

SUPPORTING INFORMATION

Silver(I)-Catalyzed Oxidative Coupling of Hydrosilanes with DMF to Symmetrical and Unsymmetrical Disiloxanes

Nan Wu,^{†a} Chuang Li,^{†a} Guichao Dong,^{†a} Mengfei Jiang,^a Zhou Xu^{*a}

^aJiangsu Key Laboratory of New Drug Research and Clinical Pharmacy, School of Pharmacy,
Xuzhou Medical University, Tongshan Road 209, Xuzhou, 221004, China.

Corresponding author email: xuzhou@xzhmu.edu.cn

Table of Contents

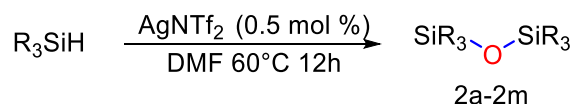
I. General procedures	2
II. General procedures for oxidative coupling of hydrosilanes with DMF	2
III. Characterization data of disiloxanes	3
V. Copies of the ¹ H, ¹⁹ F and ¹³ C NMR spectra	8

I. General procedures

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out in air unless otherwise stated. Column chromatography was performed on silica gel (300-400 mesh, 20 gram, length of column is about 20 cm) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. ^1H , ^{13}C and ^{19}F spectra were recorded at room temperature on a JEOL ECZ400 with TMS as an internal standard and CDCl_3 as solvent. Fourier transform infrared spectra (FT-IR) were recorded on Agilent Technologies Cary 630 instrument. HRMS analyses were made by means of ESI-TOF. Melting points were measured on micro melting point apparatus and uncorrected.

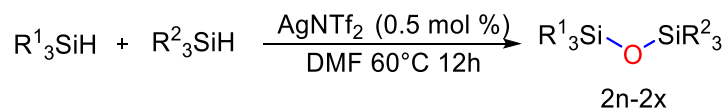
II. General procedures for oxidative coupling of hydrosilanes with DMF

1. Oxidative coupling of hydrosilanes with DMF to symmetrical disiloxanes.



AgNTf_2 (0.0125 mmol, 0.0049 g, 0.005 eq), DMF (2.5 ml), hydrosilane (2.5 mmol) were mixed in a 10 mL reaction flask and the reaction was stirred at 60 °C. After the reaction was completed (monitored by TLC), the reaction was quenched with H_2O (5 mL) and extracted with DCM (2x10 mL). The combined organic layers were dried over Na_2SO_4 and the solution was concentrated in vacuo. The disiloxane 2a was purified by flash chromatography (PE : EA = 100:1).

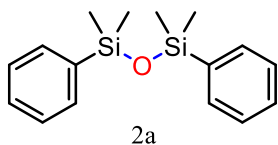
2. Synthesis of unsymmetrical disiloxanes.



AgNTf_2 (0.0125 mmol, 0.0049 g, 0.005 eq), DMF (4 ml), R^1_3SiH (3 mmol), R^2_3SiH (1 mmol) were mixed in a 10 mL reaction flask and the reaction was stirred at 60 °C. After the reaction was completed, the reaction was quenched with H_2O (5 mL) and extracted with DCM (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 , and the solution was concentrated in vacuo. The crude disiloxane was purified by flash chromatography on silica (PE : EA = 100:1).

III. Characterization data of dissiloxane

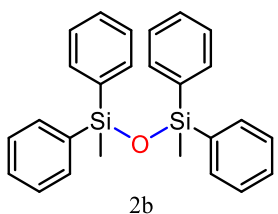
2-1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (2a)^{1,2}



2a was obtained in 96% yield (343.4 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ¹H NMR (400 MHz, CDCl₃): δ 7.55 (dd, *J* = 7.1, 2.1 Hz, 4H), 7.42-7.31 (m, 6H), 0.33 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 139.80, 132.98, 129.23, 127.68, 0.84. ²⁹Si NMR (79 MHz, CDCl₃): δ -0.52. HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₁₆H₂₂OSi₂Na⁺ 309.1101; found: 309.1102.

3-1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane (2b)¹

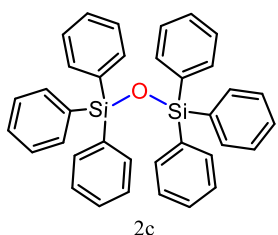


2b was obtained in 90% yield (512.7 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ¹H NMR (400 MHz, CDCl₃): δ 7.55-7.49 (m, 8H), 7.41-7.34 (m, 4H), 7.34-7.28 (m, 8H), 0.57 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 137.57, 133.99, 129.55, 127.71, -0.59.

²⁹Si NMR (79 MHz, CDCl₃): δ -9.38. HRMS (ESI-TOF) *m/z*: [M+Na]⁺

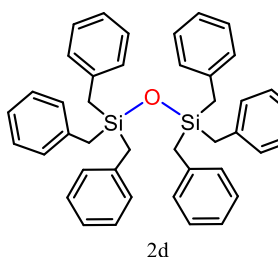
calcd. for C₁₆H₂₆OSi₂Na⁺ 433.1414; found: 433.1416.

1,1,1,3,3,3-hexaphenyldisiloxane (2c)^{2,3}



2c was obtained in 91% yield (608.3 mg) as a white solid (m.p. 221-223 °C) after silica gel column chromatography using PE/EtOAc (50:1). ¹H NMR (400 MHz, CDCl₃): δ 7.48- 7.46 (m, 10H), 7.39-7.35 (m, 5H), 7.28-7.24 (m, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 135.44, 135.12, 129.77, 127.68. ²⁹Si NMR (79 MHz, CDCl₃): δ -17.50.

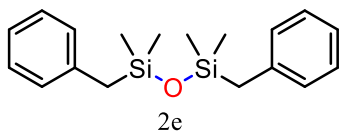
1,1,1,3,3,3-hexabenzylidisiloxane (2d)



2d was obtained in 85% yield (657.6 mg) as a white solid (m.p. 206-208°C) after silica gel column chromatography using PE/EtOAc (50:1). ¹H NMR (400 MHz, CDCl₃): δ 7.11 (t, *J* = 7.3 Hz, 12H), 7.05 (t, *J* = 7.1 Hz, 6H), 6.31 (d, *J* = 6.9 Hz, 12H), 1.95 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 138.19, 128.75, 128.29, 124.62, 24.67. ²⁹Si NMR (79 MHz, CDCl₃): δ -3.22. HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for

C₄₂H₄₂OSi₂Na⁺ 641.2672; found: 641.2674.

1,3-dibenzyl-1,1,3,3-tetramethyldisiloxane(2e)²

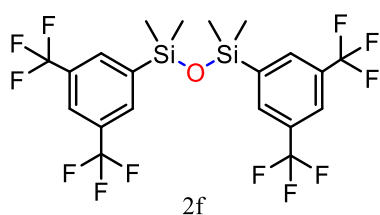


2e was obtained in 91% yield (357.8 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ¹H NMR (400 MHz, CDCl₃): δ 7.20 (t, *J* = 7.5 Hz, 4H), 7.07 (t, *J* = 7.5 Hz, 2H),

6.98 (d, *J* = 6.9 Hz, 4H), 2.05 (s, 4H), -0.02 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 139.38,

128.31, 128.11, 124.01, 28.50, -0.11. ^{29}Si NMR (79 MHz, CDCl_3): δ 5.57. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{26}\text{OSi}_2\text{Na}^+$ 337.1414; found: 337.1412.

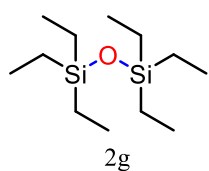
1,3-bis(3,5-bis(trifluoromethyl)phenyl)-1,1,3,3-tetramethyldisiloxane (2f)



2f was obtained in 88% yield (613.8 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1). ^1H NMR (400 MHz, CDCl_3): δ 7.87 (s, 6H), 0.43 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.27, 132.59, 130.98 (q, $J = 32.6$ Hz), 123.45 (q, $J = 273.1$ Hz), 123.36, 0.53; ^{19}F NMR (400 MHz, CDCl_3): -62.92.

^{29}Si NMR (79 MHz, CDCl_3): δ 0.72. HRMS (ESI-TOF) m/z : $[\text{M}+\text{F}]^-$ calcd. for $\text{C}_{20}\text{H}_{18}\text{F}_{12}\text{OSi}_2\text{F}^-$ 577.0694; found: 577.0685.

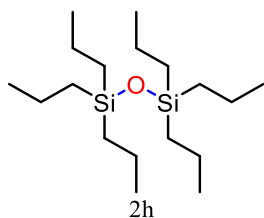
1,1,1,3,3,3-hexaethylidisiloxane (2g)^{2,3}



2g was obtained in 67% yield (206 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR (400 MHz, CDCl_3): δ 0.93 (t, $J = 16$ Hz, 18H), 0.51 (q, $J = 7.9$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 6.80, 6.38. ^{29}Si NMR (79 MHz, CDCl_3): δ 9.38. HRMS (ESI-TOF) m/z :

$[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{30}\text{OSi}_2\text{Na}^+$ 269.1727; found: 269.1725.

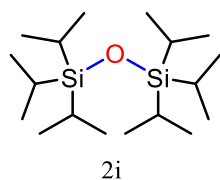
1,1,1,3,3,3-hexapropyldisiloxane (2h)



2h was obtained in 65% yield (393.2 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR (400 MHz, CDCl_3): δ 1.38-1.28 (m, 12H), 0.95 (t, $J = 7.3$ Hz, 18H), 0.50 (t, $J = 8.0$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 18.57, 18.47, 16.79. ^{29}Si NMR (79 MHz, CDCl_3): 5.83. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for

$\text{C}_{18}\text{H}_{42}\text{OSi}_2\text{Na}^+$ 353.2666; found: 353.2669.

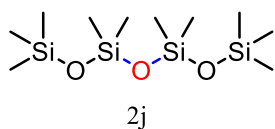
1,1,1,3,3,3-hexaisopropyldisiloxane (2i)



2i was obtained in 50% yield (206.2 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR (400 MHz, CD_3Cl): δ 1.049-0.999 (s, 42H); ^{13}C NMR (100 MHz, CDCl_3): δ 18.20, 13.67. ^{29}Si NMR (79 MHz, CDCl_3): δ 15.50. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for

$\text{C}_{18}\text{H}_{42}\text{OSi}_2\text{Na}^+$ 353.2666; found: 353.2666.

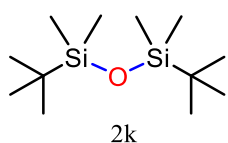
1,1,1,3,3,5,5,7,7,7-decamethyltetrasiloxane(2j)⁴



2j was obtained in 78% yield (302.2 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR (400 MHz, CDCl_3): δ 0.09 (s, 18H), 0.04 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 1.79,

1.14. ^{29}Si NMR (79 MHz, CDCl_3): δ 7.74, -21.56. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{10}\text{H}_{30}\text{O}_3\text{Si}_4\text{Na}^+$ 333.1164; found: 333.1159.

1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane (**2k**)⁵



2k

2k was obtained in 64% yield (196.8 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR (400 MHz, CDCl_3): δ 0.86 (s, 18H), -0.00 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 25.69, 18.11, -

3.04. ^{29}Si NMR (79 MHz, CDCl_3): δ 10.48. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{30}\text{OSi}_2\text{Na}^+$ 269.1727; found: 269.1727.

1,1,1,3,3,5,5,7,7,9,9,11,11-tetradecamethylhexasiloxane (**2l**)

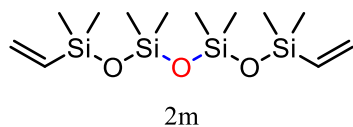


2l

2l was obtained in 76% yield (435.1 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR (400 MHz, CDCl_3): δ 0.08 (s, 18H), 0.06 (s, 12H), 0.04 (s,

12H). ^{13}C NMR (100 MHz, CDCl_3): δ 1.79, 1.14, 1.05. ^{29}Si NMR (79 MHz, CDCl_3): δ 7.80, -20.93, -42.50. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{14}\text{H}_{42}\text{O}_5\text{Si}_6\text{Na}^+$ 481.1540; found: 481.1536.

1-((dimethyl(vinyl)silyl)methyl)-1,1,3,3,5,5-hexamethyl-5-vinyltrisiloxane (**2m**)

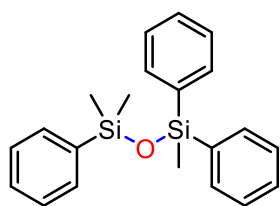


2m

2m was obtained in 80% yield (334.2 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1). ^1H NMR

(400 MHz, CDCl_3): δ 6.12 (dd, $J = 20.4, 14.9$ Hz, 2H), 5.92 (dd, $J = 14.9, 3.9$ Hz, 2H), 5.72 (dd, $J = 20.4, 3.9$ Hz, 2H), 0.18-0.12 (12H), 0.08-0.02 (12H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.34, 131.64, 1.16, 0.25. ^{29}Si NMR (79 MHz, CDCl_3): δ -2.57, -17.34. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{30}\text{O}_3\text{Si}_4\text{Na}^+$ 357.1164; found: 357.1161.

1,1,3-trimethyl-1,3,3-triphenyldisiloxane (**2n**)

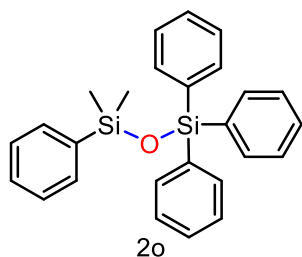


2n

2n was obtained in 59% yield (256.7 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1), $R_f = 0.33$. ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.50 (m, 6H), 7.42-7.30 (m, 9H), 0.61-0.57 (3H), 0.33 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.50, 137.85, 133.90, 132.99, 129.51, 129.29, 127.71, 0.85, -0.55. ^{29}Si NMR (79 MHz, CDCl_3): δ 0.52, -

10.48. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{21}\text{H}_{24}\text{OSi}_2\text{Na}^+$ 371.1258; found: 371.1255.

1,1-dimethyl-1,3,3,3-tetraphenyldisiloxane (**2o**)

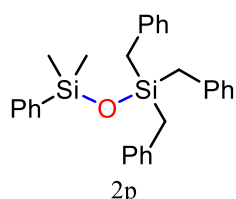


2o

2o was obtained in 65% yield (333.3 mg) as a white solid (m.p. 198-200 °C) after silica gel column chromatography using PE/EtOAc (50:1), $R_f = 0.22$. ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.55 (m, 6H), 7.55-7.50 (m, 2H), 7.42 (t, $J = 6.6$ Hz, 3H), 7.38-7.28 (m, 9H), 0.33 (s, 6H). ^{13}C NMR

(100 MHz, CDCl₃): δ 139.25, 136.38, 135.82, 134.99, 133.10, 129.77, 129.30, 127.71, 0.88. ²⁹Si NMR (79 MHz, CDCl₃): δ 1.30, -19.86. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₂₆H₂₆OSi₂Na⁺ 433.1414; found: 433.1411.

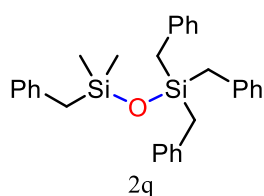
1,1,1-tribenzyl-3,3-dimethyl-3-phenyldisiloxane (2p)



2p was obtained in 58% yield (327.8 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (100:1), R_f = 0.19. ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.33 (m, 1H), 7.32-7.26 (m, 3H), 7.25-7.23 (1H), 7.18 (t, J = 7.5 Hz, 6H), 7.09 (t, J = 7.5 Hz, 3H), 6.98-6.91 (m, 6H), 2.12 (s, 6H), 0.08 (s,

6H). ¹³C NMR (100 MHz, CDCl₃): δ 139.39, 138.22, 132.98, 129.19, 128.74, 128.28, 127.63, 124.38, 24.69, 0.48. ²⁹Si NMR (79 MHz, CDCl₃): δ -0.42, -3.15. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₂₉H₃₂OSi₂Na⁺ 475.1884; found: 475.1901.

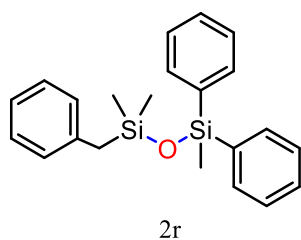
1,1,1,3-tetrabenzyl-3,3-dimethyldisiloxane (2q)



2q was obtained in 56% yield (326.3 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.28. ¹H NMR (400 MHz, CDCl₃): δ 7.25-7.15 (m, 8H), 7.15-7.00 (m, 4H), 6.92 (d, J = 7.8 Hz, 6H), 6.79 (d, J = 8.2 Hz, 2H), 2.07 (s, 6H), 1.90 (s, 2H), -0.18 (s, 6H). ¹³C

NMR (100 MHz, CDCl₃): δ 139.19, 138.34, 128.71, 128.42, 128.28, 128.15, 124.39, 124.16, 28.32, 24.67, -0.33. ²⁹Si NMR (79 MHz, CDCl₃): δ 6.29, -3.77. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₃₀H₃₄OSi₂Na⁺ 489.2040; found: 489.2040.

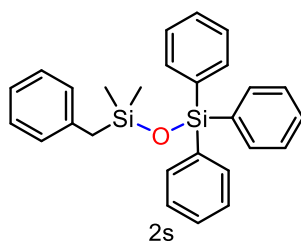
1-benzyl-1,1,3-trimethyl-3,3-diphenyldisiloxane (2r)



2r was obtained in 62% yield (280.7 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.28. ¹H NMR (400 MHz, CDCl₃): δ 7.59-7.50 (m, 4H), 7.45-7.35 (m, 6H), 7.25-7.18 (2H), 7.12 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 7.3 Hz, 2H), 2.20 (s, 2H), 0.58 (s, 3H), 0.12 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 139.11, 137.89,

133.85, 129.49, 128.31, 128.15, 127.69, 124.07, 28.51, -0.68. ²⁹Si NMR (79 MHz, CDCl₃): δ 7.43, -11.04. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₂₂H₂₆OSi₂Na⁺ 385.1414; found: 385.1424.

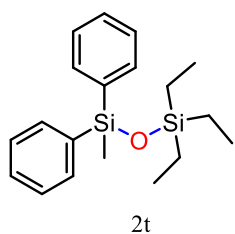
1-benzyl-1,1-dimethyl-3,3,3-triphenyldisiloxane (2s)



2s was obtained in 67% yield (355.2 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.26. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 6.4 Hz, 6H), 7.42 (d, J = 7.2 Hz, 3H), 7.35 (t, J = 7.2 Hz, 6H), 7.14 (t, J = 7.2 Hz, 2H), 7.07 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 2.16 (s, 2H), 0.05 (s, 6H). ¹³C NMR (100 MHz,

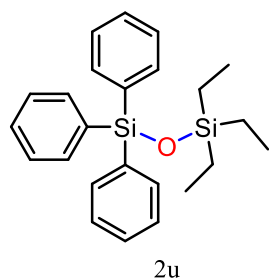
CDCl₃): δ 138.97, 135.87, 134.96, 129.74, 128.42, 128.17, 127.69, 124.07, 28.53, 0.03. ²⁹Si NMR (79 MHz, CDCl₃): δ 8.27, -20.34. HRMS (ESI-TOF) m/z: [M+K]⁺ calcd. for C₂₇H₂₈OSi₂K⁺ 463.1319; found: 463.1327.

1,1,1-triethyl-3-methyl-3,3-diphenyldisiloxane (2t)¹



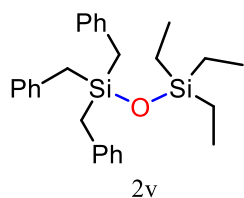
2t was obtained in 48% yield (196.9 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.47. ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 7.3 Hz, 4H), 7.37 (t, J = 6.9 Hz, 6H), 0.90 (t, J = 7.8 Hz, 9H), 0.61 (s, 3H), 0.60-0.47 (6H). ¹³C NMR (100 MHz, CDCl₃): δ 138.33, 133.81, 129.38, 127.64, 6.76, 6.27, -0.52. ²⁹Si NMR (79 MHz, CDCl₃): δ 13.09, -12.35. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₁₉H₂₈OSi₂Na⁺ 351.1571; found: 351.1573.

1,1,1-triethyl-3,3,3-triphenyldisiloxane (2u)⁶



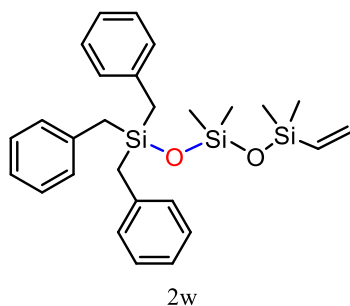
2u was obtained in 62% yield (302.4 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.42. ¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, J = 9.6 Hz, 6H), 7.42 (t, J = 7.1 Hz, 3H), 7.39-7.33 (m, 6H), 0.87 (t, J = 8.0 Hz, 9H), 0.56 (q, J = 7.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 136.28, 134.95, 129.67, 127.65, 6.76, 6.35. ²⁹Si NMR (79 MHz, CDCl₃): δ 13.97, -21.25. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₂₄H₃₀OSi₂Na⁺ 413.1727; found: 413.1735.

1,1,1-tribenzyl-3,3,3-triethyldisiloxane (2v)



2v was obtained in 56% yield (313.4 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.27. ¹H NMR (400 MHz, CDCl₃): δ 7.23 (t, J = 8.0 Hz, 6H), 7.11 (t, J = 7.3 Hz, 3H), 7.02 (d, J = 7.8 Hz, 6H), 2.22-2.04 (6H), 0.86-0.70 (m, 9H), 0.39 (q, J = 7.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 138.44, 128.68, 128.22, 124.32, 24.79, 6.71, 6.16. ²⁹Si NMR (79 MHz, CDCl₃): δ -3.98, -19.57. HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd. for C₂₇H₃₆OSi₂Na⁺ 455.2197; found: 455.2203.

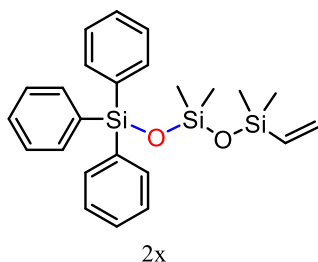
1-allyl-5,5,5-tribenzyl-1,1,3,3-tetramethyltrisiloxane (2w)



2w was obtained in 47% yield (279.8 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), R_f = 0.25. ¹H NMR (400 MHz, CDCl₃): δ 7.24-7.17 (6H), 7.09 (t, J = 7.3 Hz, 3H), 7.00 (d, J = 7.3 Hz, 6H), 6.10 (dd, J = 20.1, 14.6 Hz, 1H), 5.94 (dd, J = 14.6, 4.1 Hz, 1H), 5.72 (dd, J = 20.4, 3.9 Hz, 1H), 2.11 (s, 6H), 0.13 (s, 6H), -0.15 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 139.17,

138.36, 131.85, 128.75, 128.24, 124.34, 25.54, 1.06, 0.24. ^{29}Si NMR (79 MHz, CDCl_3): δ 12.22, -3.24, -4.46. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{27}\text{H}_{36}\text{O}_2\text{Si}_3\text{Na}^+$ 499.1915; found: 499.1929.

1-allyl-1,1,3,3-tetramethyl-5,5,5-triphenyltrisiloxane (2x)



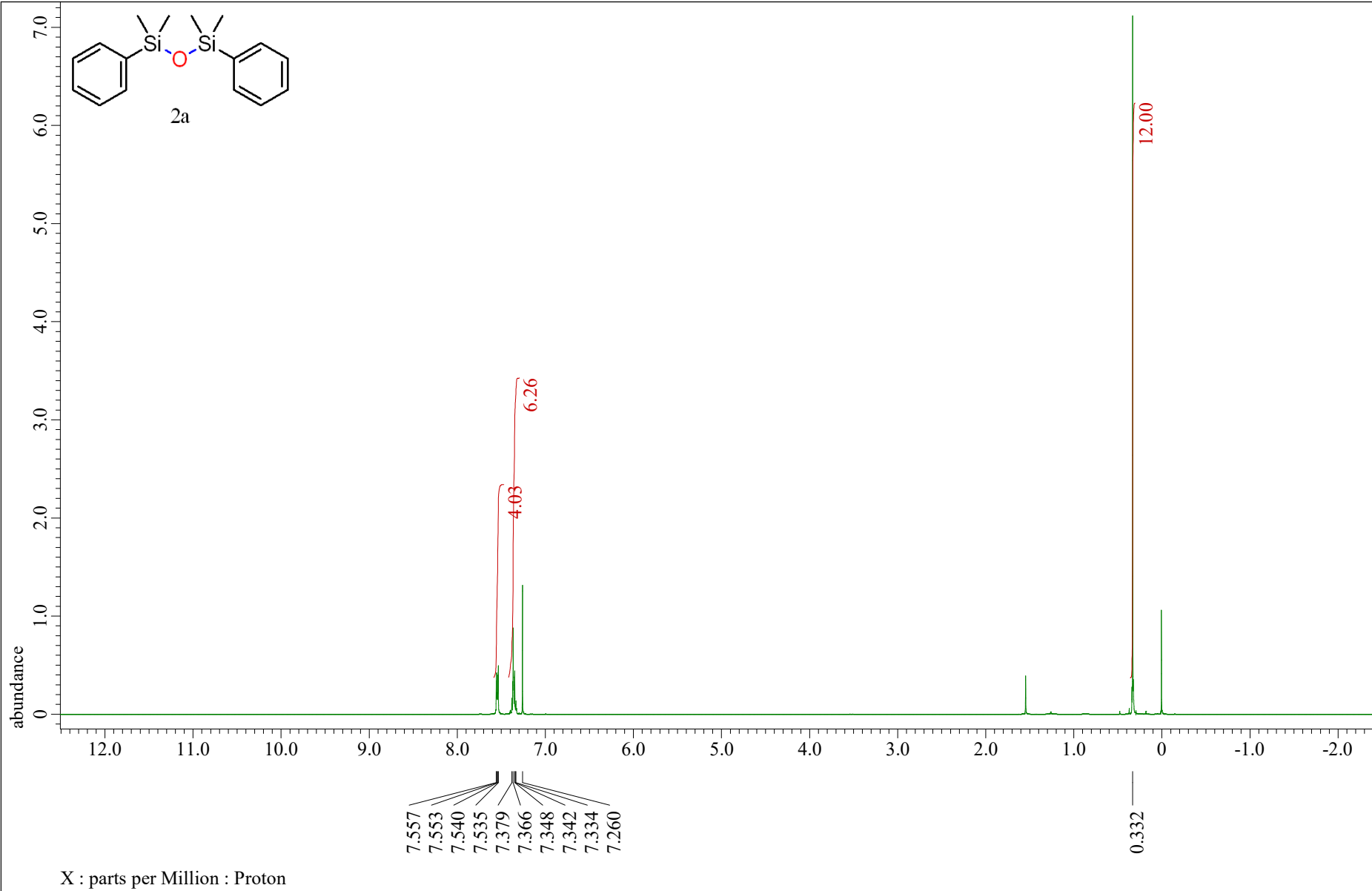
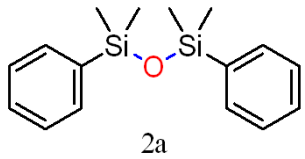
2x was obtained in 48% yield (260.5 mg) as a colorless liquid after silica gel column chromatography using PE/EtOAc (50:1), $R_f = 0.31$. ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.52 (m, 6H), 7.42 (t, $J = 6.6$ Hz, 3H), 7.38-7.33 (6H), 6.06 (dd, $J = 8.6, 4.5$ Hz, 1H), 5.88 (dd, $J = 14.6, 4.1$ Hz, 1H), 5.67 (dd, $J = 6.7, 4.5$ Hz, 1H), 0.07 (s, 6H), 0.06 (s, 6H). ^{13}C NMR (100

MHz, CDCl_3): δ 139.13, 135.93, 135.01, 131.71, 129.72, 127.65, 1.34, 0.11. ^{29}Si NMR (79 MHz, CDCl_3): δ -2.69, -17.50, -19.19. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{Si}_3\text{Na}^+$ 457.1446; found: 457.1457.

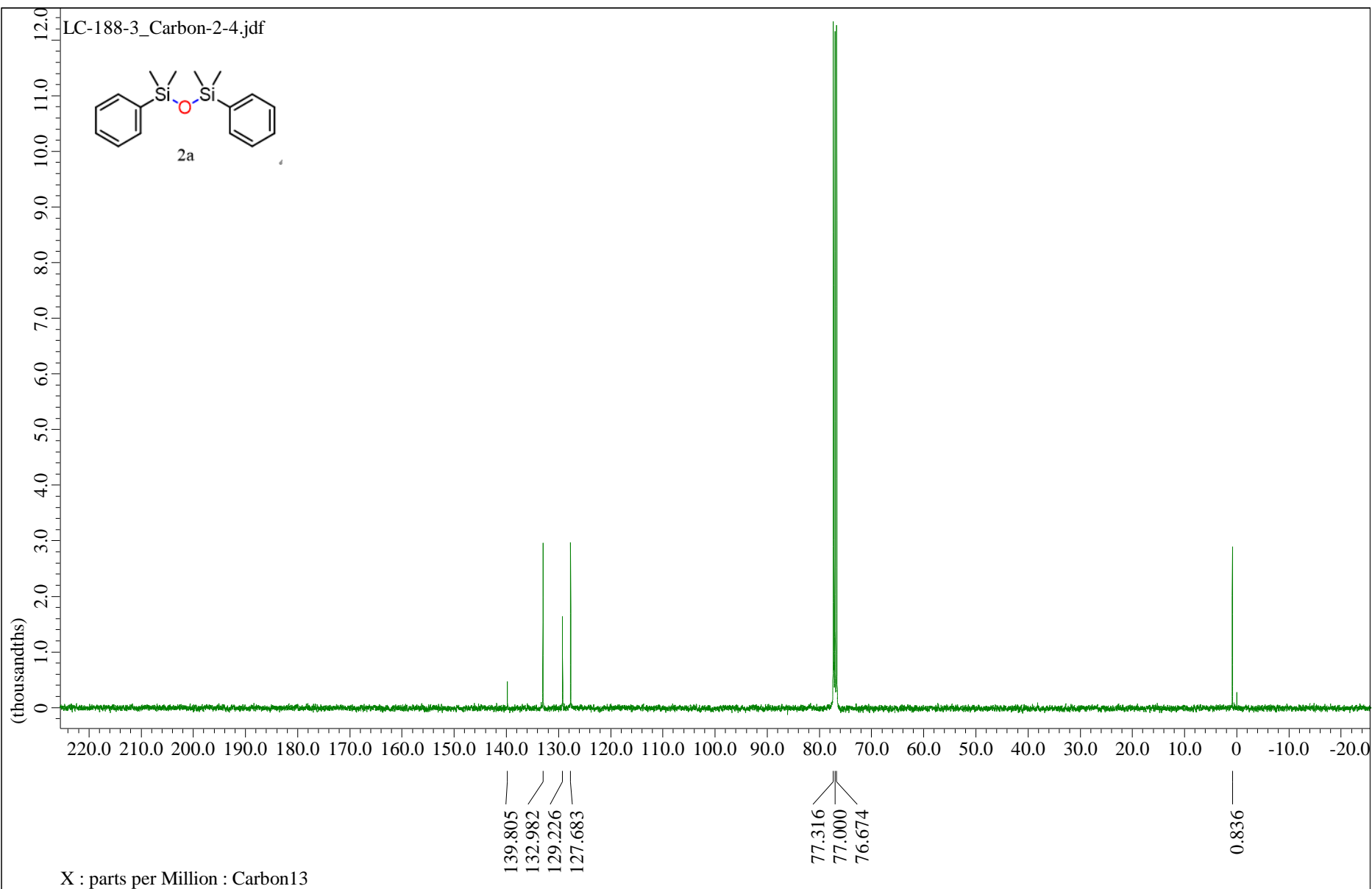
Reference

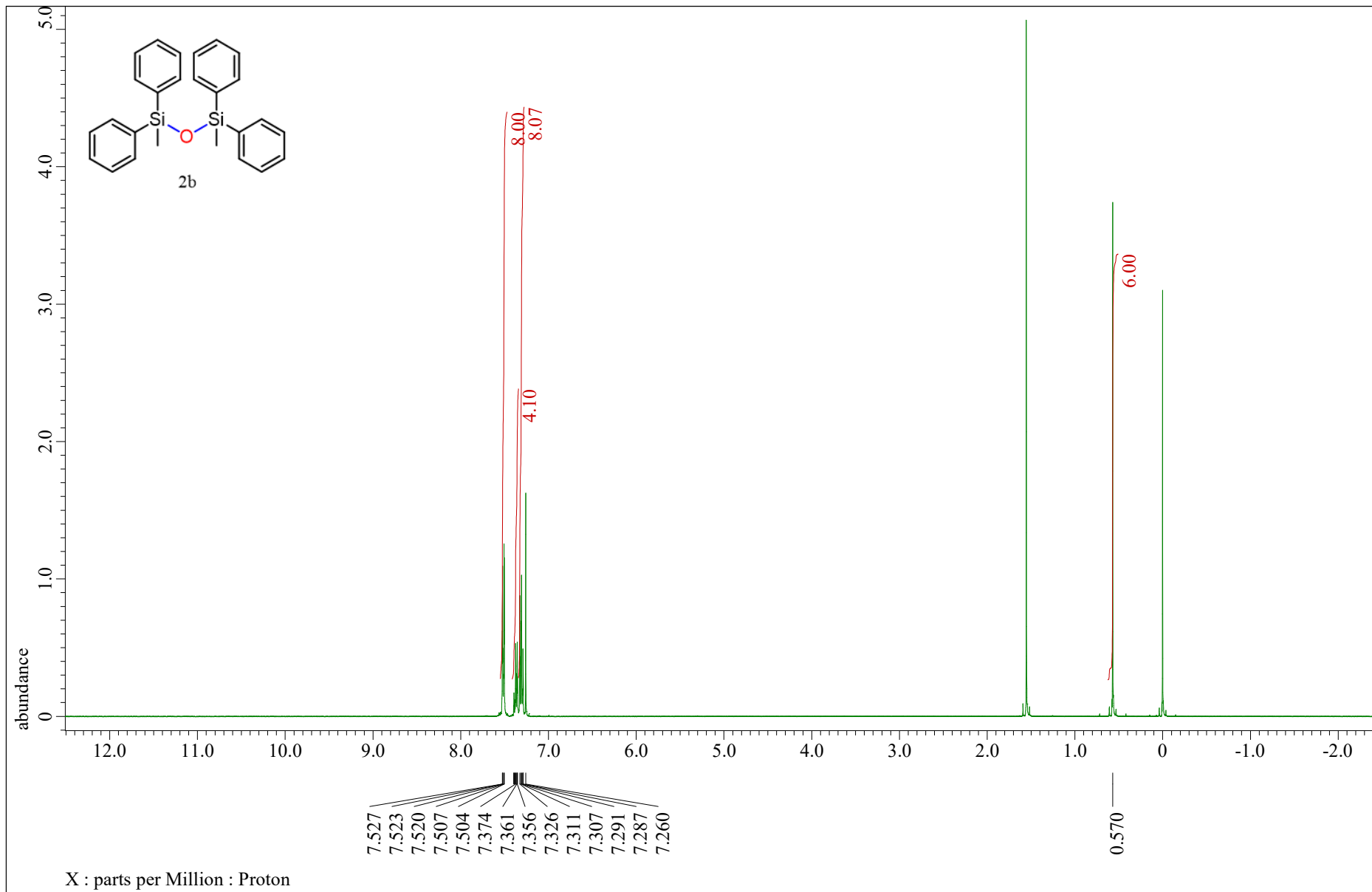
- [1] P. E. Gonzalez, H. K. Sharma, K. H. Pannell, DMF-activated Chlorosilane Chemistry: Molybdenum-catalyzed Reactions of R_3SiH , DMF and $\text{R}'_3\text{SiCl}$ to initially form $\text{R}_3\text{SiOSiR}'_3$ and R_3SiCl , *Inorg. Chim. Acta*, 2017, **466**, 376–381.
- [2] H. P. Lv, R. D. Laishram, J. Y. Li, G. R. Shi, W. Q. Sun, J. B. Xu, Y. Yang, Y. Luo, B. M. Fan, Nickel(0) catalyzed oxidation of organosilanes to disiloxanes by air as an oxidant, *Tetrahedron Lett.*, 2019, **60**, 971–974.
- [3] K. Kikushima, M. Grellier, M. Ohashi, S. Ogoshi, Transition-metal-free catalytic hydrodefluorination of polyfluoroarenes by concerted nucleophilic aromatic substitution with a hydrosilicate. *Angew. Chem. Int. Ed.*, 2017, **56**, 16191–16196.
- [4] J. Beckmann, K. Jurkschat, D. Müller, S. Rabe, M. Schürmann, 1,1,3,3,5,5,7,7-Octaphenyl-1,3,5,7-tetrasiloxane-1,7-diol and its organotin derivatives. Model compounds for diphenylsiloxane polymer, *Organometallics*, 2013, **32**, 3788–3794.
- [5] P. Patschinski, C. Zhang, H. Zipse, The Lewis base-catalyzed silylation of alcohols—a mechanistic analysis, *J. Org. Chem.*, 2014, **79**, 8348–8357.
- [6] R. T. Anderson, X. N. Zang, R. Fernando, M. J. Dzara, C. Ngo, M. Sharps, R. Pinals, S. Pylypenko, M. T. Lusk, A. Sellinger, Direct conversion of hydride- to siloxane-terminated silicon quantum dots, *J. Phys. Chem. C*, 2016, **120**, 25822–25831.

IV. Copies of the ^1H , ^{19}F and ^{13}C NMR spectra

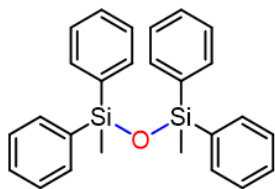


LC-188-3_Carbon-2-4.jdf

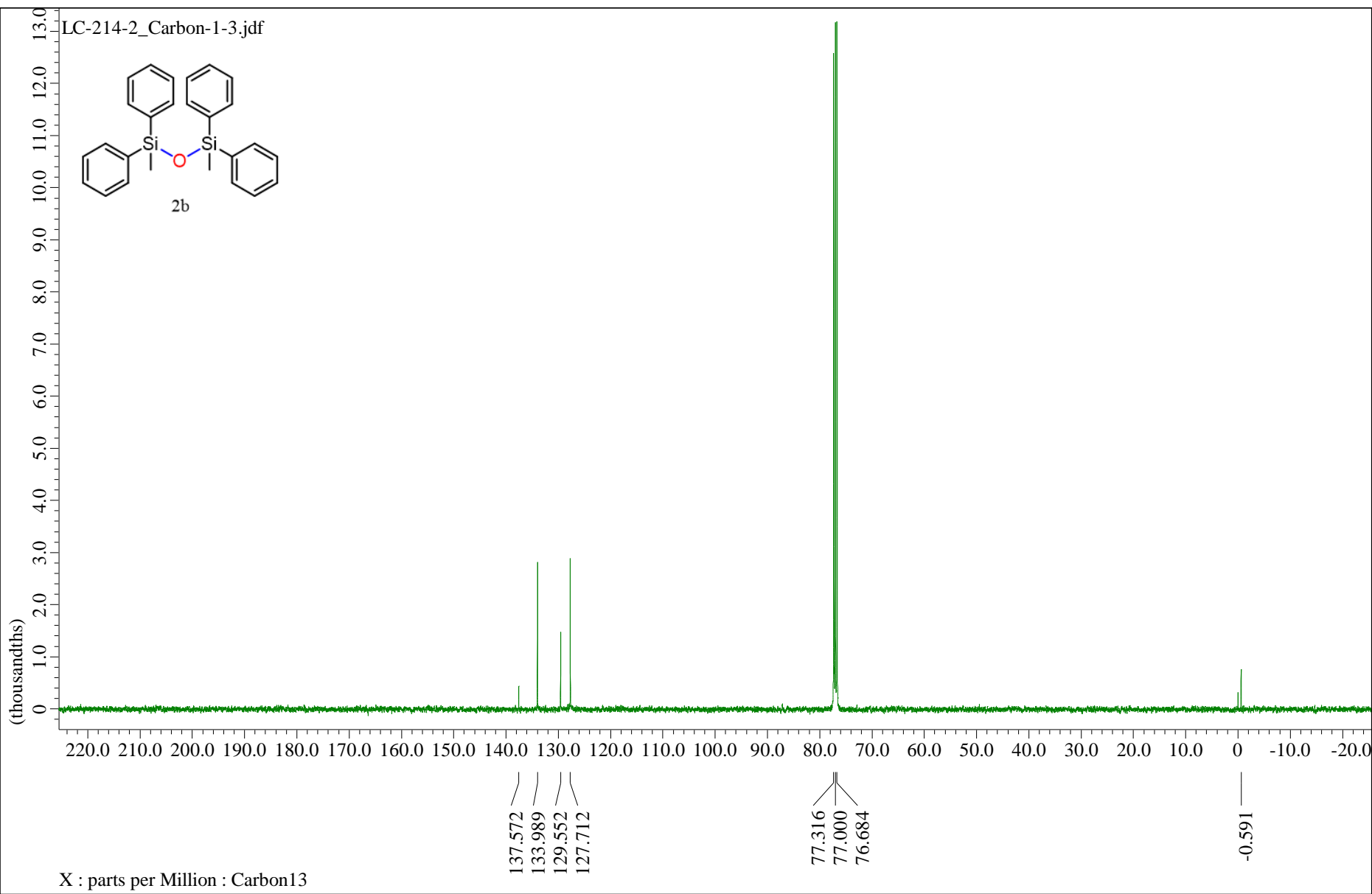


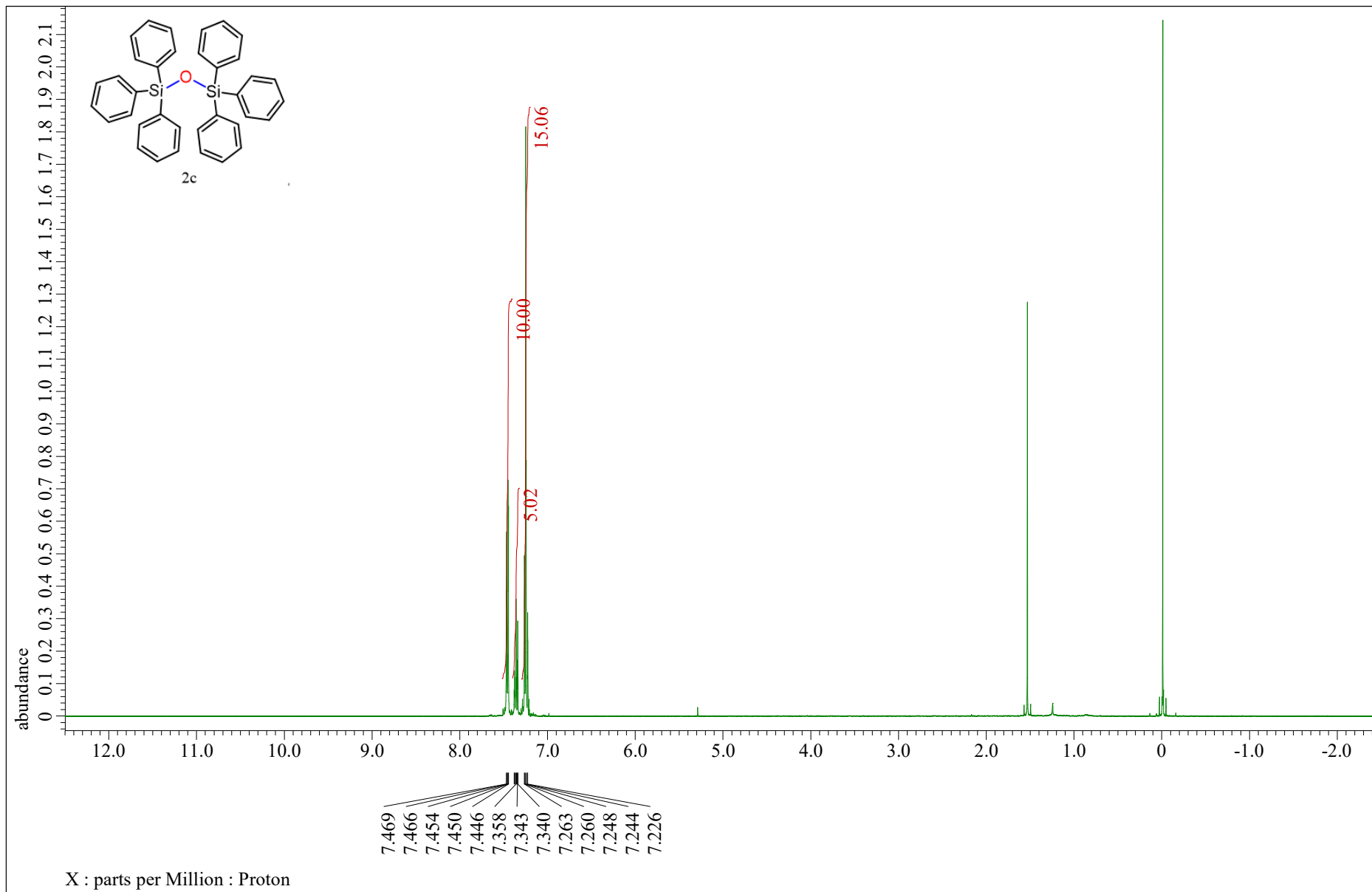


LC-214-2_Carbon-1-3.jdf

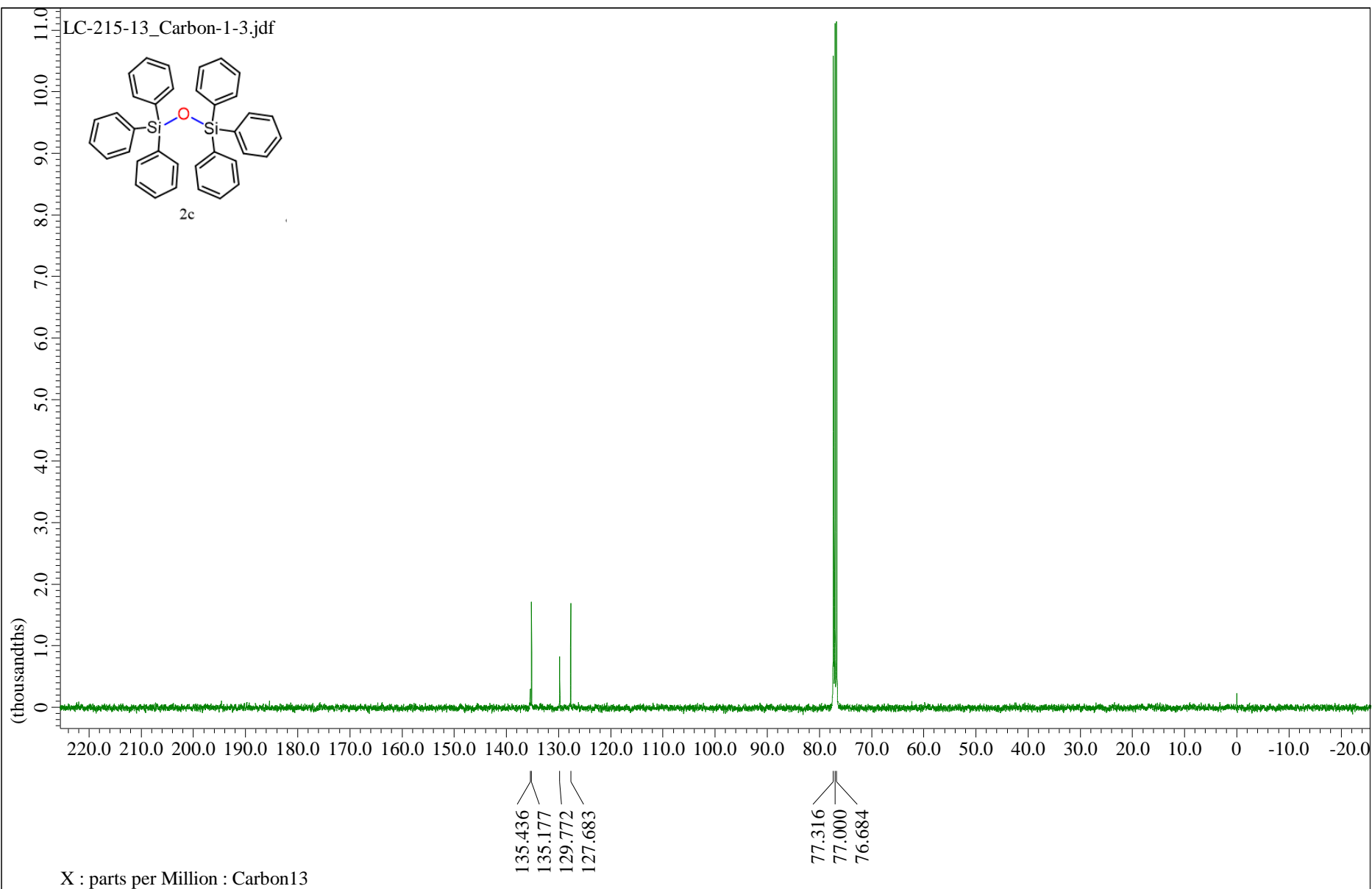
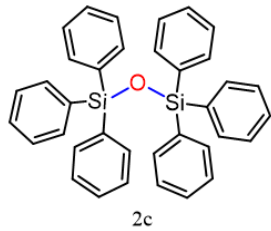


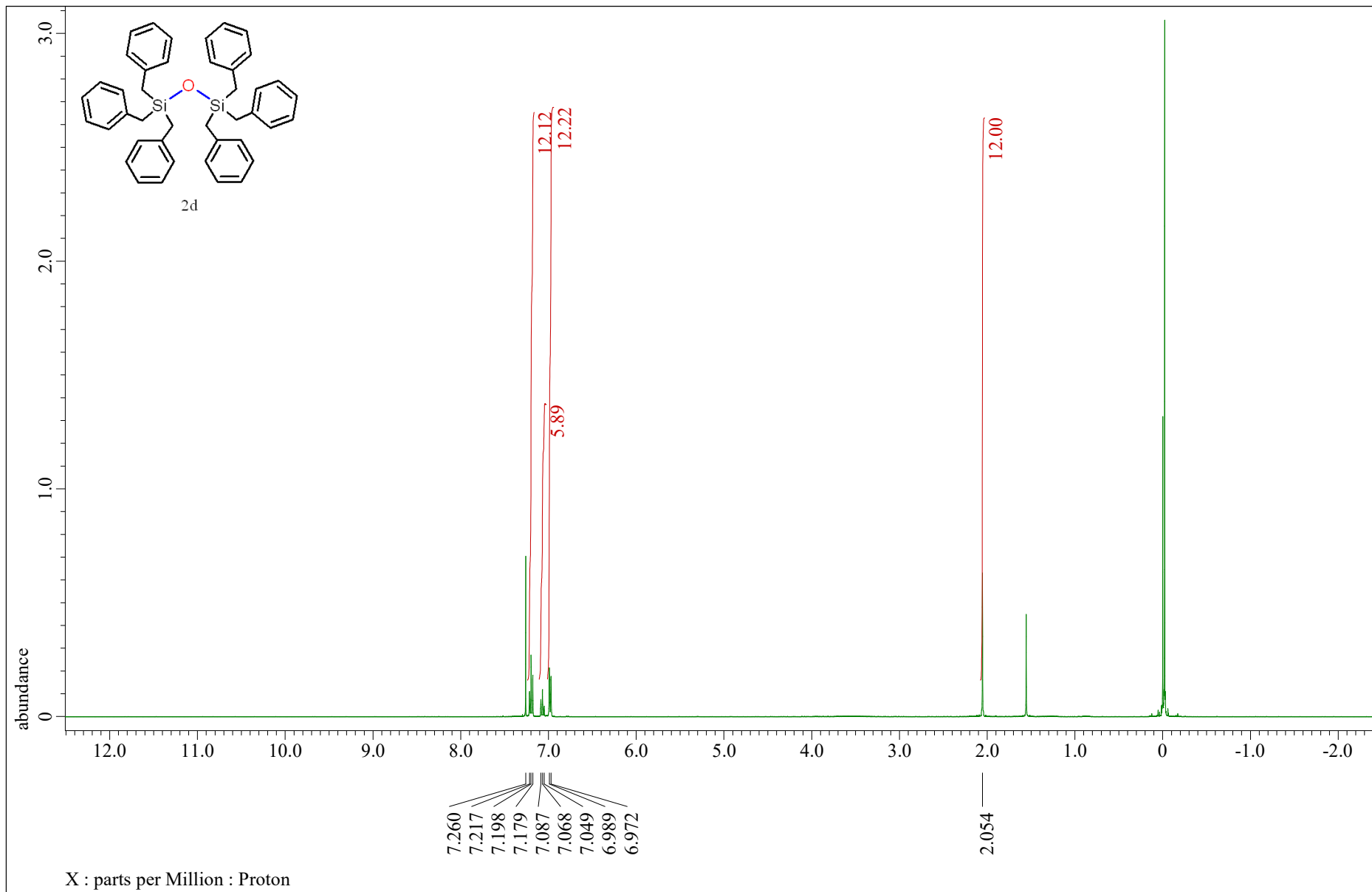
2b



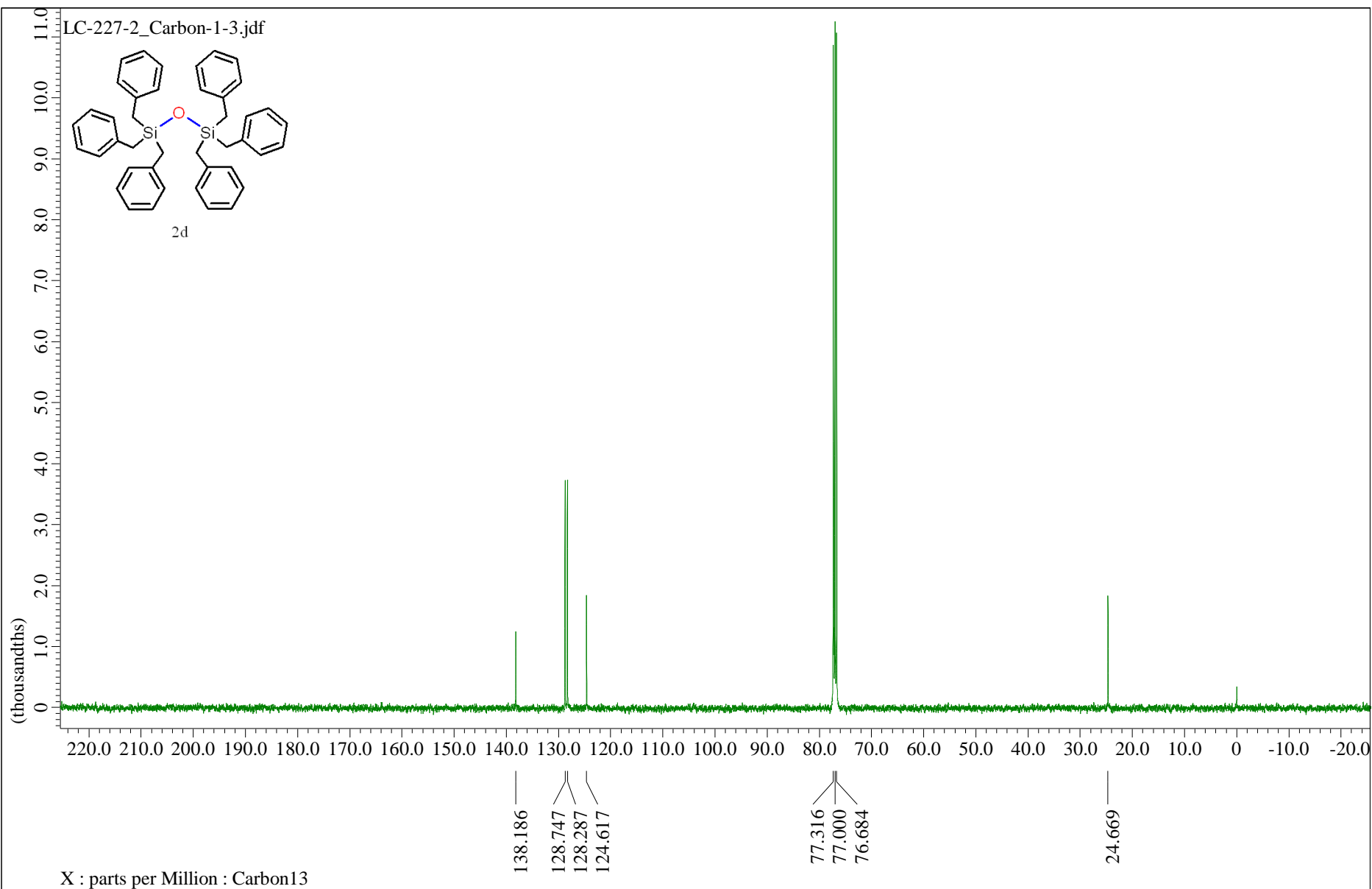
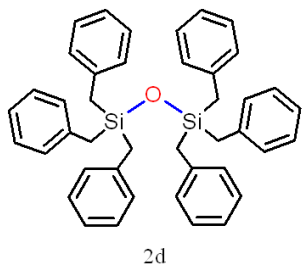


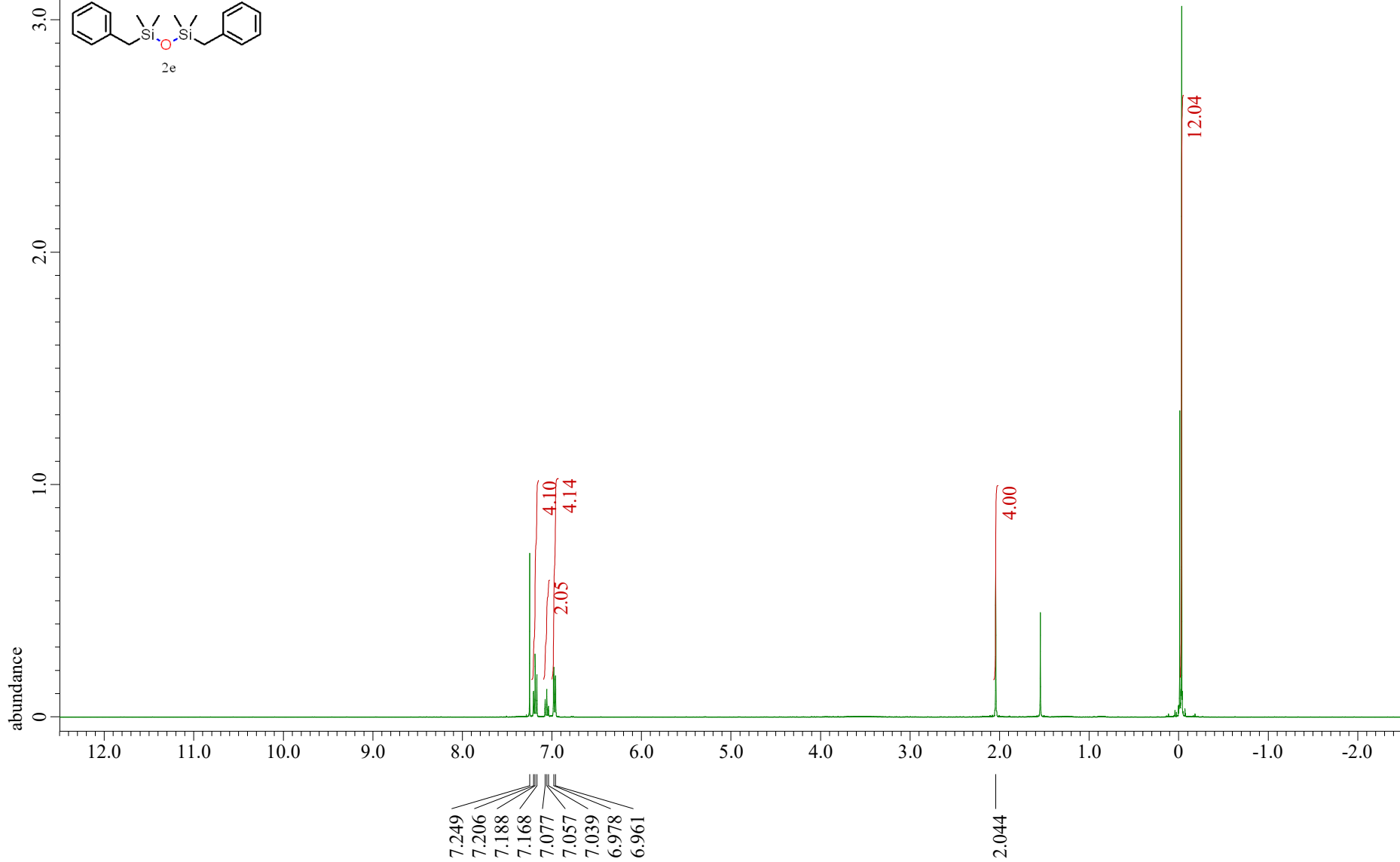
LC-215-13_Carbon-1-3.jdf





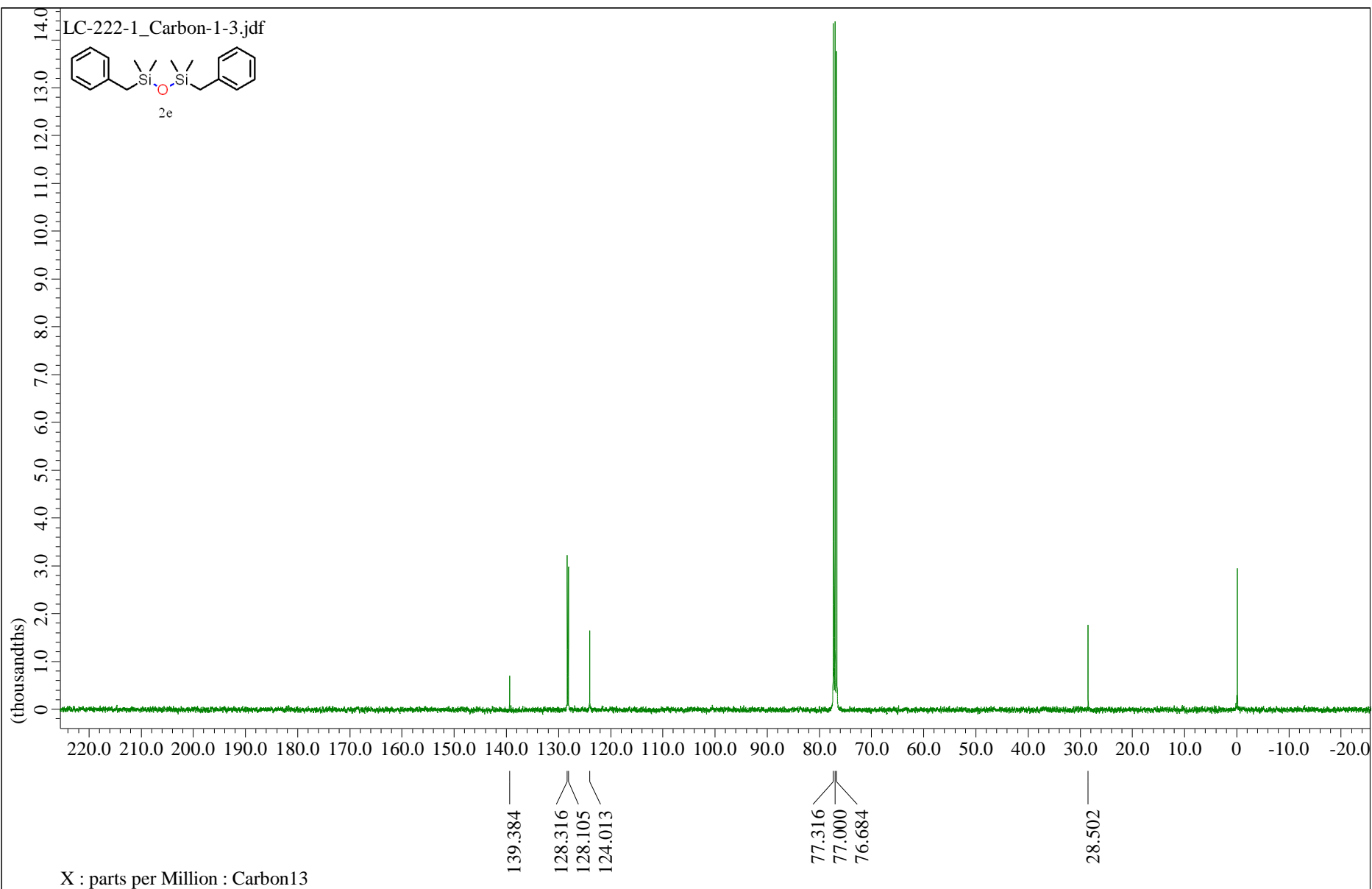
LC-227-2_Carbon-1-3.jdf



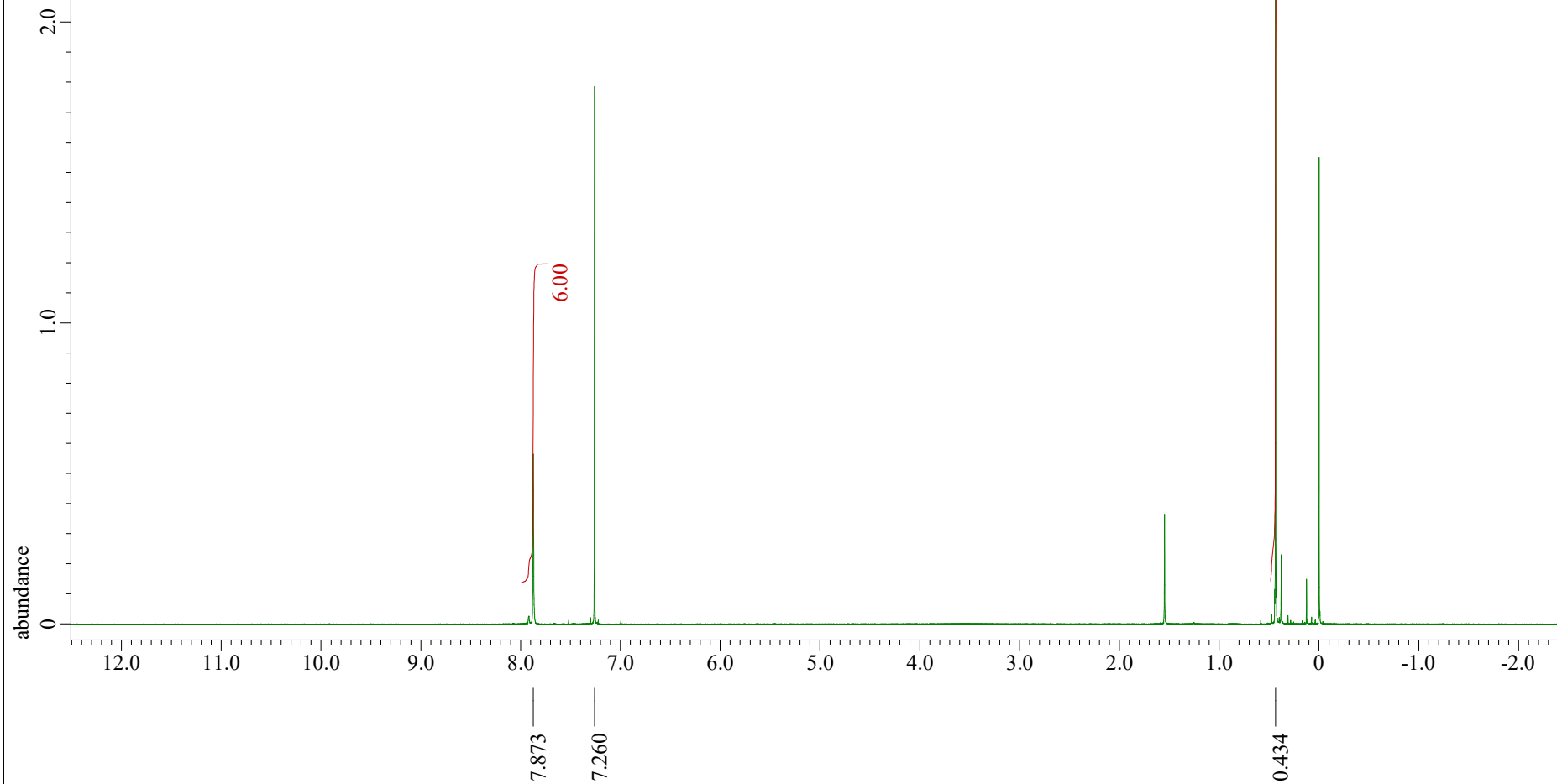
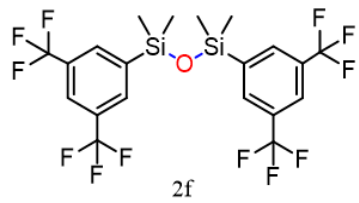


X : parts per Million : Proton

LC-222-1_Carbon-1-3.jdf

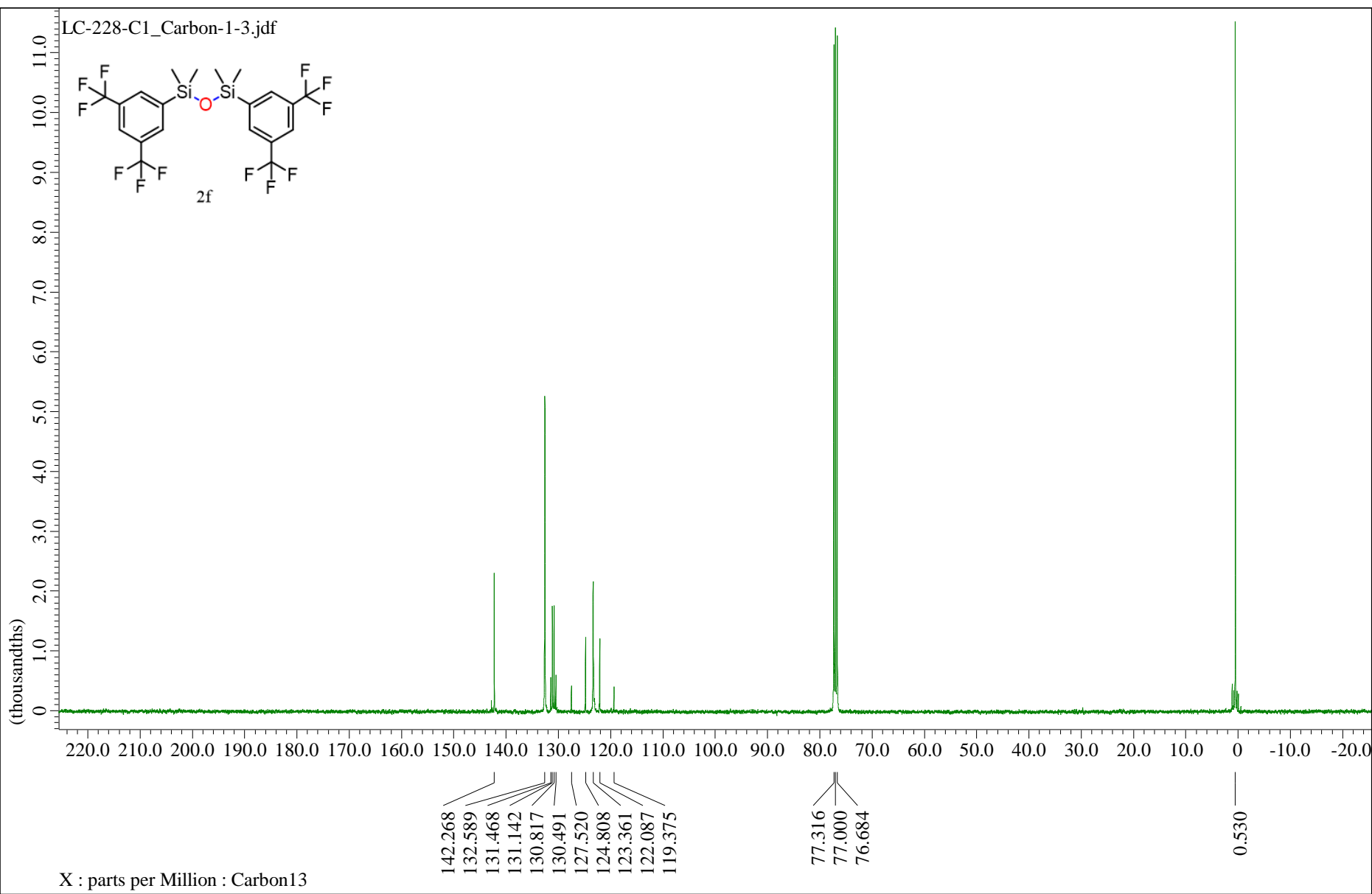
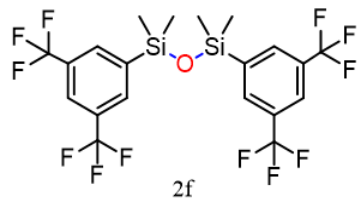


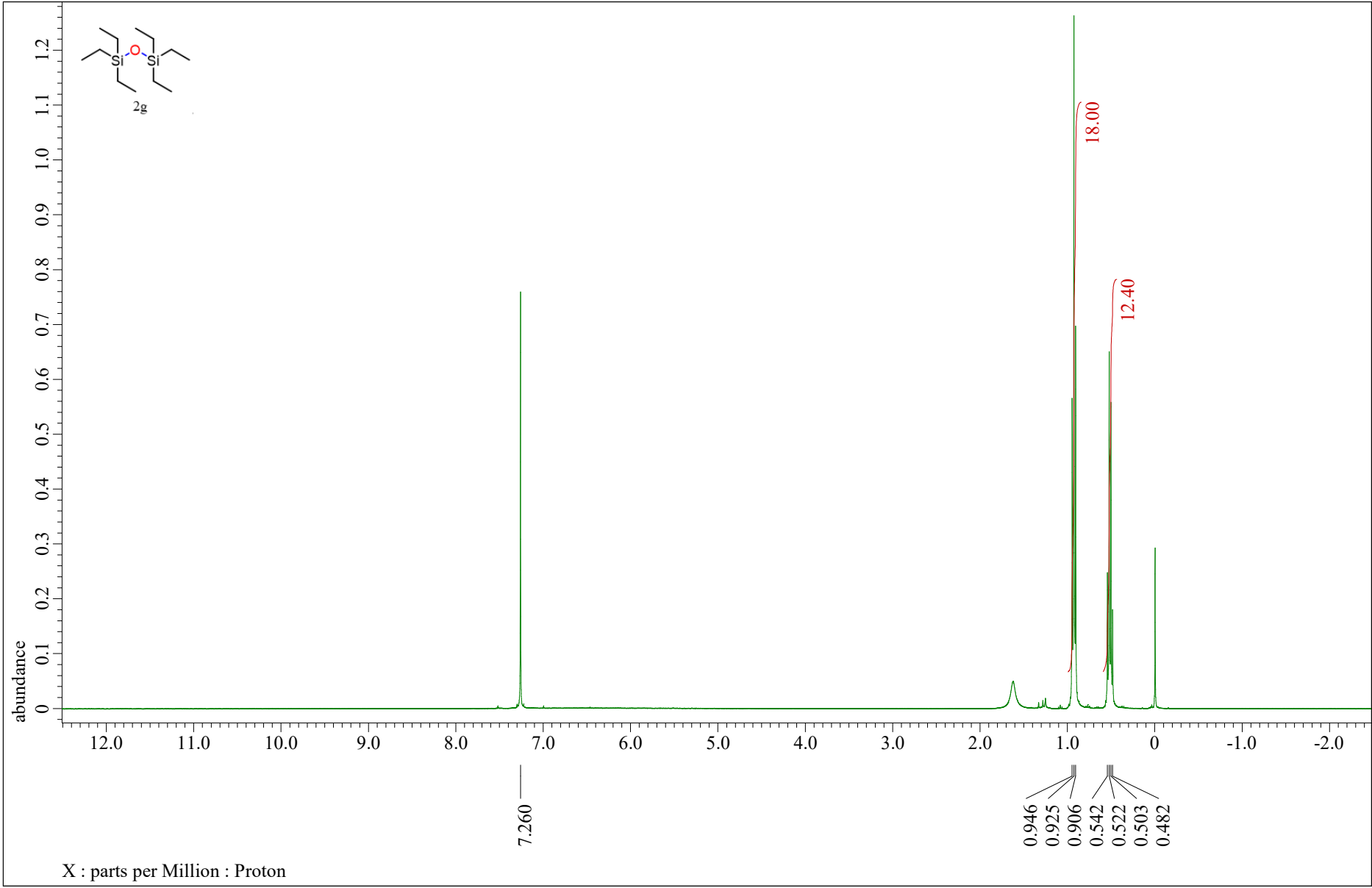
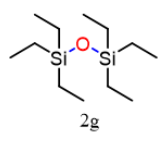
X : parts per Million : Carbon13



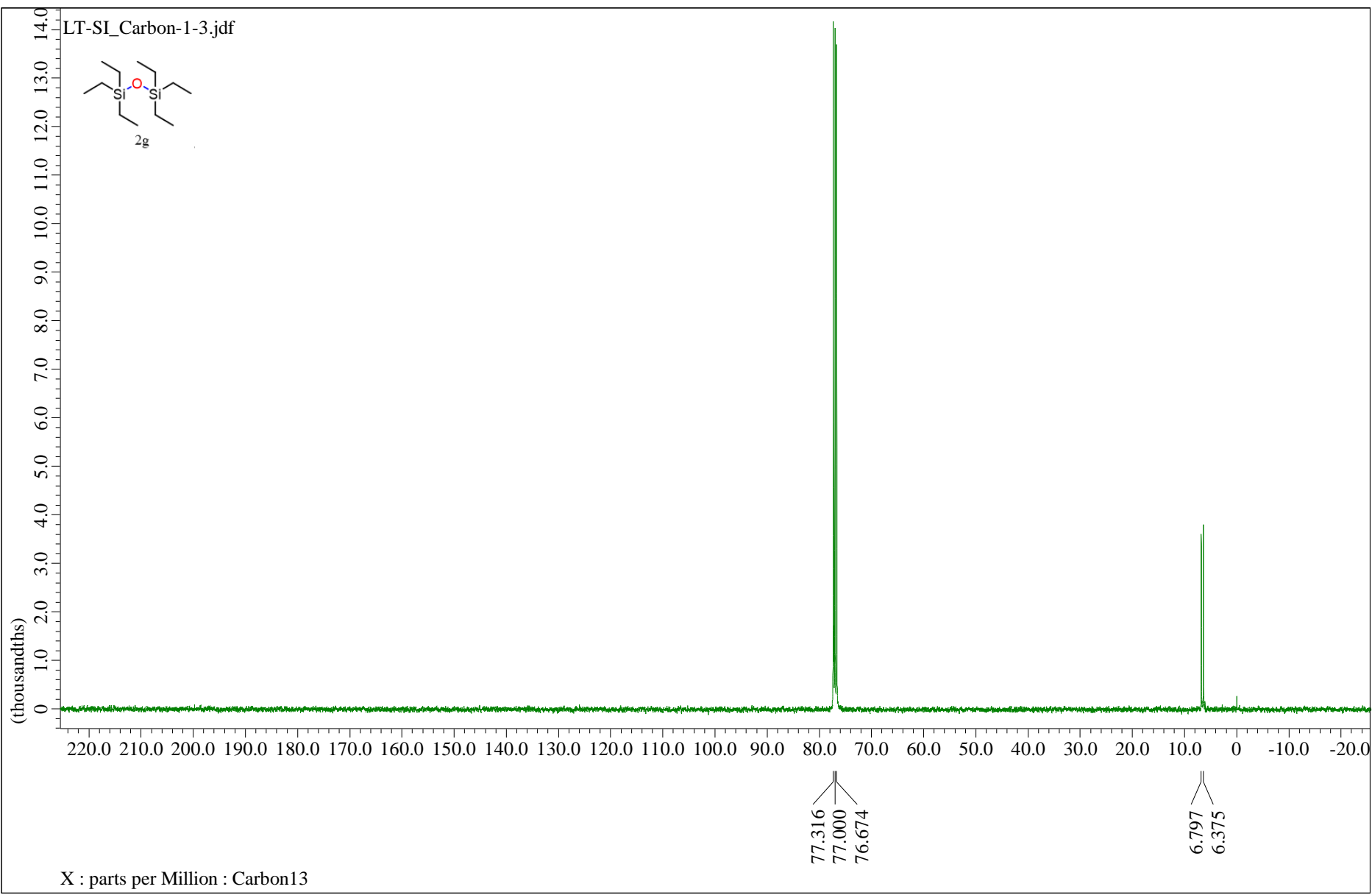
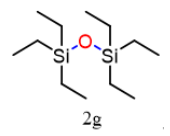
X : parts per Million : Proton

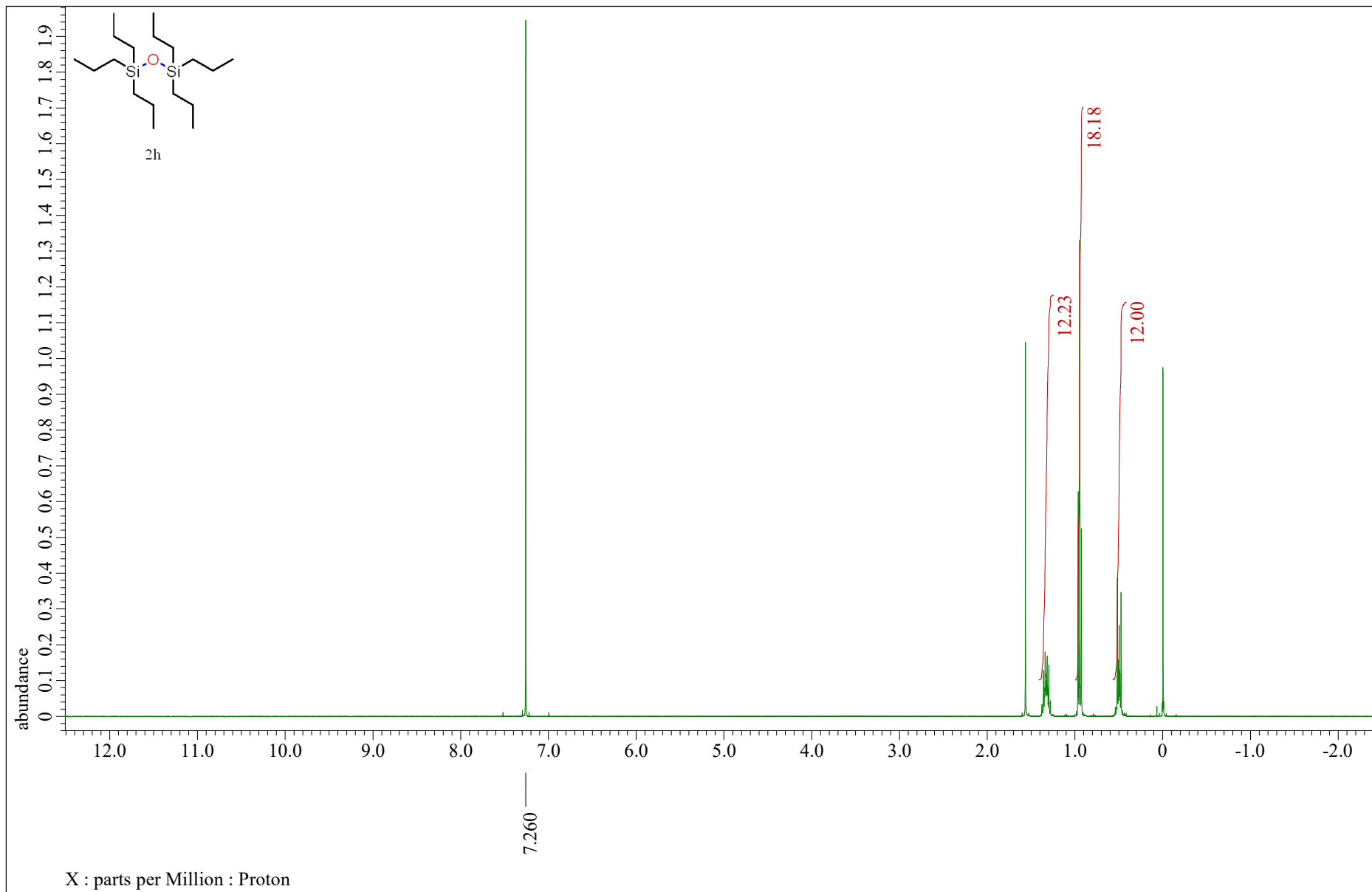
LC-228-C1_Carbon-1-3.jdf



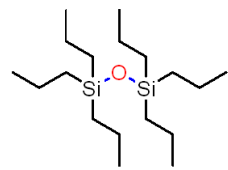


LT-SI_Carbon-1-3.jdf

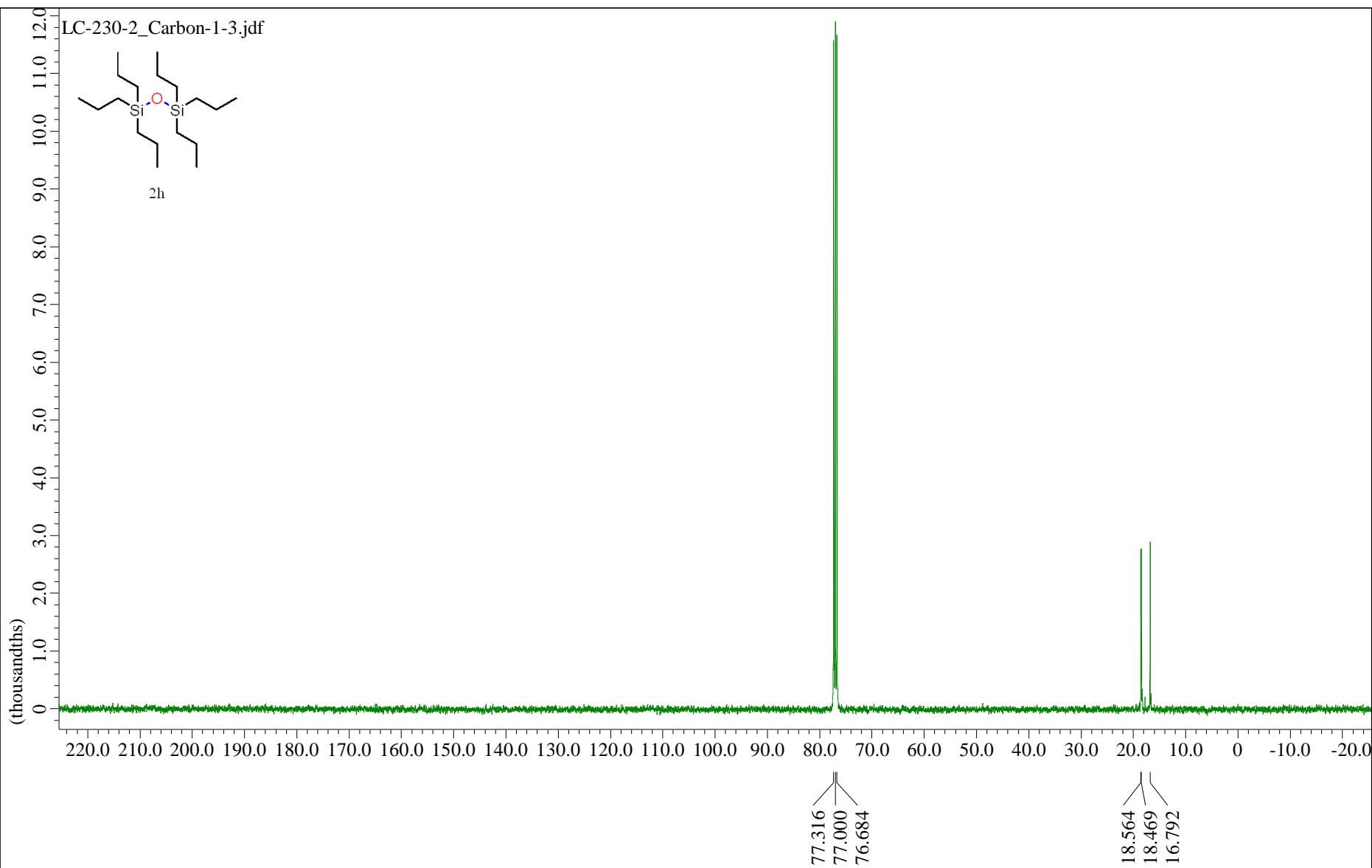




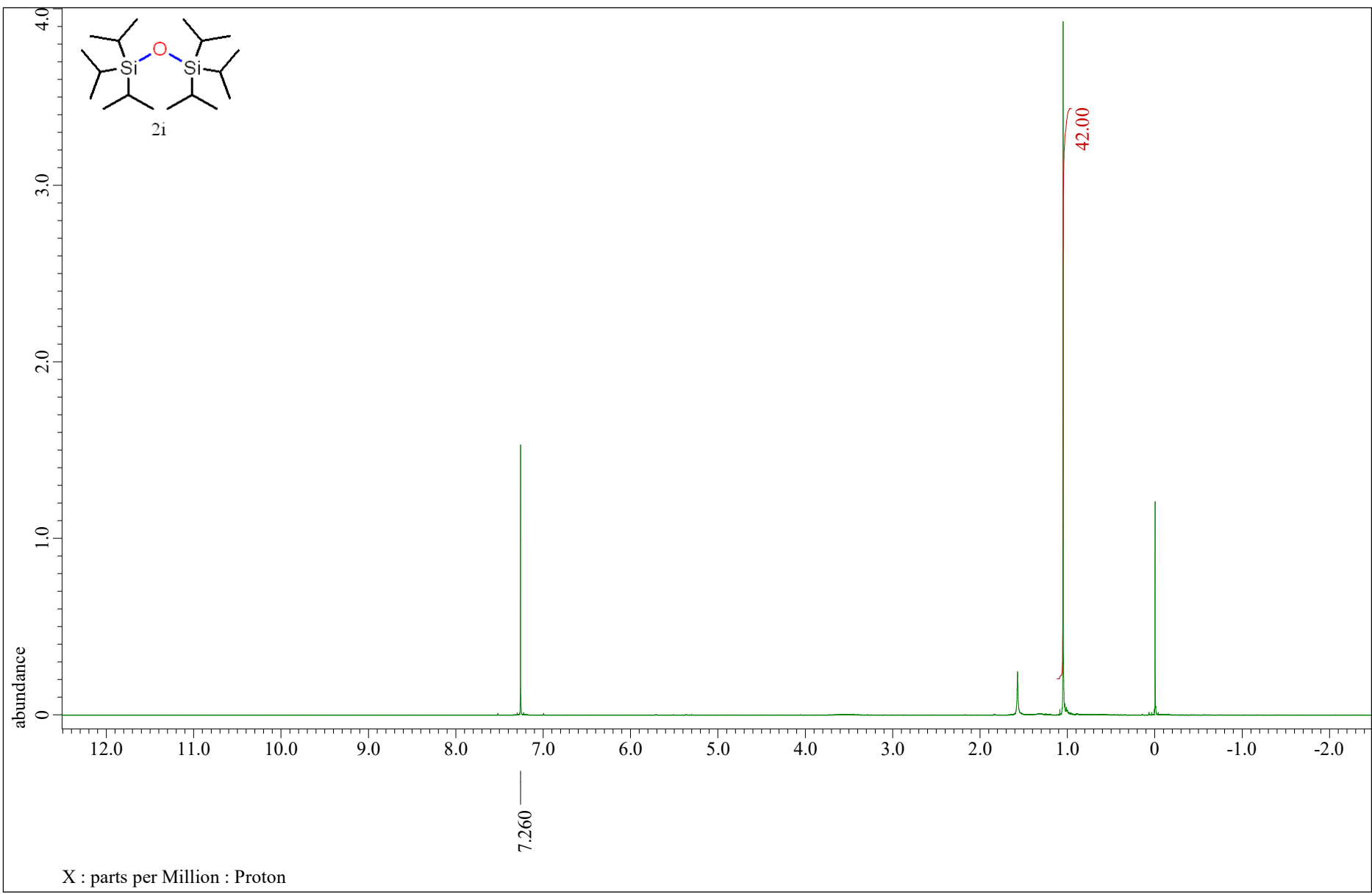
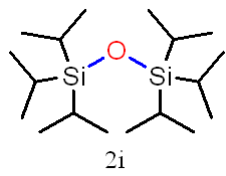
LC-230-2_Carbon-1-3.jdf



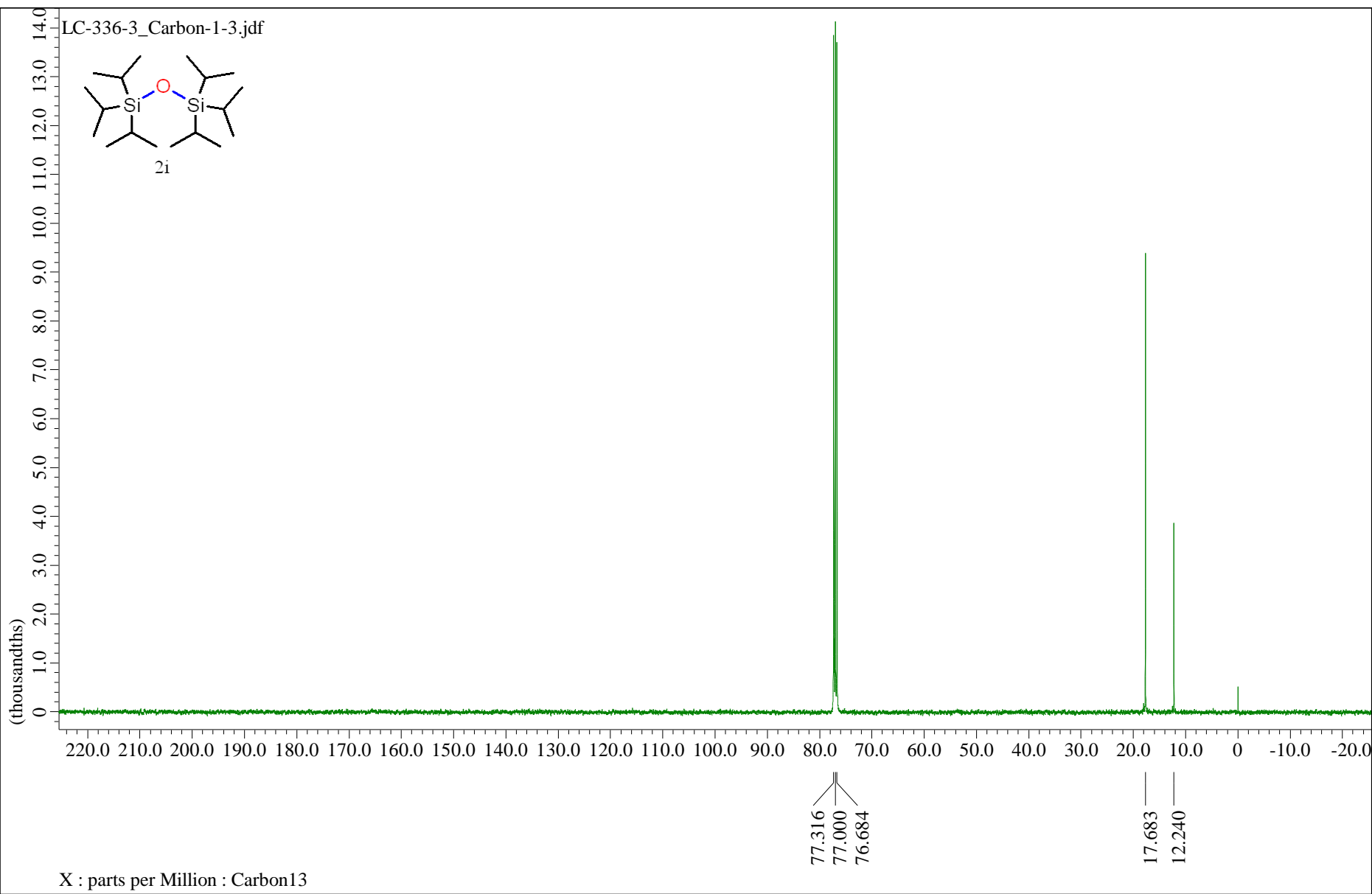
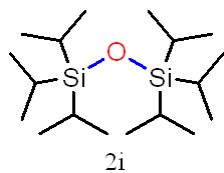
2h

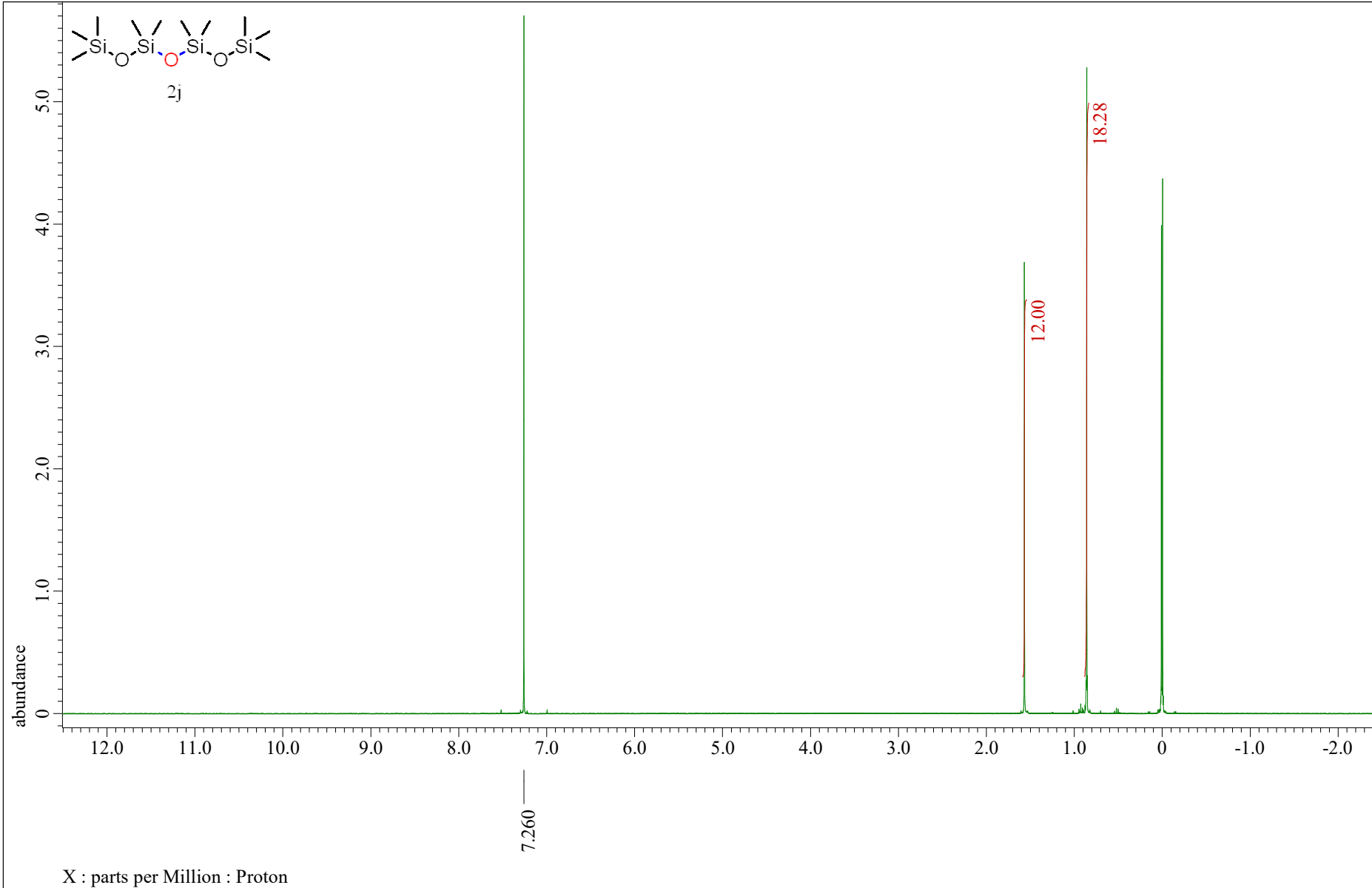
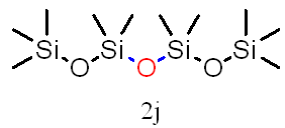


X : parts per Million : Carbon13

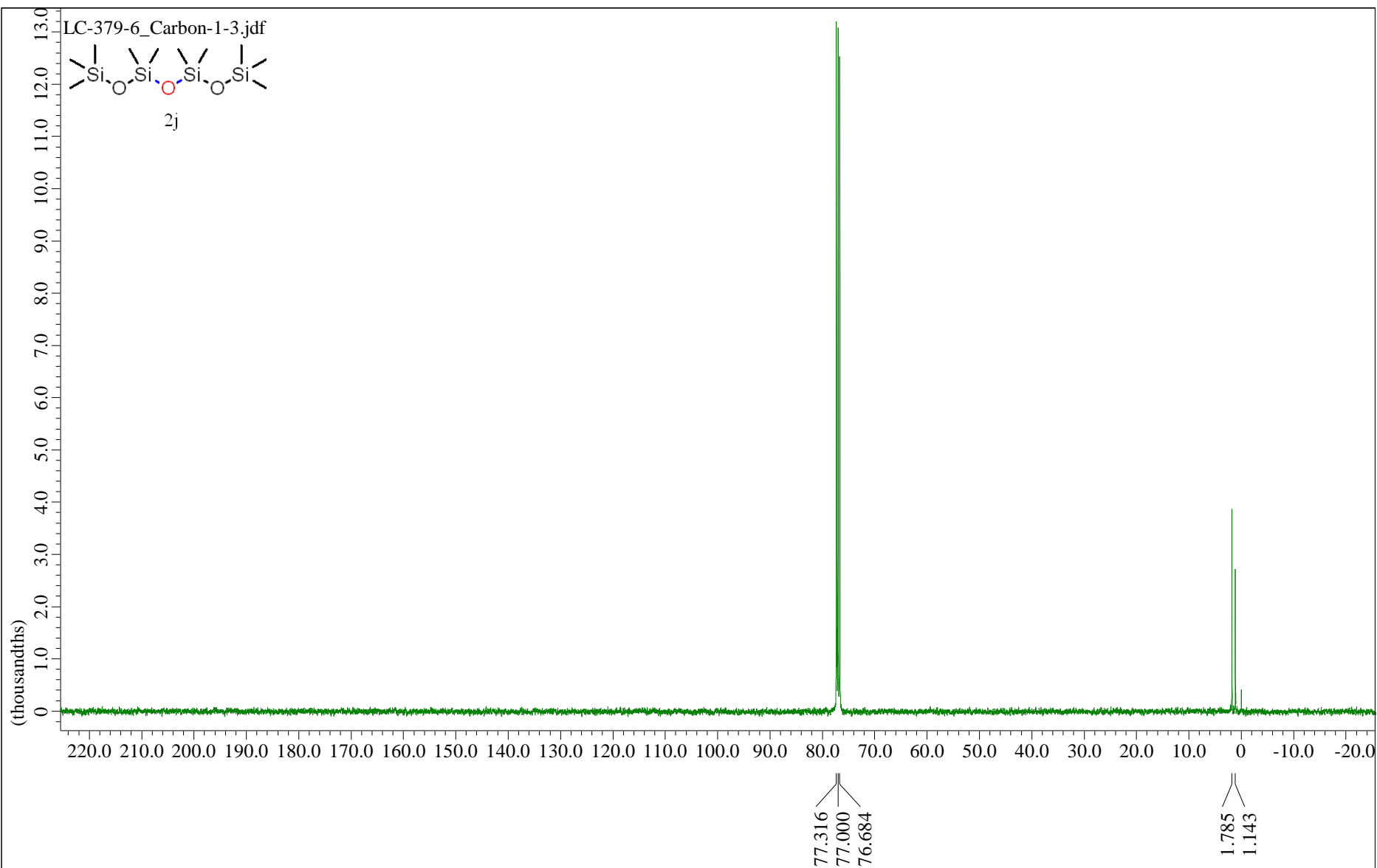
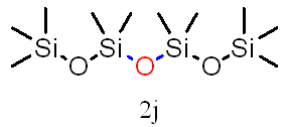


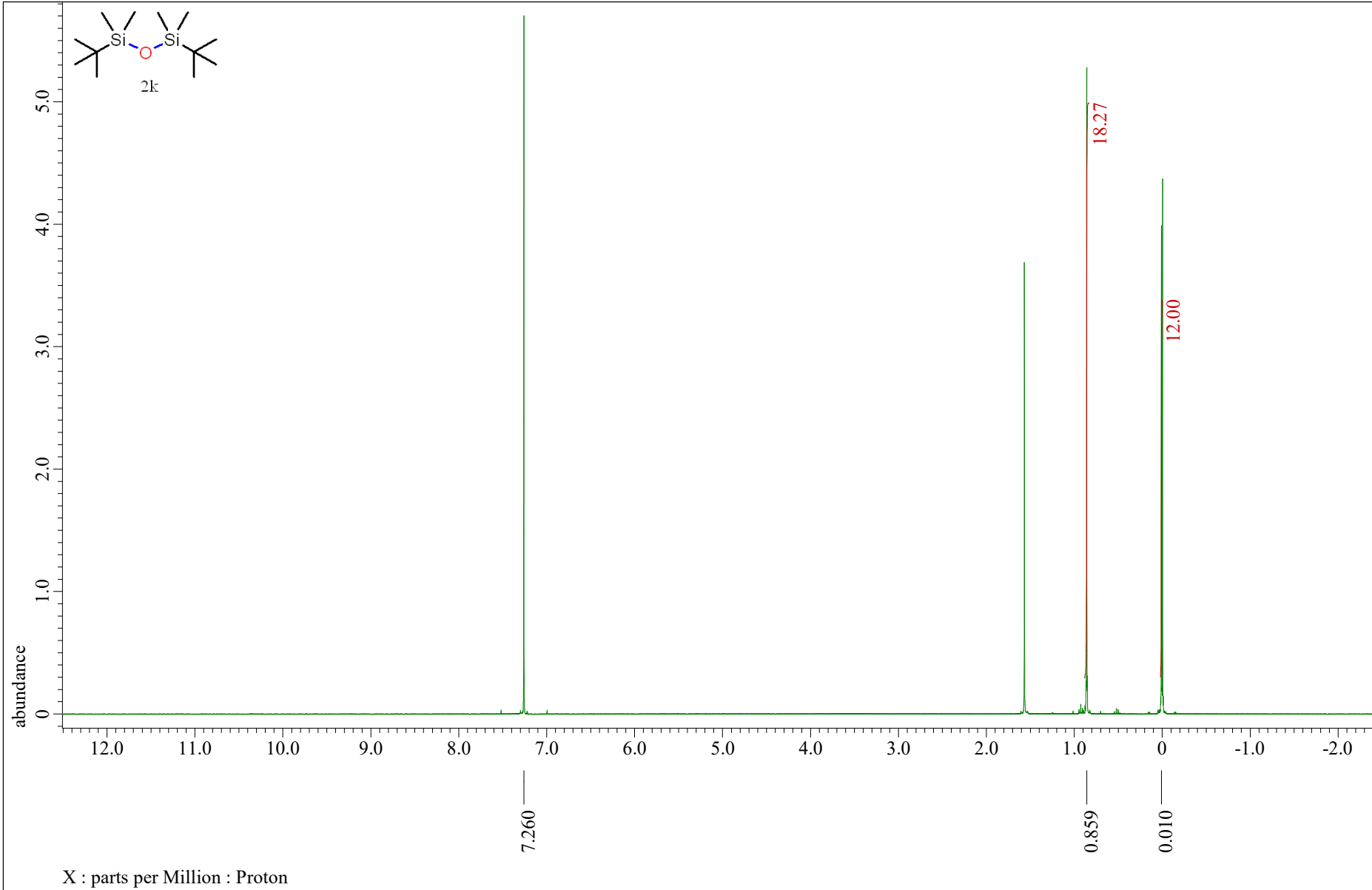
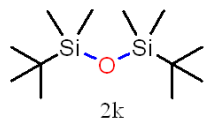
LC-336-3_Carbon-1-3.jdf



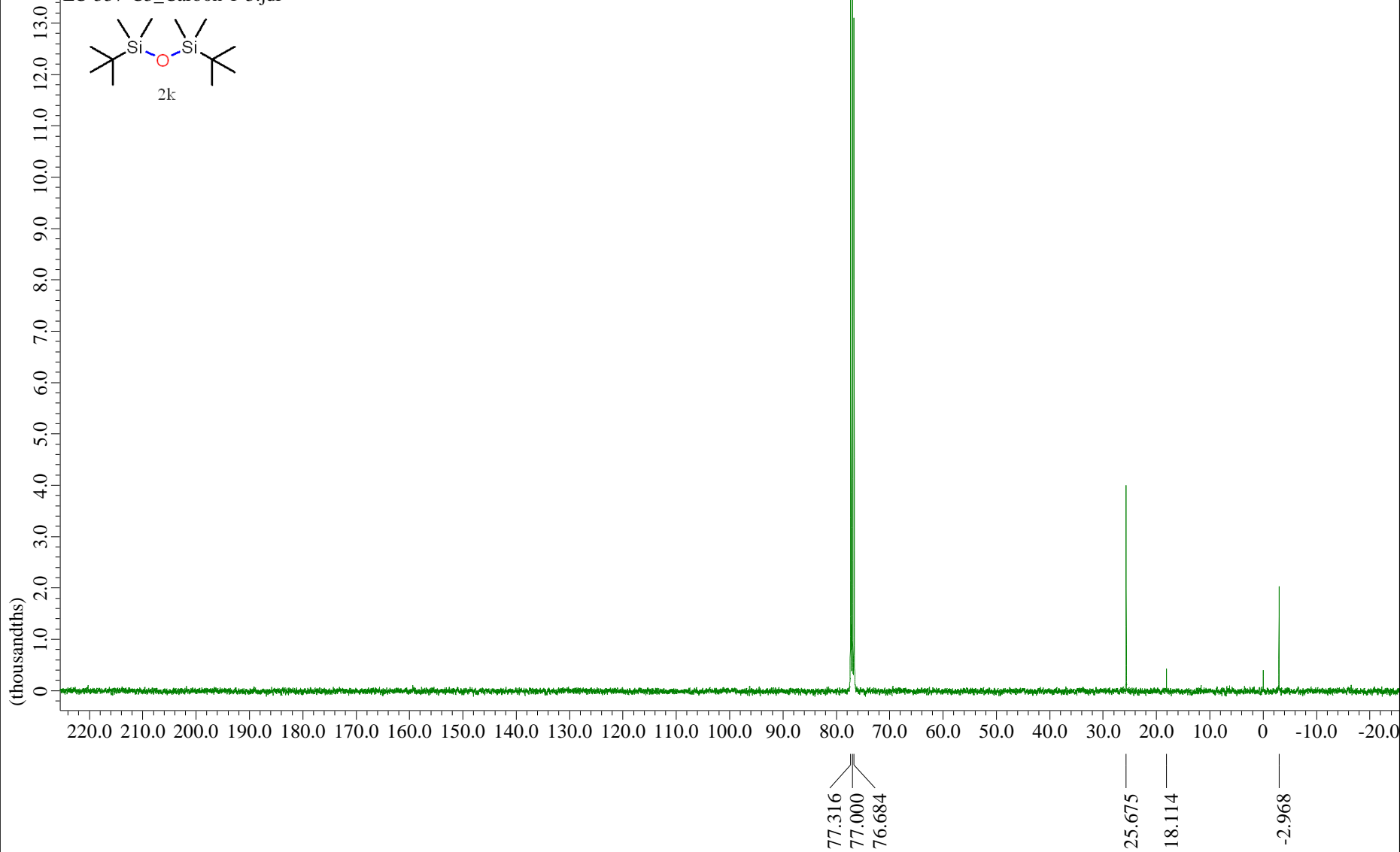
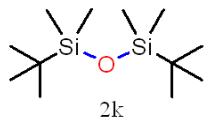


LC-379-6_Carbon-1-3.jdf

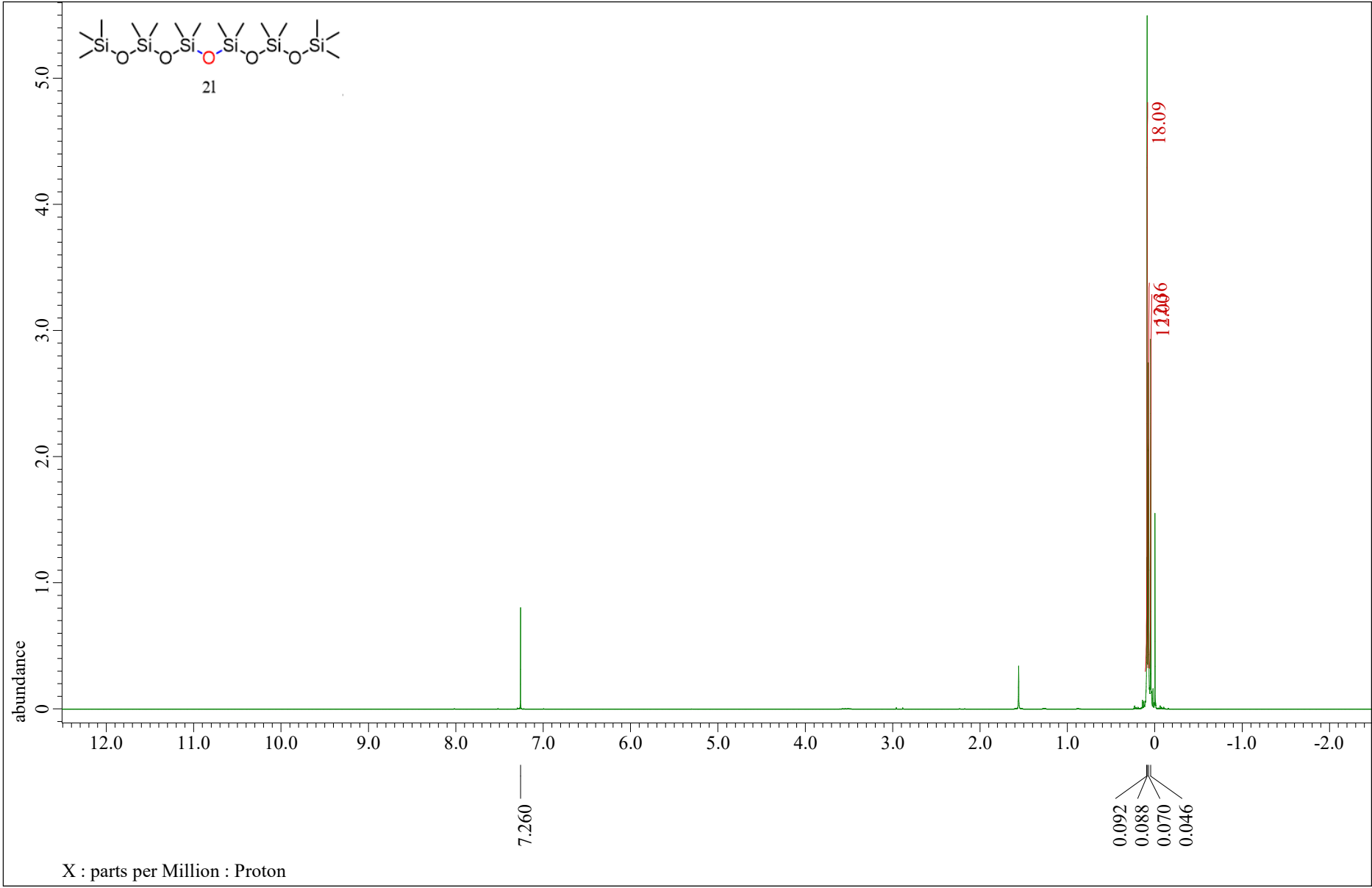
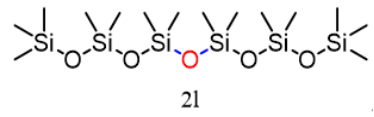




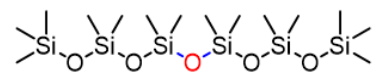
LC-337-C3_Carbon-1-3.jdf



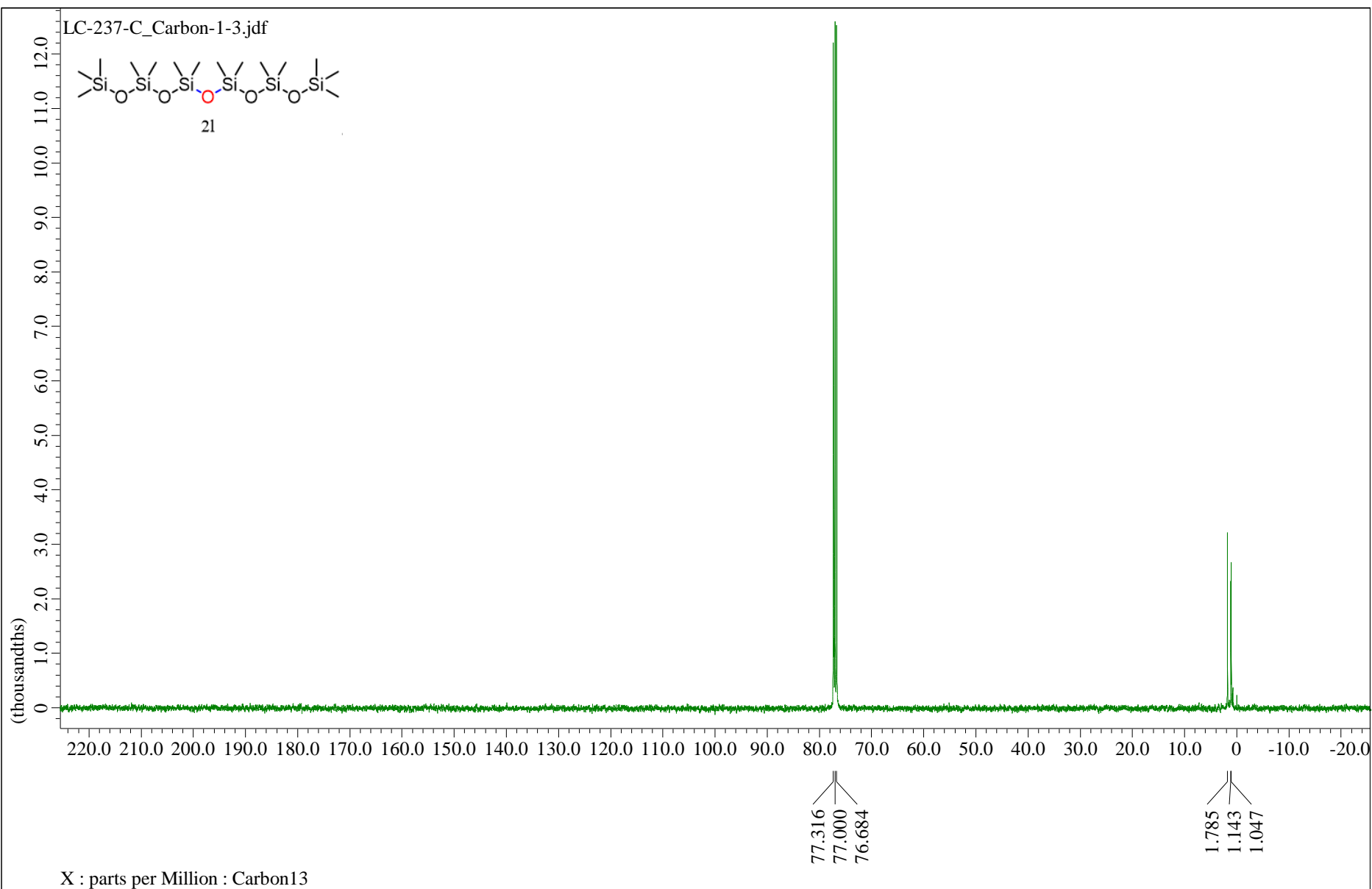
X : parts per Million : Carbon13

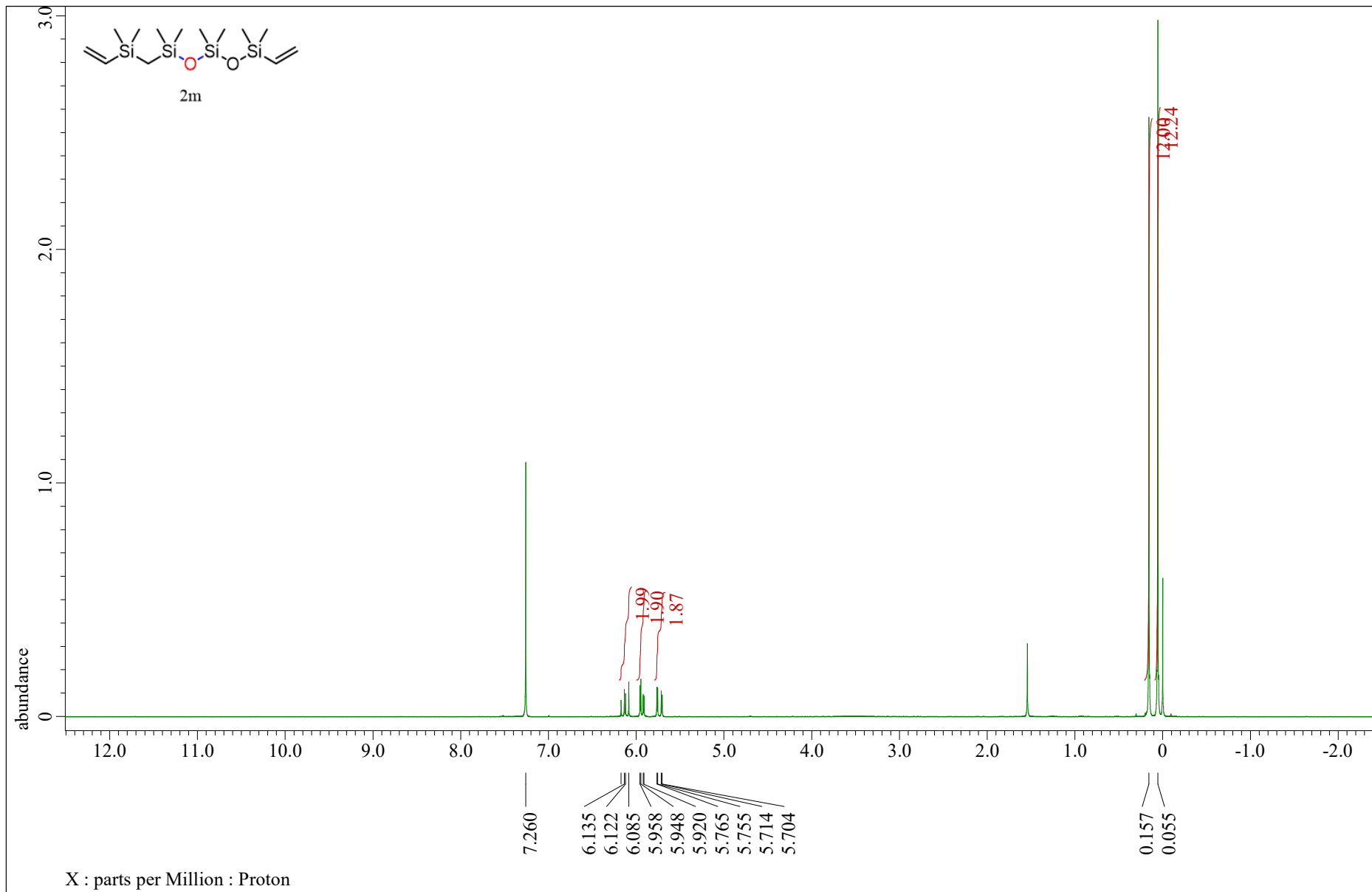


LC-237-C_Carbon-1-3.jdf

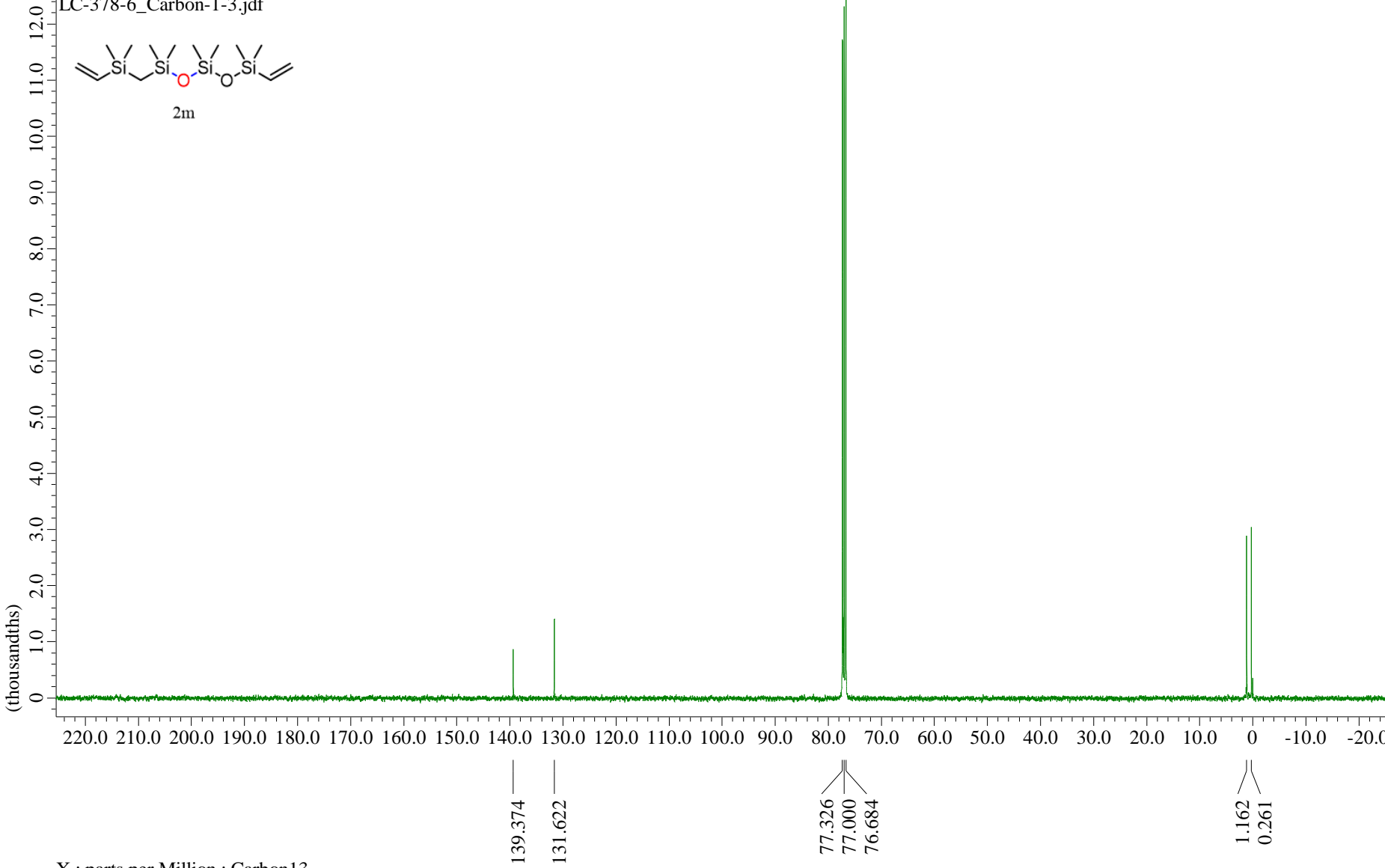


21

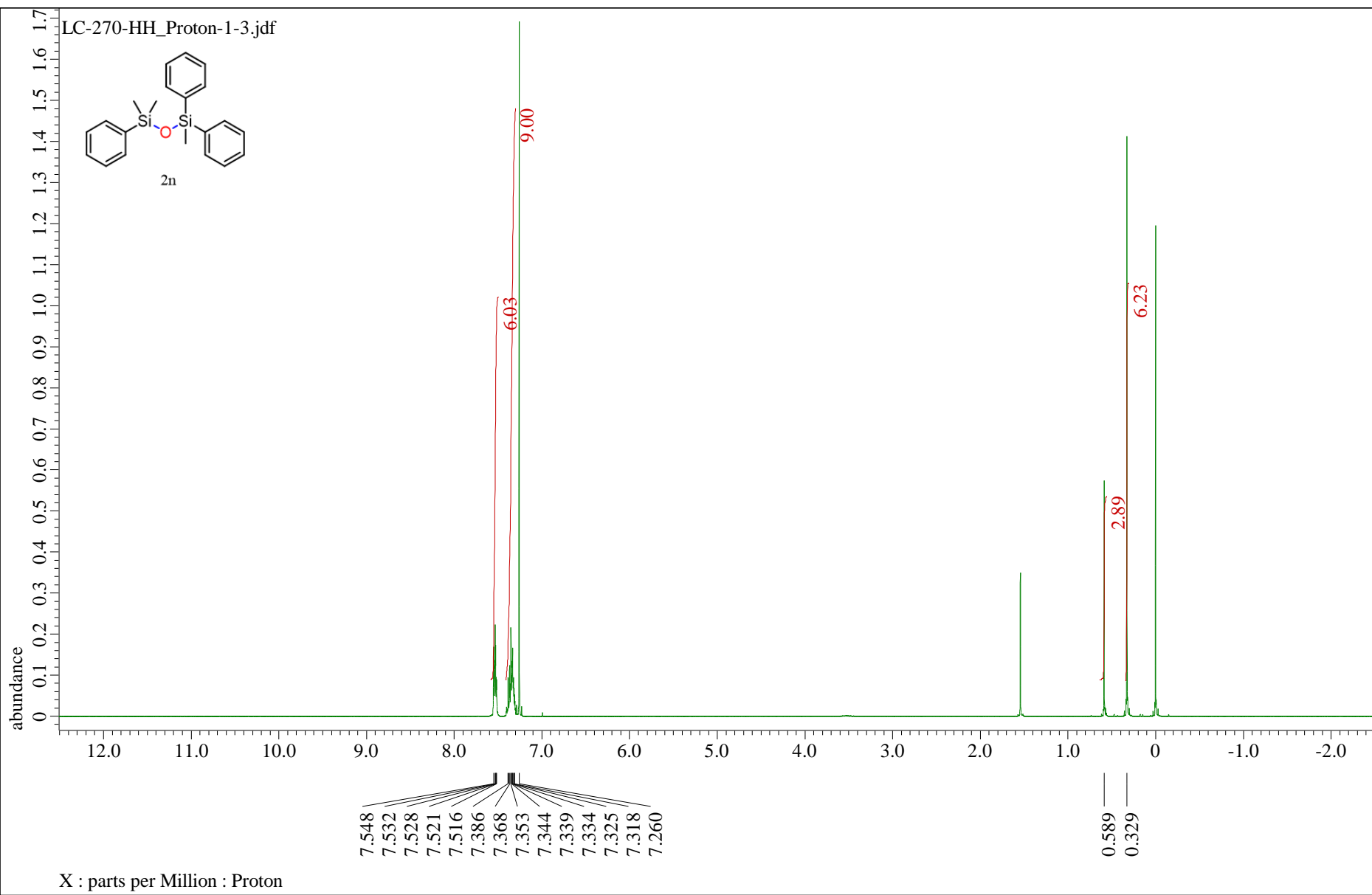
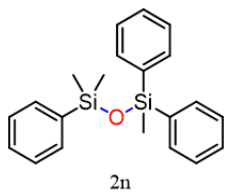




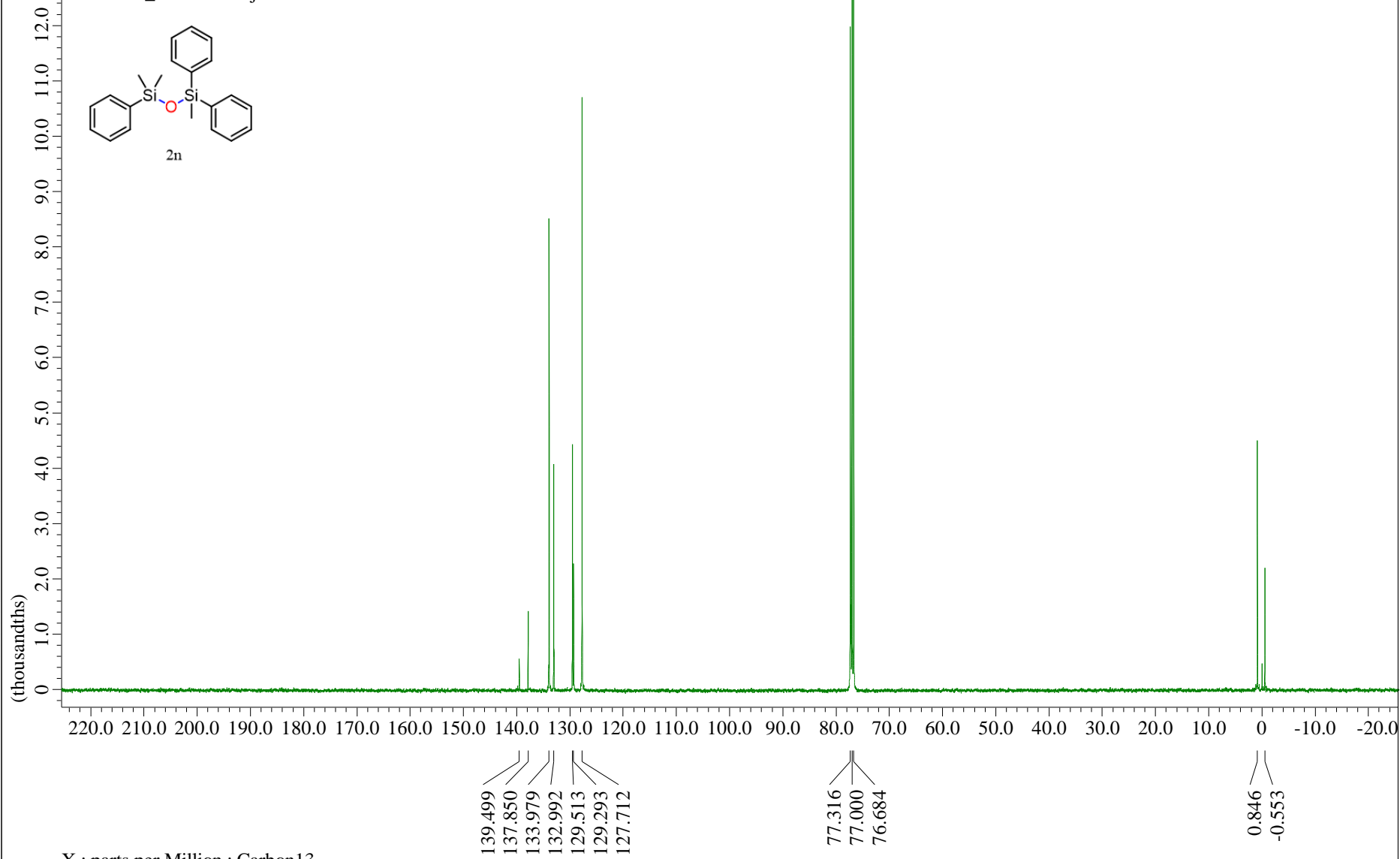
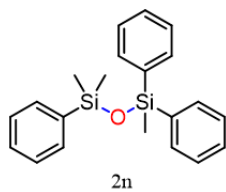
LC-378-6_Carbon-1-3.jdf



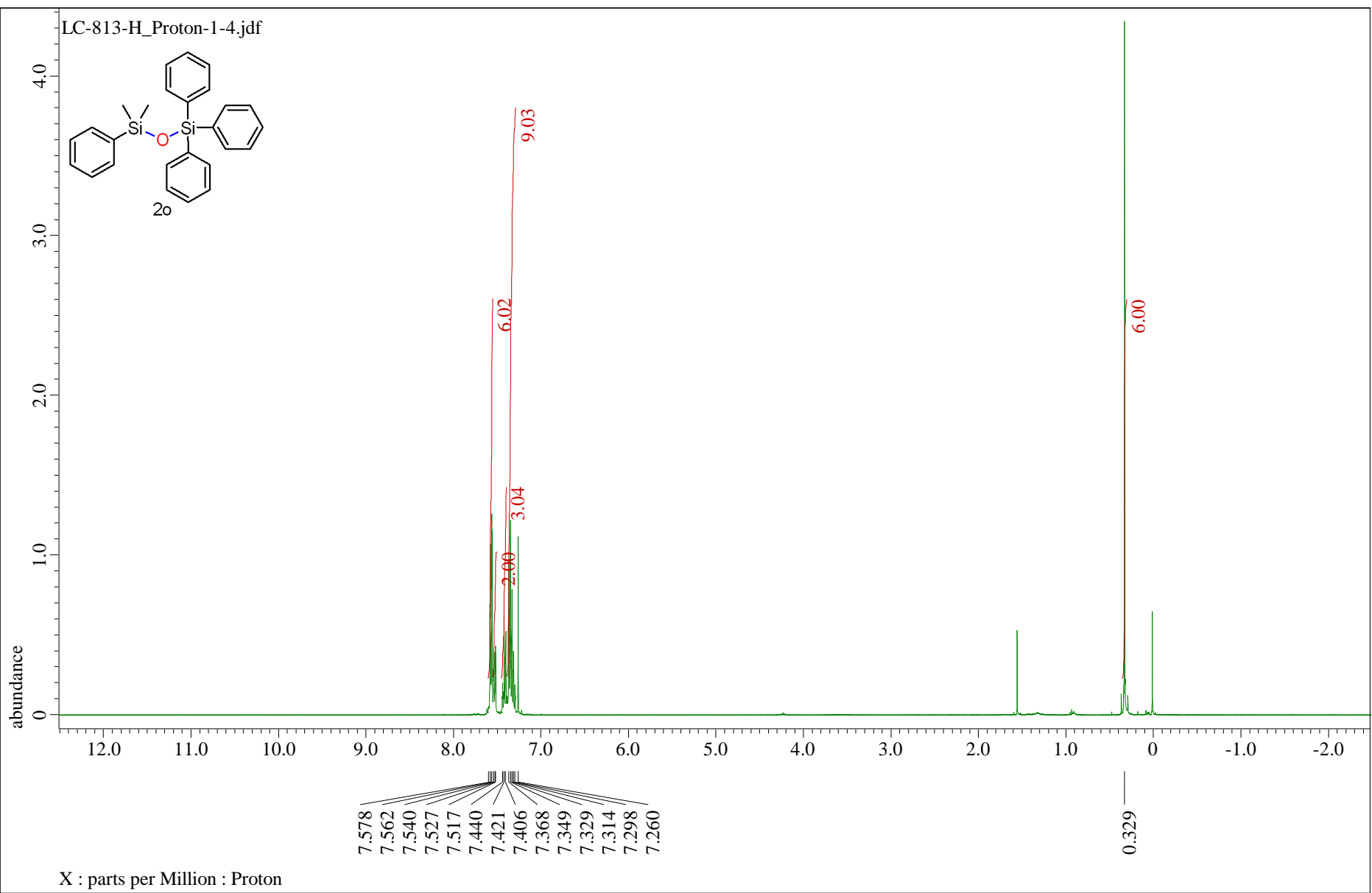
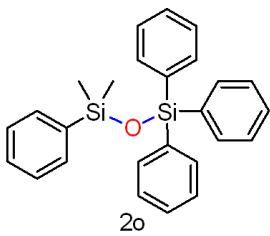
LC-270-HH_Proton-1-3.jdf



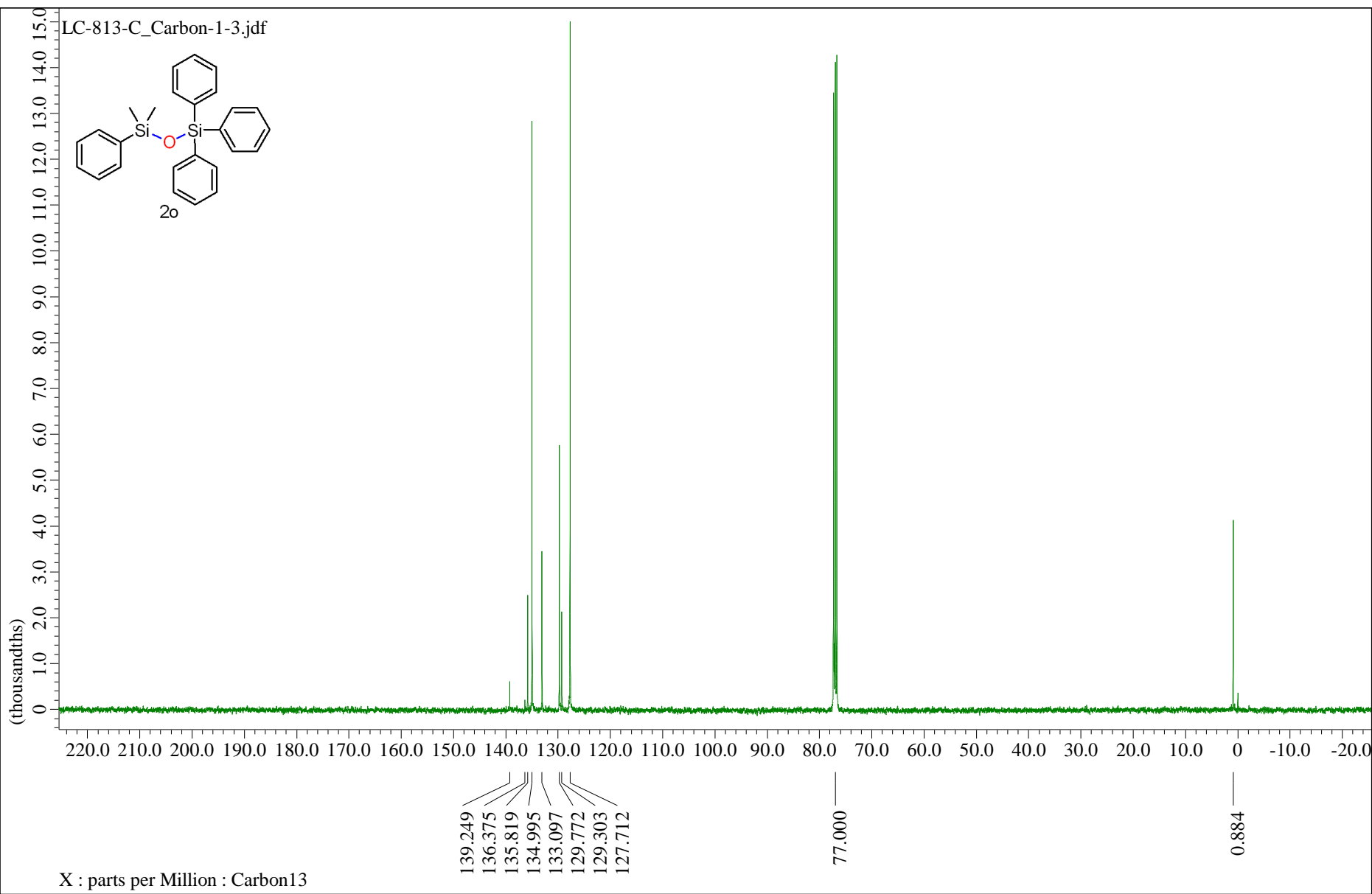
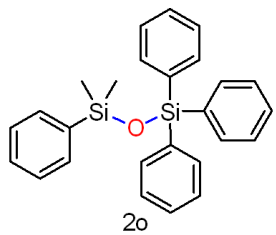
LC-270-C_Carbon-1-3.jdf



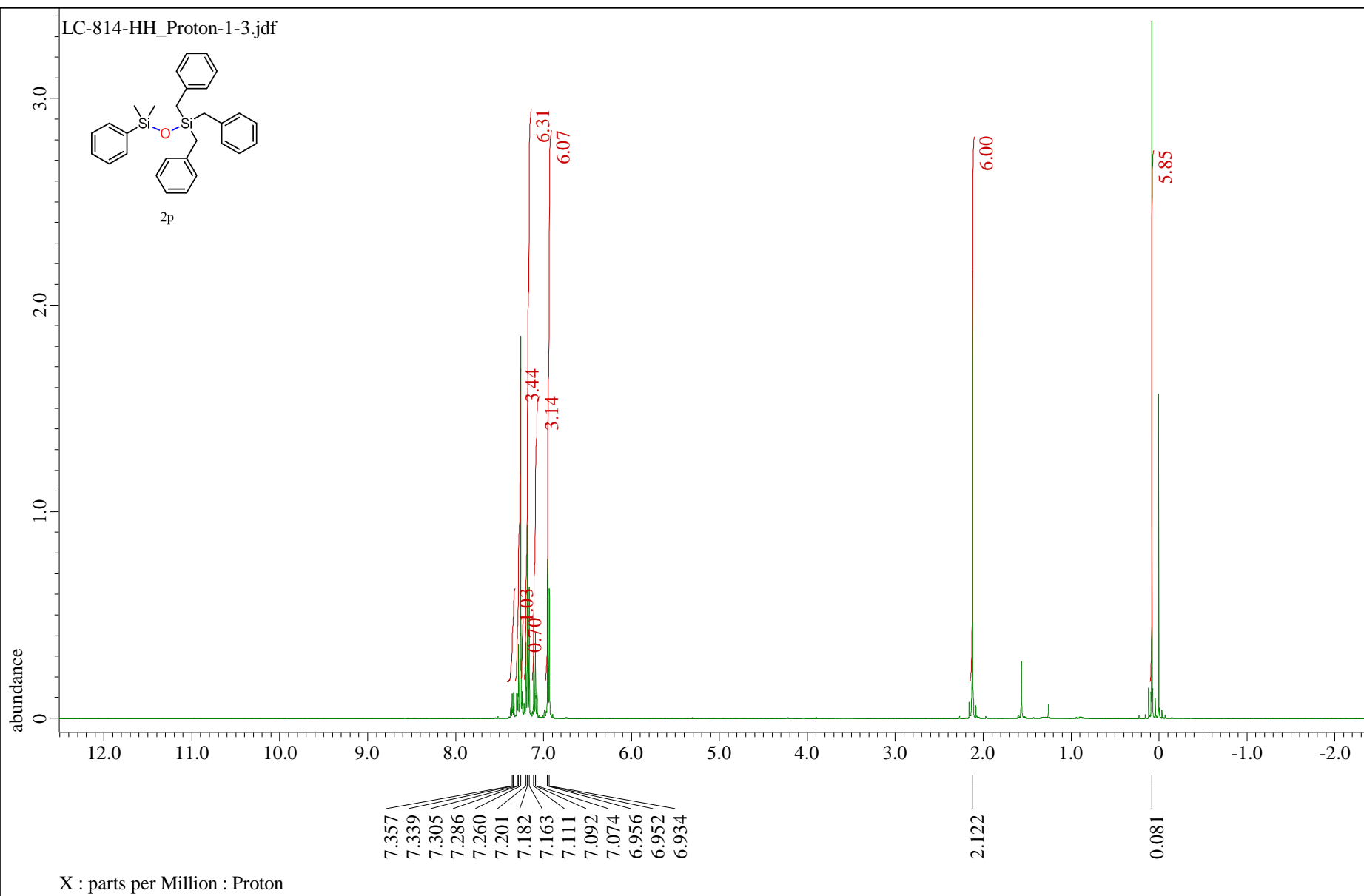
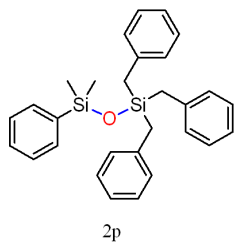
LC-813-H_Proton-1-4.jdf



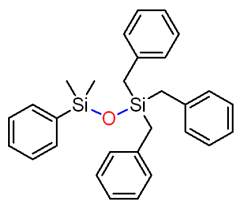
LC-813-C_Carbon-1-3.jdf



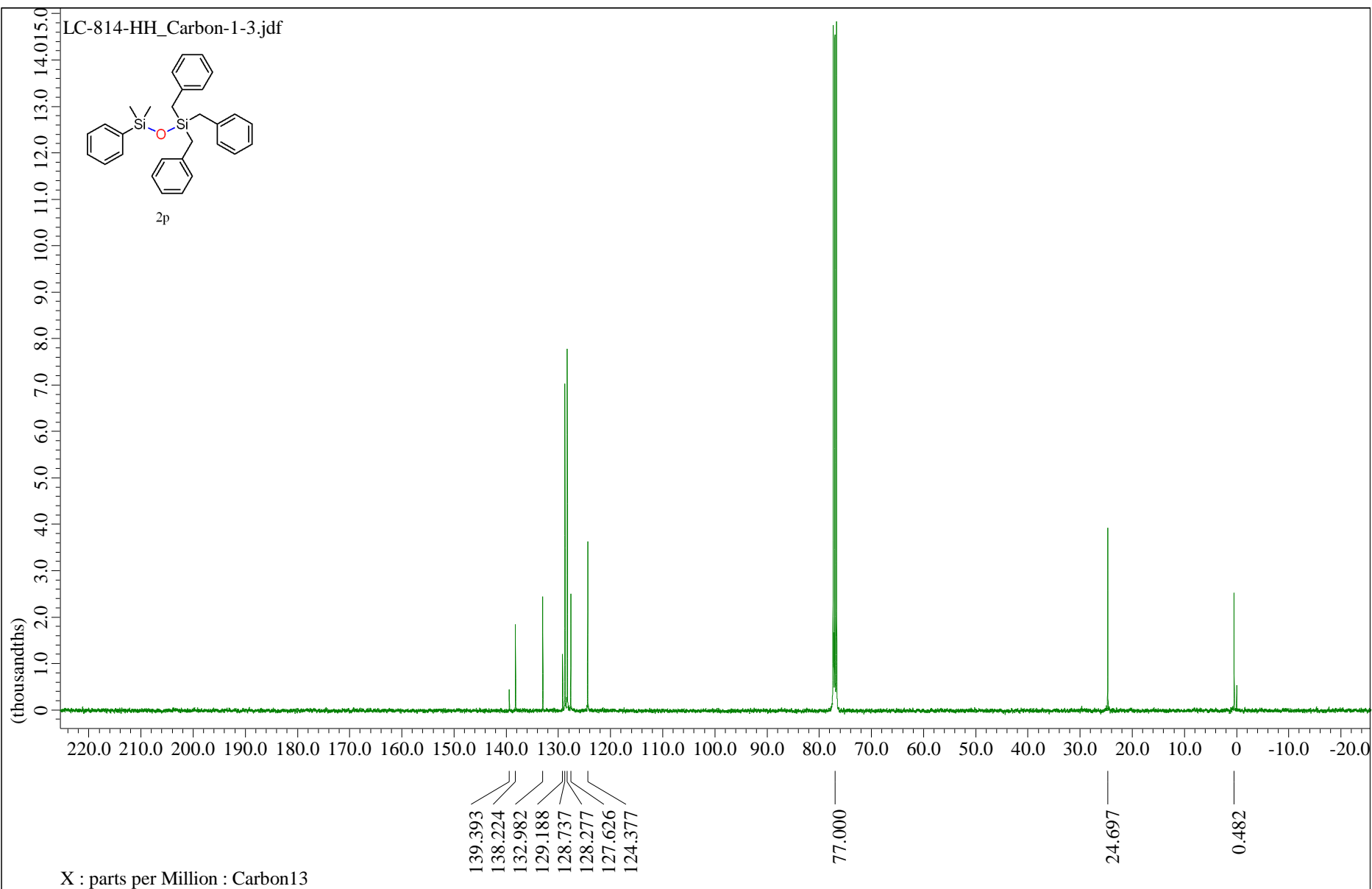
LC-814-HH_Proton-1-3.jdf



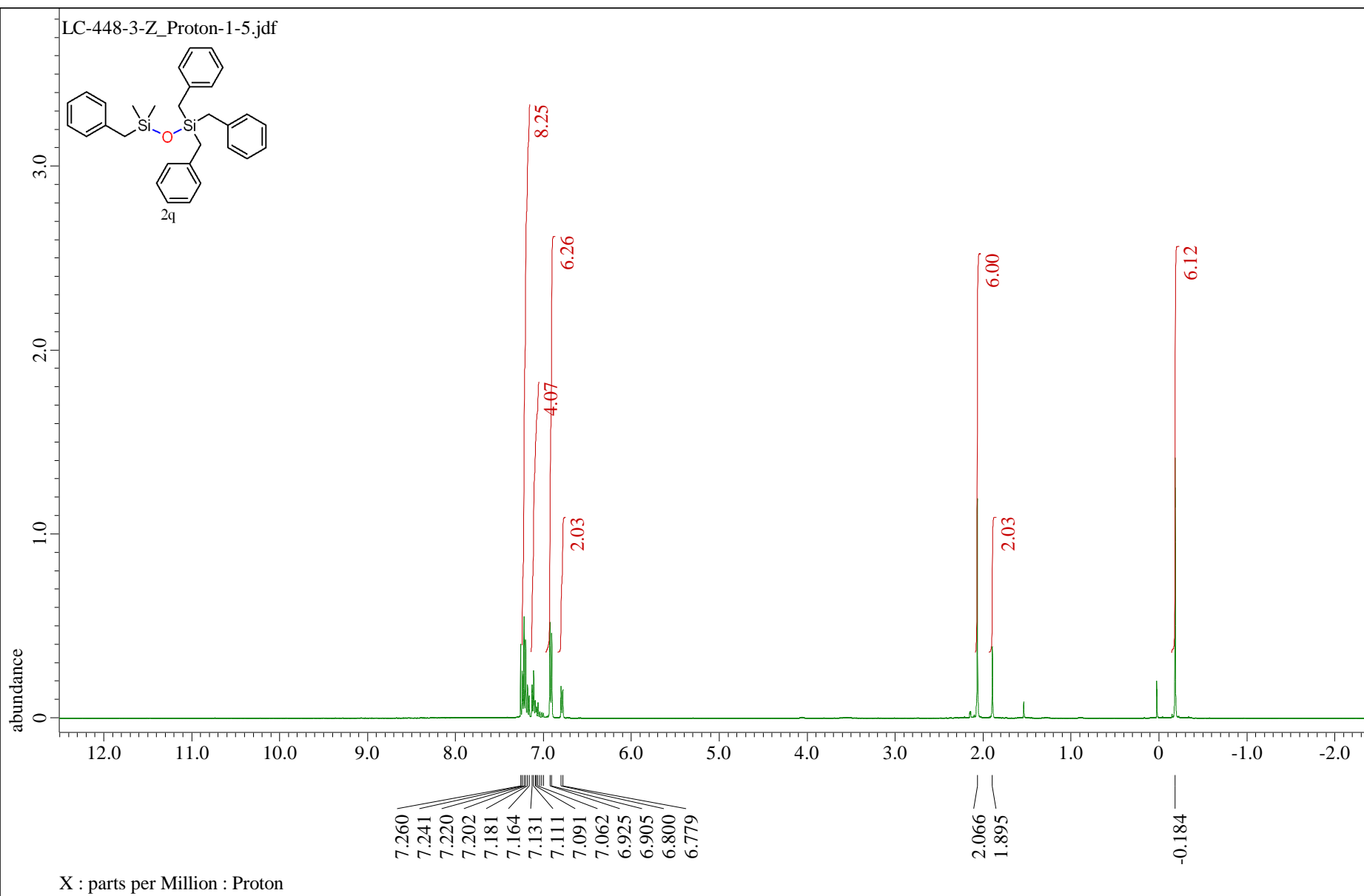
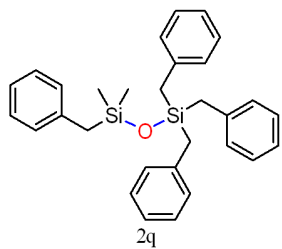
LC-814-HH_Carbon-1-3.jdf



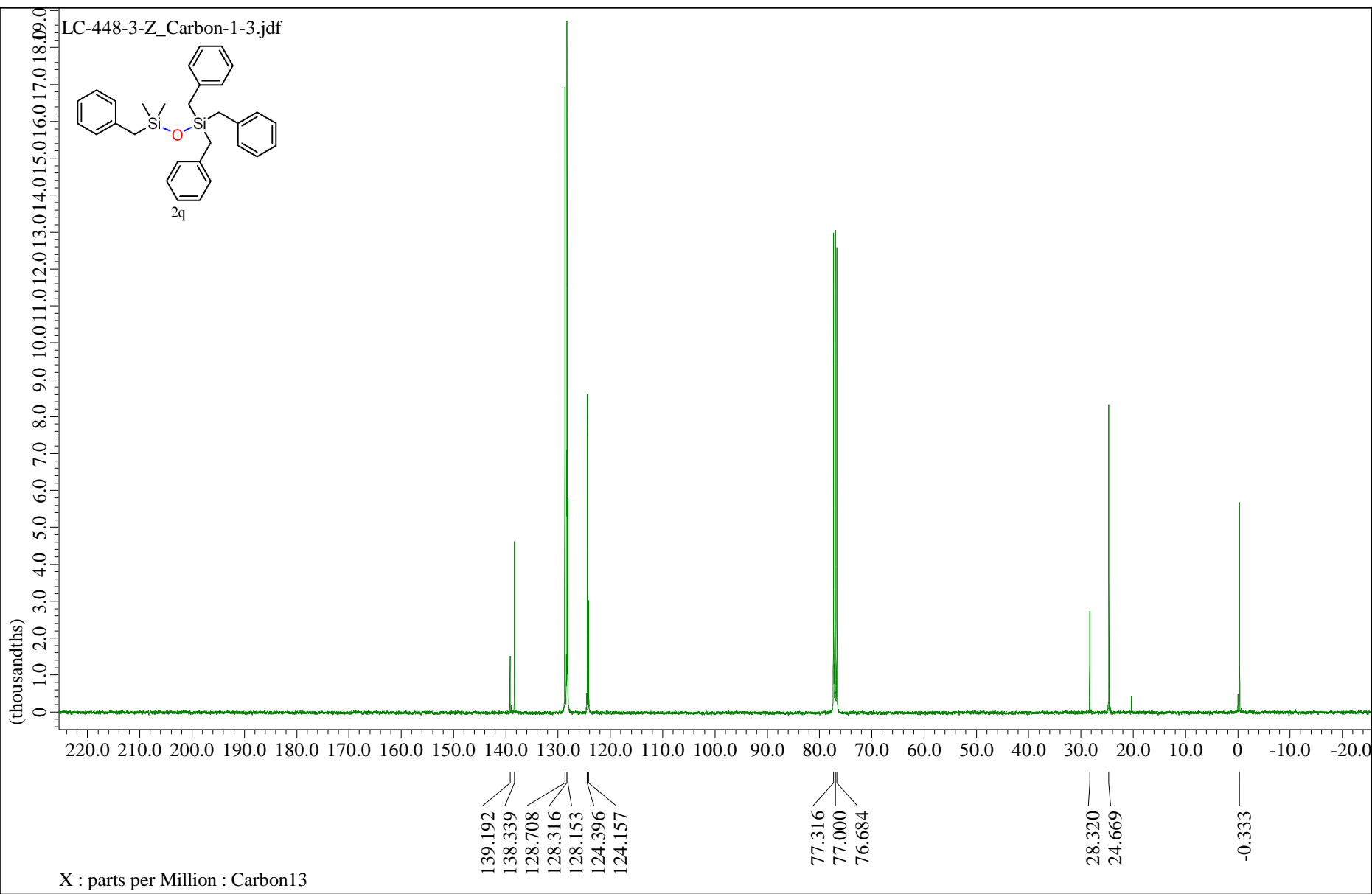
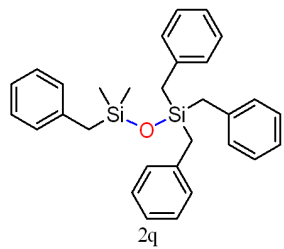
2p



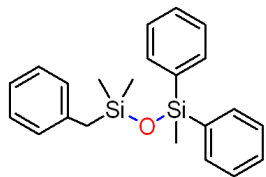
LC-448-3-Z_Proton-1-5.jdf



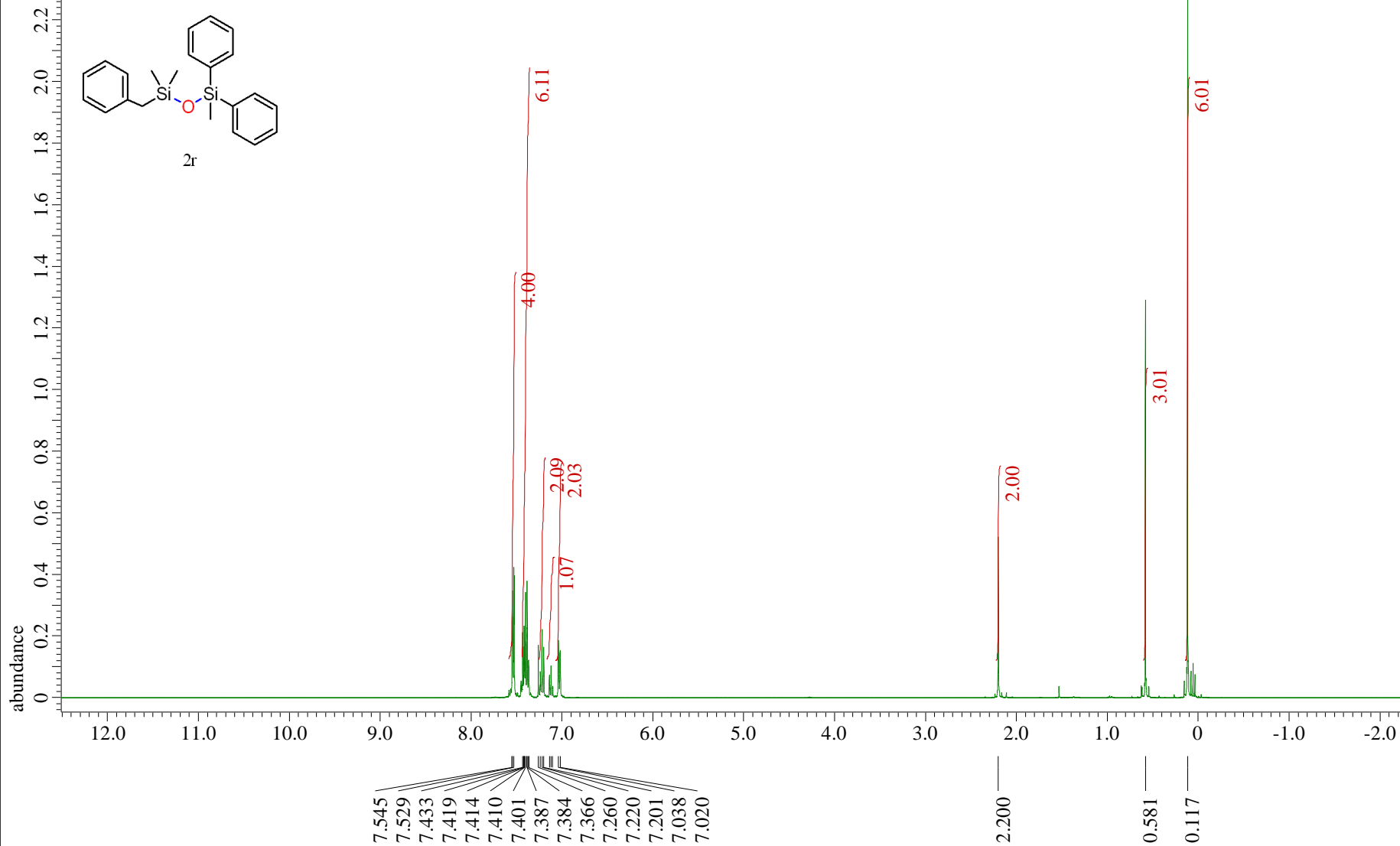
LC-448-3-Z_Carbon-1-3.jdf



LC-815-HZ_Proton-1-3.jdf

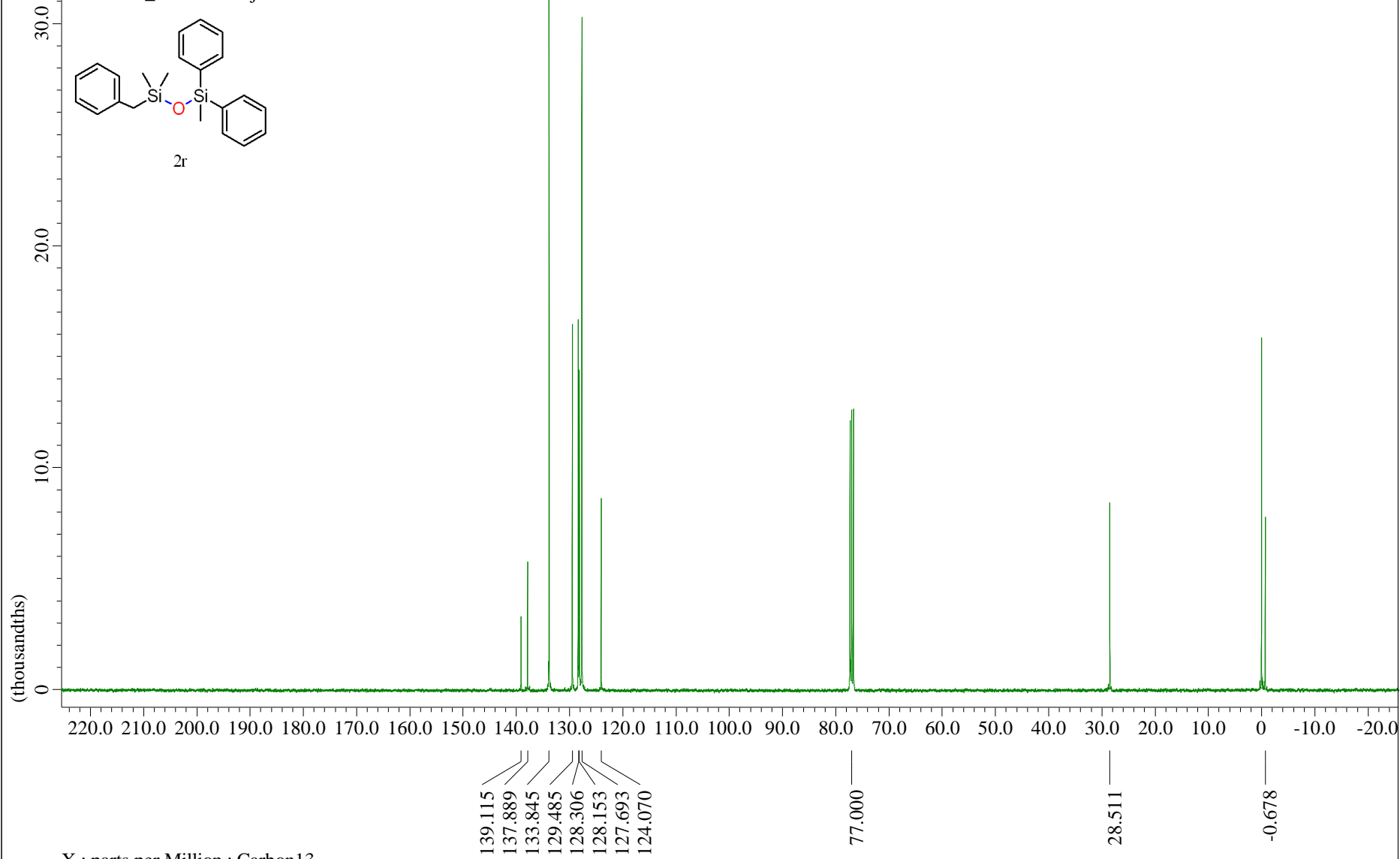
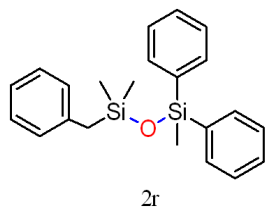


2r



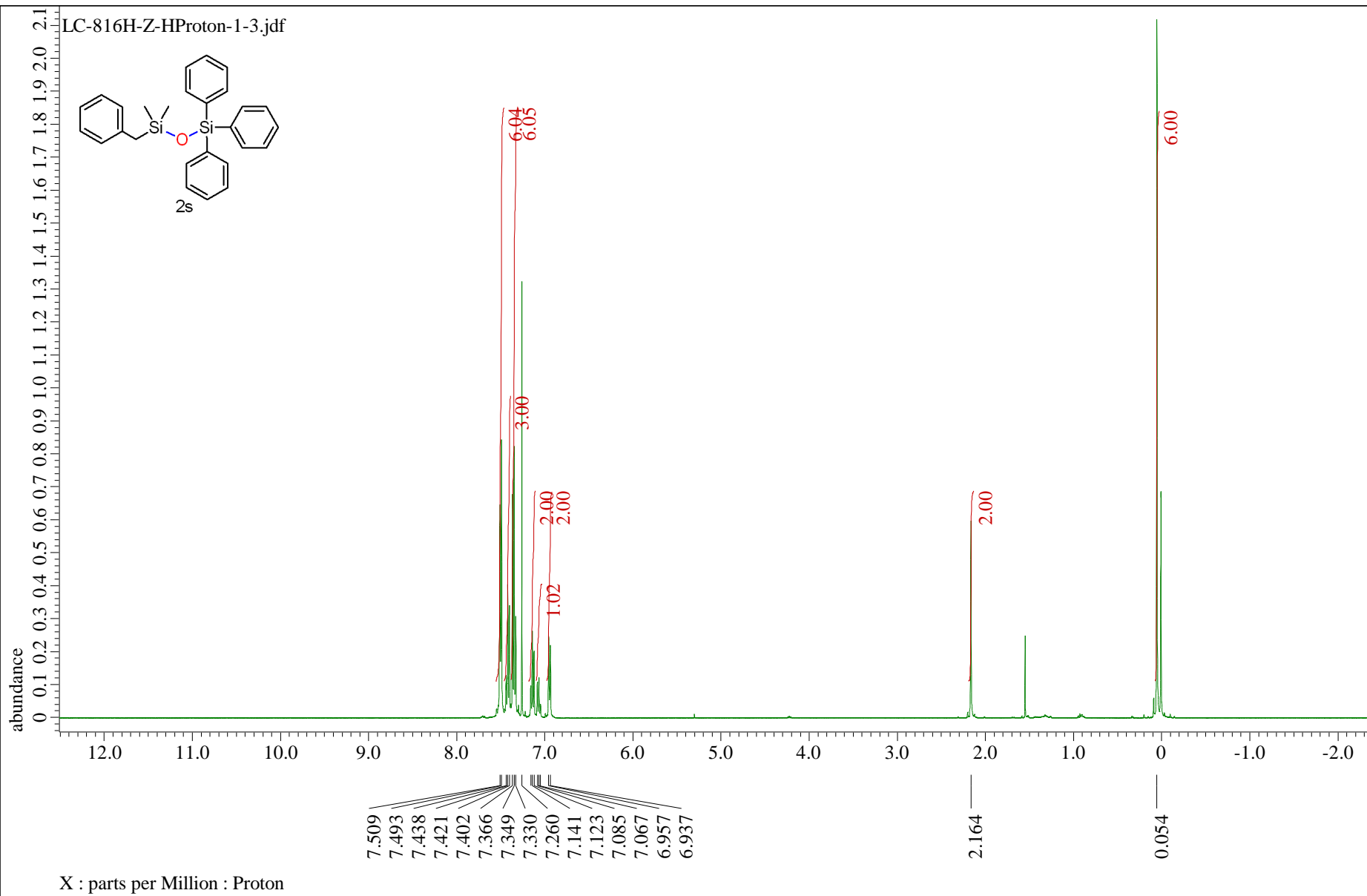
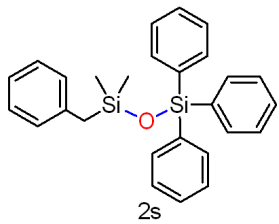
X : parts per Million : Proton

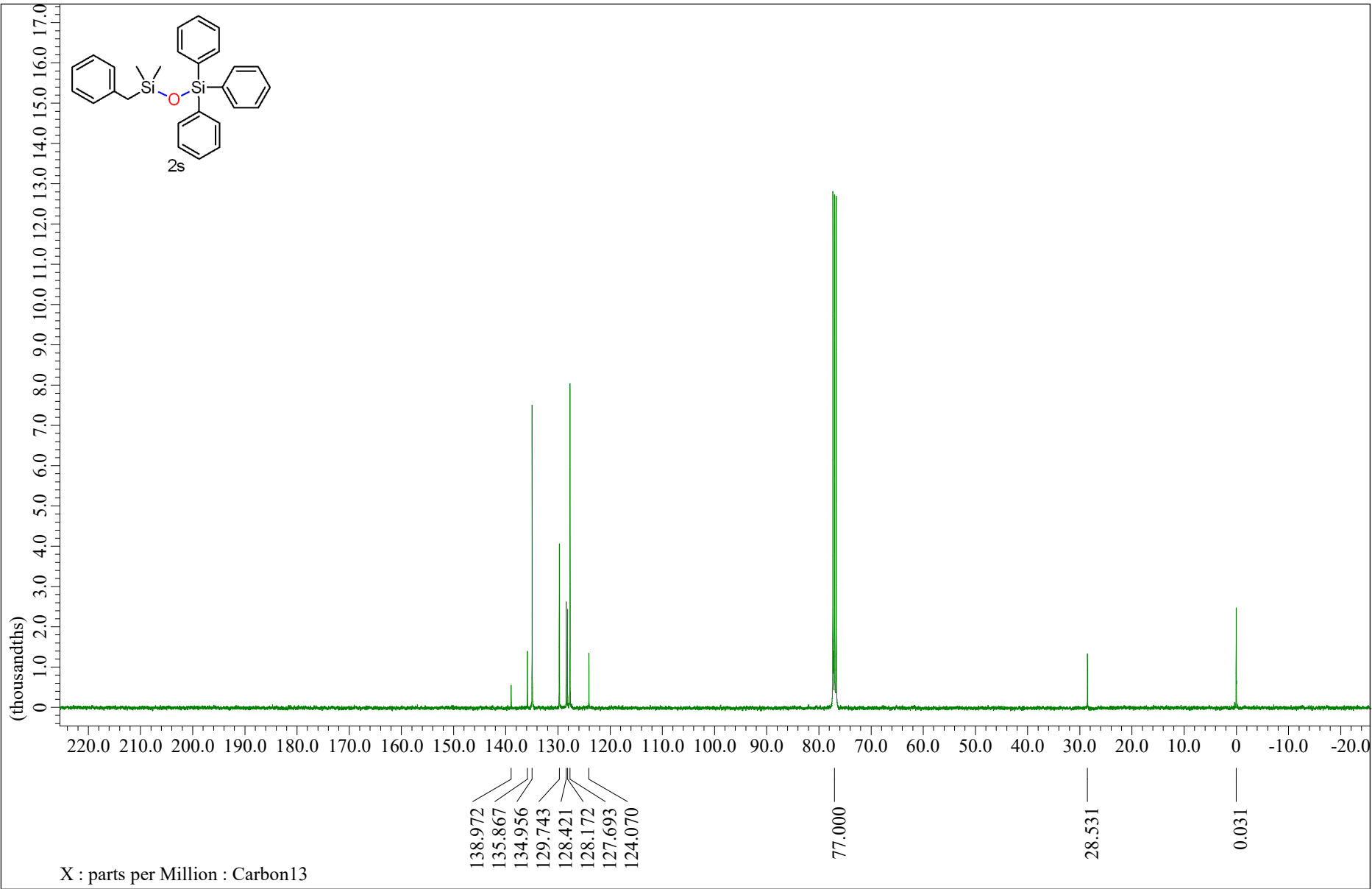
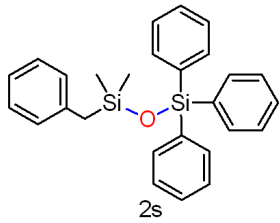
LC-815-C_Carbon-1-3.jdf



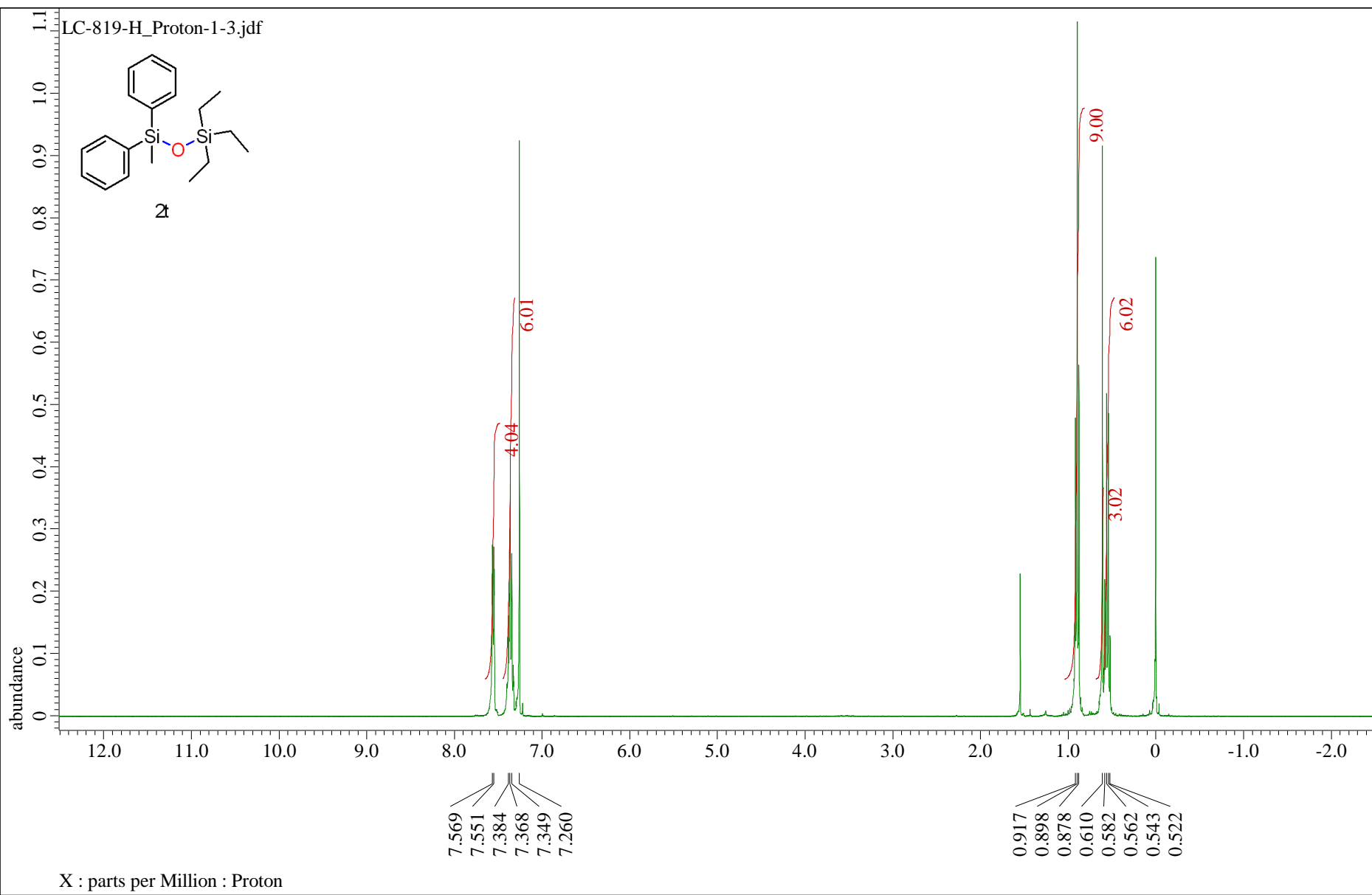
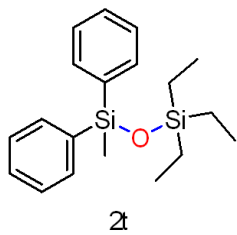
X : parts per Million : Carbon13

LC-816H-Z-HProton-1-3.jdf

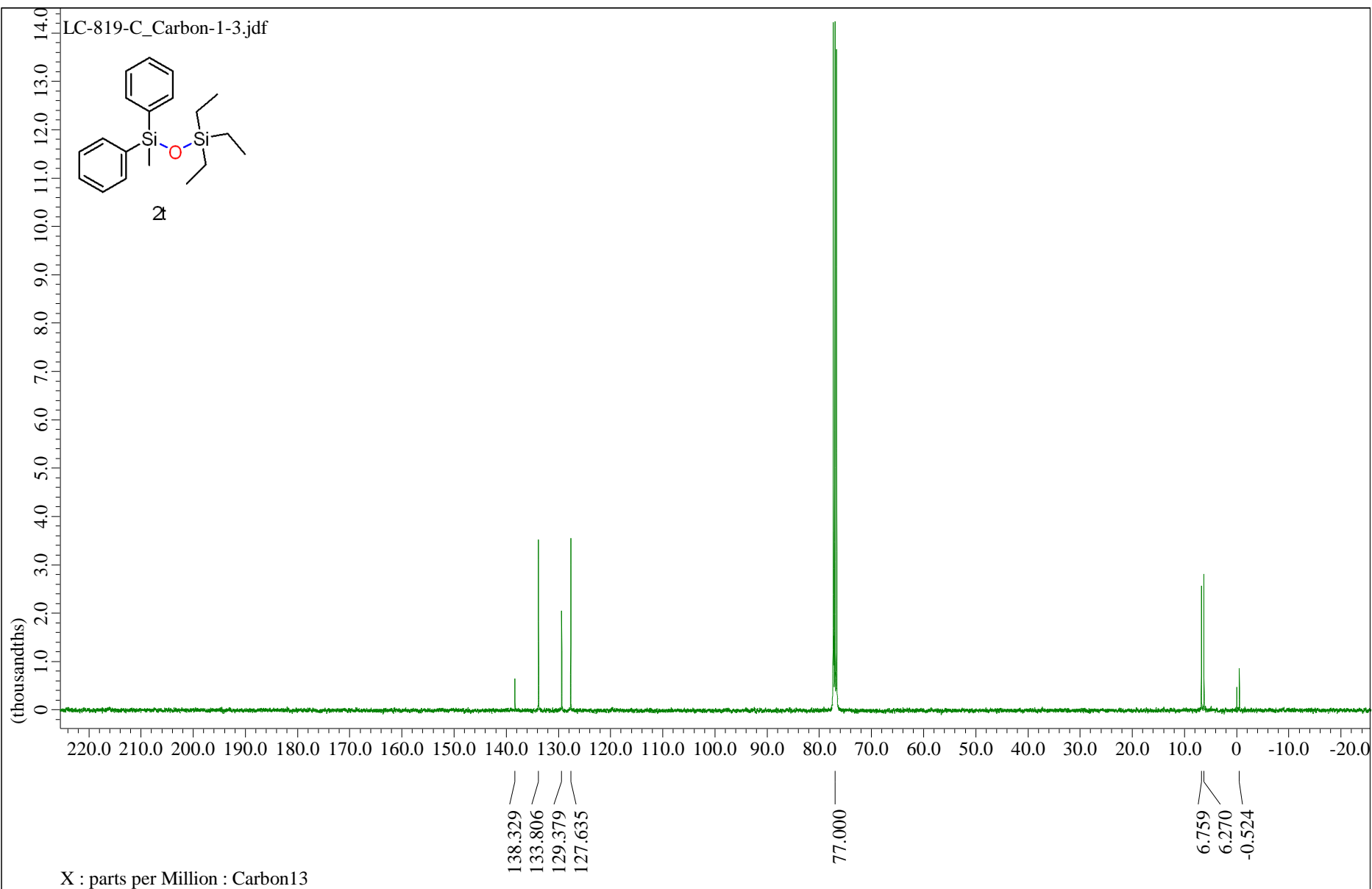
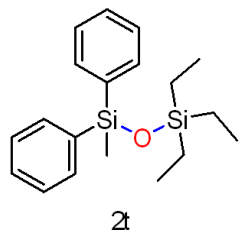




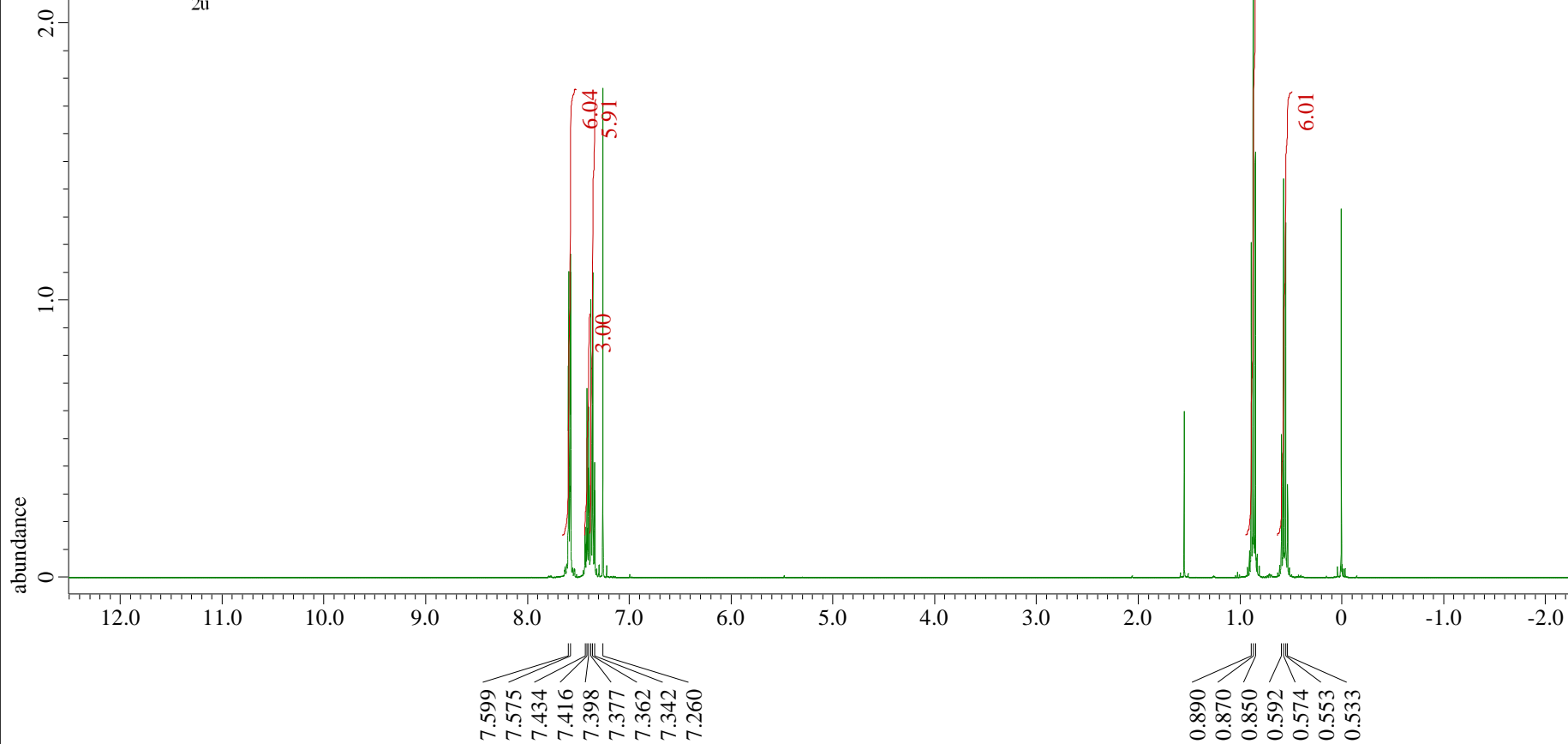
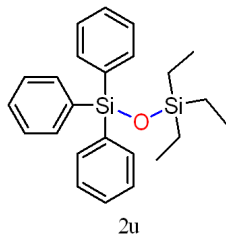
LC-819-H_Proton-1-3.jdf



LC-819-C_Carbon-1-3.jdf

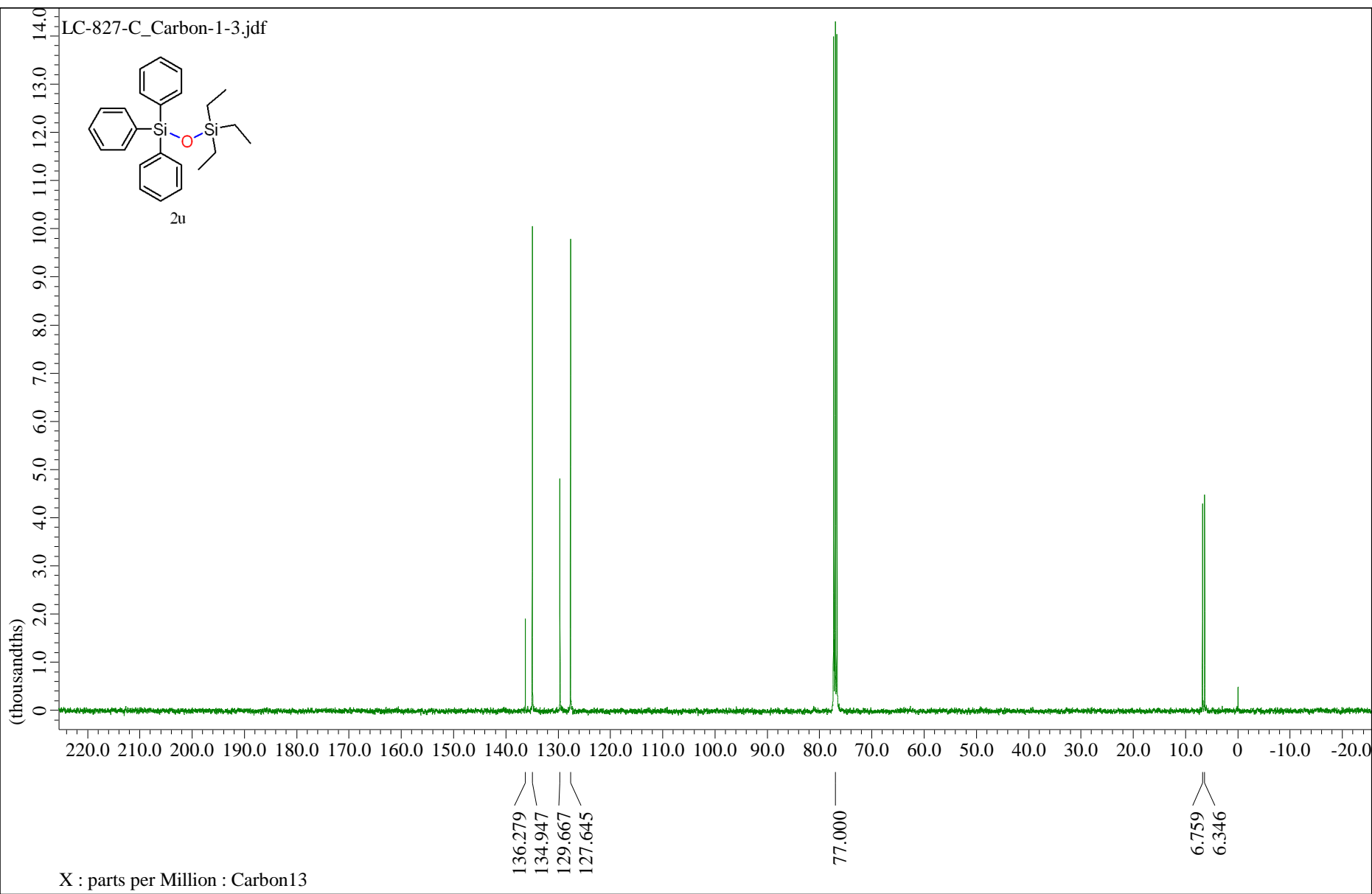
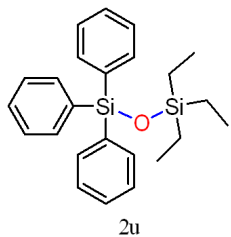


LC-827-H_Proton-1-3.jdf

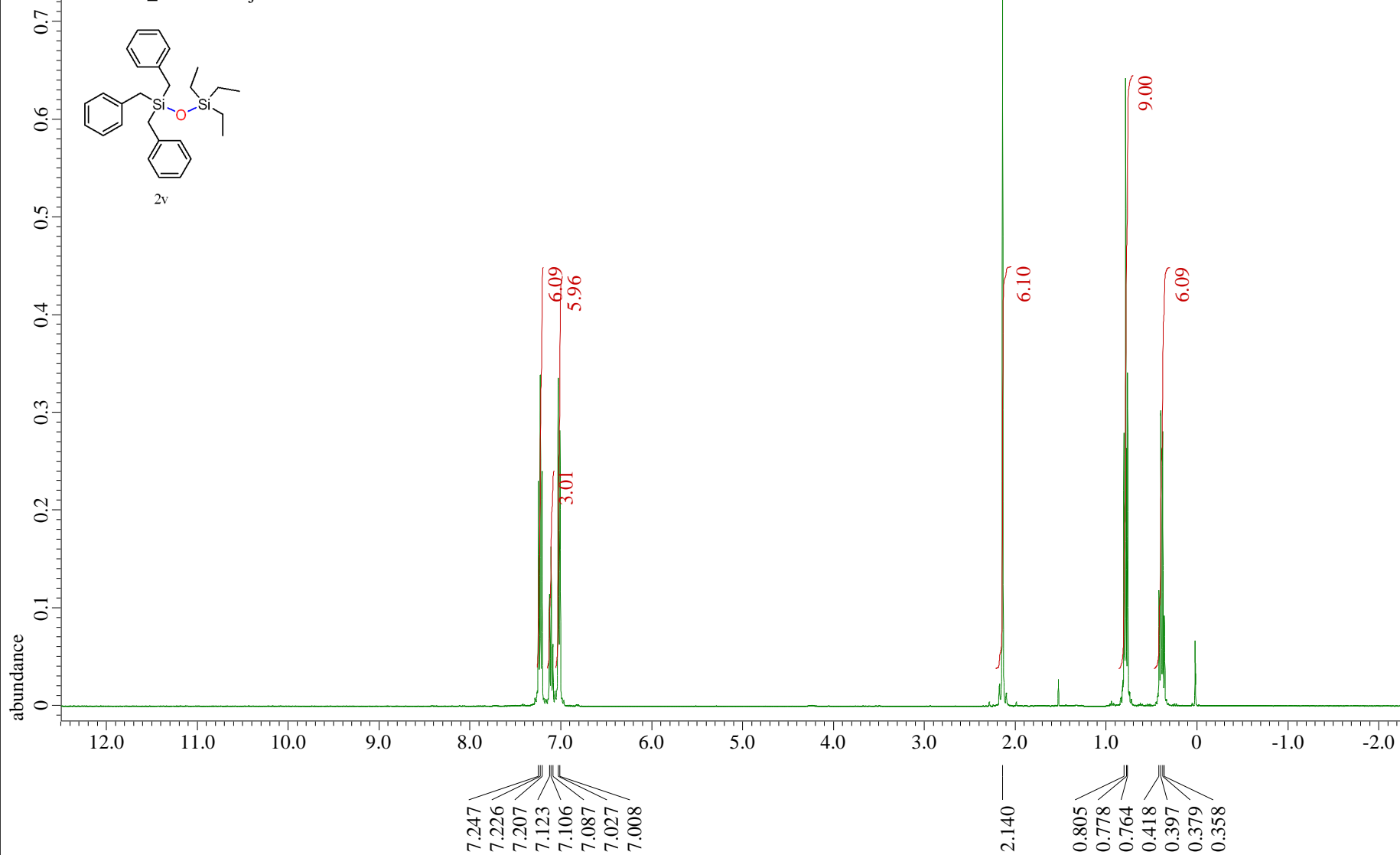
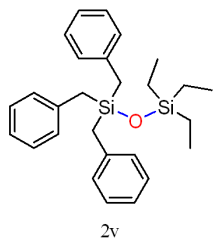


X : parts per Million : Proton

LC-827-C_Carbon-1-3.jdf

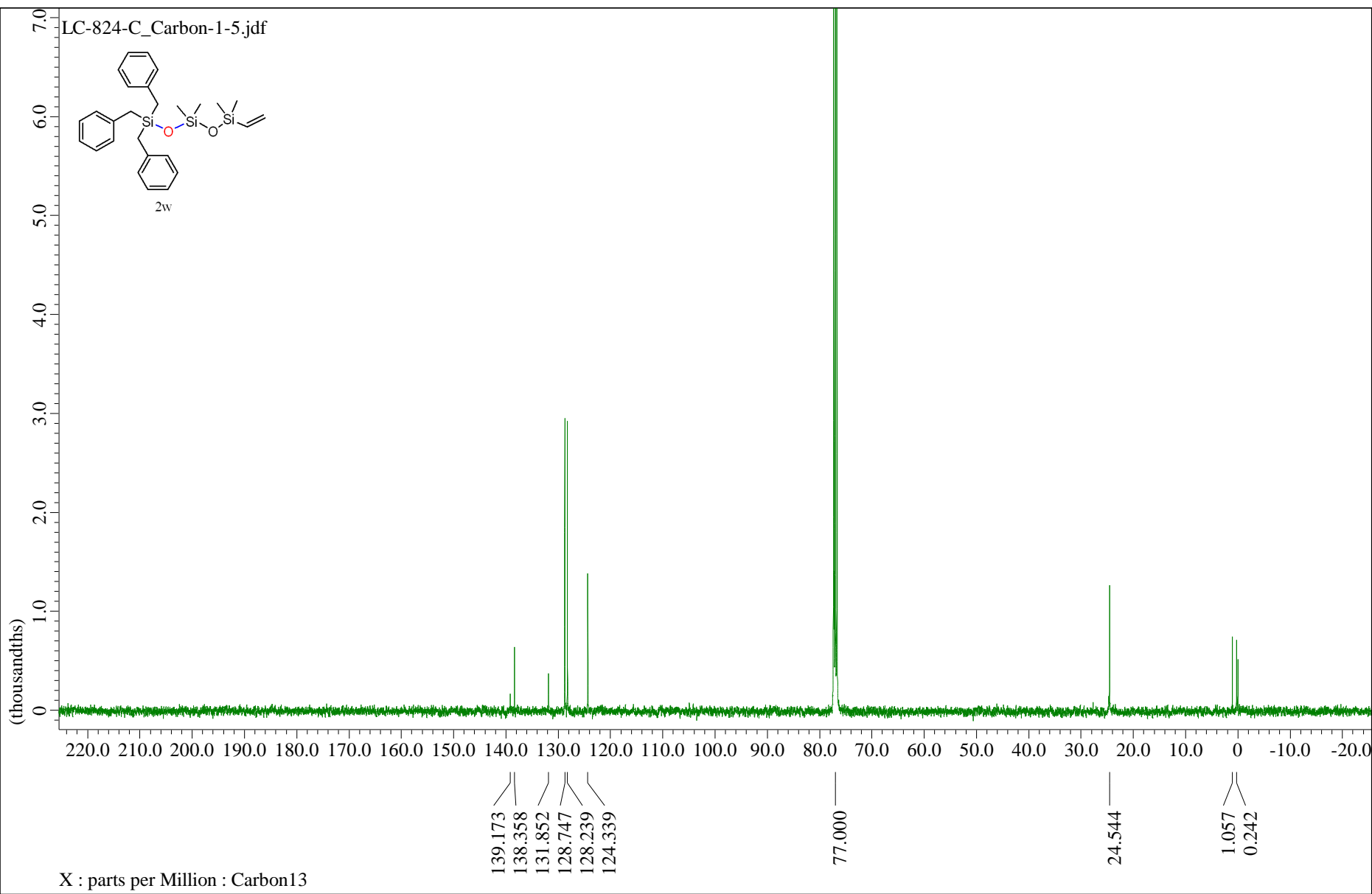
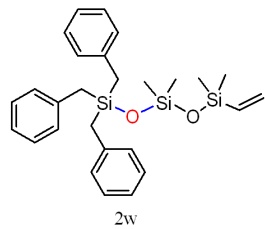


LC-828-H_Proton-1-3.jdf

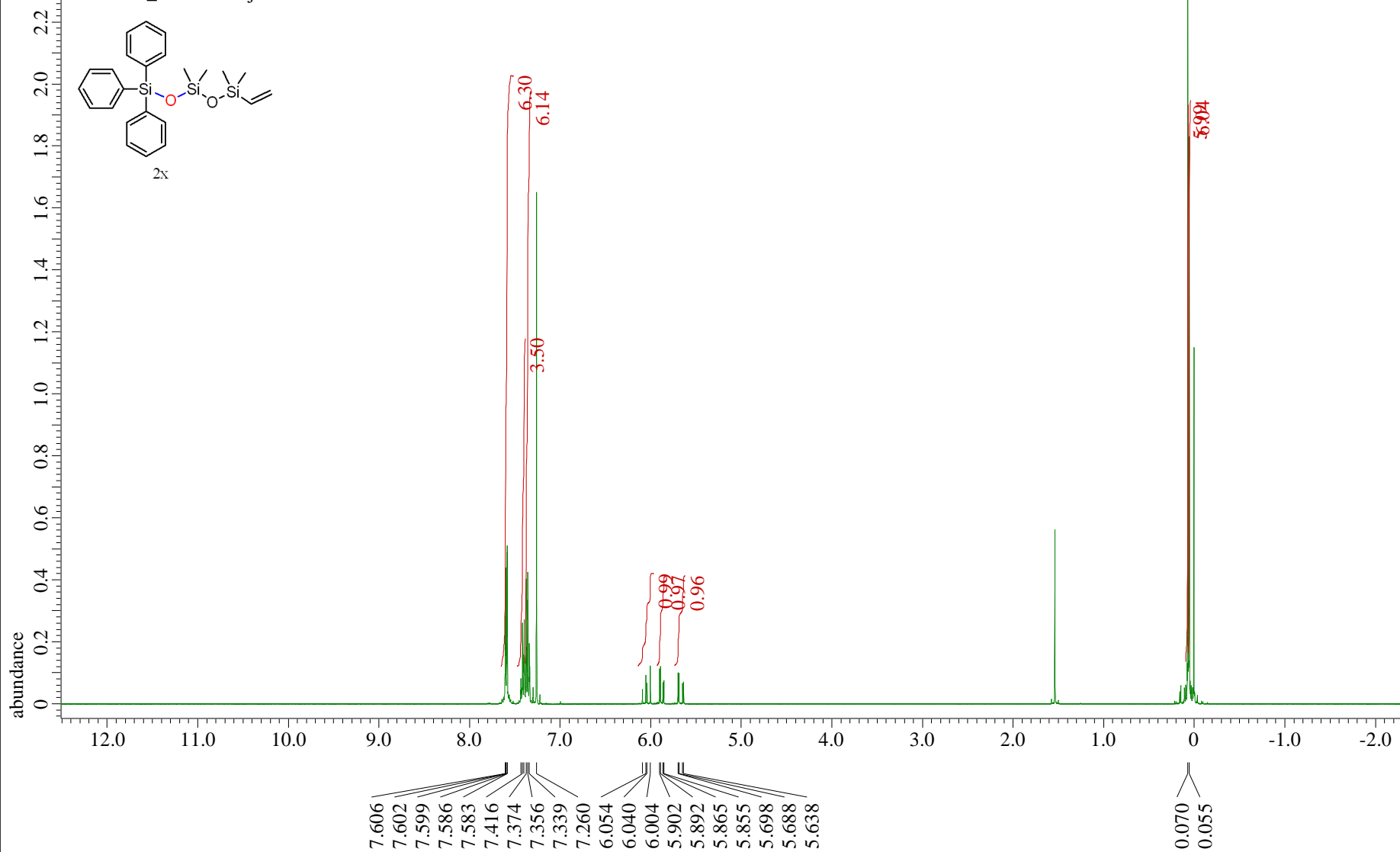
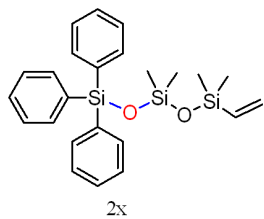


X : parts per Million : Proton

LC-824-C_Carbon-1-5.jdf



LC-825-H_Proton-1-6.jdf



X : parts per Million : Proton

LC-825-C_Carbon-1-3.jdf

