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Supporting information

Alizarin Red S-TiO_2-catalyzed cascade C(sp^3)H to C(sp^2)H bond formation/ cyclization reactions toward tetrahydroquinoline derivatives under visible light irradiation

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Contents

1. Experimental information

1.1 General Methods. TiO_2 (P25, specific surface area: 50 m^2g^{-1}) was purchased from Degussa company. Other starting materials were obtained from Sigma-Aldrich and Merck companies and used without further purification. UV–vis diffuse reflectance spectrum was performed with a Shimadzu UV-2450 spectrophotometer. All solvents were dried according to standard procedures. Melting points were measured on a Buchi 510 apparatus in open capillary tubes and the values are uncorrected. Elemental analysis was performed on a 2400 series PerkinElmer analyzer. ^{1}H NMR and ^{13}C NMR spectra were obtained using $CDCl_3$ as solvent on Bruker Advance DPX FT 250 and Bruker Ultrashield 400 (101 MHz) spectrometry respectively, with TMS as an internal standard. (FT-IR) spectra were obtained by a Shimadzu FT-IR 8300 spectrophotometer. Column chromatography: short columns of SiO_2 60 (70– 230 mesh) in glass columns (1.0 –1.5 cm); 10 –20 g of SiO_2 per nearly 0.4 gram crude mixture. Thin layer chromatography (TLC): silica gel PolyGram SIL G/UV 254 plates.

1.2 Synthesis of maleimides.

N-aryl maleimides and *N*-alky maleimides were synthesized respectively, according to the modified previous reported procedures[1, 2].

1.2.1 Synthesis of *N*-aryl maleimides.

5 mmol of maleic anhydride was put into to 50 ml three-necked round-bottom flask and dissolved in 10 ml of diethyl ether upon stirring. The flask was equipped by a dropping funnel and reflux condenser. Then, 5 mmol of the given aniline was dissolved in 3 ml diethyl ether and added to flask through the dropping funnel. The reaction mixture was stirred at room temperature for 1 h. Next, the reaction mixture was cooled to the room temperature, was filtered off and washed with diethyl ether to separate N-substituted maleanic acid. Afterward, the dried product added to flask and mixed with anhydrous sodium acetate (0.16 g, 2mmol) and acetic anhydride (2ml) then stirred for 1h at 80 ^{o}C. The reaction mixture was cooled to the room temperature and poured into an ice-water mixture. The product washed with 20 ml ice-cold water for 3 times. The dried crude was recrystallized from *n*-hexane or *n*-hexane/acetone to obtain corresponding product.

1.2.2 Synthesis of *N*-alkymaleimides.

5 mmol of maleic anhydride was put into to 50 ml three-necked round-bottom flask and dissolved in 10 ml of dichloromethane upon stirring. The flask was kept at 0-5 °C and equipped by a dropping funnel. Then, 5 mmol of the given amine was dissolved in 3 ml dichloromethane and added to flask through the dropping funnel within 20 minutes. The reaction mixture was stirred at room temperature for 1 h. Next, the reaction mixture was cooled to the room temperature, was filtered off and washed with diethyl ether to separate *N*-substituted maleanic acid. Afterward, the dried product added to flask and was mixed with triethylamine (0.28 ml, 2 mmol) and acetic anhydride (2ml) in 10 ml acetone. The reaction was refluxed for 2 h. The reaction mixture was cooled to the room temperature and poured into an ice-water mixture. The product washed with 20 ml ice-cold water for 3 times. The dried crude purified using silica gel column chromatography with petroleum ether/ethyl acetate as eluents.

1.3 Preparation of dyes-TiO_2 photocatalyst.

At first, the TiO_2 powder was heated at 110 °C in air for 3 h to remove adsorbed water on the surface. Dyes-TiO_2 were prepared by a minor modified reported procedure[3]. Typically, three different molar concentration of ARS dye (0.1 mol/L, 0.2 mol/L and 0.4 mol/L) in ethanol were added to 1g of pre-heated nano TiO_2 P25 and stirred at room temperature in the dark for 12 h. The solid was centrifuged and washed with ethanol five times and dried at 40 °C for 30 h on the vacuum oven and kept in the dark.

1.4 General Procedure for synthesis of tetrahydroquinolines.

A mixture of the *N,N*-dimethylanilines (2 mmol), maleimides (1 mmol), and ARS-TiO_2 (0.006g) in CH_3CN (8 mL) placed in a vial under air atmosphere. Subsequently, the reaction mixture was stirred under irradiation of a 12 W blue LED lamp (distance app. 4.0 cm) for 20 hours at ambient temperature (30 °C). The reaction monitored by TLC and after the completion, the reaction mixture was centrifuged to separate the catalyst. Afterward, the remaining solution was poured into water (15 mL) and extracted two times with EtOAc (15 mL), the combined organic layer was washed with brine (15 mL × 2) and dried over Na_2SO_4. The mixture concentrated in vacuo and the residue was purified on silica gel column chromatography with petroleum ether/ethyl acetate (20:1, 20:3).

2. Characterization of compounds

2-Isobutyl-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3a**)

White solid, mp = 82-84 ^{o}C. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 0.68-0.72 (m, 6H), 1.80-1.96 (m, 1H), 2.70 (s, 3H), 2.93 (dd, 1H, *J* = 6.7, 4.5 Hz), 3.22 (d, 2H, *J* = 7.5 Hz), 3.24-3.29 (m, 1H), 3.41 (dd, 1H, *J* = 8.7, 2.5 Hz), 3.88 (d, 1H, *J* = 9.2 Hz), 6.61 (d, 1H, *J* = 8.2 Hz), 6.79 (t, 1H, *J* = 7.5 Hz), 7.11 (t, 1H, *J* = 7.7 Hz), 7.37 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 19.80, 26.89, 39.30, 42.04, 43.59, 46.35, 50.90, 112.37, 119.18, 119.62, 128.50, 130.19, 148.49, 176.99, 178.98. IR (KBr) ν 2954, 1774, 1699, 1595, 1496, 1397, 1203, 1086, 1118, 748 cm^{-1}. EA Requires: C 70.56, H 7.40, N 10.29. Found: C 70.61, H 7.37, N 10.32.

5-Methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3b**)

White solid, mp = 78-80 ^{o}C (77-79 ^{o}C)[4]. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.75 (s, 3H), 2.97 (dd, 1H, *J* = 7.2, 4.2 Hz), 3.36 (dd, 1H, *J* = 6.7, 2.7 Hz), 3.44 (dd, 1H, *J* = 8.7, 2.7 Hz), 3.97 (d, 1H, *J* = 9.2 Hz), 6.69 (d, 1H, *J* = 8.2 Hz), 6.84 (td, 1H, *J* = 7.5, 1.2 Hz), 7.12-7.19 (m, 1H), 7.37 (d, 1H, *J* = 7.2 Hz), 8.37 (s, 1H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.42, 43.26, 44.81, 50.41, 112.58, 118.41, 128.73, 130.12, 148.52, 176.99, 179.01. IR (KBr) ν 3019, 2862, 1766, 1705, 1595, 1496, 1350, 1319, 1119, 794, 748 cm^{-1}.

2-Cyclohexyl-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3c**)

Yellowish oil. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.11-1.22 (m, 2H), 1.45-1.73 (m, 8H), 2.71 (s, 3H), 2.94 (dd, 1H, *J* = 6.7, 4.7 Hz), 3.16-3.24 (m, 1H), 3.37 (dd, 1H, *J* = 8.5, 3.0 Hz), 3.79-3.92 (m, 2H), 6.61 (d, 1H, *J* = 8.2 Hz), 6.72-6.82 (m, 1H), 7.11 (t, 1H, *J* = 7.00 Hz), 7.38 (d, 1H, *J* = 7.2 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 25.06, 25.82, 28.86, 39.43, 41.73, 43.07, 50.84, 58.76, 112.39, 119,49, 128.43, 129.35, 130.20 148.41, 176.87, 178.76. IR (KBr) ν 2931, 1705, 1635, 1458, 1373, 1272, 1126, 1072, 748 cm^{-1}. EA Requires: C 72.46, H 7.43, N 9.39. Found: C 72.49, H 7.49, N 9.33.

2-Benzyl-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3d**)

White solid, mp = 124 -126 ^{o}C (126-128 ^{o}C)[4]. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.69 (s, 3H), 2.93 (dd, 1H, *J* = 7.2, 4.5 Hz), 3.20-3.26 (m, 1H), 3.38 (dd, 1H, *J* = 8.75, 2.75 Hz), 3.86 (1H, d, *J* = 9.2 Hz), 4.46-4.60 (m, 2H), 6.62 (d, 1H, *J* = 8.0 Hz), 6. 79 (td, 1H, *J* = 7.2, 1.0 Hz), 7.07-7.22 (m, 6H), 7.36 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.38, 42.12, 42.81, 43.69, 50.79, 112.50, 118.91, 119.72, 127.84, 128.38, 128.52, 128.64, 130.27, 135.63, 148.52, 176.46, 178.43. IR (KBr) ν 2954, 2862, 1774, 1704, 1596, 1497, 1394, 1342, 1164, 756, 702 cm^{-1}.

5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3e**)

White solid, mp = 201-203 °C (202-204 °C)[5]. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 2.84 (s, 3H), 3.12 (dd, J = 7.2, 4.2 Hz, 1H), 3.51-3.64 (m, 2H), 4.16 (d, 1H, J = 9.5), 6.74 (d, 1H, J = 8.2 Hz), 6.90 (t, 2H, J = 7.5 Hz), 7.20-7.54 (m, 7H). ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 39.4, 42.1, 43.5, 50.6, 112.5, 118.5, 119.6, 126.3, 128.4, 128.6, 128.9, 130.3, 131.9, 148.5, 175.7, 177.7. IR (KBr) ν 2923, 1788, 1712, 1592, 1496, 1388, 1326, 1118, 756, 690 cm^{-1}.

2-(3-Bromophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3f**)

White solid, mp = 163-165 °C (164-166 °C)[6]. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 2.83 (s, 3H), 3.11 (dd, 1H, J = 11.2, 4.2 Hz), 3.49-3.63 (m, 2H), 4.15 (d, 1H, J = 9.7), 6.75 (d, 1H, J = 7.7 Hz), 6.91 (t, 1H, J = 7.5 Hz), 7.21-7.32 (m, 3H), 7.46-7.52(m, 3H) . ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 39.5, 42.1, 43.6, 50.6, 112.7, 118.3, 119.8, 122.3, 125.0, 128.8, 129.4, 130.2, 130.3, 131.6, 133.1, 148.4, 175.4, 177.3. IR (KBr) ν 2854, 1772, 1711, 1595, 1489, 1381, 1195, 786, 754 cm^{-1}.

2-(3-Chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3g**)

White solid, mp = 158-160 °C. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 2.86 (s, 3H), 3.17 (dd, 1H, J= 11.2, 4.0 Hz), 3.54-3.66 (m, 2H), 4.19 (d, 1H, J= 9.2 Hz), 6.82 (d, 1H, J = 8.0 Hz), 6.96 (td, 1H, J= 7.5, 1.0 Hz), 7.18-7.40 (m, 5H), 7.55 (d, 1H, J= 7.5 Hz). ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 39.5, 42.2, 43.7, 50.6, 112.7, 118.3, 119.8, 124.6, 126.6, 128.7, 128.8, 130.0, 130.3, 133.0, 134.5, 148.5, 175.4, 177.4. IR (KBr) ν 2844, 1774, 1712, 1596, 1481, 1388, 1195, 786, 748 cm^{-1}. EA Requires: C 66.16, H 4.63, N 8.57. Found: C 66.11, H 4.25, N 8.53.

2-(4-Chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3h**)

White solid, mp = 187-189 °C (188-190 °C)[7]. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.83 (s, 3H), 3.10 (dt, 1H, J = 11.5, 4.2 Hz), 3.49-3.63 (m, 2H), 4.15 (d, 1H, J = 9.5 Hz), 6.76 (dd, 1H, J = 8.2, 3.0 Hz), 6.88-6.95 (m, 1H), 7.21-7.27 (m, 3H), 7.36-7.41 (m, 2H), 7.51 (dd, 1H, J = 7.7, 2.2 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.51, 42.12, 43.59, 50.62, 112.66, 118.40, 119.78, 127.59, 128.79, 129.18, 130.30, 130.44, 134.22, 148.47, 175.53, 177.46. IR (KBr) ν 2958, 1782, 1712, 1595, 1488, 1396, 1326, 1203, 756 cm^{-1}.

2-(4-Methoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3i**)

White solid, mp = 221-223 °C (222-224 °C)[7]. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 2.84 (s, 3H), 3.15 (dd, 1H, J= 11.2, 4.2 Hz), 3.50-3.64 (m, 2H), 3.80 (s, 3H), 4.16 (d, 1H, J= 9.2 Hz), 6.78 (d, J = 8.2 Hz, 1H), 6.89-7.01 (m, 3H), 7.14-7.28 (m, 3H), 7.55 (d, 1H, J= 7.5 Hz). ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 39.5, 42.1, 43.5, 50.7, 55.5, 112.5, 114.3, 118.6, 119.7, 124.6, 127.6, 128.7, 130.4, 148.5, 159.4, 176.0, 178.0. IR (KBr) ν 2931, 1713, 1594, 1512, 1398, 1249, 1164, 763 cm^{-1}.

2-(4-Ethoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3j**)

White solid, mp = 151-153 ^{o}C. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 1.41 (t, 3H, J = 7.0 Hz), 2.85 (s, 3H), 3.13 (dd, 1H, J = 11.2, 4.5 Hz), 3.49-3.64 (m, 2H), 4.04 (q, 2H, J = 7.0 Hz), 4.15 (d, 1H, J = 9.5), 6.76 (d, 1H, J = 8.0 Hz), 6.89-6.94 (m, 3H), 7.15-7.28 (m, 3H), 7.55 (d, 1H, J = 7.5 Hz,) . ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 14.8, 39.5, 42.1, 43.5, 50.7, 63.7, 112.5, 114.8, 118.7, 119.7, 124.5, 127.6, 128.7, 130.4, 148.5, 158.8, 176.1, 178.0. IR (KBr) ν 2933, 1774, 1711, 1596, 1511, 1396, 1248, 1203, 1166, 810, 752 cm^{-1}. EA Requires: C 71.41, H 5.99, N 8.33. Found: C 71.45, H 5.94, N 8.29.

2-(4-Isopropylphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3k**)

White solid, mp = 157-159 ^{o}C. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 1.23 (d, J = 7.0 Hz, 6H), 2.82 (s, 3H), 2.86-2.96 (m, 1H), 3.11 (dd, 1H, J = 11.2, 4.2 Hz), 3.48-3.62 (m, 2H), 4.13 (d, 1H, J = 9.5), 6.74 (d, J = 8.2 Hz, 1H), 6.90 (t, 1H, J = 7.5 Hz), 7.15-7.29 (m, 5H), 7.53 (d, 1H, J = 7.7 Hz) . ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 23.9, 33.9, 39.5, 42.1, 43.5, 50.7, 112.5, 118.7, 119.6, 126.2, 127.1, 128.7, 129.6, 130.4, 148.5, 149.3, 175.9, 177.9. IR (KBr) ν 2962, 2861, 1712, 1595, 1504, 1388, 1272, 1195, 748 cm^{-1}. EA Requires: C 75.42, H 6.63, N 8.38. Found: C 75.45, H 6.68, N 8.42.

2-(2-Ethylphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3l**)

White solid, mp = 128-130 ^{o}C. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 0.81 (t, 3H, J = 7.5 Hz), 2.14 (qd, 2H, J= 7.5, 3.2 Hz), 2.86 (s, 3H), 3.12 (dd, 1H, J= 11.2, 3.7 Hz), 3.54-3.67 (m, 2H), 4.19 (d, 1H, J = 9.2 Hz), 6.77 (d, 1H, J = 8.2 Hz), 6.88-6.97 (m, 1H), 7.11 (d, 1H, J= 7.2 Hz), 7.20-7.37 (m, 4H), 7.52 (d, 1H, J=7.2 Hz) . ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 14.2, 24.2, 39.2, 42.9, 44.5, 51.0, 112.3, 118.8, 119.8, 126.9, 128.2, 128.4, 128.7, 129.1, 129.7, 130.3, 130.7, 148.6, 176.3, 178.3. IR (KBr) ν 2967, 2823, 1714, 1598, 1512, 1396, 1203, 756 cm^{-1}. EA Requires: C 74.98, H 6.29, N 8.74. Found: C 74.95, H 6.32, N 8.79.

2-(5-Methyl-1,3-dioxo-1,3,3a,4,5,9b-hexahydro-*2H*-pyrrolo[3,4-c]quinolin-2-yl)benzonitrile (**3m**)

White solid, mp = 177-179 ^{o}C. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.87 (s, 3H), 3.22 (dd, 1H, *J* = 7.2, 2.2 Hz), 3.61-3.72 (m, 2H), 4.29 (d, 1H, *J* = 9.2 Hz), 6.82 (1H, d, *J* = 8.0 Hz), 6.95 (td, 1H, *J* = 6.2, 1.2 Hz), 7.26 (td, 2H, *J* = 6.7, 1.5 Hz), 7.48-7.55 (m, 2H), 7.68 (t, 1H, *J* = 7.7 Hz), 7.77 (d, 1H, *J* = 7.7 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.45, 42.58, 44.07, 50.77, 112.71, 119.79, 119.84, 119.86, 128.93, 129.18, 129.20, 129.53, 130.31, 130.35, 133.58, 133.66, 148.65, 174.85, 176.71. IR (KBr) ν 2854, 2229, 1720, 1504, 1380, 1188, 763 cm^{-1}. EA Requires: C 71.91, H 4.76, N 13.24. Found: C 71.94, H 4.73, N 13.28.

2-(4-Bromophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3n**)

White solid, mp = 217-219 ^{o}C. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.76 (s, 3H), 3.04 (dd, 1H, *J* = 7.2, 4.2 Hz), 3.45-3.56 (m, 2H), 4.08 (d, 1H, *J* = 9.5 Hz), 6.68 (d, 1H, *J* = 8.2 Hz), 6.84 (td, 1H, *J* = 7.5, 1.0 Hz), 7.08-7.20 (m, 3H), 7.42-7.50 (m, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.51, 42.18, 43.74, 50.59, 112.78, 118.08, 119.91, 121.57, 123.13, 128.96, 129.78, 130.28, 132.18, 148.51, 175.19, 177.12. IR (KBr) ν 2962, 1780, 1711, 1590, 1488, 1394, 1319, 1203, 756 cm^{-1}. EA Requires: C 58.24, H 4.07, N 7.55. Found: C 58.26, H 4.03, N 7.58.

2-(4-Hydroxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3o**)

White solid, mp = 146-148 °C. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.76 (s, 3H), 3.05 (dd, 1H, *J* = 7.5, 3.7 Hz), 3.46-3.57 (m, 2H), 4.09 (d, 1H, *J* = 9.2 Hz), 6.68 (d, 1H, *J* = 8.2 Hz), 6.85 (td, 1H, *J* = 7.5, 1.0 Hz), 7.08 (d, 2H, *J* = 8.7 Hz), 7.17-7.20 (m, 1H), 7.24 (d, 2H, *J* = 9.0 Hz), 7.45 (d, 1H, *J* = 7.7 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 21.15, 39.47, 42.13, 43.60, 50.66, 112.59, 118.49, 119.73, 122.16, 127.36, 128.76, 129.41, 130.34, 148.54, 150.26, 175.68, 177.60. IR (KBr) ν 3479, 2896, 1766, 1712, 1496, 1373, 1172, 1010, 748 cm^{-1}. EA Requires: C 70.12, H 5.23, N 9.09. Found: C 70.09, H 5.19, N 9.13.

5-Methyl-2-(4-nitrophenyl)-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3p**)

Yellow solid, mp = 138-140 °C. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.85 (s, 3H), 3.16 (dd, 1H, *J* = 7.2, 4.5 Hz), 3.57-3.68 (m, 2H), 4.23 (d, 1H, *J* = 9.5 Hz), 6.78 (d, 1H, *J* = 8.2 Hz), 6.94 (td, 1H, *J* = 7.5, 1.0 Hz), 7.26 (td, 1H, *J* = 7.2, 1.5 Hz), 7.51-7.61 (m, 3H), 8.21-8.29 (dd, 2H, *J* = 9.0, 2.0 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.49, 42.17, 43.79, 50.58, 112.78, 118.03, 119.93, 124.27, 126.83, 129.02, 130.29, 137.49, 146.88, 148.55, 175.15, 177.07. IR (KBr) ν 2923, 1782, 1713, 1596, 1527, 1342, 1180, 765 cm^{-1}. EA Requires: C 64.09, H 4.48, N 12.46. Found: C 64.13, H 4.43, N 12.44.

5-Methyl-2-(3-nitrophenyl)-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3q**)

Yellow solid, mp = 188-190 °C. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.85 (s, 3H), 3.11-3.17 (m, 1H), 3.57-3.67 (m, 2H), 4.23 (d, 1H, *J* = 9.5 Hz), 6.77 (1H, d, *J* = 8.2 Hz), 6.93 (td, 1H, *J* = 7.5, 1.0 Hz), 7.22-7.29 (m, 1H), 7.52 (d, 1H, *J* = 7.5 Hz), 7.62 (t, 1H, *J* = 8.0 Hz), 7.69-7.74 (m, 1H), 8.21-8.27 (m, 2H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.52, 42.21, 43.78, 50.61, 112.79, 118.09, 119.92, 121.61, 123.16, 129.00, 129.81, 130.30, 132.22, 133.03, 148.36, 148.58, 175.23, 177.17. IR (KBr) ν 2920, 1712, 1527, 1496, 1388, 1350,1188, 756 cm^{-1}. EA Requires: C 64.09, H 4.48, N 12.46. Found: C 64.12, H 4.51, N 12.43.

8-Bromo-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3r**)

White solid, mp = 158-160 °C (157-159 °C)[4]. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.75 (s, 3H), 3.06 (dd, 1H, *J* = 7.5, 3.7 Hz), 3.45-3.56 (m, 2H), 4.03 (d, 1H, *J* = 9.2 Hz), 6.58 (1H, d, *J* = 8.7 Hz), 7.16-7.39 (m, 6H), 7.58 (d, 1H, *J* = 2.2 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.50, 41.80, 43.31, 50.40, 111.69, 114.29, 120.44, 126.34, 128.68, 129.10, 131.47, 131.85, 132.74, 147.52, 175.18, 177.31. IR (KBr) ν 2923, 1713, 1488, 1396, 1319, 1195, 694, 624 cm^{-1}.

5,8-Dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3t**)

White solid, mp = 193-195 °C (193-195°C)[5]. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.22 (s, 1H), 2.73 (s, 3H), 2.99 (dd, 1H, *J* = 7.0, 4.2 Hz), 3.44-3.54 (m, 2H), 4.05 (d, 1H, *J* = 9.5 Hz), 6.58 (d, 1H, *J* = 8.2 Hz), 6.97 (dd, 1H, *J* = 6.5, 1.7 Hz), 7.18 (t, 1H, *J* = 1.5 Hz), 7.21 (d, 1H, *J* = 1.5 Hz), 7.27-7.39 (m, 4H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 20.46, 39.59, 42.19, 43.59, 50.95, 112.55, 118.52, 126.40, 128.52, 128.82, 129.00, 129.25, 130.83, 130.92, 146.38, 175.92, 177.87. IR (KBr) ν 2932, 1712, 1505, 1388, 1272, 1195, 690, 619 cm^{-1}.

3. Indication of H_2O_2 after completing the reaction.

H_2O_2 test at the end of reaction (*Reaction conditions*: A mixture of 1 (2 mmol), 2 (1 mmol) and ARS-TiO_2 (0.006g) as photocatalyst, in the CH_3CN (8 mL) was irradiated with a 12 W blue LED in the air for 20 h at ambient temperature).

 1	 2	 3	 4	 5	 6
H_2O_2 Indicator (KI/starch)	Reaction mixture at t = 0 h	Reaction mixture at t = 24 h	Addition of 1 to 3	Addition of 1 to 30% H_2O_2	Addition of 1 to 2

Figure S1.

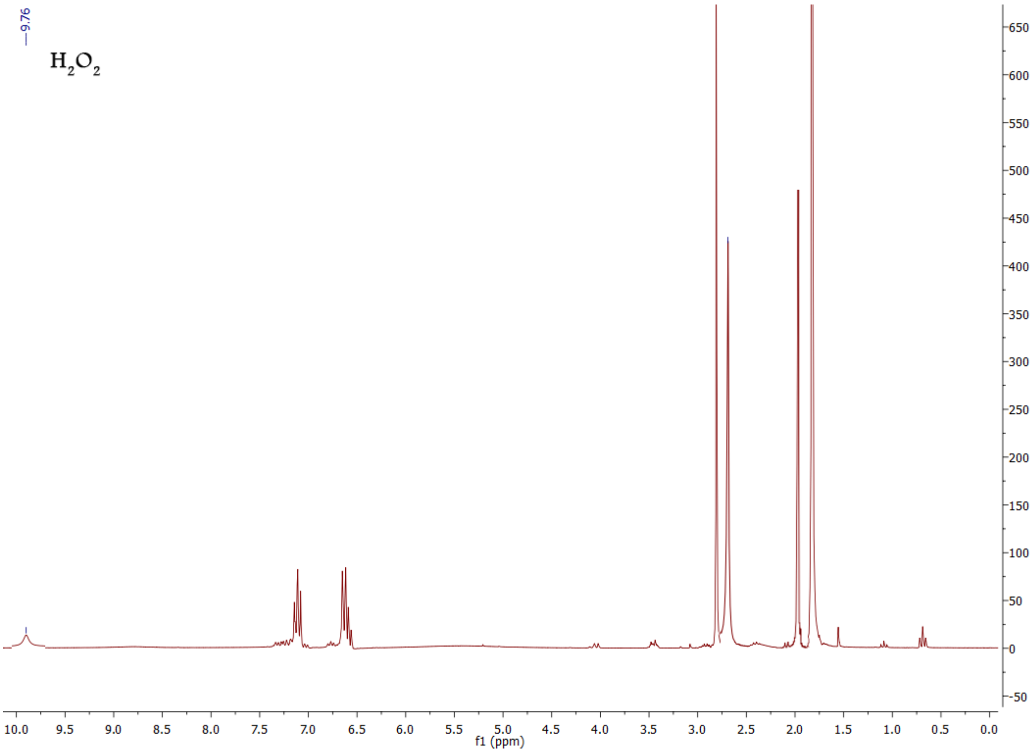


Figure S2.

4. The box used for the reactions

Figure S3.

5. Computational Details

The geometry optimizations were performed by density functional theory (DFT) calculations using the B3LYP functional and 6-31G(d,p) basis set. The default parameters for the convergence criteria were used. Subsequent frequency calculations were performed at the same level to verify the optimized structures as the minima. To obtain accurate electrochemical properties, the Gibbs free energies were computed at the G3(MP2) level of theory which has been designed particularly for the prediction of reliable thermochemical properties. The solvation model based on density (SMD) was employed to account for the solvent contribution. The Gibbs free energies of the 1-electron reduction and oxidation half-reactions were calculated in the presence of acetonitrile as solvent. The oxidation and reduction potentials were computed at 298 K and relative to NHE. The Gaussian 09 package[8] was used in all calculations. Vibrational analyses on the optimized structures were performed to confirm the structure.

6. Characterization of photocatalyst after reusability test

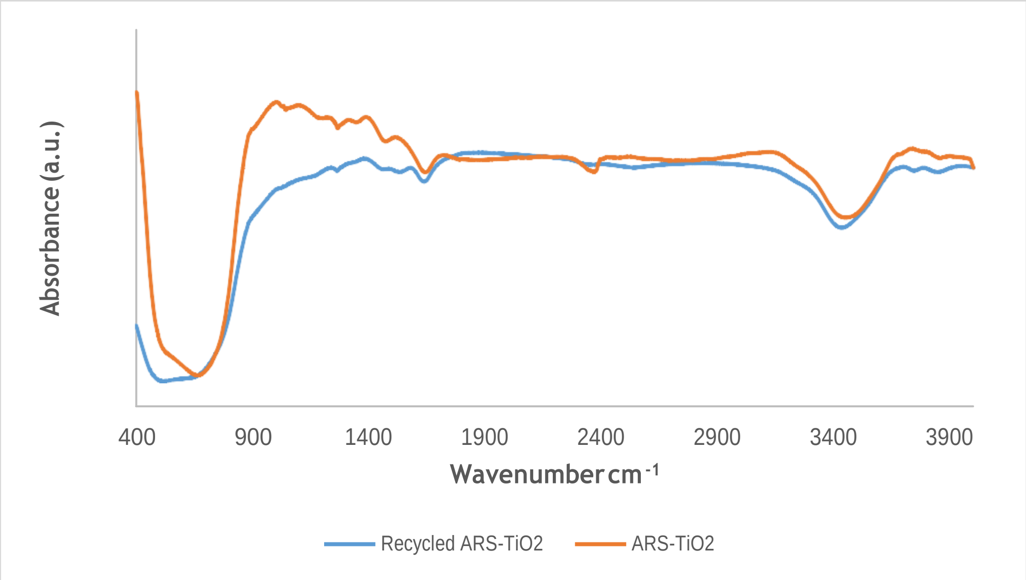


Figure S4 FT-IR spectra of ARS-TiO_2 before and after recycling

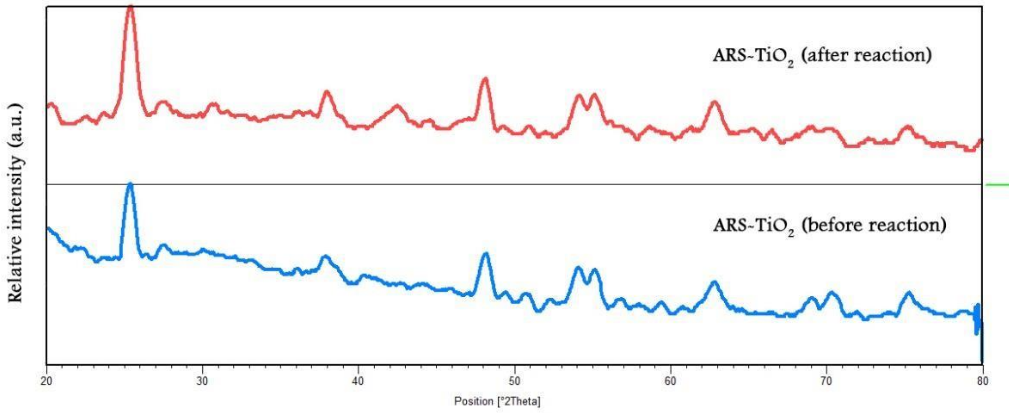
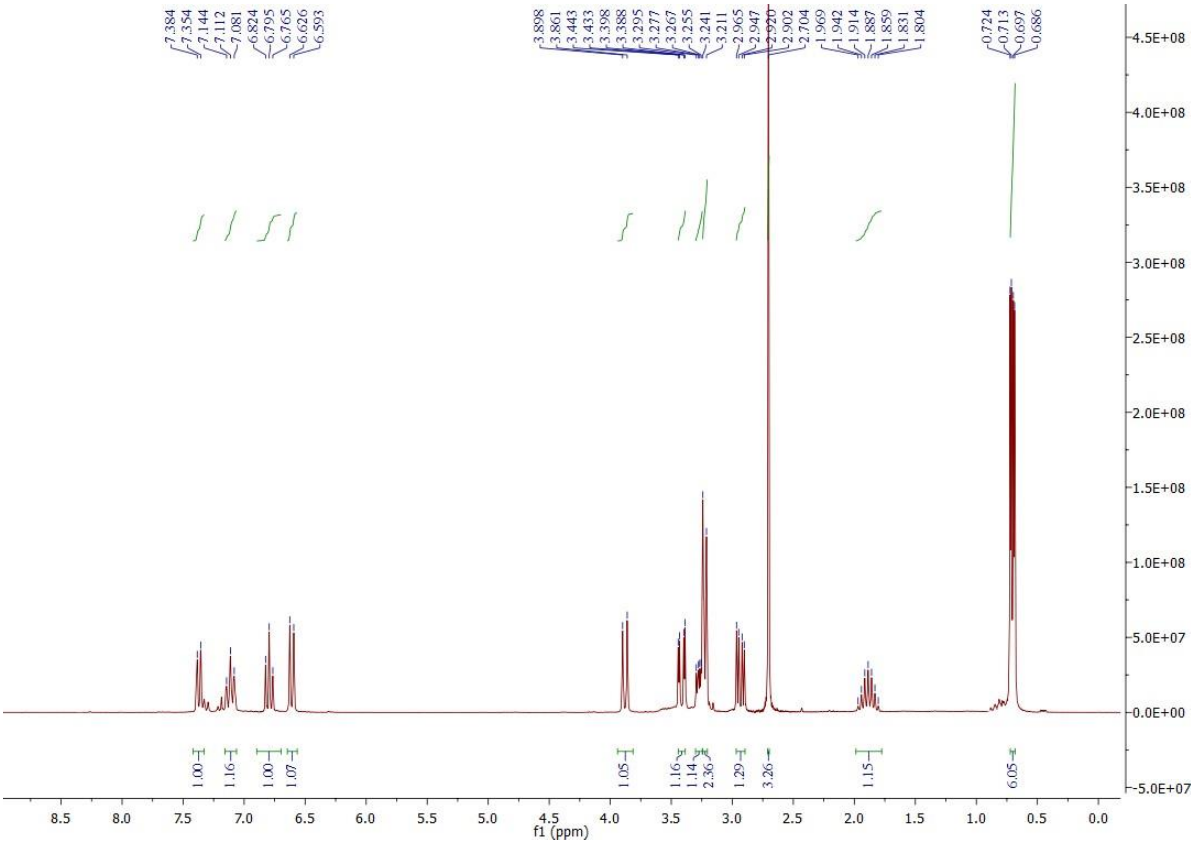


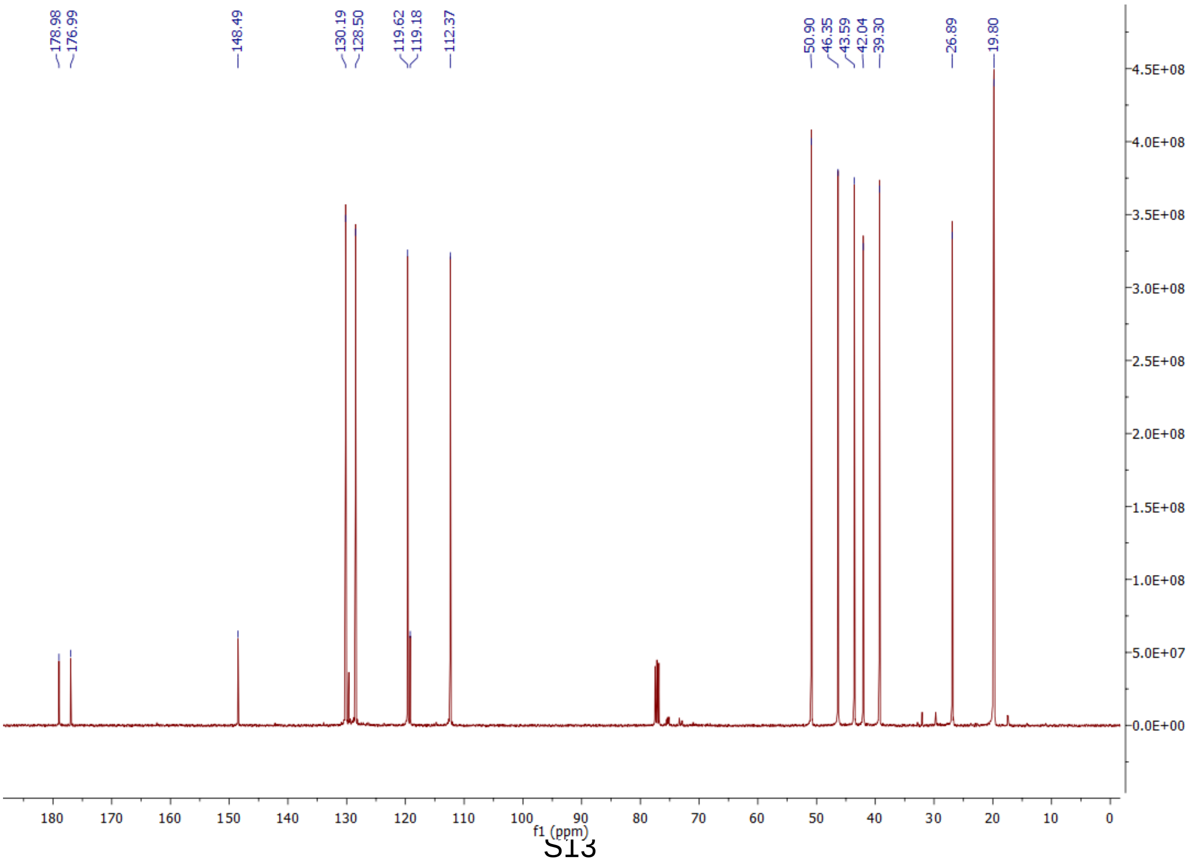
Figure S5 XRD spectra of ARS-TiO_2 before and after recycling

7. [1]H and [13]C NMR Spectra of Products

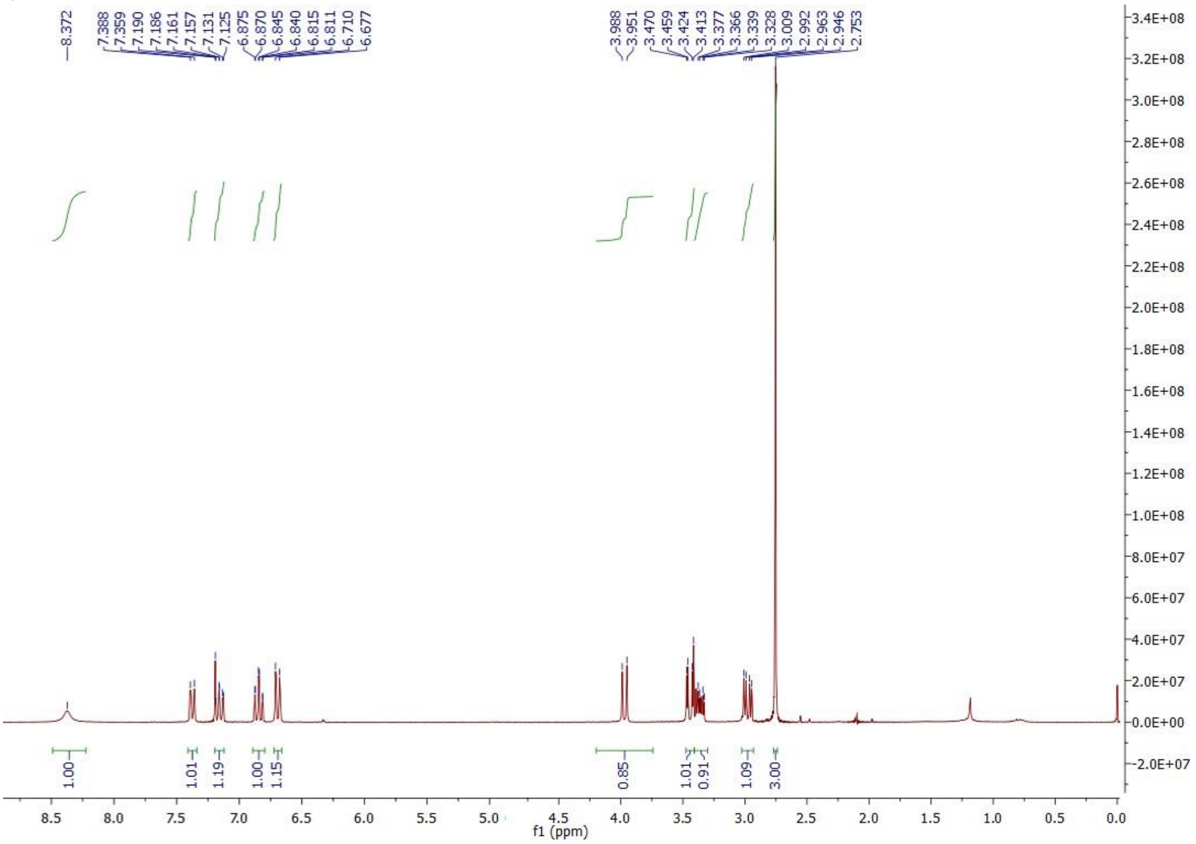
3a [1]HNMR



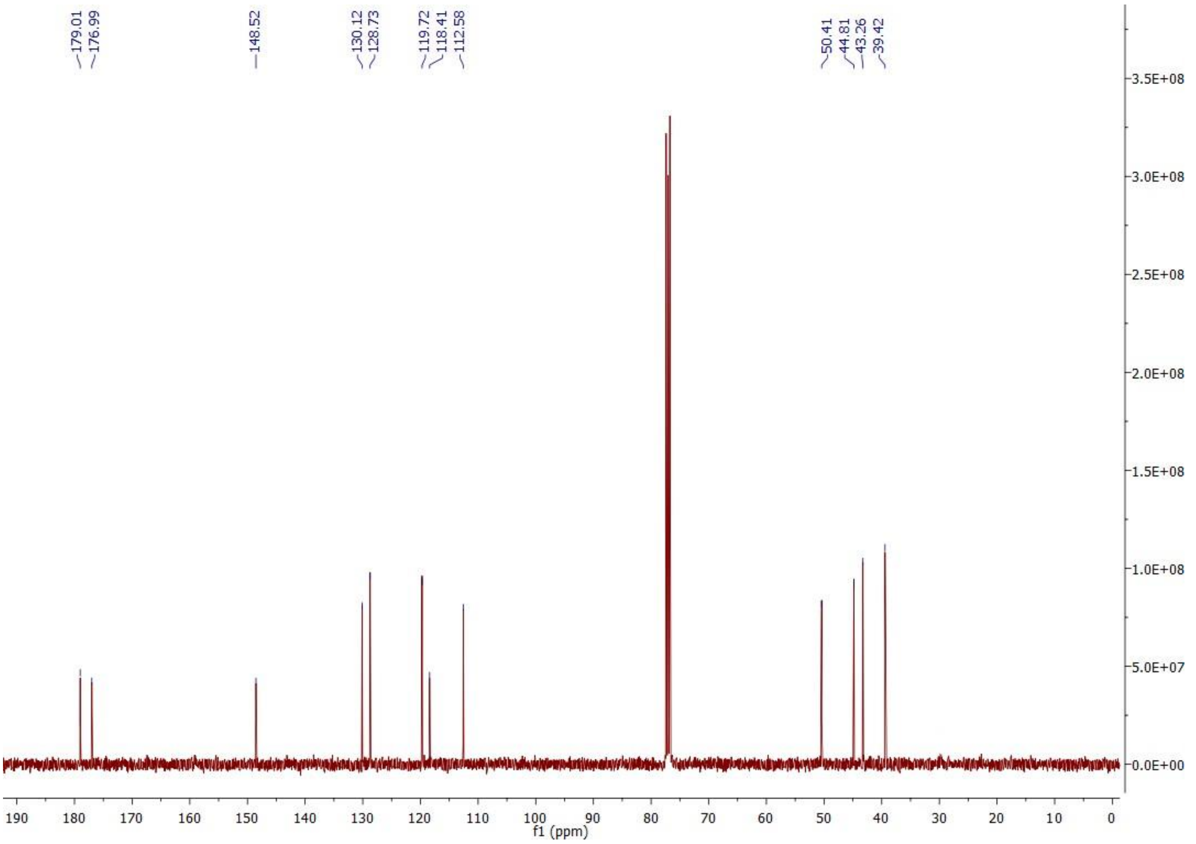
3a [13]C NMR



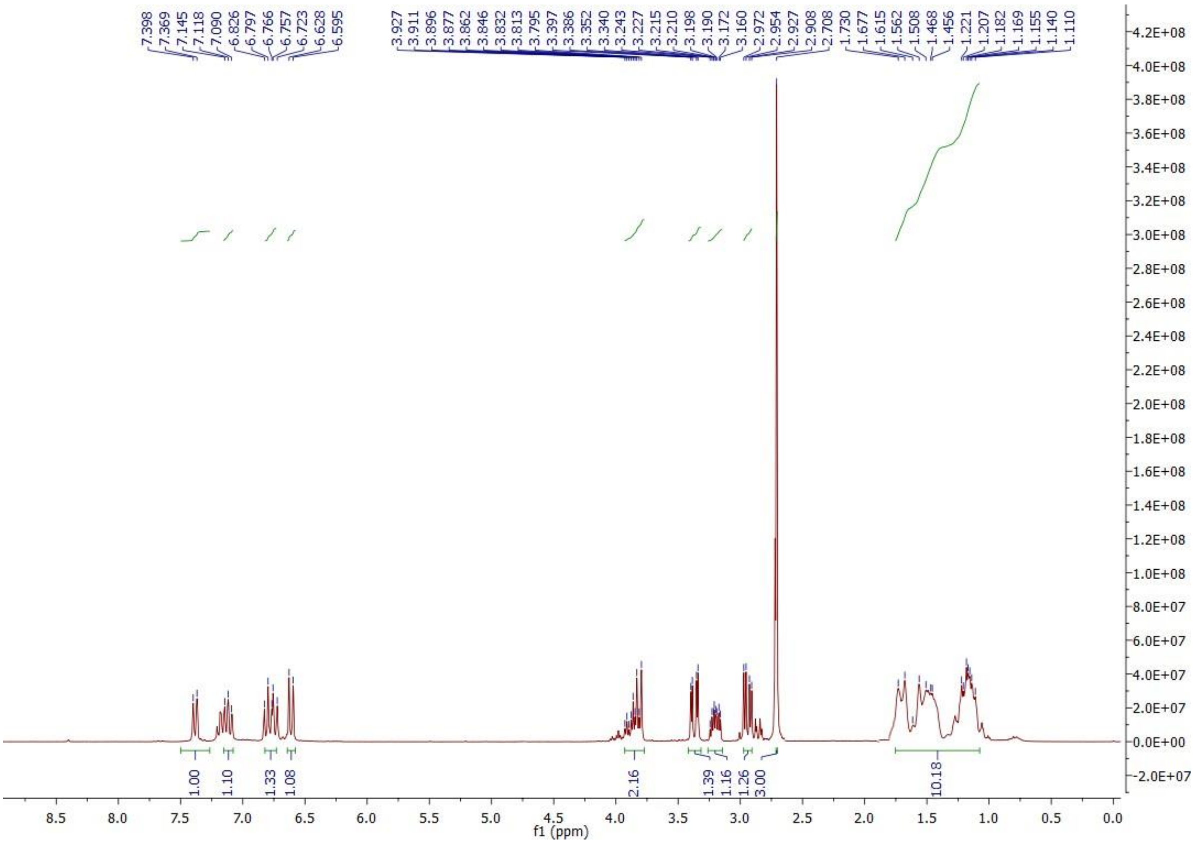
3b [1]HNMR



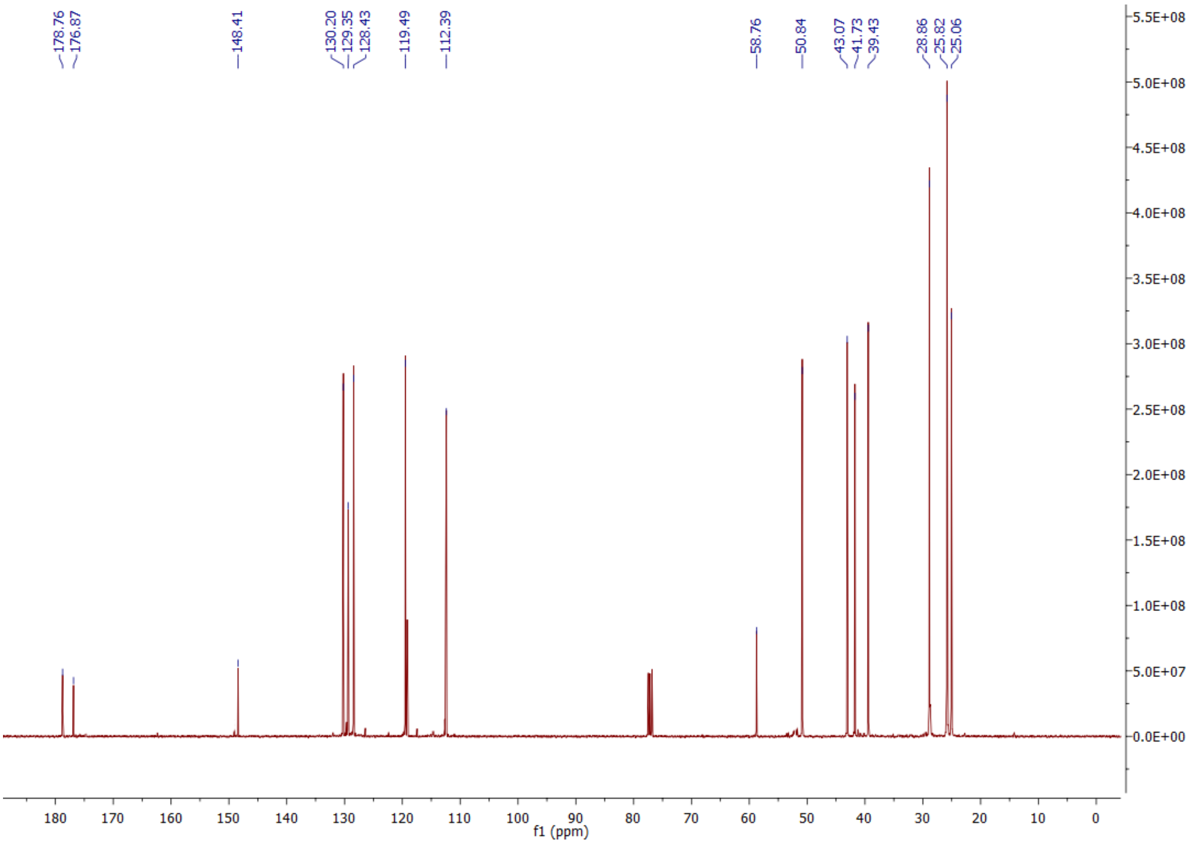
3b [13]C NMR



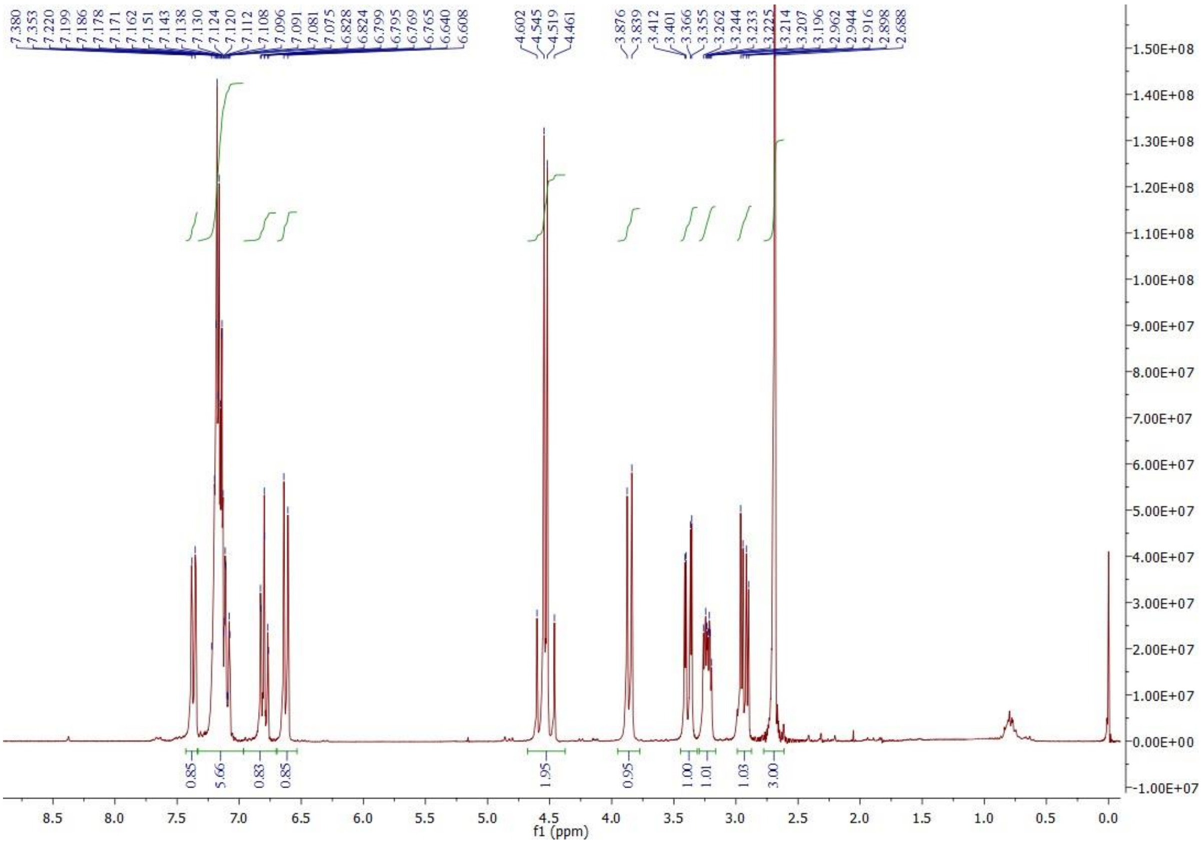
3c ¹HNMR



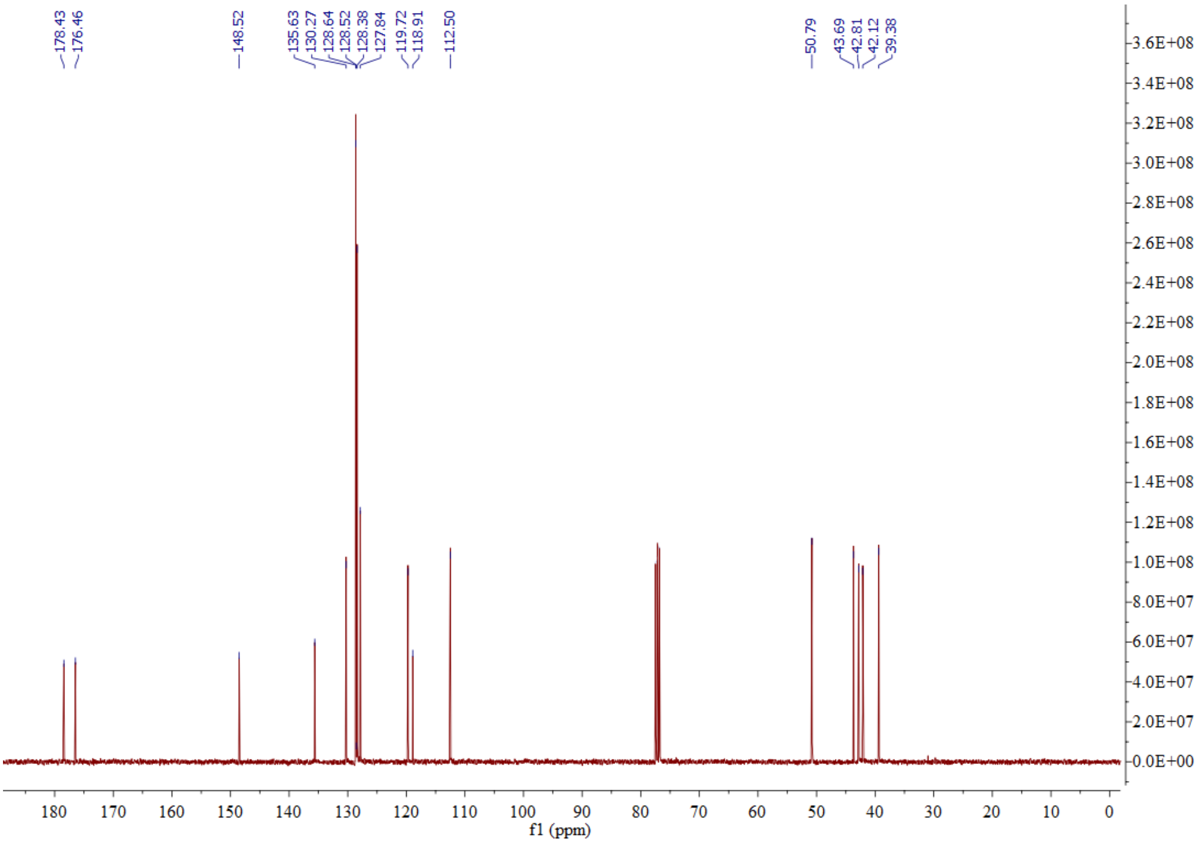
3c ¹³C NMR



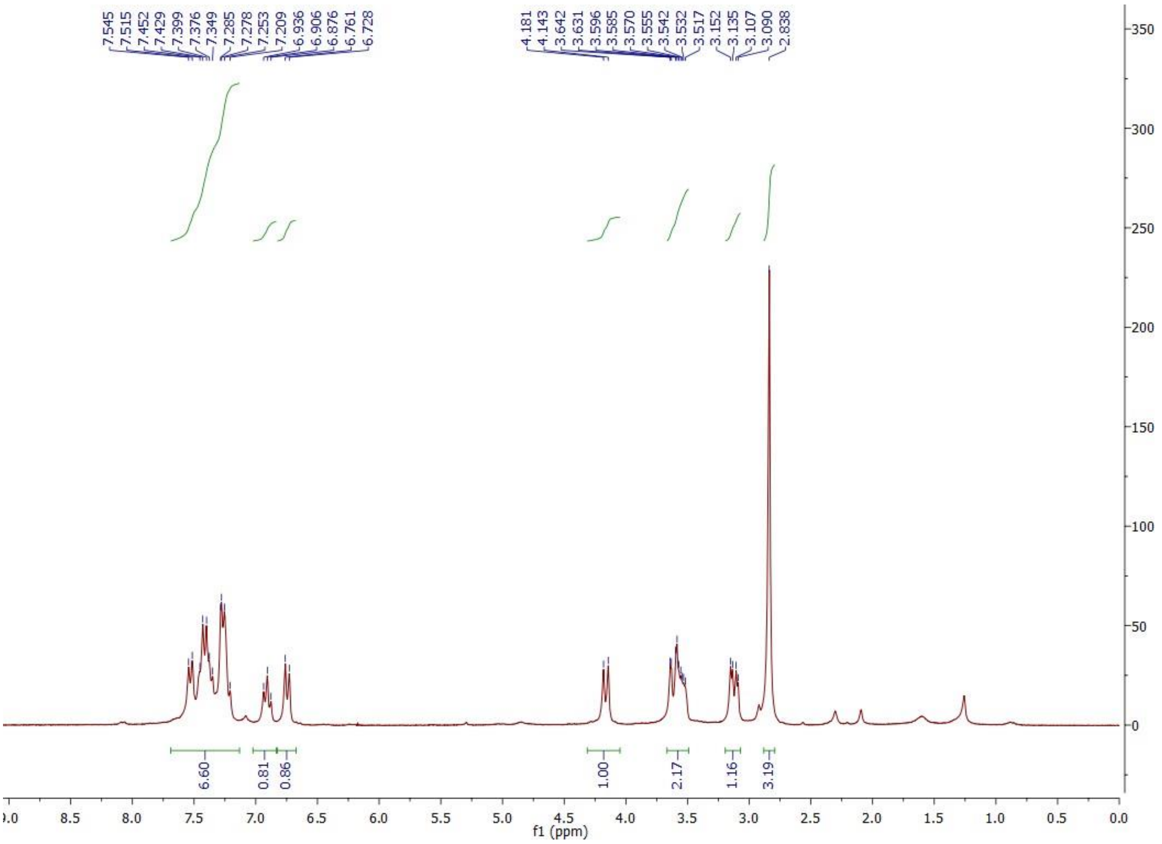
3d [1]HNMR



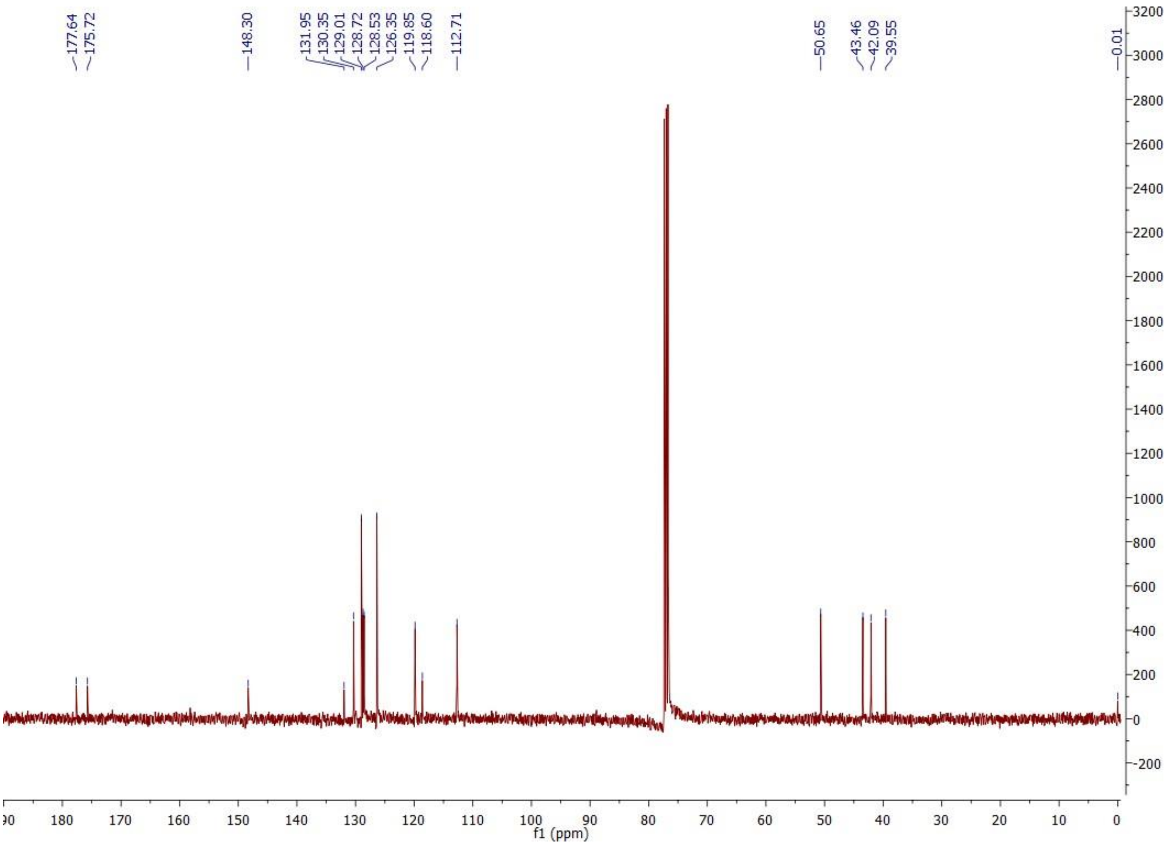
3d [13]C NMR



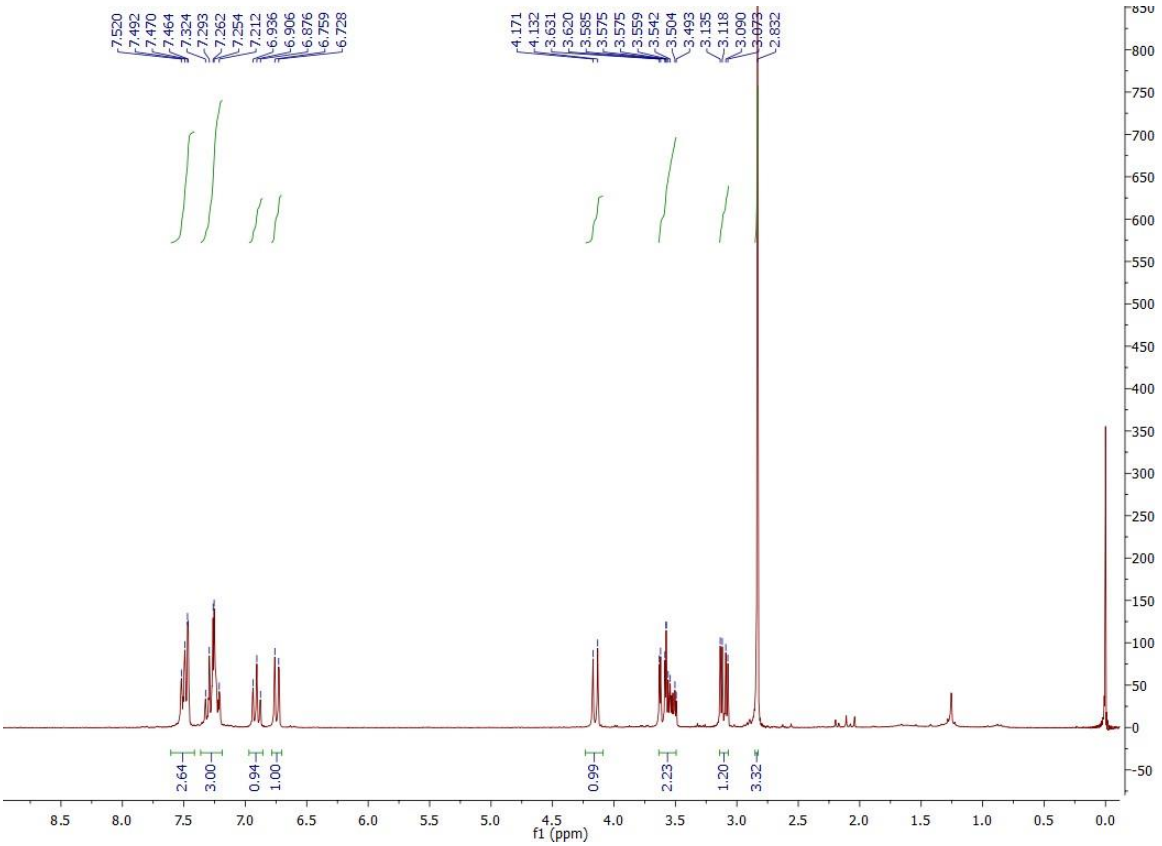
3e ¹HNMR



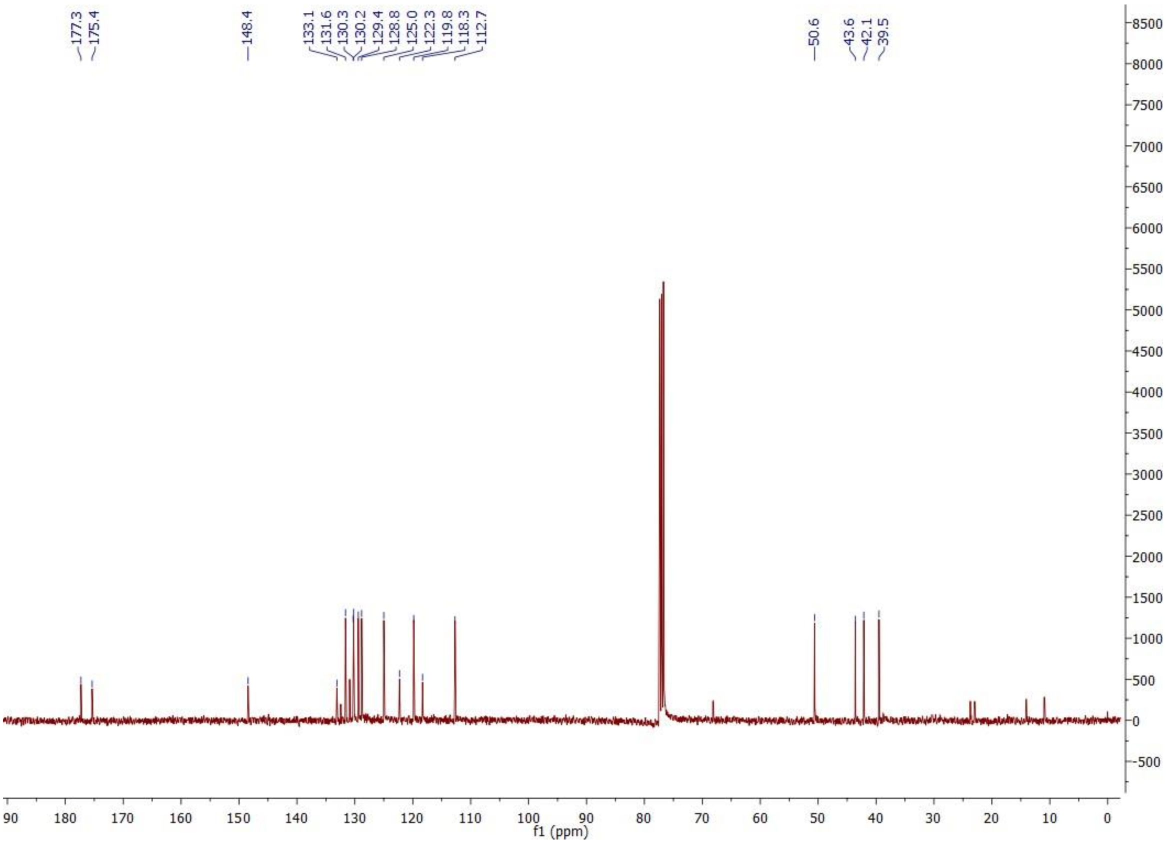
3e ¹³C NMR



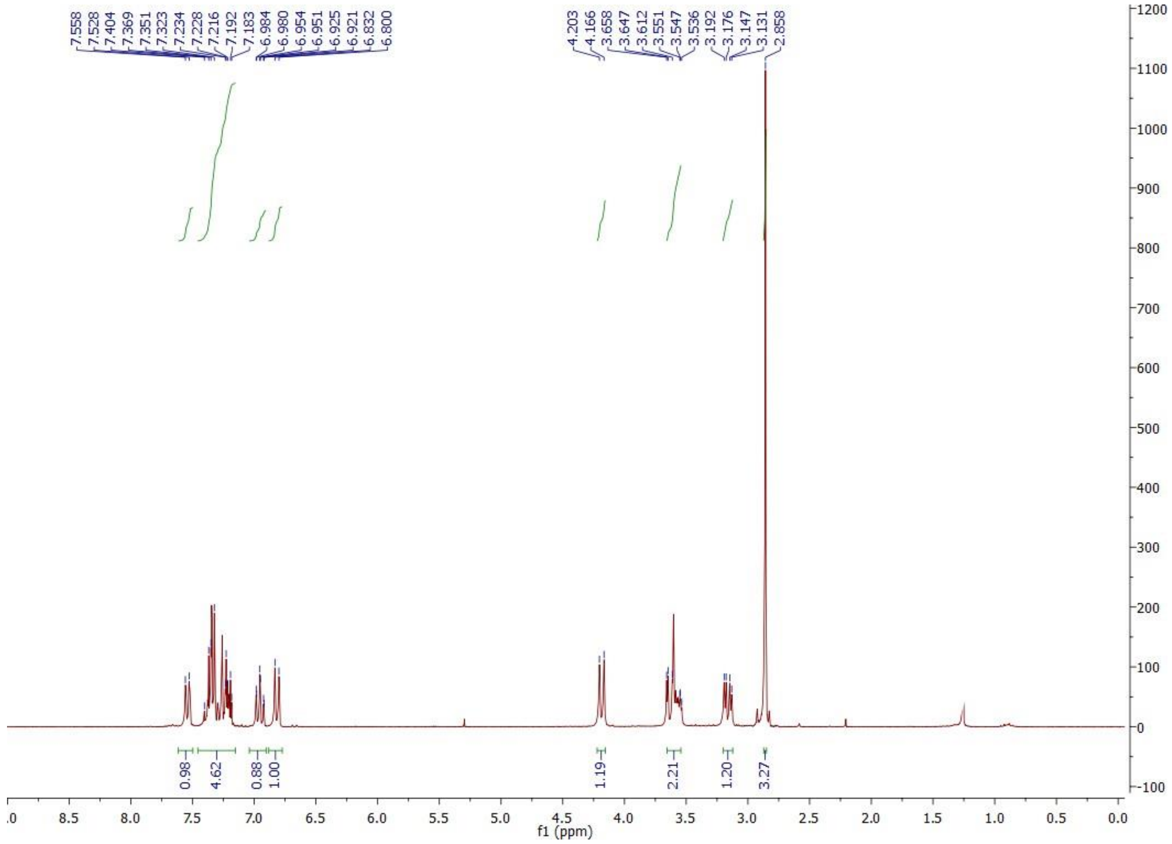
3f 1HNMR



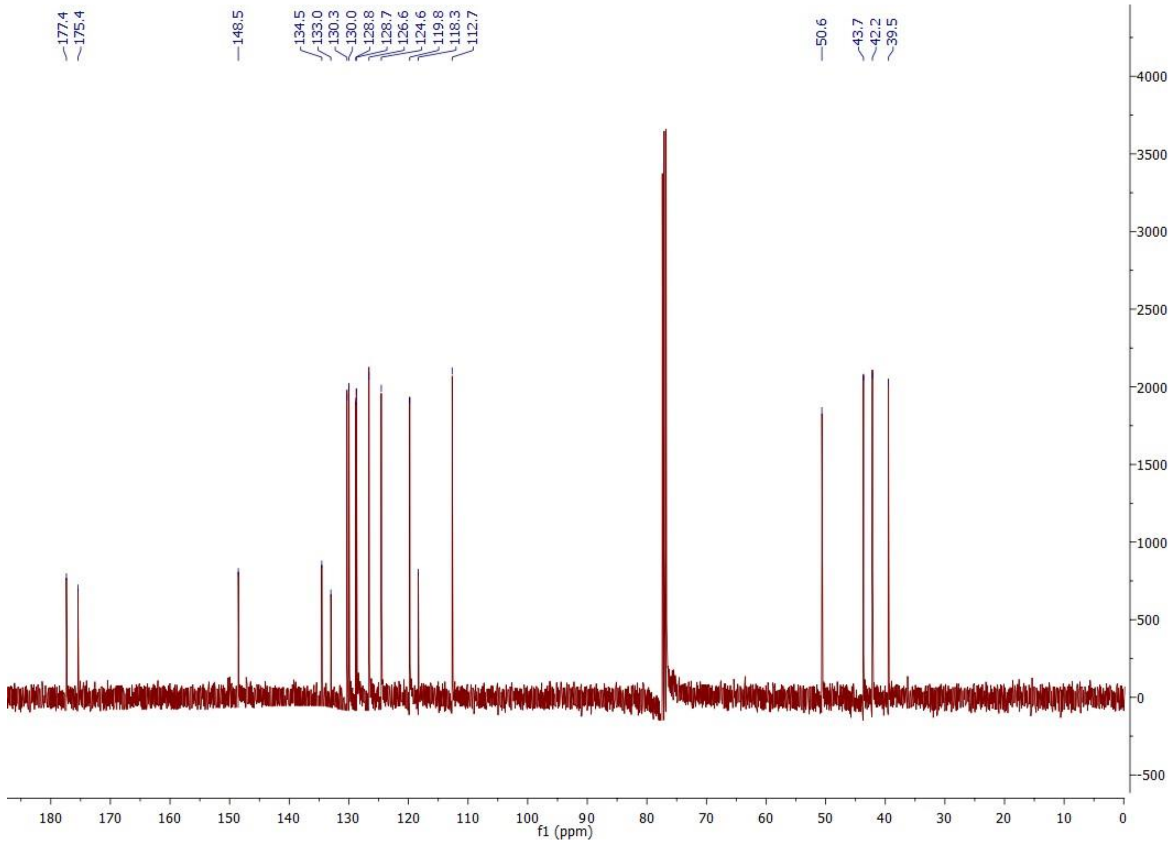
3f 13C NMR



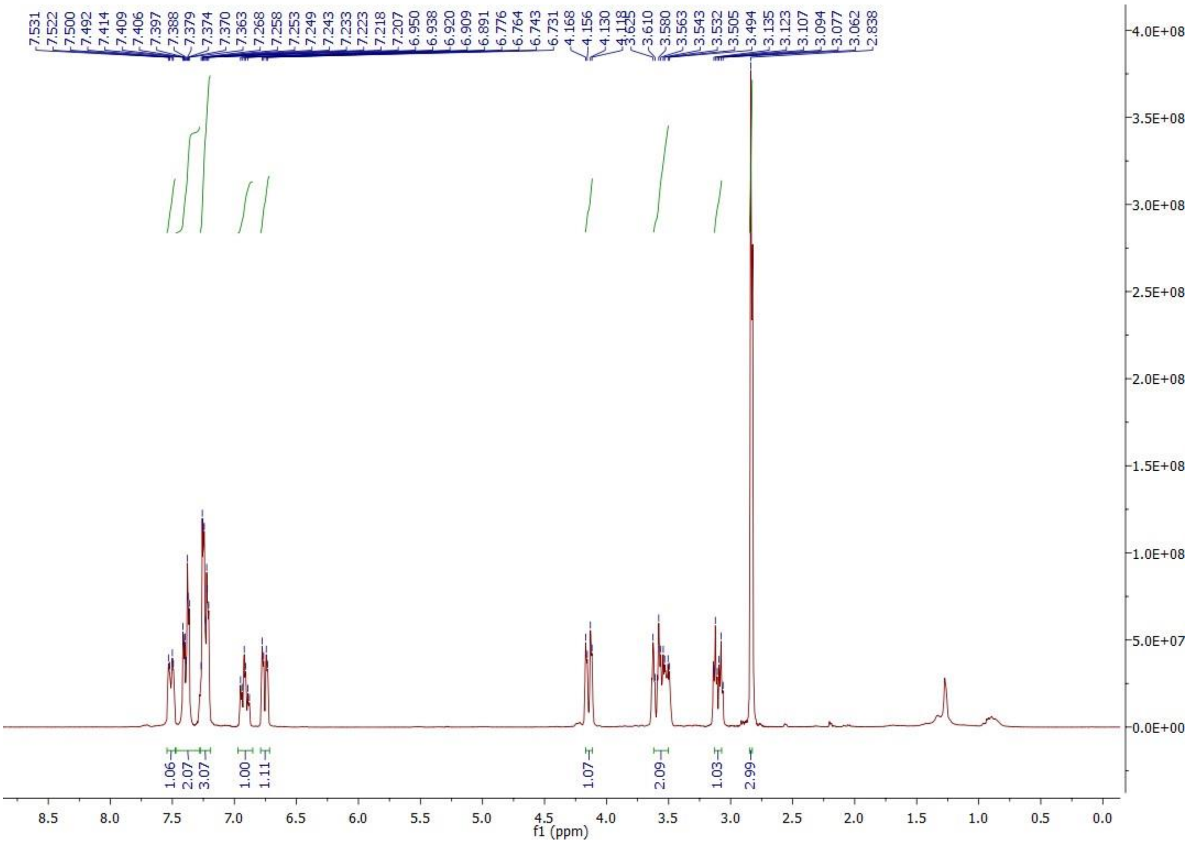
3g ¹HNMR



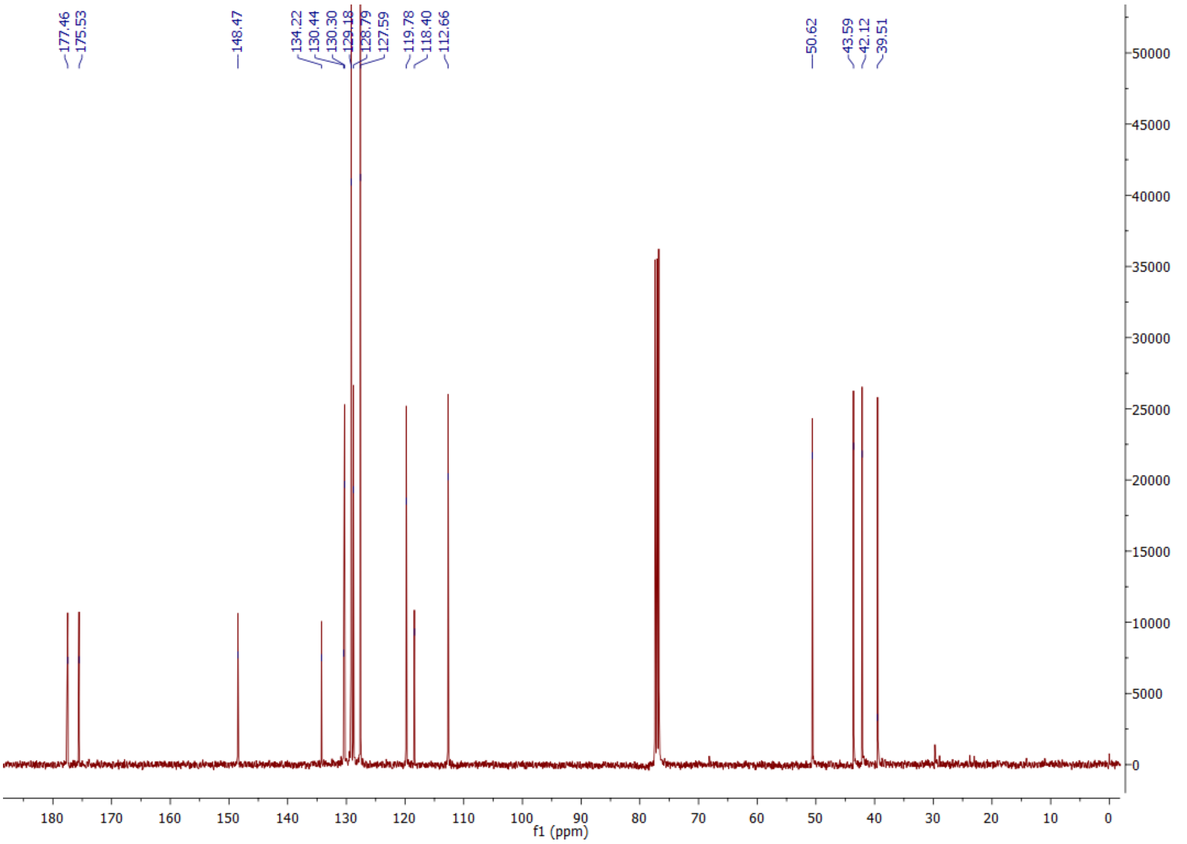
3g ¹³C NMR



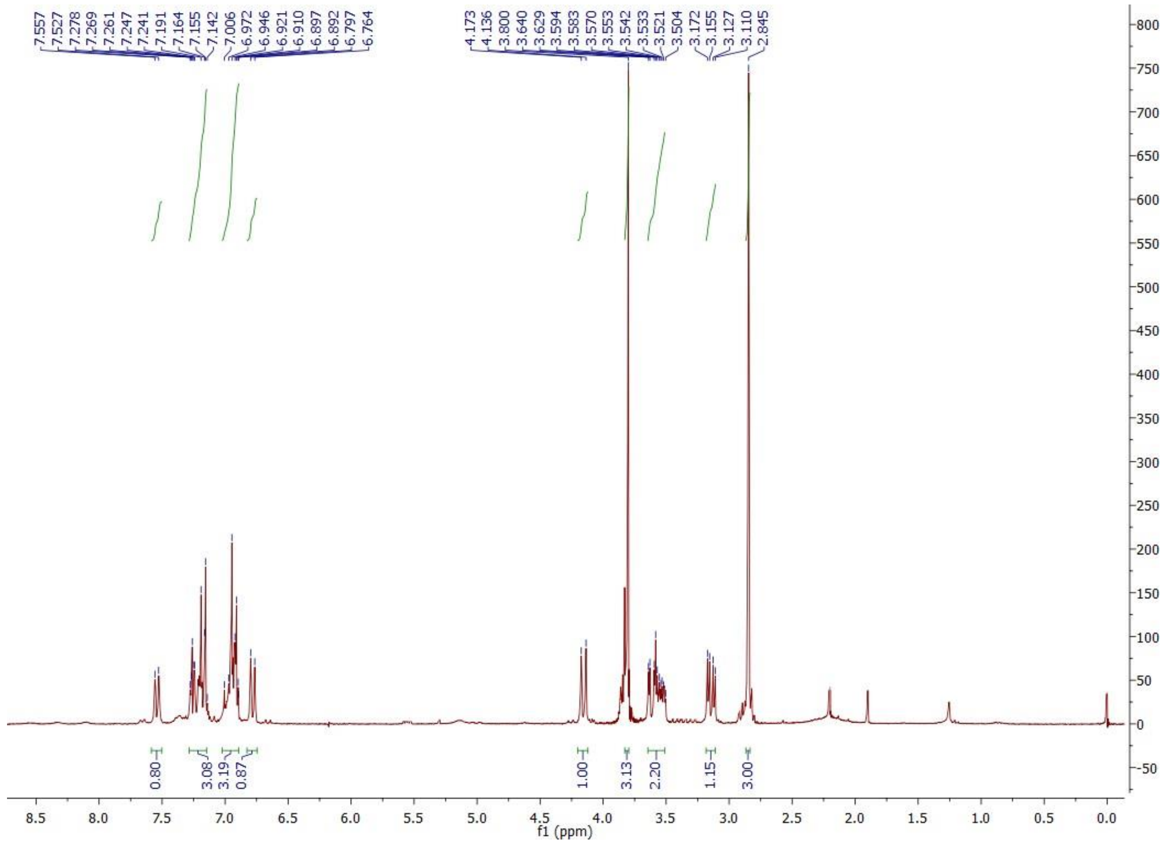
3h [1]HNMR



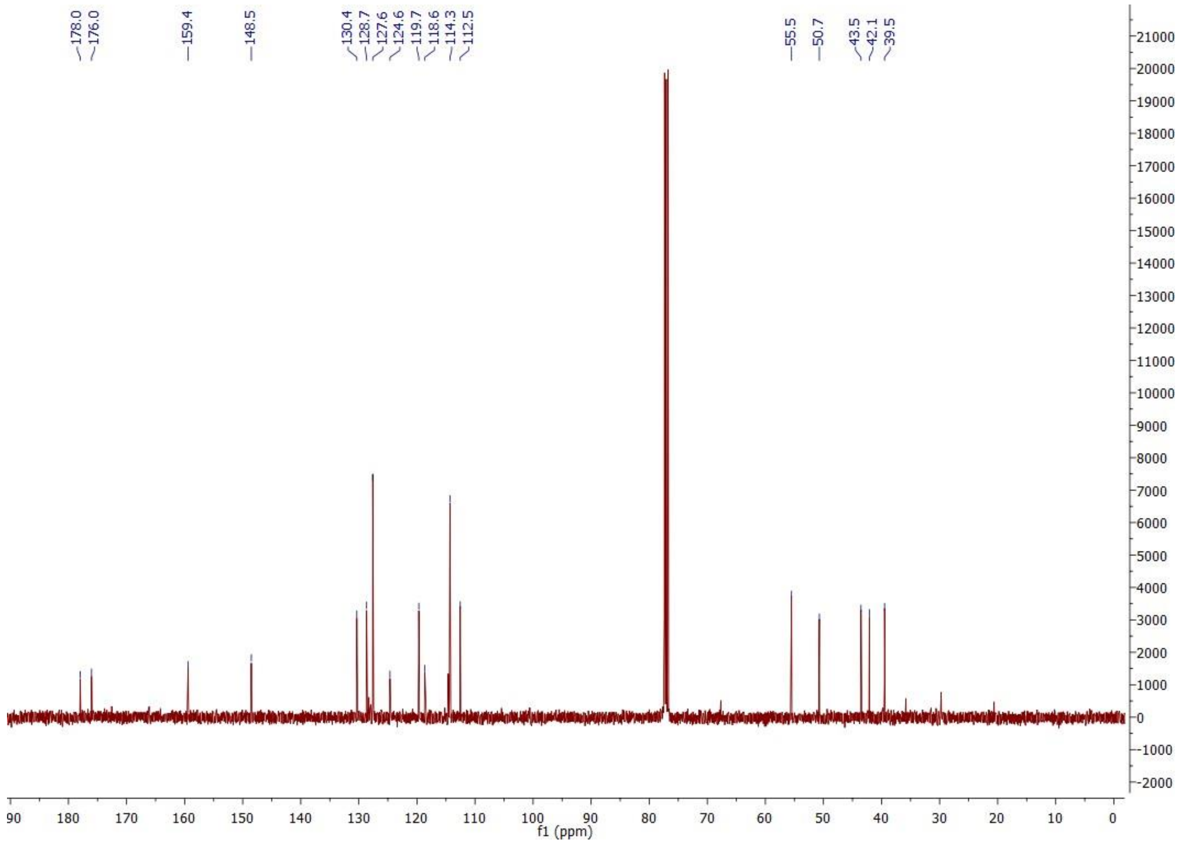
3h [13]C NMR



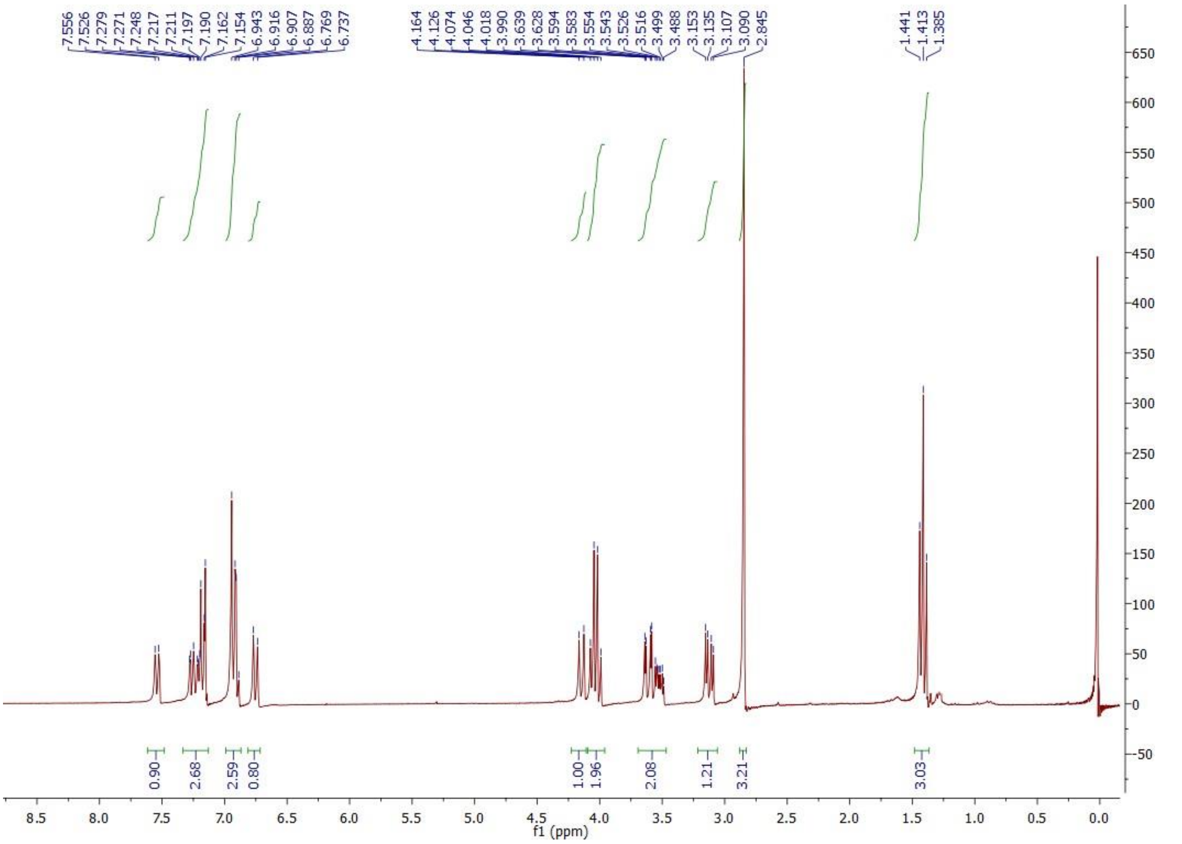
3i ¹HNMR



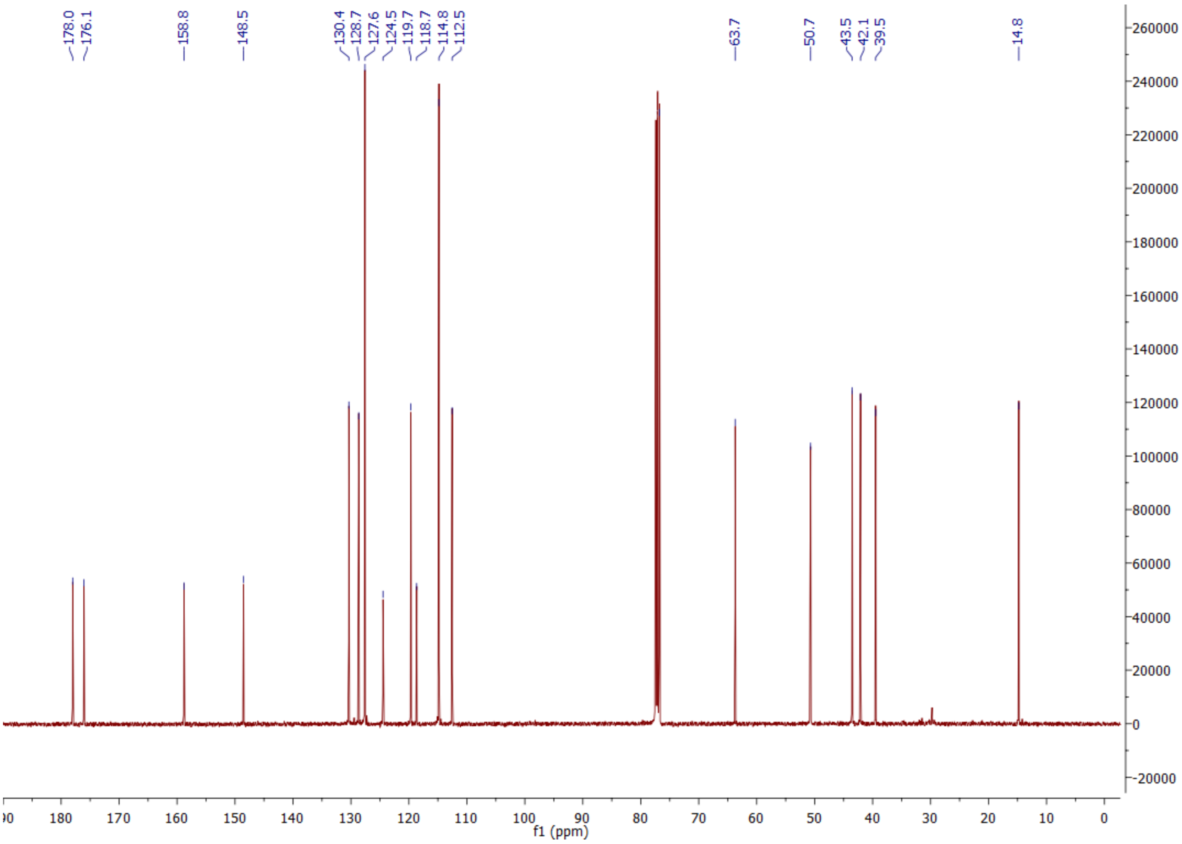
3i ¹³C NMR



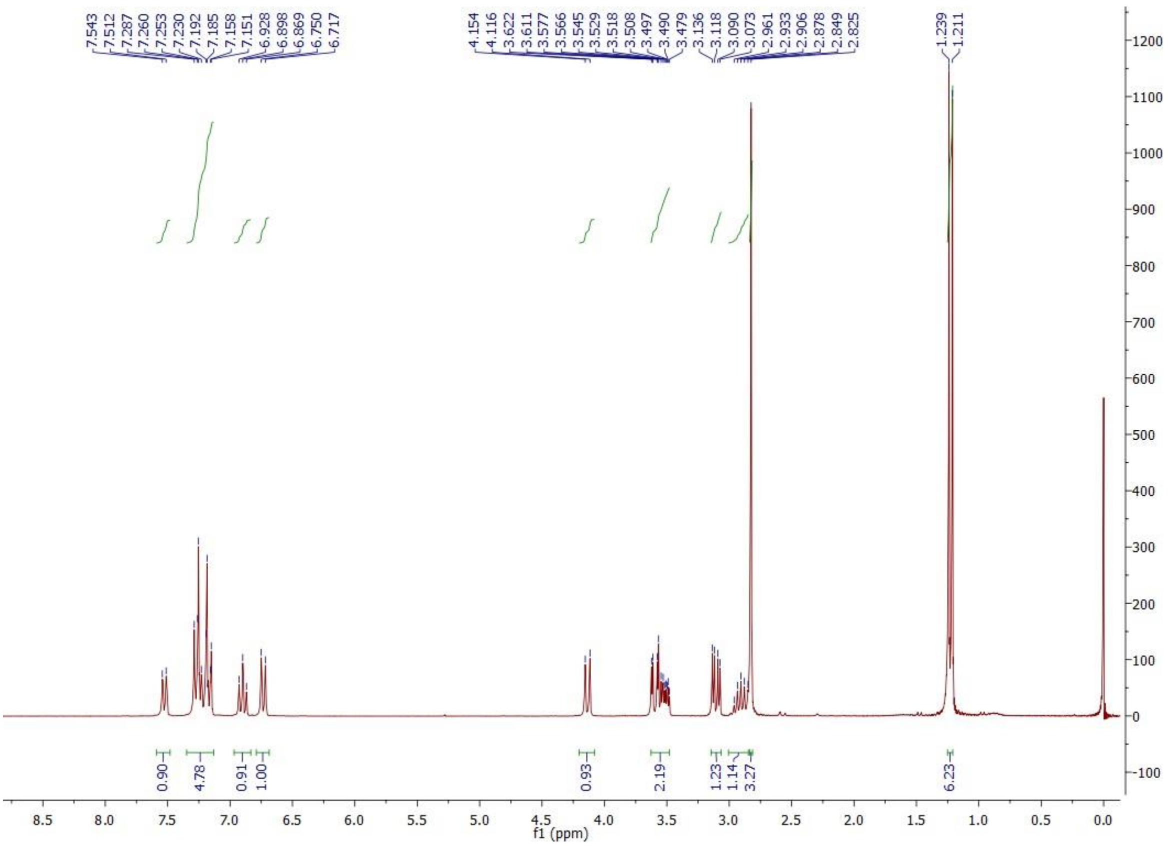
3j ¹HNMR



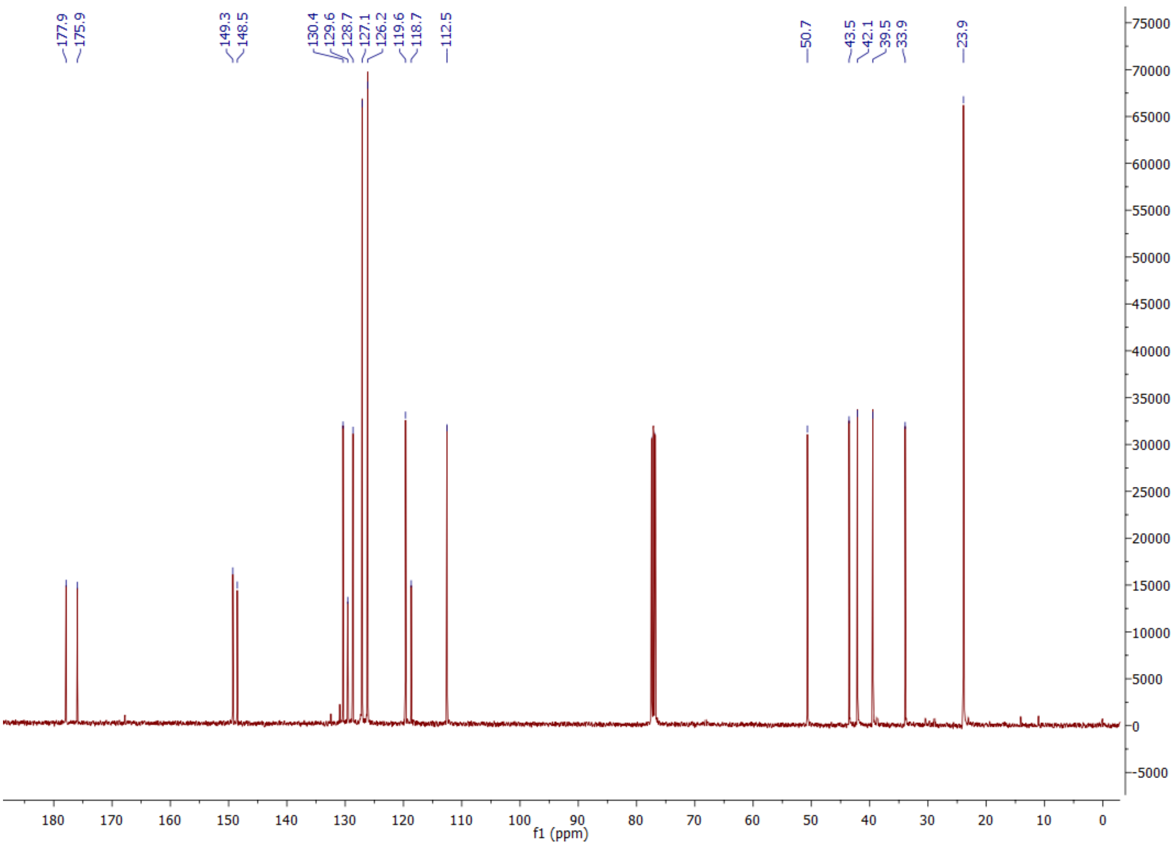
3j ¹³C NMR



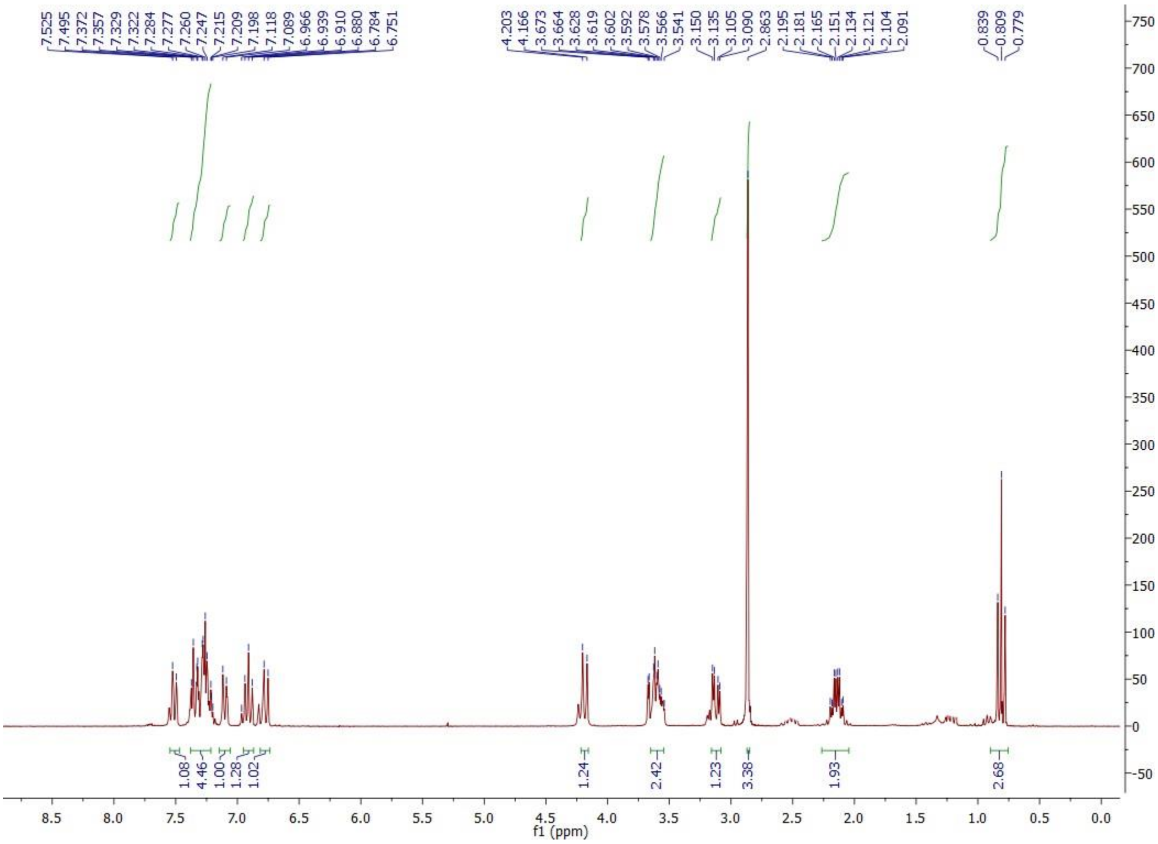
3k ^{1}HNMR



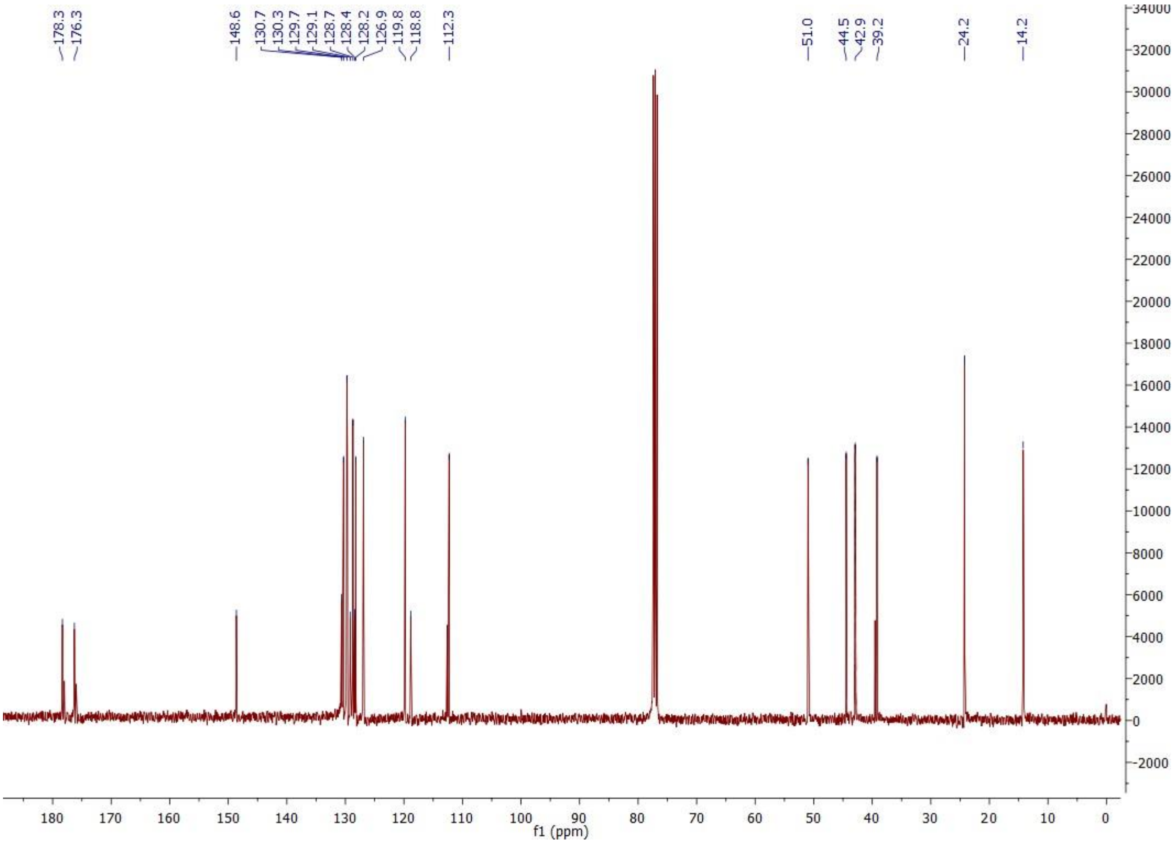
3k ^{13}C NMR



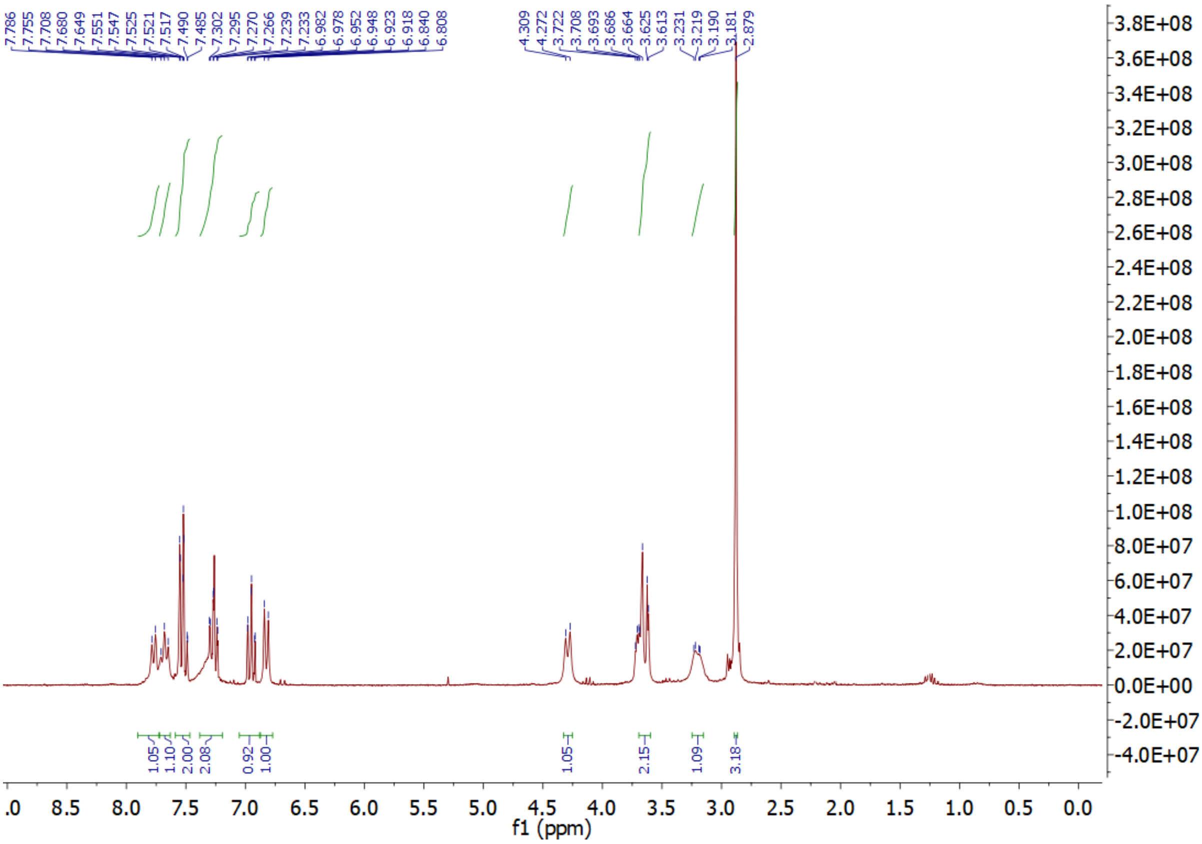
3l ^{1}HNMR



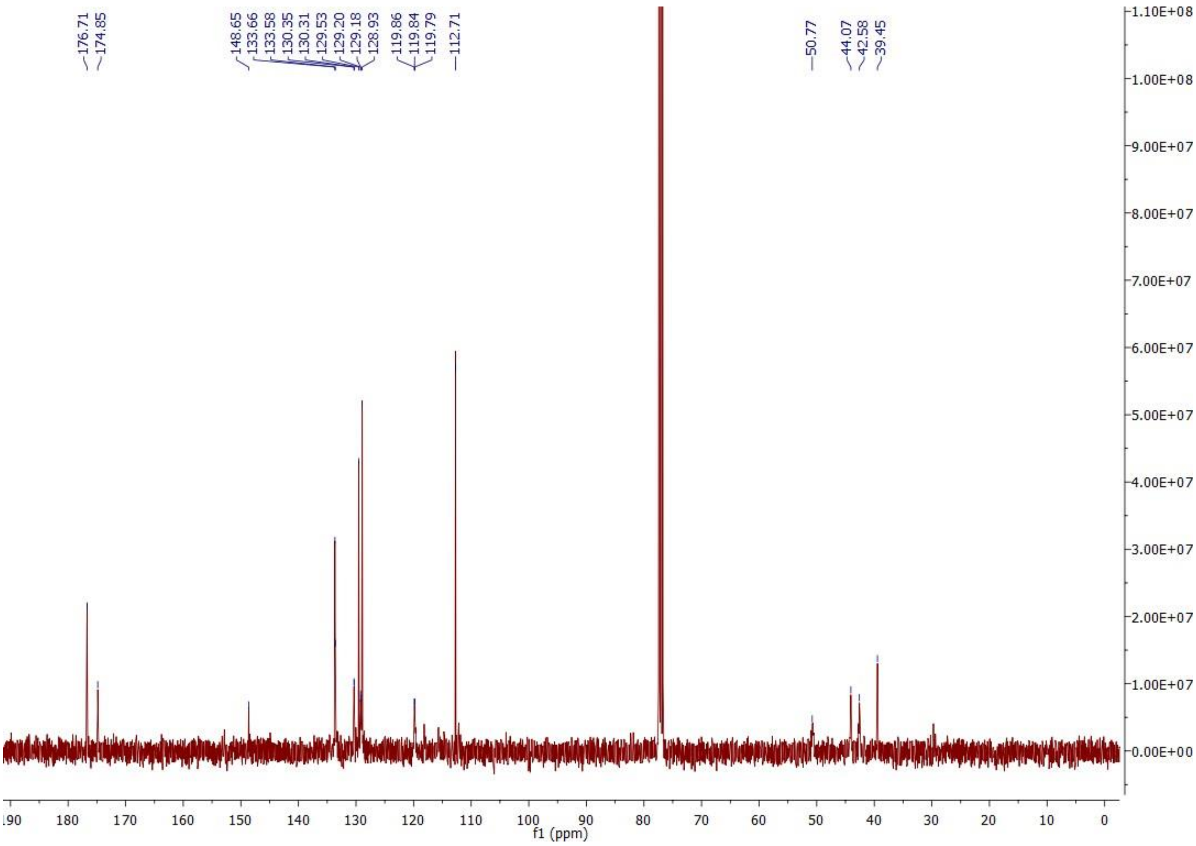
3l ^{13}C NMR



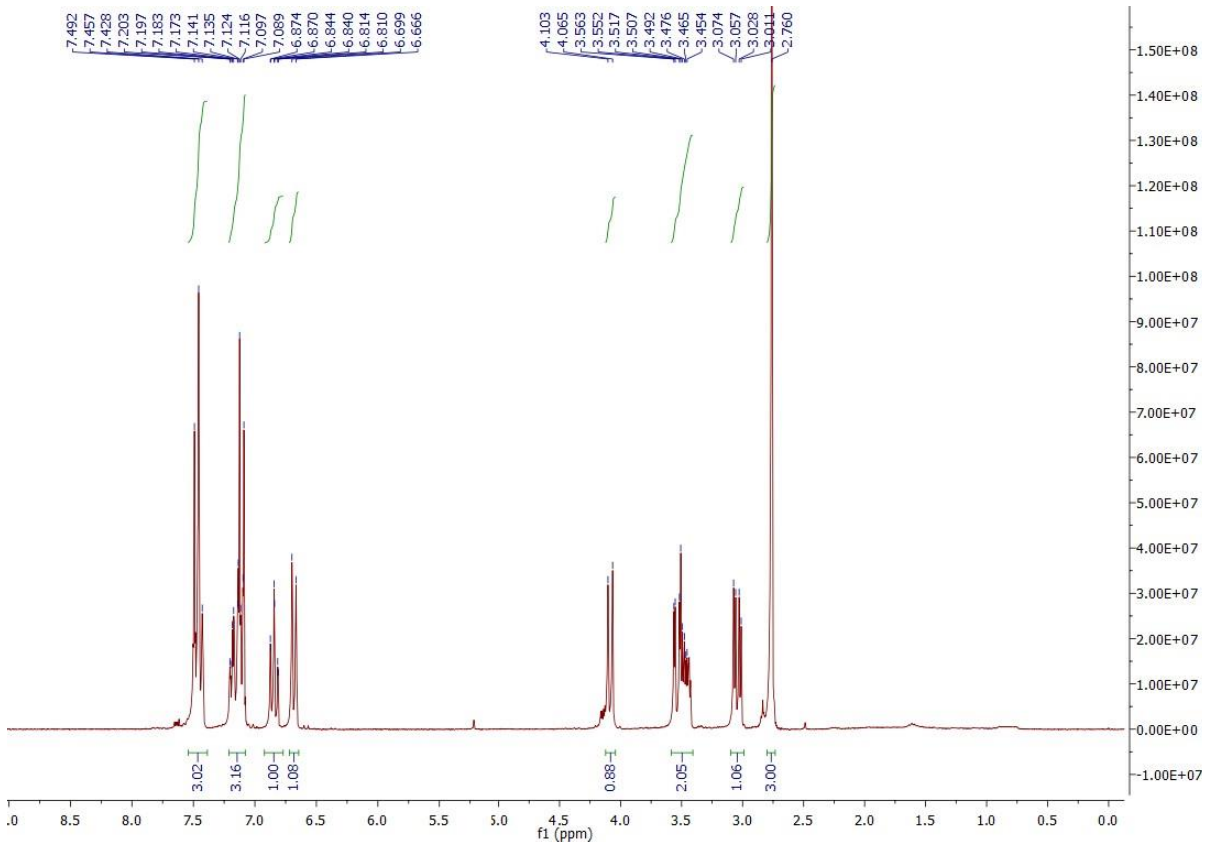
3m ¹HNMR



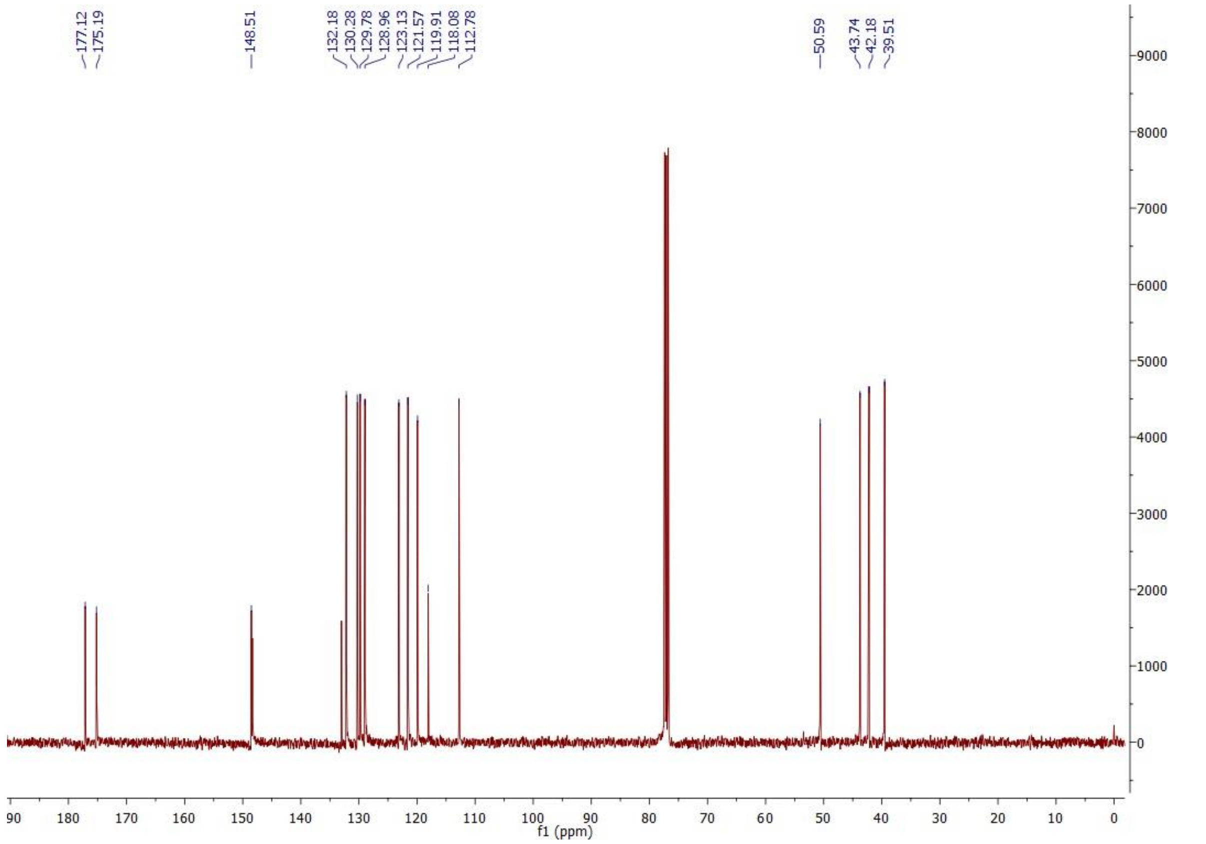
3m ¹³C NMR



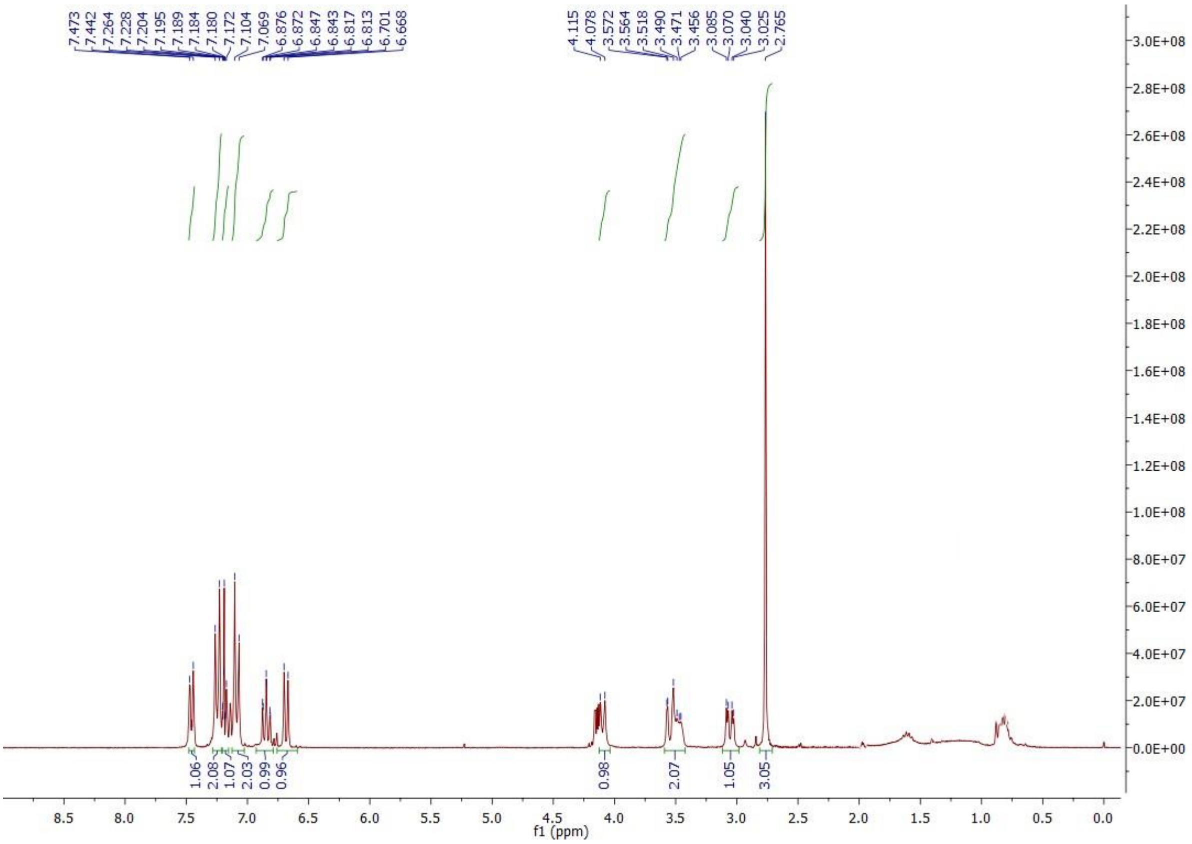
3n ¹HNMR



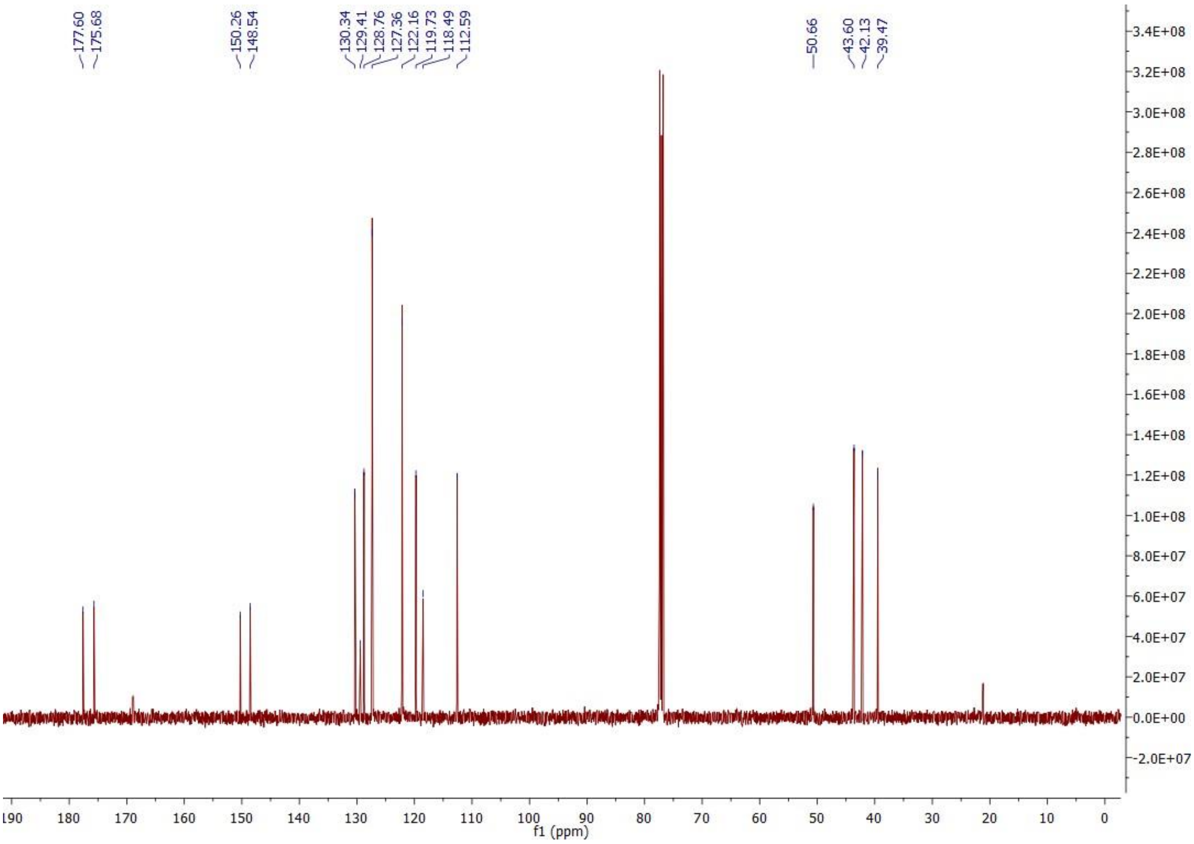
3n ¹³C NMR



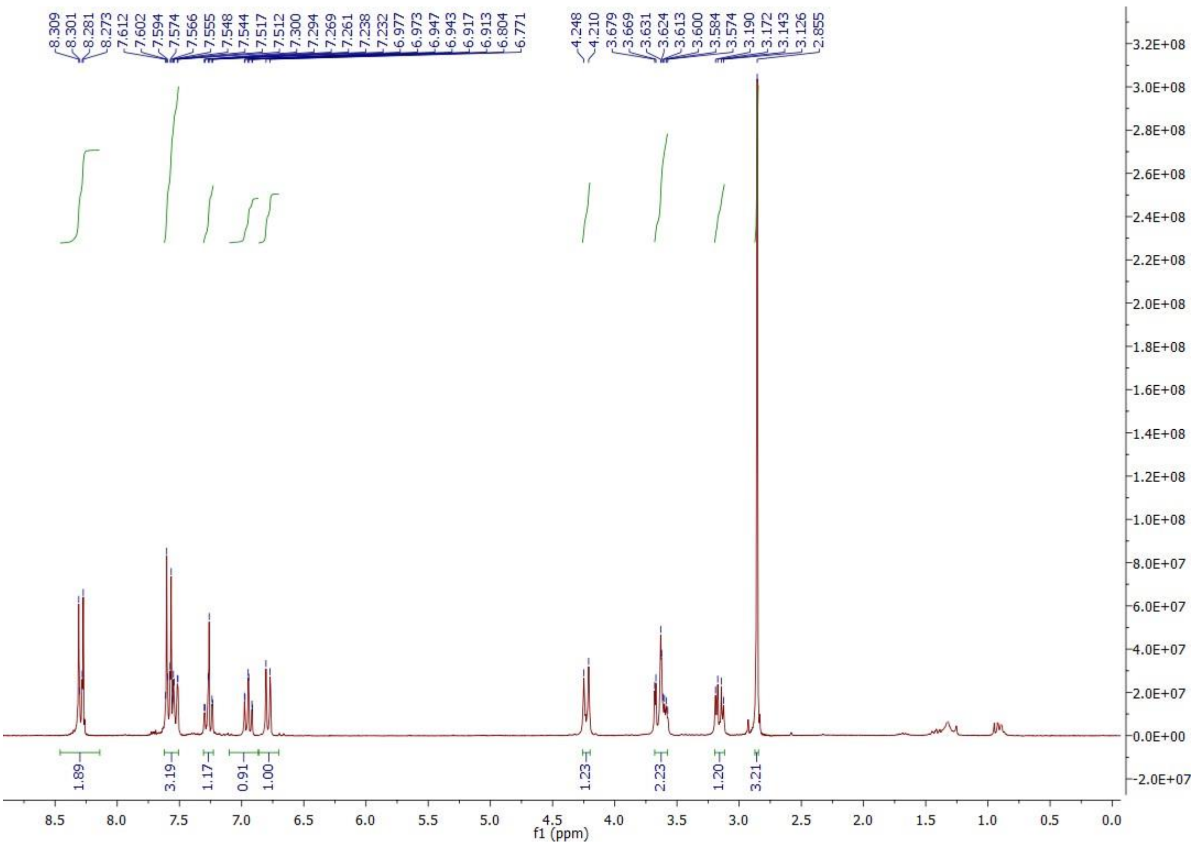
30 ¹HNMR



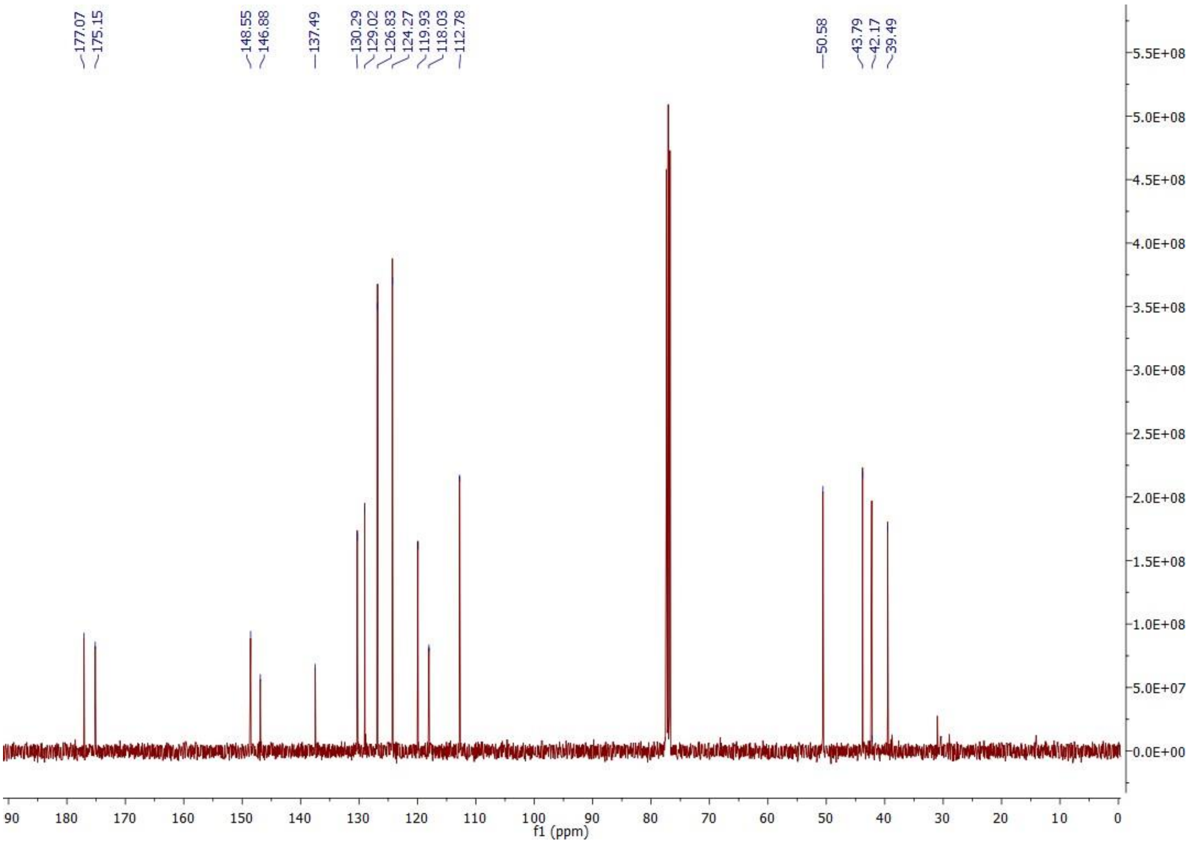
30 ¹³C NMR



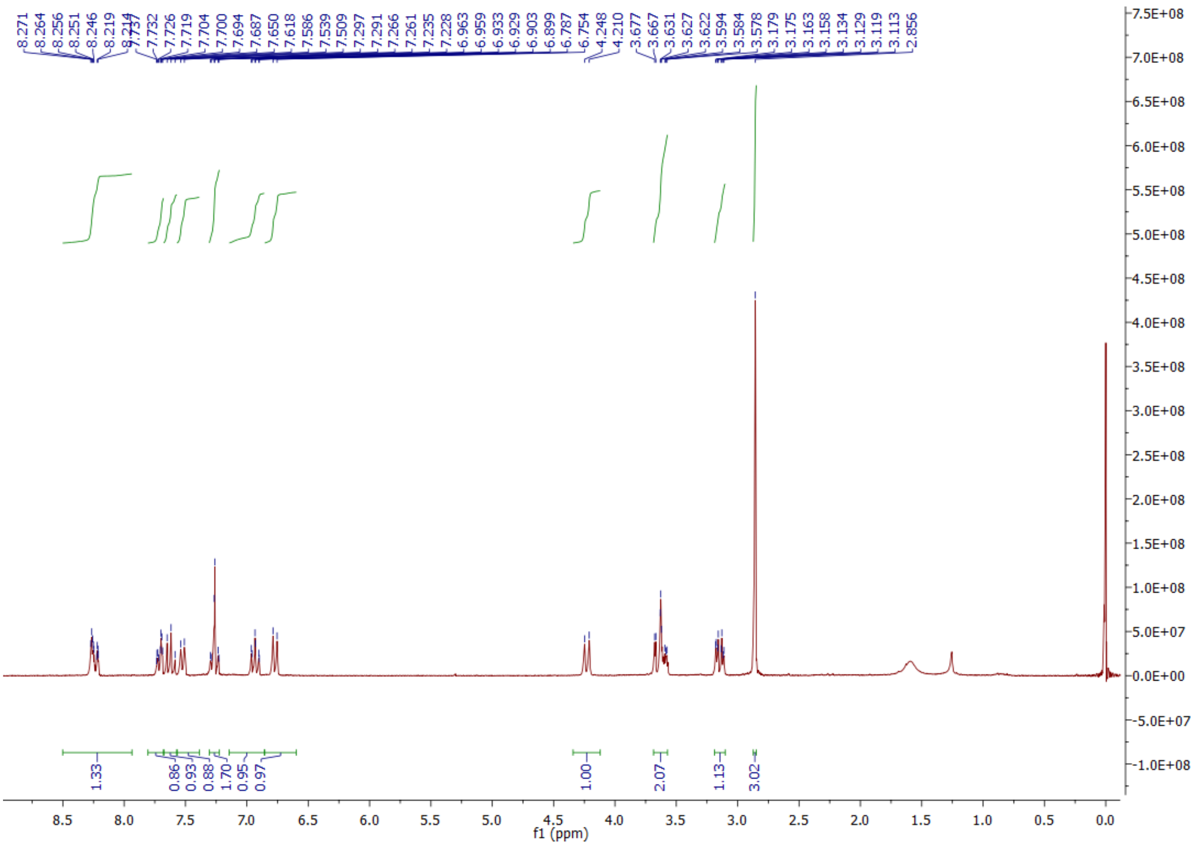
3p [1]HNMR



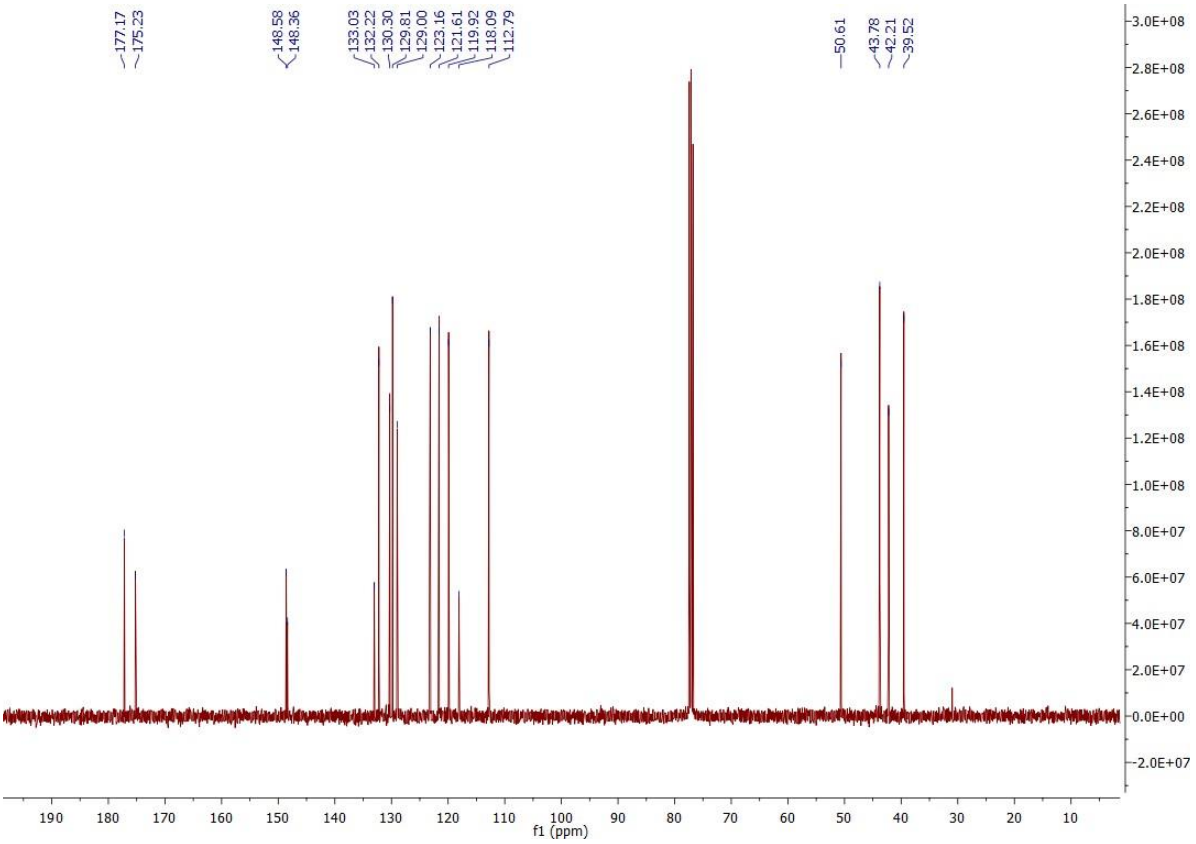
3p [13]C NMR



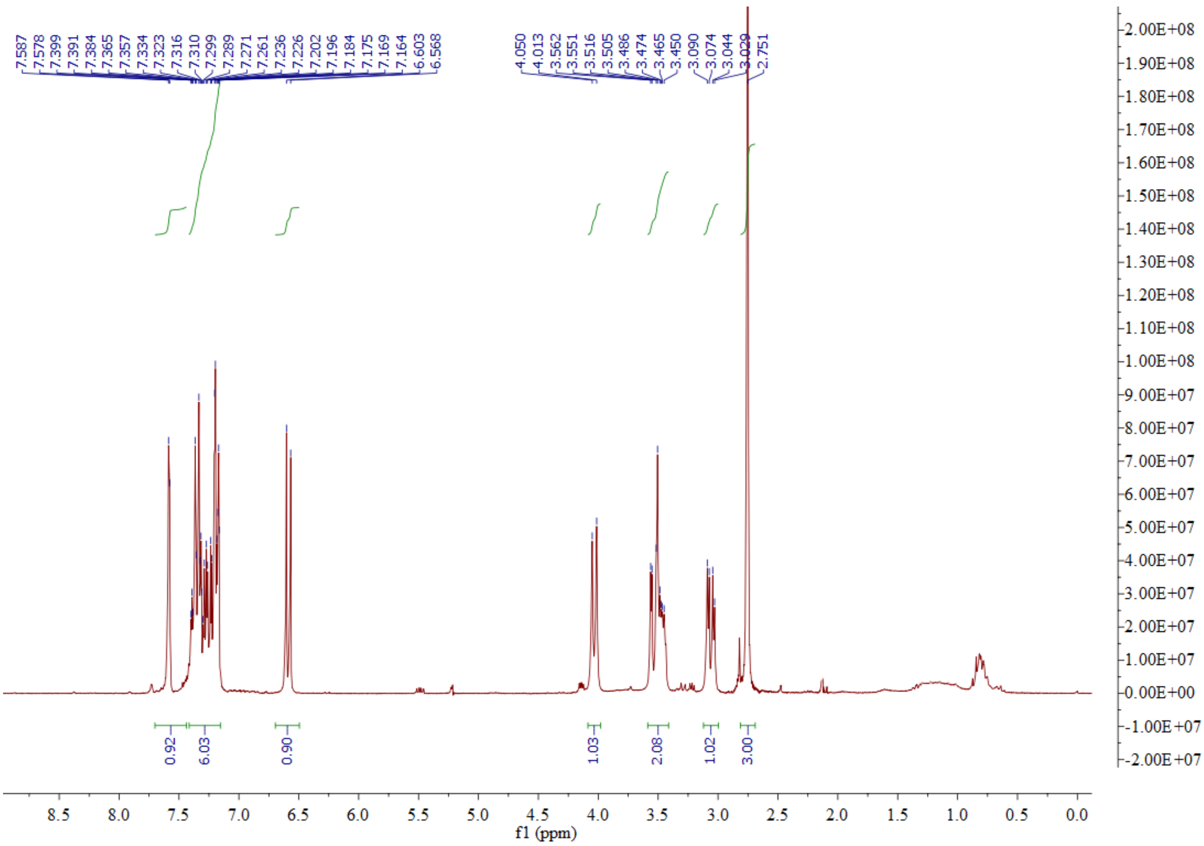
3q ^{1}HNMR



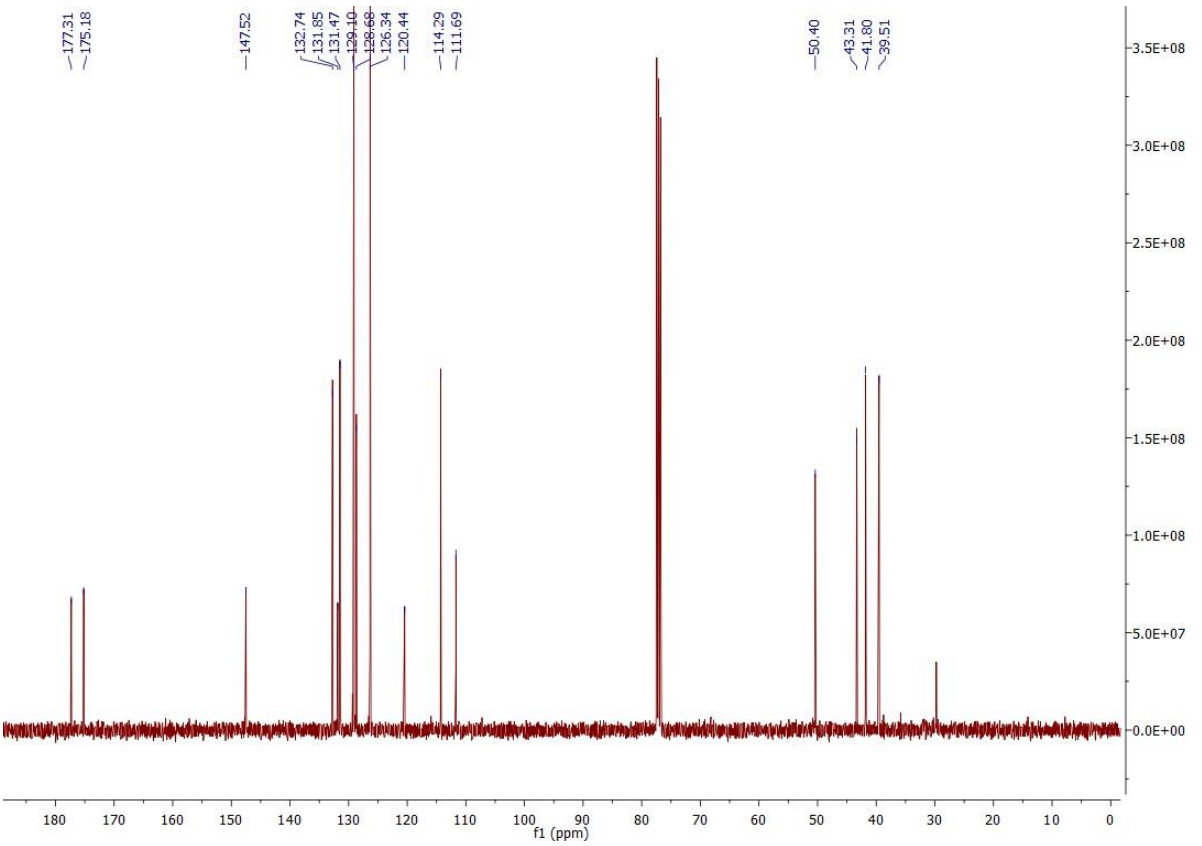
3q ^{13}C NMR



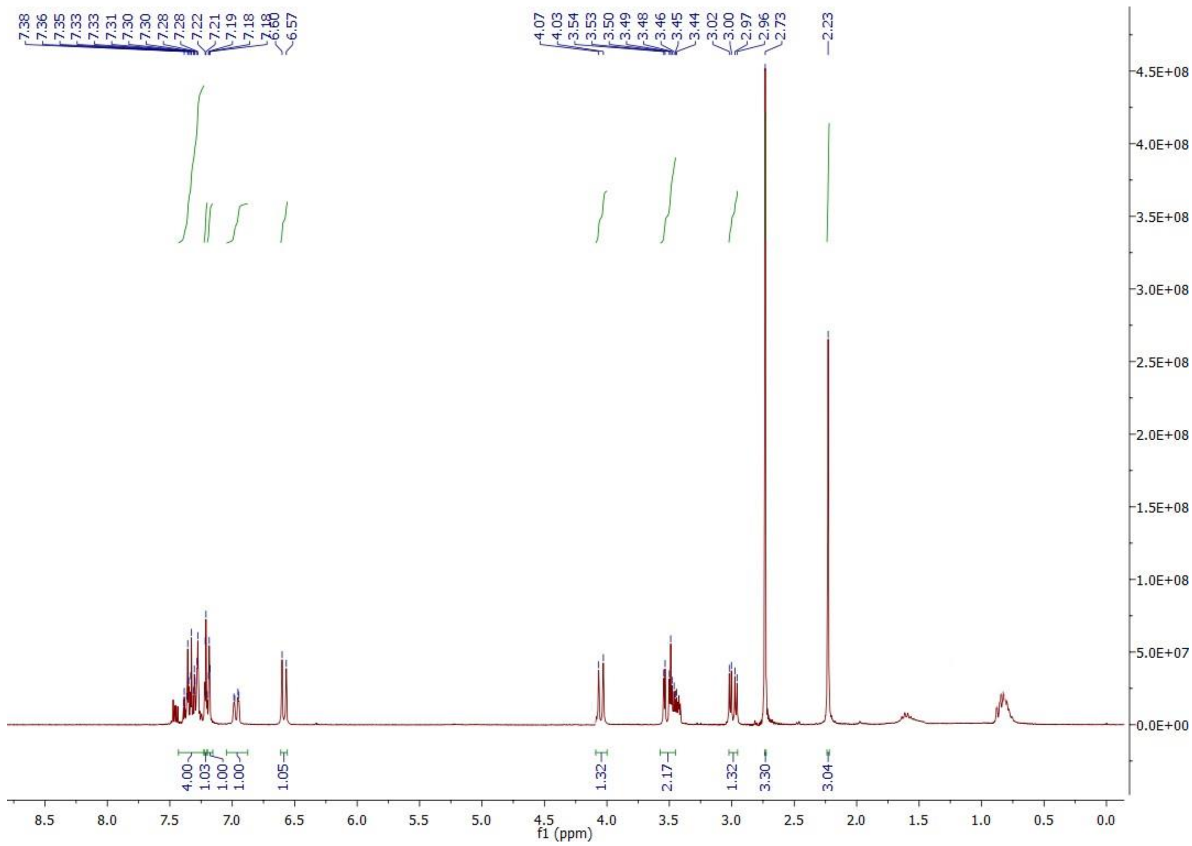
3r ¹HNMR



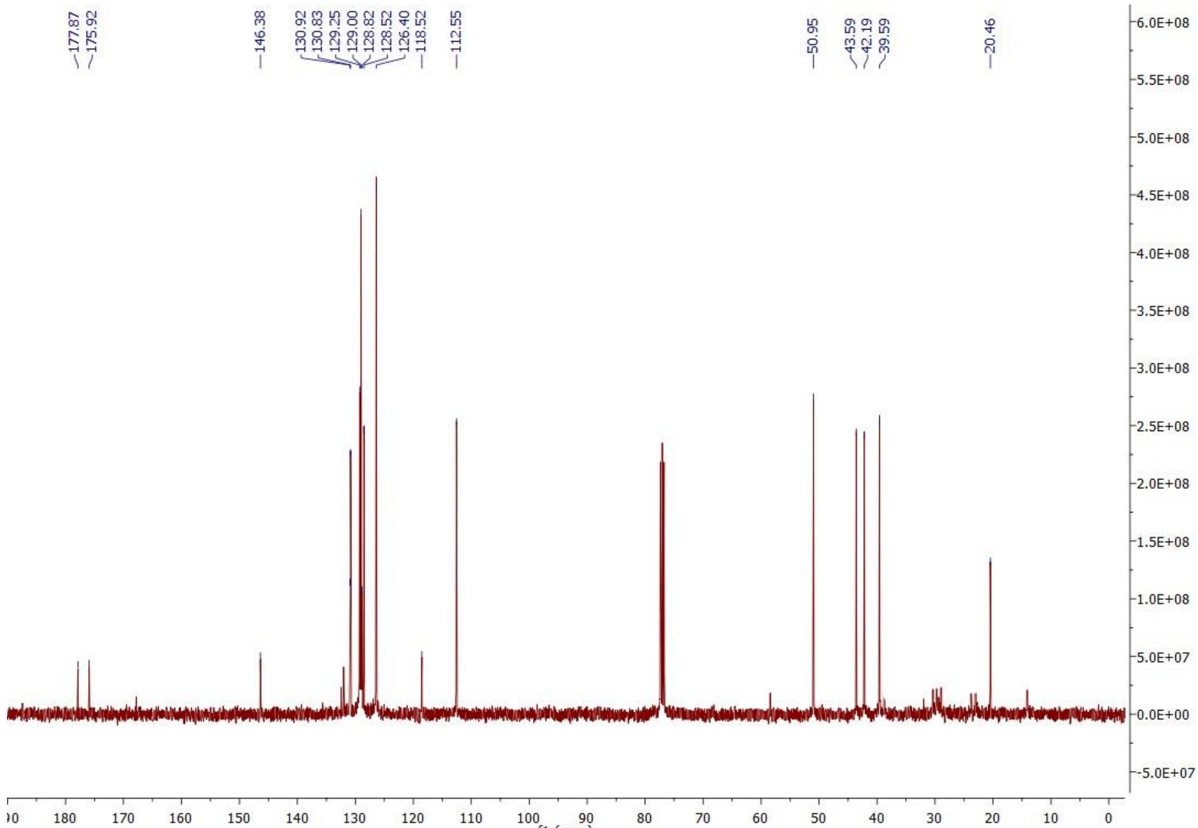
3r ¹³C NMR



3t ¹HNMR



3t ¹³C NMR



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