Electronic Supplementary Information

Au–Cu Core–Shell Nanocube-Catalyzed Click Reactions for Efficient Synthesis of Diverse Triazoles

Mahesh Madasu, Chi-Fu Hsia, and Michael H. Huang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

Experimental Section

Au–Cu core–shell nanocubes with an average edge length of 78 nm and Au–Cu octahedra with an average opposite corner distance of 45 nm were synthesized following our reported procedure.[12] Octahedral Au nanocrystal cores with an opposite corner distance of 35 nm were synthesized as described previously.[13] To perform the click reaction, alkyne (0.25 mmol, 1.0 equiv), benzyl azide (0.3 mmol, 1.2 equiv) and 2 mL of deionized water were added to a glass tube. Then 3 mg of Au@Cu nanocubes or 1 mg of Au@Cu octahedra as catalyst was introduced into the mixture. The reaction mixture was stirred at 50 ^{o}C for 3 h. After completion of the click reaction, ethyl acetate solution was added and sonicated for 1 min. Then the reaction mixture was centrifuged at 8500 rpm for 5 min. After centrifugation, the organic solvent layer was carefully collected. Next, anhydrous Na_2SO_4 was added to the organic solution, and the organic layer was filtered. Using a rotavapor, the solvent was evaporated to obtain the corresponding 1,3-dipolar cycloaddition triazole product. The product was washed with diethyl ether for purification. ^{1}H-NMR spectra were taken using $CDCl_3$ solvent to confirm the product regioselectivity and yields. ^{1}H-NMR spectra show pure compounds were formed in all the alkyne cases, so there is no need to do any column chromatography for compound separation. A JEOL JSM-7000F scanning electron microscope was used to take SEM images of the nanocrystals. TEM characterization was performed on a JEOL JEM-2100 microscope with an operating voltage of 200 kV. XRD patterns were recorded on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation. FT-IR spectra were recorded on a Bruker Vertex 80V Tensor 27 spectrometer. ^{1}H-NMR (600 MHz) and ^{13}C-NMR (150 MHz) spectra were recorded with a Bruker DMX spectrometer.

Turnover Frequency Calculations

Since surface copper atoms are considered to be the active catalytic sites, we define TOF as moles of products formed / (moles of total surface copper atoms × reaction time). The surface copper atom area density for a particular lattice plane is calculated by determining the number of surface copper atoms within a chosen area. The lattice parameter for copper is taken as 3.615 Å. For (100) plane, the surface copper atom density is $\{(4 \times 1/4) + 1\} / a^2 = 0.1530 Å^{-2}$ or 15.3 nm^{-2}. For (111)

plane, the surface copper atom density is $[\{(3 \times 1/6) + (3 \times 1/2)\} / (\sqrt{3}/2 \times a^2)] = 0.176$ Å^{-2} or 17.6 nm^{-2}

Edge lengths of cubic Au core and Au@Cu core–shell cube are 35 and 75 nm, respectively.
Surface area of a single Au@Cu nanocube = $6 \times a^2 = 6 \times (75 \times 10^{-7}\text{cm})^2 = 3.375 \times 10^{-10}$ cm^2
Volume of a single Au@Cu nanocube = $a^3 = (75 \times 10^{-7}$ cm$)^3 = 4.218 \times 10^{-16}$ cm^3
Edge length of the octahedral Au core ~ (opposite corner distance) / 1.4 = 25 nm
Volume of the octahedral Au core = $(1/3)\sqrt{2}\, a^3 = 7.366 \times 10^{-18}$ cm^3
Volume of the cubic Cu shell = $(4.218 \times 10^{-16}$ cm$^3 - 7.366 \times 10^{-18}$ cm$^3) = 4.144 \times 10^{-16}$ cm^3
Weight of a single Au@Cu cube = $(\rho_{Au} \times V_{Au} + \rho_{Cu} \times V_{Cu}) = (19.6 \times 7.366 \times 10^{-18} + 8.96 \times 4.144 \times 10^{-16}) = 3.86 \times 10^{-15}$ g
Weight of total Au@Cu cubes = 0.003 g
Number of Au@Cu nanocubes = $0.003 / 3.86 \times 10^{-15} = 7.77 \times 10^{11}$
Total surface area of Au@Cu nanocubes = $7.77 \times 10^{11} \times 3.375 \times 10^{-10}$ cm^2 = 262.2 cm^2 = 2.62×10^{16} nm^2
Assume Au@Cu octahedra have the same total surface area of 2.62×10^{16} nm^2
Total surface Cu atoms in Au@Cu cubes = $(2.62 \times 10^{16}$ nm$^2 \times 15.3$ nm$^{-2}) / (6.023 \times 10^{23}) = 6.66 \times 10^{-7}$ mol
Total surface Cu atoms in Au@Cu octahedra = $(2.62 \times 10^{16}$ nm$^2 \times 17.6$ nm$^{-2}) / (6.023 \times 10^{23}) = 7.66 \times 10^{-7}$ mol

For the reaction shown in Table 1, 0.0255 g (0.25 mmol) of phenyl acetylene was used for each case. The phenylacetylene molecular weight is 102.13 g/mol and that of triazole product is 235.28 g/mol.
For Au@Cu cubes, isolated triazole product weight is 0.053 g or 2.25×10^{-4} mol.
For Au@Cu octahedra, isolated triazole product weight is 0.027 g or 1.15×10^{-4} mol.
TOF of nanocubes = 2.25×10^{-4} mol / $(6.66 \times 10^{-7}$ mol $\times$ 3 h) = 112.6 h^{-1}
TOF of octahedra = 1.15×10^{-4} mol / $(7.66 \times 10^{-7}$ mol $\times$ 3 h) = 50.0 h^{-1}

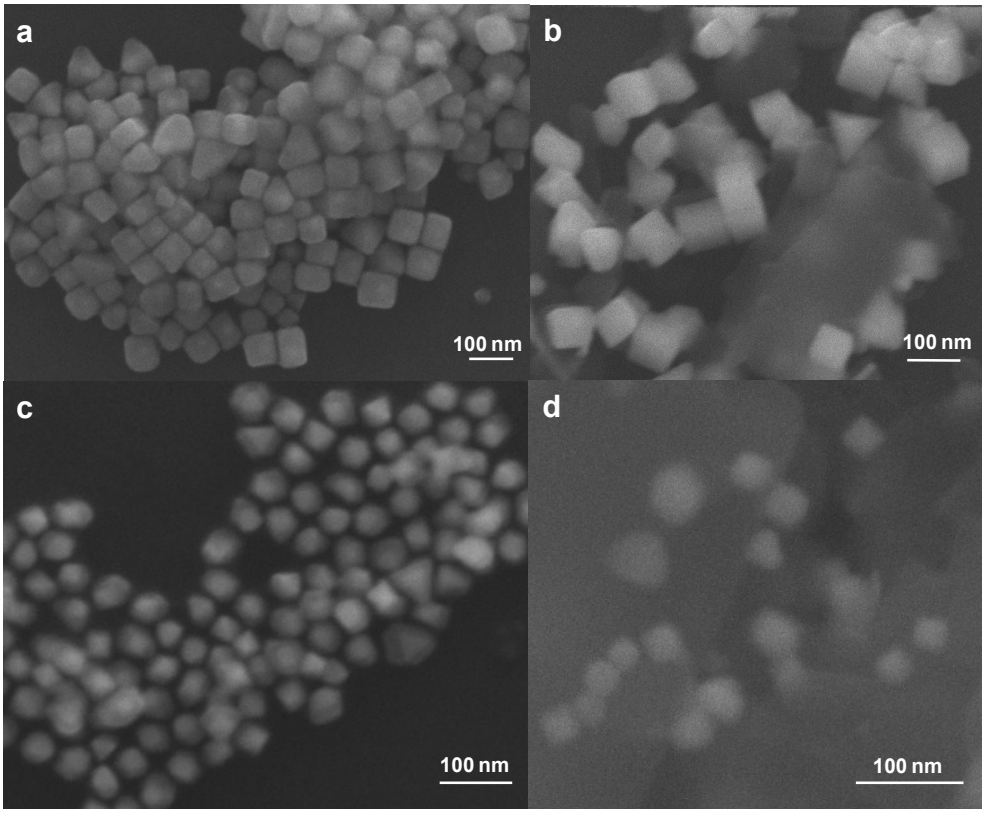

Fig. S1 SEM images of Au–Cu (a, b) nanocubes and (c, d) octahedra (a, c) before and (b, d) after the catalytic reaction. The organic product partially covers the nanocrystals.

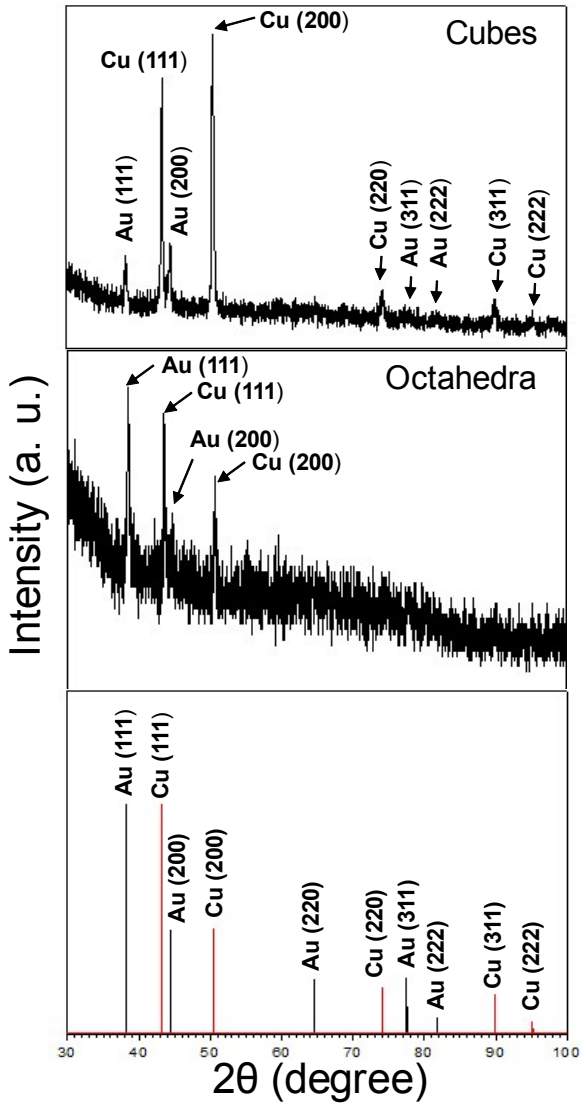

Fig. S2 XRD patterns of Au–Cu (a) nanocubes and (b) octahedra. Standard XRD patterns of Au and Cu are provided. Au–Cu nanocubes have exceptionally strong Cu (200) peak. The Au (111) and Cu (111) peaks in Au–Cu octahedra have similar intensities because of the thin Cu shell.

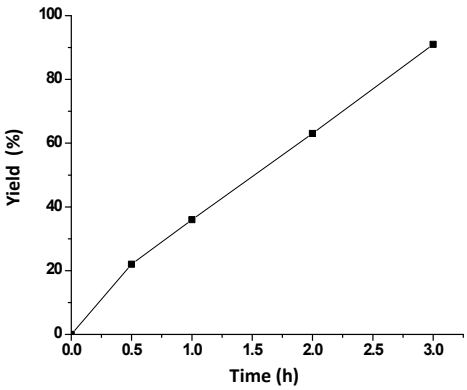

Figure S3. Plot showing percent yields of 1-benzyl-4-phenyl-1H-1,2,3-triazole (Table 1 reaction) as a function of reaction time.

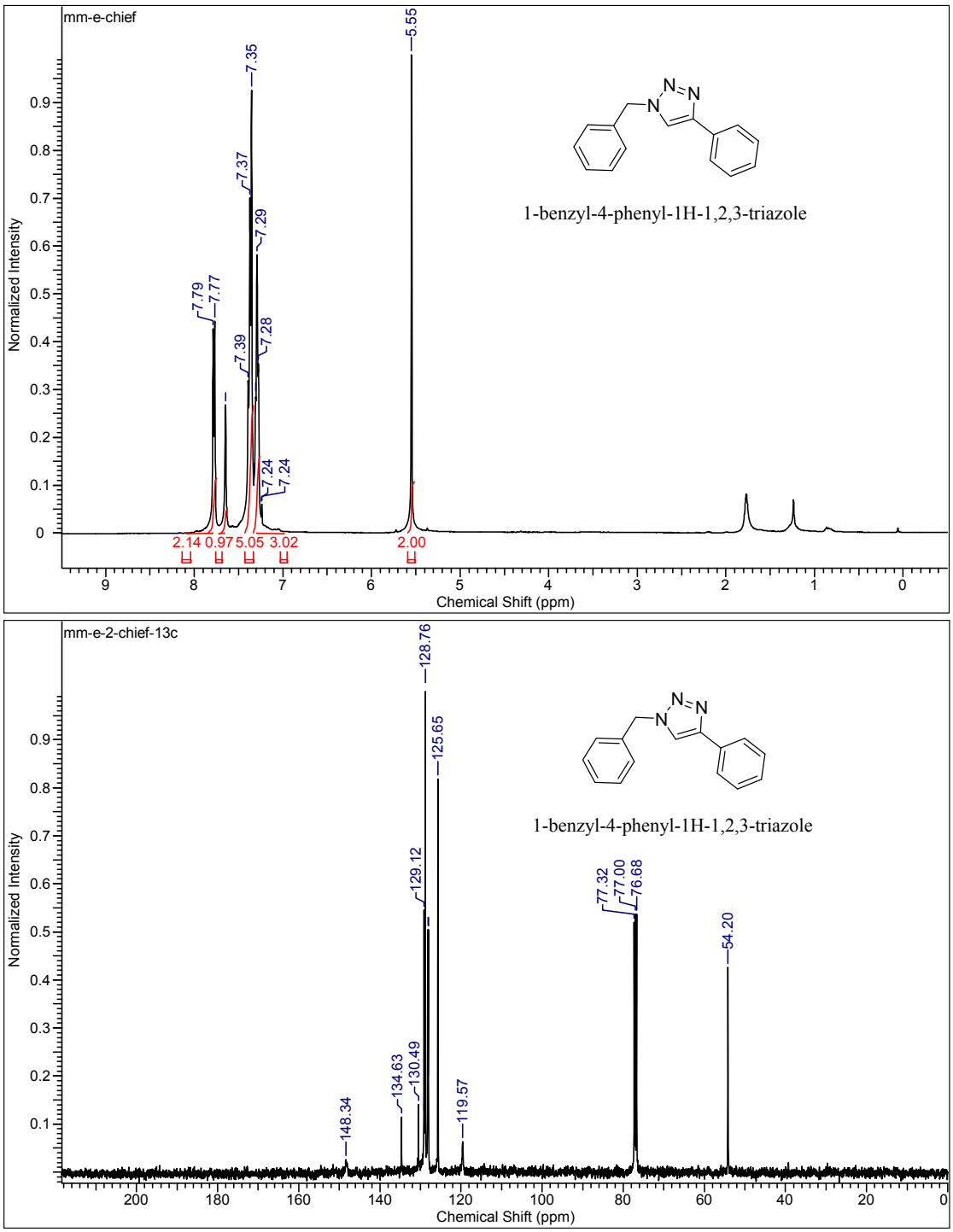

Fig. S4 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-phenyl-1H-1,2,3-triazole.

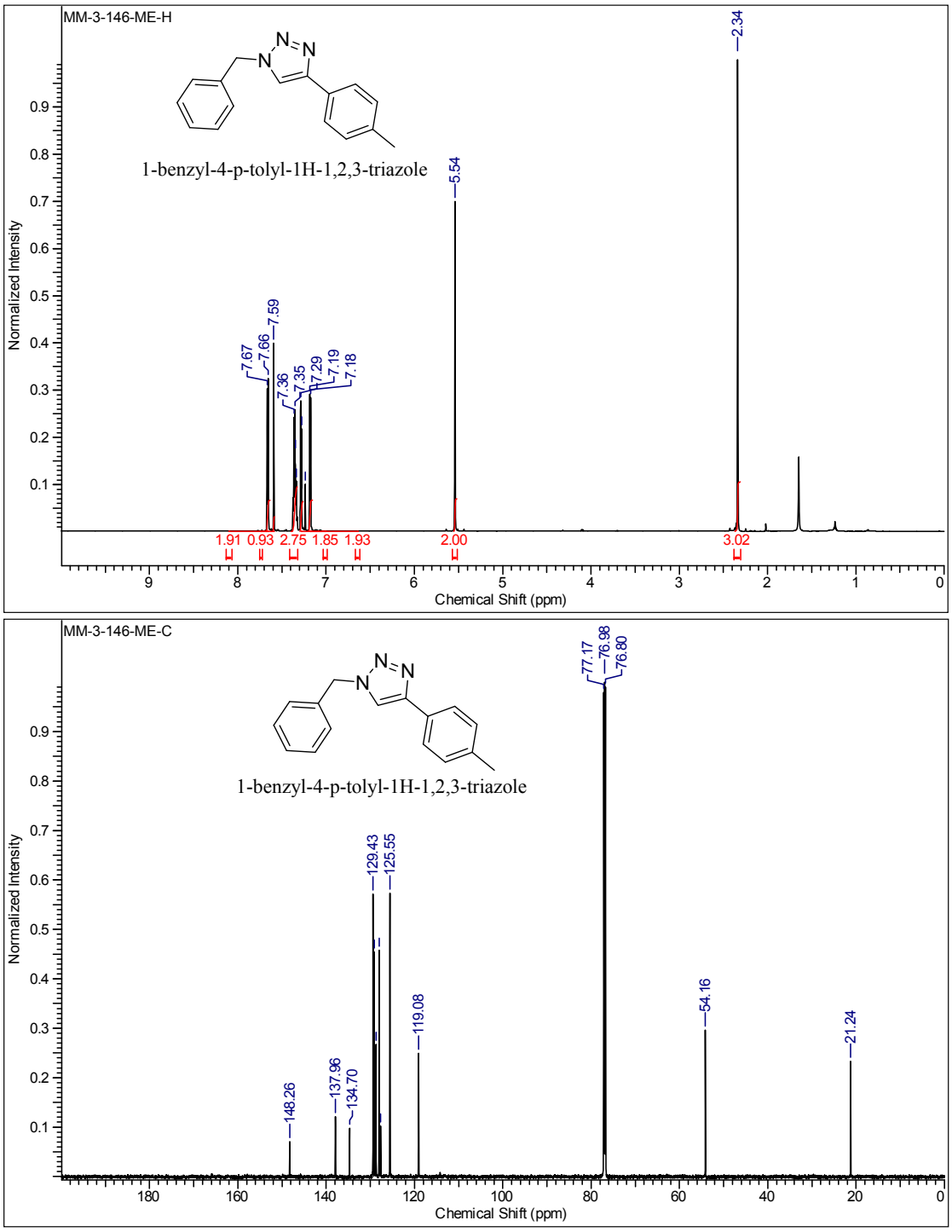

Fig. S5 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-p-tolyl-1H-1,2,3-triazole.

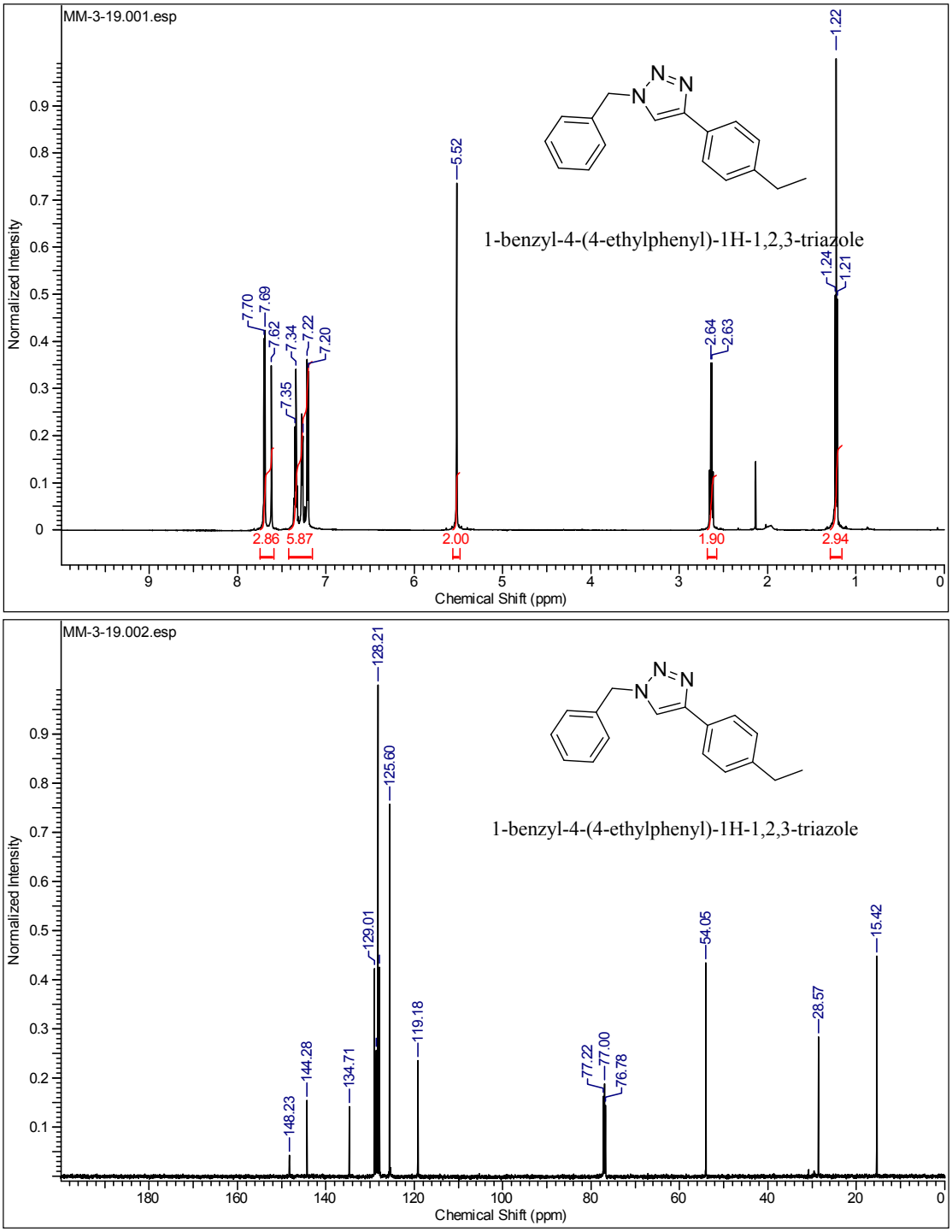

Fig. S6 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(4-ethylphenyl)-1H-1,2,3-triazole.

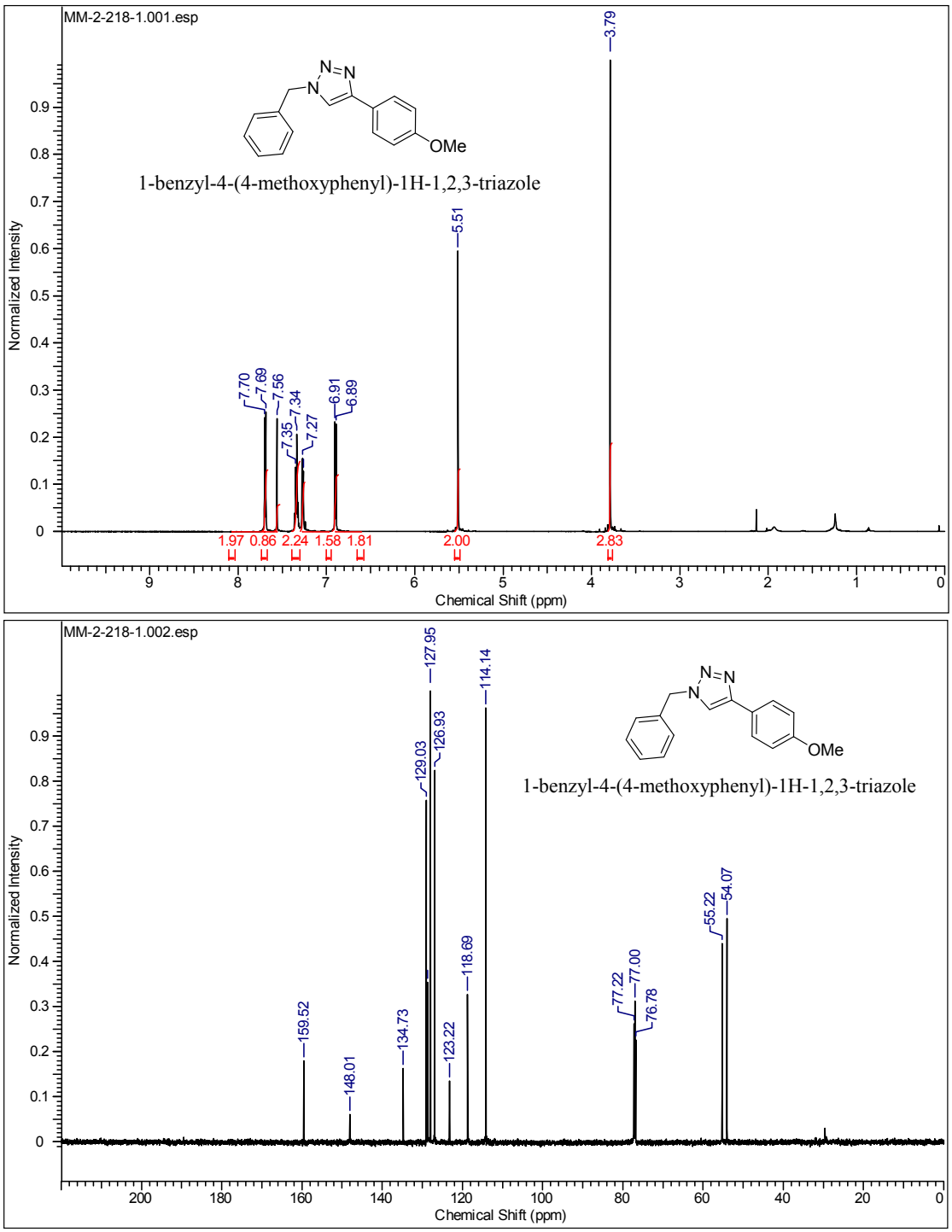

Fig. S7 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole.

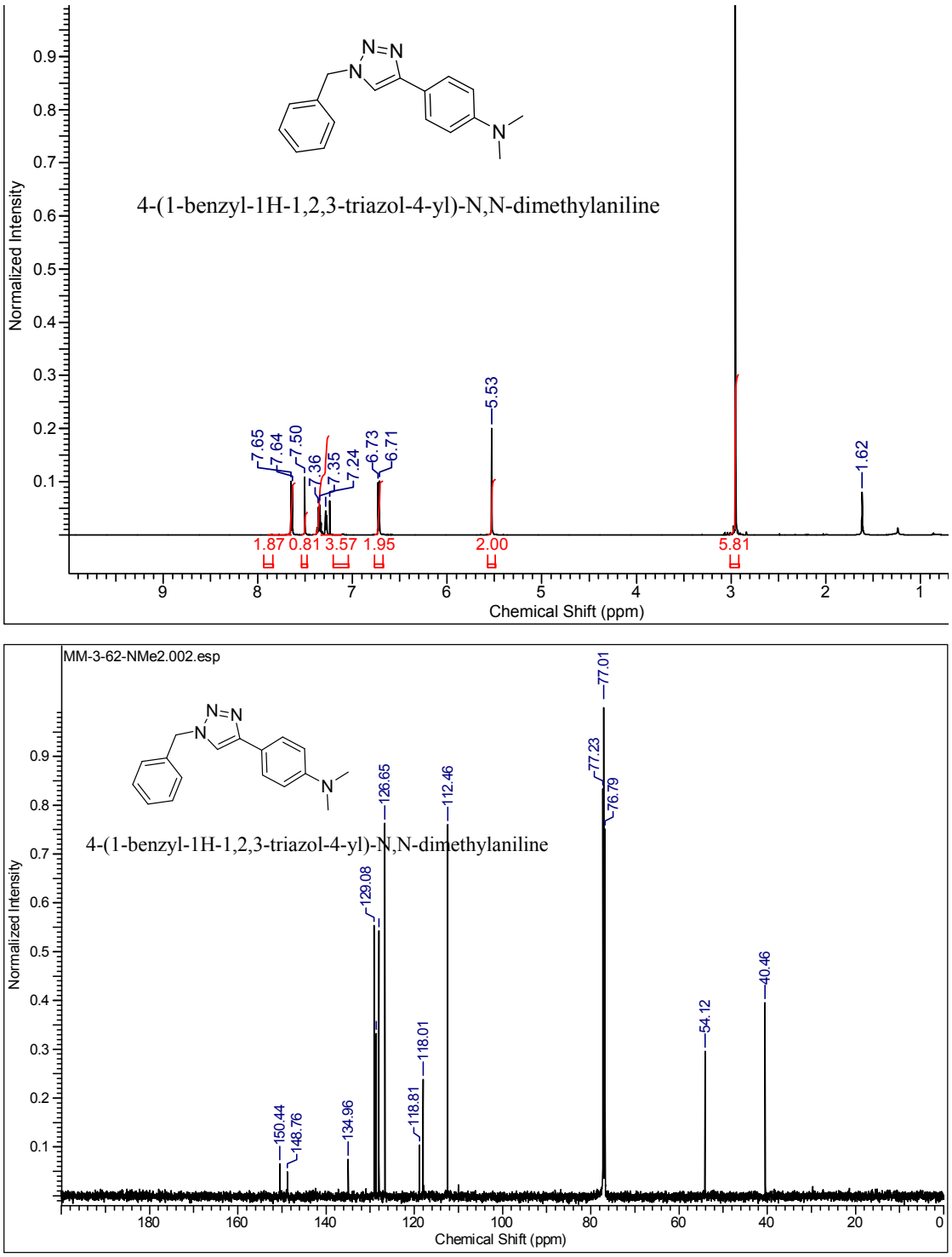

Fig. S8 ^{1}H- and ^{13}C-NMR spectra of 4-(1-benzyl-1H-1,2,3-triazol-4-yl)-N,N-dimethylaniline.

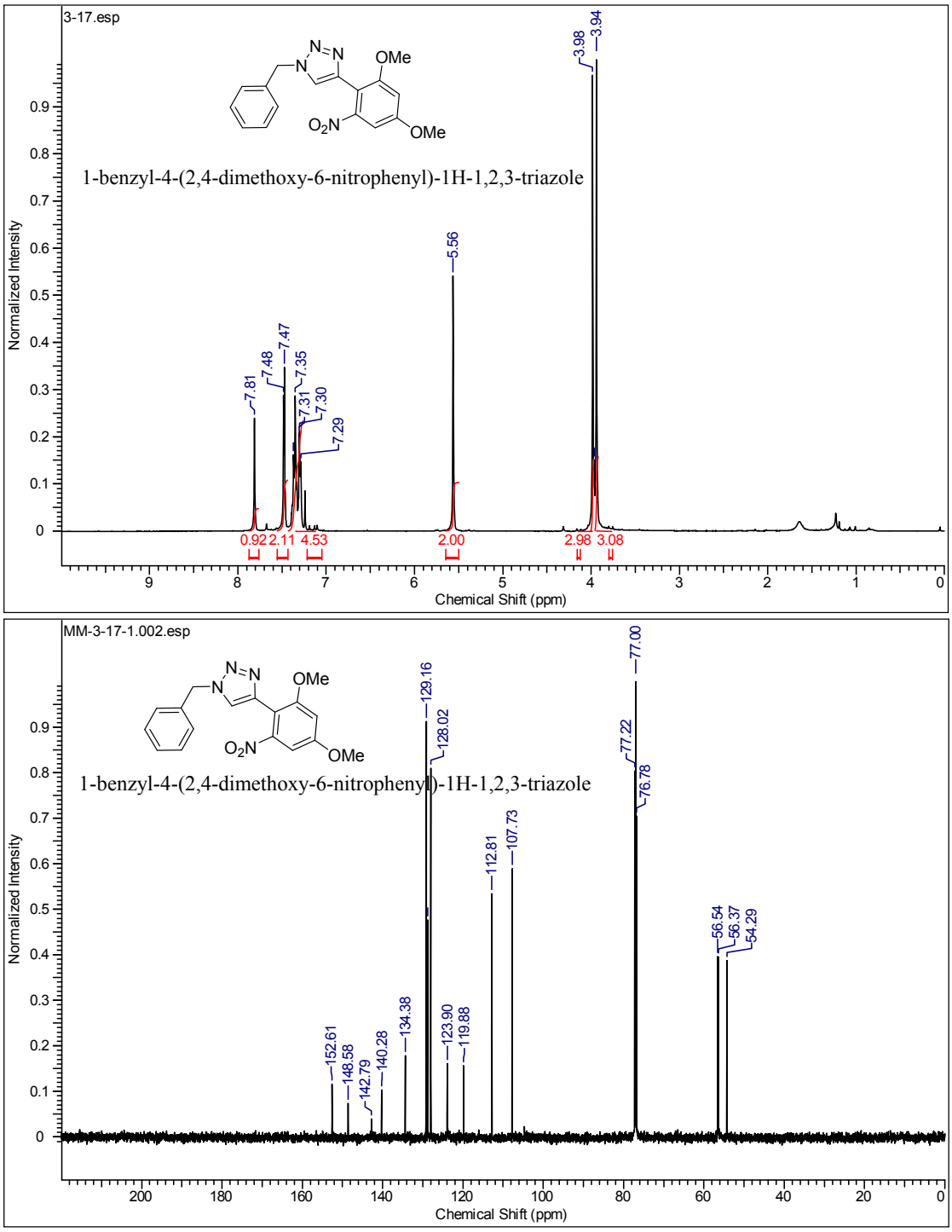

Fig. S9 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(2,4-dimethoxy-6-nitrophenyl)-1H-1,2,3-triazole.

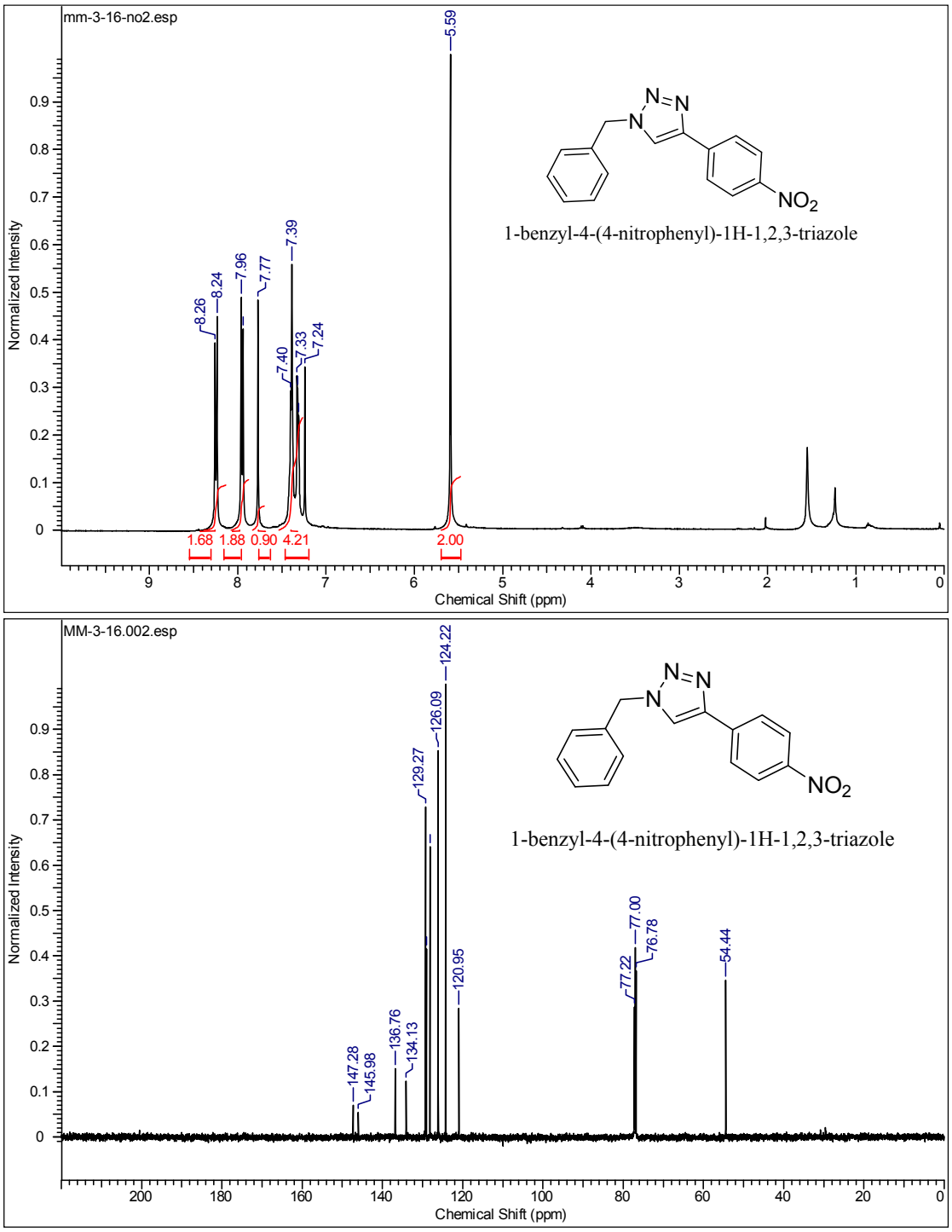

Fig. S10 ^{1}H and ^{13}C NMR spectrum of 1-benzyl-4-(4-nitrophenyl)-1H-1,2,3-triazole.

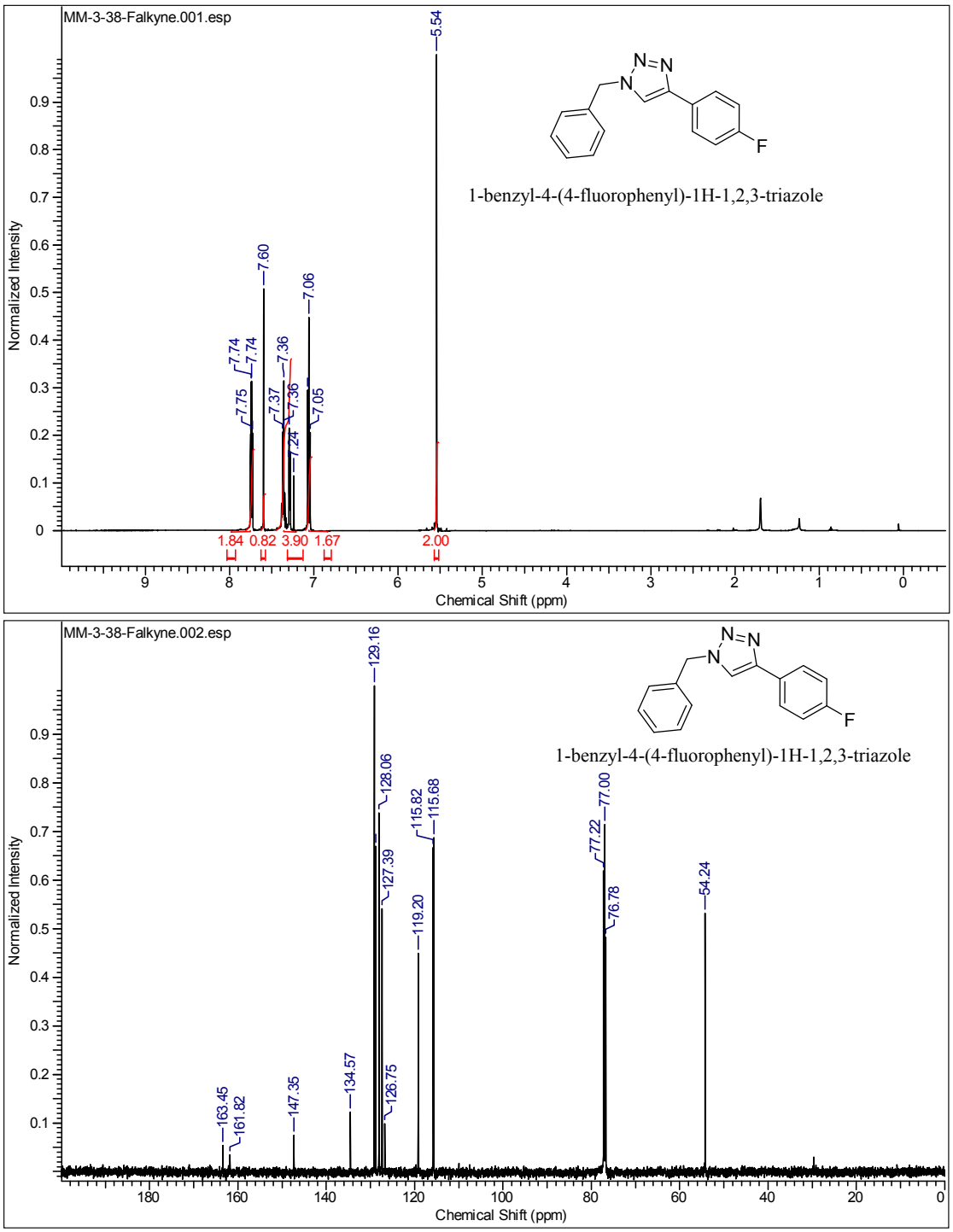

Fig. S11 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(4-fluorophenyl)-1H-1,2,3-triazole.

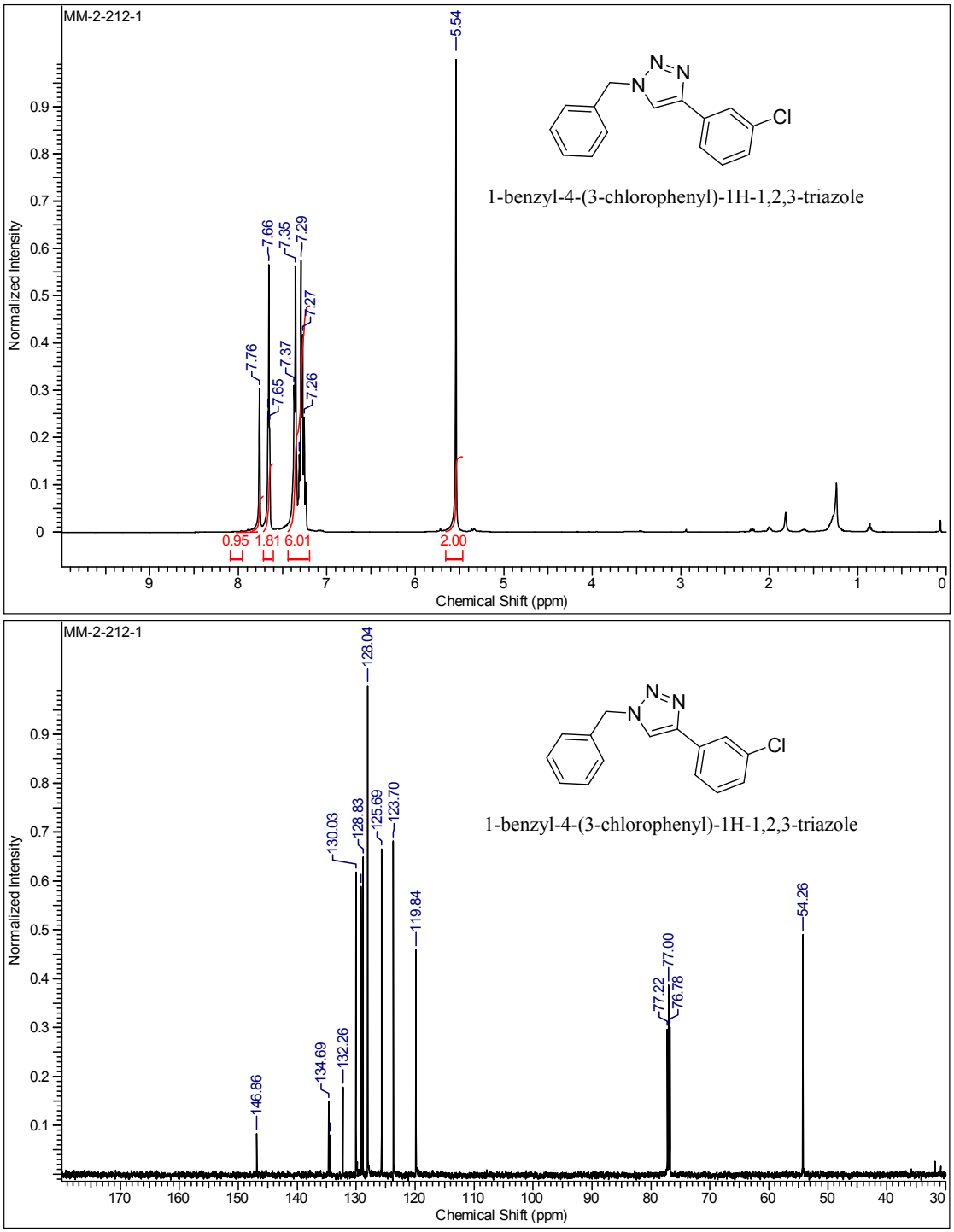

Fig. S12 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(3-chlorophenyl)-1H-1,2,3-triazole.

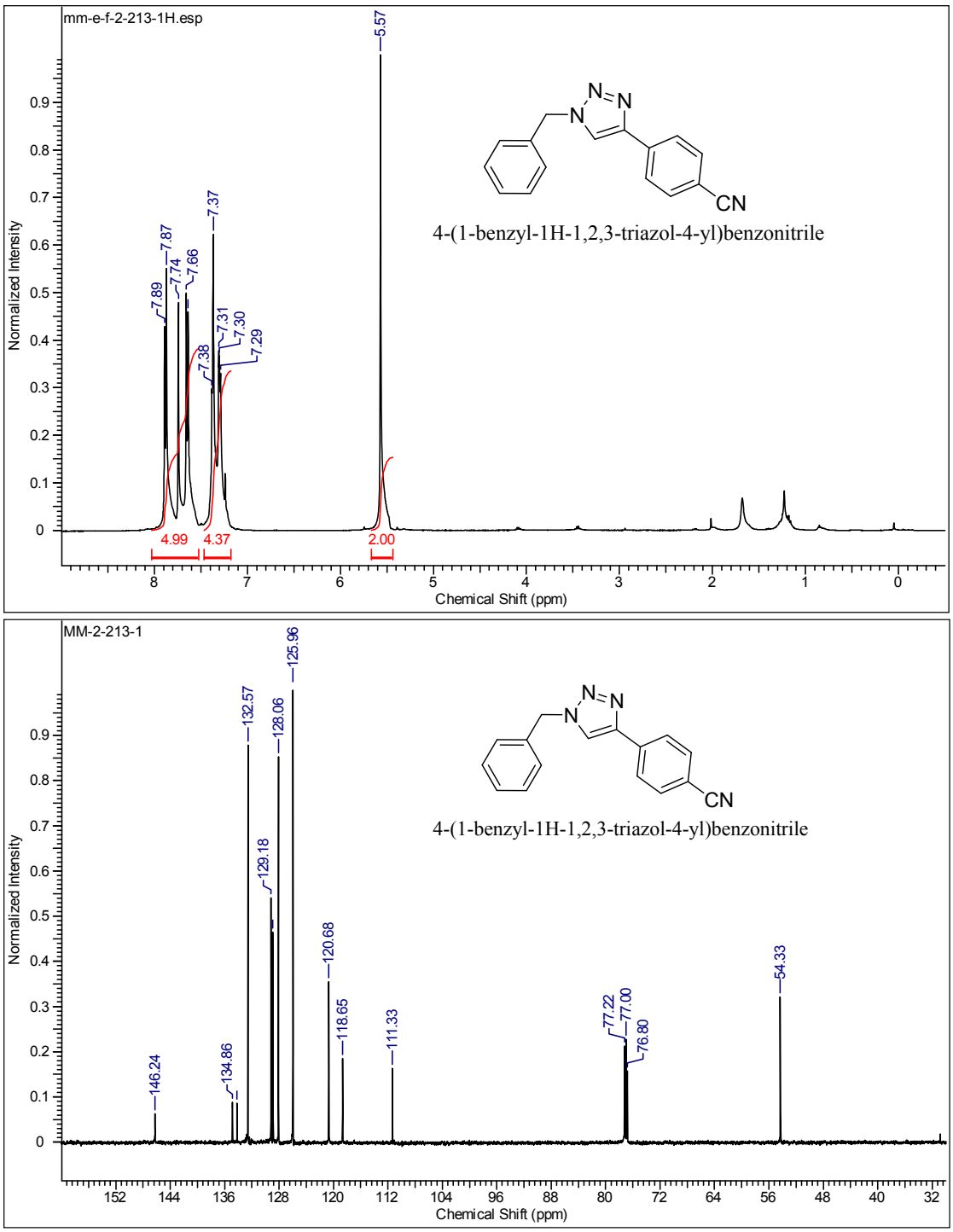

Fig. S13 ^{1}H- and ^{13}C-NMR spectra of 4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzonitrile.

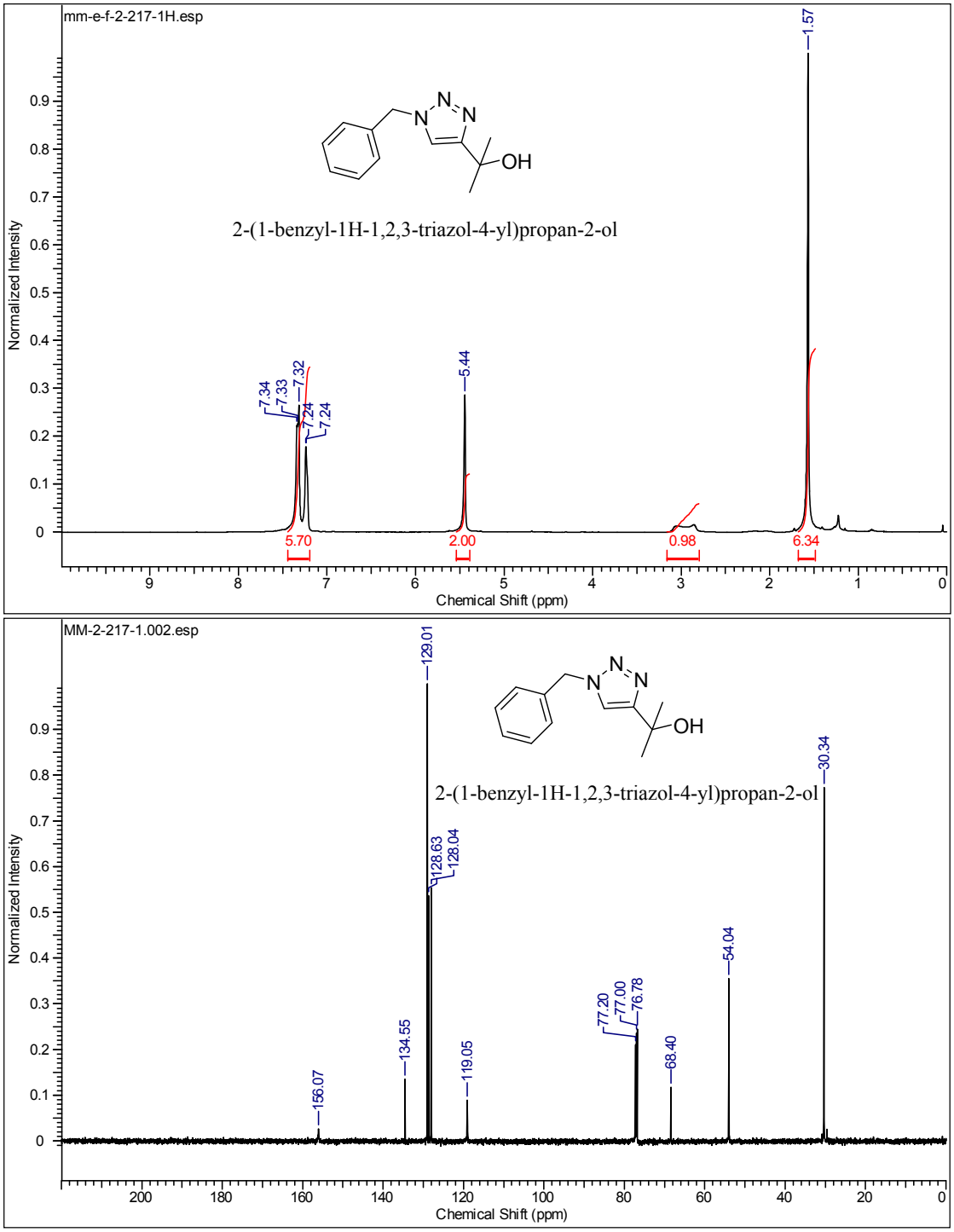

Fig. S14 ^{1}H- and ^{13}C-NMR spectra of 2-(1-benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol.

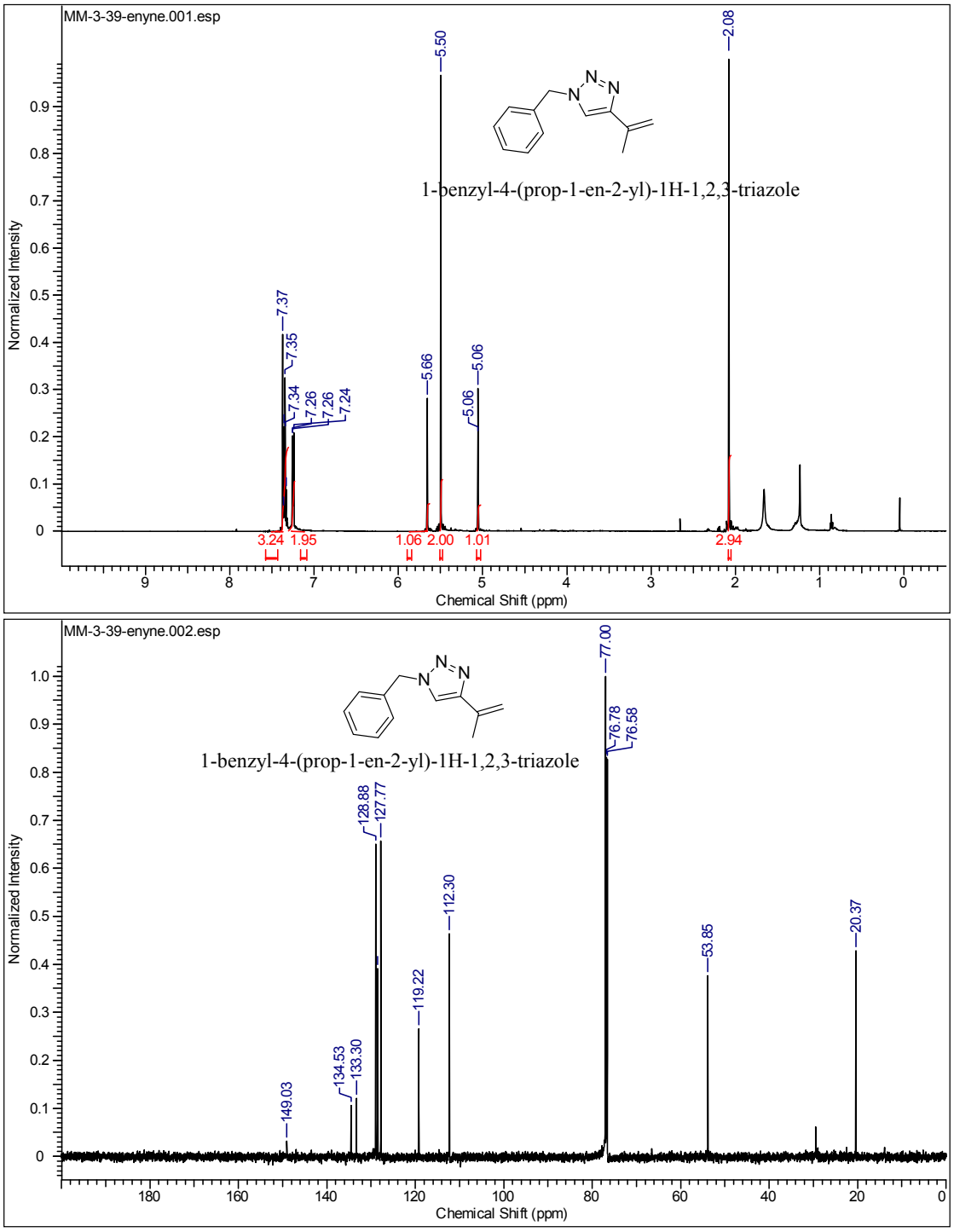

Fig. S15 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(prop-1-en-2-yl)-1H-1,2,3-triazole.

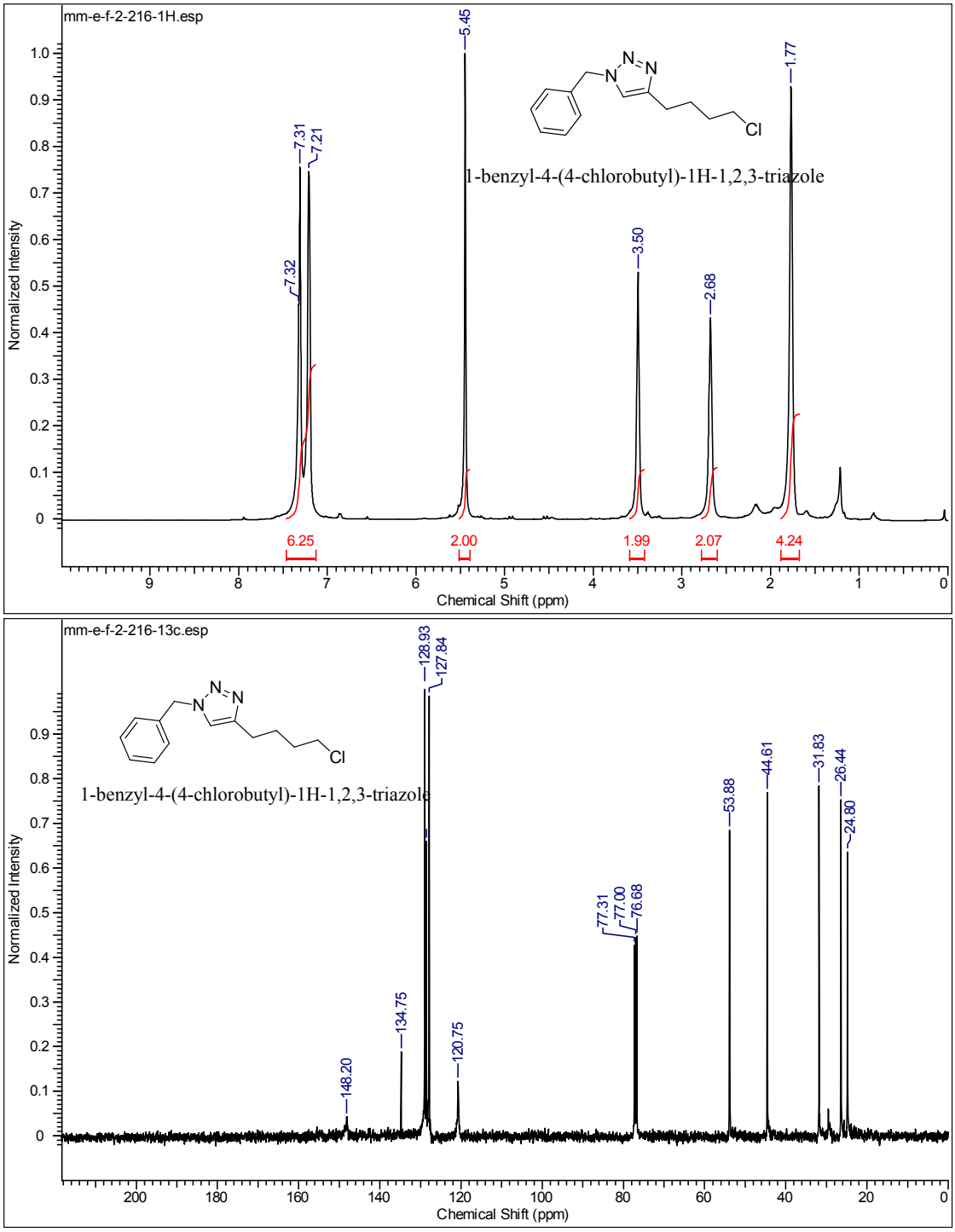

Fig. S16 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(4-chlorobutyl)-1H-1,2,3-triazole.

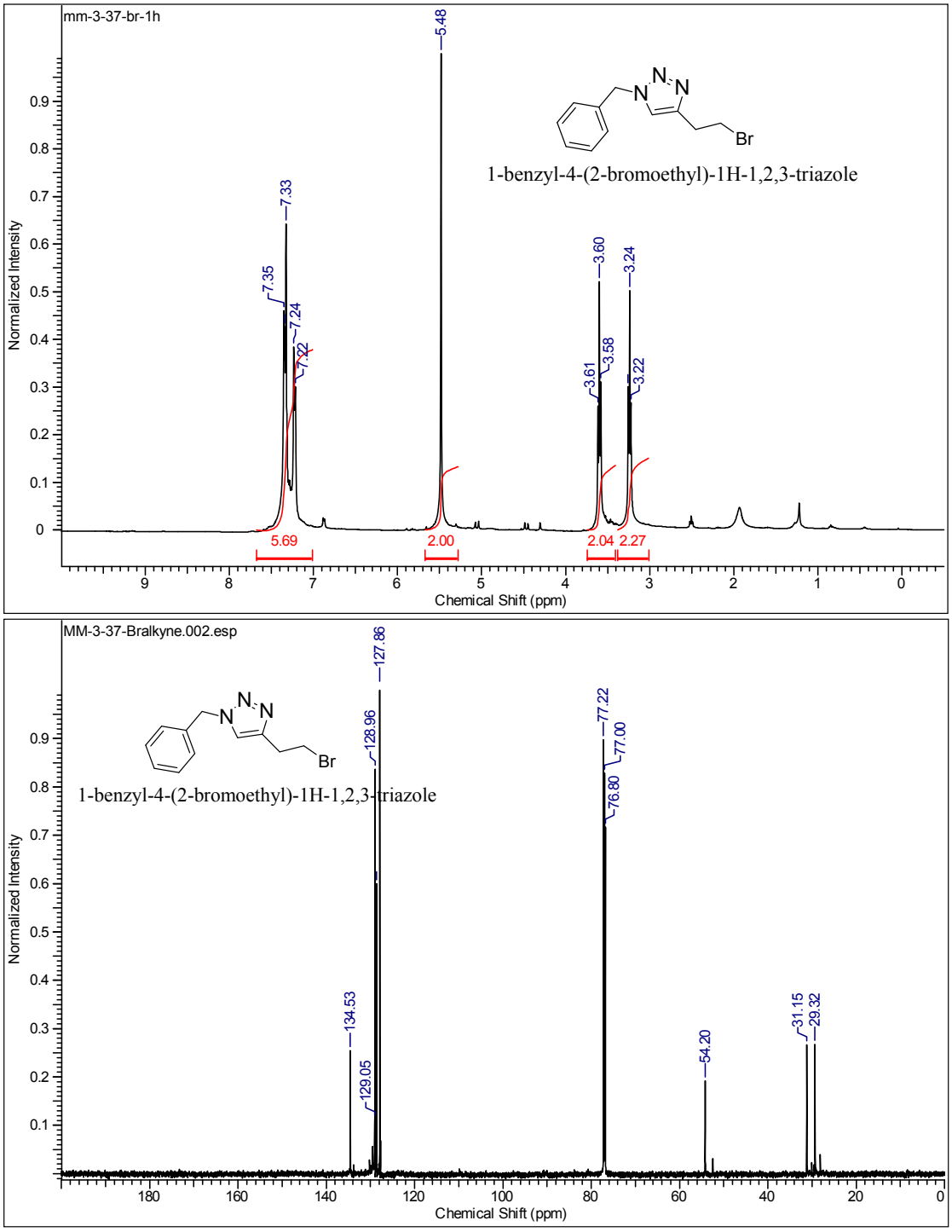

Fig. S17 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(2-bromoethyl)-1H-1,2,3-triazole.

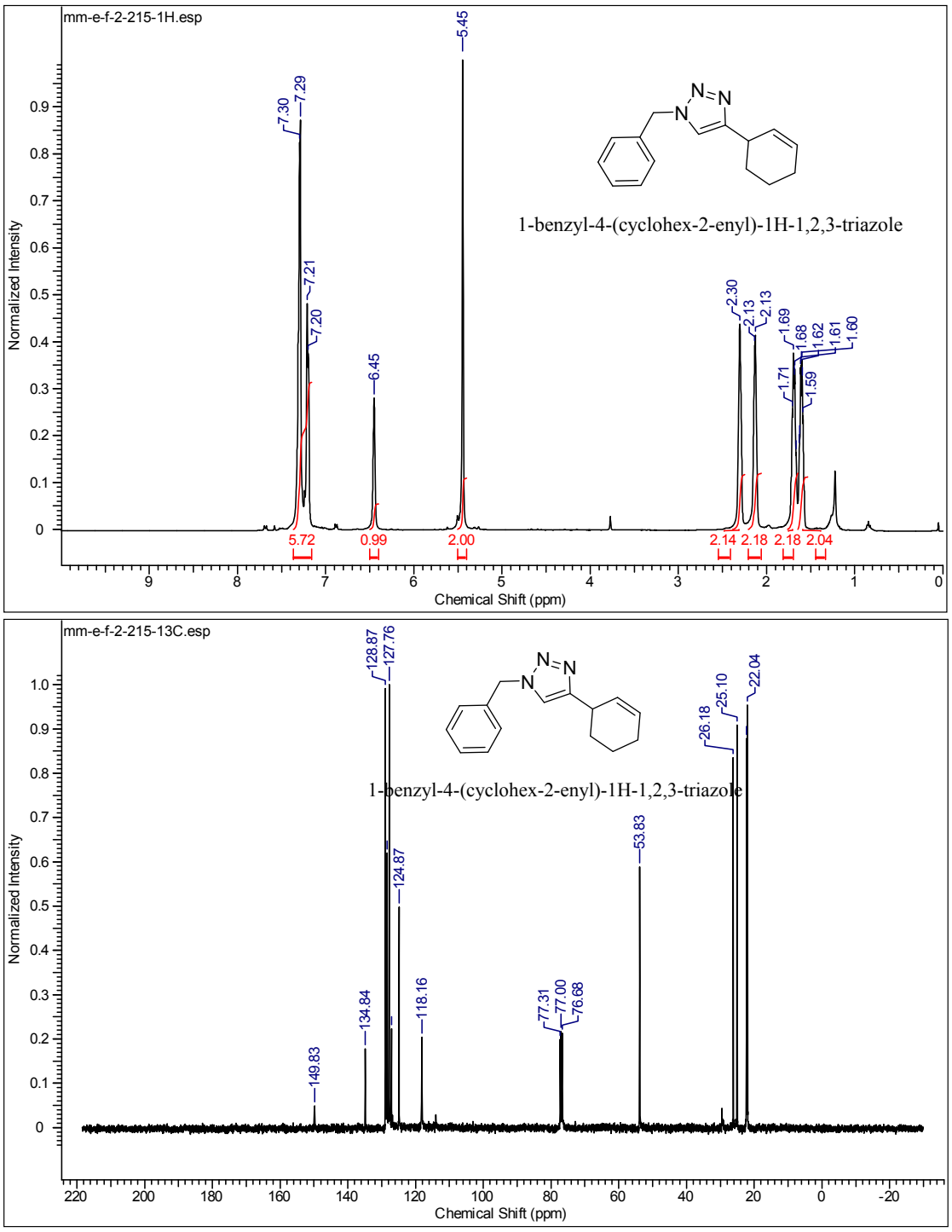

Fig. S18 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-(cyclohex-2-enyl)-1H-1,2,3-triazole.

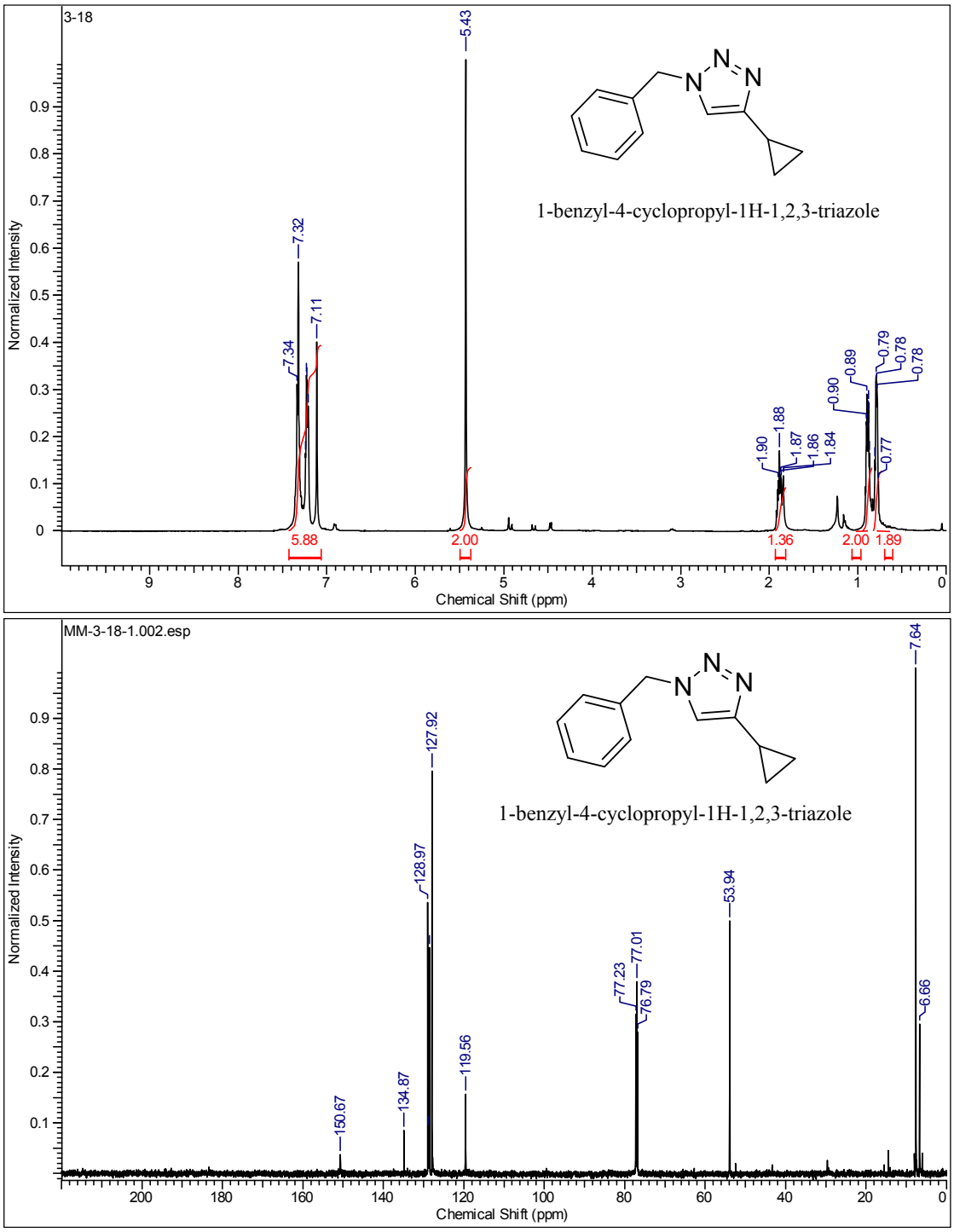

Fig. S19 ^{1}H- and ^{13}C-NMR spectra of 1-benzyl-4-cyclopropyl-1H-1,2,3-triazole.