Supplementary Material (ESI) for Green Chemistry

A rapid, versatile and green method for the MW-assisted grafting of organic components onto a pure mesoporous silica matrix: study of the dependence on time irradiation and solvent.

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Supplementary Informations

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Experimental

Elemental analysis were carried out using a CHN Perkin Elmer PE2004 analyzer. Measures of TOC were performed in duplicate for each sample on a Analitik Jena multi N/C 2100 analyzer equipped with a HT 1300 oven. Raman spectra were recorded on a Renishaw inVia microRaman spectrophotometer using a laser power of 1.2 mW and laser excitation wavelength and a λ of 514 nm. FT-IR spectra were performed on a Jasco 430.
^{13}C-HRMAS NMR spectra was recorded on a Bruker Avance 500 MHz instrument at 298 K. Chemical shifts are given in parts per million (ppm) from tetramethylsilane as the internal standard (0.0 ppm). Coupling constants (J) are given in Hertz. MW-assisted reactions were performed in the sealed Teflon vessels of a microwaves oven Milestone ETHOS Touch Control with an optical fiber as temperature controller. All chemicals were used as commercially available.

General Procedures for MW-assisted functionalization of MCM-41

Pre-treatment of MCM-41 silica

10 g of MCM-43 was treated with 250 ml of an aqueous solution of HCl 25% v/v for 3 hours at reflux temperature. The temperature was lowered until room temperature and the mixture was filtered. Solid was washed with water and dried overnight at 100°C.

Functionalization of MCM-41

Pre-treated MCM-41 (300 mg) was reacted with the silylating agent (2 ml) for 15 minutes in a sealed teflon vessel of a Milestone ETHOS Touch Control MW-oven (P=500W). The temperature was fixed at 150 °C and it was continuously controlled by an internal optical fiber controller. At the end of the reaction the system was cooled until room temperature. The solid was filtered, washed three times with THF and extracted for 2 hours in CH_2Cl_2/Et_2O mixture using a Soxlet extractor, then dried under vacuum and stored overnight at 100°C. The functionalized mesoporous material obtained was stored under dried conditions.

3-aminopropyl MCM-41 (1)

Elemental analysis: (%w/w): 10.54 (%C), 3.71 (%N), 3.42 (%H).
TOC Measures (g/Kg): 148.3±15.79
FT-IR Spectrum: cm^{-1} : 1630 (bending N-H), 2938 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 9.0371 (C1), 21.2617 (C2), 42.3447 (C3).

3-mercaptopropyl MCM-41 (2)

Elemental analysis: (%w/w): 8.48 (%C), 1.86 (%H).
TOC Measures (g/Kg): 84.58±2.00
FT-IR Spectrum: cm^{-1} : 2981.4 (stretching C-H), 2936 (stretching S-H).
^{13}C-NMR (500 MHz) δ (ppm): 10.2207 (C1), 15.4664 (C2), 26.4549 (C3).

3-chloropropyl MCM-41 (3)

Elemental analysis: (%w/w): 9.06 (%C),2.0 (%H).
TOC Measures (g/Kg): 93.49±0.18
FT-IR Spectrum: cm^{-1} : 694.248 (stretching C-Cl), 1440.56 (stretching Si-CH), 2960.2 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 8.7976 (C1), 25.5882 (C2), 45.7156 (C3).

Isobutyl MCM-41 (4)

Elemental analysis: (%w/w): 6.77 (%C), 2.22 (%H).

TOC Measures (g/Kg): 90.25±20.56
FT-IR Spectrum: cm^{-1} : 1469.49 (stretching Si-CH, bending CH_3), 2775.03, 2910.06, 2961.16 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 15.2862 (C2), 22.9221 (C1, C3, C4).

3-cyanopropyl MCM-41 (5)

Elemental analysis: (%w/w): 11.56 (%C), 2.13 (%N), 2.12 (%H).
TOC Measures (g/Kg): 128.5±15.24
FT-IR Spectrum: cm^{-1} : 1395.25 (stretching Si-CH), 2255.34 (stretching C≡N), 2897.52, 2942.84, 2982.37 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 10.6564 (C1, C2), 18.5796 (C3), 118.8696 (C4).

3-isocyanatepropyl MCM-41 (6)

Elemental analysis: (%w/w): 15.91 (%C), 3.05 (%N), 3.16 (%H).
TOC Measures (g/Kg): 177.9±3.99
FT-IR Spectrum: cm^{-1} : 1447.31 (stretching Si-CH, bending C-H), 1552.42 (stretching C=N), 2200 (stretching N=C=O), 2936.09, 2979.48 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 8.4851 (C1), 16.9215 (C2), 57.9676 (C3), 157.1525 (C4).

Octyl MCM-41 (7)

Elemental analysis: (%w/w): 11.48 (%C), 2.77 (%H).
TOC Measures (g/Kg): 129.1±1.40
FT-IR Spectrum: cm^{-1} : 1447.31 (stretching Si-CH), 2858.95, 2929.34 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 11.7602 (C1, C2), 21.9642 (C7, C8), 28.6695 (C4, C5), 31.5318 (C3, C6).

3-ethylenediaminopropyl MCM-41 (8)

Elemental analysis: (%w/w): 13.86 (%C), 5.20 (%N), 4.19 (%H).
TOC Measures (g/Kg): 172.2±13.08
FT-IR Spectrum: cm^{-1} : 692.32 (wagging N-H), 1474.31 (stretching Si-CH, bending NH_2), 2945.73 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 9.4385 (C1), 21.4008 (C2), 38.0752 (C3), 49.8140 (C4, C5).

Phenyl MCM-41 (9)

Elemental analysis: (%w/w): 14.73 (%C), 1.87 (%H).
TOC Measures (g/Kg): 160.3±0.84
FT-IR Spectrum: cm^{-1} : 740.53, 689.07 (out-of-plane bending C-H), 1431.89 (in plane bending C-H), 2850.27-3075.9 (stretching C-H aromatic).
^{13}C-NMR (500 MHz) δ (ppm): 126.6012 (2 x C3, C4), 133.3750 (2 x C2, C1).

3-glycidyloxypropyl MCM-41 (10)

Elemental analysis: (%w/w): 19.67 (%C), 3.97 (%H).
TOC Measures (g/Kg): 208.3±0.19
FT-IR Spectrum: cm^{-1} : 1100 (stretching C-O-C), 1463.71 (stretching Si-CH), 2879.2, 2942.89 (stretching C-H).
^{13}C-NMR (500 MHz) δ (ppm): 8.8842 (C2), 22.6096 (C1), 57.7988 (C3), 72,7124 (C4, C5).

(N-ethylamino)-3-ethylenediaminopropyl MCM-41 (11)

Elemental analysis: (%w/w): 17.15 (%C), 6.50 (%N), 4.76 (%H).
TOC Measures (g/Kg): 213.2±8.92
FT-IR Spectrum: cm^{-1} : 692.32 (wagging N-H), 1472.58 (stretching Si-CH, bending NH_2), 2893.66, 2944.77 (stretching C-H).

^{13}C-NMR (500 MHz) δ (ppm): 9.4020 (C1), 20.4680 (C2), 39.1083 (C7), 47.3440 (C3, C4, C5, C6).

3-propylurea MCM-41 (12)

Elemental analysis: (%w/w): 15.41 (%C), 4.88 (%N), 3.59 (%H).

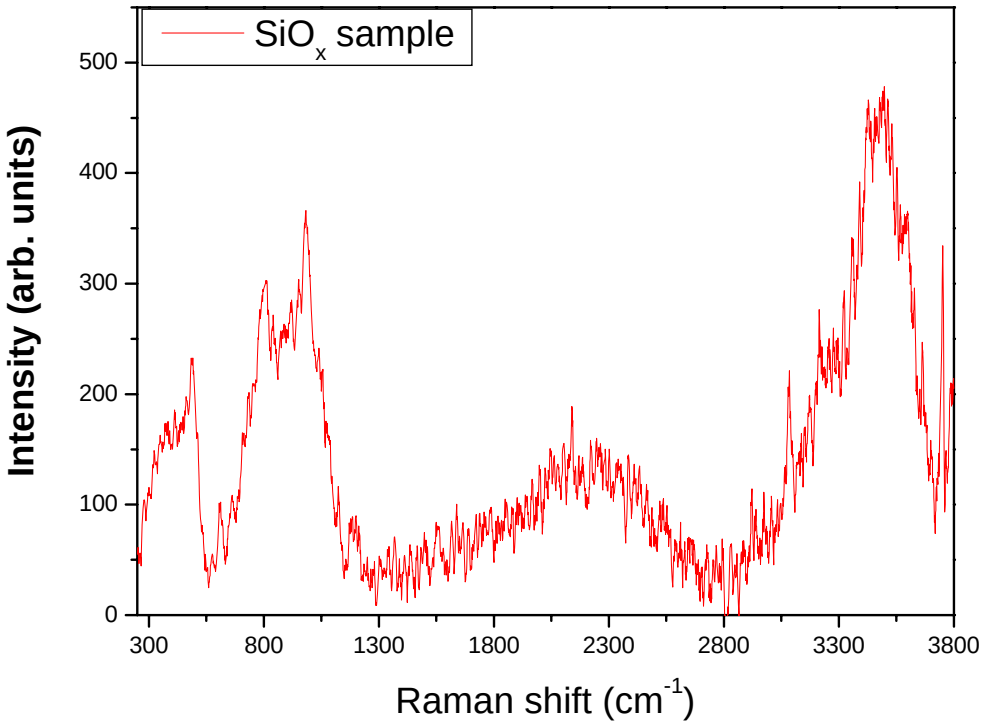
TOC Measures (g/Kg): 188.8±3.34

FT-IR Spectrum: cm^{-1} : 693.264 (wagging N-H), 1476.24(stretching Si-CH, stretching C-N), 1570,74 (bending NH), 2849.31, 2946.77 (stretching C-H).

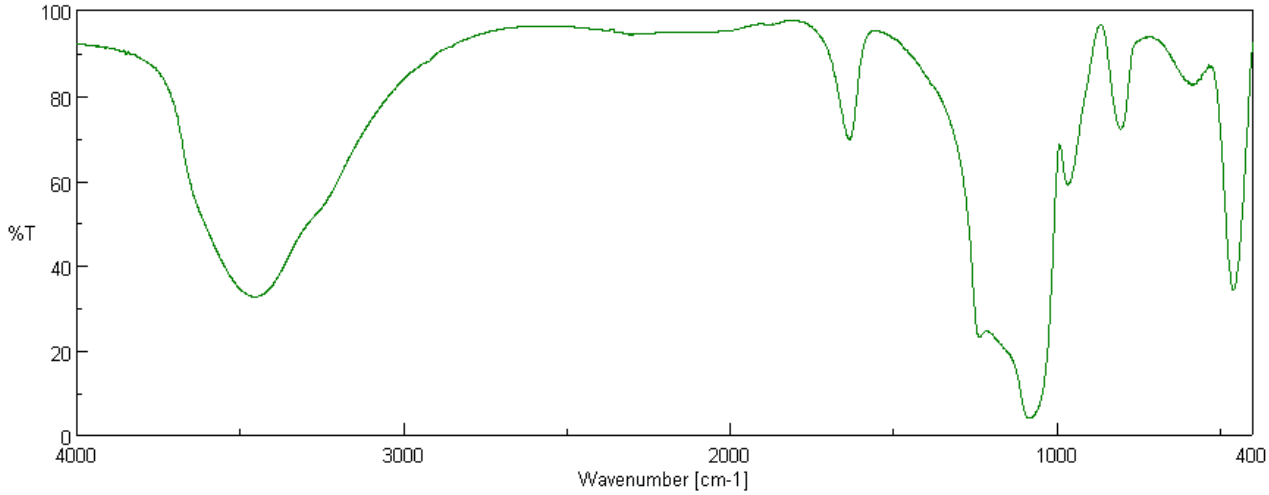
^{13}C-NMR (500 MHz) δ (ppm): 8.7611 (C1), 23.5994 (C2), 49.9212 (C3), 159.7629 (C4).

MCM-41

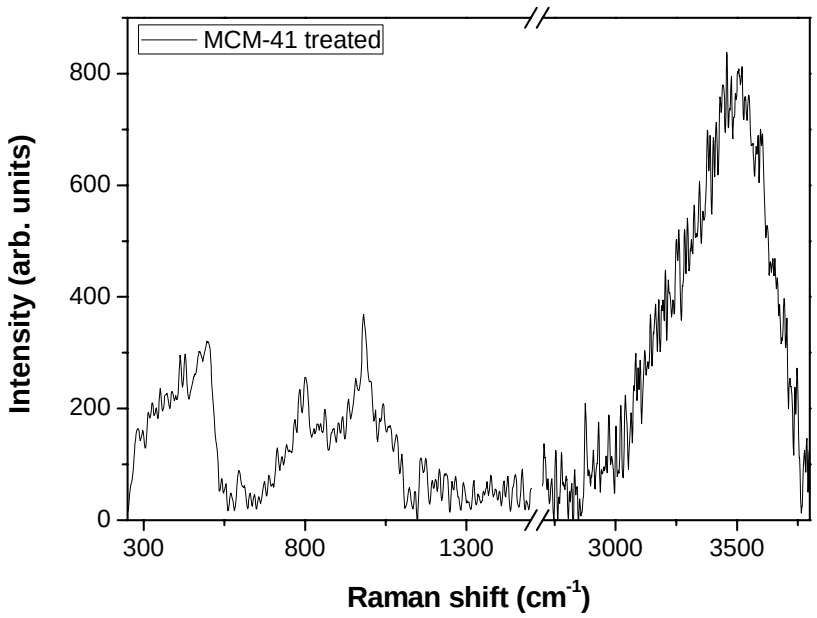
Raman Spectrum of commercial sample



FT-IR Spectrum



Raman Spectrum of MCM-41 treated sample



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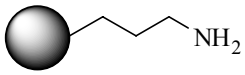
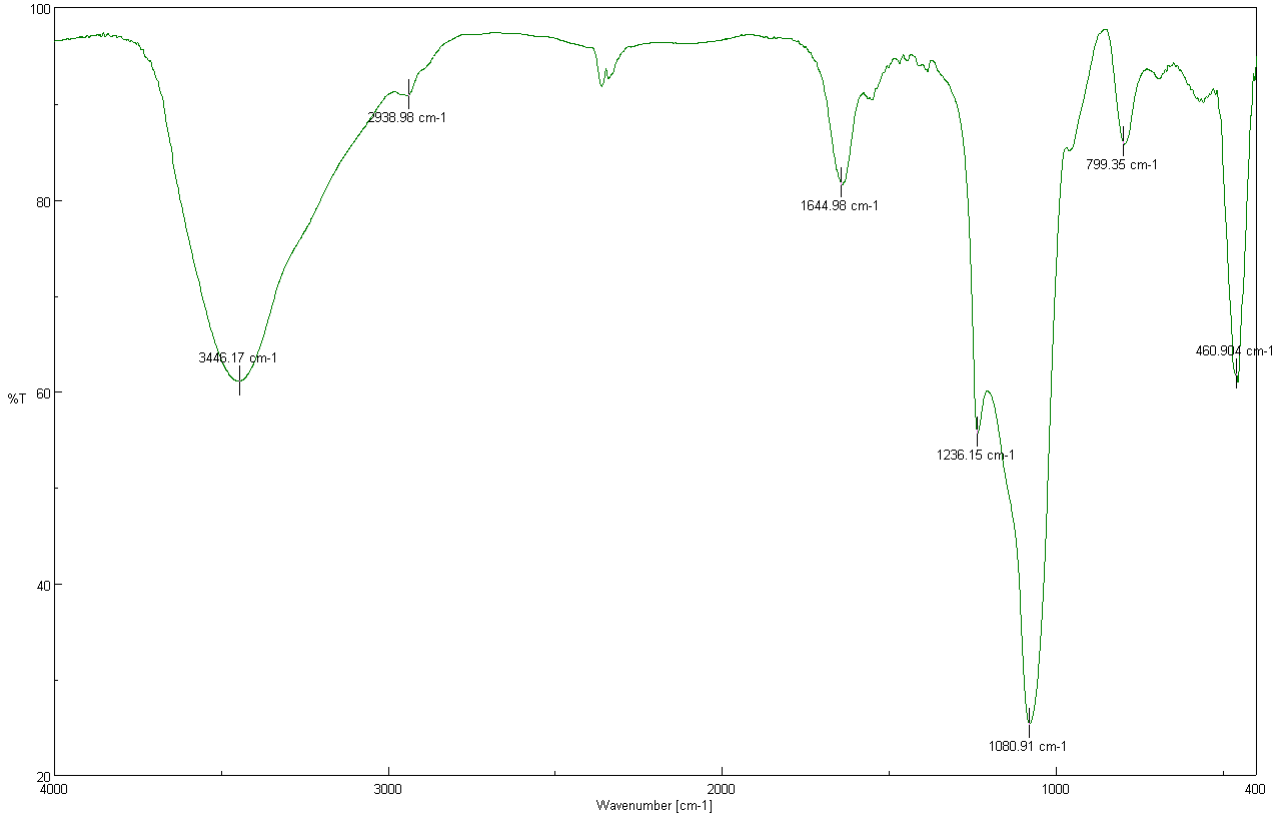


FT-IR Spectrum



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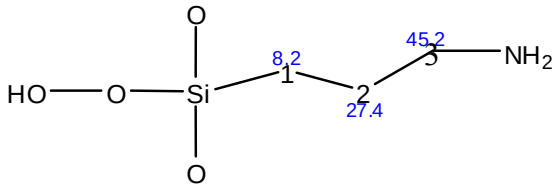

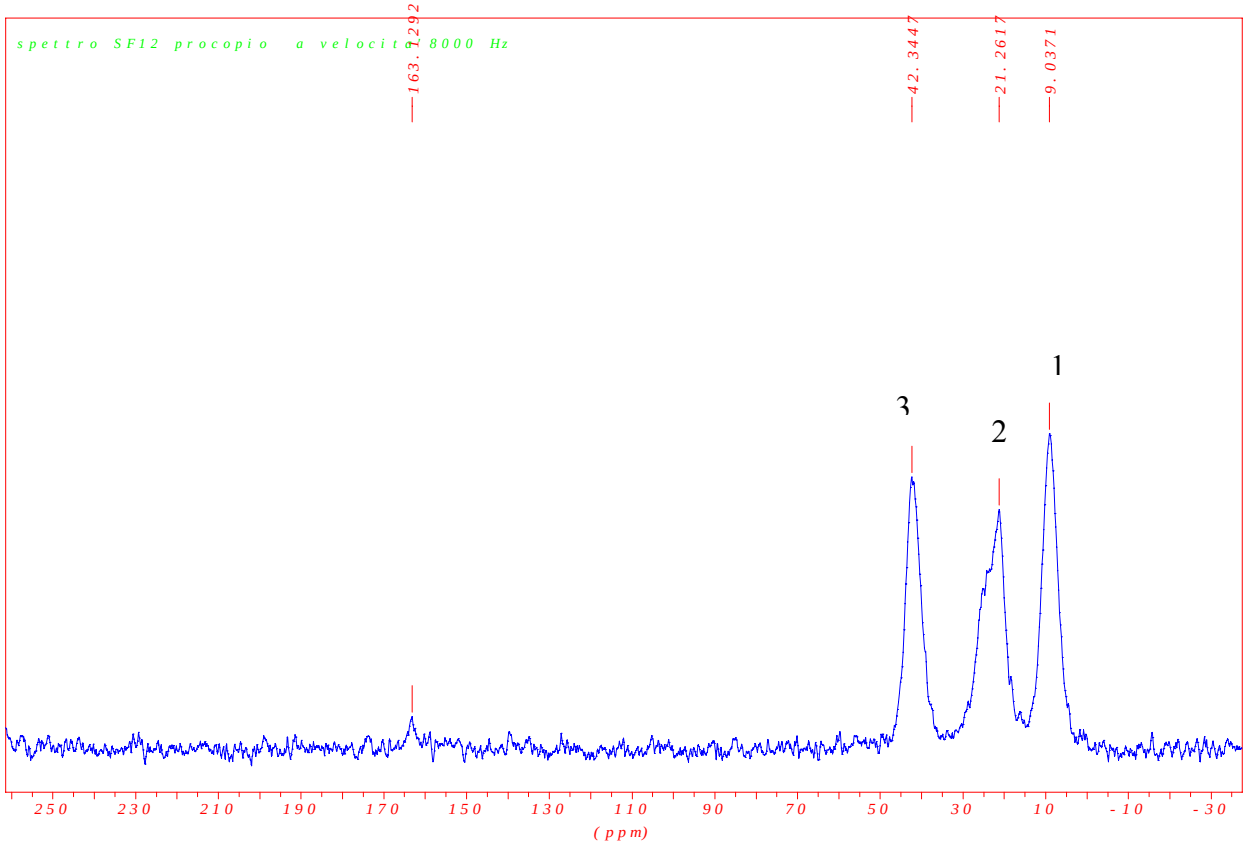

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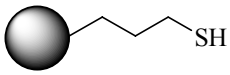

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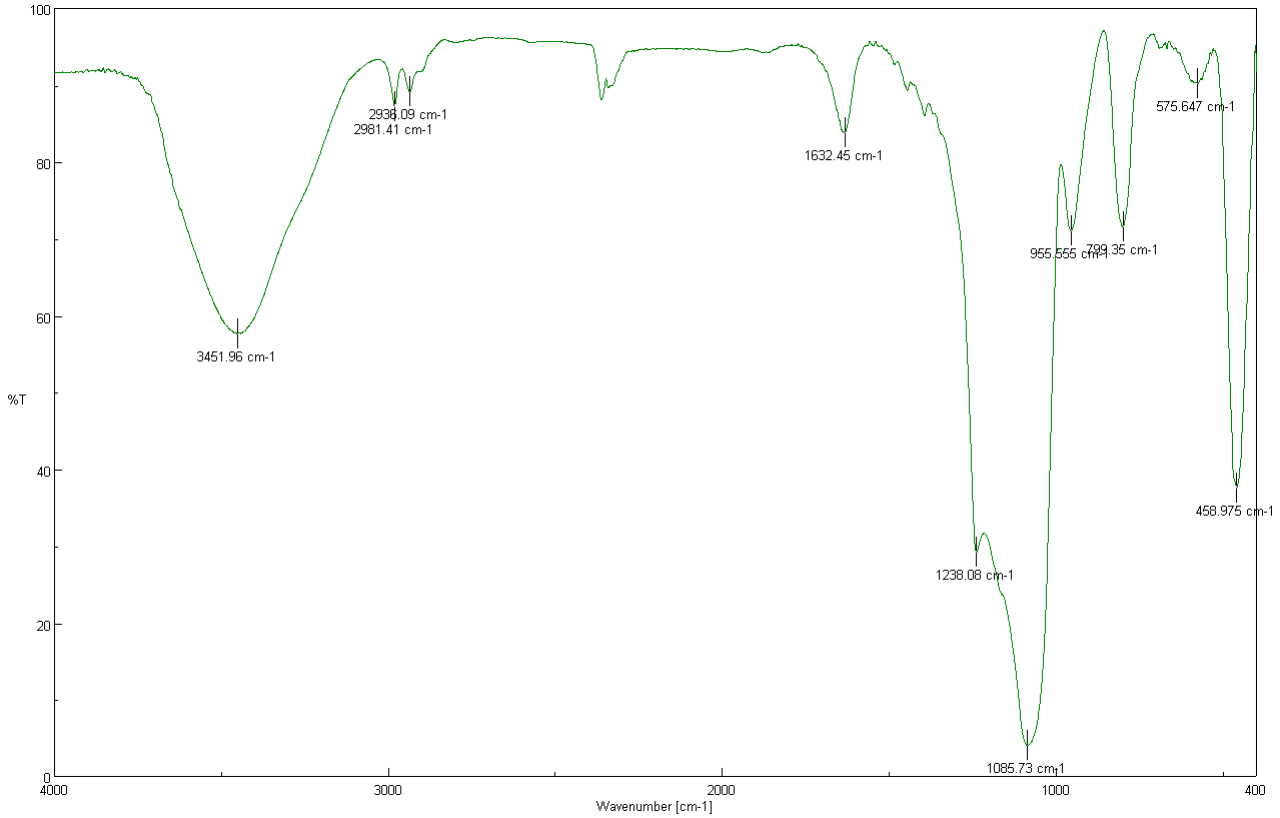

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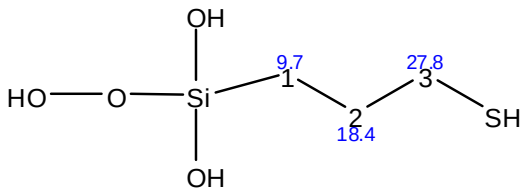

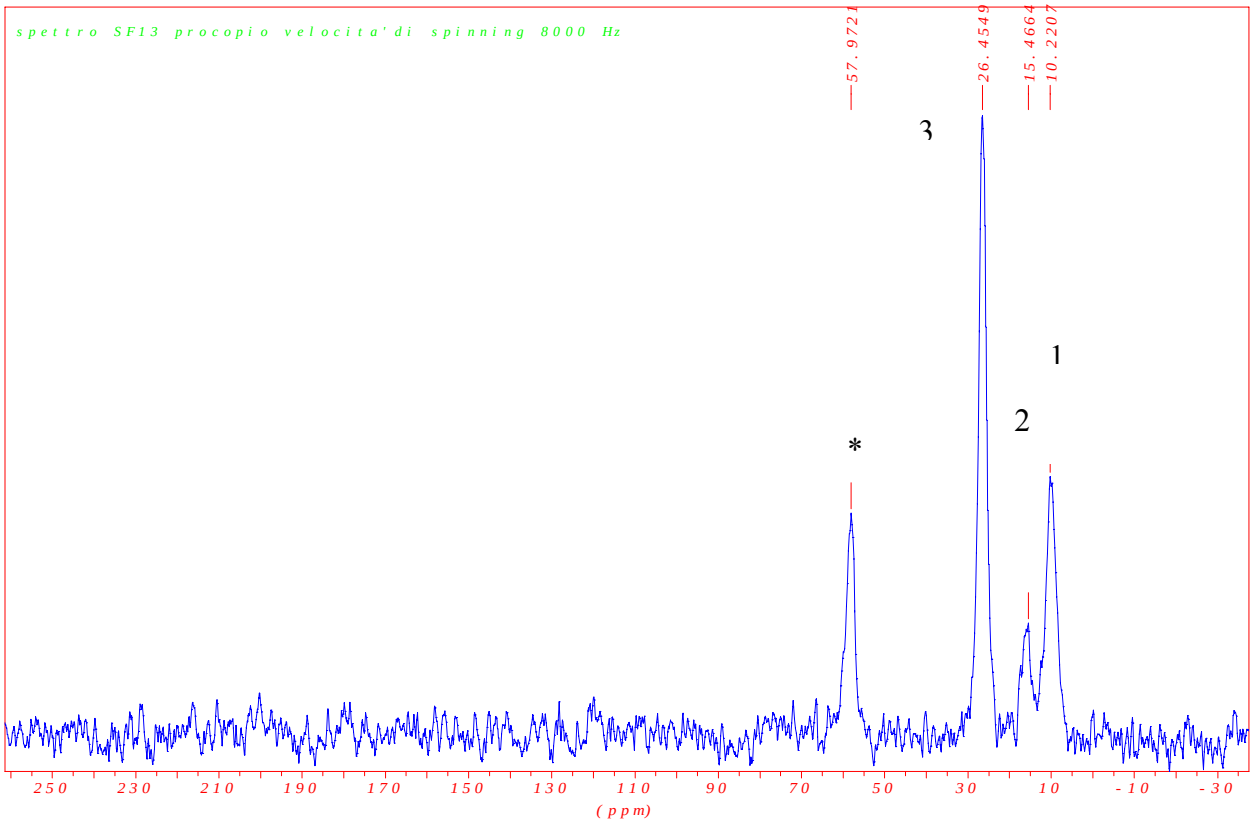

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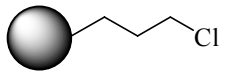
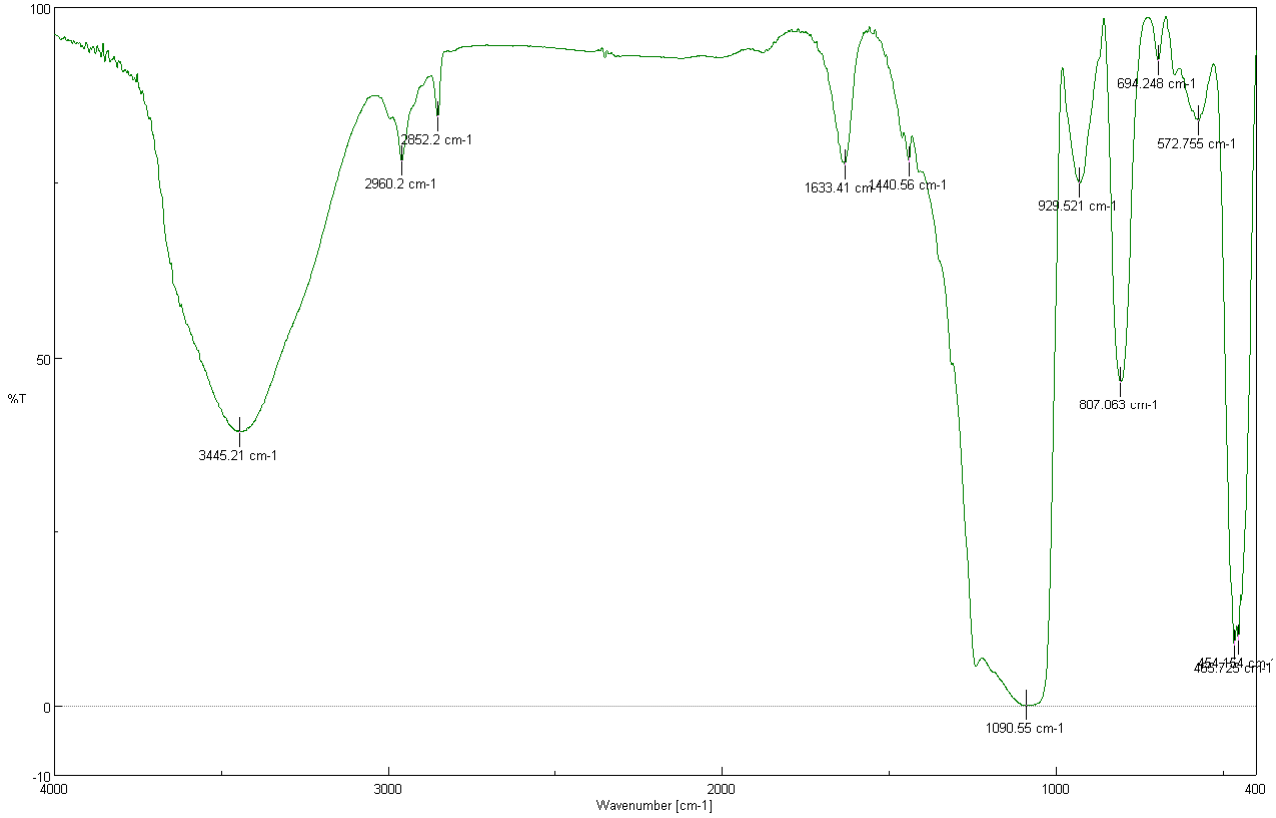


FT-IR Spectrum



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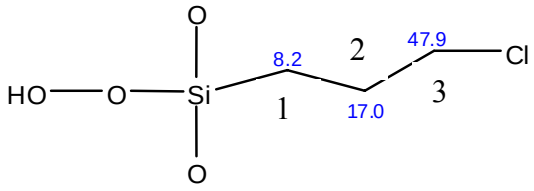

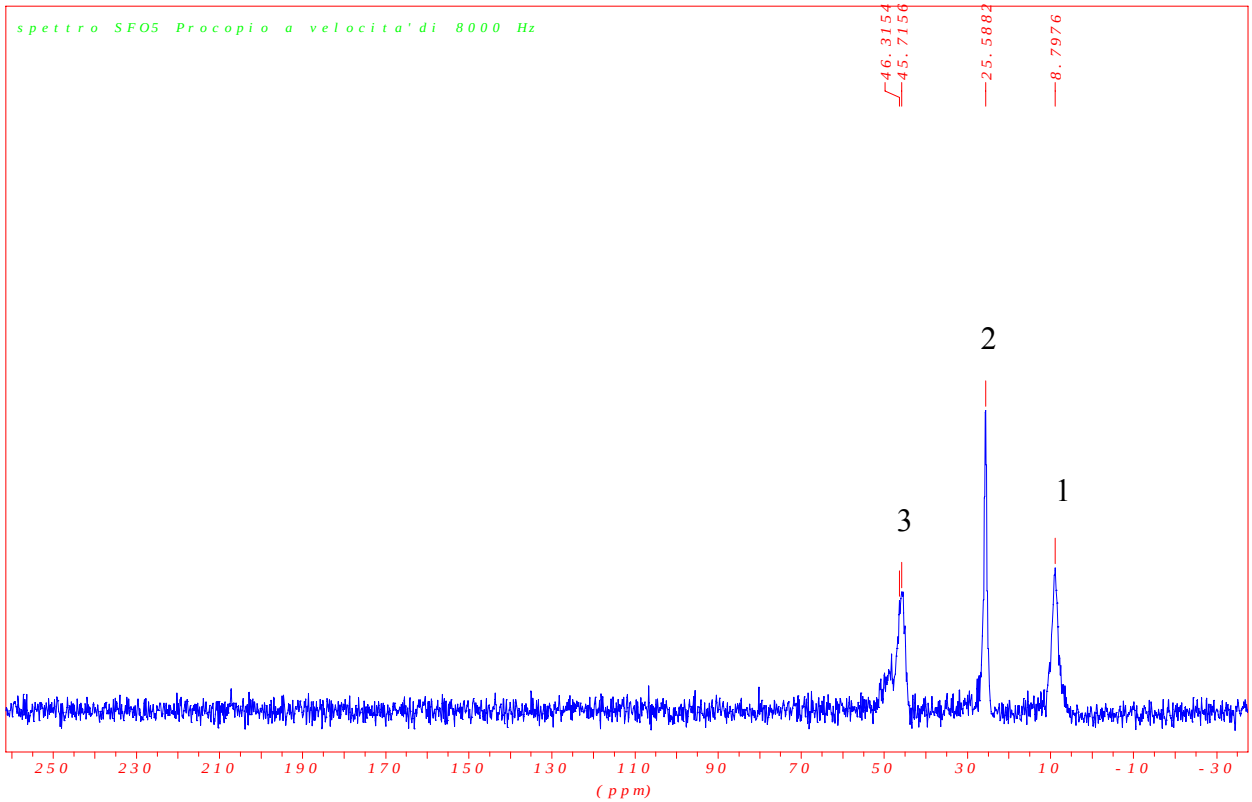

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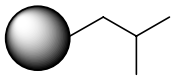
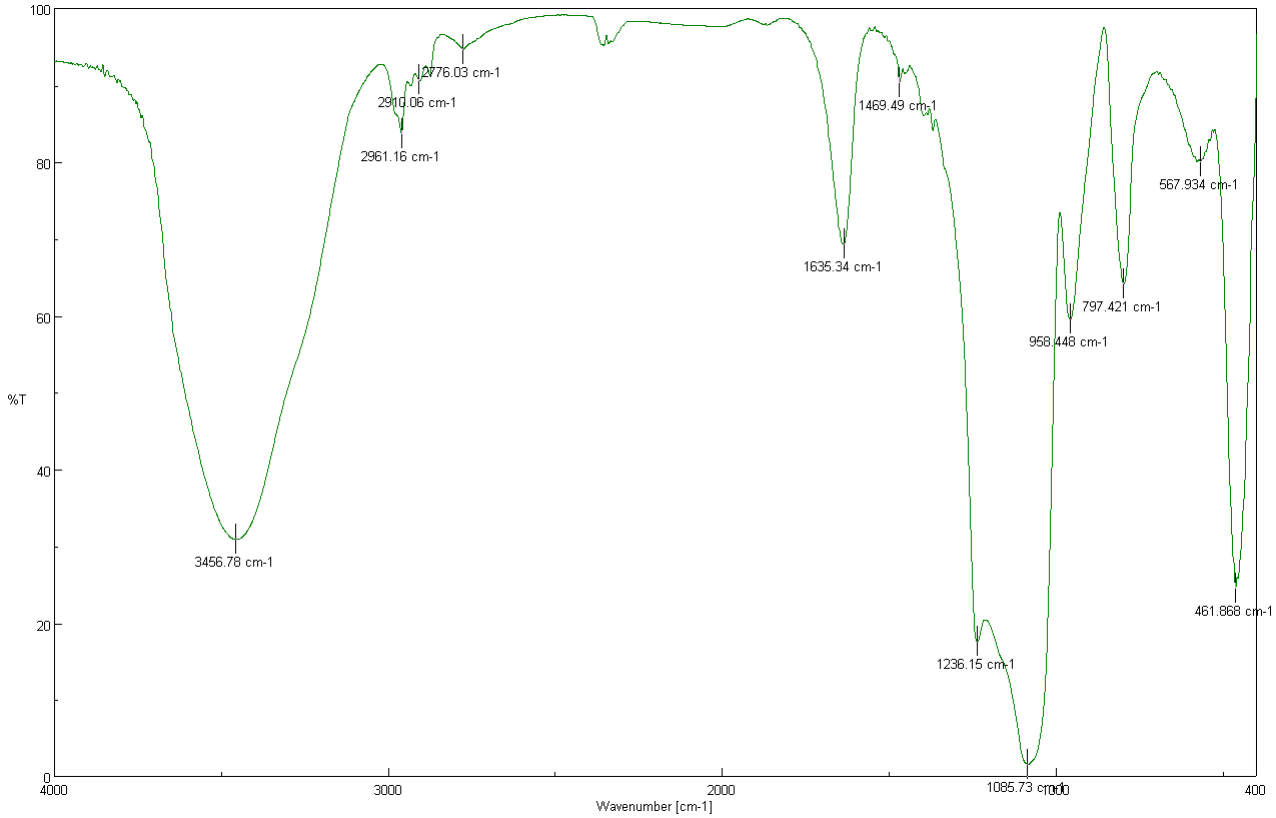


FT-IR Spectrum



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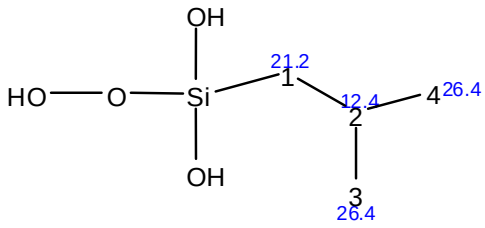

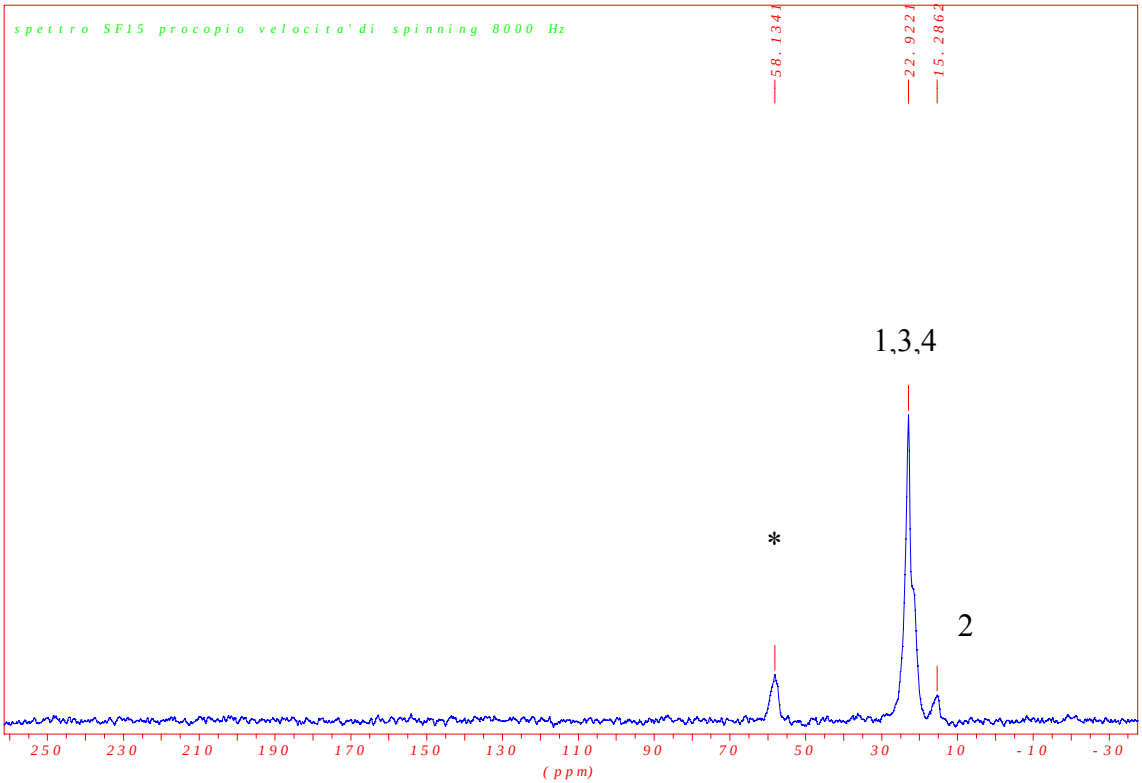

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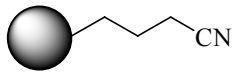
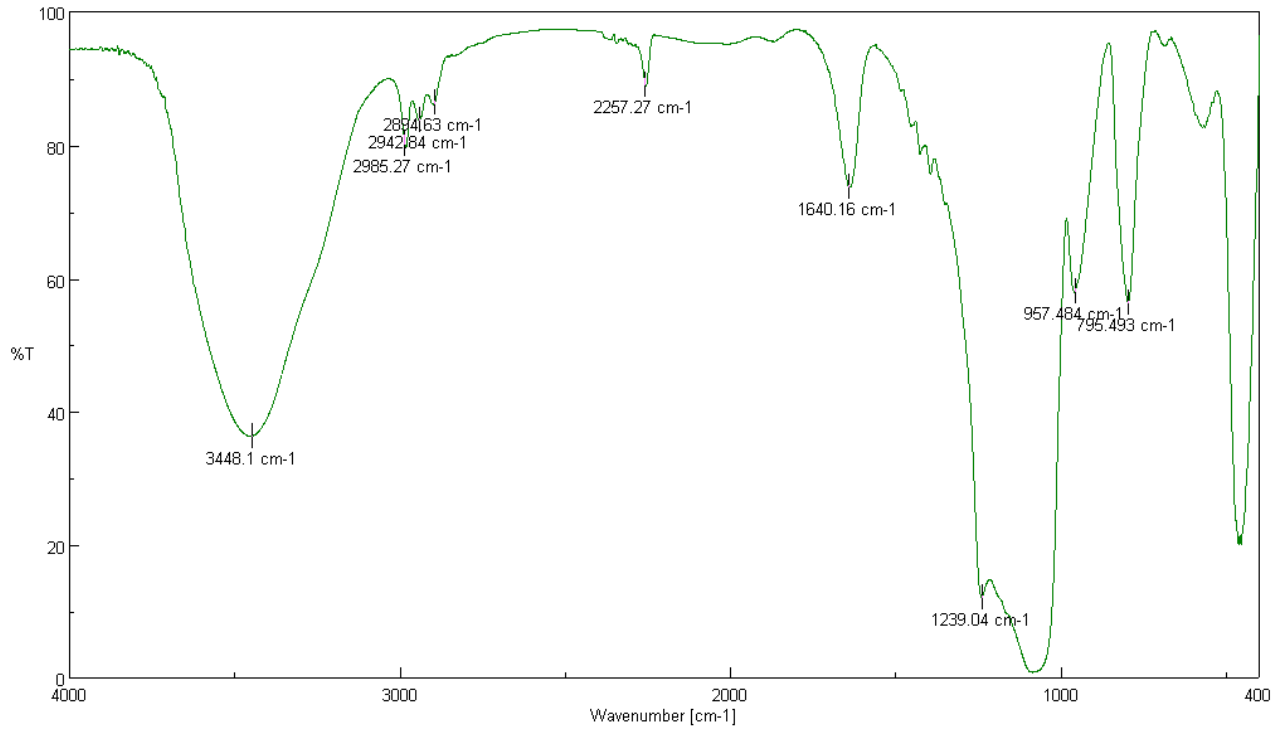


FT-IR Spectrum



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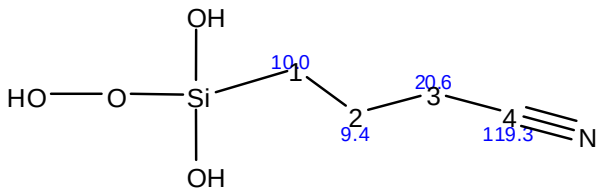

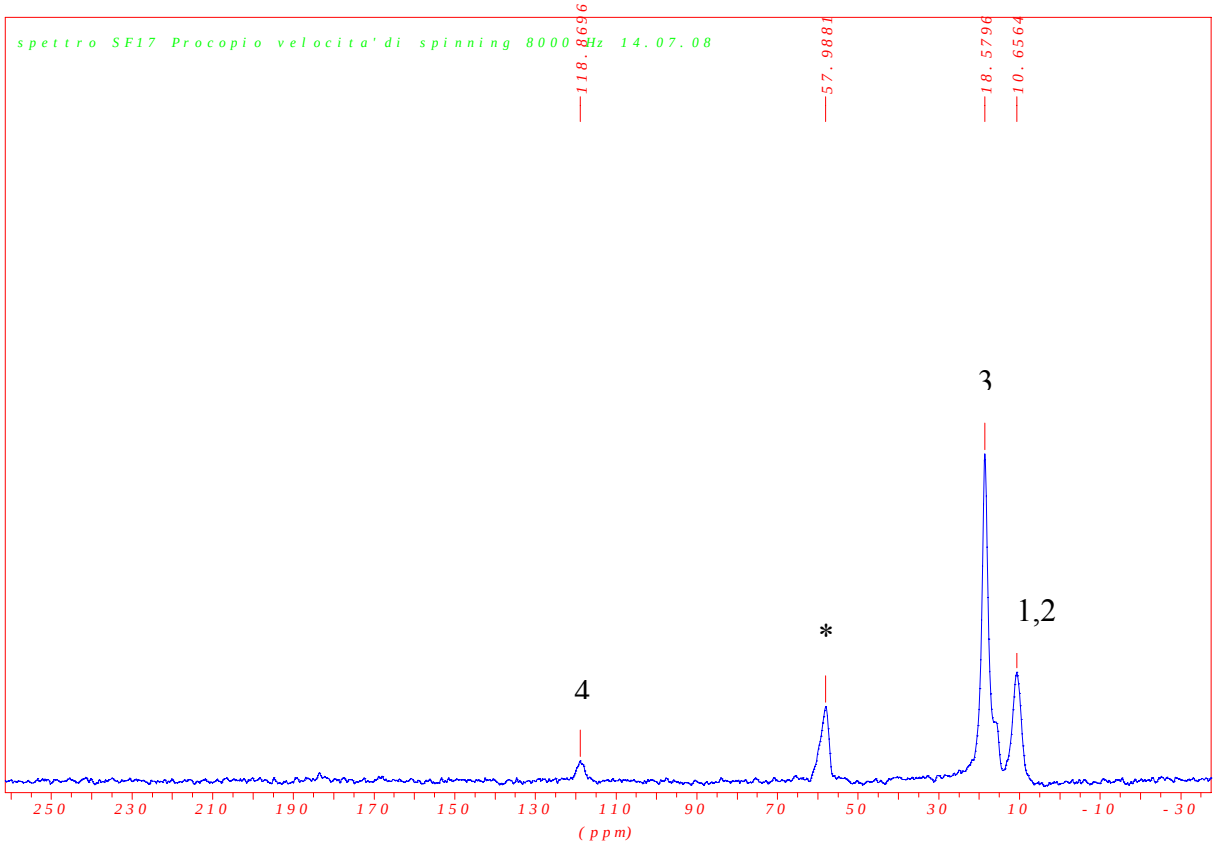

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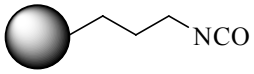
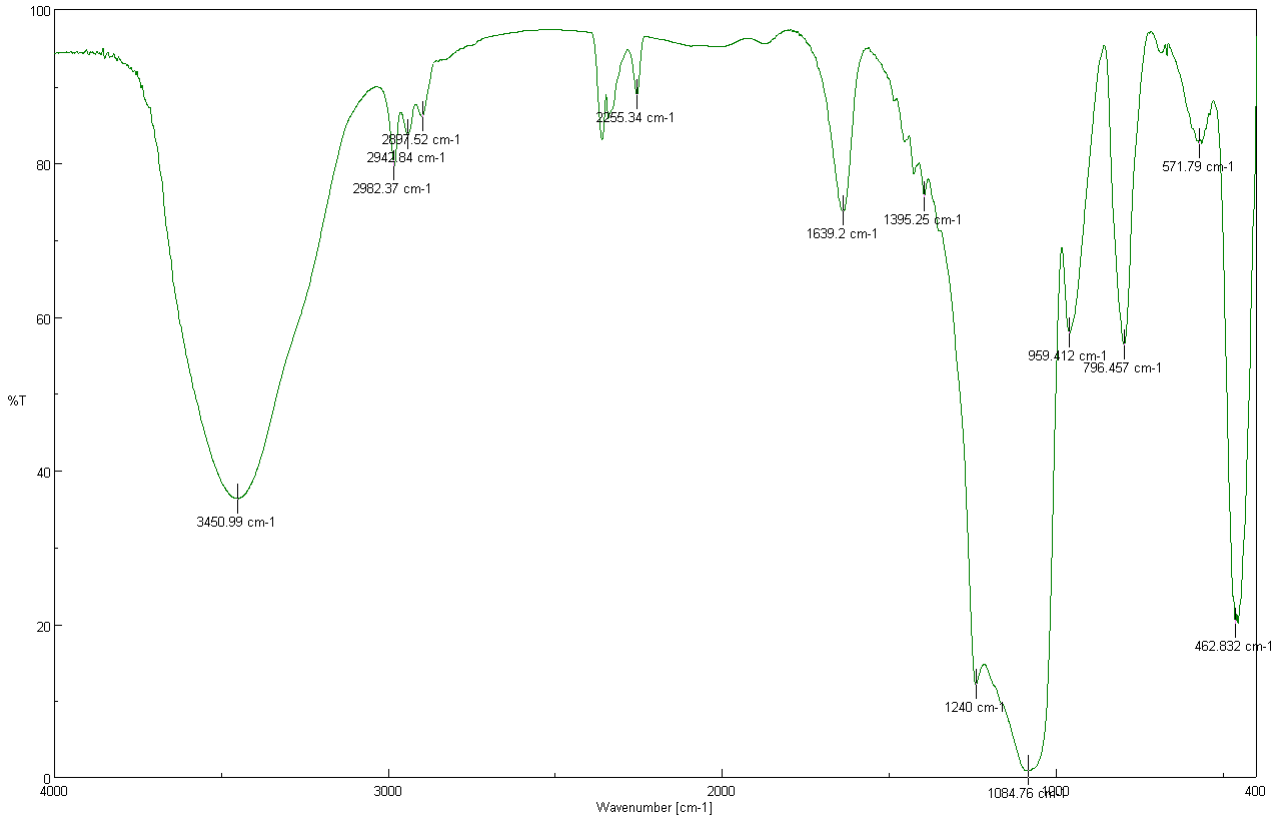


FT-IR Spectrum



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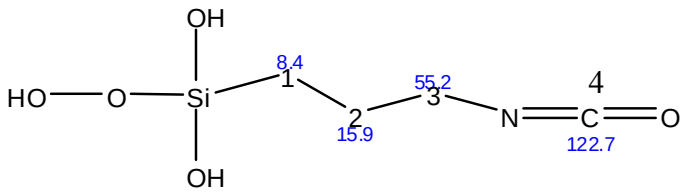

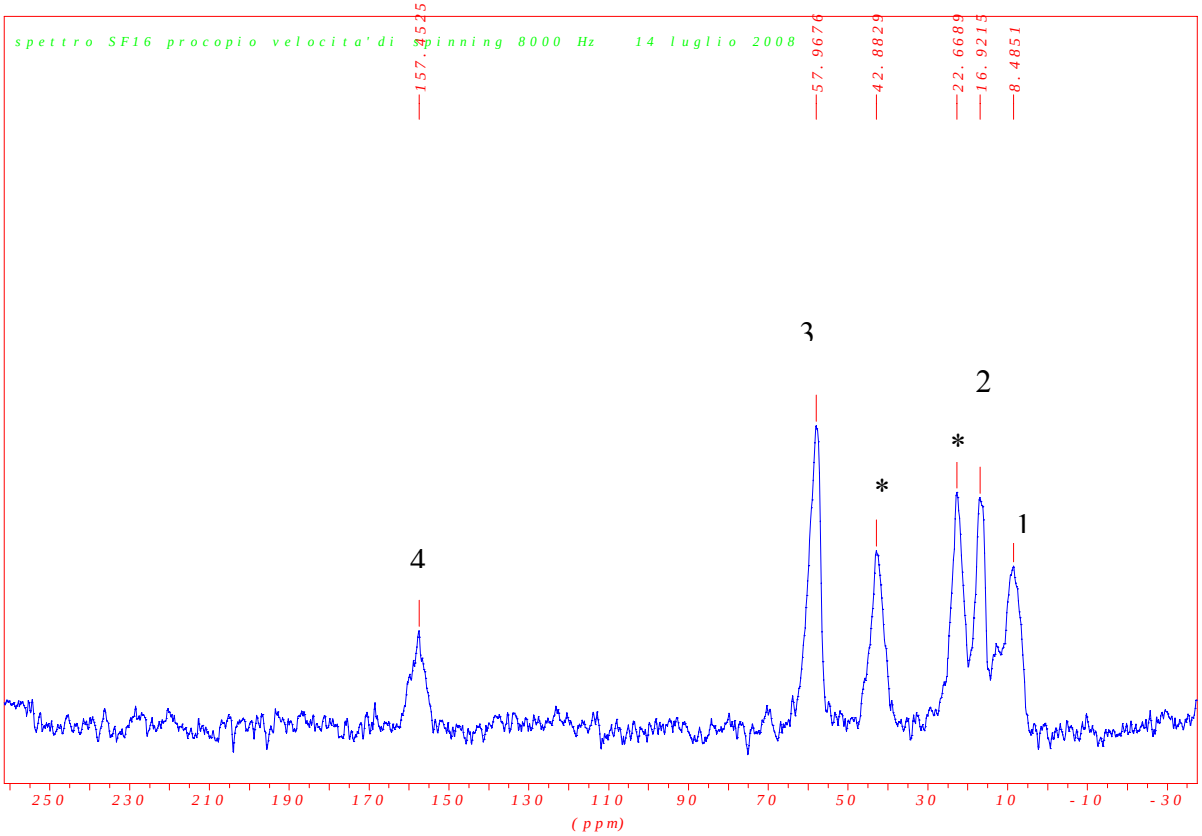

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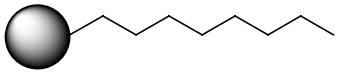
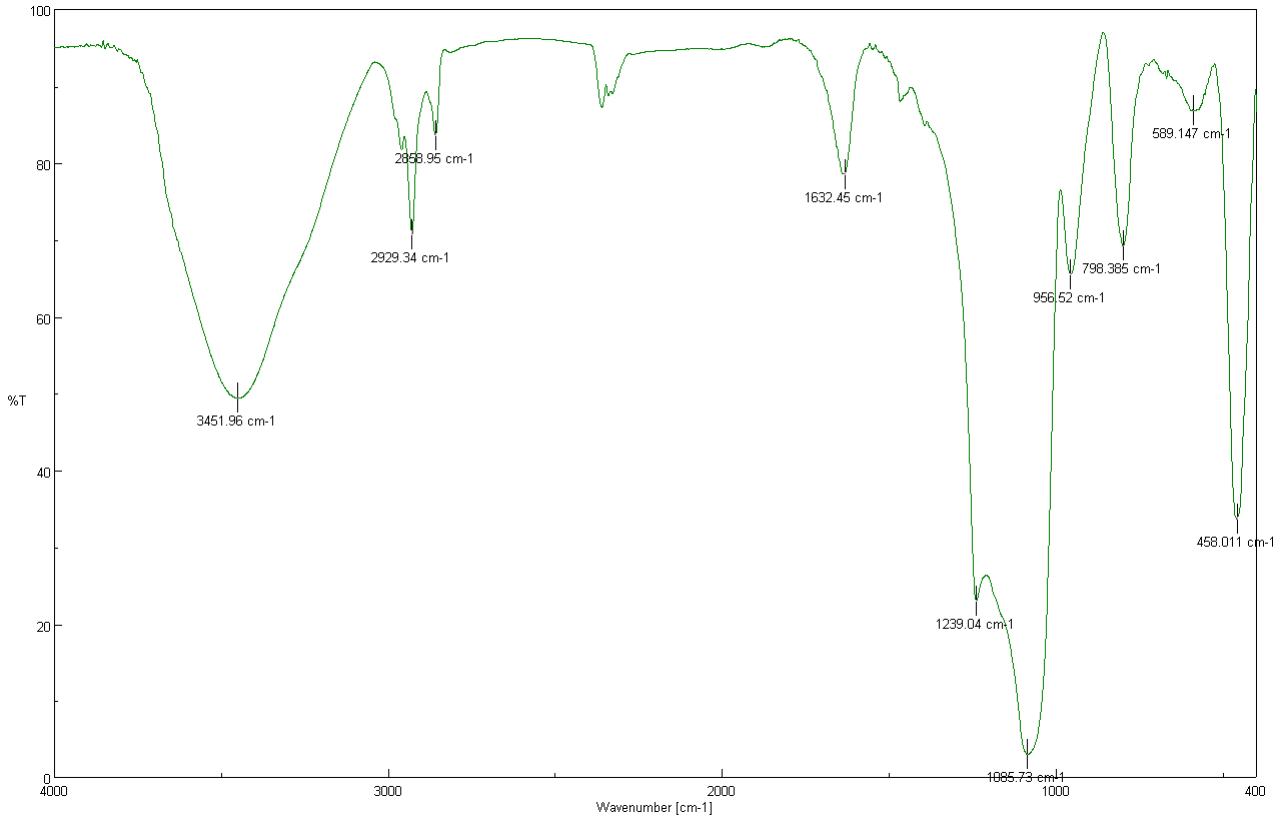
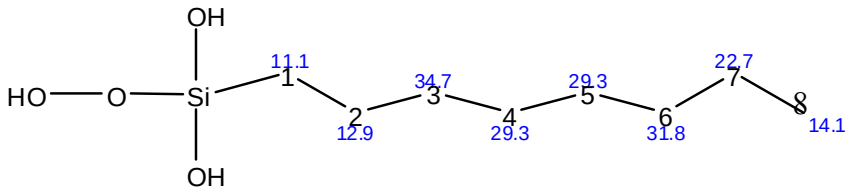
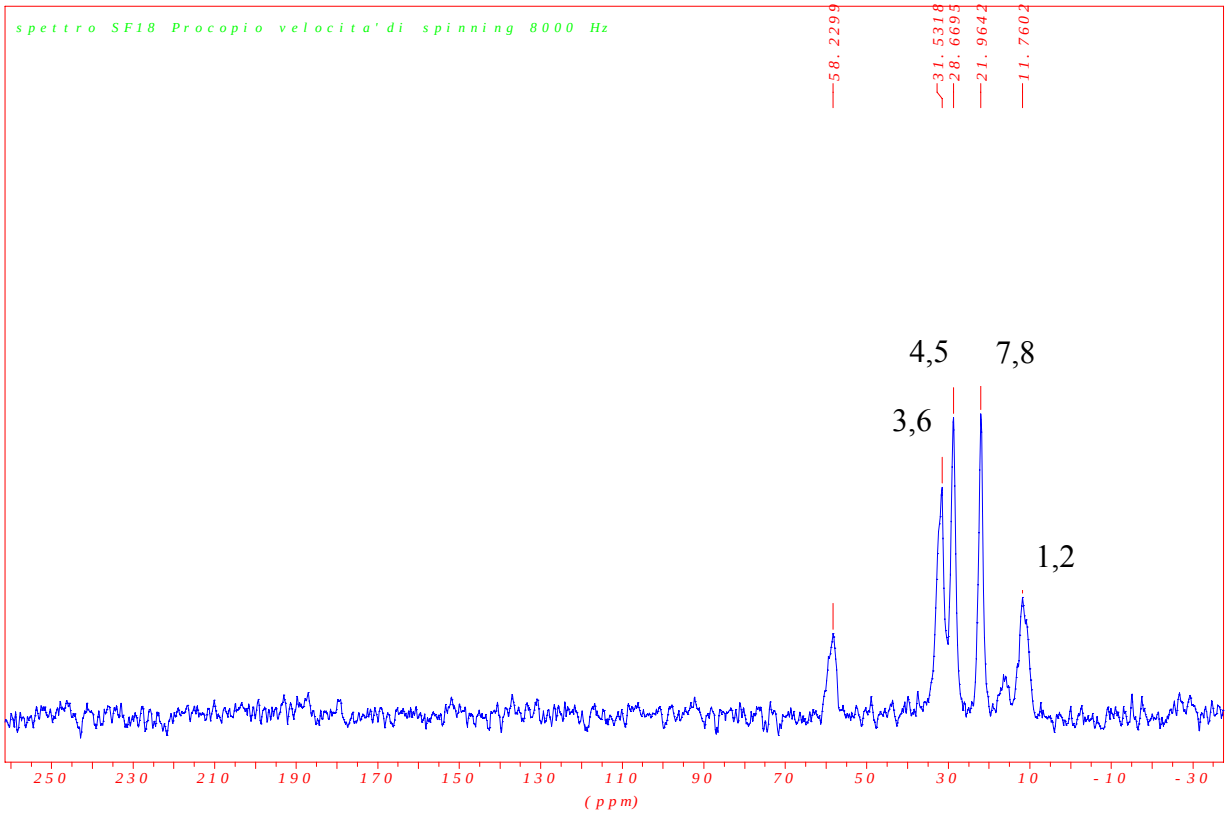


FT-IR Spectrum



^{13}C-NMR Spectrum





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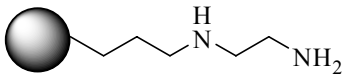
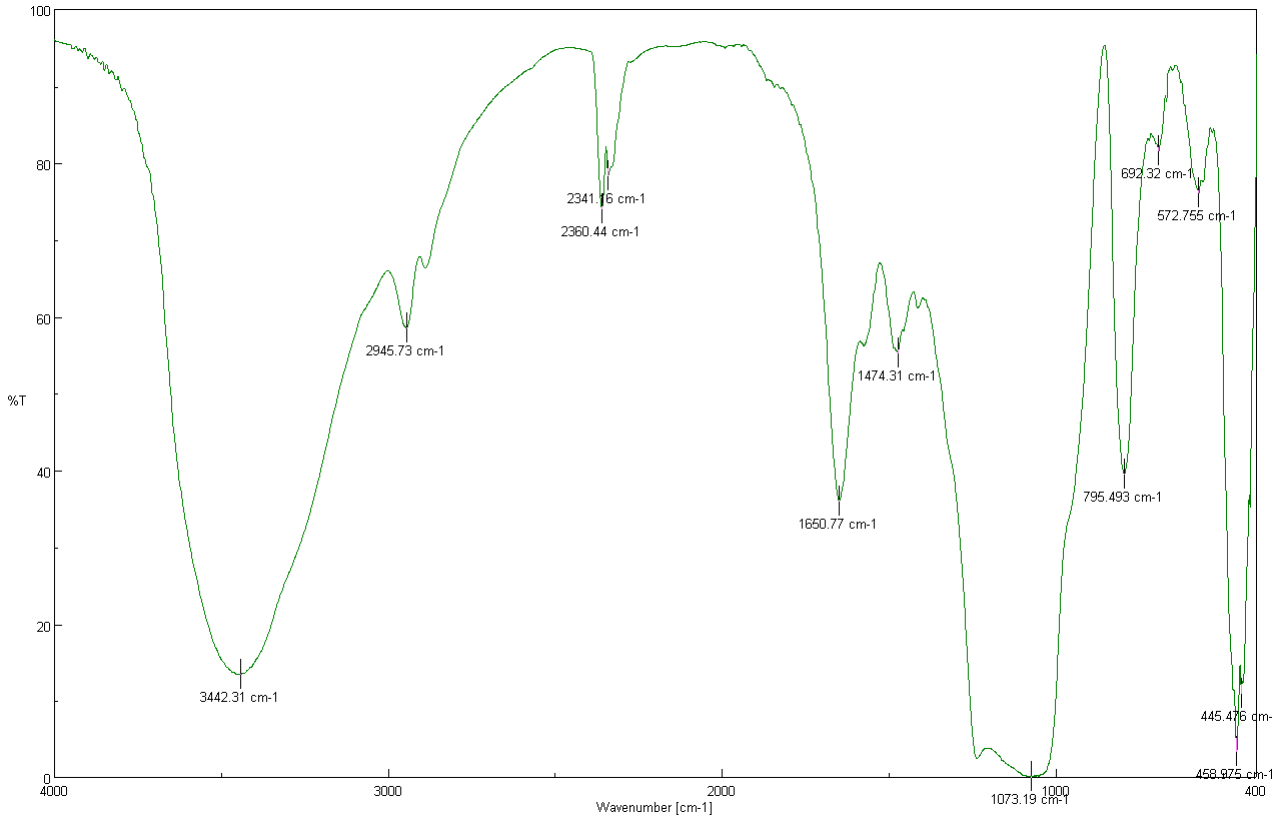
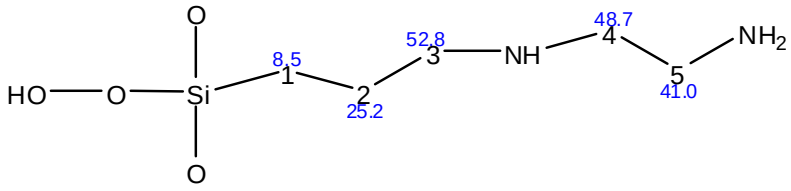
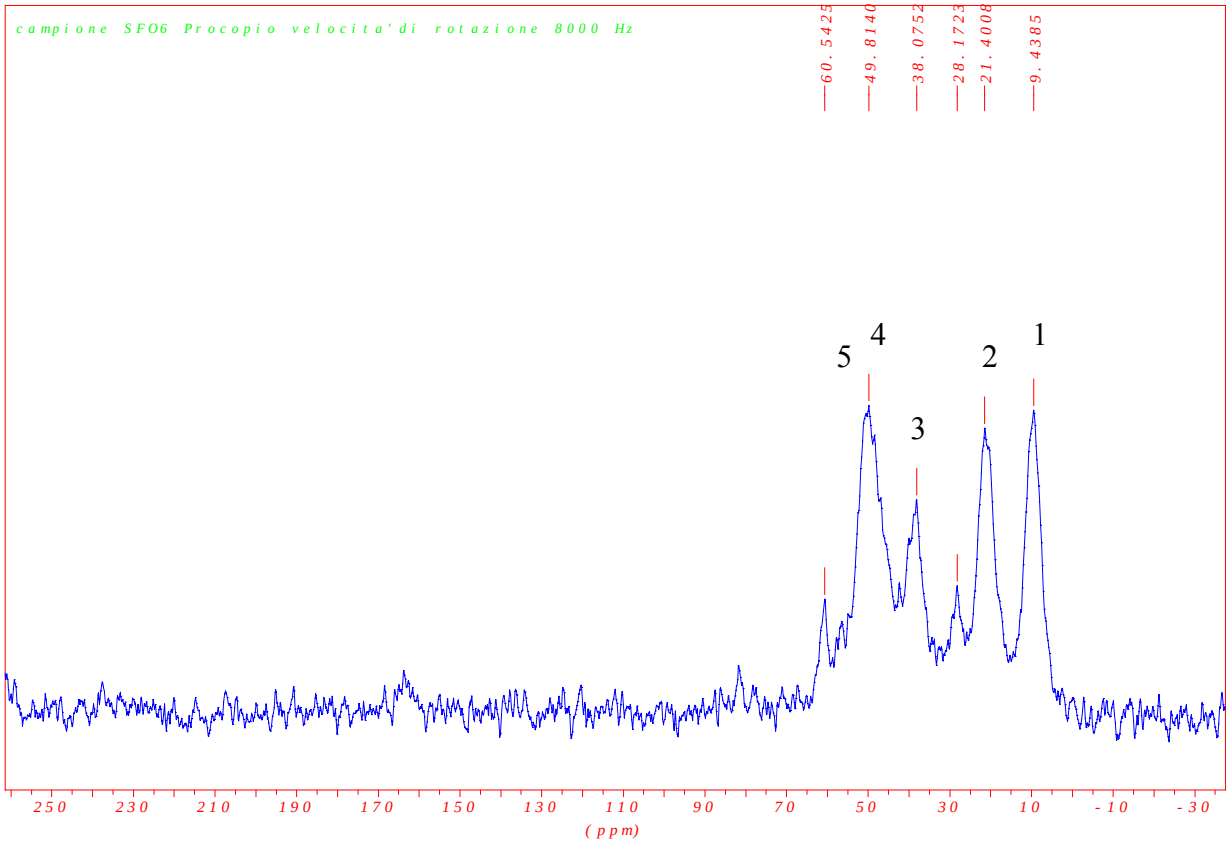


FT-IR Spectrum



^{13}C-NMR Spectrum





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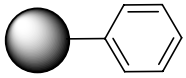
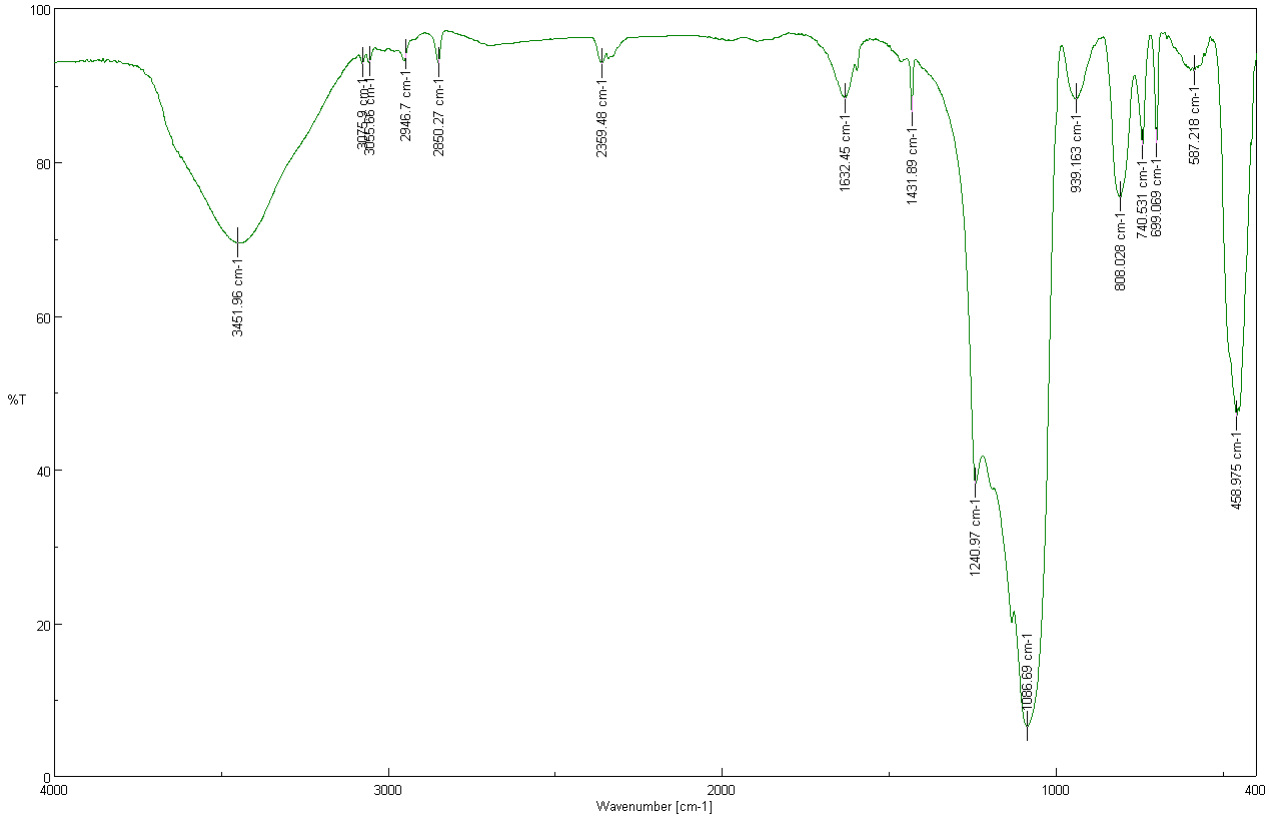
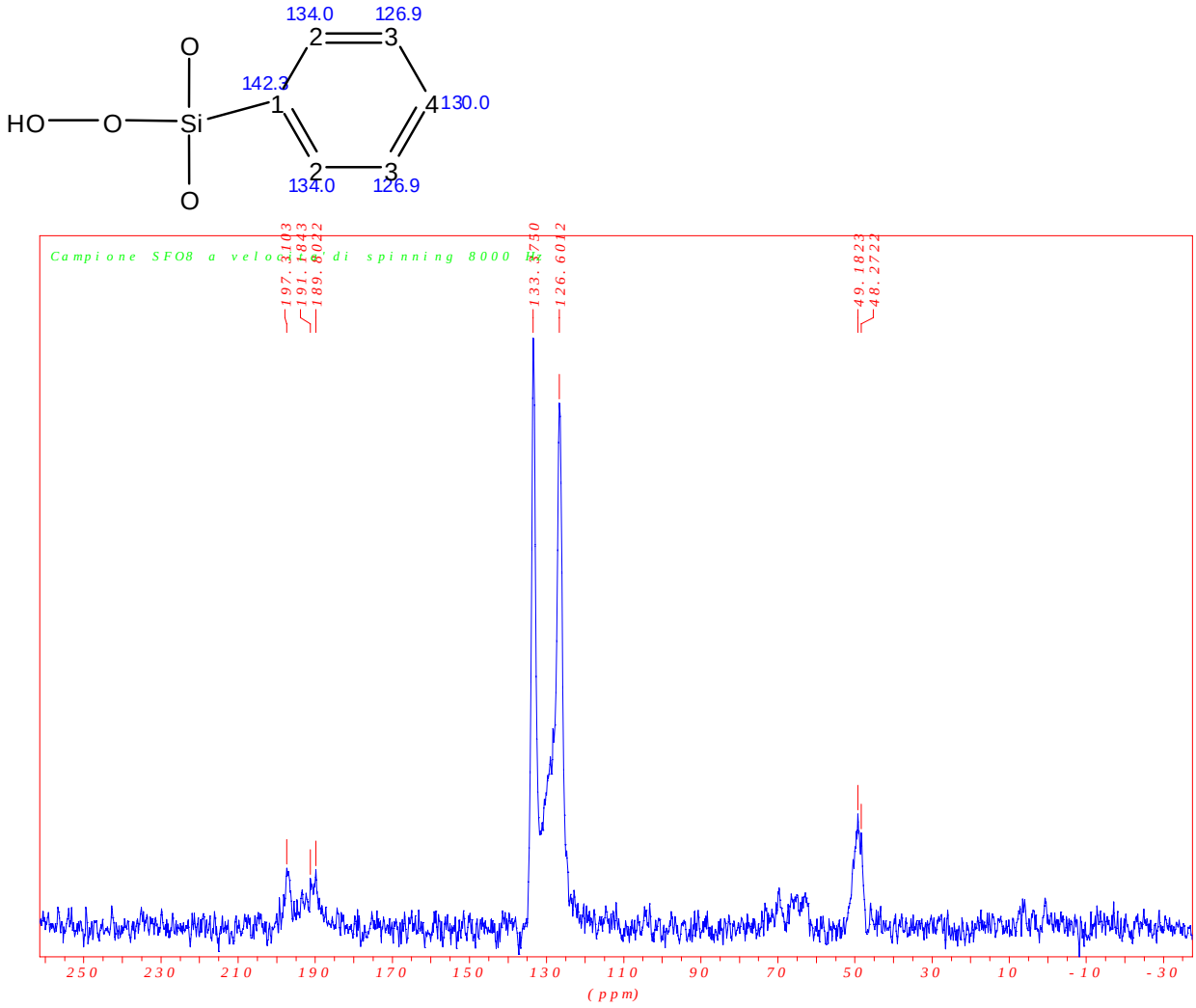


FT-IR Spectrum



^{13}C-NMR Spectrum



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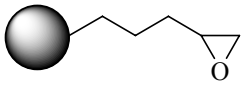
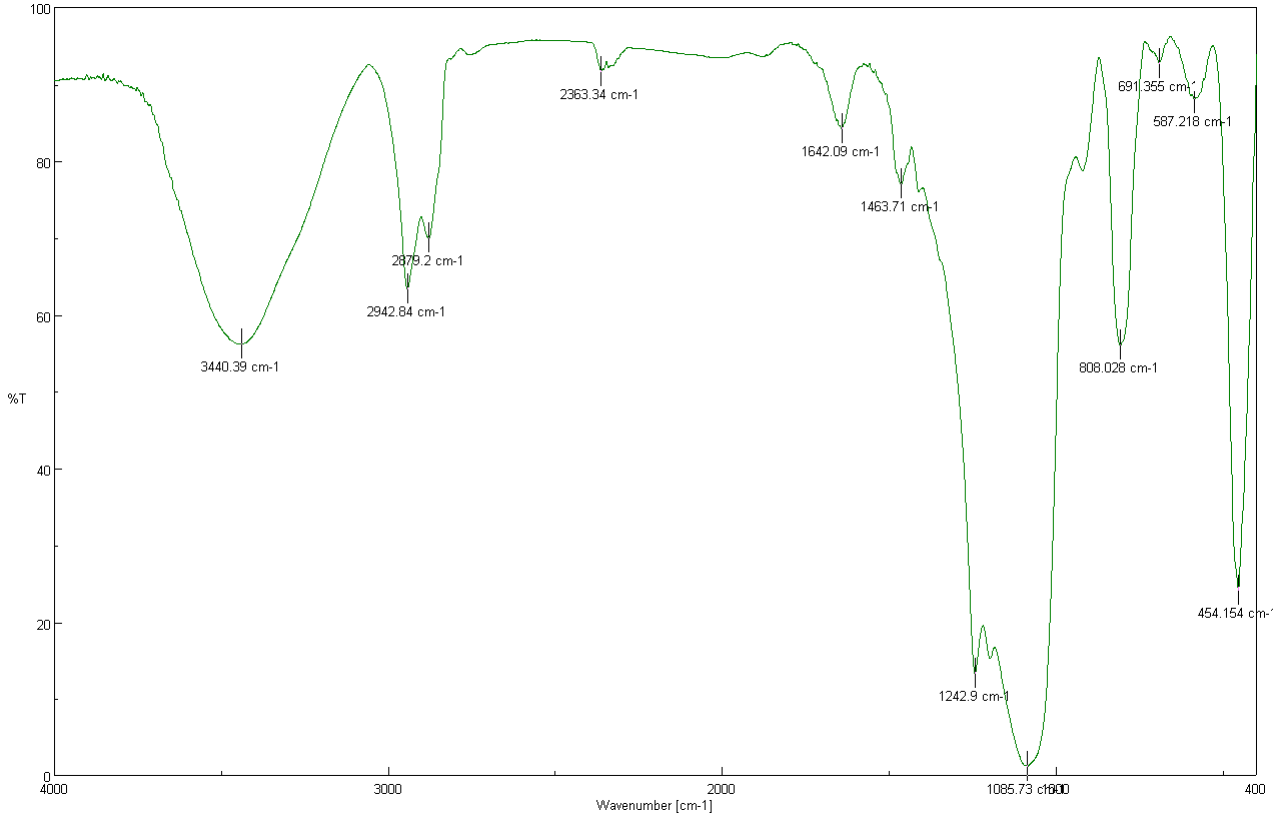
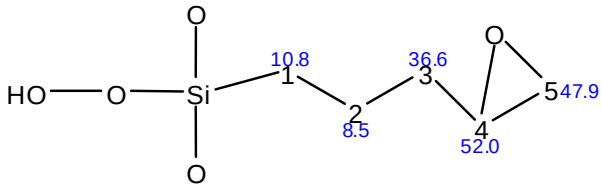
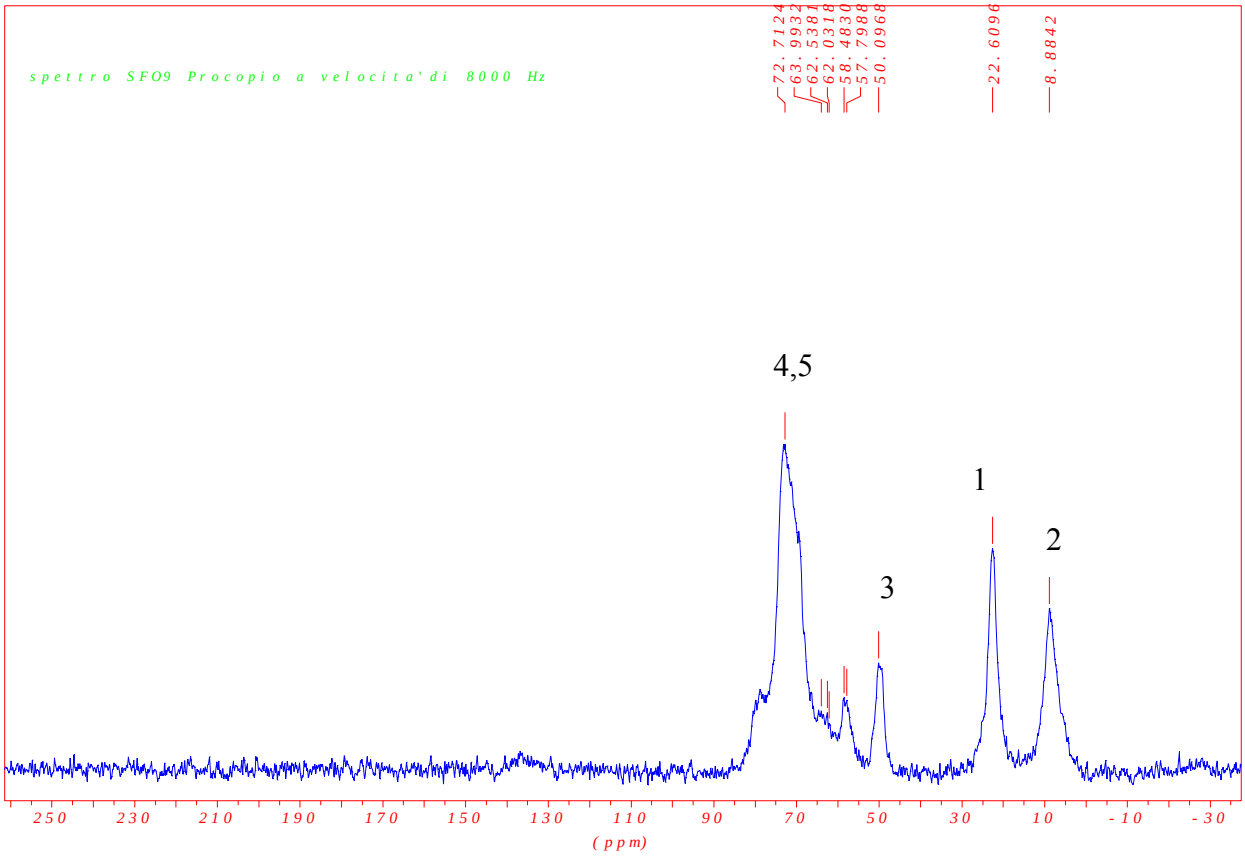


FT-IR Spectrum

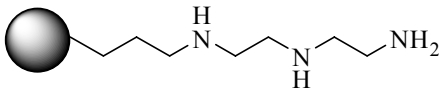


^{13}C-NMR Spectrum

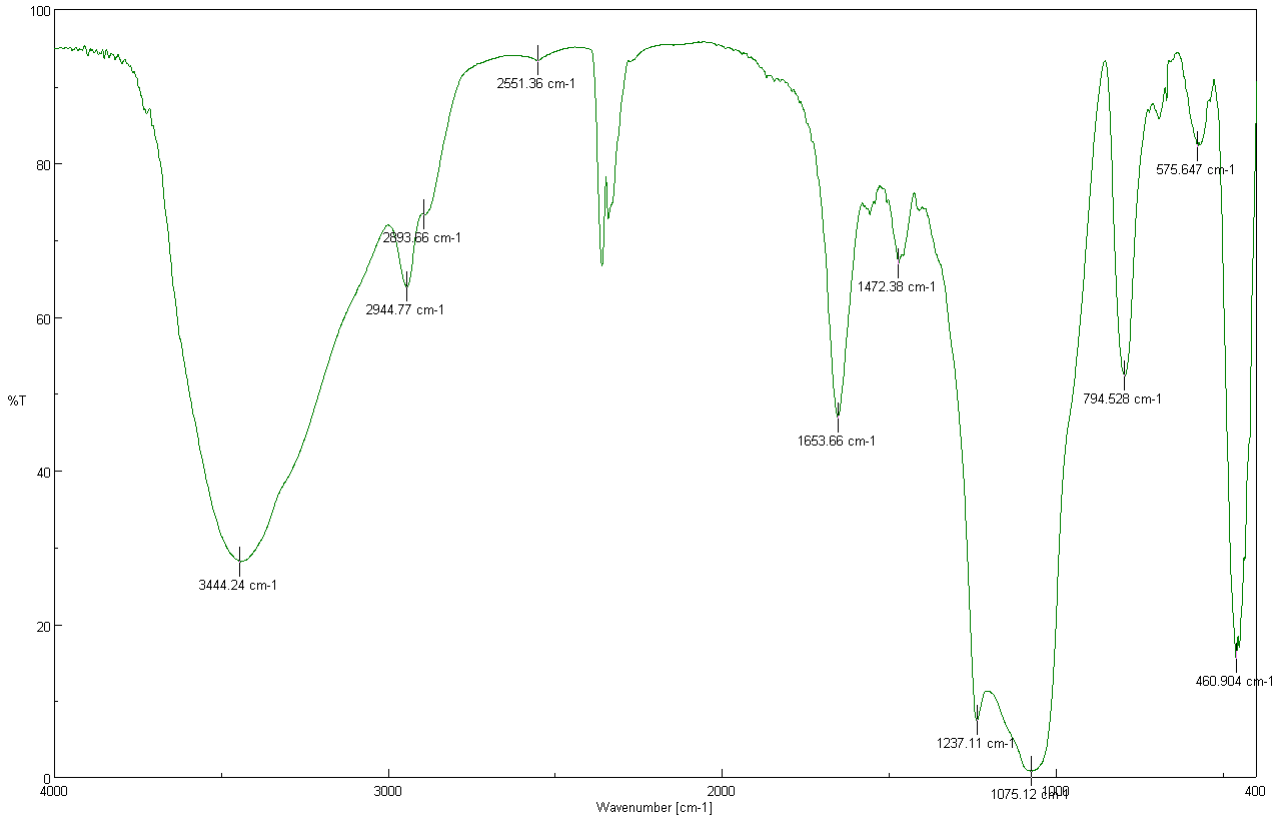




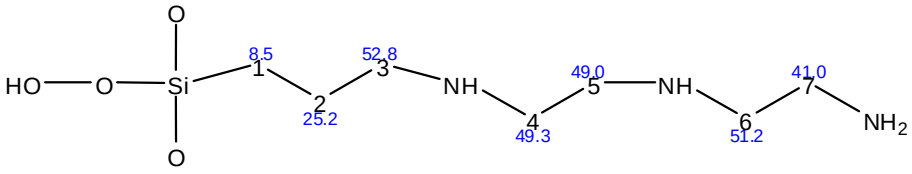
Sample 11

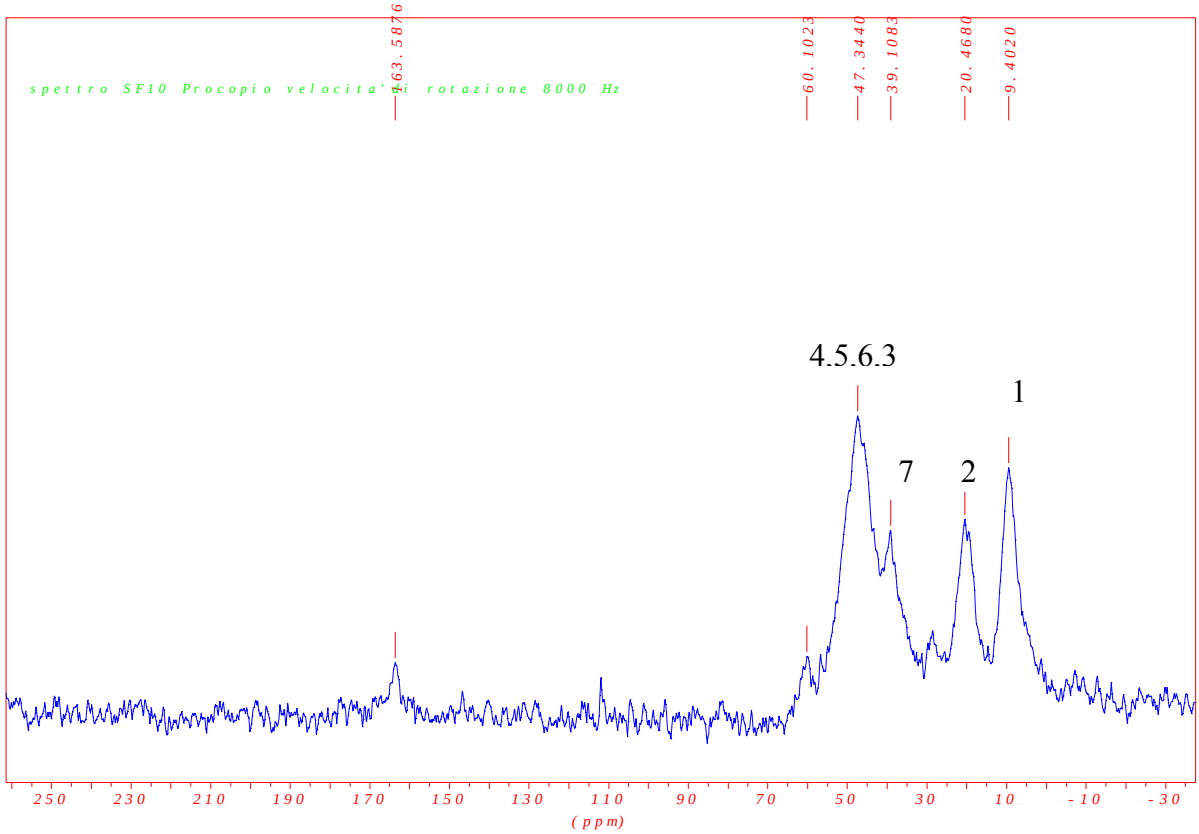


FT-IR Spectrum

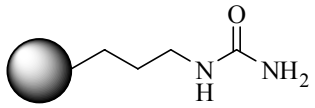


^{13}C-NMR Spectrum

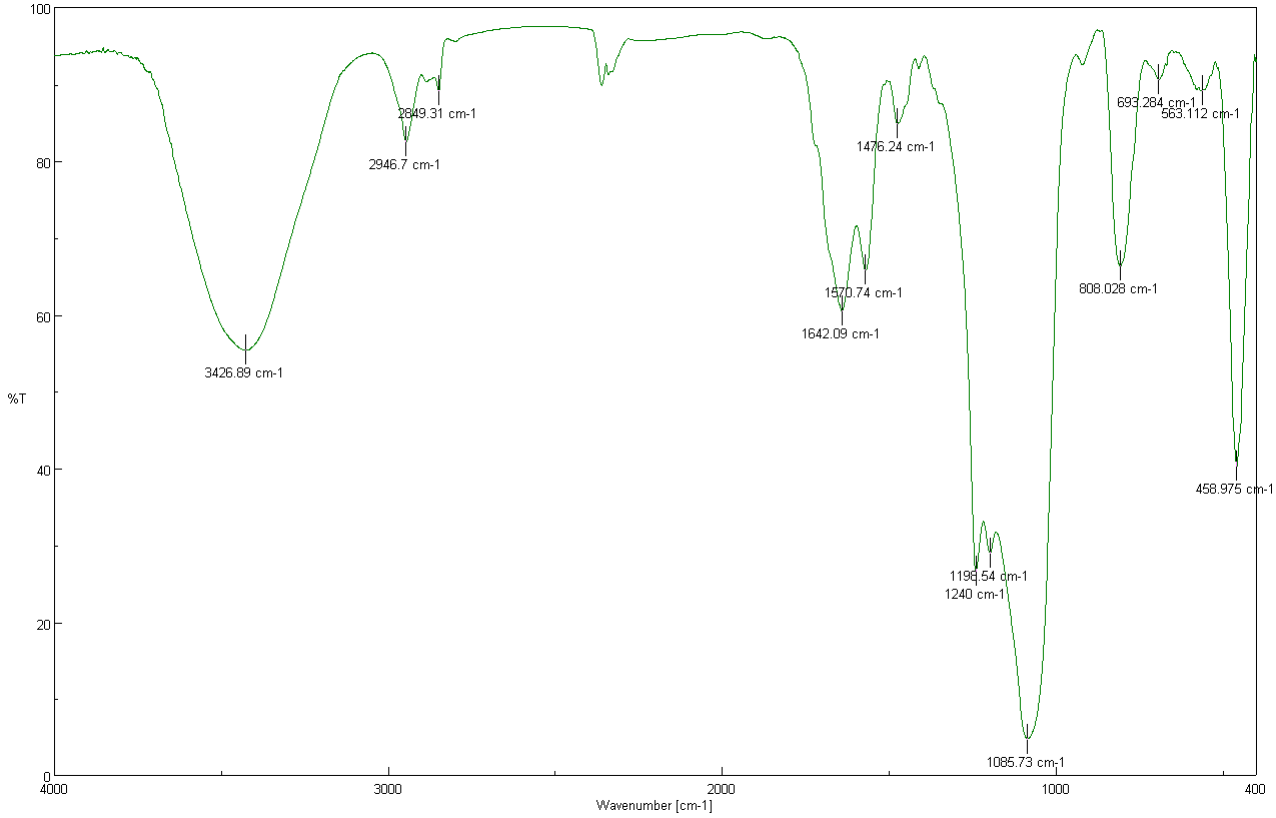




Sample 12



FT-IR Spectrum



^{13}C-NMR Spectrum