

Synthetic approach towards ‘Click’ modified chalcone based organotriethoxysilanes; UV–Vis study

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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.

5.1. 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), N,N-dimethylformamide (SDFCL), were used as supplied. Acetophenone (SDFCL), 2-hydroxyacetophenone (SDFCL), 3-hydroxyacetophenone (SDFCL), 4-hydroxyacetophenone (SDFCL), salicylaldehyde (Aldrich), 3-hydroxybenzaldehyde (SDFCL), 4-hydroxybenzaldehyde (SDFCL), p-methoxyacetophenone (HIMEDIA), 2,4-dimethoxyacetophenone (HIMEDIA) were used as supplied for synthesis of terminal alkynes **3a–3i** and **5a–5i**.

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 spectrometer (in CDCl_3) at 25 °C. HRMS data of all synthesized compounds **4a–4i** and **6a–6i** was recorded on Waters QQ–TOF micro Mass Spectrometer. UV–Vis spectra were recorded on JASCO V–530 UV–Vis spectrophotometer. The elemental data were obtained on Thermo Scientific flash 2000 organic elemental analyzer.

AzPTES was synthesized according to known procedure in literature.²⁰

Synthesis of compounds **2a(i–iii)** and **2b(i–iii)**

To a uniformly stirred solution of **1a/1b** (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 **2a(i, iii)**; **2b(i–iii)**). In case of low melting solids **2a(ii)**, extraction was carried out with ethyl acetate.

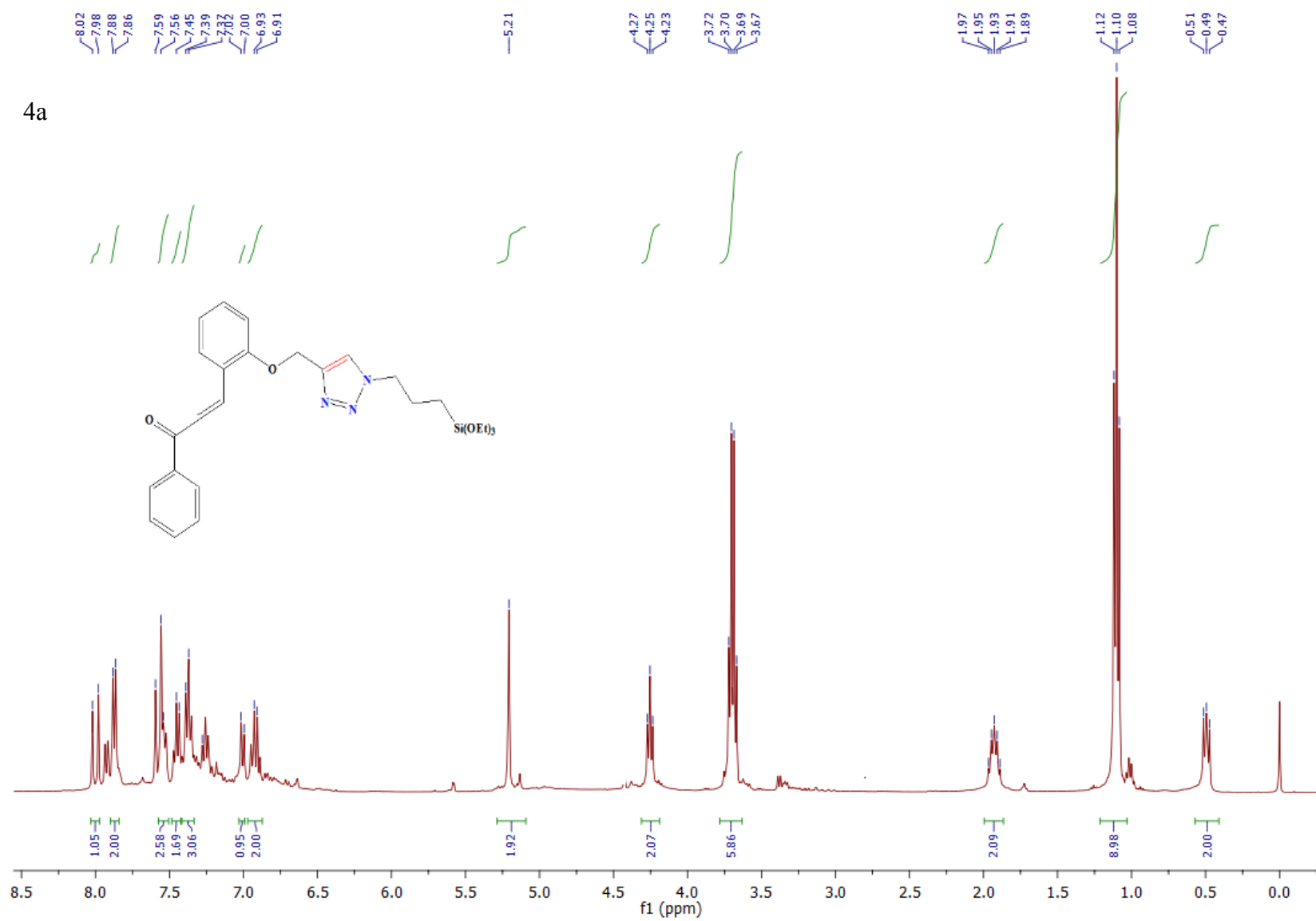
The combined organic layers were dried over anhydrous MgSO_4 and vacuum evaporation of solvent resulted into the formation of desired compound. The solid alkynes were recrystallized by dissolving in minimum amount of ethanol.

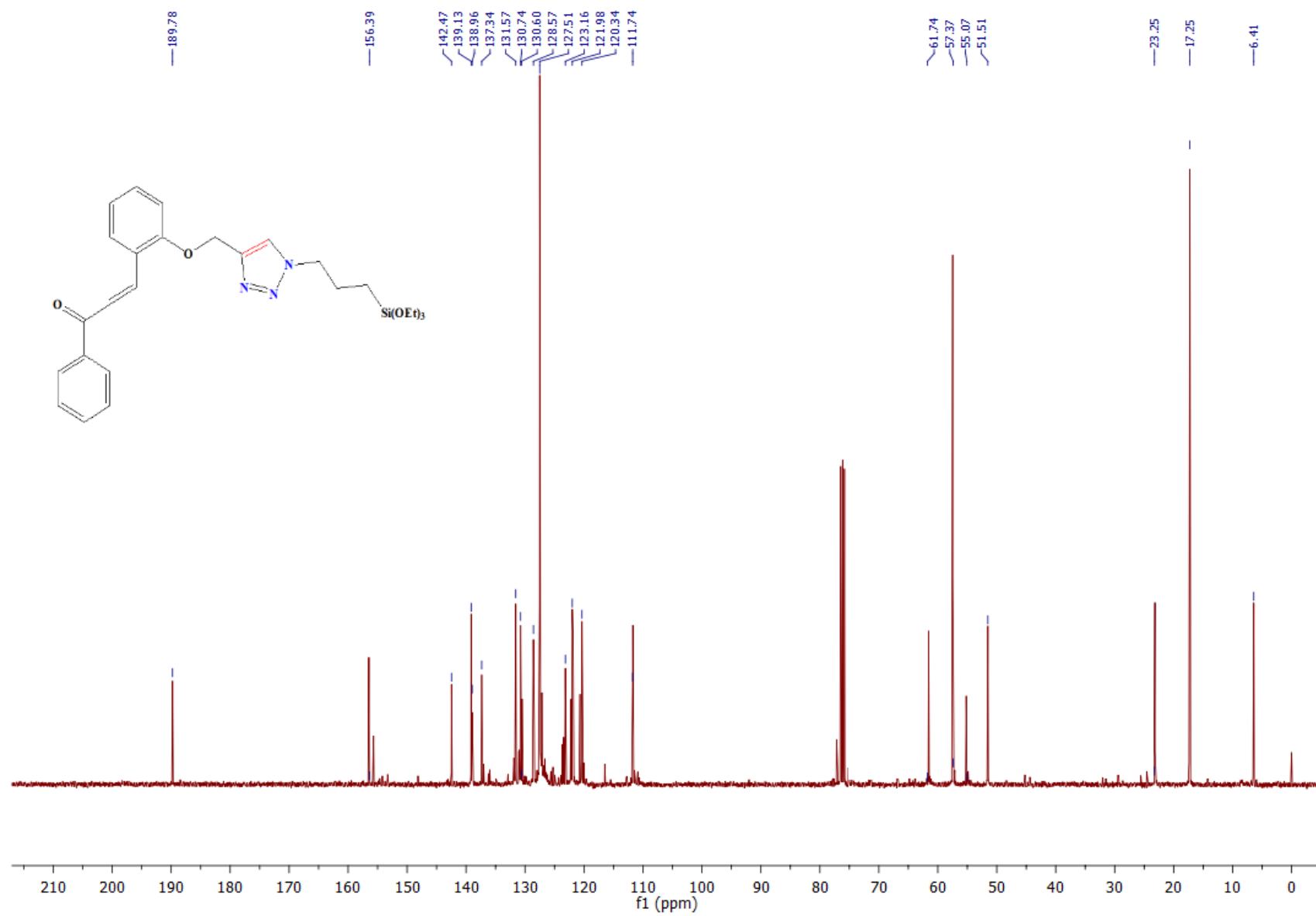
Synthesis of compounds 3a–3i/5a–5i

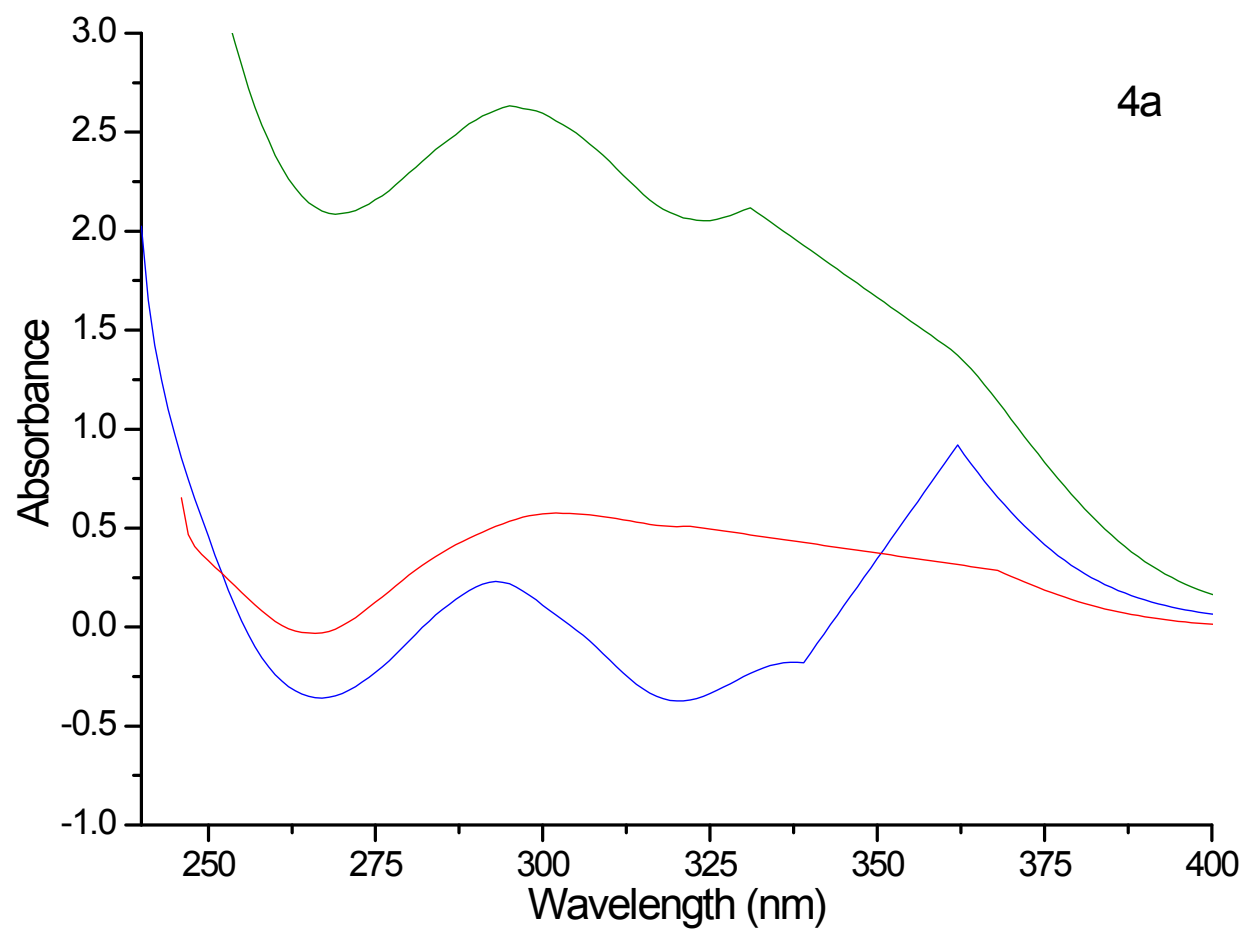
To a uniformly stirred solution of **2a** (1 equiv) and KOH (0.02 g, 0.36 mmol) in 15 ml of ethanol, ethanolic solution of substituted acetophenone **1c(a–c)** or **2b** (1 equiv) was added slowly within 10 min. The reaction was stirred for 4 h and monitored the end point using TLC (hexane:ethyl acetate (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 MgSO_4 and vacuum evaporation afforded the desired product.

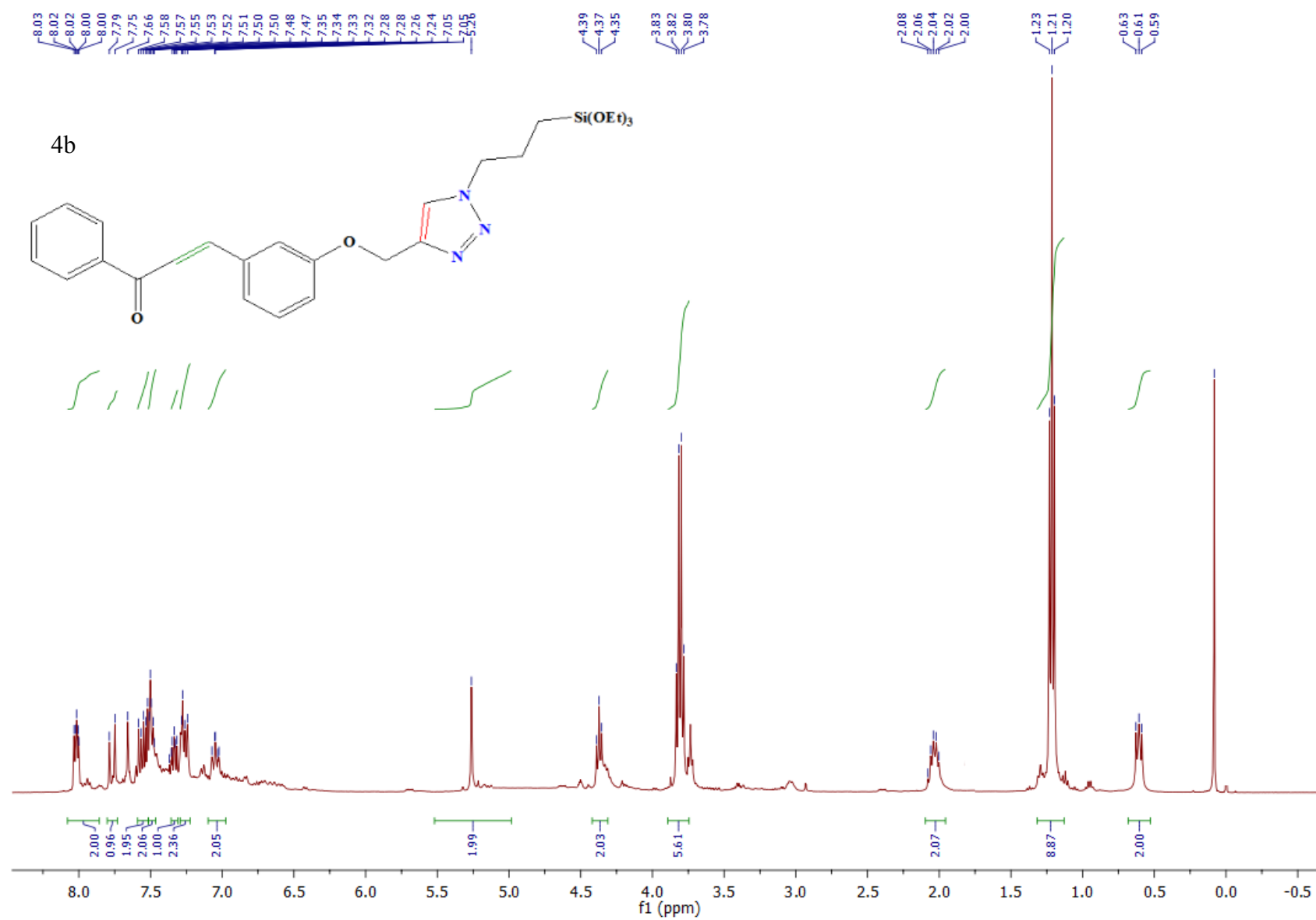
Synthesis of compounds 4a–4i/6a–6i

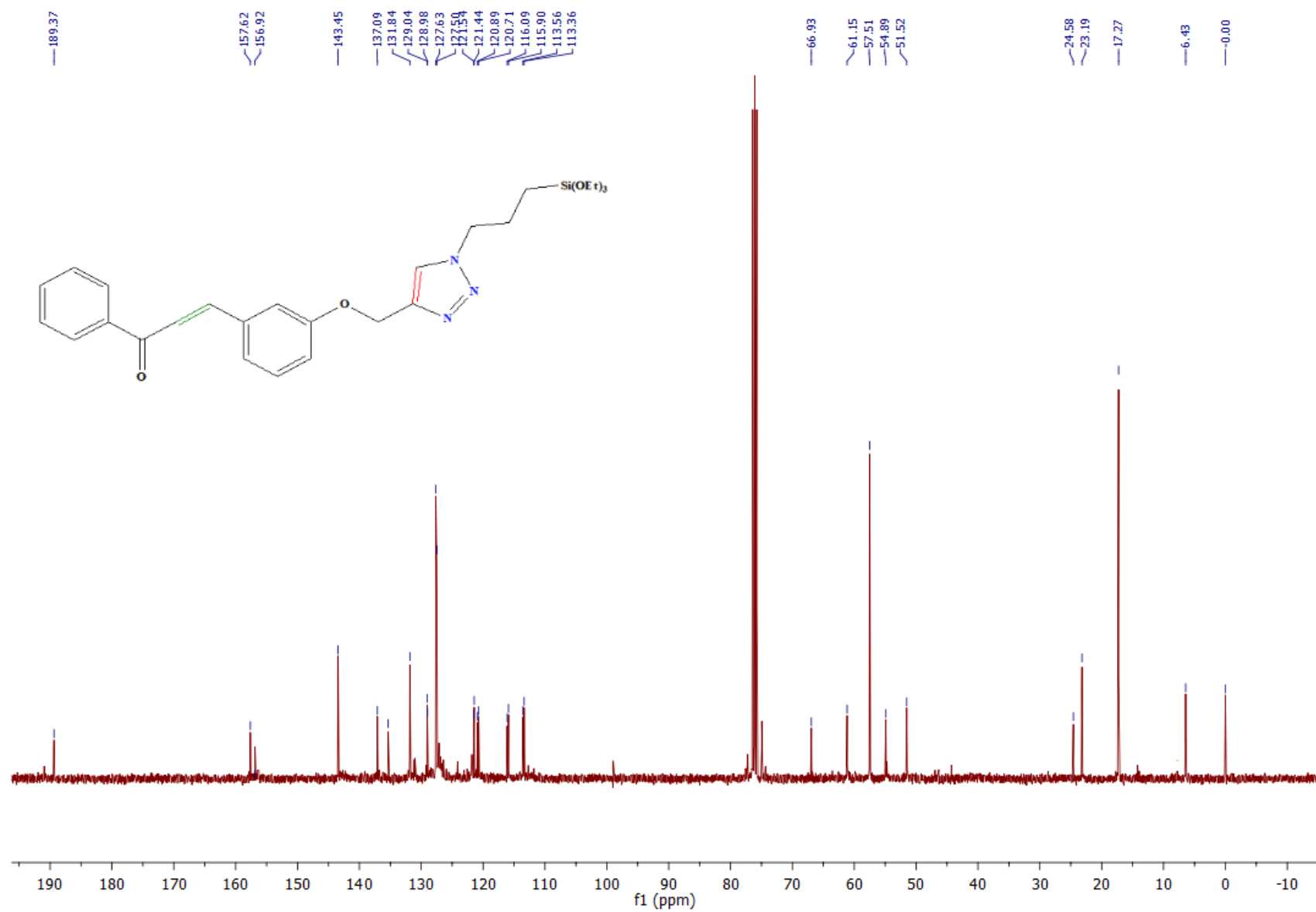
In a 25 ml two neck round bottom flask, to stirred solution of alkyne **3a–3i/5a–5i** in 1:1 solution of THF:TEA (3ml), added AzPTES (1 equiv for **3a–3i** and 2 equiv for **5a–5i**) followed by catalyst (0.02 mmol for **3a–3i** and 0.04 mmol for **5a–5i**) loading under inert atmosphere. Slowly the 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 **4a–4i/6a–6i**.

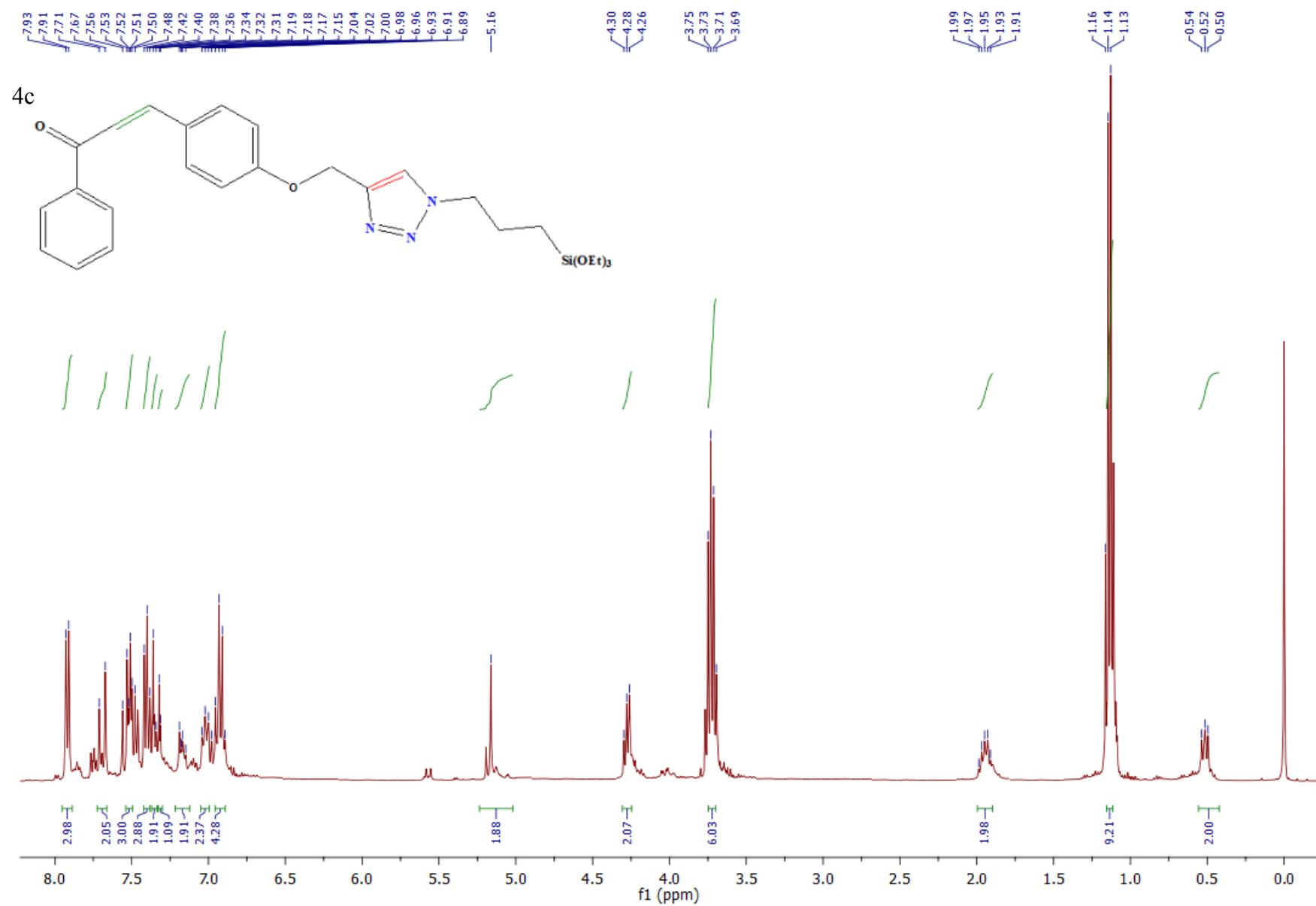


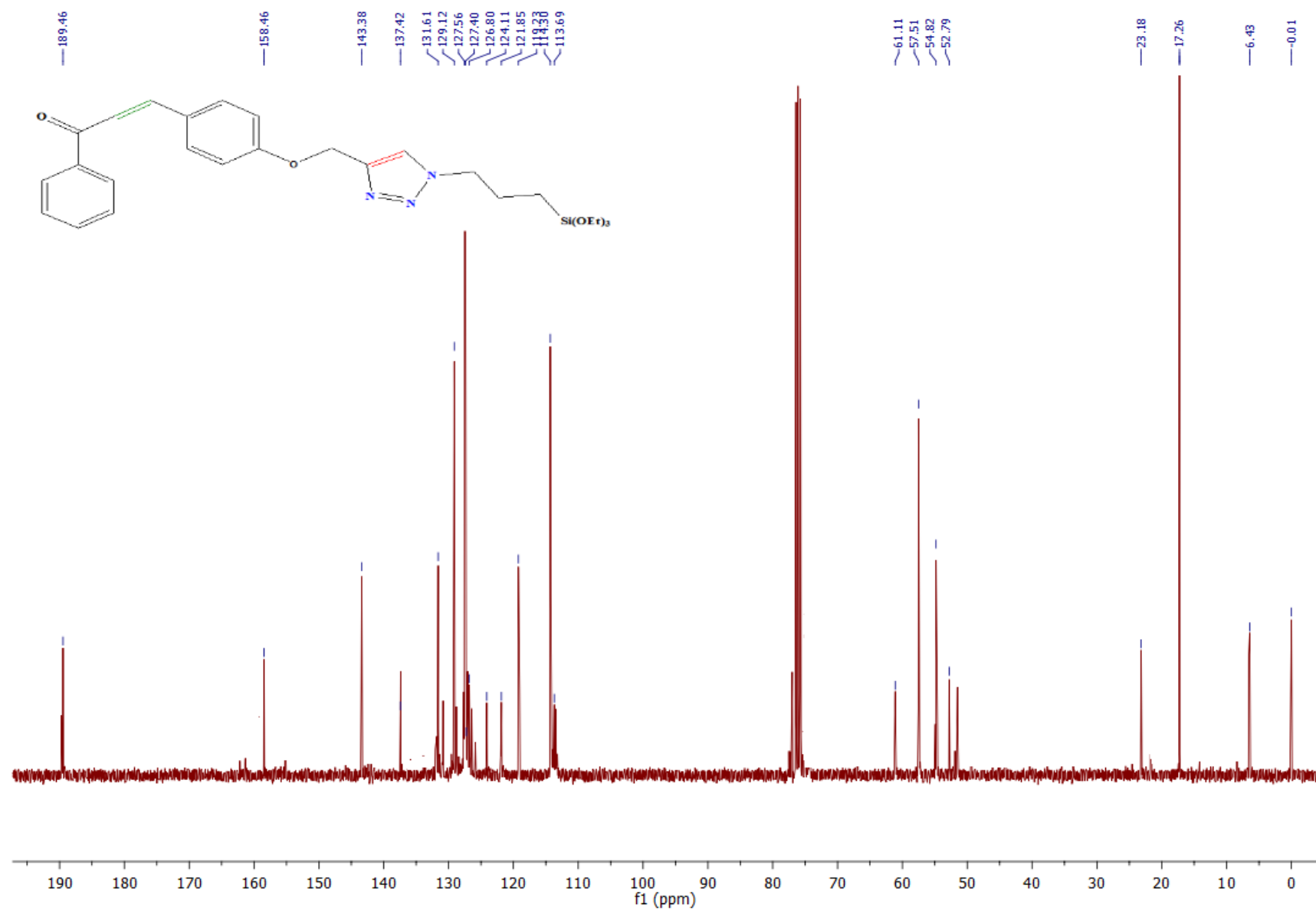










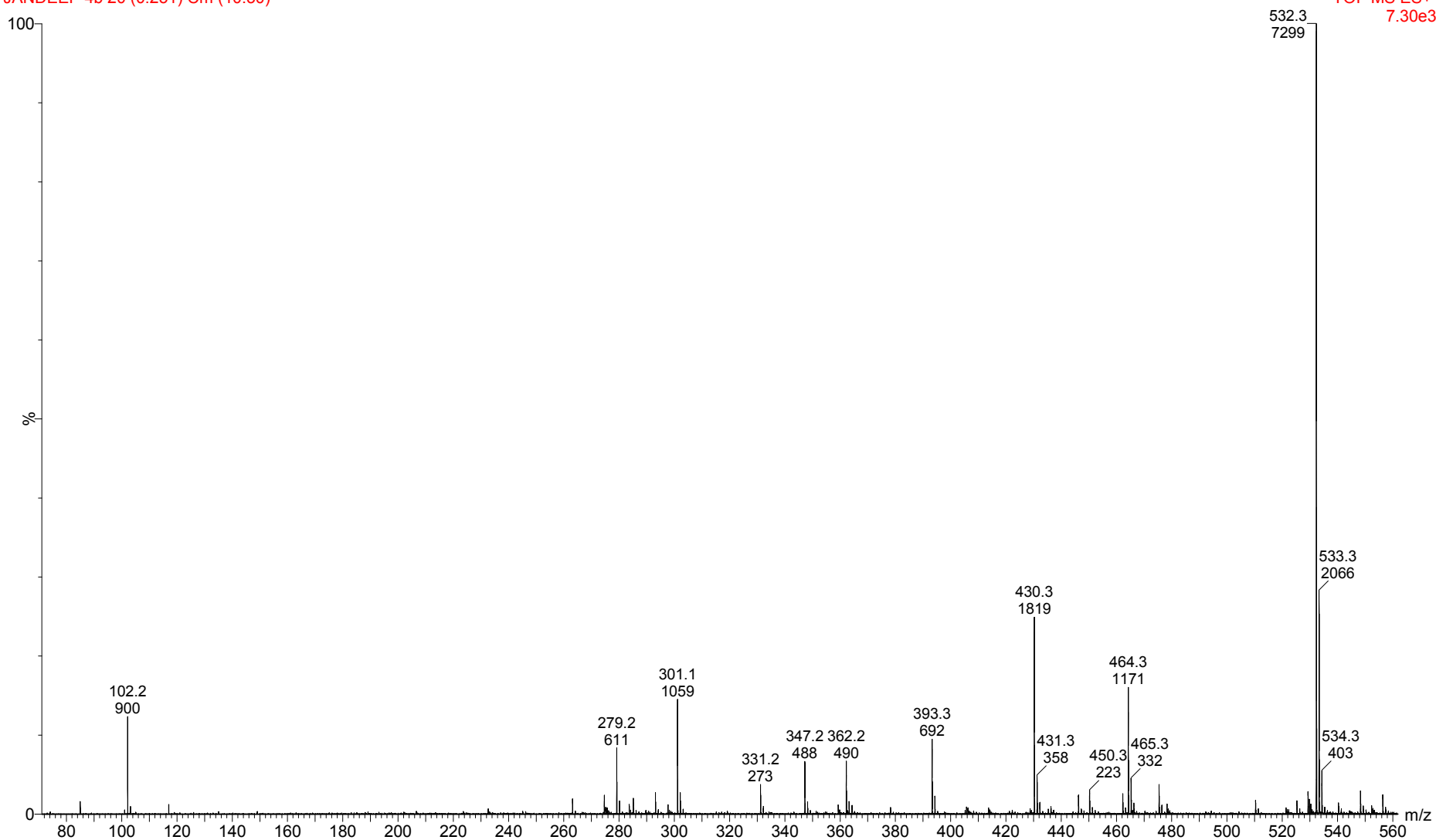


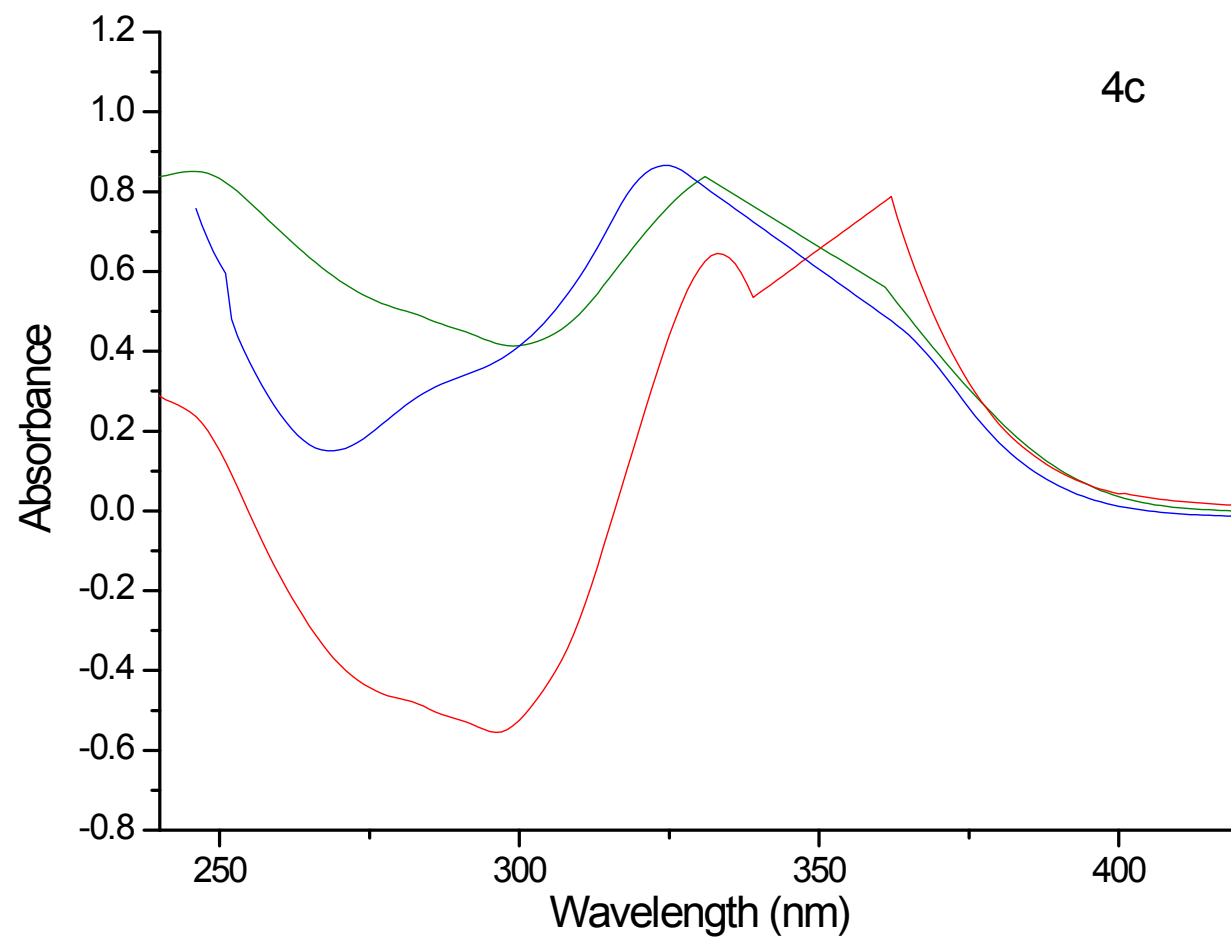
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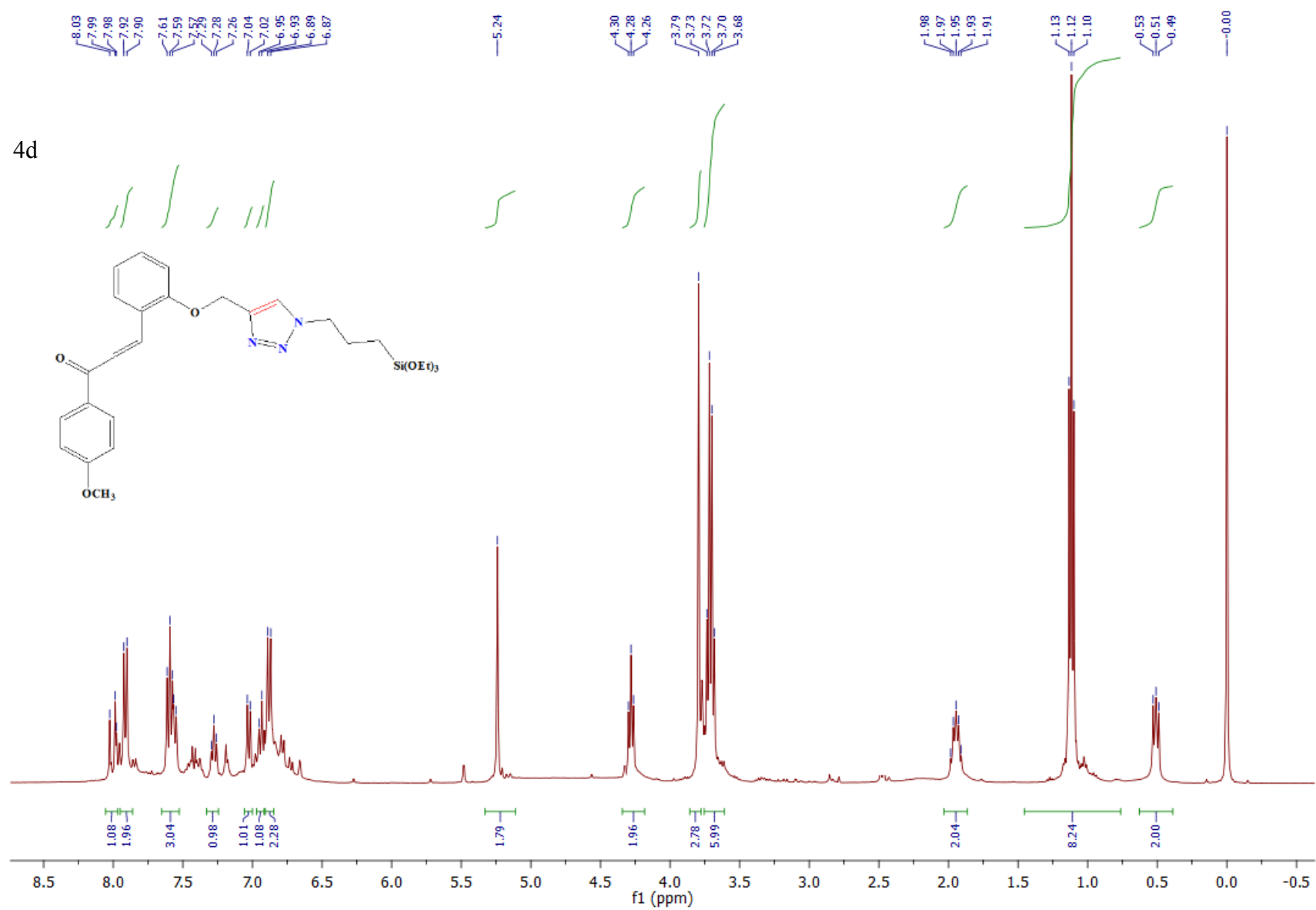
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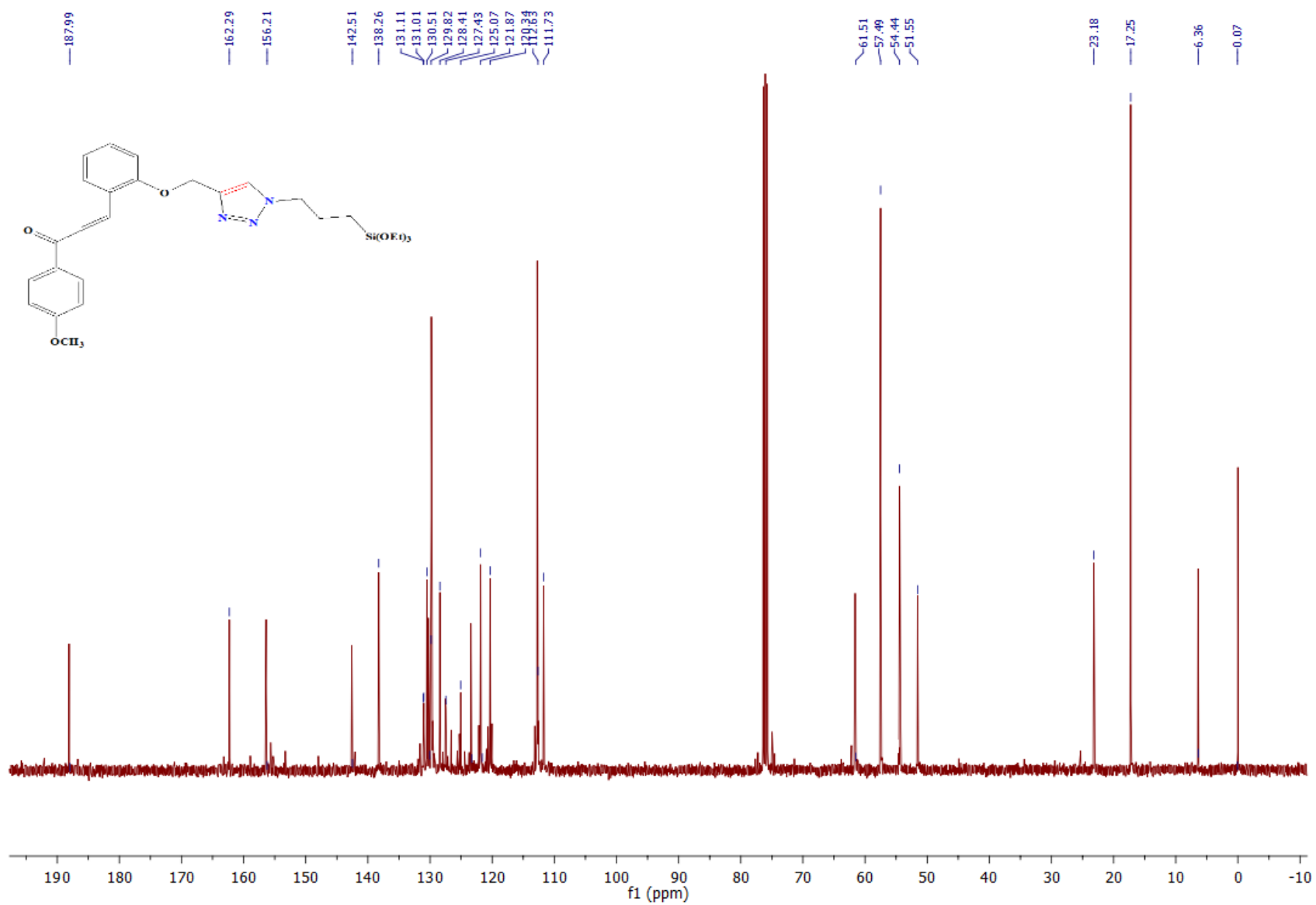
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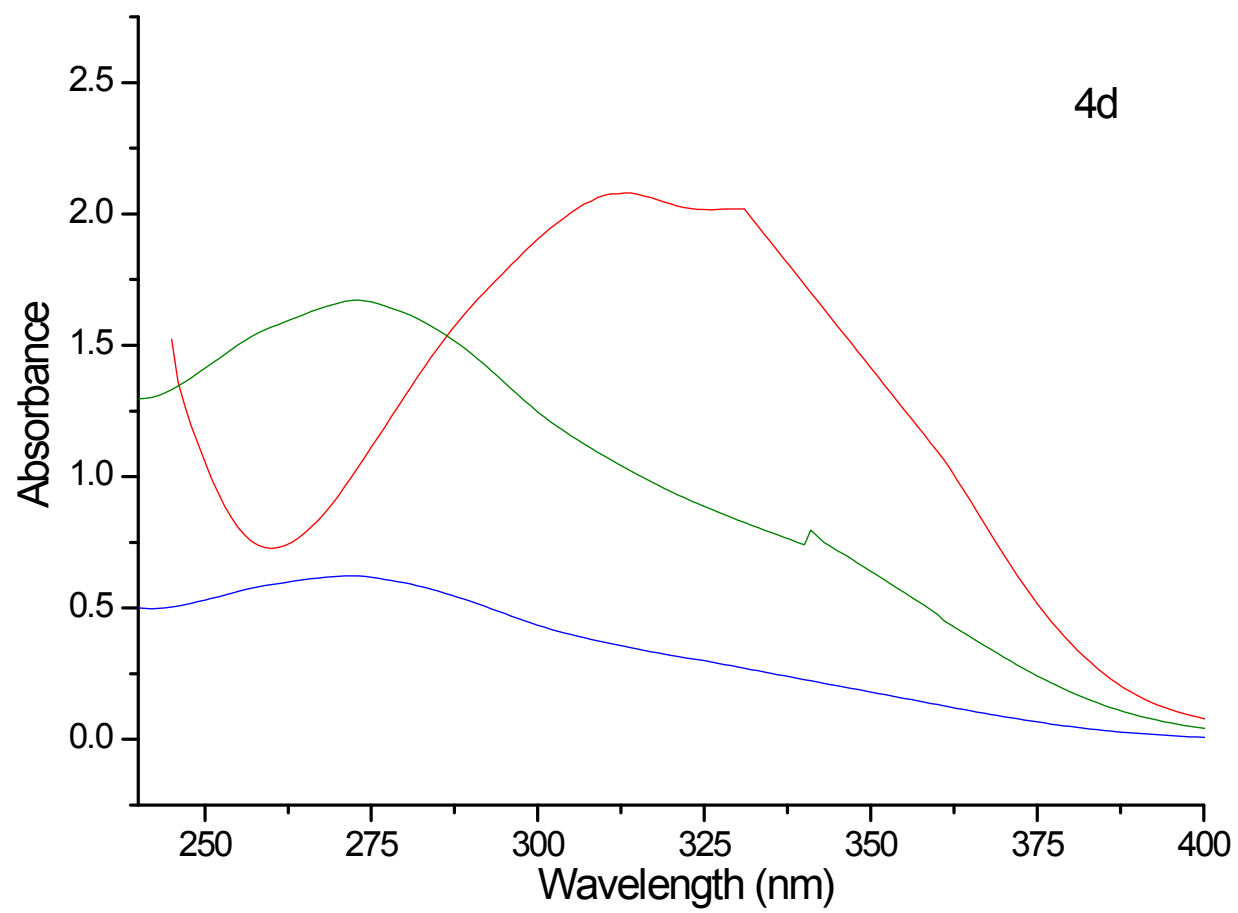
TOF MS ES+
7.30e3

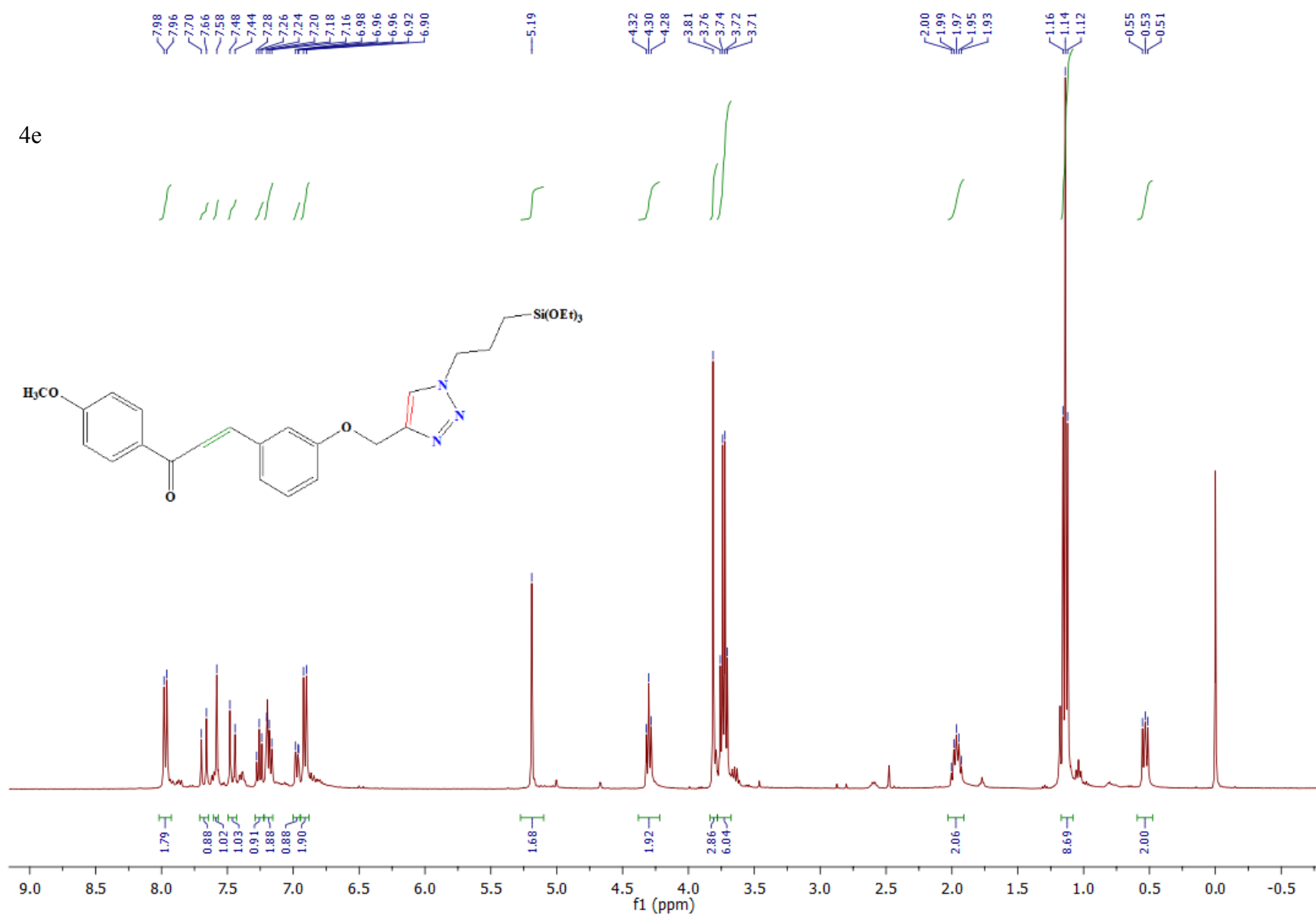


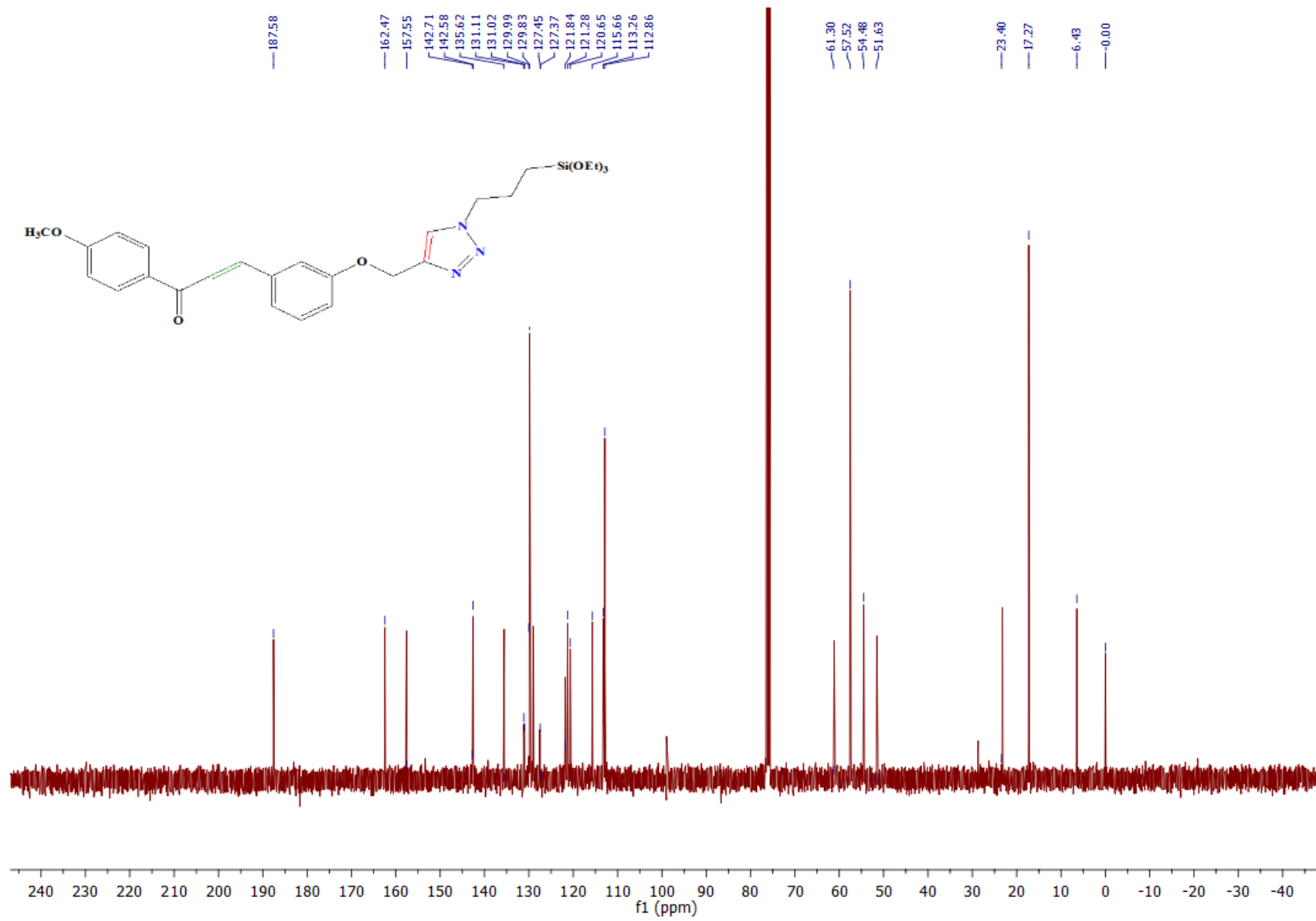


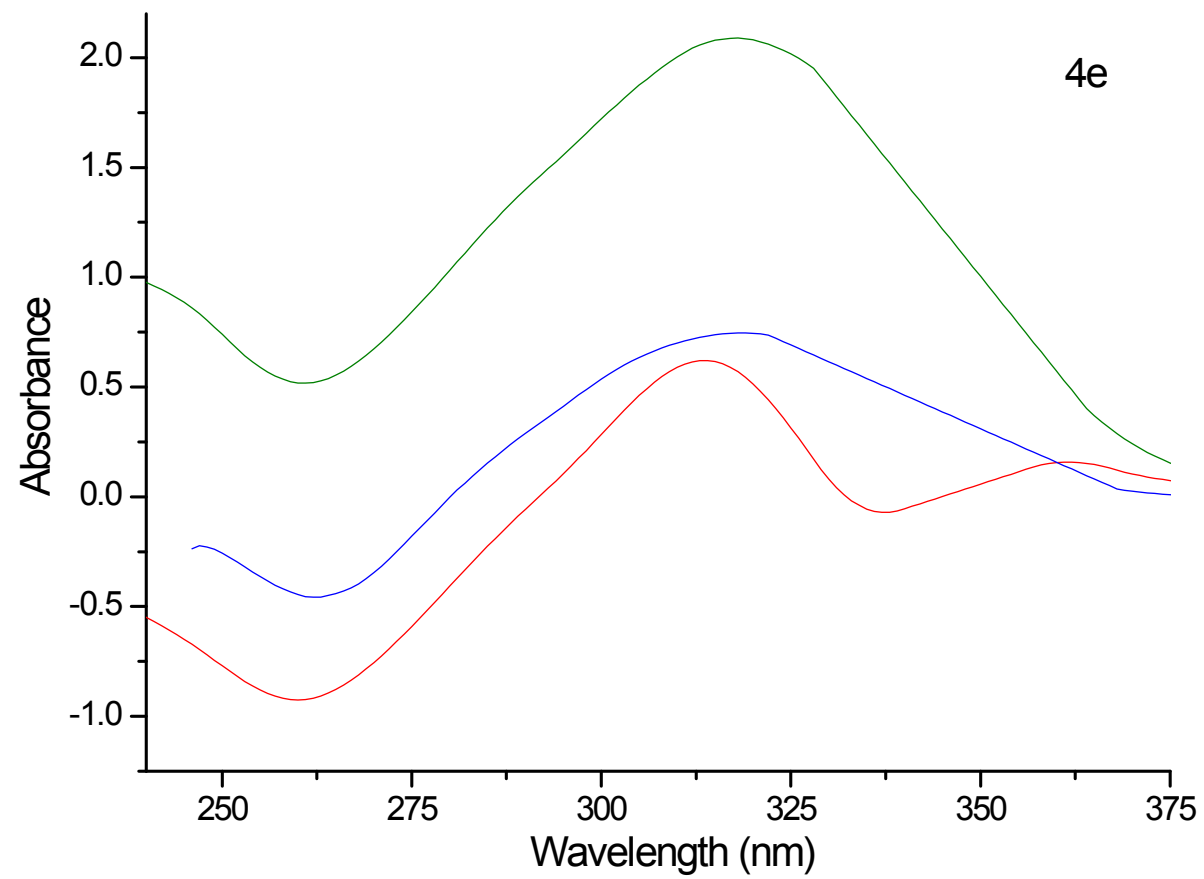


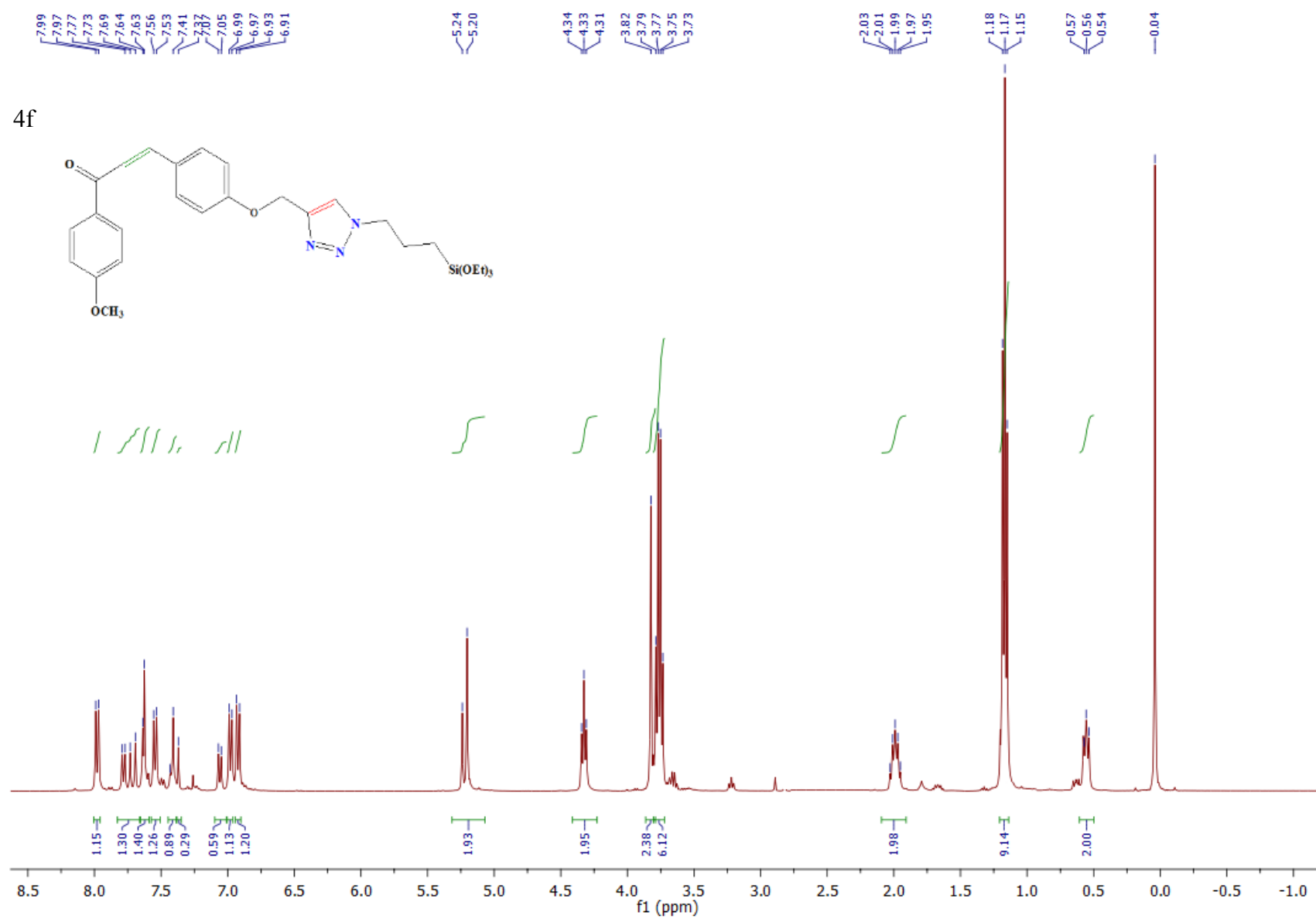


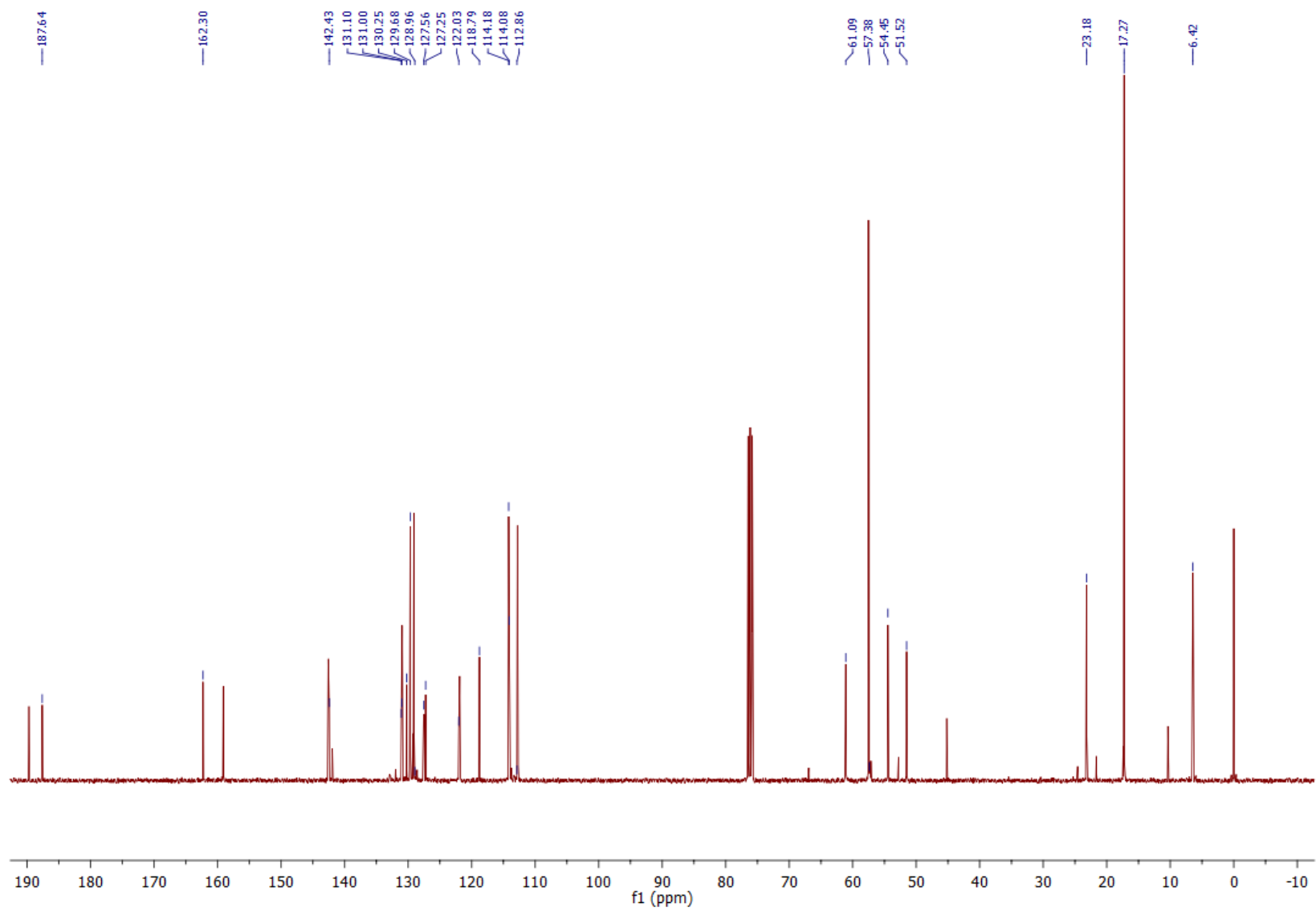










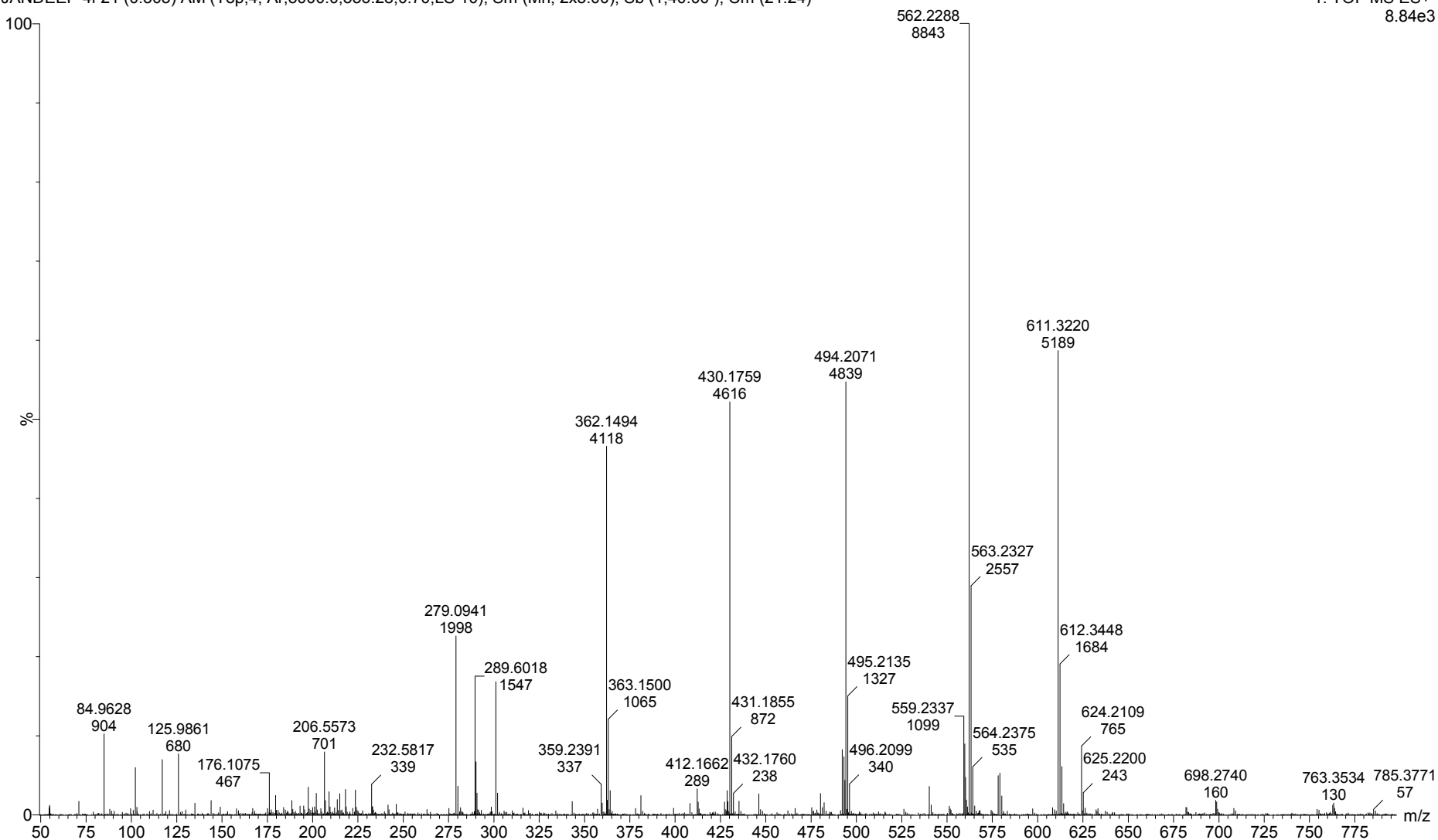


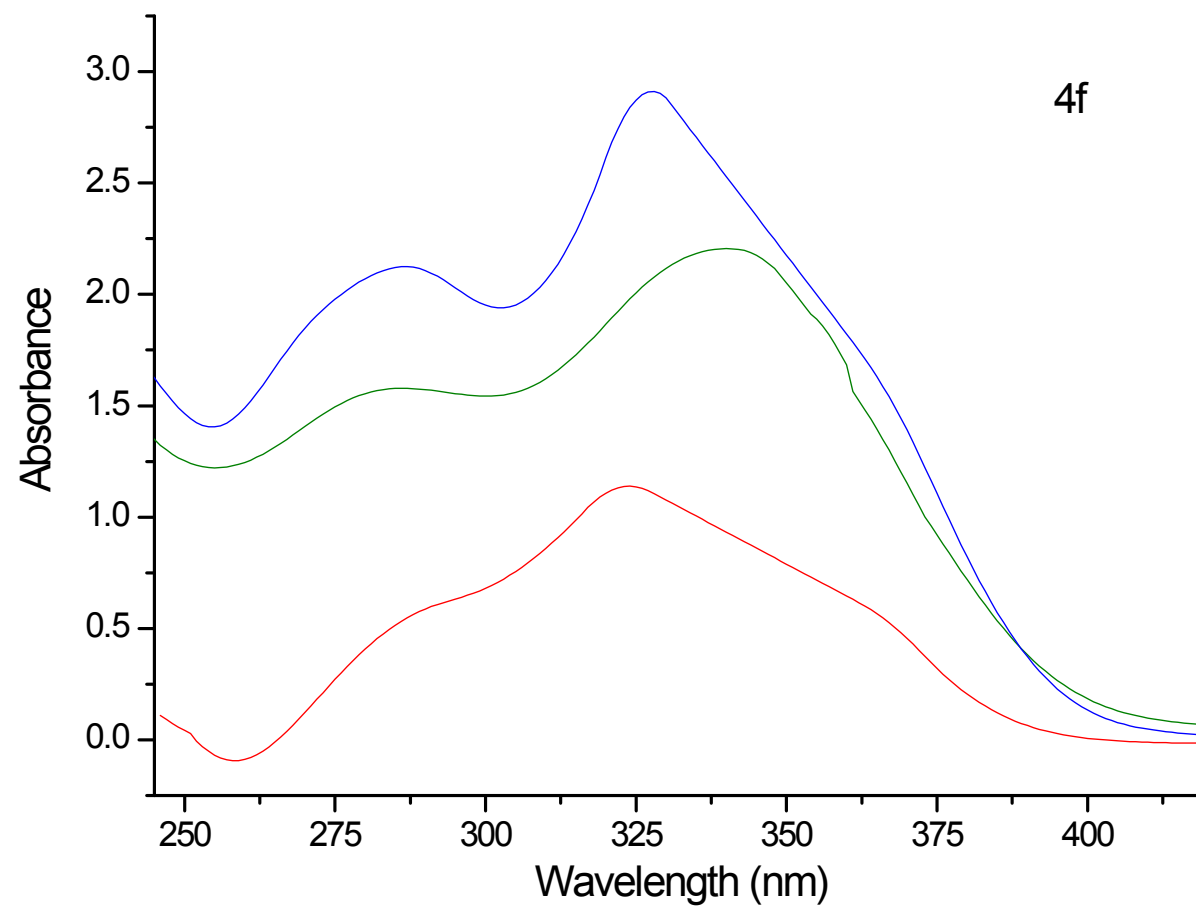
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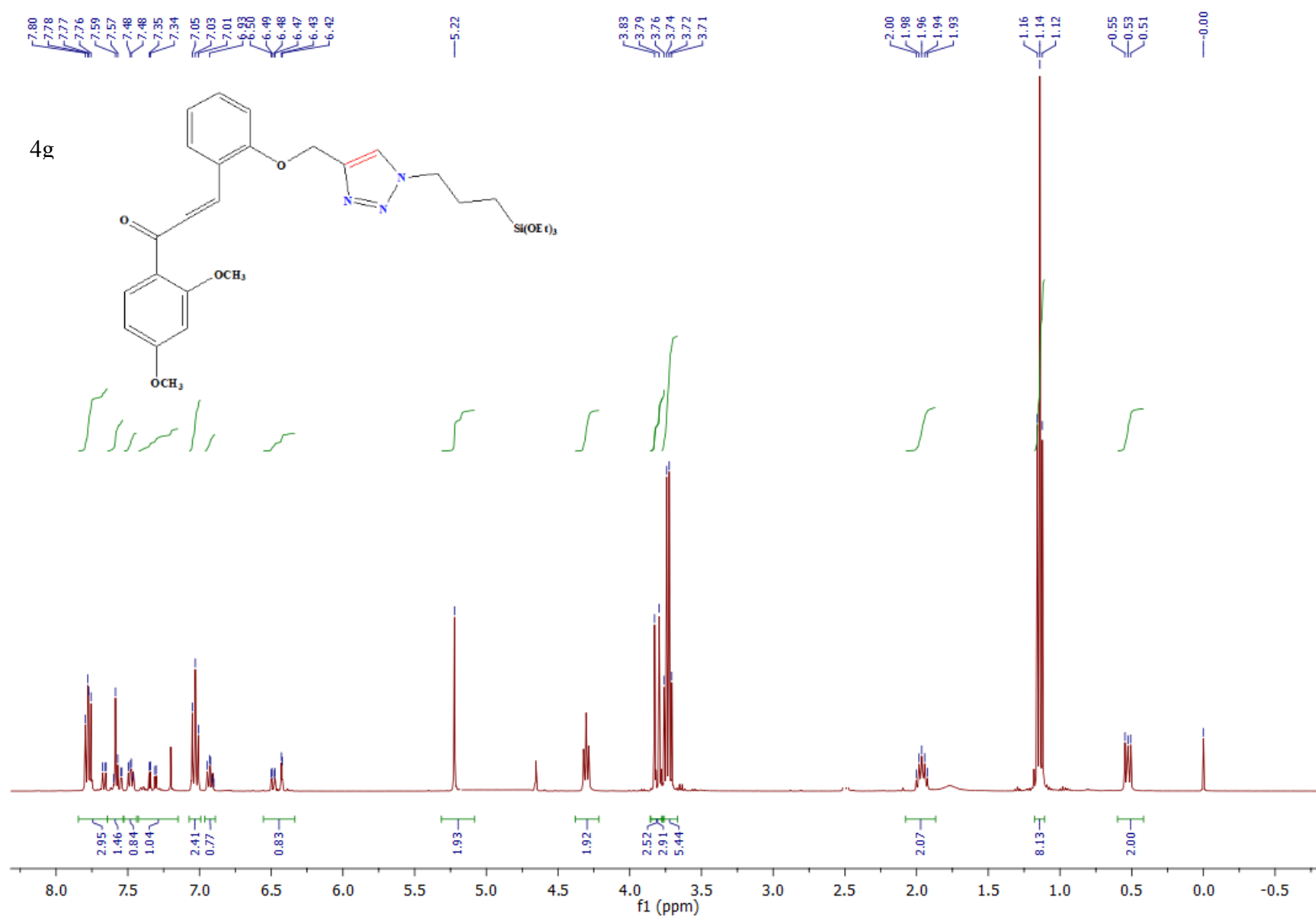
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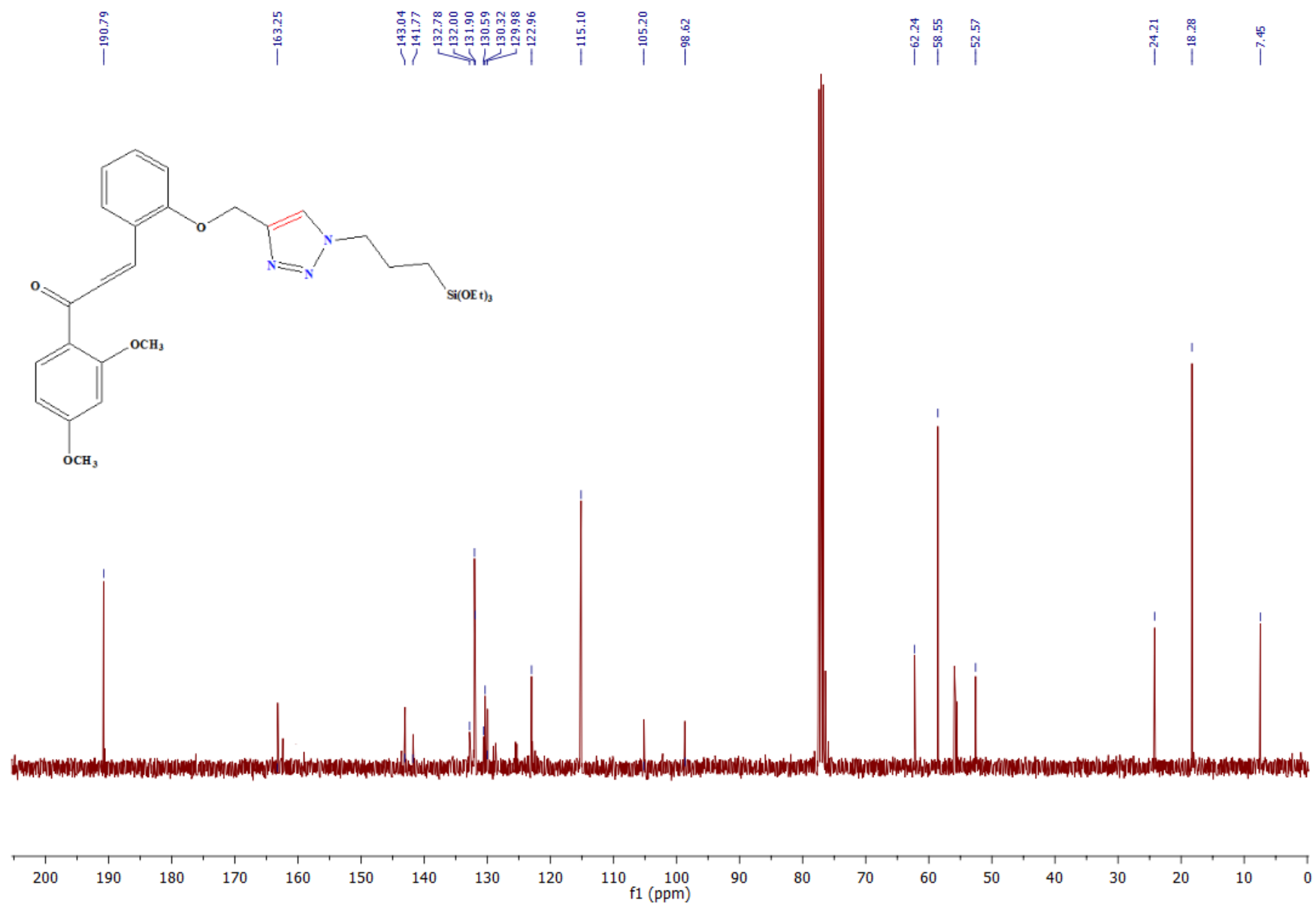
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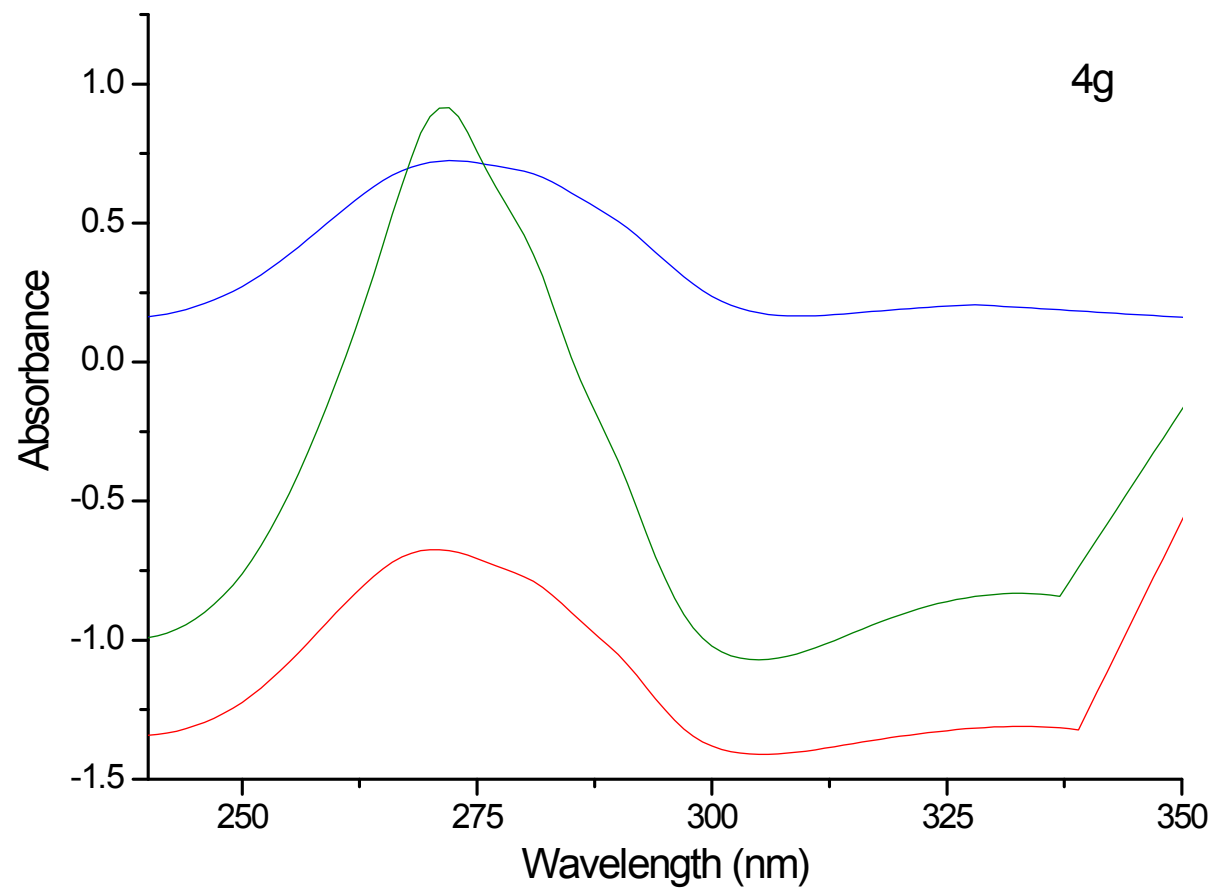
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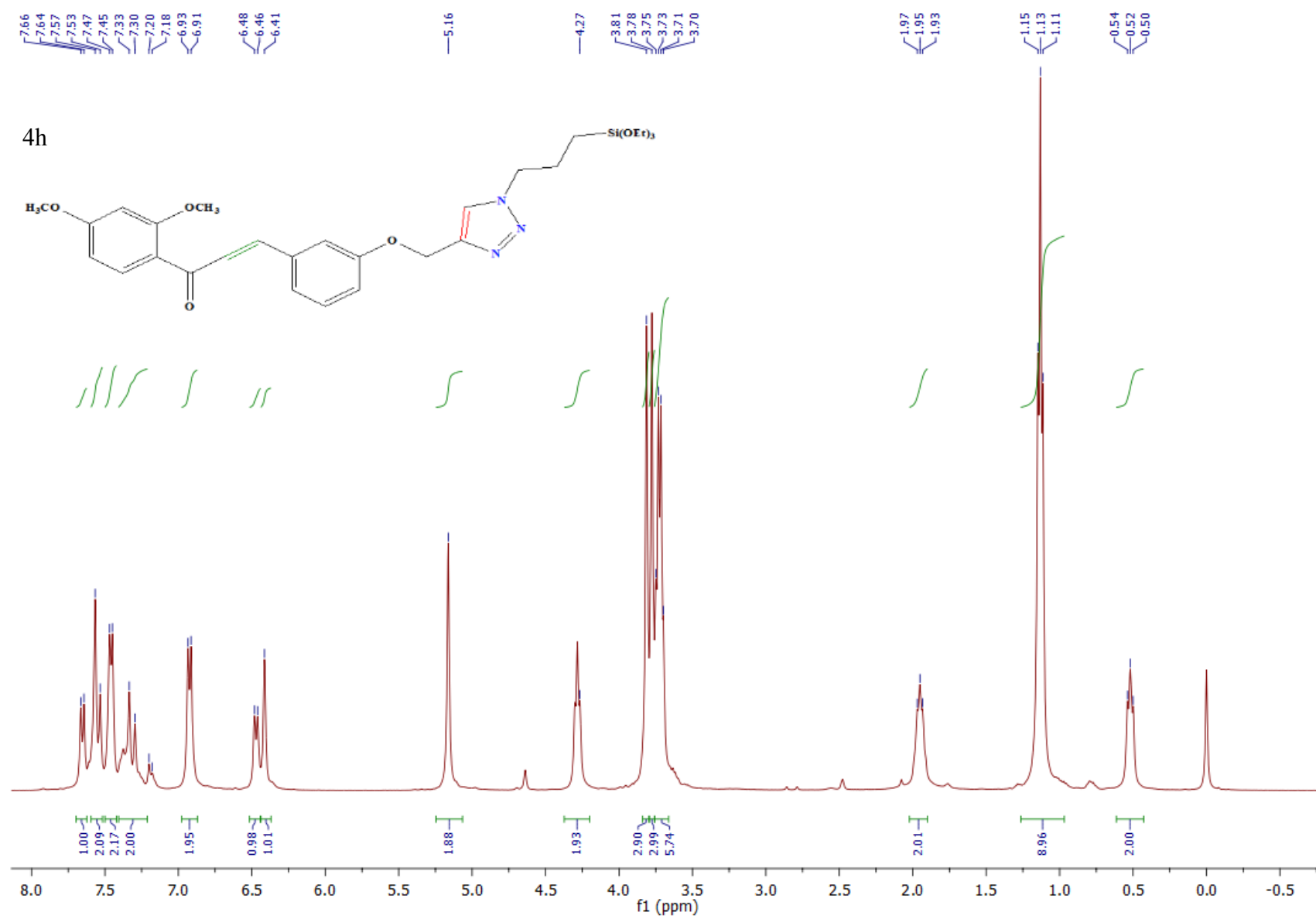


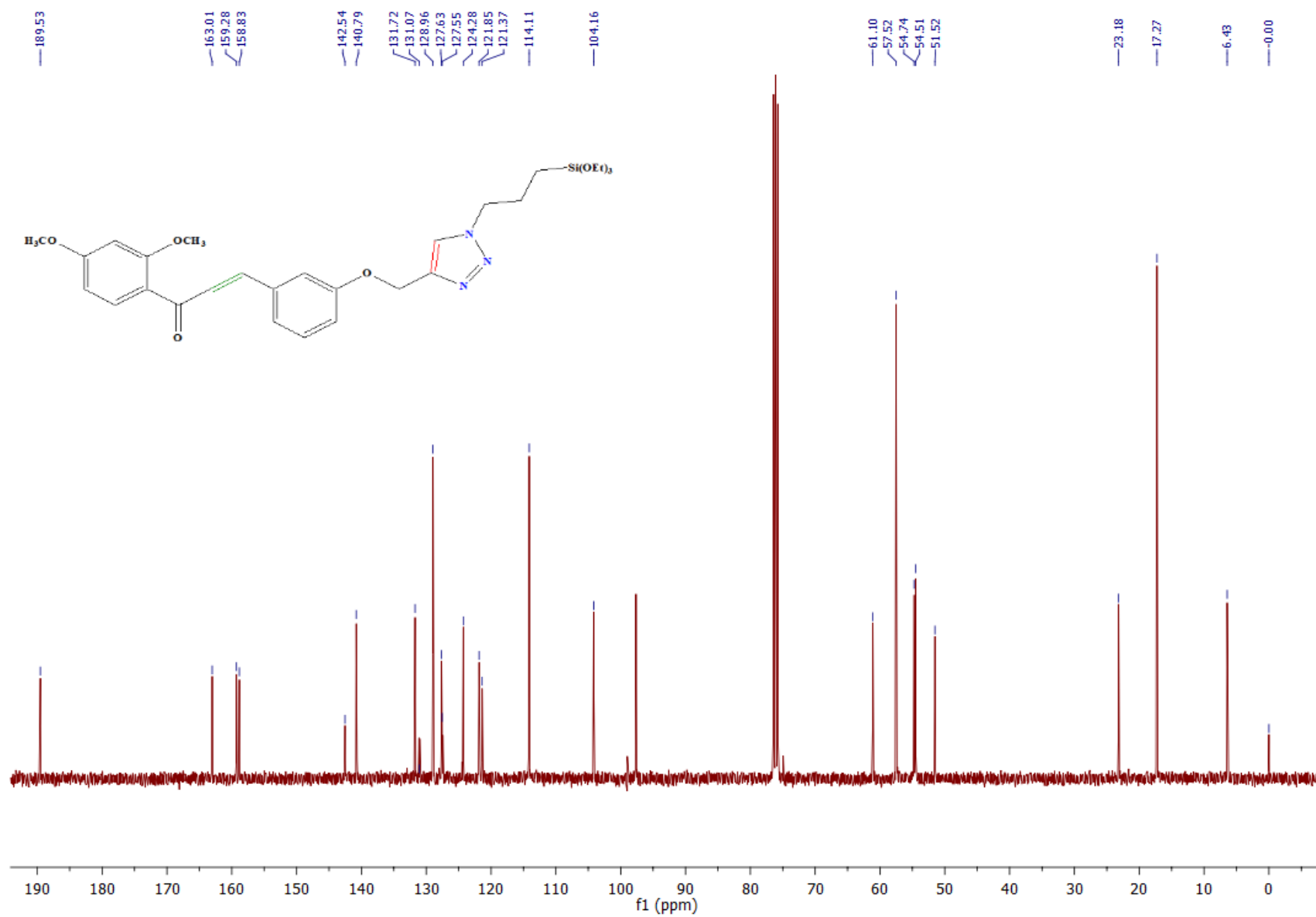


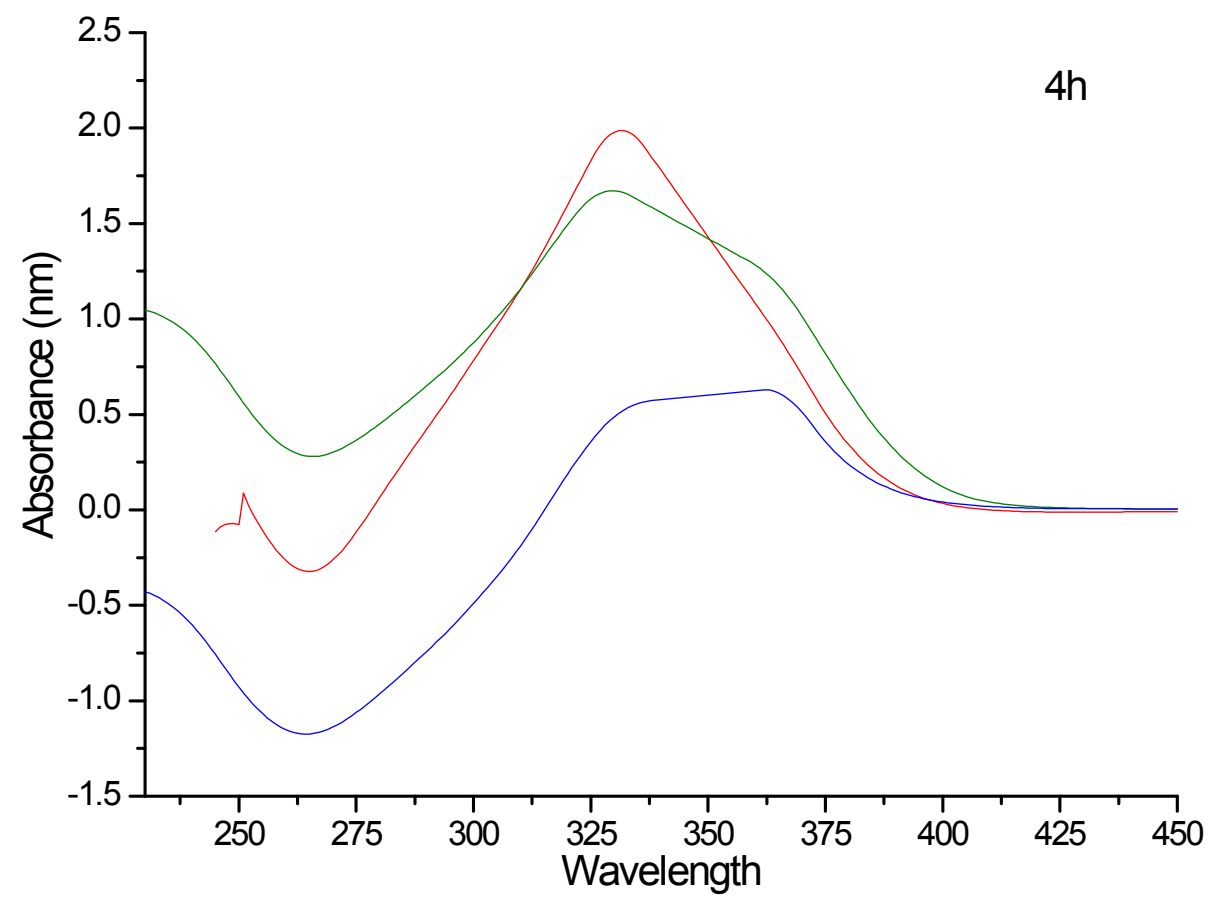


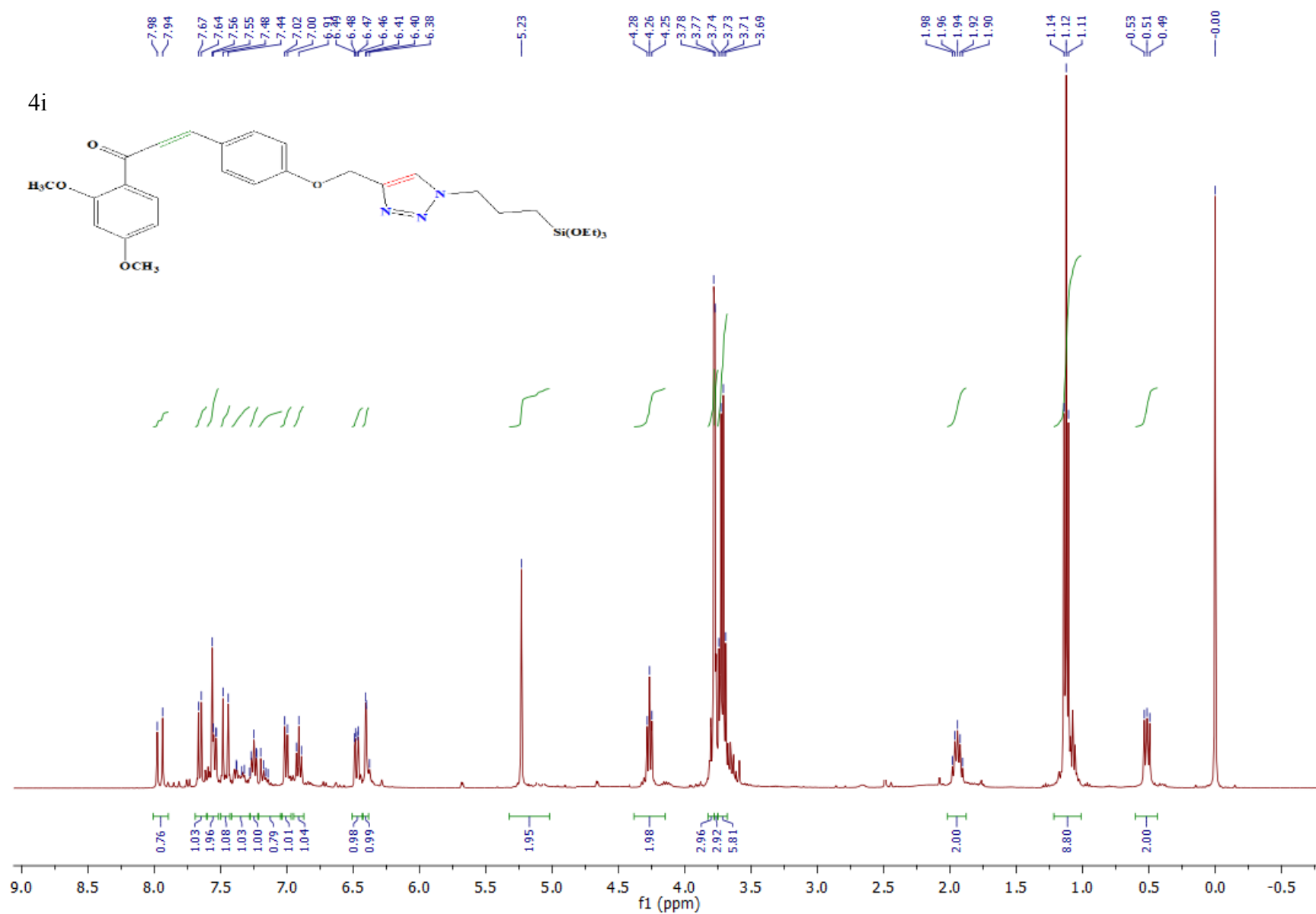


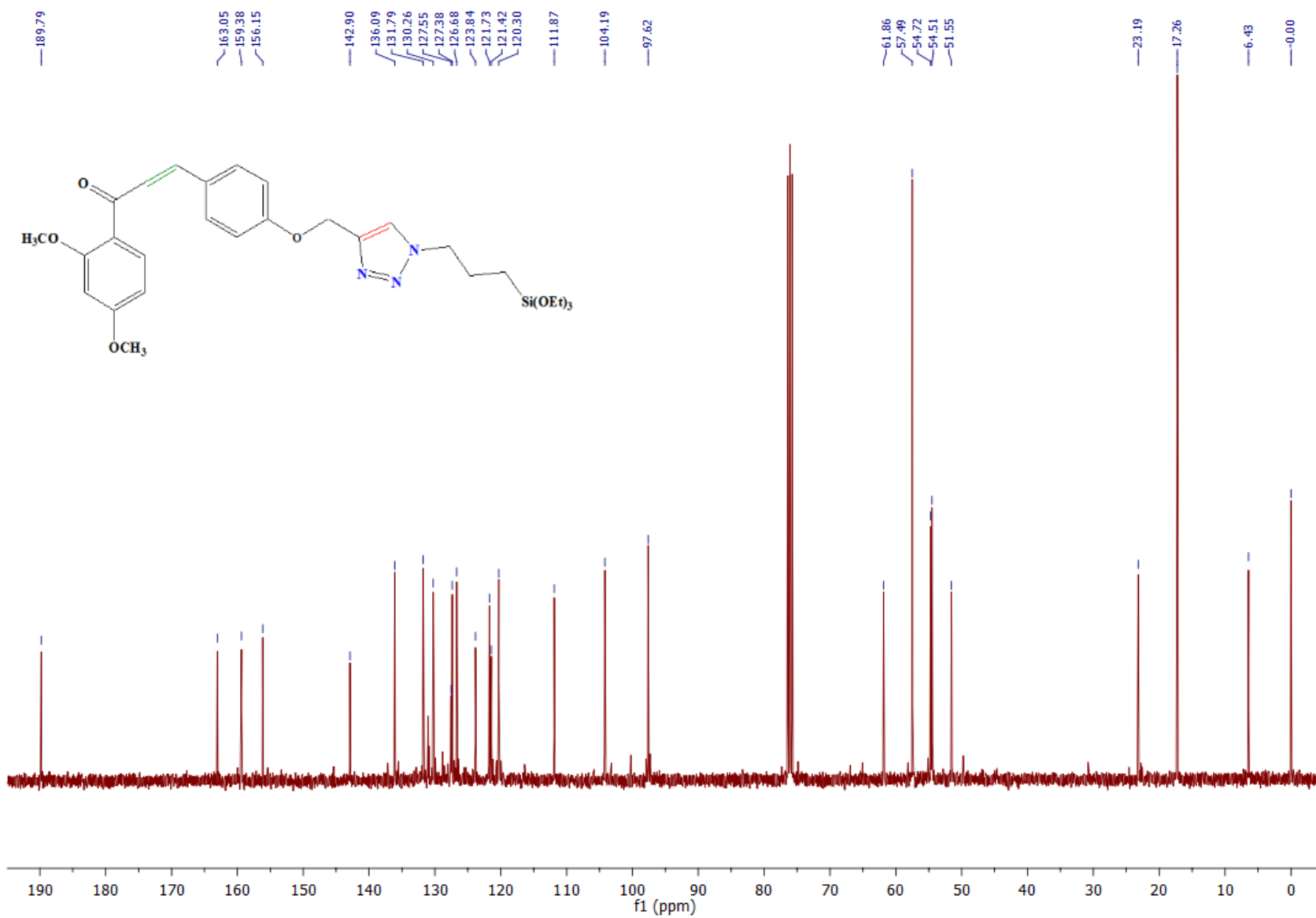










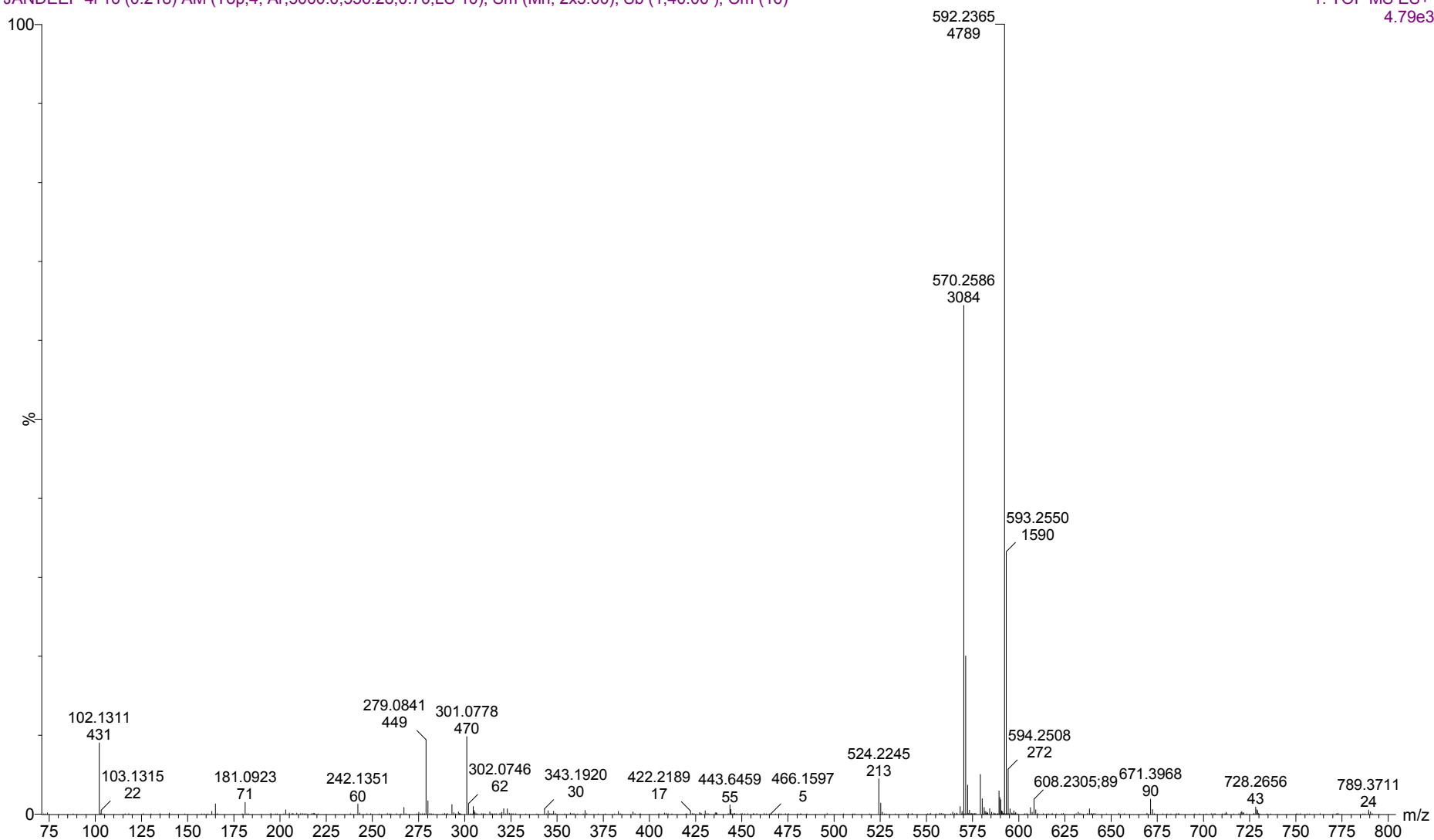


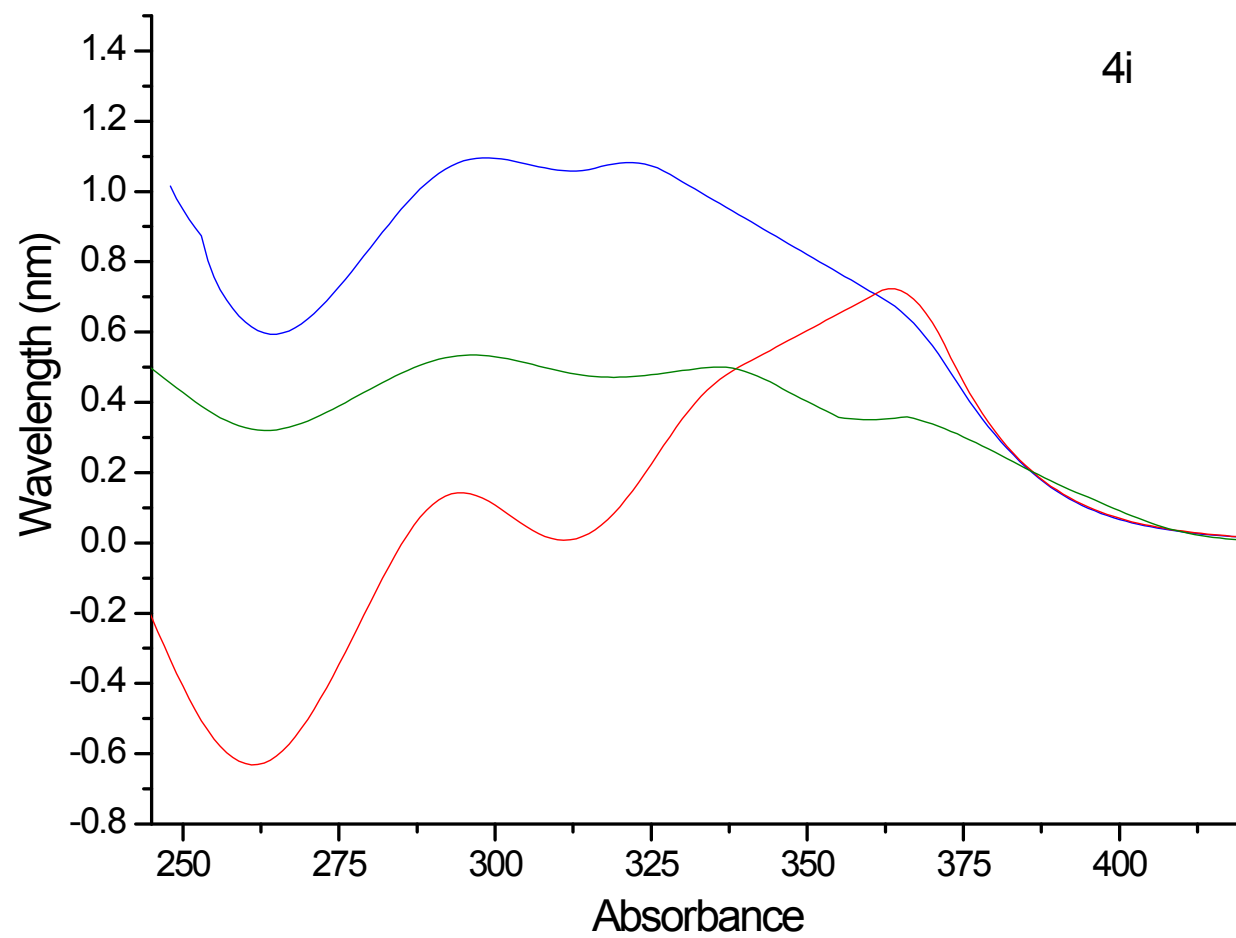
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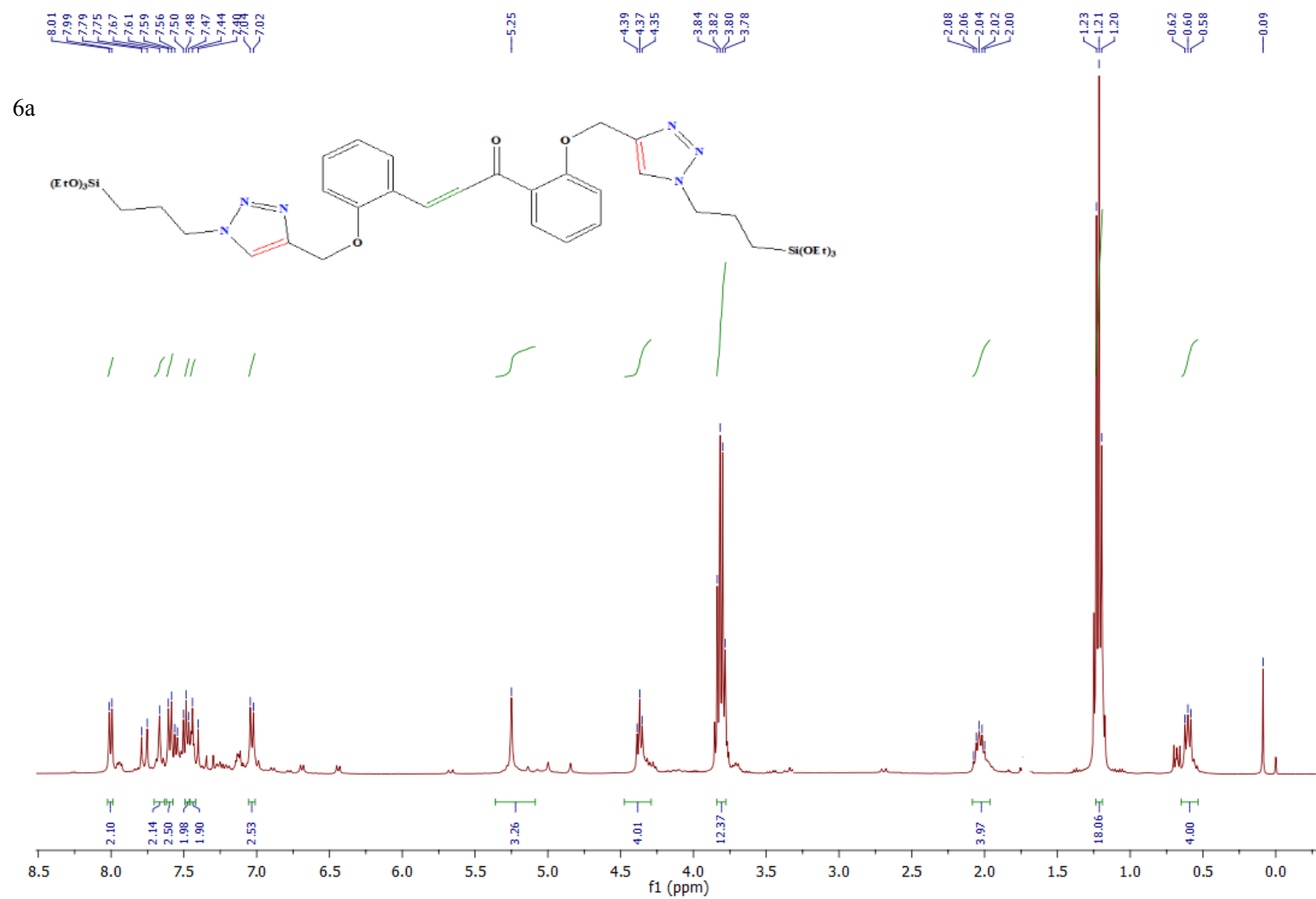
JANDEEP 4i 16 (0.218) AM (Top,4, Ar,5000.0,556.28,0.70,LS 10); Sm (Mn, 2x3.00); Sb (1,40.00); Cm (16)

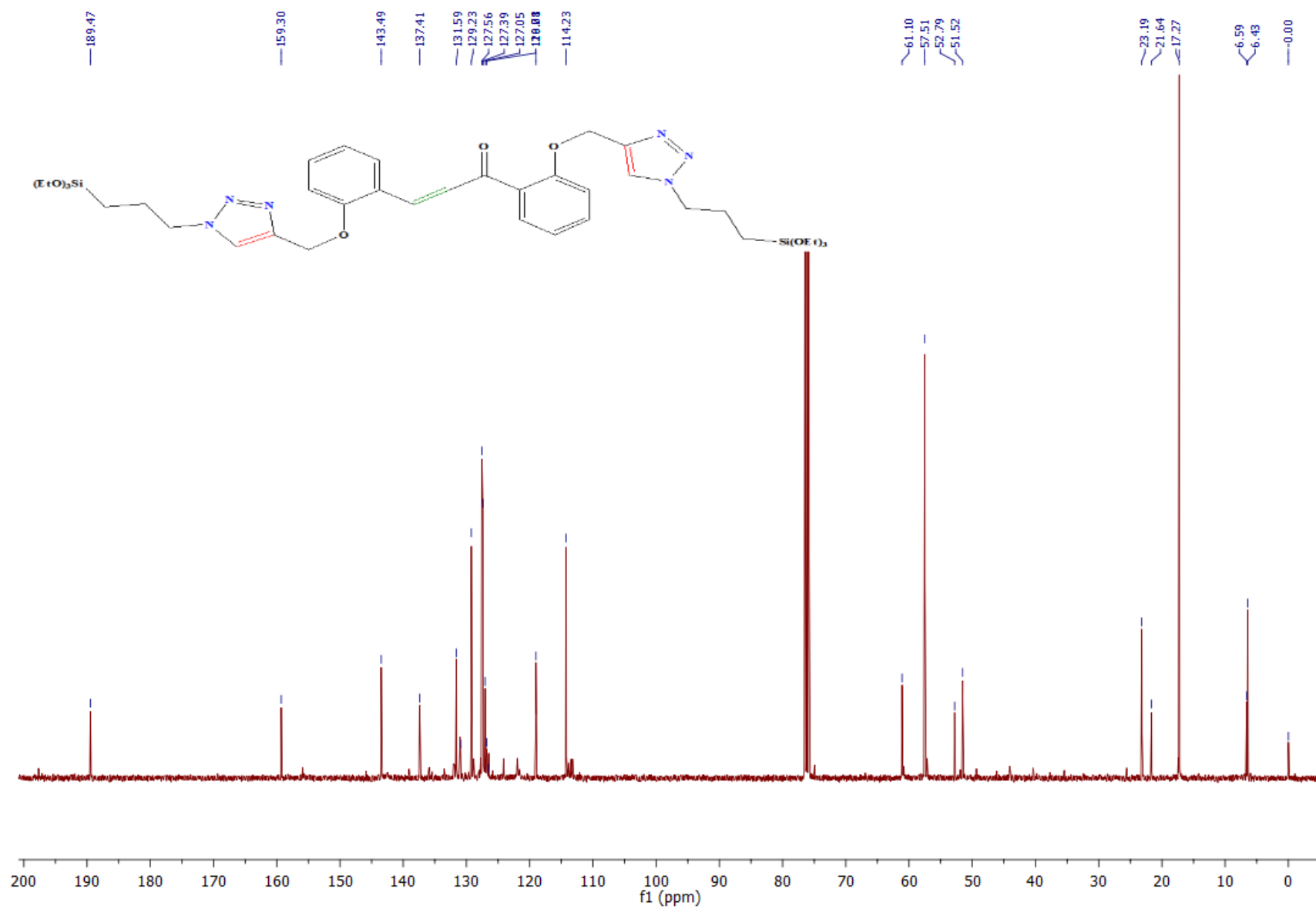
SAIF/CIL,PANJAB UNIVERSITY,CHANDIGARH

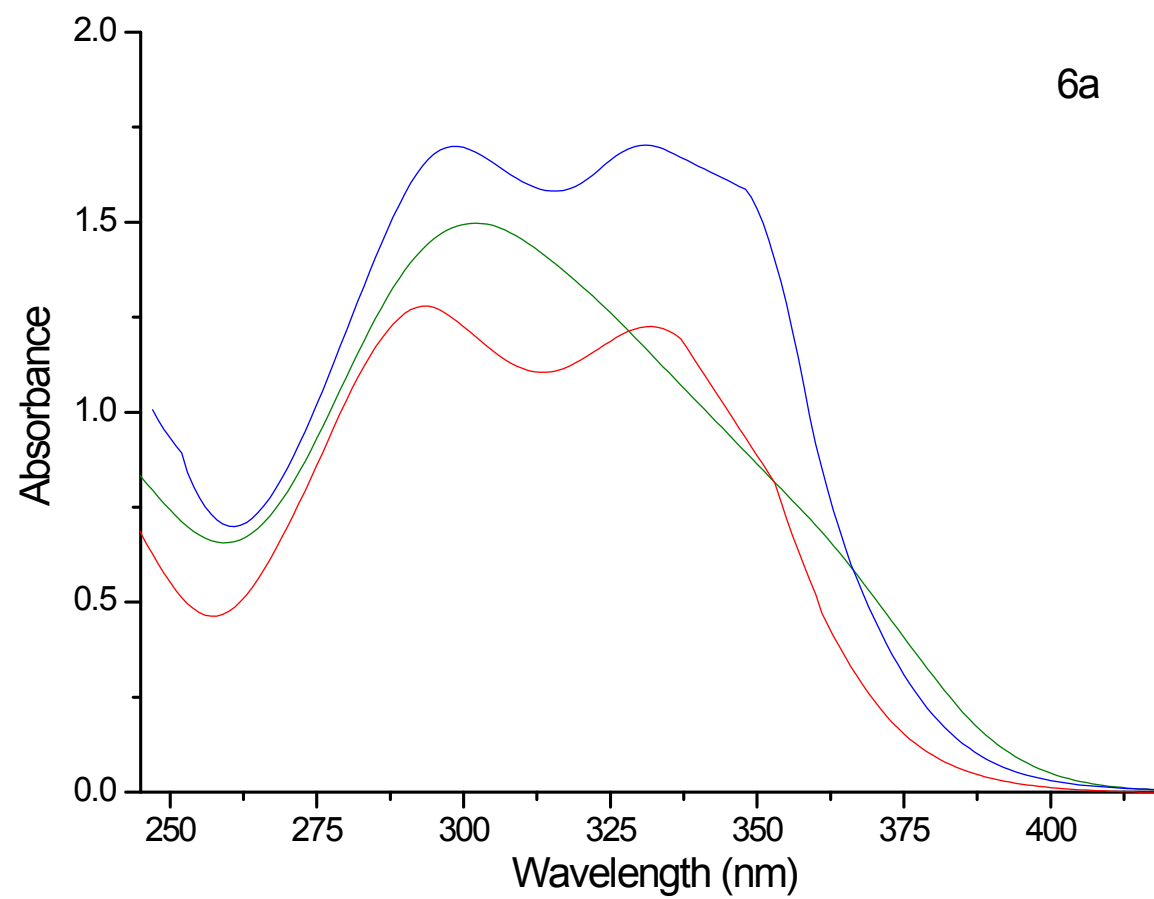
1: TOF MS ES+
4.79e3



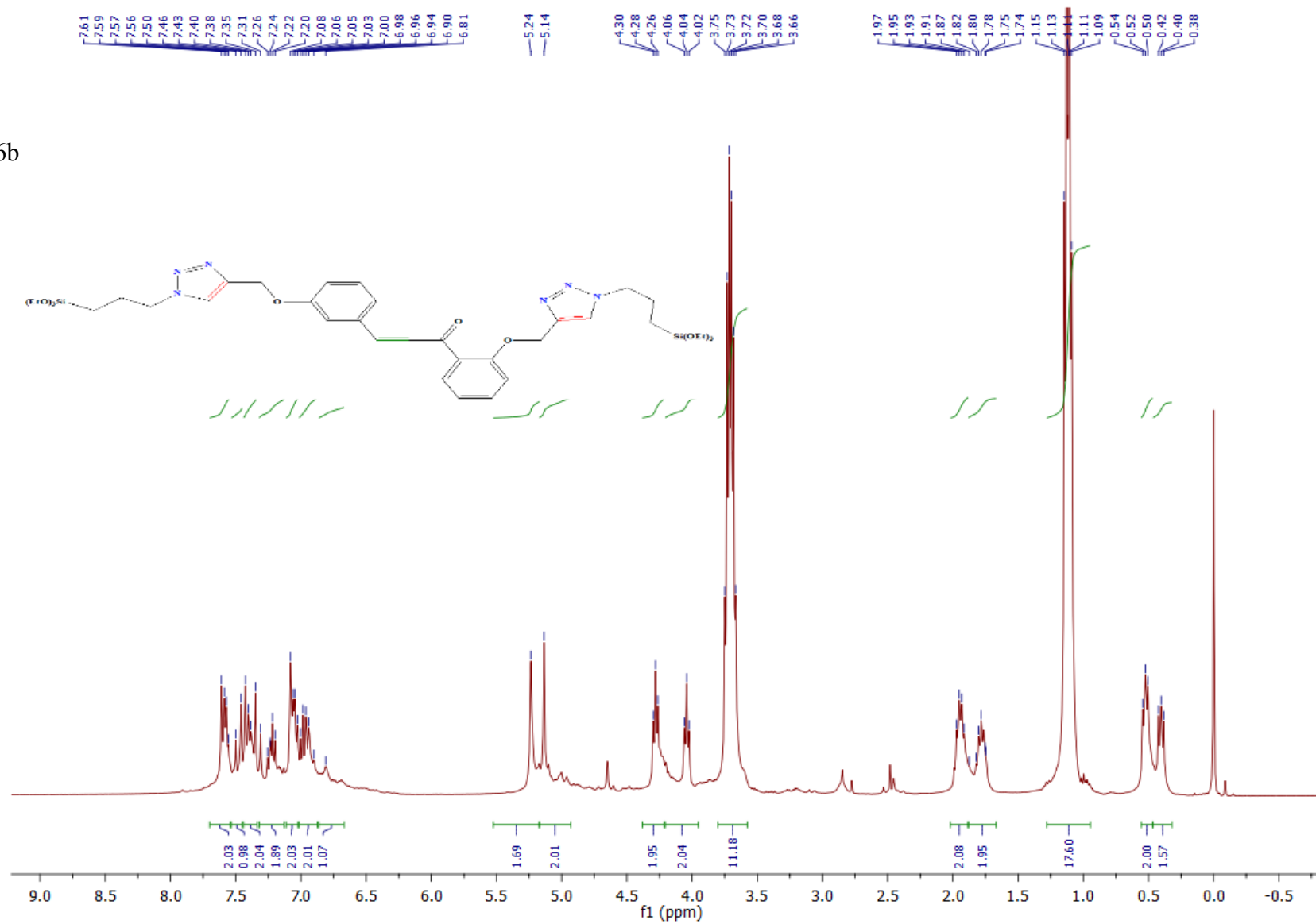


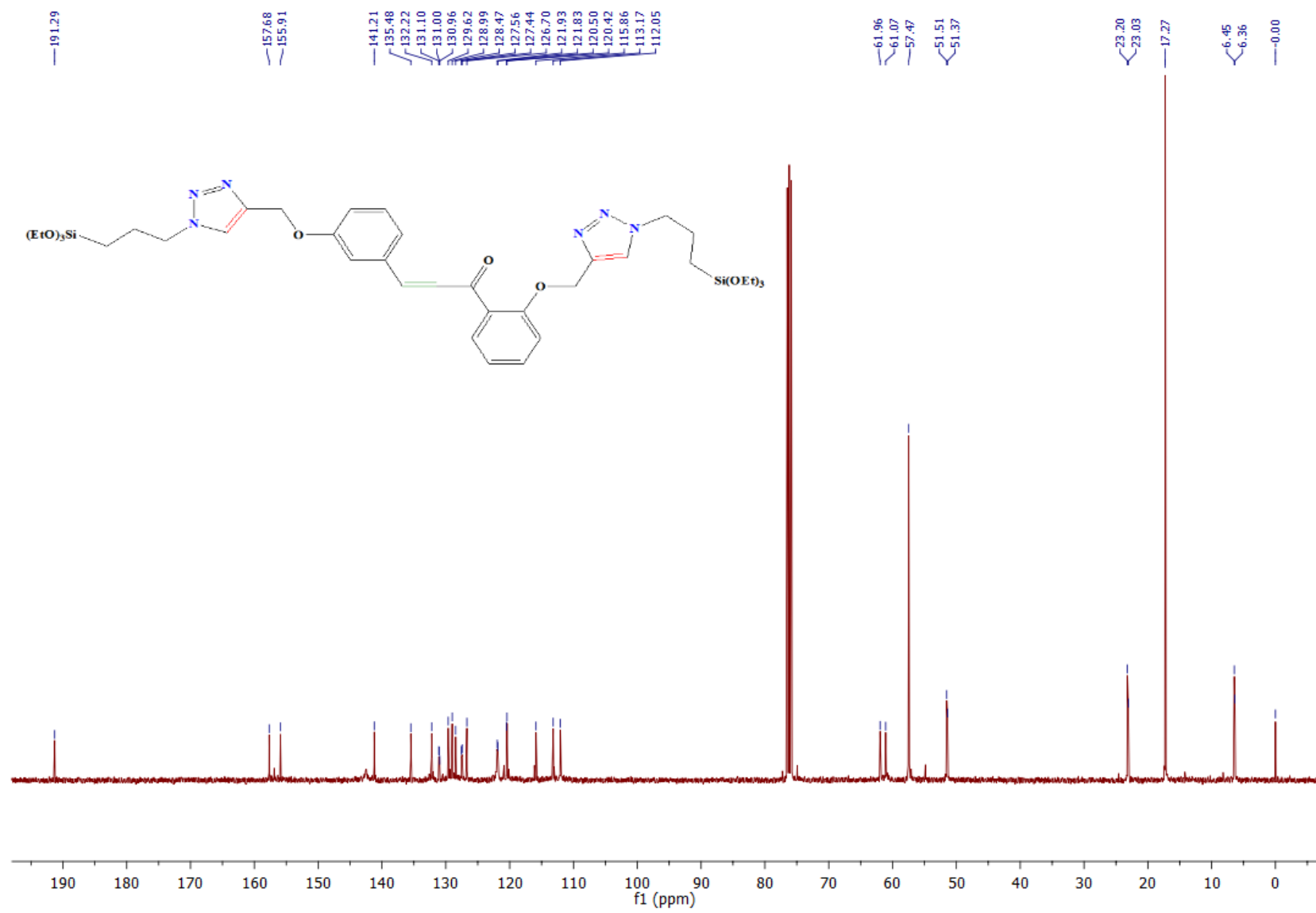


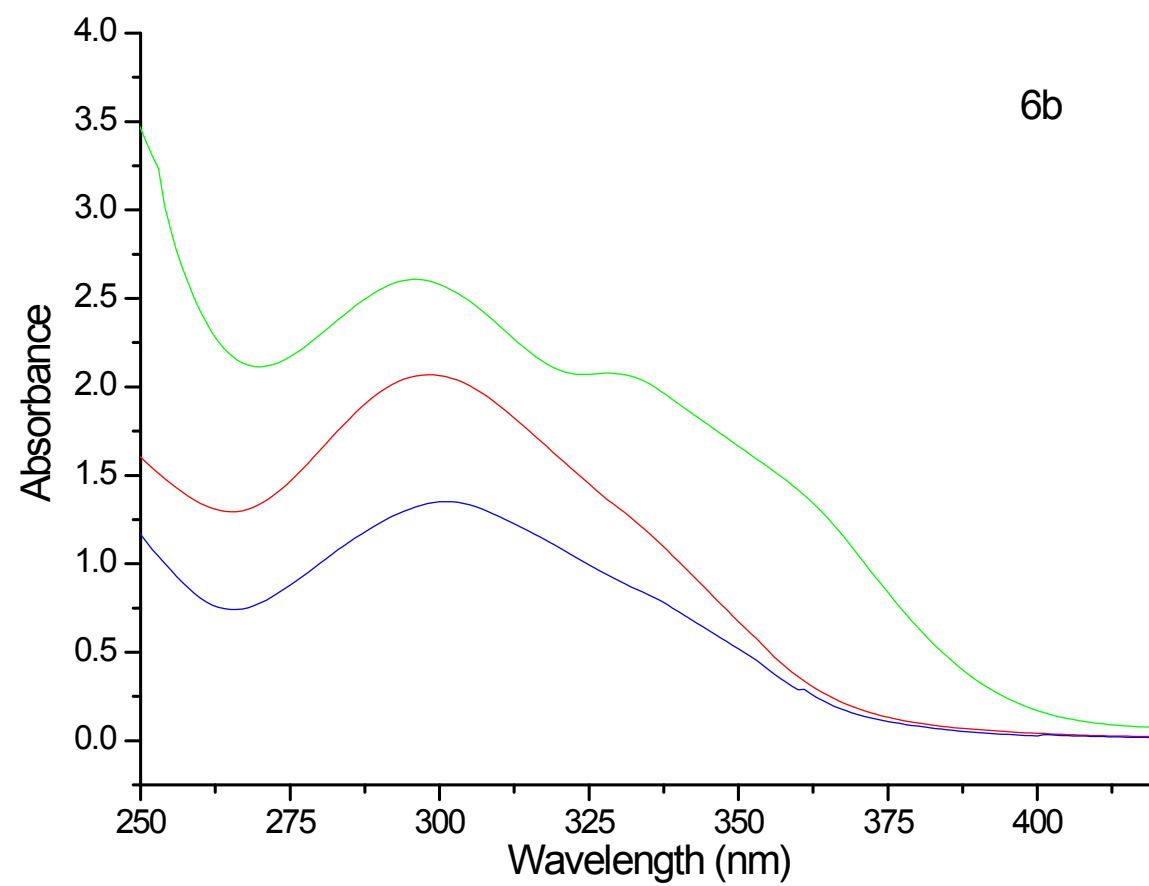


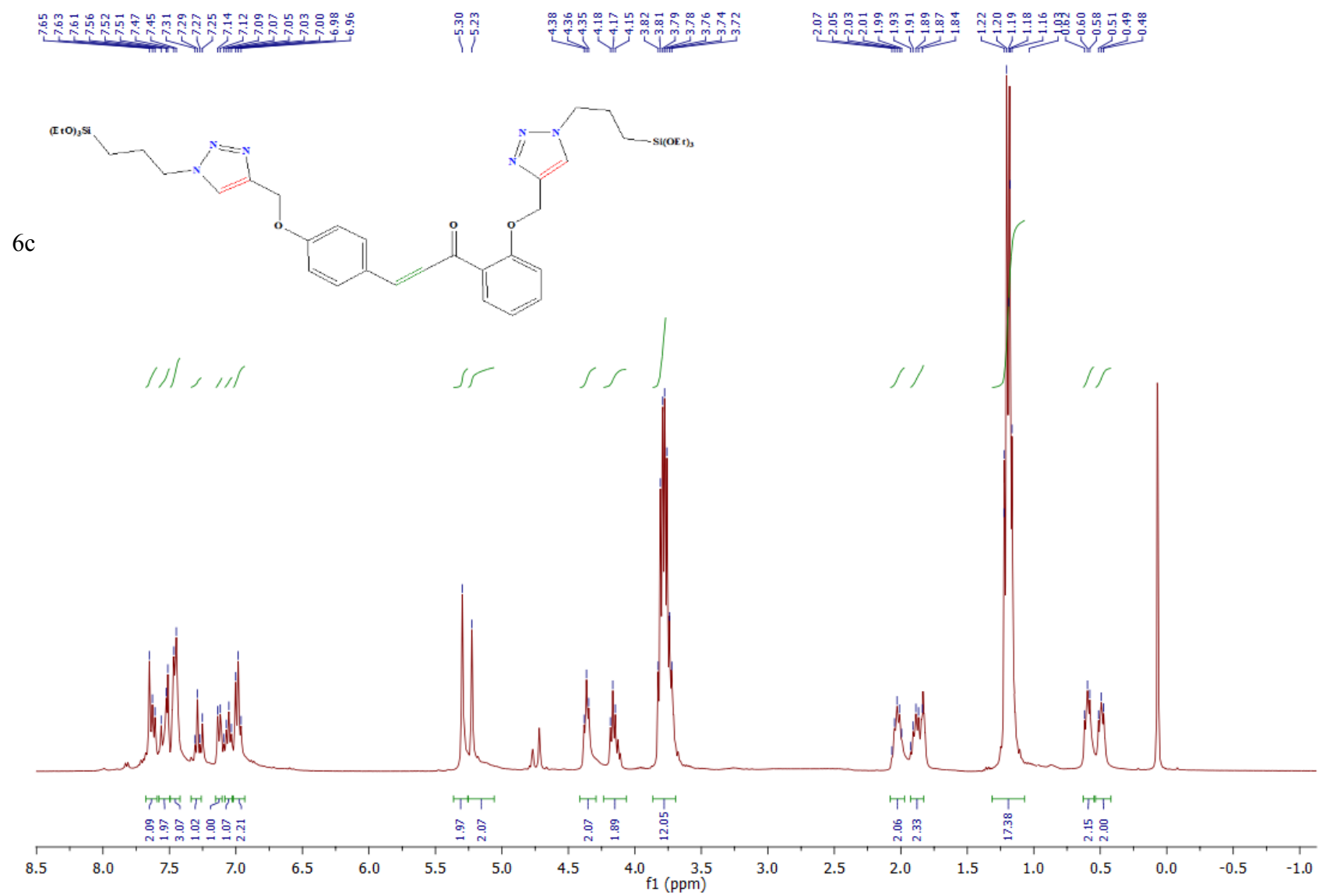


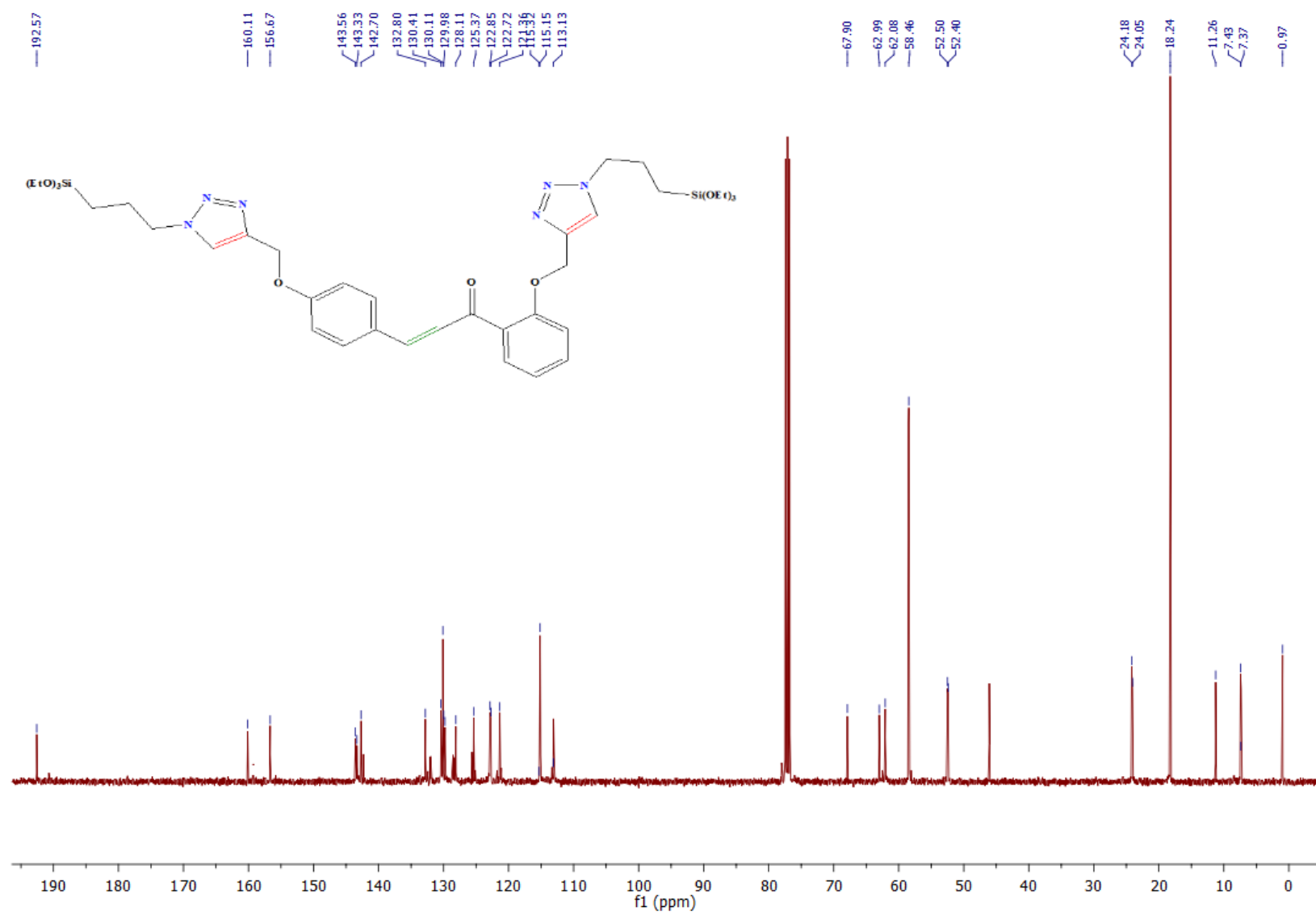
6b









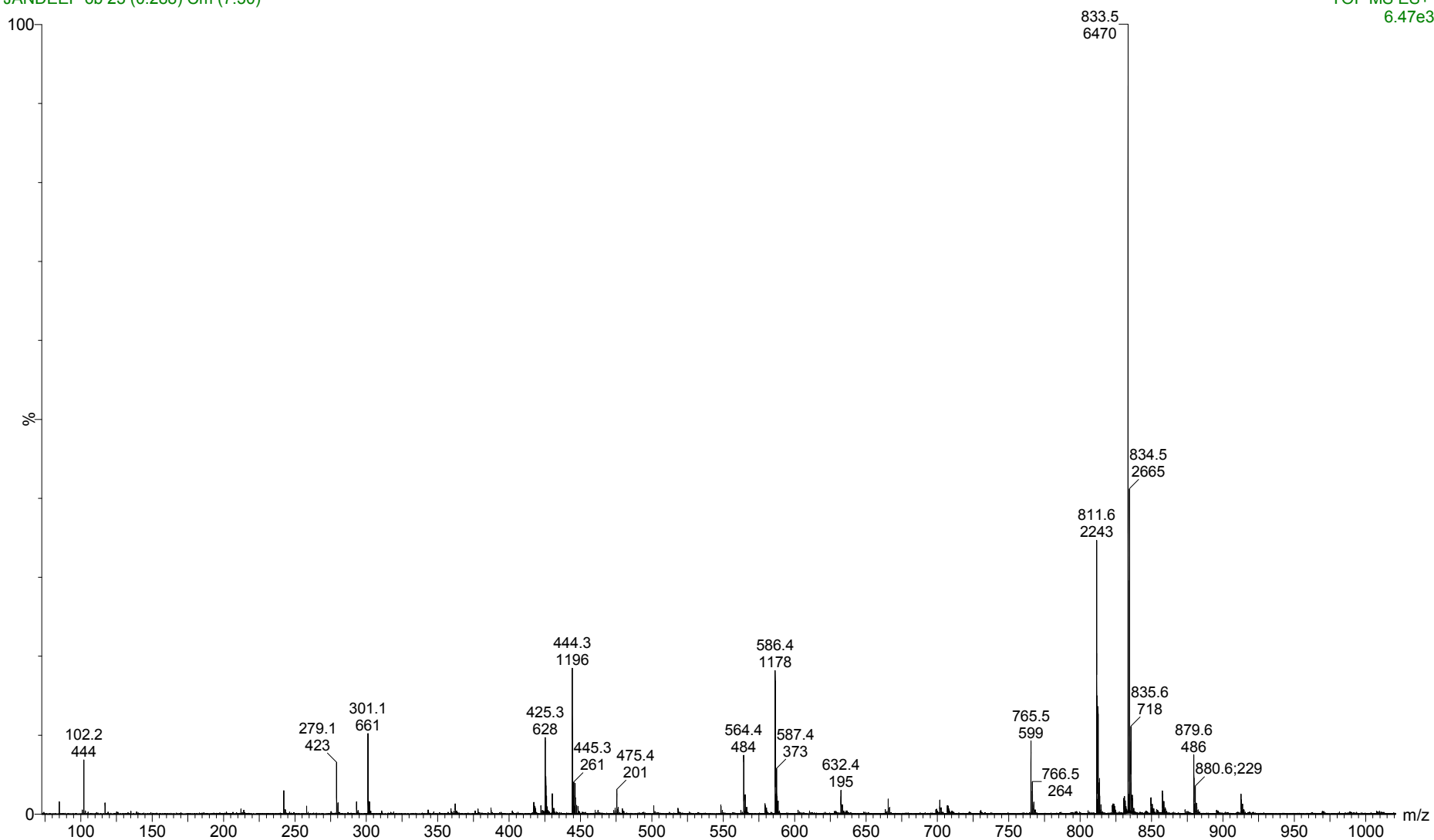


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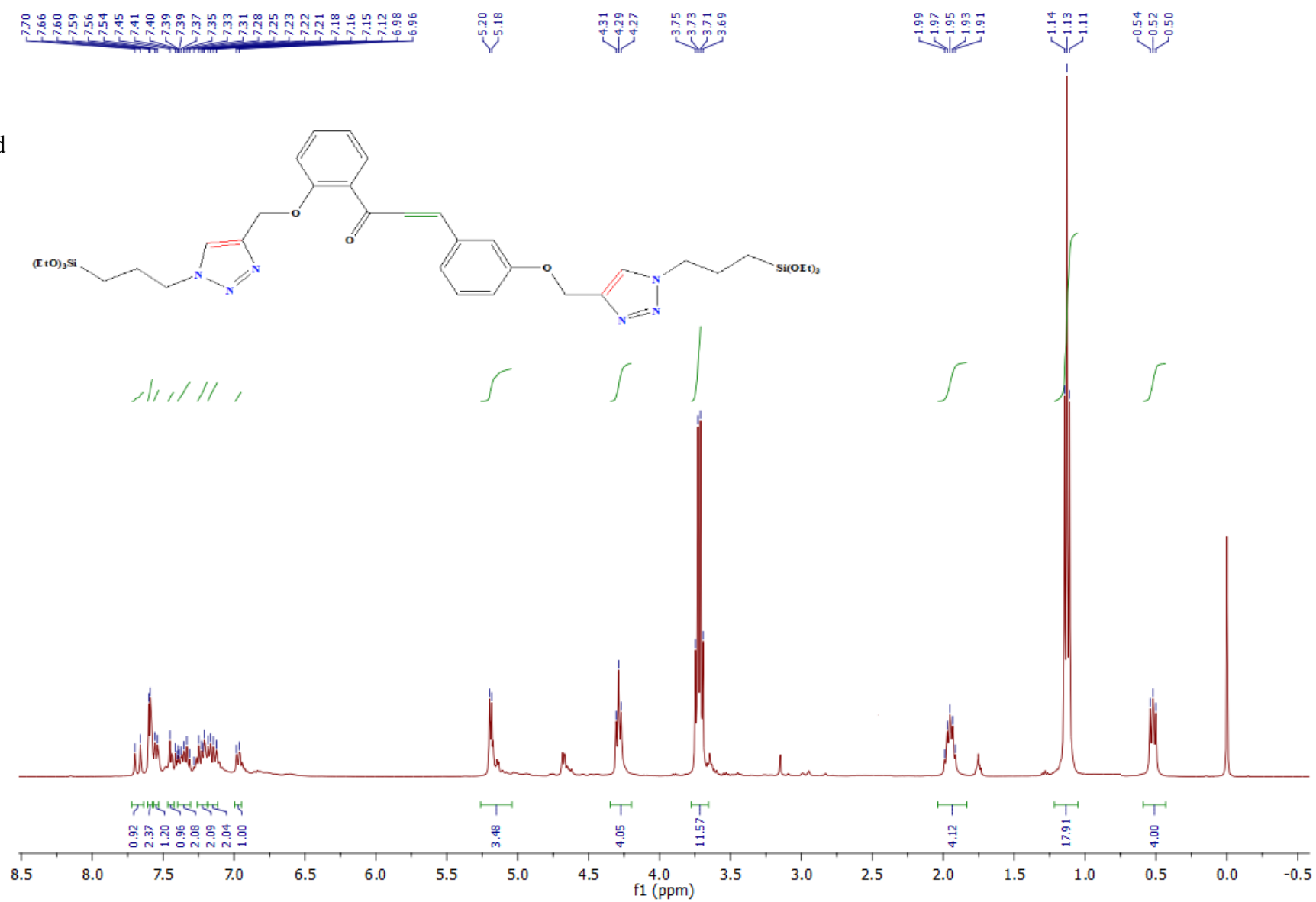
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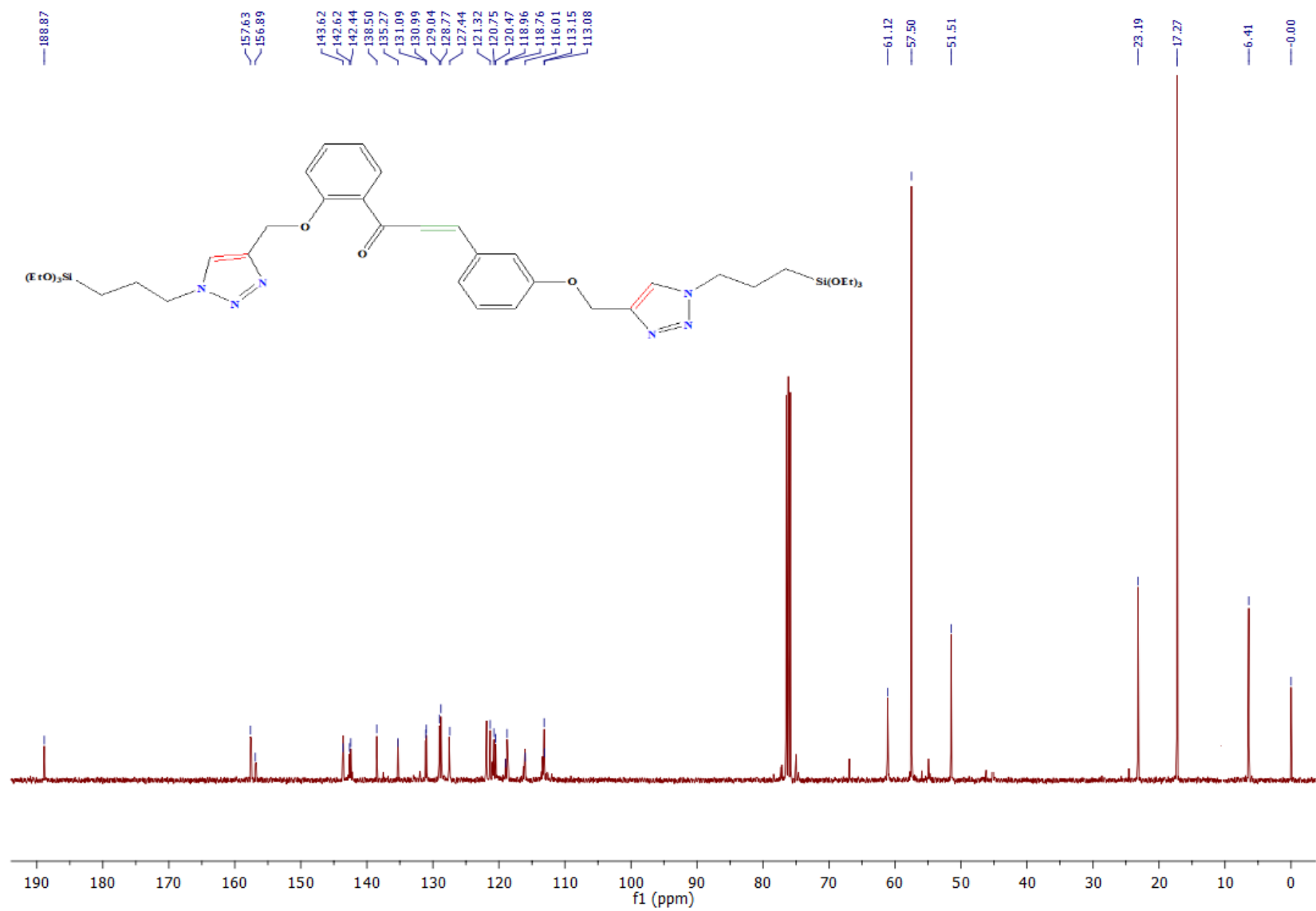
SAIF/CIL,PANJAB UNIVERSITY,CHANDIGARH

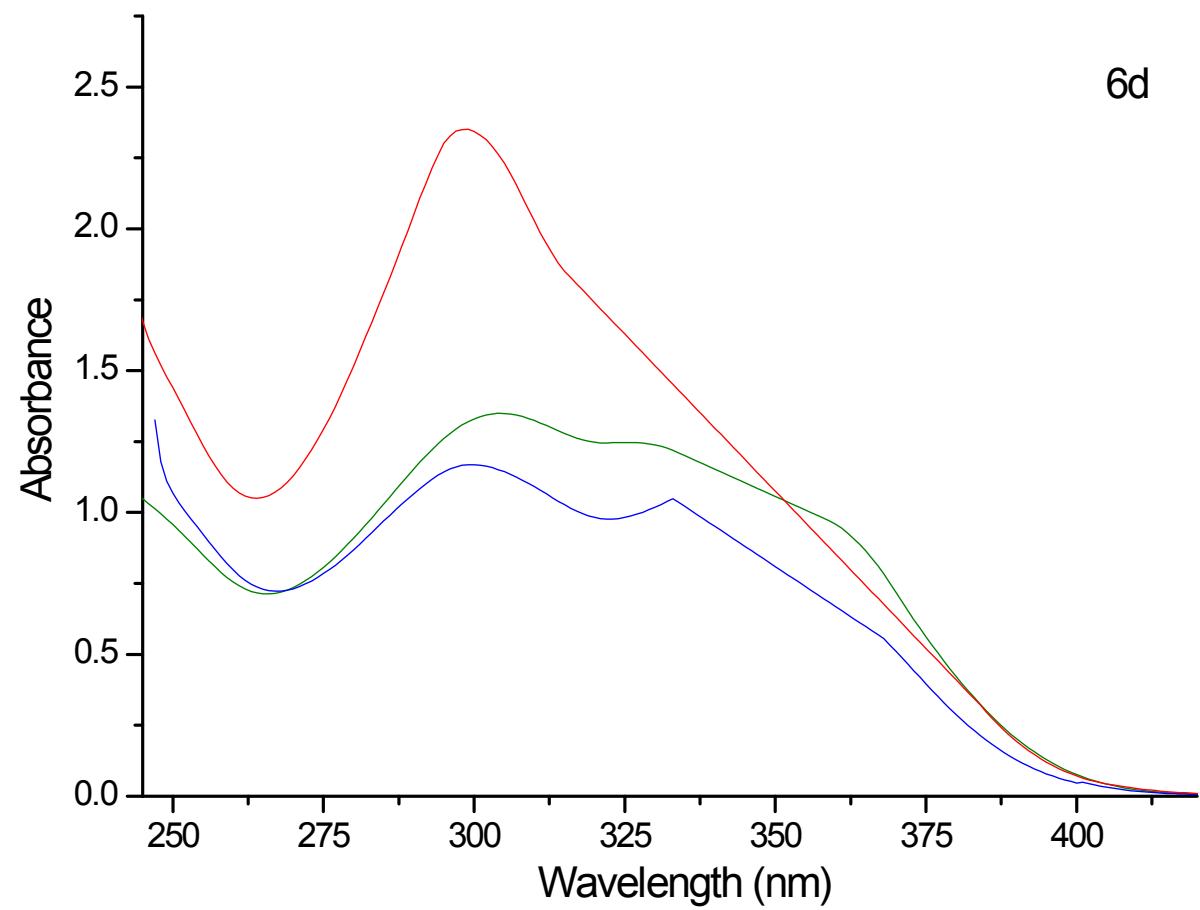
TOF MS ES+
6.47e3



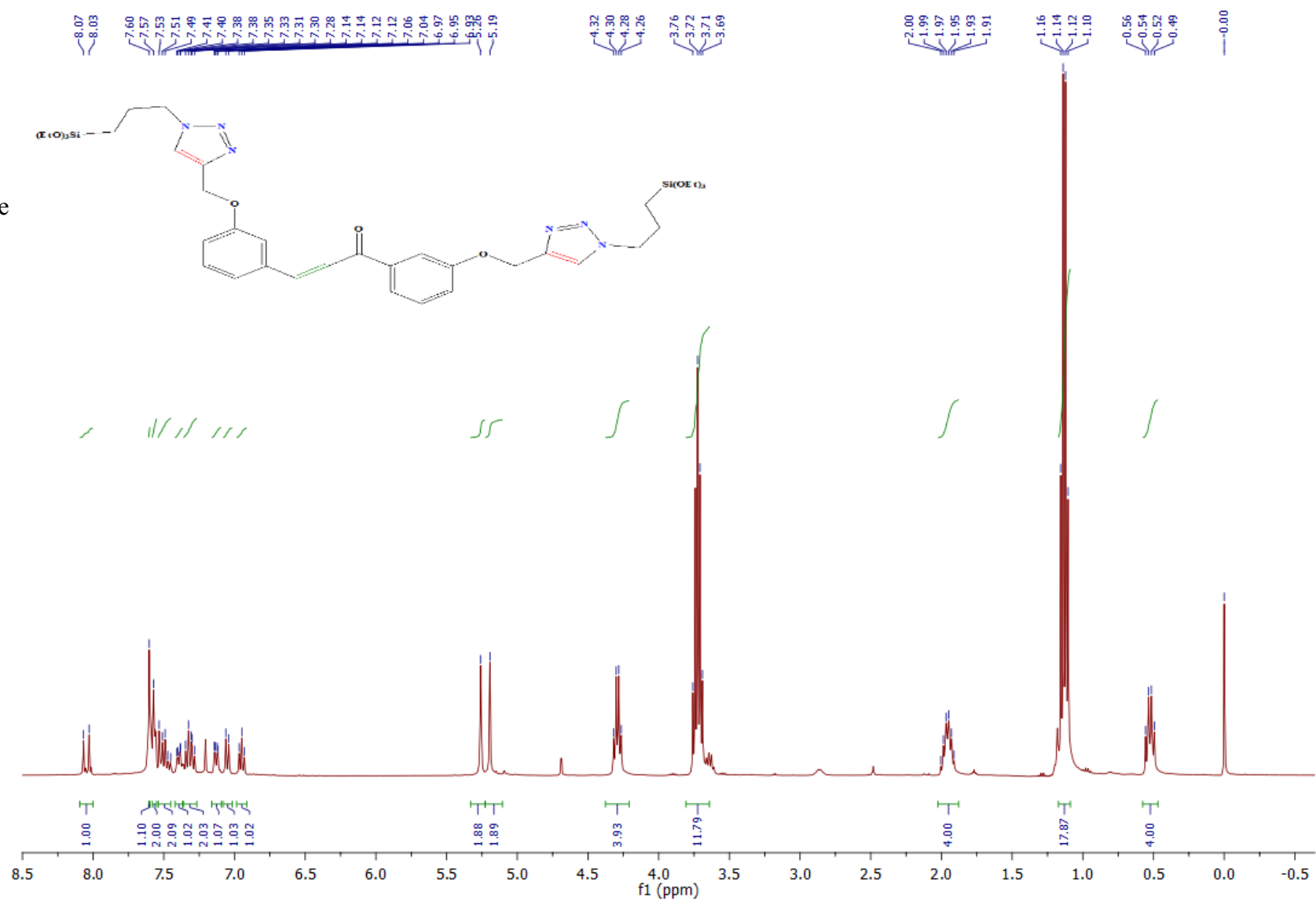
6d

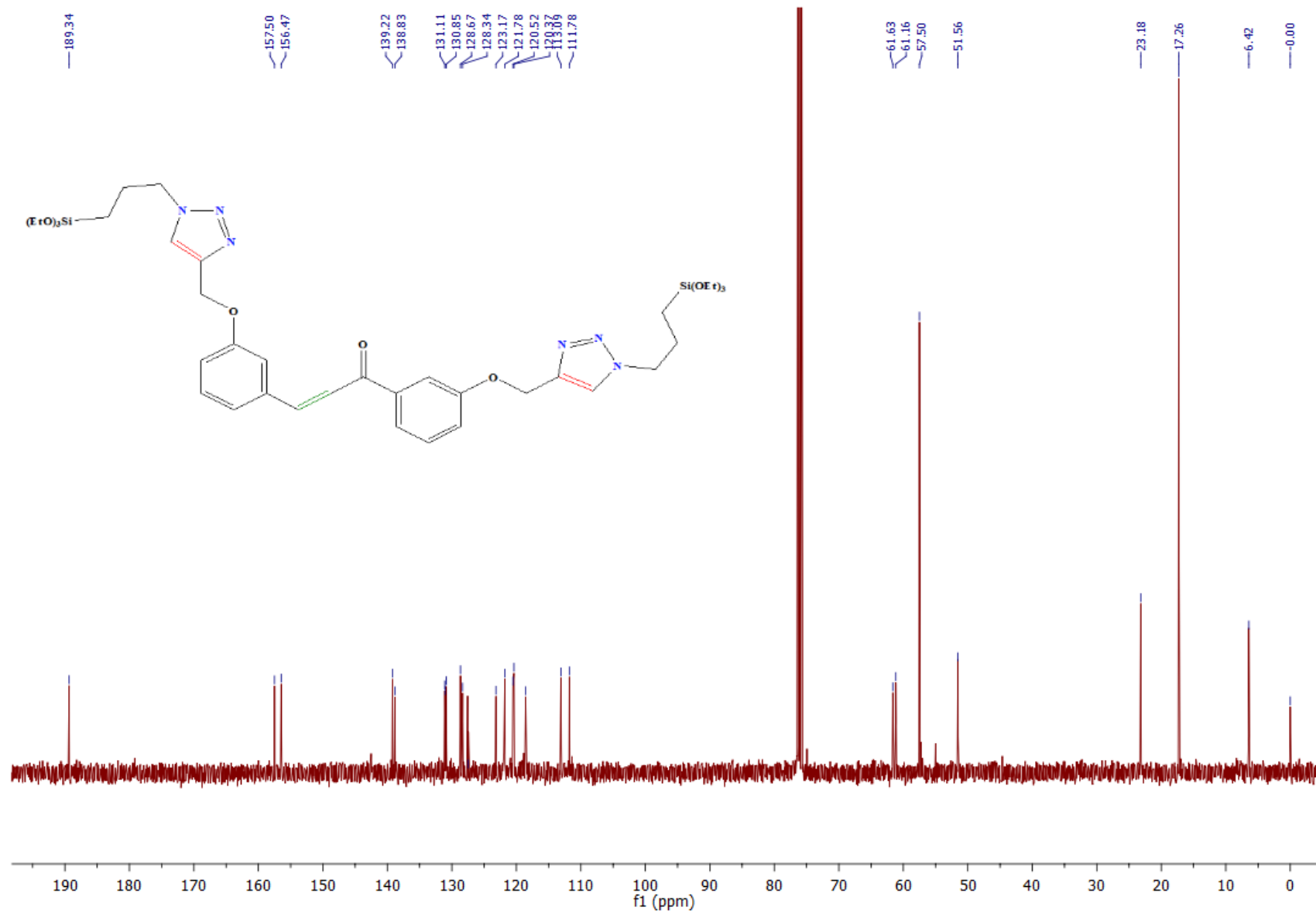


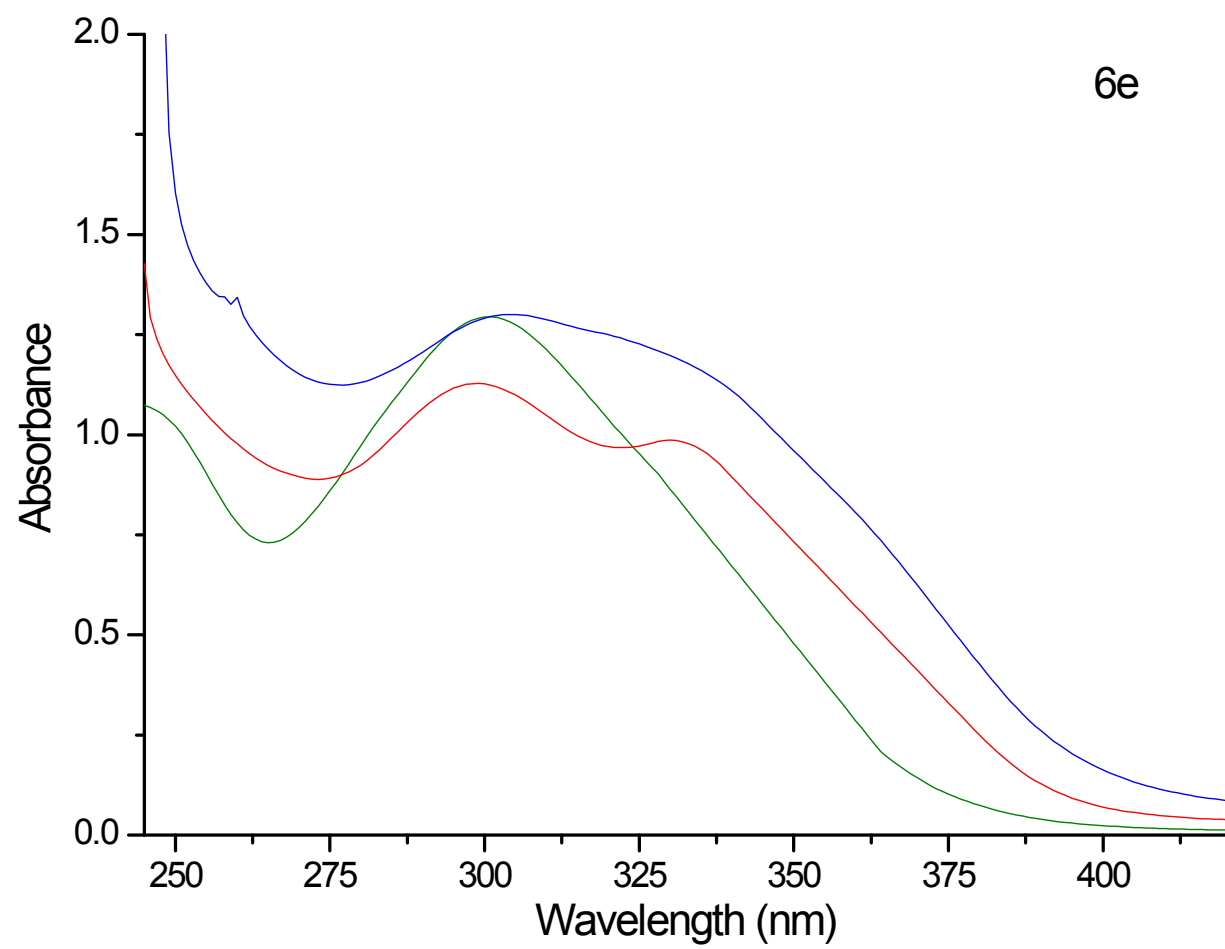




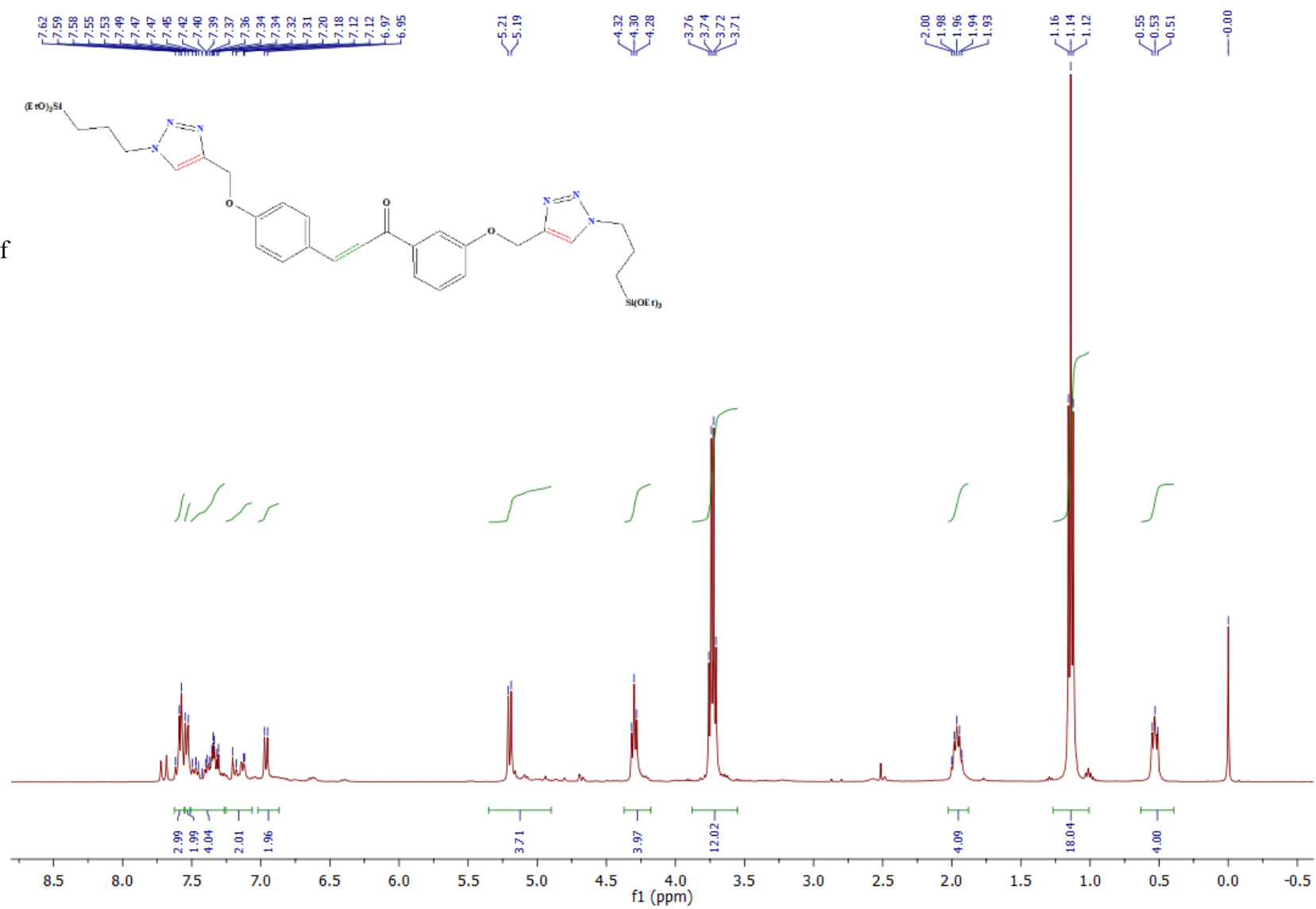
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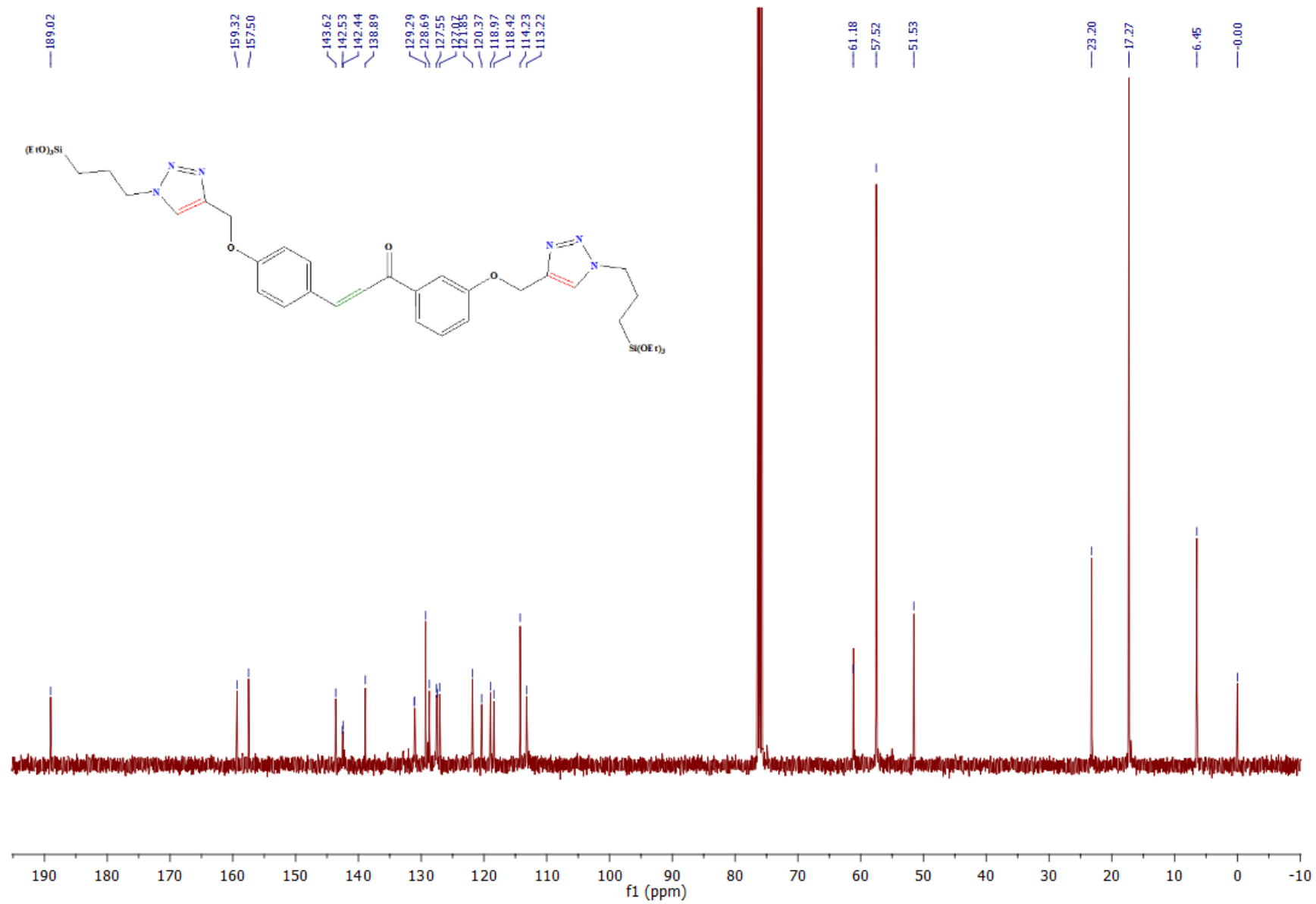


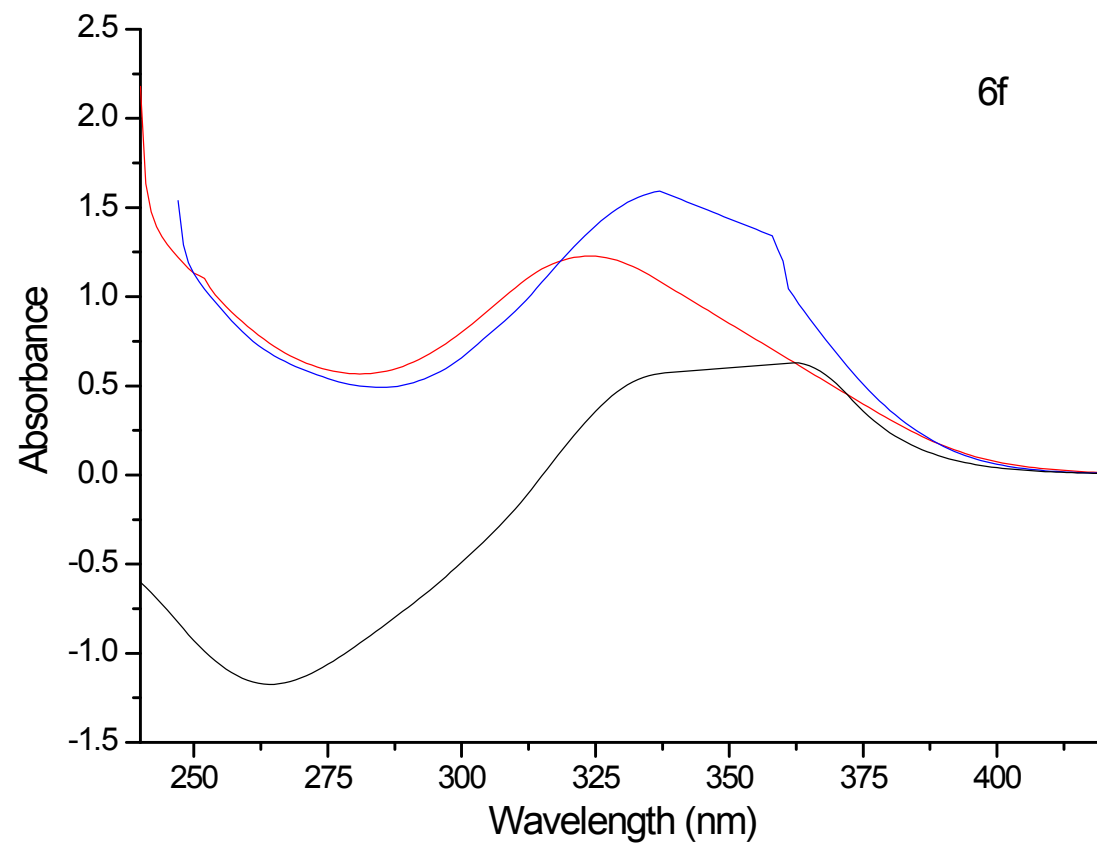


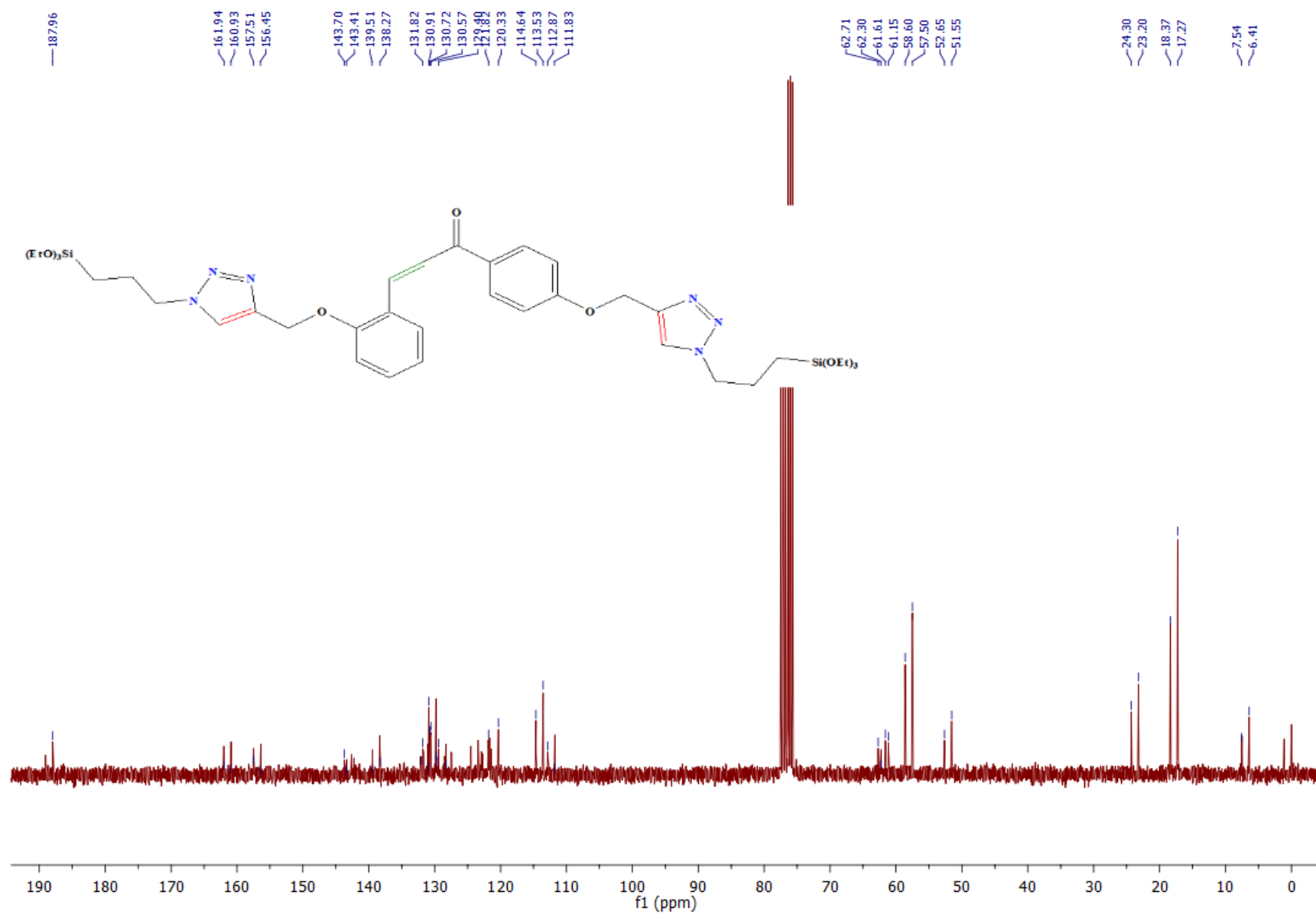


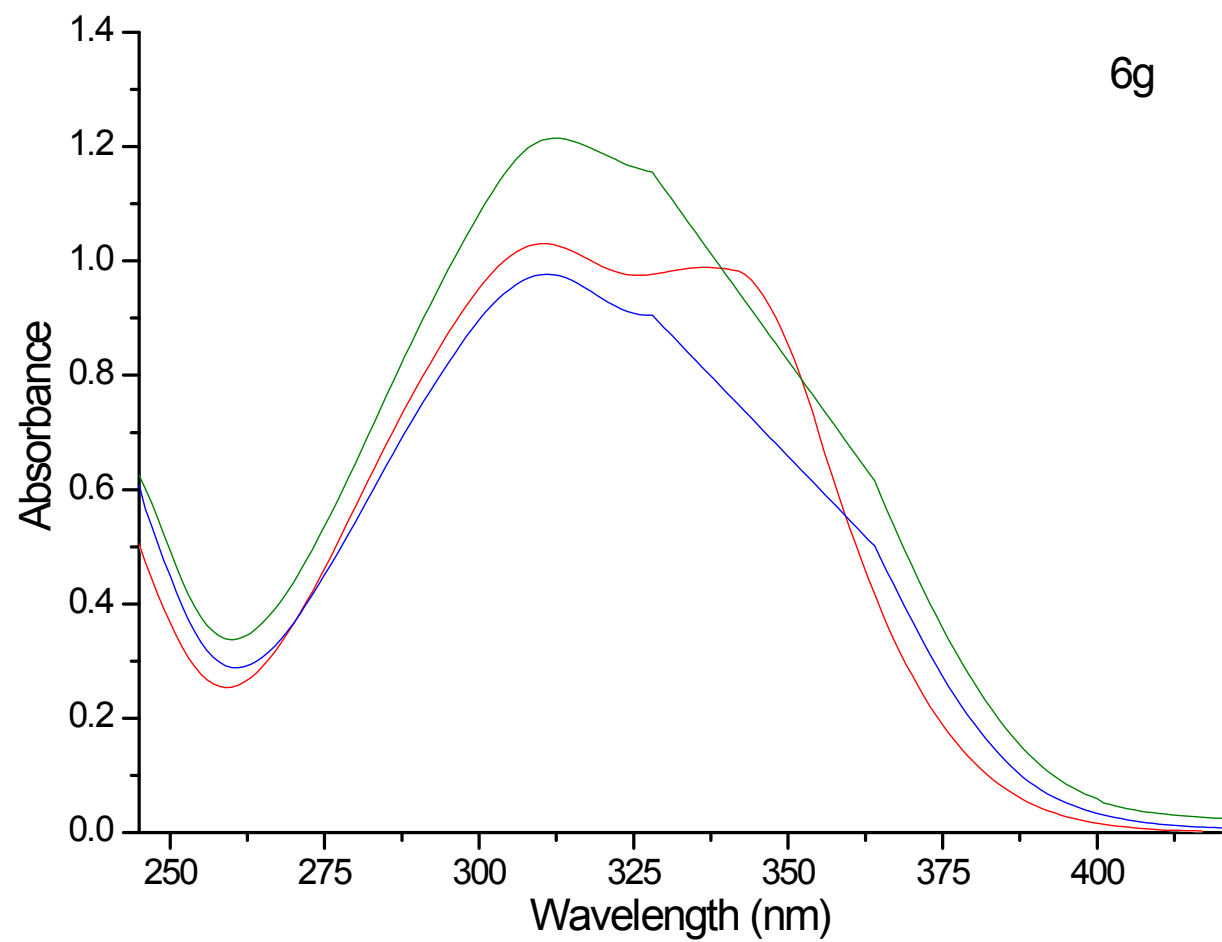
6f











6h

