Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of *Sym*-Pentaalkylfunctionalized Corannulene

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Supporting Information

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1. General notes

Synthetic procedures were carried out under an inert atmosphere of nitrogen, in drysolvents (by passage through alumina columns in a MC Brown solvent system anddegassed with N_2), using standard Schlenk techniques, unless otherwise noted. Allreagents and solvents were reagent grade and were used without further purification unless otherwise specified. Flash chromatographic purification was performed using silica gel Merck 60 (particle size 0.040–0.063 mm); the eluting solvent for each purification was determined by thin layer chromatography (TLC). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. Solvents for chromatography were technical grade and freshly distilled before use. ^{1}H NMR spectra were recorded on a Bruker AV2-500 (500MHz) or Bruker AV2-400 (400MHz) spectrometers. Solvent for NMR spectroscopy were purchased from ARMARchemicals, degassed with nitrogen and dried over molecular sieves. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak: $CDCl_3$ = 7.26 ppm, d^4-MeOD = 3.31 ppm, d^6-DMSO = 2.50 ppm. Multiplicities are given as: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), dd (doublet of

doublets), dt (doublet of triplets), m (multiplet). ^{1}H-decoupled ^{13}C NMR spectra were obtained on Bruker AV2-500 (125 MHz) or Bruker AV2-400 (100MHz) spectrometer. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak: CDCl3 =77.23 ppm, d^4-MeOD = 49.00 ppm, d^6-DMSO = 39.52 ppm. HR-ESI-MS and HR-ACPI-MS: Finnigan Mat 900 MS. UV/Vis measurements were carried out on a Agilent 8453 UV/Vis spectrophotometer using a 1 mm path quartz cuvette. Emission spectra were recorded on an Edinburgh Instruments FLS920 spectrometer. Circular dichroism (CD) spectra were recorded at room temperature on a Jasco J-810 spectropolarimeter using 1 mm path quartz cuvette. [α] values were recorded on JASCO P-2000 Polarimeter at 25 °C.

2. Synthetic details

***sym*-Penta-methyl-corannulene (2).** Methyl magnesium bromide (3.0 ml, 9.0 mmol, 3 M in THF) was added to a suspension of *sym*-pentachlorocorannulene (347 mg, 0.82 mmol) and Fe(acac)$_3$ (72 mg, 0.20 mmol) in THF (7 ml) and NMP (0.7 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with hexane. The solvent was evaporated to yield a pale yellow solid (174 mg, 66%). The spectroscopic data were identical with those reported.[1]

***sym*-Penta-ethyl-corannulene (3).** Ethyl magnesium bromide (4.6 ml, 9.2 mmol, 2 M in THF) was added to a suspension of *sym*-pentachlorocorannulene (350 mg, 0.83 mmol) and Fe(acac)$_3$ (73 mg, 0.21 mmol) in THF (7 ml) and NMP (0.7 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with hexane. The solvent was evaporated to yield a pale yellow solid (188 mg, 58%). The spectroscopic data were identical with those reported.[2]

***sym*-Penta-((*S*)-2-methyl-butyl)-corannulene (4).** *(S)*-2-methyl-butylbromide (1.0 g, 6.6 mmol) was added to a suspension of Mg (194 mg, 8.0 mmol) and a crystal of iodine in THF (5 ml) at 0 °C; the mixture was stirred at room temperature for 2.5 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (254 mg, 0.60 mmol) and $Fe(acac)_3$ (53 mg, 0.15 mmol) in THF (5 ml) and NMP (0.5 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with hexane. The solvent was evaporated to yield a yellow solid (222 mg, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.76 (s, 5H), 3.40 (dd, ^2J = 13.5 Hz, ^3J = 6.0 Hz, 5H), 3.02 (dd, ^2J = 13.5 Hz, ^3J = 8.0 Hz, 5H), 2.24 (m, 5H), 1.85-1.80 (m, 5H), 1.62-1.56 (m, 5H), 1.26-1.23 (m, 30H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 140.47, 135.02, 130.14, 123.87, 41.09, 37.75, 30.02, 19.73, 12.02. UV (THF) λ_{max}, nm: 261, 299. $[\alpha]^{25}_D$ = +68.9 (*c*=1.88 in $CHCl_3$) HRMS (ACPI) m/z: found 601.4765 (M + H); calc ($C_{45}H_{61}$) 601.4768.

***sym*-Penta-(1-methyl-adamantyl)-corannulene (5).** 1-bromo-methyl-adamantane[3] (2.2 g, 9.6 mmol) was added to a suspension of Mg (1.0 g, 42.8 mmol) and a crystal of iodine in diethyl ether (70 ml) at 0 °C; the mixture was stirred at room temperature for 5 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (368 mg, 0.87 mmol) and $Fe(acac)_3$ (77 mg, 0.22 mmol) in THF (5 ml) and NMP (0.5 ml) at 0 °C. The reaction was stirred at room temperature for 18 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with hexane. The solvent was evaporated to yield a pale yellow solid (302 mg, 35%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 5H), 2.87 (s, 10H), 2.01 (s, 15H), 1.80 (s, 30H), 1.70 (dd, ^2J = 12.5 Hz, ^3J = 9.0 Hz, 30H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ

136.78, 134.05, 130.48, 126.57, 47.89, 43.28, 37.31, 34.84, 29.20. UV (THF) λ_{max}, nm: 263, 301. HRMS (APCI) m/z: found 991.7109 (M + H); calc ($C_{75}H_{91}$) 991.7115.

***sym*-Penta-(1-buten-4-yl)-corannulene (6).** 4-bromo-1-butene (1.1 g, 8.1 mmol) was added to a suspension of Mg (219 mg, 9.0 mmol) and a crystal of iodine in THF (30 ml) at 0 °C; the mixture was stirred at room temperature for 2 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (311 mg, 0.74 mmol) and $Fe(acac)_3$ (65 mg, 0.18 mmol) in THF (5 ml) and NMP (0.5 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with a mixture hexane:ethyl acetate 98:2. The solvent was evaporated to yield a yellow solid (235 mg, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 5H), 6.11 (m, 5H), 5.27 (dd, ^2J = 17.0 Hz, ^3J = 1.5 Hz, 5H), 5.17 (dd, ^2J = 10.0 Hz, ^3J = 1.5 Hz, 5H), 3.31 (t, ^3J = 7,5 Hz, 10H), 2.76 (m, 10H). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.80, 138.38, 135.13, 129.91, 122.75, 115.38, 36.54, 33.12. UV (THF) λ_{max}, nm: 261, 298. HRMS (ESI) m/z: found 521.3205 (M + H); calc ($C_{40}H_{41}$) 520.3203.

***sym*-Penta-(1-(trimethylsilyl)-1-butyn-4-yl)-corannulene (7).** 1-bromo-4-trimethylsilyl-3-butyne[4] (2.4 g, 11.7 mmol) was added to a suspension of Mg (575 mg, 19.7 mmol) and a crystal of iodine in THF (40 ml) at 0 °C; the mixture was stirred at room temperature for 3.5 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (465 mg, 1.1 mmol) and $Fe(acac)_3$ (97 mg, 0.27 mmol) in THF (10 ml) and NMP (1.0 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with a mixture hexane:diethyl ether 98:2. The solvent was evaporated to yield a yellow solid (537 mg, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 5H), 3.33 (t, ^{3}J = 7.5 Hz, 10H), 2.75 (t, ^{3}J = 7.5 Hz, 10H), 1,53 (s, 45H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.65, 135.22, 129.64, 123.26, 106.53, 86.02, 32.86, 23.10, 0.35. UV (THF) λ_{max}, nm: 262, 299. HRMS (APCI) m/z: found 871.4396 (M + H); calc ($C_{55}H_{71}Si_5$) 871.4397.

***sym*-Penta-(1-[1,3]-dioxolane-2-ethyl)-corannulene (8).** 2-(1,3-dioxa-2-cyclopentyl)-ethyl bromide (2.6 g, 14.4 mmol) was added to a suspension of Mg (367 mg, 15.1 mmol) and a crystal of iodine in THF (60 ml) at 0 °C; the mixture was stirred at room temperature for 2.5 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (553 mg, 1.3 mmol) and $Fe(acac)_3$ (115 mg, 0.33 mmol) in THF (10 ml) and NMP (1.0 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with ethyl acetate. The solvent was evaporated to yield a yellow solid (674 mg, 69%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.65 (s, 5H), 5.04 (t, ^{3}J = 4.8 Hz, 10H), 4.09 (m, 10H), 3,92 (m, 10H), 3.23 (t, ^{3}J = 8.4 Hz, 10H), 2.24 (m, 10H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 140.68, 135.15, 130.00, 122.83, 104.17, 65.28, 36.45, 27.80. UV (THF) λ_{max}, nm: 263, 298. HRMS (ESI) m/z: found 773.3294 (M + Na); calc ($C_{45}H_{50}NaO_{10}$) 773.3296.

***sym*-Penta-(1-(triisopropylsilyloxy)-3-propyl)-corannulene (9).** 3-(triisopropylsilyloxy)-propylbromide[5] (3.5 g, 11.9 mmol) was added to a suspension of Mg (356 mg, 14.6 mmol) and a crystal of iodine in THF (25 ml) at 0 °C; the mixture was stirred at room temperature for 1 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (457 mg, 1.1 mmol) and $Fe(acac)_3$ (97 mg, 0.27 mmol) in THF (5 ml) and NMP (0.5 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel

eluted with ethyl acetate. The solvent was evaporated to yield a yellow oil (887 mg, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.62 (s, 5H), 3.87 (t, ^{3}J = 6.0 Hz, 10H), 3.19 (t, ^{3}J = 7.5 Hz, 10H), 2.11 (m, 10H), 1.10 (m, 105H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 141.38, 135.14, 130.06, 122.82, 63.17, 36.00, 30.06, 18.35, 12.33. UV (THF) λ_{max}, nm: 263, 298. HRMS (ESI) m/z: found 1321.9610 (M + H); calc ($C_{80}H_{141}O_5Si_5$) 1321.9620.

***sym*-Penta-(3-(2,5-dimethylpyrrole)-1-propyl)-corannulene (10).** 1-(3-bromopropyl)-2,5-dimethylpyrrole[6] (4.1 g, 19.0 mmol) was added to a suspension of Mg (557 mg, 22.3 mmol) and a crystal of iodine in THF (15 ml) at 0 °C; the mixture was stirred at room temperature for 2 hours. The Grignard solution was added to a suspension of *sym*-pentachlorocorannulene (730 mg, 1.7 mmol) and $Fe(acac)_3$ (152 mg, 0.43 mmol) in THF (15 ml) and NMP (1.5 ml) at 0 °C. The reaction was stirred at room temperature for 2.5 hours. The solution was then cooled to 0 °C and quenched by slowly addition of diethyl ether followed by a 1 M solution of HCl in water. The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with a mixture hexane:ethyl acetate 8:2. The solvent was evaporated to yield a pale yellow solid (976 mg, 62%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 5H), 5.83 (s, 10H), 3.97 (t, ^{3}J = 7.0 Hz, 10H), 3.10 (t, ^{3}J = 7.0 Hz, 10H), 2.25 (m, 40H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 140.64, 135.35, 129.53, 127.62, 122.33, 105.59, 43.44, 33.37, 30.57, 12.87. UV (THF) λ_{max}, nm: 262, 299. HRMS (ESI) m/z: found 948.5905 (M + Na); calc ($C_{65}H_{75}N_5Na$) 948.5915.

***sym*-Penta-(1-butyn-4-yl)-corannulene (11).** A solution of NaOH 10% in water was added to a solution of **7** (156 mg, 0.18 mmol) in MeOH (1.5 ml); THF was added until a clear solution was obtained. The reaction was stirred at room temperature for 24 hours. The solution was then cooled to 0 °C, acidified with a 1 M solution of HCl in water and extracted with diethyl ether. The collected organic phases were dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with a mixture hexane:dichloromethane 6:4. The solvent was evaporated to yield a pale yellow solid (77 mg, 84%). ^{1}H-NMR

(500 MHz, $CDCl_3$): δ 7.68 (s, 5H), 3.37 (t, ^3J = 7.5 Hz, 10H), 2.73 (dt, ^3J = 7.5 Hz, ^4J = 2.5 Hz, 10H), 2.05 (t, ^4J = 2.5 Hz, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.35, 135.26, 129.66, 123.32, 83.88, 69.80, 32.54, 21.48. UV (THF) λ_{max}, nm: 262, 299. HRMS (ESI) m/z: found 511.2420 (M + 23); calc ($C_{40}H_{31}$) 511.2420.

***sym*-Penta-(1-al-3-propyl)-corannulene (12).** Acetic acid (1.0 ml) and HCl 1 M (1.0 ml) were added to a solution of **8** (55 mg, 73.3 μmol) in THF (1.0 ml) and was heated to reflux and stirred for 2 hours. The mixture was cooled to 0 °C, neutralized with $NaHCO_3$ and extracted with ethyl acetate. The collected organic phases were dried over Na_sSO_4 and evaporated to yield an orange solid (41 mg, 99%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.92 (s, 5H), 7.60 (s, 5H), 3.45 (dt, ^3J = 7.5 Hz, ^3J = 7.0 Hz, 10H), 3.05 (t, ^3J = 7.5 Hz, 10H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 201.18, 139.89, 135.32, 129.70, 123.02, 46.03, 25.68. UV (THF) λ_{max}, nm: 261, 298. HRMS (ESI) m/z: found 553.1983 (M + Na); calc ($C_{35}H_{30}NaO_5$) 553.1986.

***sym*-Penta-(1-carboxy-2-ethyl)-corannulene (13).** A suspension of Oxone® (1.8 g, 2.88 mmol) in water (2 ml) was added to a solution of **8** (54 mg, 71.9 μmol) in THF (400 μl) at 0 °C. The reaction was stirred at room tamperature for 2 days. The mixture was then diluted with water and ethyl acetate; the organic player was separated and the aqueous phase was extracted with ethyl acetate. The collected organic phases were dried over Na_2SO_4 and evaporated. The crude was then dissolved in MeOH and a NaOH 1 M was slowly added until basic pH was reached; the aqueous phase was washed with ethyl acetate. The aqueous layer was then acidified with HCl 1 M to pH 1 and extractions with ethyl acetate were performed. The collected organic phases were dried over Na_sSO_4 and evaporated to yield a yellow solid (39 mg, 89%).

^{1}H-NMR (500 MHz, d^4-MeOD): δ 7.68 (s, 5H), 3.24 (t, ^3J = 7.0 Hz, 10H), 2.87 (t, ^3J = 7.0 Hz, 10H). ^{13}C-NMR (125 MHz, d^4-MeOD): δ 176.90, 141.21, 136.14, 130.81, 123.93, 37.54, 29.64. UV (THF) λ_{max}, nm: 263, 298. HRMS (ESI) m/z: found 609.1773 (M - H); calc ($C_{35}H_{29}O_{10}$) 609.1766.

***sym*-Penta-(1-ol-3-propyl)-corannulene (14).** Trifluoroacetic acid (2.0 ml, 26.1 mmol) was added to a well stirred solution of **9** (250 mg, 0.19 mmol) in acetone (2.5 ml), THF (1.75 ml) and water (1.0 ml). The reaction was heated to reflux for 2 days.

The mixture was cooled to room temperature and the organic solvents were evaporated. The solid was then filtrated and was washed with water and diethyl ether. The product was purified by column chromatography on silica gel eluted with a mixture dichloromethane:methanol 9:1. The solvent was evaporated to yield a pale yellow solid (93 mg, 91%).

^{1}H-NMR (500 MHz, *d*^{4}-MeOD): δ 7.59 (s, 5H), 4.47 (br, 5H), 3.64 (t, ^{3}J = 6.0 Hz, 10H), 3.11 (t, ^{3}J = 7.5 Hz, 10H), 2.01 (m, 10H). ^{13}C-NMR (125 MHz, *d*^{4}-MeOD): δ 142.50, 136.04, 131.09, 123.86, 62.58, 36.45, 30.73. UV (THF) λ_{max}, nm: 261, 298. HRMS (ESI) m/z: found 563.2766 (M + Na); calc ($C_{35}H_{40}NaO_5$) 563.2768.

***sym*-Penta-(1-bromo-3-propyl)-corannulene (15).** NBS (106 mg, 0.60 mmol) was added to a solution of **14** (37 mg, 68.4 μmol) and triphenylphosphine (149 mg, 0.57 mmol) in DMF (2.0 ml) at 0 °C. The reaction was stirred at room temperature for 1 hour. The DMF was evaporated at reduced pressure and the crude was diluted in dichloromethane. The organic phase was washed with water and brine, dried over Na_sSO_4 and evaporated to yield the crude product. The product was purified by column chromatography on silica gel eluted with a mixture hexane:ethyl acetate 9:1; hexane:ethyl acetate 1:1 and then ethyl acetate:methanol 9:1. The solvent was evaporated to yield a pale yellow solid (45 mg, 77%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 5H), 3.56 (t, ^{3}J = 6.4 Hz, 10H), 3.30 (t, ^{3}J = 7.2 Hz, 10H), 2.45 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 139.87, 135.24, 129.86, 123.36, 34.96, 33.61, 31.67. UV (THF) λ_{max}, nm: 261, 299. HRMS (ESI) m/z: found 850.8714 (M + H); calc ($C_{35}H_{36}Br_5$) 850.8728.

***sym*-Penta-(1-thiol-3-propyl)-corannulene (16).** A solution of **15** (40 mg, 46.8 μmol), thiourea (64 mg, 0.84 mmol) in ethanol (3.0 ml) and THF (1.0 ml) was heated to reflux and stirred for 2 hours. The mixture was cooled down and the solvent was evaporated. The crude was dissolved in NaOH 7.5 M (5.0 ml), heated to reflux and stirred for 2 hours. The mixture was cooled down to 0 °C and acidified to pH 1 with HCl 1 M. The solid was filtrated and washed with water and diethyl ether to yield a pale yellow solid (28 mg, 96%).

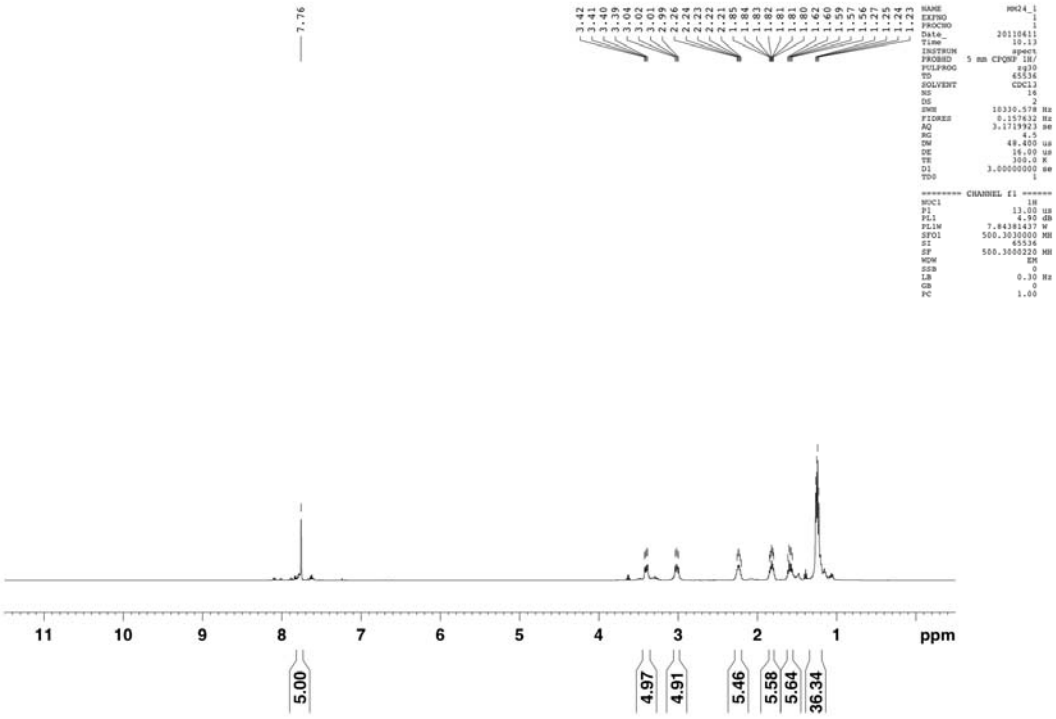
^{1}H-NMR (400 MHz, *d*^{6}-DMSO): δ 7.79 (s, 5H), 3.24 (t, ^{3}J = 7.5 Hz, 10H), 2.66 (dt, ^{3}J = 7.5 Hz, ^{3}J = 7.0 Hz, 10H), 2.11 (m, 10H). ^{13}C-NMR (100 MHz, *d*^{6}-DMSO): δ

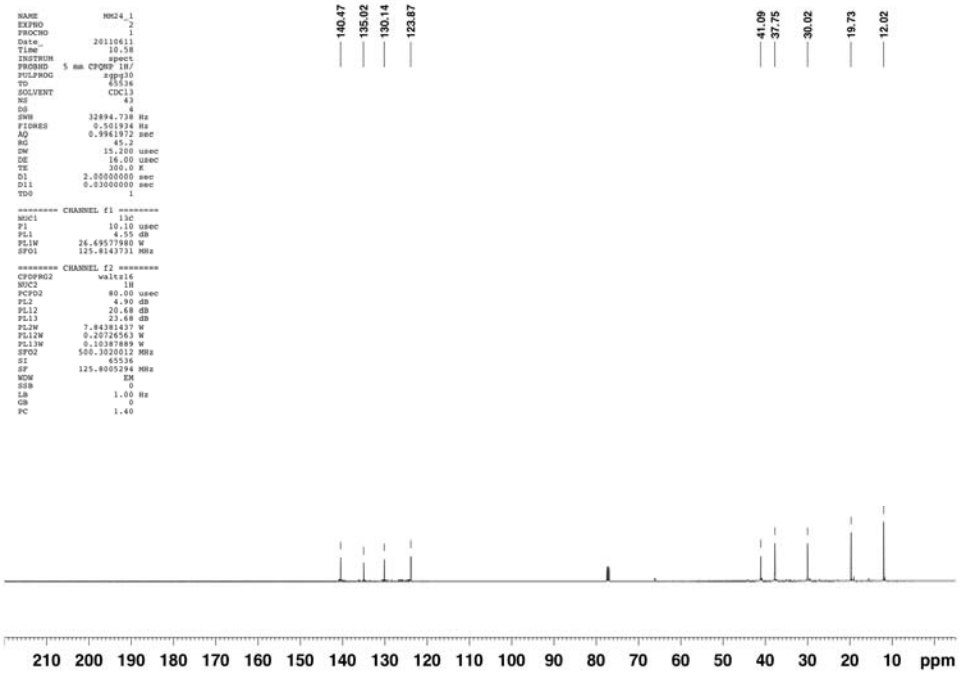
140.75, 133.96, 129.47, 122.86, 36.11, 31.20, 23.61. UV (DMSO) λ_{max}, nm: 263, 301. HRMS (ESI) m/z: found 621.1812 (M + H); calc ($C_{35}H_{41}S_5$) 621.1806.

***sym*-Penta-(2-(1,2,3-triazole-4-ethyl)-ethyl-®-D-galactopyranoside)-corannulene (21).** A mixture of **20**[7, 8] (42.0 mg, 0.17 mmol), **11** (11.6 mg, 23 μmol) and copper nanoparticles (10.8 mg, 0.17 mmol) in DMF (1 ml) in a microwave vessel was heated at 60 °C in a microwave reactor (200 W) for 2 hours. The mixture was then filtrated over celite, the solvent was evaporated and MeOH was added to the crude. The solid was then filtrated and washed with cold MeOH to yield a white solid (24 mg, 59%) ^{1}H-NMR (500 MHz, *d*^{6}-DMSO): δ 8.19 (s, 5H), 7.81 (s, 5H), 5.01 (d, ^{3}J = 4.5 Hz, 5H), 4.77 (d, ^{3}J = 5.5 Hz, 5H), 4.62-4.51 (m, 15H), 4.17 (d, ^{3}J = 7.5 Hz, 5H), 4.08 (m, 5H), 3.86 (m, 5H), 3.62 (t, ^{3}J = 4.0 Hz, 5H), 3.51 (m, 20H), 3.16 (t br, ^{3}J = 7.0 Hz, 10H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.14, 140.6, 134.02, 129.48, 123.08, 103.45, 75.36, 73.30, 70.41, 68.16, 67.26, 60.48, 49.50, 32.43, 27.99. UV (DMSO) λ_{max}, nm: 264, 300. $[\alpha]^{25}_D$ = +349.3 (*c*=0.15 in H_2O). HRMS (ESI) m/z: found 878.8647 (M + 2H); calc ($C_{80}H_{107}N_{15}O_{30}$) 878.8649.

3. ^{1}H-NMR and ^{13}C-NMR spectra of compounds 4-16

Spectra of 4

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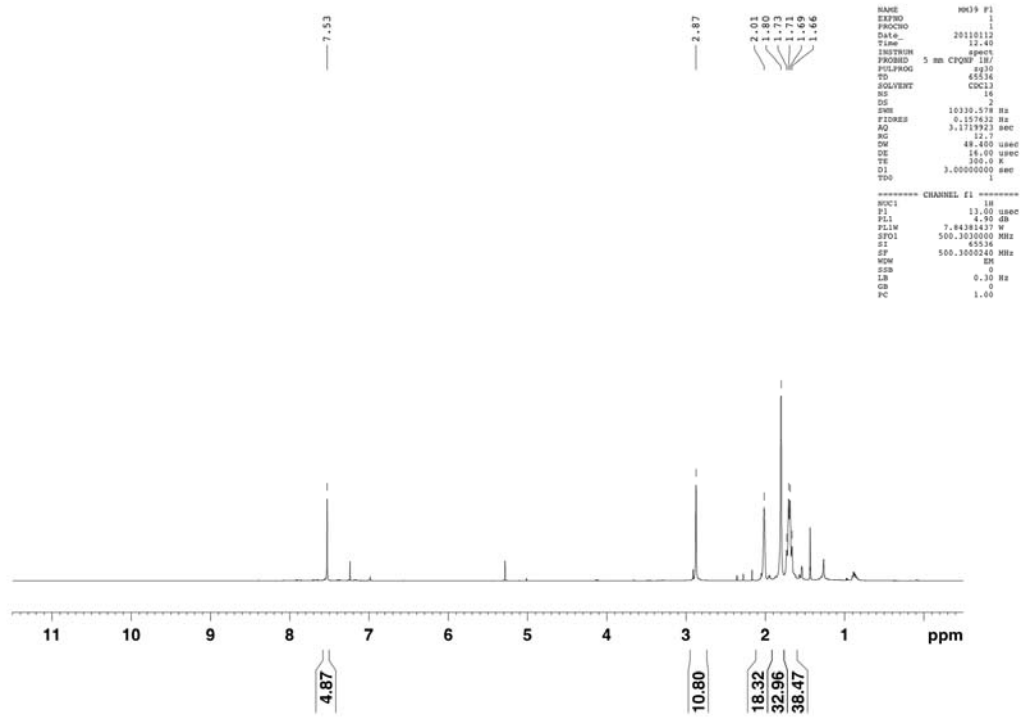
Spectra of 5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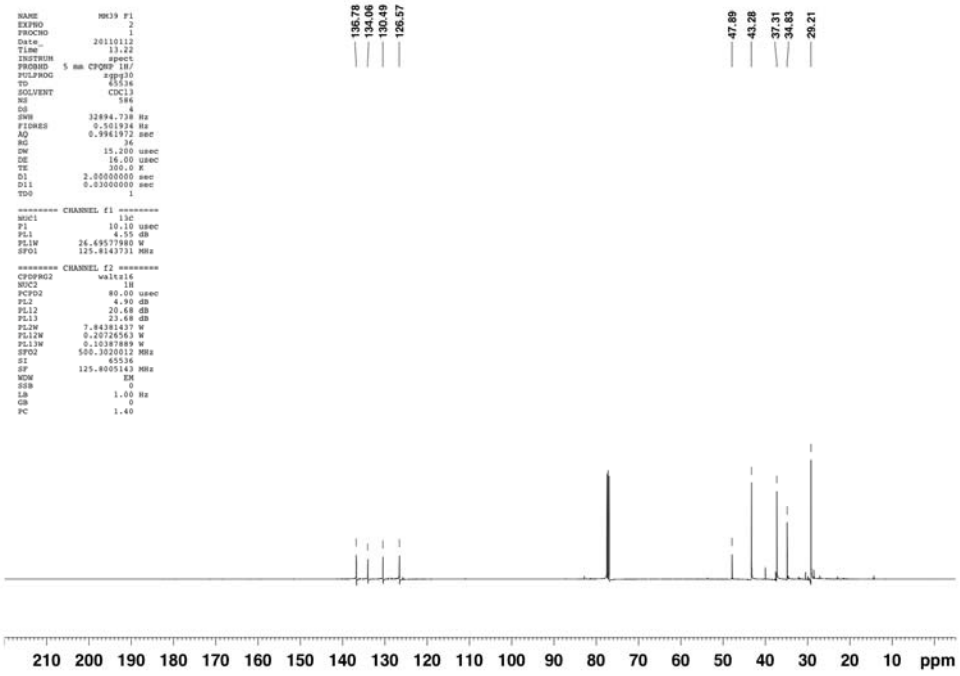
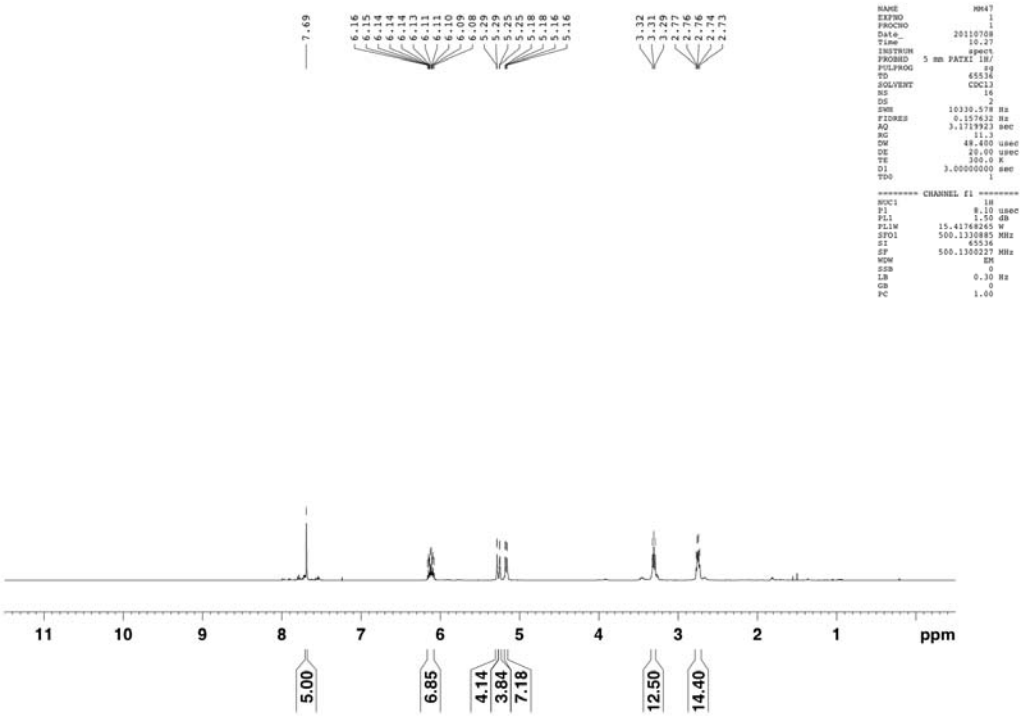
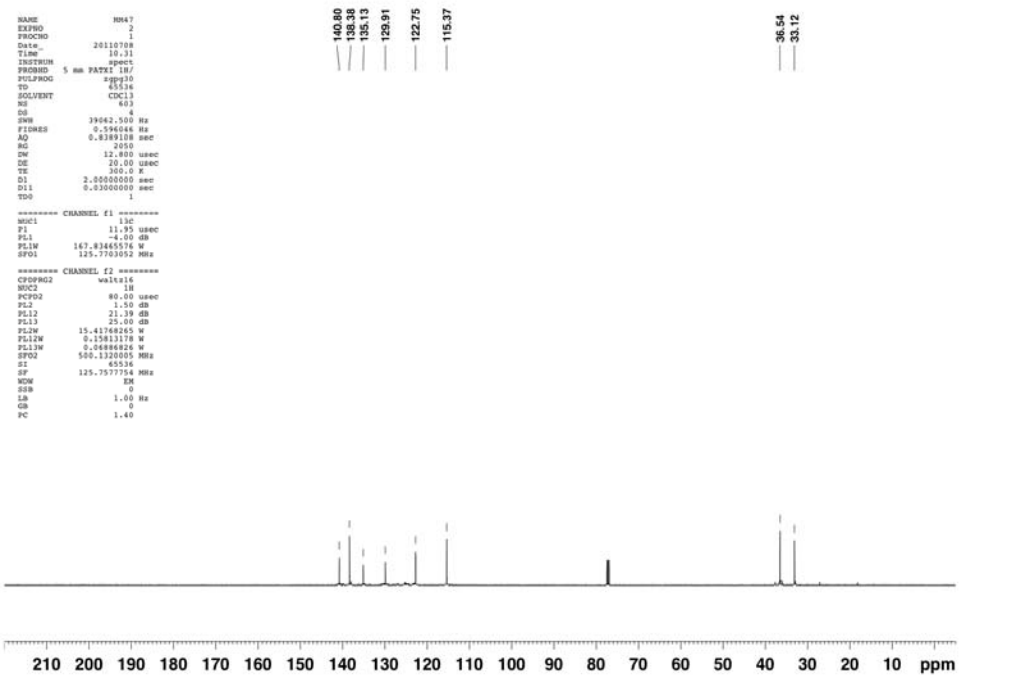
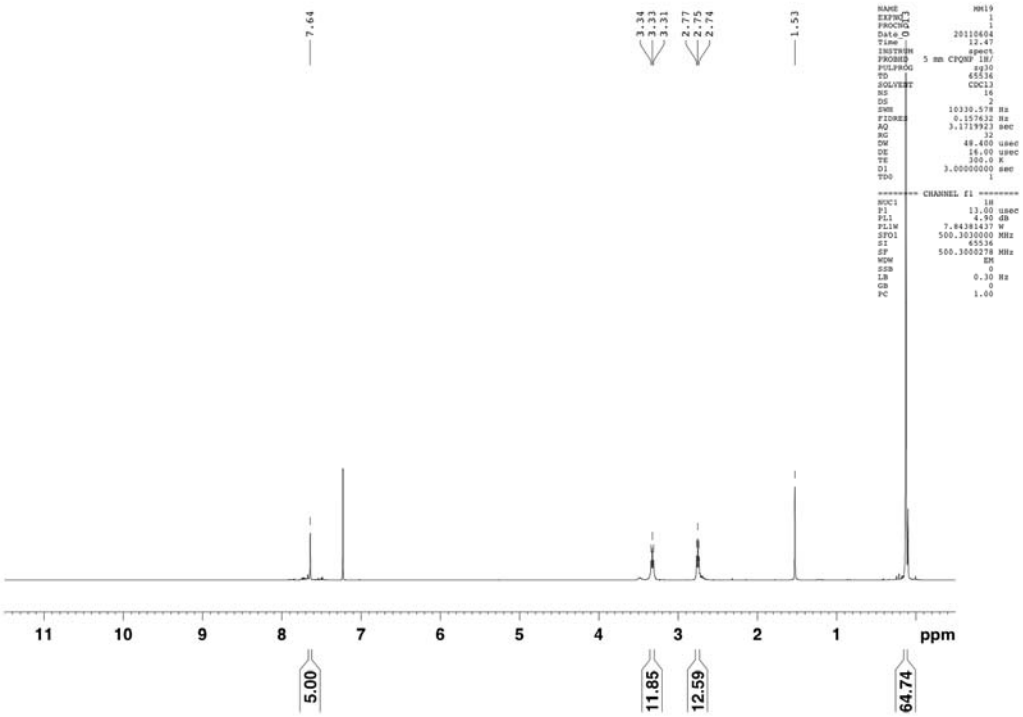


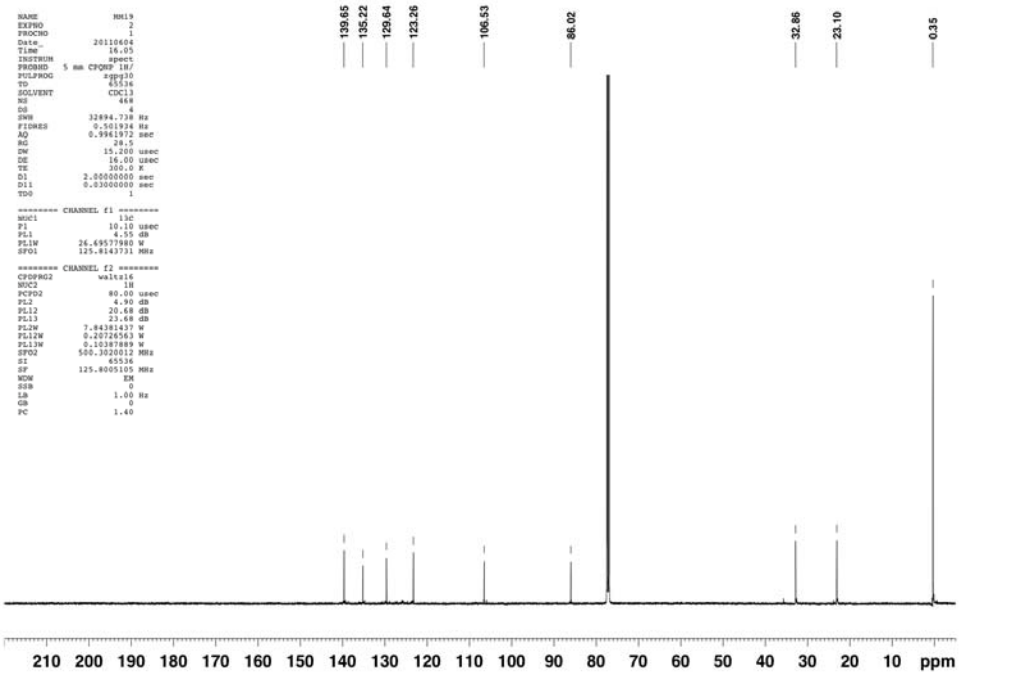
Spectra of 6





Spectra of 7





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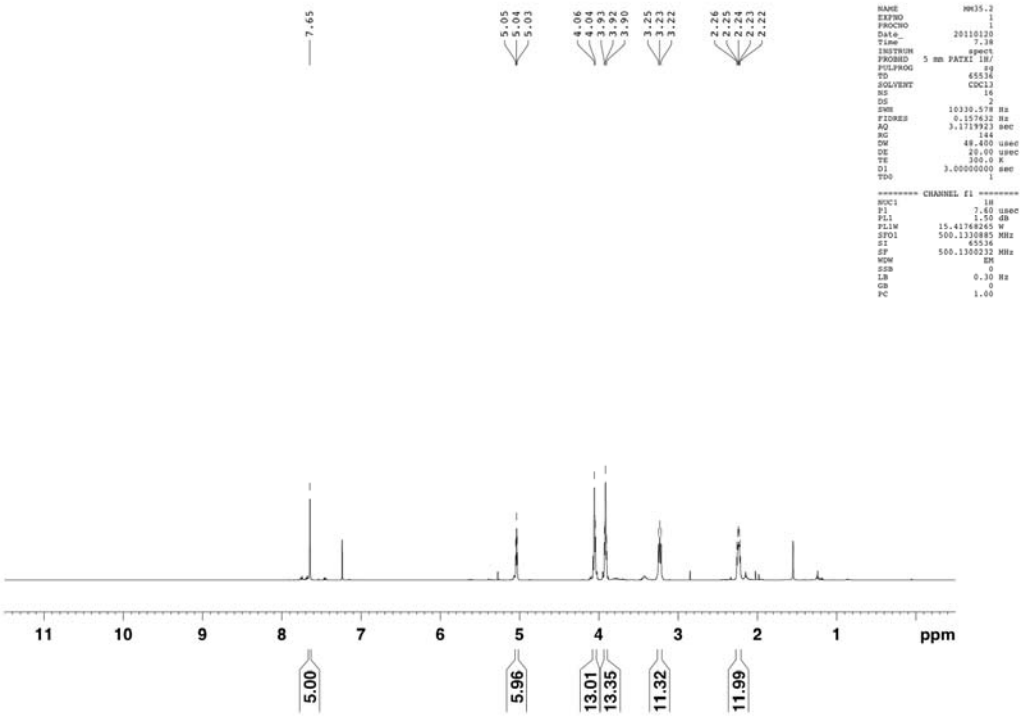

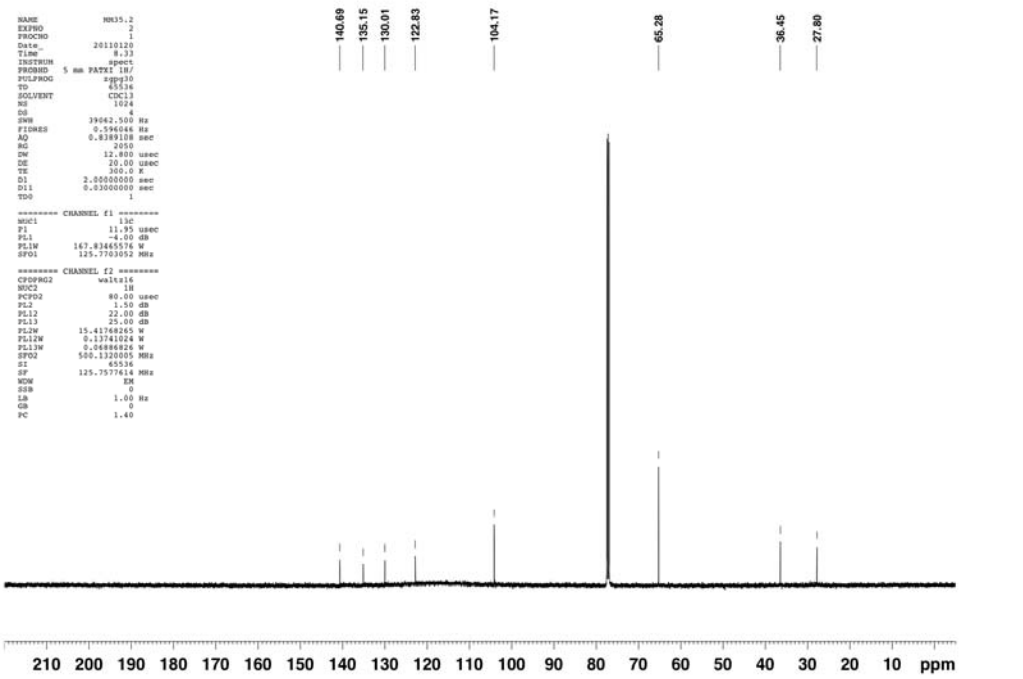

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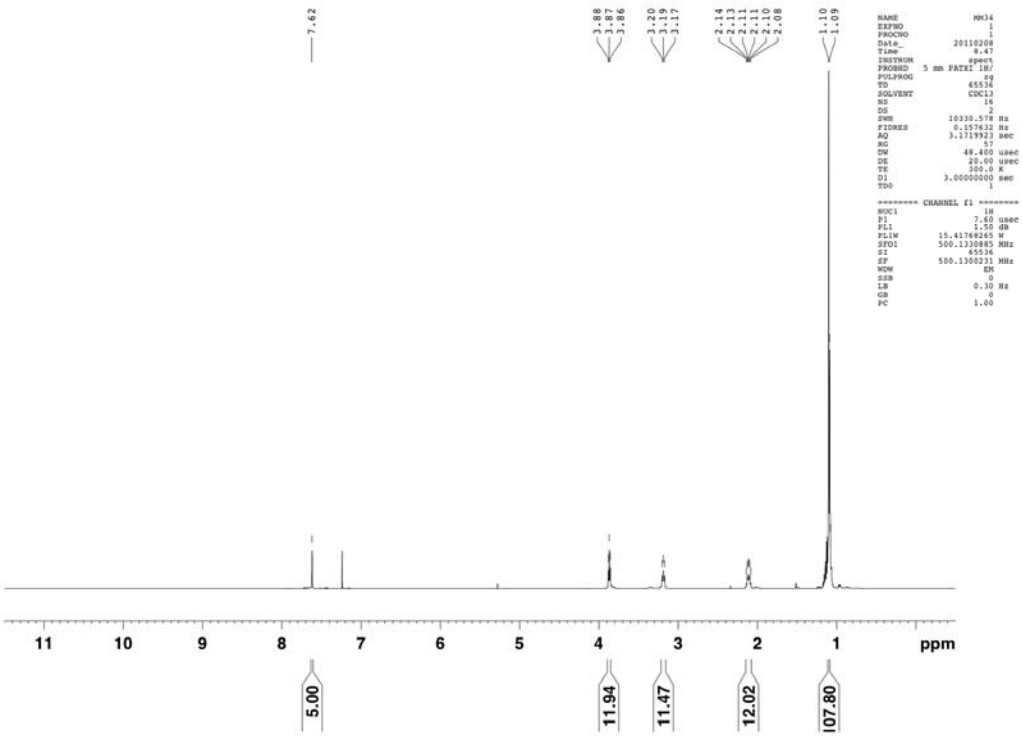

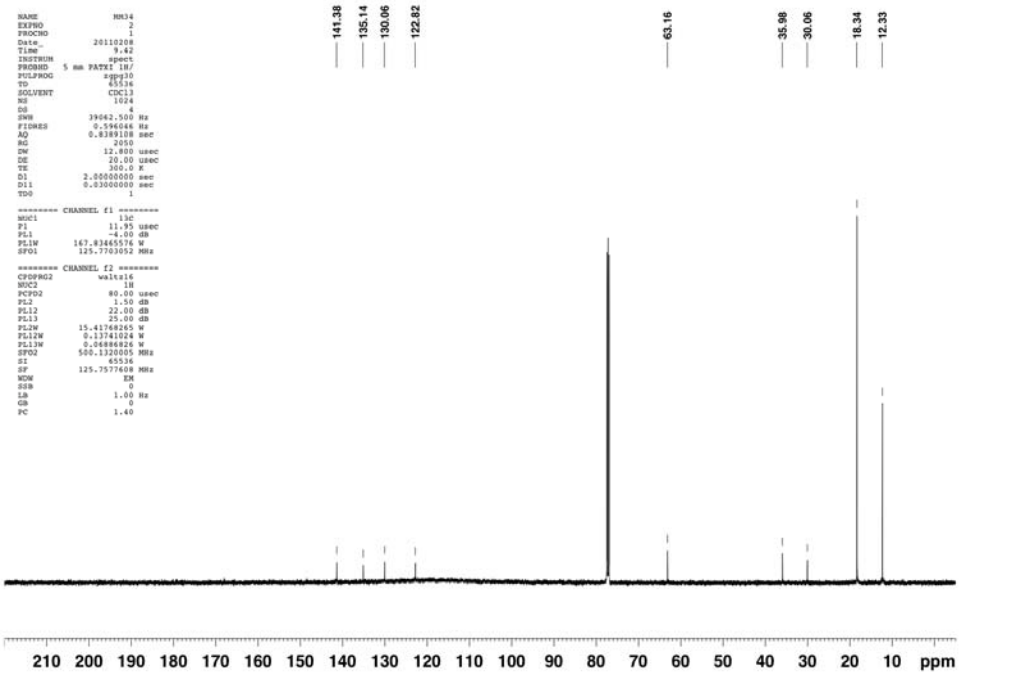

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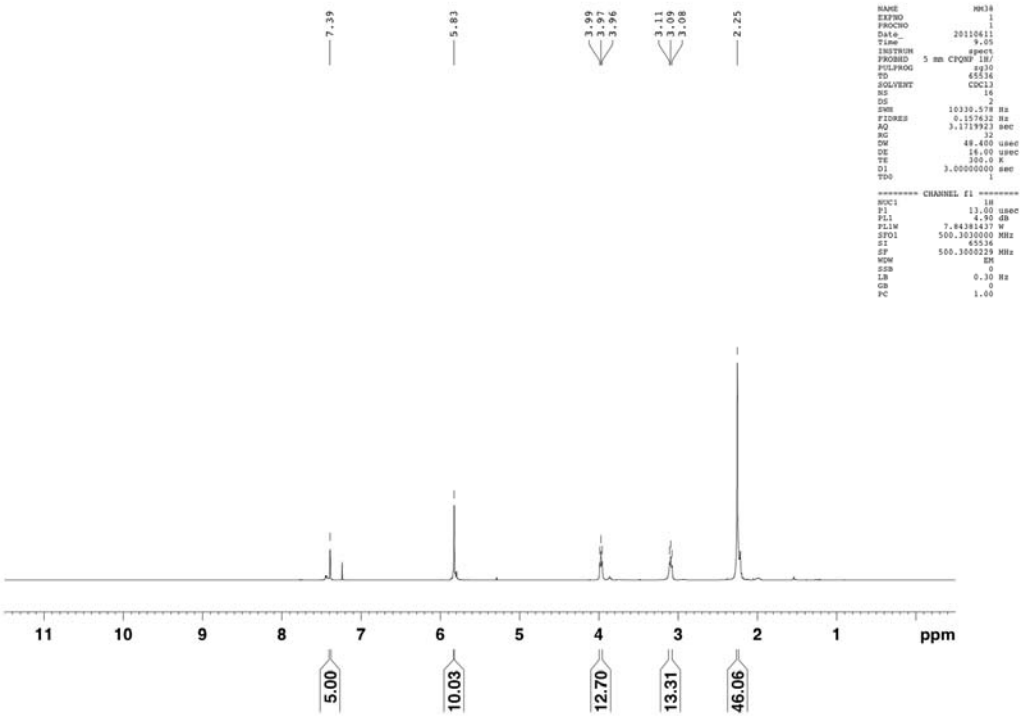

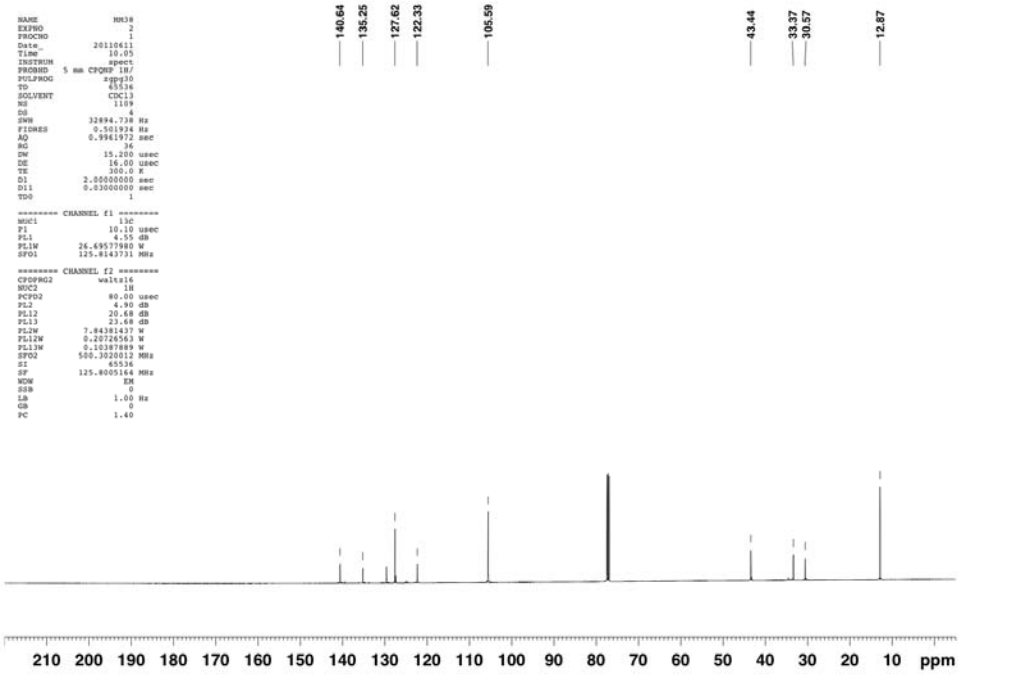

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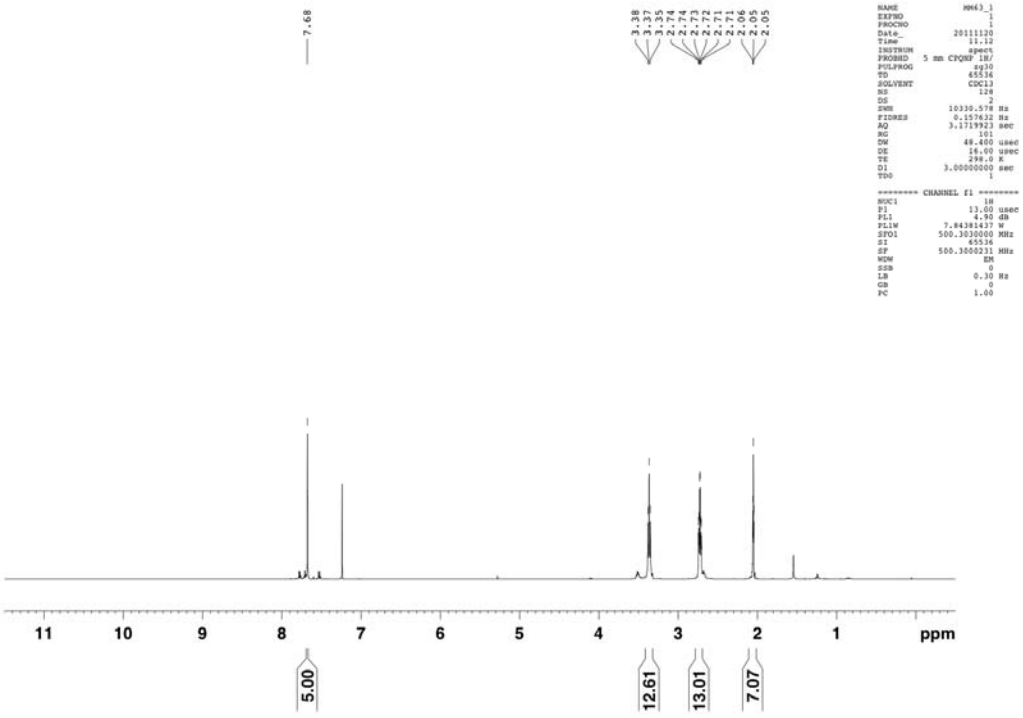

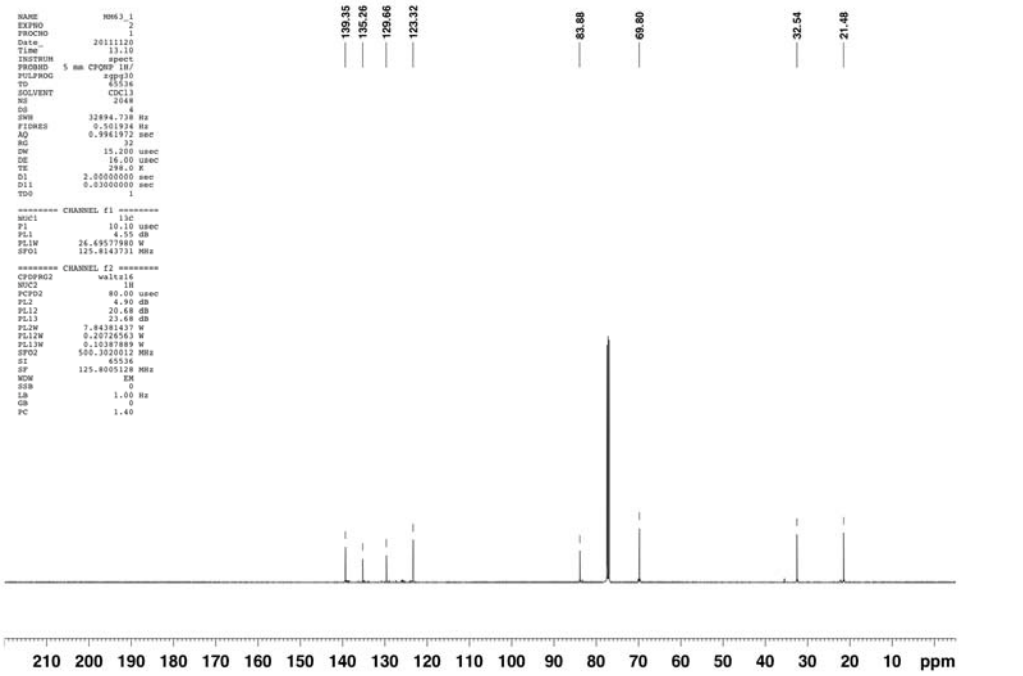

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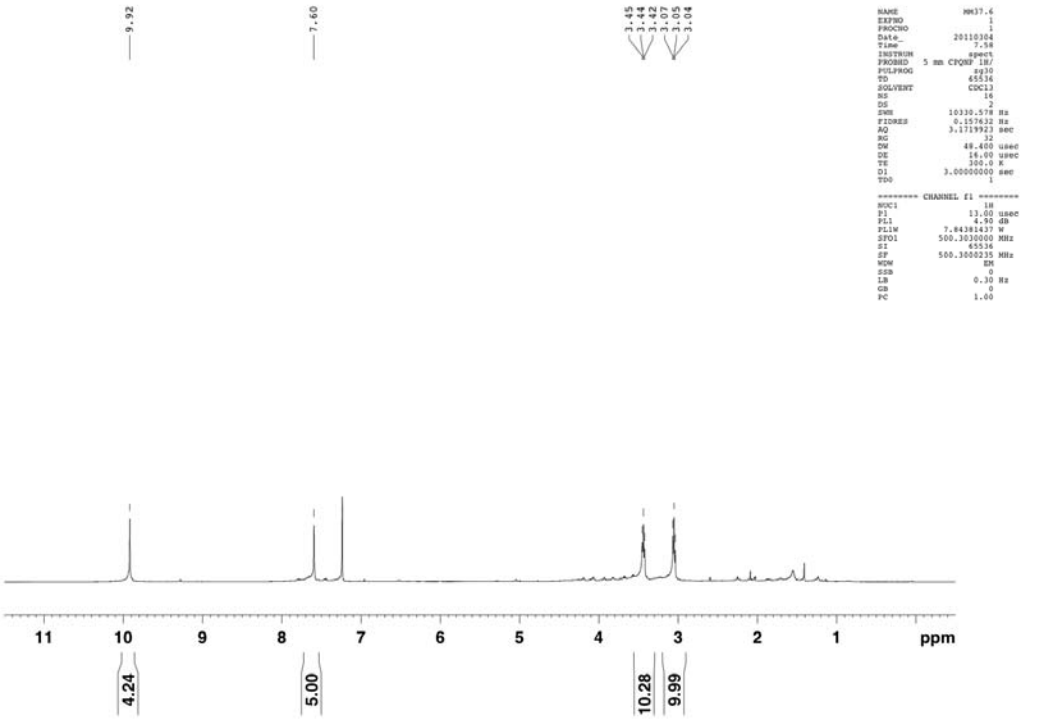

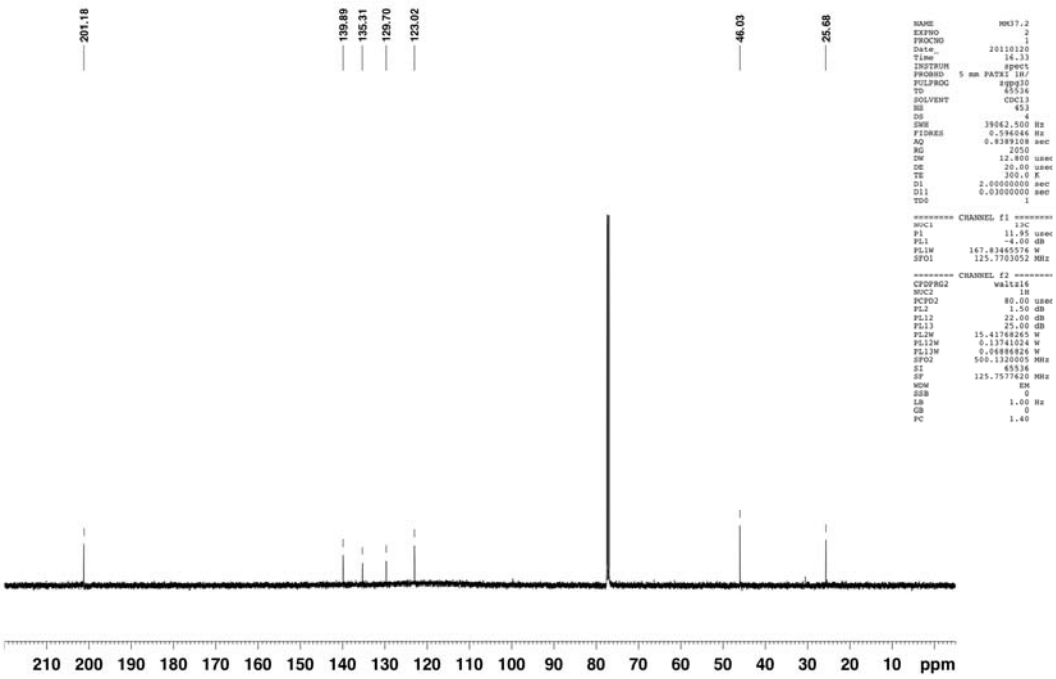

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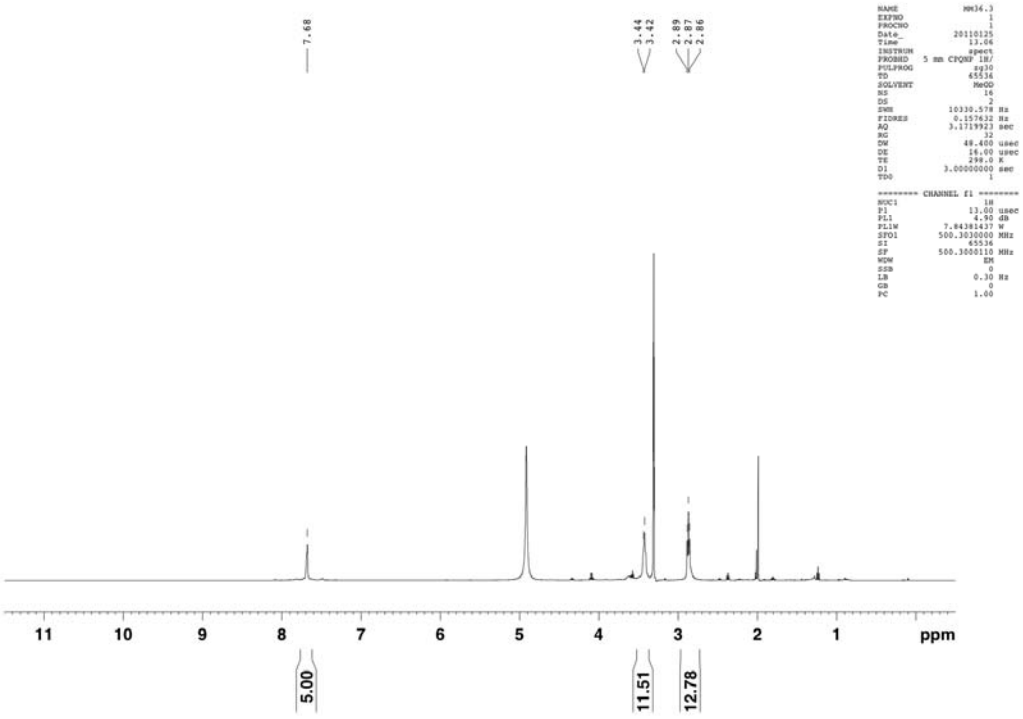
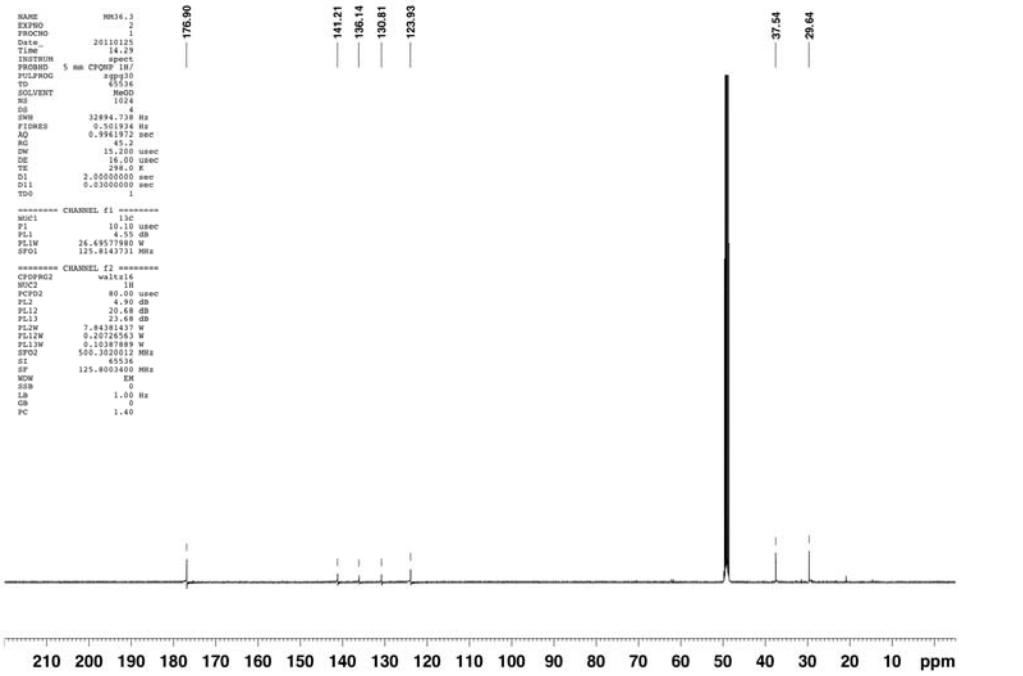
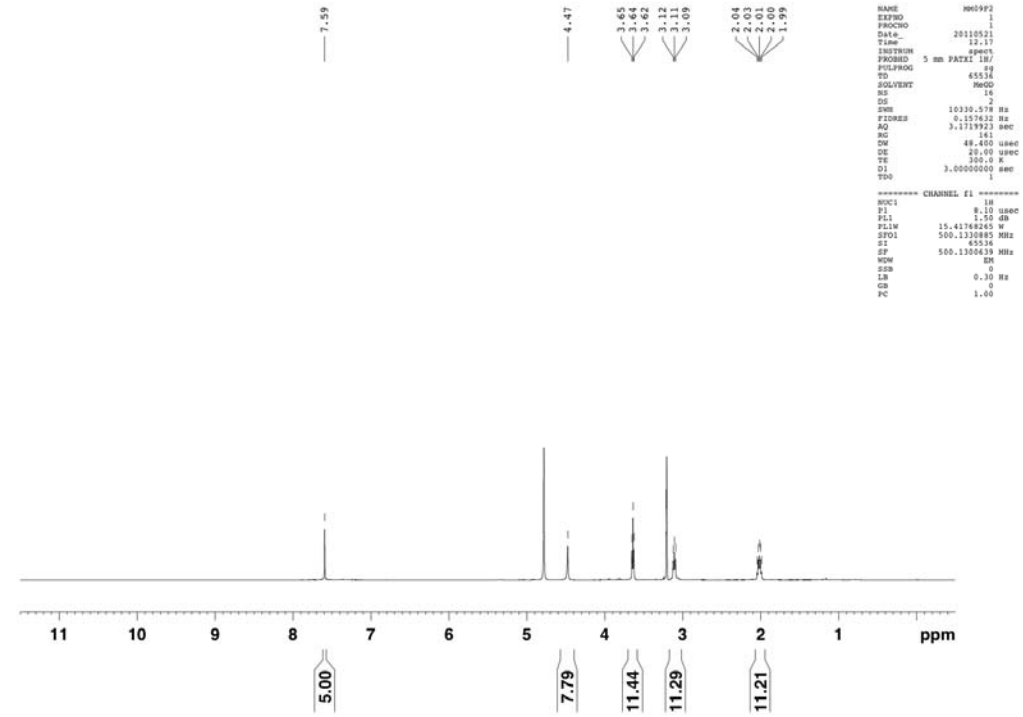
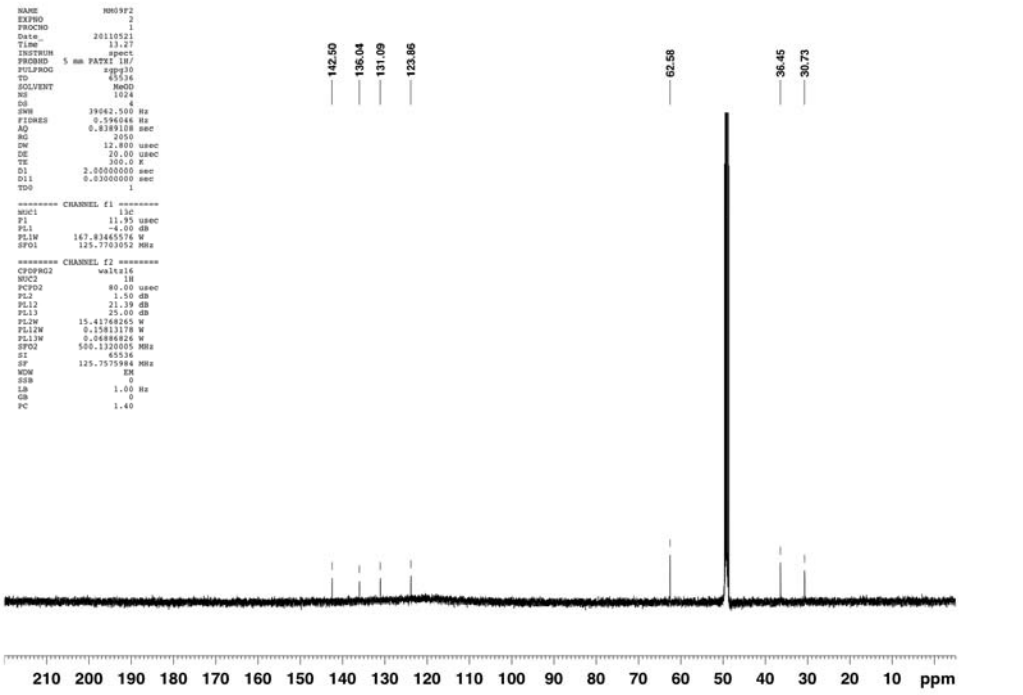


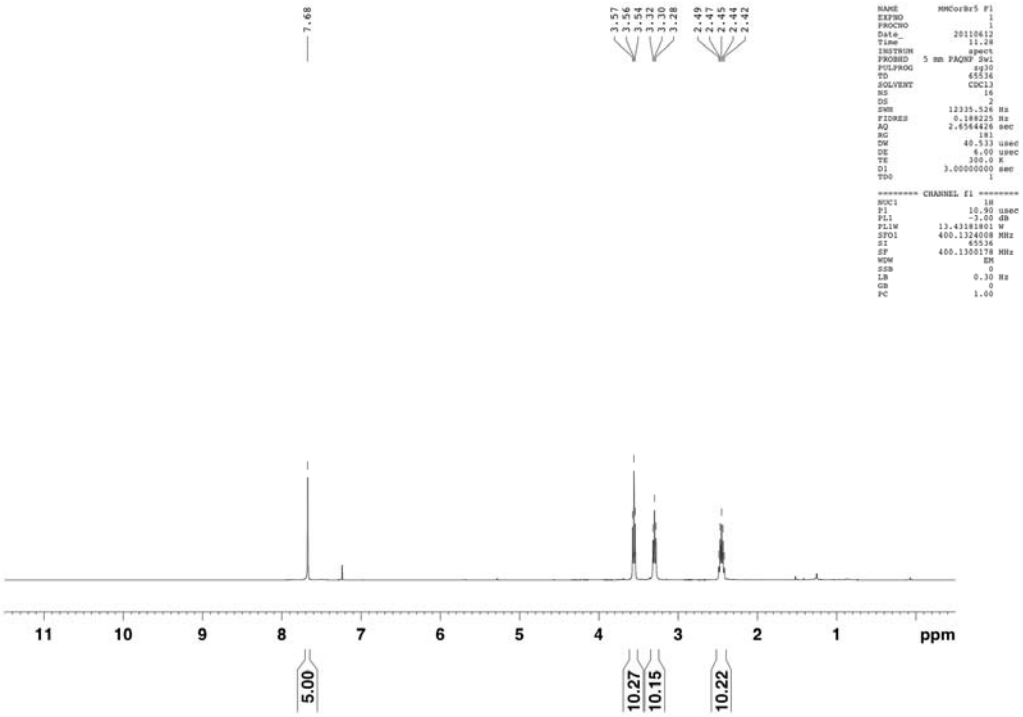


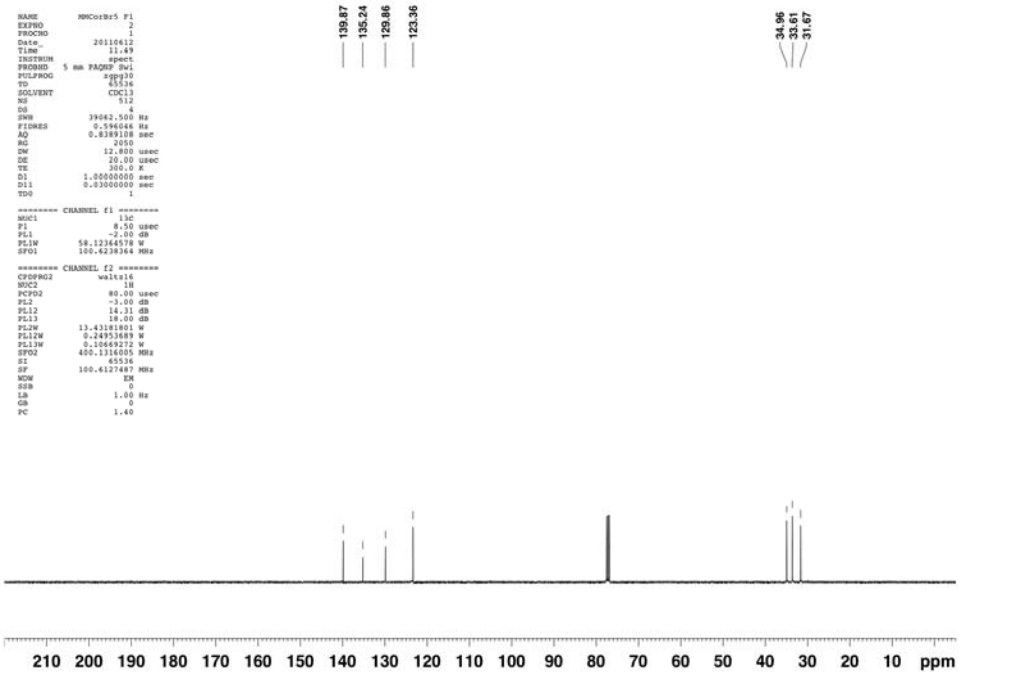
Spectra of 14



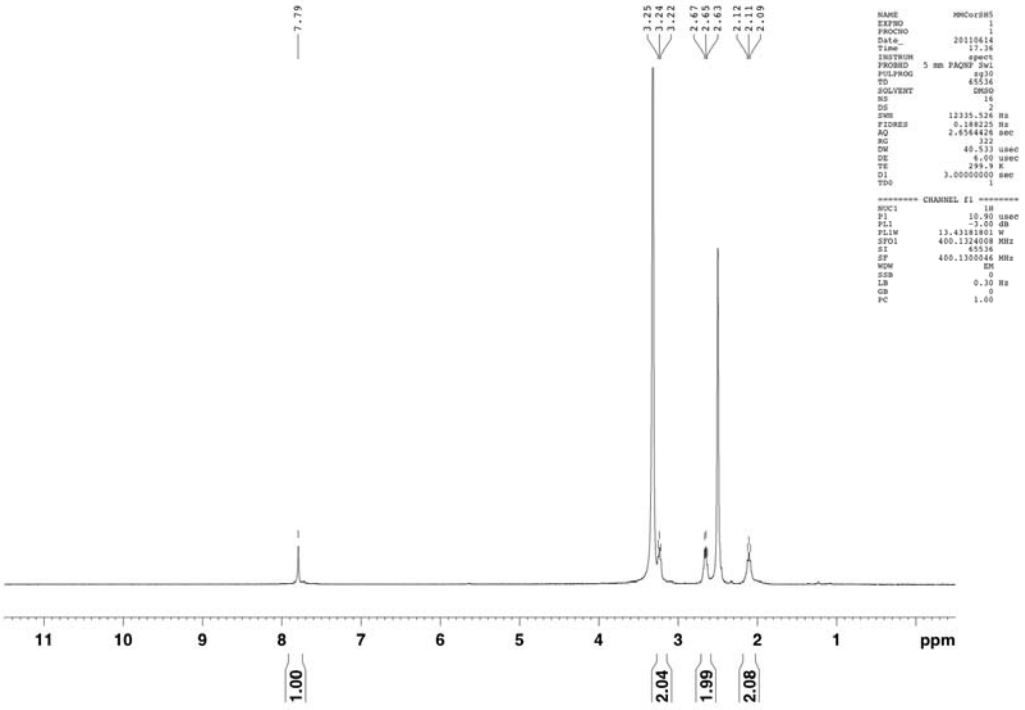


Spectra of 15





Spectra of 16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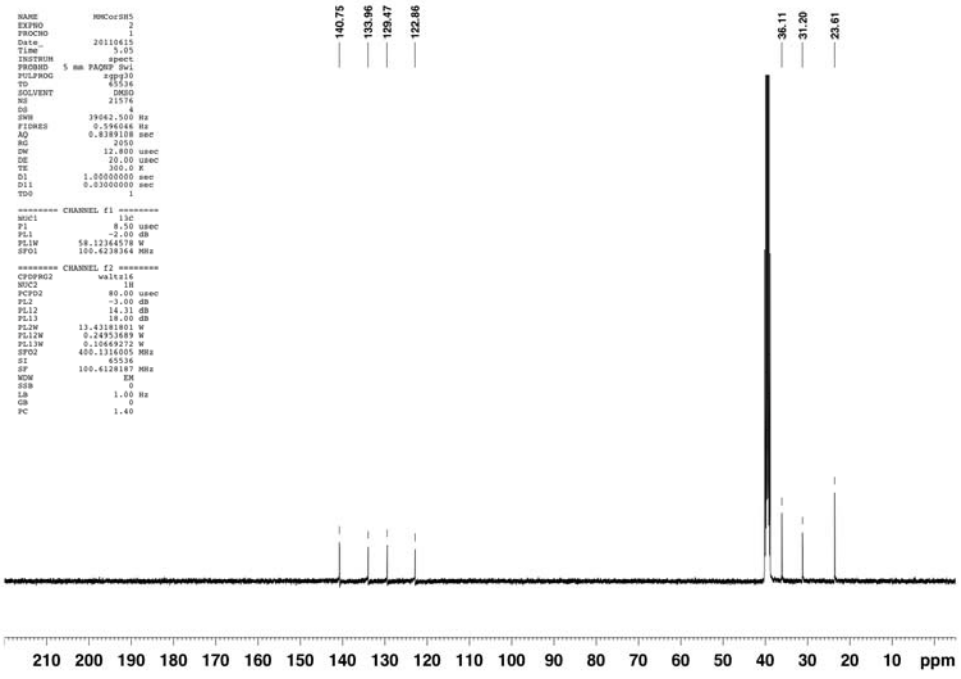
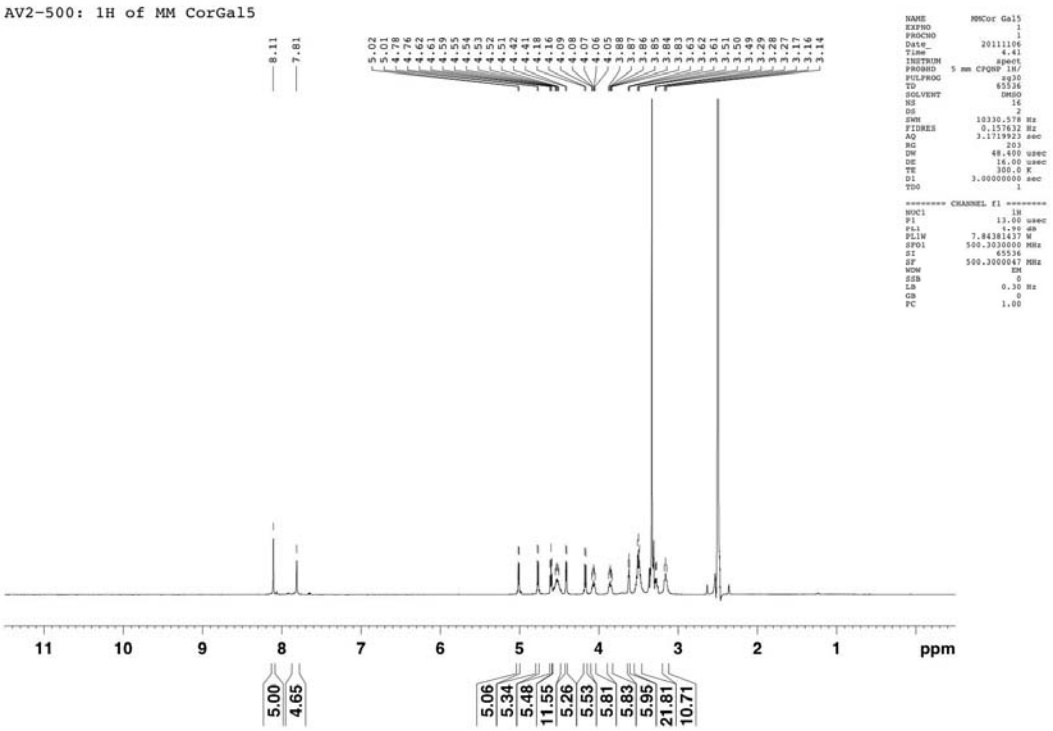
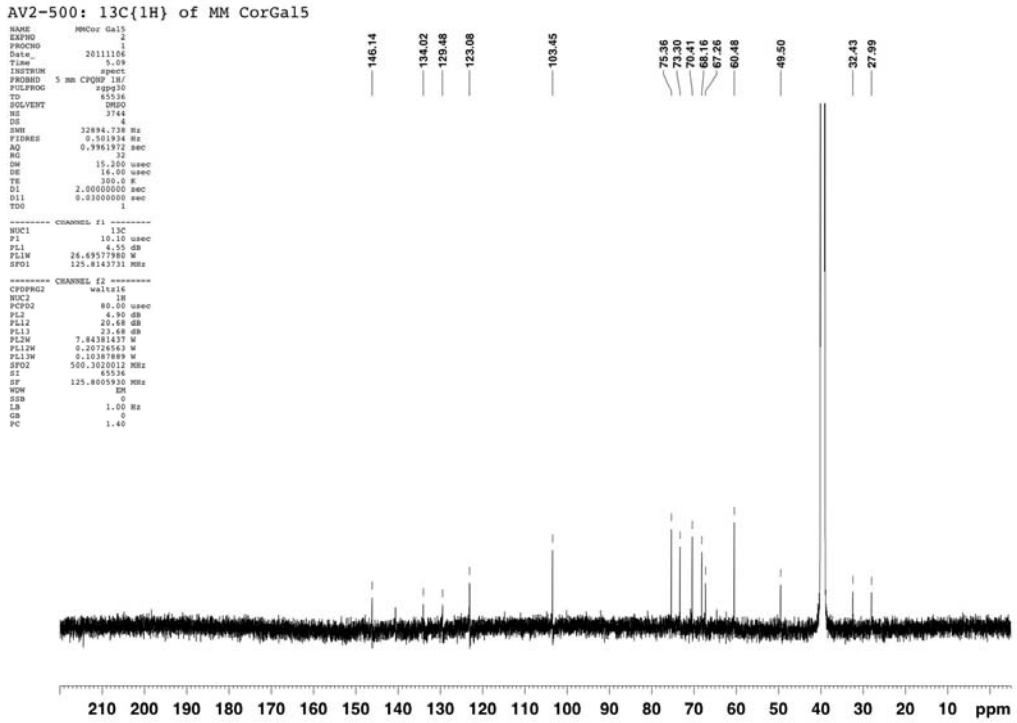
3.25
3.24
3.22
2.67
2.65
2.63
2.12
2.11
2.09
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.04
1.99
2.08


140.75
133.96
129.47
122.86
36.11
31.20
23.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

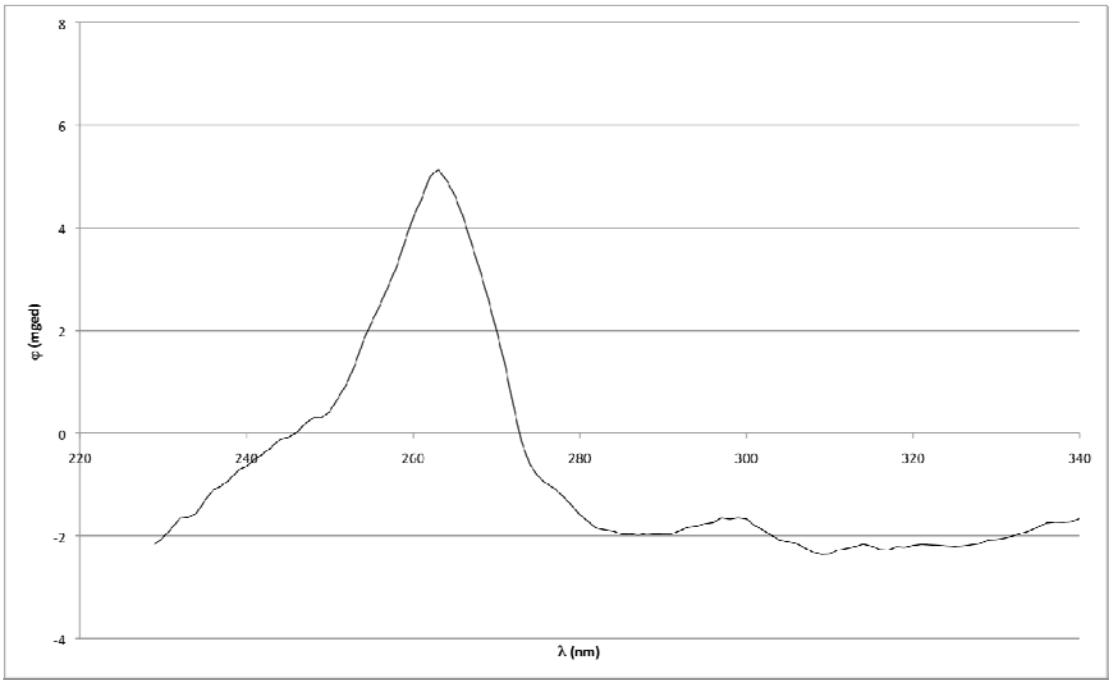
Spectra of 21



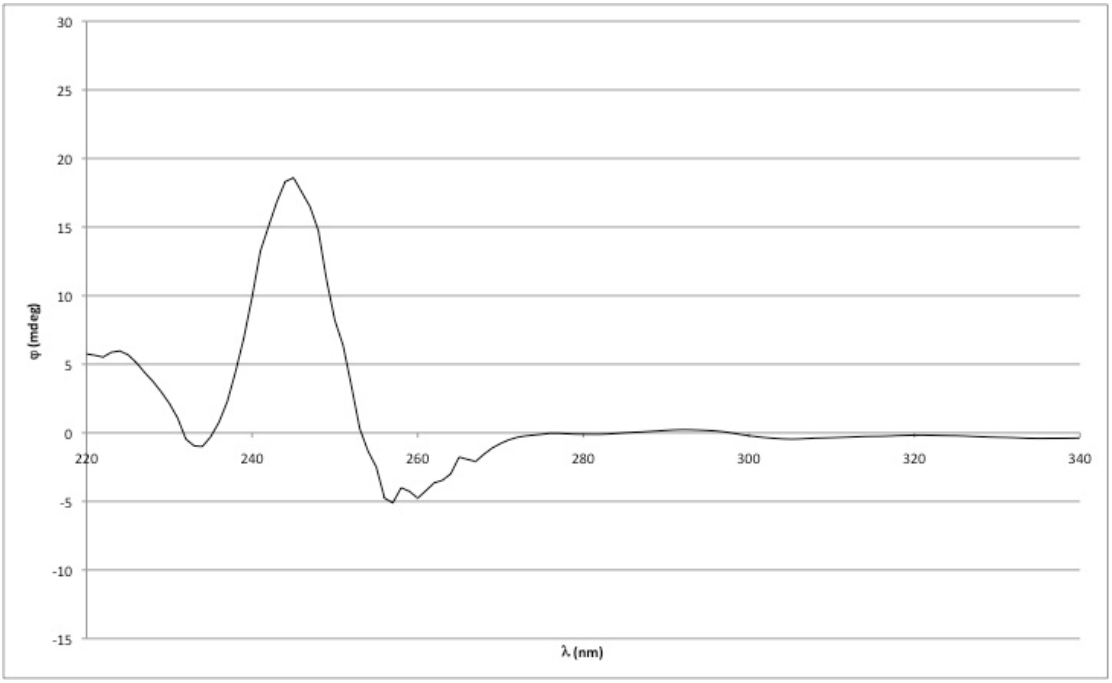


4. Circular Dichroism

Spectra of 4



Spectra of 21



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