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Electronic Supporting Information (ESI)

Copper-loaded Hypercrosslinked Polymer Decorated with Pendant Amine Groups: A Green and Retrievable Catalytic System for Quick [3+2] Huisgen Cycloaddition in Water

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1. Experimental Section

1.1. General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies and used without further purification. Products were characterized by physical data, IR, ^{1}HNMR, ^{13}CNMR and HRMS spectra. Melting points were determined on a Thermo Scientific 9200 apparatus. IR spectra were obtained on a Bomen MB:102 FT-IR spectrophotometer. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ or DMSO with tetramethylsilane as an internal standard. HRMS spectra were measured on an Agilent 5975 mass spectrometer and elemental analyses were performed on a Thermo Finnigan Flash EA 1112 CHNS-Analyzer. The polymer morphology was examined by AFM (Nano Wizard II) and FE-SEM (MIRA3 TESCAN)). The thermal stability of functionalized polymer was investigated by NETZSCH STA 409 PC/PG under a nitrogen atmosphere (rate of $N_2 \approx 1$ L h^{-1}). The catalyst copper content was determined by atomic absorption spectrophotometer (GBC Avanta instrument) and EDS (SAME, France) analysis.

Monitoring of the reactions and the purity determination of the products were accomplished by TLC on PolyGram SILG/UV 254 silica gel plates.

*1.2. Synthesis of calix[4]resorcinarene **1***

Calix[4]resorcinarene was prepared according to a previously reported procedure.

*1.3. Synthesis of the 3D-network polymer based on calix[4]resorcinarene **2***

The desired polymer was synthesized by adding 42 mmol of formaldehyde to 14 mmol of the prepared calix[4]resorcinarene dissolved in 40 mL NaOH solution (10%) at room temperature. The resultant mixture was heated to 90 °C and maintained at this temperature for 20 h. Next, the excess alkali was washed out of the gel formed with cold water. The gel was allowed to stand at 100 °C for 1 h. Then, the gel was transformed into the acidic form by treatment with the 0.1 M HCl solution. The resulting solid was dried at 100 °C for 10 h.

*1.4. Synthesis of novel amine-functionalized polymer **3***

The synthesized polymer **2** obtained from the above procedure (1.0 g), 3-(triethoxysilyl)propylamine (4.0 g, 18 mmol) were introduced into 50-mL round-bottomed flask containing 10 mL H_2O/EtOH at room temperature. The reaction mixture was heated to 90 °C and stirred at this temperature for 20 h. The desired amine-functionalized polymer **3** was collected by filtration and washed several times with hot toluene before being dried at 100 °C.

1.4.1. Determination of the amount of amine functionalities grafted onto the polymer

The amount of amine functionalities grafted onto the polymer was determined by elemental analysis to be 3.5 mmol per gram of dry polymer.

1.5. Preparation of copper(I) iodide salt

To a stirred solution of 10 g copper(II) iodide in 10 mL water was added slowly at room temperature a solution of 7.6 g of anhydrous sodium sulfite, Na_2SO_3, in 50 mL water. The copper(I) iodide solution first became very dark brown, and then white copper(I) iodide slowly separated. After all the sodium sulfite solution was added and the mixture stirred thoroughly, the copper(I) iodide settled readily and the supernatant liquid was faintly green. The precipitate and supernatant liquid were then poured into about a liter of water to which 1 g of sodium sulfite and 2 mL of concentrated hydrochloric acid were added, and the mixture was stirred well and allowed to stand until all the copper(I) iodide was settled. The supernatant liquid was carefully decanted and the precipitate was quickly washed onto a suction filter (sintered glass type preferred) with dilute sulfurous acid solution. Care should be taken that a layer of liquid covers the salt in the funnel at all times. The copper(I) iodide was then washed four or five times with 20 to 25 mL of glacial acetic acid. During this washing process the suction should be adjusted so that the washed liquid would be sucked through rather slowly. When only a thin film of liquid covered the solid, the next portion of glacial acetic acid was added. The walls of the funnel should be washed each time with the washing liquid. The washed copper(I) iodide with glacial acetic acid was then washed by three 30-mL of absolute alcohol and six 15-mL of anhydrous ether in exactly the same way. After the last portion of ether was removed fairly completely by applying suction for about 30 seconds, the white solid (with filter paper removed) was transferred quickly to a previously dried watch glass and placed in an oven (75 to 100 ºC) for 20 to 25 minutes. The sample should be preserved in an airtight bottle. The copper(I) iodide prepared by this method is a white crystalline powder that remains practically unchanged for an indefinite period if kept dry. If all the alcohol is not removed during the washing process, the copper(I) iodide may become slightly discolored on heating or standing. Some samples of anhydrous ether tend to impart a gray tint to the product.

*1.6. Preparation of novel polymer-supported copper(I) catalyst **4***

In a small Schlenk tube, amine-functionalized polymer **3** (1.0 g) was mixed with CuI (0.017 g, 0.1 mmol) in DMF (5 mL). The mixture was stirred for 4 h under a N_2 atmosphere at r.t. The solid was isolated by filtration and washed consecutively with acetone (5 mL) and MeOH (5 mL). Finally the resultant product was dried at r.t. for 16 h.

*1.6.1. Determination of the copper content of catalyst **4***

The catalyst copper content was measured using a GBC Avanta, Australia, atomic absorption spectrophotometer (AAS) to be 1.26 percent of the resulted catalyst **4**.

*1.7. General procedure for the one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles **7A-F***

Benzyl bromide (0.118 mL, 1 mmol) and sodium azide (0.065 g, 1 mmol) were charged into a 25 mL round-bottomed flask containing 3 mL water. Then, phenylacetylene (0.102 g, 1 mmol) and polymer-supported copper catalyst **4** (0.258 g, 0.05 mmol) were added to the reaction mixture. The mixture was heated and stirred under reflux condition till the reaction completion (TLC monitoring). After cooling to r.t., the reaction mixture was vacuum-filtered through a sintered glass funnel and washed with ethyl acetate (5 mL). The resulting solution was poured in a water/ethyl acetate mixture. After extraction of the aqueous phase with ethyl acetate, the combined organic phase was dried over magnesium sulfate and filtered. The resultant solution was concentrated and pure crystalline product was isolated through filtration.

*1.8. Recycling of the polymer-supported copper catalyst **4***

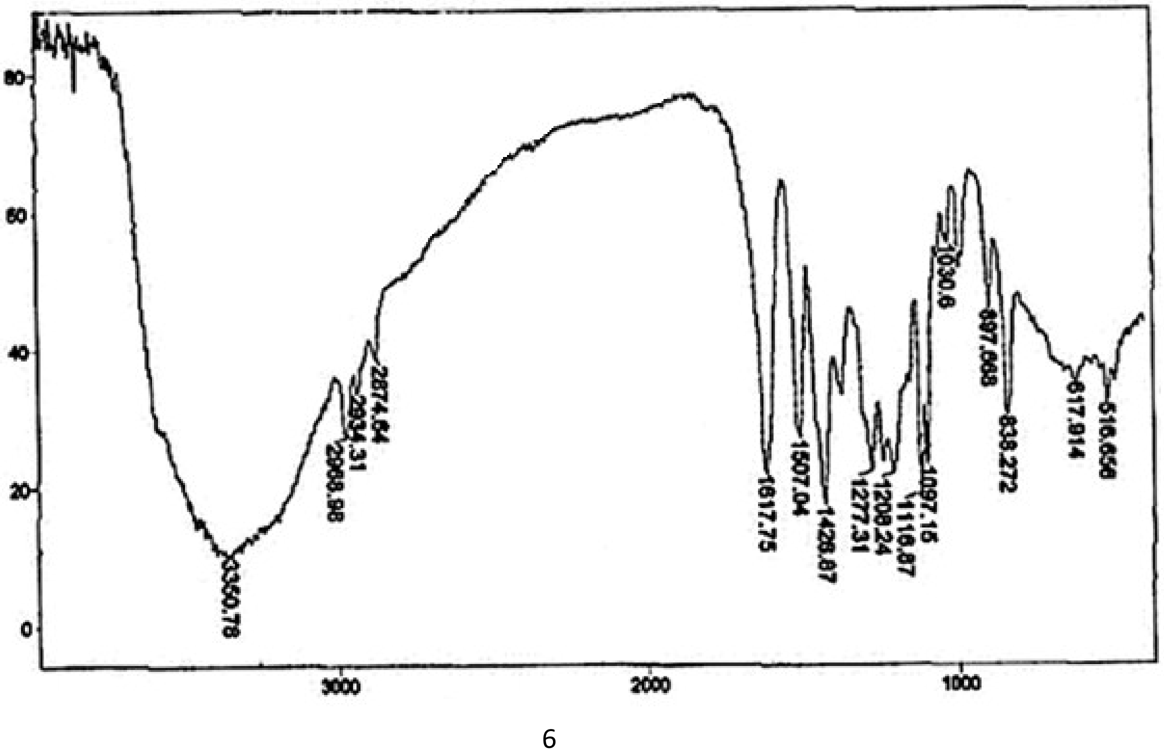
After the reaction had been carried out, the mixture was vacuum-filtered onto a sintered-glass funnel. The residue was consecutively washed with CH_2Cl_2 (5 mL), Et_2O (5 mL), EtOH (5 mL), and n-hexane (5 mL). The solid catalyst dried under vacuum after each cycle, and then reused for the next reaction.

2. Characterization of calix[4]resorcinarene (1)

2,8,14,20-tetraalkylpentacyclo-[19.3.1.1.1.1]octacosa-1(25),3,5,7,(28),9,11,13 (27),15,17,19(26),21,23-dodecane-4,6,10,12,16,18,22,24-octol (***c*-methylcalix[4]resorcinarene**, $C_{32}H_{32}O_8$)

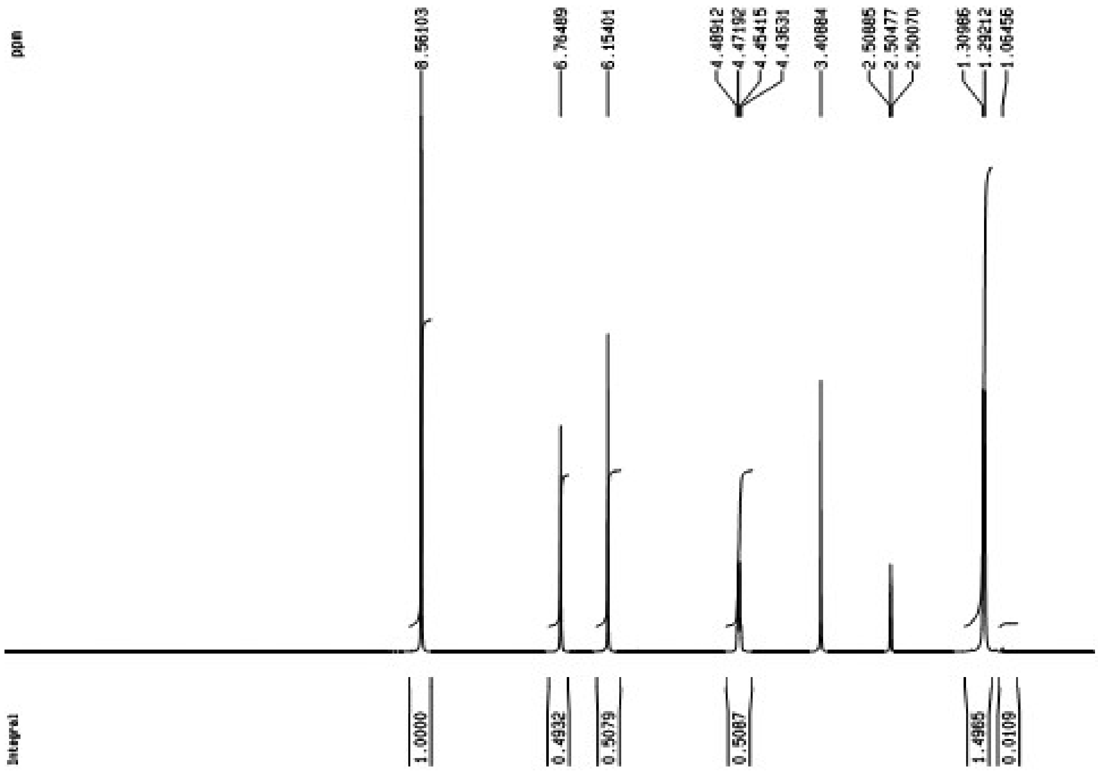
Yield 60%; white powder, m.p.: > 360˚C; IR (KBr): ν = 3000-3500 (OH) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ =1.29-1.30 (d, 12H, CH_3),4.43-4.49 (q, 4H, H-5), 6.15 (s, 4H, H-1), 6.76 (s, 4H, H-4), 8.56 (s, 8H, OH) ppm;^{13}CNMR (100MHz, DMSO-d_6): δ = 22.0 (CH_3), 29.0 (C-5), 102.5 (C-3), 123.5 (C-1), 125.7 (C-2), 152.3 (C-4) ppm.

2.1. IR Spectra

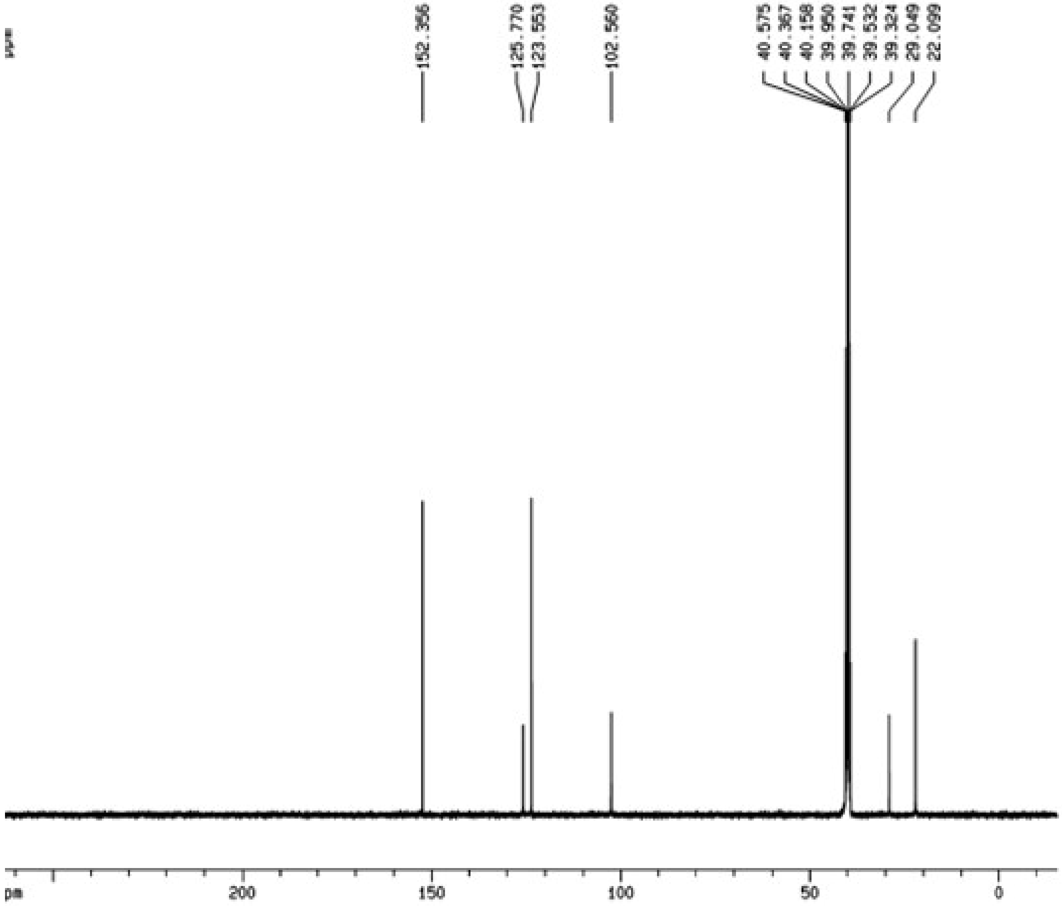


2.2.

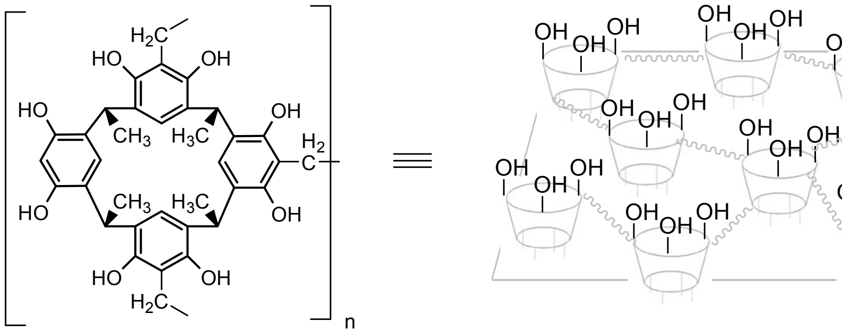
^{1}HNMR Spectra



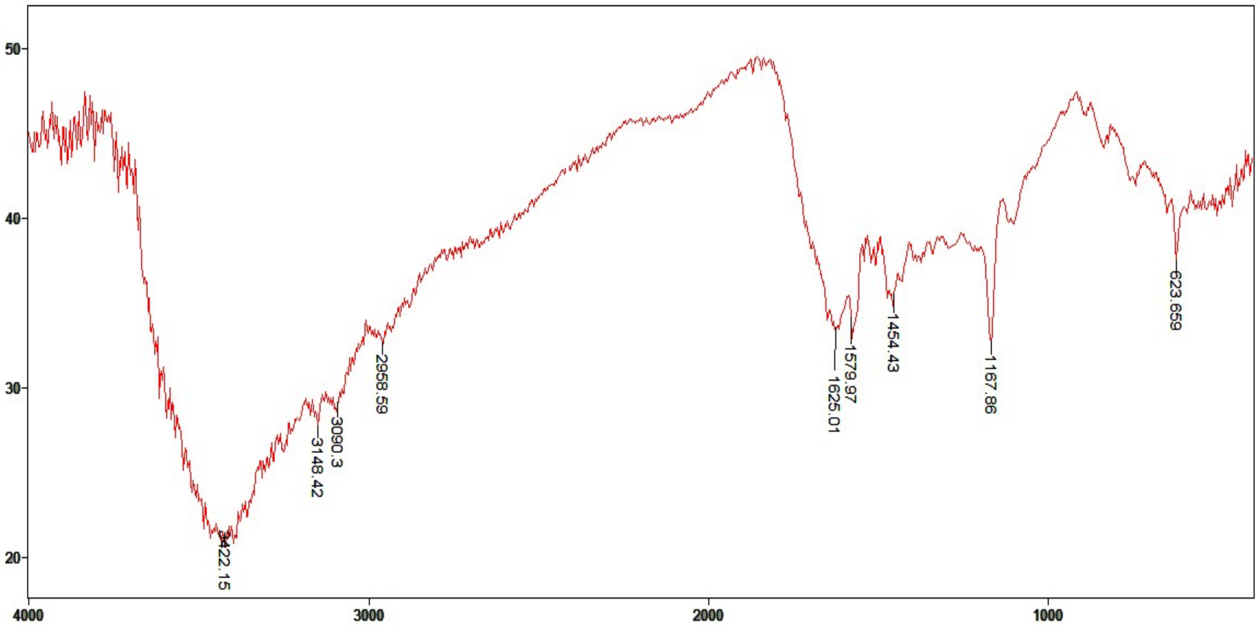
2.3. ^{13}CNMR Spectra



3. Characterization of 3D-network polymer (2)

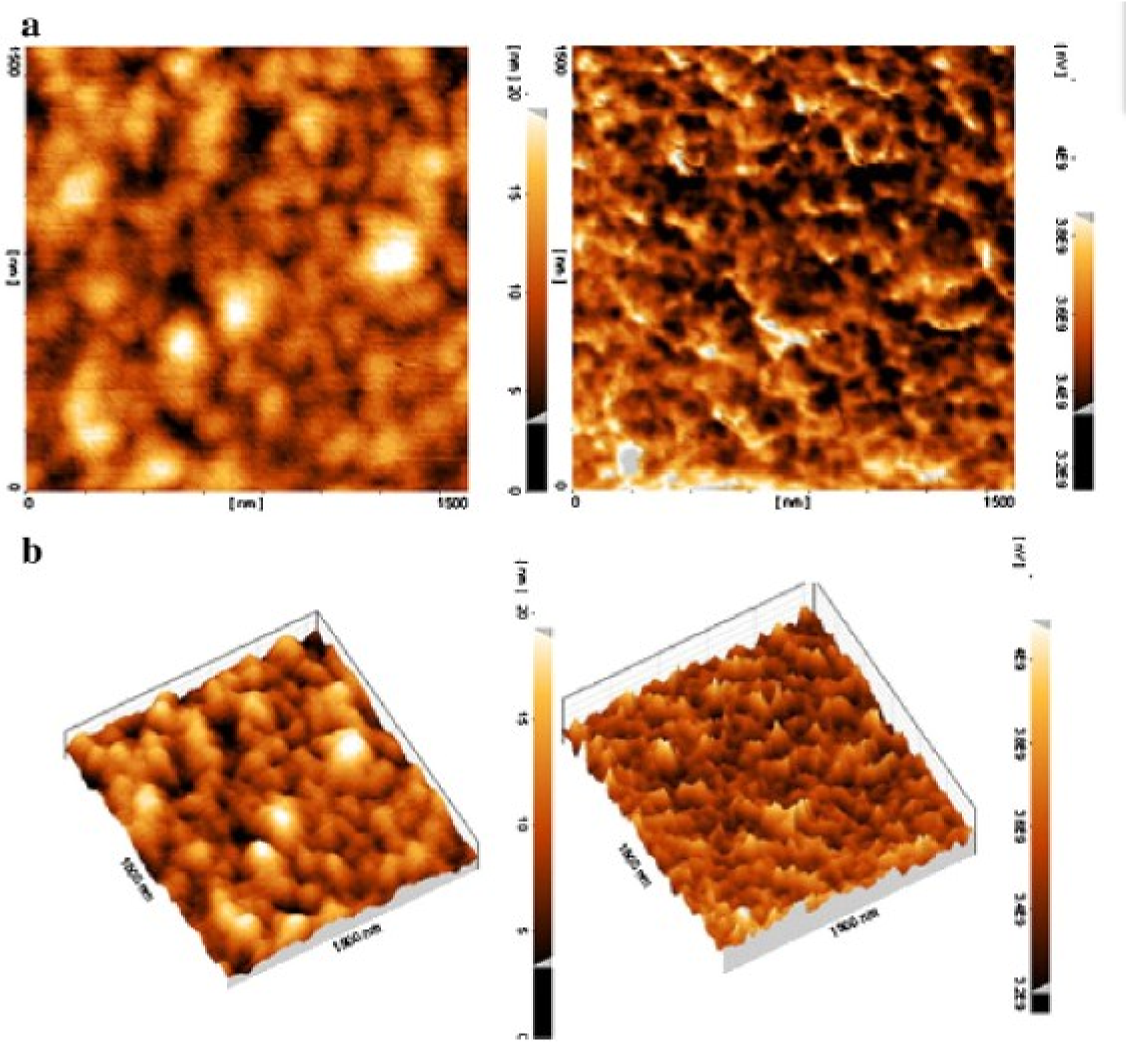


3.1. IR Spectra

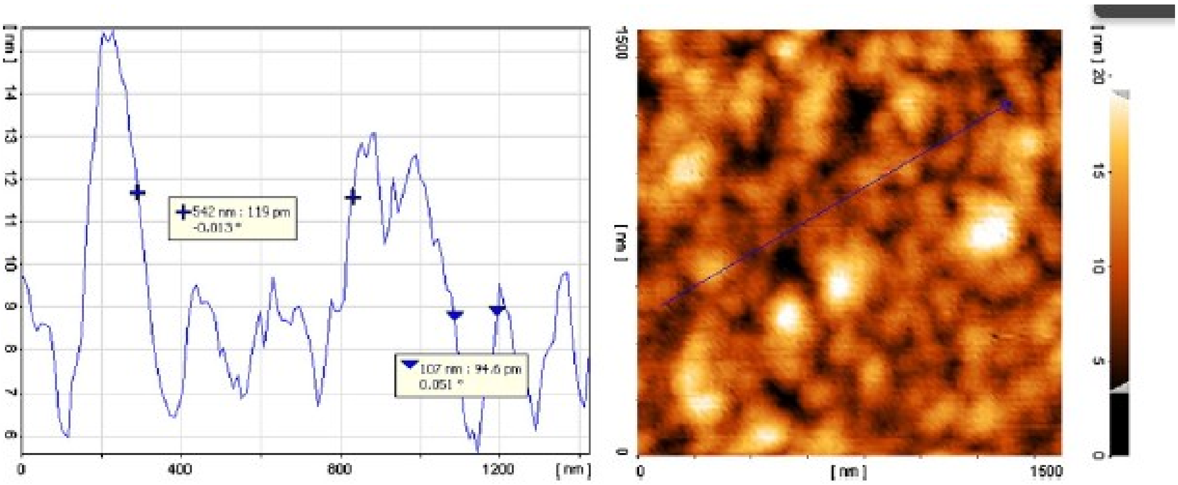


IR Spectra of 3D-network polymer **2**

3.2. AFM images



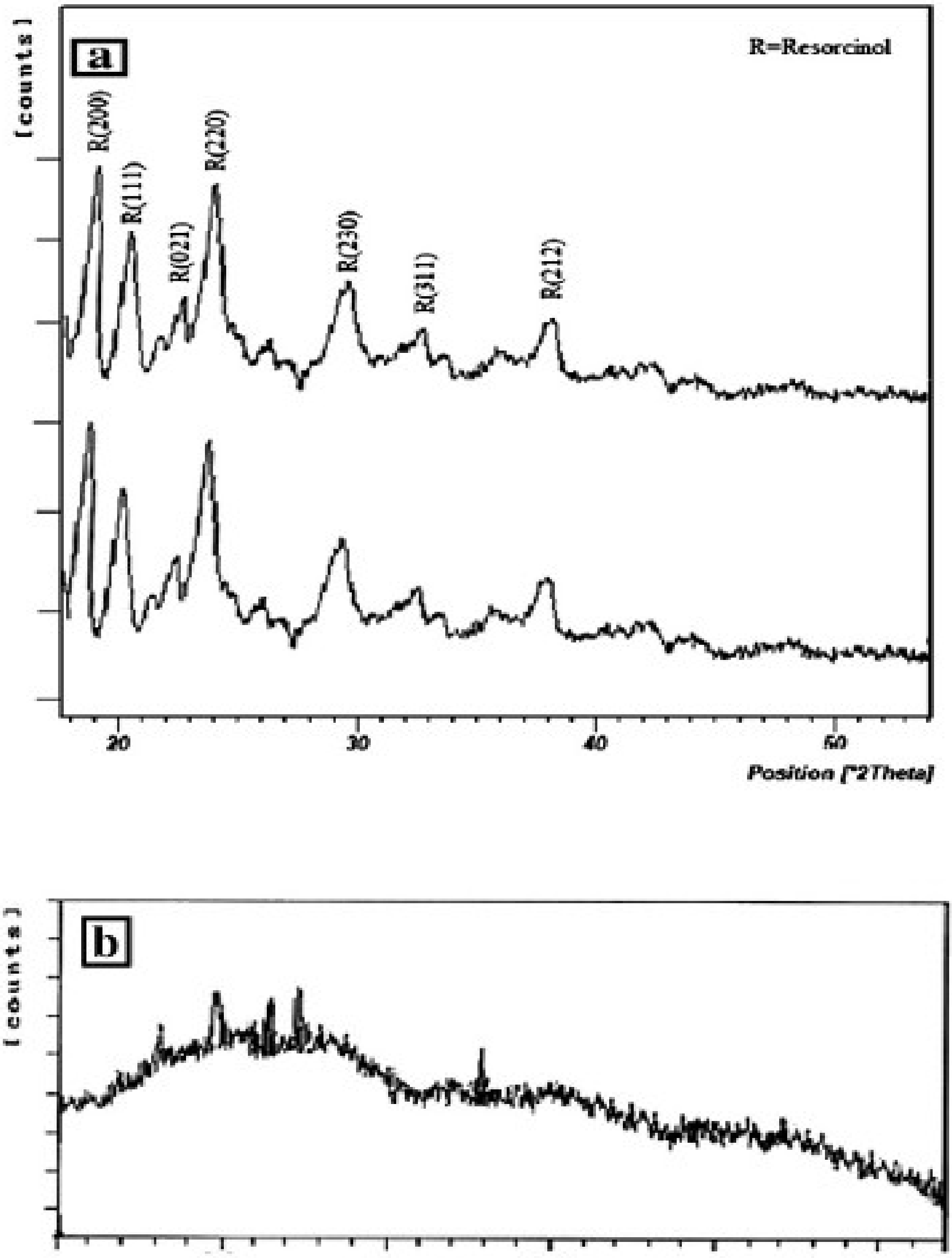
(a) AFM images (1 μ× 1 μ) of network polymer and (b) AFM surface plot of network polymer.



Section analyses of network polymer.

3.3. X-ray diffraction

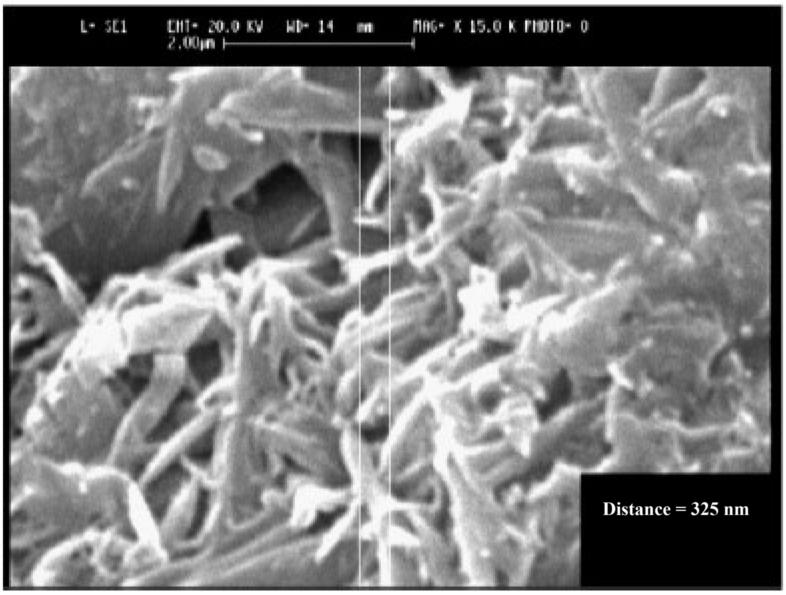
The XRD patterns of the prepared network polymer and calix[4]resorcinarene are depicted. It seems that to the intense and sharp diffraction peaks of calix[4]resorcinarene, it exhibited a high degree of crystallinity and this may be attributed to the hydrogen bonding between the resorcinarene units (a). As it can be seen in this figure, most of the peaks in the XRD patterns of the methylcalix[4]resorcinarene samples can be completely indexed with resorcinol in the standard card (JCPDS No. 00-038-1969). It can be observed that when the calix[4]resorcinarene is incorporated into a polymer system crystalline peaks are still exhibited but the intensity of the peaks decreases and a broad spectrum appears. In other words, the amorphous nature of the polymer increases and almost the fine disrupts crystals of the calix[4]resorcinarene were existed (b). Some distinct peaks were observed for the network polymer which indicated that the network polymer molecules have the semi crystalline nature but broad spectrum shows that its composition consists predominantly of an amorphous phase.



XRD pattern a) calix[4]resorcinarene (**1**) and b) polymer (**2**)

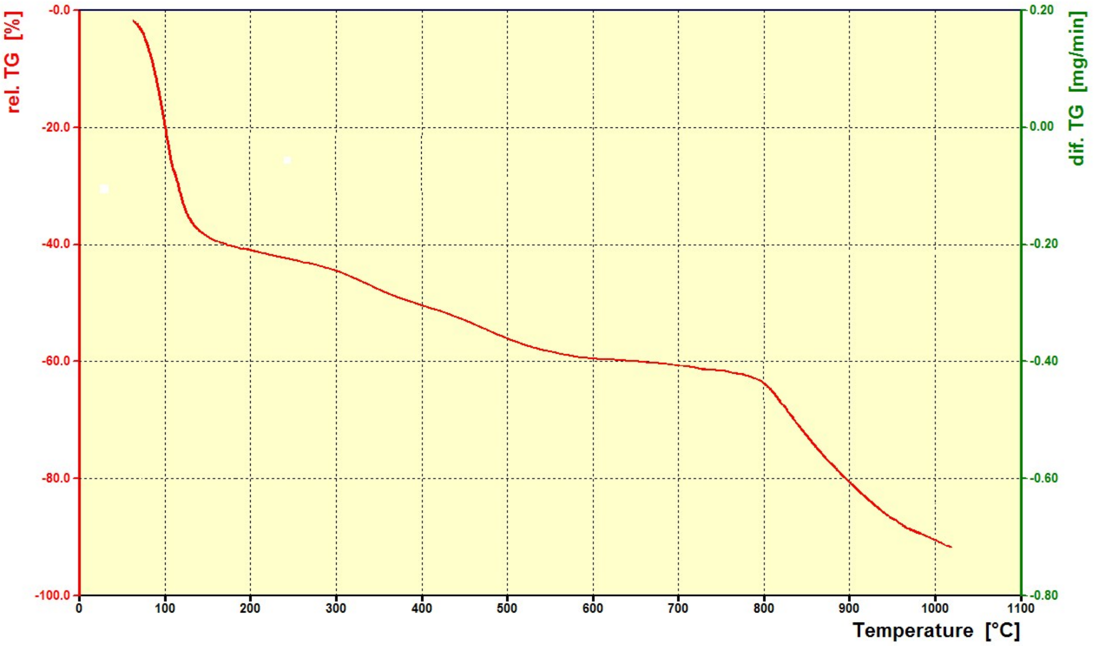
3.4. SEM image

In this image, one can observe that more porous structure with meshwork was obtained for network polymer. SEM confirmed that the average size of pores network polymer is in agreement with the AFM data.



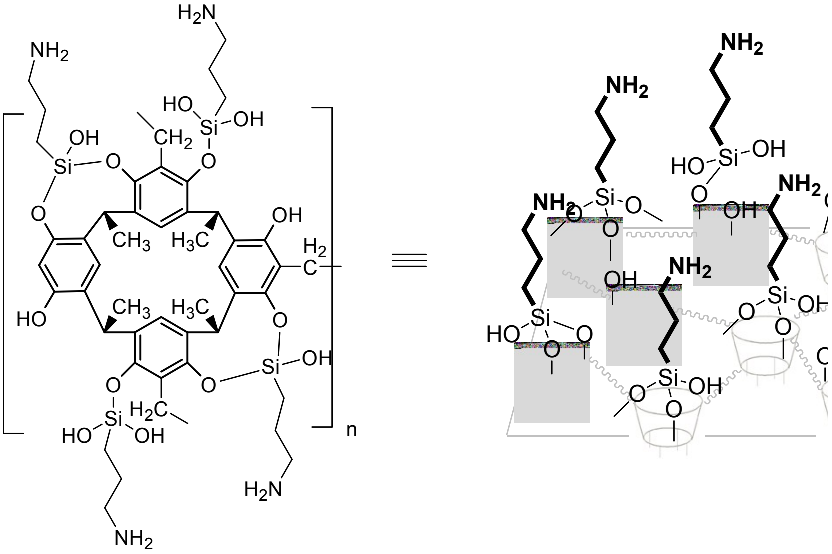
SEM image of 3D-network polymer **2**

3.5. TGA curve



TGA curve of 3D-network polymer **3**

4. Characterization of novel amine functionalized 3D-network polymer (3)



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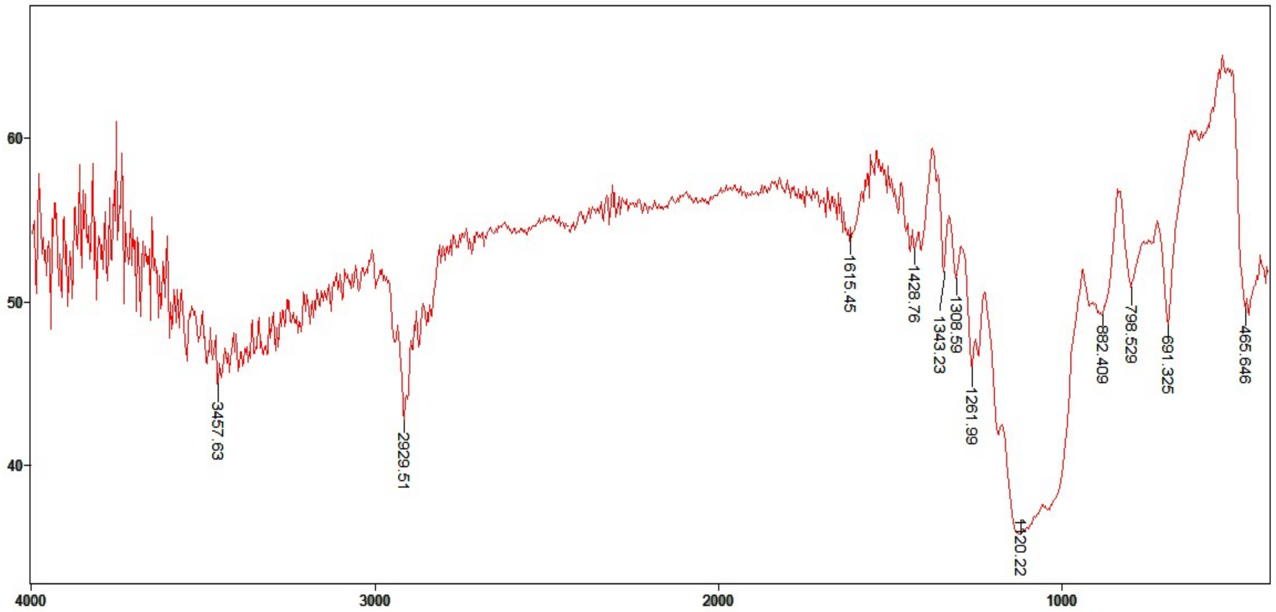
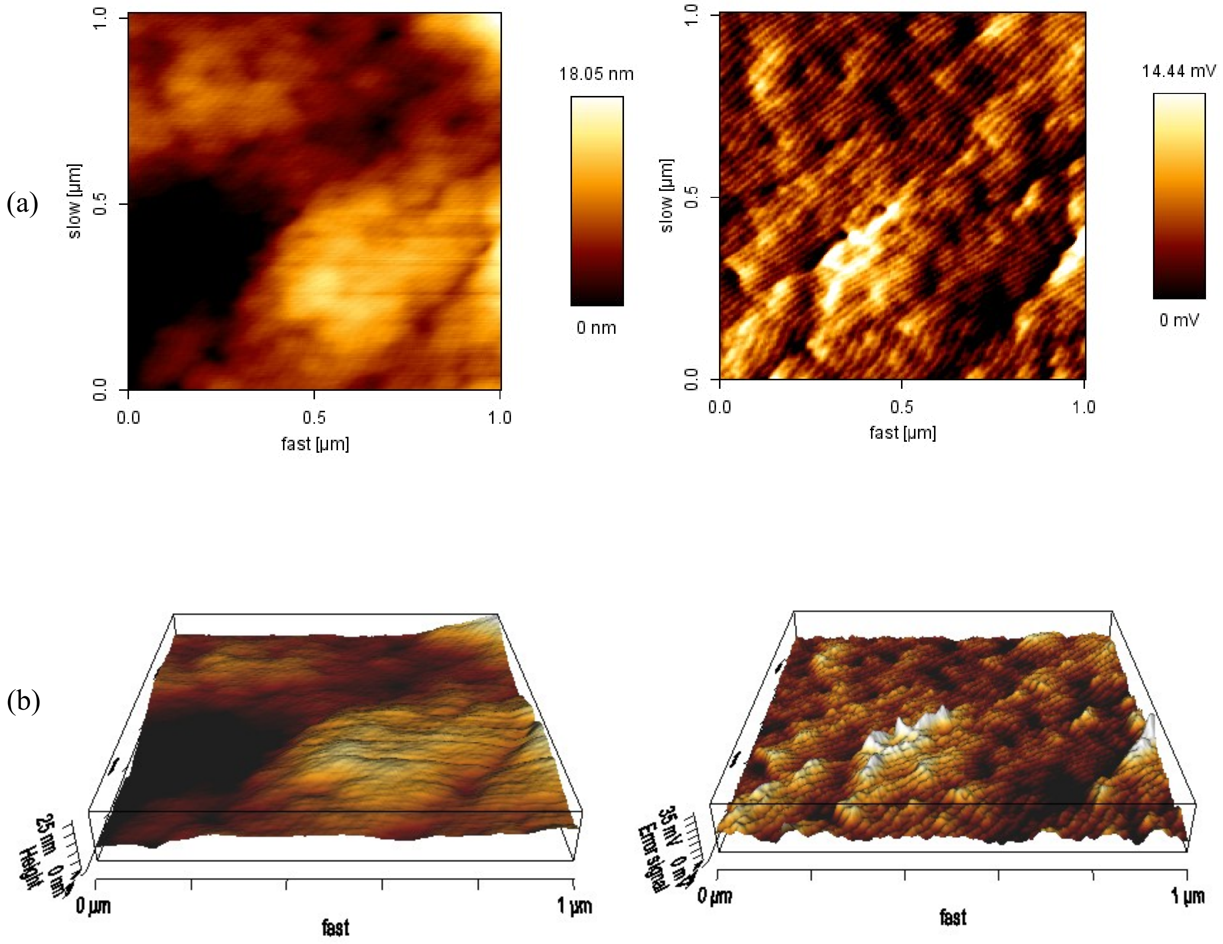


IR Spectra of amine functionalized polymer **3**

4.2. AFM images



AFM images (1.0 µm × 1.0 µm) of amine functionalized polymer **3**, (a) 2D and (b) 3D height and phase plots

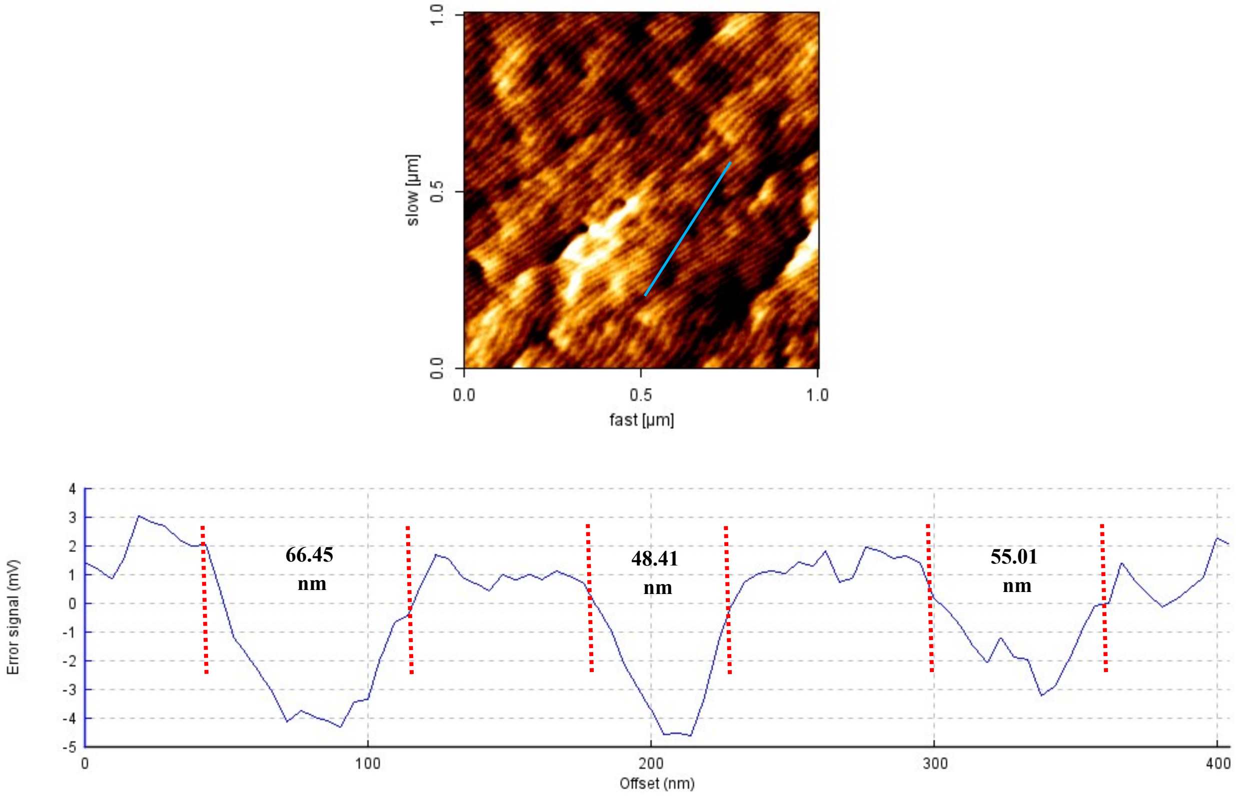
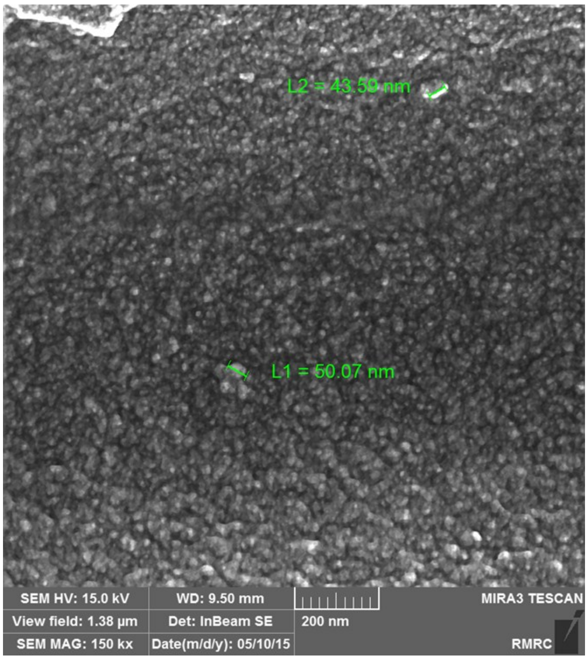


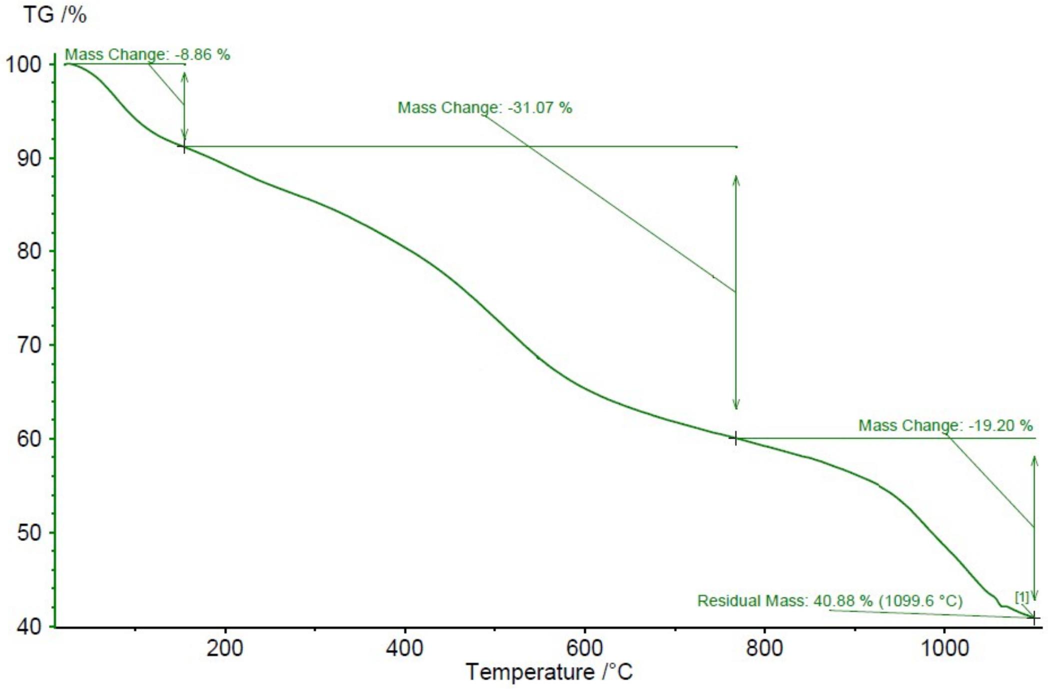
Image profile (the analysis of the height along a linear path) of amine functionalized polymer **3**

4.3. SEM image



SEM image of amine functionalized polymer **3**

4.4. TGA curve

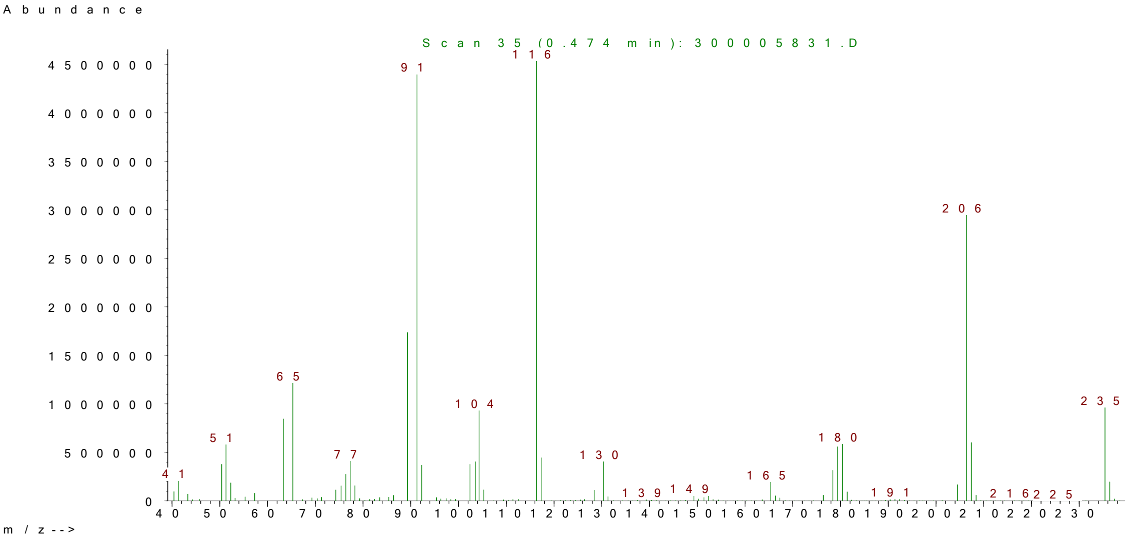


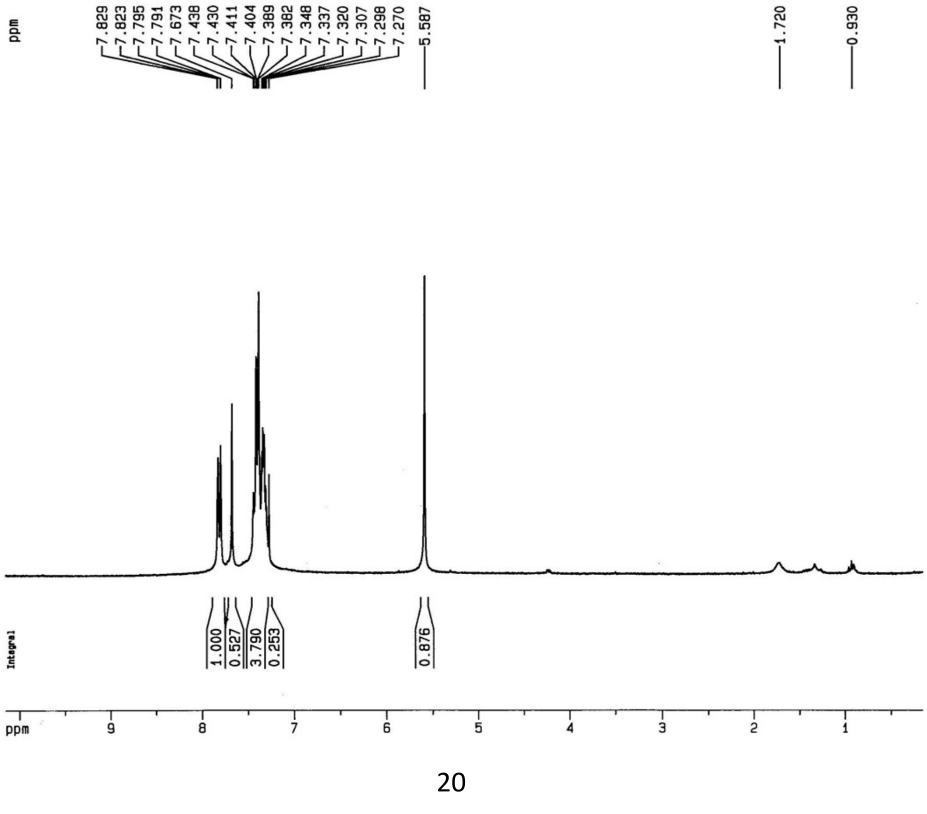
TGA profile of amine functionalized polymer **3**

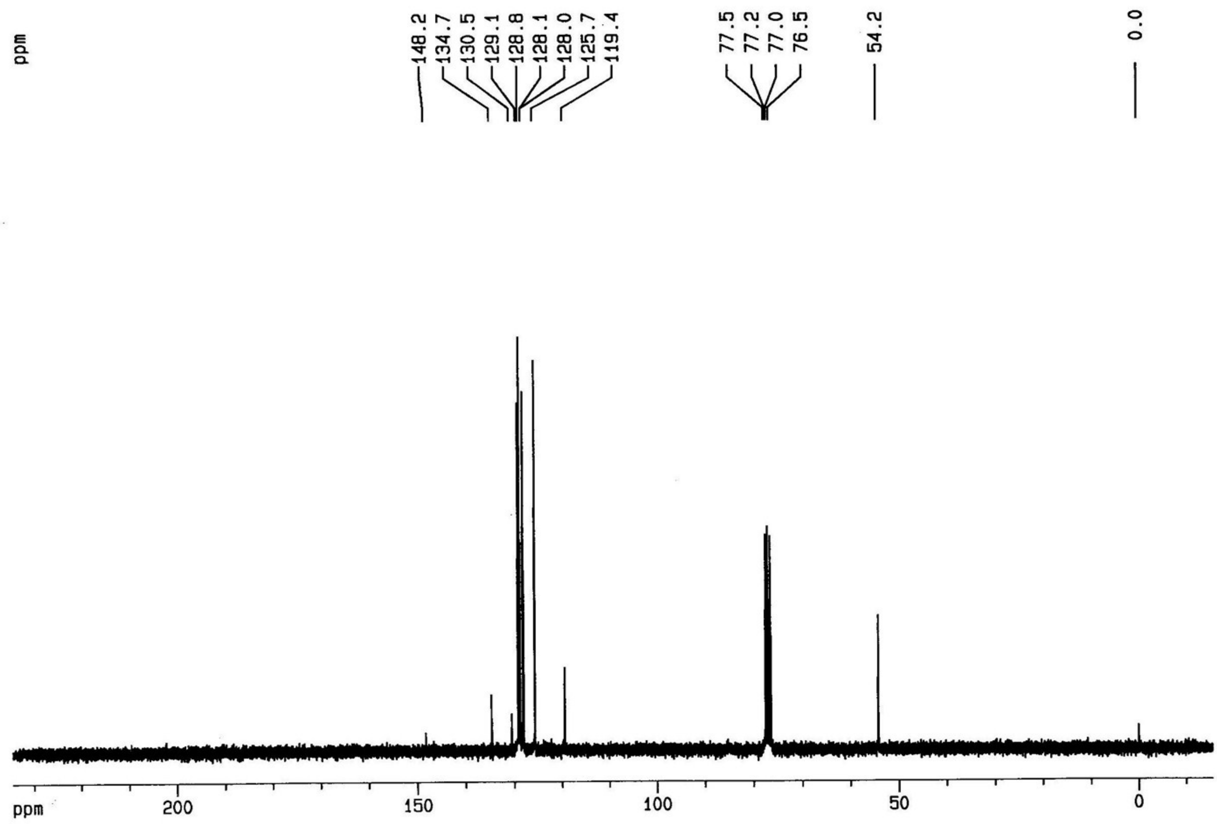
5. Characterization of synthesized 1,2,3-triazole derivatives (7)

1-benzyl-4-phenyl-1H-1,2,3-triazole (7A)

Yield 97%; white crystals, m.p.: 126-128 ˚C; MS m/z: 235 [M$^+$]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.58 (s, 2H, C-6-H_2), 7.29-7.823 (m, 10H, Ar-H), 7.829 (s, 1H, C-1-H) ppm; ^{13}CNMR (100MHz, $CDCl_3$): δ = 54.2 (C-6), 119.4 (C-1), 125.7, 128.0, 128.1, 128.8, 129.1 (ArC), 130.5, 134.7 (ArC$_q$), 148.2 (C-2) ppm.



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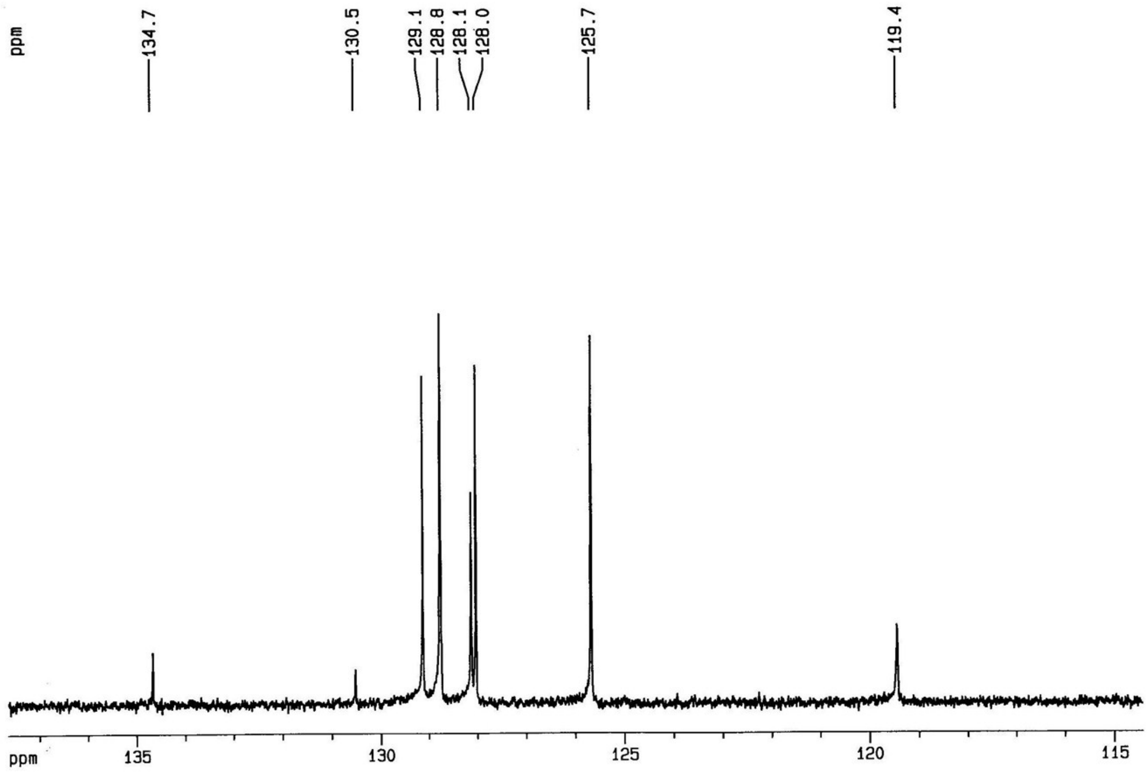
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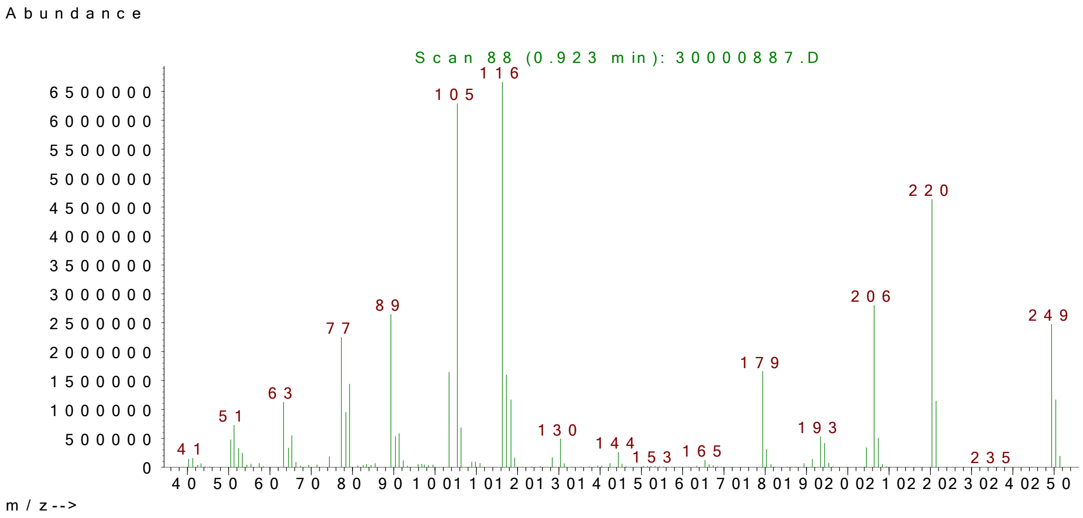
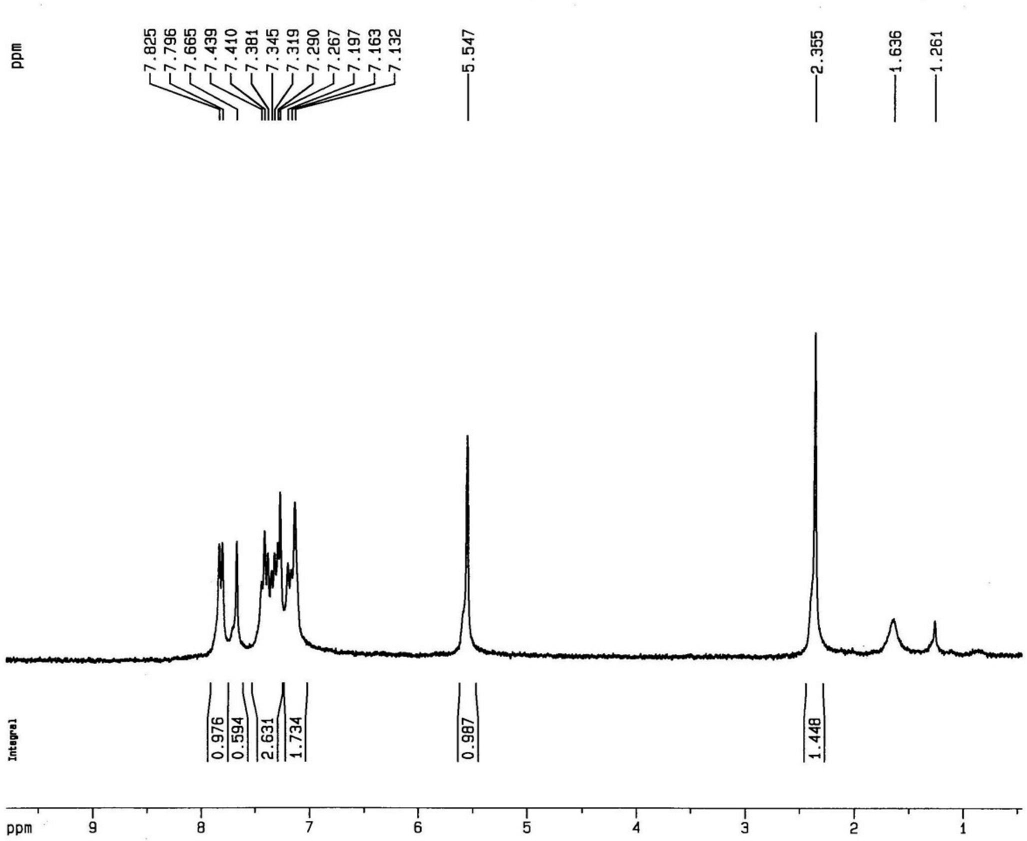
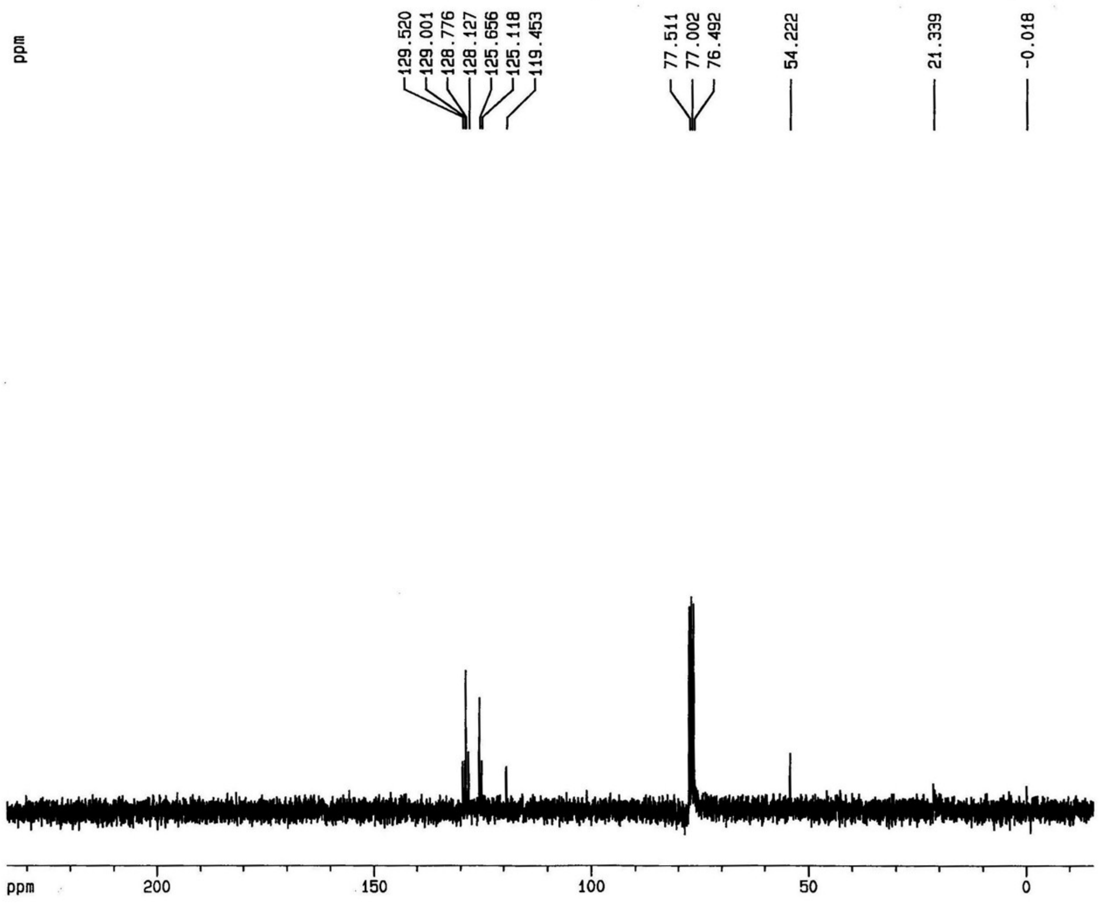
*1-(3-methylbenzyl)-4-phenyl-1H-1,2,3-triazole (7**D**)*

Yield 88%; white crystals, m.p.: 95-97 ˚C; MS m/z: 249 [M$^+$]; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.35 (s, 3H, CH$_3$), 5.54 (s, 2H, C-6-H$_2$), 7.13-7.79 (m, 9H, Ar-H), 7.82 (s, 1H, C-1-H) ppm; ^{13}CNMR (100MHz, CDCl$_3$): δ = 21.3 (CH$_3$), 54.2 (C-6), 119.4 (C-1), 125.1 (ArC$_q$), 125.6 (ArC), 128.1 (ArC$_q$), 128.7 (ArC), 129.0 (C-2), 129.5 (ArC$_q$) ppm.



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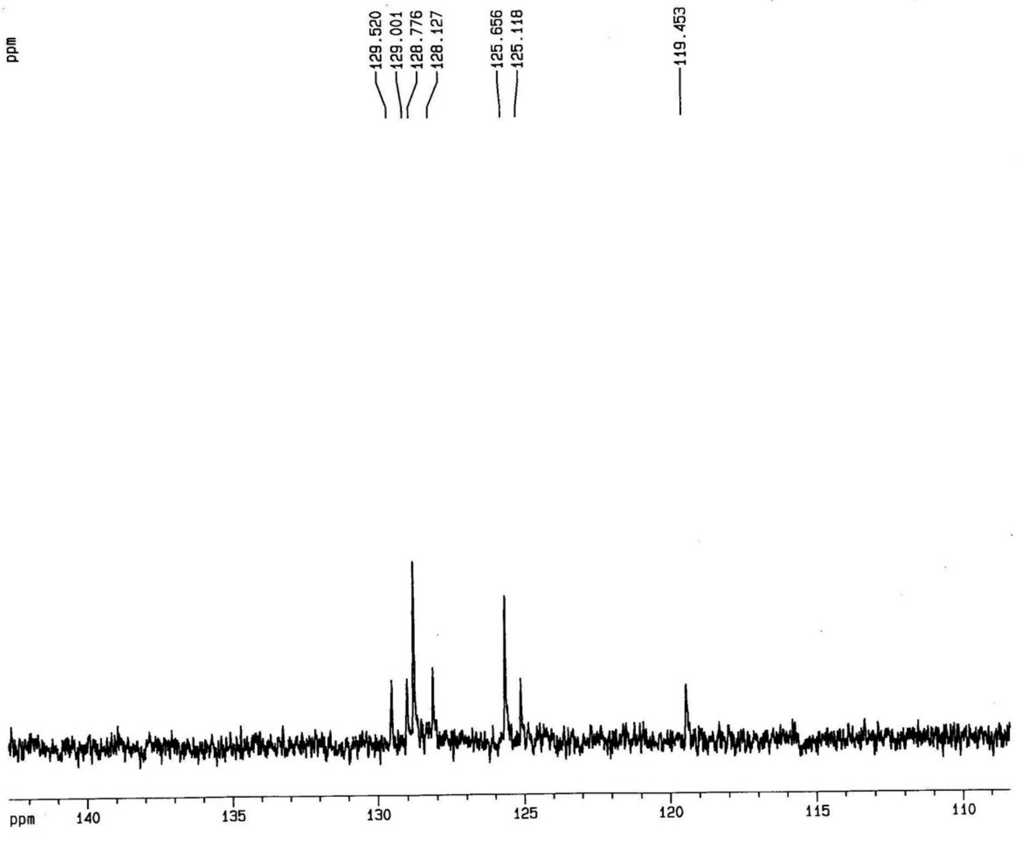
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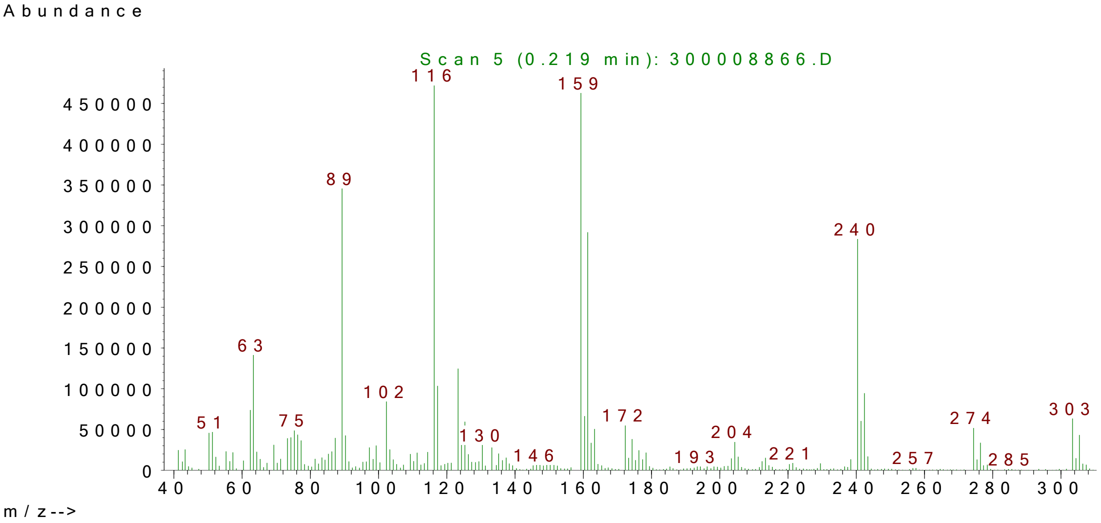
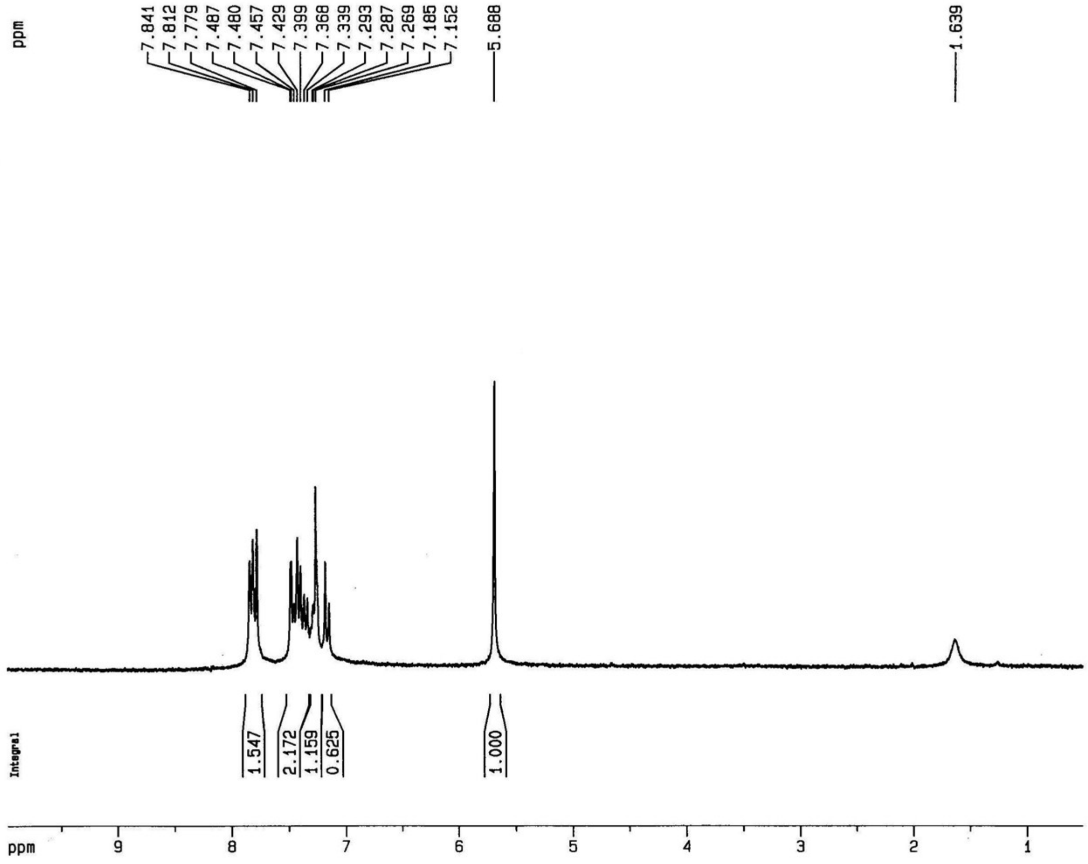
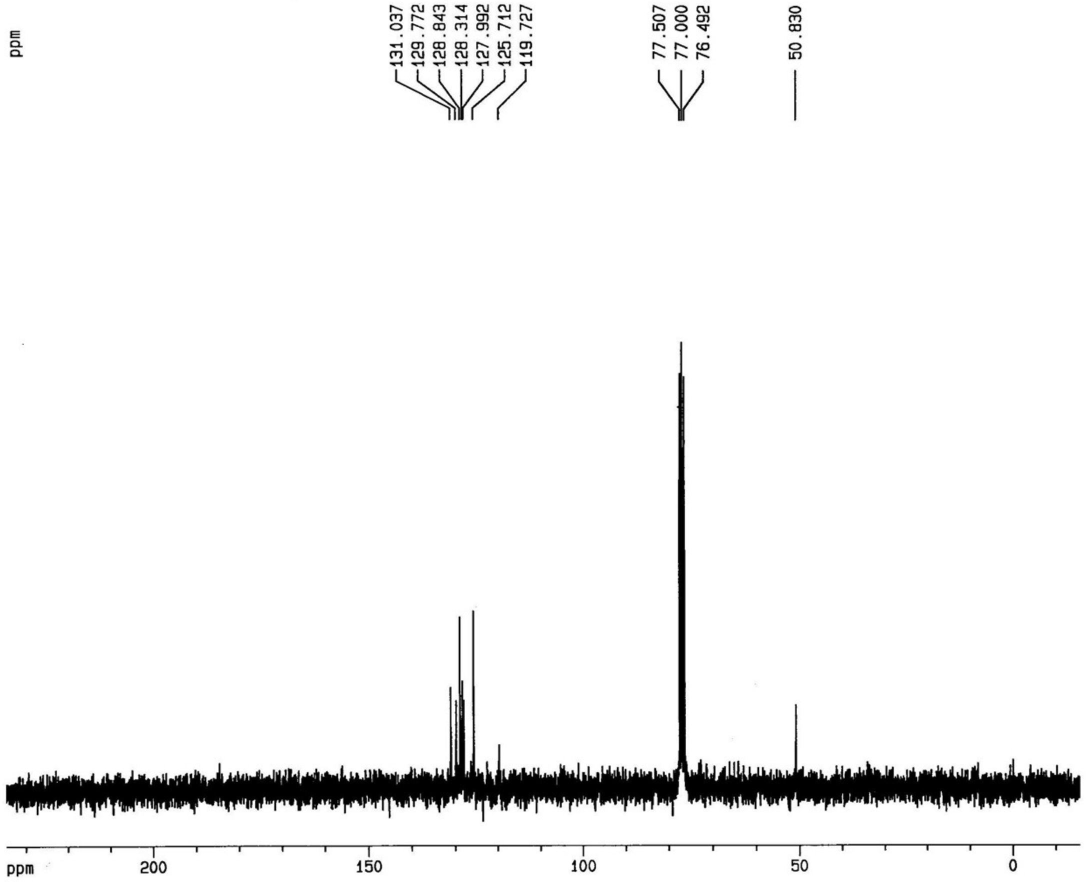
*1-(2,4-dichlorobenzyl)-4-phenyl-1H-1,2,3-triazole (7**E**)*

Yield 80%; white crystals, m.p.: 116-117 ˚C; MS m/z: 303 [M$^+$]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68 (s, 2H, C-6-H_2), 7.15-7.81 (m, 8H, Ar-H), 7.84 (s, 1H, C-1-H) ppm; ^{13}CNMR (100MHz, $CDCl_3$): δ = 50.8 (C-6), 119.7 (C-1), 125.7 (ArC), 127.9, 128.3, 128.8, 129.7 (ArC$_q$), 131.0 (C-2) ppm.



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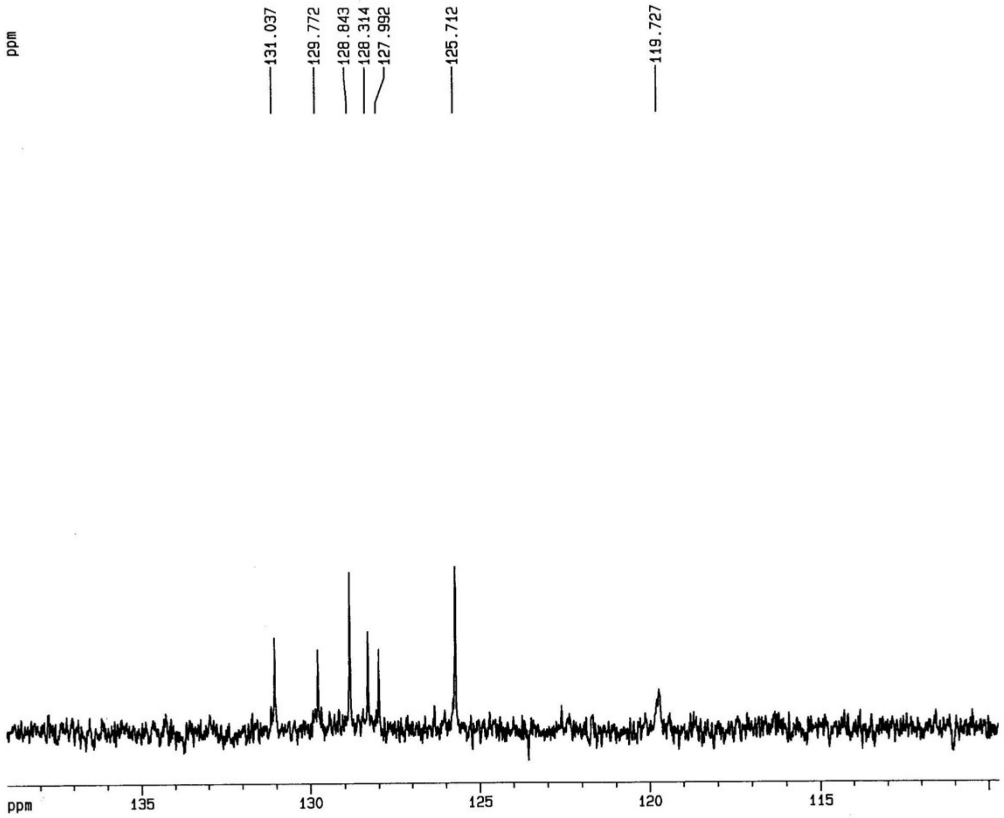
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