

Electronic Supporting Information

Bis-triazole appended azobenzene chromophore for selective sensing of copper (II) ion

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Experimental details

Synthesis of N, N-dipropargyl aniline (2)

In a three-necked round-bottomed flask, equipped with a stirrer, dropping funnel, and a reflux condenser topped by a calcium chloride tube, is placed 15.83 g of potassium carbonate (114 mmol) in dry acetone (80 ml). To a stirred mixture 1.78 g of aniline (19 mmol) then 5 g of propargyl bromide (42 mmol) is added dropwise with stirring and reflux for two days with catalytic amount of potassium iodide. Then the reaction mixture was poured into the crushed ice and extracted with ethyl acetate. The solvent was removed by rotary evaporator; the crude product was subjected to column chromatography using ethyl acetate: hexane (1:5) as solvent mixture to obtain a pale yellow liquid as product, weighs 1.9g (56%). ¹H NMR (300 MHz, CDCl₃) δ (ppm) : 2.22 (s, C≡C-H), 4.09 (s, -CH₂-), 6.95(m, Ar-H), 7.24 (d, J= 8.7 Hz, Ar-H). ¹³C NMR (300 MHz, CDCl₃; Me₄Si) δ (ppm): 43.45, 76.64, (aliphatic), 118.33, 125.23, 157.54 (aromatic). Anal. Calcd(%) for C₁₂H₁₁N: C 85.17, H 6.55, N 8.28. Found: C 85.29, H 6.70, N 8.01.

Synthesis of 4-((4-nitrophenyl) diazenyl)-N, N-dipropargyl aniline (6)

The diazonium salt of 4-nitroaniline was prepared by adding an aqueous solution of sodium nitrite (0.269 g, 3.9 mmol) drop wise into a solution of 4-nitroaniline (0.490 g, 3 mmol) dissolved in HCl: H₂O mixture. The mixture was stirred at 0 °C for 30 min. The diazonium salt solution was added drop wise into a solution containing 500 mg of N, N-dipropargyl aniline (2), 100 mg (1.2 mmol) of sodium acetate, 4 ml of water, and 13.1 ml of ethanol immediately the color of the solution turned to red, and in a few seconds a red-

orange crystalline precipitate of the azo compound formed. The mixture was allowed to stir for another hour and the reaction mixture poured into an excess amount of water. The precipitate was collected by filtration and washed with water repeatedly. The crude product was subject to column chromatography using solvent mixture of (1: 10) ethyl acetate and hexane to obtain as fine red-orange needles with yield of 86% (0.8g) and melts at 138-139° C. ¹H NMR (300 MHz, CDCl₃) δ (ppm) : 2.24 (s, C≡C-H), 4.17 (s, -CH₂-), 6.94(d, J=7.8 Hz, Ar-H), 7.8 (d, j=6.8 Hz, Ar-H), 8.2 (d, J= 7.8 Hz, NO₂-Ar-H), ¹³C NMR (300 MHz, CDCl₃; Me₄Si) δ (ppm): 39.26, 72.11(aliphatic), 112.90, 121.89, 123.67, 124.63, 144.41, 146.86, 149.70, 155.38 (aromatic). Anal. Calcd (%) for C₁₈H₁₄N₄O₂: C 67.91, H 4.43, N 17.60, O 10.05. Found: C 67.77, H 4.77, N 17.32, O 10.14.

Synthesis of 4-((phenyl) diazenyl)-N, N-dipropargylaniline (5)

The aforementioned procedure was performed for the synthesis of 4-((phenyl)diazenyl)-N,N-dipropargyl aniline as orange yellow needle like crystals with yield of 73% and melts at 110° C. ¹H NMR (300 MHz, CDCl₃) δH (ppm) : 2.22 (s, C≡C-H), 4.15(s, N-CH₂), 6.96(d, J= 8.7 Hz, Ar-H), 7.41 (m, Ar-H), 7.83 (dd, N-Ar-N), ¹³C NMR (300 MHz, CDCl₃; Me₄Si) δ (ppm): 40.31, 72.92(aliphatic), 114.35, 122.43, 124.46, 128.97, 129.96, 145.69, 149.74, 155.03 (aromatic). Anal. Calcd(%) for C₁₈H₁₅N₃: C 79.10, H 5.53, N 15.37. Found: C 78.88, H 5.64, N 15.48.

Synthesis of 6-azidohexanol

6-bromohexanol (15g, 82 mmol) and sodium azide (1.85g, 248 mmol) were dissolved in a DMF solution and the resulting solution was stirred overnight at 60° C. The reaction mixture was cooled and poured into ice water and extracted with ethyl acetate (3 x 50 mL). The organic layers collected were dried over sodium sulfate, after removal of the solvent under reduced pressure; 6-azidohexanol was isolated as light yellow oil with yield of 77%.

Synthesis of receptor II

6-azidohexanol (0.282g, 1.9 mmol) and 4-((4-nitrophenyl) diazenyl)-N, N-dipropargyl aniline (6) (0.25g, 0.7 mmol) were dissolved in tert-butanol: H₂O (10: 5 mL). CuSO₄•5H₂O (0.0494g, 20 mol%) and

sodium ascorbate (0.0792 g, 10 mol%) were added and the solution was stirred for 2 days at room temperature. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into ice water. The combined organic layers were washed with water and extracted with ethyl acetate, dried over sodium sulfate and the solvent was evaporated. The compound was dried in vacuum to give the desired product as a dark red syrupy liquid and purified by column chromatography using chloroform and ethyl acetate as solvent mixture in ratio the of 80:20 with 74% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 1.36 (m, $-\text{CH}_2-$) 3.60 (t, $-\text{CH}_2-\text{O}$), 4.34 (t, $-\text{CH}_2-$), 4.84 (s, $-\text{N}-\text{CH}_2-\text{C}-$), 6.98 (d, Ar-H), 7.93(d, Ar-H), 8.33 (s, triazole ring). ^{13}C NMR (300 MHz, CDCl_3 ; Me_4Si) δ (ppm): 20.78, 24.91, 25.95, 30.01, 32.01, 36.75, 46.58, 50.34, 62.27 (aliphatic), 112.90, 122.81, 123.67, 124.63, 125.97, 144.62, 147.40, 151.38, 156.46, 163.19 (aromatic) 176.85 (triazole ring). Anal. Calcd(%) for $\text{C}_{30}\text{H}_{40}\text{N}_{10}\text{O}_4$: C 59.9, H 6.67, N 23.16, O 10.58. Found: 59.38, H 6.71, N 23.29, O 10.62.

2.7. Synthesis of receptor I

The similar procedure for synthesis of receptor II was adopted for the preparation of receptor I. ^1H NMR (300 MHz, CDCl_3) δ (ppm) : 1.38 (m, $-\text{CH}_2-$) 3.56 (t, $-\text{CH}_2-\text{O}$), 4.34 (t, $-\text{CH}_2-$), 4.80 (s, $-\text{N}-\text{CH}_2-\text{C}-$), 6.98 (d, $J = 9.3$ Hz, Ar-H), 7.86(d, $J = 6.3$ Hz, Ar-H), 7.91(s, triazole ring). ^{13}C NMR (300 MHz, CDCl_3 ; Me_4Si) δ (ppm): 20.78, 24.91, 25.95, 30.01, 32.01, 36.75, 46.58, 50.34, 62.27 (aliphatic), 112.90, 122.81, 123.67, 124.63, 125.97, 144.62, 147.40, 151.38, 156.46, 163.19 (aromatic) 176.85 (triazole ring). Anal. Calcd (%) for $\text{C}_{30}\text{H}_{41}\text{N}_9\text{O}_2$: C 64.38, H 7.38, N 22.52, O 5.72. Found: 64.52, H 7.85, N 22.07, O 5.56.

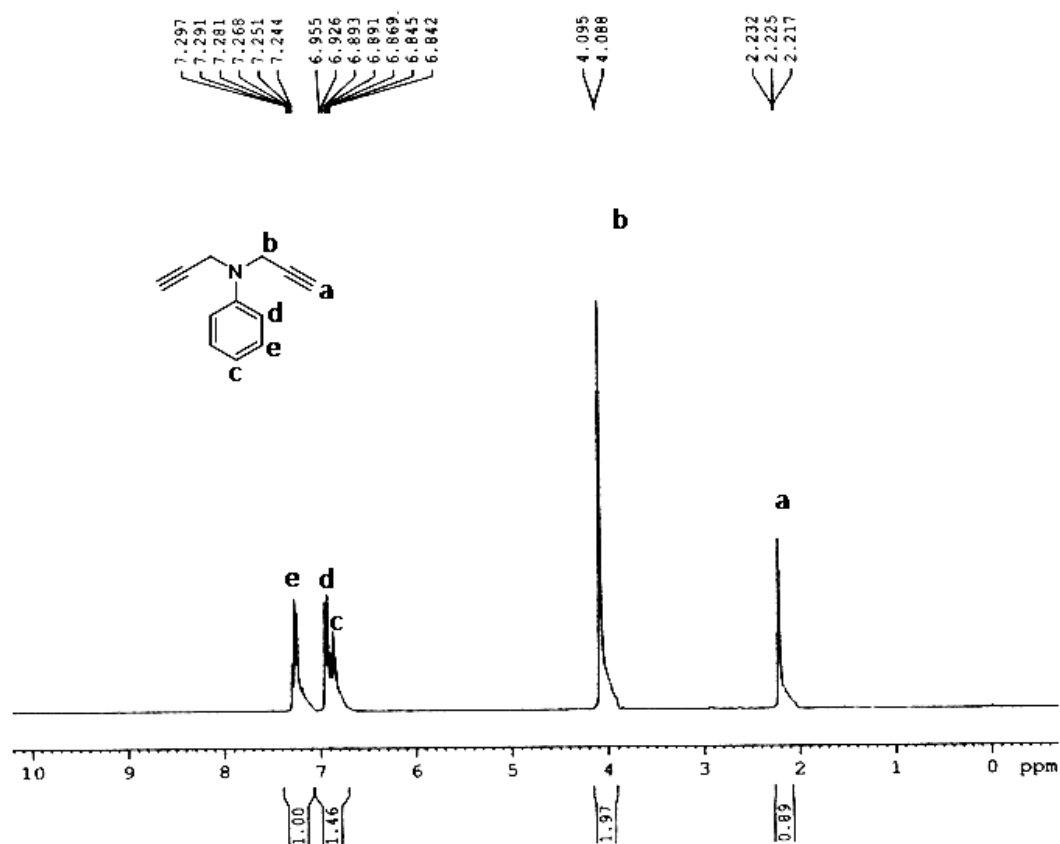


Figure S1. ^1H - NMR spectrum of N,N-dipropargyl aniline (2).

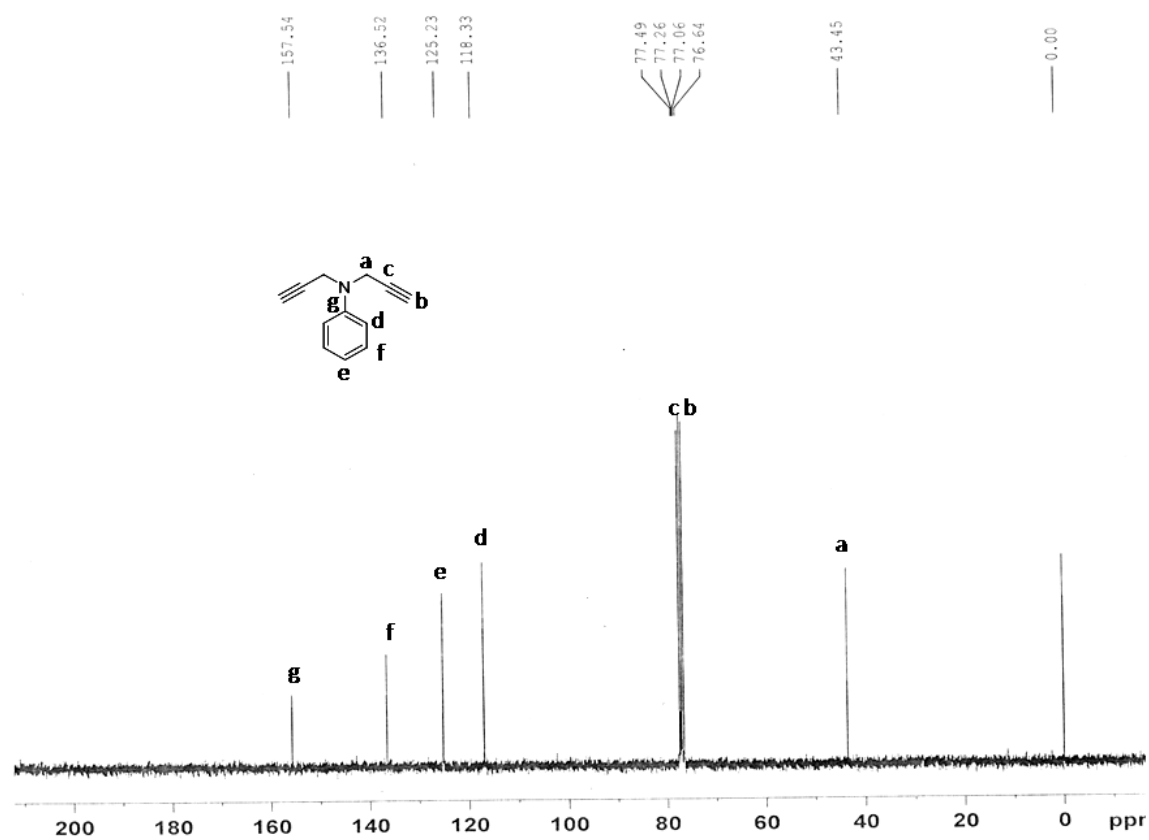


Figure S2. ^{13}C -NMR spectrum of N, N-dipropargyl aniline (2).

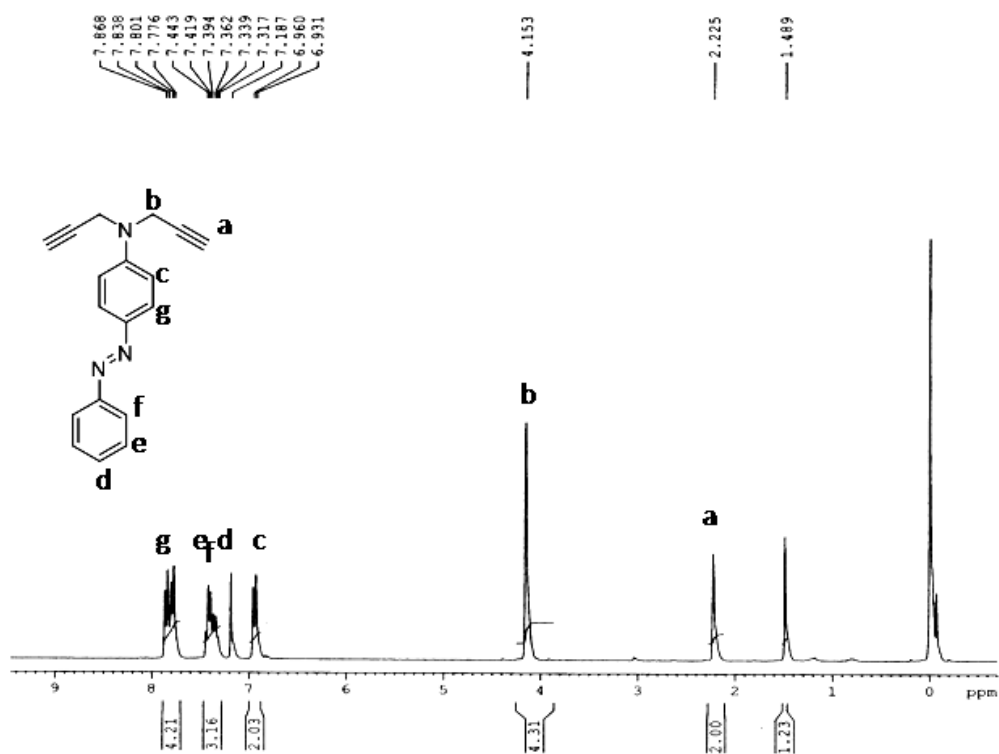


Figure S3. ^1H - NMR spectrum of 4-((phenyl)diazenyl)-N,N-dipropargylaniline(5)

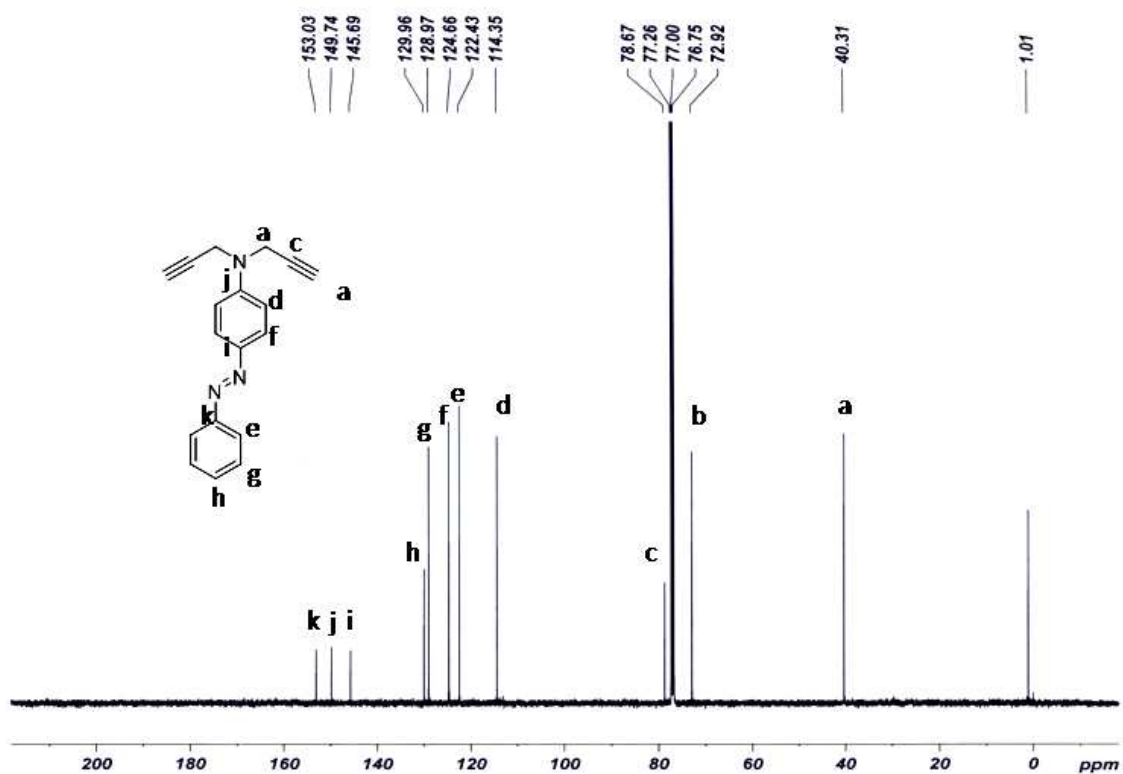


Figure S4. ^{13}C - NMR spectrum of 4-((phenyl)diazenyl)-N,N-dipropargylaniline(5)

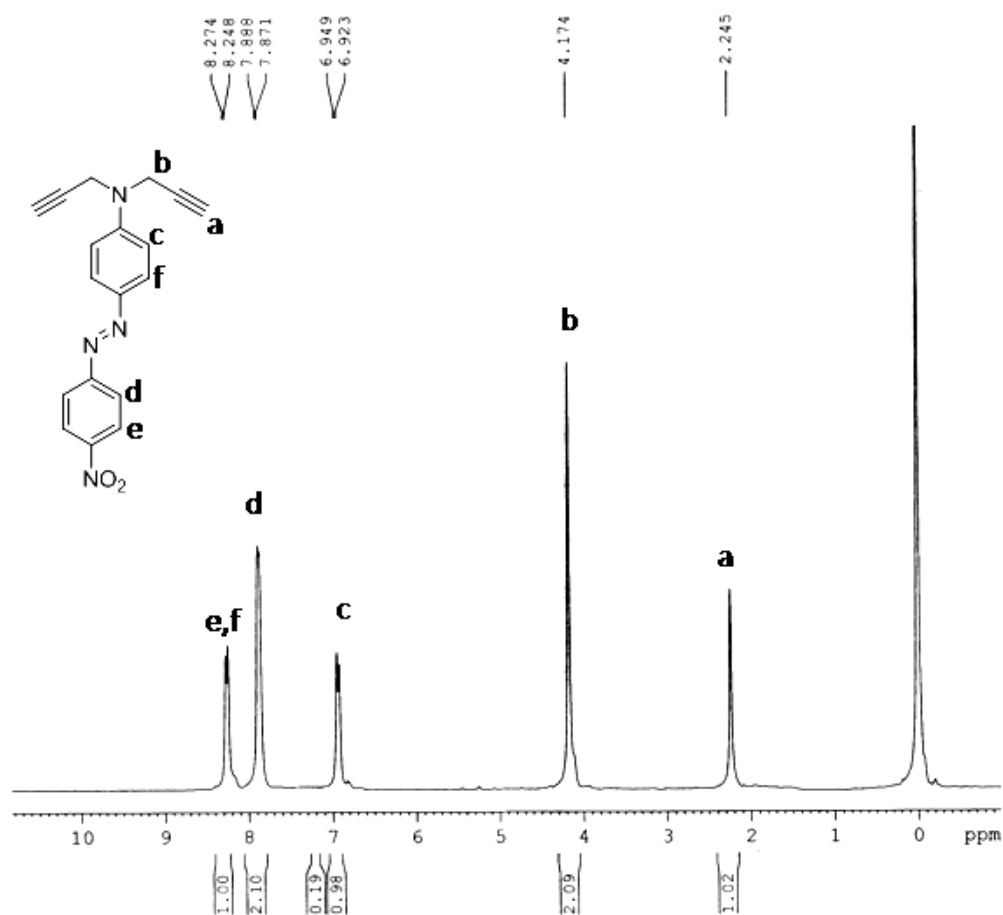


Figure S5. ¹H-NMR spectrum of 4-((4-nitrophenyl)diazenyl)-N,N-dipropargylaniline (6).

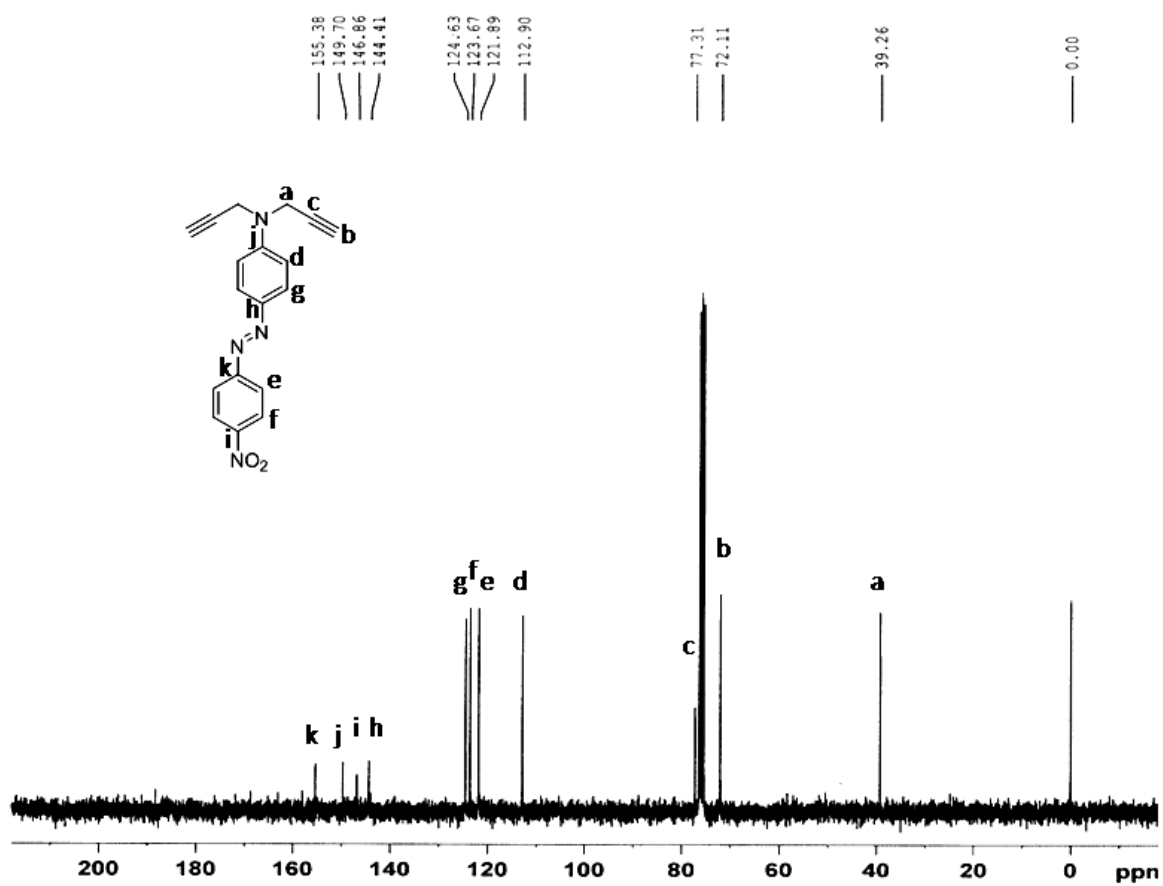


Figure S6. ^{13}C -NMR spectrum of 4-((4-nitrophenyl)diazenyl)-N,N-dipropargylaniline (6).

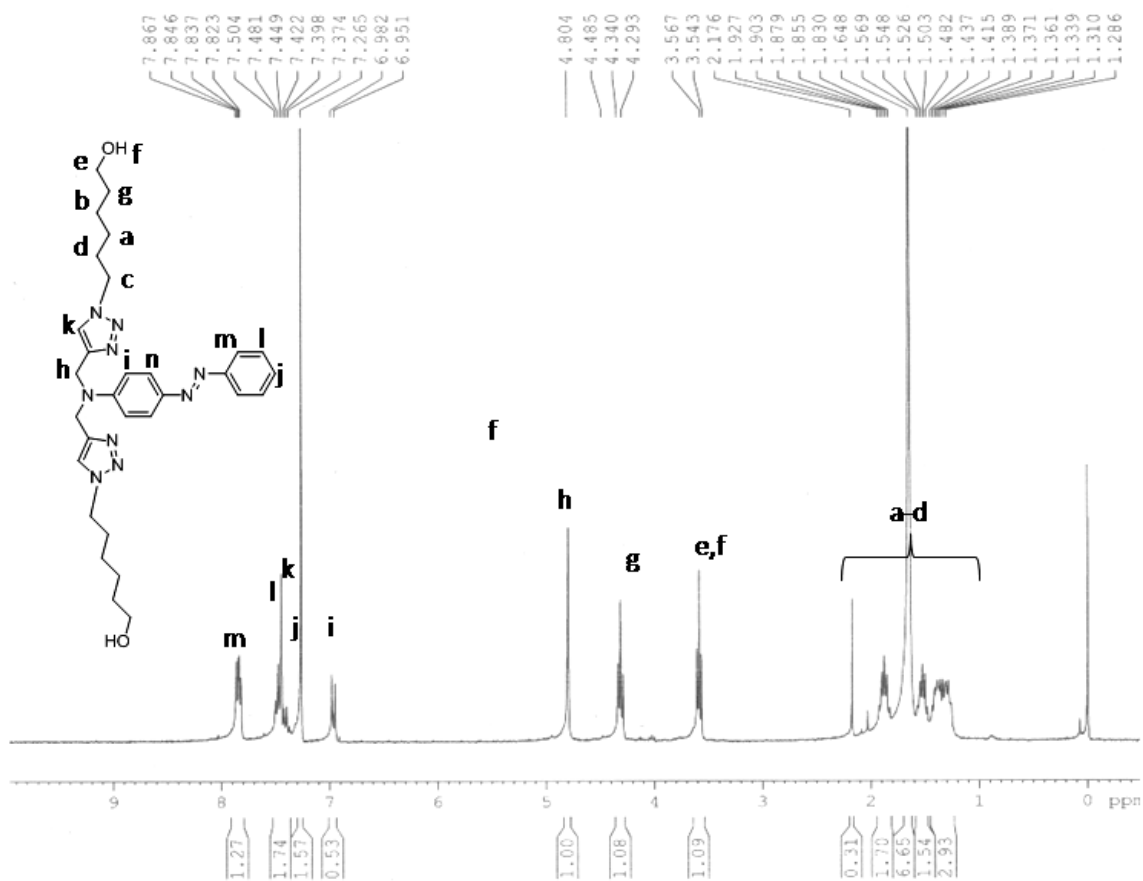


Figure S7. ¹H-NMR spectrum of receptor I.

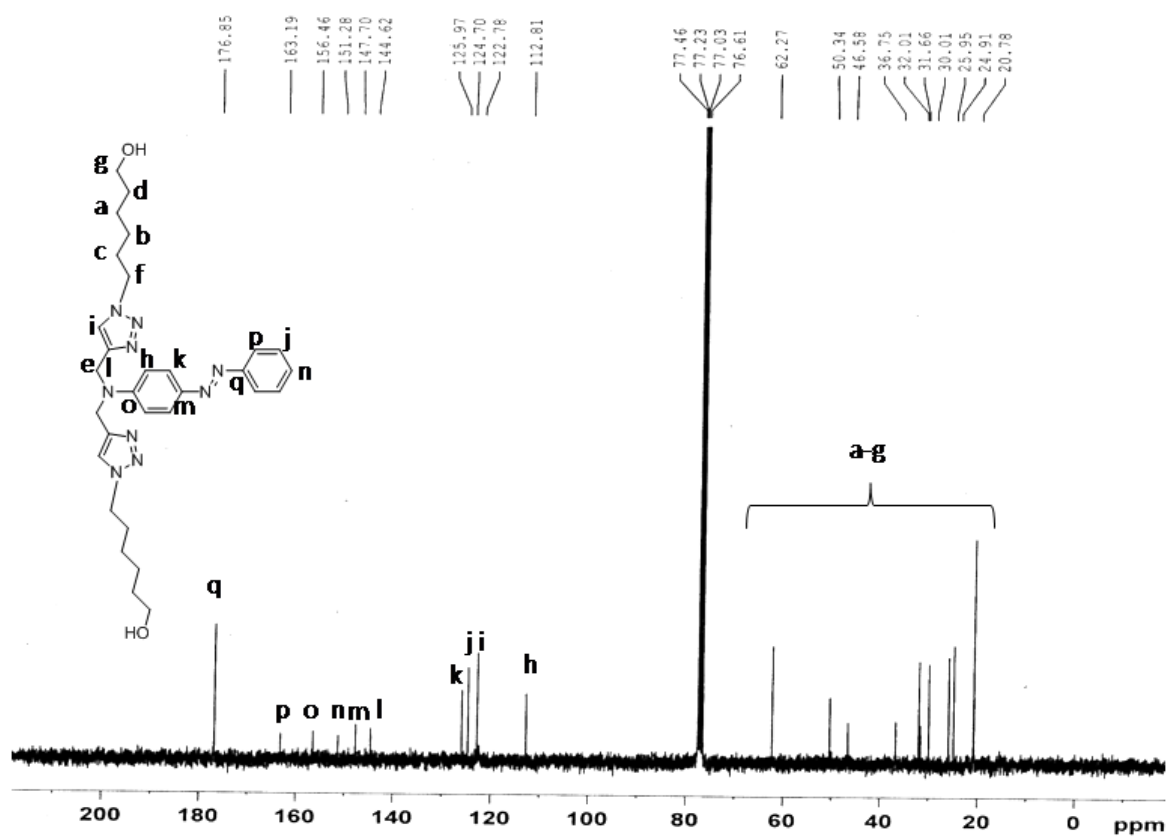


Figure S8. ^{13}C -NMR spectrum of receptor I.

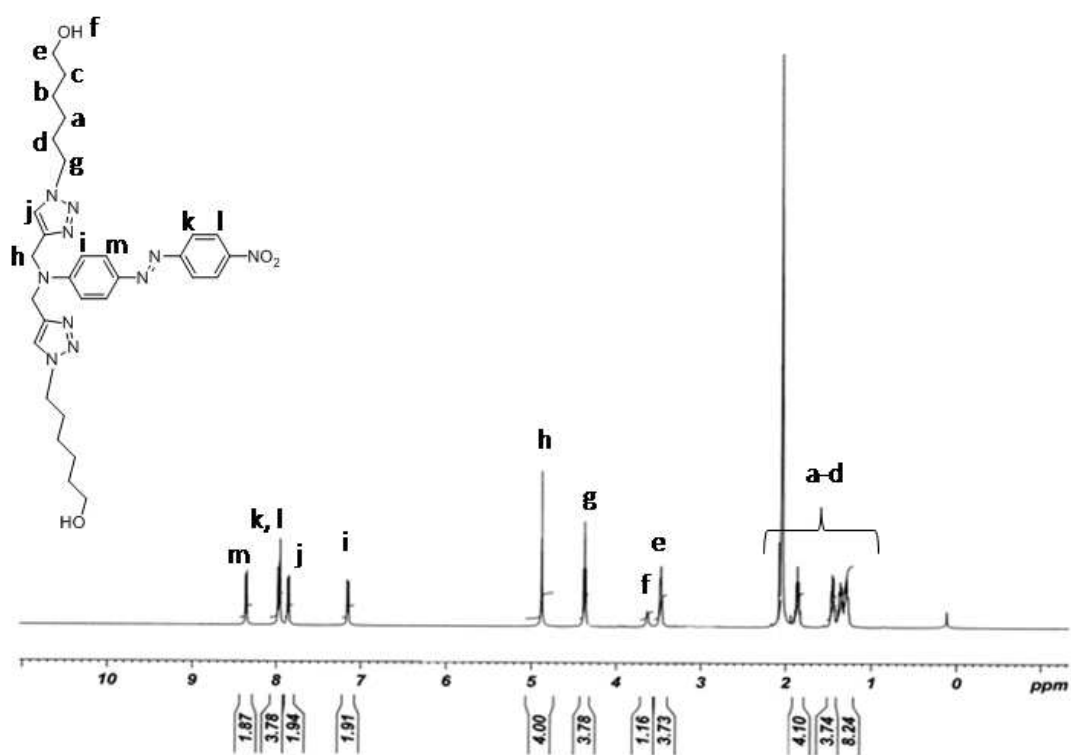


Figure S9. ¹H-NMR spectrum of receptor II.

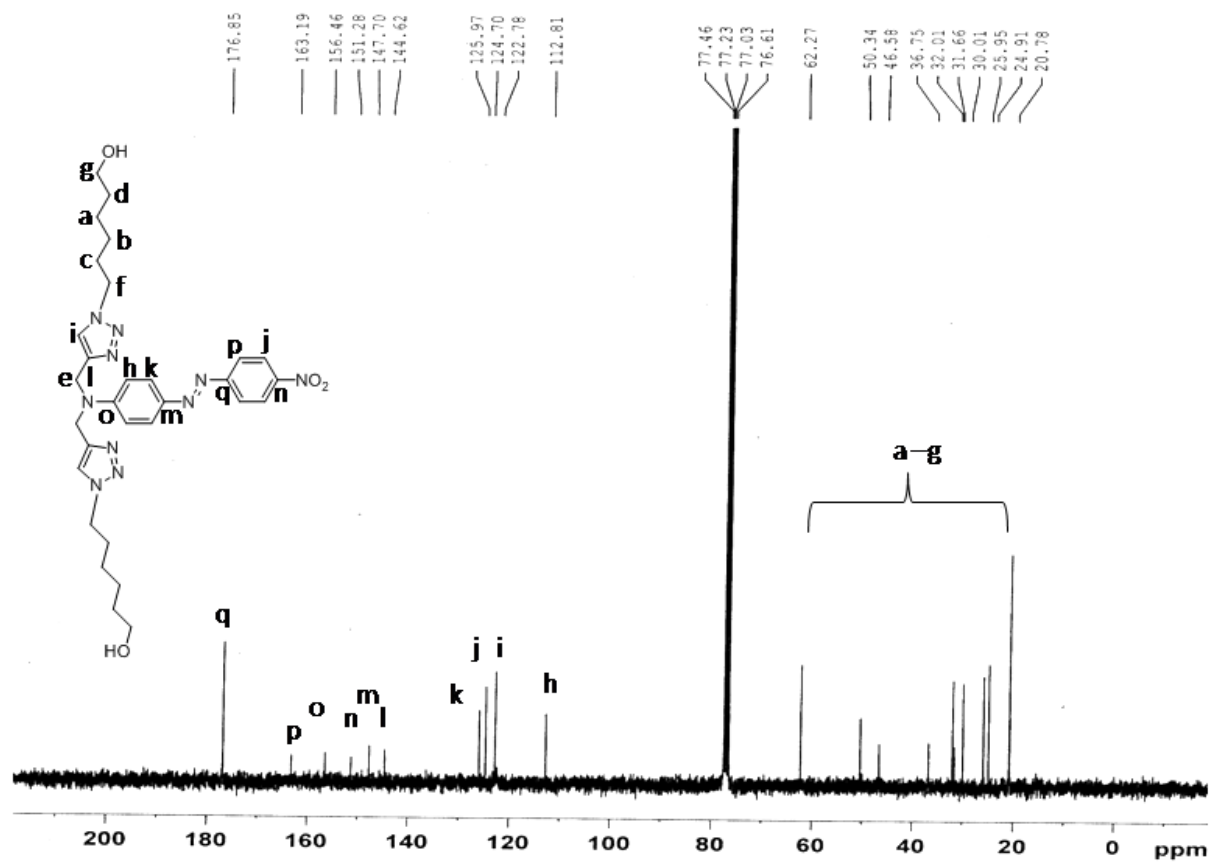


Figure S10. ^{13}C -NMR spectrum of receptor II.

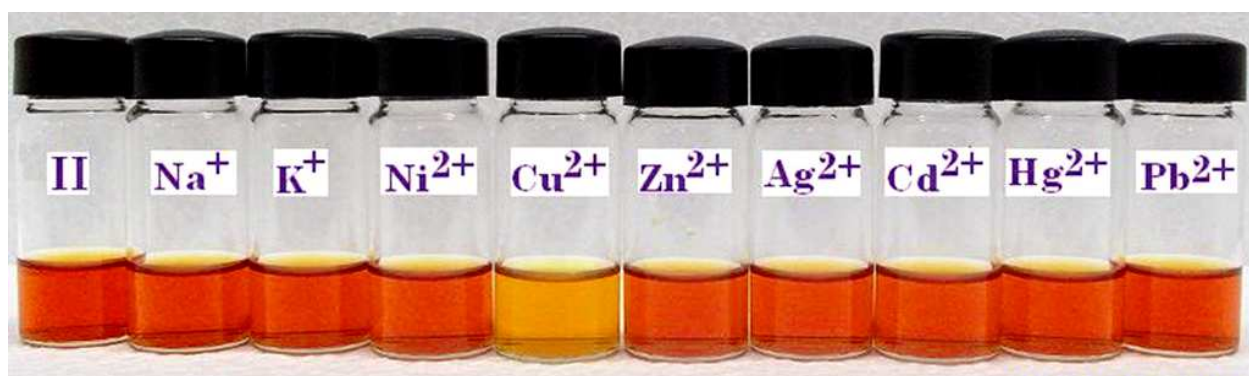


Figure S11. Pictures of receptor II (200 μ M) upon addition of various metal ions (10.0 equiv) in CH₃CN/H₂O (80:20, v/v).

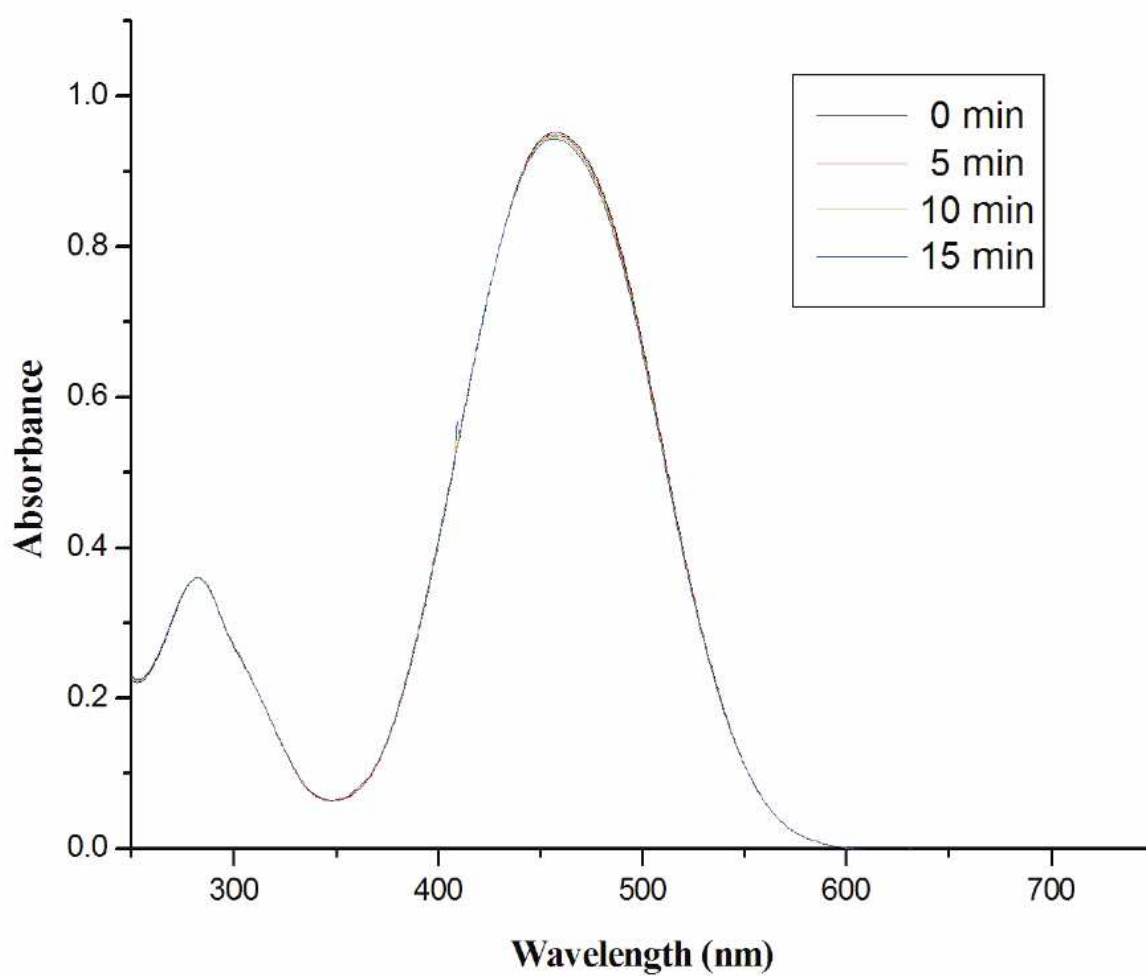


Figure S12. UV-vis spectrum of receptor II with 460 nm visible light irradiation with a time period (0, 5 , 10 and 15 min) for isomerization reaction.

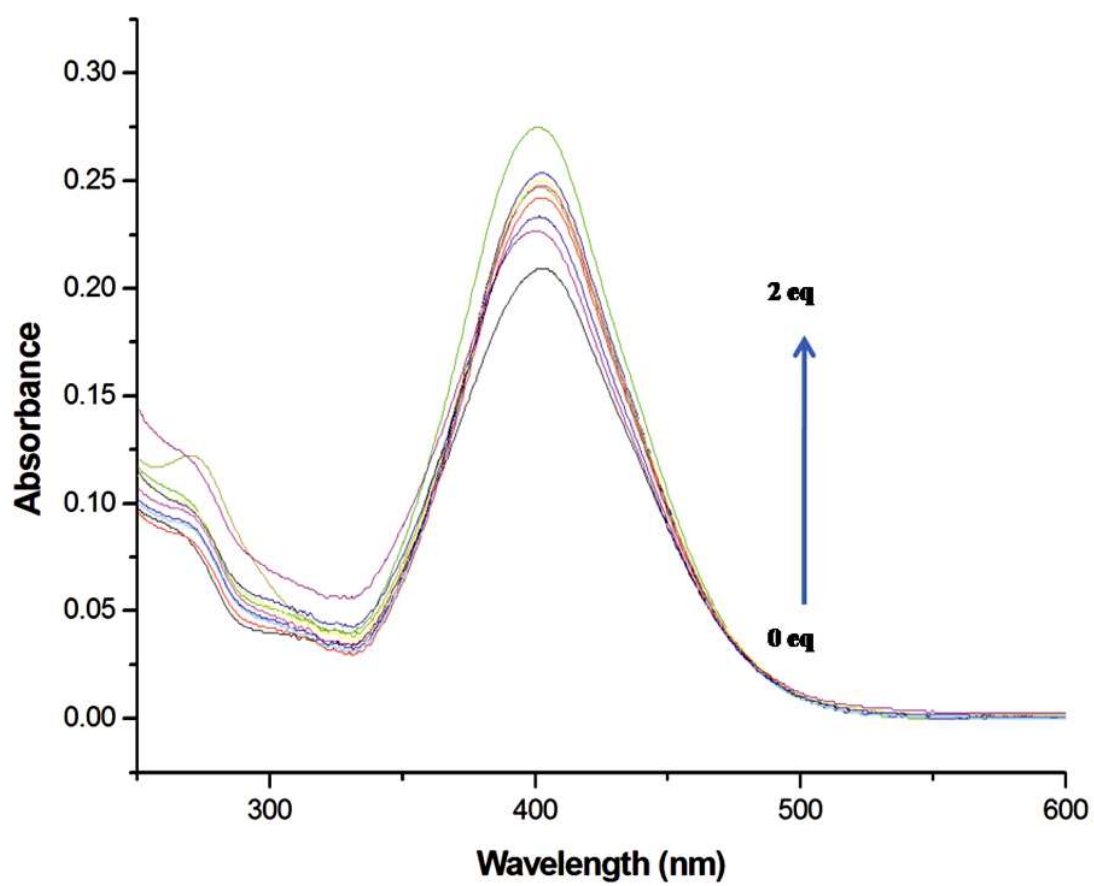


Figure S13. UV-vis spectra of receptor I with addition Cu²⁺ in CH₃CN/H₂O (80:20, v/v).