

Chalcomer assembly of optical chemosensors for selective Cu²⁺ and Ni²⁺ ion recognition

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Experimental

Caution! Azide compounds are explosive to heat and shock. Great care and protection is required for handling of these compounds.

2.1. General material and methods: All the syntheses were carried out under dry nitrogen atmosphere using vacuum glass line. The organic solvents used were dried and purified according to the standard procedure and stored under dry nitrogen atmosphere. bromotris(triphenylphosphine)copper(I) (Aldrich), γ -chloropropyltriethoxysilane (CIPTES) (Aldrich), propargyl bromide (80% wt. solution in toluene) (Aldrich), sodium azide (SDFCL), potassium carbonate (THOMAS BAKER), 2-hydroxyacetophenone (SDFCL), 3-hydroxyacetophenone (SDFCL), 4-hydroxyacetophenone (SDFCL), salicylaldehyde (Aldrich), 3-hydroxybenzaldehyde (SDFCL), 4-hydroxybenzaldehyde (SDFCL) and triethanolamine (SDFCL) were used as supplied for synthesis of compounds **CTSI 1–9**.

Melting points were uncorrected and measured in a Mel Temp II device using sealed capillaries. Infrared spectrum was obtained neat on a Thermo Scientific Fischer spectrometer. Multinuclear NMR (^1H , ^{13}C) spectra were recorded on a Bruker advance II 400 NMR spectrometer (in CDCl_3) at 298K. MS data of synthesized compounds **CTSI 1–9** was recorded on Waters QQ–TOF micro Mass Spectrometer. UV–Vis spectra were recorded on JASCO V–530 UV–Vis spectrophotometer. CHN analyses were obtained on a Perkin Elmer Model 2400 CHNS elemental analyser. Fluorescence spectroscopy was performed on Perkin Elmer LS55 Fluorescence Spectrophotometer.

Synthesis of terminal alkynes **A1–A6**

To a uniformly stirred solution of **hydroxy aldehyde/ hydroxy acetophenone** (2g, 16.40 mmol, 1 equiv) in 15 ml of DMF cooled in ice bath, added K_2CO_3 (6.76 g, 47.2 mmol, 3 equiv) and propargyl bromide (2.15 g, 1.61 ml, 18.06 mmol, 1.1 equiv) dropwise within 5 min. After complete addition of reactants, the temperature of reaction mixture was slowly raised to 30 °C and stirred for 14 h. The reaction was then quenched by addition of ice cold water and filtered the solid product (in case of aldehyde **A1–A3** and acetophenone **A4–A6**). In case of low melting solids extraction was carried out with ethyl acetate. The combined organic layers were dried over anhydrous MgSO_4 and vacuum

evaporation of solvent resulted into the formation of desired compound. The solid alkynes were recrystallized by dissolving in minimum amount of ethanol.

Synthesis of chalcones B1–B9

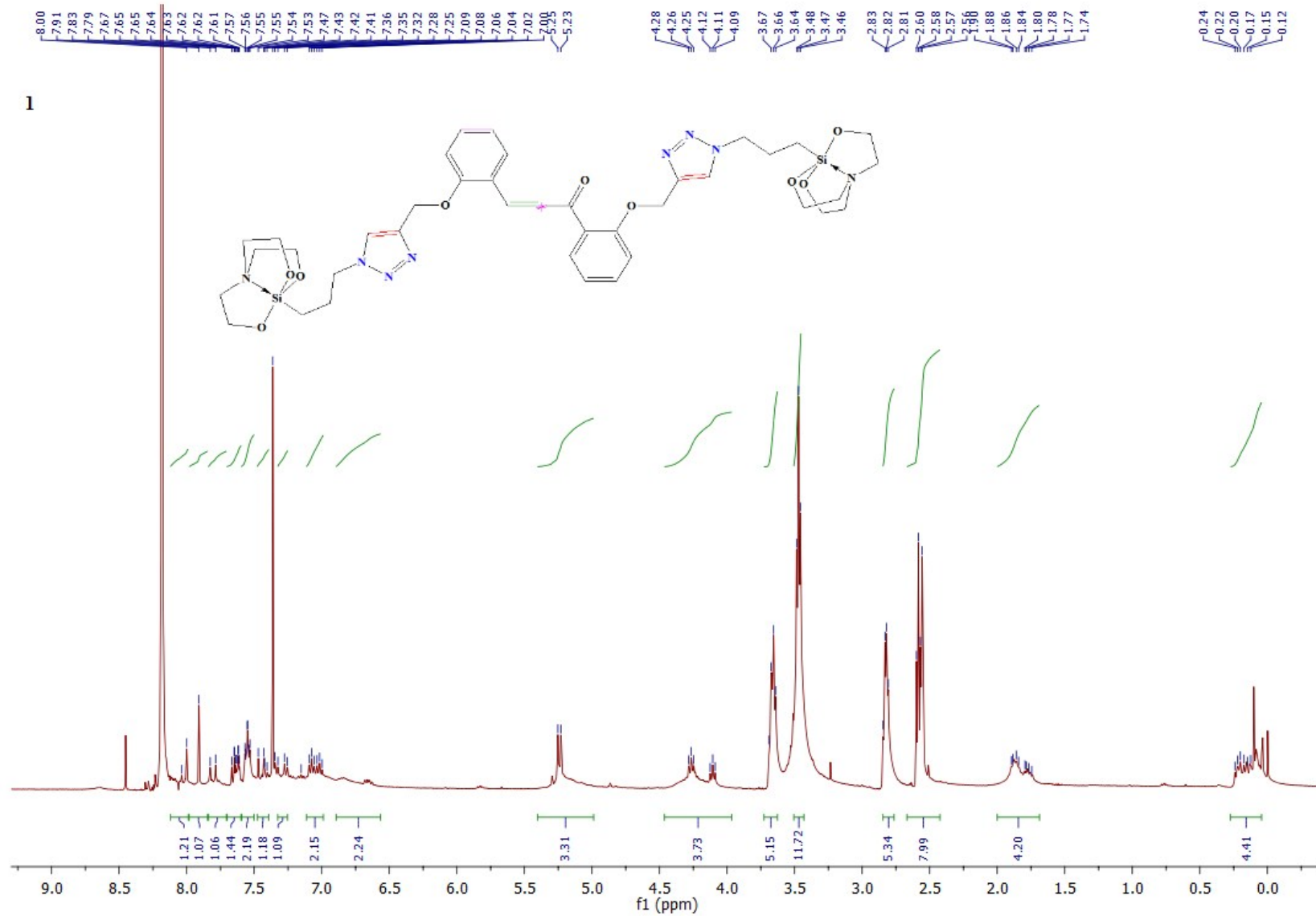
To a uniformly stirred solution of above aldehyde alkynes **A1–A3** (1 equiv) in 15 ml of ethanol, added KOH (0.02 g, 0.36 mmol), ethanolic solution of substituted acetophenone **A4–A6** (1 equiv) was added slowly within 10 min. The reaction was stirred for 4 h and monitored the end point using TLC (hexane:ethyl acetate (8:2)). On completion, the reaction was quenched by ice cold water, extracted with methylene chloride and washed twice with brine solution. The combined organic phases were dried over anhydrous MgSO₄ and vacuum evaporation afforded the desired product.

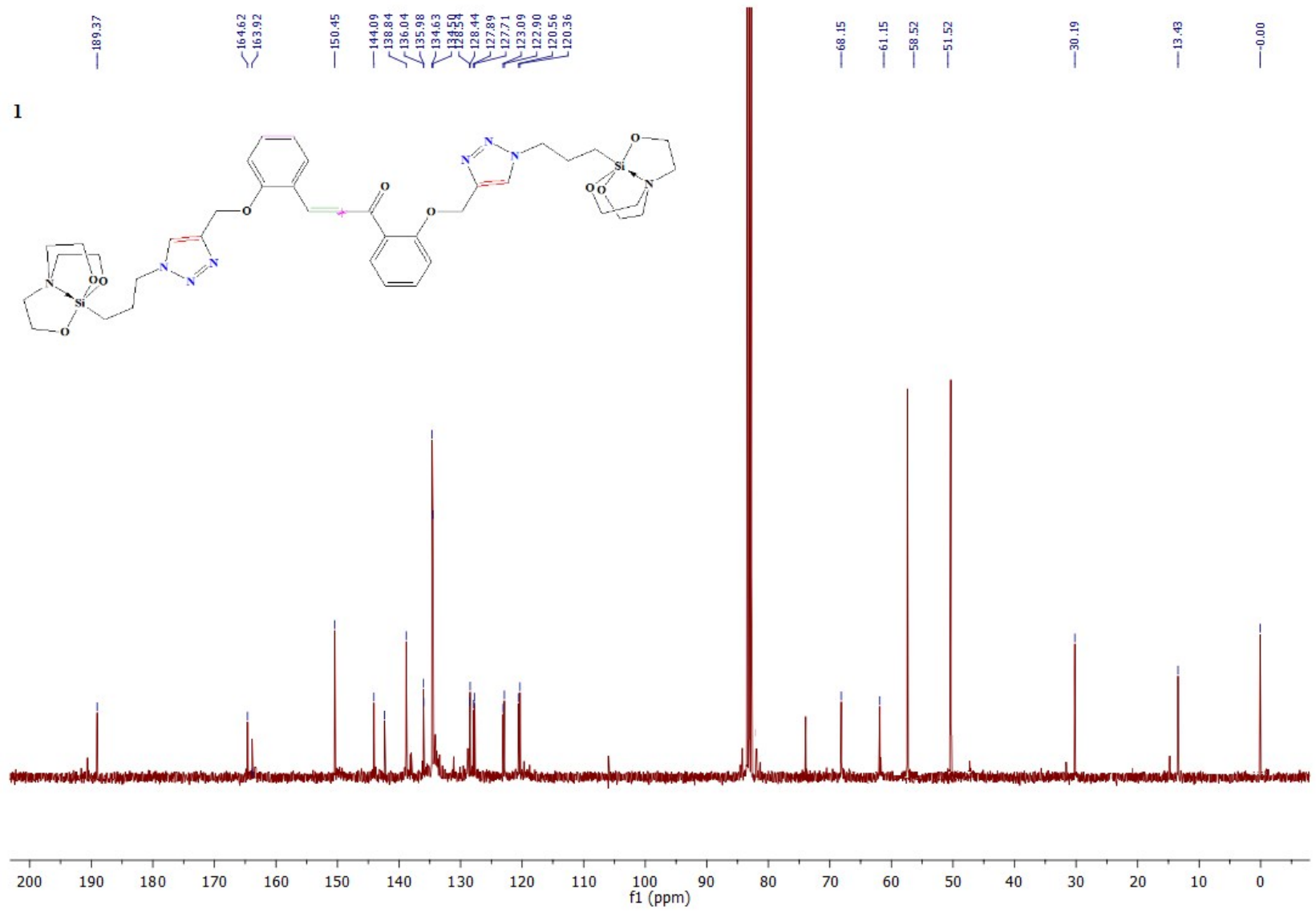
Synthesis of triethoxysilanes (CTTES) C1–C9

In a 25 ml two neck round bottom flask, to stirred solution of chalcone alkyne **B1–B9** in 1:1 solution of THF:TEA (3ml), added AzPTES followed by catalyst loading under inert atmosphere. Slowly the temperature of reaction mixture was raised to 65 °C and stirred vigorously for 3 h. After completion of reaction, it was cooled to room temperature, filtered and vacuum evaporation of solvent resulted in desired nPTES **C1–C9**.

2.2. Synthesis of compounds CTSI 1–9

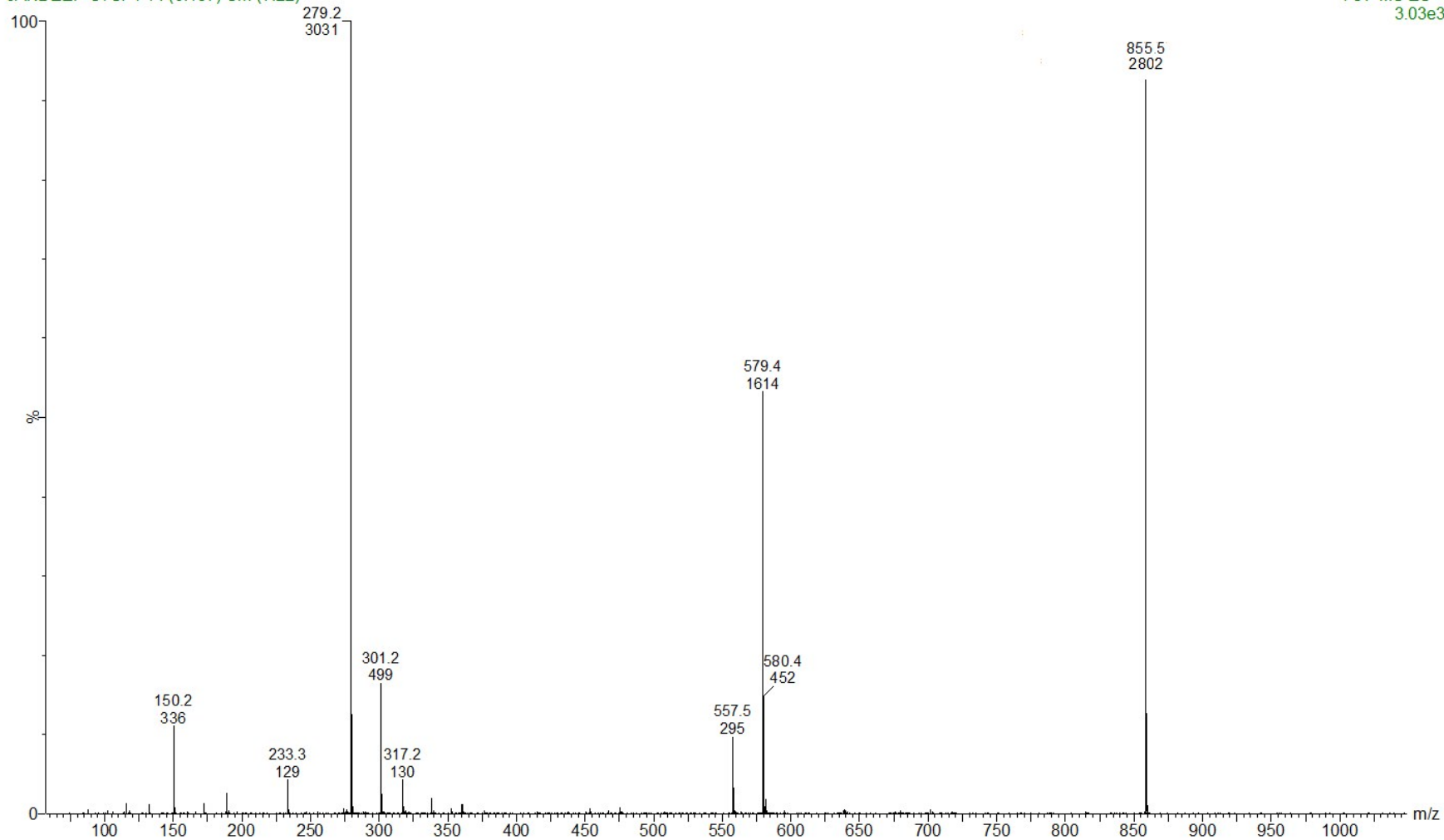
General procedure for the synthesis of different positional isomers of CTS involve following methodology. To uniformly stirred solution of triethanolamine (1 equiv) and potassium hydroxide (cat. amt.) in toluene, slowly added **C 1–9** dropwise within 2 min. The mixture was refluxed for 5 h and after completion of reaction was allowed to cool at room temperature. The solvent volume in mixture was reduced to 3 ml by vacuum evaporation and addition of 10 ml of n-pentane resulted into separation of slightly coloured solid. The solid so obtained was stirred for 48 h, filtered and washed with 2x5 ml n-pentane to afford **CTSI 1–9**.





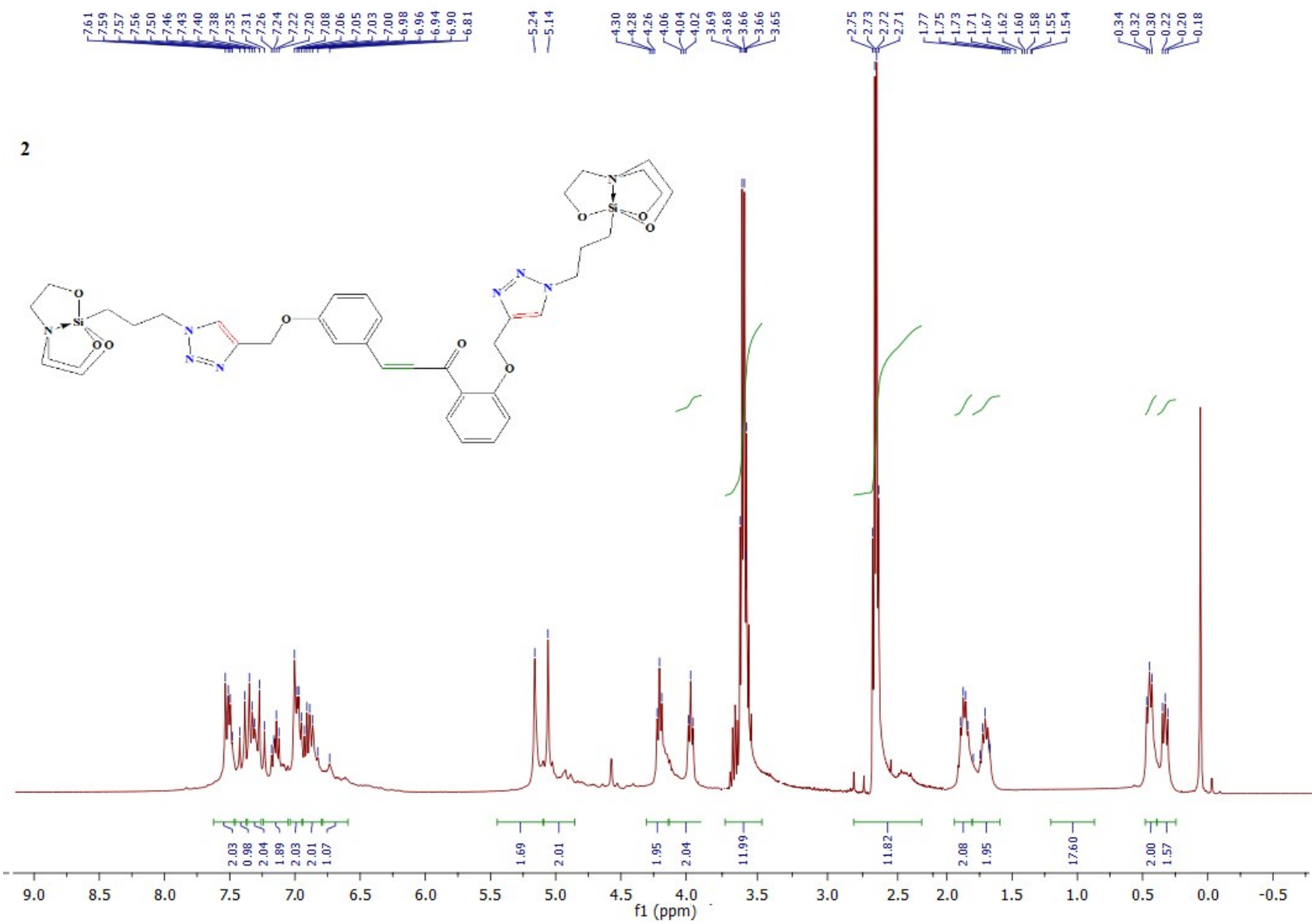
WATERS, Q-TOF MICROMASS (LC-MS)

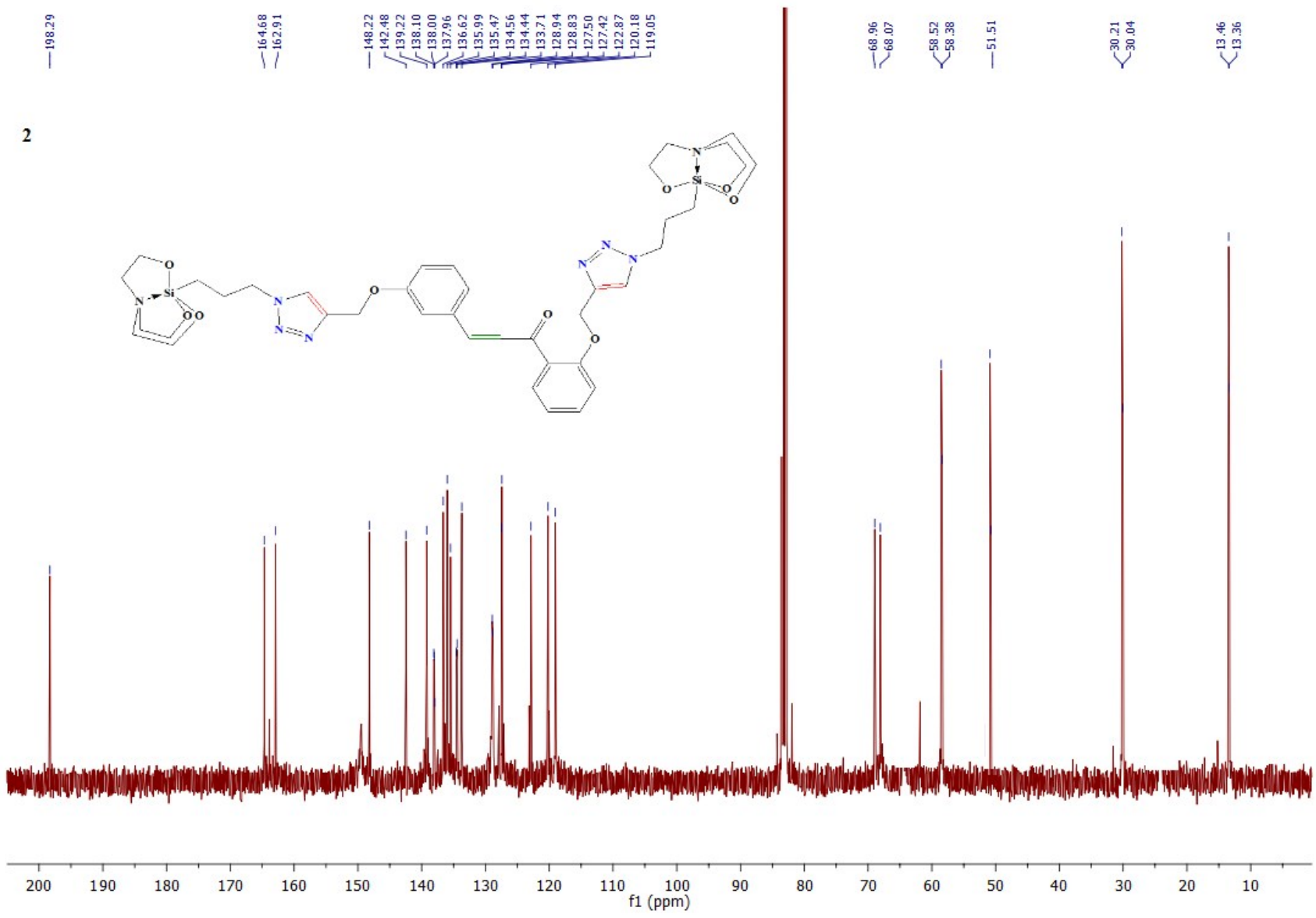
JANDEEP CTSI-1 14 (0.157) Cm (7:22)

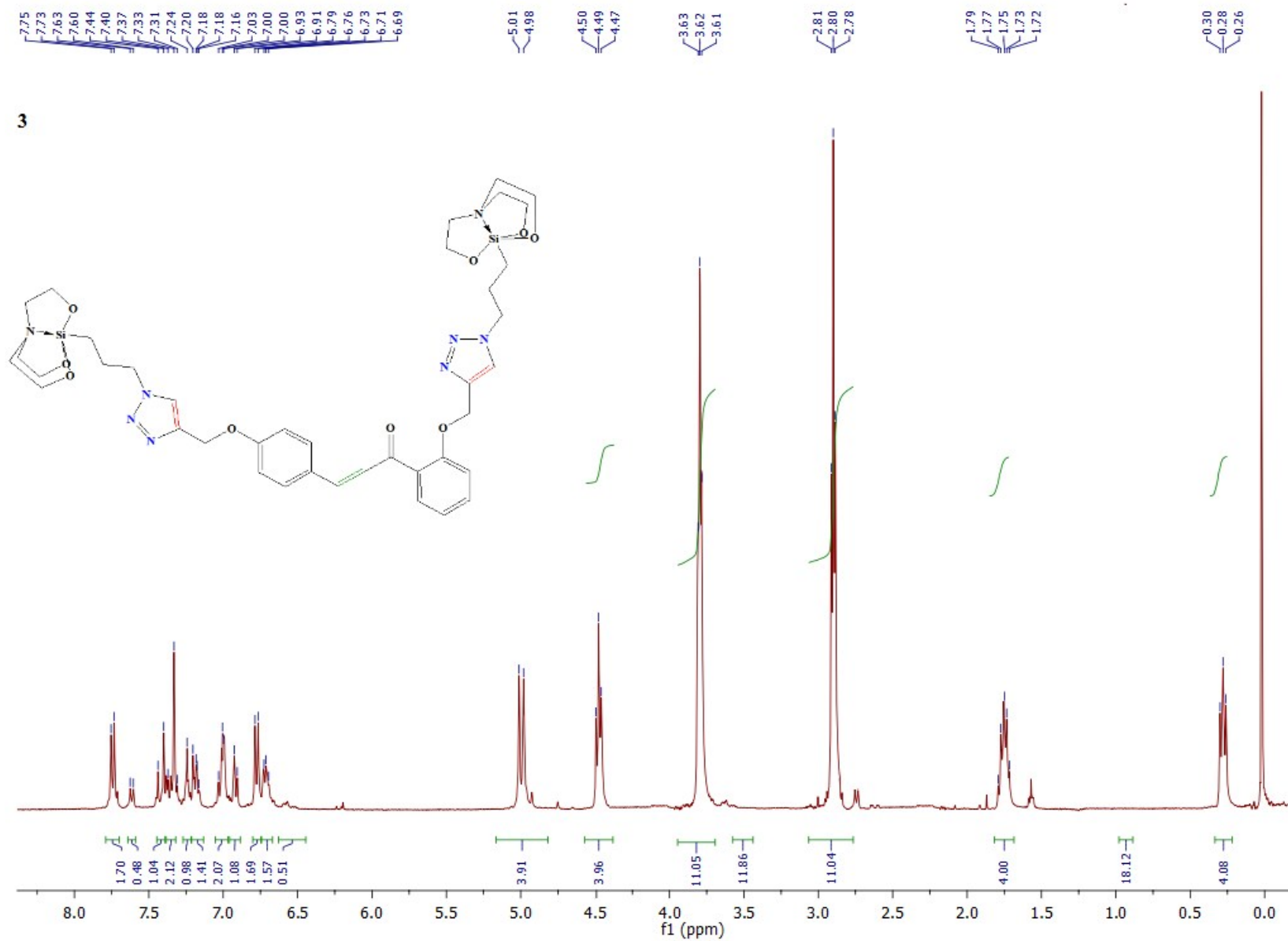


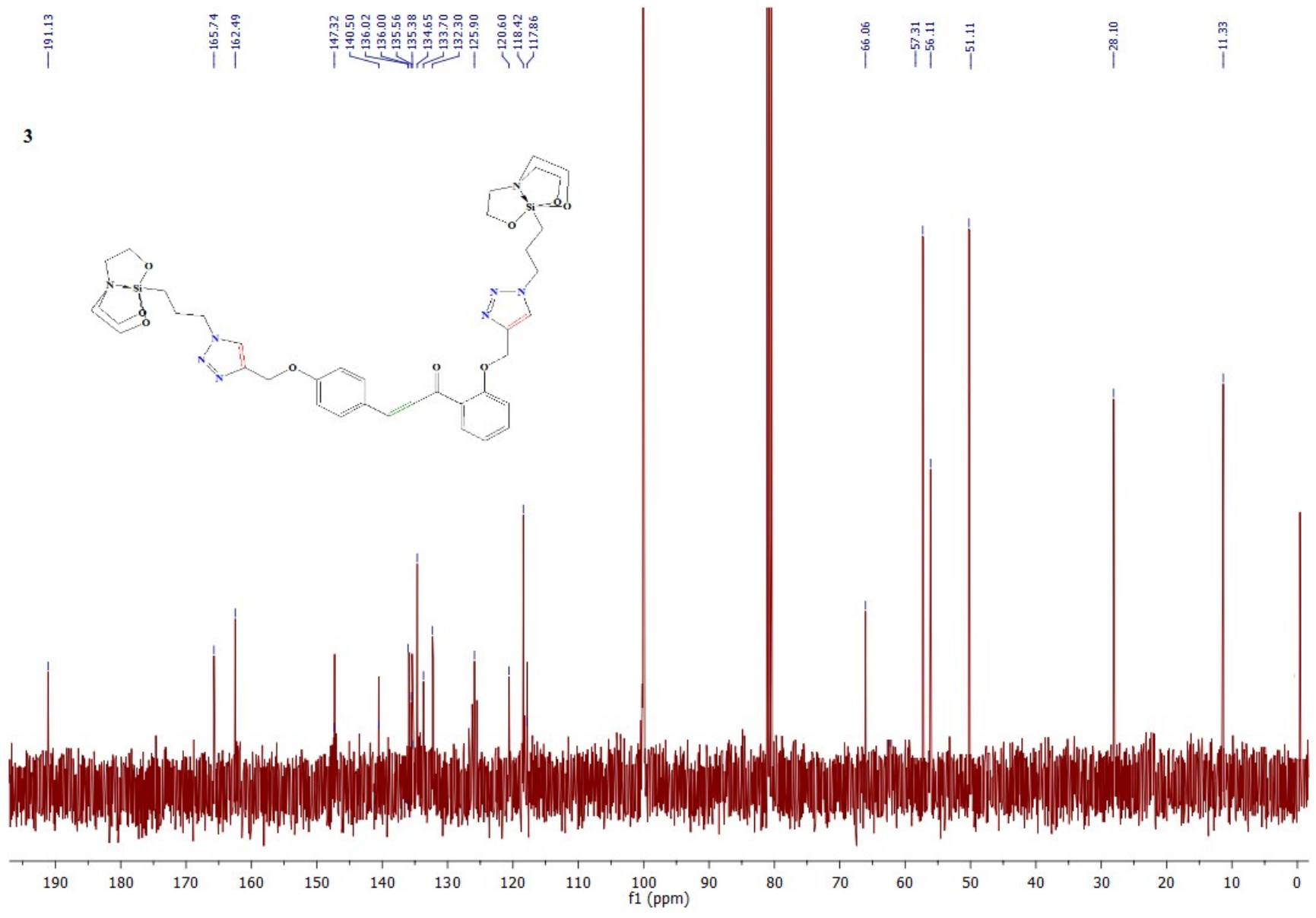
SAIF/CIL, PANJAB UNIVERSITY, CHANDIGARH

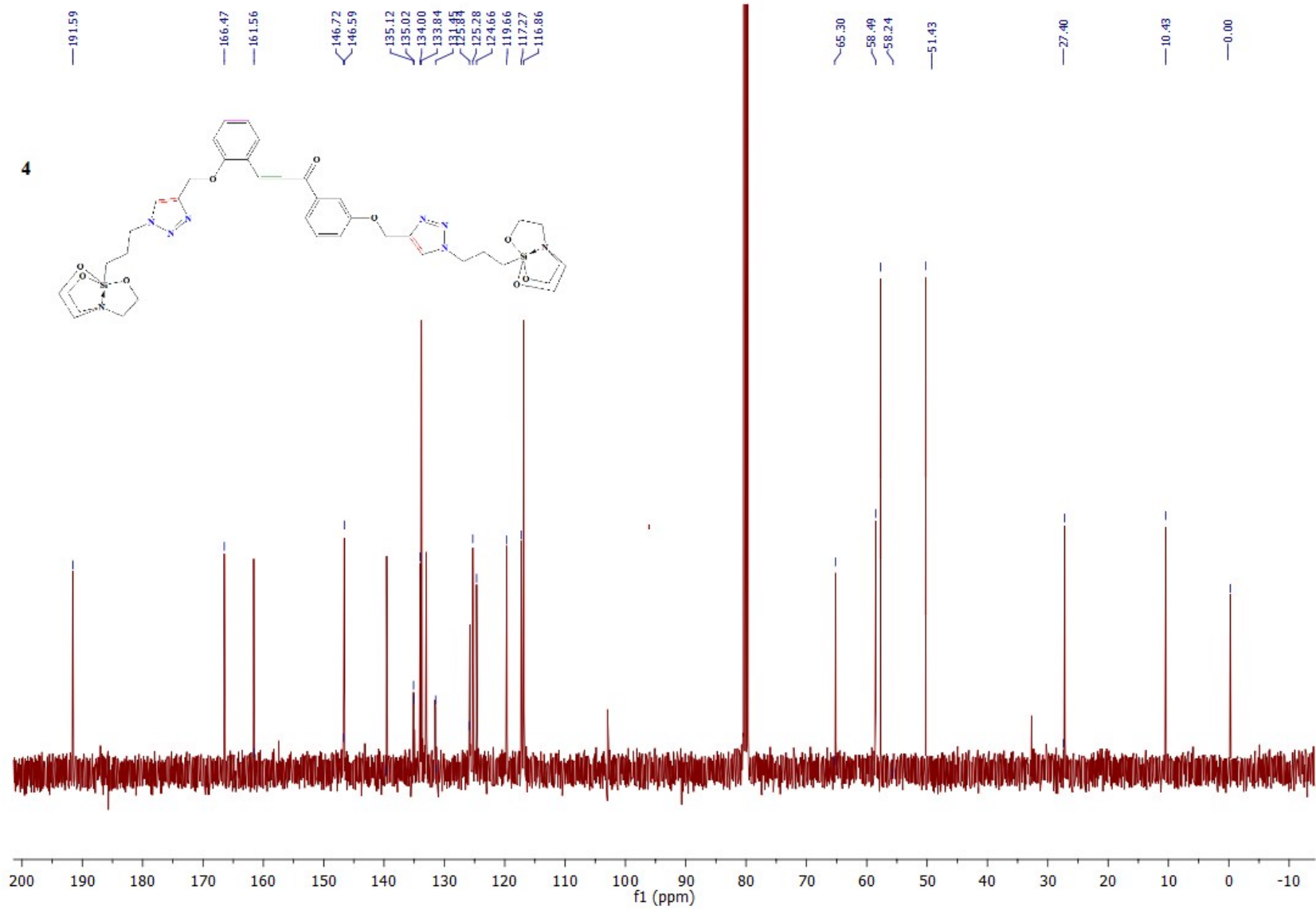
TOF MS ES+
3.03e3

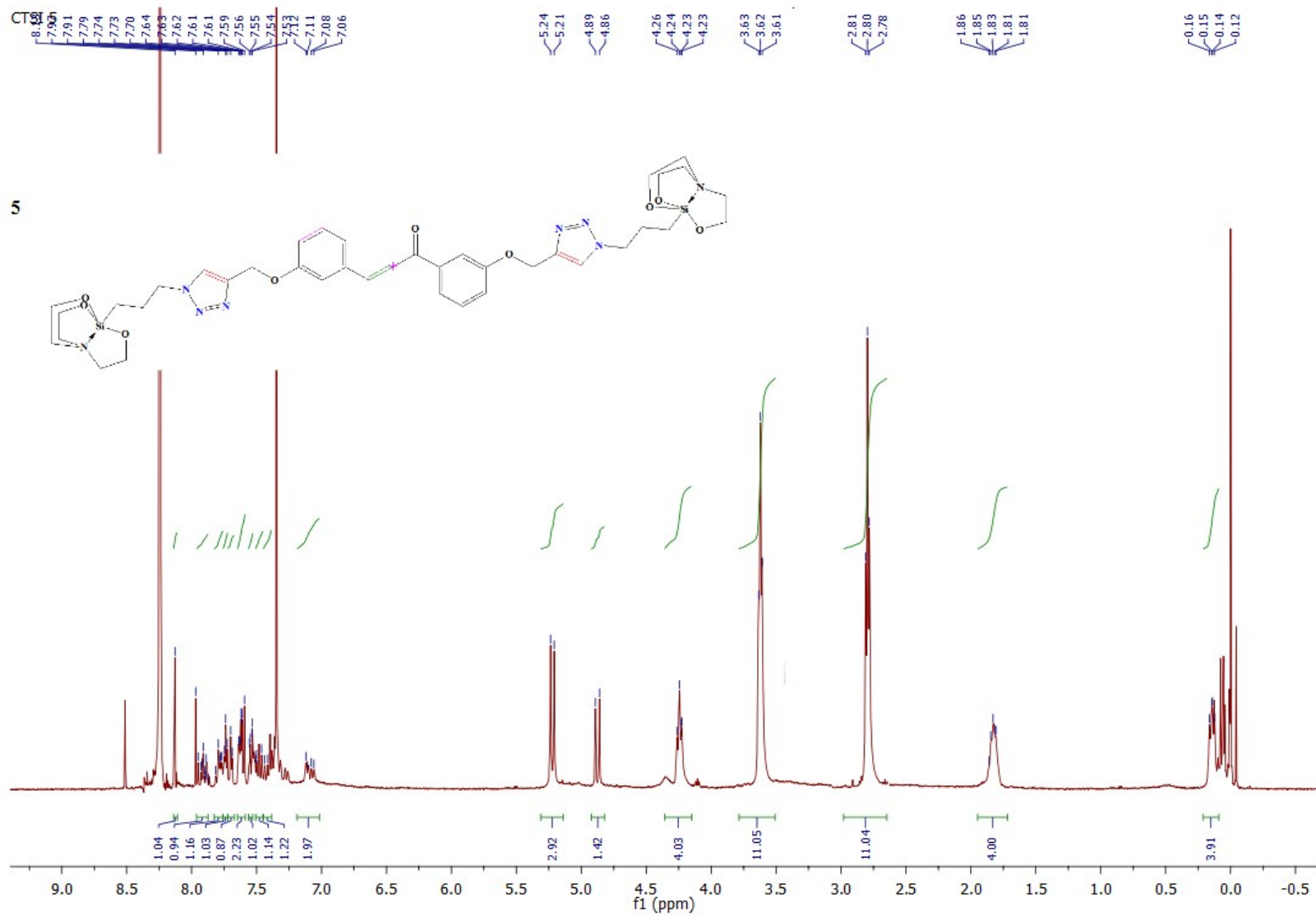


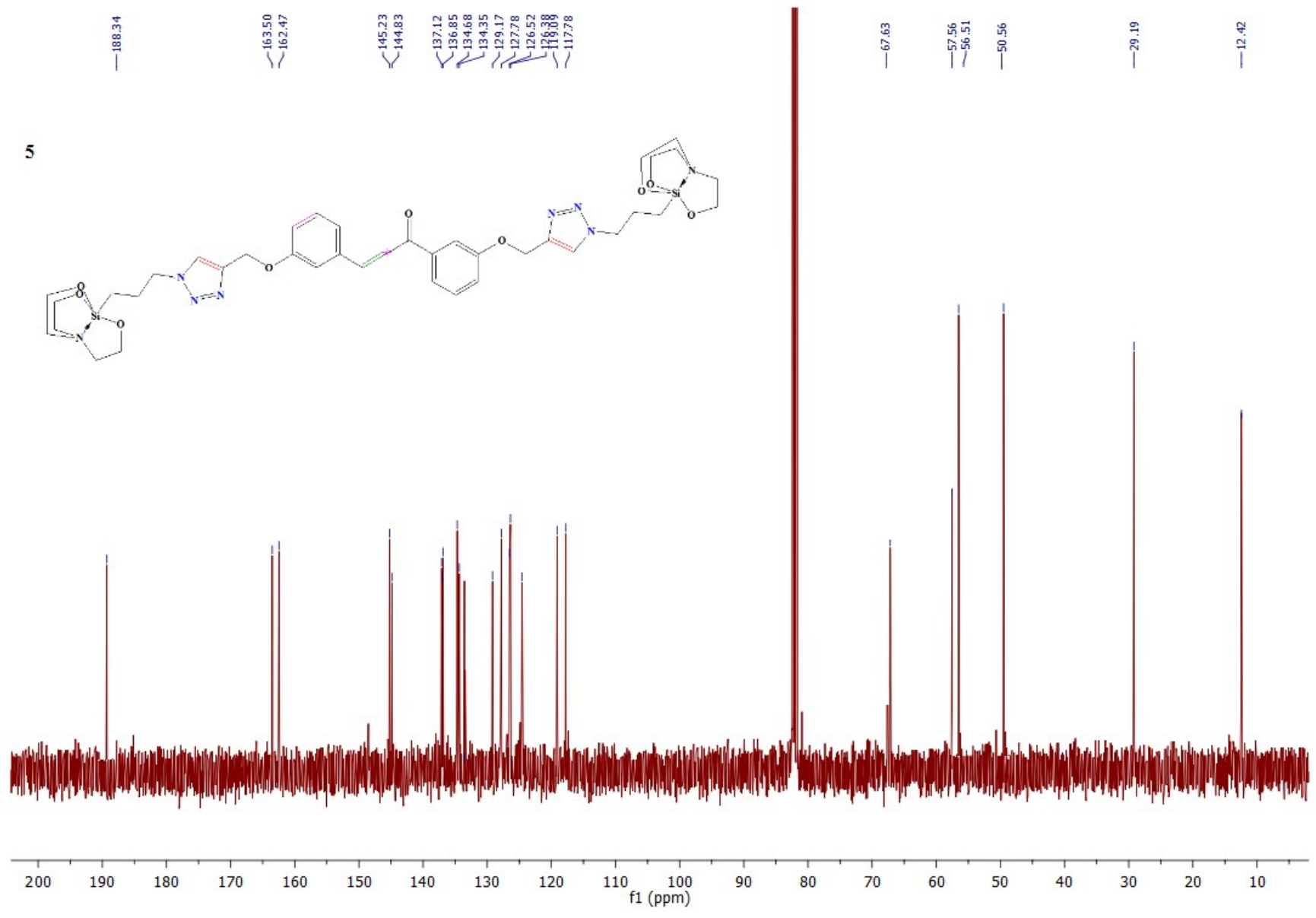


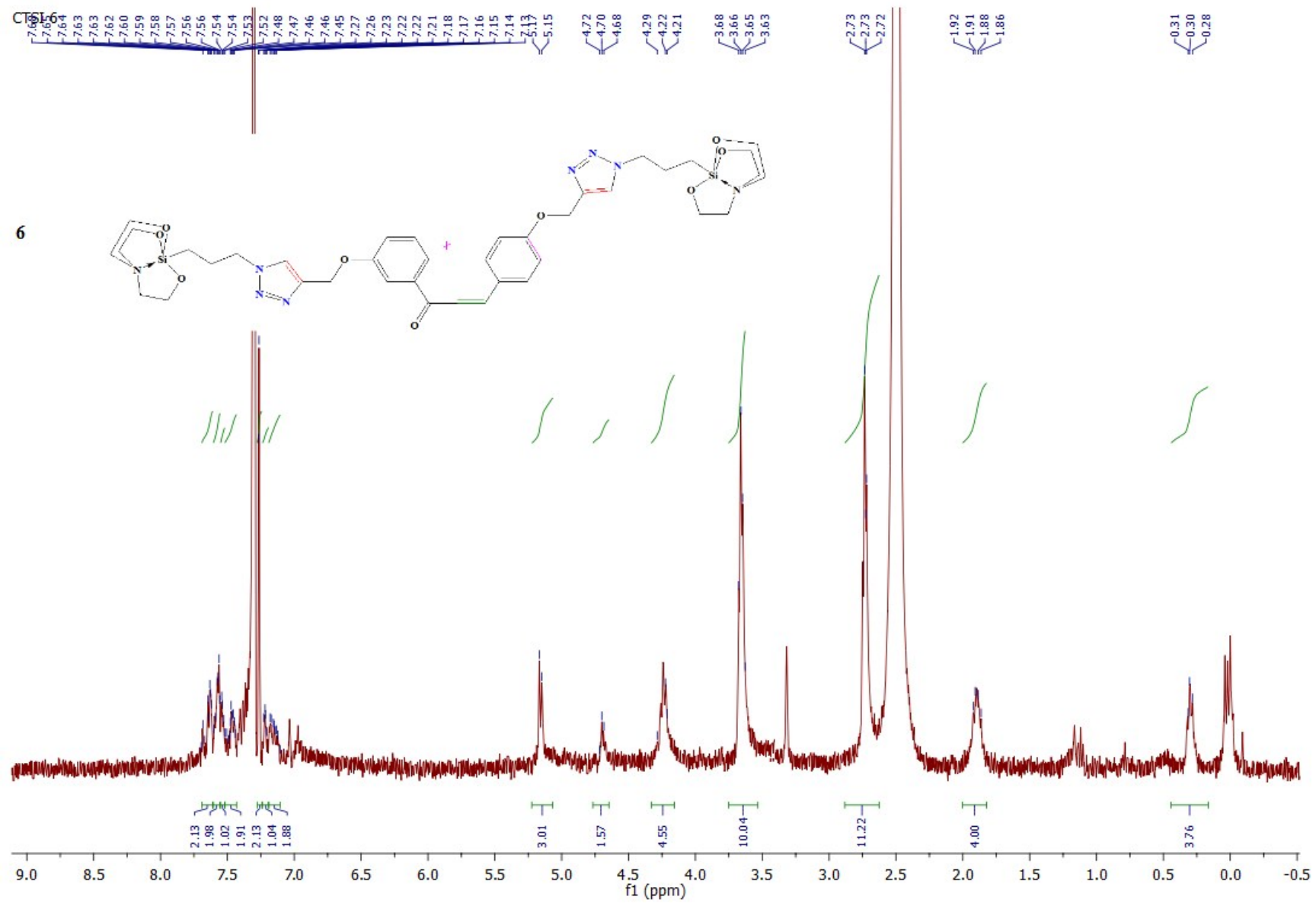


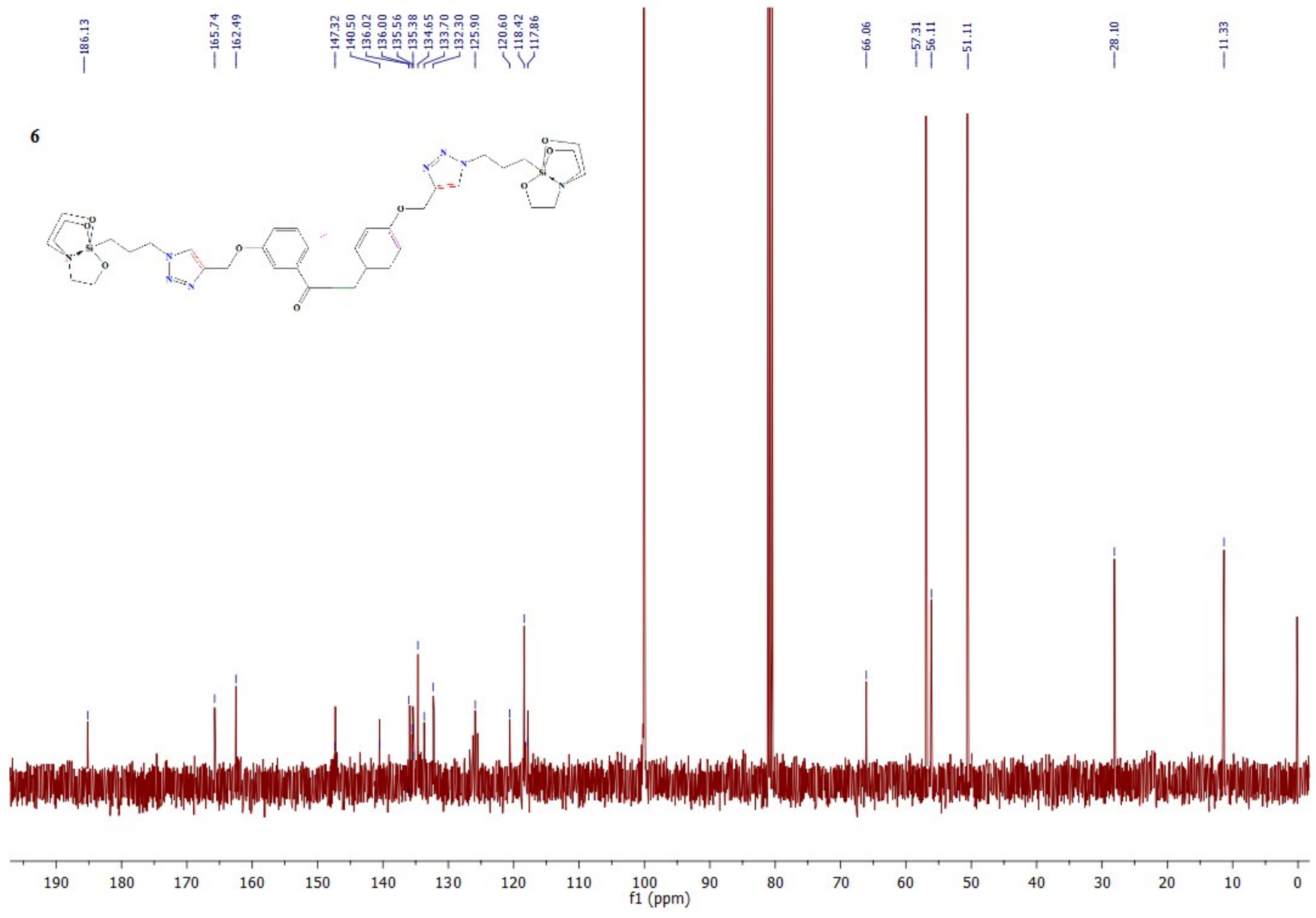


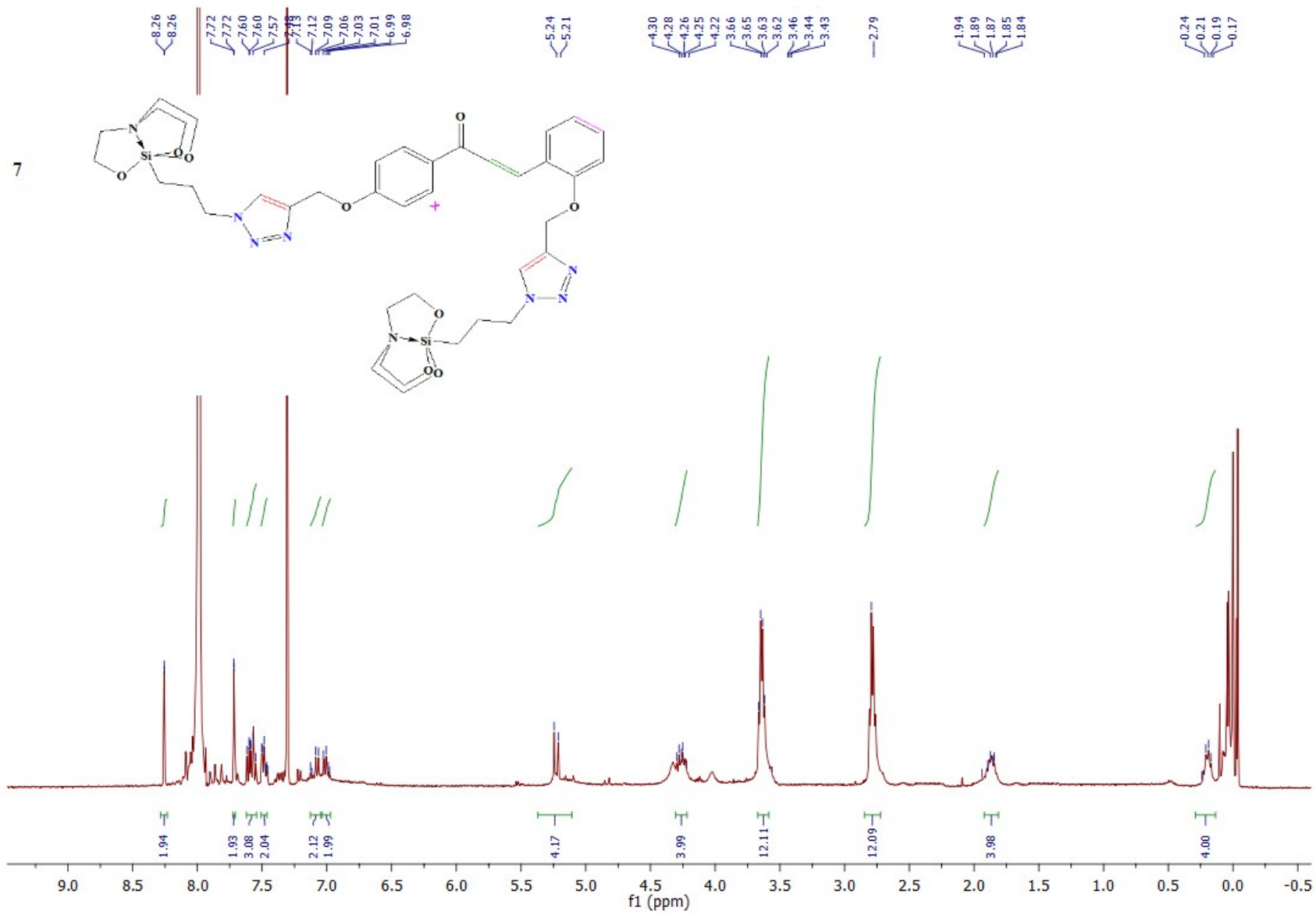


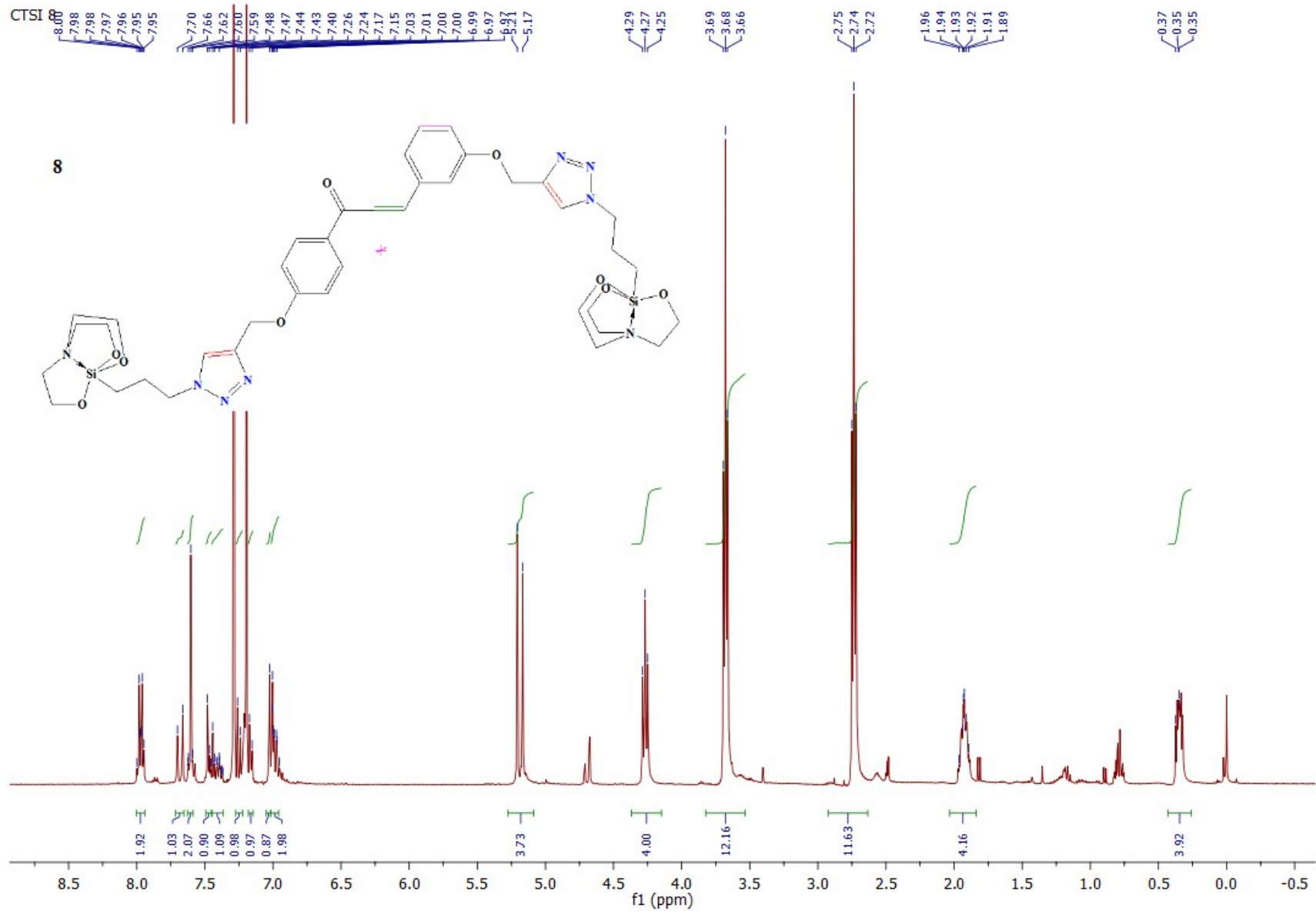


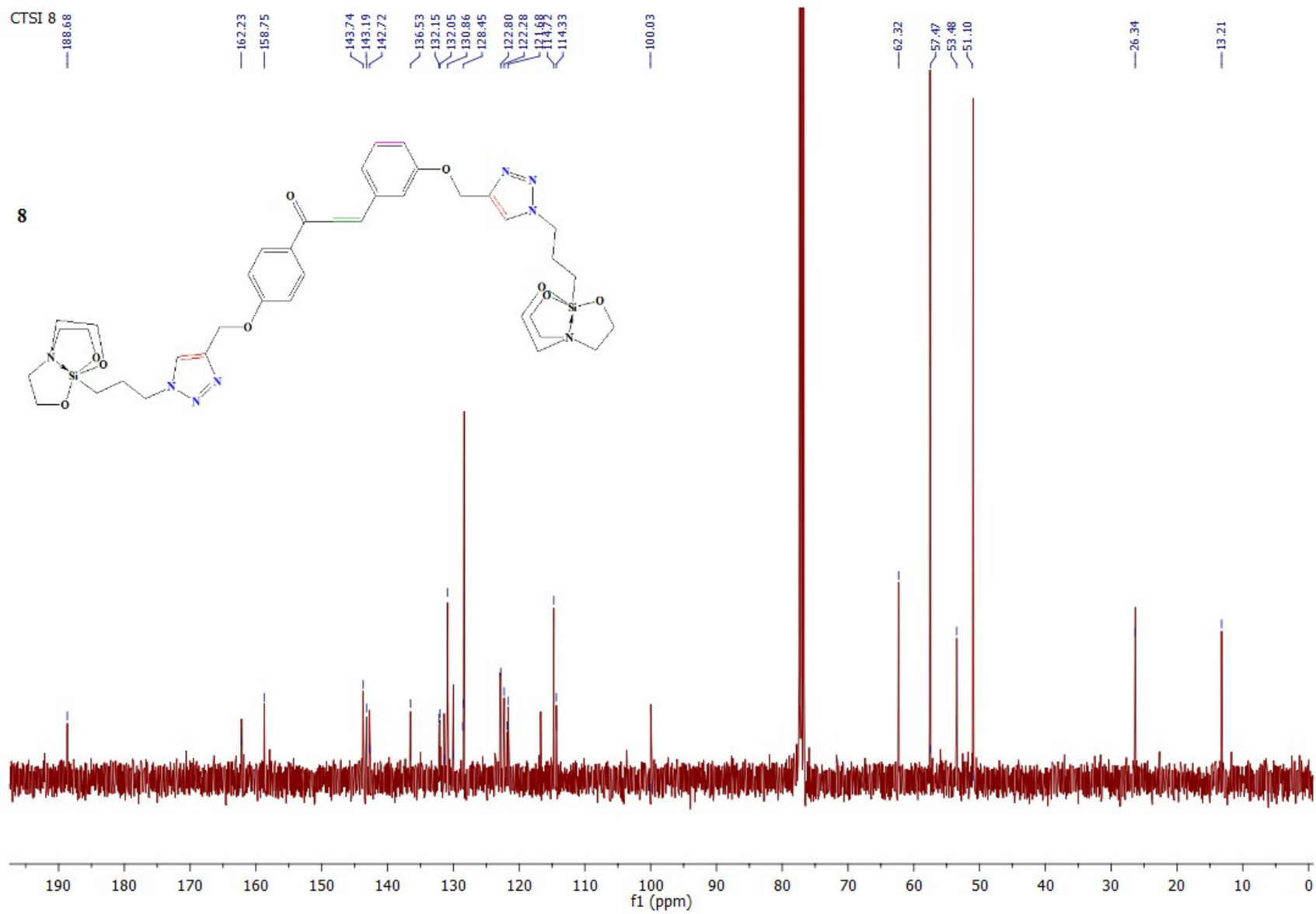


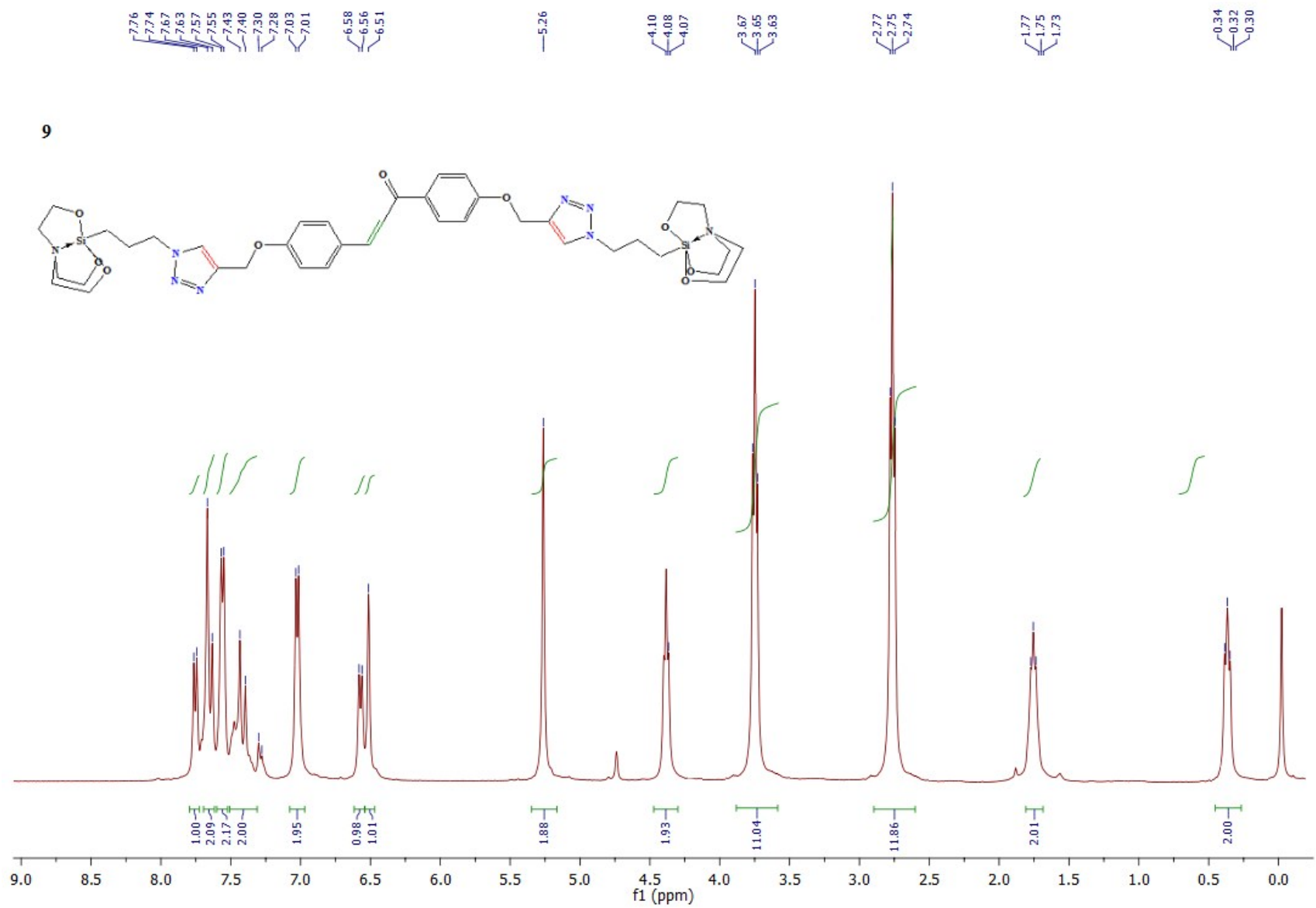


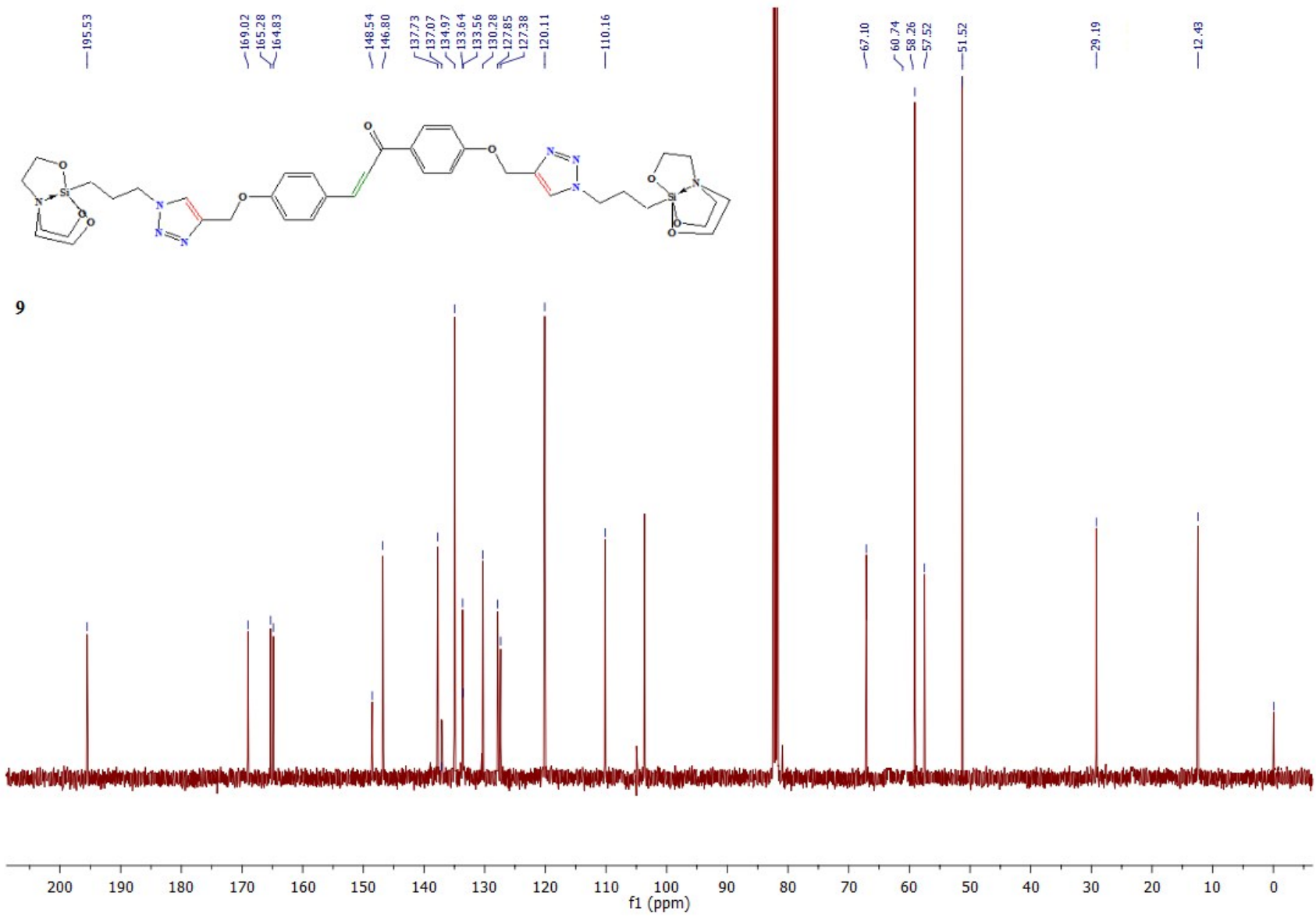












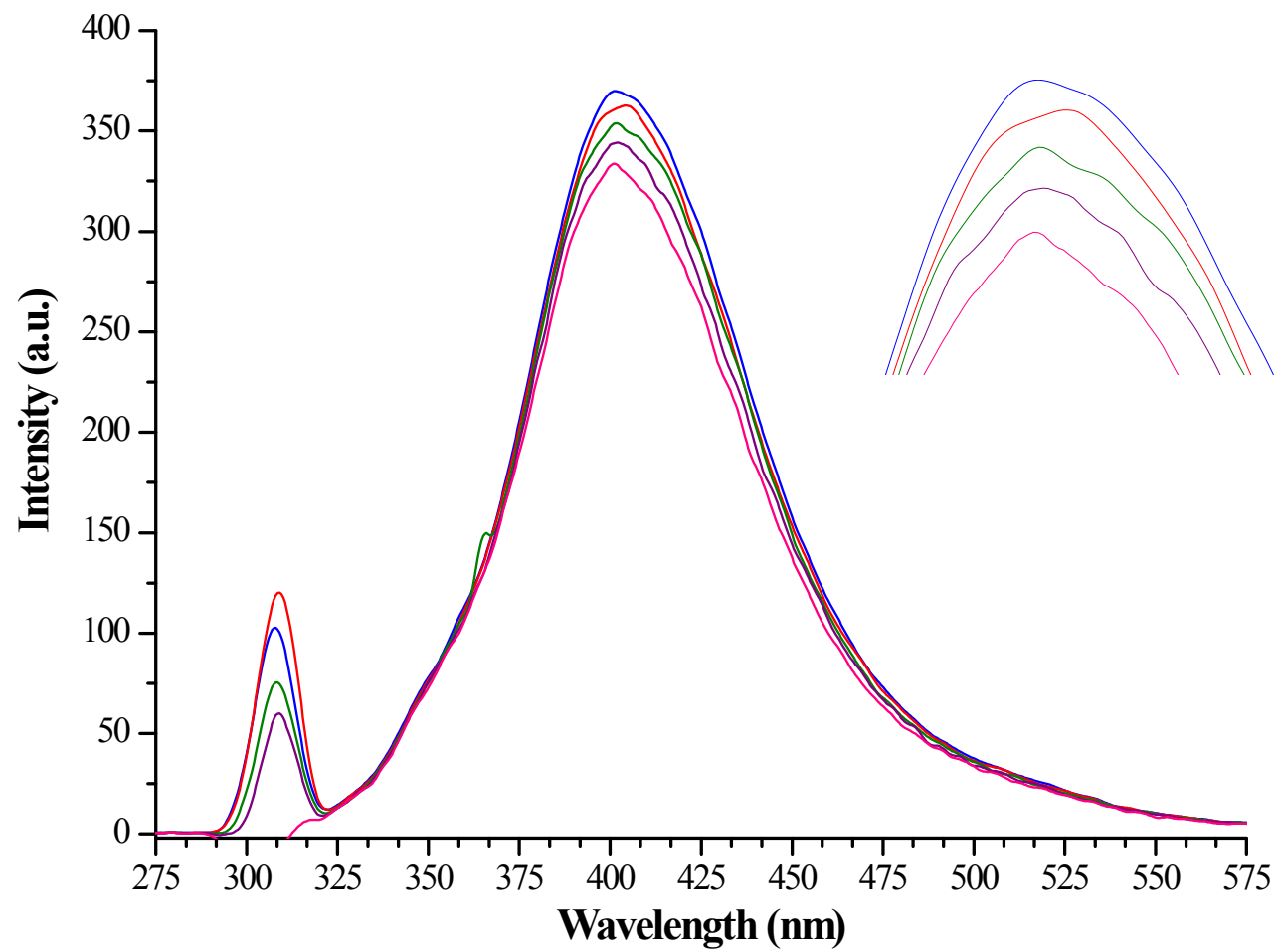


Figure S1: Effect of change in pH value on CTSI 1 in MeOH:H₂O (v/v) (8:2) with $\lambda_{\text{ex}} = 311$ nm

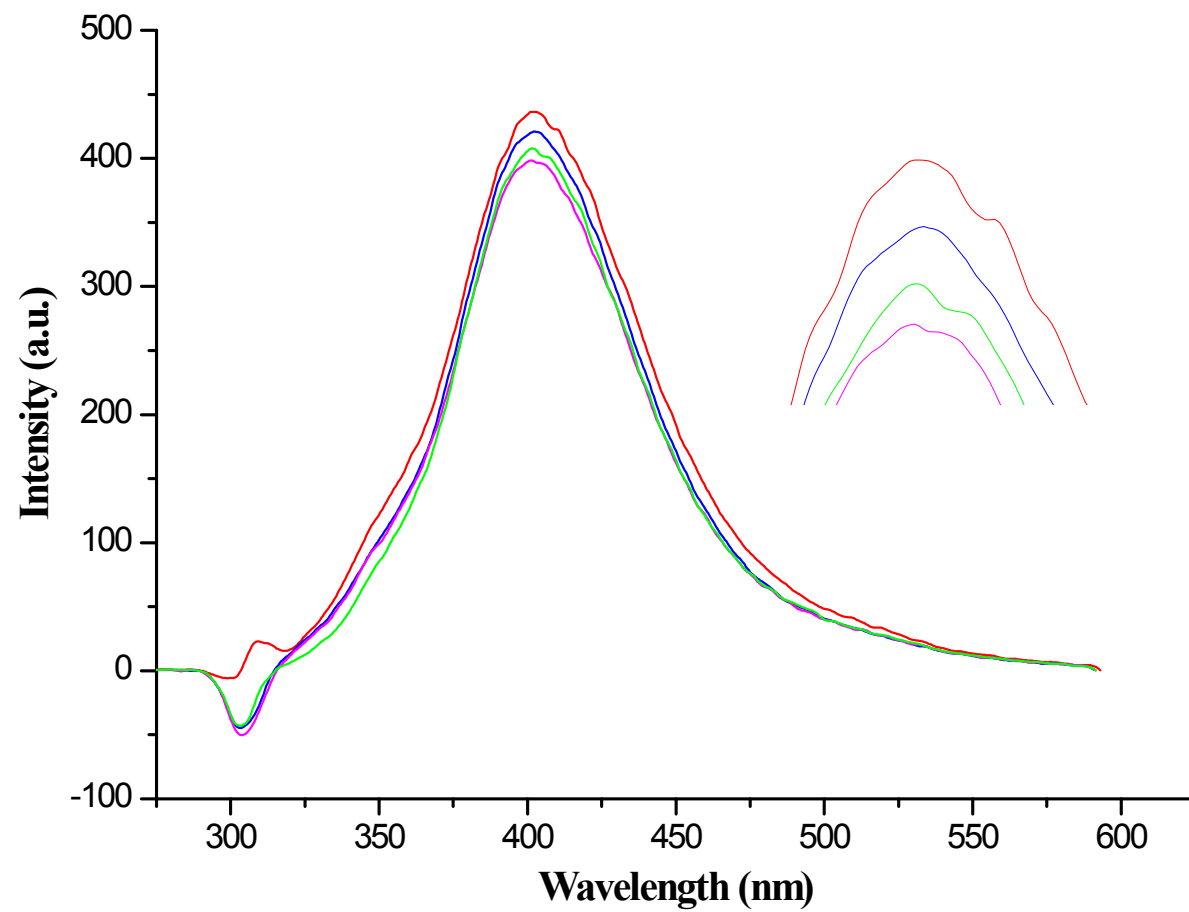


Figure S2: Effect of change in pH value on CTSI 1 in presence of Cu^{2+} and Ni^{2+} in $\text{MeOH}:\text{H}_2\text{O}$ (v/v) (8:2) with $\lambda_{\text{ex}} = 311 \text{ nm}$

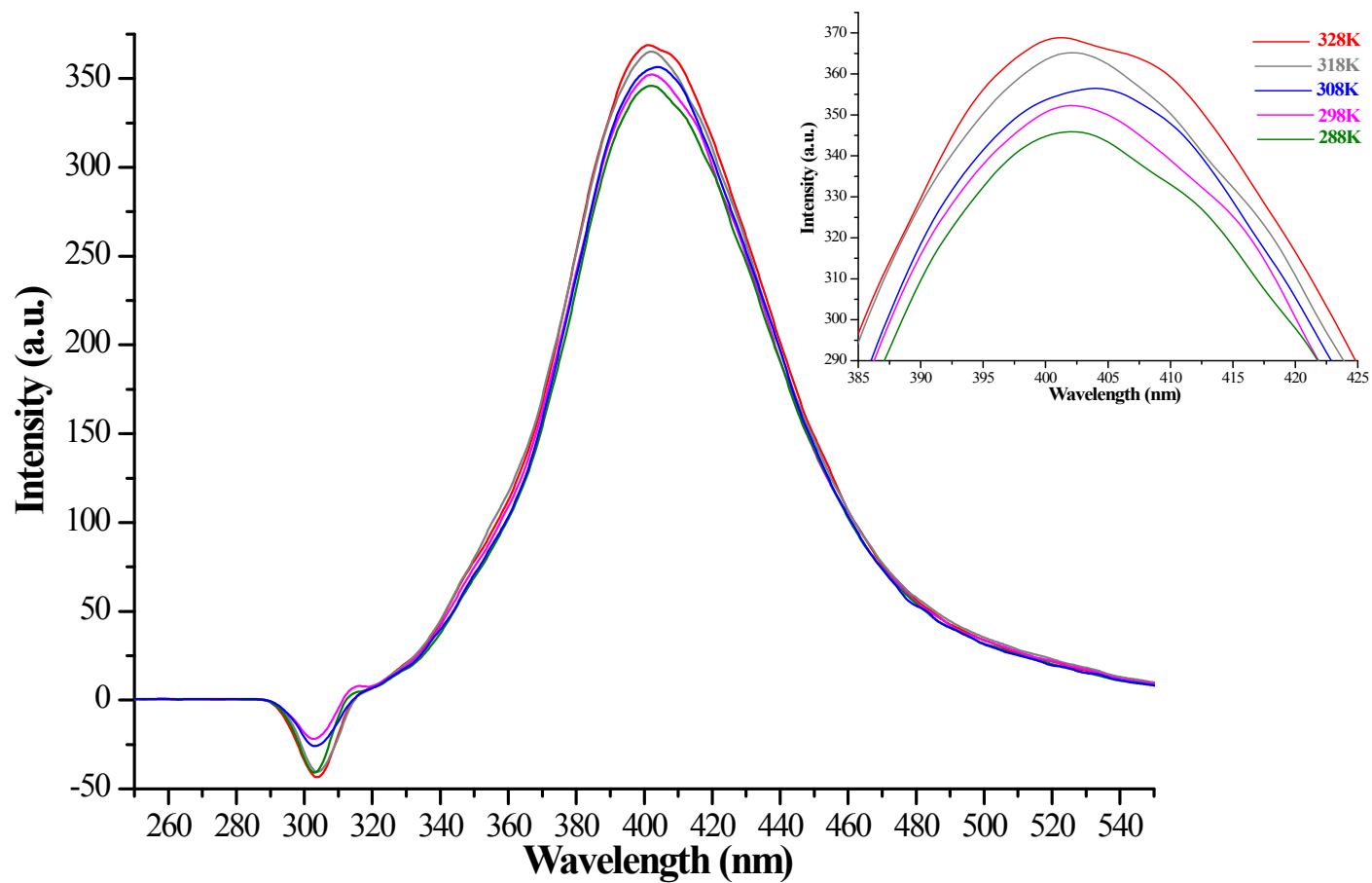


Figure S3: Effect of change in temperature on CTSI 1 in MeOH:H₂O (v/v) (8:2) with $\lambda_{\text{ex}} = 311 \text{ nm}$