

## Supporting Information

### Synthesis of Azasilacyclopentenes and Silanols via Huisgen Cycloaddition-Initiated C-H Bond Insertion Cascades

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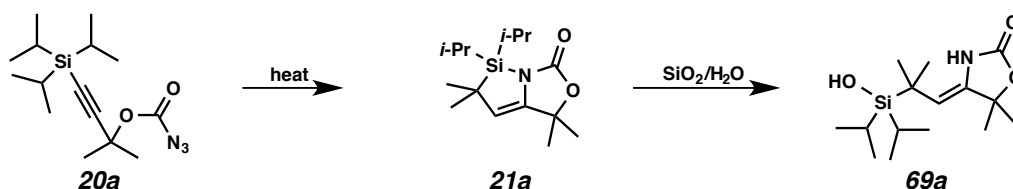
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#### General Considerations

All reactions were carried out in flame or oven-dried glassware. Hexanes, THF, toluene, dichloroethane, and CH<sub>2</sub>Cl<sub>2</sub> were purged with argon and dried over activated alumina columns. Isopropyl acetate was dried over Na<sub>2</sub>SO<sub>4</sub> before usage. Flash chromatography was performed on 60 Å silica gel (Sorbent Technologies). Analytical thin layer chromatography was performed on EMD silica gel/TLC plates with fluorescent indicator 254 nm. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL ECA-500 or ECX-400P spectrometer using the residual solvent peak as an internal reference (CDCl<sub>3</sub>: 7.24 ppm for <sup>1</sup>H NMR and 77.0 ppm for <sup>13</sup>C NMR). NMR yields were determined by addition of 0.5 equivalents of methyl (4-nitrophenyl) carboxylate as an internal standard to the crude reaction mixture. IR spectra were obtained using a ThermoNicolet Avatar 370 FT-IR instrument. GCMS analyses were performed on a Shimadzu GCMS-QP2010S chromatographer equipped with a Shimadzu column (SHRXL-5MS, 0.25 mm x 0.25 μ x 30 M). HRMS analyses were performed under contract by UT Austin's mass spectrometric facility via positive mode ESI or CI methods on a US10252005 instrument. Commercially available compounds were purchased from Aldrich Chemical Co., Acros Organics, Alfa Aesar or TCI America and were used without further purification.

## Reaction Optimization

A 2 dram vial was charged with a magnetic spin bar, carbonazidate **20a** (30.9 mg, 0.1 mmol, 1 equiv), additive, and dry solvent (0.1M, 1 mL). The reaction vessel was sealed and heated in an oil bath at 90 °C (or 100 °C). (**Warning: Pressure buildup may occur during the reaction.**) The progress of the reaction was monitored by TLC. After the reaction was finished, the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. To the crude product was added methyl-4-nitro-benzoate (9.1 mg, 0.05 mmol, 0.5 equiv) and CDCl<sub>3</sub> (0.7 mL). The yield of the azasilacyclopentene was calculated based on <sup>1</sup>H NMR peak integration relative to the methyl group of methyl-4-nitro-benzoate. NMR data was collected using a relaxation delay of 30 sec. (The experiments were conducted to show that RD = 30 sec was required to achieve quantitative information.) The crude product was purified by column chromatography on silica gel to give silanol **69a**.



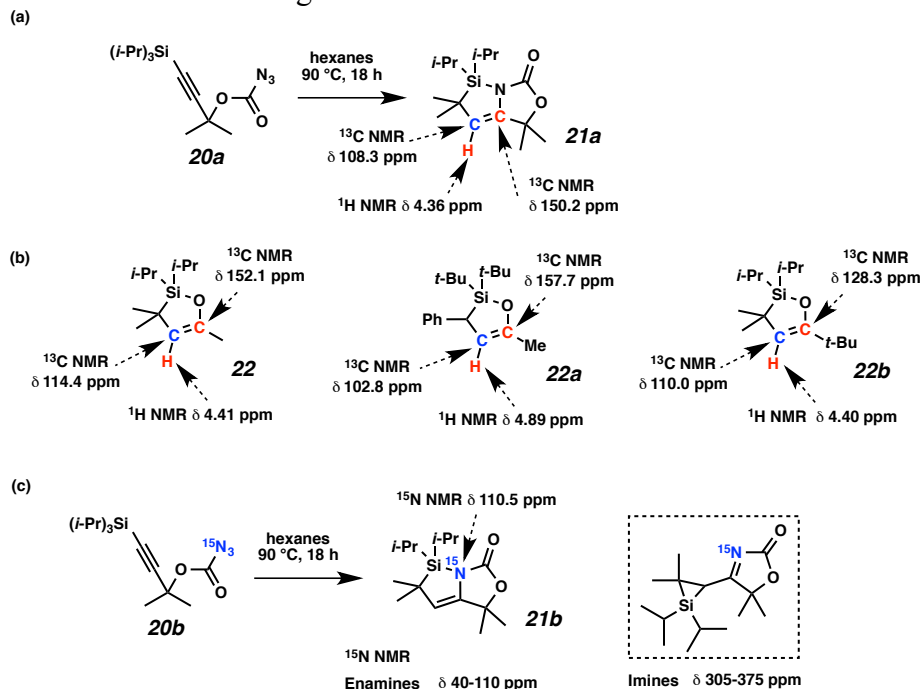
Entry	Solvent	Additive	T, °C	Rxn time	c, M	NMR yield% of <b>21a</b> (isolated of <b>69a</b> )
1	<i>i</i> -PrOAc	-	90	18	0.1	48 (48)
2	PhMe	-	90	18	0.1	31
3	hexanes	-	90	18	0.1	53 (50)
4	MeCN	-	90	18	0.1	5
5	THF	-	90	18	0.1	48
6	CH <sub>2</sub> Cl <sub>2</sub>	1 mol% Rh <sub>2</sub> (esp) <sub>2</sub>	R.T.	48	0.1	-
7	hexanes	silica gel	100	6	0.1	-
8	hexanes	-	100	6	0.05	49
9	hexanes	-	100	6	0.2	47
10	acetone	-	90	12	0.1	18
11	hexanes	1 mol% Rh <sub>2</sub> (oct) <sub>4</sub>	90	12	0.1	29
12	hexanes	1 mol% Rh <sub>2</sub> (esp) <sub>2</sub>	90	18	0.1	43
13	hexanes	2 mol% Cp* <i>Ru</i> Cl(cod)	90	18	0.1	19
14	hexanes	0.5 equiv K <sub>2</sub> CO <sub>3</sub>	90	18	0.1	38
15	heptane	-	90	18	0.1	31
16	cyclohexane	-	90	18	0.1	31

Figure 1. Optimization Table.

## The Identification of the Azasilacyclopentene

Carbonazidate **20b** was synthesized from alcohol **SI-13** and Na<sup>15</sup>N<sub>3</sub> using General Procedure C. Azasilacyclopentene **21b** was synthesized from carbonazidate **20b** using General Procedure D1 (Figure 2). The NMR signals of **21a** (the vinyl proton: 4.36 ppm; enamine carbons: 108.3, 150.2 ppm) matched those of oxasilacyclopentenes (**22** to **22b**)

In addition, the  $^{15}\text{N}$  NMR analysis of  $^{15}\text{N}$  enriched azasilacyclopentene **21b** (110.5 ppm, no signals from 305 to 375 ppm) suggested the nitrogen was involved in an enamine motif, which confirmed the assignment from  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

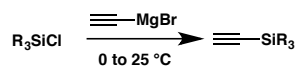


**Figure 2.** The Identification of the Azasilacyclopentene.

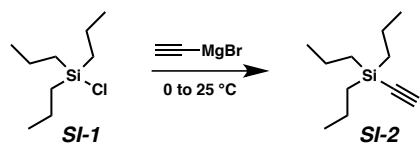
## Synthesis of Compounds

### Synthesis of Alkynylsilanes

#### General Procedure A

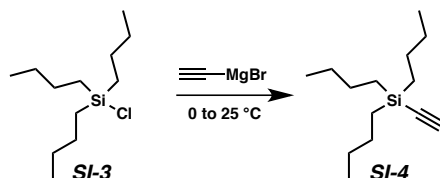


A flame-dried round-bottom flask was charged ethynylmagnesium bromide (1.2 equiv, 0.5 M) under an argon atmosphere. The reaction was cooled to 0 °C in an ice bath. The chlorosilane (1.0 equiv) was then added dropwise into the reaction, and the reaction mixture was allowed to warm up to 25 °C and stirred for 12 hours. Afterwards, the reaction was quenched with  $\text{H}_2\text{O}$  and saturated  $\text{NH}_4\text{Cl}_{(\text{aq})}$ , and the mixture was extracted with hexanes (3x). The organic phases were combined and washed with brine, dried over anhydrous  $\text{MgSO}_4$ , filtered through a short plug of silica gel and concentrated under reduced pressure to yield the product. No further purification was necessary.

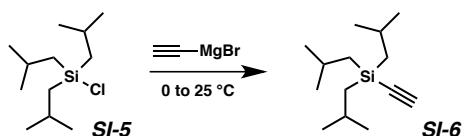


**ethynyltri-*n*-propylsilane (SI-2)** was synthesized from tri-*n*-propylsilyl chloride (2 mL, 1.764 g, 9.15 mmol) using General Procedure A. The product was obtained as a colorless

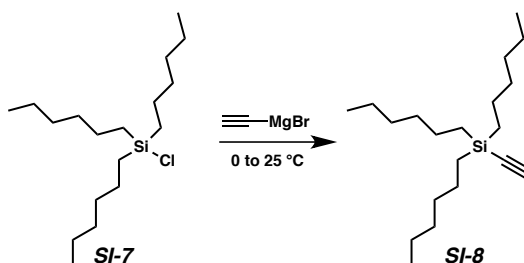
oil. (1.5221 g, 91% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.35 (s, 1H), 1.49–1.33 (m, 6H), 0.96 (t,  $J = 7.3$  Hz, 9H), 0.65–0.55 (m, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  94.0, 88.3, 18.2, 17.4, 15.8. **IR(neat)** 3294, 2955, 2926, 2869, 2033, 1455, 1408, 1333, 1066, 1005, 710, 669  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 182.1485 [(M) $^+$ ]; calculated for  $\text{C}_{11}\text{H}_{22}\text{Si}$ : 182.1491]. **R<sub>F</sub>**: 0.79 in 5% EtOAc/Hex.



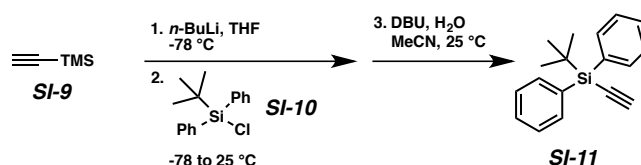
**tri-*n*-butyl(ethynyl)silane (SI-4)** was synthesized from tri-*n*-butylsilyl chloride (2 mL, 1.766 g, 7.52 mmol) using General Procedure A. The product was obtained as a colorless oil. (1.6663 g, 99% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.35 (s, 1H), 1.41–1.26 (m, 12H), 0.94–0.80 (m, 9H), 0.67–0.54 (m, 6H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  94.0, 88.3, 26.4, 26.0, 13.8, 12.8. **IR(neat)** 3294, 2956, 2921, 2872, 2857, 2033, 1464, 1408, 1377, 1192, 1081, 1028, 1000, 963, 885, 787, 758, 711, 669  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 224.1957 [(M) $^+$ ]; calculated for  $\text{C}_{14}\text{H}_{28}\text{Si}$ : 224.1960]. **R<sub>F</sub>**: 0.79 in 5% EtOAc/Hex.



**ethynyltriisobutylsilane (SI-6)** was synthesized from triisobutylsilyl chloride (0.8 mL, 0.7096 g, 3 mmol) using General Procedure A. The product was obtained as a colorless oil. (0.651 g, 90% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.39 (s, 1H), 1.92–1.79 (m, 3H), 0.96 (d,  $J = 6.8$  Hz, 18H), 0.63 (d,  $J = 6.9$  Hz, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  94.6, 89.5, 26.2, 25.0, 24.7. **IR(neat)** 3284, 2952, 2896, 2867, 2033, 1464, 1400, 1381, 1364, 1328, 1217, 1163, 1093, 1039, 950, 830, 762, 669  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 223.1882 [(M-H) $^+$ ]; calculated for  $\text{C}_{14}\text{H}_{27}\text{Si}$ : 223.1882]. **R<sub>F</sub>**: 0.8 in 5% EtOAc/Hex.



**ethynyltri-*n*-hexylsilane (SI-8)** was synthesized from tri-*n*-hexylsilyl chloride (2 mL, 1.7420 g, 5.3 mmol) using General Procedure A. The product was obtained as a colorless oil. (1.6460 g, 99% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34 (s, 1H), 1.40–1.18 (m, 24H), 0.92–0.81 (m, 9H), 0.67–0.53 (m, 6H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  94.0, 88.4, 33.1, 31.5, 23.7, 22.6, 14.1, 13.0. **IR(neat)** 3294, 2956, 2920, 2872, 2854, 2033, 1466, 1408, 1377, 1340, 1182, 1101, 995, 961, 889, 846, 764, 710, 669  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 308.2888 [(M) $^+$ ]; calculated for  $\text{C}_{20}\text{H}_{40}\text{Si}$ : 308.2899]. **R<sub>F</sub>**: 0.8 in 5% EtOAc/Hex.

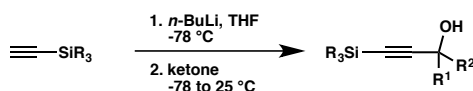


### ***tert*-butyl(ethynyl)diphenylsilane (SI-11)**

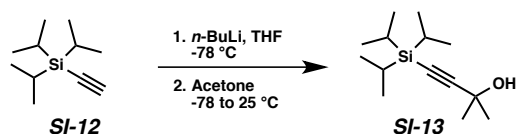
A flame-dried round-bottom flask was charged with *n*-BuLi (2.5 M, 1.3 equiv, 39 mmol, 15.6 mL) under an argon atmosphere. Anhydrous THF (0.5 M, 50 mL) was added, and the mixture was cooled to -78 °C in a dry ice/acetone bath. Trimethylsilylacetylene (1.3 equiv, 39 mmol, 5.6 mL) was then added dropwise. After the reaction was stirring for 15 minutes at -78 °C, *tert*-butyl(chloro)diphenylsilane (7.8 mL, 30 mmol) was added dropwise. The reaction mixture was allowed to warm up to 25 °C and stirred for 2 hours. After completion, saturated NH<sub>4</sub>Cl solution was added. The mixture was extracted with Et<sub>2</sub>O (3x), and the organic phases were combined and washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated to yield crude product. The crude product was subjected to the next step without further purification. The crude product was dissolved in MeCN (0.5 M, 60 mL) and water (10.0 M, 3 mL). Diazobicycloundecene (DBU, 1.0 equiv, 4.5 mL, 30 mmol) was added into the reaction. The progress of the reaction was monitored by TLC. After completion (5 h), the reaction was concentrated to yield crude product, and purification was done by column chromatography on silica gel using a gradient of 0 to 1 % EtOAc in hexanes as eluents. The product was obtained as a white solid. (4.4788 g, 56.5% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.83–7.78 (m, 4H), 7.45–7.33 (m, 6H), 2.71 (s, 1H), 1.11 (s, 9H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 135.5, 132.6, 129.6, 127.8, 97.2, 85.4, 26.9, 18.4. IR(neat) 3266, 3065, 2959, 2946, 2857, 2035, 1485, 1468, 1426, 1390, 1372, 1361, 1259, 1105, 1007, 820, 742, 691, 660 cm<sup>-1</sup>. HRMS (CI) *m/z*: 264.1333 [(M)<sup>+</sup>; calculated for C<sub>18</sub>H<sub>20</sub>Si: 264.1334]. R<sub>F</sub>: 0.5 in 2% EtOAc/Hex. MP: 66–68 °C.

### **Synthesis of Propargyl Alcohols**

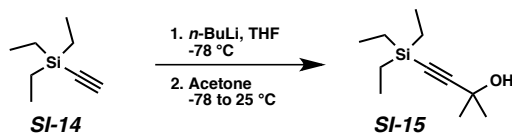
#### *General Procedure B*



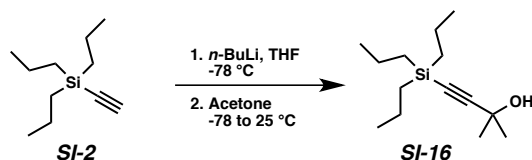
A flame-dried round-bottom flask was charged with *n*-BuLi (2.5 M, 1.2 equiv, 4.8 mmol) under Argon atmosphere. Anhydrous THF (0.5 M, 8 mL) was added, and the reaction was cooled to -78 °C in a dry ice/acetone bath. The silyl acetylene (1.3 equiv, 5.2 mmol) was then added dropwise. The reaction was allowed to stir for 20 minutes at -78 °C. Then, ketone (1 equiv, 4 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and stirred for 2 hours. After completion, saturated NH<sub>4</sub>Cl solution was added to quench the reaction. The mixture was extracted with Et<sub>2</sub>O three times, and the organic phases were combined and washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered through a celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.



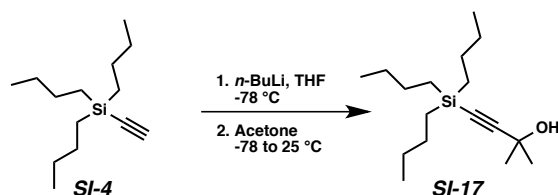
**2-methyl-4-(triisopropylsilyl)but-3-yn-2-ol (SI-13)** was synthesized from triisopropylsilylacetylene and acetone using General Procedure B. The crude product was purified by column chromatography on silica gel using 10% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.777 g, 88% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.92 (s, 1H), 1.51 (s, 6H), 1.08–0.99 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  112.7, 82.1, 65.5, 31.6, 18.6, 11.1. **IR(neat)** 3343, 2942, 2892, 2865, 2167, 2032, 1463, 1364, 1220, 1164, 996, 968, 912, 881, 786, 674, 658  $\text{cm}^{-1}$ . **HRMS (CI)  $m/z$** : 240.1906  $[(\text{M})^+]$ ; calculated for  $\text{C}_{14}\text{H}_{28}\text{OSi}$ : 240.1909]. **R<sub>F</sub>**: 0.27 in 10% EtOAc/Hex.



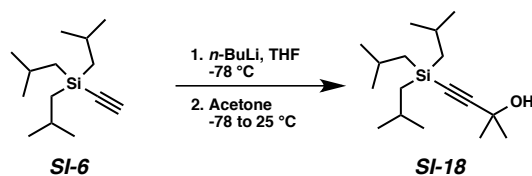
**2-methyl-4-(triethylsilyl)but-3-yn-2-ol (SI-15)** was synthesized from triethylsilylacetylene and acetone using General Procedure B. The crude product was purified by column chromatography on silica gel using 10%  $\text{Et}_2\text{O}$  in pentane as an eluent. The product was obtained as a colorless oil. (0.7801 g, 98% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.92 (s, 1H), 1.50 (s, 6H), 0.96 (t,  $J = 8.0$  Hz, 9H), 0.56 (q,  $J = 8.0$  Hz, 6H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  111.9, 83.2, 65.5, 31.5, 7.4, 4.3. **IR(neat)** 3340, 2955, 2912, 2875, 2168, 1457, 1362, 1220, 1164, 1005, 912, 789, 722, 701  $\text{cm}^{-1}$ . **HRMS (CI)  $m/z$** : 198.1441  $[(\text{M})^+]$ ; calculated for  $\text{C}_{11}\text{H}_{22}\text{OSi}$ : 198.1440]. **R<sub>F</sub>**: 0.15 in 10%  $\text{Et}_2\text{O}$ /pentane.



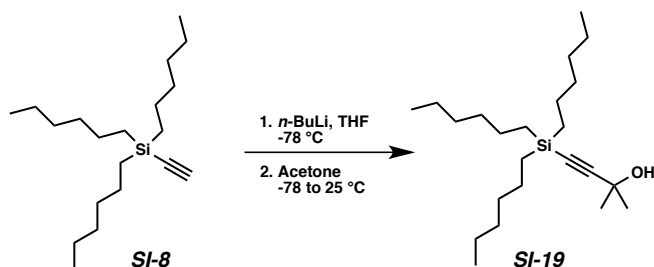
**2-methyl-4-(tripropylsilyl)but-3-yn-2-ol (SI-16)** was synthesized from tri-*n*-propylsilylacetylene and acetone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.9908 g, 98% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89 (s, 1H), 1.49 (s, 6H), 1.43–1.31 (m, 6H), 0.95 (t,  $J = 7.2$  Hz, 9H), 0.61–0.51 (m, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  111.8, 84.1, 65.5, 31.4, 18.2, 17.4, 16.0. **IR(neat)** 3344, 2954, 2926, 2868, 2168, 1455, 1408, 1374, 1362, 1333, 1217, 1164, 1065, 1031, 1004, 912, 786, 814, 739, 699  $\text{cm}^{-1}$ . **HRMS (CI)  $m/z$** : 240.1905  $[(\text{M})^+]$ ; calculated for  $\text{C}_{14}\text{H}_{28}\text{OSi}$ : 240.1909]. **R<sub>F</sub>**: 0.36 in 10% EtOAc/Hex.



**2-methyl-4-(tributylsilyl)but-3-yn-2-ol (SI-17)** was synthesized from tri-*n*-butylsilylacetylene and acetone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (1.0730 g, 95% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.88 (s, 1H), 1.49 (s, 6H), 1.40–1.19 (m, 12H), 0.94–0.77 (m, 9H), 0.66–0.47 (m, 6H).  $^{13}\text{C}$  NMR (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  111.7, 84.1, 76.9, 65.5, 31.4, 26.4, 26.1, 13.8, 12.9. IR(neat) 3295, 2951, 2895, 2867, 2168, 2033, 1463, 1400, 1380, 1163, 1093, 912, 793, 670  $\text{cm}^{-1}$ . HRMS (CI)  $m/z$ : 282.2374 [(M) $^+$ ; calculated for  $\text{C}_{17}\text{H}_{34}\text{OSi}$ : 282.2379].  $R_F$ : 0.42 in 10% EtOAc/Hex.

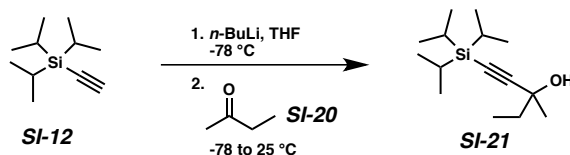


**2-methyl-4-(triisobutylsilyl)but-3-yn-2-ol (SI-18)** was synthesized from triisobutylsilylacetylene and acetone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (1.0730 g, 95% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.90–1.72 (m, 3H), 1.48 (s, 6H), 0.95 (d,  $J = 6.5$  Hz, 18H), 0.59 (d,  $J = 6.9$  Hz, 6H).  $^{13}\text{C}$  NMR (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  112.0, 9.5, 65.4, 31.2, 26.2, 25.0, 24.9. IR(neat) 3347, 2951, 2895, 2867, 2168, 1463, 1400, 1379, 1364, 1217, 1163, 1092, 912, 829, 793, 768  $\text{cm}^{-1}$ . HRMS (CI)  $m/z$ : 282.2374 [(M) $^+$ ; calculated for  $\text{C}_{17}\text{H}_{34}\text{OSi}$ : 282.2379].  $R_F$ : 0.42 in 10% EtOAc/Hex.

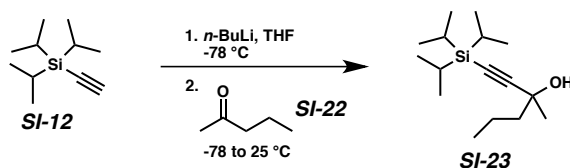


**2-methyl-4-(tri-n-hexylsilyl)but-3-yn-2-ol (SI-19)** was synthesized from tri-*n*-hexylsilylacetylene and acetone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (1.3544 g, 92% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.49 (s, 6H), 1.37–1.17 (m, 24H), 0.95–0.80 (m, 9H), 0.64–0.48 (m, 6H).  $^{13}\text{C}$  NMR (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  111.7, 84.2, 65.4, 33.1, 31.5, 31.4, 23.8, 22.6, 14.2, 13.2. IR(neat) 3345, 2956, 2920, 2872, 2854, 2167, 1457, 1408, 1362, 1219,

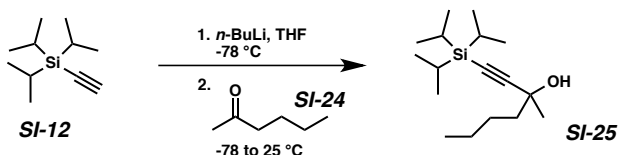
1165 968, 913, 846, 791, 700  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 367.3386  $[(M+H)^+]$ ; calculated for  $\text{C}_{23}\text{H}_{47}\text{OSi}$ : 367.3396]. **R<sub>F</sub>**: 0.45 in 10% EtOAc/Hex.



**3-methyl-1-(triisopropylsilyl)pent-1-yn-3-ol (SI-21)** was synthesized from triisopropylsilylacetylene and 2-butanone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.813 g, 89% yield). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89 (s, 1H), 1.77–1.56 (m, 2H), 1.46 (s, 3H), 1.08–0.96 (m, 24H). **<sup>13</sup>C NMR** (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  111.4, 83.4, 69.1, 36.6, 29.5, 18.6, 11.1, 9.1. **IR(neat)** 3360, 2941, 2891, 2865, 2165, 1462, 1382, 1366, 1323, 1288, 1157, 1126, 1073, 1053, 1034, 1012, 995, 930, 909, 881, 793, 766, 674, 658  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 254.2065  $[(M)^+]$ ; calculated for  $\text{C}_{15}\text{H}_{30}\text{OSi}$ : 254.2066]. **R<sub>F</sub>**: 0.42 in 10% EtOAc/Hex.

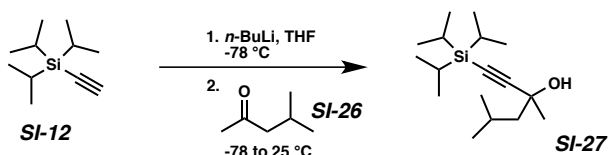


**3-methyl-1-(triisopropylsilyl)hex-1-yn-3-ol (SI-23)** was synthesized from triisopropylsilylacetylene and 2-pentanone using General Procedure B. The crude product was purified by column chromatography on silica gel using 5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.902 g, 84% yield). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89 (s, 1H), 1.70–1.48 (m, 4H), 1.46 (s, 3H), 1.13–0.97 (m, 21H), 0.94 (t,  $J = 7.2$  Hz, 3H). **<sup>13</sup>C NMR** (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  111.7, 83.2, 68.6, 46.0, 30.0, 18.6, 18.1, 14.3, 11.1. **IR(neat)** 3373, 2958, 2941, 2892, 2865, 2165, 1463, 1366, 1382, 1284, 1253, 1159, 1131, 1073, 1051, 1017, 995, 934, 904, 882, 794, 674, 659  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 268.2229  $[(M)^+]$ ; calculated for  $\text{C}_{16}\text{H}_{32}\text{OSi}$ : 268.2222]. **R<sub>F</sub>**: 0.4 in 10% EtOAc/Hex.

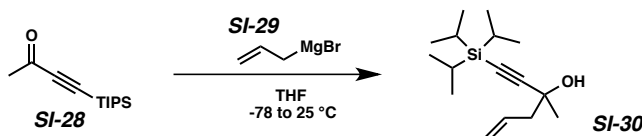


**3-methyl-1-(triisopropylsilyl)hept-1-yn-3-ol (SI-25)** was synthesized from triisopropylsilylacetylene and 2-hexanone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (904 mg, 80% yield). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.88 (s, 1H), 1.67–1.45 (m, 4H), 1.46 (s, 3H), 1.41–1.26 (m, 2H), 1.11–0.97 (m, 21H), 0.90 (t,  $J = 7.3$  Hz, 3H). **<sup>13</sup>C NMR** (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  111.8, 83.3, 68.6, 43.4, 29.9, 27.0, 22.8, 18.6, 14.1, 11.1. **IR(neat)** 3374, 2941, 2864, 2164, 1463, 1129, 1087, 949, 909, 675, 659  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 282.2386  $[(M)^+]$ ; calculated for  $\text{C}_{17}\text{H}_{34}\text{OSi}$ : 282.2379]. **R<sub>F</sub>**: 0.3 in 5% EtOAc/Hex.



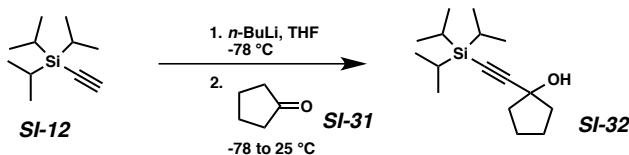


**3,5-dimethyl-1-(triisopropylsilyl)hex-1-yn-3-ol (SI-27)** was synthesized from triisopropylsilylacetylene and methyl isobutyl ketone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (1.1075 g, 98% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.04–1.88 (m, 1H), 1.85 (s, 1H), 1.57 (d,  $J$  = 6.2 Hz, 2H), 1.48 (s, 3H), 1.09–0.95 (m, 27H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  112.0, 94.7, 8.6, 68.5, 51.7, 31.3, 25.3, 24.3, 24.1, 18.5, 11.1. **IR(neat)** 3440, 2943, 2865, 2164, 2032, 1463, 1383, 1073, 1045, 1017, 944, 919, 881, 673, 660  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 282.2381 [ $\text{M}$ ] $^+$ ; calculated for  $\text{C}_{17}\text{H}_{34}\text{OSi}$ : 282.2379]. **R<sub>F</sub>**: 0.42 in 10% EtOAc/Hex.



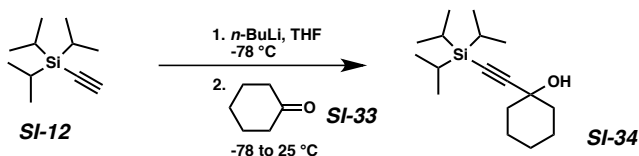
**3-methyl-1-(triisopropylsilyl)hex-5-en-1-yn-3-ol (SI-30)**

To a flame-dried round-bottom flask was added ynone **SI-28** (1.12 g, 5 mmol, 1 equiv) and THF (6 mL). The reaction was cooled to  $-78\text{ }^\circ\text{C}$ . After stirring for 10 min at  $-78\text{ }^\circ\text{C}$ , allylmagnesium bromide (1 M in  $\text{Et}_2\text{O}$ , 6 mL, 6 mmol, 1.2 equiv) was added to the reaction. The reaction was allowed to warm to  $25\text{ }^\circ\text{C}$ . After completion, saturated  $\text{NH}_4\text{Cl}$  solution was added to quench the reaction. The mixture was extracted with  $\text{Et}_2\text{O}$  three times, and the organic phases were combined and washed with brine, dried over anhydrous  $\text{MgSO}_4$ , filtered through a celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with a gradient of 1 to 2% ethyl acetate in hexanes as eluents. The product was obtained as colorless oil. (1 g, 75% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.02–5.91 (m, 1H), 5.24–5.11 (m, 2H), 2.47 (dd,  $J$  = 13.4, 6.5 Hz, 1H), 2.36 (dd,  $J$  = 13.5, 8.1 Hz, 1H), 1.48 (s, 3H), 1.10–0.98 (m, 21H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.4, 119.5, 111.1, 83.7, 67.3, 48.3, 29.5, 18.6, 11.1. **IR(neat)** 3373, 2942, 2892, 2865, 2166, 1642, 1463, 1382, 1367, 1260, 1110, 1073, 995, 942, 916, 882, 799, 675  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 289.1962 [ $\text{M}+\text{Na}$ ] $^+$ ; calculated for  $\text{C}_{16}\text{H}_{30}\text{OSi}$ : 289.1958]. **R<sub>F</sub>**: 0.21 in 5% EtOAc/Hex.

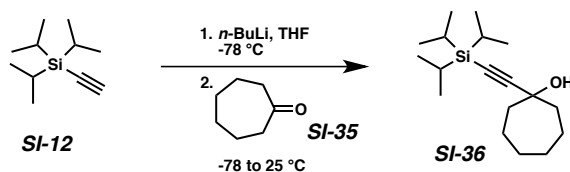


**1-((triisopropylsilyl)ethynyl)cyclopentan-1-ol (SI-32)** was synthesized from triisopropylsilylacetylene and cyclopentanone using General Procedure B. The crude product was purified by column chromatography on silica gel using 5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.9167 g, 86% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.06–1.62 (m, 8H), 1.09–0.98 (m, 21H).  $^{13}\text{C NMR}$

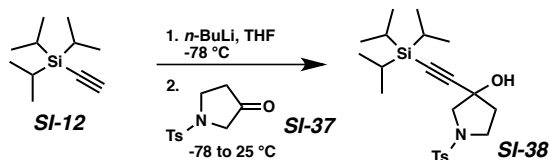
(125.77 MHz, CDCl<sub>3</sub>)  $\delta$  111.9, 83.1, 74.9, 42.7, 23.5, 18.6, 11.1. **IR(neat)** 3334, 2942, 2891, 2864, 2161, 1462, 1382, 1366, 1314, 1208, 1073, 994, 944, 918, 672 cm<sup>-1</sup>. **HRMS** (CI)  $m/z$ : 266.2066 [(M)<sup>+</sup>; calculated for C<sub>16</sub>H<sub>30</sub>OSi: 266.2066]. **R<sub>F</sub>**: 0.18 in 5% EtOAc/Hex.



**1-((triisopropylsilyl)ethynyl)cyclohexan-1-ol (SI-34)** was synthesized from triisopropylsilylacetylene and cyclohexanone using General Procedure B. The crude product was purified by column chromatography on silica gel using 5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.9875 g, 88% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.18 (s, 1H), 1.96–1.83 (m, 2H), 1.72–1.62 (m, 2H), 1.60–1.45 (m, 6H), 1.11–0.92 (m, 21H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  111.5, 84.5, 69.2, 40.1, 25.2, 23.5, 18.6, 11.1. **IR(neat)** 3339, 2934, 2891, 2863, 2163, 1446, 1462, 1382, 1366, 1281, 1257, 1132, 1032, 995, 918, 881, 760, 658 cm<sup>-1</sup>. **HRMS** (CI)  $m/z$ : 280.2217 [(M)<sup>+</sup>; calculated for C<sub>17</sub>H<sub>32</sub>OSi: 280.2222]. **R<sub>F</sub>**: 0.2 in 5% EtOAc/Hex.

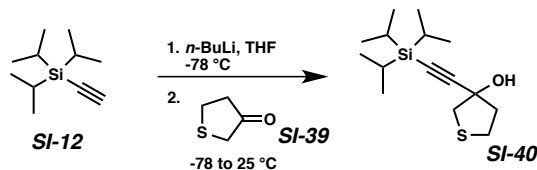


**1-((triisopropylsilyl)ethynyl)cycloheptan-1-ol (SI-36)** was synthesized from triisopropylsilylacetylene and cycloheptanone using General Procedure B. The crude product was purified by column chromatography on silica gel using 5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (1.1546 g, 98% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.06–1.89 (m, 2H), 1.86–1.72 (m, 2H), 1.72–1.46 (m, 8H), 1.12–0.87 (m, 21H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  112.5, 83.8, 72.3, 43.2, 27.7, 22.3, 18.6, 11.1. **IR(neat)** 2939, 2863, 2163, 2031, 1461, 1383, 1366, 1242, 1200, 1058, 1018, 995, 920, 882, 795, 750, 723, 673 cm<sup>-1</sup>. **HRMS** (CI)  $m/z$ : 294.2369 [(M)<sup>+</sup>; calculated for C<sub>18</sub>H<sub>34</sub>OSi: 294.2379]. **R<sub>F</sub>**: 0.36 in 10% EtOAc/Hex.

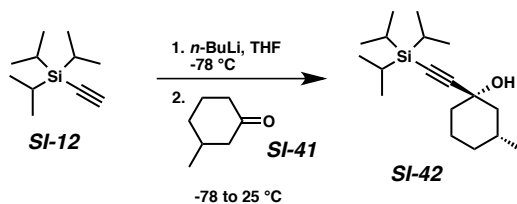


**1-tosyl-3-((triisopropylsilyl)ethynyl)pyrrolidin-3-ol (SI-38)** synthesized from triisopropylsilylacetylene and 1-tosylpyrrolidin-3-one using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 15 to 20% EtOAc in hexanes as eluents. The product was obtained as a white solid. (1.2800 g, 76% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d,  $J$  = 8.4 Hz, 2H), 7.29 (d,  $J$  = 8.0 Hz, 2H), 3.58–3.42 (m, 3H), 3.41–3.31 (m, 1H), 2.40 (s, 3H), 2.16–2.03 (m, 2H), 1.86 (s, 1H), 1.07–0.90 (m, 21H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  143.5, 133.9, 129.6,

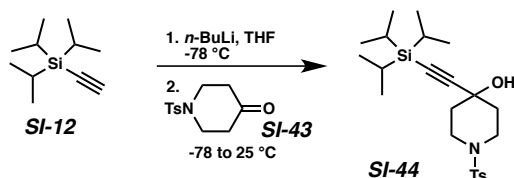
127.5, 106.2, 86.7, 72.0, 61.1, 46.5, 40.9, 21.5, 18.5, 10.9. **IR(neat)** 3455, 2942, 2891, 2864, 2167, 1597, 1462, 1383, 1323, 1304, 1290, 1242, 1153, 1110, 1037, 1017, 997, 925, 881, 804, 756, 699  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 444.2004  $[(M+Na)^+]$ ; calculated for  $\text{C}_{22}\text{H}_{35}\text{NO}_3\text{SSiNa}$ : 444.1999]. **R<sub>F</sub>**: 0.3 in 20% EtOAc/Hex. **MP**: 86-87 °C.



**3-((triisopropylsilyl)ethynyl)tetrahydrothiophen-3-ol (SI-40)** was synthesized from triisopropylsilylacetylene and dihydrothiophen-3(2H)-one using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.455 g, 40% yield). **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.18 (d,  $J$  = 11.5 Hz, 1H), 3.06–2.86 (m, 3H), 2.40–2.29 (m, 1H), 2.27 (s, 1H), 2.21–2.09 (m, 1H), 1.15–0.88 (m, 21H). **<sup>13</sup>C NMR** (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  107.4, 85.6, 75.6, 44.8, 44.5, 28.7, 18.5, 11.0. **IR(neat)** 3382, 2941, 2890, 2864, 2163, 1462, 1428, 1382, 1366, 1270, 1233, 1209, 1061, 1029, 950, 918, 881, 831, 781, 751, 671  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 284.1629  $[(M)^+]$ ; calculated for  $\text{C}_{15}\text{H}_{28}\text{OSSi}$ : 284.1630]. **R<sub>F</sub>**: 0.36 in 10% EtOAc/Hex.

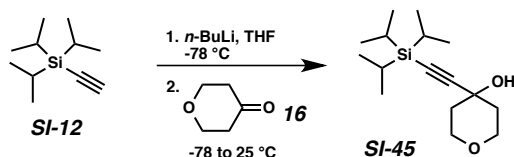


**(1S,3R)-3-methyl-1-((triisopropylsilyl)ethynyl)cyclohexan-1-ol (SI-42)** was synthesized from triisopropylsilylacetylene and 3-methylcyclohexanone using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of 1 to 2% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.685 g, 56% yield). **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.12 (s, 1H), 1.98–1.87 (m, 2H), 1.79–1.50 (m, 4H), 1.42–1.29 (m, 1H), 1.20–0.95 (m, 22H), 0.90 (d,  $J$  = 6.8 Hz, 3H), 0.84–0.69 (m, 1H). **<sup>13</sup>C NMR** (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  111.3, 84.9, 69.9, 48.7, 39.9, 34.0, 30.6, 23.7, 22.1, 18.6, 11.1. **IR(neat)** 3349, 2927, 2892, 2864, 2159, 1460, 1366, 1327, 1073, 1051, 1001, 953, 942, 918, 882, 854, 813, 762, 675  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 294.2371  $[(M)^+]$ ; calculated for  $\text{C}_{18}\text{H}_{34}\text{OSi}$ : 294.2379]. **R<sub>F</sub>**: 0.2 in 5% EtOAc/Hex.

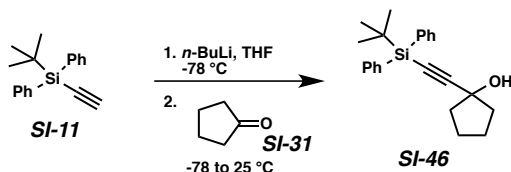


**1-tosyl-4-((triisopropylsilyl)ethynyl)piperidin-4-ol (SI-44)** synthesized from triisopropylsilylacetylene and 1-tosylpiperidin-4-one using General Procedure B. The crude product was purified by column chromatography on silica gel using a gradient of

15 to 20% EtOAc in hexanes as eluents. The product was obtained as a white solid. (1.436 g, 72% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 8.4$  Hz, 2H), 7.29 (d,  $J = 8.1$  Hz, 2H), 3.63–3.40 (m, 2H), 2.83–2.64 (m, 2H), 2.42 (s, 3H), 2.08–1.80 (m, 5H), 0.99–0.84 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 132.7, 129.6, 127.6, 108.6, 86.9, 66.6, 43.7, 38.6, 21.5, 18.5, 10.9. **IR(neat)** 3493, 2940, 2864, 2170, 1743, 1597, 1494, 1379, 1351, 1319, 1190, 1169, 1158, 1141, 1047, 1002, 955, 801, 766, 730, 706  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 458.2158  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{37}\text{NO}_3\text{SSiNa}$ : 458.2156]. **R<sub>F</sub>**: 0.24 in 20% EtOAc/Hex. **MP**: 153–154 °C.



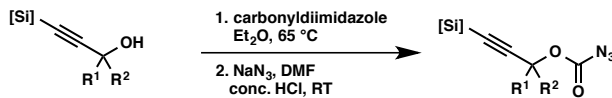
**4-((triisopropylsilyl)ethynyl)tetrahydro-2H-pyran-4-ol (SI-45)** was synthesized from triisopropylsilylacetylene and tetrahydro-4H-pyran-4-one using General Procedure B. The crude product was purified by column chromatography on silica gel using 10% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (1.0396 g, 92% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.99–3.82 (m, 2H), 3.73–3.55 (m, 2H), 2.28 (s, 1H), 1.98–1.84 (m, 2H), 1.84–1.74 (m, 2H), 1.13–0.88 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  109.9, 85.9, 66.4, 65.2, 40.2, 18.6, 11.1. **IR(neat)** 3416, 2942, 2891, 2864, 2162, 1463, 1425, 1384, 1366, 1335, 1300, 1275, 1233, 1160, 1134, 1011, 987, 958, 882, 842, 768, 674  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 282.2021  $[(\text{M})^+]$ ; calculated for  $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$ : 282.2015]. **R<sub>F</sub>**: 0.3 in 20% EtOAc/Hex.



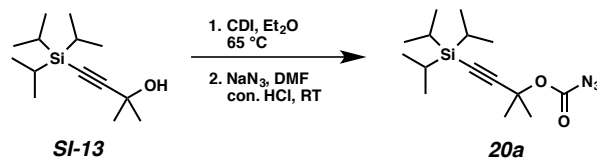
**1-((tert-butyl)diphenylsilyl)ethynylcyclopentan-1-ol (SI-46)** was synthesized from *tert*-butyl(ethynyl)diphenylsilane and cyclopentanone using General Procedure B. The crude product was purified by column chromatography on silica gel using 5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.976 g, 70% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81–7.72 (m, 4H), 7.44–7.29 (m, 6H), 2.18–1.95 (m, 4H), 1.95–1.69 (m, 4H), 1.06 (s, 9H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  135.5, 133.2, 129.5, 127.7, 114.0, 82.4, 75.0, 42.6, 27.0, 23.5, 18.5. **IR(neat)** 3343, 3070, 2957, 2929, 2856, 2162, 1471, 1428, 1389, 1361, 1258, 1208, 1106, 997, 941, 914, 883, 819, 740  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 348.1905  $[(\text{M})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{28}\text{OSi}$ : 348.1909]. **R<sub>F</sub>**: 0.3 in 10% EtOAc/Hex.

## Synthesis of Carbonazidates

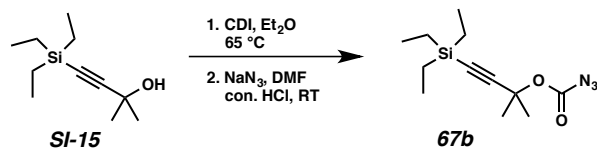
### General Procedure C



A flame-dried heavy wall pressure vessel was charged with the propargyl alcohol (1.0 equiv, 3 mmol), carbonyldiimidazole (CDI, 2.0 equiv, 6 mmol, 973 mg), and anhydrous Et<sub>2</sub>O (0.5 M, 6 mL) under an argon atmosphere. The reaction vessel was sealed and heated to reflux in an oil bath (65 °C). (**Warning: Pressure buildup may occur during the reaction.**) The progress of the reaction was monitored by TLC. (The reaction vessel should only be opened when cooled to room temperature!) After the reaction was done, the reaction vessel was cooled to room temperature, and the solvent was evaporated under a stream of nitrogen gas. The residue was then dissolved in DMF (0.5 M, 6 mL), and NaN<sub>3</sub> (5.0 equiv, 15 mmol, 975 mg) was added in one portion. The reaction mixture was acidified with concentrated HCl until pH ~ 6 (monitored by pH paper). The progress of the reaction was monitored by TLC. After the reaction was finished, deionized water was added and the mixture was extracted with Et<sub>2</sub>O three times. The organic phases were combined and washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel. No decomposition of the carbonazidates was observed at room temperature after more than a month, but it is recommended to keep them at -20 °C for long-term storage.

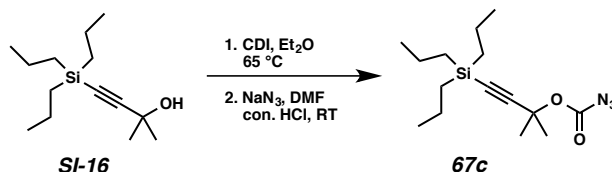


**2-methyl-4-(triisopropylsilyl)but-3-yn-2-yl carbonazidate (20a)** was synthesized from alcohol **SI-13** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0.5 to 1% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.680 g, 73% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.70 (s, 6H), 1.09–0.94 (m, 21H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 154.8, 106.5, 86.6, 76.3, 28.9, 18.5, 11.0. IR(neat) 2942, 2866, 2174, 2129, 1735, 1463, 1383, 1366, 1231, 1193, 1120, 1072, 996, 947, 919, 878, 796, 775, 676 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 332.1764 [(M+Na)<sup>+</sup>; calculated for C<sub>15</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>SiNa: 332.1765]. R<sub>F</sub>1 = 0.24 in 10% EtOAc/Hex. R<sub>F</sub>2 = 0.42 in 5% EtOAc/Hex.

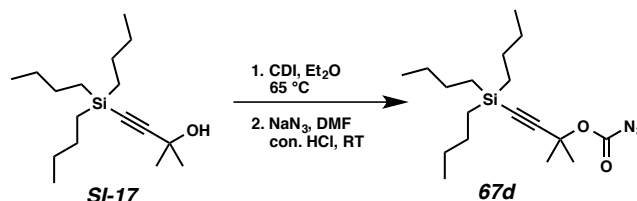


**2-methyl-4-(triethylsilyl)but-3-yn-2-yl carbonazidate (67b)** was synthesized from alcohol **SI-15** using General Procedure C. The crude product was purified by column

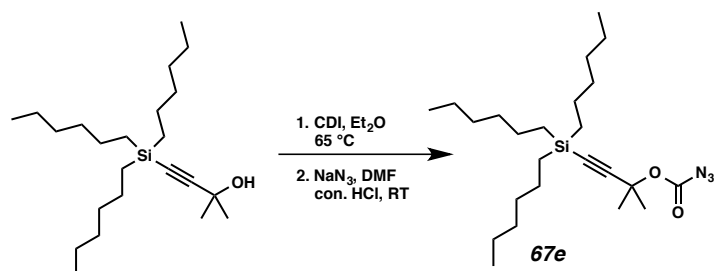
chromatography on silica gel using a gradient of 0.5 to 1% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.625 g, 78% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.69 (s, 6H), 0.96 (t,  $J = 7.9$  Hz, 9H), 0.57 (q,  $J = 8.0$  Hz, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 105.8, 87.6, 76.3, 28.8, 7.36, 4.2. **IR(neat)** 2956, 2913, 2876, 2174, 2129, 1735, 1458, 1415, 1383, 1366, 1229, 1192, 1119, 1015, 947, 875, 775, 724  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 268.1476 [(M+H) $^+$ ]; calculated for  $\text{C}_{12}\text{H}_{22}\text{N}_3\text{O}_2\text{Si}$ : 268.1481]. **R<sub>F</sub>1** = 0.24 in 10% EtOAc/Hex. **R<sub>F</sub>2** = 0.5 in 5% EtOAc/Hex.



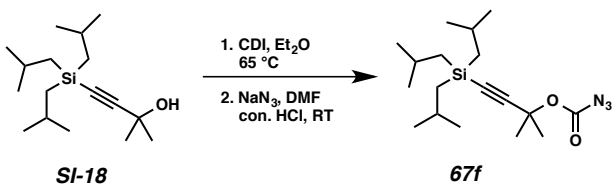
**2-methyl-4-(tripropylsilyl)but-3-yn-2-yl carbonazidate (67c)** was synthesized from alcohol **SI-16** using General Procedure C. The crude product was purified by column chromatography on silica gel using 0.5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.750 g, 80% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.68 (s, 6H), 1.44–1.29 (m, 6H), 0.95 (t,  $J = 7.4$  Hz, 9H), 0.62–0.53 (m, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 105.7, 88.4, 76.4, 28.8, 18.1, 17.4, 15.8. **IR(neat)** 2955, 2926, 2869, 2174, 2129, 1760, 1736, 1462, 1365, 1231, 1193, 1119, 1065, 1005, 947, 875, 801, 749  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 310.1947 [(M+H) $^+$ ]; calculated for  $\text{C}_{15}\text{H}_{28}\text{N}_3\text{O}_2\text{Si}$ : 310.1951]. **R<sub>F</sub>1** = 0.24 in 10% EtOAc/Hex. **R<sub>F</sub>2** = 0.54 in 2% EtOAc/Hex.



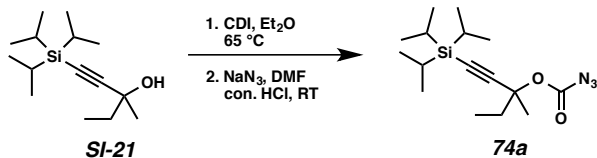
**2-methyl-4-(tributylsilyl)but-3-yn-2-yl carbonazidate (67d)** was synthesized from alcohol **SI-17** using General Procedure C. The crude product was purified by column chromatography on silica gel using 0.5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.824 g, 78% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.69 (s, 6H), 1.38–1.22 (m, 12H), 0.93–0.80 (m, 9H), 0.65–0.50 (m, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 105.6, 88.5, 76.4, 28.8, 26.3, 26.0, 13.8, 12.7. **IR(neat)** 2956, 2922, 2872, 2174, 2129, 1736, 1465, 1408, 1378, 1365, 1232, 1192, 1120, 1081, 1028, 999, 947, 876, 799, 749  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 352.2422 [(M+H) $^+$ ]; calculated for  $\text{C}_{18}\text{H}_{34}\text{N}_3\text{O}_2\text{Si}$ : 352.2420]. **R<sub>F</sub>1** = 0.24 in 10% EtOAc/Hex. **R<sub>F</sub>2** = 0.6 in 5% EtOAc/Hex.



**2-methyl-4-(trihexylsilyl)but-3-yn-2-yl carbonazidate (67e)** was synthesized from alcohol **SI-19** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0 to 2% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (1.0995 g, 84% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.68 (s, 6H), 1.38–1.15 (m, 24H), 0.92–0.81 (m, 9H), 0.63–0.51 (m, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 105.6, 88.5, 76.3, 33.0, 31.5, 28.8, 23.8, 22.6, 14.1, 13.0. **IR(neat)** 2956, 2921, 285, 2175, 2129, 1737, 1466, 1381, 1365, 1232, 1192, 1121, 975, 875, 799, 749, 721  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 436.3347 [(M+H) $^+$ ; calculated for  $\text{C}_{24}\text{H}_{46}\text{N}_3\text{O}_2\text{Si}$ : 436.3359].  $\mathbf{R}_F1$  = 0.3 in 10% EtOAc/Hex.  $\mathbf{R}_F2$  = 0.45 in 2% EtOAc/Hex.

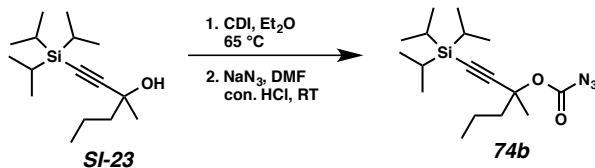


**2-methyl-4-(triisobutylsilyl)but-3-yn-2-yl carbonazidate (67f)** was synthesized from alcohol **SI-18** using General Procedure C. The crude product was purified by column chromatography on silica gel using 0.5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.990 g, 94% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89–1.74 (m, 3H), 1.67 (s, 6H), 1.00–0.90 (m, 18H), 0.60 (d,  $J$  = 7.0 Hz, 6H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 105.9, 89.8, 76.4, 28.5, 26.2, 25.0, 24.7. **IR(neat)** 2952, 2895, 2867, 2174, 2130, 2070, 1737, 1531, 1464, 1233, 1193, 1163, 1120, 1093, 1039, 974, 947, 875, 829, 800, 749  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 374.2240 [(M+Na) $^+$ ; calculated for  $\text{C}_{18}\text{H}_{33}\text{N}_3\text{O}_2\text{SiNa}$ : 374.2234].  $\mathbf{R}_F1$  = 0.24 in 10% EtOAc/Hex.  $\mathbf{R}_F2$  = 0.6 in 5% EtOAc/Hex.

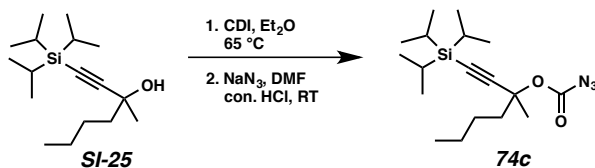


**3-methyl-1-(triisopropylsilyl)pent-1-yn-3-yl carbonazidate (74a)** was synthesized from alcohol **SI-21** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0.5 to 1% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.789 g, 81% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.06–1.93 (m, 1H), 1.89–1.77 (m, 1H), 1.69 (s, 3H), 1.09–0.98 (m, 24H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 105.3, 87.8, 80.2, 34.5, 26.0, 18.5, 11.0, 8.7.

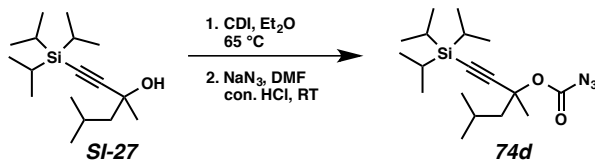
**IR(neat)** 2942, 2865, 2180, 2129, 1741, 1463, 1382, 1299, 1227, 1185, 1152, 1120, 1056, 1032, 997, 951, 881, 786, 748, 676  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 346.1920  $[(M+Na)^+]$ ; calculated for  $\text{C}_{16}\text{H}_{29}\text{N}_3\text{O}_2\text{SiNa}$ : 346.1921].  $R_F1 = 0.24$  in 5% EtOAc/Hex.  $R_F2 = 0.63$  in 5% EtOAc/Hex.



**3-methyl-1-(triisopropylsilyl)hex-1-yn-3-yl carbonazidate (74b)** was synthesized from alcohol **SI-23** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0.5 to 2% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.737 g, 73% yield).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.94 (ddd,  $J = 13.4, 10.8, 5.6$  Hz, 1H), 1.78 (ddd,  $J = 13.6, 10.6, 5.9$  Hz, 1H), 1.70 (s, 3H), 1.59–1.43 (m, 2H), 1.14–0.98 (m, 21H), 0.93 (t,  $J = 7.4$  Hz, 3H).  **$^{13}\text{C}$  NMR** (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 105.6, 87.6, 79.7, 43.4, 26.5, 18.5, 17.6, 14.0, 11.0. **IR(neat)** 2942, 2866, 2182, 2131, 1736, 1463, 1375, 1225, 1181, 1151, 1111, 1078, 1048, 1018, 996, 967, 916, 881, 800, 773, 749, 676  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 360.2075  $[(M+Na)^+]$ ; calculated for  $\text{C}_{17}\text{H}_{31}\text{N}_3\text{O}_2\text{SiNa}$ : 360.2078].  $R_F1 = 0.3$  in 10% EtOAc/Hex.  $R_F2 = 0.45$  in 5% EtOAc/Hex.



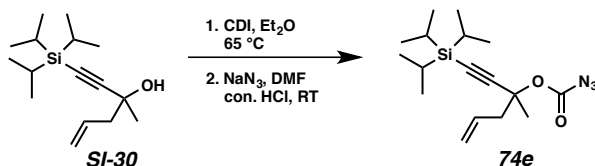
**3-methyl-1-(triisopropylsilyl)hept-1-yn-3-yl carbonazidate (74c)** was synthesized from alcohol **SI-25** using General Procedure C. The crude product was purified by column chromatography on silica gel using 0.5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.739 g, 70% yield).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.96 (ddd,  $J = 13.7, 11.1, 5.3$  Hz, 1H), 1.79 (ddd,  $J = 13.6, 11.1, 5.7$  Hz, 1H), 1.70 (s, 3H), 1.52–1.39 (m, 2H), 1.39–1.26 (m, 2H), 1.11–0.97 (m, 21H), 0.89 (t,  $J = 7.3$  Hz, 3H).  **$^{13}\text{C}$  NMR** (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 105.6, 87.7, 79.8, 41.0, 26.4, 26.4, 22.6, 18.5, 14.0, 11.0. **IR(neat)** 2942, 2865, 2182, 2129, 1737, 1463, 1375, 1223, 1129, 1114, 1151, 1082, 1043, 996, 920, 881, 806, 774, 749, 676, 660  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 374.2232  $[(M+Na)^+]$ ; calculated for  $\text{C}_{18}\text{H}_{33}\text{N}_3\text{O}_2\text{SiNa}$ : 374.2234].  $R_F1 = 0.2$  in 5% EtOAc/Hex.  $R_F2 = 0.6$  in 5% EtOAc/Hex.



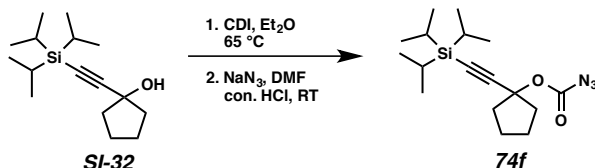
**3,5-dimethyl-1-(triisopropylsilyl)hex-1-yn-3-yl carbonazidate (74d)** was synthesized from alcohol **SI-27** using General Procedure C. The crude product was purified by column chromatography on silica gel using 0.5% EtOAc in hexanes as an eluent. The



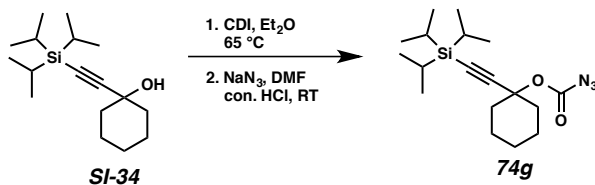
product was obtained as a colorless oil. (0.526 g, 50% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.05–1.92 (m, 1H), 1.92–1.85 (m, 1H), 1.77–1.65 (m, 4H), 1.13–1.00 (m, 21H), 1.00–0.91 (m, 6H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 105.6, 88.0, 79.8, 49.3, 27.3, 25.0, 24.1, 23.6, 18.5, 11.0. **IR(neat)** 2942, 2866, 2182, 2129, 1736, 1463, 1367, 1274, 1225, 1127, 1040, 996, 953, 903, 881, 802, 749, 676, 660  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 352.2426 [(M+H) $^+$ ; calculated for  $\text{C}_{18}\text{H}_{34}\text{N}_3\text{O}_2\text{Si}$ : 352.2420]. **R<sub>F</sub>1** = 0.2 in 5% EtOAc/Hex. **R<sub>F</sub>2** = 0.75 in 5% EtOAc/Hex.



**3-methyl-1-(triisopropylsilyl)hex-5-en-1-yn-3-yl carbonazidate (74e)** was synthesized from alcohol **SI-30** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0 to 0.5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.5940 g, 59% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.88–5.80 (m, 1H), 5.19–5.16 (m, 1H), 5.18–5.10 (m, 1H), 2.74 (dd,  $J$  = 13.8, 6.9 Hz, 1H), 2.62 (dd,  $J$  = 13.8, 7.5 Hz, 1H), 1.68 (s, 3H), 1.04 (s, 21H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.64, 131.66, 119.61, 105.20, 88.21, 78.44, 45.45, 26.17, 18.51, 11.02. **IR(neat)** 2943, 2865, 2183, 2130, 1737, 1463, 1224, 1143, 1089, 1061, 995, 920, 902, 881, 773, 749  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 358.1924 [(M+Na) $^+$ ; calculated for  $\text{C}_{17}\text{H}_{29}\text{N}_3\text{O}_2\text{Si}$ : 358.1921]. **R<sub>F</sub>1** = 0.3 in 10% EtOAc/Hex. **R<sub>F</sub>2** = 0.6 in 5% EtOAc/Hex.

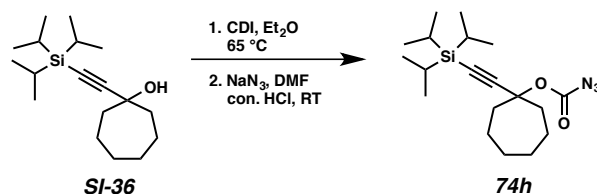


**1-(triisopropylsilyl)ethynylcyclopentyl carbonazidate (74f)** was synthesized from alcohol **SI-32** using General Procedure C. The crude product was purified by column chromatography on silica gel using 0.5% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.804 g, 80% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34–2.20 (m, 2H), 2.20–2.08 (m, 2H), 1.81–1.65 (m, 4H), 1.12–0.88 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 105.9, 87.3, 84.8, 40.4, 23.2, 18.5, 11.0. **IR(neat)** 2943, 2865, 2173, 2128, 1737, 1463, 1383, 1329, 1228, 1170, 1071, 995, 919, 881, 749, 675  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 358.1921 [(M+Na) $^+$ ; calculated for  $\text{C}_{17}\text{H}_{29}\text{N}_3\text{O}_2\text{SiNa}$ : 358.1921]. **R<sub>F</sub>1** = 0.24 in 20% EtOAc/Hex. **R<sub>F</sub>2** = 0.6 in 20% EtOAc/Hex.

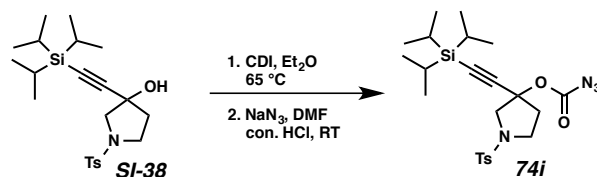


**1-(triisopropylsilyl)ethynylcyclohexyl carbonazidate (74g)** was synthesized from alcohol **SI-34** using General Procedure C. The crude product was purified by column

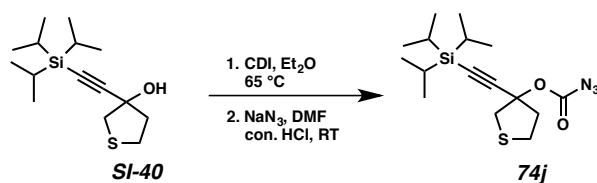
chromatography on silica gel using a gradient of 0.5 to 1% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.785 g, 75% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.20 (dt,  $J = 11.5, 4.4$  Hz, 2H), 1.79 (dt,  $J = 11.8, 3.8$  Hz, 2H), 1.72–1.50 (m, 4H), 1.14–0.90 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.5, 105.2, 88.9, 80.2, 37.0, 25.0, 22.9, 18.5, 11.1. **IR(neat)** 2939, 2864, 2183, 2135, 1739, 1463, 1383, 1366, 1296, 1262, 1205, 1170, 1140, 1119, 1071, 941, 918, 881, 852, 839, 676  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 372.2069  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{18}\text{H}_{31}\text{N}_3\text{O}_2\text{SiNa}$ : 372.2078].  $\mathbf{R}_\text{F}1 = 0.27$  in 10% EtOAc/Hex.  $\mathbf{R}_\text{F}2 = 0.7$  in 10% EtOAc/Hex.



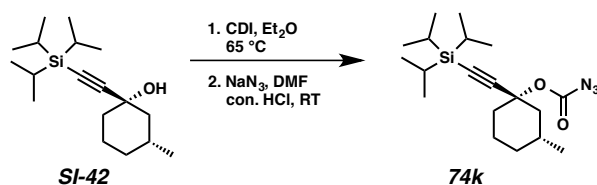
**1-((triisopropylsilyl)ethynyl)cycloheptyl carbonazidate (74h)** was synthesized from alcohol **SI-36** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0.5 to 1% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.816 g, 75% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.28 (ddd,  $J = 14.0, 7.4, 3.1$  Hz, 2H), 2.06 (ddd,  $J = 14.3, 8.8, 3.1$  Hz, 2H), 1.72–1.50 (m, 8H), 1.14–0.91 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 106.2, 88.3, 83.6, 40.0, 27.9, 22.2, 18.5, 11.1. **IR(neat)** 2940, 2864, 2181, 2130, 2069, 1735, 1527, 1462, 1367, 1286, 1223, 1192, 1176, 1065, 996, 881, 802, 749, 676  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 386.2234  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}_2\text{SiNa}$ : 386.2234].  $\mathbf{R}_\text{F}1 = 0.3$  in 10% EtOAc/Hex.  $\mathbf{R}_\text{F}2 = 0.67$  in 10% EtOAc/Hex.



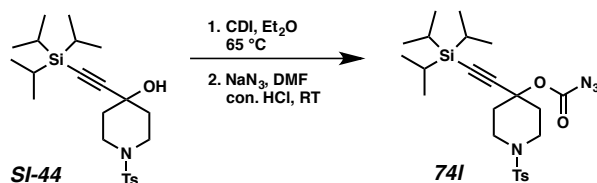
**1-tosyl-3-((triisopropylsilyl)ethynyl)pyrrolidin-3-yl carbonazidate (74i)** was synthesized from alcohol **SI-38** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 10% EtOAc in hexanes as eluents. The product was obtained as a white solid. (1.1762 g, 80% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.2$  Hz, 2H), 4.00 (dd,  $J = 12.8, 1.7$  Hz, 1H), 3.64 (d,  $J = 12.7$  Hz, 1H), 3.54 (ddd,  $J = 9.6, 8.1, 3.1$  Hz, 1H), 3.29 (ddd,  $J = 9.8, 9.7, 6.6$  Hz, 1H), 2.50–2.34 (m, 4H), 2.26 (ddd,  $J = 13.7, 10.0, 8.2$  Hz, 1H), 1.08–0.87 (m, 21H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 143.8, 133.3, 129.7, 127.6, 100.4, 90.9, 80.1, 57.8, 46.1, 38.9, 21.5, 18.4, 10.8. **IR(neat)** 2942, 2891, 2865, 2174, 2129, 1731, 1463, 1384, 1222, 1174, 1086, 1029, 1016, 972, 944, 919, 848, 814, 708, 697, 678  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 513.1967  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{34}\text{N}_4\text{O}_4\text{SSiNa}$ : 513.1962].  $\mathbf{R}_\text{F}1 = 0.2$  in 25% EtOAc/Hex.  $\mathbf{R}_\text{F}2 = 0.6$  in 25% EtOAc/Hex. **MP**: 72–74  $^\circ\text{C}$ .



**3-((triisopropylsilyl)ethynyl)tetrahydrothiophen-3-yl carbonazidate (74j)** was synthesized from alcohol **SI-40** using General Procedure C. The crude product was purified by column chromatography on silica gel using 2% EtOAc in hexanes as an eluent. The product was obtained as a colorless oil. (0.773 g, 73% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.47 (dd,  $J = 12.3, 1.2$  Hz, 1H), 3.31 (d,  $J = 12.1$  Hz, 1H), 3.05–2.87 (m, 2H), 2.73–2.62 (m, 1H), 2.44–2.24 (m, 1H), 1.12–0.97 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 102.1, 89.6, 84.1, 42.9, 41.2, 28.1, 18.5, 11.0. **IR(neat)** 2942, 2891, 2865, 2177, 2132, 1763, 1734, 1463, 1384, 1247, 1228, 1199, 1176, 1072, 1004, 959, 910, 881, 848, 747, 669  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 353.1590  $[(\text{M})^+]$ ; calculated for  $\text{C}_{16}\text{H}_{27}\text{N}_3\text{O}_2\text{SSi}$ : 353.1593].  $\text{R}_\text{F}1 = 0.2$  in 10% EtOAc/Hex.  $\text{R}_\text{F}2 = 0.48$  in 5% EtOAc/Hex.

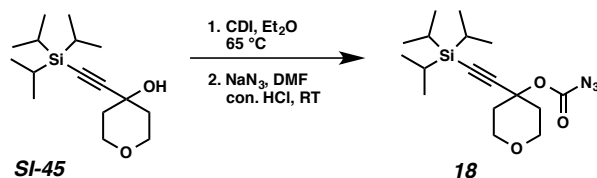


**3-methyl-1-((triisopropylsilyl)ethynyl)cyclohexyl carbonazidate (74k)** was synthesized from alcohol **SI-42** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 0.5 to 1% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (1.09 g, 92% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.46–2.29 (m, 1H), 1.88–1.57 (m, 4H), 1.53–1.42 (m, 1H), 1.27–1.15 (m, 1H), 1.05 (s, 21H), 0.92 (d,  $J = 6.7$  Hz, 3H), 0.89–0.74 (m, 1H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  154.5, 104.9, 89.5, 81.0, 45.1, 36.8, 33.9, 30.2, 23.1, 21.9, 18.6, 11.1. **IR(neat)** 2940, 2865, 2177, 2133, 1738, 1462, 1383, 1298, 1281, 1229, 1209, 1174, 1052, 1016, 974, 914, 881, 748, 675, 660  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 386.2232  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}_2\text{SiNa}$ : 386.2234].  $\text{R}_\text{F}1 = 0.3$  in 10% EtOAc/Hex.  $\text{R}_\text{F}2 = 0.67$  in 10% EtOAc/Hex.

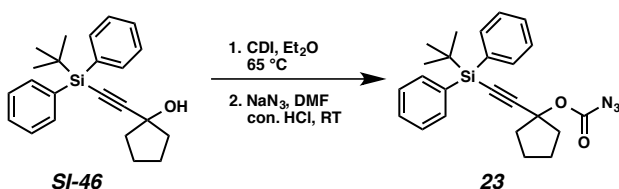


**1-tosyl-4-((triisopropylsilyl)ethynyl)piperidin-4-yl carbonazidate (74l)** was synthesized from alcohol **SI-44** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 10% EtOAc in hexanes as eluents. The product was obtained as a white solid. (1.089 g, 72% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 8.4$  Hz, 2H), 7.29 (d,  $J = 8.1$  Hz, 2H), 3.57 (ddd,  $J = 12.4, 4.2, 4.2$  Hz, 2H), 2.73 (ddd,  $J = 11.4, 11.4, 2.8$  Hz, 2H), 2.41 (s, 3H), 2.37–2.25 (m, 2H), 2.04 (ddd,  $J = 12.8, 11.0, 4.0$  Hz, 2H), 1.00–0.77 (m, 21H).  $^{13}\text{C NMR}$  (100.52

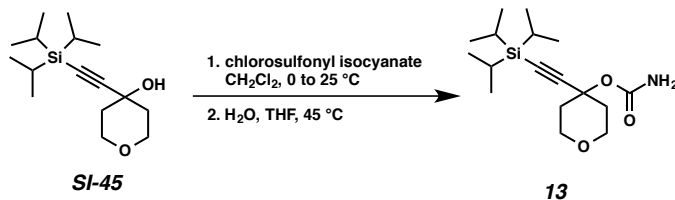
MHz, CDCl<sub>3</sub>)  $\delta$  154.8, 143.7, 132.4, 129.7, 127.6, 102.5, 91.4, 77.2, 43.3, 35.8, 21.5, 18.4, 10.8. **IR(neat)** 2941, 2864, 2159, 2128, 1736, 1494, 1382, 1302, 1260, 1231, 1211, 1200, 1154, 1109, 1094, 1062, 1032, 960, 800, 767, 746, 729, 709, 679 cm<sup>-1</sup>. **HRMS** (ESI)  $m/z$ : 527.2112 [(M+Na)<sup>+</sup>; calculated for C<sub>24</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>SSiNa: 527.2119]. **R<sub>F</sub>1** = 0.2 in 25% EtOAc/Hex. **R<sub>F</sub>2** = 0.6 in 25% EtOAc/Hex. **MP**: 107-108 °C.



**4-((triisopropylsilyl)ethynyl)tetrahydro-2H-pyran-4-yl carbonazidate (18)** was synthesized from alcohol **SI-45** using General Procedure C. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 5% EtOAc in hexanes as eluents. The product was obtained as a colorless oil. (0.815 g, 77% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.89 (ddd,  $J$  = 12.1, 4.1, 4.1 Hz, 2H), 3.70 (ddd,  $J$  = 12.6, 10.2, 2.4 Hz, 2H), 2.25 (ddd,  $J$  = 13.1, 2.2, 2.2 Hz, 2H), 2.00 (ddd,  $J$  = 13.8, 10.2, 4.2 Hz, 2H), 1.13–0.98 (m, 21H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  154.7, 103.7, 90.3, 76.9, 64.7, 37.5, 18.5, 11.0. **IR(neat)** 2941, 2864, 2184, 2136, 2070, 1738, 1463, 1385, 1267, 1221, 1153, 1098, 988, 935, 881, 849, 748, 660 cm<sup>-1</sup>. **HRMS** (CI)  $m/z$ : 352.2045 [(M+H)<sup>+</sup>; calculated for C<sub>17</sub>H<sub>30</sub>N<sub>3</sub>O<sub>3</sub>Si: 352.2056]. **R<sub>F</sub>1** = 0.24 in 20% EtOAc/Hex. **R<sub>F</sub>2** = 0.45 in 10% EtOAc/Hex.



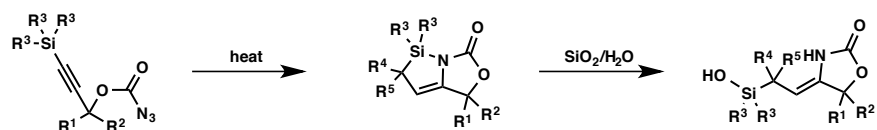
**1-((tert-butylidiphenylsilyl)ethynyl)cyclopentyl carbonazidate (23)** was synthesized from alcohol **SI-46** using General Procedure C. The crude product was purified by column chromatography on silica gel using 2% EtOAc in hexanes as an eluent. The product was obtained as a white solid. (0.806 g, 77% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.86–7.75 (m, 4H), 7.46–7.33 (m, 6H), 2.46–2.25 (m, 4H), 1.90–1.77 (m, 4H), 1.10 (s, 9H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  155.4, 135.5, 132.8, 129.5, 127.7, 108.1, 86.4, 84.6, 40.4, 26.9, 23.3, 18.6. **IR(neat)** 3069, 2954, 2931, 2856, 2180, 2129, 1737, 1470, 1444, 1427, 1361, 1329, 1239, 1177, 1107, 998, 964, 950, 899, 819, 701 cm<sup>-1</sup>. **HRMS** (ESI)  $m/z$ : 440.1763 [(M+Na)<sup>+</sup>; calculated for C<sub>24</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>SiNa: 440.1765]. **R<sub>F</sub>1** = 0.2 in 10% EtOAc/Hex. **R<sub>F</sub>2** = 0.2 in 2% EtOAc/Hex. **MP**: 44-45 °C.



**4-((triisopropylsilyl)ethynyl)tetrahydro-2H-pyran-4-yl carbamate (13)**

A flame-dried round-bottom flask was charged with chlorosulfonyl isocyanate (1.5 equiv) under an argon atmosphere. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.1M) was added, and the mixture was cooled to 0 °C in an ice/H<sub>2</sub>O bath. The propargyl alcohol **SI-45** (0.31 g, 0.26 mmol, 1.0 equiv) dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.3M) was then added dropwise. The reaction mixture was allowed to warm to room temperature. After 30 minutes, H<sub>2</sub>O (1/10 of the total volume of CH<sub>2</sub>Cl<sub>2</sub> added) and THF (1/5 of the total volume) were added. The reaction mixture was refluxed (45 °C oil bath) for 30 minutes. Then saturated NaCl solution was added, and the layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2x), and the organic phases were combined, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated to yield crude product. The crude product was purified by column chromatography on silica gel using 30% EtOAc in hexanes as an eluent. The product was obtained as a white solid. (0.24 g, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.70 (s, 2H), 3.86 (ddd, *J* = 11.9, 4.1, 4.1 Hz, 2H), 3.71 (ddd, *J* = 12.0, 10.3, 2.5 Hz, 2H), 2.23 (ddd, *J* = 13.4, 4.5, 2.2 Hz, 2H), 1.97 (ddd, *J* = 13.4, 10.3, 4.2 Hz, 2H), 1.16–0.93 (m, 21H). <sup>13</sup>C NMR (100.52 MHz, CDCl<sub>3</sub>) δ 154.6, 105.8, 88.1, 73.0, 64.7, 38.0, 18.6, 11.1. IR(neat) 3429, 3333, 3272, 2941, 2864, 2166, 1723, 1362, 1245, 1204, 1098, 1057, 1025, 972, 906, 845, 819, 780, 718, 680, 663 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 348.1966 [(M+Na)<sup>+</sup>; calculated for C<sub>17</sub>H<sub>31</sub>NO<sub>3</sub>SiNa: 348.1965]. R<sub>F</sub>: 0.36 in 30% EtOAc/Hex. MP: 82-84 °C.

### Synthesis of Azasilacyclopentenes and Silanols



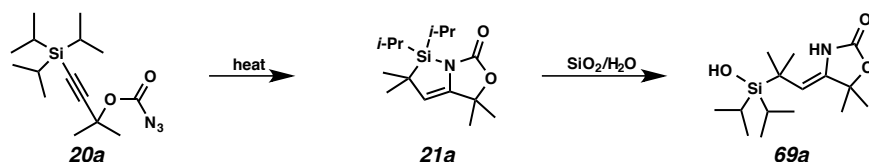
#### General Procedure D1

A 2 dram vial was charged with a magnetic spin bar, carbonazidate (0.1 mmol), and dry hexanes (0.1 M, 1 mL). The reaction vessel was sealed and heated in an oil bath at 90 °C. **(Warning: Pressure buildup may occur during the reaction.)** The progress of the reaction was monitored by TLC. After the reaction was finished (18 h), the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. To the crude product was added methyl-4-nitro-benzoate (9.1 mg, 0.05 mmol, 0.5 equiv) and CDCl<sub>3</sub> (0.7 mL). The yield of the azasilacyclopentene was calculated based on <sup>1</sup>H NMR peak integration relative to the methyl group of methyl-4-nitro-benzoate. NMR data was collected using a relaxation delay of 30 sec. (The experiments were conducted to show that RD = 30 sec was required to achieve quantitative information.) The azasilacyclopentenes were identified by their correspondence to the <sup>1</sup>H NMR data of 21a and their mass as determined by GC/MS. The crude product was purified by column chromatography on silica gel to give silanol.

#### General Procedure D2

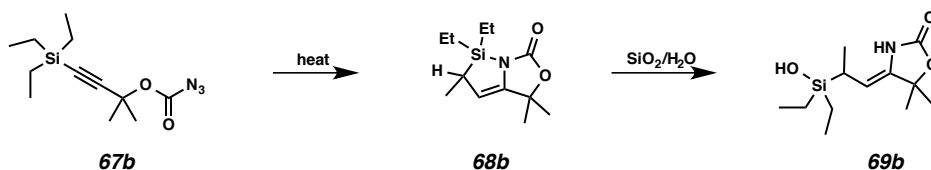
A 2 dram vial was charged with a magnetic spin bar, carbonazidate (0.1 mmol), and dry isopropylacetate (0.1 M, 1 mL). The reaction vessel was sealed and heated in an oil bath

at 100 °C. (**Warning: Pressure buildup may occur during the reaction.**) The progress of the reaction was monitored by TLC. After the reaction was finished (14 h), the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. To the crude product was added methyl-4-nitro-benzoate (9.1 mg, 0.05 mmol, 0.5 equiv) and CDCl<sub>3</sub> (0.7 mL). The yield of the azasilacyclopentene was calculated based on <sup>1</sup>H NMR peak integration relative to the methyl group of methyl-4-nitro-benzoate. NMR data was collected using a relaxation delay of 30 sec. (The experiments were conducted to show that RD = 30 sec was required to achieve quantitative information.) The azasilacyclopentenes were identified by their correspondence to the <sup>1</sup>H NMR data of 21a and their mass as determined by GC/MS. The crude product was purified by column chromatography on silica gel to give silanol.



**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-5,5-dimethyloxazolidin-2-one (69a)** was synthesized from carbonazidate **20a** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 20% EtOAc in hexanes as eluents. The silanol **69a** was obtained as an amorphous yellowish solid. (trial 1: 15.6 mg, 52% yield; trial 2: 15.0 mg, 50% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.21 (s, 1H), 4.52 (s, 1H), 4.22 (s, 1H), 1.44 (s, 6H), 1.13 (s, 6H), 1.10–0.93 (m, 14H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 156.8, 139.4, 107.5, 84.9, 28.1, 25.6, 23.9, 18.4, 18.4, 13.3. IR(neat) 3351, 2944, 2866, 1739, 1718, 1690, 1463, 1386, 1207, 1171, 963, 917, 824, 673 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 322.1813 [(M+Na)<sup>+</sup>]; calculated for C<sub>15</sub>H<sub>29</sub>NO<sub>3</sub>SiNa: 322.1809]. R<sub>F</sub>: 0.2 in 20% EtOAc/Hex.

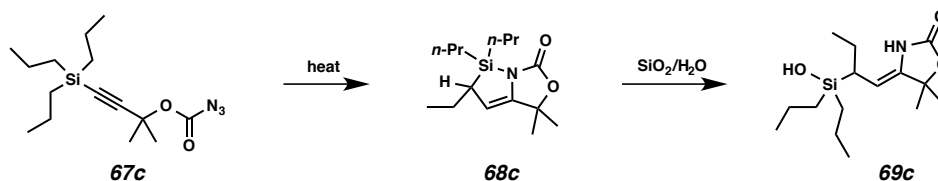
**1,1-diisopropyl-2,2,4,4-tetramethyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (21a)** was observed in crude NMR (53% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.36 (s, 1H), 1.45 (s, 6H), 1.20–1.15 (m, 20H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.0, 150.2, 108.3, 81.5, 27.7, 26.0, 17.9, 17.5, 11.7. MS (EI) *m/z*: 281 [(M)<sup>+</sup>]; calculated for C<sub>15</sub>H<sub>27</sub>NO<sub>2</sub>Si: 281.18]



**(Z)-4-(2-(diethyl(hydroxy)silyl)propylidene)-5,5-dimethyloxazolidin-2-one (69b)** was synthesized from carbonazidate **67b** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 20 to 25% EtOAc in hexanes as eluents. The silanol **69b** was obtained as an amorphous yellowish solid. (trial 1: 10.0 mg, 39% yield; trial 2: 9.8 mg, 38% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 1H), 4.17 (d, *J* = 9.9 Hz, 1H), 3.00 (s, 1H), 1.66 (dq, *J* = 10.2, 7.4 Hz, 1H), 1.47 (s, 6H), 1.06 (d, *J* = 7.4 Hz, 3H), 1.02–0.90 (m, 6H), 0.68–0.49 (m, 4H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 157.9, 138.1, 100.9, 85.0, 28.1, 28.0, 20.6, 15.0, 6.8, 6.5, 4.9, 4.3.

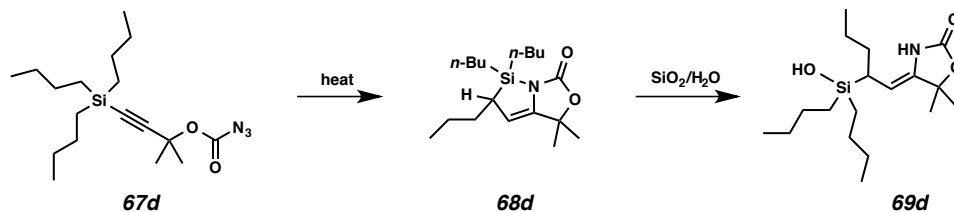
**IR(neat)** 3463, 3231, 2953, 2875, 1723, 1698, 1388, 1369, 1325, 1299, 1204, 1186, 1153, 1017, 912, 888, 850, 770, 715, 669  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 280.1342 [(M+Na)<sup>+</sup>; calculated for C<sub>12</sub>H<sub>23</sub>NO<sub>3</sub>SiNa: 280.1339]. **R<sub>F</sub>**: 0.2 in 25% EtOAc/Hex.

**1,1-diethyl-2,4,4-trimethyl-2,4-dihydro-1*H*,6*H*-[1,2]azasilolo[1,5-*c*]oxazol-6-one (68b)** was observed in crude NMR (38% yield). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.57 (d,  $J$  = 3.2 Hz, 1H, vinyl proton), **MS** (EI)  $m/z$ : 239 [(M<sup>+</sup>); calculated for C<sub>12</sub>H<sub>21</sub>NO<sub>2</sub>Si: 239.13]



**(*Z*)-4-(2-(hydroxydipropylsilyl)butylidene)-5,5-dimethyloxazolidin-2-one (69c)** was synthesized from carbonazidate **67c** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 20 to 25% EtOAc in hexanes as eluents. The silanol **69c** was obtained as a yellow oil. (trial 1: 12.5 mg, 42% yield; trial 2: 13.7 mg, 46% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (s, 1H), 4.11 (d,  $J$  = 10.5 Hz, 1H), 2.64 (s, 1H), 1.68–1.56 (m, 1H), 1.49 (d,  $J$  = 3.4 Hz, 6H), 1.45–1.17 (m, 5H), 1.03–0.90 (m, 6H), 0.88 (t,  $J$  = 7.2 Hz, 3H), 0.65–0.50 (m, 4H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  157.6, 139.7, 98.8, 85.0, 29.9, 28.1, 28.0, 22.7, 18.4, 18.4, 16.7, 16.7, 16.5, 16.2, 14.3. **IR(neat)** 3248, 2954, 2927, 2867, 1744, 1699, 1385, 1305, 1178, 1150, 1130, 1008, 894, 838, 752, 675  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 298.1835 [(M-H)<sup>+</sup>; calculated for C<sub>15</sub>H<sub>28</sub>NO<sub>3</sub>Si: 298.1838]. **R<sub>F</sub>**: 0.15 in 20% EtOAc/Hex.

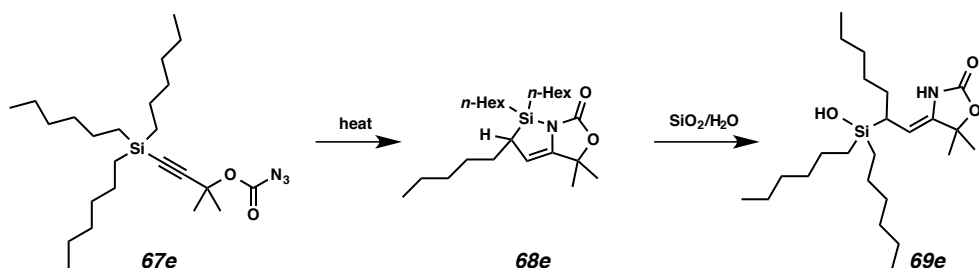
**2-ethyl-4,4-dimethyl-1,1-dipropyl-2,4-dihydro-1*H*,6*H*-[1,2]azasilolo[1,5-*c*]oxazol-6-one (68c)** was observed in crude NMR (42% yield). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.65 (d,  $J$  = 3.2 Hz, 1H, vinyl proton), **MS** (EI)  $m/z$ : 281 [(M<sup>+</sup>); calculated for C<sub>15</sub>H<sub>27</sub>NO<sub>2</sub>Si: 281.18]



**(*Z*)-4-(2-(dibutyl(hydroxy)silyl)pentylidene)-5,5-dimethyloxazolidin-2-one (69d)** was synthesized from carbonazidate **67d** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 15 to 20% EtOAc in hexanes as eluents. The silanol **69d** was obtained as an amorphous yellowish solid. (trial 1: 14.7 mg, 43% yield; trial 2: 14.3 mg, 42% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.59 (s, 1H), 4.11 (d,  $J$  = 10.4 Hz, 1H), 2.65 (s, 1H), 1.56 (td,  $J$  = 11.1, 2.9 Hz, 1H), 1.48 (s, 6H), 1.43–1.07 (m, 12H), 0.93–0.78 (m, 9H), 0.67–0.48 (m, 4H). **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  157.6, 139.2, 99.2, 85.0, 31.7, 28.1, 28.0, 27.6, 26.6, 26.6, 25.3, 25.1, 22.6, 13.9, 13.7, 13.7, 13.5, 13.1. **IR(neat)** 3238, 2955, 2923, 2870, 1746, 1699, 1464, 1385, 1307, 1196, 1174, 1132, 1009, 887, 767, 731, 676  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ :

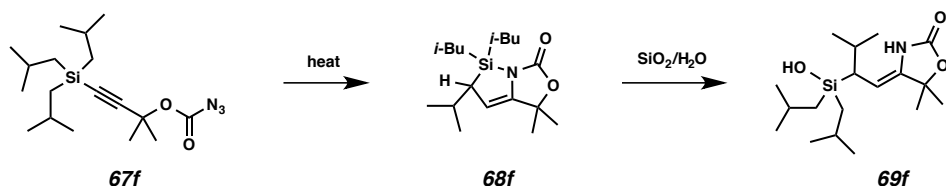
364.2274 [(M+Na)<sup>+</sup>; calculated for C<sub>18</sub>H<sub>35</sub>NO<sub>3</sub>SiNa: 364.2278]. **R<sub>F</sub>**: 0.2 in 25% EtOAc/Hex.

**1,1-dibutyl-4,4-dimethyl-2-propyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (68d)** was observed in crude NMR (56% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.63 (d, *J* = 2.9 Hz, 1H, vinyl proton), **MS** (EI) *m/z*: 323 [(M<sup>+</sup>); calculated for C<sub>18</sub>H<sub>33</sub>NO<sub>2</sub>Si: 323.22]



**(Z)-4-(2-(dihexyl(hydroxy)silyl)heptylidene)-5,5-dimethyloxazolidin-2-one (69e)** was synthesized from carbonazidate **67e** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 15% EtOAc in hexanes as eluents. The silanol **69e** was obtained as an amorphous yellowish solid. (trial 1: 18.7 mg, 44% yield; trial 2: 19.1 mg, 45% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.58 (s, 1H), 4.11 (d, *J* = 10.6 Hz, 1H), 2.65 (s, 1H), 1.59–1.42 (m, 8H), 1.42–1.05 (m, 23H), 0.94–0.76 (m, 9H), 0.65–0.46 (m, 4H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 157.6, 139.2, 99.3, 85.0, 33.4, 33.3, 31.6, 31.5, 31.5, 29.4, 29.2, 28.1, 28.0, 27.8, 23.1, 22.8, 22.6, 22.6, 22.6, 14.1, 14.1, 14.1, 13.9, 13.4. **IR(neat)** 3397, 3096, 2957, 2919, 2871, 2852, 1744, 1704, 1461, 1382, 1366, 1328, 1209, 1167, 1031, 1006, 953, 895, 845, 764, 722, 676 cm<sup>-1</sup>. **HRMS** (ESI) *m/z*: 448.3221 [(M+Na)<sup>+</sup>; calculated for C<sub>24</sub>H<sub>47</sub>NO<sub>3</sub>SiNa: 448.3217]. **R<sub>F</sub>**: 0.15 in 10% EtOAc/Hex.

**1,1-dihexyl-4,4-dimethyl-2-pentyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (48e)** was observed in crude NMR (56% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.63 (d, *J* = 2.9 Hz, 1H, vinyl proton), **MS** (EI) *m/z*: 407 [(M<sup>+</sup>); calculated for C<sub>24</sub>H<sub>45</sub>NO<sub>2</sub>Si: 407.32]

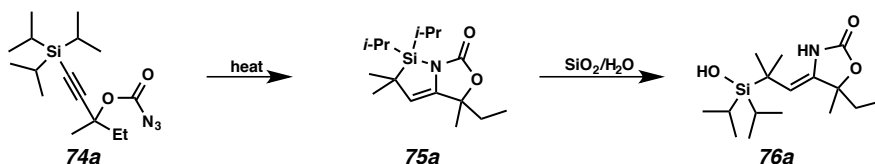


**(Z)-4-(2-(hydroxydiisobutylsilyl)-3-methylbutylidene)-5,5-dimethyloxazolidin-2-one (69f)** was synthesized from carbonazidate **67f** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 15 to 20% EtOAc in hexanes as eluents. The silanol **69f** was obtained as an amorphous yellowish solid. (trial 1: 15.0 mg, 44% yield; trial 2: 14.0 mg, 41% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.74 (s, 1H), 4.25 (d, *J* = 11.4 Hz, 1H), 2.04–1.91 (m, 1H), 1.91–1.74 (m, 2H), 1.50 (s, 3H), 1.49 (s, 3H), 1.01–0.82 (m, 19H), 0.67–0.49 (m, 4H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 157.7, 140.4, 95.7, 85.0, 36.0, 28.4, 28.0, 28.0, 26.6, 26.5, 26.4,



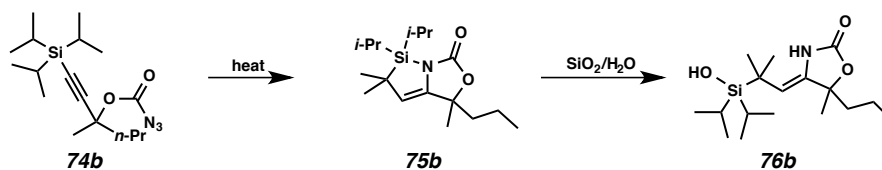
26.3, 26.2, 25.8, 24.3, 24.2, 23.6, 20.4. **IR(neat)** 3241, 2952, 2866, 1743, 1697, 1464, 1384, 1316, 1218, 1184, 1089, 1009, 822, 797, 757, 744, 674  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 364.2282  $[(M+Na)^+]$ ; calculated for  $\text{C}_{18}\text{H}_{35}\text{NO}_3\text{SiNa}$ : 364.2278]. **R<sub>F</sub>**: 0.2 in 25% EtOAc/Hex.

**1,1-diisobutyl-2-isopropyl-4,4-dimethyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (68f)** was observed in crude NMR (55% yield). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.71 (d,  $J = 3.2$  Hz, 1H, vinyl proton), **MS** (EI)  $m/z$ : 323  $[(M)^+]$ ; calculated for  $\text{C}_{18}\text{H}_{33}\text{NO}_2\text{Si}$ : 323.22]



**(Z)-5-ethyl-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-5-methyloxazolidin-2-one (76a)** was synthesized from carbonazidate **74a** using General Procedure D1. The crude product was purified by column chromatography on silica gel using 10% EtOAc in hexanes as an eluent. The silanol **76a** was obtained as an amorphous yellowish solid. (trial 1: 16.3 mg, 52% yield; trial 2: 15.9 mg, 51% yield). **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.19 (s, 1H), 4.28 (s, 1H), 4.17 (s, 1H), 1.76 (dq,  $J = 14.6, 7.3$  Hz, 1H), 1.59 (dq,  $J = 14.5, 7.3$  Hz, 1H), 1.41 (s, 3H), 1.14 (d,  $J = 6.2$  Hz, 6H), 1.11–0.99 (m, 14H), 0.89 (t,  $J = 7.3$  Hz, 3H). **<sup>13</sup>C NMR** (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 137.7, 108.1, 87.7, 33.9, 26.7, 26.0, 25.3, 24.0, 18.4, 18.4, 18.4, 18.3, 13.4, 13.4, 7.3. **IR(neat)** 3350, 2969, 2943, 2866, 1736, 1717, 1687, 1462, 1331, 1281, 1248, 1143, 1099, 1033, 1004, 957, 904, 882, 824, 673  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 336.1970  $[(M+Na)^+]$ ; calculated for  $\text{C}_{16}\text{H}_{31}\text{NO}_3\text{SiNa}$ : 336.1965]. **R<sub>F</sub>**: 0.3 in 20% EtOAc/Hex.

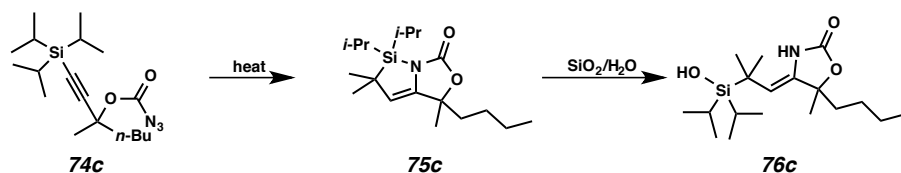
**4-ethyl-1,1-diisopropyl-2,2,4-trimethyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (75a)** was observed in crude NMR (57% yield). **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.33 (s, 1H, vinyl proton), **MS** (EI)  $m/z$ : 295  $[(M)^+]$ ; calculated for  $\text{C}_{16}\text{H}_{29}\text{NO}_2\text{Si}$ : 295.20]



**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-5-methyl-5-propyloxazolidin-2-one (76b)** was synthesized from carbonazidate **74b** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 15% EtOAc in hexanes as eluents. The silanol **76b** was obtained as an amorphous yellowish solid. (trial 1: 17.3 mg, 53% yield; trial 2: 17.7 mg, 54% yield; ). **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.17 (s, 1H), 4.31 (s, 1H), 4.17 (s, 1H), 1.77–1.61 (m, 1H), 1.58–1.46 (m, 1H), 1.40 (s, 3H), 1.39–1.29 (m, 2H), 1.13 (d,  $J = 2.4$  Hz, 6H), 1.10–1.01 (m, 14H), 0.88 (t,  $J = 7.3$  Hz, 3H). **<sup>13</sup>C NMR** (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 138.1, 108.1, 87.4, 43.3, 26.9, 26.0, 25.3, 24.0, 18.4, 18.4, 18.3, 16.3, 14.0, 13.5. **IR(neat)** 3207, 2941, 2863, 1747, 1687, 1463, 1366, 1332, 1291, 1231, 1146, 1078,

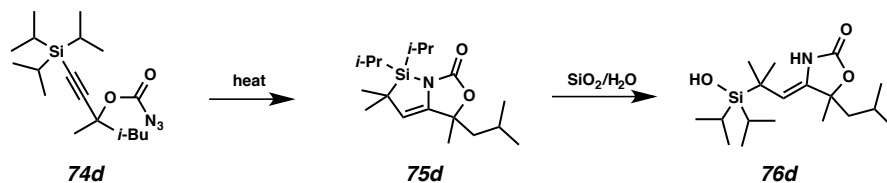
1006, 915, 880, 861, 837, 707, 666  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 350.2126 [(M+Na)<sup>+</sup>; calculated for C<sub>17</sub>H<sub>33</sub>NO<sub>3</sub>SiNa: 350.2122]. **R<sub>F</sub>**: 0.27 in 20% EtOAc/Hex.

**1,1-diisopropyl-2,2,4-trimethyl-4-propyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (75b)** was observed in crude NMR (55% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.33 (s, 1H, vinyl proton), **MS** (EI)  $m/z$ : 309 [(M+); calculated for C<sub>17</sub>H<sub>31</sub>NO<sub>2</sub>Si: 309.21]



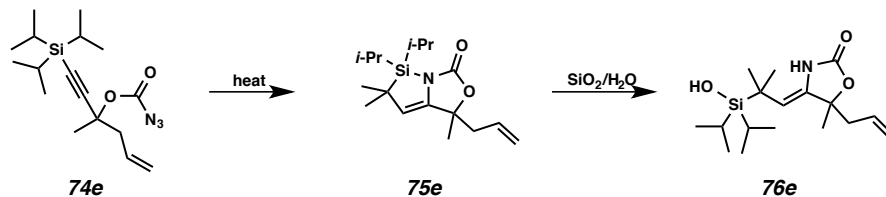
**(Z)-5-butyl-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-5-methyloxazolidin-2-one (76c)** was synthesized from carbonazidate **74c** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 15% EtOAc in hexanes as eluents. The silanol **76c** was obtained as a yellowish oil. (trial 1: 20.2 mg, 59% yield; trial 2: 20.1 mg, 59 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.29 (s, 1H), 4.64 (s, 1H), 4.18 (s, 1H), 1.80–1.65 (m, 1H), 1.59–1.48 (m, 1H), 1.40 (s, 3H), 1.36–1.21 (m, 4H), 1.13 (d,  $J$  = 3.7 Hz, 6H), 1.09–1.03 (m, 14H), 0.85 (t,  $J$  = 6.9 Hz, 3H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  157.7, 138.1, 108.2, 87.7, 40.8, 27.1, 25.9, 25.4, 25.1, 24.0, 22.6, 18.4, 18.4, 18.4, 18.3, 13.9, 13.5, 13.4. **IR**(neat) 3221, 2942, 2865, 1742, 1689, 1464, 1330, 1288, 1144, 1005, 961, 915, 829, 767, 731, 672  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 364.2282 [(M+Na)<sup>+</sup>; calculated for C<sub>18</sub>H<sub>35</sub>NO<sub>3</sub>SiNa: 364.2278]. **R<sub>F</sub>**: 0.3 in 20% EtOAc/Hex.

**4-butyl-1,1-diisopropyl-2,2,4-trimethyl-2,4-dihydro-1H,6H-[1,2]azasilolo[1,5-c]oxazol-6-one (75c)** was observed in crude NMR (60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.30 (s, 1H, vinyl proton), **MS** (EI)  $m/z$ : 323 [(M+); calculated for C<sub>18</sub>H<sub>33</sub>NO<sub>2</sub>Si: 323.23]



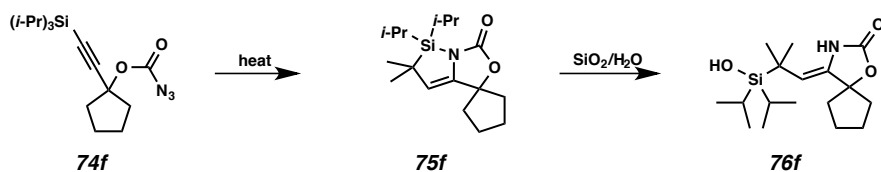
**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-5-isobutyl-5-methyloxazolidin-2-one (76d)** was synthesized from carbonazidate **74d** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 15% EtOAc in hexanes as eluents. The silanol **76d** was obtained as a yellowish oil. (trial 1: 14.8 mg, 43% yield; trial 2: 15.4 mg, 45 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.25 (s, 1H), 4.46 (s, 1H), 4.16 (s, 1H), 1.85–1.72 (m,  $J$  = 6.5 Hz, 1H), 1.65 (dd,  $J$  = 14.7, 6.5 Hz, 1H), 1.52 (dd,  $J$  = 14.8, 5.6 Hz, 1H), 1.40 (s, 3H), 1.14 (d,  $J$  = 5.6 Hz, 6H), 1.10–0.98 (m, 14H), 0.91 (t,  $J$  = 6.6 Hz, 6H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  157.5, 138.6, 108.3, 87.8, 49.2, 27.7, 26.1, 25.1, 24.3, 24.3, 24.3, 24.0, 24.0, 18.5, 18.4, 18.4, 18.3, 13.4. **IR**(neat) 3221, 2947, 2866, 1742, 1689, 1464, 1376, 1314, 150, 1007, 915, 880, 829, 792, 767, 731, 672  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 364.2282 [(M+Na)<sup>+</sup>; calculated for C<sub>18</sub>H<sub>35</sub>NO<sub>3</sub>SiNa: 364.2278]. **R<sub>F</sub>**: 0.24 in 20% EtOAc/Hex.

**4-isobutyl-1,1-diisopropyl-2,2,4-trimethyl-2,4-dihydro-1*H*,6*H*-[1,2]azasilolo[1,5-*c*]oxazol-6-one (75d)** was observed in crude NMR (49% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.32 (s, 1H, vinyl proton), MS (EI) *m/z*: 323 [(M<sup>+</sup>); calculated for C<sub>18</sub>H<sub>33</sub>NO<sub>2</sub>Si: 323.23]



**(*Z*)-5-allyl-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-5-methyloxazolidin-2-one (76e)** was synthesized from carbonazidate **74e** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 15% EtOAc in hexanes as eluents. The silanol **76e** was obtained as a yellowish oil. (trial 1: 16.3 mg, 50% yield; trial 2: 16.1 mg, 49 % yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.20 (s, 1H), 5.89–5.56 (m, 1H), 5.14–5.12 (m, 1H), 5.11 (d, *J* = 4.4 Hz, 1H), 4.32 (s, 1H), 4.22 (s, 1H), 2.43 (dd, *J* = 14.3, 7.7 Hz, 1H), 2.36 (dd, *J* = 14.2, 6.5 Hz, 1H), 1.42 (s, 3H), 1.13 (s, 6H), 1.10–1.00 (m, 14H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 157.3, 137.6, 131.1, 119.8, 108.7, 86.3, 45.4, 26.3, 26.0, 25.4, 24.1, 18.4, 18.4, 18.3, 13.4, 13.4. IR(neat) 3235, 2944, 2865, 1744, 1690, 1463, 1374, 1329, 1239, 1099, 1046, 1003, 918, 880, 829, 765, 672 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 348.1975 [(M+Na)<sup>+</sup>; calculated for C<sub>17</sub>H<sub>31</sub>NO<sub>3</sub>Si: 348.1965]. R<sub>F</sub>: 0.15 in 15% EtOAc/Hex.

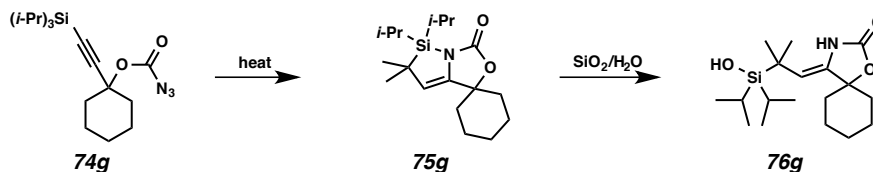
**4-allyl-1,1-diisopropyl-2,2,4-trimethyl-2,4-dihydro-1*H*,6*H*-[1,2]azasilolo[1,5-*c*]oxazol-6-one (75e)** was observed in crude NMR (52% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.35 (s, 1H, vinyl proton), MS (EI) *m/z*: 307 [(M<sup>+</sup>); calculated for C<sub>17</sub>H<sub>29</sub>NO<sub>2</sub>Si: 307.20]



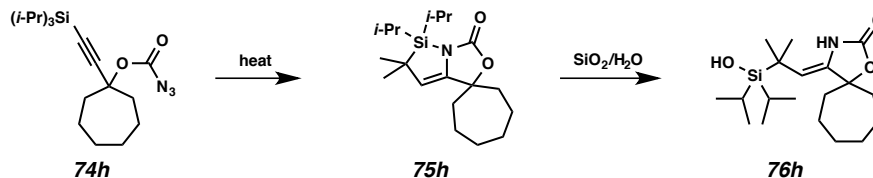
**(*Z*)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-1-oxa-3-azaspiro[4.4]nonan-2-one (76f)** was synthesized from carbonazidate **74f** using General Procedure D1. The crude product was purified by column chromatography on silica gel using 10% EtOAc in hexanes as an eluent. The silanol **76f** was obtained as an amorphous yellowish solid. (trial 1: 16.6 mg, 51% yield; trial 2: 14.6 mg, 45% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.30 (s, 1H), 4.76 (s, 1H), 4.26 (s, 1H), 2.17–2.03 (m, 2H), 1.92–1.66 (m, 6H), 1.13 (s, 6H), 1.09–1.01 (m, 14H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 157.4, 137.7, 107.9, 95.1, 41.1, 41.1, 25.6, 25.6, 24.2, 24.2, 24.0, 18.4, 18.4, 18.4, 18.4, 13.4, 13.4. IR(neat) 3350, 2941, 2864, 1746, 1692, 1464, 1432, 1340, 1311, 1247, 1080, 991, 880, 791, 765, 674 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 348.1970 [(M+Na)<sup>+</sup>; calculated for C<sub>17</sub>H<sub>31</sub>NO<sub>3</sub>SiNa: 348.1965]. R<sub>F</sub>: 0.2 in 20% EtOAc/Hex.

**1',1'-diisopropyl-2',2'-dimethyl-1',2'-dihydro-6'*H*-spiro[cyclopentane-1,4'-[1,2]azasilolo[1,5-*c*]oxazol]-6'-one (75f)** was observed in crude NMR (52% yield). <sup>1</sup>H

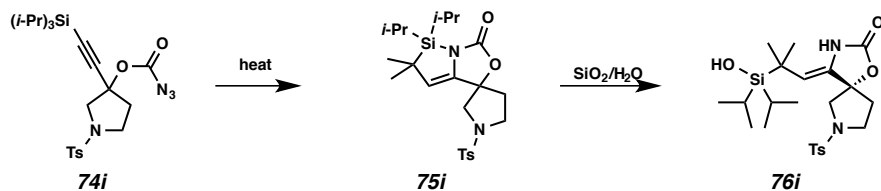
NMR (400 MHz, CDCl<sub>3</sub>) δ 4.39 (s, 1H, vinyl proton), MS (EI) *m/z*: 307 [(M+); calculated for C<sub>17</sub>H<sub>29</sub>NO<sub>2</sub>Si: 307.20]



**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-1-oxa-3-azaspiro[4.5]decan-2-one (76g)** was synthesized from carbonazidate **74g** using General Procedure D1. The crude product was purified by column chromatography on silica gel using 10% EtOAc in hexanes as an eluent. The silanol **76g** was obtained as a yellowish solid. (trial 1: 16.9 mg, 50% yield; trial 2: 16.2 mg, 48% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.15 (s, 1H), 4.44 (s, 1H), 4.20 (s, 1H), 1.94–1.81 (m, 2H), 1.78–1.54 (m, 6H), 1.53–1.33 (m, 2H), 1.12 (s, 6H), 1.09–0.90 (m, 14H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 157.6, 139.3, 108.3, 86.8, 37.1, 37.1, 25.7, 25.7, 24.7, 23.9, 21.7, 21.7, 18.4, 18.4, 13.4, 13.4. IR(neat) 3195, 2931, 2866, 1754, 1690, 1463, 1421, 1306, 1148, 1005, 945, 885, 867, 727, 699, 662 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 362.2127 [(M+Na)<sup>+</sup>; calculated for C<sub>18</sub>H<sub>33</sub>NO<sub>3</sub>SiNa: 362.2122]. R<sub>F</sub>: 0.24 in 20% EtOAc/Hex. MP: 123–125 °C. **1',1'-diisopropyl-2',2'-dimethyl-1',2'-dihydro-6'H-spiro[cyclohexane-1,4'-[1,2]azasilolo[1,5-c]oxazol]-6'-one (75g)** was observed in crude NMR (51% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.34 (s, 1H, vinyl proton), MS (EI) *m/z*: 321 [(M+); calculated for C<sub>18</sub>H<sub>31</sub>NO<sub>2</sub>Si: 321.21]

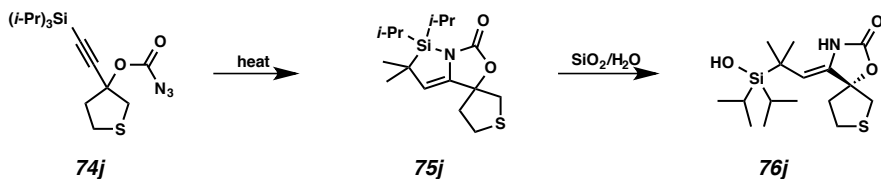


**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-1-oxa-3-azaspiro[4.6]undecan-2-one (76h)** was synthesized from carbonazidate **74h** using General Procedure D1. The crude product was purified by column chromatography on silica gel using 10% EtOAc in hexanes as an eluent. The silanol **76h** was obtained as an amorphous white solid. (trial 1: 16.5 mg, 47% yield; trial 2: 16.2 mg, 46% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.20 (s, 1H), 4.61 (s, 1H), 4.25 (s, 1H), 2.05–1.92 (m, 2H), 1.83–1.59 (m, 6H), 1.59–1.45 (m, 4H), 1.12 (s, 6H), 1.09–0.89 (m, 14H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 157.6, 140.9, 108.1, 90.1, 40.8, 28.8, 25.7, 21.9, 18.4, 18.4, 13.5. IR(neat) 3282, 2924, 2861, 1740, 1683, 1455, 1444, 1368, 1276, 1143, 1086, 1058, 1003, 952, 869, 849, 821, 786, 663 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 376.2282 [(M+Na)<sup>+</sup>; calculated for C<sub>19</sub>H<sub>35</sub>NO<sub>3</sub>SiNa: 376.2278]. R<sub>F</sub>: 0.27 in 20% EtOAc/Hex. **1',1'-diisopropyl-2',2'-dimethyl-1',2'-dihydro-6'H-spiro[cycloheptane-1,4'-[1,2]azasilolo[1,5-c]oxazol]-6'-one (75h)** was observed in crude NMR (56% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.39 (s, 1H, vinyl proton), MS (EI) *m/z*: 335 [(M+); calculated for C<sub>19</sub>H<sub>33</sub>NO<sub>2</sub>Si: 335.23]



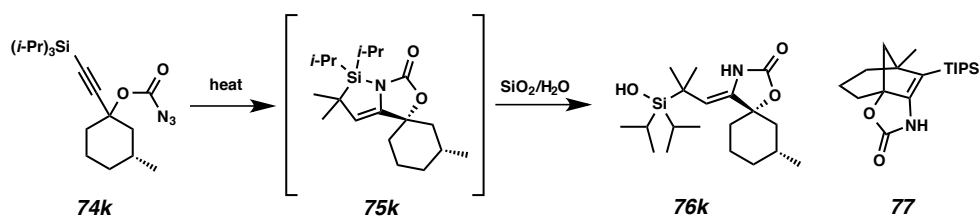
**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-7-tosyl-1-oxa-3,7-diazaspiro[4.4]nonan-2-one (76i)** was synthesized from carbonazidate **74i** using General Procedure D2. The crude product was purified by column chromatography on silica gel using 25% EtOAc in hexanes as an eluent. The silanol **76i** was obtained as a white solid. (trial 1: 23.5 mg, 49% yield; trial 2: 23.0 mg, 48% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 1H), 7.69 (d,  $J = 8.4$  Hz, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 4.31 (s, 1H), 3.74–3.66 (m, 1H), 3.50 (q,  $J = 12.1$  Hz, 2H), 3.36 (s, 1H), 3.23 (ddd,  $J = 11.2, 9.6, 6.1$  Hz, 1H), 2.42 (s, 3H), 2.16 (dd,  $J = 13.6, 5.9$  Hz, 1H), 2.04–1.89 (m, 1H), 1.11 (s, 6H), 1.09–0.86 (m, 14H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 144.0, 133.4, 133.3, 129.9, 127.6, 110.3, 90.4, 59.5, 47.2, 39.8, 25.4, 25.2, 24.2, 21.6, 18.4, 18.4, 18.3, 18.3, 13.2, 13.2. **IR**(neat) 2943, 2865, 1747, 1699, 1597, 1494, 1462, 1360, 1342, 1239, 1167, 1149, 1039, 1017, 993, 949, 910, 815, 732, 764, 706, 660  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 503.2011  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{36}\text{N}_2\text{O}_5\text{SSiNa}$ : 503.2006]. **R<sub>F</sub>**: 0.24 in 30% EtOAc/Hex. **MP**: 150–152 °C.

**1',1'-diisopropyl-2',2'-dimethyl-1-tosyl-1',2'-dihydro-6'H-spiro[pyrrolidine-3,4'-[1,2]azasilolo[1,5-c]oxazol]-6'-one (75i)** was observed in crude NMR (50% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.41 (s, 1H, vinyl proton), **MS** (EI)  $m/z$ : 462  $[(\text{M}+)]$ ; calculated for  $\text{C}_{23}\text{H}_{34}\text{N}_2\text{O}_4\text{SSi}$ : 462.20]



**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-1-oxa-7-thia-3-azaspiro[4.4]nonan-2-one (76j)** was synthesized from carbonazidate **74j** using General Procedure D2. The crude product was purified by column chromatography on silica gel using 25% EtOAc in hexanes as an eluent. The silanol **76j** was obtained as an amorphous white solid. (trial 1: 14.5 mg, 42% yield; trial 2: 14.0 mg, 41% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.36 (s, 1H), 4.48 (s, 1H), 4.45 (s, 1H), 3.16 (d,  $J = 12.1$  Hz, 1H), 3.13–3.04 (m, 1H), 3.00 (d,  $J = 12.3$  Hz, 1H), 2.98–2.92 (m, 1H), 2.44–2.36 (m, 1H), 2.06–1.95 (m, 1H), 1.14 (s, 6H), 1.10–0.99 (m, 14H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 133.7, 109.9, 94.3, 43.2, 42.6, 29.3, 25.5, 25.4, 24.3, 18.4, 18.3, 13.3. **IR**(neat) 3391, 2945, 2864, 1749, 1690, 1623, 1462, 1385, 1371, 1334, 1297, 1278, 1246, 1067, 992, 881, 824, 755, 666  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 366.1534  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{16}\text{H}_{29}\text{NO}_3\text{SSiNa}$ : 366.1530]. **R<sub>F</sub>**: 0.21 in 20% EtOAc/Hex.

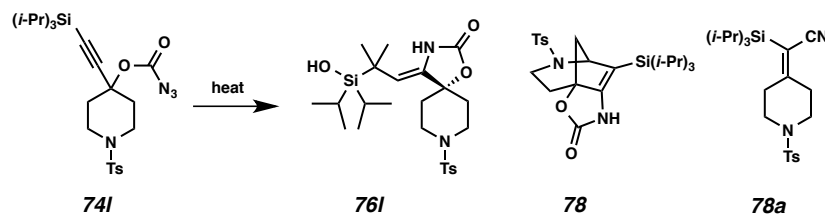
**1',1'-diisopropyl-2',2'-dimethyl-1',2',4,5-tetrahydro-2H,6'H-spiro[thiophene-3,4'-[1,2]azasilolo[1,5-c]oxazol]-6'-one (75j)** was observed in crude NMR (45% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.58 (s, 1H, vinyl proton), **MS** (EI)  $m/z$ : 325  $[(\text{M}+)]$ ; calculated for  $\text{C}_{16}\text{H}_{27}\text{NO}_2\text{SSi}$ : 325.15]



**(5*S*,7*R*,*Z*)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-7-methyl-1-oxa-3-azaspiro[4.5]decan-2-one (76k)** was synthesized from carbonazidate **74k** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 10% EtOAc in hexanes as eluents. The silanol **76k** was obtained as an amorphous yellowish solid. (trial 1: 12.4 mg, 35% yield; trial 2: 12.3 mg, 35% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.23 (s, 1H), 4.60 (s, 1H), 4.43 (s, 1H), 2.00–1.41 (m, 9H), 1.14 (s, 6H), 1.05 (s, 14H), 0.98 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 139.3, 109.8, 86.7, 43.4, 36.2, 32.0, 28.0, 25.8, 25.7, 24.2, 21.4, 19.8, 18.4, 18.4, 18.4, 18.3, 13.5, 13.5. **IR(neat)** 3088, 2926, 2863, 1745, 1678, 1463, 1367, 1323, 1286, 1250, 1206, 1155, 1134, 1058, 972, 935, 921, 826, 791, 668  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 376.2283 [( $\text{M}+\text{Na}$ ) $^+$ ; calculated for  $\text{C}_{19}\text{H}_{35}\text{NO}_3\text{SiNa}$ : 376.2278]. **R<sub>F</sub>**: 0.18 in 15% EtOAc/Hex.

**(1*S*,3*R*)-1',1'-diisopropyl-2',2',3-trimethyl-1',2'-dihydro-6'*H*-spiro[cyclohexane-1,4'-[1,2]azasilolo[1,5-*c*]oxazol]-6'-one (75k)** was observed in crude NMR (36% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.50 (s, 1H, vinyl proton), **MS** (EI)  $m/z$ : 335 [( $\text{M}+$ ); calculated for  $\text{C}_{19}\text{H}_{33}\text{NO}_2\text{Si}$ : 335.23]

**(5*S*,8*aS*)-5-methyl-4-(triisopropylsilyl)-5,6,7,8-tetrahydro-5,8a-methanocyclohepta[*d*]oxazol-2(3*H*)-one (77)** was synthesized from carbonazidate **74k** using General Procedure D1. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 10% EtOAc in hexanes as eluents. The tricyclic **77** was obtained as a white solid. (trial 1: 11.3 mg, 34% yield; trial 2: 11.8 mg, 35% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.66 (s, 1H), 2.15–2.01 (m, 1H), 1.86–1.68 (m, 3H), 1.65 (d,  $J = 9.1$  Hz, 1H), 1.62–1.52 (m, 1H), 1.43 (d, 1H), 1.32–1.19 (m, 4H), 1.19–0.94 (m, 21H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 152.4, 106.1, 92.7, 57.7, 53.7, 32.6, 28.8, 27.8, 20.8, 19.1, 19.1, 19.1, 19.1, 19.1, 17.7, 12.5, 12.5, 12.2. **IR(neat)** 3230, 2938, 2864, 1756, 1629, 1465, 1321, 1277, 1229, 1008, 976, 944, 881, 846, 745, 712, 665  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 358.2177 [( $\text{M}+\text{Na}$ ) $^+$ ; calculated for  $\text{C}_{19}\text{H}_{33}\text{NO}_2\text{SiNa}$ : 358.2173]. **R<sub>F</sub>**: 0.39 in 15% EtOAc/Hex. **MP** 120–122 °C

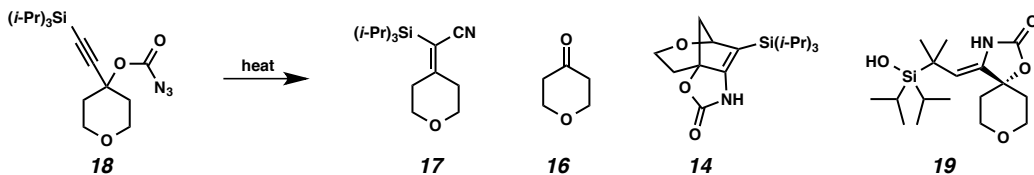


**(*Z*)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-8-tosyl-1-oxa-3,8-diazaspiro[4.5]decan-2-one (76l)** was synthesized from carbonazidate **74l** using General Procedure D2. The crude product was purified by column chromatography on silica gel

using a gradient of 10 to 20% EtOAc in hexanes as eluents. The silanol **76I** was obtained as a white solid. (trial 1: 25.7 mg, 52% yield; trial 2: 26.2 mg, 53% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (s, 1H), 7.60 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 7.9$  Hz, 2H), 4.25 (s, 1H), 3.84–3.67 (m, 3H), 3.35 (t,  $J = 6.1$  Hz, 1H), 2.59–2.47 (m, 3H), 2.43 (s, 3H), 1.90–1.82 (m, 2H), 1.11 (s, 6H), 1.06–0.92 (m, 14H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 143.9, 136.9, 132.7, 129.9, 127.6, 109.6, 82.9, 45.9, 42.34, 40.6, 36.1, 25.4, 24.0, 21.5, 18.4, 13.3. **IR(neat)** 3335, 2946, 2867, 1745, 1698, 1595, 1464, 1376, 1314, 1259, 1180, 1085, 1003, 944, 932, 913, 894, 877, 765, 742, 721, 675  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 517.2167  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{24}\text{H}_{38}\text{N}_2\text{O}_5\text{SSiNa}$ : 517.2163]. **R<sub>F</sub>**: 0.24 in 30% EtOAc/Hex. **MP**: 201–202 °C.

**(5S,8aS)-6-tosyl-4-(triisopropylsilyl)-5,6,7,8-tetrahydro-5,8a-methanooxazolo[4,5-d]azepin-2(3H)-one (78)** was synthesized from carbonazidate **74I** using General Procedure D2. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 20% EtOAc in hexanes as eluents. The tricycle **56** was obtained as a white solid. (trial 1: 9.5 mg, 20% yield; trial 2: 10.0 mg, 21% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 8.1$  Hz, 2H), 7.16 (s, 1H), 5.07 (d,  $J = 4.0$  Hz, 1H), 3.91 (dd,  $J = 14.7, 6.8$  Hz, 1H), 3.47 (ddd,  $J = 14.7, 11.9, 5.4$  Hz, 1H), 2.42 (s, 3H), 2.09–2.02 (m, 1H), 1.97–1.86 (m, 1H), 1.65 (d,  $J = 9.7$  Hz, 1H), 1.62–1.53 (m, 2H), 1.18–0.93 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 156.3, 143.6, 137.5, 129.9, 127.1, 100.5, 91.6, 65.3, 48.2, 40.9, 30.8, 21.6, 18.5, 11.5. **IR(neat)** 3206, 2942, 2863, 1770, 1655, 1597, 1459, 1339, 1297, 1223, 1207, 1165, 1153, 1094, 1009, 959, 926, 902, 767, 729, 706, 661  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 499.2060  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_4\text{SSiNa}$ : 499.2057]. **R<sub>F</sub>**: 0.42 in 30% EtOAc/Hex. **MP**: 199–200 °C.

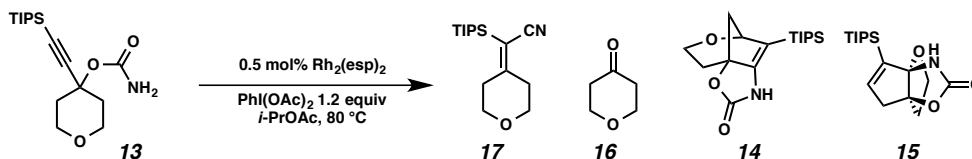
**2-(1-tosylpiperidin-4-ylidene)-2-(triisopropylsilyl)acetonitrile (78a)** was synthesized from carbonazidate **74I** using General Procedure D2. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 20% EtOAc in hexanes as an eluent. The nitrile **78a** was obtained as a white solid. (trial 1: 4.3 mg, 10% yield; trial 2: 4.8 mg, 11% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 8.3$  Hz, 2H), 7.32 (d,  $J = 8.1$  Hz, 2H), 3.15 (t,  $J = 5.9$  Hz, 2H), 3.11 (t,  $J = 5.7$  Hz, 2H), 2.86 (t,  $J = 5.9$  Hz, 2H), 2.51 (t,  $J = 5.9$  Hz, 2H), 2.42 (s, 3H), 1.37–1.24 (m, 3H), 1.11–0.90 (m, 18H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 144.0, 133.2, 129.8, 127.5, 119.9, 106.3, 46.8, 46.5, 35.9, 34.4, 21.6, 18.5, 12.6. **IR(neat)** 2946, 2863, 2190, 1766, 1656, 1596, 1494, 1357, 1227, 1162, 1101, 1072, 954, 935, 903, 815, 800, 732, 712, 701, 676  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 455.2165  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{36}\text{N}_2\text{O}_2\text{SSiNa}$ : 455.2159]. **R<sub>F</sub>**: 0.6 in 30% EtOAc/Hex. **MP**: 96–98 °C.



**2-(tetrahydro-4H-pyran-4-ylidene)-2-(triisopropylsilyl)acetonitrile (17)** was synthesized from carbonazidate **18** using General Procedure D2. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 20% EtOAc in hexanes as an eluent. The nitrile **17** was obtained as a white solid. (trial 1: 1.4 mg, 5% yield; trial 2: 1.3 mg, 4% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.80 (t,  $J = 5.7$  Hz, 2H), 3.74 (t,  $J = 5.7$  Hz, 2H), 2.82 (t,  $J = 5.7$  Hz, 2H), 2.47 (t,  $J = 5.7$  Hz, 2H), 1.41–1.31 (m, 3H), 1.11 (m, 18H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 120.5, 104.2, 69.0, 68.5, 38.0, 36.6, 18.7, 13.0. **IR(neat)** 2941, 2889, 2863, 2846, 2195, 1756, 1574, 1459, 1430, 1374, 1318, 1288, 1222, 1264, 1172, 1021, 916, 882, 872, 709, 678  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 280.2095  $[(\text{M}+\text{H})^+]$ ; calculated for  $\text{C}_{16}\text{H}_{30}\text{NOSi}$ : 280.2097]. **R<sub>F</sub>**: 0.51 in 20% EtOAc/Hex. **MP** 53–55 °C.

**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-1,8-dioxa-3-azaspiro[4.5]decan-2-one (19)** was synthesized from carbonazidate **18** using General Procedure D2. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 20% EtOAc in hexanes as eluents. The silanol **19** was obtained as a white solid. (trial 1: 15.6 mg, 46% yield; trial 2: 14.0 mg, 41% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.10 (s, 1H), 4.28 (s, 1H), 3.99 (s, 1H), 3.93–3.82 (m, 2H), 3.75 (ddd,  $J = 11.8, 11.9, 2.3$  Hz, 2H), 1.91–1.65 (m, 4H), 1.14 (s, 6H), 1.05 (s, 14H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 137.8, 109.2, 83.5, 63.8, 37.1, 25.6, 24.0, 18.4, 13.4. **IR(neat)** 3280, 3064, 2951, 2968, 2858, 1748, 1701, 1427, 1385, 1301, 1255, 1244, 1125, 1100, 1021, 1005, 947, 895, 843, 822, 778, 728, 677  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 364.1918  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{17}\text{H}_{31}\text{NO}_4\text{SiNa}$ : 364.1915]. **R<sub>F</sub>**: 0.18 in 20% EtOAc/Hex. **MP**: 76–78 °C.

**(5S,8aS)-4-(triisopropylsilyl)-3,5,7,8-tetrahydro-2H-5,8a-methanooxepino[4,5-d]oxazol-2-one (14)** was synthesized from carbonazidate **18** using General Procedure D2. The crude product was purified by column chromatography on silica gel using a gradient of 5 to 20% EtOAc in hexanes as eluents. The tricyclic **14** was obtained as a white solid. (trial 1: 9.1 mg, 28% yield; trial 2: 10.1 mg, 31% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 (s, 1H), 4.98 (d,  $J = 2.9$  Hz, 1H), 4.09–4.01 (m, 1H), 3.88 (dd,  $J = 10.9, 6.9$  Hz, 1H), 2.34–2.26 (m, 2H), 2.18 (d,  $J = 9.2$  Hz, 1H), 1.69–1.63 (m, 1H), 1.19–1.10 (m, 3H), 1.09–1.04 (m, 18H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 156.5, 98.2, 91.9, 84.9, 60.6, 52.3, 32.6, 31.1, 18.8, 18.6, 11.8. **IR(neat)** 3204, 2942, 2864, 1752, 1690, 1651, 1337, 1316, 1248, 1219, 162, 1297, 1100, 1069, 1040, 968, 940, 914, 881, 855, 729, 700  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 346.1814  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{SiNa}$ : 346.1809]. **R<sub>F</sub>**: 0.39 in 20% EtOAc/Hex. **MP**: 95–97 °C.

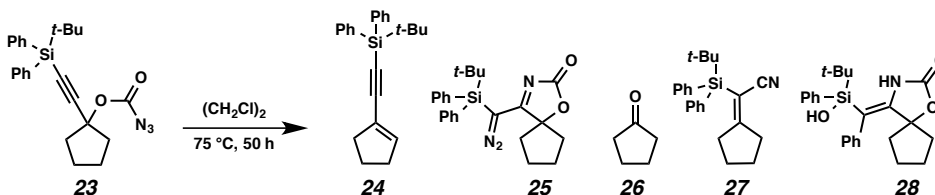


A 2 dram vial was charged with magnetic stir bar, alkynyl carbamate **13** (65 mg, 0.2 mmol, 1.0 equiv),  $\text{PhI}(\text{OAc})_2$  (77.3 mg, 0.24 mmol, 1.2 equiv) and  $\text{Rh}_2(\text{esp})_2$  (0.8 mg, 0.0001 mmol, 0.5 mol%). Isopropyl acetate (2 mL, 0.1 M) was added and the vial was sealed. The reaction mixture was heated at 80 °C for 21 hours. When cooled to room

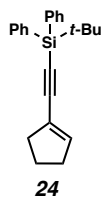


temperature, solvents were removed via rotary evaporation and the residue was purified by flash column chromatography on silica gel using a gradient of 5 to 20% EtOAc in hexanes as eluents. **2-(tetrahydro-4H-pyran-4-ylidene)-2-(triisopropylsilyl)acetonitrile (17)** was obtained as a white solid. (9 mg, 16% yield). **(5S,8aS)-4-(triisopropylsilyl)-3,5,7,8-tetrahydro-2H-5,8a-methanooxepino[4,5-d]oxazol-2-one (14)** was obtained as a white solid. (8 mg, 12% yield).

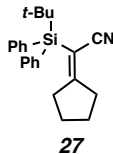
**(3aR,6aR)-6-(triisopropylsilyl)-2,3-dihydro-4H-3a,6a-(epoxymethanoimino)cyclopenta[b]furan-8-one (15)** was obtained as a white solid. (17 mg, 27% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.02 (t,  $J = 2.3$  Hz, 1H), 5.54 (s, 1H), 4.10–4.05 (m, 1H), 3.98–3.91 (m, 1H), 2.97–2.80 (m, 2H), 2.52–2.45 (m, 1H), 1.98–1.88 (m, 1H), 1.19–1.01 (m, 21H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 144.2, 139.8, 112.1, 97.4, 67.4, 45.1, 38.9, 18.8, 18.7, 18.7, 11.4. **IR**(neat) 3258, 2941, 2864, 1745, 1651, 1574, 1462, 1383, 1335, 1274, 1298, 1066, 1144, 999, 985, 959, 937, 922, 880, 818, 766, 710, 679  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 346.1814  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{SiNa}$ : 346.1809]. **R<sub>F</sub>**: 0.3 in 20% EtOAc/Hex. **MP**: 95–97 °C.



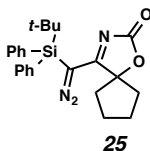
A 2 dram vial was charged with a magnetic spin bar, carbonazidate **23** (0.3 mmol, 1 equiv), and distilled 1,2-dichloroethane (0.1 M, 3 mL). The reaction vessel was sealed and heated in an oil bath at 75 °C. The progress of the reaction was monitored by TLC. After 50 h, the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 20% EtOAc in hexanes as eluents.



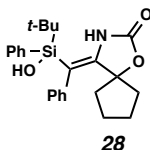
**tert-butyl(cyclopent-1-en-1-ylethynyl)diphenylsilane (24)** was obtained as a colorless oil. (19.8 mg, 20% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85–7.75 (m, 4H), 7.44–7.31 (m, 6H), 6.26–6.20 (m, 1H), 2.62–2.51 (m, 2H), 2.50–2.40 (m, 2H), 2.03–1.88 (m, 2H), 1.08 (s, 9H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 135.6, 133.6, 129.4, 127.6, 124.7, 106.7, 90.3, 36.4, 33.4, 27.1, 23.3, 18.6. **IR**(neat) 3069, 2956, 2928, 2891, 2855, 2143, 1470, 1427, 1389, 1360, 1259, 1157, 1107, 1008, 998, 875, 819, 741, 724, 697  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 330.1800  $[(\text{M})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{26}\text{Si}$ : 330.1804]. **R<sub>F</sub>**: 0.75 in 10% EtOAc/Hex.



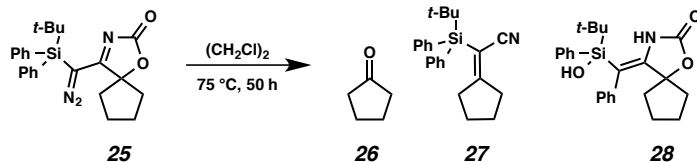
**2-((tert-butyl)diphenylsilyl)-2-cyclopentylideneacetonitrile (27)** was obtained as a white solid. (15.4 mg, 15% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72–7.66 (m, 4H), 7.45–7.34 (m, 6H), 2.84 (td,  $J = 7.4, 1.7$  Hz, 2H), 1.70–1.58 (m, 4H), 1.50–1.39 (m, 2H), 1.12 (s, 9H).  $^{13}\text{C NMR}$  (125.77 MHz,  $\text{CDCl}_3$ )  $\delta$  189.7, 135.7, 132.4, 129.7, 128.0, 121.3, 98.4, 38.0, 35.9, 27.1, 26.9, 24.9, 18.7. **IR(neat)** 3048, 2955, 2861, 2194, 1751, 1576, 1450, 1427, 1391, 1362, 1336, 1105, 1011, 997, 941, 821, 742, 700, 686  $\text{cm}^{-1}$ . **HRMS** (CI)  $m/z$ : 346.1995  $[(\text{M}+\text{H})^+]$ ; calculated for  $\text{C}_{23}\text{H}_{27}\text{NSi}$ : 346.1991]. **R<sub>F</sub>**: 0.51 in 10% EtOAc/Hex. **MP**: 103–105 °C.



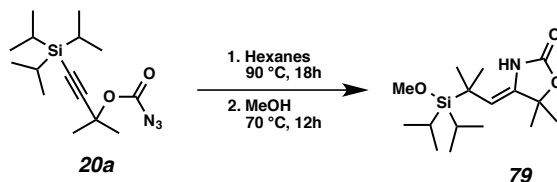
**4-((tert-butyl)diphenylsilyl)(diazo)methyl-1-oxa-3-azaspiro[4.4]non-3-en-2-one (25)** was obtained as a yellow solid. (18.8 mg, 15% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61–7.55 (m, 4H), 7.49–7.41 (m, 2H), 7.41–7.34 (m, 4H), 2.21–2.06 (m, 4H), 2.06–1.90 (m, 2H), 1.89–1.70 (m, 2H), 1.25 (s, 9H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 165.6, 136.5, 135.9, 130.9, 130.4, 128.3, 128.1, 96.6, 37.8, 37.0, 29.0, 27.7, 26.0, 23.4, 19.9. **IR(neat)** 3071, 2955, 2856, 2196, 1579, 1427, 1388, 1359, 1258, 1107, 998, 956, 819, 739, 698  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 440.1767  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_2\text{SiNa}$ : 440.1765]. **R<sub>F</sub>**: 0.21 in 10% EtOAc/Hex. **MP**: 108–109 °C.



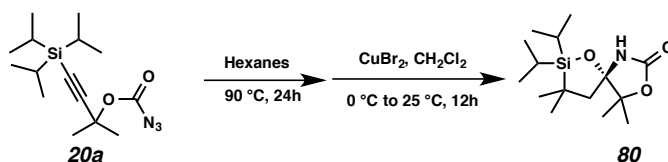
**(Z)-4-((tert-butyl(hydroxy)(phenyl)silyl)(phenyl)methylene)-1-oxa-3-azaspiro[4.4]nonan-2-one (28)** was obtained as a white solid. (12.3 mg, 10% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (s, 1H), 7.46–7.01 (m, 10H), 5.76 (s, 1H), 2.18–1.98 (m, 2H), 1.83–1.72 (m, 1H), 1.72–1.43 (m, 3H), 1.20–1.07 (m, 1H), 0.95 (s, 10H).  $^{13}\text{C NMR}$  (100.52 MHz,  $\text{CDCl}_3$ )  $\delta$  157.1, 149.6, 136.8, 134.7, 134.1, 129.5, 127.5, 127.4, 126.5, 107.1, 97.1, 40.7, 38.7, 26.6, 24.2, 20.7. **IR(neat)** 3074, 2949, 2862, 2196, 1980, 1741, 1579, 1428, 1390, 1363, 1262, 1108, 999, 823, 739, 699  $\text{cm}^{-1}$ . **HRMS** (ESI)  $m/z$ : 430.1813  $[(\text{M}+\text{Na})^+]$ ; calculated for  $\text{C}_{24}\text{H}_{29}\text{NO}_3\text{SiNa}$ : 430.1809]. **R<sub>F</sub>**: 0.15 in 20% EtOAc/Hex. **MP**: 166–168 °C.



A 2 dram vial was charged with a magnetic spin bar, diazo **25** (62 mg, 0.15 mmol, 1 equiv), and distilled 1,2-dichloroethane (0.1 M, 1.5 mL). The reaction vessel was sealed and heated in an oil bath at 75 °C. The progress of the reaction was monitored by TLC. After 50 h, the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 2 to 20% EtOAc in hexanes as eluents. Cyclopentanone **26** was observed on TLC (~30% yield). **Nitrile 27** was obtained as a white solid. (15.1 mg, 30% yield). Silanol **28** was obtained as a white solid. (15.0 mg, 25% yield).



**(Z)-4-(2-(diisopropyl(methoxy)silyl)-2-methylpropylidene)-5,5-dimethyloxazolidin-2-one (79)** A 2 dram vial was charged with a magnetic stir bar, carbonazidate **20a** (0.1 mmol), and dry hexanes (0.1 M, 1 mL). The reaction vessel was sealed and heated in an oil bath at 90 °C. (**Warning: Pressure buildup may occur during the reaction.**) The progress of the reaction was monitored by TLC. After the reaction was finished (18 h), the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. The crude product was then dissolved in dry methanol (0.1M, 1 mL) in a 2 dram vial. The vial was sealed and the reaction was heated to 70 °C. The progress of the reaction was monitored by TLC. After 12 h, the reaction mixture was cooled and concentrated. The crude product was purified by column chromatography on silica gel using a gradient of 0 to 5% EtOAc in hexanes as eluents. Compound **79** was obtained as a colorless oil. (16.0 mg, 51% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 4.15 (s, 1H), 3.59 (s, 3H), 1.41 (s, 6H), 1.23–0.98 (m, 20H). <sup>13</sup>C NMR (150.91 MHz, CDCl<sub>3</sub>) δ 156.1, 139.6, 107.0, 84.5, 51.8, 28.0, 25.9, 24.5, 18.6, 18.2, 12.8. IR(neat) 2945, 2866, 1757, 1688, 1464, 1384, 1297, 1171, 1104, 1067, 1002, 902, 885, 798, 731, 679 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 336.1969 [(M+Na)<sup>+</sup>; calculated for C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>SiNa: 336.1965]. R<sub>F</sub>: 0.36 in 20% EtOAc/Hex.



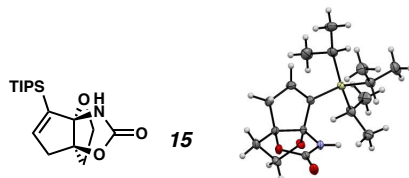
**2,2-diisopropyl-3,3,9,9-tetramethyl-1,8-dioxa-6-aza-2-silaspiro[4.4]nonan-7-one (80)** A 2 dram vial was charged with a magnetic stir bar, carbonazidate **20a** (0.2 mmol), and dry hexanes (0.1 M, 2 mL). The reaction vessel was sealed and heated in an oil bath at 90

°C. (**Warning: Pressure buildup may occur during the reaction.**) The progress of the reaction was monitored by TLC. After the reaction was finished (24 h), the reaction vessel was cooled to room temperature and the mixture was concentrated under reduced pressure. The crude product was then dissolved in dry dichloromethane (0.1 M, 2 mL). The mixture was cooled to 0 °C and stirred for 10 min. CuBr<sub>2</sub> (4.5 mg, 0.02 mmol, 0.1 equiv) was added in one portion. The progress of the reaction was monitored by TLC. After 12 h, the reaction mixture was filtered through a short celite pad and concentrated. The crude product was purified by column chromatography on silica gel using a gradient of 10 to 15% EtOAc in hexanes as eluents. Compound **80** was obtained as a white solid. (trial 1: 29.3 mg, 49% yield; trial 2: 28.7 mg, 48% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.14 (s, 1H), 1.85 (d, *J* = 14.0 Hz, 1H), 1.71 (d, *J* = 13.9 Hz, 1H), 1.38 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H), 1.16 (s, 3H), 1.14–0.92 (m, 14H). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>) δ 158.3, 95.3, 87.9, 48.8, 26.2, 26.2, 24.1, 23.6, 20.6, 17.9, 17.8, 17.6, 17.6, 13.4, 12.4. IR(neat) 3255, 2935, 2863, 1746, 1464, 1386, 1370, 1352, 1191, 1105, 1014, 989, 857, 907, 881, 846, 776, 683 cm<sup>-1</sup>. HRMS (ESI) *m/z*: 322.1813 [(M+Na)<sup>+</sup>; calculated for C<sub>15</sub>H<sub>29</sub>NO<sub>3</sub>SiNa: 322.1809]. R<sub>F</sub>: 0.15 in 20% EtOAc/Hex. MP: 114–116 °C.

### Crystallographic Data

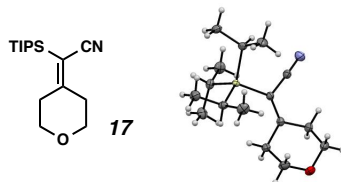
#### (3*aR*,6*aR*)-6-(triisopropylsilyl)-2,3-dihydro-4*H*-3*a*,6*a*-epoxymethanoimino)cyclopenta[*b*]furan-8-one (**15**)

The solved structure of **15** has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1477662.



#### 2-(tetrahydro-4*H*-pyran-4-ylidene)-2-(triisopropylsilyl)acetonitrile (**17**)

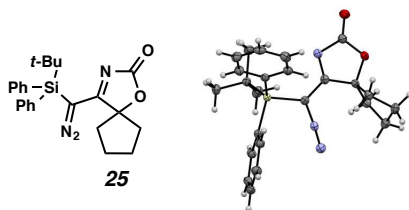
The solved structure of **17** has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1477728.



#### 4-((*tert*-butyldiphenylsilyl)(diazomethyl)-1-oxa-3-azaspiro[4.4]non-3-en-2-one (**25**)

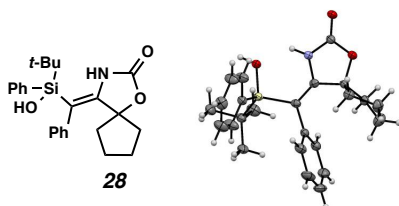
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Centre. CCDC 1477664.



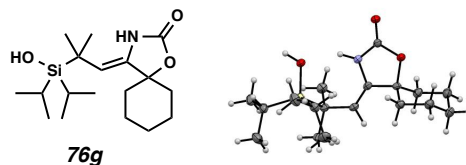
**(Z)-4-((*tert*-butyl(hydroxy)(phenyl)silyl)(phenyl)methylene)-1-oxa-3-azaspiro[4.4]nonan-2-one (28)**

The solved structure of **28** has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1477665.



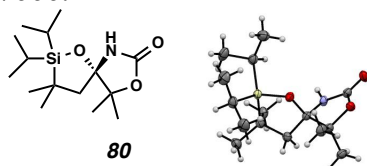
**(Z)-4-(2-(hydroxydiisopropylsilyl)-2-methylpropylidene)-1-oxa-3-azaspiro[4.5]decan-2-one (76g)**

The solved structure of **76g** has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1477663.

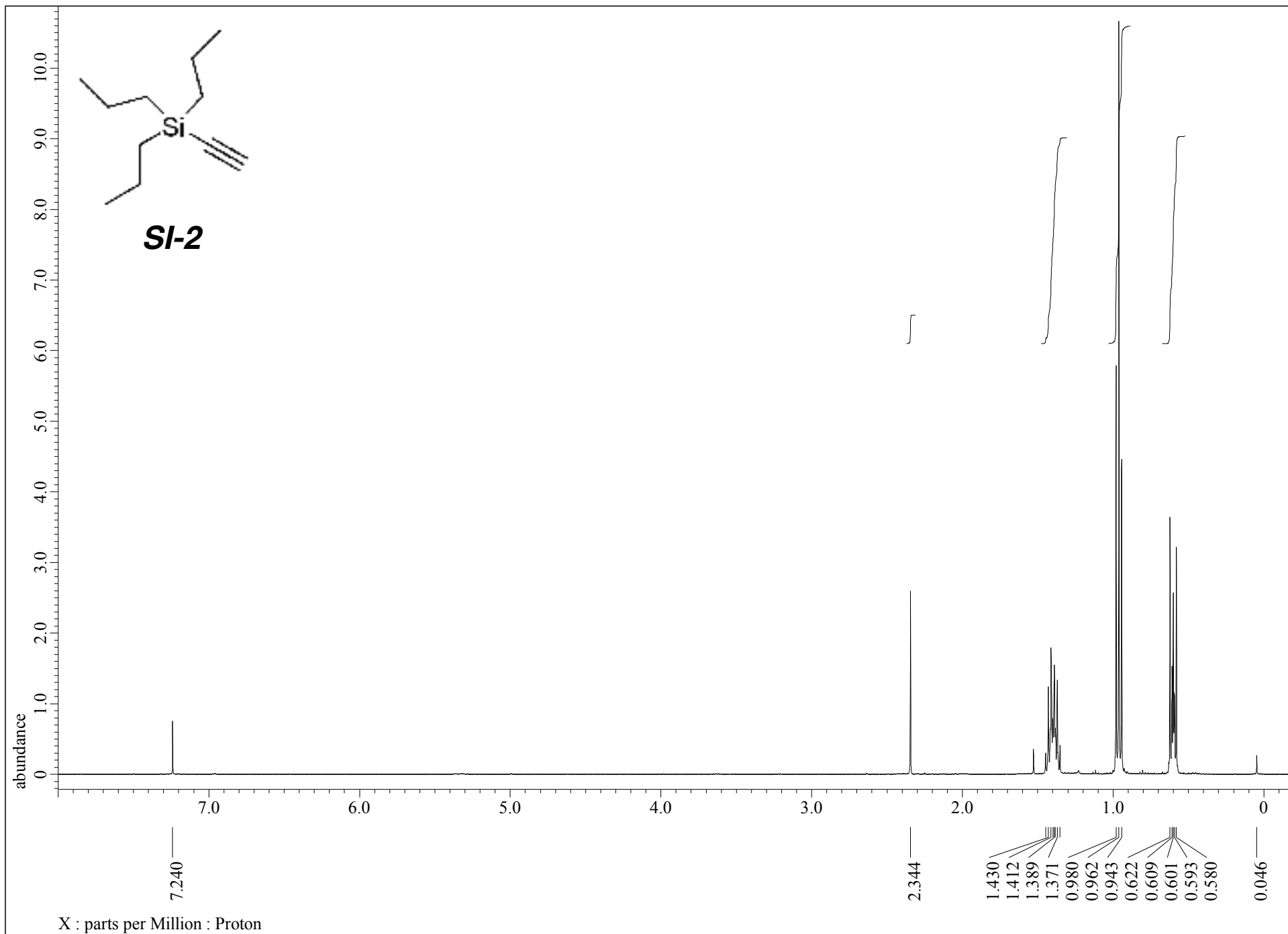


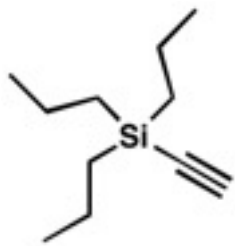
**2,2-diisopropyl-3,3,9,9-tetramethyl-1,8-dioxa-6-aza-2-silaspiro[4.4]nonan-7-one (80)**

The solved structure of **58** has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1477666.

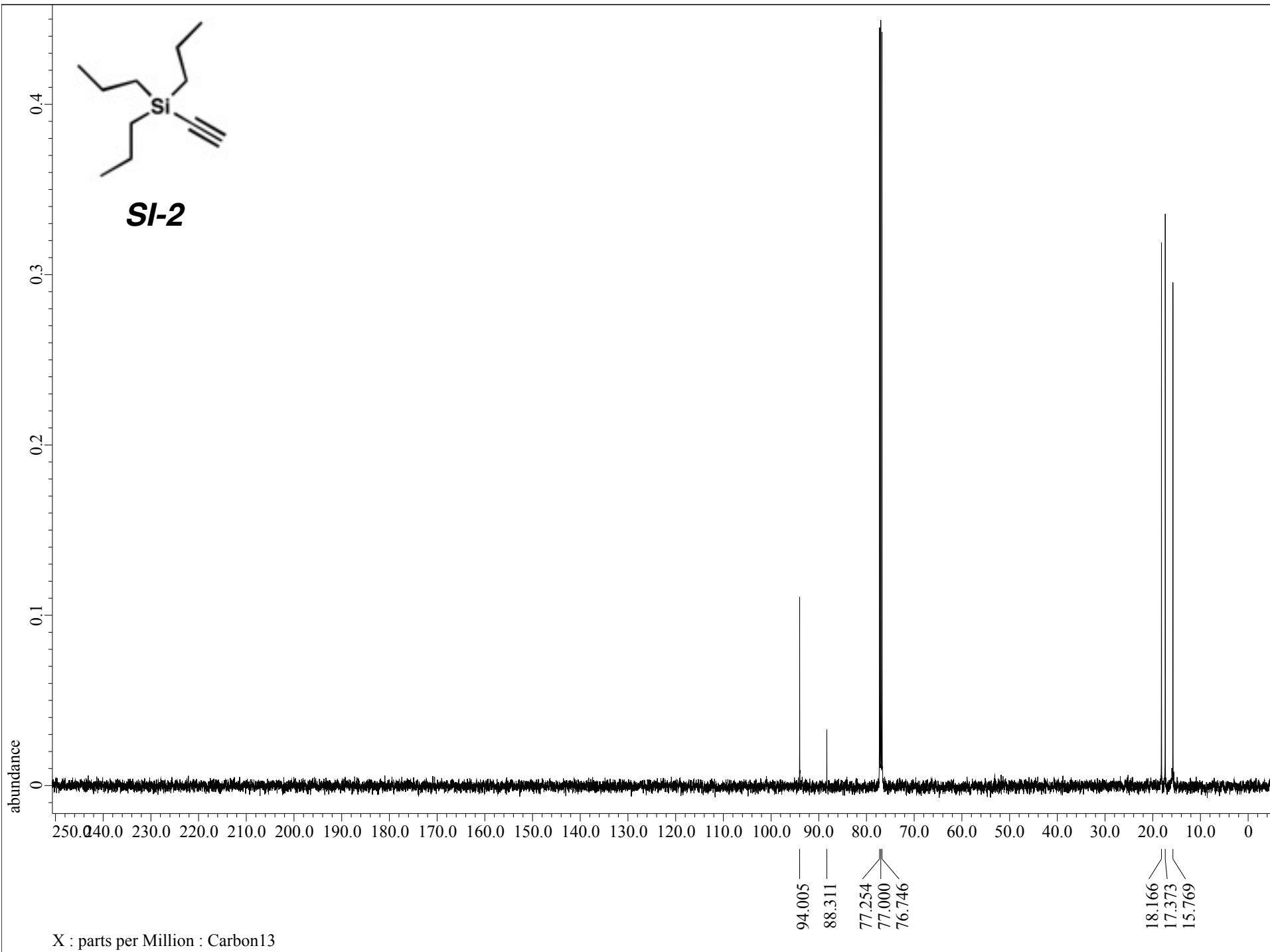


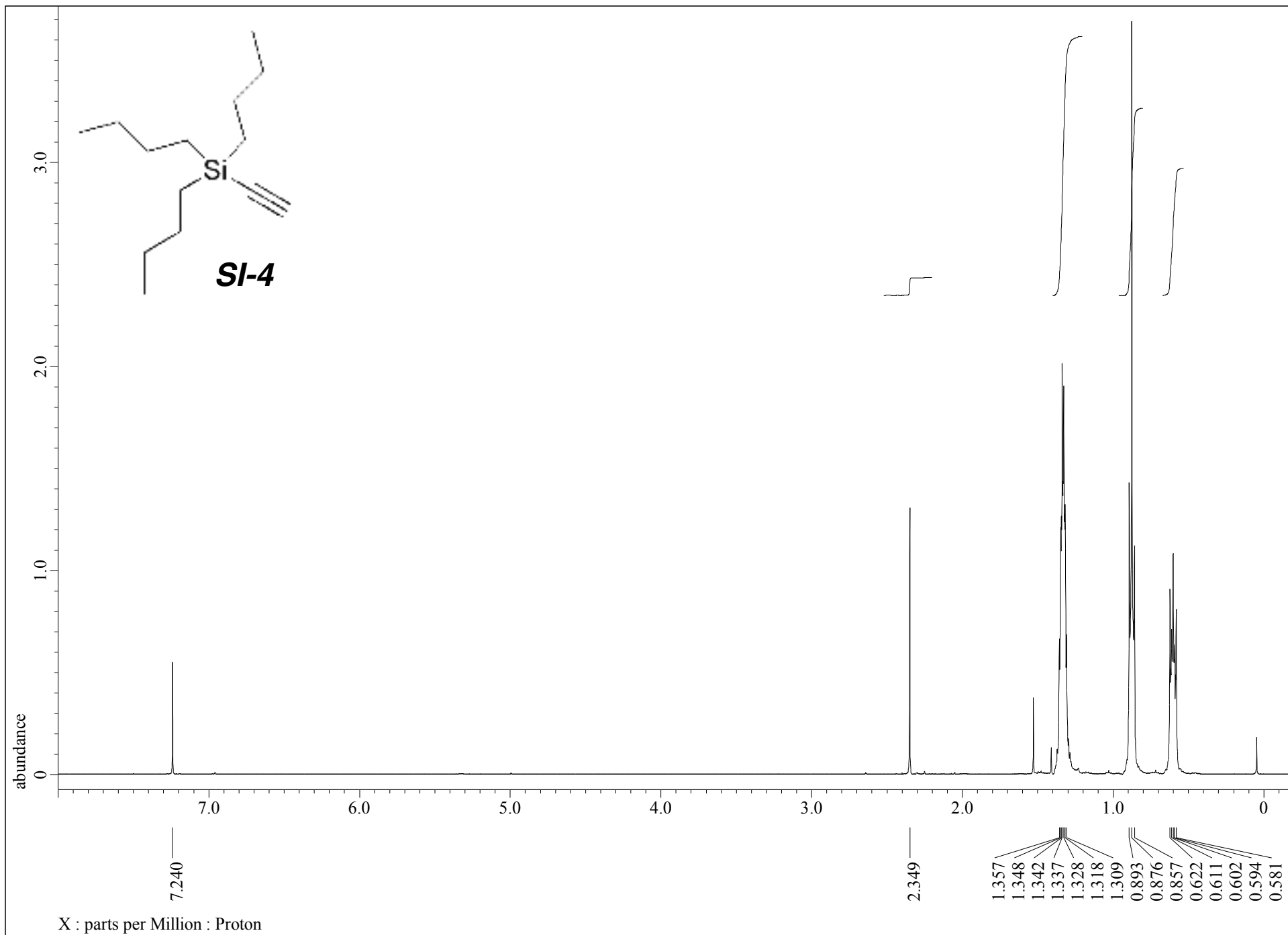
**Spectral Data**



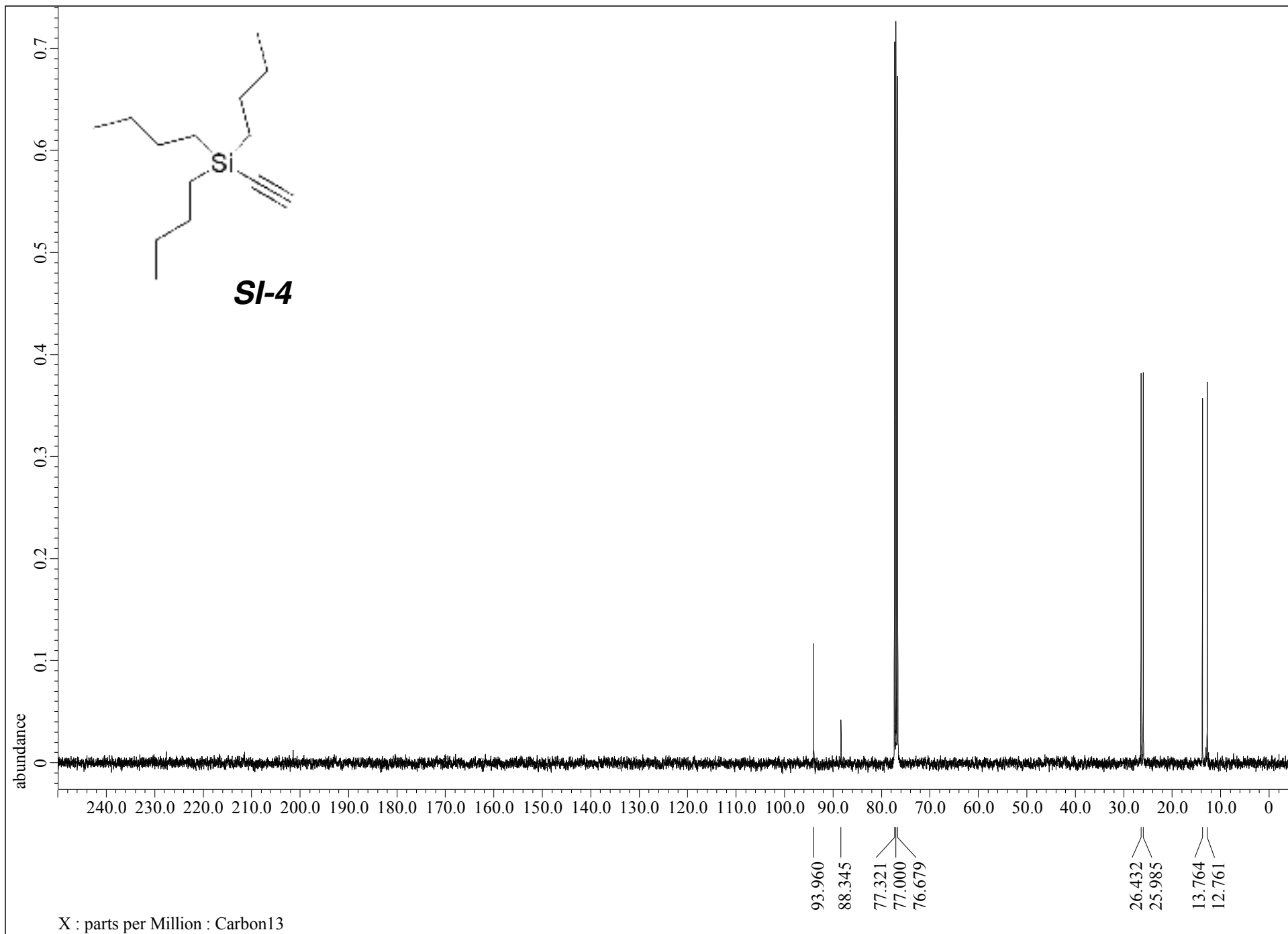


**SI-2**

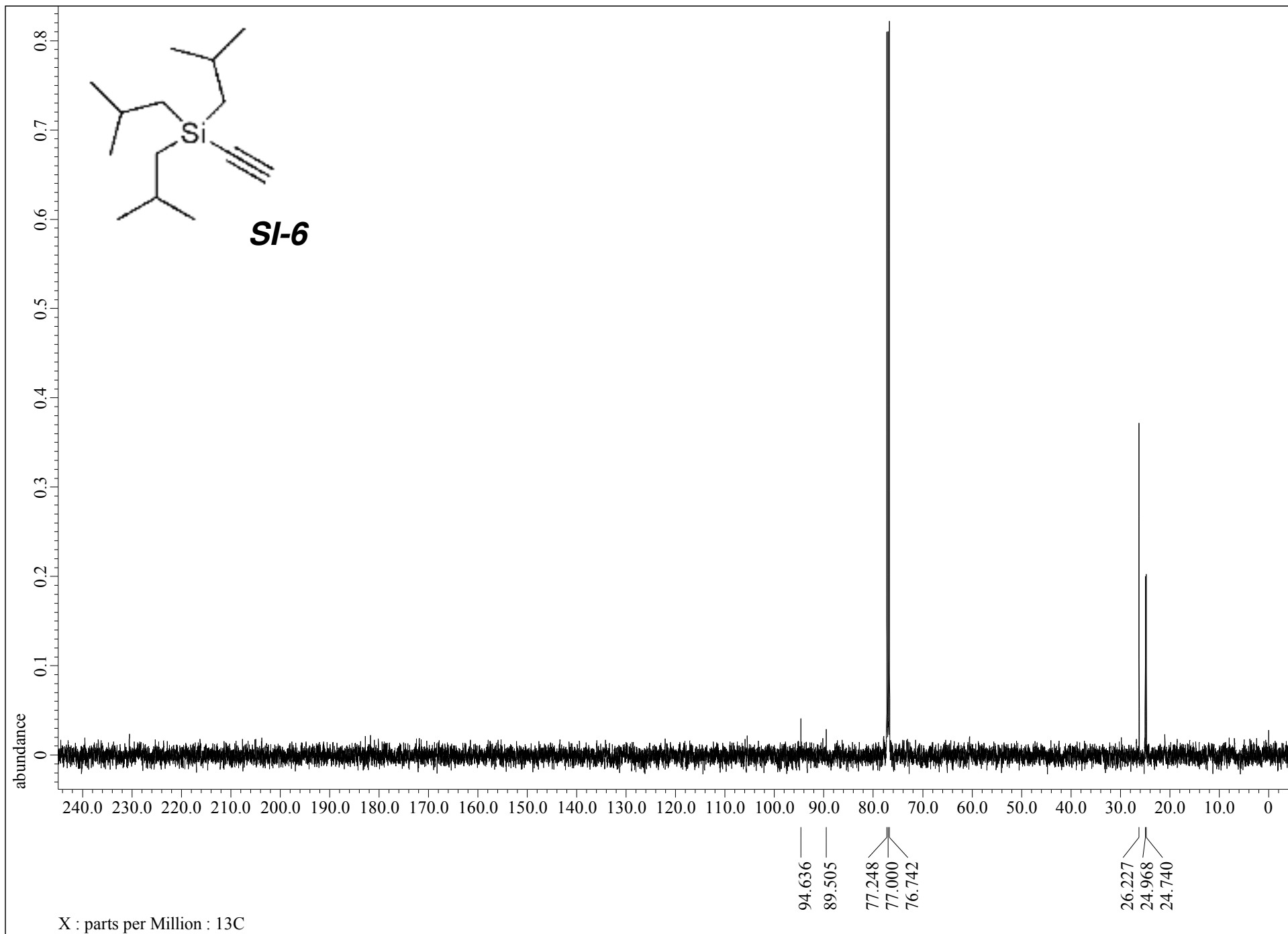


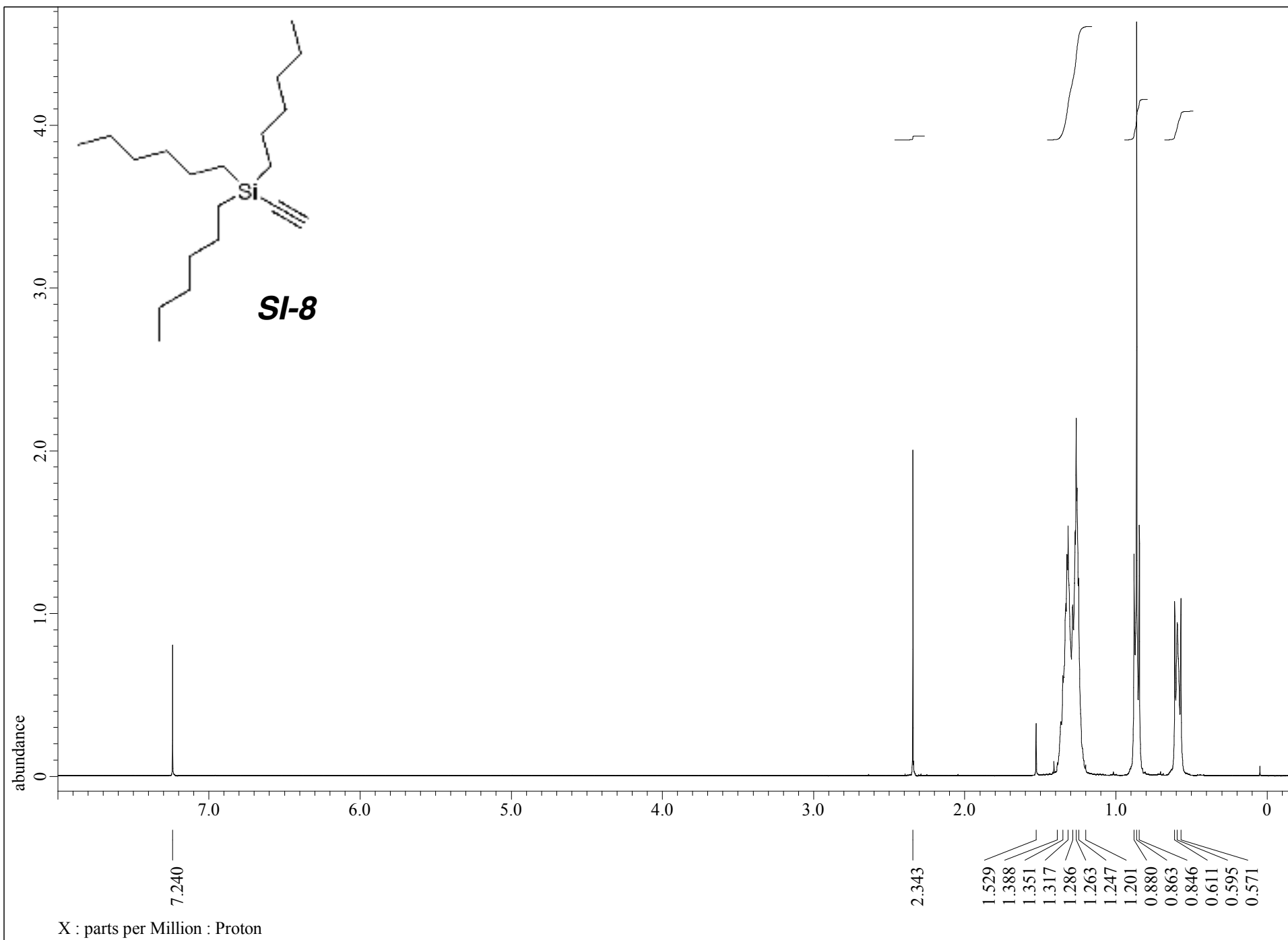


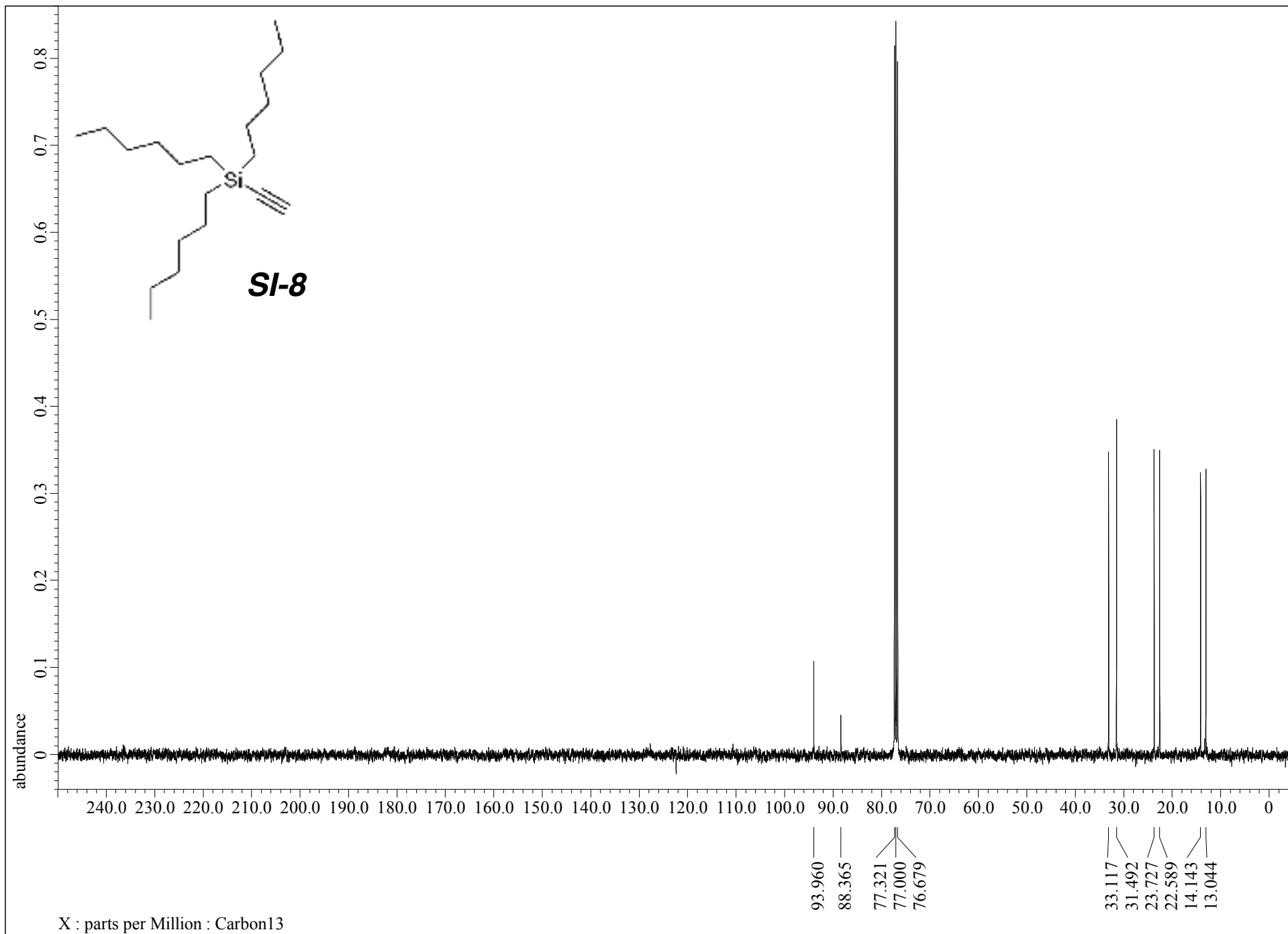


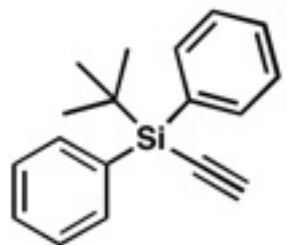




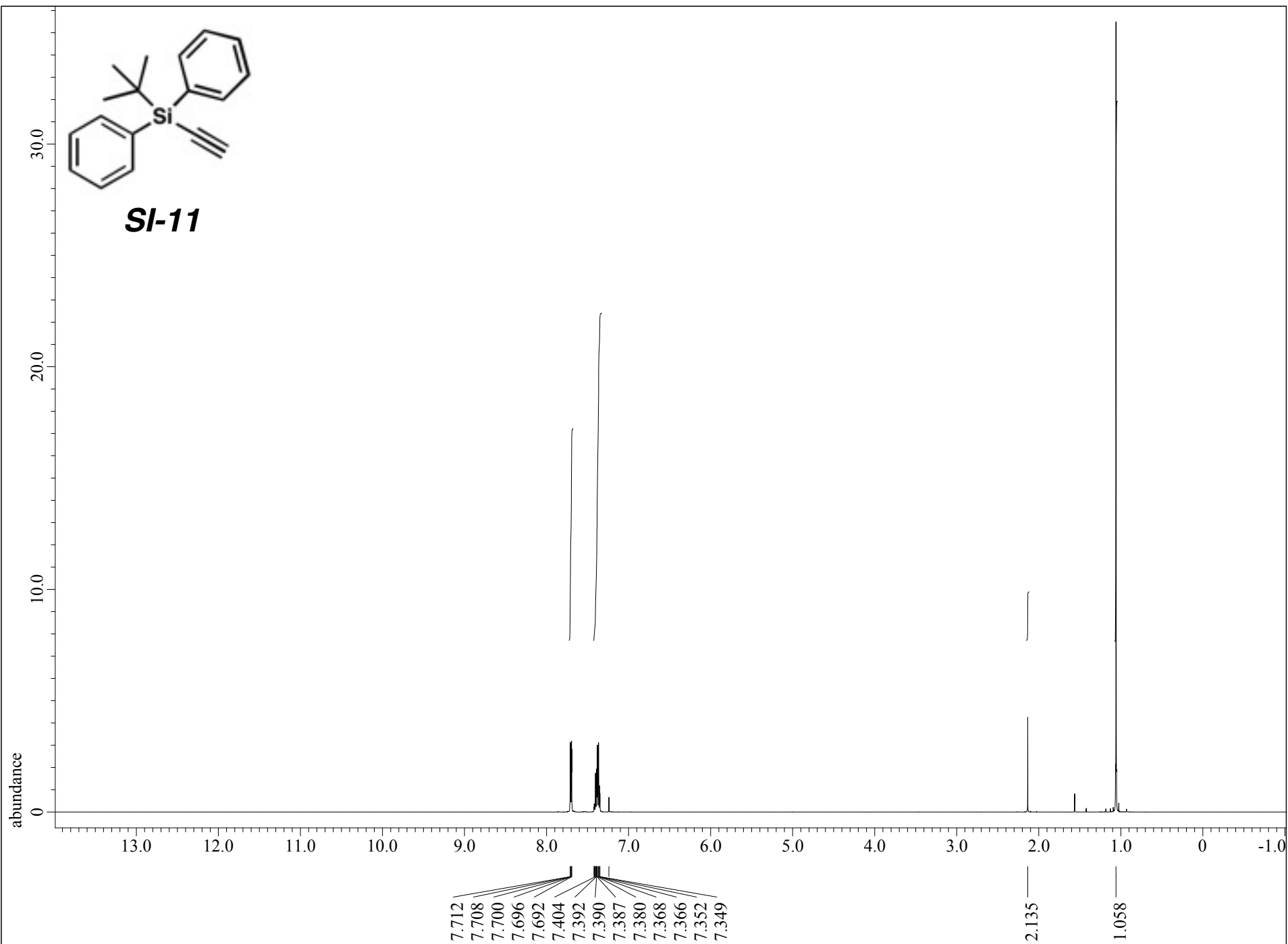


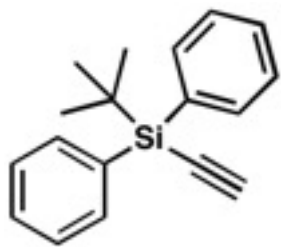




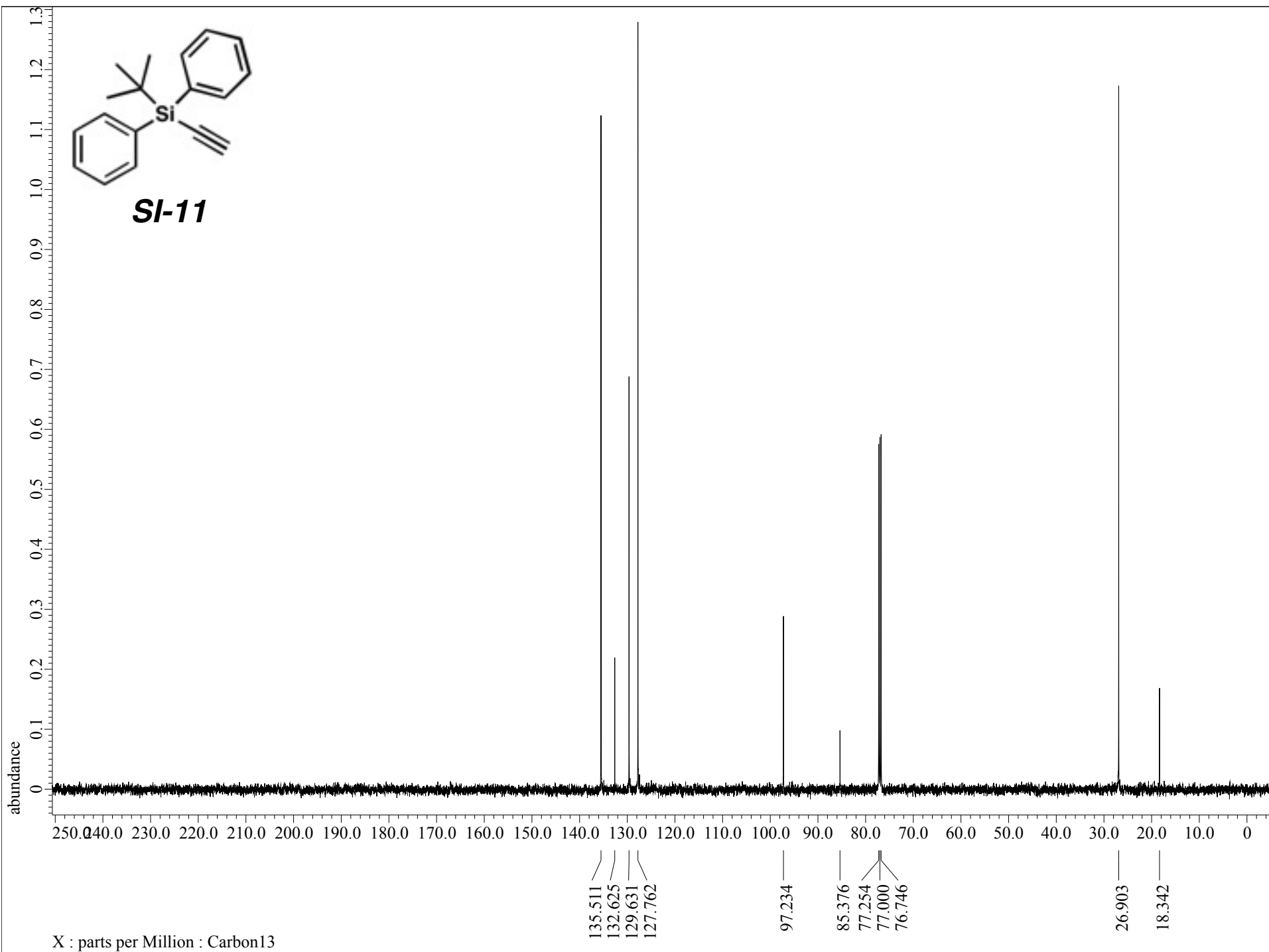


**SI-11**



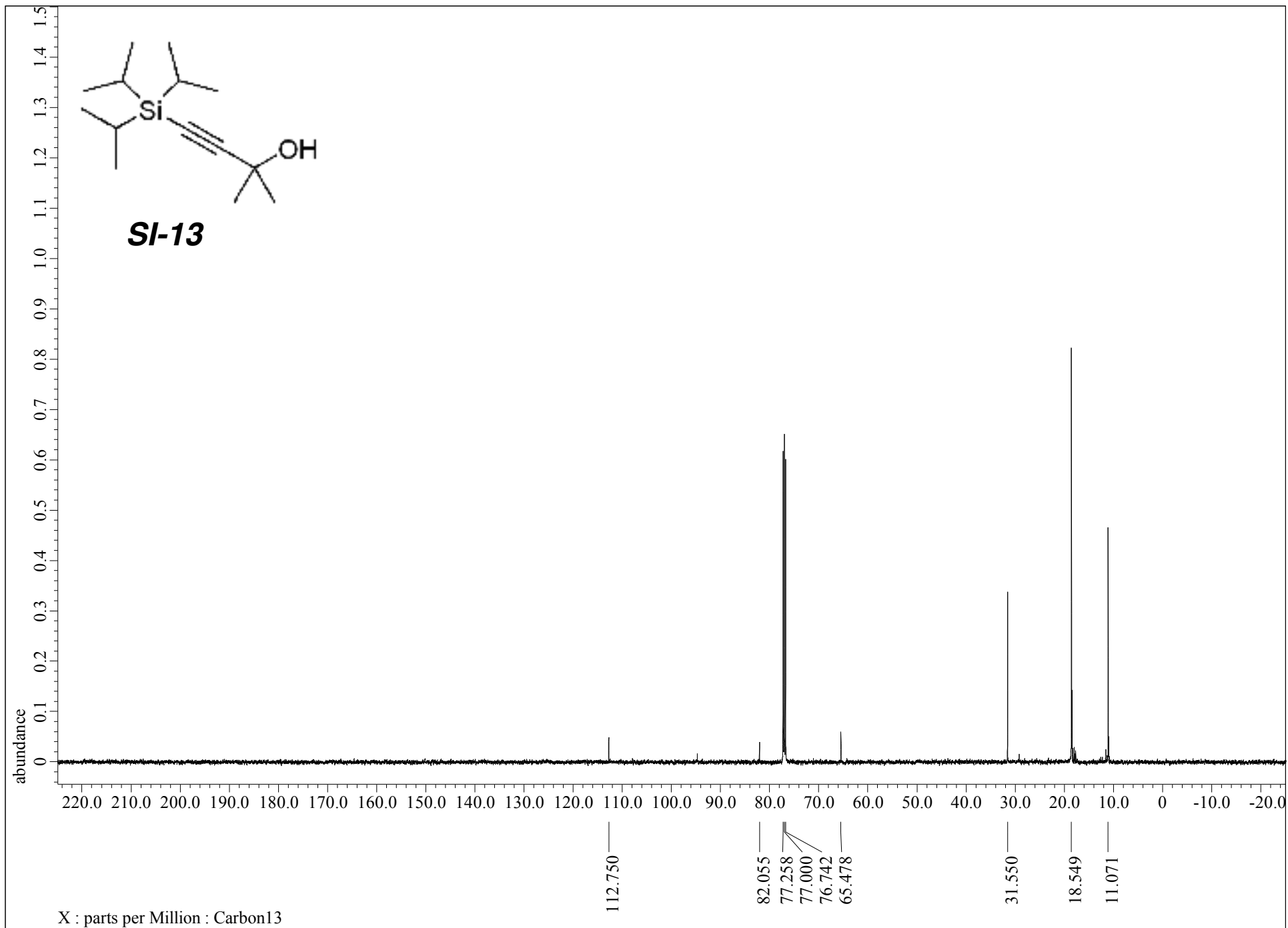


**SI-11**



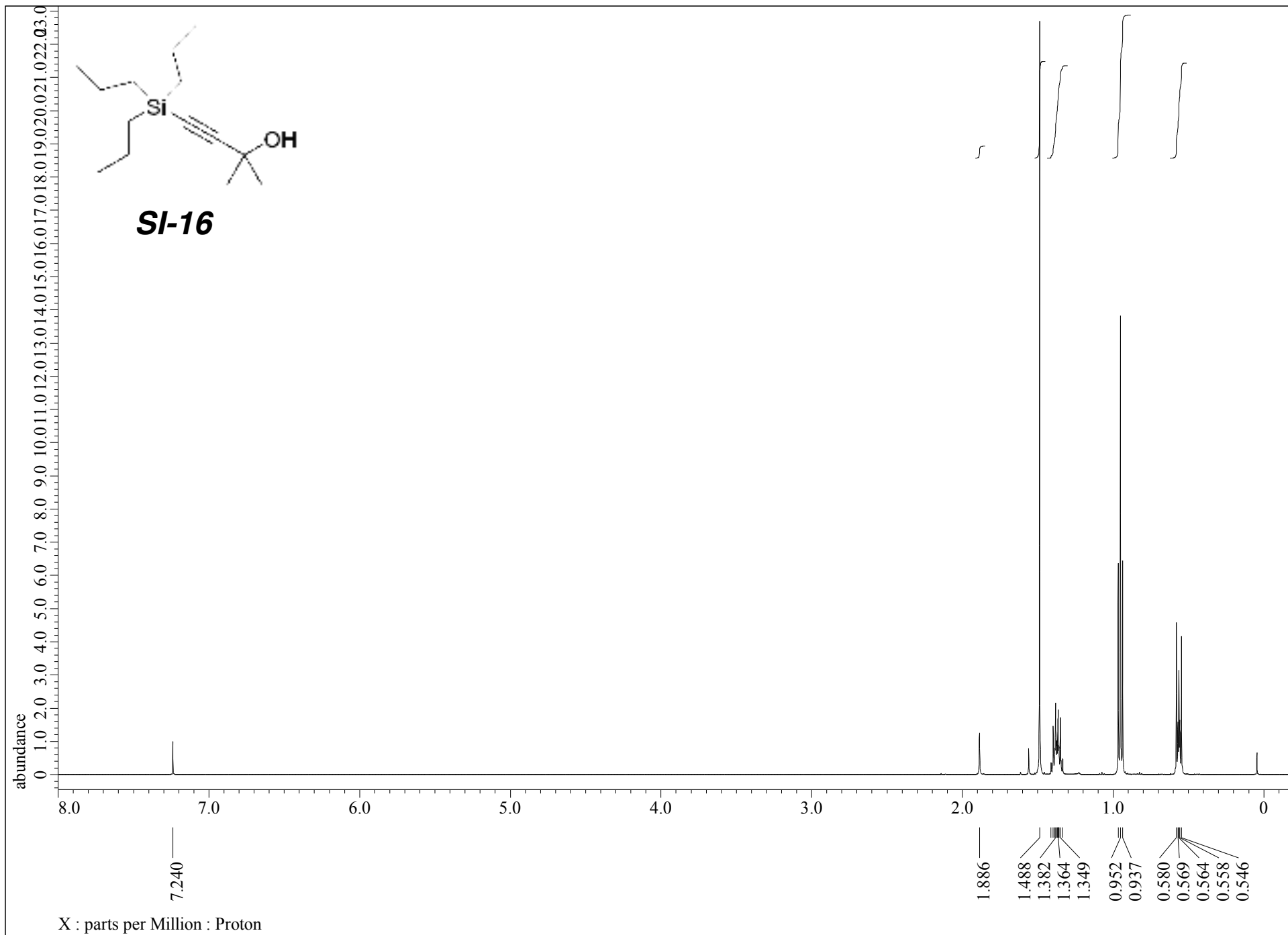


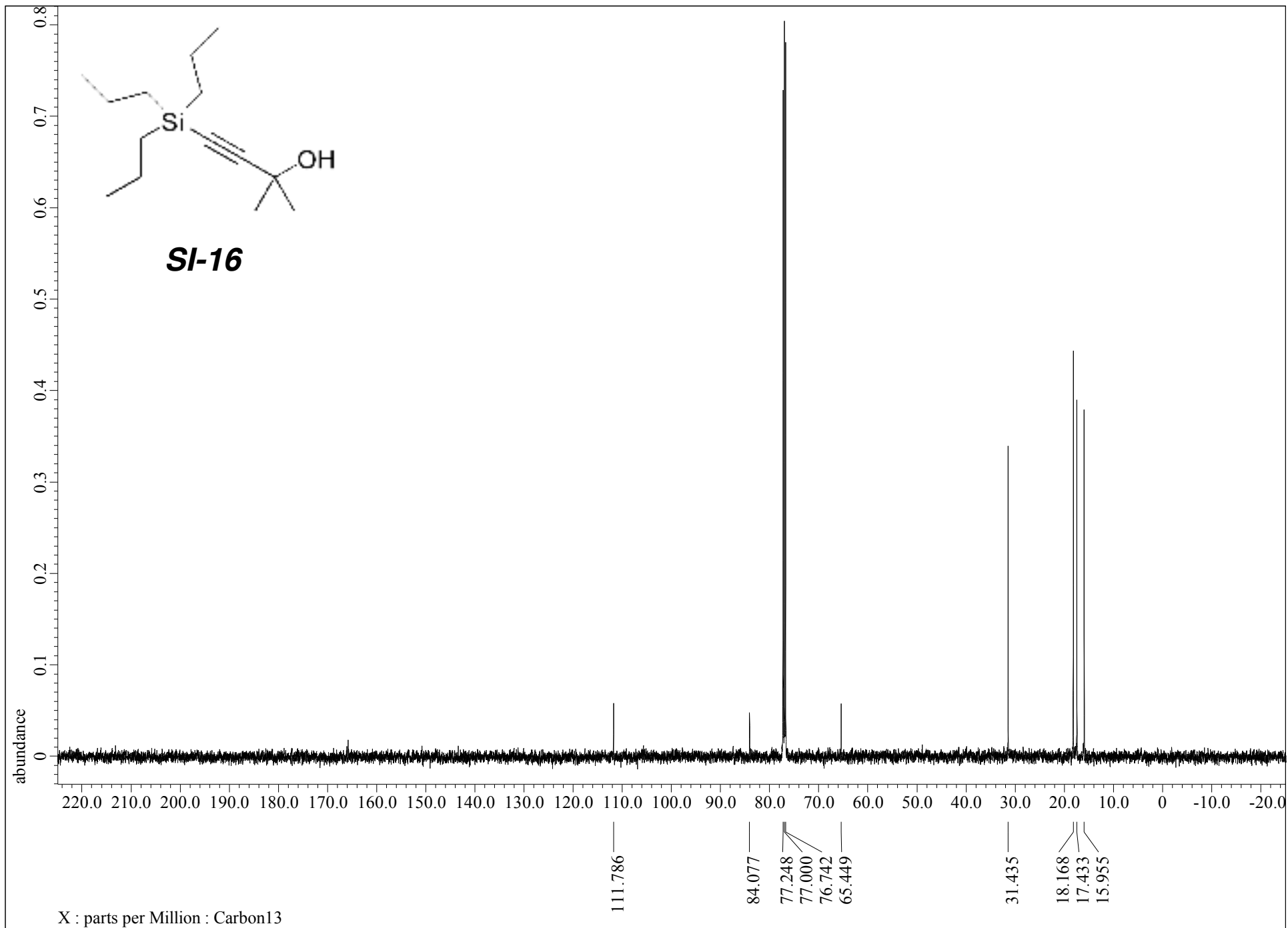




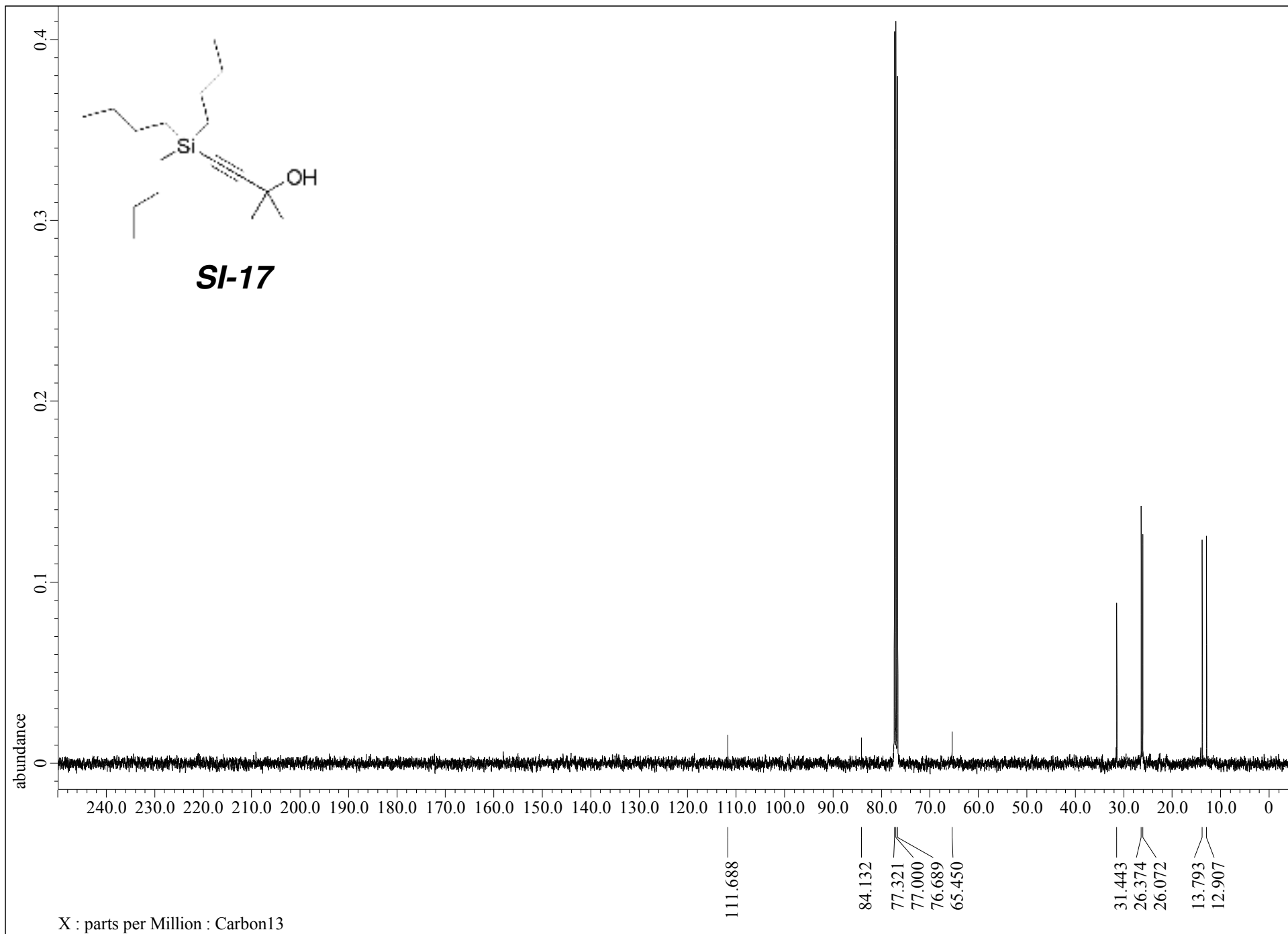


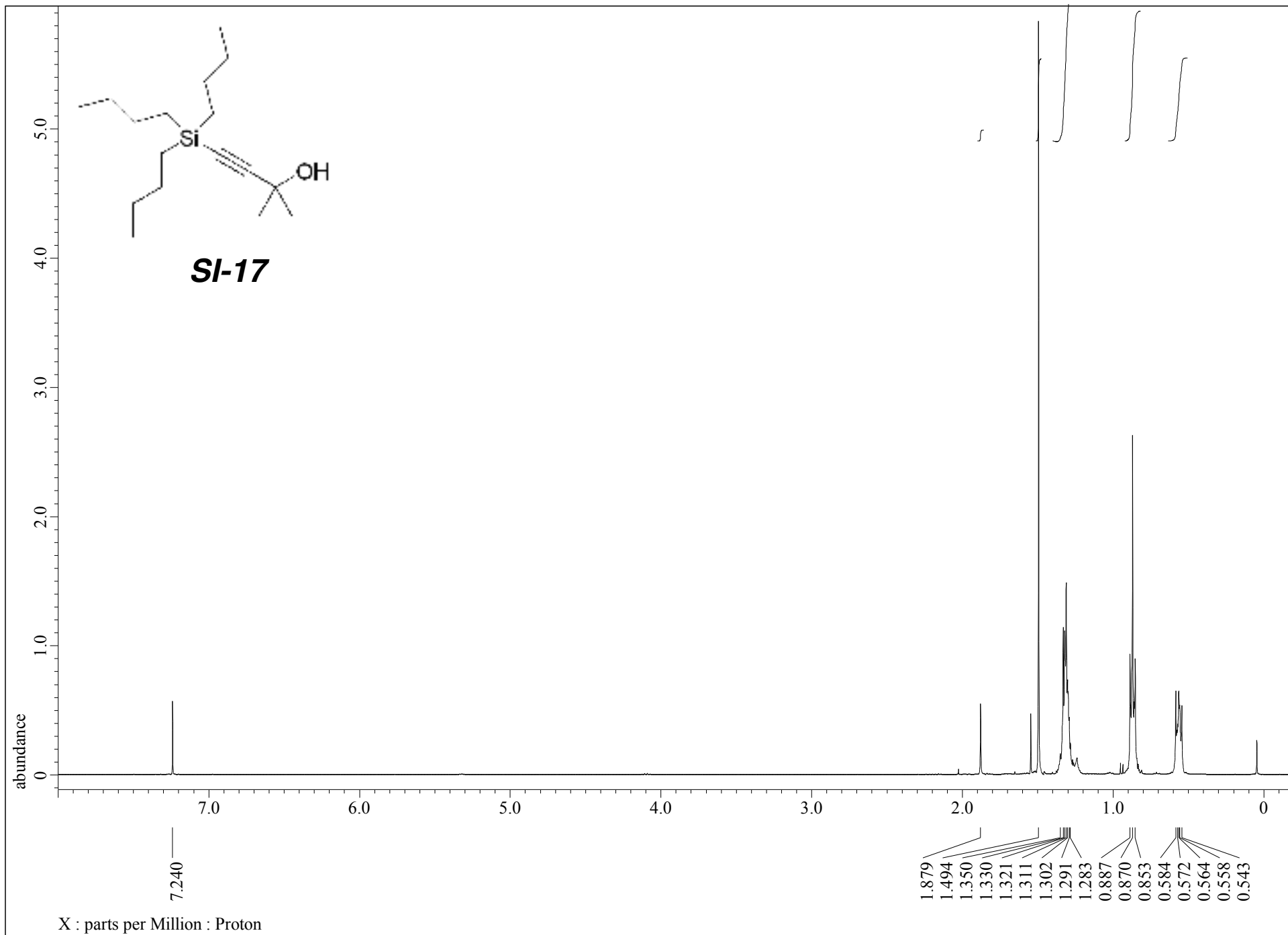






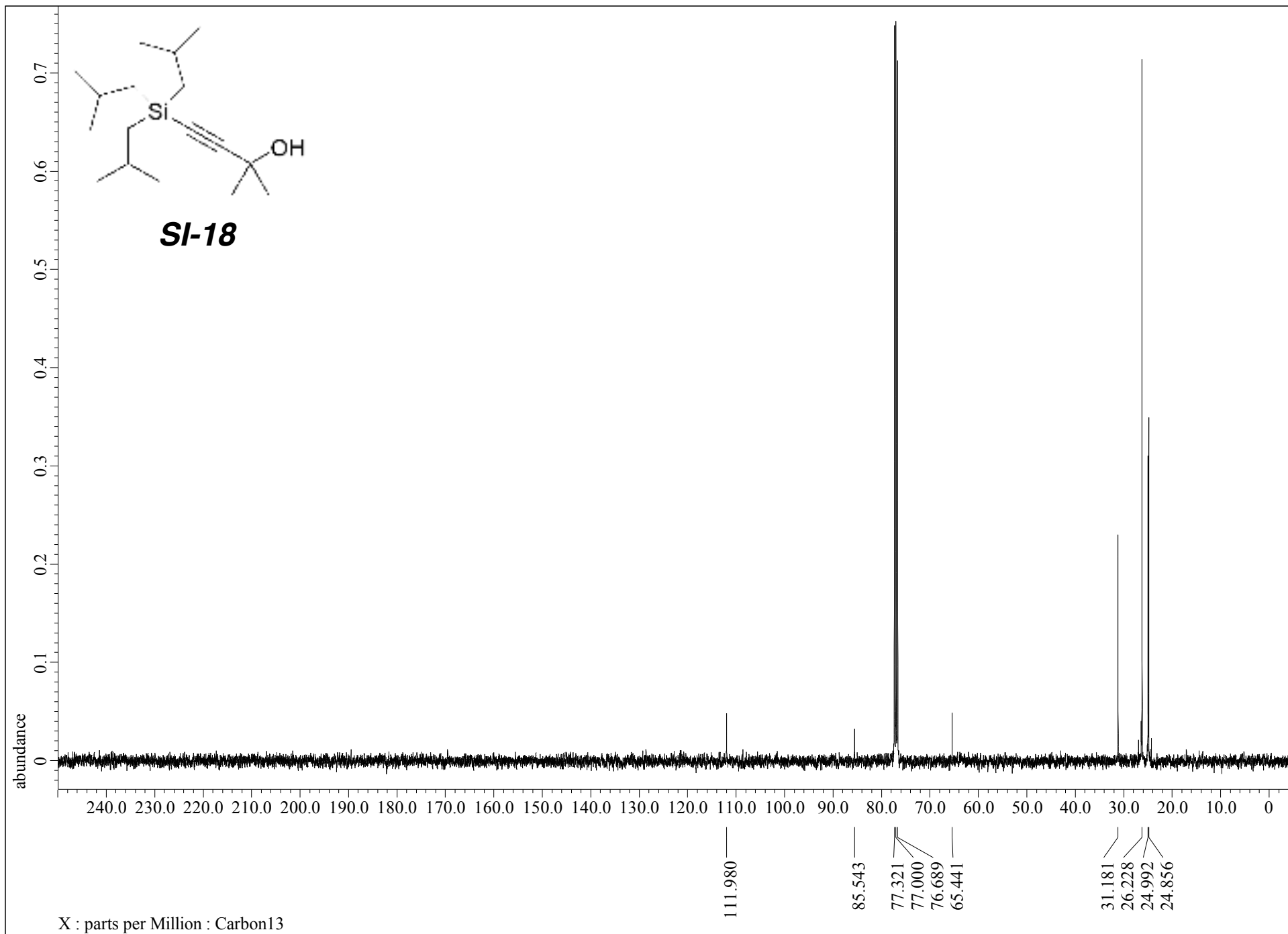
SI-54

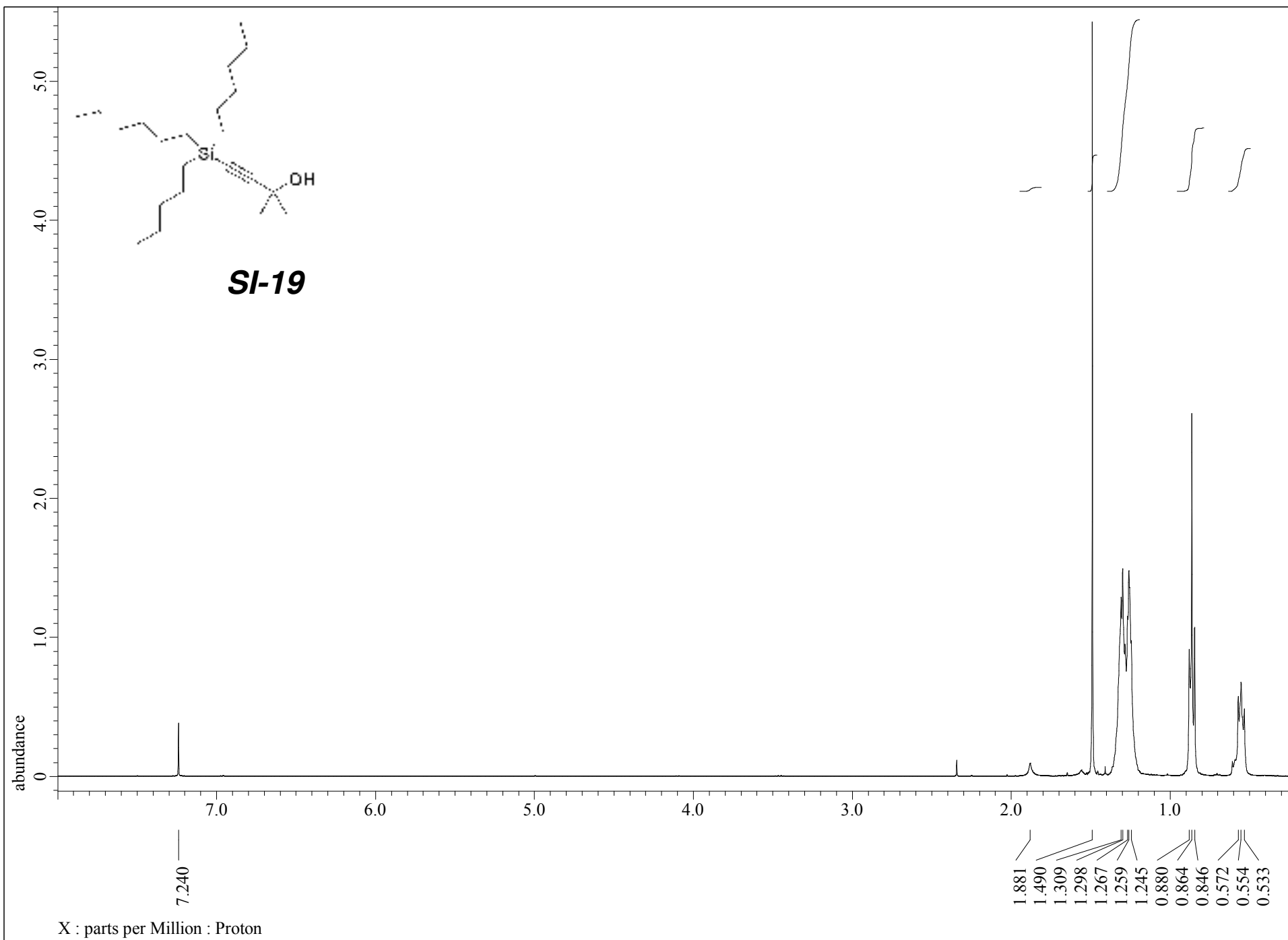


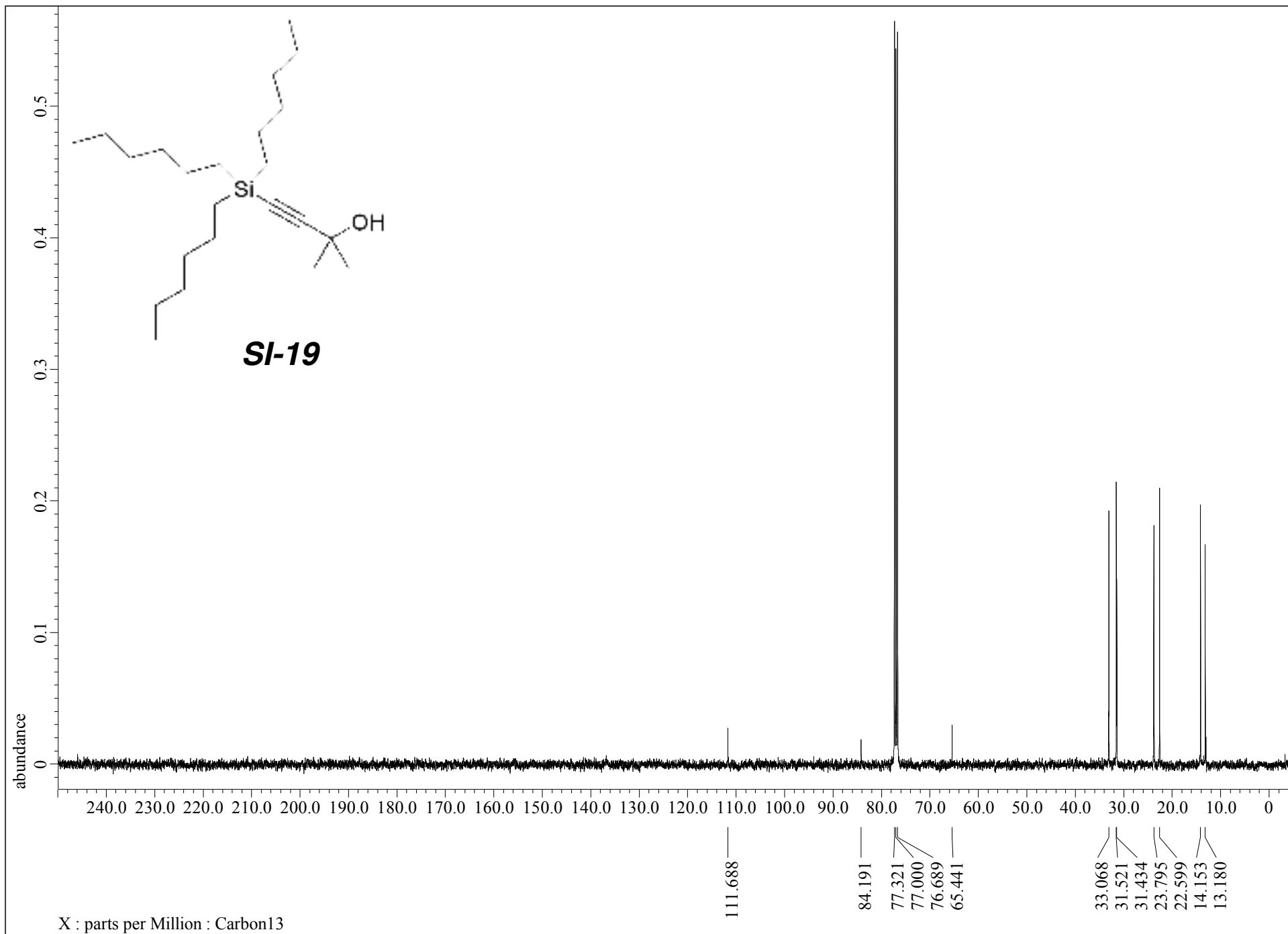


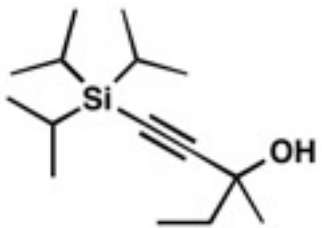




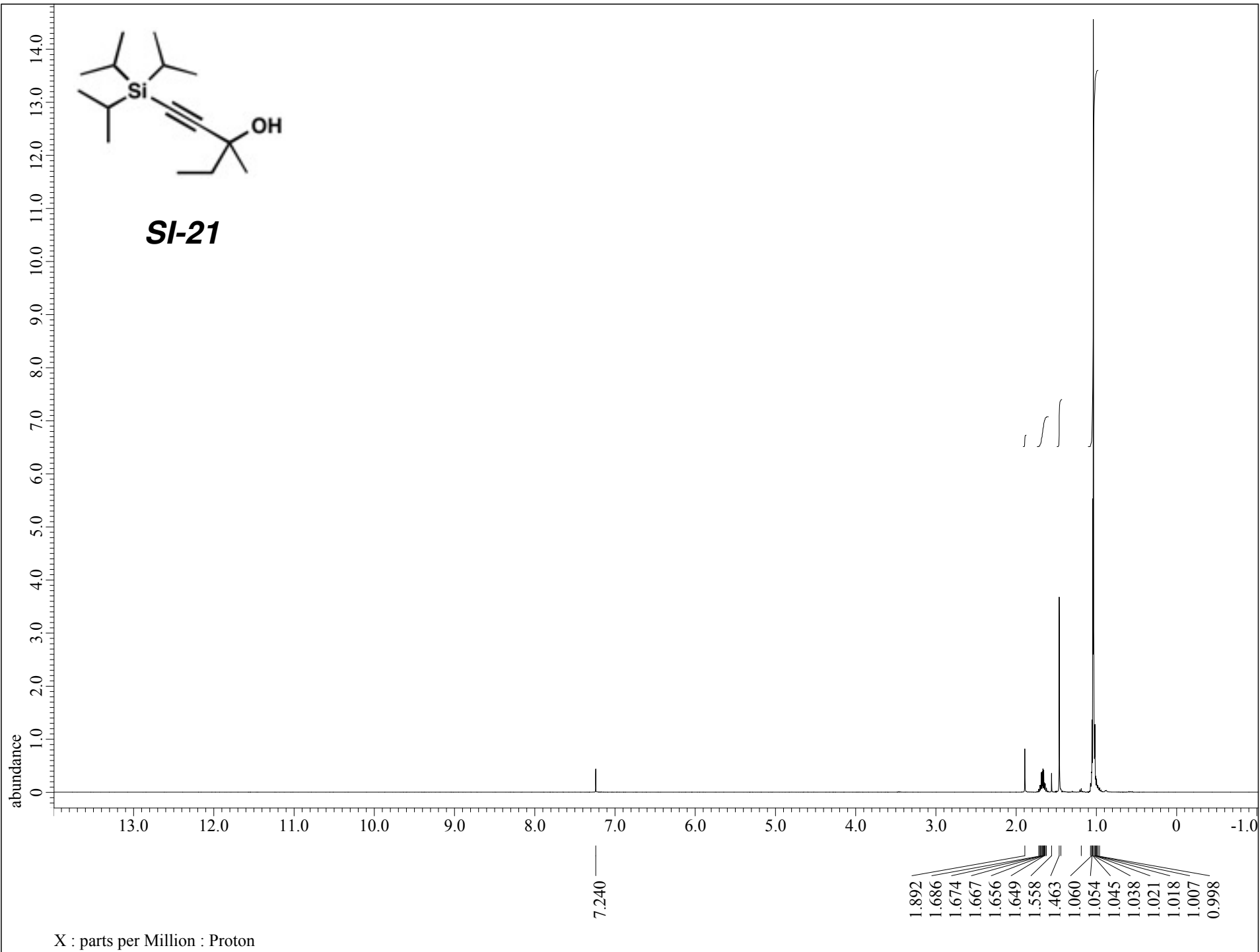




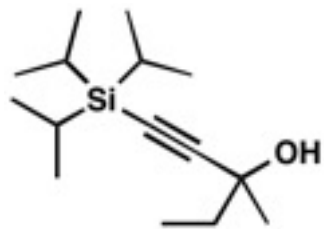




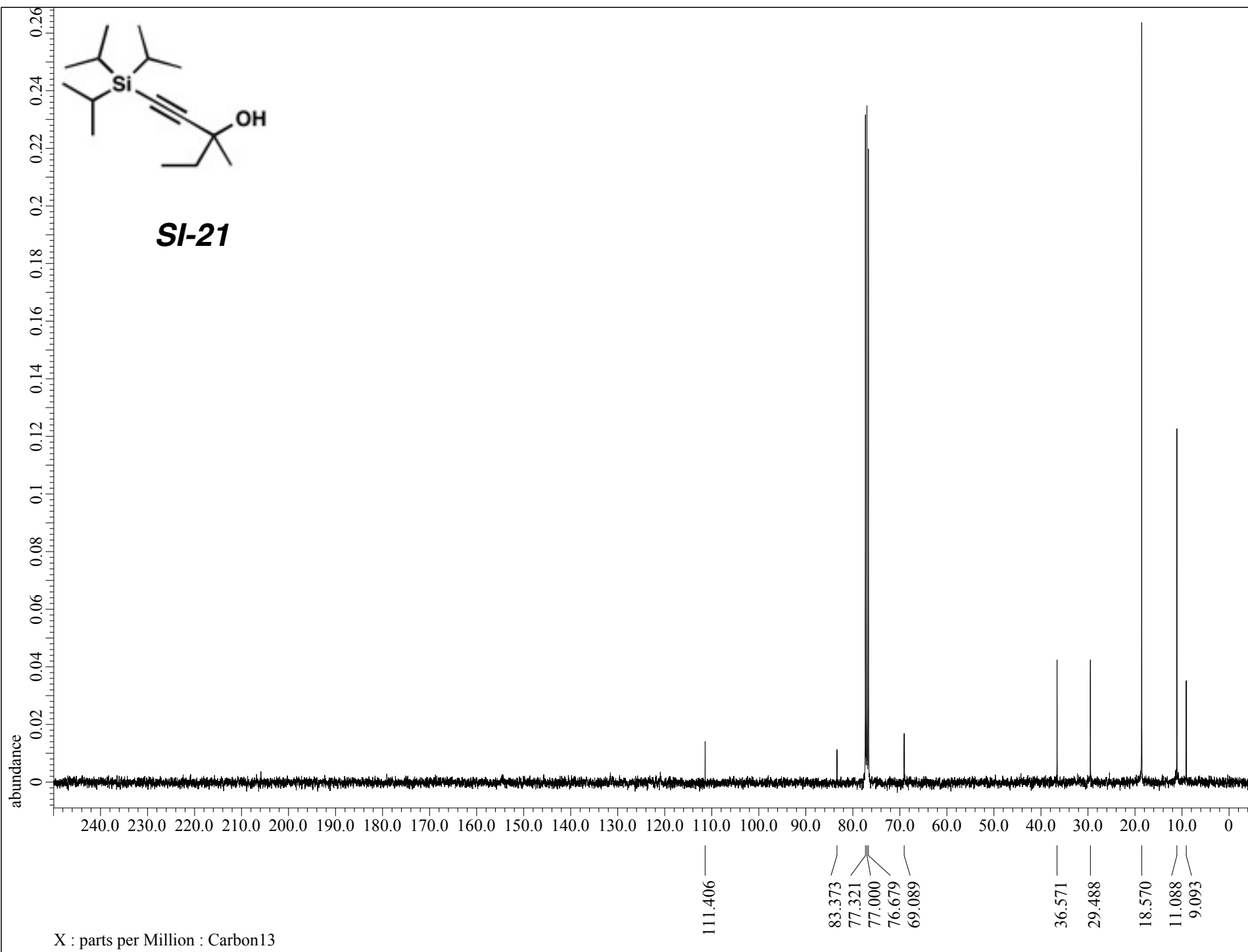
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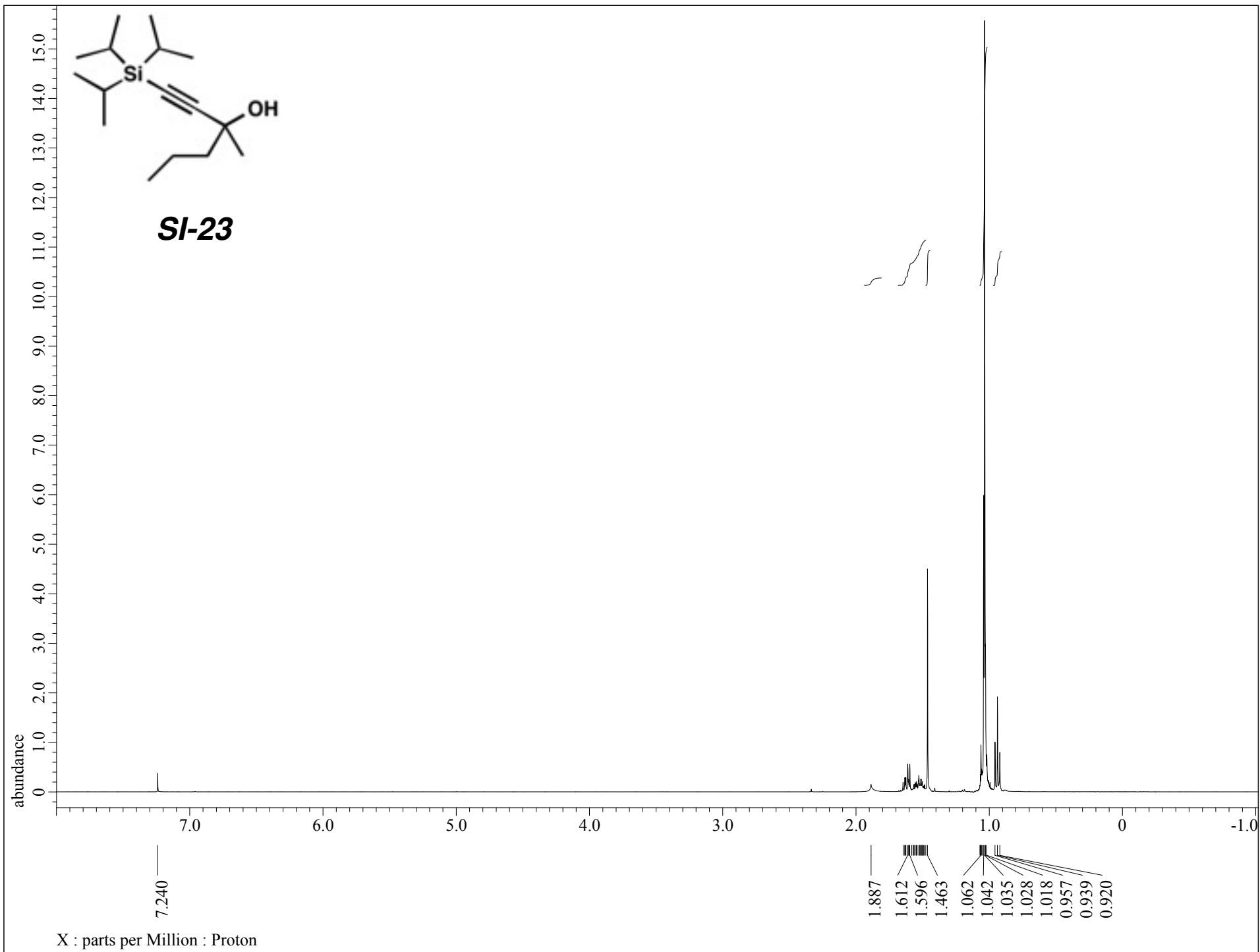


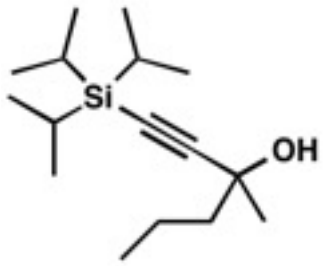
SI-61



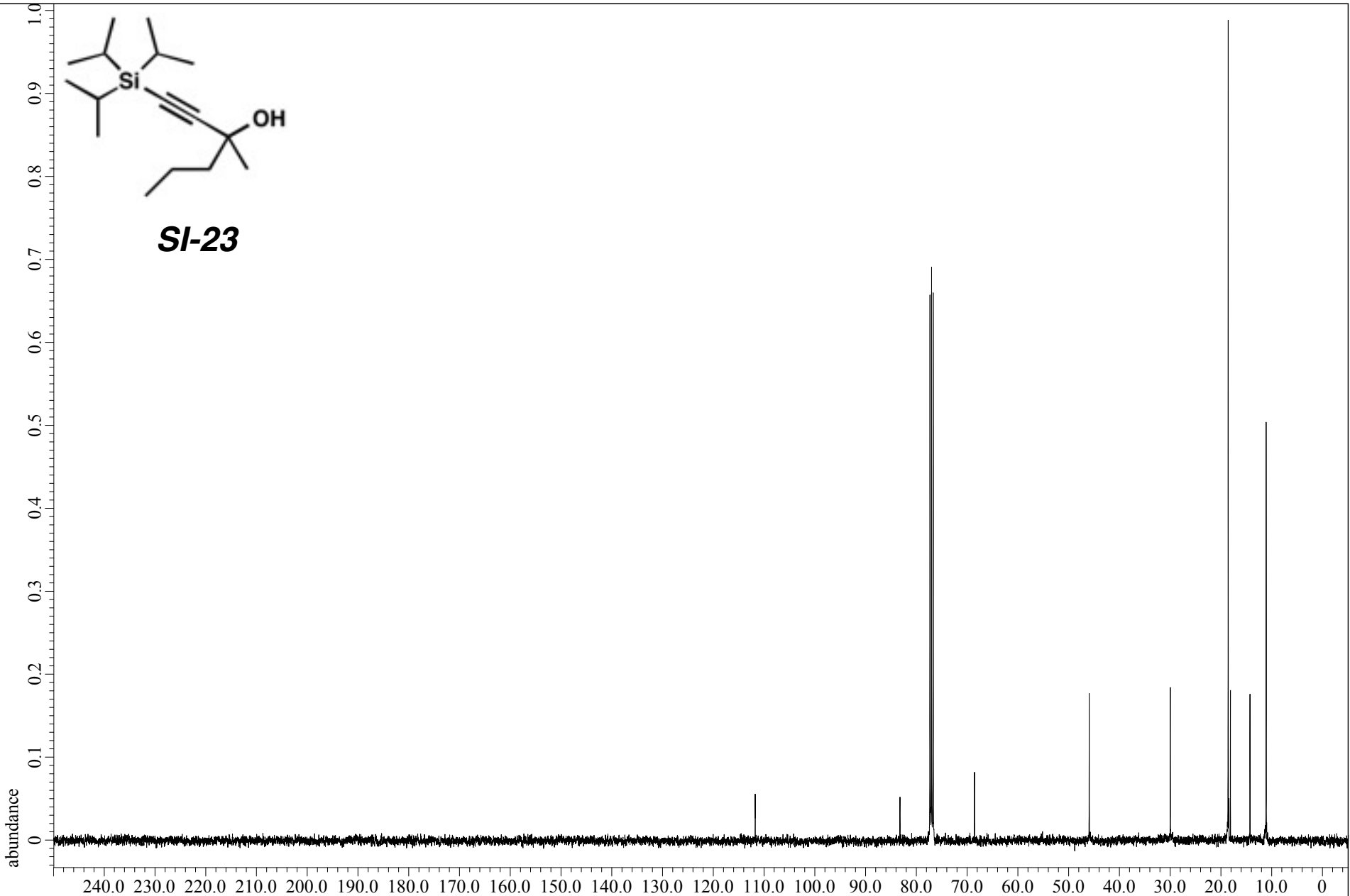
**SI-21**







**SI-23**

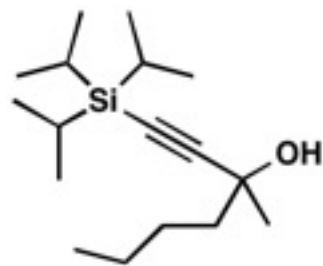


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- 76.679
- 68.554
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- 18.123
- 14.270
- 11.078

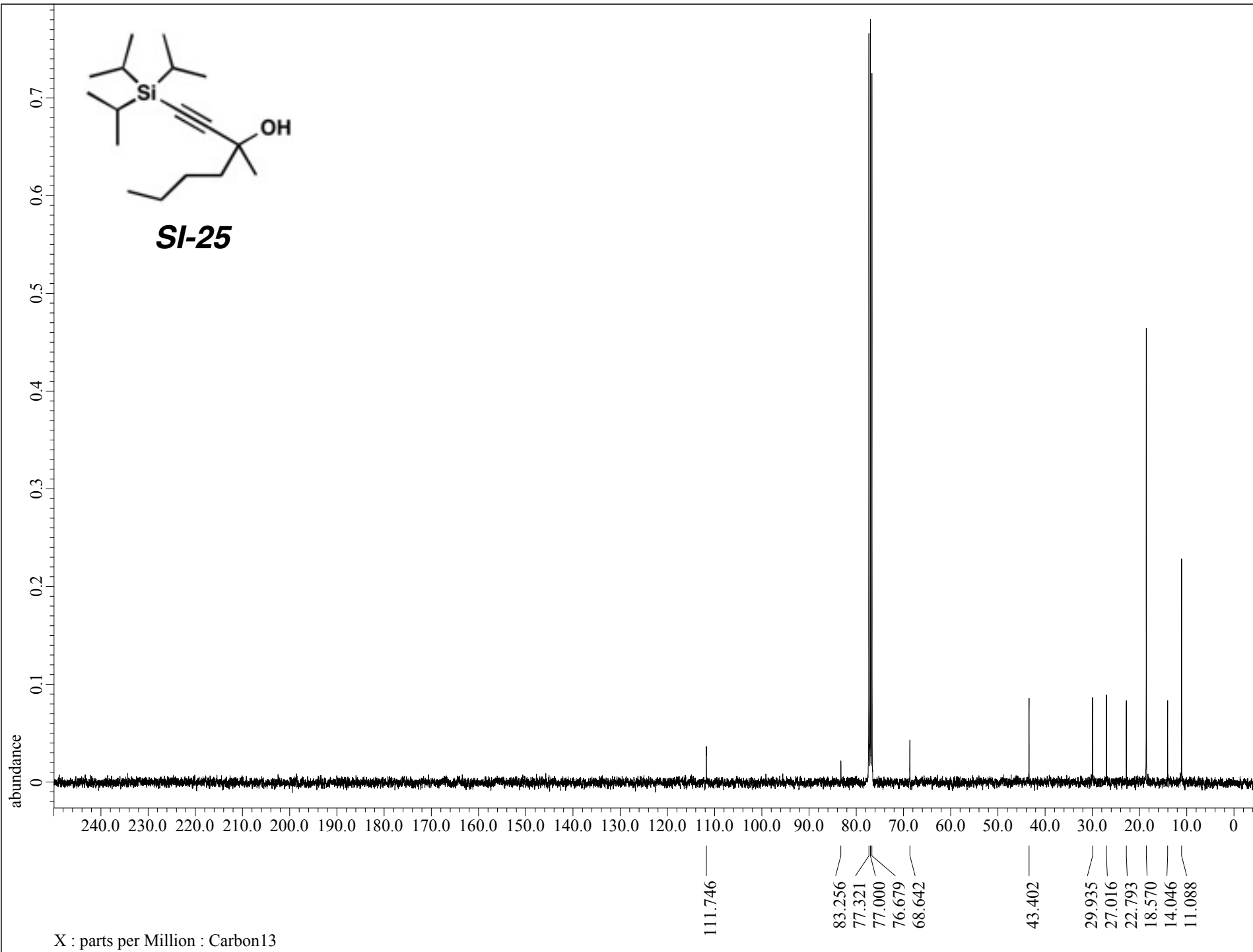
X : parts per Million : Carbon13



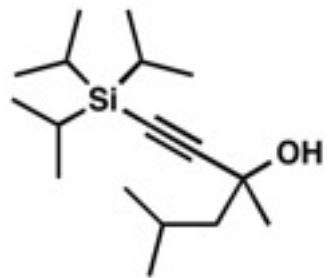




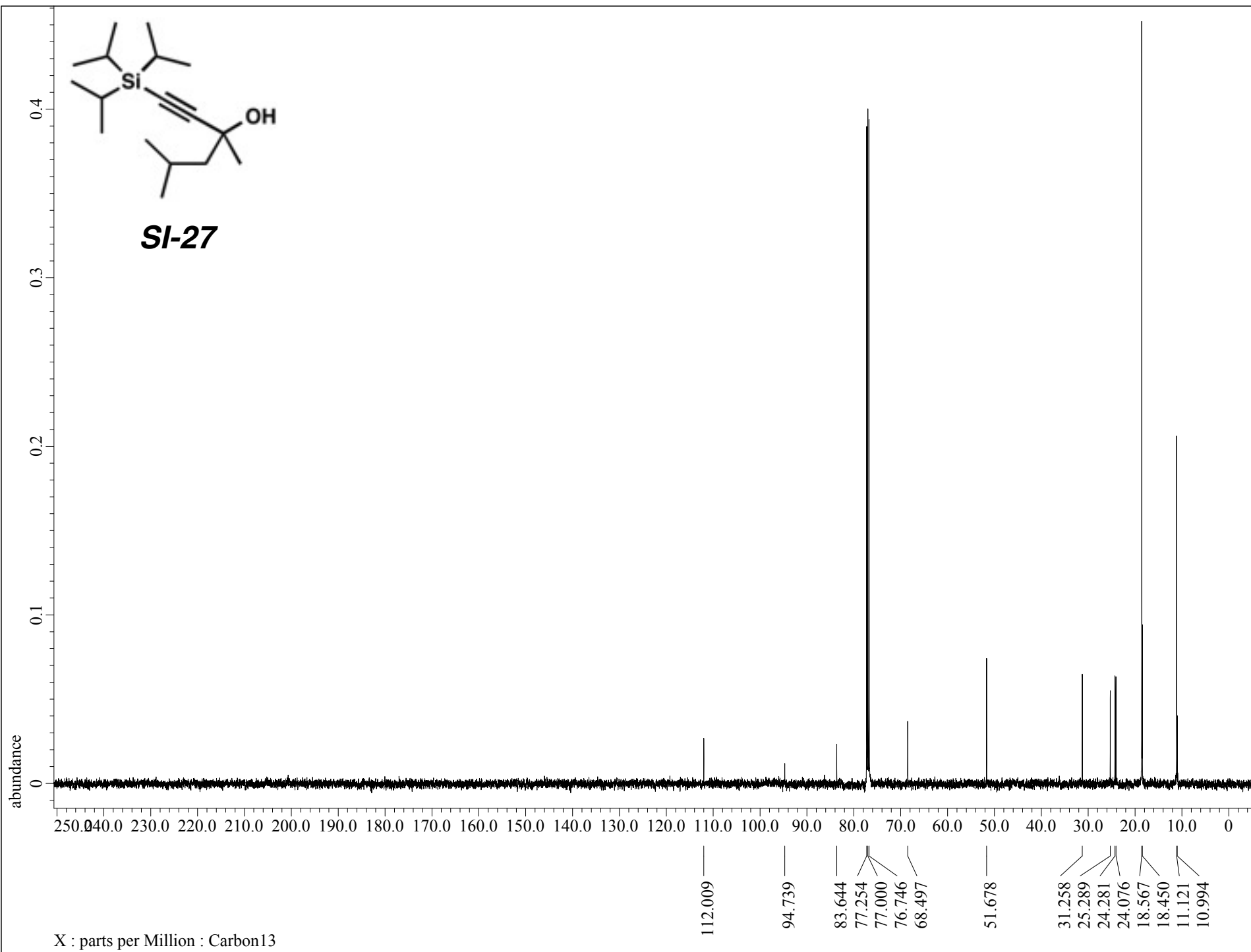
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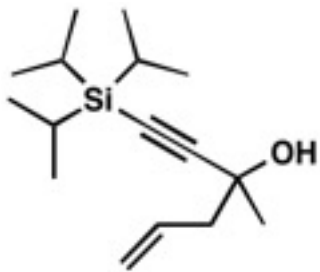




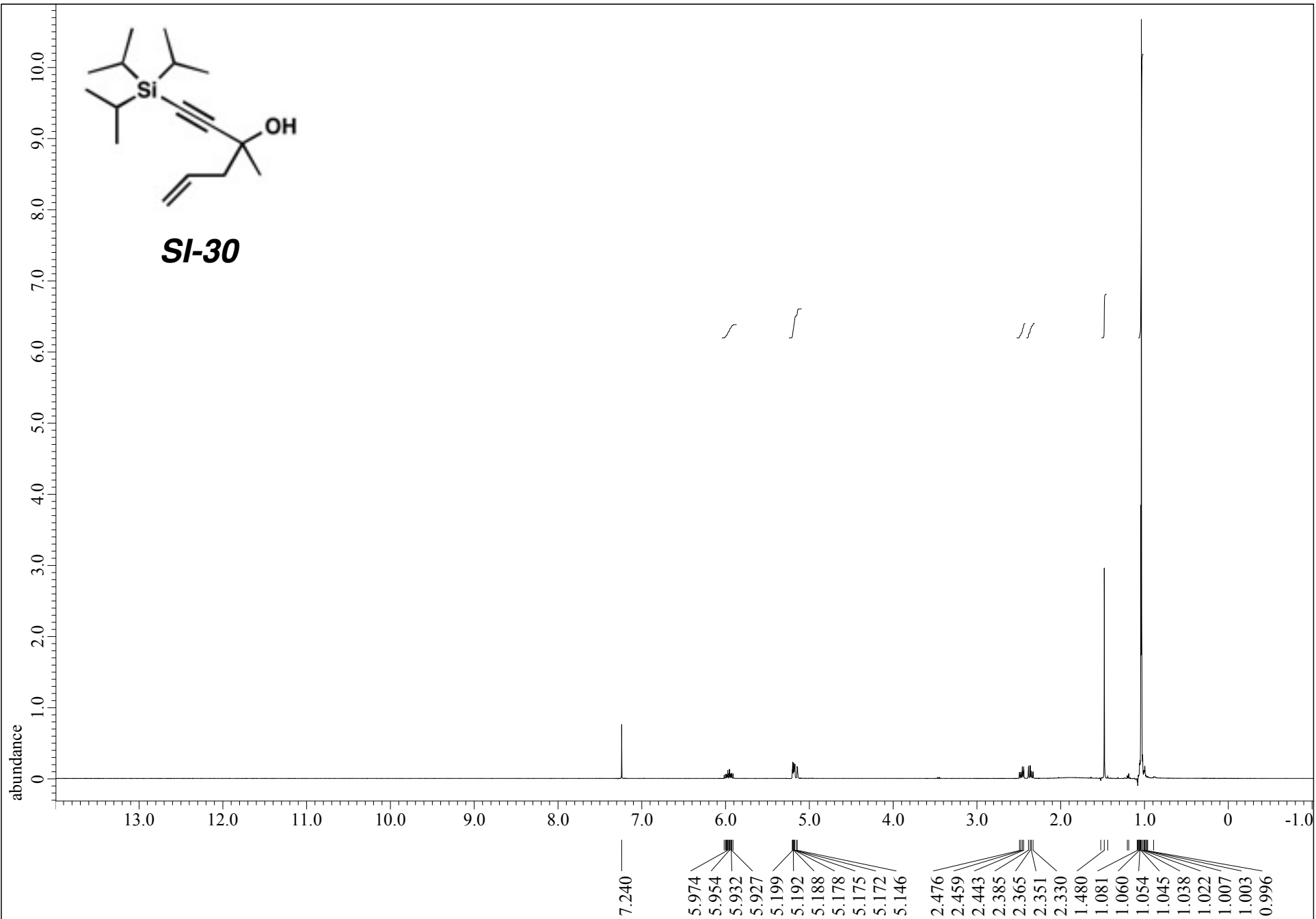


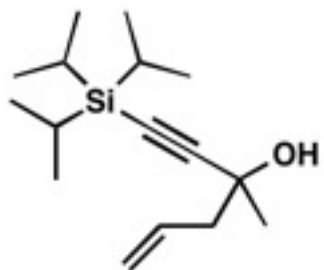
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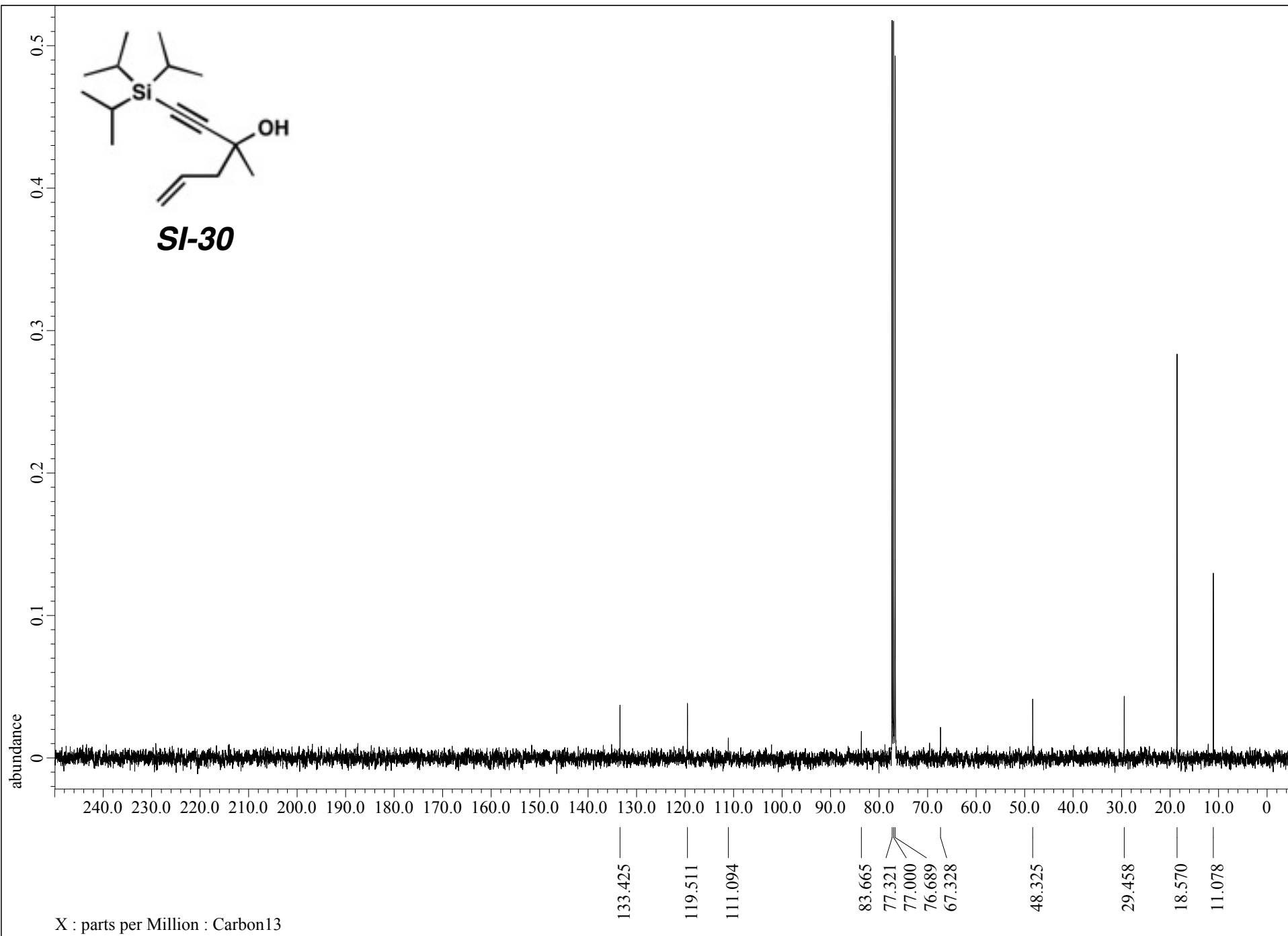


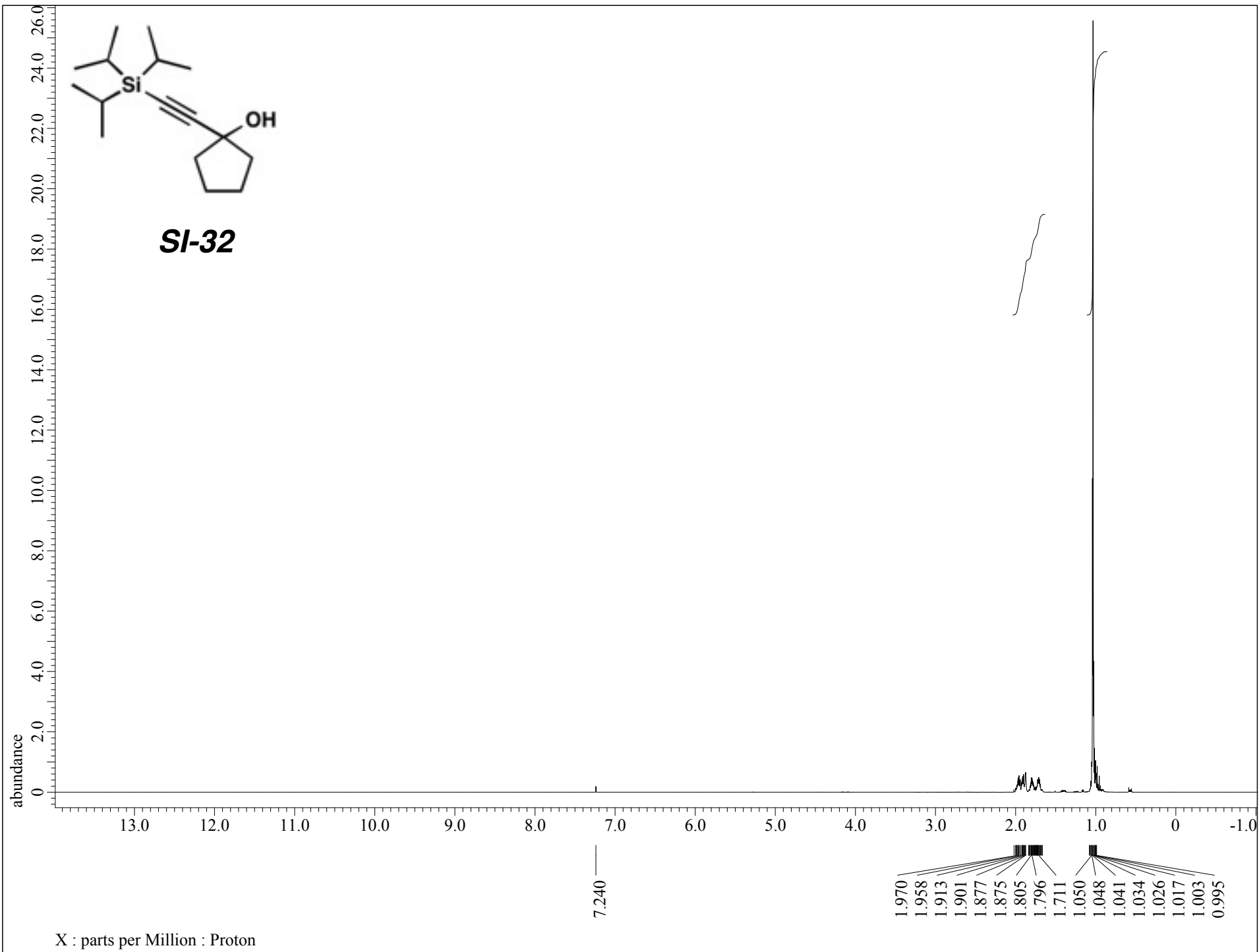
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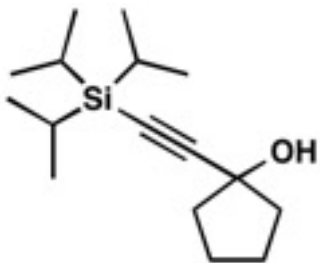




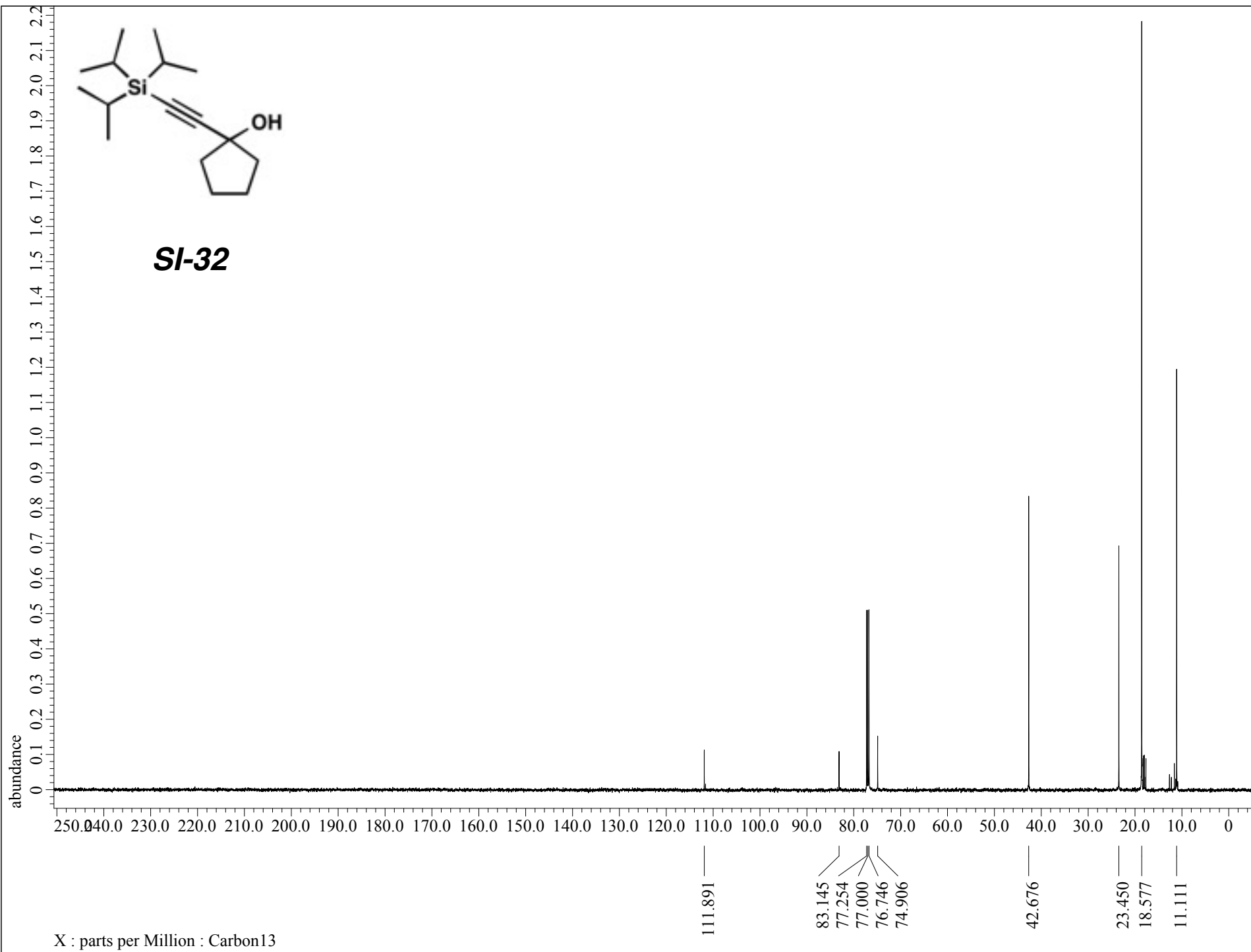
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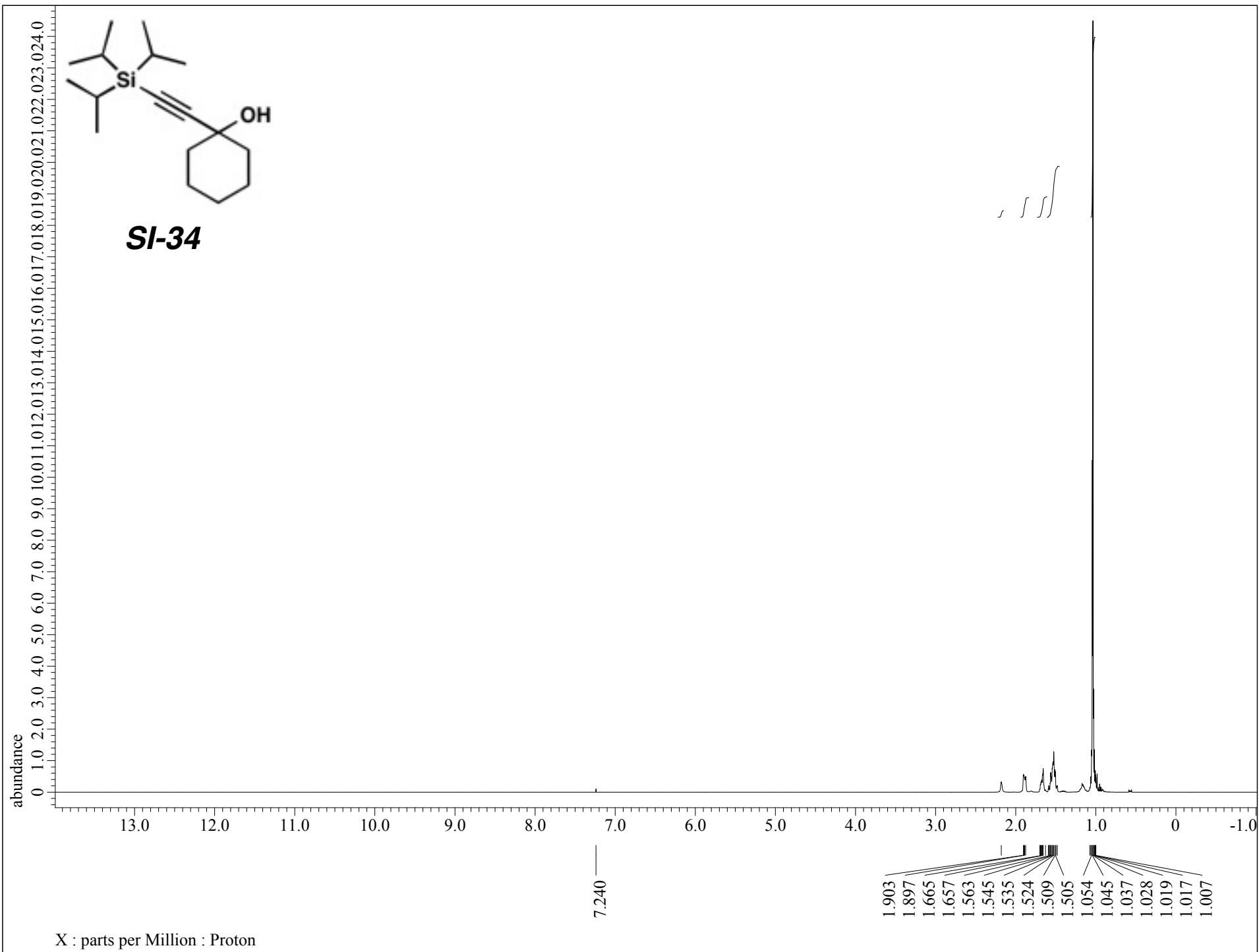




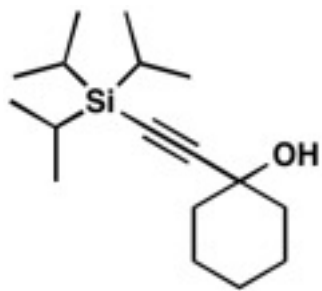


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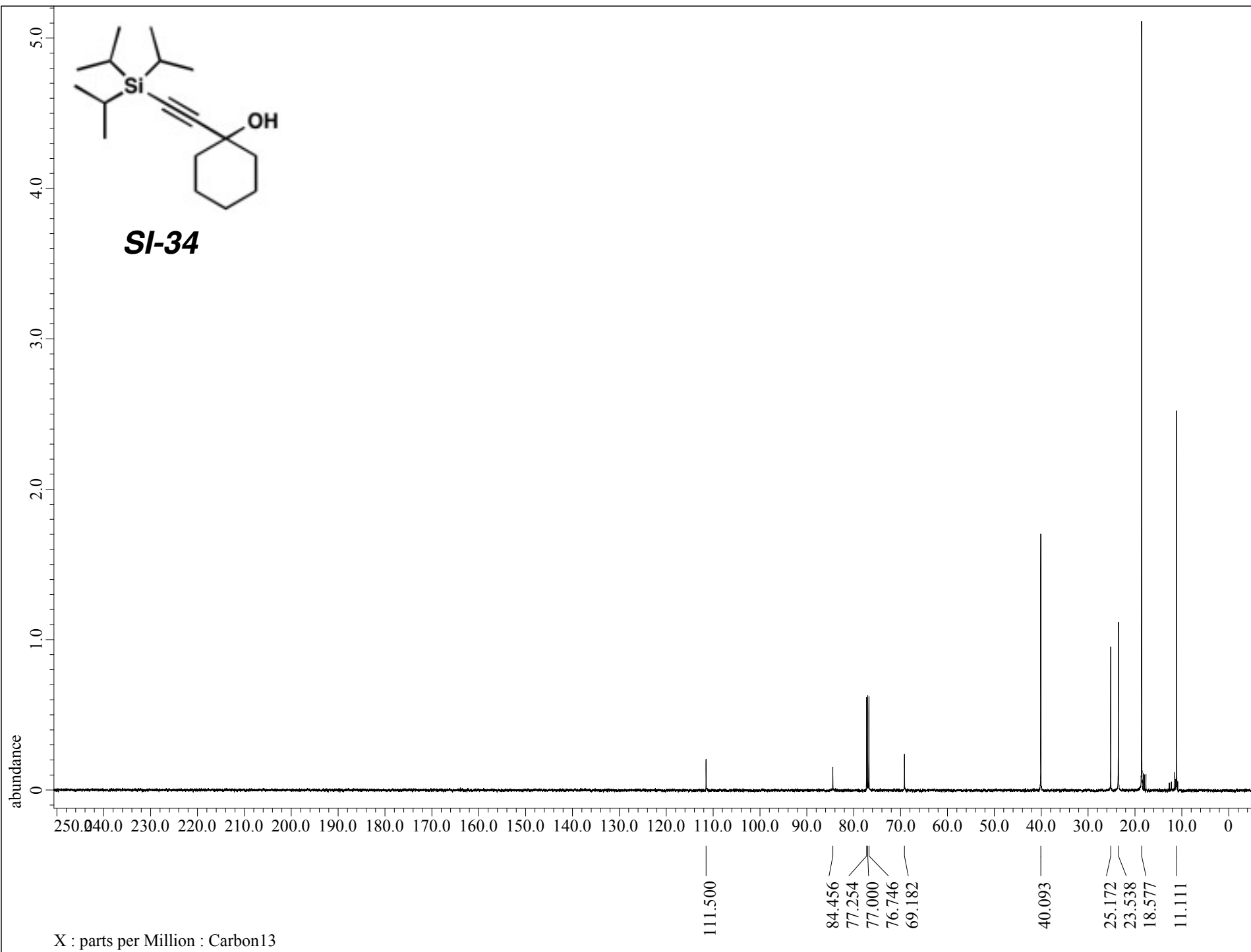


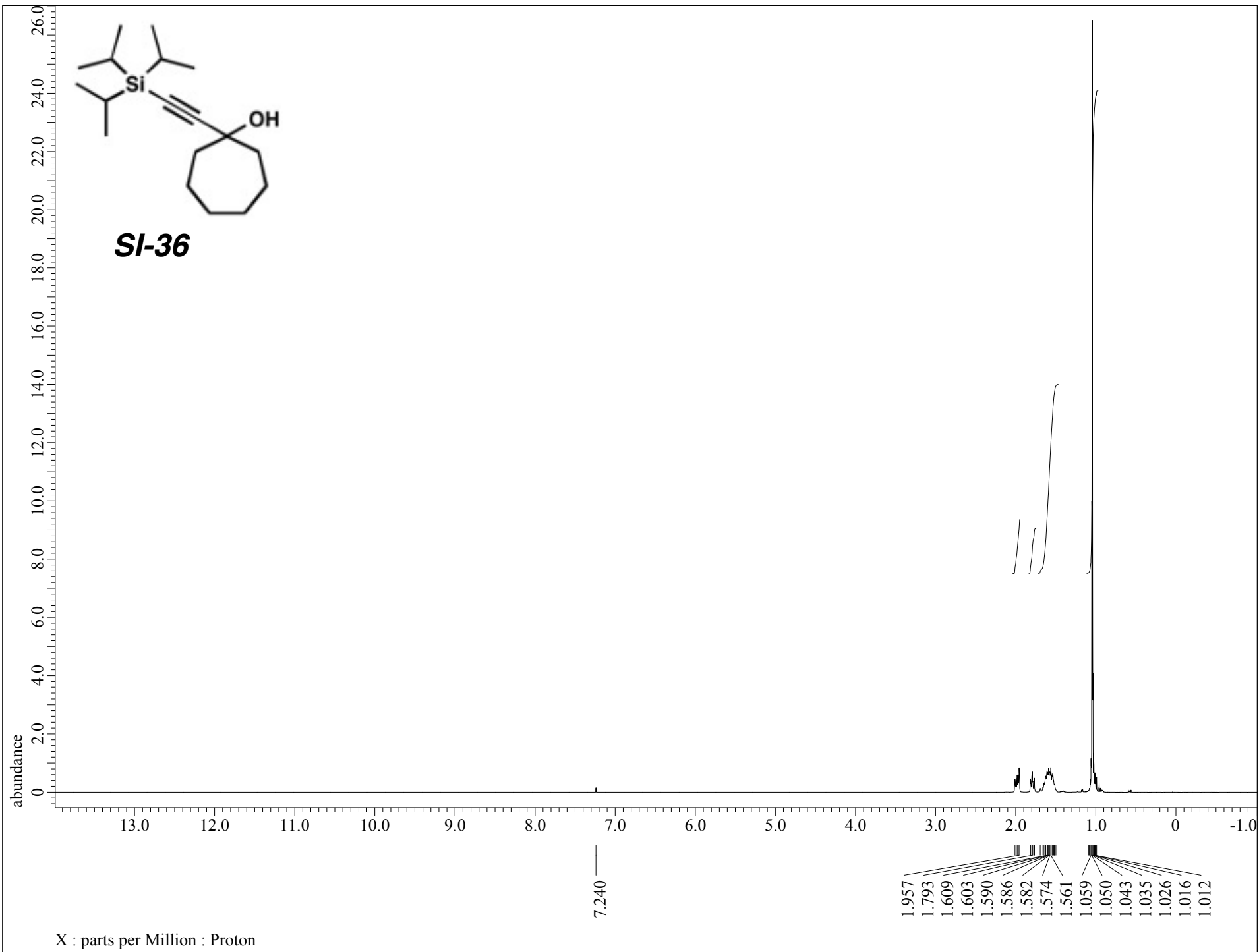


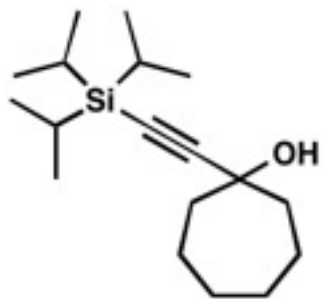




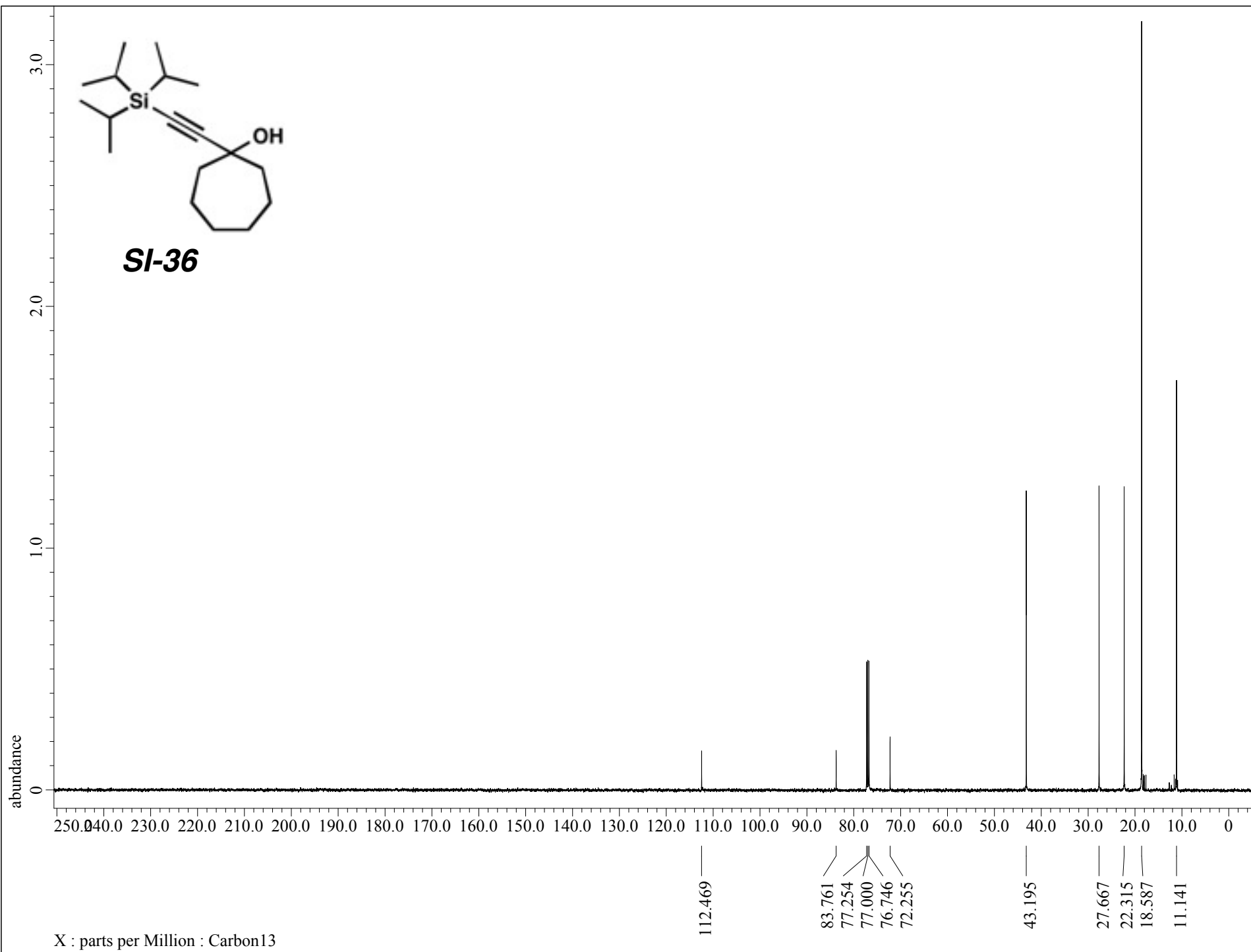
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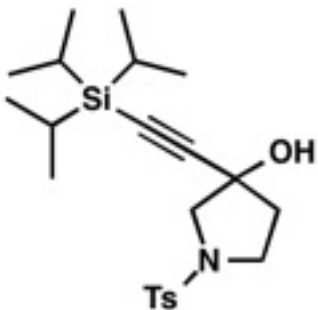




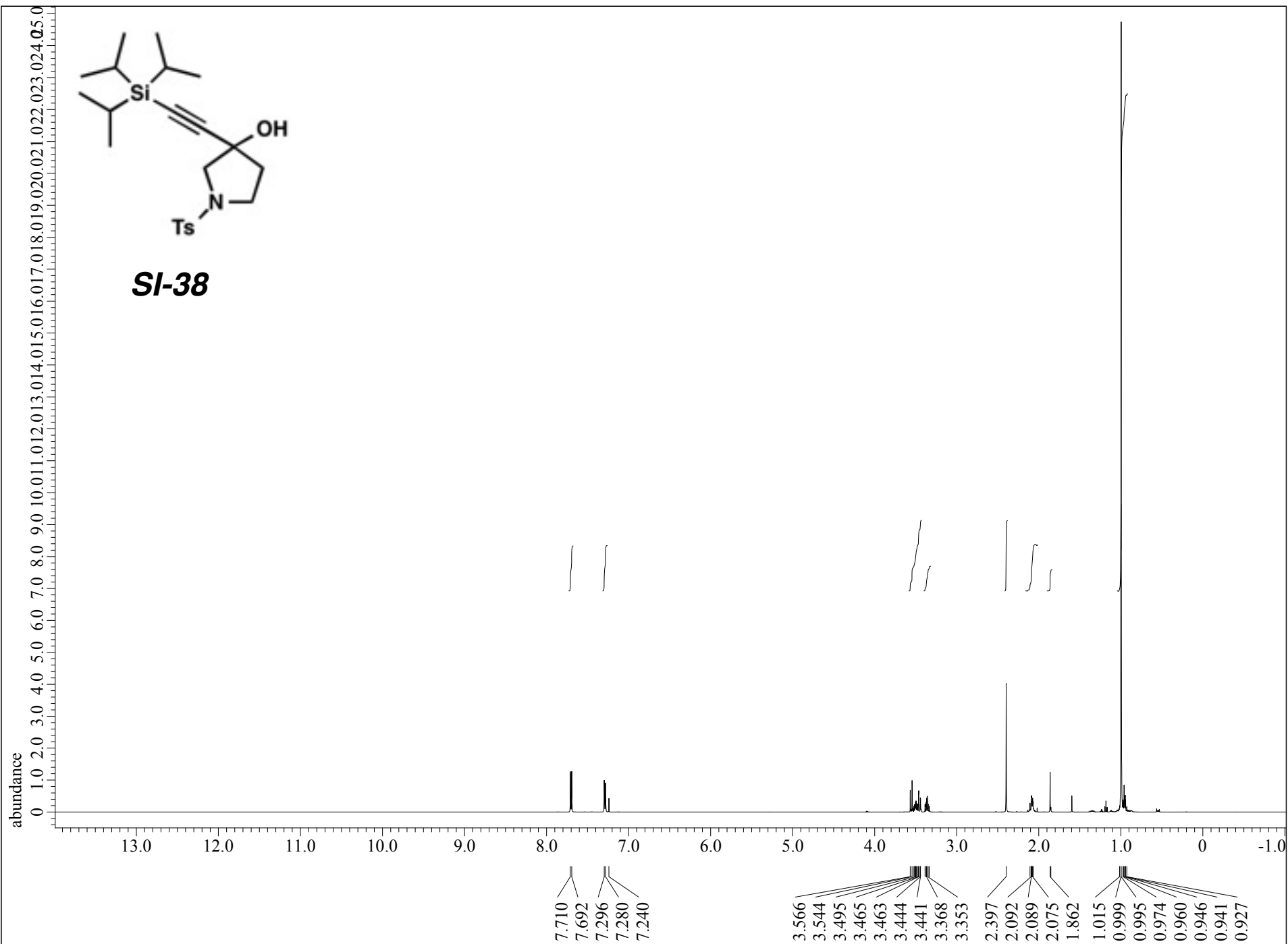


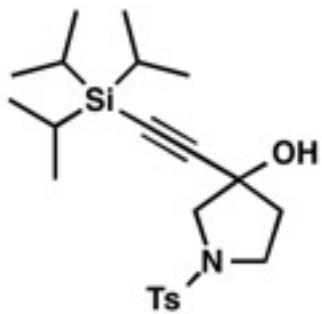
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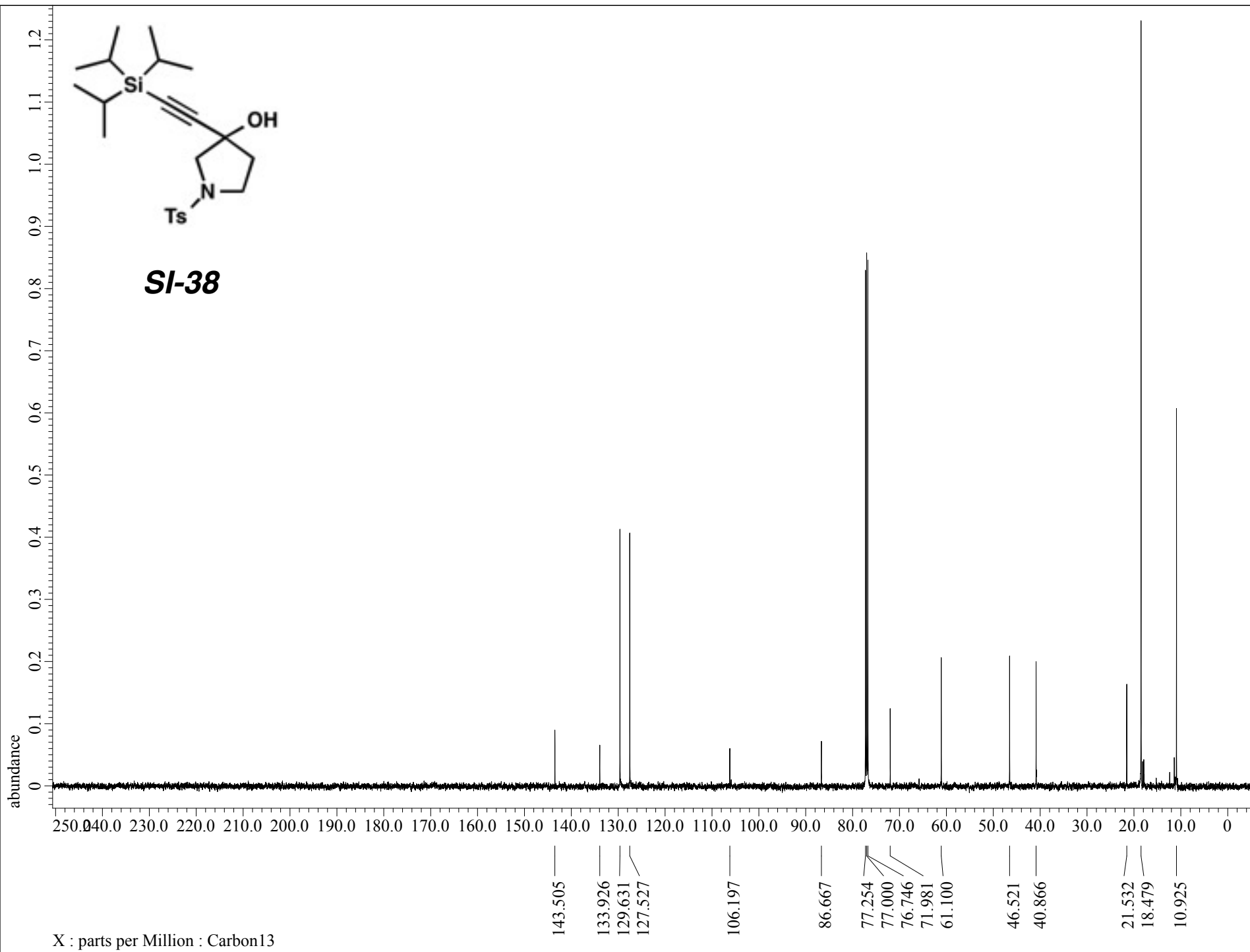


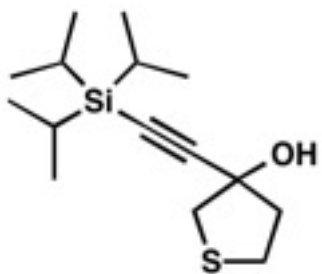
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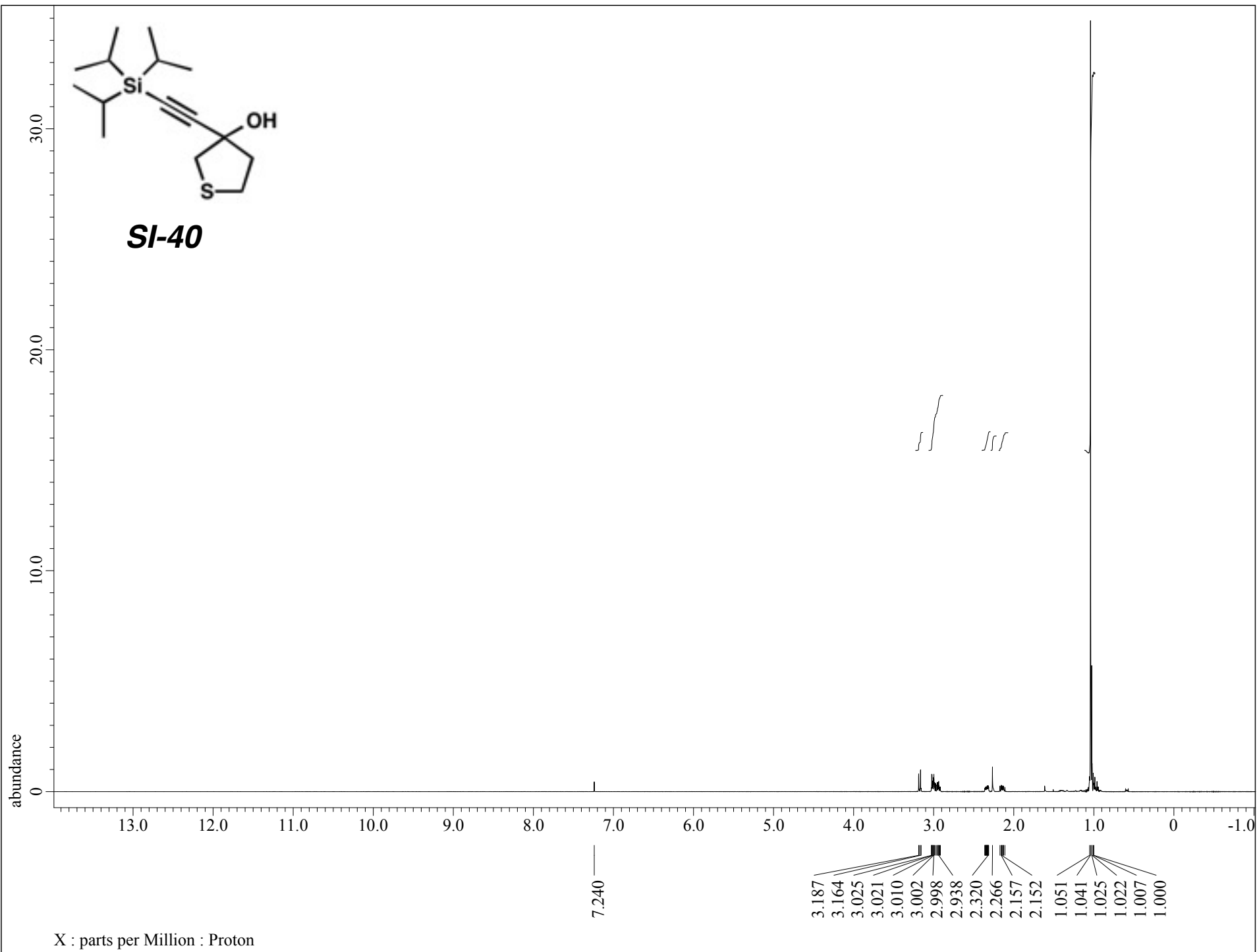


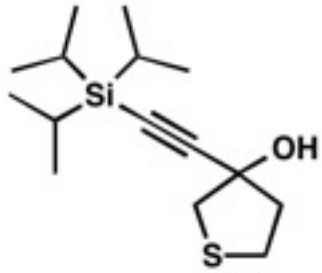
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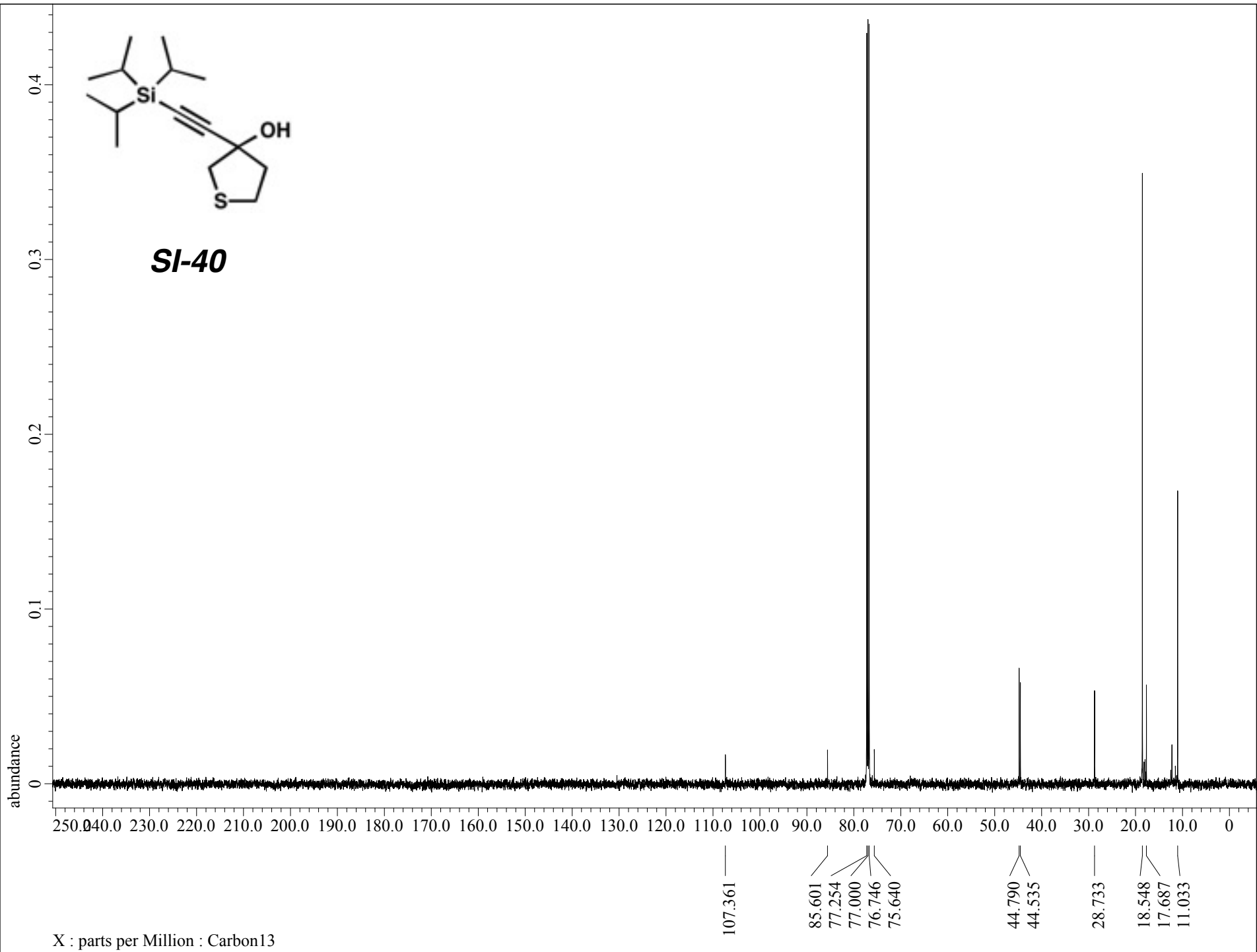


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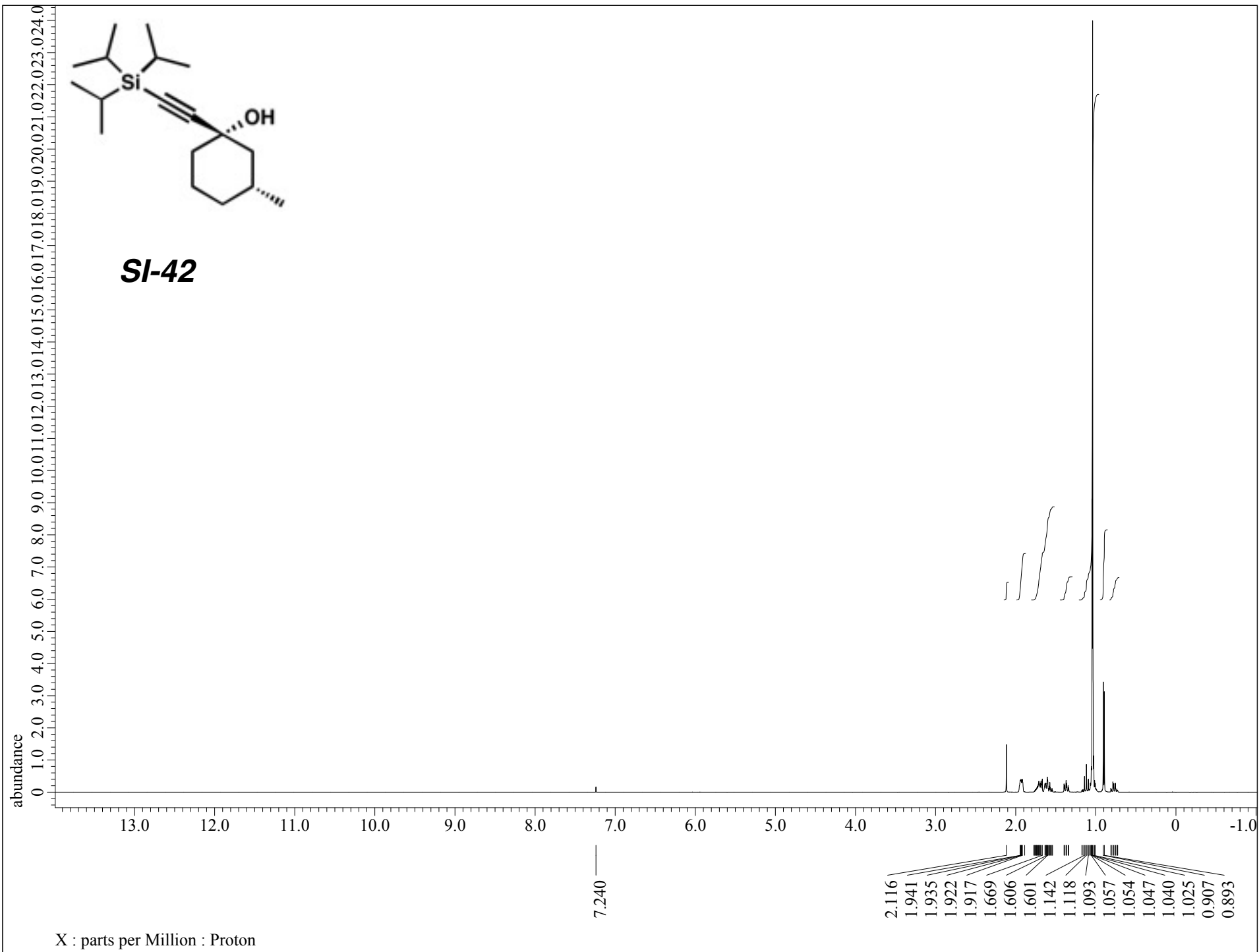




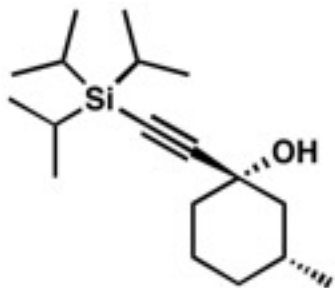
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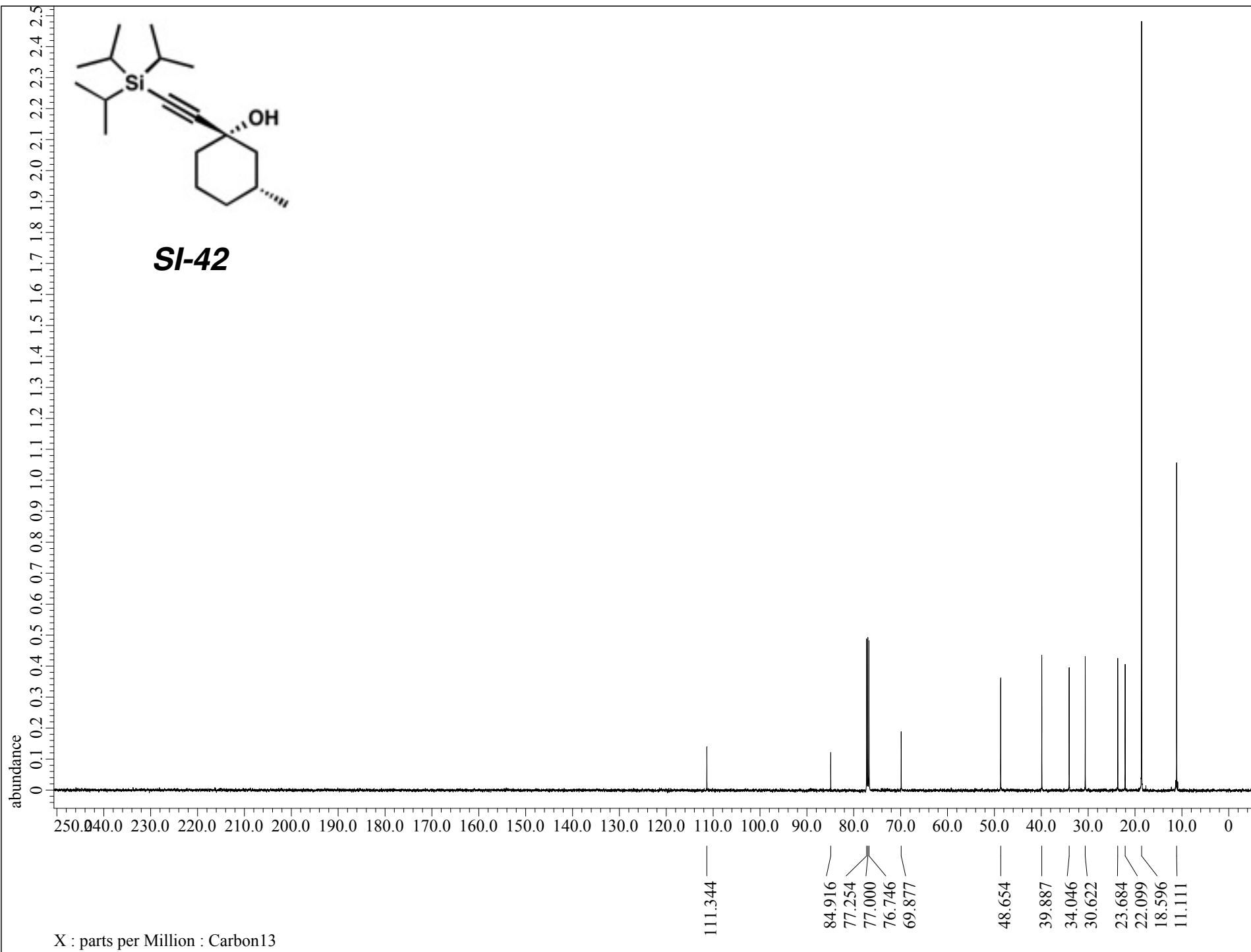
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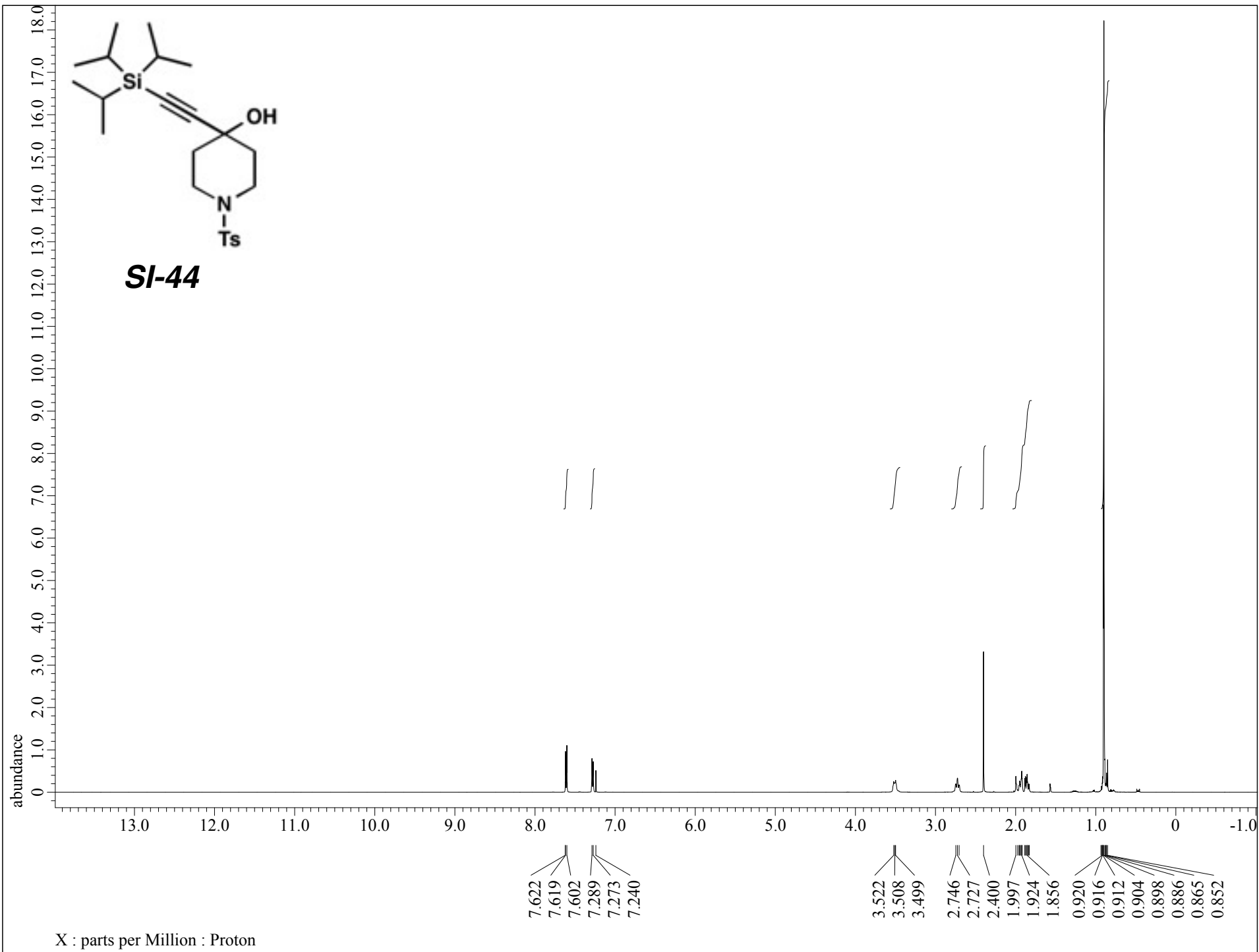


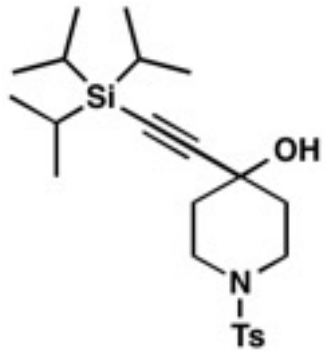




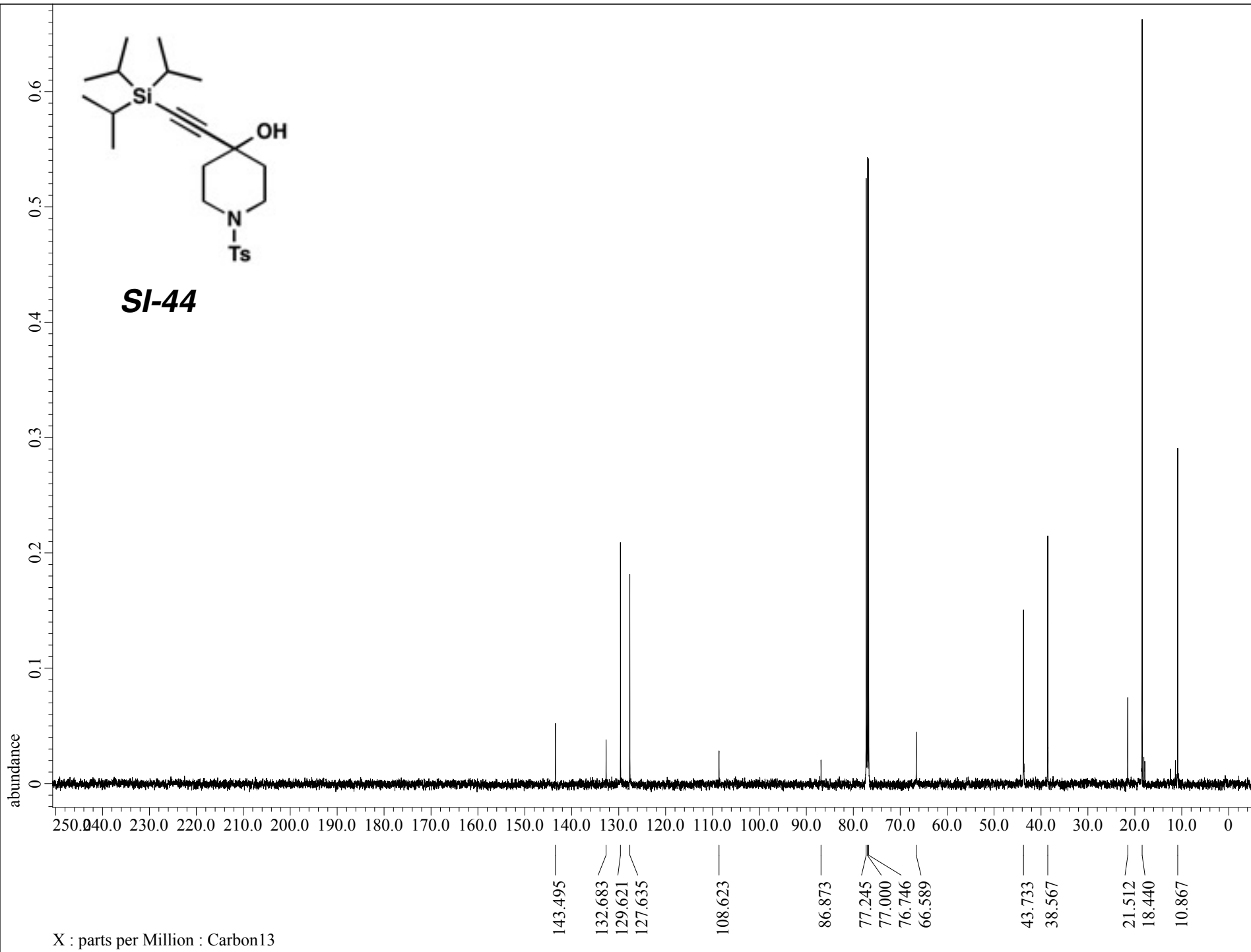
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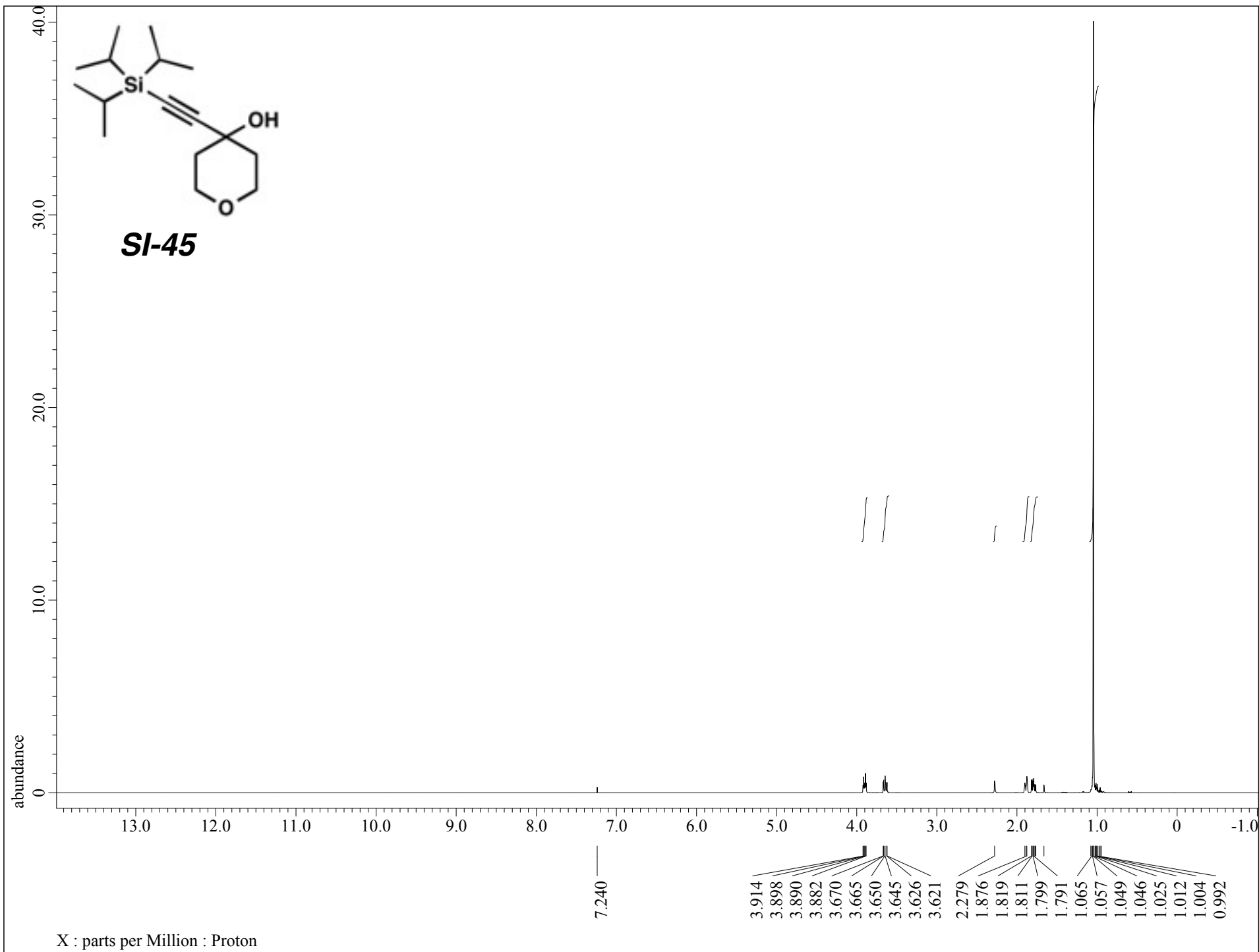




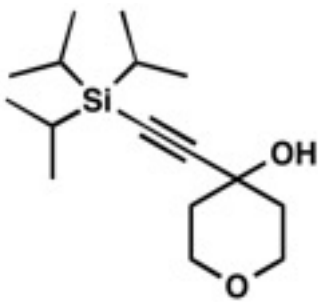


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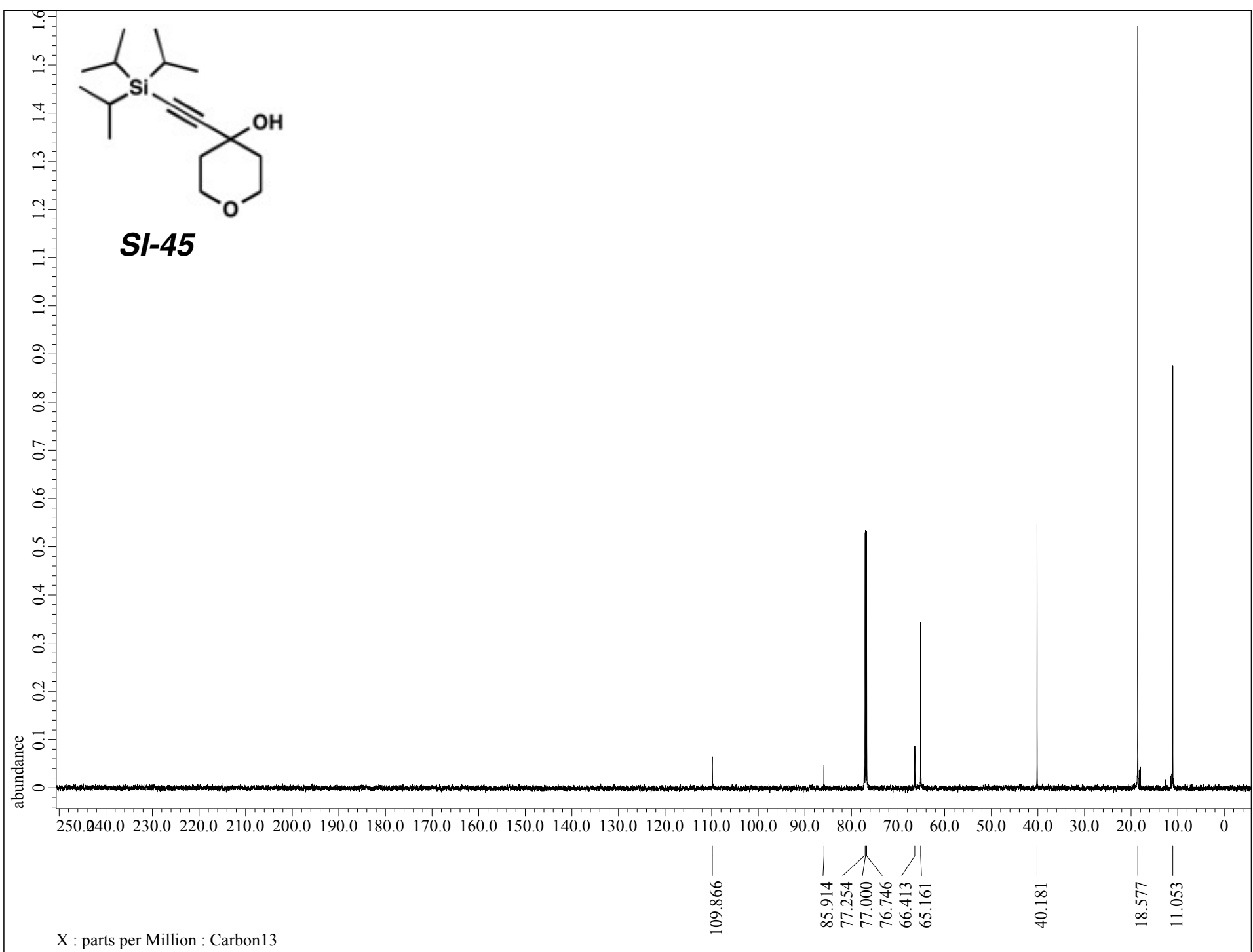


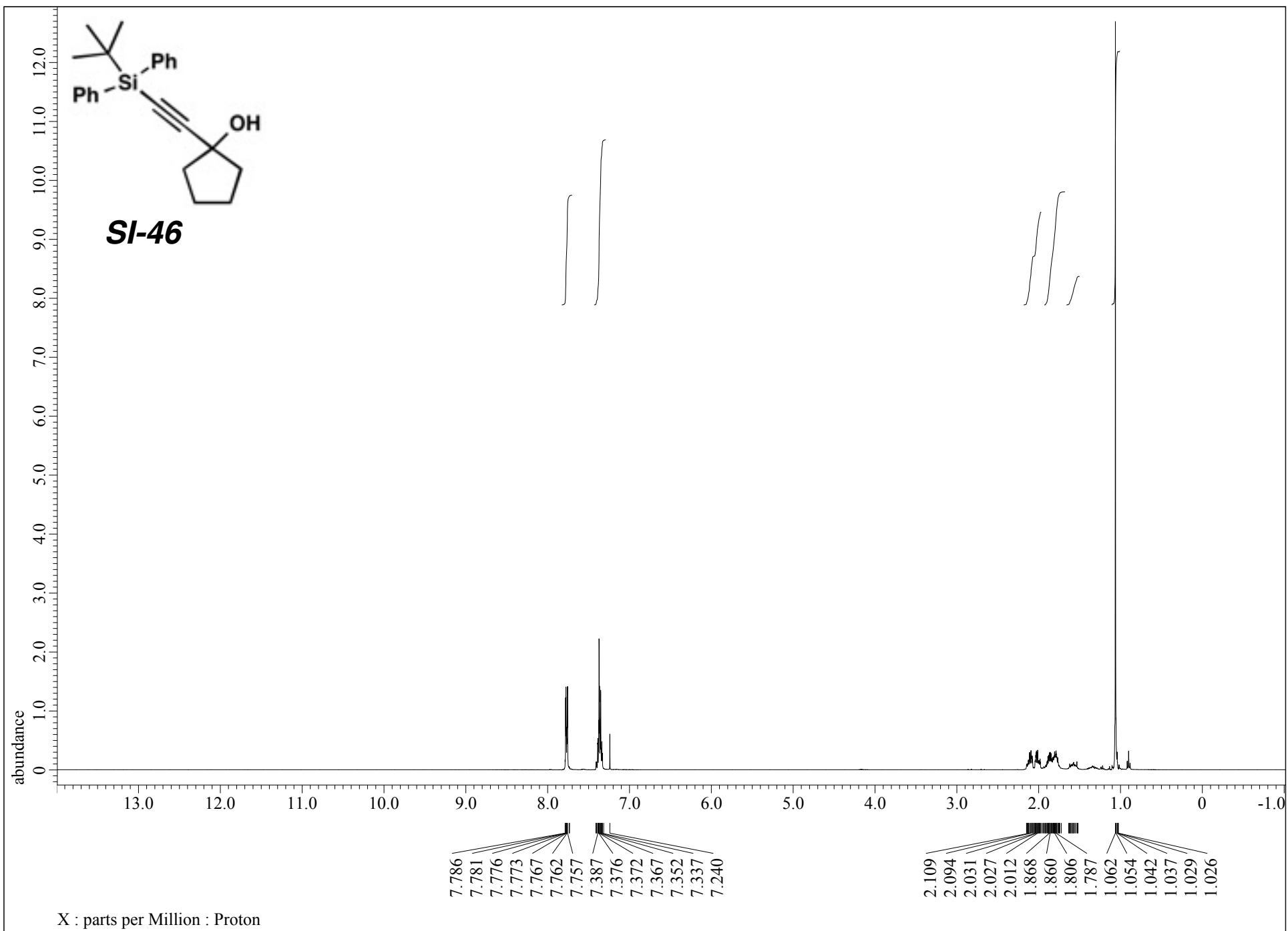


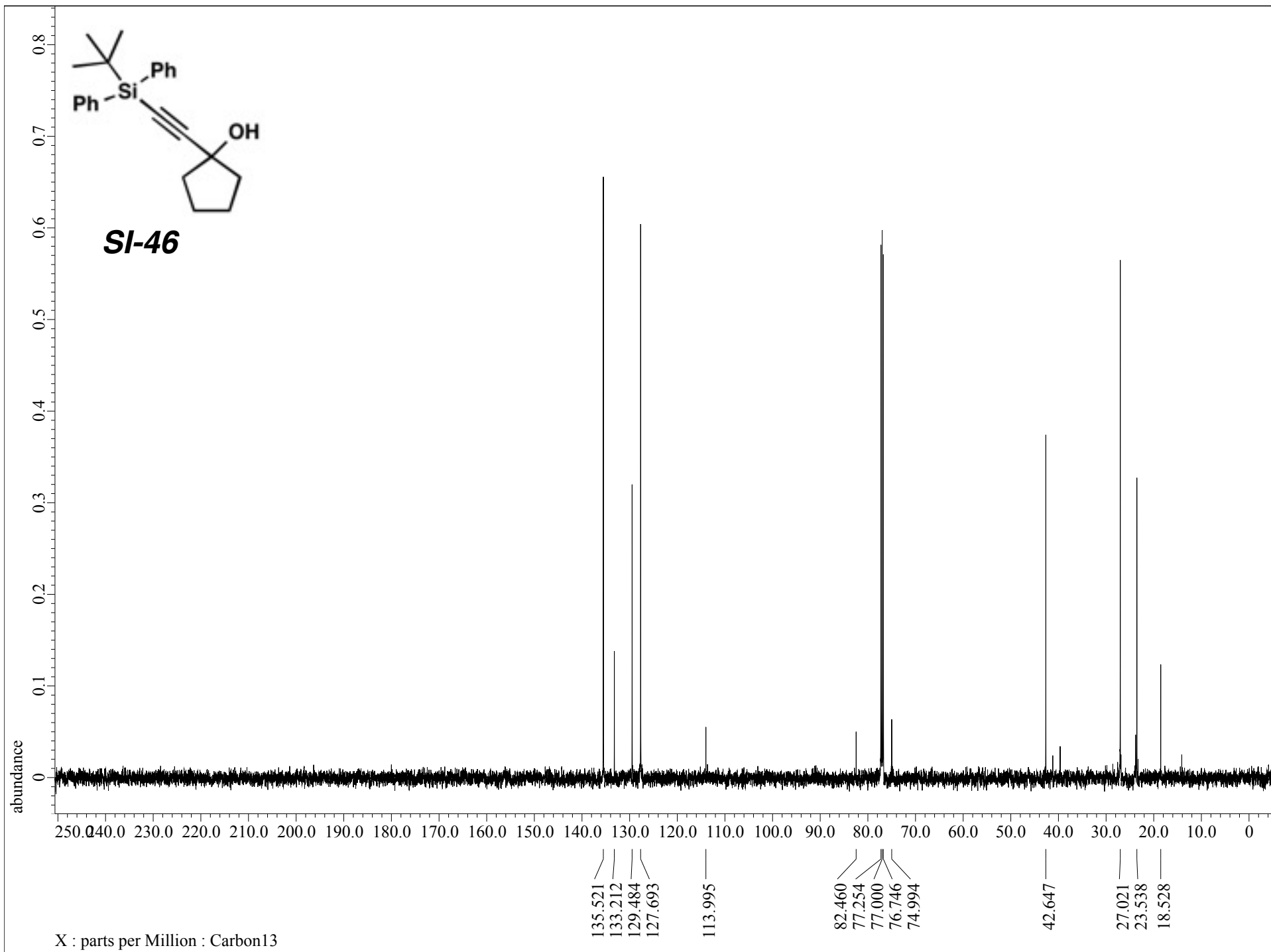
SI-85



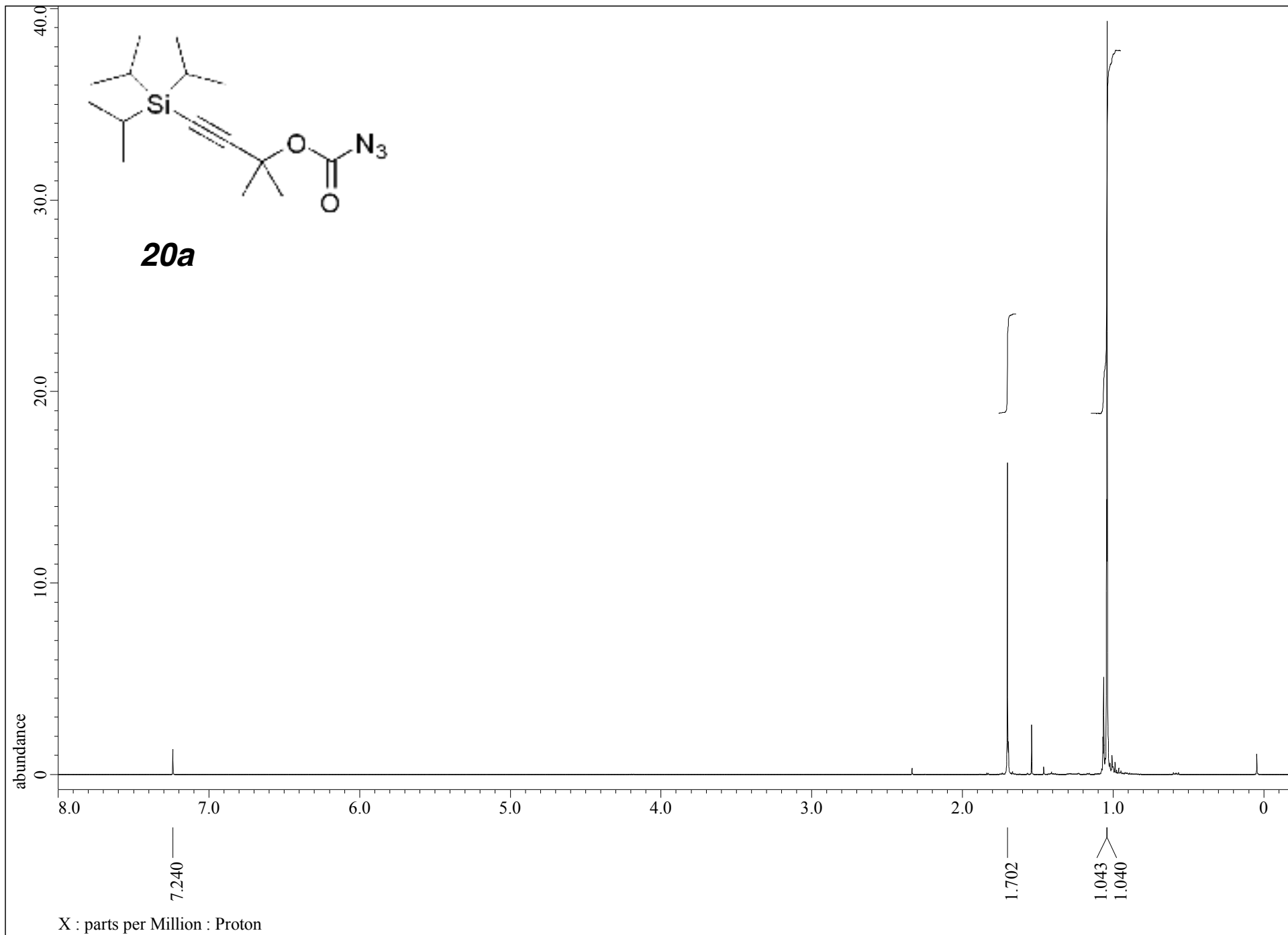
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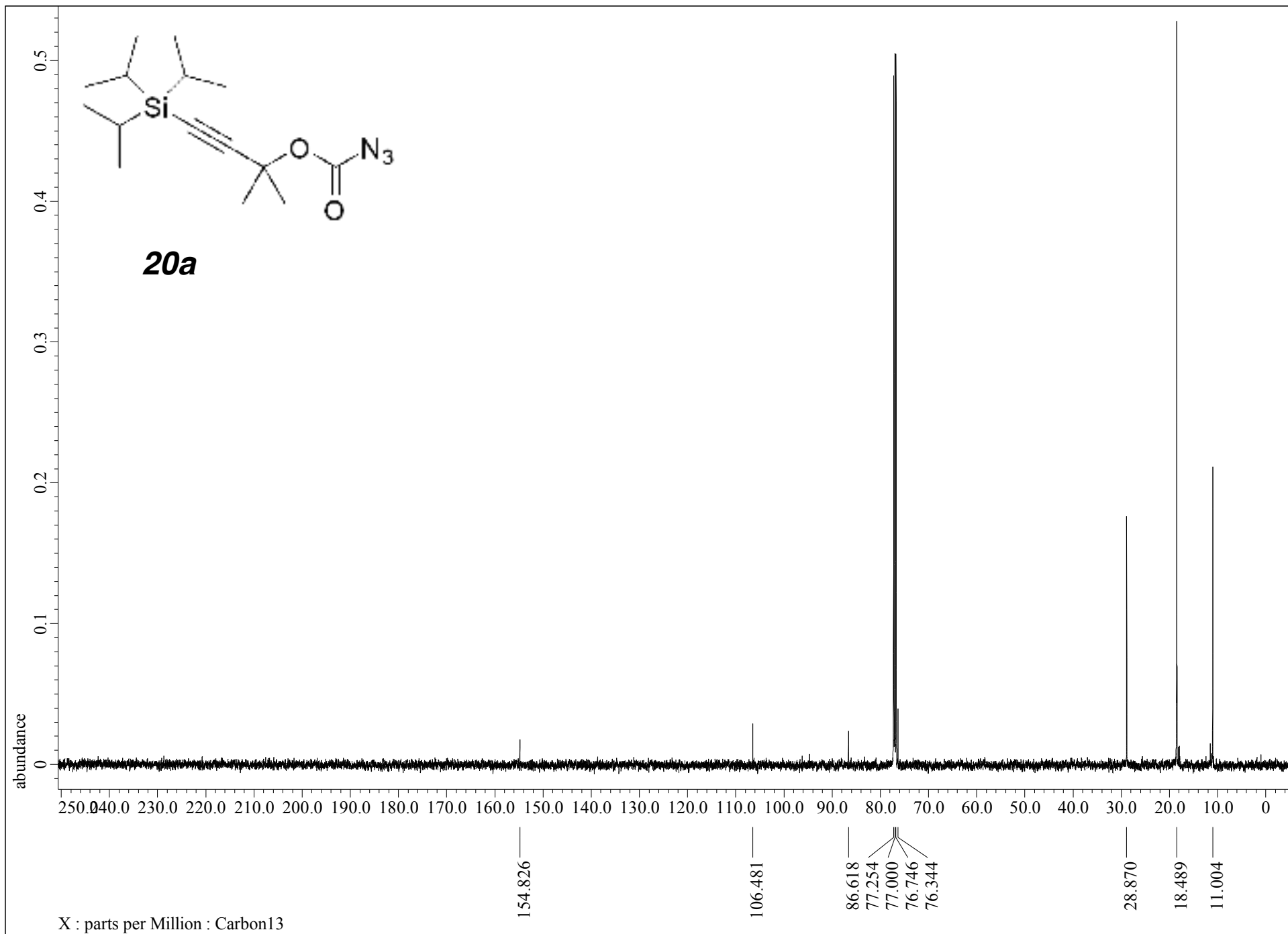


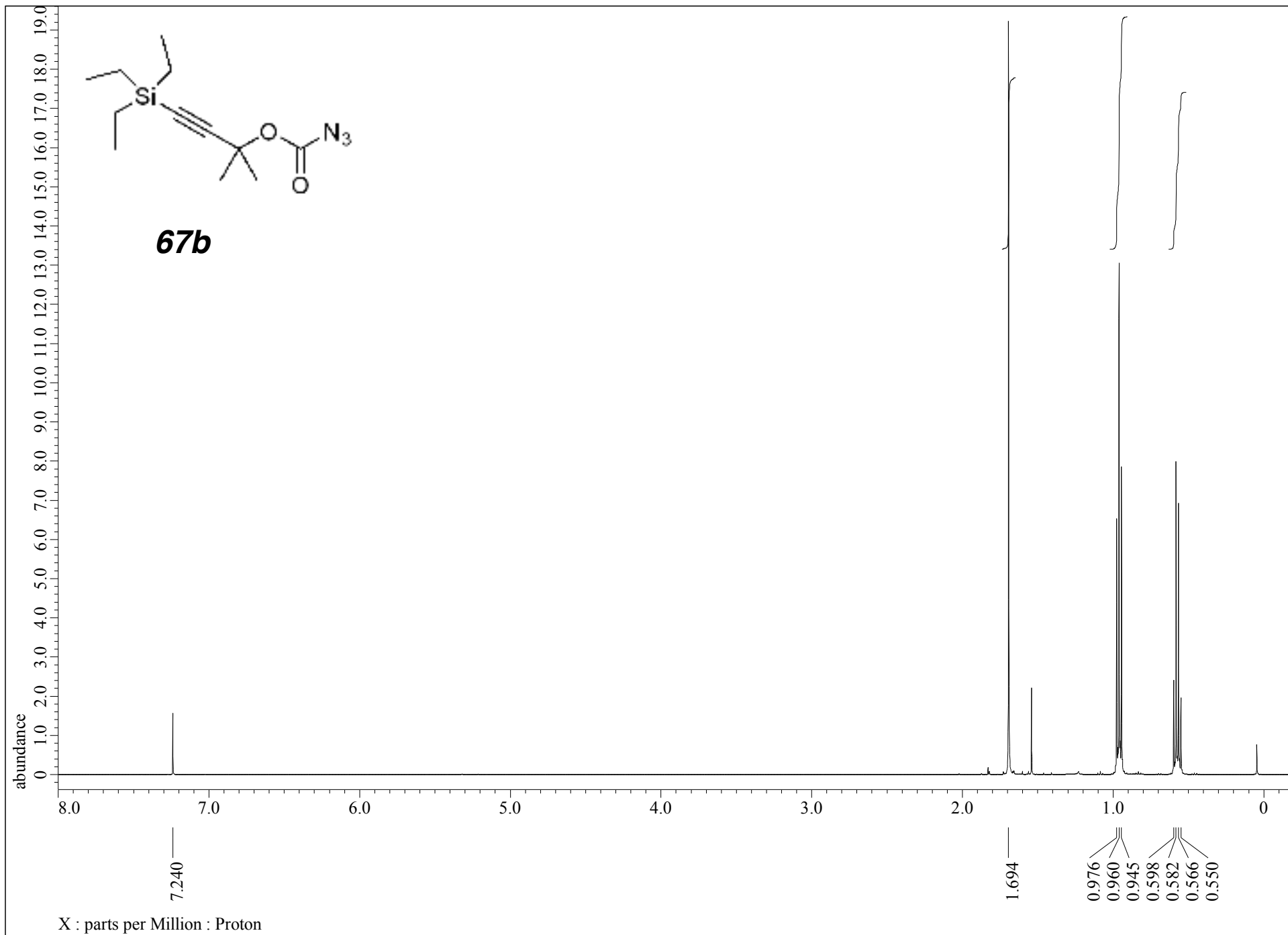


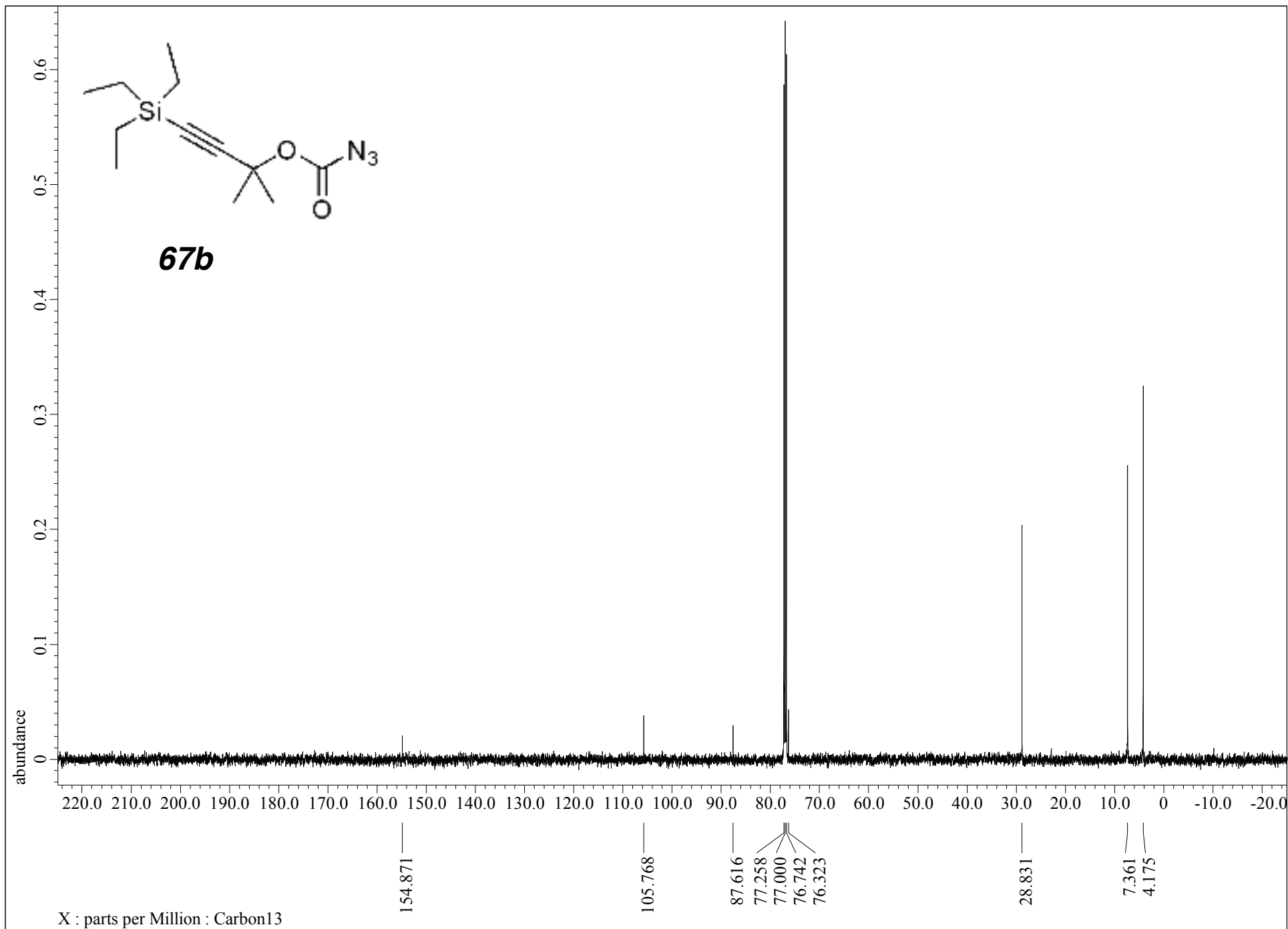
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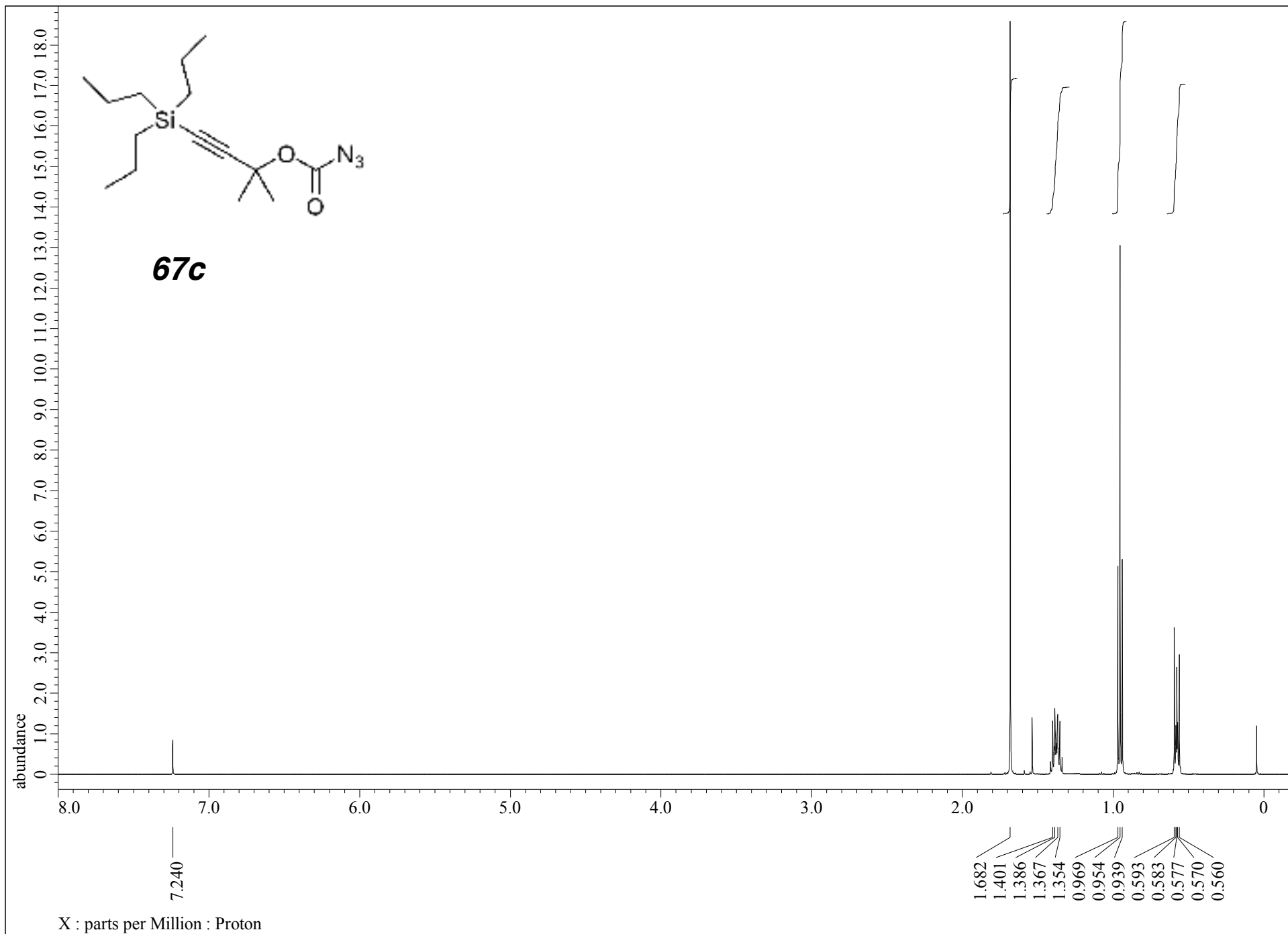


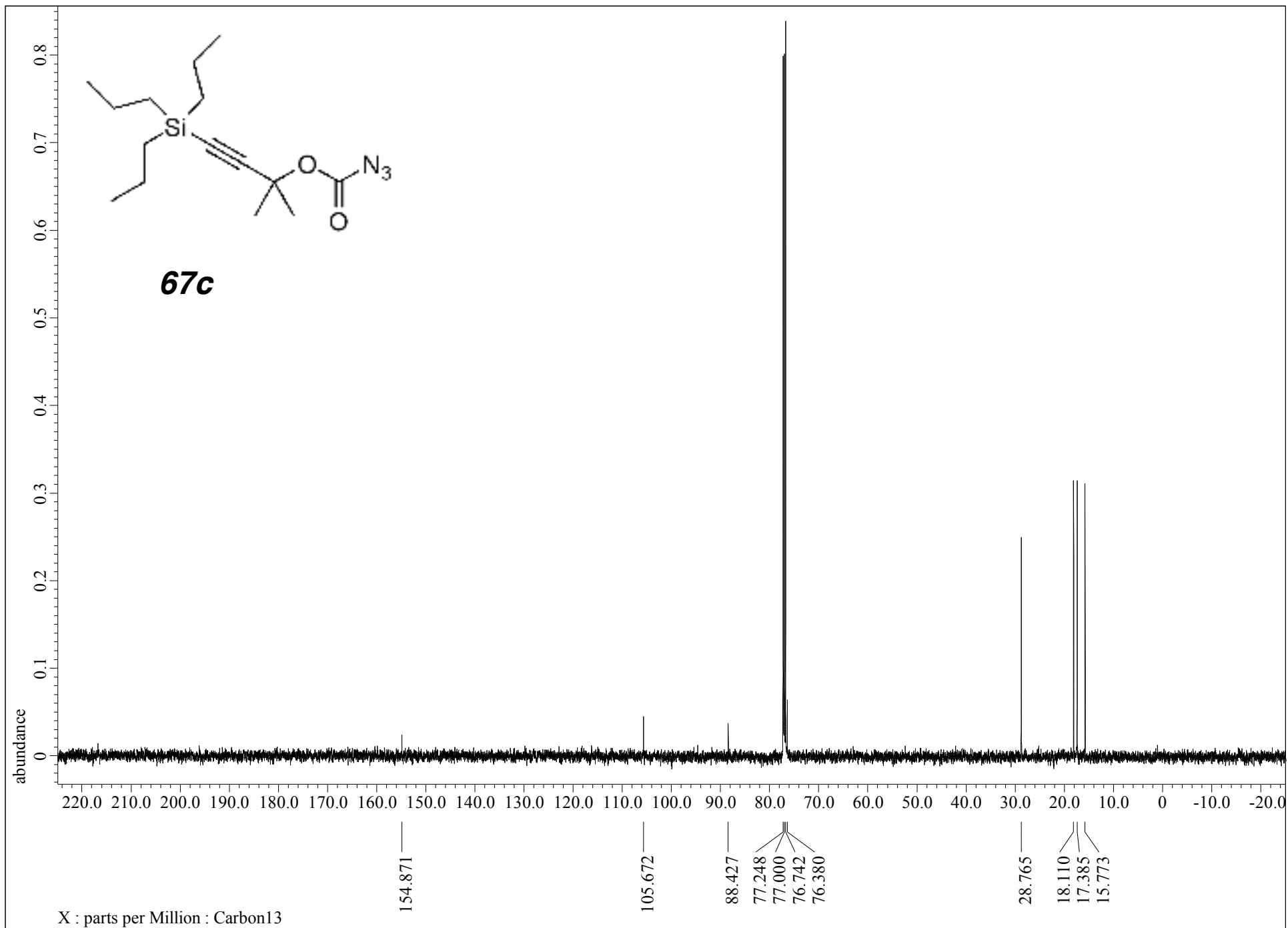


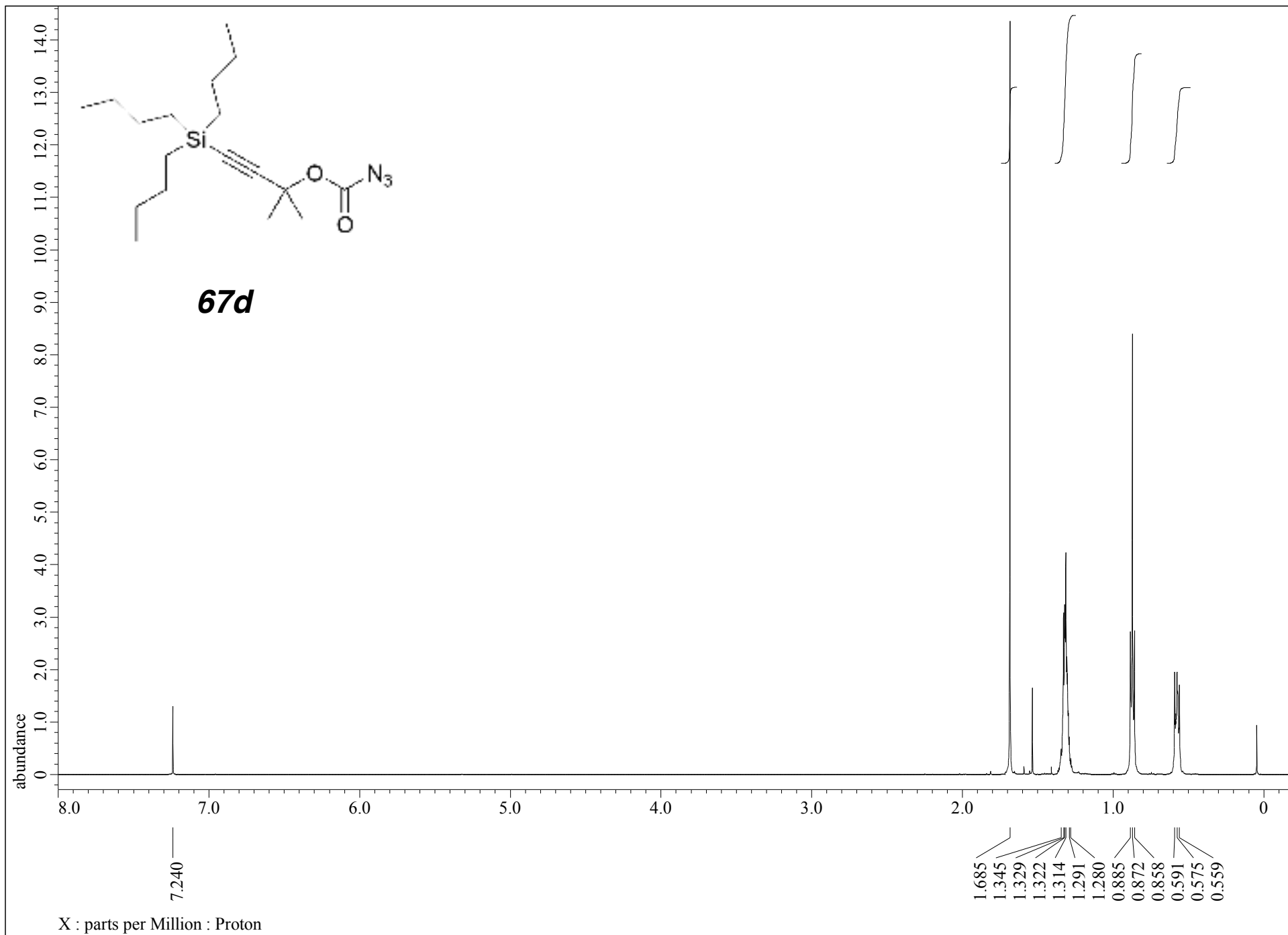


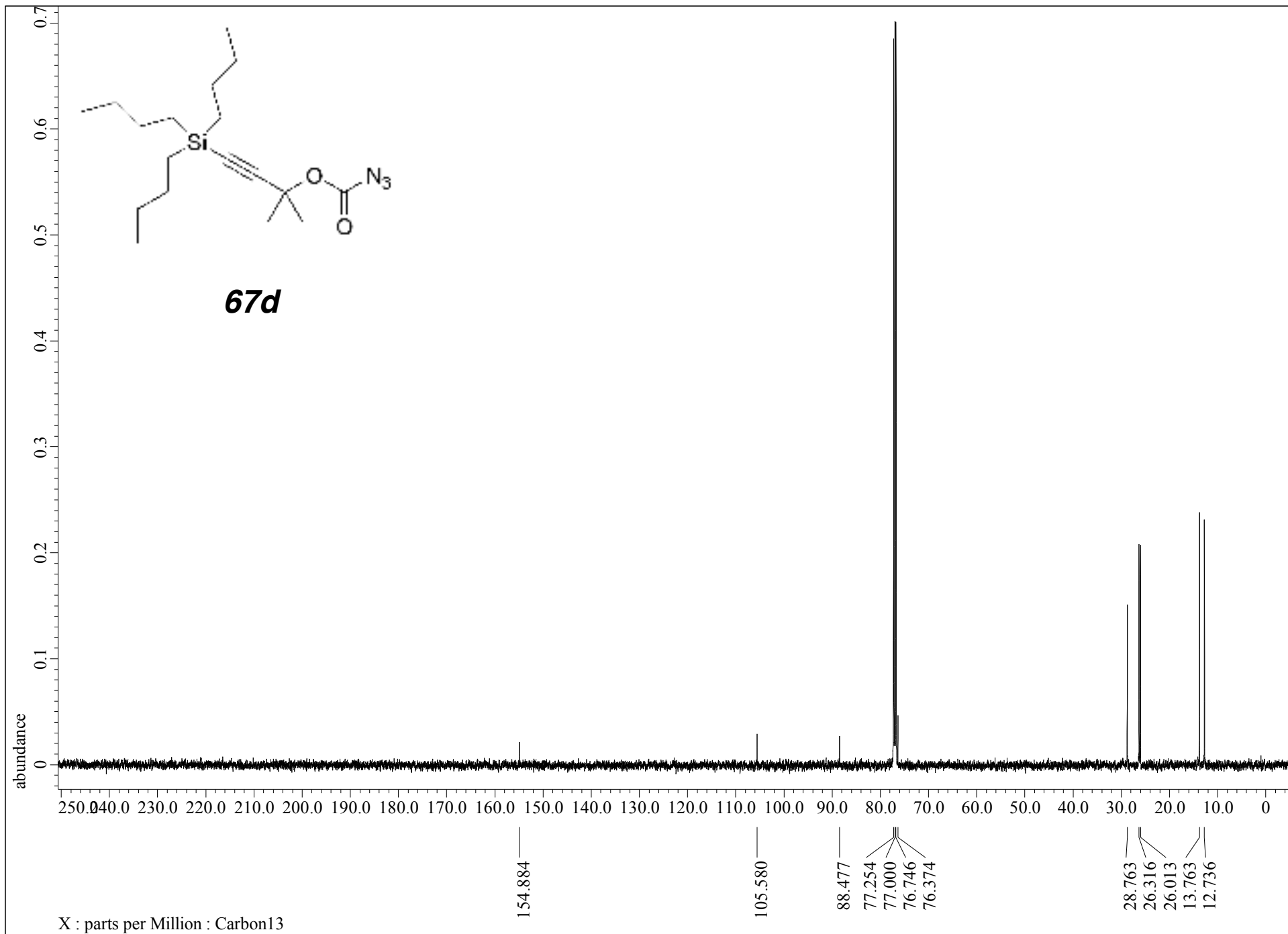


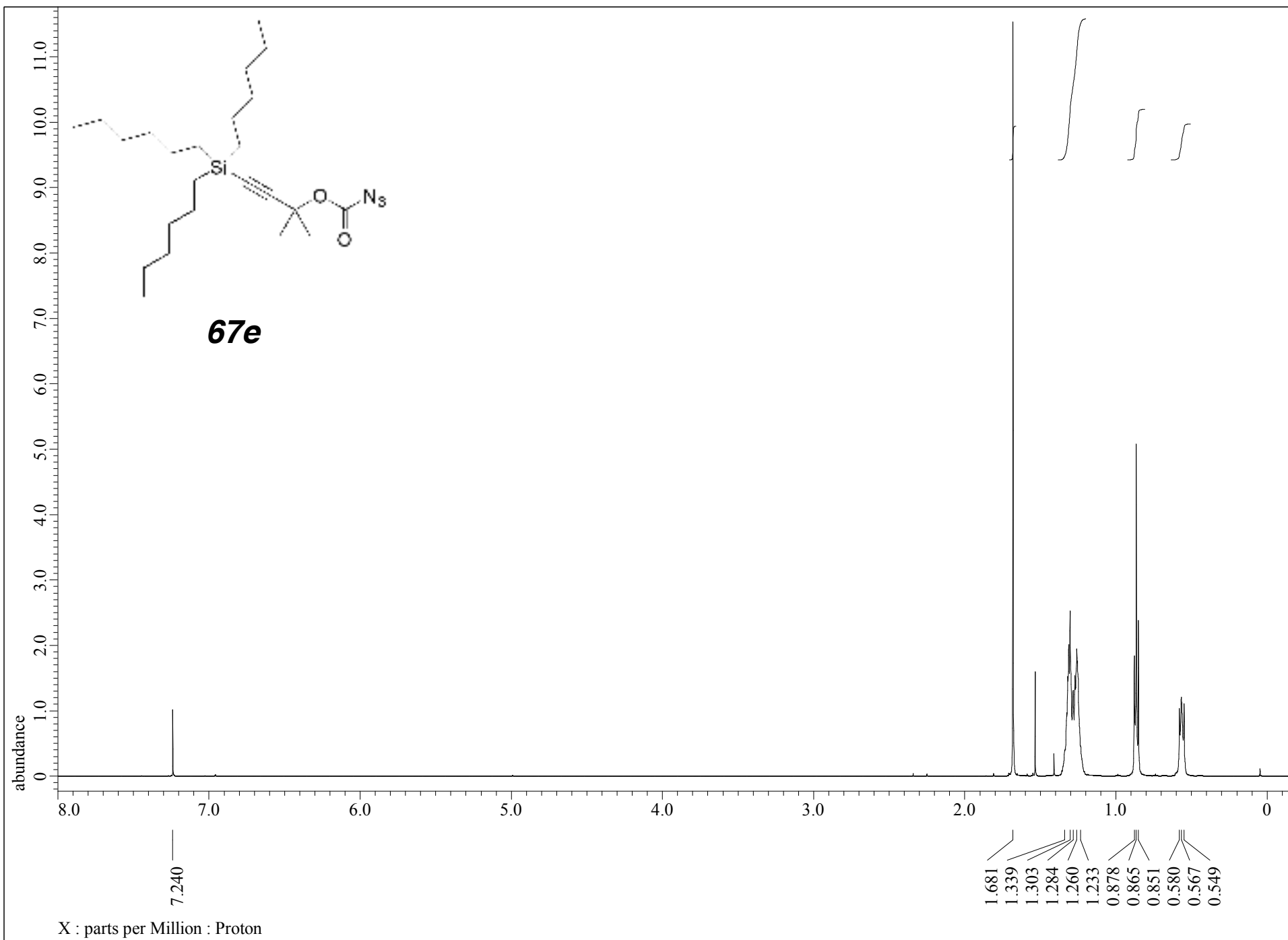




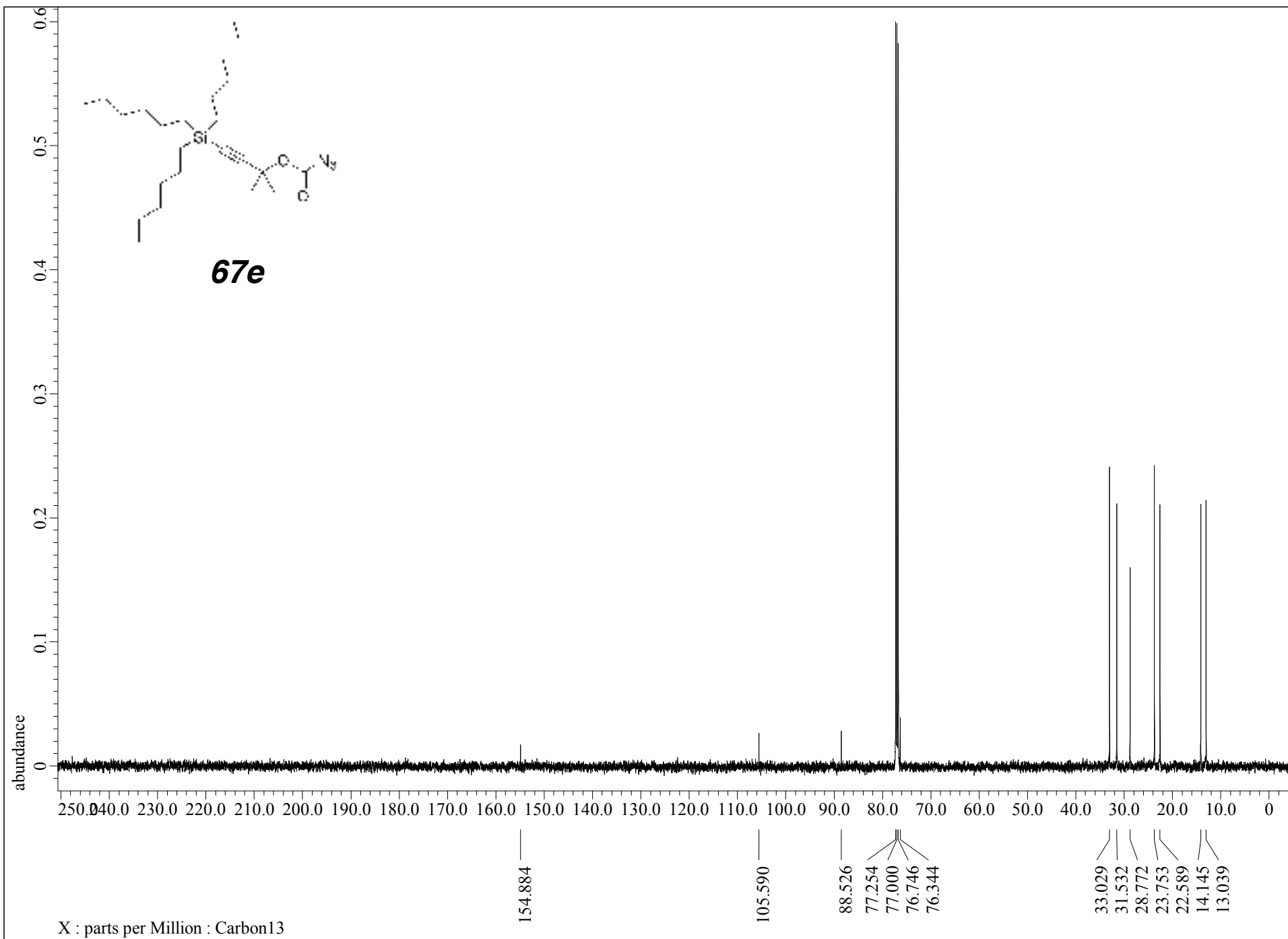


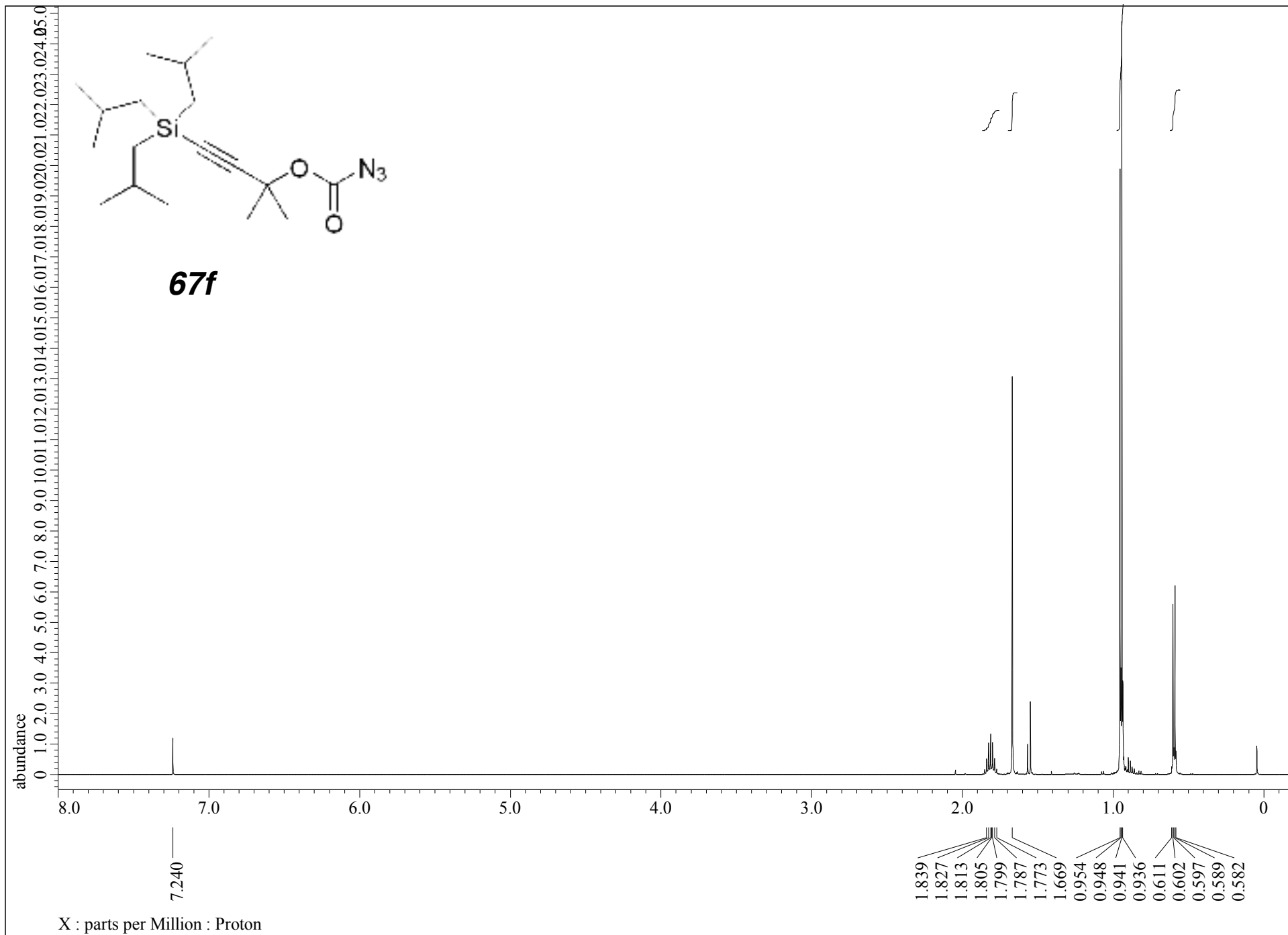


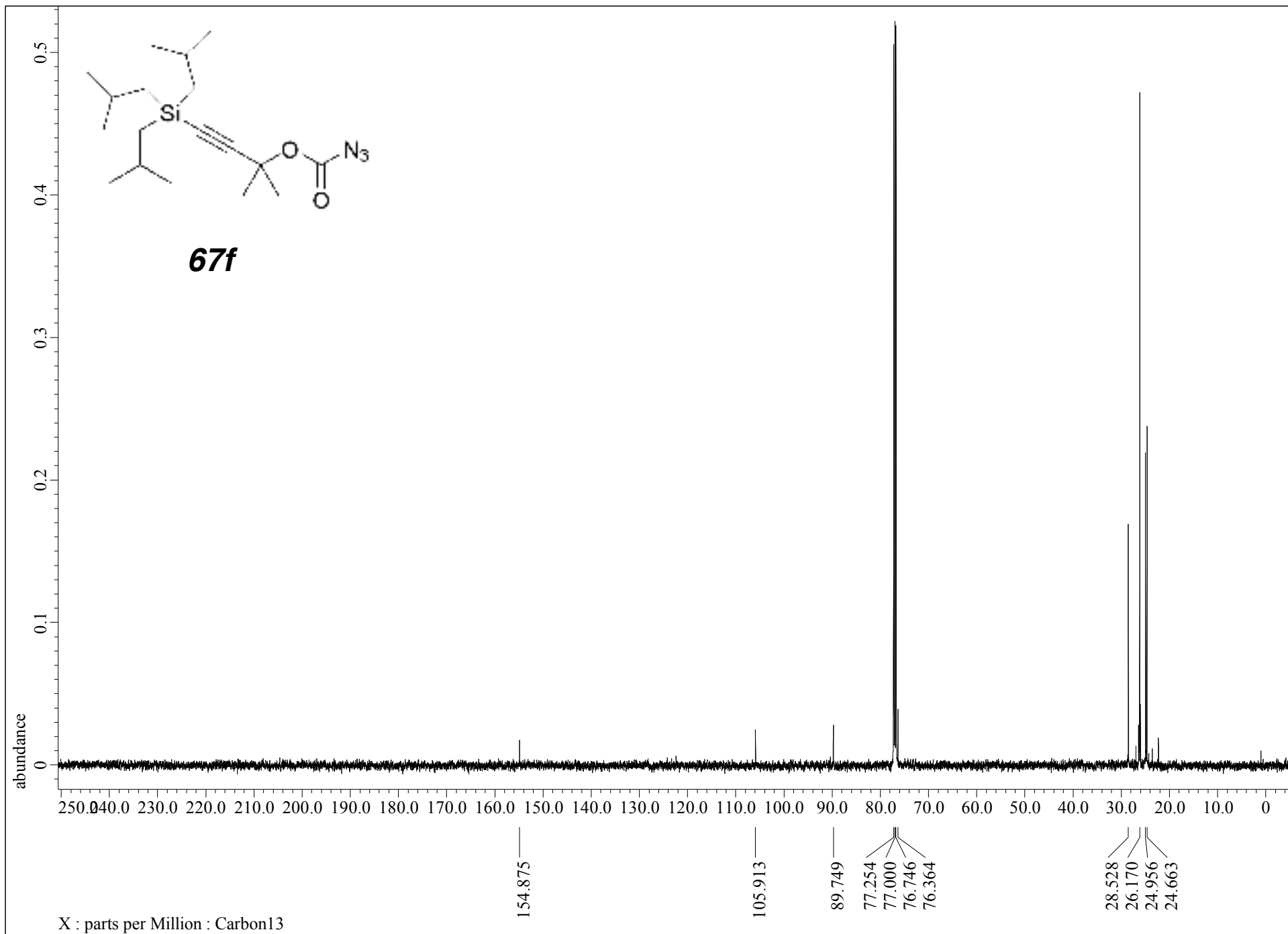


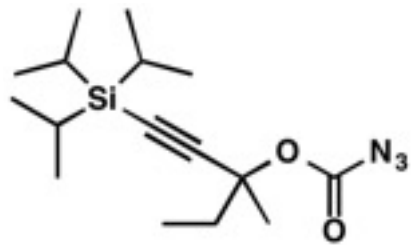




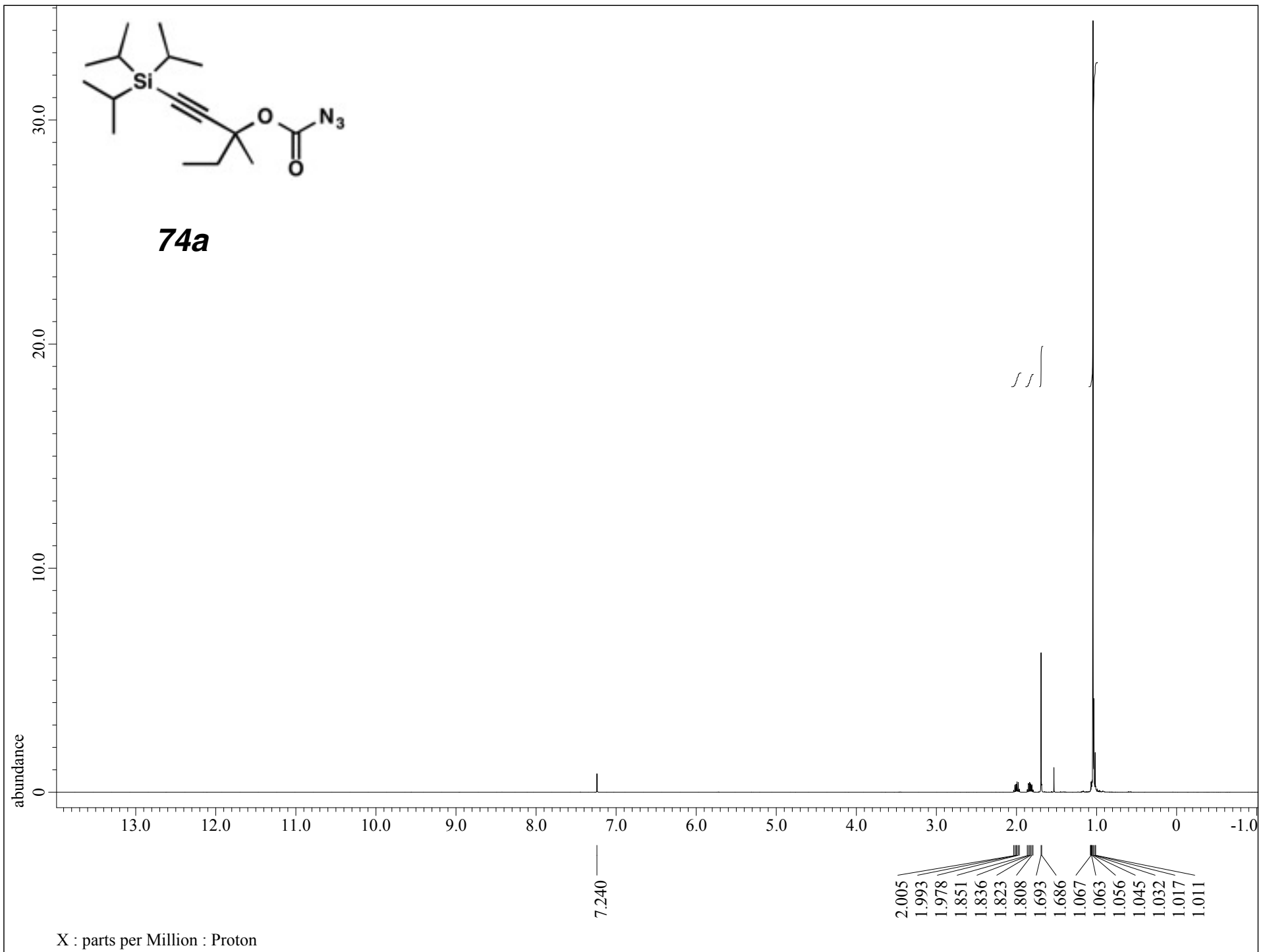


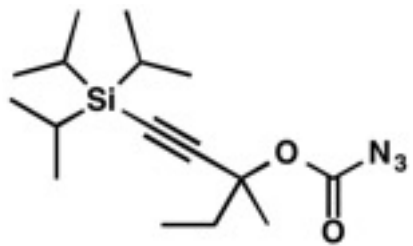




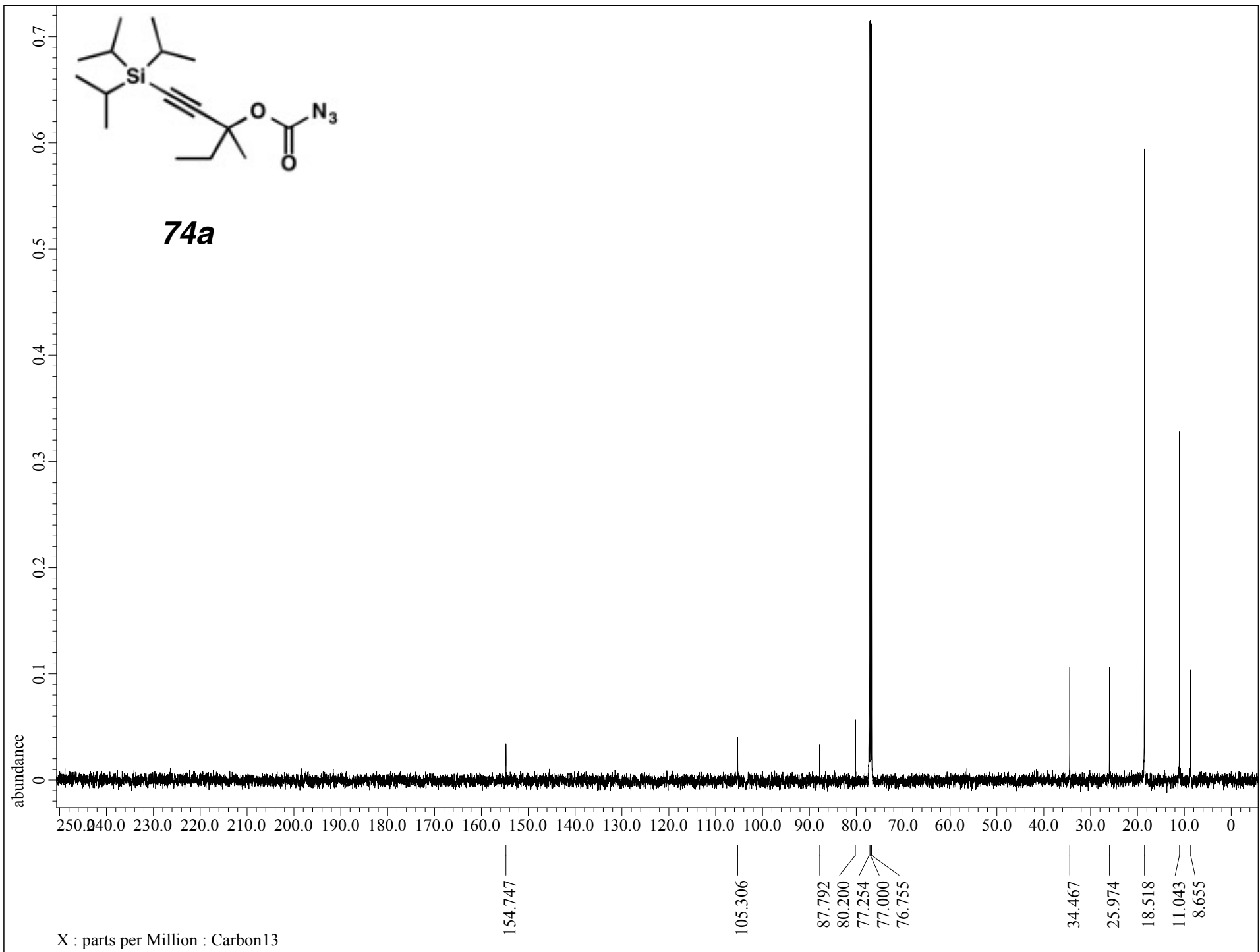


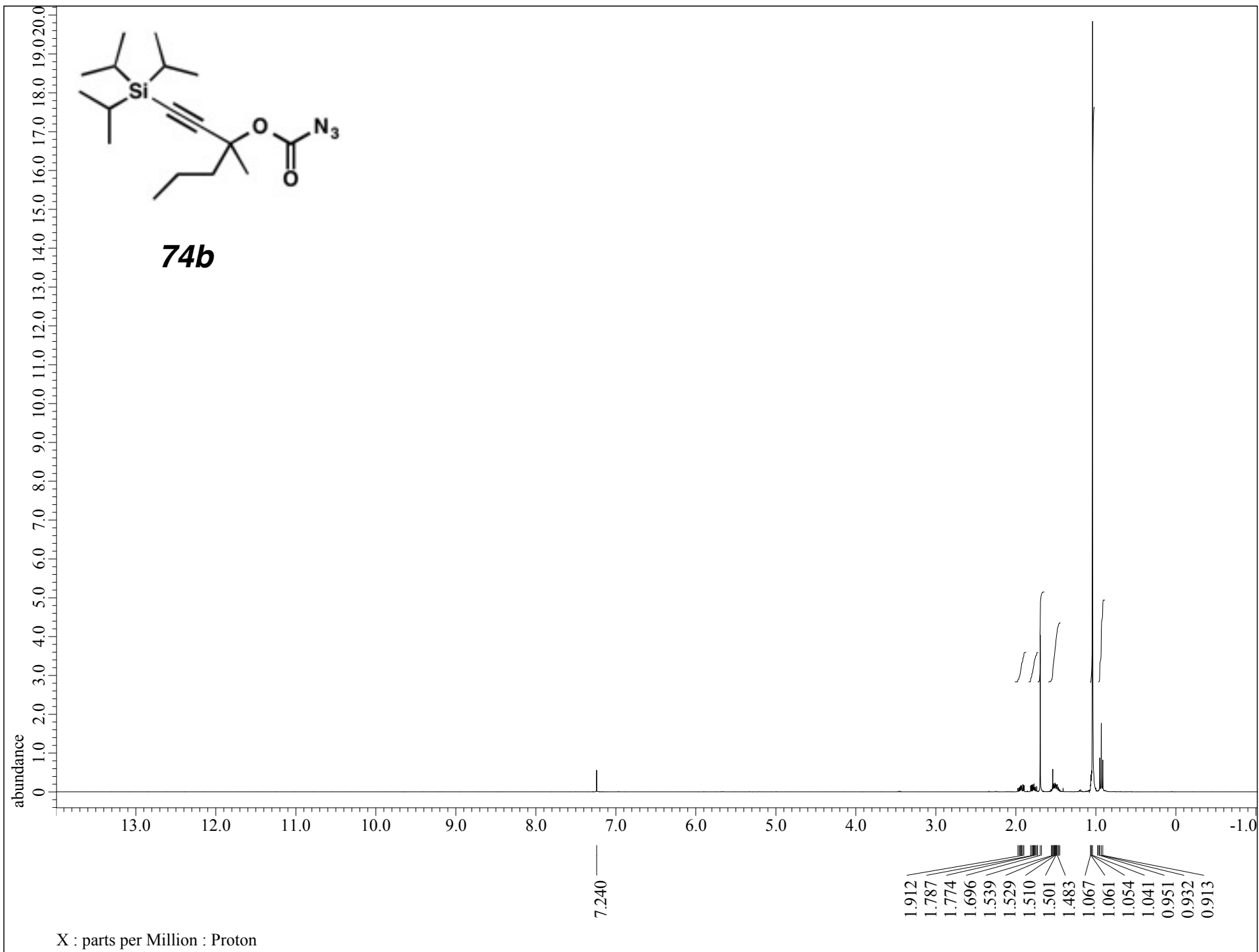
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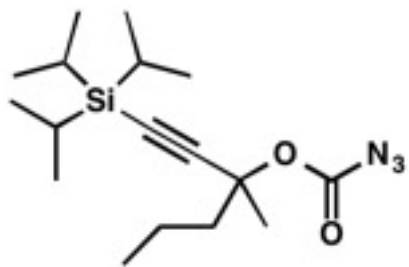




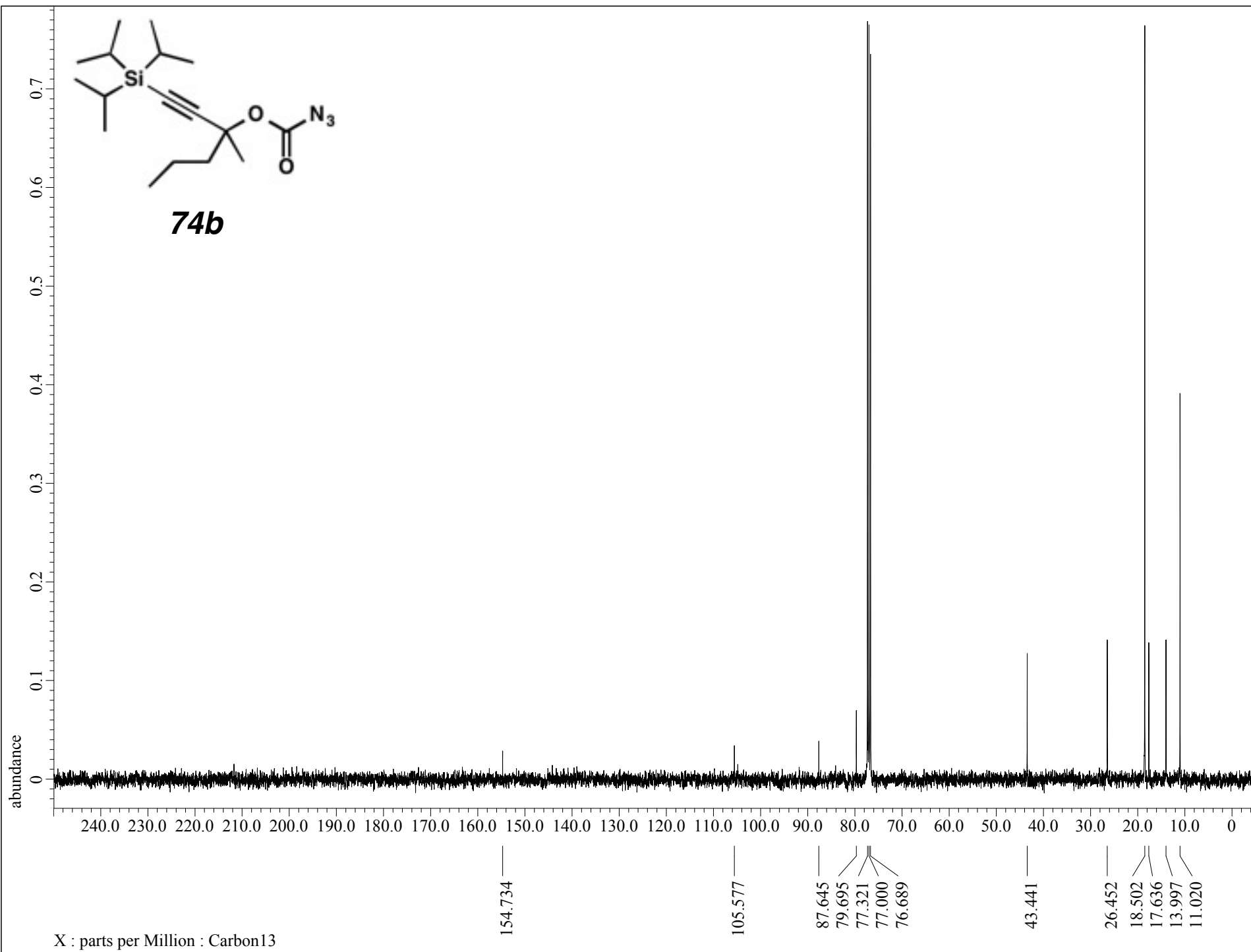
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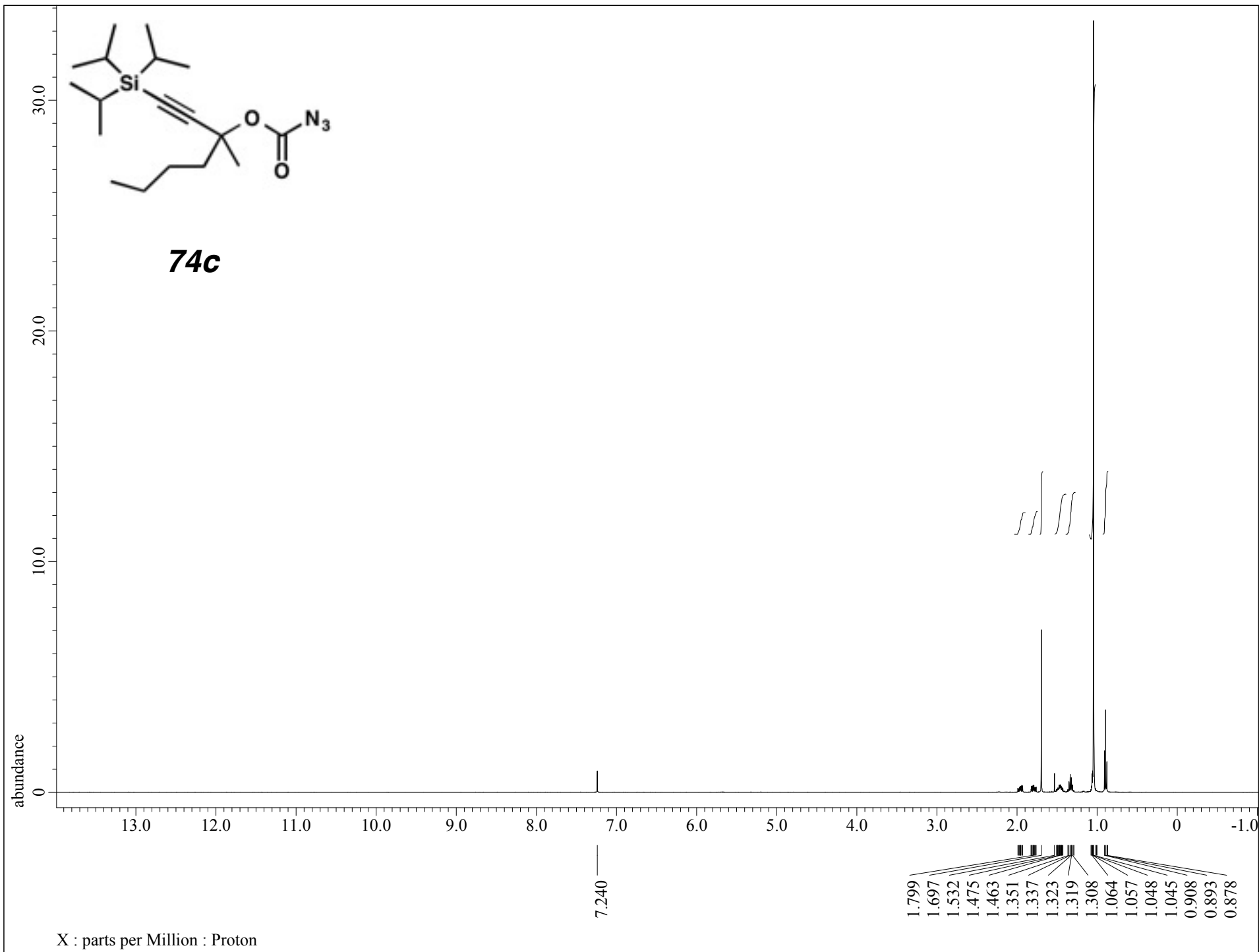




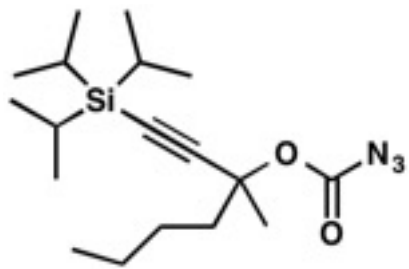


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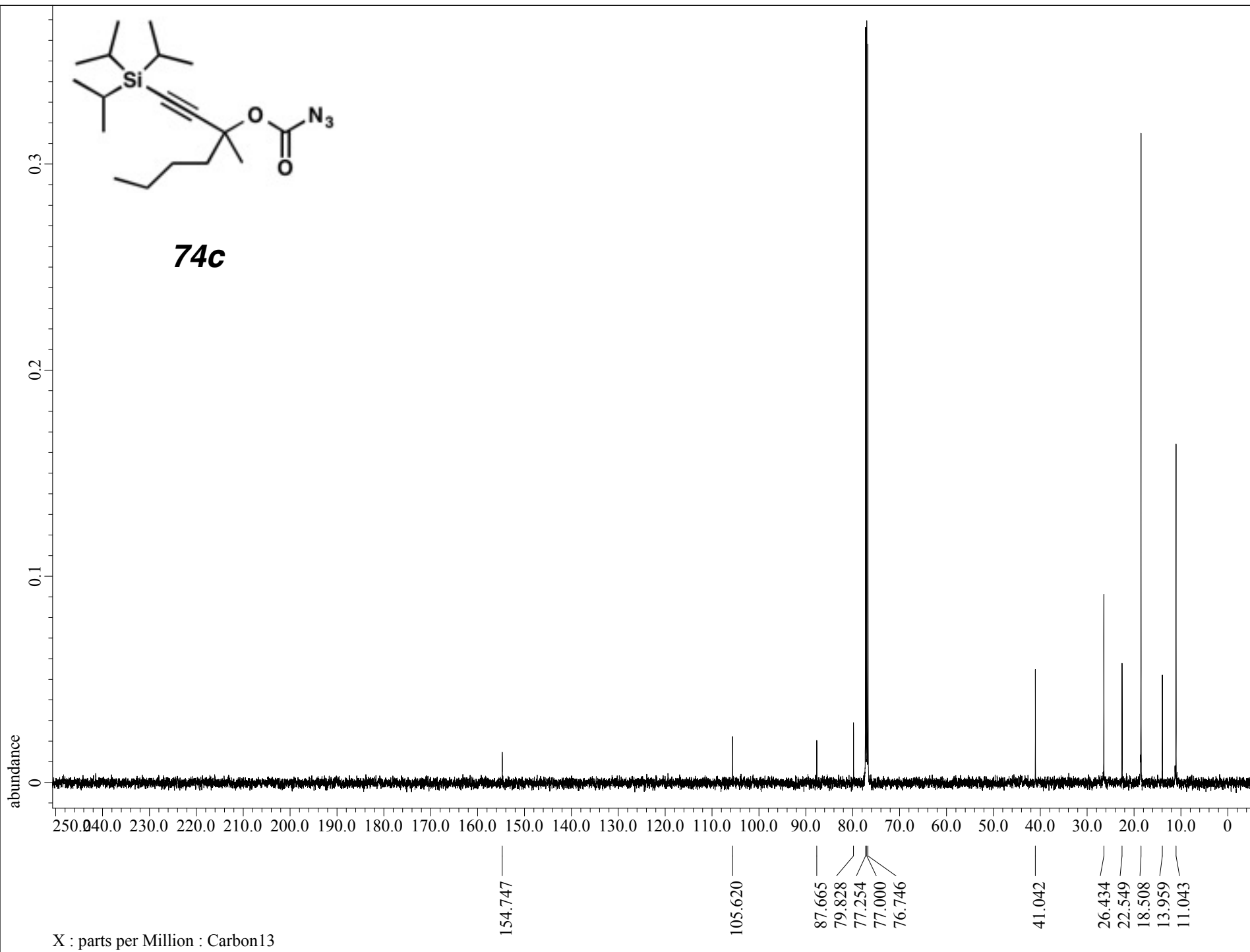


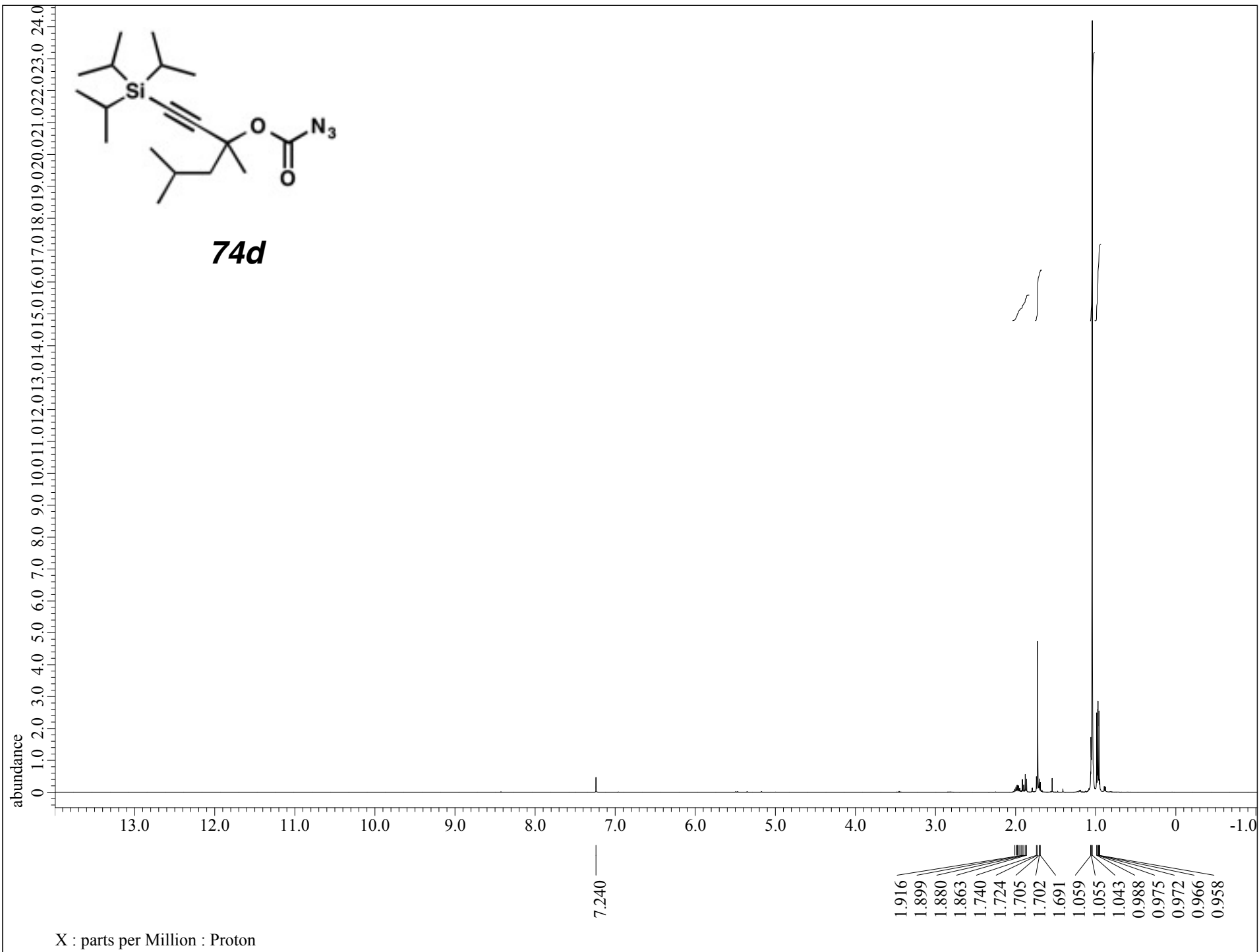


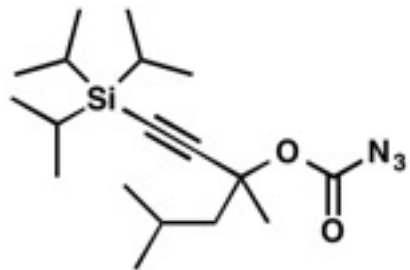




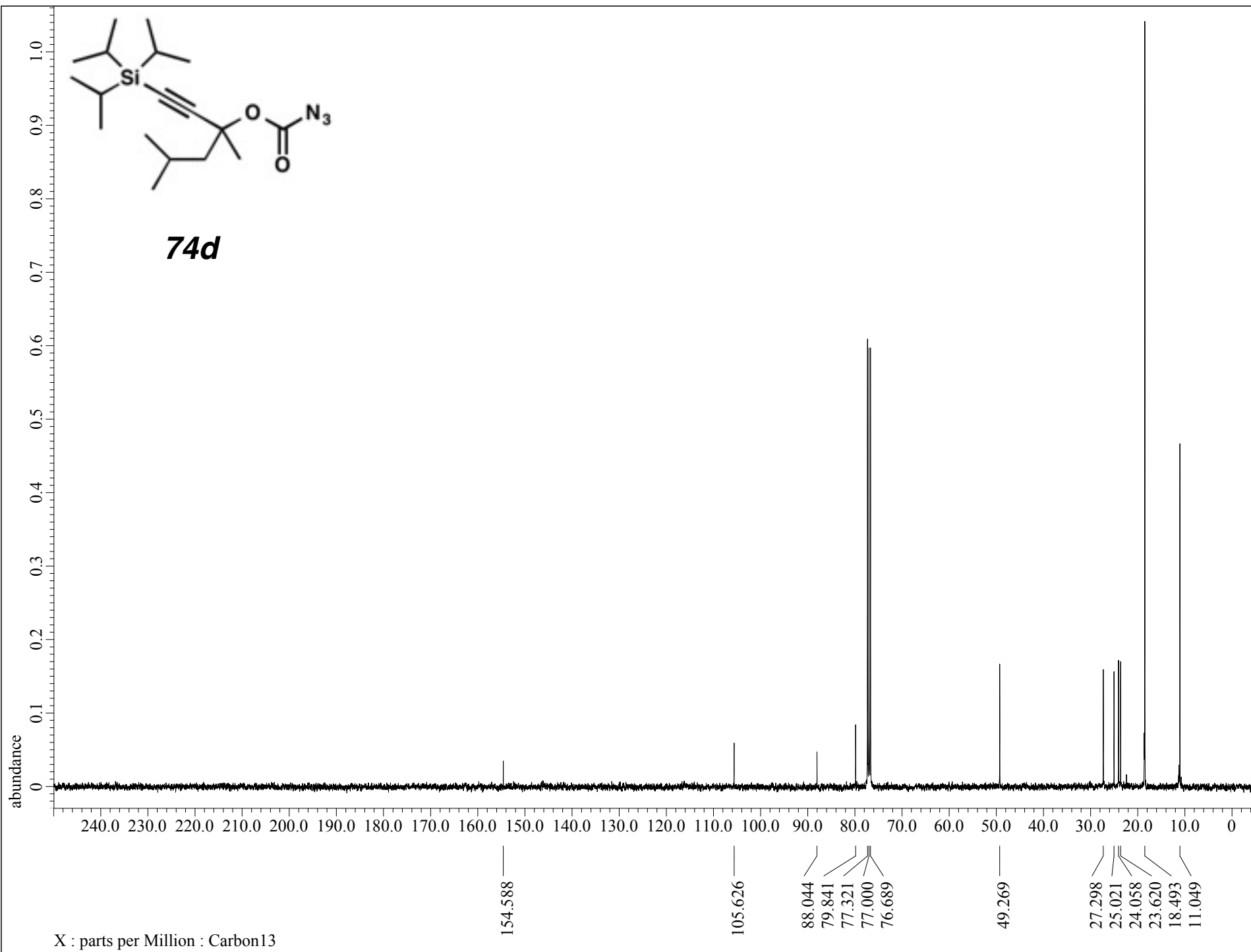
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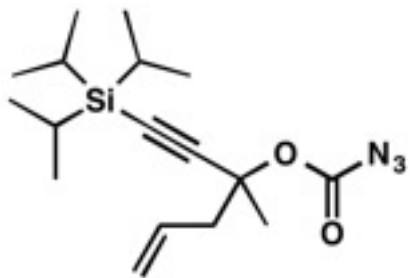




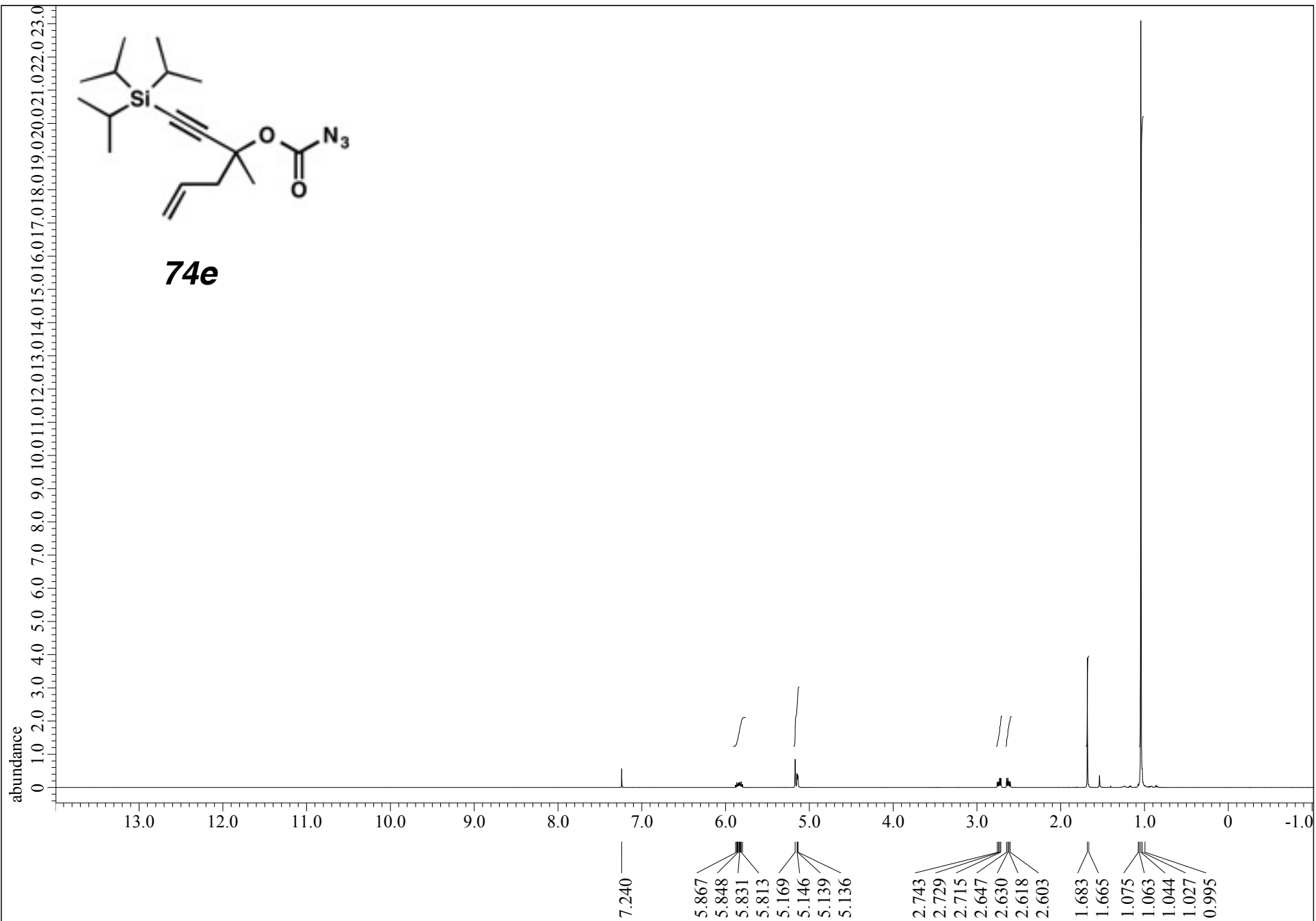


**74d**

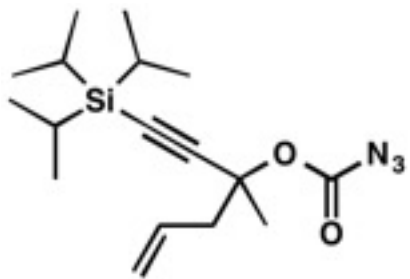




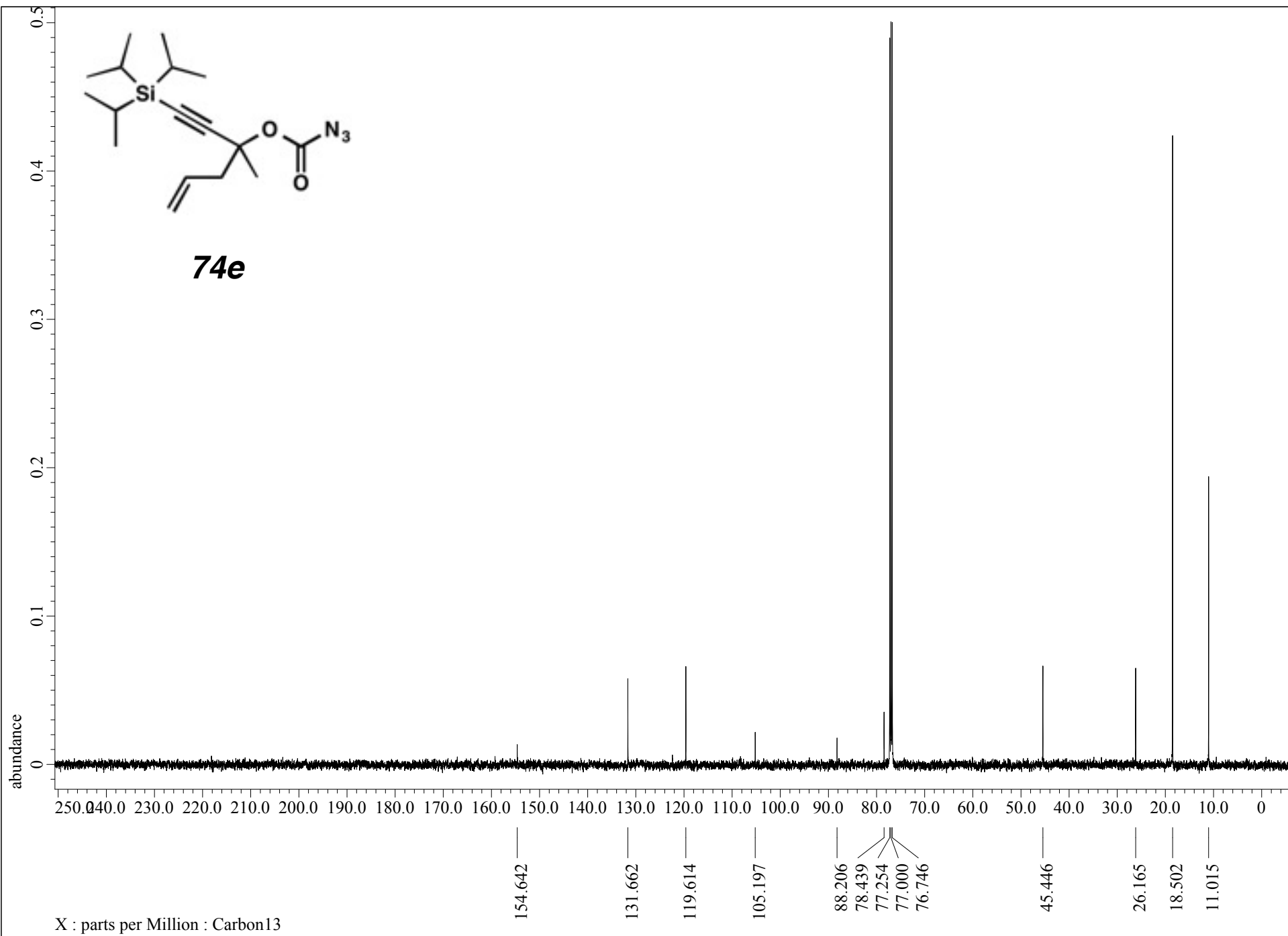
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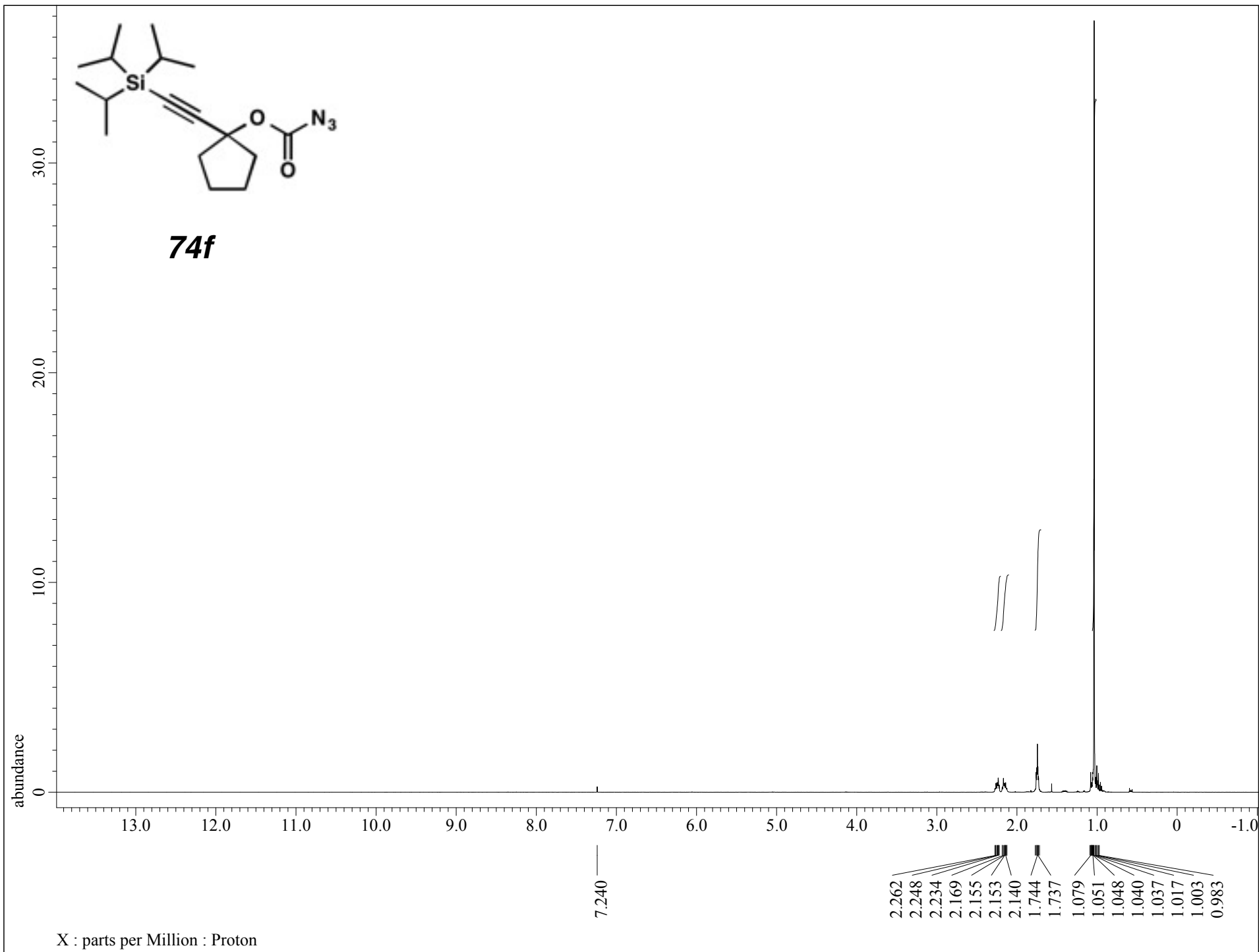


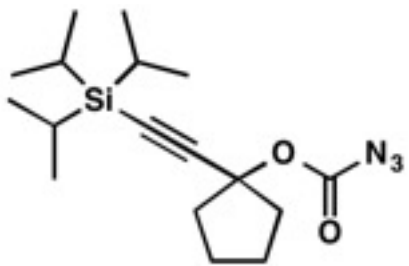
X : parts per Million : Proton



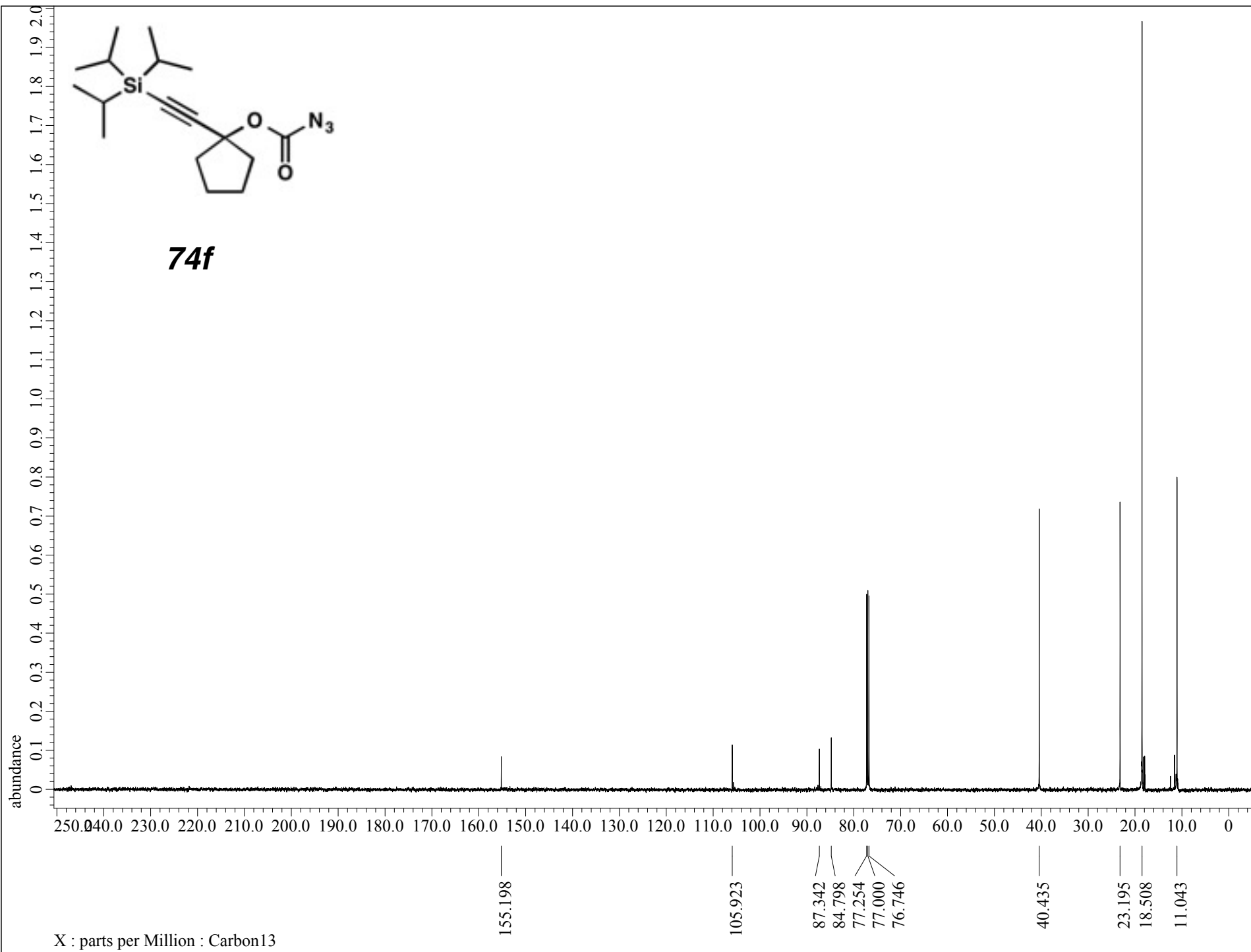
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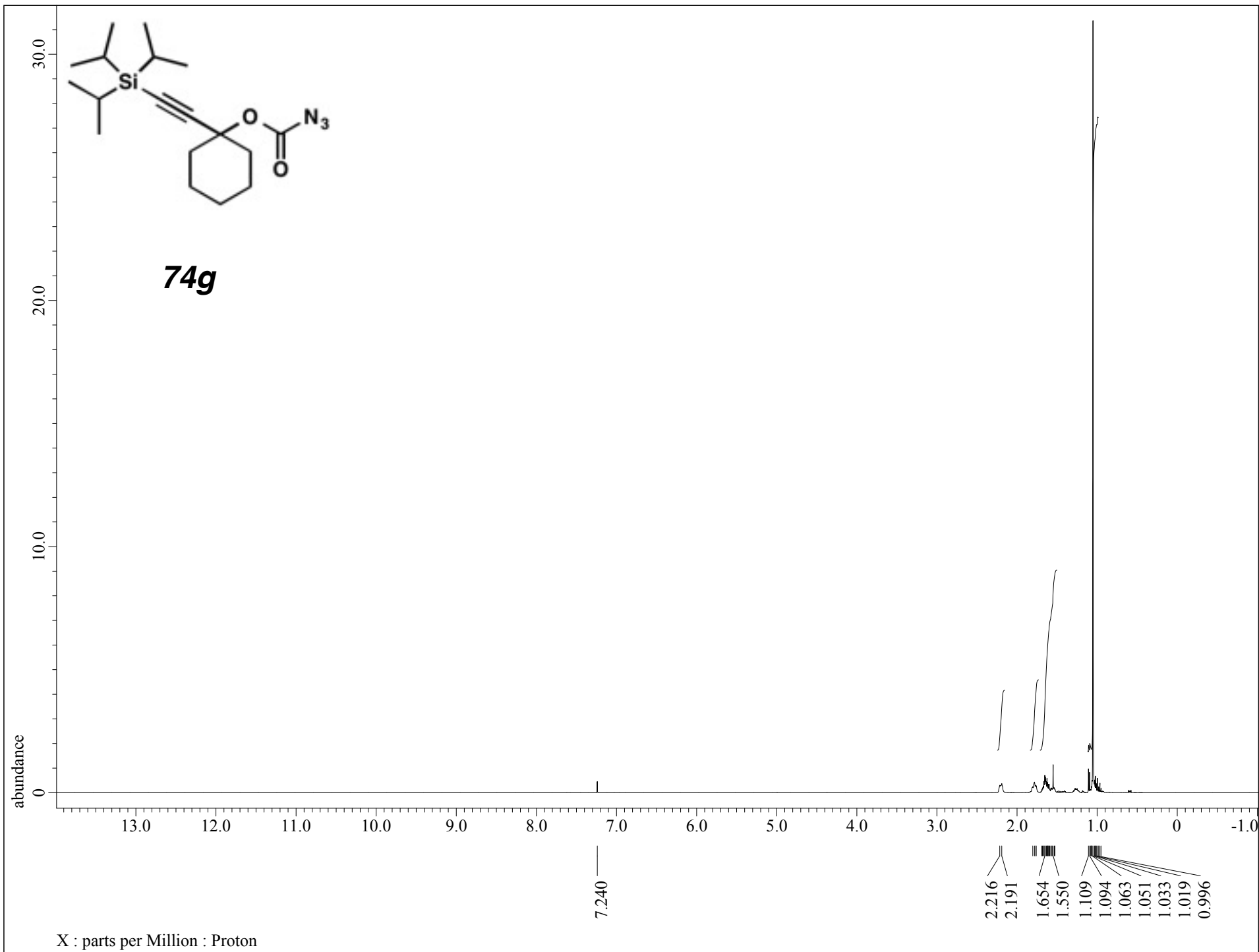




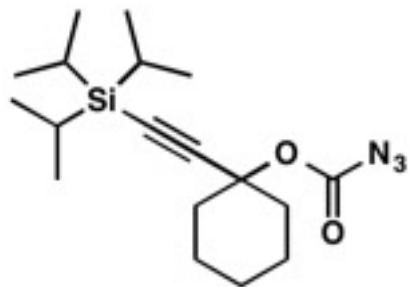


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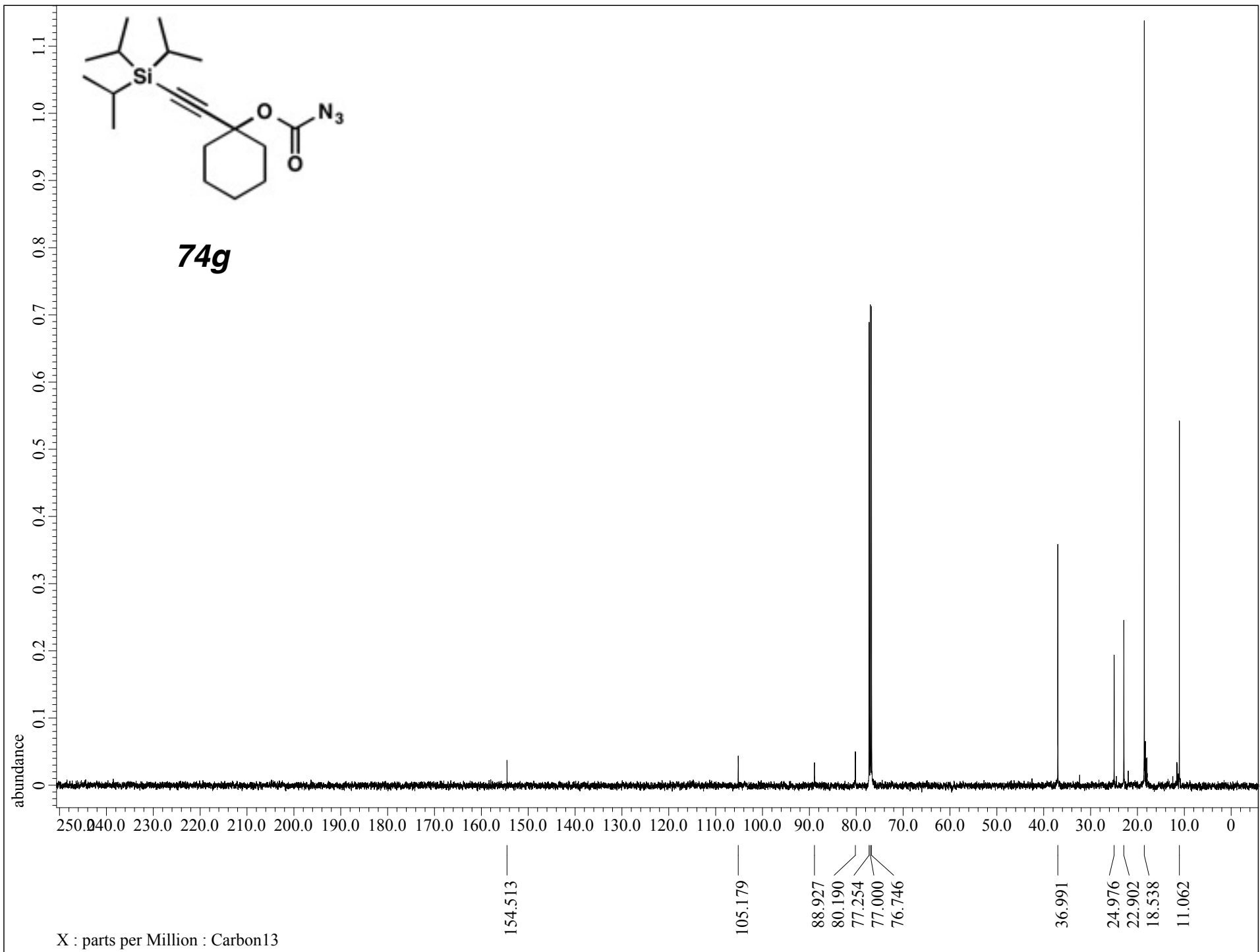




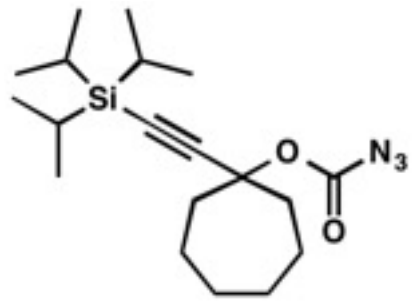




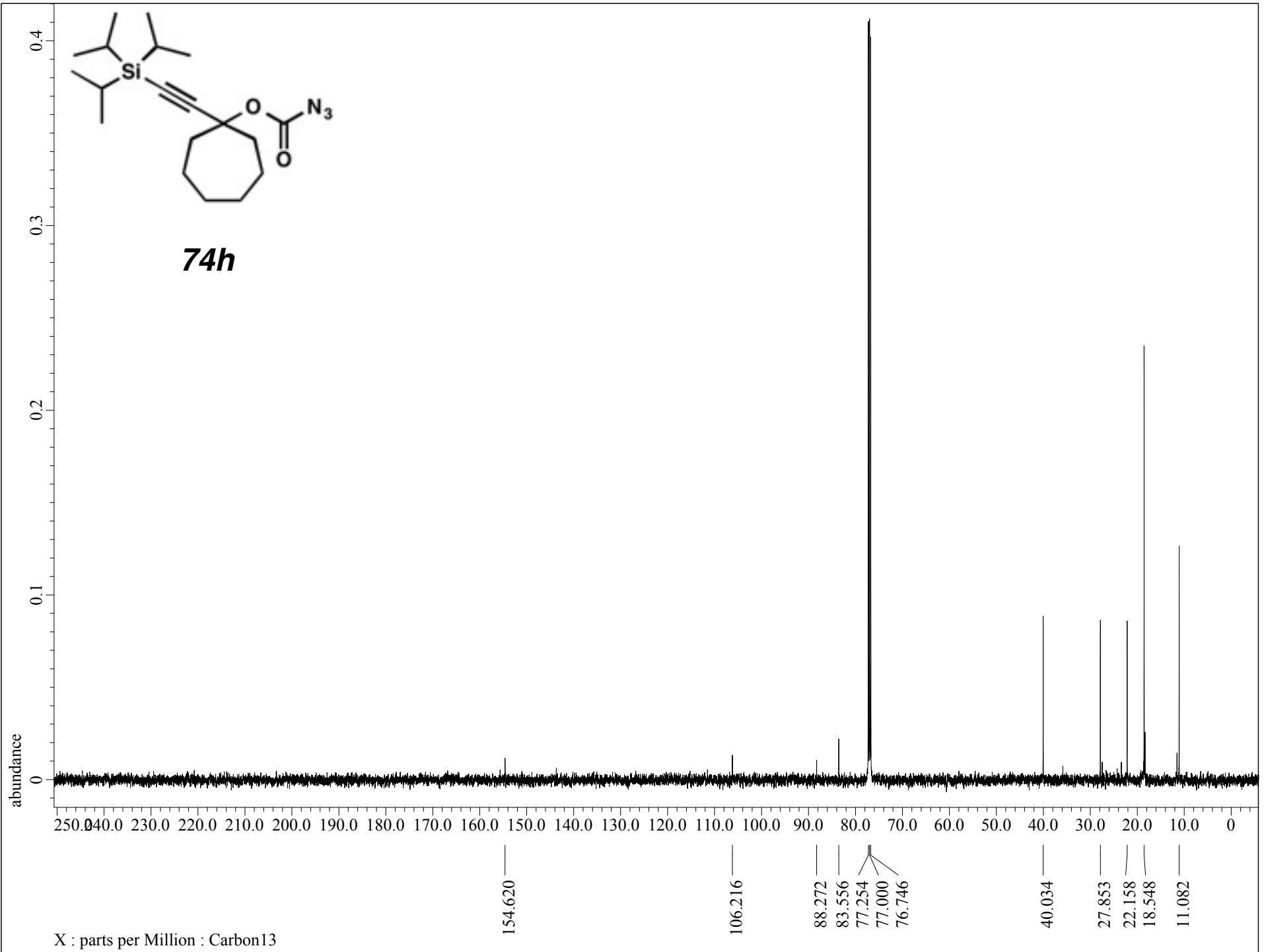
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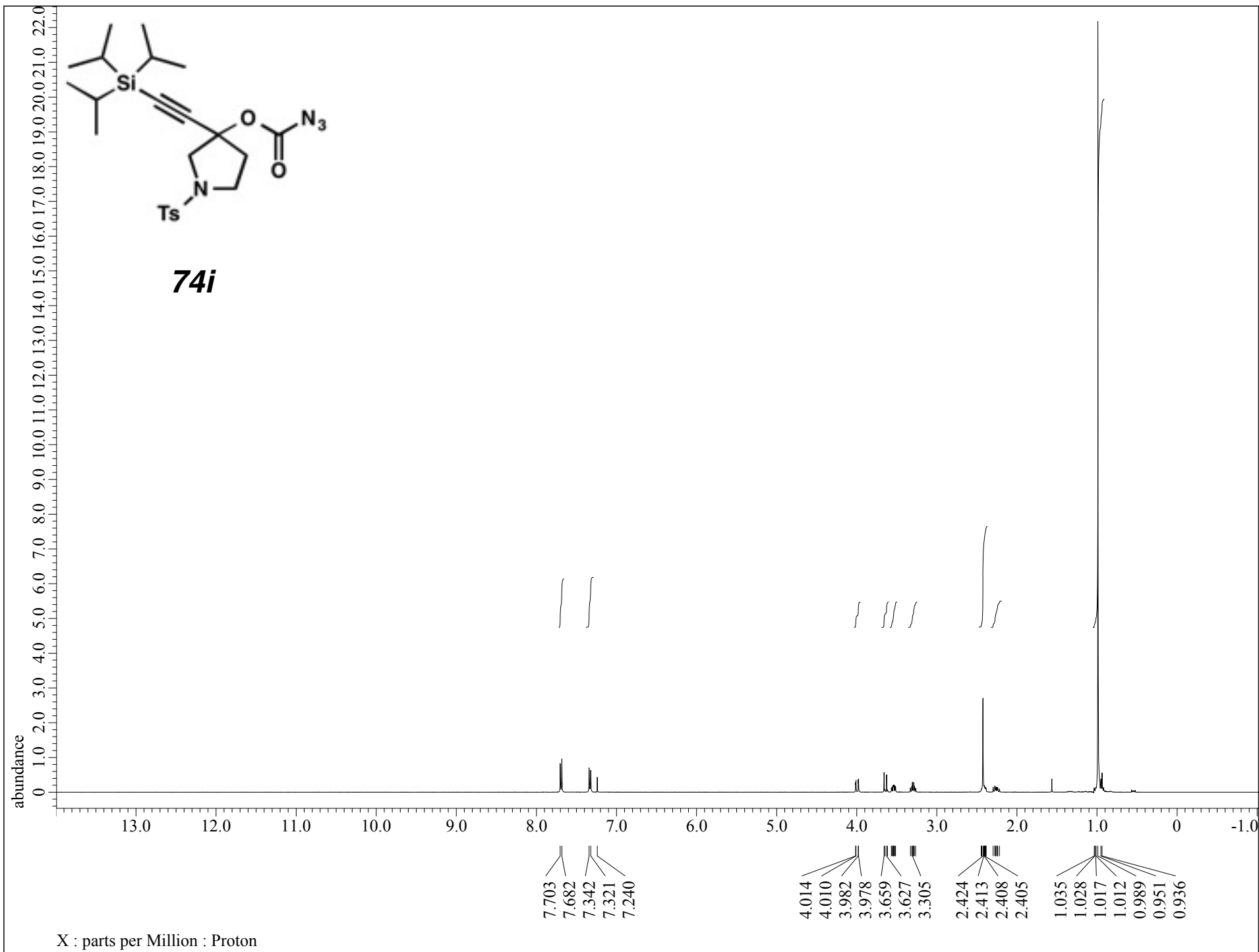


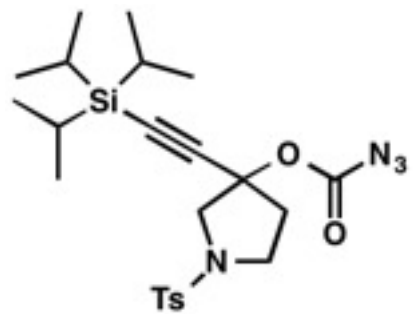




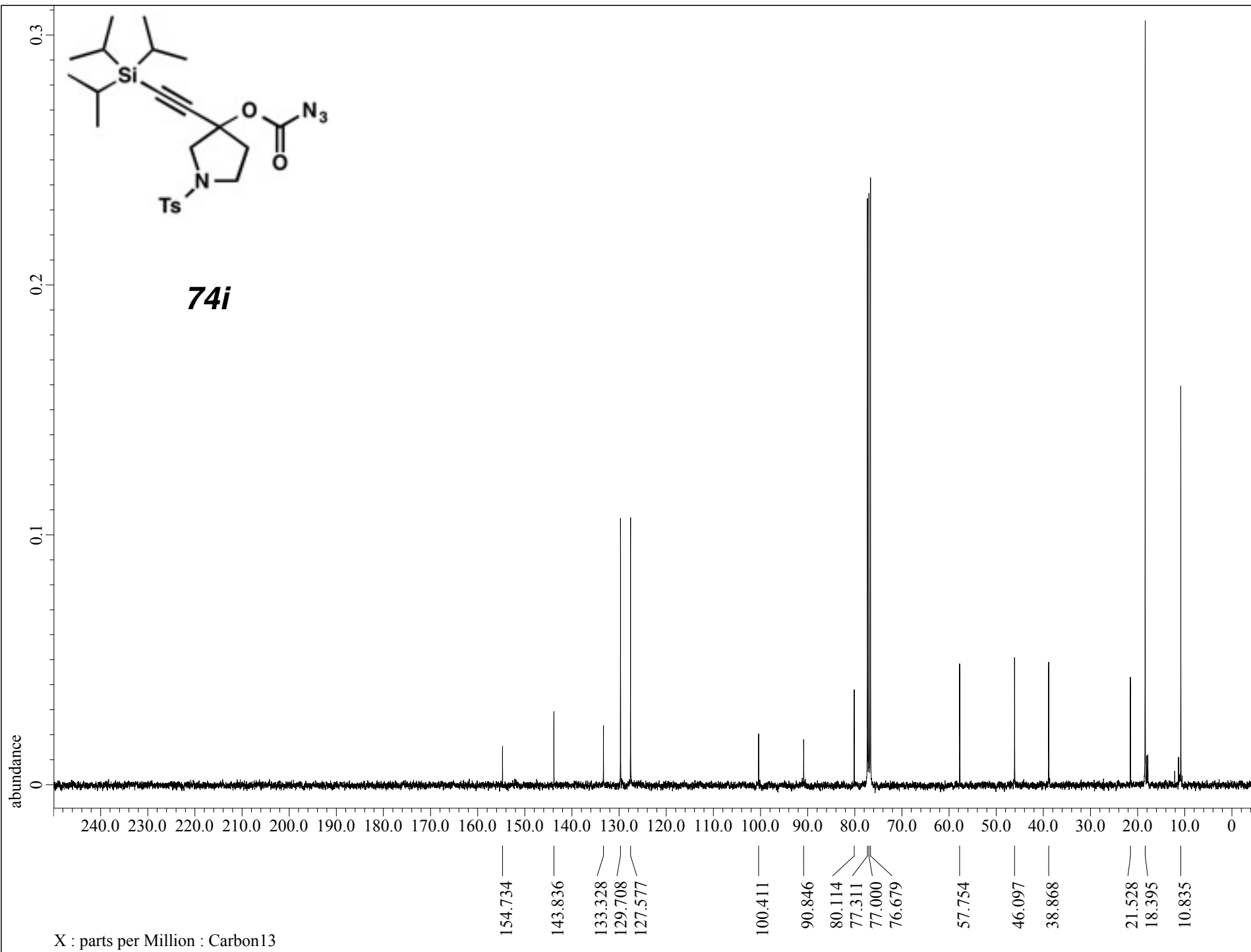
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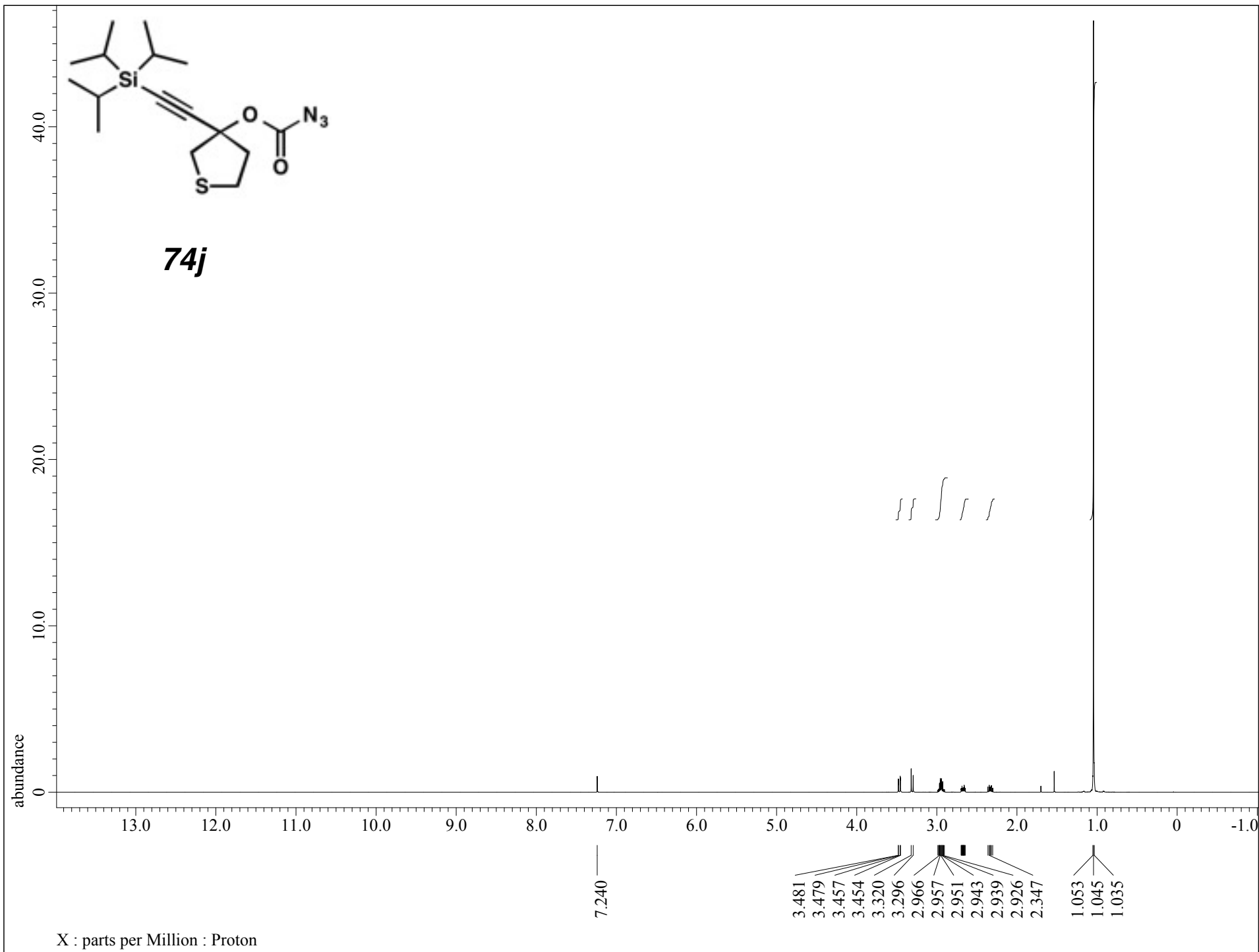


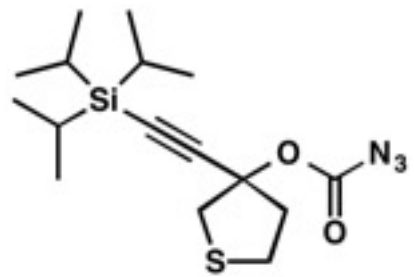




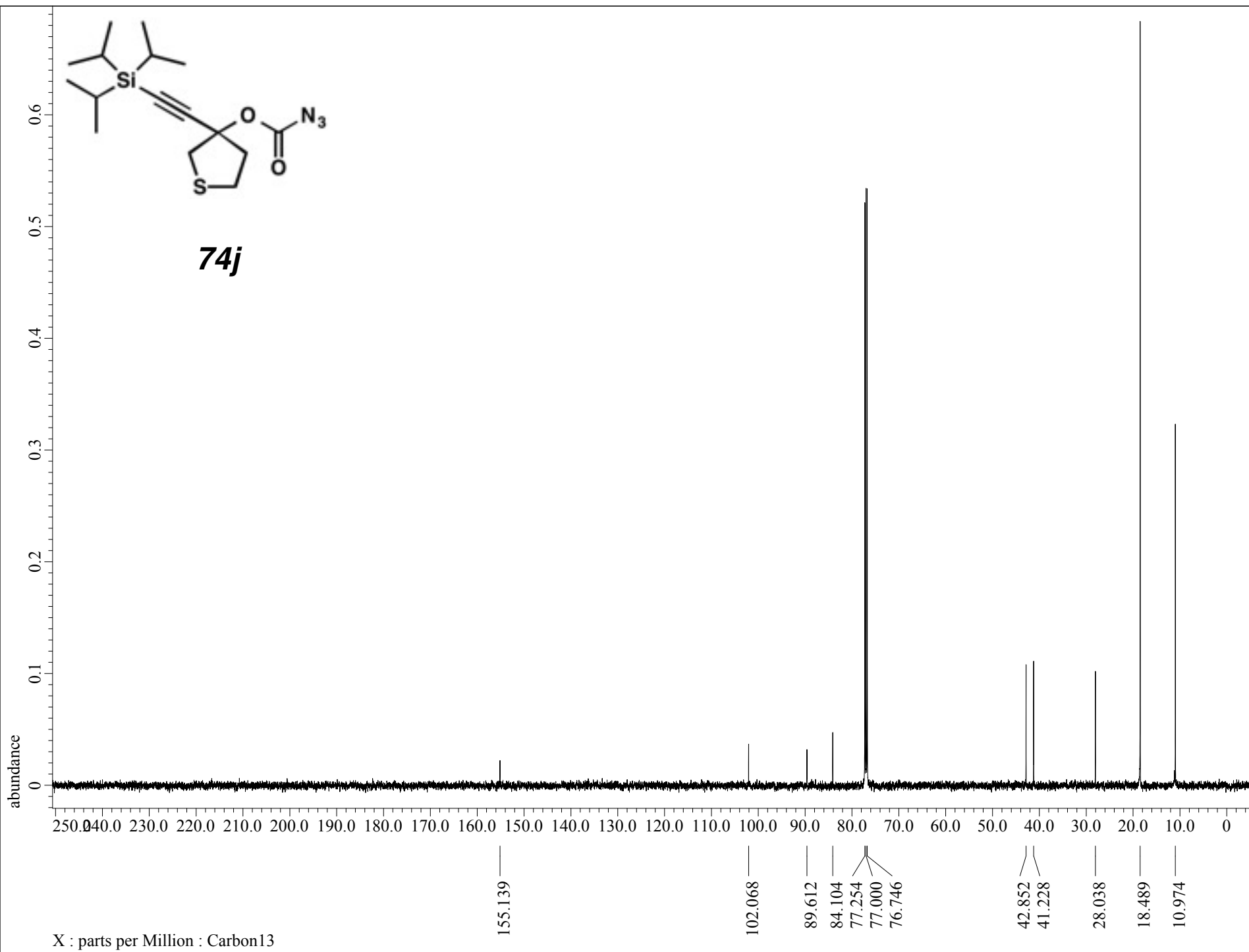
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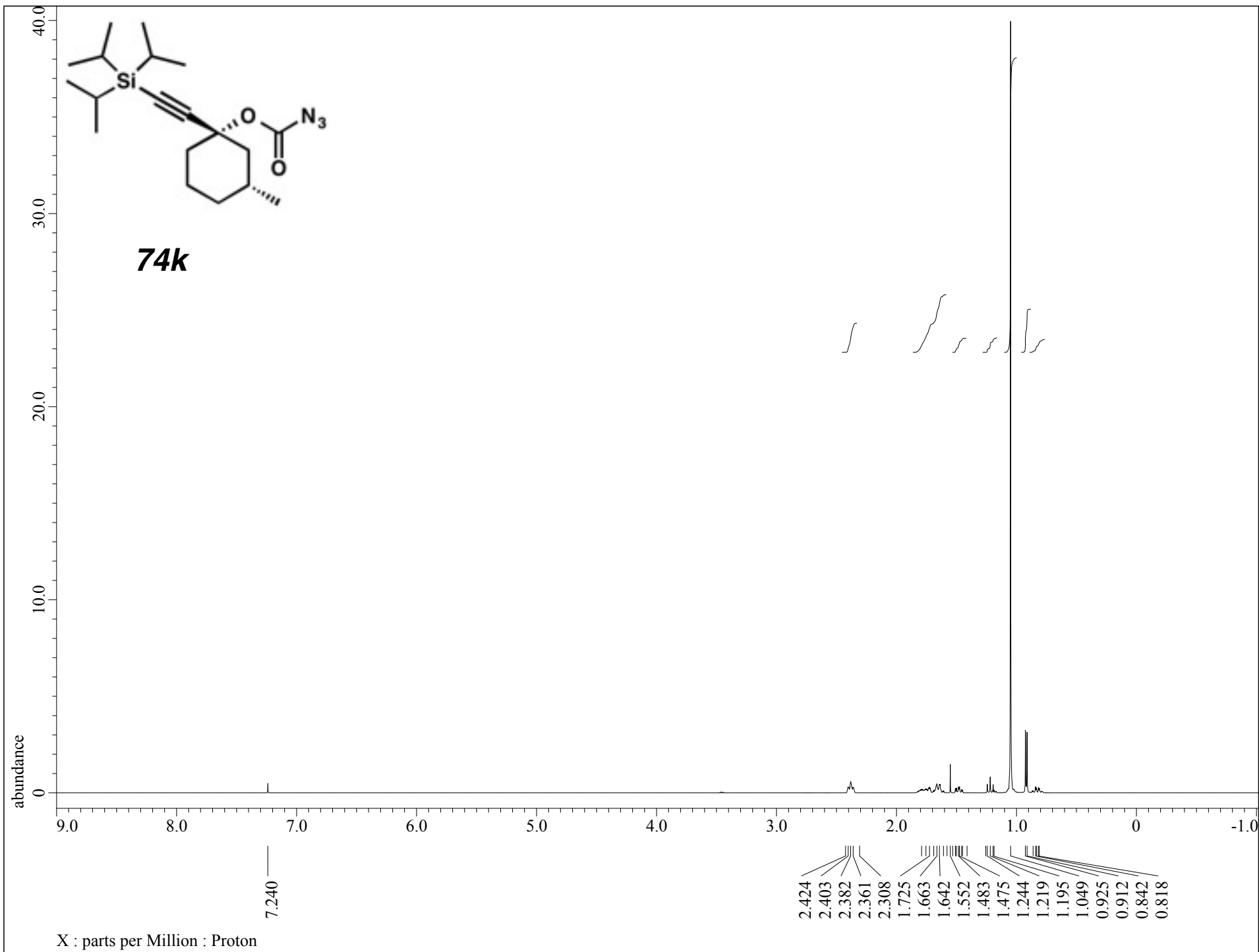




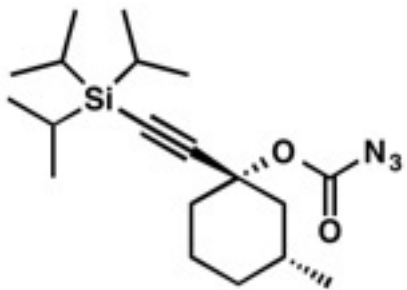


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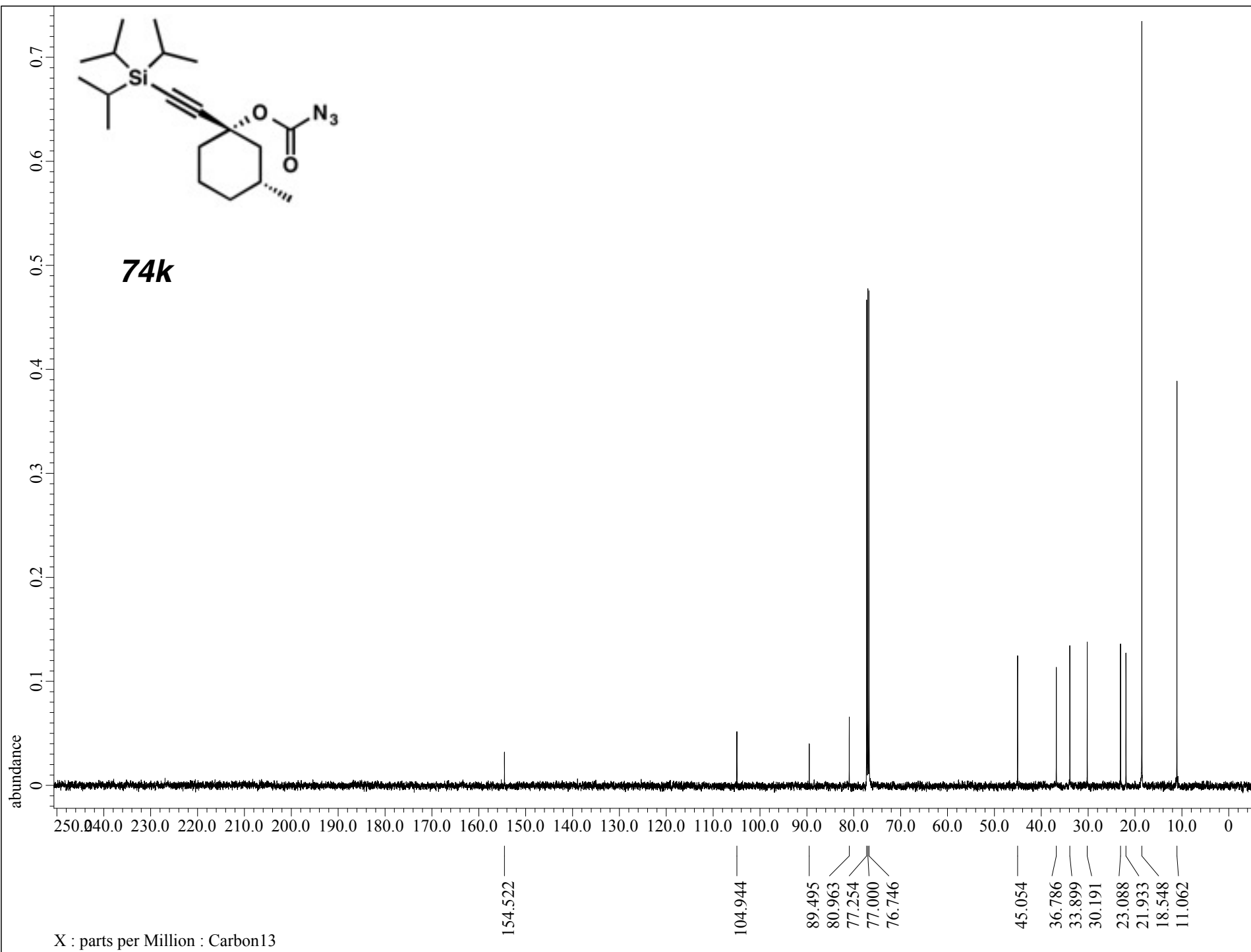


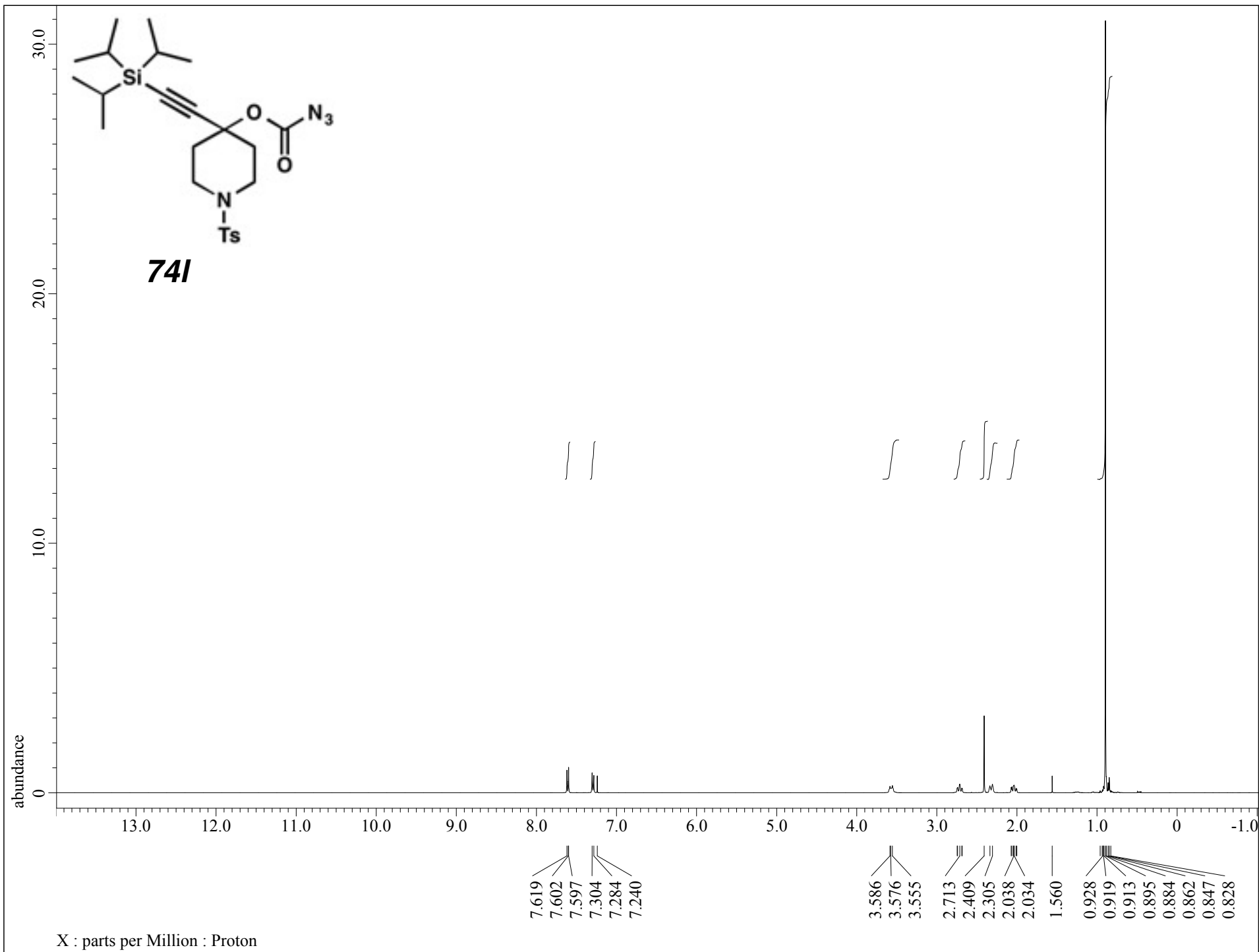




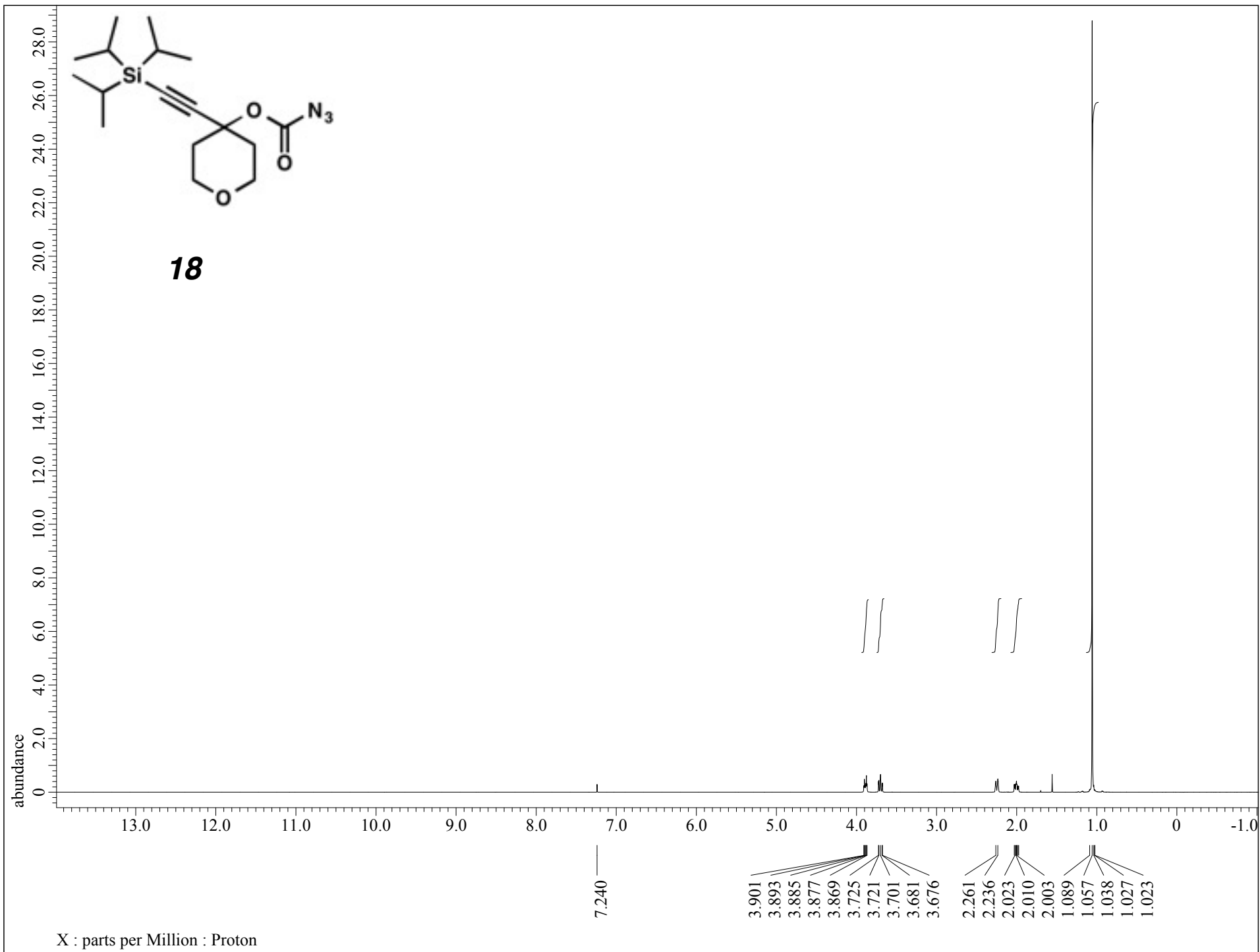


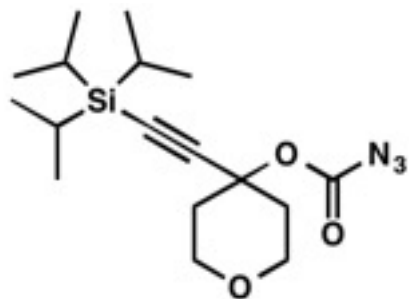
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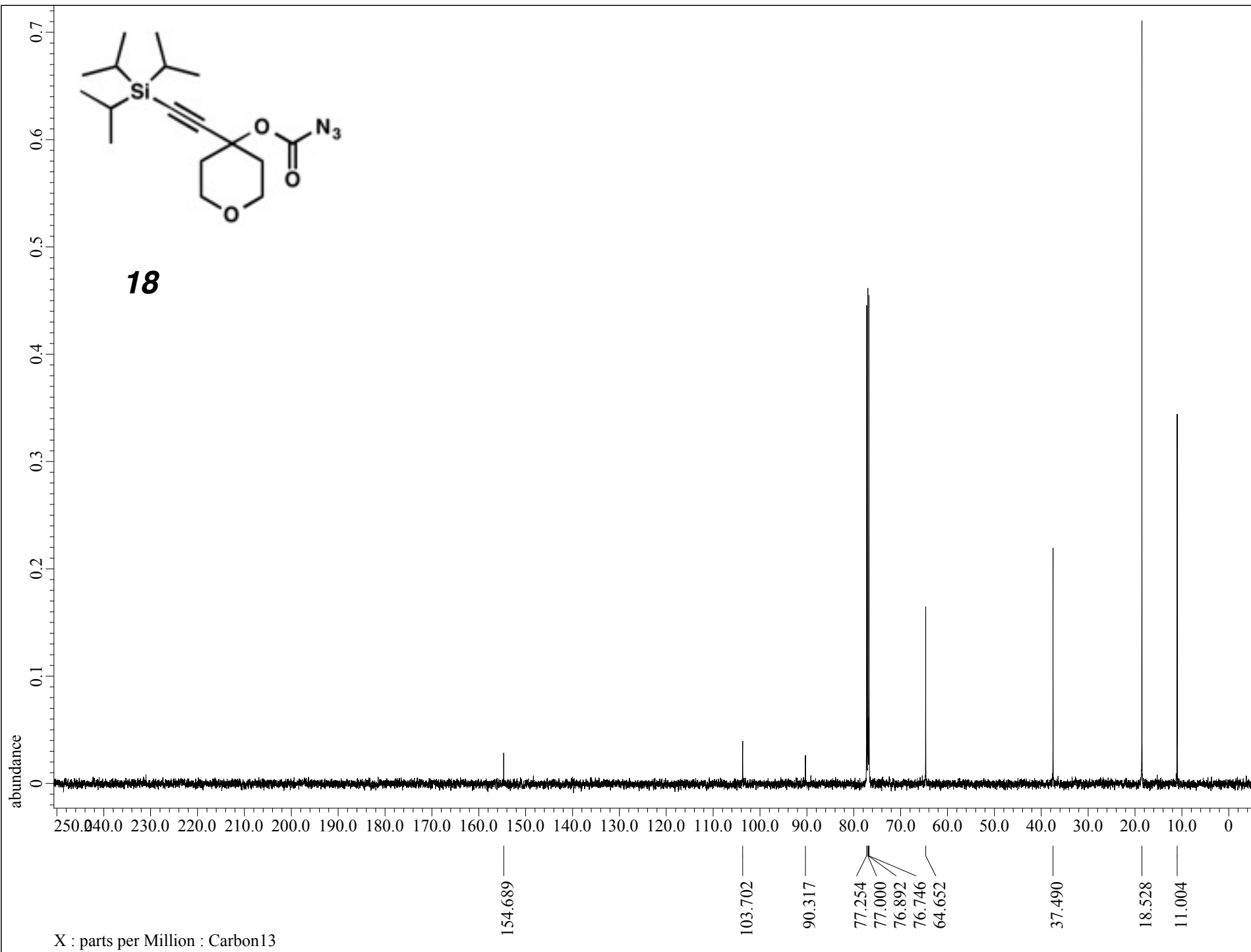


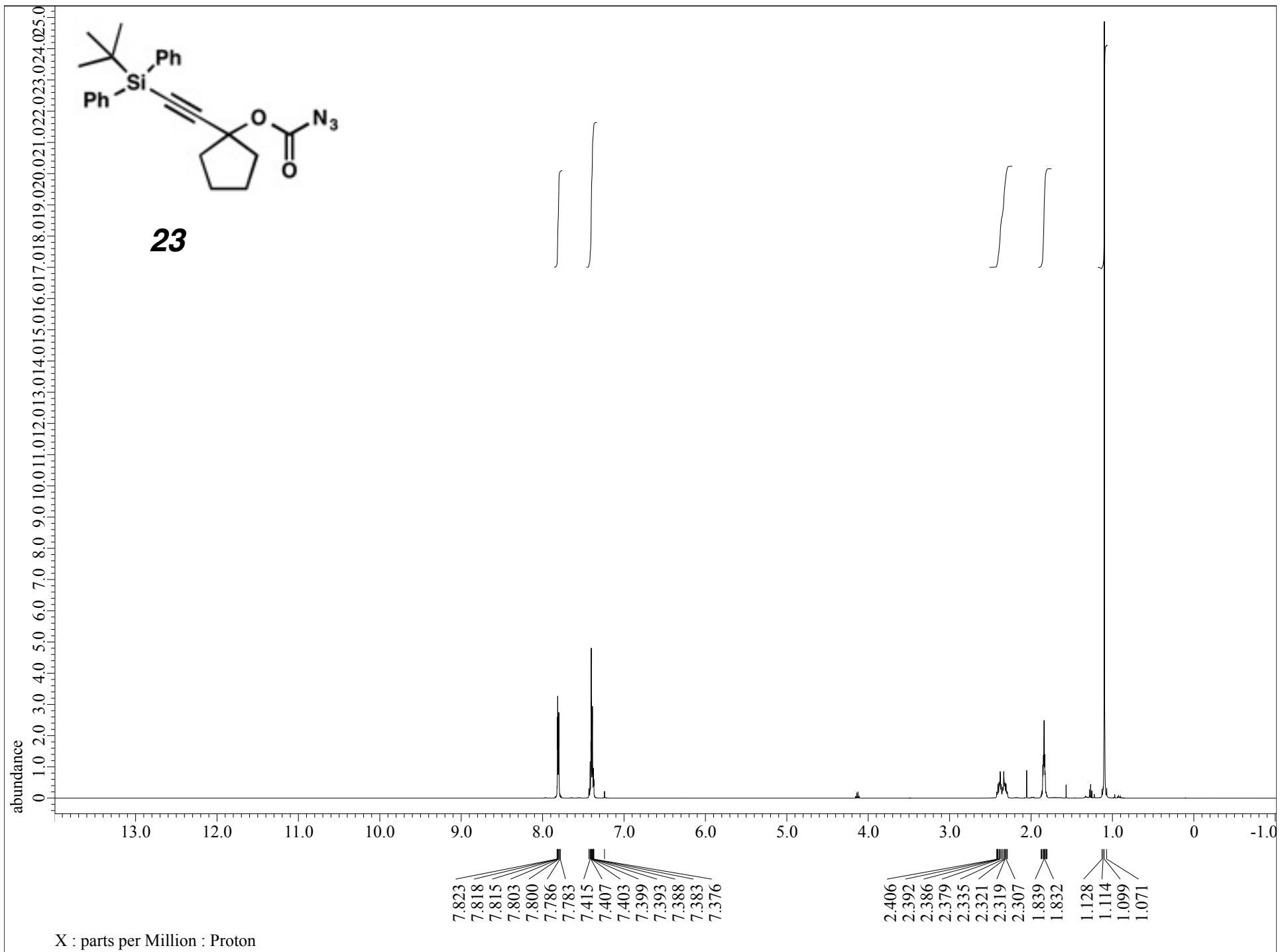


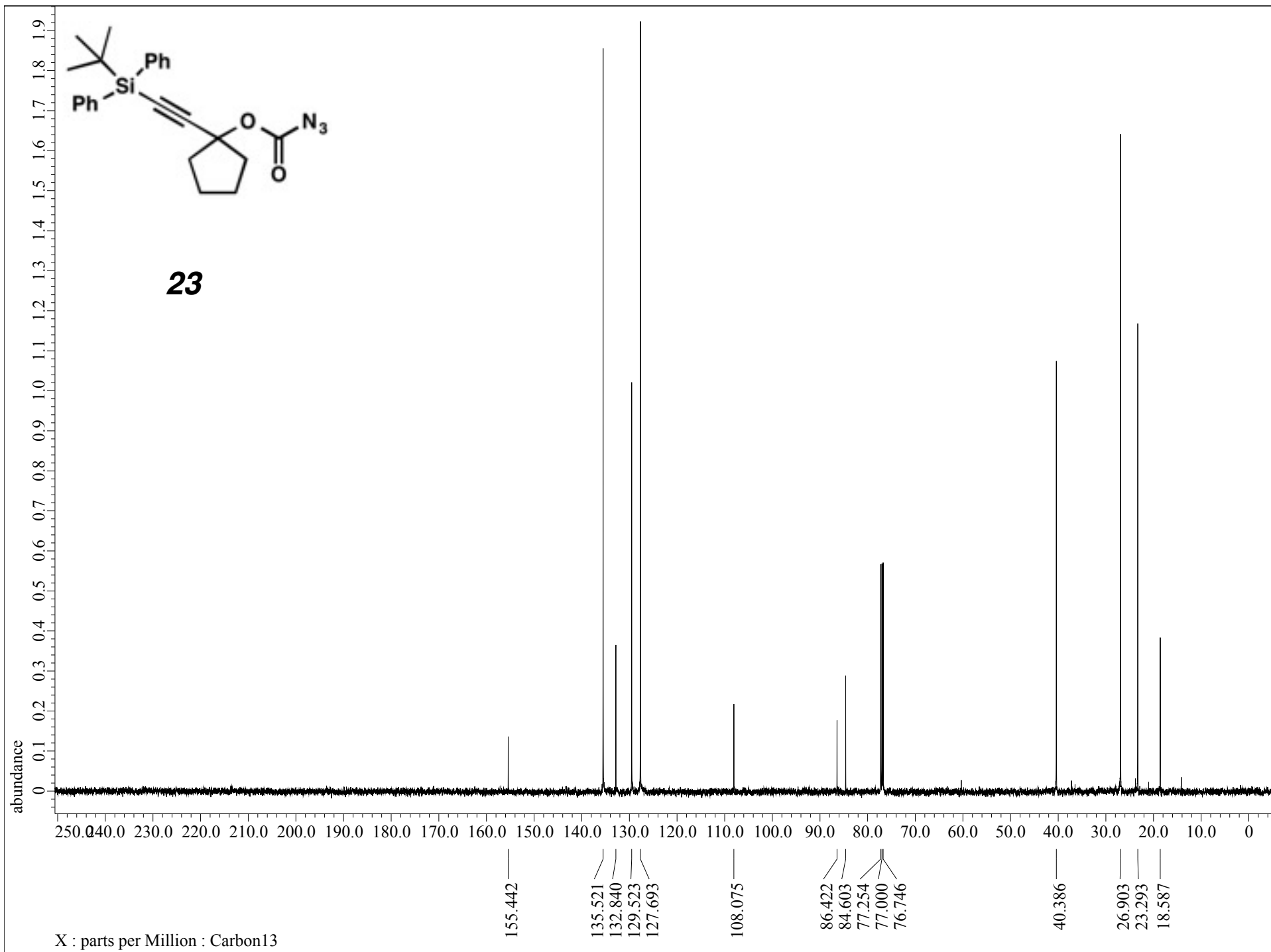




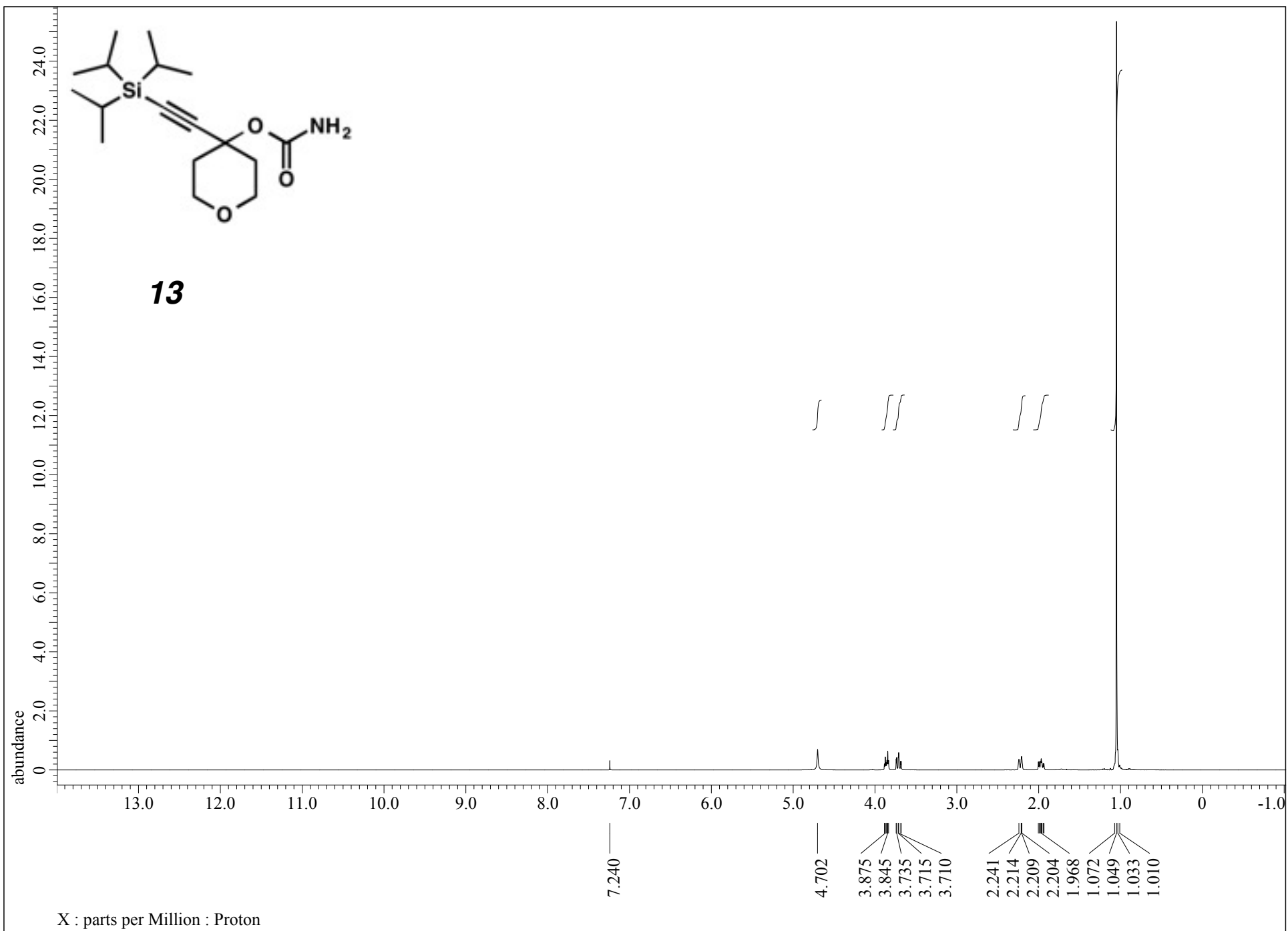
**18**



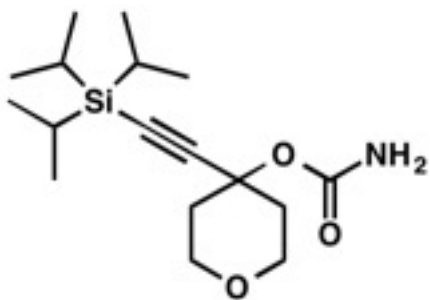




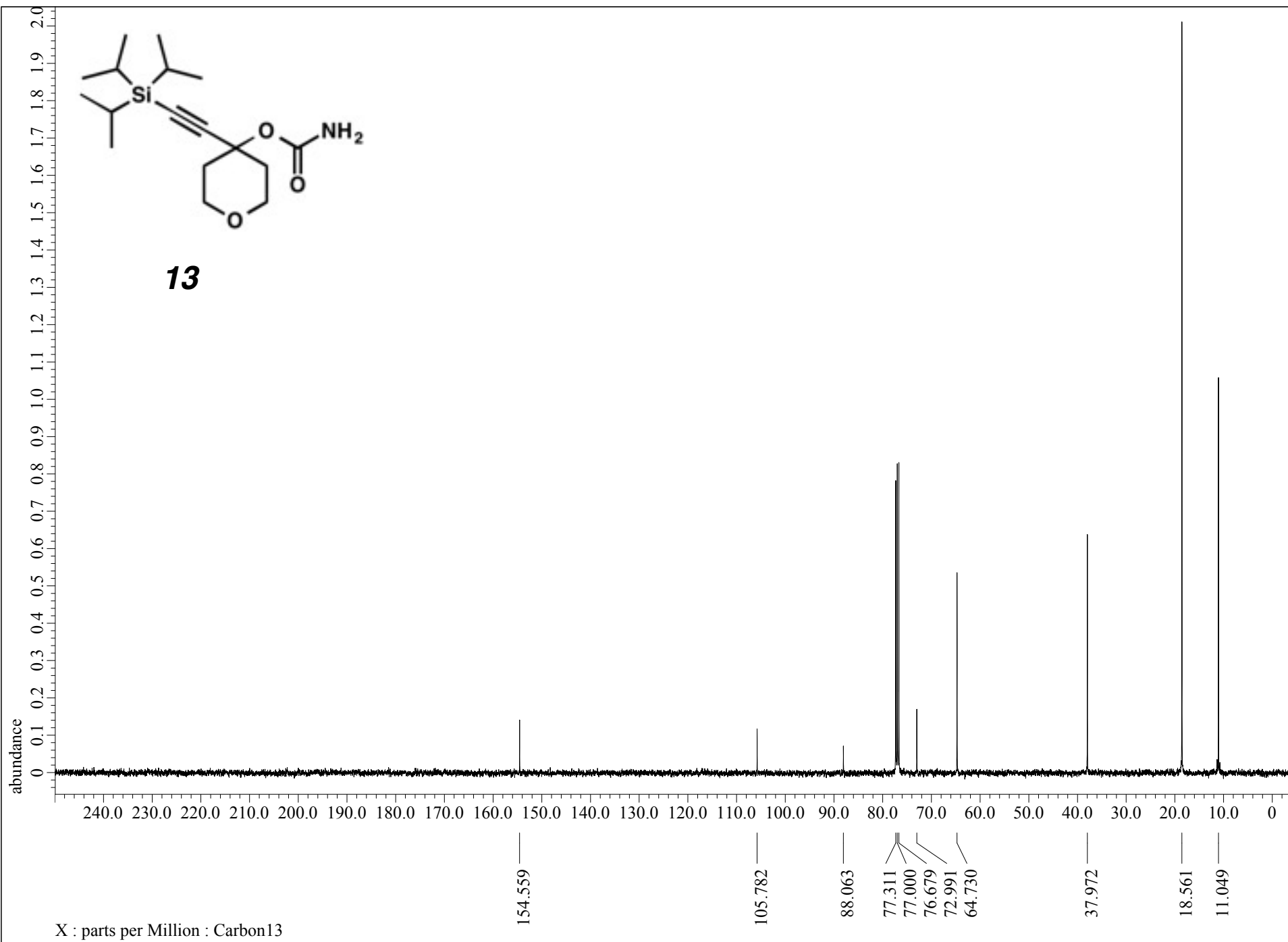
SI-128

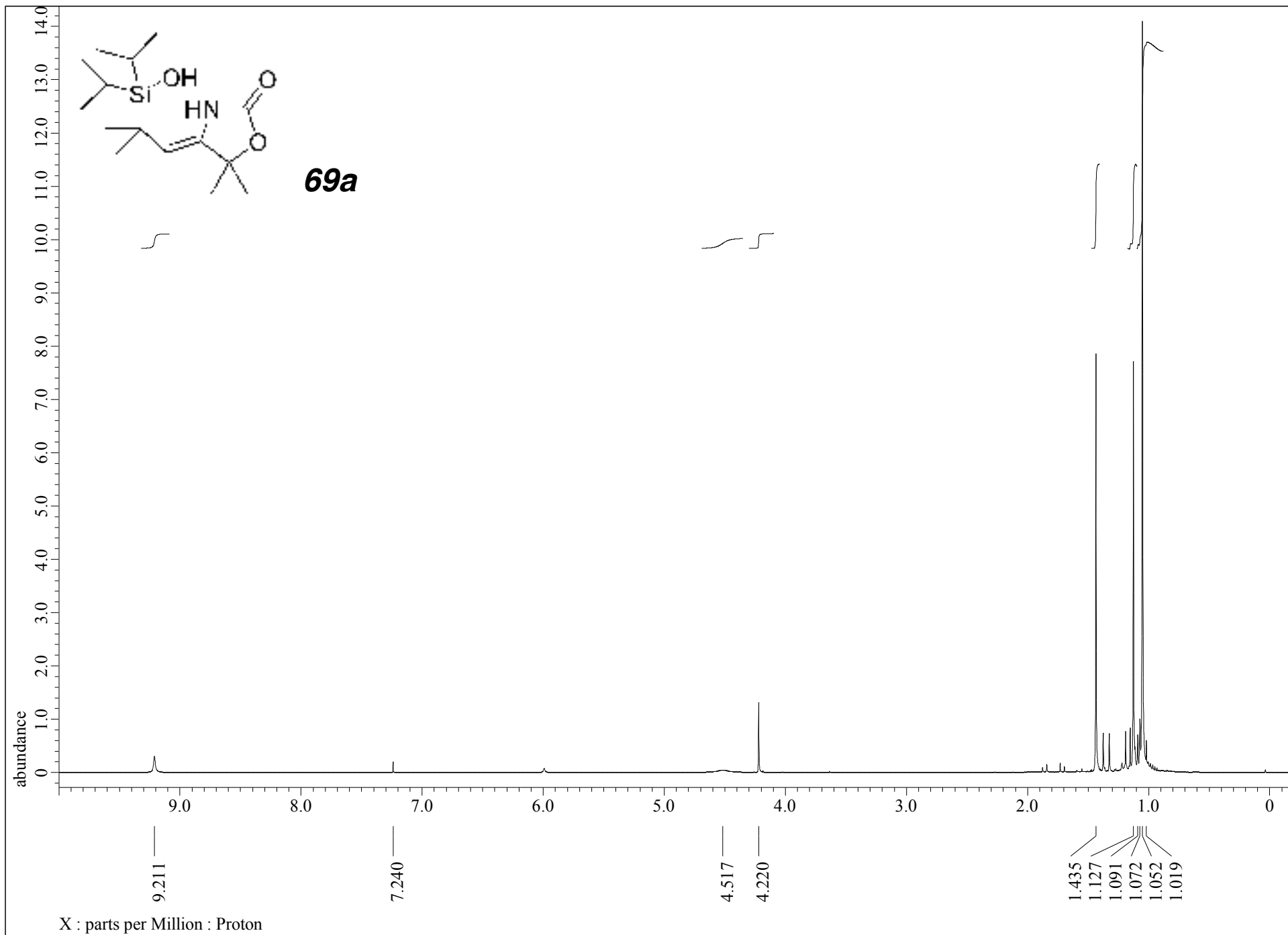


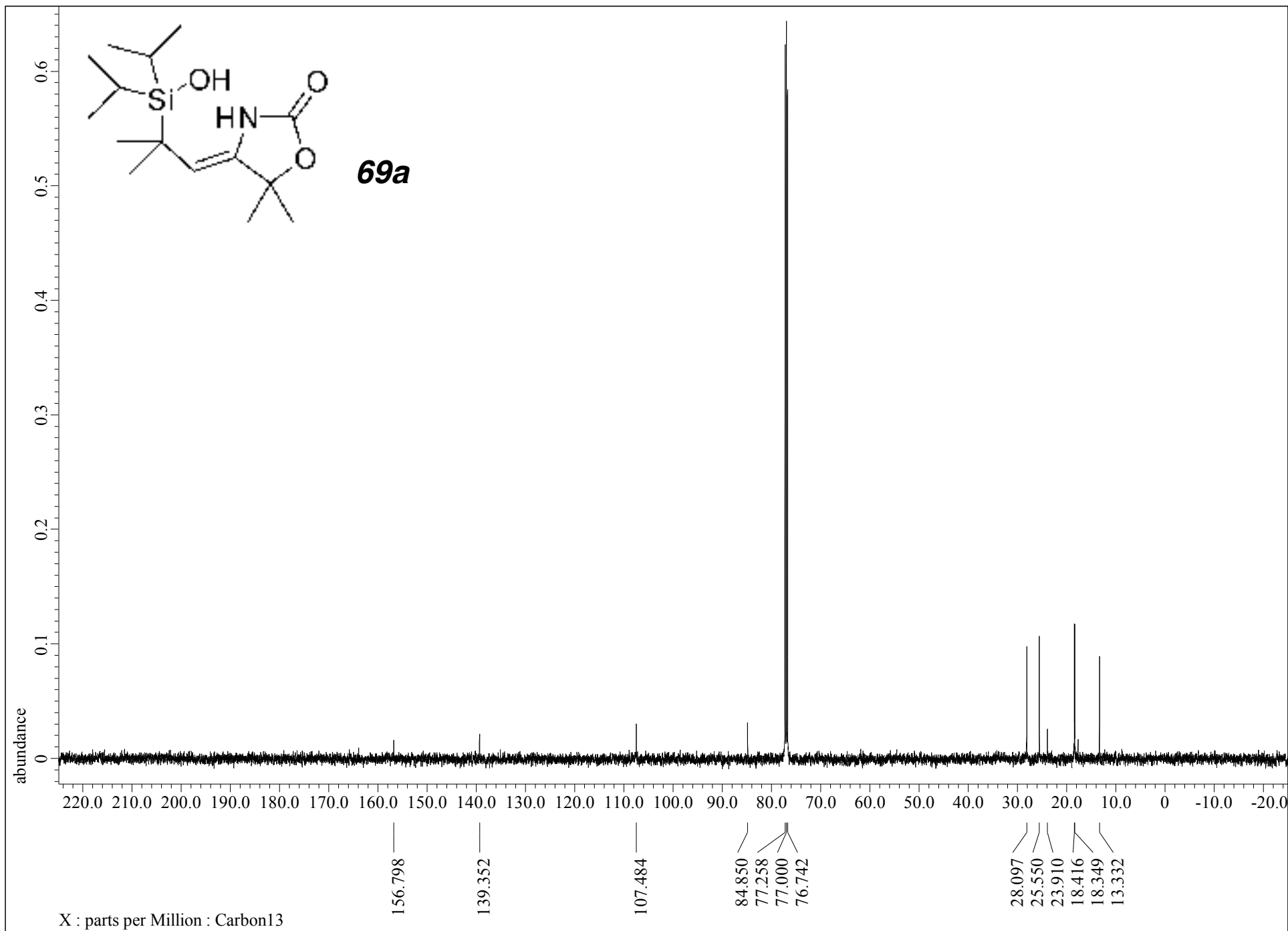


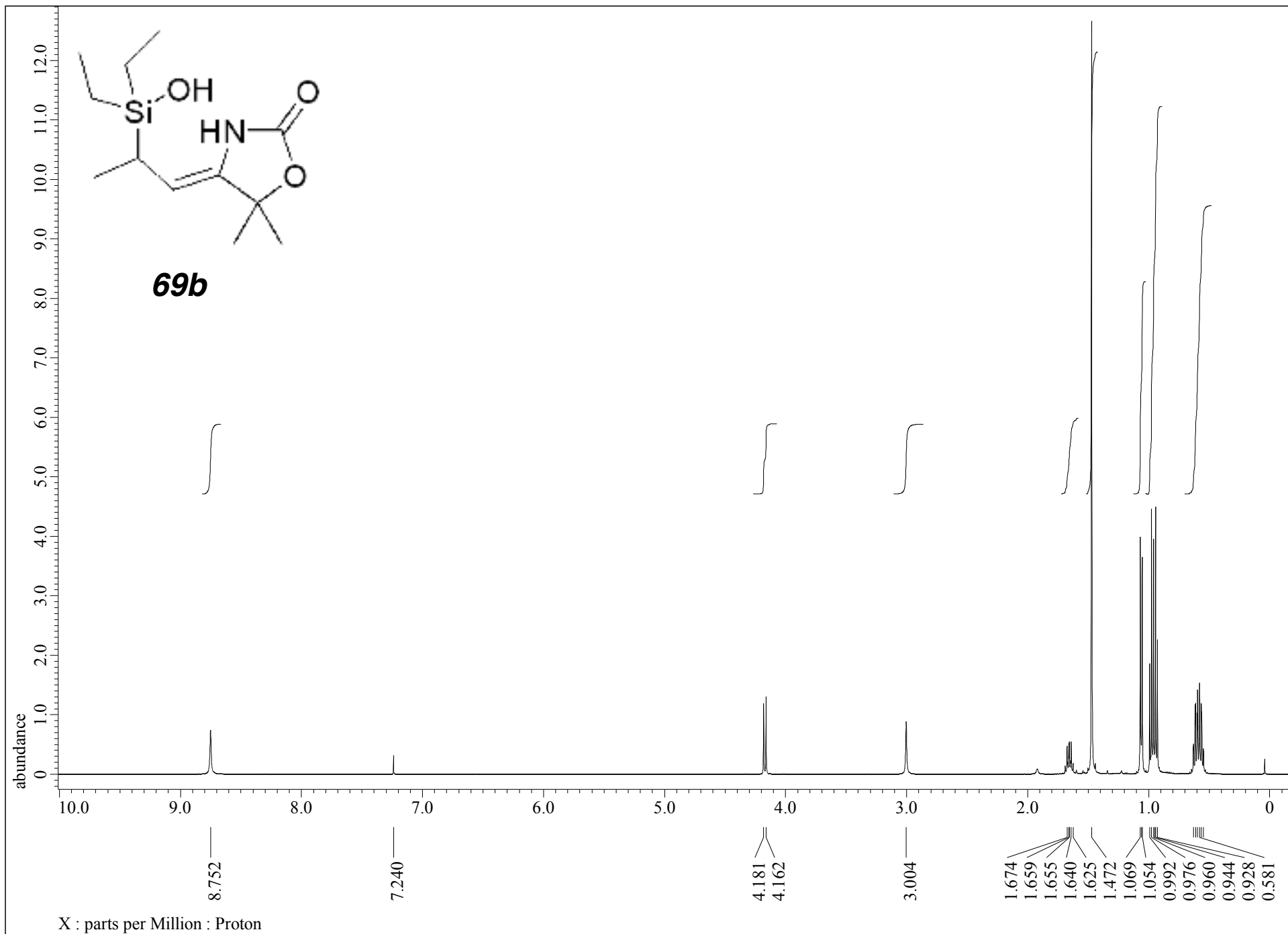


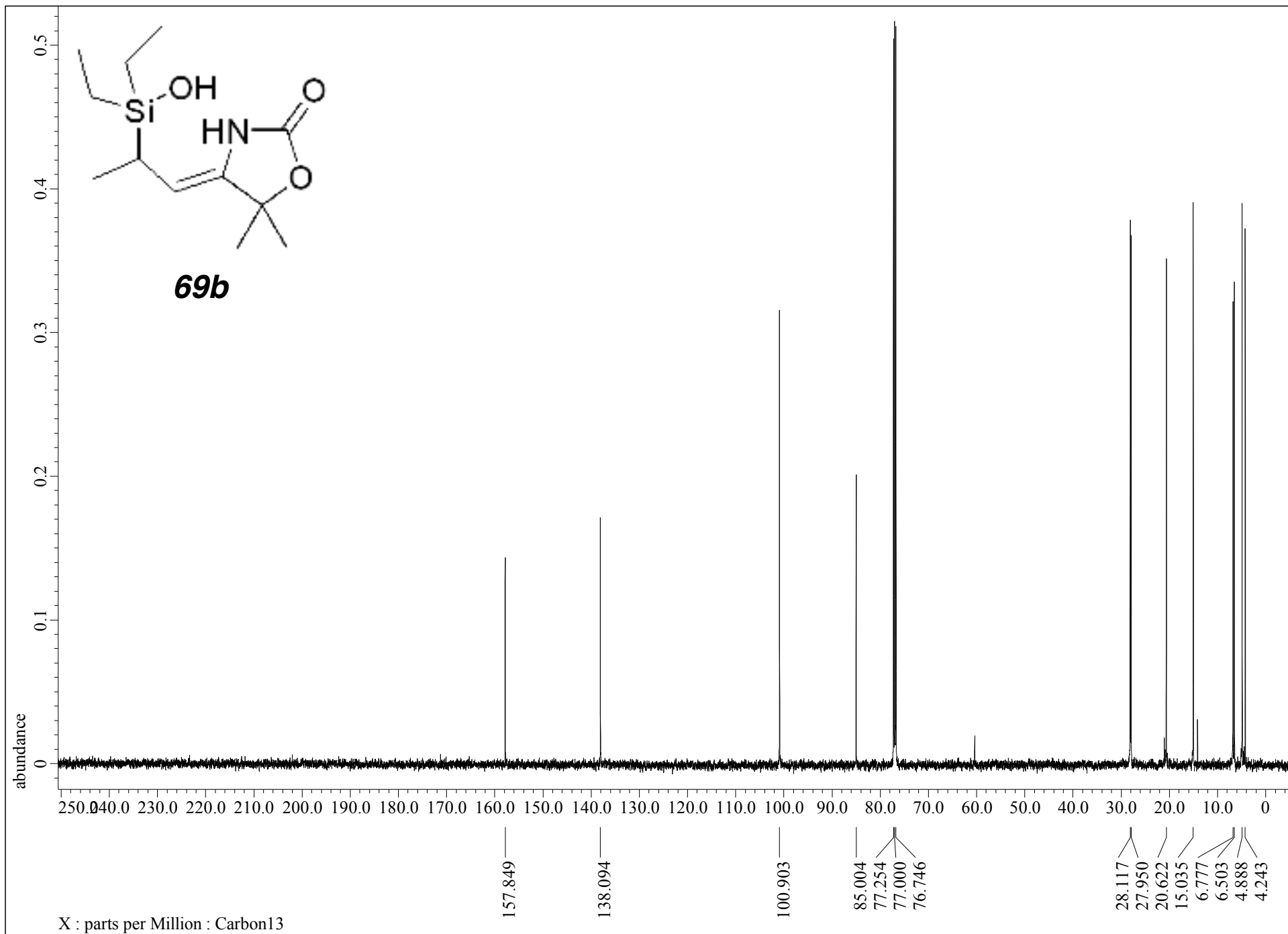
**13**



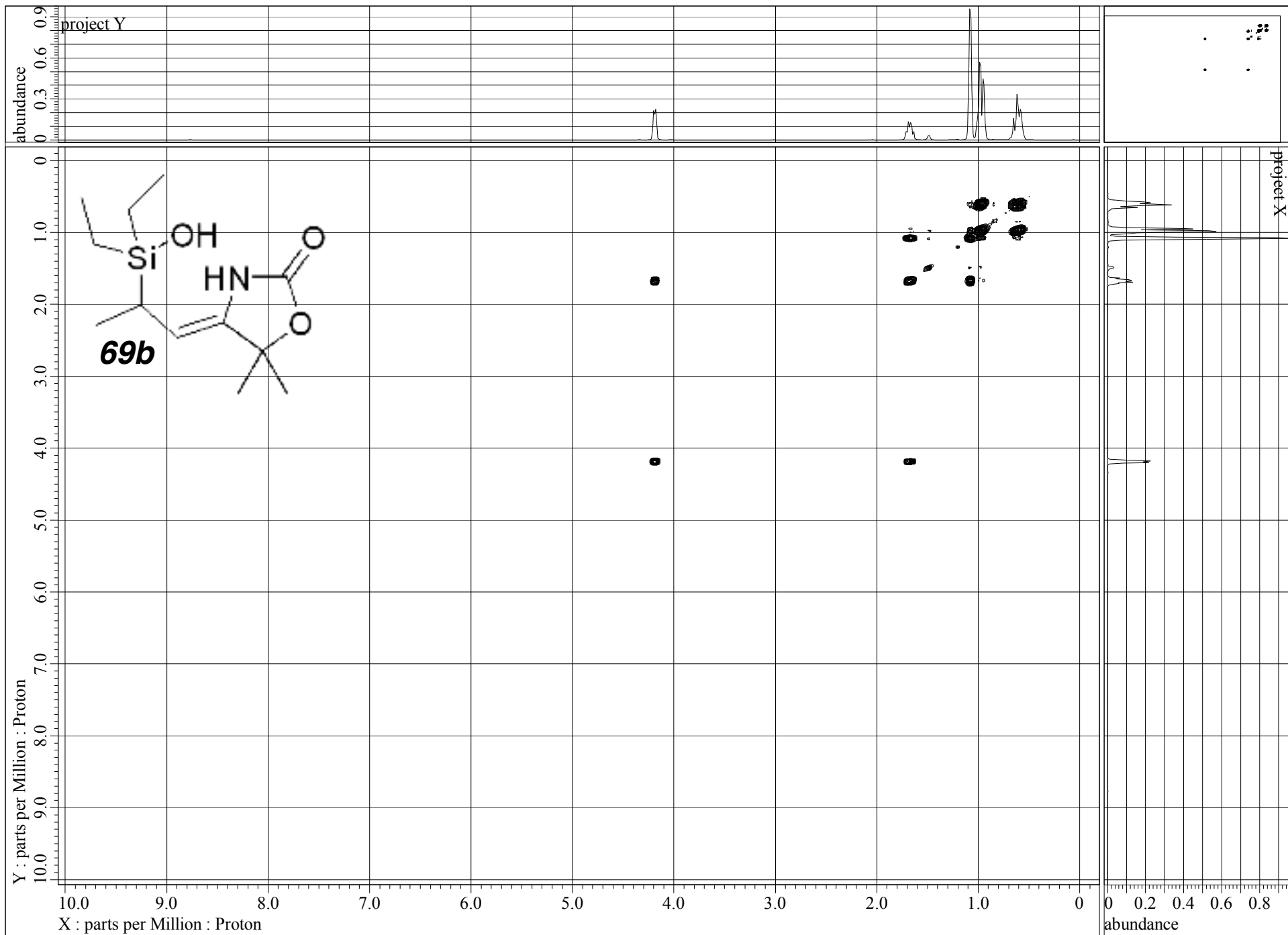




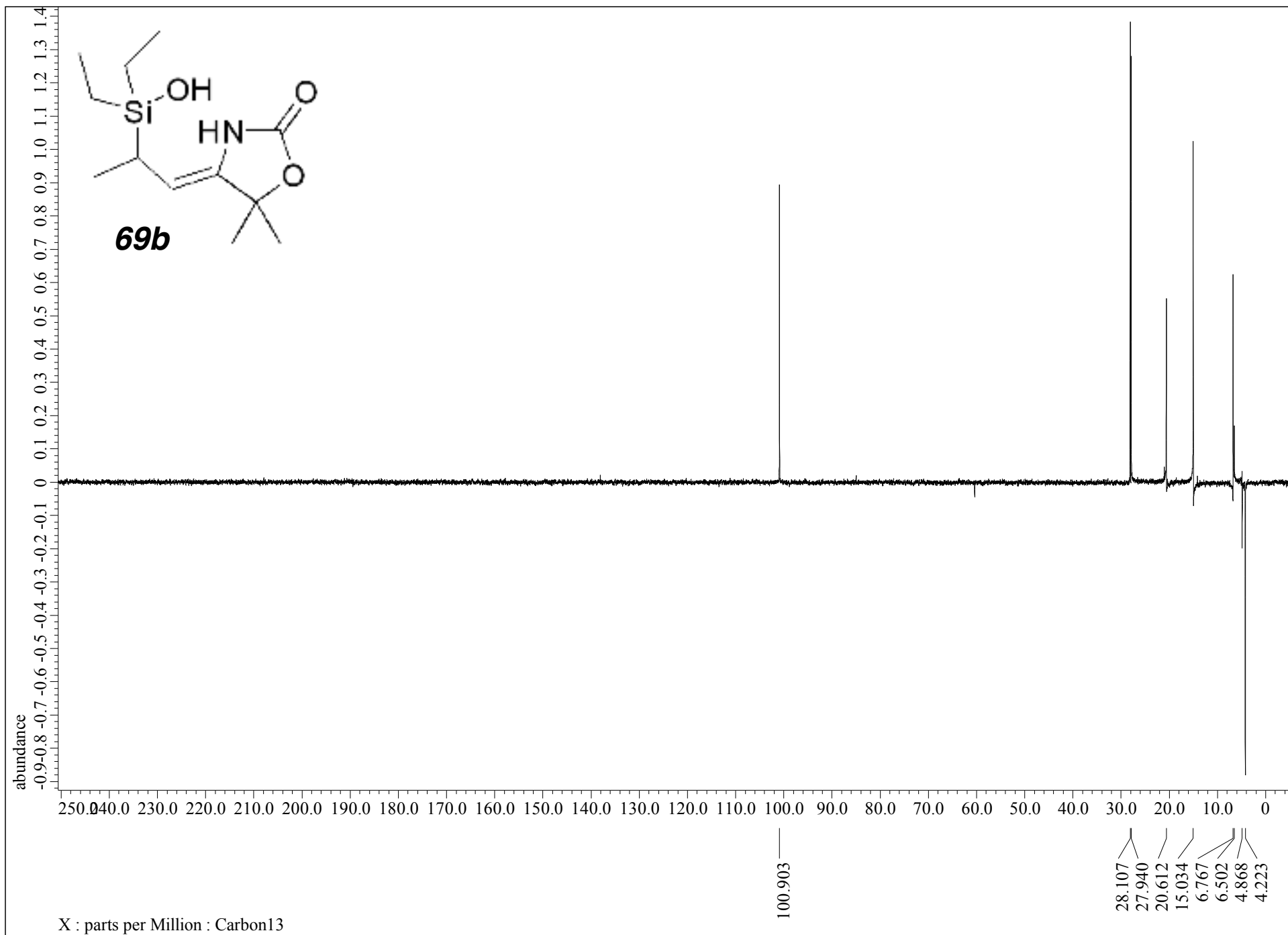


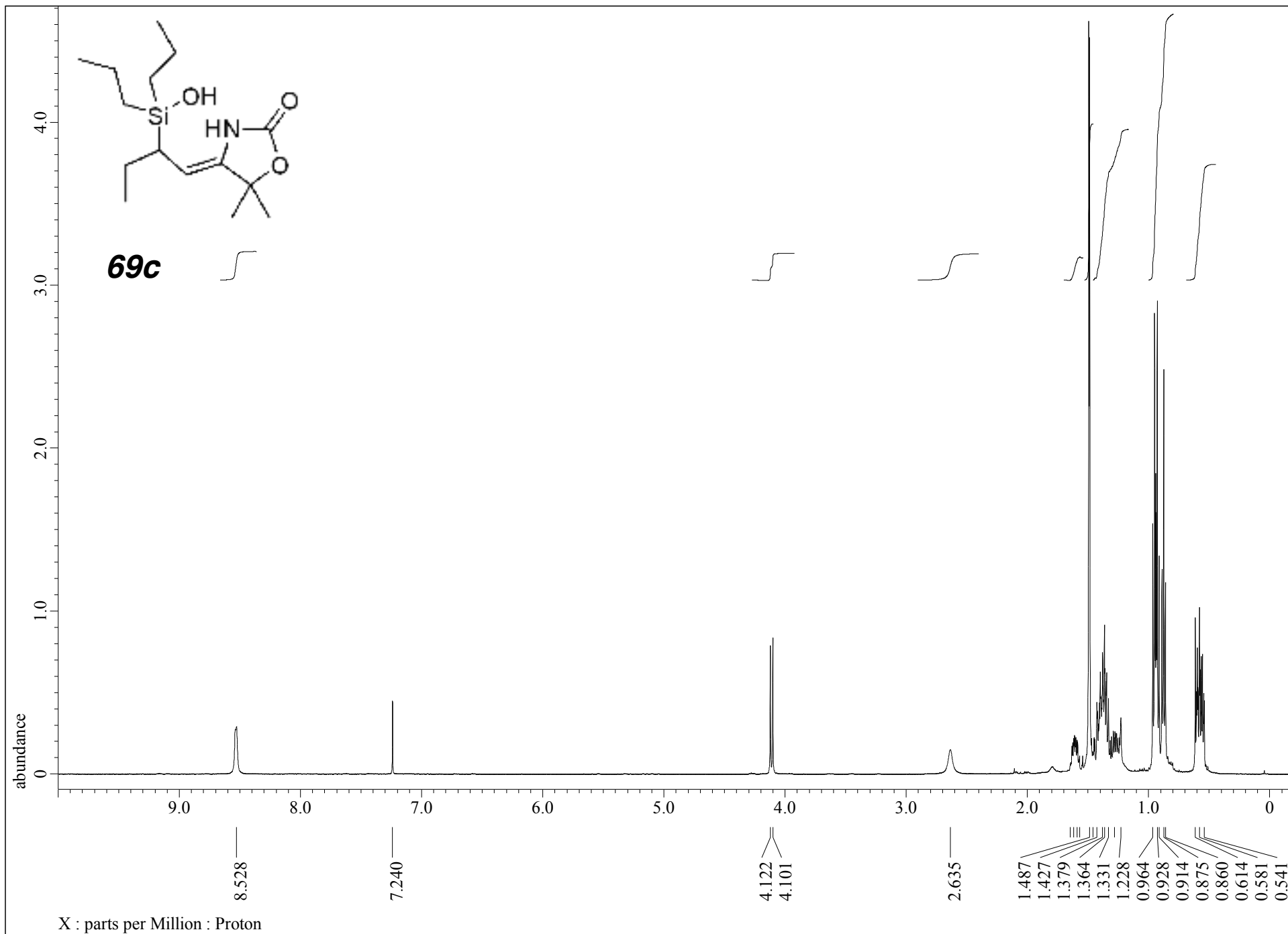


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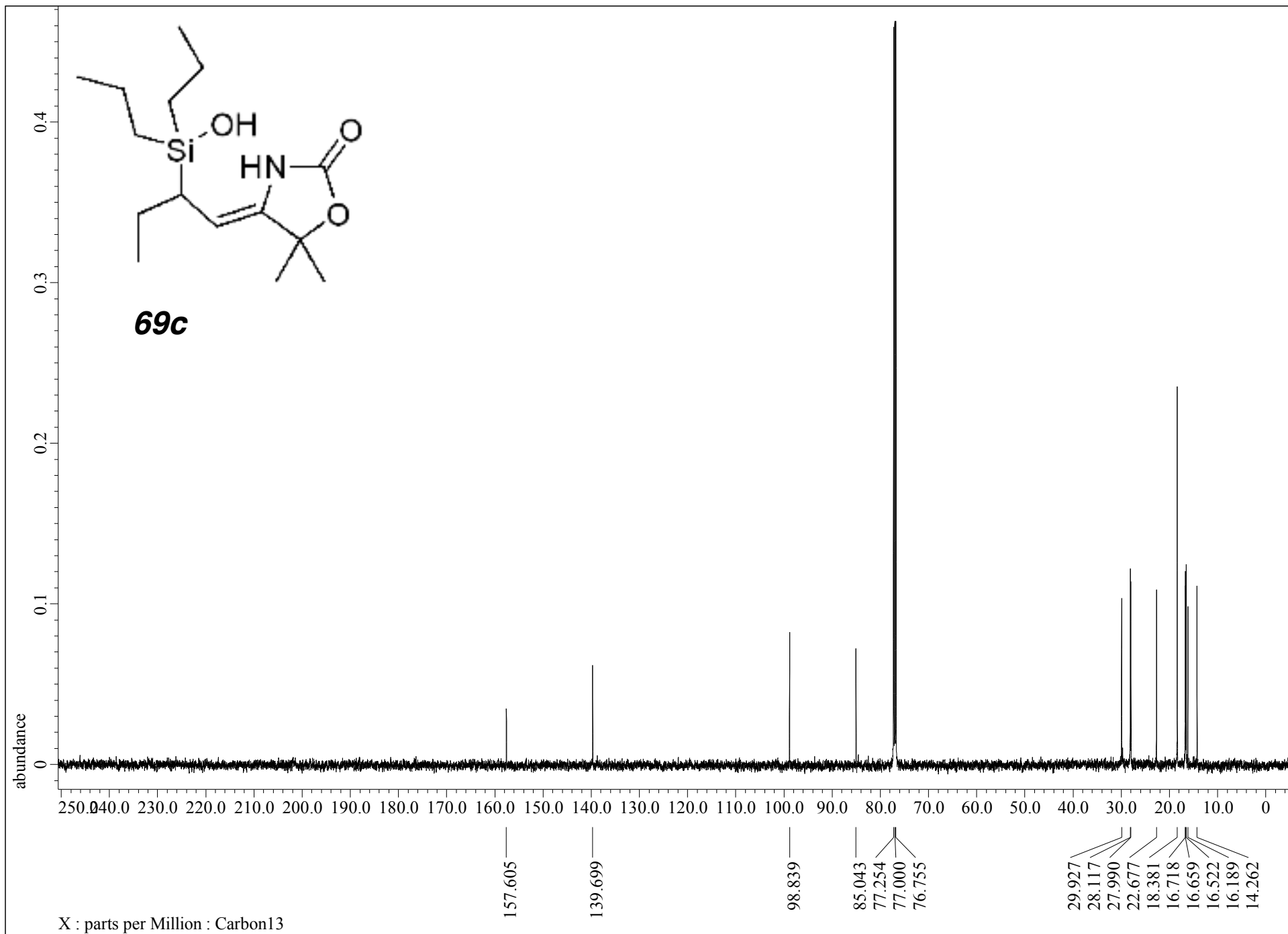


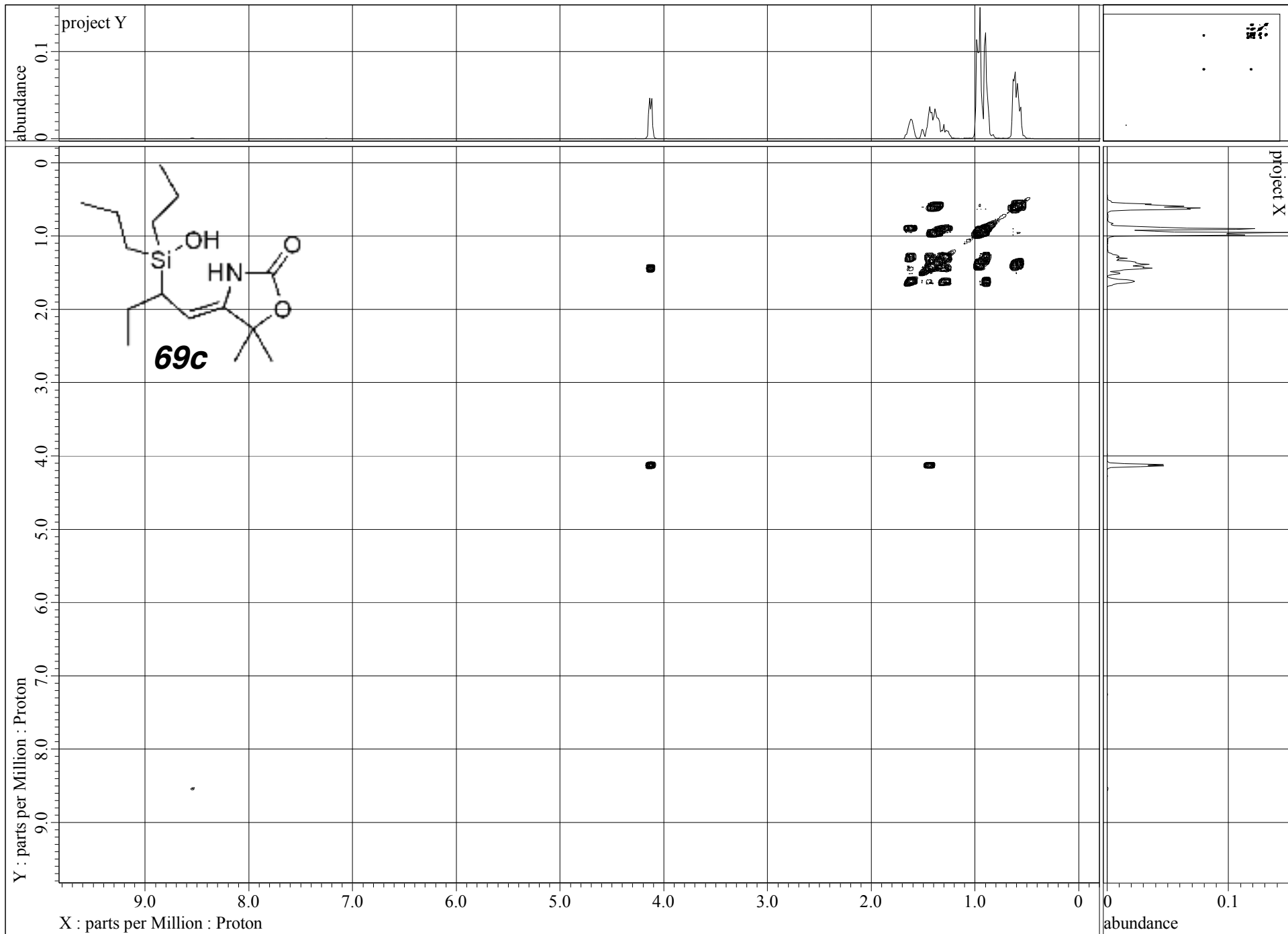
DEPT

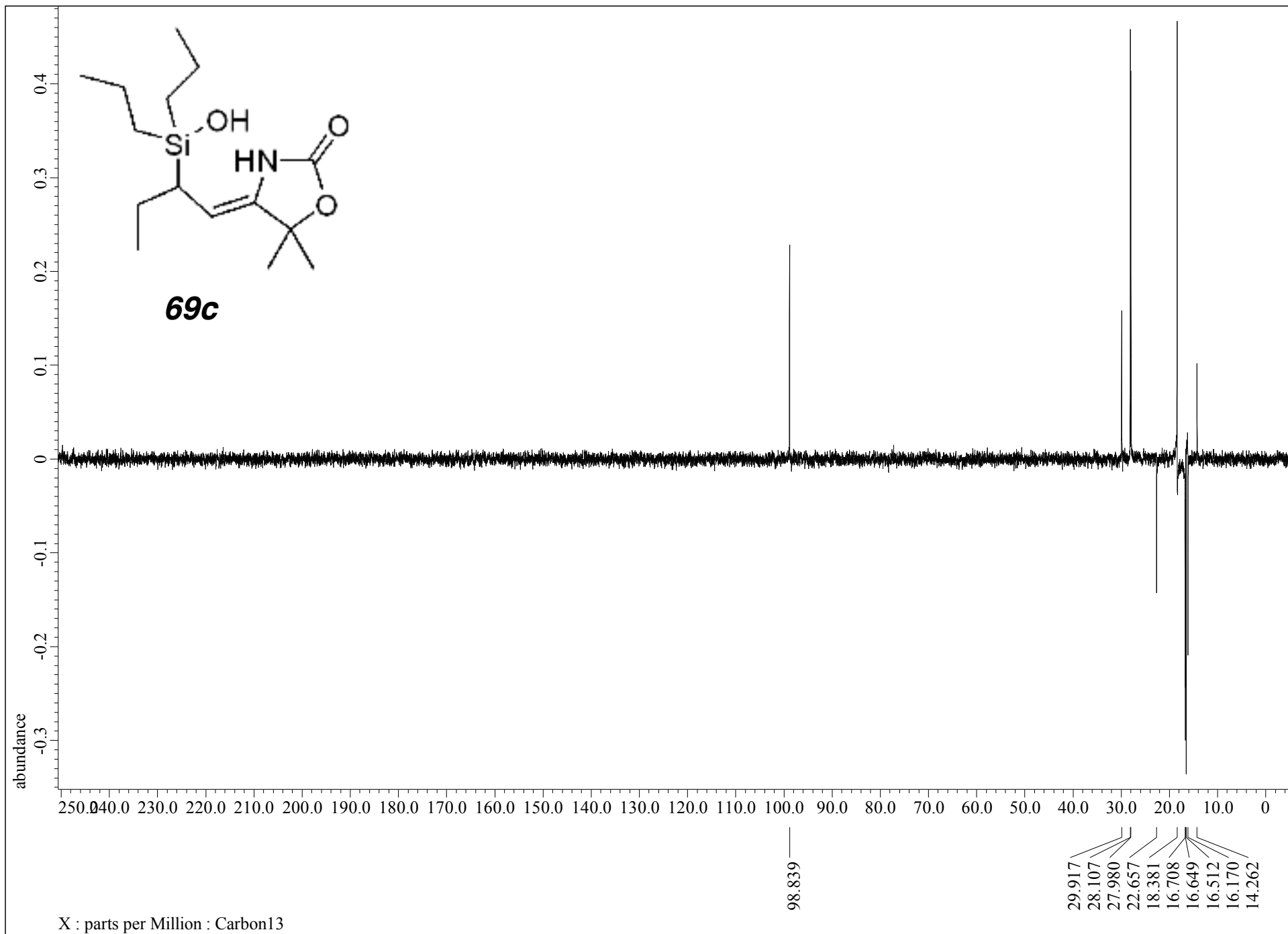


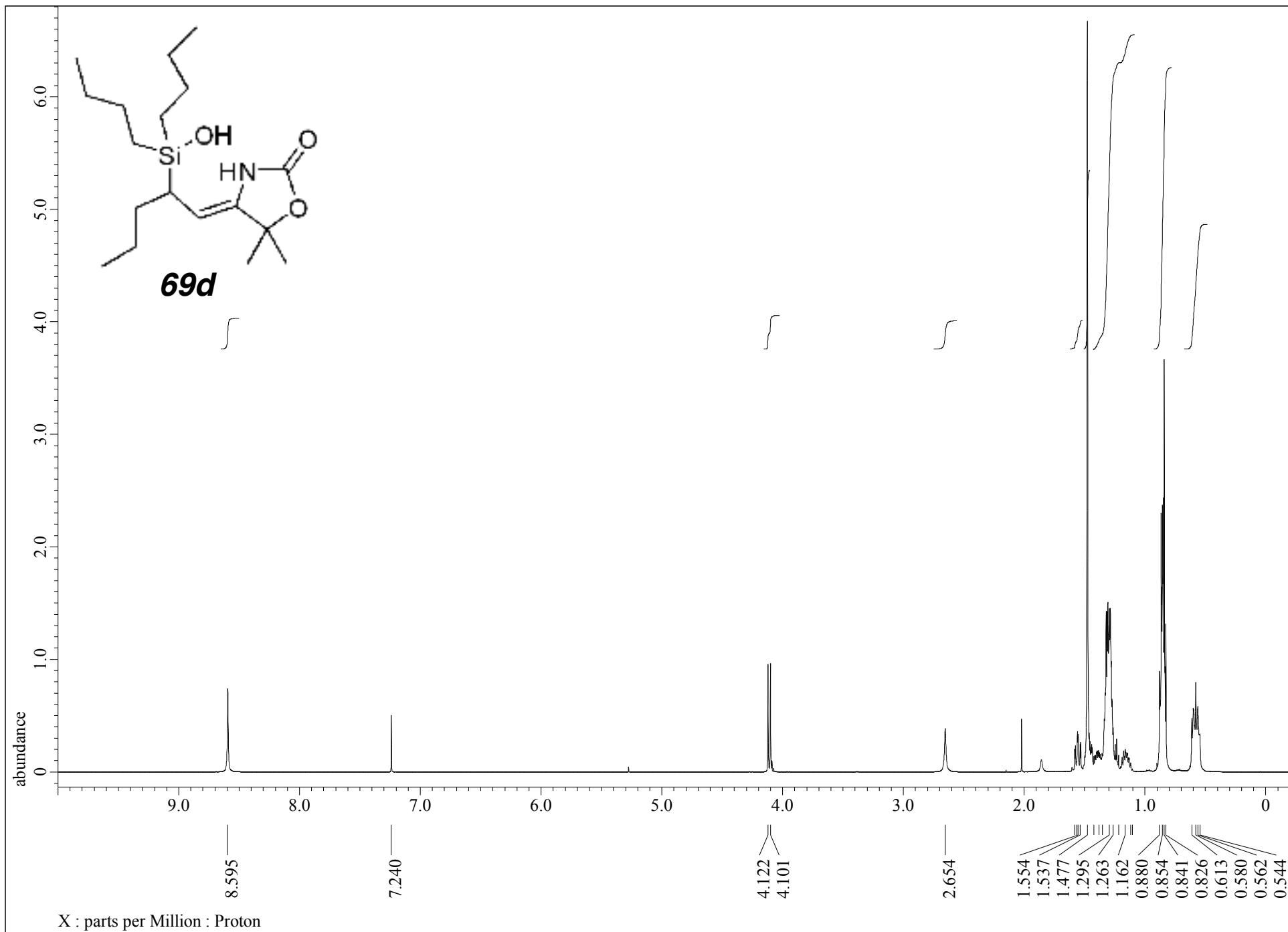


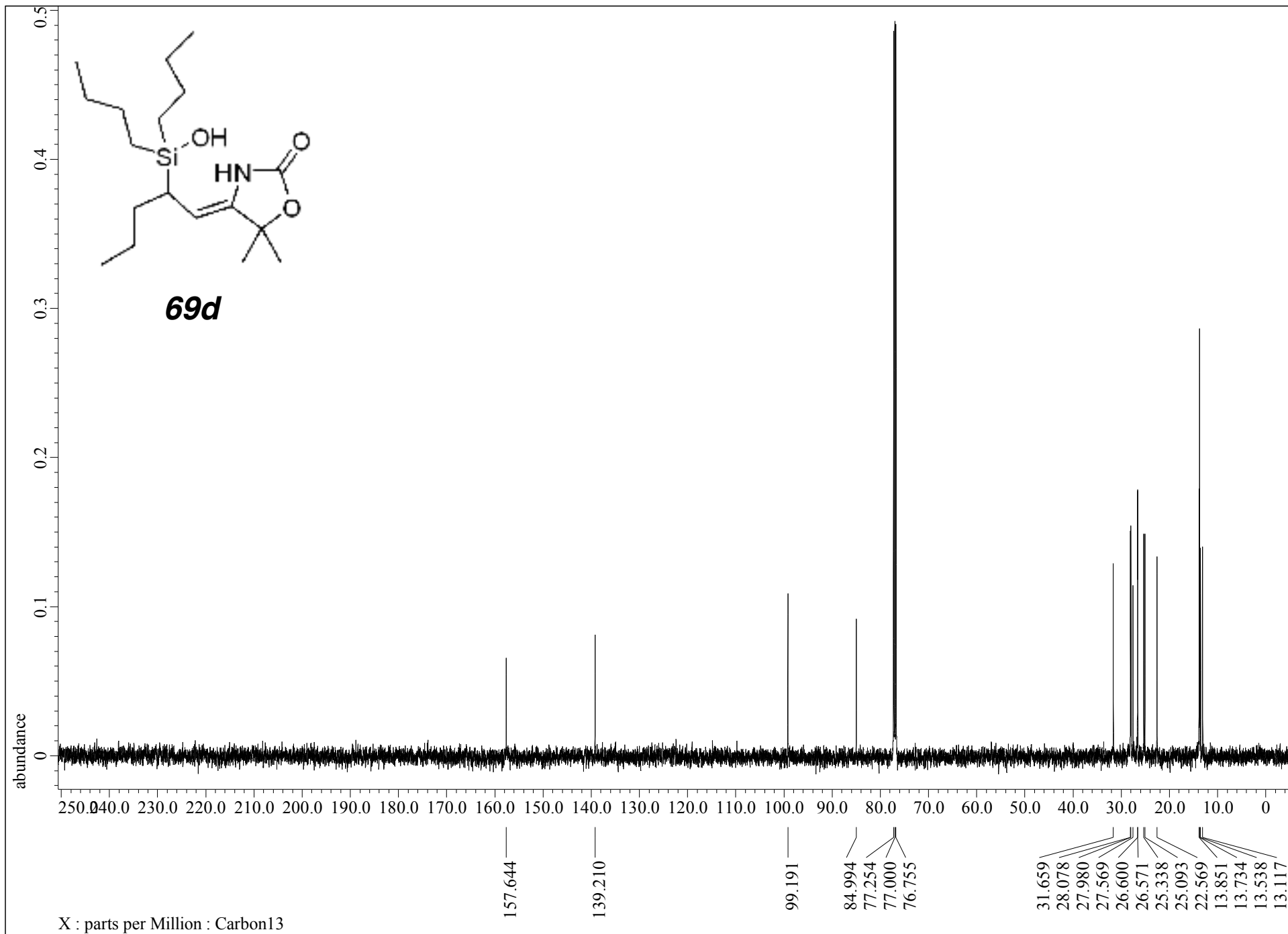


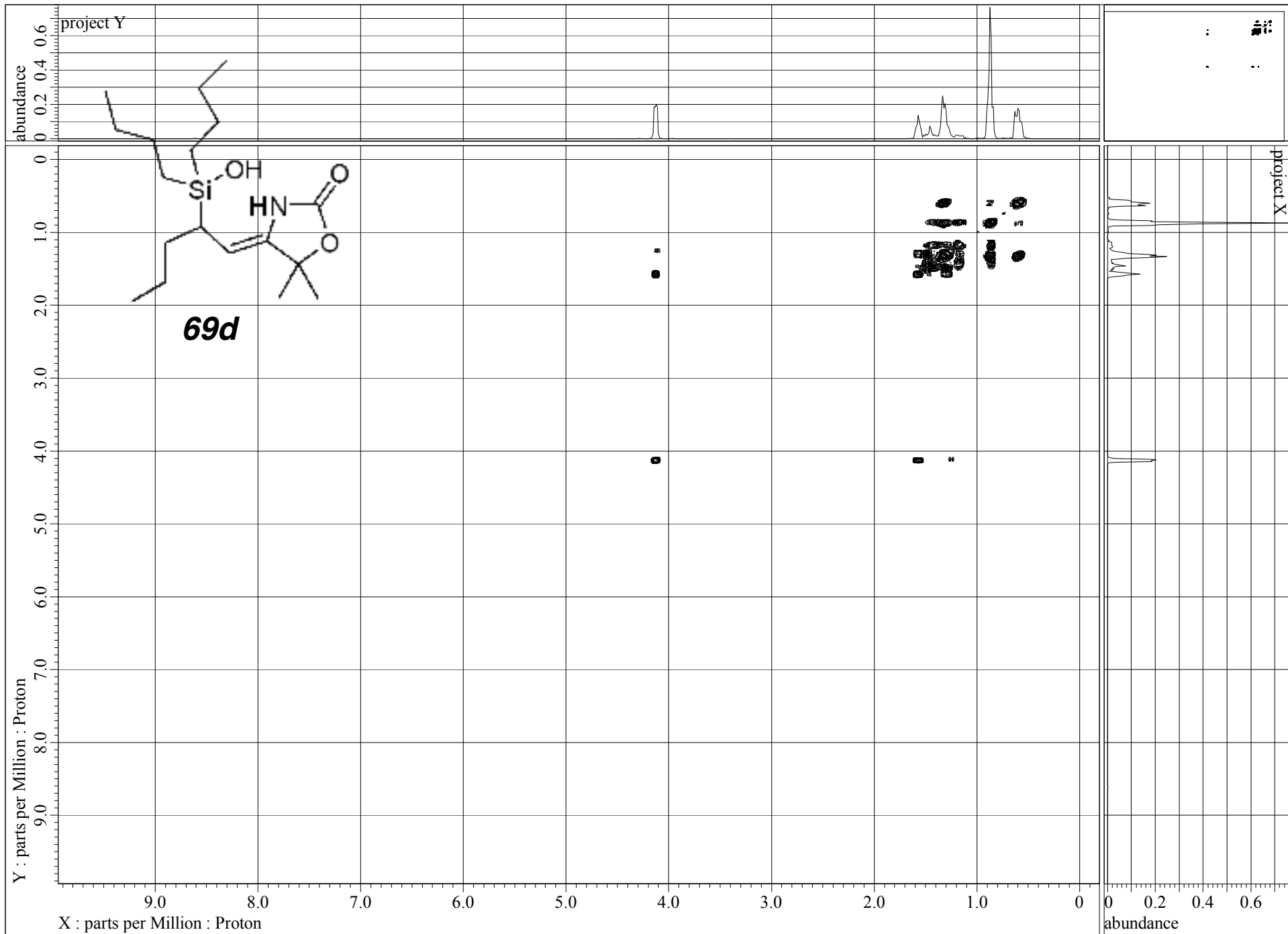


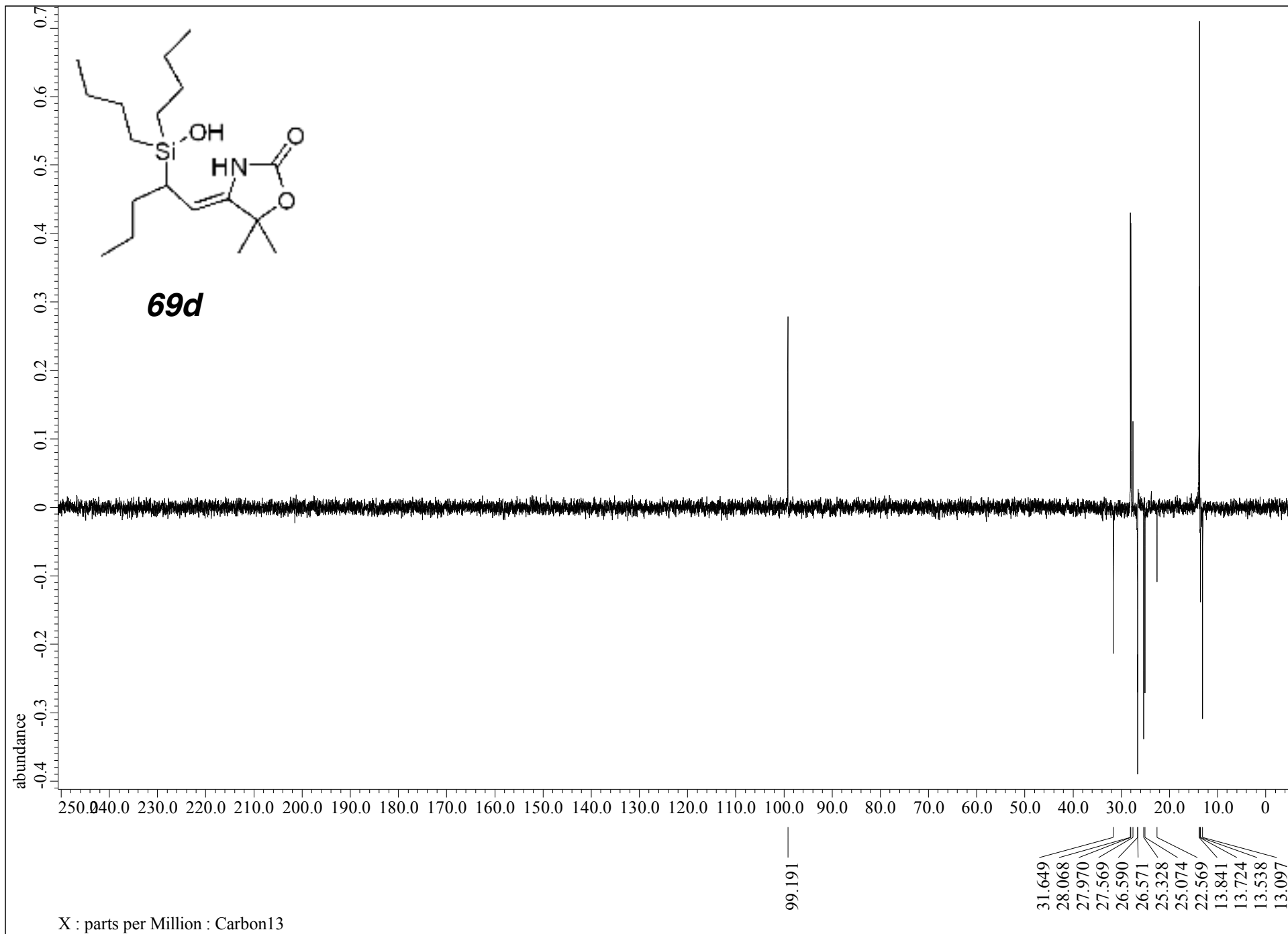


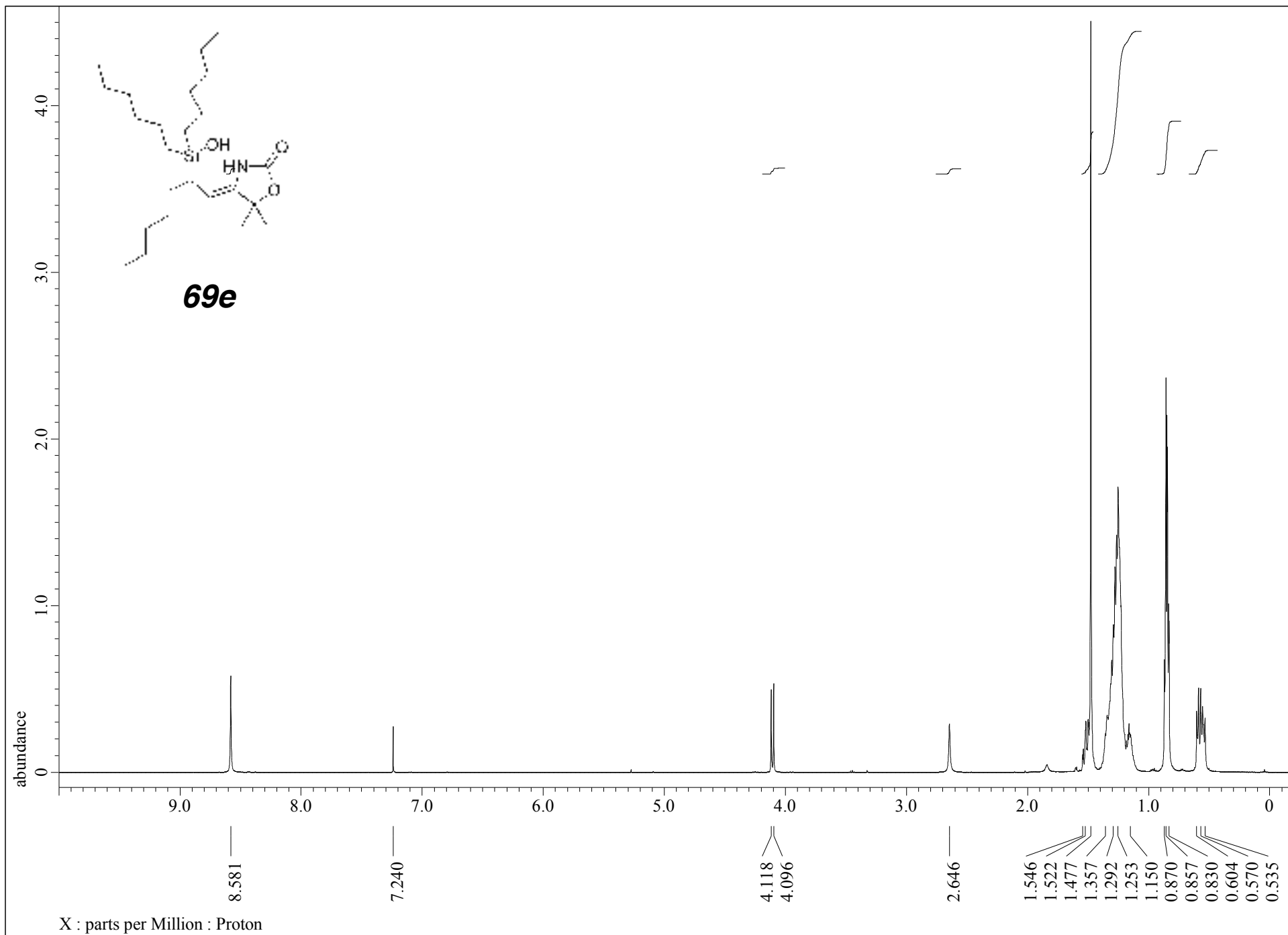




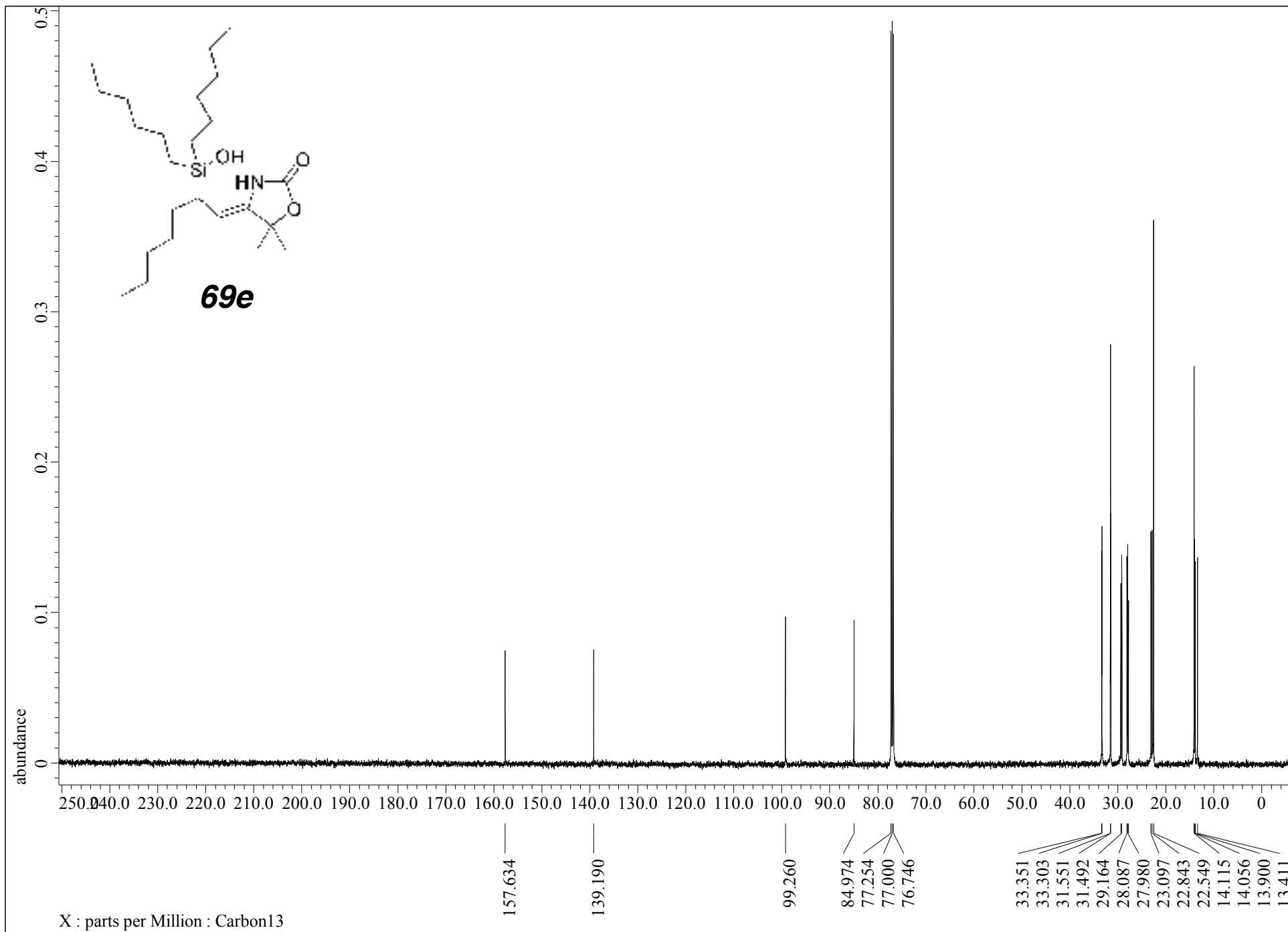


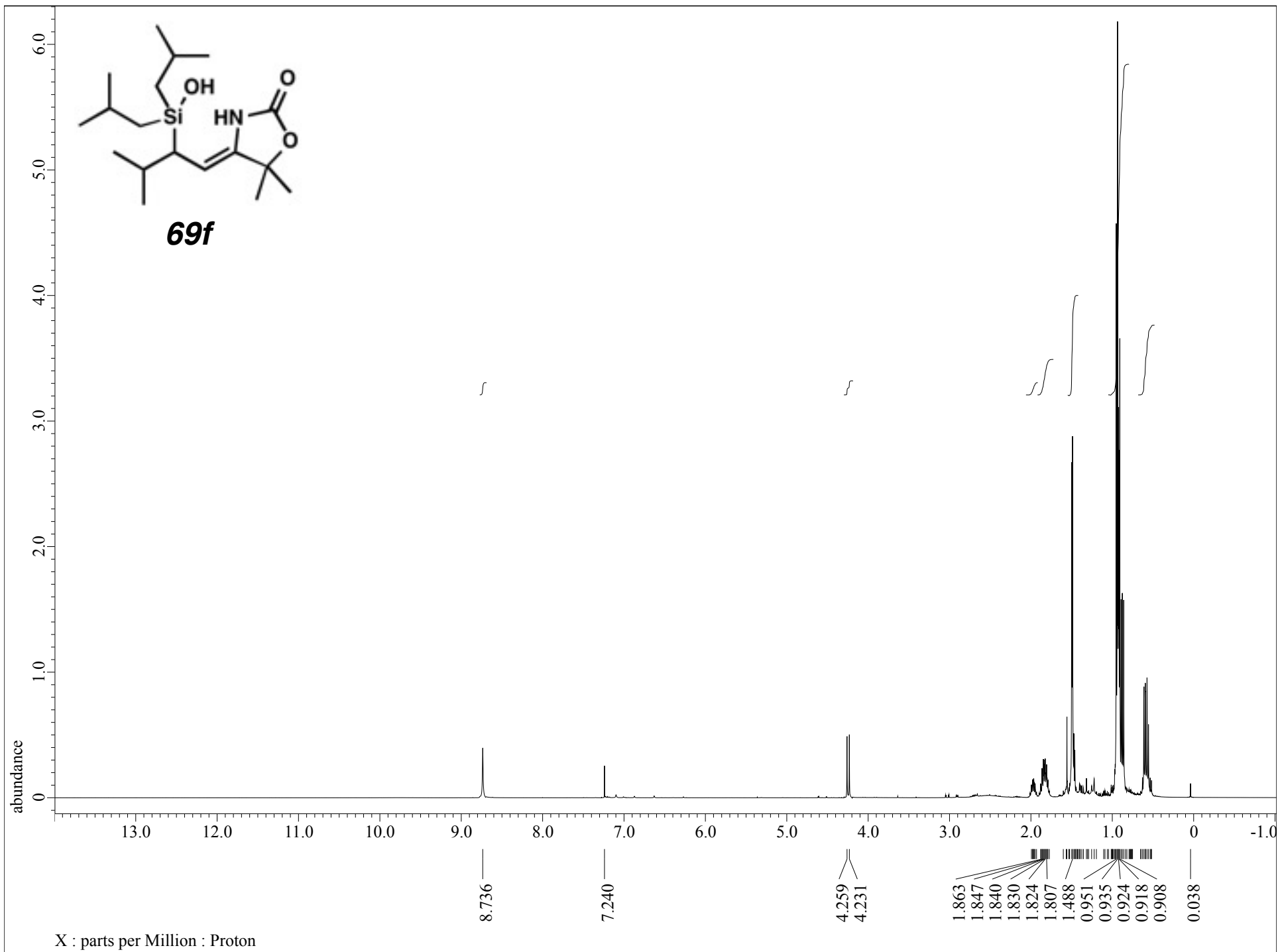


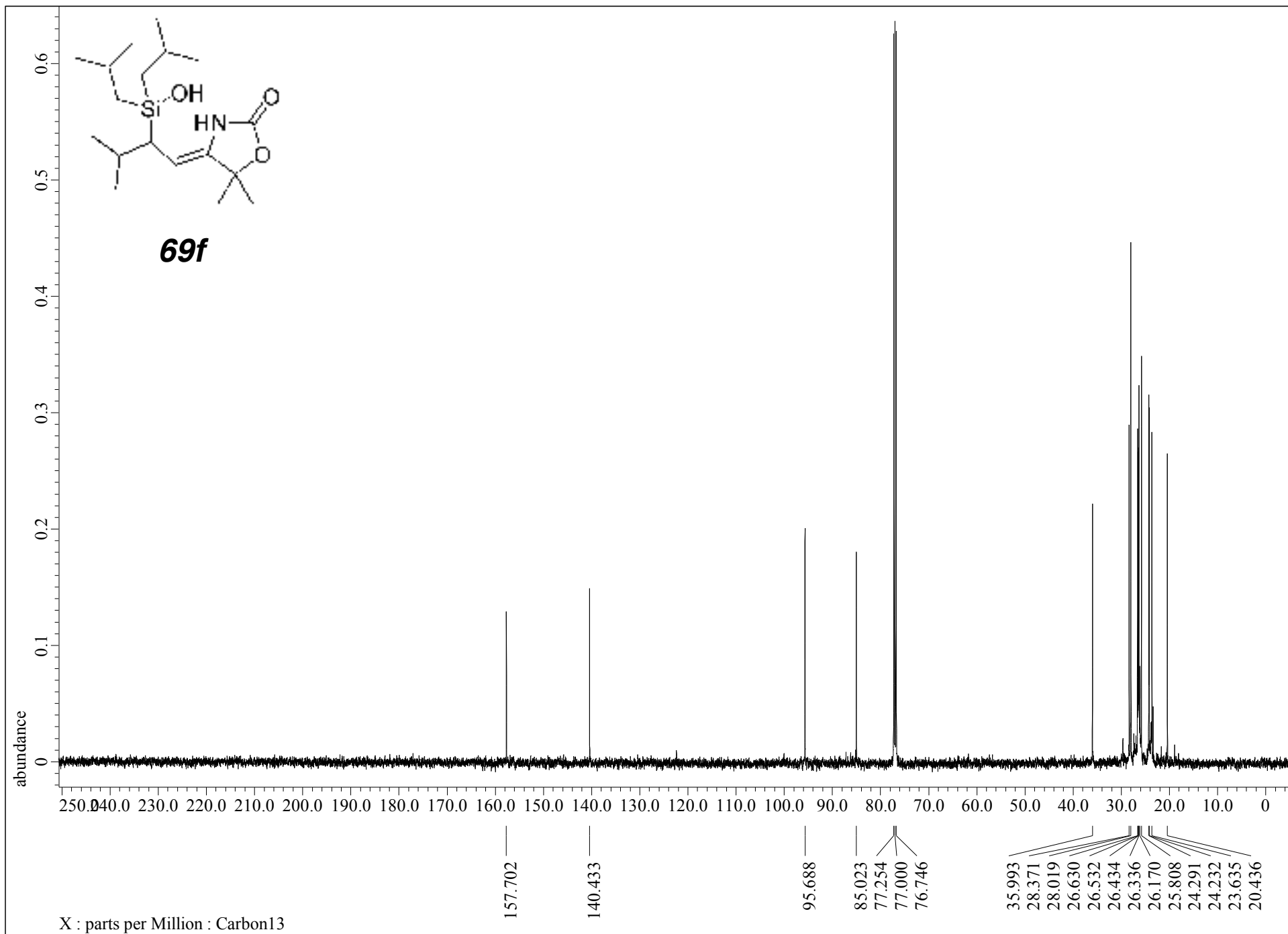


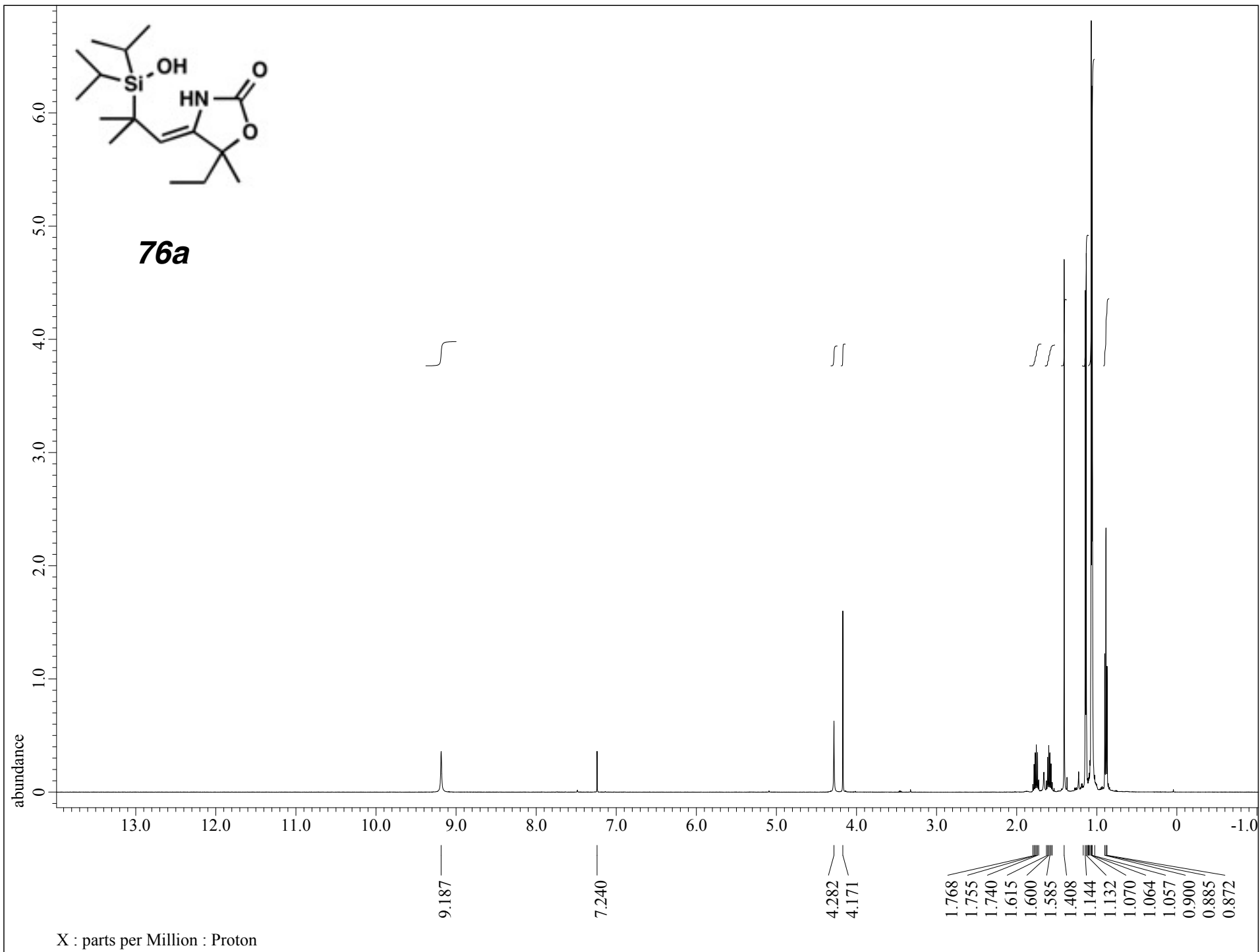






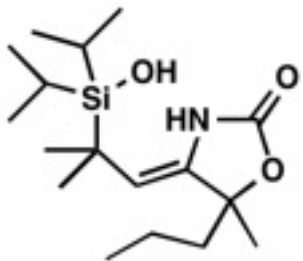




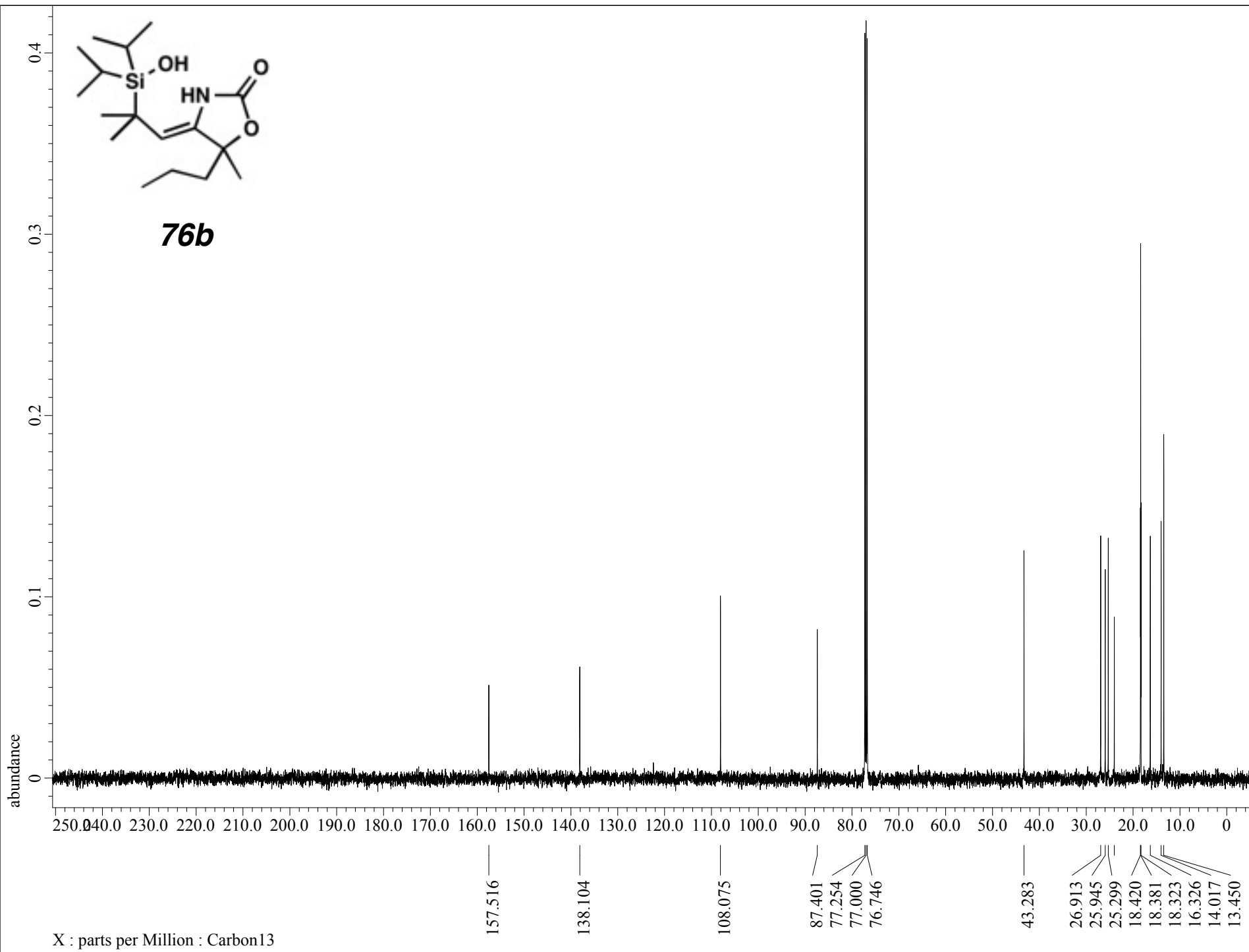


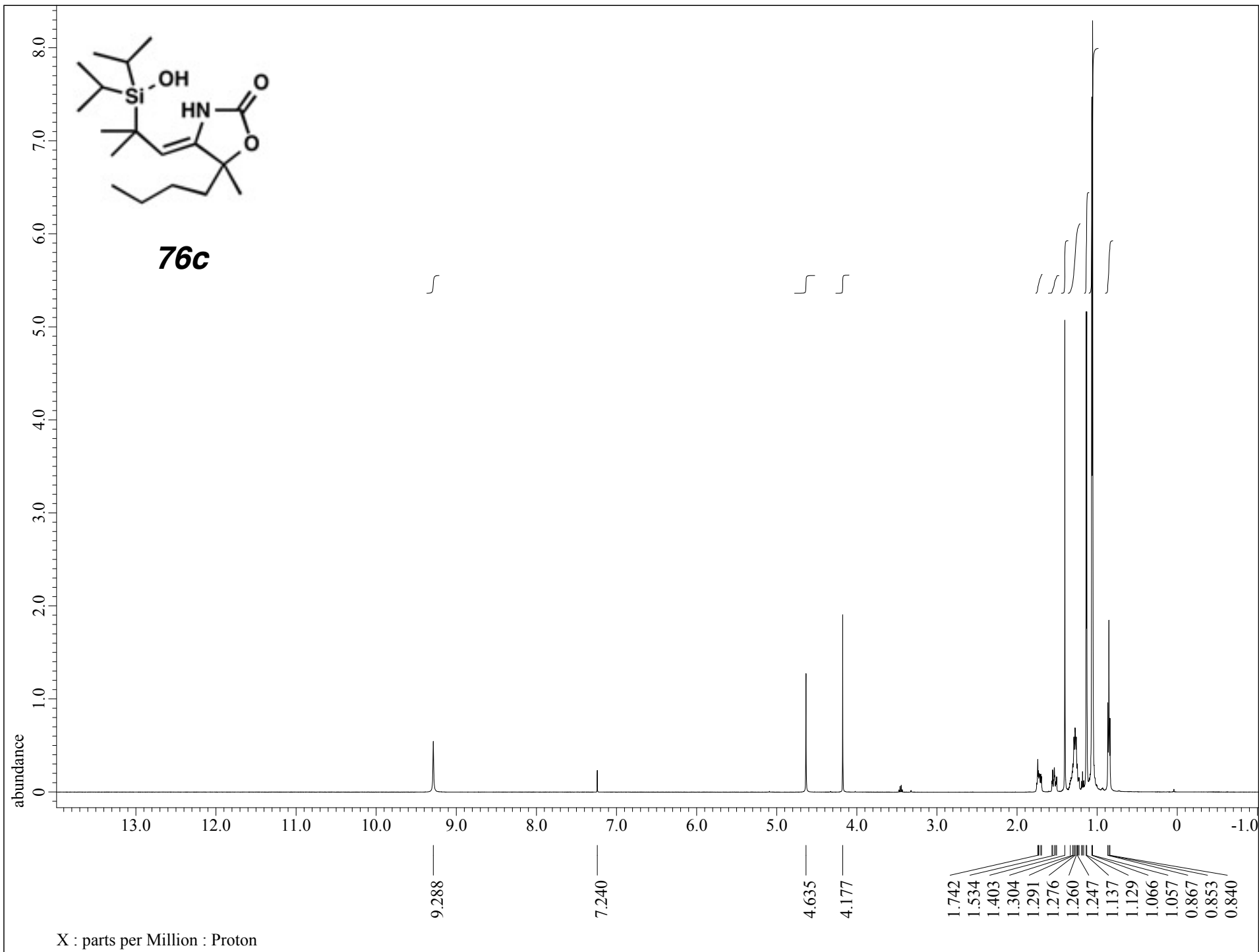






**76b**



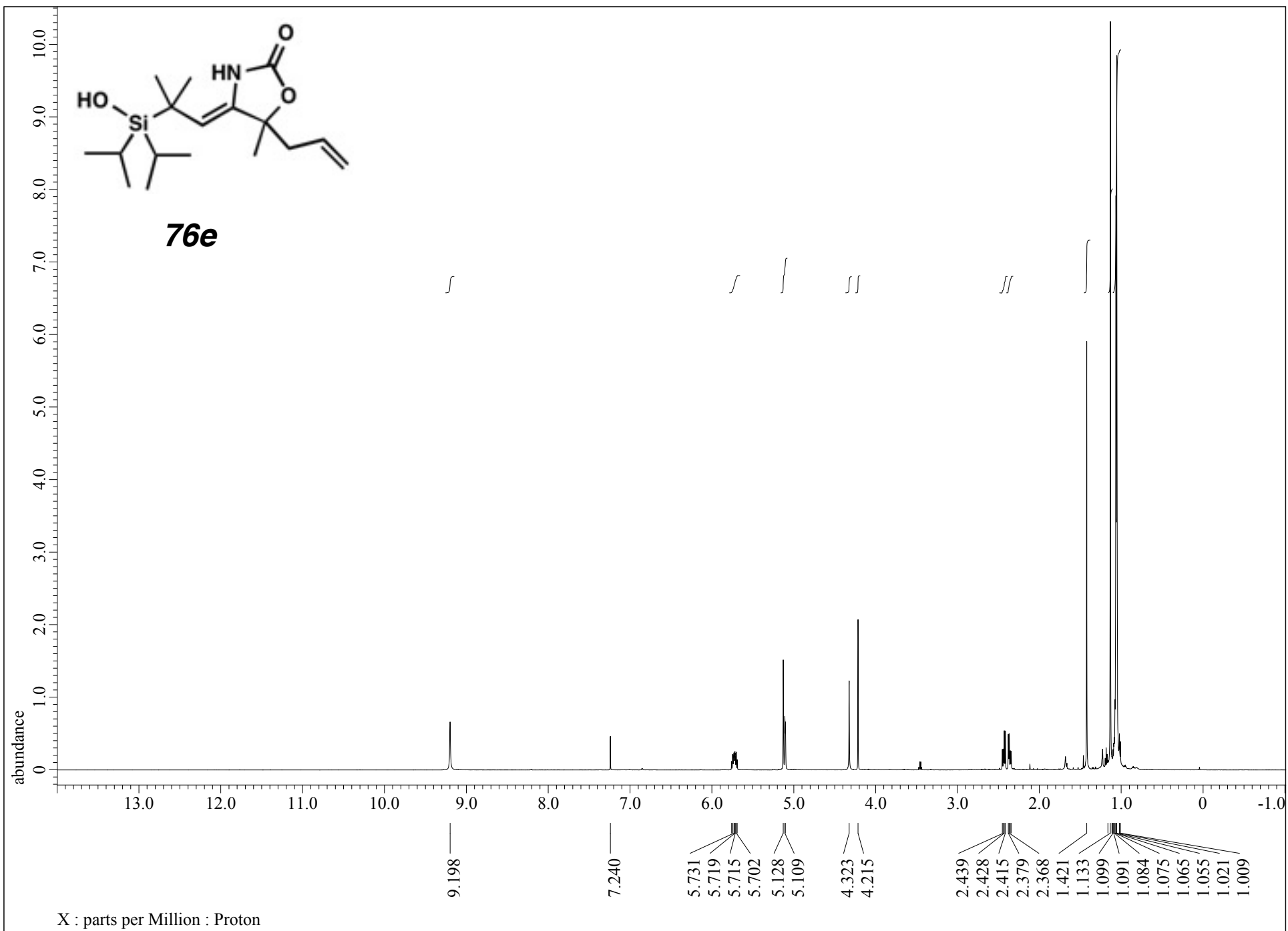


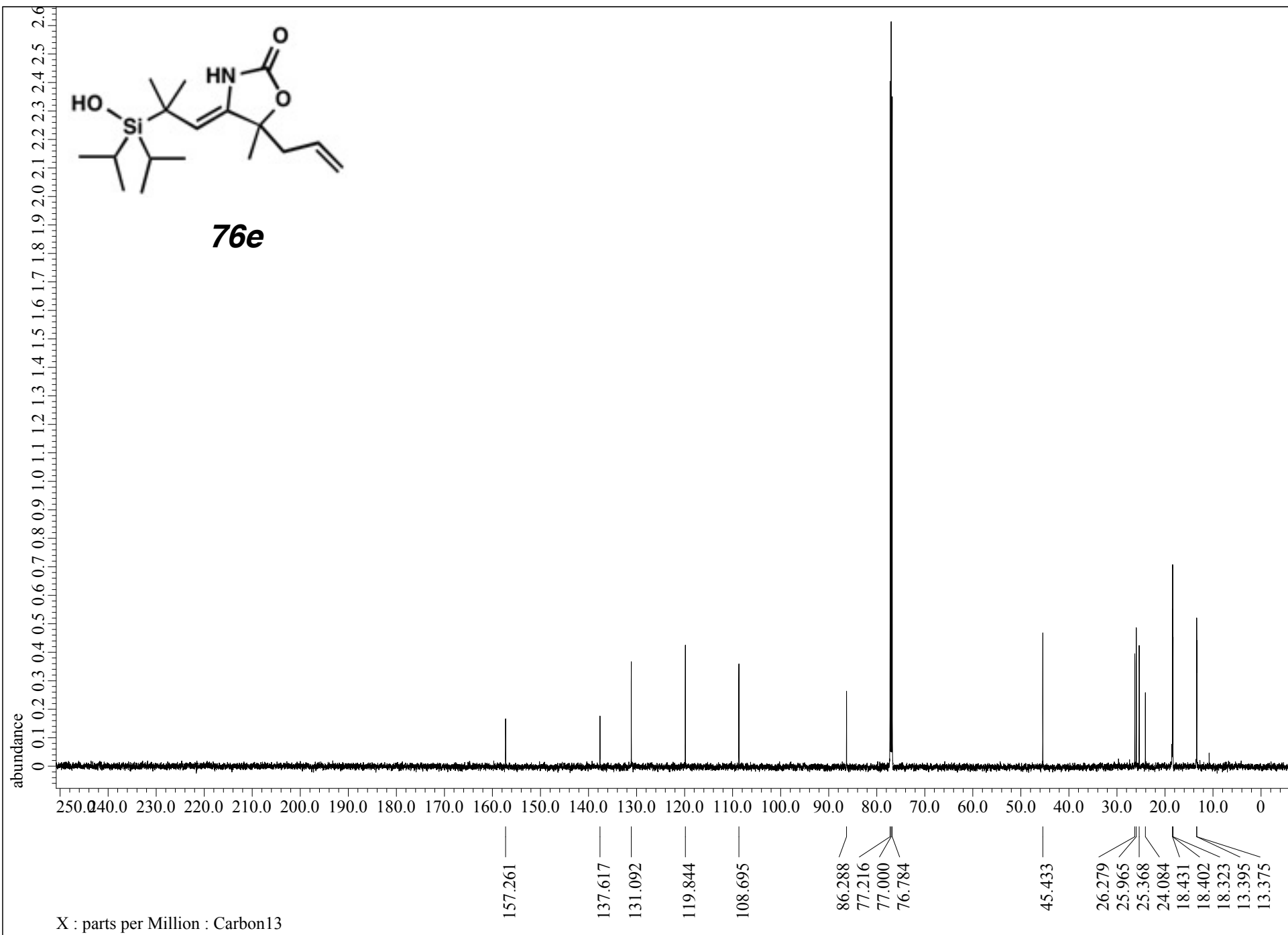


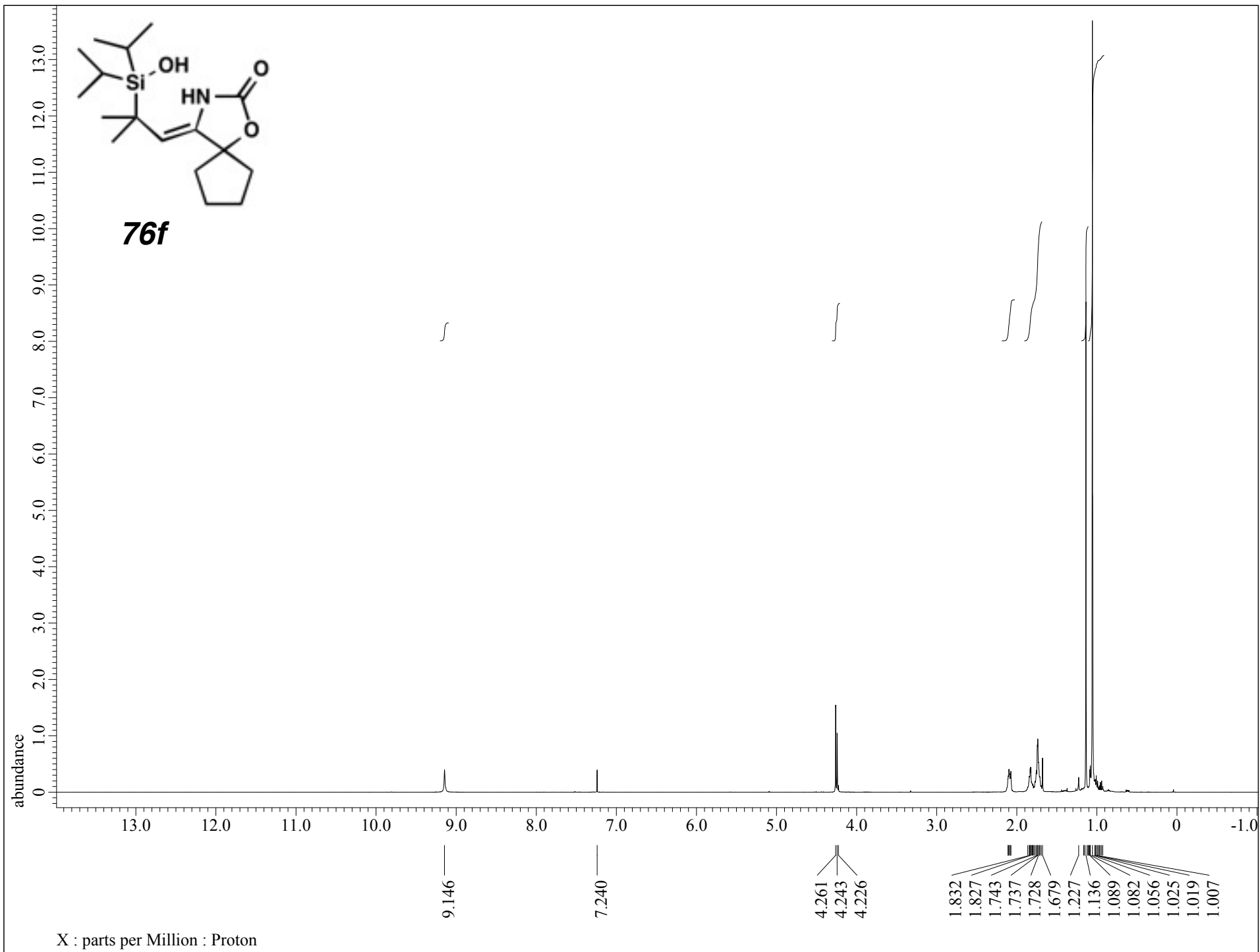


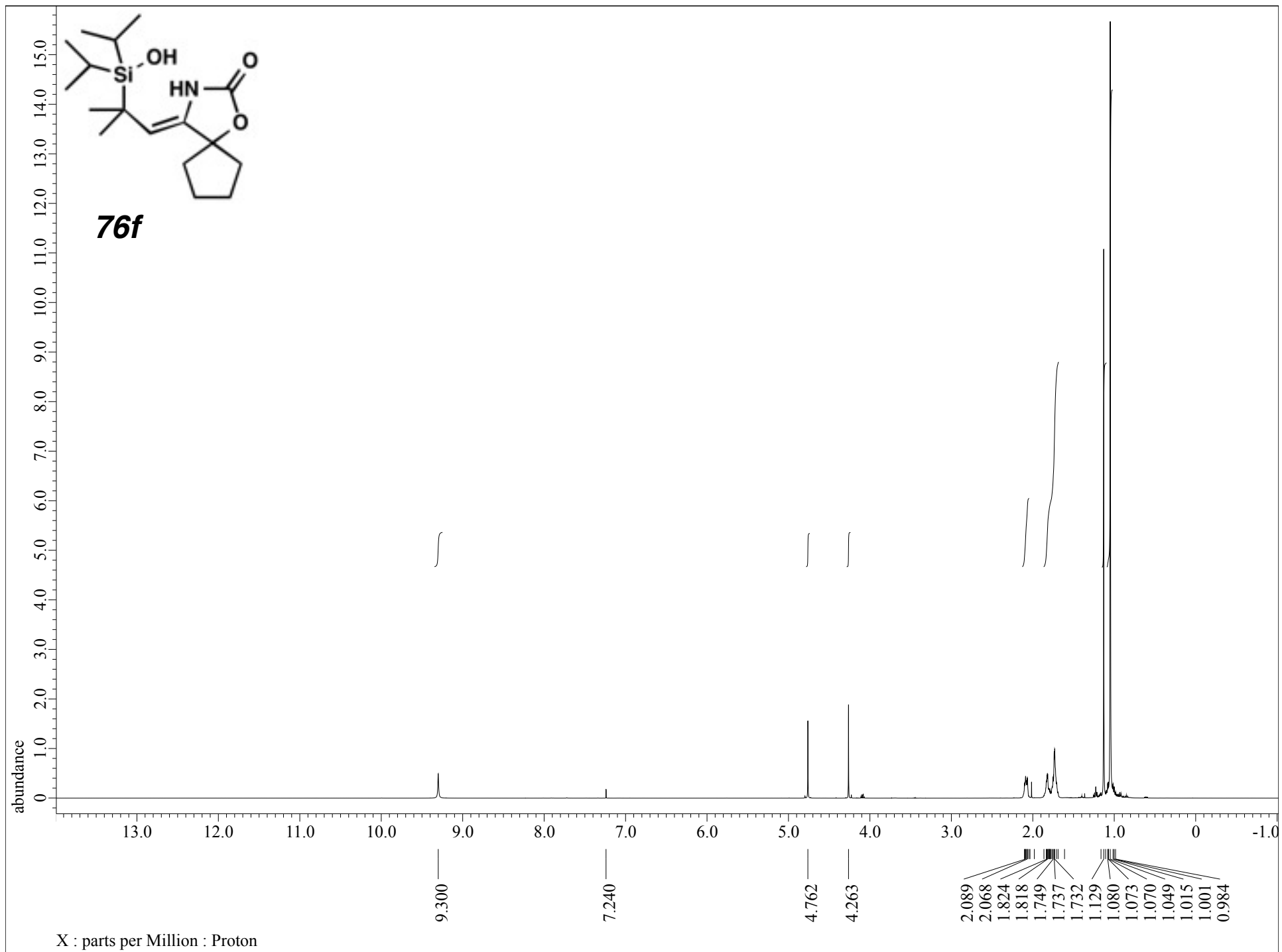


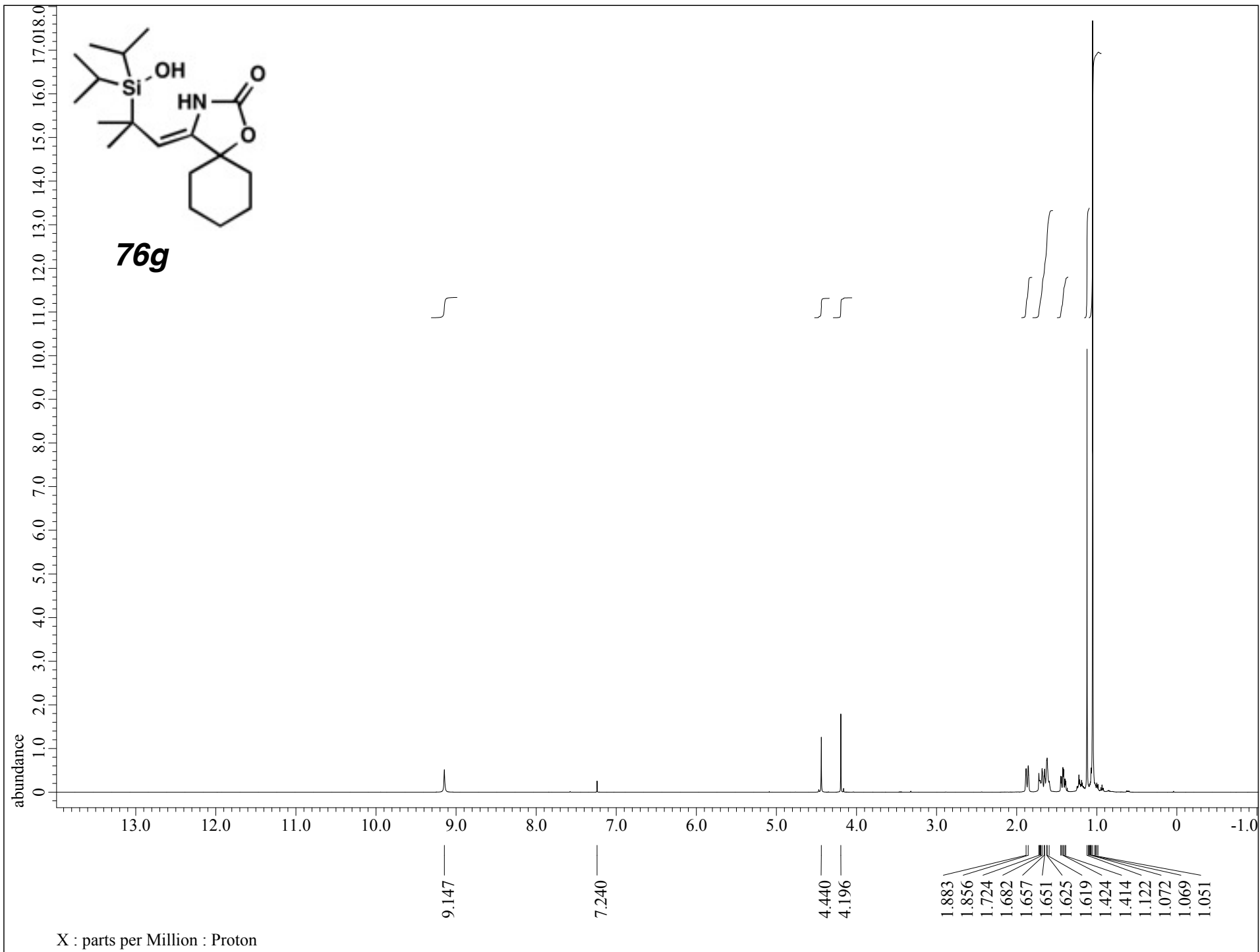




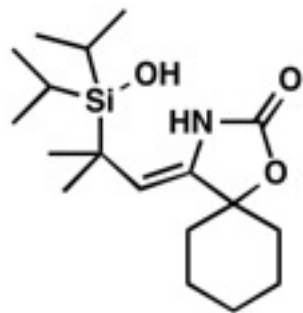




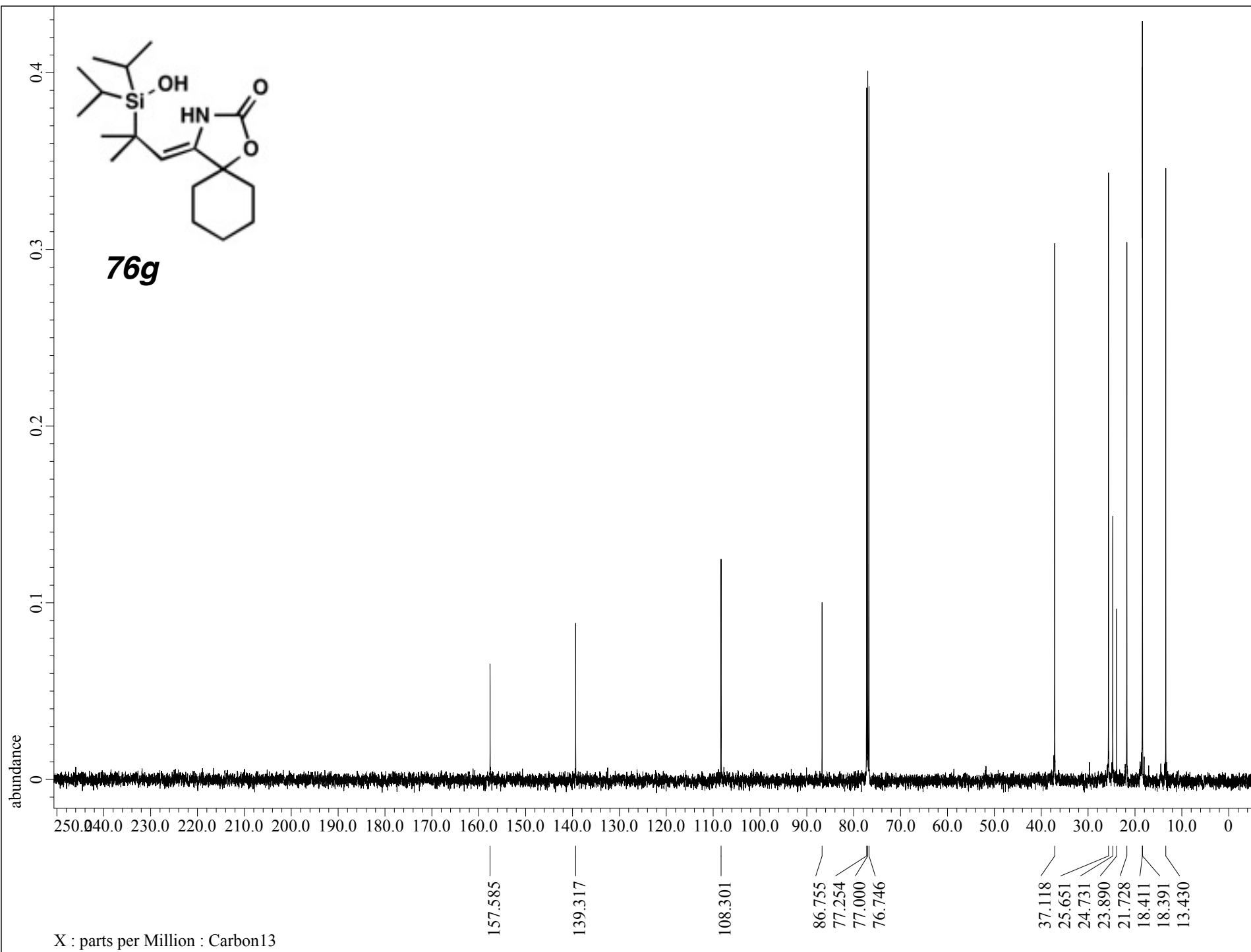


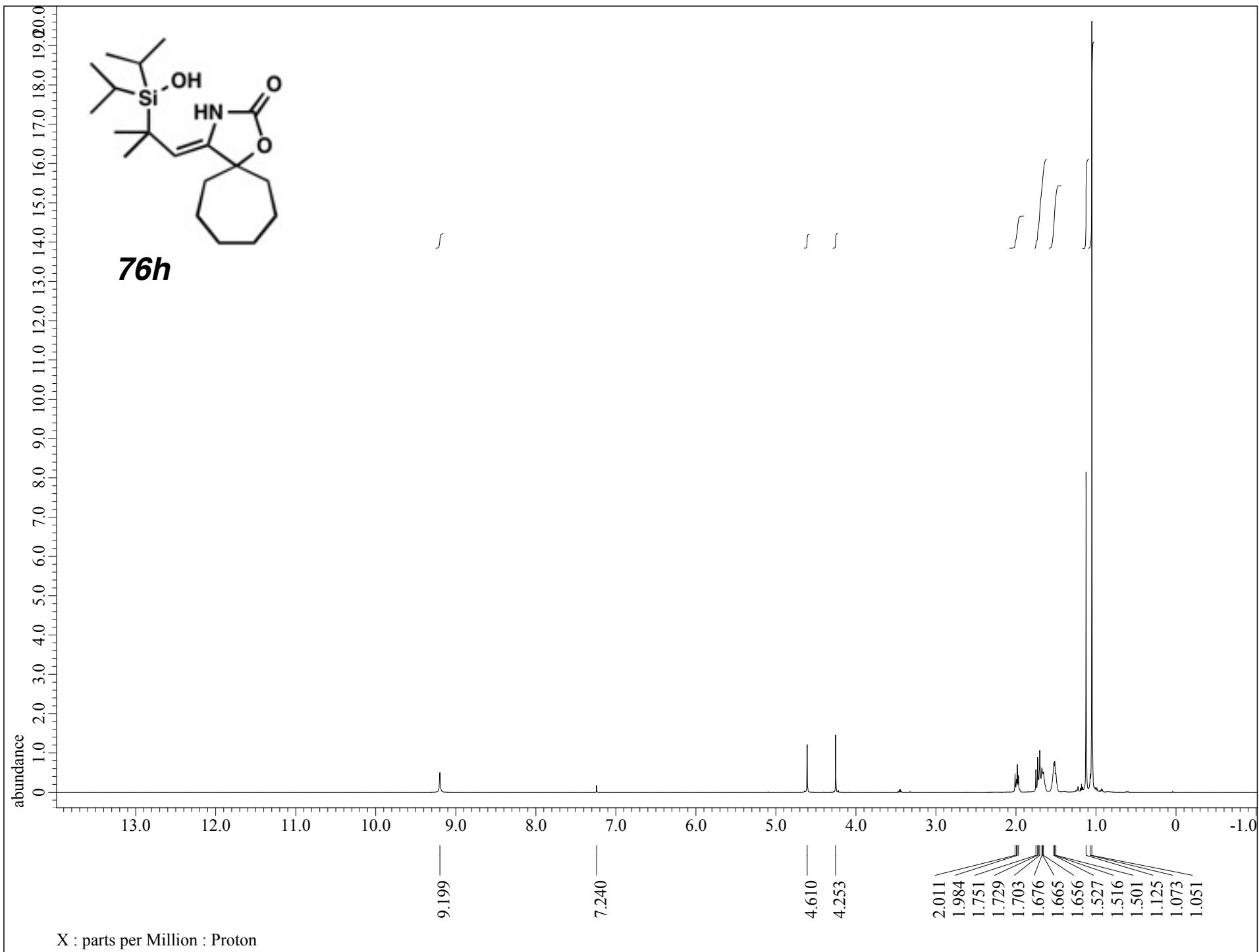


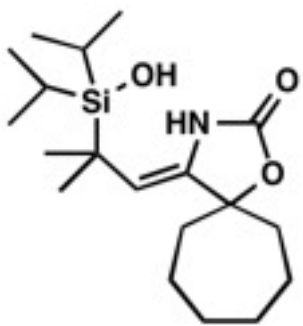




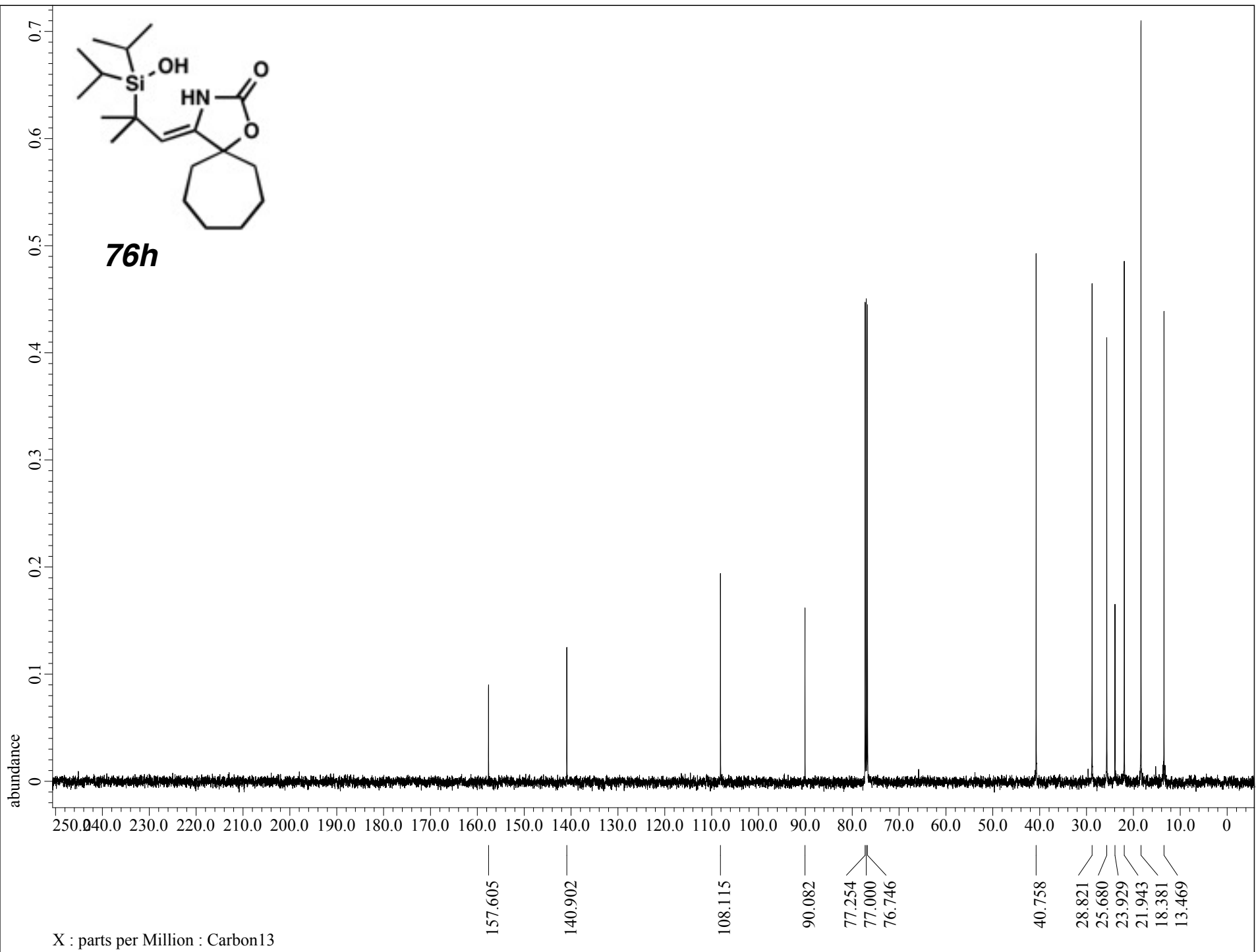
**76g**

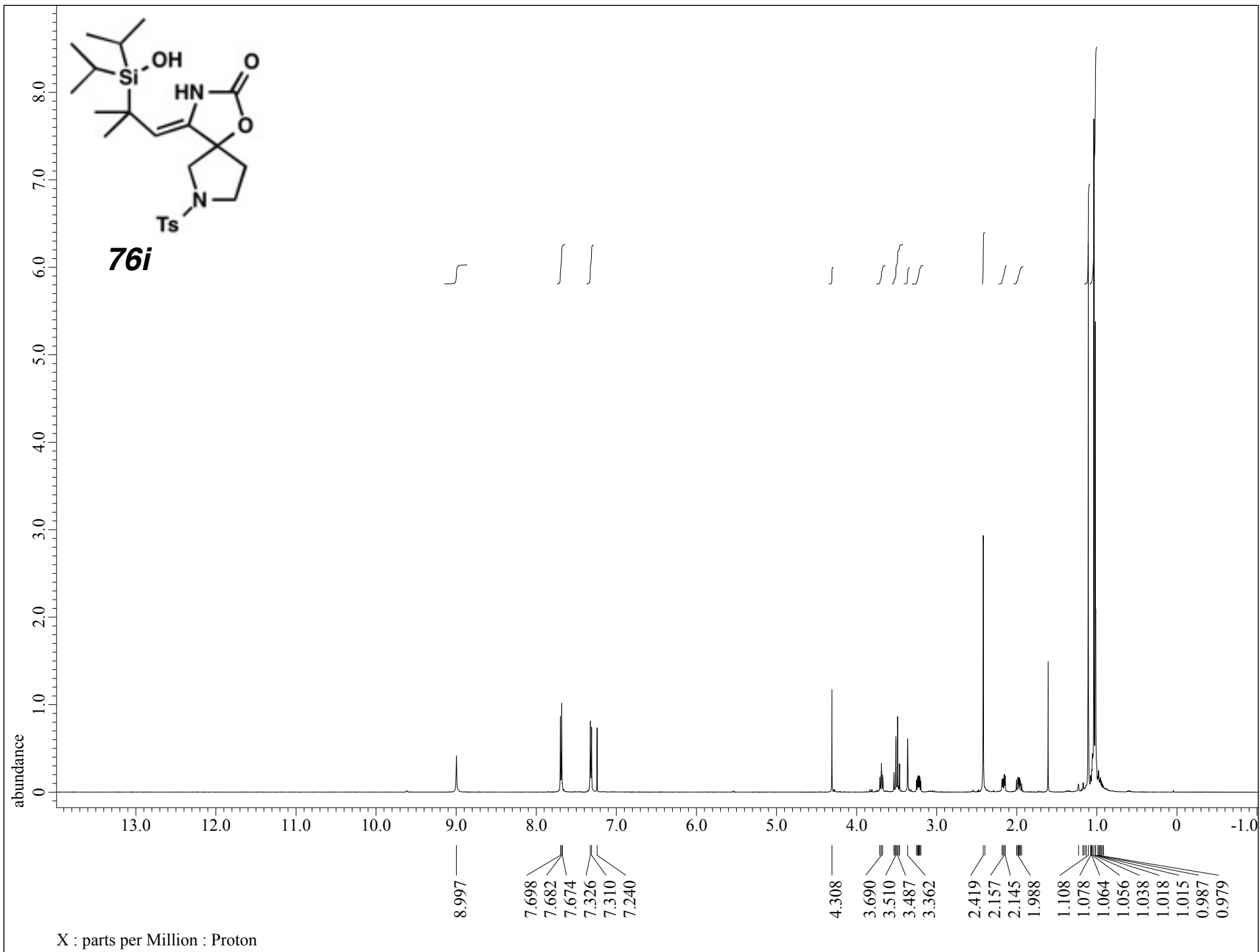


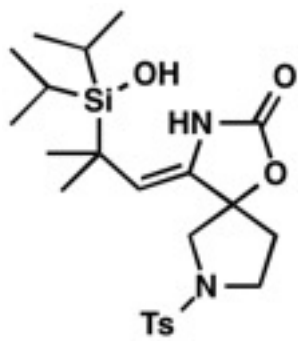




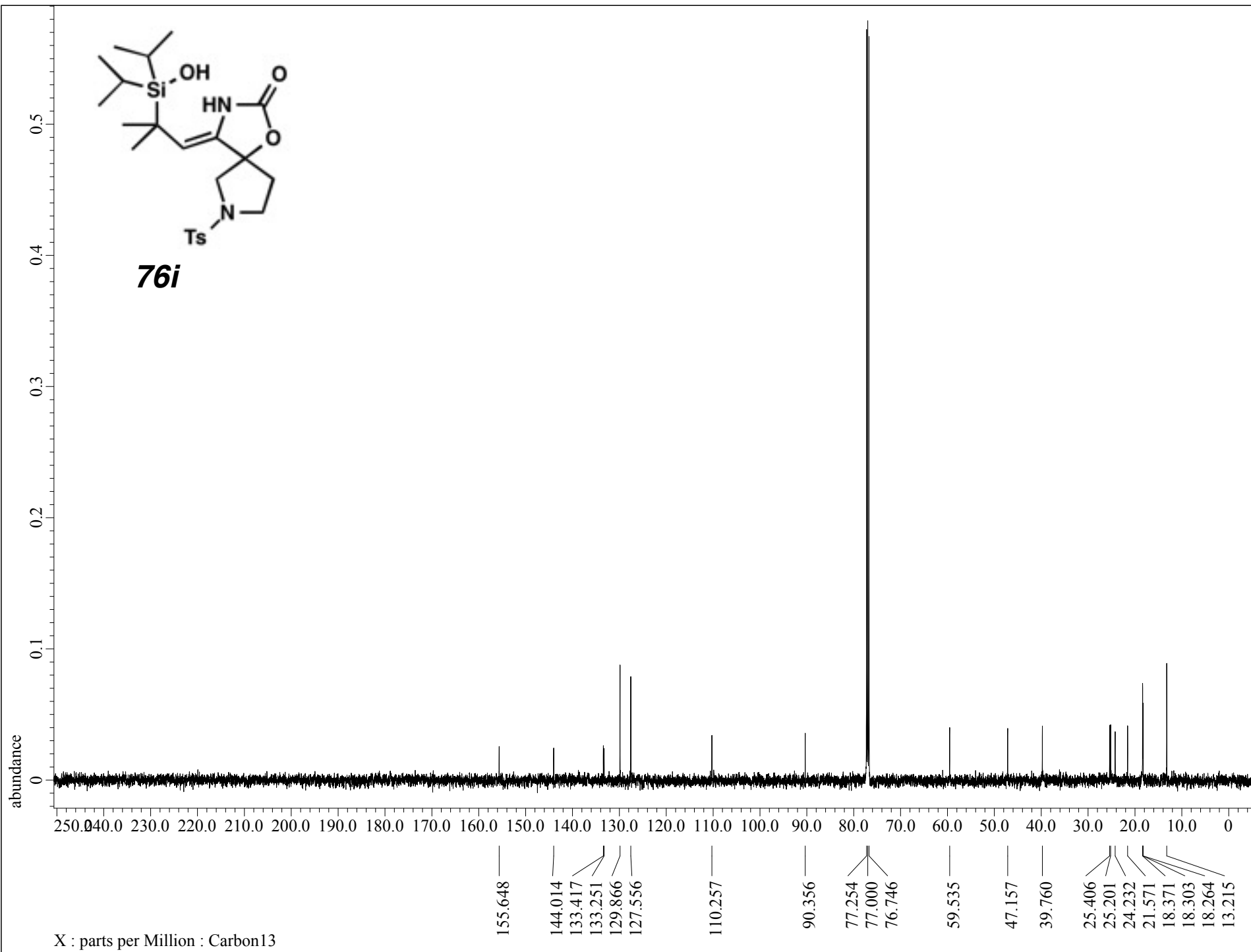
**76h**

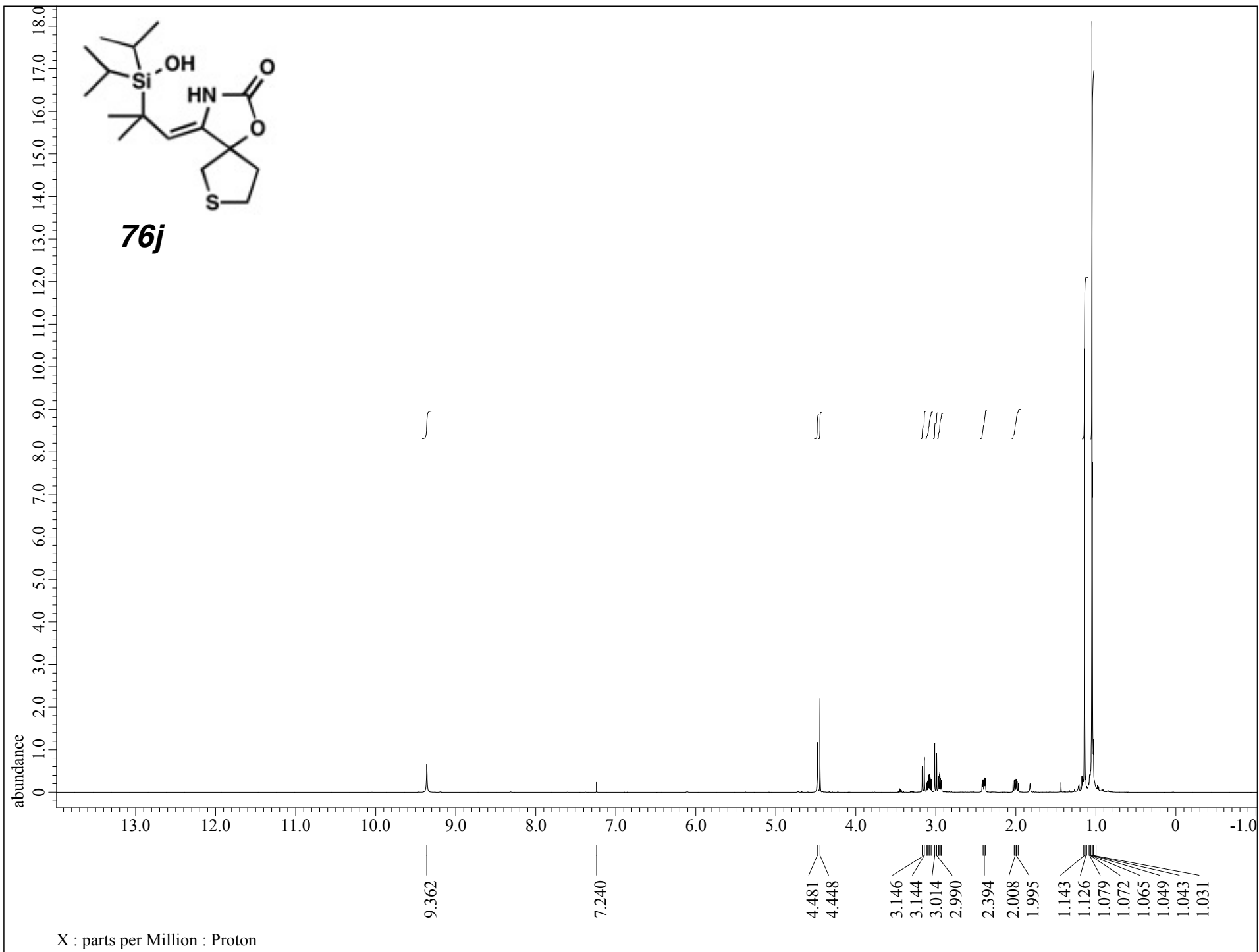


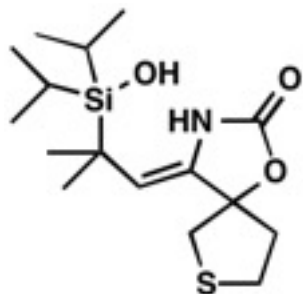




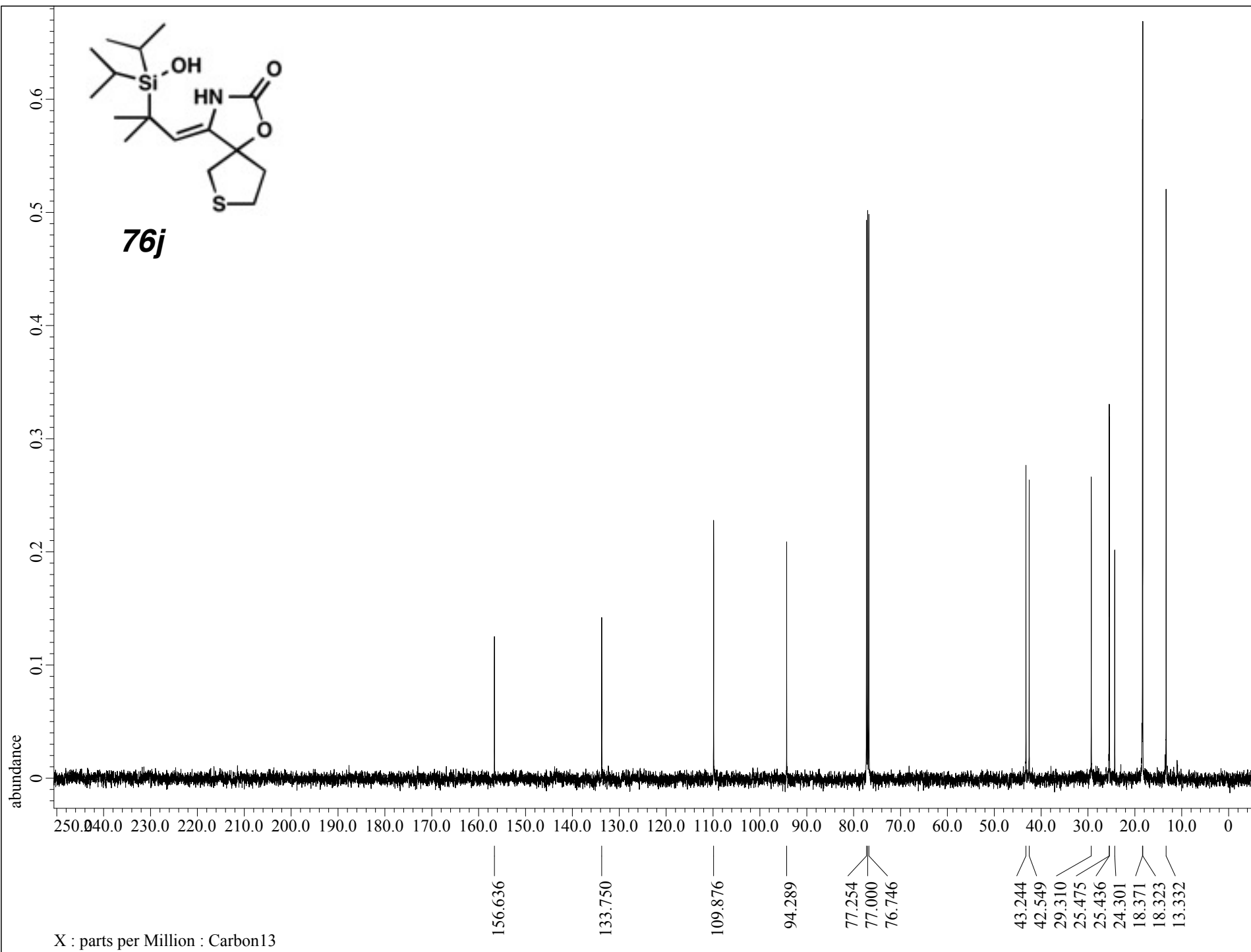
**76i**

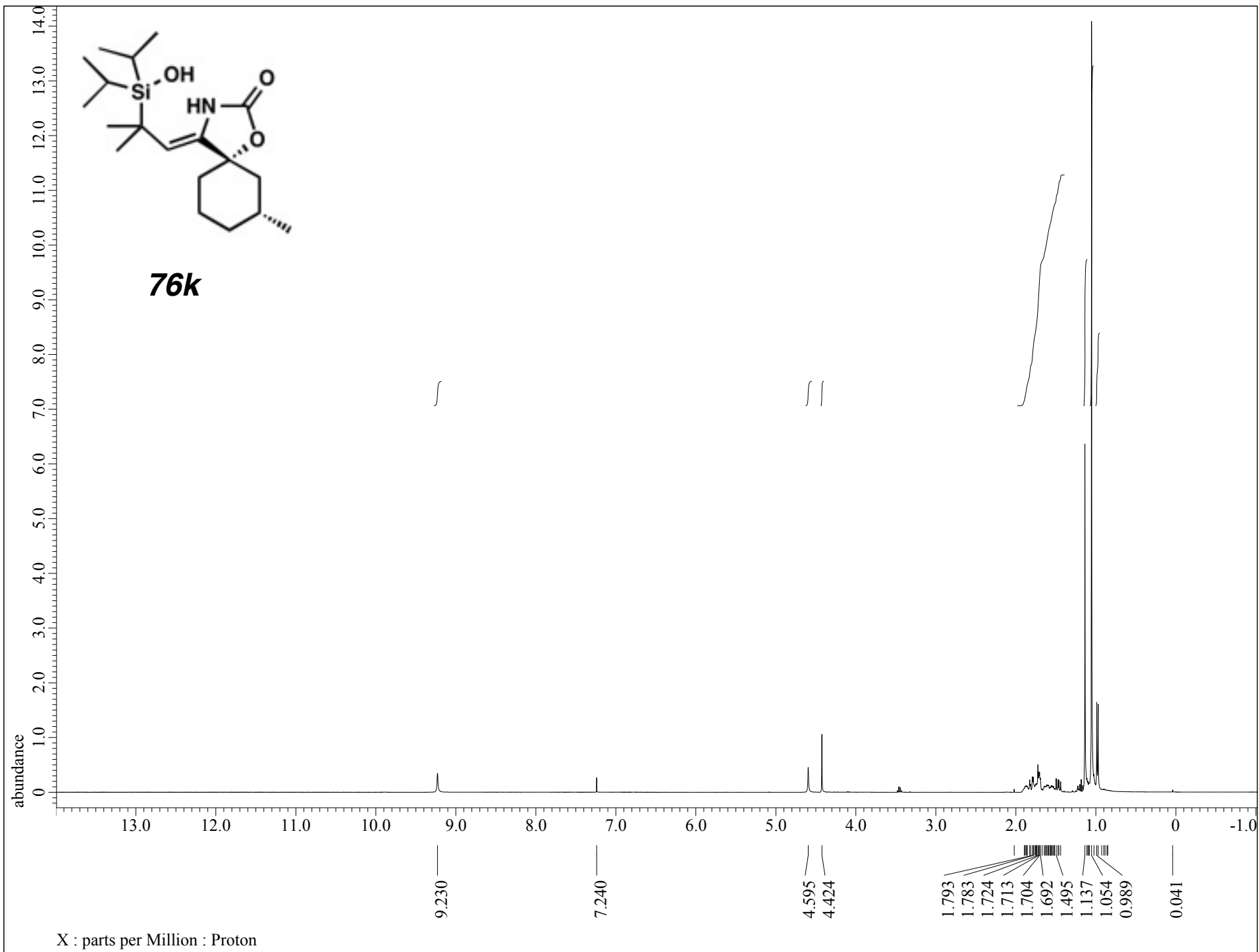




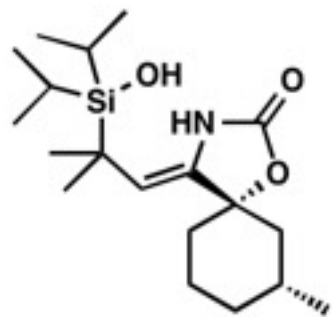


**76j**

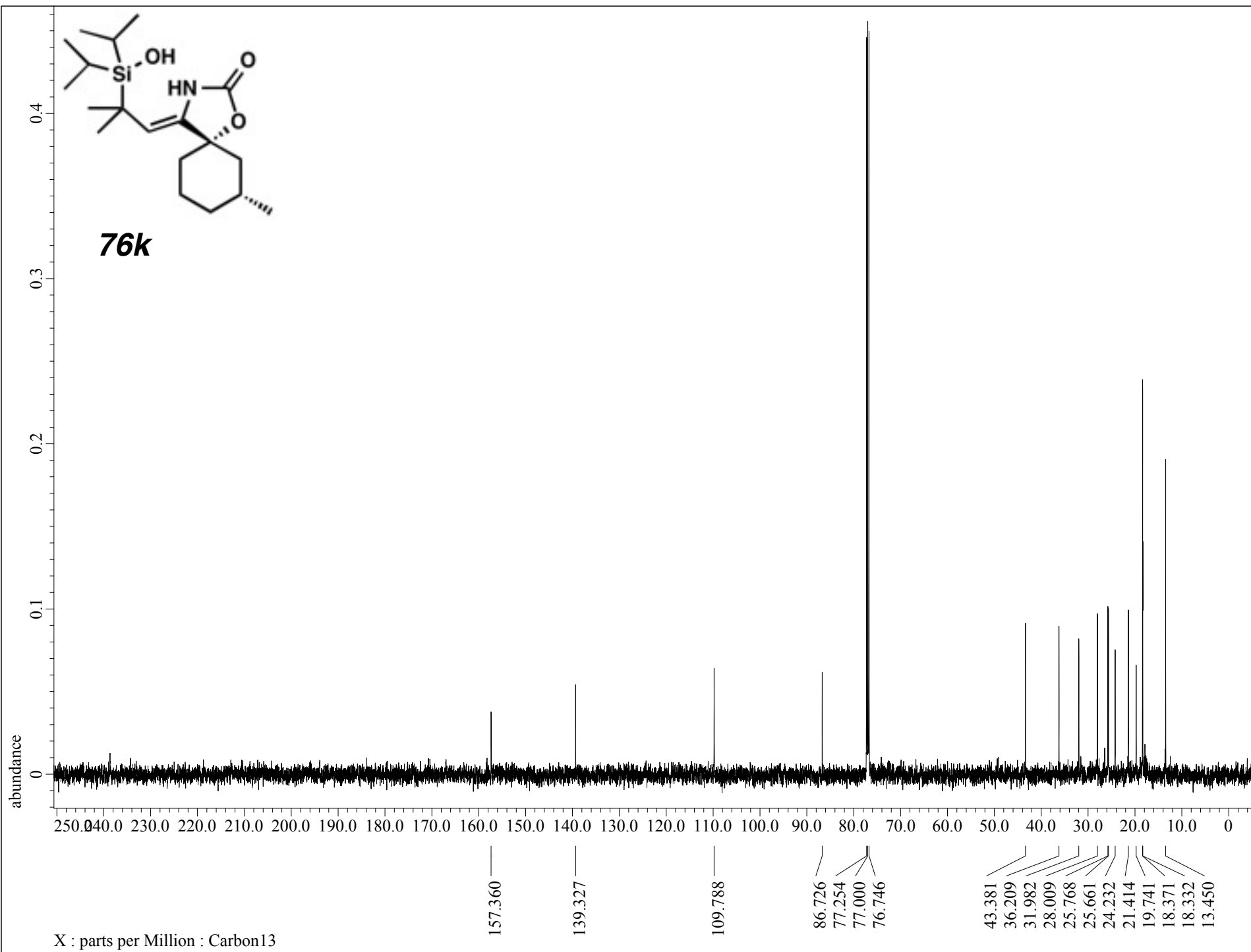




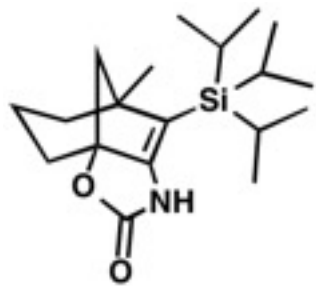




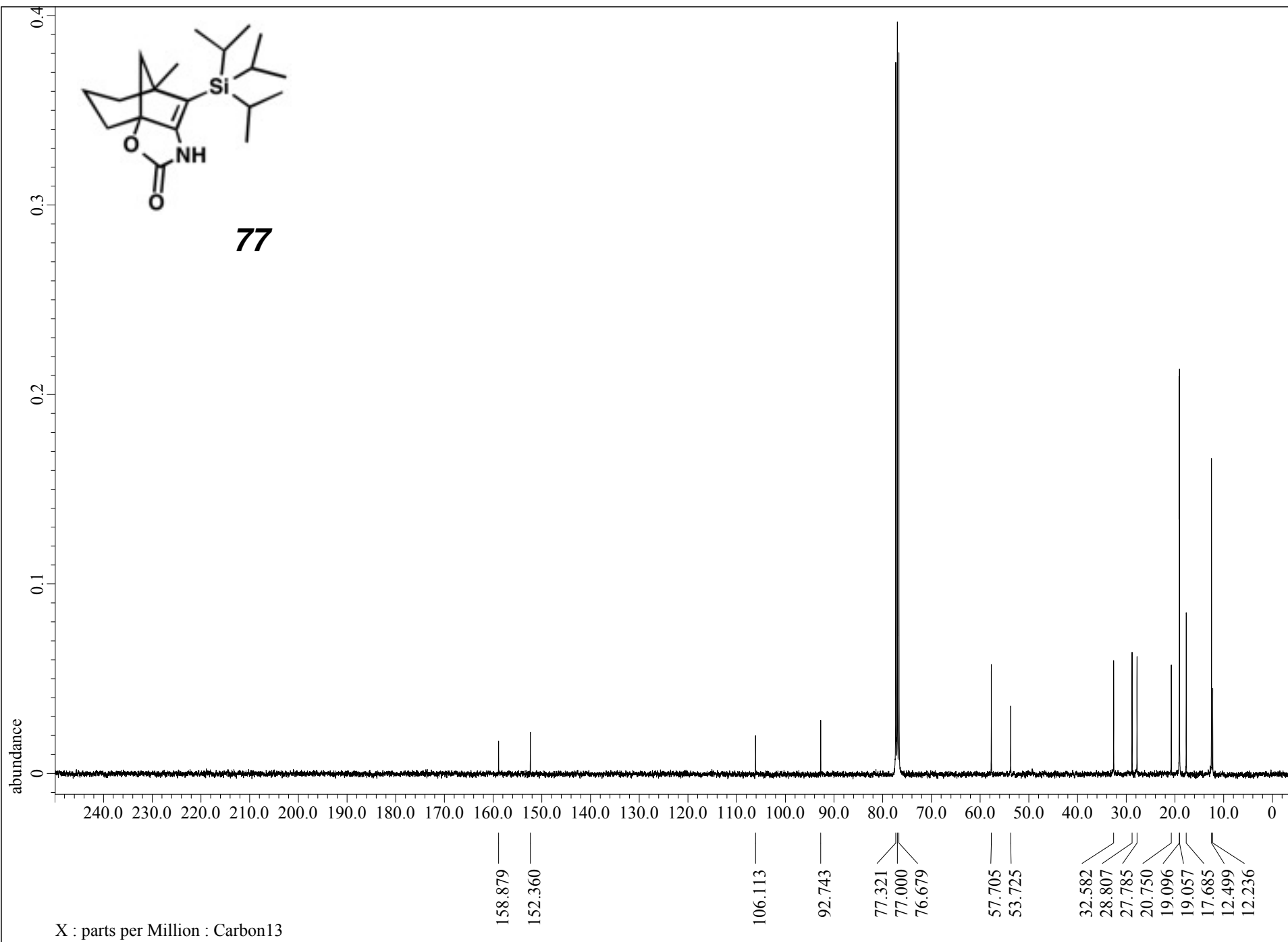
**76k**

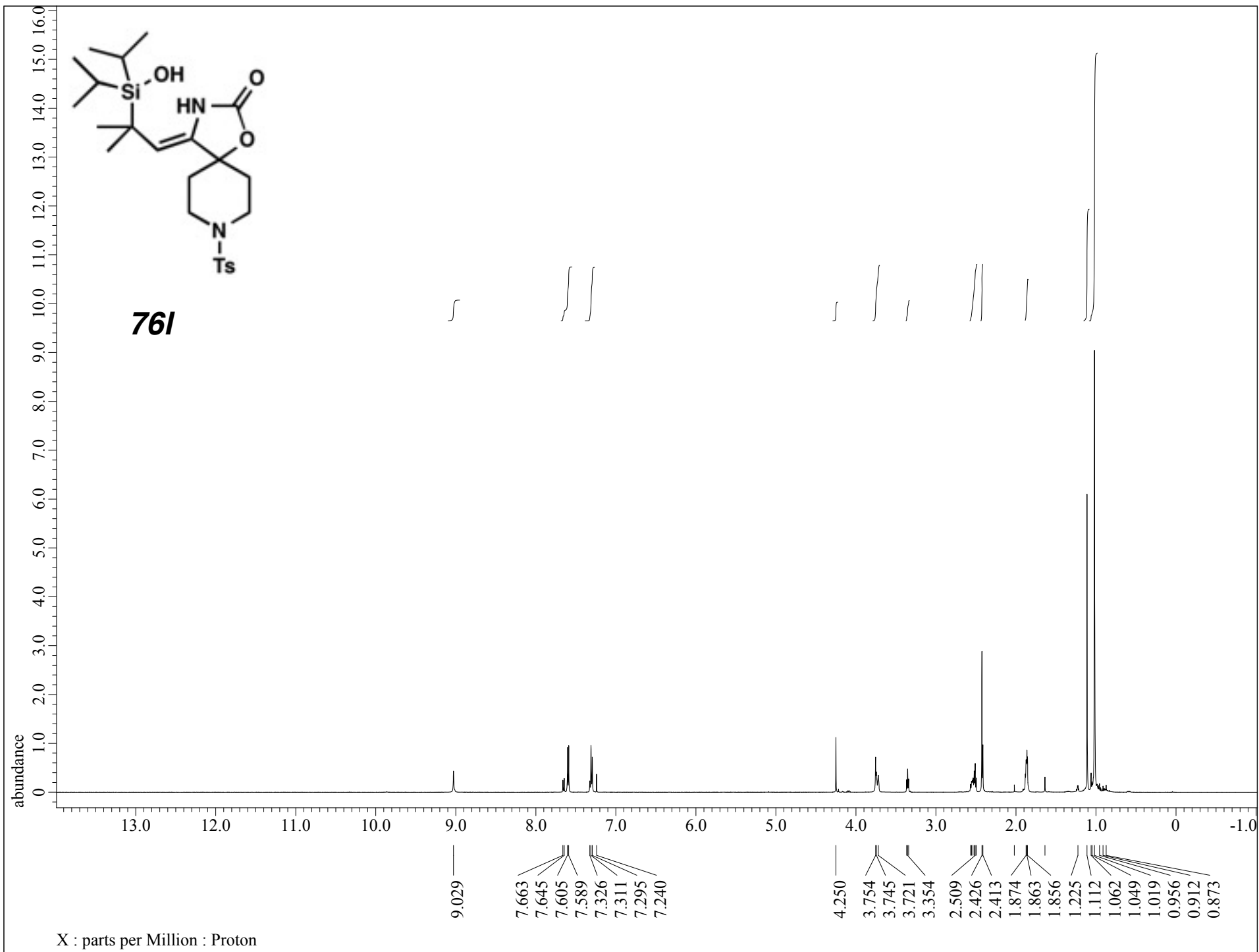


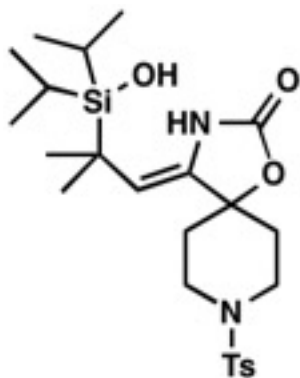




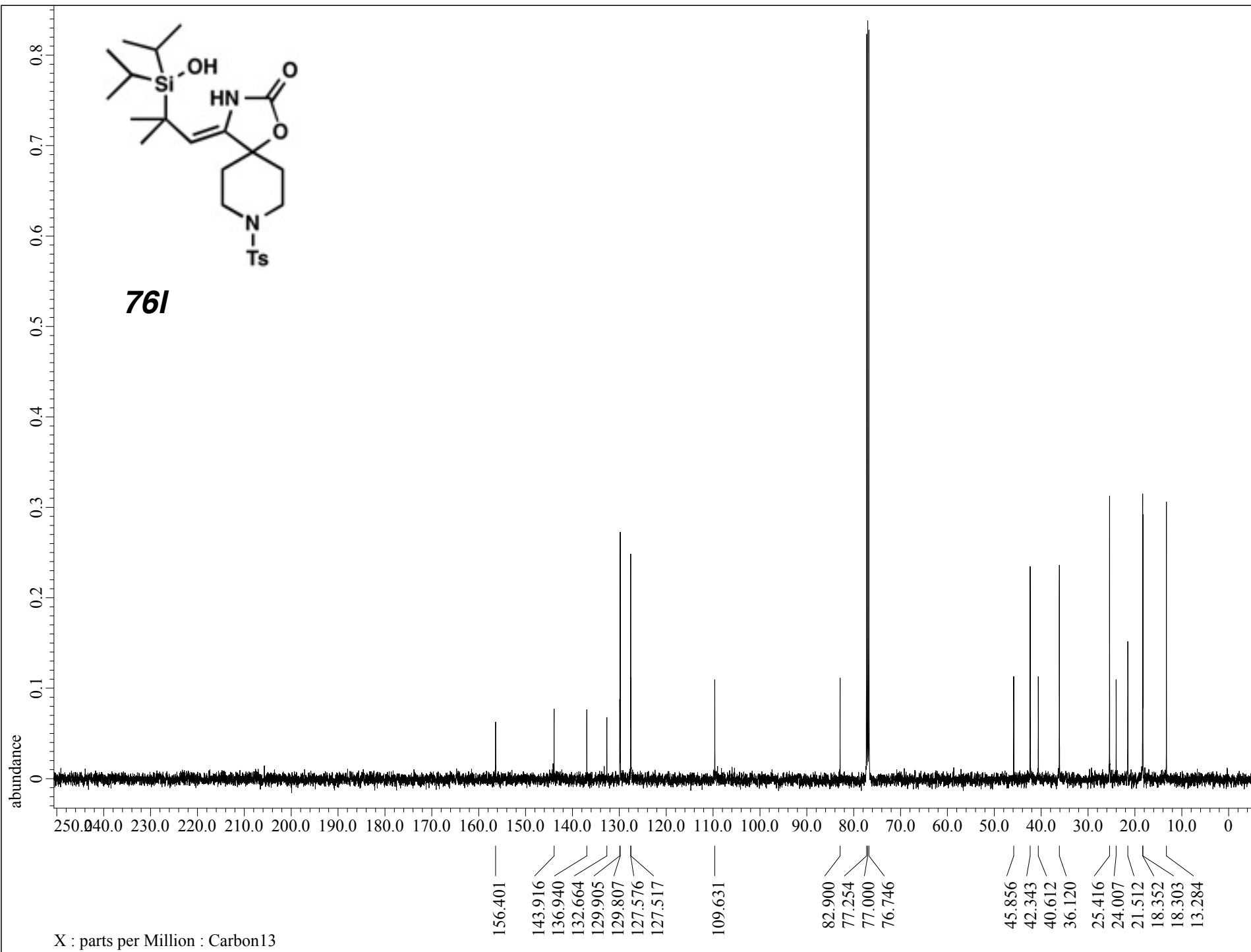
**77**

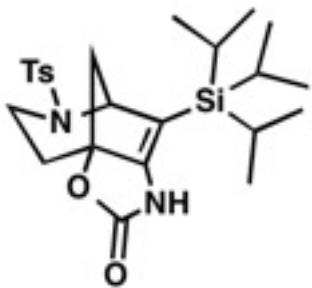




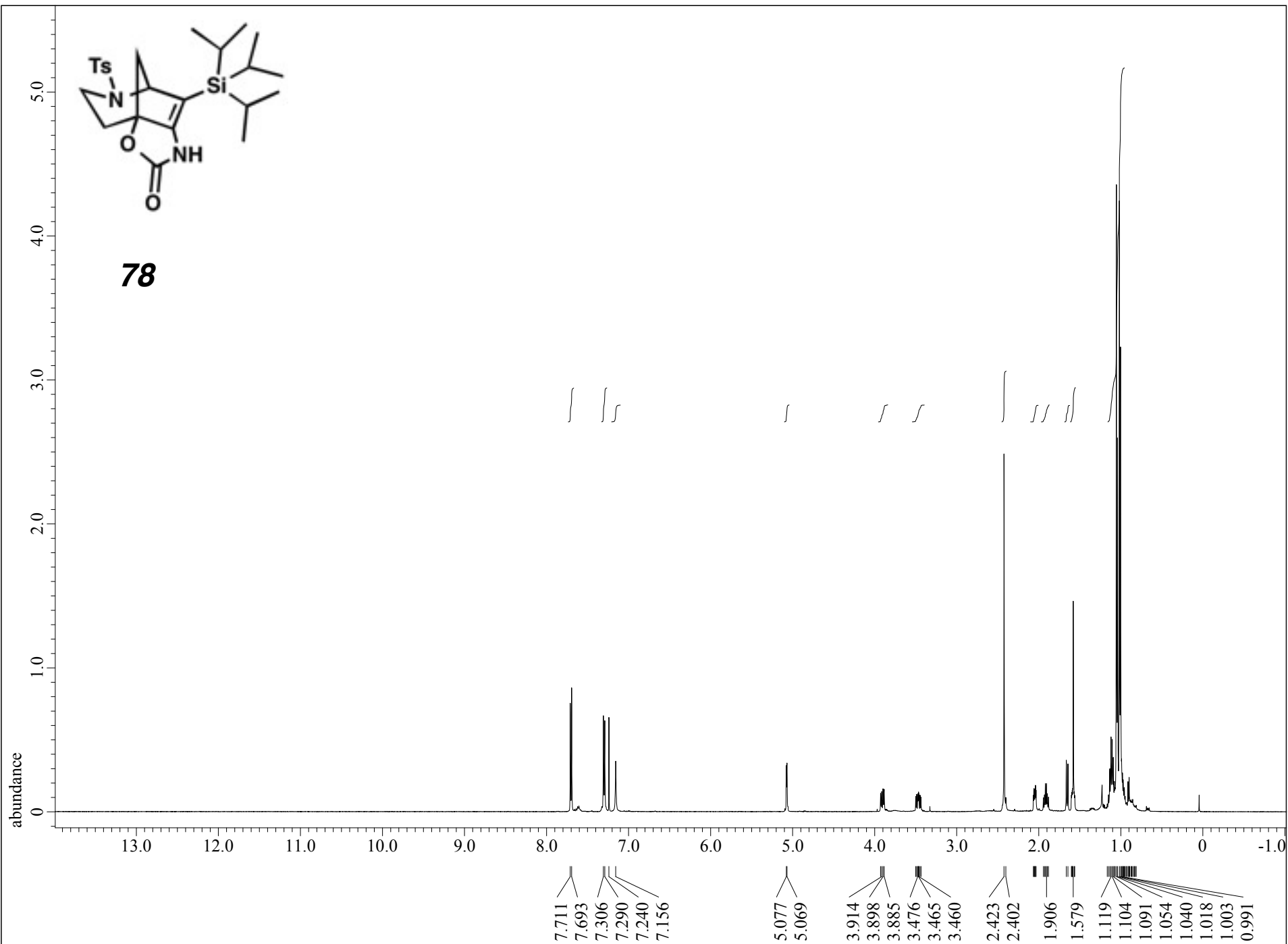


**761**

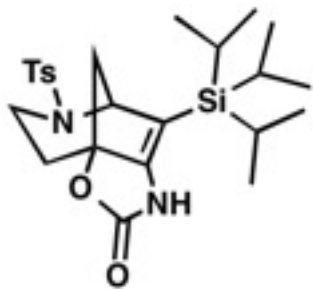




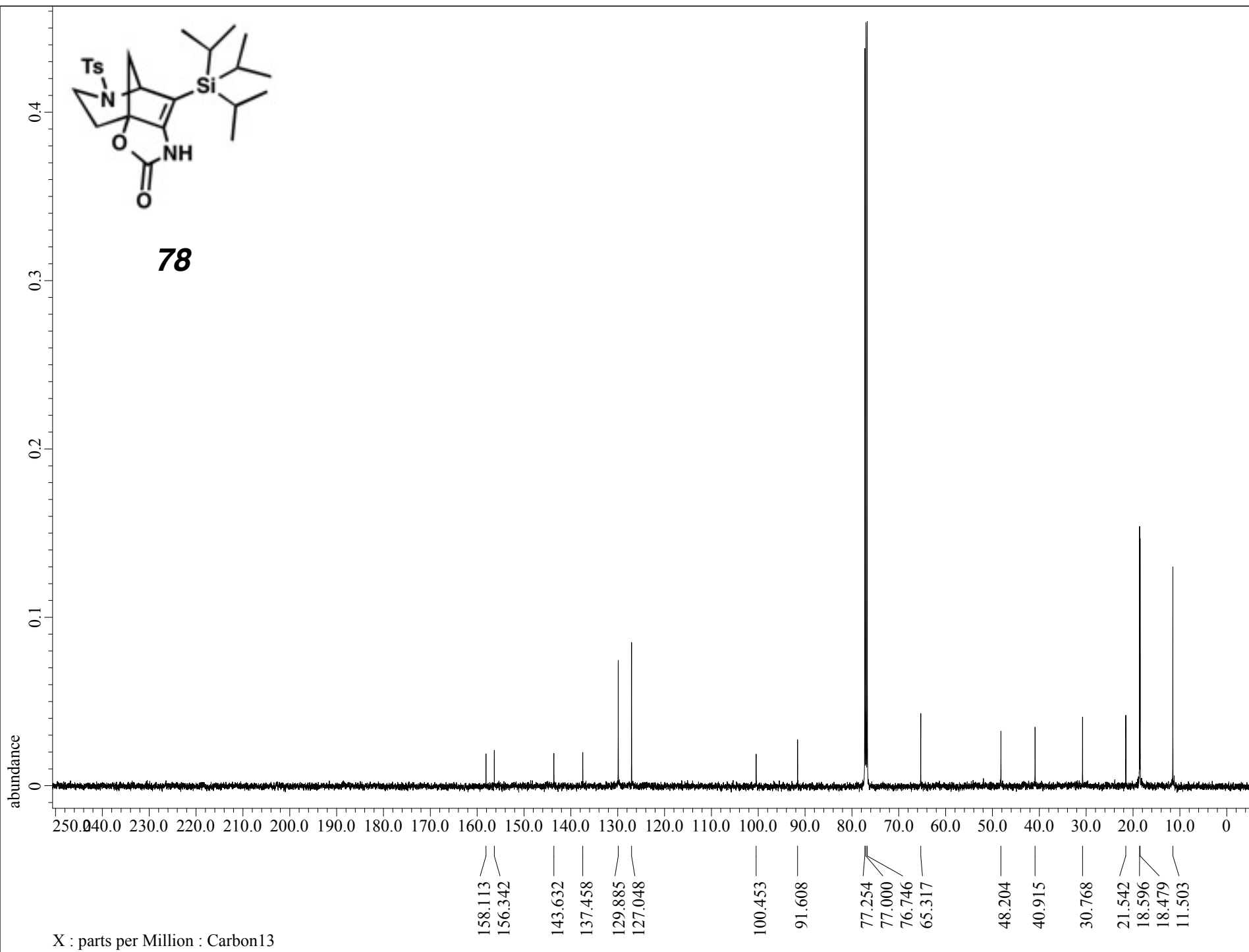
**78**

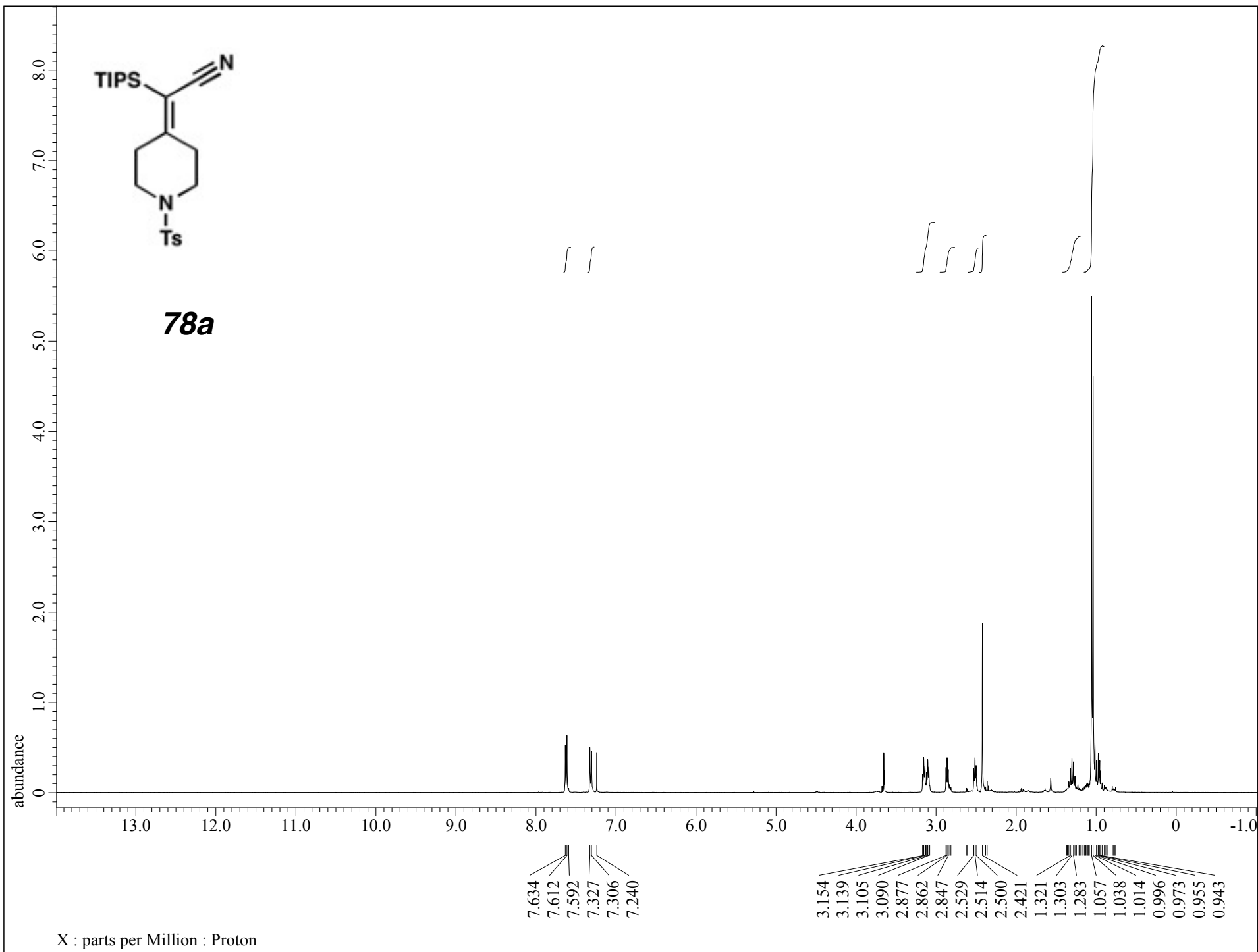


X : parts per Million : Proton

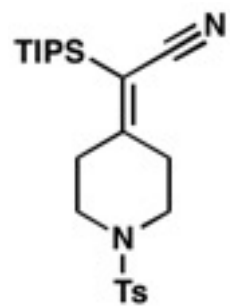


78

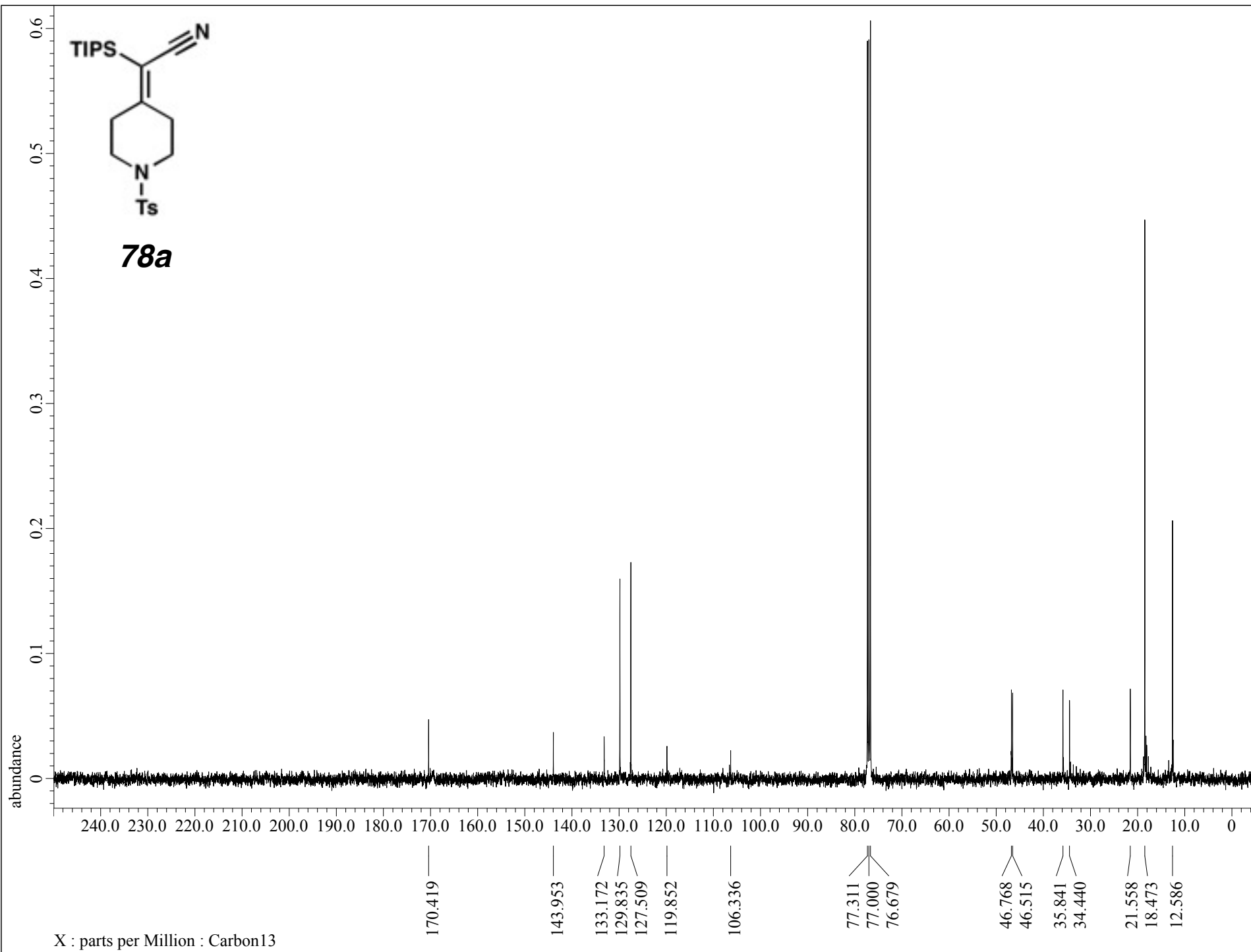


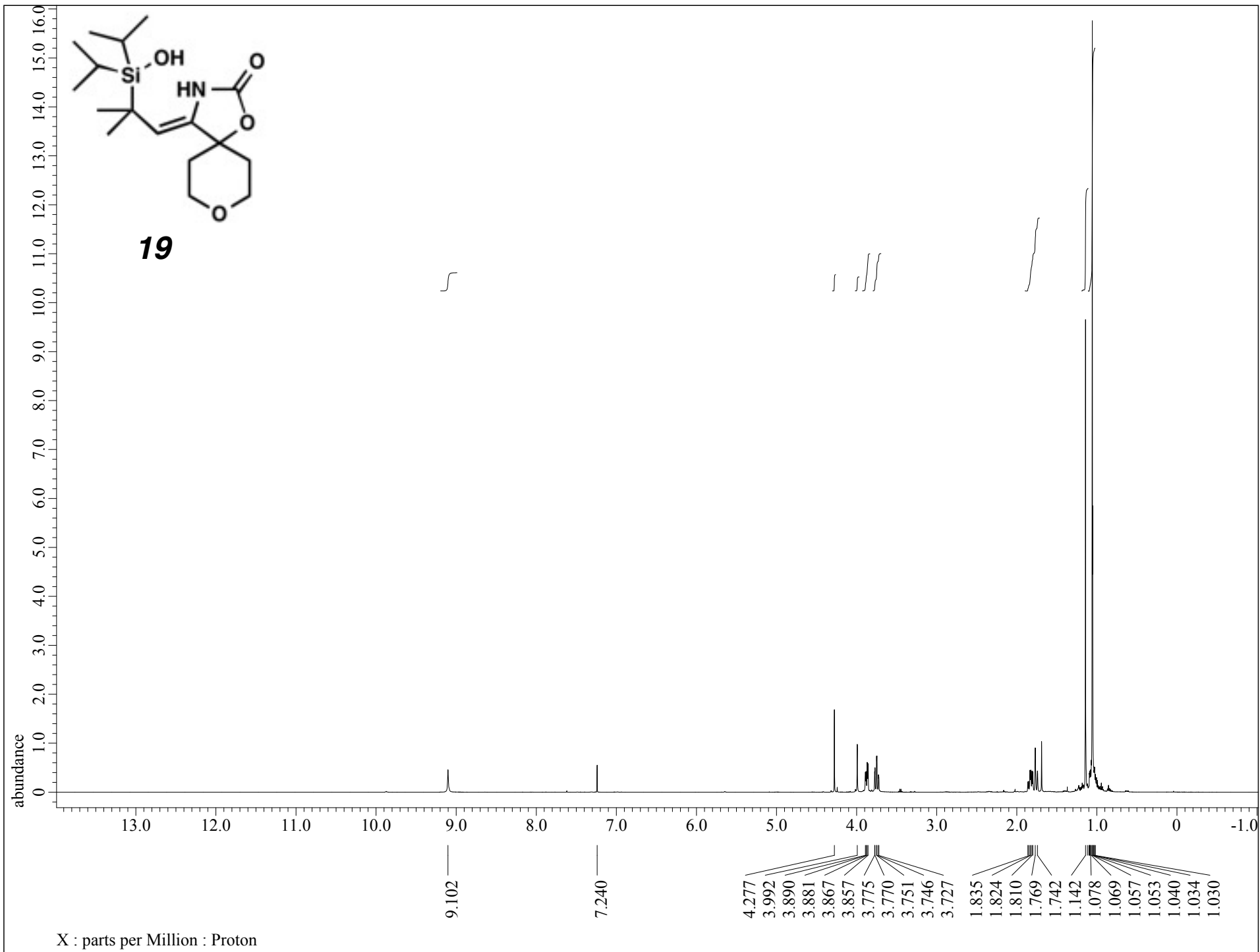


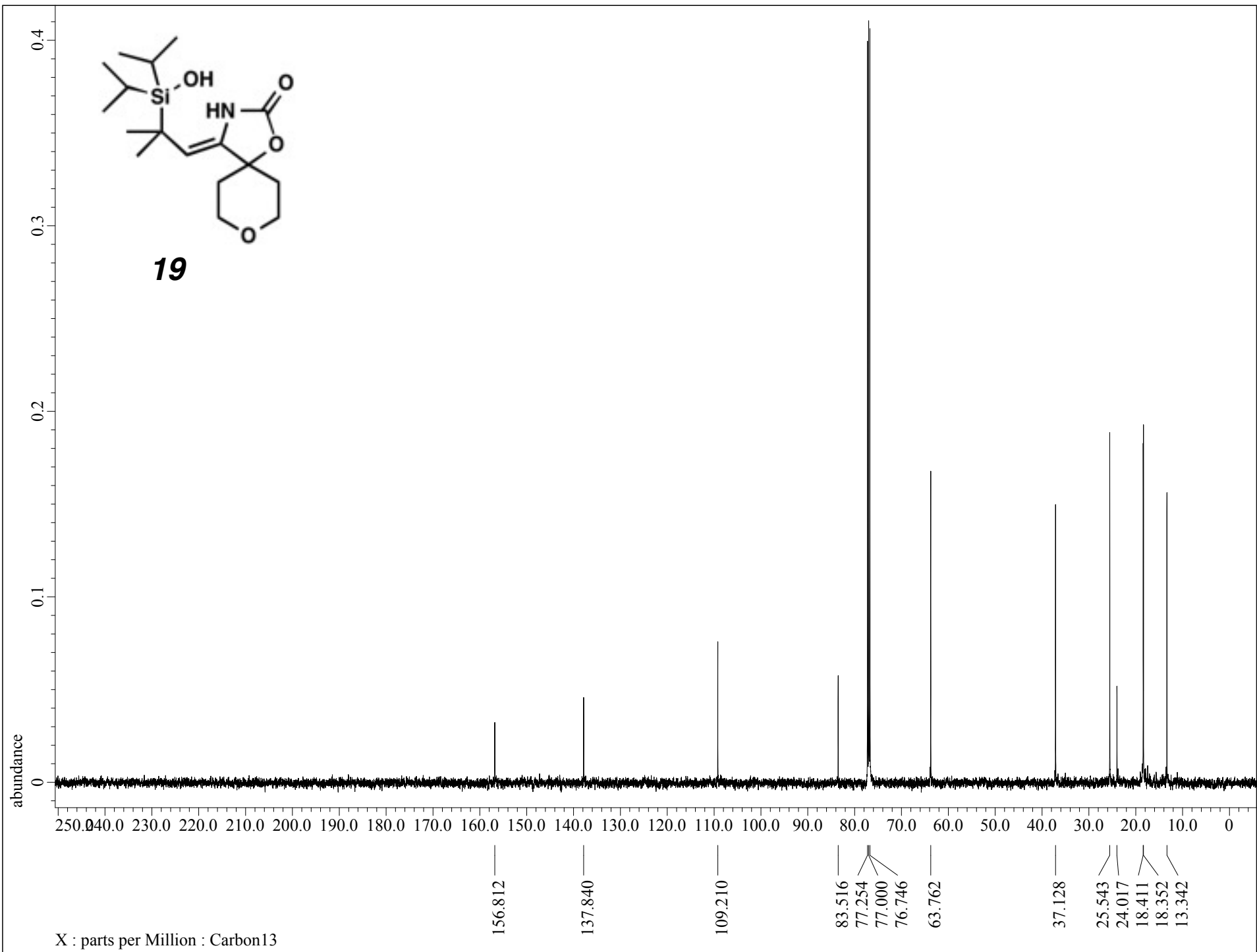


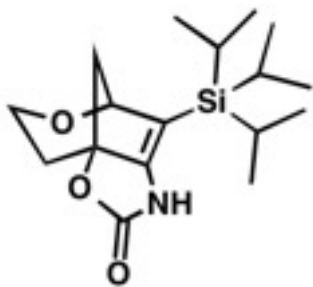


**78a**

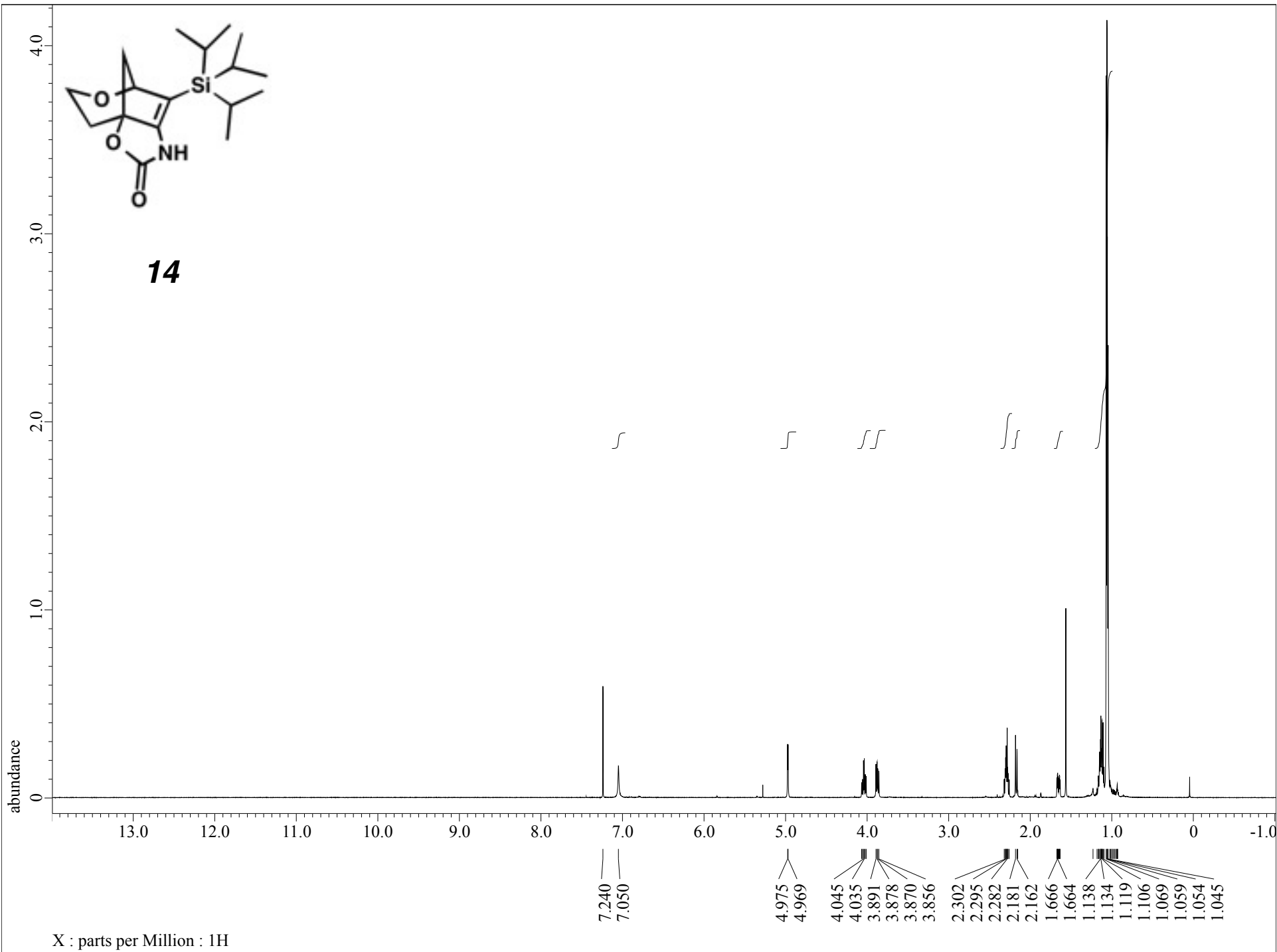


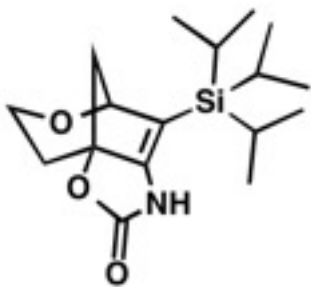




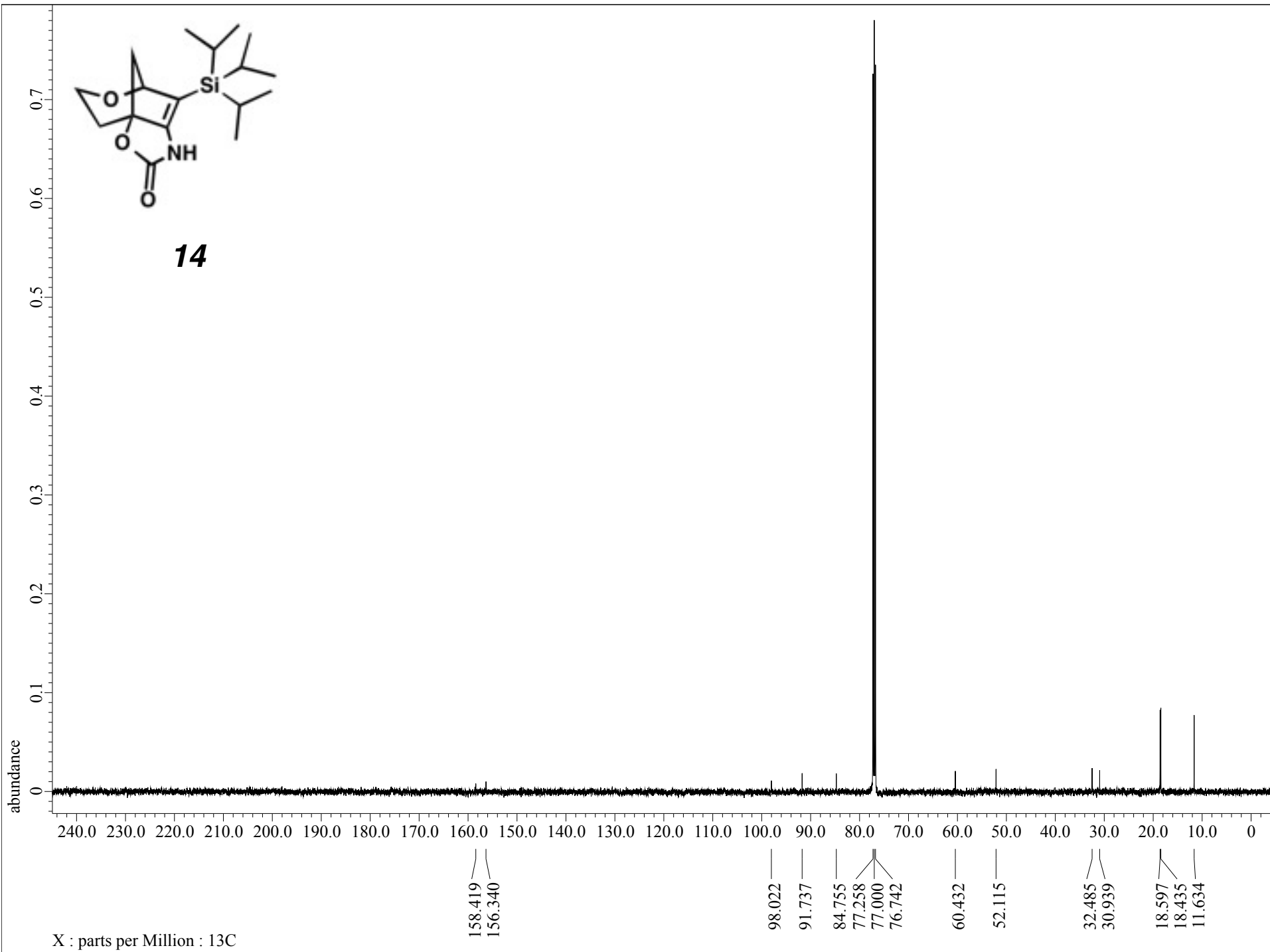


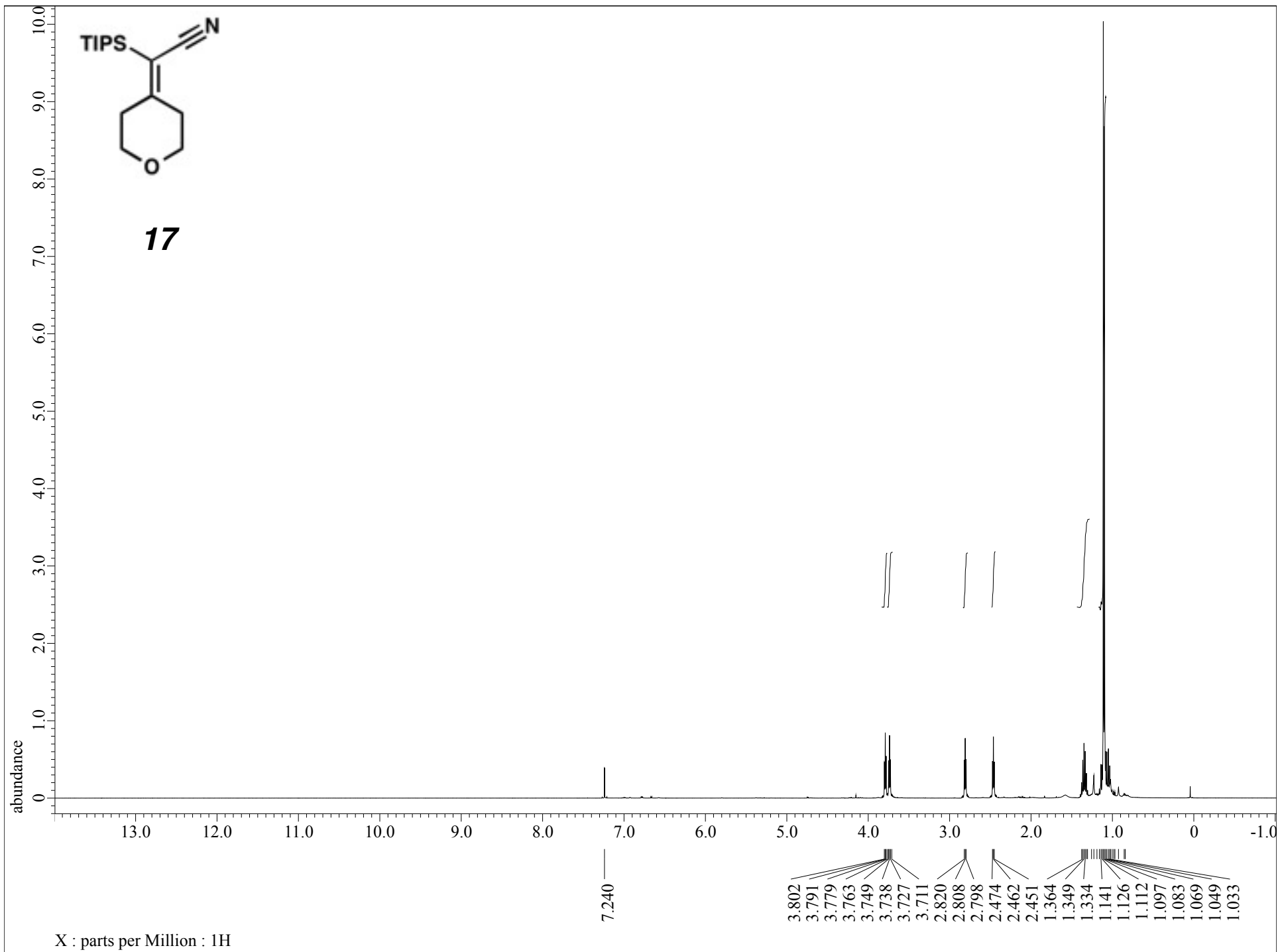
**14**

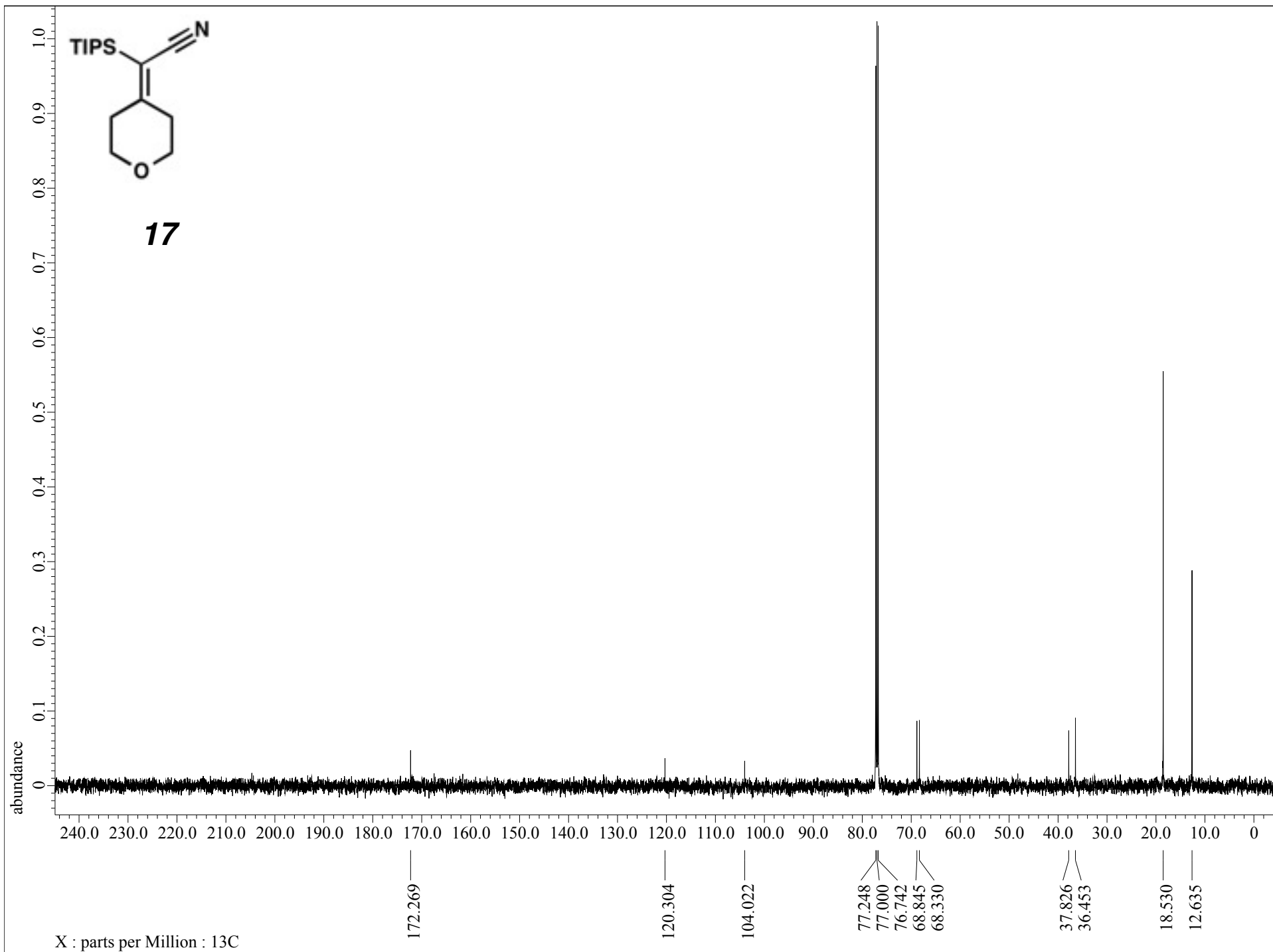


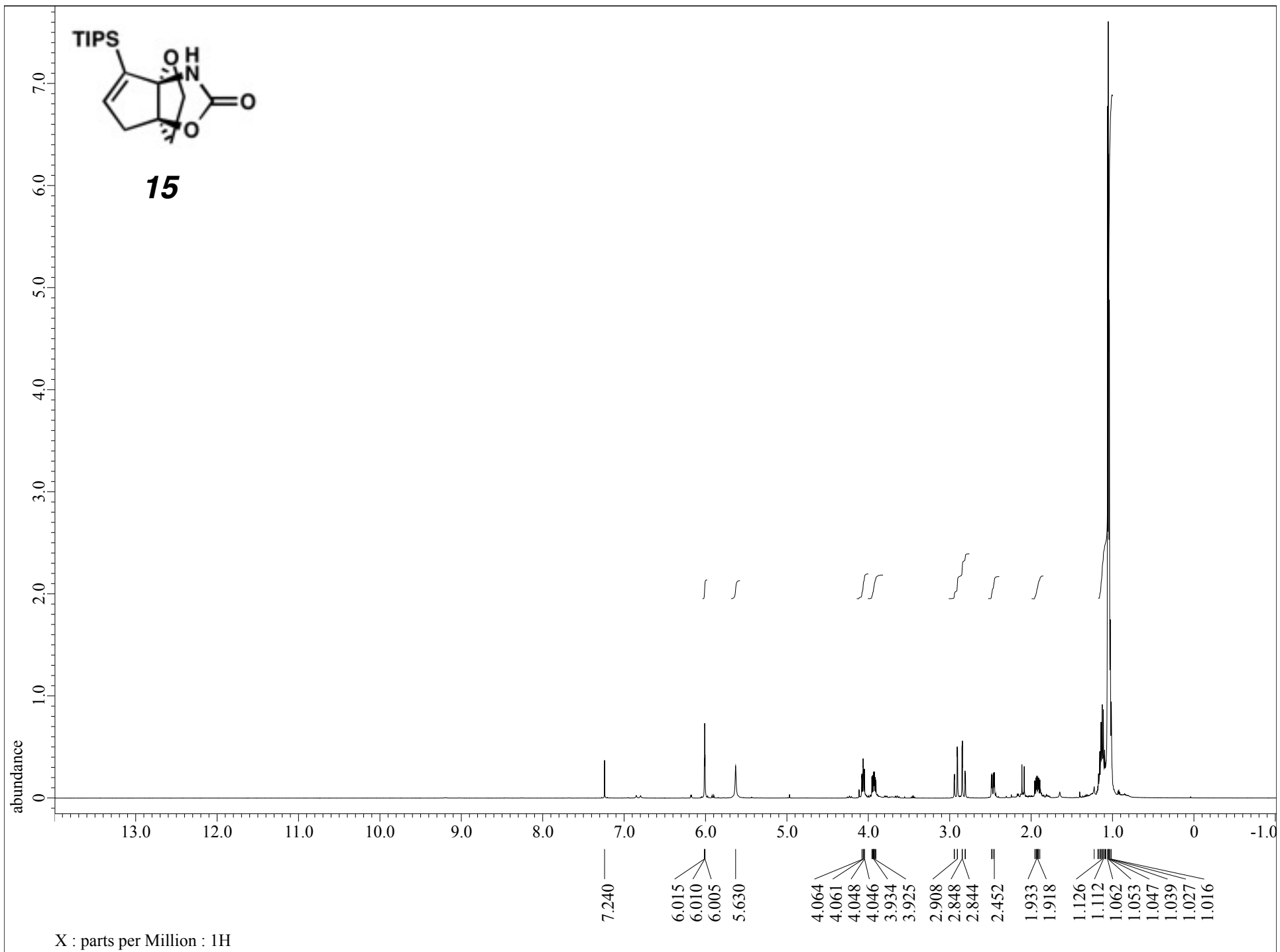


**14**

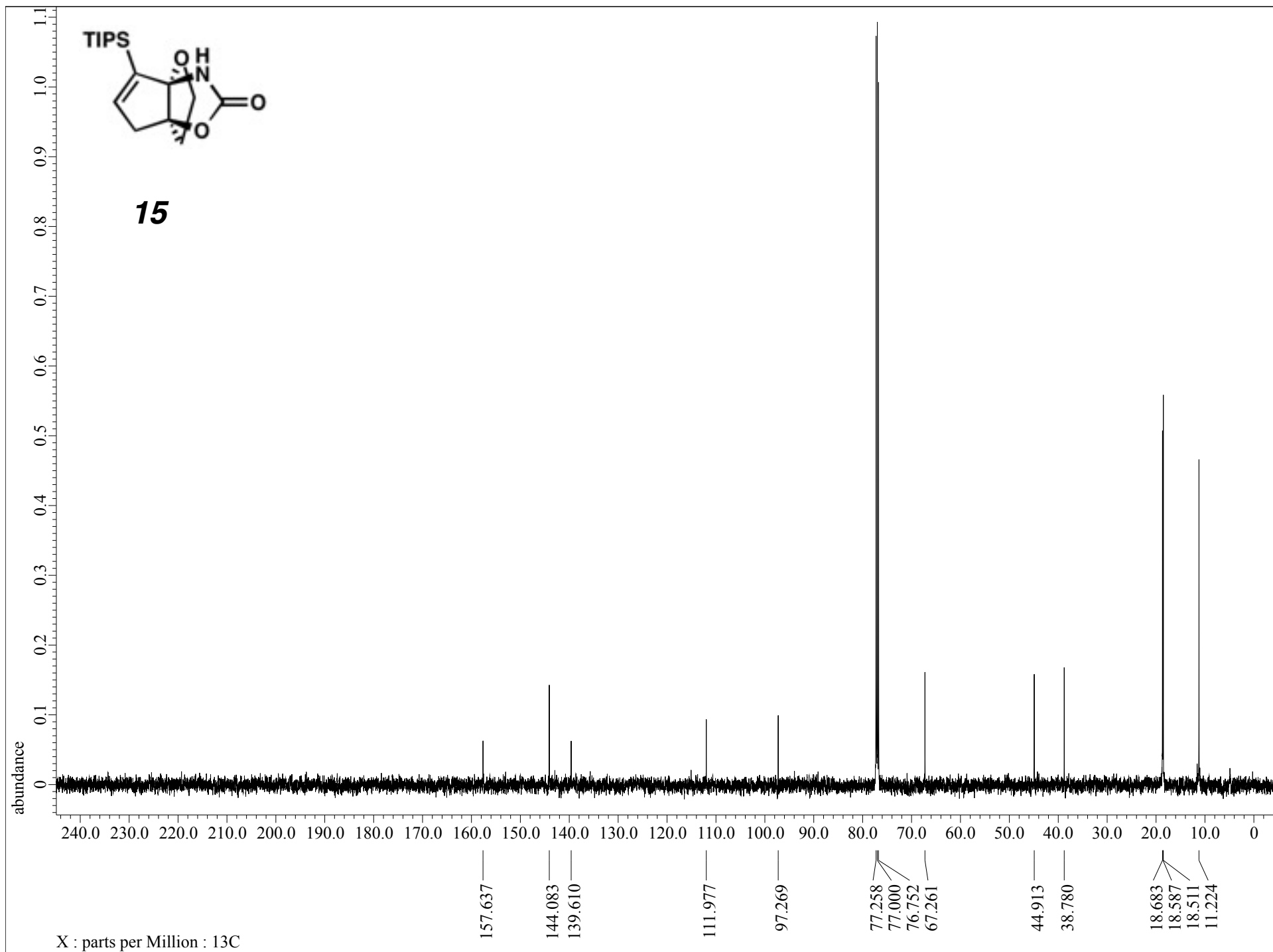


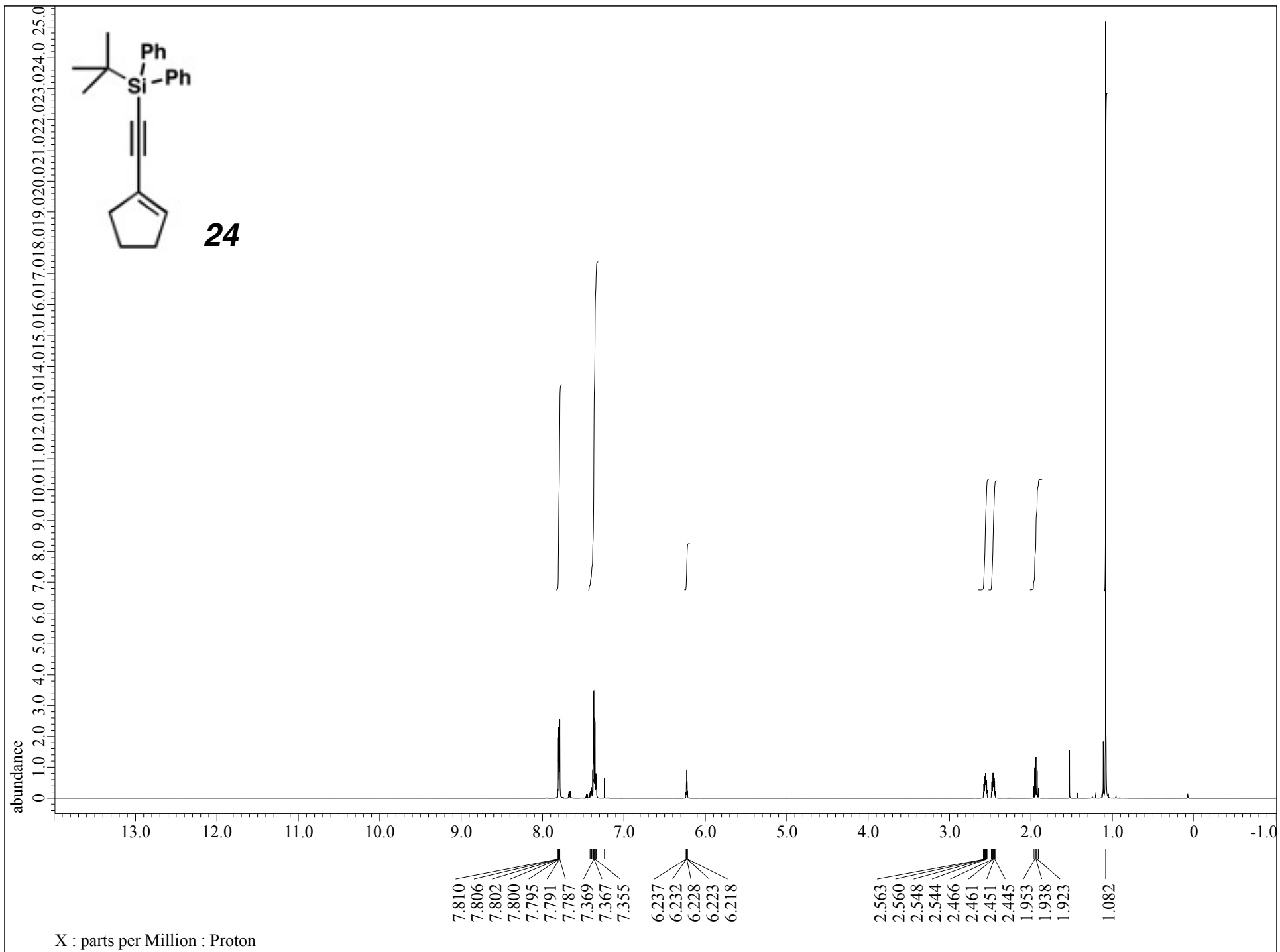


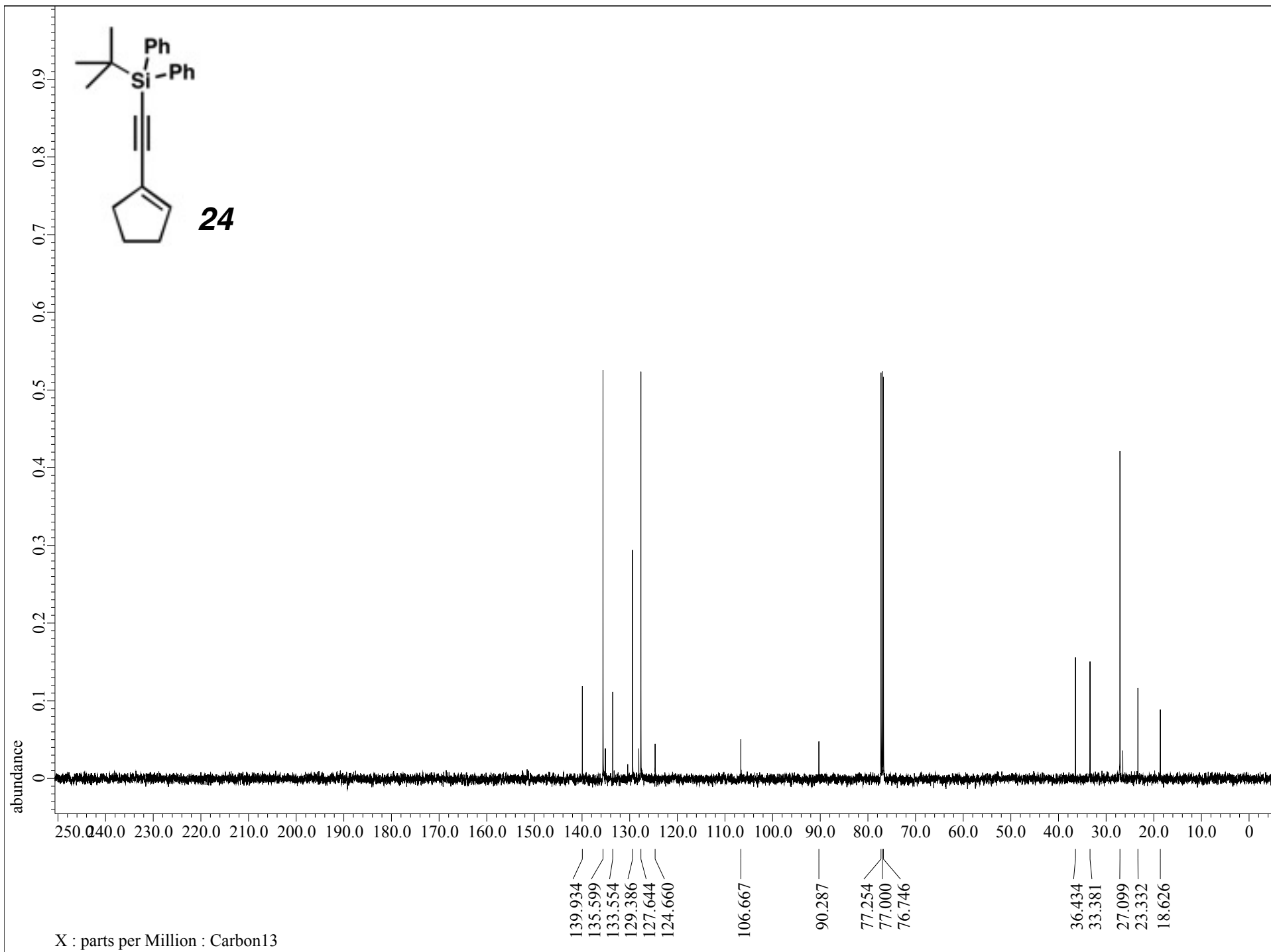


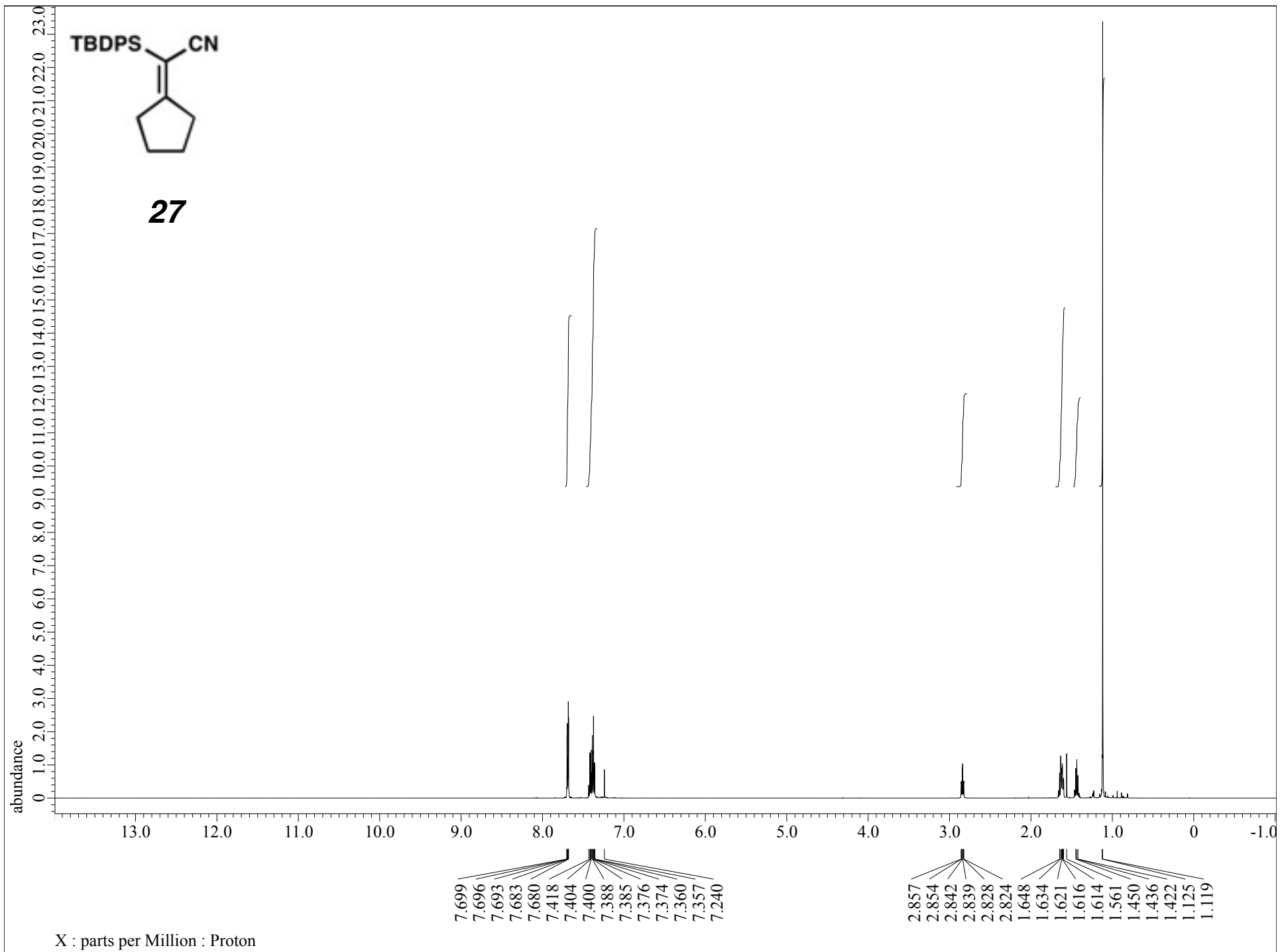




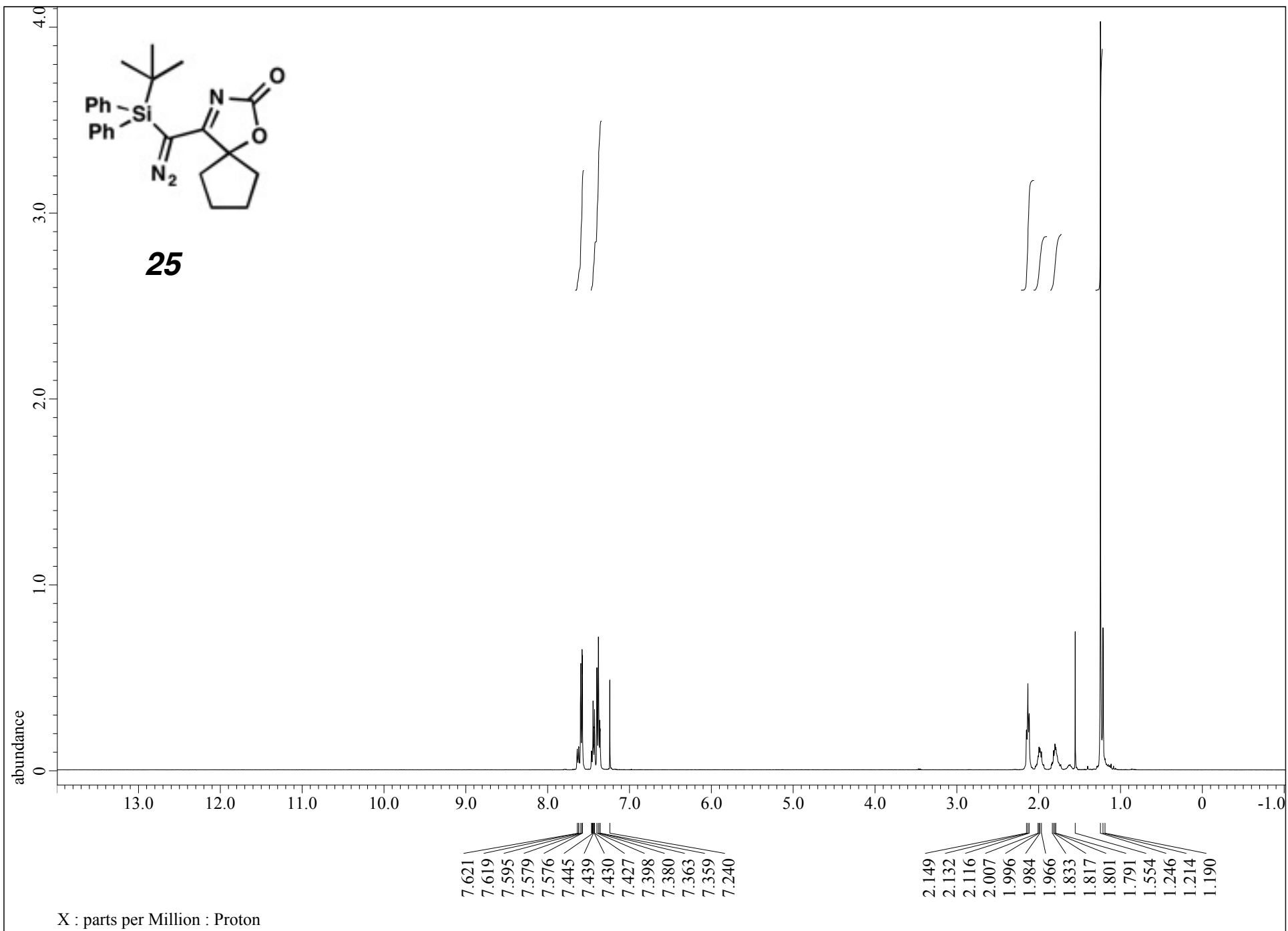


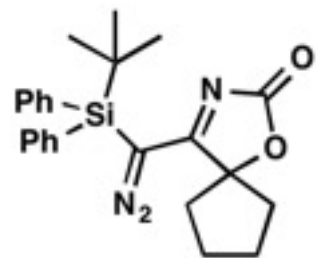




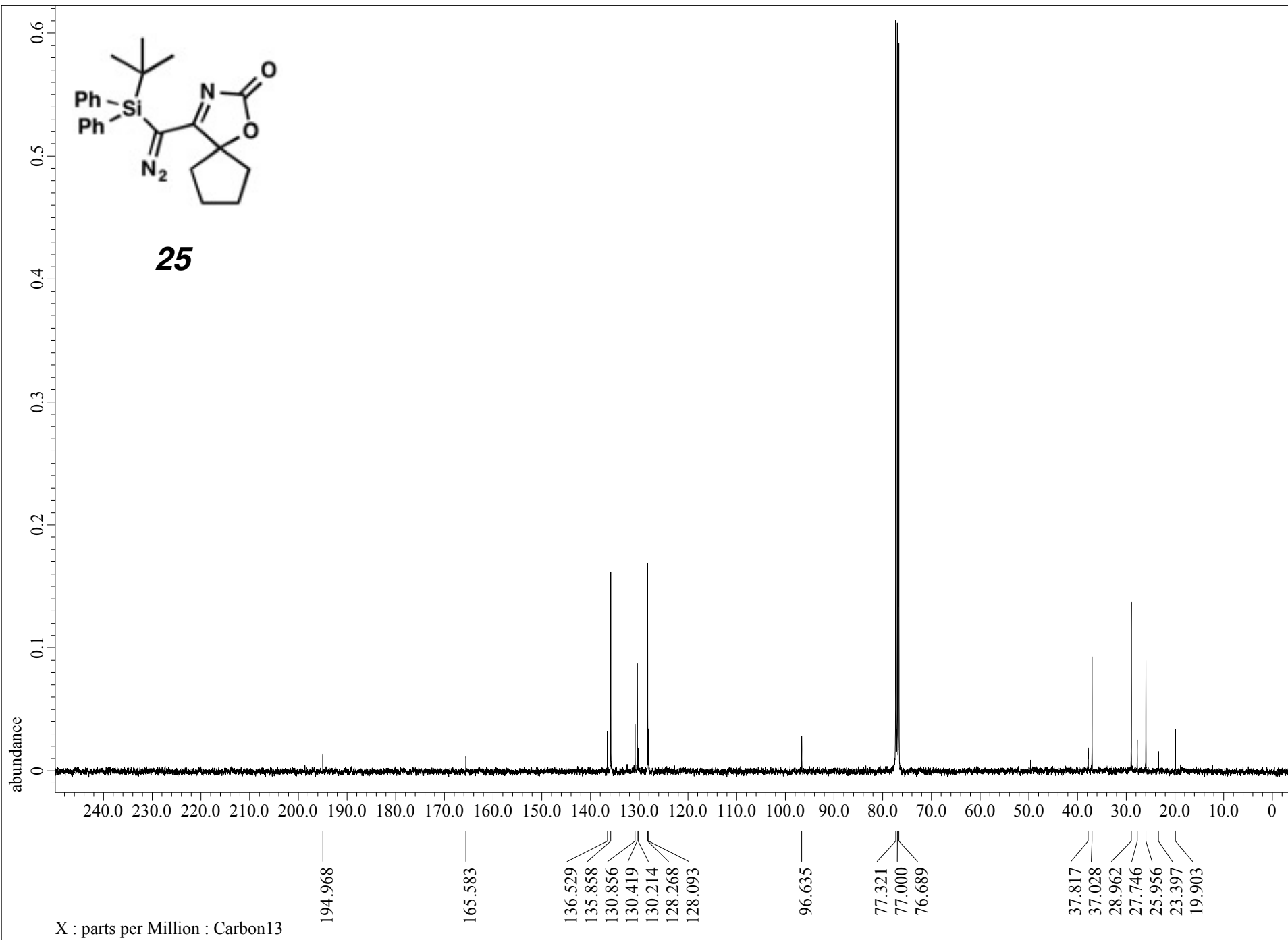


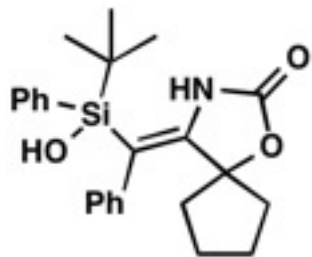




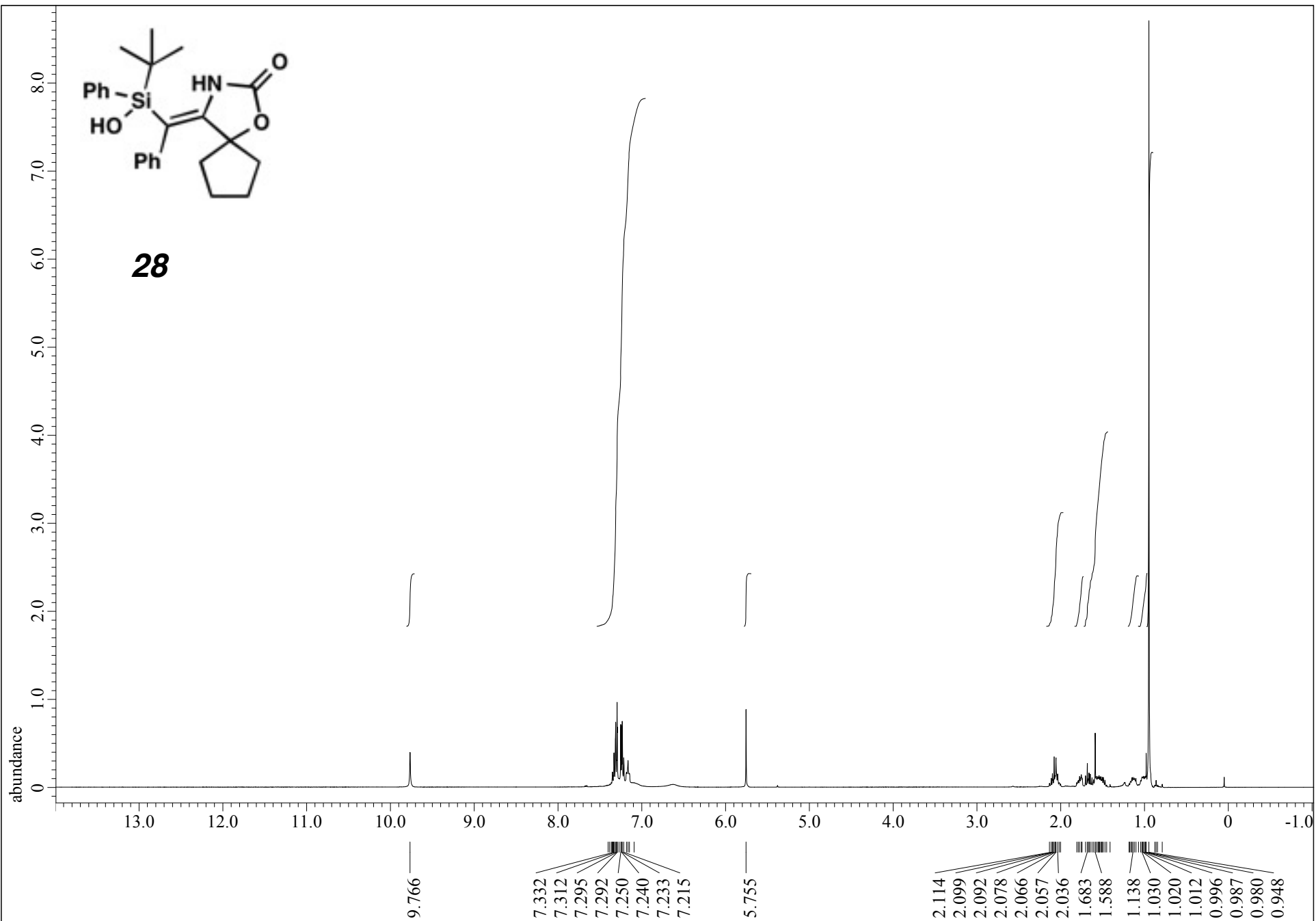


**25**



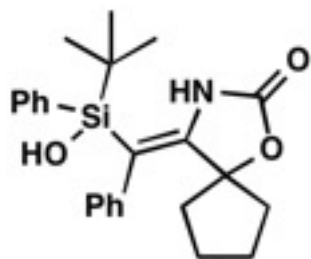


**28**

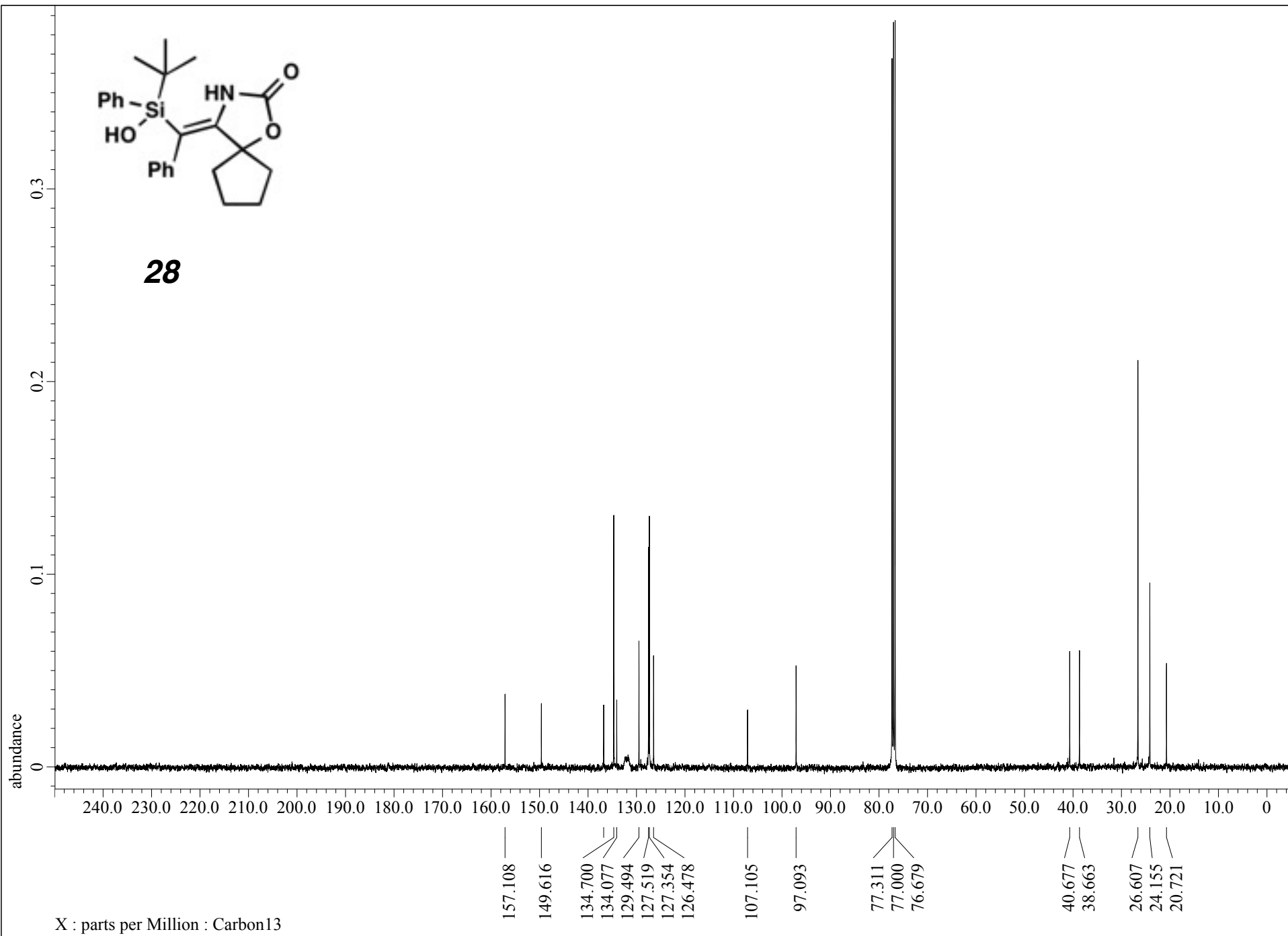


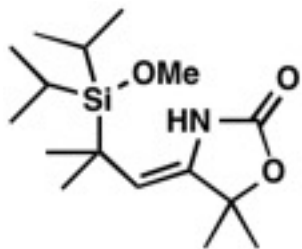
X : parts per Million : Proton



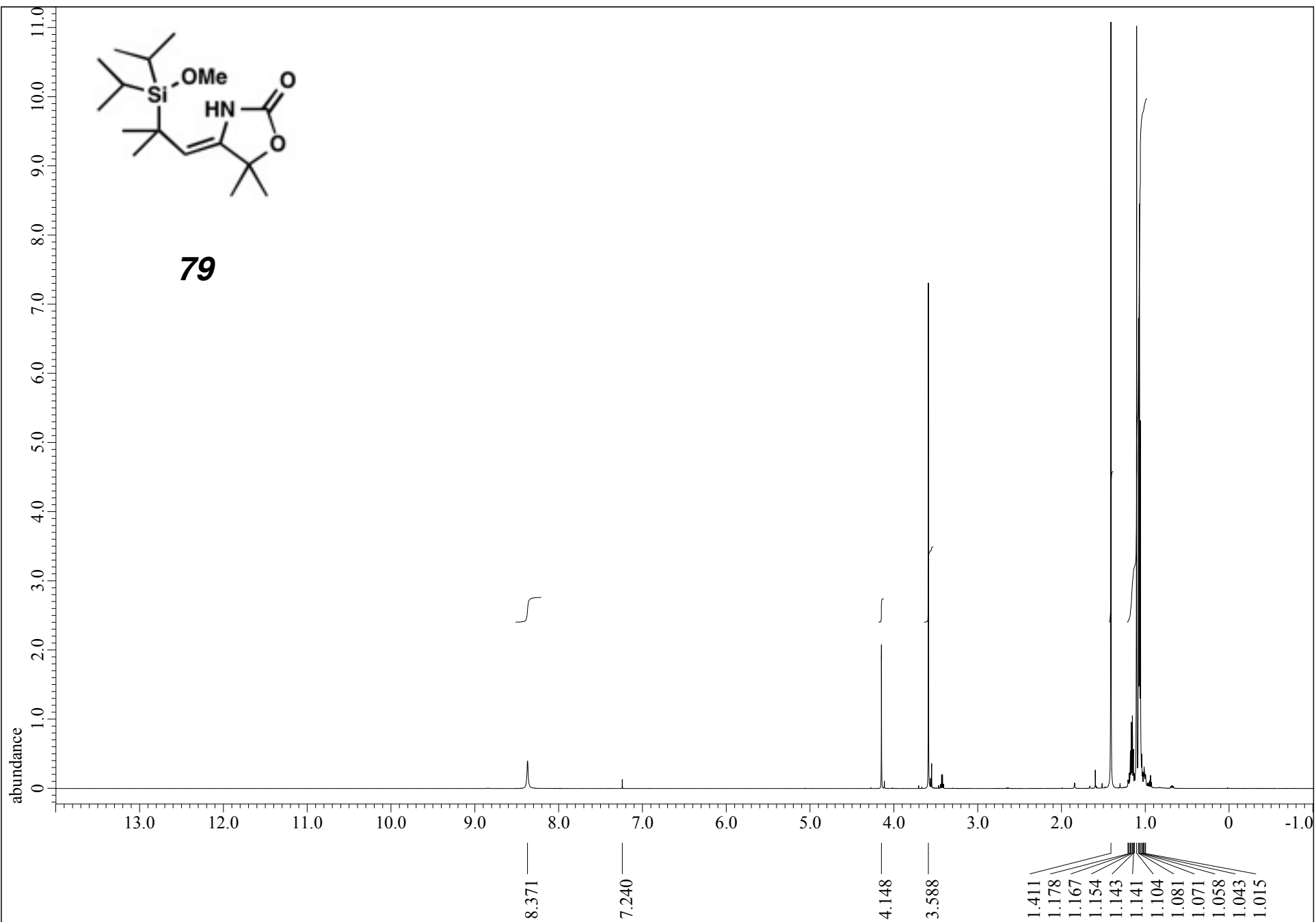


**28**





**79**

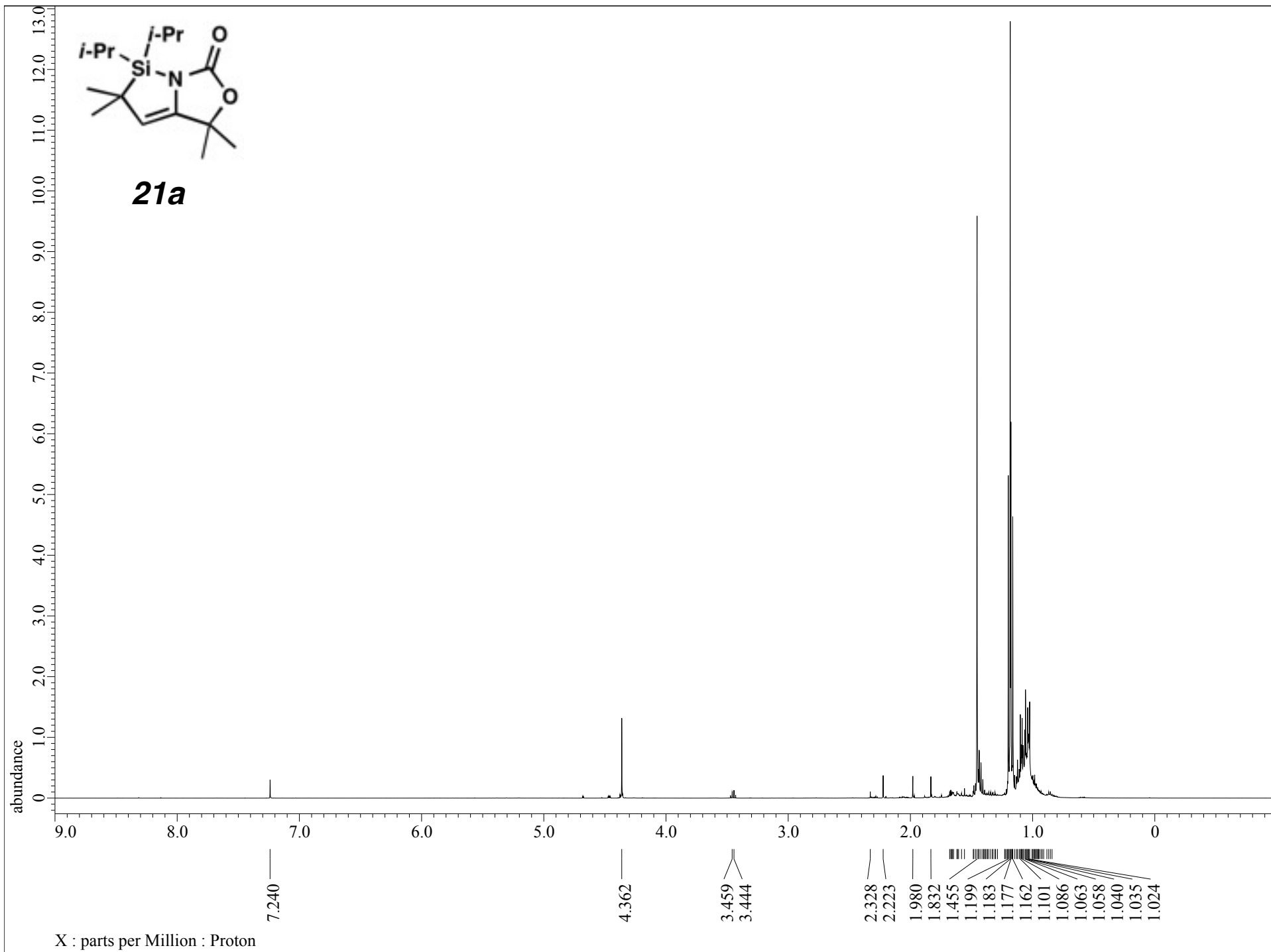




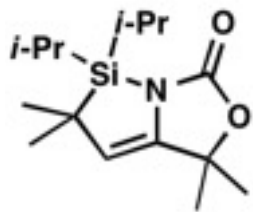




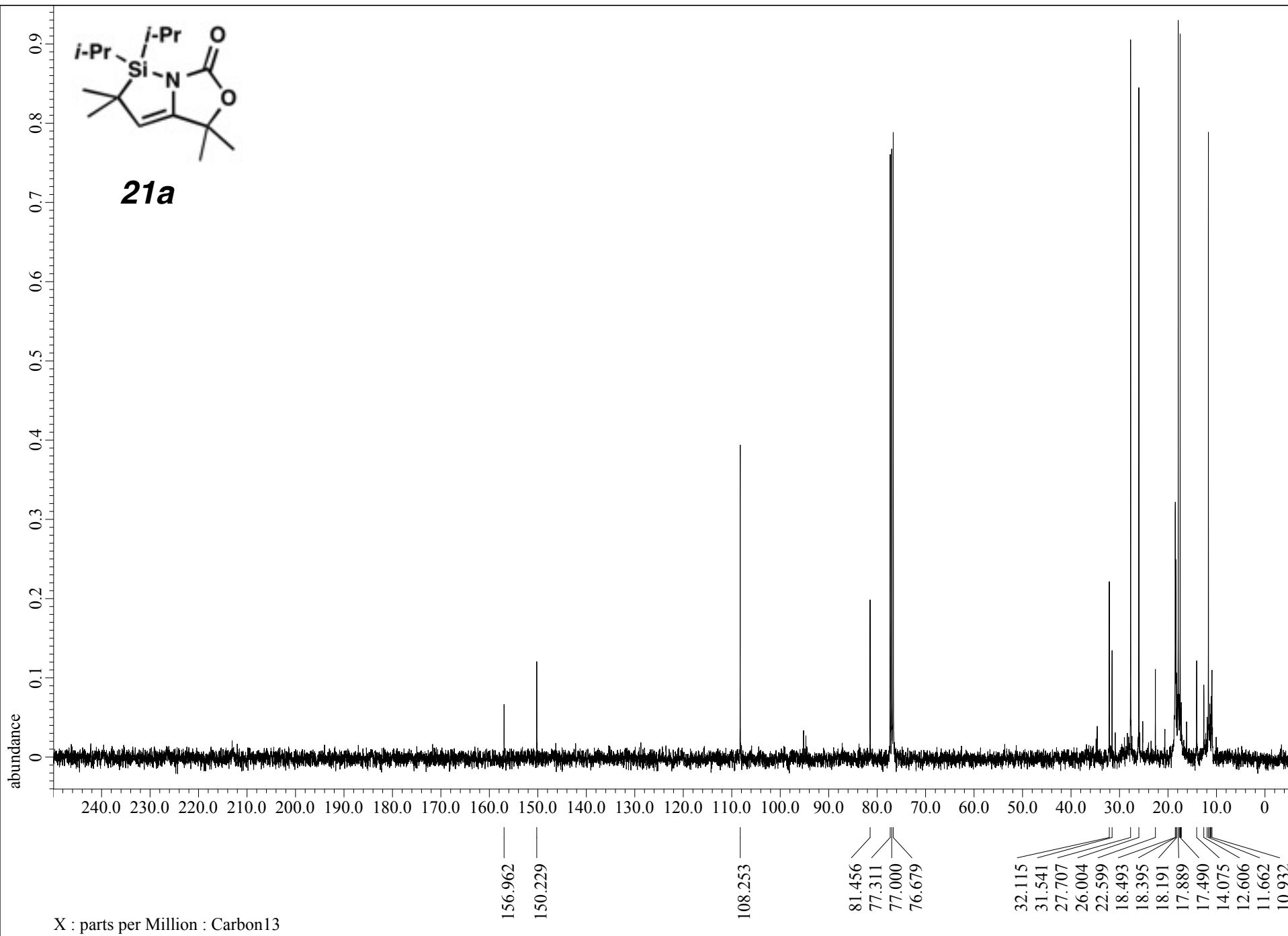




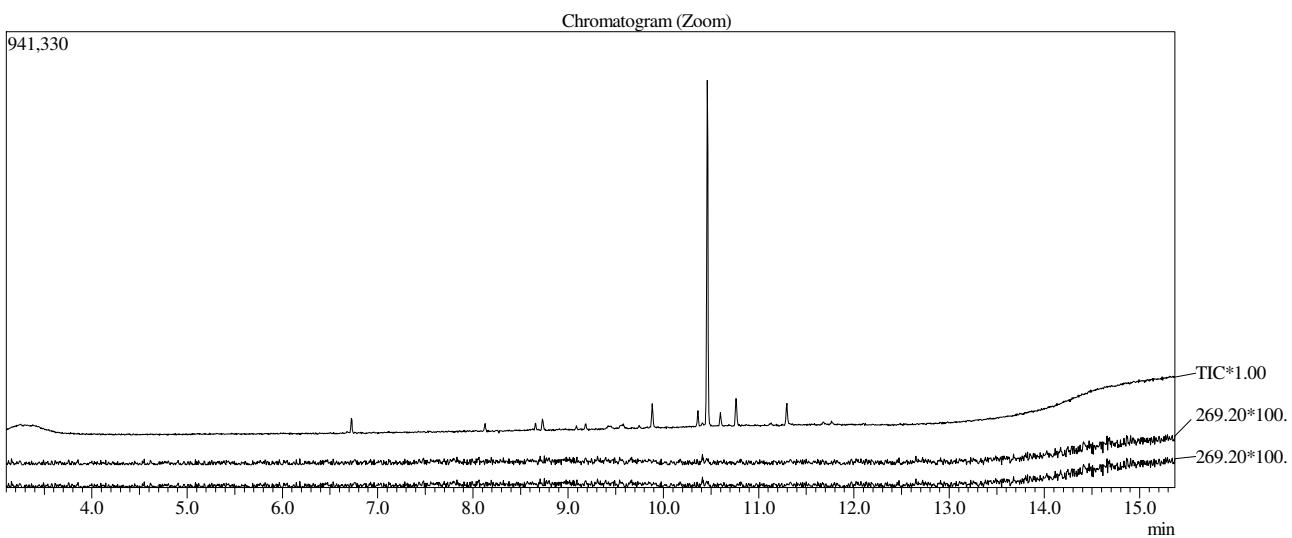
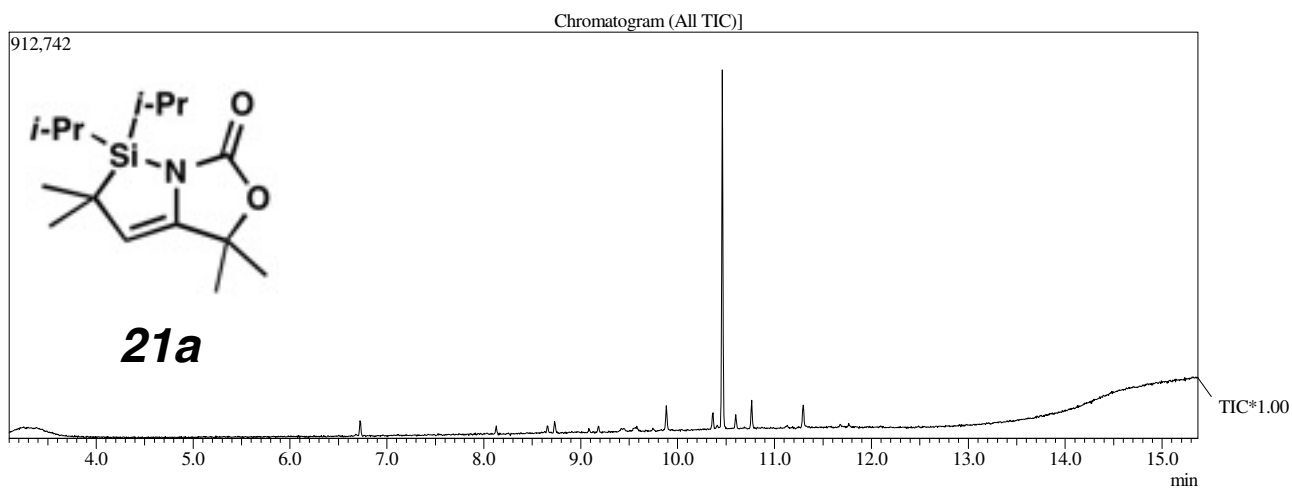
SI-200



**21a**

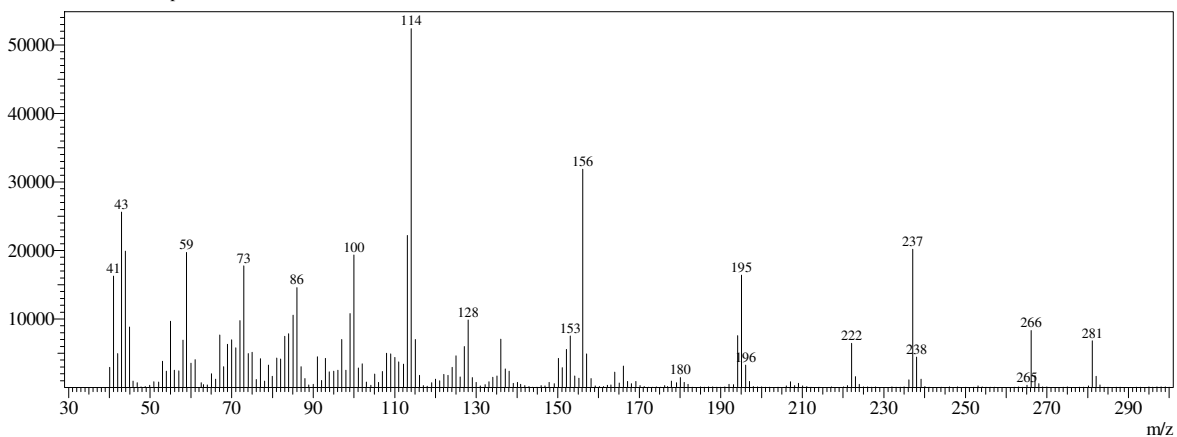


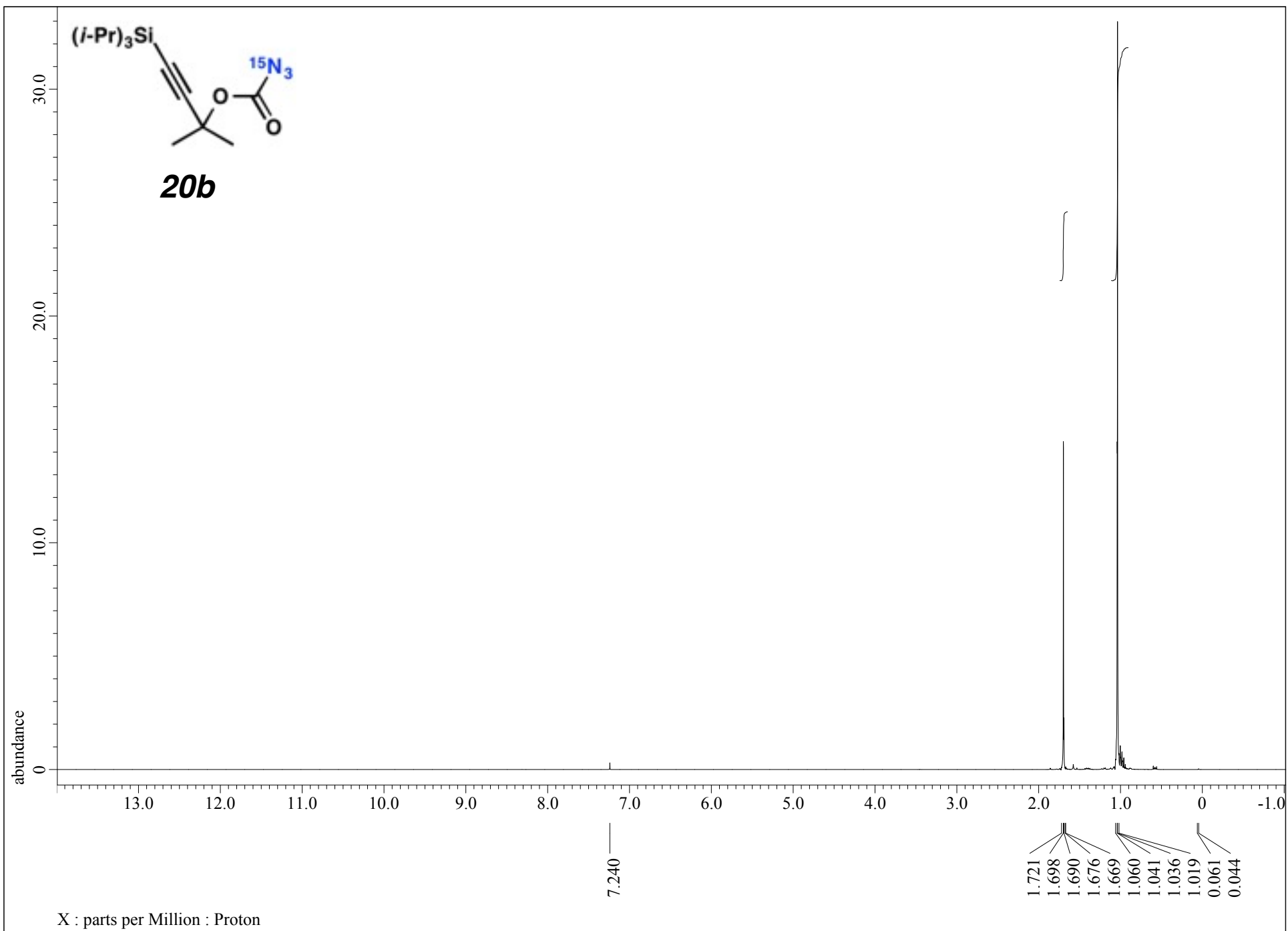


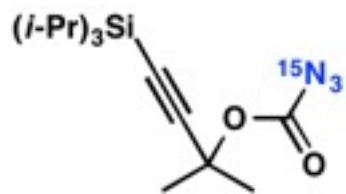


Spectrum

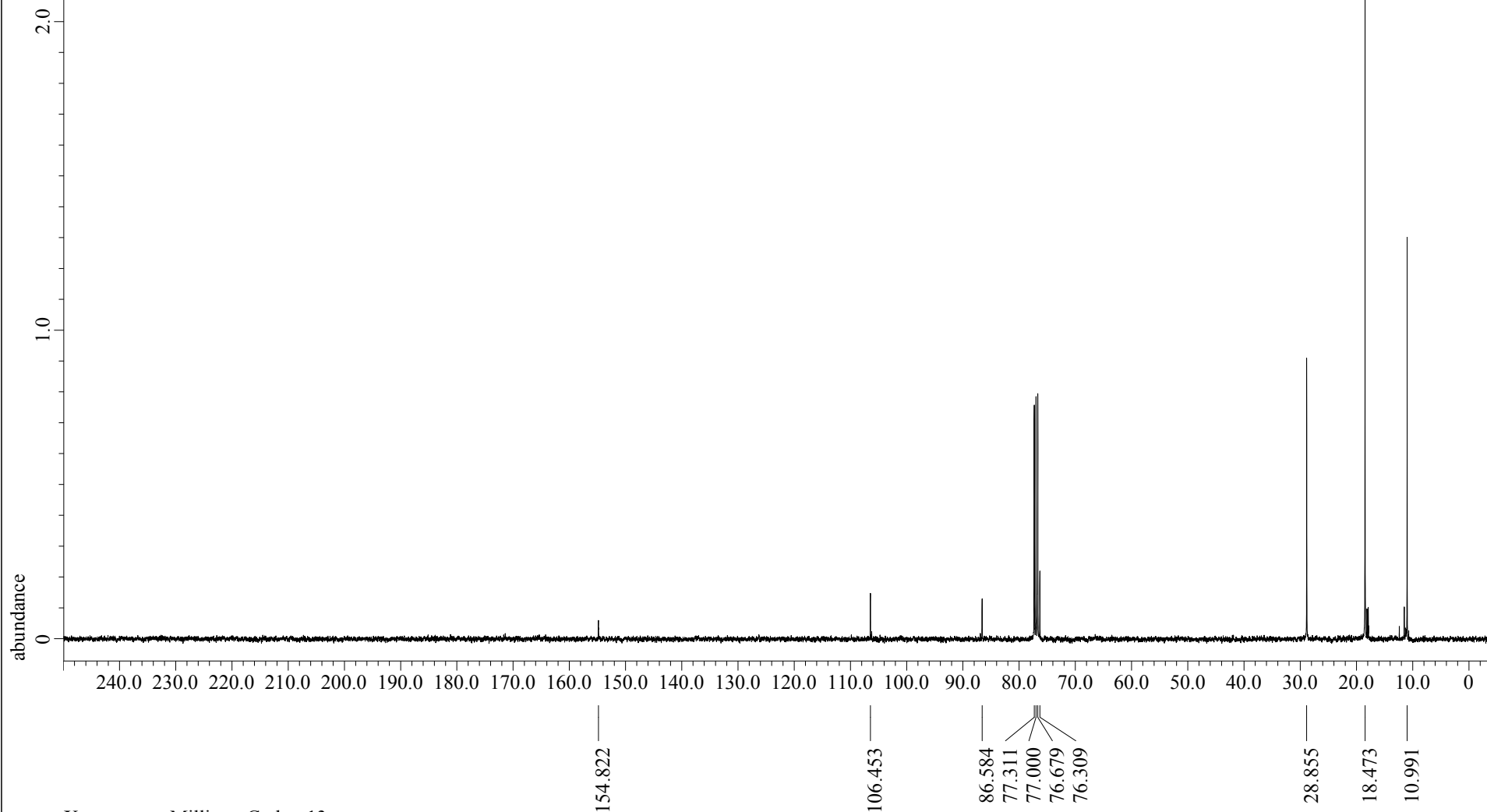
Line#:1 R.Time:10.466(Scan#:1164)  
 MassPeaks:300  
 RawMode:Single 10.466(1164) BasePeak:114.05(52381)  
 BG Mode:None Group 1 - Event 1



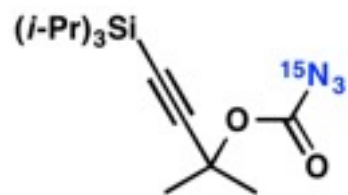




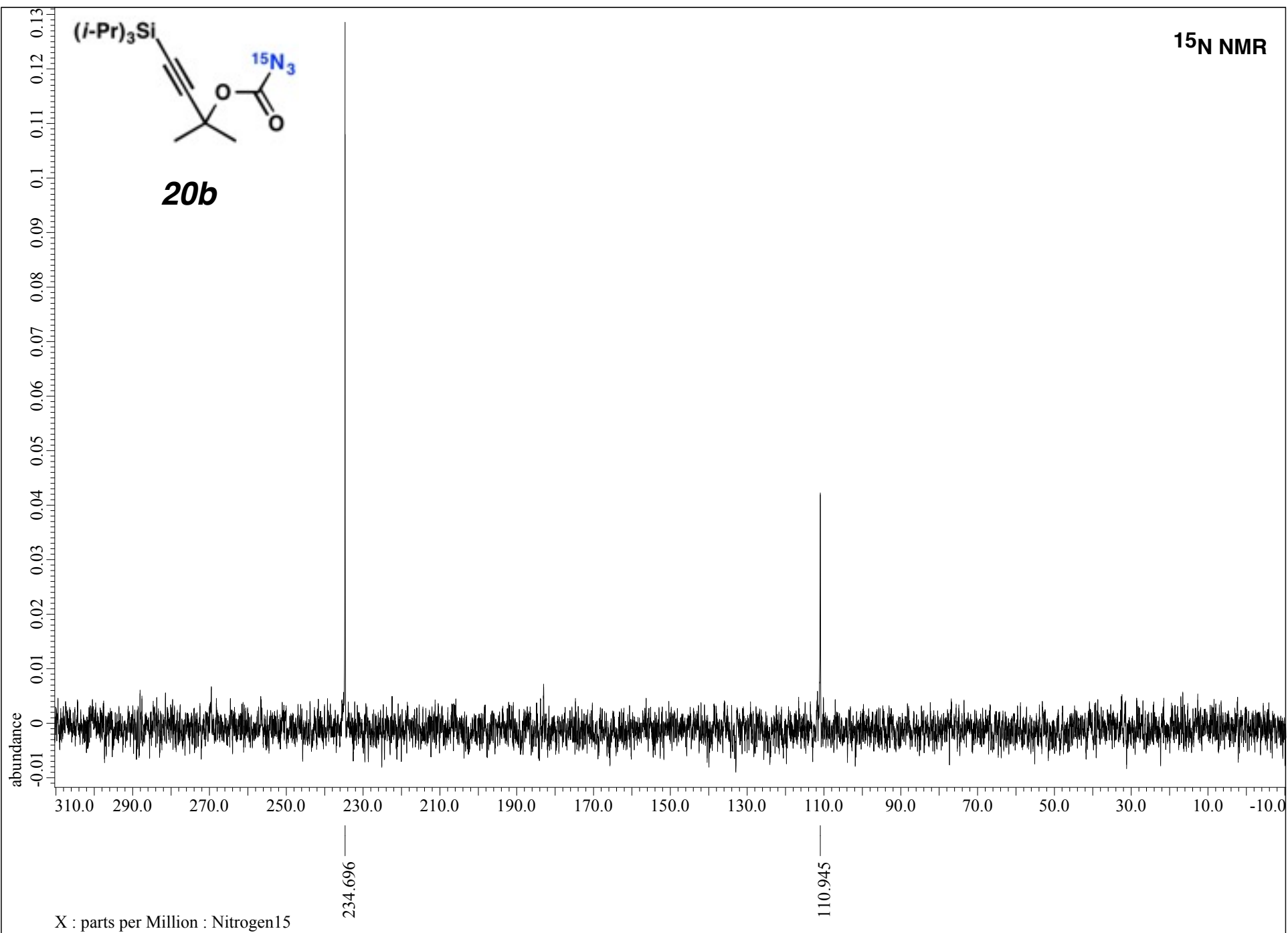
**20b**



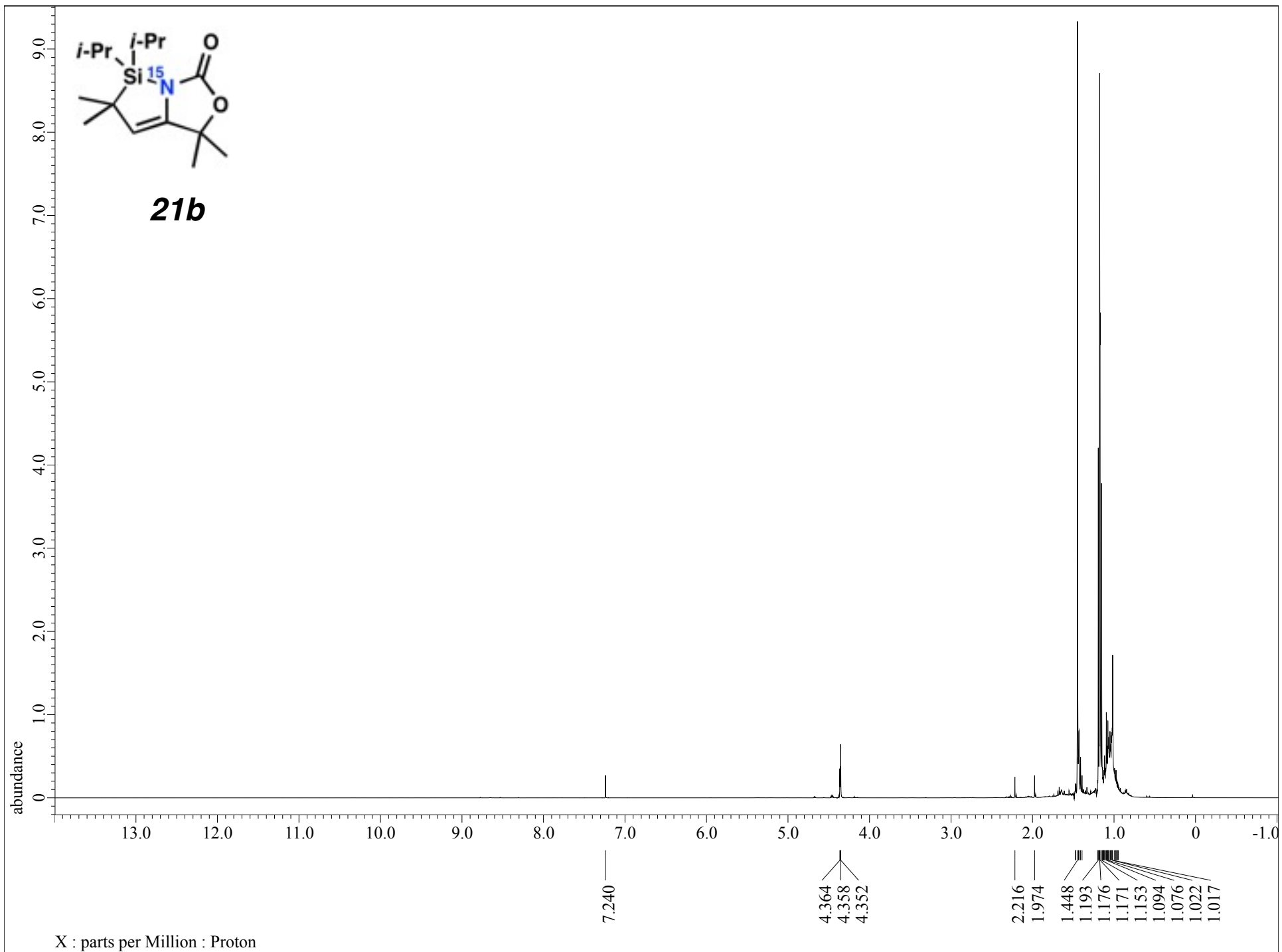
<sup>15</sup>N NMR

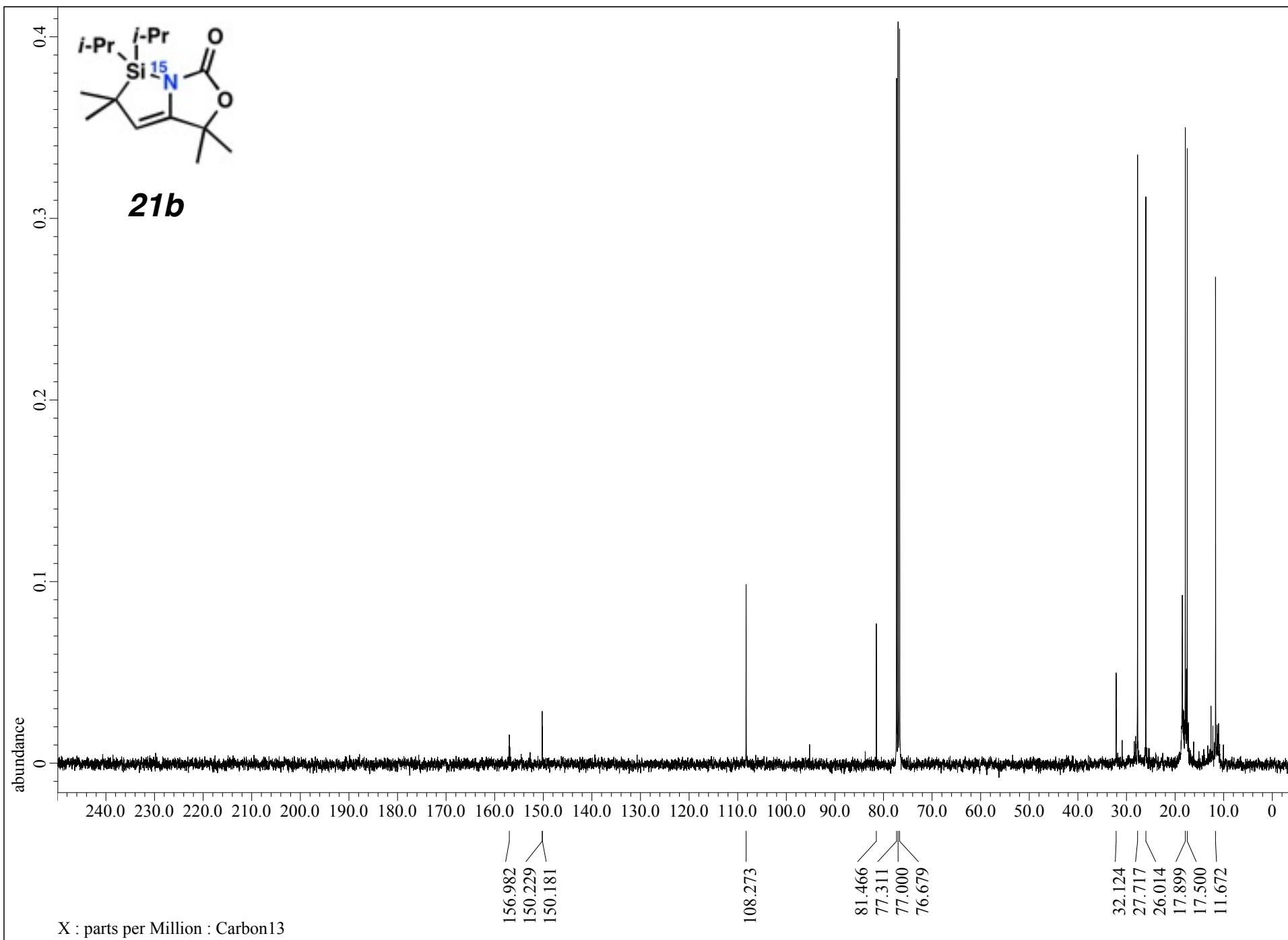


**20b**

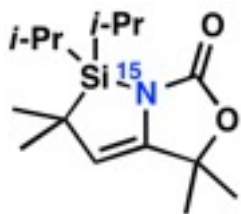


X : parts per Million : Nitrogen15

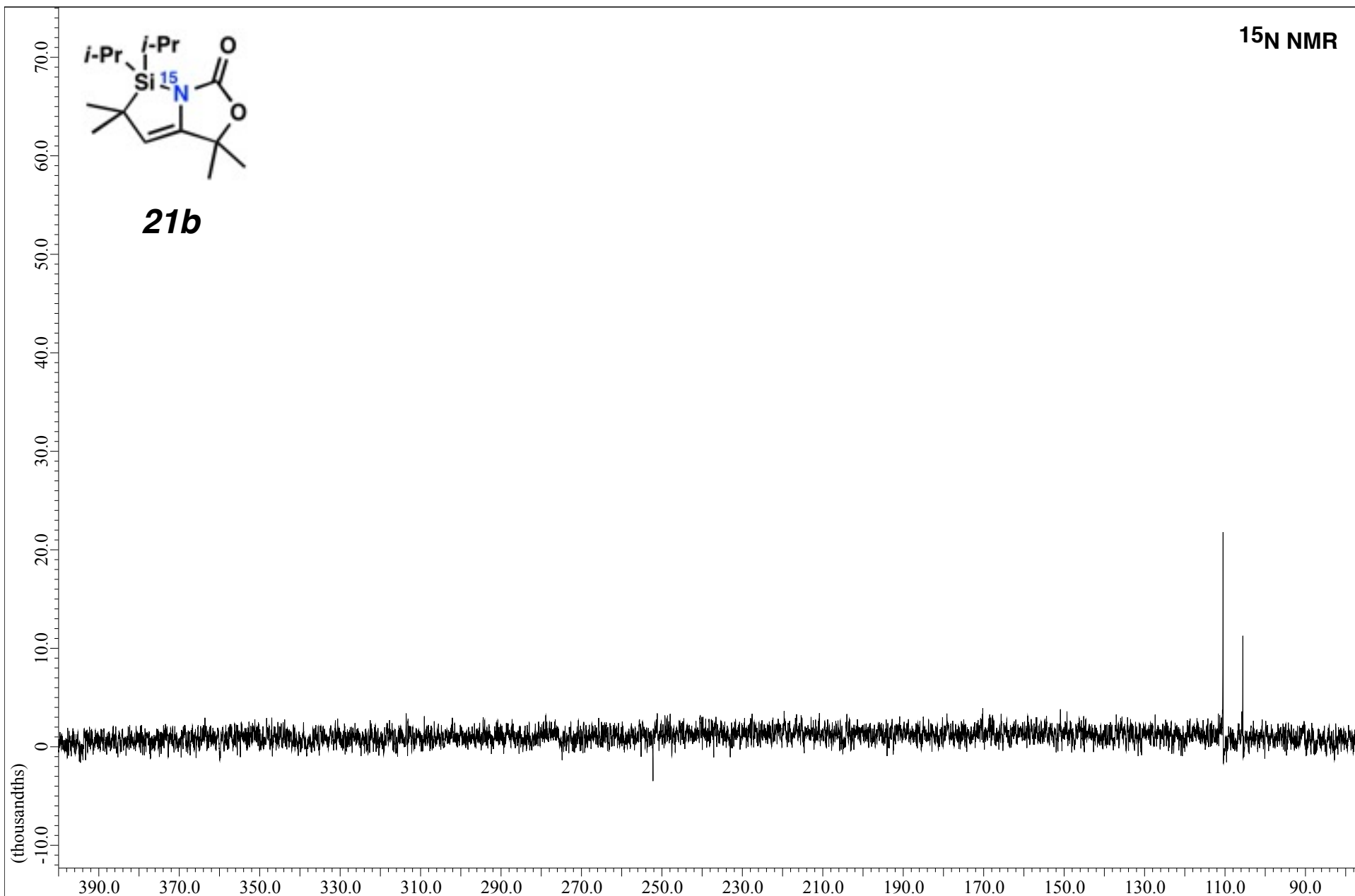




<sup>15</sup>N NMR

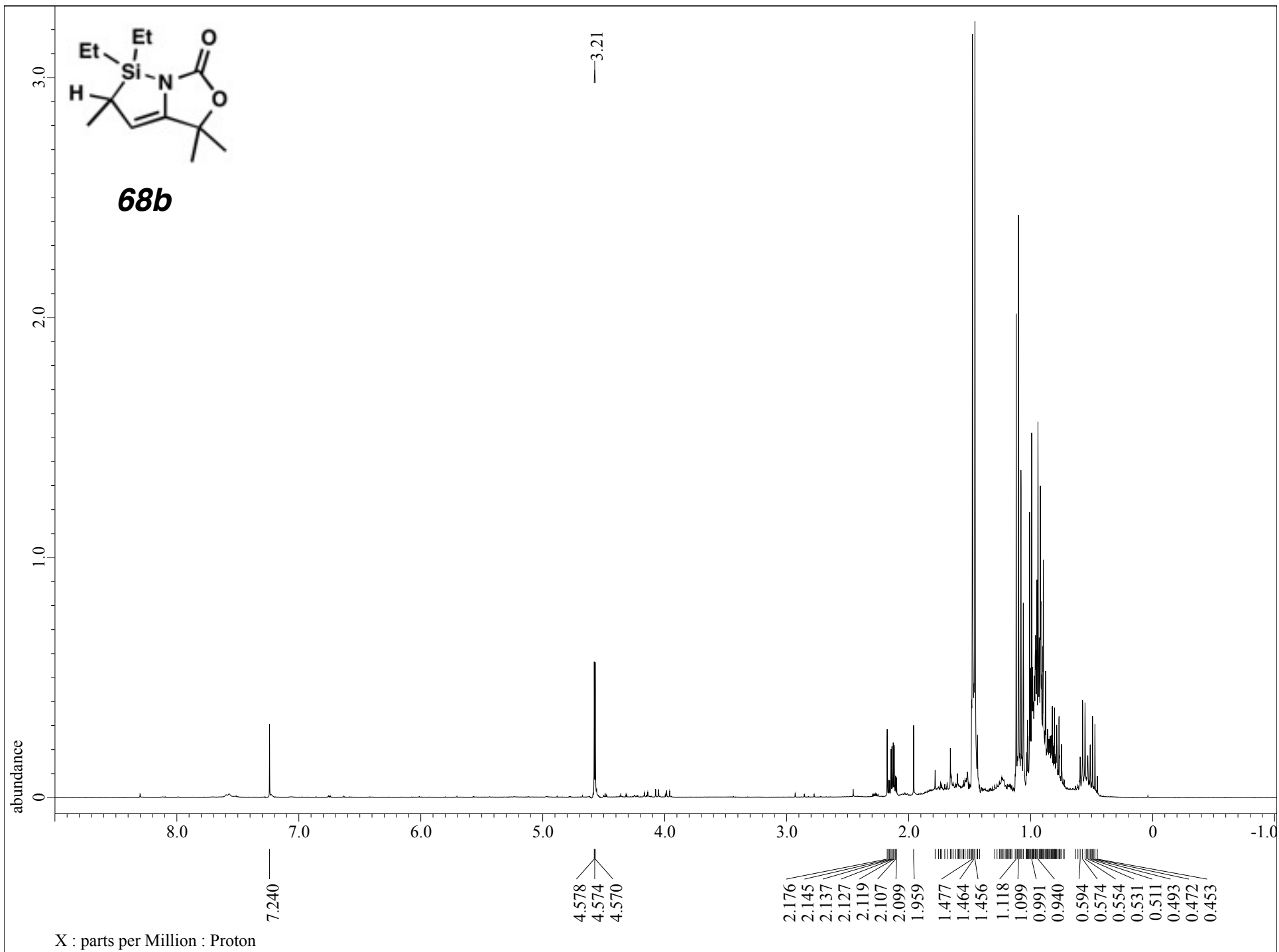


**21b**

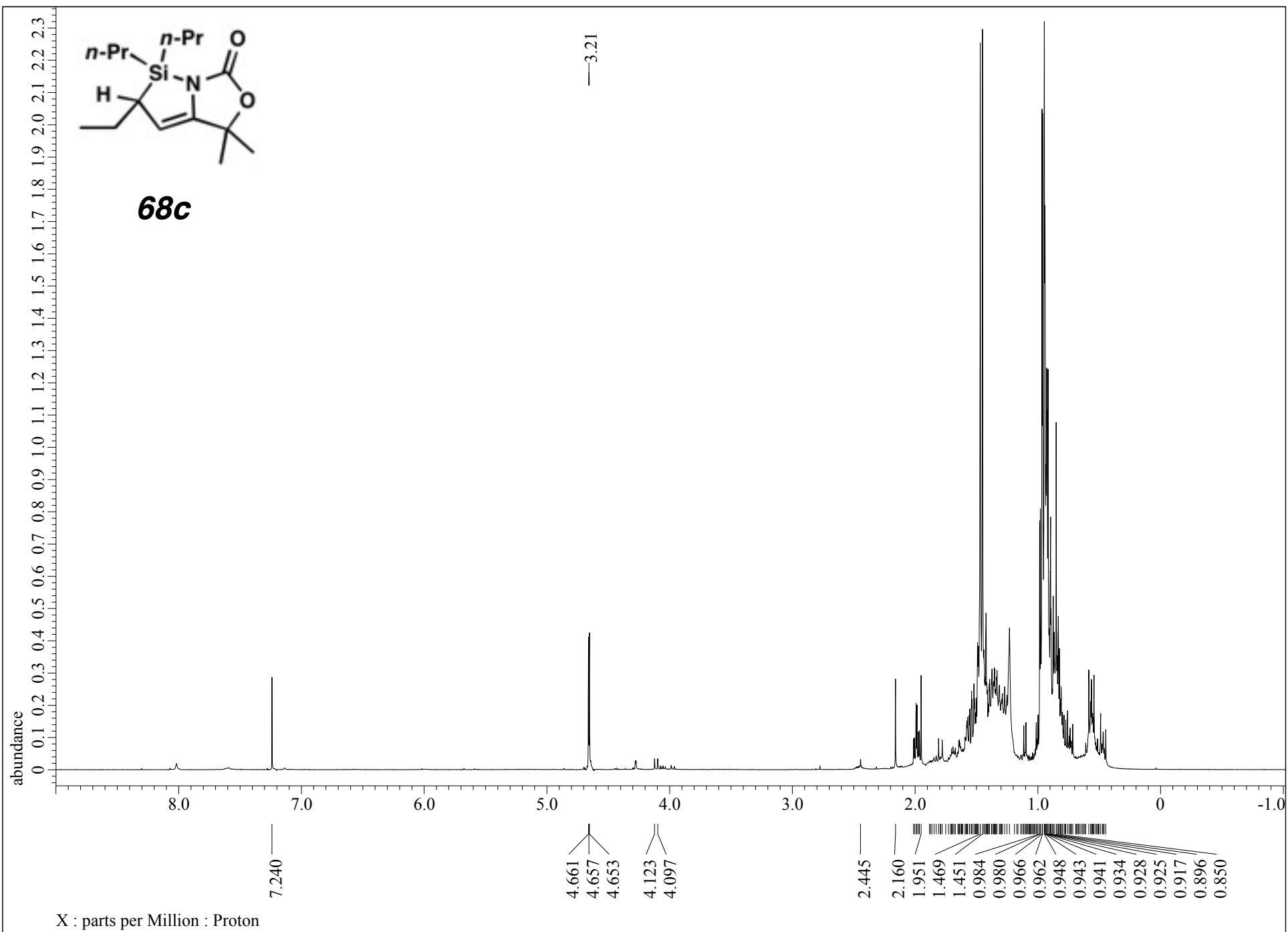


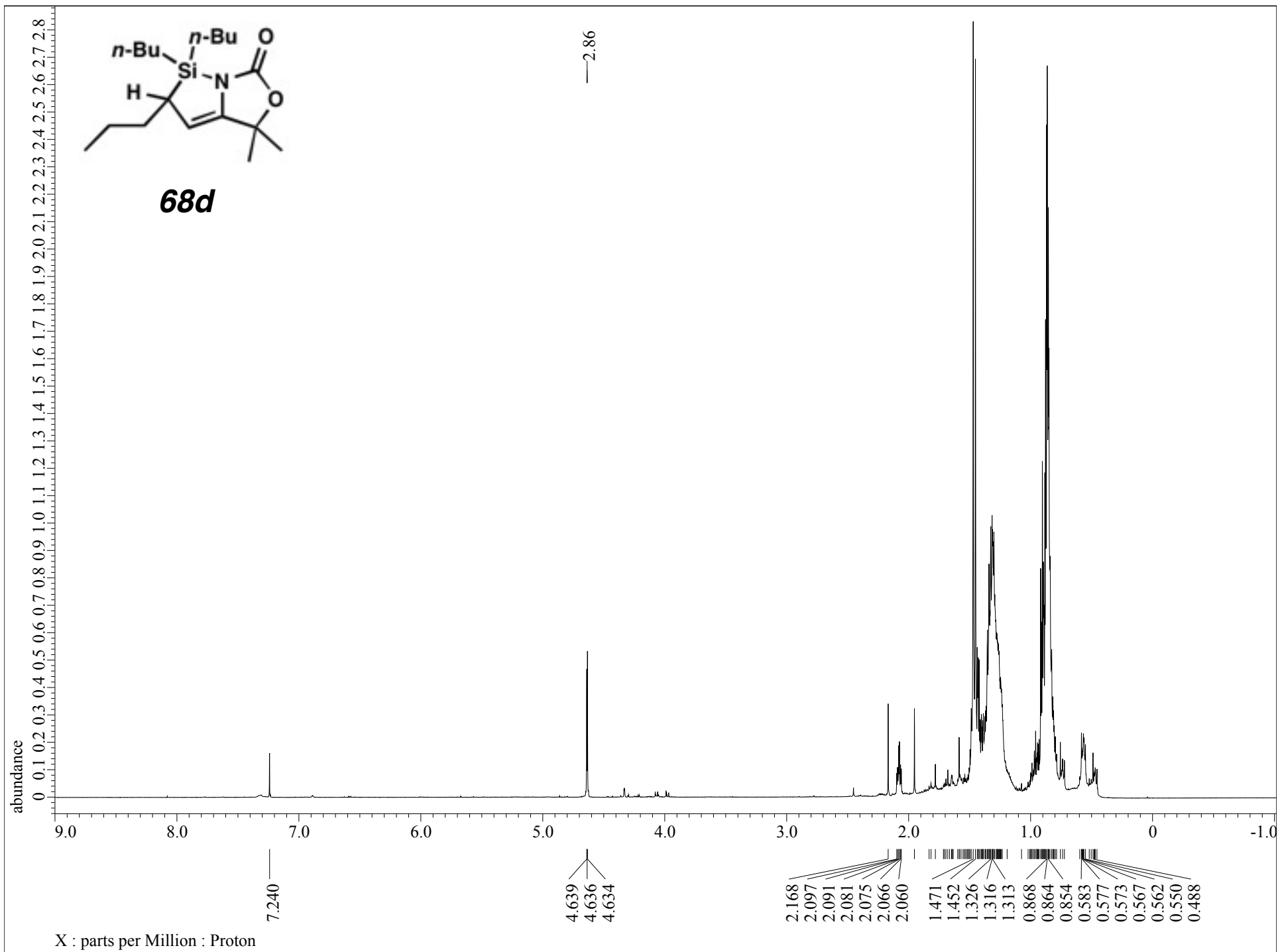
X : parts per Million : Nitrogen15

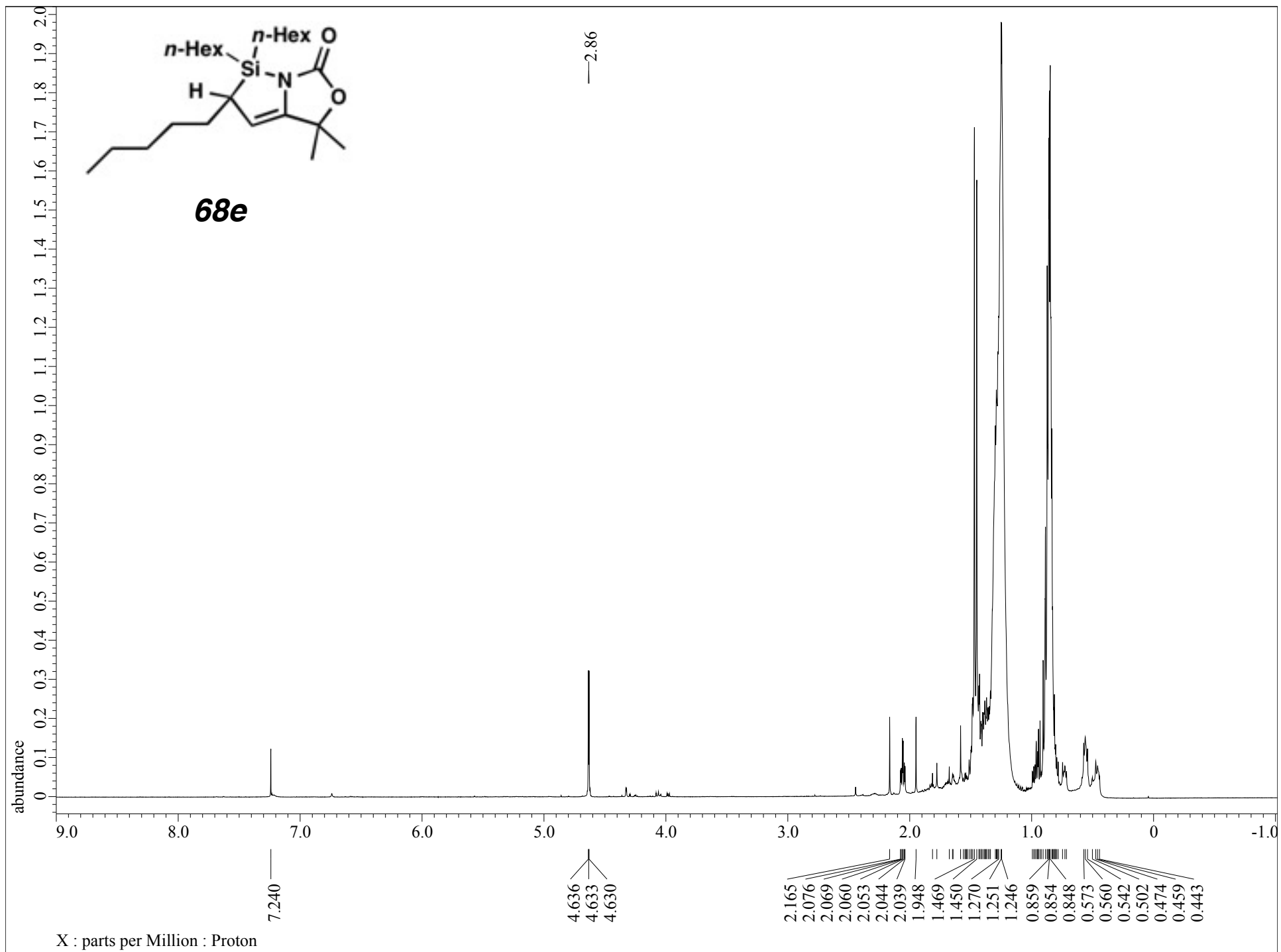
110.484

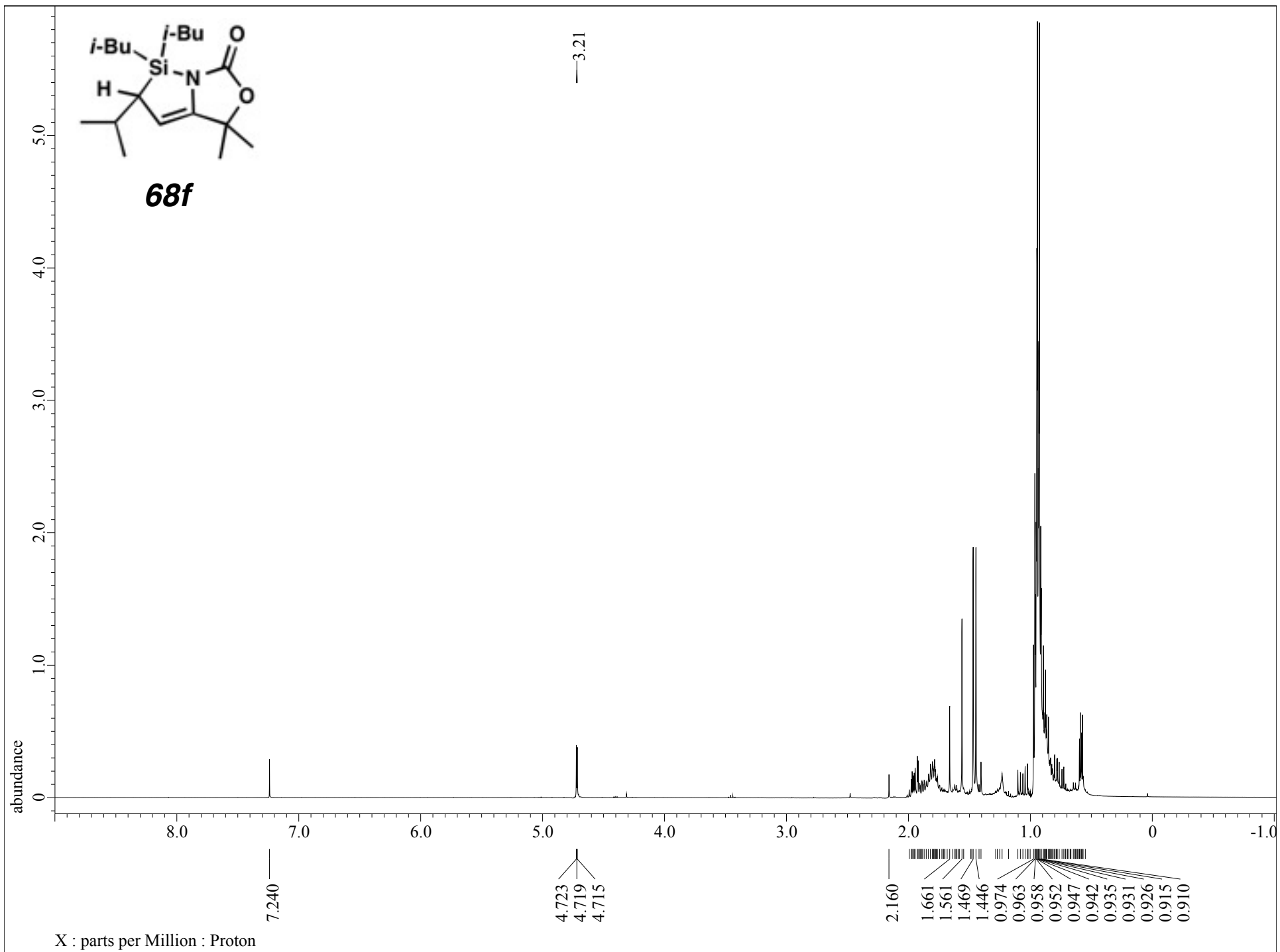


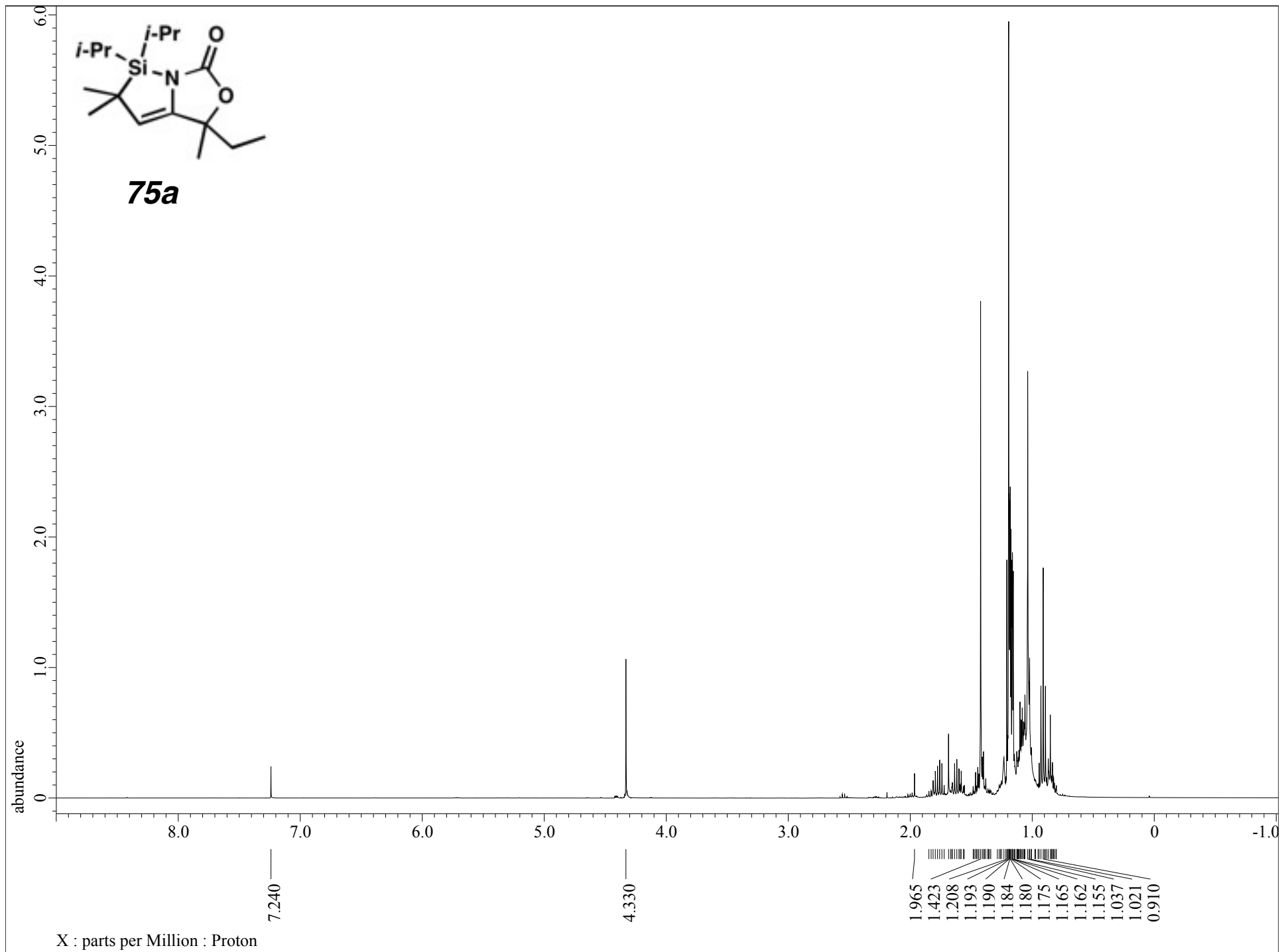


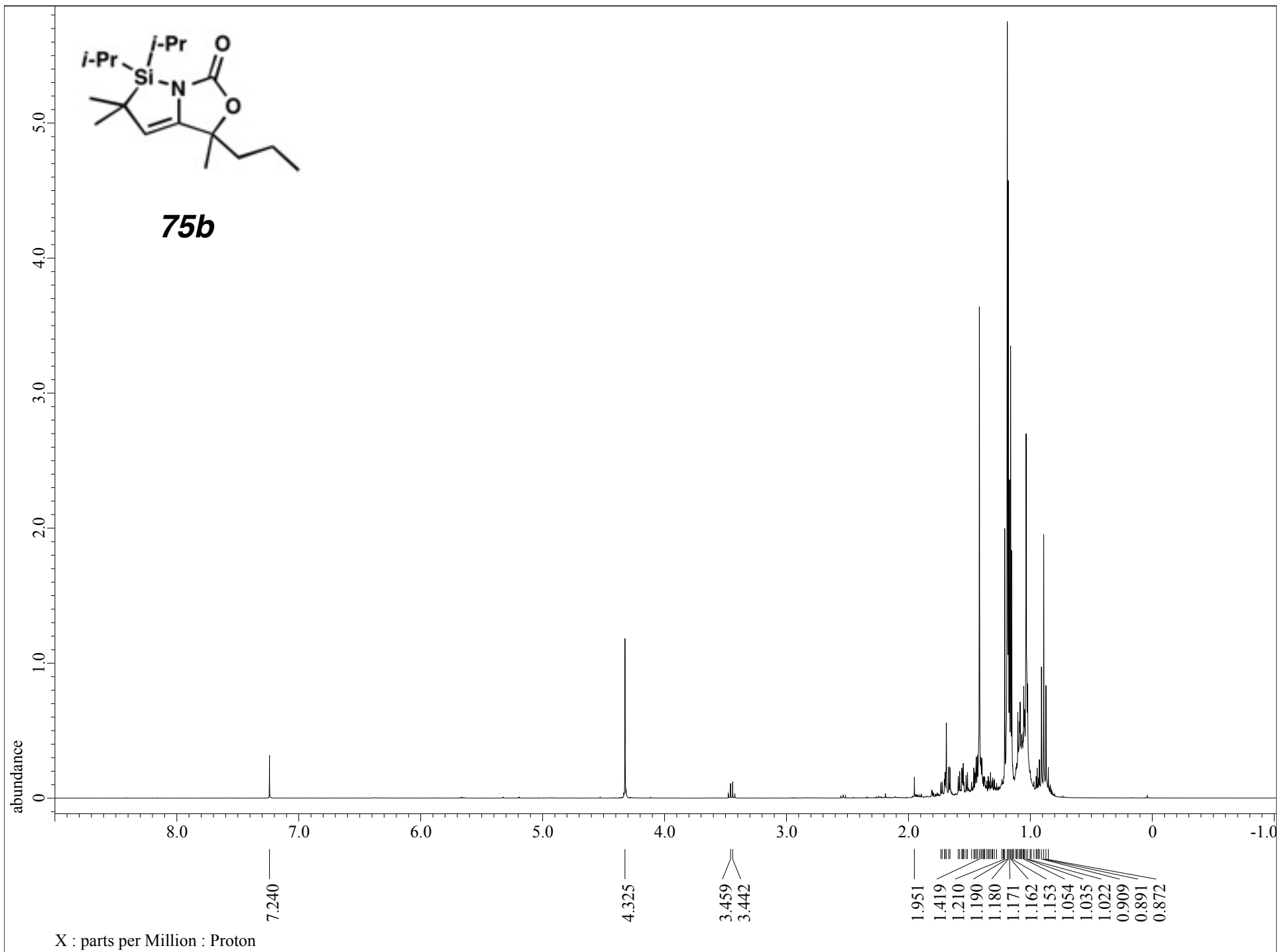


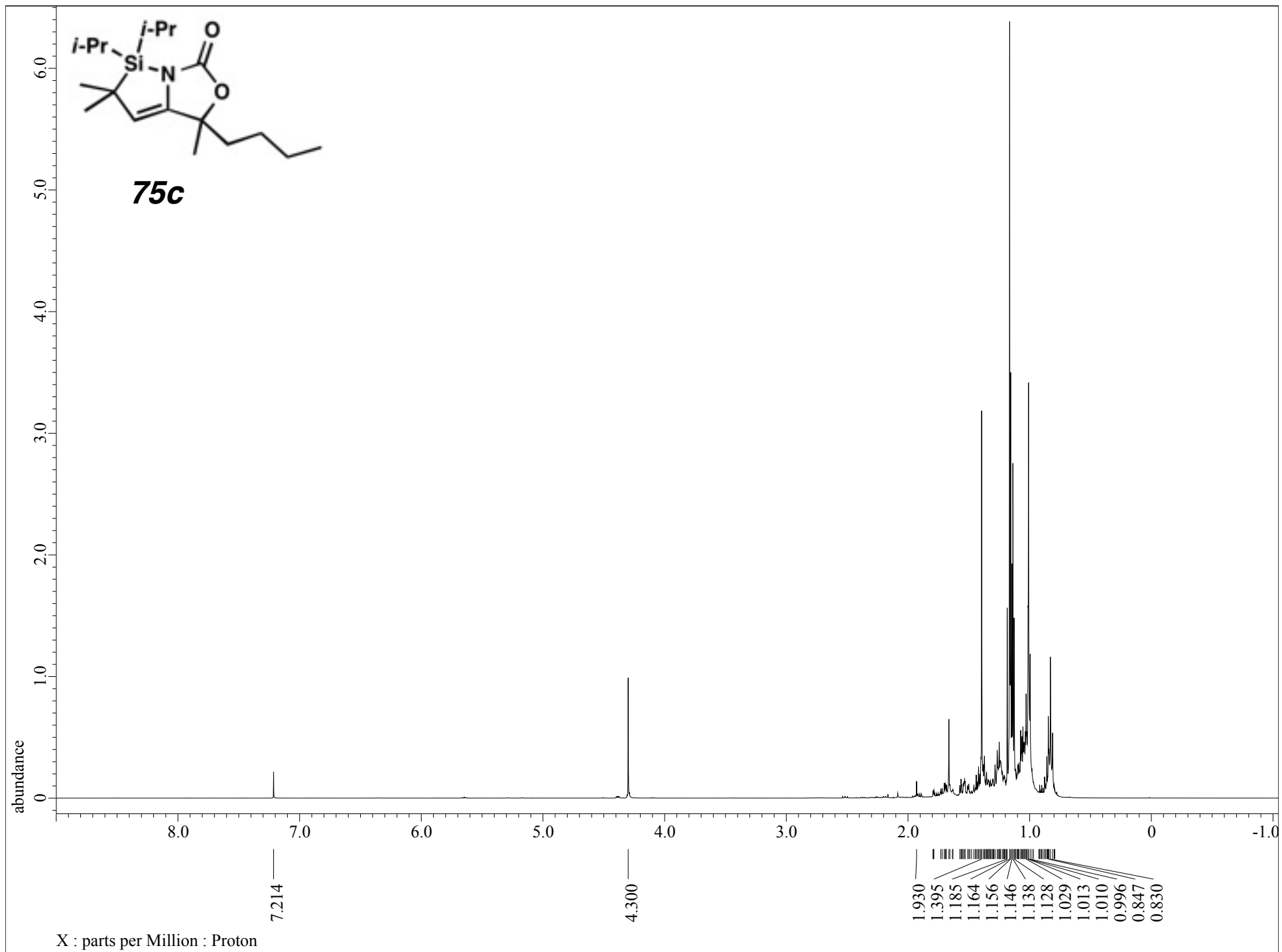


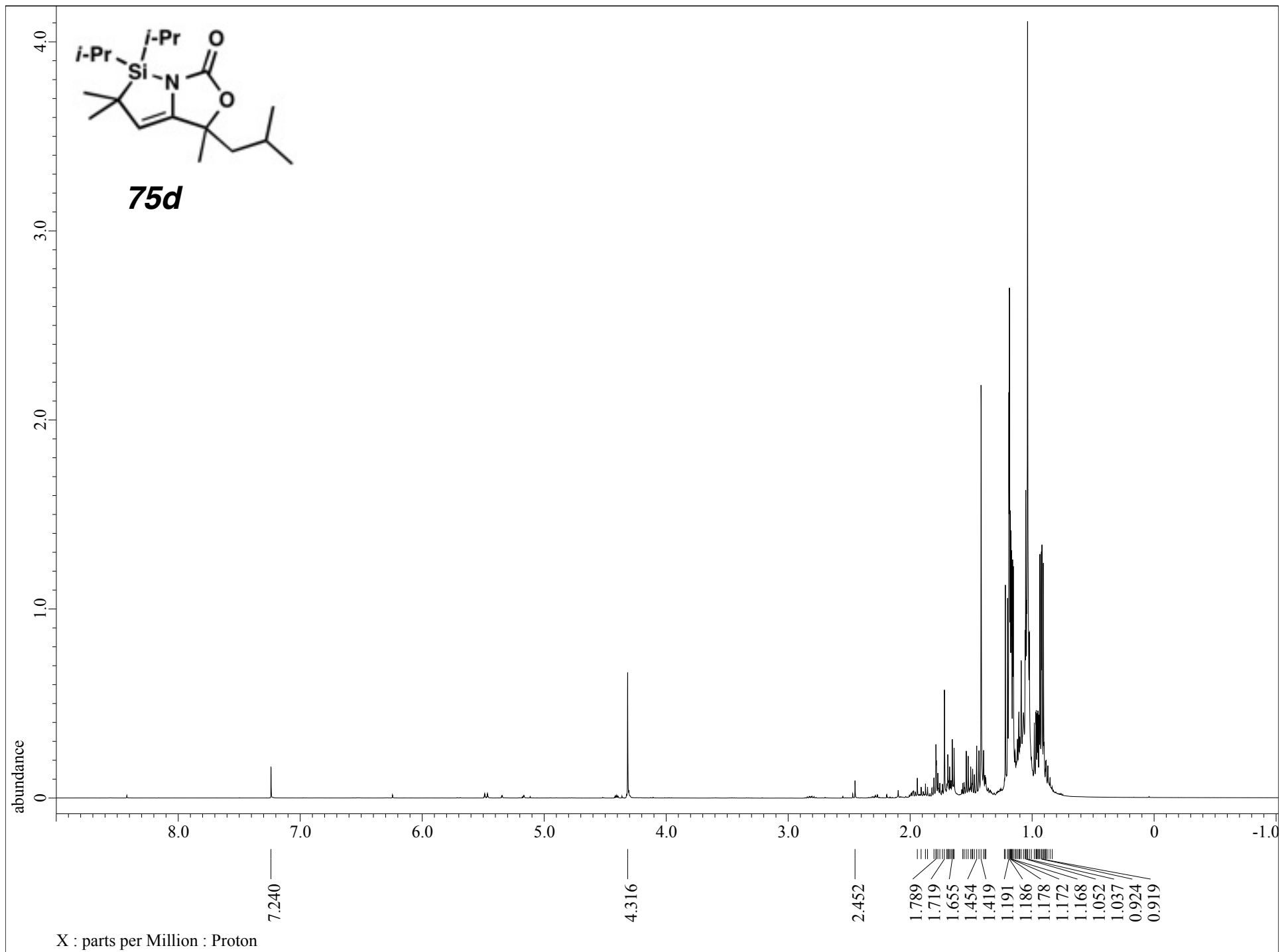




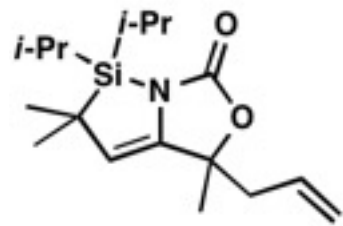












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