Electronic Supporting Information (ESI)

Heterobimetallic propargyl gold complexes with π-bound copper or silver with enhanced anticancer activity

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1. Experimental

1.1. Starting Materials

The starting materials [AuCl(tht)],[1] [AuCl(PPh_3)],[2] [Au(acac)(PPh_3)],[3] [Ag(OTf)(PPh_3)$_2$],[4] [Cu(NO_3)(PPh_3)$_2$],[5] *N*-propargyl-di(2-picolyl)amine[6-7] and *N*-propargylcarbazole[8] were prepared according to published procedures. 3-Dimethylamino-1-propyne, 1-propargyl-1H-benzotriazole, 3-(allyloxy)-1-propyne, propargylether and phenylpropargyl sulfide were purchased from Sigma-Aldrich and used without further purification. Bis(2-dipyridylmethyl)amine and propargyl bromide were purchased from TCI chemicals and used without further purification. Solvents were dried with a SPS solvent purification system.

1.2. Instrumentation

Mass spectra were recorded on a Bruker Esquire 3000 PLUS, with the electrospray (ESI) technique and on a Bruker Microflex (MALDI-TOF). ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F NMR, including 2D experiments, were recorded at room temperature on a Bruker Avance 400 spectrometer (^{1}H 400.0 MHz, ^{13}C 100.6 MHz, ^{31}P 162.0 MHz, ^{19}F 376.5 MHz) or on a Bruker Avance II 300 spectrometer (^{1}H 300.0 MHz, ^{13}C 75.5 MHz, ^{31}P 121.5 MHz, ^{19}F 282.3 MHz), with chemical shifts (δ, ppm) reported relative to the solvent peaks of the deuterated solvent. All *J* values are given in Hz. IR spectra were recorded in neat samples in the range 4000-250 cm^{-1} on a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

1.3. Crystallography

Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of an Xcalibur Oxford Diffraction (**2**) or a Smart APEX CCD diffractometer (**3-5**, **7**, **8**) equipped with a low-temperature attachment. Data were collected using monochromated MoKα radiation (λ = 0.71073 Å). Scan type ϖ. Absorption corrections based on multiple scans were applied using SADABS[9] or spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.[10] The structures were solved by direct methods and refined on F2 using the program SHELXT-2016,[11] or Olex2.[12] All non-hydrogen atoms were refined anisotropically. CCDC deposition numbers 2009440 (**2**), 2009441 (**3**), 2009442 (**4**), 2009443 (**5**), 2009444 (**7**), 2009445 (**8**) and 2009446 (**9**) contain the supplementary crystallographic data. These data can be obtained free of charge by The Cambridge Crystallography Data Centre.

1.4. Cell culture

A549 (human lung carcinoma) cells were maintained in high glucose DMEM (Dulbecco's Modified Eagle's Medium) supplemented with 5% fetal bovine serum (FBS), 200 μg ml^{-1} penicillin, 100 μg ml^{-1} streptomycin and 2 mM L-glutamine.

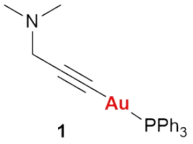
1.5. Antiproliferative studies: MTT assay

Exponentially growing cells (A549) were seeded at a density of approximately 10^4 cells per well in 96-well flat-bottomed microplates and allowed to attach for 24 h prior to addition of compounds. Various concentrations of the compounds (0.1-100 μM) were added and incubated for 24 h at 37 °C (total volume 200 μl). Stock solutions of the compounds were prepared as 10 mM DMSO solutions and diluted using DMEM media. The final concentration of DMSO in each well was ≤0.25 %. After 24 h, 10 μl of MTT (5mg ml^{-1} in PBS) was added to each well and the plates incubated for an additional 2

h at 37 °C. The media/MTT mixture was eliminated and DMSO (100 µl per well) was added to dissolve the formazan precipitates. The optical density was measured at 550 nm using a 96-well multiscanner autoreader (ELISA). Absorbance values were normalised to (DMSO-containing) control wells and plotted as concentration of compound versus % cell viability. IC_{50} values were calculated by nonlinear regression analysis. The reported IC_{50} values are the average of three independent experiments, each consisting of four replicates per concentration level (overall n = 12).

1.6. Syntheses

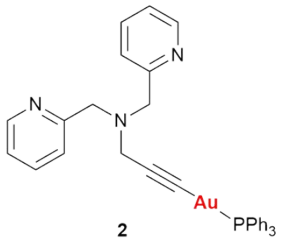
Synthesis of **1**



1

Method 1: To a solution of 3-dimethylamine-1-propyne (16.3 µl, 0.1 mmol) in CH_2Cl_2 (5 ml) was added [Au(acac)(PPh_3)] (0.0559 g, 0.1 mmol) and the solution stirred for 2 h. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.0540 g, 99%). Method 2: To a solution of 3-dimethylamine-1-propyne (32.6 µl, 0.2 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.0989 g, 0.2 mmol) and KOH (0.0168 g, 0.3 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.0129 g, 12%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.62 – 7.38 (m, 15H, PPh_3), 3.28 (s, 2H, CH_2), 2.25 (s, 6H, Me). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 42.30 (s, PPh_3).

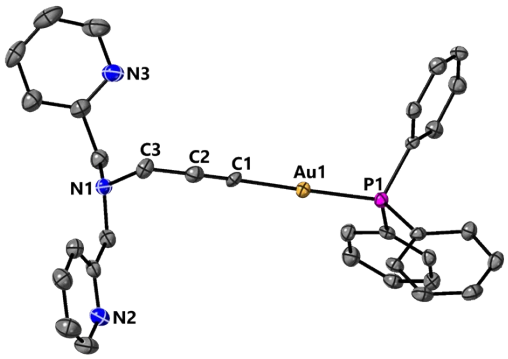
Synthesis of **2**



2

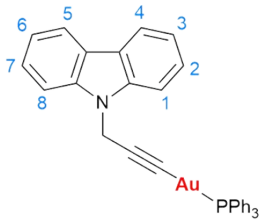
Method 1: To a solution of *N*-propargyl-di(2-picolyl)amine (0.0237 g, 0.1 mmol) in CH_2Cl_2 (5 ml) was added [Au(acac)(PPh_3)] (0.0559 g, 0.1 mmol) and the solution stirred for 2 h. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O added to precipitate a pale-yellow solid (0.0494 g, 71%). Method 2: To a solution of *N*-propargyl-di(2-picolyl)amine (0.0942 g, 0.4 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.1964 g, 0.4 mmol) and KOH (0.0336 g, 0.6 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.0341 g, 12%). HRMS (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_{33}H_{30}AuN_3P$ 696.1837; Found 696.1807. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.51 (ddd, $^3J_{HH}$ = 4.9, $^4J_{HH}$ = 1.9, $^5J_{HH}$ = 1.0 Hz, 2H, Py), 7.70 – 7.41 (m, 18H, PPh_3/Py), 7.14 (ddd, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 4.9, $^5J_{HH}$ = 1.4 Hz, 2H, Py), 3.91 (s, 4H, CH_2Py), 3.42 (s, 2H, CH_2C≡C). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 42.20 (s, PPh_3). ^{13}C APT (75 MHz, CD_2Cl_2) δ 160.35 (s, Py), 149.56 (s, Py), 136.74 (s, Py), 134.86 (d, $^2J_{CP}$ = 13.9 Hz, *o*-PPh_3), 132.08 (s, *p*-PPh_3), 129.71 (d, $^3J_{CP}$ = 11.2 Hz, *m*-PPh_3), 123.58 (s, Py), 122.36 (s, Py), 97.68 (s, CH_2C≡*C*Au), 60.00 (s, *C*H_2Py), 44.15 (s, *C*H_2C≡CAu).

Molecular structure:



Molecular structures of complex **2** determined by single crystal X ray diffraction. Ellipsoids drawn at 50%. Selected bond lengths [Å] and angles [°]: Au(1)-C(1) 2.024(5), Au(1)-P(1) 2.2711(13), C(1)-C(2) 1.173(7), C(2)-C(3) 1.487(8), C(1)-Au(1)-P(1) 178.95(15), C(1)-C(2)-C(3) 176.6(6).

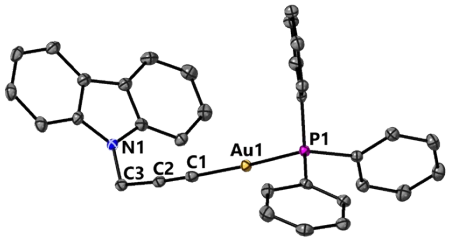
Synthesis of **3**



3

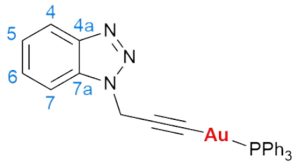
To a solution of *N*-propargylcarbazole (0.0410 g, 0.2 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.0989 g, 0.2 mmol) and KOH (0.0168 g, 0.3 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.1075 g, 81%) HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}AuNNaP$ 686.1282; Found 686.1263. ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H4/H5 carbazole), 7.61 (dt, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, H1/H8, carbazole), 7.52 – 7.36 (m, 17H, PPh_3 + H2/H7 carbazole), 7.21 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, H3/H6 carbazole), 5.21 (d, $^5J_{HP}$ = 1.4 Hz, 2H, $CH_2C{\equiv}CAu$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.11 (s, PPh_3). ^{13}C APT (75 MHz, $CDCl_3$) δ 134.39 (d, $^2J_{CP}$ = 13.8 Hz, *o*-PPh_3), 131.65 (d, $^4J_{CP}$ = 2.4 Hz, *p*-PPh_3), 129.24 (d, $^3J_{CP}$ = 11.3 Hz, *m*-PPh_3), 125.77 (s, C2/C7 carbazole), 120.29 (s, C4/C5 carbazole), 119.06 (s, C3/C6 carbazole), 109.38 (s, C1/C8 carbazole), 33.55 (s, $CH_2C{\equiv}CAu$).

Molecular structure:



Molecular structures of complex **3** determined by single crystal X ray diffraction. Ellipsoids drawn at 50%. Selected bond lengths [Å] and angles [°]: Au(1)-C(1) 2.0004(18), Au(1)-P(1) 2.2686(8), C(1)-C(2) 1.200(2), C(2)-C(3) 1.472(2), C(1)-Au(1)-P(1) 175.56(5), C(1)-C(2)-C(3) 173.60(17).

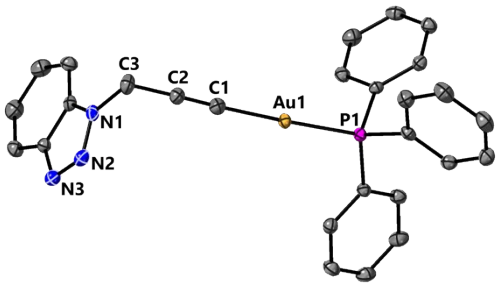
Synthesis of **4**



4

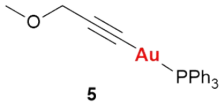
Method 1: To a solution of 1-propargyl-1H-benzoltriazole (0.0157 g, 0.1 mmol) in CH_2Cl_2 (5 ml) was added [Au(acac)(PPh_3)] (0.0559 g, 0.1 mmol) and the solution stirred for 2 h. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.0455 g, 74%). Method 2: To a solution of 1-propargyl-1H-benzoltriazole (0.0315 g, 0.2 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.0989 g, 0.2 mmol) and KOH (0.0168 g, 0.3 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.0895 g, 73%). HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}AuN_3NaP$ 638.1031; Found 638.1041. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.02 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H4), 7.90 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H7), 7.59 – 7.42 (m, 16H, PPh_3/H5), 7.38 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ =1.1 Hz, 1H, H5), 5.54 (s, 2H, CH_2C≡CAu). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 41.67 (s, PPh_3). ^{13}C APT (75 MHz, CD_2Cl_2) δ 146.23 (s, C7a), 134.20 (d, $^2J_{CP}$ = 13.8 Hz, *o*-PPh_3), 132.60 (s, C4a), 131.58 (d, $^4J_{CP}$ = 2.5 Hz, *p*-PPh_3), 129.13 (d, $^3J_{CP}$ = 11.3 Hz, *m*-PPh_3), 127.00 (s, C6), 123.69 (s, C5), 119.54 (s, C4), 110.66 (C7), 93.46 (s, CH_2C≡*C*Au), 39.34 (s, *C*H_2C≡CAu).

Molecular structure:



Molecular structures of complex **4** determined by single crystal X ray diffraction. Ellipsoids drawn at 50%. Selected bond lengths [Å] and angles [°]: Au(1)-C(1) 1.997(3), Au(1)-P(1) 2.2772(8), C(1)-C(2) 1.198(4), C(2)-C(3) 1.468(4), C(1)-Au(1)-P(1) 175.31(8), C(1)-C(2)-C(3) 178.7(3).

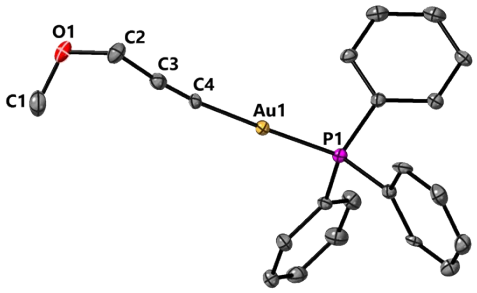
Synthesis of **5**



5

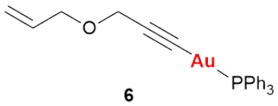
To a solution of propargyl bromide (10.8 µl, 0.1 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.0495 g, 0.1 mmol) and KOH (0.0168 g, 0.3 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.0388 g, 73%). HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{20}AuNaOP$ 551.0809; Found 551.0831. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.69 – 7.36 (m, 15H, PPh_3), 4.16 (s, 2H, CH_2), 3.35 (s, 3H, Me). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 42.07 (s, PPh_3). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.86 (d, $^2J_{CP}$ = 13.9 Hz, *o*-PPh_3), 132.13 (d, $^4J_{CP}$ = 2.5 Hz, *p*-PPh_3), 130.48 (d, $^1J_{CP}$ = 55.6 Hz, *i*-PPh_3), 129.72 (d, $^3J_{CP}$ = 11.2 Hz, *m*-PPh_3), 61.17 (s, CH_2), 57.34 (s, Me).

Molecular structure:



Molecular structures of complex **5** adetermined by single crystal X ray diffraction. Ellipsoids drawn at 50%. Selected bond lengths [Å] and angles [°] 5: Au(1)-C(4) 2.005(5), Au(1)-P(1) 2.2870(12), C(2)-C(3) 1.489(7), C(3)-C(4) 1.205(7), C(4)-Au(1)-P(1) 178.38(15), C(4)-C(3)-C(2) 174.4(5).

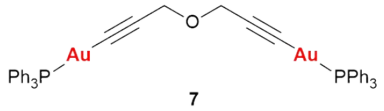
Synthesis of **6**



6

Method 1: To a solution of 3-(allyloxy)-1-propyne (16.7 µl, 0.1 mmol) in CH_2Cl_2 (5 ml) was added [Au(acac)(PPh_3)] (0.0559 g, 0.1 mmol) and the solution stirred for 2 h. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.0484 g, 87%). Method 2: To a solution of 3-(allyloxy)-1-propyne (66.9 µl, 0.6 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.2474 g, 0.5 mmol) and KOH (0.0336 g, 0.6 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.2070 g, 62%). HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}AuNaOP$ 557.0966; Found 557.0977. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.66 – 7.39 (m, 15H, PPh_3), 5.92 (ddt, $^3J_{HH}$ = 17.3 Hz, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 5.5 Hz, 1H), 5.27 (m, 1H, *trans* H), 5.15 (ddt, $^3J_{HH}$ = 10.4 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *cis* H), 4.23 (s, 2H, C*H*$_2$C≡C), 4.07 (ddd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, C*H*$_2$CHC=CH_2). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 42.05 (s, PPh_3). ^{13}C APT (75 MHz, CD_2Cl_2) δ 135.63 (s, CH_2*C*H=CH_2), 134.85 (d, $^2J_{CP}$ = 13.8 Hz, *o*-PPh_3), 132.12 (d, $^4J_{CP}$ = 2.4 Hz, *p*-PPh_3), 130.45 (d, $^1J_{CP}$ = 55.8 Hz, *i*-PPh_3), 129.71 (d, $^3J_{CP}$ = 11.2 Hz, *m*-PPh_3), 116.86 (s, CH_2CH=*C*H_2), 99.16 (d, $^2J_{CP}$ = 26.4 Hz, CH_2C≡*C*Au), 70.45 (s, *C*H_2CH=CH_2), 58.89 (s, *C*H_2C≡C).

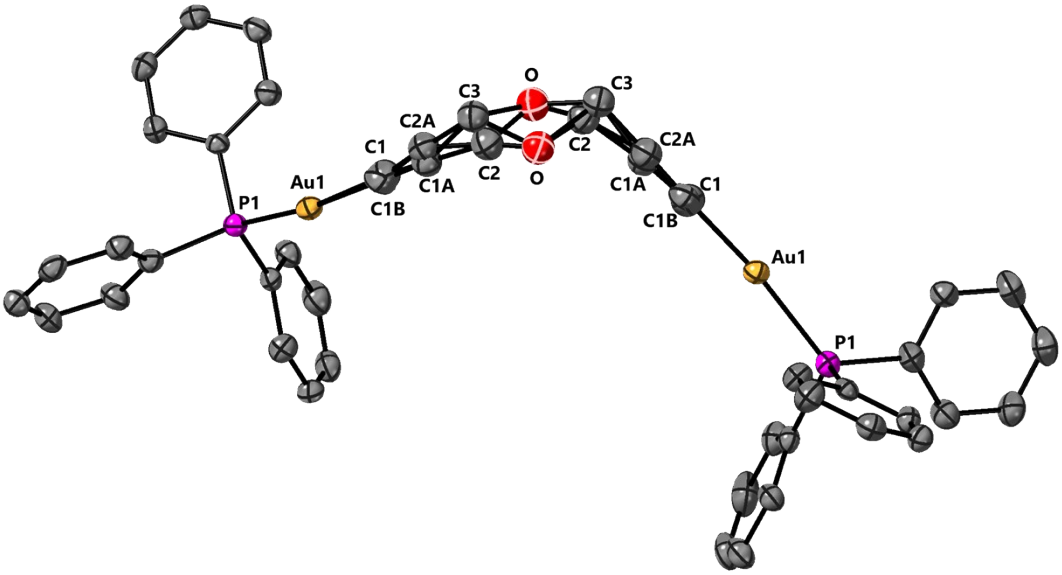
Synthesis of **7**



7

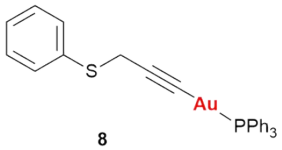
Method 1: To a solution of propargylether (7.7 µl, 0.05 mmol) in CH_2Cl_2 (5 ml) was added [Au(acac)(PPh_3)] (0.0559 g, 0.1 mmol) and the solution stirred for 2 h. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.0242 g, 48%). Method 2: To a solution of dipropargylether (15.4 µl, 0.1 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.0989 g, 0.2 mmol) and KOH (0.0168 g, 0.3 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.0534 g, 53%). HRMS (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_{42}H_{35}Au_2OP_2$ 1011.1489; Found 1011.1454. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.66 – 7.43 (m, 30H, PPh_3), 4.34 (s, 4H, CH_2). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 42.07 (s, PPh_3). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.89 (d, $^2J_{CP}$ = 13.9 Hz, *o*-PPh_3), 132.08 (d, $^4J_{HH}$ = 2.4 Hz, *p*-PPh_3), 130.54 (d, $^1J_{CP}$ = 55.5 Hz, *i*-PPh_3), 129.70 (d, $^3J_{CP}$ = 11.3 Hz, *m*-PPh_3), 98.99 (d, $^2J_{CP}$ = 26.5 Hz, $CH_2C{\equiv}CAu$), 57.33 (s, $CH_2C{\equiv}C$).

Molecular structure:



Molecular structure of complex **7** determined by single crystal X-ray diffraction. Ellipsoids drawn at 50%. Selected bond lengths [Å] and angles [°]: Au(1)-Au(1)#1 3.2907(4), Au(1)-C(1) 2.060(9), Au(1)-C(1B)#2 1.951(9), Au(1)-P(1) 2.2733(12), C(1)-C(2A) 1.205(2), C(3)-C(2A) 1.439(2), C(3)-O 1.409(2), O-C(2) 1.408(2), C(2)-C(1A) 1.439(2), C(1A)-C(1B) 1.205(2), C(1)-Au(1)-P(1) 168.0(7), C(1B)#2-Au(1)-P(1) 169.9(8), C(3)-C(2A)-C(1) 177.6(18), C(1B)-C(1A)-C(2) 174(2).

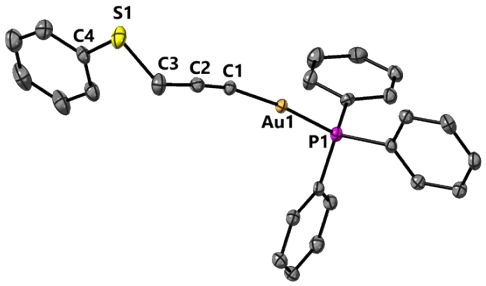
Synthesis of **8**



8

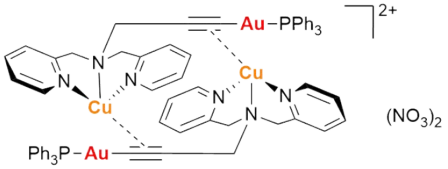
Method 1: To a solution of phenyl propargylsulfide (20.6 µl, 0.1 mmol) in CH_2Cl_2 (5 ml) was added [Au(acac)(PPh_3)] (0.0559 g, 0.1 mmol) and the solution stirred for 2 h. The solution was filtered through celite, the filtrate concentrated under reduced pressure to approximately 1 ml and Et_2O (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.0606 g, 99%). Method 2: To a solution of phenyl propargylsulfide (20.6 µl, 0.1 mmol) in MeOH (15 ml) was added [AuCl(PPh_3)] (0.0495 g, 0.1 mmol) and KOH (0.0168 g, 0.3 mmol) and the mixture stirred for 12 h. A white precipitate formed which was collected, washed with Et_2O and vacuum dried to give the product (0.0551 g, 91%). HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}AuNaPS$ 629.0738; Found 629.0744. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.62 – 7.13 (m, 20H, PPh_3 + Ph), 3.78 (s, 2H, CH_2). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 41.97 (s, PPh_3). ^{13}C APT (75 MHz, CD_2Cl_2) δ 136.86 (s, Ph), 134.23 (d, $^2J_{CP}$ = 13.9 Hz, *o*-PPh_3), 131.50 (d, $^4J_{HH}$ = 2.4 Hz, *p*-PPh_3), 129.84 (d, $^1J_{CP}$ = 55.6 Hz, *i*-PPh_3), 129.09 (d, $^3J_{CP}$ = 11.4 Hz, *m*-PPh_3), 128.75 (s, Ph), 128.50 (s, Ph), 125.78 (s, Ph), 23.34 (s, CH_2).

Molecular structure:



Molecular structures of complex **8** determined by single crystal X ray diffraction. Ellipsoids drawn at 50%. Selected bond lengths [Å] and angles [°]: Au(1)-C(1) 1.994(3), Au(1)-P(1) 2.2766(7), C(1)-C(2) 1.206(4), C(2)-C(3) 1.467(4), C(1)-Au(1)-P(1) 173.51(9), C(1)-C(2)-C(3) 175.1(3).

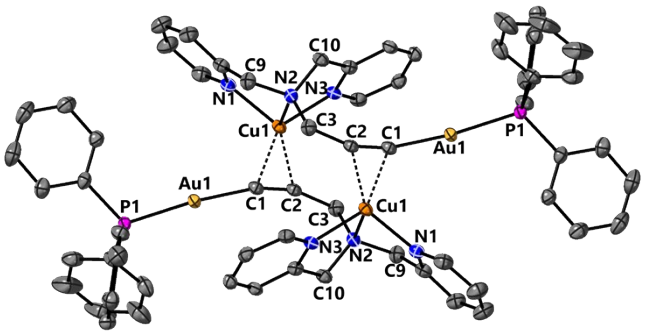
Synthesis of **9**



9

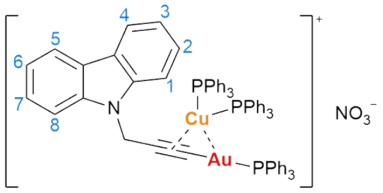
To a solution of **2** (0.0315 g, 0.045 mmol) in CH_2Cl_2 (5 ml) was added $[Cu(NO_3)(PPh_3)_2]$ (0.0294 g, 0.045 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.0332 g, 88%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.30 (d, $^3J_{HH}$ = 5.2 Hz, 2H, Py), 7.82 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Py), 7.63 – 7.09 (m, 19H, PPh_3 / Py), 4.60 – 3.73 (m, 4H, C*H*$_2$), 3.62 (s, 2H, C*H*$_2$C≡C). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 41.31 (s, br). ^{13}C APT (75 MHz, CD_2Cl_2) δ 157.31 (s, *ipso*-Py), 150.04 (s, Py), 139.08 (s, Py), 134.64 (d, $^3J_{CP}$ = 14.0 Hz, *m*-PPh_3), 133.83 (d, $^2J_{CP}$ = 15.5 Hz, *o*-PPh_3), 130.97 (s, *p*-PPh_3), 124.93 (s, Py), 124.52 (s, Py), 59.55 (s, *C*H_2), 48.35 (s, *C*H_2C≡C).

Molecular structure:



Molecular structure of complex **9** determined by single crystal X-ray diffraction. Ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Au(1)-P(1) 2.2694(6), Au(1)-C(1) 1.999(3), Cu(1)-N(1) 2.033(2), Cu(1)-N(2) 2.264(2), Cu(1)-N(3) 2.017(2), Cu(1)-C(1) 2.019(2), Cu(1)-C(2) 2.004(2), C(1)-Au(1)-P(1) 171.15(7), N(2)-Cu(1)-N(1) 79.63(8), N(3)-Cu(1)-N(1) 109.17(8), N(3)-Cu(1)-N(2) 80.69(8), C(1)-Cu(1)-N(1) 108.27(9), C(1)-Cu(1)-N(2) 111.27(9), C(1)-Cu(1)-N(3) 142.18(9), C(2)-Cu(1)-N(1) 142.73(9), C(2)-Cu(1)-N(2) 116.78(9), C(2)-Cu(1)-N(3) 106.54(9), C(2)-Cu(1)-C(1) 35.70(10), C(3)-C(2)-C(1) 160.1(3).

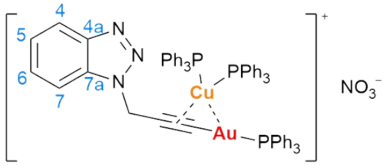
Synthesis of **10**



10

To a solution of **3** (0.1327 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added $[Cu(NO_3)(PPh_3)_2]$ (0.1300 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2657 g, 99%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.09 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H4/H5 carbazole), 7.62 – 7.13 (m, 51H, PPh_3/carbazole), 5.14 (s, 2H, CH_2C≡CAu). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 41.61 (s, $AuPPh_3$), 0.73 (s, $CuPPh_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 140.53 (s, C1a/C8a carbazole), 134.33 (d, $^2J_{CP}$ = 14.6 Hz, *o*-PPh_3), 131.25 (s, *p*-PPh_3), 129.49 (d, $^3J_{CP}$ = 10.0 Hz, *m*-PPh_3), 126.20 (s, C2/C7 carbazole), 123.52 (s, C4a/C5a carbazole), 120.70 (s, C4/C5 carbazole), 119.59 (s, C3/C6 carbazole), 109.67 (s, C1/C8 carbazole), 33.96 (s, *C*H_2C≡CAu).

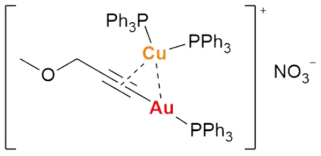
Synthesis of **11**



11

To a solution of **4** (0.615 g, 0.1 mmol) in CH_2Cl_2 (5 ml) was added $[Cu(NO_3)(PPh_3)_2]$ (0.0650 g, 0.1 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.1242 g, 97%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.00 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H4), 7.82 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H7), 7.58 – 7.26 (m, 47H, PPh_3/H5/H6), 5.46 (s, 2H, CH_2C≡CAu). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 40.83 (s, $AuPPh_3$), 0.97 (s, $CuPPh_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.40 (d, $^2J_{CP}$ = 14.4 Hz, *o*-PPh_3), 131.34 (s, *p*-PPh_3), 129.54 (d, $^3J_{CP}$ = 10.0 Hz, *m*-PPh_3), 127.95 (s, C6), 124.62 (s, C5), 120.19 (s, C4), 111.14 (s, C7), 40.20 (s, *C*H_2C≡CAu).

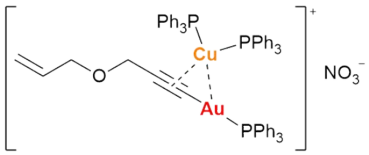
Synthesis of **12**



12

To a solution of **5** (0.1057 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added $[Cu(NO_3)(PPh_3)_2]$ (0.1300 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2339 g, 98%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58 – 7.22 (m, 45H, PPh_3), 4.14 (s, 2H, CH_2), 3.33 (s, 3H, Me). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 41.41 (s, $AuPPh_3$), 2.01 (s, $CuPPh_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.36 (d, J_{CP} = 14.5 Hz, *o*-PPh_3), 131.42 (s, *p*-PPh_3), 129.56 (d, $^3J_{CP}$ = 10.2 Hz, *m*-PPh_3), 61.30 (s, CH_2C≡CAu), 57.39 (s, Me).

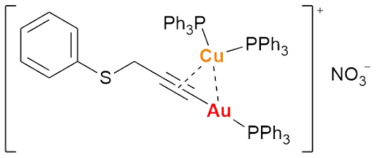
Synthesis of **13**



13

To a solution of **6** (0.1109 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added $[Cu(NO_3)(PPh_3)_2]$ (0.1300 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2354 g, 91%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.52 – 7.30 (m, 45H, PPh_3), 5.90 (ddt, $^3J_{HH}$ = 17.3 Hz, $^3J_{HH}$ = 10.4 Hz, 5.5 Hz, 1H, C*H*), 5.27 (dd, $^3J_{HH}$ = 17.3 Hz, $^4J_{HH}$ 1.8 Hz, 1H, *trans* H), 5.20 – 5.10 (m, 1H, *cis* H), 4.05 (ddd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH_2CHC=CH_2). ^{31}P NMR (162 MHz, CD_2Cl_2, -80 °C) δ 40.08 (s, $AuPPh_3$), -1.15 (s, $CuPPh_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 135.48 (s, CH_2*C*H=CH_2), 134.36 (d, $^2J_{CP}$ = 14.5 Hz, *o*-PPh_3), 131.39 (s, *p*-PPh_3), 129.55 (d, $^3J_{CP}$ = 10.3 Hz, *m*-PPh_3), 116.94 (s, CH_2CH=*C*H_2), 100.01 (s, CH_2CH=*C*H_2), 70.50 (s, *C*H_2CH=CH_2), 59.02 (s, *C*H_2C≡CAu).

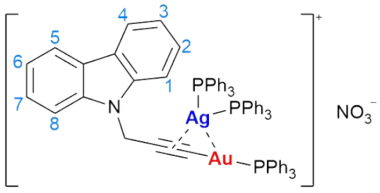
Synthesis of **14**



14

To a solution of **8** (0.1185 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added $[Cu(NO_3)(PPh_3)_2]$ (0.1300 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.1843 g, 72%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58 – 7.08 (m, 50H, Ph), 3.74 (s, 2H, CH_2). ^{31}P NMR (162 MHz, CD_2Cl_2, -80 °C) δ 38.46 (s, $AuPPh_3$), -1.16 (s, $CuPPh_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.36 (d, $^2J_{CP}$ = 14.6 Hz, *o*-PPh_3), 131.36 (s, *p*-PPh_3), 129.54 (d, $^3J_{CP}$ = 10.2 Hz, *m*-PPh_3), 129.36 (s, *o*-Ph), 129.19 (s, *p*-Ph), 126.48 (s, *m*-Ph), 24.14 (s, *C*H_2).

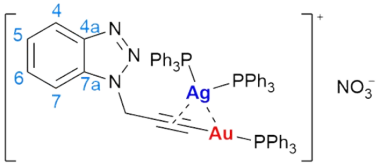
Synthesis of **15**



15

To a solution of **3** (0.1227 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added $[Ag(OTf)(PPh_3)_2]$ (0.1563 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2719 g, 99%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.06 – 7.94 (m, 2H, H4/H5 carbazole), 7.46 – 7.40 (m, 10H, Ph/carbazole), 7.25 – 7.15 (m, 41H, Ph/carbazole), 4.90 (s, 2H, CH_2C≡CAu). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 39.802 (s, $AuPPh_3$), 11.04 (s, $AgPPh_3$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 140.17 (s, C1a/C8a carbazole), 134.23 (d, $^2J_{CP}$ = 14.4 Hz, *o*-PPh_3), 131.88 (s, *p*-PPh_3), 129.82 (d, $^3J_{CP}$ = 9.6 Hz, *m*-PPh_3), 126.45 (s, C2/C7 carbazole), 123.62 (s, C4a/C5a carbazole), 120.91 (s, C4/C5 carbazole), 120.09 (s, C3/C6 carbazole), 109.15 (s, C1/C8 carbazole), 102.11 (s, $CH_2C{\equiv}CAu$), 33.80 (s, $CH_2C{\equiv}CAu$).

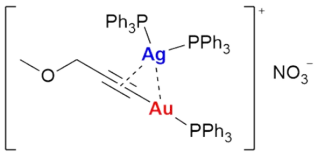
Synthesis of **16**



16

To a solution of **4** (0.1231 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added [Ag(OTf)(PPh_3)$_2$] (0.1563 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2411 g, 91%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.90 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H4), 7.59 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H7), 7.53 – 7.16 (m, 47H, PPh_3/H5/H6), 5.25 (s, 2H, CH_2C≡CAu). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 40.60 (s, AuPPh$_3$), 10.63 (s, AgPPh$_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 146.66 (s, C7a), 134.34 (d, $^2J_{CP}$ = 14.9 Hz, *o*-PPh$_3$), 132.95 (s, C4a), 131.74 (s, *p*-PPh$_3$), 129.74 (d, $^3J_{CP}$ = 10.2 Hz, *m*-PPh$_3$), 128.43 (s, C6), 124.91 (s, C5), 120.30 (s, C4), 110.40 (s, C7), 95.53 (s, CH_2C≡*C*Au), 39.72 (s, *C*H_2C≡CAu).

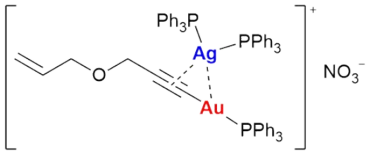
Synthesis of **17**



17

To a solution of **5** (0.1057 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added [Ag(OTf)(PPh_3)$_2$] (0.1563 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2169 g, 88%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.56 – 7.24 (m, 45H, PPh_3), 3.92 (s, 2H, CH_2), 3.07 (s, 3H, Me). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 40.30 (s, AuPPh$_3$), 9.38 (s, AgPPh$_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.32 (d, $^2J_{CP}$ = 14.0 Hz, *o*-PPh$_2$), 131.92 (s, *p*-PPh$_3$), 129.87 (d, $^3J_{CP}$ = 9.1 Hz, *m*-PPh$_3$), 60.91 (s, *C*H_2), 57.92 (s, Me).

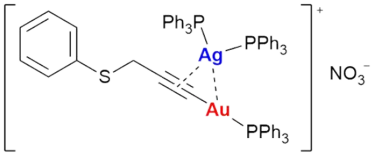
Synthesis of **18**



18

To a solution of **6** (0.1109 g, 0.2 mmol) in CH_2Cl_2 (5 ml) was added [Ag(OTf)$(PPh_3)_2$] (0.1563 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2502 g, 99%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58 – 7.15 (m, 45H, PPh_3), 5.75 – 5.58 (m, 1H, C*H*), 5.15 – 4.99 (m, 2H, CH=CH_2), 4.02 (s, 2H, CH_2C≡C), 3.83 (d, $^3J_{HH}$ = 5.6 Hz, 2H, CH_2CHC=CH_2). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 39.55 (s, AuPPh$_3$), 10.78 (s, AgPPh$_3$). ^{13}C APT (75 MHz, CD_2Cl_2) δ 134.34 (d, $^2J_{CP}$ = 15.1 Hz, *o*-PPh$_3$), 131.81 (s, *p*-PPh$_3$), 129.80 (d, $^3J_{CP}$ = 10.4 Hz, *m*-PPh$_3$), 117.48 (s, CH_2CH=*C*H_2), 71.04 (s, *C*H_2CH=CH_2), 58.59 (s, *C*H_2C≡C).

Synthesis of **19**



19

To a solution of **8** (0.1185 g, 0.1 mmol) in CH_2Cl_2 (5 ml) was added [Ag(OTf)$(PPh_3)_2$] (0.1563 g, 0.2 mmol) and the solution stirred for 1 h. The solution was concentrated under reduced pressure to approximately 1 ml and hexane (10 ml) added to precipitate a white solid which was collected and vacuum dried to give the product (0.2106 g, 80%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.57 – 6.97 (m, 50H, Ph), 3.47 (s, 2H, CH_2). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 40.28 (s, AuPPh$_3$), 9.40 (s, AgPPh$_3$)

1.7. Crystallographic Data

Table S1. Selected Crystallographic Data for Complexes 2-5

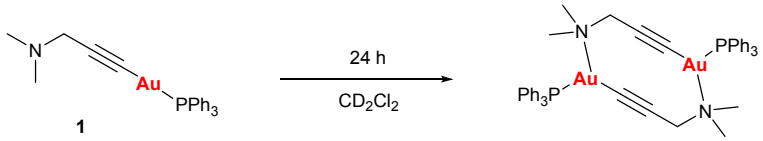
Complex	2	3	4	5
Empirical formula	$C_{33}H_{29}AuN_3P$	$C_{33}H_{25}AuNP$	$C_{27}H_{21}AuN_3P$	$C_{22}H_{20}AuOP$
Formula weight	695.53	663.47	615.40	528.32
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$
Unit cell dimensions				
a (Å)	18.2164(17)	8.7346(17)	12.7122(9)	13.413(4)
b (Å)	8.9192(8)	9.4044(19)	10.3660(8)	10.891(4)
c (Å)	17.6329(17)	16.195(3)	18.2237(13)	13.413(4)
α (°)	90	88.70(3)	90	90
β (°)	107.9050(10)	77.31(3)	107.6570(10)	100.08
γ (°)	90	78.99(3)	90	90
Volume ($Å^3$)	2726.2(4)	1273.7(5)	2288.3(3)	1929.2(11)
Z	4	2	4	4
Density (calculated) (Mg/m^3)	1.695	1.730	1.786	1.819
Absorption coefficient (mm^{-1})	5.483	5.861	6.519	7.715
θ range (°)	2.350 to 27.832	3.135 to 31.162	2.288 to 28.558	2.424 to 28.608
Reflections collected	23312	46269	20377	16809
R_{int}	0.0590	0.0280	0.0290	0.1706
Completeness (%)	99.8	99.7	99.8	99.9
Data / restraints / parameters	6304 / 0 / 343	7697 / 0 / 325	5407 / 0 / 289	4613 / 0 / 227
Goodness-of-fit on F^2	1.023	1.038	1.060	1.047
R_1 [I>2σ(I)]	0.0386	0.0163	0.0249	0.0398
wR_2 (all data)	0.0834	0.0345	0.0671	0.1110
Largest diff. peak and hole ($e.Å^{-3}$)	1.549 and -1.973	0.616 and -0.934	1.930 and -1.451	3.406 and -2.475

Table S2. Selected Crystallographic Data for Complexes 7-9

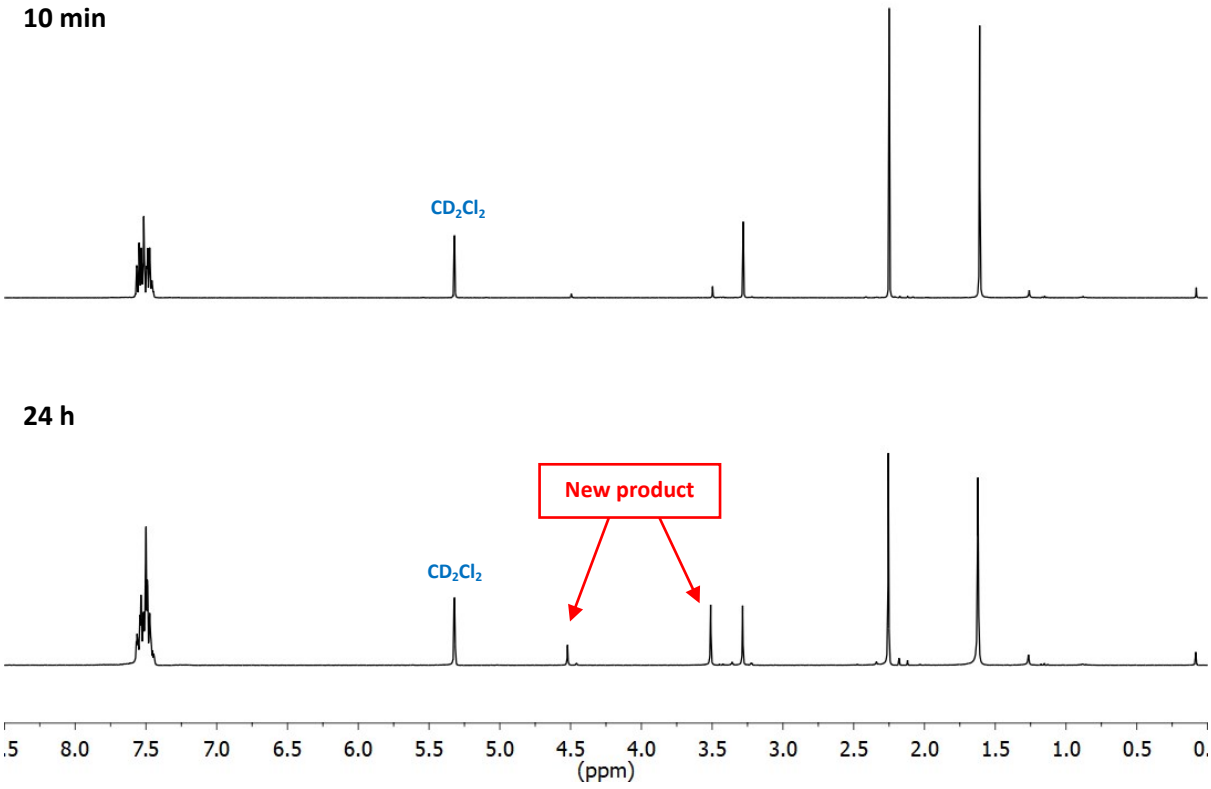
Complex	7	8	9
Empirical formula	$C_{42}H_{34}Au_2OP_2$	$C_{27}H_{22}AuPS$	$C_{70}H_{66}Au_2Cl_8Cu_2N_8O_8P_2$
Formula weight	1010.618	606.44	2013.86
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	Pccn	$P2_1/c$	P-1
Unit cell dimensions			
a (Å)	21.9189(13)	8.9759(7)	10.6521(6)
b (Å)	9.0536(6)	16.5724(12)	11.9337(7)
c (Å)	17.5745(11)	15.6715(12)	15.9069(9)
α (°)	90	90	72.6560(10)
β (°)	90	102.7590(10)	76.3360(10)
γ (°)	90	90	83.1630(10)
Volume ($Å^3$)	3487.6(4)	2273.6(3)	1872.92(19)
Z	4	4	1
Density (calculated) (Mg/m^3)	1.925	1.772	1.785
Absorption coefficient (mm^{-1})	8.528	6.644	4.852
θ range (°)	1.86 to 28.66	2.458 to 28.671	1.79 to 28.68
Reflections collected	39861	20660	22593
R_{int}	0.0435	0.0299	0.0206
Completeness (%)	100.0	99.8	99.7
Data / restraints / parameters	4314 / 75 / 232	5430 / 0 / 271	8705 / 655 / 538
Goodness-of-fit on F^2	1.0559	1.073	1.0513
R_1 [I>2σ(I)]	0.0312	0.0232	0.0224
wR_2 (all data)	0.0675	0.0591	0.0572
Largest diff. peak and hole ($e.Å^{-3}$)	3.3862 and -1.2712	1.442 and -1.037	2.2178 and -0.7914

1.8. Stability of Complex 1 - NMR Studies

Complex **1** (10 mg) was dissolved in CD_2Cl_2 (0.6 ml) under air. NMR spectra were recorded after 10 min and after 24 h, showing the slow formation of a new dimeric/oligomeric product.

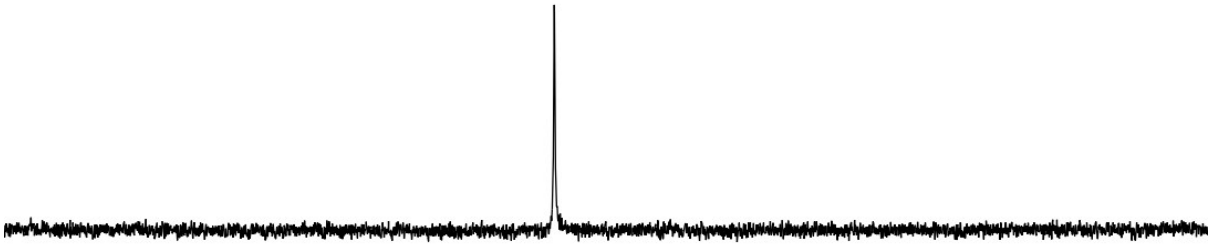


^{1}H NMR (300 MHz. CD_2Cl_2)

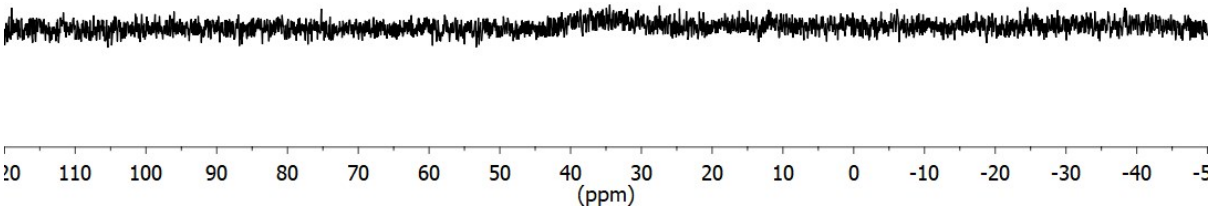


^{31}P NMR (121 MHz, CD_2Cl_2)

10 min

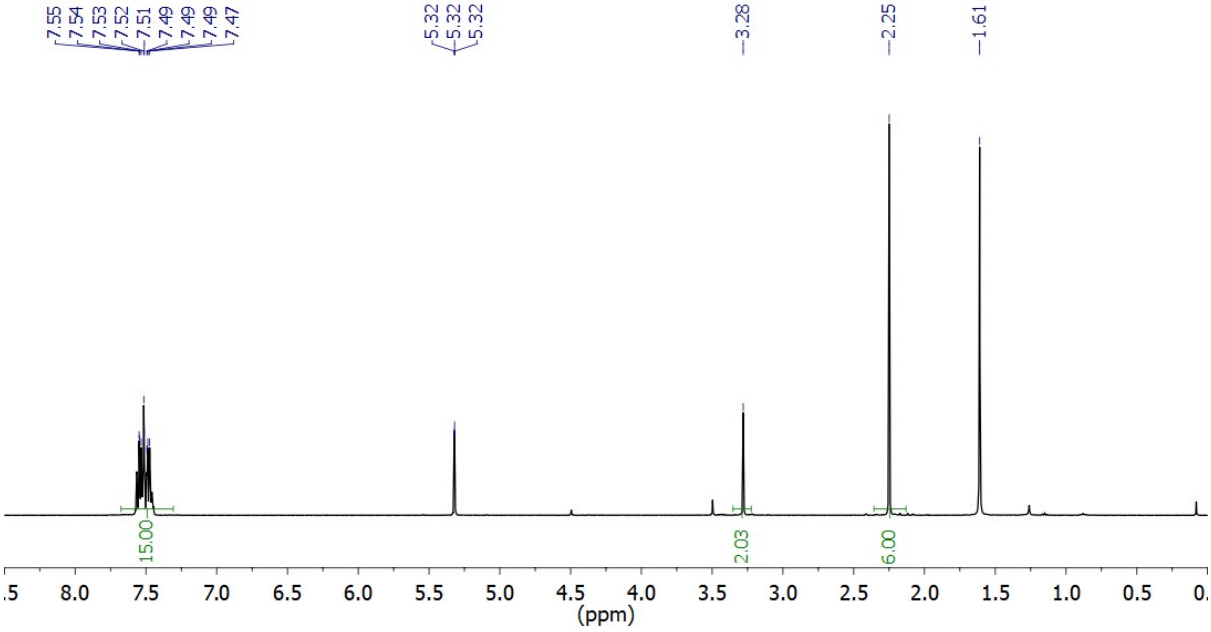


24 h

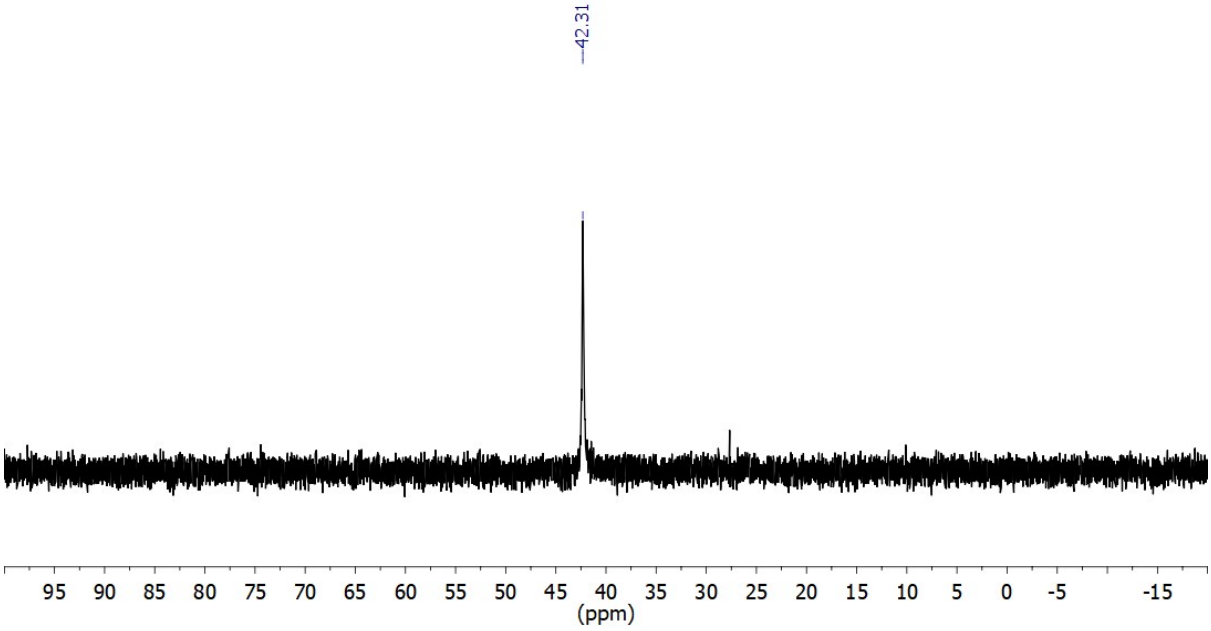


1.9. NMR Spectra for Complex 1

^{1}H NMR (400 MHz, CD_2Cl_2)

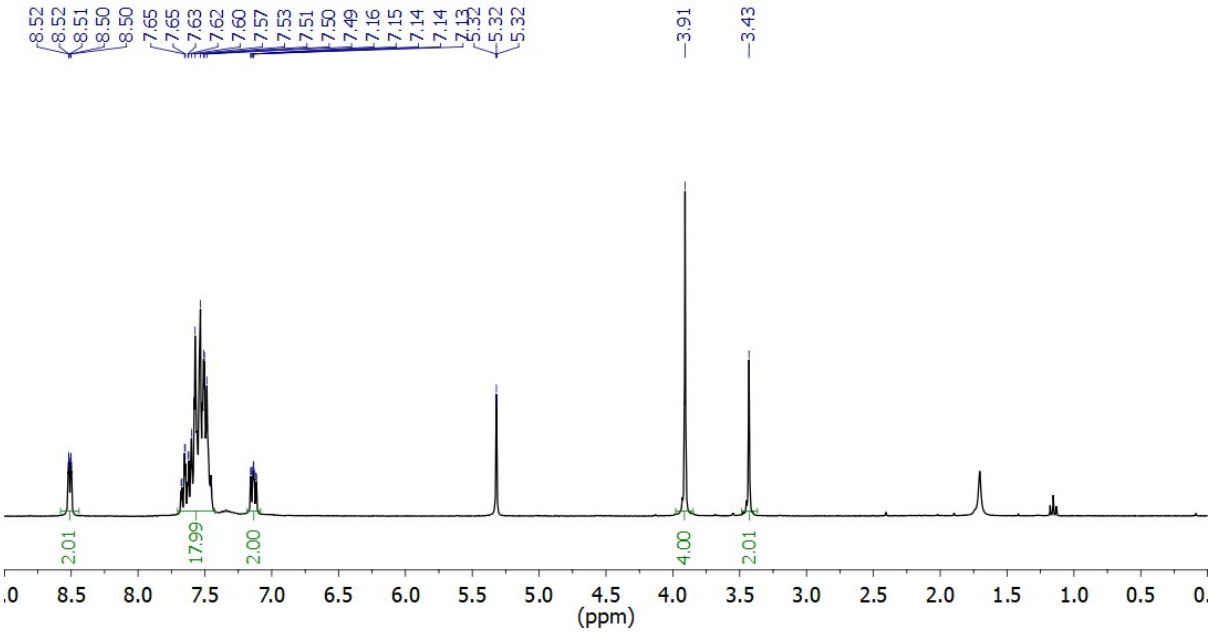


^{31}P NMR (162 MHz, CD_2Cl_2)

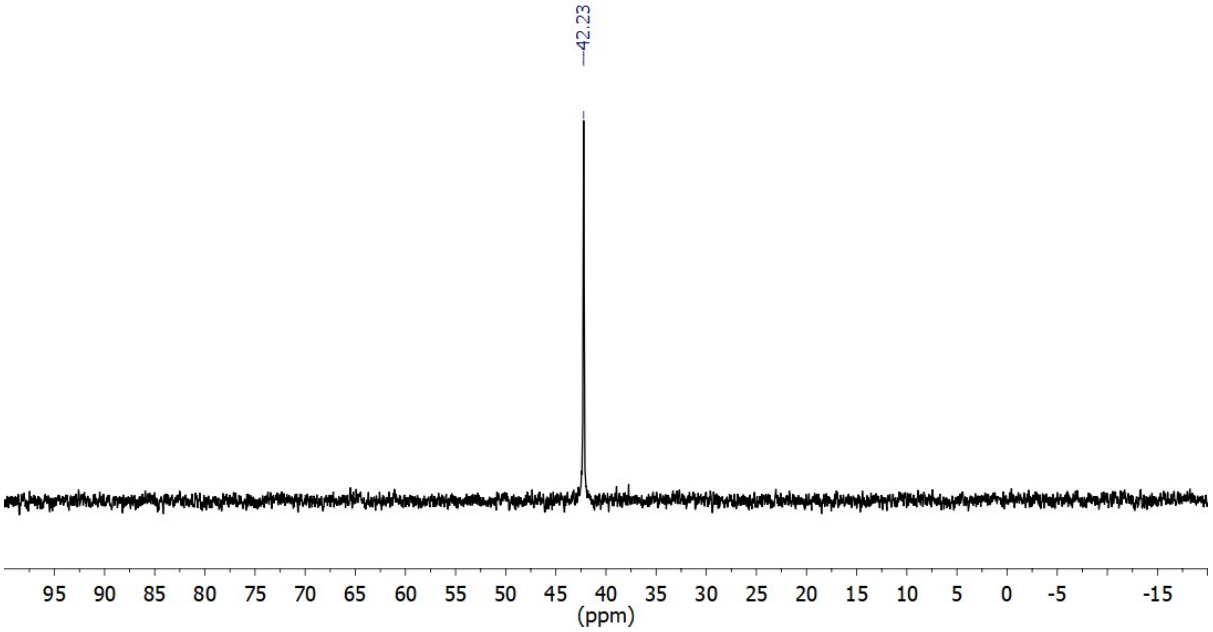


1.10. NMR Spectra for Complex 2

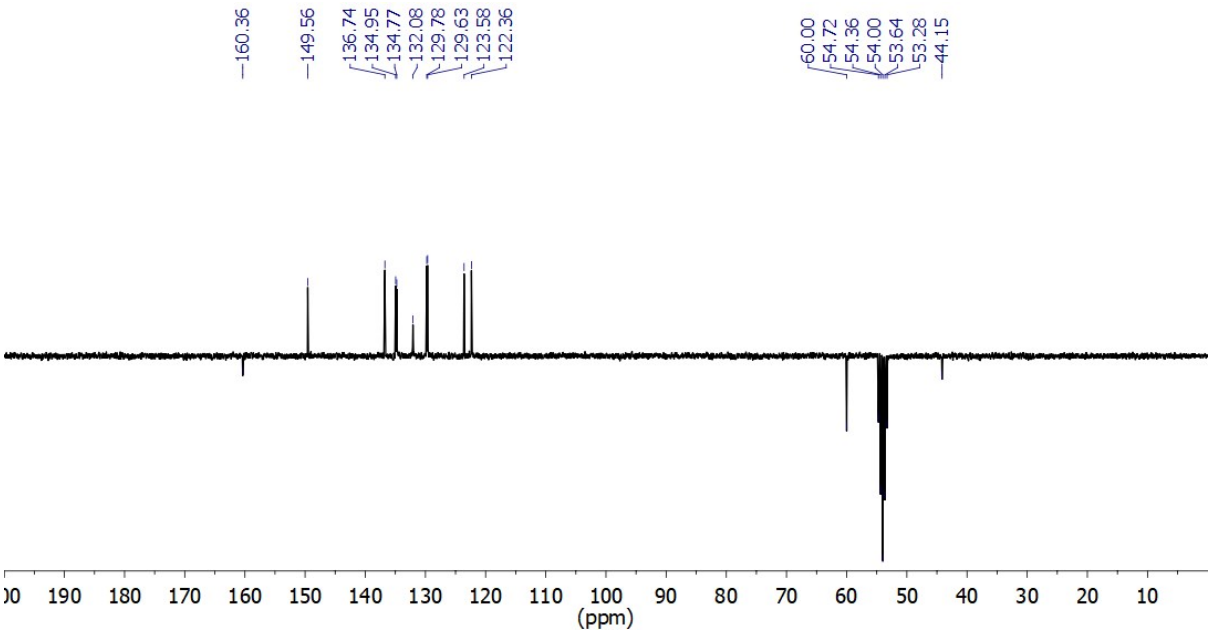
^{1}H NMR (300 MHz, CD_2Cl_2)



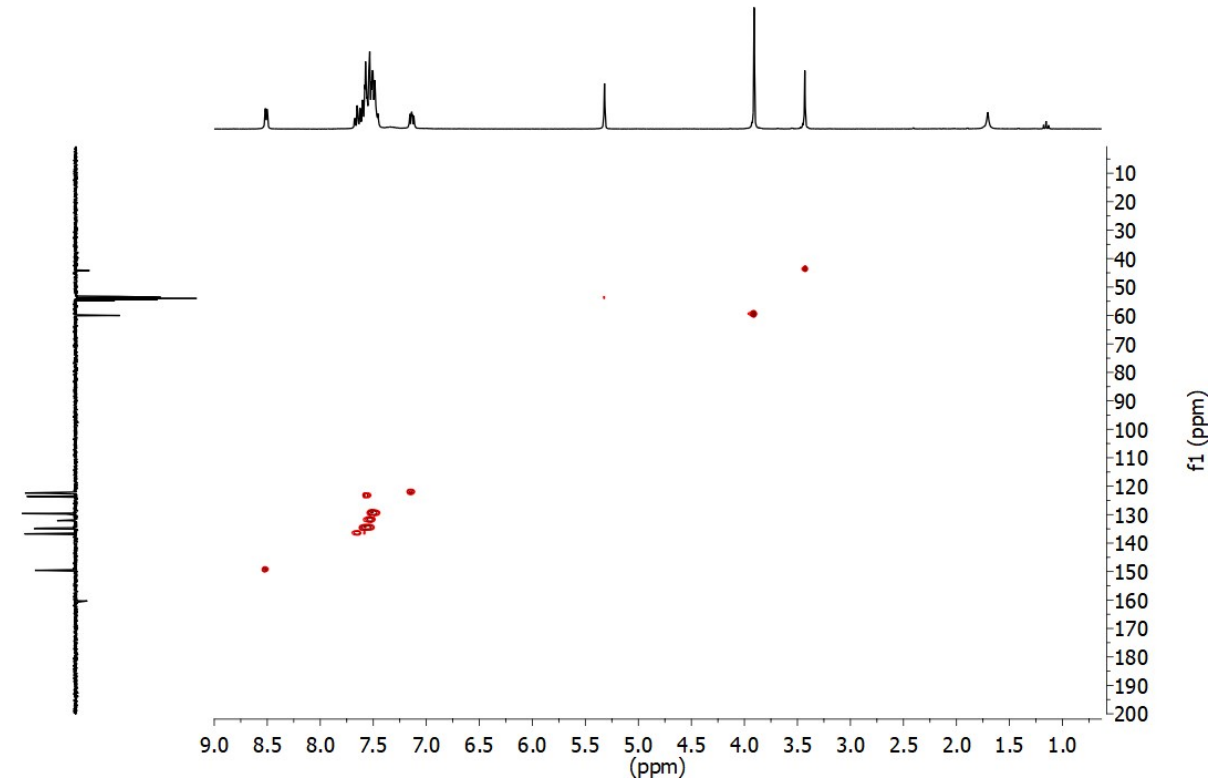
^{31}P NMR (121 MHz, CD_2Cl_2)



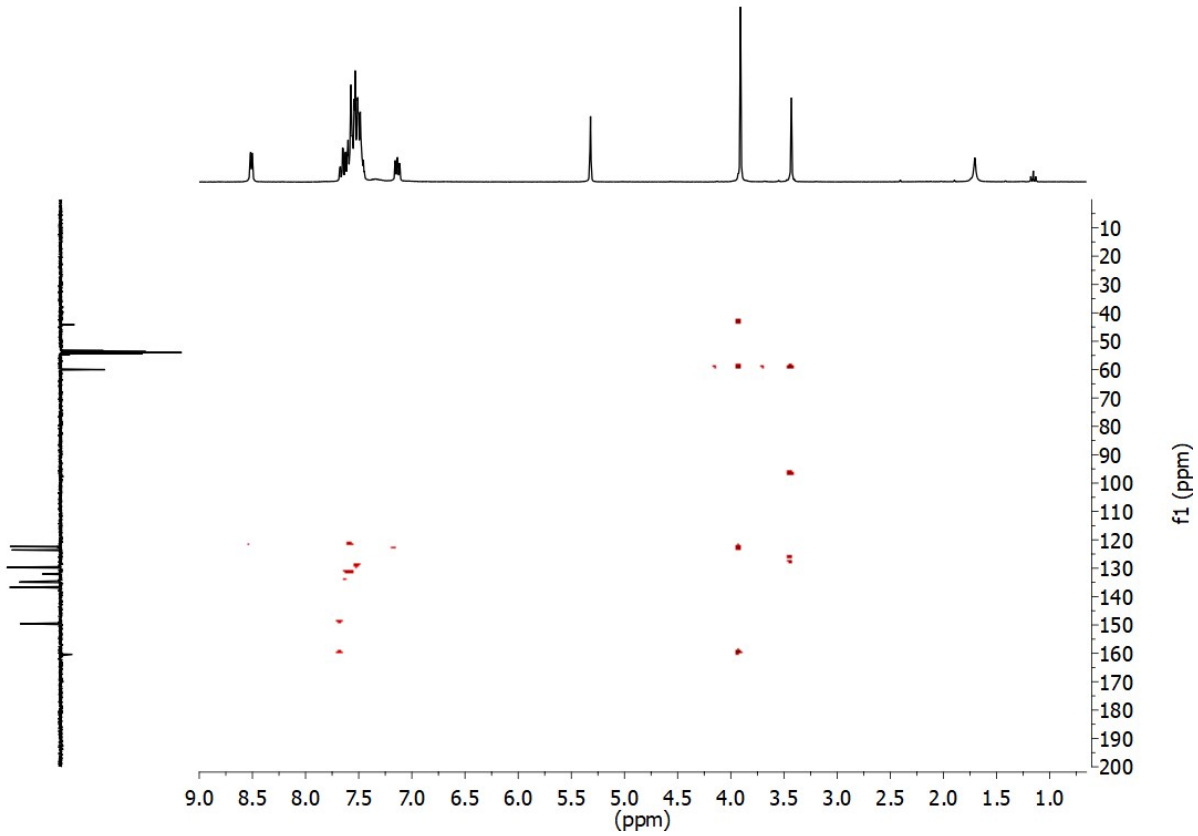
^{13}C APT (75 MHz, CD_2Cl_2)


160.36
149.56
136.74
134.95
134.77
132.08
129.78
129.63
123.58
122.36
60.00
54.72
54.36
54.00
53.64
53.28
44.15
(ppm)

HSQC


f1 (ppm)
(ppm)

HMBC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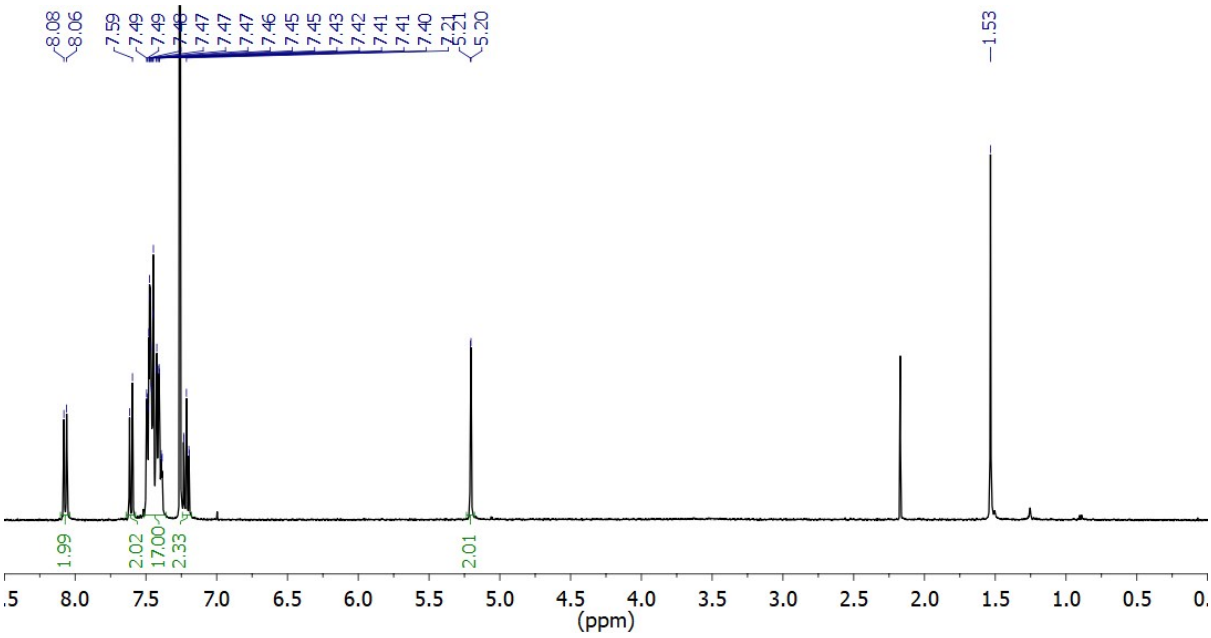
190
200
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

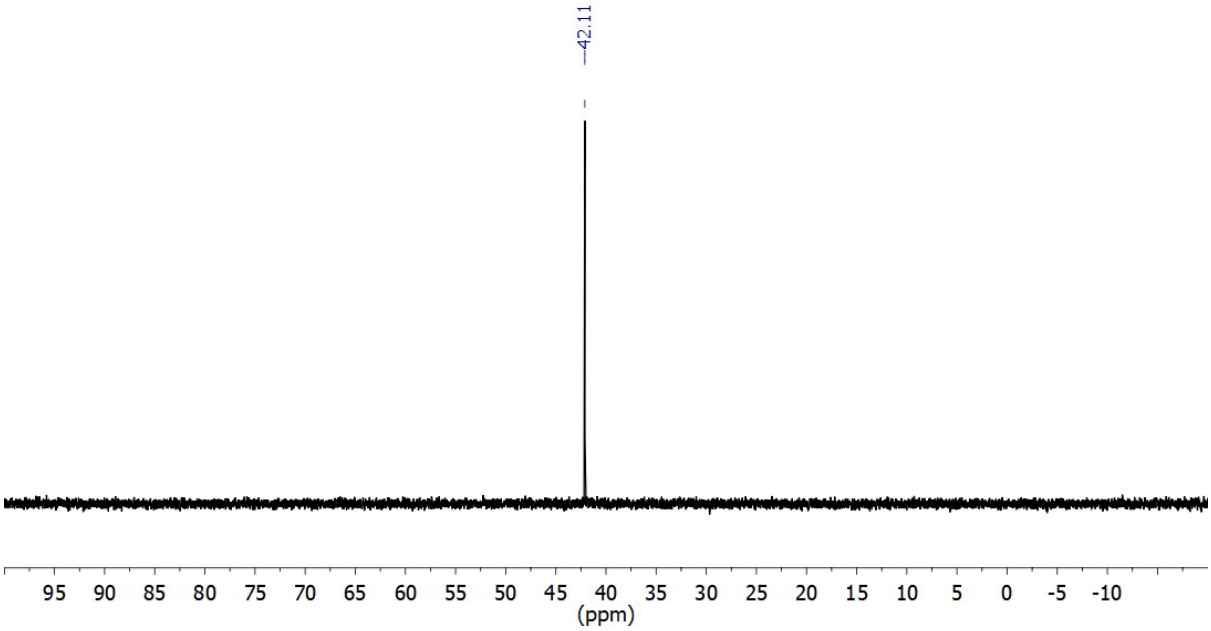
1.11. NMR Spectra for Complex 3

3

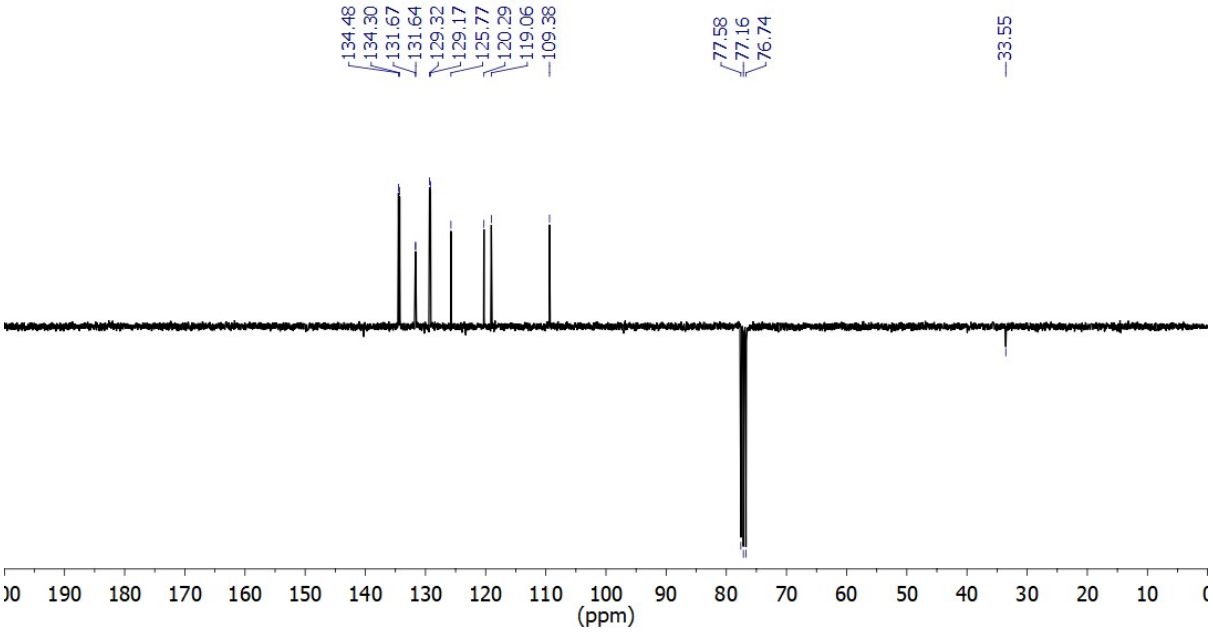
^{1}H NMR (300 MHz, $CDCl_3$)



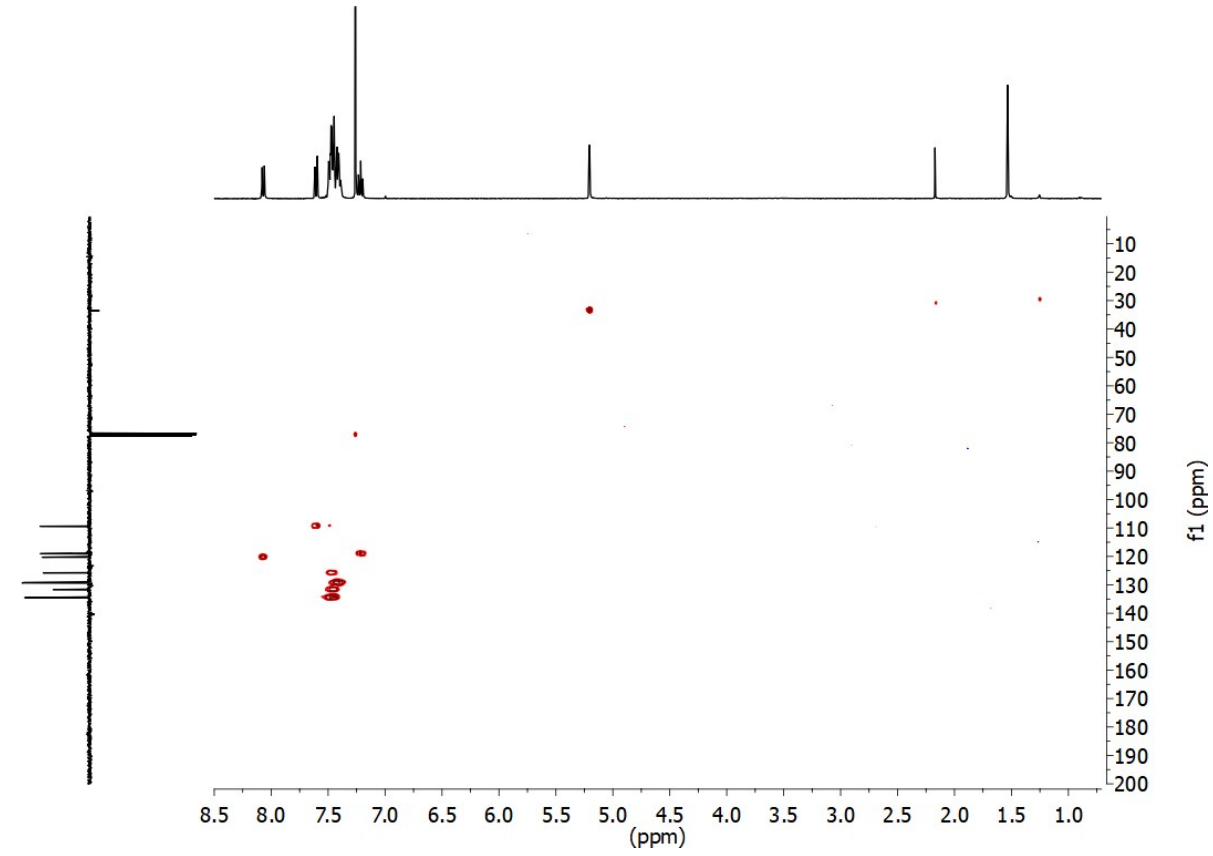
^{31}P NMR (162 MHz, $CDCl_3$)



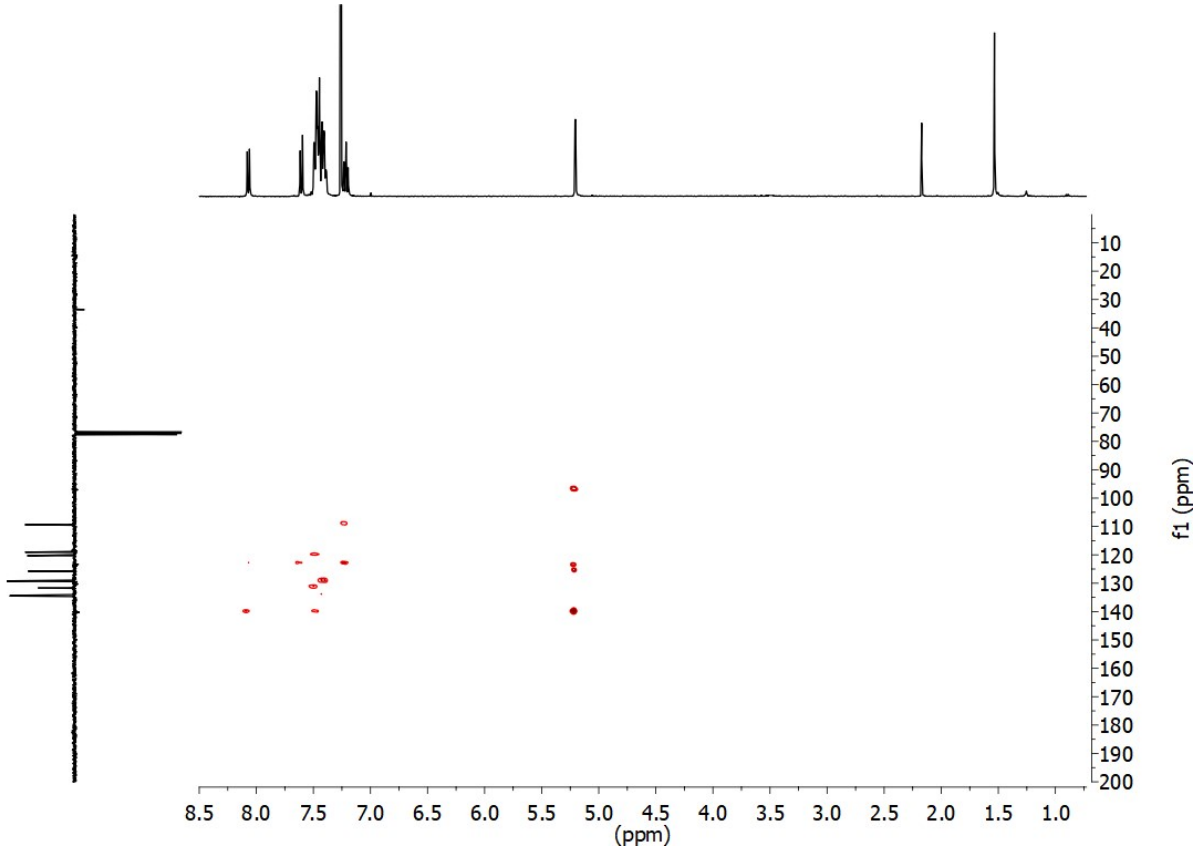
^{13}C APT (75 MHz, $CDCl_3$)



HSQC



HMBC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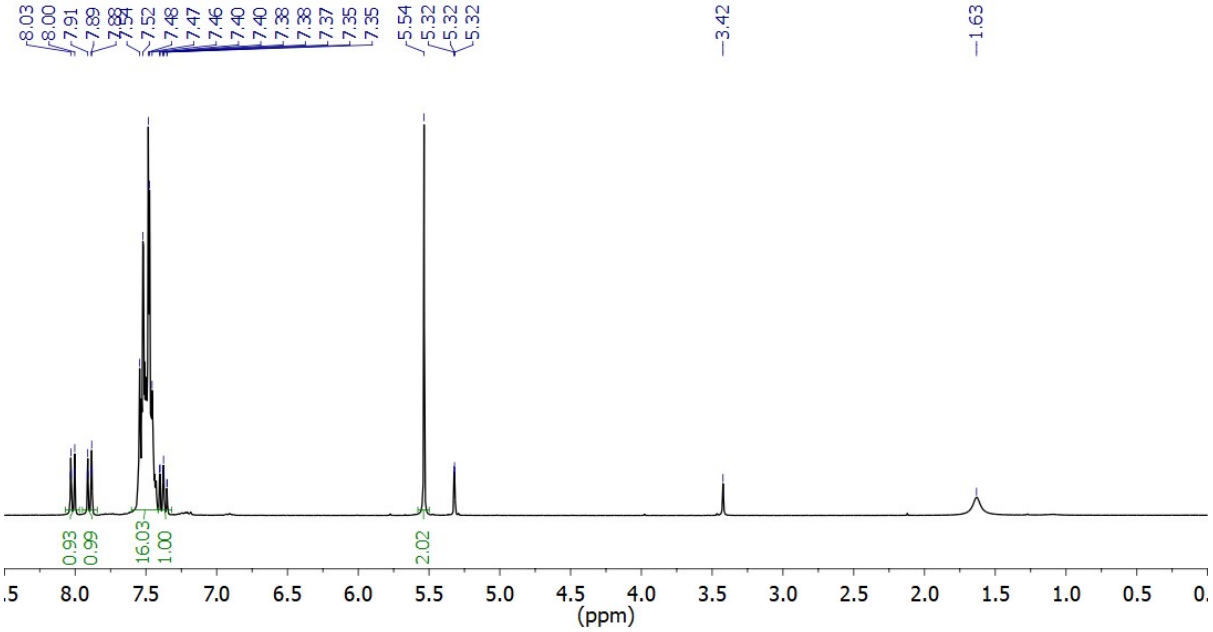
190
200
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

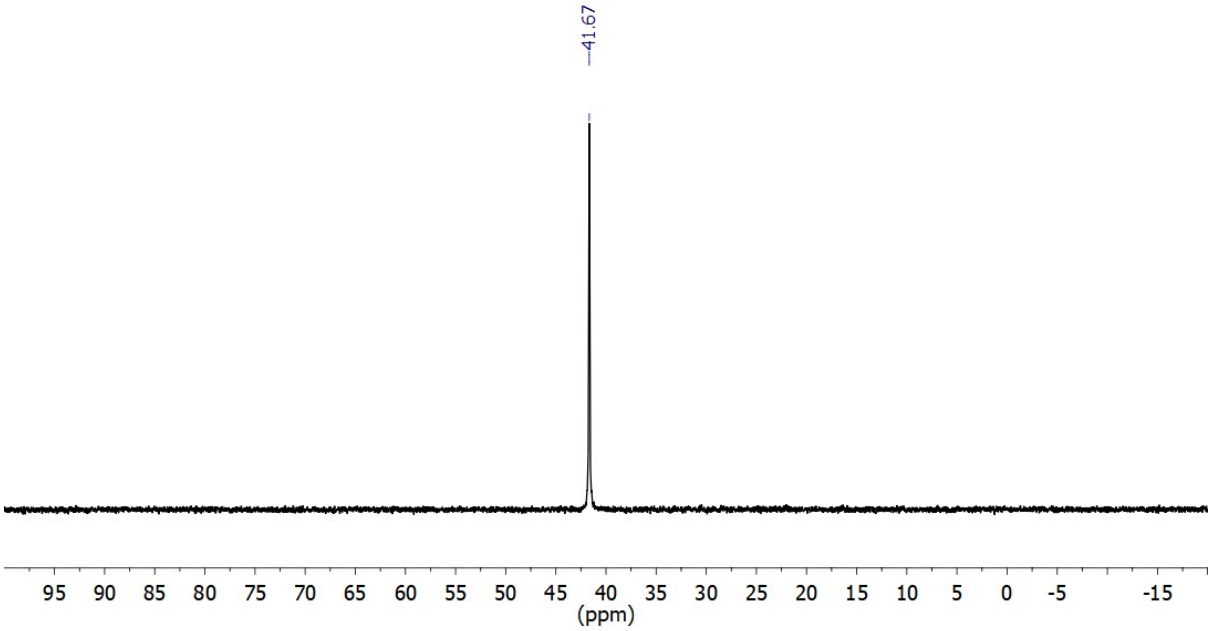
1.12. NMR Spectra for Complex 4

4

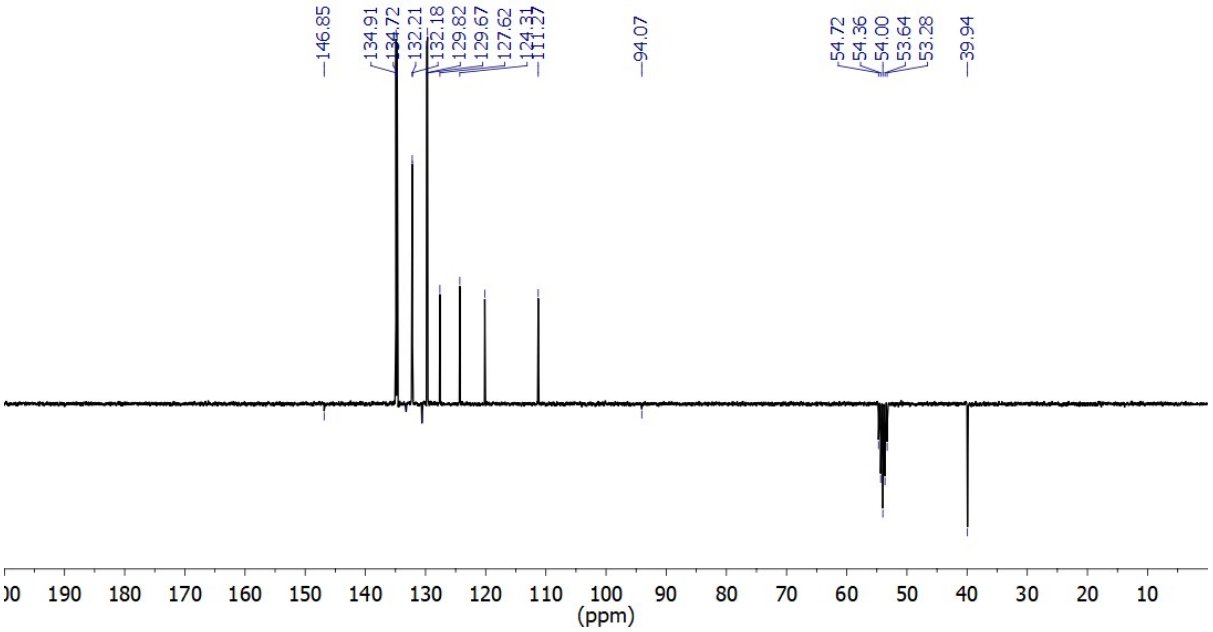
^{1}H NMR (300 MHz, CD_2Cl_2)



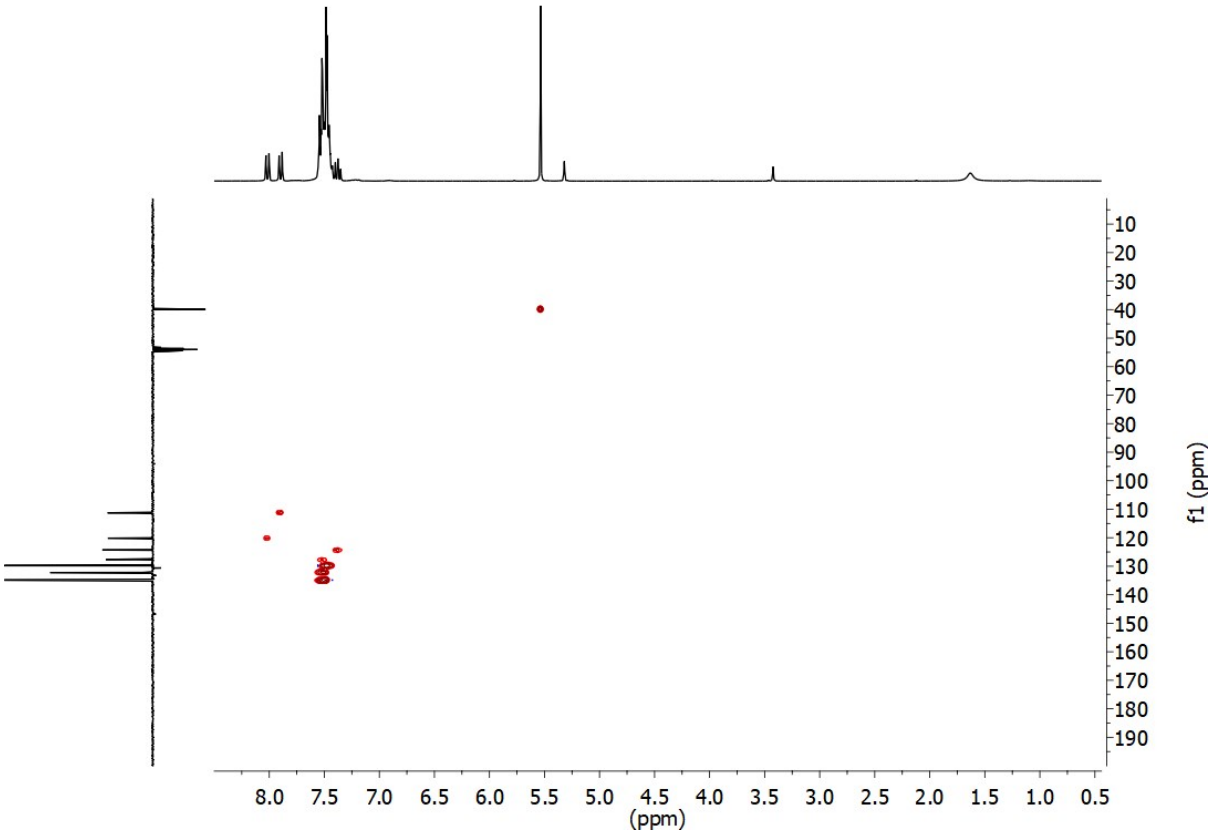
^{31}P NMR (121 MHz, CD_2Cl_2)



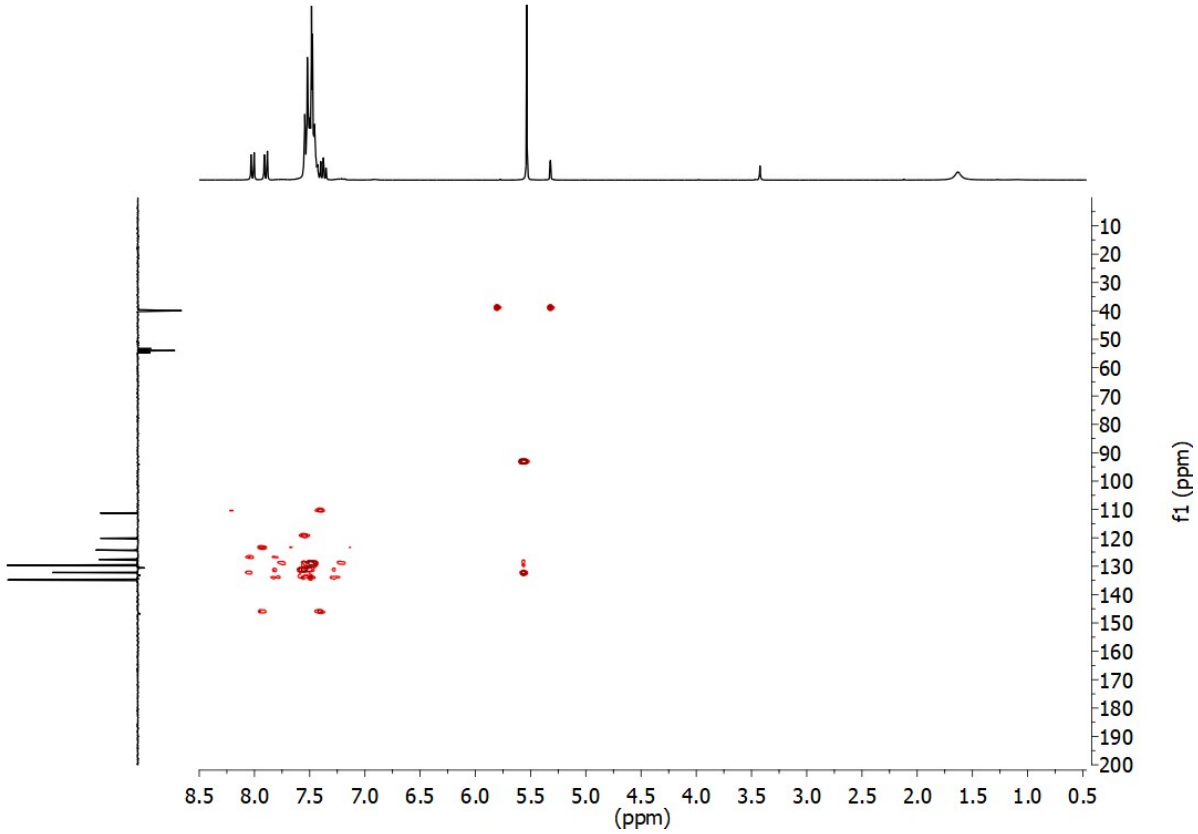
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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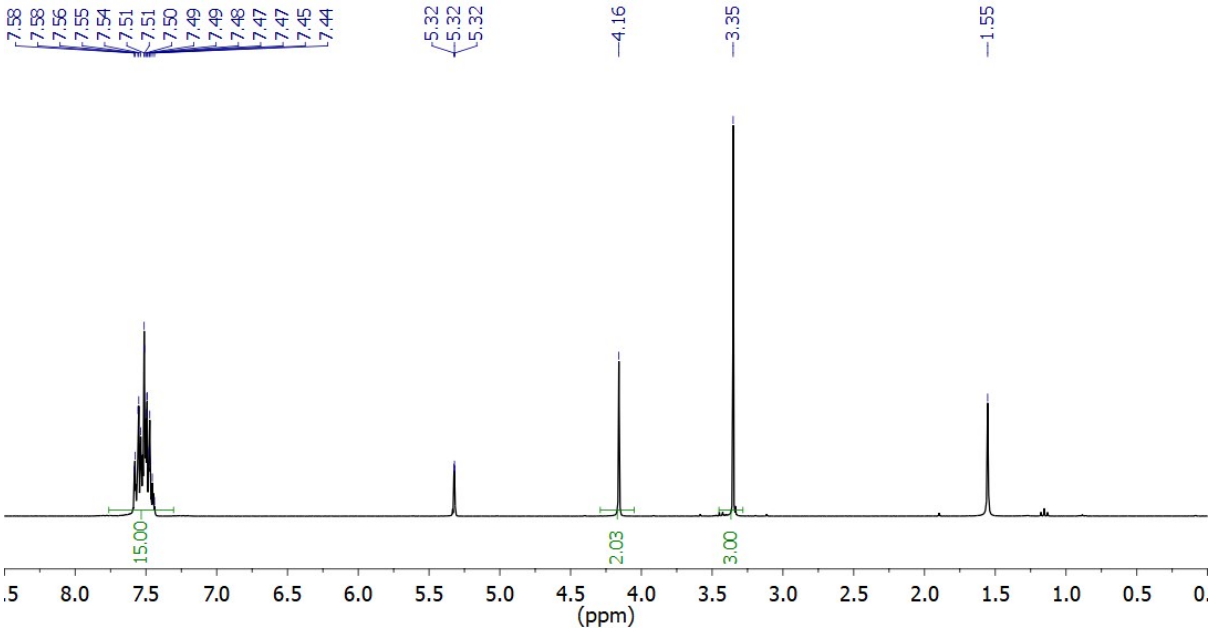
190
200
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

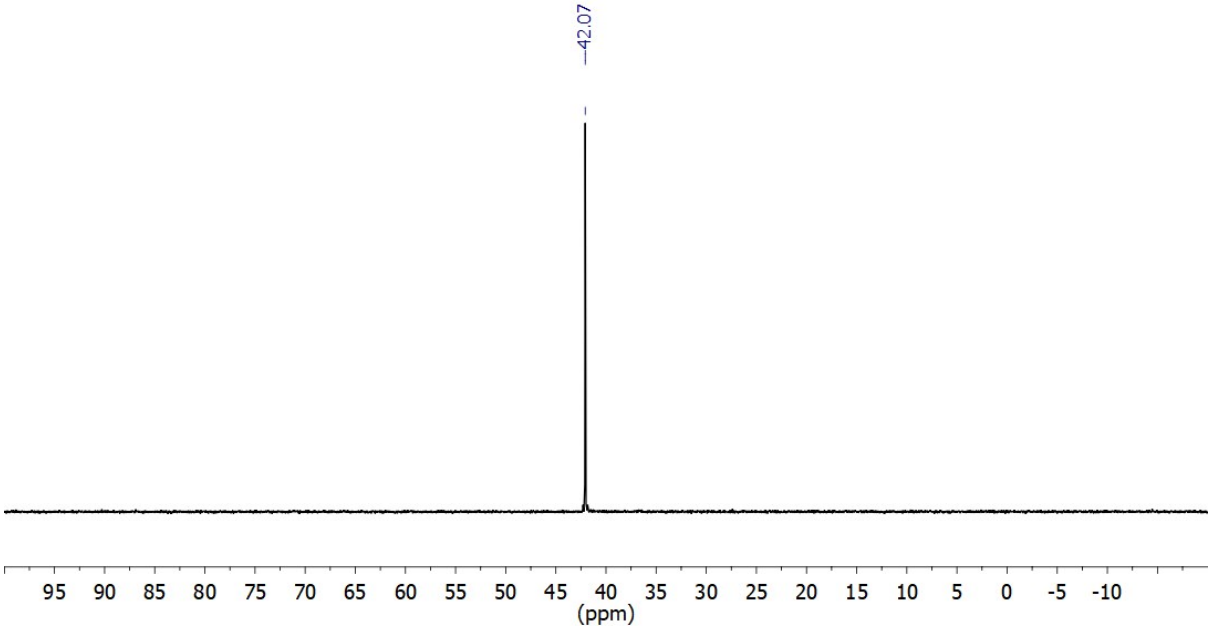
1.13. NMR Spectra for Complex 5

5

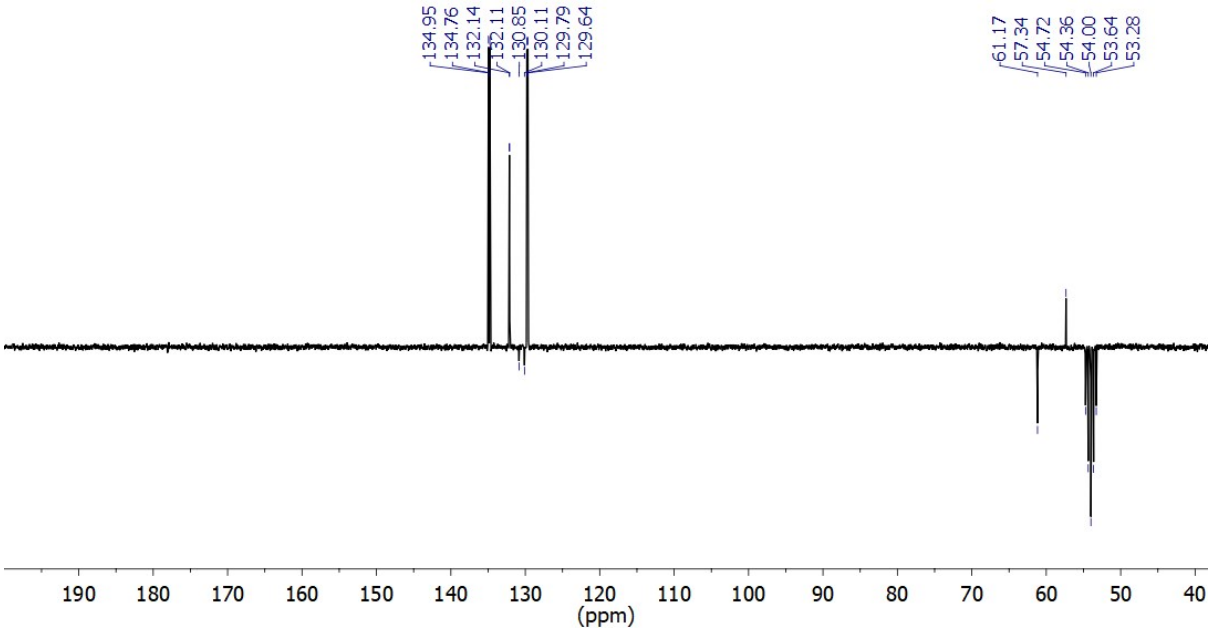
^{1}H NMR (300 MHz, CD_2Cl_2)



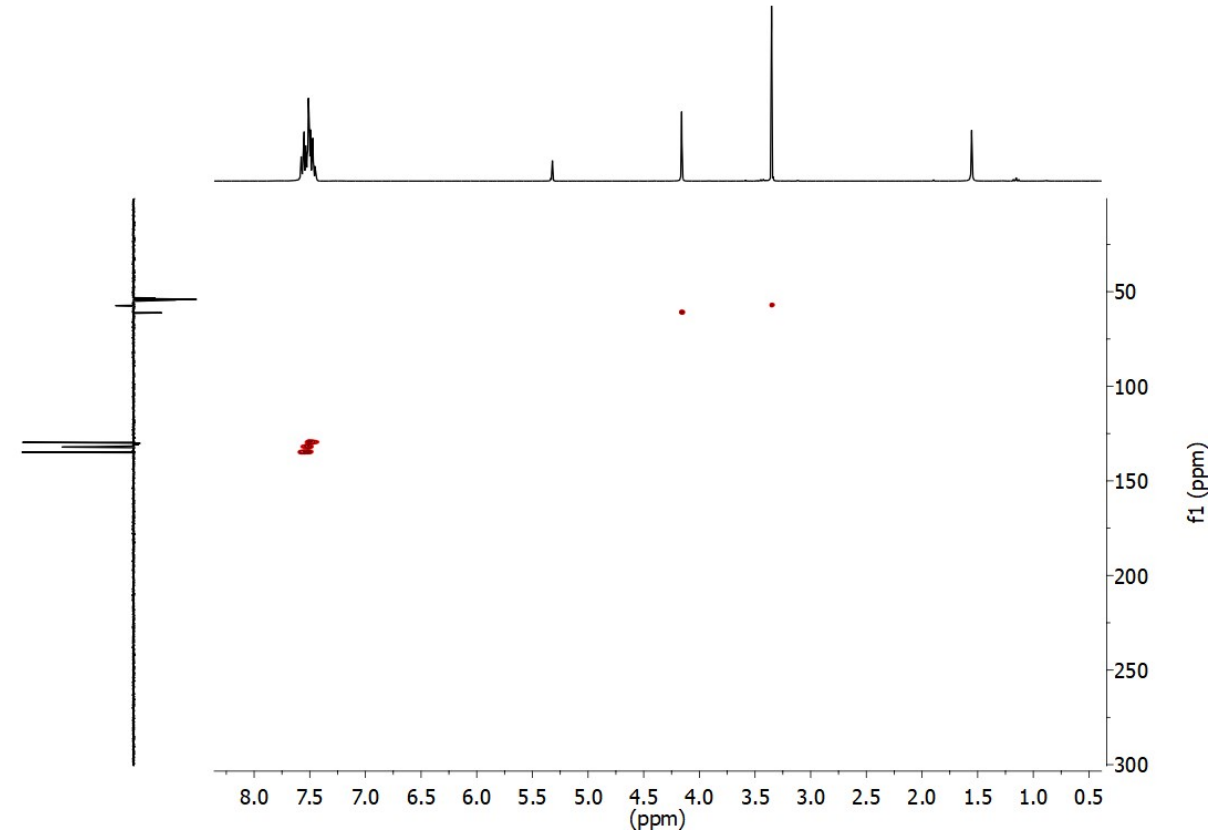
^{31}P NMR (121 MHz, CD_2Cl_2)



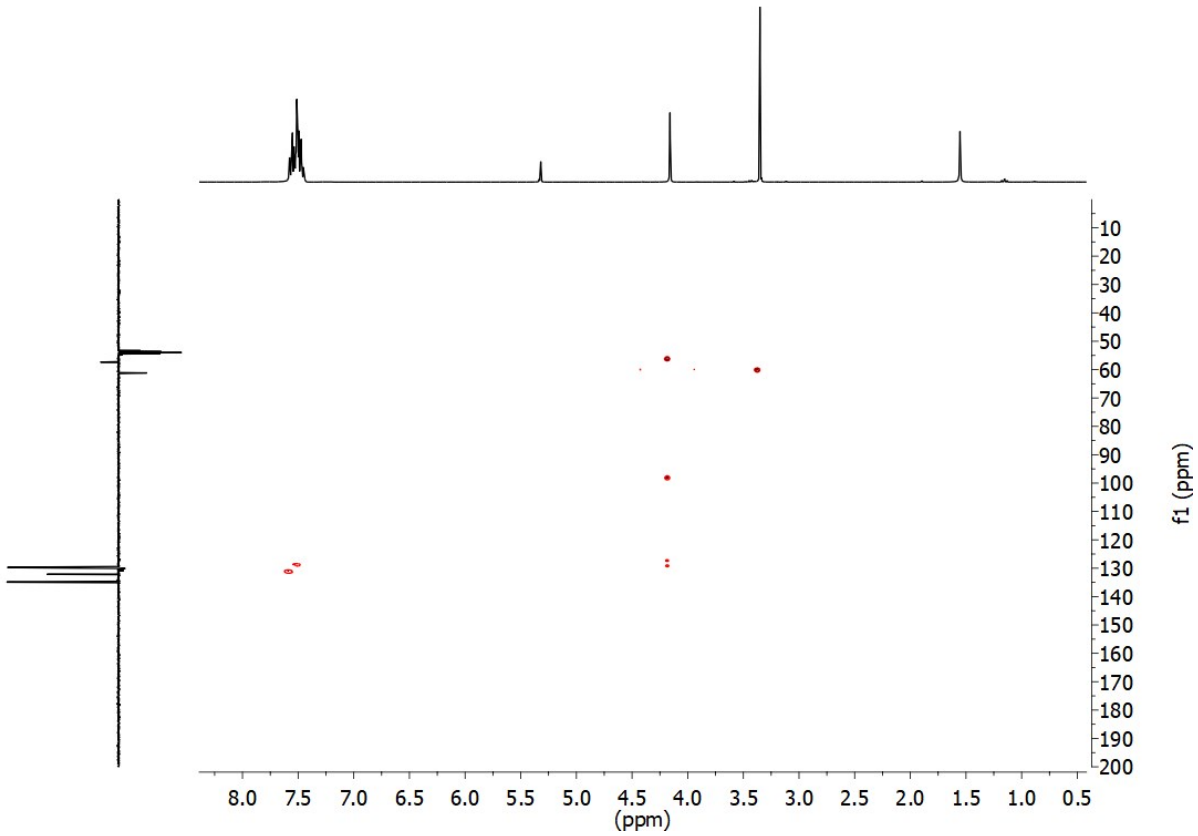
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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170
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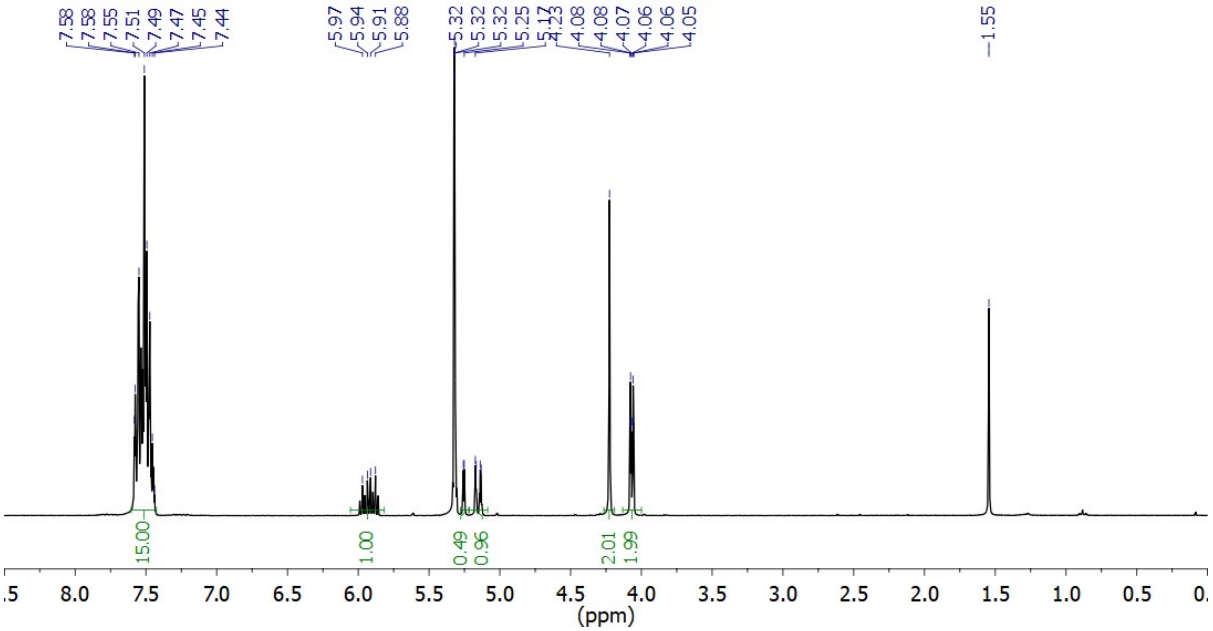
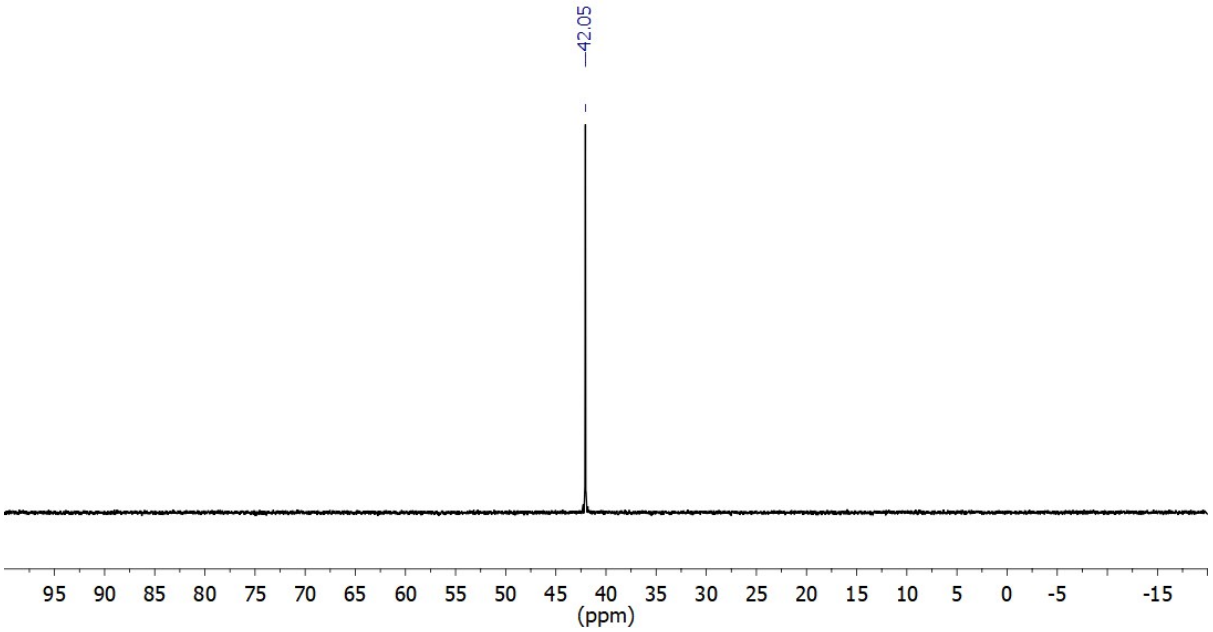
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

1.14. NMR Spectra for Complex 6

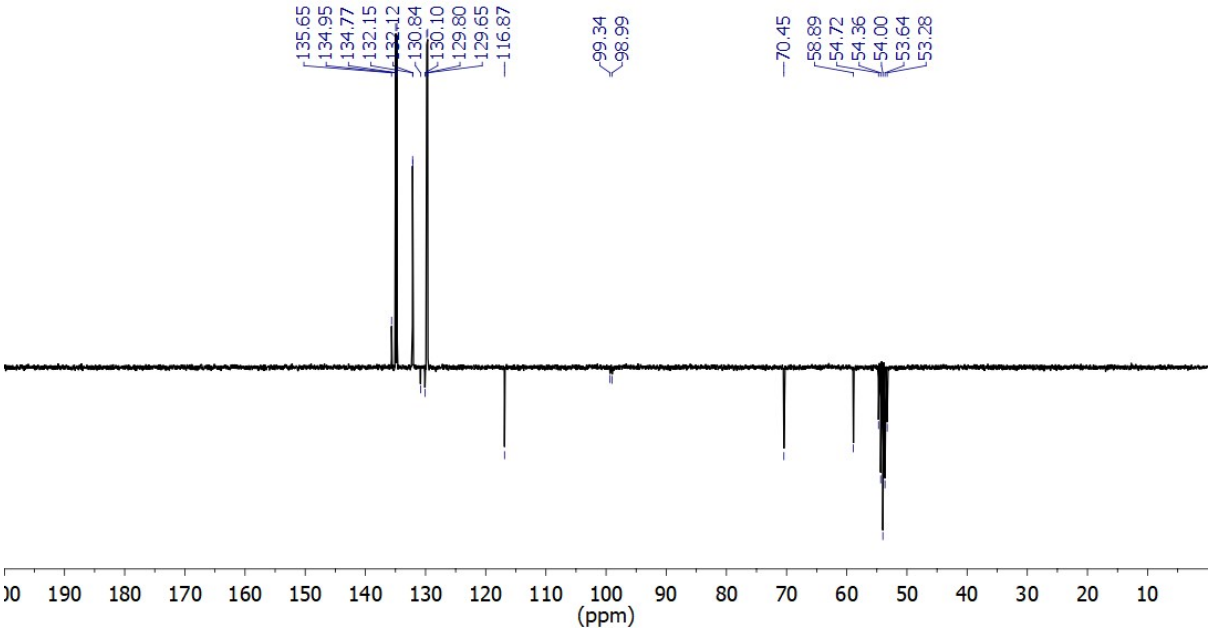
^{1}H NMR (300 MHz, CD_2Cl_2)



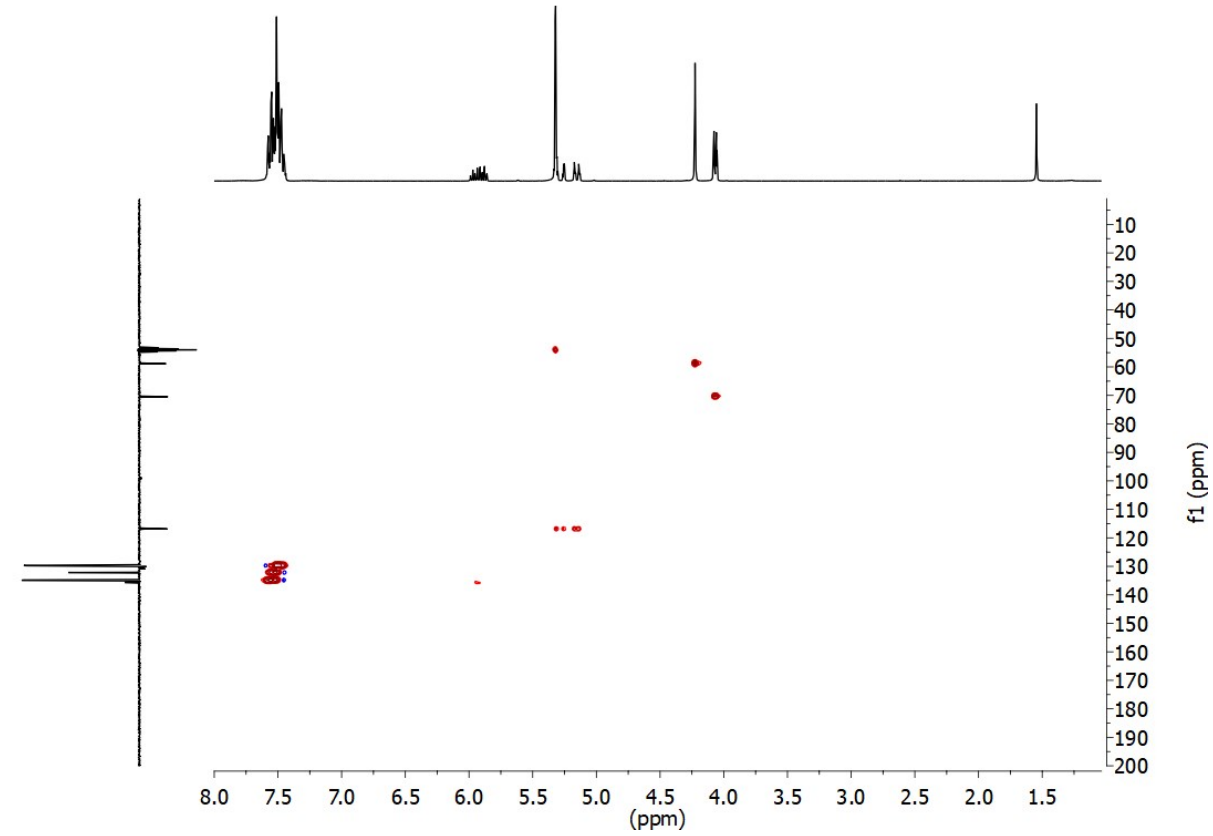
^{31}P NMR (121 MHz, CD_2Cl_2)



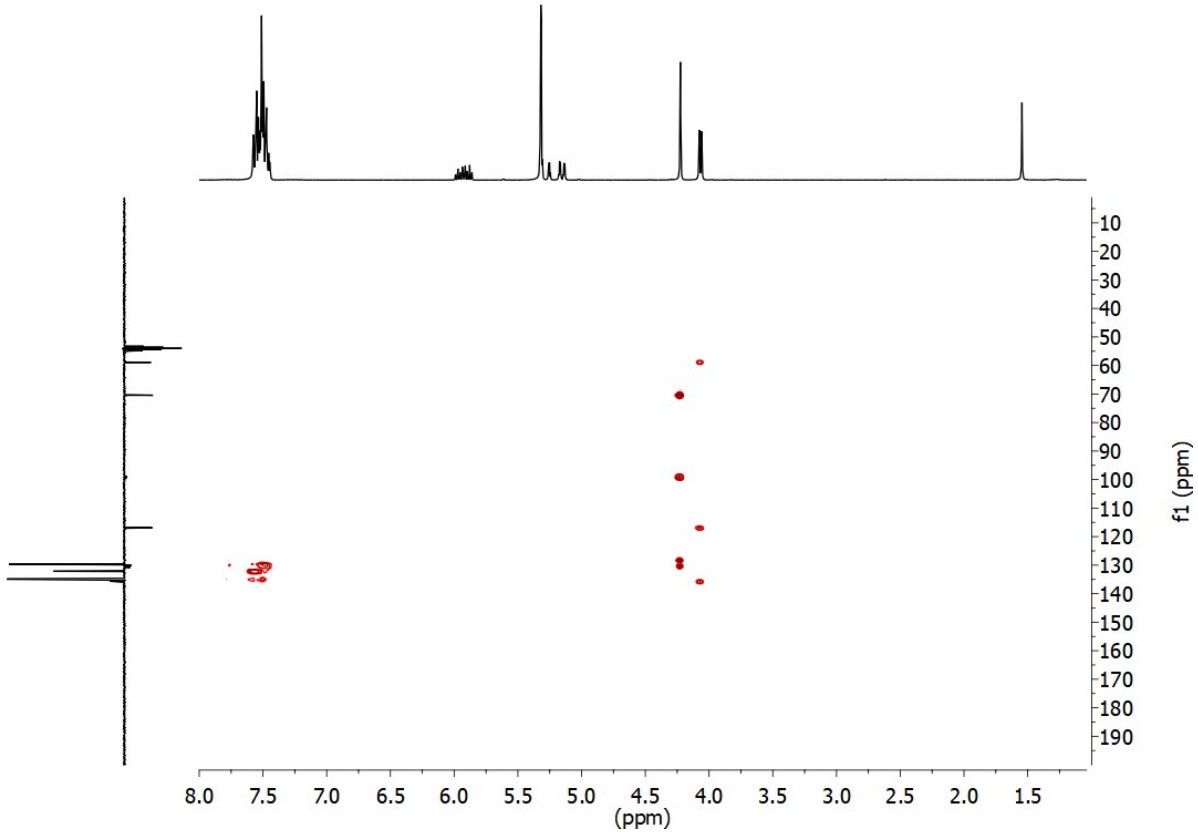
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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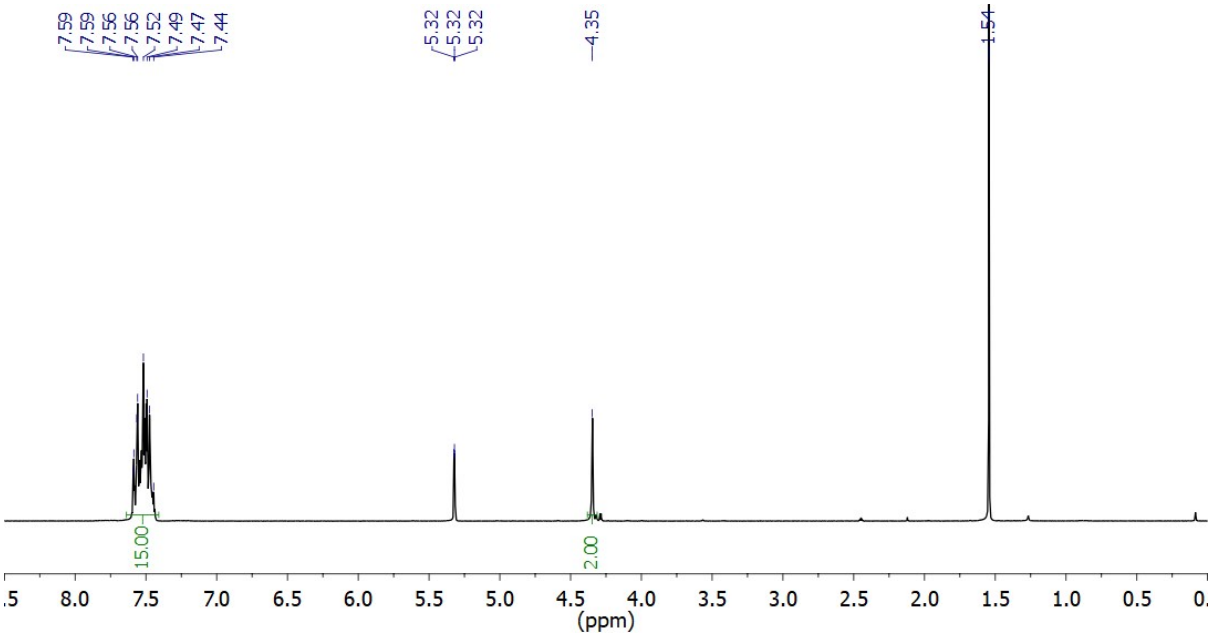
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

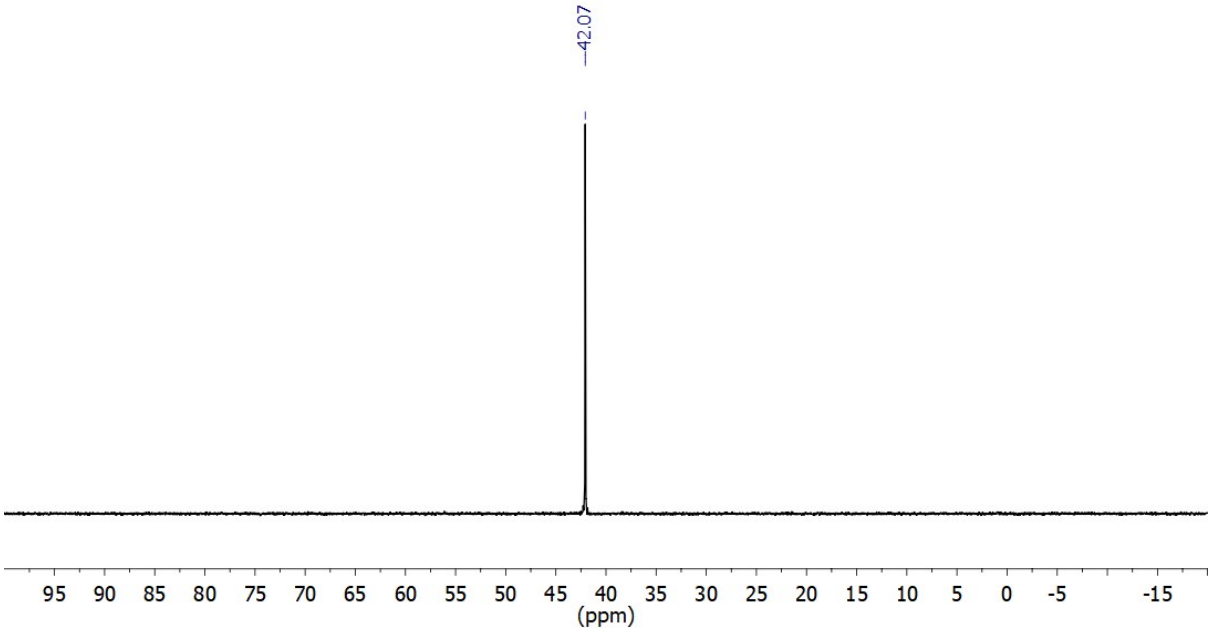
1.15. NMR Spectra for Complex 7

7

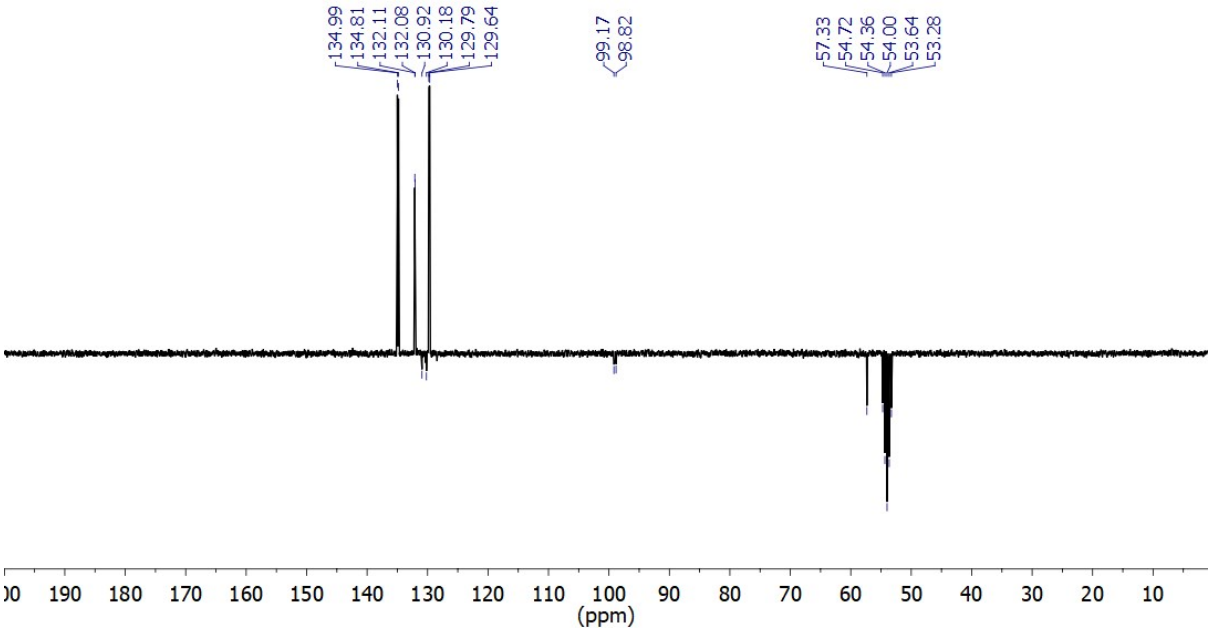
^{1}H NMR (300 MHz, CD_2Cl_2)



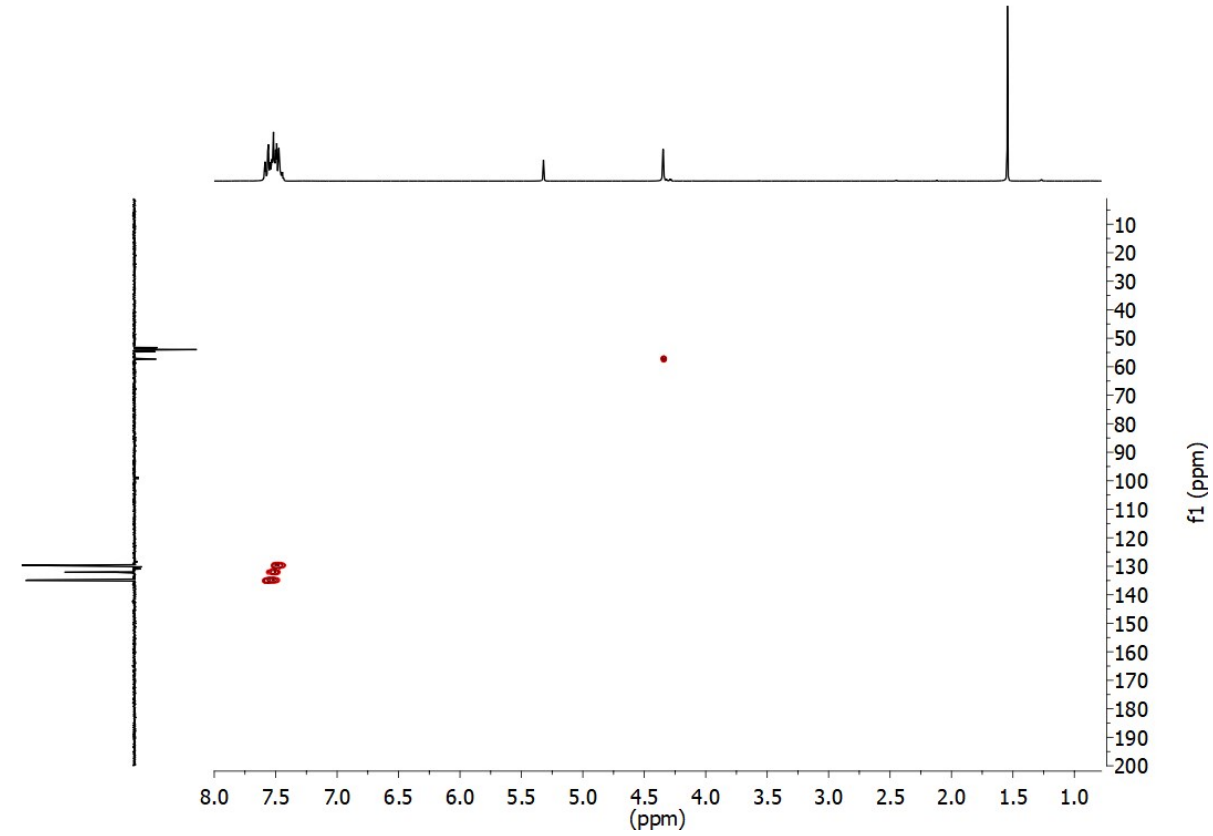
^{31}P NMR (121 MHz, CD_2Cl_2)



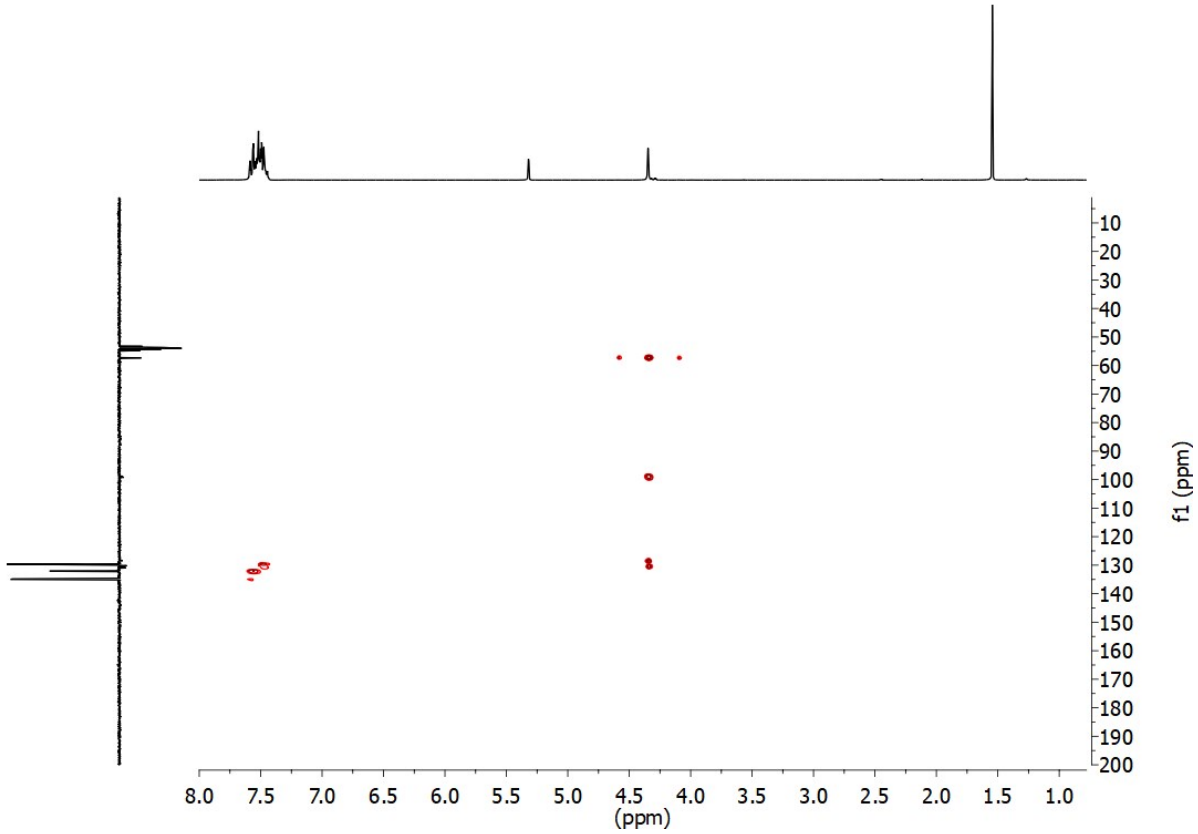
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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170
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190
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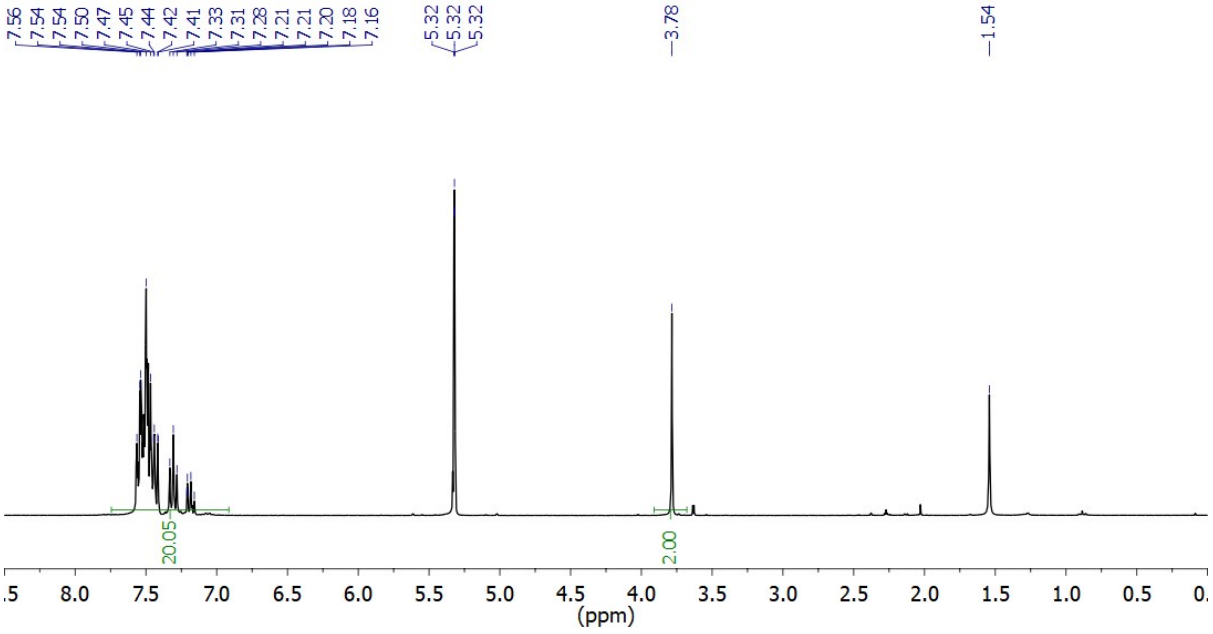
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

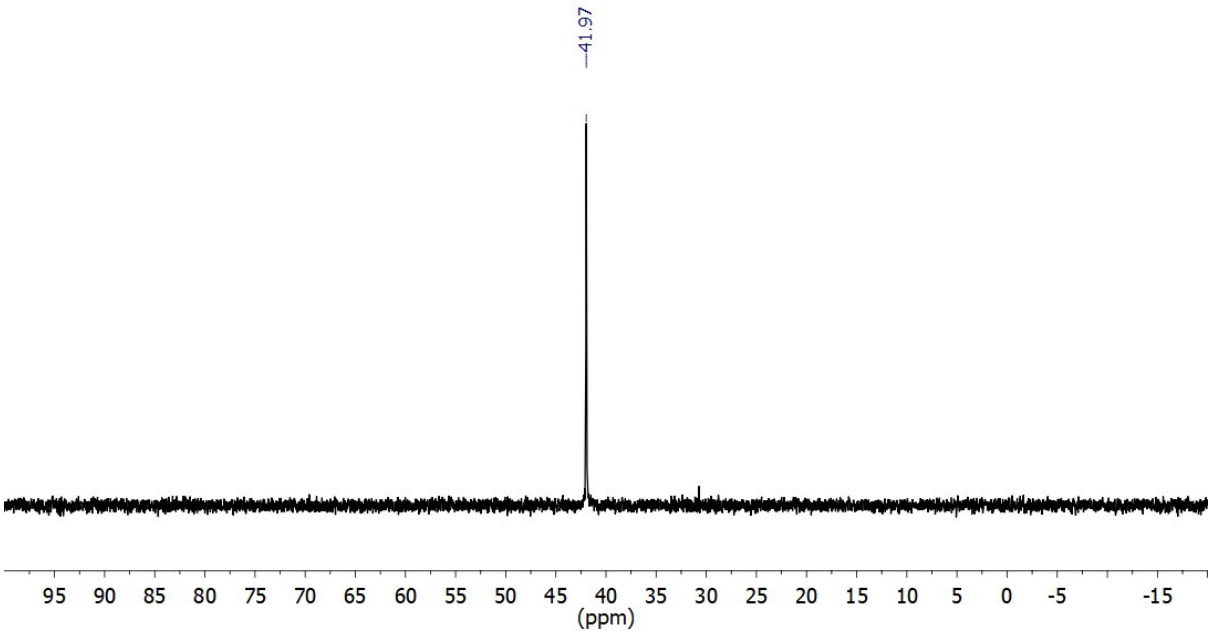
1.16. NMR Spectra for Complex 8

8

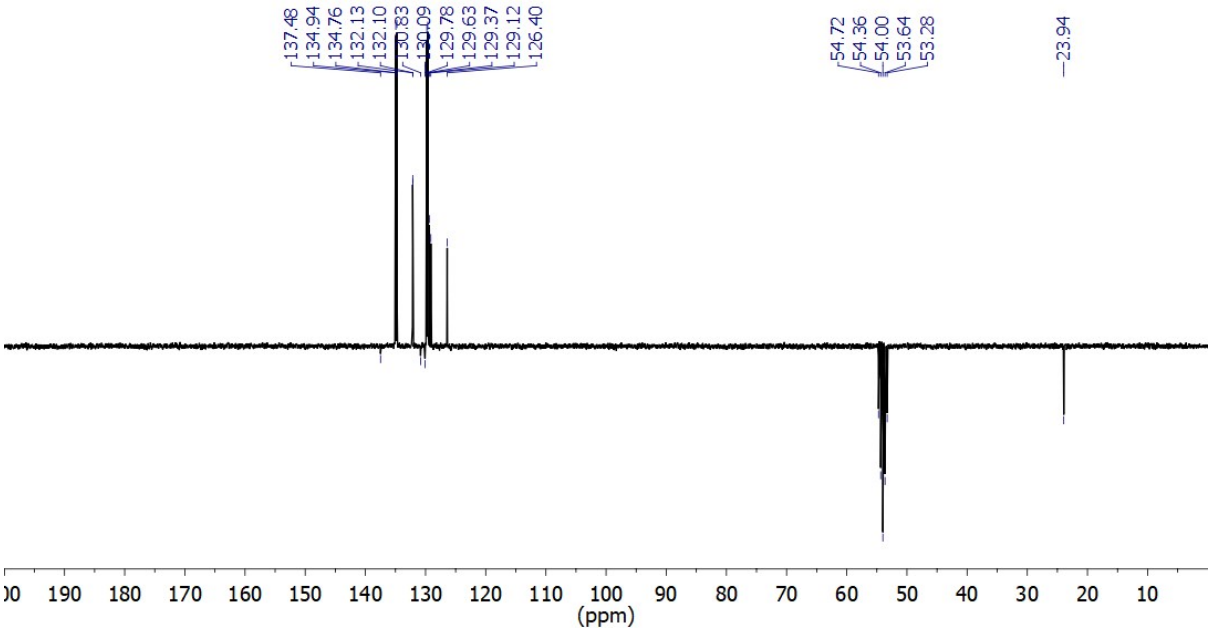
^{1}H NMR (300 MHz, CD_2Cl_2)



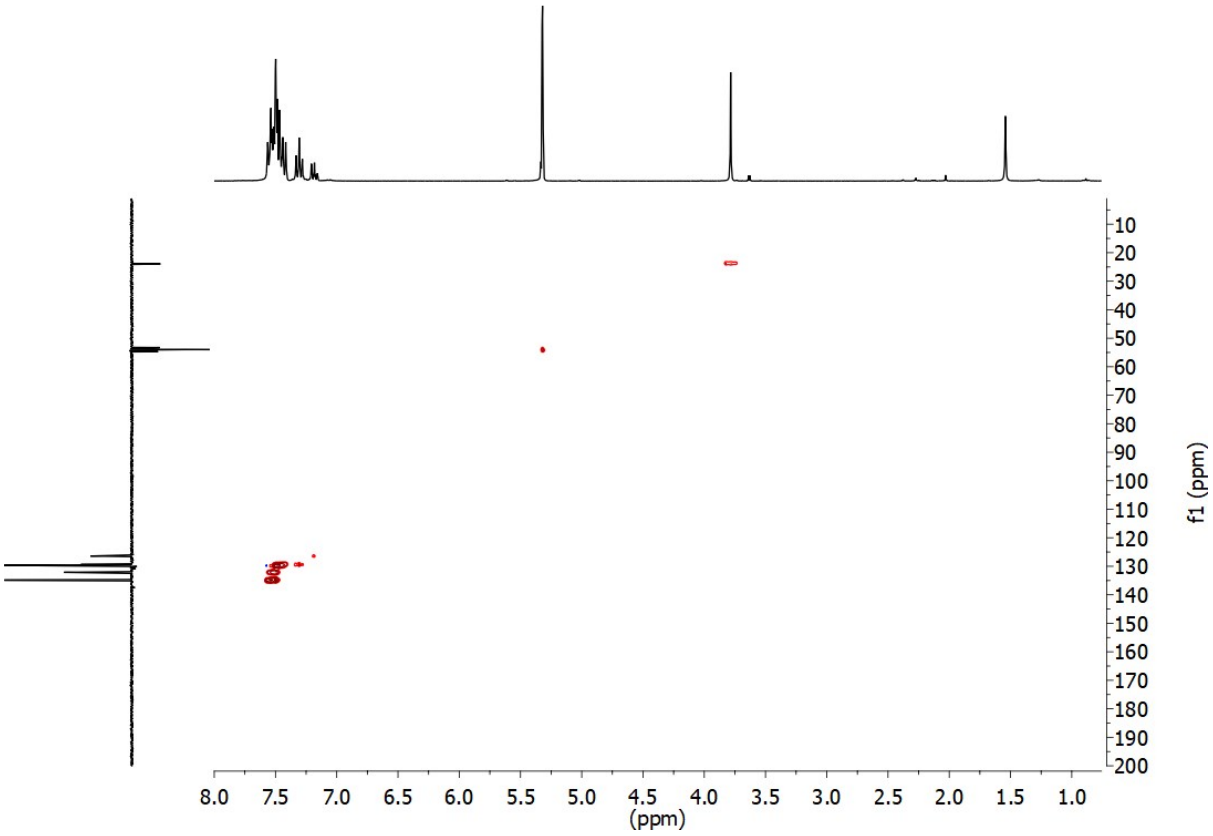
^{31}P NMR (121 MHz, CD_2Cl_2)



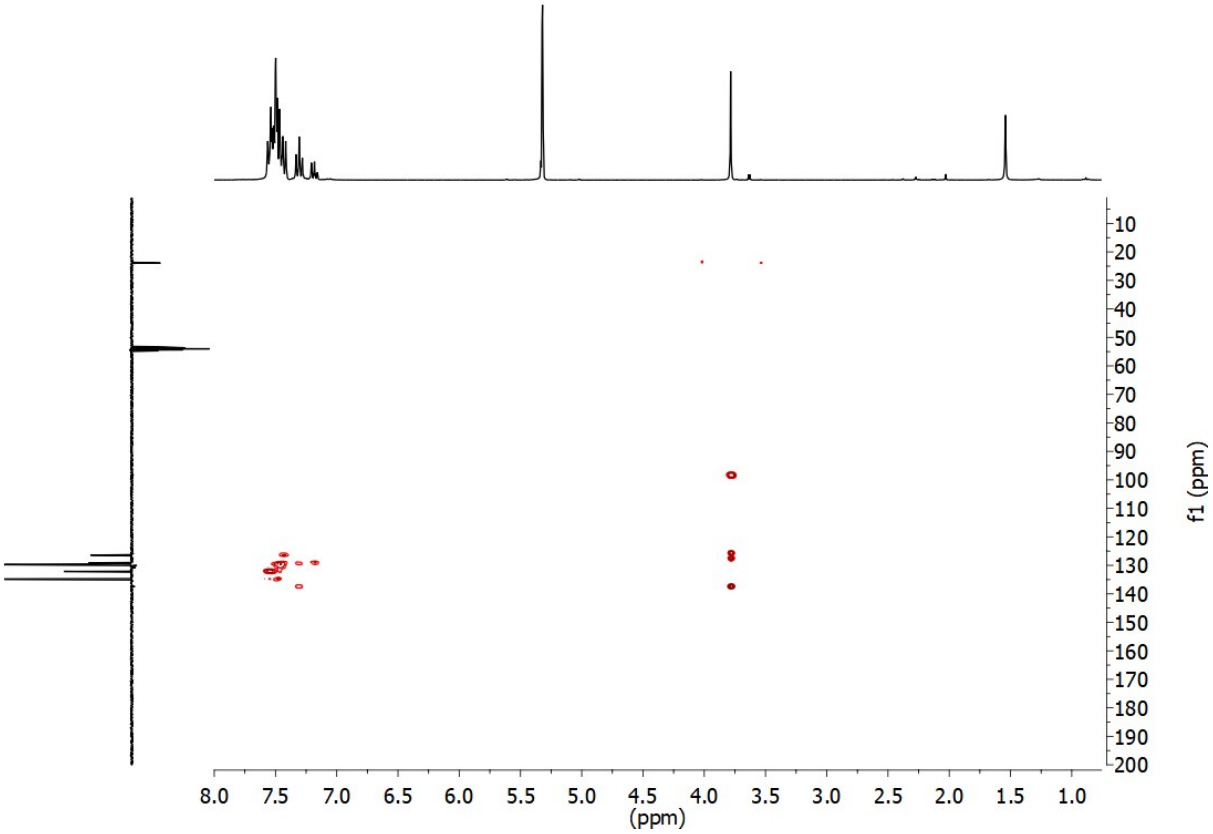
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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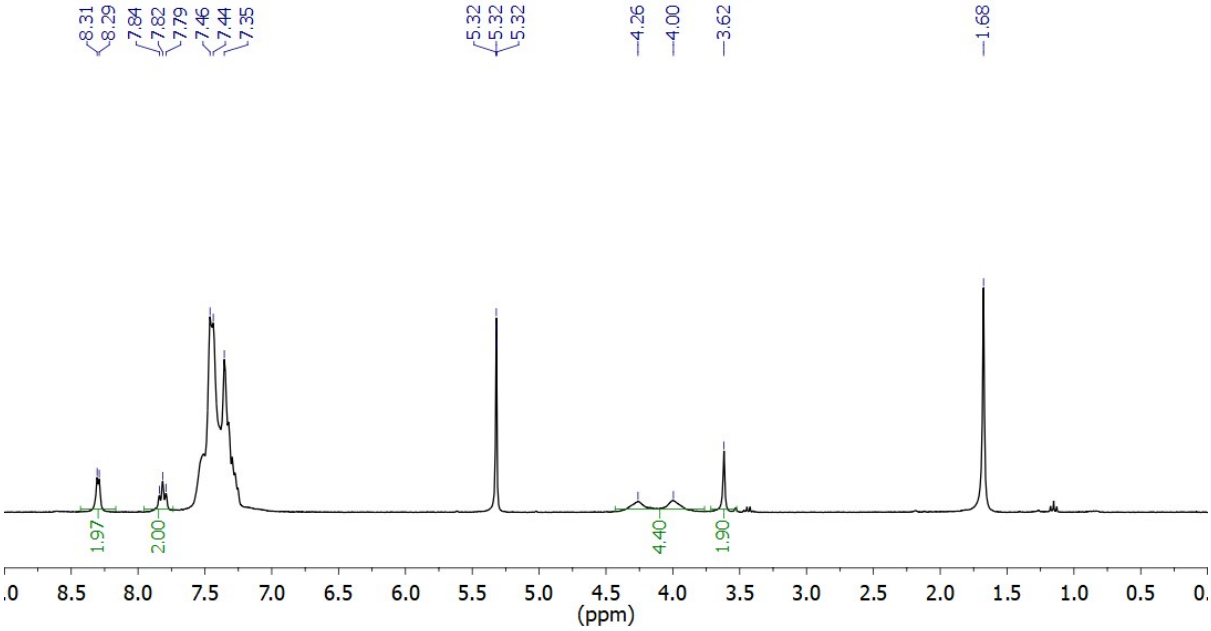
130
140
150
160
170
180
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

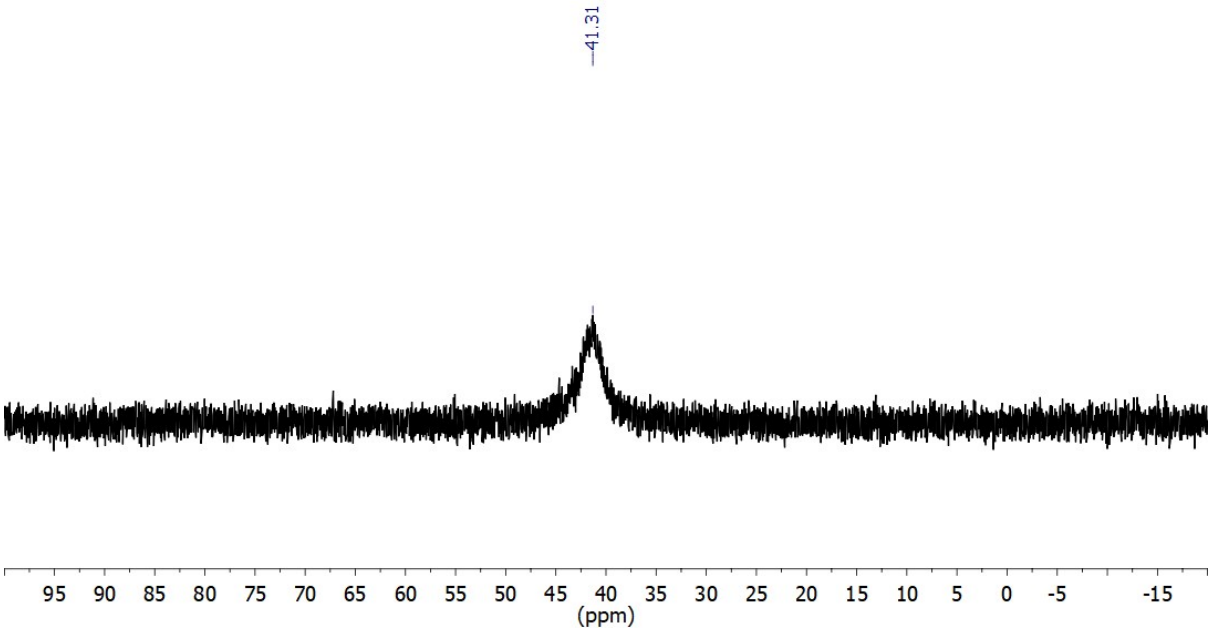
1.17. NMR Spectra for Complex 9

9

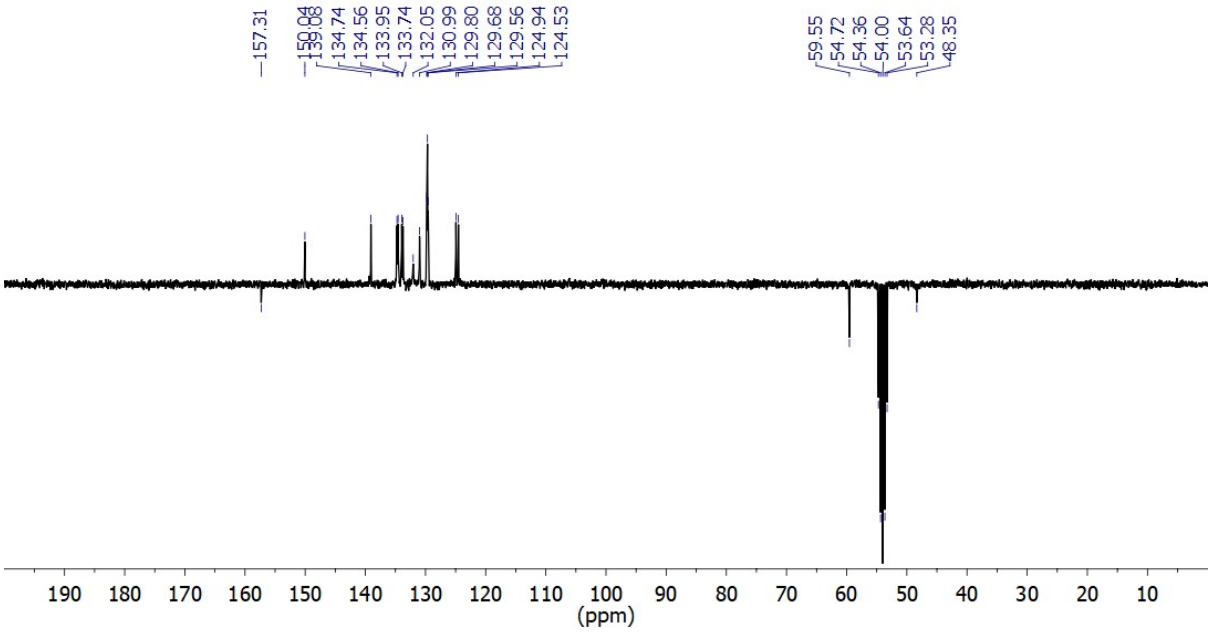
^{1}H NMR (300 MHz, CD_2Cl_2)



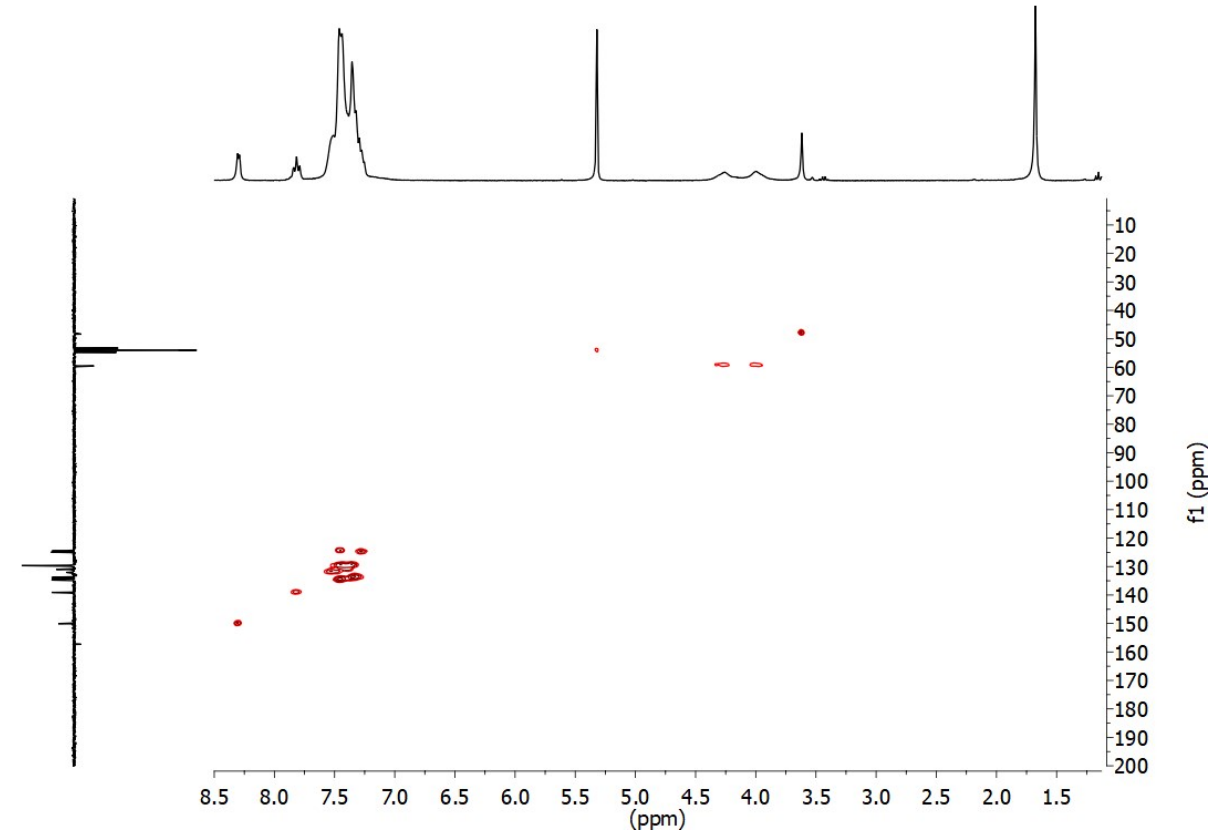
^{31}P NMR (121 MHz, CD_2Cl_2, RT)



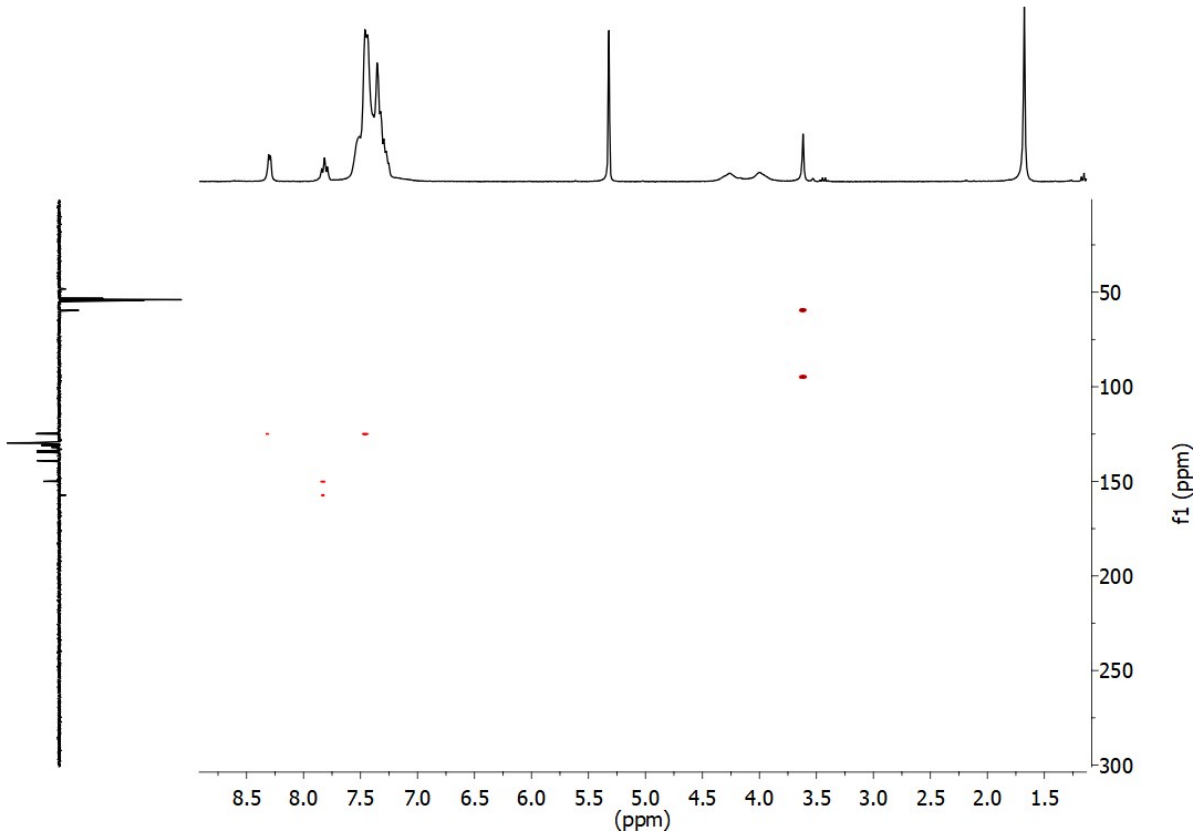
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC

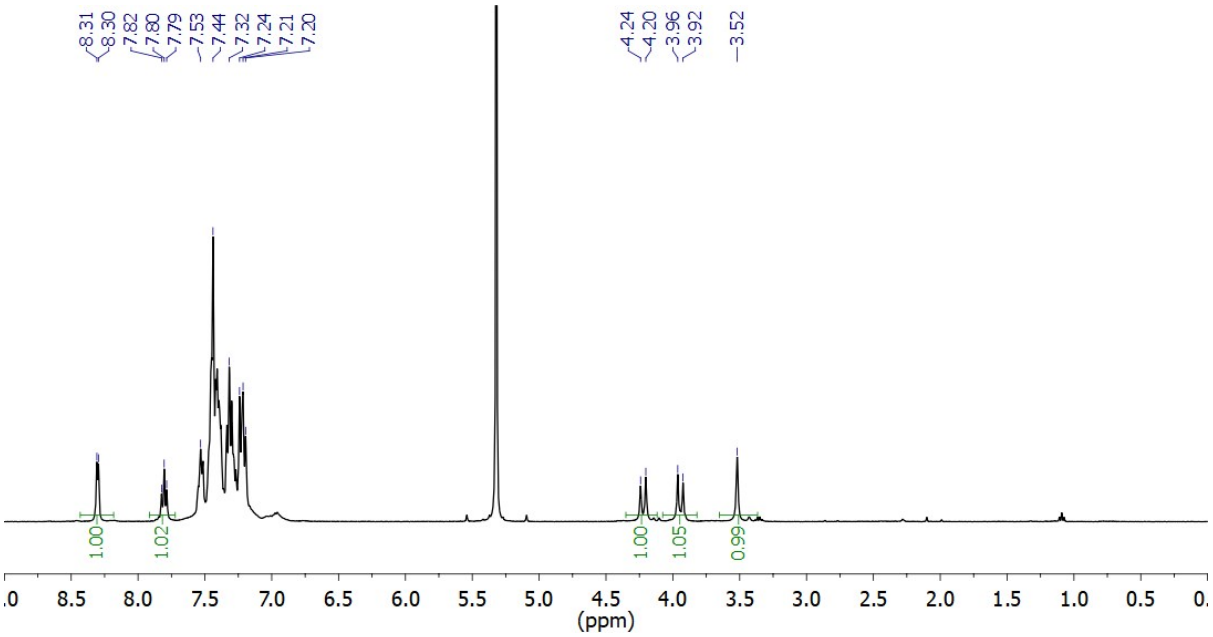


HMBC

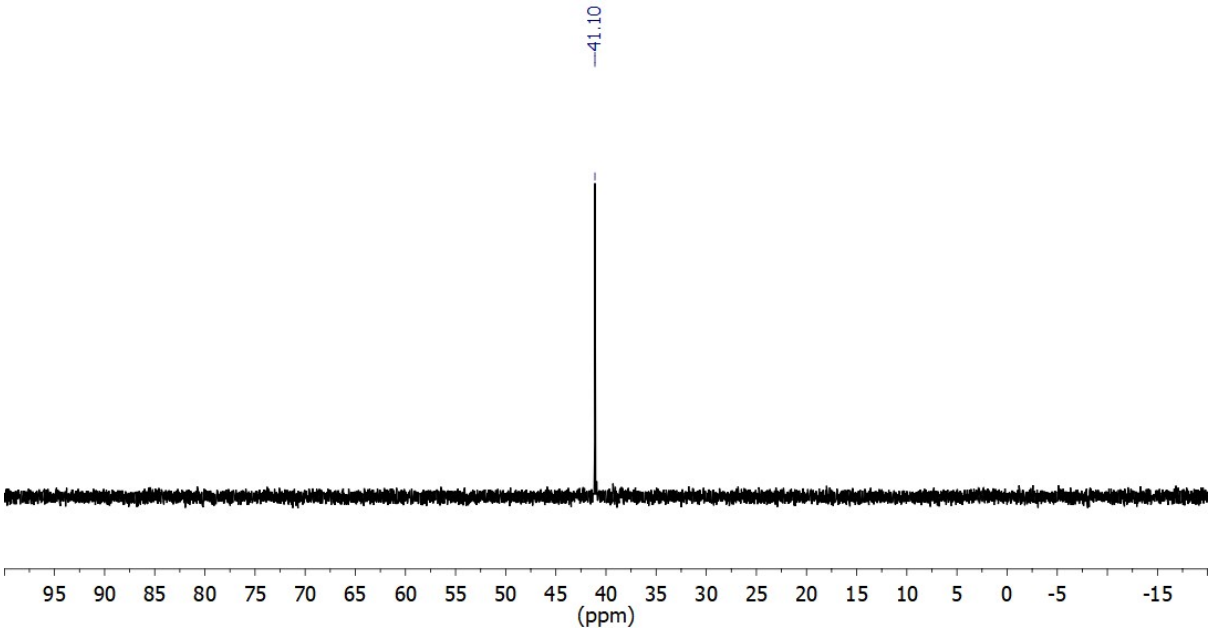

50
100
150
200
250
300
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

1.18. VT NMR Complex 9

^{1}H NMR 193K (300 MHz, CD_2Cl_2)



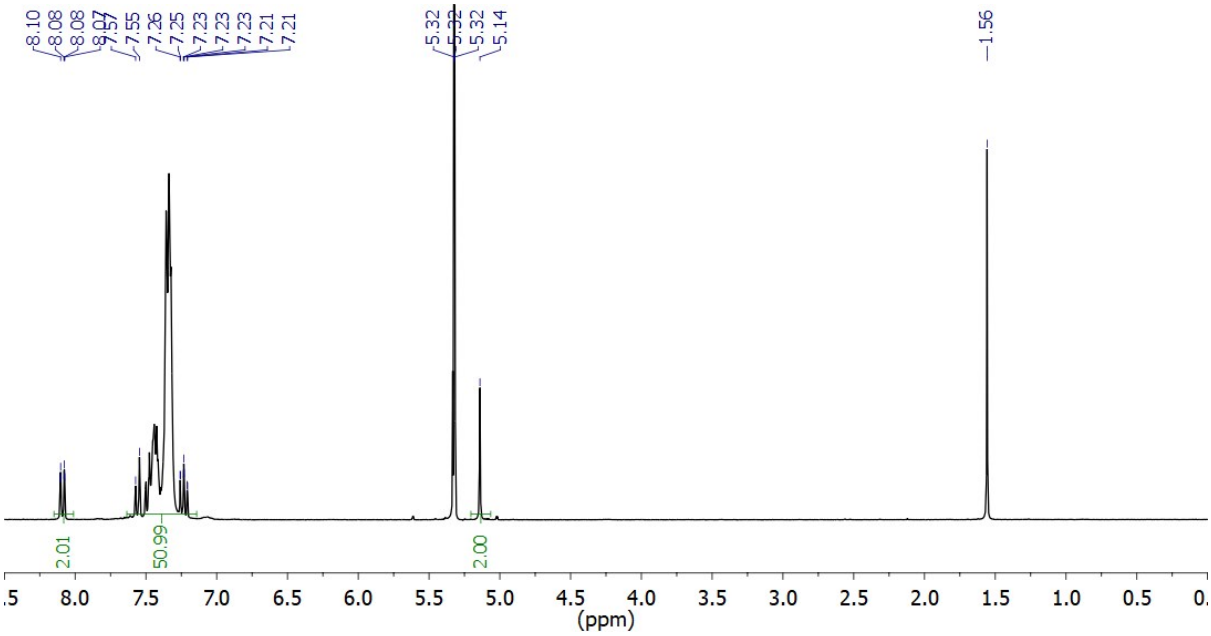
^{31}P NMR 193 K (121 MHz, CD_2Cl_2)



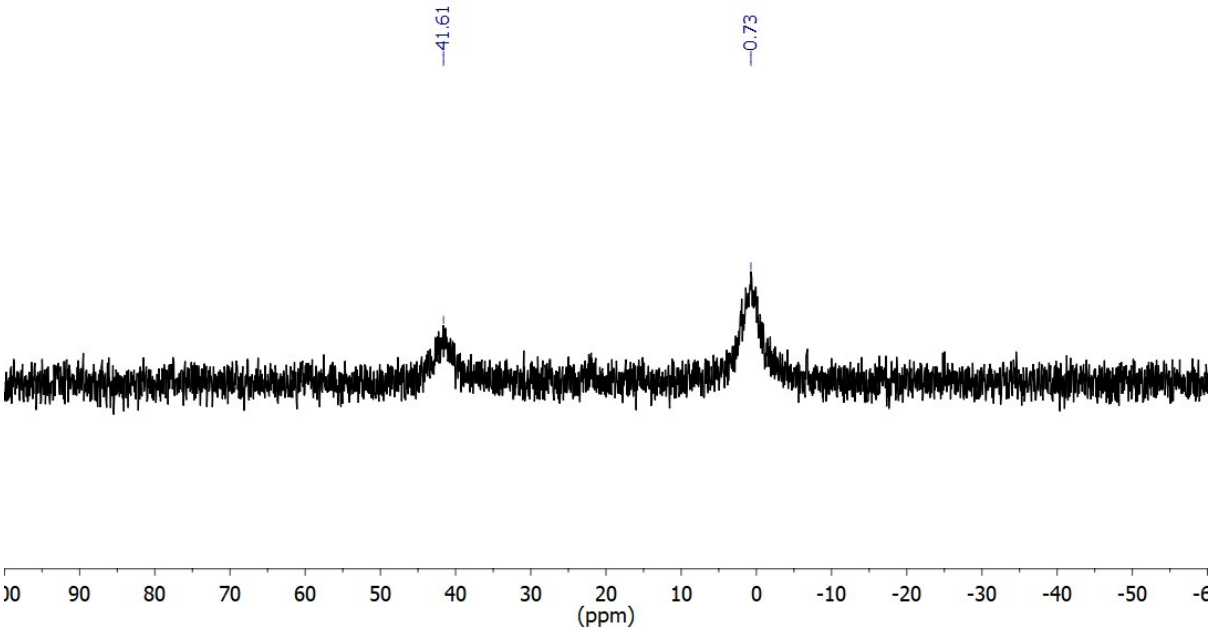
1.19. NMR Spectra Complex 10

10

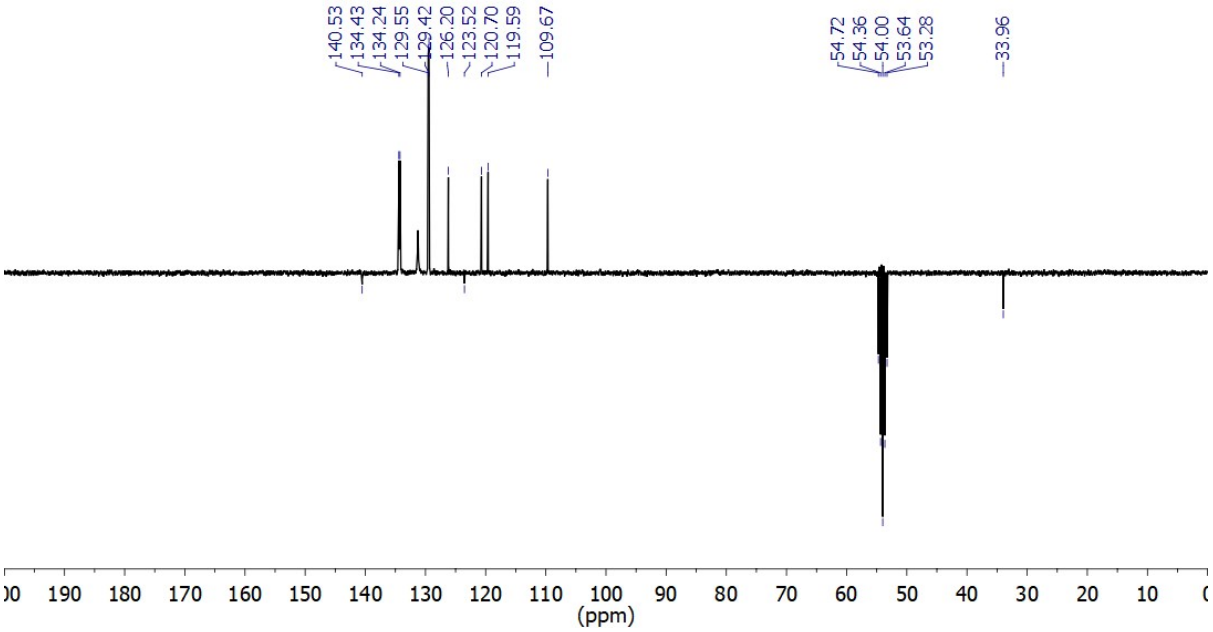
^{1}H NMR (300 MHz, CD_2Cl_2)



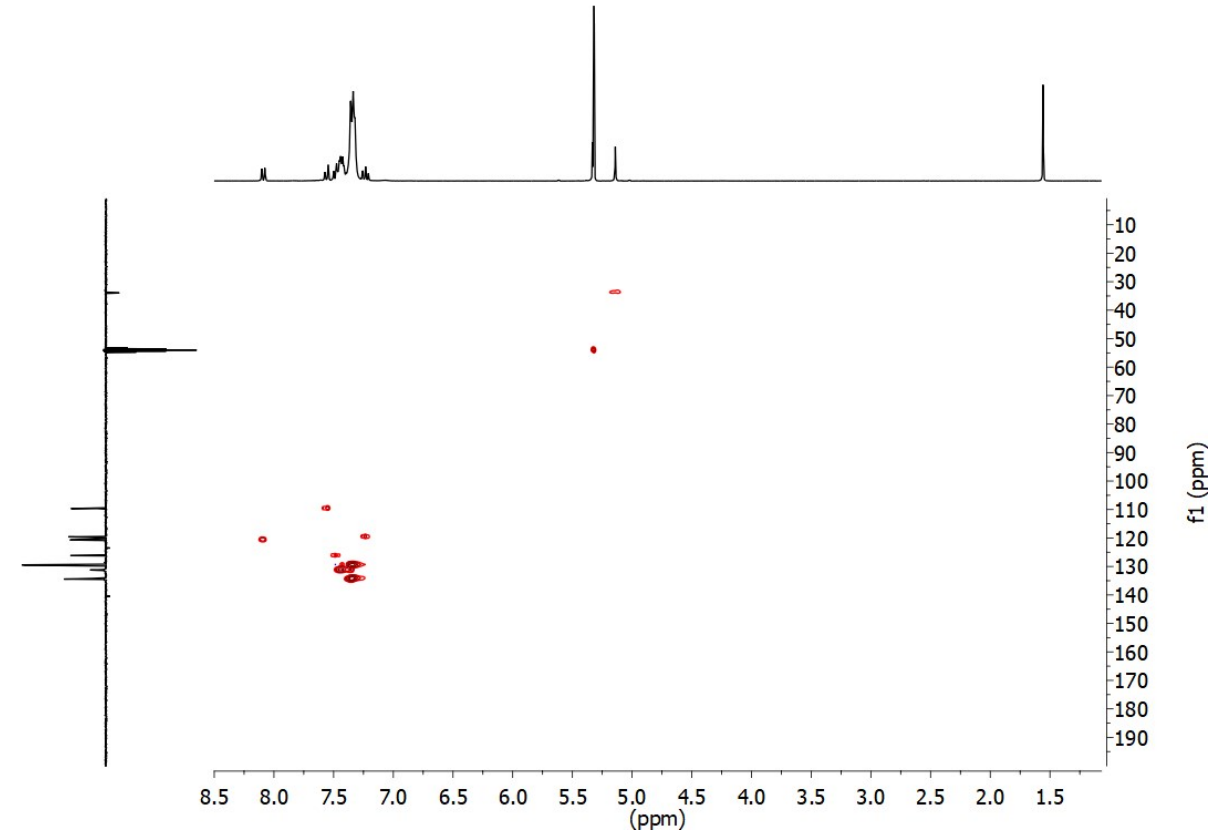
^{31}P NMR (162 MHz, CD_2Cl_2)



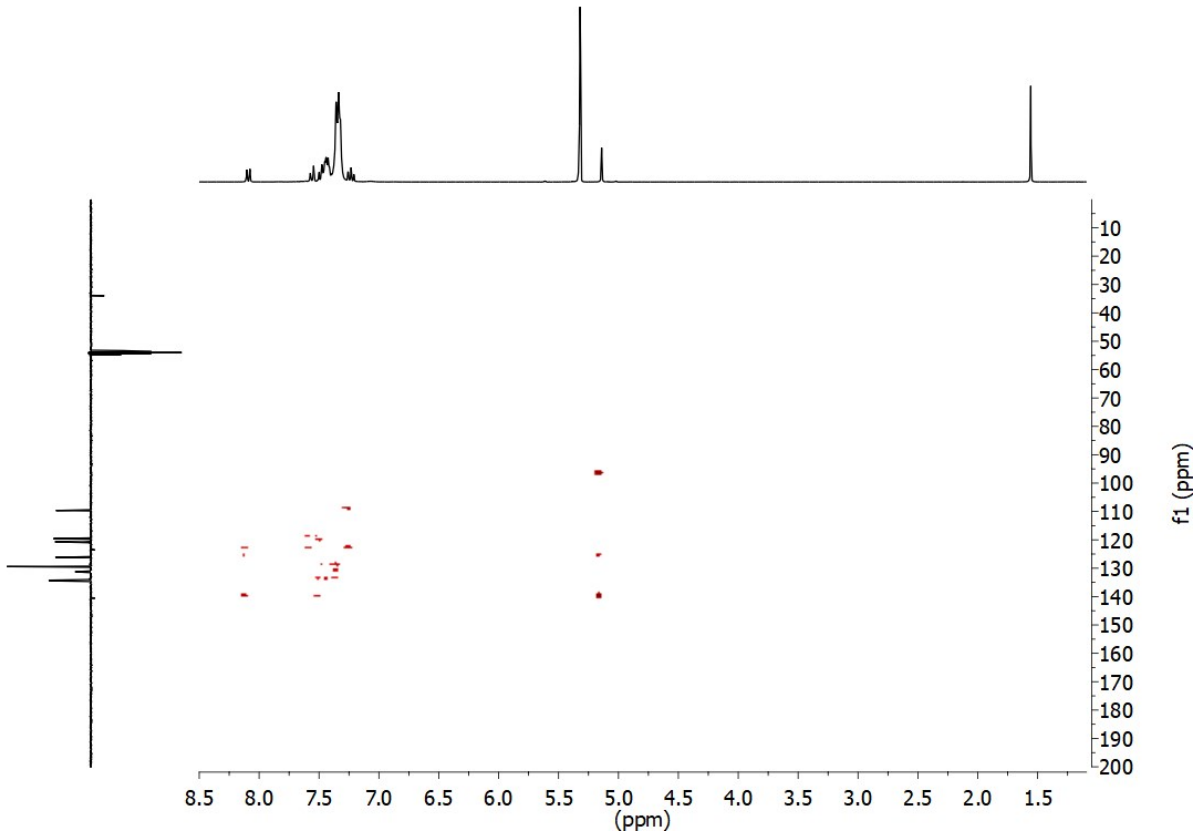
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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190
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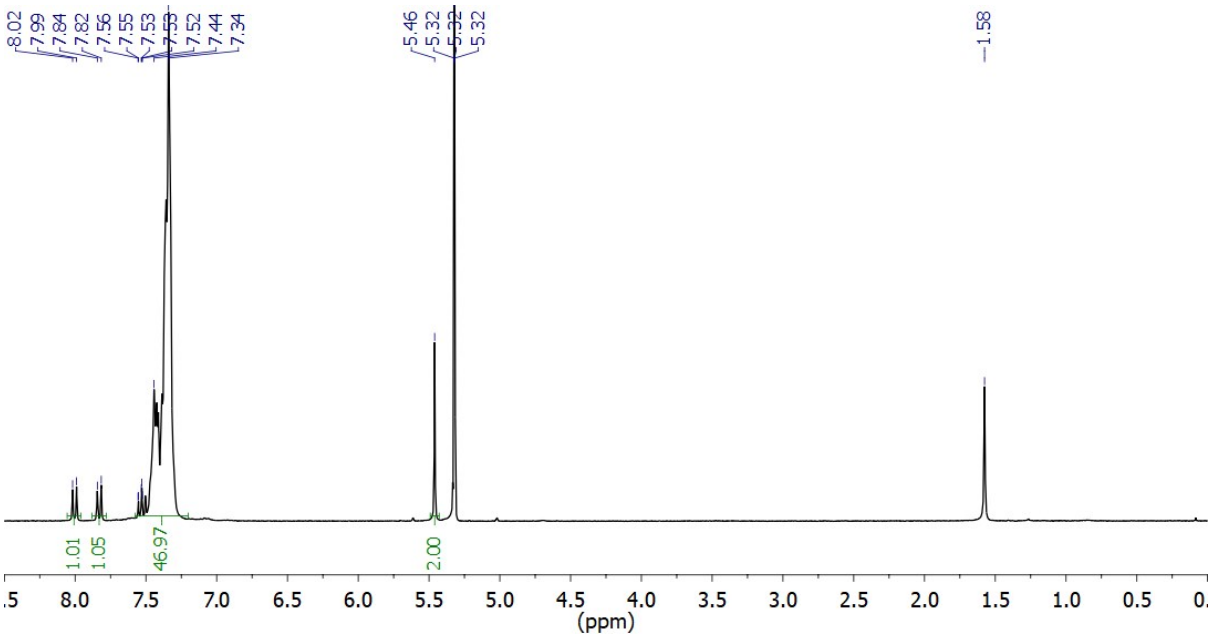
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

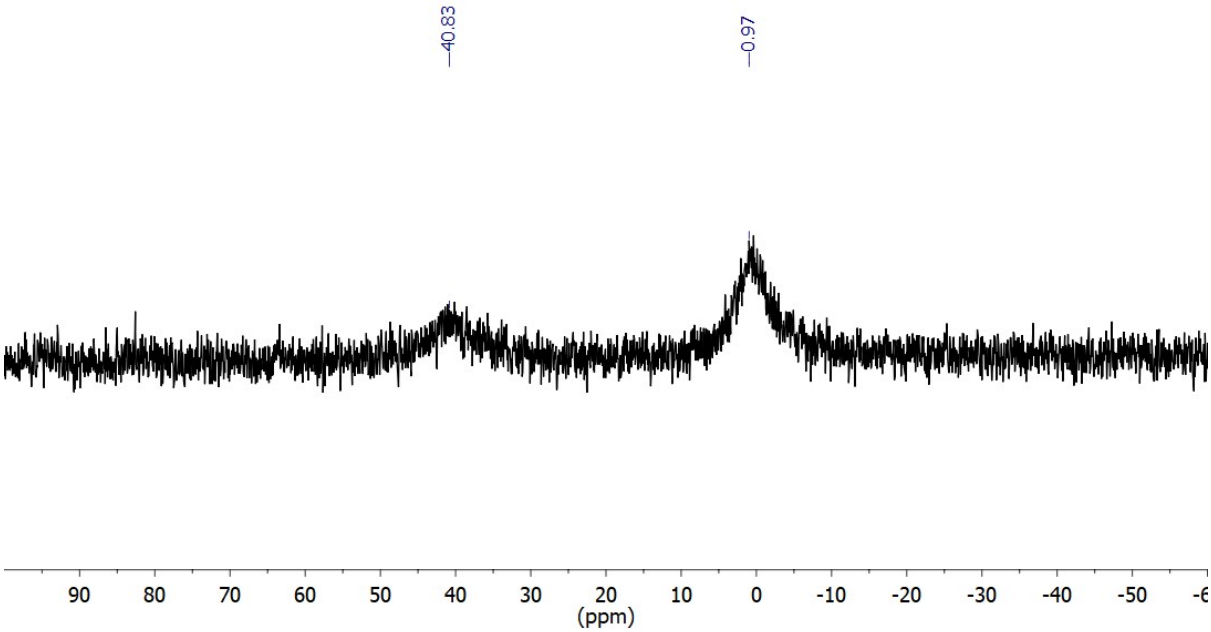
1.20. NMR Spectra Complex 11

11

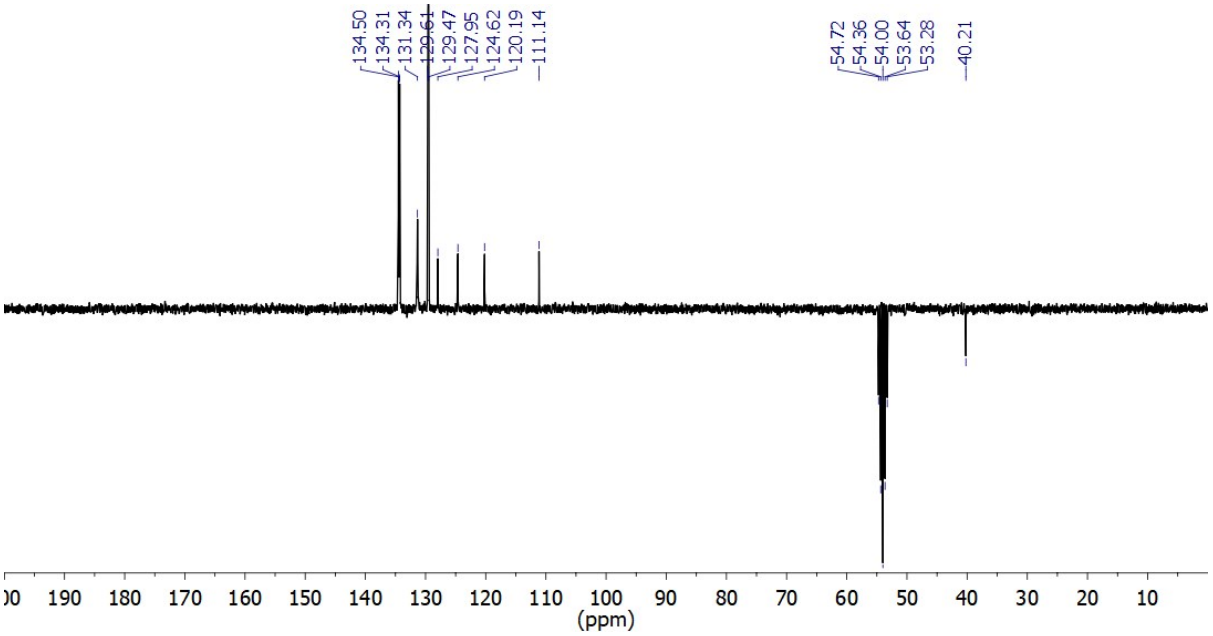
^{1}H NMR (300 MHz, CD_2Cl_2)



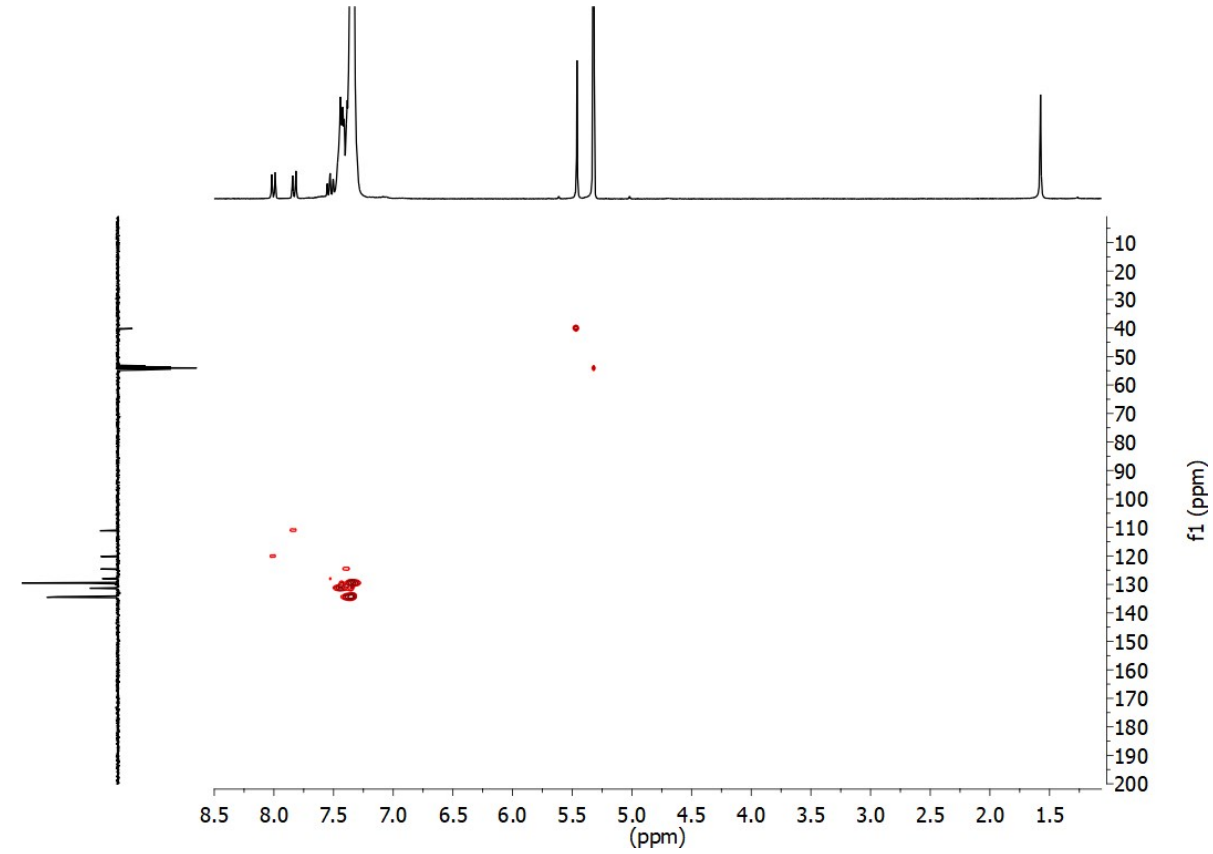
^{31}P NMR (162 MHz, CD_2Cl_2)



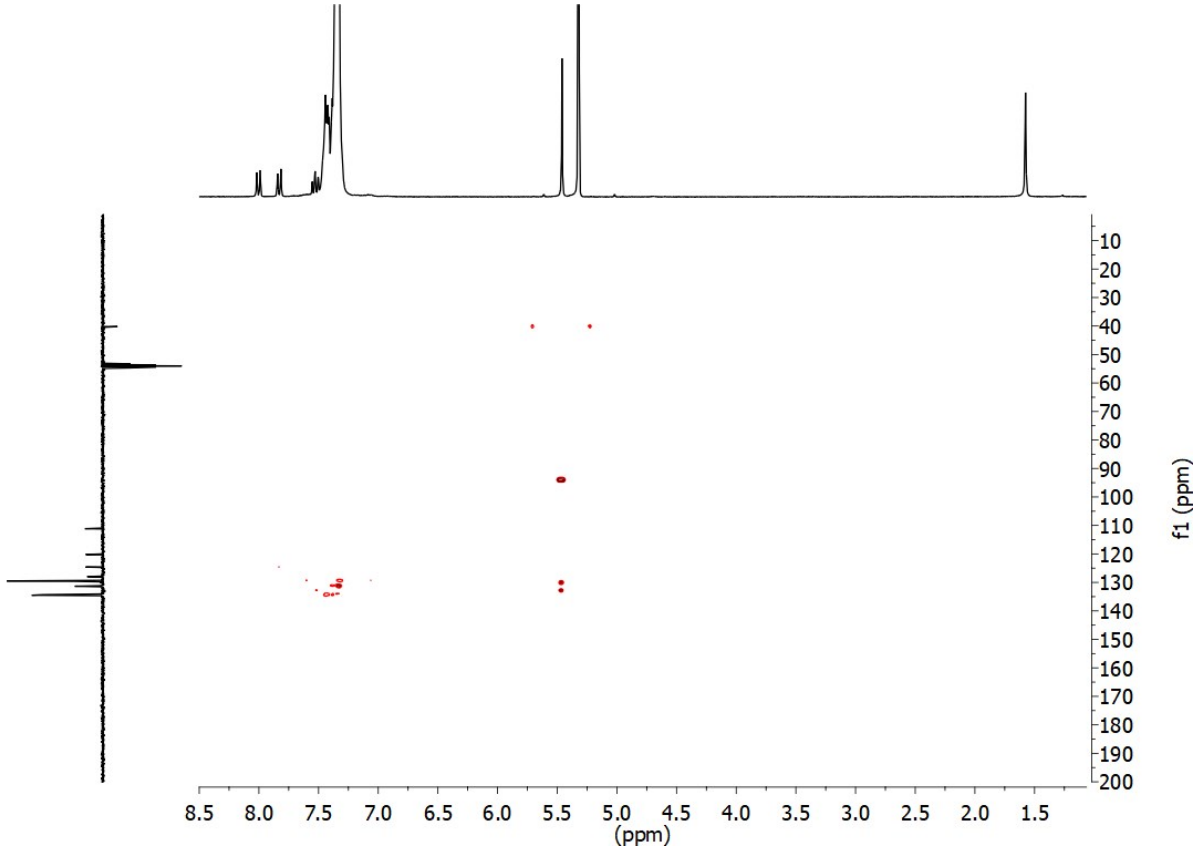
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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170
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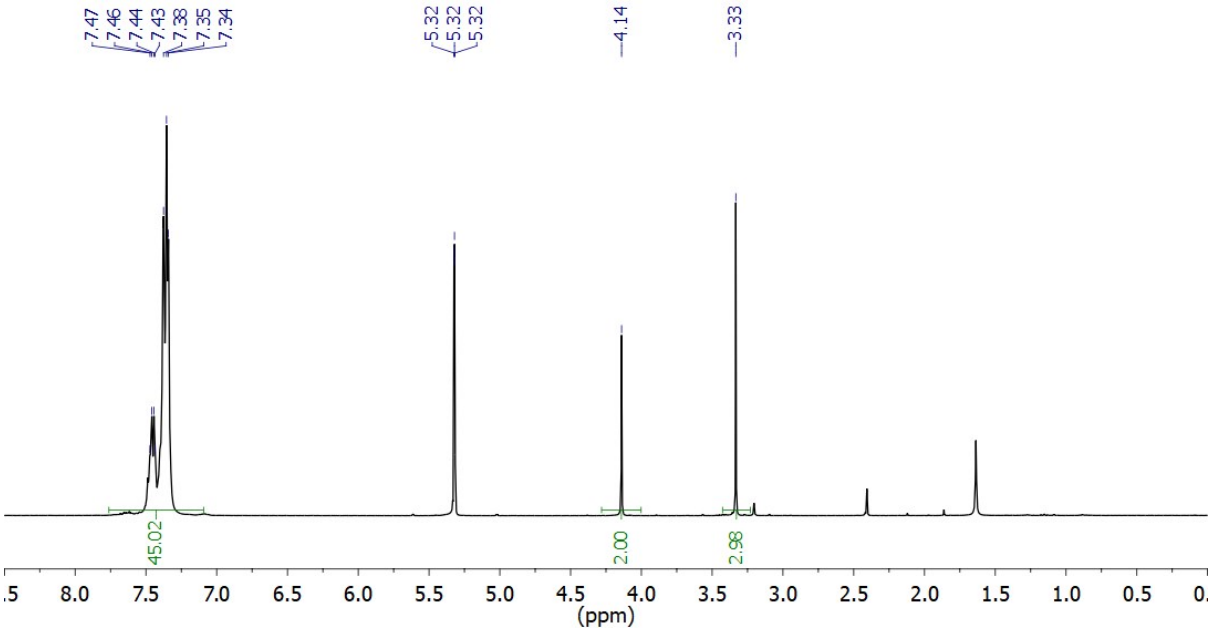
190
200
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

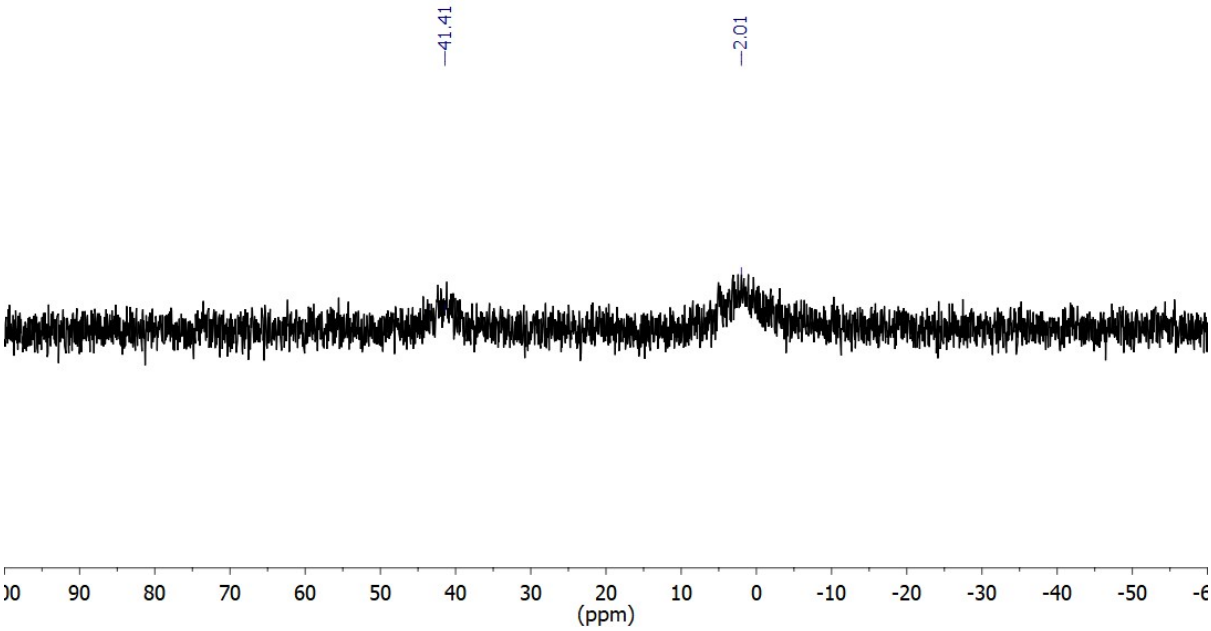
1.21. NMR Spectra Complex 12

12

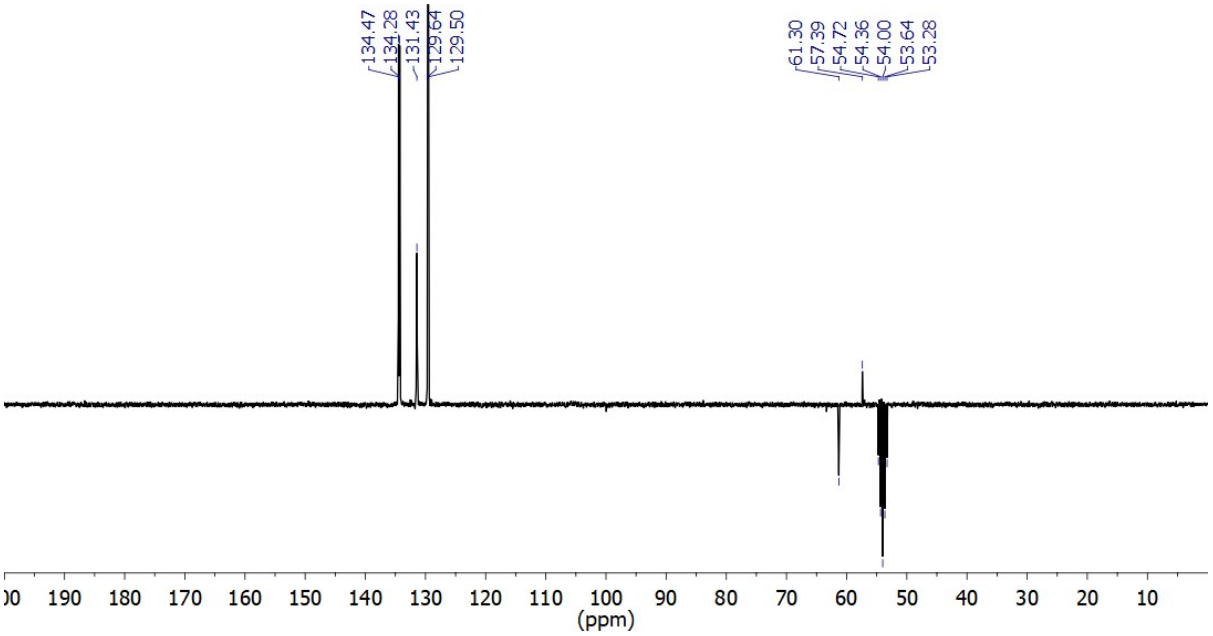
^{1}H NMR (300 MHz, CD_2Cl_2)



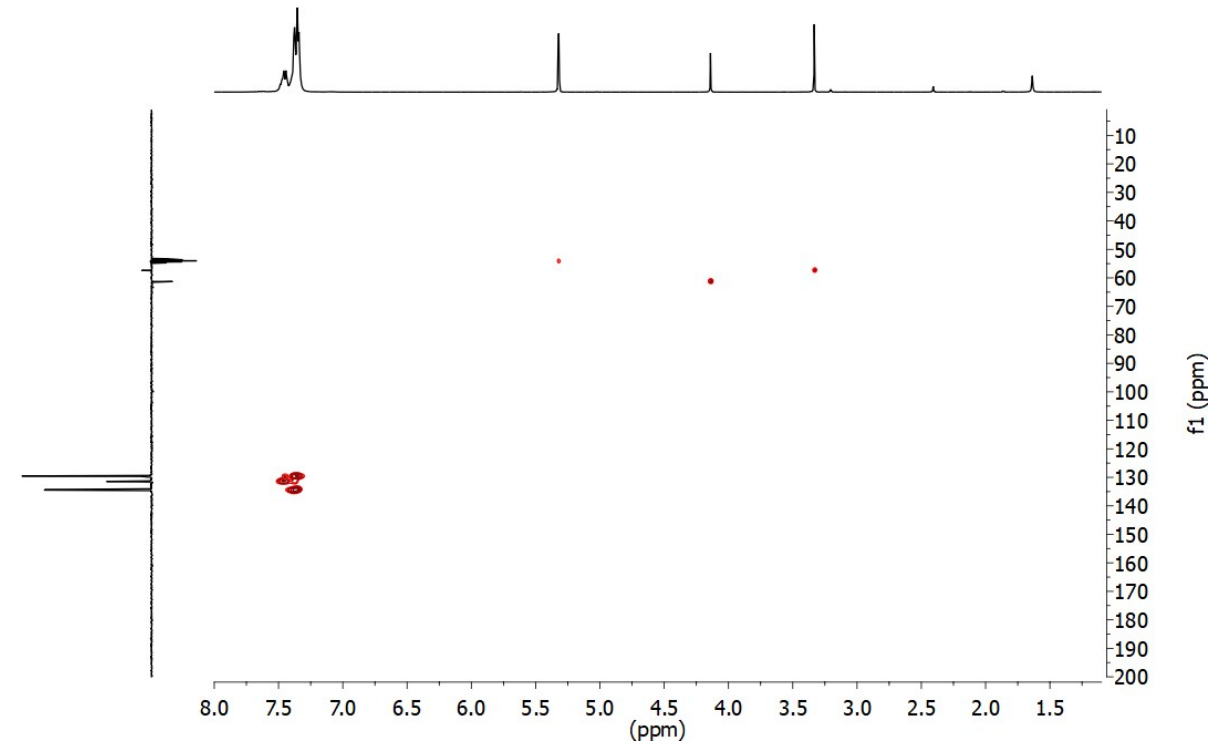
^{31}P NMR (162 MHz, CD_2Cl_2)



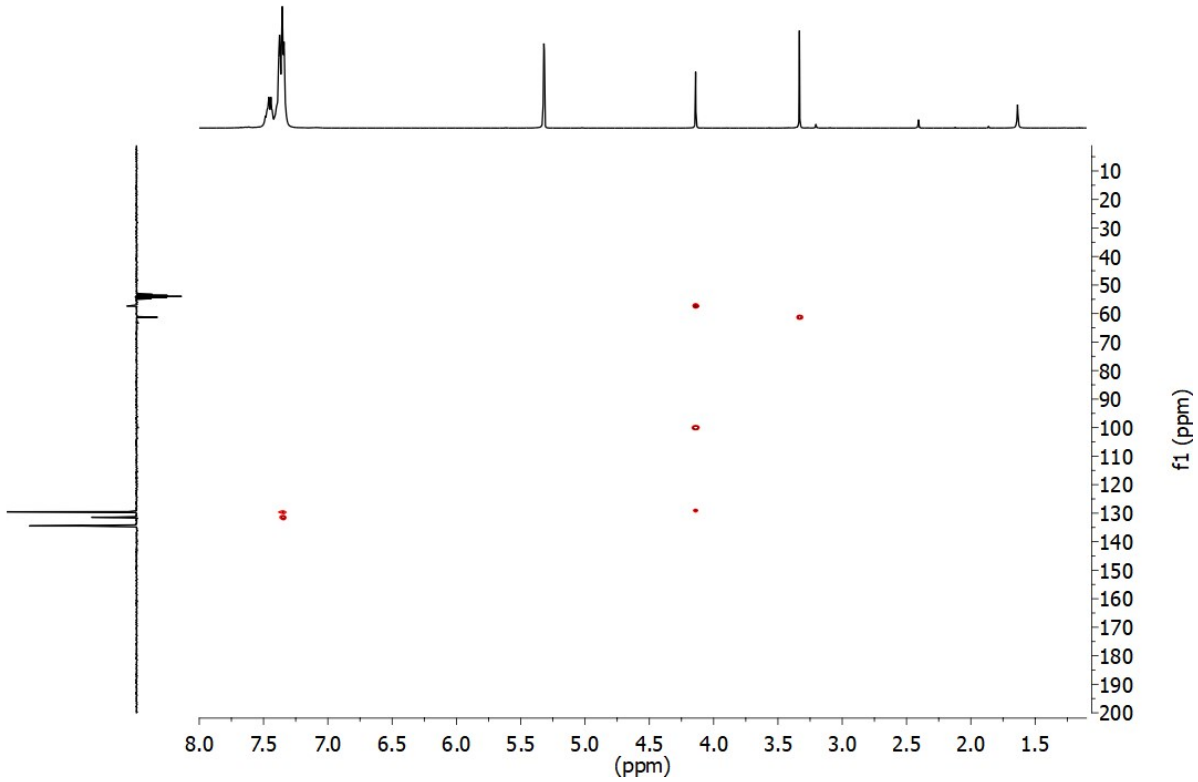
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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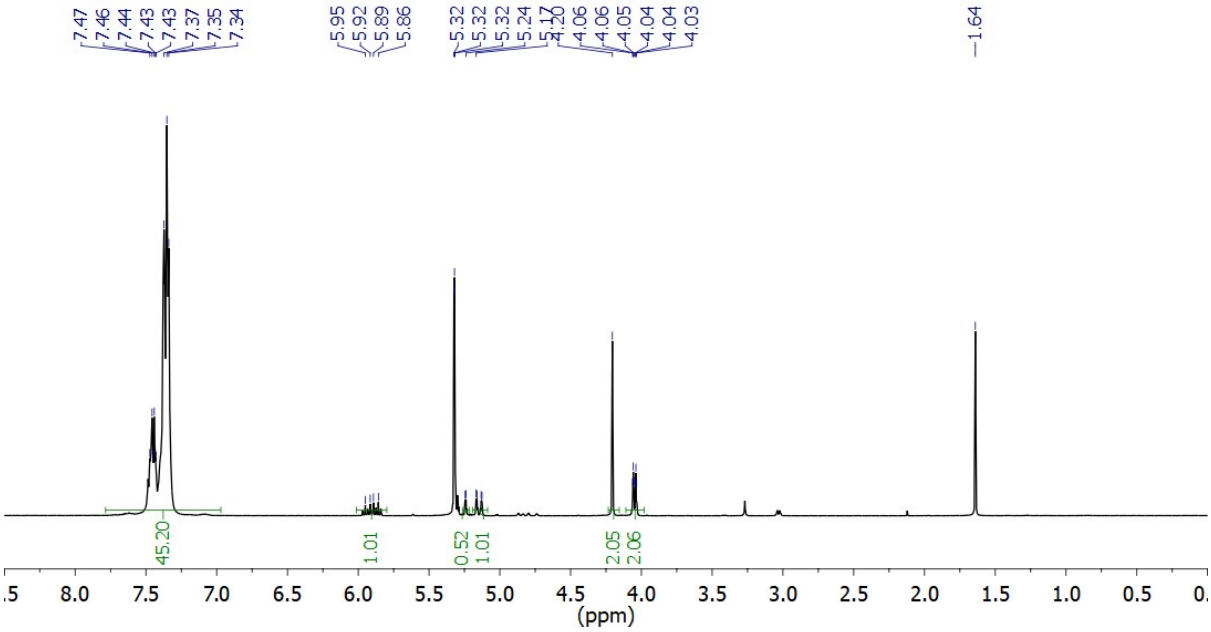
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

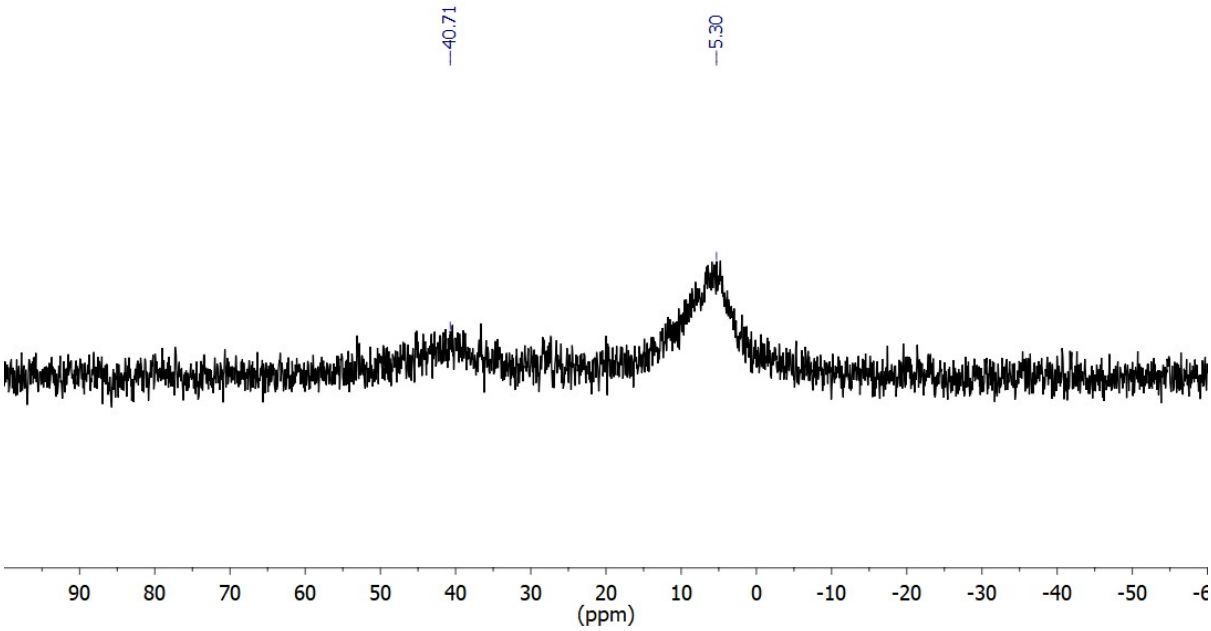
1.22. NMR Spectra for Complex 13

13

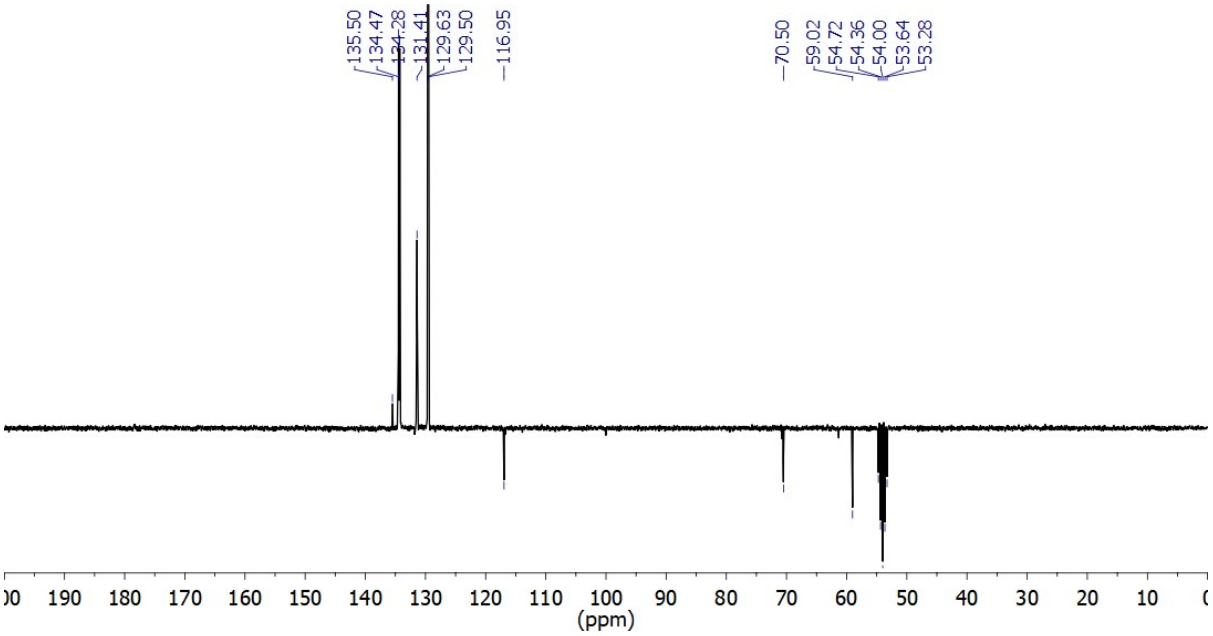
^{1}H NMR (300 MHz, CD_2Cl_2)



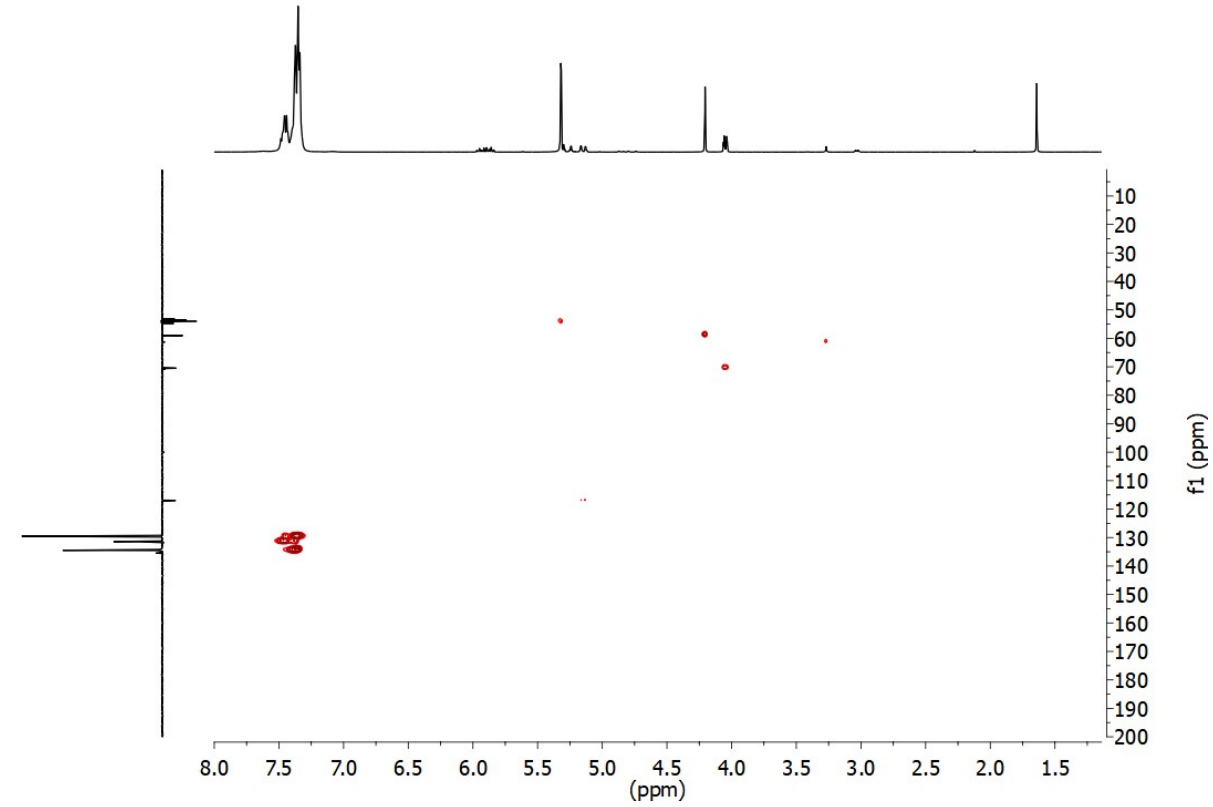
^{31}P NMR (162 MHz, CD_2Cl_2)



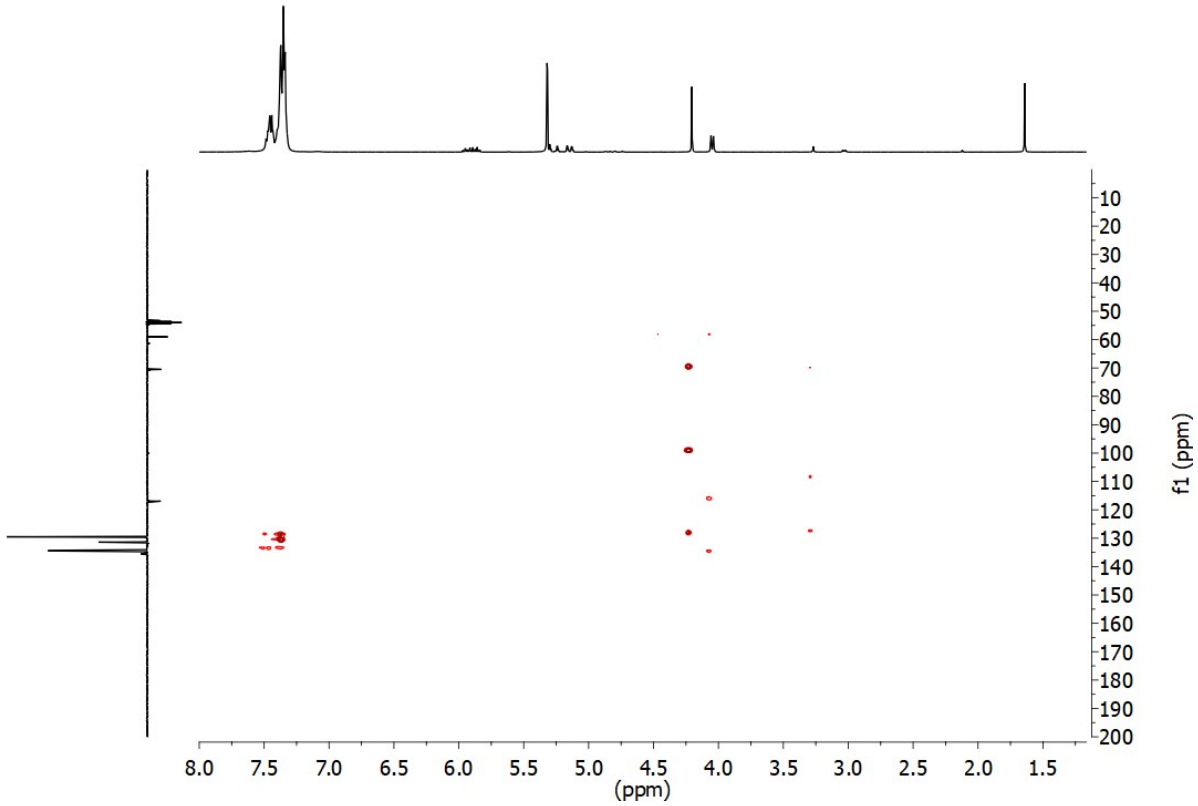
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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130
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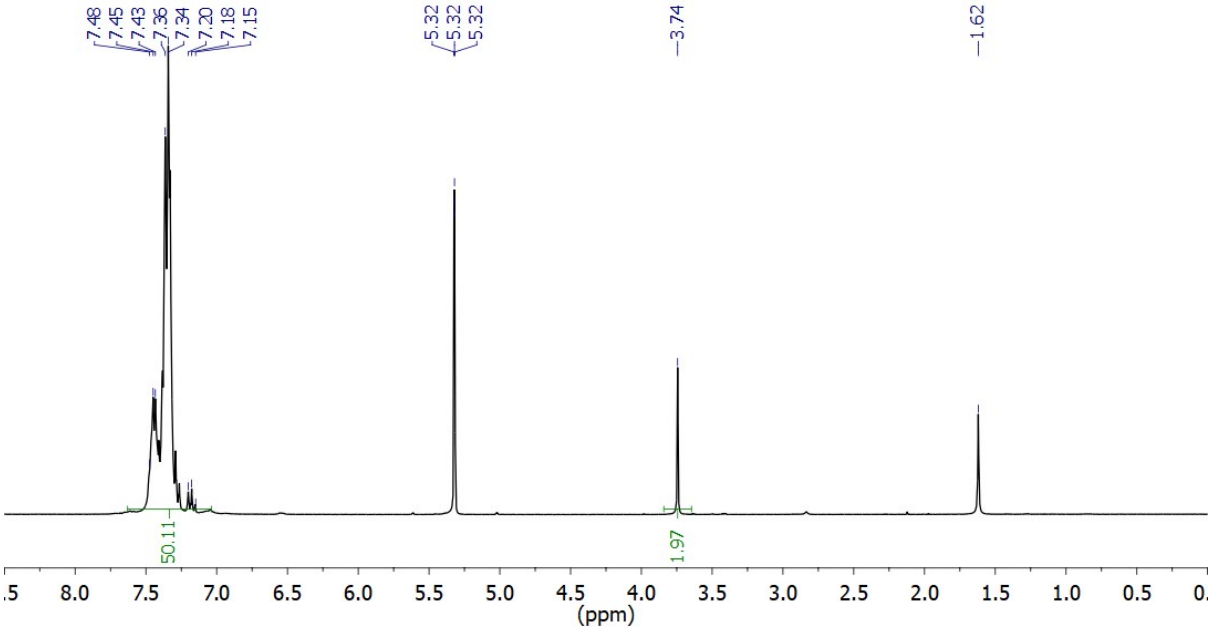
150
160
170
180
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

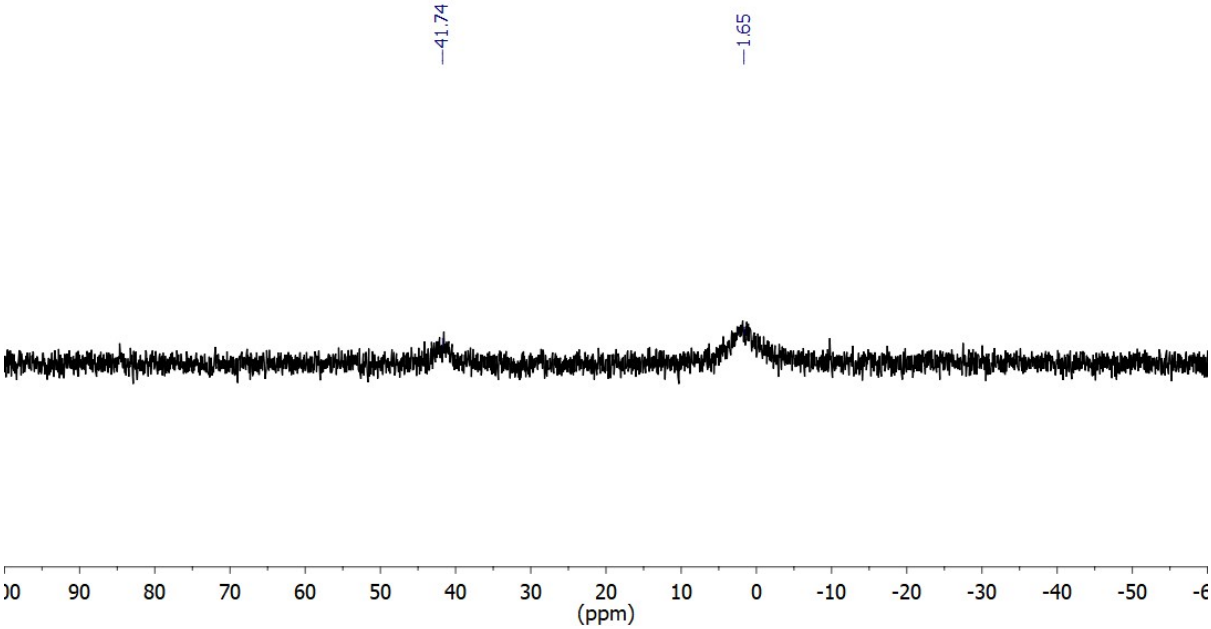
1.23. NMR Spectra for Complex 14

14

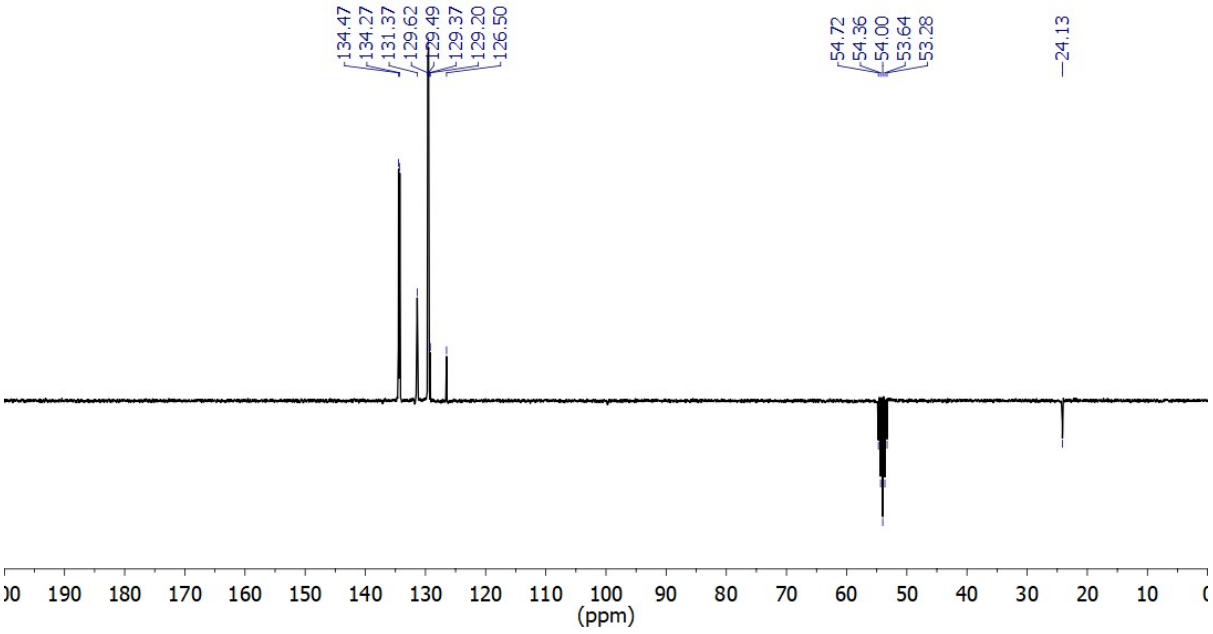
^{1}H NMR (300 MHz, CD_2Cl_2)



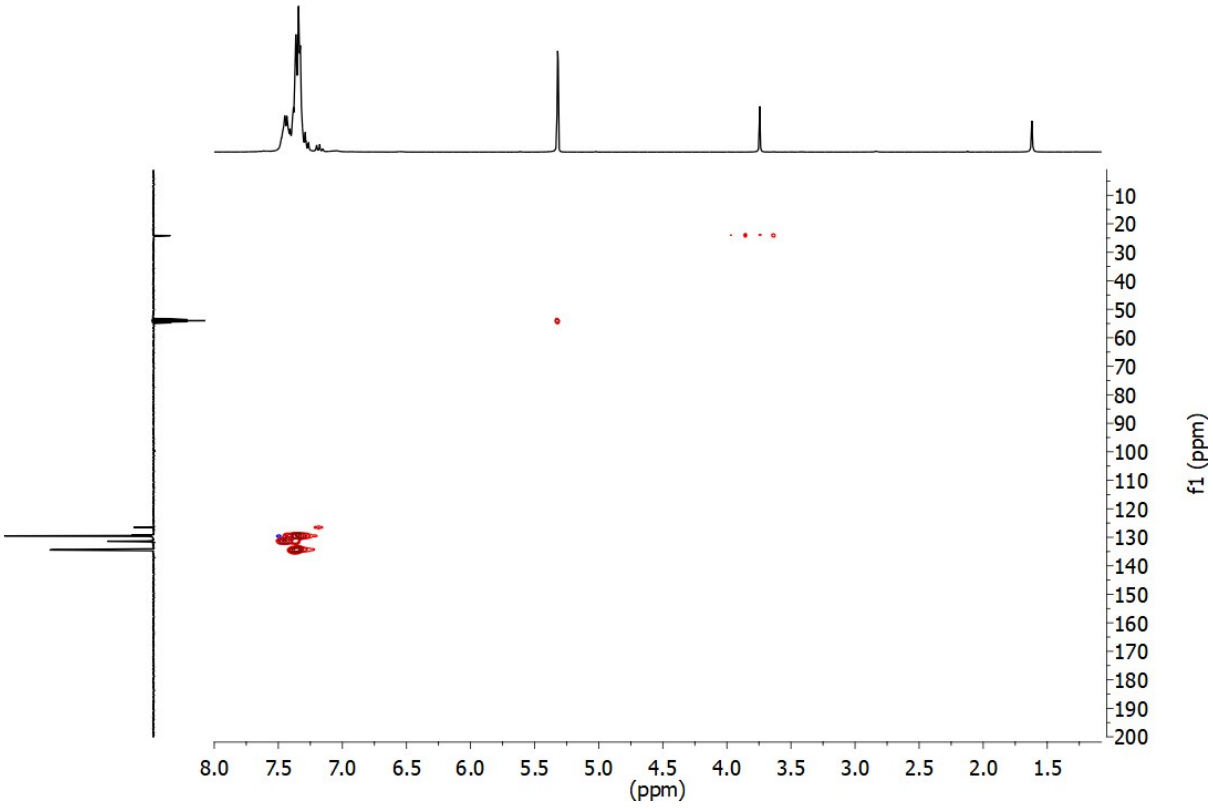
^{31}P NMR (162 MHz, CD_2Cl_2)



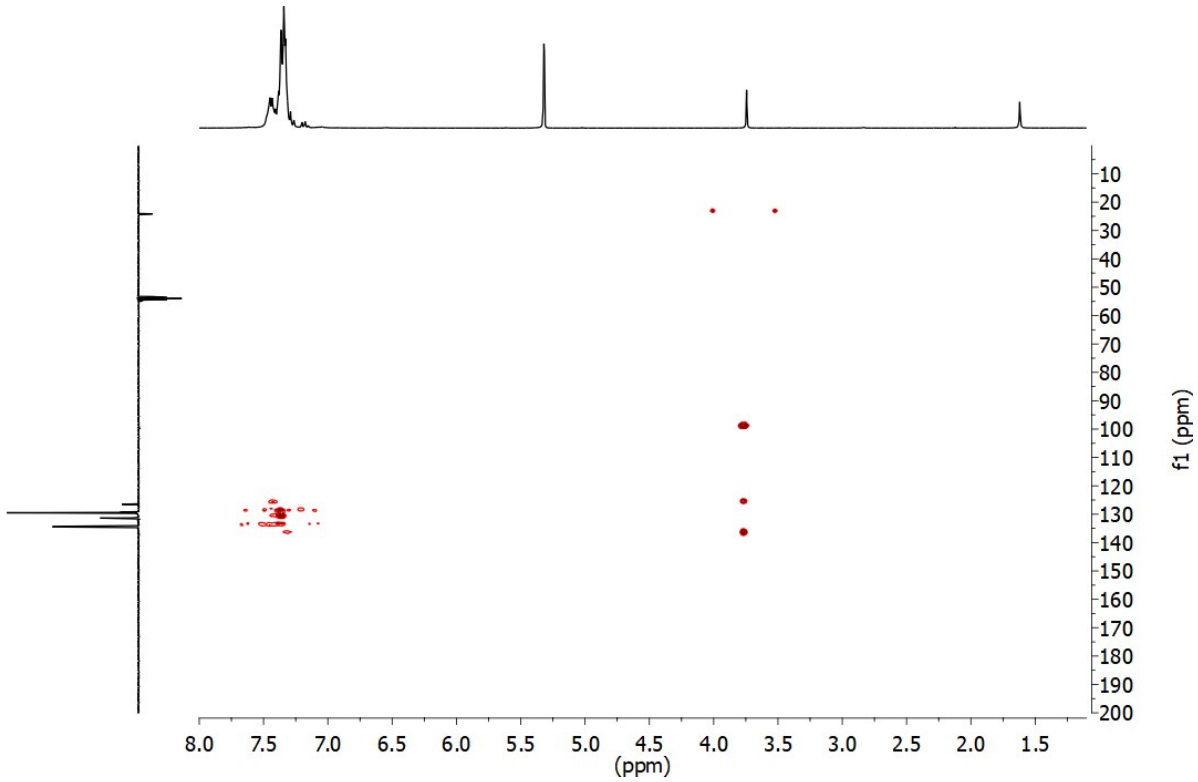
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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150
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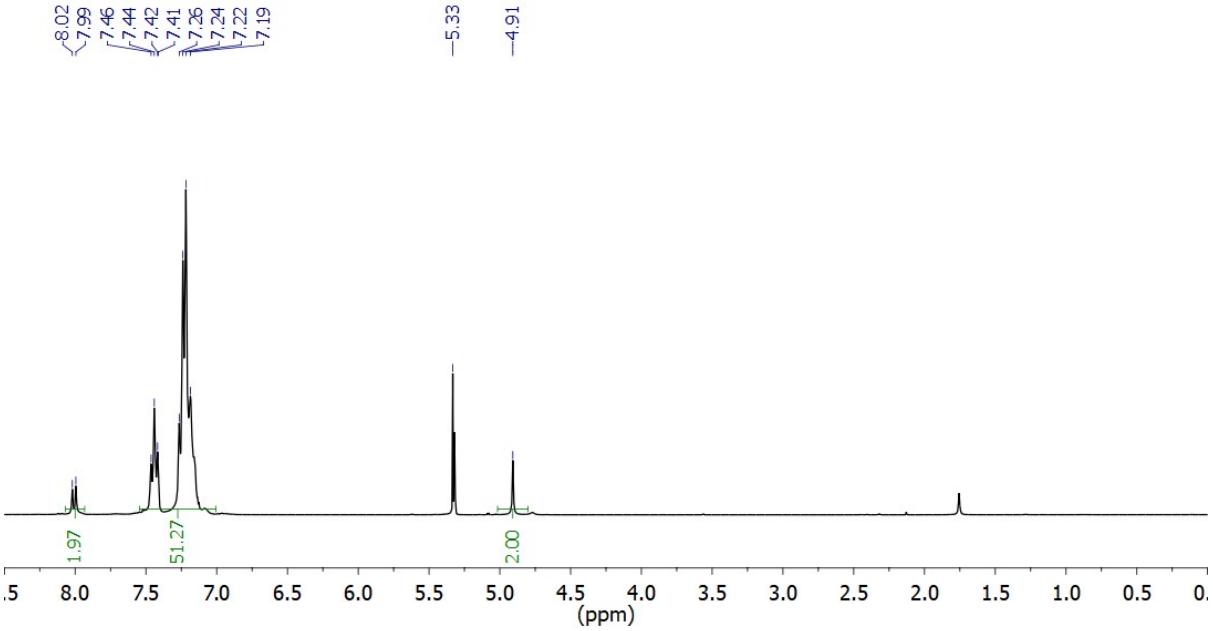
170
180
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

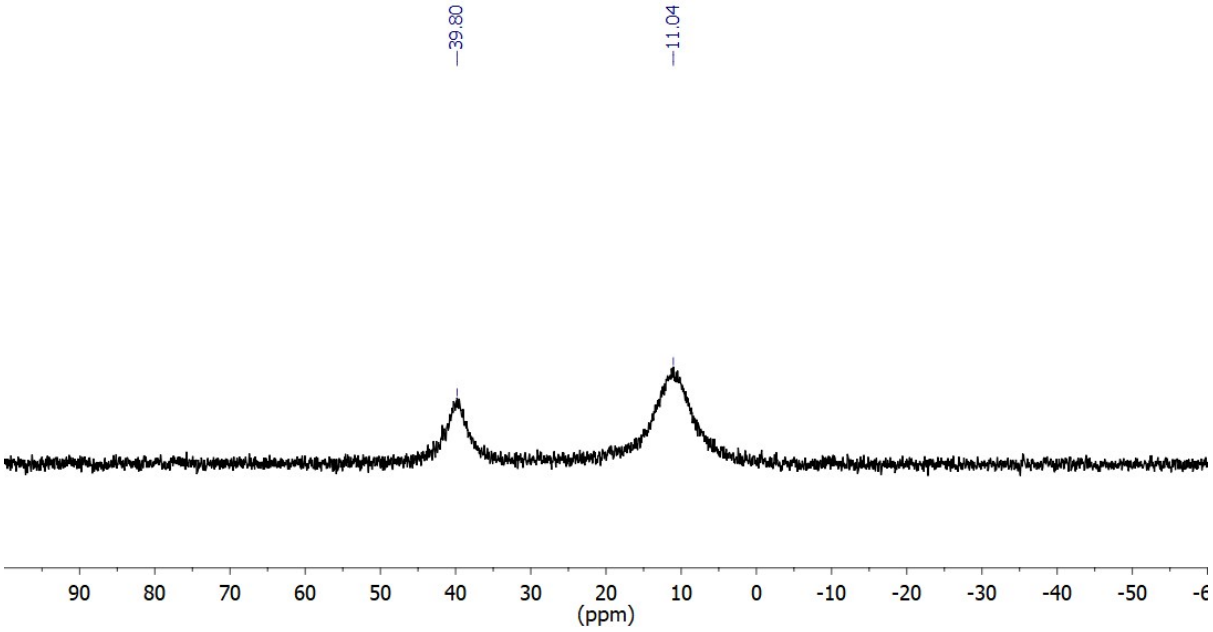
1.24. NMR Spectra for Complex 15

15

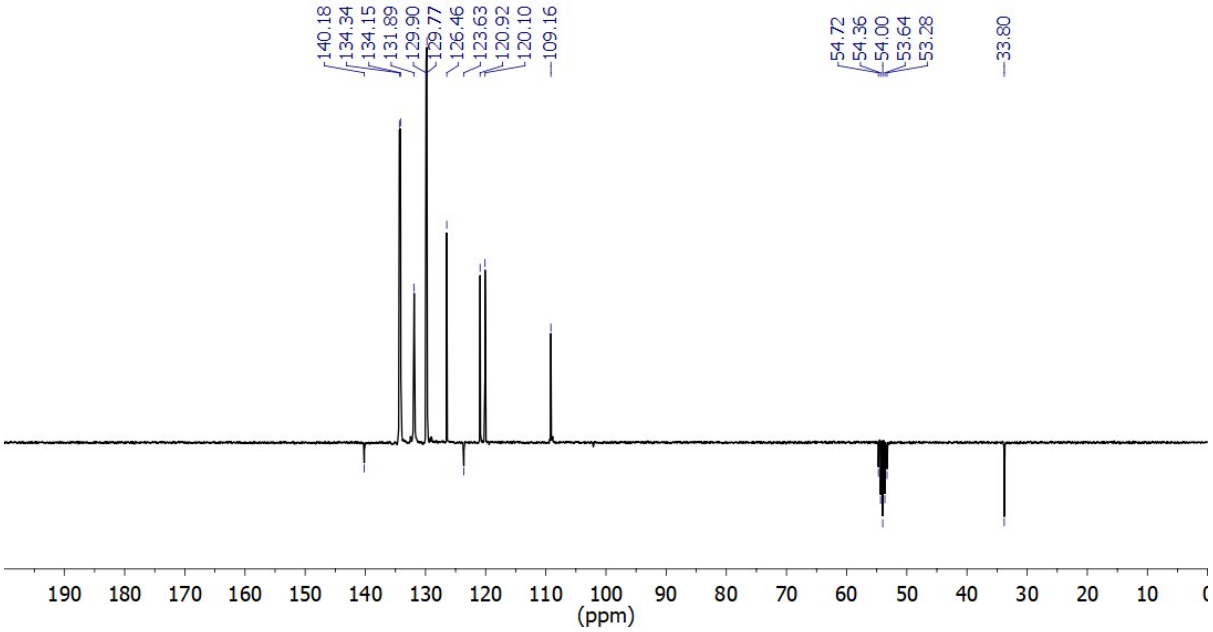
^{1}H NMR (300 MHz, CD_2Cl_2)



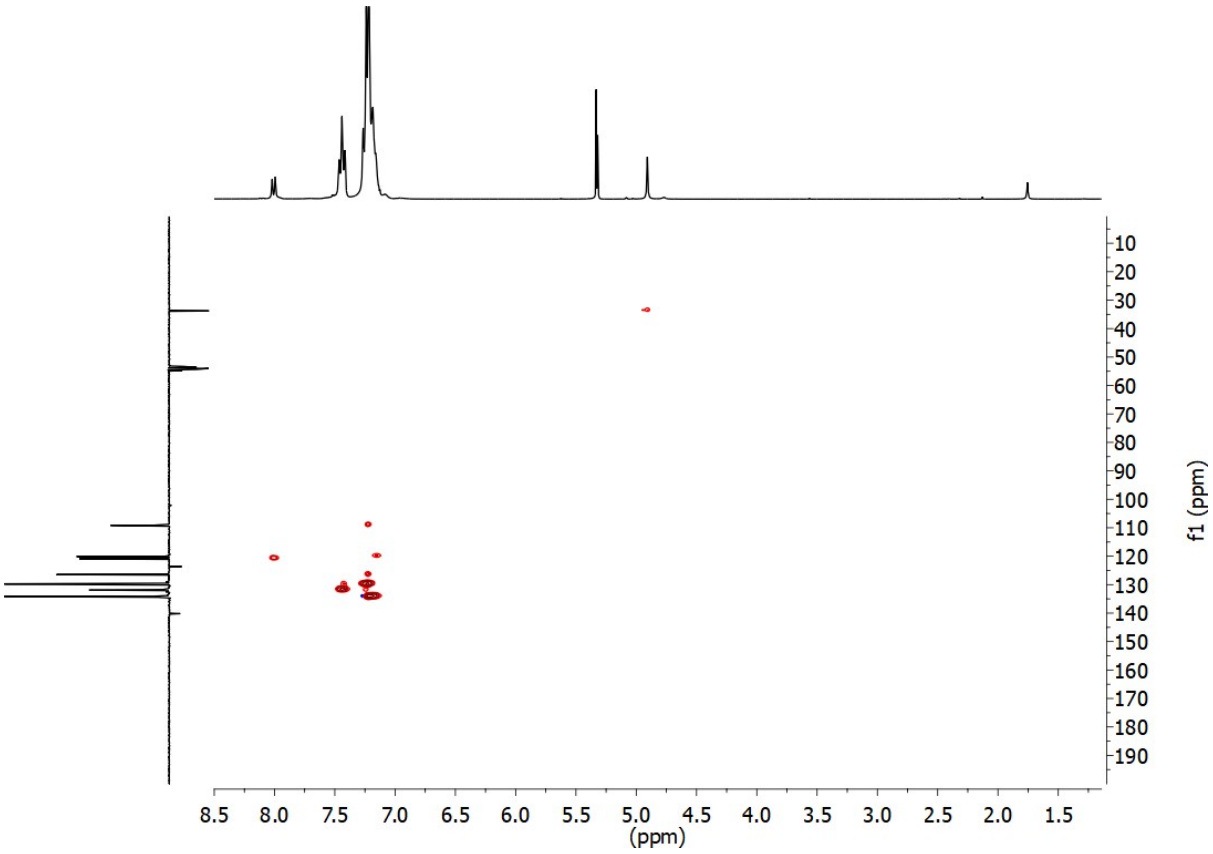
^{31}P NMR (162 MHz, CD_2Cl_2)



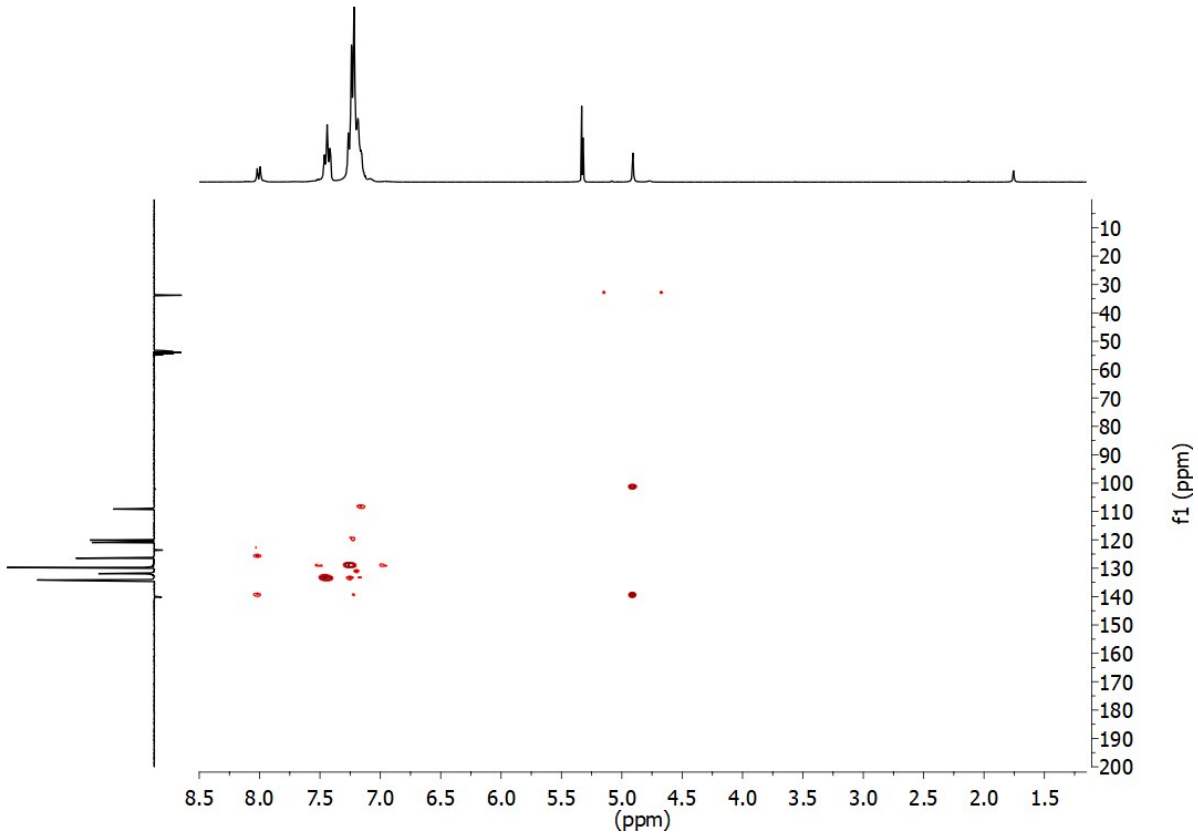
^{13}C NMR (75 MHz, CD_2Cl_2)



HSQC



HMBC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190
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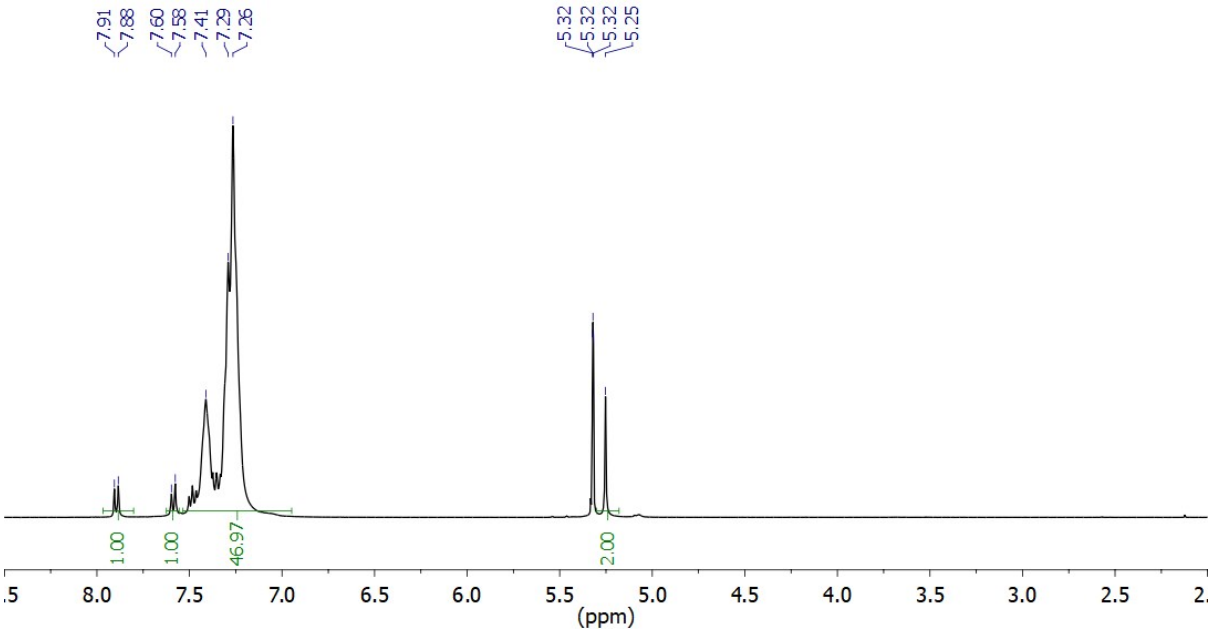
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

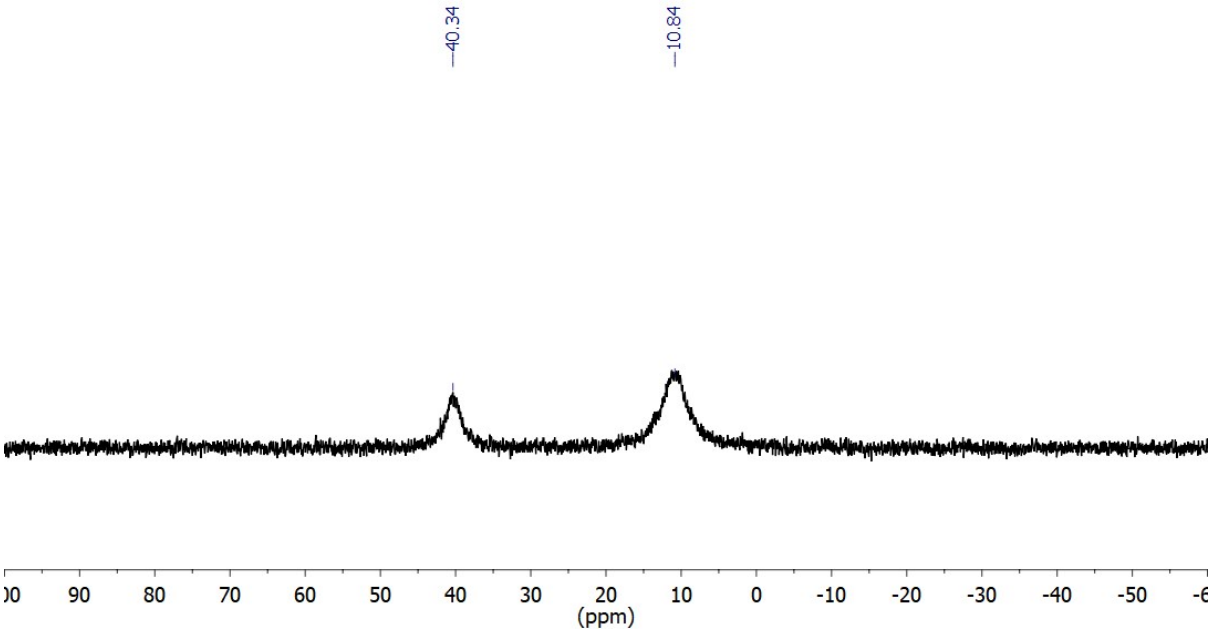
1.25. NMR Spectra for Complex 16

16

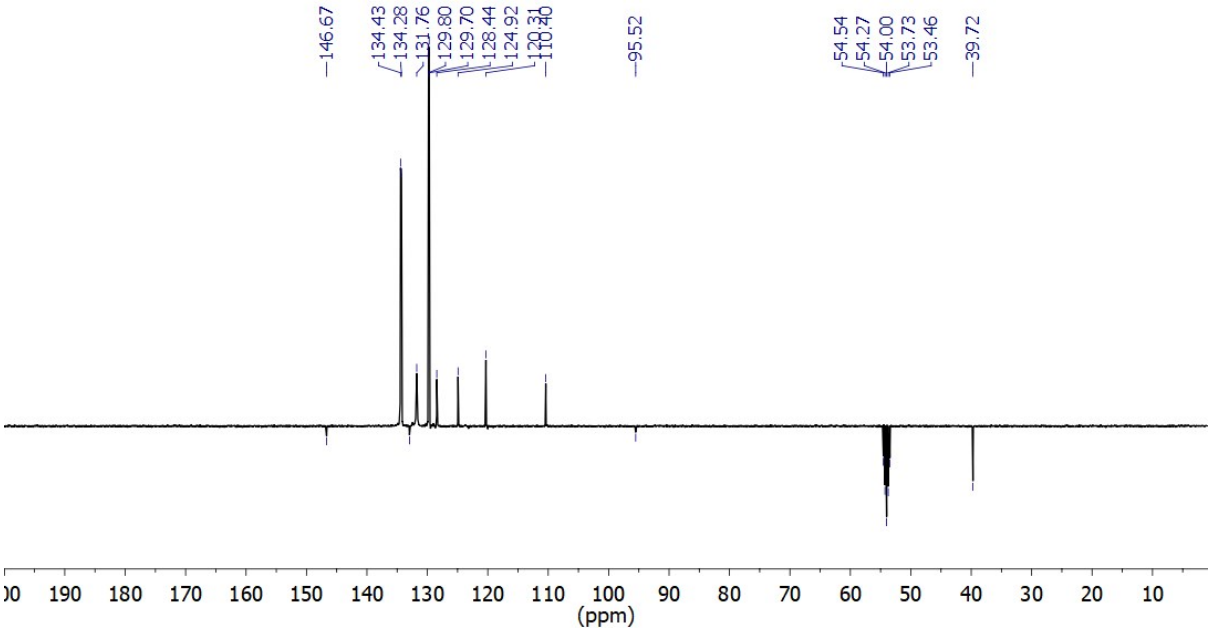
^{1}H NMR (300 MHz, CD_2Cl_2)



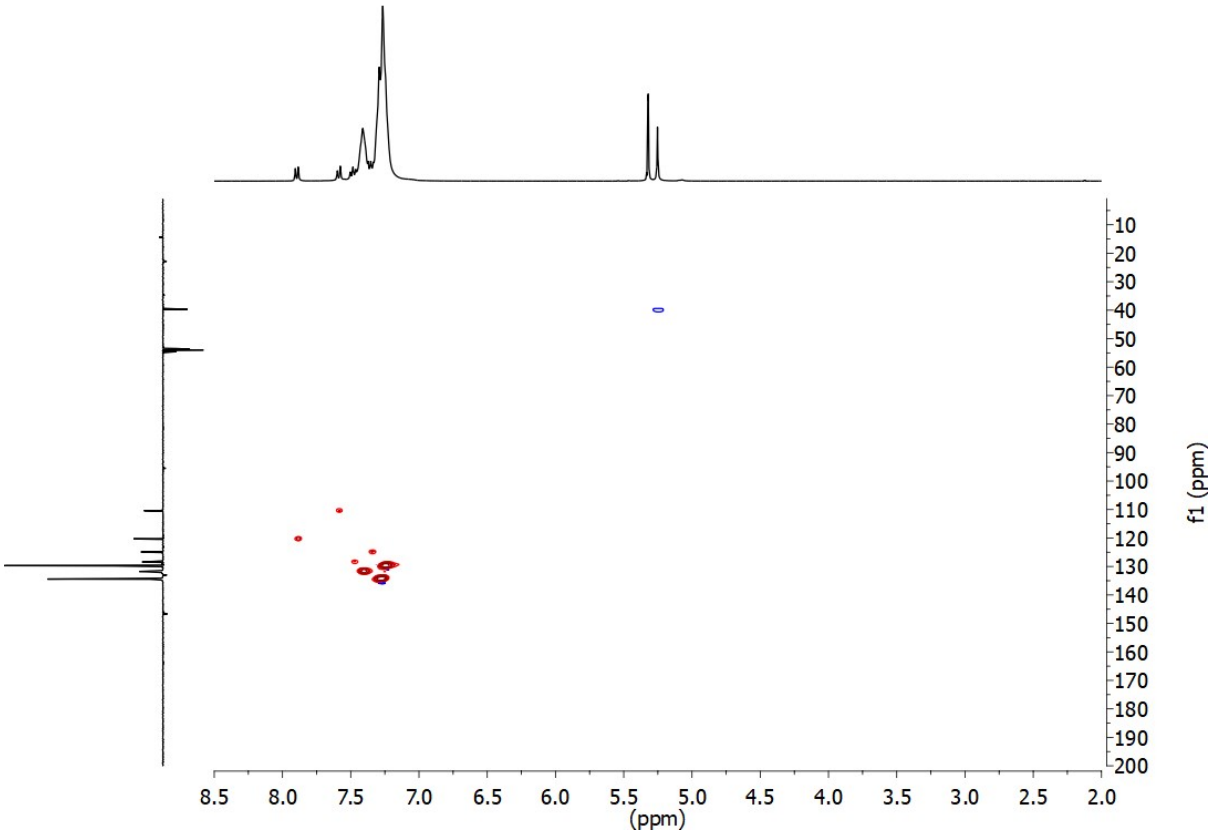
^{31}P NMR (162 MHz, CD_2Cl_2)



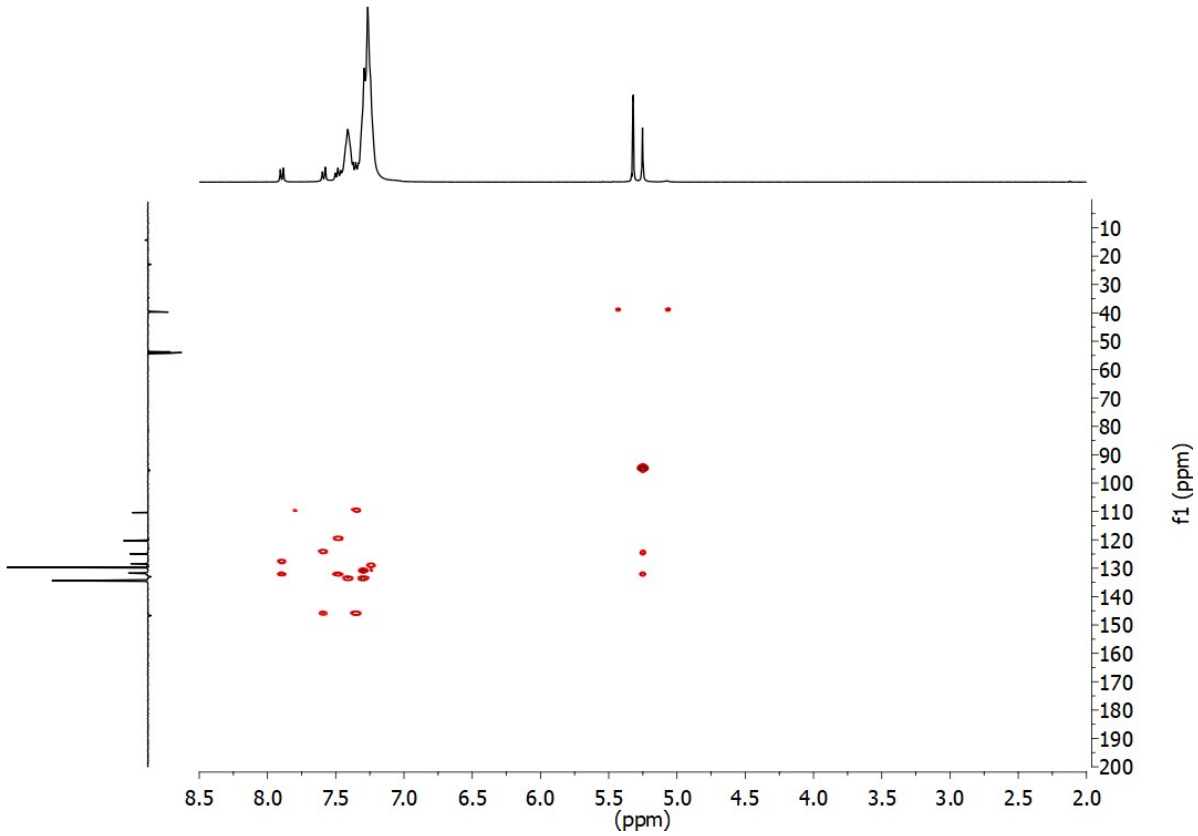
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



HMBC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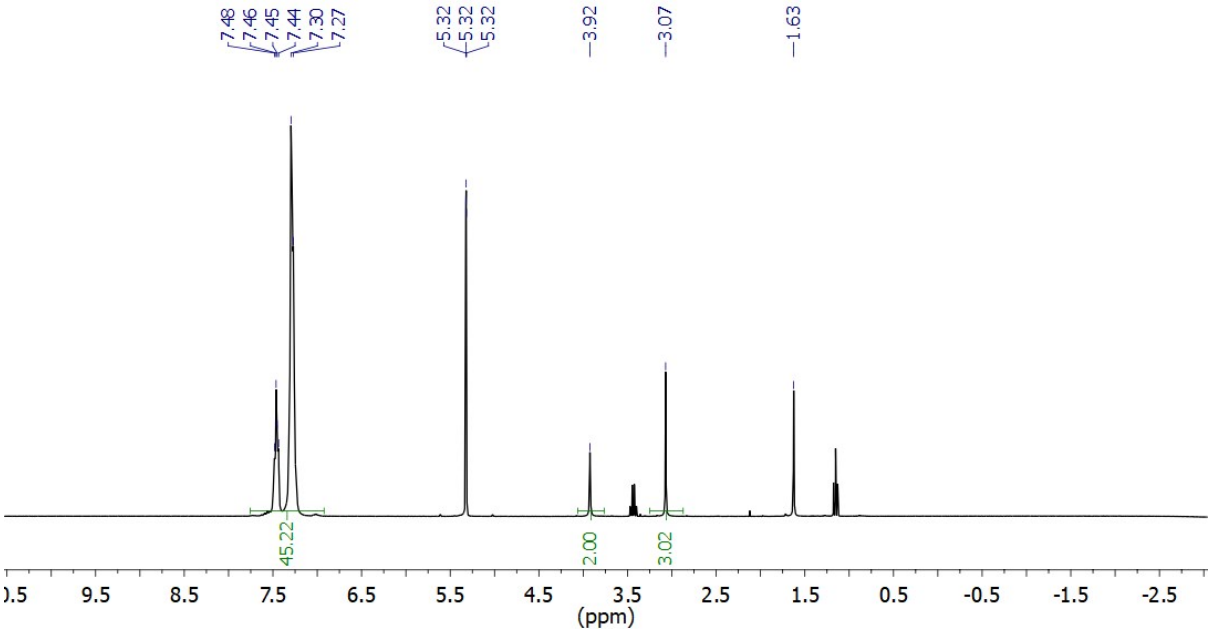
160
170
180
190
200
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
(ppm)

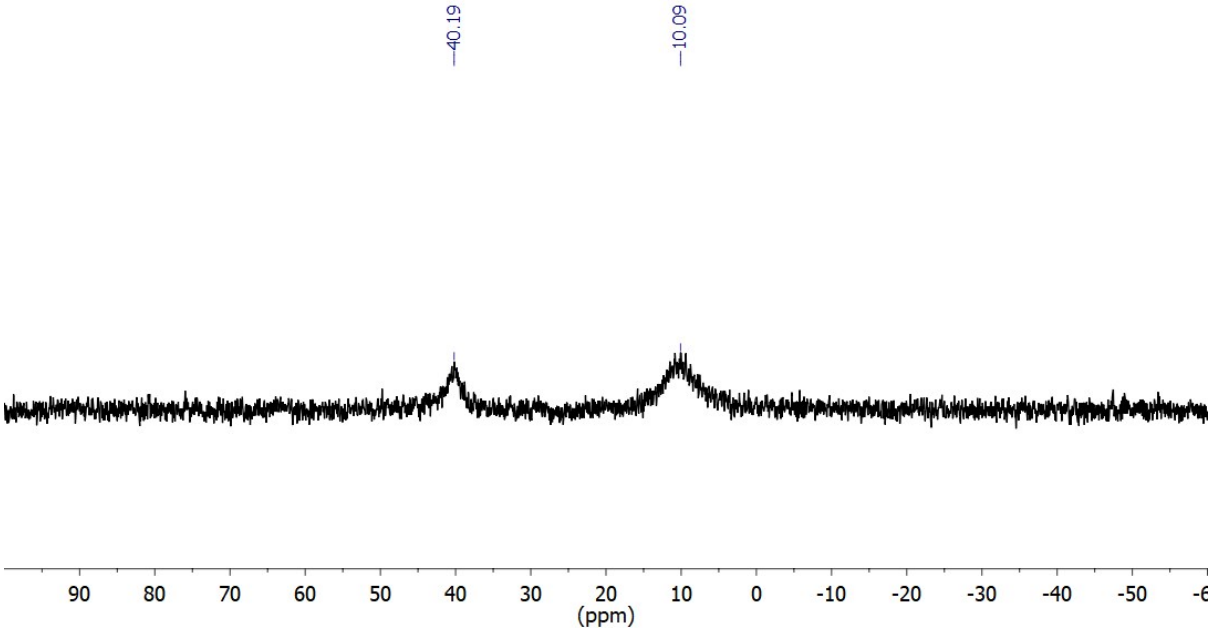
1.26. NMR Spectra for Complex 17

17

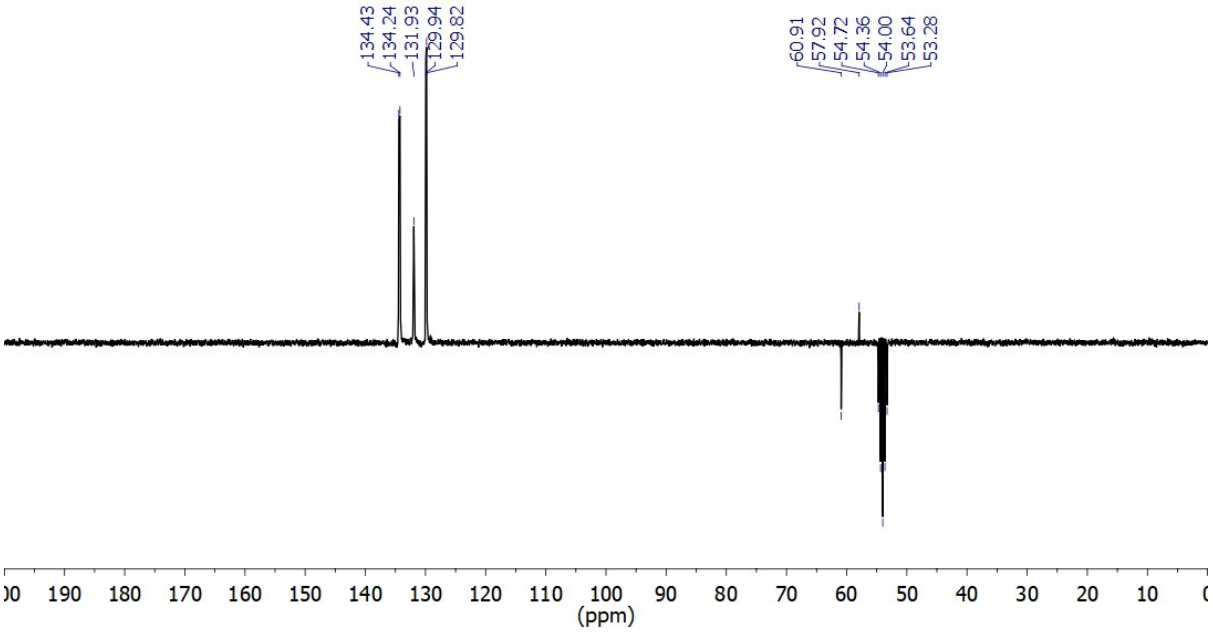
^{1}H NMR (300 MHz, CD_2Cl_2)



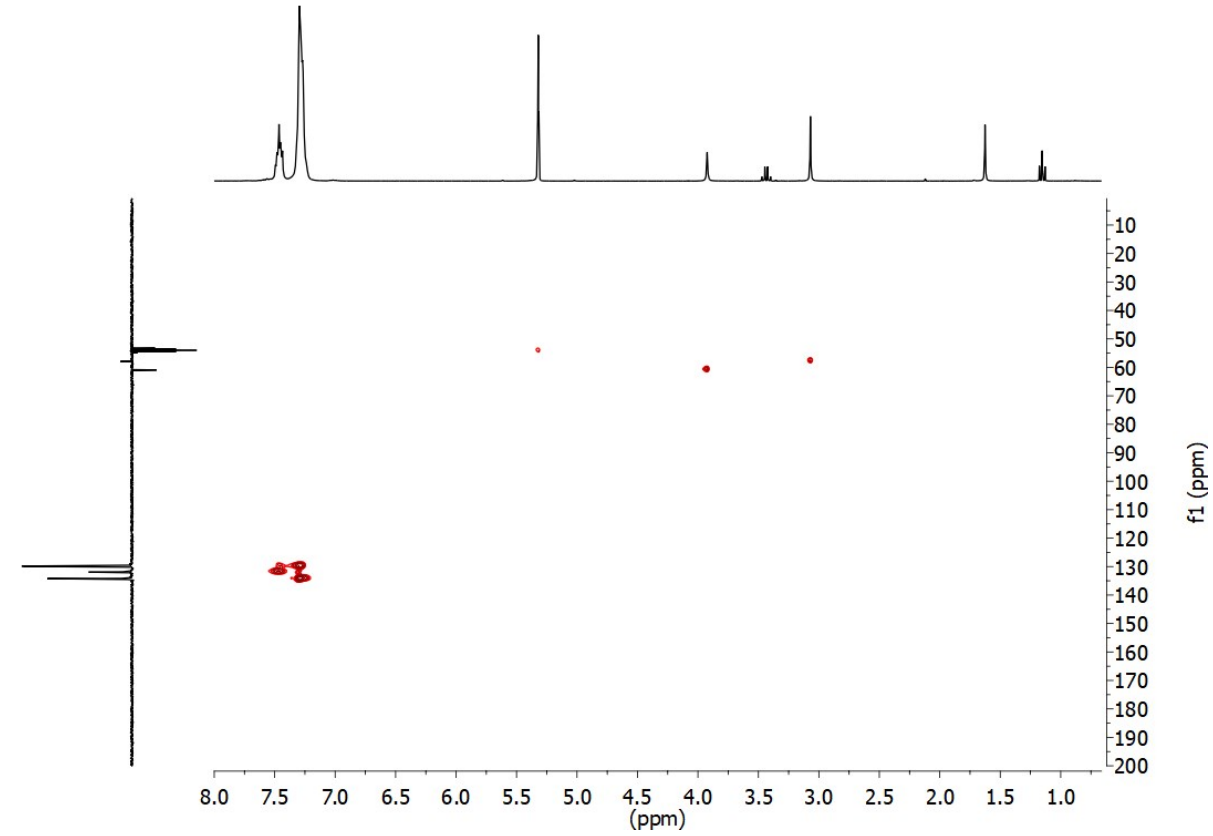
^{31}P NMR (162 MHz, CD_2Cl_2)



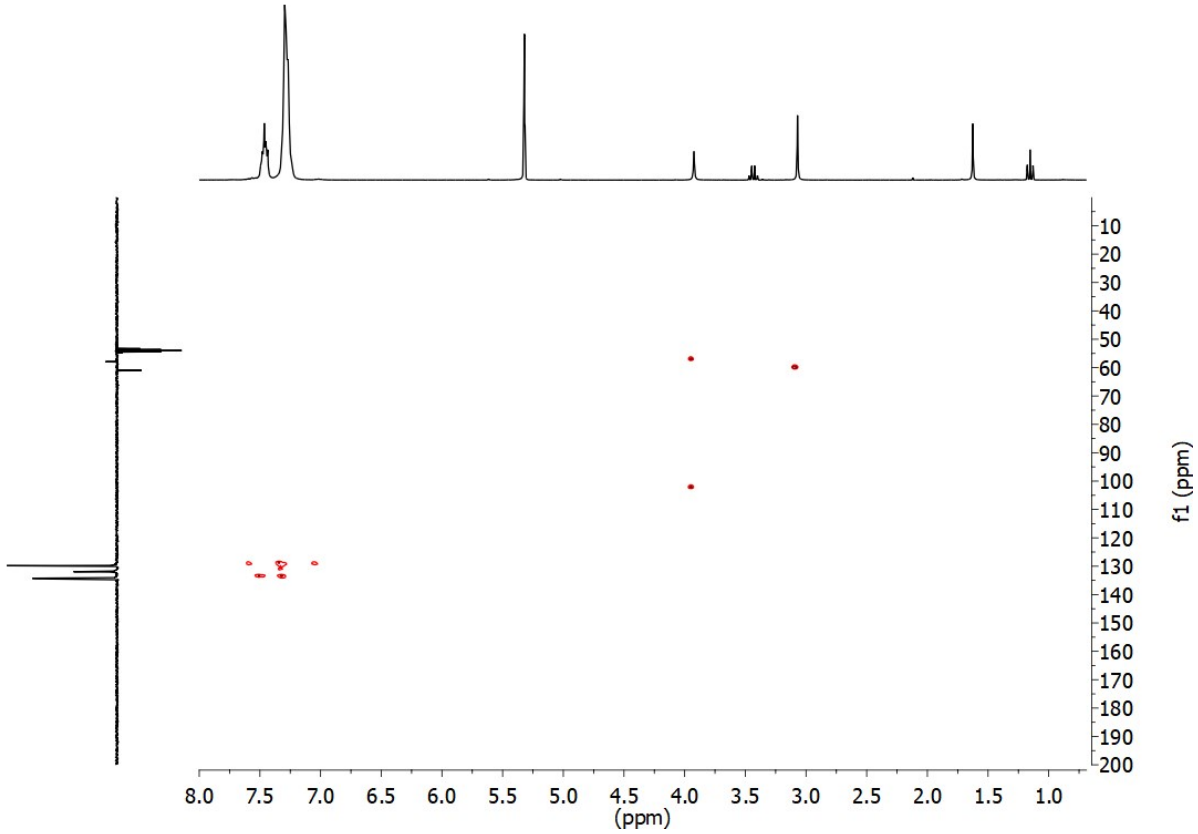
^{13}C APT (75 MHz, CD_2Cl_2)



HSCQ



HMBC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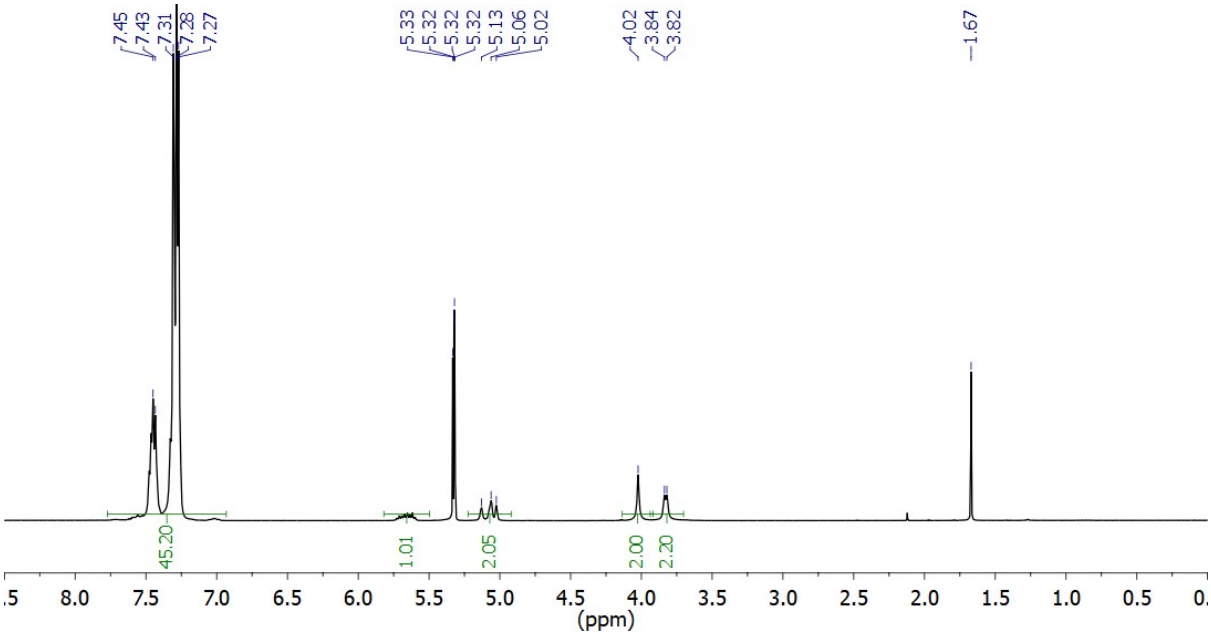
130
140
150
160
170
180
190
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

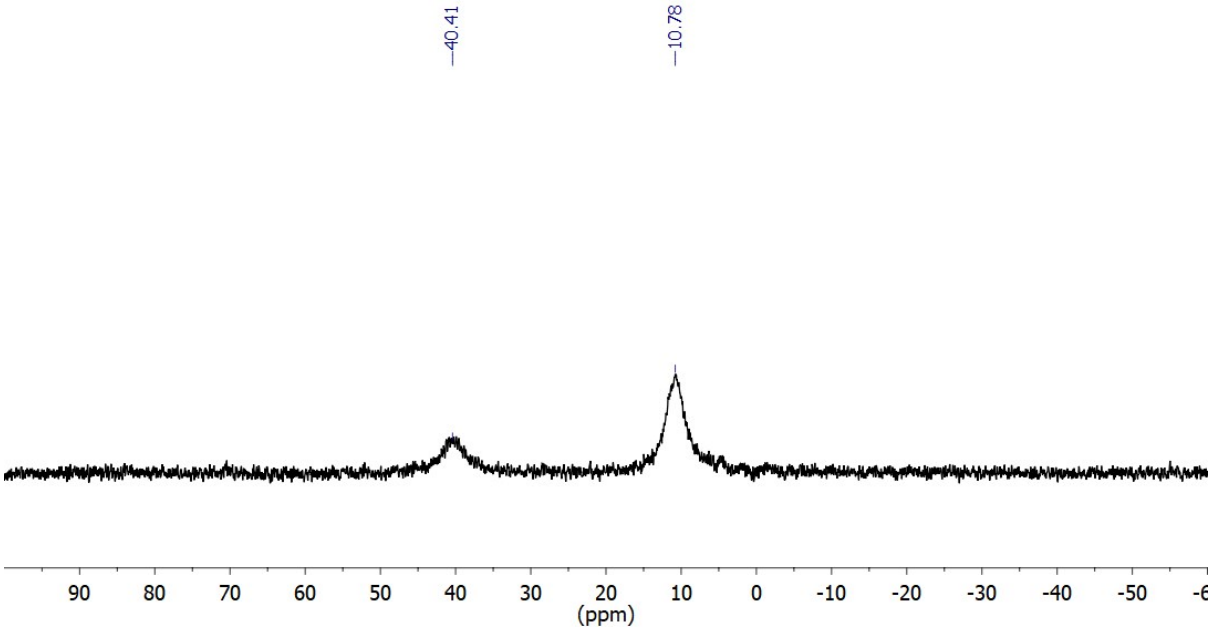
1.27. NMR Spectra for Complex 18

18

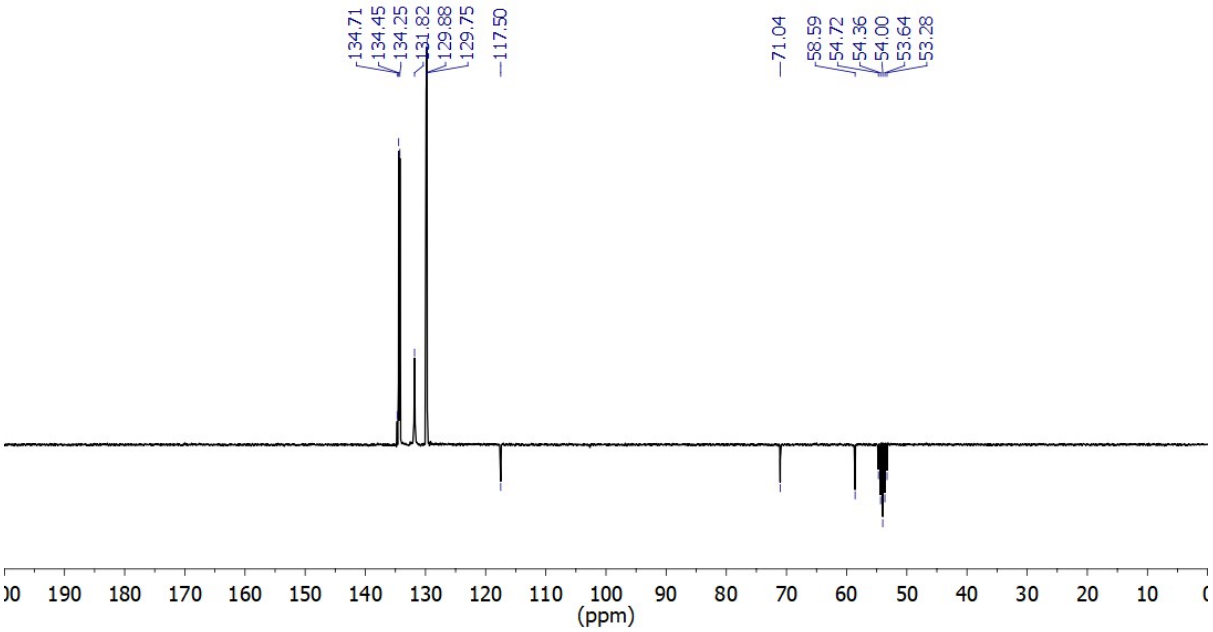
^{1}H NMR (300 MHz, CD_2Cl_2)



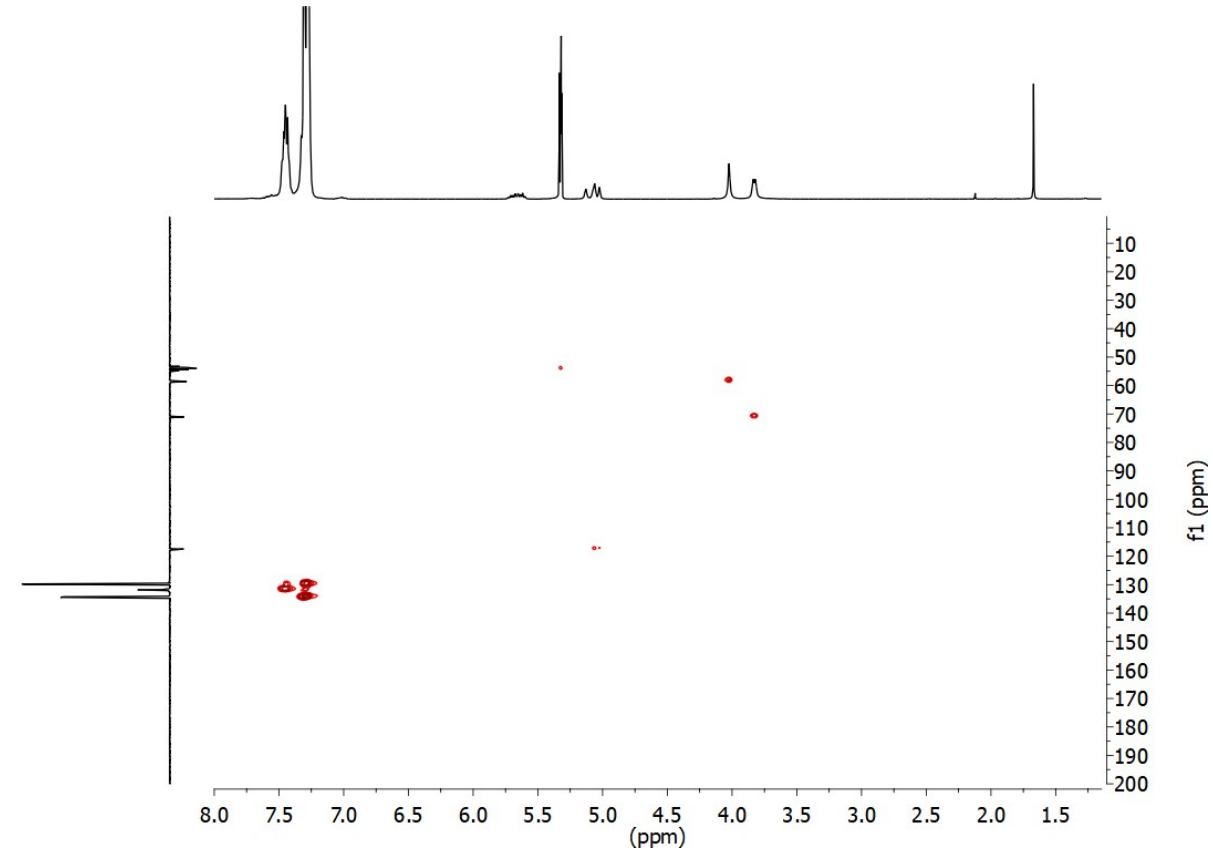
^{31}P NMR (162 MHz, CD_2Cl_2)



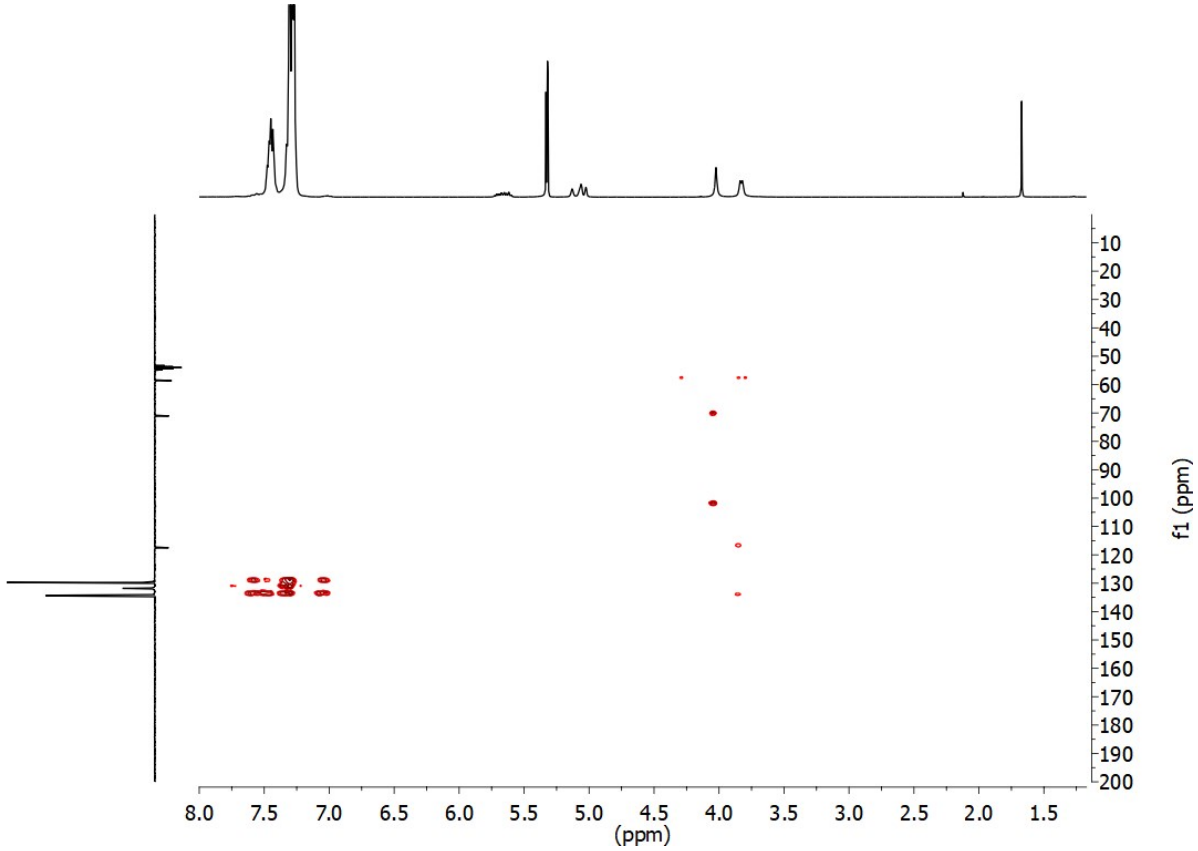
^{13}C APT (75 MHz, CD_2Cl_2)



HSQC



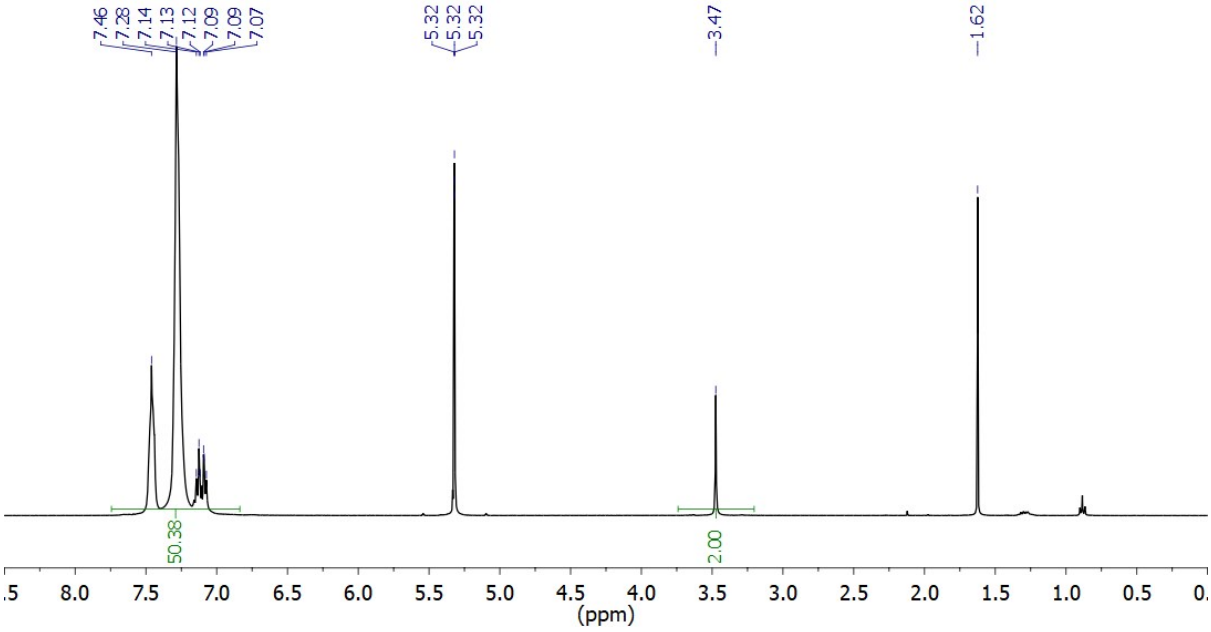
HMBC


10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
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
(ppm)

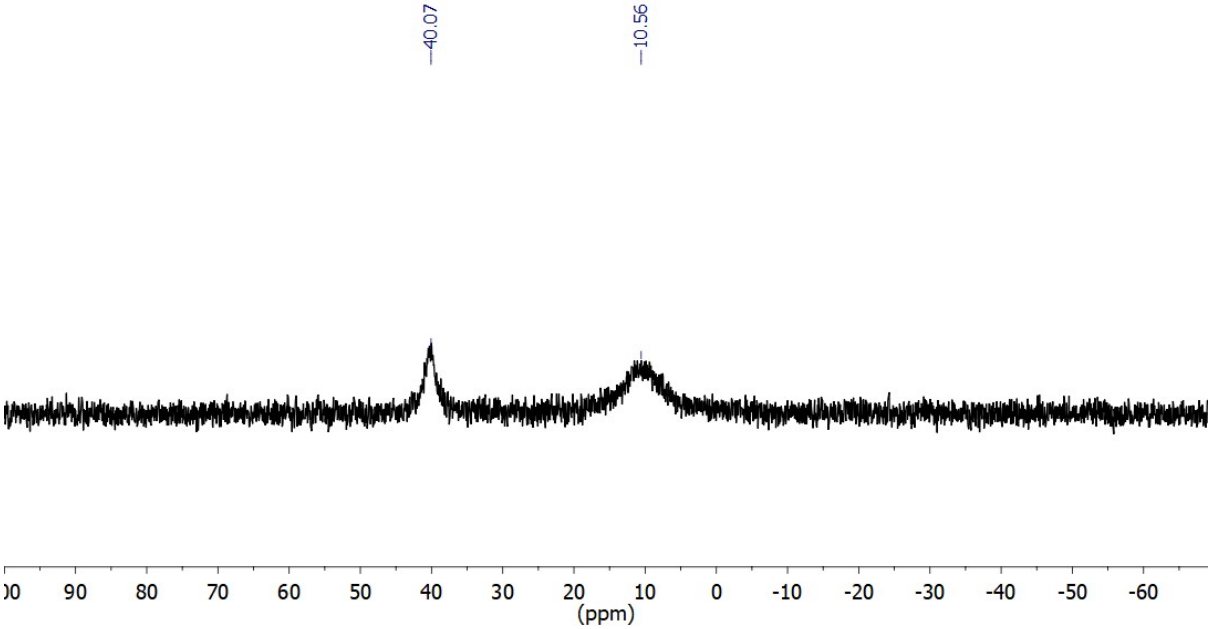
1.28. NMR Spectra for Complex 19

19

^{1}H NMR (400 MHz, CD_2Cl_2)



^{31}P NMR (162 MHz, CD_2Cl_2)



1.29. NMR Stability Studies

Approx. 10 mg of complex was dissolved in DMSO-d_6 (0.6 ml) and NMR spectra recorded after 1 h, 6 h and 24 h.

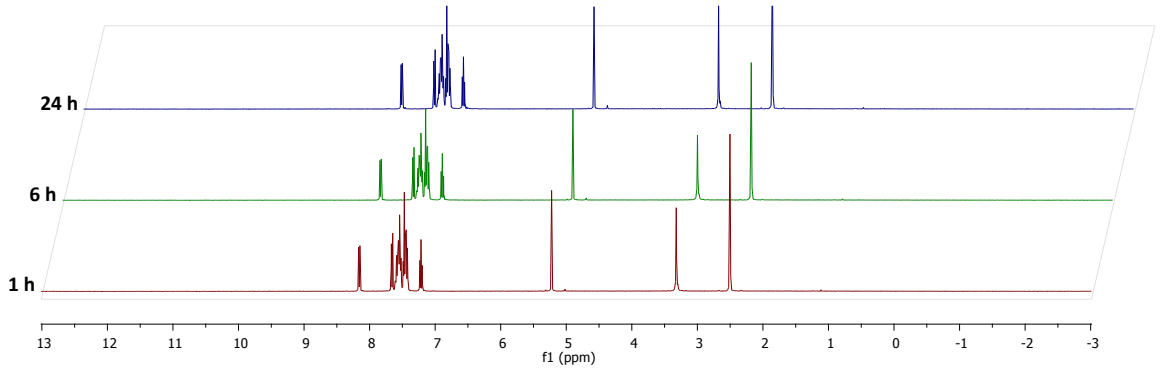


Figure S1. Stability of compound **3** after 24 h in DMSO (400 MHz).

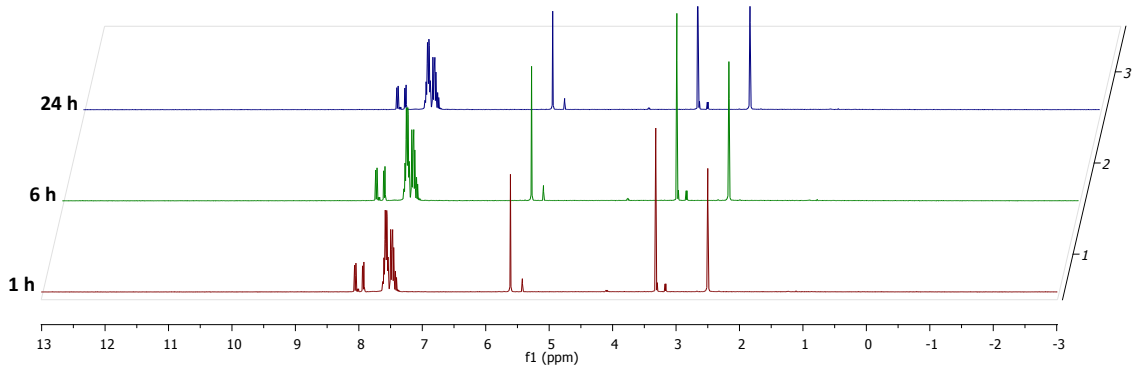


Figure S2. Stability of compound **4** after 24 h in DMSO (400 MHz).

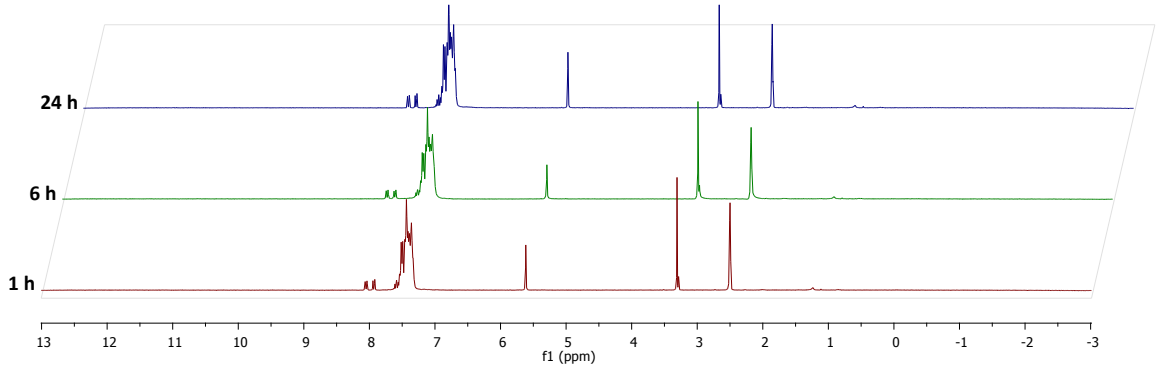


Figure S3. Stability of compound **11** after 24 h in DMSO (400 MHz).

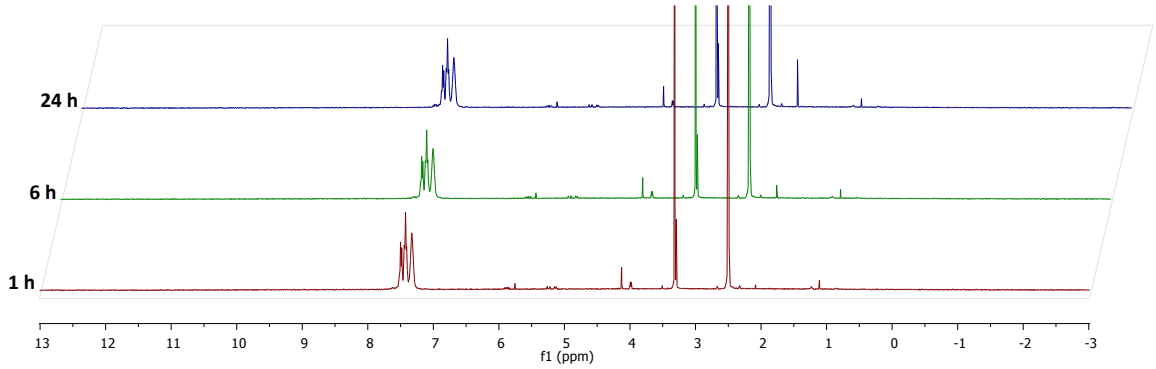


Figure S4. Stability of compound **13** after 24 h in DMSO (400 MHz).

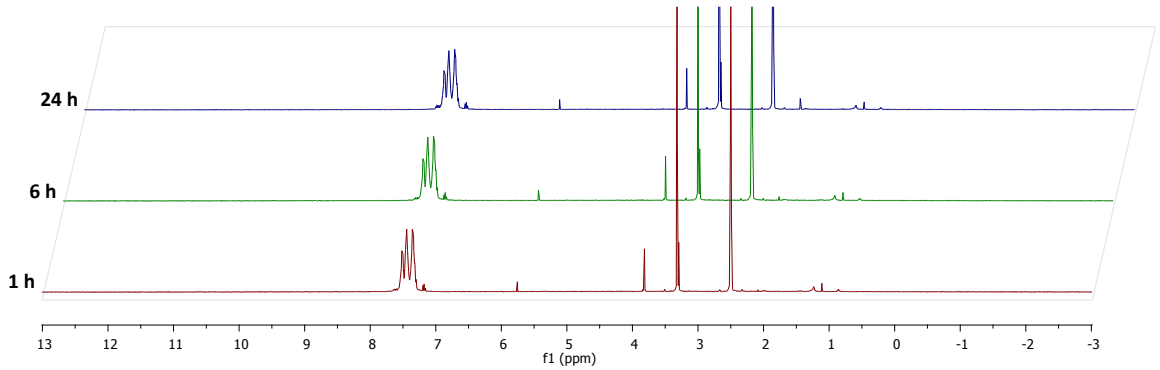


Figure S5. Stability of compound **14** after 24 h in DMSO (400 MHz).

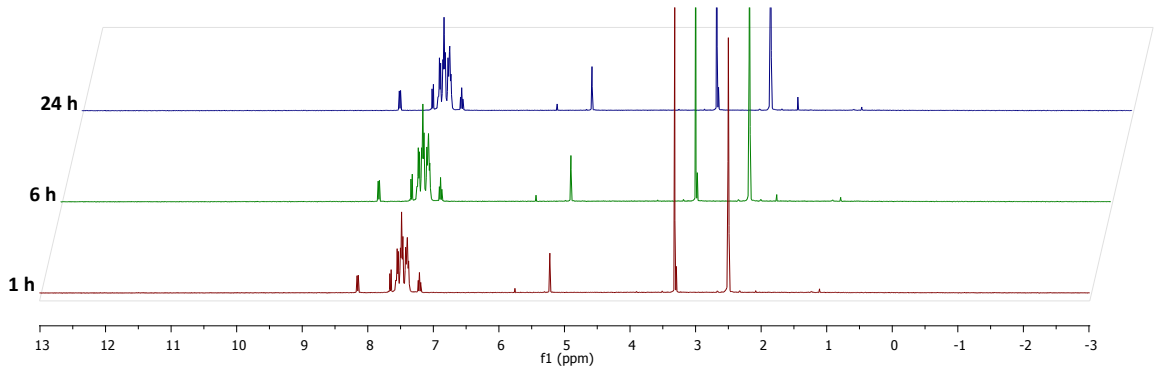


Figure S6. Stability of compound **15** after 24 h in DMSO (400 MHz).

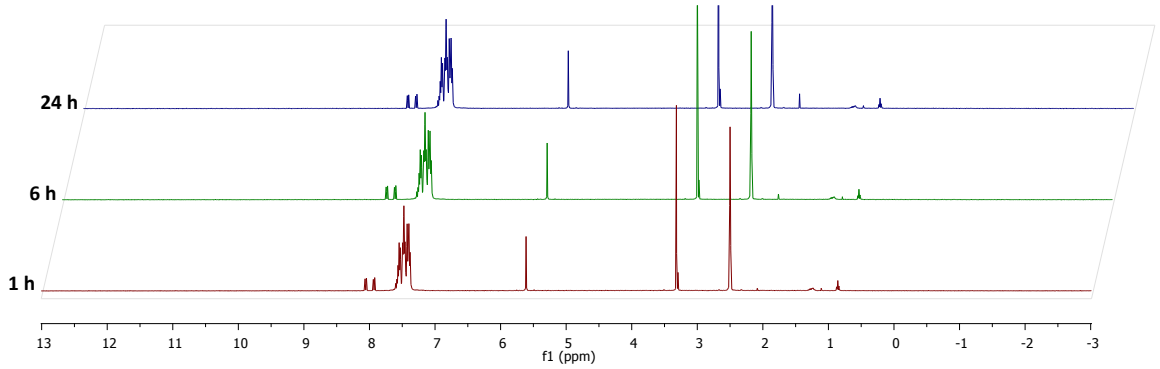


Figure S7. Stability of compound **16** after 24 h in DMSO (400 MHz).

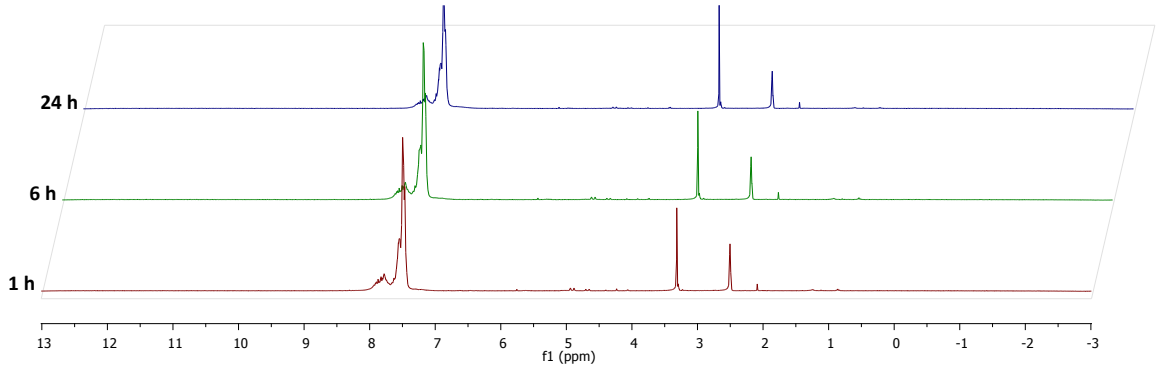


Figure S8. Stability of compound **17** after 24 h in DMSO (400 MHz).

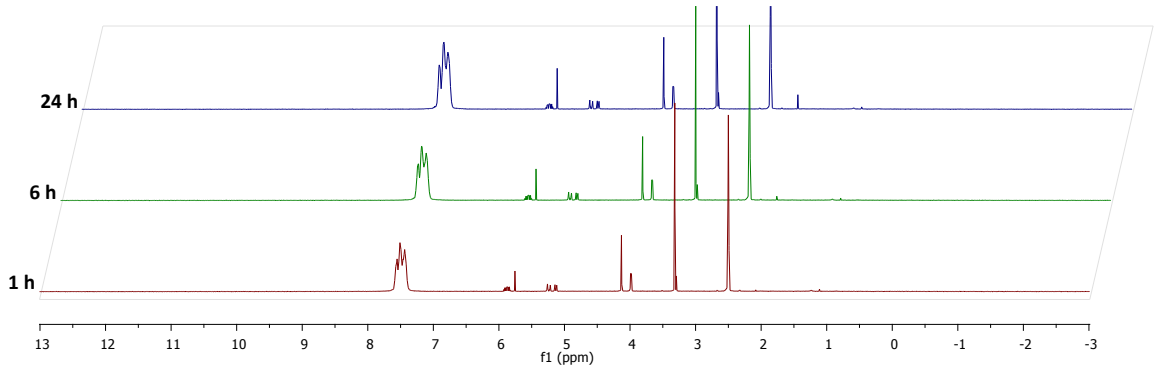


Figure S9. Stability of compound **18** after 24 h in DMSO (400 MHz).

1.30. UV-Vis Stability Studies

UV-Vis spectra were recorded using a Thermo Fisher Scientific Evolution 600 UV–Visible Spectrophotometer with 1 × 1 cm quartz cuvettes at 240–600 nm and 298 K. Stock solutions of the compounds were prepared in DMSO to a final concentration of 0.02 M. An intermediary solution of the compound was prepared in DMSO to a final concentration of 2 mM. The final solution of the selected compound was prepared with DMSO and PBS buffer to a final concentration of 20 µM (20 µL of the intermediary solution, 380 µL of DMSO and 1.600 µL of the PBS buffer solution) A baseline correction was done using the corresponding dimethyl sulfoxide DMSO solution in the buffer (400 µL in 2 mL, 20 %). Spectra were recorded at times 0 h, 1 h, 3 h and 24 h.

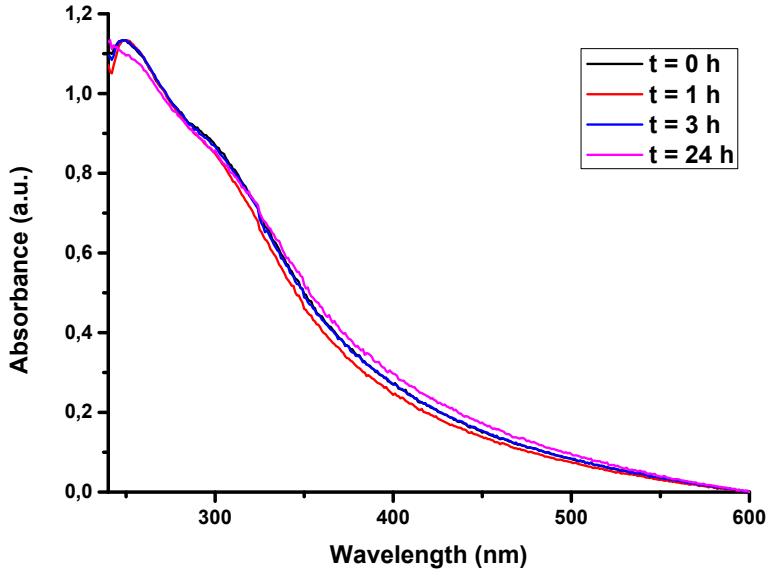


Figure S10. Stability of compound **11** after 24 h in DMSO/PBS

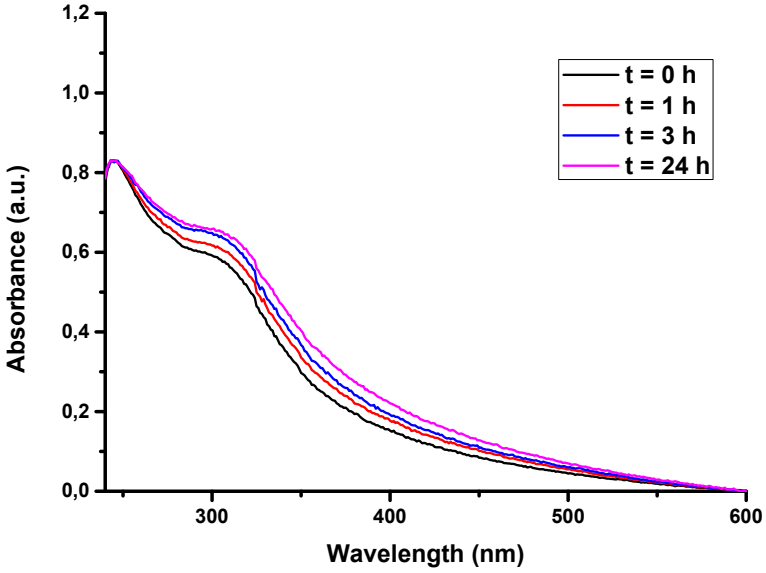


Figure S11. Stability of compound **13** after 24 h in DMSO/PBS

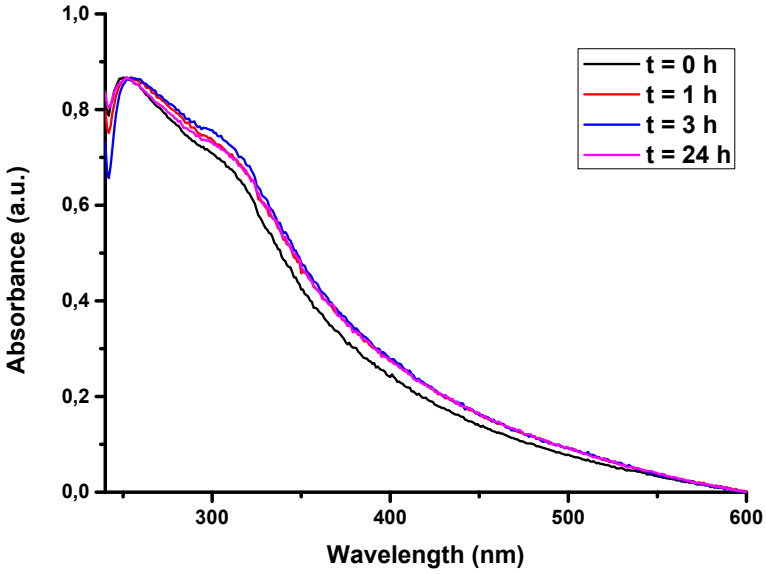


Figure S12. Stability of compound **14** after 24 h in DMSO/PBS

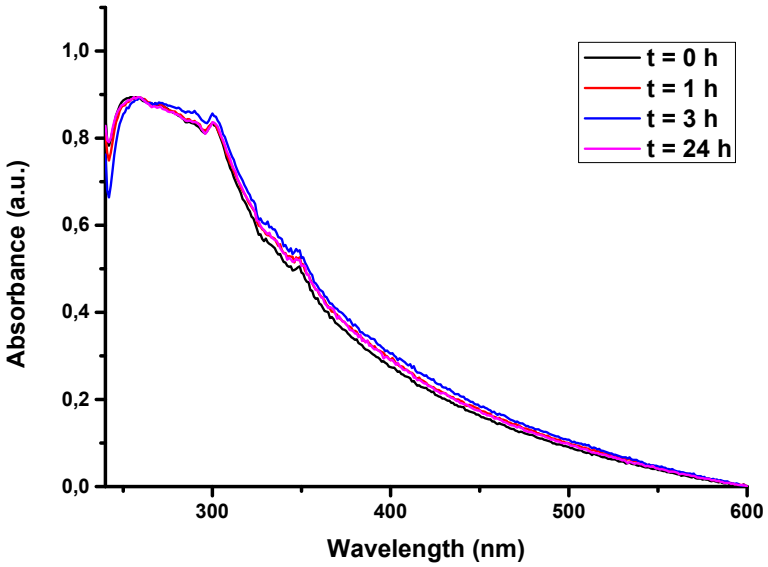


Figure S13. Stability of compound **15** after 24 h in DMSO/PBS

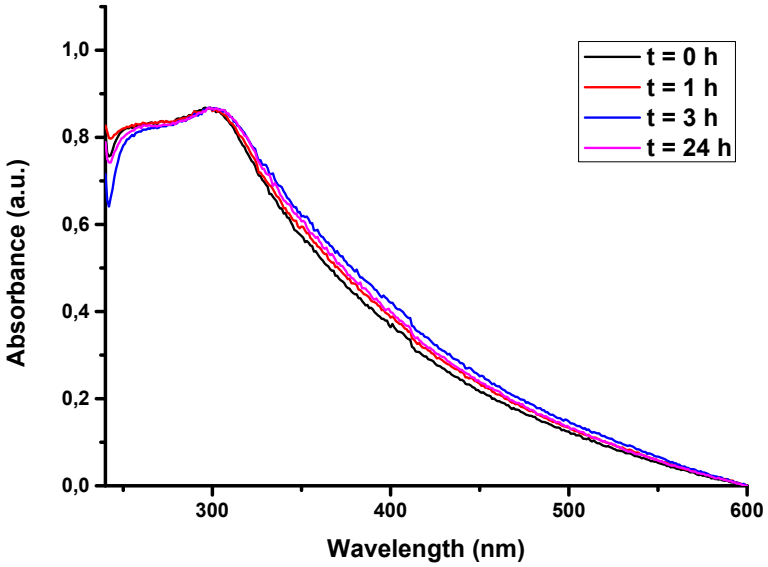


Figure S14. Stability of compound **16** after 24 h in DMSO/PBS

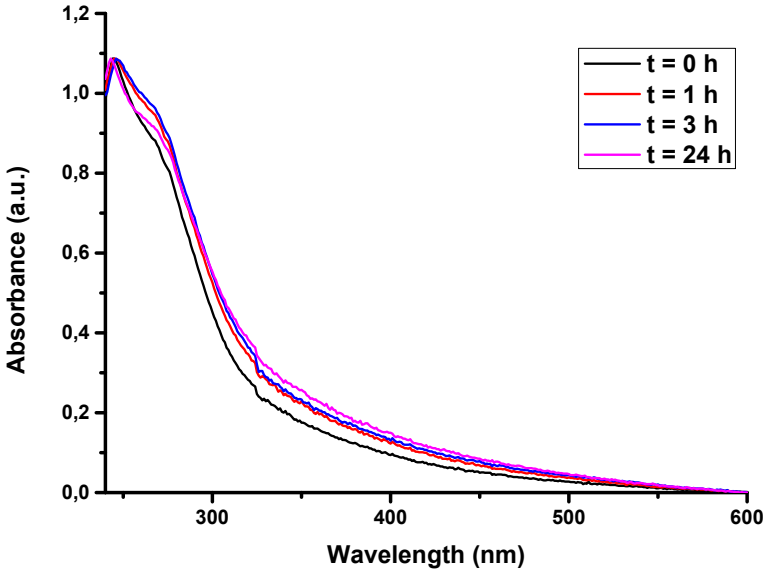


Figure S15. Stability of compound **17** after 24 h in DMSO/PBS

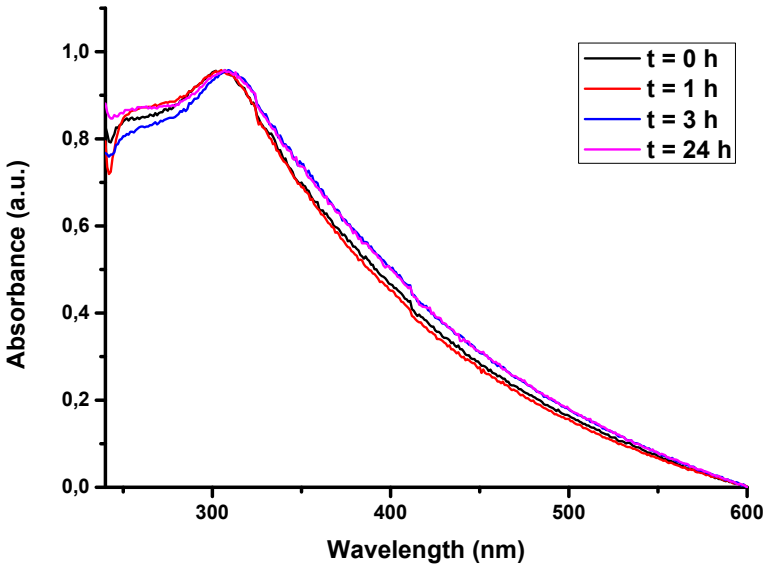


Figure S16. Stability of compound **18** after 24 h in DMSO/PBS

1.31. Dose Response Curves for MTT Assays

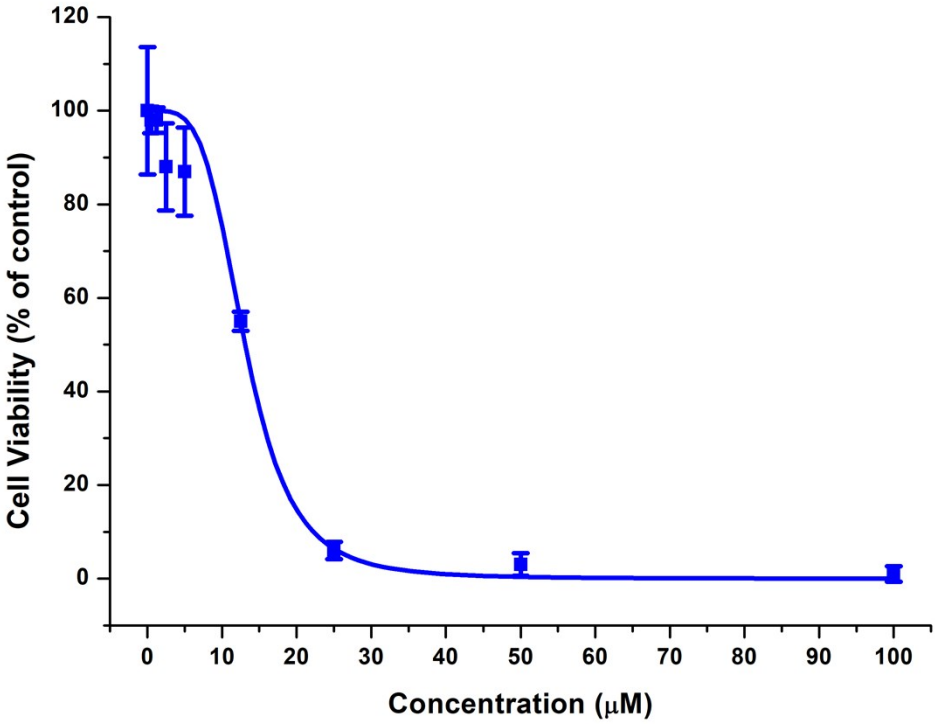


Figure S17. Cell viability (% of control) vs concentration (μM) for complex **2**

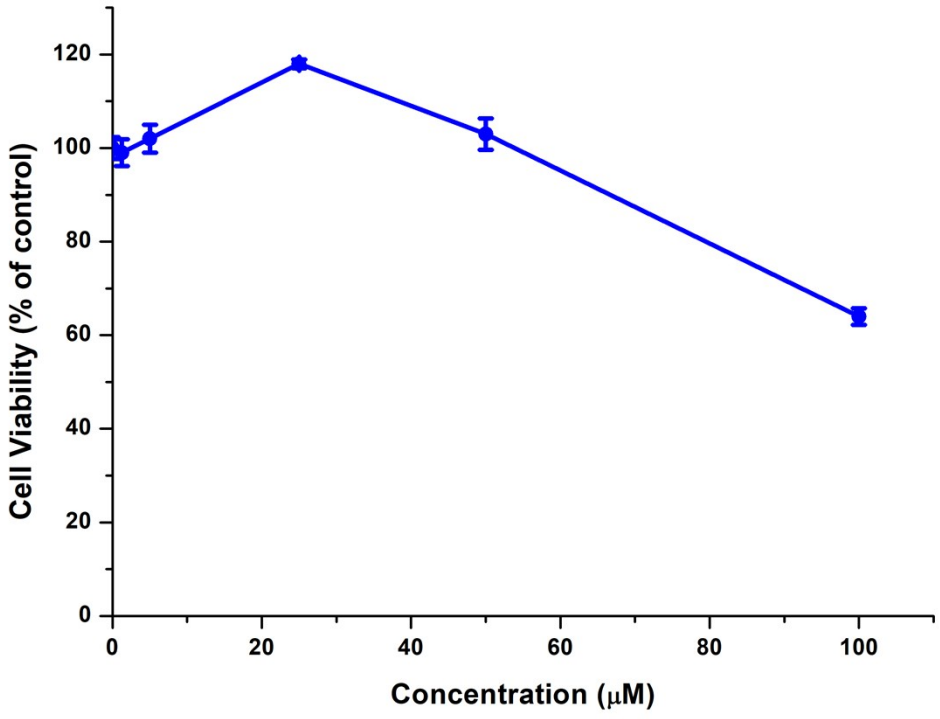


Figure S18. Cell viability (% of control) vs concentration (μM) for complex **3**

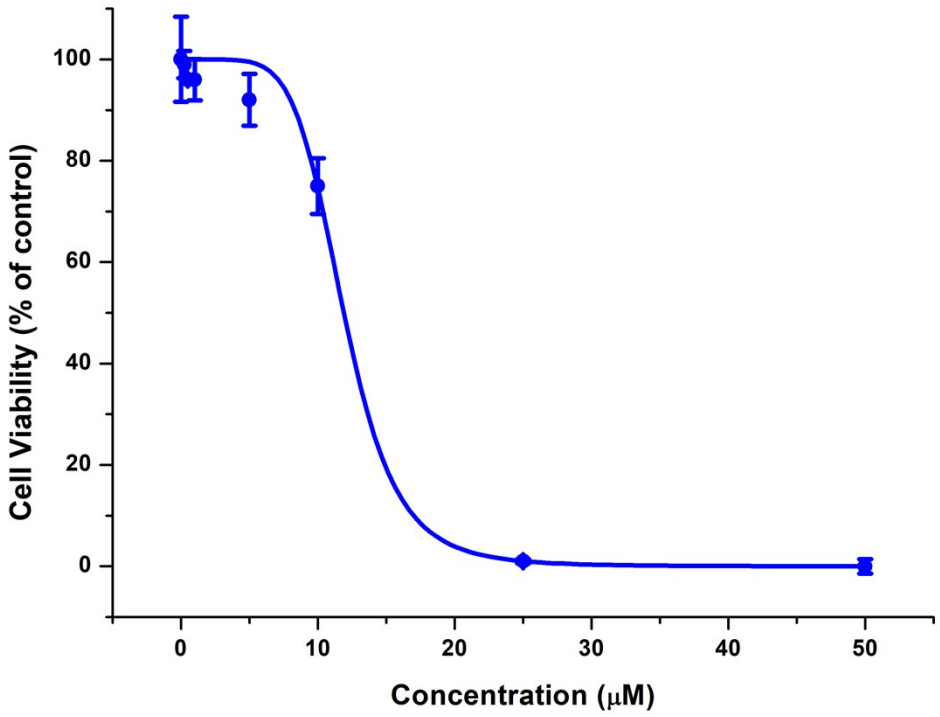


Figure S19. Cell viability (% of control) vs concentration (μM) for complex **4**

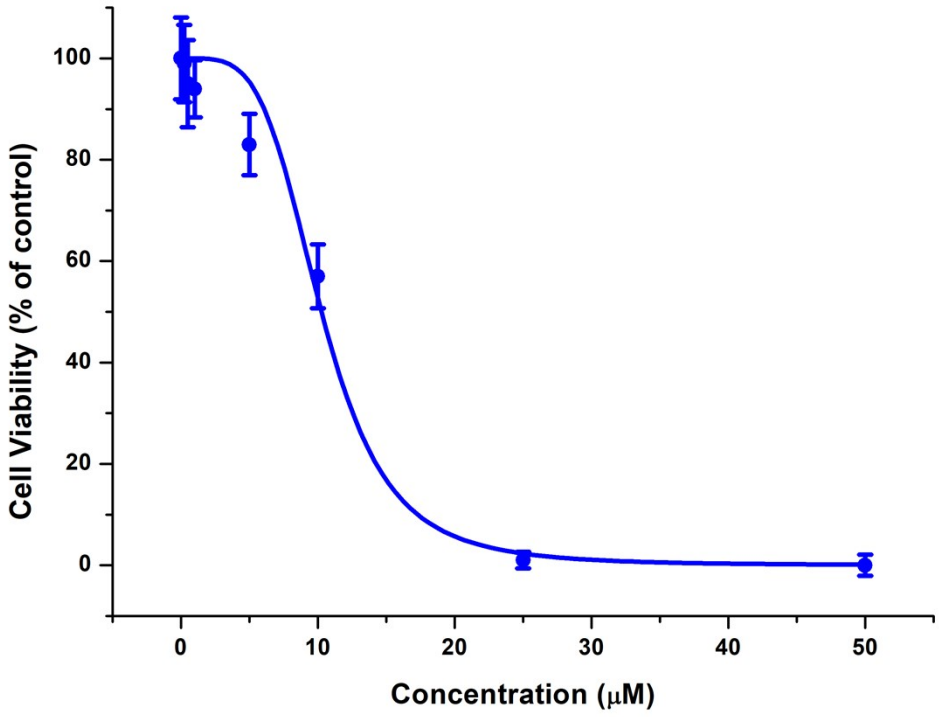


Figure S20. Cell viability (% of control) vs concentration (μM) for complex **5**

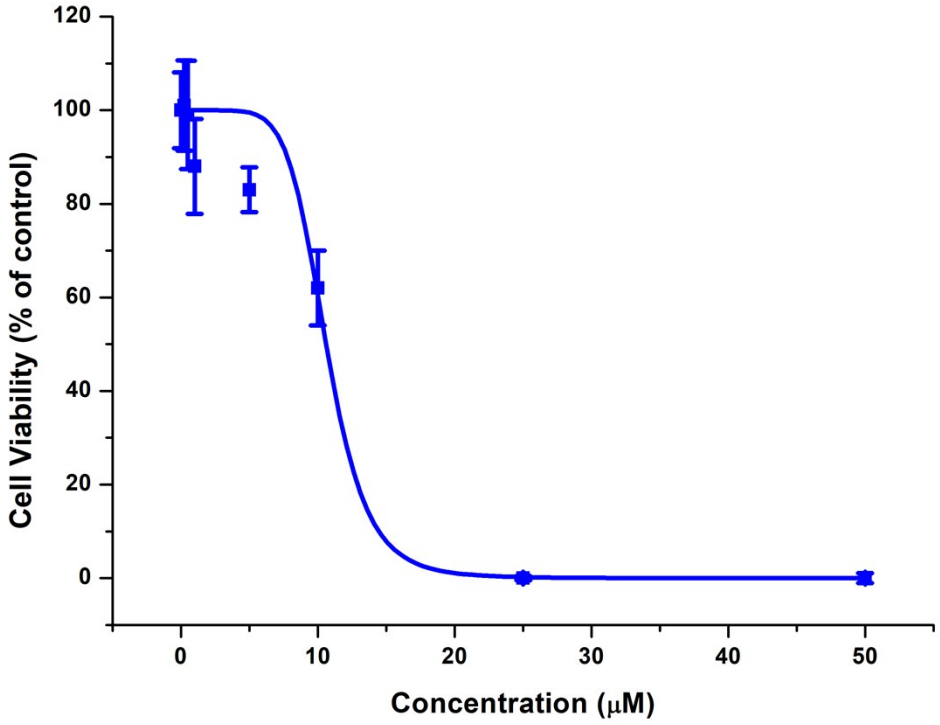


Figure S21. Cell viability (% of control) vs concentration (μM) for complex **6**

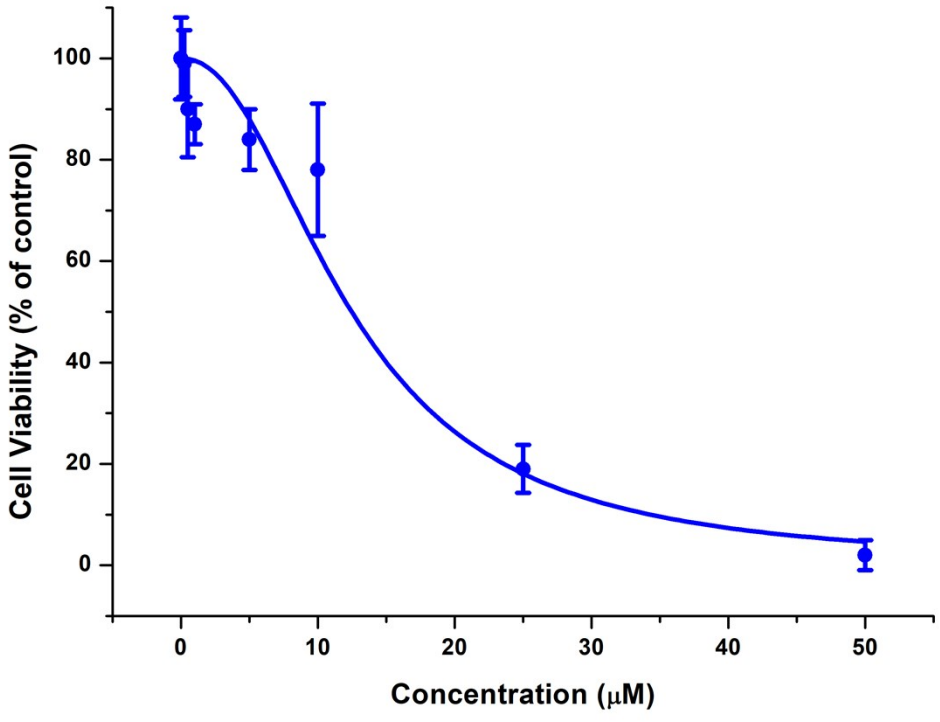


Figure S22. Cell viability (% of control) vs concentration (μM) for complex **7**

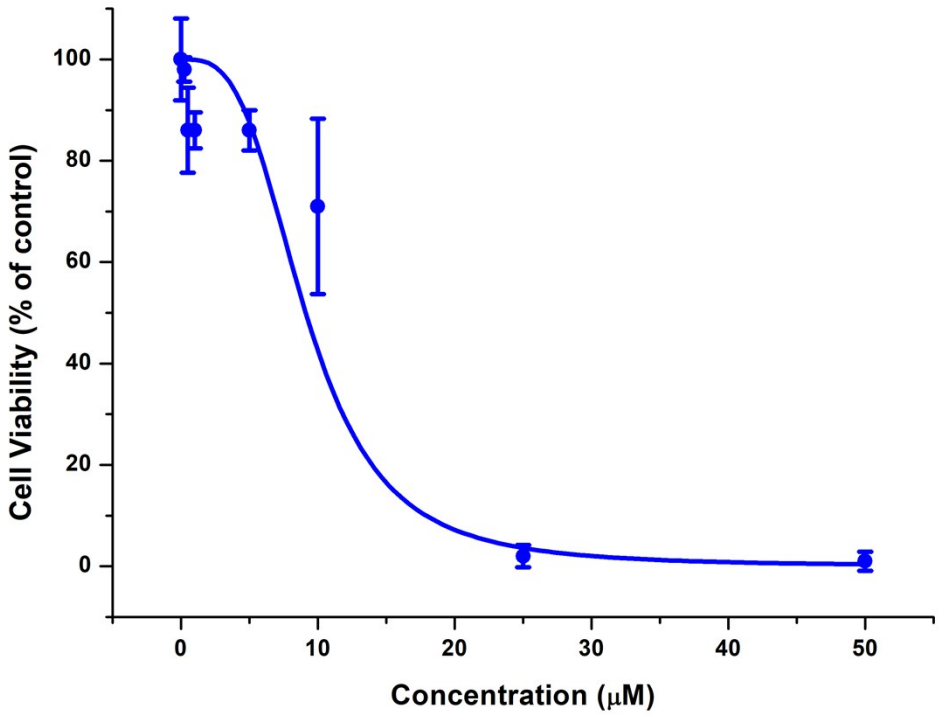


Figure S23. Cell viability (% of control) vs concentration (μM) for complex **8**

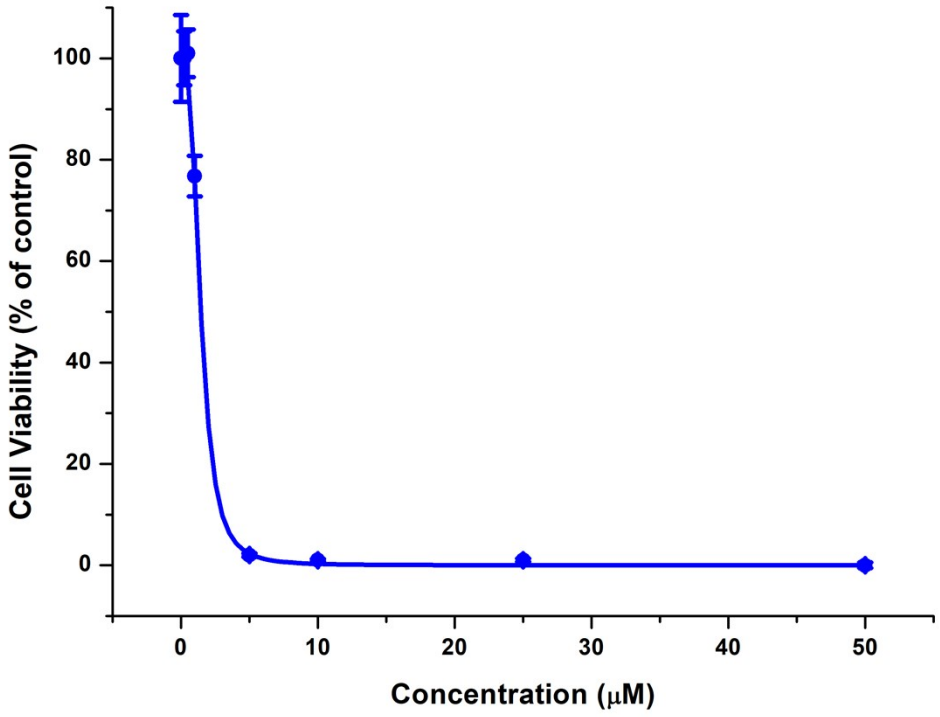


Figure S24. Cell viability (% of control) vs concentration (μM) for complex **9**

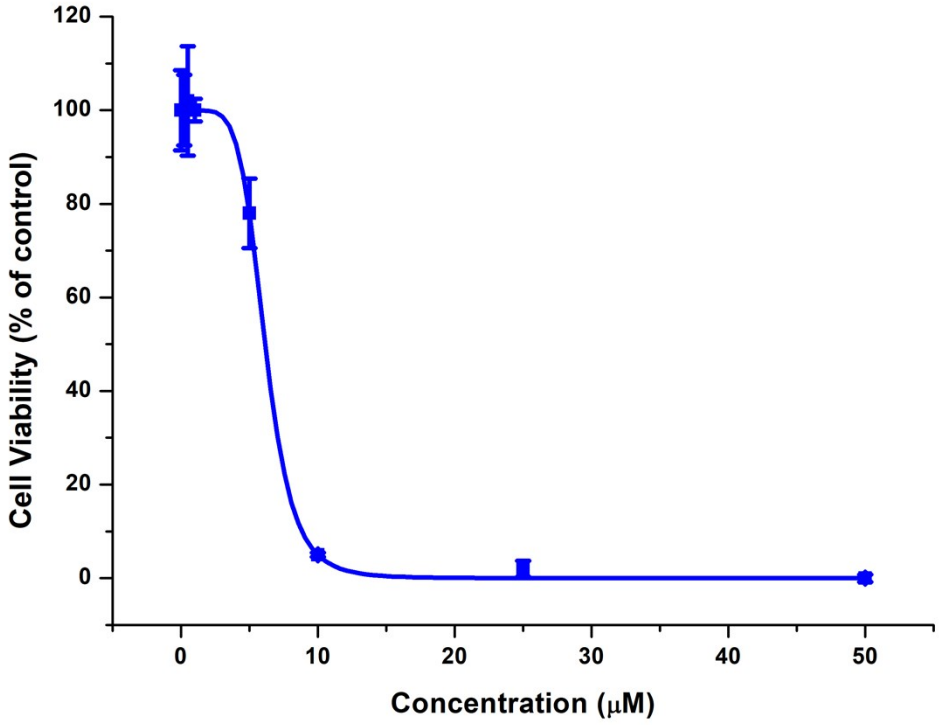


Figure S25. Cell viability (% of control) vs concentration (μM) for complex **10**

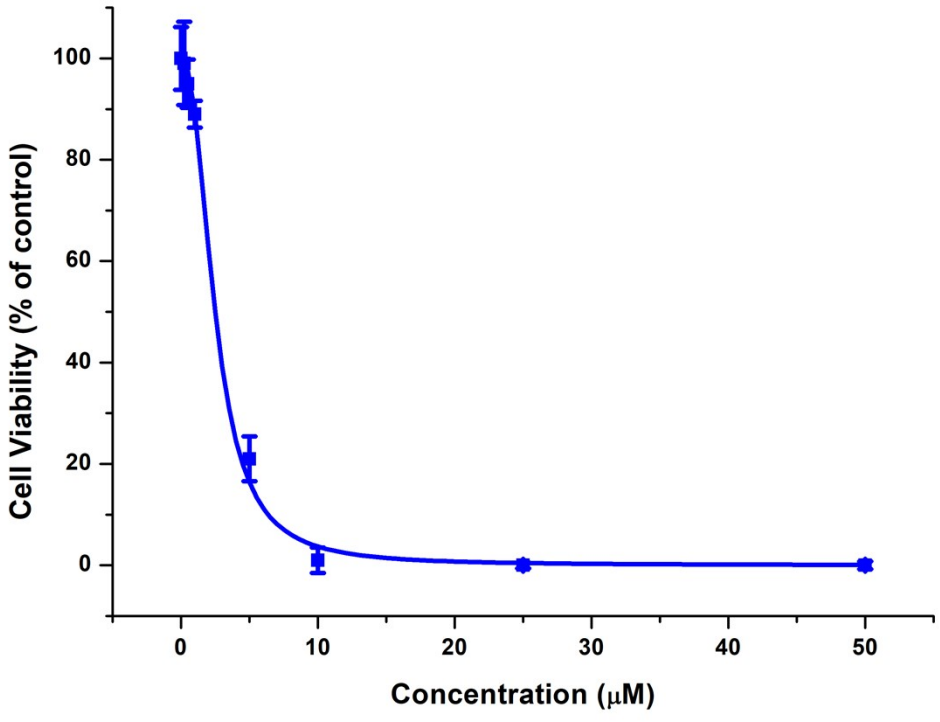


Figure S26. Cell viability (% of control) vs concentration (μM) for complex **11**

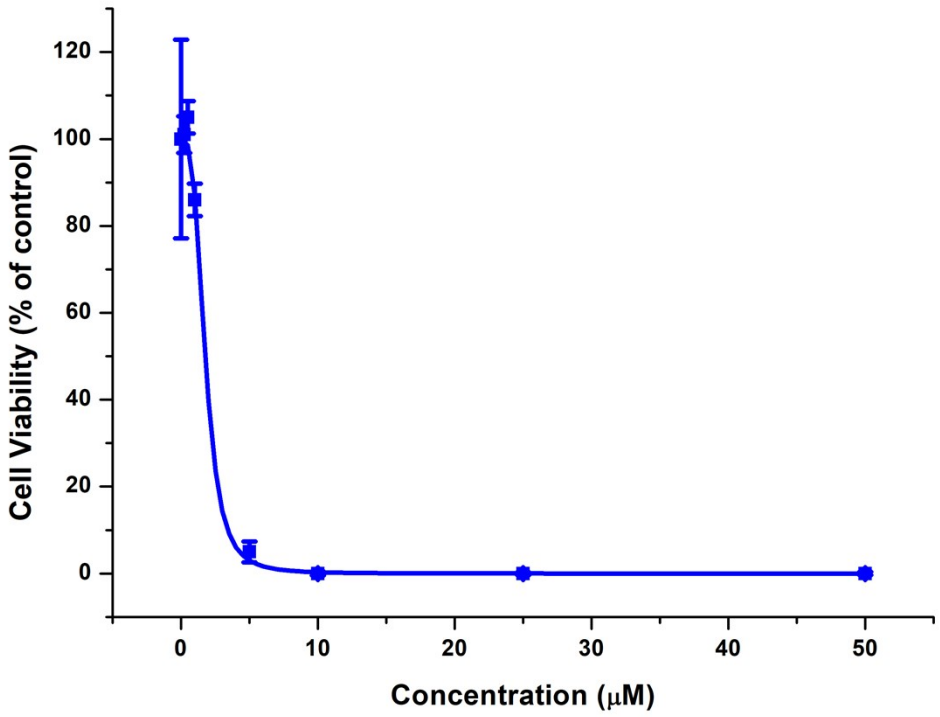


Figure S27. Cell viability (% of control) vs concentration (μM) for complex 1**2**

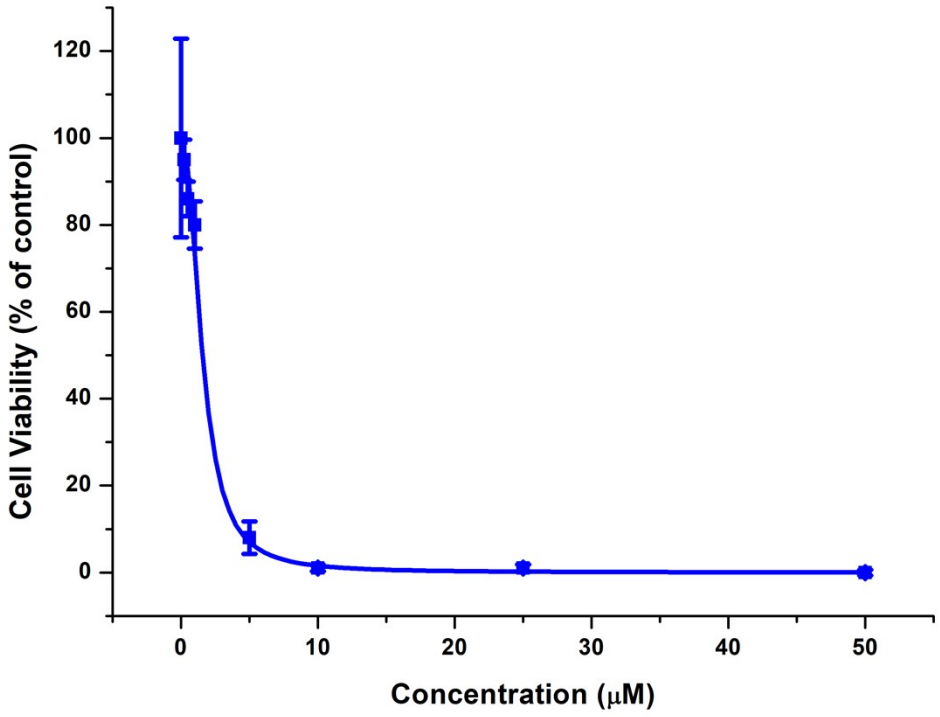


Figure S28. Cell viability (% of control) vs concentration (μM) for complex **13**

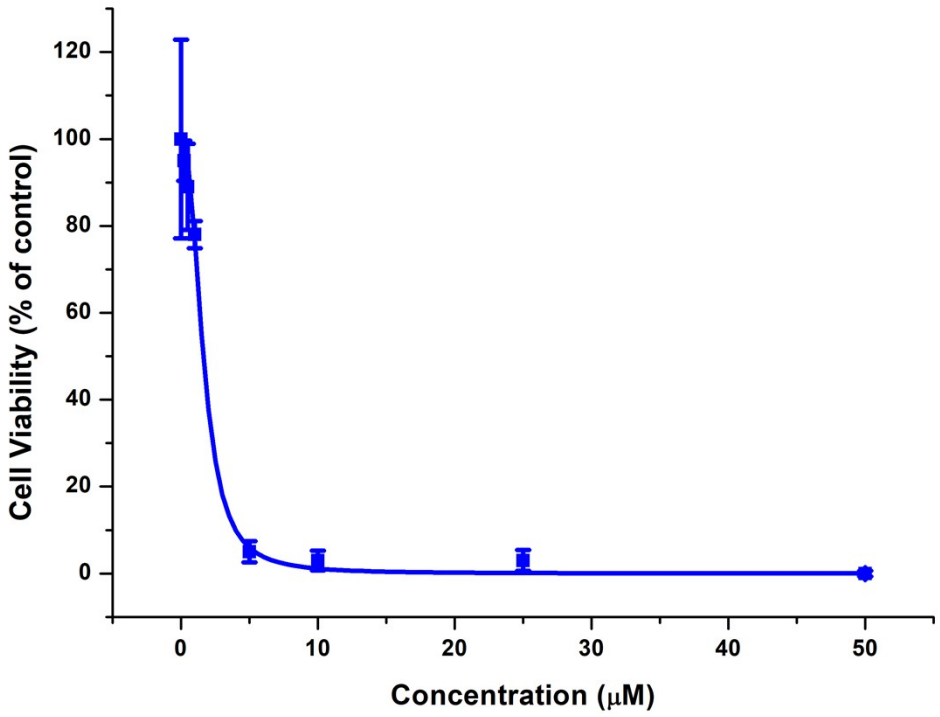


Figure S29. Cell viability (% of control) vs concentration (μM) for complex **14**

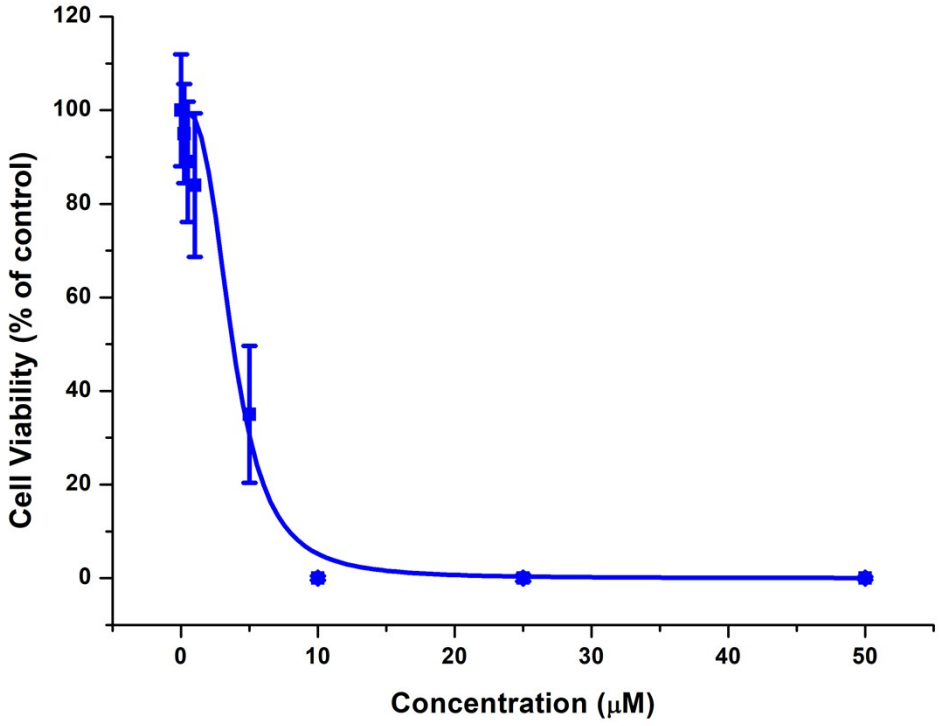


Figure S30. Cell viability (% of control) vs concentration (μM) for complex **15**

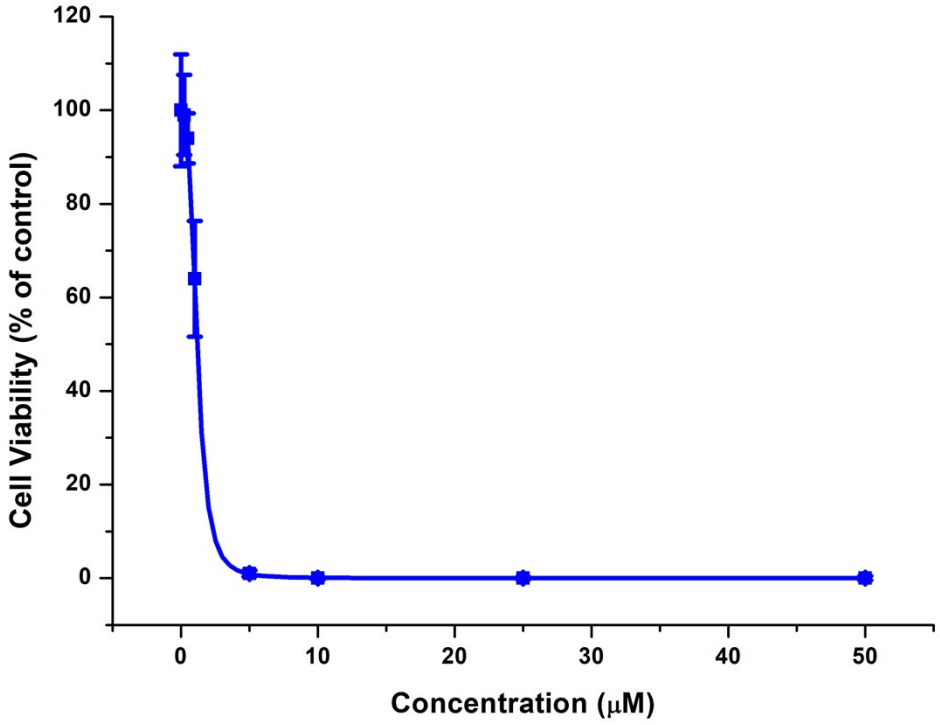


Figure S31. Cell viability (% of control) vs concentration (μM) for complex **16**

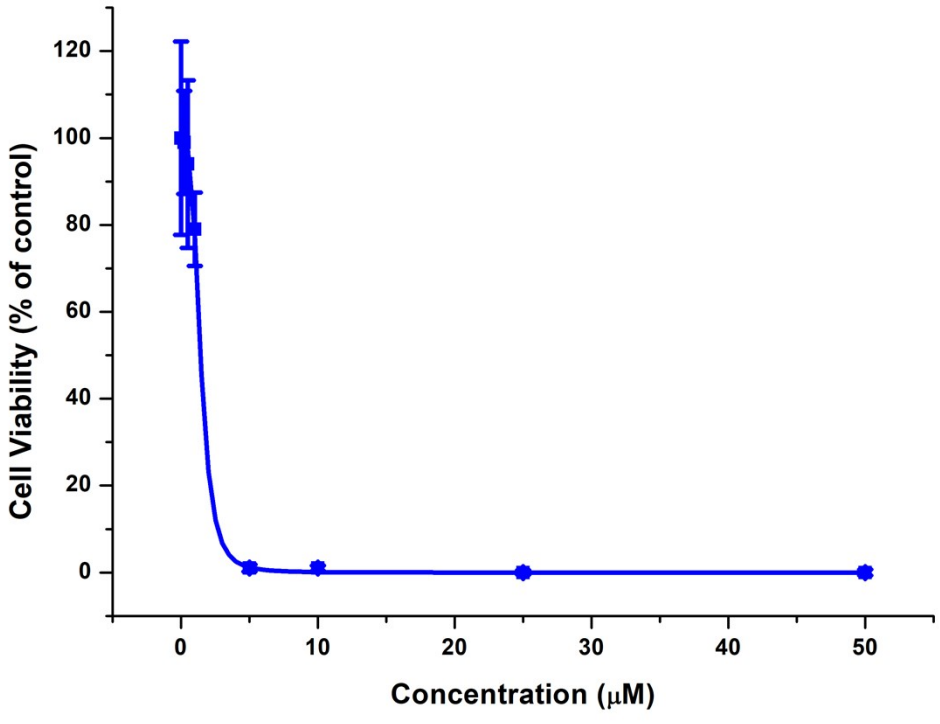


Figure S32. Cell viability (% of control) vs concentration (μM) for complex **17**

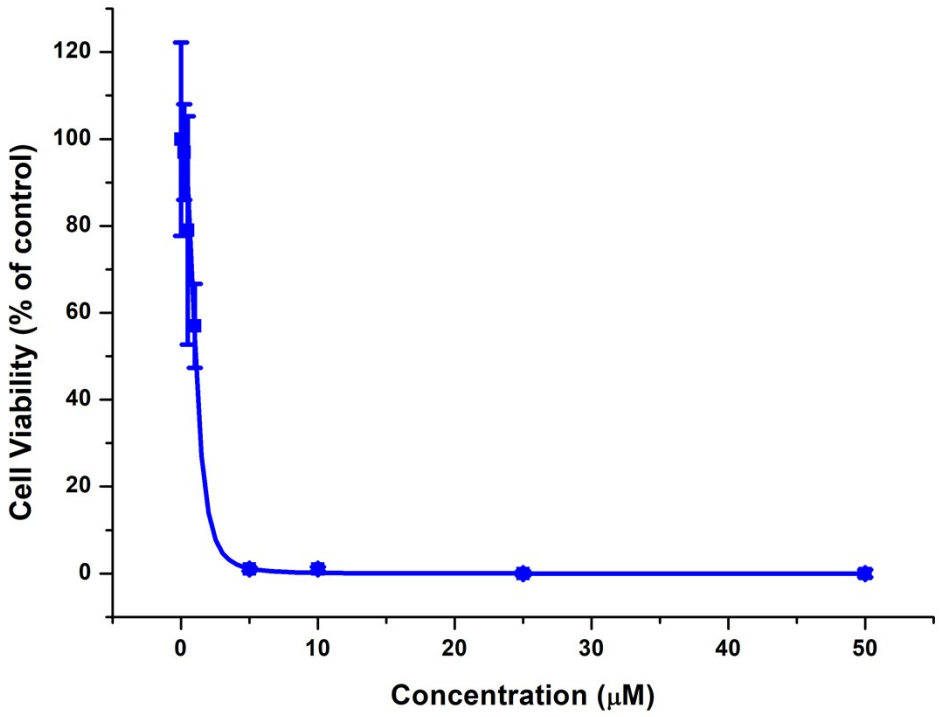


Figure S33. Cell viability (% of control) vs concentration (μM) for complex **18**

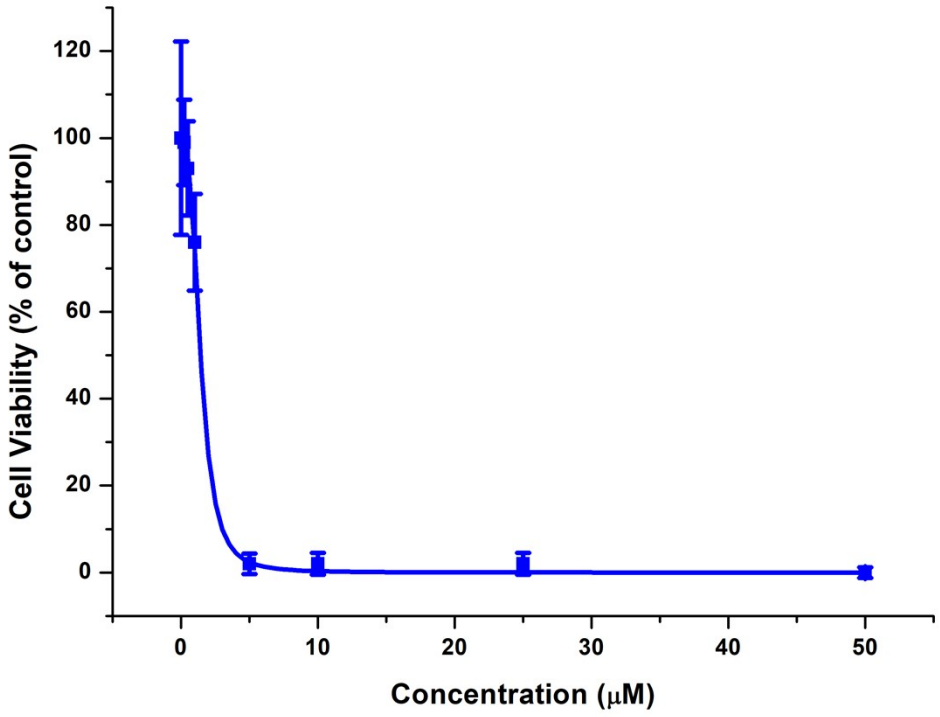


Figure S34. Cell viability (% of control) vs concentration (μM) for complex **19**

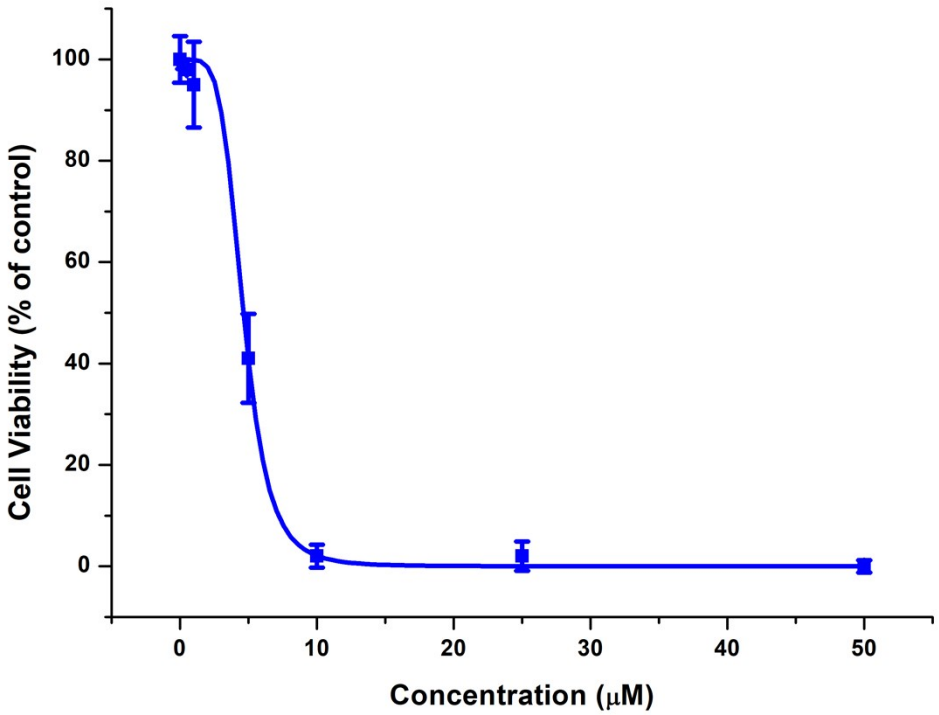


Figure S35. Cell viability (% of control) vs concentration (μM) for complex $[Cu(NO_3)(PPh_3)_2]$

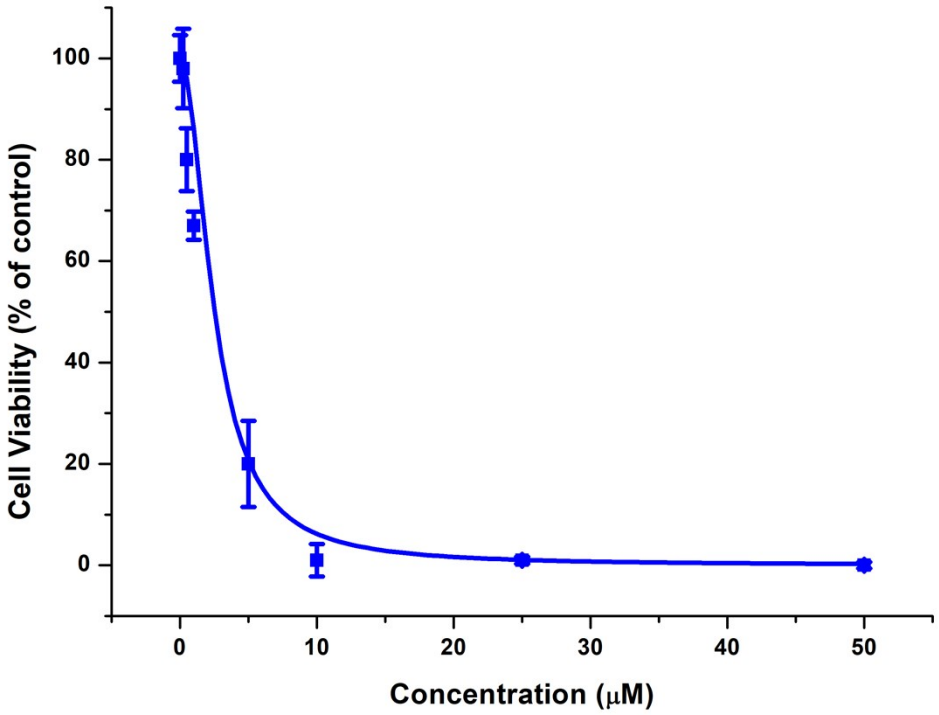


Figure S36. Cell viability (% of control) vs concentration (μM) for complex $[Ag(OTf)(PPh_3)_2]$

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