

Supporting Information

Synthesis of Divalent Ytterbium Terphenylamide and Catalytic Application for Regioselective Hydrosilylation of Alkenes

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X-ray Crystallography

Table S1. Crystallographic detail for **1***C₇H₈.

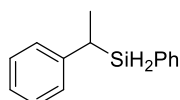
Empirical formula	C ₆₃ H ₈₈ N ₄ Si ₄ Yb ₂
Formula weight	1359.81
temperature	113(2)
wavelength	0.71075 Å
Crystal system, space group	Monoclinic, P 2 ₁ /n
Unit cell dimensions	a=14.368(3) Å alpha= 90.00 ° b=23.236(4) Å beta = 106.498(3) ° c=19.877(4) Å gamma=90.00 °
volume	6363(2) Å ³
Z, Calculated density	4, 1.420 Mg/m ³
F(000)	2760
Absorption coefficient	3.036 mm ⁻¹
Crystal size	0.32 × 0.24 × 0.20 mm
Theta range for data collection	2.66 to 27.88 deg
Limiting indices	-14 ≤ h ≤ 13, -15 ≤ K ≤ 13, -18 ≤ l ≤ 18
Reflections collected / unique	14713 / 7126 [R(int) = 0.0304]
Completeness to theta = 27.88	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4736 and 0.3979
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7126 / 92 / 357
Goodness-of-fit on F ²	1.075
Final R indices [I > 2σ(I)]	R1 = 0.0243, wR2 = 0.0596
R indices (all data)	R1 = 0.0264, wR2 = 0.0603
Largest diff. Peak and hole	0.991 and -1.374 e.Å ⁻³
CCDC number	1545004

Table S2. Crystallographic detail for **2***C₇H₈.

Empirical formula	C ₆₁ H ₆₆ N ₂ O ₂ Si Yb	
Formula weight	1060.29	
Temperature	113(2)K	
Wavelength	0.71075 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a=17.100(2) Å	α =71.668(6) deg.
	b=17.5072(17) Å	β =85.793(6) deg.
	c=19.438(2) Å	γ =71.566(5) deg.
Volume	5238.3(11) Å ³	
Z, Calculated density	4, 1.344 Mg/m ³	
Absorption coefficient	1.852 mm ⁻¹	
F(000)	2184	
Crystal size	0.26 × 0.24 × 0.22 mm	
Theta range for data collection	1.26 to 27.88 deg.	
Limiting indices	-22 ≤ h ≤ 22, -23 ≤ k ≤ 20, -25 ≤ l ≤ 25	
Reflections collected/unique	58425/24765 [R(int)= 0.0409]	
Completeness to theta=27.88	99/1%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6861 and 0.6445	
Refinement method	Full-matrix least-squares on F ²	
CCDC number	1545003	

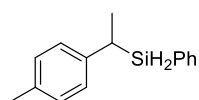
General Procedures for the Catalytic Hydrosilylation Reactions. In an Ar glove box, a Schlenk tube (10 ml) was charged with catalyst **1** (0.005-0.01 mmol) and toluene (0.2 mL). And then silane (1.0 mmol) and the appropriate alkene or diene (1.0 mmol) were added by microsyringe. The Schlenk tube was quickly removed from the glovebox. The reaction mixture was stirred 4-8 h at 60-90 °C using oil bath, and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent.

Phenyl(1-phenylethyl)silane (**4a**)¹



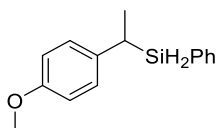
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), Styrene (104 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 60 °C for 4 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (201 mg, 95 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (m, 2H, Ar-*H*), 7.63 – 7.56 (m, 2H, Ar-*H*), 7.50 (m, 4H, Ar-*H*), 7.35 (m, 2H, Ar-*H*), 4.62 (s, 2H, SiH₂), 2.86 (m, 1H, C-*H*), 1.71 (d, ³J_{H-H} = 7.4 Hz, 3H, Me). ¹³C NMR (101 MHz, CDCl₃): δ 144.7, 135.9, 131.6, 130.0, 128.6, 128.1, 127.4, 125.3 (Ar-C), 25.6 (Me), 16.6 (CHSi). ²⁹Si NMR (79 MHz, CDCl₃): δ -20.6 (SiH₂). GC-MS (EI): Calcd for C₁₄H₁₆Si: 212.10, found: 212.21. This compound was known.

Phenyl(1-(*p*-tolyl)ethyl)silane (**4b**)²



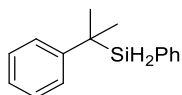
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 4-Methylstyrene (118 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 60 °C for 4 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (215 mg, 95 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.53 (m, 2H, Ar-*H*), 7.44 (m, 2H, Ar-*H*), 7.41–7.36 (m, 2H, Ar-*H*), 7.16–7.11 (m, 3H, Ar-*H*), 4.47 (s, 2H, SiH₂), 2.68 (m, 1H, CH), 2.40 (s, 3H, Ar-Me), 1.55 (d, ³J_{H-H} = 7.4 Hz, 3H, CH-Me). ¹³C NMR (101 MHz, CDCl₃): δ 141.7, 136.0, 130.0, 129.4, 128.1, 127.3 (Ar-C), 25.1 (CH-Me), 21.2 (Ar-Me), 16.9 (CHSi). ²⁹Si NMR (79 MHz, CDCl₃): δ -20.8 (SiH₂). GC-MS (EI): Calcd for C₁₅H₁₈Si: 226.12, found: 226.24. This compound was known.

(1-(4-Methoxyphenyl)ethyl)(phenyl)silane (**4c**)³



The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 4-Methoxystyrene (134 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 60 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (230 mg, 95 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (m, 2H, Ar-*H*), 7.52 (m, 3H, Ar-*H*), 7.21 (m, 2H, Ar-*H*), 7.00 (m, 2H, Ar-*H*), 4.54 (s, 2H, SiH₂), 3.92 (s, 3H, ArO-Me), 2.75 (m, 1H, CH), 1.63 (d, ³J_{H-H} = 7.3 Hz, 3H, Me). ¹³C NMR (101 MHz, CDCl₃): δ 158.1, 137.3, 136.6, 132.4, 130.6, 129.0, 128.9, 128.8 (Ar-C), 56.0 (ArO-Me), 25.1 (Me), 17.7 (CHSi). ²⁹Si NMR (79 MHz, CDCl₃): δ -21.2 (SiH₂). GC-MS (EI): Calcd for C₁₅H₁₈OSi: 242.11, found: 242.23. This compound was known.

PhCH₃C(SiH₂Ph)CH₃ (**4d**)³



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 2-Phenyl-1-propene (118 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (208 mg, 92 %) as a colorless oil. ¹H NMR (400 MHz, C₆D₆): δ 7.53–7.05 (m, 10H, Ar-*H*), 4.44 (s, 2H, SiH₂), 1.36 (s, 6H, Me). ¹³C NMR (101 MHz, C₆D₆): δ 136.2, 135.9, 129.9, 128.4, 127.9, 126.3, 125.7, 125.2 (Ar-C), 26.5 (Me), 25.3 (Me₂-C). ²⁹Si NMR (79 MHz, C₆D₆): δ -13.3 (SiH₂). GC-MS (EI): Calcd for C₁₅H₁₈Si: 226.12, found: 226.17. This compound was known.

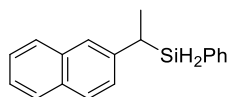
Ph₂C(CH₃)SiH₂Ph (**4e**)³



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1,1-Diphenylethylene (180 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (268 mg, 93 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.61–7.39 (m, 15H, Ar-*H*), 5.04 (s, 2H, SiH₂), 2.09 (s, 3H, Me). ¹³C

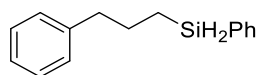
NMR (101 MHz, CDCl_3): δ 146.3, 135.2, 134.6, 129.8, 128.7, 127.2, 126.5, 124.5 (Ar-C), 36.5 ($\text{Ph}_2\text{-C}$), 24.5 (Me). ^{29}Si NMR (79 MHz, C_6D_6): δ -19.3 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{20}\text{H}_{20}\text{Si}$: 228.13, found: 228.20. This compound was known.

[1-(2-Naphthyl)-1-ethyl](phenyl)silane (**4f**)³



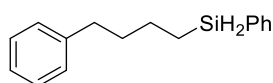
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 2-Vinylnaphthalene (154 mg, 1.0 mmol) and PhSiH_3 (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (250 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.09–8.01 (m, 3H, Ar-*H*), 7.85 (s, 1H, Ar-*H*), 7.76–7.71 (m, 3H, Ar-*H*), 7.67 (m, 2H, Ar-*H*), 7.62–7.55 (m, 3H, Ar-*H*), 4.78 (m, 2H, SiH_2), 3.16–3.04 (m, 1H, CH), 1.89 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3): δ 141.0, 134.5, 132.7, 130.5, 130.1, 128.7, 126.8, 126.7, 126.5, 126.2, 125.5, 124.8, 123.7, 123.4 (Ar-C), 24.5 (Me), 15.3 (CH). ^{29}Si NMR (79 MHz, C_6D_6): δ -21.4 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{18}\text{Si}$: 262.12, found: 262.18. This compound was known.

phenyl(3-phenylpropyl)silane (**4g**)³



The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), Allylbenzene (118 mg, 1.0 mmol) and PhSiH_3 (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (204 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 7.46 (m, 2H, Ar-*H*), 7.13 (m, 5H, Ar-*H*), 7.08–7.04 (m, 1H, Ar-*H*), 6.99 (m, 2H, Ar-*H*), 4.43 (m, 2H, SiH_2), 2.46 (m, 2H, Ar- CH_2), 1.65 (m, 2H, CH_2), 0.79 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 141.9, 135.2, 132.2, 129.5, 128.5, 128.3, 128.0, 125.8 (Ar-C), 39.0 (Ar- CH_2), 27.0 (CH_2), 9.7 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -31.0 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{18}\text{Si}$: 226.12, found: 226.20.

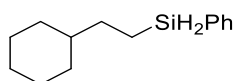
Phenyl(4-phenylbutyl)silane (**4h**)⁴



The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 4-Phenyl-1-butene (132 mg, 1.0 mmol) and PhSiH_3 (108 mg, 1.0 mmol) at 70 °C for 6 h and then the

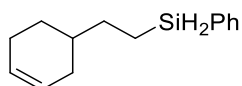
reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (215 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 7.50–7.45 (m, 2H, Ar-*H*), 7.16 (m, 2H, Ar-*H*), 7.14 (m, 3H, Ar-*H*), 7.07 (m, 1H, Ar-*H*), 7.02 (m, 2H, Ar-*H*), 4.50–4.39 (m, 2H, SiH_2), 2.43–2.37 (m, 2H, Ar- CH_2), 1.58–1.48 (m, 2H, CH_2), 1.44–1.30 (m, 2H, CH_2), 0.78 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 142.3, 135.2, 132.3, 129.5, 128.4, 128.3, 128.0, 125.7 (Ar-C), 35.6 (Ar- CH_2), 34.6 (CH_2), 24.7 (CH_2), 9.9 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -31.1 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{Si}$: 240.13, found: 240.22.

(2-Cyclohexylethyl)(phenyl)silane (**4i**)⁵



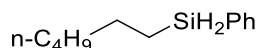
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), Vinylcyclohexane (110 mg, 1.0 mmol) and PhSiH_3 (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (160 mg, 70 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.71 (m, 2H, Ar-*H*), 7.48 (m, 3H, Ar-*H*), 4.44 (s, 2H, SiH_2), 1.83 (m, 6H, CH_2 , CH), 1.46–1.31 (m, 5H, CH_2), 1.05–0.85 (m, 4H, CH_2 , CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 135.9, 135.4, 129.6, 128.3 (Ar-C), 40.5 (CH), 33.1, 32.7, 27.0, 26.6 (CH_2), 7.3 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -29.9 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{22}\text{Si}$: 218.15, found: 218.27.

4-[2-(Phenylsilyl)ethyl]cyclohex-1-ene (**4j**)⁶



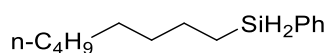
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 4-Vinylcyclohexene (108 mg, 1.0 mmol) and PhSiH_3 (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (195 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.73 (m, 2H, Ar-*H*), 7.51 (m, 3H, Ar-*H*), 5.82 (s, 2H, $\text{CH}=\text{CH}$), 4.48 (s, 2H, SiH_2), 2.19 (s, 2H, CH_2), 1.88–1.76 (m, 2H, CH_2), 1.59–1.35 (m, 3H, CH_2), 1.12 (s, 2H, CH_2), 0.92 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 135.4, 132.7, 129.7, 128.1 (Ar-C), 127.2, 126.7 ($\text{CH}=\text{CH}$), 36.3 (CH), 32.0, 31.6, 28.6, 25.5 (CH_2), 7.4 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -29.9 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{20}\text{Si}$: 216.13, found: 216.21.

(1-Hexyl)(phenyl)silane (**4k**)³



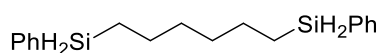
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1-Hexene (84 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (145 mg, 75 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (m, 2H, Ar-*H*), 7.49 (m, 3H, Ar-*H*), 4.46 (s, 2H, SiH₂), 1.4–1.08 (m, 8H, CH₂), 0.9–0.75 (m, 5H, Me, CH₂Si). ¹³C NMR (101 MHz, CDCl₃): δ 134.6, 134.2, 128.4, 126.9 (Ar-C), 31.5, 30.5, 24.0, 21.5 (CH₂), 13.1 (Me), 9.0 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -31.3 (SiH₂). GC-MS (EI): Calcd for C₁₂H₂₀Si: 192.13, found: 192.24.

(1-Octyl)(phenyl)silane (**4l**)⁷



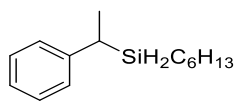
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1-Octene (112 mg, 1.0 mmol) and PhSiH₃ (108 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (175 mg, 80 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (m, 2H, Ar-*H*), 7.44 (m, 3H, Ar-*H*), 4.45 (s, 2H, SiH₂), 1.48–1.35 (m, 12H, CH₂), 1.08–0.97 (m, 5H, Me, SiH₂). ¹³C NMR (101 MHz, CDCl₃): δ 134.6, 134.1, 128.4, 126.9 (Ar-C), 32.0, 30.9, 28.3, 24.5, 24.1, 21.6 (CH₂), 13.1 (Me), 9.0 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -30.6 (SiH₂). GC-MS (EI): Calcd for C₁₄H₂₄Si: 220.16, found: 220.26.

1,6-bis(phenylsilyl)hexane (**4m**)⁸



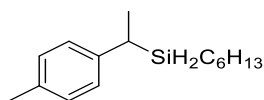
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1,5-Hexadiene (82 mg, 1.0 mmol) and PhSiH₃ (216 mg, 2.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (210 mg, 70 %) as a colorless oil. ¹H NMR (400 MHz, C₆D₆): δ 7.53 (m, 4H, Ar-*H*), 7.21 (m, 6H, Ar-*H*), 4.50 (s, 4H, SiH₂), 1.39 (m, 4H, CH₂), 1.25 (m, 4H, CH₂), 0.84 (s, 4H, SiH₂). ¹³C NMR (101 MHz, C₆D₆): δ 135.9, 135.4, 129.7, 128.2 (Ar-C), 32.6 (CH₂), 25.2 (CH₂), 10.3 (CH₂Si). ²⁹Si NMR (79 MHz, C₆D₆): δ -31.0 (SiH₂). GC-MS (EI): Calcd for C₁₈H₂₆Si: 298.16, found: 298.18.

Hexyl(1-phenylethyl)silane (**5a**)



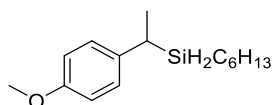
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), Styrene (104 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 60 °C for 4 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (213 mg, 97 %) as a colorless oil. ¹H NMR (400 MHz, C₆D₆): δ 7.14 (m, 2H, Ar-*H*), 7.07–6.97 (m, 3H, Ar-*H*), 3.95–3.82 (m, 2H, SiH₂), 2.31–2.20 (m, 1H, CH), 1.35 (d, ³J_{H-H} = 7.5 Hz, 3H, CH-Me), 1.27–1.11 (m, 8H, CH₂), 0.86 (t, ³J_{H-H} = 6.9 Hz, 3H, CH₂-Me), 0.52 (s, 2H, CH₂Si). ¹³C NMR (101 MHz, C₆D₆): δ 145.4, 128.6, 127.0, 125.1 (Ar-C), 32.8 (CH₂), 31.7 (CH₂), 25.4 (CH₂), 24.6 (CH-Me), 22.8 (CH₂), 16.9 (CHSi), 14.2 (CH₂-Me), 8.4 (CH₂Si). ²⁹Si NMR (79 MHz, C₆D₆): δ -18.5 (SiH₂). GC-MS (EI): Calcd for C₁₄H₂₄Si: 220.16, found: 220.25.

Hexyl(1-(*p*-tolyl)ethyl)silane (**5b**)



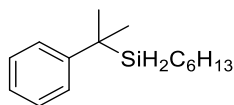
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 4-Methylstyrene (118 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 60 °C for 4 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (227 mg, 97 %) as a colorless oil. ¹H NMR (400 MHz, C₆D₆): δ 6.97 (m, 4H, Ar-*H*), 3.88 (m, 2H, Ar-*H*), 2.32–2.22 (m, 1H, CH), 2.15 (s, 3H, Ar-Me), 1.36 (t, ³J_{H-H} = 9.5 Hz, 3H, CH-Me), 1.30–1.12 (m, 8H, CH₂), 0.86 (t, ³J_{H-H} = 6.9 Hz, 3H, CH₂-Me), 0.54 (m, 2H, CH₂Si). ¹³C NMR (101 MHz, C₆D₆): δ 142.2, 134.1, 129.3, 126.9 (Ar-C), 32.8 (CH₂), 31.7 (CH₂), 25.6 (CH₂), 24.1 (CH-Me), 22.8 (CH₂), 20.8 (Ar-Me), 17.1 (CHSi), 14.2 (CH₂-Me), 8.4 (CH₂Si). ²⁹Si NMR (79 MHz, C₆D₆): δ -18.7 (SiH₂). GC-MS (EI): Calcd for C₁₅H₂₆Si: 234.18, found: 234.32.

(1-(4-Methoxyphenyl)ethyl)(hexyl)silane (**5c**)



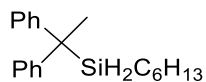
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 4-Methoxystyrene (134 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 60 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (237 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 6.96 (m, 2H, Ar-*H*), 6.74 (m, 2H, Ar-*H*), 3.93–3.81 (m, 2H, SiH_2), 3.38 (s, 3H, ArO-Me), 2.24 (m, 1H, CH), 1.35 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 3H, CH-Me), 1.28–1.10 (m, 8H, CH_2), 0.84 (t, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, CH_2 -Me), 0.55 (d, $^3J_{\text{H-H}} = 2.4$ Hz, 2H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 157.7, 137.1, 127.8, 114.2 (Ar-C), 54.6 (ArO-Me), 32.8 (CH_2), 31.7 (CH_2), 25.4 (CH_2), 23.5 (CH-Me), 22.8 (CH_2), 17.3 (CHSi), 14.2 (CH_2 -Me), 8.4 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -19.0 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{26}\text{OSi}$: 250.18, found: 250.37.

$\text{PhCH}_2\text{C}(\text{SiH}_2\text{C}_6\text{H}_{13})\text{CH}_3$ (5d)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 2-Phenyl-1-propene (118 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (215 mg, 92 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 7.21 (m, 2H, Ar-*H*), 7.16 (m, 2H, Ar-*H*), 7.00 (m, 1H, Ar-*H*), 3.86 (m, 2H, SiH_2), 1.38 (s, 6H, Me), 1.22–1.09 (m, 8H, CH_2), 0.84 (m, 3H, CH_2 -Me), 0.49 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 148.3, 128.4, 125.8, 124.9 (Ar-C), 32.8 (CH_2), 31.7 (CH_2), 25.9 (CH_2), 25.4 (Me), 25.3 ($\text{Me}_2\text{-C}$), 22.8 (CH_2), 14.2 (CH_2 -Me), 8.1 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -10.21 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{26}\text{Si}$: 234.18, found: 234.27.

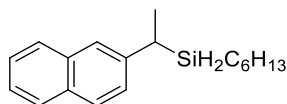
$\text{Ph}_2\text{C}(\text{CH}_3)\text{SiH}_2\text{C}_6\text{H}_{13}$ (5e)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1,1-Diphenylethylene (180 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (276 mg, 93 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 7.28–7.19 (m, 4H, Ar-*H*), 7.14–7.09 (m, 4H, Ar-*H*), 7.01 (m, 2H, Ar-*H*), 4.24 (m, 2H, SiH_2), 1.70 (s, 3H, $\text{Ph}_2\text{C-Me}$), 1.24–1.08 (m, 8H, CH_2), 0.89–0.79 (m, 3H, CH_2 -Me), 0.54

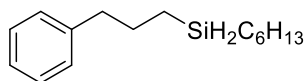
(d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 148.30, 128.52, 128.17, 125.61 (Ar-C), 37.2 ($\text{Ph}_2\text{-C}$), 32.7 (CH_2), 31.7 (CH_2), 26.3 (CH_2), 25.5 ($\text{Ph}_2\text{-C-Me}$), 22.8 (CH_2), 14.3 ($\text{CH}_2\text{-Me}$), 8.6 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -15.3 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{20}\text{H}_{28}\text{Si}$: 296.20, found: 296.24.

[1-(2-Naphthyl)-1-ethyl](hexyl)silane (**5f**)



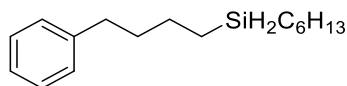
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 2-Vinylnaphthalene (154 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 6 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (251 mg, 93 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (m, 3H, Ar-H), 7.51 (m, 1H, Ar-H), 7.39–7.33 (m, 2H, Ar-H), 7.25 (m, 1H, Ar-H), 3.81–3.71 (m, 2H, SiH_2), 2.59–2.48 (m, 1H, CH), 1.50 (m, 3H, CH-Me), 1.27–1.16 (m, 8H, CH_2), 0.83 (t, $^3J_{\text{H-H}} = 6.9$ Hz, 3H, $\text{CH}_2\text{-Me}$), 0.60 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 142.08, 132.78, 130.45, 126.75, 126.50, 126.20, 125.41, 124.78, 123.66, 123.03 (Ar-C), 31.4 (CH_2), 30.4 (CH_2), 24.0 (CH_2), 23.6 (CH-Me), 21.5 (CH_2), 15.7 (CH), 13.0 ($\text{CH}_2\text{-Me}$), 7.2 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -21.4 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{26}\text{Si}$: 270.18, found: 270.24.

Hexyl(3-phenylpropyl)silane (**5g**)



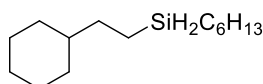
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), Allylbenzene (118 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (223 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 7.14 (m, 2H, Ar-H), 7.04 (m, 3H, Ar-H), 3.90–3.78 (m, 2H, SiH_2), 2.51 (m, 2H, Ar- CH_2), 1.63 (m, 2H, Ar $\text{CH}_2\text{-CH}_2$), 1.26 (m, 8H, CH_2), 0.88 (t, $^3J_{\text{H-H}} = 6.9$ Hz, 3H, $\text{CH}_2\text{-Me}$), 0.65–0.53 (m, 4H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 142.1, 128.6, 128.4, 125.9 (Ar-C), 39.3 (Ar- CH_2), 32.8 (CH_2), 31.8 (CH_2), 27.7 (CH_2), 25.6 (CH_2), 22.8 (CH_2), 14.2 ($\text{CH}_2\text{-Me}$), 9.3 (CH_2Si), 9.0 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -28.8 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{26}\text{Si}$: 234.18, found: 234.28.

Hexyl(4-phenylbutyl)silane (**5h**)



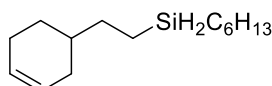
The reaction was carried out according to general method by using catalyst A (6.4 mg, 0.005 mmol), 4-Phenyl-1-butene (132 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (236 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, C_6D_6): δ 7.18–7.10 (m, 2H, Ar-H), 7.04 (m, 3H, Ar-H), 3.86–3.78 (m, 2H, SiH_2), 2.54–2.39 (m, 2H, Ar- CH_2), 1.63–1.50 (m, 2H, CH_2), 1.32 (m, 10H, CH_2), 0.87 (m, 3H, CH_2 -Me), 0.61 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, CH_2Si). ^{13}C NMR (101 MHz, C_6D_6): δ 142.4, 128.5, 128.3, 125.8 (Ar-C), 35.8 (CH_2), 34.9 (CH_2), 32.9 (CH_2), 31.8 (CH_2), 25.7 (CH_2), 25.3 (CH_2), 22.8 (CH_2), 14.2 (CH_2 -Me), 9.3 (CH_2Si), 9.2 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -28.9 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{28}\text{Si}$: 248.20, found: 248.29.

(2-Cyclohexylethyl)(hexyl)silane (**5i**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), Vinylcyclohexane (110 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (208 mg, 92 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.72 (s, 2H, SiH_2), 1.77 (m, 5H, CH_2 , CH), 1.32 (m, 14H, CH_2), 0.96 (m, 5H, CH_2 , CH_2 -Me), 0.74 (m, 4H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 40.4 (CH), 33.1 (CH_2), 33.0 (CH_2), 32.7 (CH_2), 31.6 (CH_2), 26.8 (CH_2), 26.5 (CH_2), 25.5 (CH_2), 22.7 (CH_2), 14.1 (CH_2 -Me), 9.2 (CH_2Si), 6.3 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -27.8 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{30}\text{Si}$: 226.21, found: 226.29.

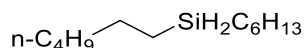
4-[2-(Hexylsilyl)ethyl]cyclohex-1-ene (**5j**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 4-Vinylcyclohexene (108 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (213 mg, 95 %) as a

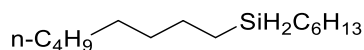
colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 5.70 (s, 2H, $\text{CH}=\text{CH}$), 3.72 (s, 2H, SiH_2), 2.25–2.02 (m, 4H, CH_2), 1.74 (m, 1H, CH), 1.52–1.26 (m, 12H, CH_2), 0.94 (s, 3H, $\text{CH}_2\text{-Me}$), 0.74 (s, 4H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 127.0, 126.5 ($\text{CH}=\text{CH}$), 36.2 (CH), 32.7 (CH_2), 32.3 (CH_2), 31.6 (CH_2), 28.5 (CH_2), 25.5 (CH_2), 25.3 (CH_2), 22.6 (CH_2), 14.1 (Me), 9.2 (CH_2Si), 6.3 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -27.8 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{28}\text{Si}$: 224.20, found: 224.28.

(1-Hexyl)(hexyl)silane (**5k**)



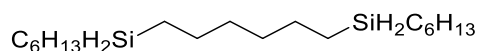
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1-Hexene (84 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (191 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.71 (s, 2H, SiH_2), 1.38 (m, 16H, CH_2), 0.95 (m, 6H, $\text{CH}_2\text{-Me}$), 0.73 (m, 4H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 32.7 (CH_2), 31.6 (CH_2), 25.5 (CH_2), 22.6 (CH_2), 14.1 (Me), 9.20 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -28.9 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{12}\text{H}_{28}\text{Si}$: 200.20, found: 200.29.

(1-Octyl)(hexyl)silane (**5l**)



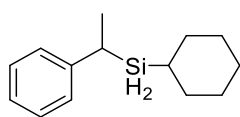
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1-Octene (112 mg, 1.0 mmol) and hexylsilane (116 mg, 1.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (217 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.70 (s, 2H, SiH_2), 1.32 (m, 20H, CH_2), 0.93 (m, 6H, $\text{CH}_2\text{-Me}$), 0.72 (m, 4H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 33.0 (CH_2), 32.6 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 25.5 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 ($\text{CH}_2\text{-Me}$), 9.2 (CH_2Si). ^{29}Si NMR (79 MHz, C_6D_6): δ -28.9 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{32}\text{Si}$: 228.23, found: 228.33.

1,6-Bis(hexylsilyl)hexane (**5m**)



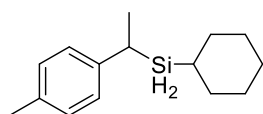
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1,5-Hexadiene (82 mg, 1.0 mmol) and hexylsilane (232 mg, 2.0 mmol) at 70 °C for 8 h and then the reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (285 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.71 (s, 4H, SiH_2), 1.40 (m, 24H, CH_2), 0.94 (s, 6H, $\text{CH}_2\text{-Me}$), 0.73 (s, 8H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 32.7 (CH_2), 32.6 (CH_2), 31.6 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 22.6 (CH_2), 14.1 ($\text{CH}_2\text{-Me}$), 9.2 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -28.6 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{42}\text{Si}$: 314.28, found: 314.37.

Cyclohexyl(1-phenylethyl)silane (**6a**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), styrene (104 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 70 °C for 5 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (207 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.40 (m, 2H, Ar-*H*), 7.30–7.21 (m, 3H, Ar-*H*), 3.77 (m, 1H, SiHH), 3.72 (m, 1H, SiHH), 2.63–2.53 (m, 1H, Ar-*CH*), 1.86–1.72 (m, 5H, CH_2), 1.63–1.54 (m, 3H, CH-Me), 1.40–1.27 (m, 5H, CH_2), 1.04–0.92 (m, 1H, CHSi). ^{13}C NMR (101 MHz, CDCl_3): δ 145.8, 128.5, 127.0, 124.9 (Ar-C), 29.3 (CH_2), 27.8 (CH_2), 26.7 (CH_2), 23.7 ($\text{CH}_2\text{-Me}$), 20.9 (CHSi), 17.5 (Ar-*CH*). ^{29}Si NMR (79 MHz, CDCl_3): δ -11.4 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{22}\text{Si}$: 218.15, found: 218.24.

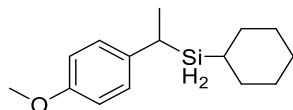
Cyclohexyl(1-(*p*-tolyl)ethyl)silane (**6b**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 4-methylstyrene (118 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 70 °C for 5 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (220 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.34–7.11 (m, 4H, Ar-*H*), 3.78 (m, 2H, SiH_2), 2.65–2.54 (m, 1H, Ar-*CH*), 2.48 (s, 3H, Ar-Me), 1.84 (s, 5H, CH_2), 1.60 (d, $^3J_{\text{H-H}} = 7.3$ Hz, CH-Me), 1.38 (s, 5H, CH_2), 1.03 (s, 1H, CHSi). ^{13}C NMR (101 MHz, CDCl_3): δ 142.7, 134.2, 129.2, 126.9 (Ar-C), 29.3 (CH_2), 27.8 (CH_2), 26.8 (CH_2),

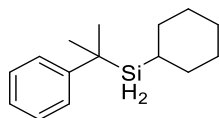
23.1 (Ar-Me), 21.1 (Me), 21.0 (CHSi), 17.7 (Ar-CH). ^{29}Si NMR (79 MHz, CDCl_3): δ -11.5 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{24}\text{Si}$: 232.16, found: 232.22.

(1-(4-Methoxyphenyl)ethyl)(cyclohexyl)silane (6c)



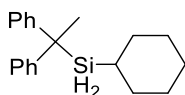
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 4-methoxystyrene (134 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 80 °C for 6 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (235 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 6.98–6.90 (m, 2H, Ar-*H*), 6.75–6.67 (m, 2H, Ar-*H*), 3.64 (s, 3H, ArO-Me), 3.52 (m, 1H, SiHH), 3.46 (m, 1H, SiHH), 2.27 (m, 1H, ArCH), 1.63–1.50 (m, 5H, CH_2), 1.35–1.26 (m, 3H, CH-Me), 1.14–1.01 (m, 5H, CH_2), 0.75 (m, 1H, CHSi). ^{13}C NMR (101 MHz, CDCl_3): δ 156.0, 136.5, 126.7, 112.8 (Ar-C), 54.04 (ArO-Me), 28.10 (CH_2), 26.6 (CH_2), 25.6 (CH_2), 21.4 (Me), 19.8 (CHSi), 16.7 (Ar-CH). ^{29}Si NMR (79 MHz, CDCl_3): δ -12.0 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{24}\text{OSi}$: 248.16, found: 248.22.

$\text{PhCH}_2\text{C}(\text{SiH}_2\text{C}_6\text{H}_{11})\text{CH}_3$ (6d)



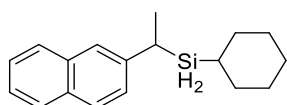
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 2-Phenyl-1-propene (118 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (210 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.51–7.44 (m, 4H, Ar-*H*), 7.34–7.27 (m, 1H, Ar-*H*), 3.84 (m, 2H, SiH_2), 1.80 (m, 3H, Me), 1.74–1.63 (m, 8H, CH_2 , Me), 1.32 (m, 5H, CH_2), 1.06–0.97 (m, 1H, CHSi). ^{13}C NMR (101 MHz, CDCl_3): δ 147.4, 127.0, 124.7, 123.6 (Ar-C), 28.5 (CH_2), 26.5 (CH_2), 25.5 (CH_2), 25.3 (Me), 24.8 (Me₂-C), 19.9 (CHSi). ^{29}Si NMR (79 MHz, CDCl_3): δ -3.31 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{24}\text{Si}$: 232.16, found: 232.24.

$\text{Ph}_2\text{C}(\text{CH}_3)\text{SiH}_2\text{C}_6\text{H}_{11}$ (6e)



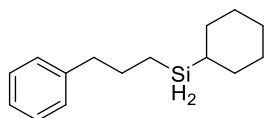
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1,1-Diphenylethylene (180 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (265 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.52 (m, 8H, Ar-H), 7.41 (m, 2H, Ar-H), 4.30 (m, 2H, SiH_2), 2.09 (s, 3H, Me), 1.88–1.75 (m, 5H, CH_2), 1.45 (m, 5H, CH_2), 1.11 (s, 1H, CHSi). ^{13}C NMR (101 MHz, CDCl_3): δ : 146.9, 127.1, 126.8, 124.2 (Ar-C), 43.6 (Ph_2C), 36.1 (CH_2), 28.7 (CH_2), 26.5 (CH_2), 25.2 (Me), 20.0 (CHSi). ^{29}Si NMR (79 MHz, CDCl_3): δ -7.93 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{20}\text{H}_{26}\text{Si}$: 294.18, found: 294.24.

[1-(2-Naphthyl)-1-ethyl](cyclohexyl)silane (**6f**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 2-Vinylnaphthalene (154 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (241 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.93–7.87 (m, 3H, Ar-H), 7.71 (m, 1H, Ar-H), 7.57 (m, 2H, Ar-H), 7.45 (m, 1H, Ar-H), 3.88–3.76 (m, 2H, SiH_2), 2.76 (m, 1H, CH), 1.91–1.76 (m, 5H, CH_2), 1.70 (m, 3H, Me), 1.43–1.36 (m, 5H, CH_2), 1.04 (s, 1H, CHSi). ^{13}C NMR (101 MHz, CDCl_3): δ 142.4, 132.8, 130.4, 126.7, 126.5, 126.2, 125.5, 124.8, 123.7, 123.2 (Ar-C), 28.12 (CH_2), 26.51 (CH_2), 25.5 (CH_2), 22.8 (Me), 19.8 (CHSi), 16.36 (Ar-CH). ^{29}Si NMR (79 MHz, CDCl_3): δ -11.6 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{24}\text{Si}$: 268.16, found: 268.24.

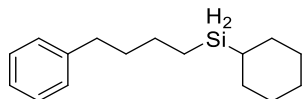
Cyclohexyl(3-phenylpropyl)silane (**5g**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), Allylbenzene (118 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (210 mg, 90 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.36 (m, 2H, Ar-H), 7.30–7.21 (m, 3H, Ar-H), 3.63 (s, 2H, SiH_2), 2.73 (m, 2H, CH_2), 1.80 (m, 7H, CH_2), 1.29 (m, 5H, CH_2), 1.00–0.93 (m, 1H, CHSi), 0.80 (s, 2H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 142.4, 128.6, 128.3, 125.7 (Ar-C), 39.2 (Ar- CH_2), 29.3 (CH_2), 27.8 (CH_2), 27.7

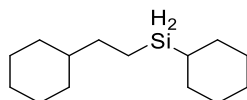
(CH₂), 26.7 (CH₂), 21.2 (CHSi), 7.62 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -22.3 (SiH₂). GC-MS (EI): Calcd for C₁₅H₂₄Si: 232.16, found: 232.22.

Cyclohexyl(4-phenylbutyl)silane (**6h**)



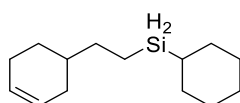
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 4-Phenyl-1-butene (132 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (222 mg, 90 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (m, 2H, Ar-*H*), 7.31 (m, 3H, Ar-*H*), 3.69 (s, 2H, SiH₂), 2.75 (s, 2H, Ar-CH₂), 1.84 (m, 7H, CH₂), 1.59 (s, 2H, CH₂), 1.38 (s, 5H, CH₂), 1.02 (m, 1H, CHSi), 0.85 (s, 2H, CH₂Si). ¹³C NMR (101 MHz, CDCl₃): δ 142.7, 128.5, 128.3, 125.7 (Ar-C), 35.8 (Ar-CH₂), 34.8 (CH₂), 29.4 (CH₂), 27.8 (CH₂), 26.8 (CH₂), 25.5 (CH₂), 21.3 (CHSi), 7.7 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -22.1 (SiH₂). GC-MS (EI): Calcd for C₁₆H₂₆Si: 246.18, found: 246.24.

(2-Cyclohexylethyl)(cyclohexyl)silane (**6i**)



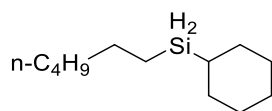
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), Vinylcyclohexane (110 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (208 mg, 93 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 3.56 (s, 2H, SiH₂), 1.75 (s, 10H, CH₂), 1.26 (m, 11H, CH₂, CH), 0.96–0.80 (m, 3H, CH₂, CHSi), 0.69 (s, 2H, CH₂Si). ¹³C NMR (101 MHz, CDCl₃): δ 39.4 (CH), 32.2 (CH₂), 31.9 (CH₂), 28.2 (CH₂), 26.7 (CH₂), 25.8 (CH₂), 25.7 (CH₂), 25.4 (CH₂), 20.2 (CHSi), 3.79 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -21.2 (SiH₂). GC-MS (EI): Calcd for C₁₄H₂₈Si: 224.20, found: 224.26

4-[2-(Cyclohexylsilyl)ethyl]cyclohex-1-ene (**6j**)



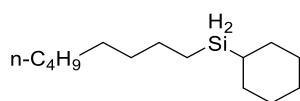
The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 4-Vinylcyclohexene (108 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (206 mg, 93 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 5.69 (s, 2H, $\text{CH}=\text{CH}$), 3.57 (m, 2H, SiH_2), 2.21–2.02 (m, 3H, CH_2 , CH), 1.80 (m, 2H, CH_2), 1.77–1.61 (m, 5H, CH_2), 1.57–1.48 (m, 1H, CH), 1.43–1.36 (m, 2H, CH_2), 1.31–1.18 (m, 6H, CH_2), 0.94 (m, 1H, CHSi), 0.73 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 126.0, 125.5 ($\text{CH}=\text{CH}$), 35.2 (CH), 31.4 (CH_2), 30.6 (CH_2), 28.2 (CH_2), 27.4 (CH_2), 26.7 (CH_2), 25.7 (CH_2), 24.3 (CH_2), 20.2 (CHSi), 3.8 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -21.3 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{26}\text{Si}$: 222.18, found: 222.30.

(1-Hexyl)(cyclohexyl)silane (**6k**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1-Hexene (84 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (188 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.57 (m, 2H, SiH_2), 1.77 (m, 5H, CH_2), 1.33 (m, 13H, CH_2), 0.93 (m, 4H, Me, CHSi), 0.70 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 32.7 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 27.8 (CH_2), 26.7 (CH_2), 25.6 (CH_2), 22.6 (CH_2), 21.2 (CHSi), 14.1 (Me), 7.7 (CH_2Si). ^{29}Si NMR (79 MHz, CDCl_3): δ -22.1 (SiH_2). GC-MS (EI): Calcd for $\text{C}_{12}\text{H}_{26}\text{Si}$: 198.18, found: 198.24.

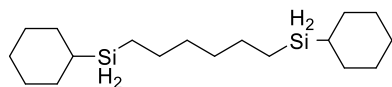
(1-Octyl)(hexyl)silane (**6l**)



The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1-Octene (112 mg, 1.0 mmol) and cyclohexylsilane (114 mg, 1.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (215 mg, 95 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.56 (m, 2H, SiH_2), 1.76 (m, 5H, CH_2), 1.44–1.21 (m, 17H, CH_2), 0.92 (m, 4H, Me, CHSi), 0.74–0.66 (m, 2H, CH_2Si). ^{13}C NMR (101 MHz, CDCl_3): δ 33.0 (CH_2), 31.9 (CH_2), 29.3

(CH₂), 29.2 (CH₂), 27.7 (CH₂), 26.7 (CH₂), 25.6 (CH₂), 22.7 (CH₂), 21.2 (CHSi), 14.1 (Me), 7.7 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -22.1 (SiH₂). GC-MS (EI): Calcd for C₁₄H₃₀Si: 226.21, found: 226.28.

1,6-Bis(cyclohexylsilyl)hexane (**6m**)

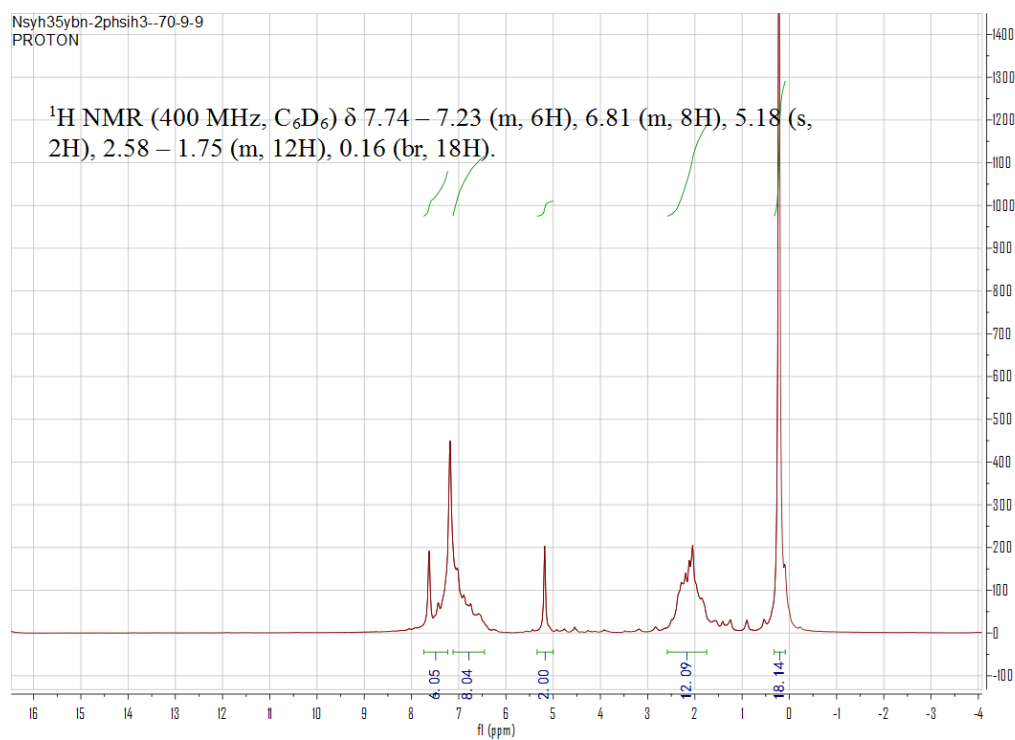


The reaction was carried out according to general method by using catalyst A (12.7 mg, 0.01 mmol), 1,5-Hexadiene (82 mg, 1.0 mmol) and cyclohexylsilane (228 mg, 2.0 mmol) at 90 °C for 8 h and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent. The title compound was isolated (249 mg, 80 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 3.56 (s, 4H, SiH₂), 1.76 (m, 10H, CH₂), 1.40 (m, 8H, CH₂), 1.25 (m, 10H, CH₂), 0.93 (m, 2H, CHSi), 0.70 (m, 4H, CH₂Si). ¹³C NMR (101 MHz, CDCl₃): δ 32.6 (CH₂), 29.2 (CH₂), 27.7 (CH₂), 26.7 (CH₂), 25.5 (CH₂), 21.2 (CHSi), 7.7 (CH₂Si). ²⁹Si NMR (79 MHz, CDCl₃): δ -22.1 (SiH₂). GC-MS (EI): Calcd for C₁₈H₃₈Si: 310.25, found: 310.32.

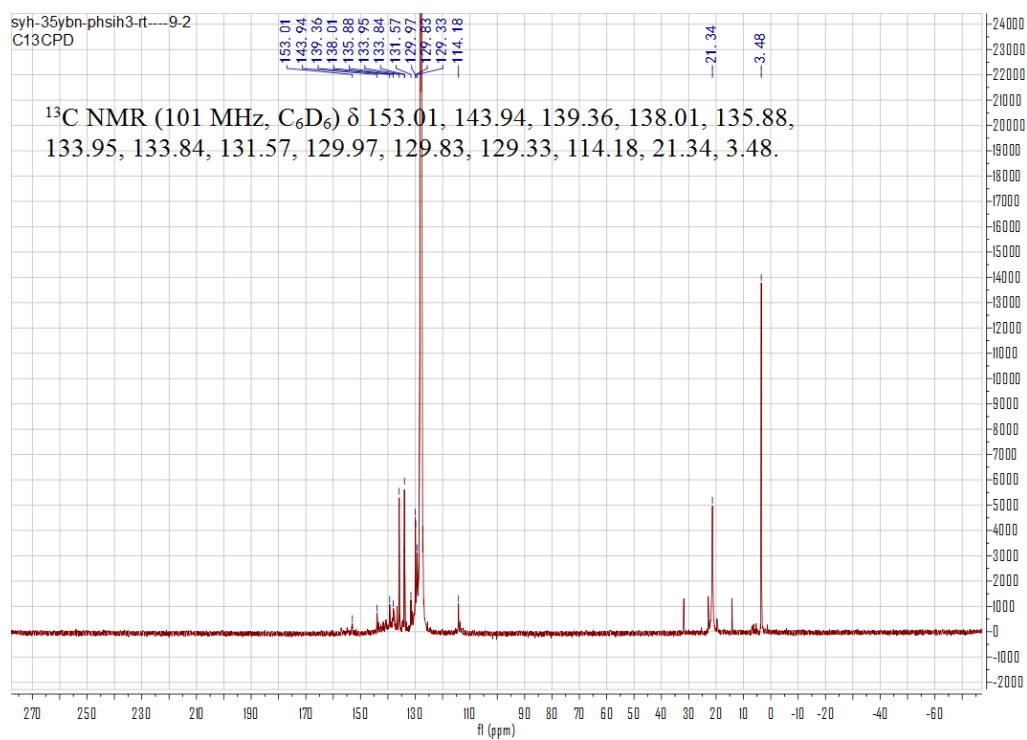
References

- 1 P. F. Fu, L. Brard, Y. W. Li and T. J. Marks, *J. Am. Chem. Soc.* 1995, **117**, 7157-7168.
- 2 L. B. Junquera, M. C. Puerta and P. Valerga, *Organometallics*. 2012, **31**, 2175-2183.
- 3 A. K. Dash, I. Gourevich, J.- Q. Wang, J. -X. Wang, M.Kapon, and M. S. Eisen
Organometallics 2001, **20**, 5084-5104.
- 4 M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.* 2014, **356**, 584-590.
- 5 C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix and P. L. Holland,
J. Am. Chem. Soc. 2015, **137**, 13244-13247.
- 6 A. A. Trifonov, T. P. Spaniol and J. Okuda, *Dalton Trans.* 2004, 2245-2250.
- 7 X. Du, Y. Zhang, D. Peng and Z. Haung, *Angew. Chem. Int. Ed.* 2016, **55**, 6671-6675.
- 8 M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron, J. Okuda, *J. Am. Chem. Soc.* 2008,
130, 6920-6921.

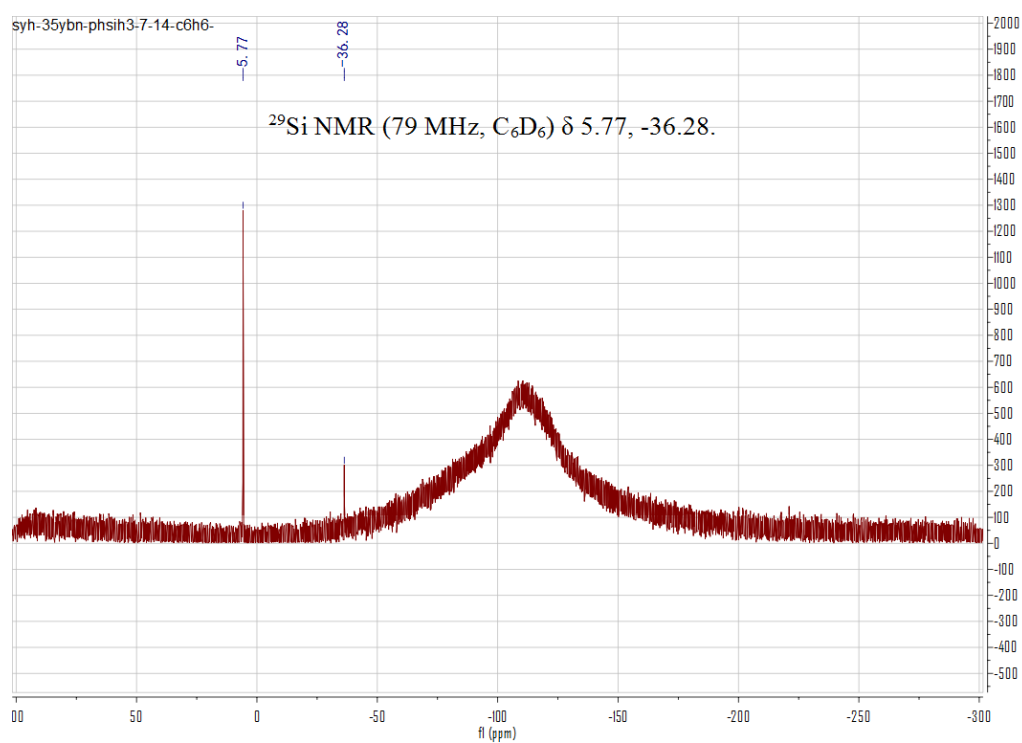
¹H NMR Spectrum of A



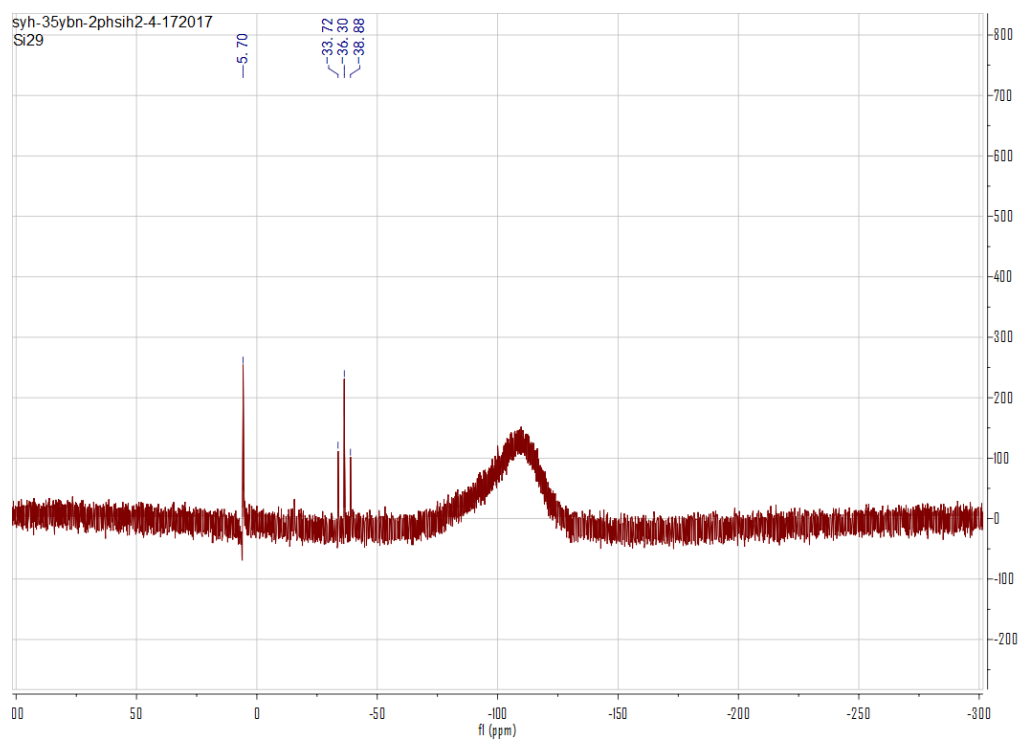
¹³C NMR Spectrum of A



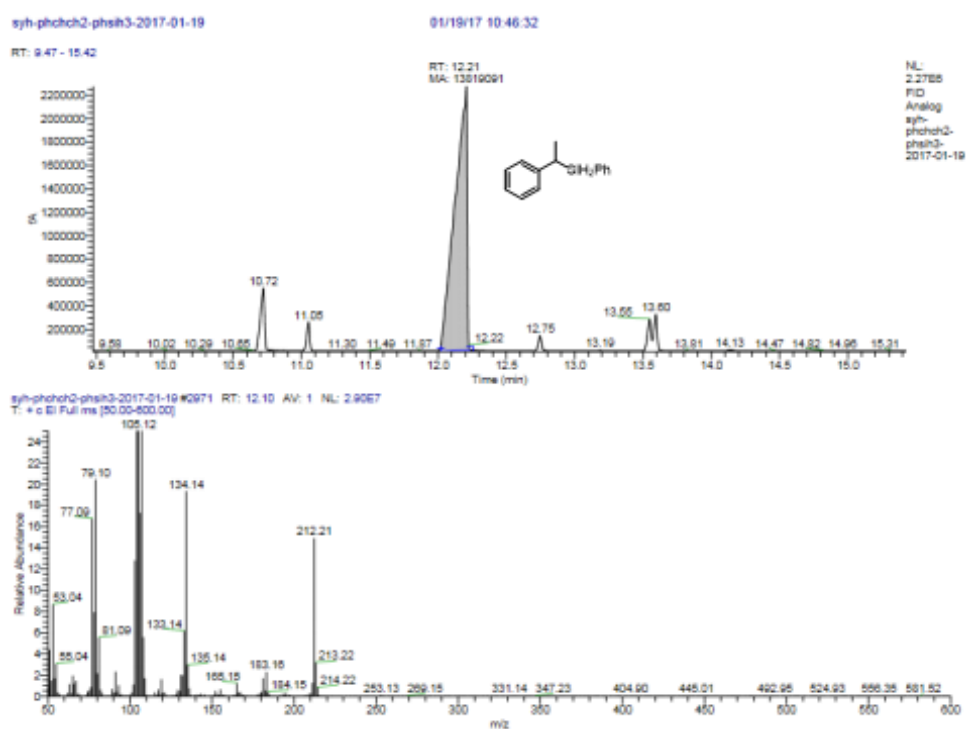
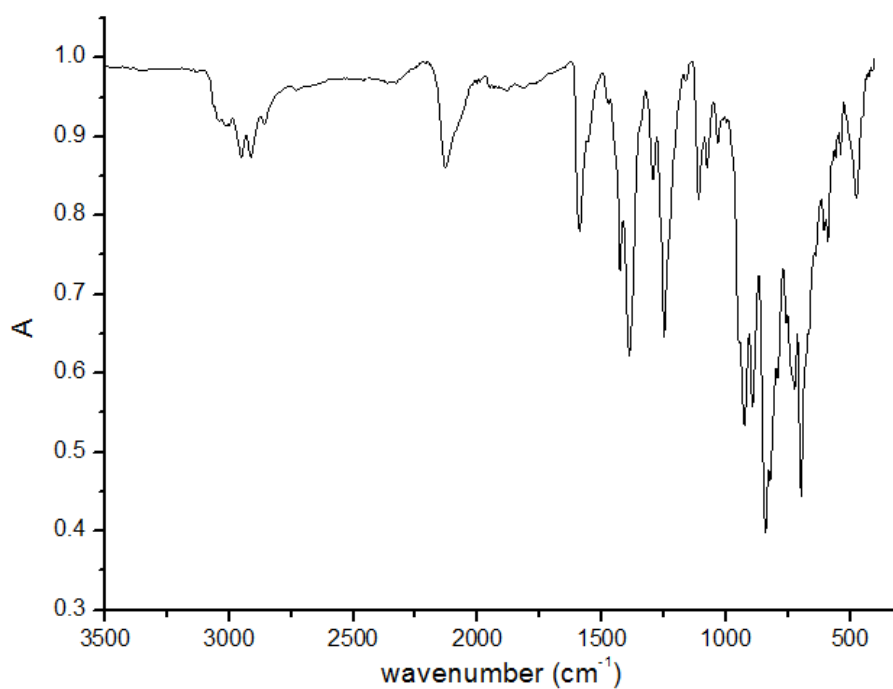
Proton-decoupled ^{29}Si NMR Spectrum of A

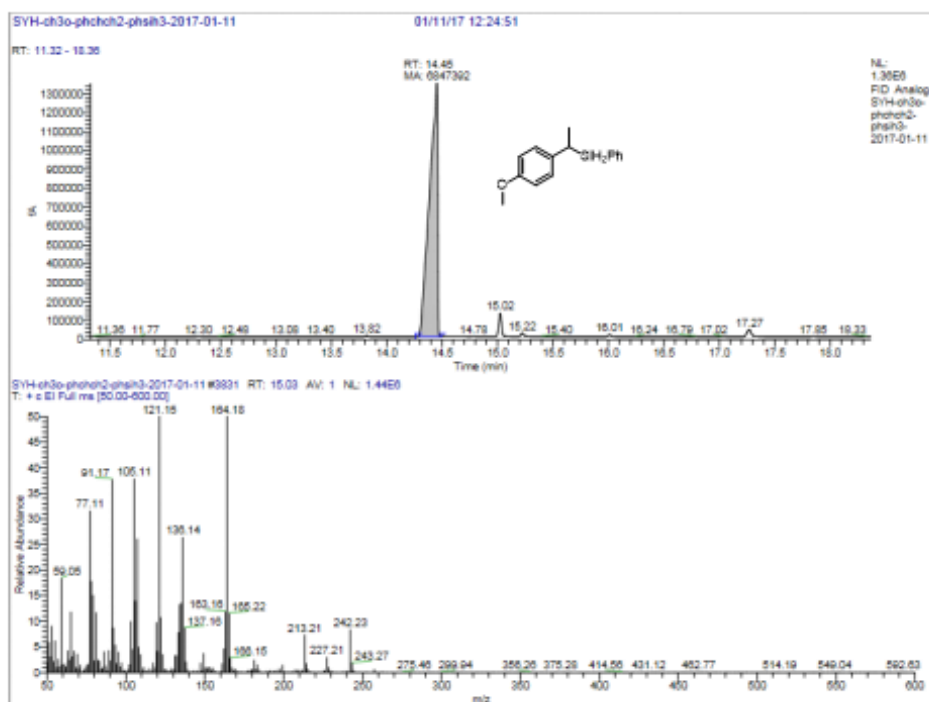
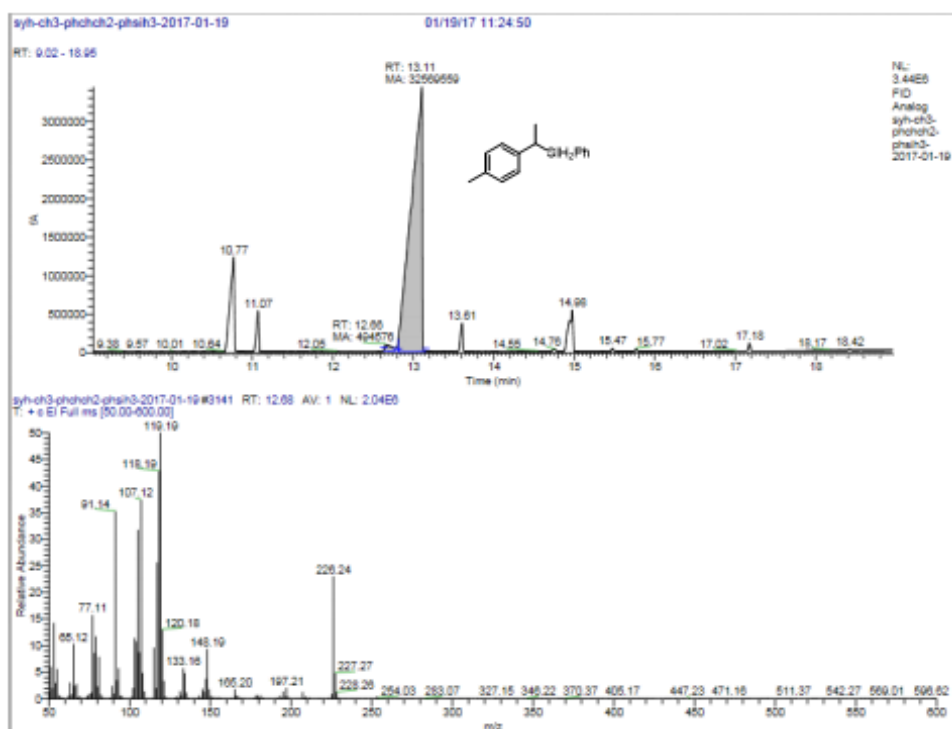


Proton-coupled ^{29}Si NMR Spectrum of A



IR Spectrum of A

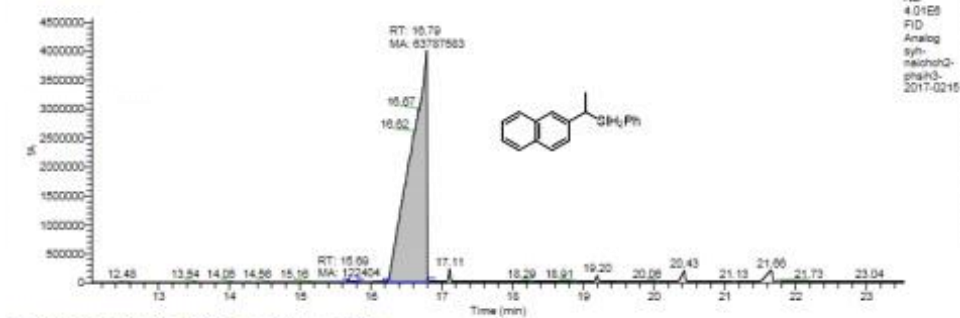




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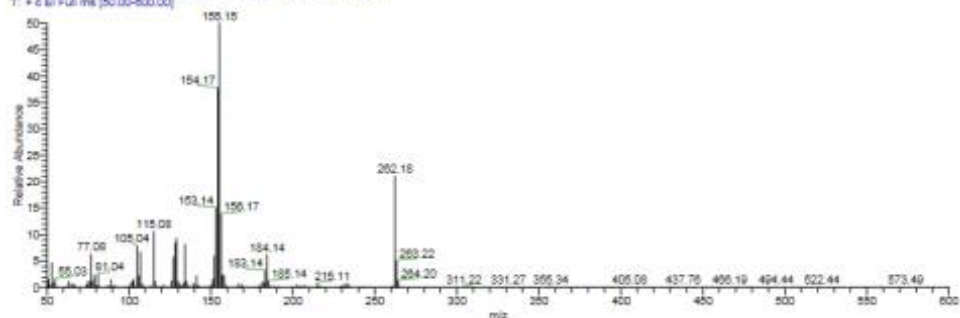
02/15/17 10:19:05

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NL: 4.01E8
FID
Analog
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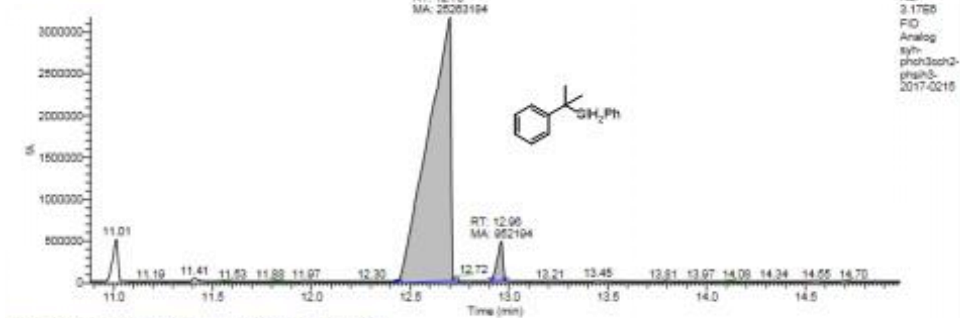
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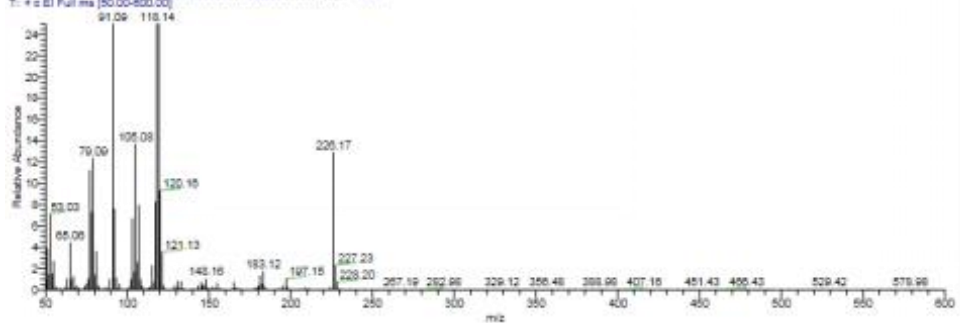
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Analog
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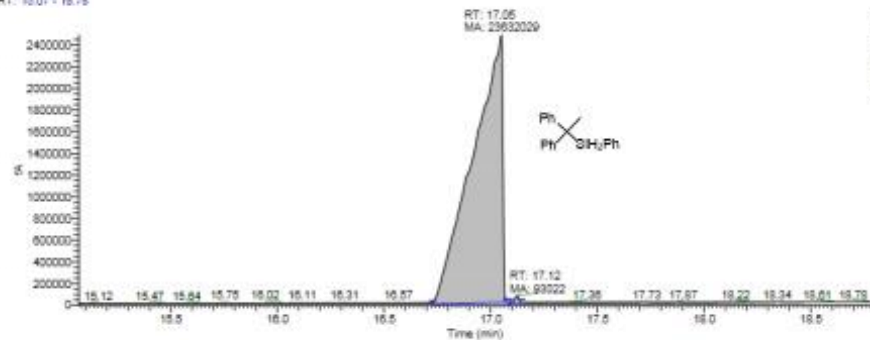
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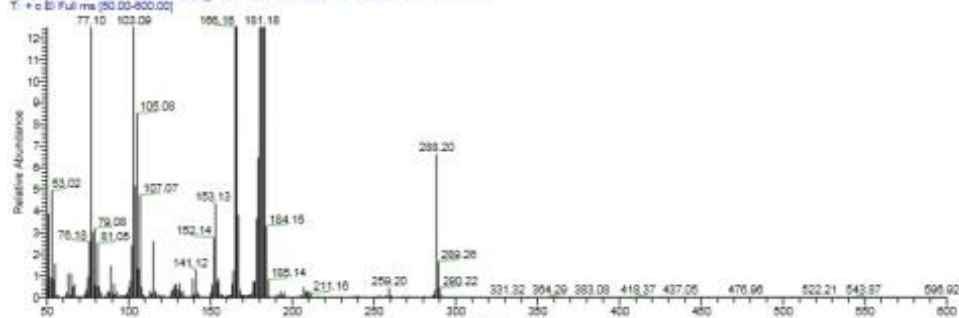
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RT: 15.07 - 16.78



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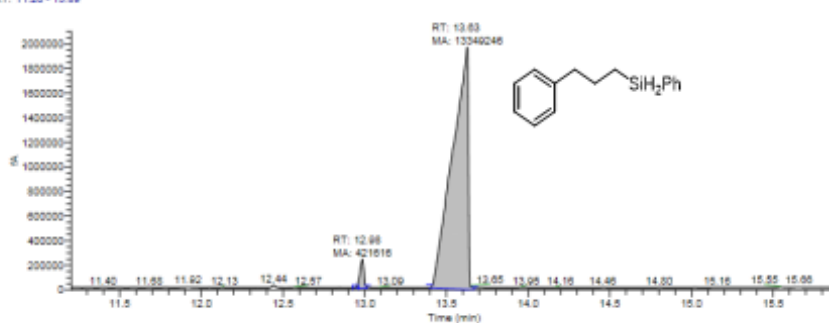
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syh-phch2chch2-phsih3-70du-2017-0217

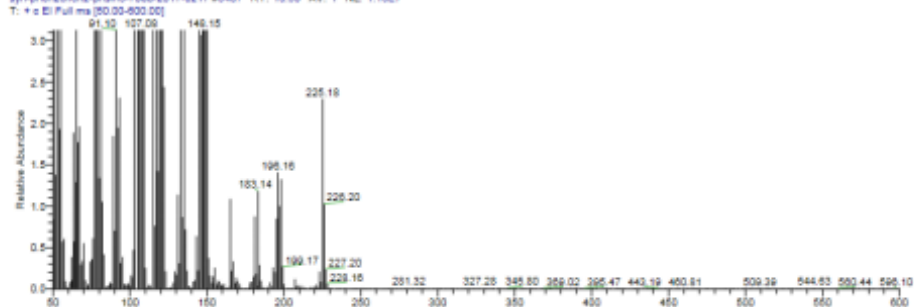
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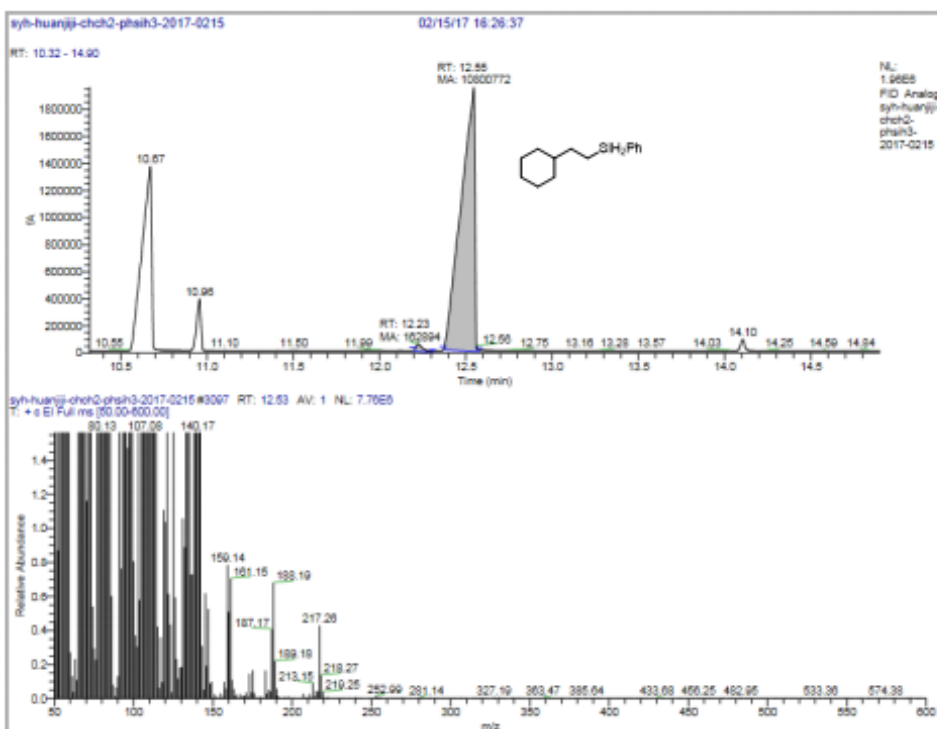
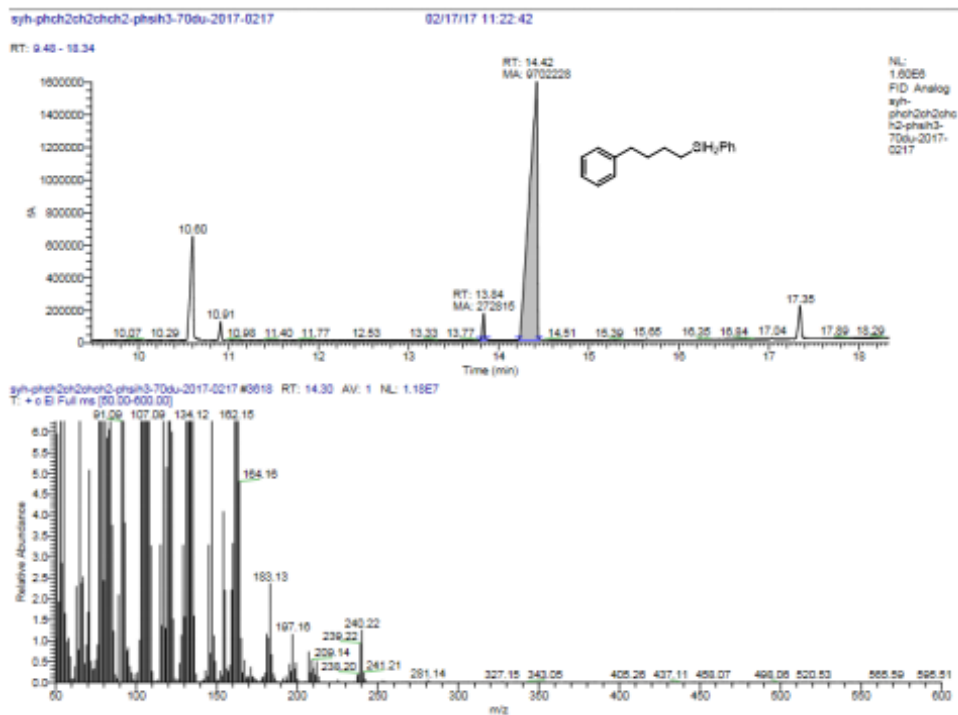
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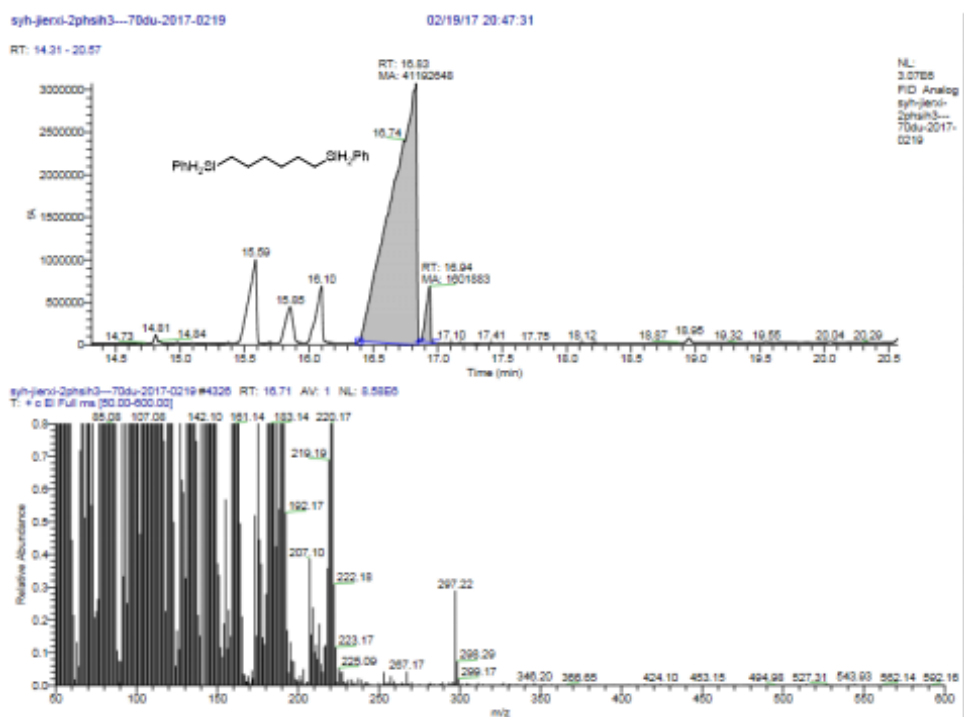
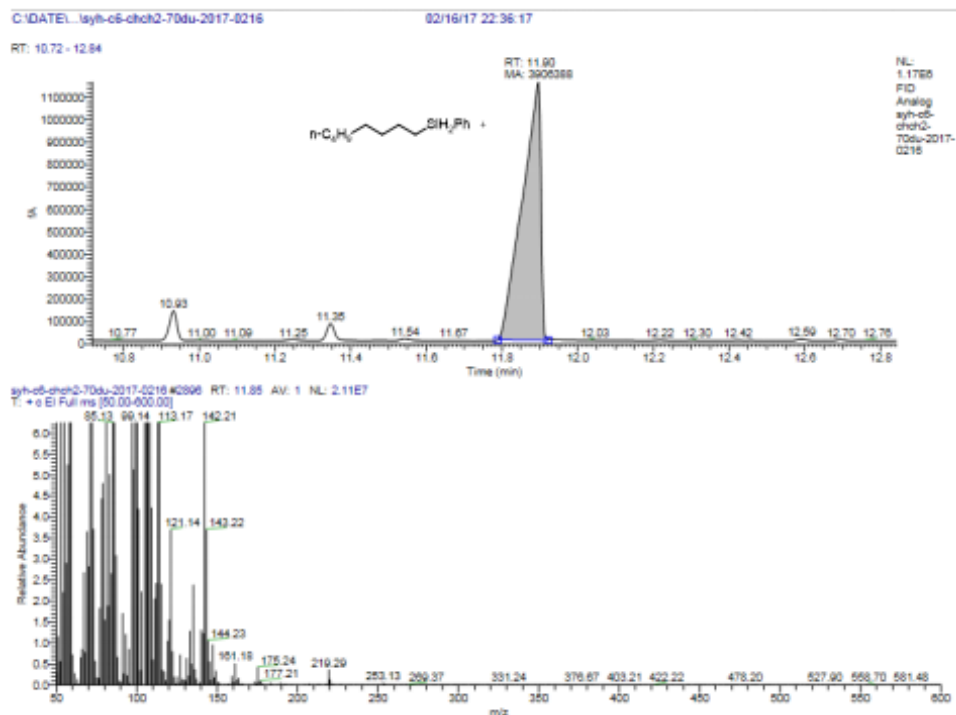


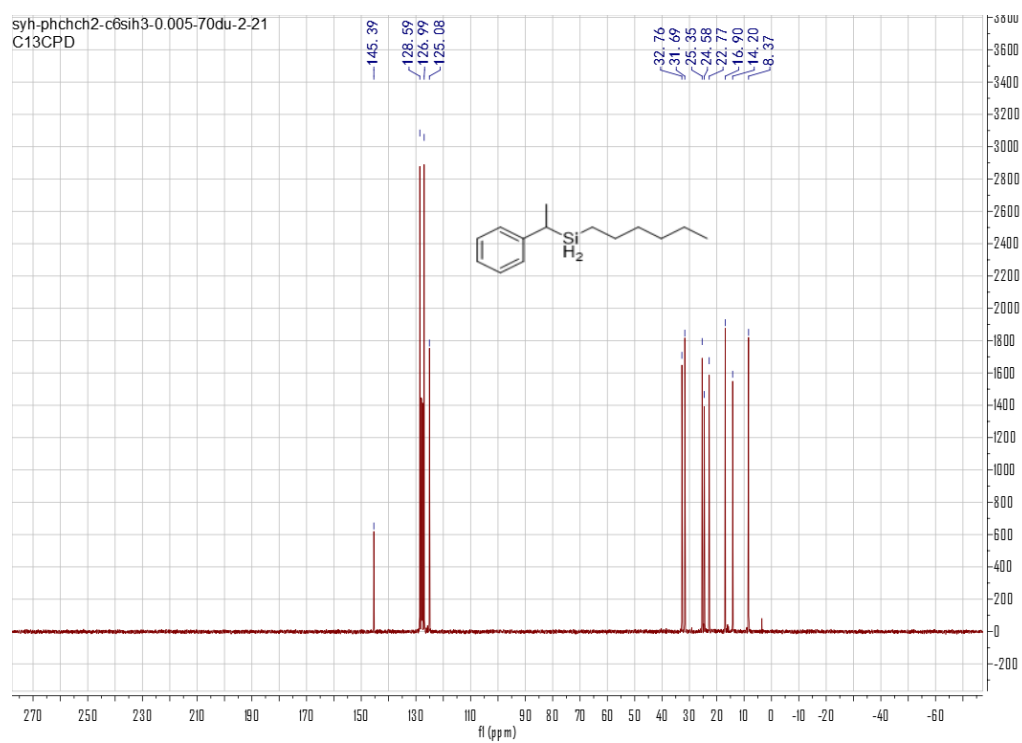
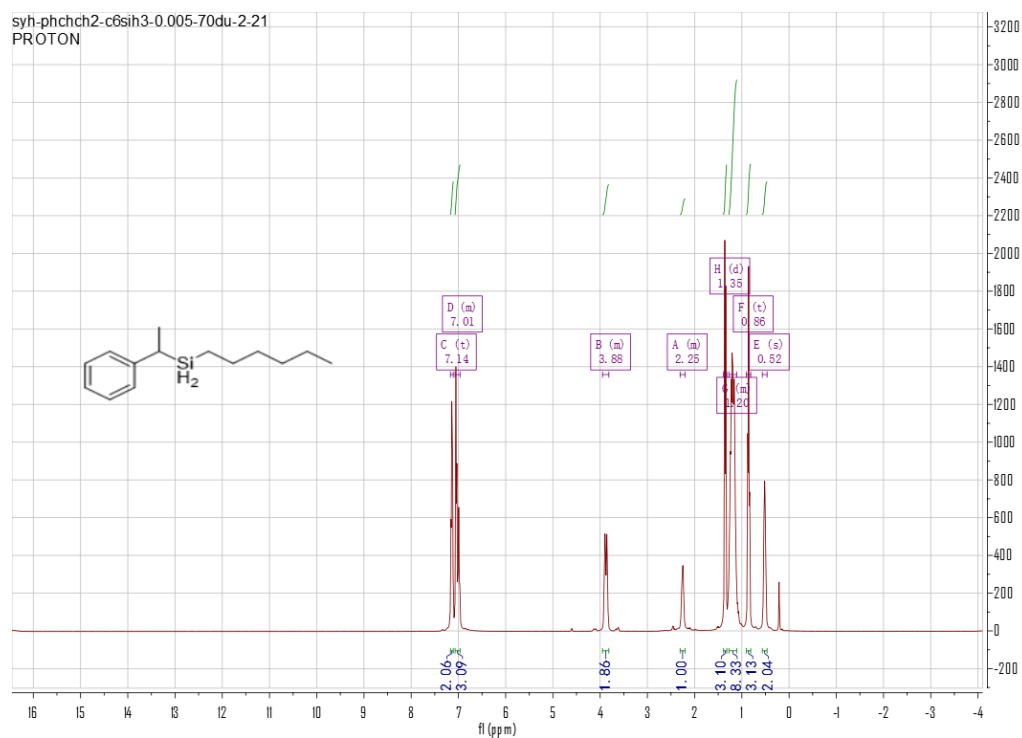
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FID Analog
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phch2chch2-
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70du-2017-
0217

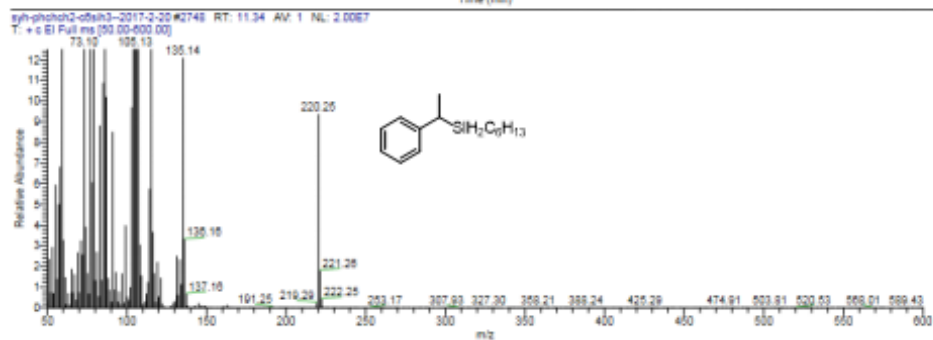
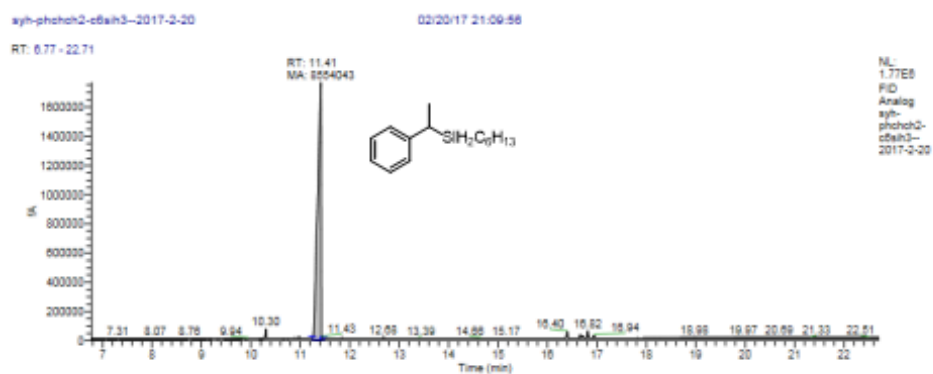
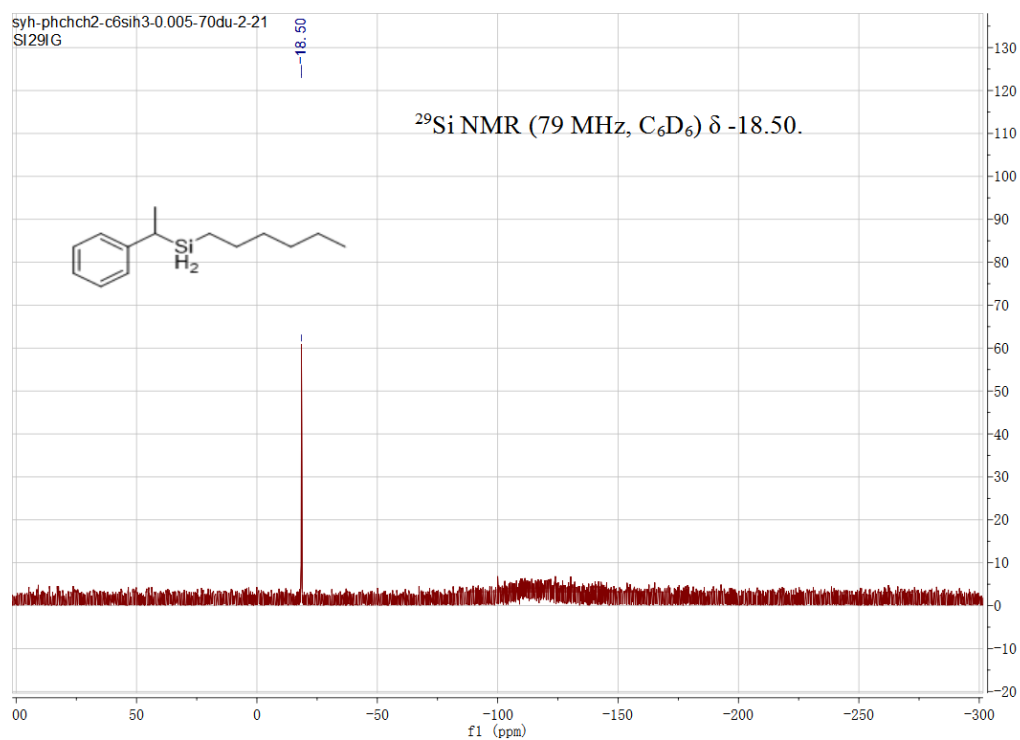
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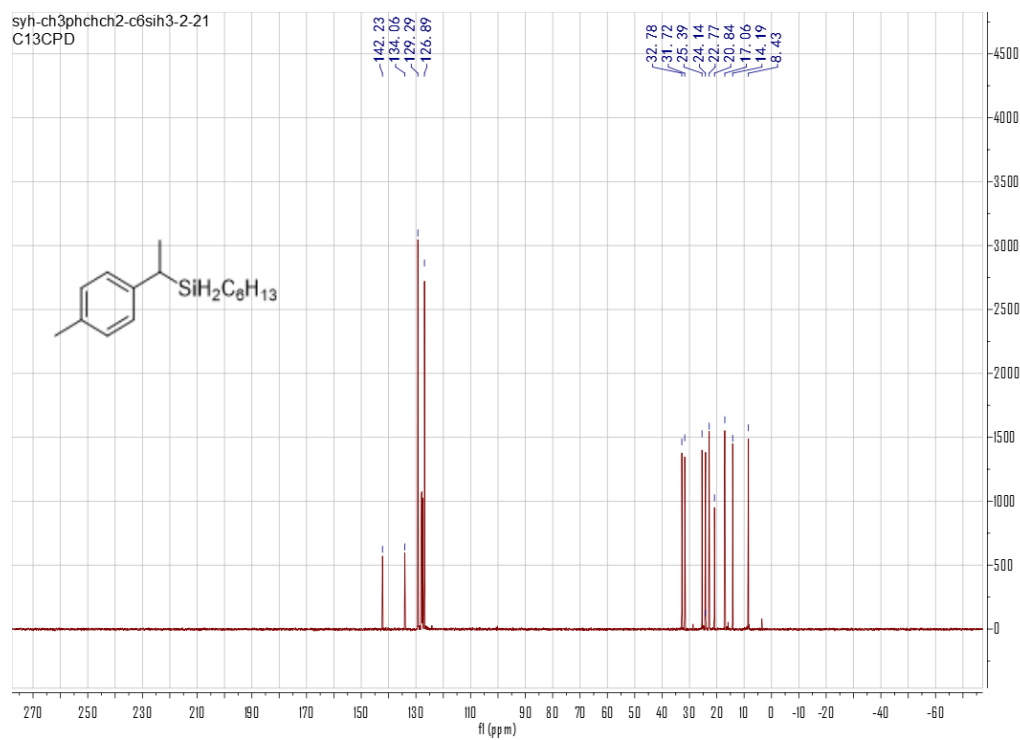
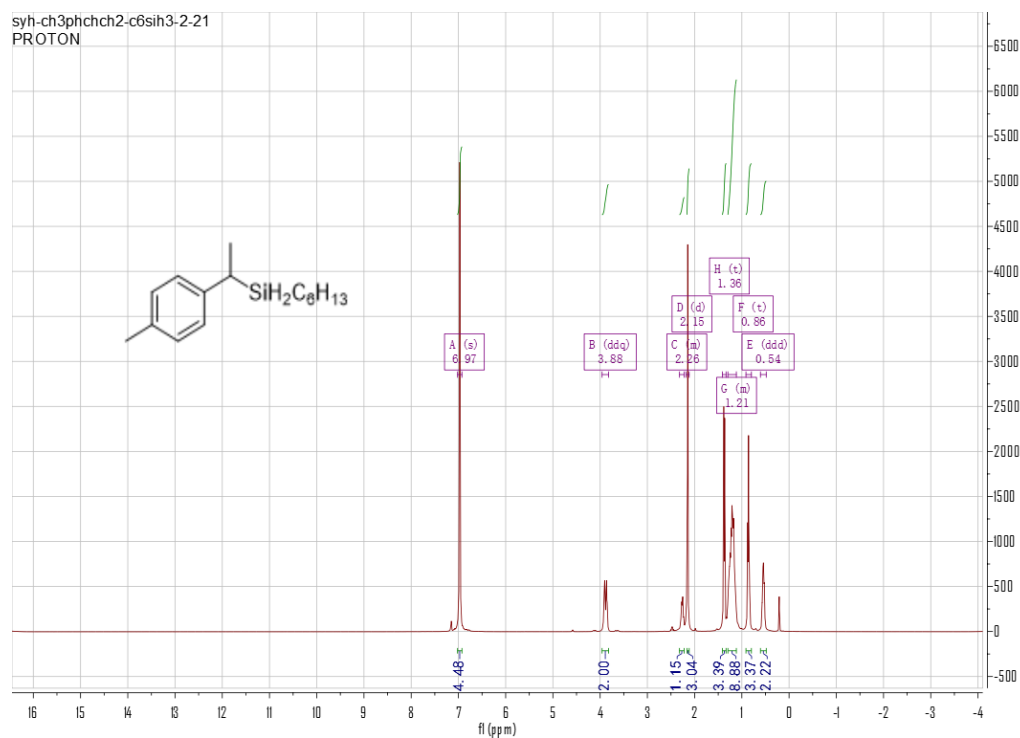


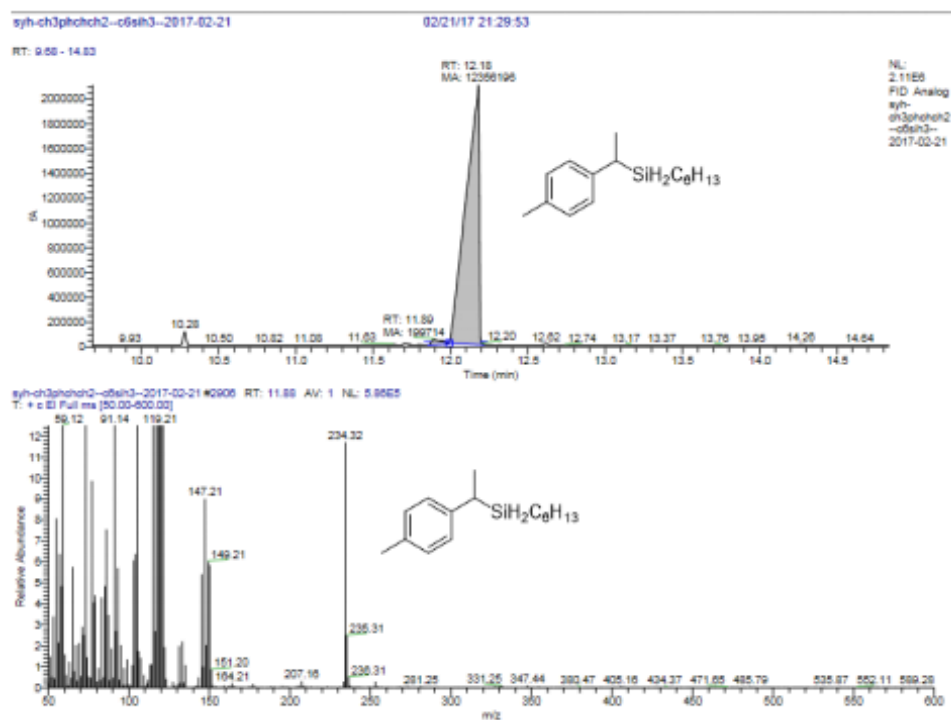
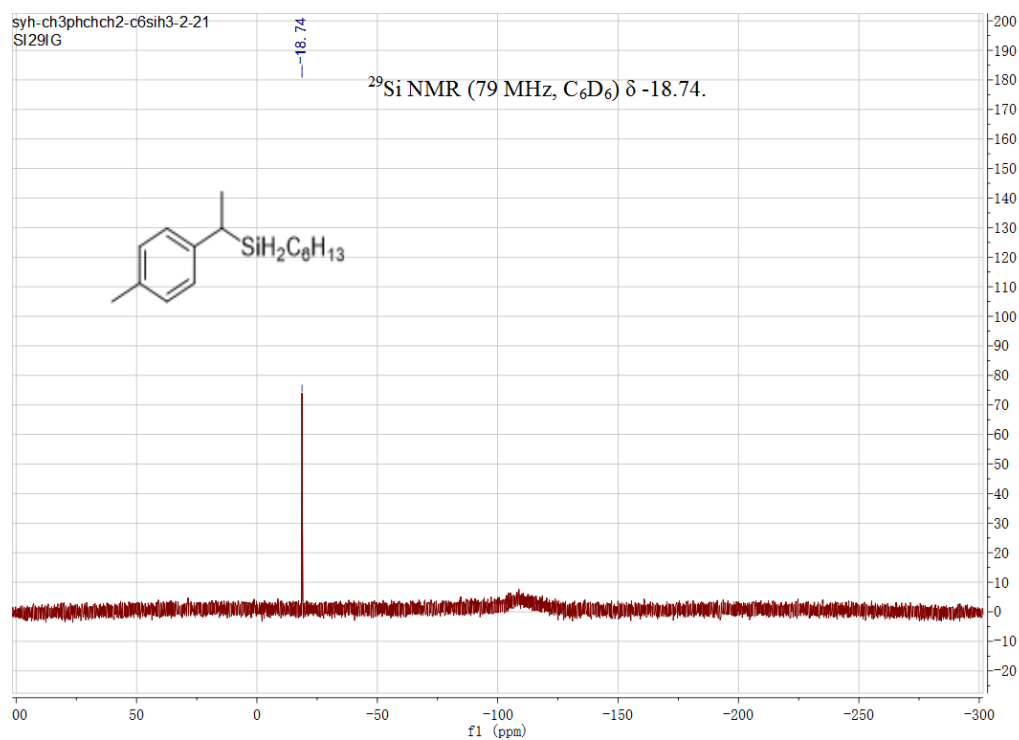


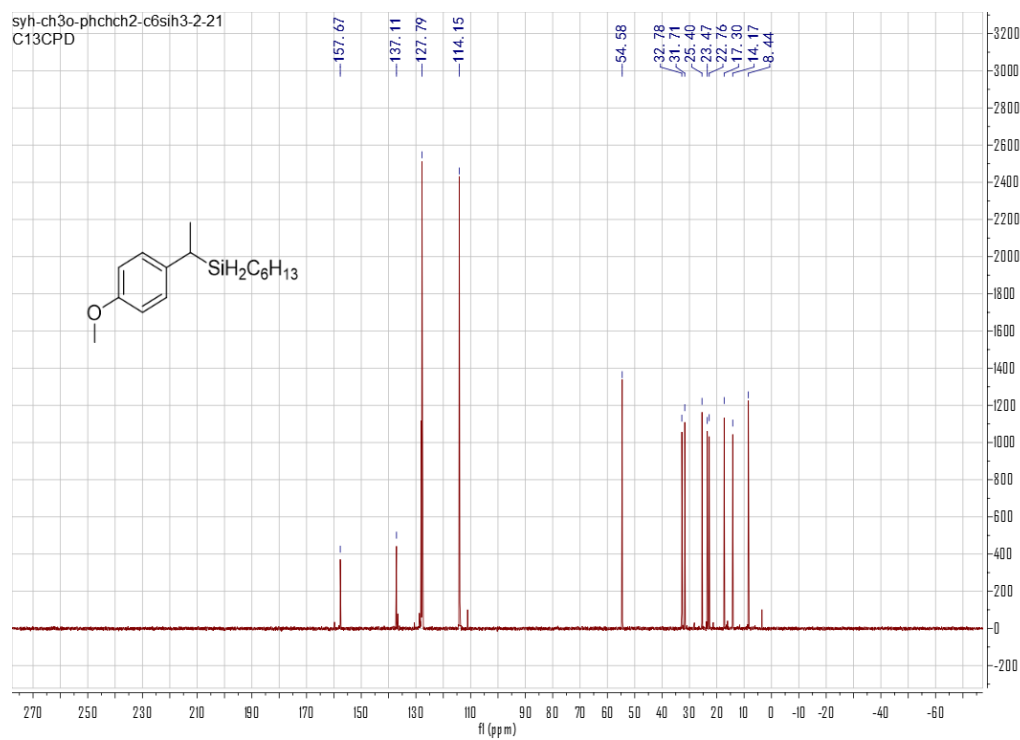
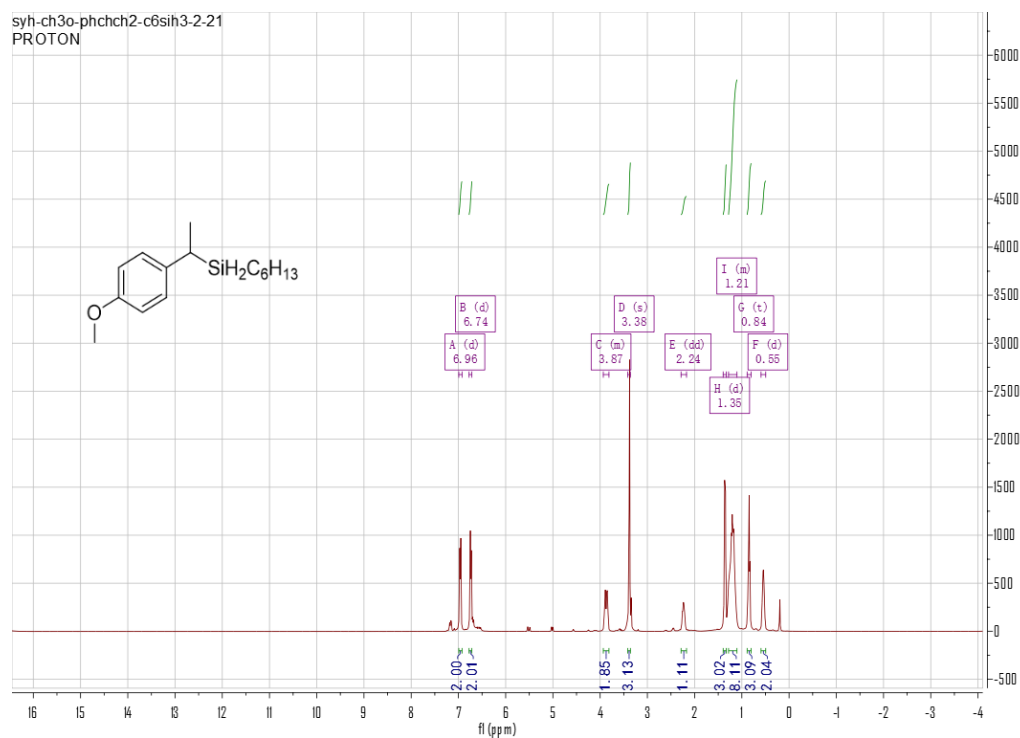


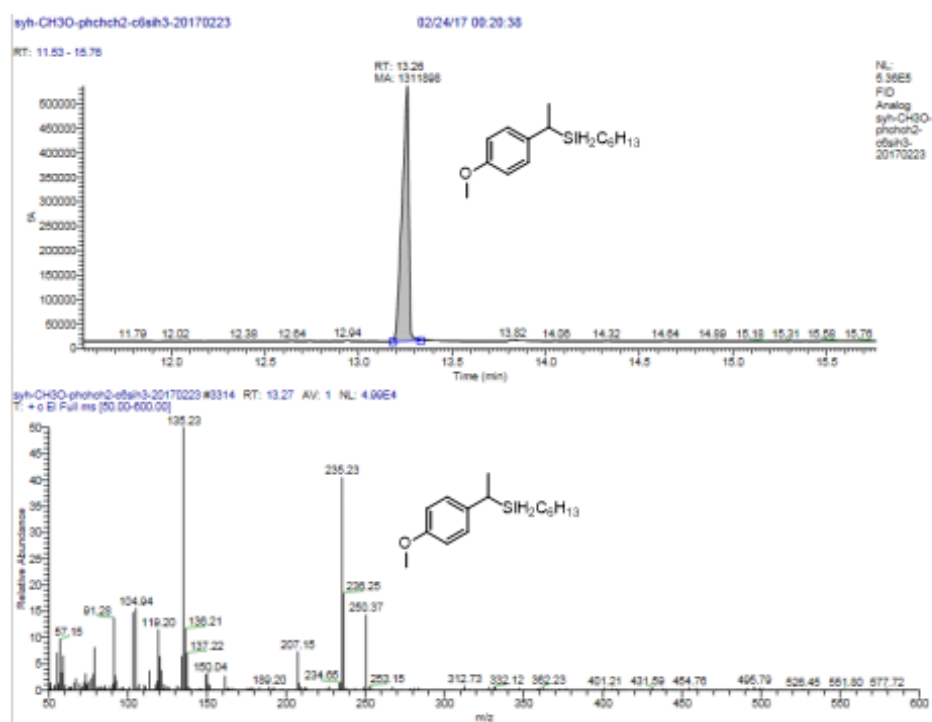
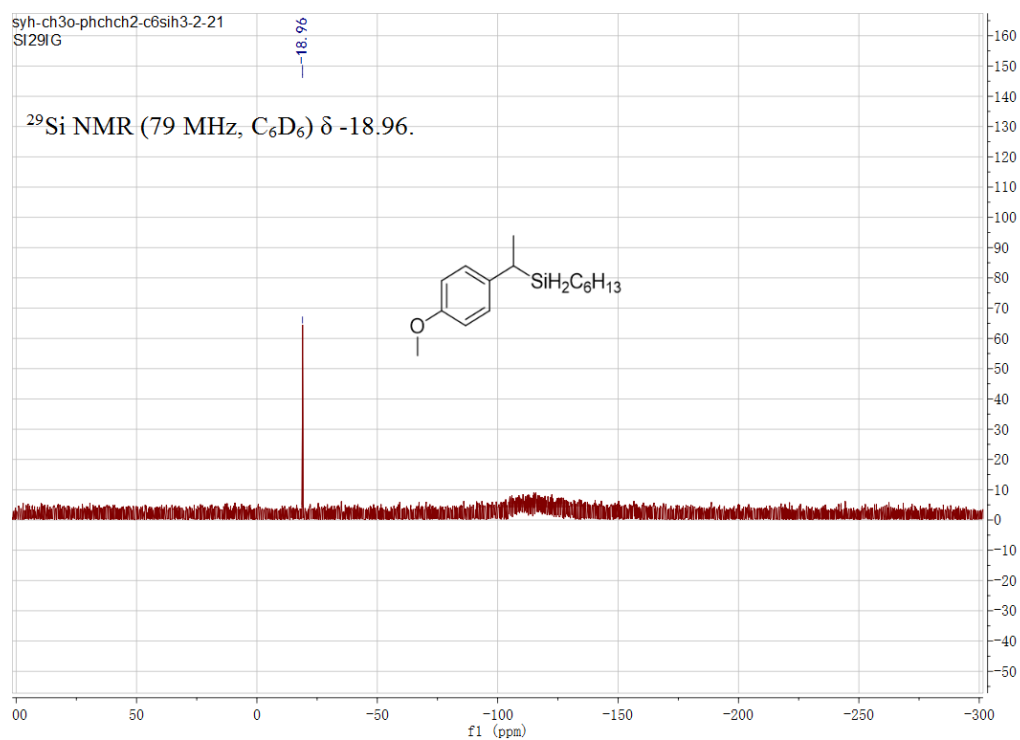




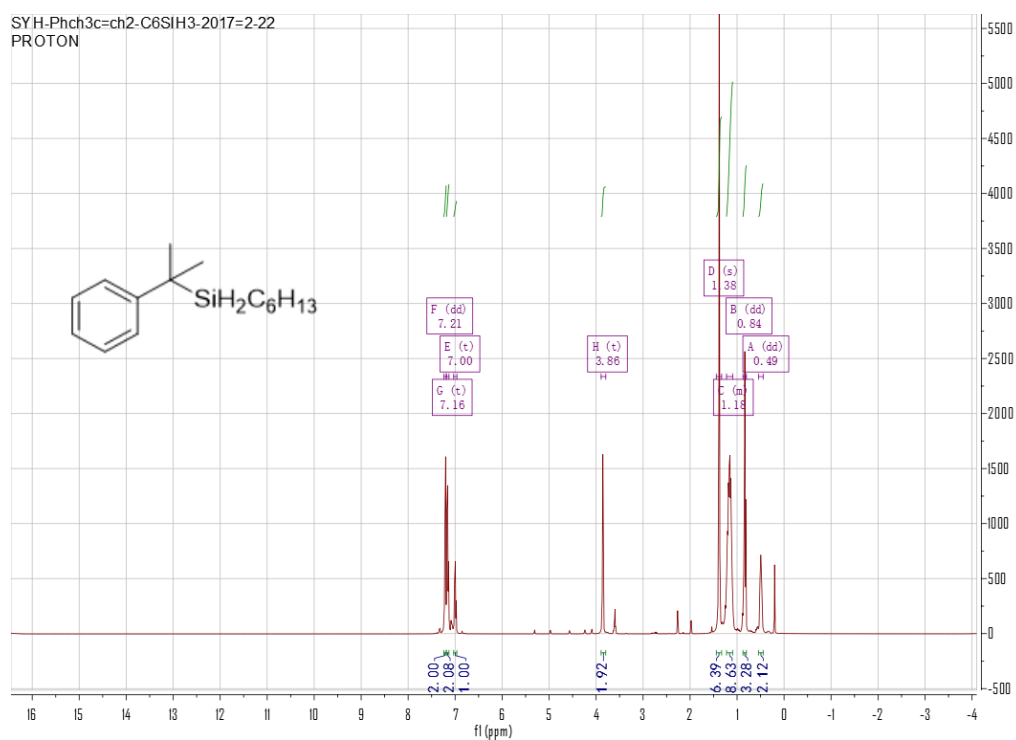




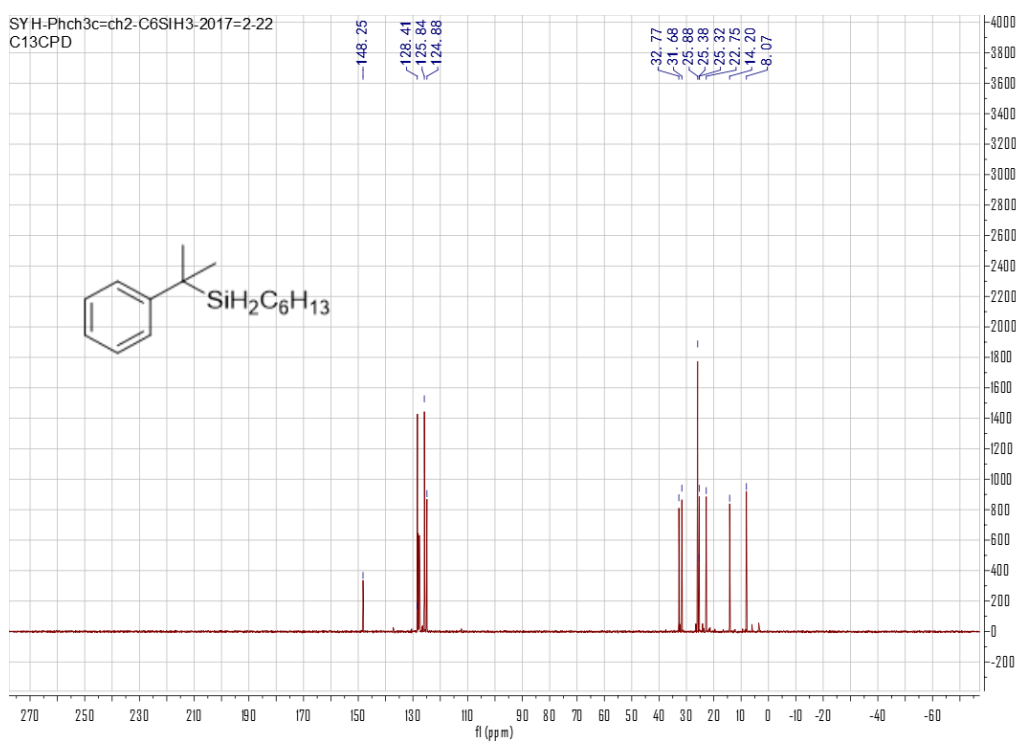


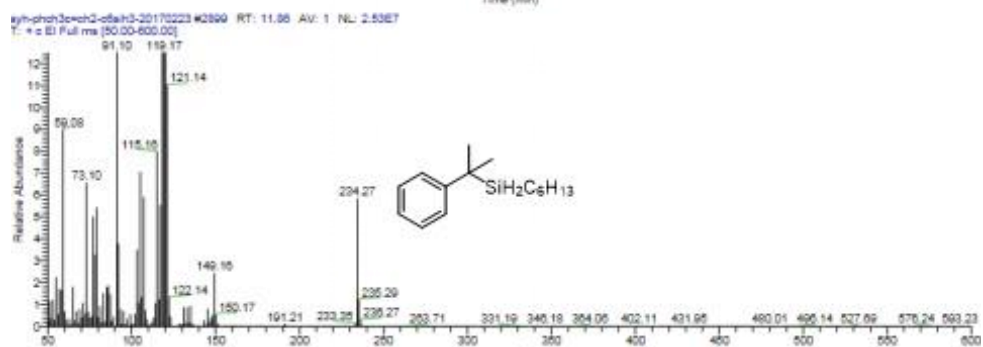
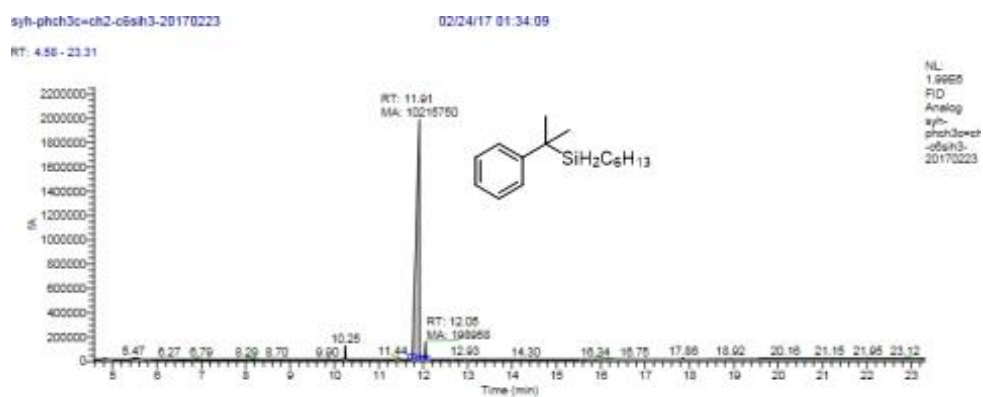
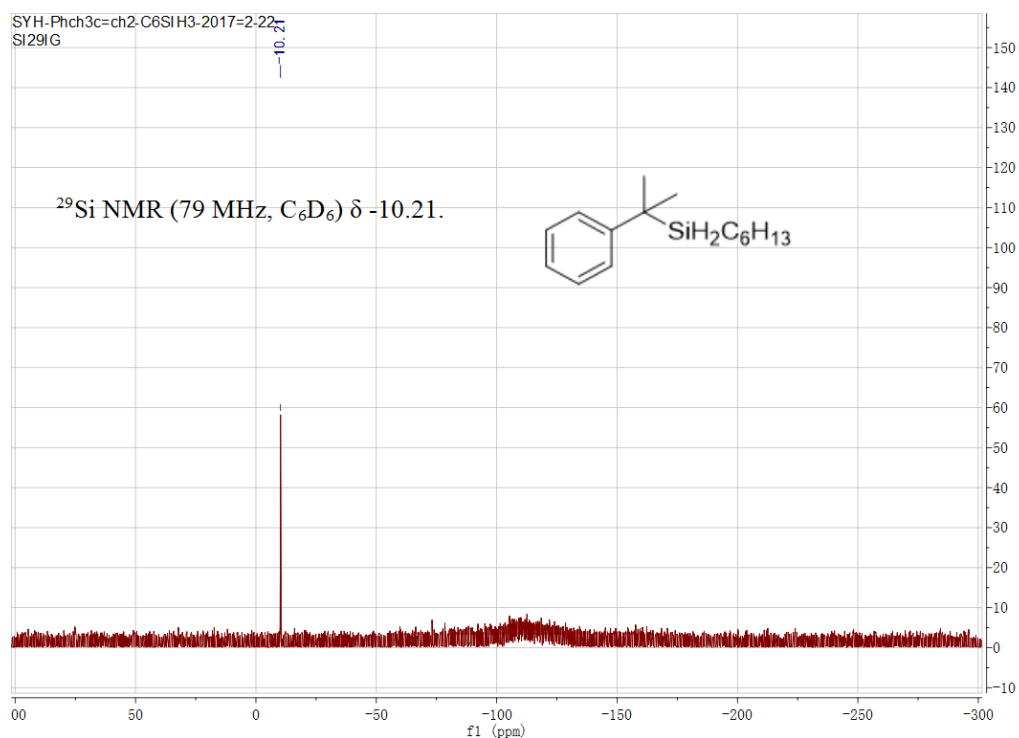


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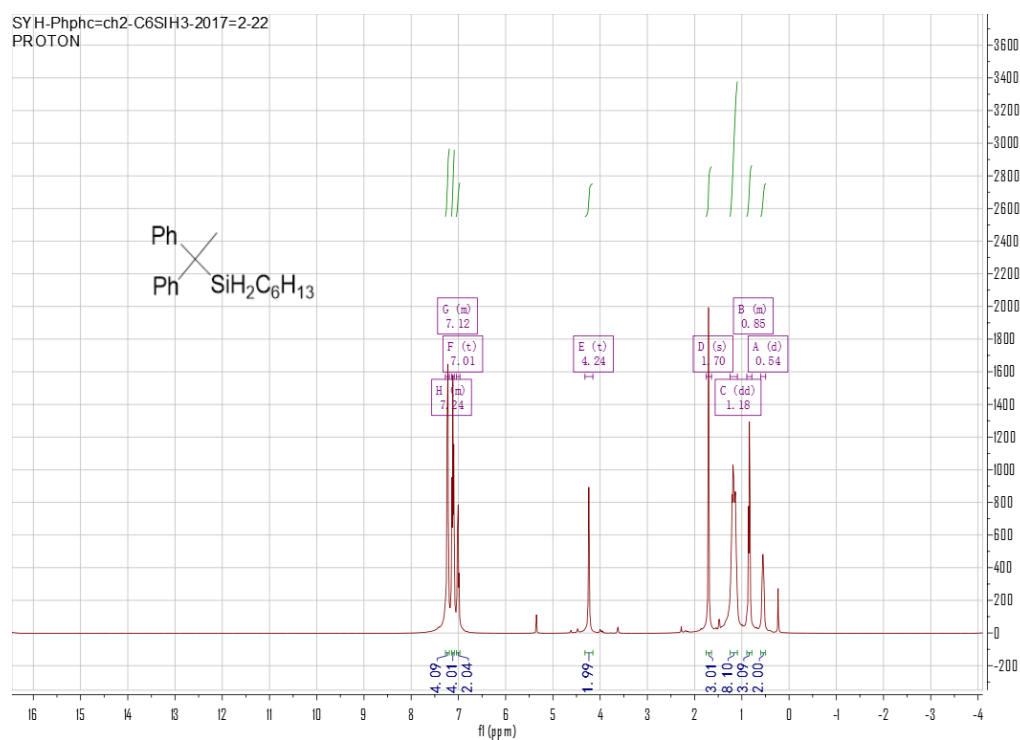


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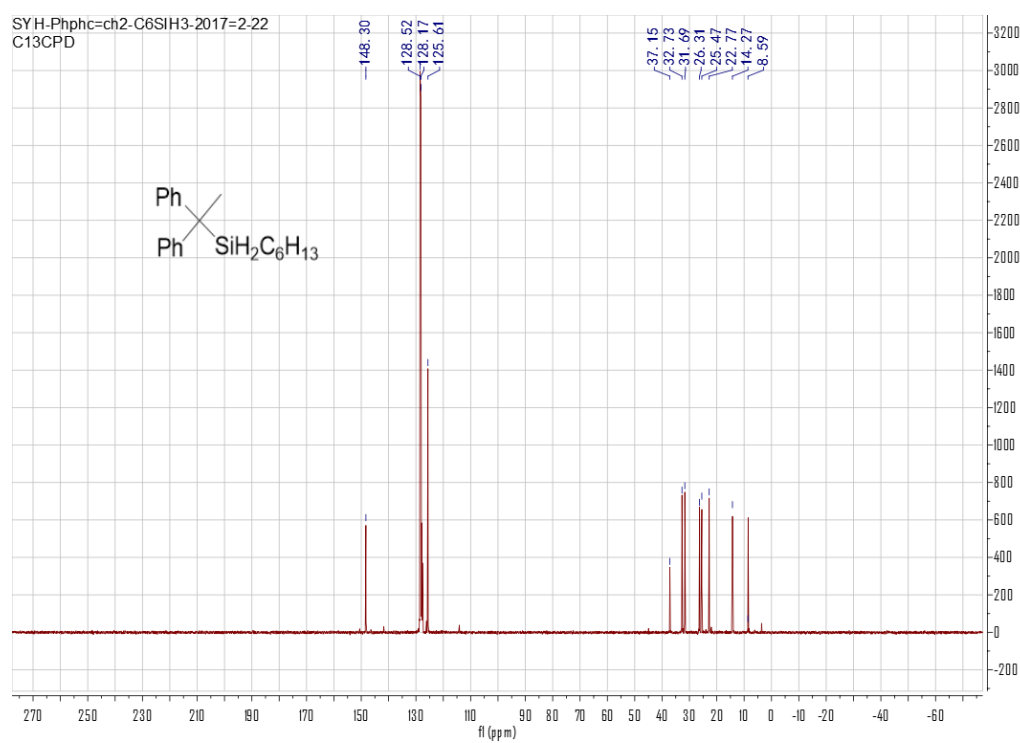


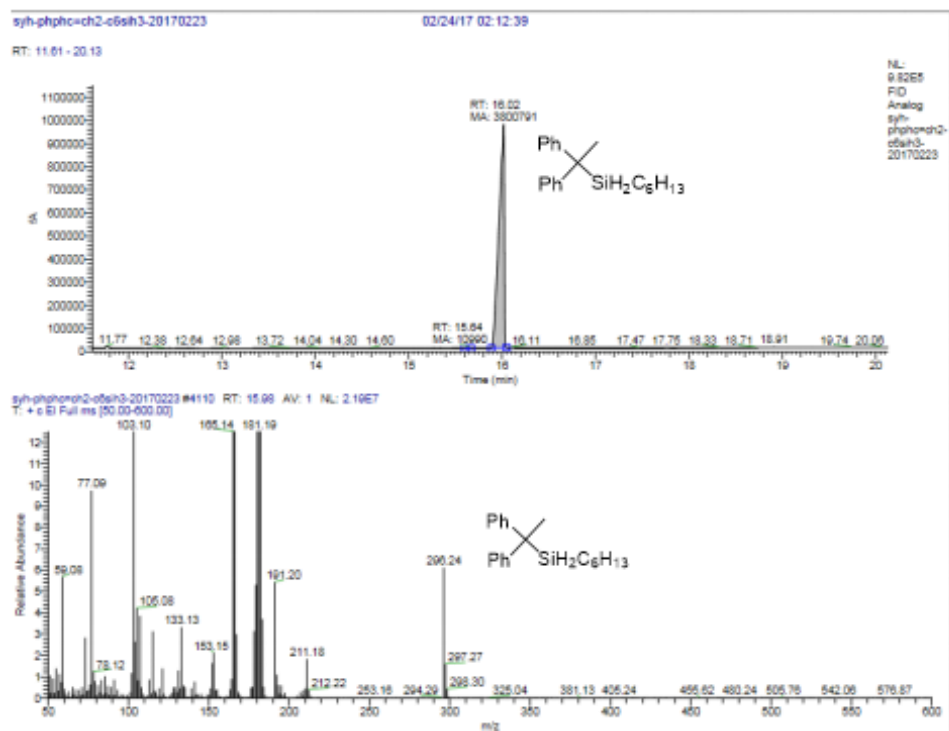
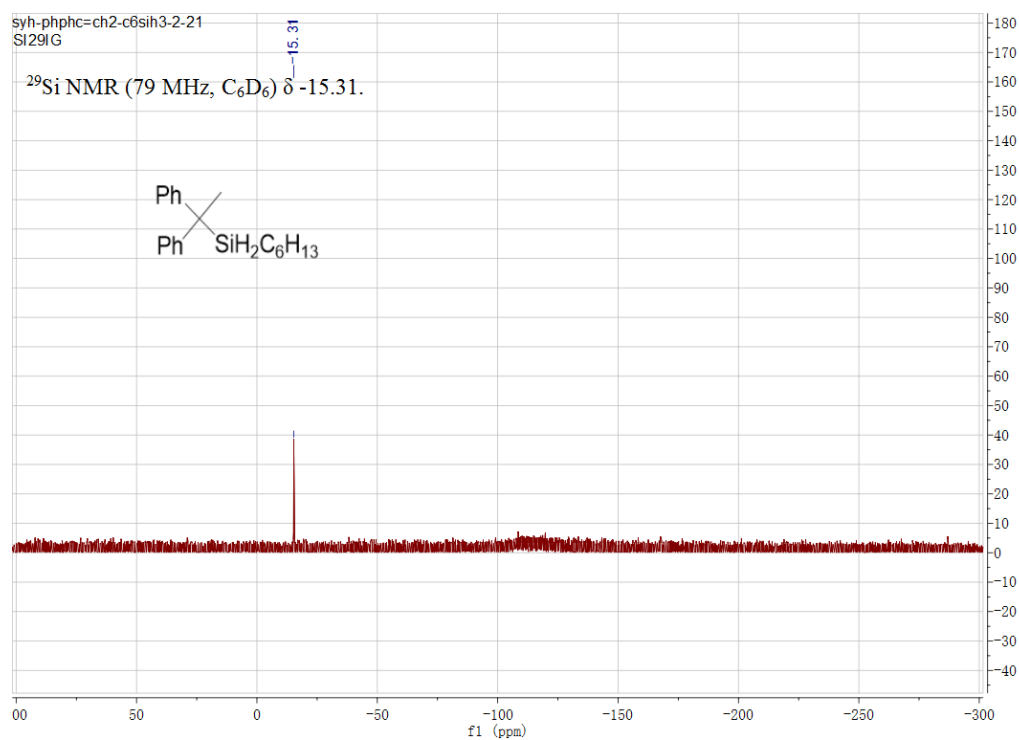


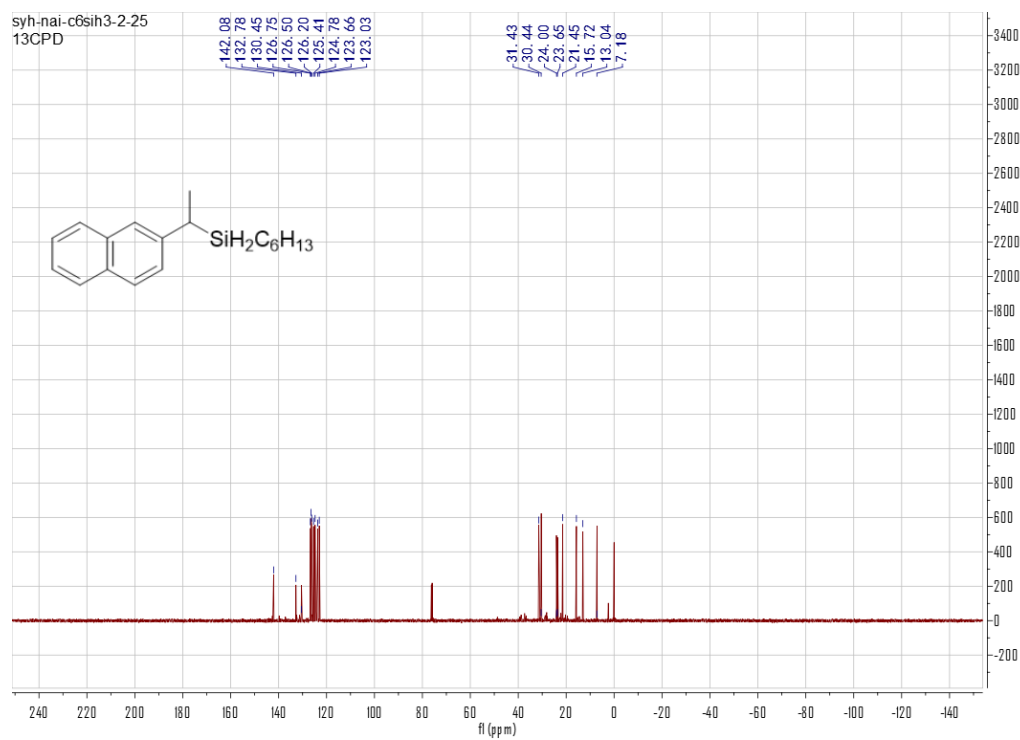
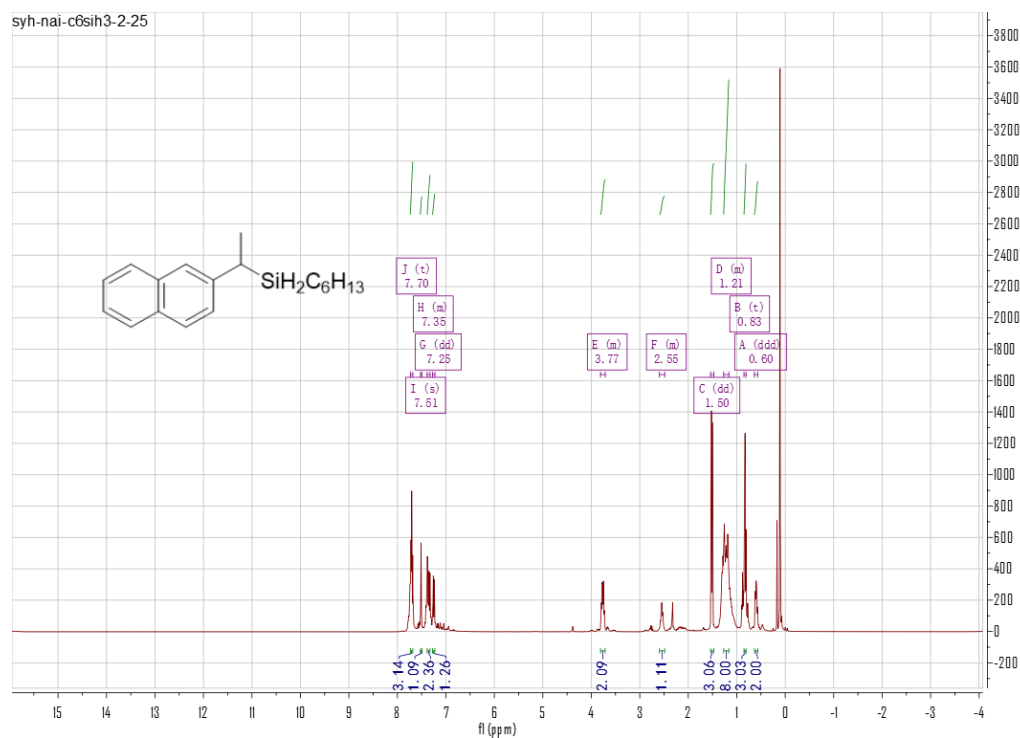
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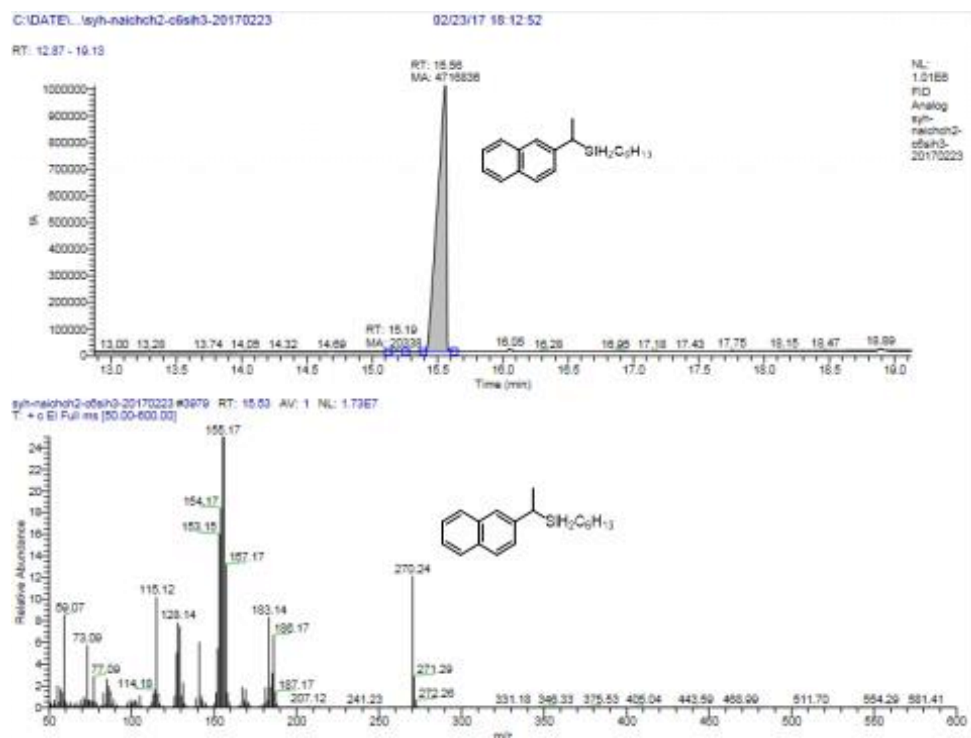
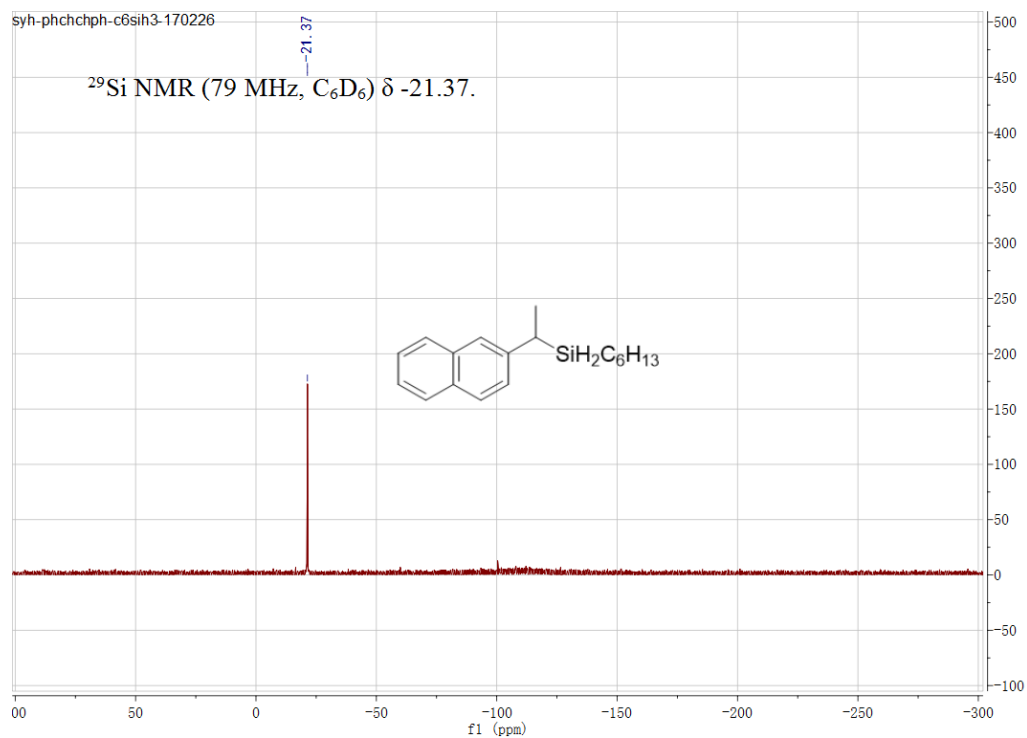


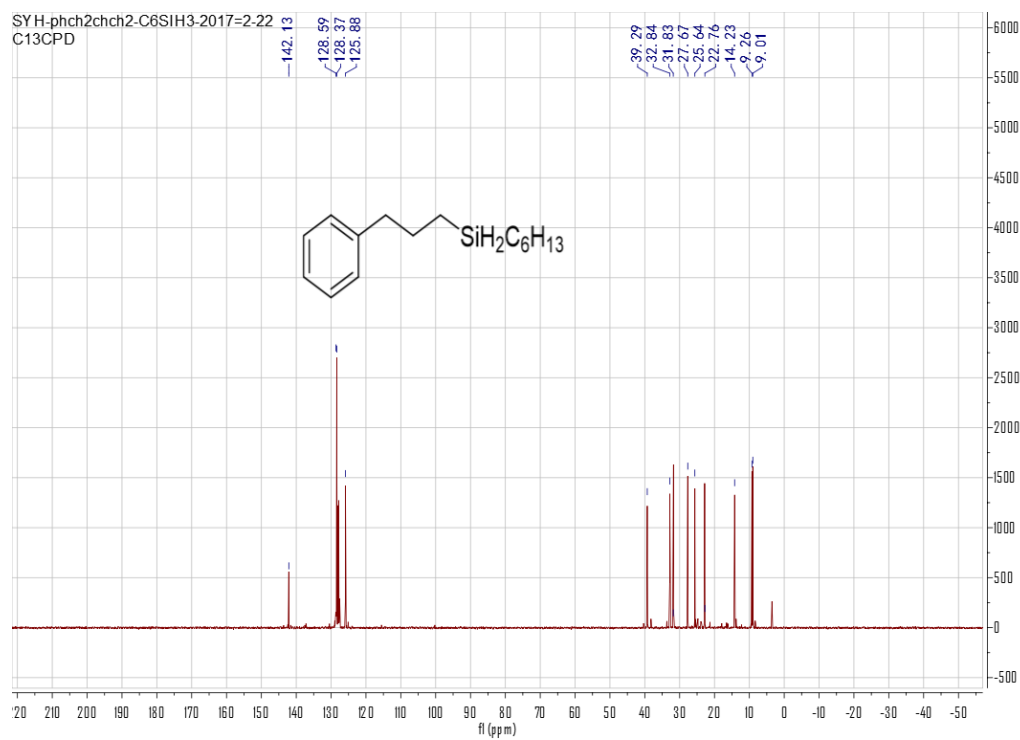
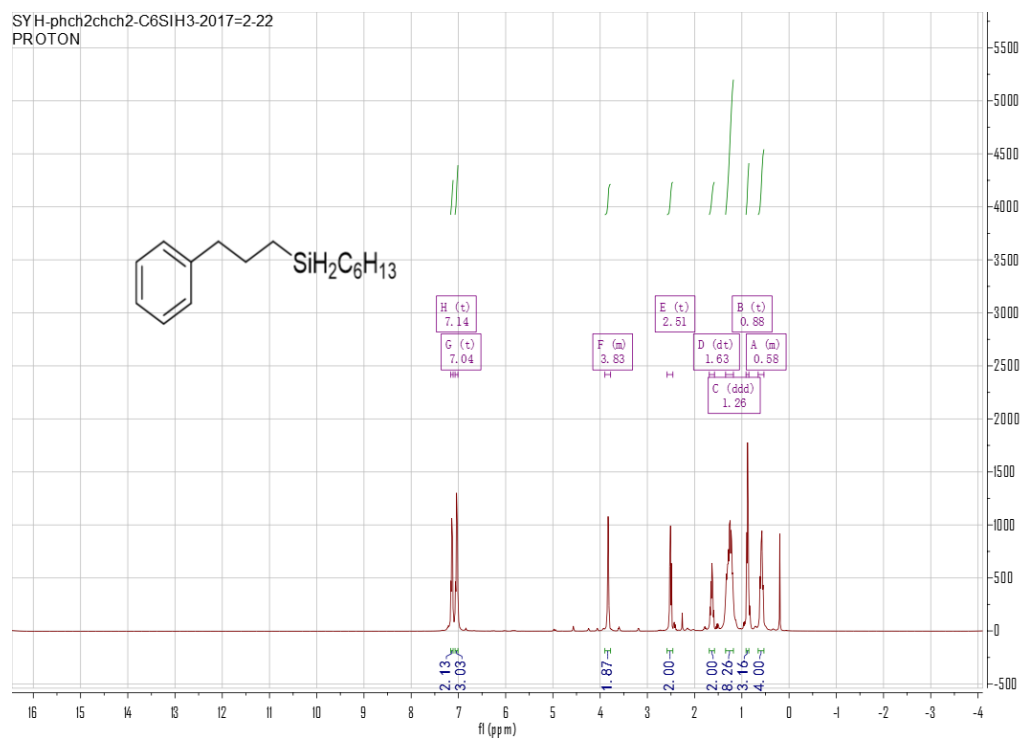
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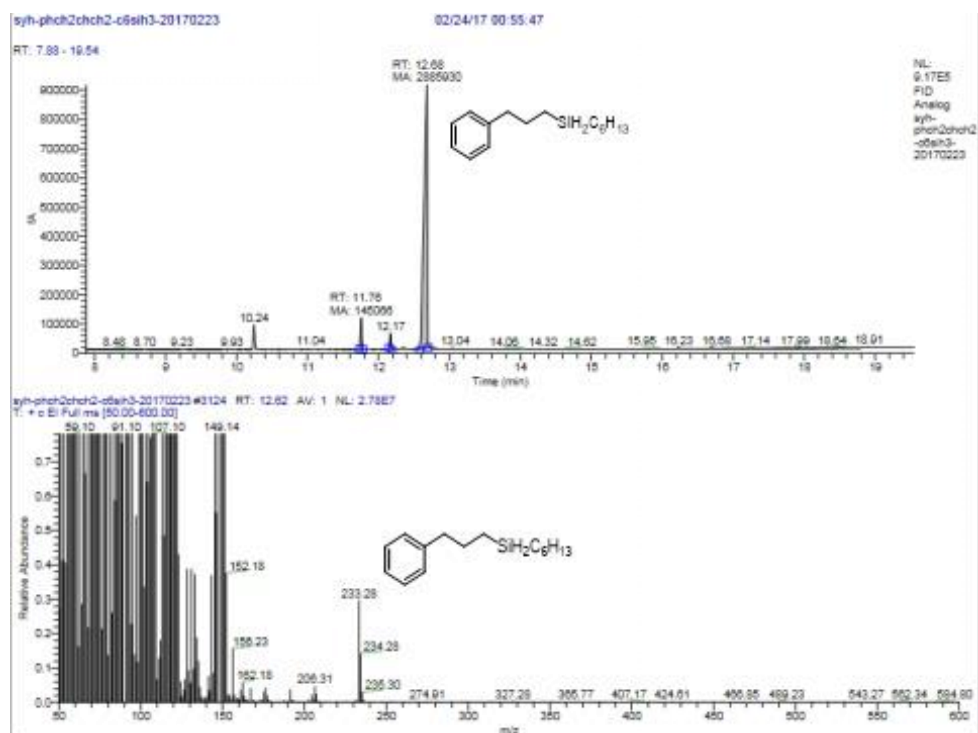
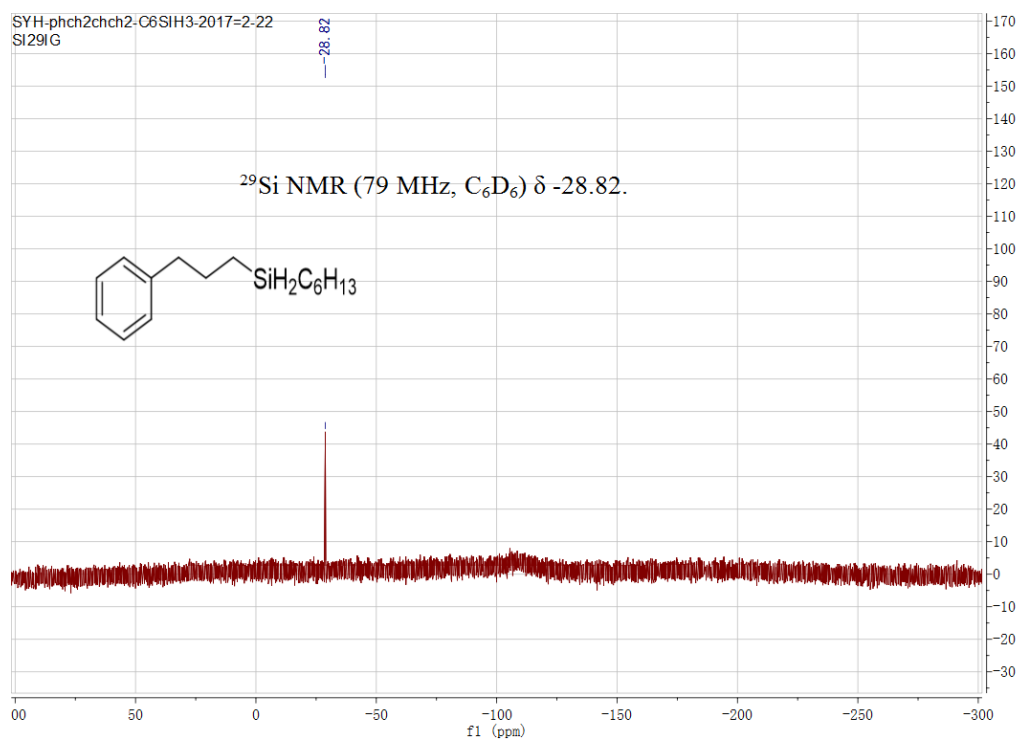


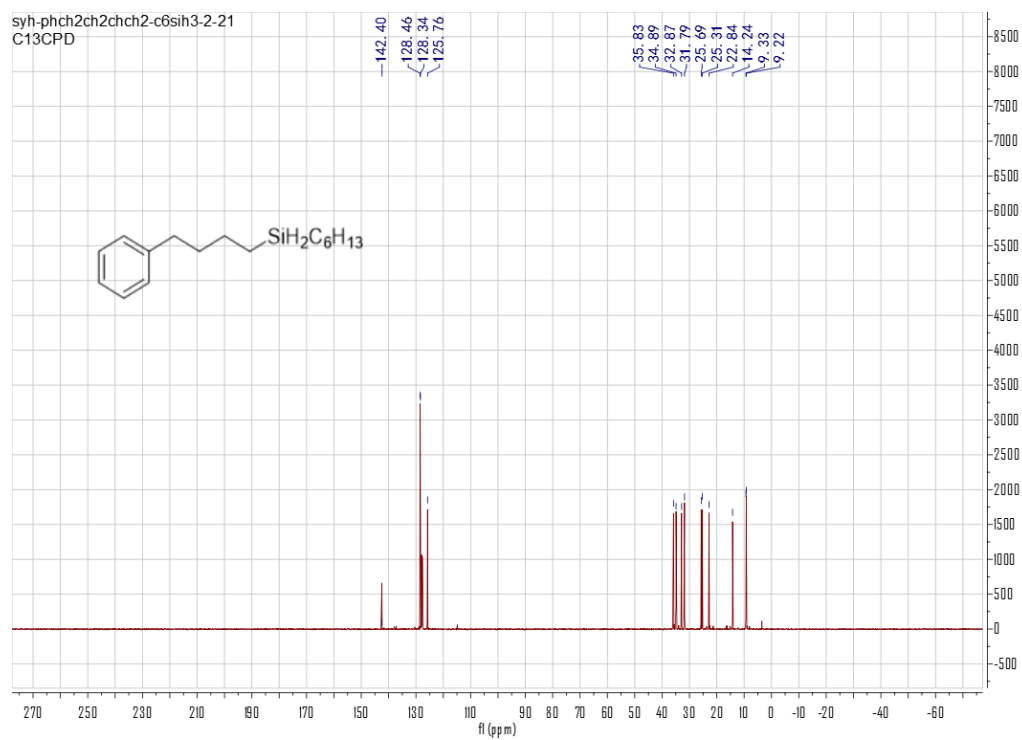
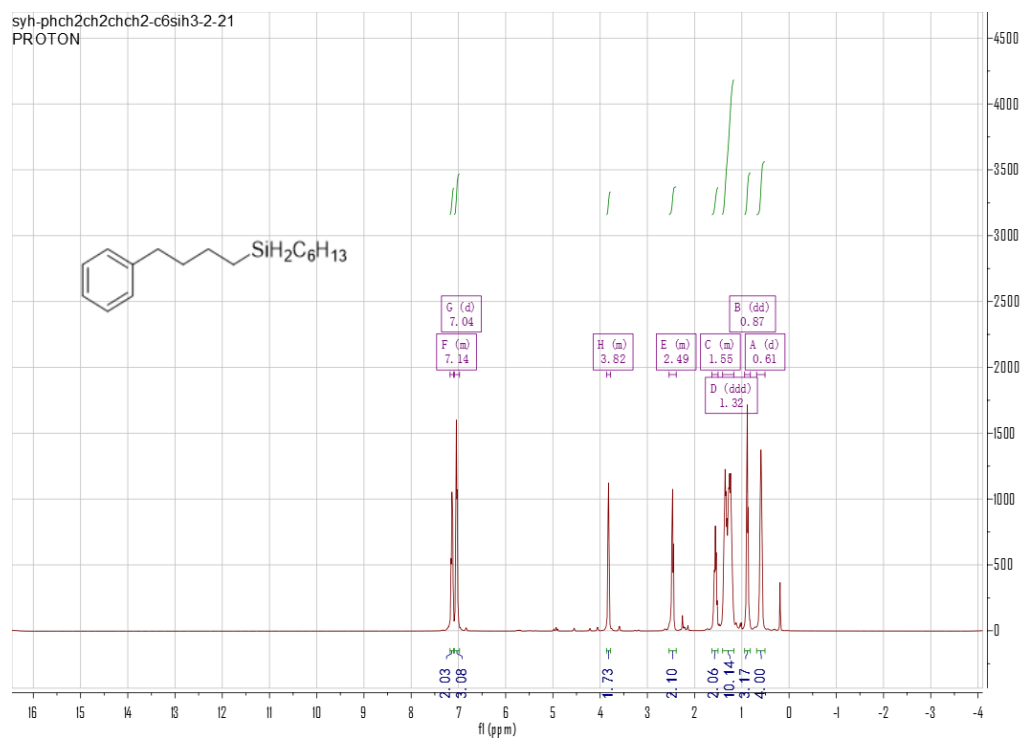


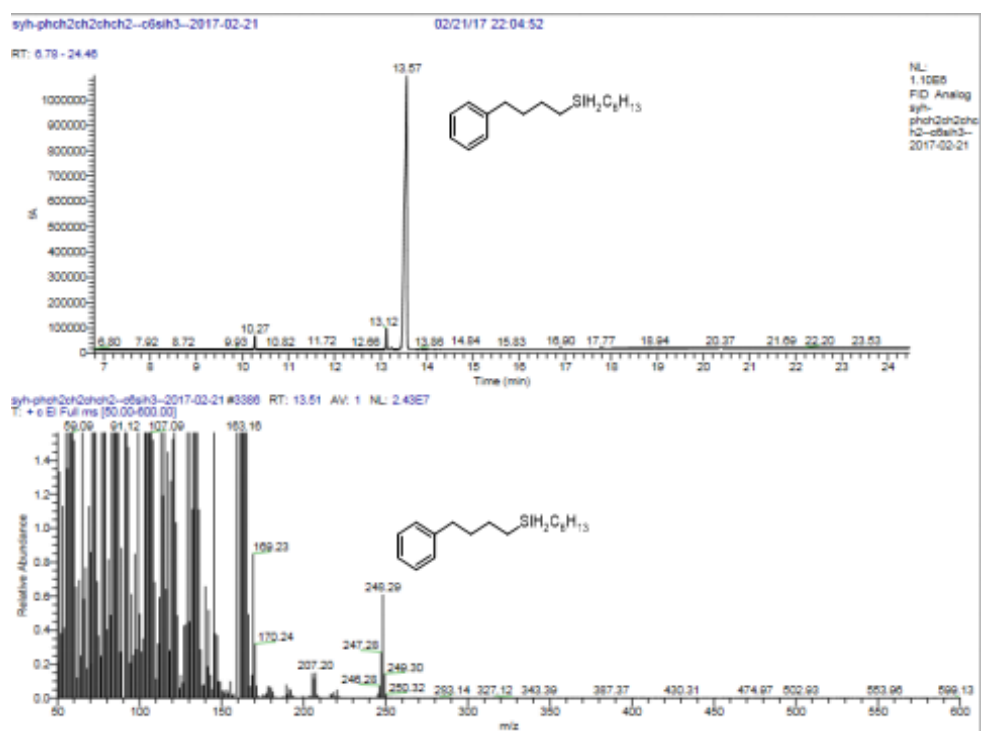
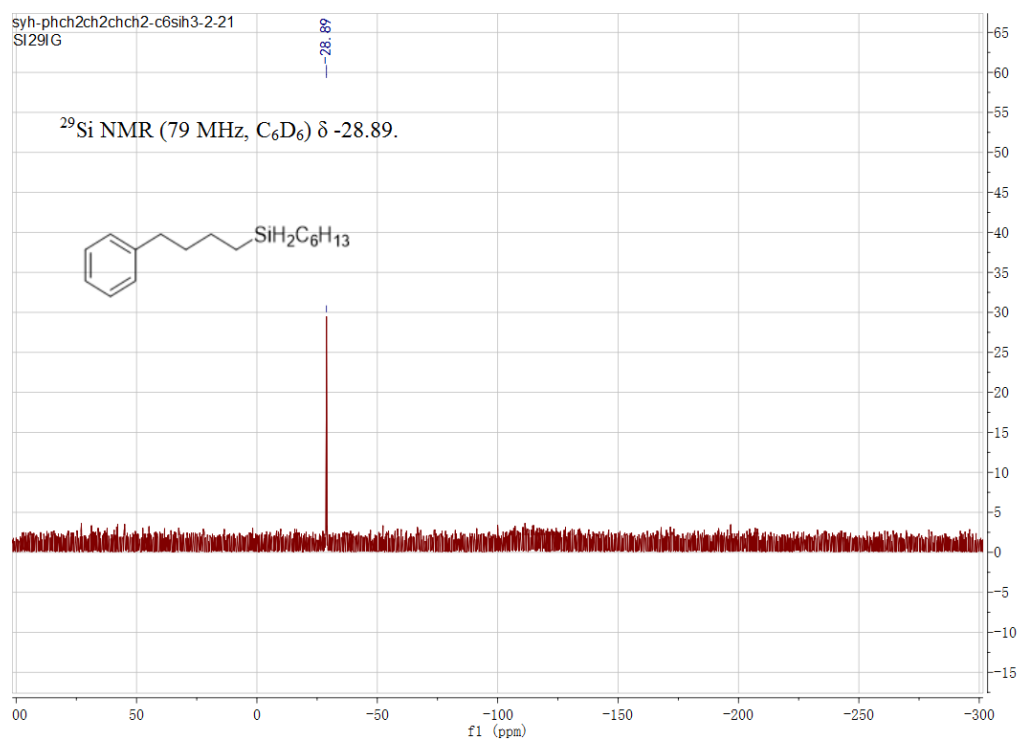


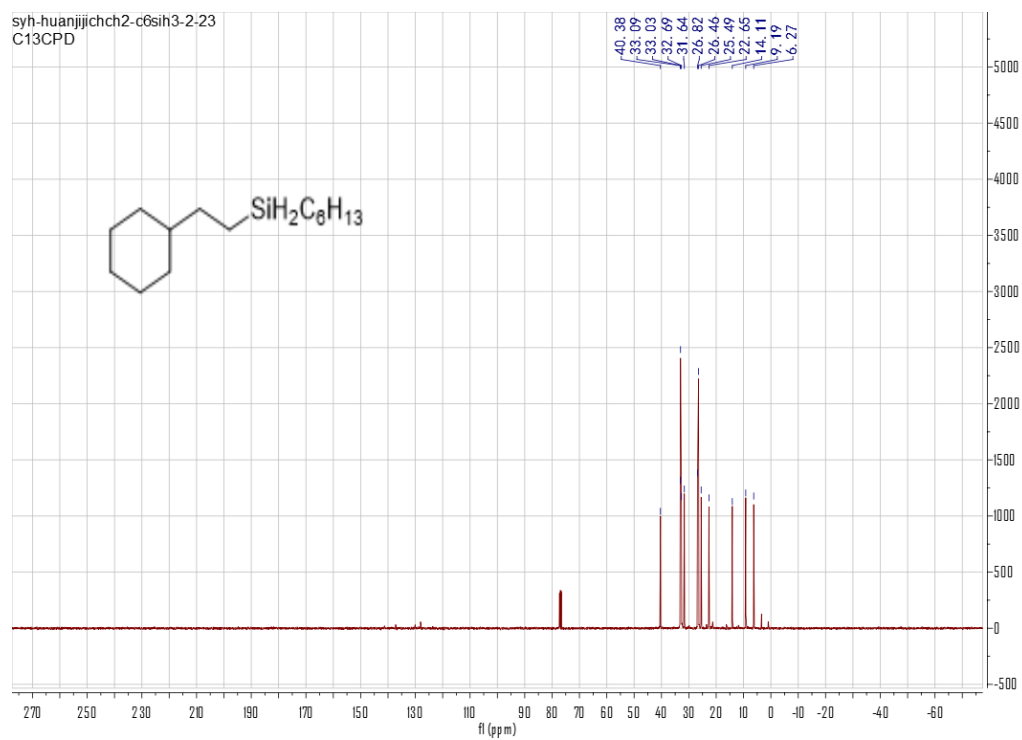
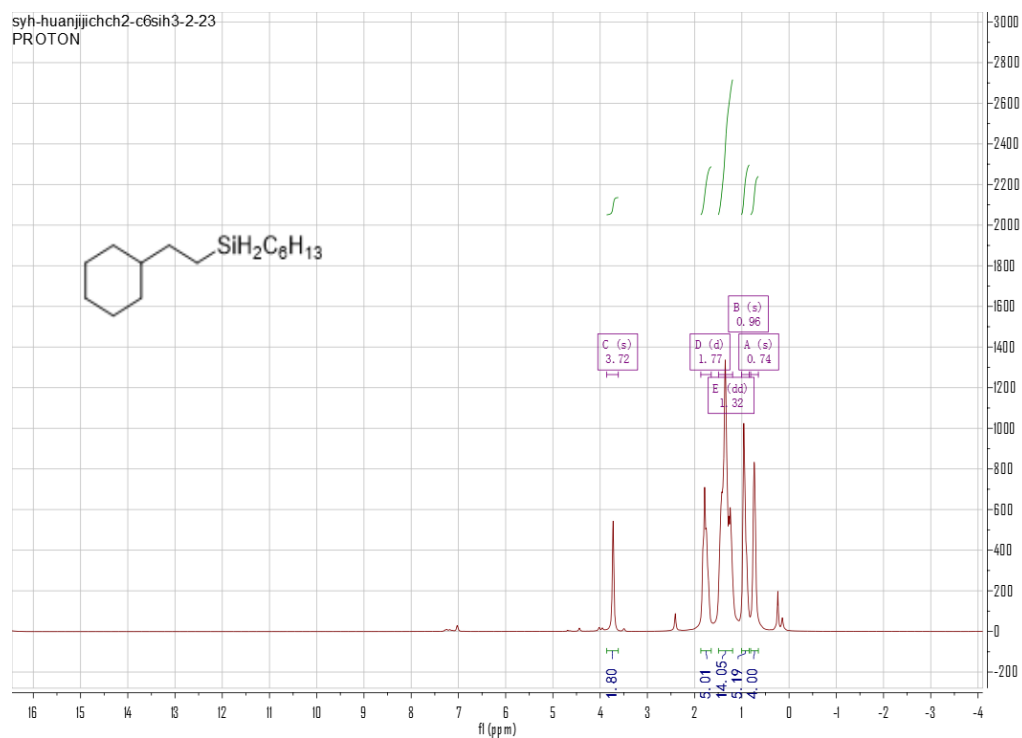


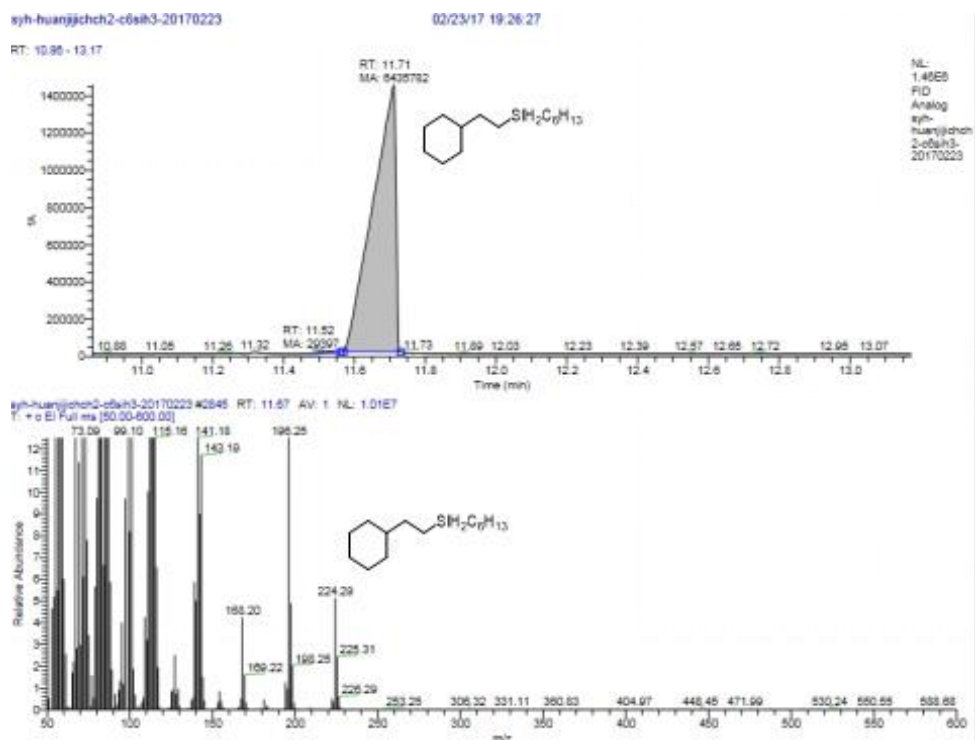
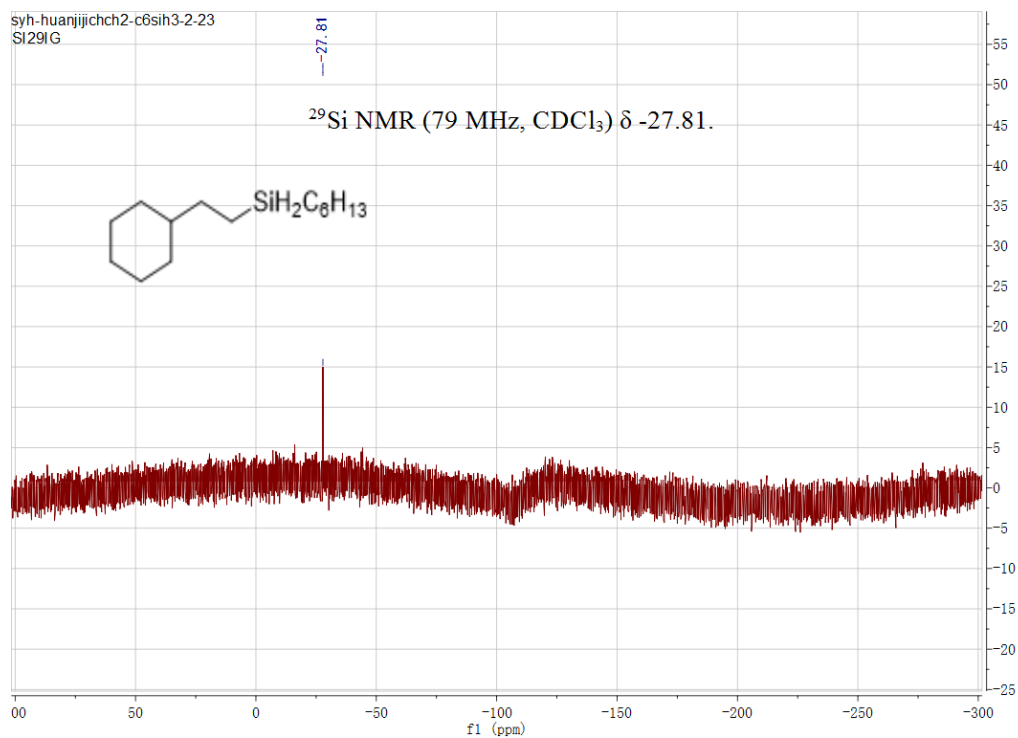


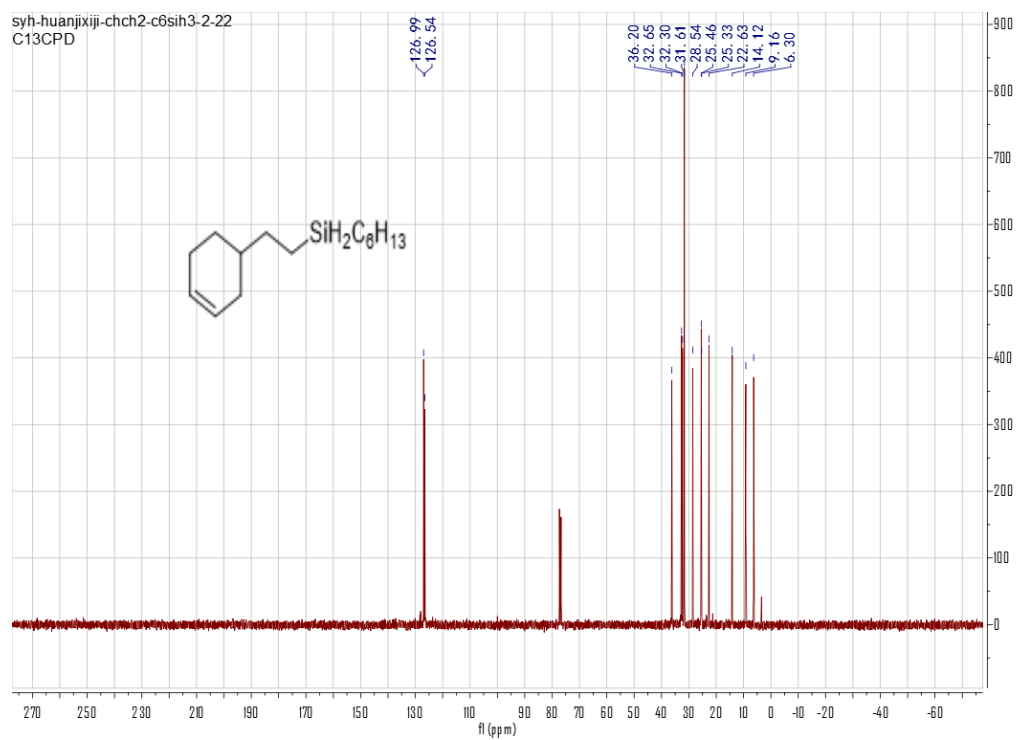
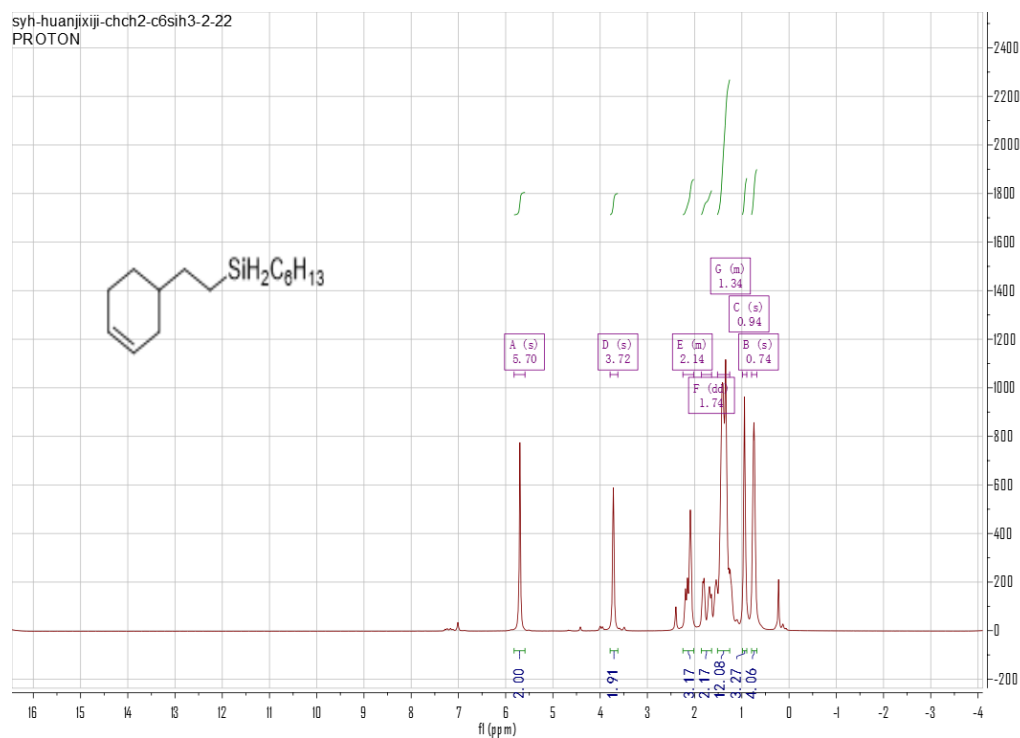


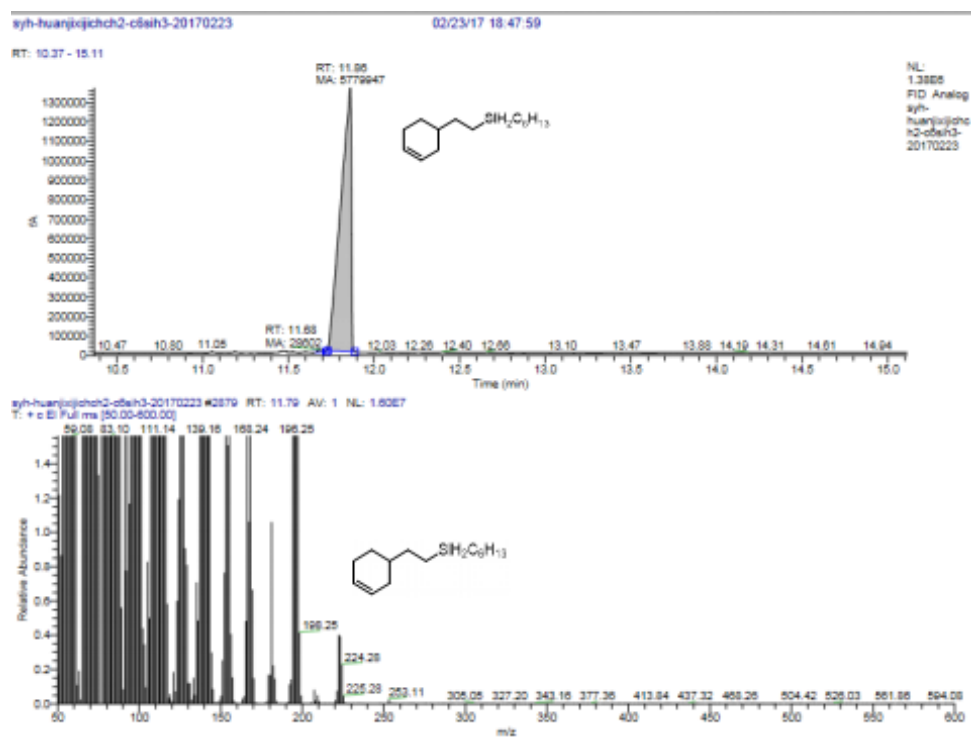
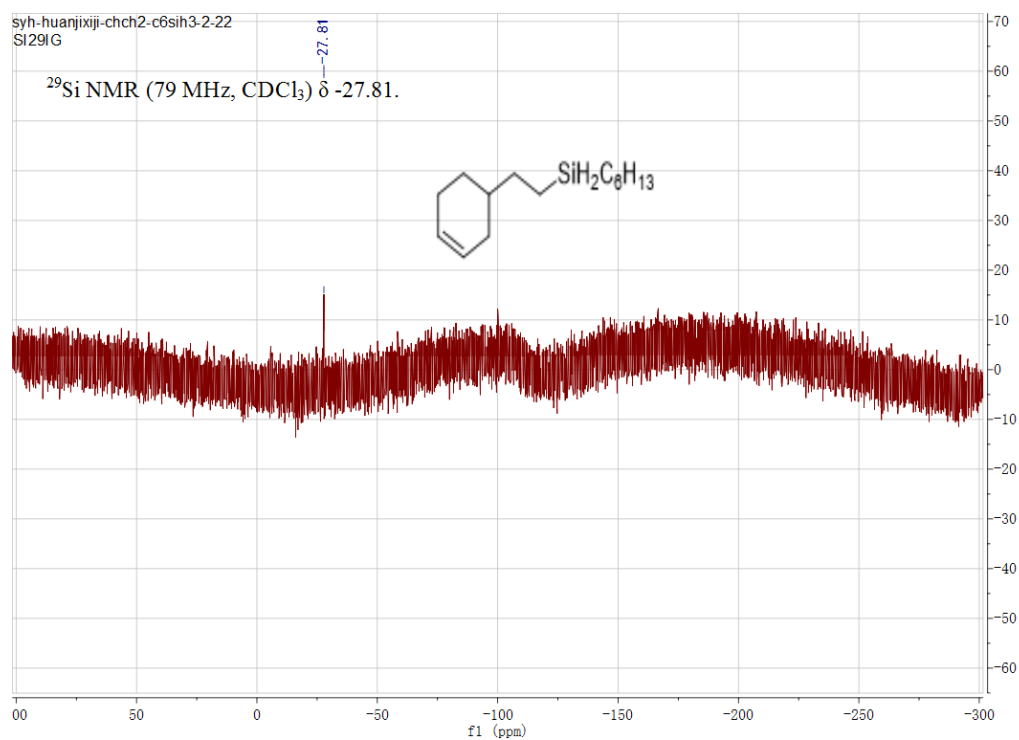


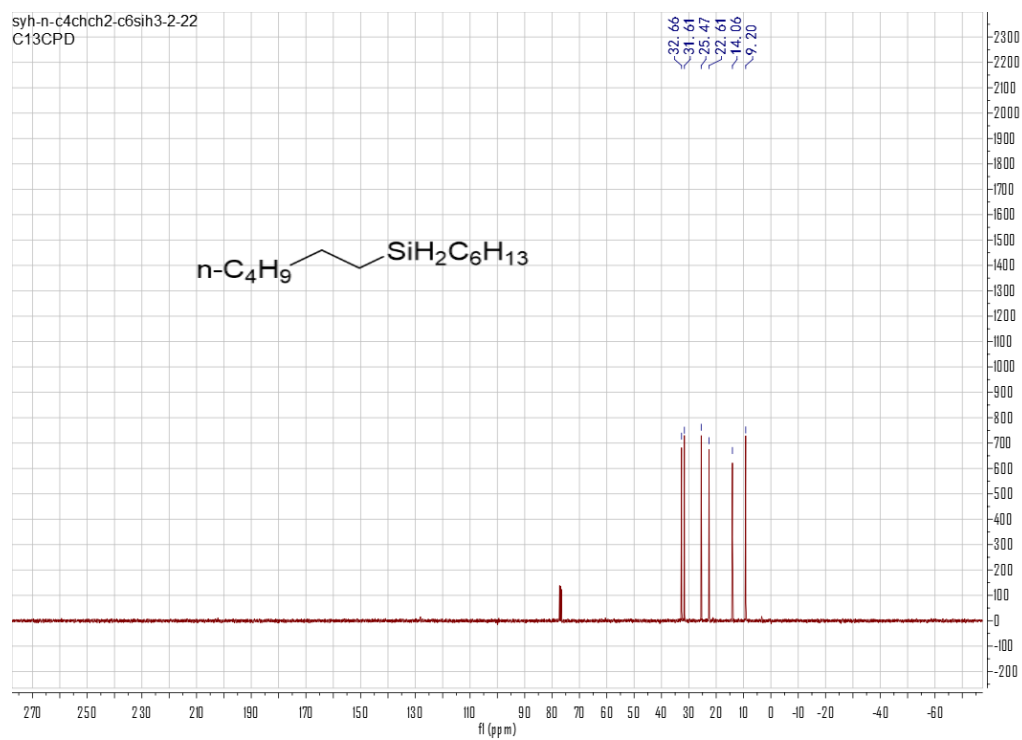
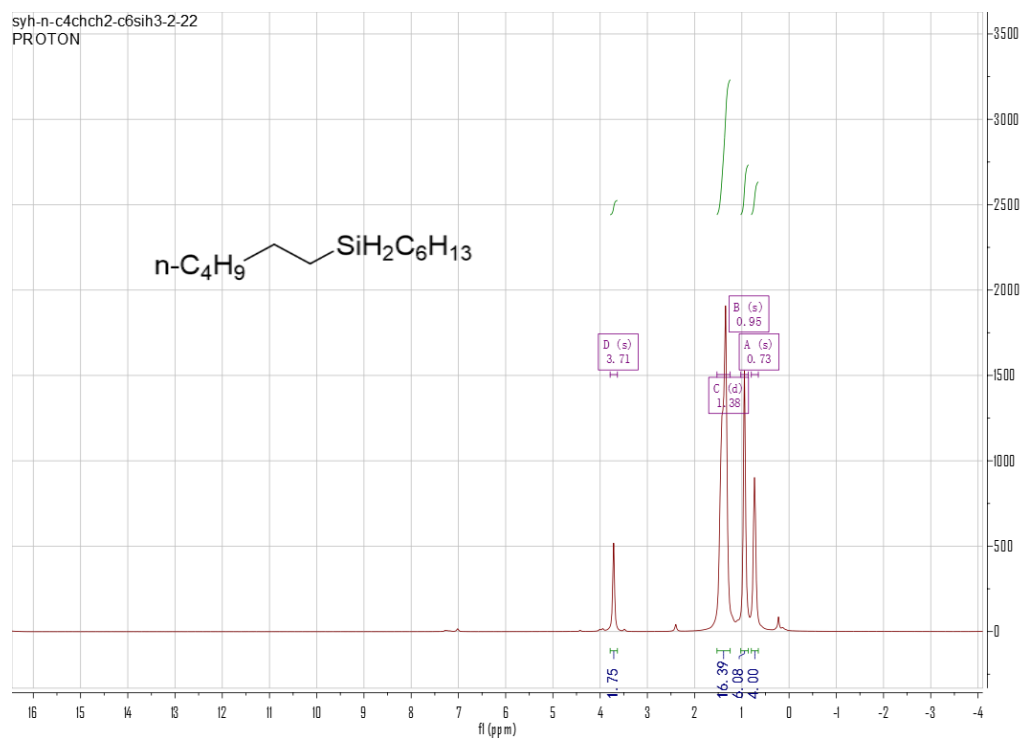


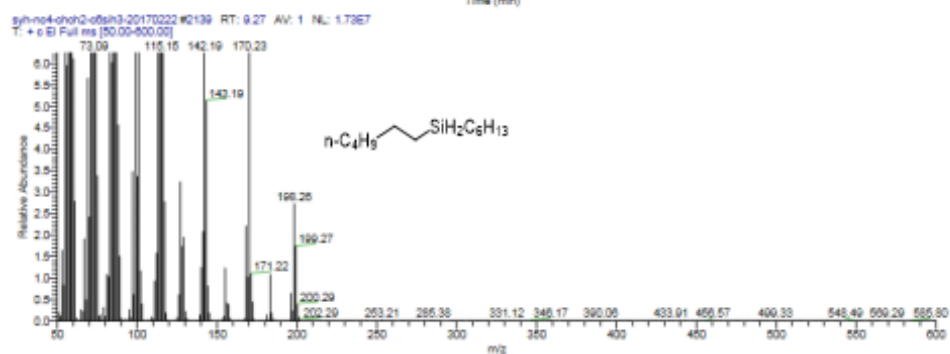
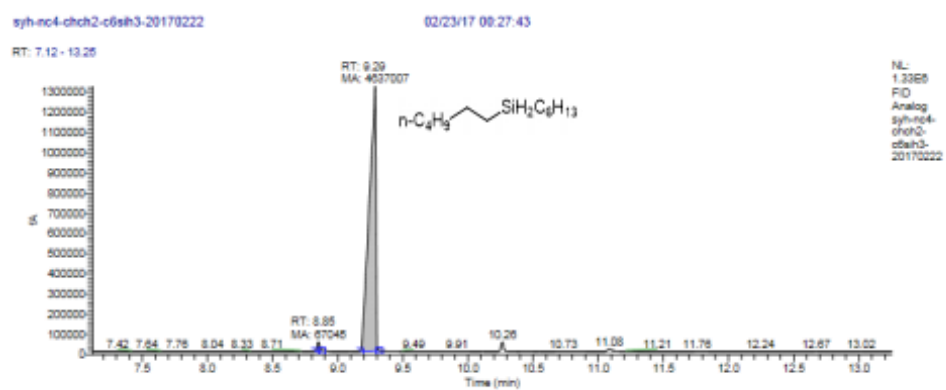
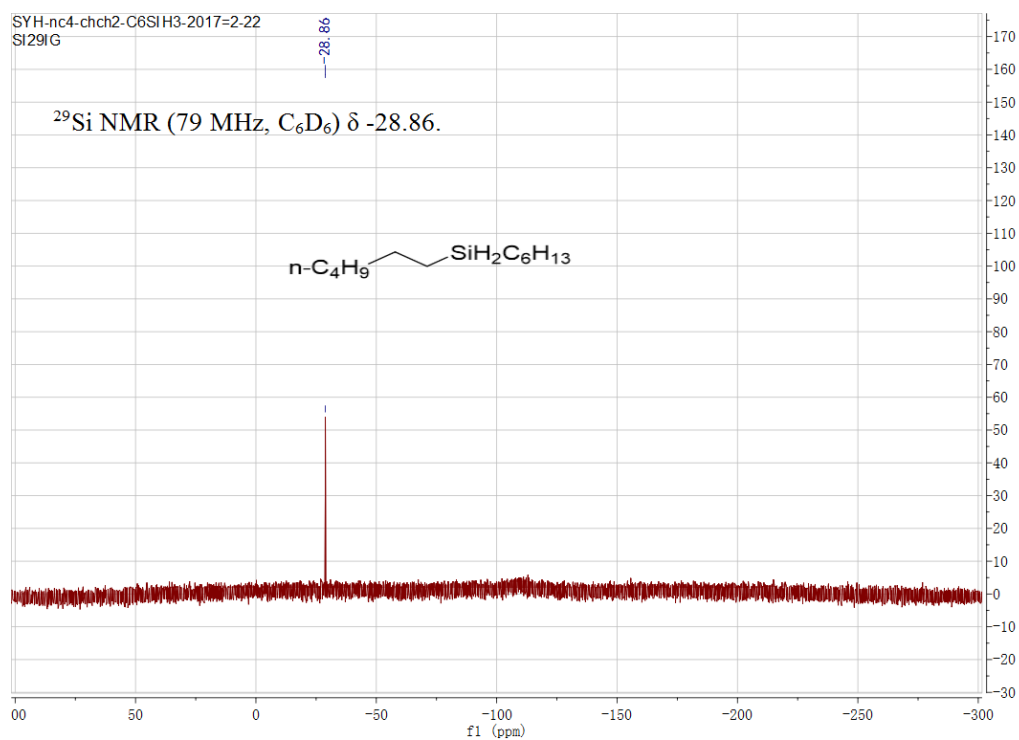


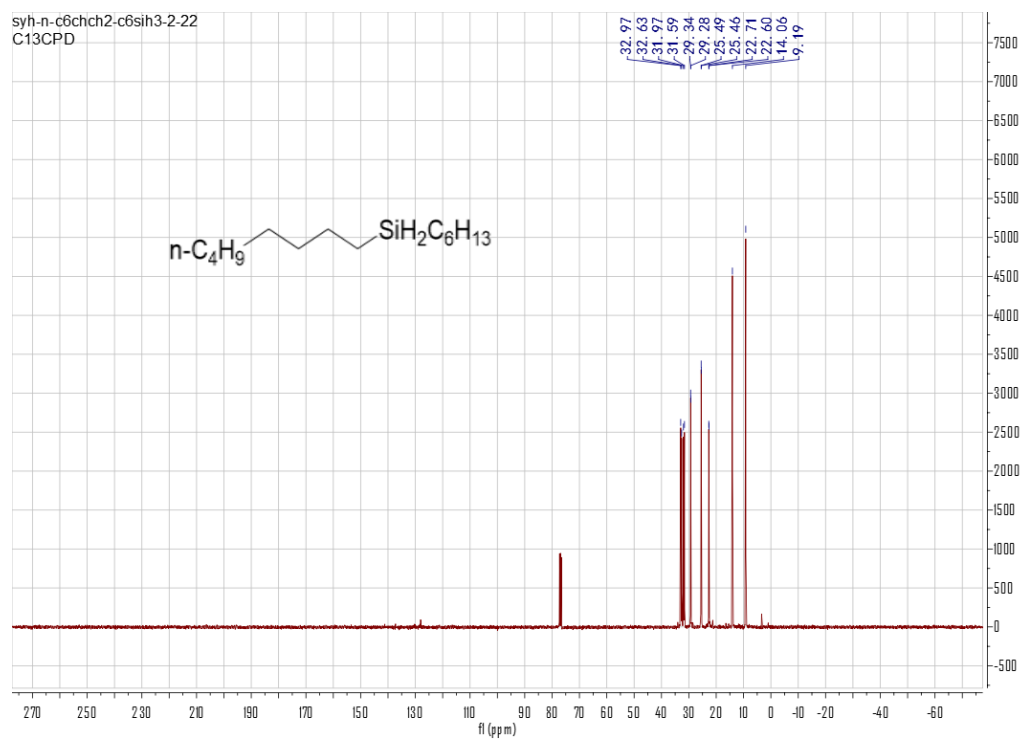
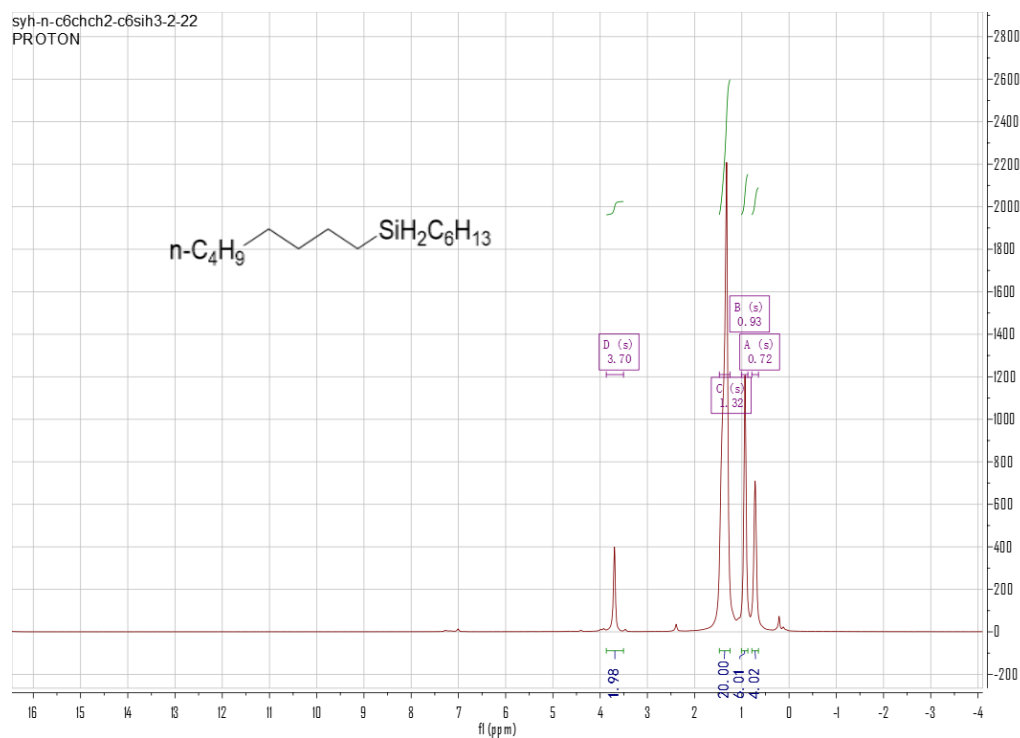




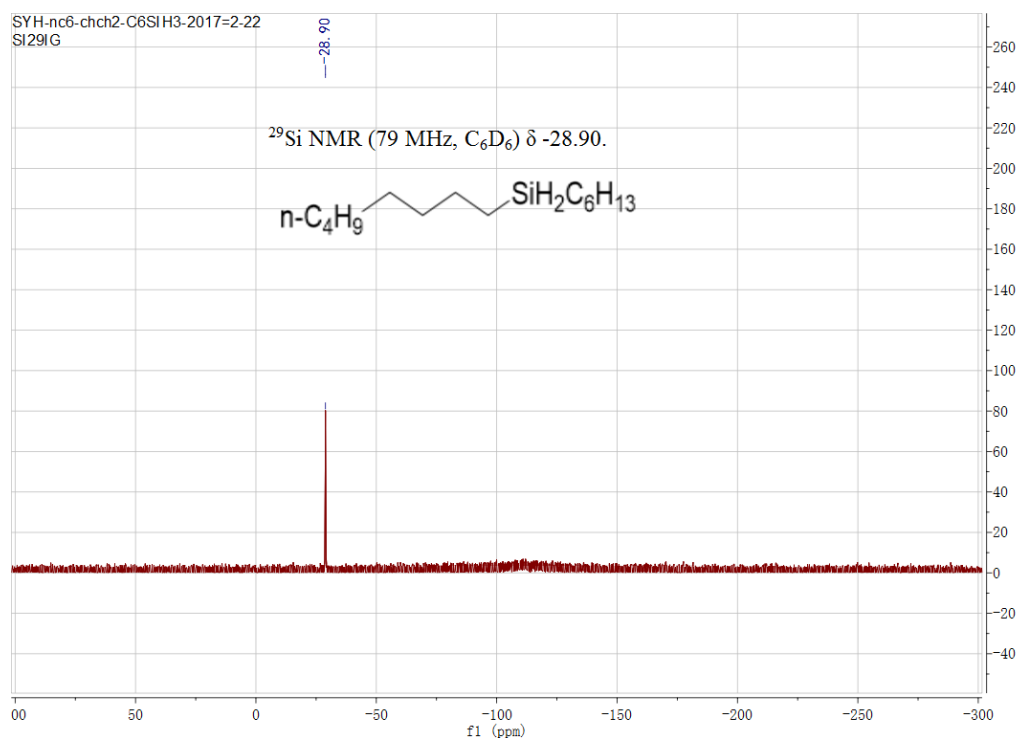








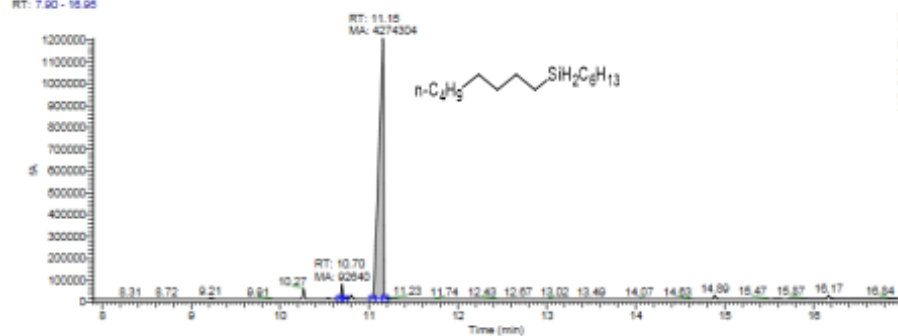
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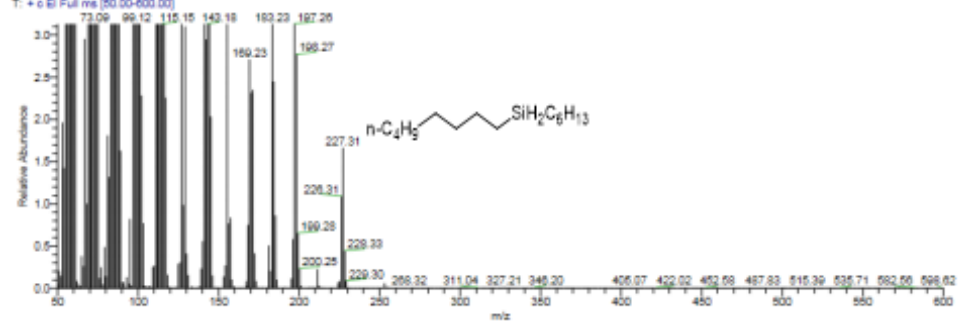
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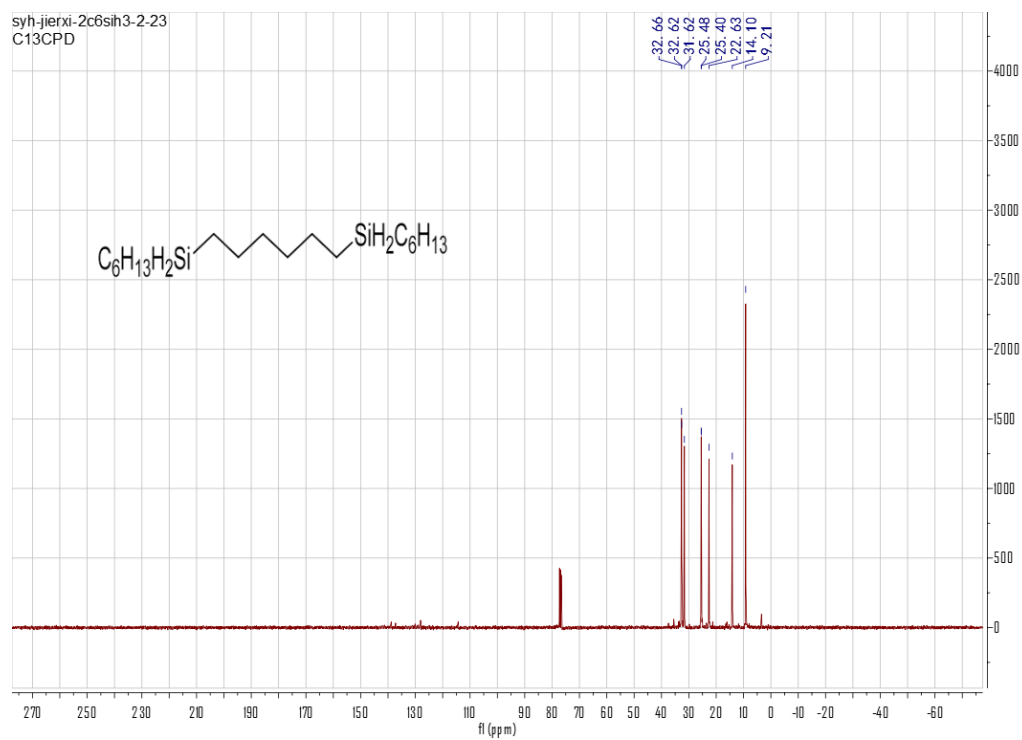
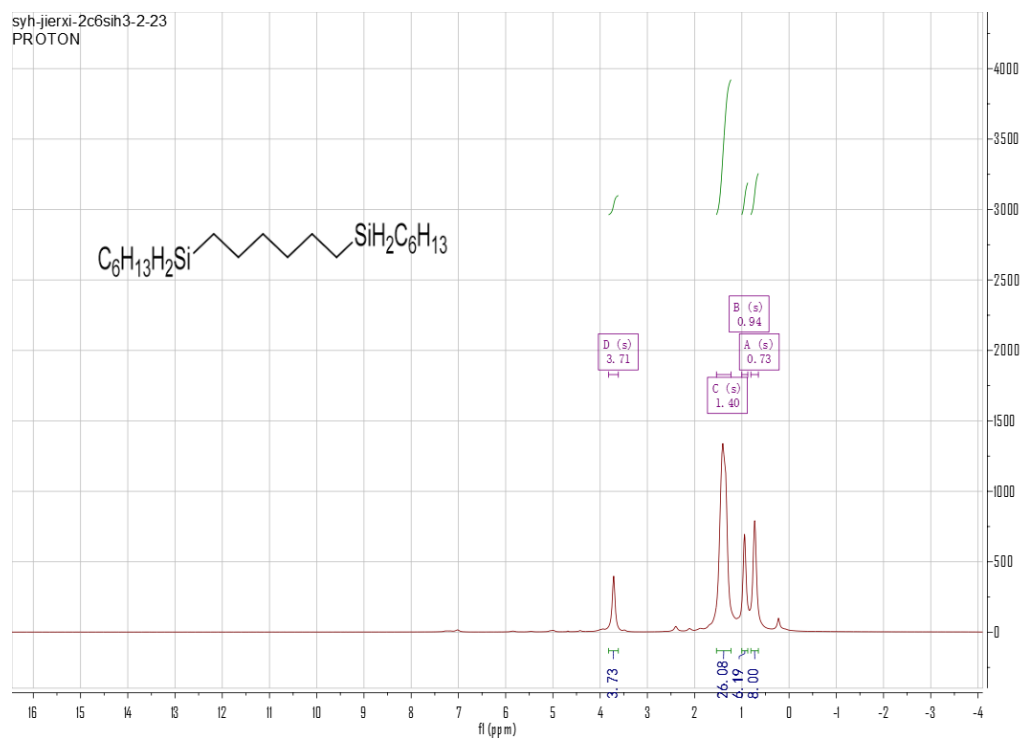
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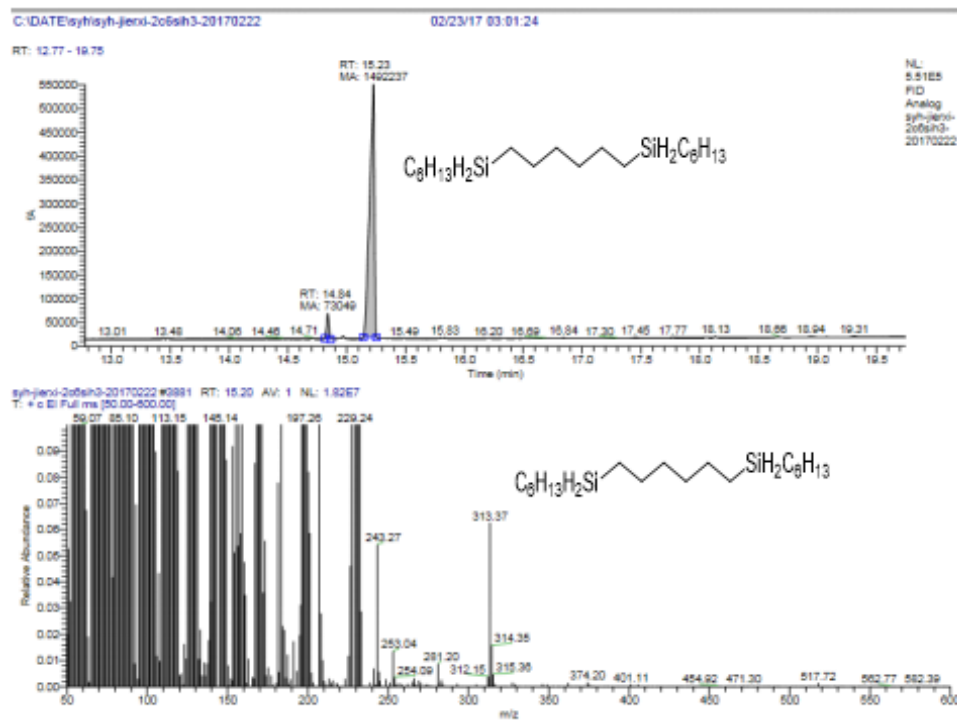
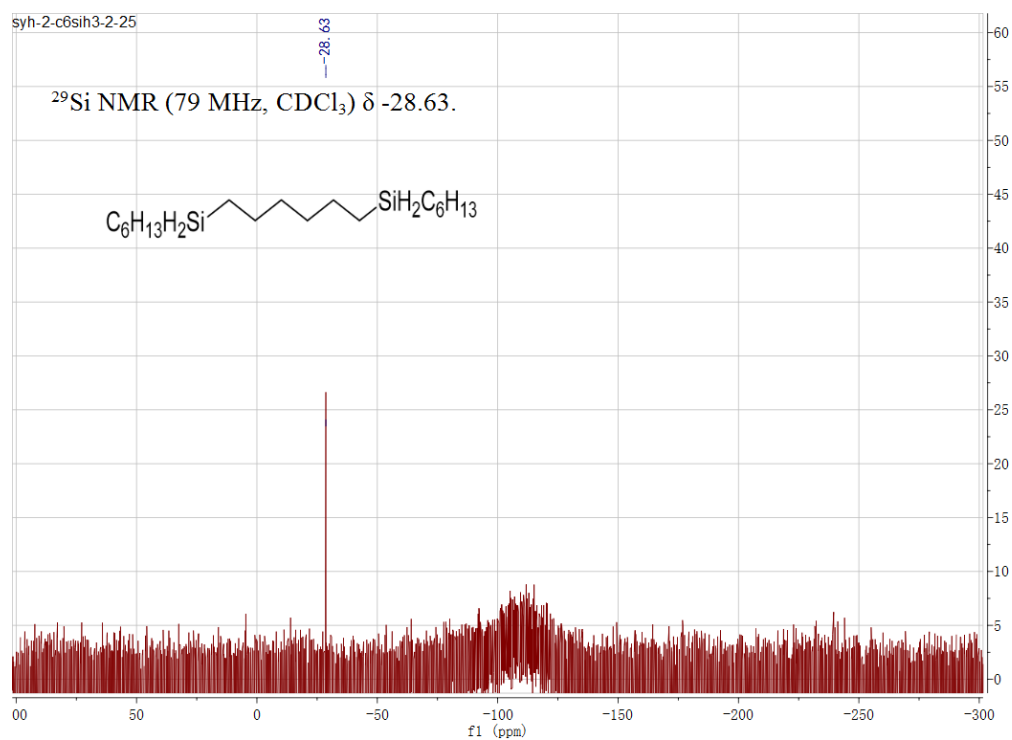


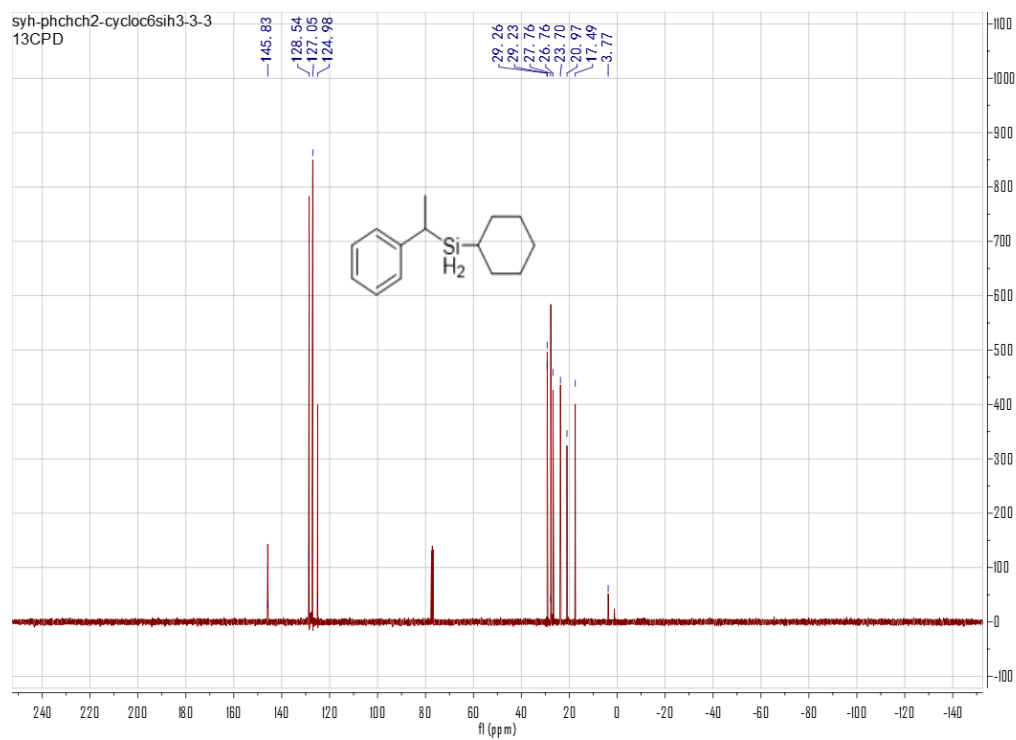
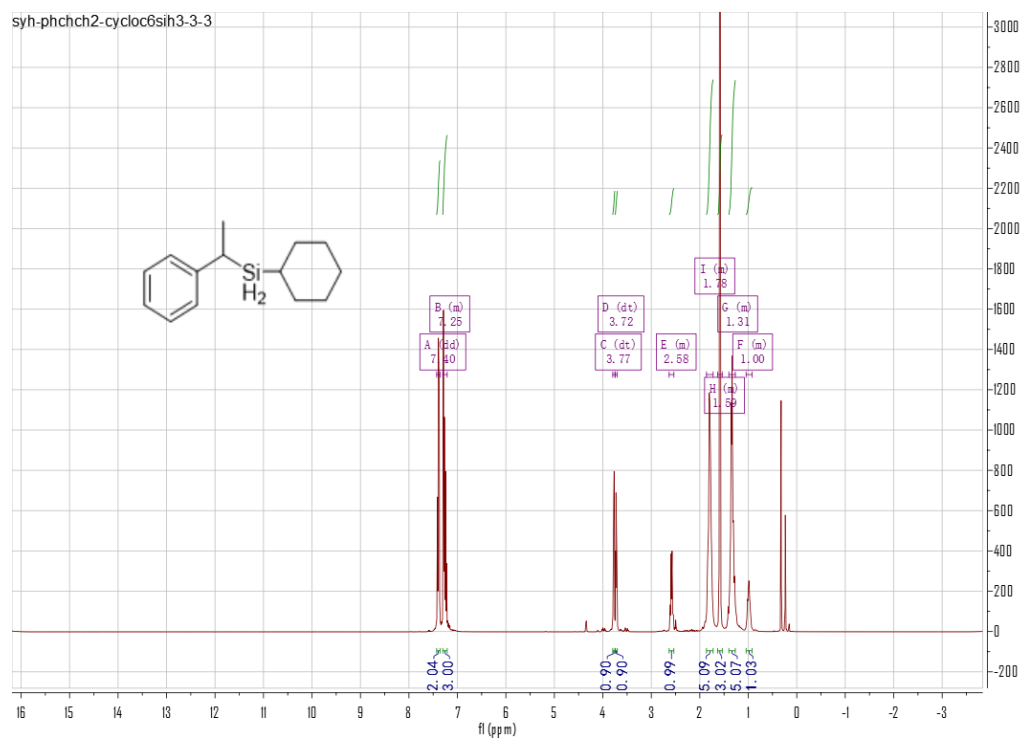
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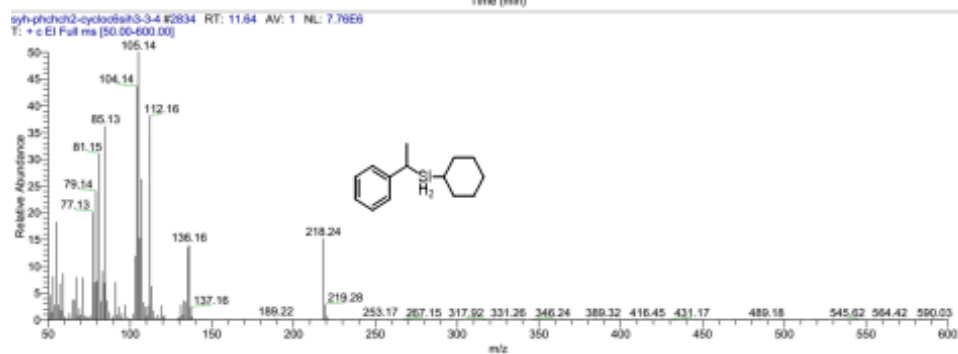
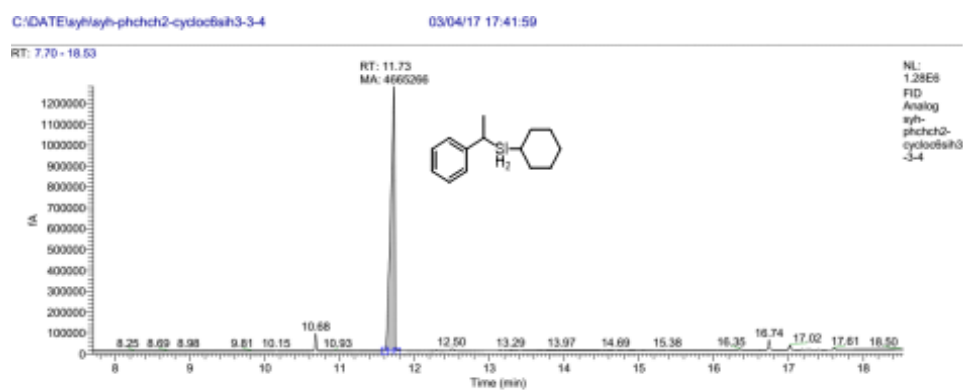
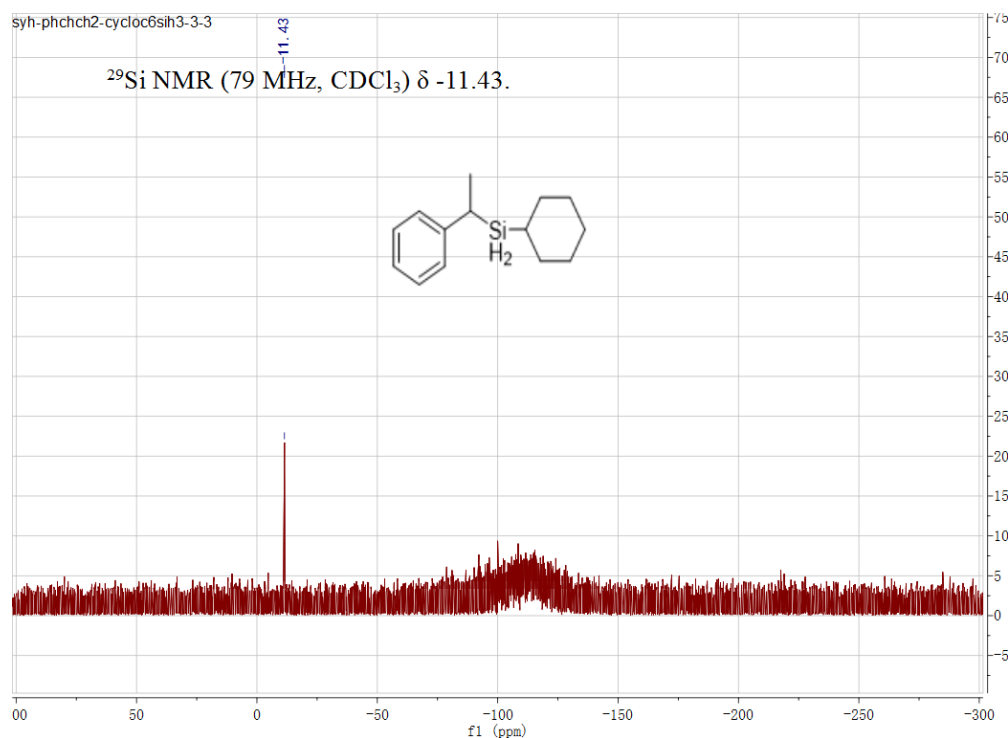
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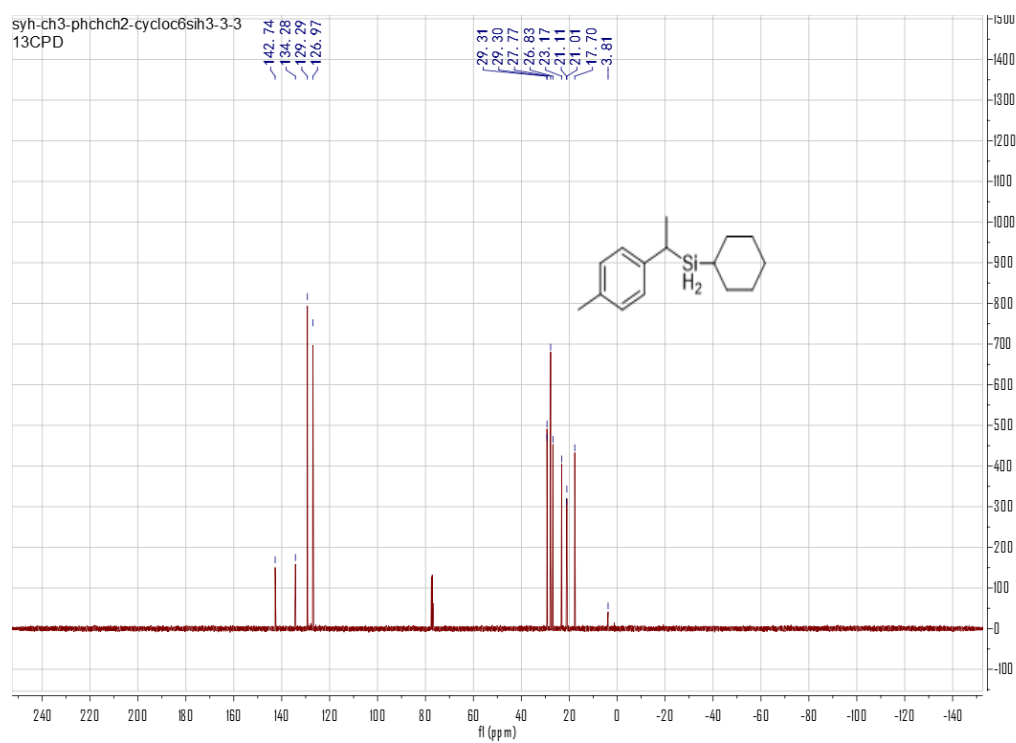
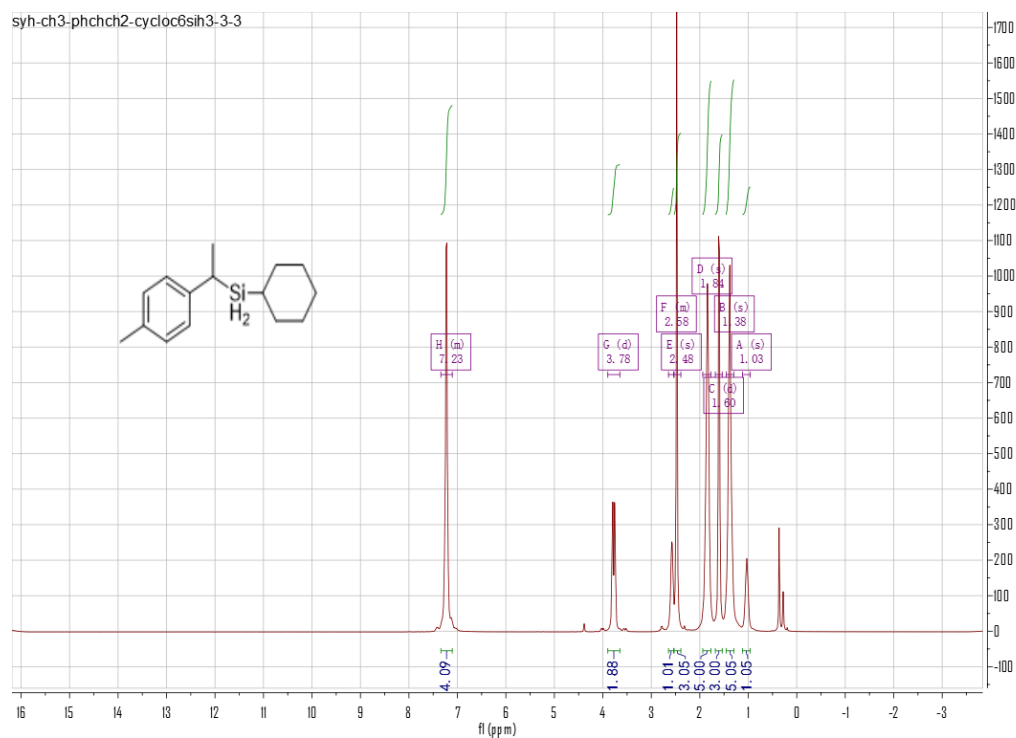


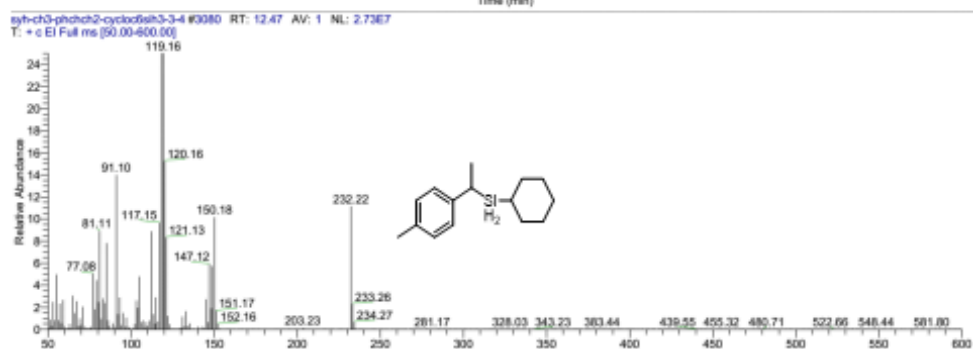
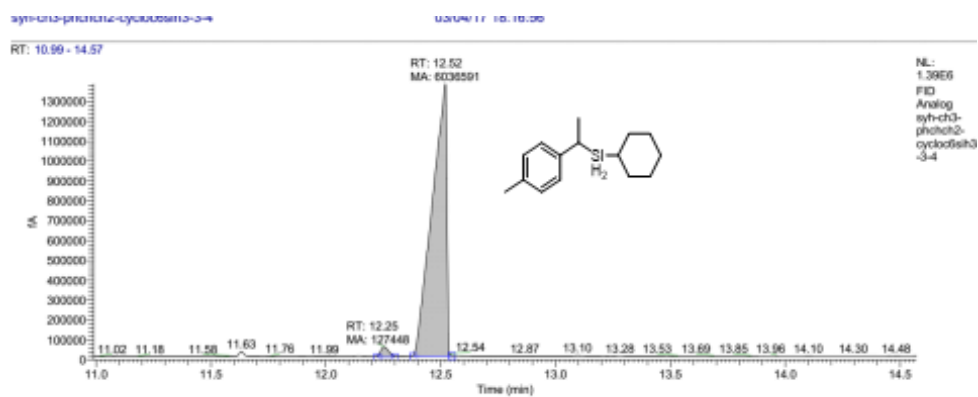
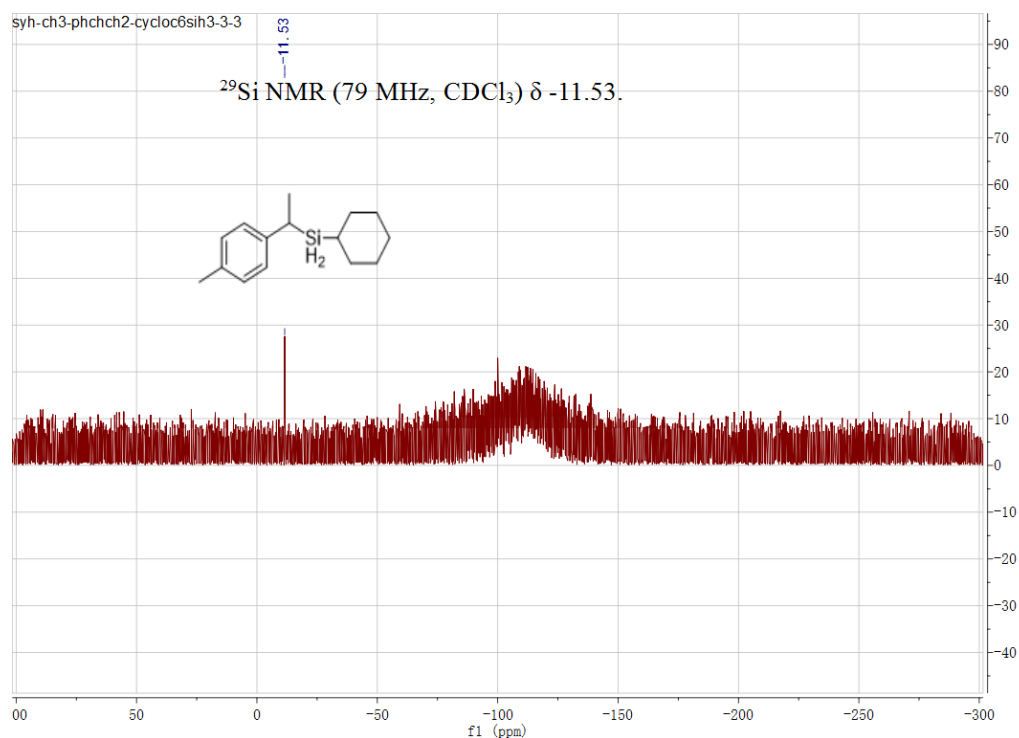


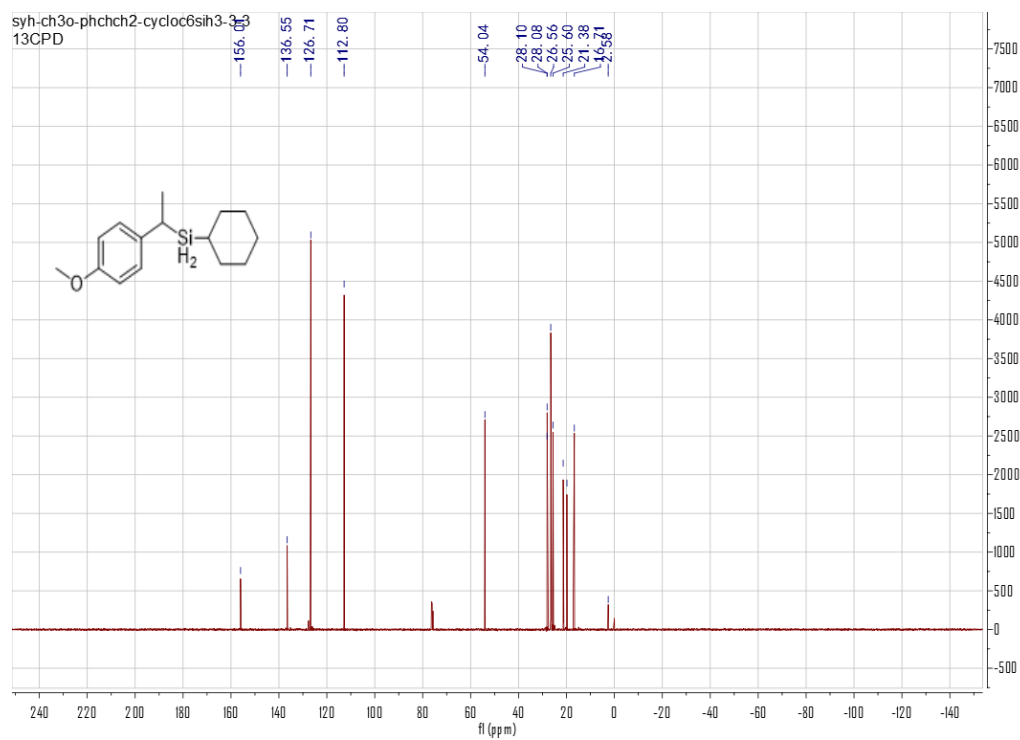
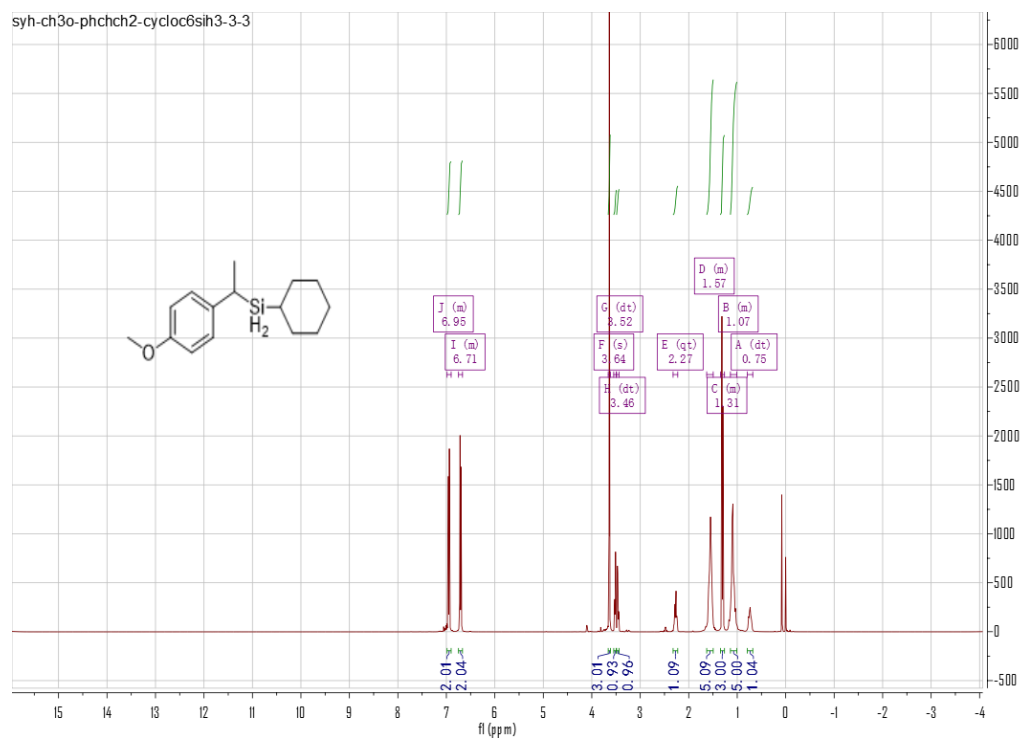


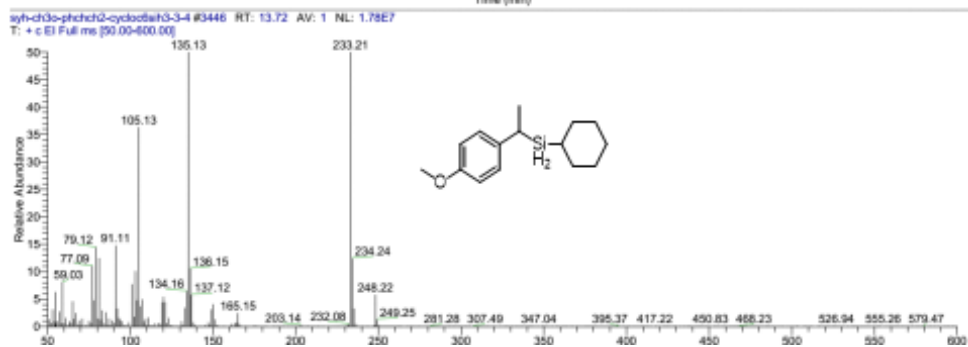
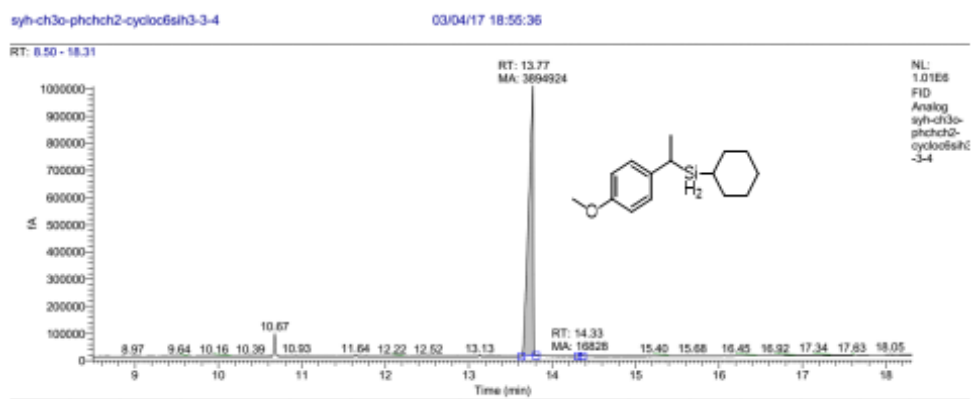
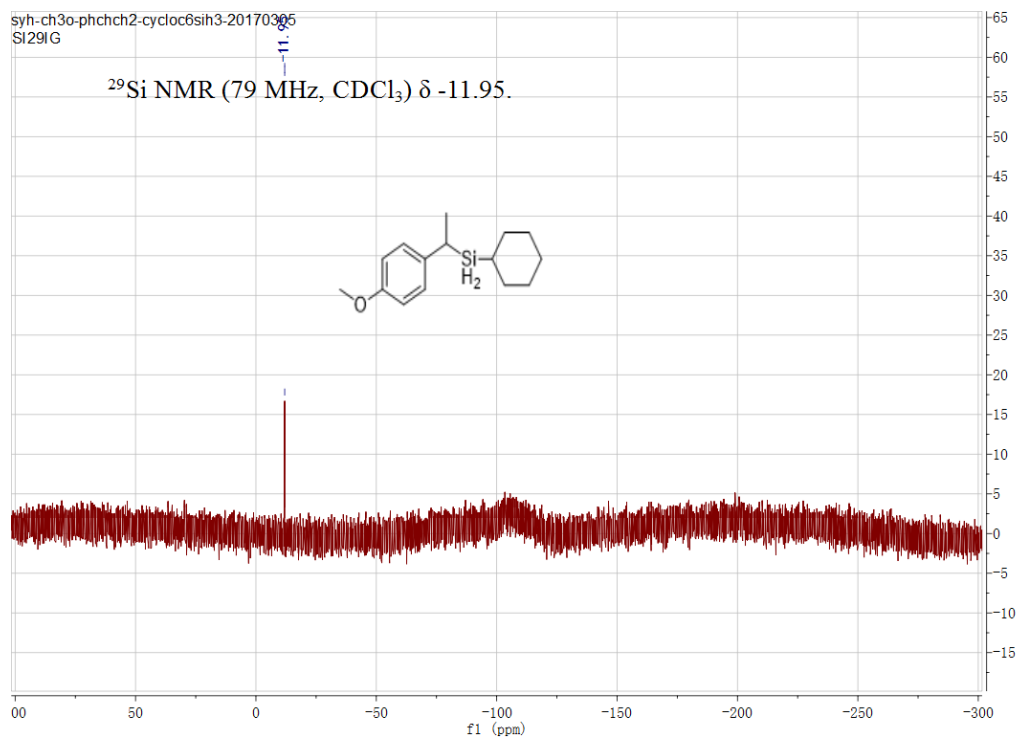


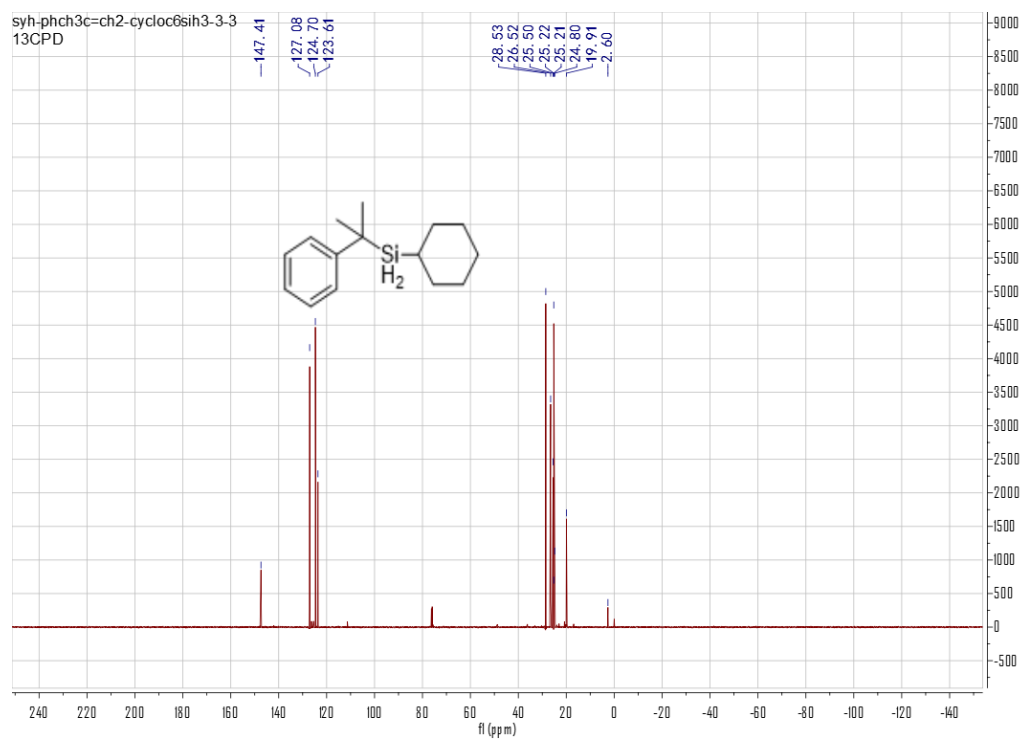
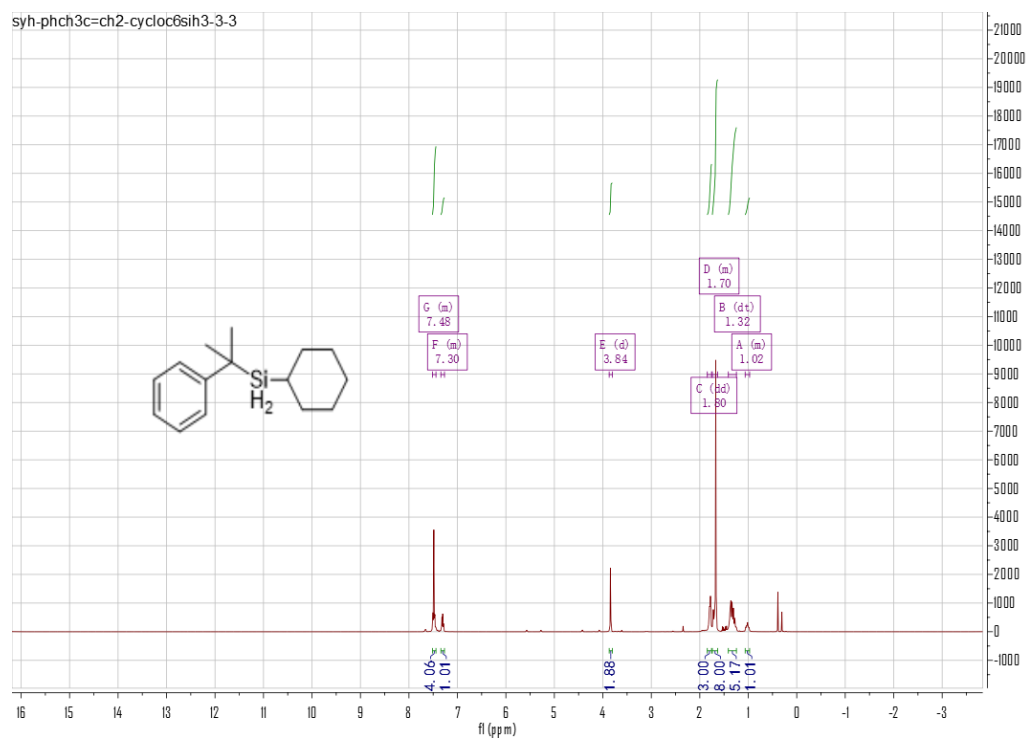


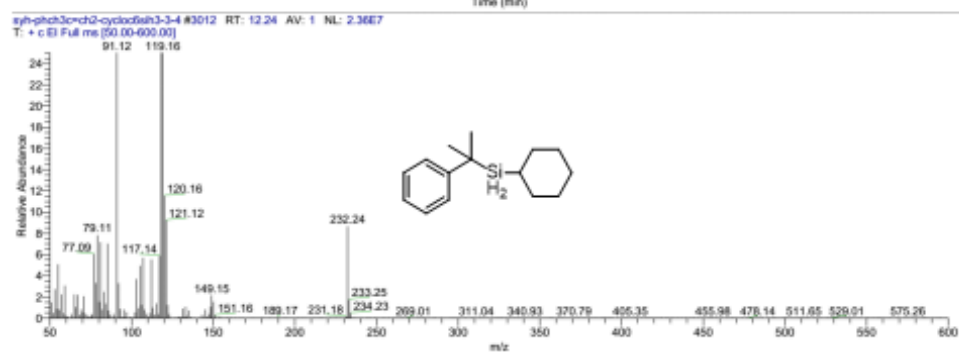
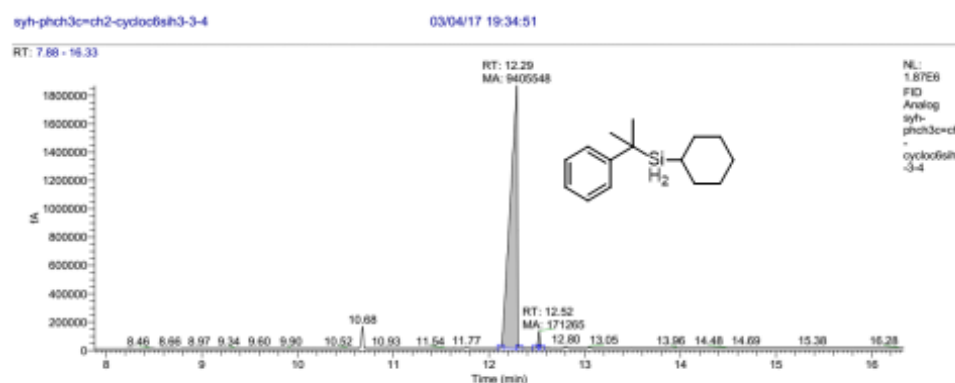
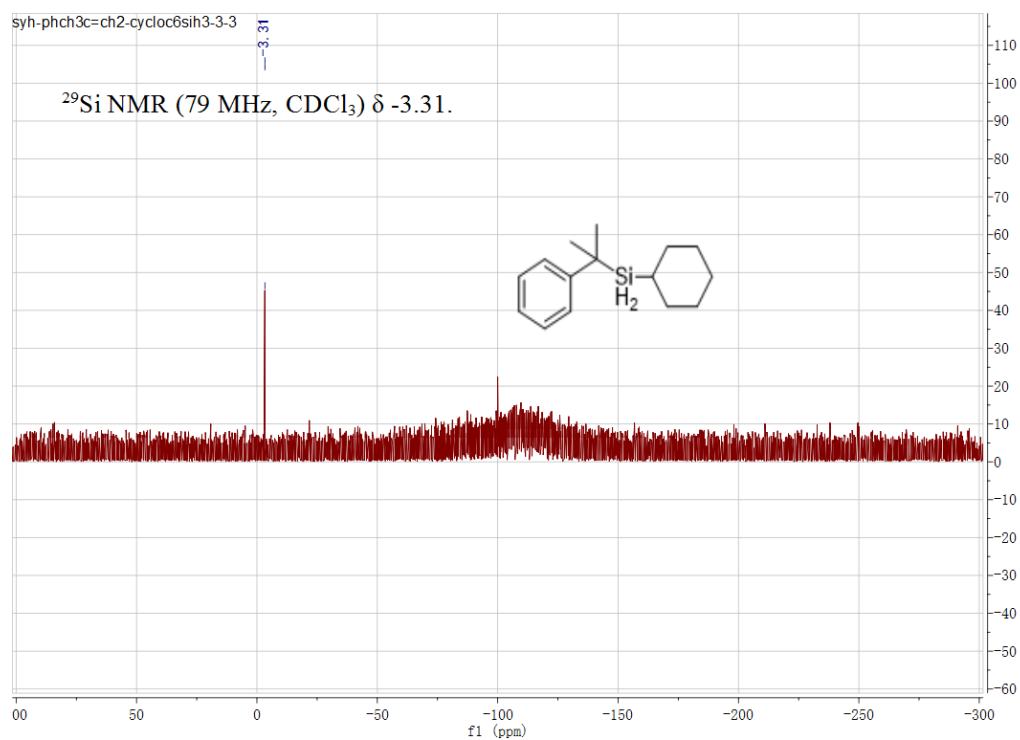


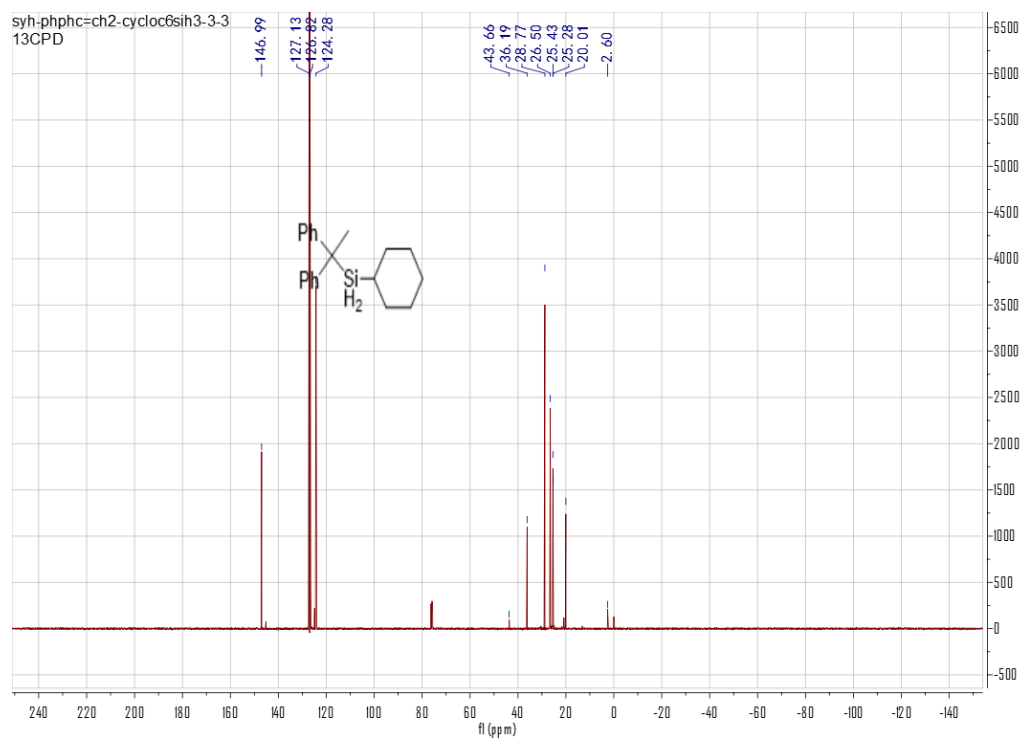
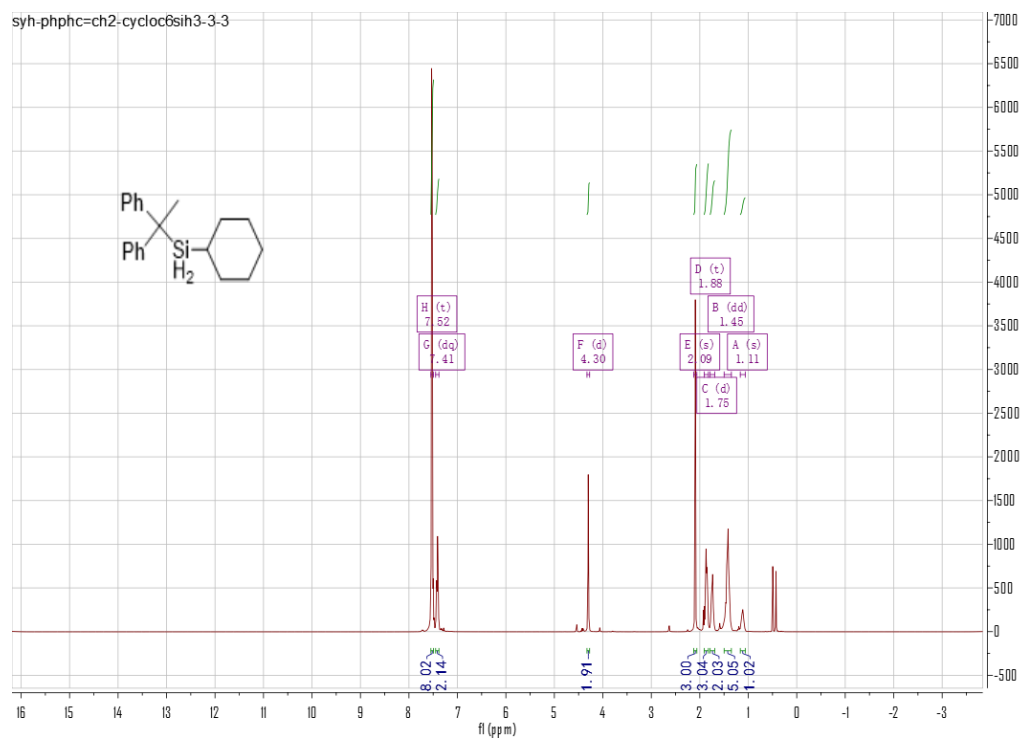


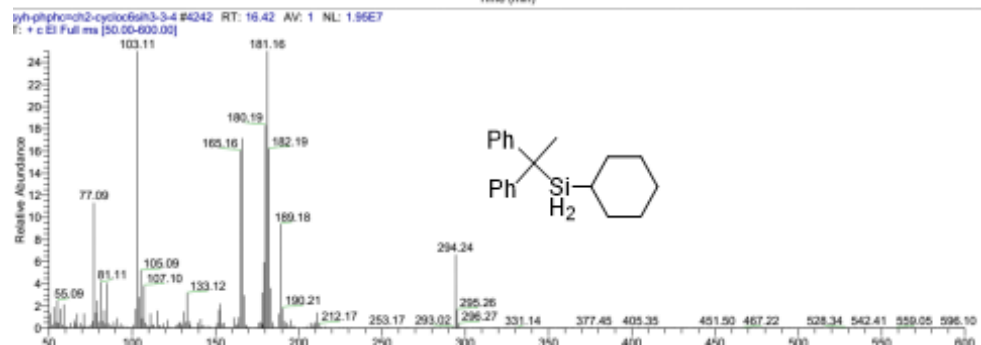
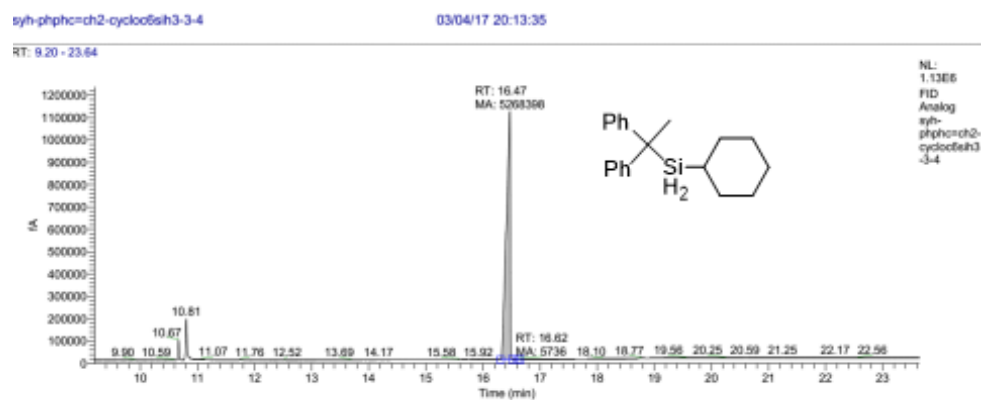
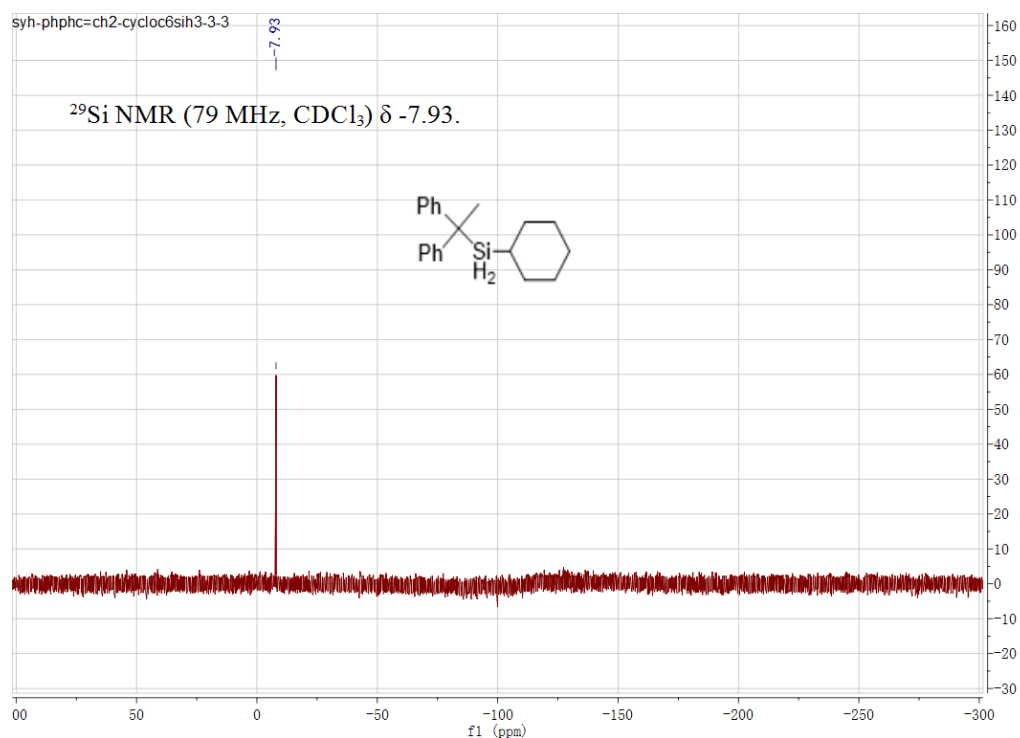


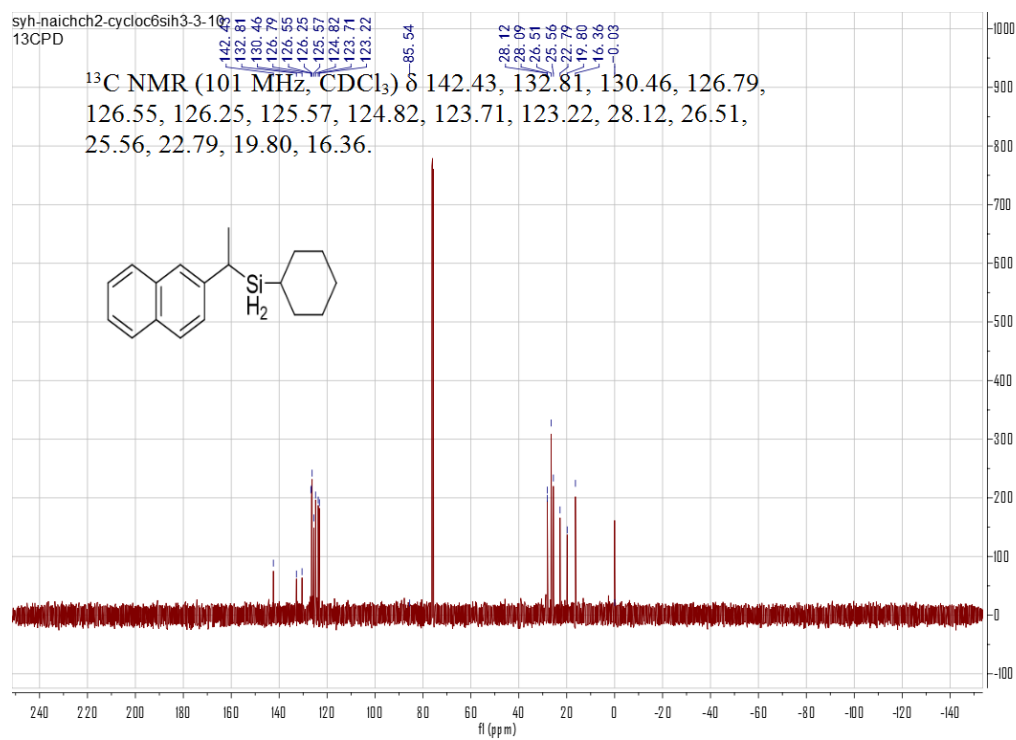
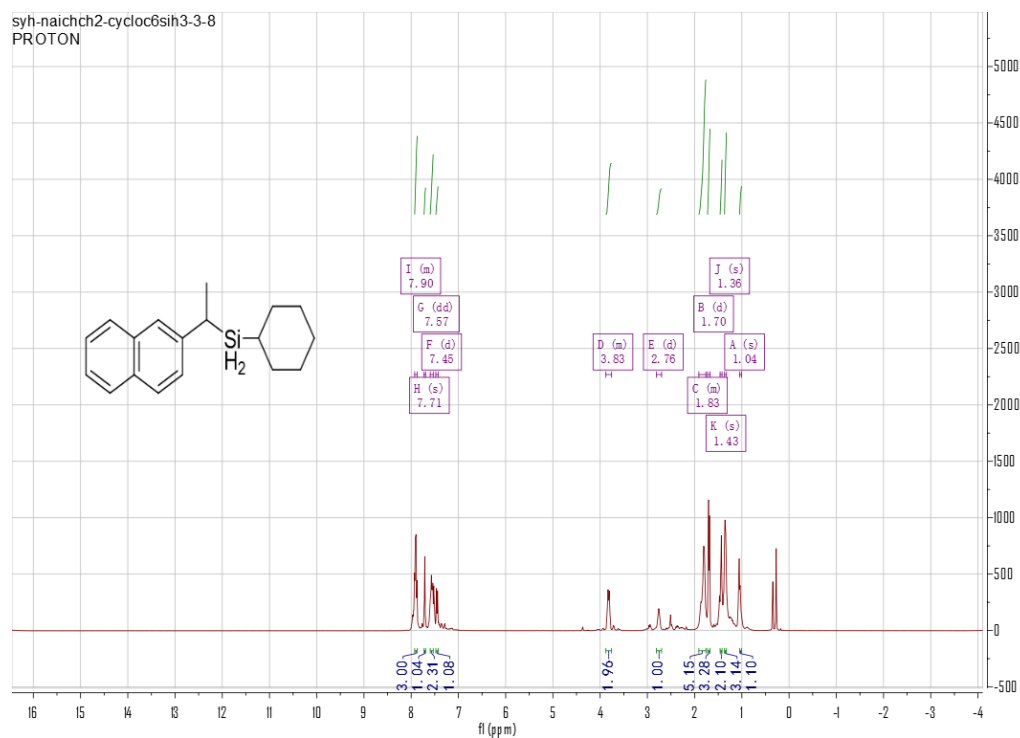


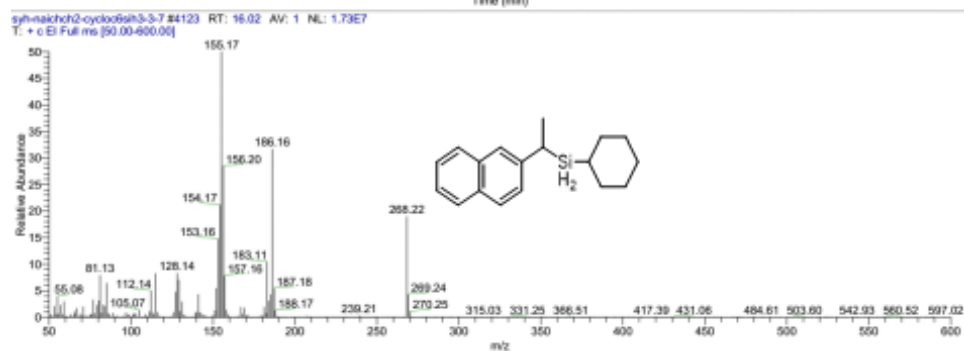
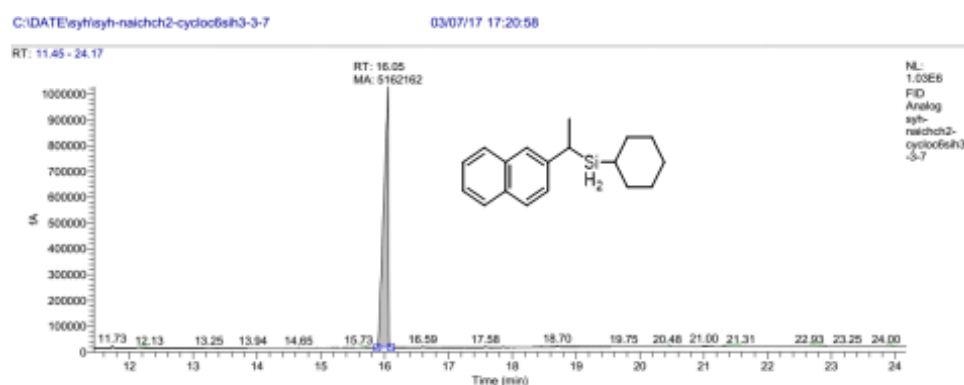
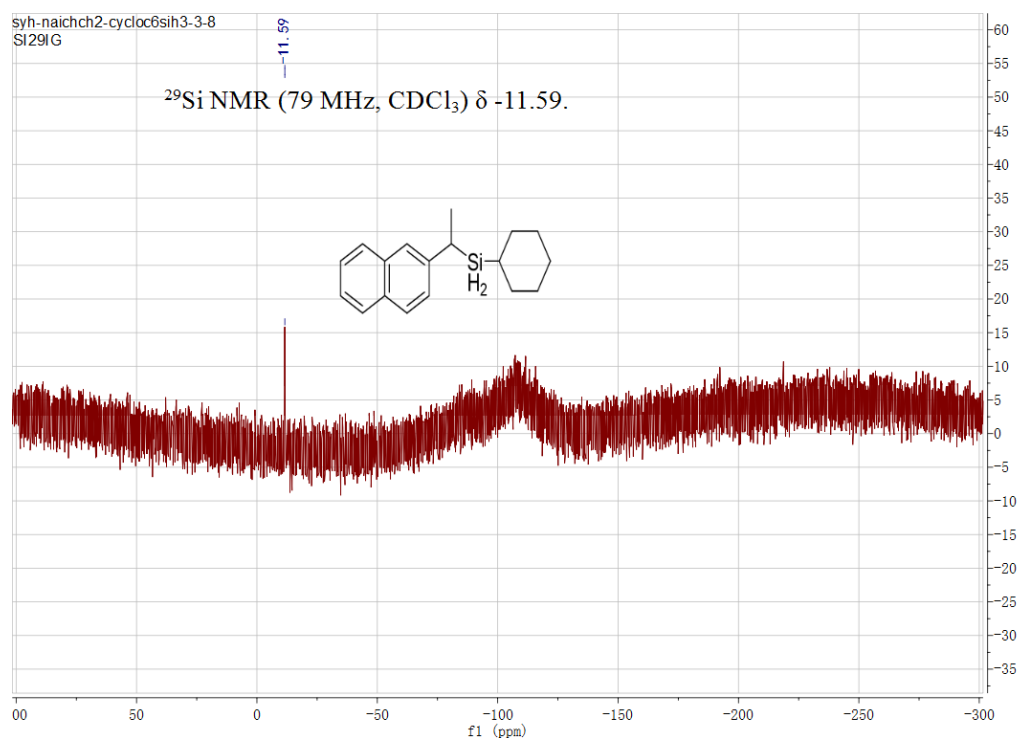


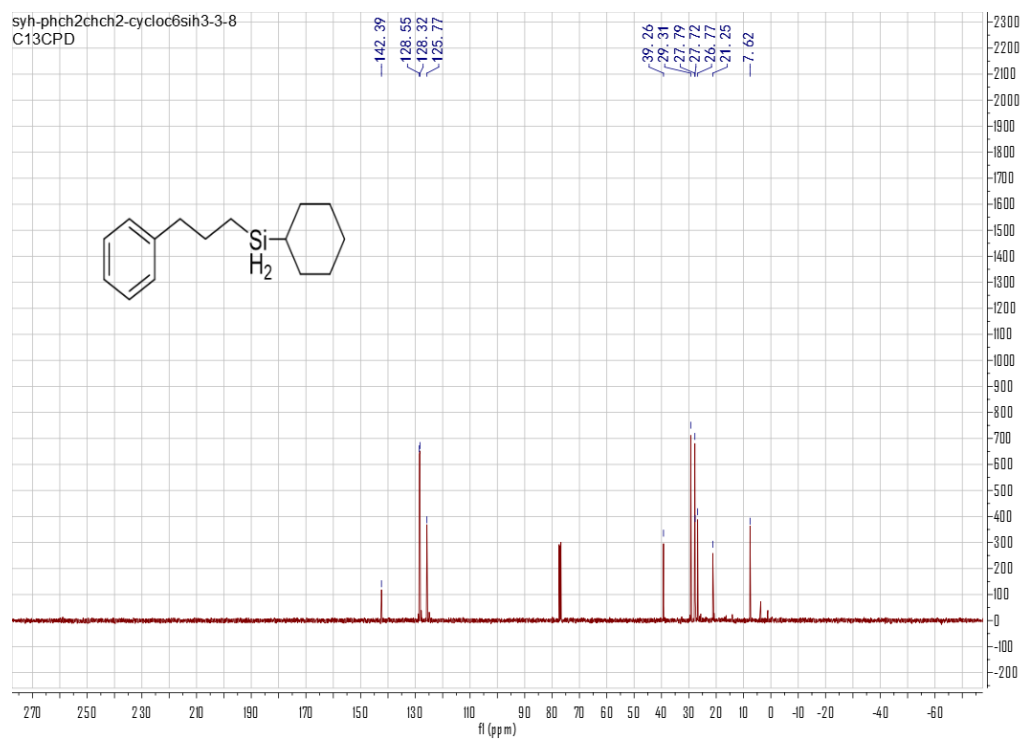
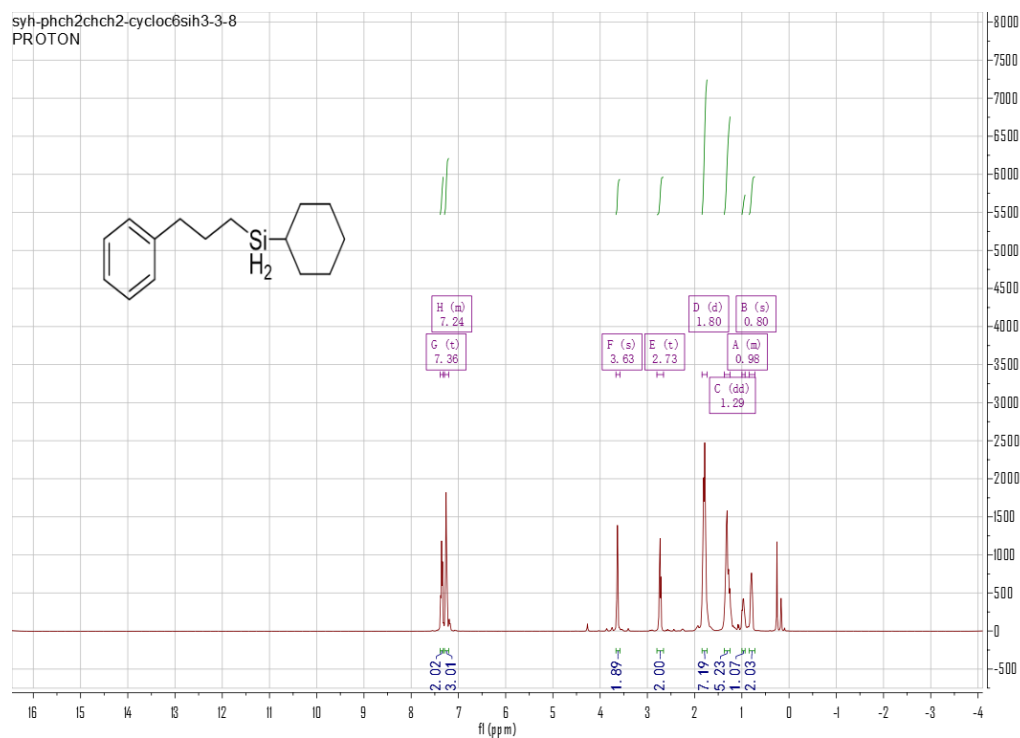


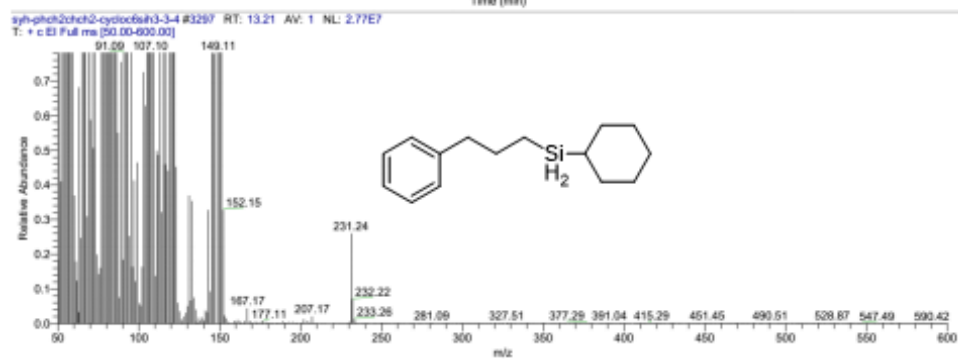
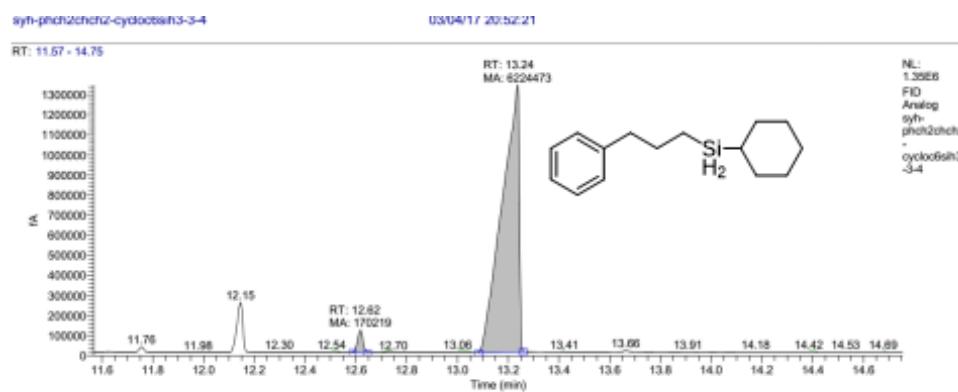
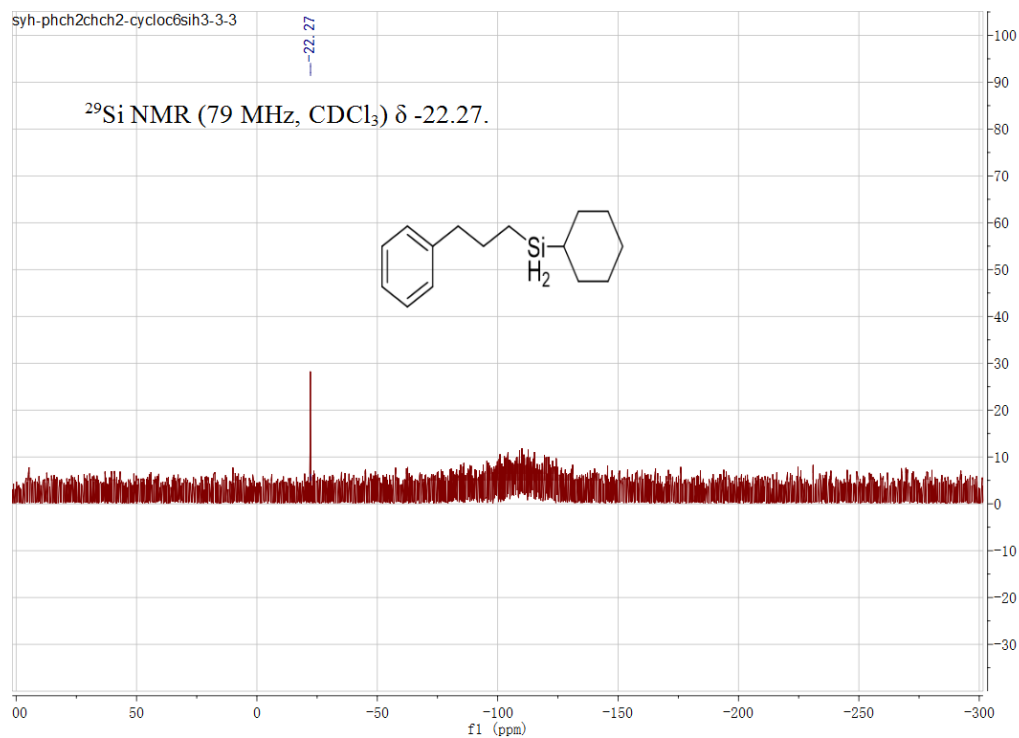


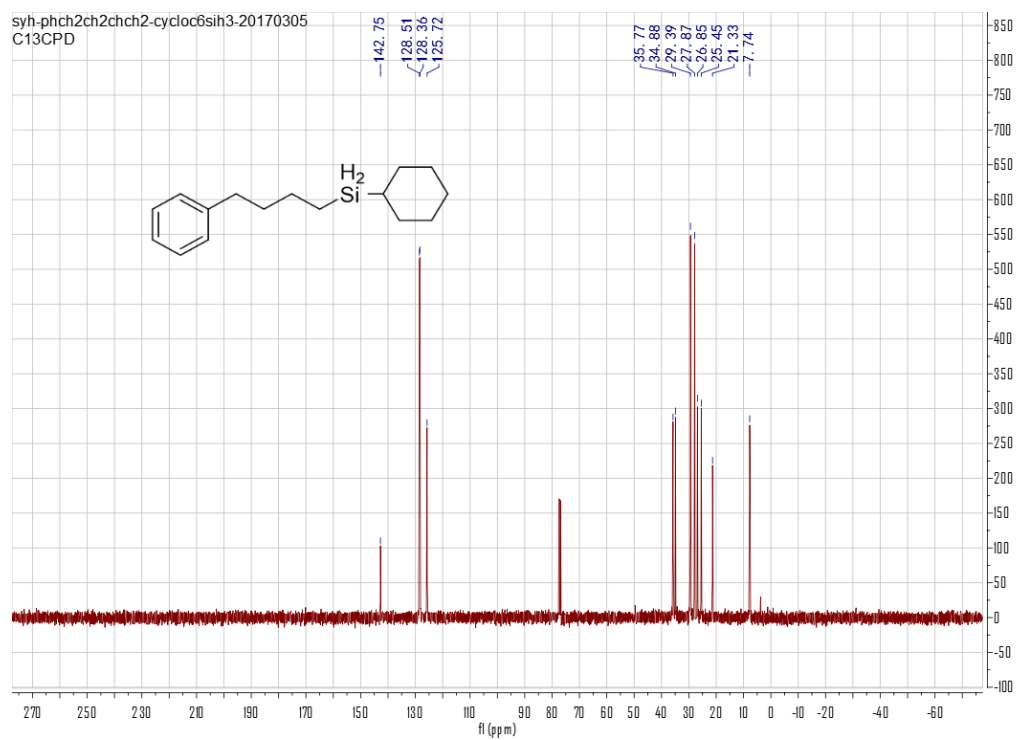
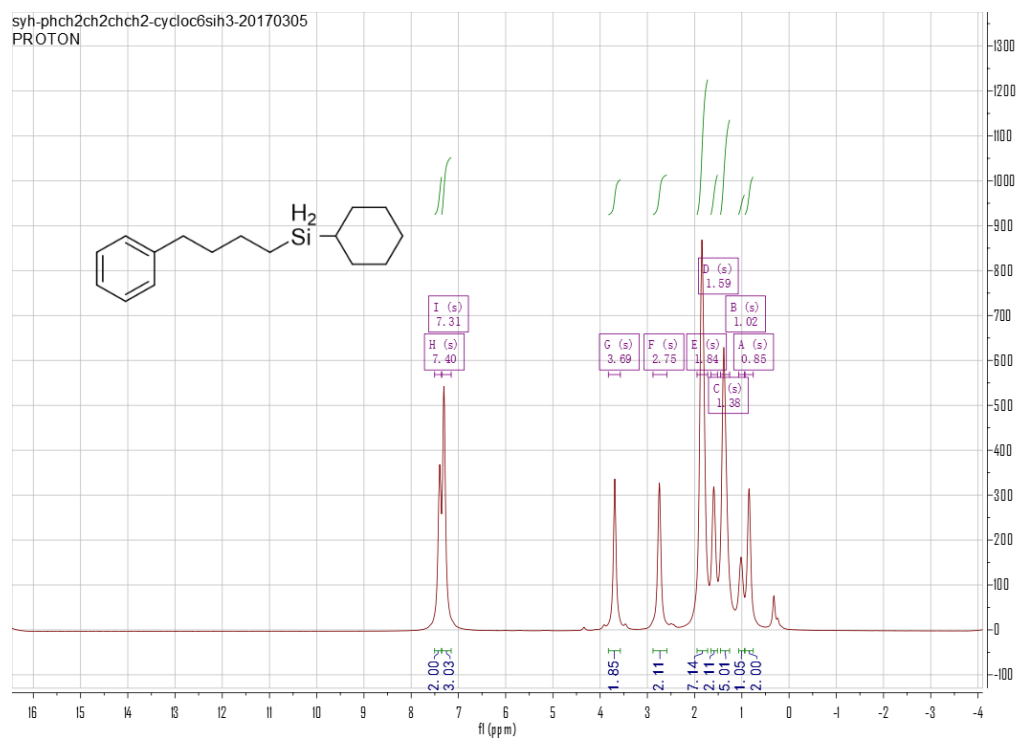


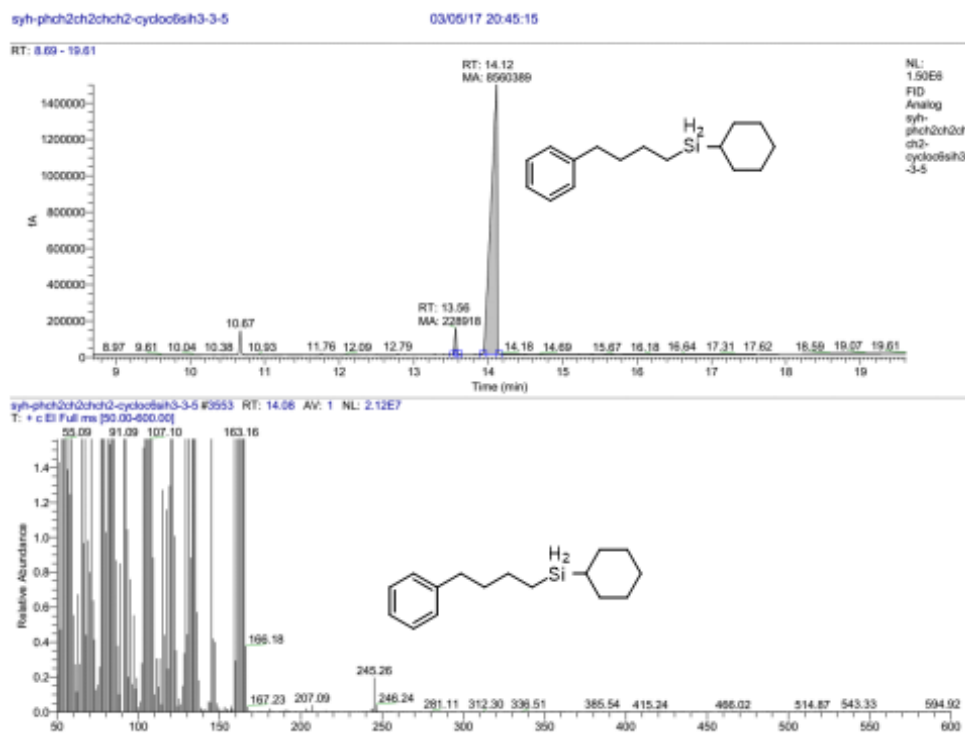
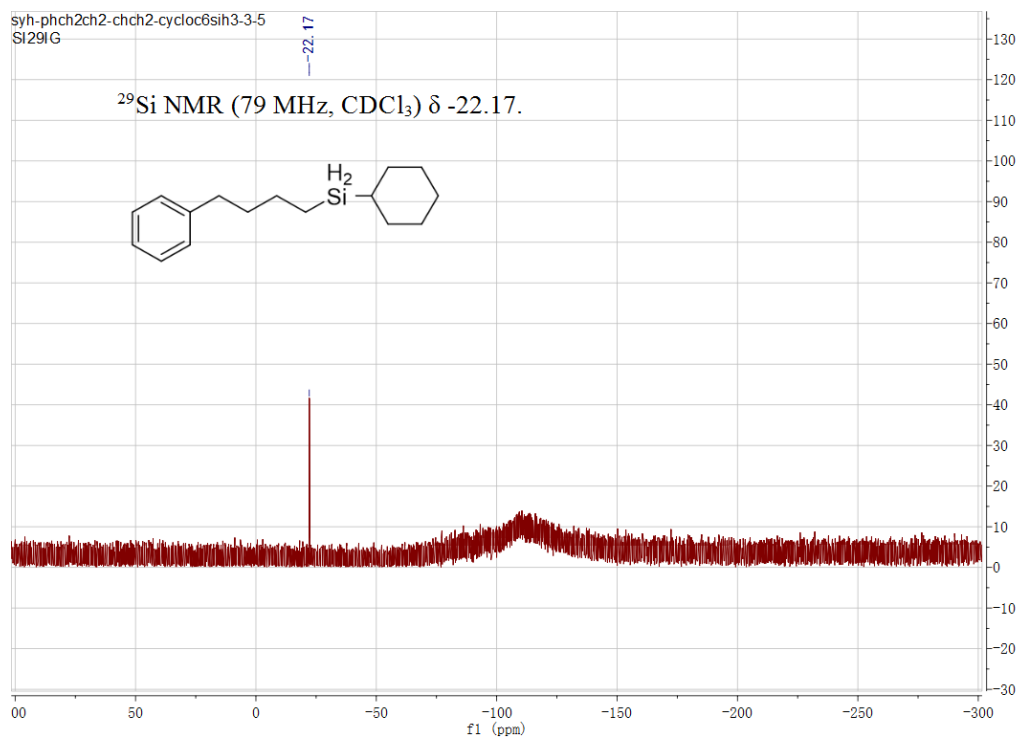




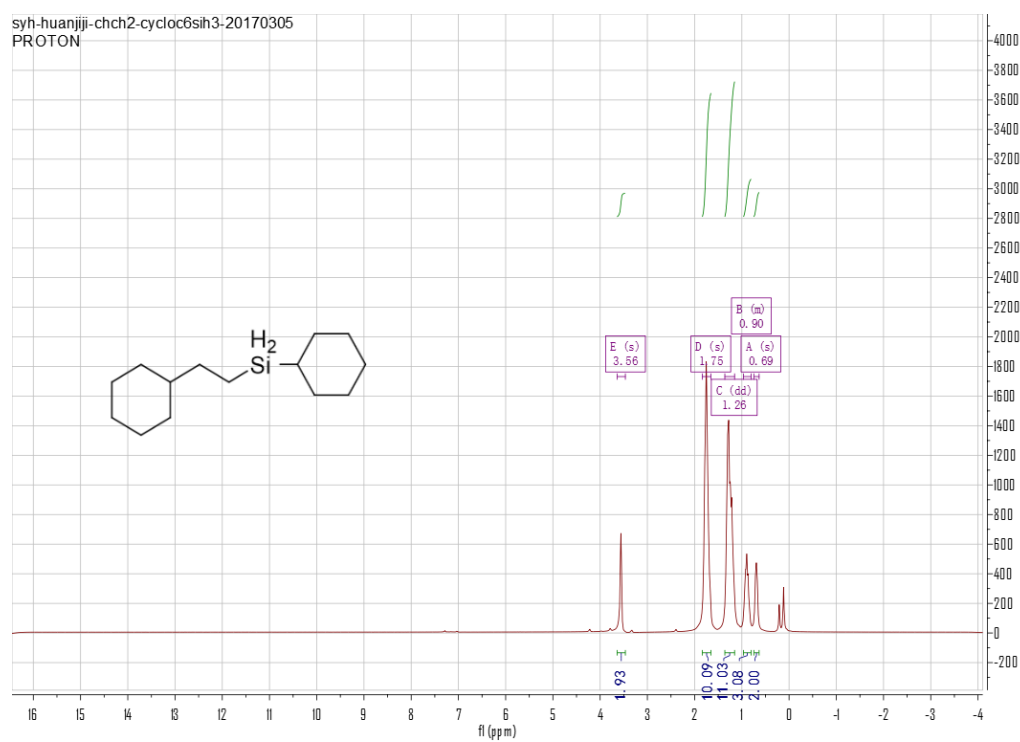




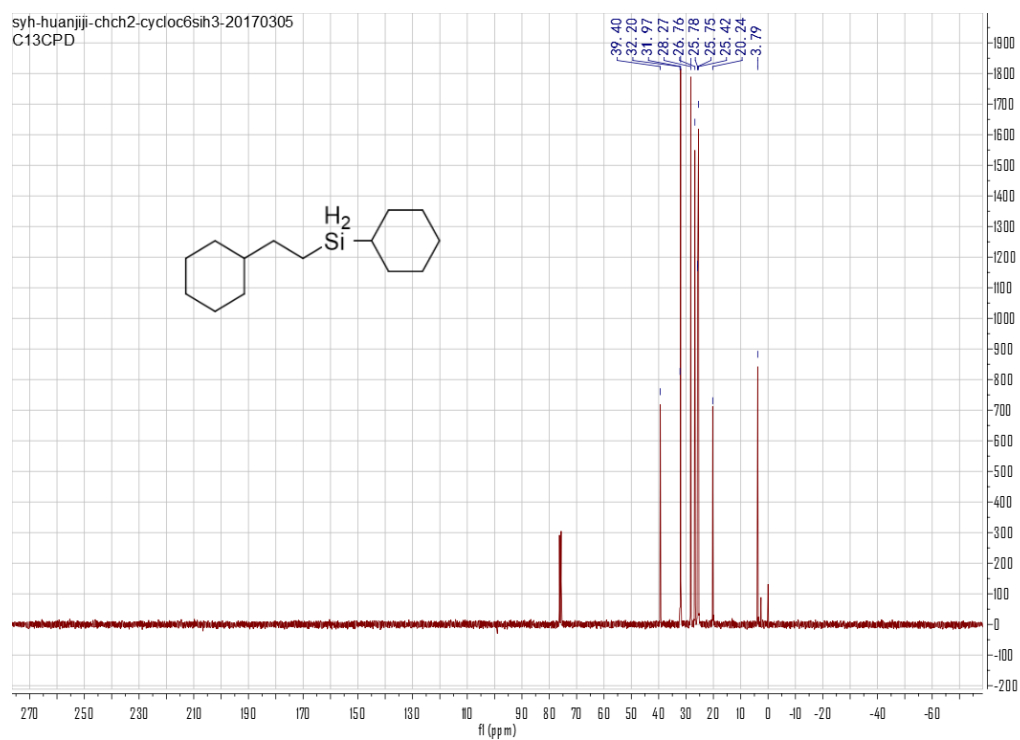


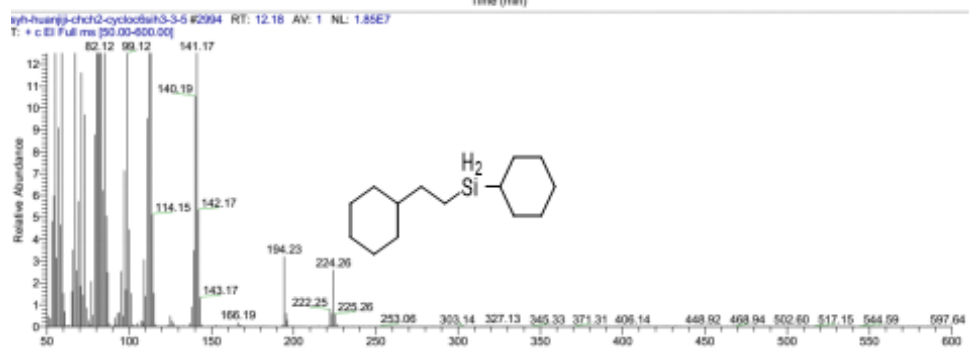
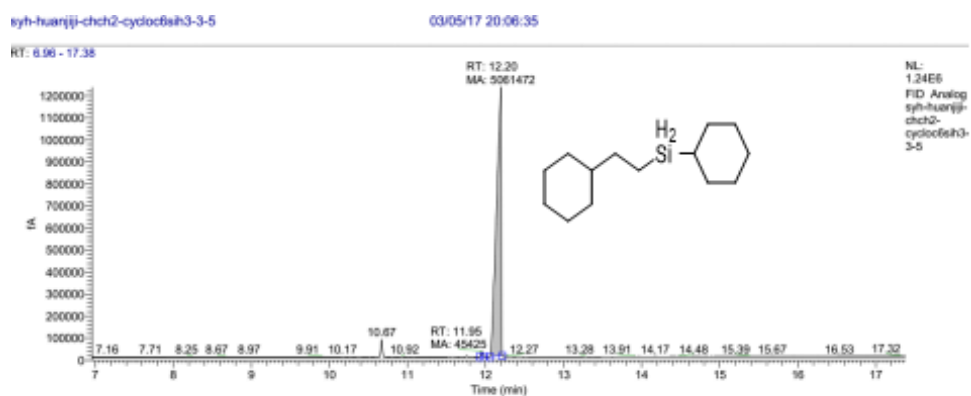
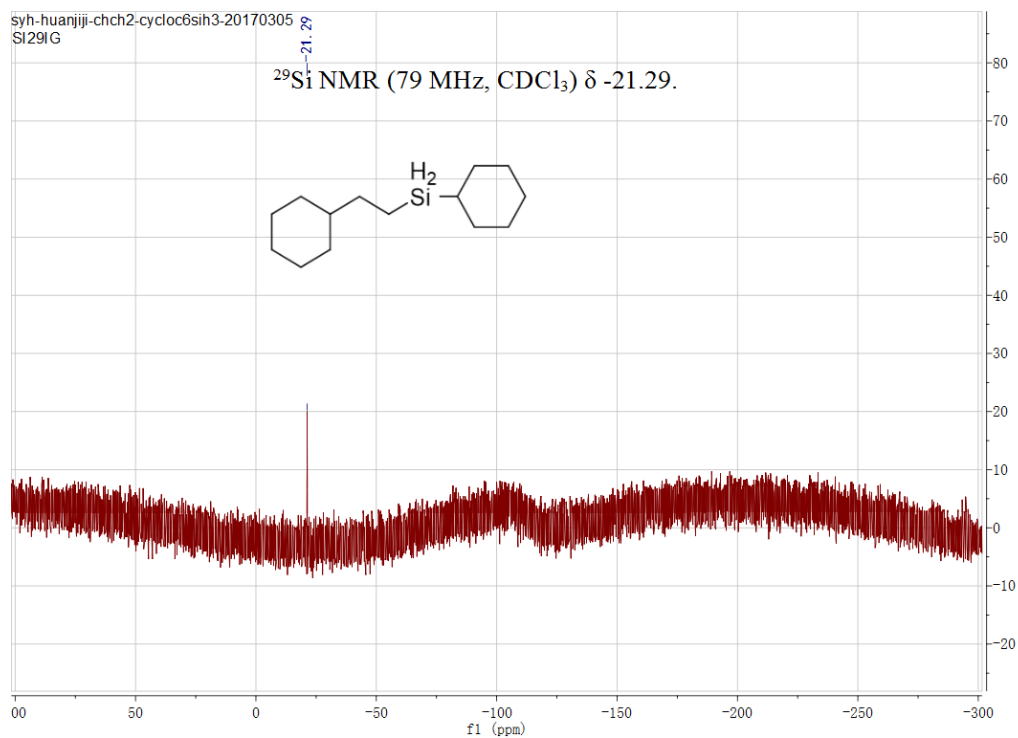


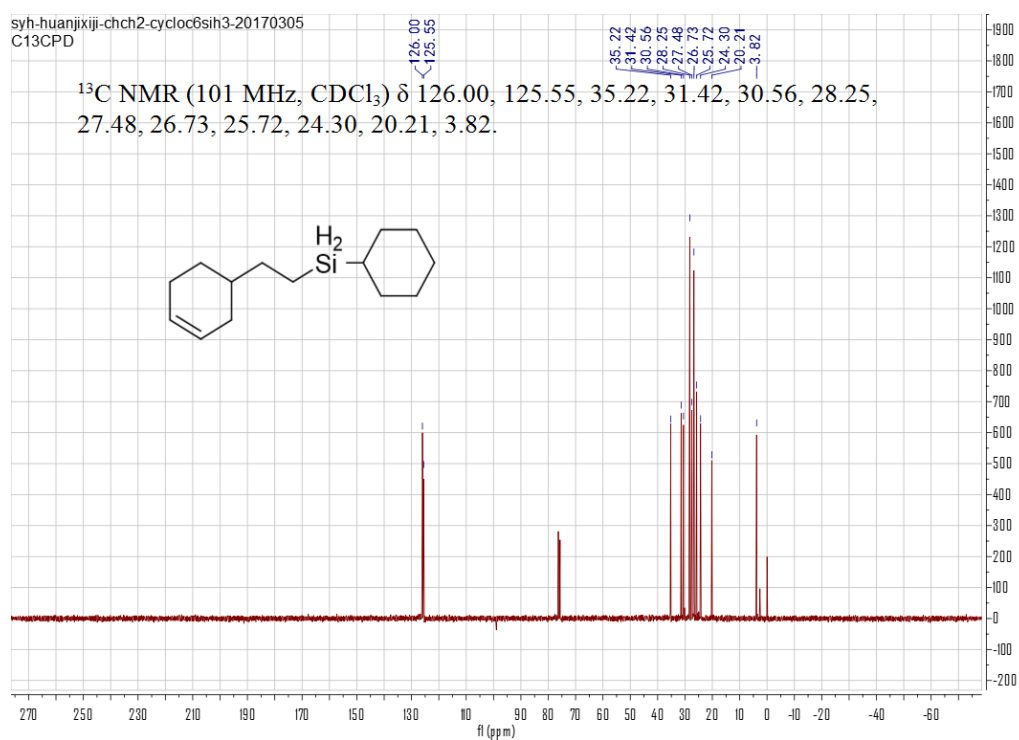
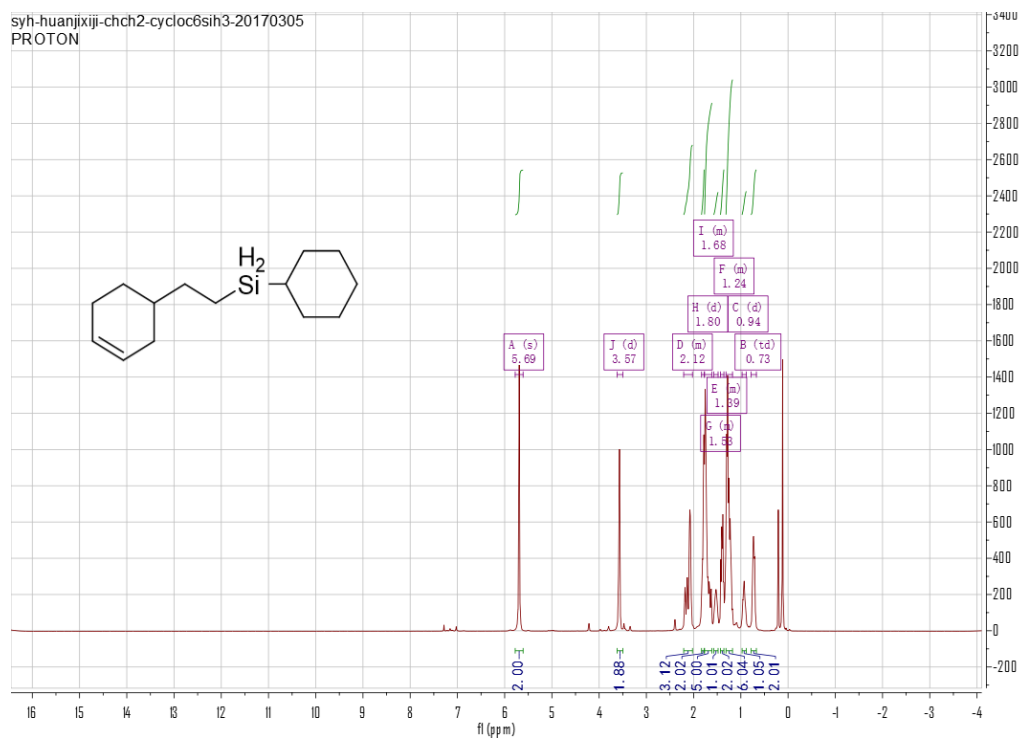
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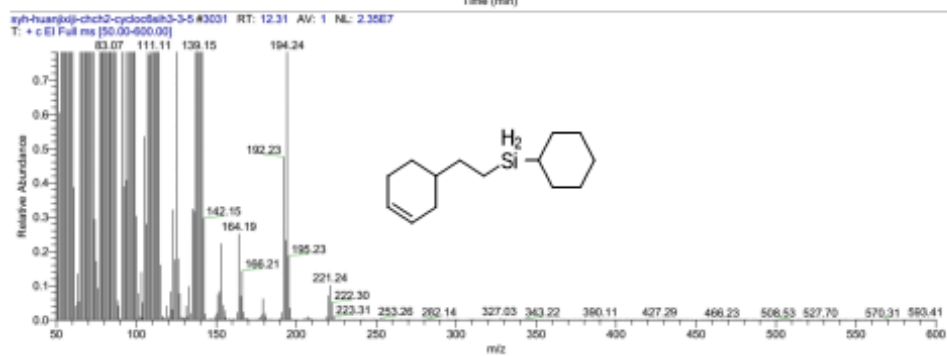
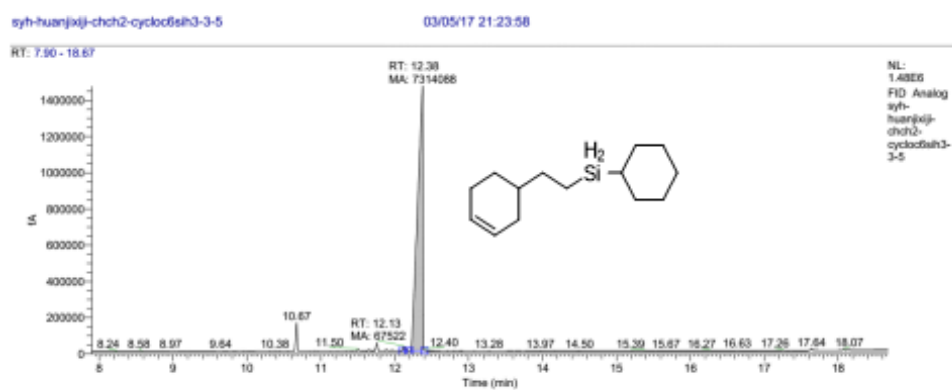
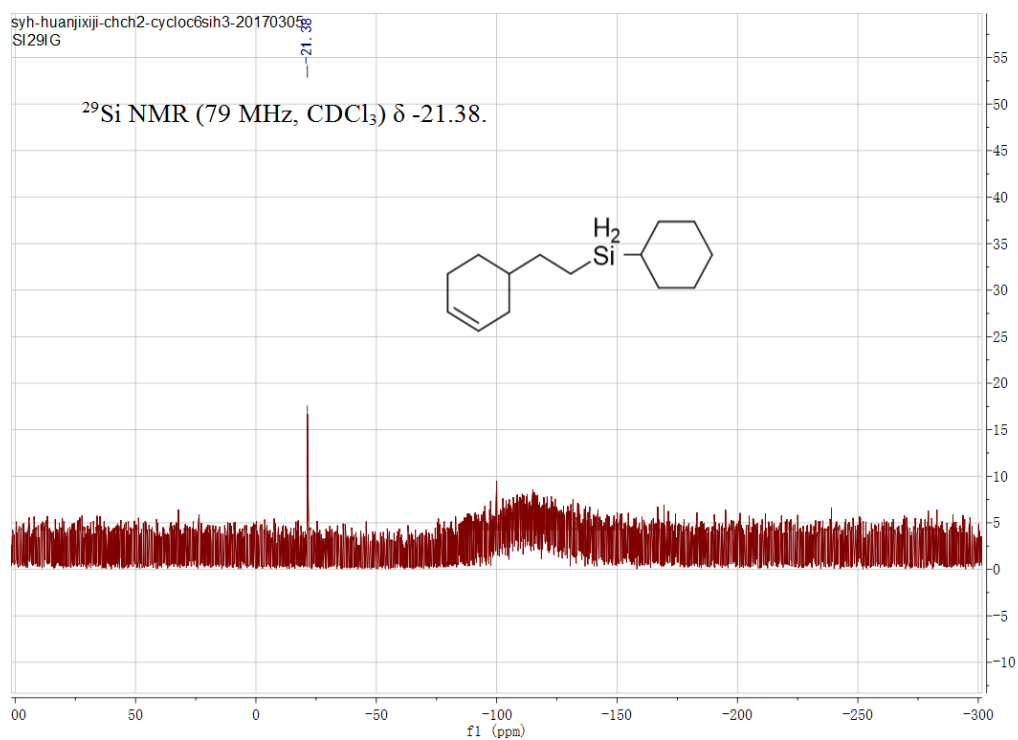
syh-huanjiji-chch2-cycloc6sih3-20170305
C13CPD



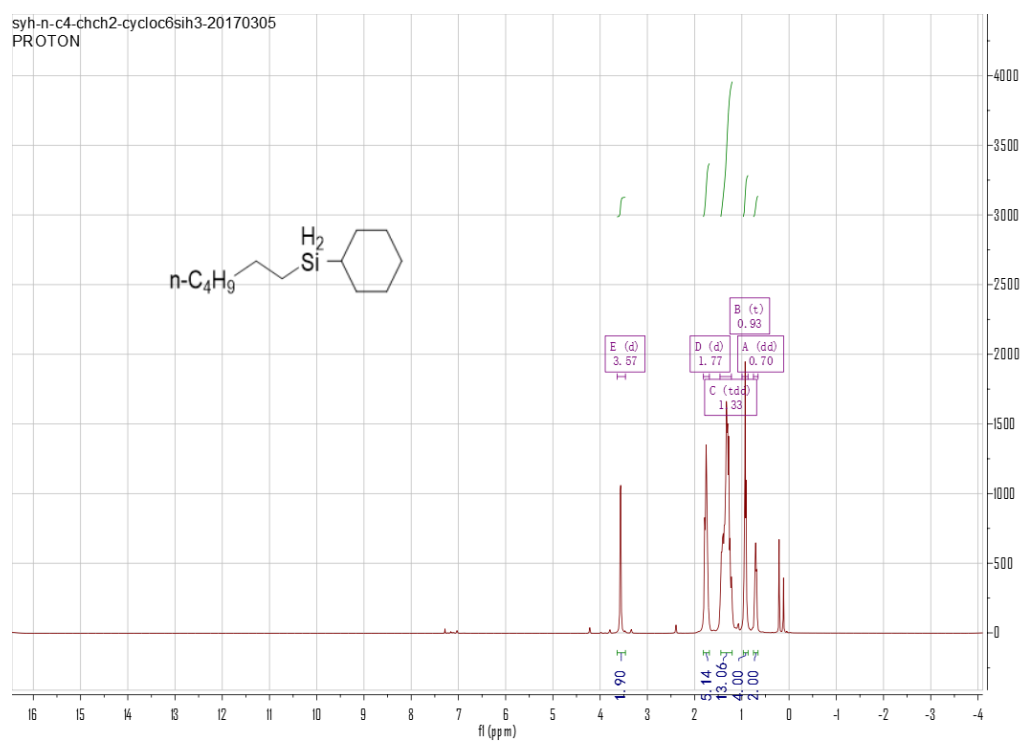




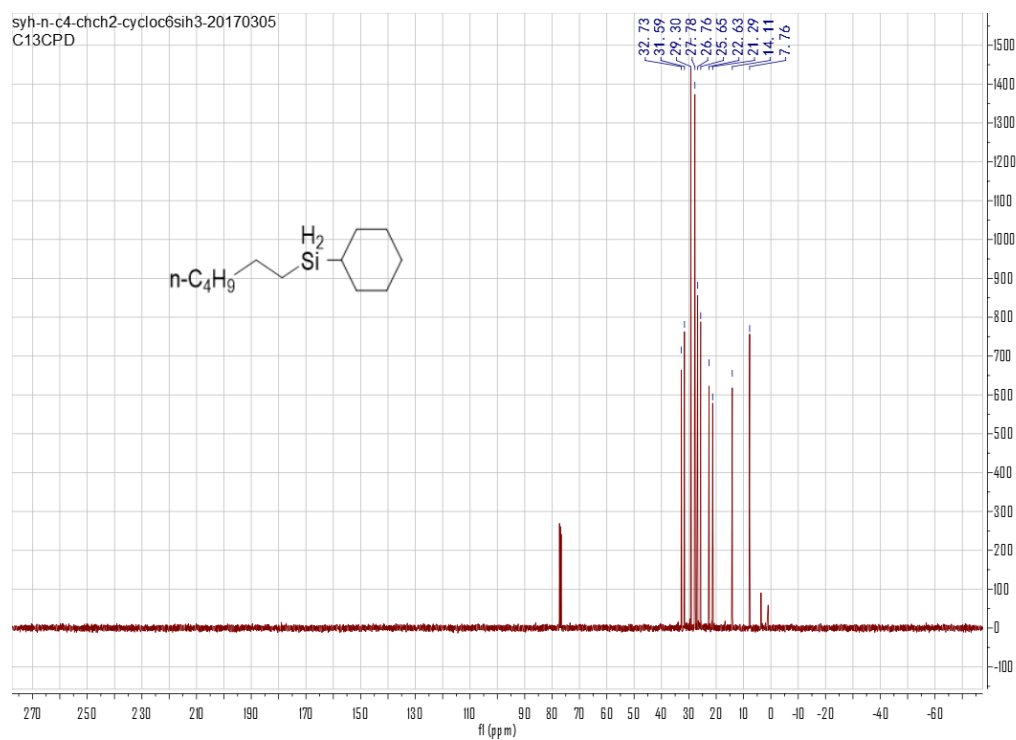
^{13}C NMR (101 MHz, CDCl_3) δ 126.00, 125.55, 35.22, 31.42, 30.56, 28.25, 27.48, 26.73, 25.72, 24.30, 20.21, 3.82.

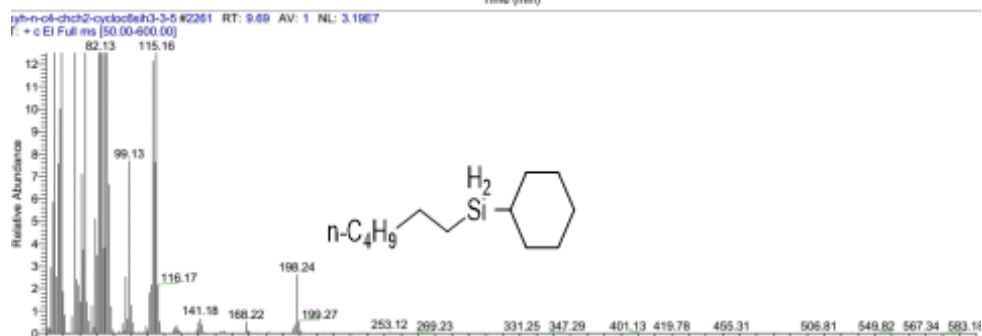
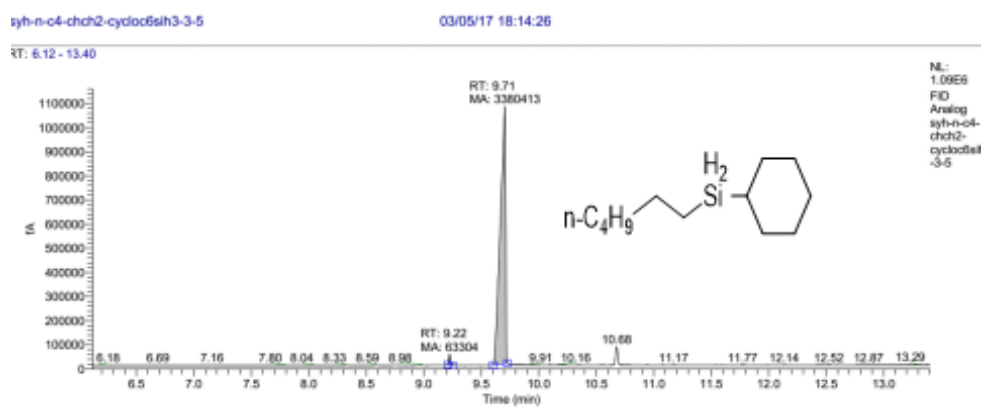
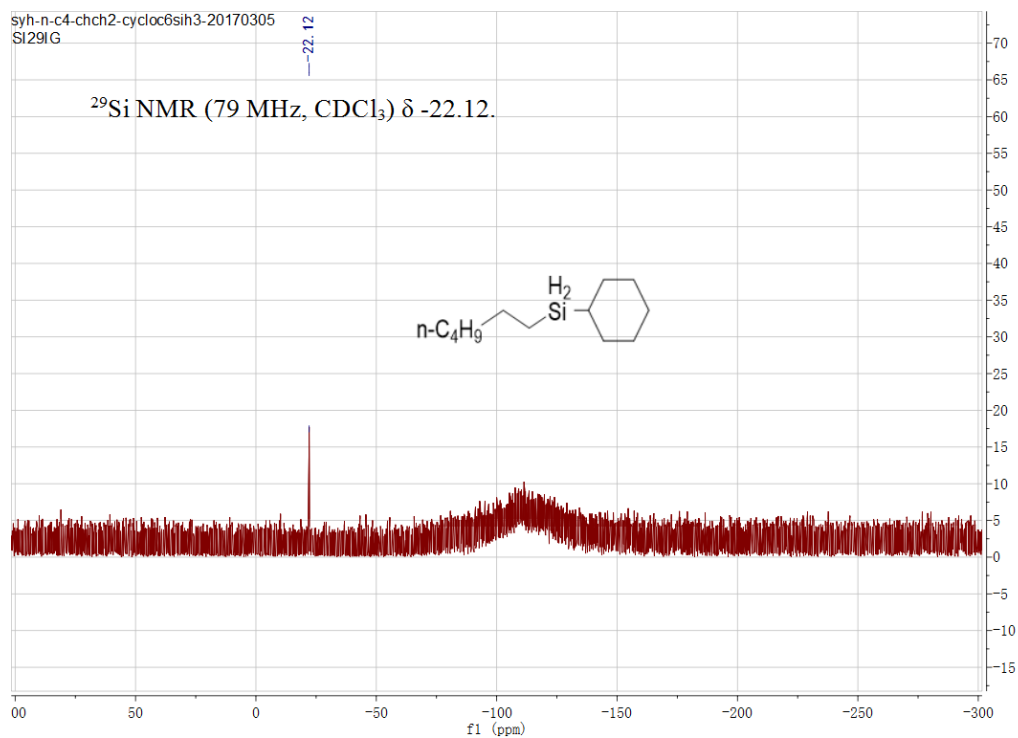


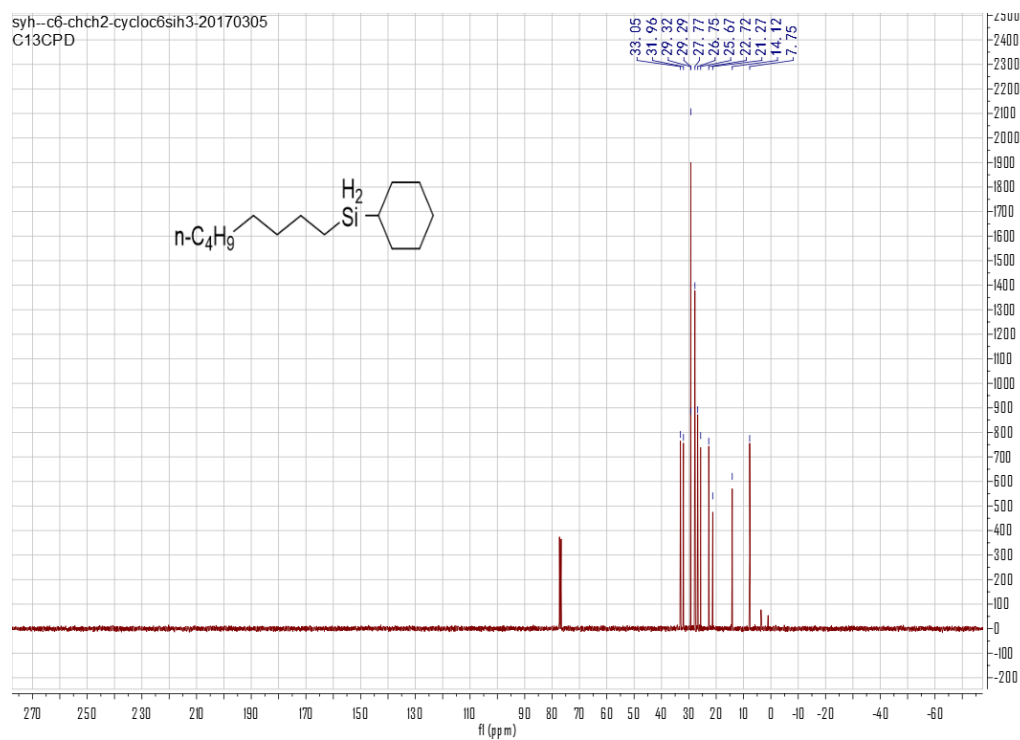
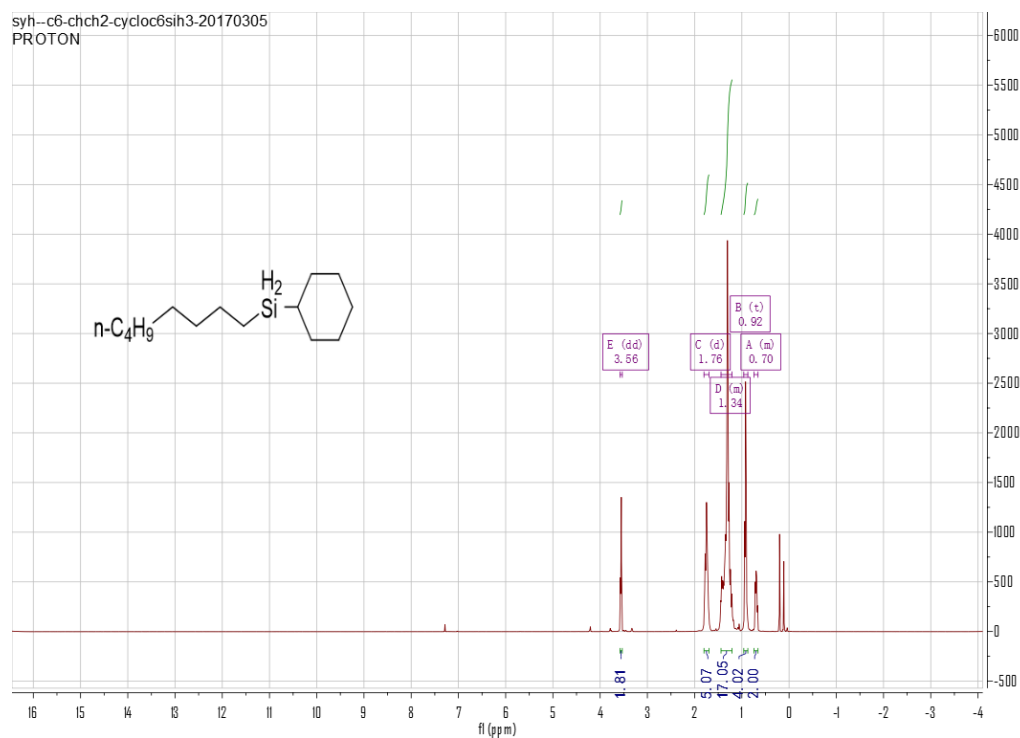
syh-n-c4-chch2-cycloc6sih3-20170305
PROTON

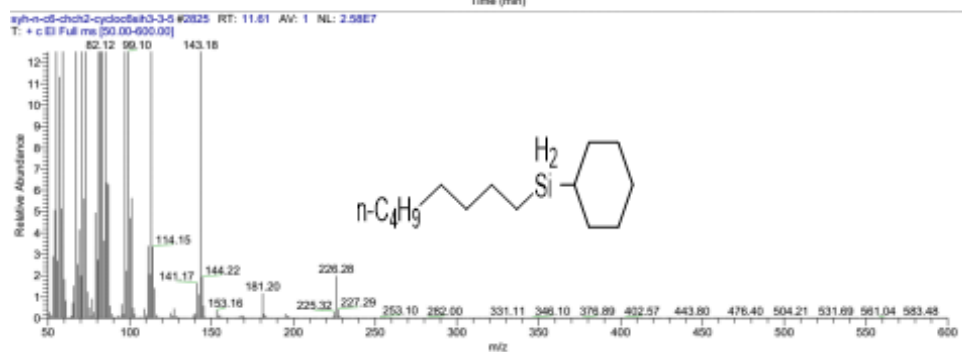
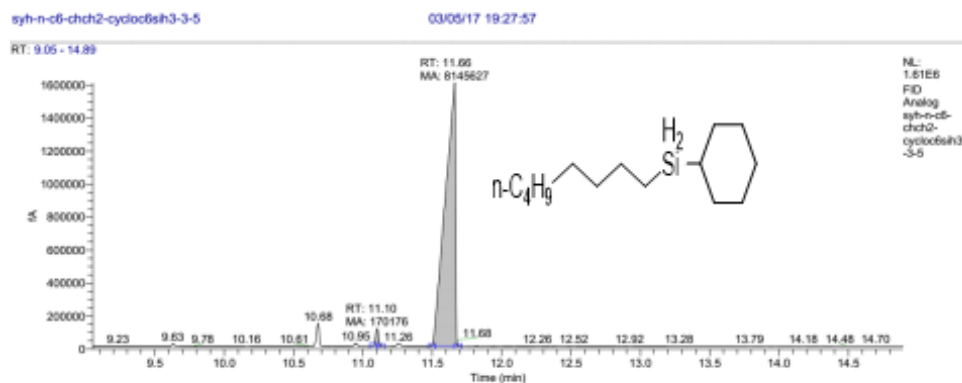
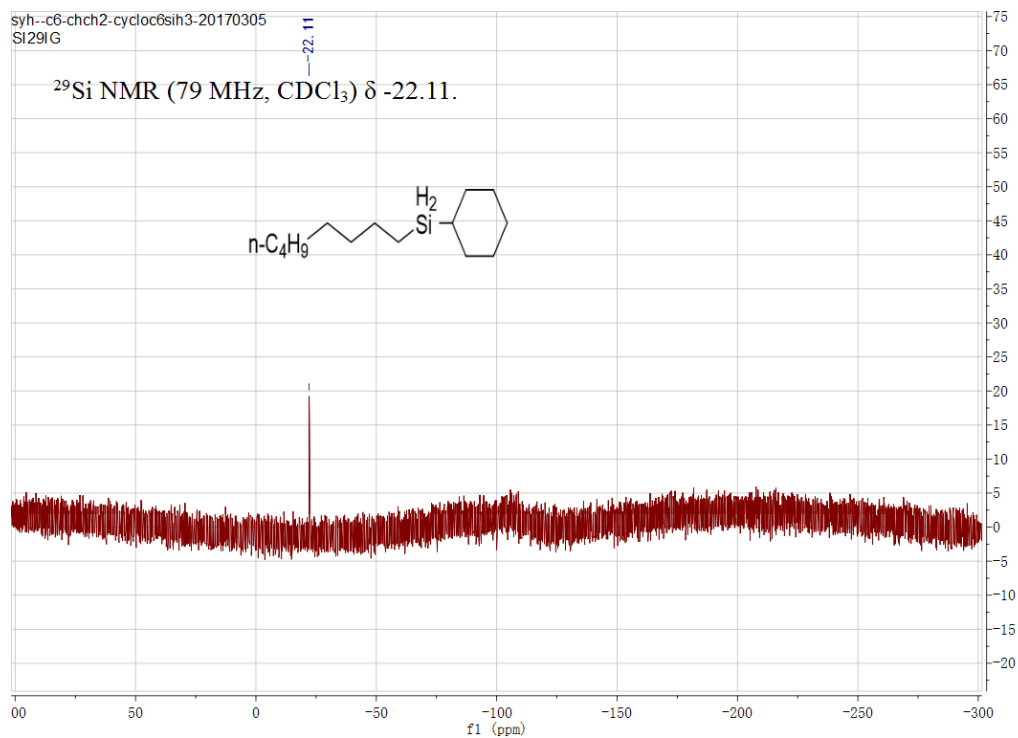


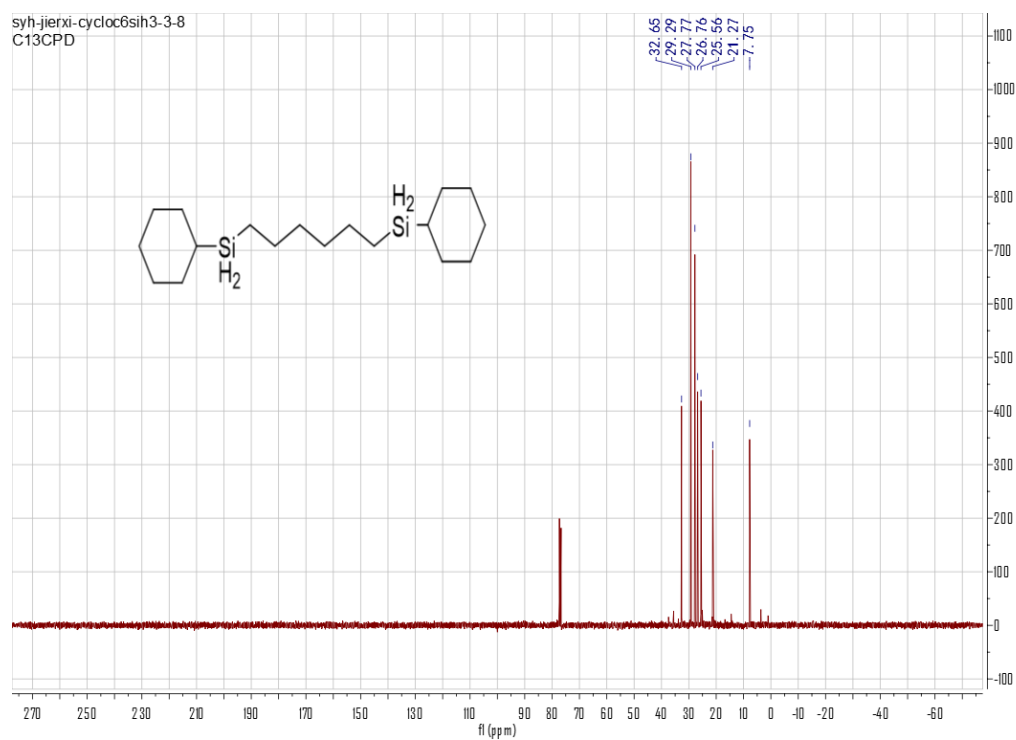
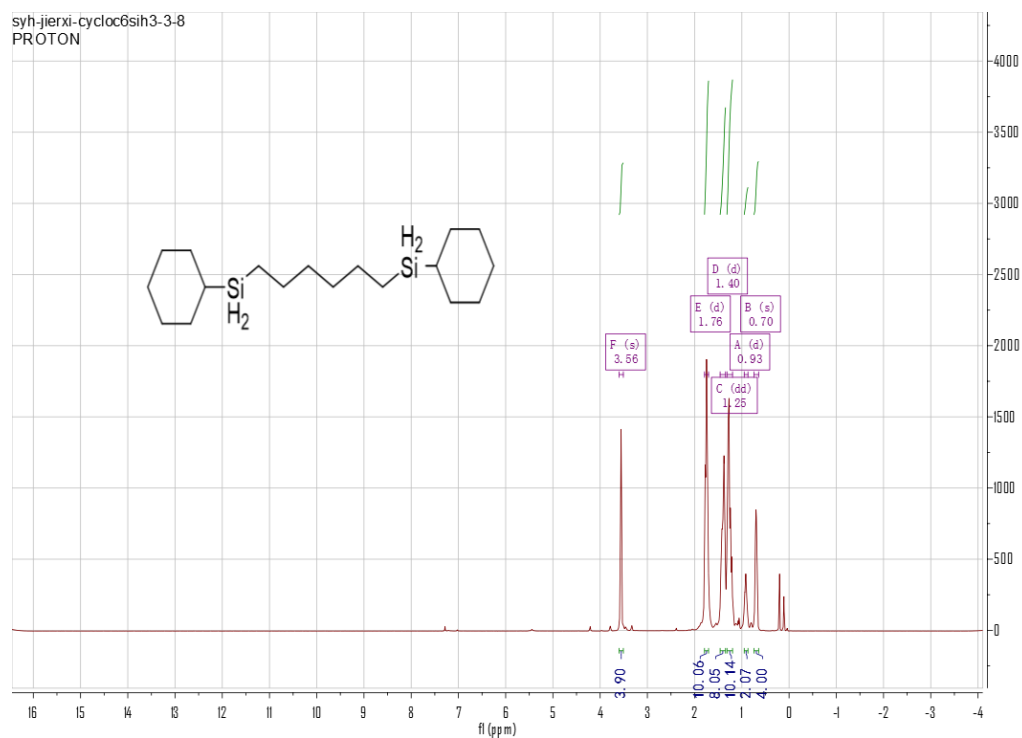
syh-n-c4-chch2-cycloc6sih3-20170305
C13CPD

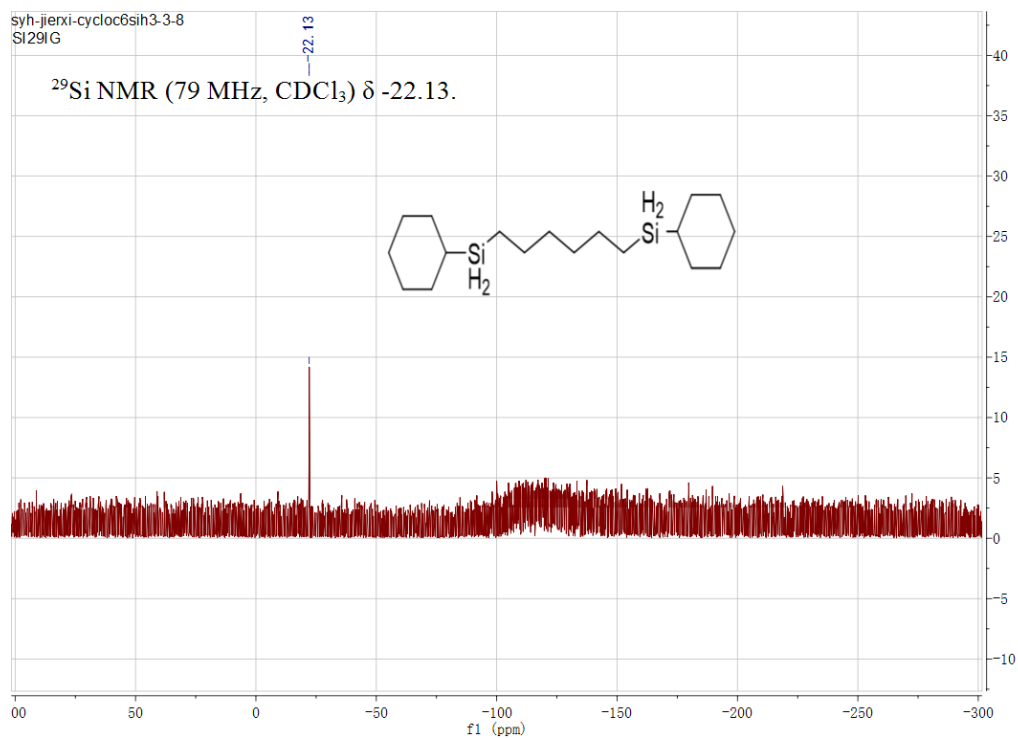








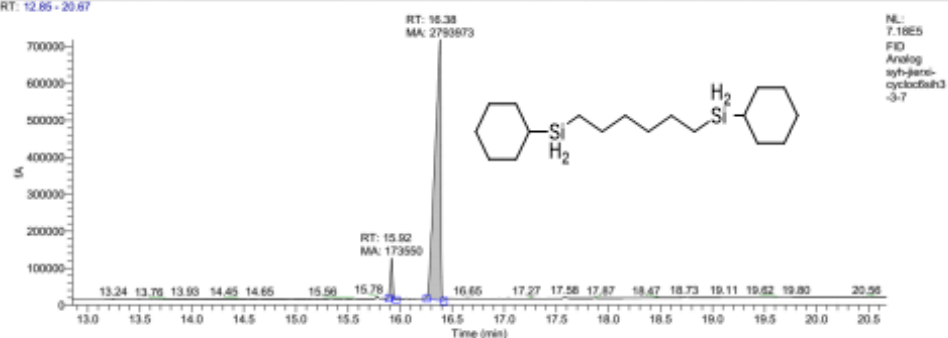




C:\DATE\syh-jierxi-cycloc6sih3-3-7

03/07/17 17:59:30

RT: 12.85 - 20.87



syh-jierxi-cycloc6sih3-3-7 64216 RT: 16.34 AV: 1 NL: 1.68E7
T: + c EI Full ms [50.00-600.00]

