiv) in 5 mL of THF was added. The mixture was stirred until completion of the reaction as judged by GC/MS analysis. To this mixture, hexanes (10 mL) was added and then filtered. The filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography in hexanes.

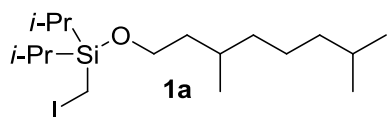
Method B: To a stirred mixture of primary/secondary alcohol (2 mmol, 1 equiv) and THF (5 mL), MeLi (1.34 mL, 1.5 M, 2 mmol, 1 equiv) was added dropwise at 0 °C under Ar atmosphere. To this mixture, HMPA (0.35 mL, 2 mmol, 1 equiv) was added, followed by, **T₁-Cl** (640 mg, 2.2 mmol, 1.1 equiv) in 5 mL of THF at 0 °C. The mixture was stirred until completion of the reaction as judged by GC/MS analysis. Then, the mixture was quenched with NH₄Cl_(sat) solution (30 mL) and extracted with Et₂O (3 x 20 mL). The combined organic layer was washed with brine. The organic layer was dried and filtered. The filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography in hexanes.



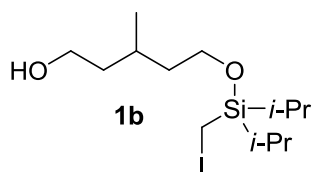
Method C: To a stirred mixture of imidazole (410 mg, 4 mmol, 2 equiv) and THF (5 mL), chlorosilane **T₂-Cl** (520 mg, 2.2 mmol, 1.1equiv) was added at rt under Ar atmosphere. To this mixture, secondary/tertiary alcohol (2 mmol, 1 equiv) in 5 mL of THF was added. The mixture was stirred until completion of the reaction as judged by GC/MS analysis. To this mixture, hexanes (10 mL) was added and then filtered. The filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography in hexanes.

Method D: To a stirred mixture of imidazole (410 mg, 4 mmol, 2 equiv) and MeCN (3 mL), dimethyl(bromomethyl-)chlorosilane (0.3 mL, 2.2 mmol, 1.1 equiv) was added at rt under Ar atmosphere. To this mixture, secondary/tertiary alcohol (2 mmol, 1 equiv) in 2 mL of MeCN was added. The mixture was stirred until completion of the reaction as judged by GC/MS analysis. Then, NaI (900 mg, 3 equiv) was added directly to the reaction mixture. The mixture was heated to 85 °C for 2-12 h. After completion, the mixture was cooled to rt, diluted with EtOAc (60 mL), then washed with Na₂S₂O_{3(sat)} solution (30 mL) and water (30 mL), dried over Na₂SO_{4(anh)}, concentrated and purified by flash chromatography in hexanes.

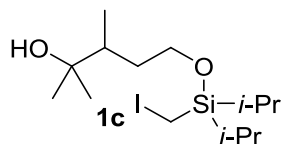
Alcohol tethered analytics (1):



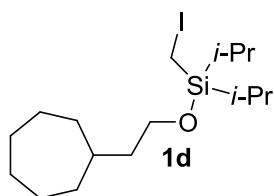
1a was prepared according to the general Method A in 71% yield. Clear and colorless liquid. R_f (hexanes): 0.60. ¹H NMR (500 MHz, CDCl₃): δ ppm 3.79-3.72 (m, 1H), 2.08 (s, 2H), 1.59-1.50 (m, 3H), 1.38-1.12 (m, 6H), 1.16-1.03 (m, 16H), 0.87 (t, *J* = 6.6 Hz, 9H). ¹³C NMR (126 MHz, CDCl₃): δ ppm 12.3, 17.4, 17.6, 19.9, 22.6, 22.7, 24.7, 27.9, 29.4, 39.2, 39.9, 62.2. HRMS (EI+) calcd. for C₁₇H₃₇OISi [M]: 412.1658, found: 412.1658.



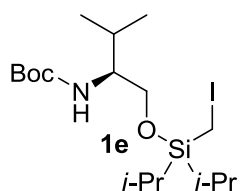
1b was prepared according to the general Method A in 40% yield. Clear and colorless liquid. R_f (hexanes:EtOAc = 9:1): 0.20. ¹H NMR (500 MHz, CDCl₃): δ ppm 3.81-3.68 (m, 4H), 2.80-2.07 (s, 2H), 1.77-1.75 (m, 1H), 1.64-1.60 (m, 2H), 1.46-1.40 (m, 2H), 1.32 (bs, 1H), 1.25-1.19 (m, 2H), 1.09-1.06 (m, 13H), 0.94-0.92 (m, 3H). ¹³C NMR (126 MHz, CDCl₃): δ ppm 12.3, 17.4, 17.7, 19.9, 26.3, 39.7, 39.9, 61.1, 61.9. HRMS (EI+) calcd. for C₁₇H₃₇OISi [M]: 412.1658, found: 412.1658.



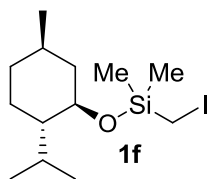
1c was prepared according to the general Method A in 62% yield. Clear and colorless liquid. R_f (hexanes:EtOAc = 9:1): 0.38. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.89-3.87 (m, 1H), 3.78-3.76 (m, 1H), 2.09 (s, 2H), 1.98 (bs, 1H), 1.90-1.85 (m, 1H), 1.65-1.62 (m, 1H), 1.38-1.32 (m, 1H), 1.27-1.21 (m, 2H), 1.19 (s, 3H), 1.17-1.15 (m, 3H), 1.10-1.07 (m, 12H), 0.94 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.3, 17.4, 17.7, 25.8, 27.7, 35.0, 41.3, 62.7, 72.8. LRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{31}\text{O}_2\text{ISi}$ [M]: 386.39, found: 386.01.



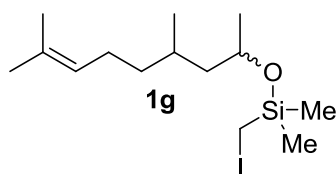
1d was prepared according to the general Method A in 58% yield. Clear and colorless liquid. R_f (hexanes): 0.58. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.76 (t, $J = 6.7$ Hz, 1H), 2.08 (s, 2H), 1.72-1.40 (m, 14H), 1.26-1.15 (m, 4H), 1.09-1.03 (m, 12H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.3, 17.4, 17.7, 26.4, 28.5, 34.6, 35.6, 40.9, 62.3. LRMS (EI+) calcd. for $\text{C}_{16}\text{H}_{33}\text{OISi}$ [M]: 396.43, found: 396.01



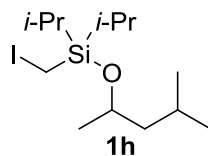
1e was prepared according to the general Method A in 58% yield. Clear and colorless oil. R_f (hexanes): 0.48. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.72-4.74 (m, 1H), 3.79 (dd, $J = 10.2, 3.8$ Hz, 1H), 3.87-3.83 (dd, $J = 9.9, 3.8$ Hz, 1H), 3.39 (m, 1H), 2.09 (s, 2H), 1.93-1.84 (m, 1H), 1.44 (m, 9H), 1.29-1.18 (m, 2H), 1.09-1.06 (m, 12H), 0.96-0.93 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.3, 17.3, 17.4, 17.5, 17.6, 17.7, 18.8, 19.7, 28.4, 29.0, 57.1, 63.9, 79.9, 155.9. HRMS (EI+) calcd. for $\text{C}_{17}\text{H}_{36}\text{O}_2\text{NISi}$ [M+Na]: 480.1407, found: 480.1413.



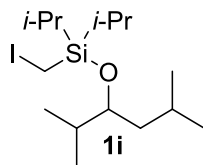
1f was prepared according to the general Method **D** in 58% yield. Clear and colorless liquid. R_f (hexanes): 0.20. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.48-3.43 (m, 1H), 2.16-2.13 (m, 1H), 2.04 (s, 2H), 1.85-1.84 (m, 1H), 1.65-1.58 (m, 2H), 1.39-1.36 (m, 1H), 1.16-1.12 (m, 1H), 1.06-0.99 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 7H), 0.87-0.81 (m, 1H), 0.74 (d, $J = 6.9$ Hz, 3H), 0.30 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -1.8, 15.9, 21.2, 22.3, 22.9, 25.3, 31.7, 34.4, 45.4, 49.9, 73.2. HRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{27}\text{OISi}$ [M]: 354.0876, found: 354.0876.



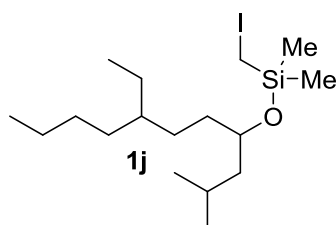
1g was prepared according to the general Method **D** in 53% yield. dr = 1:1. Clear and colorless liquid. R_f (hexanes): 0.71. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.09-5.08 (m, 1H), 3.96-3.91 (m, 1H), 2.02-1.93 (m, 5H), 1.68 (s, 3H), 1.60 (s, 3H), 1.53-1.47 (m, 1H), 1.36-1.26 (m, 3H), 1.17-1.09 (m, 6H), 0.88 (q, 4H), 0.29 (d, $J = 4.4$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -2.0, 17.6, 19.5, 20.0, 23.9, 24.6, 25.4, 25.7, 28.8, 29.3, 37.1, 37.6, 47.1, 67.3, 67.6, 124.8, 131.1. LRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{29}\text{OISi}$ [M]: 368.37, found: 368.01.



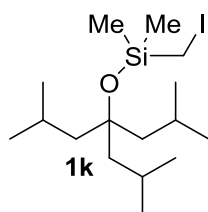
1h was prepared according to the general Method **A** in 84% yield. Colorless liquid. R_f (hexanes): 0.59. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.03-4.07 (m, 1H), 2.08 (s, 1H), 1.68 (q, $J = 7.0$ Hz, 1H), 1.47-1.41 (m, 1H), 1.27-1.17 (m, 7H), 1.10-1.06 (m, 12H), 0.90 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.4, 17.2, 17.3, 17.7, 17.6, 22.6, 22.8, 23.8, 24.5, 48.9, 67.4. HRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{29}\text{IOSi}$ [M]-1: 355.1032, found: 355.09492.



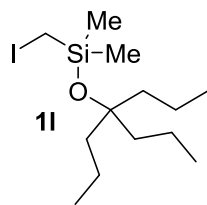
1i was prepared according to the general Method **A** in 78% yield. Colorless liquid. R_f (hexanes): 0.62. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.83-3.80 (m, 1H), 2.08 (s, 2H), 1.79-1.76 (m, 1H), 1.67-1.65 (m, 1H), 1.31-1.18 (m, 4H), 1.09 (t, $J = 7.34$ Hz, 12H), 0.92-0.88 (m, 9H), 0.82 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.8, 16.7, 17.6, 17.8, 17.9, 22.8, 23.2, 24.5, 32.8, 42.2, 75.5. LRMS (EI+) calcd. for $\text{C}_{15}\text{H}_{33}\text{OISi}$ [M]: 384.42, found: 384.01.



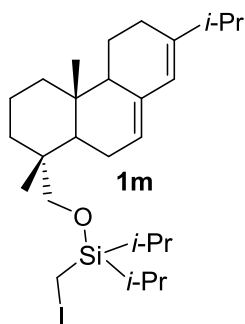
1j was prepared according to the general Method **D** in 94% yield. 92% Purity. Clear and colorless liquid. R_f (hexanes): 0.43. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.75-3.70 (m, 1H), 2.04 (m, 2H), 1.71-1.63 (m, 1H), 1.43-1.23 (m, 15H), 0.91-0.82 (m, 12H), 0.29 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -1.9, 10.9, 14.2, 22.5, 23.1, 23.3, 24.5, 25.8, 28.6, 28.9, 32.7, 34.7, 38.9, 46.5, 72.1. HRMS (EI+) calcd. for $\text{C}_{17}\text{H}_{36}\text{OISi}$ [M-H]: 411.1180, found: 411.1178.



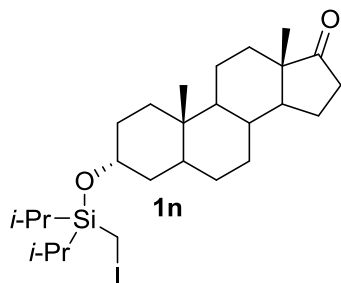
1k was prepared according to the general Method **C** in 50% yield. Clear and colorless liquid. R_f (hexanes): 0.79. ^1H NMR (500 MHz, CDCl_3): δ ppm 2.06 (s, 2H), 1.75-1.68 (m, 3H), 1.43 (d, $J = 5.5$ Hz, 6H), 0.94 (d, $J = 6.7$ Hz, 18H), 0.3 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -14.0 (not shown), 0.4, 24.2, 25.1, 49.1, 81.4. LRMS (EI+) calcd. for $\text{C}_{16}\text{H}_{35}\text{OISi}$ [M]: 398.44, found: 398.01.



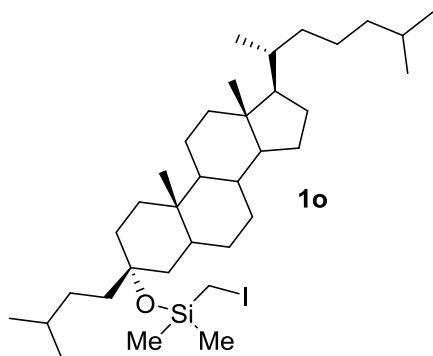
1l was prepared according to the general Method **C** in 65% yield. Clear and colorless liquid. R_f (hexanes): 0.61. ^1H NMR (500 MHz, CDCl_3): δ ppm 2.02 (s, 2H), 1.41-1.38 (m, 6H), 1.30-1.25 (m, 6H), 0.90-0.87 (m, 9H), 0.28 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -14.0 (not shown), 0.2, 14.7, 17.1, 42.2, 79.4. LRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{29}\text{OISi}$ [M]: 356.36, found: 356.01.



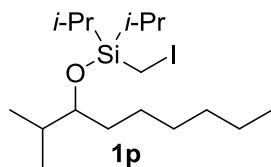
1m was prepared according to the general Method **B** in 36% yield. Clear and colorless thick liquid. R_f (hexanes): 0.77. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.78 (s, 1H), 5.40-5.39 (m, 1H), 3.44 (d, $J = 9.4$ Hz, 1H), 3.25 (d, $J = 9.4$ Hz, 1H), 2.24-2.19 (d, 1H), 2.10-2.08 (m, 3H), 2.05 (s, 2H), 1.98-1.95 (m, 1H), 1.90-1.79 (m, 3H), 1.63-1.16 (m, 8H), 1.09-1.00 (m, 20H), 0.86 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.2, 12.3, 14.2, 17.5, 17.6, 17.7, 18.3, 20.8, 21.4, 22.7, 24.0, 27.4, 34.6, 34.8, 36.1, 37.9, 38.9, 43.6, 50.7, 72.6, 121.2, 122.6, 135.3, 144.9. HRMS (EI+) calcd. for $\text{C}_{27}\text{H}_{47}\text{OISi}$ [M]: 542.2241, found: 542.2254.



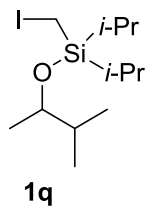
1n was prepared according to the general Method **A** in 40% yield. Clear and colorless thick liquid. R_f (hexanes:EtOAc = 9:1): 0.47. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.16-4.15 (m, 1H), 2.43 (dd, $J = 19.1$ Hz, 8.4 Hz, 1H), 2.06 (s, 2H), 1.95-1.90 (m, 1H), 1.80-1.79 (m, 2H), 1.69-1.16 (m, 18H), 1.09-1.00 (m, 14H), 0.85 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 11.4, 12.6, 13.8, 17.6, 17.7, 17.8, 20.1, 21.8, 28.3, 29.8, 30.9, 31.6, 32.4, 35.1, 35.9, 36.2, 36.8, 39.1, 47.8, 51.5, 54.5, 67.7, 221.6. LRMS (EI+) calcd. for $\text{C}_{26}\text{H}_{45}\text{O}_2\text{ISi}$ [M]: 544.63, found: 544.01.



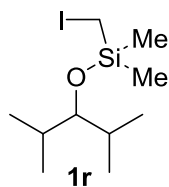
1o was prepared according to the general Method **C** in 46% yield. White-pale solid. R_f (hexanes): 0.78. ^1H NMR (500 MHz, CDCl_3): δ ppm 2.04 (s, 2H), 2.02 (s, 1H), 1.98-1.95 (m, 1H), 1.83-0.96 (m, 36H), 0.91-0.85 (m, 16H), 0.72 (s, 3H), 0.65 (s, 3H), 0.3 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -14.0 (not shown), 0.36, 0.23, 11.6, 12.1, 18.7, 21.0, 22.5, 22.7, 22.8, 23.8, 24.2, 28.0, 28.3, 28.5, 28.7, 32.2, 32.7, 33.4, 34.1, 35.6, 35.7, 35.8, 36.2, 39.5, 40.1, 40.4, 40.7, 42.4, 42.6, 54.4, 56.3, 56.3, 76.9. LRMS (EI+) calcd. for $\text{C}_{35}\text{H}_{65}\text{OISi}$ [M]: 656.89, found: 656.01.



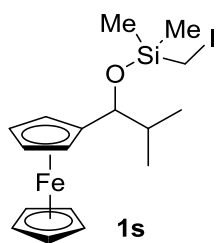
1p was prepared according to the general Method **A** in 67% yield. Colorless liquid. R_f (hexanes): 0.61. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.70-3.67 (q, 1H), 2.08 (s, 2H), 1.78-1.74 (m, 1H), 1.41-1.41 (m, 2H), 1.32-1.19 (m, 10H), 1.09 (t, $J = 7.34$ Hz, 12H), 0.90-0.84 (m, 9H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.8, 14.1, 17.3, 17.5, 18.1, 22.7, 25.6, 29.6, 31.9, 32.7, 33.2, 77.8. HRMS (EI+) calcd. for $\text{C}_{17}\text{H}_{37}\text{OISi}$ [M]: 412.1658 found: 412.63.



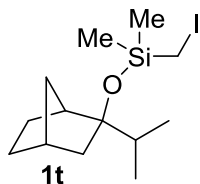
1q was prepared according to the general Method **A** in 42% yield. Clear and colorless liquid. R_f (hexanes): 0.58. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.85-3.81 (m, 1H), 2.08 (s, 2H), 1.71-1.65 (m, 1H), 1.23-1.18 (m, 2H), 1.12-1.05 (m, 15H), 0.87 (d, $J = 7.0$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.6, 12.7, 17.4, 17.5, 17.6, 17.8, 17.9, 18.0, 19.6, 35.3, 73.6. HRMS (EI+) calcd. for $\text{C}_{12}\text{H}_{27}\text{OISi}$ [M]: 342.0876, found: 342.0879.



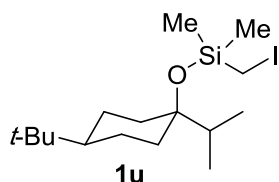
1r was prepared according to the general Method **D** in 48% yield. Colorless liquid. R_f (hexanes): 0.55. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.17-3.14 (m, 1H), 2.07 (s, 2H), 1.78-1.72 (m, 2H), 0.86 (dd, $J = 6.8$ Hz, $J = 3.3$ Hz, 12H), 0.32 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -1.8, 17.7, 20.4, 30.9, 84.3. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{23}\text{OISi}$ [M-H]: 313.0485, found: 313.0485.



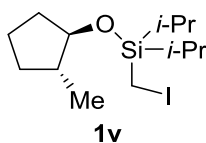
1s was prepared according to the general Method **C** in 20% yield. Yellow liquid. R_f (hexanes:EtOAc = 20:1): 0.40. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.55 (d, $J = 4.0$ Hz, 1H), 4.23 (s, 1H), 4.11 (s, 5H), 4.08 (s, 2H), 4.05 (s, 1H), 2.09 (s, 2H), 1.93-1.86 (m, 1H), 0.83 (d, $J = 8.5$ Hz, 3H), 0.77 (d, $J = 8.5$ Hz, 3H), 0.39 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -1.8, -1.6, 17.4, 18.1, 35.5, 66.4, 66.7, 67.2, 67.8, 68.6. HRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{18}\text{OISiFe}$ [M]: 456.0069 found: 456.0069.



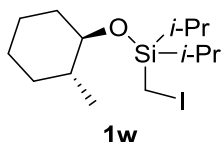
1t was prepared according to the general Method C in 31% yield. Clear and colorless liquid. R_f (hexanes): 0.70. ^1H NMR (500 MHz, CDCl_3): δ ppm 2.29 (s, 1H), 2.17 (s, 1H), 2.09 (s, 2H), 1.80-1.75 (m, 1H), 1.68-1.62 (m, 2H), 1.56-1.51 (m, 1H), 1.40-1.23 (m, 3H), 1.20-1.09 (m, 2H), 0.92-0.84 (m, 6H), 0.34 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 0.0, 17.2, 17.7, 17.8, 23.3, 28.5, 36.9, 37.0, 37.5, 43.7, 45.1, 86.9. HRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{25}\text{OISi}$ [M]: 352.0719, found: 352.0724.



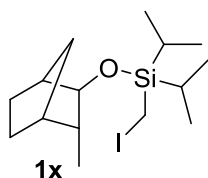
1u was prepared according to the general Method C in 45% yield. Clear and colorless liquid. R_f (hexanes): 0.56. ^1H NMR (500 MHz, CDCl_3): δ ppm 2.08-2.03 (m, 2H), 1.64-1.52 (m, 5H), 1.32-1.25 (m, 4H), 0.92-0.83 (m, 16H), 0.34-0.23 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 0.1, 0.4, 16.2, 17.7, 22.5, 22.6, 24.1, 27.6, 32.4, 34.0, 37.6, 39.0, 47.9, 79.1. HRMS (EI+) calcd. for $\text{C}_{16}\text{H}_{33}\text{OISi}$ [M]: 396.1345, found: 398.1346.



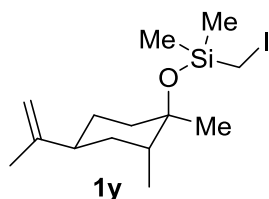
1v was prepared according to the general Method A in 67% yield. Colorless liquid. R_f (hexanes): 0.58. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.84 (m, 1H), 2.08 (s, 2H), 1.89-1.81 (m, 2H), 1.71-1.66 (m, 1H), 1.58-1.52 (m, 2H), 1.24-1.18 (m, 2H), 1.09-1.06 (m, 12H), 0.96-0.94 (d, $J = 6.9$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.4, 17.4, 17.7, 17.8, 18.4, 21.4, 31.1, 34.6, 42.7, 81.3. HRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{27}\text{OISi}$ [M]: 354.0876, found: 354.0878.



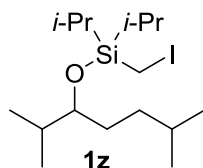
1w was prepared according to the general Method **A** in 75% yield. Clear and colorless liquid. R_f (hexanes): 0.60. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.37-3.32 (m, 1H), 2.09 (s, 2H), 1.91-1.86 (m, 1H), 1.72-1.67 (m, 2H), 1.59-1.53 (m, 1H), 1.41-1.08 (m, 6H), 1.11-1.06 (m, 12H), 0.99-0.96 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.7, 12.8, 17.5, 17.6, 17.8, 18.0, 19.2, 25.0, 25.3, 33.3, 35.9, 40.3, 77.7. LRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{29}\text{O}_2\text{ISi}$ [M]: 368.37, found: 368.01.



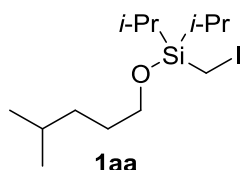
1x was prepared according to the general Method **A** in 75% yield. Colorless liquid. R_f (hexanes/EtOAc = 50:1): 0.66. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.19 (s, 1H), 2.08-2.04 (m, 3H), 2.03-2.00 (m, 1H), 1.74-1.70 (m, 2H), 1.48-1.44 (m, 1H), 1.38-1.33 (m, 1H), 1.22-1.15 (m, 4H), 1.10-1.03 (m, 14H), 0.95 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.4, 15.3, 17.4, 17.5, 17.7, 17.8, 21.3, 24.7, 36.5, 40.7, 46.0, 46.8, 83.5. HRMS (CI+) calcd. for $\text{C}_{16}\text{H}_{25}\text{OISi}$ [M]: 380.1032, found: 380.0941.



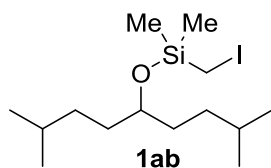
1y was prepared according to the general Method **C** in 35% yield. Colorless liquid. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.72-4.68 (m, 2H), 2.06-2.01 (m, 3H), 1.96-1.92 (m, 1H), 1.80-1.77 (m, 1H), 1.71 (s, 3H), 1.66-1.61 (m, 1H), 1.57-1.48 (m, 3H), 1.49-1.44 (m, 1H), 1.31-1.25 (m, 1H), 1.20 (s, 3H), 0.95-0.92 (m, 3H), 0.89-0.87 (m, 1H), 0.30 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 0.2, 16.3, 20.9, 26.9, 28.0, 34.0, 34.7, 37.9, 38.0, 40.0, 108.4, 150.6. HRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{27}\text{OISi}$ [M]: 366.36, found: 366.01.



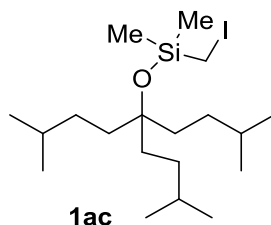
1z was prepared according to the general Method A in 82% yield. Colorless liquid. R_f (hexanes): 0.46. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.71-3.65 (m, 1H), 2.09 (s, 2H), 1.80-1.74 (m, 1H), 1.54-1.49 (m, 1H), 1.45-1.43 (m, 2H), 1.26-1.18 (m, 4 H), 1.12-1.09 (m, 12H), 0.92-0.86 (m, 12H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.8, 17.2, 17.6, 17.9, 18.2, 22.6, 22.7, 28.3, 31.2, 32.6, 34.7, 78.0. LRMS (EI+) calcd. for $\text{C}_{16}\text{H}_{35}\text{OISi}$ [M]: 398.15, found: 398.01.



1aa was prepared according to the general Method A in 70% yield. Clear and colorless liquid. R_f (hexanes): 0.30. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.71 (t, $J = 6.7$ Hz, 2H), 2.08 (s, 2H), 1.59-1.53 (m, 3H), 1.24-1.18 (m, 4H), 1.08 (t, $J = 7.3$ Hz, 12H), 0.88 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.3, 17.4, 17.7, 22.6, 27.8, 30.7, 34.9, 84.2. LRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{29}\text{OISi}$ [M]: 356.36, found: 356.01.

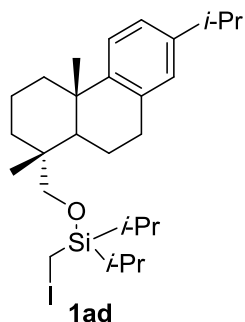


1ab was prepared according to the general Method C in 40% yield. Clear and colorless liquid. R_f (hexanes): 0.39. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.67-3.61 (m, 1H), 2.03 (s, 2H), 1.56-1.41 (m, 6H), 1.28-1.10 (m, 4H), 0.90-0.86 (m, 12H), 0.29 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -2.0, 22.5, 22.6, 28.1, 34.6, 34.7, 35.0, 35.2, 74.0. HRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{31}\text{OISi}$ [M]: 370.1189, found: 370.1192.



1ac was prepared according to the general Method C in 29% yield. Clear and colorless liquid. R_f (hexanes): 0.65. ^1H NMR (500 MHz, CDCl_3): δ ppm 2.02 (s, 2H), 1.50-1.38 (m, 9H), 1.17-1.10

(m, 6H), 0.89 (d, $J = 8.2$ Hz, 18H), 0.29 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 0.4, 22.8, 28.7, 32.8, 37.4, 79.6. LRMS (EI+) calcd. for $\text{C}_{19}\text{H}_{41}\text{OISi}$ [M]: 440.52, found: 440.01.



1ad was prepared according to the general Method **B** in 36% yield. Clear and colorless oil. R_f (hexanes): 0.50. ^1H NMR (500 MHz, CDCl_3): δ ppm 7.18 (d, $J = 8.0$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.9 (s, 1H), 3.60 (d, $J = 9.5$ Hz, 1H), 3.26 (d, $J = 9.5$ Hz, 1H), 2.86-2.82 (m, 3H), 2.25 (d, $J = 12.5$ Hz, 1H), 2.07 (s, 2H), 1.80-1.73 (m, 3H), 1.66-1.50 (m, 5H), 1.39-1.30 (m, 2H), 1.25-1.20 (m, 9H), 1.08-1.02 (m, 12H), 0.85 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 12.3, 17.4, 17.5, 17.8, 18.8, 19.0, 24.0, 25.6, 30.5, 33.4, 35.3, 38.3, 38.4, 43.6, 72.4, 123.7, 124.4, 126.8, 135.0, 147.5. HRMS (EI+) calcd. for $\text{C}_{27}\text{H}_{45}\text{OISi}$ [M]: 540.2284, found: 540.2285.

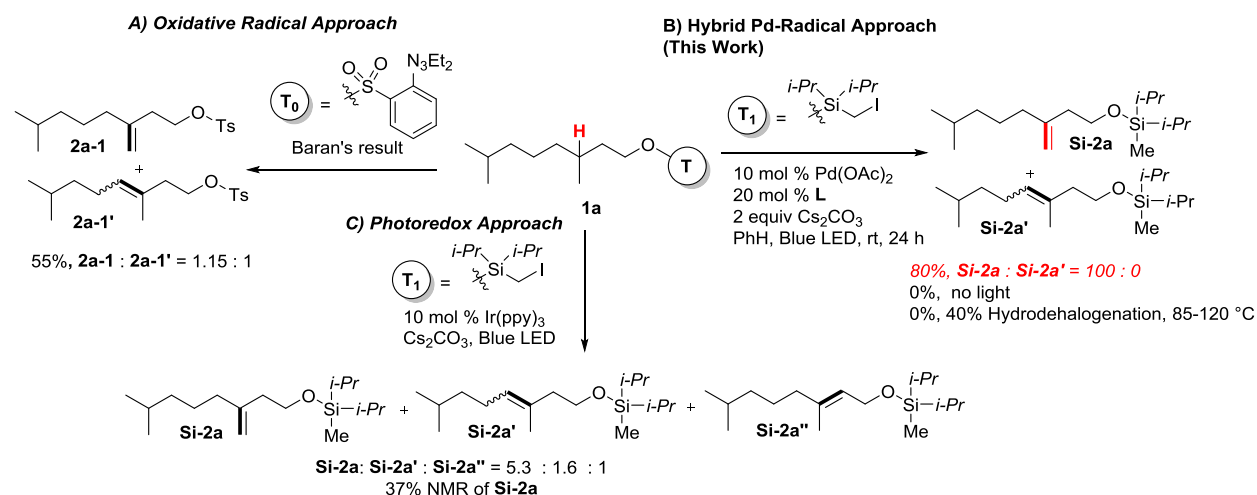
3. Optimization of the Reaction Parameters

Rationale for the design of silylmethyl hydrogen abstracting tethers.

Apparently, alkyl radicals are poor hydrogen atom abstracting species compared to aryl radicals due to BDEs. However, the C–H bond of methyl silanes has a BDE of 100 kcal/mol, thus silyl methyl radicals are capable of abstracting unactivated tertiary C–H sites (BDE = 96 kcal/mol) and secondary C–H sites (BDE = 98 kcal/mol).¹

The design of the iodomethylsilane moiety was based upon our prior work on endo-selective silylmethyl-Heck reaction (see ref 12 in the manuscript). To achieve the desired HAT event, the distance from the formed radical and abstraction site is vital. For the HAT involving the alkyl tether, the proximal α -position would be in a 1,4 relationship, which is disfavored for the HAT. Conversely, the remote C–H sites are in a favorable distance (1,5, 1,6 and 1,7) for the HAT to occur with the flexible silyl alkyl-based auxiliary. Therefore, due to sufficient reactivity of silyl methyl radicals and favorable distance for HAT for our systems, desaturation occurs at remote C–H sites. In contrast to the carbon-chain systems preferring 1,5-HAT, the most preferred HAT distance for our system is 1,6 (see note 14 in the manuscript).

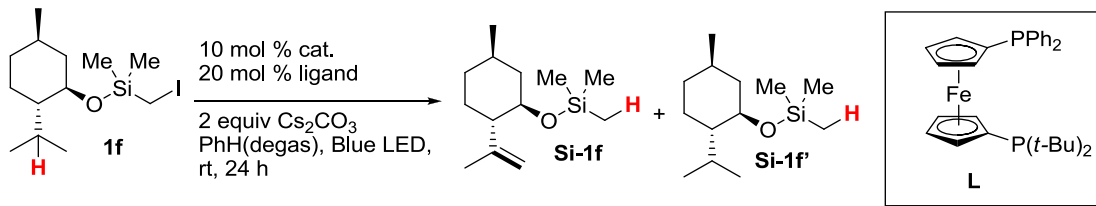
Initial Studies and Comparison Studies of Primary Alcohol **1a**:



Application of Baran's groundbreaking method (**A**) for desaturation of challenging substrate **1a** resulted in γ -/ δ - desaturated adducts (**2a-1** and **2a-1'**) with low regiocontrol. Applying our strategy (**B**), using a designed tether **T₁** and our previously optimized conditions,² resulted in γ -

γ -desaturation product **Si-2a** in 80% yield as the sole regioisomer. Next, we examined the possibility of desaturation of **T**₁-containing substrate under typical photoredox conditions. To this end, desaturation of **1a** was tested in the presence of a conventional Ir-photosensitizer. Not surprisingly, due to the formation of cationic intermediates (similar mechanistic feature in Baran's approach (**A**)), the photoredox approach resulted in low yields and low regioselectivity of γ - δ -desaturation product **Si-2a**. Based on the high regioselective outcome in our transformation (**B**), it is very likely that our mechanism is distinct from other pathways (**A** and **C**), which involves a controlled β -Pd-H elimination endgame step.

Optimization studies on secondary alcohol **1f** using **T**₂:

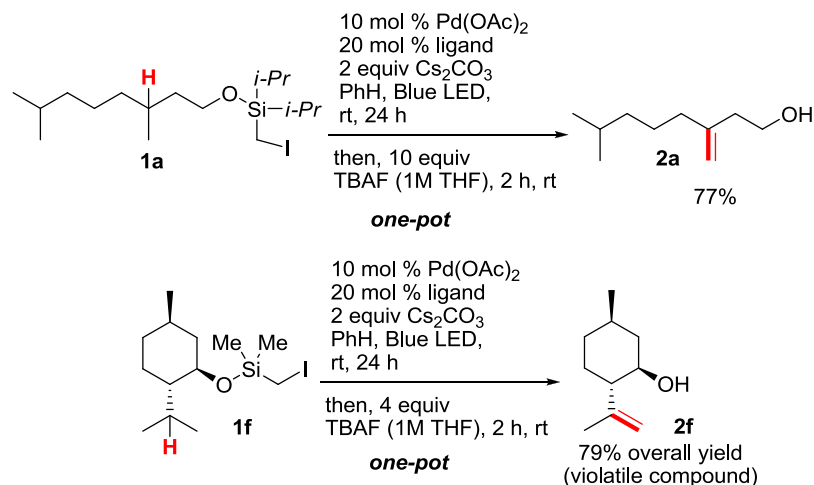


#	catalyst	ligand	Si-1f : Si-1f'	GC yield, ^a %
1	Pd(OAc) ₂	bipy	-	NR
2	Pd(OAc) ₂	1,10-phen	-	NR
3	Pd(PPh ₃) ₄	-	4 : 1	57
4	Pd(OAc) ₂	SiPr	-	NR
5	Pd(OAc) ₂	dppe	-	Traces
6	Pd(OAc) ₂	Triphos	1 : 1	28
7	Pd(OAc) ₂	DPEphos	-	NR
8	Pd(OAc) ₂	Binap	1 : 0	47
9	Pd(OAc) ₂	dppf	1 : 1	12
10	Pd(OAc) ₂	xantphos	-	72
11	Pd(OAc)₂	L	20 : 1	94
12 ^b	Pd(OAc) ₂	L	20 : 1	60
13	Pd(OAc) ₂	-	-	<2
14	-	L	-	<2

^aGC yields were calibrated using pentadecane as an internal standard. ^b5 mol % Pd/ 10 mol % L

Table S1. Optimization of the reaction parameters.

One-pot procedure for desaturation/desilylation of **1a/1f**:



4. Remote Desaturation of Alcohols

4.1 General Procedure A for Desaturation of Alcohols using T₁.

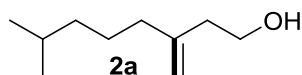
An oven dried 5 mL Wheaton V-vial containing a stirring bar was charged with silyl tethered alcohols **1** (0.2 mmol), Pd(OAc)₂ (4.49 mg, 0.02 mmol), ligand **L** (20.6 mg, 0.04 mmol) and Cs₂CO₃ (130 mg, 0.4 mmol) under N₂ atmosphere (glovebox). Dry degassed benzene (2 mL) was added and the reaction vessel was capped with a pressure screw cap. The vial was irradiated with 34 W Blue LED lamp (Kessil KSH150B LED Grow Light) for 12-48 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. After completion, judged by GC/MS analysis, 10 equiv of TBAF (2 mL, 1 M THF) was added directly to the reaction mixture. The reaction was stirred for an additional 2-12 h (monitored by GC/MS). The resulting mixture was diluted with DCM (10 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by filtration through silica gel (hexanes:EtOAc = 9:1 to 4:1) affording the corresponding desaturated alcohols.

4.2 General Procedure B for Desaturation of Alcohols using T₂.

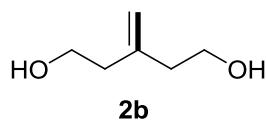
An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with silyl tethered alcohols **1** (0.2 mmol), Pd(OAc)₂ (4.49 mg, 0.02 mmol), ligand **L** (20.6 mg, 0.04 mmol) and Cs₂CO₃ (130 mg, 0.4 mmol) under N₂ atmosphere (glovebox). Dry degassed benzene (2 mL)

was added and the reaction vessel was capped with a pressure screw cap. The vial was irradiated with 34 W Blue LED lamp (Kessil KSH150B LED Grow Light) for 12-48 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. After completion, judged by GC/MS analysis, 5 equiv of TBAF (1 mL, 1 M THF) was added directly to the reaction mixture. The reaction was stirred for an additional 2-12 h (monitored by GC/MS). The resulting mixture was diluted with DCM (10 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by filtration through silica gel (hexanes:EtOAc = 9:1 to 4:1) affording the corresponding desaturated alcohols.

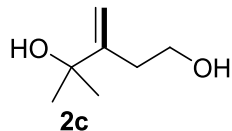
Desaturated Alcohols analytics (2):



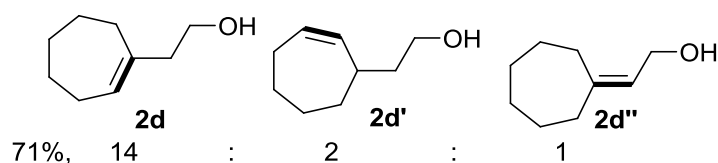
2a was prepared according to the general procedure **A** in 77% yield. Slightly yellow oil. R_f (hexanes/EtOAc = 4:1): 0.44. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ ppm 4.86 (s, 1H), 4.81 (s, 1H), 3.71 (t, $J = 6.3$ Hz, 2H), 2.29 (t, $J = 6.6$ Hz, 2H), 2.01 (t, $J = 7.7$ Hz, 2H), 1.57-1.51 (m, 3H), 1.46-1.40 (m, 2H), 1.20-1.13 (s, 2H), 0.90-0.86 (m, 7H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ ppm 12.7, 17.1, 22.6, 25.5, 27.9, 36.7, 39.1, 62.9, 110.4, 146.9. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{20}\text{O}$ [M]: 156.1514, found: 155.1512.



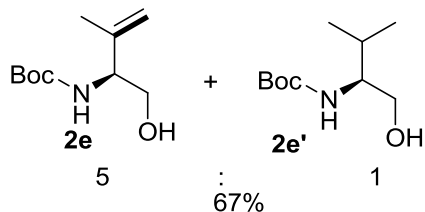
2b was prepared according to the general procedure **A** (two-step procedure) in 48% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 1:4): 0.25. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ ppm 5.01 (s, 2H), 3.79 (t, $J = 6.2$ Hz, 4H), 2.36 (t, $J = 6.2$ Hz, 4H), 1.75 (bs, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ ppm 38.8, 60.6, 114.3, 143.0. LRMS (EI+) calcd. for $\text{C}_6\text{H}_{12}\text{O}_2$ [M]- H_2O : 98.16, found 98.10.



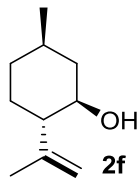
2c was prepared according to the general procedure **A** (two-step procedure) in 47% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 1:4): 0.61. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.18 (s, 1H), 4.90 (s, 1H), 3.83 (t, $J = 5.8$ Hz, 2H), 2.46 (t, $J = 5.1$ Hz, 2H), 1.42 (2, 6H), 1.28 (bs, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 29.7, 34.7, 63.1, 72.7, 110.1, 153.3. HRMS (EI+) calcd. for $\text{C}_7\text{H}_{14}\text{O}_2$ [M]: 129.09156, found: 129.09097.



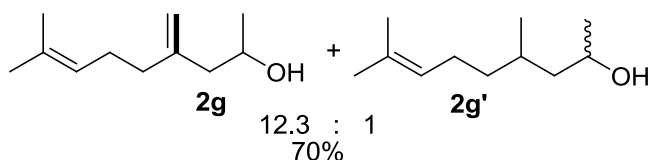
2d was prepared according to the general procedure **A** in calcd. 58% yield of **2d**. Yellow oil. R_f (hexanes/EtOAc = 4:1): 0.40. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.67 (t, $J = 6.6$ Hz, 1H), 3.63 (t, $J = 6.2$ Hz, 2H), 2.24 (t, $J = 5.8$ Hz, 2H), 2.13-2.09 (m, 4H), 1.77-1.72 (m, 2H), 1.51-1.45 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 26.4, 26.9, 27.3, 28.4, 32.5, 43.3, 59.3, 129.8, 140.7. LRMS (EI+) calcd. for $\text{C}_9\text{H}_{16}\text{O}$ [M]: 140.23, found: 140.00.



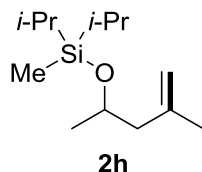
2e was prepared according to the general procedure **A** in calcd. 56% yield of **2e**. White solid. R_f (hexanes/EtOAc = 1:1): 0.48. ^1H NMR (500 MHz, CDCl_3): δ 4.97 (s, 1H), 4.94 (s, 1H), 4.11 (br, 1H), 3.68 (s, 2H), 1.79 (s, 3H), 1.45 (s, 9H), 1.25 (bs, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ 20.4, 28.4, 57.4, 63.8, 79.8, 112.3, 142.6, 155.9. HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{19}\text{O}_3$ [M]+Na: 224.1263, found: 224.1260.



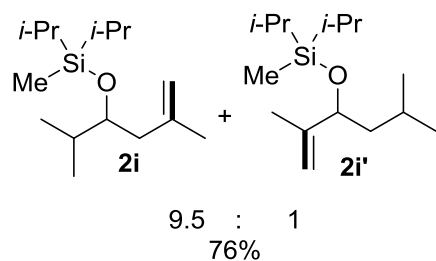
2f was prepared according to the general procedure **B** in 79% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.39. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.90 (s, 1H), 4.85 (s, 1H), 3.46 (t, $J = 5.4$ Hz, 1H), 2.04 (d, $J = 12.5$ Hz, 1H), 1.90-1.85 (m, 2H), 1.71 (s, 3H), 1.69-1.66 (m, 1H), 1.50 (bs, 1H), 1.36-1.25 (m, 2H), 0.98-0.92 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 19.2, 22.2, 29.6, 31.4, 34.3, 42.6, 55.1, 70.3, 112.9, 146.6. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{18}\text{O}$ [M]: 154.1358, found: 154.1360.



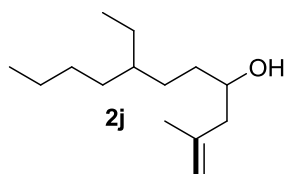
2g was prepared according to the general procedure **B** in calcd. 65% yield of **2g**. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.40. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.09 (t, $J = 6.4$ Hz, 1H), 4.89 (s, 1H), 4.85 (s, 1H), 3.93-3.87 (m, 1H), 2.24-2.02 (m, 6H), 1.75 (bs, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.21 (d, $J = 6.1$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 17.7, 22.9, 25.6, 26.3, 35.8, 46.5, 65.1, 70.3, 112.3, 123.7, 131.9, 146.6. HRMS (ES+) calcd. for $\text{C}_{11}\text{H}_{20}\text{O}$ [M]+1: 169.1592, found: 169.1597.



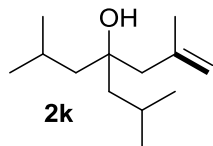
2h was prepared according to the general procedure **A** in 77% yield. Yellow oil. R_f (hexanes): 0.58. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.75 (s, 1H), 4.69 (s, 1H), 4.02-3.94 (m, 1H), 2.31-2.23 (m, 1H), 2.15-2.06 (m, 1H), 1.72 (s, 3H), 1.15-1.55 (m, 3H), 1.05-0.97 (m, 12H), 0.93-0.87 (m, 2H), 0.02 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -8.1, 13.3, 17.4, 22.9, 23.1, 48.5, 67.3, 112.6, 143.0. HRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{28}\text{OSi}$ [M]+1: 229.1909, found: 229.19967.



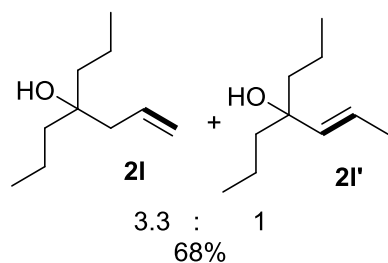
2i was prepared according to the general procedure **A** (two-steps) in calcd. 69% yield of **2i**. Clear and colorless oil. R_f (hexanes): 0.62. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.75 (s, 1H), 4.72 (s, 1H), 3.74-3.71 (m, 1H), 2.20-2.10 (m, 2H), 1.72 (s, 3H), 1.00 (d, $J = 7.0$ Hz, 14H), 0.91-0.88 (m, 8H), 0.84 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -7.3, 13.6, 16.1, 17.5, 17.6, 18.8, 22.8, 32.2, 42.6, 74.9, 112.6, 143.2. LRMS (ES+) calcd. for $\text{C}_{15}\text{H}_{32}\text{OSi}$ [M]: 256.49, found: 255.20.



2j was prepared according to the general procedure **B** in 80% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.55. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.88 (s, 1H), 4.80 (s, 1H), 3.68 (m, 1H), 2.23 (dd, $J = 13.6, 2.9$ Hz, 1H), 2.08 (dd, $J = 13.6, 9.5$ Hz, 1H), 1.76 (s, 3H), 1.47-1.34 (m, 4H), 1.28-1.24 (m, 10H), 0.93-0.83 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 10.8, 14.1, 22.4, 24.6, 25.7, 28.9, 29.1, 32.7, 34.3, 38.9, 46.2, 69.1, 113.4, 142.9. HRMS (EI+) calcd. For $\text{C}_{14}\text{H}_{28}\text{O}$ [M]: 212.2140, found 212.2140.

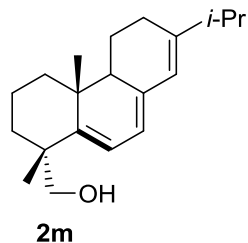


2k was prepared according to the general procedure **B** in 73% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.61. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.93 (s, 1H), 4.75 (s, 1H), 2.2 (s, 1H), 1.84-1.78 (m, 5H), 1.44-1.36 (m, 5H), 0.97-0.95 (m, 14H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 24.0, 24.7, 24.9, 24.6, 48.3, 48.6, 75.3, 114.9, 143.0. LRMS (ES+) calcd. for $\text{C}_{13}\text{H}_{26}\text{O}$ [M]: 198.35, found: 198.20.

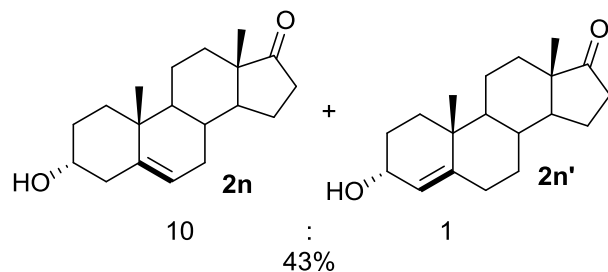


2I was prepared according to the general procedure **B** in calcd. 52% yield of **2I**. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.62. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.88-5.80 (m, 1H), 5.14-5.08 (m, 2H), 2.20 (d, $J = 6.6$ Hz, 2H), 1.49-1.25 (m, 8H), 0.93-0.88 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 14.6, 16.7, 41.5, 43.4, 43.9, 74.9, 118.4, 134.0. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{19}\text{O}$ [M]-1: 155.1436, found 155.1431.

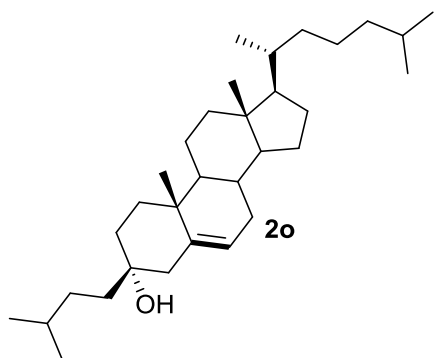
2I' ^1H NMR (500 MHz, CDCl_3): δ ppm 5.61-5.57 (m, 1H), 5.44 (dd, $J = 15.4, 1.5$ Hz, 1H), 1.70 (dd, $J = 7.7, 1.5$ Hz, 2H), 1.49-1.25 (m, 8H), 0.93-0.88 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 14.7, 16.8, 17.7, 41.7, 74.9, 122.7, 137.2. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{19}\text{O}$ [M]-1: 155.1436, found 155.1431.



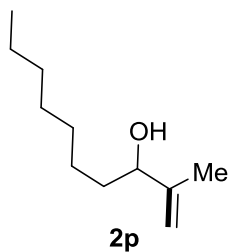
2m was prepared according to the general procedure **A** (two-steps) in 53% yield. White solid. R_f (hexanes/EtOAc = 4:1): 0.39. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.95 (s, 1H), 5.91 (d, $J = 5.5$ Hz, 1H), 5.69 (s, 1H), 3.78 (d, $J = 11.3$ Hz, 1H), 3.16 (d, $J = 11.0$ Hz, 1H), 2.30-2.22 (m, 2H), 2.13-2.01 (m, 2H), 1.88-1.17 (m, 6H), 1.07-0.98 (m, 12H), 0.89 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 17.1, 17.4, 17.8, 20.1, 21.3, 22.3, 27.9, 28.2, 33.8, 35.3, 38.2, 40.9, 47.7, 70.5, 117.3, 119.5, 121.7, 136.2, 148.3, 148.6. HRMS (ES+) calcd. for $\text{C}_{20}\text{H}_{30}\text{O}$ [M]+1: 287.2375, found: 287.2367.



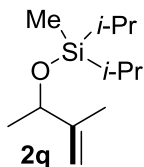
2n was prepared according to the general procedure **A** in calcd. 40% yield of **2n**. White solid. R_f (hexanes/EtOAc = 1:1): 0.59. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ ppm 5.44 (m, 1H), 4.03 (m, 1H), 2.59 (d, $J = 15.5$ Hz, 1H), 2.46 (dd, $J = 19.1, 8.8$ Hz, 1H), 2.13-1.15 (m, 18H), 1.04 (s, 3H), 0.89 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ ppm 13.5, 18.7, 20.1, 21.9, 28.9, 30.9, 31.4, 33.1, 35.8, 37.8, 39.8, 47.5, 50.4, 51.8, 66.9, 132.0, 138.9, 221.2. HRMS (ES+) calcd. for $\text{C}_{19}\text{H}_{28}\text{O}_2$ $[\text{M}]^+1$: 289.2168, found: 289.2161.



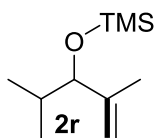
2o was prepared according to the general procedure **B** in 65% yield. White solid. R_f (hexanes/EtOAc = 9:1): 0.62. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ ppm 5.40 (d, $J = 5.4$ Hz, 1H), 2.38 (dd, $J = 14.3, 2.2$ Hz, 1H), 2.03-0.85 (m, 51H), 0.68 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ ppm 11.8, 18.6, 18.7, 20.9, 22.5, 22.6, 22.7, 22.8, 23.8, 24.9, 28.0, 28.2, 28.6, 31.9, 32.0, 32.2, 33.0, 35.1, 35.8, 36.2, 37.0, 39.5, 39.8, 40.6, 42.3, 44.1, 50.4, 56.1, 56.7, 71.9, 123.9, 139.9. HRMS (ES+) calcd. For $\text{C}_{32}\text{H}_{56}\text{O}$: 456.4331, found 456.4331.



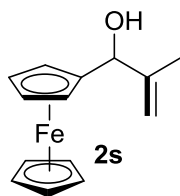
2p was prepared according to the general procedure **A** in calcd. 56% yield (80% yield, r.r. = 3.1:1). Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.47. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.93 (s, 1H), 4.83 (s, 1H), 4.05 (s, 1H), 1.72 (s, 3H), 1.55-1.51 (m, 2H), 1.44 (bs, 1H), 1.34-1.26 (m, 8H), 0.88 (t, $J = 5.4$ Hz, 3H). ^{13}C NMR (500 MHz, CDCl_3): δ ppm 14.1, 17.5, 22.6, 25.5, 29.2, 31.8, 34.9, 76.0, 110.9, 147.7. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{20}\text{O}$ [M]: 140.1201, found: 140.1197.



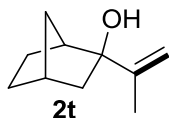
2q was prepared according to the general procedure **B** in 76% yield (NMR). ^1H NMR (500 MHz, C_6D_6): δ ppm 5.09 (s, 1H), 4.83 (s, 1H), 4.31-4.26 (m, 1H), 1.77 (s, 3H), 1.31 (d, $J = 6.4$ Hz, 1H), 1.19-1.11 (m, 14H), 0.12 (s, 3H). LRMS (EI+) calcd. for $\text{C}_{12}\text{H}_{26}\text{OSi}$ [M]+1: 214.42, found: 214.10.



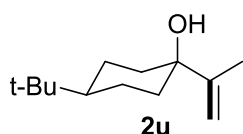
2r was prepared according to the general procedure **B** in 87% yield (NMR). ^1H NMR (500 MHz, C_6D_6): δ ppm 4.97 (s, 1H), 4.89 (s, 1H), 3.70 (d, $J = 7.3$ Hz, 1H), 1.83-1.79 (m, 3H), 1.73 (s, 3H), 1.10 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H), 0.24 (s, 9H). HRMS (ES+) calcd. for $\text{C}_{10}\text{H}_{22}\text{OSi}$ [M]+1: 186.37, found: 186.10.



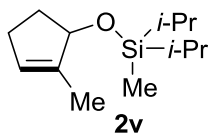
2s was prepared according to the general procedure **B** in 48% yield. R_f (hexanes/EtOAc = 9:1): 0.38. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.02 (s, 1H), 4.80 (s, 2H), 4.27-4.17 (m, 9H), 2.20 (bs, 1H), 1.69 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 18.2, 65.2, 67.8, 67.9, 68.4, 73.6, 92.9, 110.9, 146.6. HRMS (ES+) calcd. for $\text{C}_{14}\text{H}_{16}\text{OFe}$ [M]+1: 257.029, found: 257.0638.



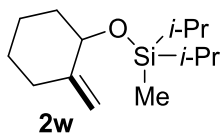
2t was prepared according to the general procedure **B** in 82% yield. R_f (hexanes/EtOAc = 4:1): 0.60. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.91 (s, 1H), 4.78 (s, 2H), 2.40 (bs, 1H), 2.20 (bs, 1H), 2.04-1.94 (m, 2H), 1.82 (s, 3H), 1.59-0.89 (m, 7H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 18.7, 22.1, 28.8, 37.0, 38.9, 44.1, 44.8, 81.2, 109.4, 149.8. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{16}\text{O}$ [M]: 152.12012, found: 152.11963.



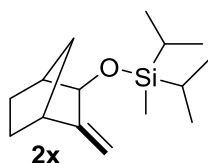
2u was prepared according to the general procedure **B** 66% yield. R_f (hexanes/EtOAc = 4:1): 0.60. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.01 (s, 1H), 4.79 (s, 1H), 1.80 (s, 3H), 1.68-1.57 (m, 6H), 1.45-1.40 (m, 2H), 0.97-0.90 (m, 1H), 0.87 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 16.8, 9.0, 22.5, 27.5, 29.1, 32.3, 36.2, 46.6, 73.2, 108.7, 152.5. HRMS (ES+) calcd. for $\text{C}_{13}\text{H}_{24}\text{O}$ [M]: 196.18272, found: 196.18239.



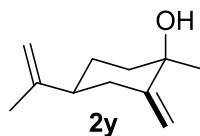
2v was prepared according to the general procedure **A** (without TBAF) 49% yield. R_f (hexanes): 0.24. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.46 (s, 1H), 4.86 (s, 1H), 2.36-2.15 (m, 4H), 1.73 (s, 3H), 1.04-0.92 (m, 14H), 0.60 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -7.7, 13.2, 17.4, 29.6, 34.5, 39.3, 80.1, 126.8, 142.2. HRMS (EI+) calcd. for $\text{C}_{13}\text{H}_{26}\text{OSi}$ [M]: 226.17530, found: 226.17480.



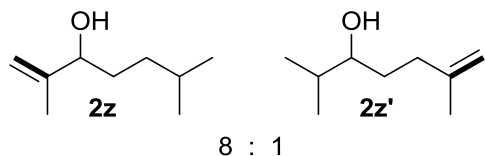
2w was prepared according to the general procedure **A** (without TBAF) 50% yield. R_f (hexanes): 0.42. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.91 (s, 1H), 4.69 (s, 1H), 4.06 (s, 1H), 2.40-2.38 (m, 1H), 1.99-1.94 (m, 1H), 1.84-1.79 (m, 2H), 1.60-1.56 (m, 1H), 1.46-1.38 (m, 3H), 1.02-0.90 (m, 14H), 0.02 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -8.1, 13.2, 17.5, 23.8, 27.9, 33.6, 37.6, 73.2, 105.4, 151.5. HRMS (EI+) calcd. for $\text{C}_{14}\text{H}_{28}\text{OSi}$ [M]: 240.19095, found: 240.19050.



2x was prepared according to the general procedure **A** (without the TBAF step) in 42% yield. Slightly yellow oil. R_f (hexanes/EtOAc = 50:1): 0.61. ^1H NMR (500 MHz, CDCl_3): δ ppm 5.01 (s, 1H), 4.92 (s, 1H), 3.89 (s, 1H), 2.69 (s, 1H), 2.17 (s, 1H), 1.82-1.79 (m, 1H), 1.55 (s, 2H), 1.27-1.26 (m, 1H), 1.21-1.16 (m, 2H), 1.02-0.95 (m, 12H), 0.95-0.91 (m, 2H), 0.07 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -7.9, 13.2, 13.4, 17.4, 17.5, 23.9, 29.2, 35.4, 43.9, 44.9, 106.2, 159.2. LRMS (ES+) calcd. for $\text{C}_{15}\text{H}_{28}\text{OSi}$ [M]: 252.1, found: 252.1.

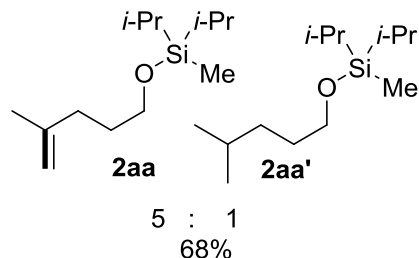


2y was prepared according to the general procedure **B** 70% yield. R_f (hexanes/EtOAc = 9:1): 0.42. ^1H NMR (500 MHz, CDCl_3): δ ppm 4.88 (s, 1H), 4.78 (s, 1H), 4.74 (s, 1H), 4.71 (m, 1H), 2.46 (m, $J = 12.1$ Hz, 1H), 2.20 (d, $J = 12.4$ Hz, 2H), 1.98 (t, $J = 11.4$ Hz, 1H), 1.89-1.84 (m, 1H), 1.74 (m, 3H), 1.62-1.60 (m, 1H), 1.47-1.43 (m, 1H), 1.40 (s, 3H), 1.36 (bs, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 20.8, 26.9, 27.5, 37.5, 40.2, 46.7, 70.8, 107.5, 108.3, 149.5, 152.4. LRMS (EI+) calcd. for $\text{C}_{11}\text{H}_{18}\text{O}$ [M]: 166.26, found: 166.10.

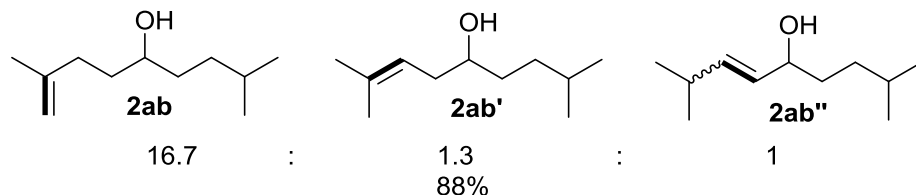


2z was prepared according to the general Method **D** in 73% yield. 85% purity. Colorless liquid. R_f (hexanes/EtOAc 9:1): 0.40. For major isomer **2z**, ^1H NMR (500 MHz, CDCl_3): δ ppm 4.94 (s,

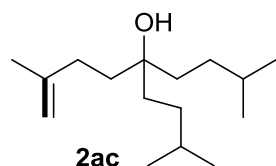
1H), 4.84 (s, 1H) 4.06-4.03 (m, 1H), 1.74 (s, 3H), 1.57-1.53 (m, 2H), 1.27-1.25 (m, 1H), 1.04-0.99 (m, 2H), 0.93-0.89 (m, 6 H). ¹³C NMR (126 MHz, CDCl₃): δ ppm 17.2, 17.4, 22.6, 32.7, 34.6, 76.3, 111.1, 147.6. LRMS (EI+) calcd. for C₉H₁₈O [M]: 142.1, found: 142.1.



2aa was prepared according to the general procedure **A** (without the TBAF step) in calcd. 57% yield. Yellow oil. R_f (hexanes/EtOAc = 20:1): 0.41. ¹H NMR (500 MHz, CDCl₃): δ ppm 4.69 (d, *J* = 11.6 Hz, 2H), 3.64-3.56 (m, 2H), 2.07-1.99 (m, 2H), 1.72 (s, 3H), 1.69-1.64 (m, 2H), 1.03-0.99 (m, 14H), 0.01 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ ppm -8.7, 12.9, 17.4, 22.4, 30.9, 33.9, 63.0, 109.7, 127.2. LRMS (EI+) calcd. for C₁₃H₂₈OSi [M]: 228.45, found: 229.10.

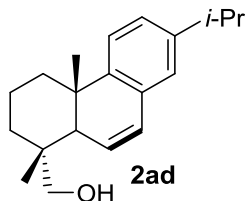


2ab was prepared according to the general procedure **B** in calcd. 77% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.54. ¹H NMR (500 MHz, CDCl₃): δ ppm 4.72 (s, 2H), 3.60-3.54 (m, 1H), 2.17-2.08 (m, 2H), 1.74 (s, 3H), 1.65-1.16 (m, 8H), 0.99-0.88 (m, 6H). ¹³C NMR (126 MHz, CDCl₃): δ ppm 22.4, 22.5, 22.7, 28.1, 34.1, 35.2, 35.3, 72.1, 110.0, 145.9. HRMS (EI+) calcd. for C₁₁H₂₂O [M]: 170.16707, found: 170.16688.



2ac was prepared according to the general procedure **B** in 89 % yield. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.63. ¹H NMR (500 MHz, CDCl₃): δ ppm 4.70 (s, 2H), 2.03-2.00 (m,

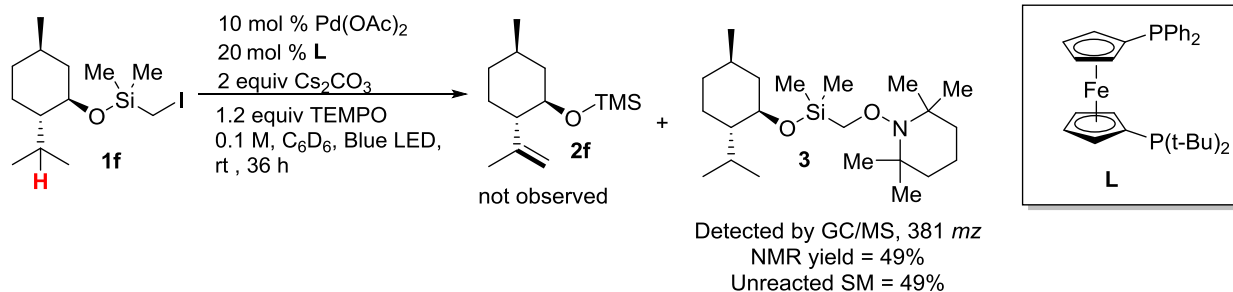
2H), 1.54 (s, 3H), 1.49-1.38 (m, 9H), 1.19-1.14 (m, 4H), 0.90-0.89 (m, $J = 6.6$ Hz, 12H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 22.7, 28.6, 31.7, 32.4, 36.8, 37.2, 74.3, 109.7, 146.4. HRMS (ESI+) calcd. for $\text{C}_{16}\text{H}_{32}\text{O}$ $[\text{M}] + \text{Na}$: 263.2351, found: 263.2359.



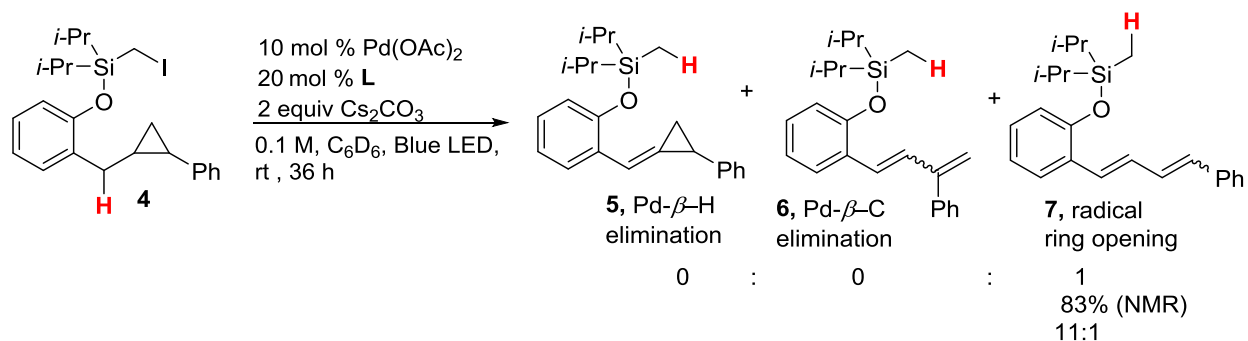
2ad was prepared according to the general procedure **A** (two-steps) in 40% yield. Clear and colorless oil. R_f (hexanes/EtOAc = 4:1): 0.28. ^1H NMR (500 MHz, CDCl_3): δ ppm 7.10 (d, $J = 7.7$ Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 1H), 6.90 (s, 1H), 6.55 (dd, $J = 9.5, 2.9$ Hz, 1H), 5.97 (d, $J = 9.2, 2.2$ Hz, 1H), 3.49 (d, $J = 11.0$ Hz, 1H), 3.27 (d, $J = 11.0$ Hz, 1H), 2.89-2.82 (m, 1H), 2.40 (bs, 1H), 2.18 (d, 12.8 Hz, 1H), 1.83-1.74 (m, 2H), 1.64-1.41 (m, 4H), 1.28-1.23 (m, 6H), 1.08 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm 18.2, 18.3, 20.8, 24.0, 33.5, 29.7, 33.7, 34.4, 35.7, 37.2, 45.1, 71.6, 121.8, 124.6, 125.7, 128.5, 128.7, 132.6, 145.6, 146.2. HRMS (ES+) calcd. for $\text{C}_{20}\text{H}_{28}\text{O}$ $[\text{M}] + 1$: 285.2218, found: 285.2224.

5. Mechanistic Studies

1. Trapping with TEMPO:



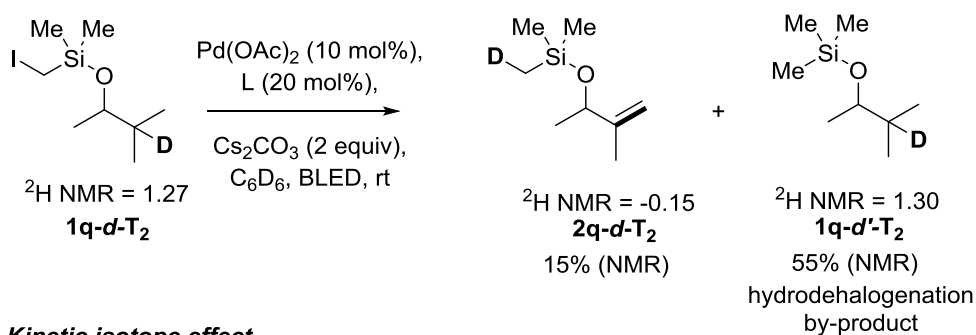
2. Radical clock experiment:



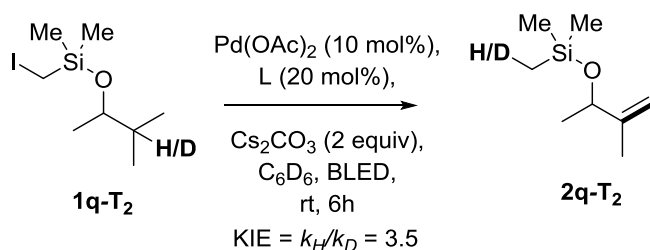
7 was prepared according to the general procedure **A** in 83% NMR yield. ¹H NMR (500 MHz, C₆D₆): δ ppm 7.62 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (d, *J* = 10.3 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.14-7.06 (m, 5H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8, 1H), 6.66 (d, *J* = 15.0, 1H), 1.22-1.11 (m, 14H), 0.25 (s, 3H). ¹³C-dept displayed no CH₂ signals in the olefin region. LRMS (EI+) calcd. for C₂₃H₃₀OSi [M]: 350.58, found: 350.20.

3. Isotope labeling study and kinetic isotope effect :

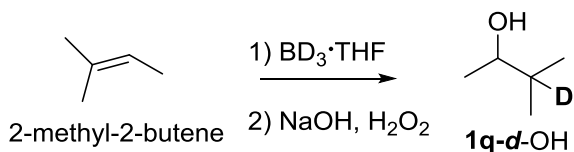
Isotope labeling study



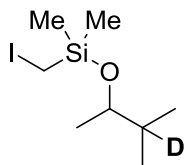
Kinetic isotope effect



To gain more evidence for the HAT process, an isotope labeling study was conducted. It was found that deuterium atom at the β -position of **1q-d-T₂** was transferred to the silyl methyl group, which strongly supports the 1,5-HAT step in this transformation. Besides, formation of the desaturation product **2q-d-T₂** was observed in low yield, along with the major hydrodehalogenation by-product. This result indicates that HAT step of **1q-d-T₂** is much slower than that for its hydrogen derivative **1q-T₂**, and HAT could be the rate-determining-step. To verify this hypothesis, kinetic isotope effect studies were performed. Indeed, the parallel KIE studies resulted in a k_H/k_D of 3.5, which indicates that the HAT step maybe the rate limiting event in the transformation.



1q-d-OH was prepared according to reported procedure³ and was used without further purification.



1q-d-T₂

1q-d-T₂ was prepared according to the Method **C** in 41% yield (2 steps yield from 2-methyl-2-butene). Colorless liquid. R_f (hexanes): 0.49. ^2H NMR(77 MHz, CCl_4): δ ppm 1.27. ^1H NMR (500 MHz, CDCl_3): δ ppm 3.62-3.58 (m, 1H), 2.03 (d, $J = 1.8$ Hz, 2H), 1.10 (d, $J = 6.2$ Hz, 3H), 0.85 (d, $J = 5.9$ Hz, 2H), 0.28 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -2.1, 18.1, 20.5, 20.6, 74.0. LRMS (EI+) calcd. for $\text{C}_8\text{H}_{18}\text{DIOSi}$ [M]: 287.0, found: 287.0.

4. Photophysical studies:

A series of photophysical studies was conducted in order to understand the role of visible light. For these studies, $\text{Pd}(\text{PPh}_3)_4$ was used to represent Pd(0) species instead of $\text{Pd}(\text{II})(\text{OAc})_2$ and ligand since $\text{Pd}(\text{PPh}_3)_4$ was found to be a competent catalyst for the reaction (see Optimization Table S1, entry 3 in Section 3). First, the absorption spectrum of $\text{Pd}(\text{PPh}_3)_4$ in THF previously reported by J. Caspar⁴ was reproduced to confirm that Pd catalyst absorbs visible light between 400 and 500 nm. In contrast, **1f** did not show any absorption in visible light region, which shows that Pd(0) is the only light absorbing species (Fig. S1). Next, emission spectrum was recorded by irradiated Pd(0) catalyst at 450 nm (where Kessil blue LED has the maximum absorption, see insert Fig. S1), to show the emission band at 620 nm. Subsequently, different amounts of alkyl iodide **1f** were added to Pd(0) catalyst. The emission intensity was found to decrease gradually by increasing concentration of alkyl iodide **1f** (Fig. S2). The obtained linear correlation between I_0/I and concentration of **1f** for Stern–Volmer studies (Fig. S3) indicated that **1f** quenches excited Pd(0) species, presumably via an SET event.

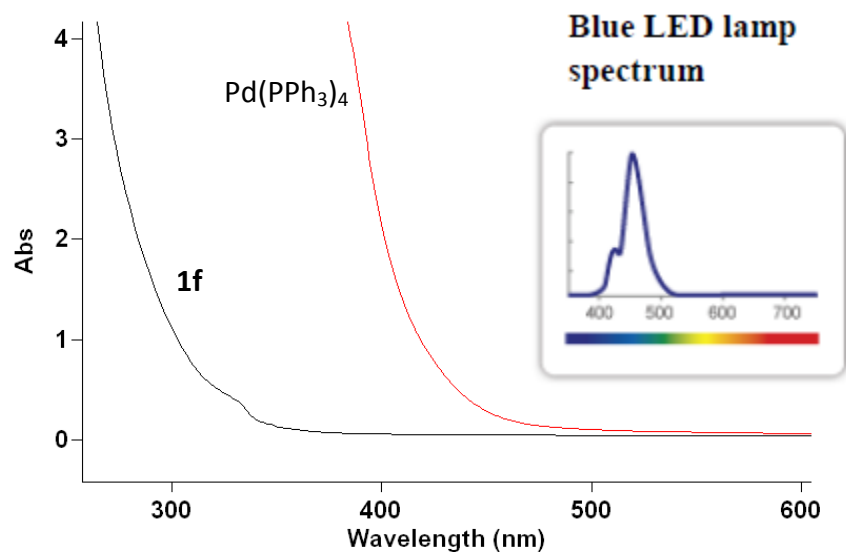


Fig. S1. Absorption spectra of Pd(PPh₃)₄ (8.65×10^{-4} M in THF, red line) and alkyl iodide **1f** (blue line).

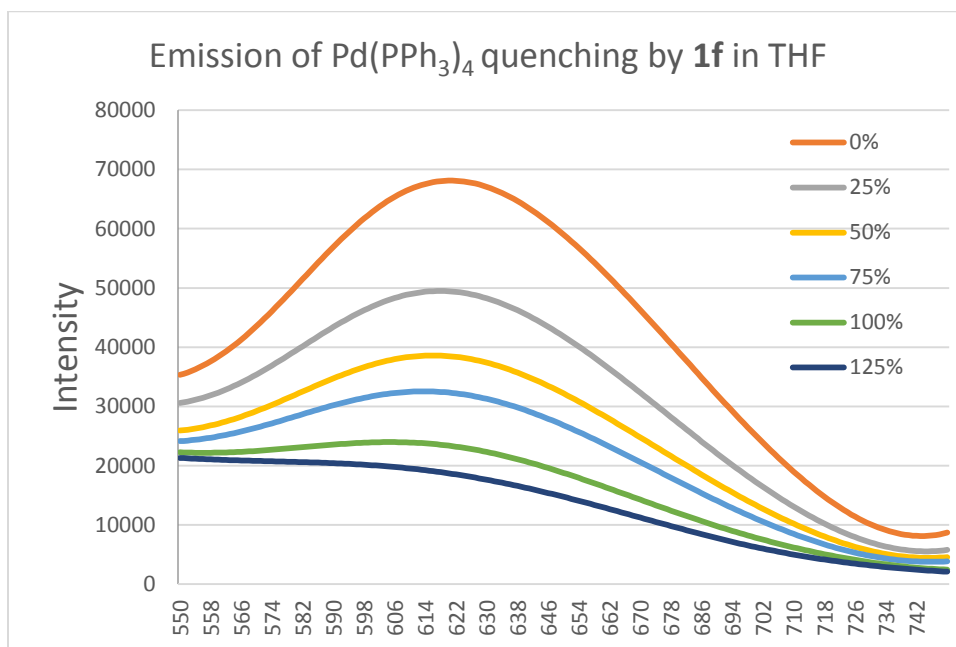


Fig. S2. Emission quenching of Pd(PPh₃)₄ (8.65×10^{-4} M in THF) by alkyl iodide **1f** in the concentration range of 0-125 mol% with respect to Pd(PPh₃)₄ after irradiation at 450 nm at 25 °C.

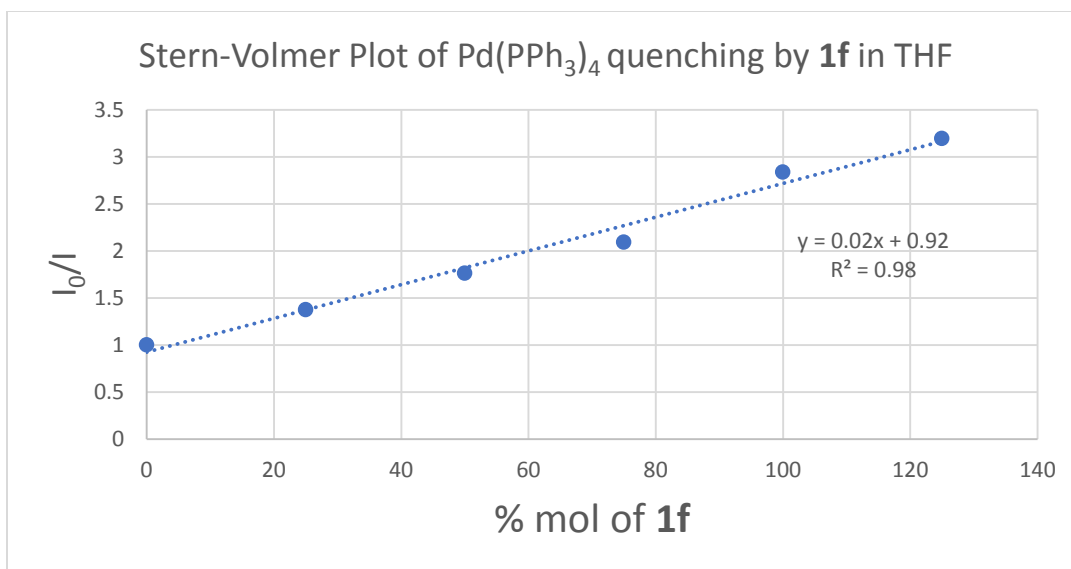
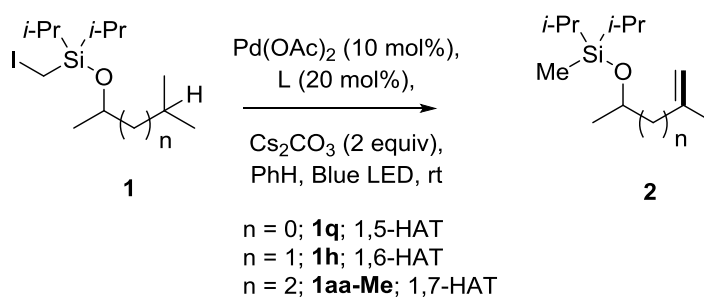


Fig. S3. Stern-Volmer plot for the emission quenching of Pd(PPh₃)₄ by various concentrations of alkyl iodide **1f** (from 0 to 125 mol% with respect to Pd(PPh₃)₄ in THF).

5. Kinetic study for 1,*n*-HAT (n = 5, 6, 7):

In order to uncover the kinetic preference for HAT, a kinetic study of desaturation of **1q** via 1,5-HAT, **1h** via 1,6-HAT, and **1aa-Me** via 1,7-HAT, was conducted. By monitoring the rate of conversion for each substrate over time in a series of experiments (average of 2 runs is presented). The following kinetic preference of HAT was found (Table S2): 1,6-HAT > 1,5-HAT > 1,7-HAT. This trend relates well to the regiochemical outcome of desaturation of substrates possessing ambiguous C-H abstraction sites with similar BDEs, such as **1i**, **1j**, and **1z** (see Table 1, 2).



Reaction time (min)	%GC 2q (1,5-HAT)	%GC 2h (1,6-HAT)	%GC 2aa-Me (1,7-HAT)
15	1.2	3.2	0.5

30	3.7	6.5	1.8
45	6.5	10.3	3.0
60	9.5	11.9	4.7
90	16.7	21.9	8.8
120	20.3	25.4	14.3
180	25.4	32.5	20.3
480	52.5	67.4	42.2
1080	66.0	86.7	46.6
1440	70.1	86.2	45.3

Table S2. Kinetic study for 1,*n*-HAT (n = 5, 6, 7).

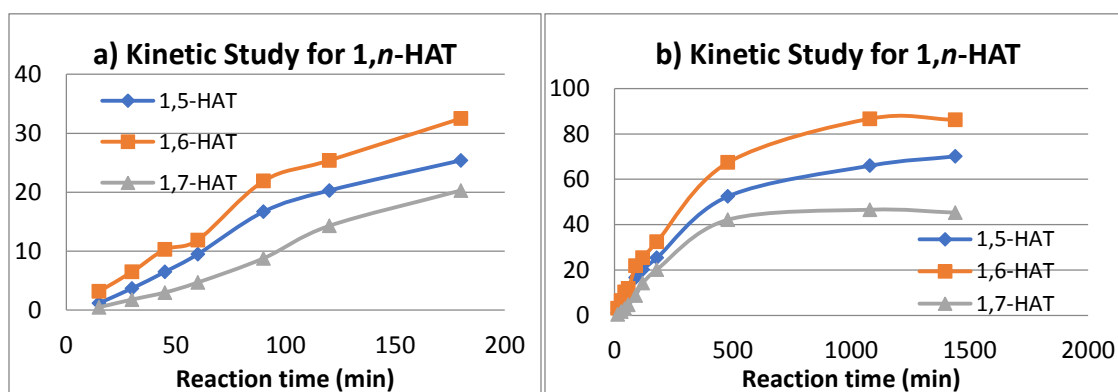
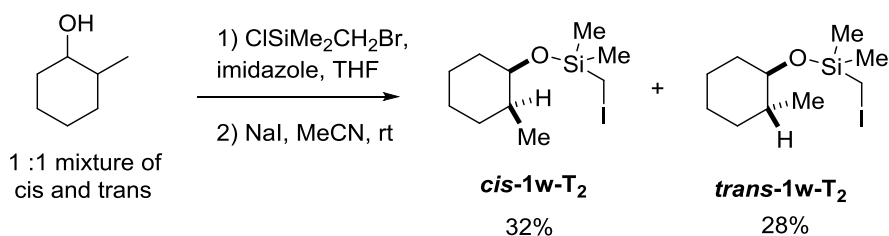
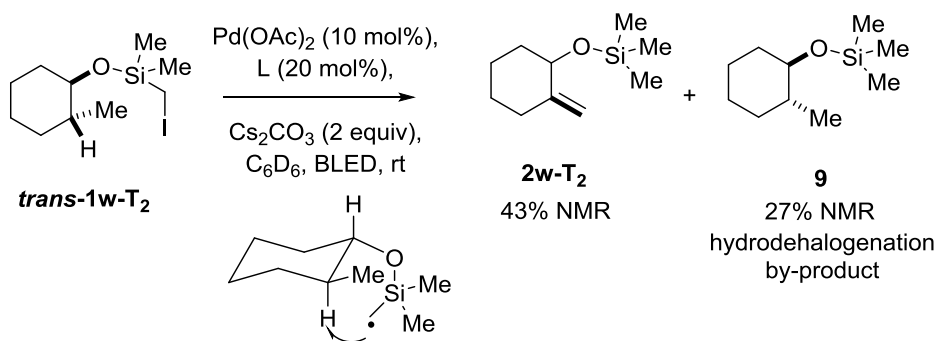
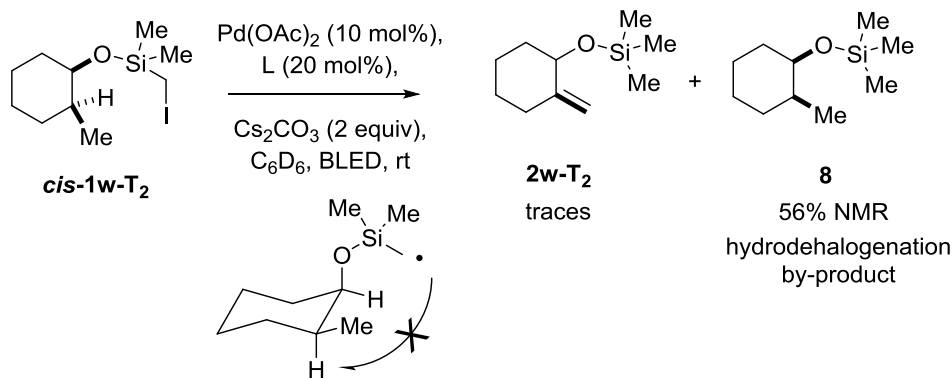


Fig. S4. % GC yield vs reaction time for 1,*n*-HAT: a) 0-180 min; b) 0-1440 min.

6. Study on stereoselectivity of HAT step in 1w:

In order to investigate the stereoselectivity of the HAT step, desaturation of *cis*- and *trans*-**1w-T₂** was tested. It was found that the *cis* isomer resulted in only trace amounts of allylic ether **2w-T₂**, presumably due to incapability to form quasi-linear TS required for an HAT event (see below). Conversely, the *trans*-isomer resulted in 43% NMR yield of the **2w-T₂**.



cis-1w-T₂ and **trans-1w-T₂** was prepared according to the general Method **D** in 32 and 28% yields respectively. The two stereoisomers were separated. Colorless oil. R_f (hexanes): cis 0.56, trans 0.54.

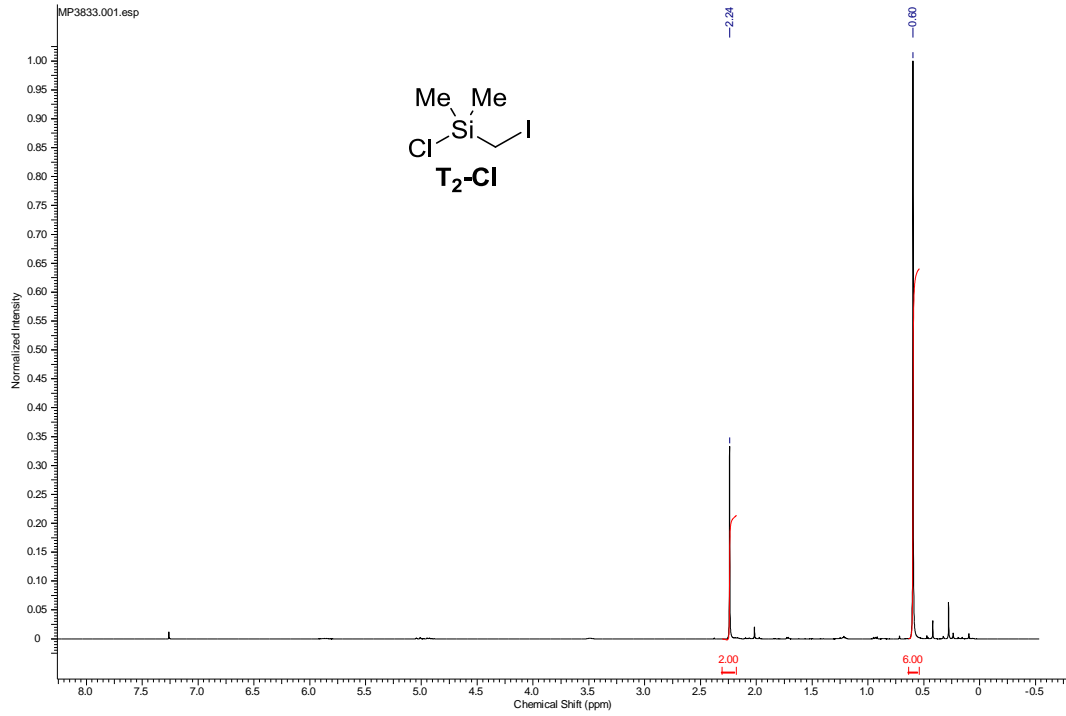
For **cis-1w-T₂**: ¹H NMR (500 MHz, CDCl₃): δ ppm 3.83-3.78 (m, 1H), 2.03 (s, 2H), 1.68-1.51 (m, 4H), 1.45-1.38 (m, 2H), 1.34-1.29 (m, 2H), 1.26-1.18 (m, 1H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.27 (s, 6H). ¹³C NMR (126 MHz, CDCl₃): δ ppm -2.0, -0.4, 17.5, 20.8, 24.6, 28.8, 33.3, 36.5, 72.5. HRMS (EI⁺) calcd. for C₁₀H₂₁IOSi [M]: 312.0406, found: 312.04015.

For **trans-1w-T₂**: ¹H NMR (500 MHz, CDCl₃): δ ppm 3.18-3.13 (m, 1H), 2.03 (d, *J* = 2.9 Hz, 2H), 1.99-1.91 (m, 1H), 1.75-1.66 (m, 2H), 1.61-1.55 (m, 1H), 1.37-1.12 (m, 5H), 0.93 (d, *J* =

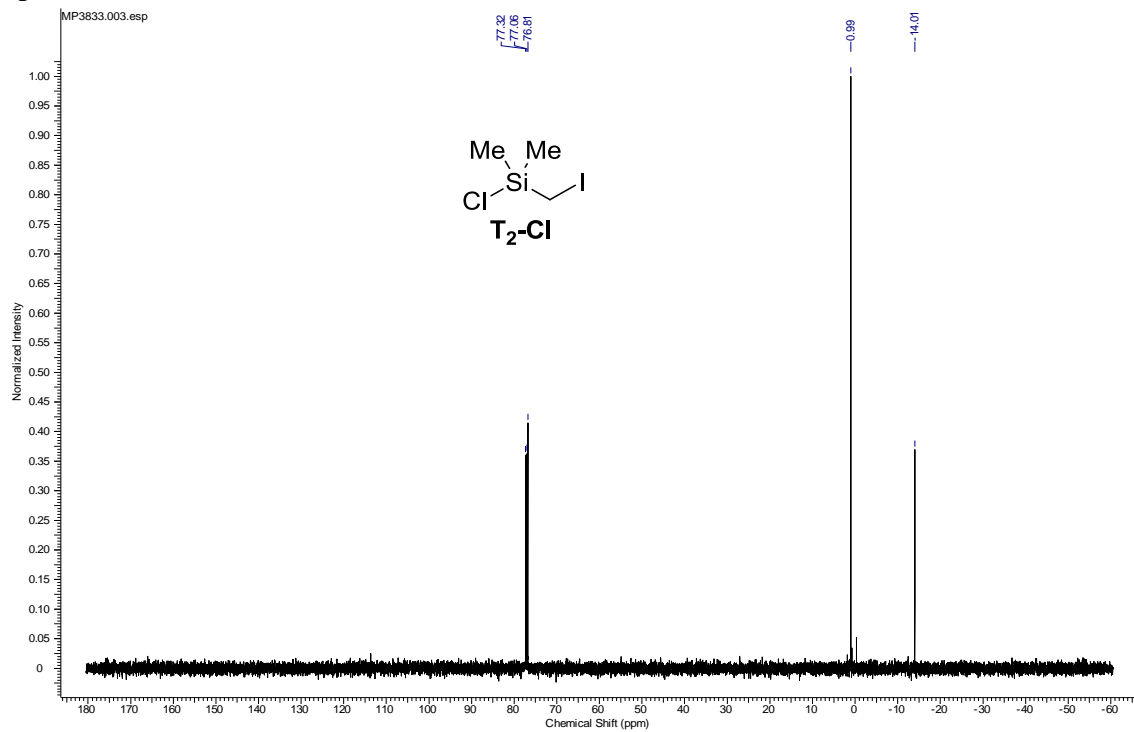
6.6 Hz, 3H), 0.30 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ ppm -1.9, 19.6, 25.2, 25.6, 33.7, 36.1, 40.1, 78.0. HRMS (EI+) calcd. for $\text{C}_{10}\text{H}_{21}\text{IOSi}$ [M]: 312.0406, found: 312.03987

6. NMR Spectral Data

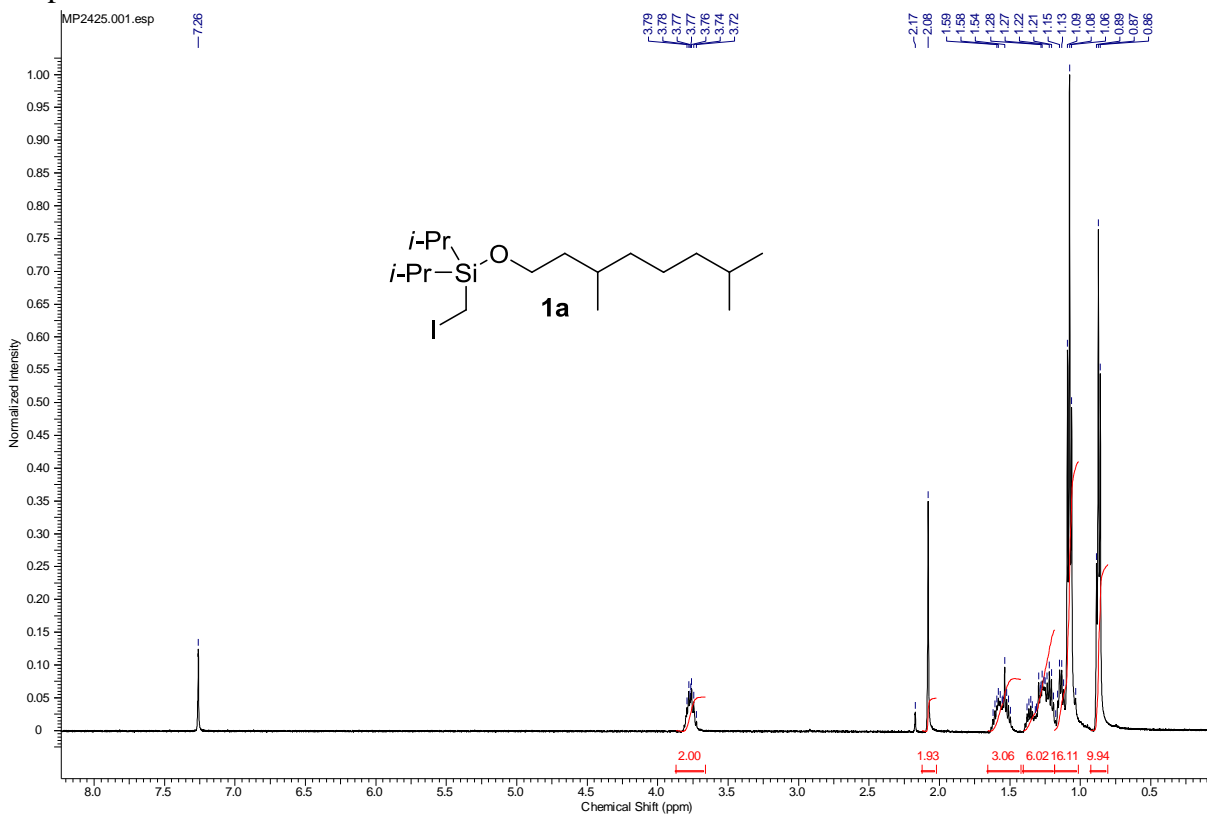
^1H Spectrum of $\text{T}_2\text{-Cl}$



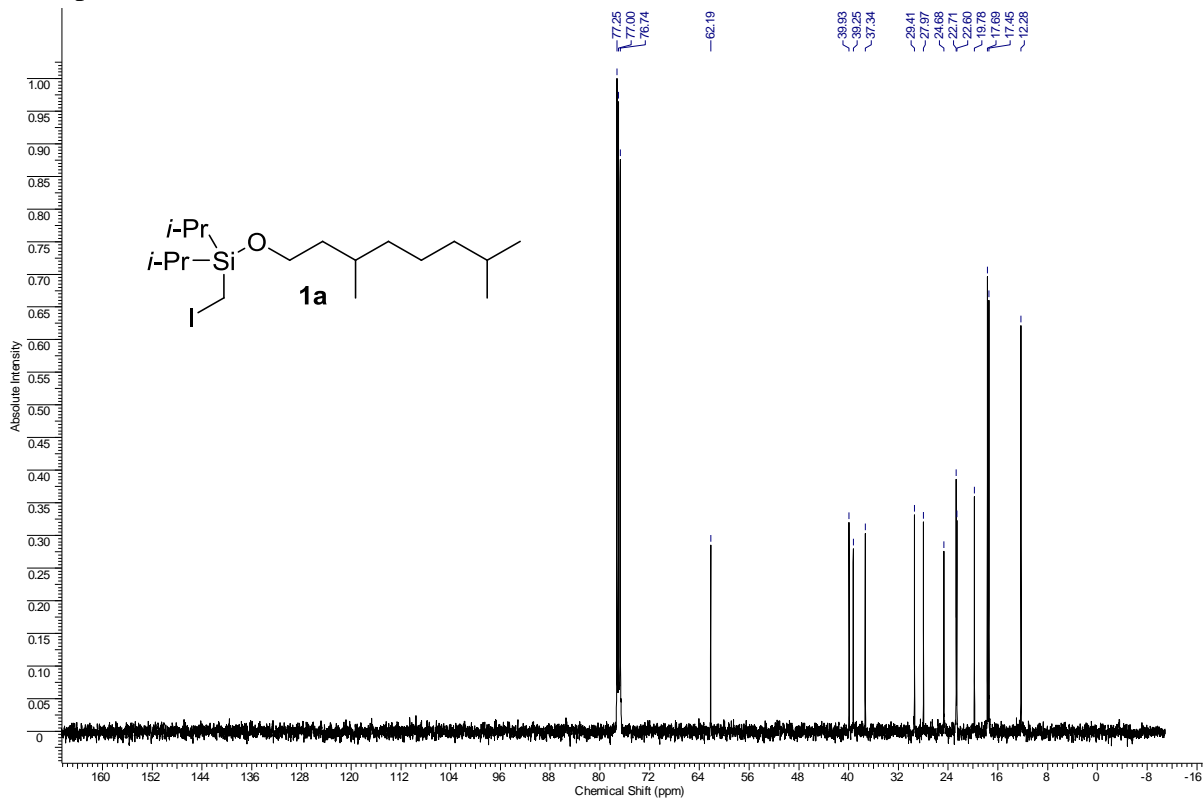
^{13}C Spectrum of $\text{T}_2\text{-Cl}$



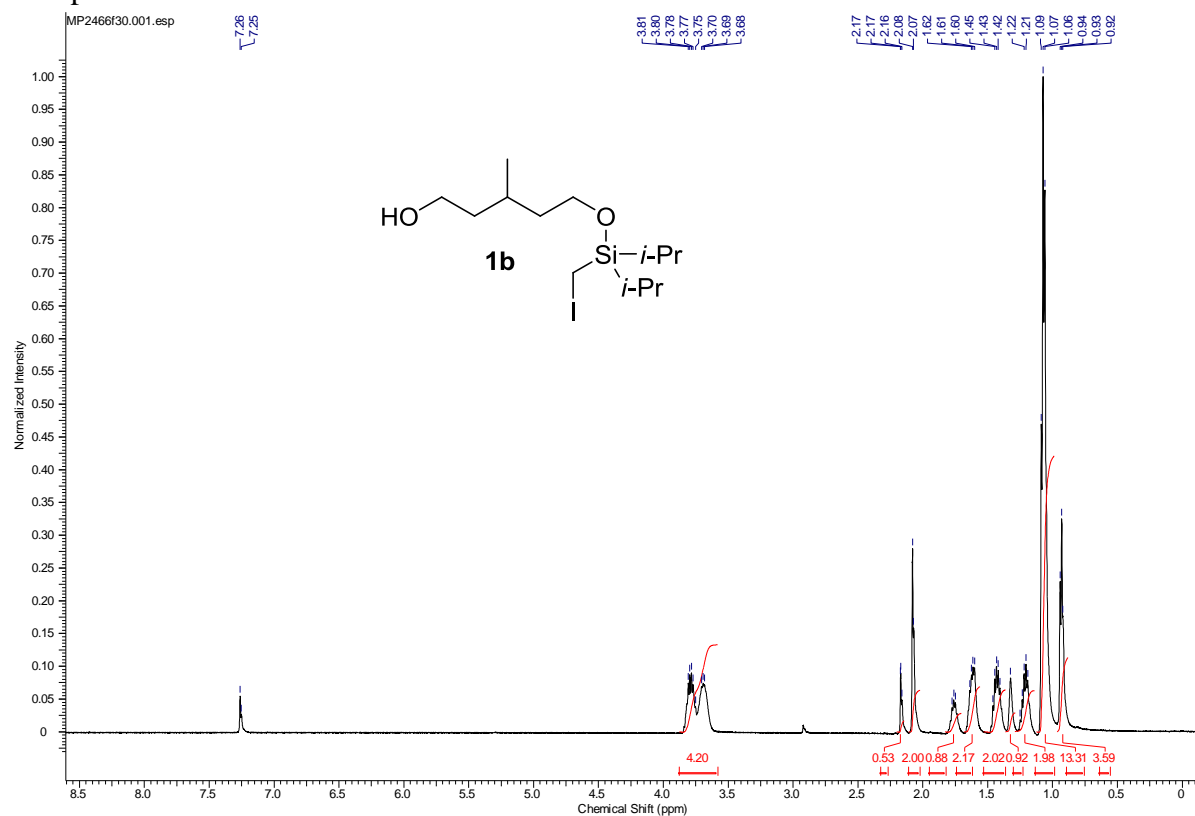
¹H Spectrum of 1a



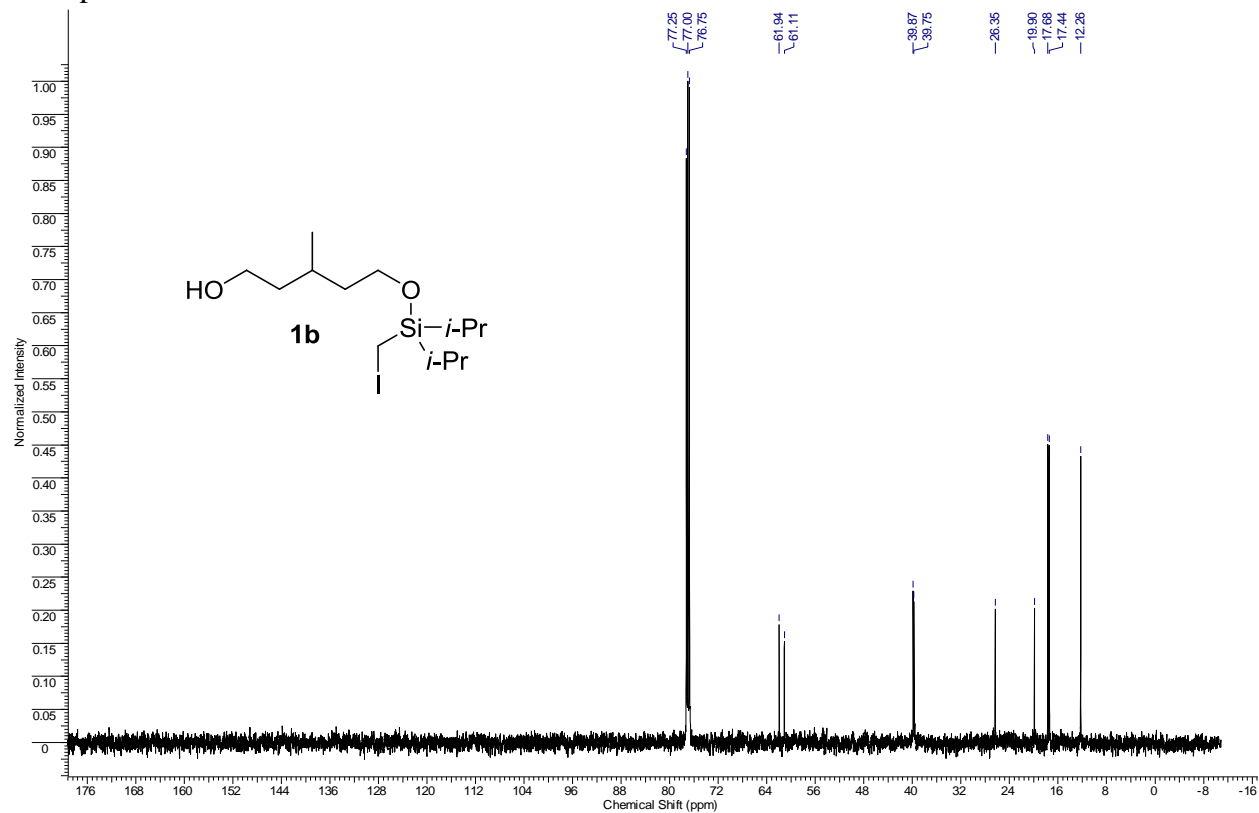
¹³C Spectrum of 1a



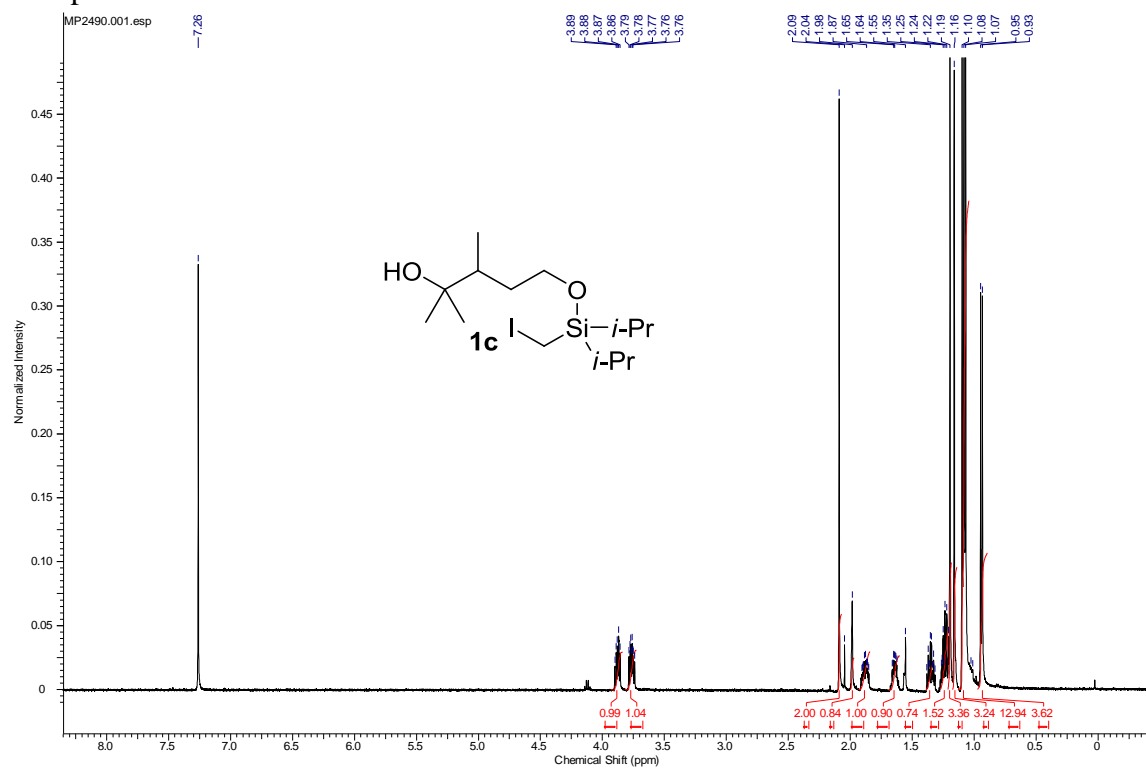
¹H Spectrum of **1b**



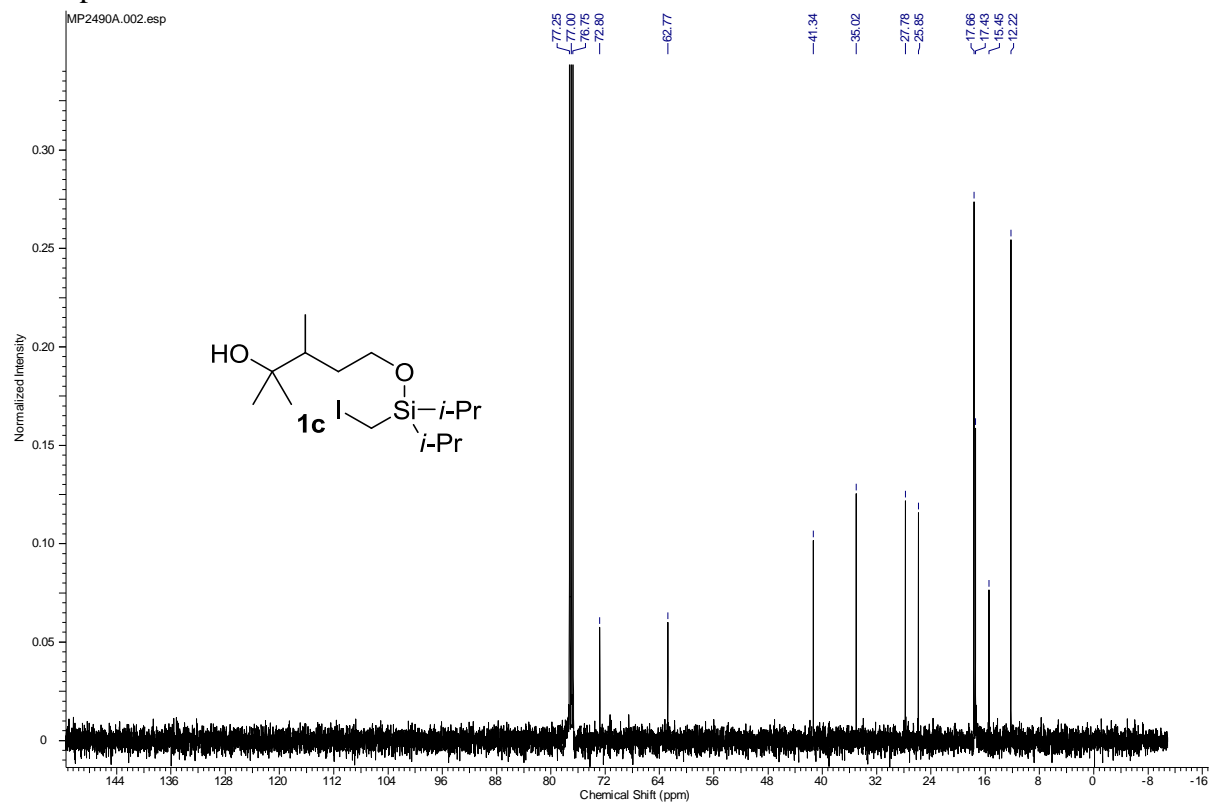
¹³C Spectrum of **1b**



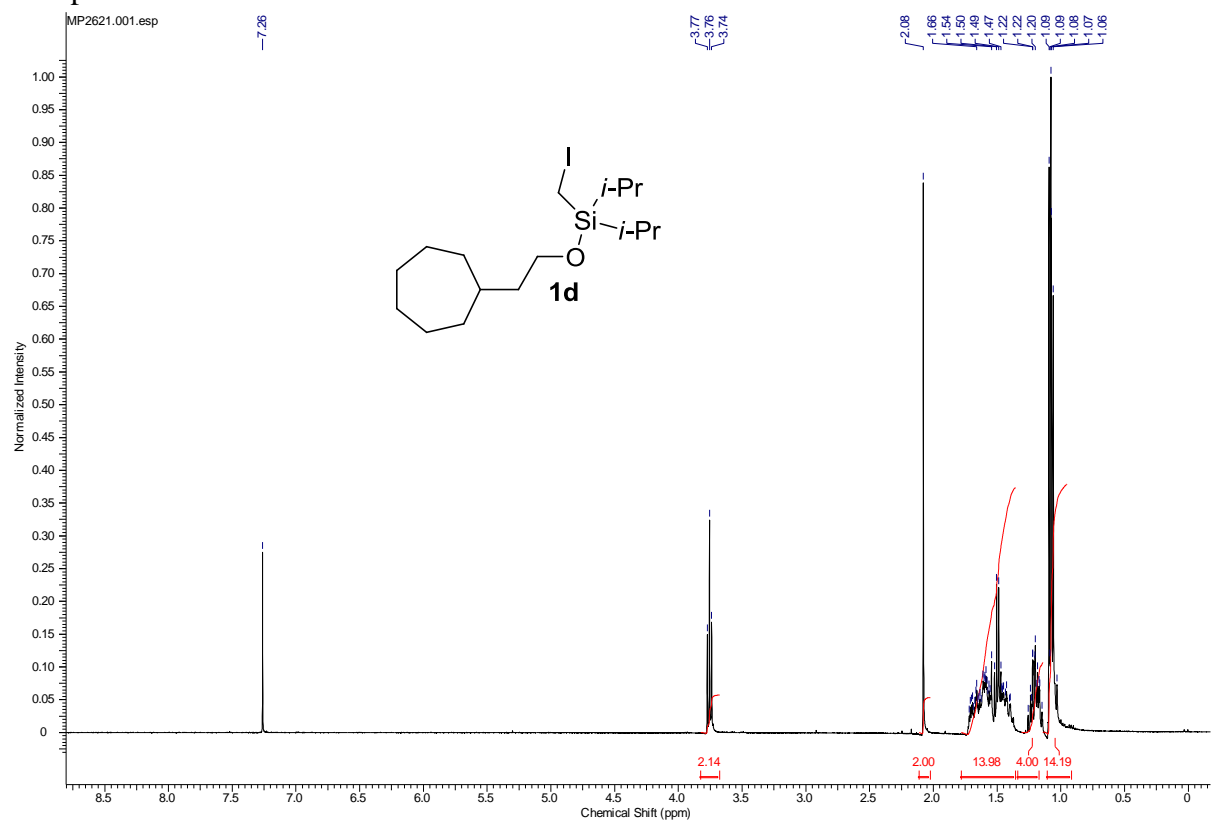
¹H Spectrum of 1c



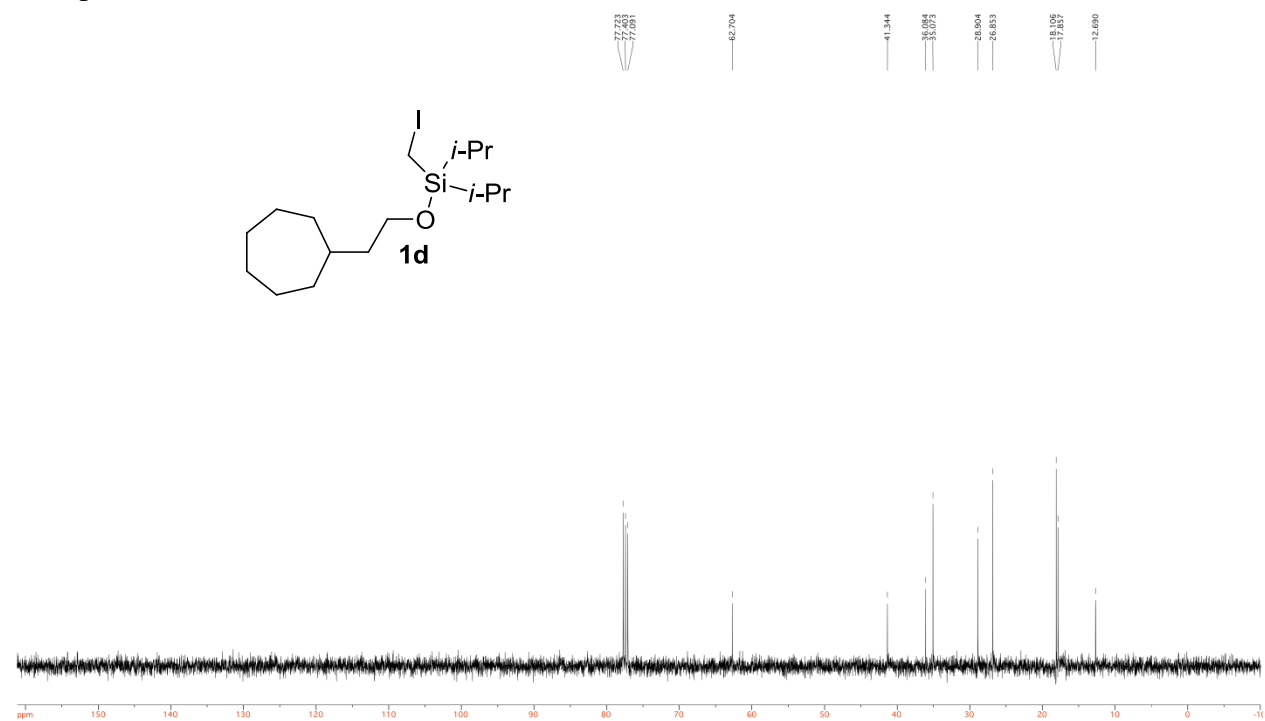
¹³C Spectrum of 1c



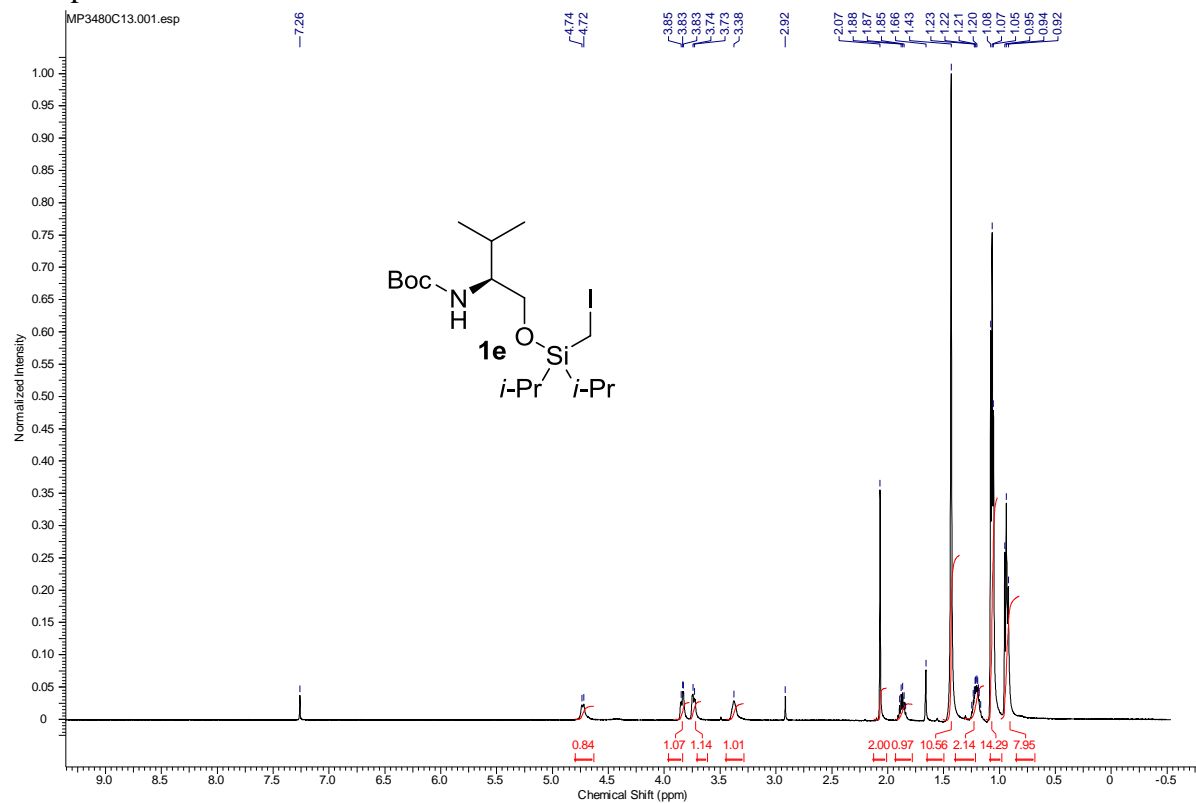
¹H Spectrum of **1d**



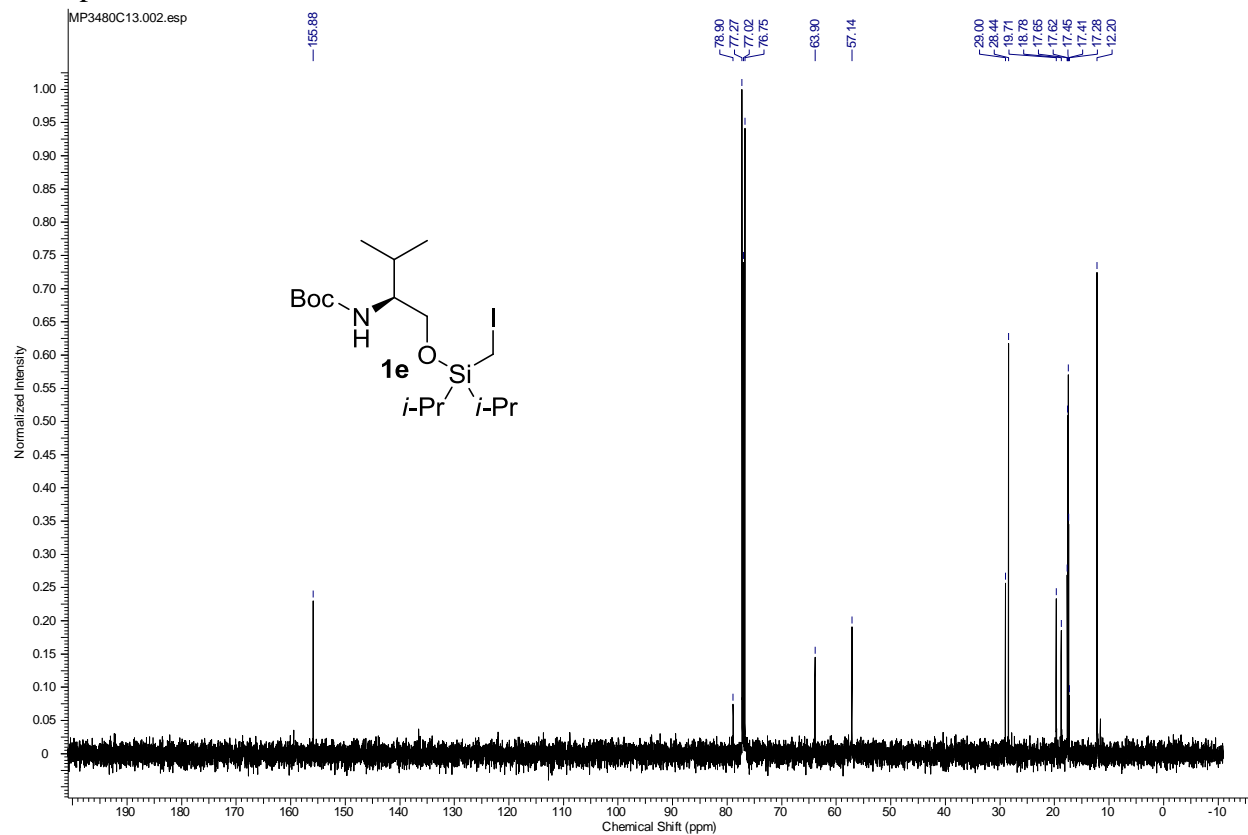
¹³C Spectrum of **1d**



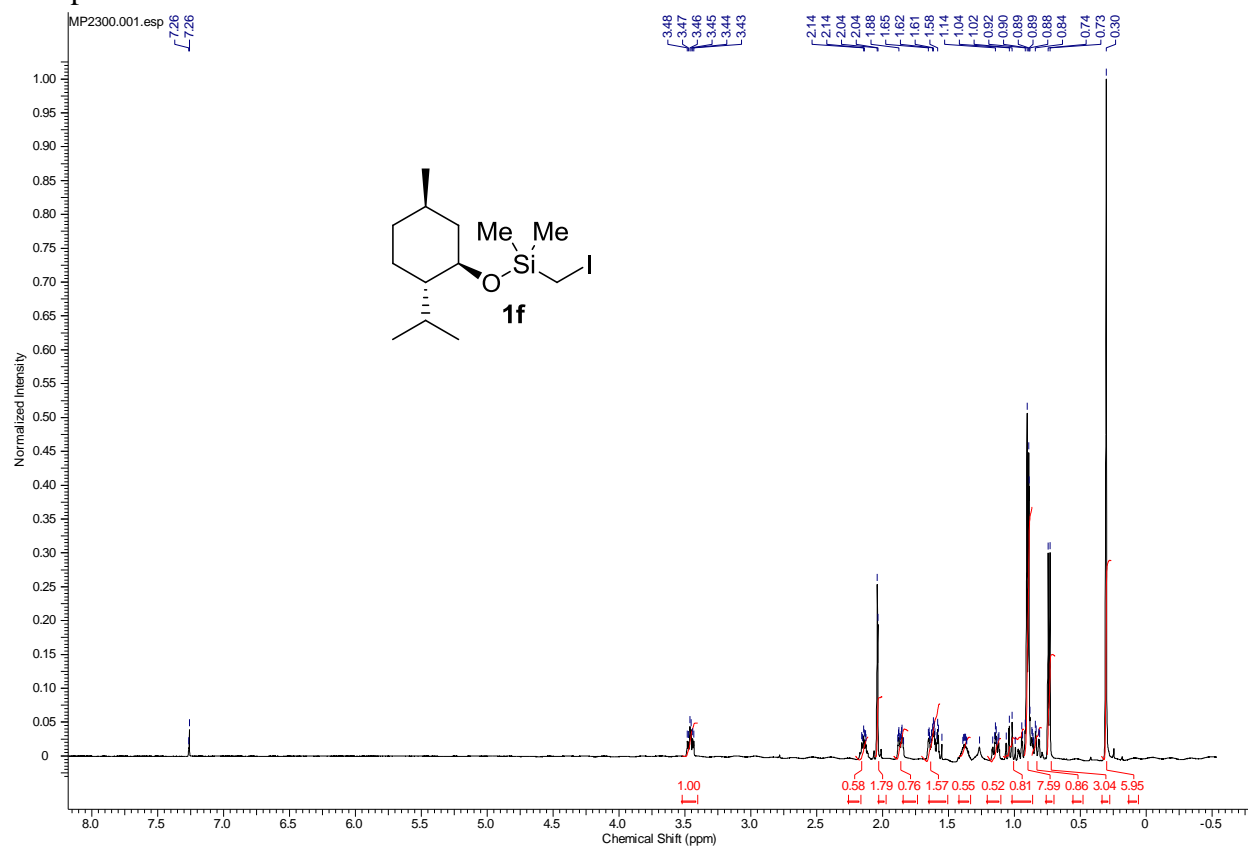
¹H Spectrum of **1e**



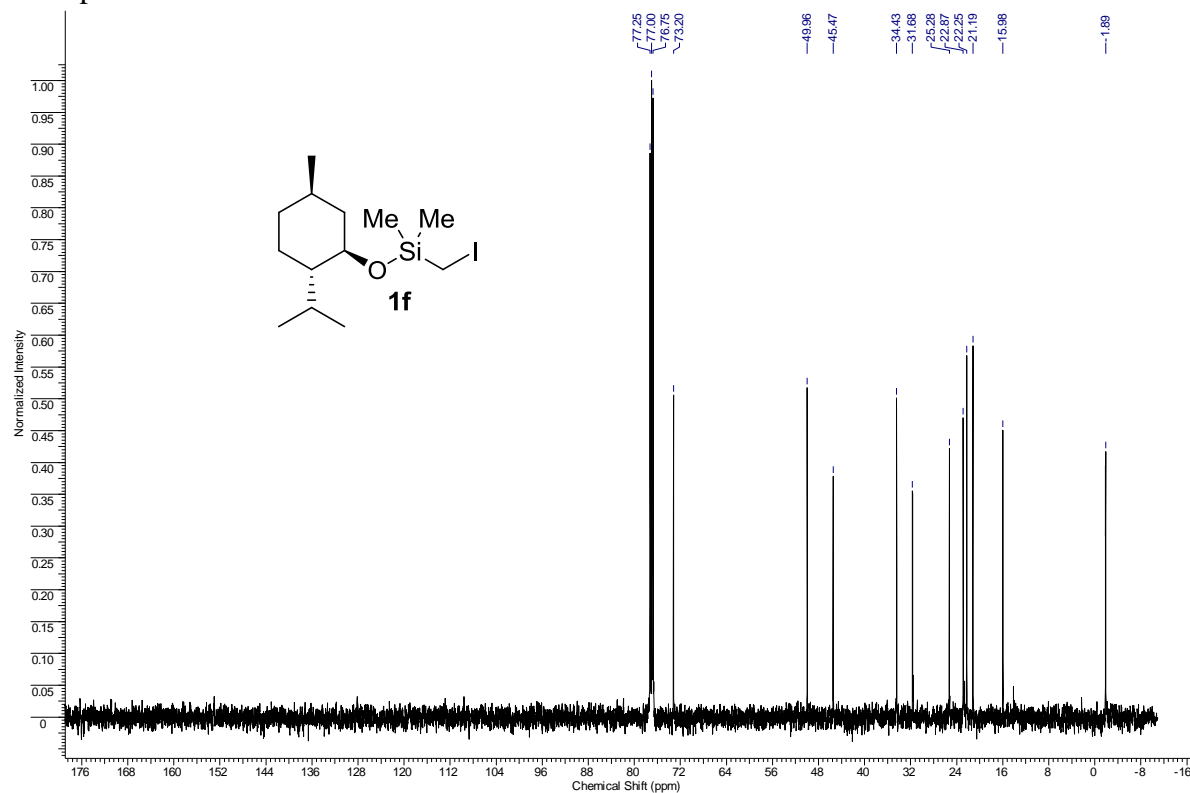
¹³C Spectrum of **1e**



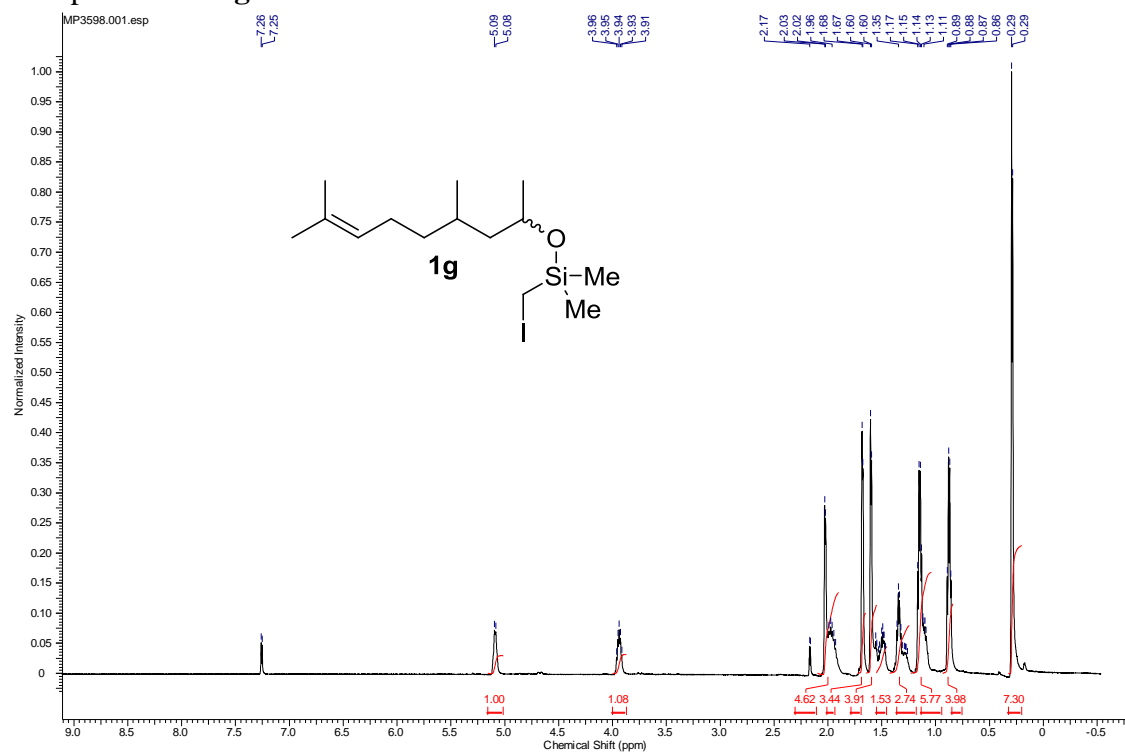
¹H Spectrum of **1f**



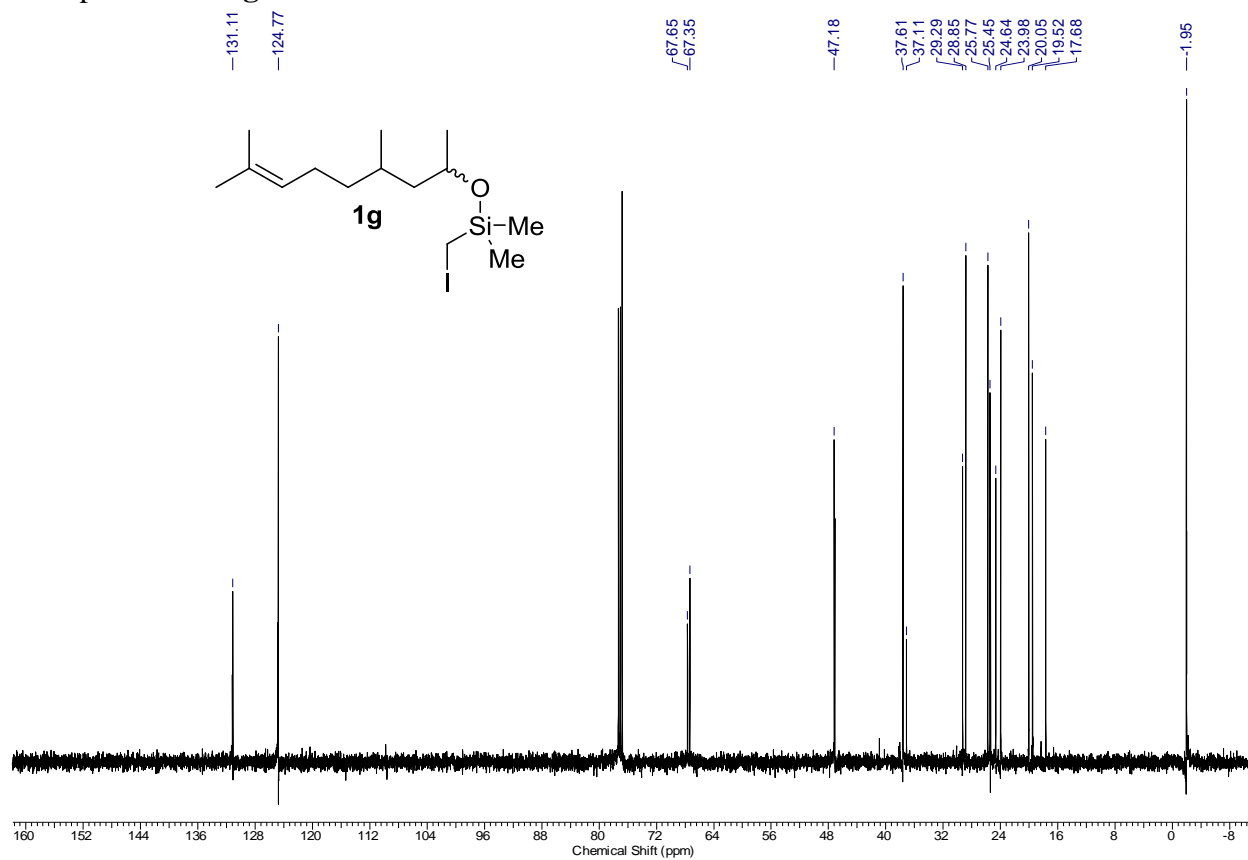
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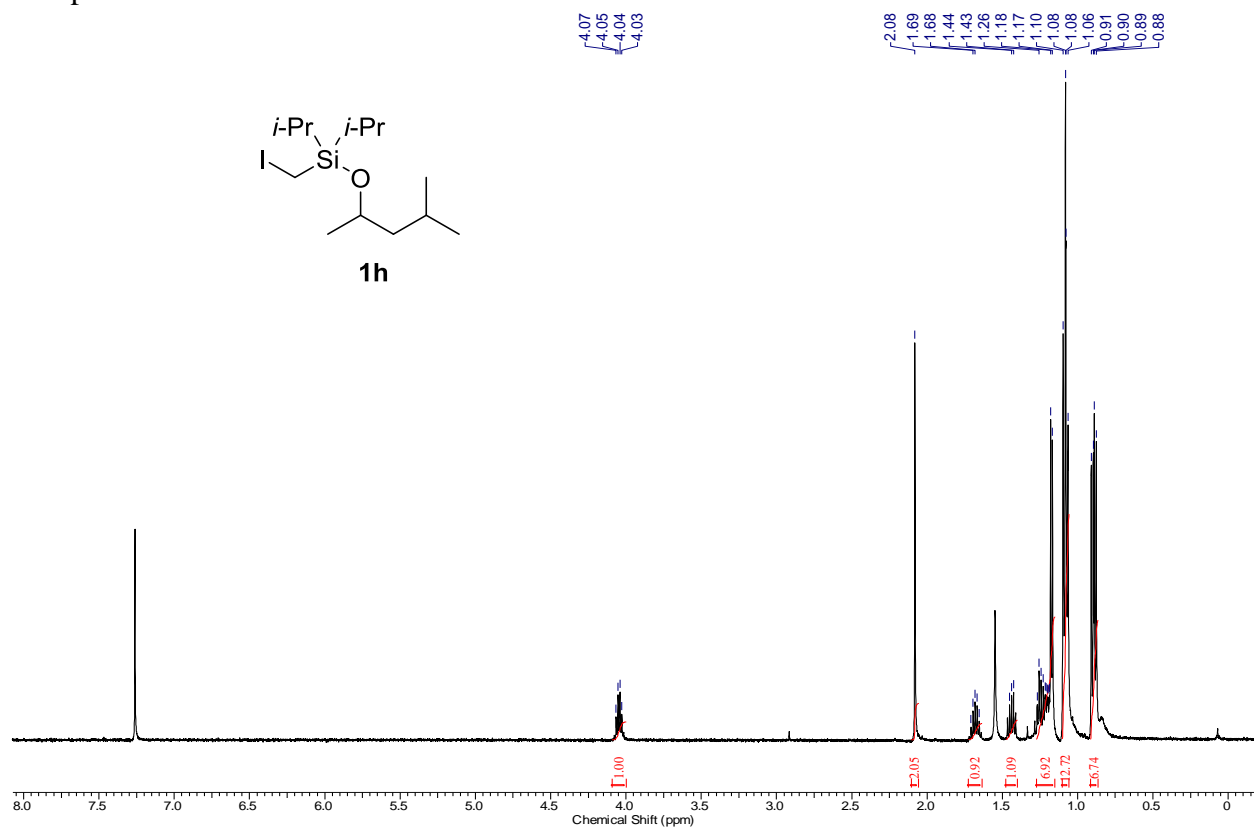
¹H Spectrum of **1g**



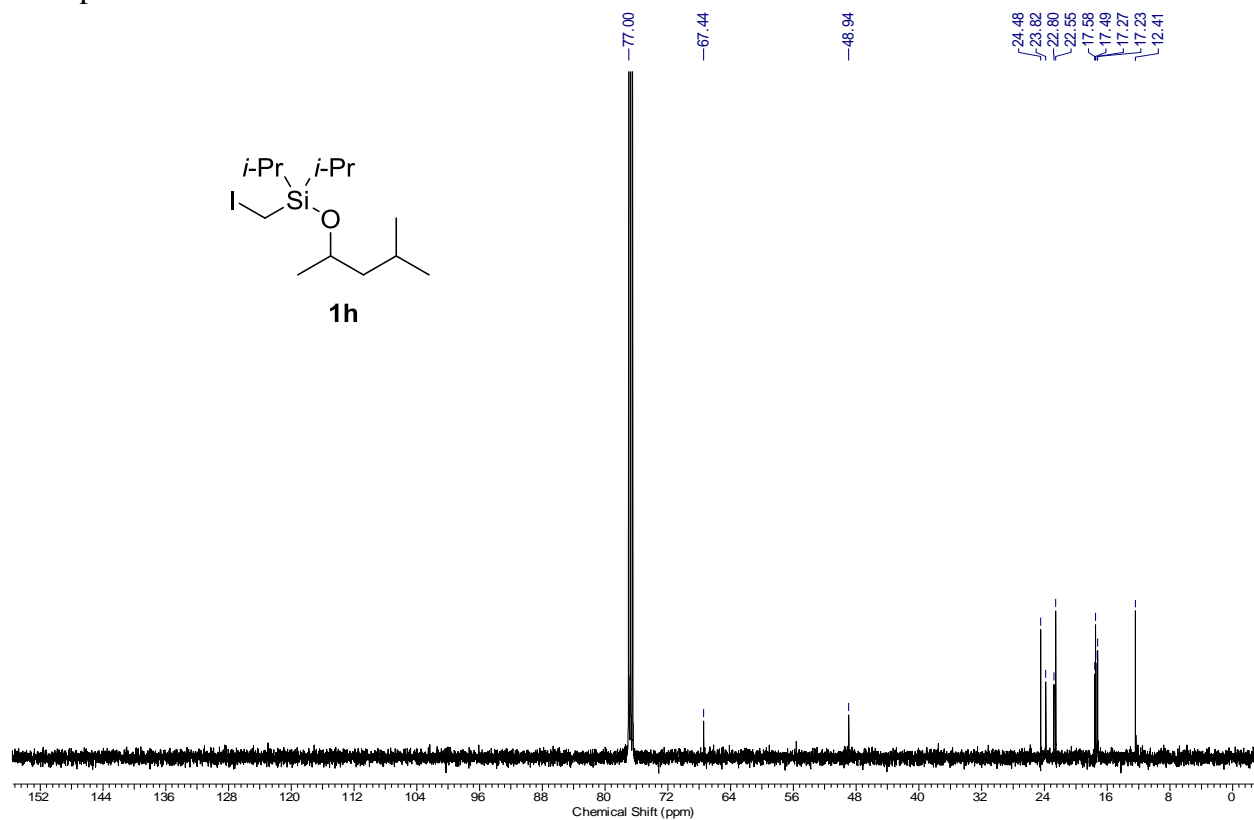
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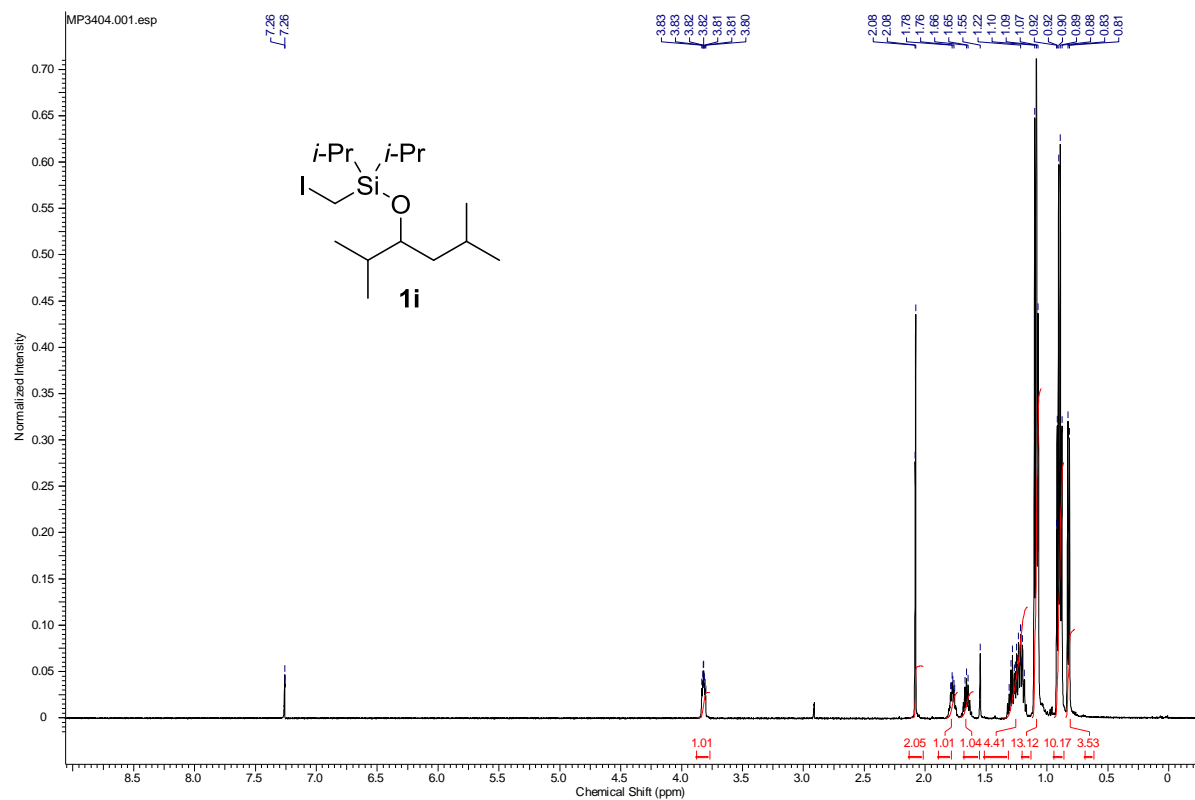
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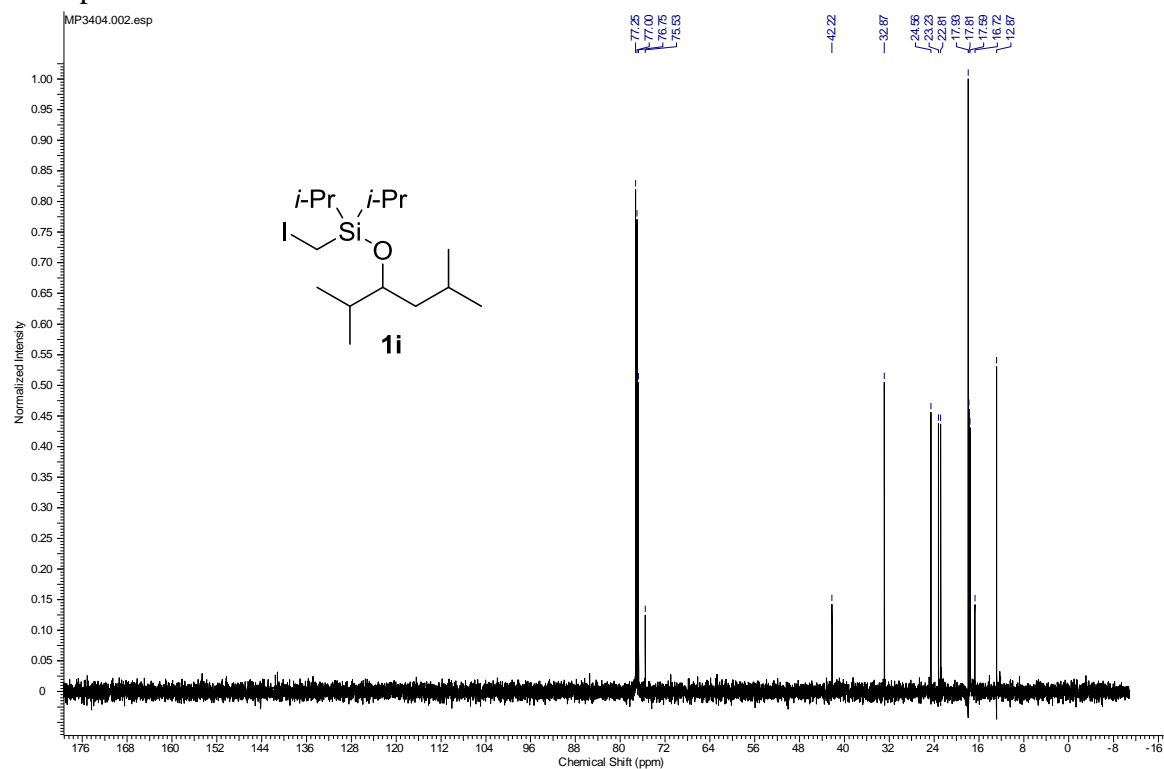
¹³C Spectrum of **1h**



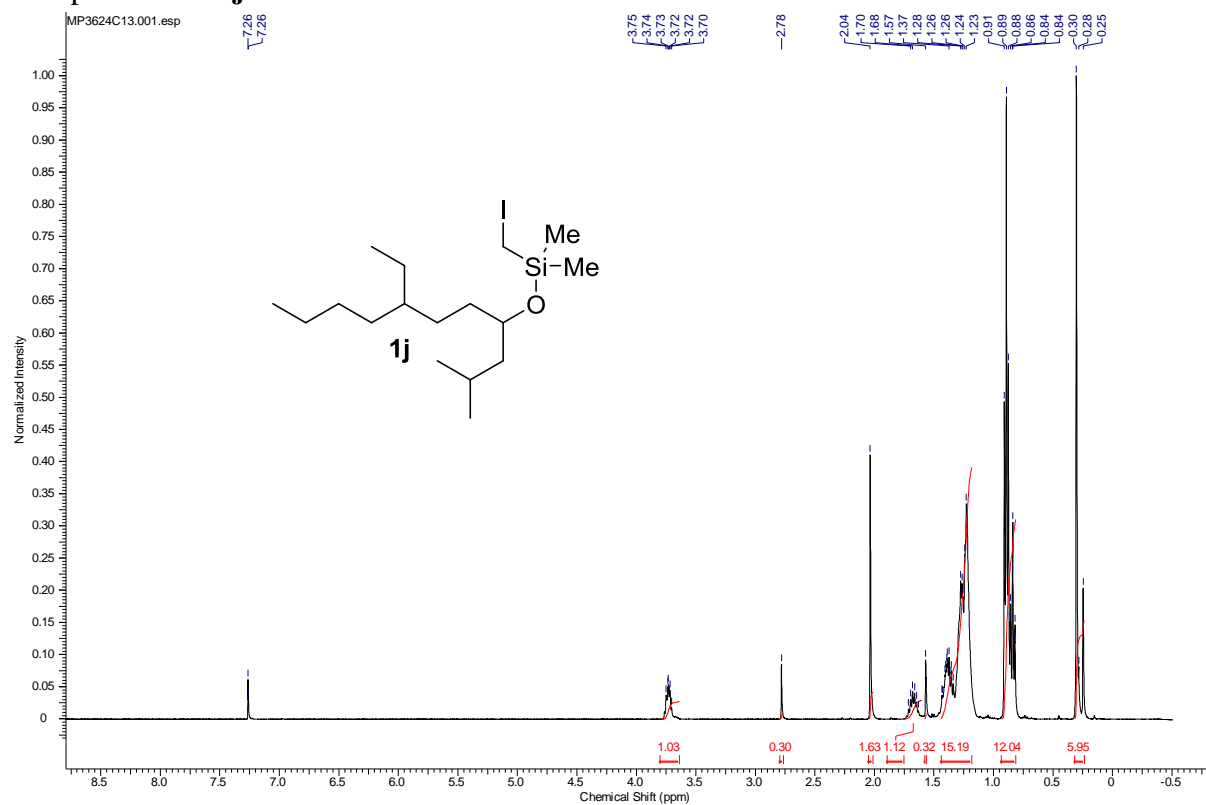
¹H Spectrum of **1i**



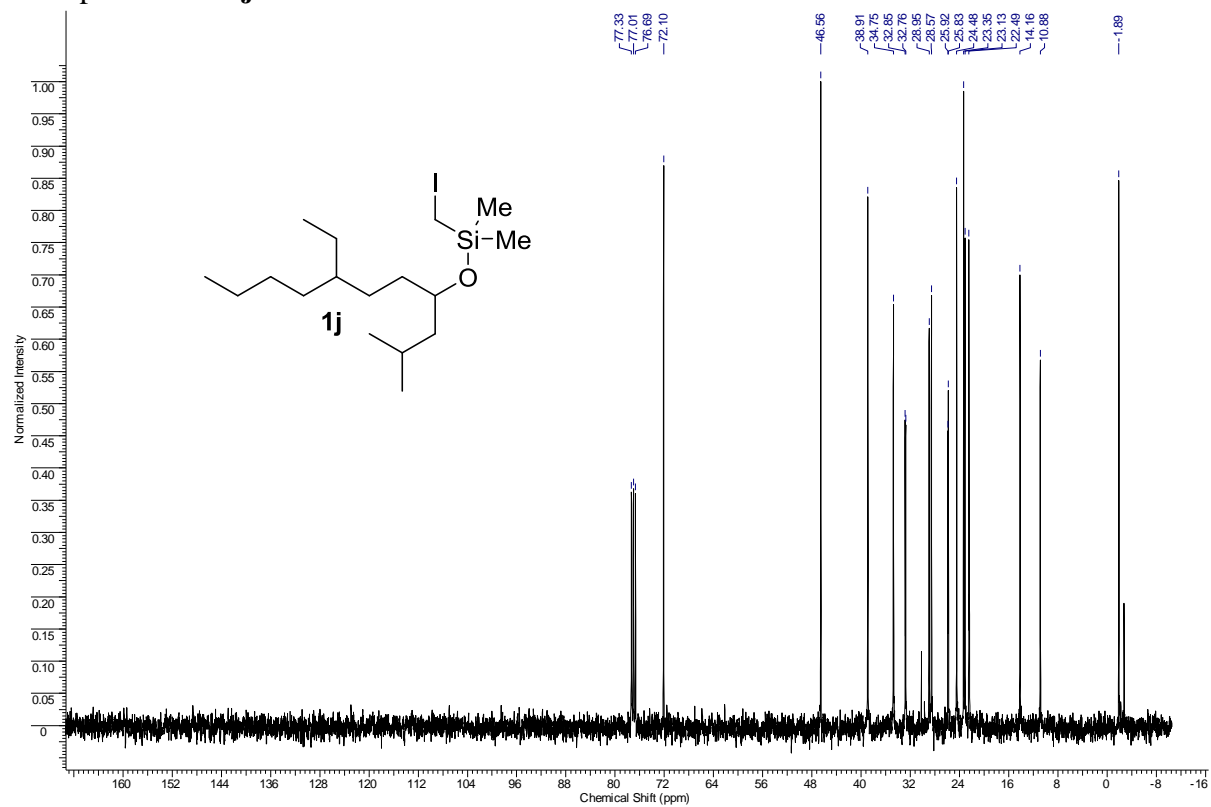
¹³C Spectrum of **1i**



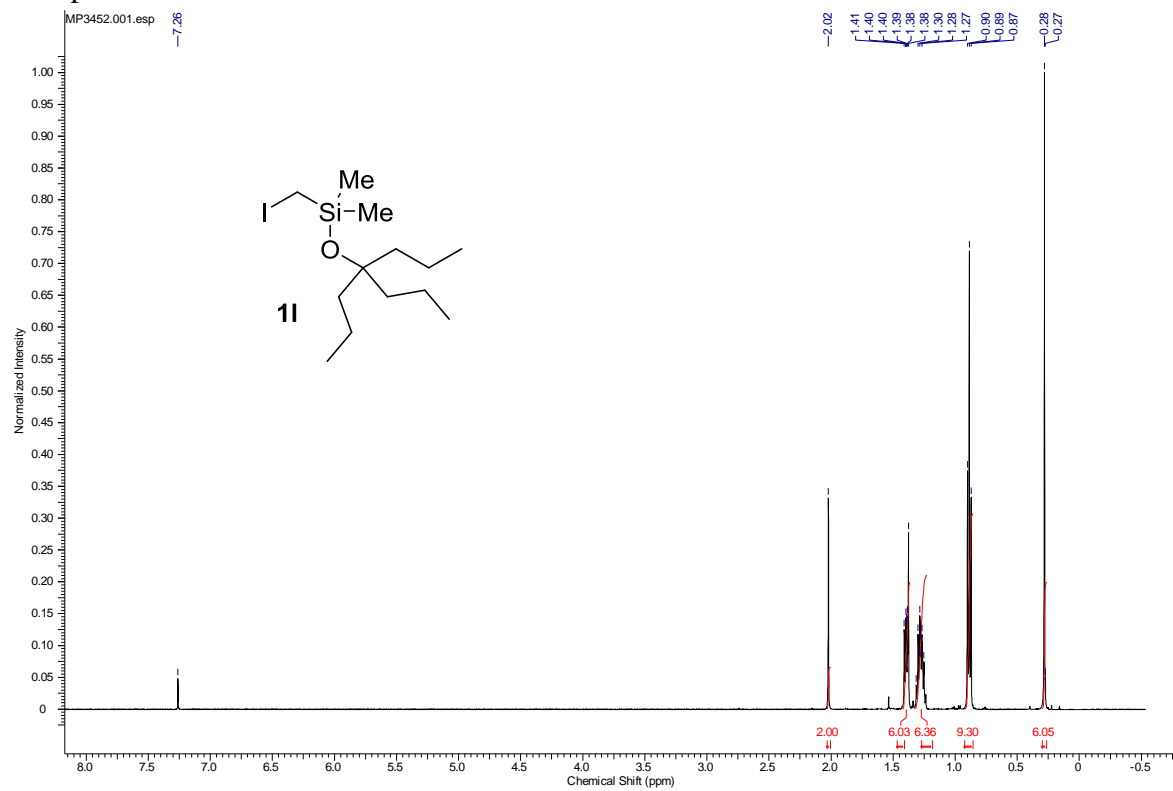
¹H Spectrum of **1j**



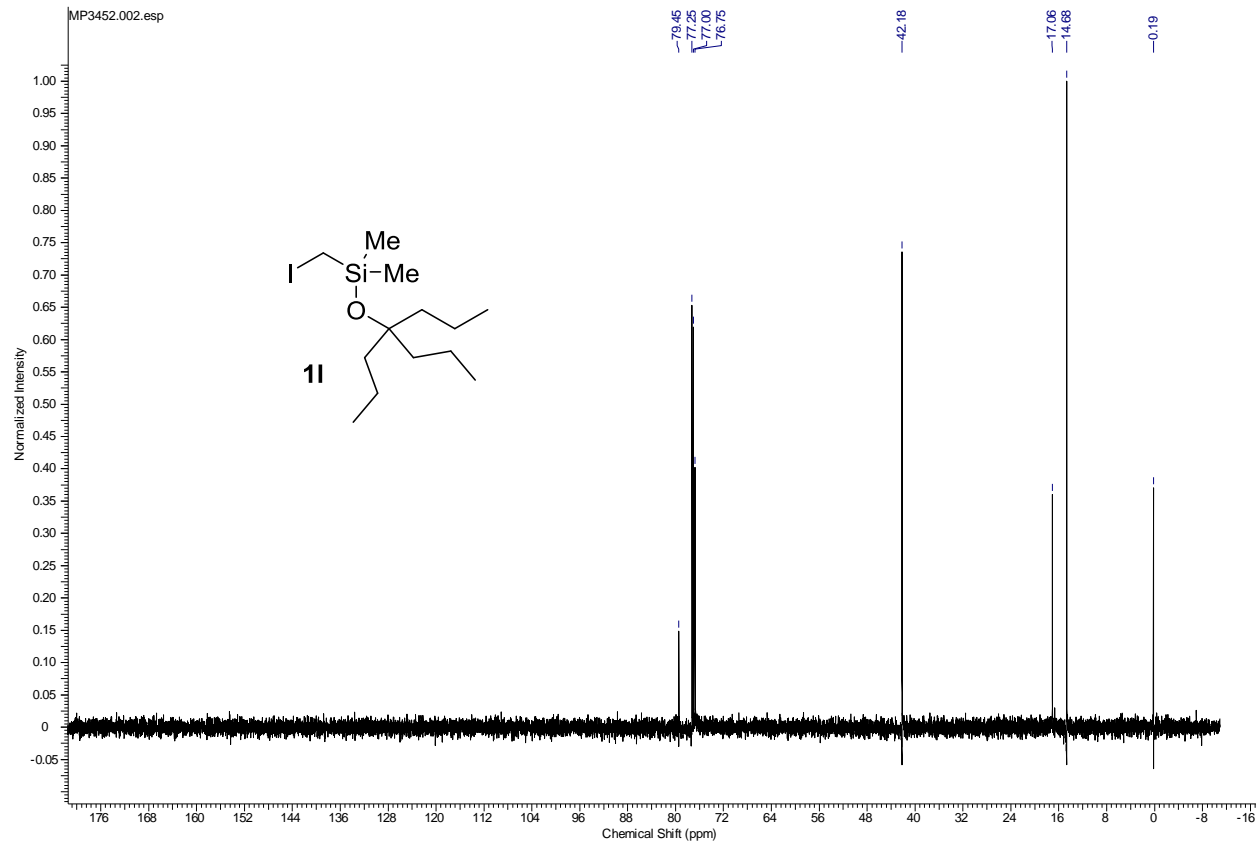
¹³C Spectrum of **1j**



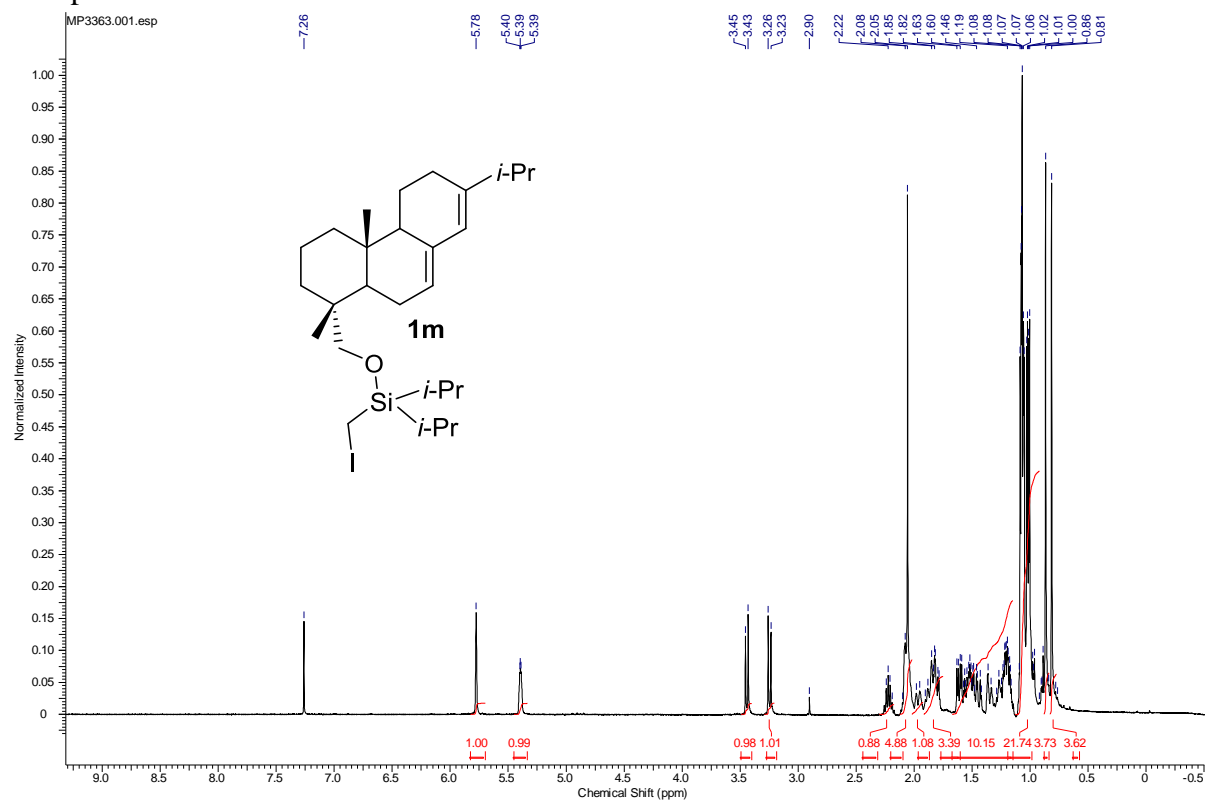
¹H Spectrum of **11**



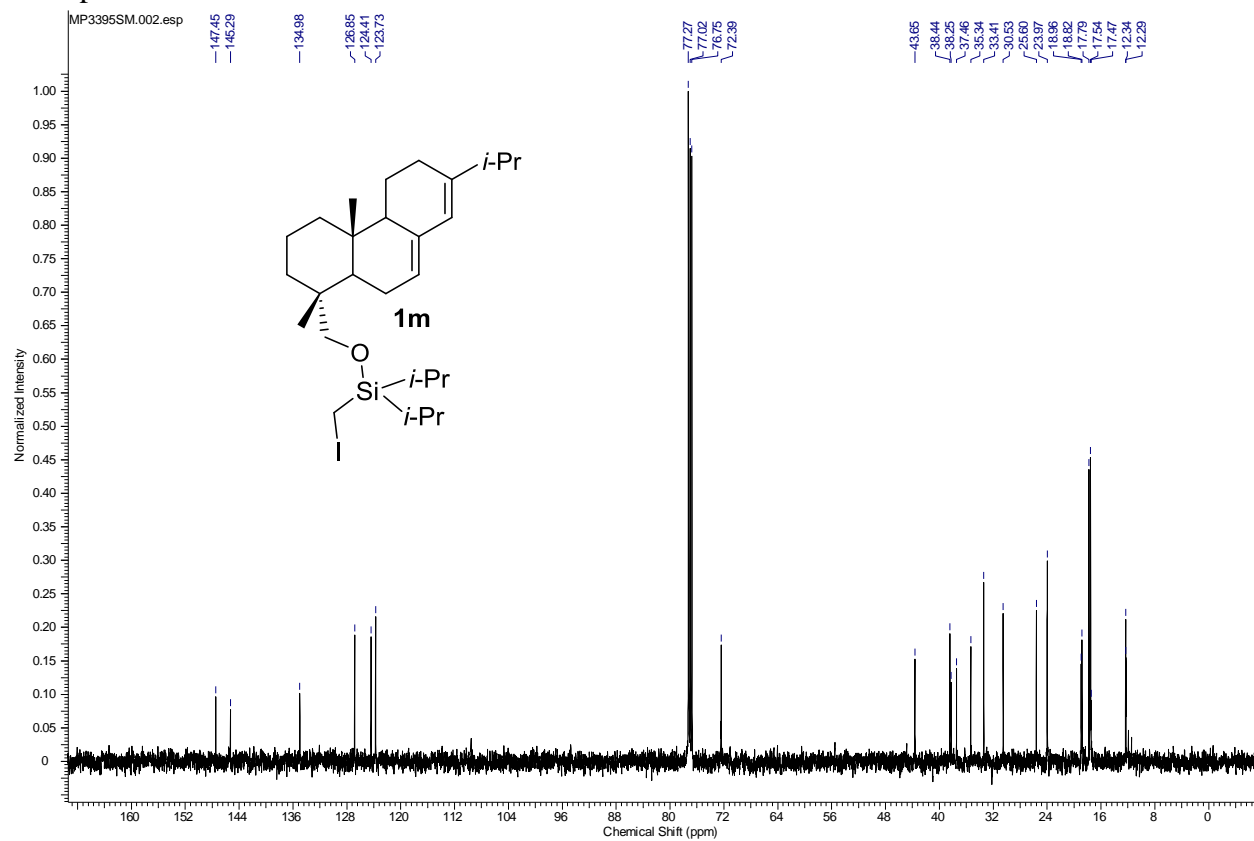
¹³C Spectrum of **11**



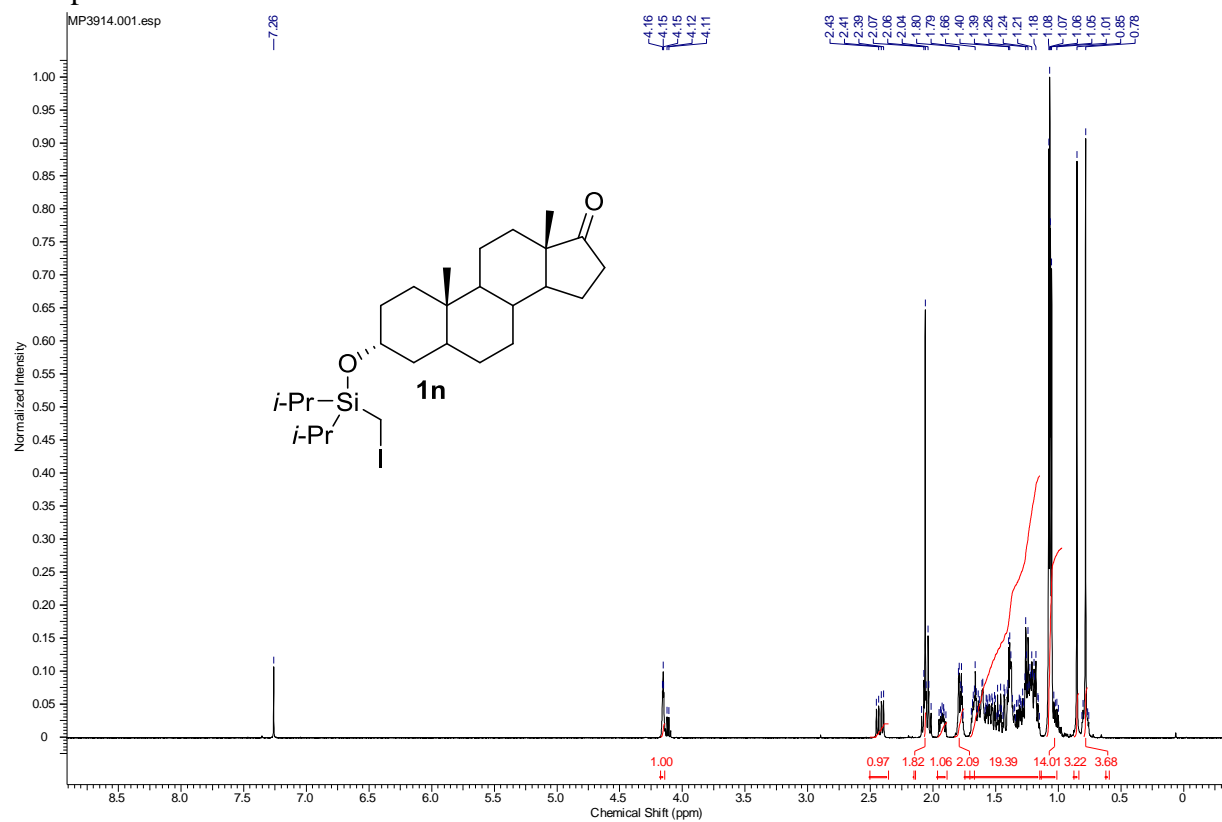
¹H Spectrum of **1m**



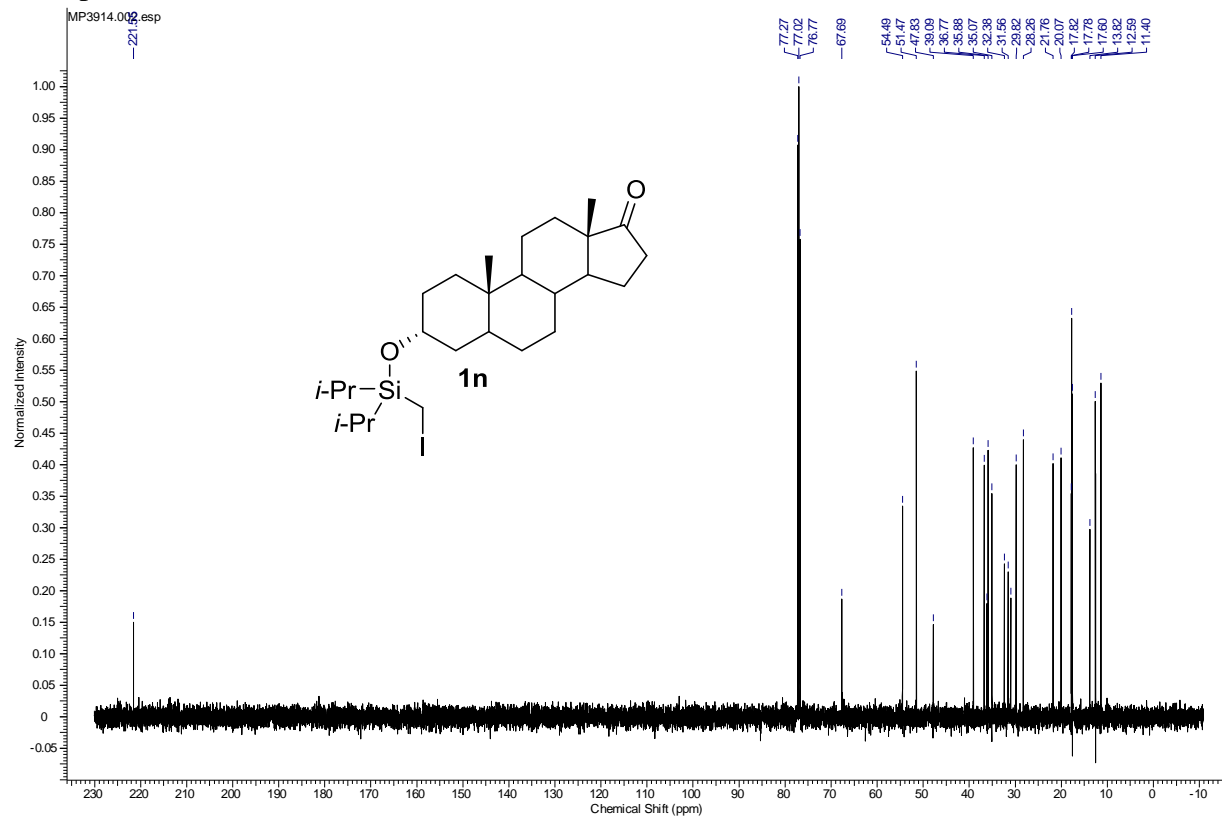
¹³C Spectrum of **1m**



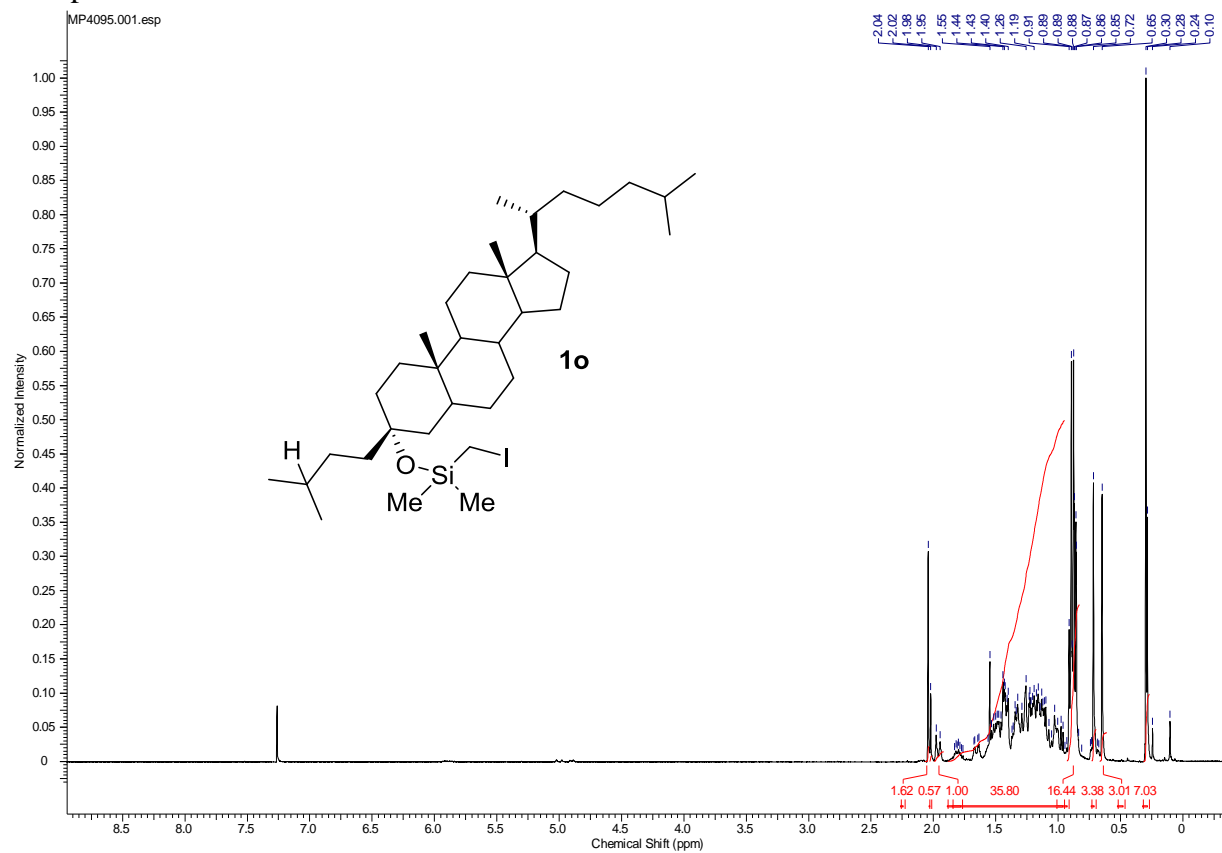
¹H Spectrum of **1n**



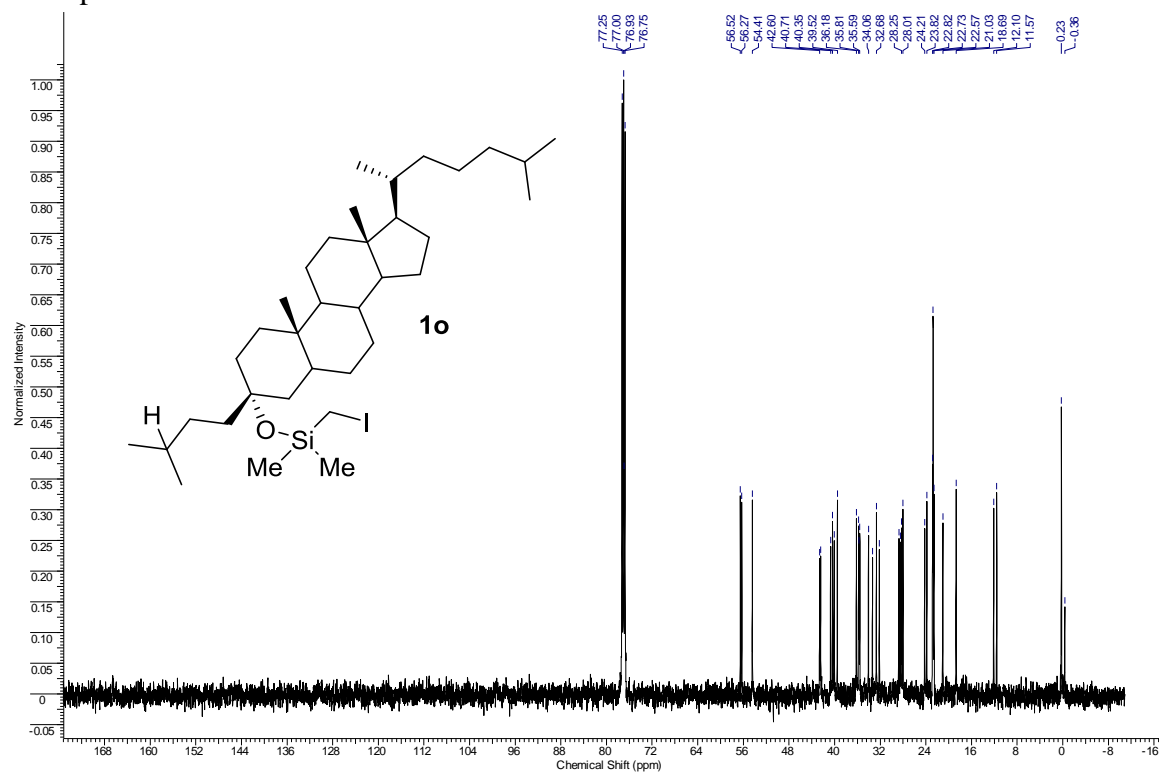
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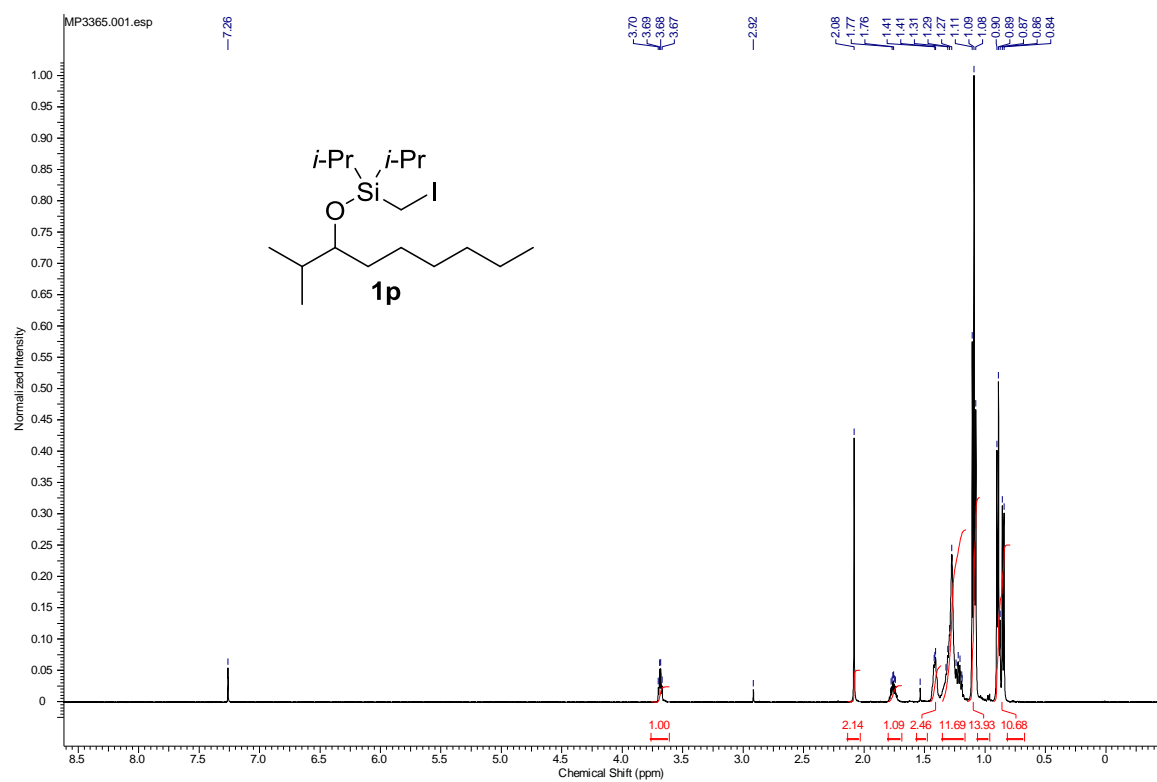
¹H Spectrum of **1o**



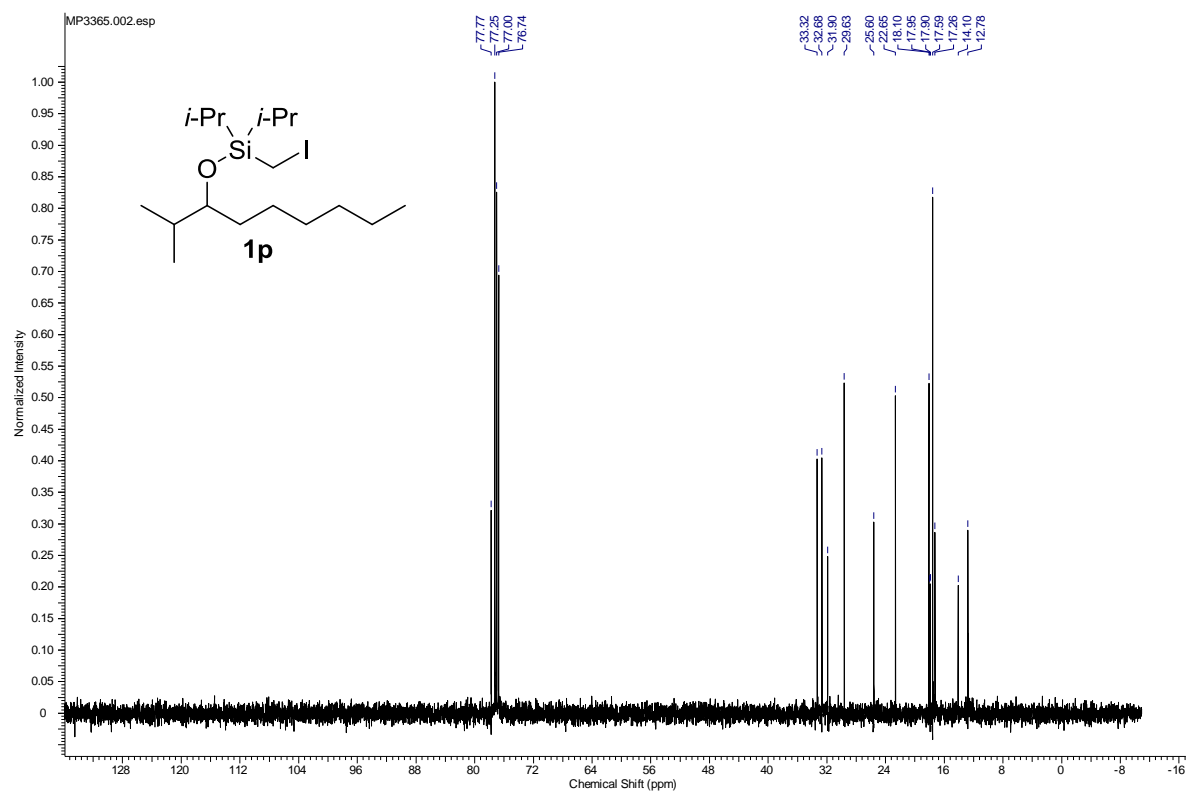
¹³C Spectrum of **1o**



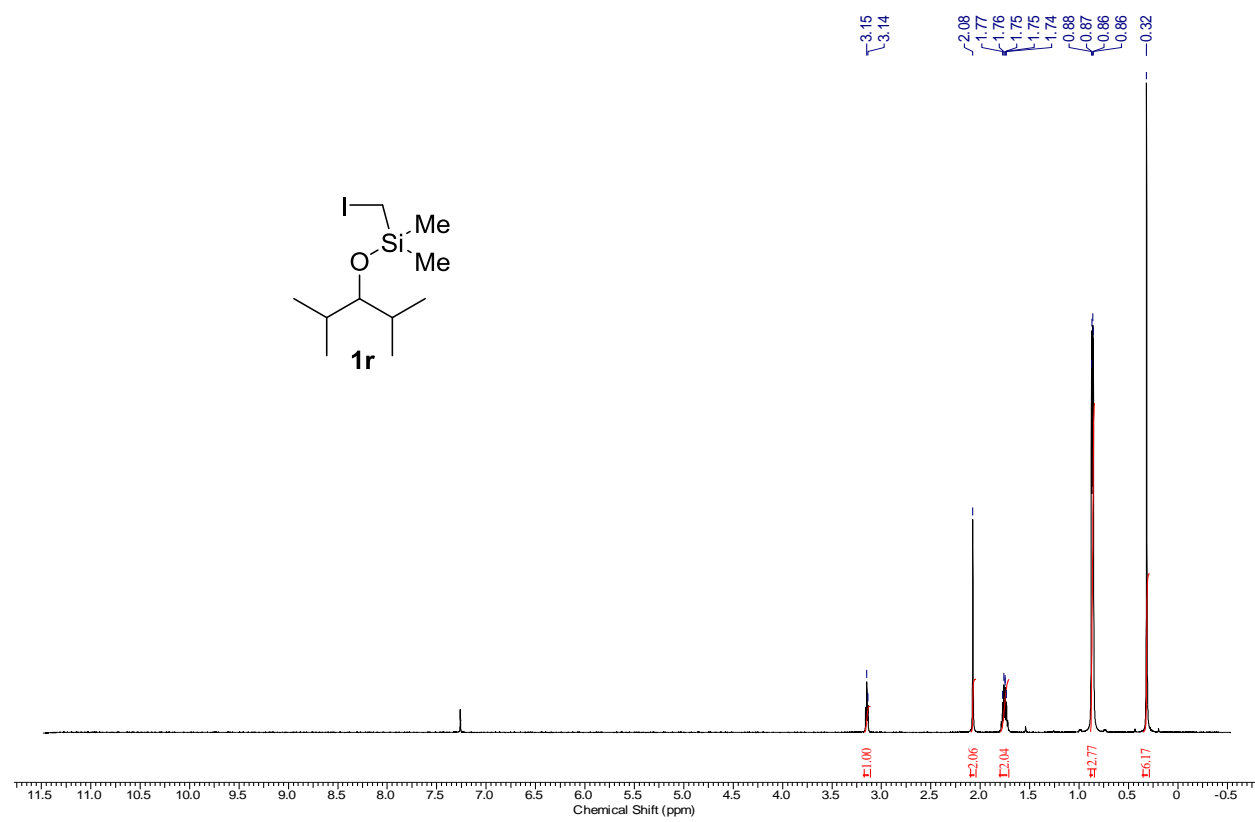
¹H Spectrum of **1p**



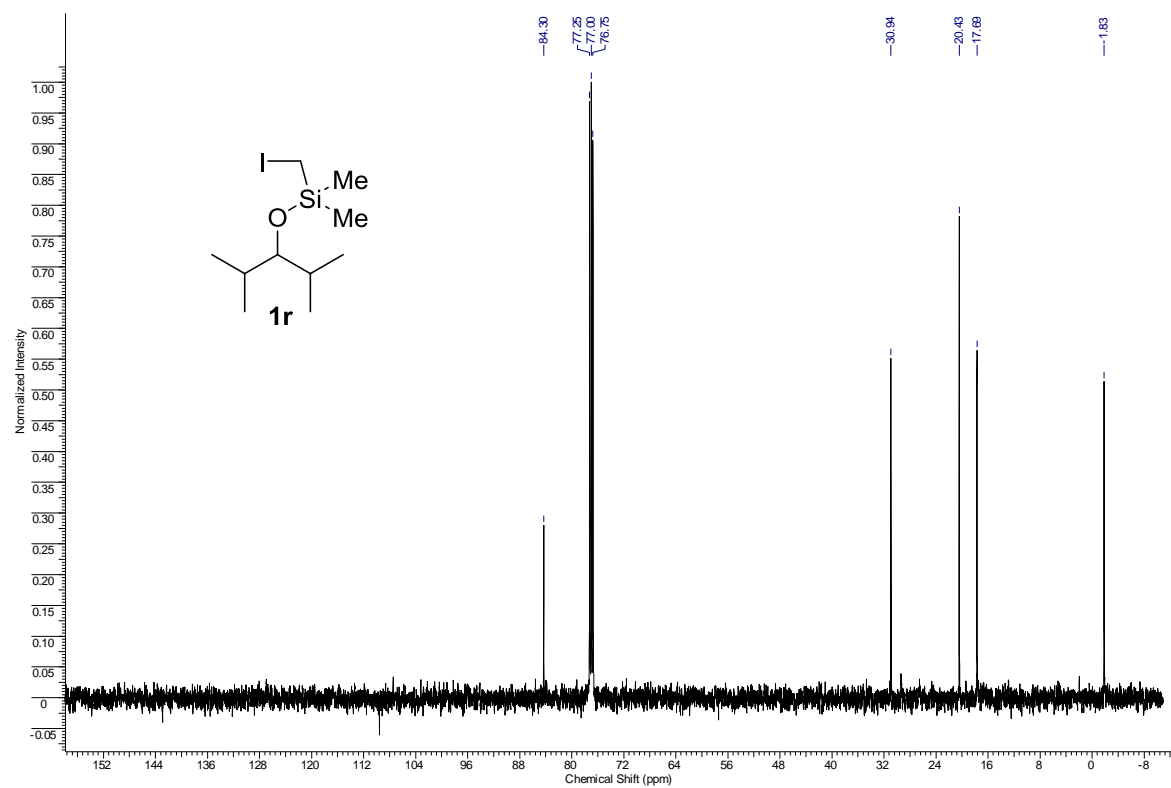
¹³C Spectrum of **1p**



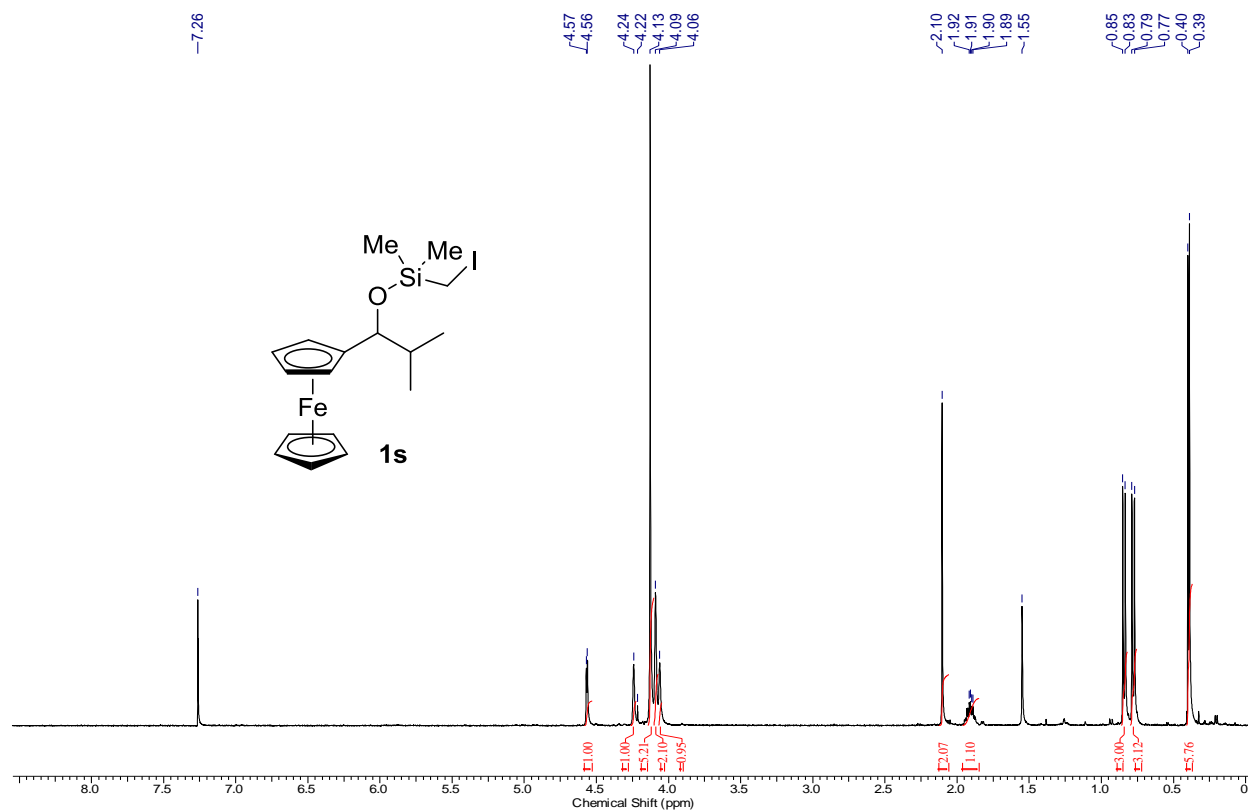
^1H NMR of **1r**



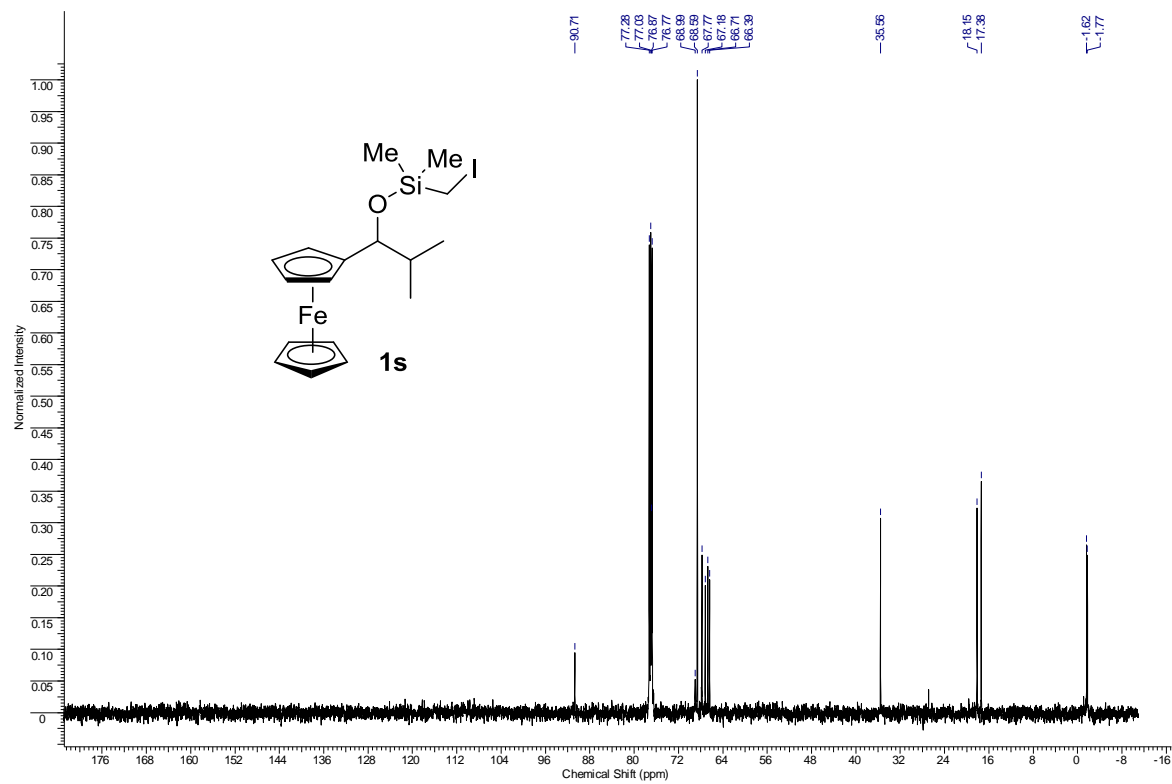
^{13}C NMR of **1r**



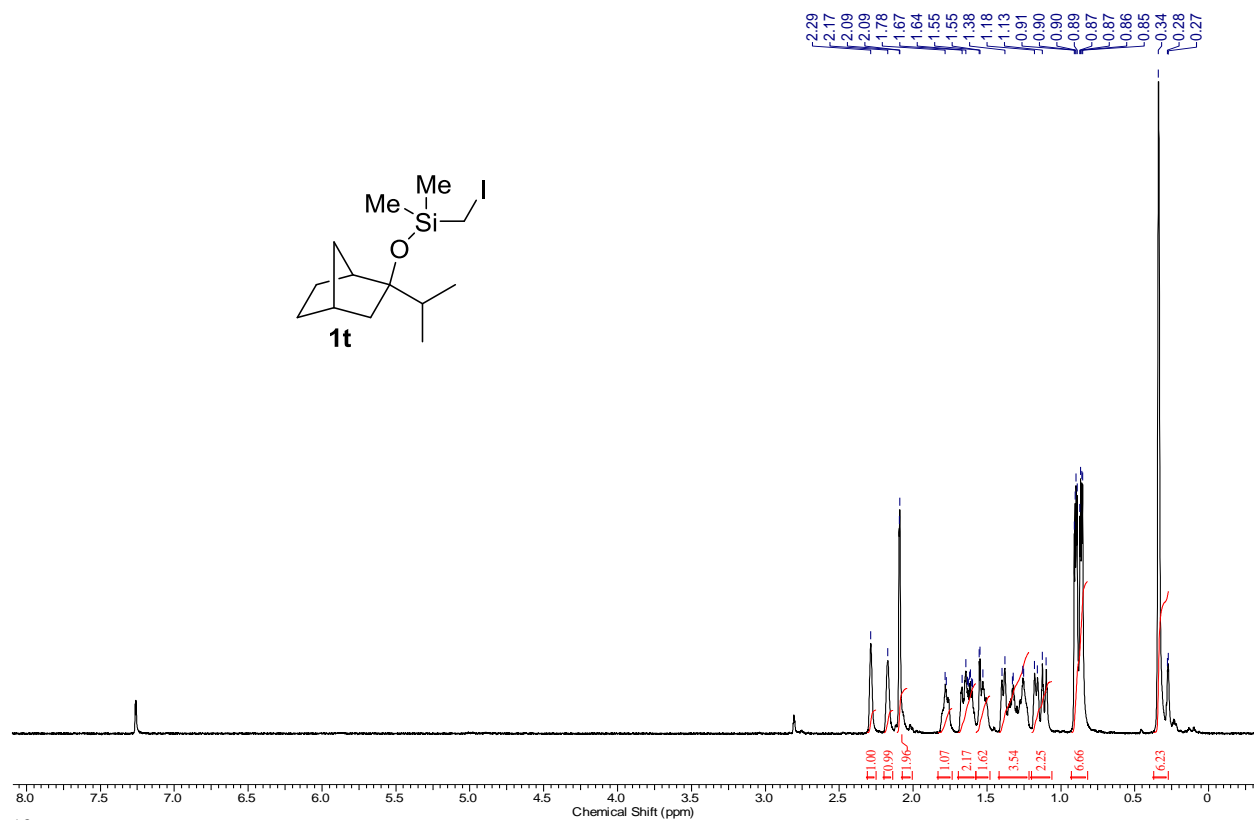
¹H NMR of **1s**



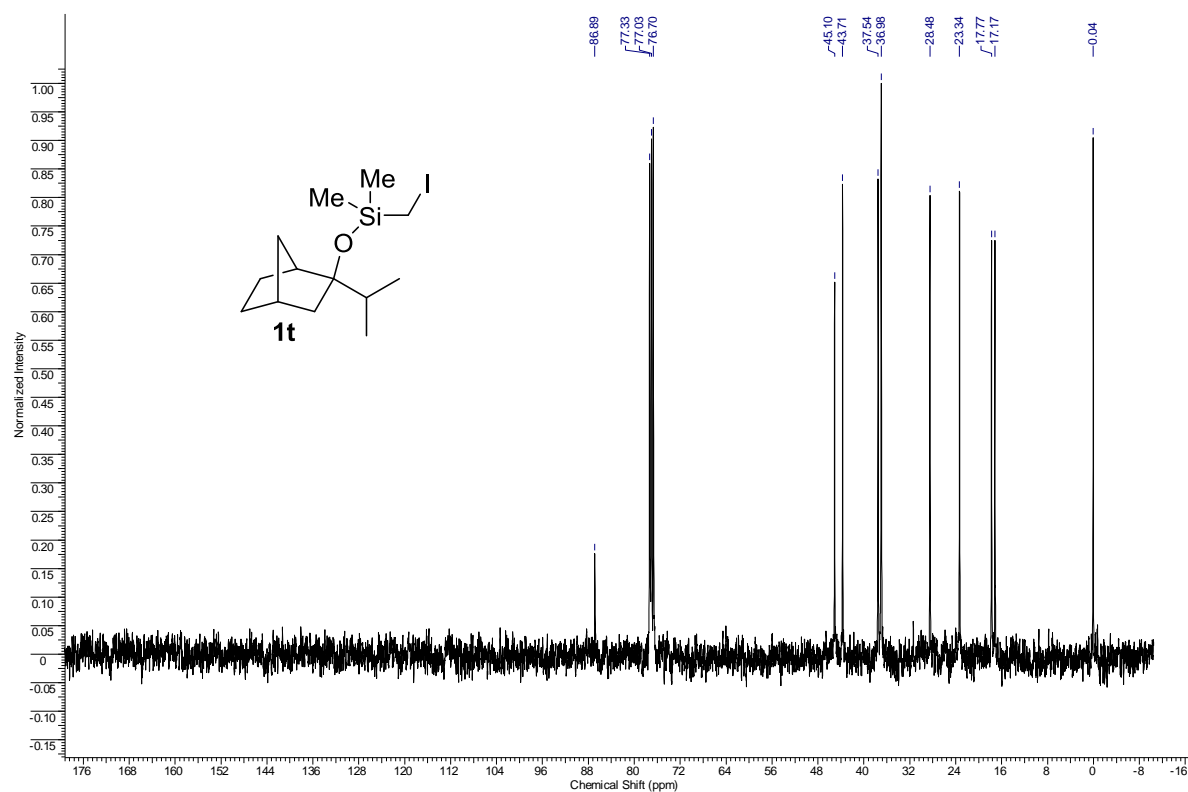
¹³C NMR of **1s**



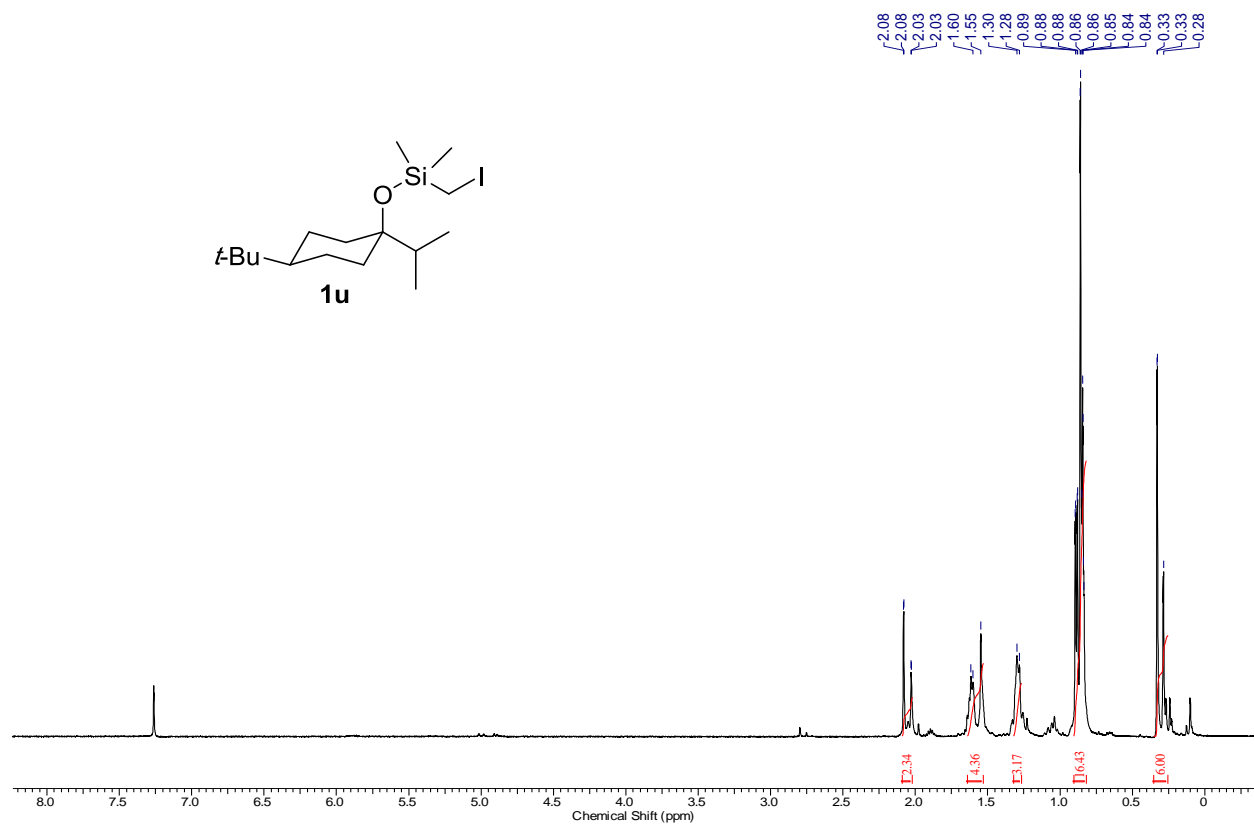
¹H NMR of **1t**



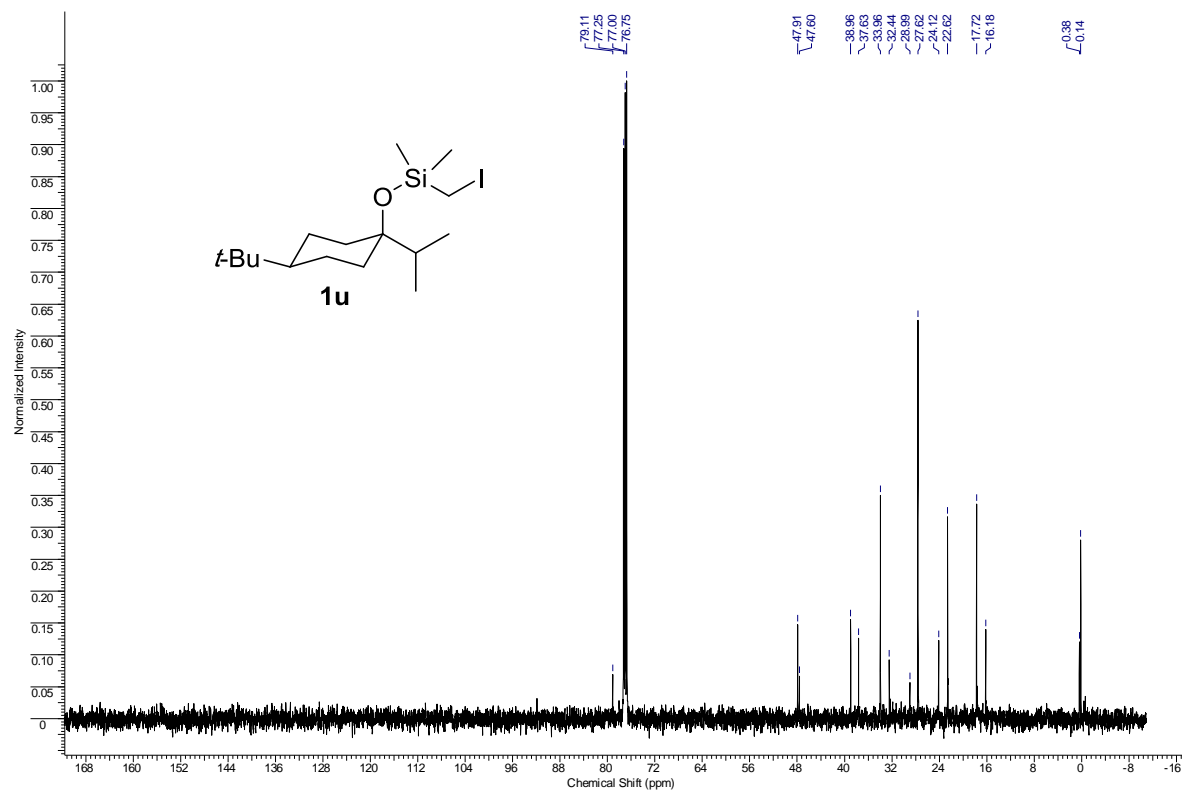
¹³C NMR of **1t**



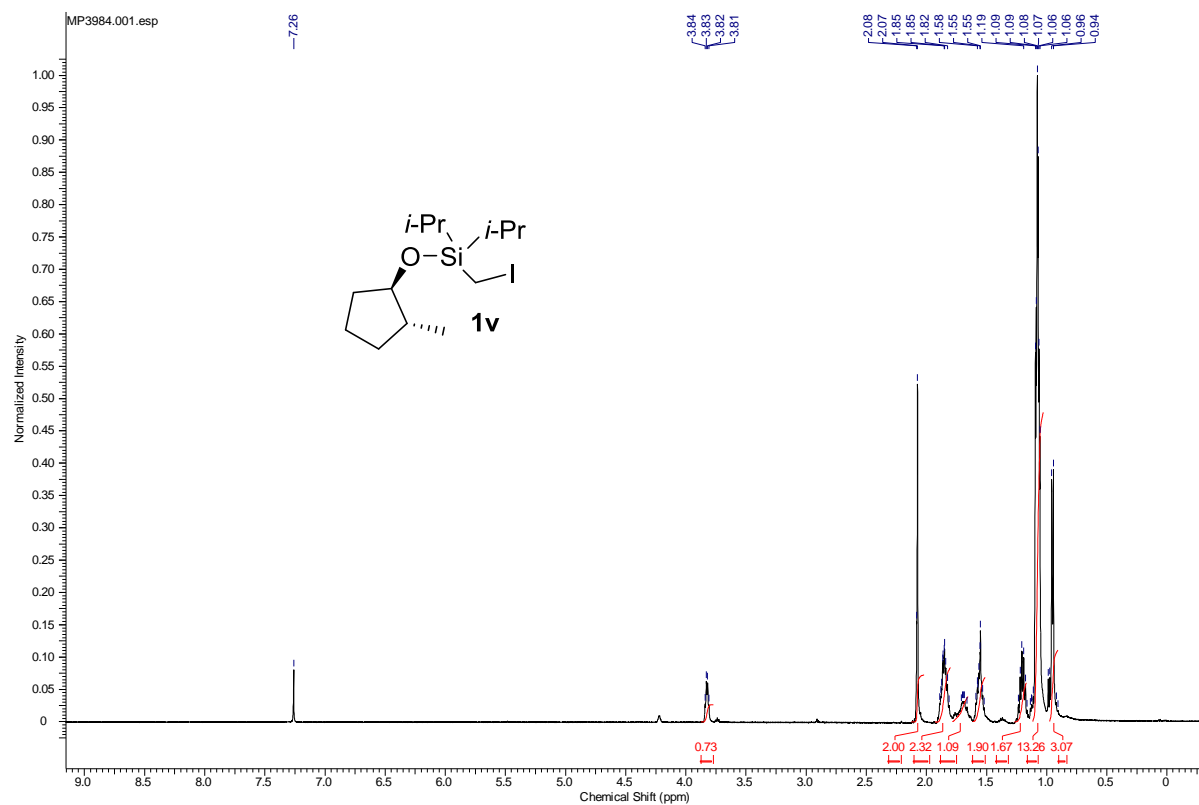
¹H NMR of **1u**



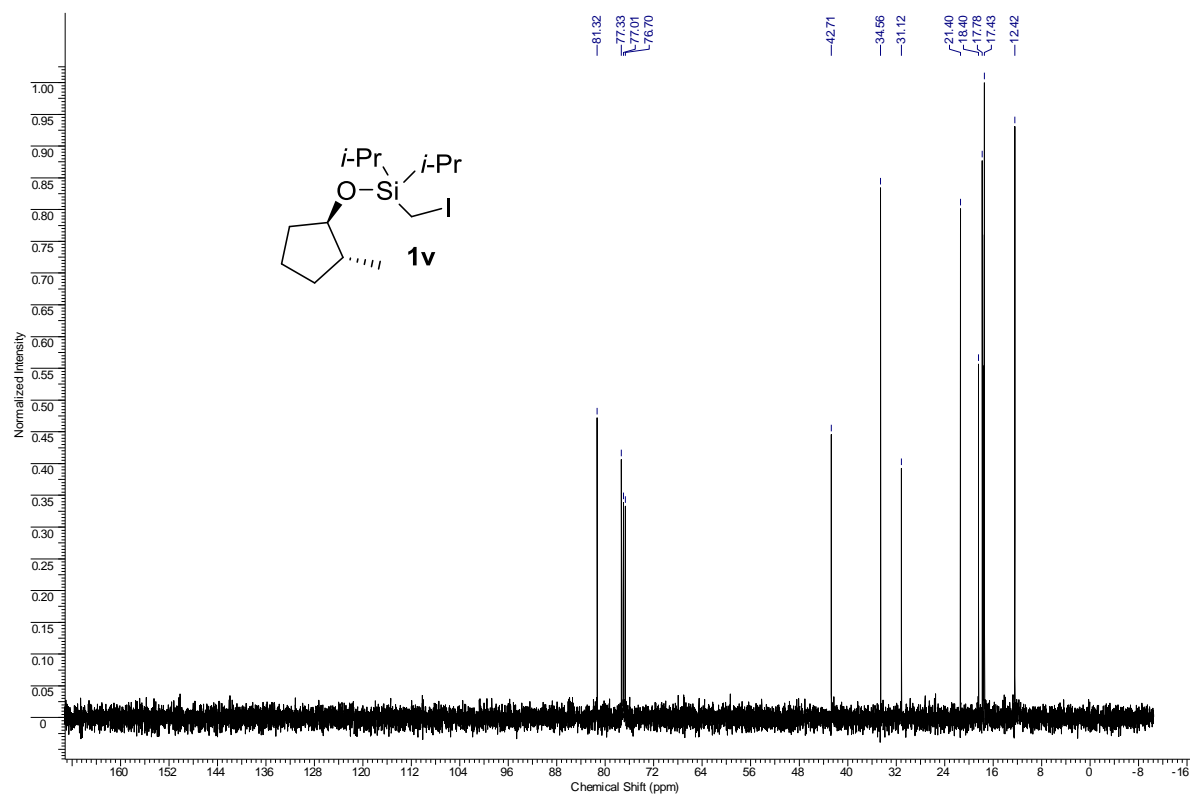
¹³C NMR of **1u**



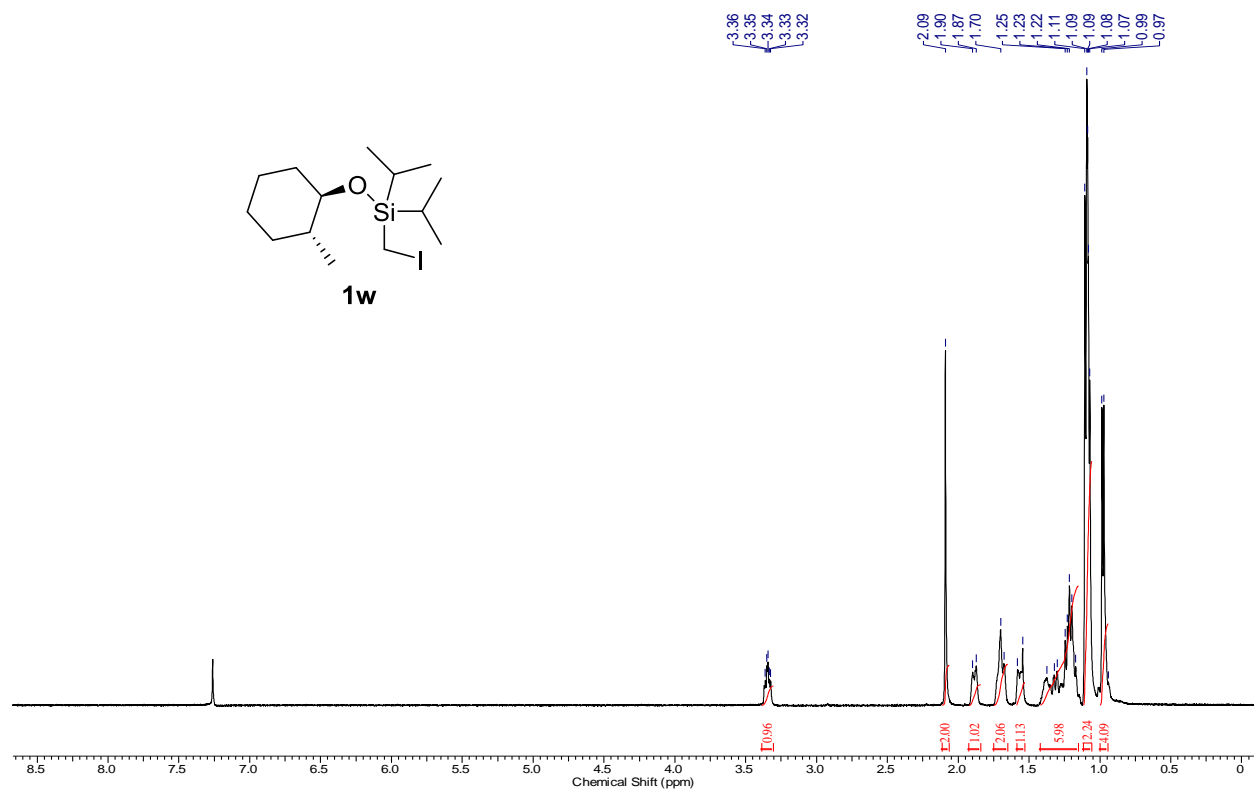
¹H Spectrum of **1v**



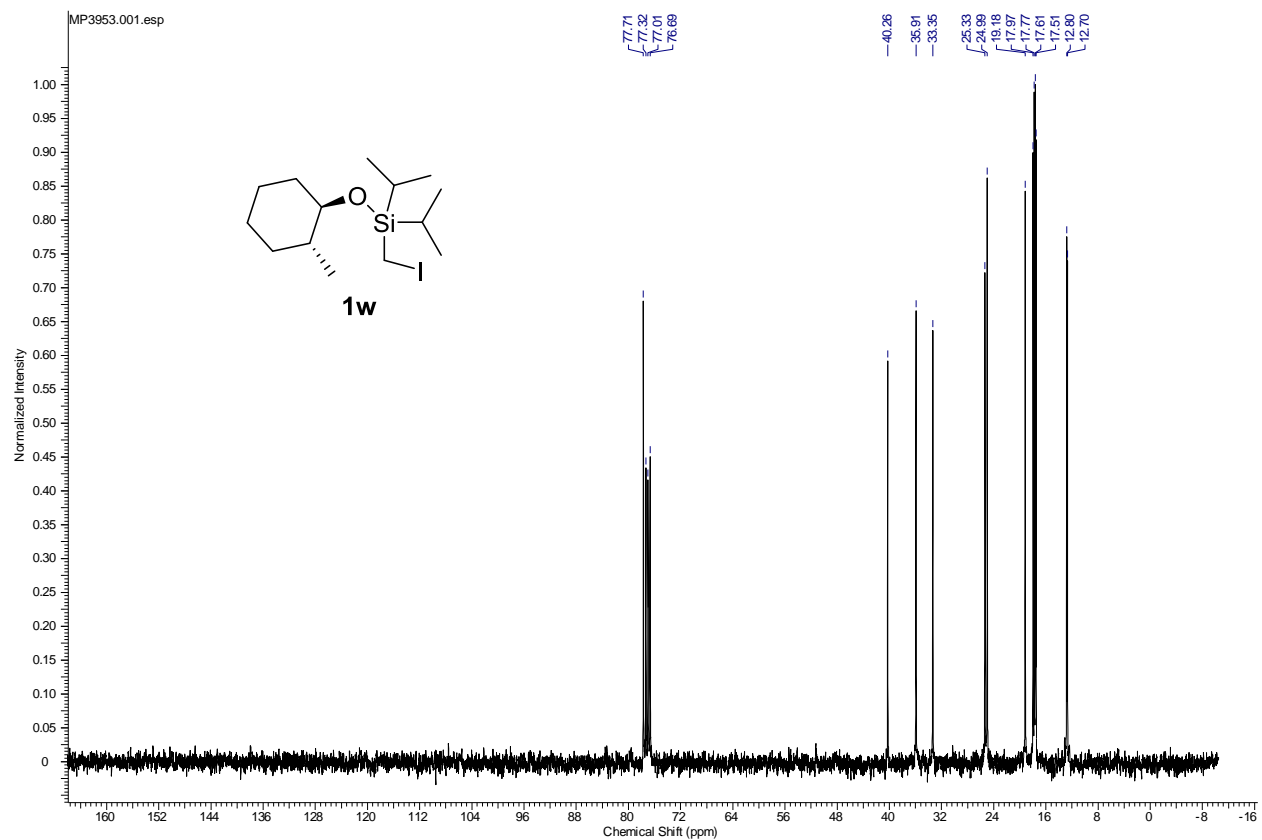
¹³C Spectrum of **1v**



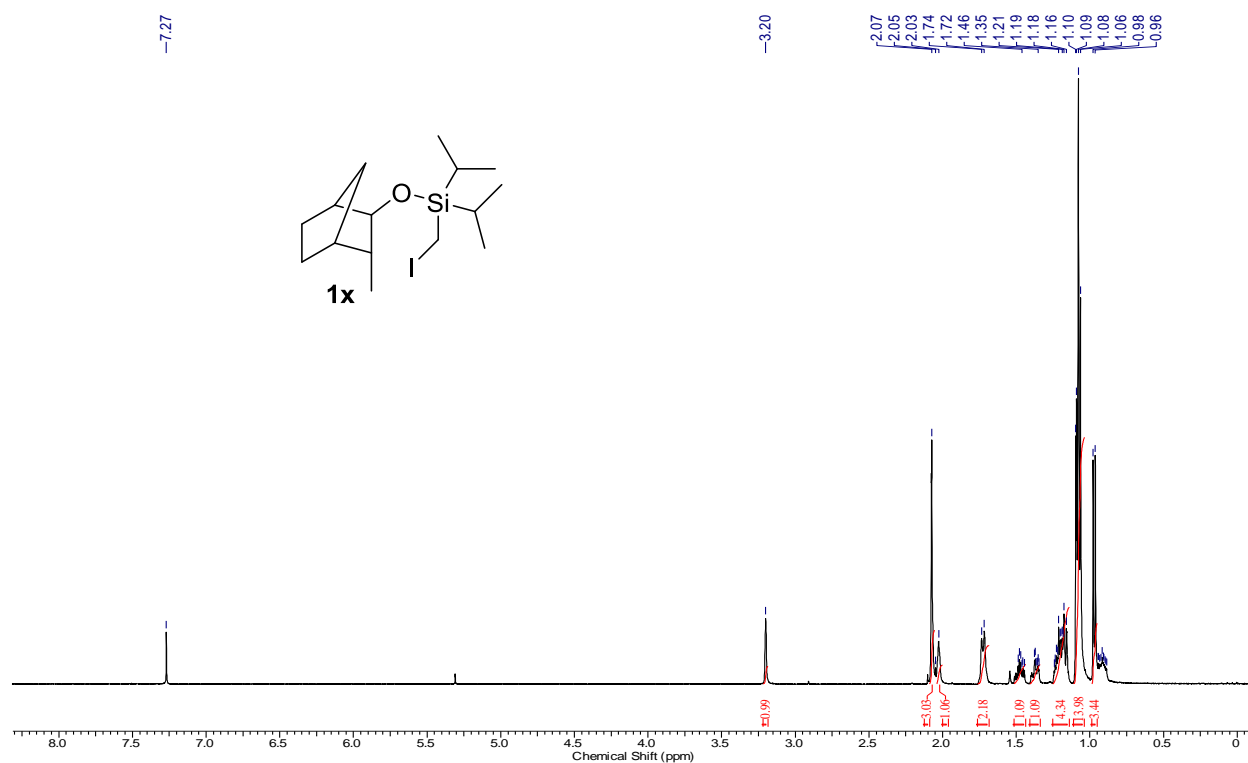
¹H NMR of **1w**



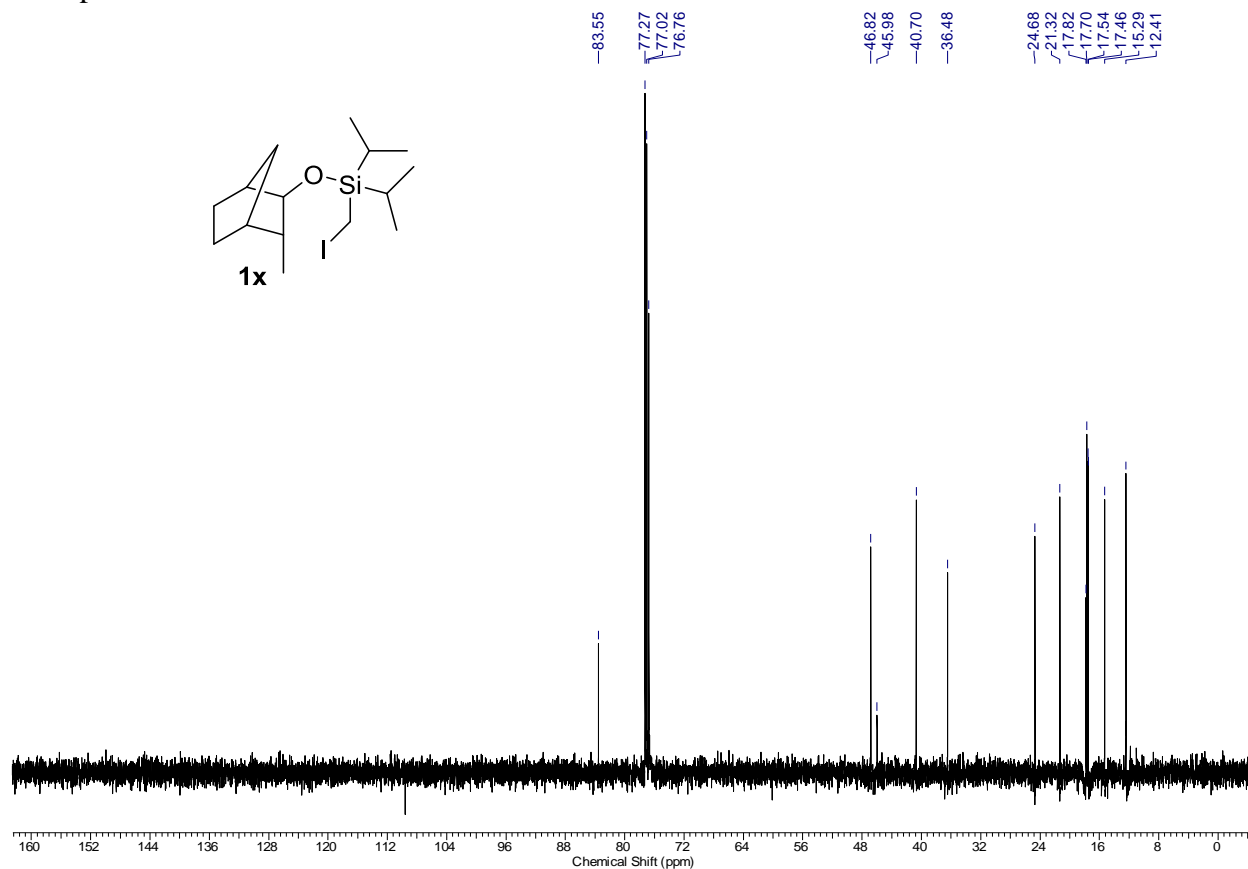
¹³C NMR of **1w**



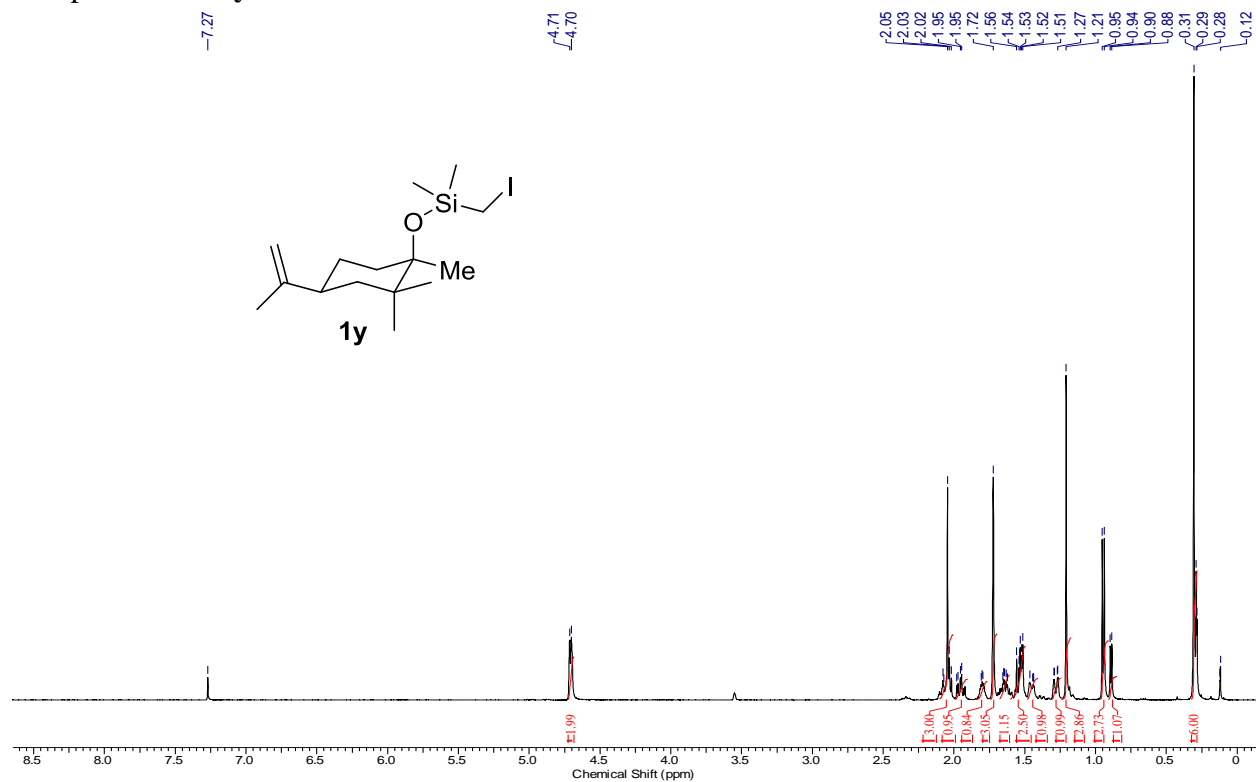
¹H Spectrum of **1x**



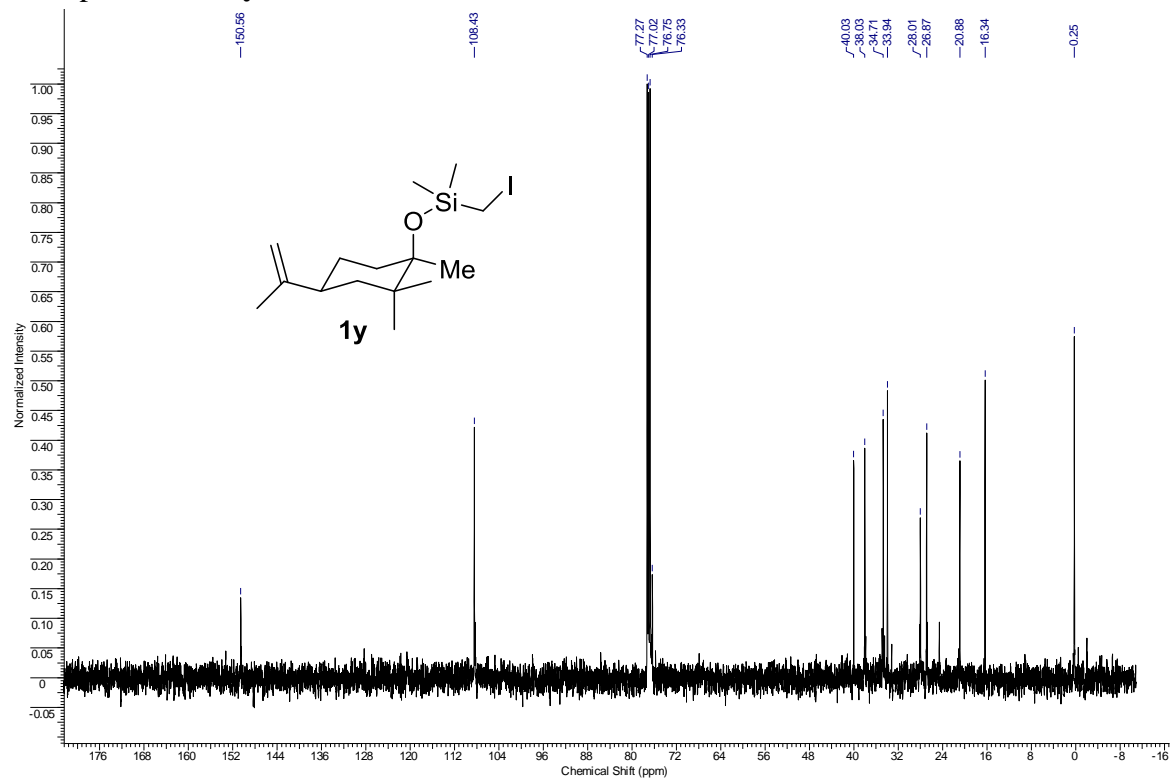
¹³C Spectrum of **1x**



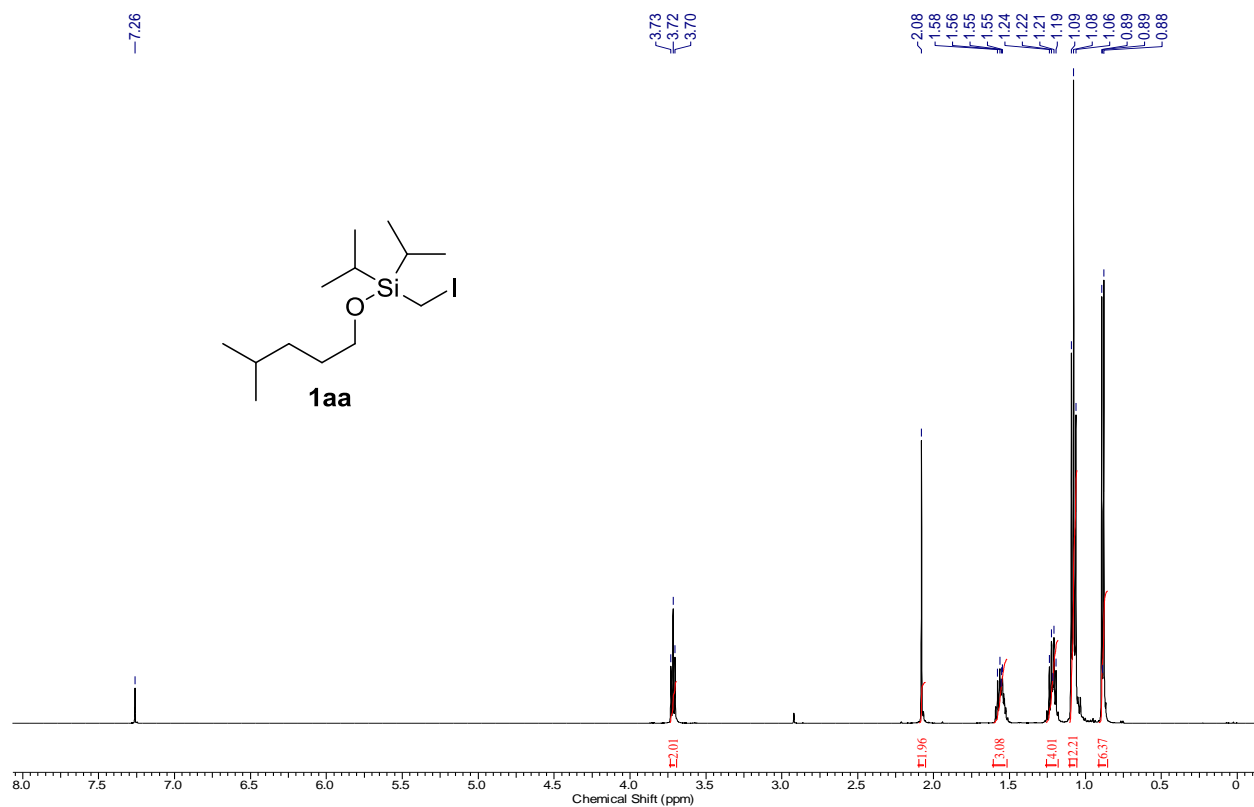
¹H Spectrum of **1y**



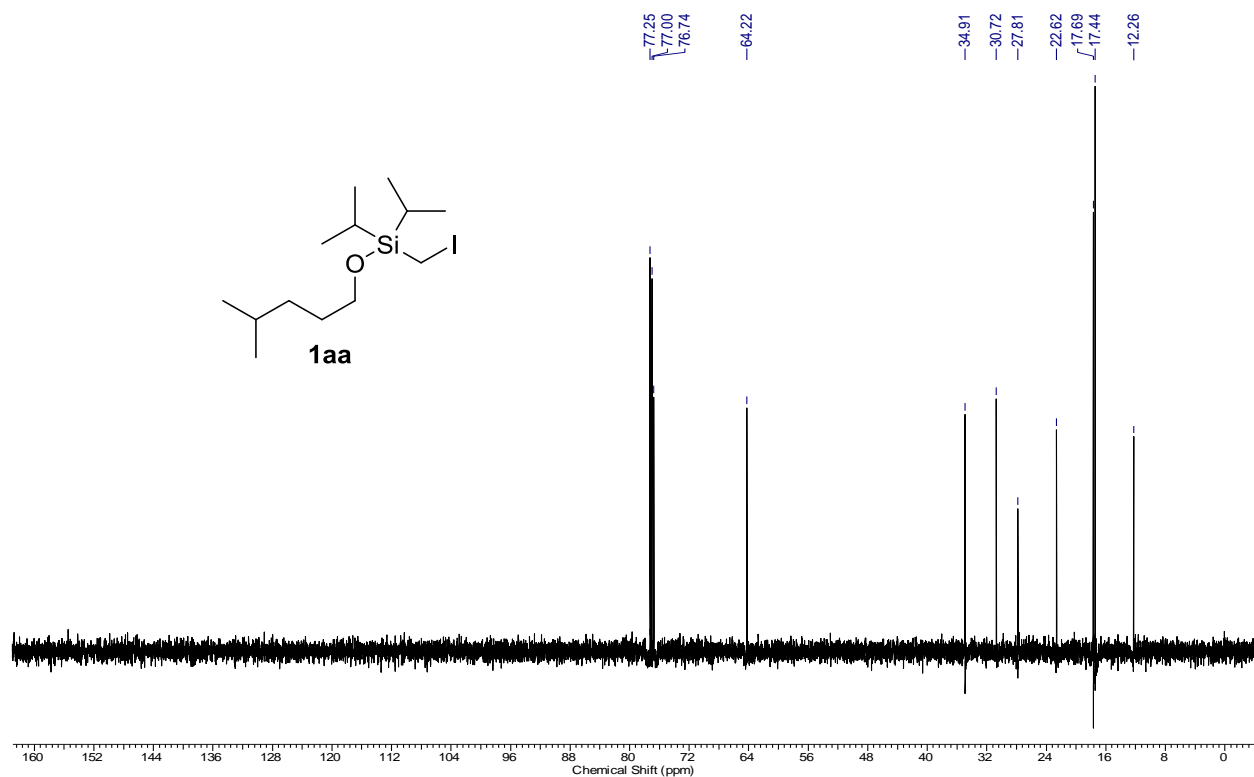
¹³C Spectrum of **1y**



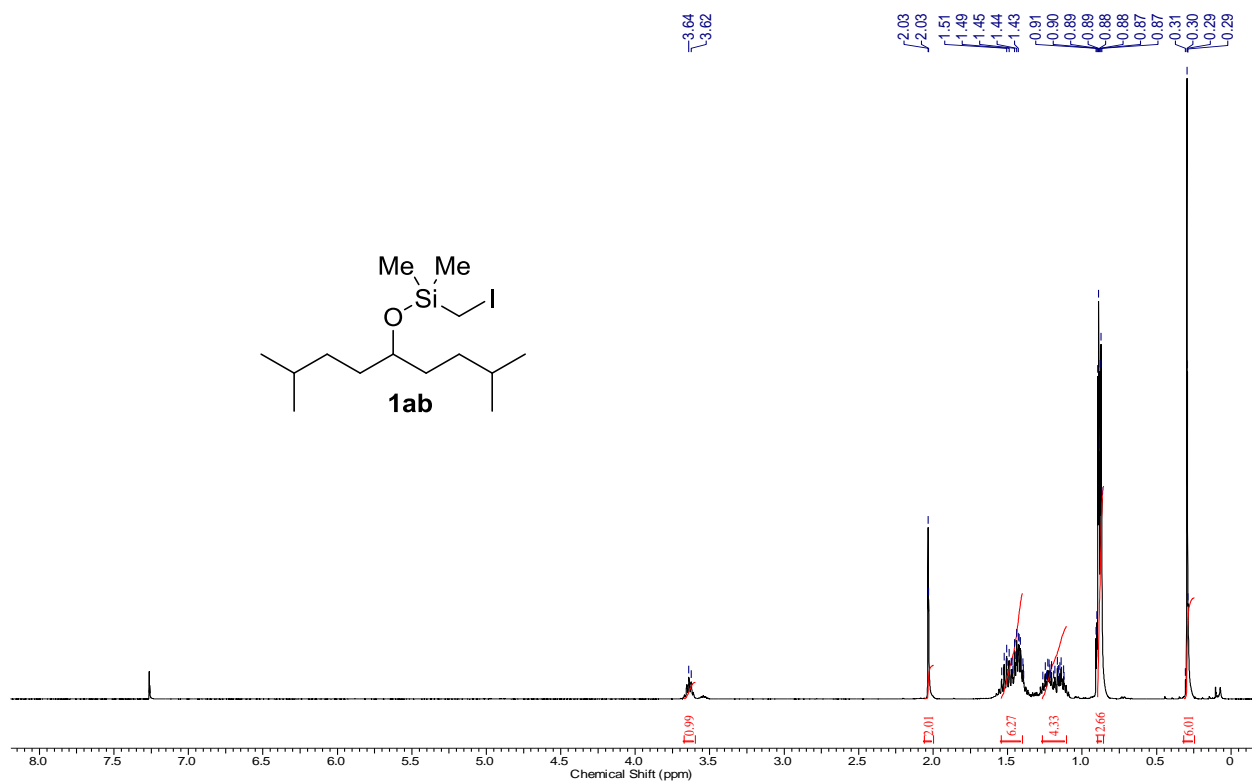
¹H NMR of **1aa**



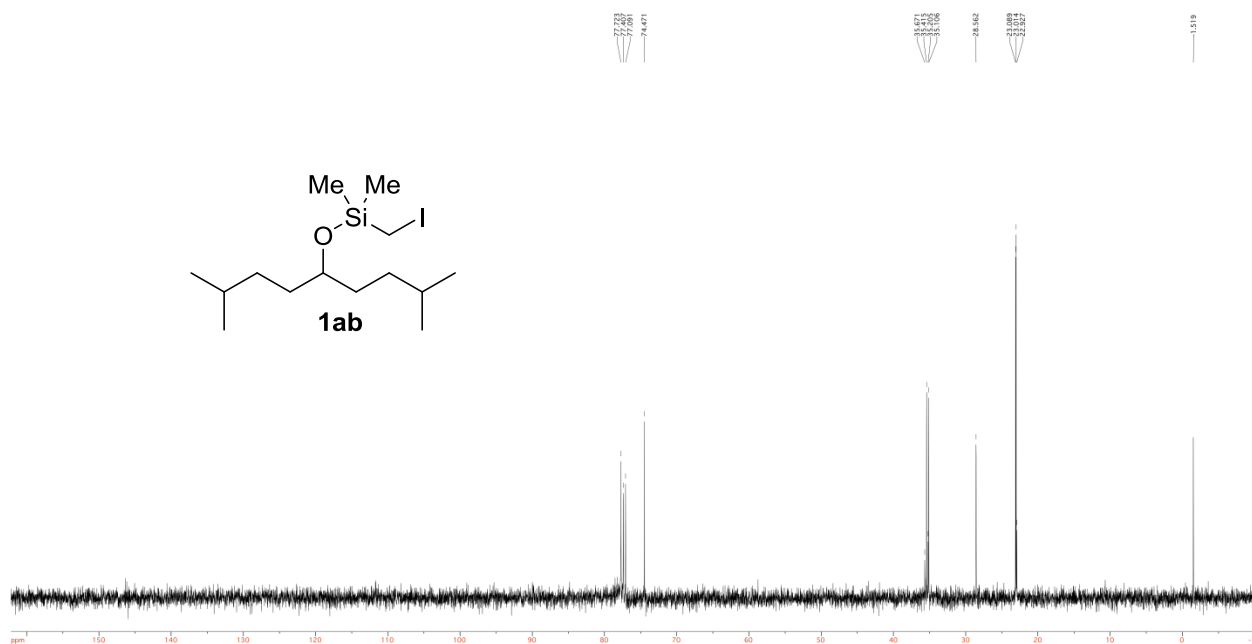
¹³C NMR of **1aa**



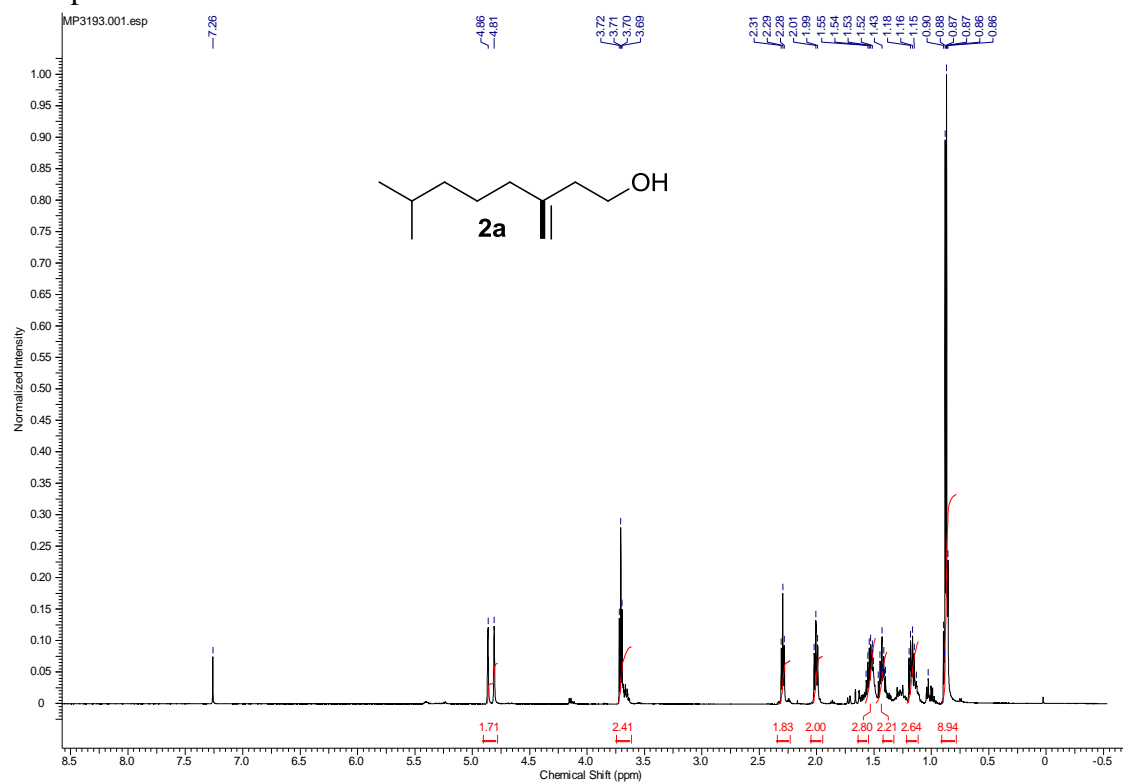
¹H NMR of **1ab**



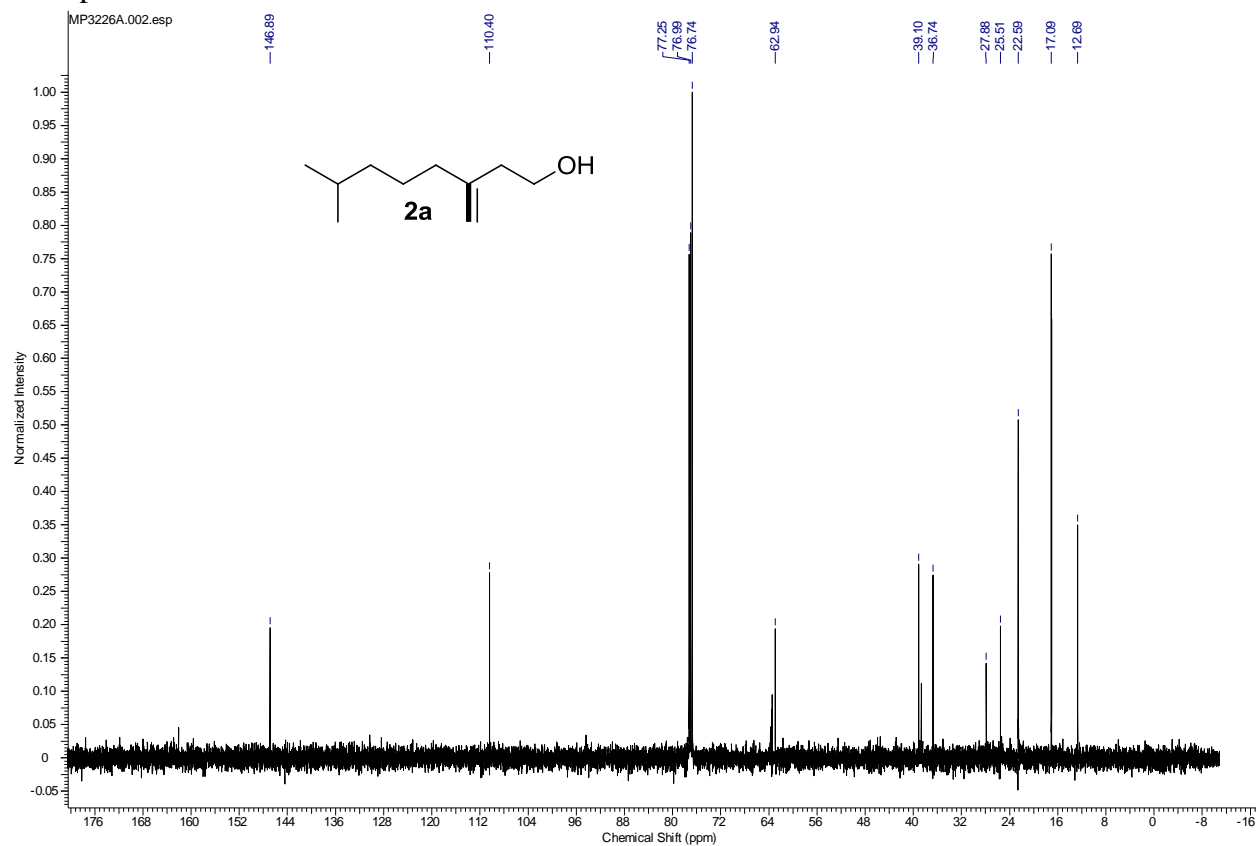
¹³C NMR of **1ab**



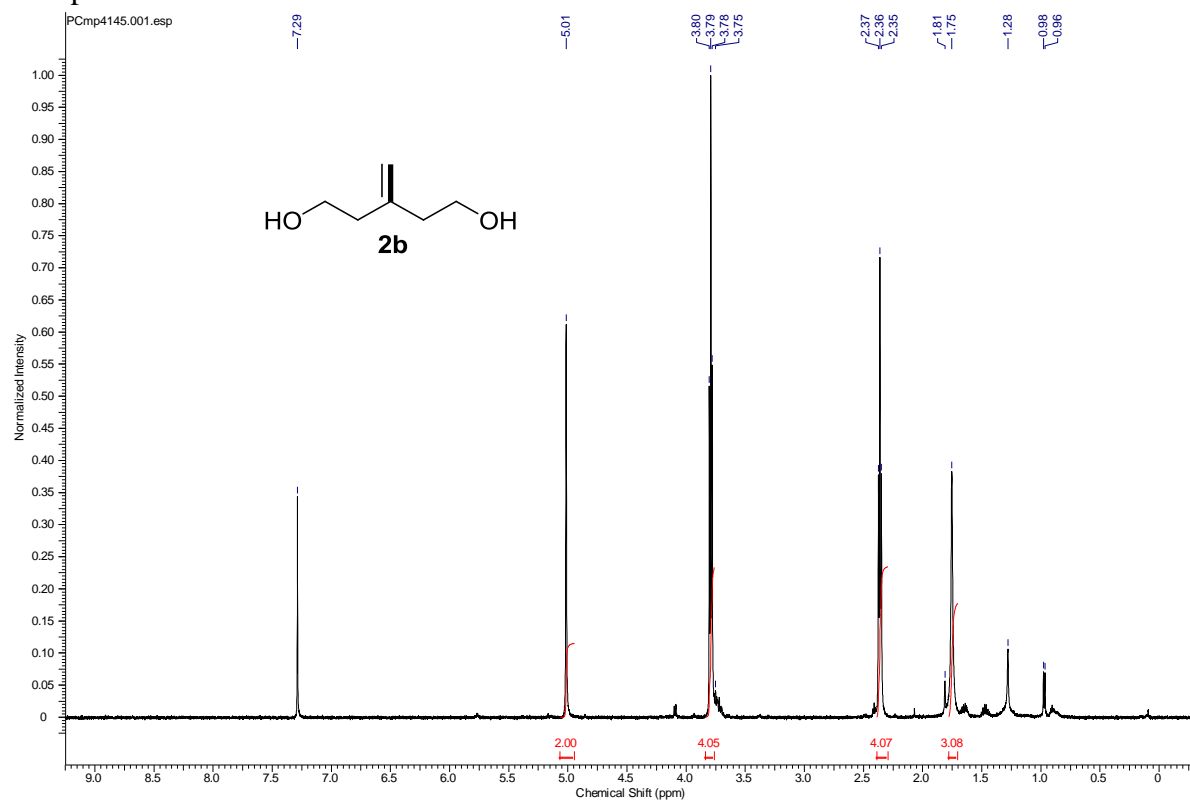
¹H Spectrum of 2a



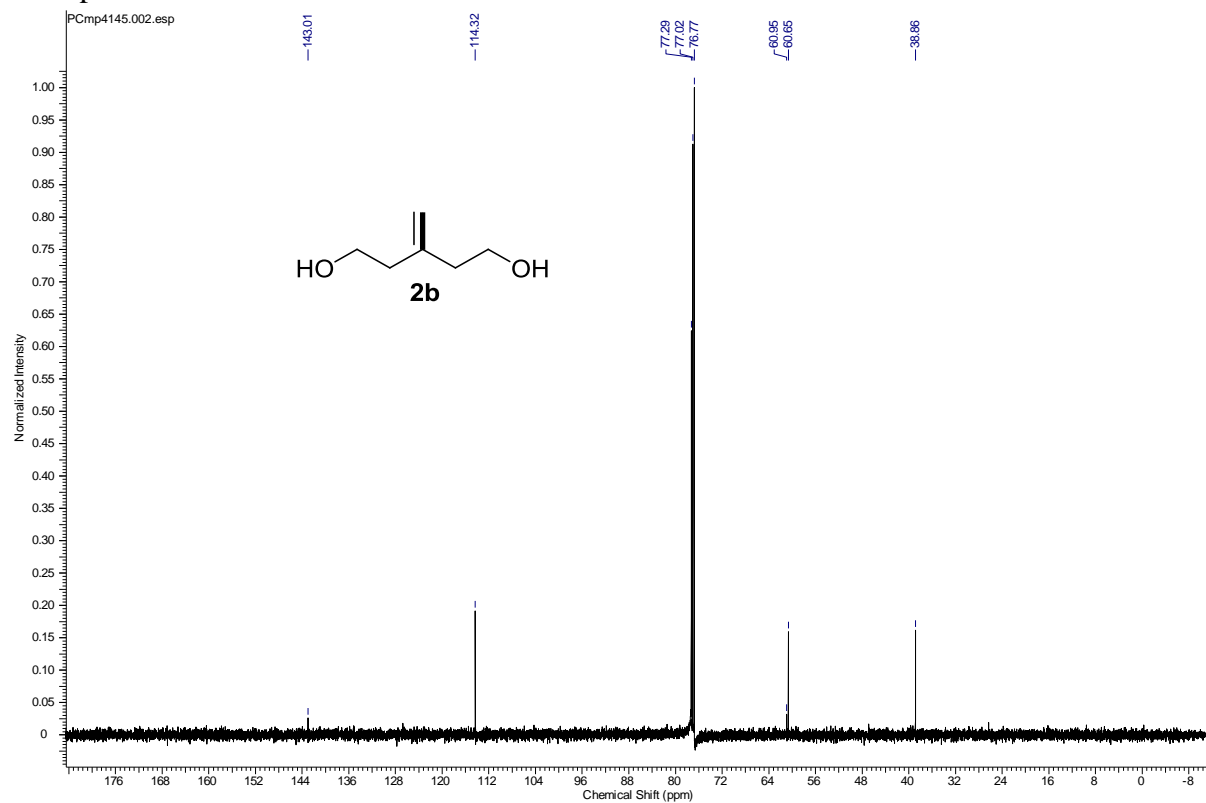
¹³C Spectrum of 2a



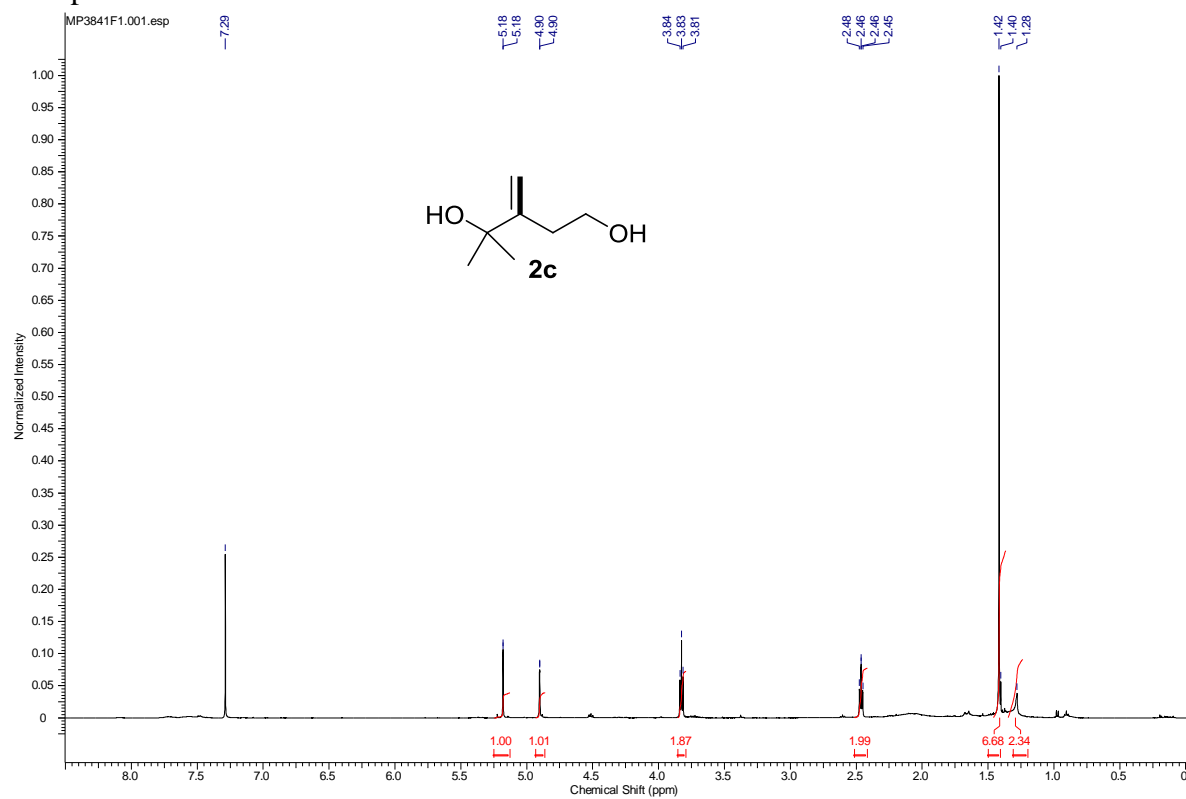
¹H Spectrum of 2b



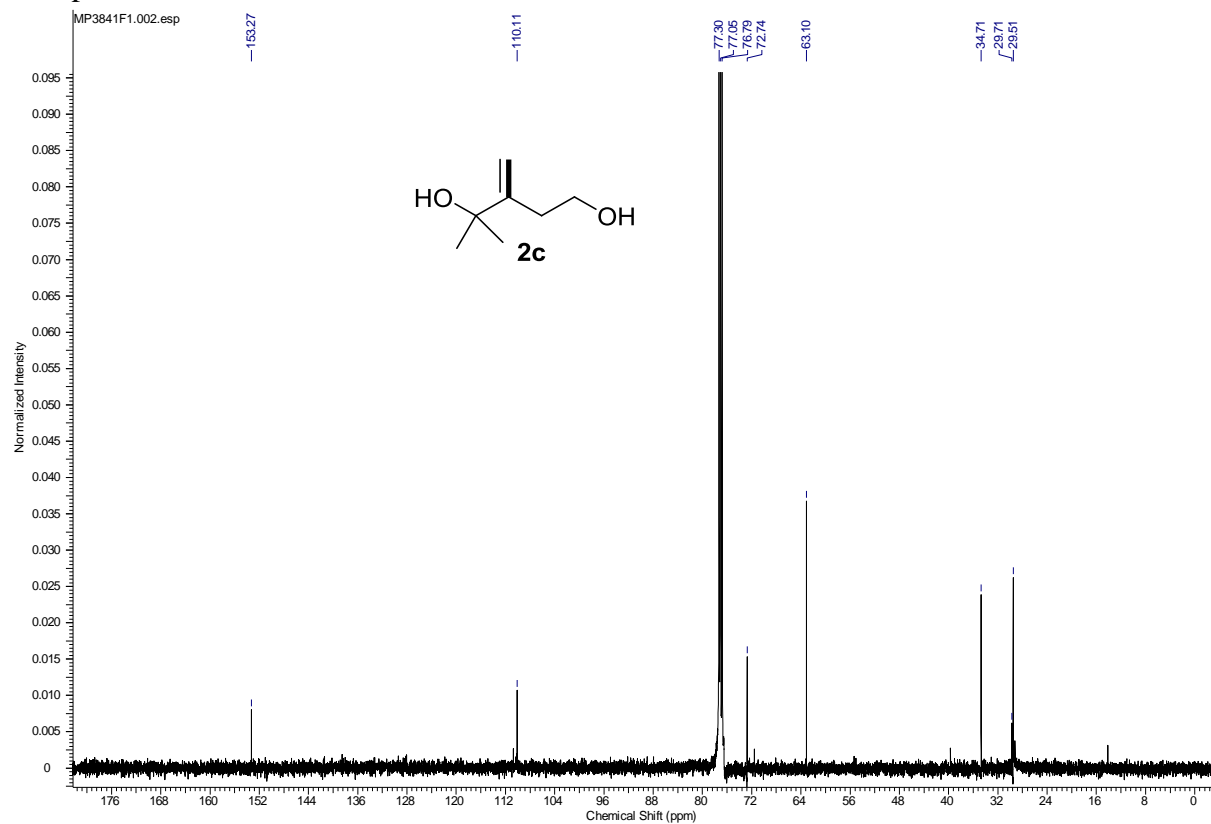
¹³C Spectrum of 2b



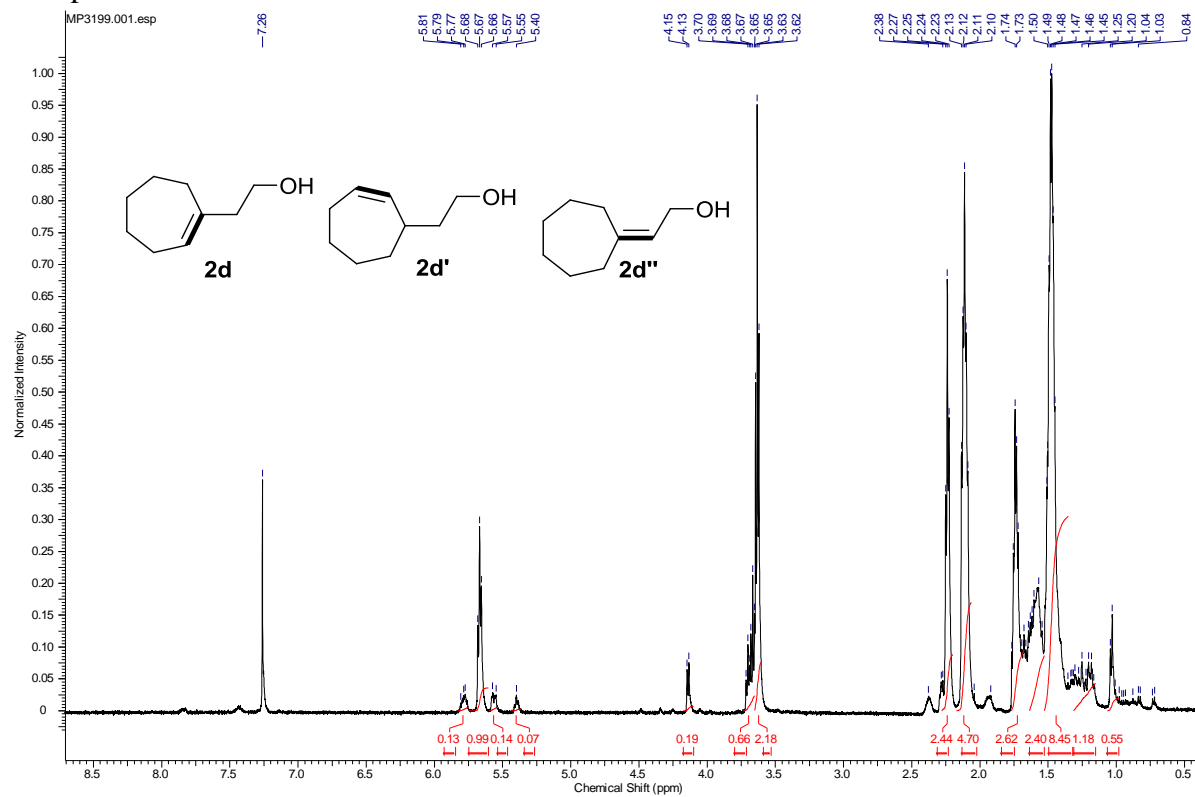
¹H Spectrum of 2c



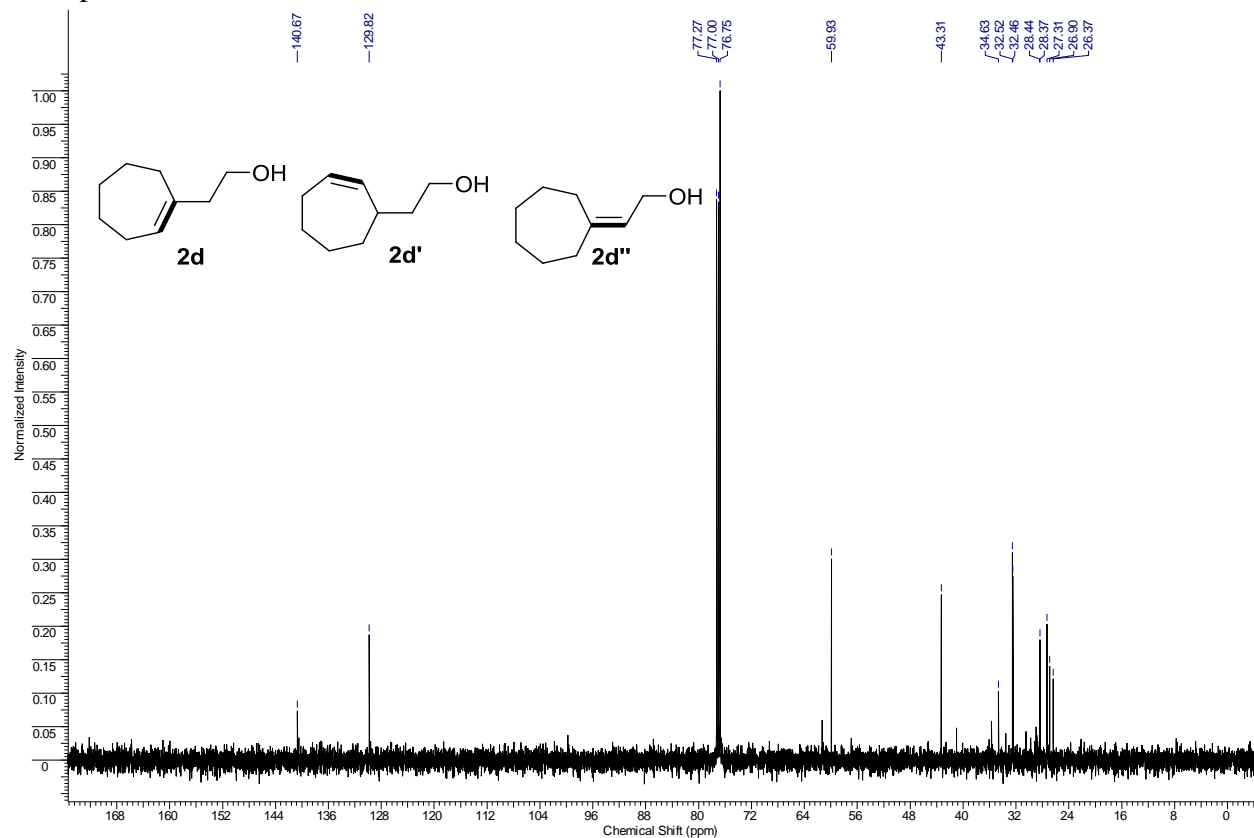
¹³C Spectrum of 2c



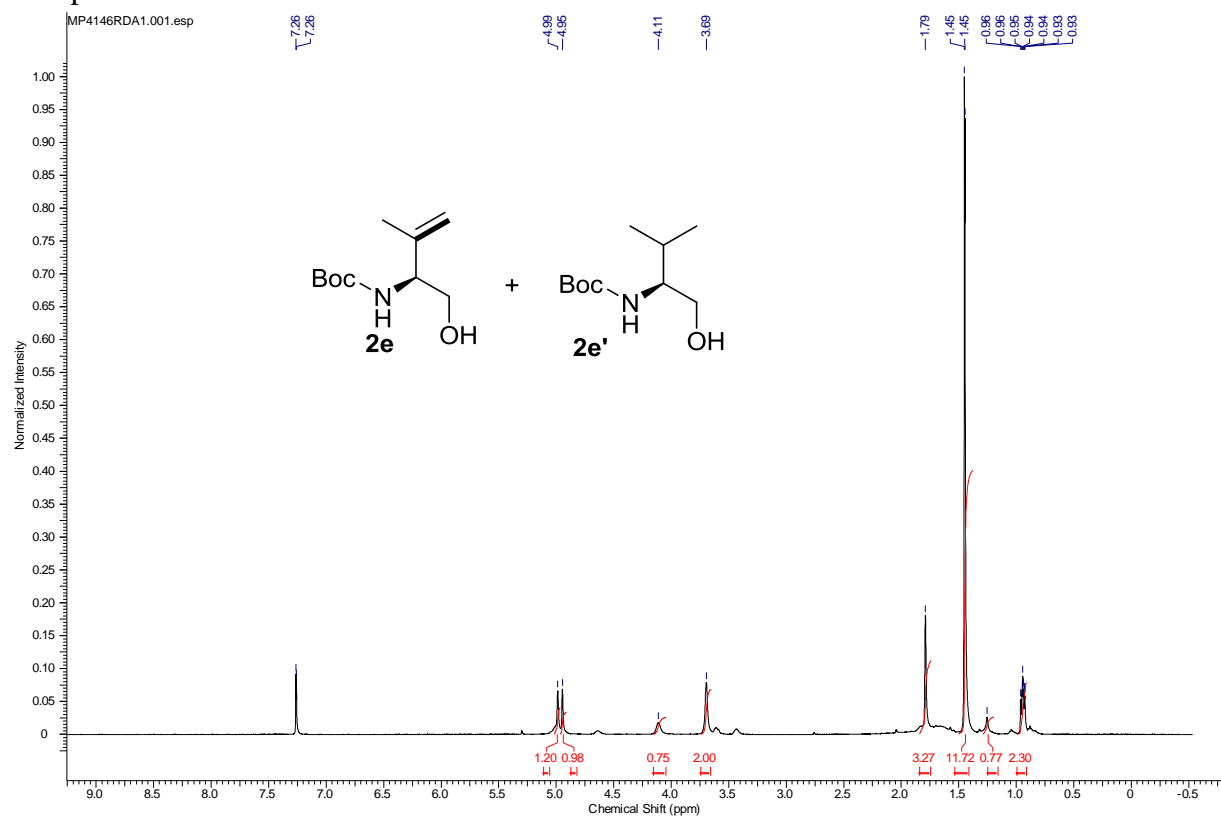
¹H Spectrum of 2d



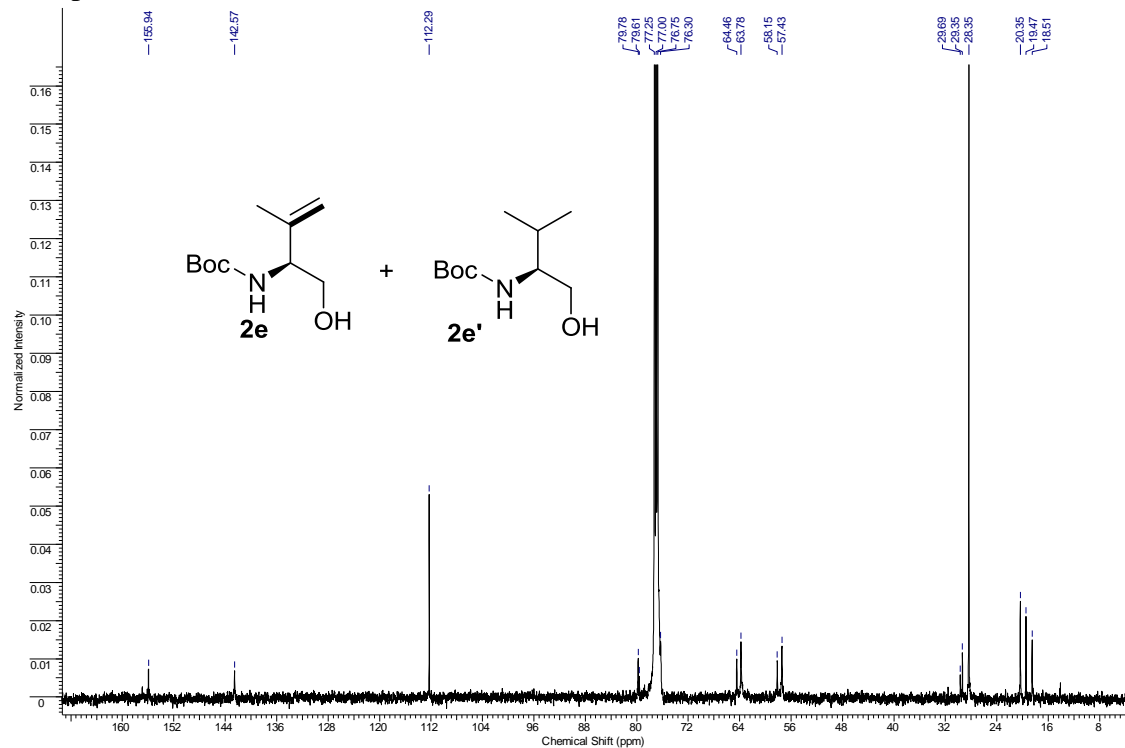
¹³C Spectrum of 2d



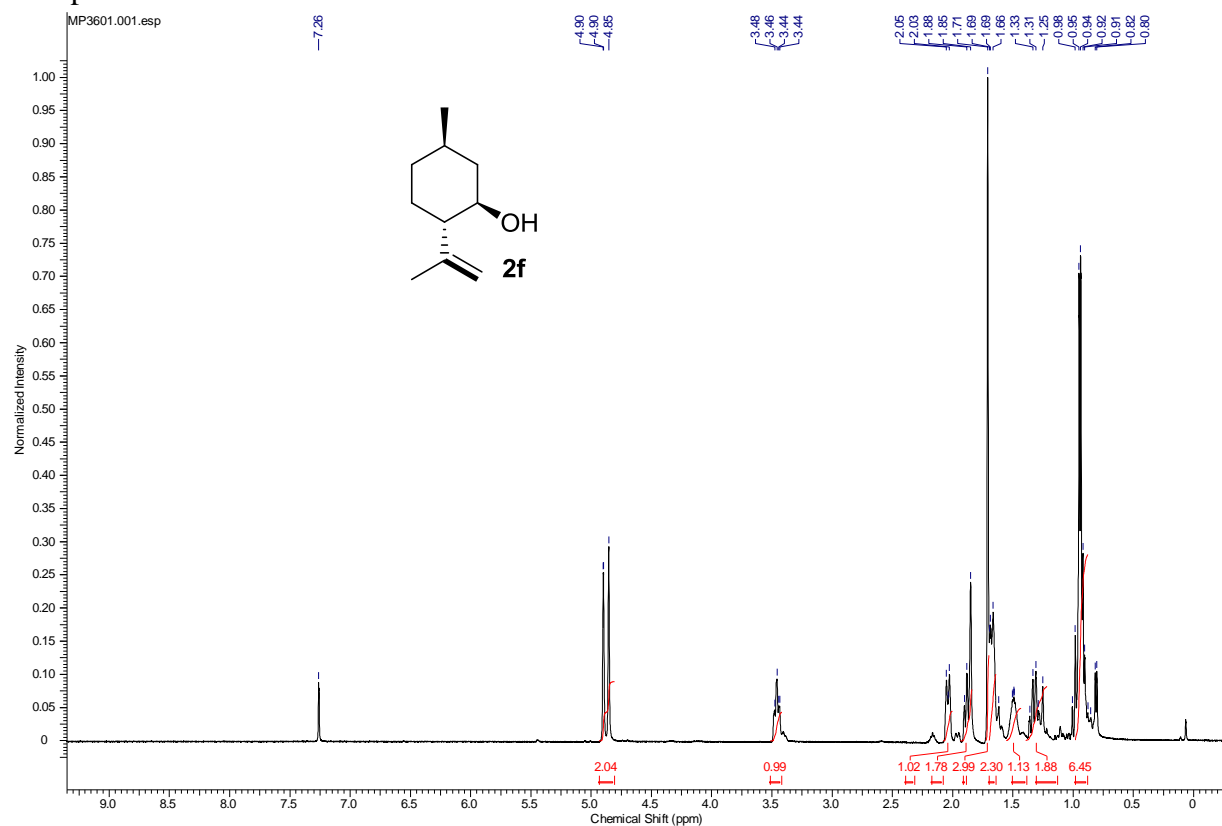
¹H Spectrum of 2e



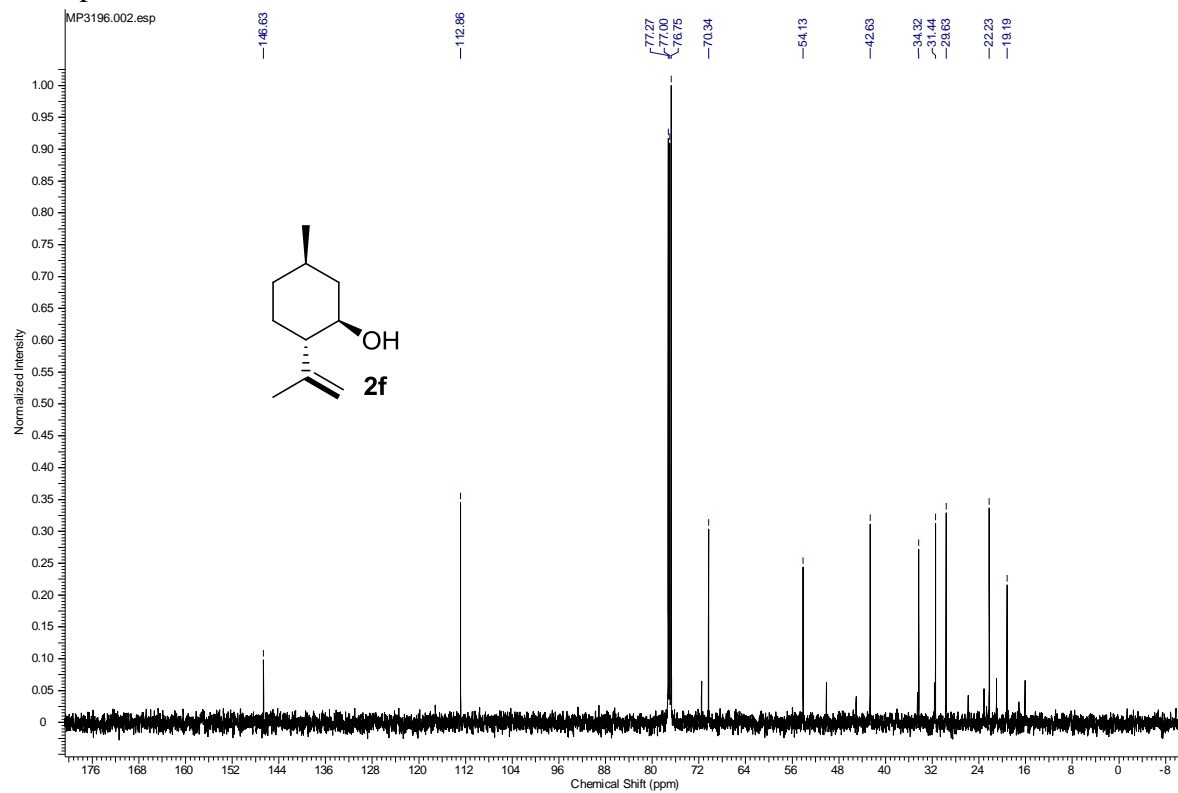
¹³C Spectrum of 2e



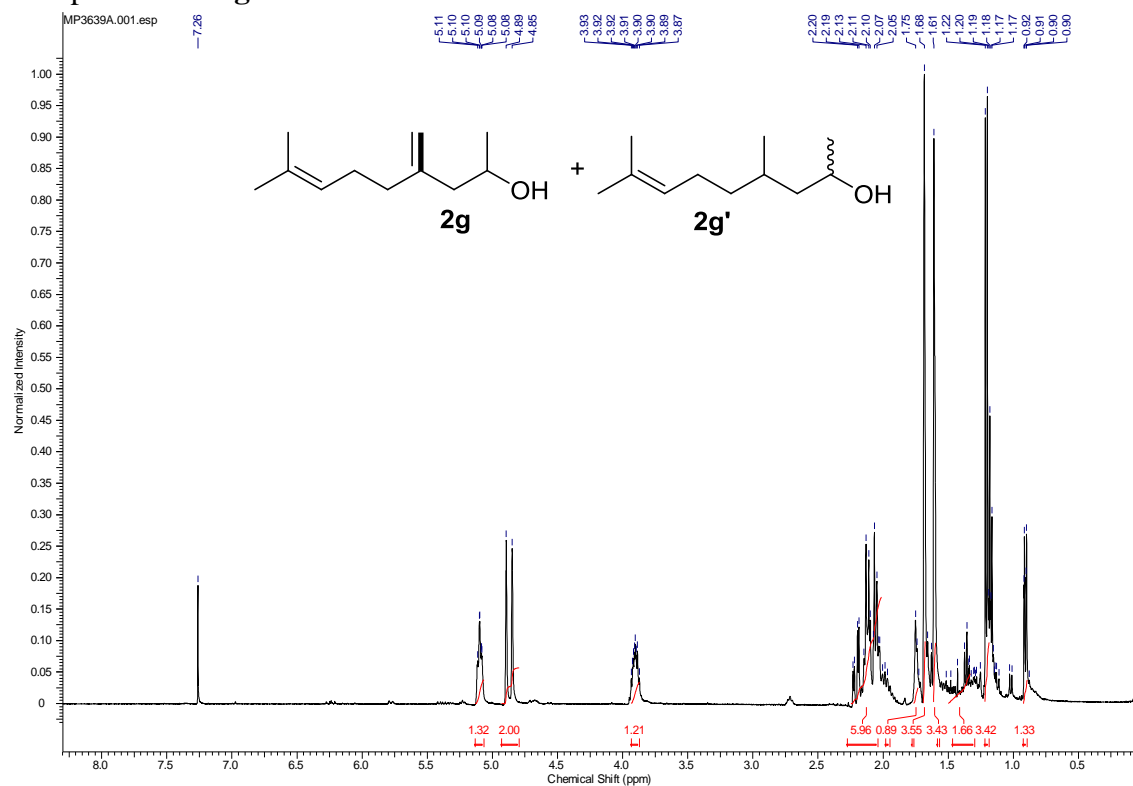
¹H Spectrum of 2f



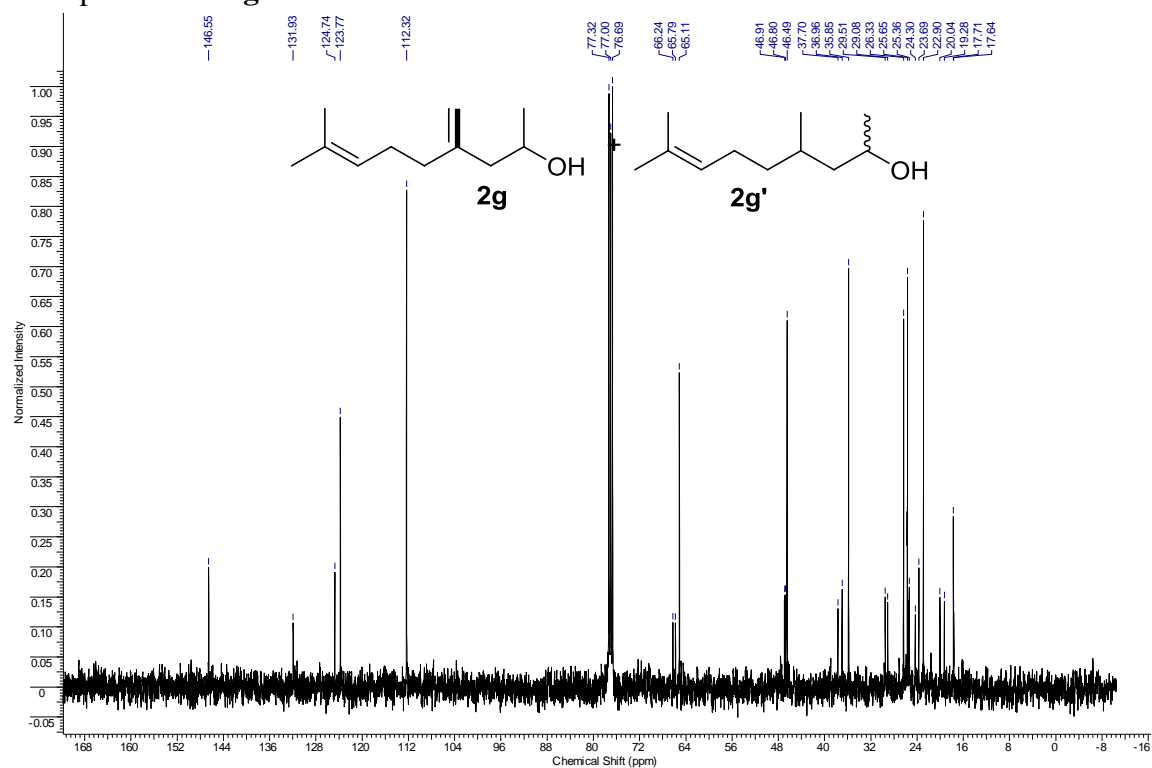
¹³C Spectrum of 2f



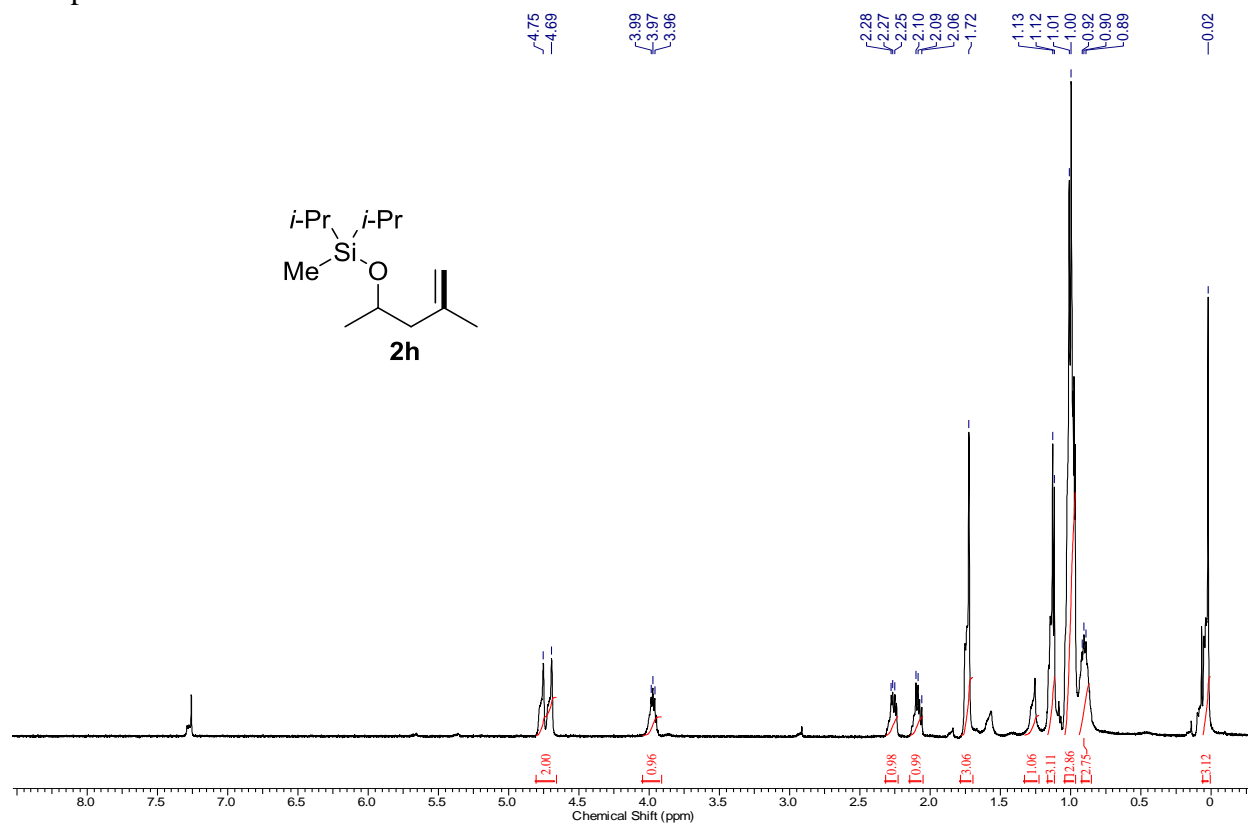
¹H Spectrum of 2g



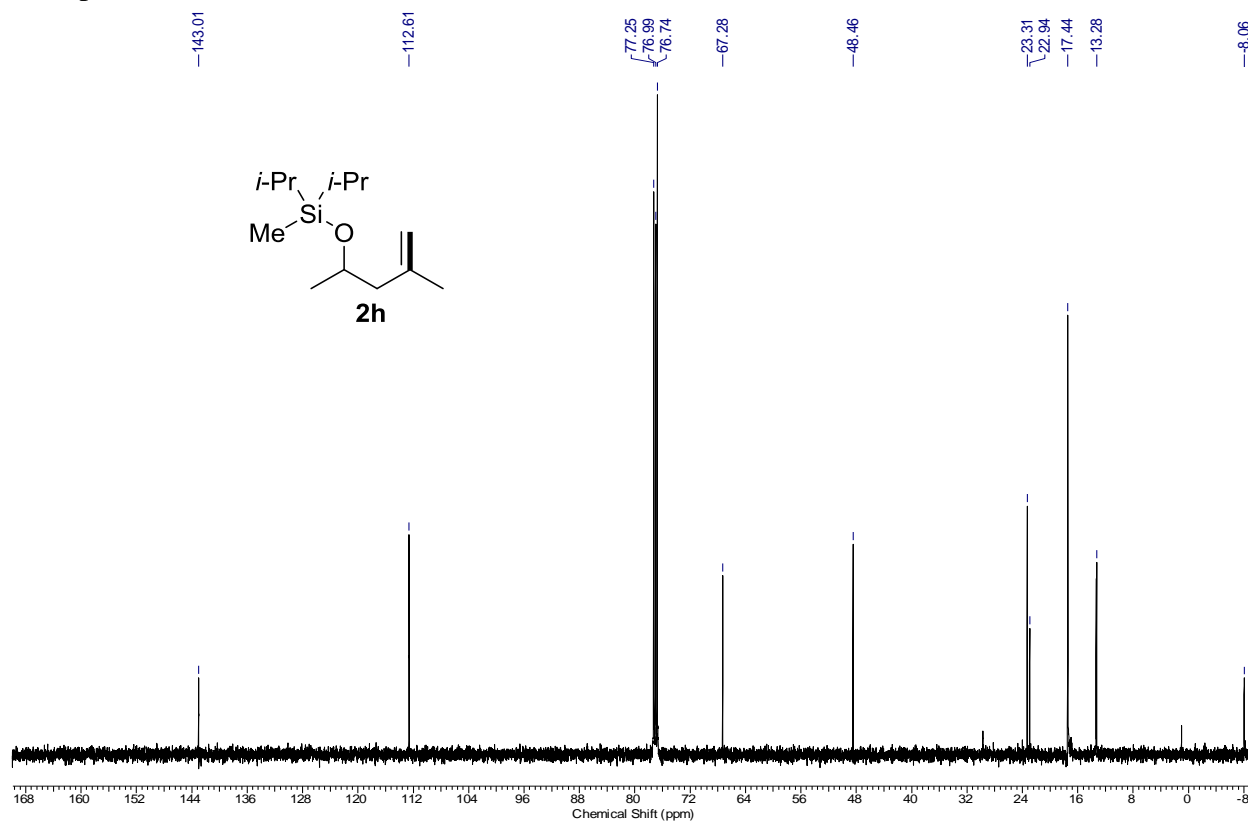
¹³C Spectrum of 2g



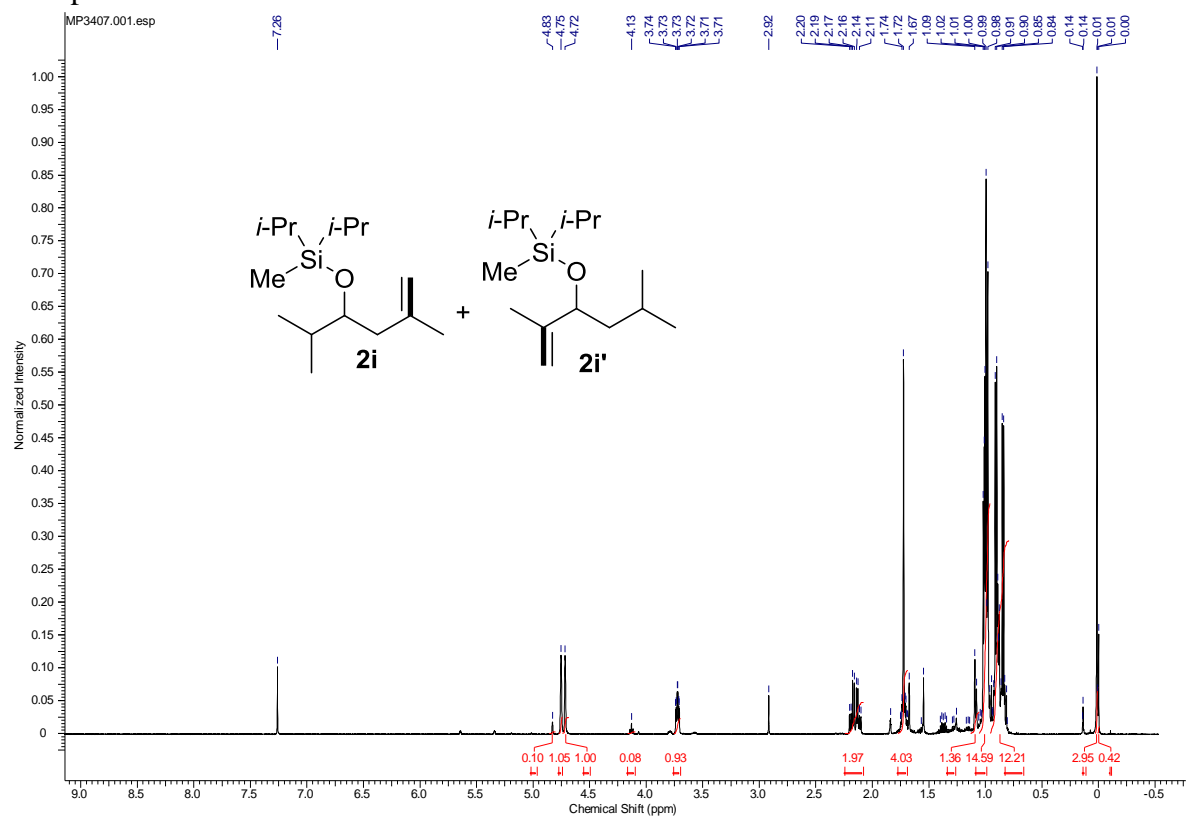
¹H Spectrum of **2h**



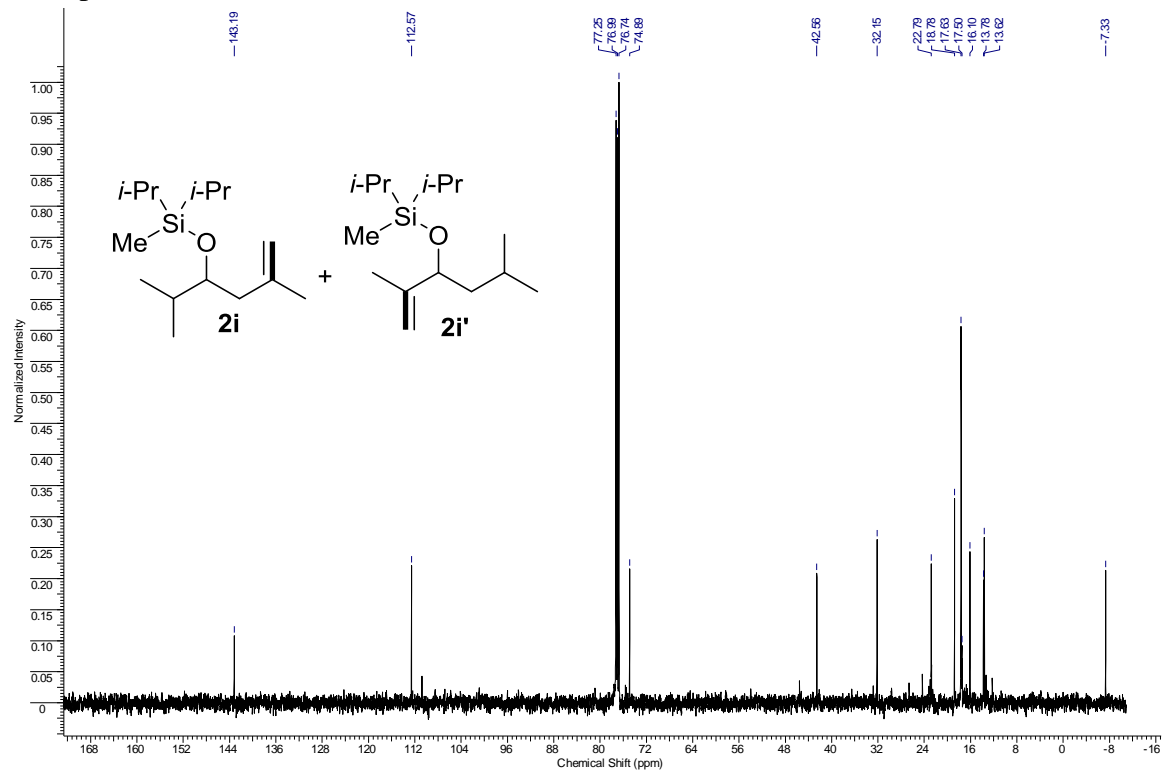
¹³C Spectrum of **2h**



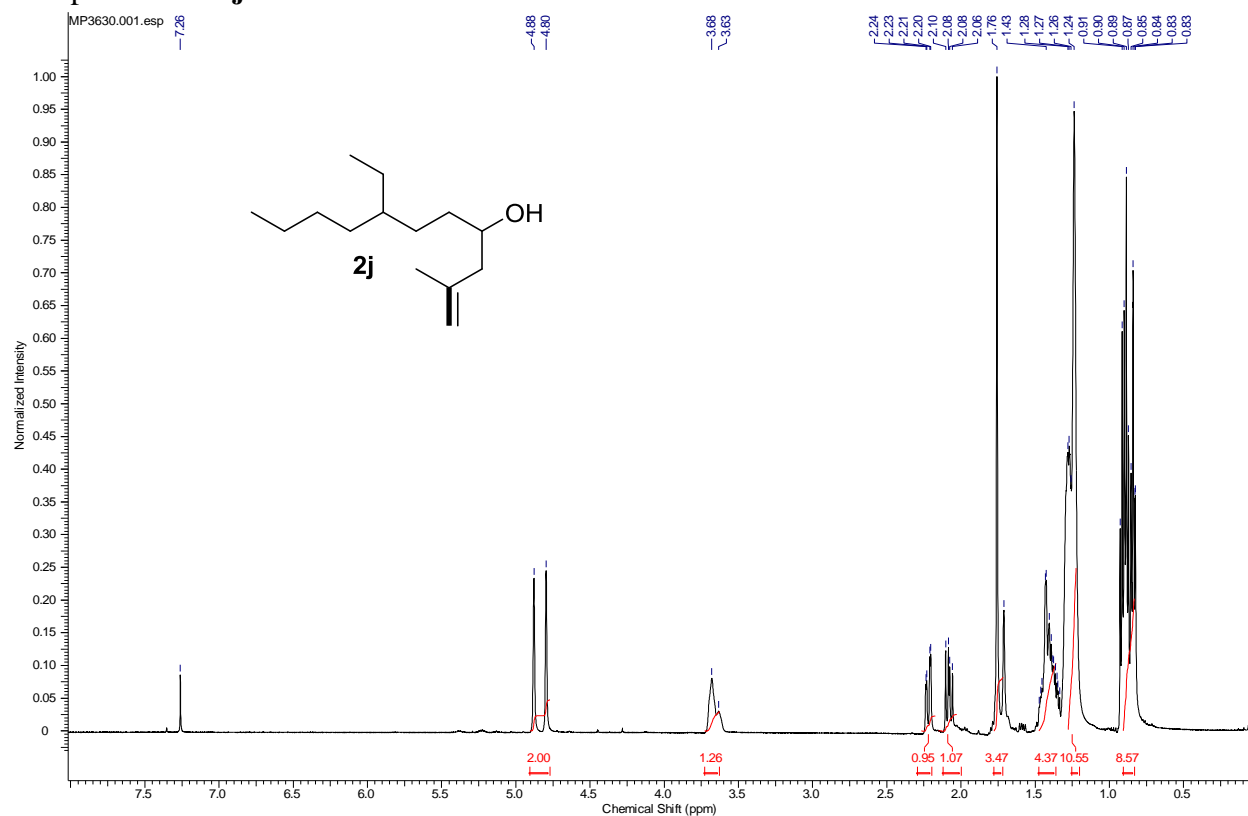
¹H Spectrum of **2i**



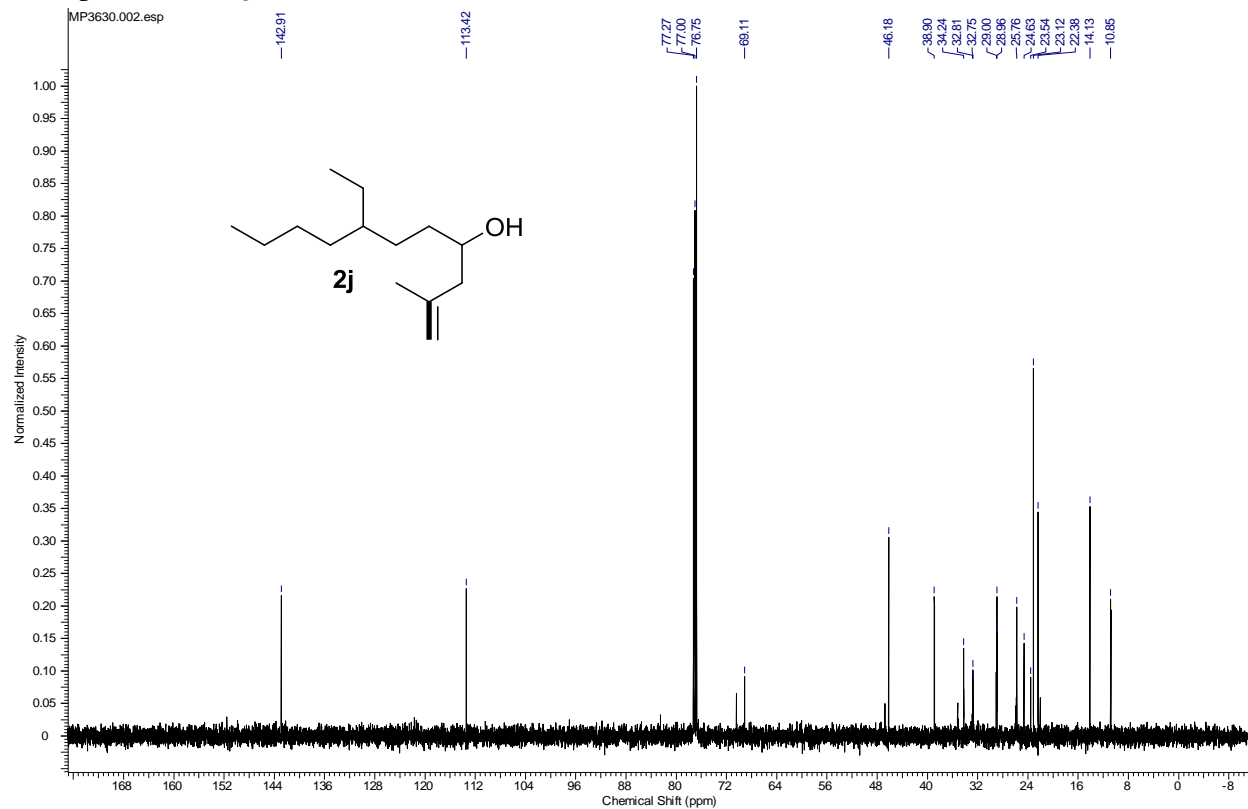
¹³C Spectrum of **2i**



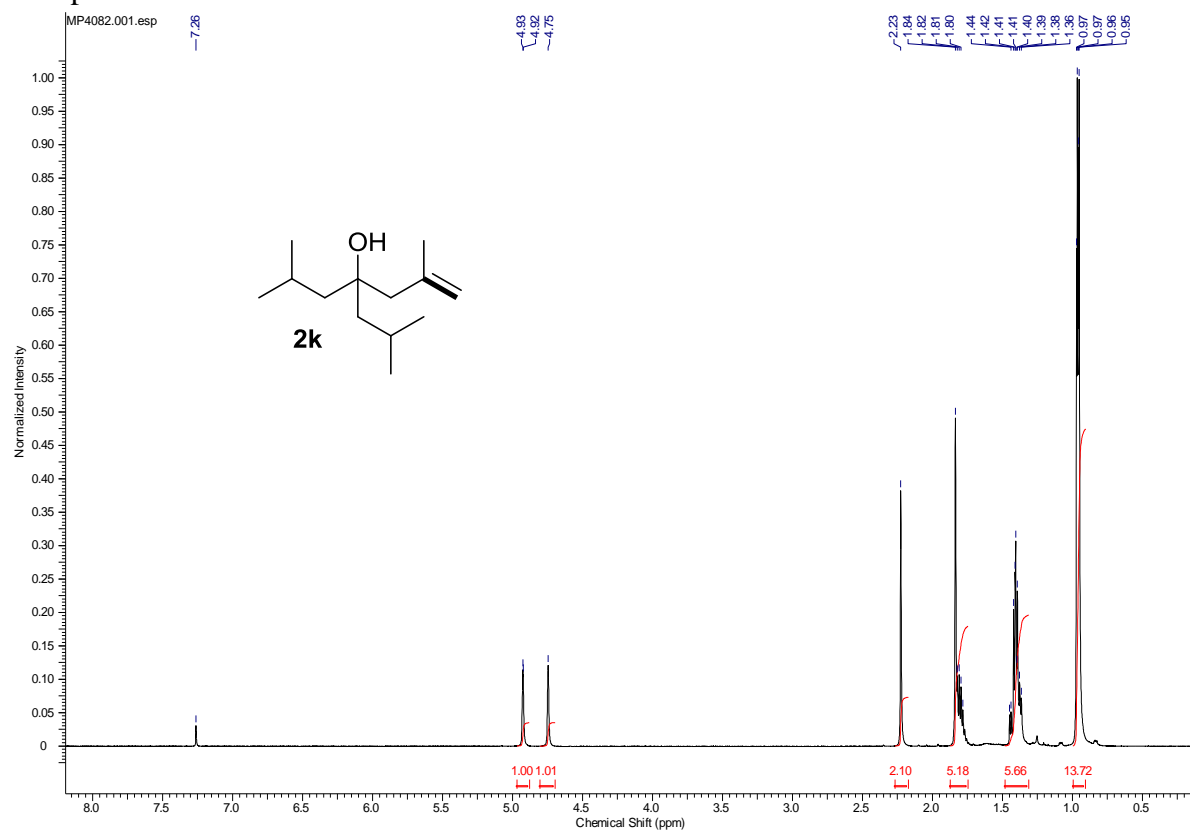
¹H Spectrum of 2j



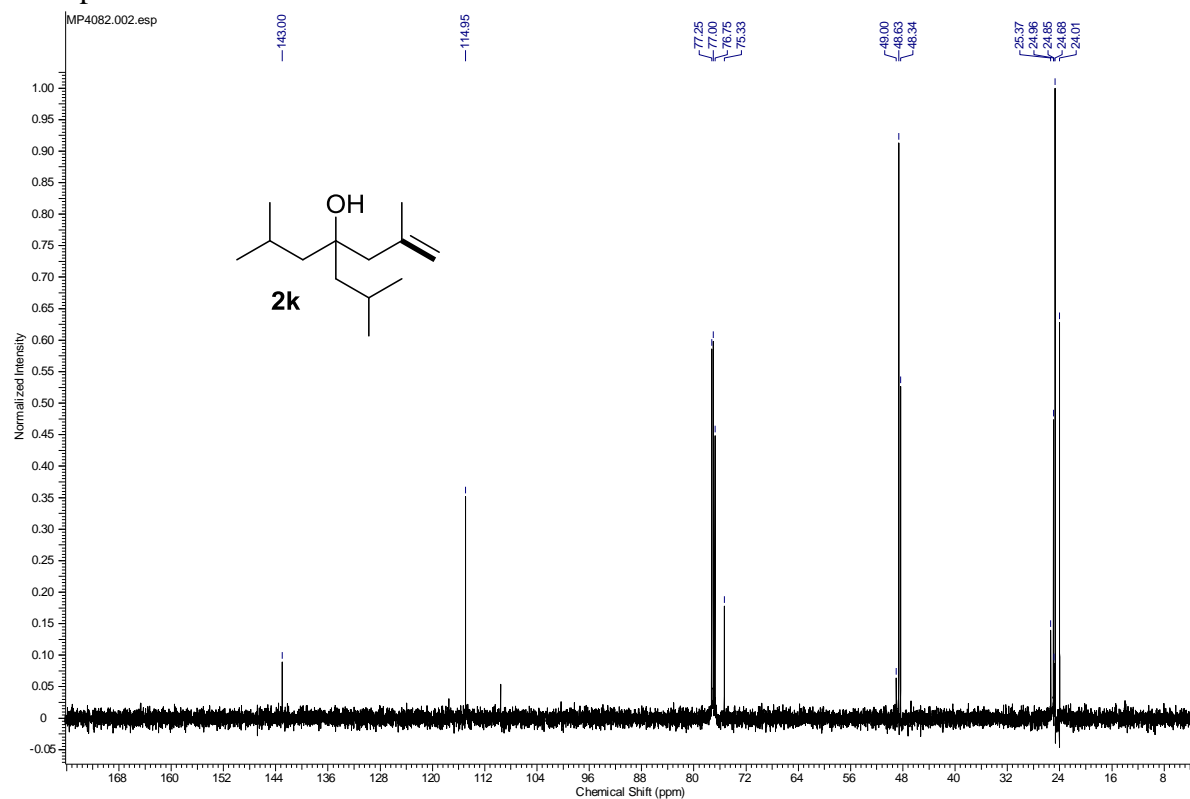
¹³C Spectrum of 2j



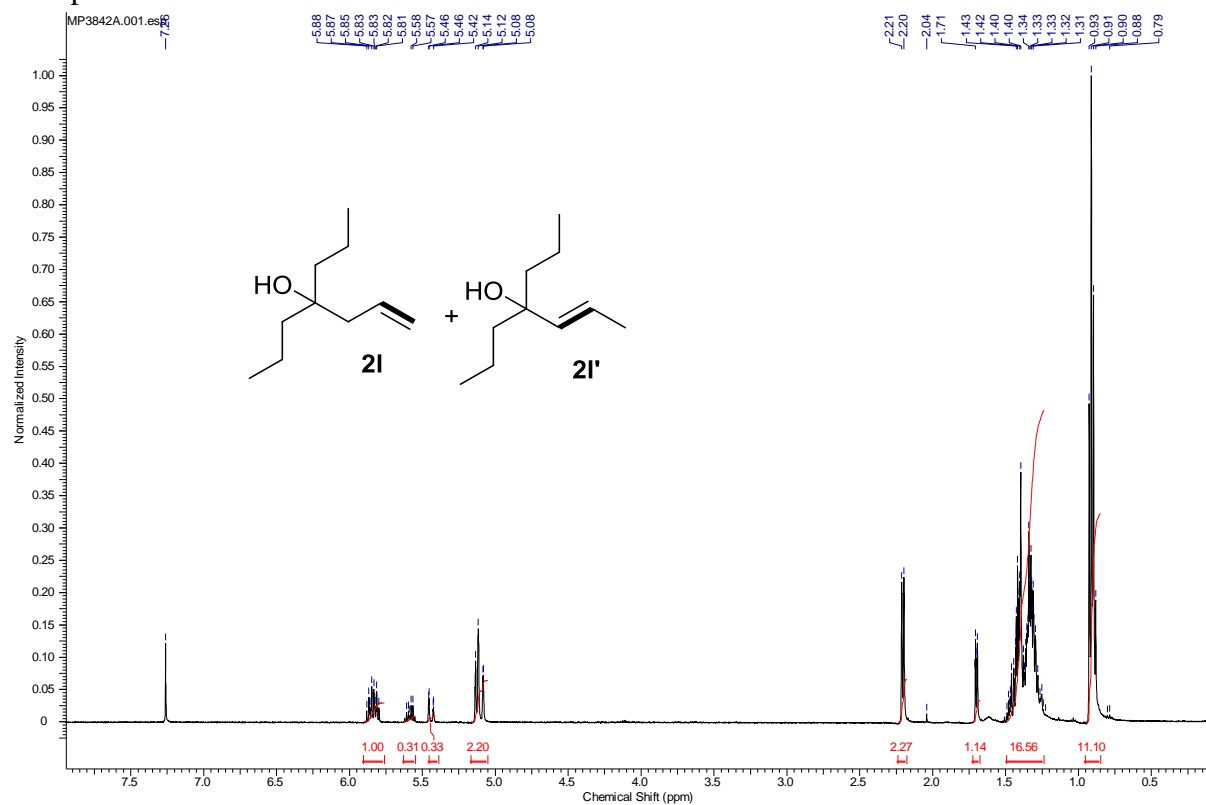
¹H Spectrum of 2k



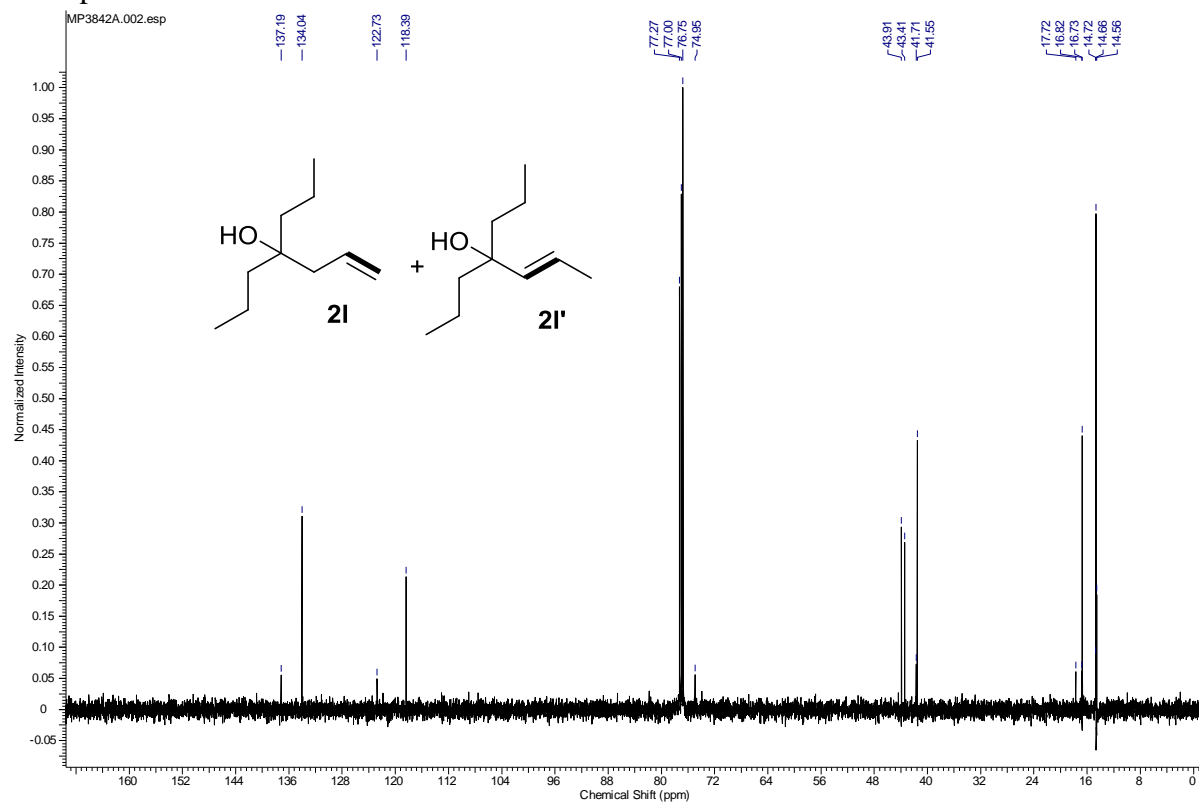
¹³C Spectrum of 2k



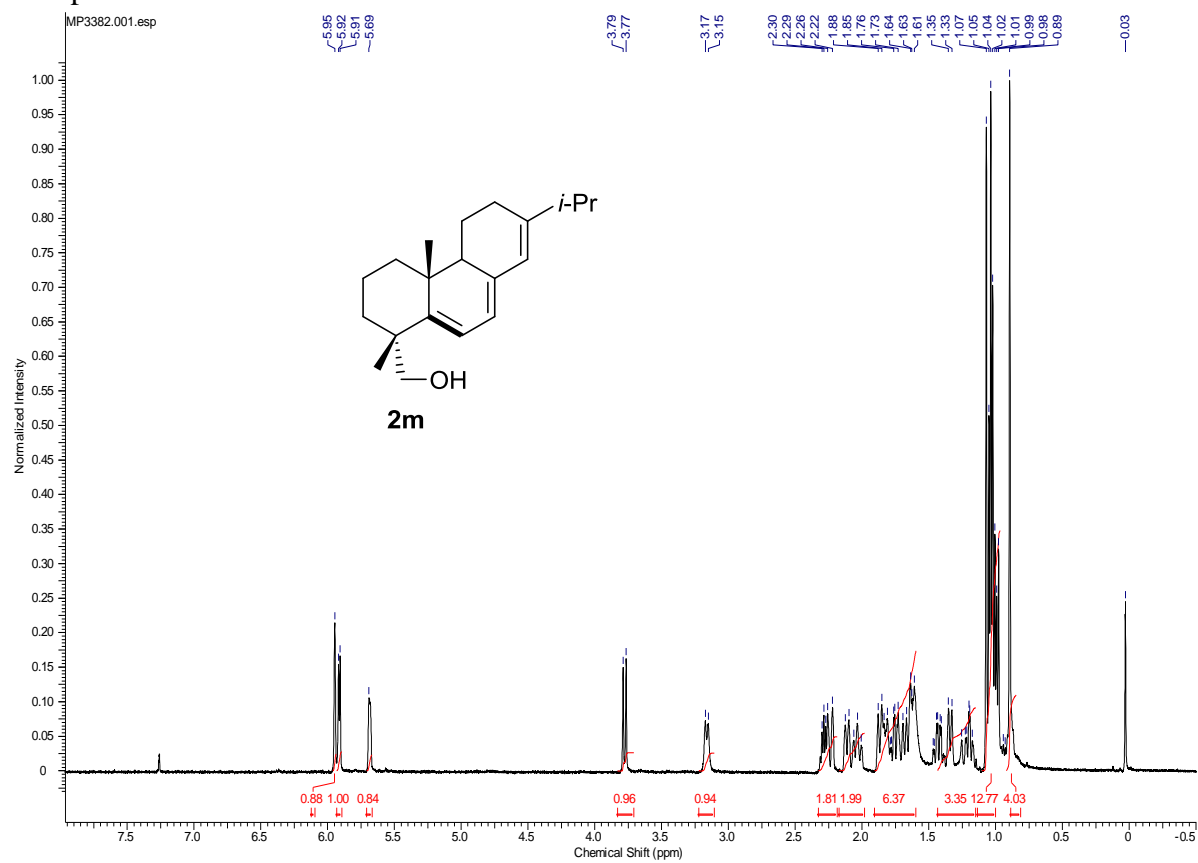
¹H Spectrum of 21



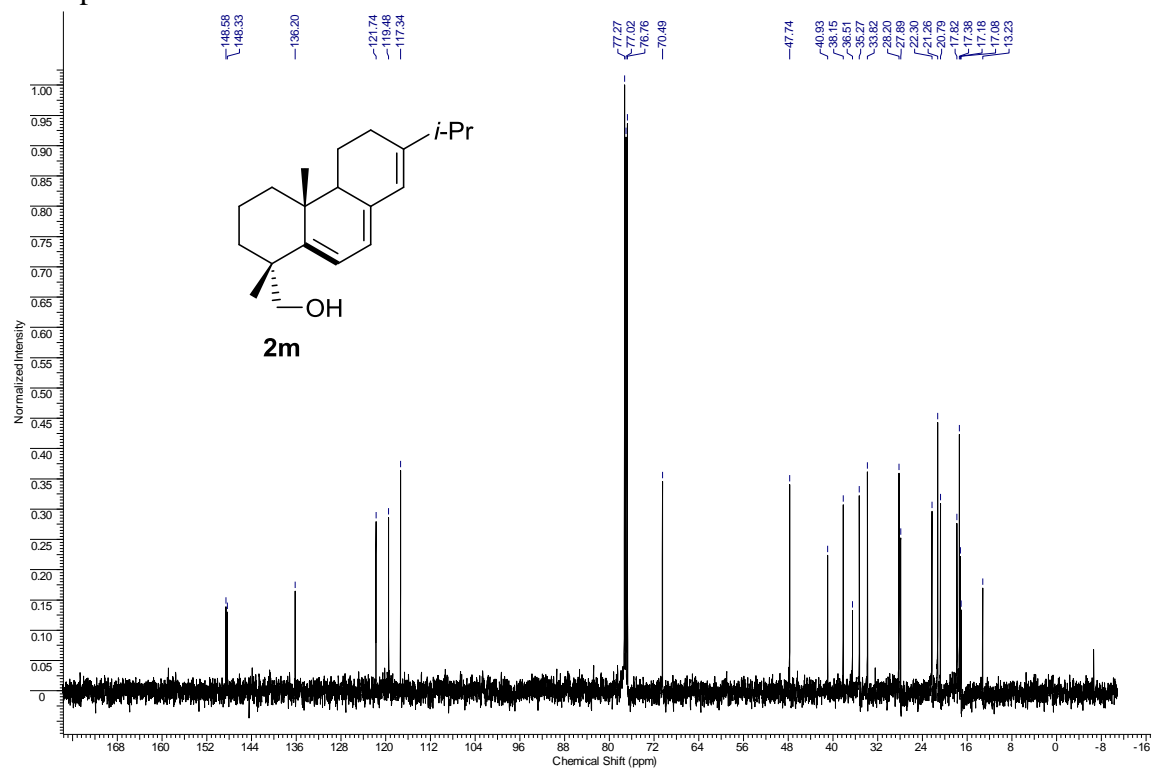
¹³C Spectrum of 21



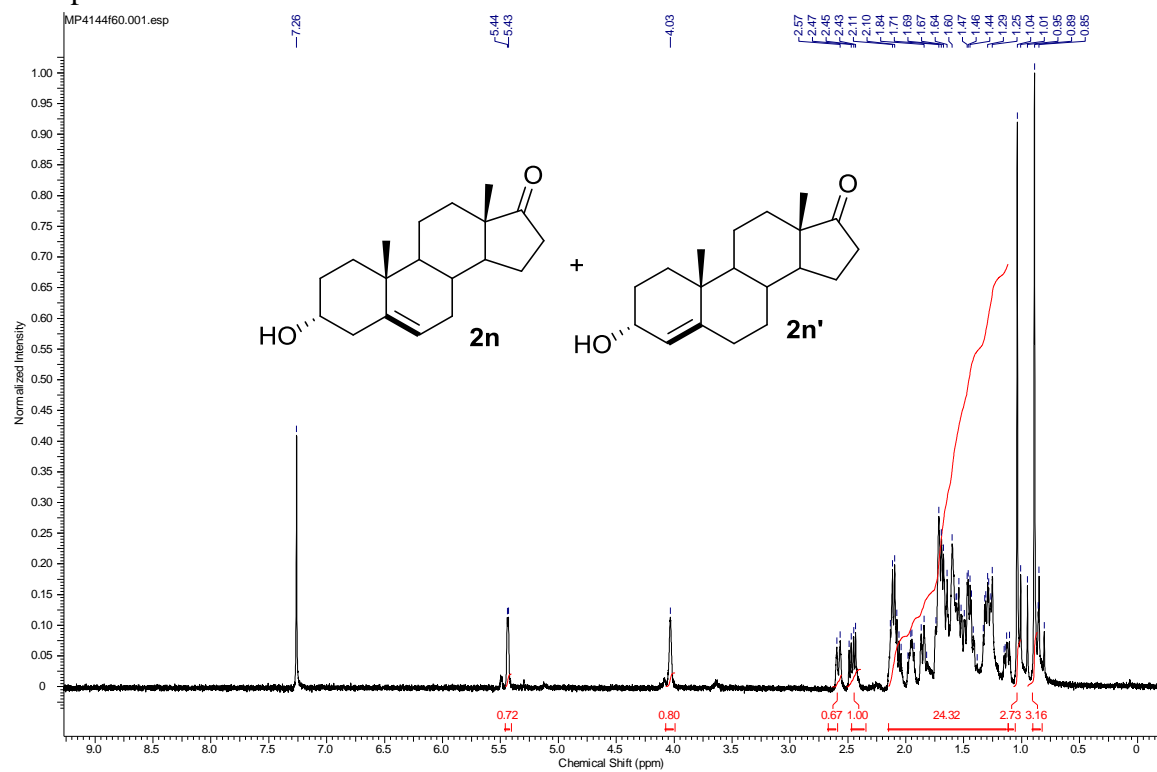
¹H Spectrum of 2m



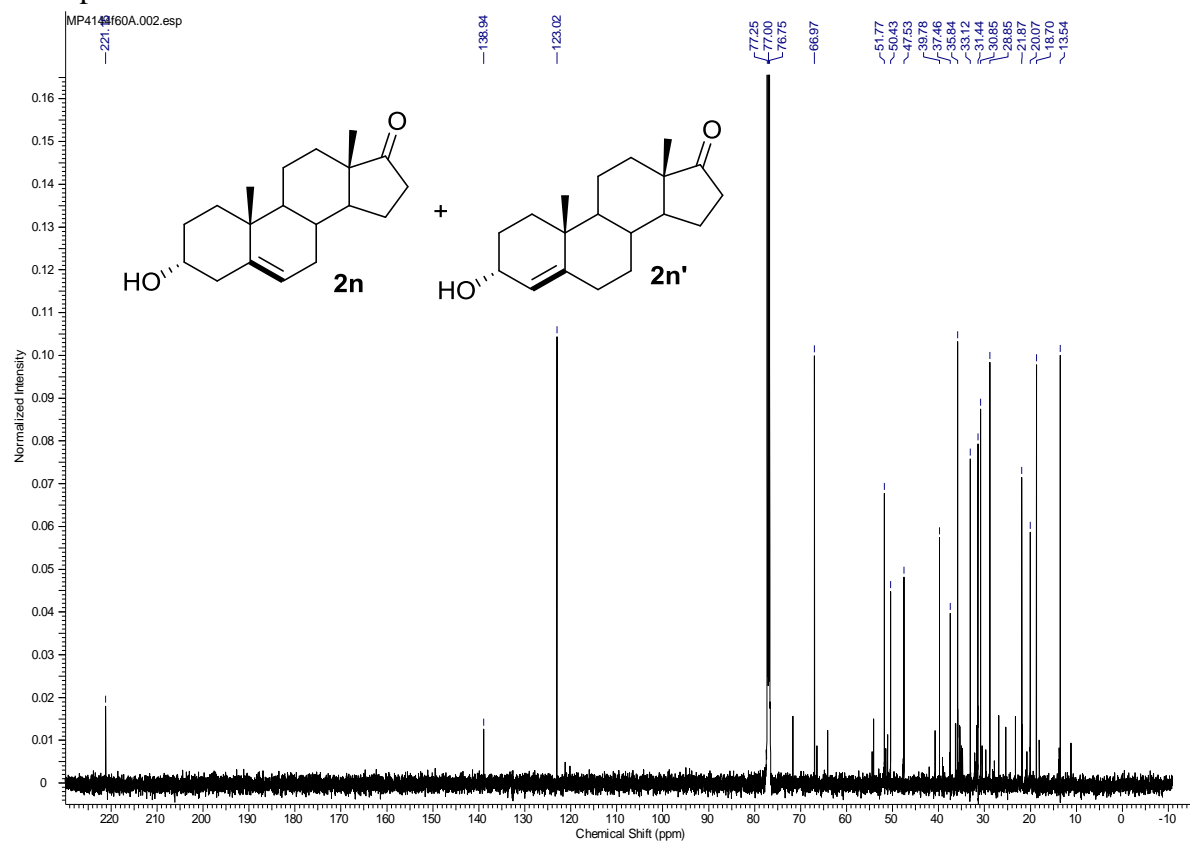
¹³C Spectrum of 2m



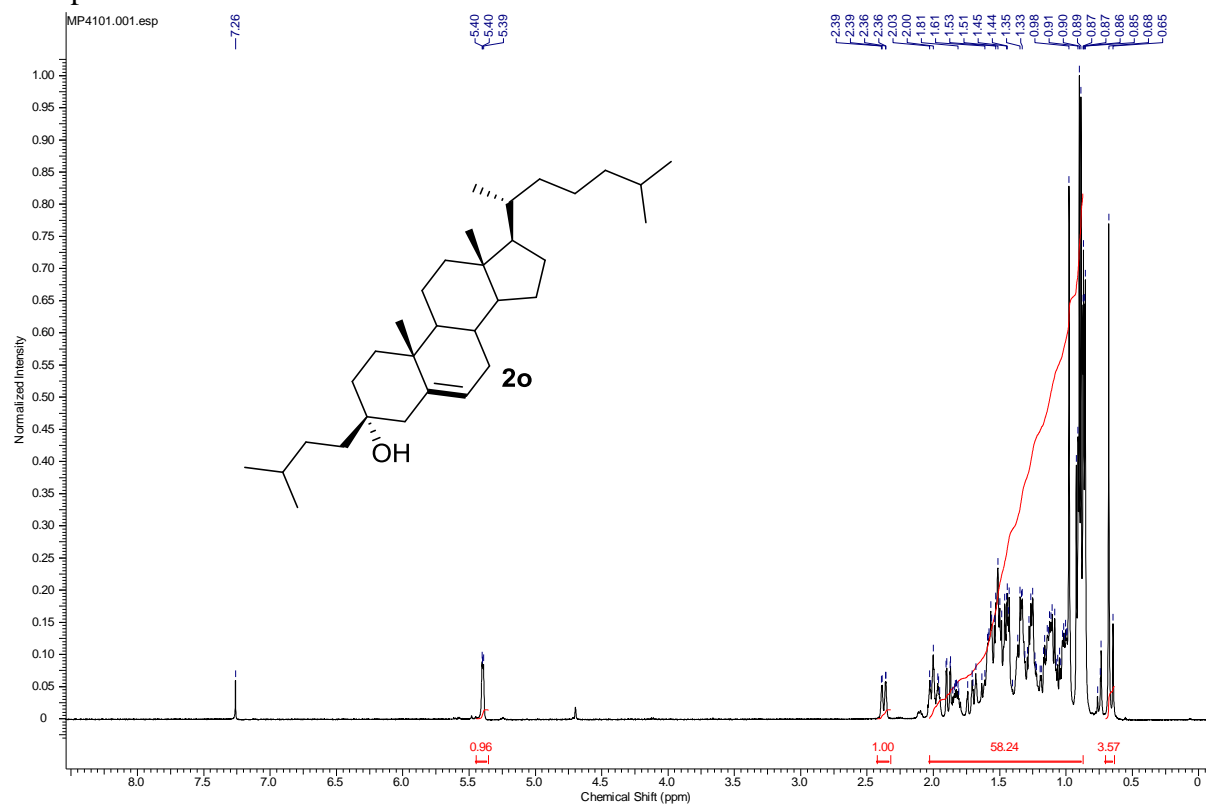
¹H Spectrum of 2n



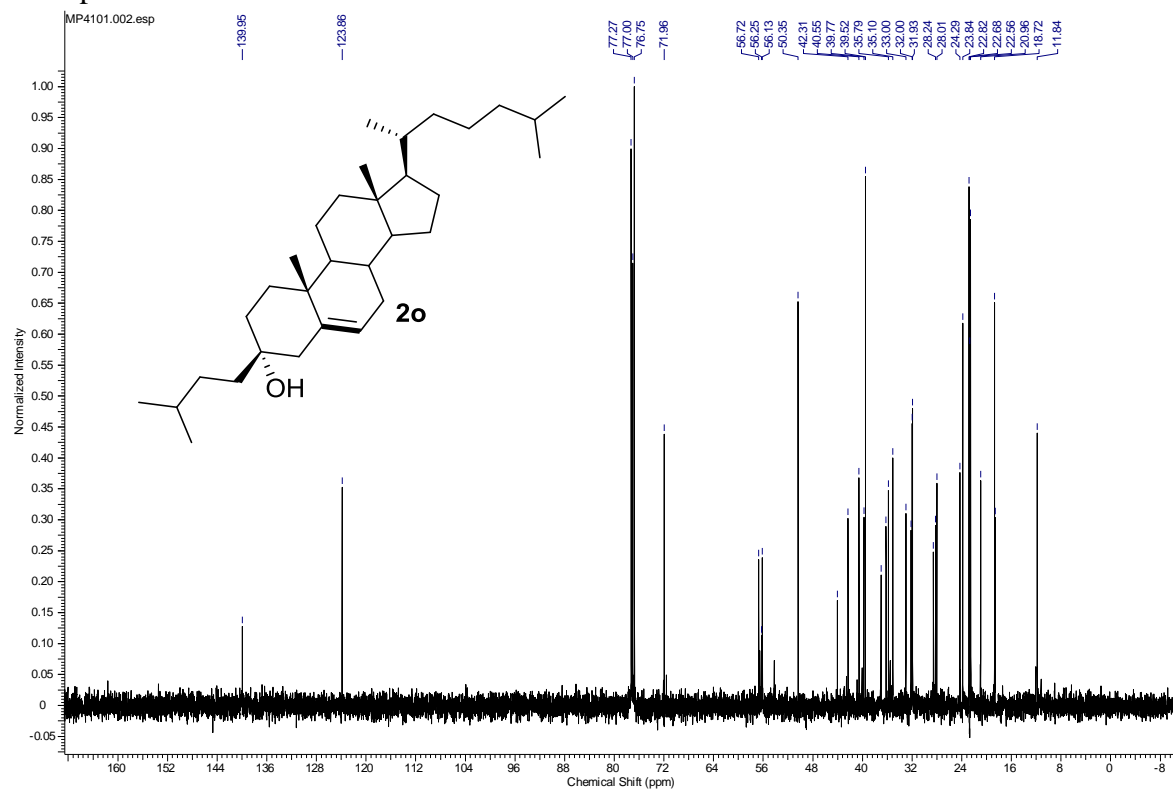
¹³C Spectrum of 2n



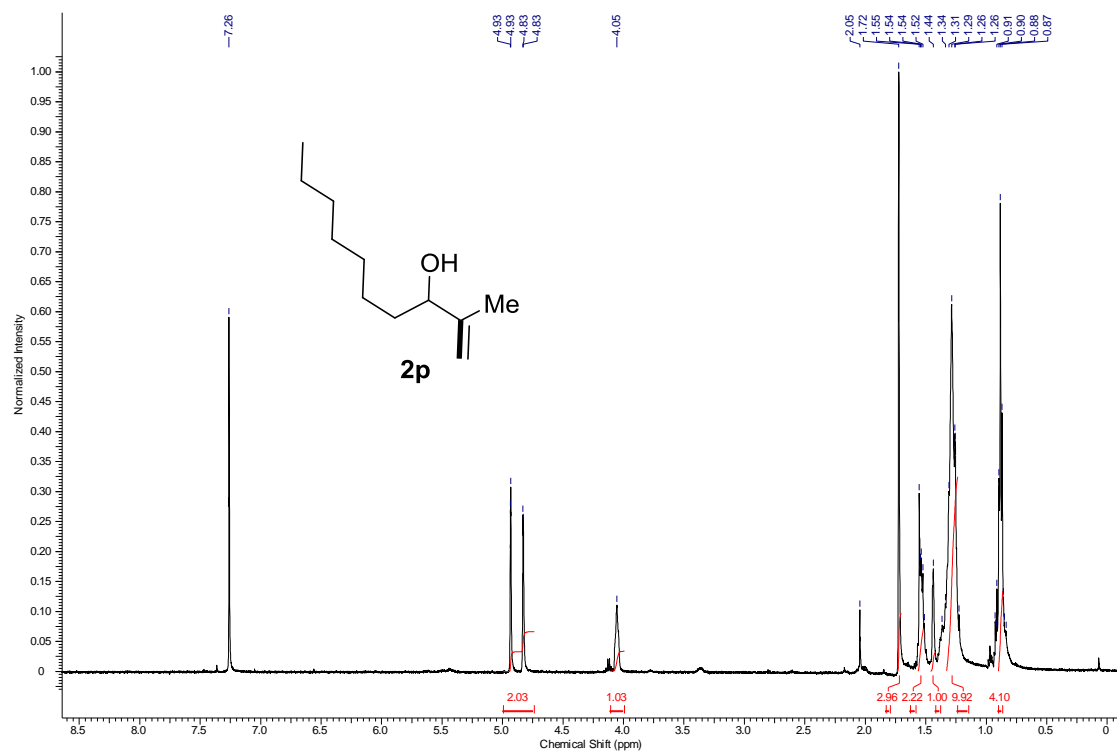
¹H Spectrum of 2o



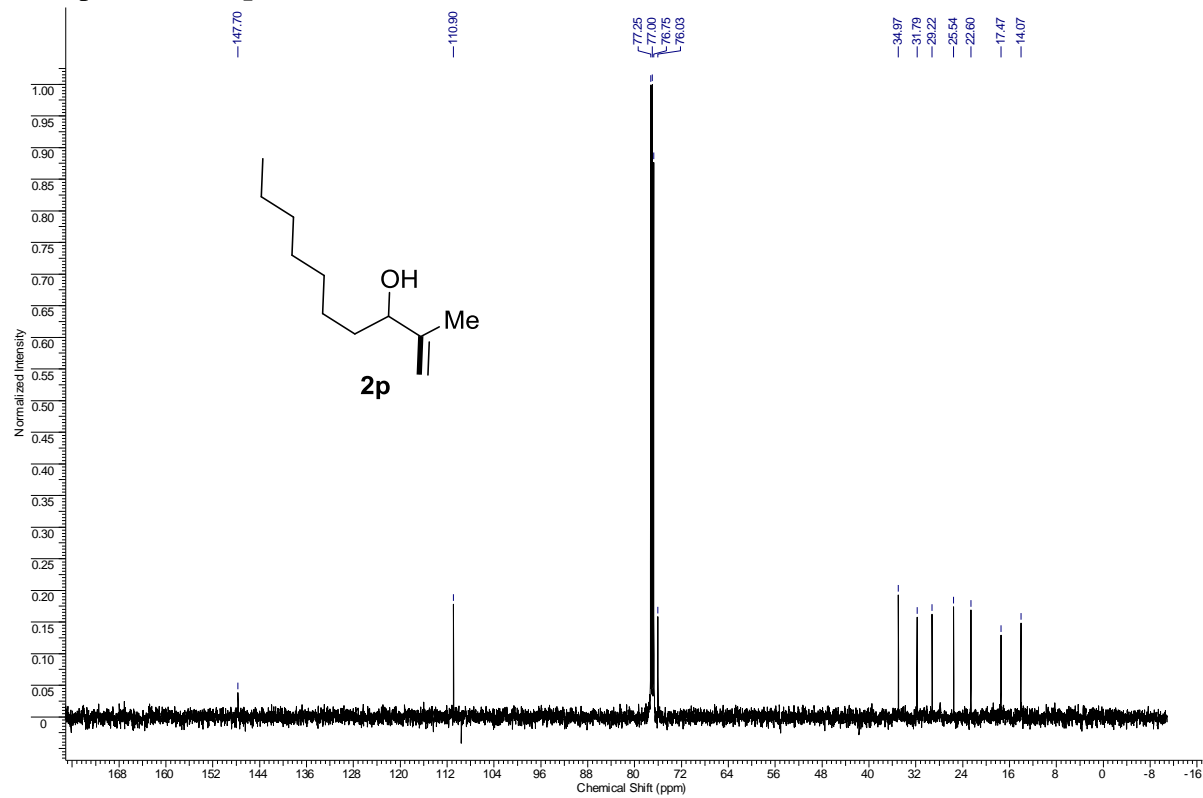
¹³C Spectrum of 2o



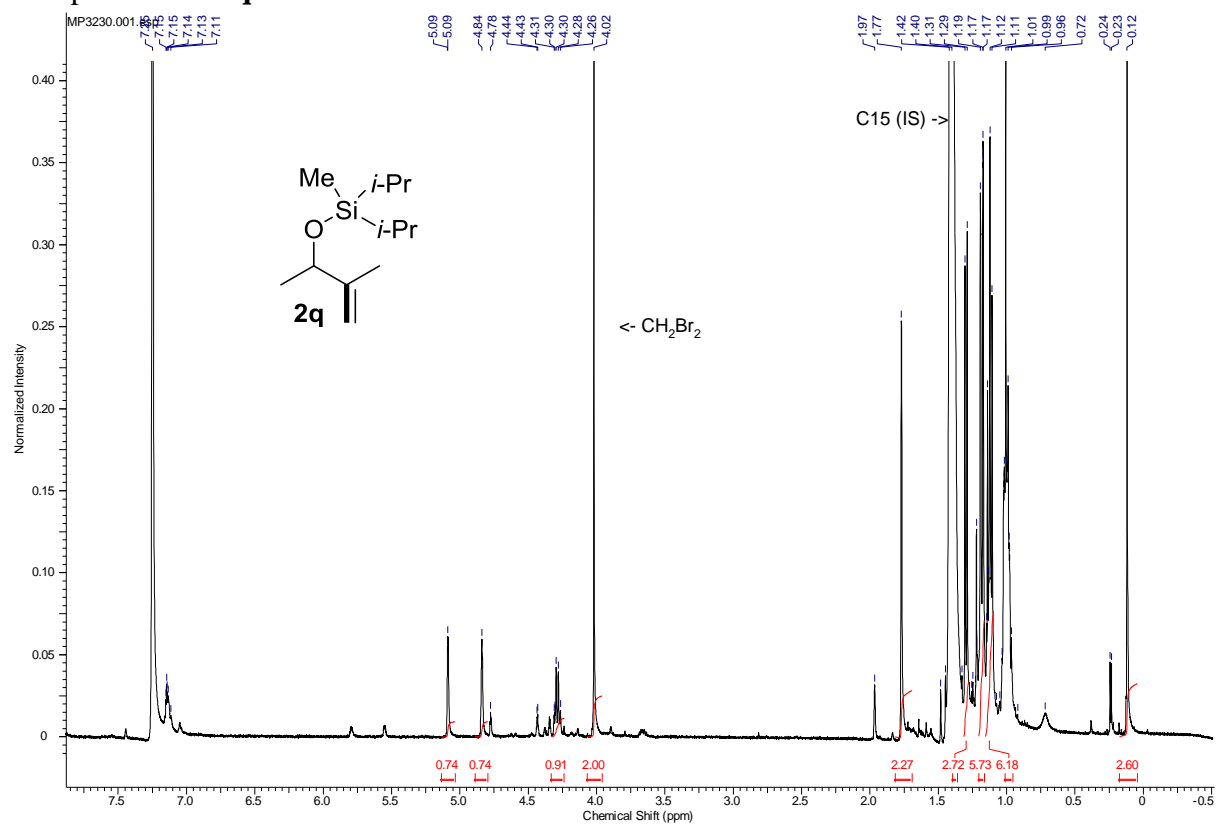
¹H Spectrum of 2p



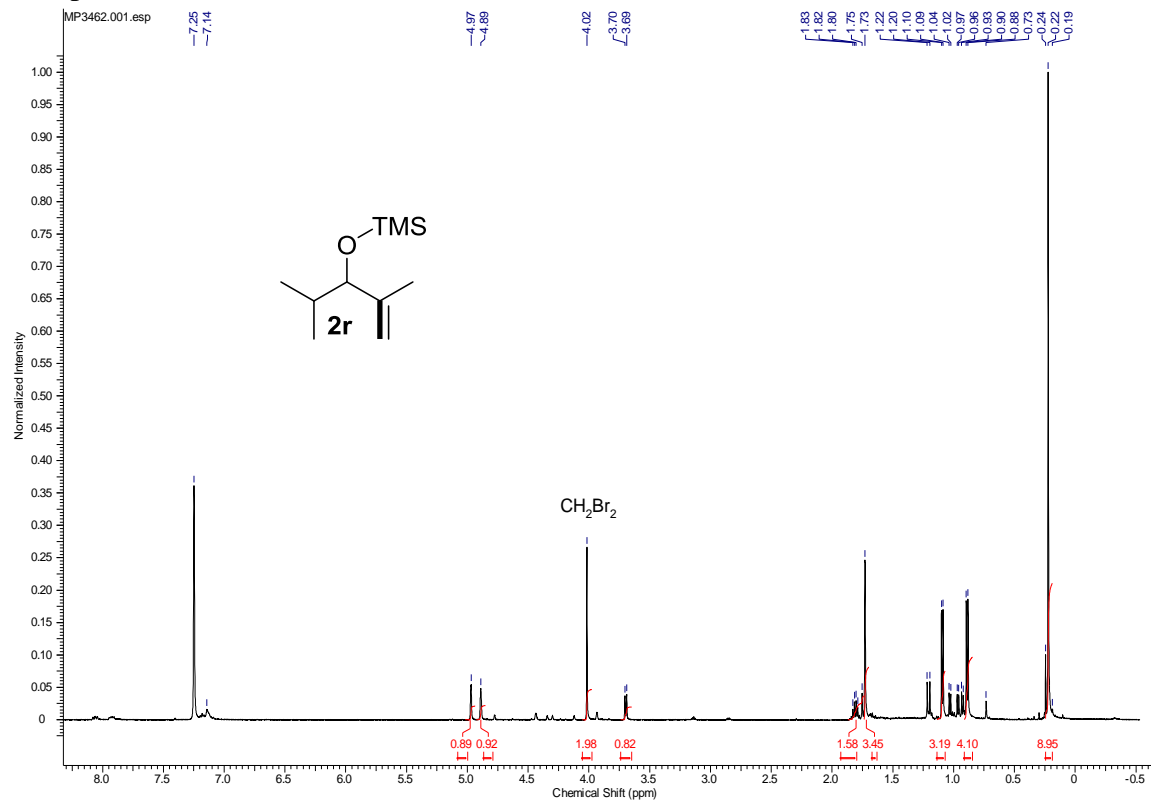
¹³C Spectrum of 2p



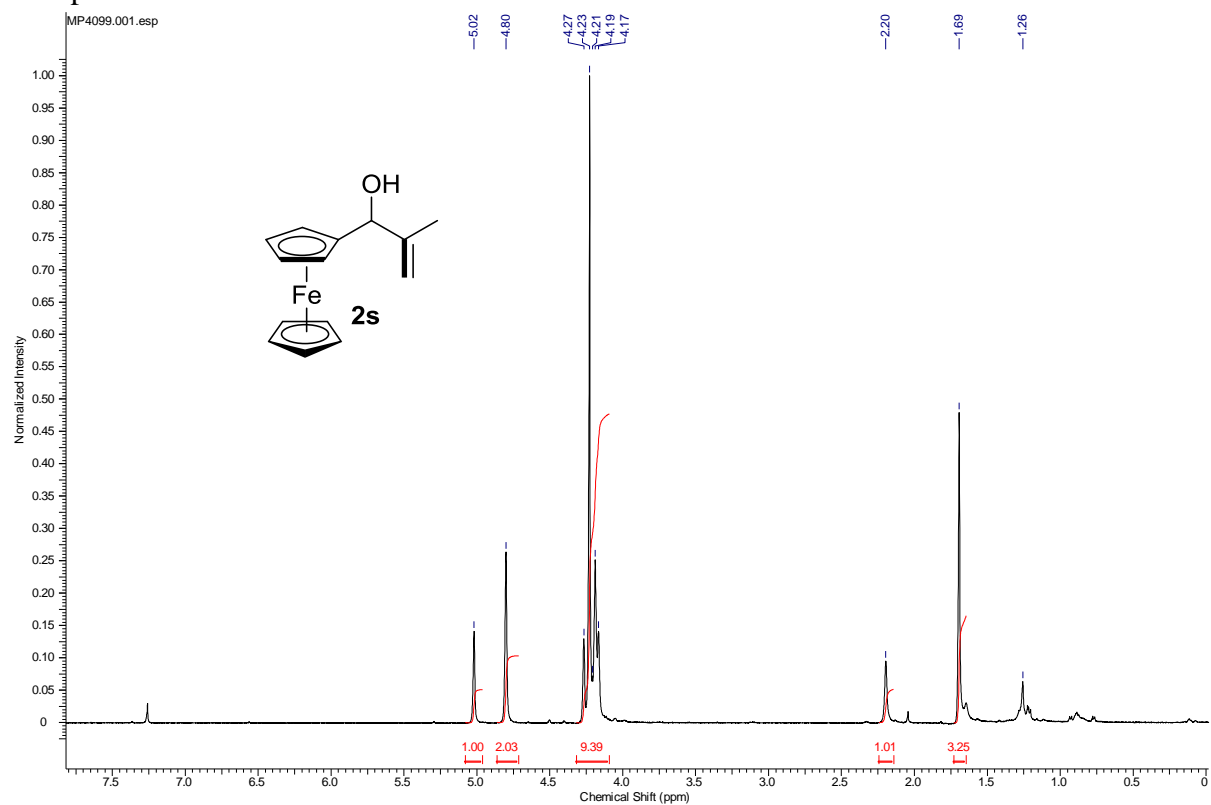
¹H Spectrum of 2q



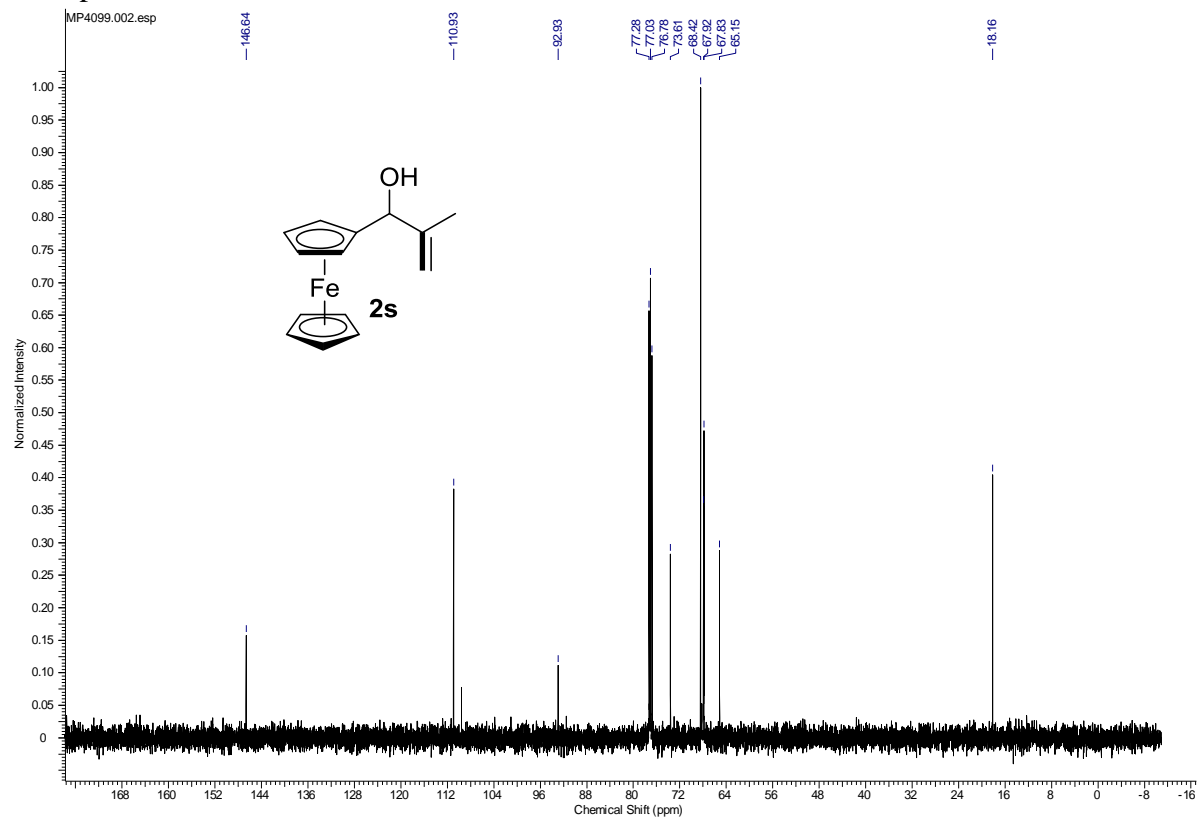
¹H Spectrum of 2r



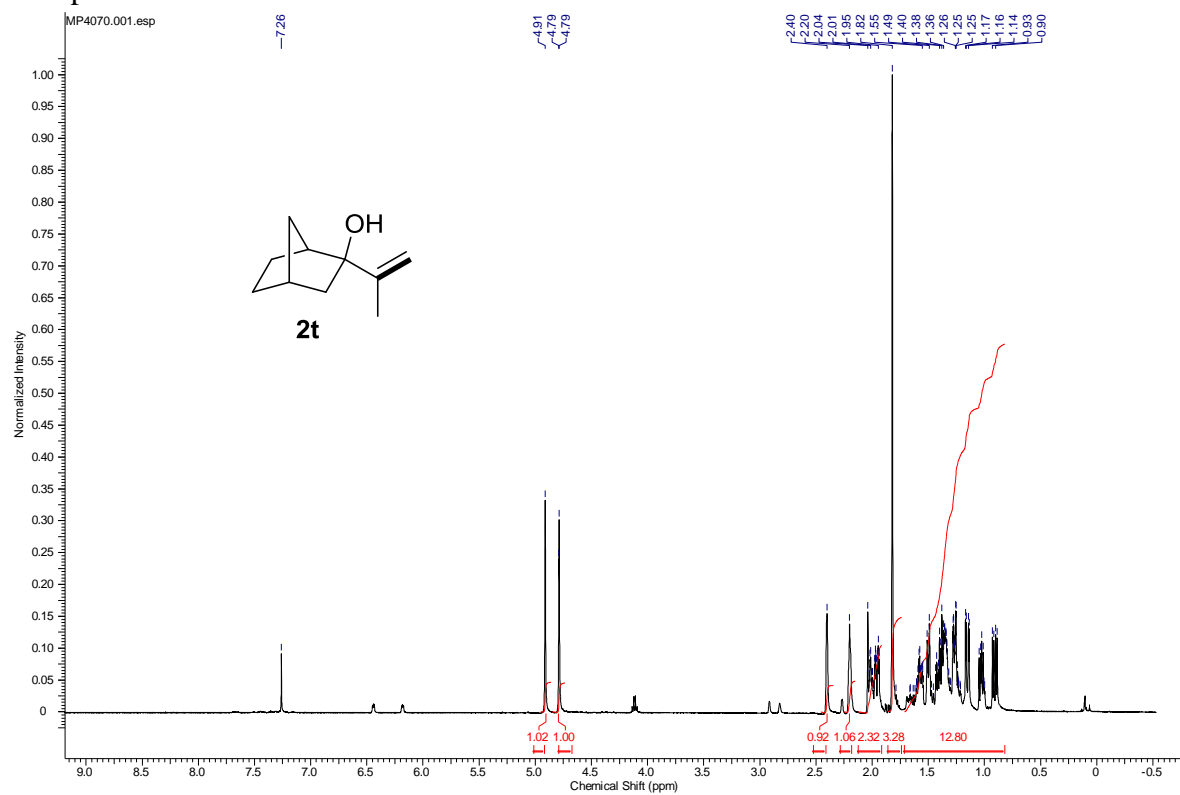
¹H Spectrum of 2s



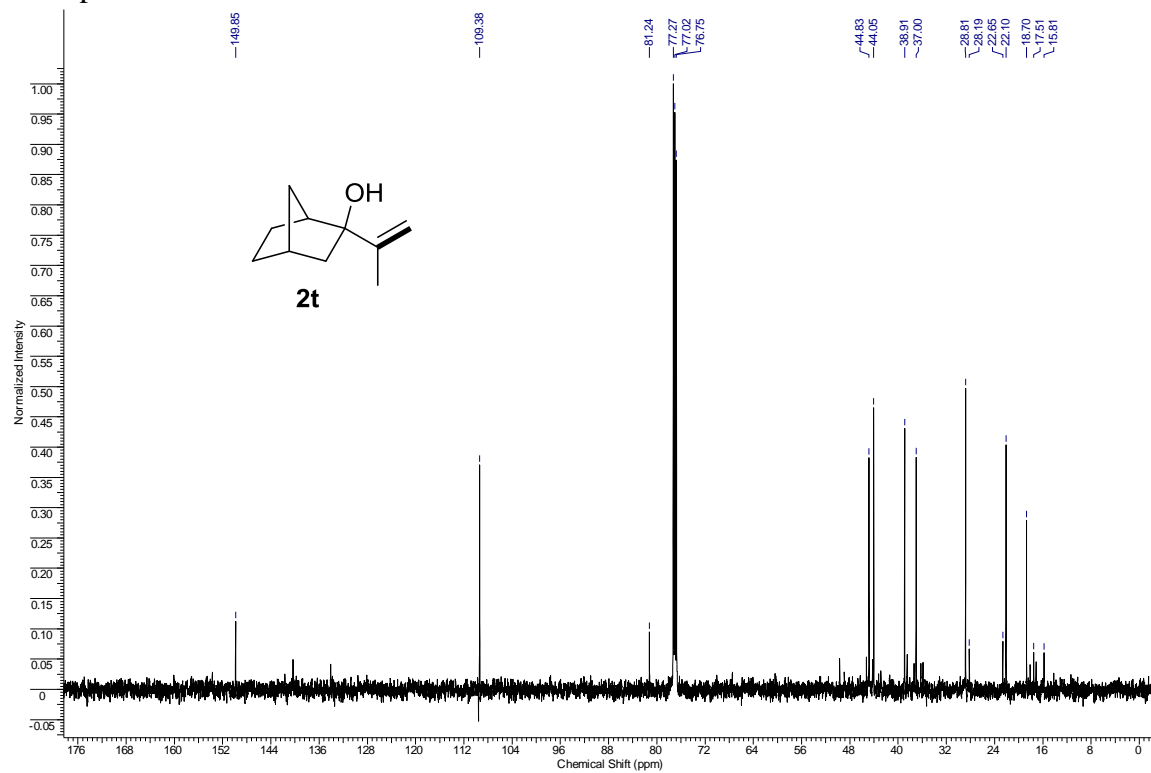
¹³C Spectrum of 2s



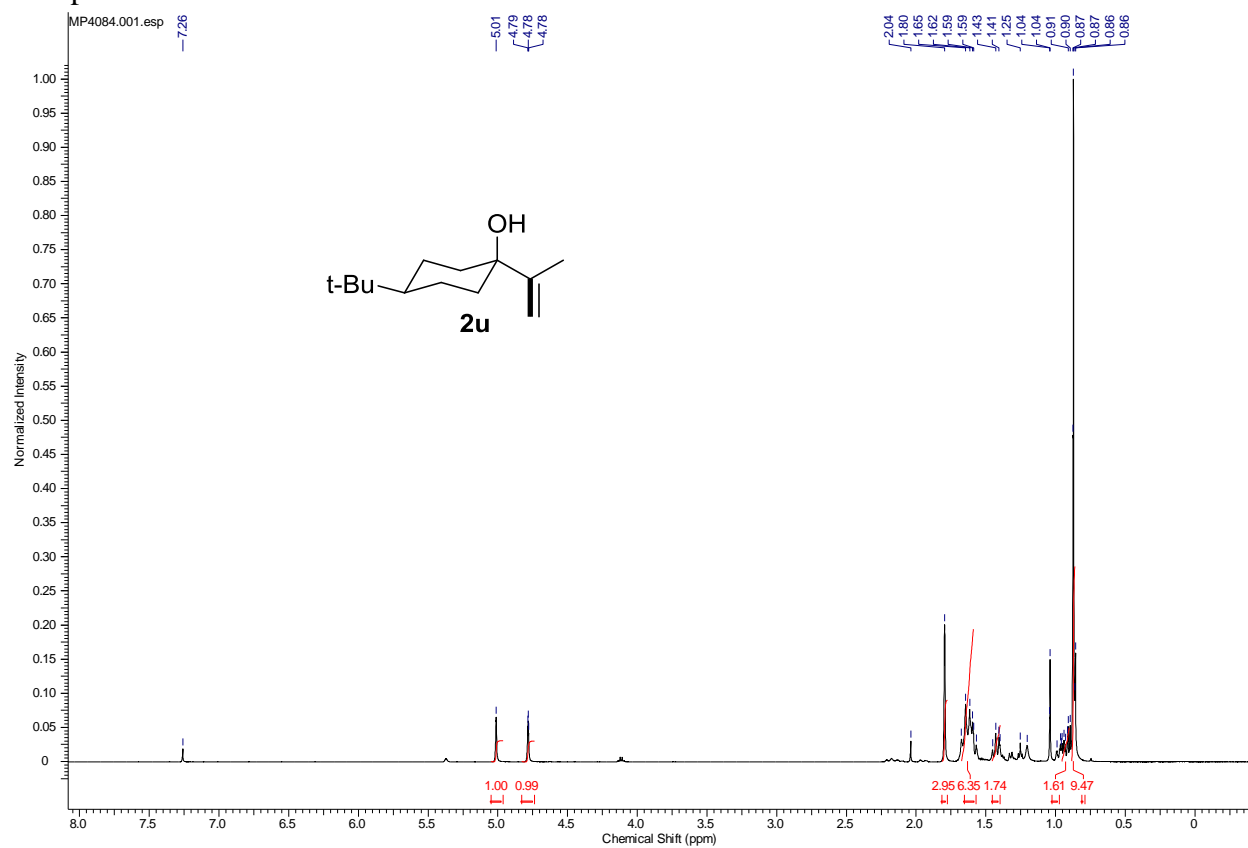
¹H Spectrum of 2t



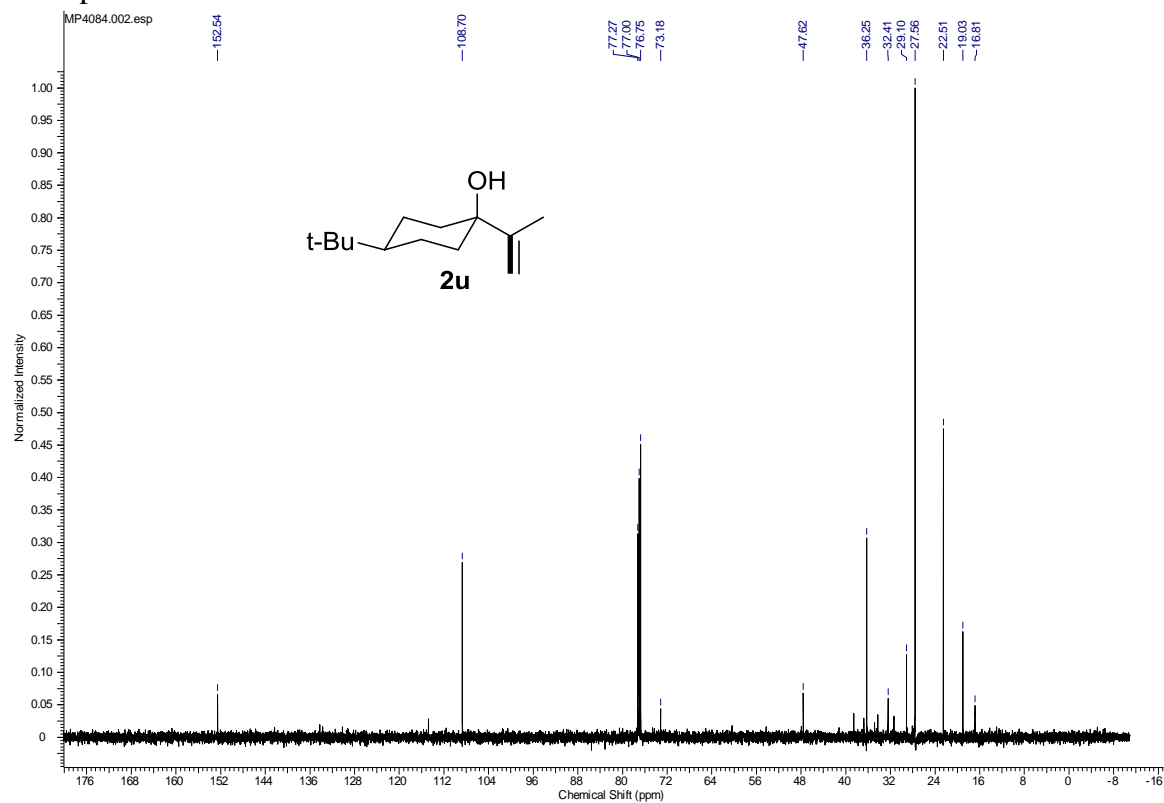
¹³C Spectrum of 2t



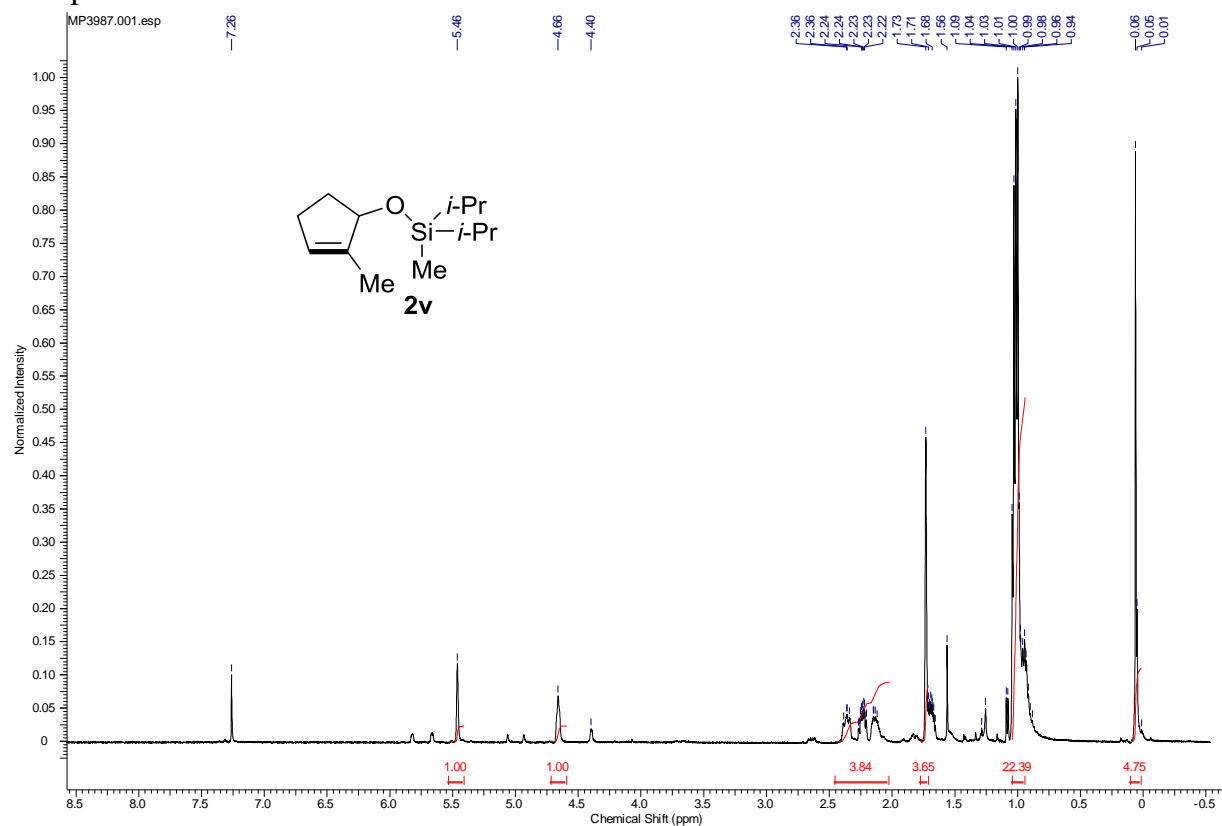
¹H Spectrum of **2u**



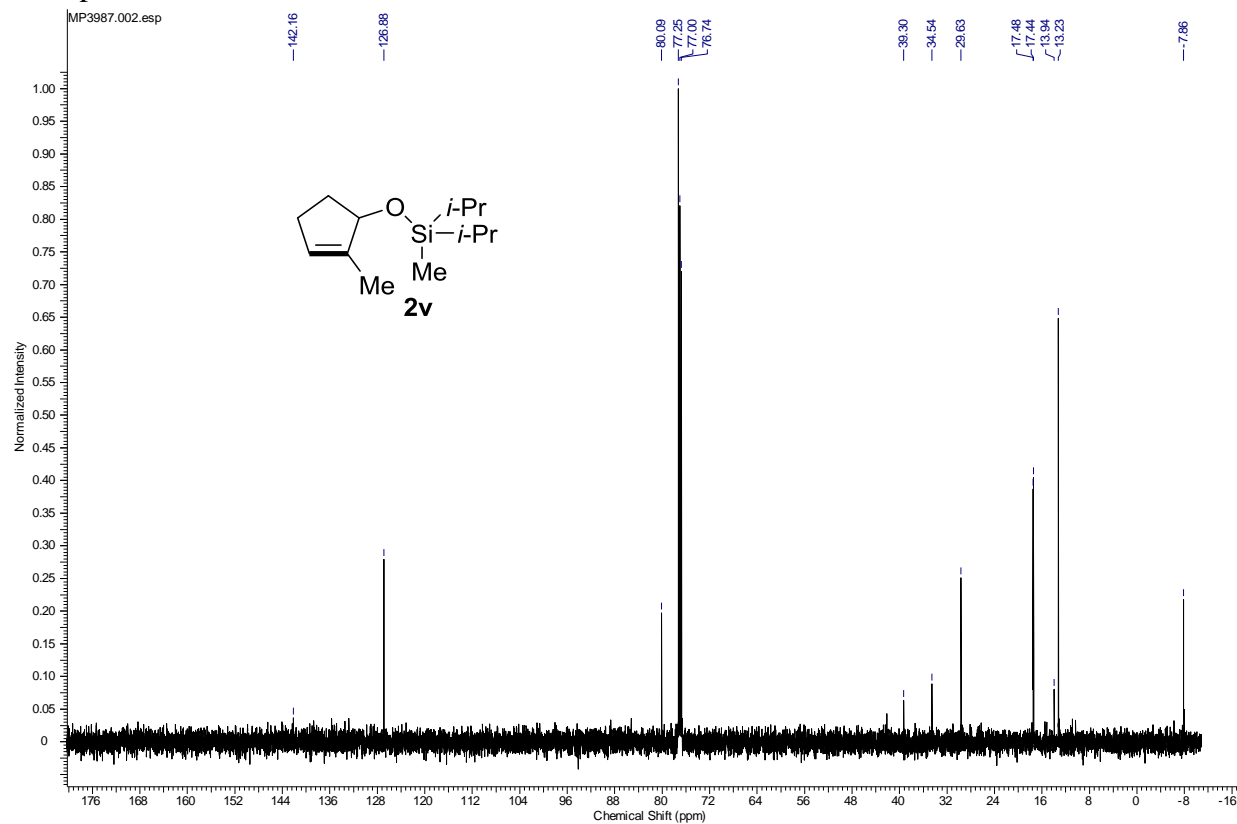
¹³C Spectrum of **2u**



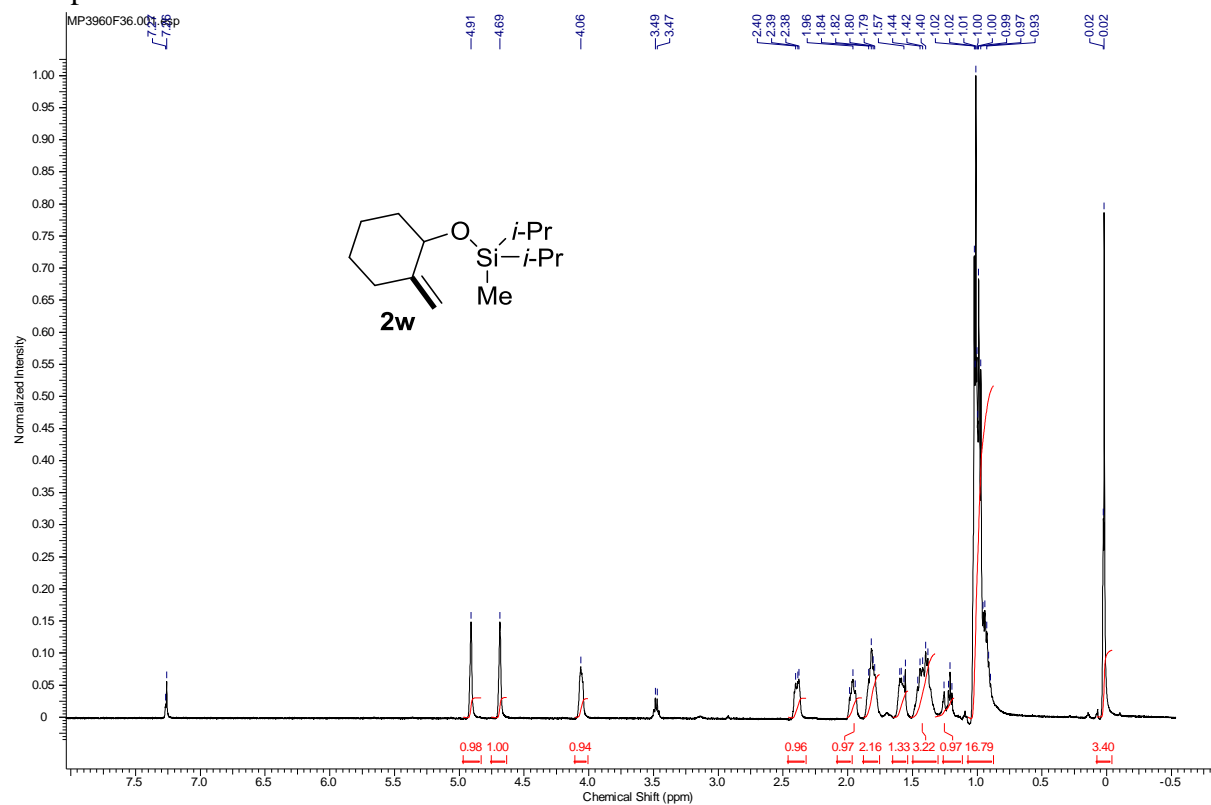
¹H Spectrum of 2v



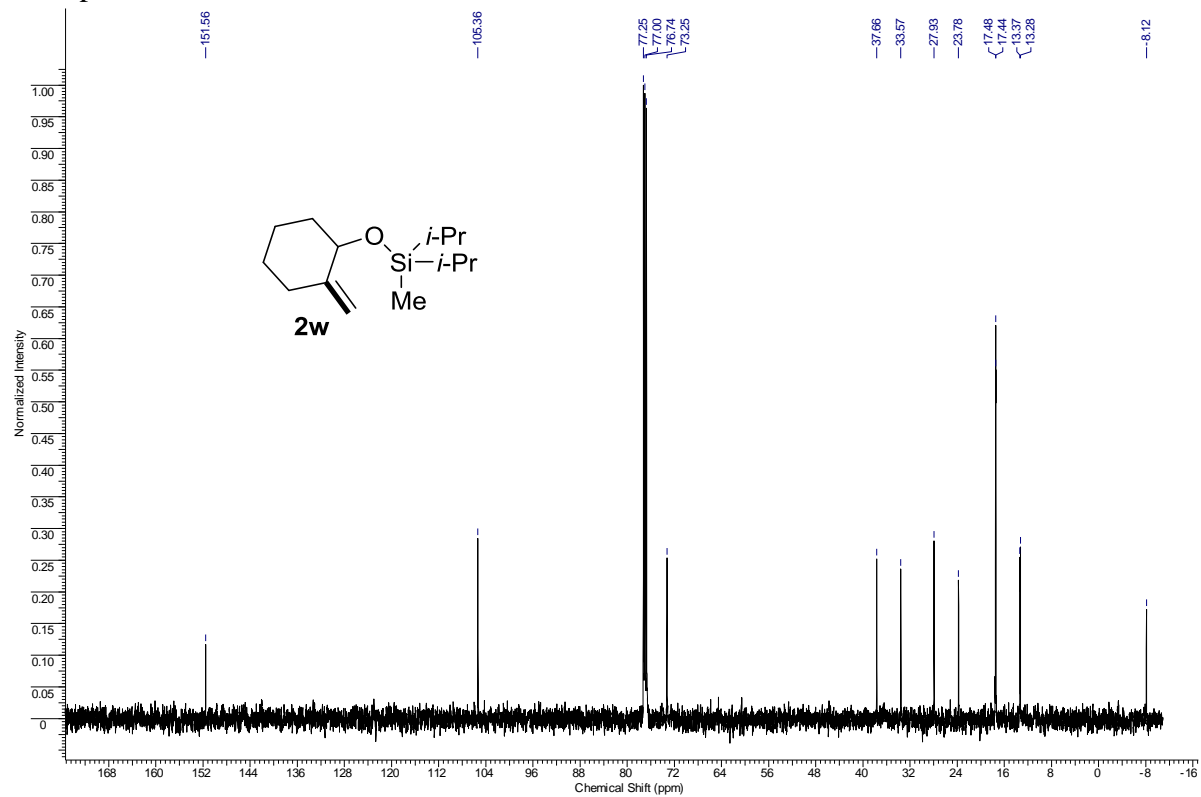
¹³C Spectrum of 2v



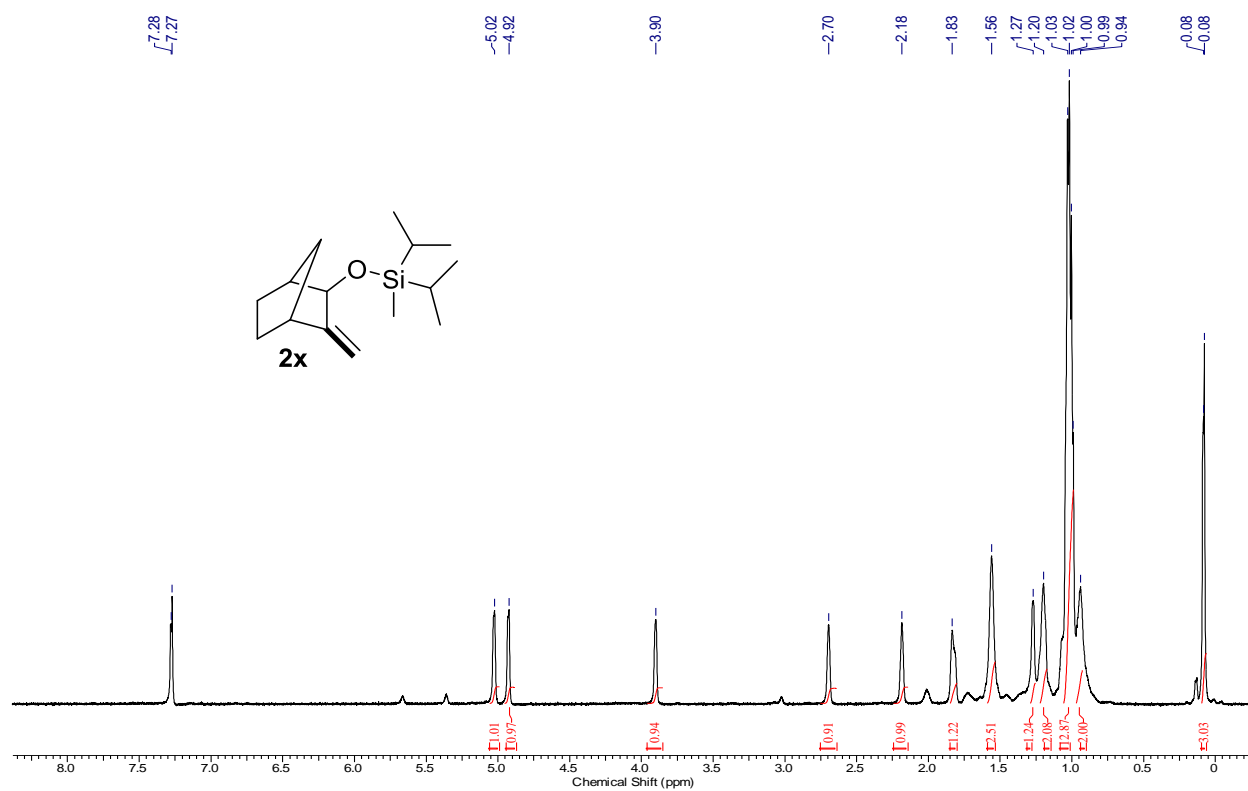
¹H Spectrum of 2w



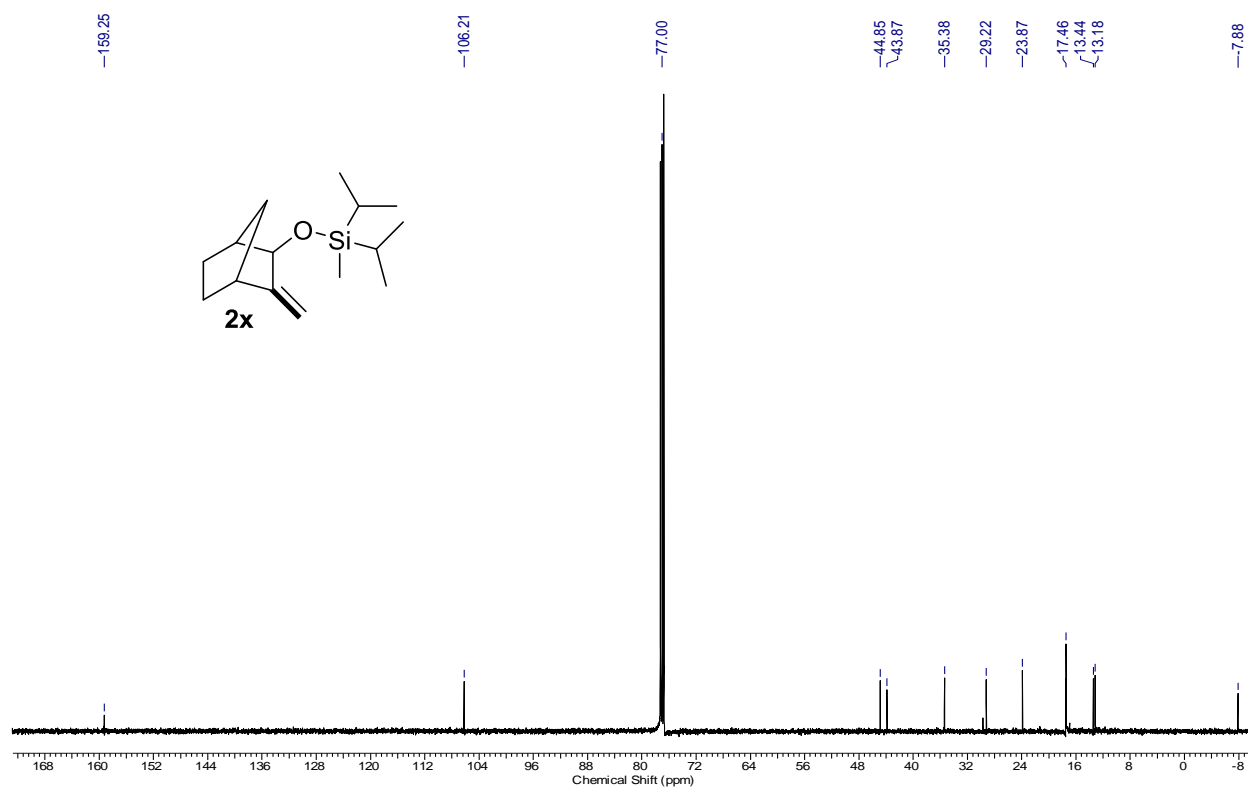
¹³C Spectrum of 2w



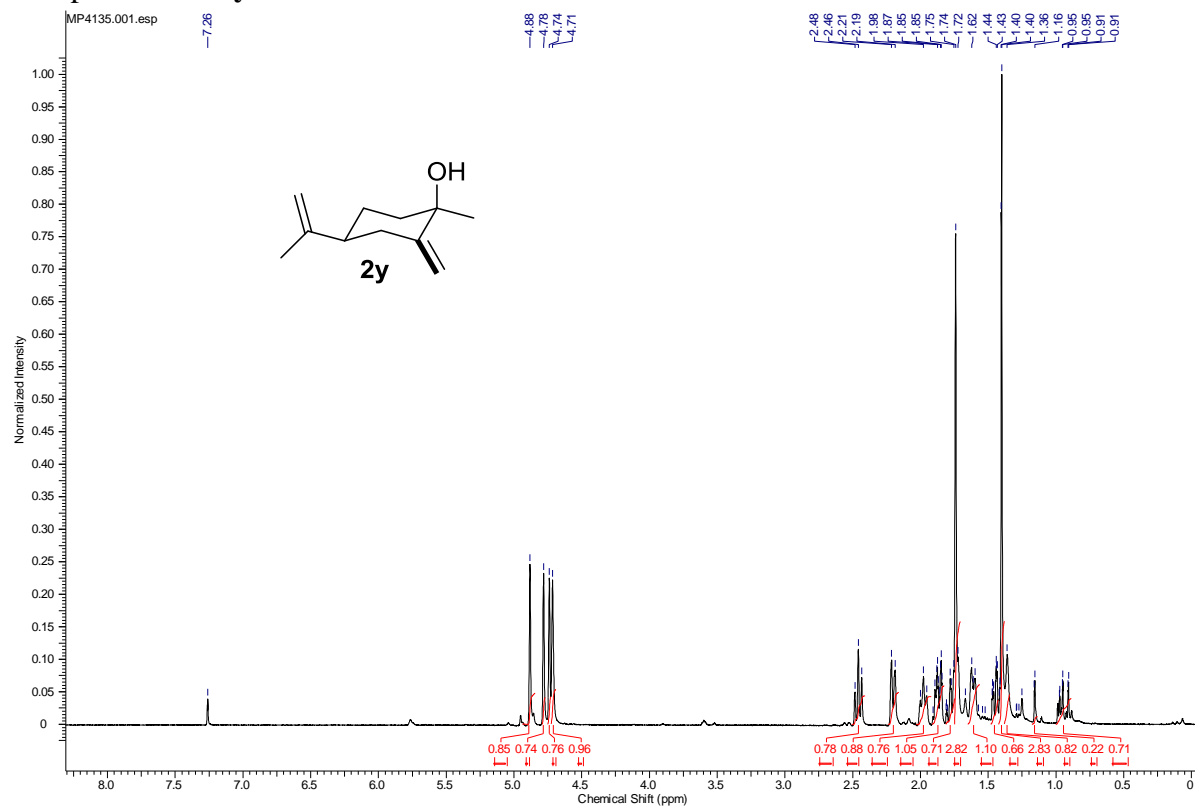
¹H Spectrum of 2x



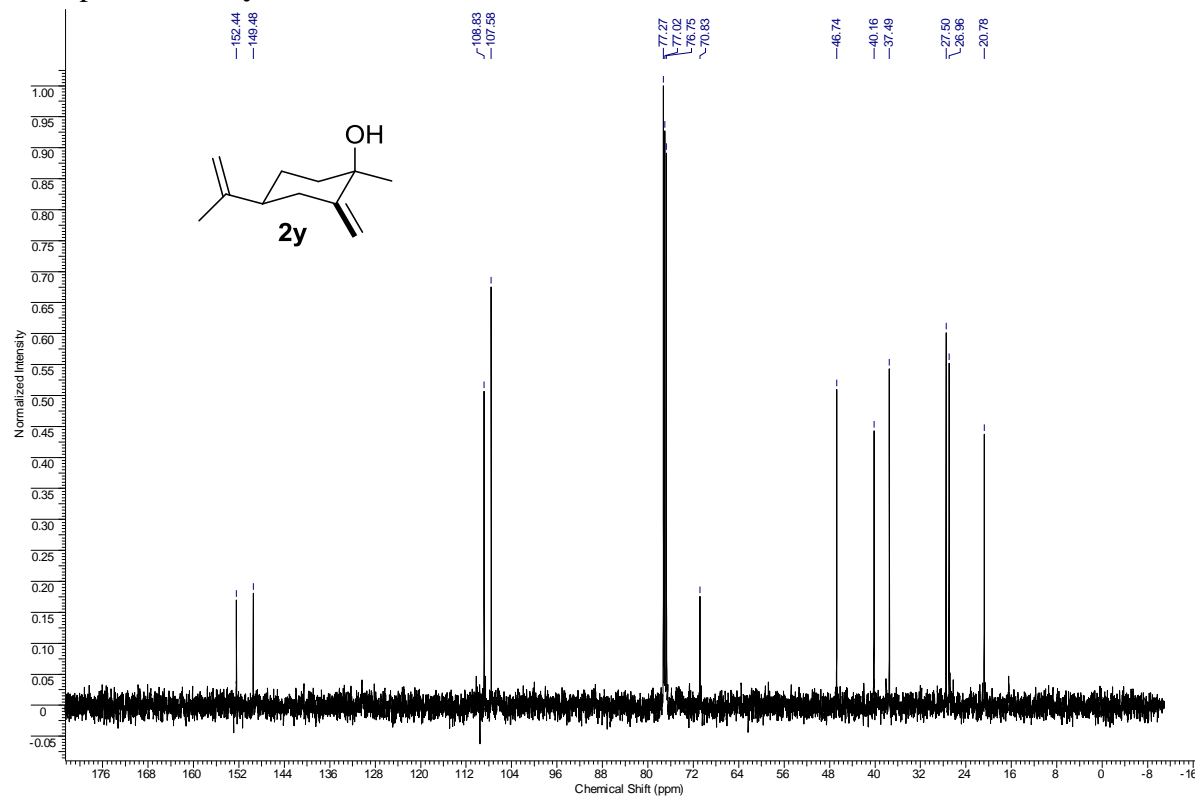
¹³C Spectrum of 2x



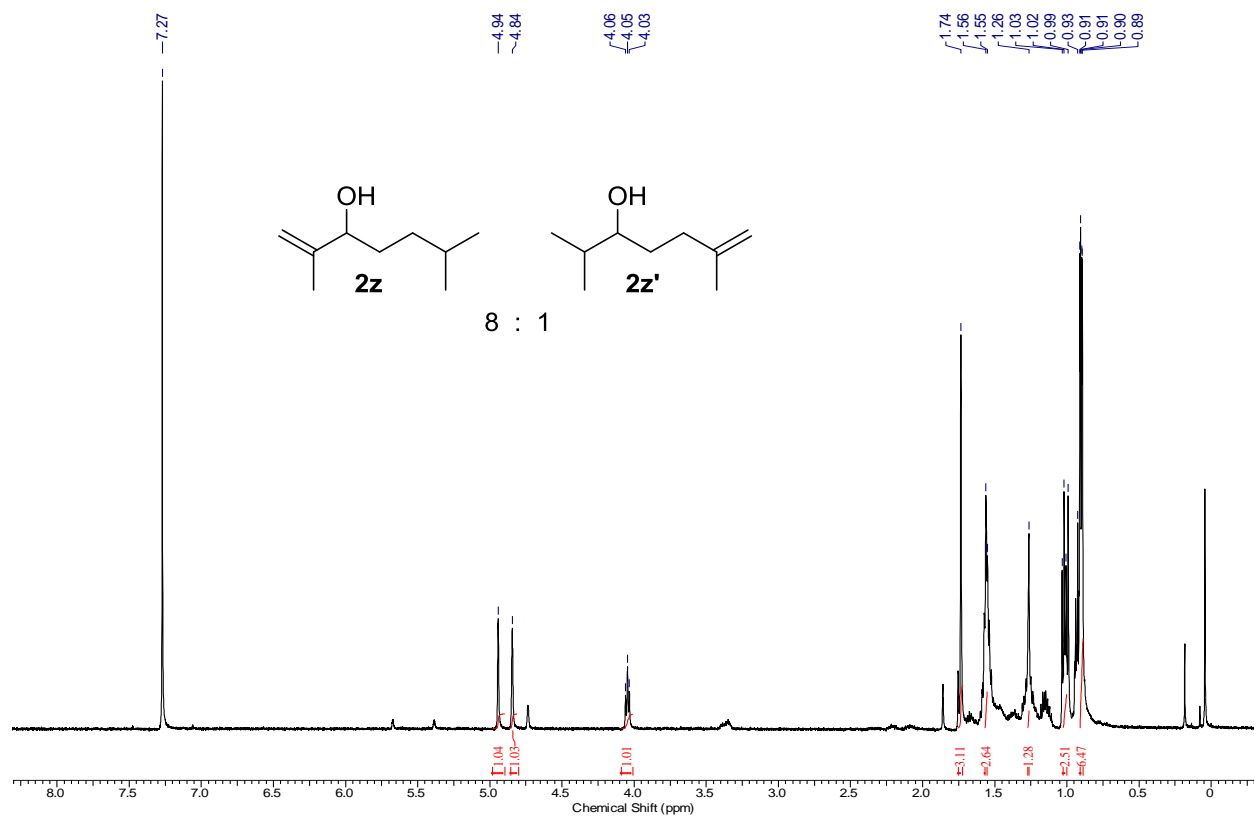
¹H Spectrum of 2y



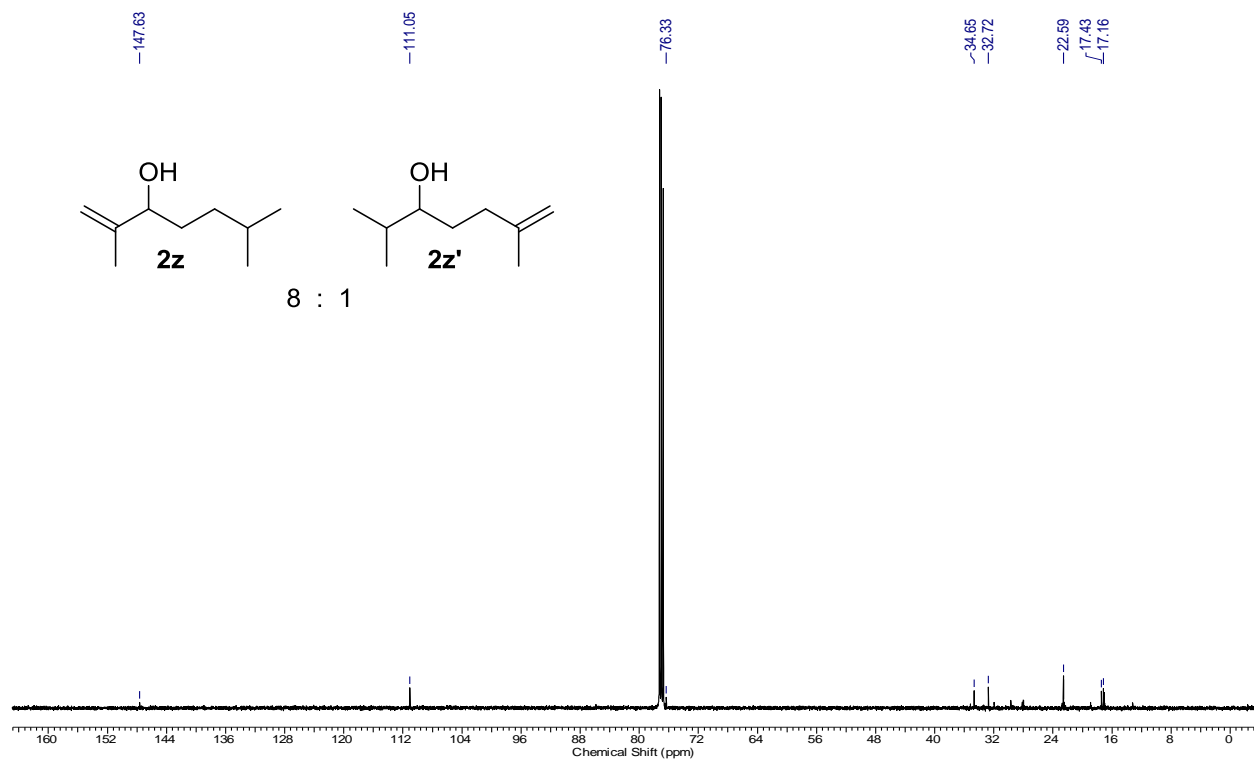
¹³C Spectrum of 2y



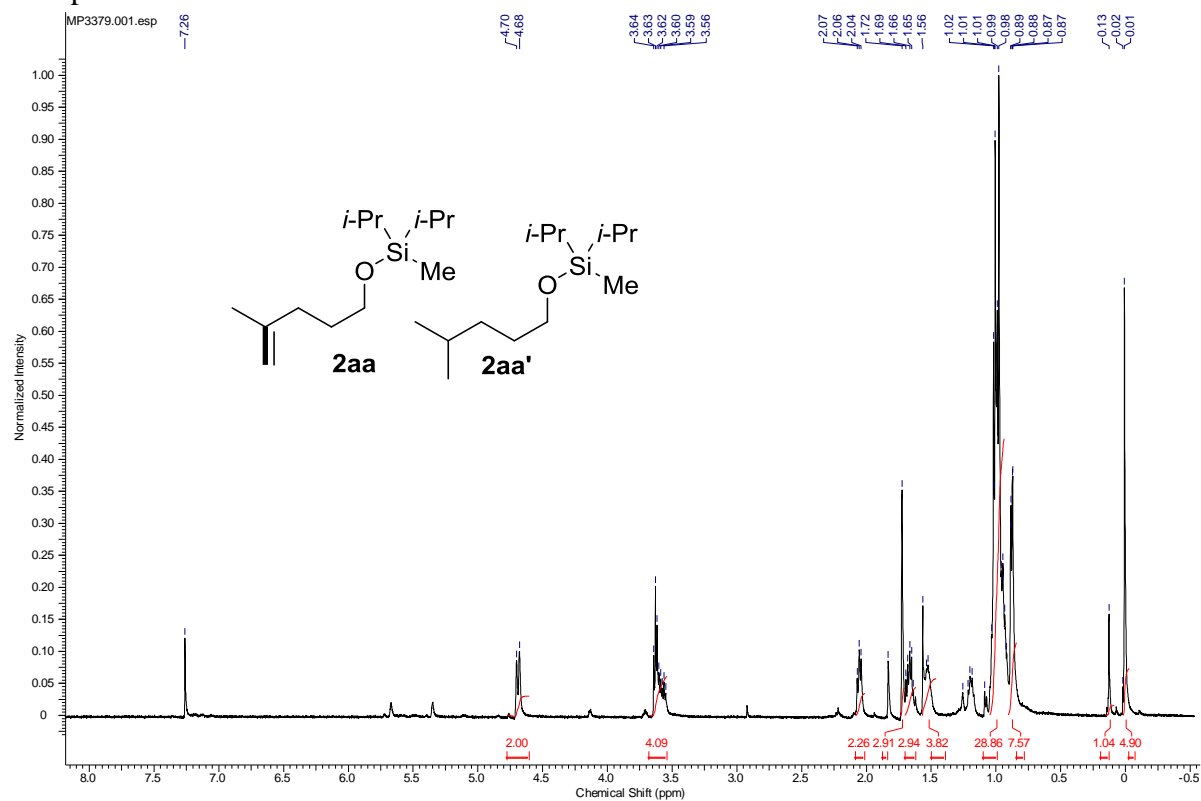
¹H Spectrum of **2z**



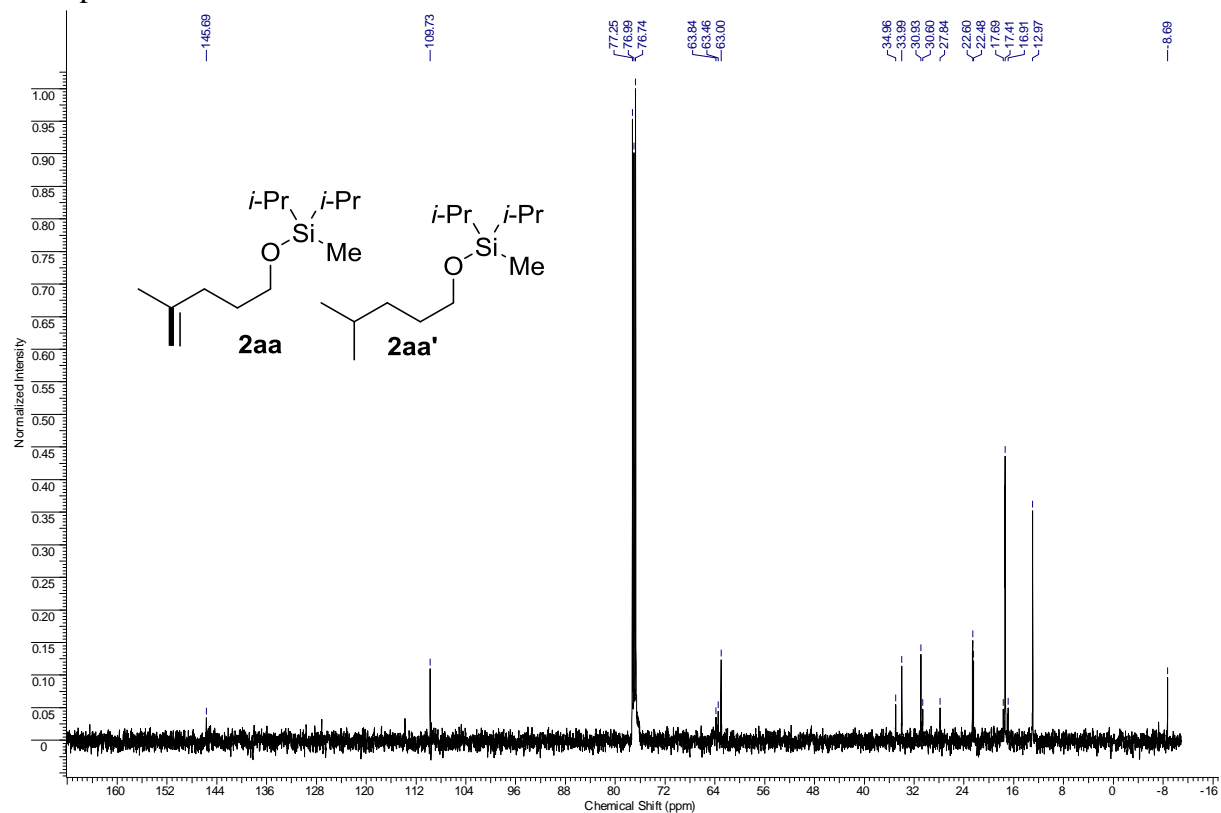
¹³C Spectrum of **2z**



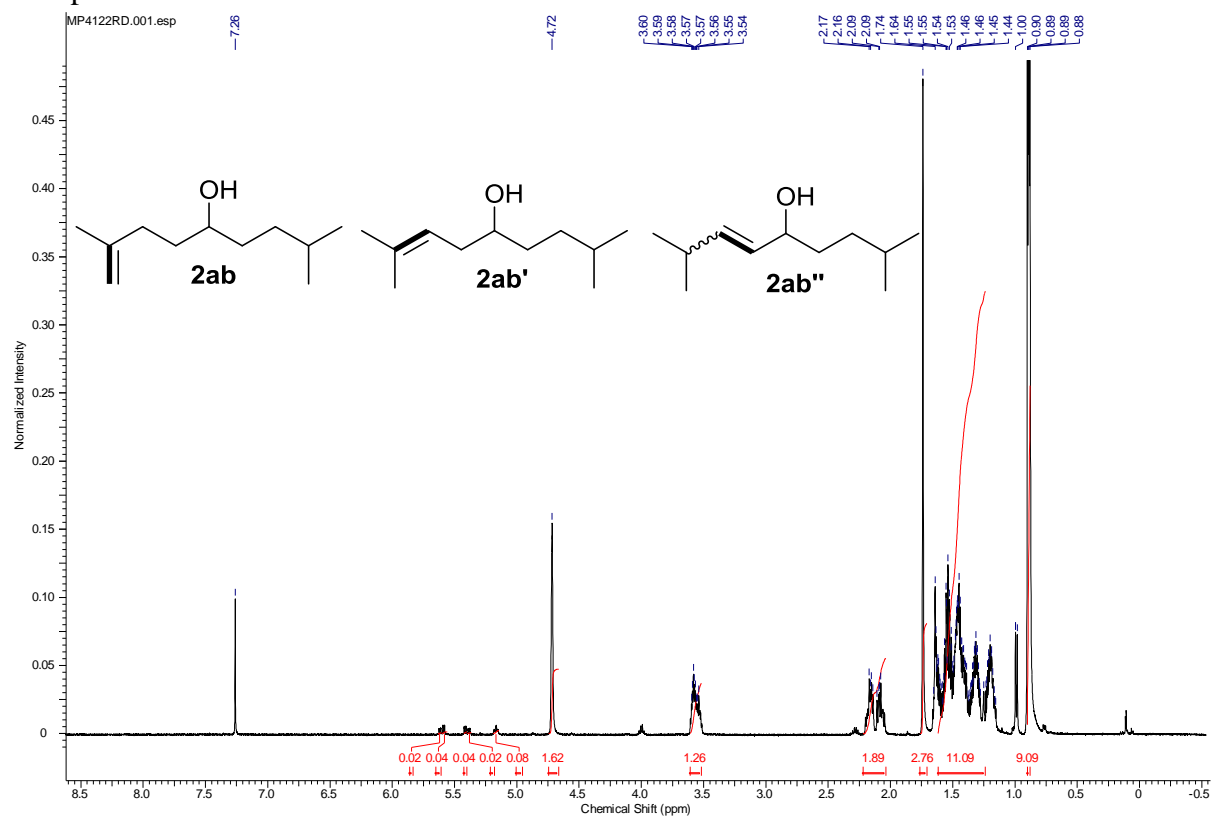
¹H Spectrum of 2aa



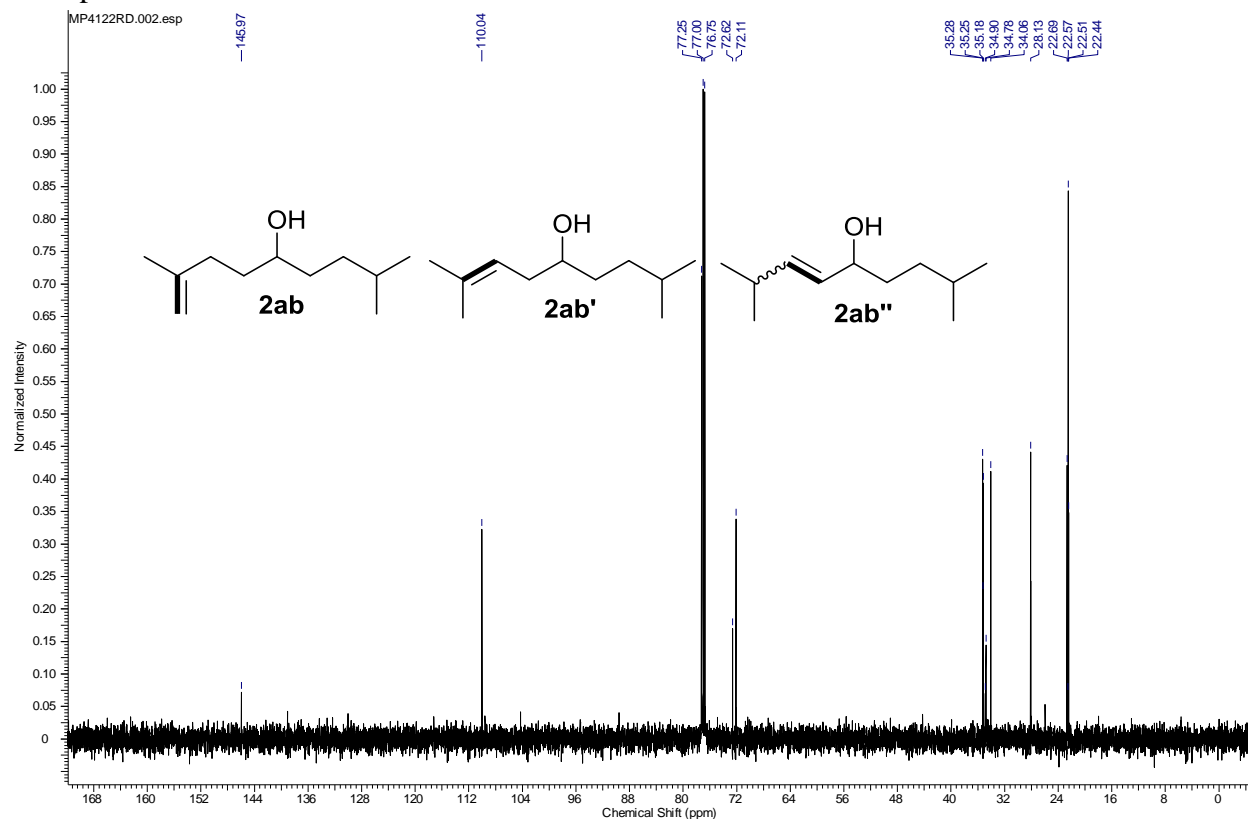
¹³C Spectrum of 2aa



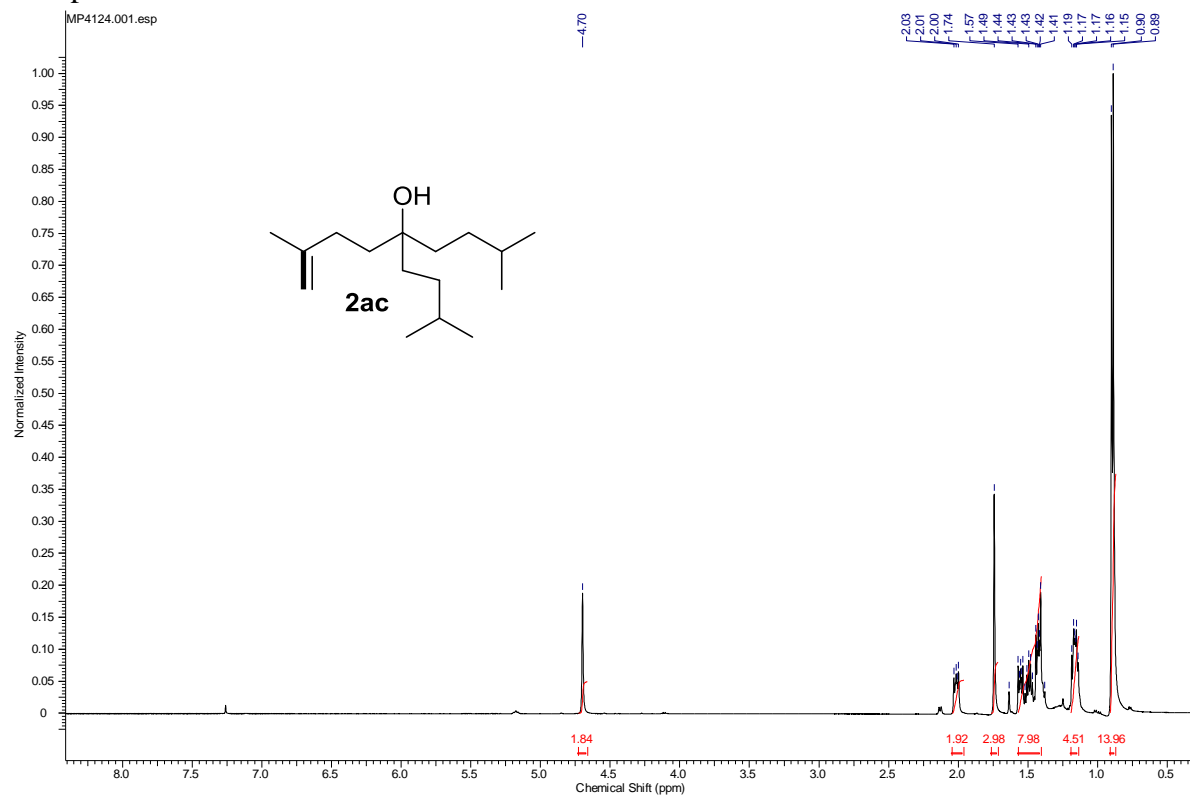
¹H Spectrum of 2ab



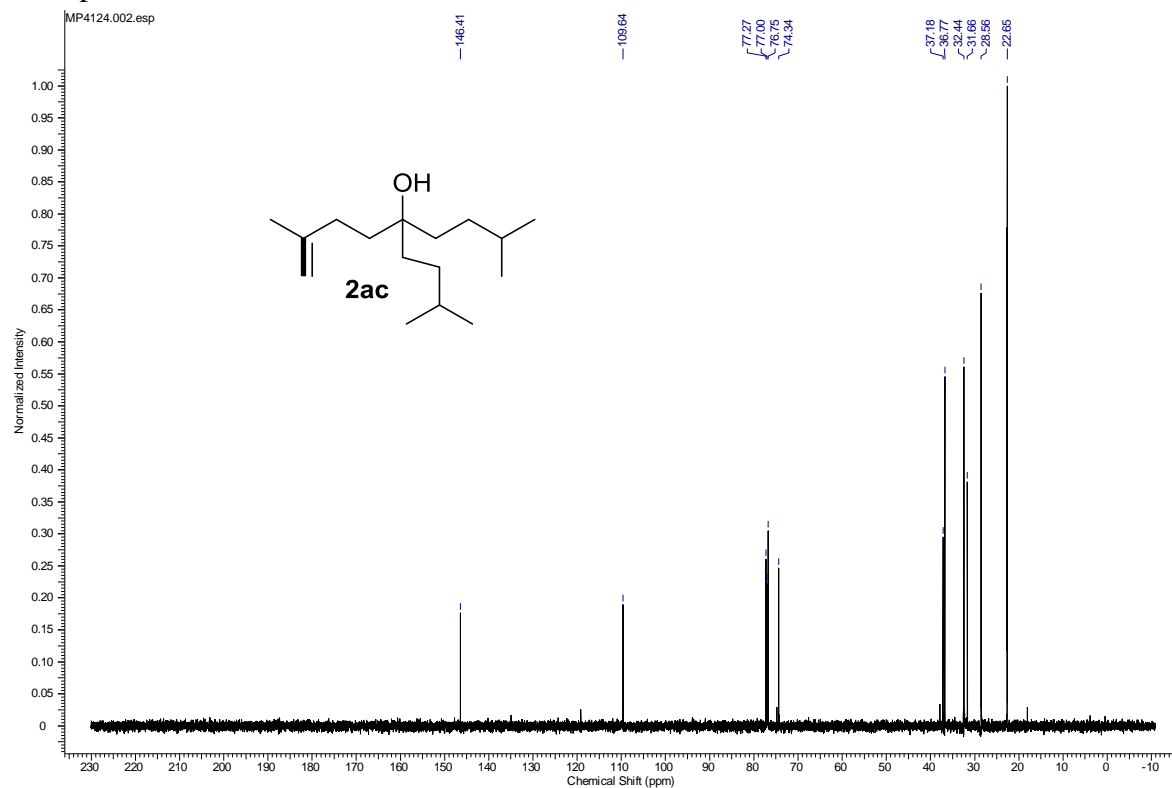
¹³C Spectrum of 2ab



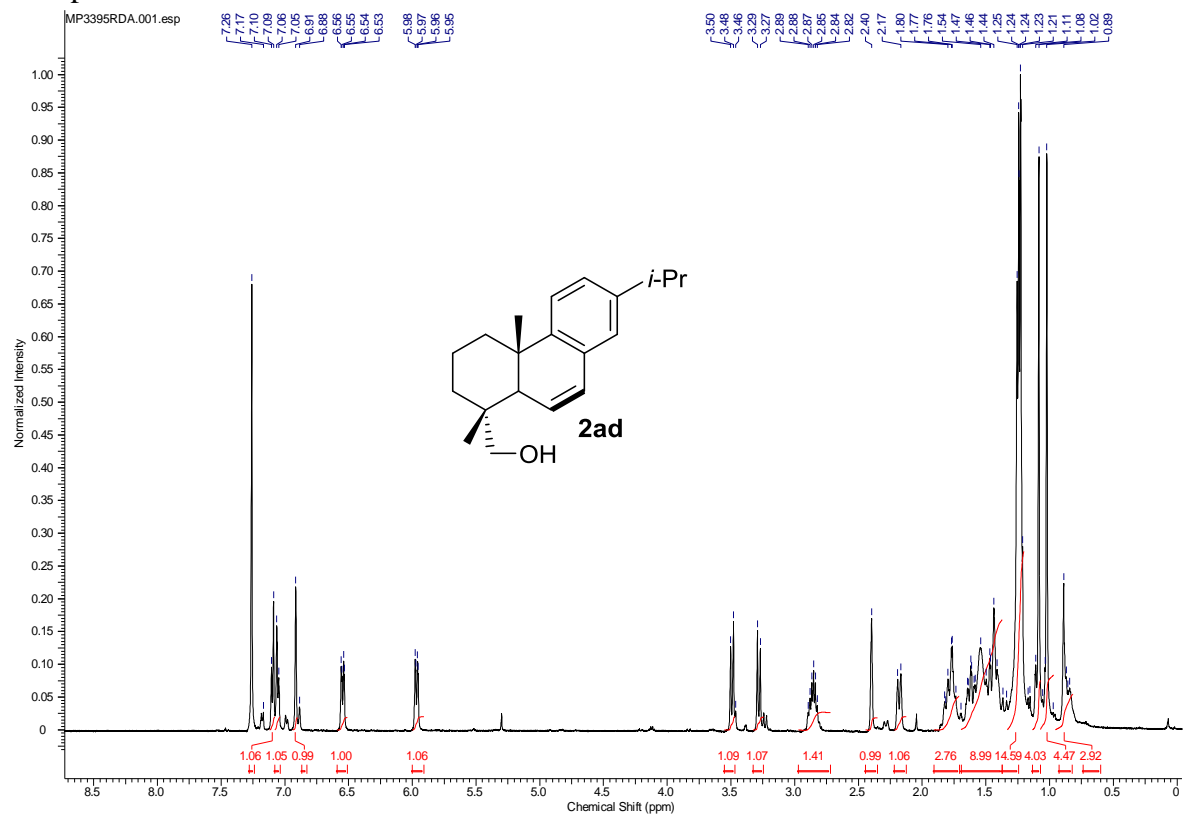
¹H Spectrum of 2ac



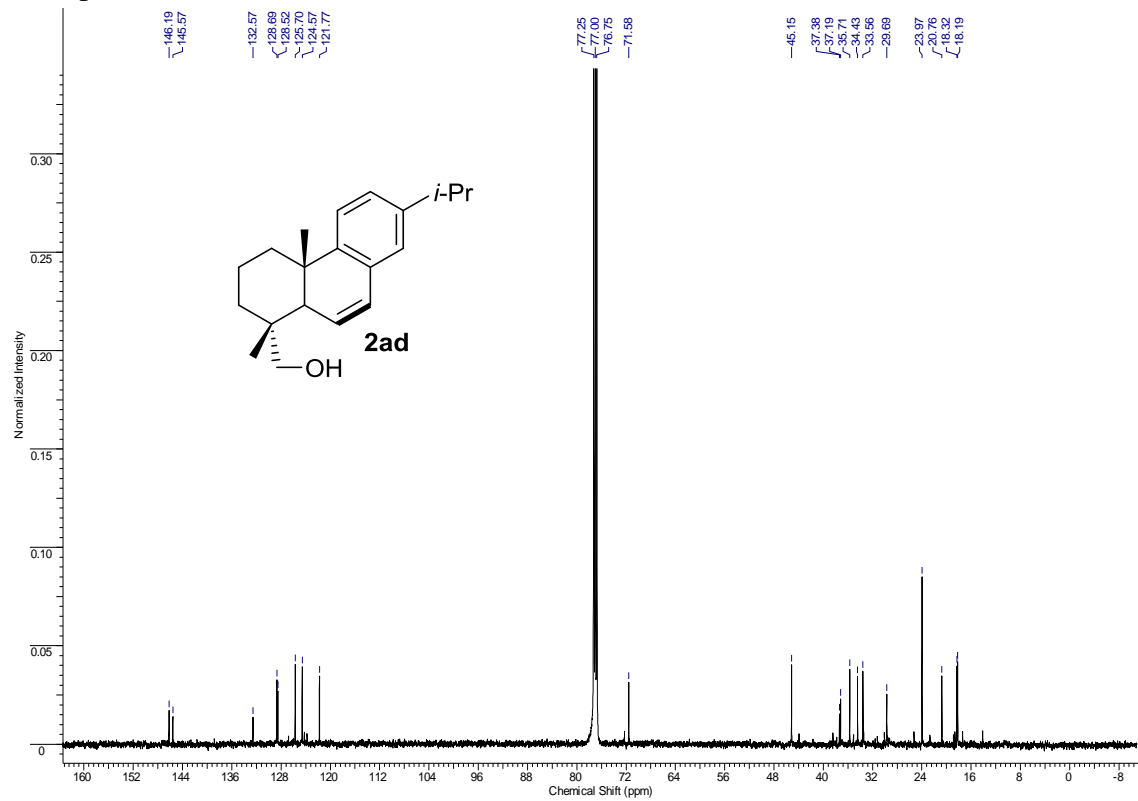
¹³C Spectrum of 2ac



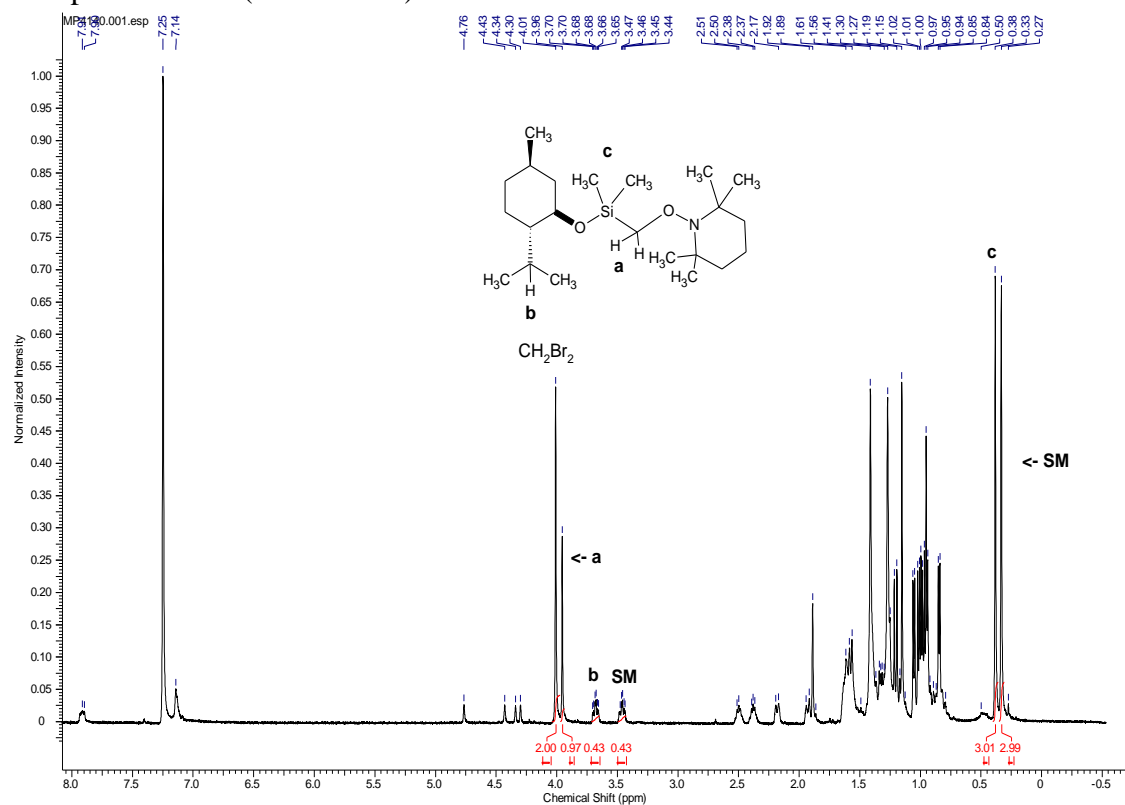
¹H Spectrum of 2ad



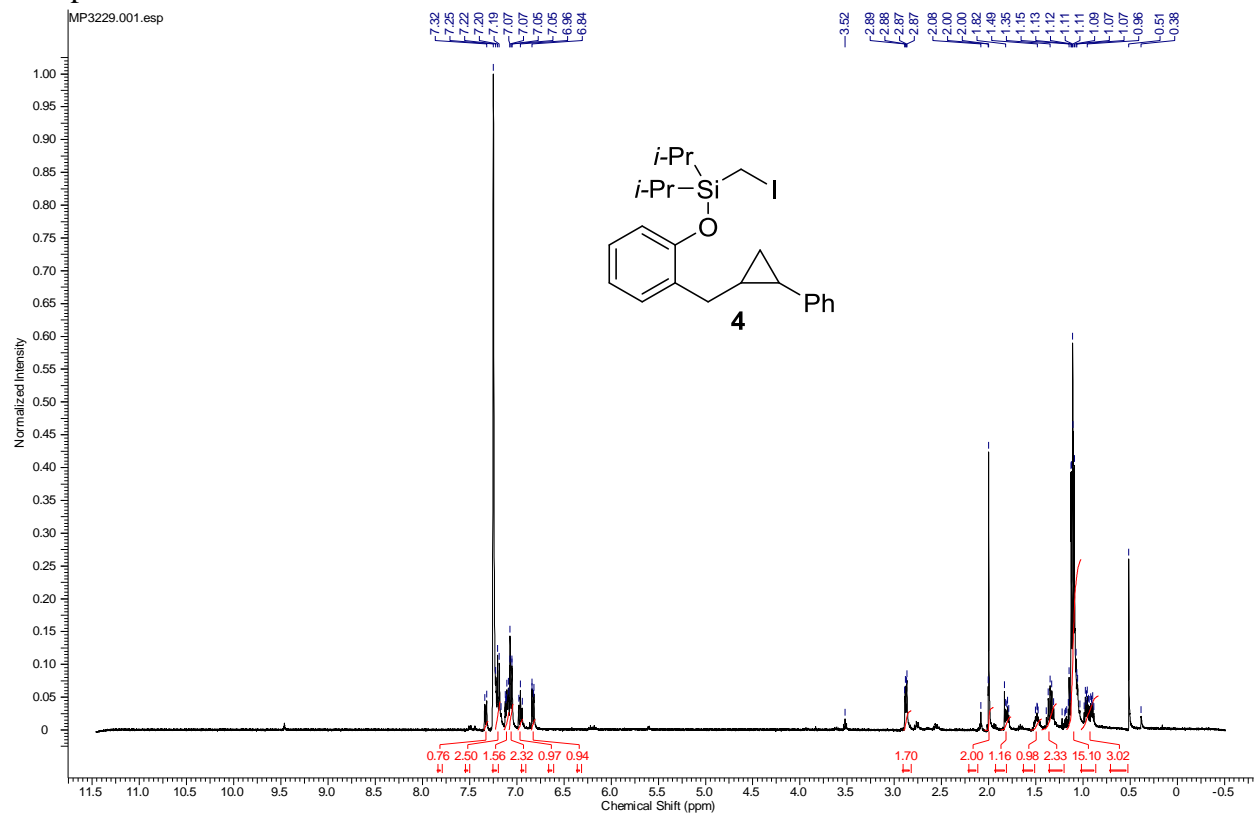
¹³C Spectrum of 2ad



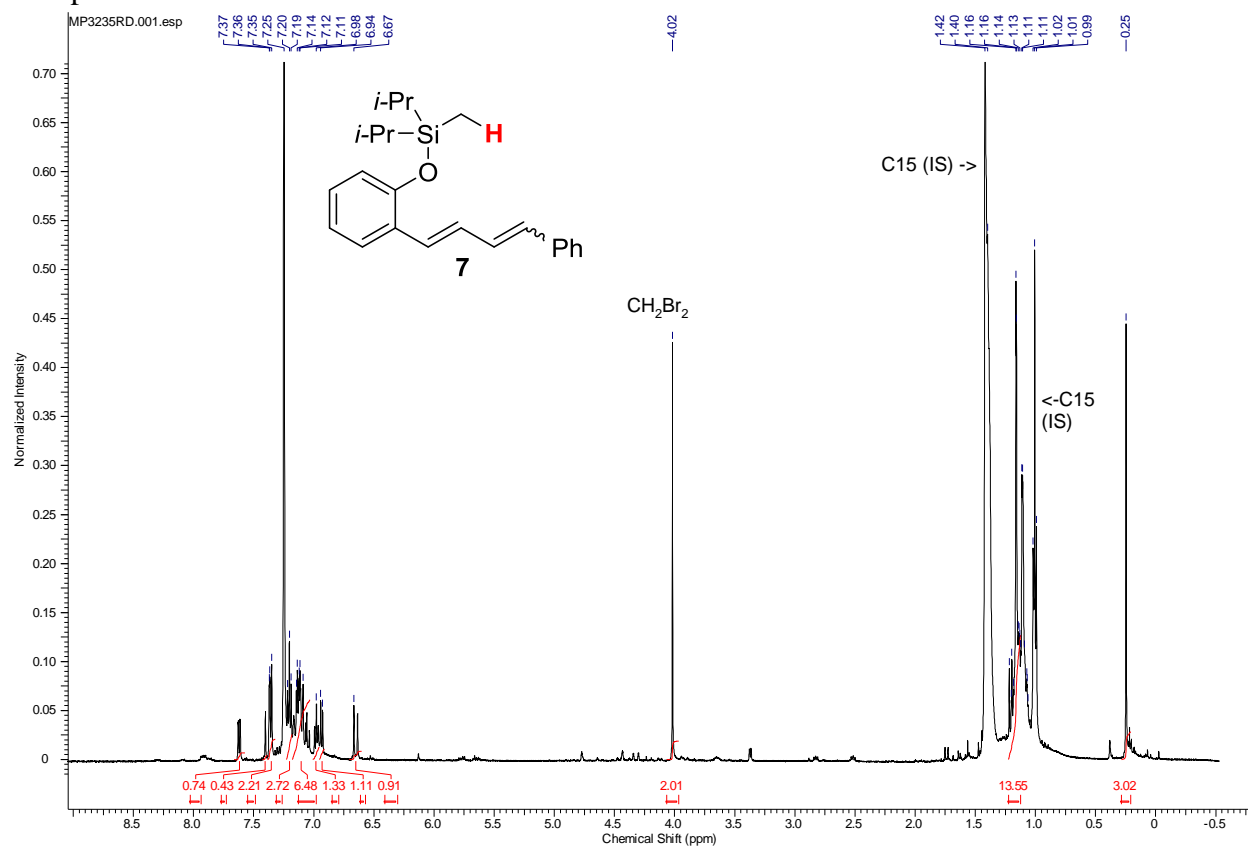
¹H Spectrum of 3 (NMR Yield)



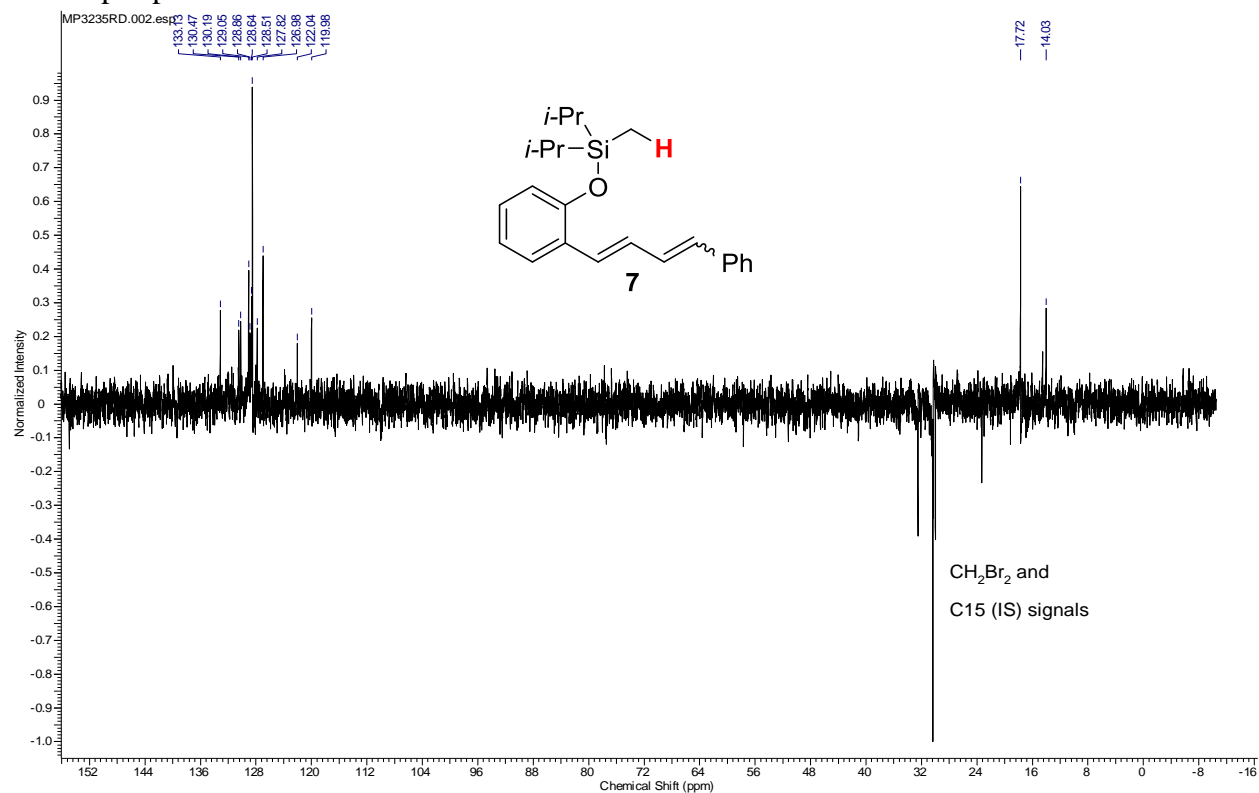
¹H Spectrum of 4



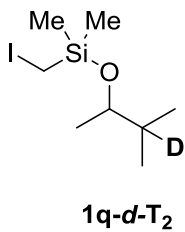
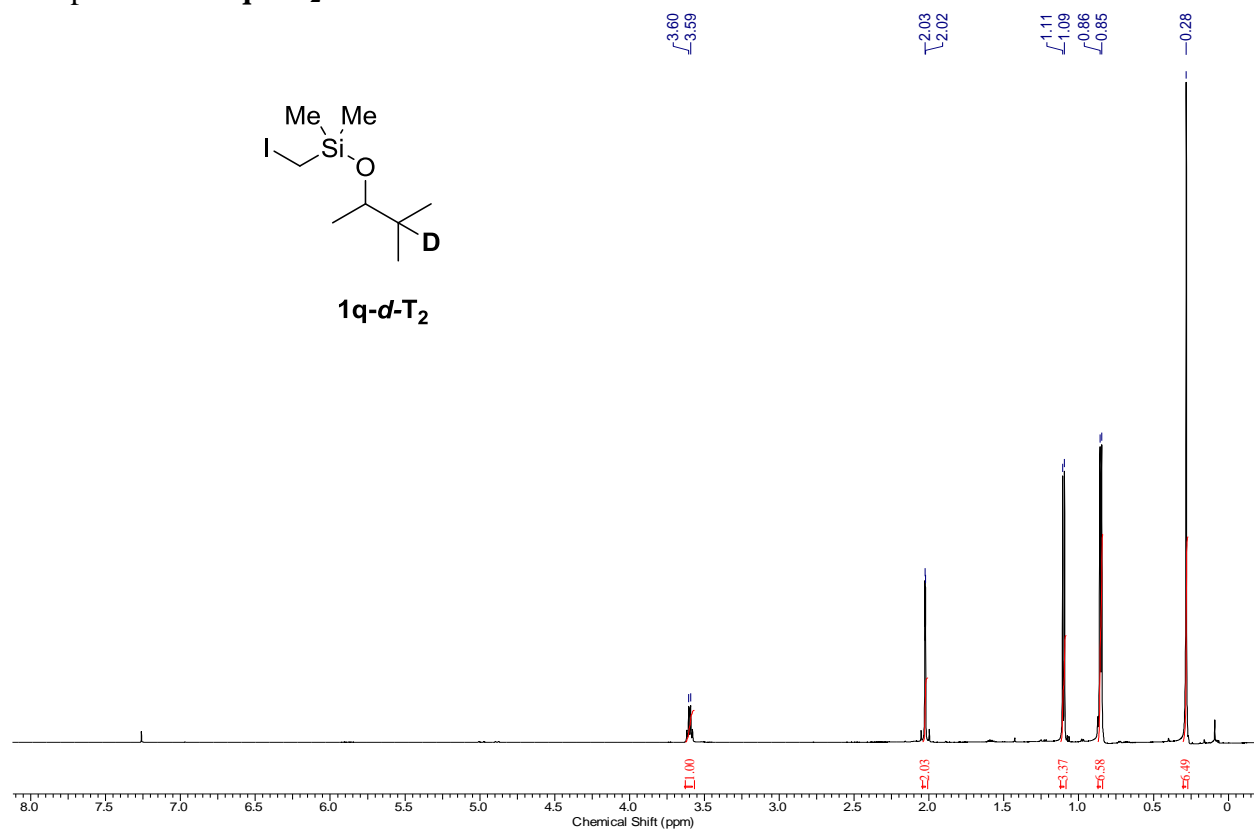
¹H Spectrum of 7



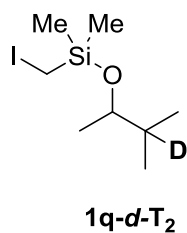
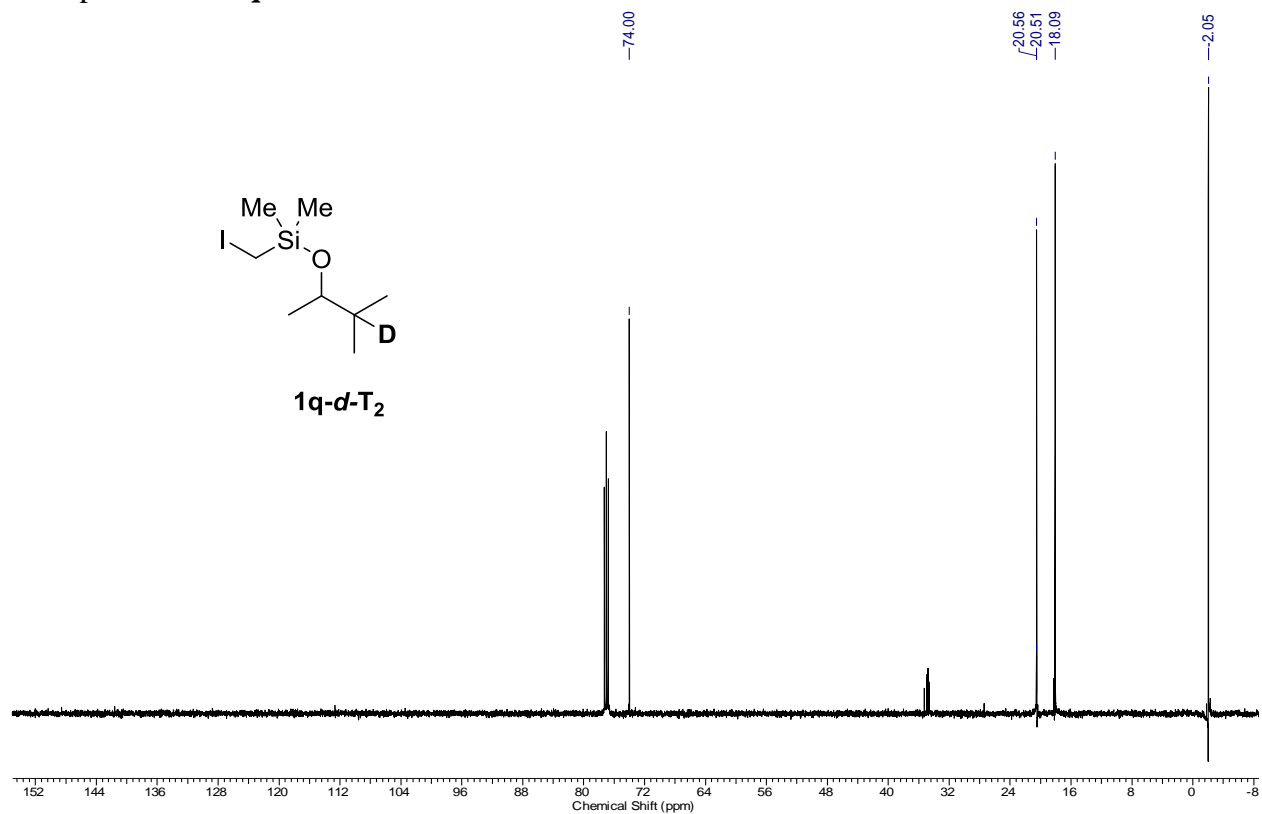
¹³C-Dept Spectrum of 7



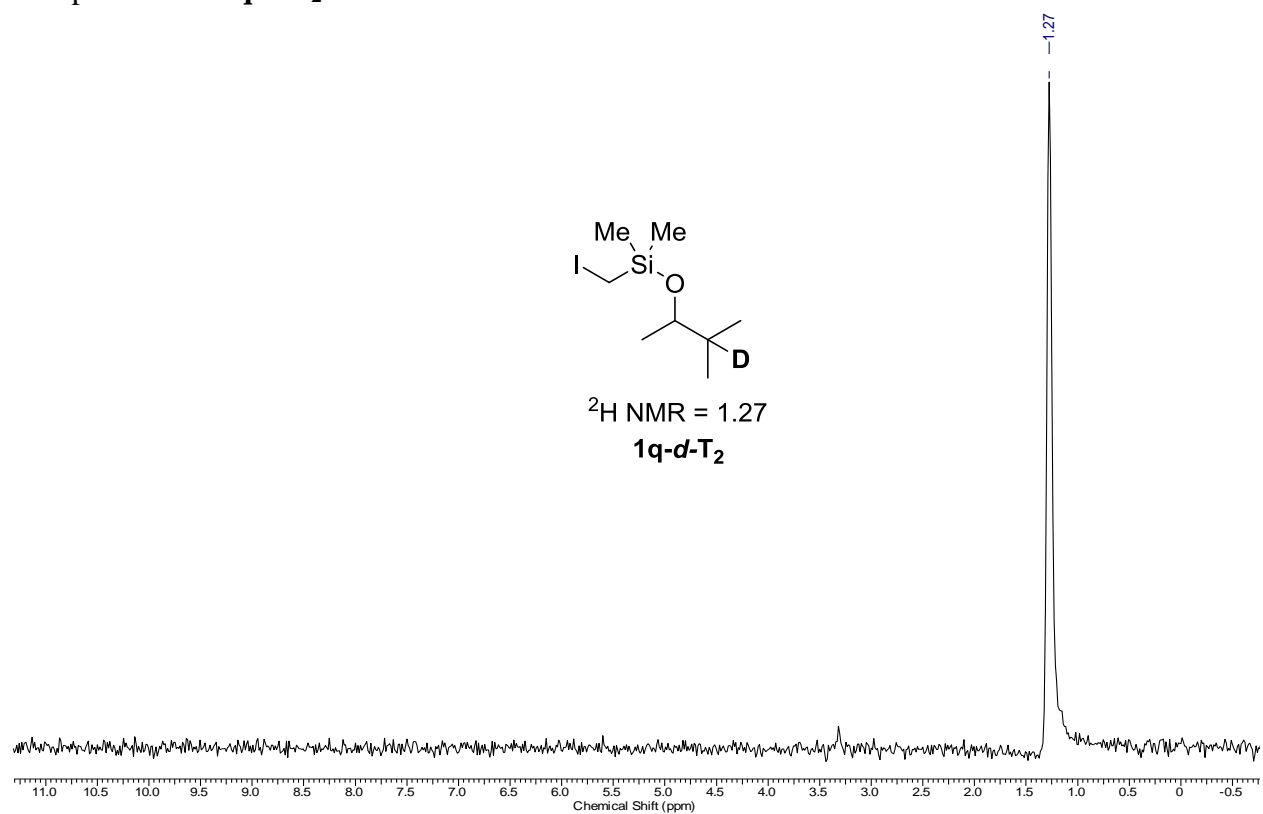
¹H Spectrum of **1q-d-T₂**



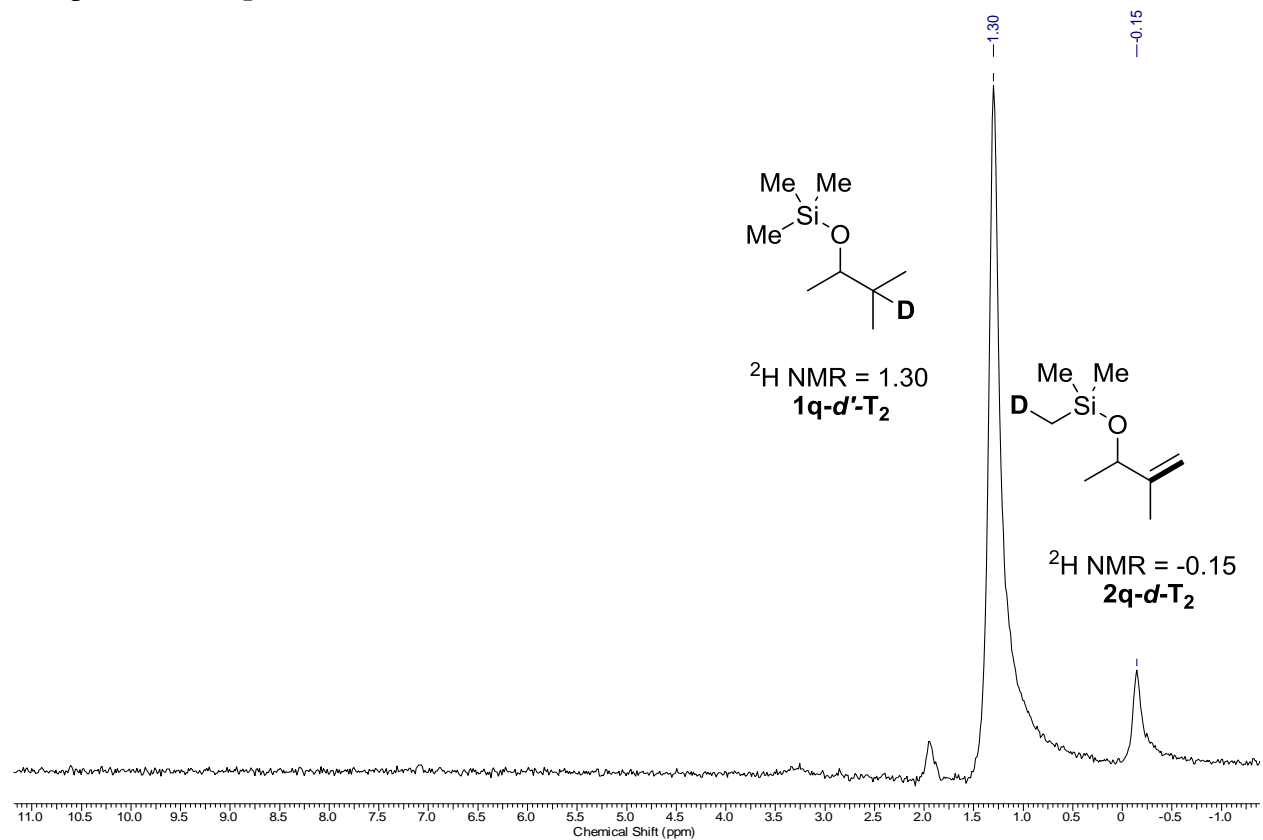
¹³C Spectrum of **1q-d-T₂**



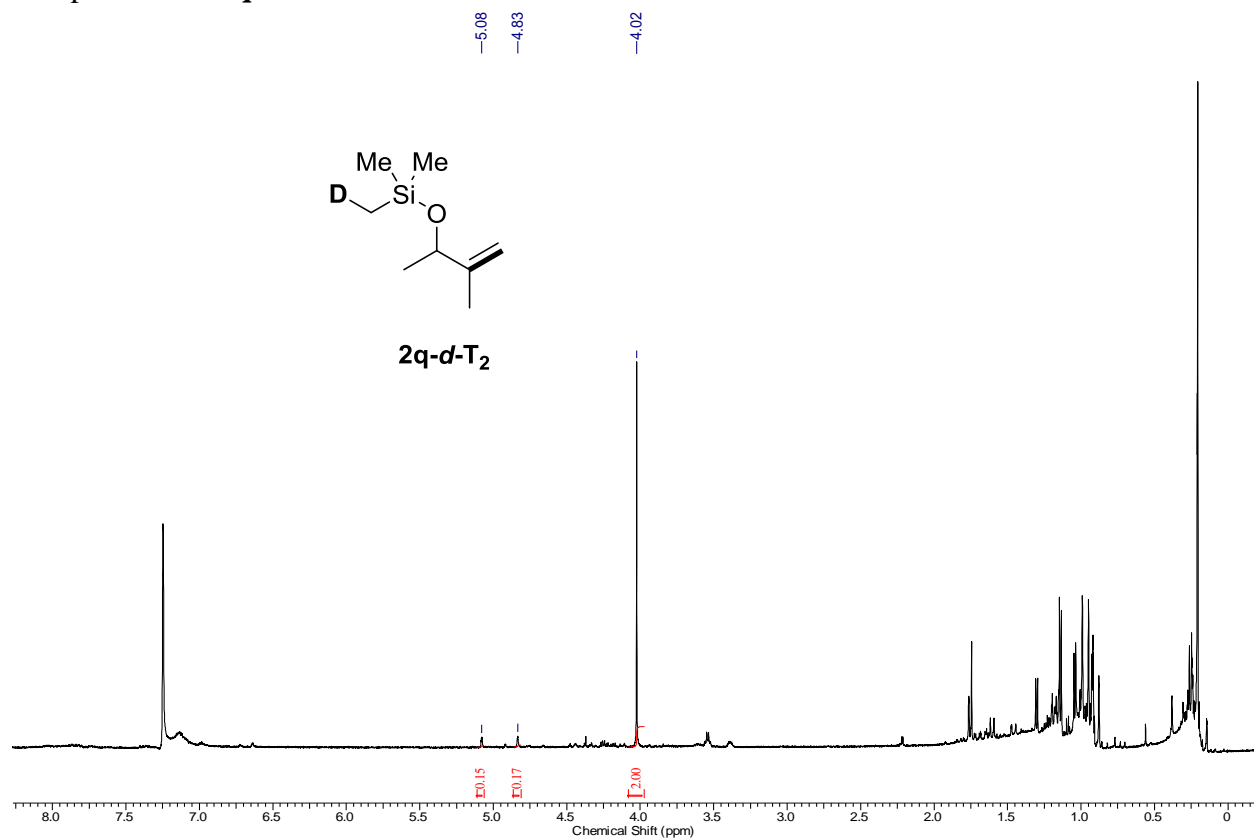
^2H Spectrum of **1q-d-T₂**



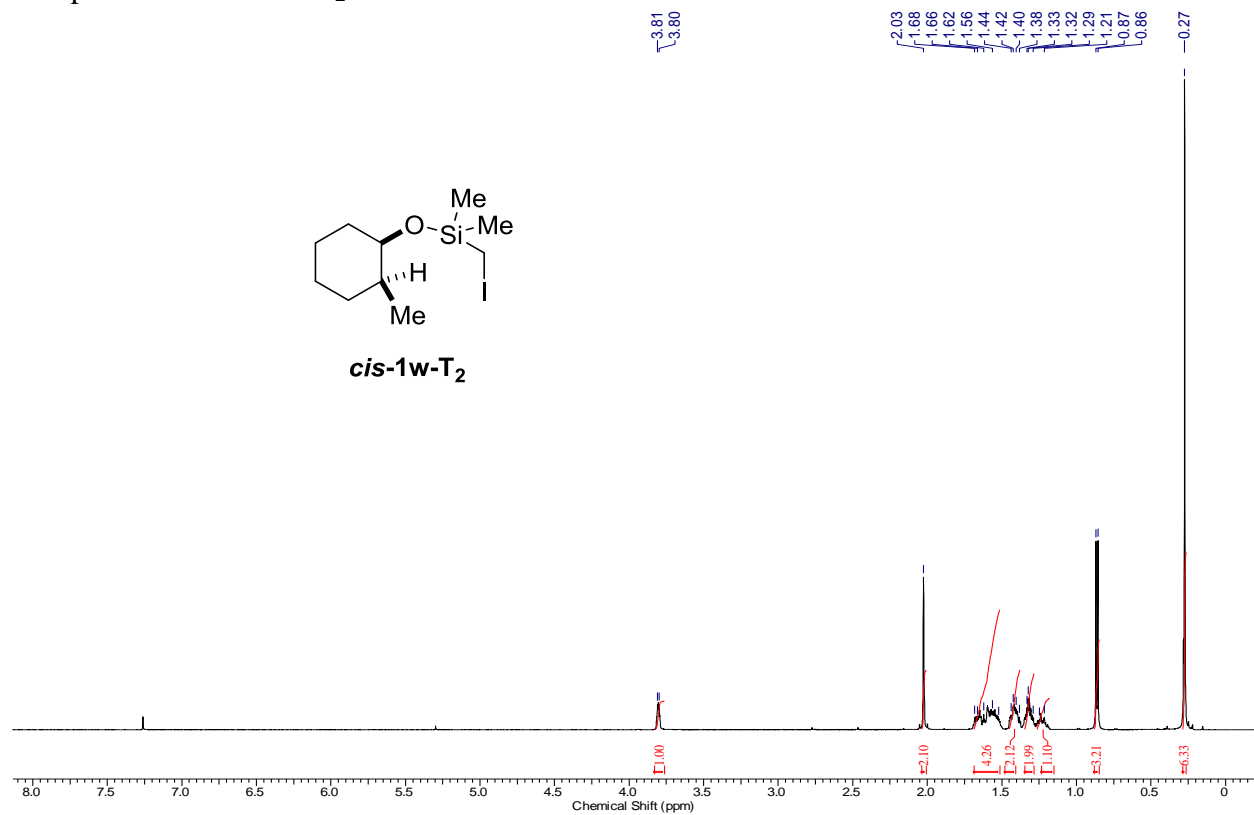
^2H Spectrum of **2q-d-T₂**



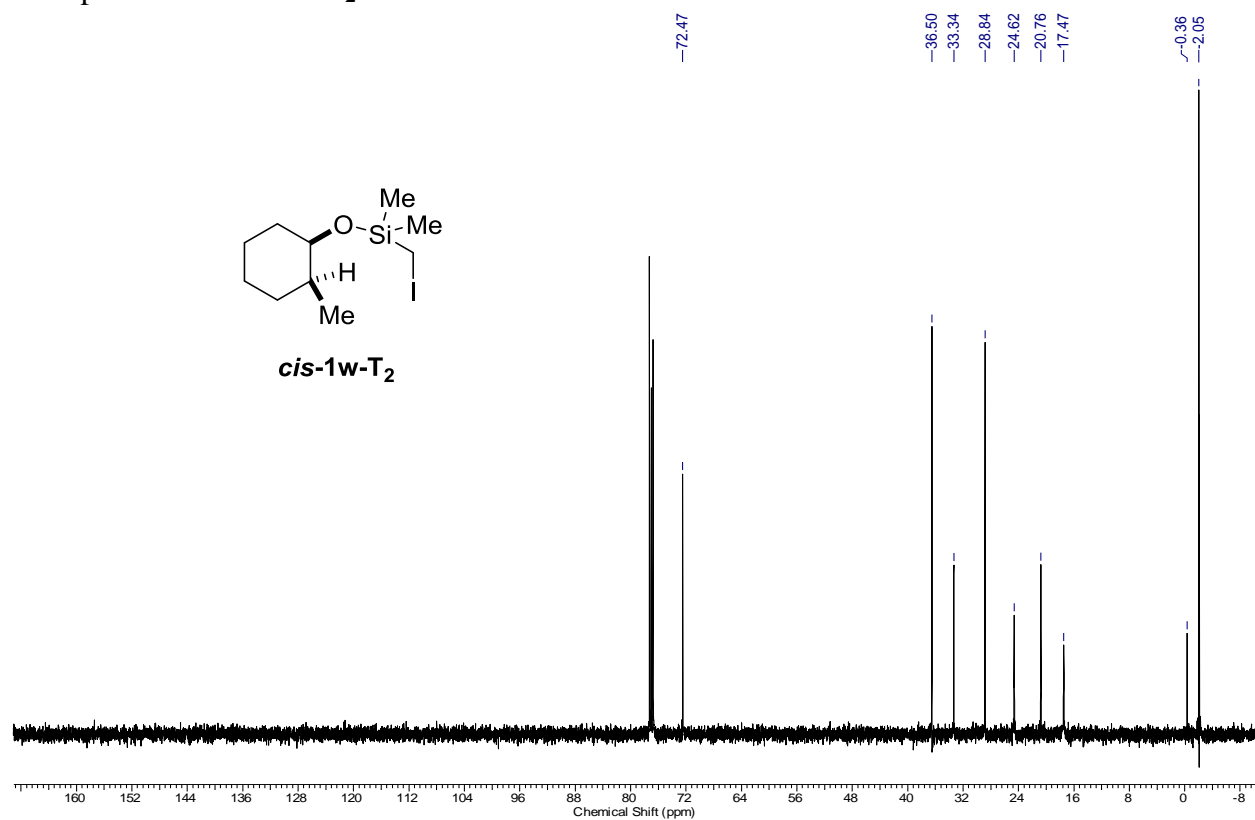
¹H Spectrum of **2q-d-T₂**



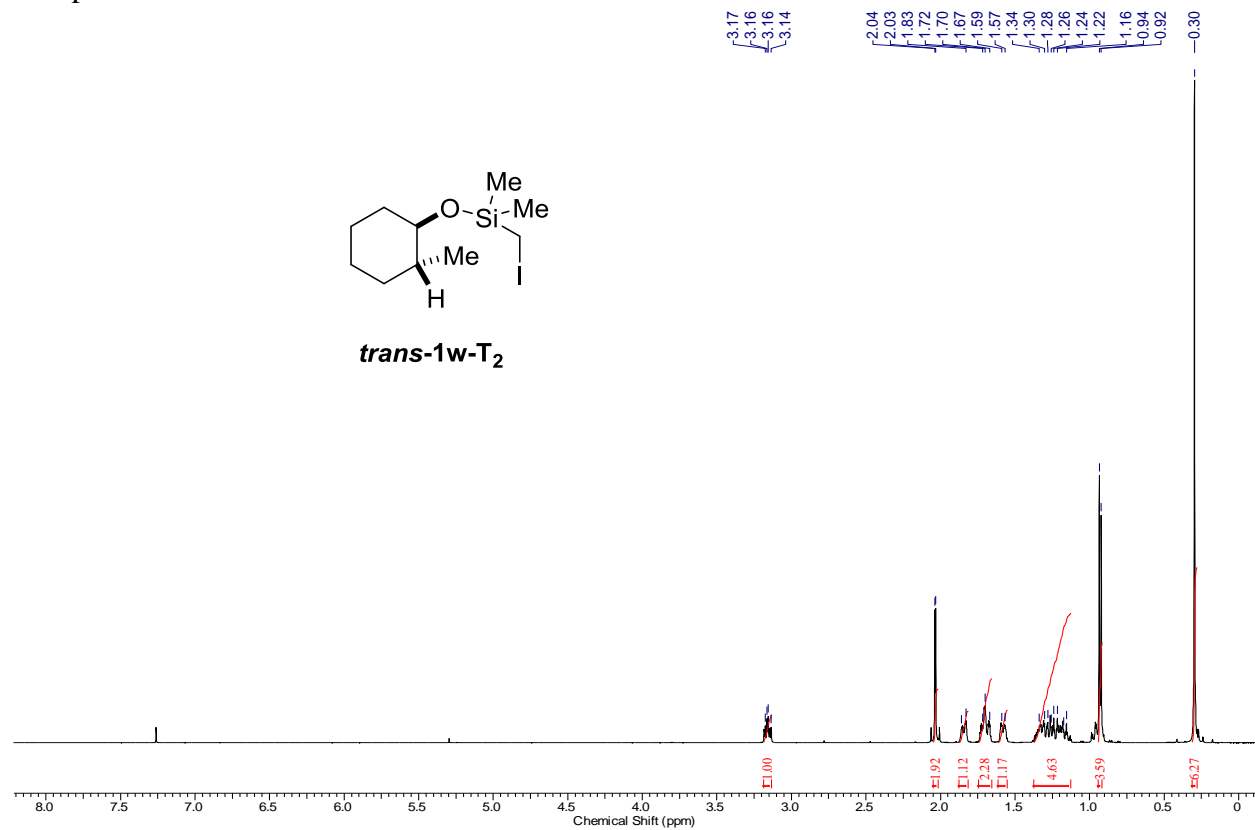
¹H Spectrum of **cis-1w-T₂**



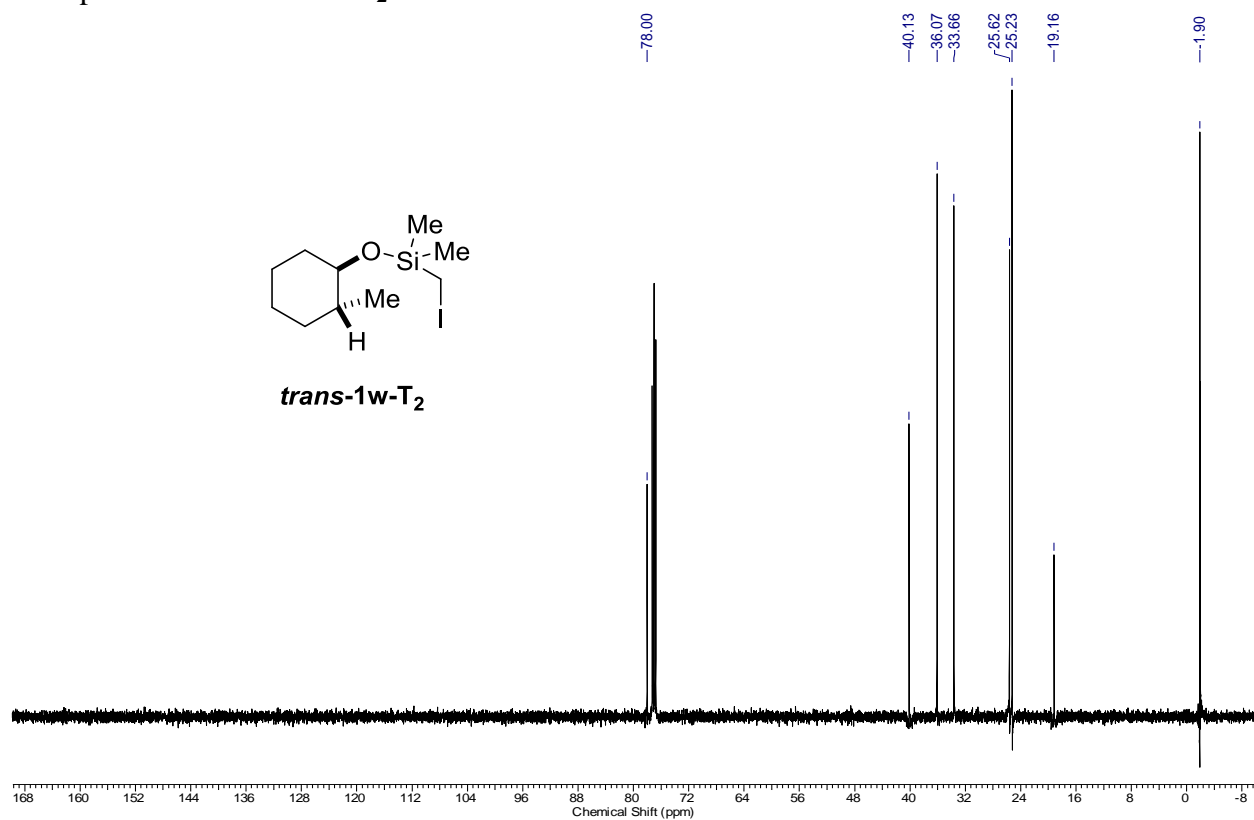
^{13}C Spectrum of *cis-1w-T₂*



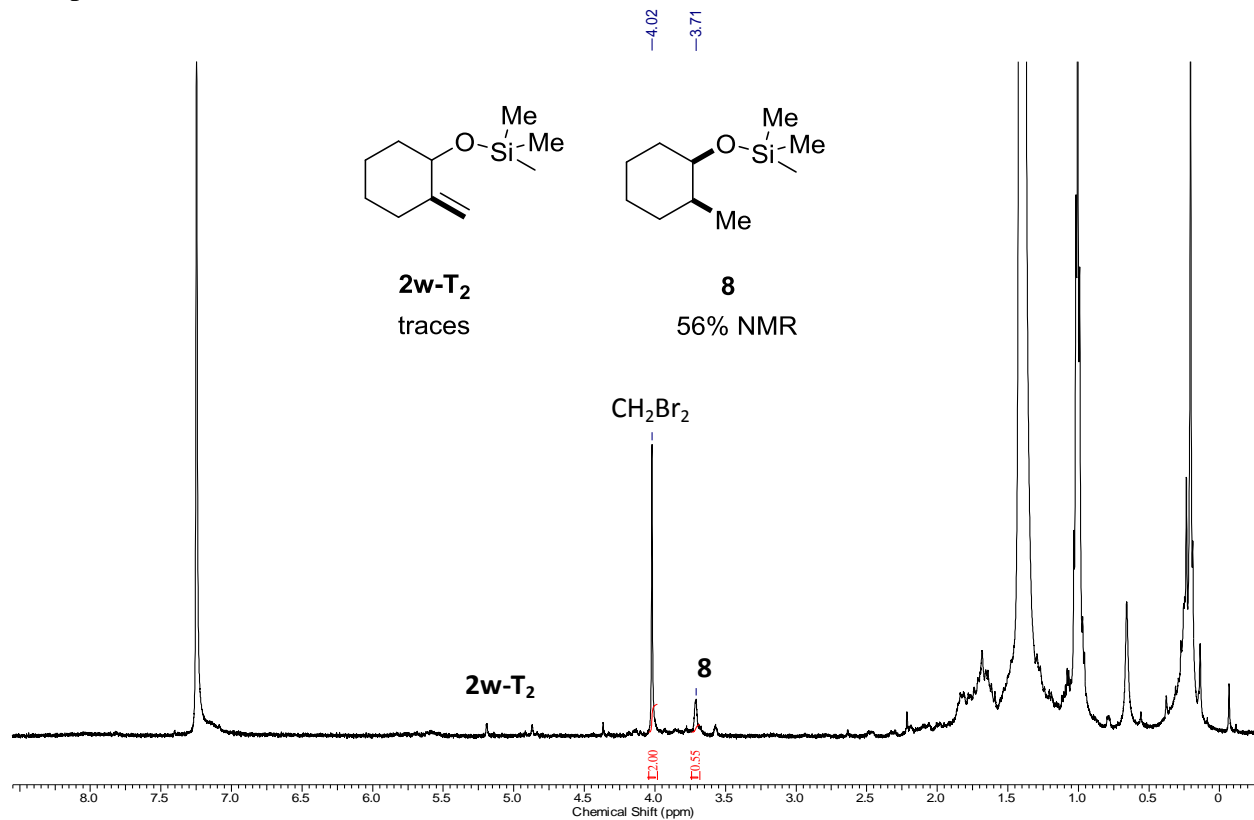
^1H Spectrum of *trans-1w-T₂*



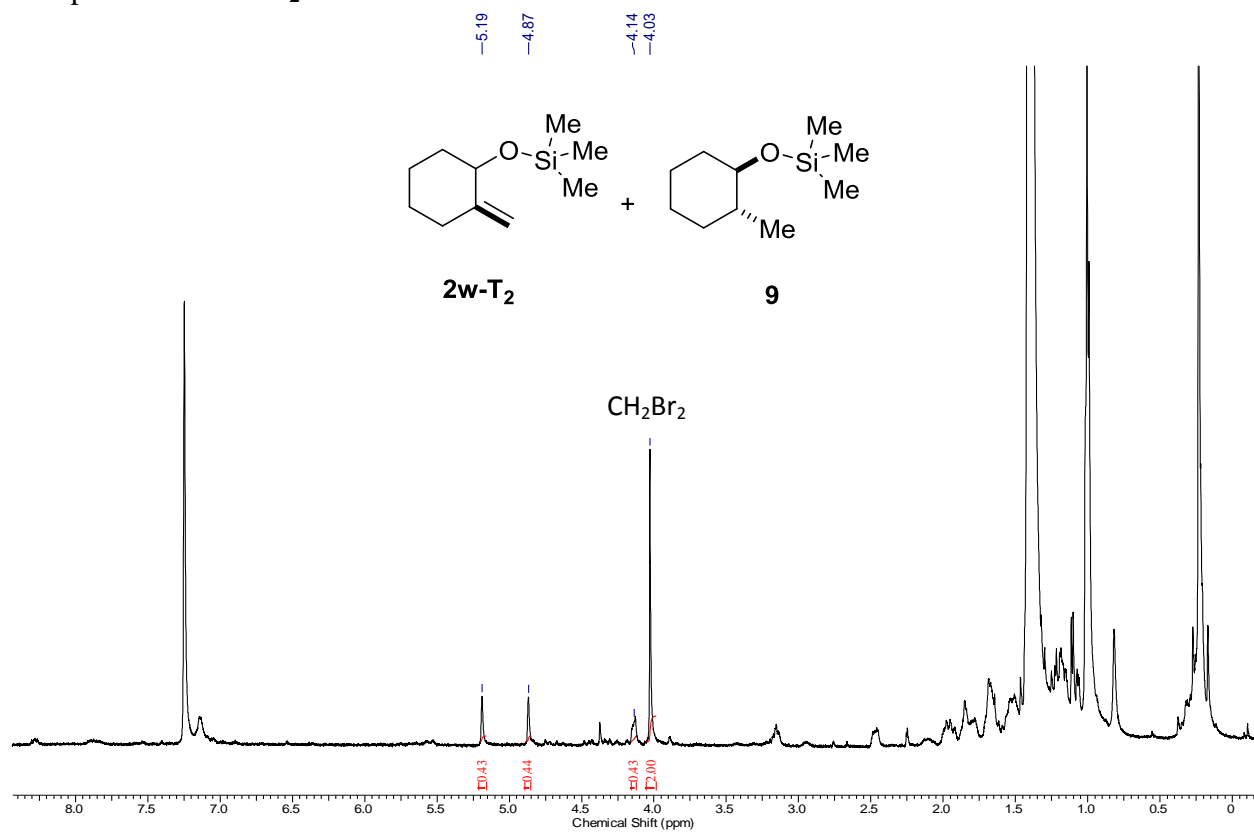
¹³C Spectrum of *trans*-1w-T₂



¹H Spectrum of 2w-T₂ + 8



^1H Spectrum of **2w-T₂** + **9**



7. References

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