

Supporting Information

belonging to the manuscript

A direct access to heterobimetallic complexes by roll-over cyclometallation

by

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Experimental details and spectroscopic data

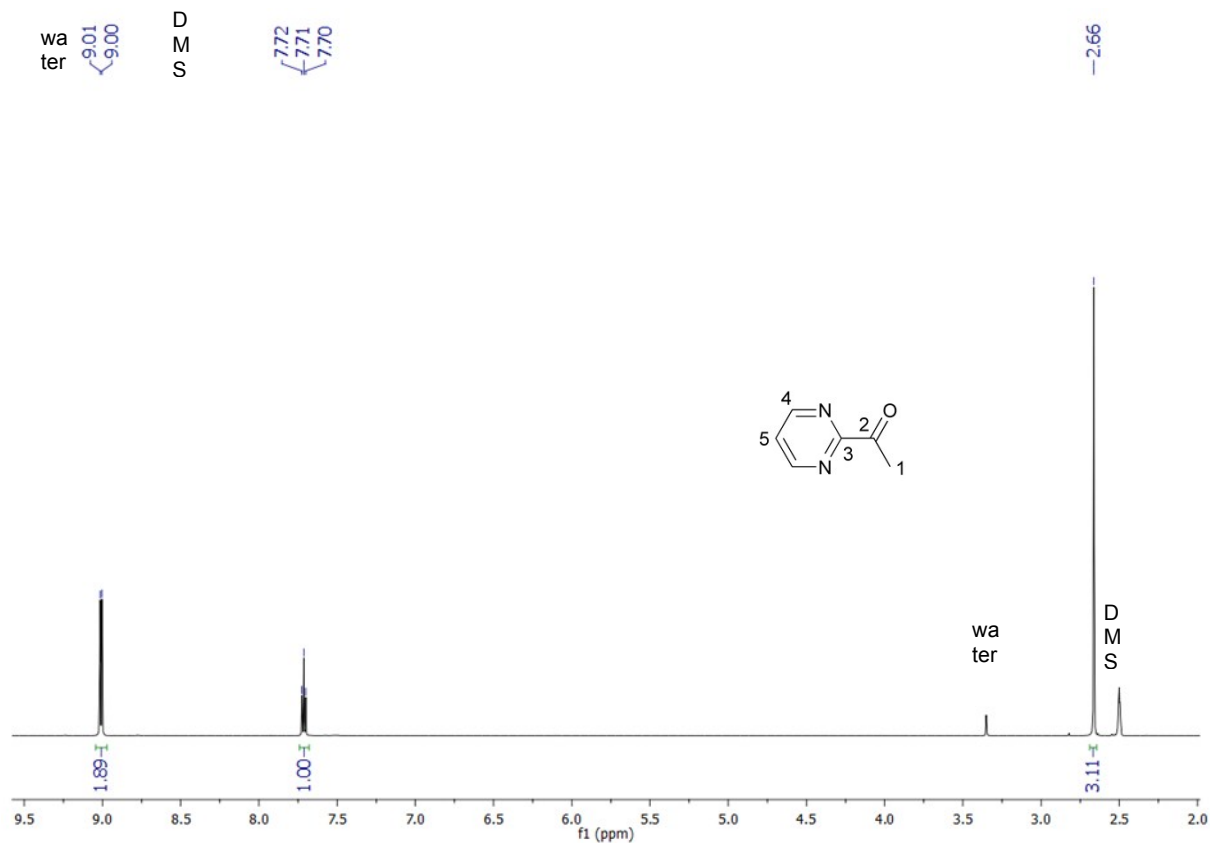
General information

Pyrimidine-2-carbonitrile was purchased from Sigma-Aldrich, $[(\text{Cp}^*)\text{IrCl}_2]_2$ from Strem. Solvents were purchased from Sigma Aldrich and dried over molecular sieves in a Braun MB SPS solvent dryer. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk-techniques. The NMR spectra were obtained on Bruker Avance 400 and 600 systems. For the assignment of the peaks, see the structures presented in the Supporting Information. The ^{195}Pt NMR spectra are calibrated to the resonance of a 1.2 M solution of Na_2PtCl_6 in D_2O (δ 0 ppm). The IR spectra were recorded with a Perkin Elmer FT-IR Spectrum 100 device equipped with an ATR sample assembly. For data refining the Perkin Elmer software Spectrum 6.3.5 was used. Elemental analyses were performed with a Hanau Elemental Analyzer Vario Micro cube.

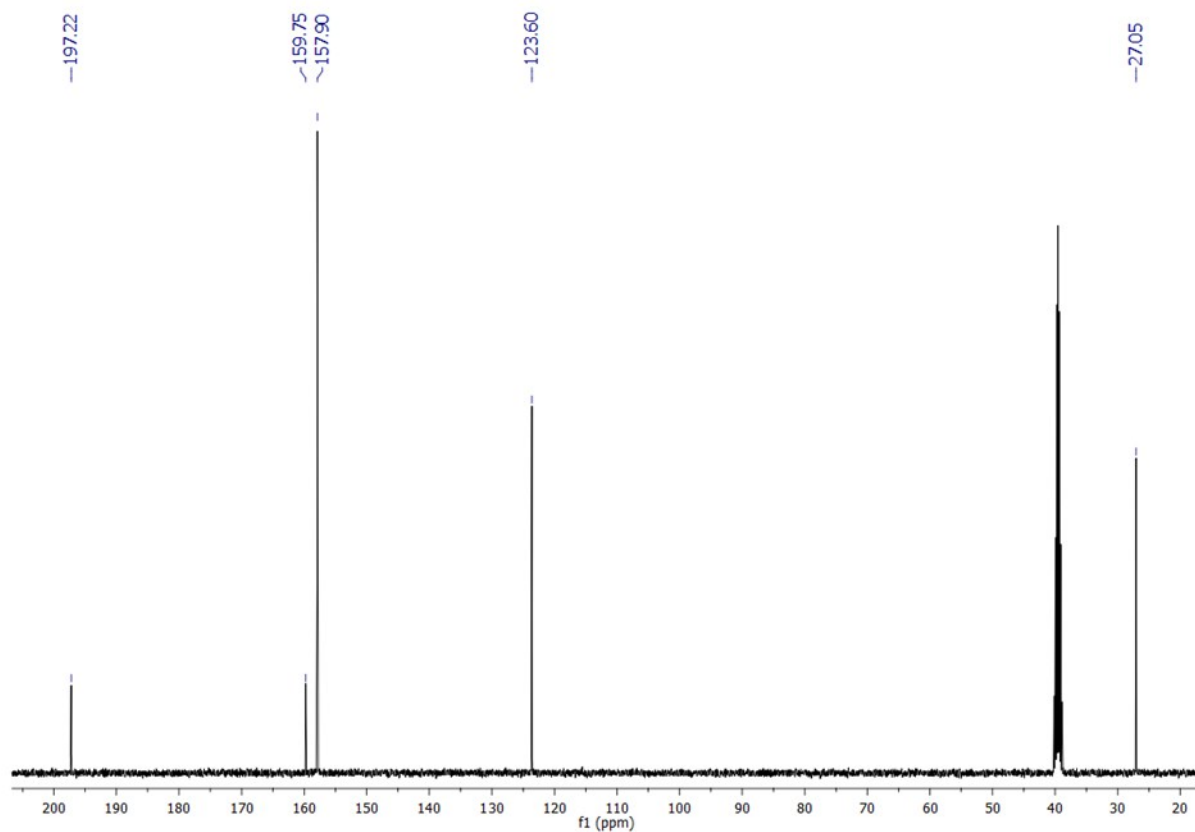
2-Acetylpyrimidine (2): Compound **2** was synthesized following a procedure published in a patent.¹ A solution of 42 mL of a 1 M solution of CH_3MgBr was added to 90 mL of dry thf. This solution was added at $-5\text{ }^\circ\text{C}$ drop-wise to a solution of 9.00 g (83.9 mmol) of pyrimidine-2-carbonitrile and the mixture was stirred for 18 h at $0\text{ }^\circ\text{C}$. After the addition of 30 mL of a saturated aqueous solution of NH_4Cl , 60 mL of 4 M HCl were added and the mixture was stirred for 1 h at r.t.. Then the mixture was cooled again to $0\text{ }^\circ\text{C}$ and its pH value was adjusted to 6.5-7 by careful addition of a saturated aqueous solution of K_2CO_3 . After the resulting solution was extracted five times with 90 mL of EtOAc, the pH value was raised to 7-8 and the aqueous solution was extracted further three times with 90 mL of EtOAc. The combined organic phases were washed once with a saturated NaCl solution, dried over MgSO_4 and the solvent was evaporated under vacuum. The resulting brown residue was purified by column chromatography (EtOAc/n-hexane: 1/1). Compound **2** was obtained in 47% yield as a colorless solid. Anal. calcd. for $\text{C}_6\text{H}_6\text{N}_2\text{O}$ (122.13): C 59.01, H 4.95, N 22.94, found: C 58.94, H 5.05, N 22.95%. ^1H NMR (400.1 MHz, DMSO-d_6): δ 9.01 (d, $^3J_{\text{HH}} = 4.9\text{ Hz}$, 2H, H4), 7.72 (t, $^3J_{\text{HH}} = 4.9\text{ Hz}$, 1H, H5), 2.67 (s, 3H, H1). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, DMSO-d_6): δ 197.2 (C2), 159.8 (C3), 157.9 (C4), 123.6 (C5), 27.1 (C1) ppm. IR (ATR, cm^{-1}): ν 3401w, 3127w, 3045w, 3004w, 2978w, 2924w, 1705s, 1558s, 1409m, 1361s, 1301s, 1270s, 1132m, 1132s, 1094m, 995m, 958m, 815s, 788s.

¹ T. Nowak and S. C. Purkiss, A. P. Thomas, WO 2008117051 A1, 2008.

^1H NMR spectrum



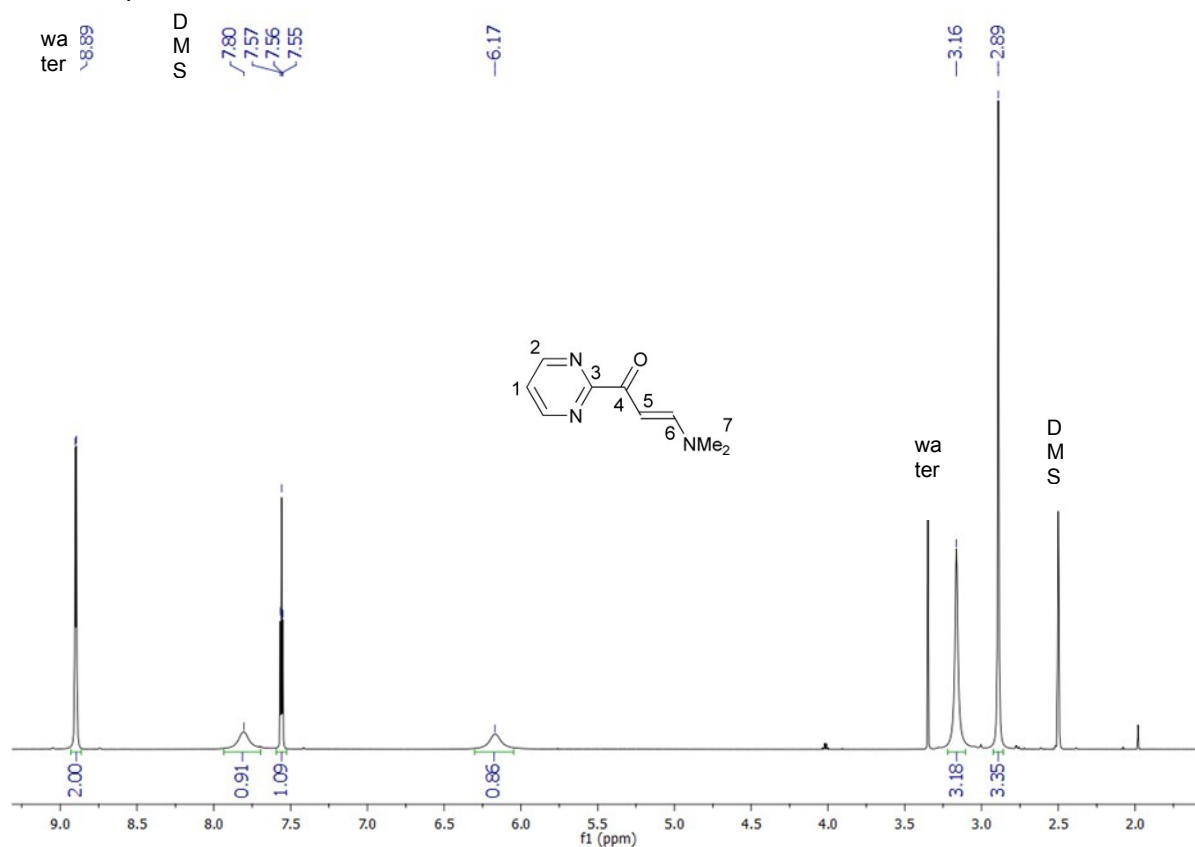
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



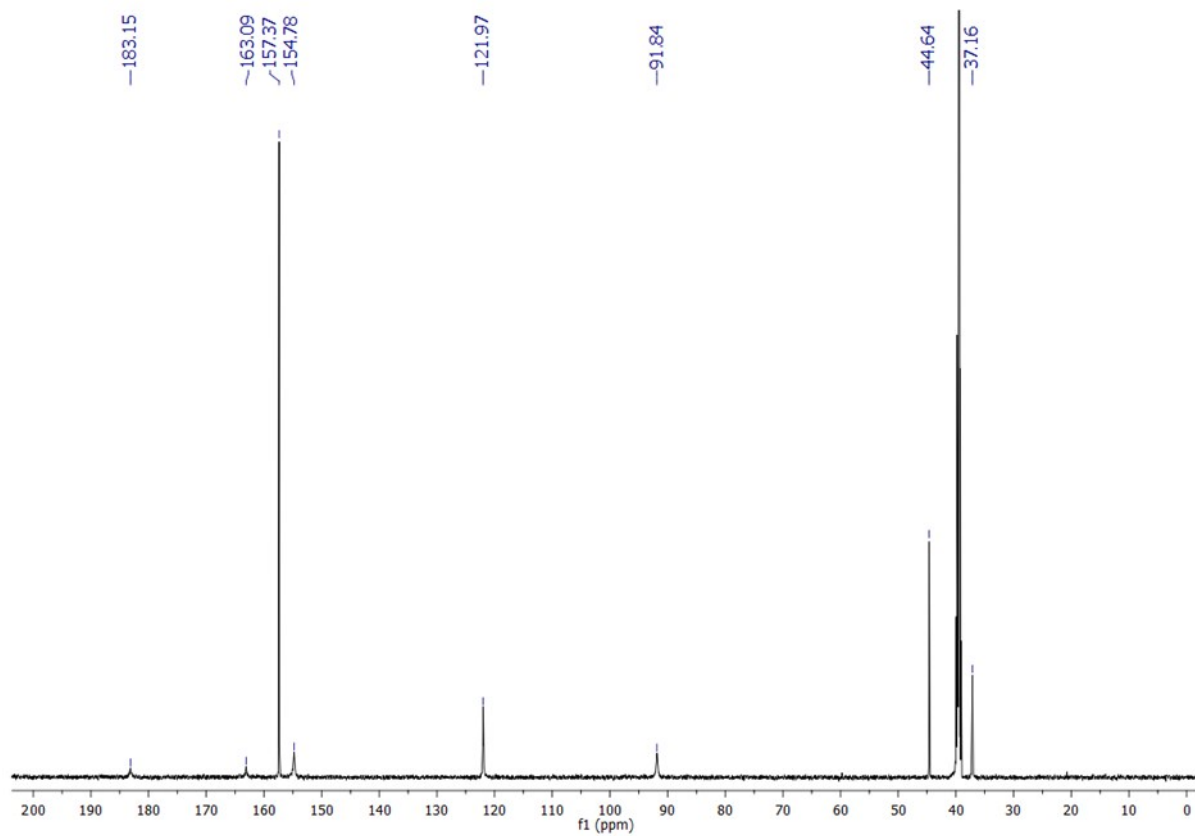
3-Dimethylamino-1-pyrimidin-2-yl-propenon (3): Compound **3** was synthesized following a procedure published in the literature.² 1.70 g (13.9 mmol) of **2** and 3.56 g (29.9 mmol) of *N,N*-dimethylformamide

dimethylacetale heated up to 110 °C for 3 h in a flask equipped with a distillation bridge do remove methanol formed during the reaction. The reddish-brown residue was washed twice with 10 mL of Et₂O and twice with 10 mL of pentane and finally recrystallized from ethyl acetate. Compound **3** was obtained in 83% yield as a reddish-brown solid. Anal. calcd. for C₉H₁₁N₃O (177.21): C 60.95, H 6.43, N 23.93, found: C 61.00, H 6.26, N 23.71%. ¹H NMR (400.1 MHz, DMSO-d₆): δ 8.90 (d, ³J_{HH} = 4.8 Hz, 1H, H2), 7.80 (br, 1H, H6), 7.56 (t, ³J_{HH} = 4.8 Hz, 1H, H1), 6.17 (br, 1H, H3), 3.16 (s, 3H, H7), 2.89 (s, 3H, H7). ¹³C{¹H} NMR (100.6 MHz, DMSO-d₆): δ 183.2 (C4), 163.1 (C3), 157.4 (C2), 154.7 (C6), 122.0 (C1), 91.8 (C5), 44.6 (C7), 37.2 (C7). IR (ATR, cm⁻¹): ν 3050w, 1645m, 1542s, 1411m, 1357m, 1266m, 1112w, 1078m, 981m, 905m, 853w, 821w, 775m, 694m.

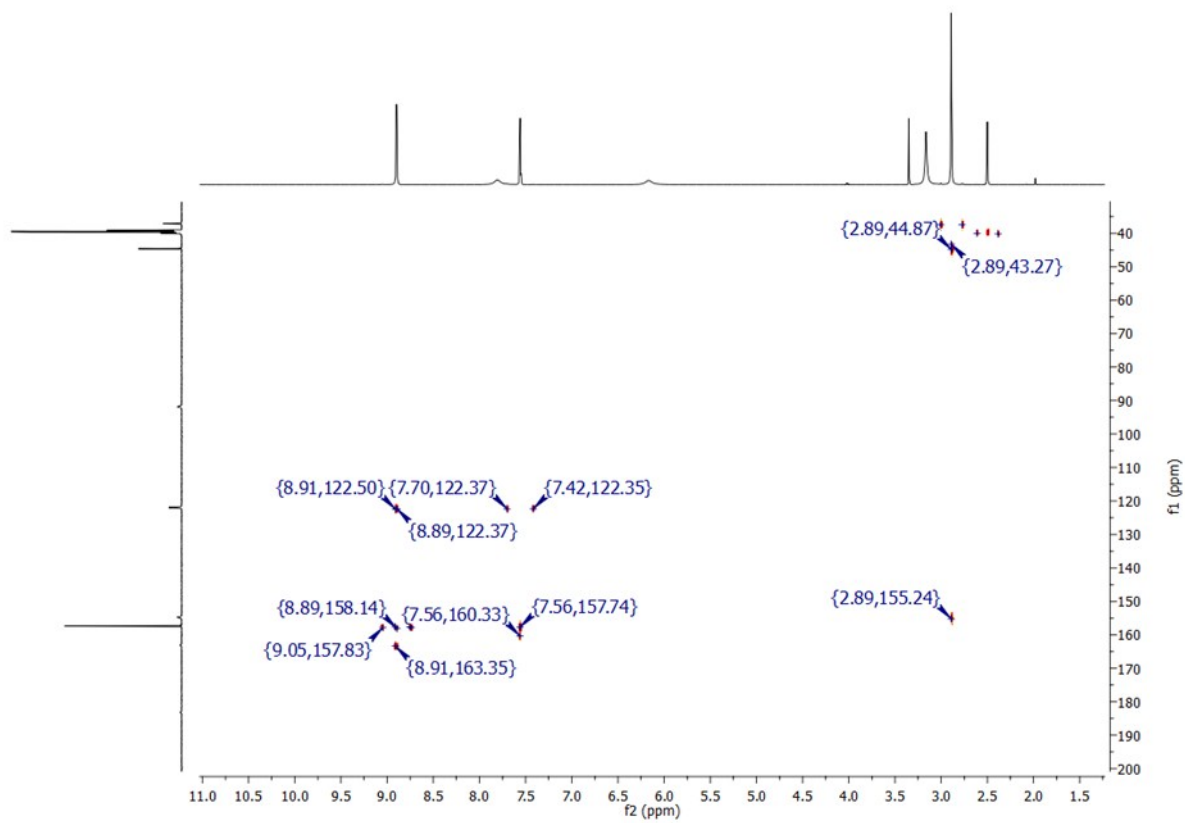
¹H NMR spectrum



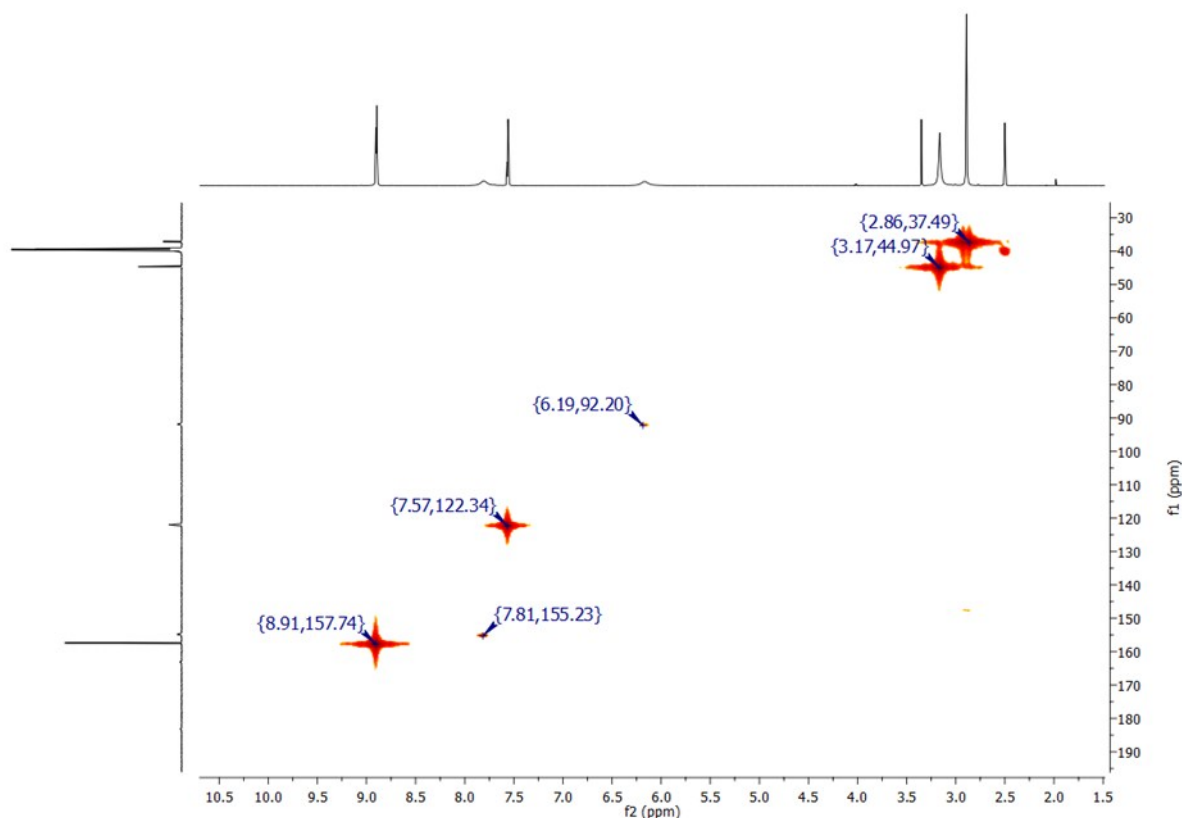
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



HMBC spectrum

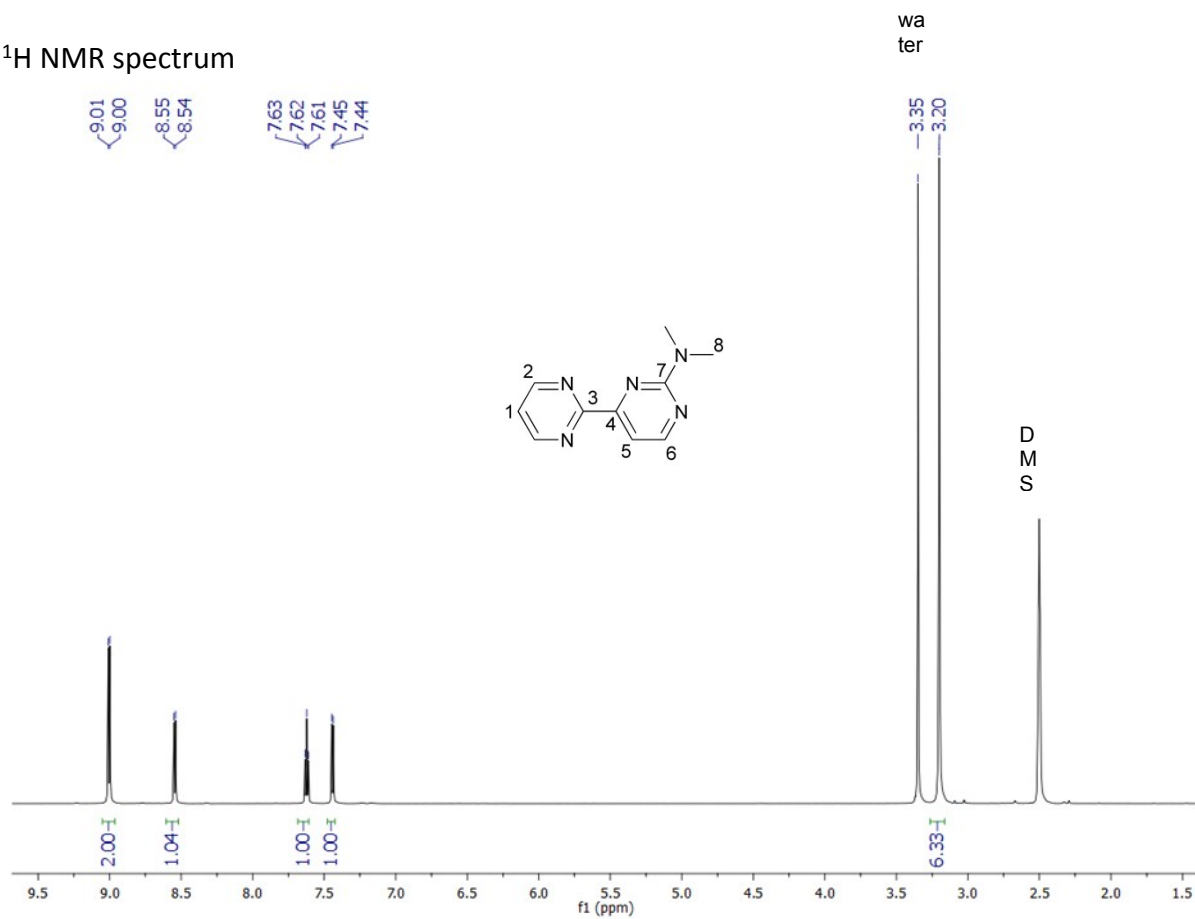


HMQC spectrum

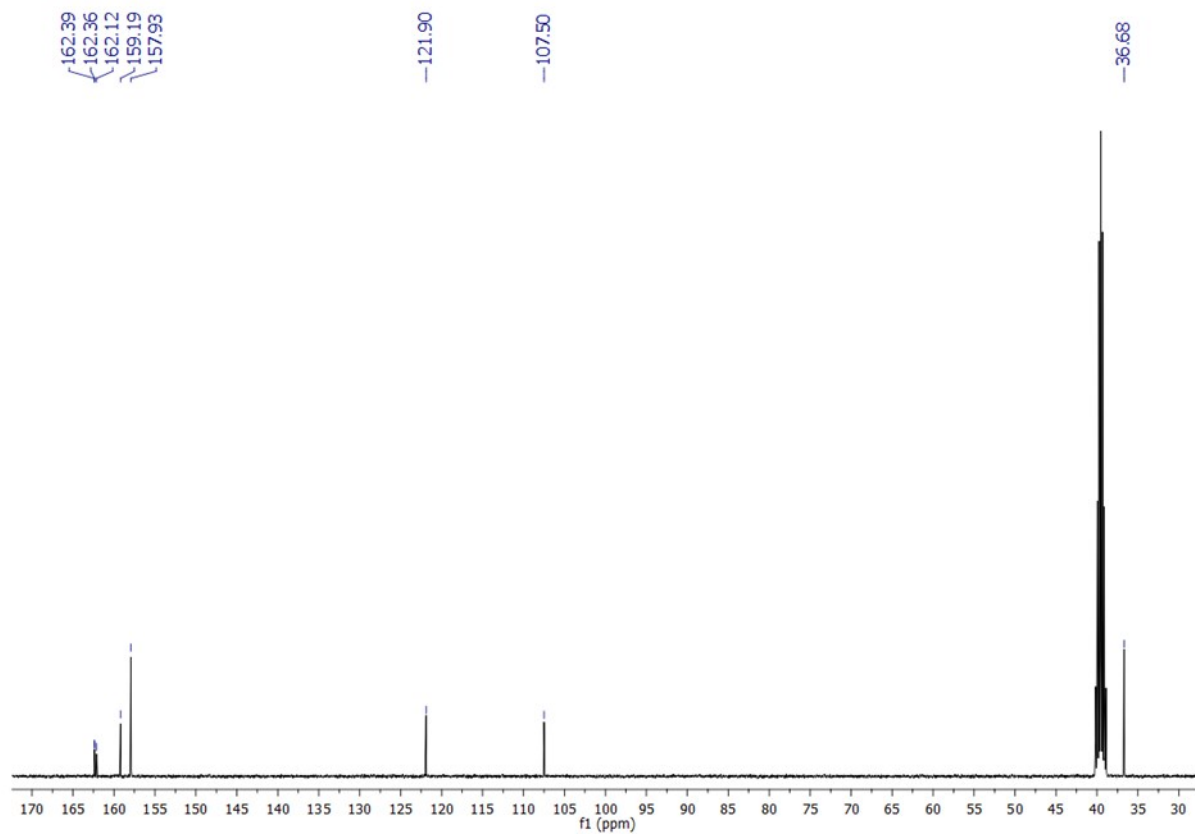


***N,N*-Dimethyl-(2,4-bipyrimidin)-2-amine (5a):** Compound **5a** was synthesized following a procedure published in the literature.² 2.43 g (8.74 mmol) of *N,N*-dimethylguanidinium sulphate (**4a**) and 1.00 g (5.64 mmol) of compound **3** were suspended in 60 mL of dry EtOH. 914 mg (8.74 mmol) of NaOMe were added and the mixture was heated to reflux for 48 h. The solvent was removed under vacuum. 25 mL of water were added and the aqueous mixture was extracted three times with 20 mL of toluene. The combined organic solutions were dried over MgSO₄ and toluene was removed under vacuum. Compound **5a** was obtained in 81% yield as a brownish solid. Anal. calcd. for C₁₀H₁₁N₅ (201.23): C 59.69, H 5.51, N 34.80, found: C 59.61, H 5.43, N 34.60%. ¹H NMR (400.1 MHz, DMSO-*d*₆): δ 9.00 (d, ³J_{HH} = 4.8 Hz, 2H, H2), 8.54 (d, ³J_{HH} = 4.9 Hz, 1H, H6), 7.62 (t, ³J_{HH} = 4.9 Hz, 1H, H1), 7.44 (d, ³J_{HH} = 4.9 Hz, 1H, H5), 3.20 (s, 6H, H8). ¹³C{¹H} NMR (100.6 MHz, DMSO-*d*₆): δ 162.4 (C4), 162.4 (C3), 162.1 (C7), 159.2 (C6), 157.9 (C2), 121.9 (C1), 107.5 (C5), 36.7 (C8). IR (ATR, cm⁻¹): ν 3036w, 2935m, 2862m, 2974w, 1544s, 1446m, 1397s, 1342s, 1199m, 1138m, 998s, 789s, 659s.

^1H NMR spectrum

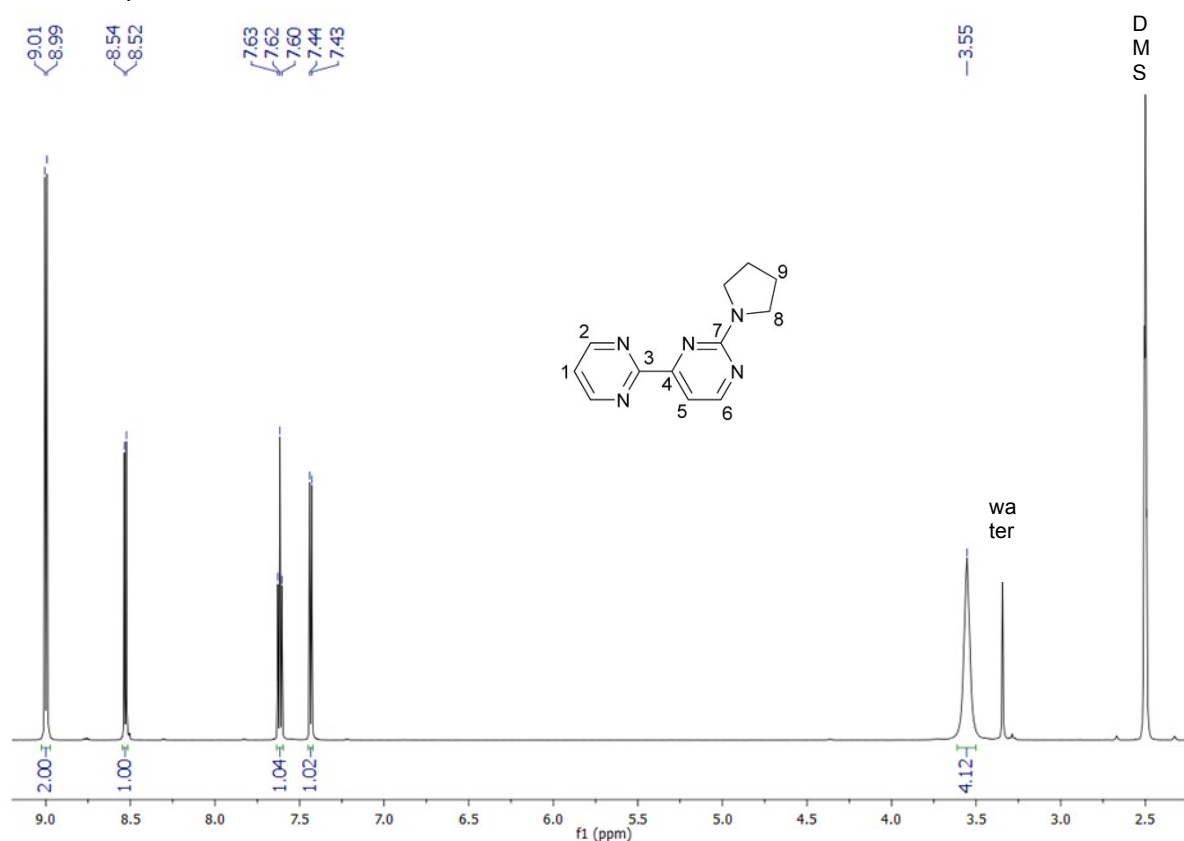


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

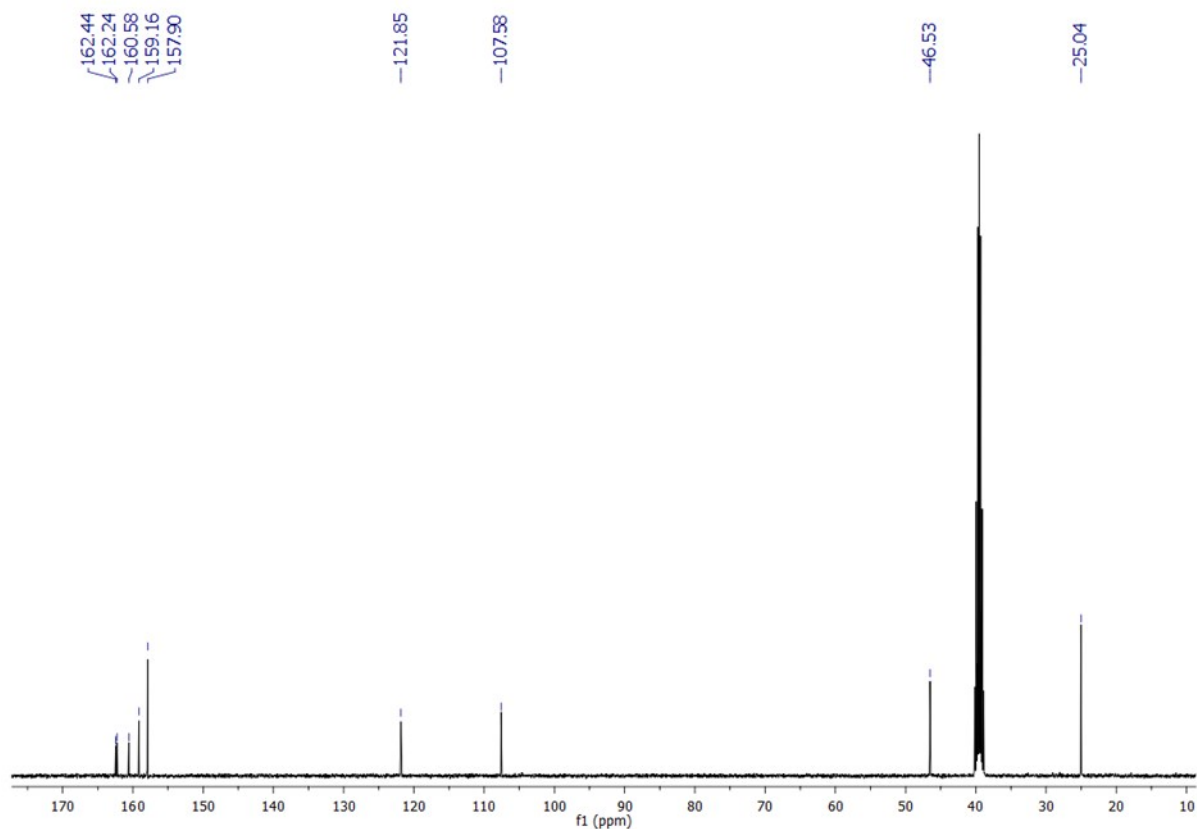


2'-(Pyrrolidinyl)-2-4'-bipyrimidine (5b): Compound **5b** was synthesized following a procedure published in the literature.² 5.18 g (16.00 mmol) of amidinopyrrolidin hemisulphate (**4b**) and 1.83 g (10.30 mmol) of compound **3** were suspended in 120 mL of dry EtOH. 1.67 g (30.90 mmol) of NaOMe were added and the mixture was heated to reflux for 48 h. The solvent was removed under vacuum. 50 mL of water were added and the aqueous mixture was extracted three times with 30 mL of toluene. The combined organic solutions were dried over MgSO₄ and toluene was removed under vacuum. Compound **5a** was obtained in 71% yield as a yellow solid. Anal. calcd. for C₁₂H₁₃N₅ (227.27): C 63.42, H 5.77, N 30.82, found: C 63.48, H 5.86, N 30.64%. ¹H NMR (400.1 MHz, DMSO-d₆): δ 9.00 (d, ³J_{HH} = 4.9 Hz, 2H, H2), 8.53(d, ³J_{HH} = 5.0 Hz, 1H, H6), 7.62 (t, ³J_{HH} = 4.9 Hz, 1H, H1), 7.43 (d, ³J_{HH} = 5.0 Hz, 1H, H5), 3.55 (br, 4H, H8), 1.94 (m, 4H, H9). ¹³C{¹H} NMR (100.6 MHz, DMSO-d₆): δ 162.4 (C4), 162.2 (C3), 160.6 (C7), 159.2 (C6), 157.9 (C2), 121.9 (C1), 107.6 (C5), 46.5 (C8), 25.0 (C9). IR (ATR, cm⁻¹): ν 3030w, 2963m, 2936m, 2872m, 2851m, 1573m, 1543s, 1506s, 1481s, 1461s, 1404s, 1360m, 1323m, 1298m, 1221m, 1203m, 1168m, 1183m, 1084m, 1056m, 1022m, 968m, 916m, 865m, 794s, 657s.

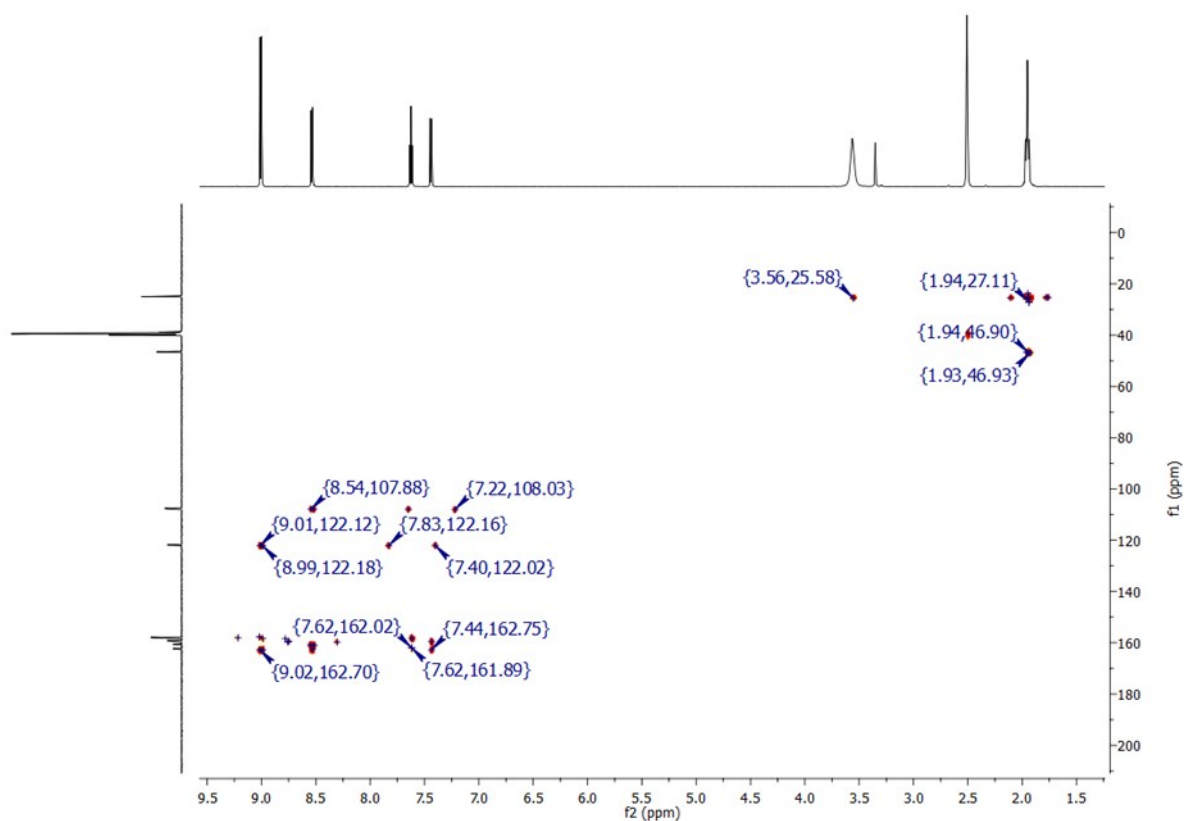
¹H NMR spectrum



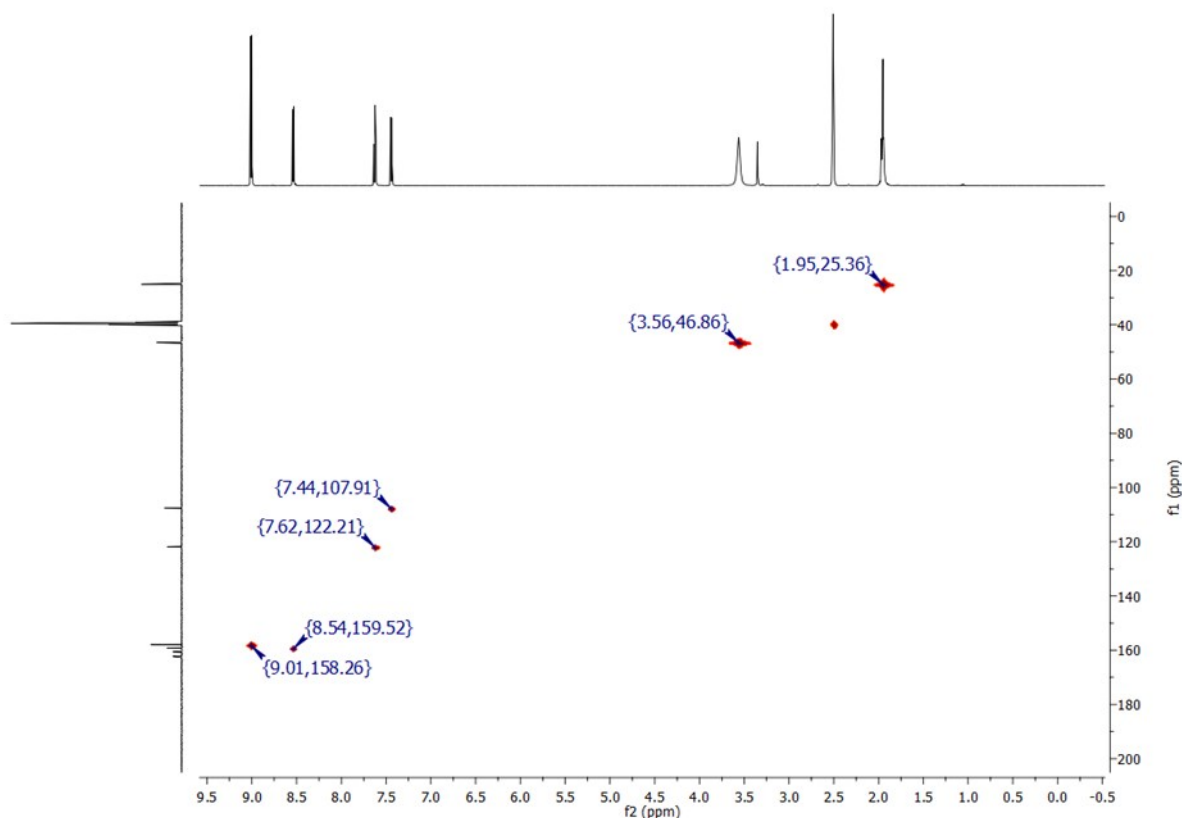
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



HMBC spectrum

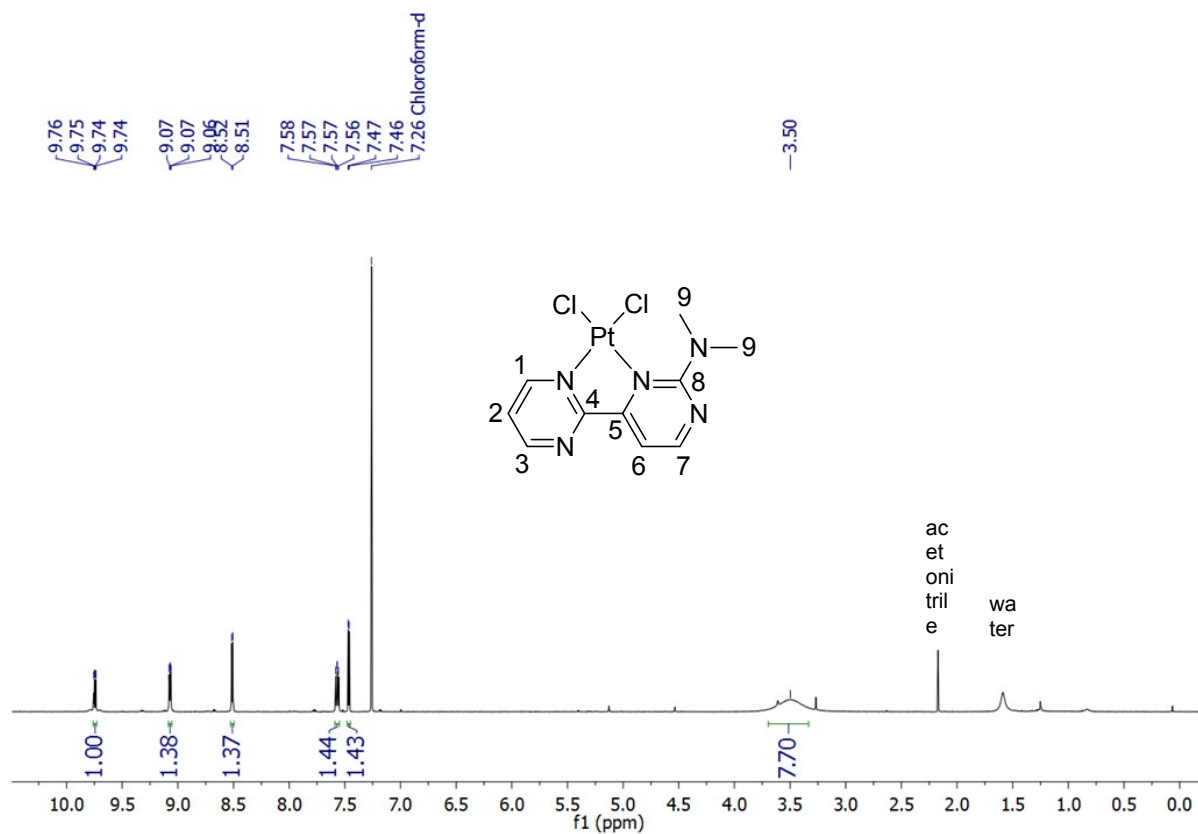


HMQC spectrum

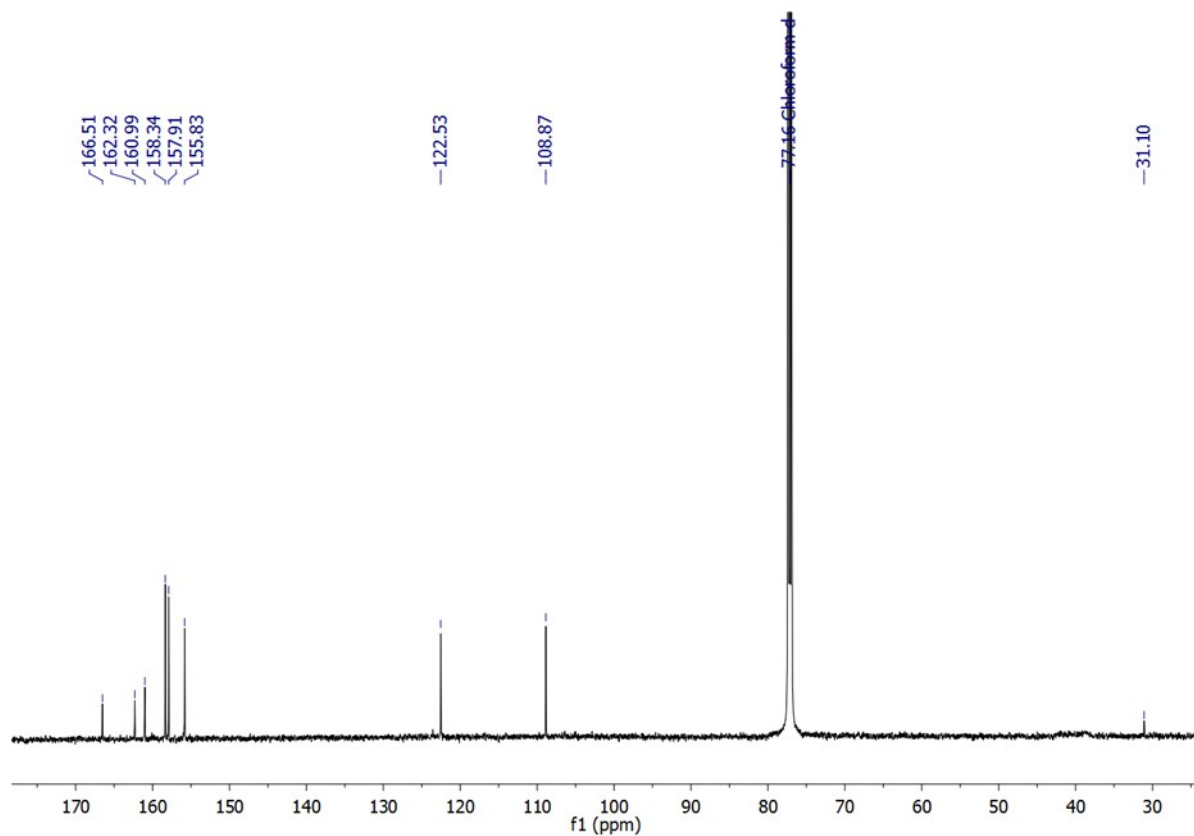


Dichlorido(*N,N*-dimethyl-(2,4-bipyrimidin)-2-amine)platinum (5aPt): 28.6 mg (142 μmol) of compound **5a** and 54.9 mg (142 μmol) of $\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3]$ were suspended in 10 mL of acetone. The mixture was stirred at room temperature for 96 h. The solvent was removed under vacuum and the residue was washed with 20 mL of Et_2O . Compound **5aPt** was obtained in 45% yield as an orange colored microcrystalline solid. Anal. calcd. for $\text{C}_{10}\text{H}_{11}\text{Cl}_2\text{N}_5\text{Pt}$ (467.22): C 25.71, H 2.37, N 14.99, found: C 25.85, H 2.48, N 15.06%. ^1H NMR (400.1 MHz, CDCl_3): δ 9.75 (dd, $^3J_{\text{HH}} = 5.9, 2.1$ Hz, 1H, H1), 9.07 (dd, $^3J_{\text{HH}} = 4.8, 2.1$ Hz, 1H, H3), 8.51 (d, $^3J_{\text{HH}} = 4.1$ Hz, 1H, H7), 7.57 (dd, $^3J_{\text{HH}} = 5.9, 4.8$ Hz, 1H, H2), 7.47 (d, $^3J_{\text{HH}} = 4.1$ Hz, 1H, H6), 3.50 (s, br 6 H, H9). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz, CDCl_3): δ 166.5 (C5), 162.3 (C4), 160.9 (C8), 158.3 (C7), 157.9 (C3), 155.8 (C1), 122.5 (C2), 108.8 (C6), 31.1 (C9). ^{195}Pt NMR (129.01 MHz, CDCl_3): δ -2075.20. IR (ATR, cm^{-1}): ν 3085w, 2942w, 1618m, 1578m, 1528m, 1463m, 1408m, 1358m, 1218m, 1183m, 1133m, 1012m, 987m, 832m, 772m.

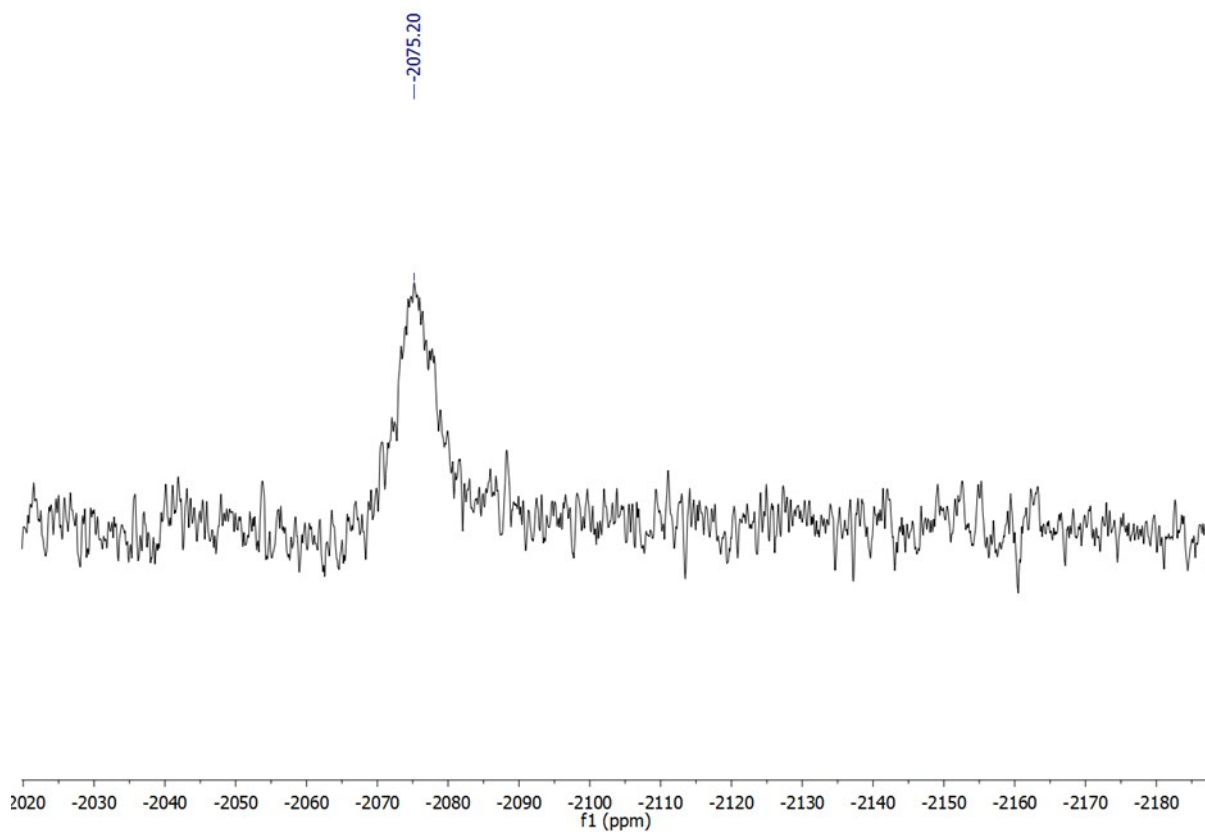
^1H NMR spectrum



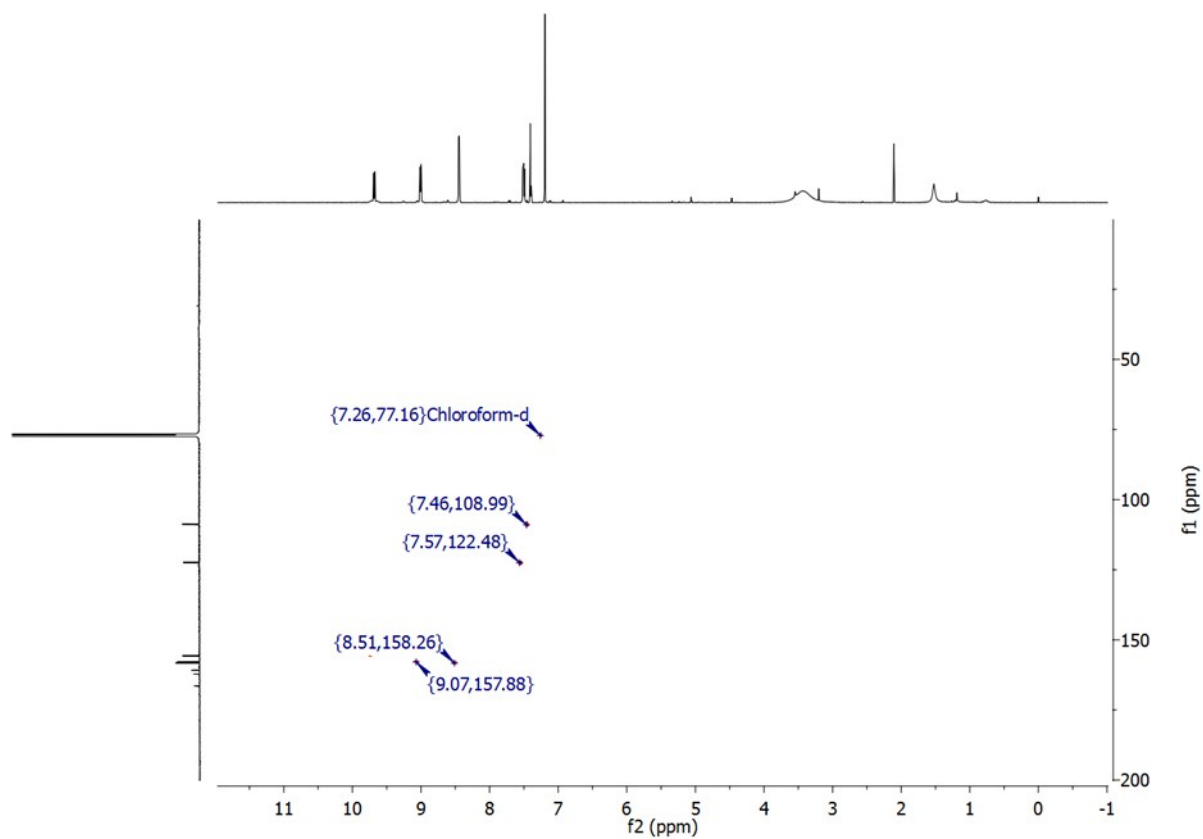
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



^{195}Pt NMR spectrum

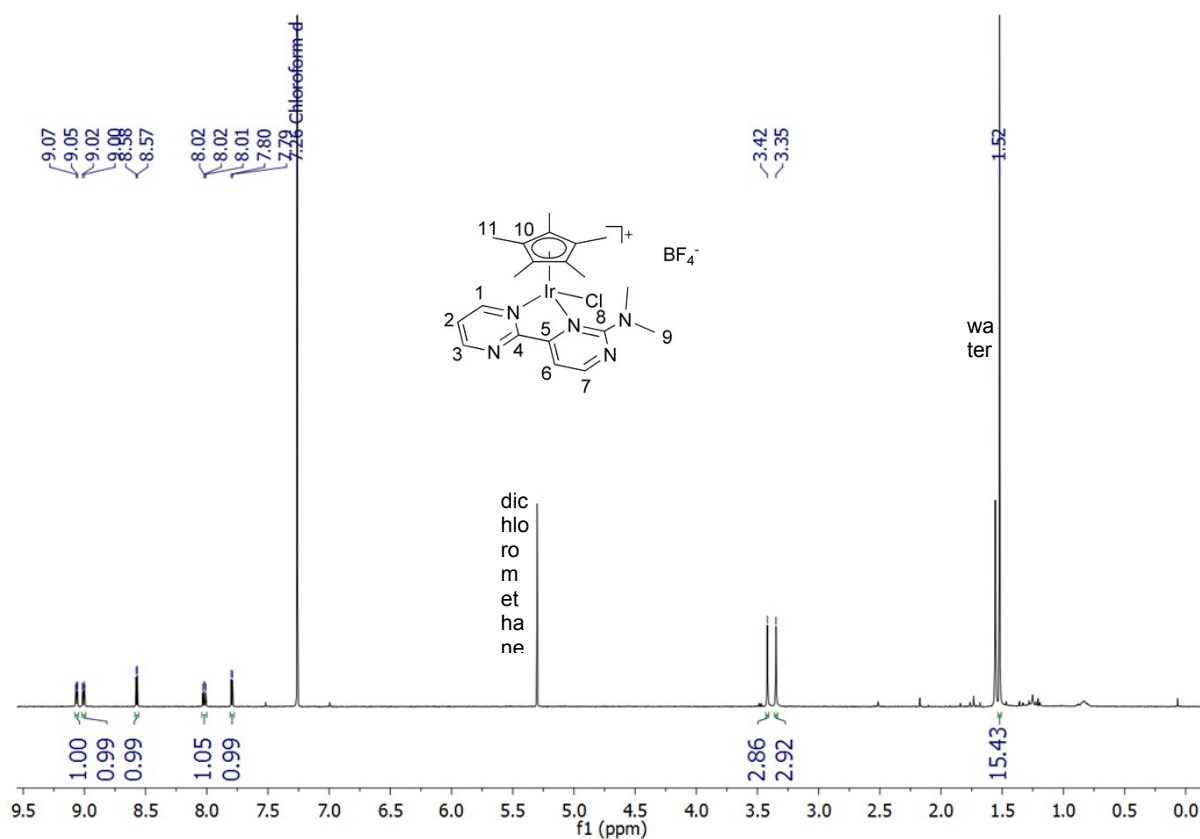


HMQC spectrum

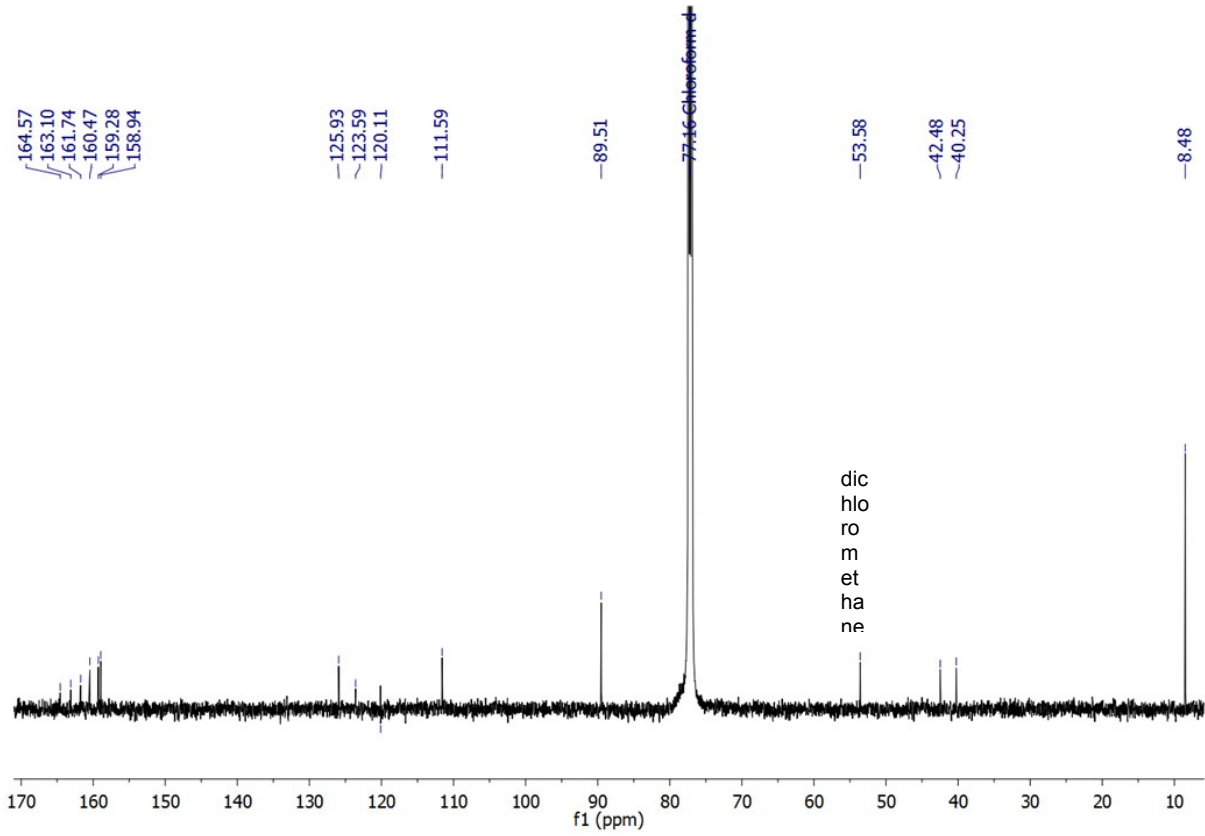


[Chlorido(*N,N*-dimethyl-(2,4-bipyrimidin)-2-amine)(η^5 -pentamethylcyclopentadienyl)iridium] tetrafluoroborate (6a**):** 16.1 mg (146 μ mol) of NaBF₄, 53 mg (66.5 μ mol) of [Cp*IrCl₂]₂ and 26.8 mg (133 μ mol) of compound **5a** were suspended in 20 mL of CH₂Cl₂. The mixture was stirred at room temperature for 20 h. The mixture was stirred for 20 h at r.t. and then filtrated. After removing the solvent under vacuum, the residue was recrystallized by vapor diffusion of Et₂O into a solution in CH₂Cl₂. Compound **6a** was obtained in 93% yield as orange colored crystals. Anal. calcd. for C₂₀H₂₆BClF₄IrN₅·(CH₂Cl₂) (735.87): C 34.28, H 3.84, N 9.52, found: C 34.12, H 4.01, N 9.38%. ¹H NMR (400.1 MHz, CDCl₃): δ 9.06 (dd, ³J_{HH} = 4.8, 2.0 Hz, 1H, H1), 9.01 (dd, ³J_{HH} = 5.8, 2.0 Hz, 1H, H3), 8.57 (d, ³J_{HH} = 4.3 Hz, 1H, H7), 8.02 (dd, ³J_{HH} = 5.7, 4.8 Hz, 1H, H2), 7.79 (d, ³J_{HH} = 4.3 Hz, 1H, H6), 3.42 (s, 3 H, H9), 3.35 (s, 3H, H9), 1.52 (s, 15 H, H11). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 163.9 (C4), 162.2 (C5 o. C8), 161.0 (C5 o. C8), 160.8 (C1), 159.8 (C7), 159.5 (C3), 125.7 (C2), 110.9 (C6), 89.5 (C11), 52.4 (C9), 50.5 (C9), 26.8 (C10), 25.0 (C10), 8.6 (C12). IR (ATR, cm⁻¹): ν 3102w, 2963w, 1603w, 1583w, 1556m, 1457m, 1401m, 1357m, 1273w, 1178w, 1027s, 823m, 736m, 705m.

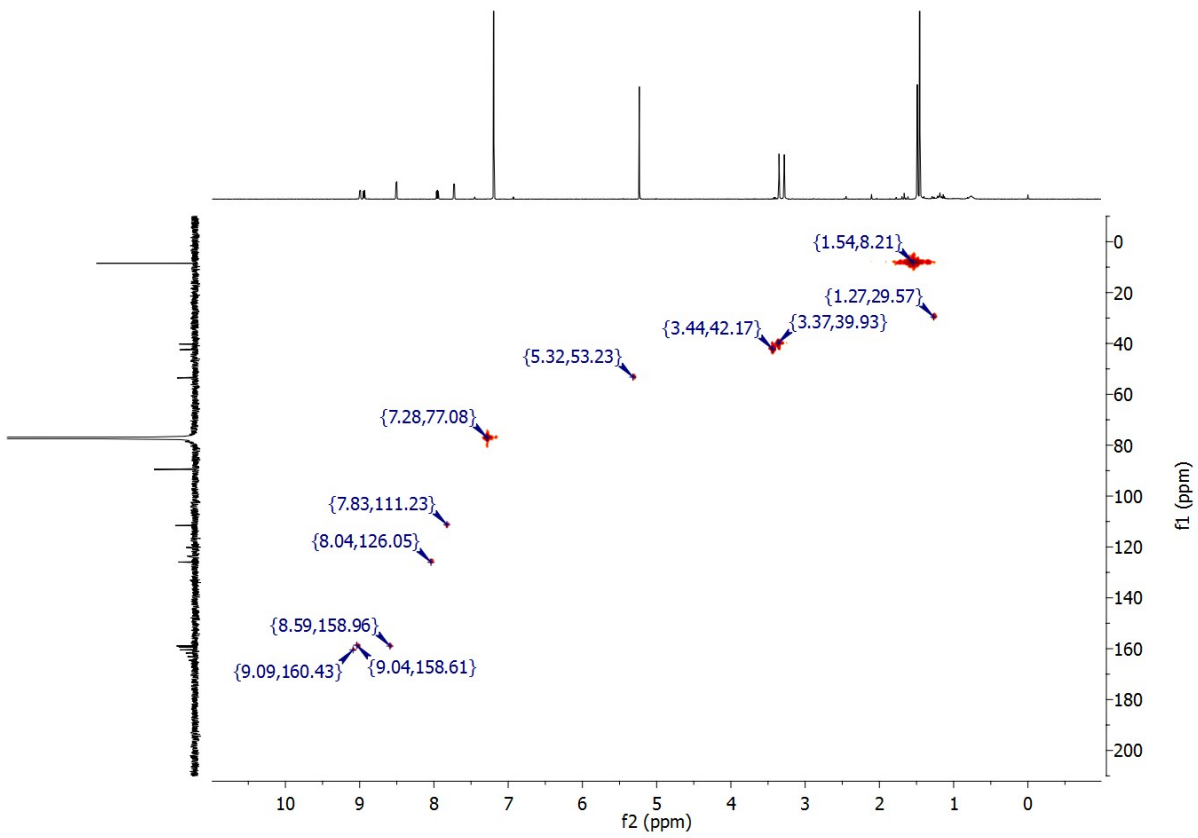
¹H NMR spectrum



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

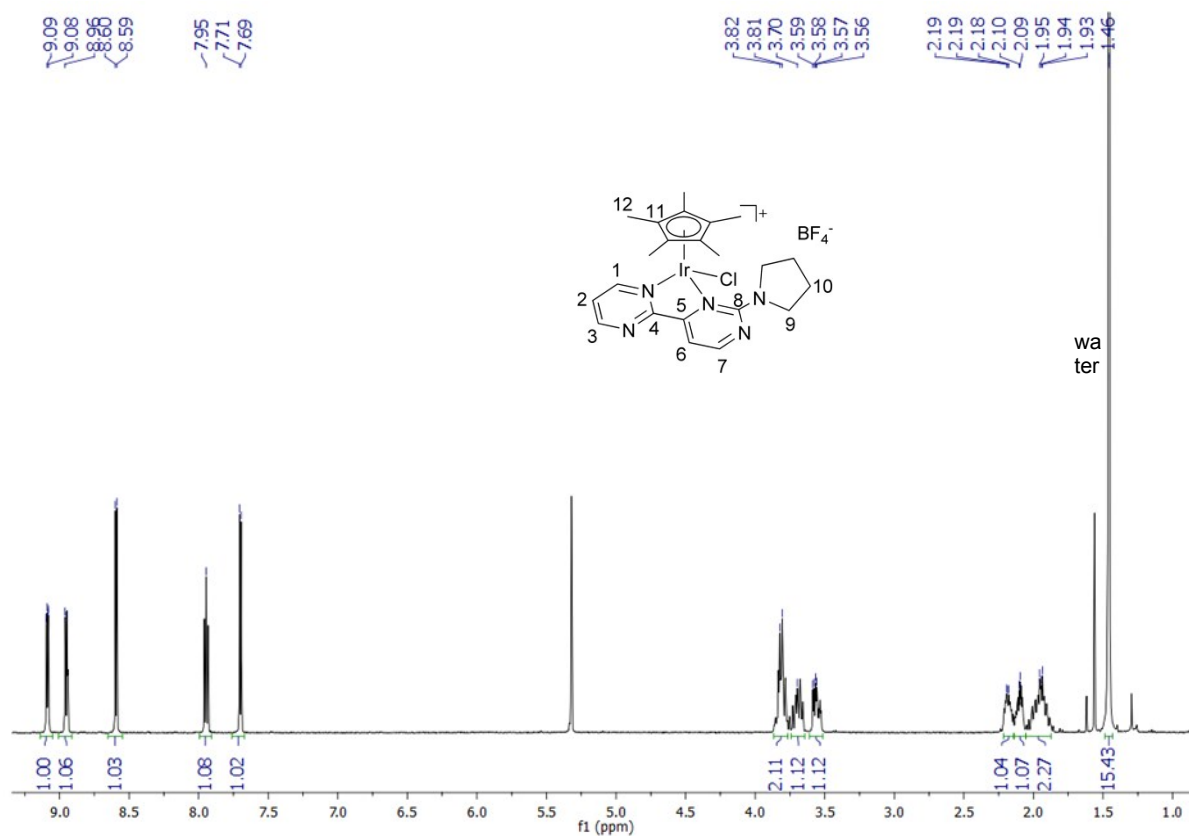


HMQC spectrum

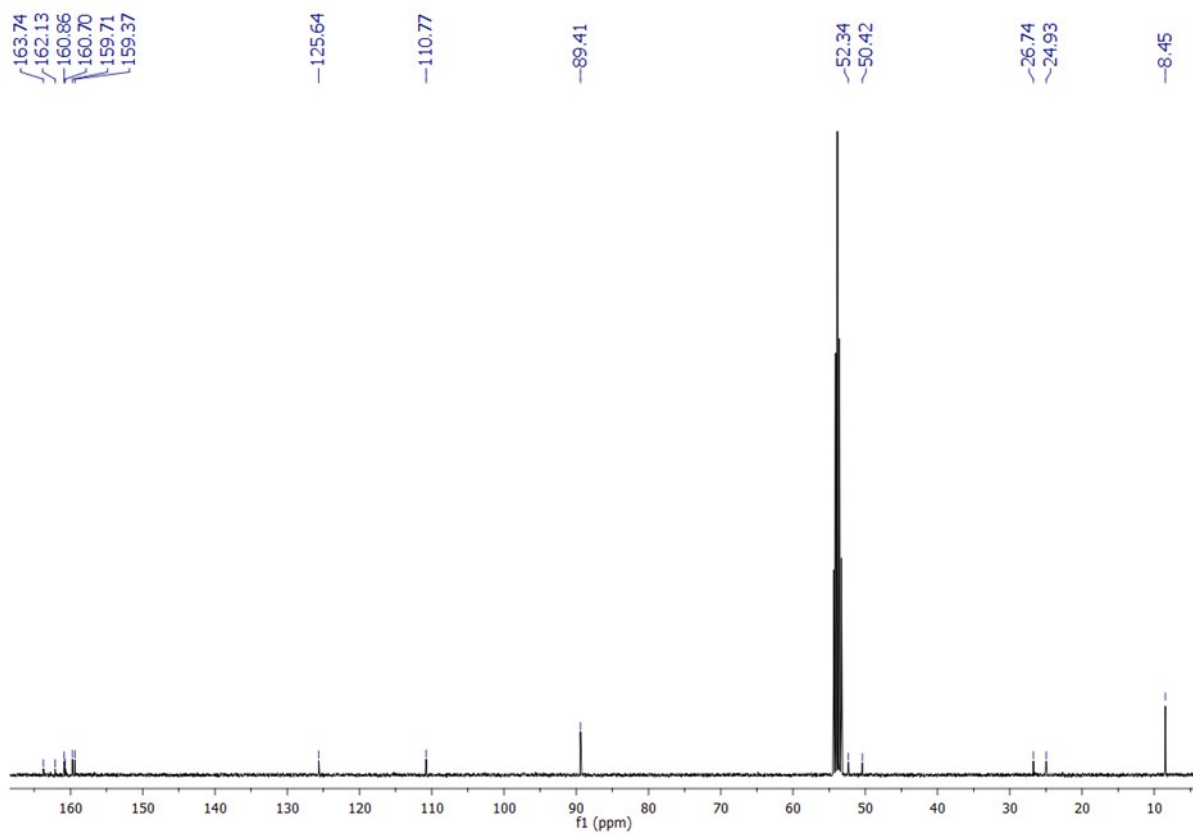


[Chlorido(η^5 -pentamethylcyclopentadienyl)(2'-(pyrrolidinyl)-2-4'-bipyrimidine)iridium] tetrafluoroborate (6b**):** 61 mg (557 μ mol) of NaBF₄, 193 mg (242 μ mol) of [Cp*IrCl₂]₂ and 110 mg (484 μ mol) of compound **5b** were suspended in 20 mL of CH₂Cl₂. The mixture was stirred for 20 h at r.t. and then filtrated. After removing the solvent under vacuum, the residue was recrystallized by vapor diffusion of Et₂O into a solution in CH₂Cl₂. Compound **6b** was obtained in 93% yield as orange colored crystals. Anal. calcd. for C₂₂H₂₈BClF₄IrN₅ (676.97): C 39.03, H 4.17, N 10.35, found: C 38.92, H 4.27, N 10.42%. ¹H NMR (400.1 MHz, CD₂Cl₂): δ 9.09 (dd, ³J_{HH} = 4.8, 2.0 Hz, 1H, H1), 8.95 (dd, ³J_{HH} = 5.7, 2.0 Hz, 1H, H3), 8.59 (d, ³J_{HH} = 4.3 Hz, 1H, H7), 7.95 (t, ³J_{HH} = 5.28 Hz, 1H, H2), 7.70 (d, ³J_{HH} = 4.3 Hz, 1H, H6), 3.89-3.76 (m, 2H, H9), 3.76-3.63 (m, 1H, H9), 3.60-3.51 (m, 1H, H9), 2.22-2.13 (m, 1H, H10), 2.13-2.05 (m, 1H, H10), 2.03-1.84 (m, 2H, H10), 1.46 (s, 15 H, H12). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ 163.9 (C4), 162.3 (C5 or C8), 161.0 (C5 or C8), 160.9 (C1), 159.9 (C7), 159.5 (C3), 125.8 (C2), 110.9 (C6), 89.6 (C11), 52.5 (C9), 50.6 (C9), 26.9 (C10), 25.1 (C10), 8.6 (C12). IR (ATR, cm⁻¹): ν 3104w, 2990w, 2972w, 2928w, 2879w, 1603m, 1581m, 1662s, 1457s, 1341m, 1284m, 1216m, 1162w, 1025vs, 854m, 820m, 771m.

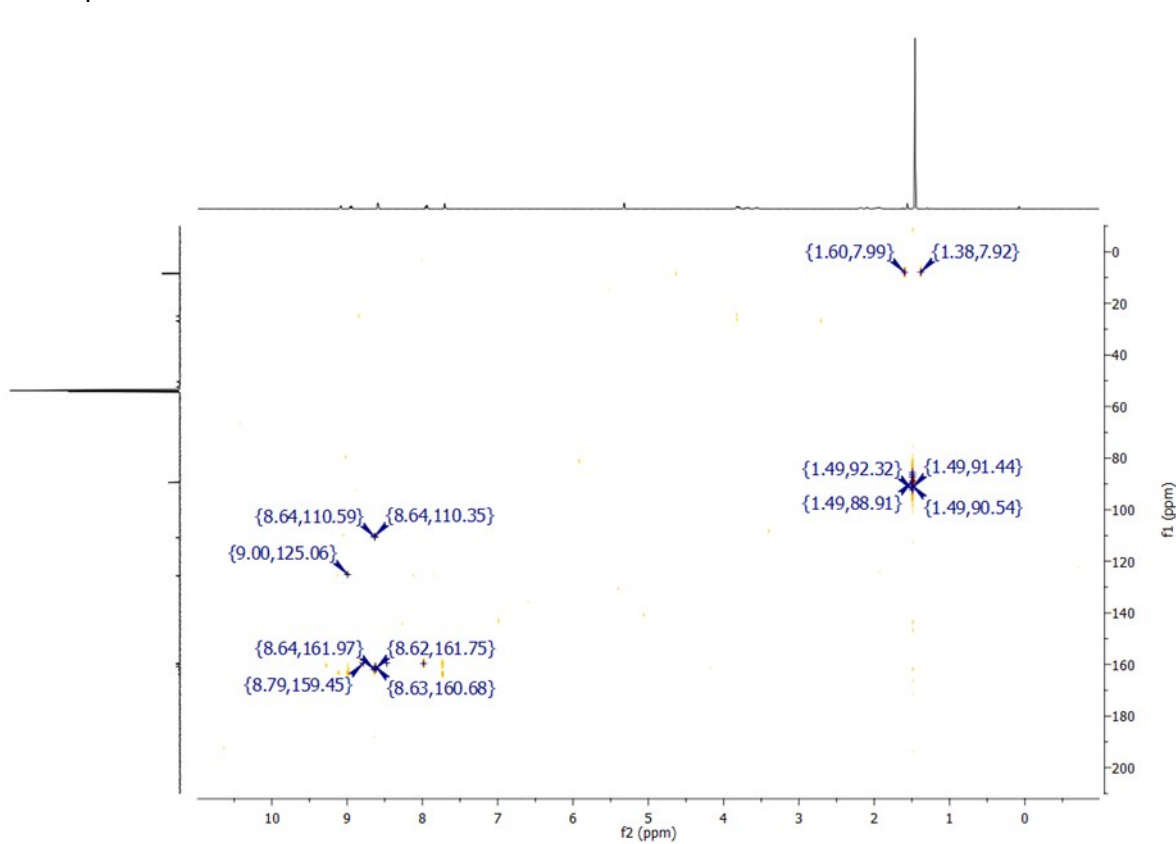
¹H NMR spectrum



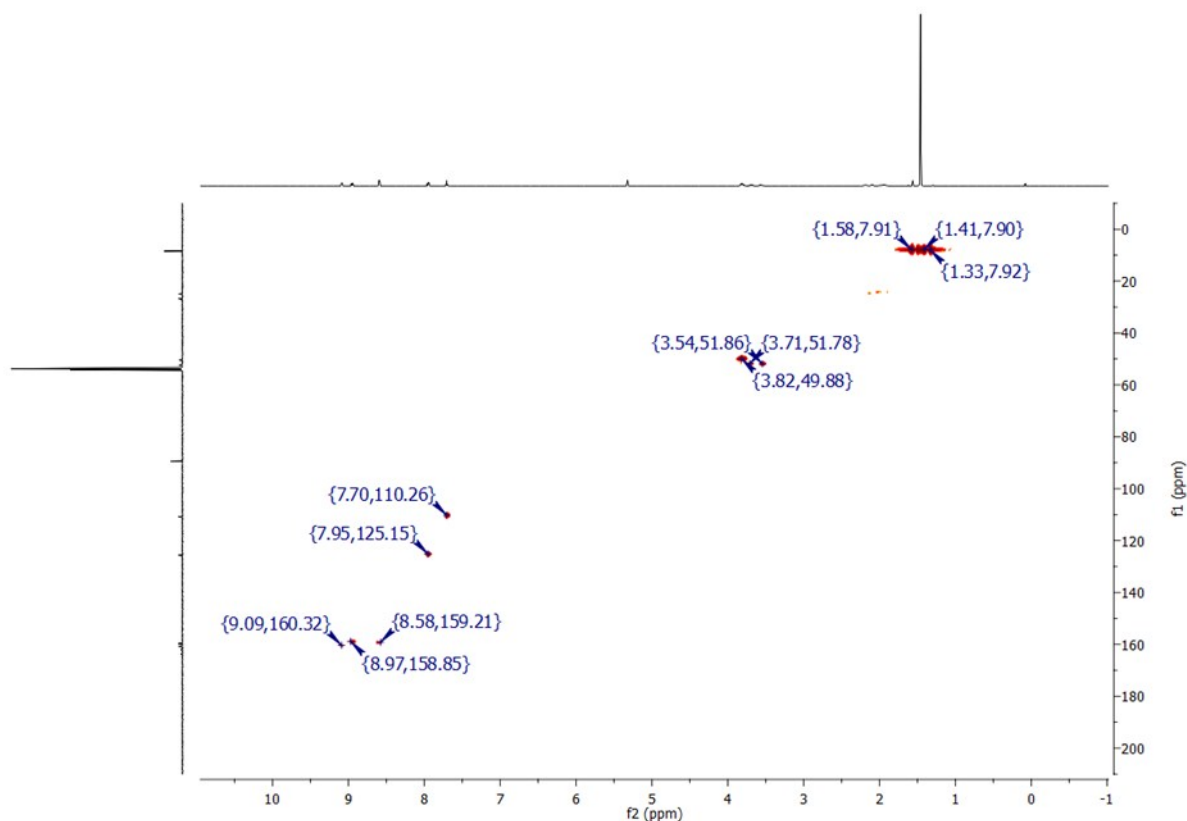
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



HMBC spectrum

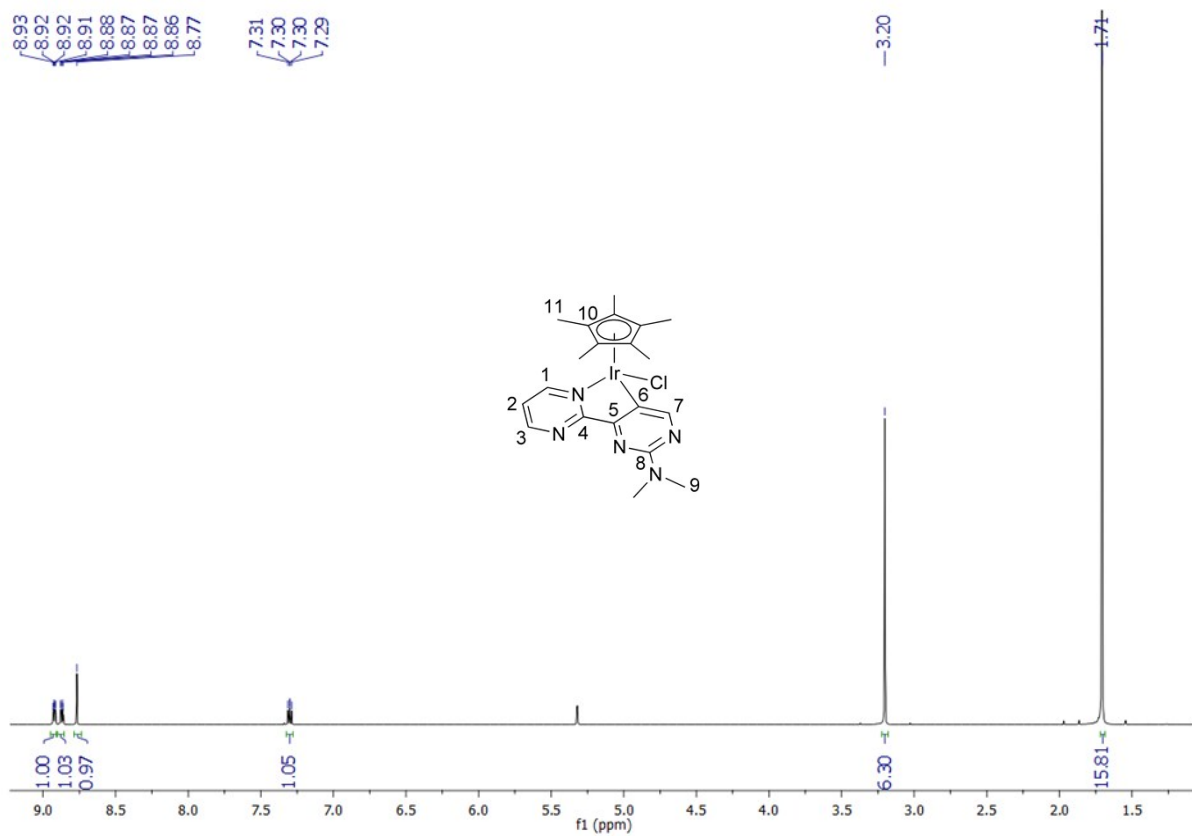


HMQC spectrum

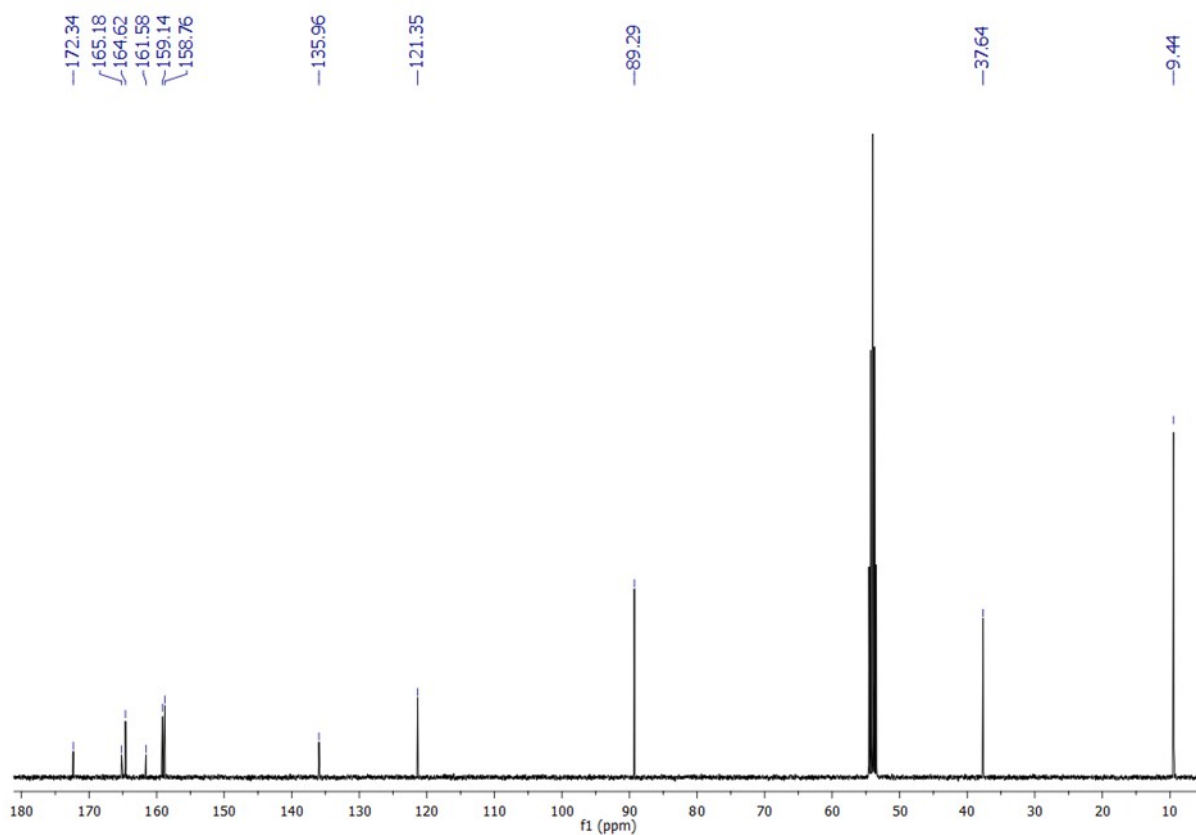


[Chlorido(2-(*N,N*-dimethylamino)-4-(pyrimidinyl)pyrimidin-5-yl)(η^5 -pentamethylcyclopentadienyl)iridium] (7a): 200 mg (252 μ mol) of [Cp*IrCl₂]₂, 49.3 mg (502 μ mol) of KOAc and 101 mg (502 μ mol) of compound **5a** were suspended in 40 mL of dry and degassed 1,2-dichlorobenzene. The mixture was stirred for 18 h at 80 °C. After removing the solvent under vacuum, the residue was purified by column chromatography (CH₂Cl₂/MeOH: 1/1) and then recrystallized by vapor diffusion of *n*-pentane into a solution in CHCl₃. Compound **7a** was obtained in 86% yield as red crystals. Anal. calcd. for C₂₀H₂₅ClIrN₅ (563.13): C 42.66, H 4.47, N 12.44, found: C 42.36, H 4.66, N 12.29%. ¹H NMR (400.1 MHz, CD₂Cl₂): δ 8.93 (dd, ³J_{HH} = 4.7, 2.2 Hz, 1H, H1), 8.87 (dd, ³J_{HH} = 5.7, 2.2 Hz, 1H, H3), 8.77 (s, 1H, H7), 7.31 (dd, ³J_{HH} = 5.7, 4.7 Hz, 1H, H2), 3.20 (s, 6H, H9), 1.71 (s, 15H, H12). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ 172.3 (C4), 165.2 (C6), 164.6 (C7), 161.6 (C8), 159.1 (C3), 158.8 (C1), 136.0 (C5), 121.4 (C2), 89.3 (C10), 37.6 (C9), 9.4 (C11). IR (ATR, cm⁻¹): ν 2921w, 2847w, 2791w, 1546s, 1511s, 1459m, 1400s, 1383s, 1206m, 1193m, 1163m, 1071m, 1027m, 1013m, 980m, 785m.

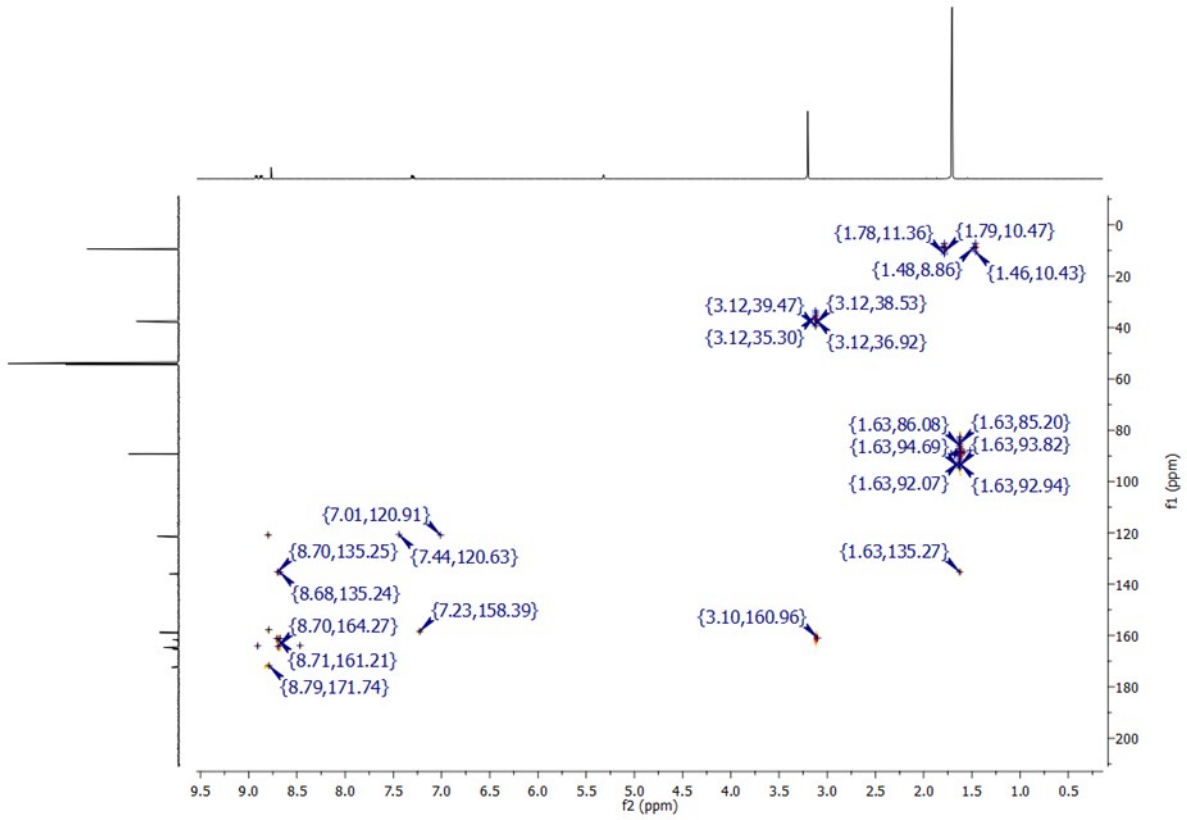
^1H NMR spectrum



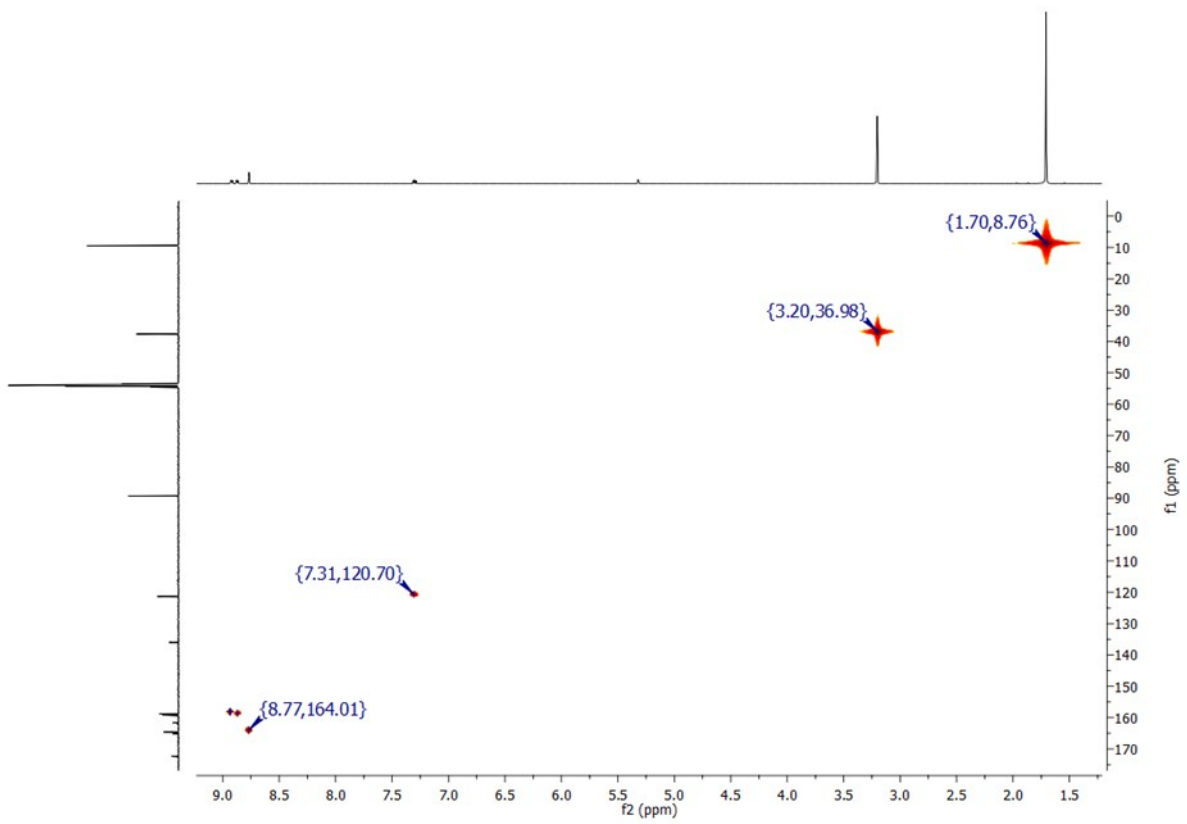
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



HMBC spectrum

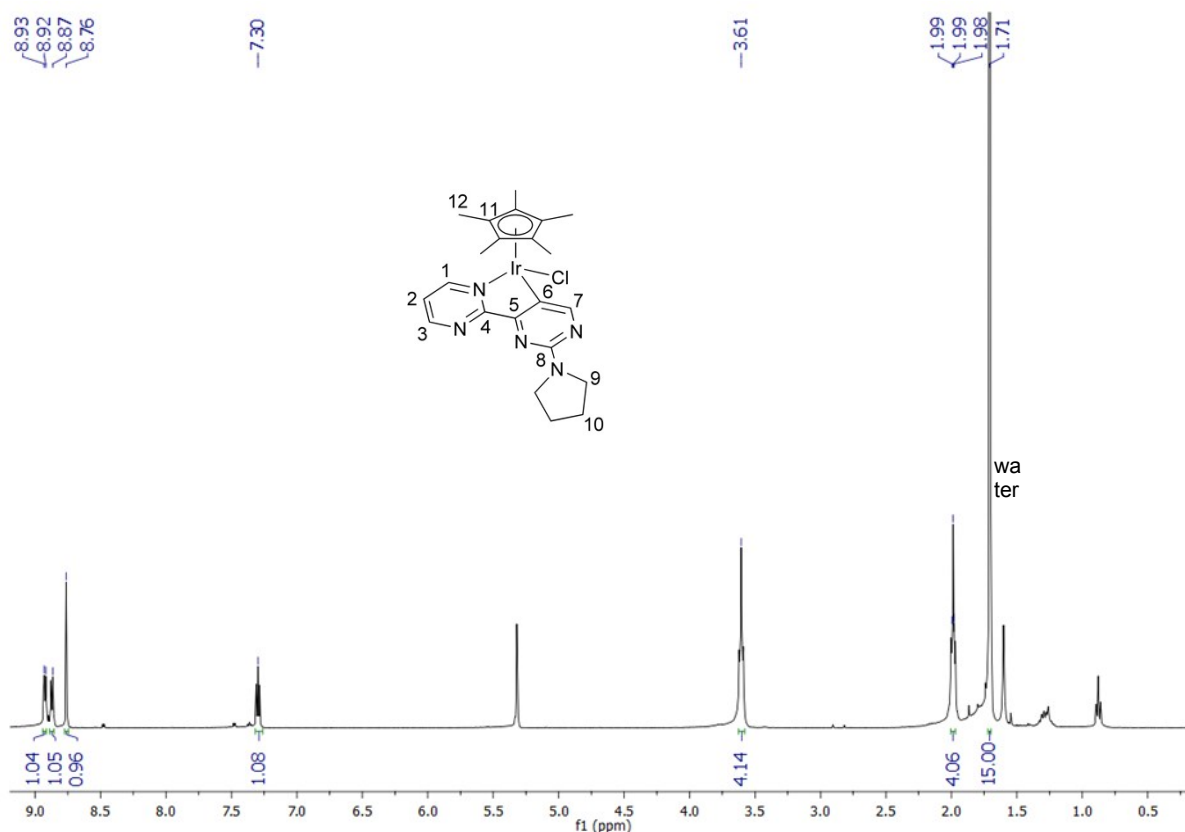


HMQC spectrum

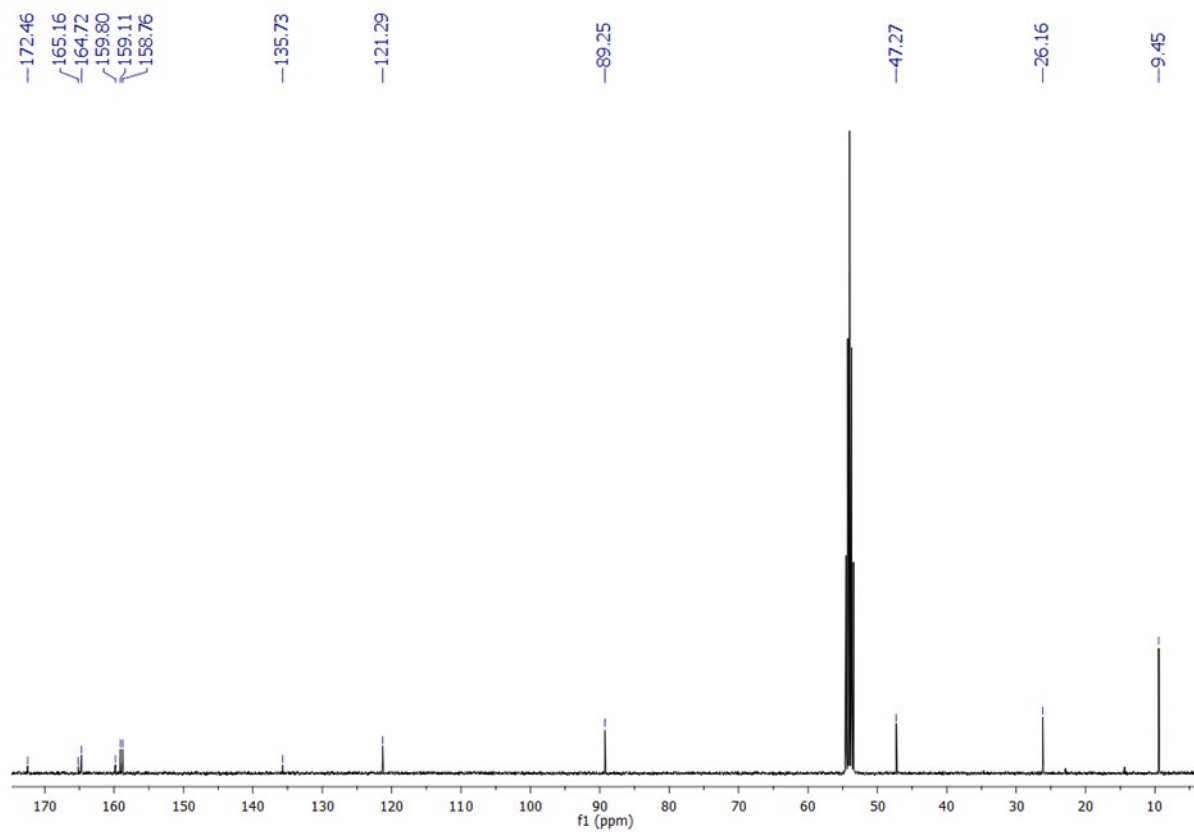


[Chlorido(2-(pyrrolidinyl)-4-(pyrimidinyl)pyrimidin-5-yl)(η^5 -pentamethylcyclopentadienyl)iridium]
(7b): 100 mg (126 μ mol) of $[\text{Cp}^*\text{IrCl}_2]_2$, 24.6 mg (251 μ mol) of KOAc and 57.0 mg (251 μ mol) of compound **5b** were suspended in 20 mL of dry and degassed 1,2-dichlorobenzene. The mixture was stirred for 18 h at 80 °C. After removing the solvent under vacuum, the residue was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$: 1/1). The solvent volume was reduced to 15 mL and the product was precipitated with *n*-pentane and dried under vacuum. Compound **7b** was obtained in 91% yield as red microcrystals. Anal. calcd. for $\text{C}_{20}\text{H}_{25}\text{ClIrN}_5$ (C_5H_{12})_{0.25} (607.20): C 45.99, H 4.98, N 11.53, found: C 45.69, H 5.22, N 11.64%. ^1H NMR (400.1 MHz, CD_2Cl_2): δ 8.93 (dd, $^3J_{\text{HH}} = 4.7, 2.1$ Hz, 1H; H1), 8.87 (dd, $^3J_{\text{HH}} = 5.7, 2.1$ Hz, 1H, H3), 8.76 (s, 1H, H7), 7.30 (t, $^3J_{\text{HH}} = 5.1$ Hz, 1H, H2), 3.64-3.57 (m, 4H, H9), 2.01-1.97 (m, 4H, H10), 1.71 (s, 15H, H12). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2): δ 172.4 (C4), 165.1 (C6), 164.7 (C7), 159.8 (C8), 159.1 (C3), 158.7 (C1), 135.7 (C5), 121.2 (C2), 89.2 (C11), 47.2 (C9), 26.1 (C10), 9.4 (C12). IR (ATR, cm^{-1}): ν 2964w, 2917w, 2863w, 1646w, 1546s, 1498m, 1480m, 1451m, 1410m, 1383m, 1198m, 1156m, 1030m, 1019m, 783m.

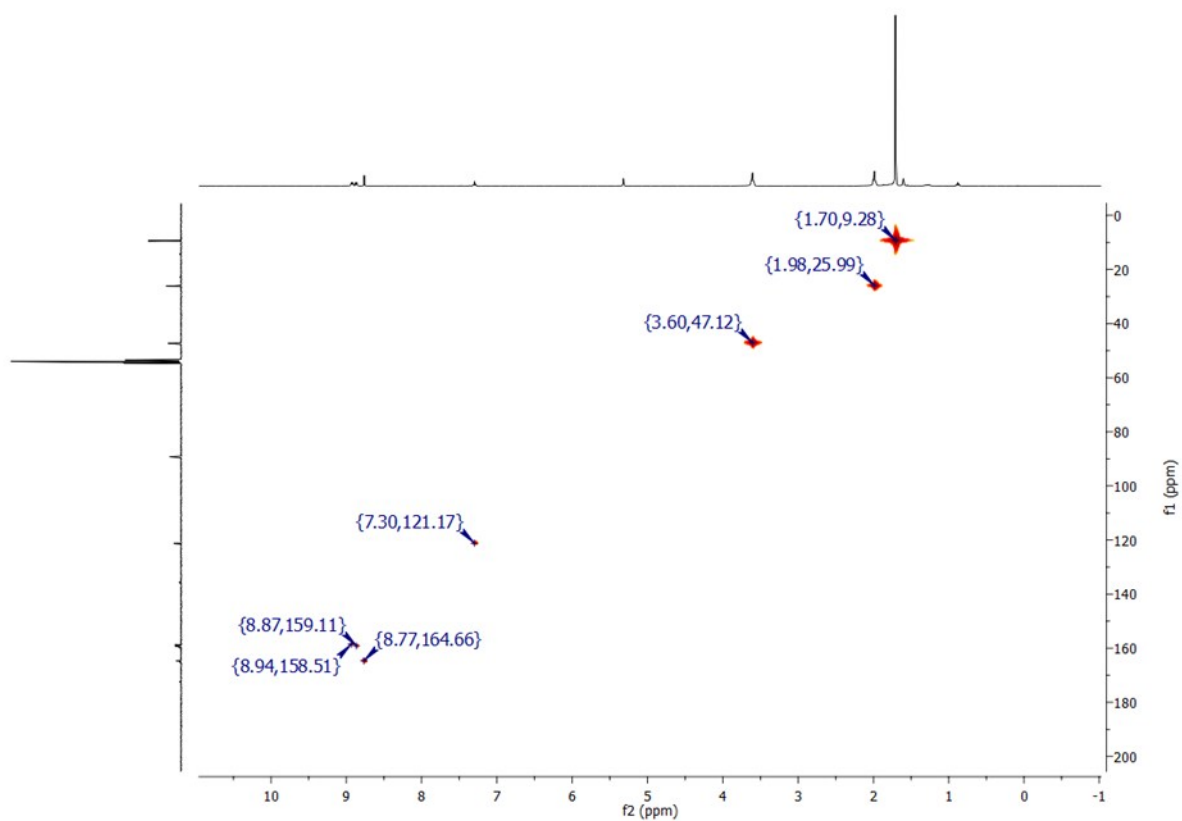
^1H NMR spectrum



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

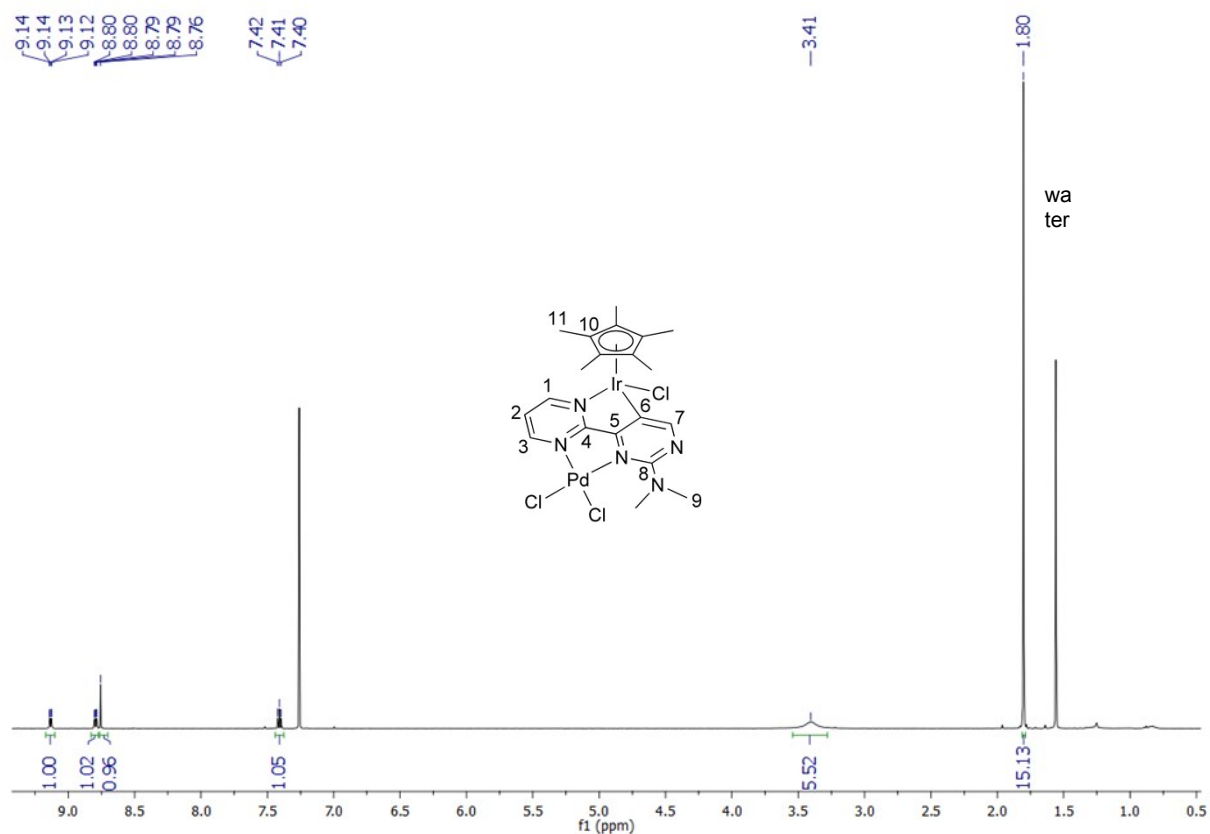


HMQC NMR spectrum

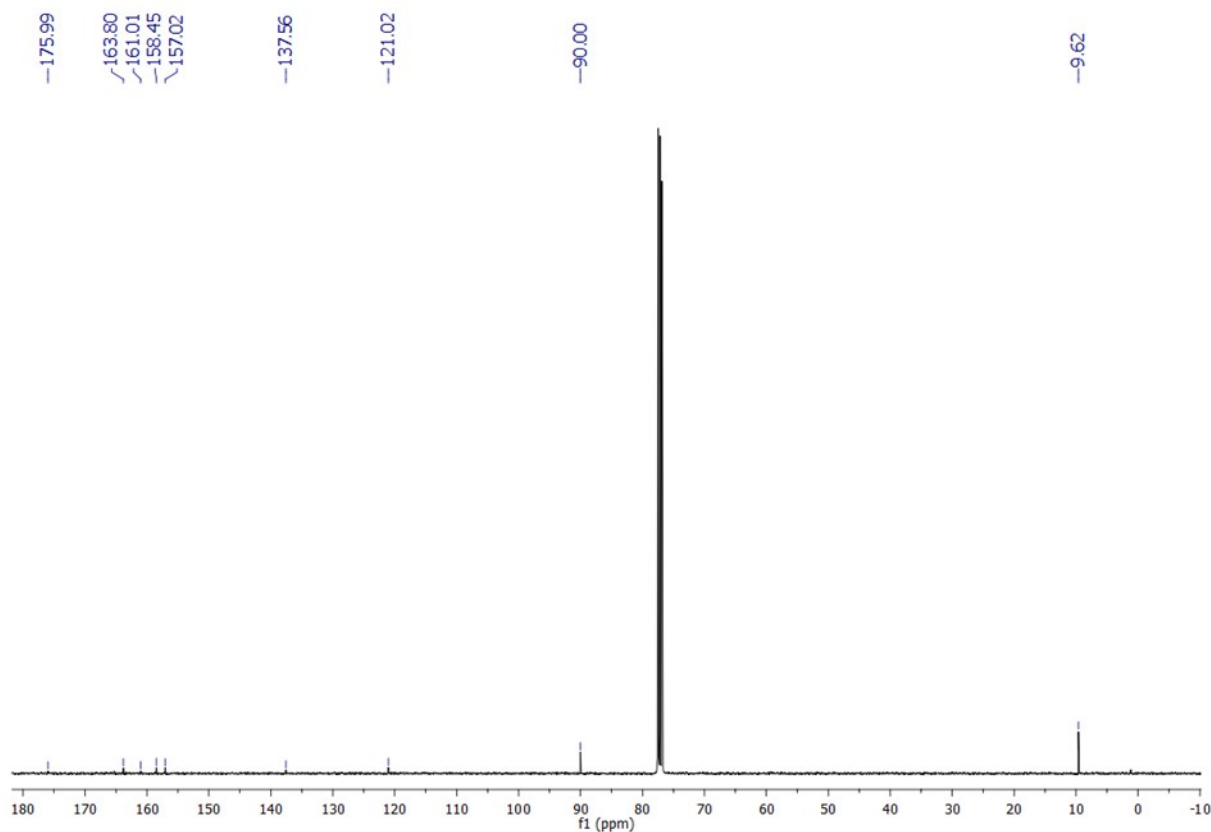


[Chlorido(2-(*N,N*-dimethylamino)-4-(pyrimidinyl)pyrimidin-5-yl)(η^5 -pentamethylcyclopentadienyl)iridium](dichlorido)palladium (8aPd**):** A solution of 50 mg (88.8 μmol) of compound 7a and 34.1 mg (88.8 μmol) of di(benzonitrile)palladium(II) dichloride in 10 mL of acetone was stirred at room temperature for 18 h. Then the solvent was removed under vacuum and the crude product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$: 1/1). The product was crystallized from THF/pentane. Compound **8aPd** was obtained in 85% yield as reddish-brown microcrystals. Anal. calcd. for $\text{C}_{20}\text{H}_{25}\text{Cl}_3\text{IrN}_5\text{Pd}\cdot(\text{C}_5\text{H}_{12})_{0.4}$ (769.29): C 34.35, H 3.90, N 9.10, found: C 34.31, H 3.95, N 9.00%. ^1H NMR (400.1 MHz, CDCl_3): δ 9.13 (dd, $^3J_{\text{HH}} = 5.6, 1.7$ Hz, 1H, H3), 8.79 (dd, $^3J_{\text{HH}} = 5.6, 1.7$ Hz, 1H, H1), 8.76 (s, 1H, H7), 7.41 (t, $^3J_{\text{HH}} = 5.6$ Hz, 1H, H2), 3.31 (s, 6H, H9), 1.80 (s, 15H, H12). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 175.9 (C4), 165.2 (C6), 163.8 (C7), 161.0 (C8), 158.4 (C1), 157.0 (C3), 137.5 (C5), 121.0 (C2), 90.0 (C10), 9.6 (C11). IR (ATR, cm^{-1}): ν 3060w, 2959w, 2915w, 2865w, 1591m, 1573m, 1557m, 1472m, 1444m, 1404m, 1378m, 1251m, 1202m, 1176m, 1126m 1064m, 1026m, 988m, 939w, 912w, 845m, 814m, 769w.

^1H NMR spectrum

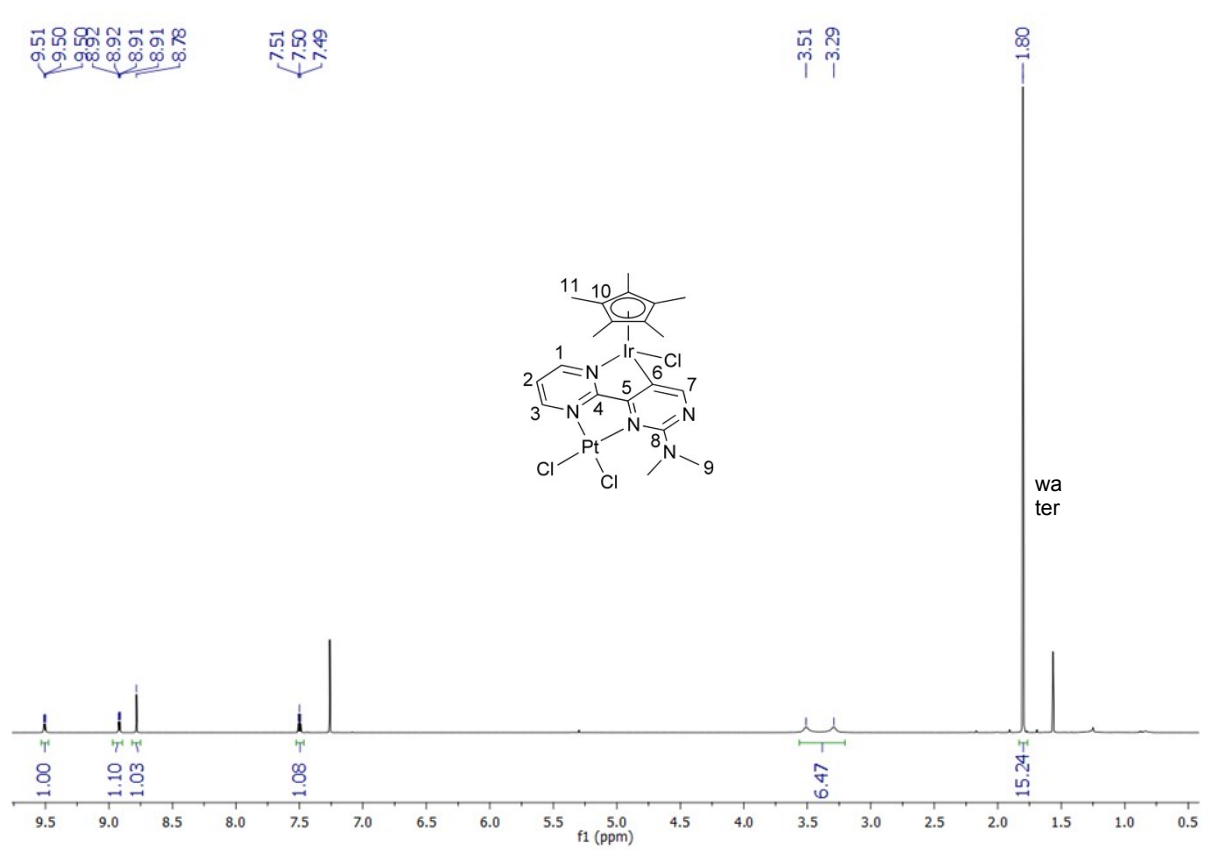


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

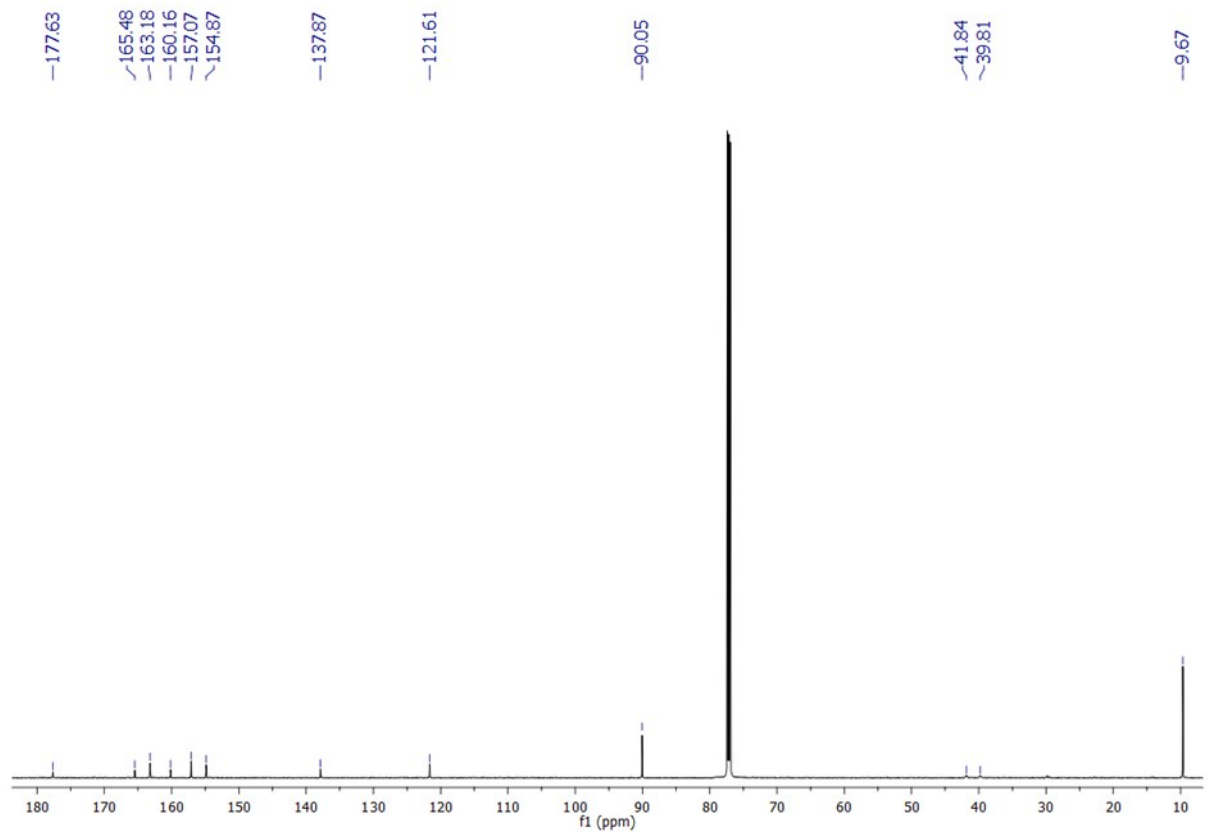


[Chlorido(2-(*N,N*-dimethylamino)-4-(pyrimidinyl)pyrimidin-5-yl)(η^5 -pentamethylcyclopentadienyl)iridium](dichlorido)platinum (8aPt**):** A solution of 92.2 mg (164 μmol) of compound **7a** and 60.3 mg (156 μmol) of $\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3](\text{H}_2\text{O})$ in 10 mL of acetone was stirred at room temperature for 68 h. The solvent was removed under vacuum and the crude product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$: 1/1). After removing of the solvents under vacuum, the product was washed twice with 5 mL of *n*-pentane and twice with 5 mL of Et_2O and then dried under vacuum. Crystals suitable for x-ray analysis were obtained by crystallisation from CDCl_3 over one week. Compound **8aPt** was obtained in 50% yield as dark purple crystals. Anal. calcd. for $\text{C}_{20}\text{H}_{25}\text{Cl}_3\text{IrN}_5\text{Pt}\cdot(\text{CHCl}_3)_{0.8}\cdot(\text{C}_5\text{H}_{12})_{0.35}$ (949.88): C 28.51, H 3.18, N 7.37, found: C 28.42, H 3.32, N 7.53%. ^1H NMR (600.1 MHz, CDCl_3): δ 9.49 (dd, $^3J_{\text{HH}} = 5.7, 1.5$ Hz, 1H, H3), 8.93 (dd, $^3J_{\text{HH}} = 5.6, 1.5$ Hz, 1H, H1), 8.78 (s, 1H, H7), 7.52 (t, $^3J_{\text{HH}} = 5.7$ Hz, 1H, H2), 3.49 (s, 3H, H9), 3.29 (s, 3H, H9), 1.80 (s, 15H, H12). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz, CDCl_3): δ 177.5 (C4), 165.6 (C6), 163.1 (C7), 160.1 (C8), 157.3 (C1), 154.8 (C3), 137.8 (C5), 121.8 (C2), 90.0 (C10), 41.6 (C9), 39.9 (C9), 9.6 (C11). ^{195}Pt NMR (129.01 MHz, CDCl_3): δ -1881.4. IR (ATR, cm^{-1}): ν 3080w, 2993w, 2919w, 1740w, 1612w, 1567m, 1463m, 1409m, 1382m, 1211w, 1122w, 1028w, 851w, 746s.

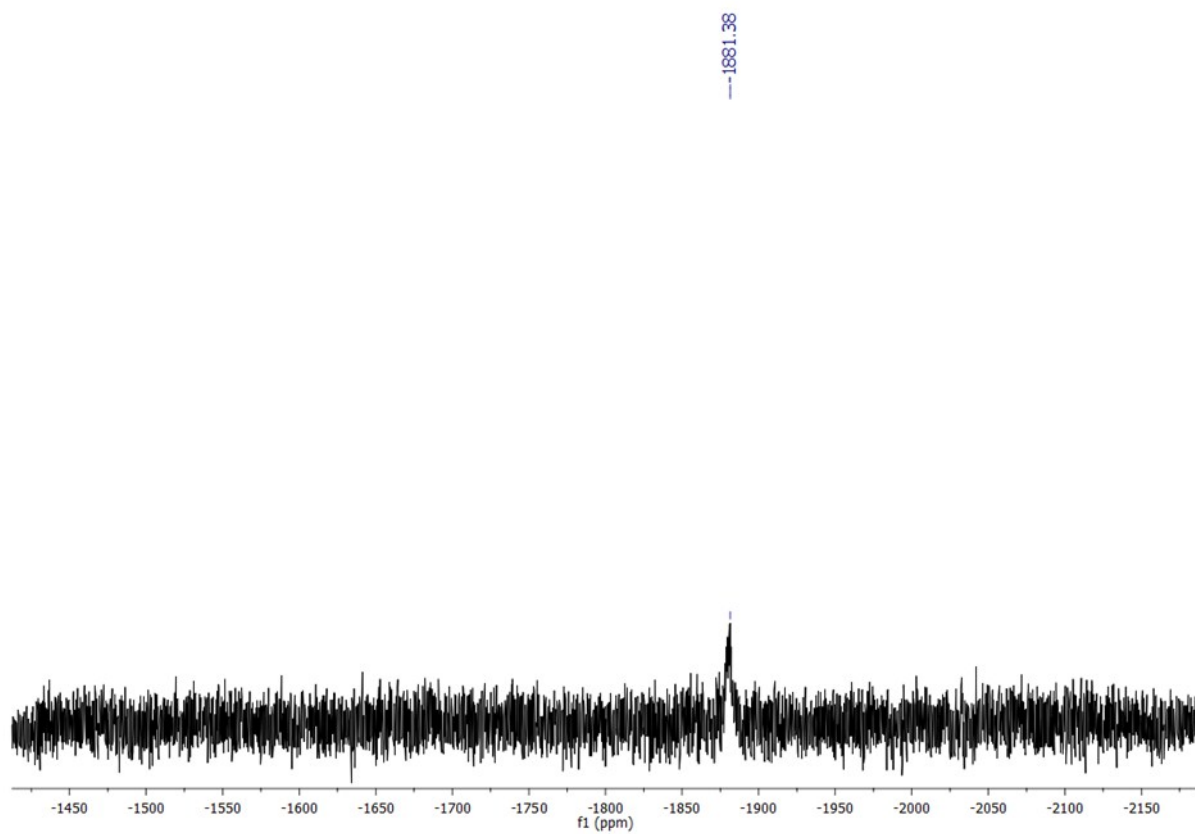
^1H NMR spectrum



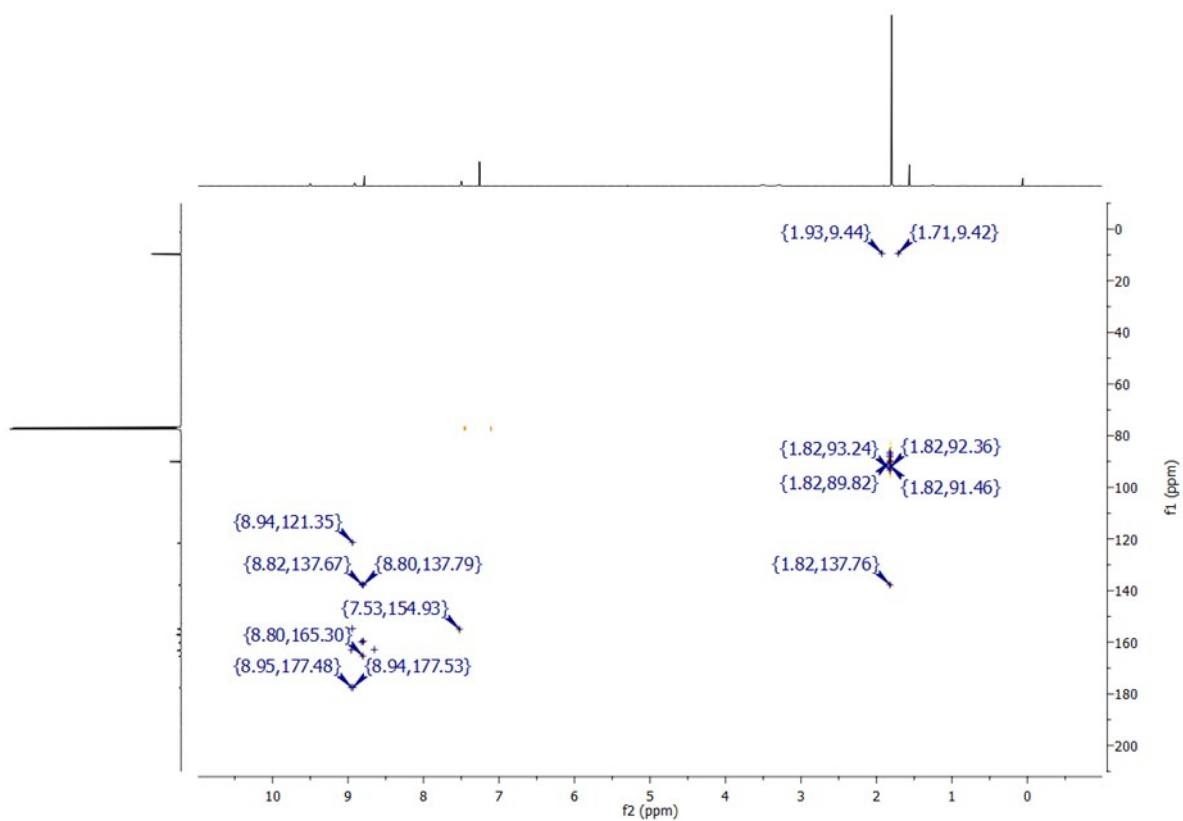
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum



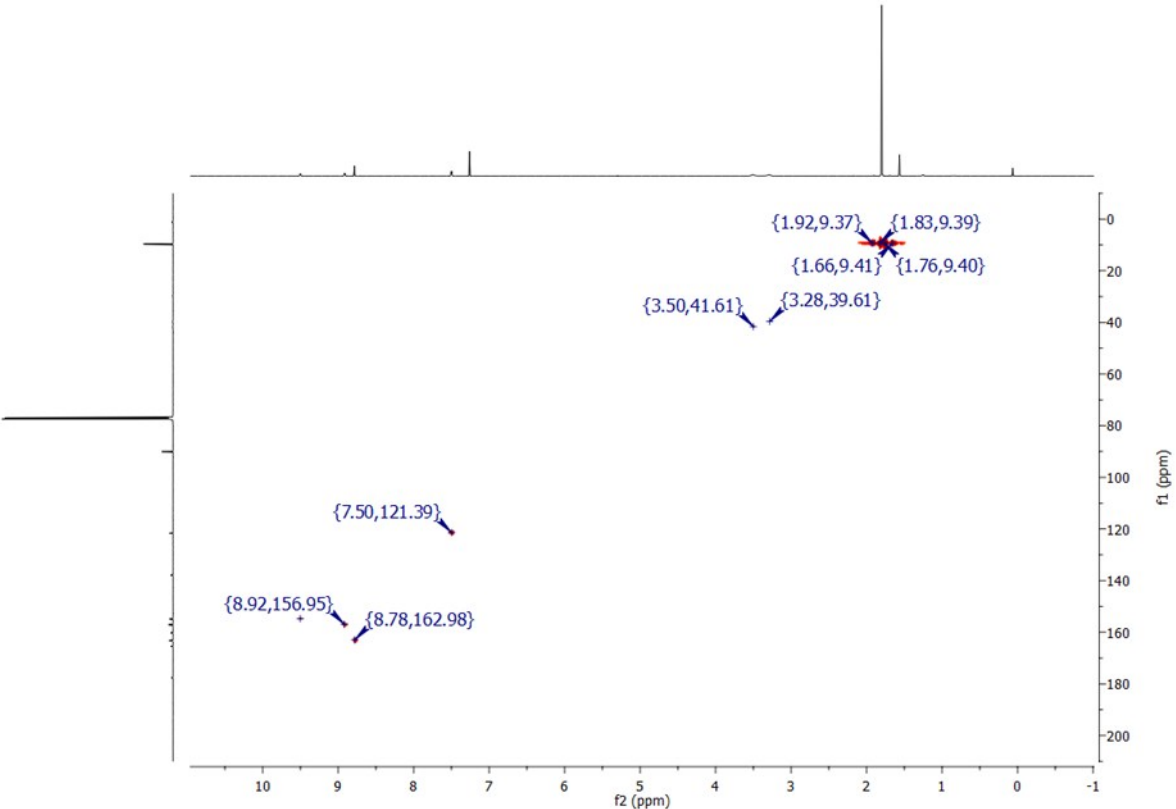
^{195}Pt NMR spectrum



HMBC spectrum



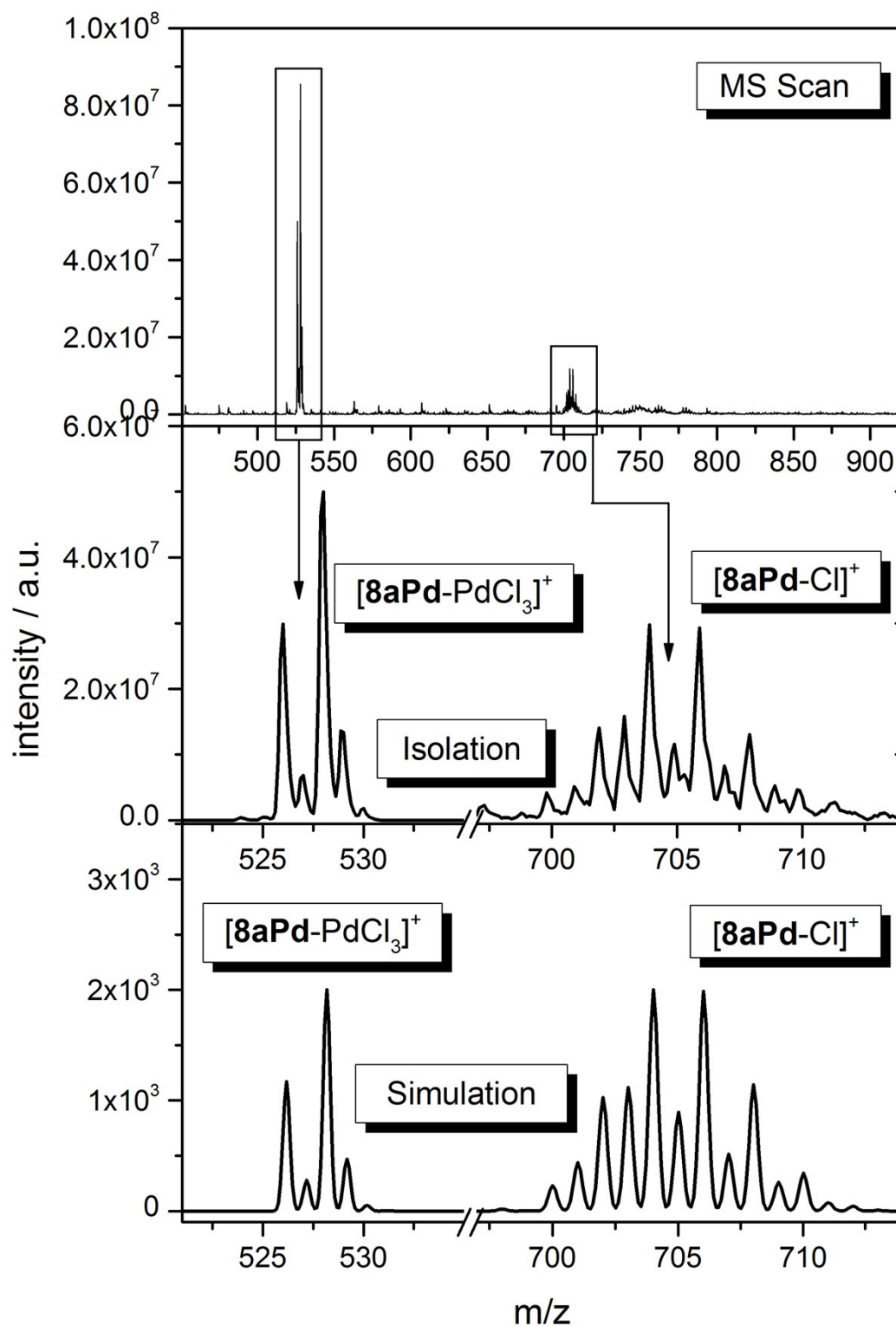
HMQC spectrum



ElectroSpray Ionization Mass Spectrometry (ESI-MS)

ESI-MS measurements were performed by a Paul-type quadrupole ion trap instrument (AmaZonETD, Bruker Daltonics) at room temperature. The ion source was set to positive and negative electrospray ionization mode to record cationic and anionic mass spectra. Scan speed was 32500 m/z / s in standard resolution scan mode (0.3 FWHM / m/z) and the scan range was 70 to 2000 m/z. Mass spectra were accumulated for at least two minutes. MSⁿ spectra were accumulated for at least twenty seconds. Sample solutions of **8aPt** and **8aPd** in acetonitrile (HPLC grade, Sigma Aldrich) at concentrations of 5×10^{-5} mol/l were continuously infused into the ESI chamber by a syringe pump at a flow rate of $2 \mu\text{L min}^{-1}$. Nitrogen was used as drying gas with a flow rate of 3.0 L min^{-1} at $220 \text{ }^\circ\text{C}$. The solutions were sprayed at a nebulizer pressure of 280 mbar (4 psi) and the electrospray needle was held at 4.5 kV. Helium was used as a buffer gas with a partial pressure of $\sim 3 \times 10^{-3}$ mbar within the ion trap.

8aPd: Positive Mode:

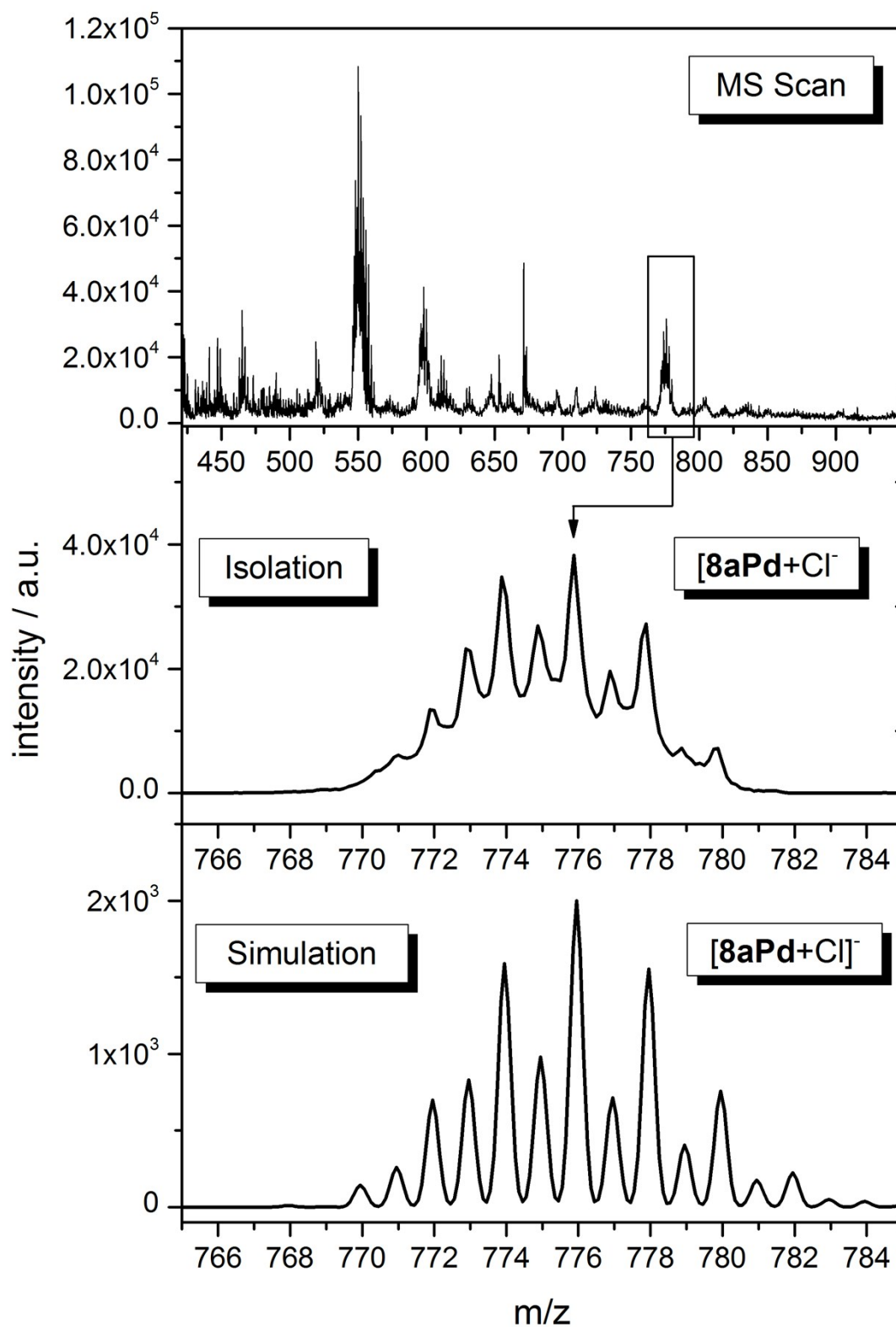


Top row: Cationic ESI mass spectrum of **8aPd** in acetonitrile.

Middle row: Recorded isotopic pattern of isolated $[8aPd-PdCl_3]^+$ and $[8aPd-Cl]^+$.

Bottom row: Simulated isotopic pattern of $[8aPd-PdCl_3]^+$ and $[8aPd-Cl]^+$.

8aPd: Negative Mode:

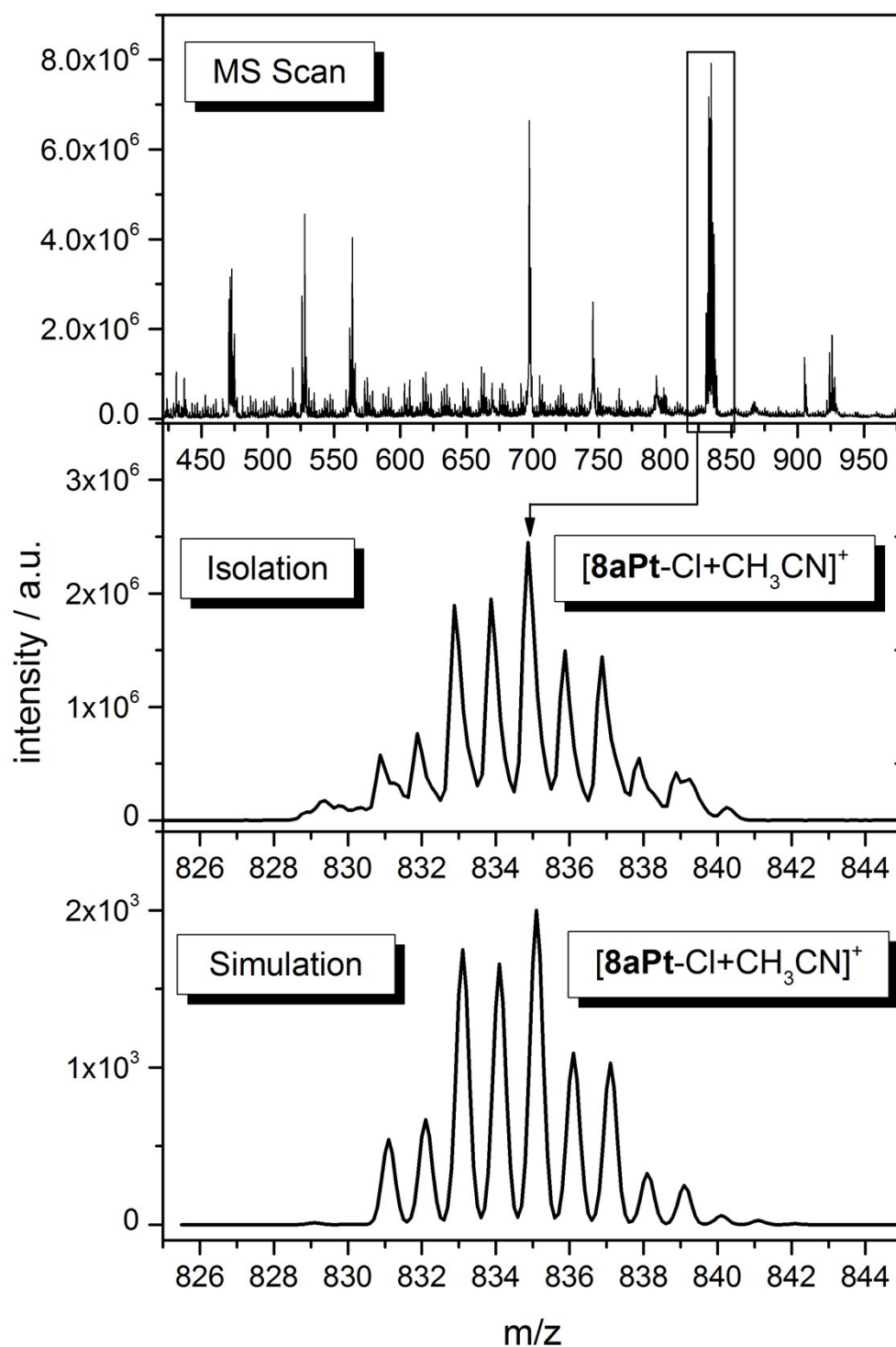


Top row: Anionic ESI mass spectrum of **8aPd** in acetonitrile.

Middle row: Recorded isotopic pattern of isolated $[8aPd+Cl]^-$.

Bottom row: Simulated isotopic pattern of $[8aPd+Cl]^-$.

8aPt: Positive Mode:

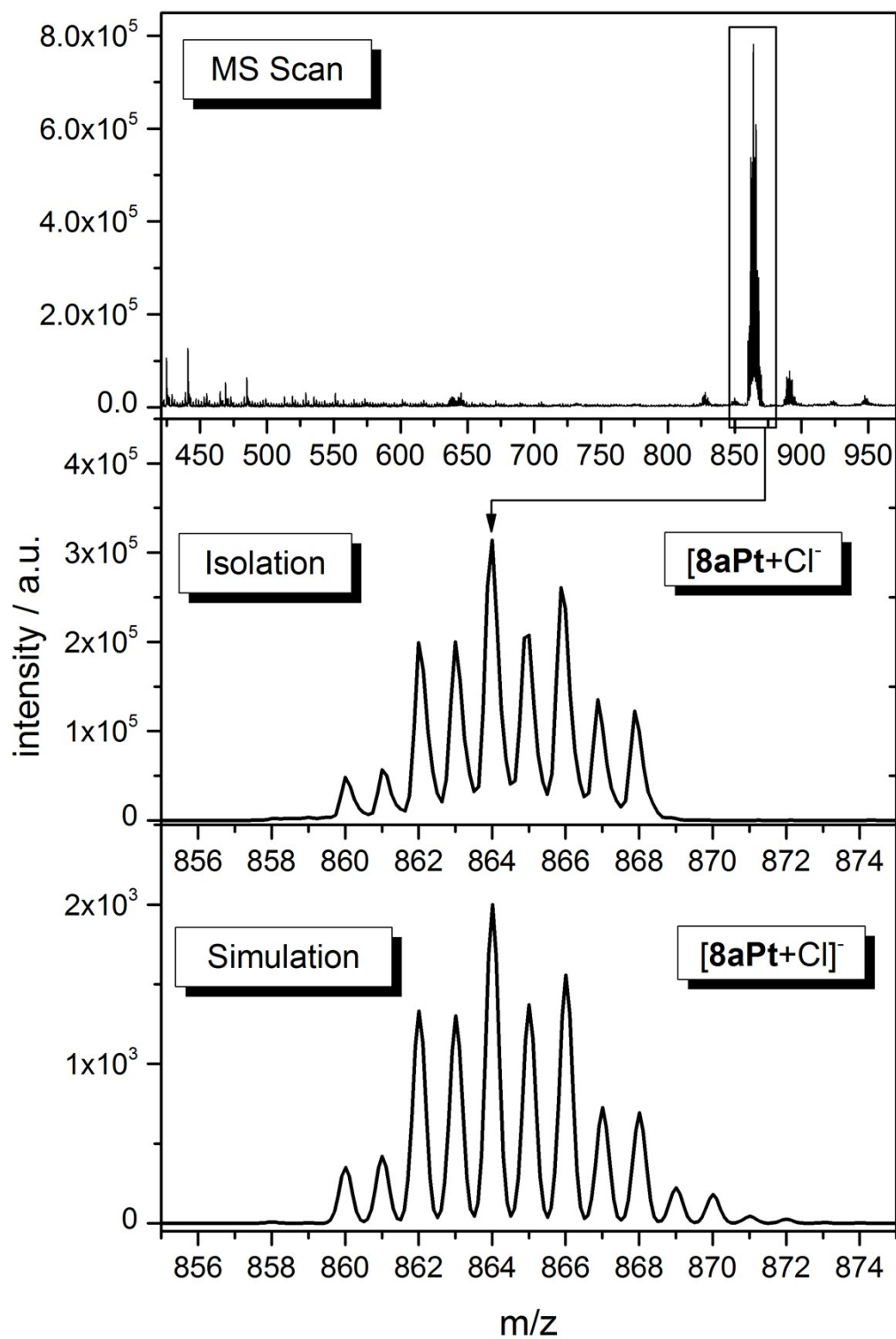


Top row: Cationic ESI mass spectrum of **8aPt** in acetonitrile.

Middle row: Recorded isotopic pattern of isolated $[8aPt-Cl+CH_3CN]^+$.

Bottom row: Simulated isotopic pattern of $[8aPt-Cl+CH_3CN]^+$.

8aPt: Negative Mode:



Top row: Anionic ESI mass spectrum of **8aPt** in acetonitrile.

Middle row: Recorded isotopic pattern of isolated **[8aPt+Cl]⁻**.

Bottom row: Simulated isotopic pattern of **[8aPt+Cl]⁻**.

Electrochemistry

Cyclic voltammograms at room temperature were performed with the PAR101 potentiostat from Metrohm in MeCN / 0.1 M NBu_4PF_6 (analyte conc. = 0.001 mol/l) with the following three electrode arrangement: Pt working electrode (1 mm diameter) or glassy carbon (GC) working electrode (1.6 mm diameter), Ag/ 0.01 M AgNO_3 , 0.1 M NBu_4PF_6 in MeCN as reference and Pt wire counter electrode. Ferrocene was added as internal standard after the measurements and all potentials are referenced relative to the Fc/Fc^+ couple. All measurements were carried out under argon atmosphere, with absolute and vented MeCN and DCM.

Cyclic voltammograms of **7a** in DCM (A and B) and MeCN (C and D) at room temperature with a scan rate of 100 mV/s (A, C: Pt tip; B, D: GC tip).

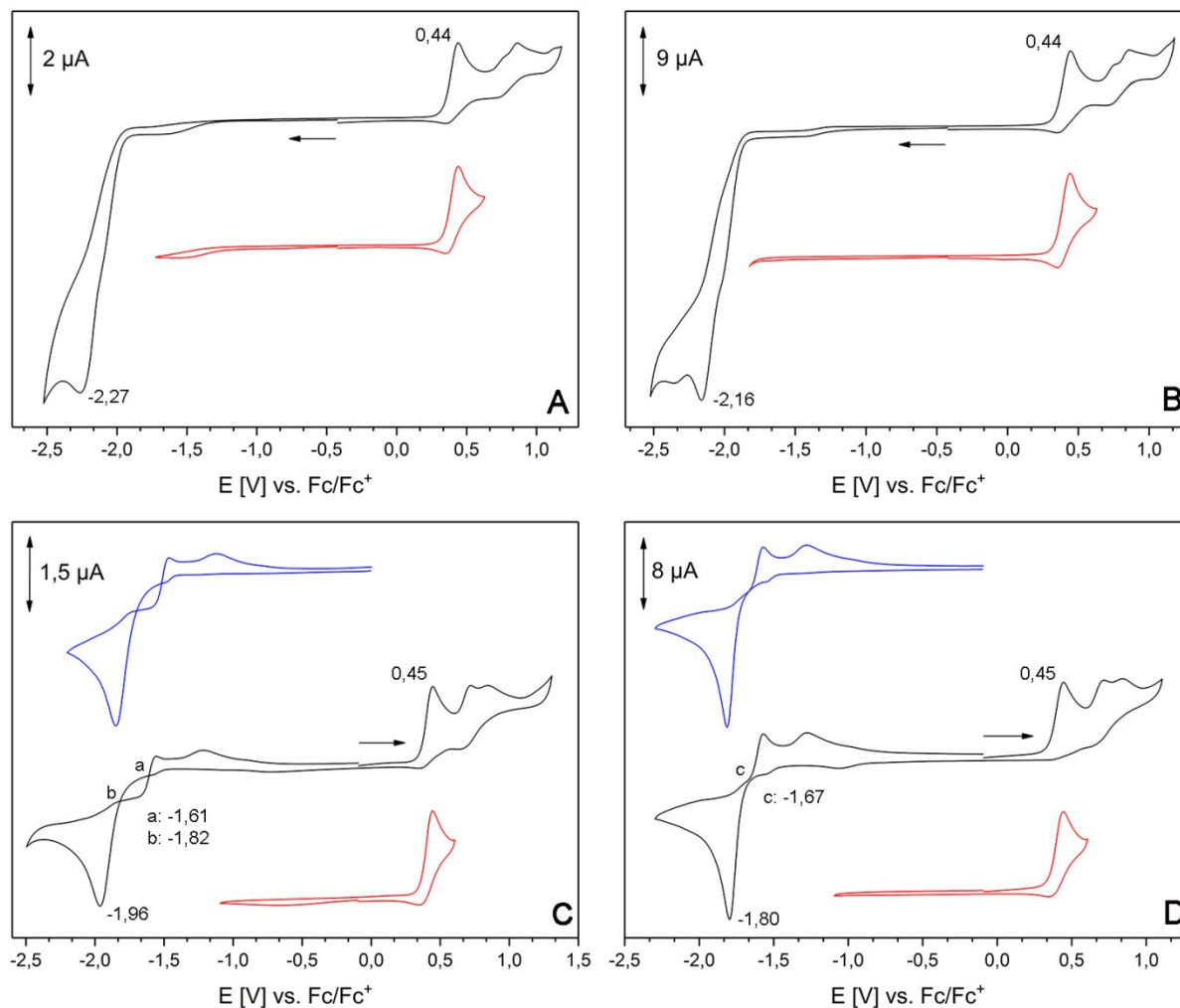
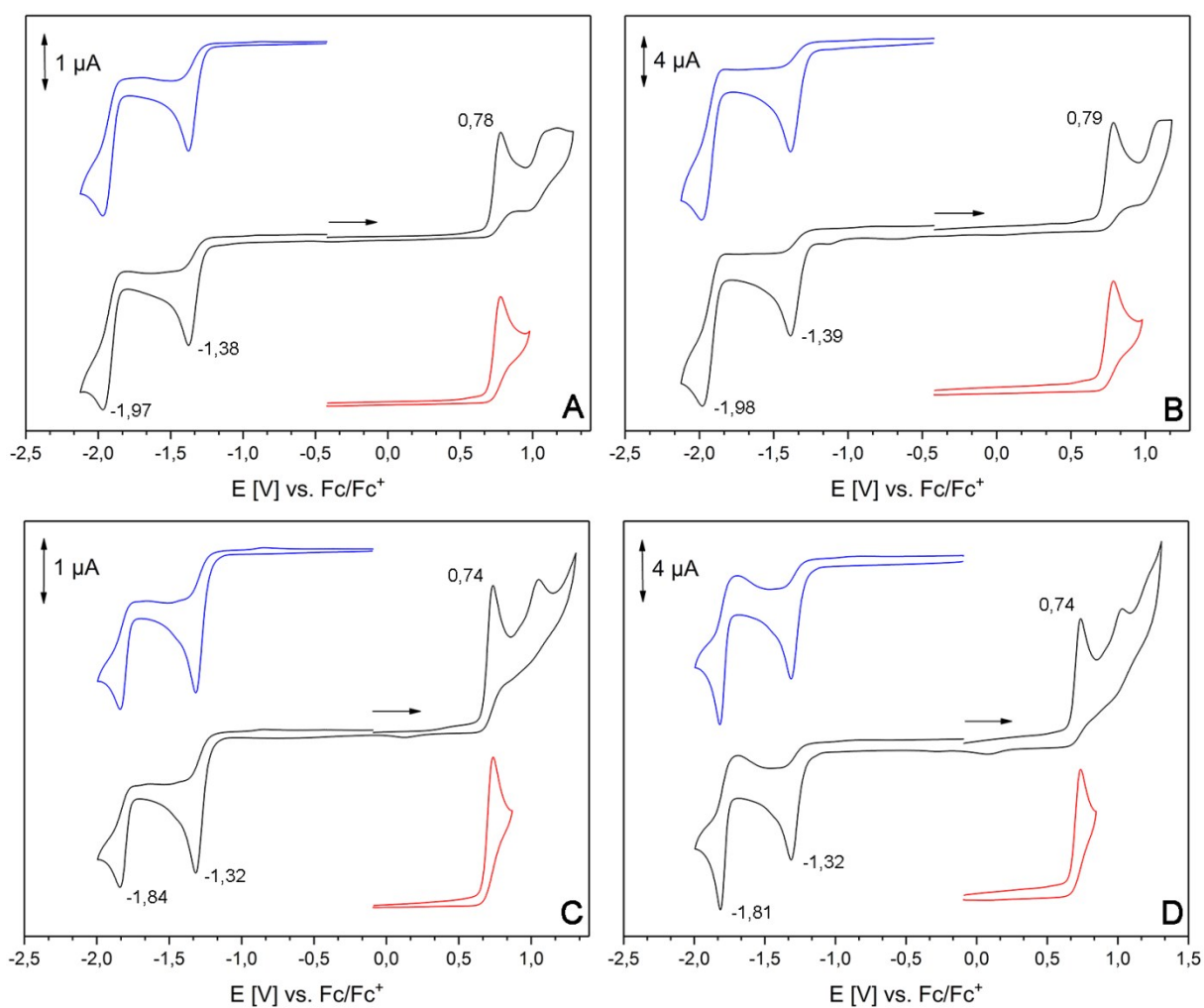
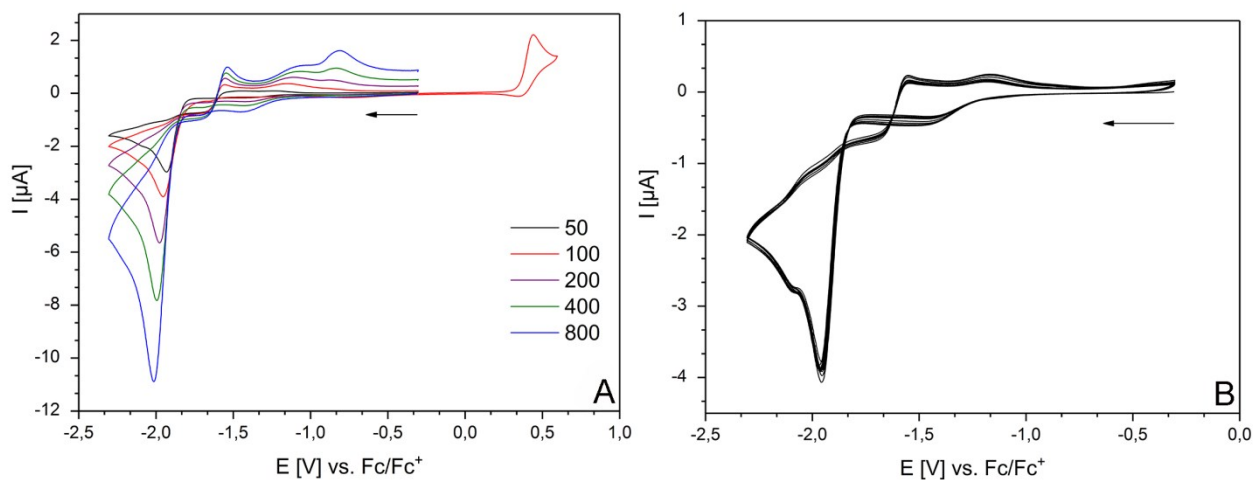


Figure y: Cyclic voltammograms of **8aPt** in DCM (A and B) and MeCN (C and D) at room temperature with a scan rate of 100 mV/s (A, C: Pt tip; B, D: GC tip).



Cyclic voltammograms of **7a** in MeCN (Pt tip) at room temperature with scan rates from 50 – 800 mV/s (A) and ten cycles of the cathodic region with 100 mV/s (B).



X-ray structure analyses

Crystal data and refinement parameters for compounds **6b**, **7a** and **8aPt** are collected in the corresponding CIF files. The structures were solved using direct methods (SIR92 for **6b** and **8aPt**, SHELXS for **7a**), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. For compounds **6b** and **8aPt**, analytical numeric absorption corrections were carried out, while a numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied on complex **7a**. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model. CCDC-xxxxxxx (**6b**), CCDC-xxxxxxx (**7a**), and CCDC-xxxxxxx (**8aPt**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.