Supporting Information

One Pot Glucose Detection by [Fe^{III}(biuret-amide)] Immobilized on Mesoporous Silica Nanoparticles: An Efficient HRP Mimic

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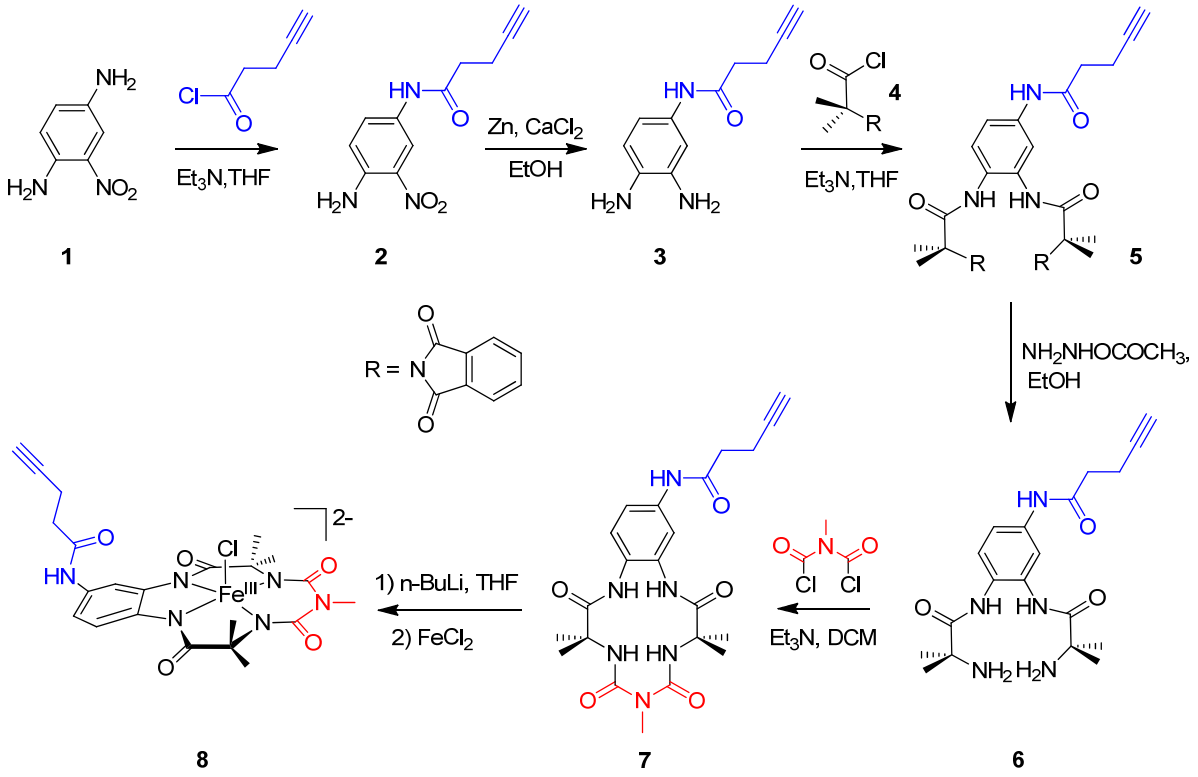
(i) Materials

Tetraethylorthosilicate (TEOS), Cetyltrimethylammonium bromide (CTAB), Amino guanidine hydrochloride (AG.HCl), glucose oxidase (GOX), 3 ,3′, 5, 5′-Tetramethylbenzidine (TBM), 4-Pentynoic acid and Hydrazine acetate were obtained from Sigma Aldrich. $CuSO_4$, Sodium ascorbate, hydrogen peroxide, glucose, fructose, Zn dust and $CaCl_2$ were obtained from Merck, India. Maltose and lactose were obtained from SRL. 3-azido-propyltriethoxysilane (AzPTES)[1] and tris(3-hydroxypropyltriazolylmethyl)amine (THPTA)[2] were prepared as reported earlier. For all the experiments de-ionized water was used.

(ii) Synthesis of clickable [Fe^{III}-(biuret-amide)]



Scheme S1. Scheme for synthesis of clickable [Fe^{III}-(biuret-amide)]

(a) Synthesis of *pent-4-ynoyl chloride*

To a solution of 4-pentynoic acid(1.50 g, 15.29 mmol) in dry benzene was added oxalyl chloride(6.56 mL, 76.45 mmol, 5 equivalent) and the reaction mixture was refluxed for 2 to 3 hours with a $CaCl_2$ guard tube fitted to the reflux condenser. The excess oxalyl chloride was distilled of under reduced pressure. The remaining little oxalyl chloride was chased off with 5 mL of benzene twice. Subsequent reactions were performed considering a 100% yield. Success of the reaction was confirmed from shift of the infrared band of cabonyl 1699 cm^{-1} (4-pentynoic acid) to 1799 cm^{-1} (pent-4-ynoyl chloride).

(b) Synthesis of *N-(4-amino-3-nitrophenyl)pent-4-ynamide*(2)

To an ice cooled solution of **1** (2 g, 13.06 mmols) and dry triethylamine (2.0 mL, 14.37 mmol, 1.1 equivalent) in dry THF, a solution of pent-4-ynoyl chloride (1.67 g, 14.37 mmol, 1.1 equivalent) in dry THF was added dropwise over a period of 30 minutes. After completion of addition the ice was removed and the reaction was stirred at room temperature for a period of 12 hours. The reaction mixture was filtered to remove the triethylamine salt. Solvent was removed under reduced pressure to have **2** as

the only product (TLC). **2** was then recrystlized from ethanol to yield 2.50g (82.08%). $C_{11}H_{11}N_3O_3$. IR (KBr, ν_{max}/cm^{-1}): 1654 (s, CO), 2119(s, C≡C), 3284 (s, NH), 3358(s, NH). ^{1}H NMR (200.13 MHz, CD_3OD): δ = 2.32(m, 1H), 2.58 (m, 4H), 6.95 (d, J = 9.10 Hz, 1H), 7.53 (dd, J_1 = 2.52 Hz, J_2 = 9.10 Hz, 1H), 8.35 (d, J = 2.66 Hz, 1H). ^{13}C NMR; (50.32 MHz, CD_3OD): δ = 15.54, 36.60, 70.39, 83.44, 117.46, 120.26, 128.57, 130.65, 131.50, 144.60, 172.29. ESI-MS: *m/z* 234.16(M-H$^+$, 100%).

(c) Synthesis of *N-(3,4-diaminophenyl)pent-4-ynamide*(3)

2 (1.5 g, 6.43 mmol) was taken in 180 ml of 95% ethanol. To it activated $CaCl_2$ powder (0.90 g, 8.10 mmol, 1.26 equivalent) and activated zinc dust (7.50 g, 114.74 mmol, 17.84 equivalent) were added. The reaction mixture was refluxed for two to three hours. The completion of reaction was followed by consumotion of **2** by TLC (60% EtOAc in petrolium ether). As soon as the starting was consumed the reaction mixture was cooled to room temperature and filtered. Ethanol was removed under reduced pressure, the solid residue was dissolved in water and the pH was adjusted to 11 by adding NaOH. Then the organic layer was extracted to 3 × 150 ml of EtOAc. Solvent evaporated to have pure **3** (1.20 g, yield 91.80%). Mol. formula: $C_{11}H_{13}N_3O$. IR (KBr, ν_{max}/cm^{-1}): 1653 (s, CO), 2111 (s, C≡C), 3275 (s, NH). ^{1}H NMR (200.13 MHz, DMSO-d_6): δ = 2.44 (brs, 4H), 2.80 (m, 1H), 4.44 (brs, 4H), 6.42 (d, J = 8.39 Hz, 1H), 6.59 (dd, J_1 =2.18 Hz, J_2 = 8.21 Hz, 1H), 6.85 (d, J = 2.23 Hz, 1H), 9.42(s, 1H). ^{13}C NMR; (50.32 MHz, DMSO-d_6): δ = 14.52, 35.26, 71.62, 84.12, 107.07, 109.11, 114.50, 130.09, 131.13, 135.31, 168.28. ESI-MS: *m/z* 204.04(M-H$^+$, 100%).

(d) Synthesis of *N,N'-(4-(pent-4-ynamido)-1,2-phenylene)bis(2-(1,3-dioxoisoindolin-2-yl)-2-methylpropanamide)* (5)

To an ice cooled solution of **3** (2 g, 9.84 mmol) and dry triethylamine (2.77 mL, 19.88 mmol, 2.02 equivalent) in dry THF, a solution of **4** (5.00g, 19.88 mmol, 2.02 equivalent) in dry THF was added dropwise over a period of 30 minutes. After completion of addition the ice was removed and the reaction was stirred at room temperature for a period of 12 hours. The reaction mixture was filtered to remove the triethlamine salt. Solvent was removed under reduced pressure and the residue was dissolved in DCM and washed with 3 × 250 mL 1N HCl and 3 × 250 mL saturated $NaHCO_3$

respectively to remove the unreacted reactants. DCM was removed by rota evaporator and the solid was recrystalized from ethanol to have crystals of **5** (4.50g, yield 72.17%). Mol. formula: $C_{35}H_{31}N_5O_7$. IR (KBr, ν_{max}/cm^{-1}): 1661 (s, CO), 1668 (s, CO), 1710 (s, CO), 2119 (s, C≡C), 3420 (br, NH). ^{1}H NMR (200.13 MHz, DMSO-d_6): δ = 1.73 (s, 6H), 1.78 (s, 6H), 2.50 (m, 4H), 2.81 (m, 1H), 7.35 (d, J = 8.75, 1H), 7.50 (dd, J_1 = 2.28, J_2 = 8.85, 1H), 7.82 (m, 9H), 9.41 (s, 1H), 9.42 (s, 1H), 10.09 (s, 1H). ^{13}C NMR; (50.32 MHz, DMSO-d_6): δ = 14.23, 24.56(4C), 35.29, 61.20, 61.33, 71.67, 83.83, 114.49, 115.85, 123.06(4C), 124.87, 125.41, 131.20, 131.85(4C), 134.66(4C), 136.63, 168.51(4C), 169.48, 171.67, 171.82,. ESI-MS: *m/z* 634.18(M-H$^+$, 100%).

(e) Synthesis of *N,N'-(4-(pent-4-ynamido)-1,2-phenylene)bis(2-amino-2-methylpropanamide)* (6)

A mixture of **5** (2 g, 3.16 mmol, 1 equivalent) and hydrazineacetate (0.767 g, 8.52 mmol, 2.7 equivalent) were taken in 50 ml of ethanol and rufluxed for 8 hrs. After two to three hour, the reaction mixture became clear and then precipitation of pthalichydrazide starts following completion of reaction with additional 5 hrs. The reaction mixture was cooled to room temperature and kept at -20 °C overnight. The reaction mixture was filtered through celite following washings with cold ethanol. Ethanol was removed under reduced pressure, the solid residue was dissolved in water and the pH was adjusted to 11 by adding NaOH . Then the organic layer was extracted to 3 × 100 ml of DCM. Solvent evaporated and the solid was recrystalized from solvent mixture of EtOAc and hexane to have pure **6** (yield 0.620 g, 52.60%). Mol. formula: $C_{19}H_{27}N_5O_3$. IR (KBr, ν_{max}/cm^{-1}): 1660 (s, CO), 1676 (s, CO), 2117 (s, C≡C), 3287 (s, NH). ^{1}H NMR (200.13 MHz, DMSO-d_6): δ = 1.32 (s, 12H), 2.50 (m, 4H), 2.82 (m, 1H), 4.69 (brs, 4H), 7.44 (m, 2H), 7.97 (m, 1H), 10.03 (s, 1H). ^{13}C NMR; (50.32 MHz, DMSO-d_6): δ = 14.31, 28.87(2C), 28.92(2C), 35.34, 55.07, 55.17, 71.73, 83.90, 114.53, 115.59, 125.02, 125.88, 131.85, 136.46, 169.45, 176.80, 177.09. ESI-MS: *m/z* 374.25(M-H$^+$, 100%).

(f) Synthesis of *N-(3,3,6,9,9-pentamethyl-2,5,7,10-tetraoxo-2,3,4,5,6,7,8,9,10,11-decahydro-1H-benzo[i][1,3,5,8,11]pentaazacyclotridecin-13-yl)pent-4-ynamide* (7)

The exact same procedure was followed as described in our previous report.[3] Yield for 0.10 g (0.268 mmol) of **6** was 0.055 g (45%). Mol. formula: $C_{22}H_{28}N_6O_5$. IR (KBr, ν_{max}/cm^{-1}): 1605 (s, CO), 1681 (s,

CO), 1703 (s, CO), 2119 (s, C≡C), 3257 (s, NH), 3315 (s, NH). ^{1}H NMR (500.20 MHz, CD_3OD): δ = 1.64 (s, 6H), 1.65 (s, 6H), 2.30 (t, J = 2.67, 1H), 2.58 (m, 4H), 3.10 (s, 3H), 7.48 (dd, J_1 = 2.43, J_2 = 8.83, 1H), 7.57 (d, J = 8.84, 1H), 8.06 (d, J = 2.16, 1H). ^{13}C NMR; (125.78 MHz, CD_3OD): δ = 15.65, 26.21(2C), 26.43(2C), 31.95, 36.99, 60.79, 60.91, 70.48, 83.66, 117.66, 118.69, 127.30, 127.37, 132.85, 138.23, 158.59, 158.98, 172.44, 176.59, 176.97. ESI-MS: *m/z* 479.18(M-Na^+, 100%).

(g) Synthesis of *alkyne tailed* $(Et_4N)_2[Fe^{III}$*(biuret-amide)]* (8)

Here also the similar procedure was followed as given in our previous report.[3] The sole difference being use of 6 equivalent of n-butyllithiun in place of 4.4 equivalents. Yield for 0.034 g (0.0745 mmol) of **7** was 0.046 g (76.53%). Mol. formula: $C_{38}H_{64}N_8O_5FeCl$. UV-Vis: $\lambda_{max}(H_2O)$/nm; 350 (ε/dm^3 mol^{-1} cm^{-1}, 5830), IR (KBr, ν_{max}/cm^{-1}): 1569 (s, CO), 1581 (s, CO), 1609 (s, CO), 3330 (s, NH). ESI-MS(negative ion mode): *m/z* 508.21(M-35, 100%). For EPR spectrum, UV-VIS and FT-IR see Figure S1.

(iii) Synthesis of Azide functionalized MSN

The azide functionalized MSN was synthesized by co-condensation of TEOS with AzPTES (3-azidopropyltriethoxysilane) by following procedure reported in literature[4,5] with slight modifications. In a typical batch synthesis, CTAB (1 g, 2.744 mmol) was dissolved in 480 mL of water and 2M aqueous NaOH (3.5 mL, 7 mmol). The mixture was stirred thoroughly at 600 rpm for 30 min at 80 °C to dissolve the surfactant completely. To this clear solution, TEOS (4.702g, 22.56 mmol) was injected rapidly followed by AzPTES (0.0563 g, 0.228 mmol). A white precipitate was observed within 1-2 min after the addition was completed. The resultant reaction mixture was allowed to stir at 600 rpm for 2 h at 80 °C . The hot contents were then filtered and the white residue was washed with copious amounts of water and methanol and dried under vacuum at 100 °C over night (yield ~1.7 g). The template was extracted by stirring the as-synthesized sample (0.8 g) in 150 mL methanol and 1 ml concentrated hydrochloric acid at 60 °C for 6 hr. The resulting template removed solid product, was filtered and washed with copious amount of methanol and then dried under vacuum at 100 °C over night (yield ~0.48 g). This azide grafted MSN will be simply denoted as N_3-MSN. Elemental analysis : C, 0.53; H, 0.1; N, 0.51%

(iv) Modification of N_3-MSN by Cu(I) catalyzed Azide-Alkyne Cycloaddition reaction (CuAAC)

For CuAAC, the azide functionalized MSN (N_3-MSN) was incubated with 3 equivalents of the alkyne tailed [Fe^{III}-(biuret-amide)] complex in 100 mM phosphate buffer containing THPTA (2.5 equivalent), AG.HCl (4 equivalent), $CuSO_4$ (0.5 equivalent) and sodium ascorbate (4 equivalent). In a typical click reaction, N_3-MSN (10 mg, 1.2 μmol of azide) was incubated with alkyne tailed [Fe^{III}-(biuret-amide)] complex (3 mg, 3.6 μmol) in 1mL, 100 mM phosphate buffer containing THPTA (1.3 mg, 3 μmol), AG.HCl (0.54 mg, 4.8 μmol), $CuSO_4$ (0.16 mg, 0.6 μmol). The reaction mixture was freeze pump thawed thrice and sodium ascorbate (0.96 mg, 4.8 μmol) was added and the mixture was stirred for 24 h. After completion of reaction, the reaction mixture was centrifuged and the residue was first washed with phosphate buffer twice and then sequentially washed with 10 mM N,N-diethyldithiocarbamate sodium solution in 100 mM phospate buffer and acetone respectively. The last two washings were repeated thrice. Finally, the yellowish white powder obtained was dried at 80°C in vacuum oven for 8 h. Yield: ~9 mg. This [Fe^{III}-(biuret-amide)] functionalized MSN will be simply denoted as Fe-MSN.

Similarly, one more click reaction was carried out with N3-MSN using propargyl alcohol. This product was denoted as PrOH-MSN.

(v) Detection of Hydrogen peroxide

Stock solutions: 50 mM solution of TBM was prepared in 0.1N aqueous hydrochloric acid. Hydrogen peoxide solutions of various concentrations were prepared in de-ionized water. 1 mg/mL of Fe-MSN catalyst solution was prepared in phosphate buffer (150 mM, pH 7) and particles were dispersed by sonication.

Procedure: In 1.5 mL eppendorf tubes 10 μL of TMB solution, 747 μL of de-ionized water, 133 μL of phosphate buffer (150 mM, pH 7), 200 μL hydrogen peroxide solutions of various concentrations and 10 μL of catalyst solution were mixed and allowed to stand at room temperature with occasional shaking for 15 min. At the 15^{th} min, the mixture was centrifuged and absorbance was noted at 650 nm.

(vi) Kinetics of TMB Oxidation

The kinetics were monitored in kinetic mode of the spectrophotometer (Perkin-Elmer –λ35) using 1 ml quartz cuvette of 1.00 cm path length at 650 nm (one of the absorption peaks of oxidized product of TMB) in an thermostatted (40.0 ± 0.5 °C) cell housing. Initial rates of TMB oxidation were calculated from the linear absorbance versus time plots using the extinction coefficients of 39000 $M^{-1}cm^{-1}$ which stands for oxidation product of TMB at 650 nm when the conversion of the TMB did not exceed 10 – 20%. 1 mg of Catalyst was dissolved in 1mL double distilled water and was treated as Stock solution. Concentration of H_2O_2 was calculated by dividing the UV absorbance at 240 nm by the characteristic molar extinction coefficient (ε = 43.6 dm^3 $M^{-1}cm^{-1}$). To investigate the mechanism assays, H_2O_2 variations was done from 4.7×10^{-3} to 3.5×10^{-1} M while keeping the TMB concentration fixed at 4.7×10^{-4} M. For TMB variation reveres procedure was followed ($[H_2O_2] = 4.0 \times 10^{-3}$ M; [TMB] = 2.8×10^{-5} – 2.8×10^{-4} M). In all kinetic runs, the catalyst concentration was kept constant. 10 µL stock catalyst solution was added in each set of H_2O_2 variation while 15 µL was added in case of TMB variation. Phosphate buffer having the appropriate pH of 4, 5, 6, 7 was used for different runs. For each set, after the reaction solution pH was measured with a pH meter (LABINDIA, PICO+) with calibrated electrode.

The kinetic parameters were calculated according to the equation, $v = V_{max} \times [S]/(K_m + [S])$ where v stands for initial rate or initial velocity, V_{max} is the maximal velocity, [S] is the concentration of the substrate and K_m is the Michaelis constant.

(vii) Detection of glucose

Stock solutions: 5mg/mL solution of glucose oxidase was prepared in phosphate buffer (10 mM, pH 7.4). 50 mM solution of TBM was prepared in 0.1N aqueous hydrochloric acid. Glucose and mannose solutions of various concentrations were prepared in phosphate buffer (10 mM, pH 7.4). 1mg/mL Fe-MSN catalyst solution was prepared in phosphate buffer (10 mM, pH 7.4) and particles were dispersed by sonication

Procedure: In 1.5 mL eppendorf tubes, 750 µL glucose solutions of various concentrations, 60 µL of glucose oxidase solution, 10 µL of TMB solution and 15 µL of catalyst solution were incubated at 37 °C with occasional shaking for 50 min. At 50^{th} min, reaction mixture was centrifuged and absorbance was noted at 650 nm.

(viii) Characterization techniques

Powder X-ray diffraction of all the samples was carried out in a PANalytical X'pert Pro dual goniometer diffractometer. A proportional counter detector was used for low angle experiments and an X'celerator solid state detector was employed in the low angle experiments. The radiation used was Cu Kα (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg–Brentano geometry (0.5 to 5°; 0.2° min^{-1}). Care was taken to avoid sample displacement effects. SEM images were obtained on Leica Stereoscan 440 microscope. HR-TEM images were taken on a FEI Technai F30 operating at 300 kV with FEG. The samples were prepared by dispersing a large number of solid particles in isopropanol by sonication, and dropping the resulting suspension on a copper grid of 400 mesh and allowed to dry in air. Nitrogen adsorption and desorption studies were carried out at 100°C using Quantachrome instrument. Samples were preheated at 100°C for 18 hours in the vacuum line. Single point BET surface area was obtained from the nitrogen adsorption-desorption data at P/P_0 ~0.249. Pore size distributions were calculated using the BJH method. Semi-quantitative FT-IR spectra were recorded on Perkin Elmer FT-IR spectrum GX instrument by making KBr pellets. Pellets were prepared by mixing 3 mg of sample with 97 mg of KBr. Yields for CuAAC reactions were calculated from corrected area under the curve characteristic for the azide stretch at ~2100 cm^{-1}. ICP experiments were performed on a Thermo IRIS Intrepid spectrum apparatus. In a typical procedure, sample was prepared by heating a known amount of solid sample in 20 mL aqua-regia to demetalate the Fe^{+3} ions from the ligand environment and then mixture was concentrated to about 3 mL by heating. This was subsequently diluted with de-ionized water and then filtered to make and the volume up to 10 mL using de-ionized water for the quantitative analysis of Fe and Cu using the ICP instrument. UV-Vis experiments were carried out on Perkin Elmer PL Lambda 950 spectrophotometer using 1 mL cuvettes with 10 mm path length. Thermogravimetric analysis (TGA) of the silica nanoparticles were carried out using a TA Instrument SDT Q600 analyzer between 100 and 800°C in air (flow 25 ml min^{-1}) at a heating rate of 5° min^{-1}. All samples were stirred in water overnight, centrifuged and dried under

vacuum at 80°C overnight prior to TGA runs. The graft density of the grafted organic moitey on the silica surface was determined by TGA using the following equation:

$$\text{graft density (mmol/g)} = \frac{\left(\frac{W_{\text{grafted MSN(150-750)}}}{100 - W_{\text{grafted MSN(150-750)}}} \times 100\right) - \left(\frac{W_{\text{MSN(150-750)}}}{100 - W_{\text{MSN(150-750)}}} \times 100\right)}{M \times 100} \times 10^3$$

where $W_{\text{grafted MSN(150-750)}}$ is the weight loss between 150^0C and 750^0C corresponding to the decomposition of the organic moiety from silica surface corrected from the thermal degradation**,** and M is the molecular weight of the decomposed organic moiety, while $W_{\text{MSN(150-750)}}$ represents the weight loss of calcined silica without organic functional groups (CAL-MSN). EPR spectrum was recorded on a Bruker EMX X-band spectrometr operating at a field modulation of 100 kHz, modulation amplitude of 4 G and microwave radiation power of 4 mW. The solid Fe(III) complex was taken in a quartz: tube and the spectrum was recorded at 94 K.

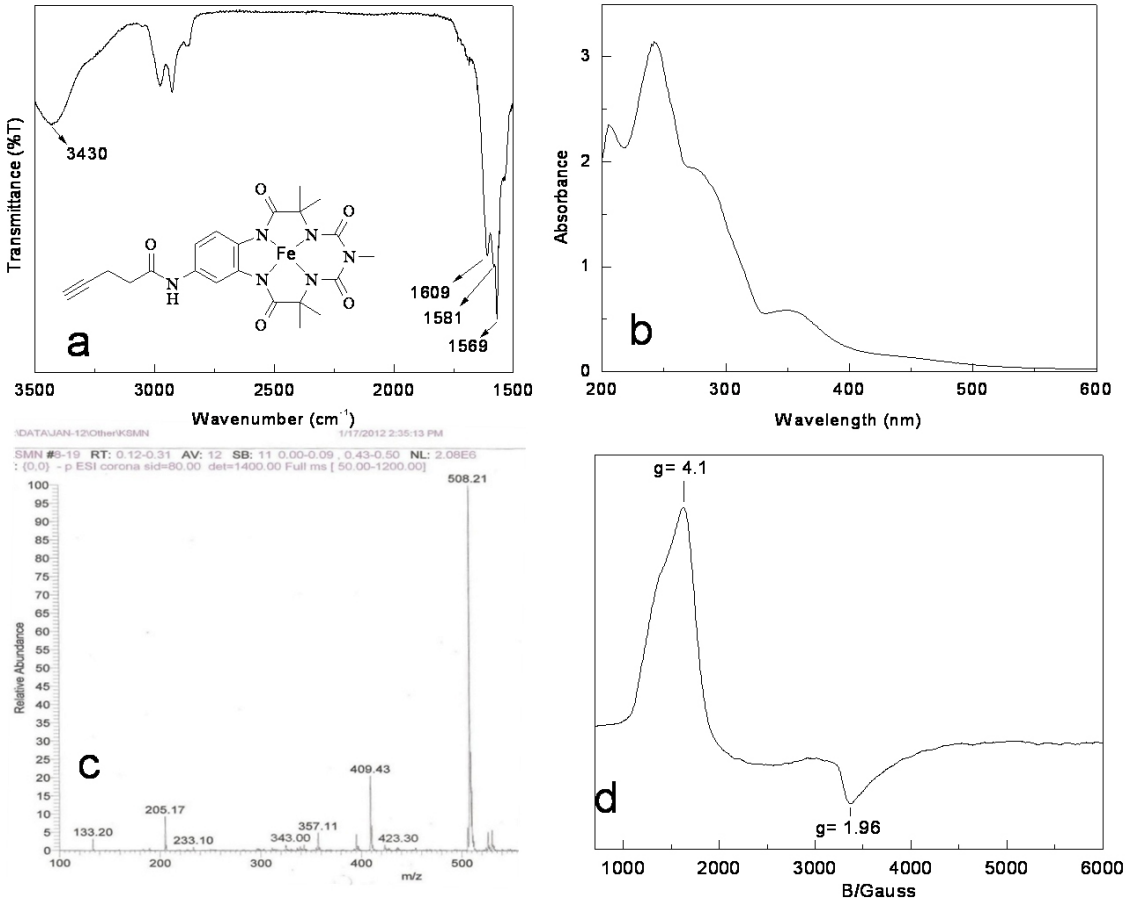


Figure S1. Characterization of alkyne tailed $(Et_4N)_2[Fe^{III}(\text{biuret-amide})]$ (**8**) by various techniques: a)FT-IR spectra of **8** in KBr pellet b)UV-Visible spectra of **8** in water (0.1 mM). c) ESI-MS of a solution of **8** in methanol (m/z 508.21). The axial chloro ligand is not observed as this ligand is labile and gets dissociated under the conditions of the mass spectrometry experiment. d) X-band EPR spectrum of **8** in acetonitrile at 90K.

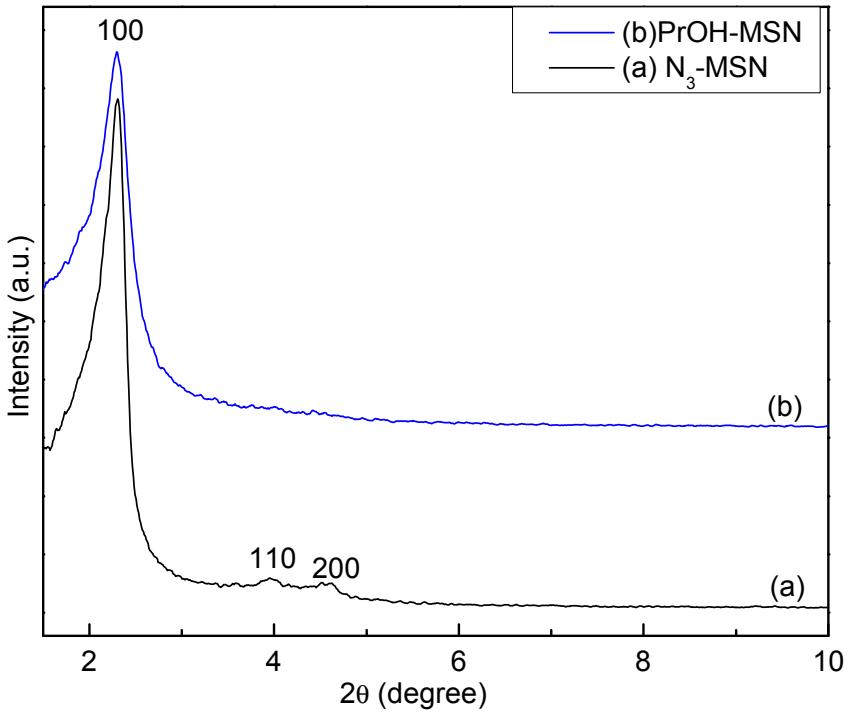


Figure S2. Powder XRD patterns of various MSN materials: (a) powder XRD patterns of N_3-MSN shows characteristic high intensity 100 peak at 2θ ~2.3º. The other significant peaks corresponding to 110 and 200 diffractions were also observed indicating that well-ordered two-dimensional hexagonal mesoporous channels were formed and remained intact under one pot co-condensation functionalization environment. (b) To characterize the click product by powder XRD, propargyl alcohol clicked MSNs (PrOH-MSN) were used to obtain p-XRD patterns. The p-XRD showed one intense (100) diffraction peak near 2θ~2.3° showing that the mesoporosity of the material does not change after under going click reaction.

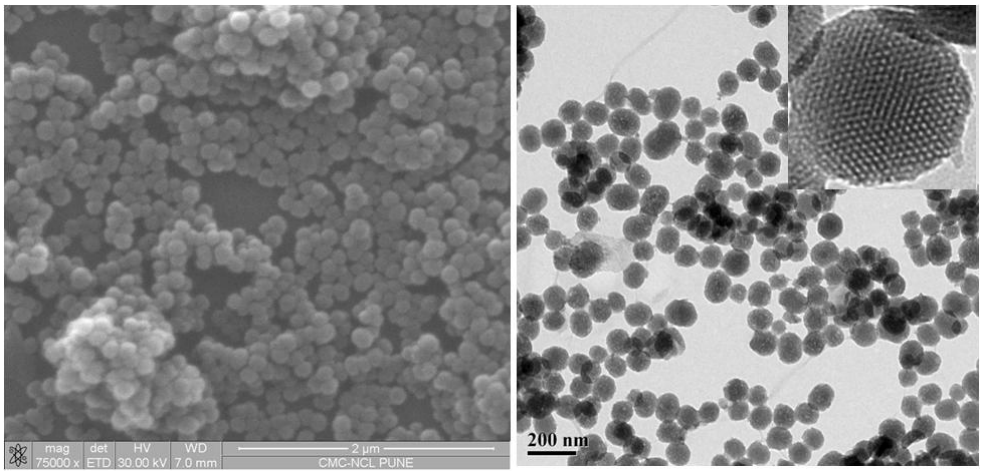


Figure S3. (a) SEM and (b) TEM images of N_3-MSN respectively

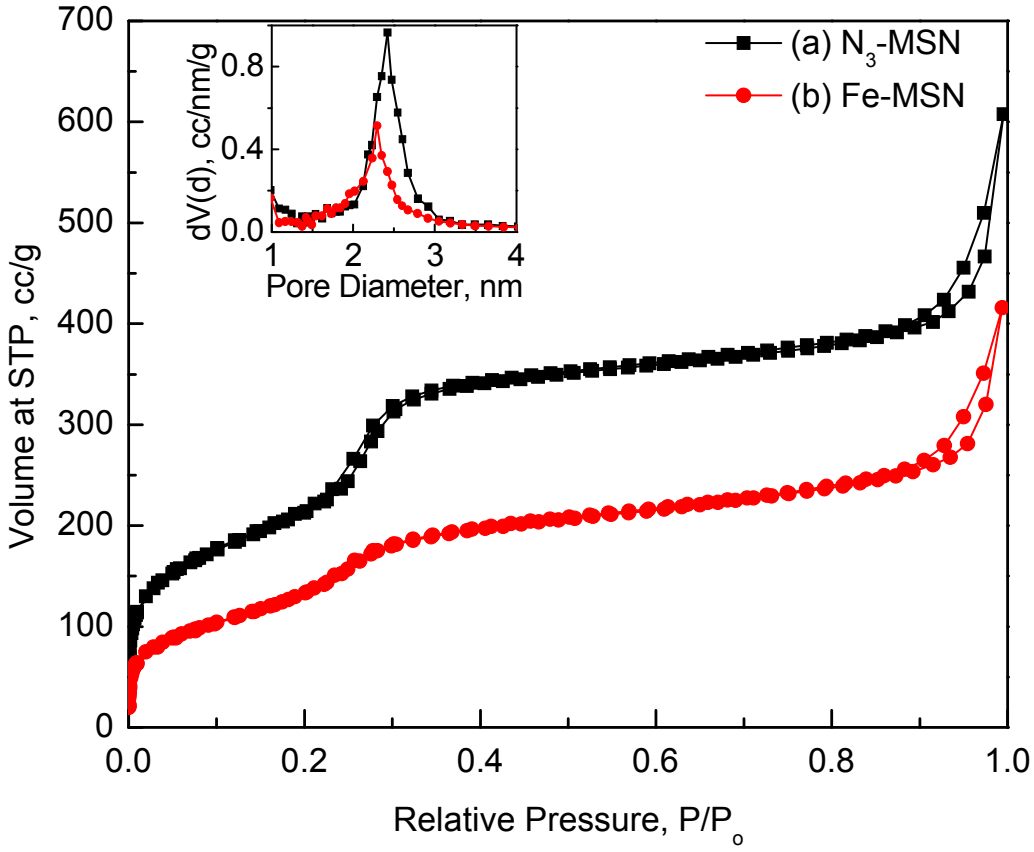


Figure S4. Nitrogen adsorption-desorption isotherms of (a) N_3-MSN and (b) Fe-MSN: Nitrogen adsorption-desorption studies of both solids showed type IV isotherm, characteristic of mesoporous materials. The BJH pore-size distribution (PSD) analysis shows very narrow PSD values in the range 2-3 nm. Physical properties of both MSN materials are listed in table S1.

Table S1. Physical properties of N_3-MSN and Fe-MSN materials

Sample Name	M_{BET} (m^2/g)	Pore Diameter (nm)	Pore Volume (cm^3/g)
N_3-MSN	724	2.4	0.93
Fe-MSN	517	2.3	0.64

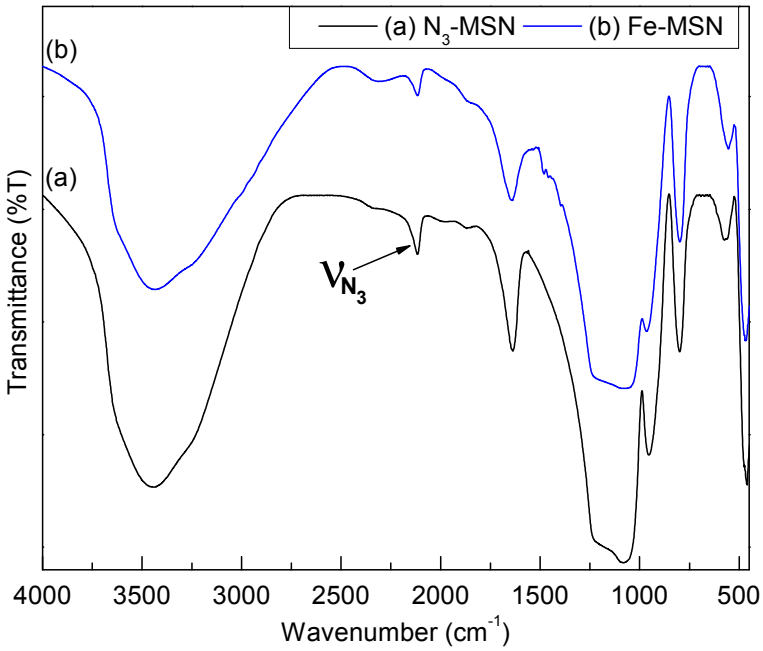


Figure S5. FT-IR spectra of (a) N_3-MSN and (b) Fe-MSN: IR spectroscopy shows about 50% decrease in the integrated intensity of $\nu_{as}(N_3)$ at 2100 cm^{-1} REF: JMC 2009

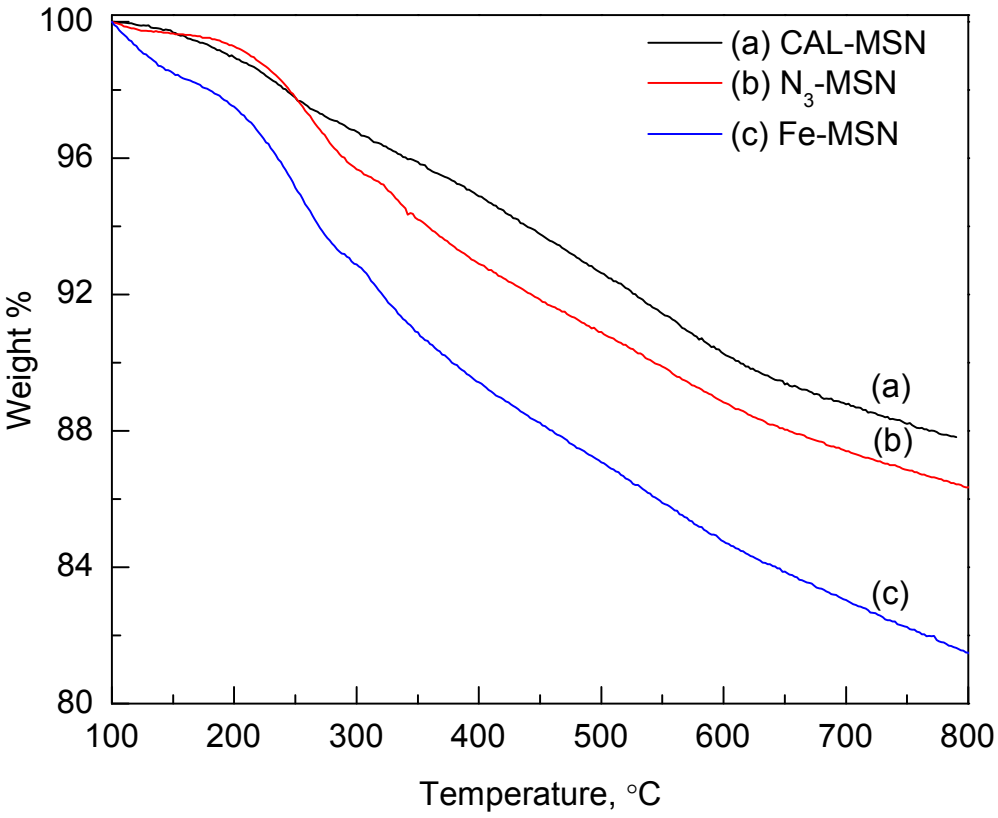


Figure S6. TGA graphs for various MSN materials (a) Calcined MSN (b) N_3-MSN and (c) Fe-MSN

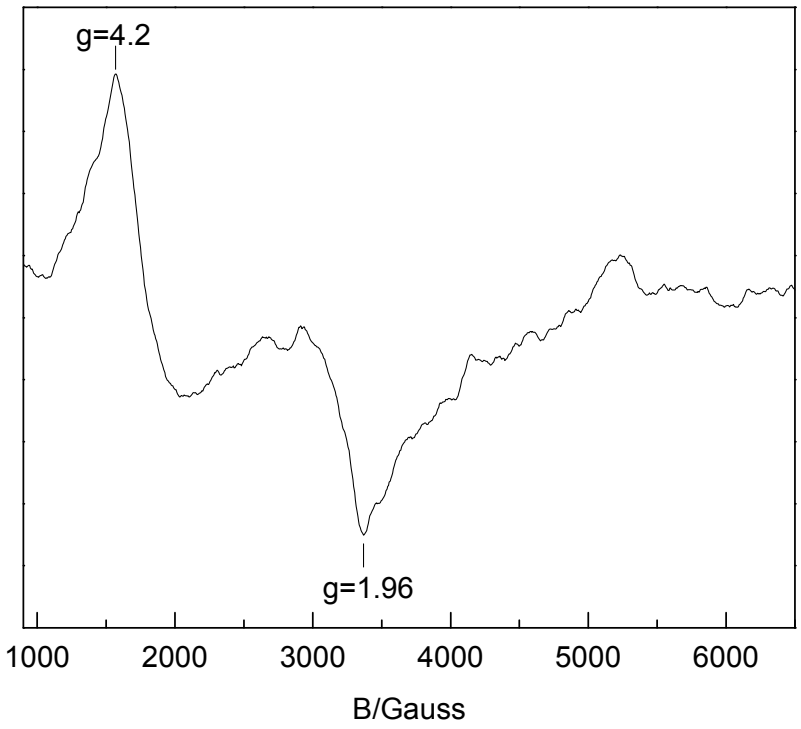


Figure S7: X-band EPR spectrum of Fe-MSN solid at 94K

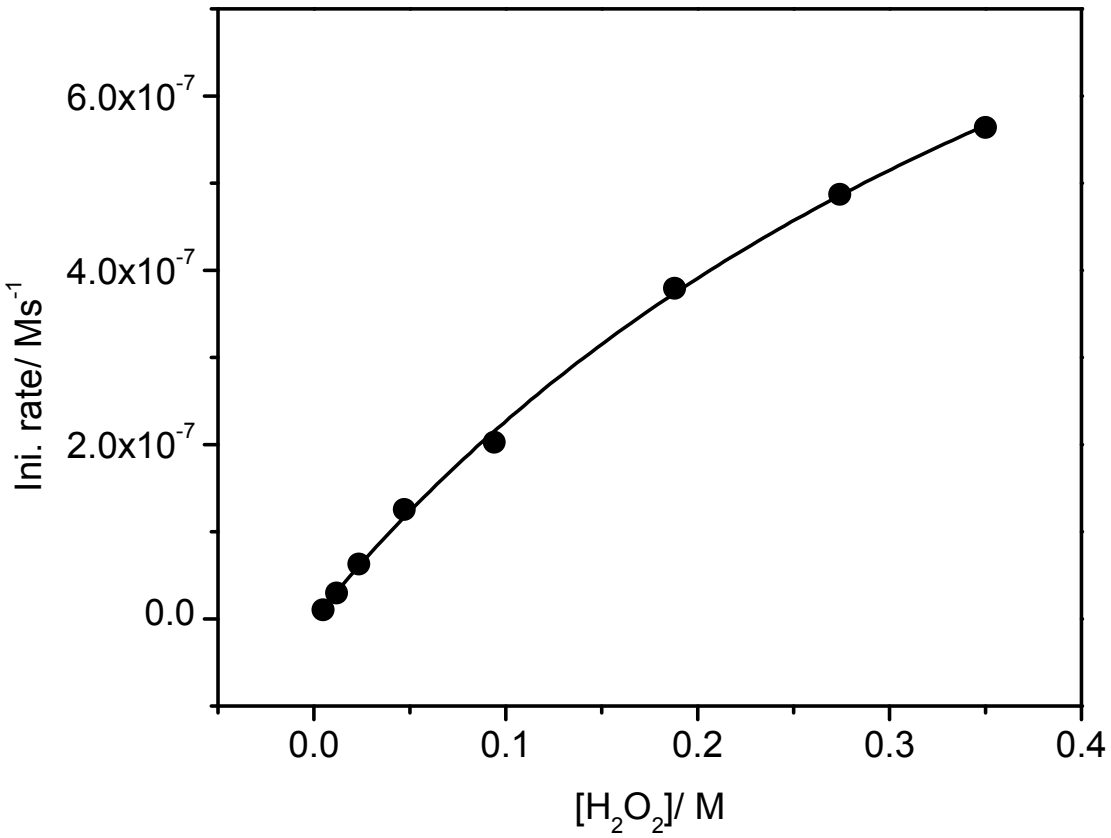


Figure S8. Polt of initial rate(v) *vs*. $[H_2O_2]$. Black dots were experimental points. The solid line was drawn according to the equation $v = V_{max} \times [S]/(K_m + [S])$. In all the kinetic runs, [TMB] = 4.7×10^{-4} M; 1 ml reaction solution contained 10 μL of 1mg/ ml catalyst solution. I = 10 mM; pH 7.4 (phosphate buffer); T = 40 °C

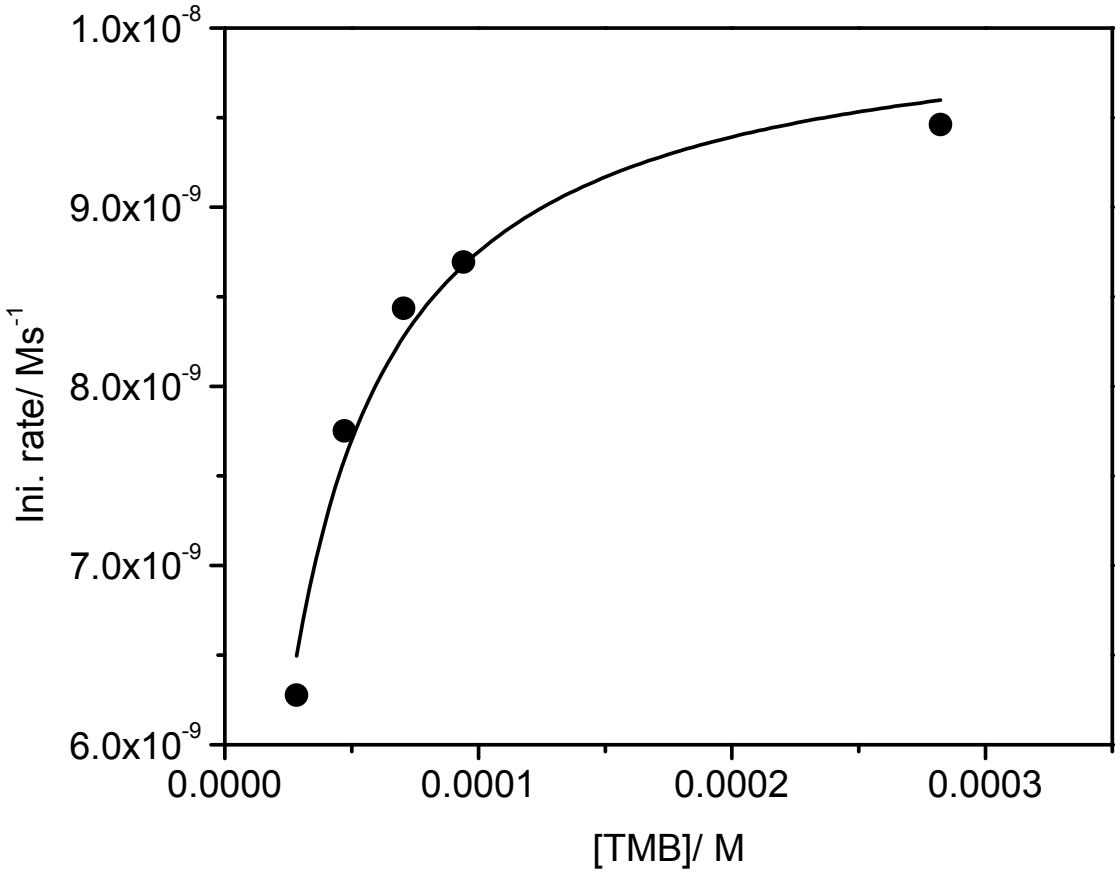


Figure S9. Plot of initial rate(v) *vs*. [TMB]. Black dots were experimental points. The solid line was drawn according to the equation $v = V_{max} \times [S]/(K_m + [S])$. In all the kinetic runs, $[H_2O_2] = 4.0 \times 10^{-3}$ M; 1 ml reaction solution contained 15 μL of 1mg/ ml catalyst solution. *I* = 10 mM; pH 7.4 (phosphate buffer); T = 40 °C (See Table 1)

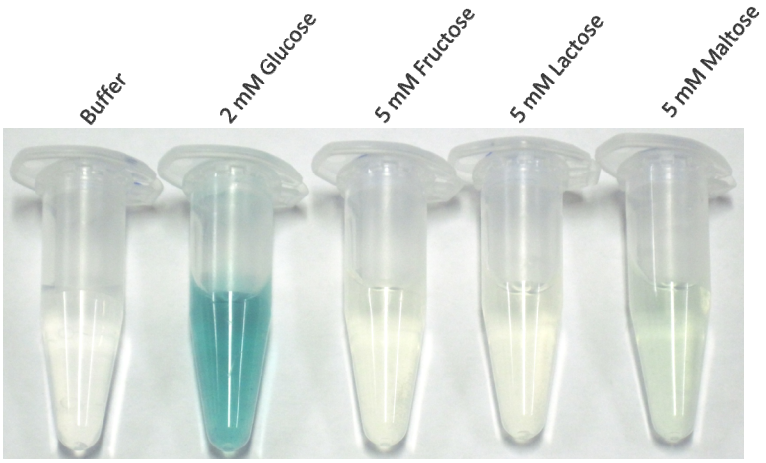
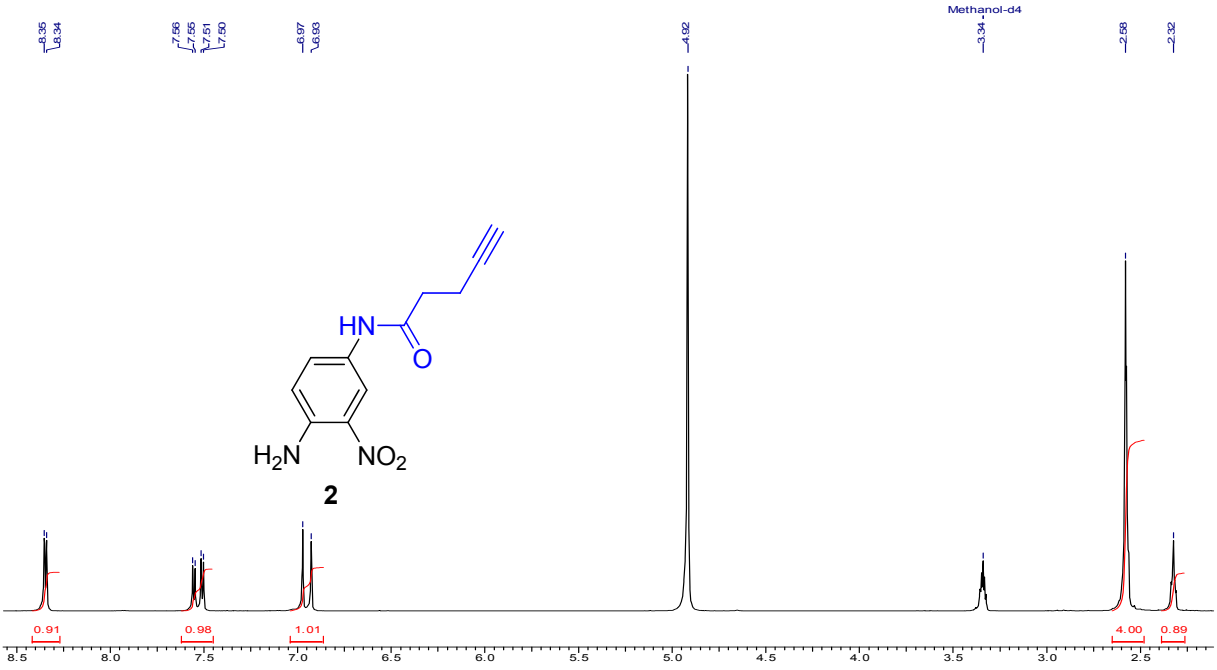
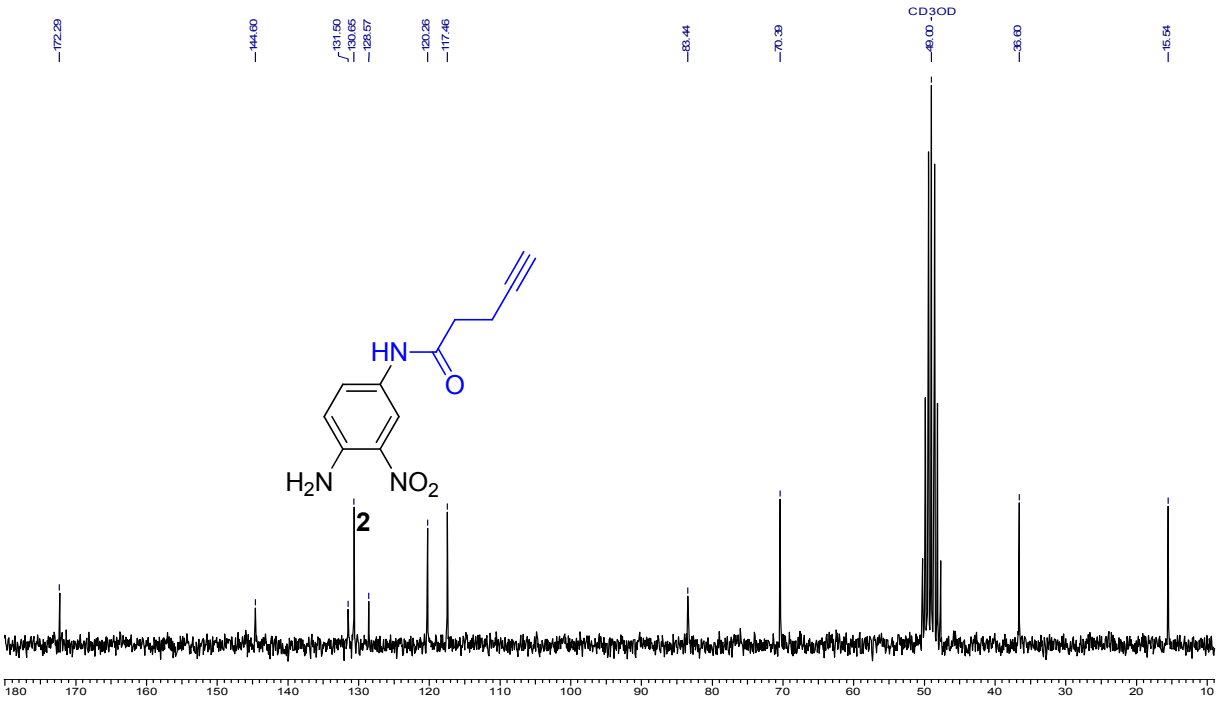
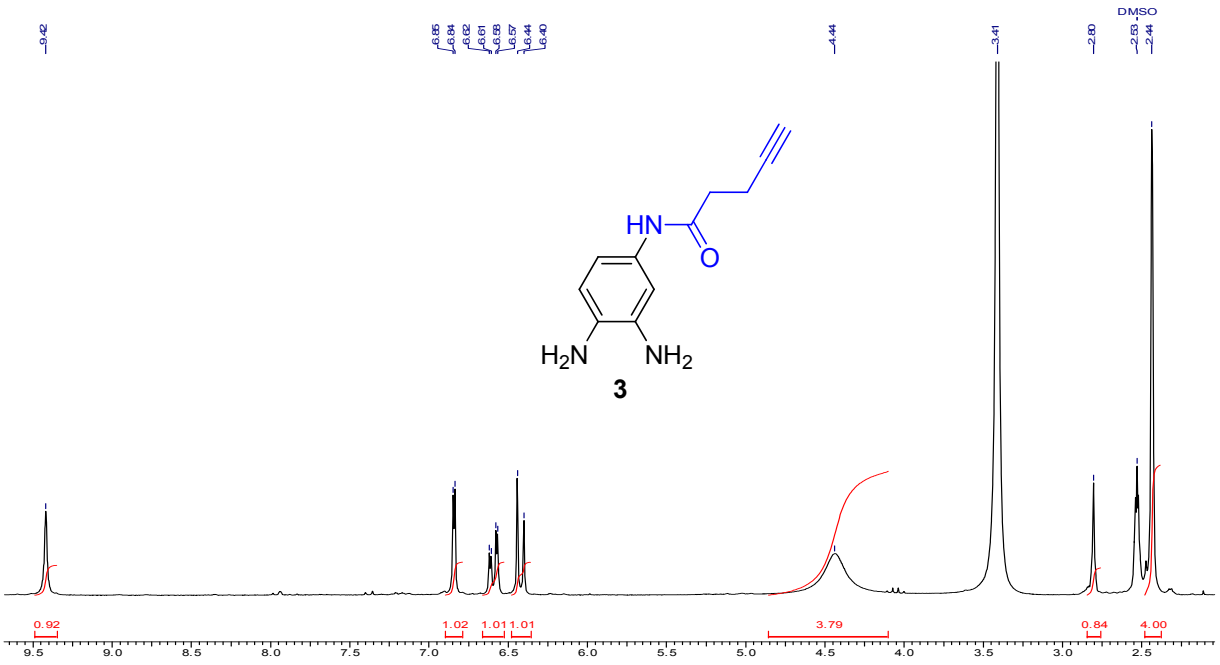


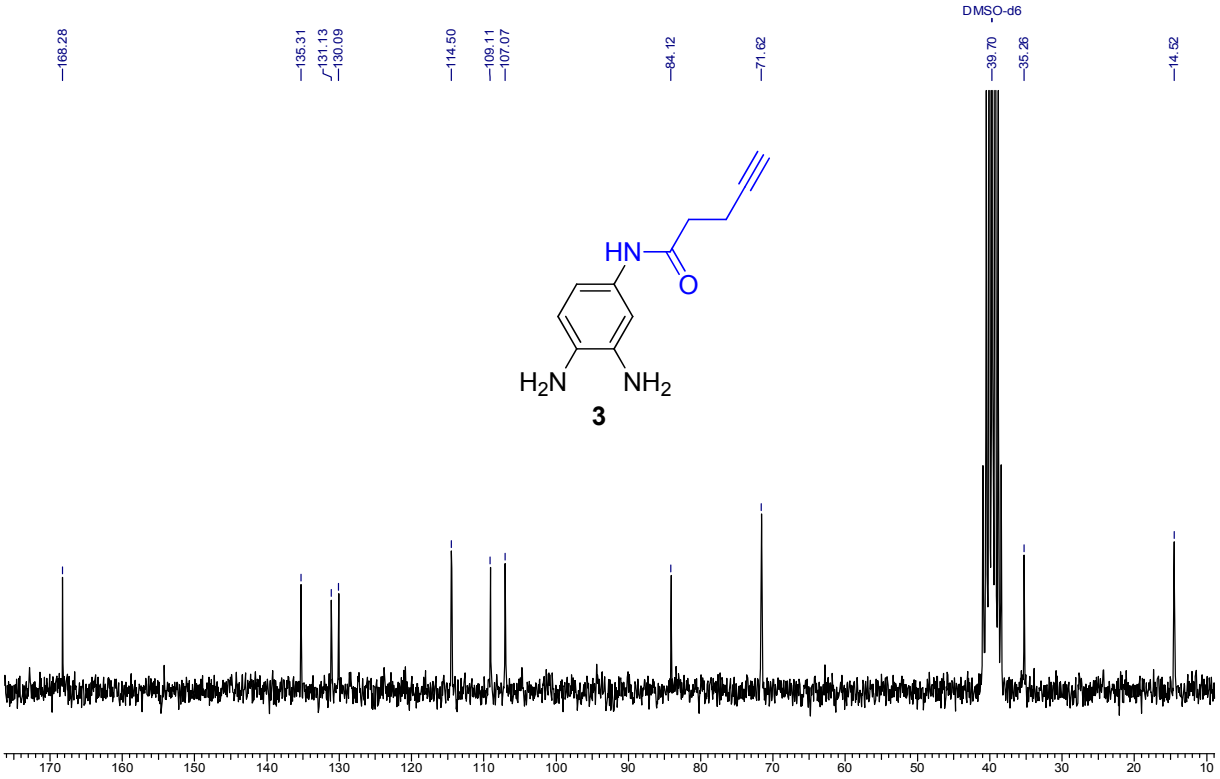
Figure S10. Typical photographs of glucose detection by the colorimetric method developed using GOX and Fe-MSN

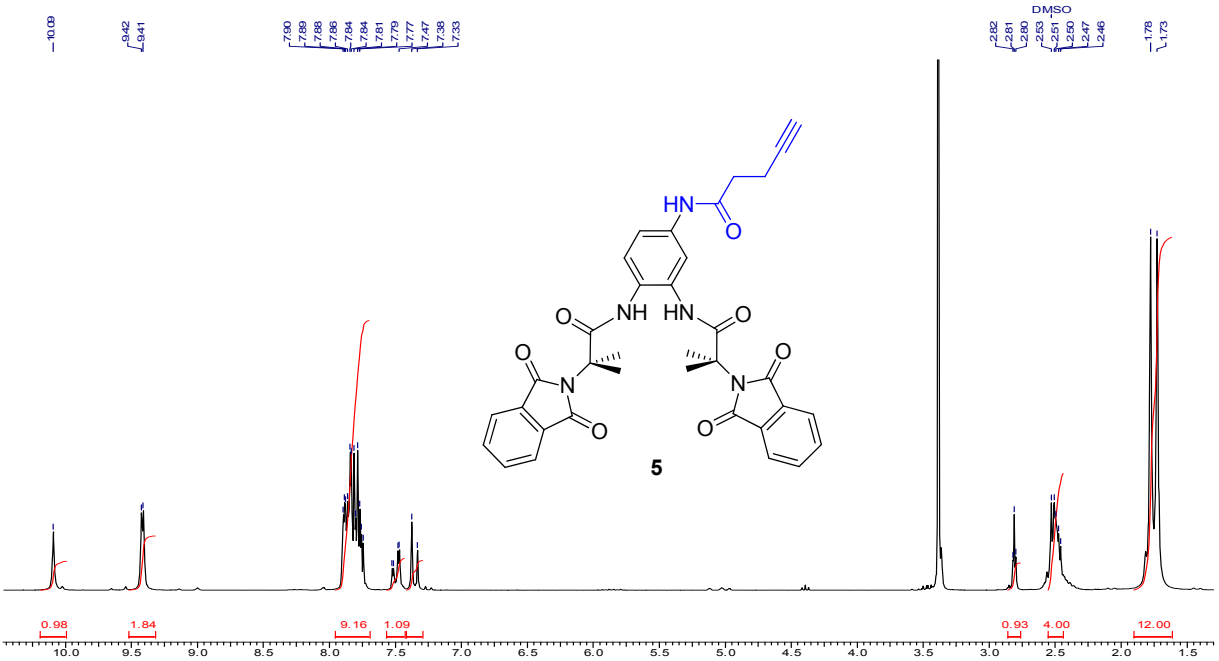
(viii) ^{1}H-NMR and ^{13}C-NMR Characterization of various compounds synthesized as shown in scheme S1

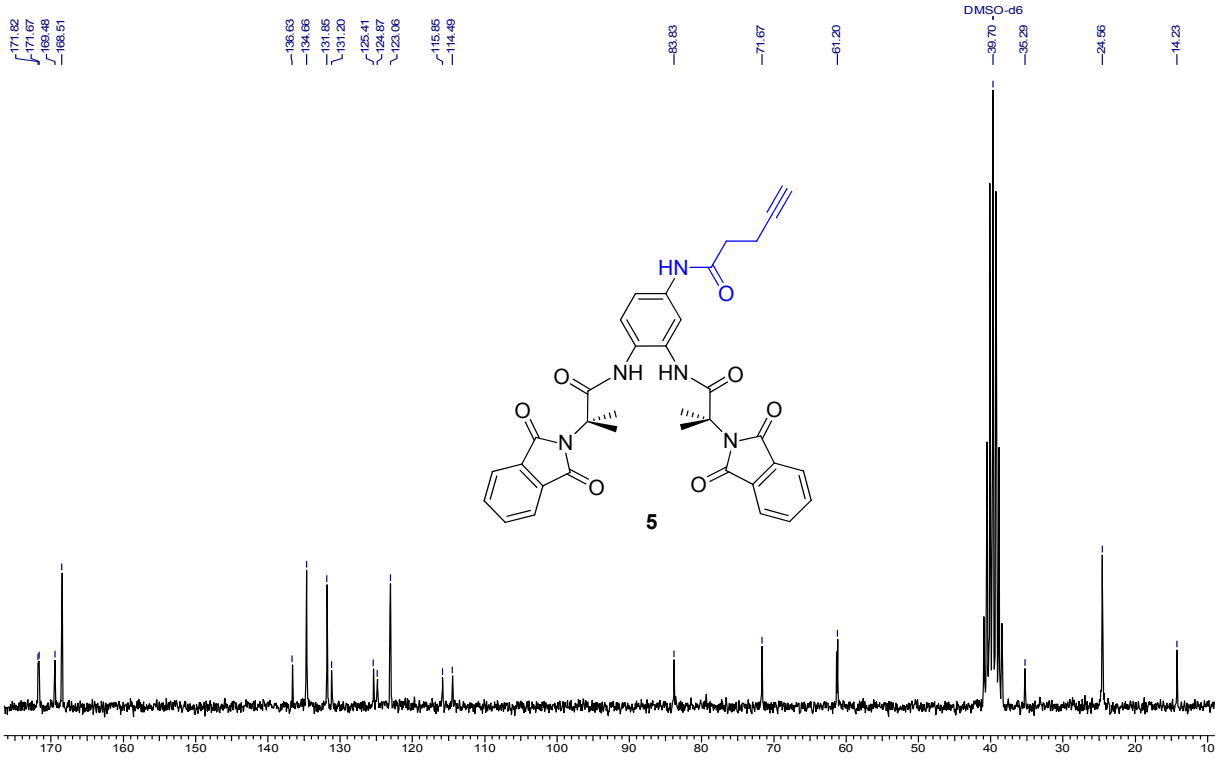


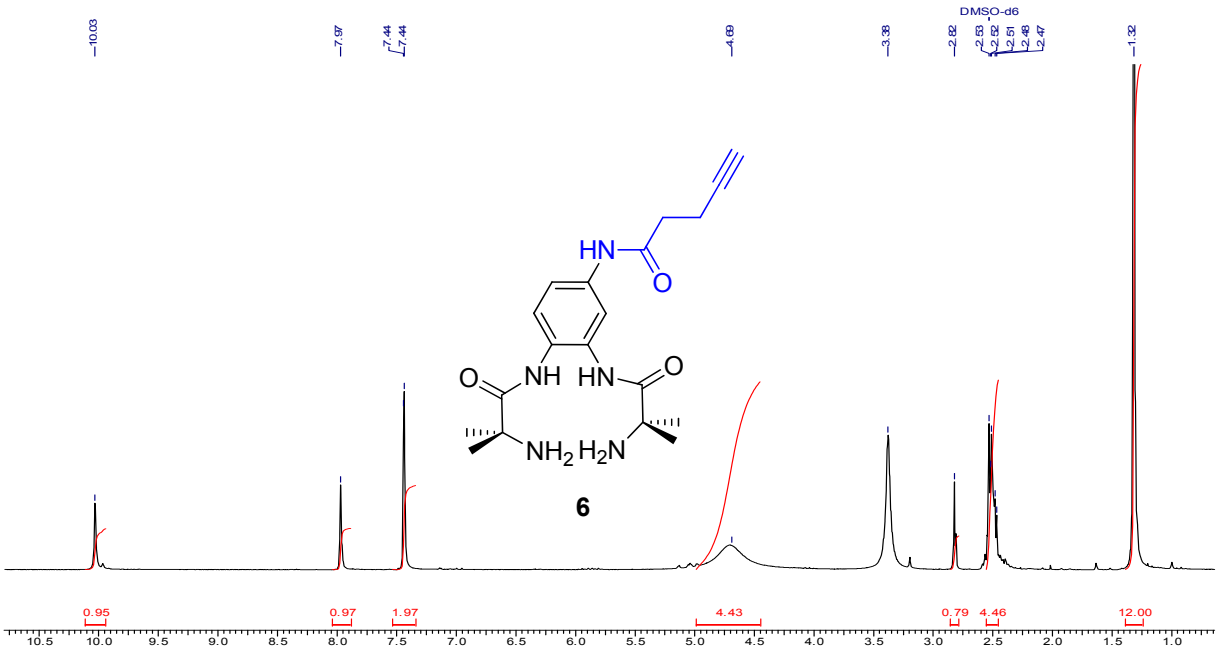



DMSO
HN
O
H_2N
NH_2
3
0.92
1.02
1.01
1.01
3.79
0.84
4.00

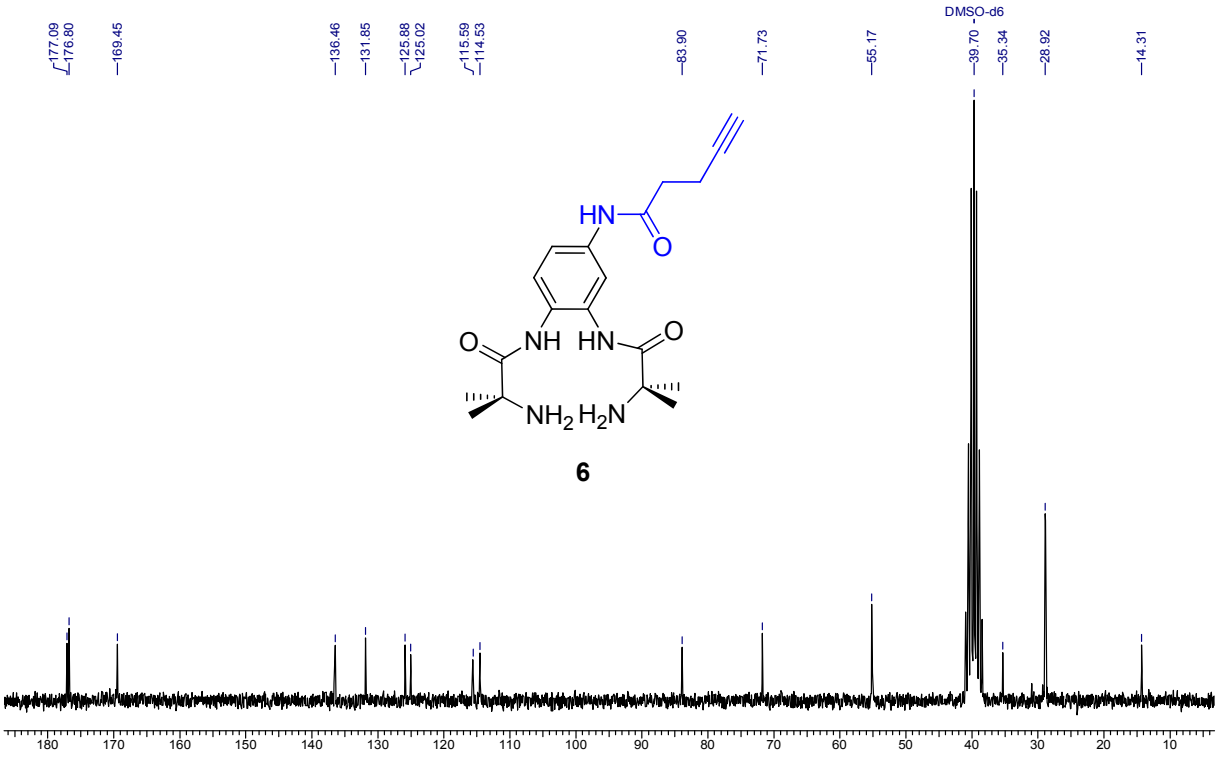

DMSO-d6
168.28
135.31
131.13
130.09
114.50
109.11
107.07
84.12
71.62
39.70
35.26
14.52
HN
O
H_2N
NH_2
3


10.09
8.42
8.41
7.90
7.89
7.88
7.86
7.84
7.84
7.81
7.79
7.77
7.47
7.38
7.33
DMSO
2.82
2.81
2.80
2.53
2.51
2.50
2.47
2.46
1.78
1.73
HN
O
NH
HN
O
N
O
5
0.98
1.84
9.16
1.09
0.93
4.00
12.00

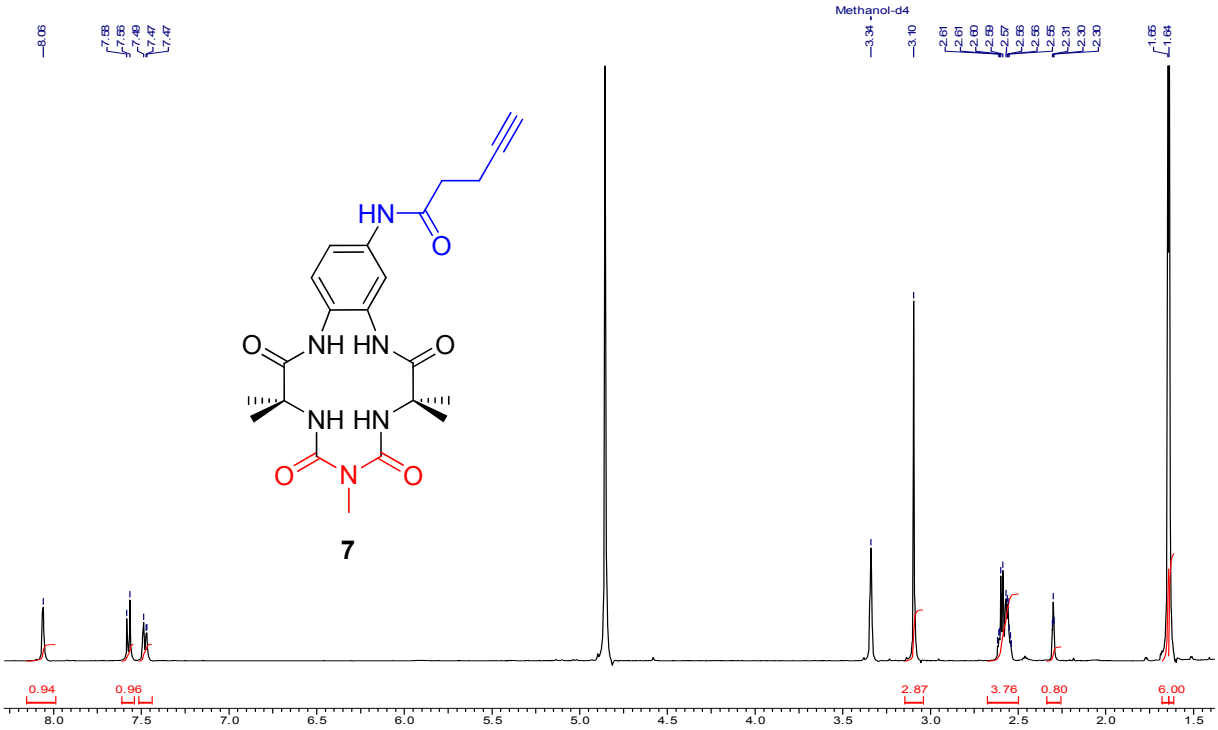

171.82
171.67
169.48
168.51
136.63
134.66
131.85
131.20
125.41
124.87
123.06
115.85
114.49
83.83
71.67
61.20
DMSO-d6
39.70
35.29
24.56
14.23
HN
O
NH
HN
O
N
O
5

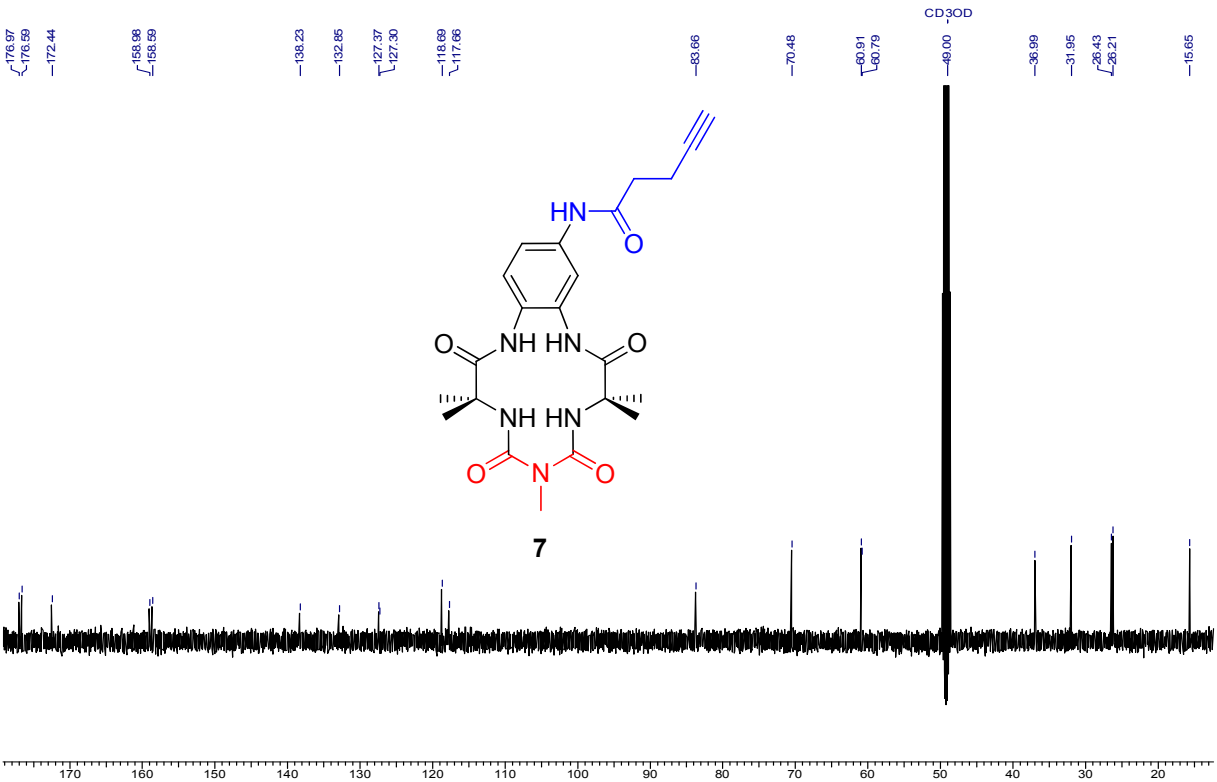

DMSO-d6
10.03
7.97
7.44
7.44
4.69
3.38
2.82
2.53
2.52
2.51
2.48
2.47
1.32
HN
O
O
NH
HN
O
NH2
H2N
0.95
0.97
1.97
4.43
0.79
4.46
12.00

6


DMSO-d6
177.09
176.80
169.45
136.46
131.85
125.88
125.02
115.59
114.53
83.90
71.73
55.17
39.70
35.34
28.92
14.31
HN
O
O
NH
HN
O
NH2
H2N

6


Methanol-d4
HN
O
NH HN
O
O
NH HN
O
N
O
7
0.94
0.96
2.87
3.76
0.80
6.00


CD3OD
HN
O
NH HN
O
O
NH HN
O
N
O
7

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