Electronic Supplementary Material (ESI) for RSC Advances.

SUPPLEMENTARY INFORMATION

Cupper Supported *β*-Cyclodextrin Grafted Magnetic Nanoparticles as an Efficient Recyclable Catalyst for One-pot Synthesis of 1-Benzyl-1*H*-1,2,3-triazoldibenzodiazepinone Derivatives via Click Reaction

General Remarks

Solvents, reagents and chemicals were obtained from Merck (Germany) and Fluka (Switzerland) Chemical Companies.

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. The IR spectra were obtained on a Nicolet Magna FT-IR 550 spectrophotometer (potassium bromide disks). Nuclear magnetic resonance spectra were recorded on a Brucker Bruker FT- 500 spectrometers using tetramethyl silane (TMS) as internal standard in pure deuterated solvents. Chemical shifts are given in the δ scale in parts per million (ppm) and singlet (s), doublet (d), triplet (t), multiplet (m) and doublets of doublet (dd) are recorded. Mass spectra were recorded on an Agilent Technology (HP) mass spectrometer operating at an ionization potential of 70 eV. The elemental analysis was performed with an Elemetar Analysen system GmbH VarioEL CHNS mode. Purification of all product were conducted by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

Thin layer chromatography was carried out on silica gel 254 analytical sheets obtained from Fluka. Column chromatography was carried out on the column of silica gel 60 Merck (230-240 mesh) in glass columns (2 or 3 cm diameter) using 15-30 grams of silica gel per one gram of the crude mixture.

Transition electron microscope images were recorded on a HITACHI S-4160. Thermogravimetric analysis of the samples were recorded by TGA Q50 V6.3 Build 189 instrument.

Preparation of the catalyst

Synthesis of SPIONs

SPIO nanoparticles was synthesized through the synthetic method reported by Mahmoudi et. al. with some modifications. 18 Briefly, two separate micro-emulsions was prepared included (micro A) toluene (29 mL) as oil phase and an aqueous solution of $FeCl_3.6H_2O$ (202 mg), $FeCl_2.4H_2O$ (75 mg), and CTAB (1.8 g) in 2.045 mL of deionized water, and (micro B) a solution of CTAB (1.8 g) in 29 mL toluene as oil phase and 25% ammonium hydroxide solution (2.65 mL) as reducing agent and aqueous phase. Both of them was separately homogenised (7000 rpm) and 1-butanol was titrated into them (as co-surfactant for the formation of micro-emulsion) until the solution was transparent. Micro A and B were mixed in a three-necked flask

using homogenizer (7000 rpm) at 50 °C and under constant flow of N_2 gas (60 min). Then, obtained magnetic residual were thoroughly washed with boiling EtOH and separated by centrifugation (or by applying an external magnetic device). The obtained SPIONs was then dried under vacuum for 12 h at room temperature (r. t.).

Preparation of β-CD@SPIONs

β-CD-Silane was synthesized via the hydrogen-transfer nucleophilic addition reaction between the end hydroxyl group of β-CD and 3-(triethoxysilyl) propyl isocyanate (TESPIC). 10 mmol of β-CD was dissolved into 50 mL of dry pyridine with vigorous stirring under argon atmosphere at 70 °C. After stirring for 6 h, 10 mmol of TESPIC was added into the later solution. After 24 h, the solvent was removed by vacuum evaporation. The residue was washed three times with n-hexane, and then recrystallized from EtOH at 0 °C. The obtained β-CD-silane was filtered at 0 °C and then dried at room temperature in vacuum. Then a solution of 0.1 g of β-CD-silane in 30 mL of EtOH was added drop-wise to a vigorous stirring solution of 50 mg of MNP in 30 mL EtOH/H_2O (1:2) and HCl (pH = 4). After vigorous stirring for 24 h, the solution was filtered off and washed thoroughly with H_2O and EtOH. The white residue was dried at 100 °C in vacuum for 12 h to obtain β-CD@SPIONs.

Immobilization of Cu onto β-CD@SPIONs

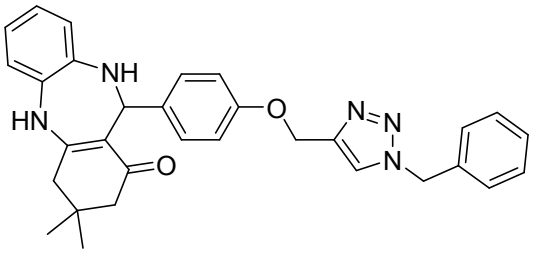
β-CD@SPIONs (0.5 g) was added to 50 mL NaOH (0.5 M) and stirred at r. t. for 30 min. Then, 75 mL of CuCl (0.04 M) was added to the later solution and was allowed to stir at r. t. for 12 h. The product was separated by an external magnet. Then it was washed with MeOH, water, and EtOH, and then air-dried at r. t. The [Cu@β-CD@SPIONs] nanocatalyst was obtained as a dark powder.

General procedure for the synthesis of 1-benzyl-1-H-1,2,3-Triazoldibenzodiazepinone Derivatives using catalytic amount of [Cu@β-CD@SPIONs]

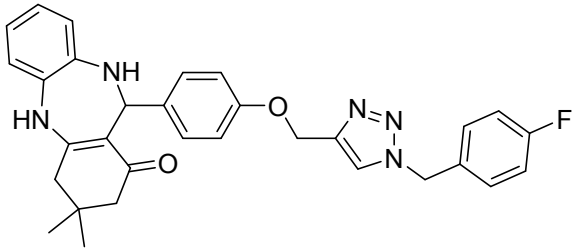
Dimedone (0.14 g, 1 mmol), *o*-phenylenediamine derivatives (1 mmol), 4-propargyloxybenzaldehyde (1 mmol), (azidomethyl) benzene derivatives (1 mmol) and triethylamine (0.12 g, 1.2 mmol) was dissolved in 10 mL of H_2O/EtOH (1:1). After 30 min, 50 mg of [Cu@β-CD@SPIONs] was added and the reaction mixture was stirred for 24 h at r. t. The reaction completion was monitored by TLC using n-hexane/ethyl acetate (8:1). After

completion of the reaction, the magnetic catalyst was separated using an external magnet and the solvent was evaporated to give the crude product, which was purified by recrystallization from EtOH.

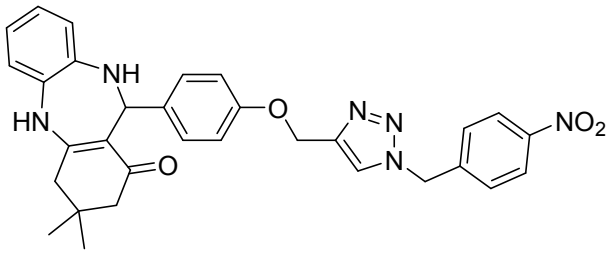
Spectral data for products



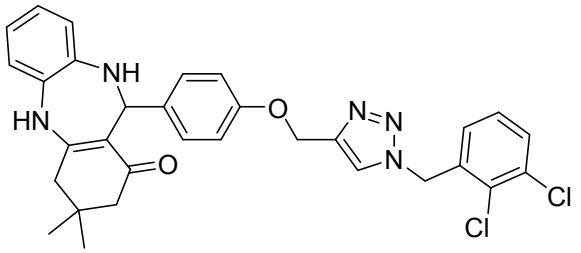
M.p. = 124.3-125.5 °C; IR (KBr): υ = 3355, 3278, 1673, 1506 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.57 (4H, m), 5.05 (2H, s), 5.49 (2H, s), 5.89 (1H, s), 6.43 (1H, d, J = 8.0 Hz), 6.68-6.73 (4H, m), 6.96 (2H, d, J = 8.0 Hz), 7.05 (2H, dd, J_1 = 8.0 Hz, J_2 = 1 Hz), 7.21-7.28 (3H, m), 7.35 (2H, d, J = 6.0 Hz), 7.42 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.1, 32.4, 37.4, 39.2, 54.1, 57.8, 62.1, 106.9, 114.5, 114.7, 118.8, 120.1, 122.5, 122.8, 123.9, 128.1, 128.4, 128.8, 129.1, 132.8, 135.6, 136.1, 137.4, 158.1, 161.0, 190.9 ppm; MS (70 eV): m/z = 506 (M^+).



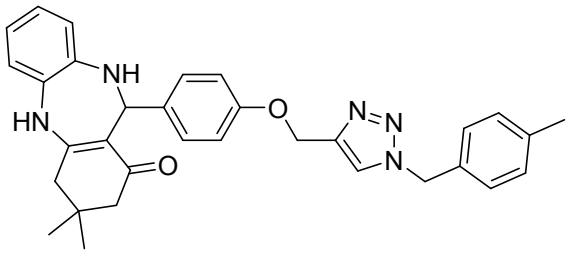
M.p. = 131.8-133.1 °C; IR (KBr): υ = 3345, 3282, 1685, 1506 1497 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.52 (4H, m), 5.05 (2H, s), 5.45 (2H, s), 5.88 (1H, s), 6.41 (1H, d, J = 6.5 Hz), 6.68-6.73 (4H, m), 6.96 (2H, d, J = 8.5 Hz), 7.05 (2H, t, J = 8.5 Hz), 7.24 (2H, dd, J_1 = 8.5 Hz, J_2 = 5 Hz), 7.30 (2H, d, J = 8.5 Hz), 7.42 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.3, 32.3, 46.5, 49.8, 53.4, 57.6, 62.1, 106.6, 114.4, 116.1, 116.2, 119.9, 121.4, 121.8, 122.4, 123.9, 128.4, 129.9, 130.0, 131.0, 132.1, 136.7, 139.6, 152.8, 156.8, 164.9 (d, J = 248 Hz), 193.8 ppm; MS (70 eV): m/z = 524 (M^+).



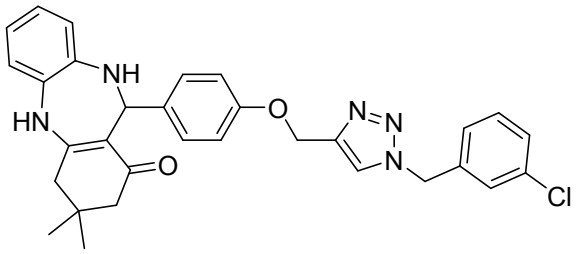
M.p. = 141.6-142.4 °C; IR (KBr): υ = 3351, 3290, 1696, 1502, 1340 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.06 (3H, s), 1.13 (3H, s), 2.19-2.56 (4H, m), 5.06 (2H, s), 5.59 (2H, s), 5.87 (1H, s), 6.40-6.42 (1H, m), 6.55 (1H, s), 6.67 (2H, d, J = 8.5 Hz), 6.70-6.72 (3H, m), 6.96 (2H, d, J = 8.5 Hz), 7.36 (2H, d, J = 8.5 Hz), 7.51 (1H, s), 8.19 (2H, d, J = 8.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.3, 32.3, 46.5, 49.8, 53.4, 57.6, 62.1, 106.6, 111.7, 114.4, 119.9, 121.3, 121.7, 122.8, 123.8, 124.3, 128.4, 128.6, 131.0, 137.0, 141.5, 145.2, 152.6, 156.6, 159.7, 193.9 ppm; MS (70 eV): m/z = 551 (M^+).



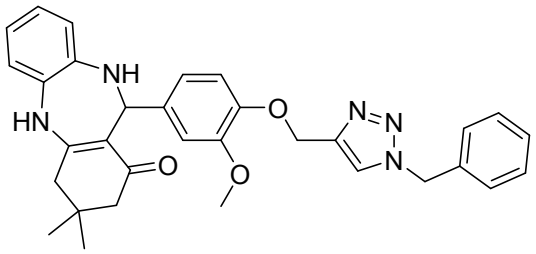
M.p. = 146.8-148.0 °C; IR (KBr): υ = 3354, 3281, 1677, 1502 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.58 (4H, m), 5.07 (2H, s), 5.64 (2H, s), 5.87 (1H, s), 6.40-6.43 (3H, m), 6.70-6.71 (3H, m), 6.97 (2H, d, J = 8.0 Hz), 6.99 (2H, d, J = 8.0 Hz), 7.18 (1H, t, J = 8.0 Hz), 7.46 (1H, dd, J_1 = 8.0 Hz, J_2 = 1 Hz), 7.55 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.2, 32.3, 46.4, 49.8, 51.9, 57.5, 62.0, 111.9, 114.4, 119.8, 121.2, 121.7, 123.0, 123.8, 124.1, 127.9, 128.1, 128.3, 129.3, 130.9, 137.3, 137.5, 144.9, 145.5, 152.7, 152.4, 156.7, 191.8 ppm; MS (70 eV): m/z = 574 (M^+).



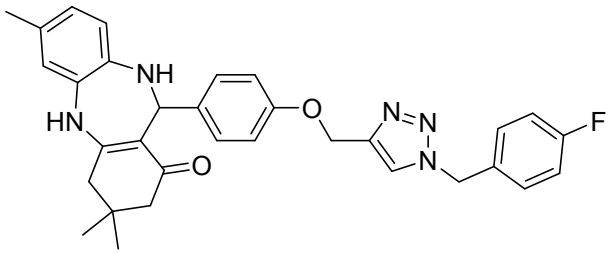
M.p. = 147.1-148.4 °C; IR (KBr): υ = 3354, 3282, 1671, 1503 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ = 1.03 (3H, s), 1.08 (3H, s), 2.07 (1H, d, J = 16.0 Hz), 2.18 (1H, d, J = 16.0 Hz), 2.27 (3H, s) 2.57 (2H, s), 4.96 (2H, s), 5.51 (2H, s), 5.87 (1H, s), 6.51-6.61 (3H, m), 6.73 (2H, d, J = 8.5 Hz), 6.92 (3H, d, J = 7.5 Hz), 7.00 (2H, d, J = 8.5 Hz), 7.15-7.20 (3H, m), 8.13 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.6, 27.4, 28.4, 31.7, 44.0, 49.5, 52.5, 55.2, 60.8, 106.6, 110.5, 113.7, 119.3, 119.9, 120.4, 122.5, 124.2, 127.9, 128.2, 129.2, 130.8, 132.9, 137.1, 138.6, 143.0, 154.5, 156.1, 191.8 ppm; MS (70 eV): m/z = 519 (M^+).



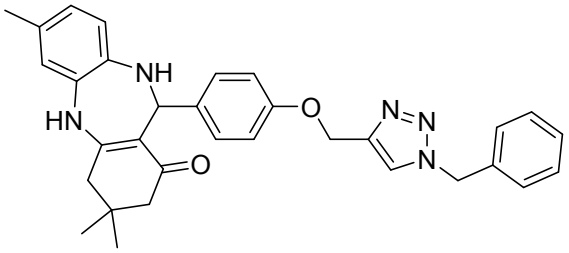
M.p. = 123.2-124.0 °C; IR (KBr): υ = 3351, 3276, 1683, 1504 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21 (1H, d, J = 16.0 Hz), 2.29 (1H, d, J = 16.0 Hz), 2.41 (1H, d, J = 17 Hz), 2.57 (1H, d, J = 17 Hz), 5.06 (2H, s), 5.46 (2H, s), 5.89 (1H, s), 6.41 (1H, d, J = 7 Hz), 6.69-6.73 (6H, m), 6.97 (2H, d, J = 8.5 Hz), 7.11 (1H, d, J = 7.5 Hz), 7.24-7.33 (2H, m), 7.44 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.5, 32.3, 46.7, 49.4, 53.5, 57.6, 62.1, 106.7 114.5, 116.7, 119.9, 121.9, 122.0, 122.5, 123.9, 126.1, 128.2, 128.4, 129.0, 130.5 131.0, 133.0, 133.1, 133.2, 136.9, 147.1, 156.8, 192.0 ppm; MS (70 eV): m/z = 539 (M^+).



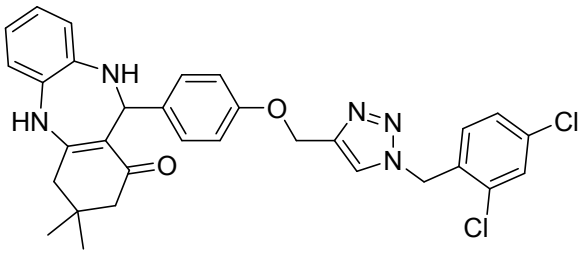
M.p. = 161.9-163.3 °C; IR (KBr): υ = 3349, 3274, 1688, 1505 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.13 (3H, s), 2.20- 2.57 (4H, m), 3.61 (3H, s), 5.12 (2H, s), 5.47 (2H, s), 5.91 (1H, s), 6.54 (1H, d, J = 7.5 Hz), 6.61-6.65 (1H, m), 6.72-6.79 (3H, m), 6.95-7.02 (3H, m), 7.23-7.25 (3H, m), 7.34-7.35 (2H, m), 7.44 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 28.1, 28.3, 32.3, 37.9, 44.3, 48.6, 54.2, 57.3, 63.3, 106.0, 111.5, 114.0, 114.8, 116.1, 119.7, 121.2, 122.7, 122.9, 123.3, 124.0, 128.1, 128.7, 129.1, 131.0, 133.4, 133.9, 135.9, 155.4, 161.7, 193.9 ppm; MS (70 eV): m/z = 535 (M^+).



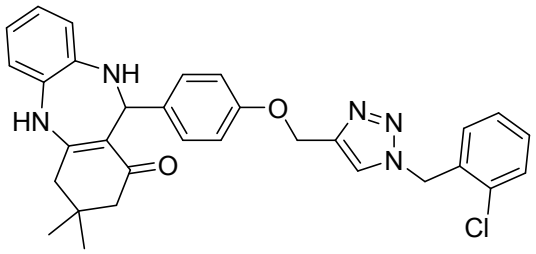
M.p. = 142.5-143.6 °C; IR (KBr): υ = 3357, 3279, 1685, 1506 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.09 (3H, s), 2.10 (3H, s), 2.17-2.58 (4H, m), 5.05 (2H, s), 5.46 (2H, s), 5.86 (1H, s), 6.23-6.25 (2H, m), 6.54 (1H, d, J = 7 Hz), 6.69 (2H, d, J = 8.5 Hz), 6.97 (2H, t, J = 8.5 Hz), 7.04 (2H, dd, J_1 = 8.5 Hz, J_2 = 5.5 Hz), 7.22-7.24 (2H, m), 7.43 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.7, 32.3, 34.3, 46.5, 49.8, 51.6, 53.5, 57.4, 62.1, 106.4, 114.4, 116.1, 116.2, 119.8, 122.1, 122.4, 124.7, 128.4, 129.6, 129.8, 130.0, 130.1, 131.1, 133.6, 139.6, 152.9, 160.8 (d, J = 253 Hz), 193.7 ppm; MS (70 eV): m/z = 537 (M^+).



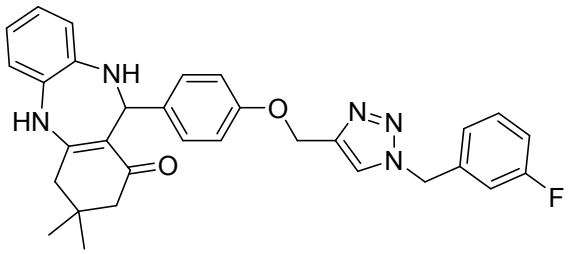
M.p. = 147.4-149.2 °C; IR (KBr): υ = 3349, 3280, 1671, 1502 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.06 (3H, s), 1.12 (3H, s), 2.10 (3H, s), 2.17-2.51 (4H, m), 5.05 (2H, s), 5.49 (2H, s), 5.82 (1H, s), 6.31 (1H, d, J = 8.5 Hz), 6.41 (1H, s), 6.54 (1H, d, J = 8.5 Hz), 6.70 (2H, d, J = 8.5 Hz), 6.97 (2H, d, J = 8.0 Hz), 7.35-7.37 (5H, m), 7.44 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.2, 26.9, 29.0, 32.3, 46.4, 49.7, 54.2, 57.5, 62.1, 106.7, 114.5, 115.8, 117.6, 121.9, 122.5, 128.1, 128.4, 128.8, 129.1, 130.4, 131.0, 133.3, 136.9, 136.9, 140.2, 152.7, 159.8, 193.9 ppm; MS (70 eV): m/z = 519 (M^+).



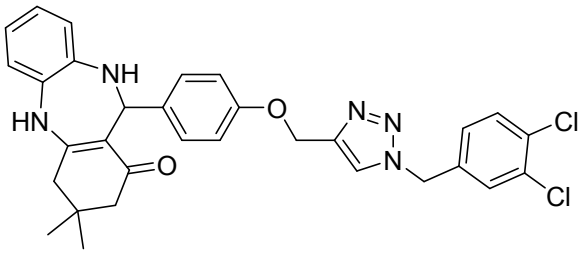
M.p. = 124.8-125.9 °C; IR (KBr): υ = 3353, 3276, 1682, 1501 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.58 (4H, m), 5.06 (2H, s), 5.58 (2H, s), 5.87 (1H, s), 6.41 (1H, d, J = 4.5 Hz), 6.50 (1H, s), 6.69-6.71 (3H, m), 6.97 (2H, d, J = 8.5 Hz), 7.08 (2H, m), 7.22 (2H, d, J = 8.5 Hz), 7.44 (1H, d, J = 2 Hz), 7.55 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.9, 32.3, 46.3, 49.8, 50.9, 57.5, 66.0, 106.0, 111.9, 114.4, 119.8, 121.2, 121.7, 122.9, 123.8, 127.7, 128.3, 129.3, 129.8, 131.0, 131.1, 135.6, 137.3, 145.0, 152.8, 153.4, 156.7, 193.8 ppm; MS (70 eV): m/z = 573 (M^+).



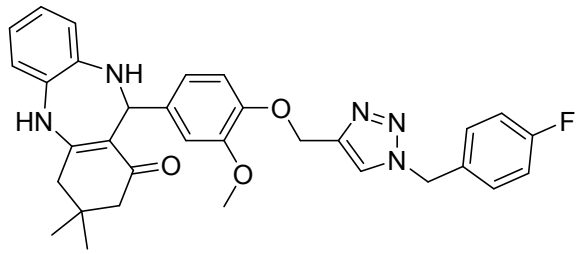
M.p. = 157.2-158.6 °C; IR (KBr): υ = 3349, 3274, 1683, 1505 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.59 (4H, m), 5.06 (2H, s), 5.63 (2H, s), 5.87 (1H, s), 6.39 (1H, d, J = 7 Hz), 6.69-6.72 (3H, m), 6.86 (2H, d, J = 8.0 Hz), 6.96 (2H, d, J = 8.0 Hz), 7.15 (2H, d, J = 7.0 Hz), 7.29 (1H, d, J = 7.5 Hz), 7.41 (1H, d, J = 7.5 Hz), 7.53 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.9, 28.9, 32.3, 49.8, 51.5, 55.6, 57.5, 62.0, 106.3, 111.9, 114.4, 119.8, 121.2, 121.7, 122.9, 123.8, 127.6, 128.3, 129.9, 130.2, 130.3, 130.9, 137.0, 137.3, 152,7 156.8, 194.0 ppm; MS (70 eV): m/z = 539 (M^+).



M.p. = 117.7-119.4 °C; IR (KBr): υ = 3357, 3273, 1673, 1505 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.59 (4H, m), 5.06 (2H, s), 5.48 (2H, s), 5.87 (1H, s), 6.37 (1H, s), 6.40 (1H, d, J = 7.5 Hz), 6.69-6.71 (3H, m), 6.93 (2H, d, J = 8.5 Hz), 6.96 (2H, d, J = 8.5 Hz), 7.01-7.05 (3H, m), 7.31-7.35 (1H, m), 7.45 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8, 28.4, 32.3, 46.6, 49.8, 53.5, 57.5, 62.1, 106.3, 114.4, 114.9, 115.1, 115.7, 115.9, 119.8, 121.2, 121.7, 122.5, 123.6, 123.8, 128.3, 130.8, 130.9, 137.0, 137.3, 145.0, 152.6, 163 (d, J = 240 Hz), 156.7, 193.8 ppm; MS (70 eV): m/z = 523 (M^+).

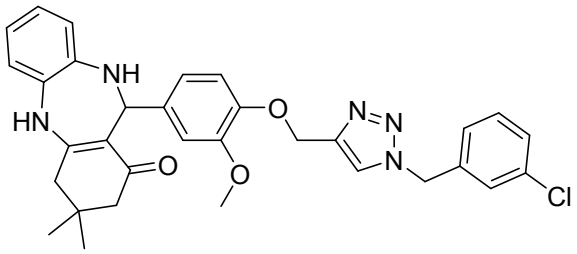


M.p. = 173.6-175.0 °C; IR (KBr): υ = 3349, 3275, 1682, 1501 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ = 1.03 (3H, s), 1.08 (3H, s), 2.08, 2.58 (4H, m), 4.99 (2H, s), 5.60 (2H, s), 5.65 (1H, s), 6.08 (1H, d, J = 7.5 Hz), 6.51-6.61 (3H, m), 6.74 (2H, d, J = 8.0 Hz), 6.93 (1H, d, J = 8.0 Hz), 7.00 (2H, d, J = 8.0 Hz), 7.27 (1H, d, J = 8.0 Hz), 7.62 (1H, s), 8.23 (1H, s), 8.75 (1H, s) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 27.4, 28.4, 31.7, 44.0, 49.5, 51.3, 55.2, 60.8, 106.8, 110.5, 113.7, 119.3, 119.9, 120.4, 122.5, 124.6, 128.2, 128.3, 130.1, 130.9, 131.1, 136.8, 137.2, 138.6, 143.2, 146.8, 154.5, 156.0, 191.8 ppm; MS (70 eV): m/z = 573 (M^+).

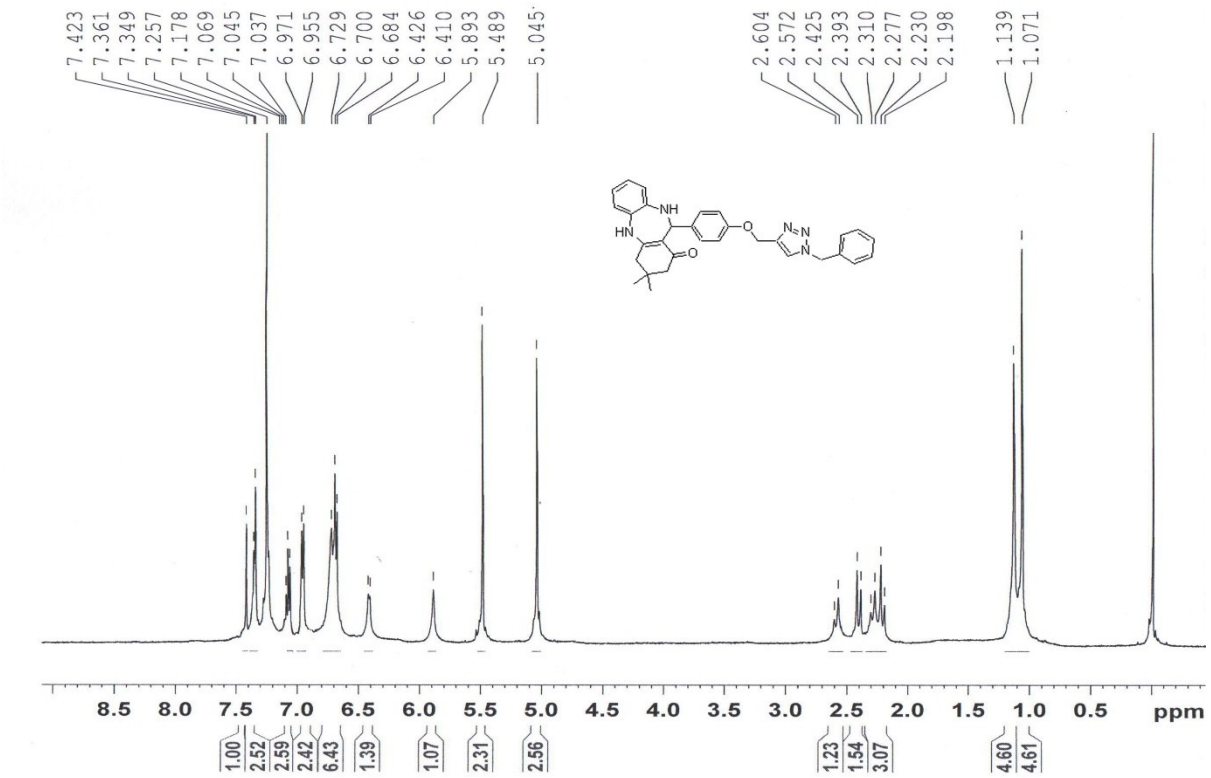


M.p. = 139.8-142.1 °C; IR (KBr): υ = 3359, 3275, 1678, 1506 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.21-2.58 (4H, m), 3.62 (3H, s), 5.12 (2H, s), 5.43 (2H, s), 5.87 (1H, s), 6.43 (1H, d, J = 6.5 Hz), 6.55 (1H, d, J = 8.0 Hz), 6.61 (1H, s), 6.71-6.74 (3H, m), 7.03 (2H, t, J = 8.5 Hz), 7.21-7.24 (2H, dd, J_1 = 8.5 Hz, J_2 = 5.0 Hz), 7.44 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.6, 29.0, 32.3, 49.8, 53.5, 55.8, 57.9, 63.3, 106.6, 111.4, 114.0, 116.0, 116.2, 119.6, 119.9, 121.6, 121.9, 122.6, 124.0, 126.1, 131.0, 132.3, 136.2, 136.7, 139.7, 152.8 (d, J = 238 Hz), 193.9 ppm; MS (70 eV): m/z = 553 (M^+).

.



M.p. = 153.3-155.6 °C; IR (KBr): υ = 3351, 3283, 1679, 1501 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (3H, s), 1.14 (3H, s), 2.20-2.58 (4H, m), 3.62 (3H, s), 5.13 (2H, s), 5.44 (2H, s), 5.88 (1H, s), 6.43 (1H, d, J = 7 Hz), 6.56 (1H, d, J = 8.0 Hz), 6.61 (1H, s), 6.71-6.75 (5H, m), 7.10 (1H, d, J = 7.5 Hz), 7.26-7.32 (2H, m), 7.47 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.4, 28.7, 32.3, 49.8, 53.5, 55.7, 57.9, 63.3, 106.6, 111.4, 114.1, 116.0, 116.4, 119.6, 119.9, 121.5, 121.9, 122.8, 124.0, 126.2, 128.2, 129.0, 130.4, 136.7, 139.7, 152.9, 193.9 ppm; MS (70 eV): m/z = 569 (M^+).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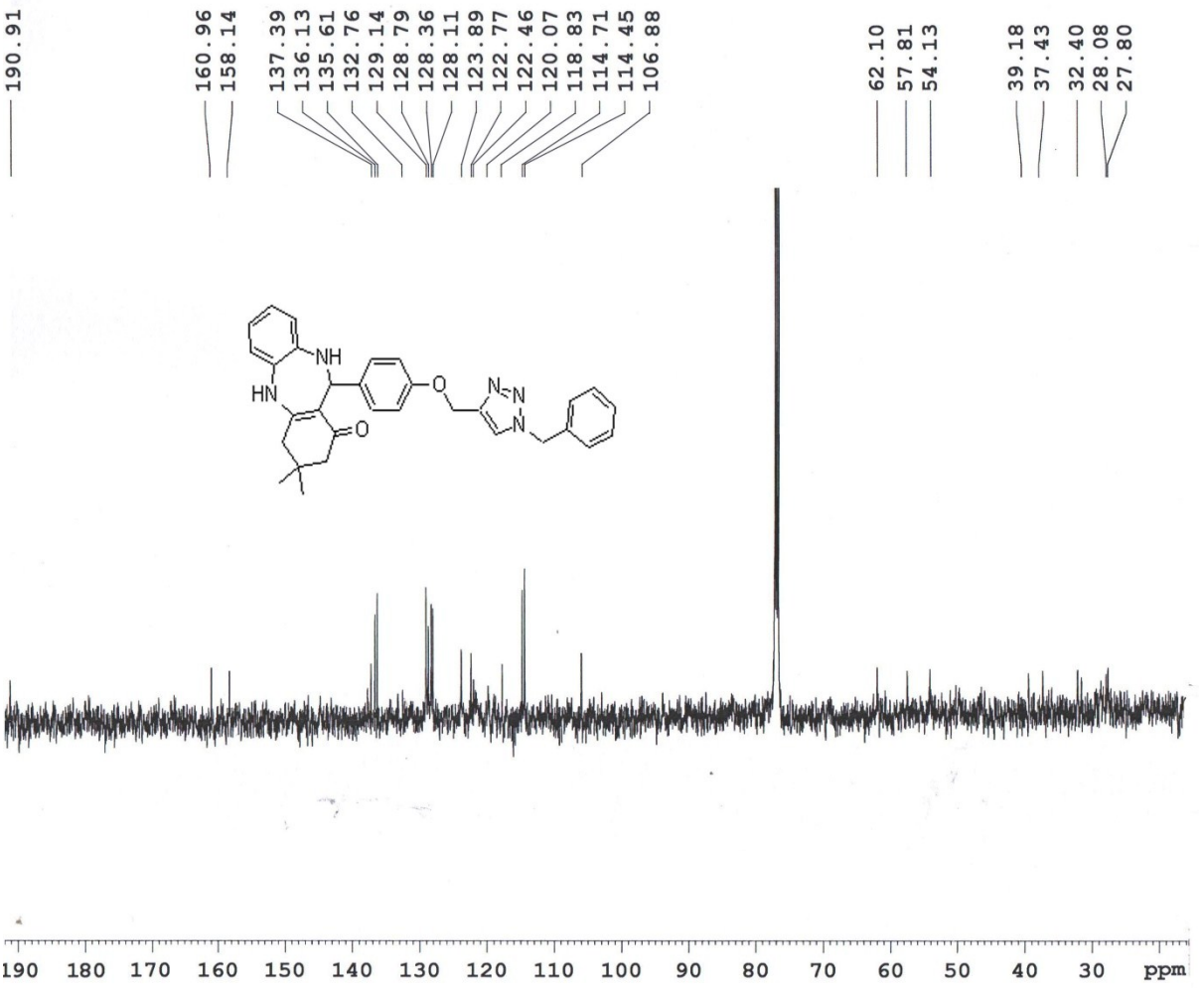
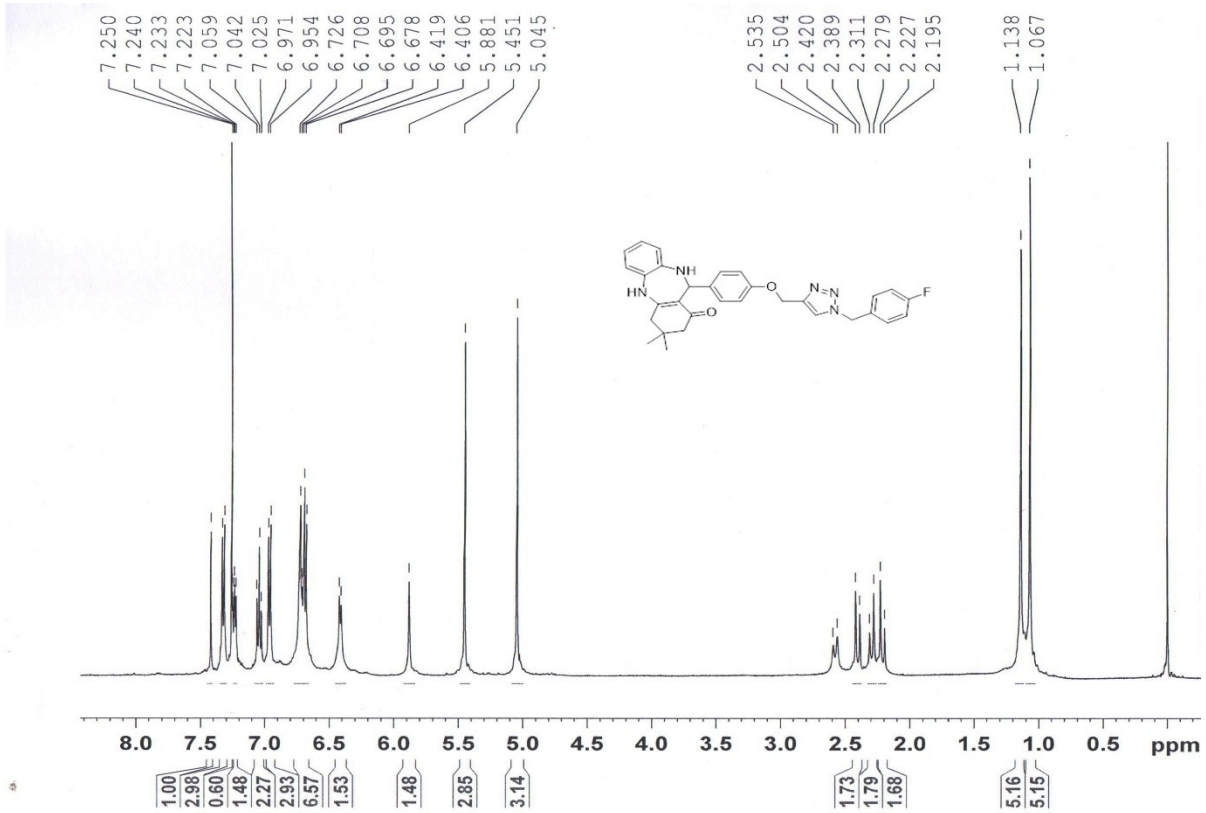
7.361
7.349
7.257
7.178
7.069
7.045
7.037
6.971
6.955
6.729
6.700
6.684
6.426
6.410
5.893
5.489
5.045
2.604
2.572
2.425
2.393
2.310
2.277
2.230
2.198
1.139
1.071
NH
HN
O
N=N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.52
2.59
2.42
6.43
1.39
1.07
2.31
2.56
1.23
1.54
3.07
4.60
4.61


190.91
160.96
158.14
137.39
136.13
135.61
132.76
129.14
128.79
128.36
128.11
123.89
122.77
122.46
120.07
118.83
114.71
114.45
106.88
62.10
57.81
54.13
39.18
37.43
32.40
28.08
27.80
NH
HN
O
N=N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm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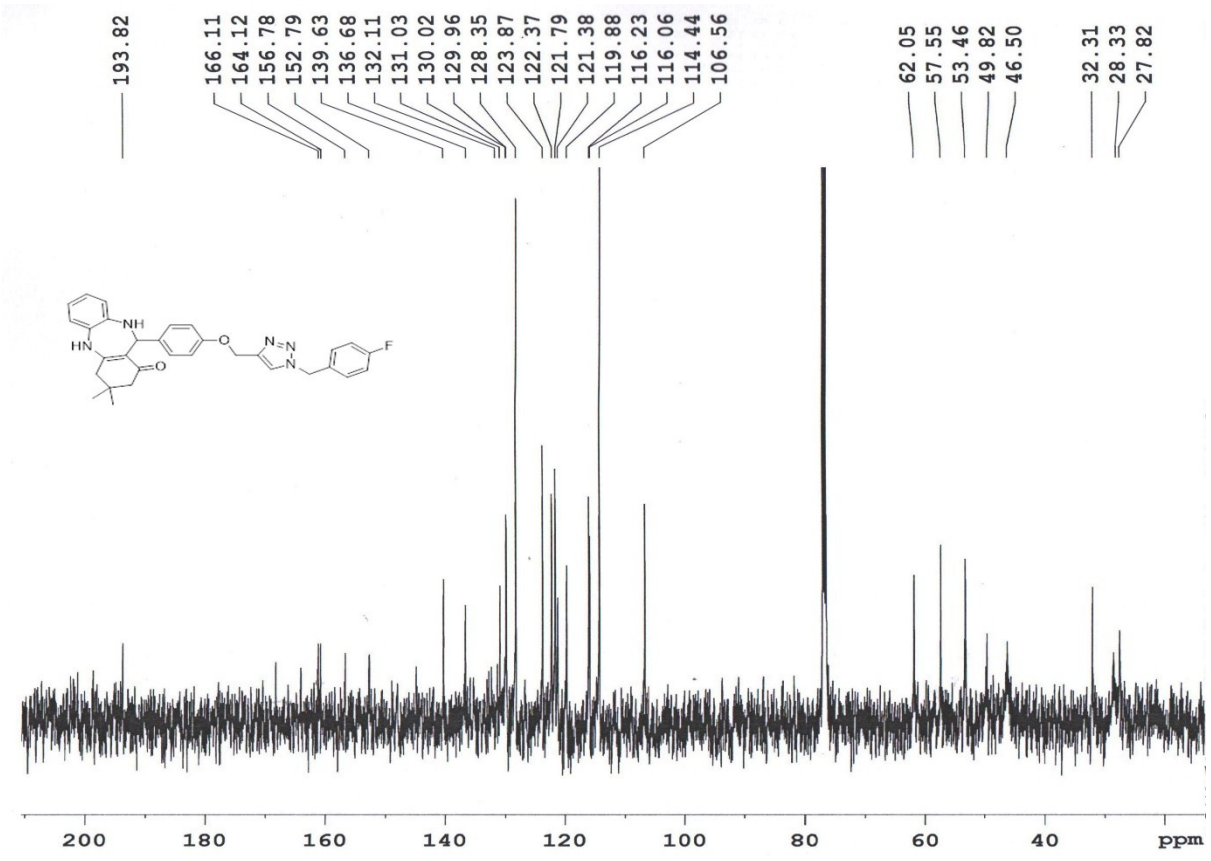
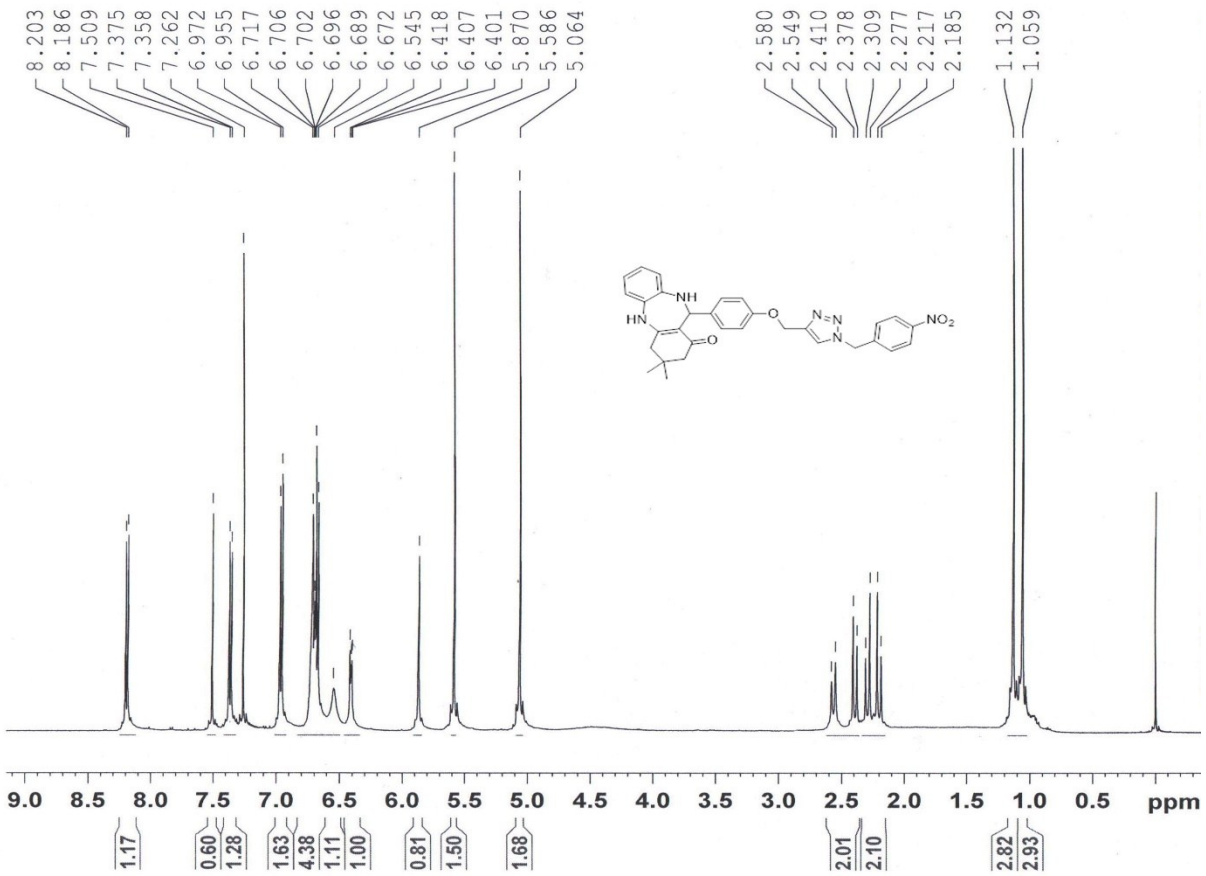
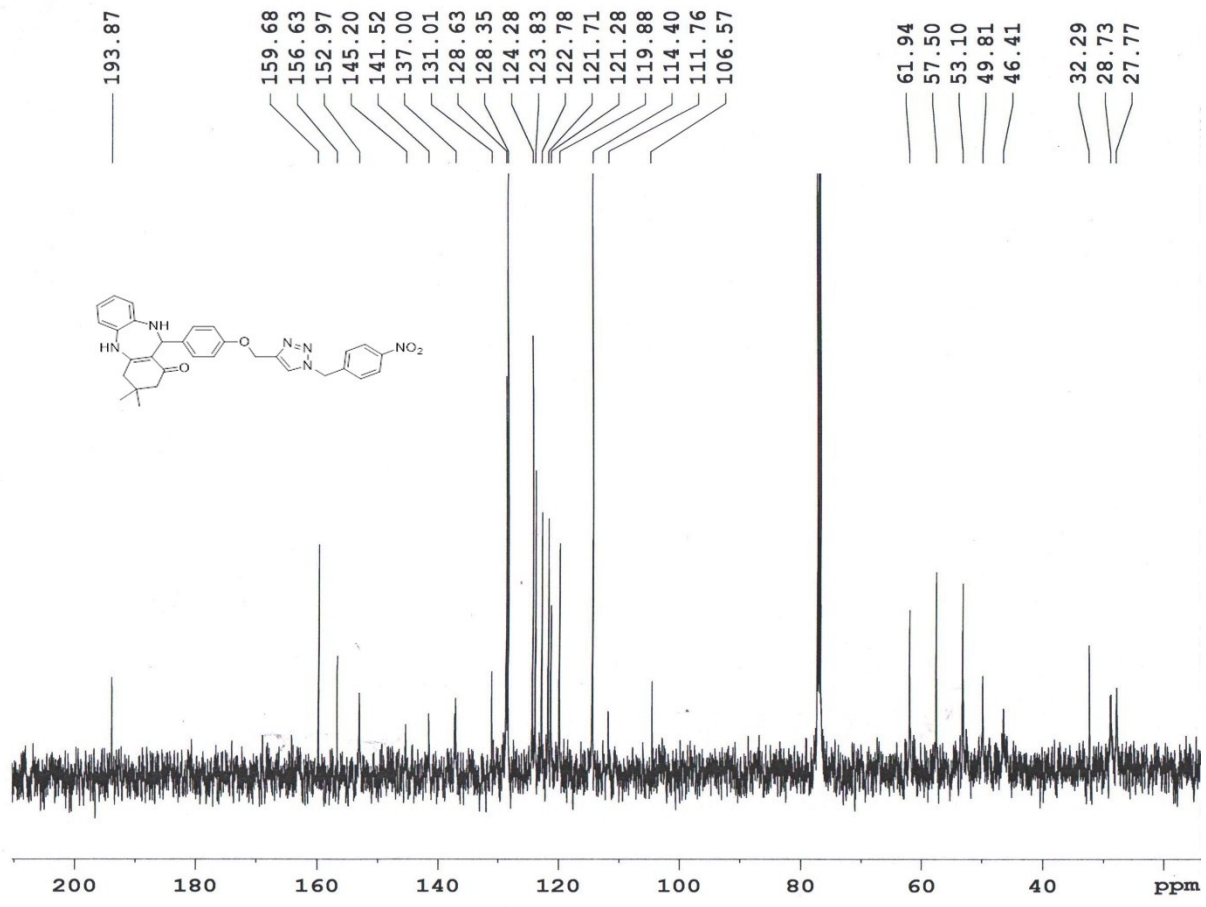
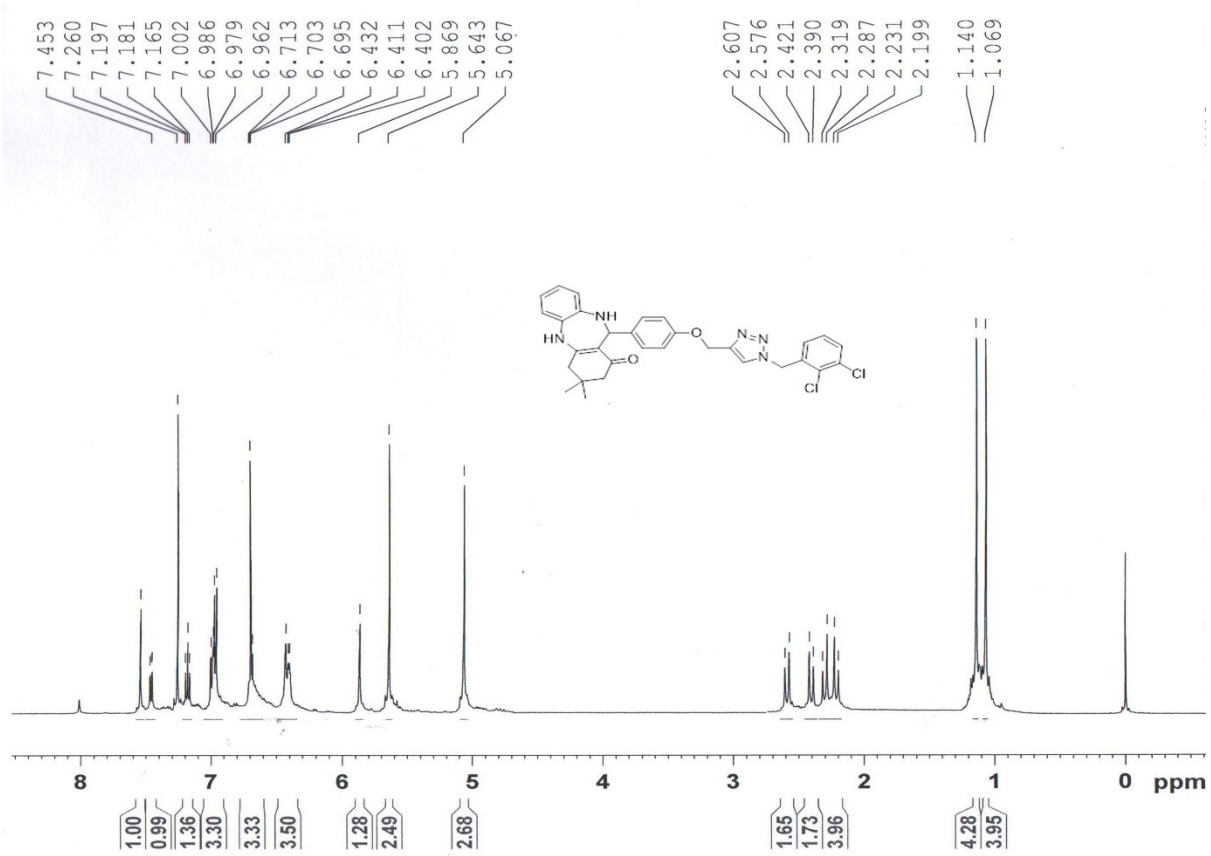
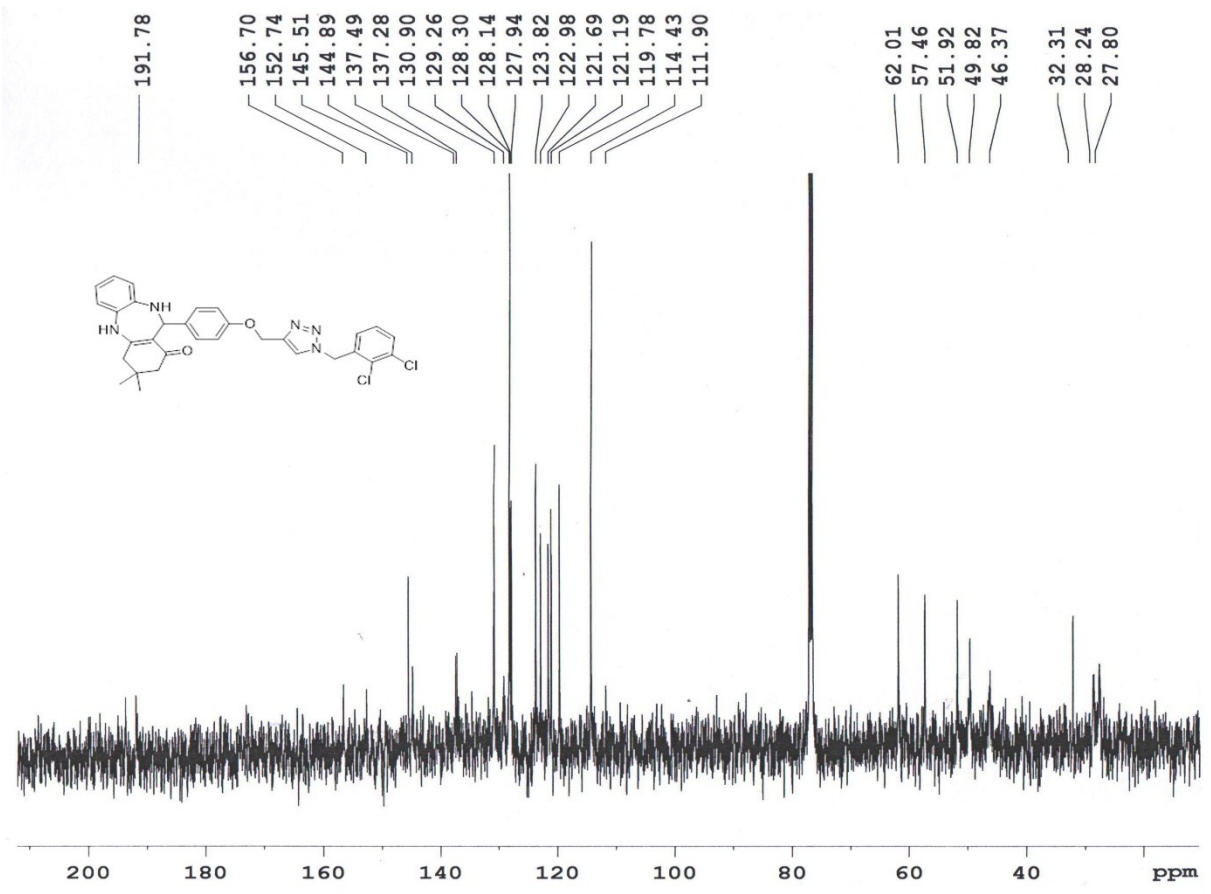
7.240
7.233
7.223
7.059
7.042
7.025
6.971
6.954
6.726
6.708
6.695
6.678
6.419
6.406
5.881
5.451
5.045
2.535
2.504
2.420
2.389
2.311
2.279
2.227
2.195
1.138
1.067
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 2.98 0.60 1.48 2.27 2.93 6.57 1.53 1.48 2.85 3.14 1.73 1.79 1.68 5.16 5.15

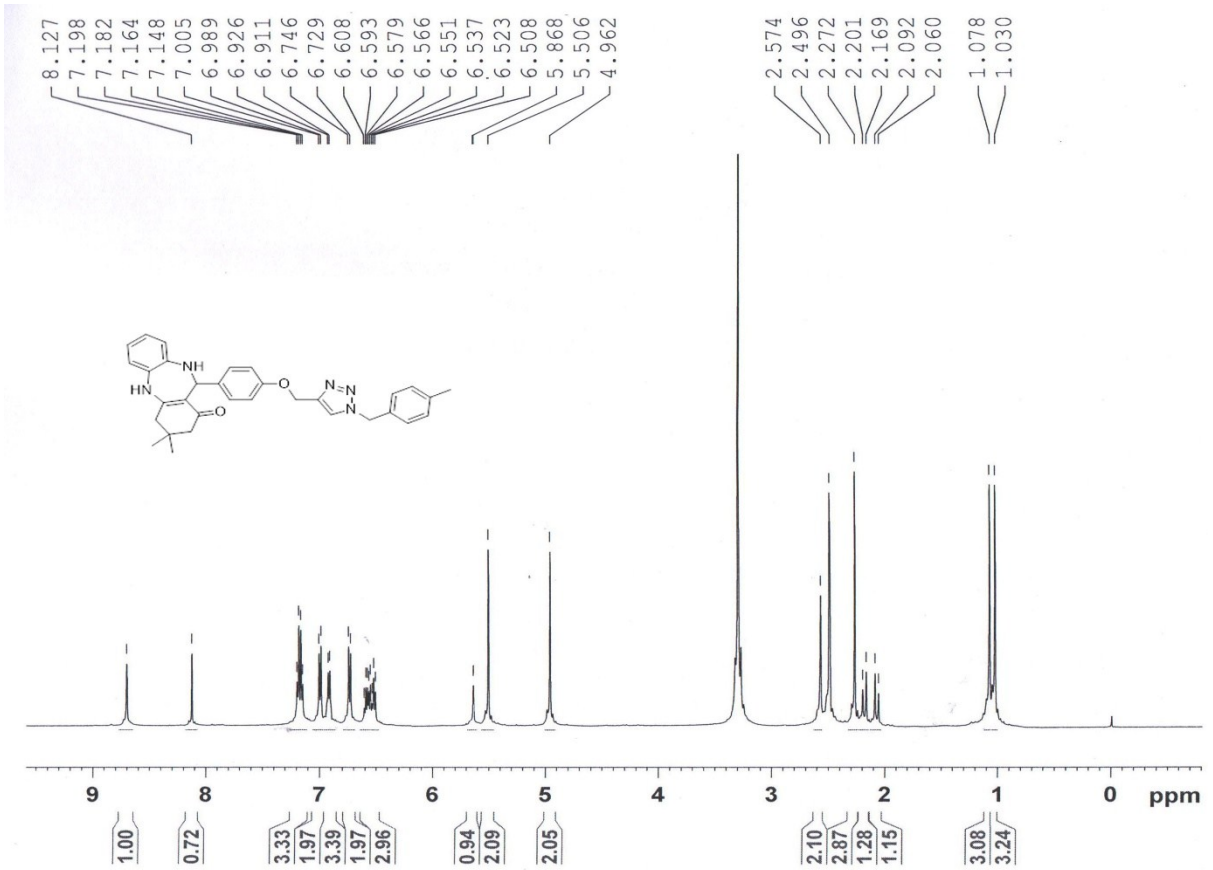

193.82
166.11
164.12
156.78
152.79
139.63
136.68
132.11
131.03
130.02
129.96
128.35
123.87
122.37
121.79
121.38
119.88
116.23
116.06
114.44
106.56
62.05
57.55
53.46
49.82
46.50
32.31
28.33
27.82
200 180 160 140 120 100 80 60 40 ppm

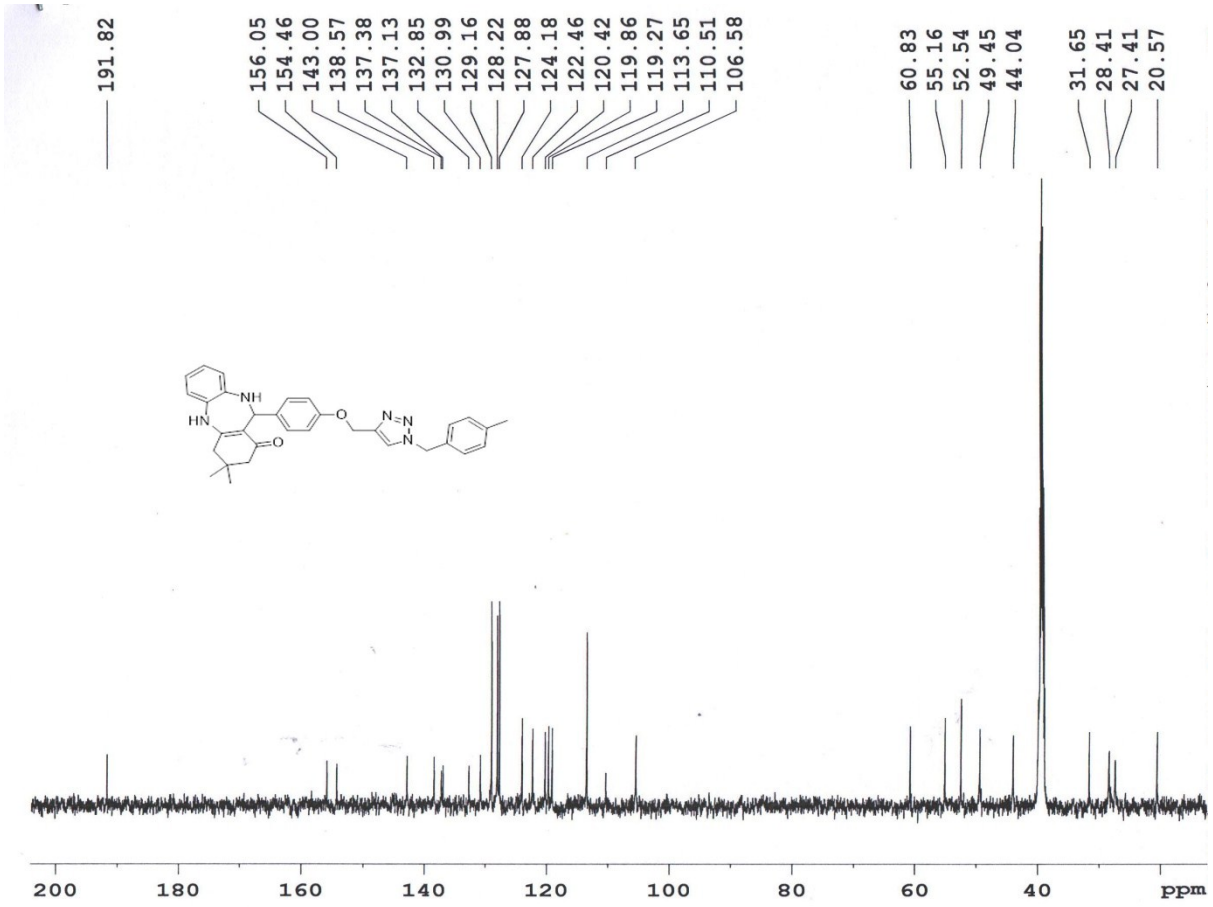

8.203
8.186
7.509
7.375
7.358
7.262
6.972
6.955
6.717
6.706
6.702
6.696
6.689
6.672
6.545
6.418
6.407
6.401
5.870
5.586
5.064
2.580
2.549
2.410
2.378
2.309
2.277
2.217
2.185
1.132
1.059
NH
HN
O
N=N
N
NO2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.17
0.60
1.28
1.63
4.38
1.11
1.00
0.81
1.50
1.68
2.01
2.10
2.82
2.93

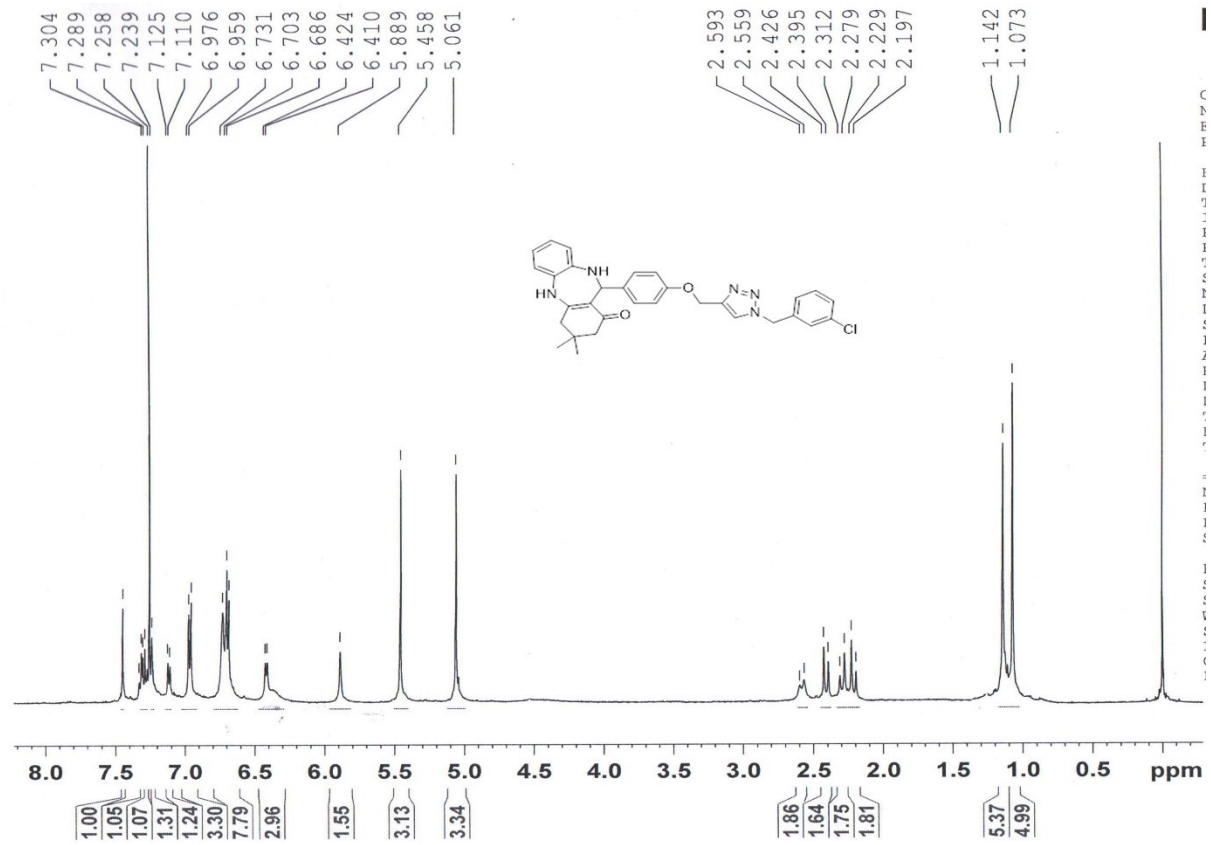

193.87
159.68
156.63
152.97
145.20
141.52
137.00
131.01
128.63
128.35
124.28
123.83
122.78
121.71
121.28
119.88
114.40
111.76
106.57
61.94
57.50
53.10
49.81
46.41
32.29
28.73
27.77
NH
HN
O
N=N
N
NO2
200 180 160 140 120 100 80 60 40 ppm


7.453
7.260
7.197
7.181
7.165
7.002
6.986
6.979
6.962
6.713
6.703
6.695
6.432
6.411
6.402
5.869
5.643
5.067
2.607
2.576
2.421
2.390
2.319
2.287
2.231
2.199
1.140
1.069
NH
HN
O
N=N
N
O
Cl
Cl
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.36
3.30
3.33
3.50
1.28
2.49
2.68
1.65
1.73
3.96
4.28
3.95


191.78
156.70
152.74
145.51
144.89
137.49
137.28
130.90
129.26
128.30
128.14
127.94
123.82
122.98
121.69
121.19
119.78
114.43
111.90
62.01
57.46
51.92
49.82
46.37
32.31
28.24
27.80
NH
HN
O
N=N
N
O
Cl
Cl
200
180
160
140
120
100
80
60
40
ppm


8.127
7.198
7.182
7.164
7.148
7.005
6.989
6.926
6.911
6.746
6.729
6.608
6.593
6.579
6.566
6.551
6.537
6.523
6.508
5.868
5.506
4.962
2.574
2.496
2.272
2.201
2.169
2.092
2.060
1.078
1.030
NH
HN
O
N=N
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.72
3.33
1.97
3.39
1.97
2.96
0.94
2.09
2.05
2.10
2.87
1.28
1.15
3.08
3.24


191.82
156.05
154.46
143.00
138.57
137.38
137.13
132.85
130.99
129.16
128.22
127.88
124.18
122.46
120.42
119.86
119.27
113.65
110.51
106.58
60.83
55.16
52.54
49.45
44.04
31.65
28.41
27.41
20.57
NH
HN
O
N=N
200
180
160
140
120
100
80
60
40
ppm


7.304
7.289
7.258
7.239
7.125
7.110
6.976
6.959
6.731
6.703
6.686
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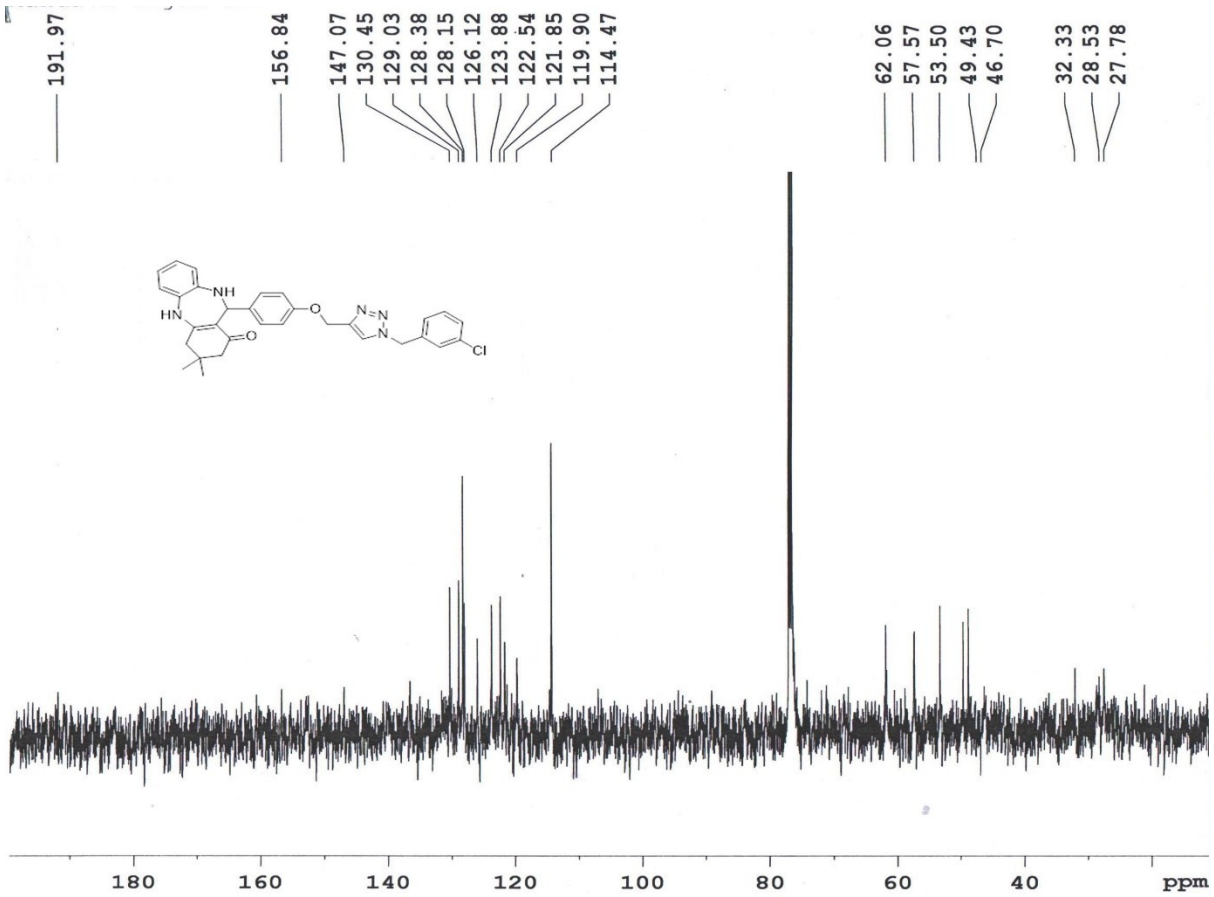
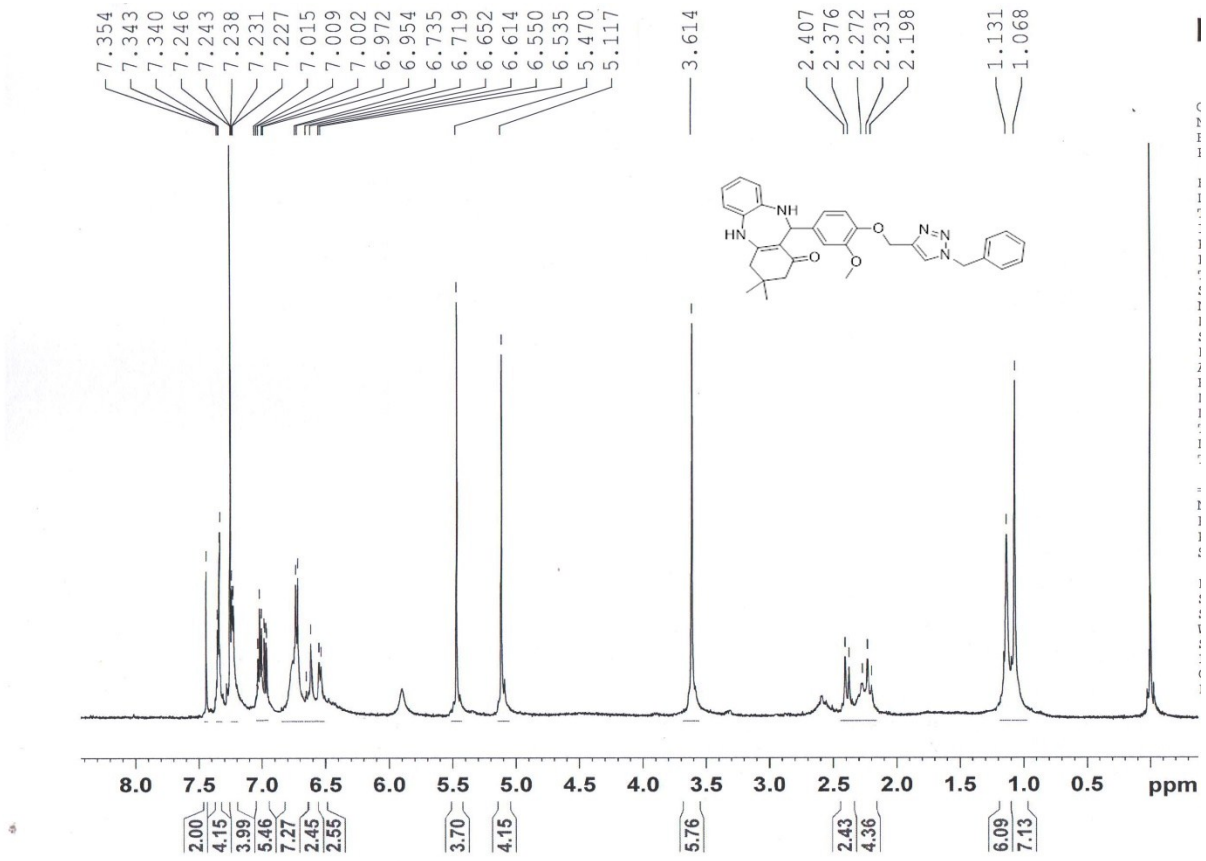
6.410
5.889
5.458
5.061
2.593
2.559
2.426
2.395
2.312
2.279
2.229
2.197
1.142
1.073
NH
HN
O
N=N
N
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.05
1.07
1.31
1.24
3.30
7.79
2.96
1.55
3.13
3.34
1.86
1.64
1.75
1.81
5.37
4.99


191.97
156.84
147.07
130.45
129.03
128.38
128.15
126.12
123.88
122.54
121.85
119.90
114.47
62.06
57.57
53.50
49.43
46.70
32.33
28.53
27.78
NH
HN
O
N=N
N
Cl
180
160
140
120
100
80
60
40
ppm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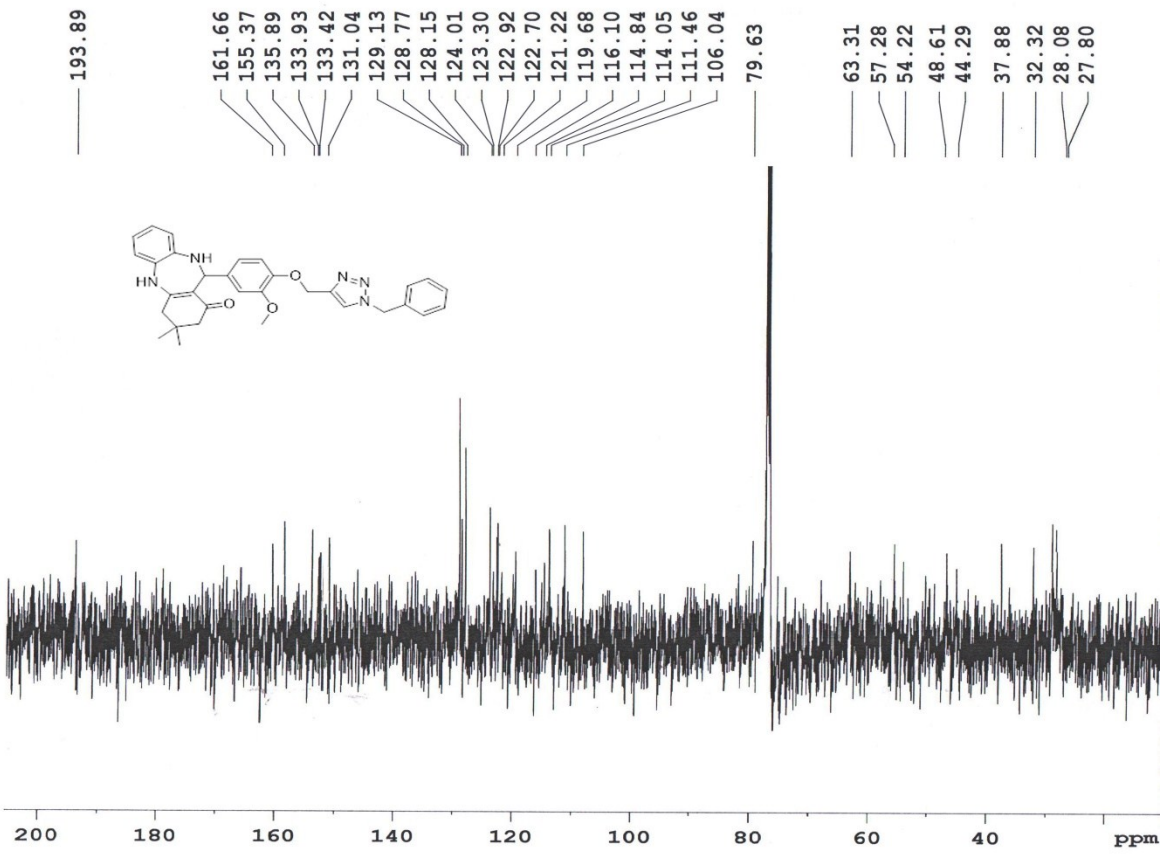
7.343
7.340
7.246
7.243
7.238
7.231
7.227
7.015
7.009
7.002
6.972
6.954
6.735
6.719
6.652
6.614
6.550
6.535
5.470
5.117
3.614
2.407
2.376
2.272
2.231
2.198
1.131
1.068
NH
HN
O
O
N=N
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
4.15
3.99
5.46
7.27
2.45
2.55
3.70
4.15
5.76
2.43
4.36
6.09
7.13


193.89
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155.37
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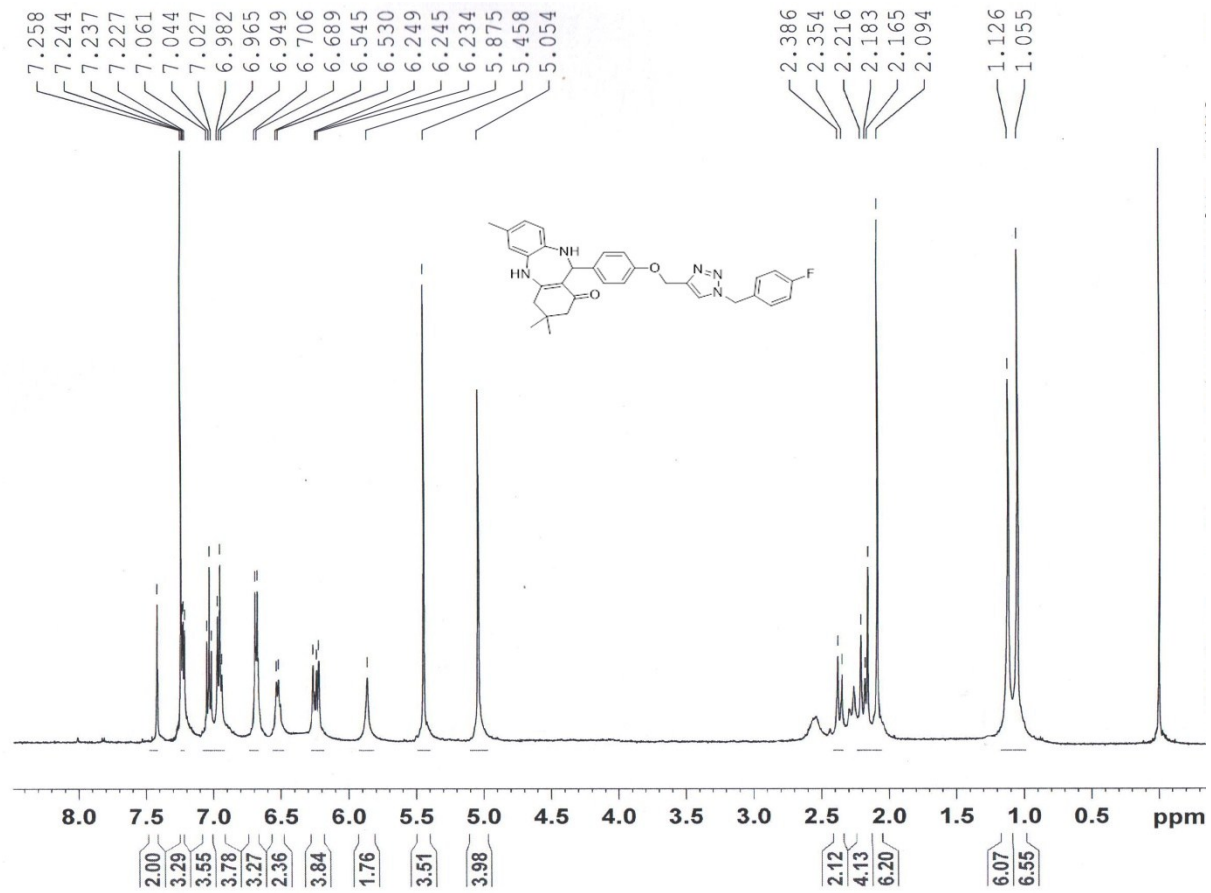
133.93
133.42
131.04
129.13
128.77
128.15
124.01
123.30
122.92
122.70
121.22
119.68
116.10
114.84
114.05
111.46
106.04
79.63
63.31
57.28
54.22
48.61
44.29
37.88
32.32
28.08
27.80
NH
HN
O
O
N=N
N
200 180 160 140 120 100 80 60 40 ppm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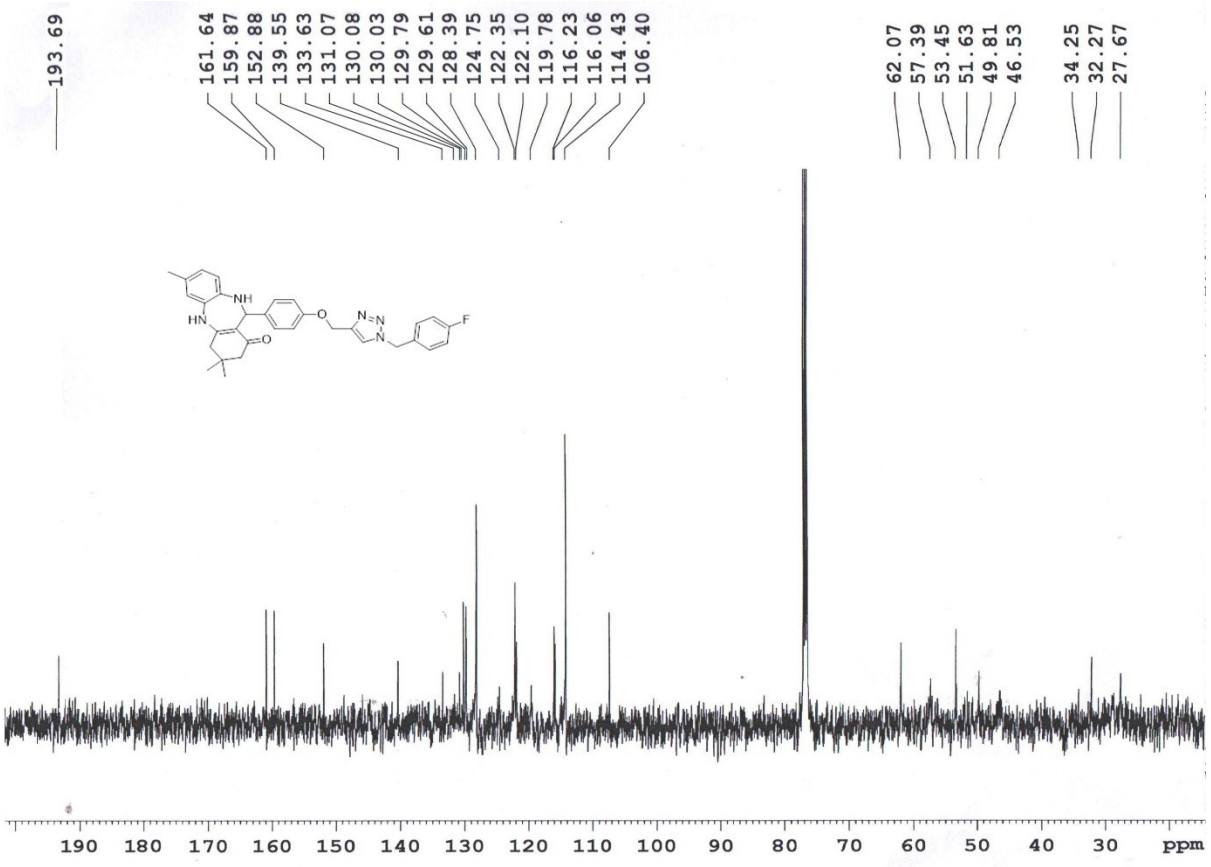
7.244
7.237
7.227
7.061
7.044
7.027
6.982
6.965
6.949
6.706
6.689
6.545
6.530
6.249
6.245
6.234
5.875
5.458
5.054
2.386
2.354
2.216
2.183
2.165
2.094
1.126
1.055
NH
HN
O
N=N
F
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
3.29
3.55
3.78
3.27
2.36
3.84
1.76
3.51
3.98
2.12
4.13
6.20
6.07
6.55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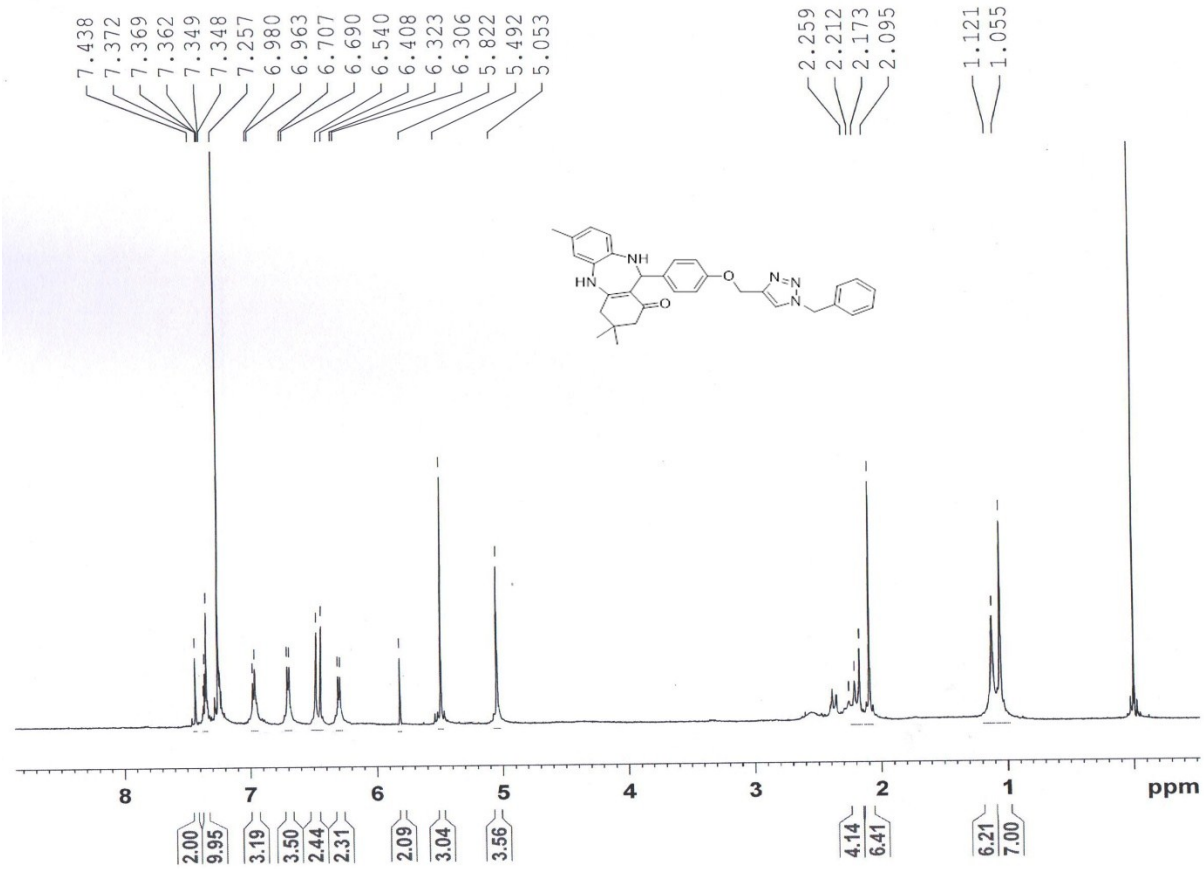
159.87
152.88
139.55
133.63
131.07
130.08
130.03
129.79
129.61
128.39
124.75
122.35
122.10
119.78
116.23
116.06
114.43
106.40
62.07
57.39
53.45
51.63
49.81
46.53
34.25
32.27
27.67
NH
HN
O
N=N
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm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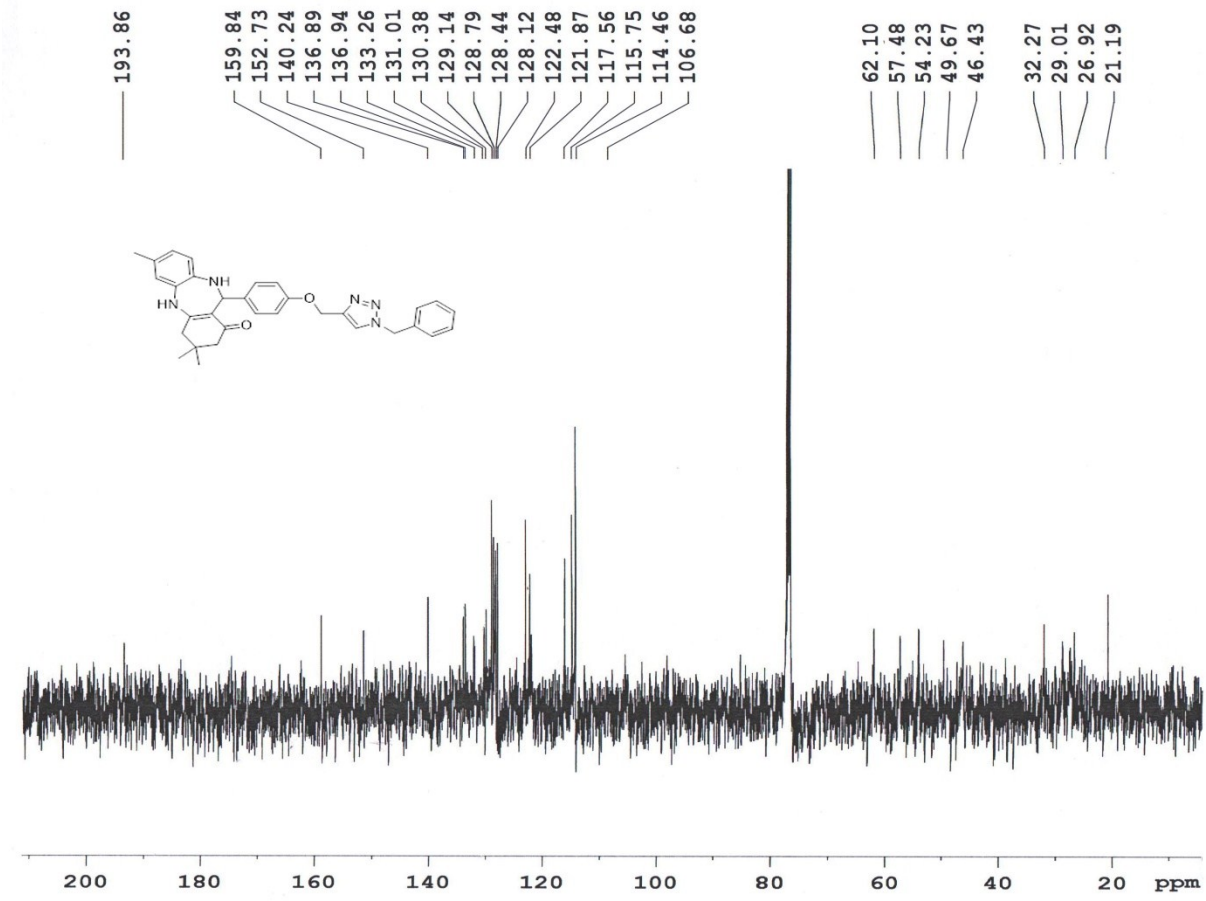
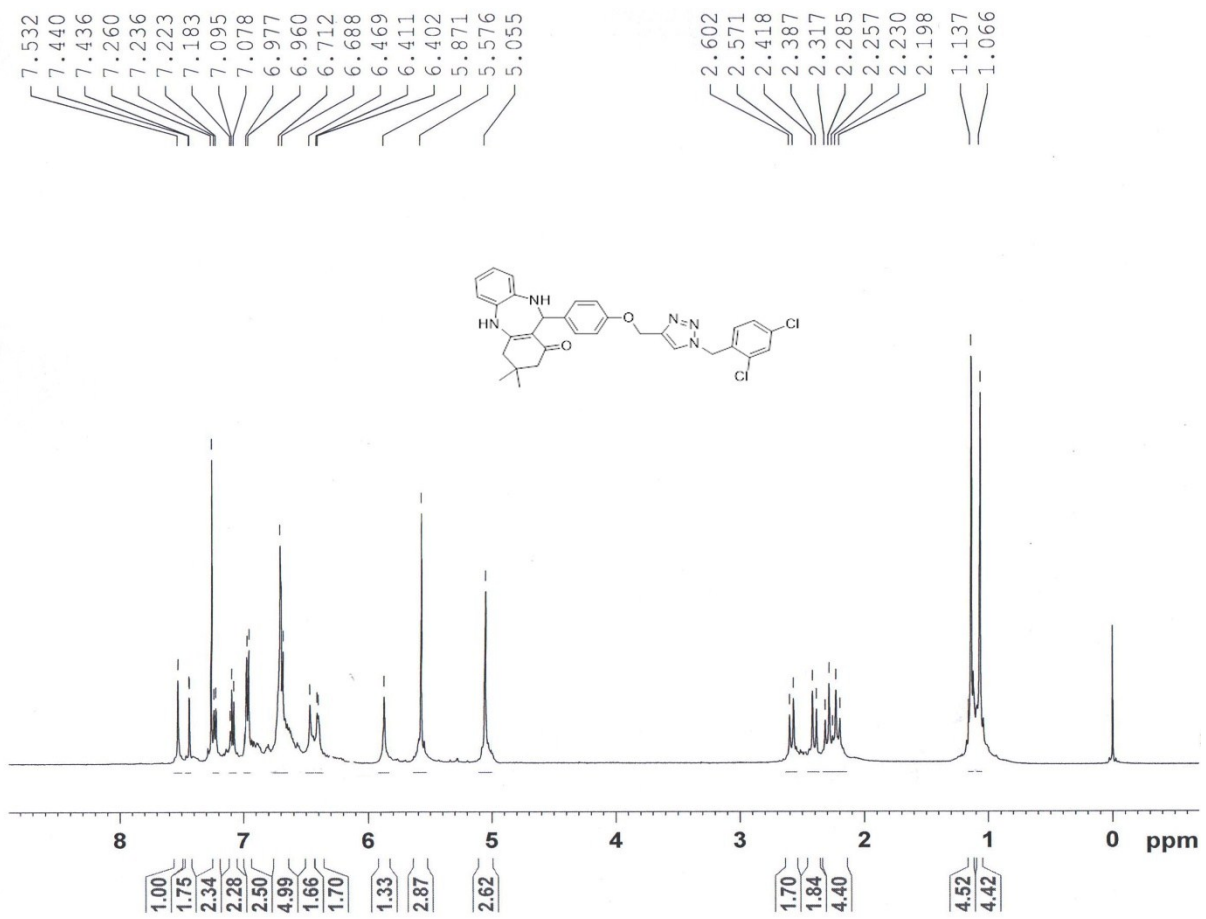
7.372
7.369
7.362
7.349
7.348
7.257
6.980
6.963
6.707
6.690
6.540
6.408
6.323
6.306
5.822
5.492
5.053
2.259
2.212
2.173
2.095
1.121
1.055
NH
HN
O
N=N
8
7
6
5
4
3
2
1
ppm
2.00
9.95
3.19
3.50
2.44
2.31
2.09
3.04
3.56
4.14
6.41
6.21
7.00


193.86
159.84
152.73
140.24
136.89
136.94
133.26
131.01
130.38
129.14
128.79
128.44
128.12
122.48
121.87
117.56
115.75
114.46
106.68
62.10
57.48
54.23
49.67
46.43
32.27
29.01
26.92
21.19
NH
HN
O
N=N
200
180
160
140
120
100
80
60
40
20
ppm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7.440
7.436
7.260
7.236
7.223
7.183
7.095
7.078
6.977
6.960
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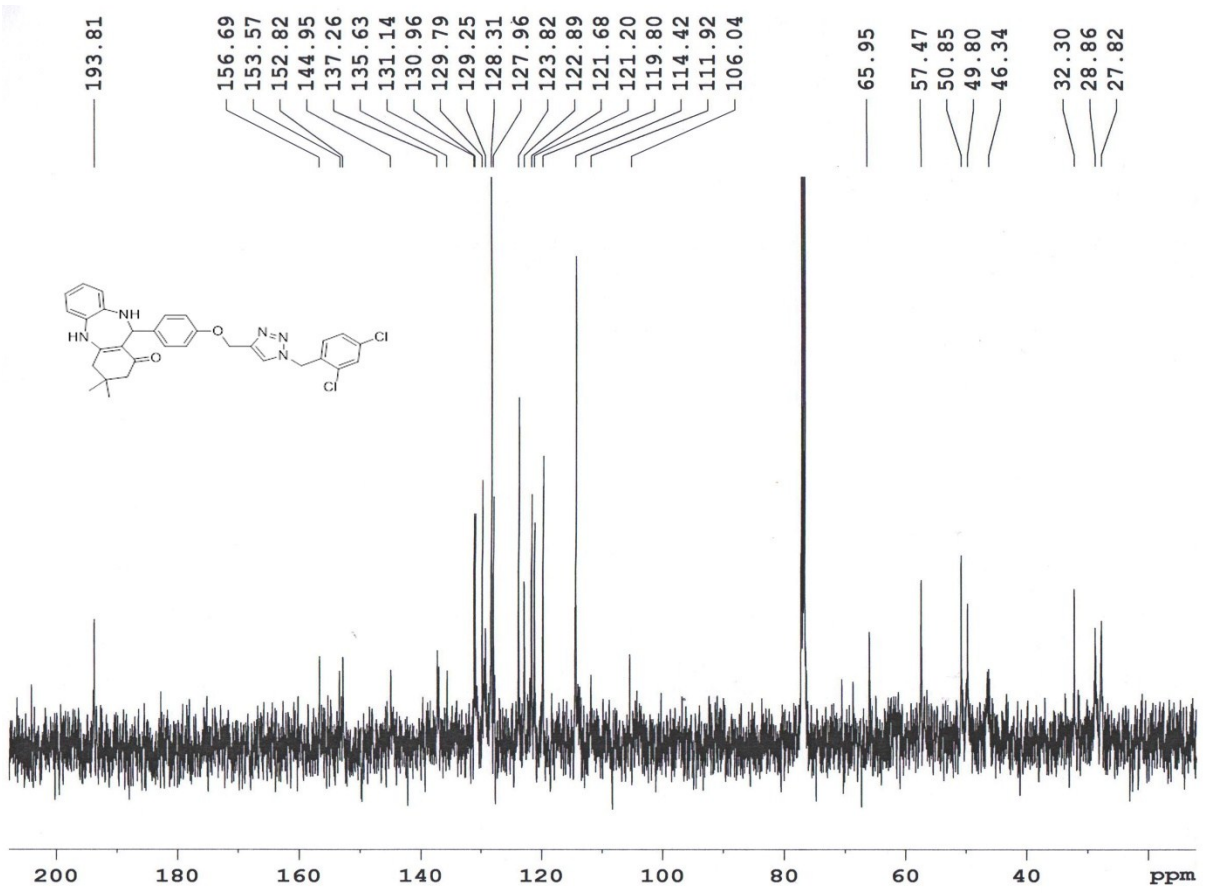
6.469
6.411
6.402
5.871
5.576
5.055
2.602
2.571
2.418
2.387
2.317
2.285
2.257
2.230
2.198
1.137
1.066
NH
HN
O
O
N=N
N
Cl
Cl
8
7
6
5
4
3
2
1
0
ppm
1.00
1.75
2.34
2.28
2.50
4.99
1.66
1.70
1.33
2.87
2.62
1.70
1.84
4.40
4.52
4.42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156.69
153.57
152.82
144.95
137.26
135.63
131.14
130.96
129.79
129.25
128.31
127.96
123.82
122.89
121.68
121.20
119.80
114.42
111.92
106.04
65.95
57.47
50.85
49.80
46.34
32.30
28.86
27.82
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O
O
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N
Cl
Cl
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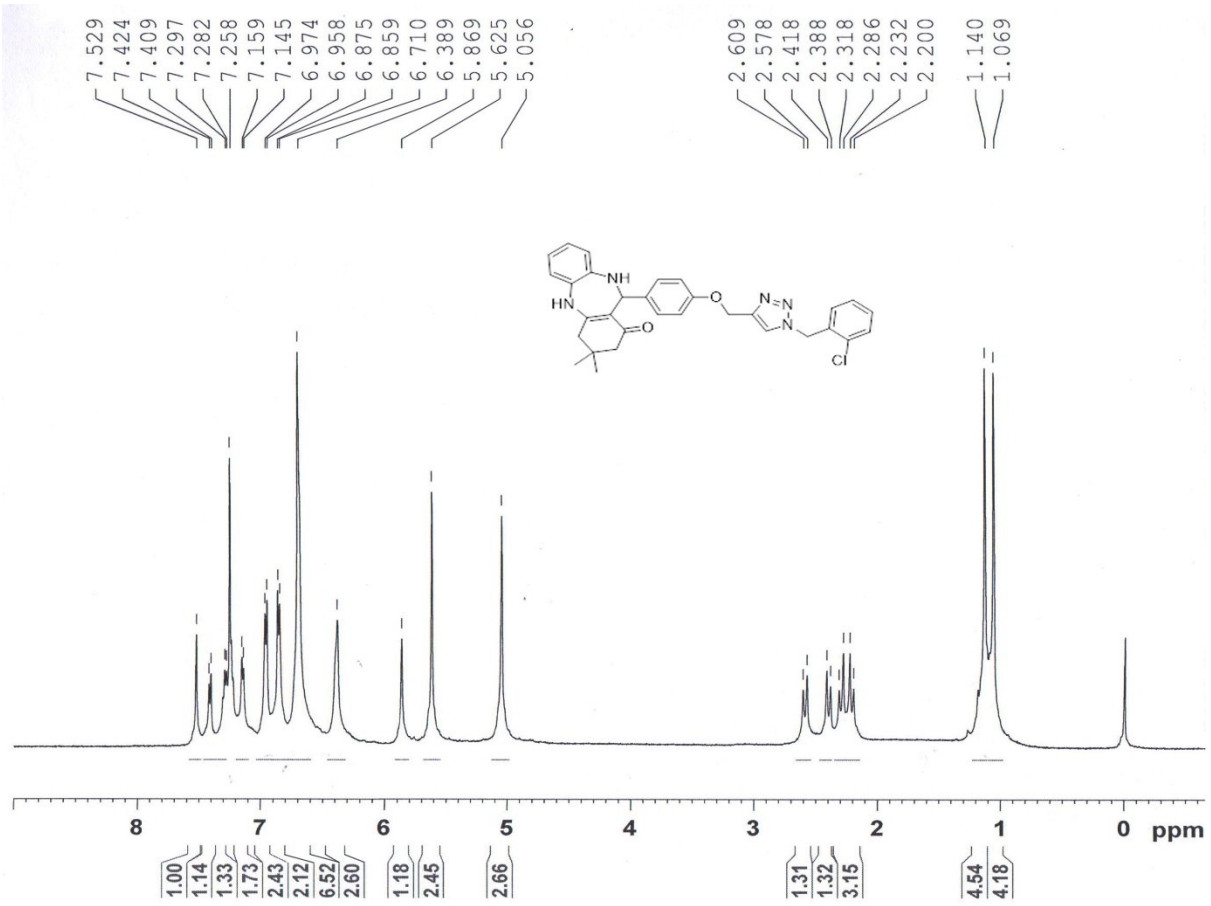
160
140
120
100
80
60
40
ppm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7.145
6.974
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6.710
6.389
5.869
5.625
5.056
2.609
2.578
2.418
2.388
2.318
2.286
2.232
2.200
1.140
1.069
NH
HN
O
N=N
N
Cl
8
7
6
5
4
3
2
1
0
ppm
1.00
1.14
1.33
1.73
2.43
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6.52
2.60
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2.45
2.66
1.31
1.32
3.15
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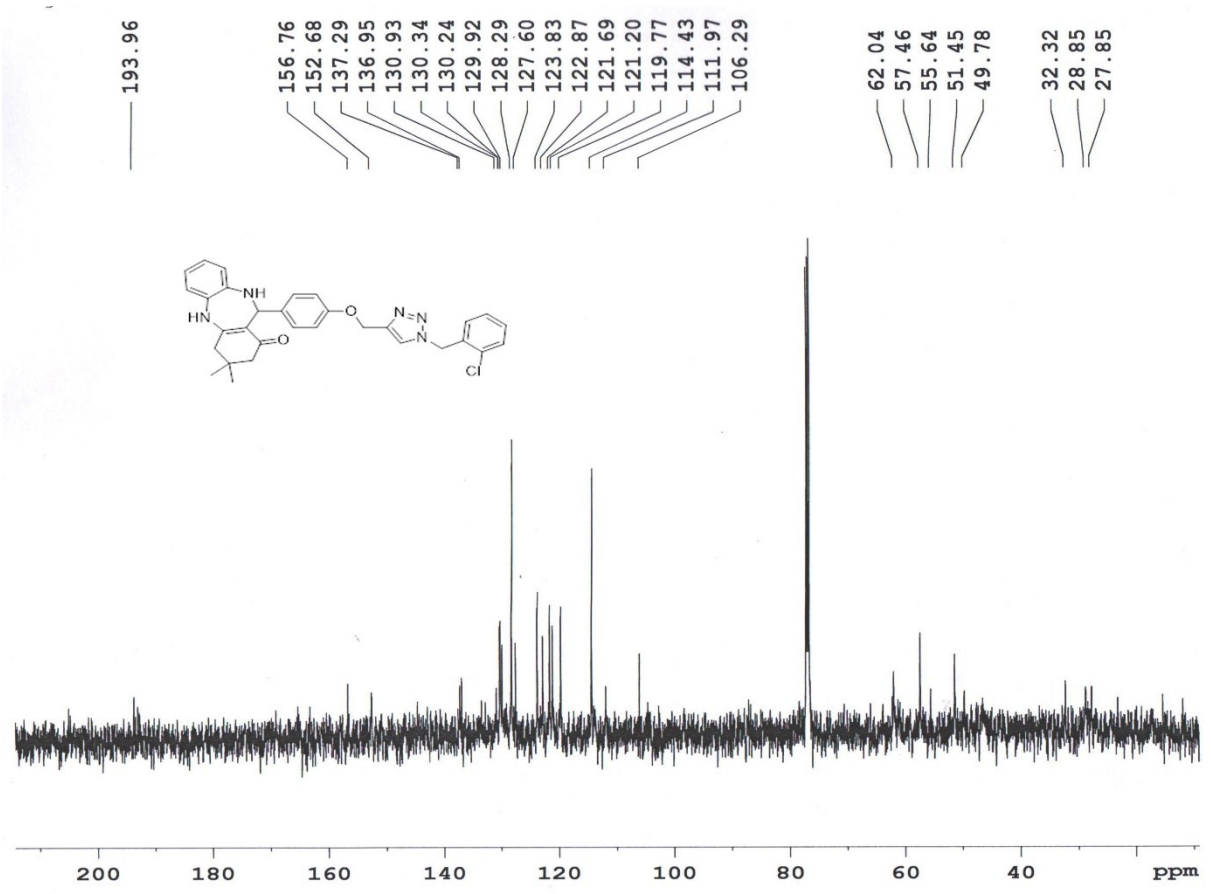
4.18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130.34
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129.92
128.29
127.60
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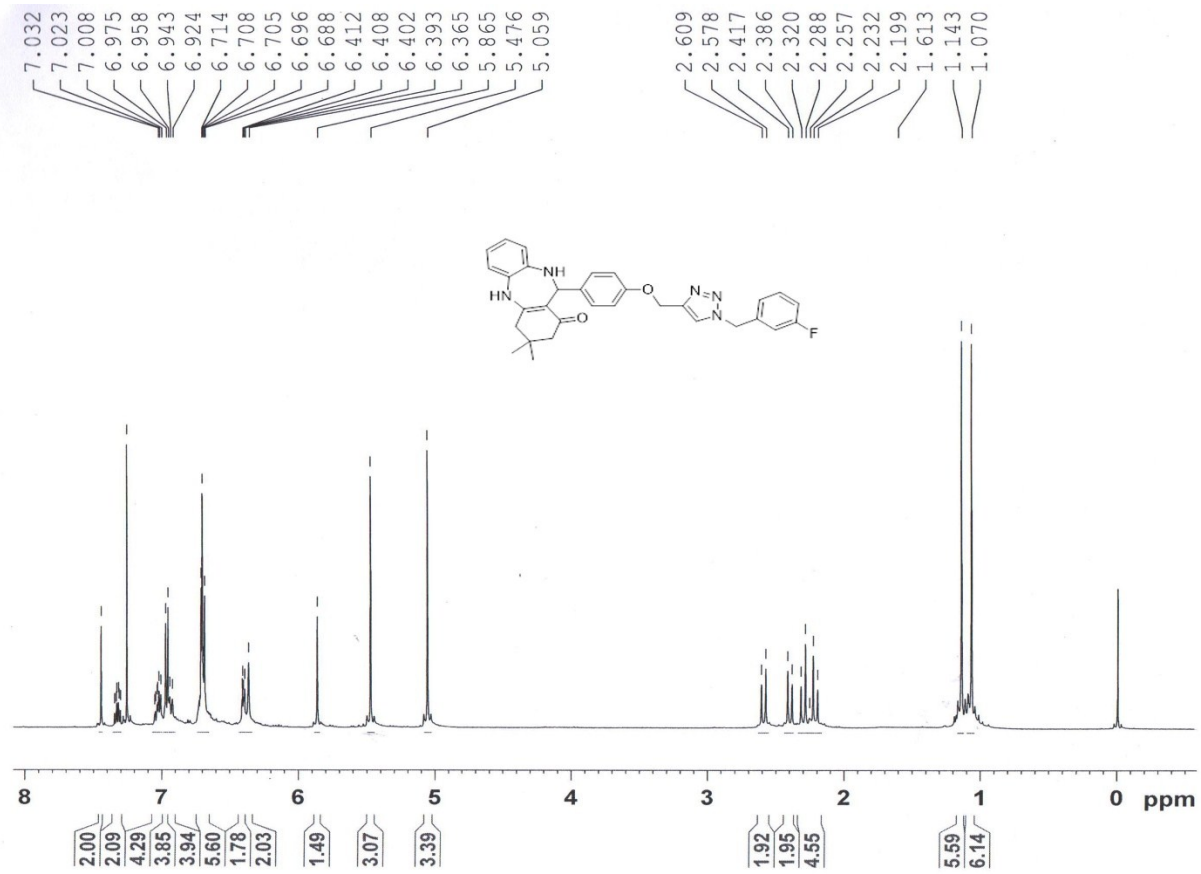
122.87
121.69
121.20
119.77
114.43
111.97
106.29
62.04
57.46
55.64
51.45
49.78
32.32
28.85
27.85
NH
HN
O
N=N
N
Cl
200
180
160
140
120
100
80
60
40
ppm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6.714
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6.705
6.696
6.688
6.412
6.408
6.402
6.393
6.365
5.865
5.476
5.059
2.609
2.578
2.417
2.386
2.320
2.288
2.257
2.232
2.199
1.613
1.143
1.070
NH
HN
O
N=N
N
F
8
7
6
5
4
3
2
1
0
ppm
2.00
2.09
4.29
3.85
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1.78
2.03
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3.39
1.92
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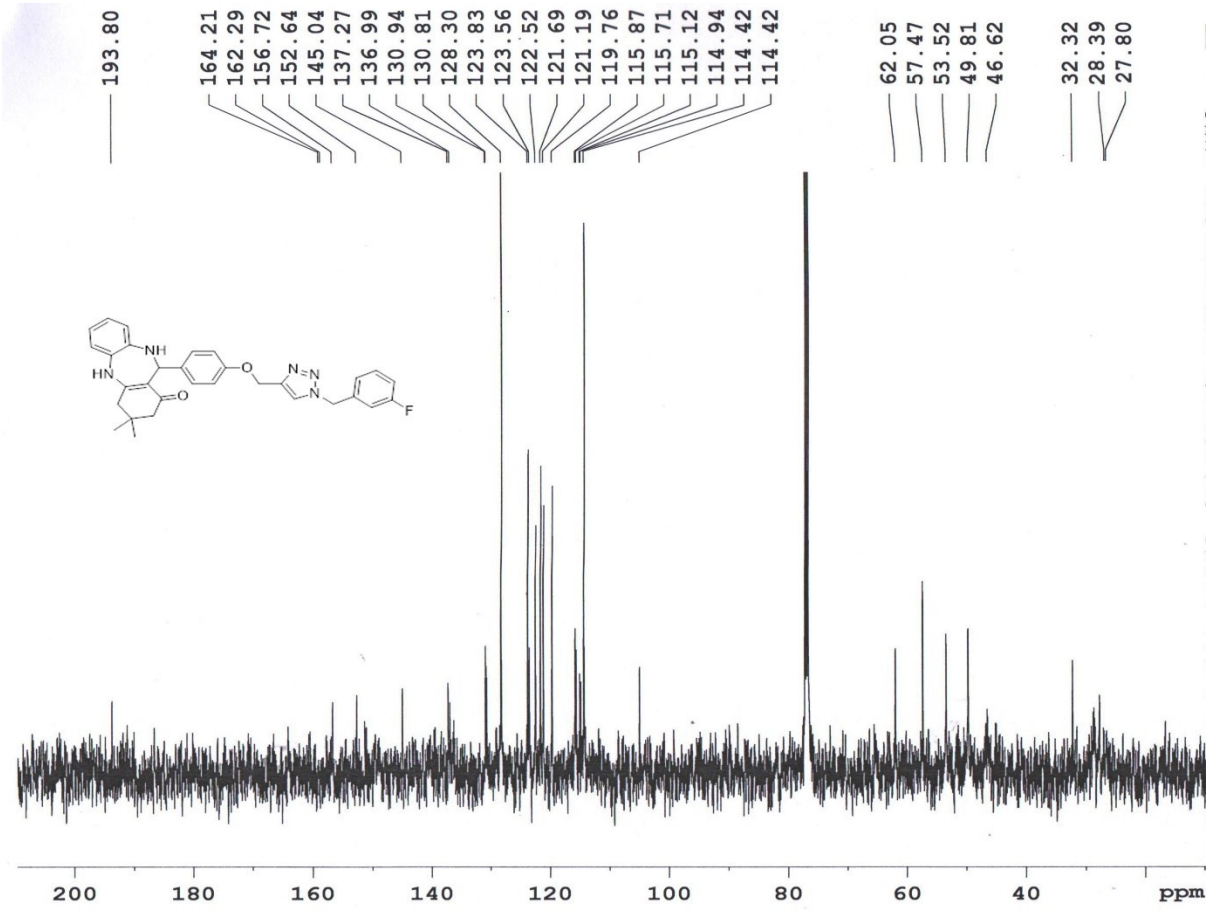
6.14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162.29
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145.04
137.27
136.99
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128.30
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123.56
122.52
121.69
121.19
119.76
115.87
115.71
115.12
114.94
114.42
114.42
62.05
57.47
53.52
49.81
46.62
32.32
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NH
HN
O
N=N
N
F
200
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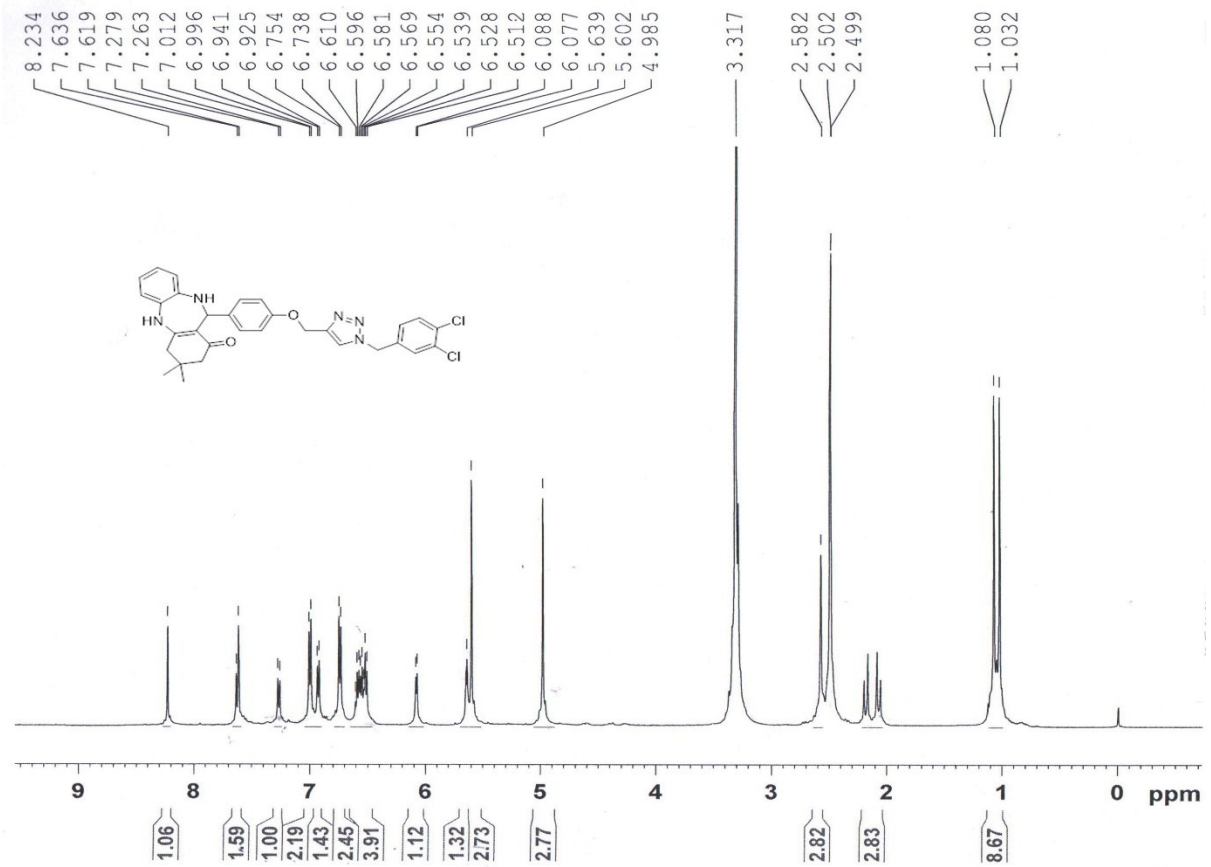
80
60
40
ppm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7.012
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6.941
6.925
6.754
6.738
6.610
6.596
6.581
6.569
6.554
6.539
6.528
6.512
6.088
6.077
5.639
5.602
4.985
3.317
2.582
2.502
2.499
1.080
1.032
NH
HN
O
N=N
Cl
Cl
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.59
1.00
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2.45
3.91
1.12
1.32
2.73
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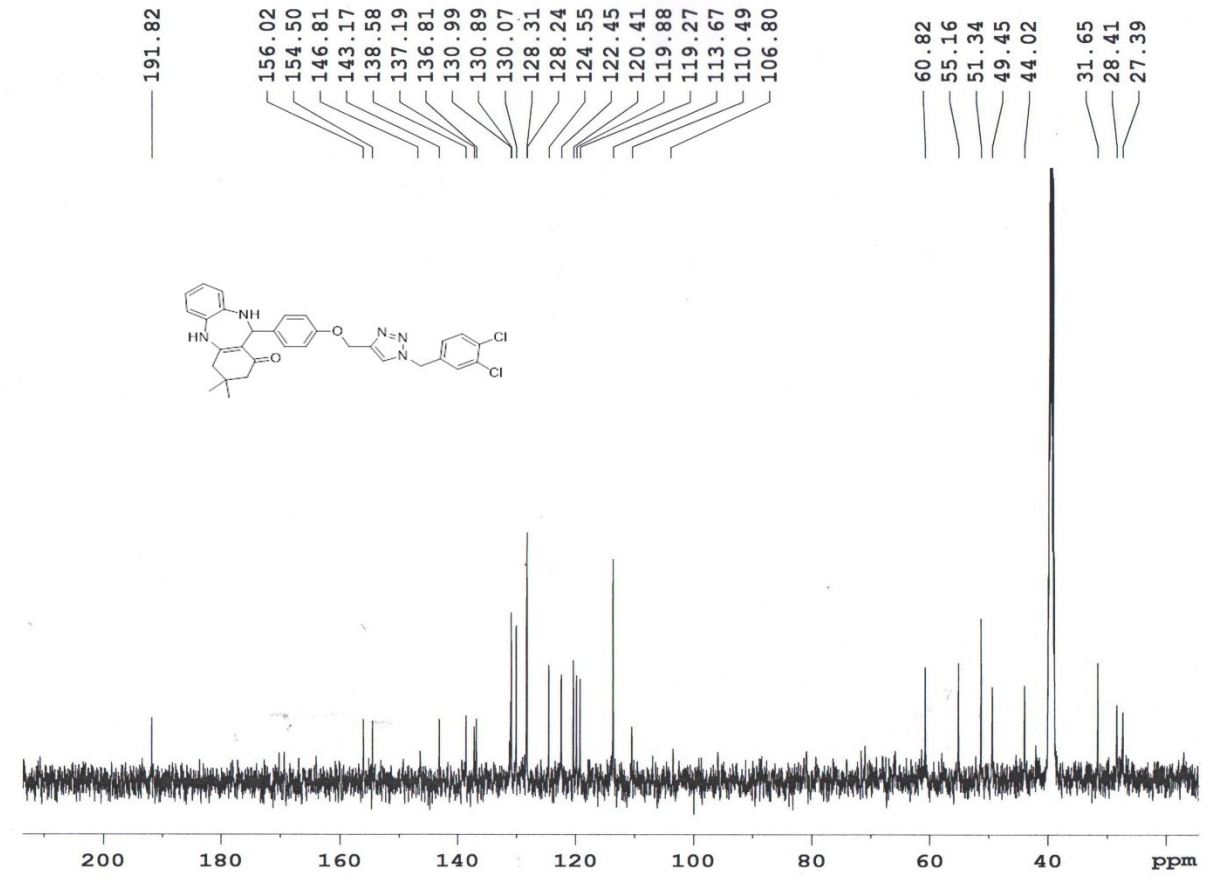
2.82
2.83
8.67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154.50
146.81
143.17
138.58
137.19
136.81
130.99
130.89
130.07
128.31
128.24
124.55
122.45
120.41
119.88
119.27
113.67
110.49
106.80
60.82
55.16
51.34
49.45
44.02
31.65
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NH
HN
O
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Cl
Cl
200
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160
140
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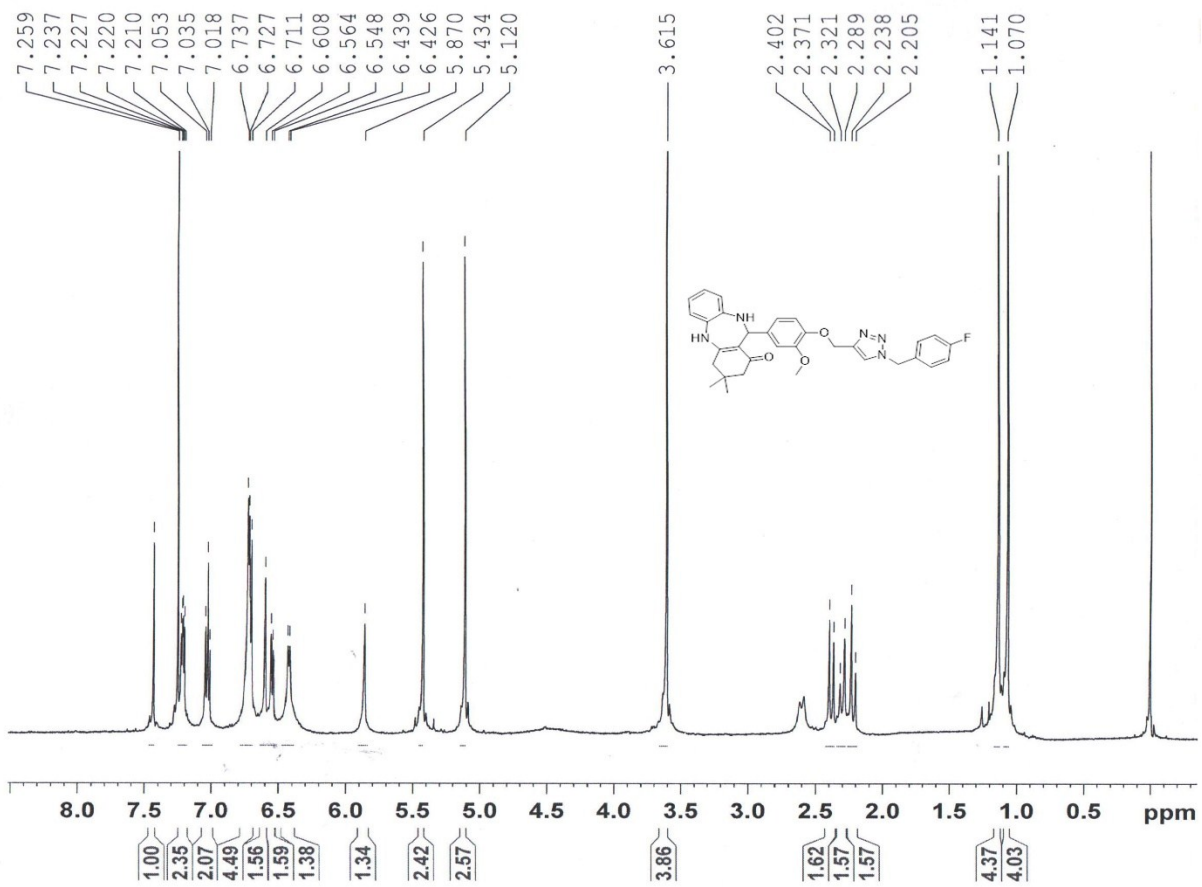
100
80
60
40
ppm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7.035
7.018
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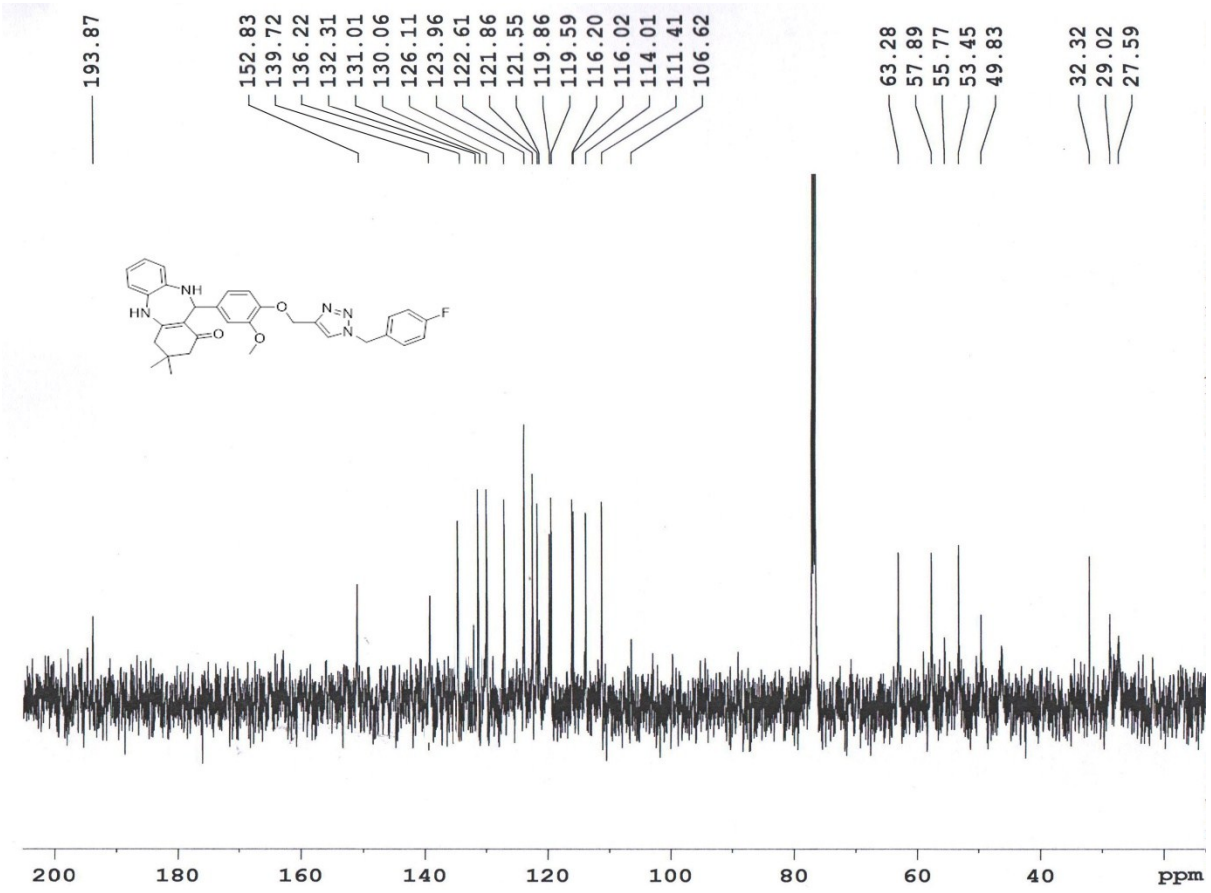
6.727
6.711
6.608
6.564
6.548
6.439
6.426
5.870
5.434
5.120
3.615
2.402
2.371
2.321
2.289
2.238
2.205
1.141
1.070
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 2.35 2.07 4.49 1.56 1.59 1.38 1.34 2.42 2.57 3.86 1.62 1.57 1.57 4.37 4.03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130.06
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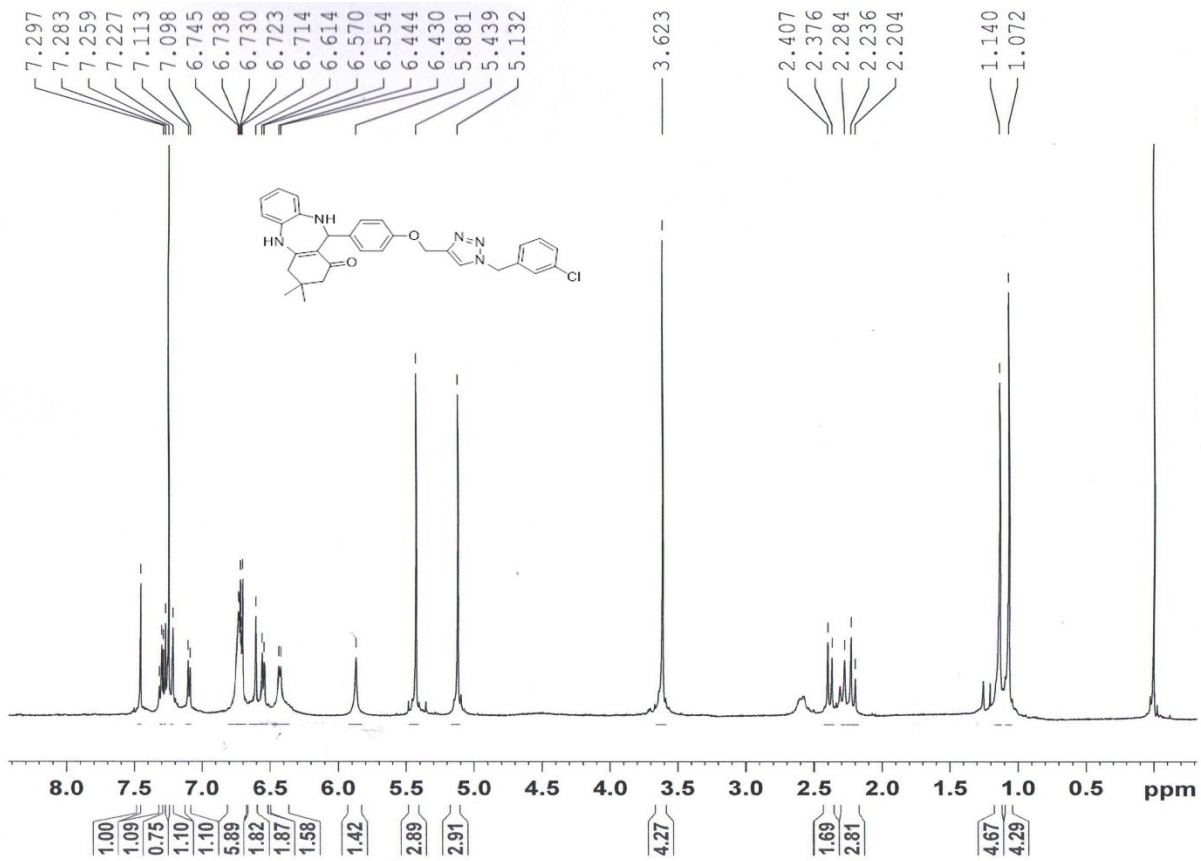
123.96
122.61
121.86
121.55
119.86
119.59
116.20
116.02
114.01
111.41
106.62
63.28
57.89
55.77
53.45
49.83
32.32
29.02
27.59
200 180 160 140 120 100 80 60 40 ppm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7.098
6.745
6.738
6.730
6.723
6.714
6.614
6.570
6.554
6.444
6.430
5.881
5.439
5.132
3.623
2.407
2.376
2.284
2.236
2.204
1.140
1.072
NH
HN
O
N=N
N
Cl
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.09
0.75
1.10
1.10
5.89
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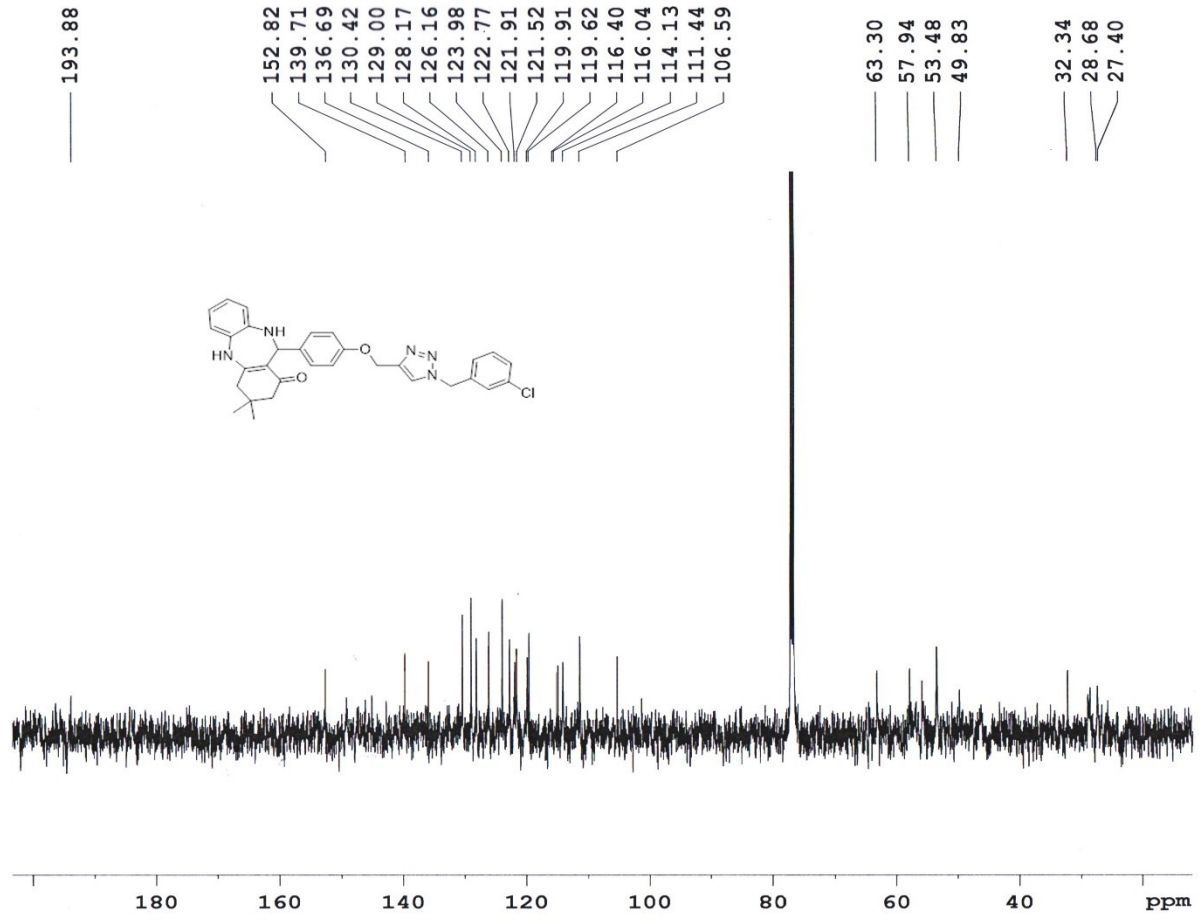
1.58
1.42
2.89
2.91
4.27
1.69
2.81
4.67
4.29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130.42
129.00
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126.16
123.98
122.77
121.91
121.52
119.91
119.62
116.40
116.04
114.13
111.44
106.59
63.30
57.94
53.48
49.83
32.34
28.68
27.40
NH
HN
O
N=N
N
Cl
180 160 140 120 100 80 60 40 ppm