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Supporting Information

Copper Supported on MWCNT-Guanidine Acetic Acid@Fe_3O_4: Synthesis, Characterization and Application as a Novel Multi-Task Nanocatalyst for Preparation of Triazoles and Bis(indolyl)methanes in Water

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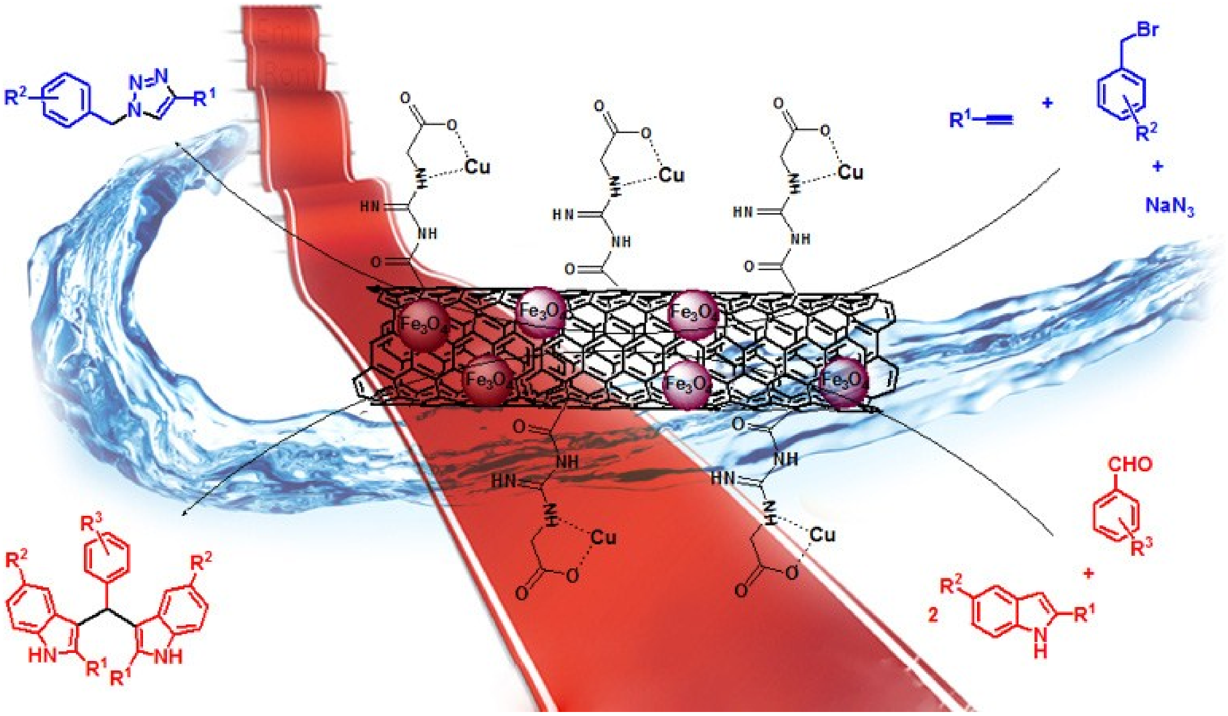

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Experimental Section

Preparation of catalyst

Preparation of MWCNT-COCl

The carbocyclic acid group of MWCNT–COOH was converted to formyl chloride *via* reaction with thionyl chloride. In a round bottom flask, excess amount of $SOCl_2$ (30 ml) was added to MWCNT–COOH (0.100 g). The suspension was refluxed for 48 h at 75 °C. Thereafter, the sample was evaporated under reduced pressure, followed by a complete removal of unreacted $SOCl_2$ on a rotary evaporator with a vacuum pump. The remaining solid (MWCNT–COCl) was washed out three times with anhydrous tetrahydrofuran (THF) and dried in an oven at 60 °C for 5 h.

Preparation of MWCNT-GAA

In a typical procedure, 0.080 g MWCNT-COCl was dispersed in 25 ml DMF and sonicated for 30 min then mixed with 0.060 g (0.001 mol) GAA. The mixture was stirred for 5 h under N_2 atmosphere at room temperature. Then the solvent was evaporated, remaining solid washed with acetone and the precipitate dried in vacuum at 60 °C to afford MWCNT-GAA.

Preparation of Cu/MWCNT-GAA

MWCNT-GAA (0.500 g) was dispersed in water, $CuCl_2$. $2H_2O$ (0.043 g, 0.00025 mmol) which was dissolved in 5 ml water added dropwise, then ascorbic acid (50 mL ,0.025M) was added, temperature of mixture was increased to 80 °C and stirring continued at 80 °C for 24h. The solvent was evaporated, and the remaining solid was washed three times with deionized water and ethanol. Finally the precipitate was dried in vacuum at 60 °C overnight to give Cu/MWCNT-GAA.

In situ preparation of Cu/MWCNT-GAA@Fe_3O_4

The next step in the accomplishment of catalyst preparation was synthesis of the magnetic Fe_3O_4 using co-precipitation technique.[44] The Fe_3O_4 NPs (1.000 g) was dispersed in water (15 mL) and sonicated for 15 min then MWCNT-GAA (1.000 g) added and sonication continued for 2 h at room temperature. In addition, a solution of $CuCl_2.2H_2O$ (0.043 g, 0.00025 mmol) in 5 mL water was added dropwise to the reaction mixture, followed by addition of ascorbic acid (50 mL, 0.025M). The reaction mixture was stirred on magnetic heater stirrer at 80 °C for 24h. Finally, by applying an external magnet, Cu/MWCNT-GAA@Fe_3O_4 nanoparticles were collected and washed three time with deionized water/ethanol and the magnetic precipitate was dried in vacuum at 60 °C.

General procedure for the synthesis of 1,2,3-triazoles

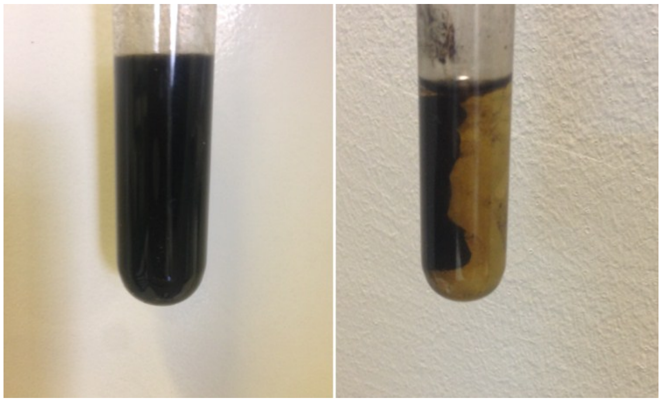
Alkynes (1 mmol), benzyl bromide derivatives (1 mmol) and sodium azide (1 mmol, 0.065 g) were added to a 10 ml round bottom flask fitted with a magnetic stirrer containing a suspension of catalyst (0.400 mol%, 0.020 g) in water (5 mL). The resultant mixture was heated at 50 °C. The progress of the reaction was followed by thin layer chromatography (TLC) (ethyl acetate/n-hexane). Upon completion, the mixture cooled to room temperature and the catalyst separated using an external magnet and the product was extracted with chloroform. The solvent was removed in vacuum to afford the pure product. If necessary the purification was performed by recrystallization from ethyl acetate or ethanol.

General procedure for the synthesis of bis(indolyl)methanes

In a 10 mL round bottom flask equipped with magnetic stir bar an indole (1 mmol), an aldehyde (0.5 mmol) and water (5 mL) were added. The catalyst (0.200 mol%, 0.01 g) was added and the mixture was stirred at 70 °C for 40-80 min. Progress of reaction was monitored by TLC (ethyl acetate/n-hexane). Then chloroform (2 × 5 mL) was added to the reaction mixture and the catalyst was separated using an external magnet. The chloroform layer was separated, evaporated under reduced pressure to give the crude product which was purified via recrystallization in ethanol–water mixture.

Materials and Instrumentation

The materials were purchased from Merck and Aldrich and used without further purification. Carboxyl multi wall carbon nanotubes (purity> 95 %, -COOH content: 2.00 wt%, outer diameter: 10-20 nm, inner diameter: 5-10 nm, length: 30µm, special surface area: 220 m^2 /g) was purchased from Atoor Sanat Abtin, Tehran, Iran. Products were analyzed using a Varian 3900 GC. X-ray diffraction (XRD) pattern of catalyst was recorded on a STOE STADI P with scintillation detector, secondary monochromator using Cu Kα radiation (λ = 0.1540 nm). Copper(II) determination was carried out on an FAAS (Shimadzu model AA-680 flame atomic absorption spectrometer) with a Cu hollow cathode lamp at 324.7 nm, using an air-acetylene flame. Transmission Electron Microscopy (TEM) was performed using a transmission microscope Philips CM-30 with an accelerating voltage of 150 Kv. Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 ºC min^{-1} in air. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer. The elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL.^1H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz. NMR spectra were obtained in DMSO-d_6 and $CDCl_3$.

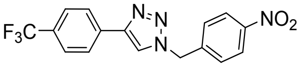


Magnetically separable catalyst

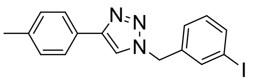
Analytical data of compounds

Spectral data for new derivatives of 1,2,3-triazoles

1-(4-Nitrobenzyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (Table 1, Entry 6). White powder; m.p.: 215-218 ^{o}C, ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 5.74 (2H, s), 7.47-7.50 (2H, m), 7.68-7.71 (2H, m), 7.84 (1H, s), 7.94-7.96 (2H, m), 8.26-8.29 (2H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) 53.1, 118.1, 120.0, 120.5, 121.8, 124.9, 125.2, 127.7, 132.5, 140.1, 147.2.

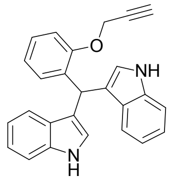


1-(3-Iodobenzyl)-4-p-tolyl-1H-1,2,3-triazole (Table 1, Entry 7).white powder; m.p. 178-181 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 2.38 (3H, s), 5.51 (2H, s), 7.09-7.14 (1H, m), 7.22-7.27 (3H, m), 7.62-7.72 (5H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) 21.3, 53.2, 94.7, 118.85, 119.25, 119.58, 125.63, 127.51, 12950, 129.63, 130.77, 136.80, 136.97, 137.86, 138.16, 148.49, 158.53.

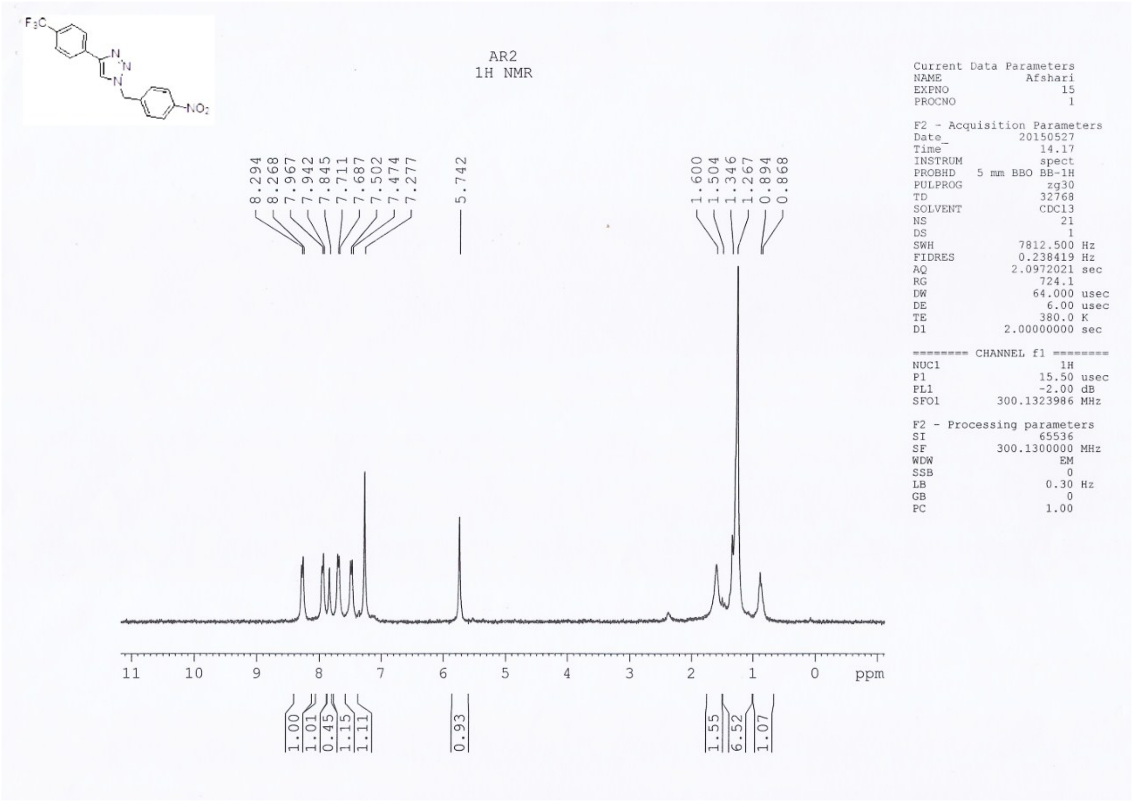


Spectral data for new derivative of bis(indolyl)methane

3-((1H-Indol-3-yl)(2-(prop-2-ynyloxy)phenyl)methyl)-1H-indole (Table 2, Entry 5). Dark red powder; m.p. 177-178 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 3.58 (1H, s), 4.87 (2H, s), 6.23 (1H, s), 6.76-6.86 (4H, m), 7.13-7.36 (10H, m), 10.79 (2H, brs); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 31.9, 56.2, 78.5, 80.1, 111.8, 113.8, 118.0, 118.5, 119.4, 121.3, 123.9, 124.0, 127.1, 127.2, 129.8, 133.7, 136.8, 137.0, 154.6; Anal. Calcd. (%) for C$_{26}$H$_{20}$N$_2$O: C, 82.95; H, 5.35; N, 7.44. Found: C, 82.90; H, 5.42; N, 7.21.



^{1}H, ^{13}C NMR for the new compounds



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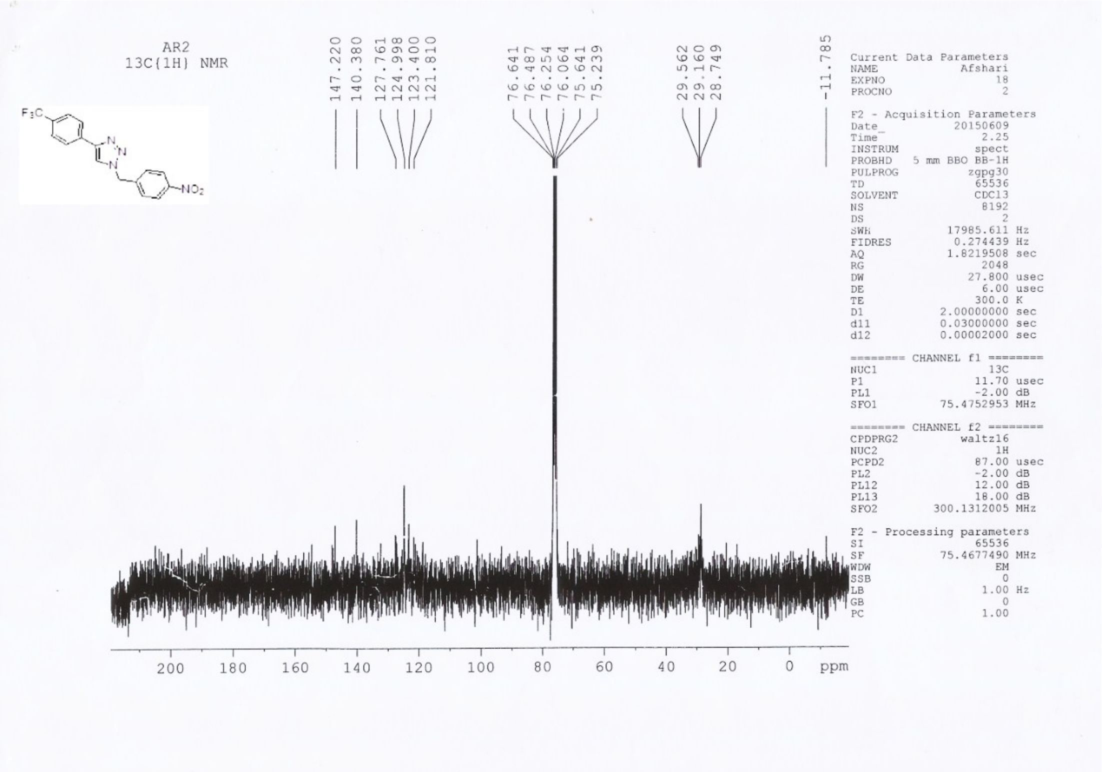

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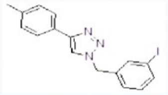

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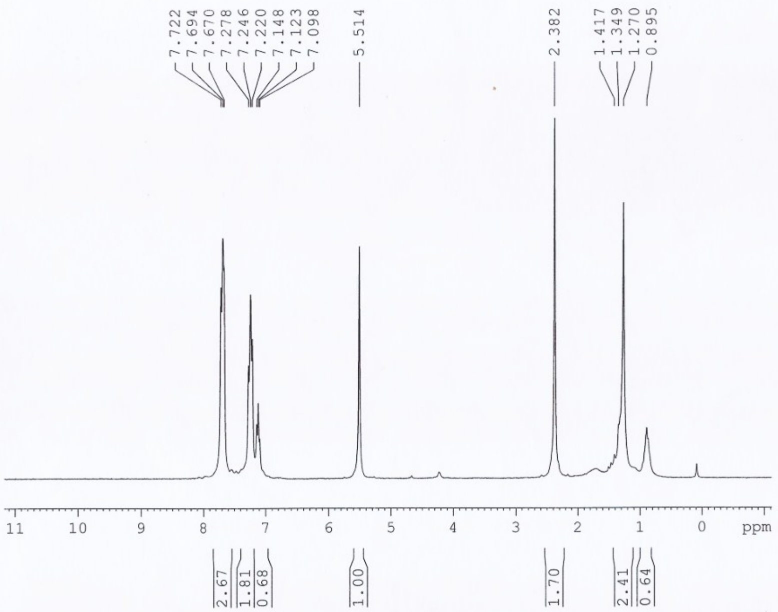

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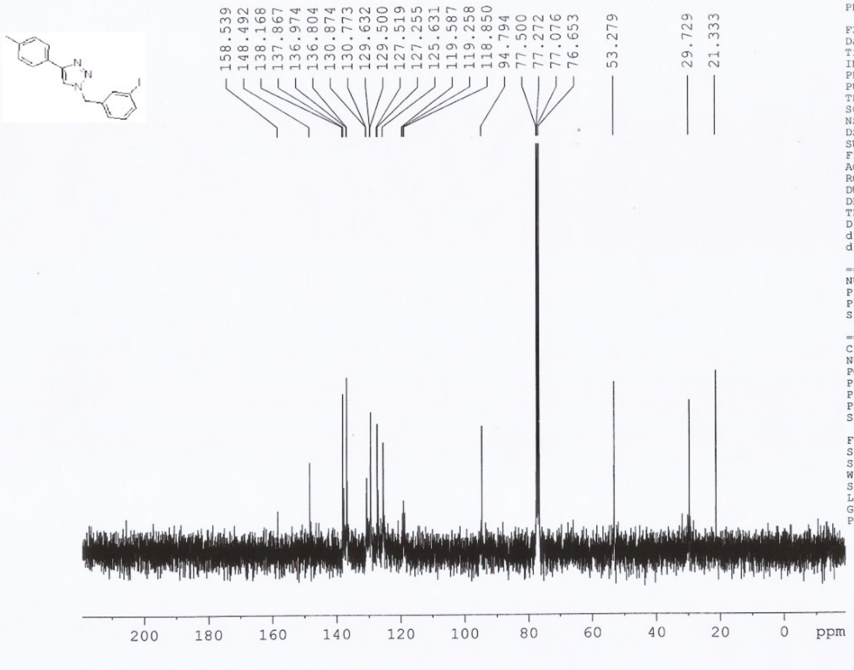

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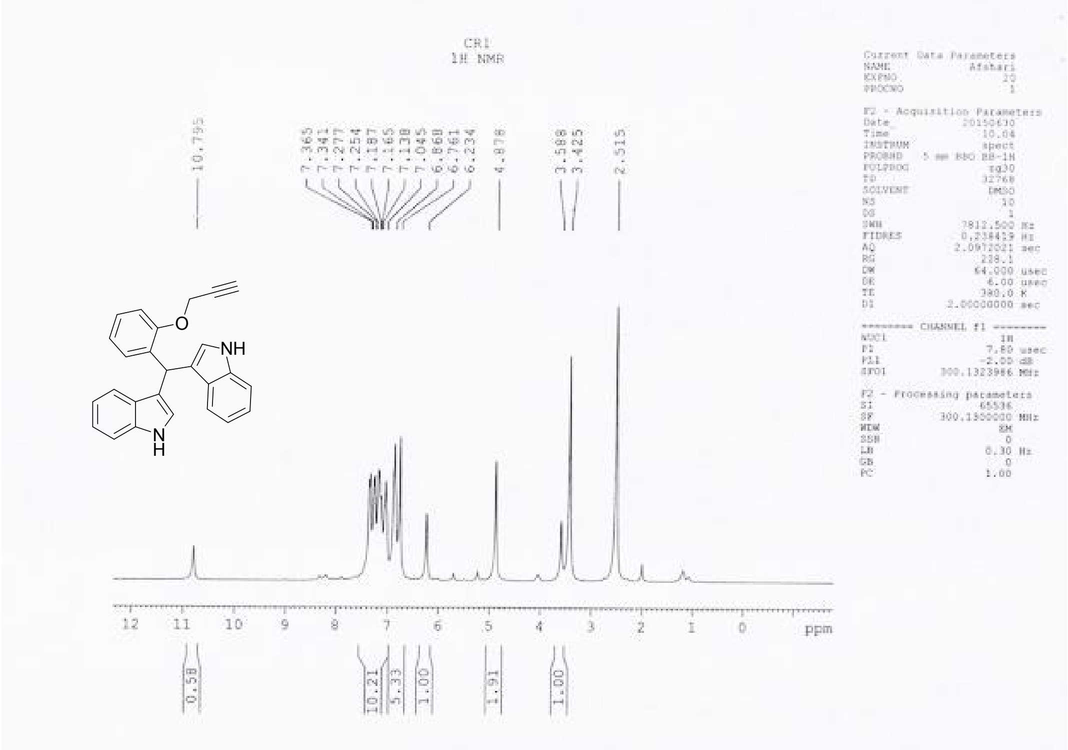

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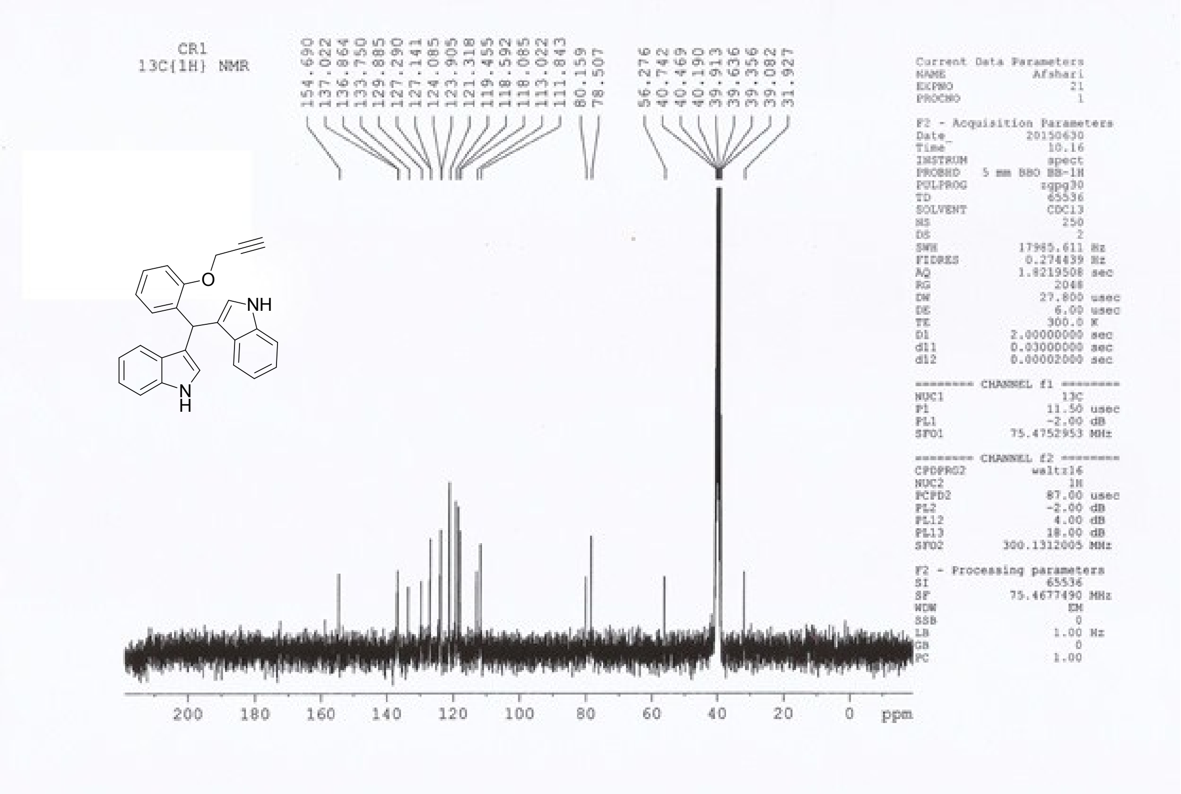

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