Supporting Information

Modifying Emission Spectral Bandwidth of Phosphorescent Platinum(II) Complexes Through Synthetic Control

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General Procedures

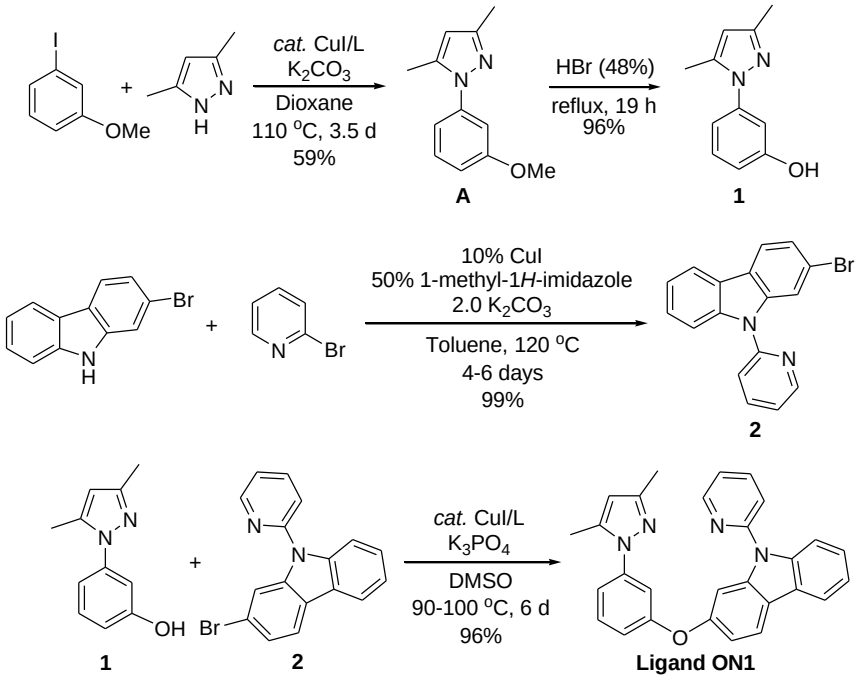
All commercial reagents were purchased and used as received without further purification. K_2PtCl_4 was purchased from Aldrich Chemical. $^nBu_4NBr$ and CuI were purchased from Aldrich Chemical. Silica gel (40-60μm) was purchased from Agela Technologies. Solvents toluene (low water) and THF were purchased from J. T. Baker and Aldrich respectively. 2-Bromopyridine was purchased from Alfa Aesar. 2-Bromo-4-tert-butylpyridine was purchased from AfferChem, Inc. 2-Bromo-4-methylpyridine, 2-bromo-5-methylpyridine and 2-bromo-4-(trifluoromethyl)pyridine were purchased from Matrix Scientific. 2-Bromo-6-methylpyridine was purchased from Oakwood Products, Inc. 2-Chloro-4-iodopyridine was purchased from Ark Pharm, Inc.

^1H NMR spectra were recorded at 400 MHz, ^{13}C NMR NMR spectra were recorded at 100 or 125 MHz on Varian Liquid-State NMR instruments in DMSO-d_6 solutions and chemical shifts were referenced to residual protiated solvent. ^1H NMR spectra were recorded with residual H_2O (δ = 3.33 ppm in DMSO-d_6; δ = 1.52 ppm in CD_2Cl_2) as internal reference; ^{13}C NMR spectra were recorded with DMSO-d_6 (δ = 39.52 ppm) or CD_2Cl_2 (δ = 53.84 ppm) as internal reference. ^{19}F NMR spectra was referenced to $PhCF_3$ in C_6D_6 (δ = -65.00 ppm) as external standard. The following abbreviations (or combinations thereof) were used to explain ^1H NMR ultiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on Shimadzu Biotech Axima Performance MALDI-TOF mass spectrometer. The Microanalysis Laboratory at Shanghai Institute of Organic Chemistry performed the elemental analysis. Density functional theory (DFT) caculations were performed using the Titan software package (wave function, Inc.) at the B3LYP/LACVP** level.

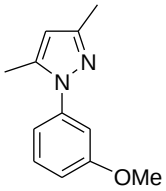
Steady state emission experiments at room temperature were performed on a Horiba Jobin Yvon FluoroLog-3 spectrometer.

Experimental Procedures

Synthesis of **Ligand ON1:**

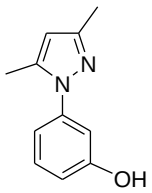


Synthesis of 1-(3-methoxyphenyl)-3,5-dimethyl-1*H*-pyrazole **A**:



A mixture of 1-iodo-3-methoxybenzene (7.15 mL, 60 mmol, 1.0 eq), 3,5-dimethyl-1*H*-pyrazole (6.92 g, 72 mmol, 1.2 eq), CuI (0.46 g, 2.4 mmol, 0.04 eq), K_2CO_3 (17.41 g, 126 mmol, 2.1 eq), *trans*-1,2-cyclohexanediamine (1.37 g, 12 mmol, 0.2 eq) and solvent dioxane (45 mL) was stirred at a temperature of 110 ^oC for 3.5 days under a nitrogen atmosphere, then cooled down to ambient temperature. The solid was filtered off and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel using hexane and ethyl acetate (10:1-3:1) as eluent to obtain the desired product 1-(3-methoxyphenyl)-3,5-dimethyl-1*H*-pyrazole **A** as a brown liquid 7.12 g in 59% yield. ^1H NMR (DMSO-d_6, 400 MHz): δ 2.18 (s, 3H), 2.30 (s, 3H), 3.80 (s, 3H), 6.06 (s, 1H), 6.95 (dd, J = 8.0, 2.4 Hz, 1H), 7.02-7.06 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H).

Synthesis of 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenol **1**:

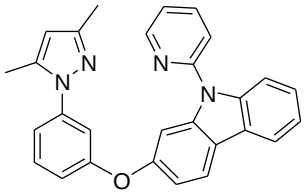


A solution of 1-(3-methoxyphenyl)-3,5-dimethyl-1*H*-pyrazole **A** (7.10 g, 35.11 mmol) in hydrogen bromide acid (45 mL, 48%) refluxed (110-120 ^{o}C) for 19 hours under a nitrogen atmosphere. Then the mixture was cooled down to ambient temperature and neutralized with a solution of K_2CO_3 in water until there was no gas to generate. Then the precipitate was filtered off and washed with water for several times. The collected solid was dried in air under reduced pressure to afford the product as a brown solid 6.33 g in 96% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.16 (s, 3H), 2.28 (s, 3H), 6.04 (s, 1H), 6.75-6.77 (m, 1H), 6.86-6.89 (m, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 9.73 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.29, 13.30, 107.07, 111.10, 113.94, 114.43, 129.71, 138.95, 140.70, 147.57, 157.84.

Improved synthesis of 2-bromo-9-(pyridin-2-yl)-9*H*-carbazole **2**:

A mixture of 2-bromocarbazole (3.91 g, 15.89 mmol, 1.0 eq), 2-bromopyridine (4.55 mL, 47.68 mmol, 3.0 eq), CuI (0.30 g, 1.59 mmol, 0.1 eq), K_2CO_3 (4.39 g, 31.78 mmol, 2.0 eq), 1-methyl-1*H*-imidazole (0.63 mL, 7.95 mmol, 0.5 eq) and toluene (60 mL) was stirred at a temperature of 120 ^{o}C for 4-6 days under a nitrogen atmosphere, then cooled down to ambient temperature. The reaction was monitored by TLC until the starting material 2-bromocarbazole was consumed completely. The solid was filtered off and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the excess 2-bromopyridine was also distillated under reduced pressure at high temperature. The residue was purified through column chromatography on silica gel using dichloromethane as eluent to obtain the desired product as a white solid 5.10 g in 99% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.37 (t, *J* = 8.0 Hz, 1H), 7.49-7.55 (m, 3H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4Hz, 1H), 7.99 (d, *J* = 1.6 Hz, 1H), 8.16 (td, *J* = 8.0, 2.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.77 (dd, *J* = 5.2, 1.2 Hz, 1H). This ^{1}H NMR data is in agreement with the reported literature[S1]. It should be noted that the starting material 2-bromocarbazole must be consumed completely and the excess must be removed from the mixture, because it is difficult to separate from the product through column chromatography.

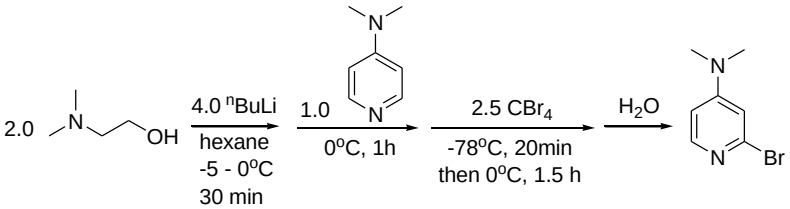
Synthesis of 2-(3-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9-(pyridin-2-yl)-9*H*-carbazole **Ligand ON1**:



Ligand ON1

To a dry pressure vessel equipped with a magnetic stir bar, added 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenol **2** (1.27 g, 6.75 mmol, 1.0 eq), 2-bromo-9-(pyridin-2-yl)-9*H*-carbazole **3** (2.62 g, 8.10 mmol, 1.2 eq), CuI (0.13 g, 0.675 mmol, 0.1 eq), picolinic acid (0.17 g, 1.35 mmol, 0.2 eq), K_3PO_4 (2.87 g, 13.50 mmol, 2.0 eq) and DMSO (20 mL). The mixture was bubbled with nitrogen for 30 minutes and then vessel was sealed. The mixture was stirred in an oil bath at a temperature of 90-100^{o}C for 6 days, then cooled down to ambient temperature. Diluted with ethyl acetate. The solid was filtered off and washed with much ethyl acetate. The filtrate was then washed with water for three time and then dried over sodium sulfate. Filtered and the solvent was removed under reduced pressure, the residue was purified through column chromatography on silica gel using hexane/ethyl acetate (10:1-3:1-2:1) as eluent to obtain the desired product as a colorless sticky liquid 2.80 g in 96% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.11 (s, 3H), 2.24 (s, 3H), 6.01 (s, 1H), 7.02-7.04 (m, 1H), 7.07-7.11 (m, 2H), 7.21-7.24 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.41-7.48 (m, 3H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 8.07 (td, *J* = 7.6, 2.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.66-8.68 (m, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.21, 13.23, 102.42, 107.48, 111.10, 113.25, 113.32, 116.26, 118.25, 119.04, 120.03, 120.19, 121.25, 121.79, 122.13, 123.24, 125.98, 130.41, 139.24, 139.34, 139.51, 139.92, 140.93, 148.08, 149.52, 150.45, 154.77, 157.93.

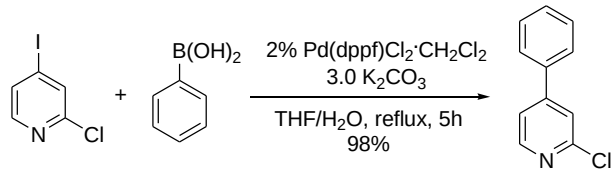
Synthesis of 2-bromo-*N*,*N*-dimethylpyridin-4-amine[S2]:



2-(Dimethylamino)ethanol (2.1 mL, 20.0 mmol, 2.0 eq) and hexane (25 mL) were added to a three-necked flask equipped with a magnetic stir bar under nitrogen. The mixture was then cooled

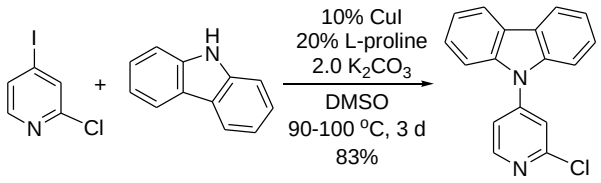
to -5 – 0 ^{o}C and ^{n}BuLi (16 mL, 40.0 mmol, 4.0 eq, 2.5 M in hexane) was added dropwise. After stirring for 30 minutes, *N*,*N*-dimethylpyridin-4-amine (1.22 g, 10.0 mmol, 1,0 eq) was added. The mixture was stirred at 0 ^{o}C for 1 hour, then cooled down to -78 ^{o}C in dry ice-acetone bath and CBr_4 (8.29 g, 25.0 mmol, 2.5 eq) was added. Then the temperature raised to 0 ^{o}C in 1.5 hours and quenched with water (50 mL). The organic layer was separated and the aqurous alyer was extracted with dichloromethane for three times. The organic layer was combined together, dried over sodium sulphate. Filtered and the solvent was removed under reduced pressure, the residue was purified through column chromatography on silica gel using hexane/ethyl acetate (2:1-1:1) as eluent to obtain the desired product as a brown solid 832 mg in 41% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.96 (s, 6H), 6.64 (dd, *J* = 6.0, 2.4 Hz, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 7.86 (d, *J* = 6.0 Hz, 1H).

Synthesis of 2-chloro-4-phenylpyridine:



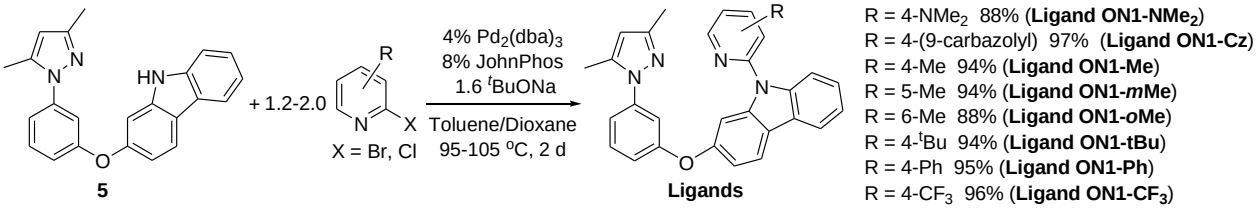
2-Chloro-4-iodopyridine (7.18 g, 30.0 mmol, 1.0 eq), phenylboronic acid (4.02 g, 33.0 mmol, 1.1 eq), Pd(dppf)Cl_2·CH_2Cl_2 (0.49 g, 0.6 mmol, 0.02 eq) and K_2CO_3 (12.44 g, 90.0 mmol, 3.0 eq) were added to a three-necked flask equipped with a magnetic stir bar. The flask was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated for another twice. Then THF (60 mL) and H_2O (15 mL) were added under nitrogen. The mixture refluxed for 5 hours and TLC monitored that the starting material 2-chloro-4-iodopyridine was consumed completely. Then water (40 mL) was added and the organic layer was separated. The aqurous layer was extracted with ethyl acetate twice. The organic layer was combined together, dried over sodium sulphate. Filtered and the solvent was removed under reduced pressure, the residue was purified through column chromatography on silica gel using hexane/ethyl acetate (10:1) as eluent to obtain the desired product as a yellow solid 5.56 g in 98% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.52-7.54 (m, 3H), 7.76 (d, *J* = 4.8 Hz, 1H), 7.85 (br, 3H), 8.47 (d, *J* = 4.8 Hz, 1H).

Synthesis of 9-(2-chloropyridin-4-yl)-9*H*-carbazole:



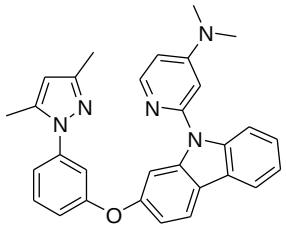
A mixture of 2-chloro-4-iodopyridine (700 mg, 2.92 mmol, 1.2 eq), carbazole (407 mg, 2.43 mmol, 1.0 eq), CuI (46 mg, 0.24 mmol, 0.1 eq), K_2CO_3 (671 mg, 4.86 mmol, 2.0 eq), L-proline (56 mg, 0.49 mmol, 0.2 eq) in DMSO (10 mL) was stirred at a temperature of 90-100 ^oC for 3 days under a nitrogen atmosphere and then cooled down to ambient temperature. The mixture was diluted with a plenty of ethyl acetate, and then washed with water three times. The organic layer was separated and dried over sodium sulphate. The solid was filtered off and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel using hexane and ethyl acetate (10:1-5:1) as eluent to obtain the desired product as a colorless sticky liquid 565 mg in 83% yield. ^1H NMR (DMSO-d_6, 400 MHz): δ 7.39 (t, J = 7.6 Hz, 2H), 7.52 (dd, J = 8.0, 0.8 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.83 (dd, J = 5.6, 0.8 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 2H), 8.69 (d, J = 5.6 Hz, 1H).

General procedure for the synthesis of ligands with a substitute on the pyridine ring:



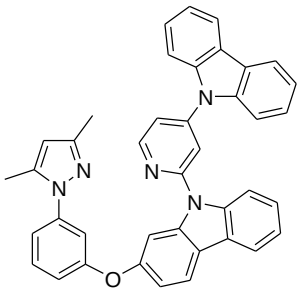
To a dry pressure Schlenk tube equipped with a magnetic stir bar, added 2-(3-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (1.0 eq, **5** was prepared according our reported literature.[S3]), 2-bromo(chloro)pyridin derrivative (1.2-2.0 eq, if it is a solid), $Pd_2(dba)_3$ (0.04 eq), JohnPhos (0.08 eq) and ^{t}BuONa (1.6 eq). The tube was evacuated and back-filled with nitrogen and this evacuation/back-fill procedure was repeated for another twice. Then the solvents toluene (4 mL/mmol **5**), dioxane (4 mL/mmol **5**) and 2-bromo(chloro)pyridin derrivative (1.2-2.0 eq, if it is a liquid) were added under the protection of nitrogen. The tube was sealed and the mixture was stirred in an oil bath at a temperature of 95-105^{o}C for 2 days. Then the mixture was cooled down to ambient temperature. The solvent was removed under reduced pressure and the residue was

purified through column chromatography on silica gel using hexane/ethyl acetate as eluent to obtain the desired product.



Ligand ON1-NMe$_2$

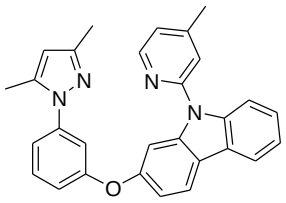
2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (530 mg, 1.5 mmol, 1.0 eq) reacted with 2-bromo-4-N,N-dimethylaminopyridine (362 mg, 1.8 mmol, 1.2 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 3:1-2:1-1:1) afforded the title compound as a colorless solid 624 mg in 88% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.10 (s, 3H), 2.23 (s, 3H), 2.94 (s, 6H), 5.99 (s, 1H), 6.63 (dd, *J* = 6.0, 1.6 Hz, 1H), 6.74 (d, *J* = 1.6 Hz, 1H), 7.02-7.07 (m, 2H), 7.12 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.37-7.46 (m, 3H), 7.74 (d, *J* = 8.4 Hz, 1H), 8.15-8.17 (m, 2H), 8.22 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.23, 13.22, 38.89, 101.14, 102.07, 105.77, 107.49, 111.33, 112.71, 113.49, 116.46, 118.27, 119.63, 119.99, 120.64, 121.63, 122.92, 125.70, 130.38, 139.21, 139.73, 140.24, 140.97, 148.07, 148.90, 151.08, 154.84, 156.09, 157.86.



Ligand ON1-Cz

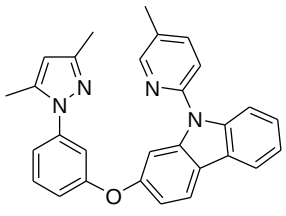
2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (589 mg, 1.66 mmol, 1.0 eq) reacted with 9-(2-chloropyridin-4-yl)-9*H*-carbazole (560 mg, 2.0 mmol, 1.2 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-3:1) afforded the title compound as a brown solid 958 mg in 97% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.07 (s, 3H), 2.17 (s, 3H), 5.95 (s, 1H), 7.01 (dd, *J* = 7.6,

2.4 Hz, 1H), 7.06-7.09 (m, 2H), 7.15-7.18 (m, 1H), 7.27-7.32 (m, 3H), 7.35-7.43 (m, 4H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 5.6, 2.0 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 8.17-8.21 (m, 3H), 8.24 (d, *J* = 8.8 Hz, 1H), 8.87 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.16, 13.21, 103.03, 107.44, 110.16, 111.38, 113.08, 113.63, 115.07, 116.06, 118.16, 118.73, 120.21, 120.33, 120.65, 121.18, 121.45, 121.76, 123.49, 123.63, 126.08, 126.57, 130.35, 138.94, 139.16, 139.38, 140.04, 140.93, 147.11, 148.04, 151.38, 152.44, 154.68, 158.04.



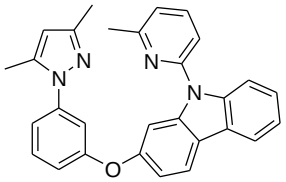
Ligand ON1-Me

2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (530 mg, 1.5 mmol, 1.0 eq) reacted with 2-bromo-4-methylpyridine (387 mg, 2.25 mmol, 1.5 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-4:1) afforded the title compound as a colorless solid 628 mg in 94% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.14 (s, 3H), 2.28 (s, 3H), 2.46 (s, 3H), 6.05 (s, 1H), 7.06 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.09-7.13 (m, 2H), 7.26 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.44-7.52 (m, 3H), 7.61 (s, 1H), 7.78 (d, *J* = 8.0, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.53 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.22, 13.22, 20.58, 102.38, 107.48, 111.18, 113.15, 113.29, 116.34, 118.25, 119.48, 119.91, 120.15, 121.12, 121.76, 123.14, 123.16, 125.92, 130.39, 139.24, 139.38, 139.98, 140.93, 148.07, 149.07, 150.47, 150.70, 154.79, 157.90.



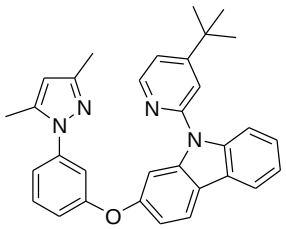
Ligand ON1-*m*Me

2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (353 mg, 1.0 mmol, 1.0 eq) reacted with 2-bromo-5-methylpyridine (258 mg, 1.5 mmol, 1.5 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-5:1) afforded the title compound as a colorless solid 420 mg in 94% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.12 (s, 3H), 2.25 (s, 3H), 2.39 (s, 3H), 6.03 (s, 1H), 7.04 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.07-7.11 (m, 2H), 7.23 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.41-7.49 (m, 3H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.0, 1H), 7.89 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.50 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.21, 13.23, 17.48, 102.16, 107.49, 110.95, 113.14, 113.26, 116.28, 118.26, 118.64, 119.87, 120.19, 121.04, 121.80, 123.07, 125.92, 130.42, 131.64, 139.25, 139.49, 139.79, 140.05, 140.92, 148.09, 148.10, 149.50, 154.74, 157.95.



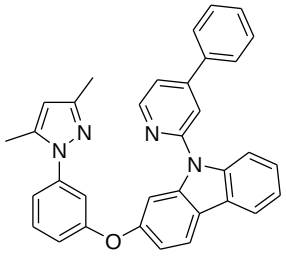
Ligand ON1-*o*Me

2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (475 mg, 1.34 mmol, 1.0 eq) reacted with 2-bromo-6-methylpyridine (461 mg, 2.68 mmol, 2.0 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-5:1) afforded the title compound as a brown solid 526 mg in 88% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.11 (s, 3H), 2.24 (s, 3H), 2.48 (s, 3H), 6.02 (s, 1H), 7.07 (td, *J* = 8.0, 2.4 Hz, 2H), 7.14 (t, *J* = 2.0 Hz, 1H), 7.24-7.29 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 2.0, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.23, 13.23, 23.82, 102.00, 107.51, 111.15, 112.98, 113.68, 115.74, 116.72, 118.42, 119.75, 120.14, 121.13, 121.28, 121.71, 123.23, 125.88, 130.42, 139.23, 139.30, 139.60, 139.93, 140.97, 148.10, 149.75, 155.13, 157.62, 158.34.



Ligand ON1-tBu

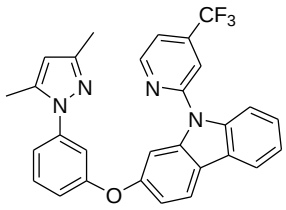
Ligand ON1tBu was prepared according our reported literature.[S2] 2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (530 mg, 1.5 mmol, 1.0 eq) reacted with 2-bromo-4-*tert*-butylpyridine (642 mg, 3.0 mmol, 2.0 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-5:1) afforded the title compound as a brown solid 685 mg in 94% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.26 (s, 9H), 2.11 (s, 3H), 2.23 (s, 3H), 6.00 (s, 1H), 7.06-7.08 (m, 1H), 7.10 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.14 (t, *J* = 2.4 Hz, 1H), 7.24-7.26 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.41-7.48 (m, 3H), 7.61 (d, *J* = 1.6, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.55 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.21, 13.22, 30.01, 34.81, 101.37, 107.50, 111.11, 113.01, 113.81, 115.78, 116.80, 118.49, 119.27, 119.72, 120.13, 121.11, 121.83, 123.20, 125.90, 130.45, 139.19, 139.43, 139.94, 141.01, 148.07, 149.37, 150.60, 155.32, 157.50, 163.03.



Ligand ON1-Ph

2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (530 mg, 1.5 mmol, 1.0 eq) reacted with 2-chloro-4-phenylpyridine (342 mg, 1.8 mmol, 1.2 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-5:1-3:1) afforded the title compound as a brown solid 725 mg in 95% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.13 (s, 3H), 2.25 (s, 3H), 6.04 (s, 1H), 7.10 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.12-7.15 (m, 2H), 7.25-7.27 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.46-7.57 (m, 6H), 7.79 (dd, *J* = 4.8, 1.6, 1H), 7.85-7.88 (m, 3H), 8.00 (d, *J* = 0.4 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.19, 13.21, 102.13,

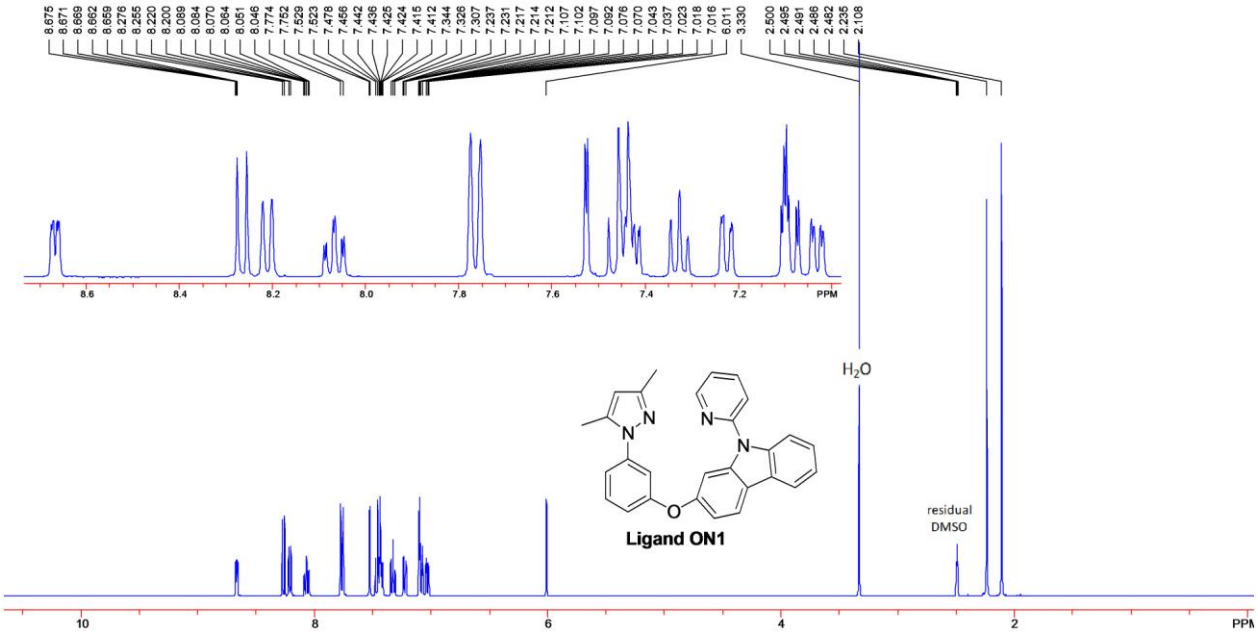
107.49, 111.22, 113.20, 113.58, 116.14, 116.49, 118.33, 119.73, 119.95, 120.14, 121.23, 121.77, 123.29, 126.01, 127.10, 129.20, 129.62, 130.37, 136.62, 139.19, 139.44, 140.01, 140.98, 148.06, 150.08, 150.46, 151.29, 155.08, 157.76.



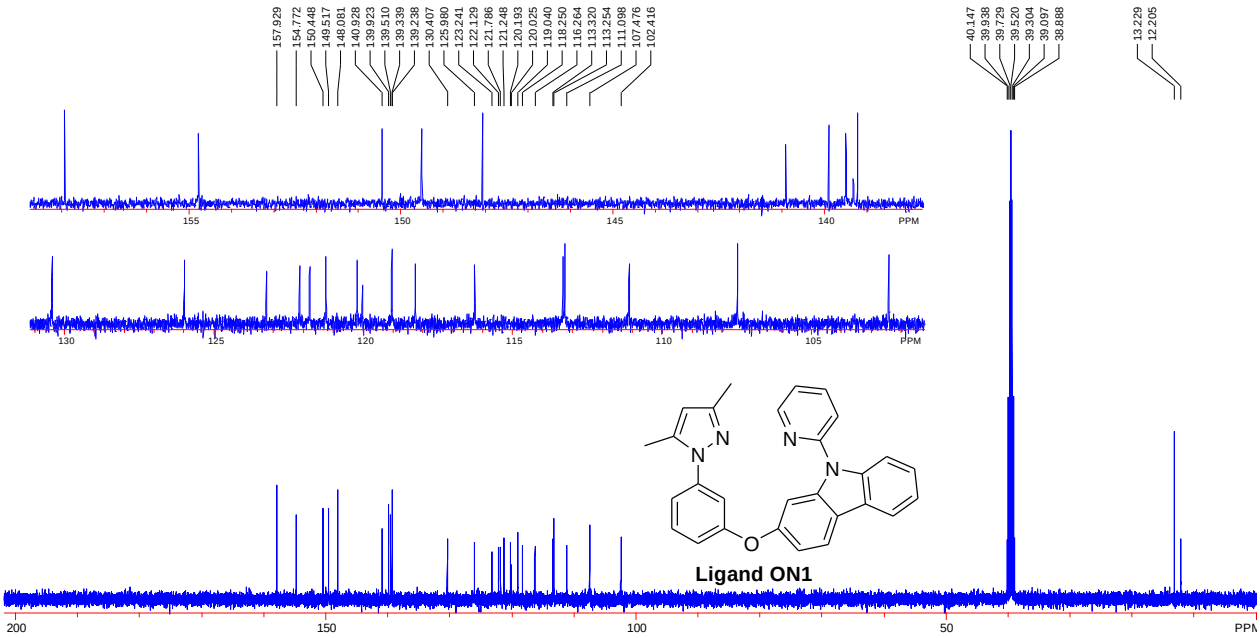
Ligand ON1-CF_3

2-(3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)-9*H*-carbazole **5** (707 mg, 2.0 mmol, 1.0 eq) reacted with 2-bromo-4-(trifluoromethyl)pyridine (904 mg, 4.0 mmol, 2.0 eq) as the general procedure. Purification of the crude product by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1-5:1) afforded the title compound as a brown solid 962 mg in 96% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.13 (s, 3H), 2.26 (s, 3H), 6.04 (s, 1H), 7.08 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.12-7.15 (m, 2H), 7.25-7.27 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.81-7.83 (m, 2H), 8.10 (s, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.95 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.16, 13.18, 102.47, 107.46, 111.09, 113.43, 113.71, 114.52 (q, *J* = 3.9 Hz), 116.37, 117.37 (q, *J* = 2.7 Hz), 118.32, 120.25, 121.77, 121.81, 122.55 (q, *J* = 272.5 Hz), 123.59, 126.16, 130.35, 139.09, 139.19, 139.56 (q, *J* = 34.7 Hz), 139.73, 140.98, 148.06, 151.32, 151.53, 155.05, 157.75. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -63.32.

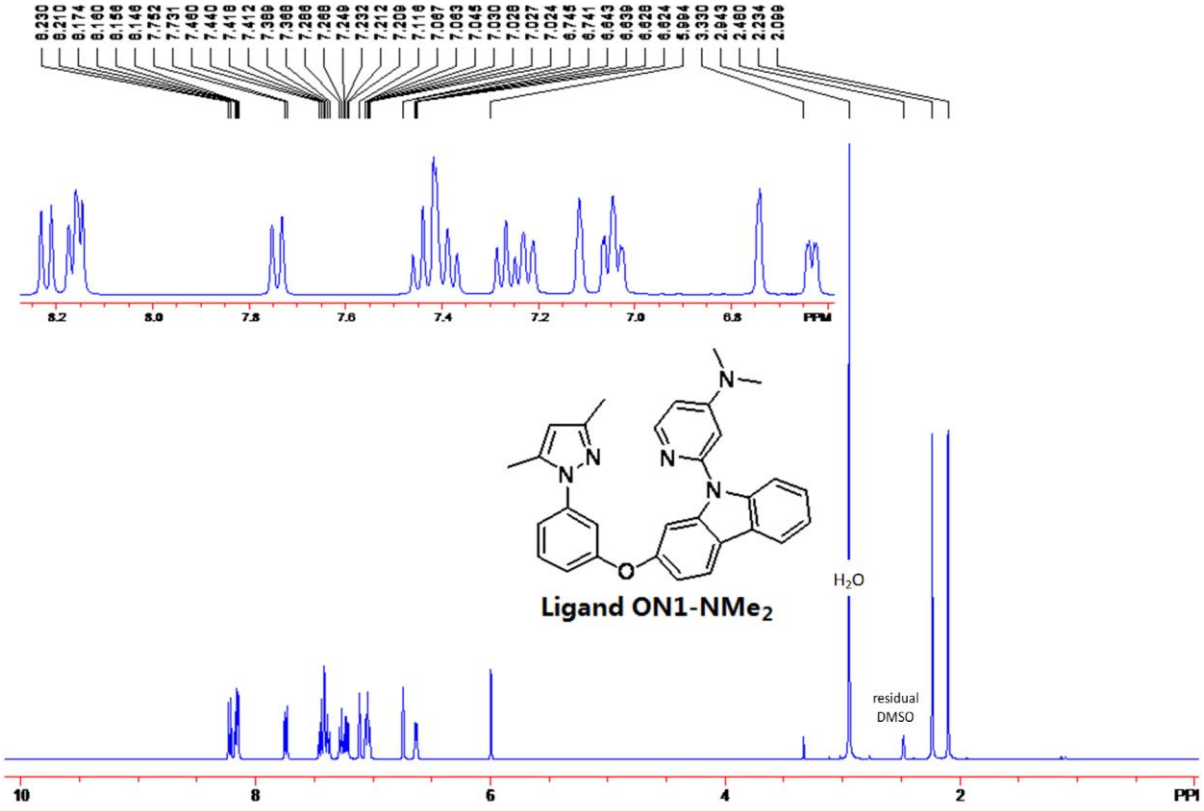
^{1}H NMR spectrum of **Ligand ON1** at 400 MHz instrument in DMSO-d_6 solution:



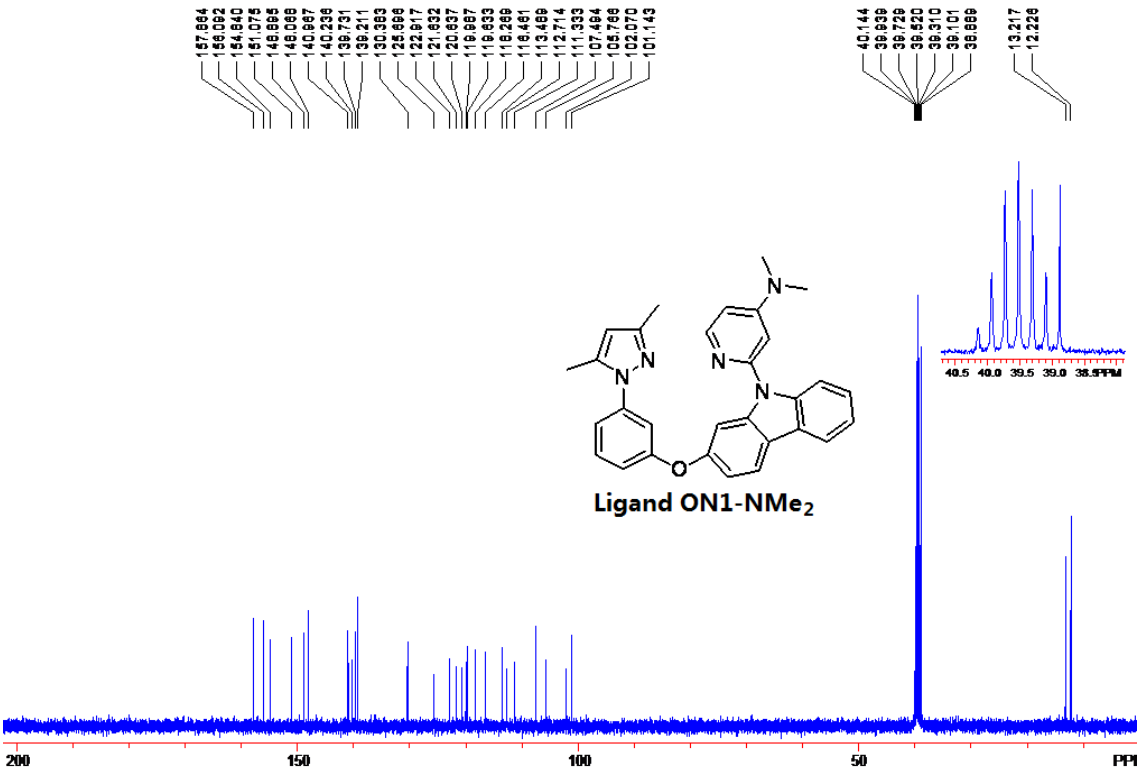
^{13}C NMR spectrum of **Ligand ON1** at 100 MHz instrument in DMSO-d_6 solution:



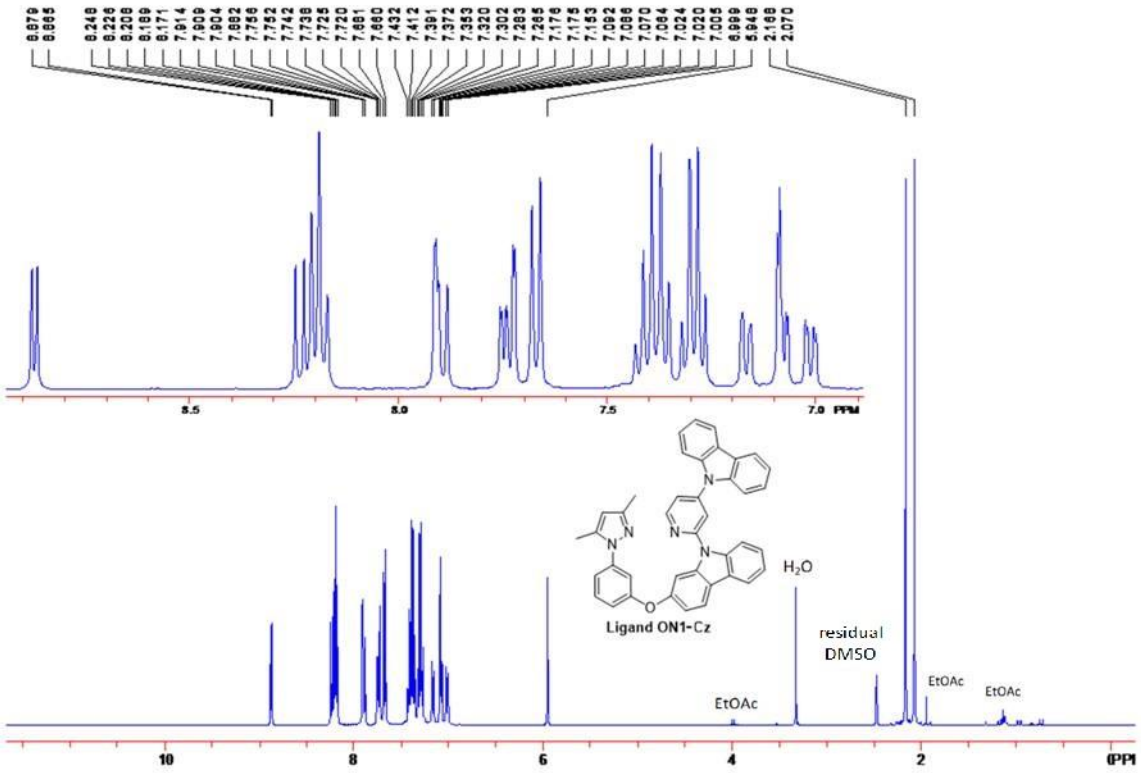
^{1}H NMR spectrum of **Ligand ON1-NMe$_2$** at 400 MHz instrument in DMSO-d_6 solution:



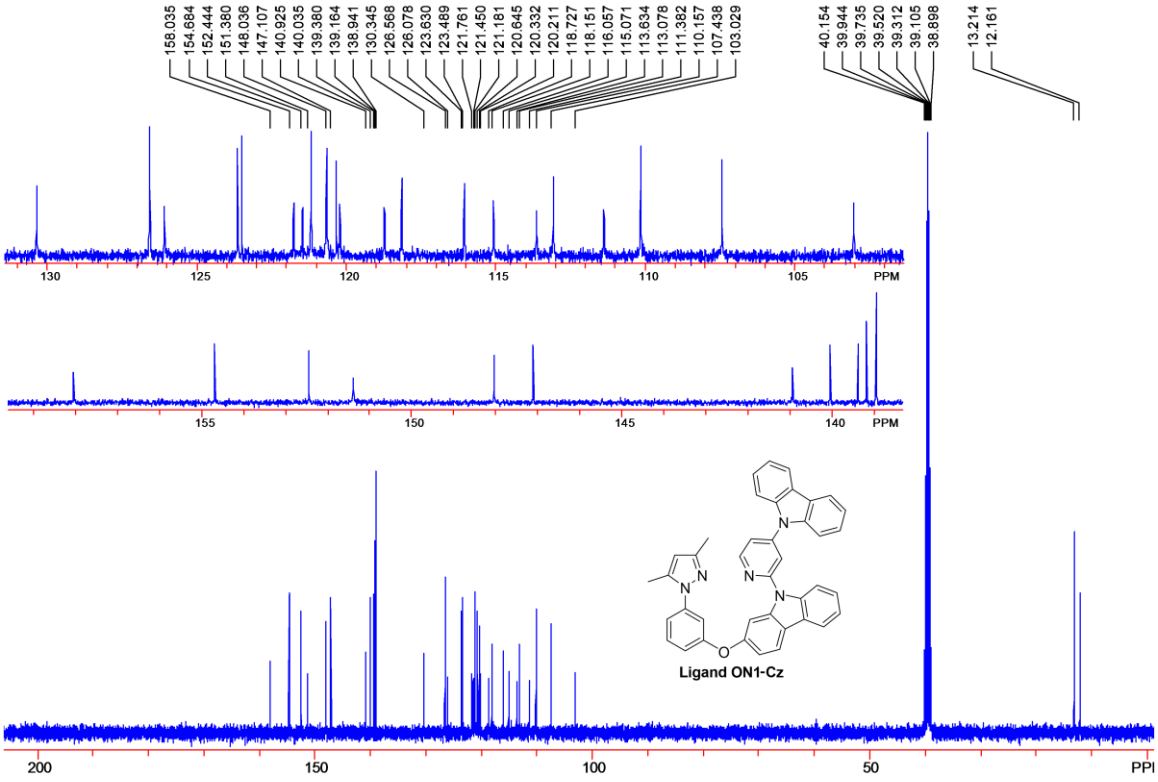
^{13}C NMR spectrum of **Ligand ON1-NMe$_2$** at 100 MHz instrument in DMSO-d_6 solution:



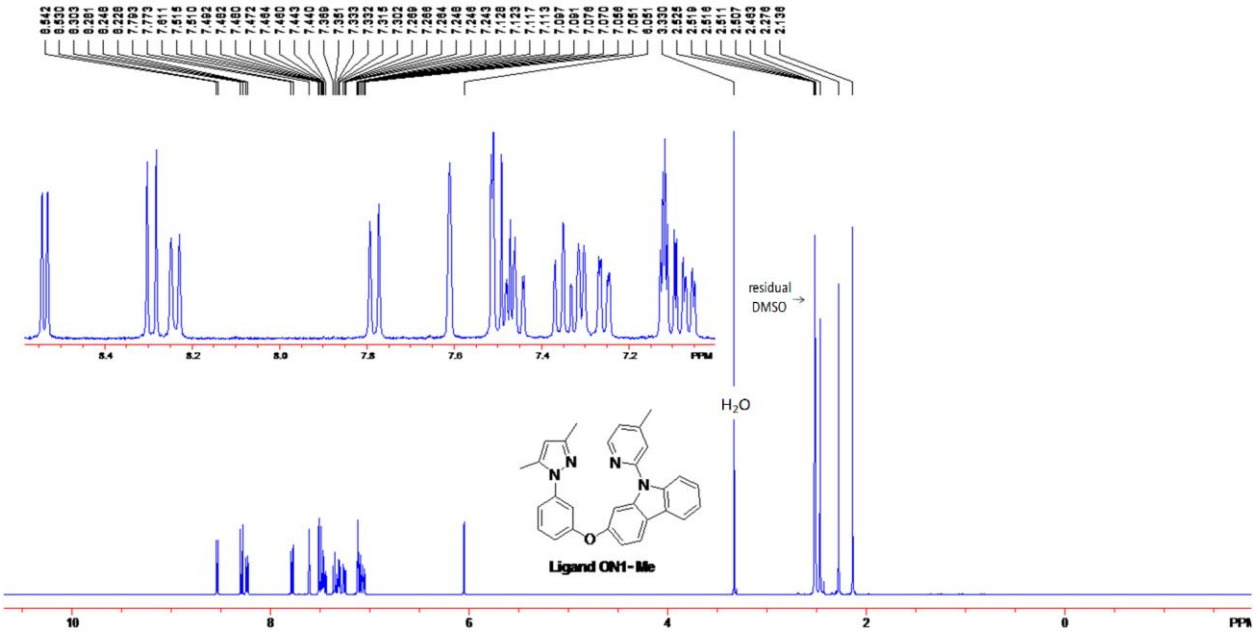
^{1}H NMR spectrum of **Ligand ON1-Cz** at 400 MHz instrument in DMSO-d_6 solution:



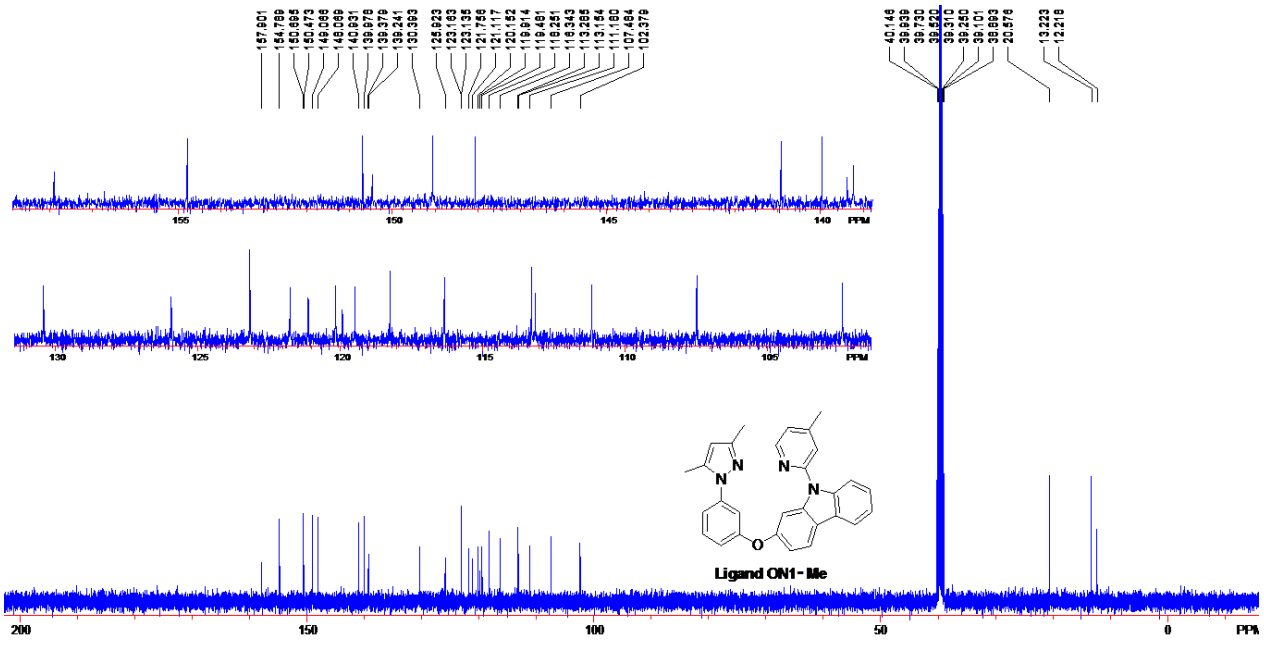
^{13}C NMR spectrum of **Ligand ON1-Cz** at 100 MHz instrument in DMSO-d_6 solution:



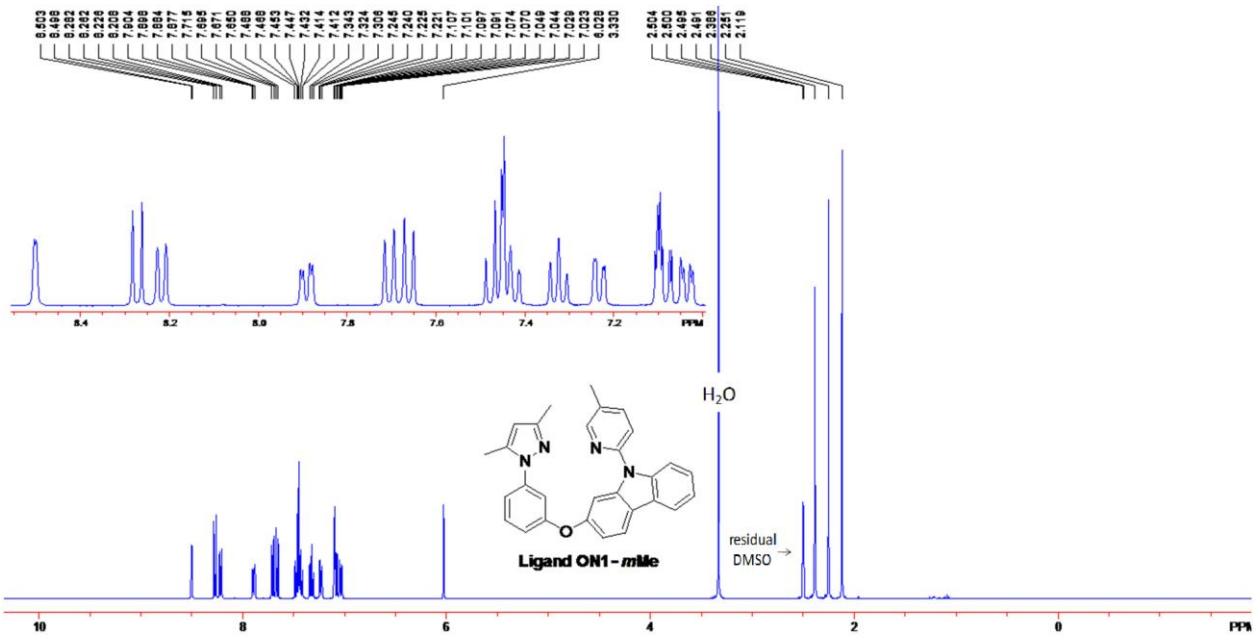
^{1}H NMR spectrum of **Ligand ON1-Me** at 400 MHz instrument in DMSO-d_6 solution:



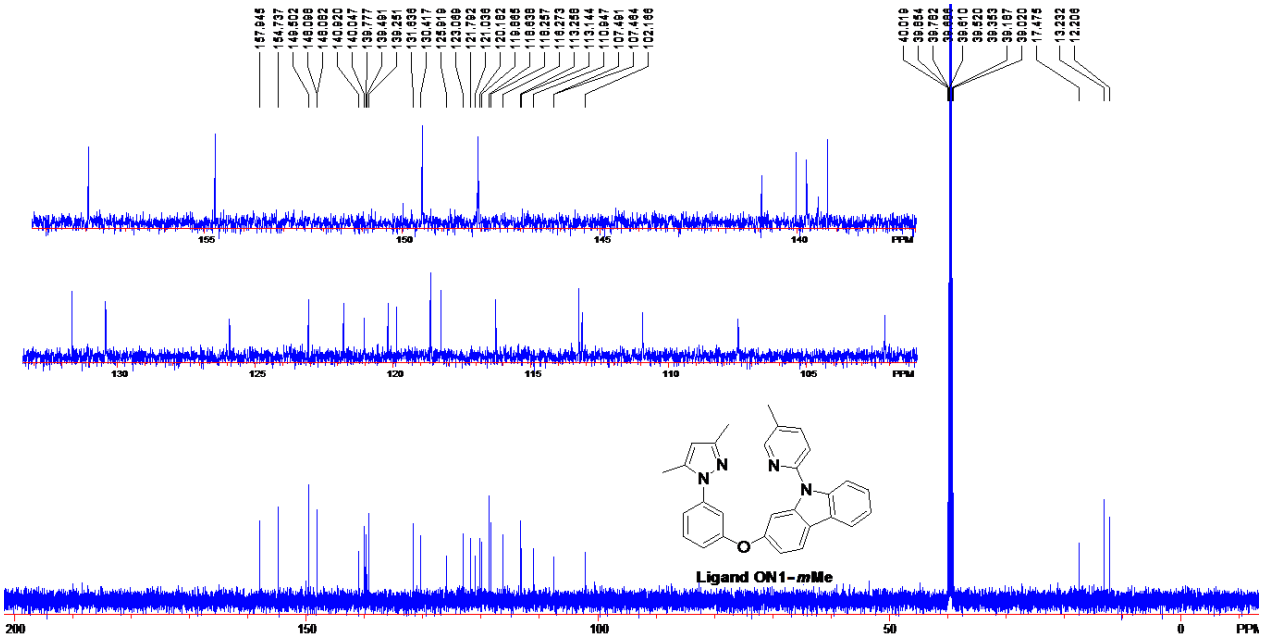
^{13}C NMR spectrum of **Ligand ON1-Me** at 100 MHz instrument in DMSO-d_6 solution:



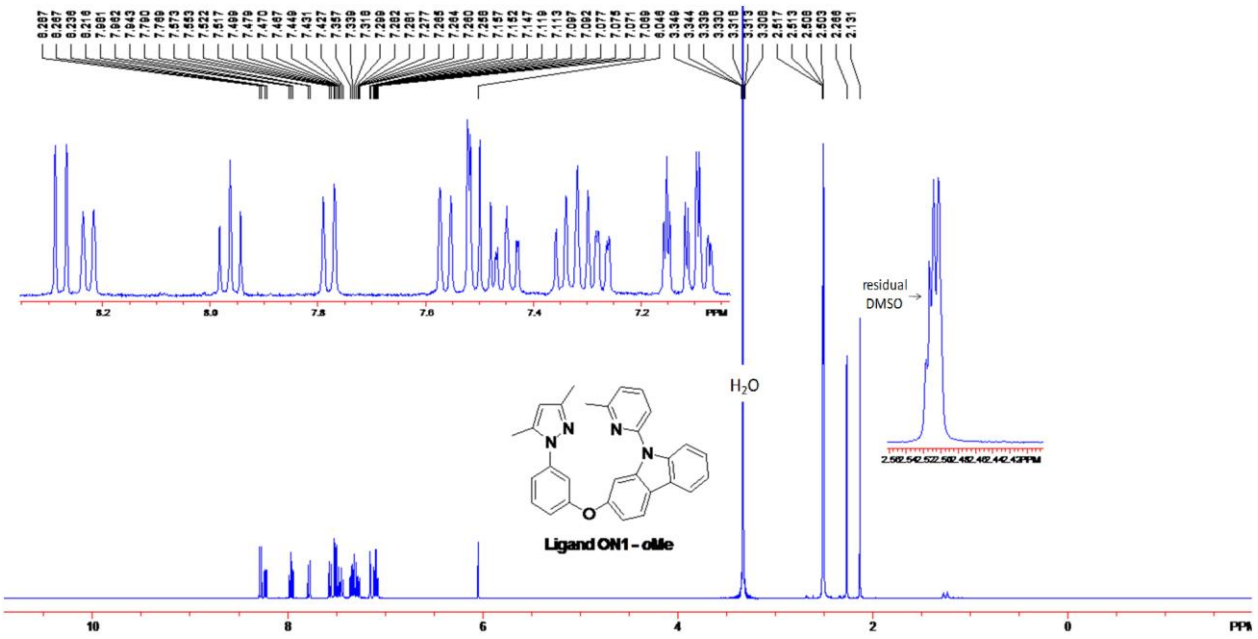
^{1}H NMR spectrum of **Ligand ON1-*m*Me** at 400 MHz instrument in DMSO-d_6 solution:



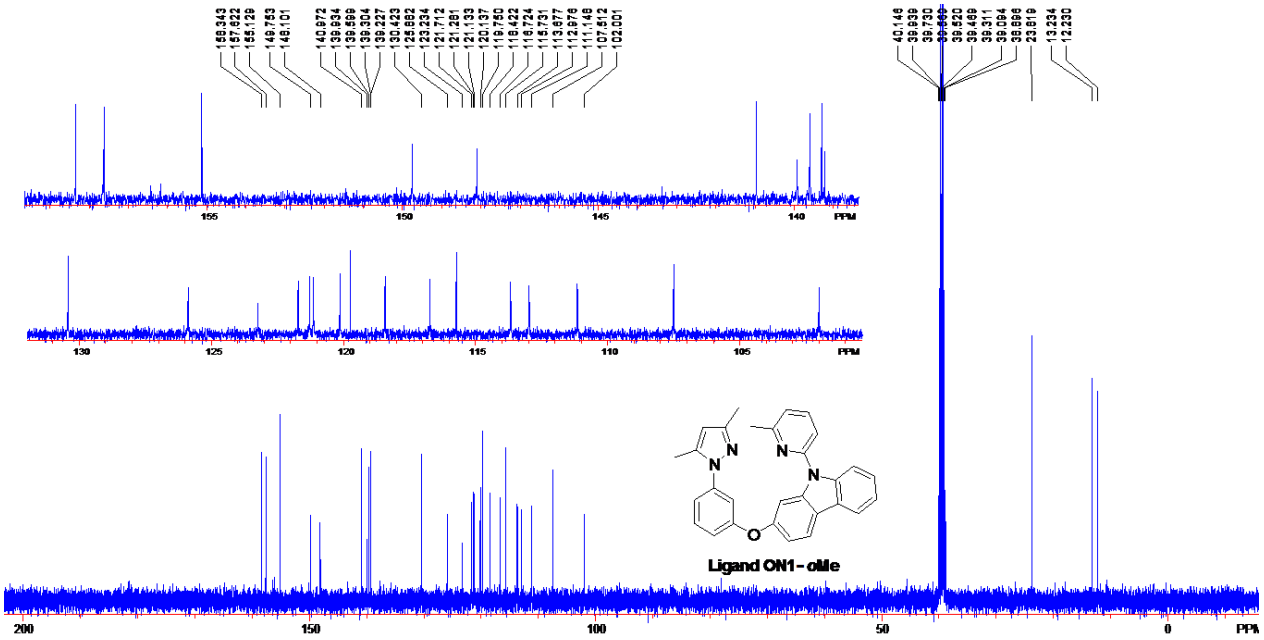
^{13}C NMR spectrum of **Ligand ON1-*m*Me** at 125 MHz instrument in DMSO-d_6 solution:



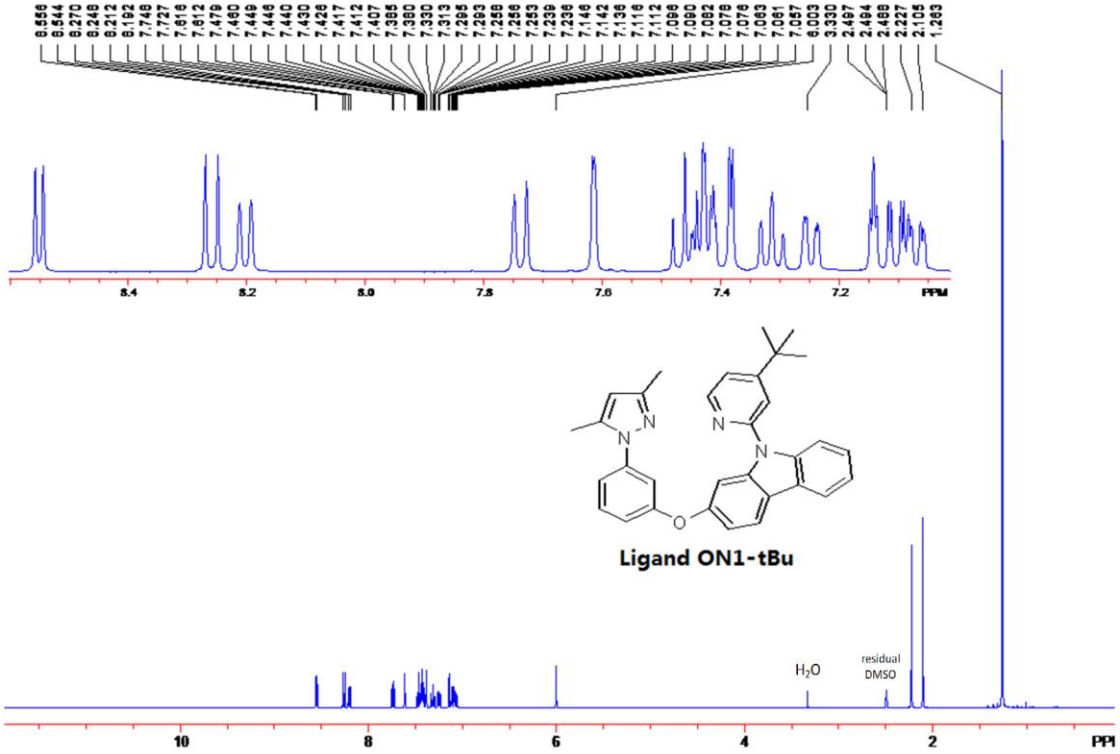
^{1}H NMR spectrum of **Ligand ON1-*o*Me** at 400 MHz instrument in DMSO-d_6 solution:



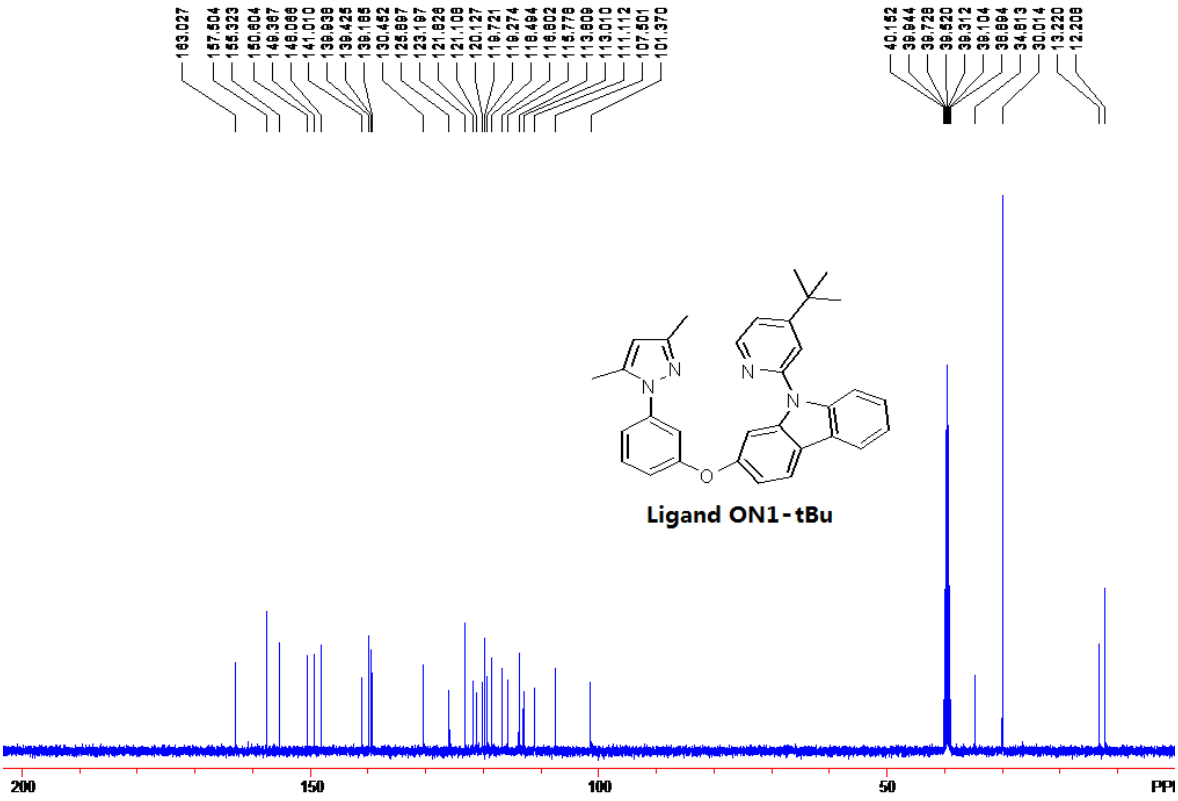
^{13}C NMR spectrum of **Ligand ON1-*o*Me** at 100 MHz instrument in DMSO-d_6 solution:



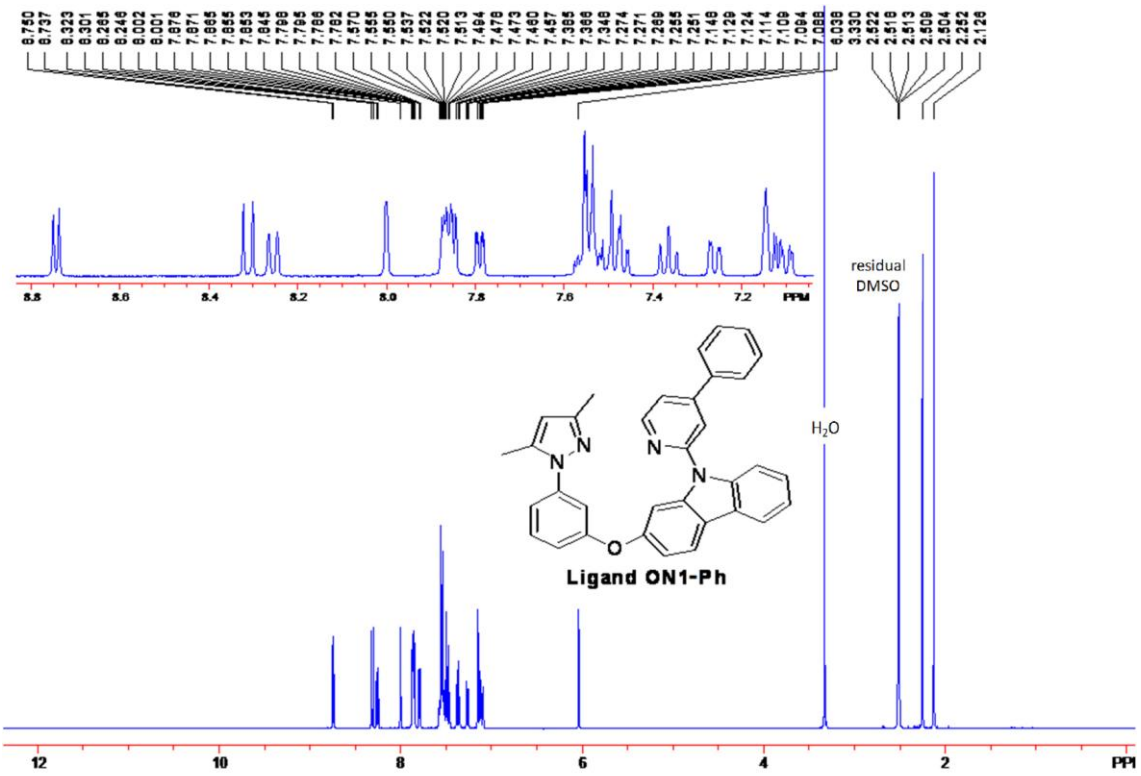
^{1}H NMR spectrum of **Ligand ON1-tBu** at 400 MHz instrument in DMSO-d_6 solution:



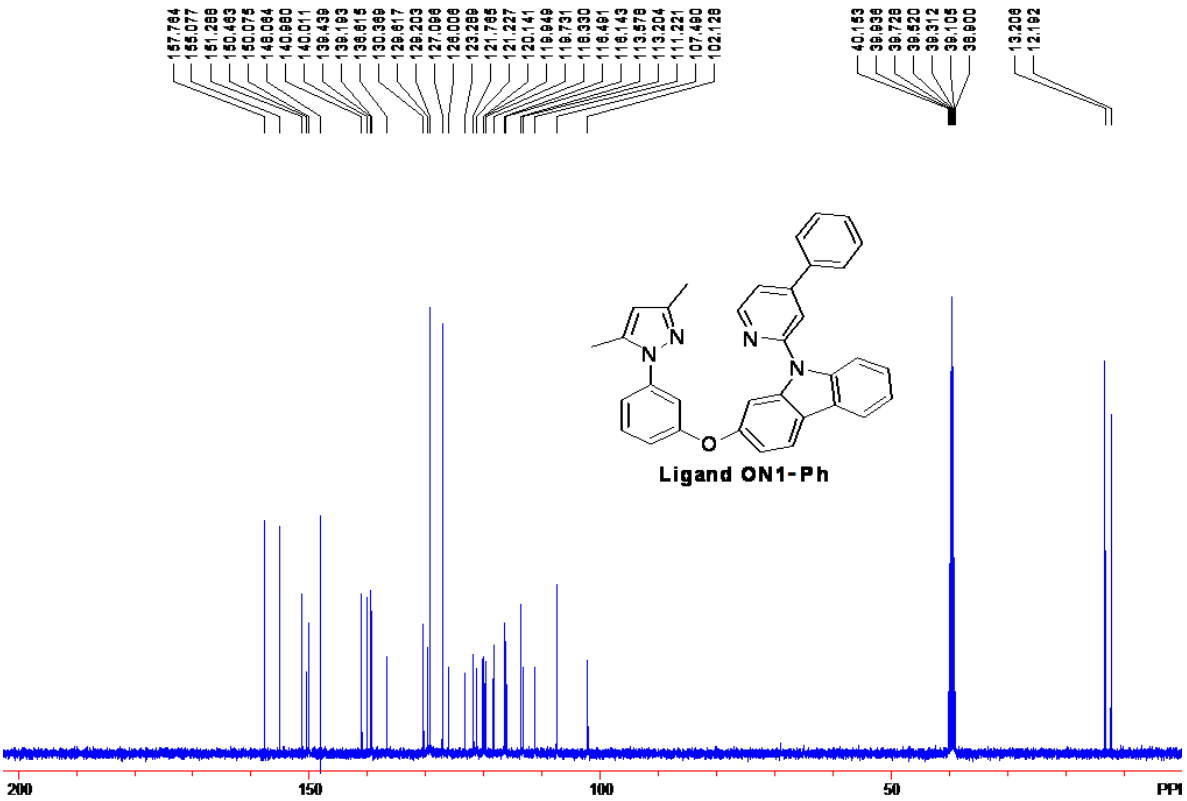
^{13}C NMR spectrum of **Ligand ON1-tBu** at 100 MHz instrument in DMSO-d_6 solution:



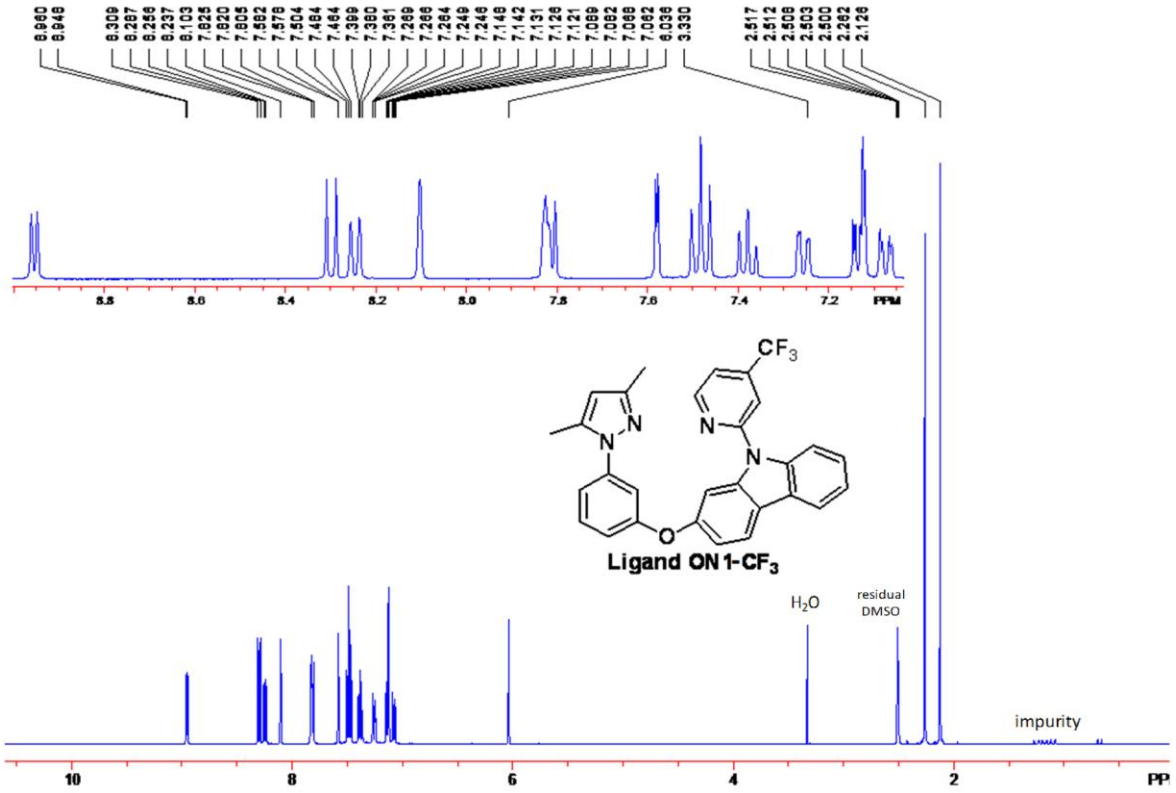
^{1}H NMR spectrum of **Ligand ON1-Ph** at 400 MHz instrument in DMSO-d_6 solution:



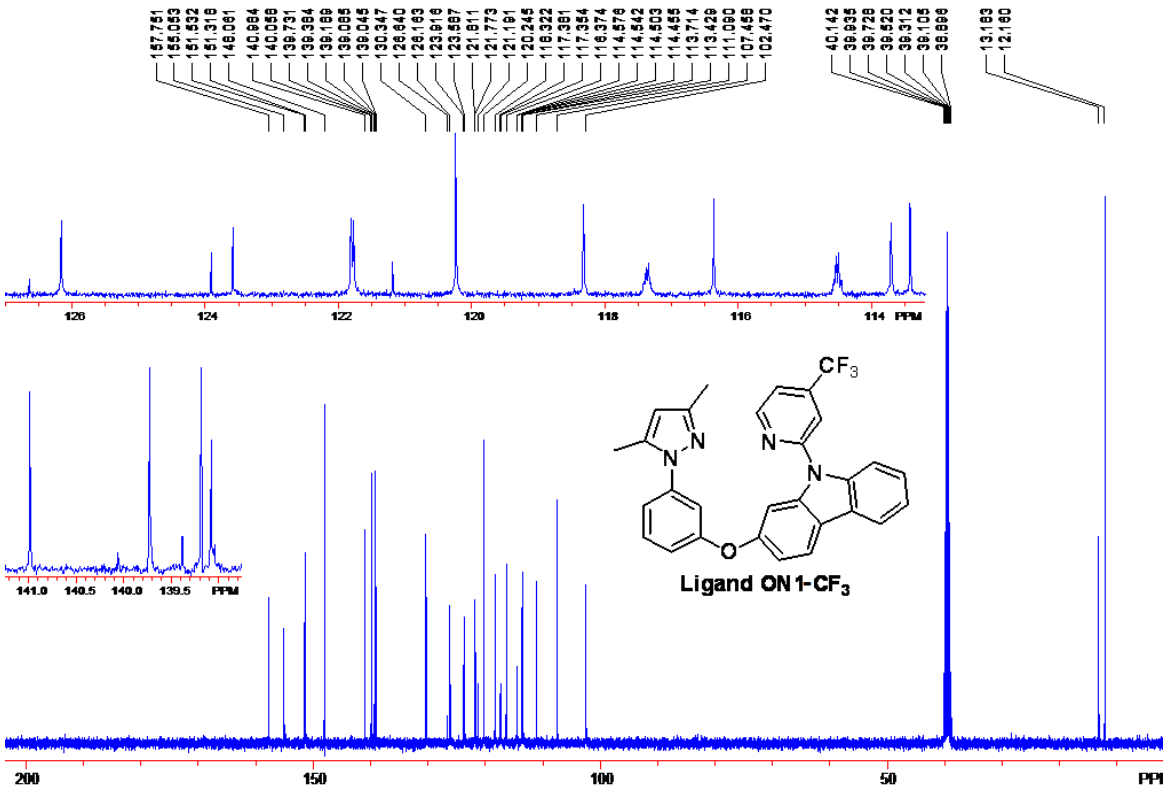
^{13}C NMR spectrum of **Ligand ON1-Ph** at 100 MHz instrument in DMSO-d_6 solution:



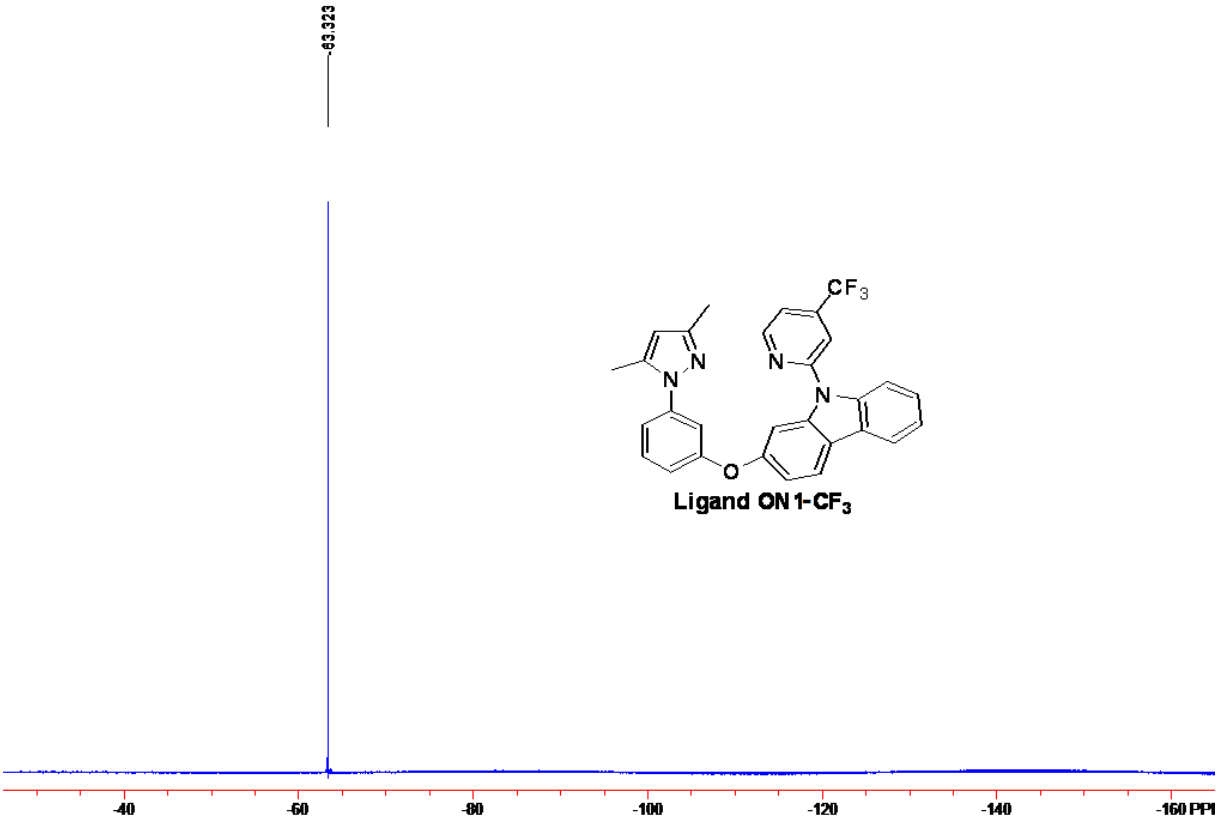
^{1}H NMR spectrum of **Ligand ON1-CF$_3$** at 400 MHz instrument in DMSO-d_6 solution:



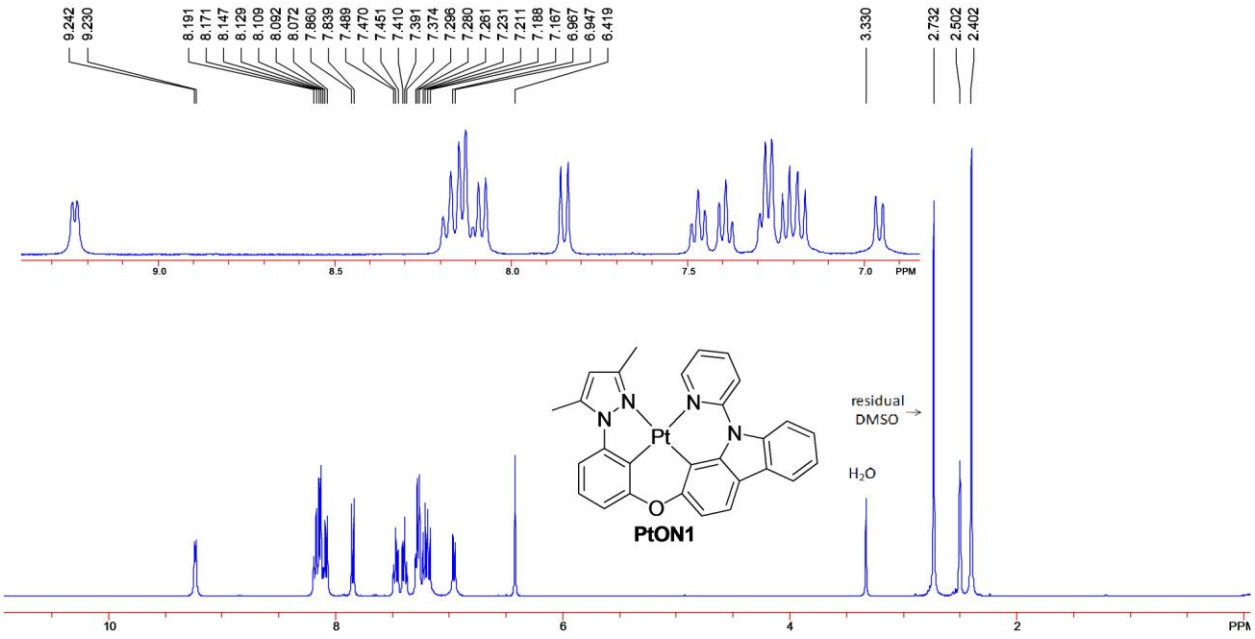
^{13}C NMR spectrum of **Ligand ON1-CF$_3$** at 100 MHz instrument in DMSO-d_6 solution:



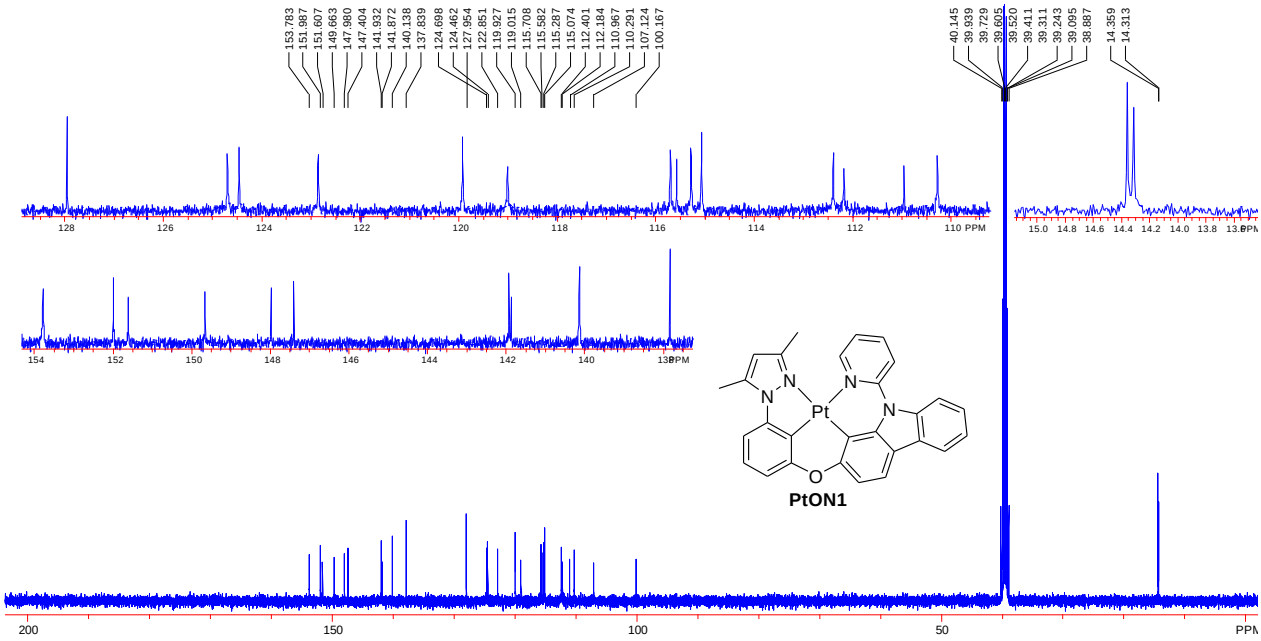
^{19}F NMR spectrum of **Ligand ON1-CF$_3$** at 376 MHz instrument in DMSO-d_6 solution:



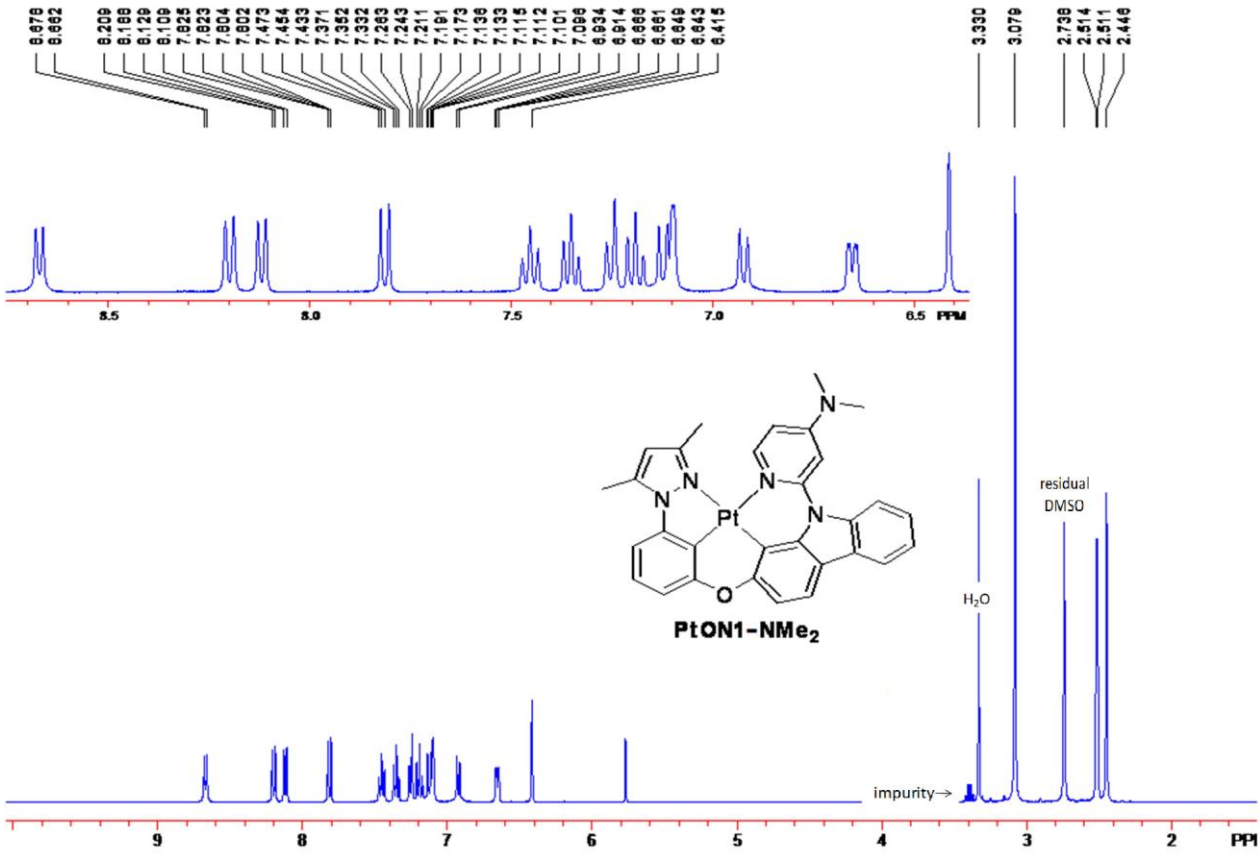
^{1}H NMR spectrum of **PtON1** at 400 MHz instrument in DMSO-d_6 solution:



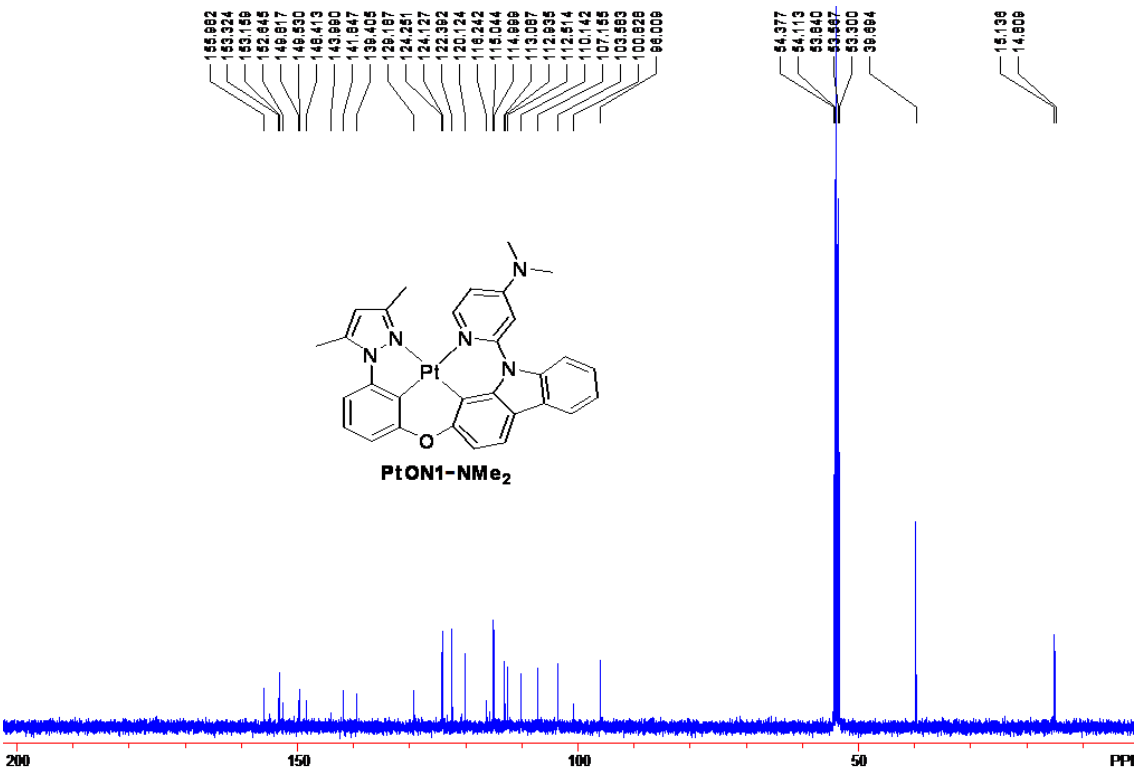
^{13}C NMR spectrum of **PtON1** at 100 MHz instrument in DMSO-d_6 solution:



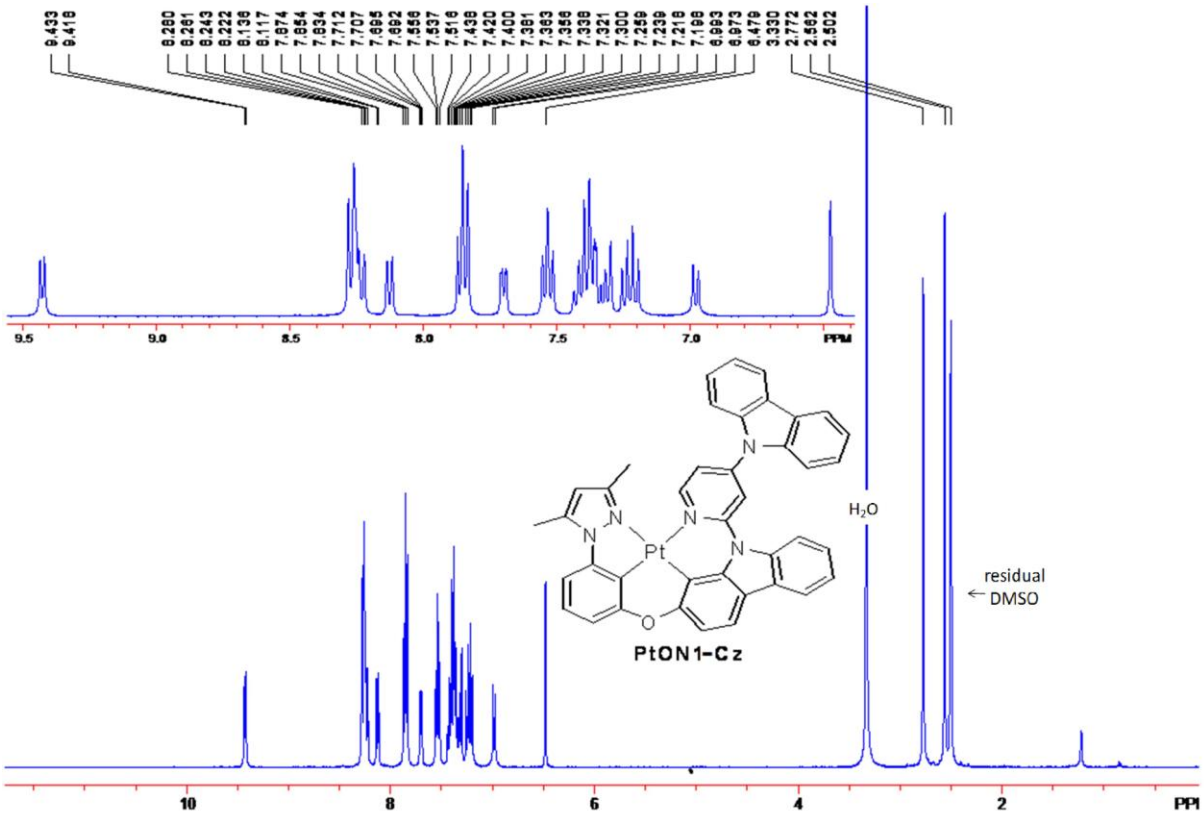
^{1}H NMR spectrum of **PtON1-NMe$_2$** at 400 MHz instrument in DMSO-d_6 solution:



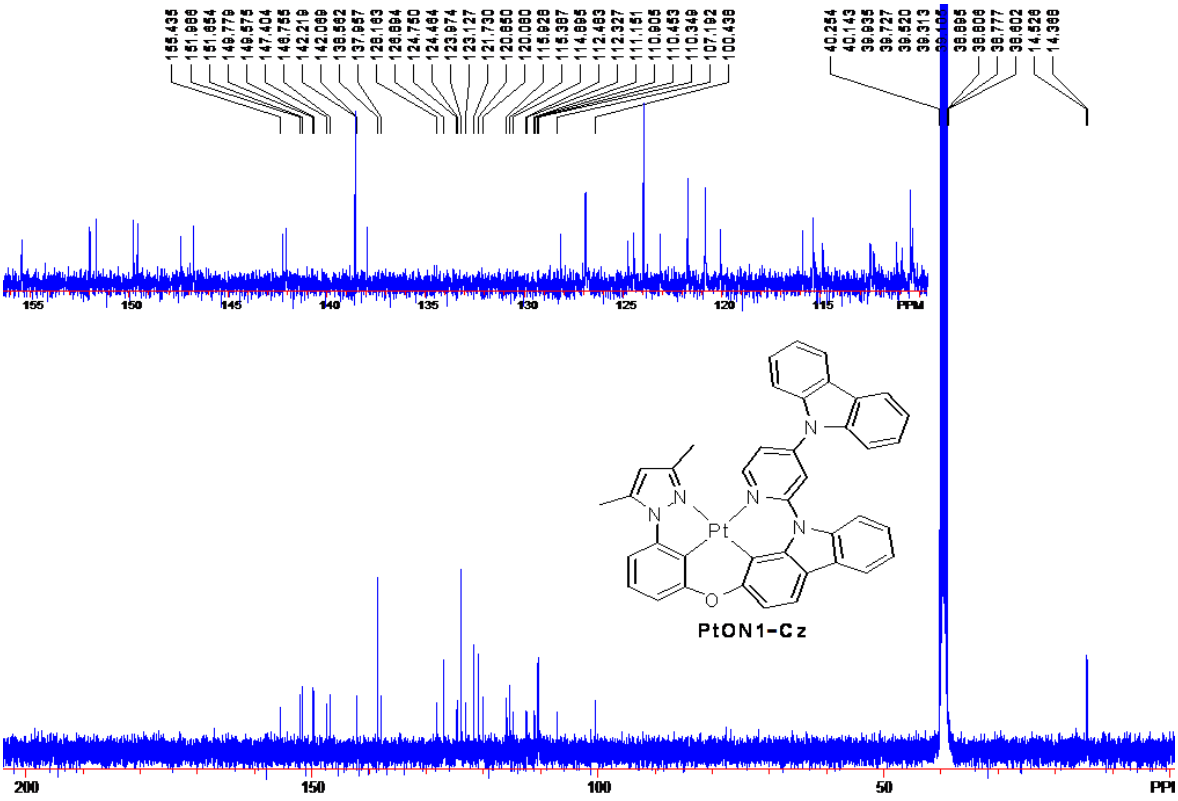
^{13}C NMR spectrum of **PtON1** at 100 MHz instrument in CD_2Cl_2 solution:



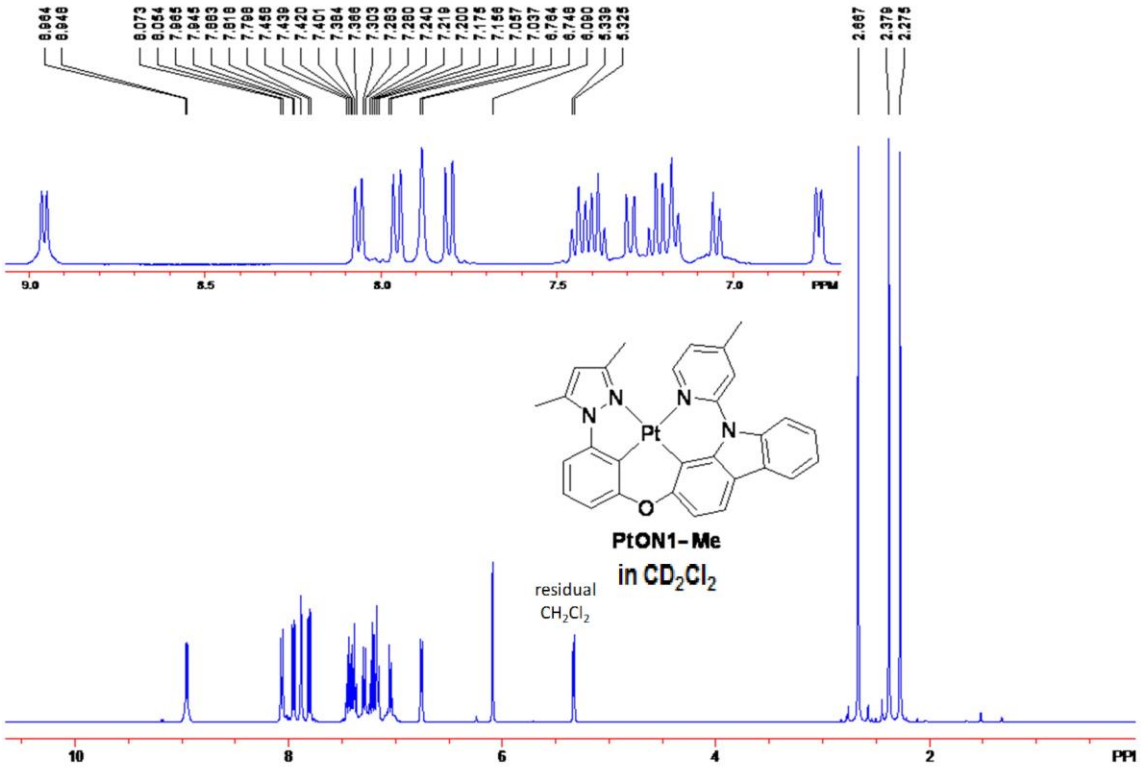
^{1}H NMR spectrum of **PtON1-Cz** at 400 MHz instrument in DMSO-d_6 solution:



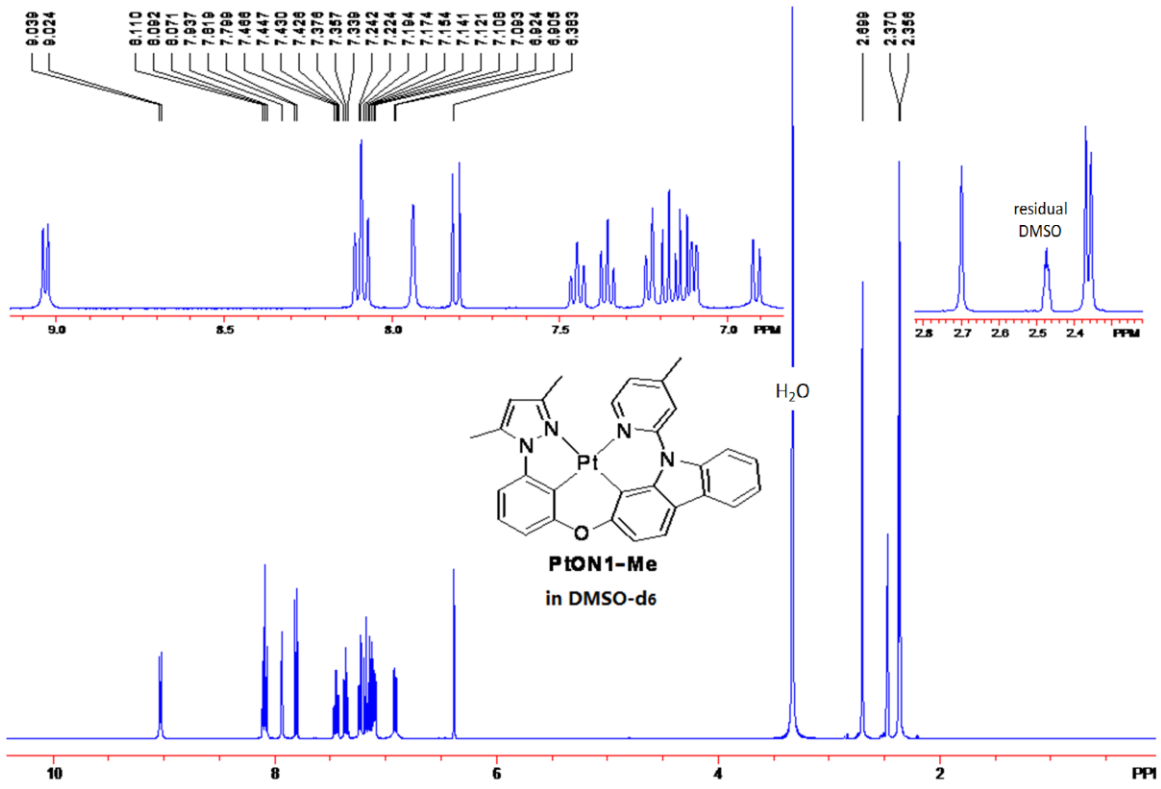
^{13}C NMR spectrum of **PtON1-Cz** at 100 MHz instrument in DMSO-d_6 solution:



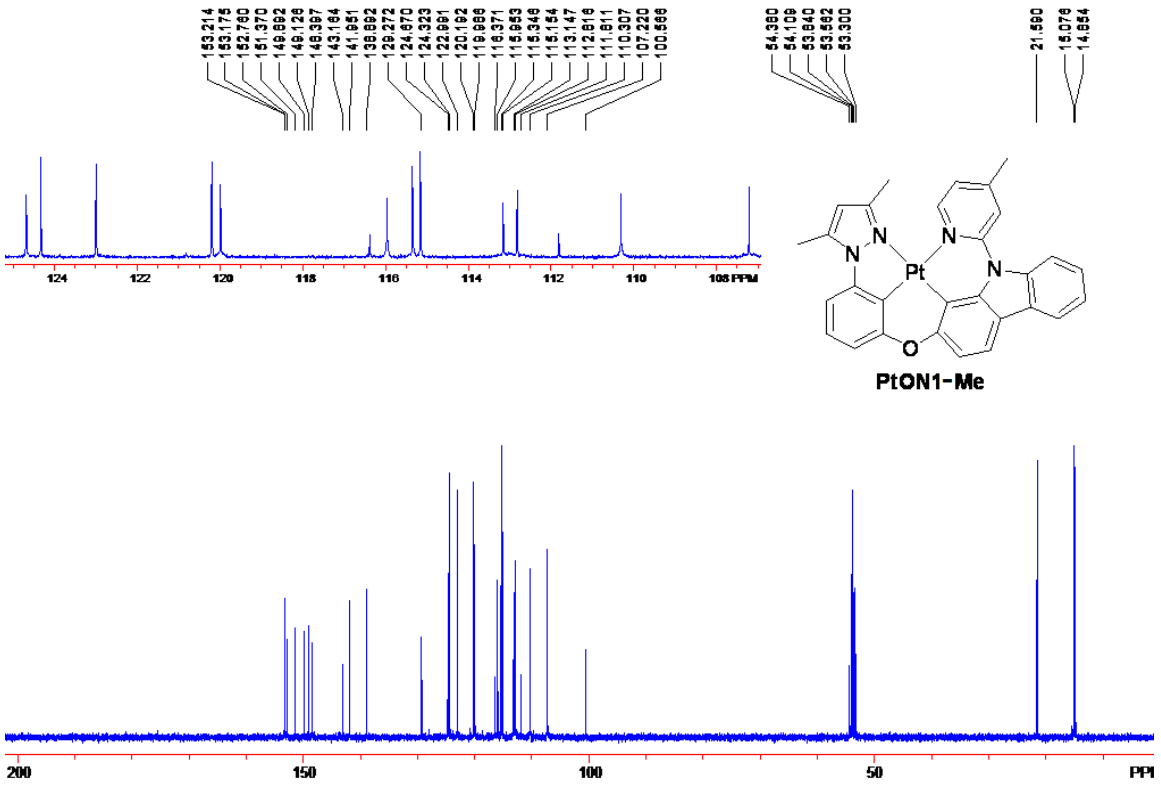
^{1}H NMR spectrum of **PtON1-Me** at 400 MHz instrument in CD_2Cl_2 solution:



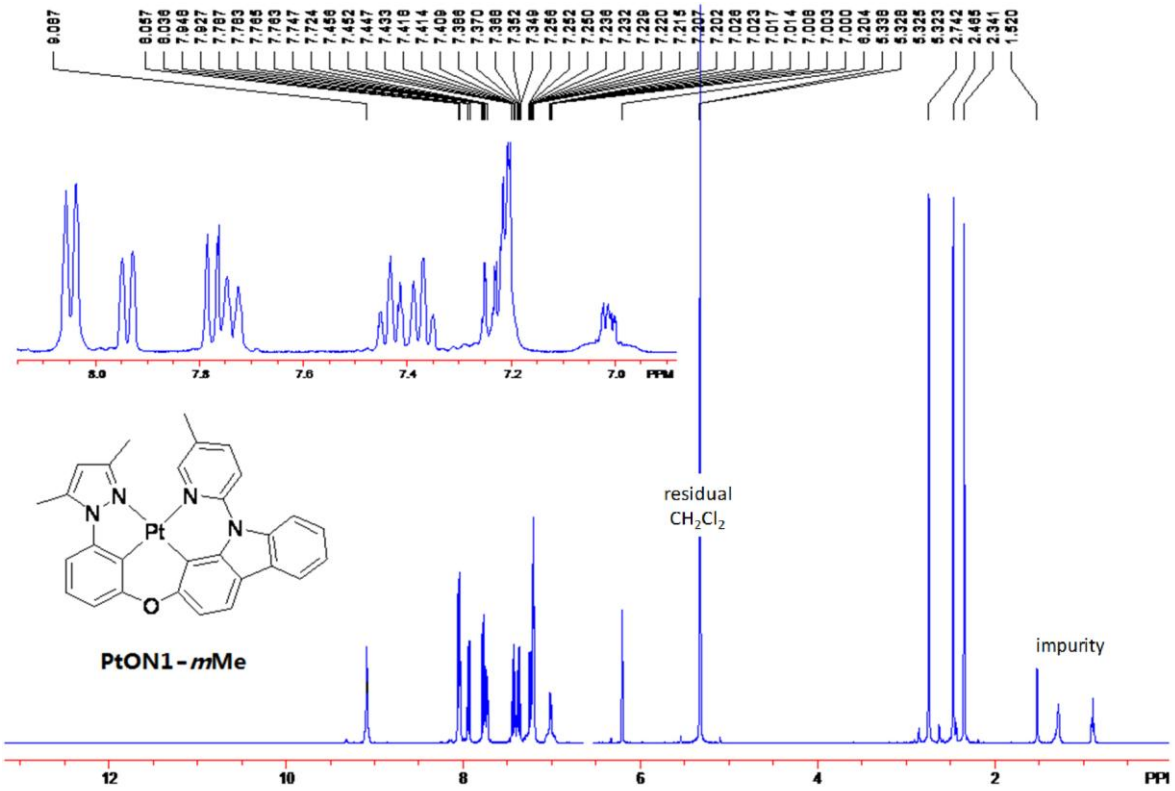
^{1}H NMR spectrum of **PtON1-Me** at 400 MHz instrument in DMSO-d_6 solution:



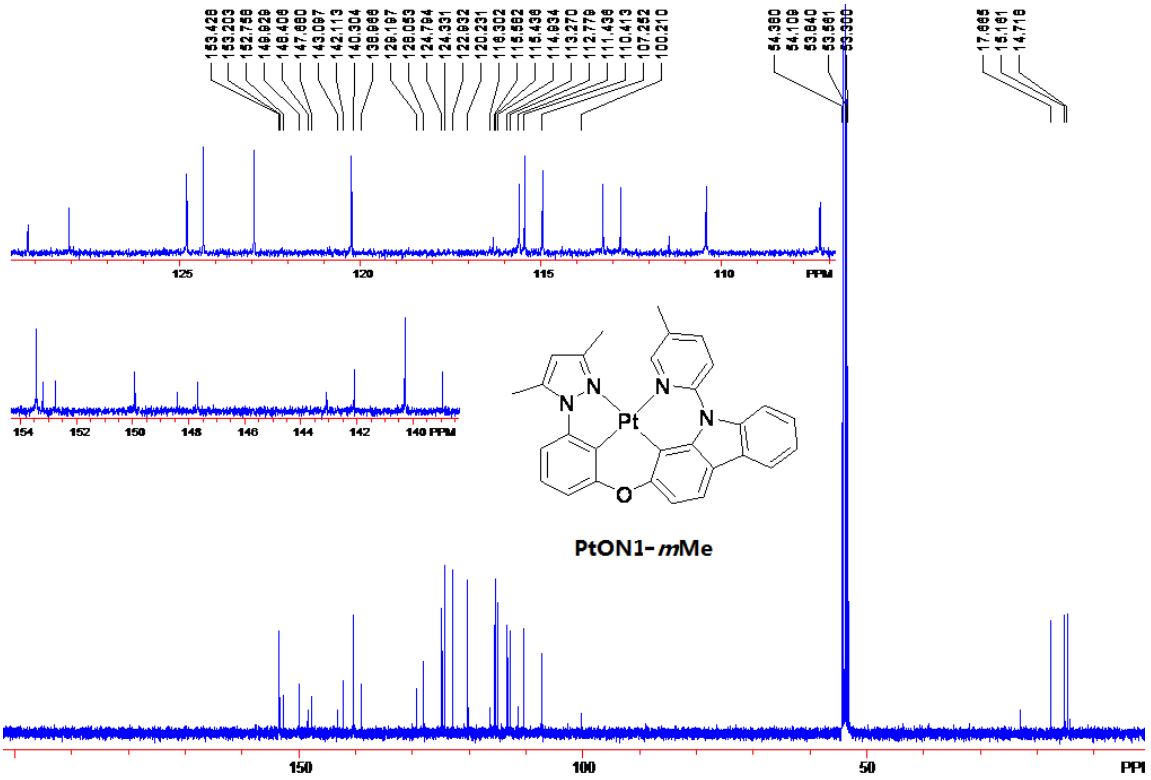
^{13}C NMR spectrum of **PtON1-Me** at 100 MHz instrument in CD_2Cl_2 solution:



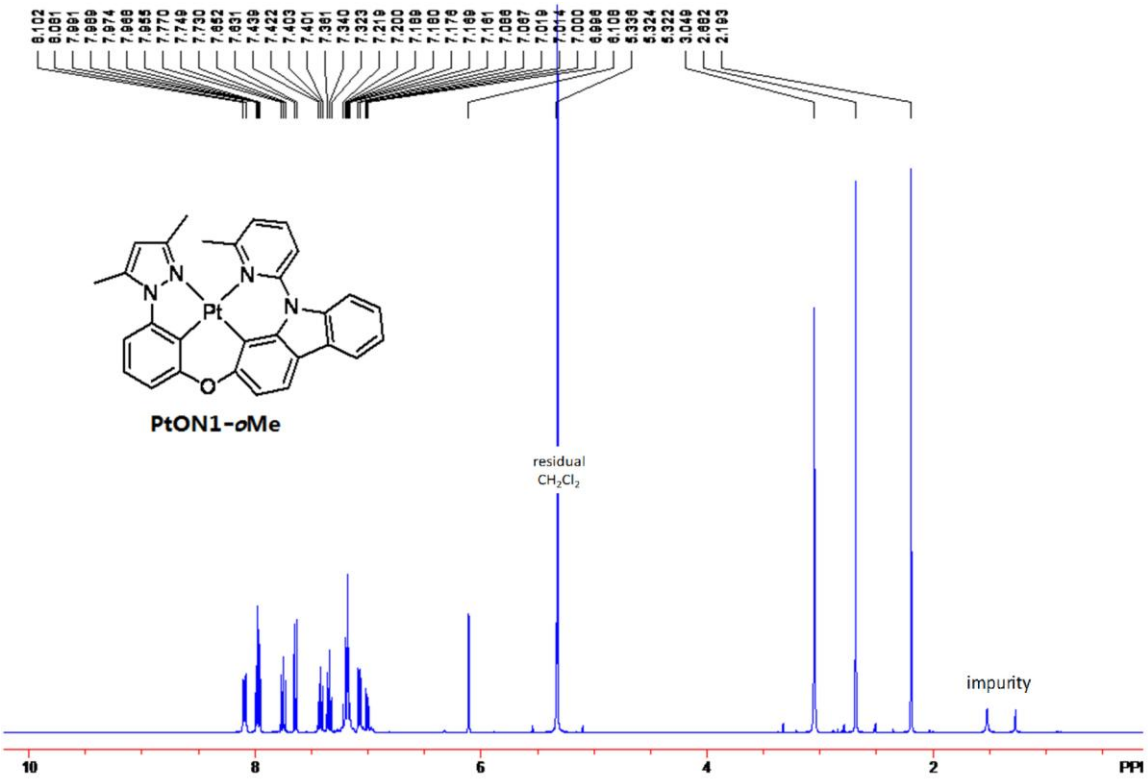
^{1}H NMR spectrum of **PtON1-*m*Me** at 400 MHz instrument in CD_2Cl_2 solution:



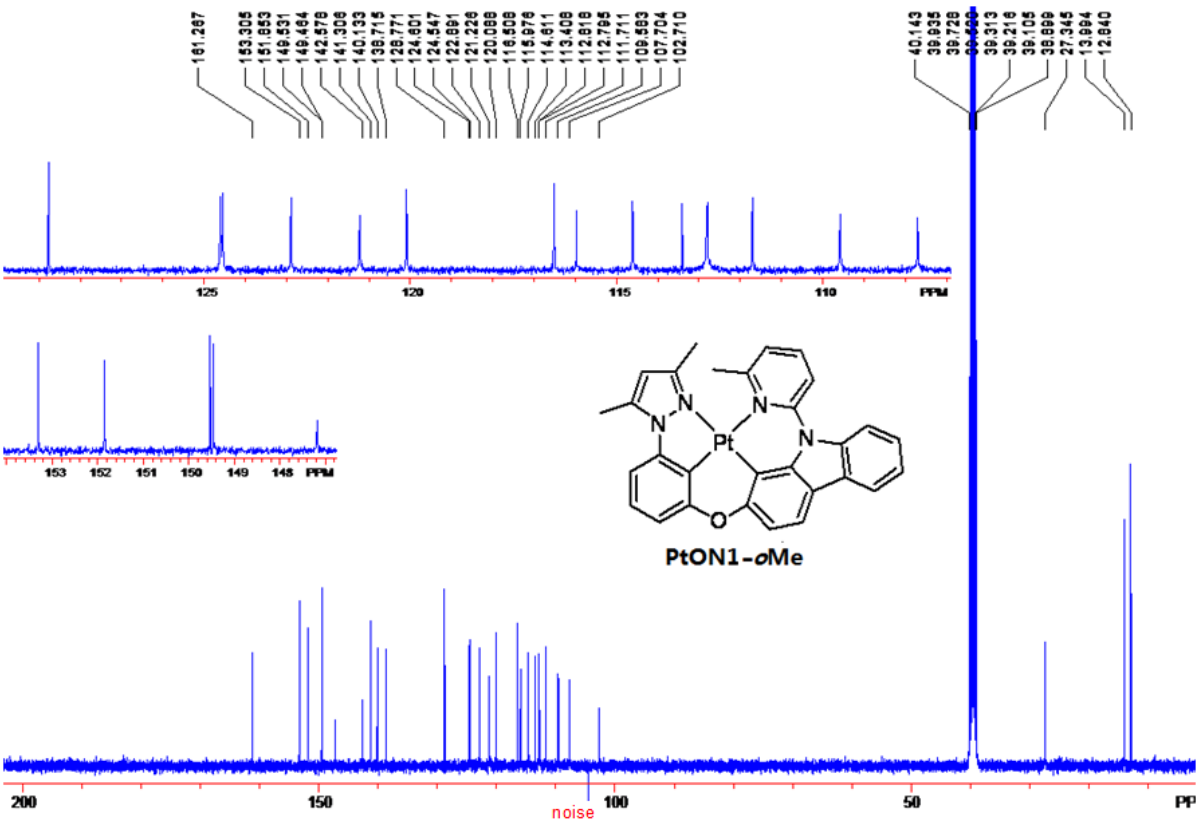
^{13}C NMR spectrum of **PtON1-*m*Me** at 100 MHz instrument in CD_2Cl_2 solution:



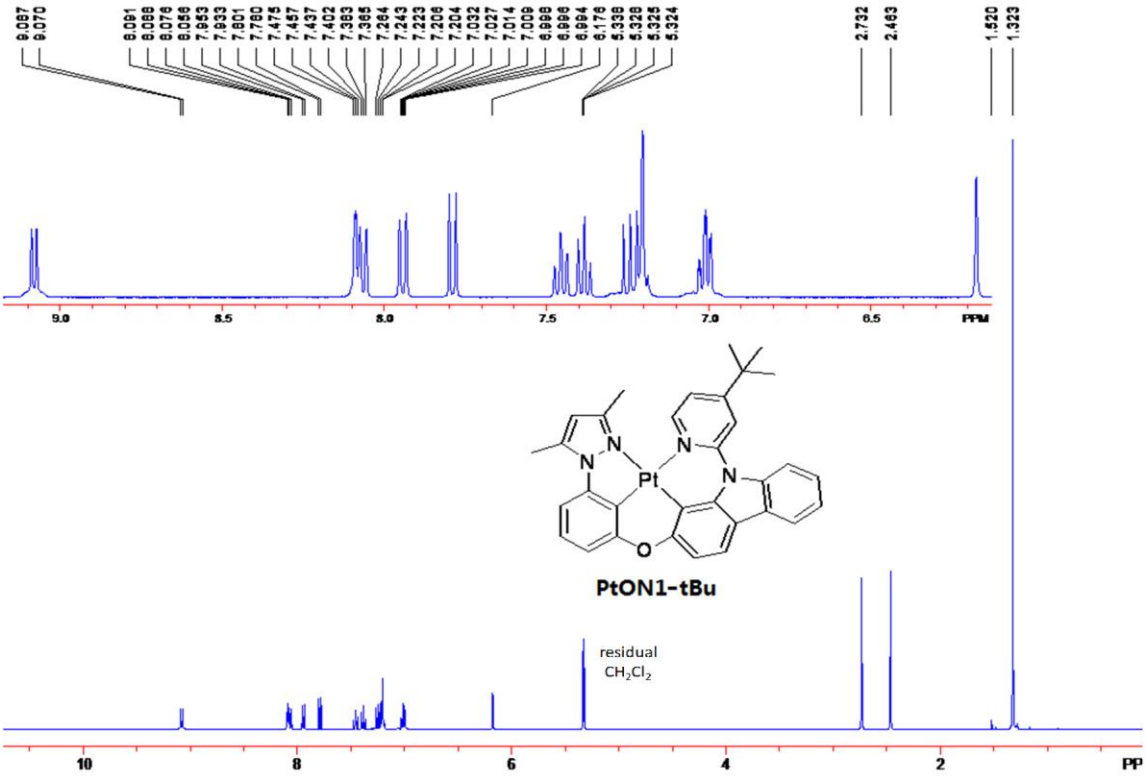
^{1}H NMR spectrum of **PtON1-*o*Me** at 400 MHz instrument in CD_2Cl_2 solution:



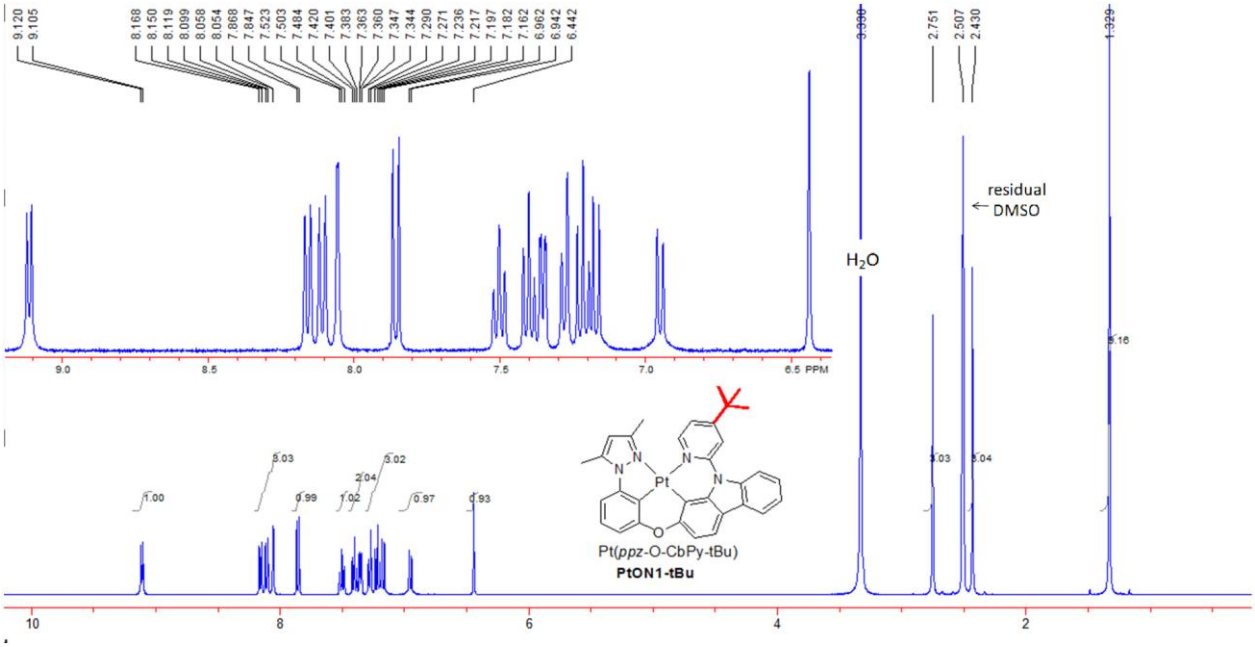
^{13}C NMR spectrum of **PtON1-*o*Me** at 100 MHz instrument in DMSO-d_6 solution:



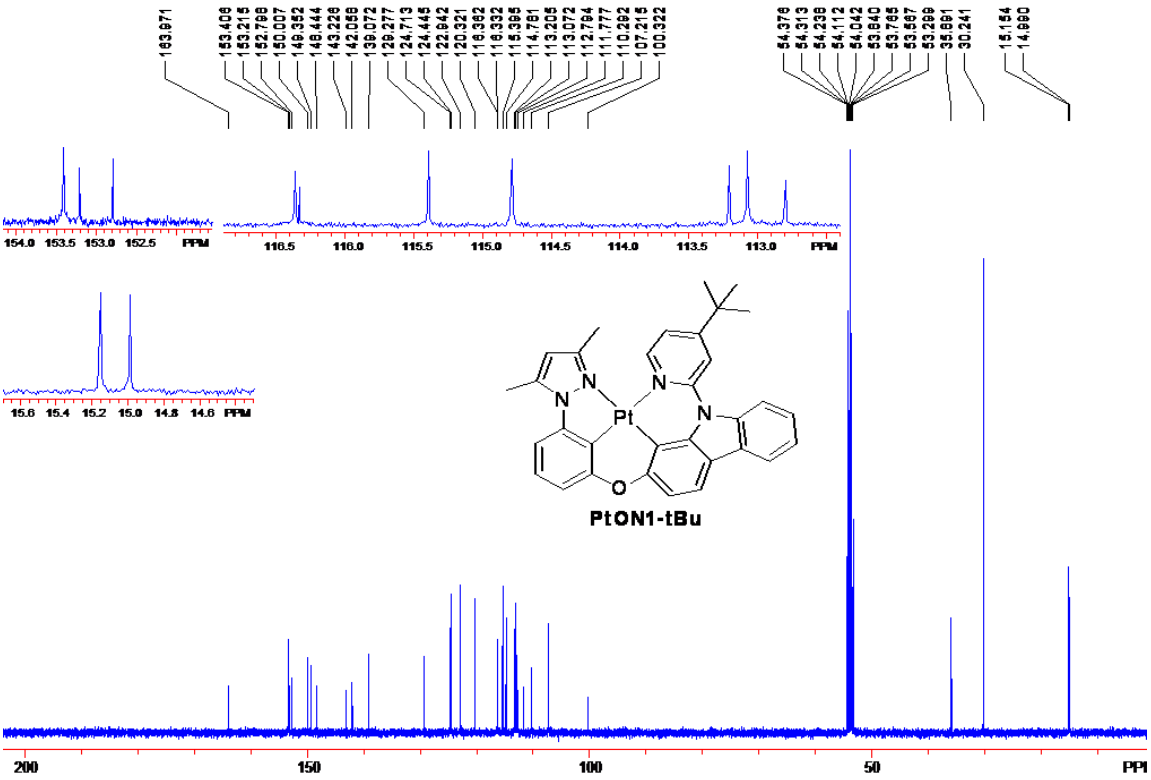
^{1}H NMR spectrum of **PtON1-tBu** at 400 MHz instrument in CD_2Cl_2 solution:[S3]



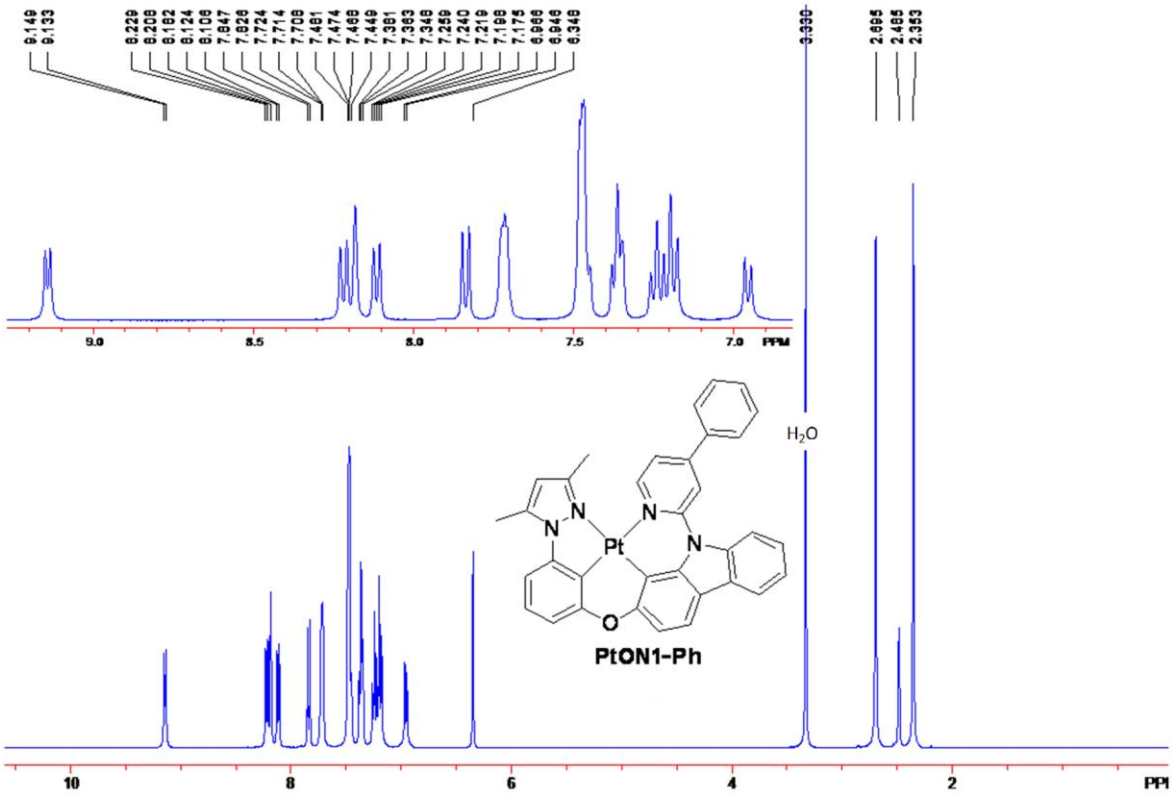
^{1}H NMR spectrum of **PtON1-tBu** at 400 MHz instrument in DMSO-d_6 solution:



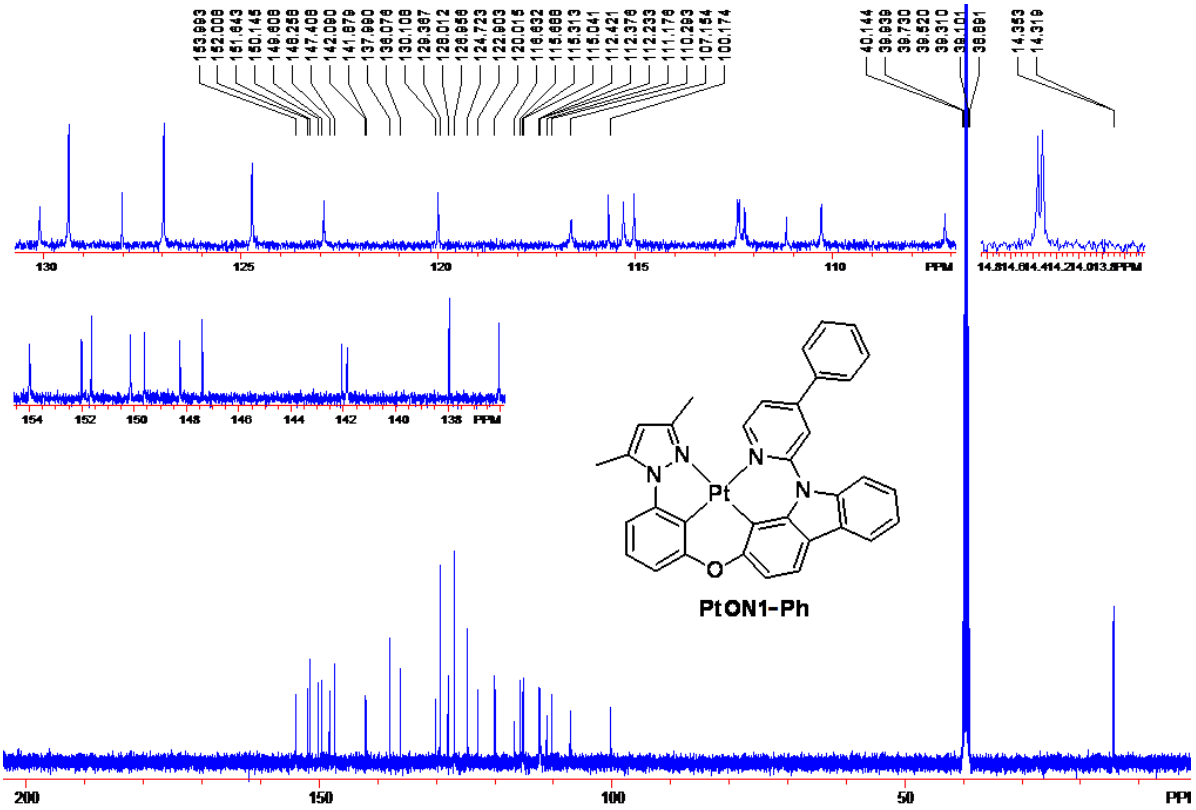
^{13}C NMR spectrum of **PtON1-tBu** at 100 MHz instrument in CD_2Cl_2 solution:[S3]



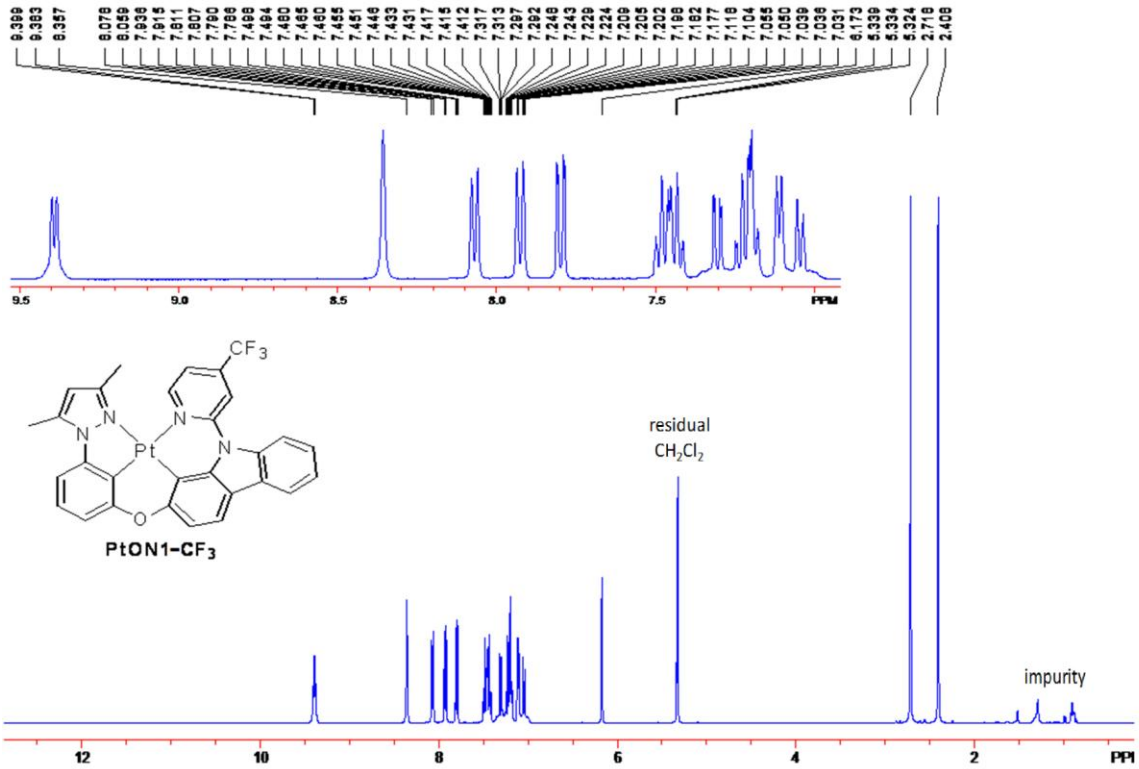
^{1}H NMR spectrum of **PtON1-Ph** at 400 MHz instrument in DMSO-d_6 solution:



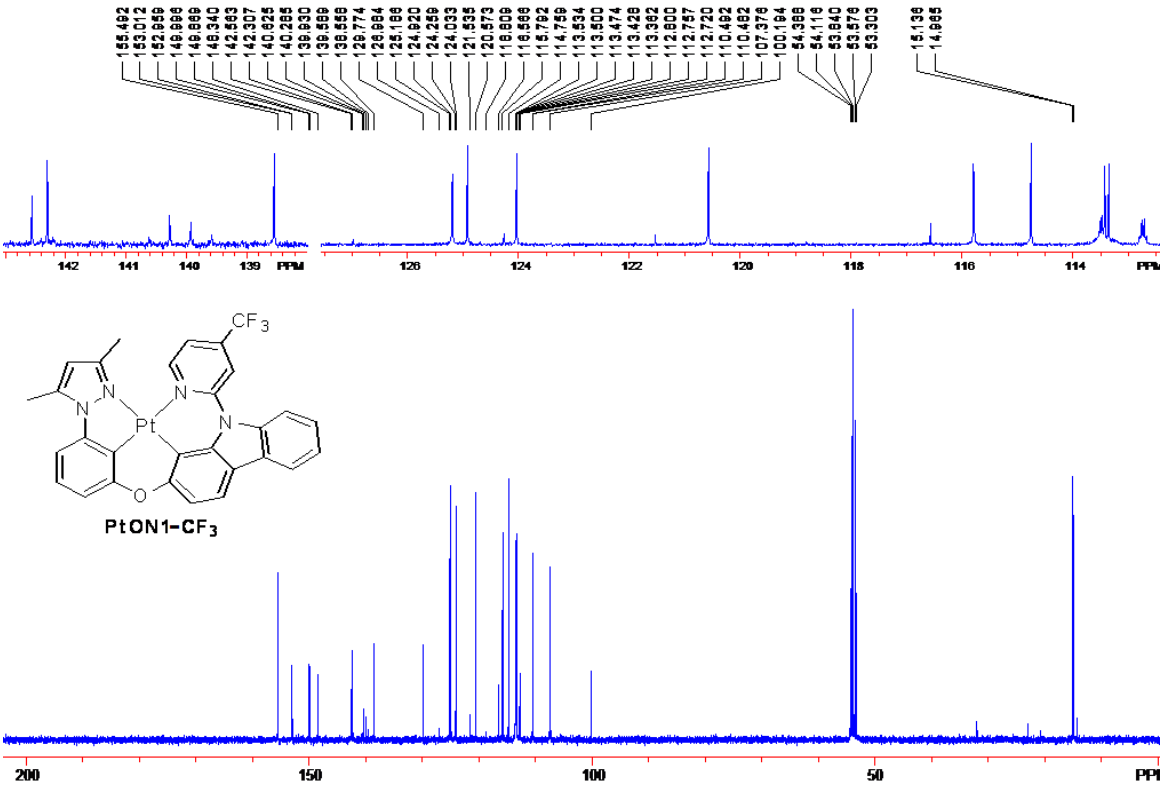
^{13}C NMR spectrum of **PtON1-Ph** at 100 MHz instrument in DMSO-d_6 solution:



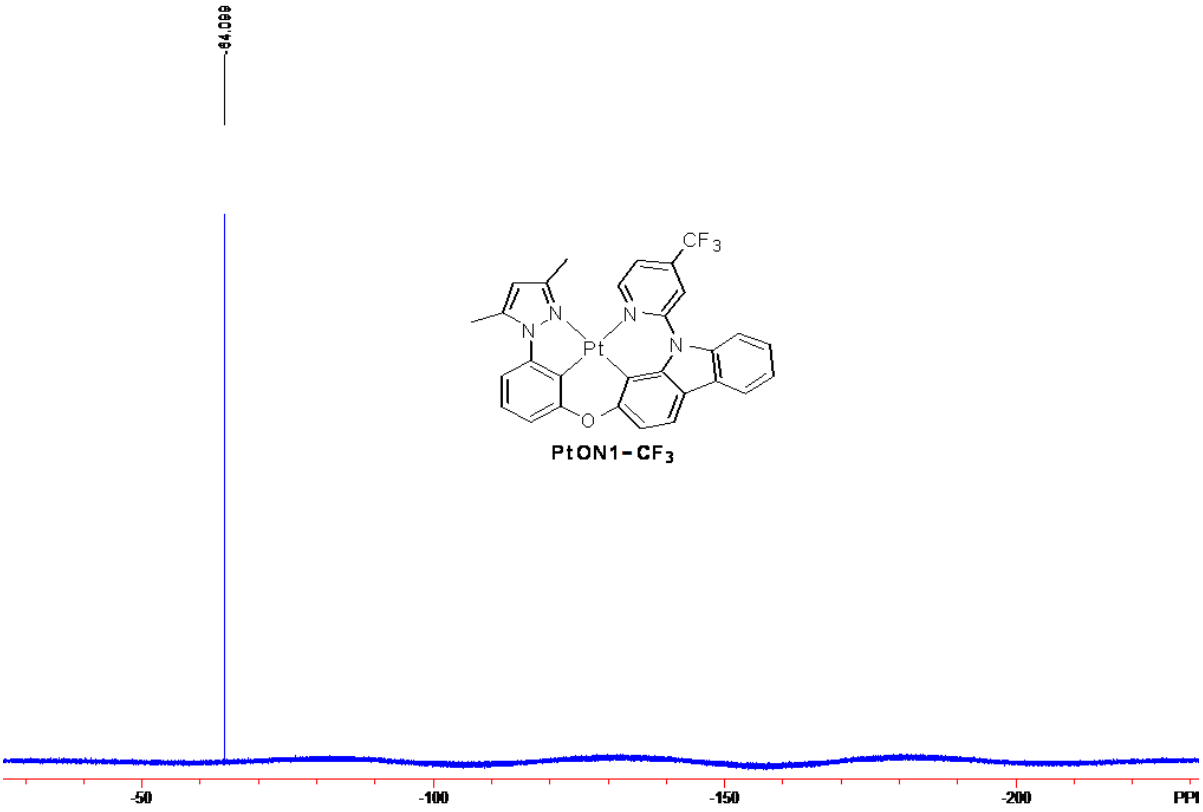
^{1}H NMR spectrum of **PtON1-CF$_3$** at 400 MHz instrument in CD_2Cl_2 solution:



^{13}C NMR spectrum of **PtON1-CF$_3$** at 100 MHz instrument in CD_2Cl_2 solution:



^{19}F NMR spectrum of **PtON1-CF$_3$** at 376 MHz instrument in DMSO-d_6 solution:



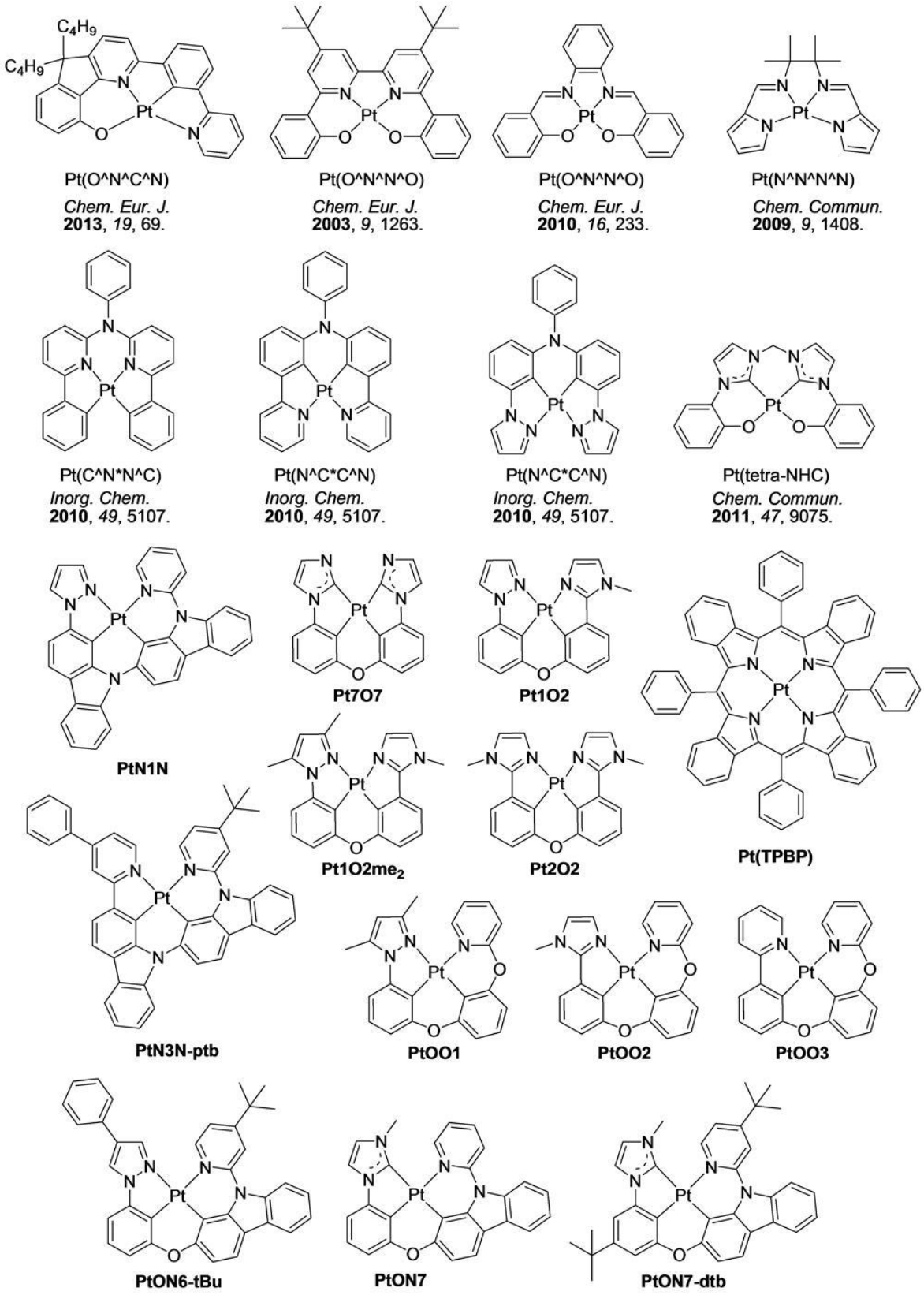


Figure S1. Molecular structures for the tertradentate Pt(II) complexes discussed in this report.

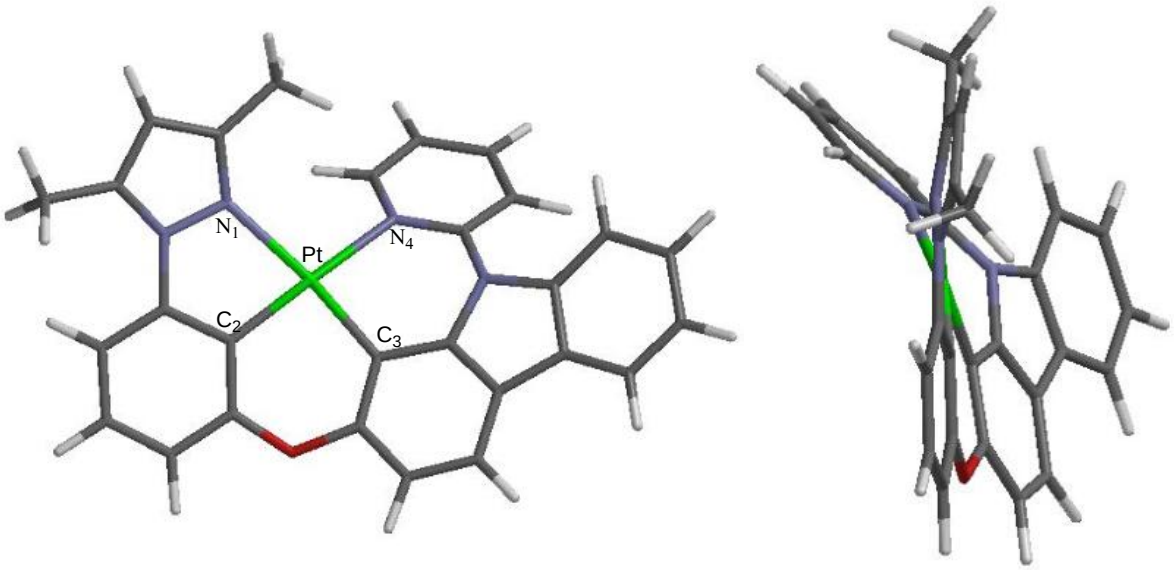


***Figure S2*:** Optimized molecular structure of **PtON1** based on the DFT calculation, top-view (left) and side-view (right)[3]

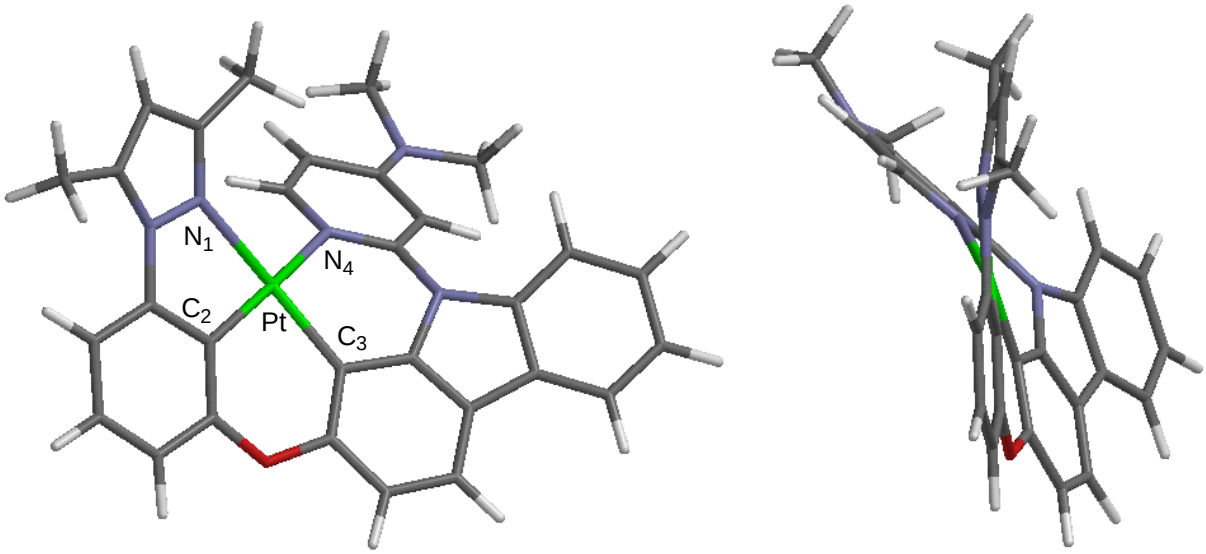


***Figure S3*:** Optimized molecular structure of **PtON1-NMe$_2$** based on the DFT calculation, top-view (left) and side-view (right)

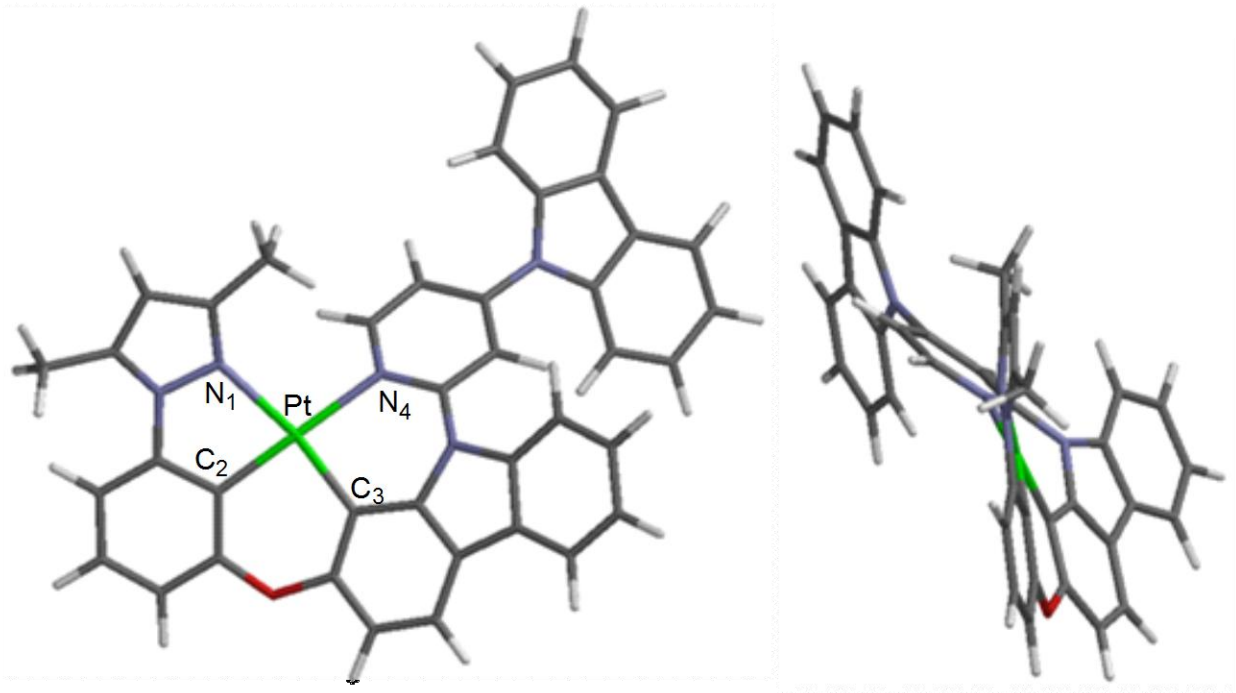


***Figure S4*:** Optimized molecular structure of **PtON1-Cz** based on the DFT calculation, top-view (left) and side-view (right)

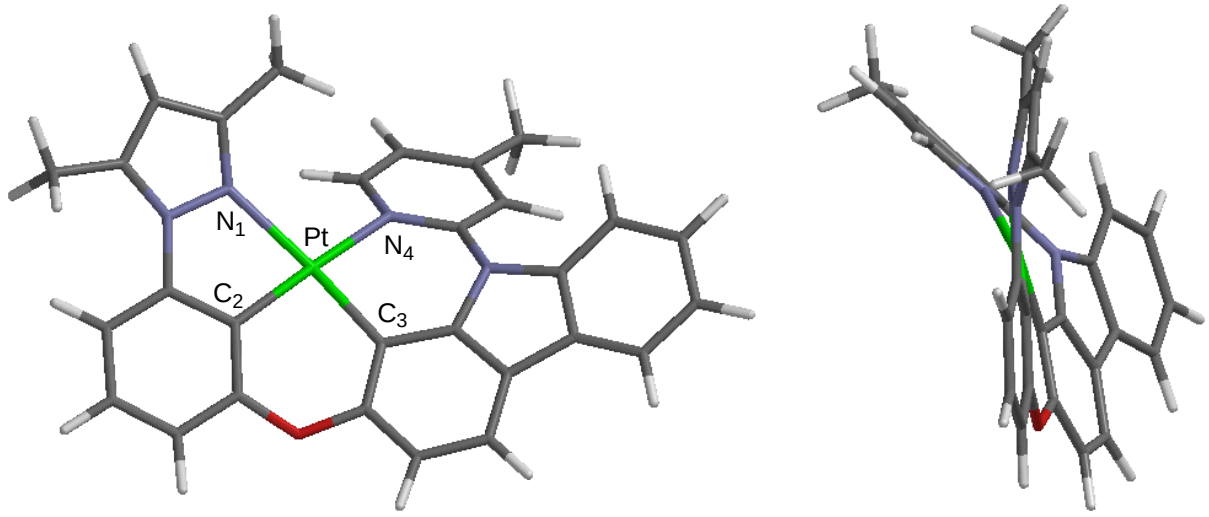


***Figure S5*:** Optimized molecular structure of **PtON1-Me** based on the DFT calculation, top-view (left) and side-view (right)

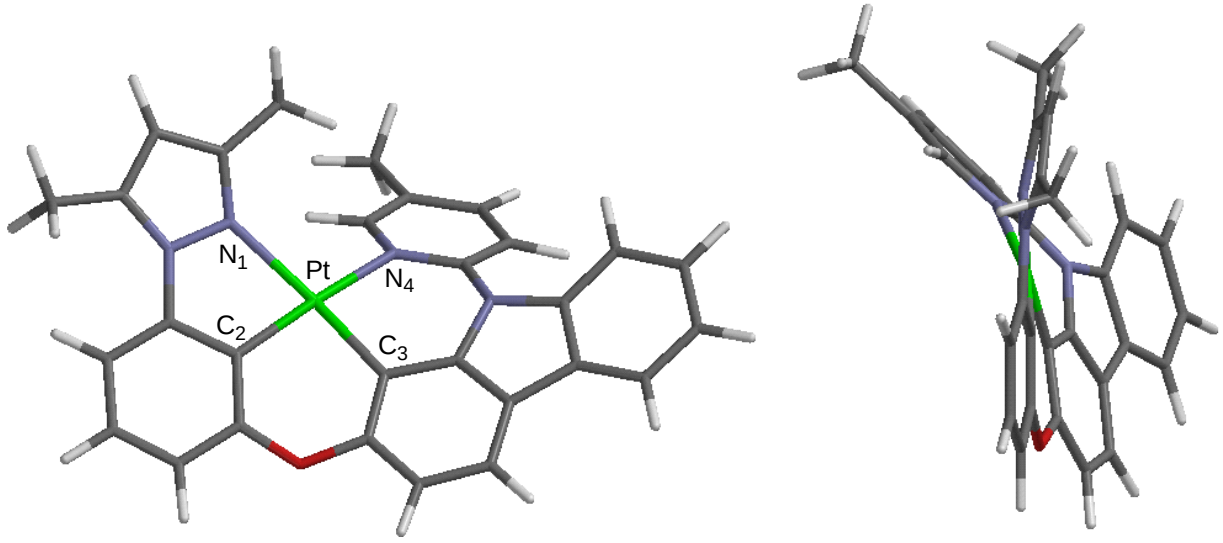


***Figure S6*: Optimized molecular structure of **PtON1-*m*Me** based on the DFT calculation, top-view (left) and side-view (right)**

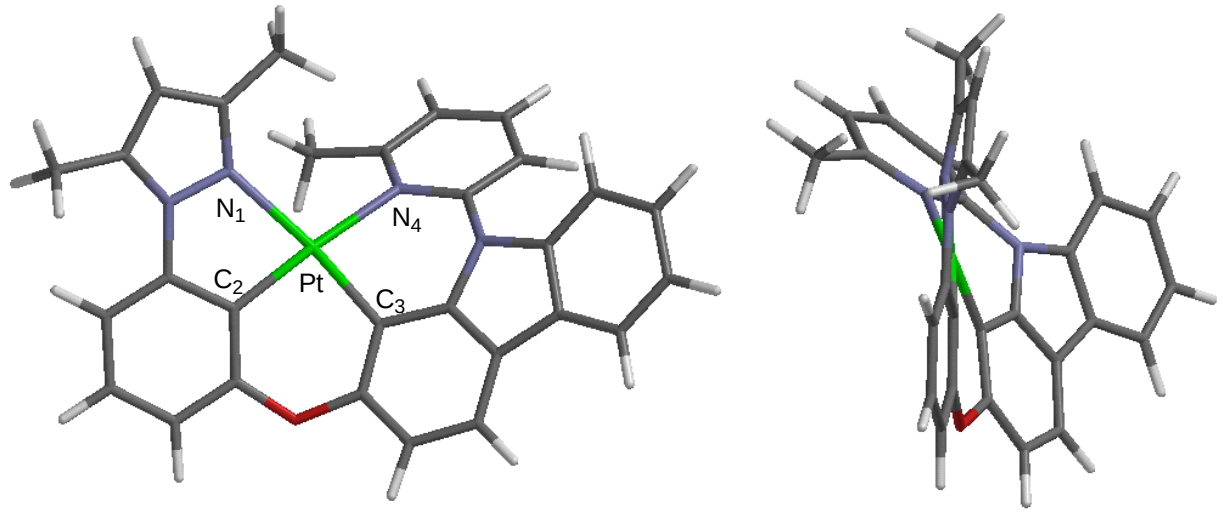


***Figure S7*: Optimized molecular structure of **PtON1-*o*Me** based on the DFT calculation, top-view (left) and side-view (right)**

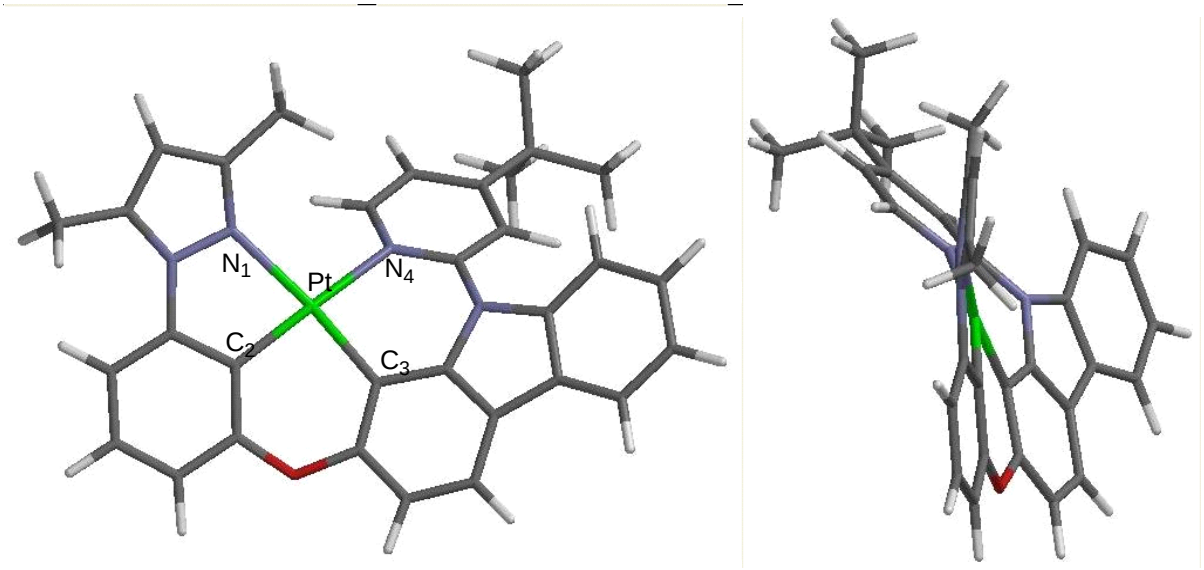


***Figure S8*:** Optimized molecular structure of **PtON1-tBu** based on the DFT calculation, top-view (left) and side-view (right)[3]

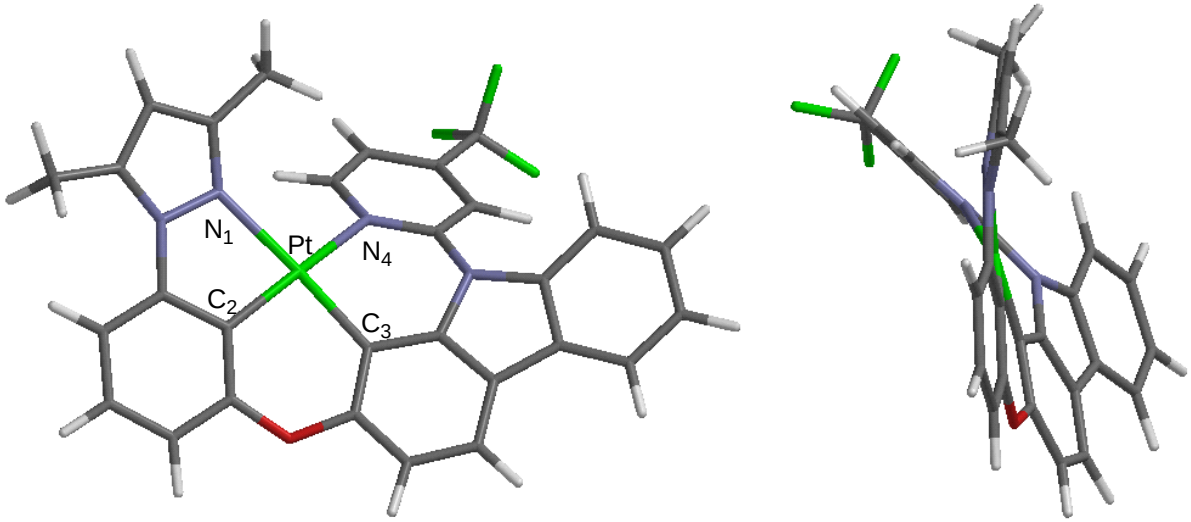


***Figure S9*:** Optimized molecular structure of **PtON1-CF_3** based on the DFT calculation, top-view (left) and side-view (right)

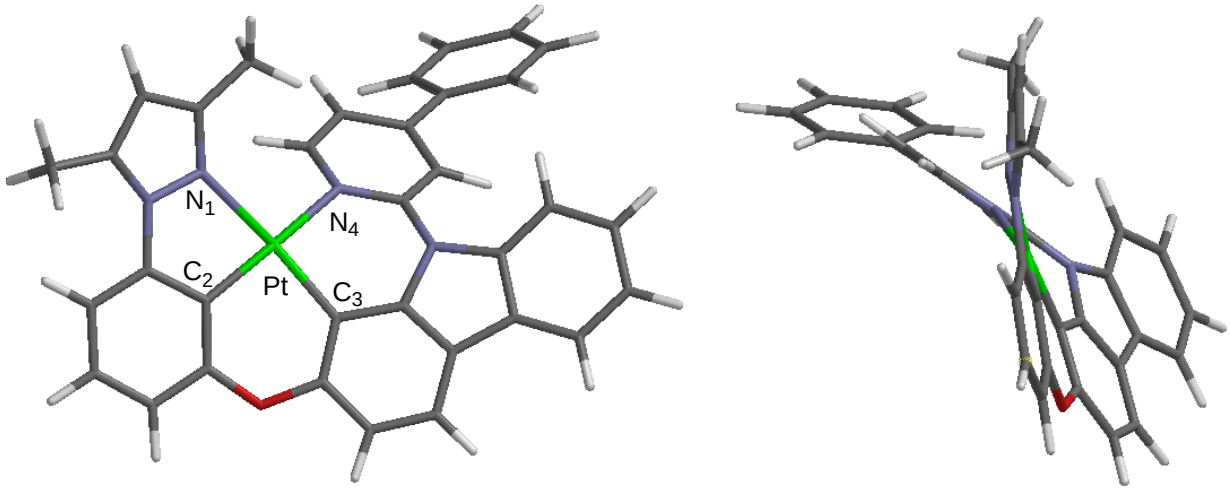


***Figure S10*:** Optimized molecular structure of **PtON1-Ph** based on the DFT calculation, top-view (left) and side-view (right)

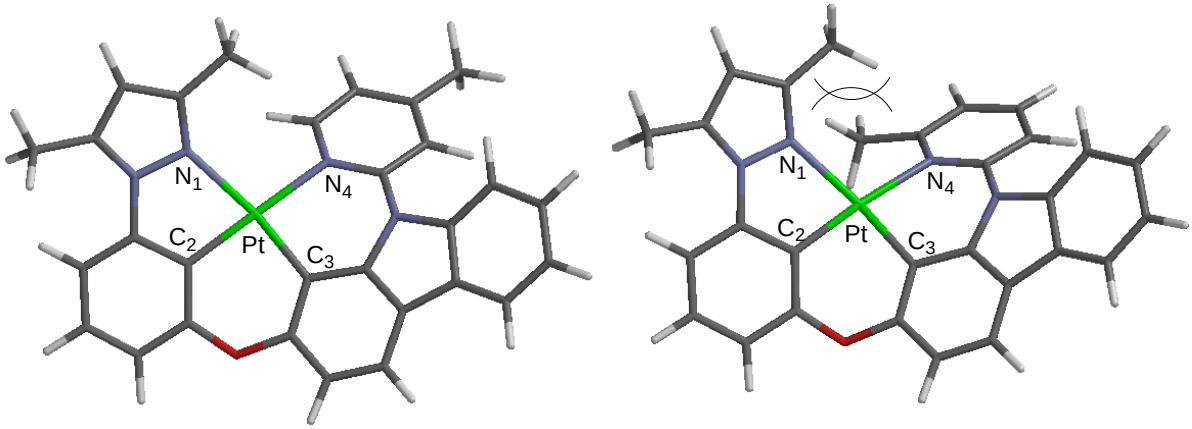


***Figure S11*:** Optimized molecular structures of **PtON1-Me** (left) and **PtON1*o*Me** (right) based on the DFT calculation, top-view.

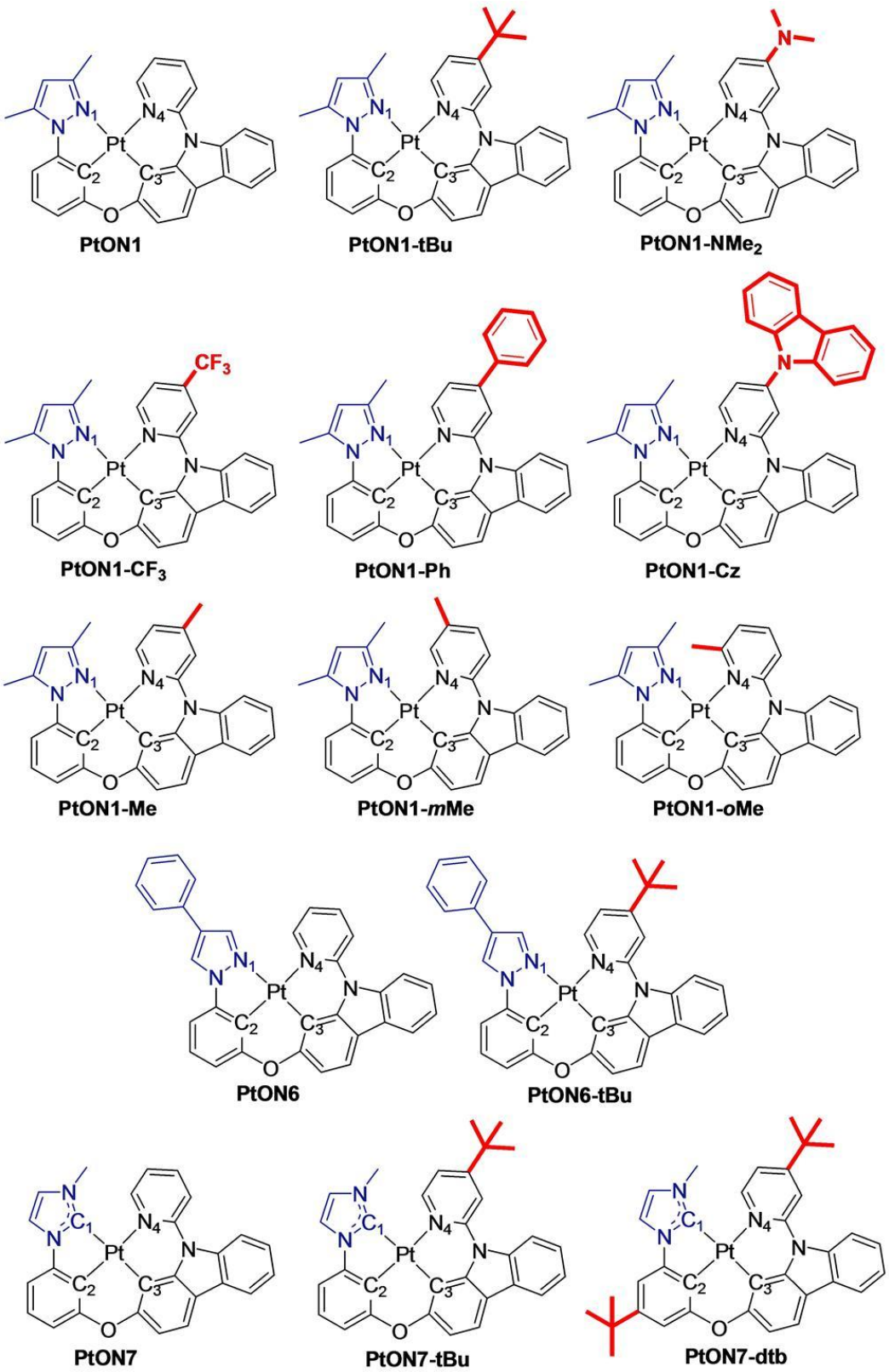


***Figure S12*:** Chemical Structures of PtON1, PtON6, PtON7 and their derivatives.

***Table S 1*:** Selected bond lengths (Å) for PtON1 and its analoges based on the DFT calculation and X-ray crystallographic analysis.

Pt complexes	Pt-$N_1(C_1)$	Pt-C_2	Pt-C_3	Pt-N_4
PtON1 (DFT)[S3]	2.18	1.98	1.98	2.19
PtON1-NMe_2 (DFT)	2.18	1.98	1.99	2.18
PtON1-Cz (DFT)	2.18	1.98	1.98	2.18
PtON1-Me (DFT)	2.18	1.98	1.99	2.18
PtON1-*m*Me (DFT)	2.18	1.98	1.99	2.19
PtON1-*o*Me (DFT)	2.19	1.98	1.98	**2.23**
PtON1-tBu (DFT)[S3]	2.18	1.98	1.99	2.18
PtON1-Ph (DFT)	2.18	1.98	1.98	2.18
PtON1-CF_3 (DFT)	2.18	1.98	1.98	2.18
PtON6 (DFT)[S3]	2.18	1.98	1.98	2.18
PtON6-tBu (DFT)[S3]	2.17	1.98	1.98	2.17
PtON7 (DFT)[S3]	2.08	1.99	2.02	2.19
PtON7-tBu (DFT)[S3]	2.08	1.99	2.02	2.19
PtON7-dtb (DFT)[S3]	2.08	1.99	2.03	2.19
PtON7-dtb (X-ray)[S3]	2.038(4)	1.973(4)	2.012(4)	2.111(3)

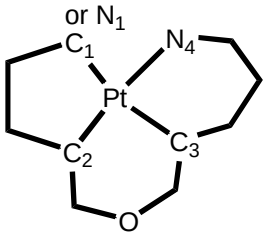
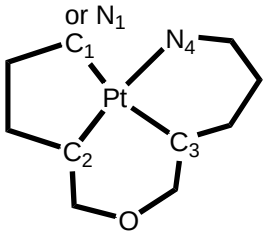


***Table S2*:** Selected bond angles (°) for PtON1 and its analoges based on the DFT calculation and X-ray crystallographic analysis.

Pt complexes	$N_1(C_1)$-Pt-C_2	C_2-Pt-C_3	C_3-Pt-N_4	N_4-Pt-$N_1(C_1)$	$N_1(C_1)$-Pt-C_3	C_2-Pt-N_4
PtON1 (DFT)[S3]	79.09	91.54	89.31	102.10	165.66	168.16
PtON1-NMe_2 (DFT)	79.03	91.43	88.93	102.53	165.33	169.19
PtON1-Cz (DFT)	79.09	91.05	88.98	102.45	165.39	168.73
PtON1-Me (DFT)	78.94	91.63	89.36	102.01	165.98	168.19
PtON1-*m*Me (DFT)	79.03	91.58	89.31	102.12	165.75	167.97
PtON1-*o*Me (DFT)	78.76	90.69	87.78	**105.33**	**162.21**	168.66
PtON1-tBu (DFT)[S3]	79.06	91.57	89.24	102.15	165.74	168.18
PtON1-Ph (DFT)	79.15	91.53	89.41	101.95	165.73	168.10
PtON1-CF_3	79.25	91.55	89.35	101.86	166.15	167.67

(DFT)						
PtON6 (DFT)[S3]	79.10	91.14	90.55	100.24	167.20	172.12
PtON6-tBu (DFT)[S3]	79.13	91.19	90.40	100.39	166.94	172.10
PtON7 (DFT)[S3]	79.74	89.90	89.06	103.25	164.74	168.89
PtON7-tBu (DFT)[S3]	79.77	89.99	89.02	103.11	165.11	168.81
PtON7-dtb (DFT)[S3]	79.58	89.78	89.06	103.40	164.86	169.11
PtON7-dtb (X-ray)[S3]	80.39(15)	89.38(16)	90.54(13)	101.58(13)	165.71(14)	167.68(13)



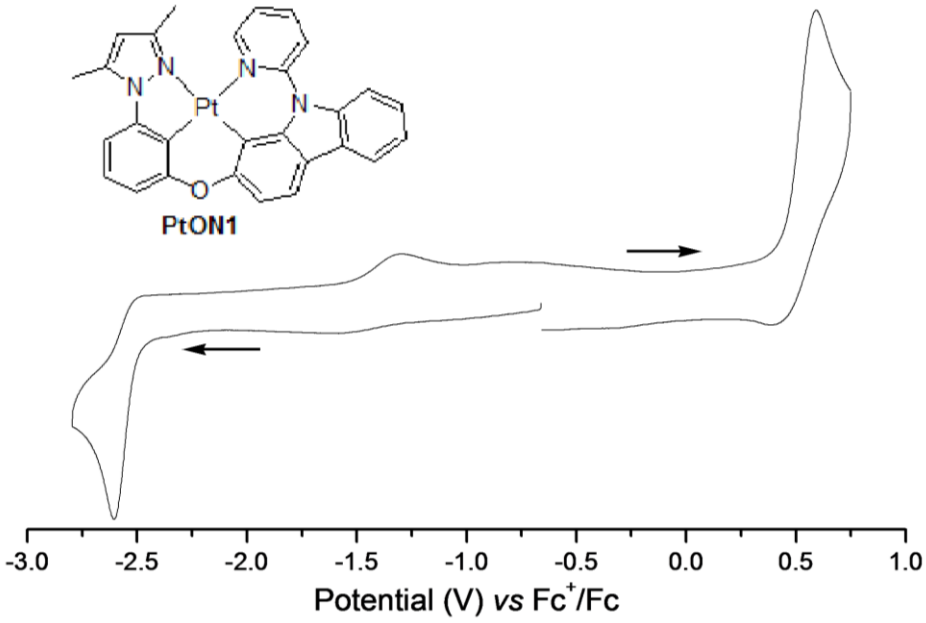


***Figure S13*:** The cyclic voltammogram for **PtON1** with the molecular structure inset in the plot.

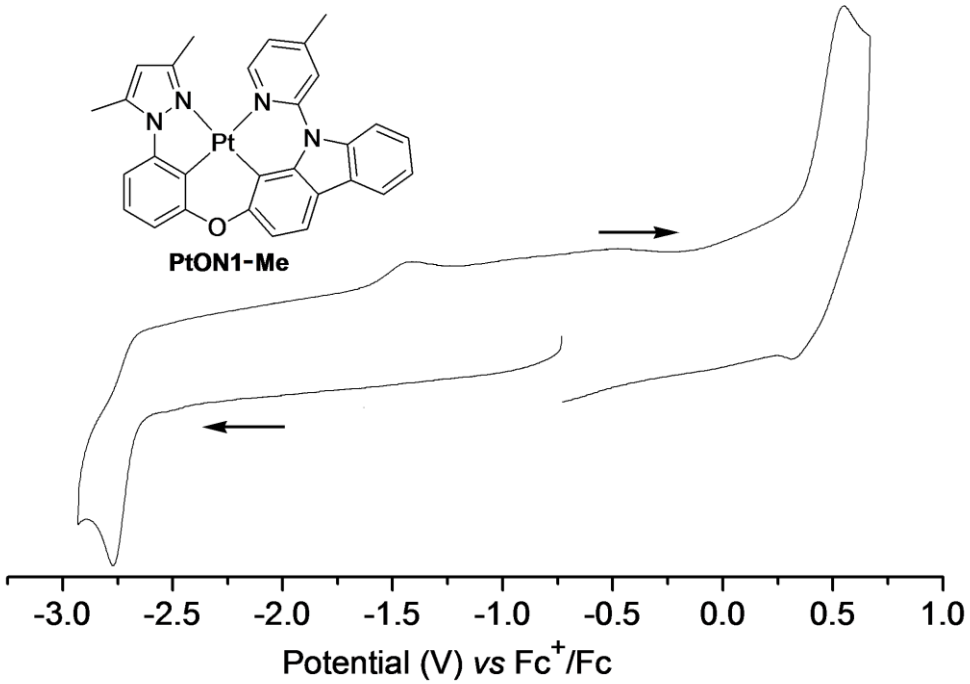


***Figure S14*:** The cyclic voltammogram for **PtON1-Me** with the molecular structure inset in the plot.

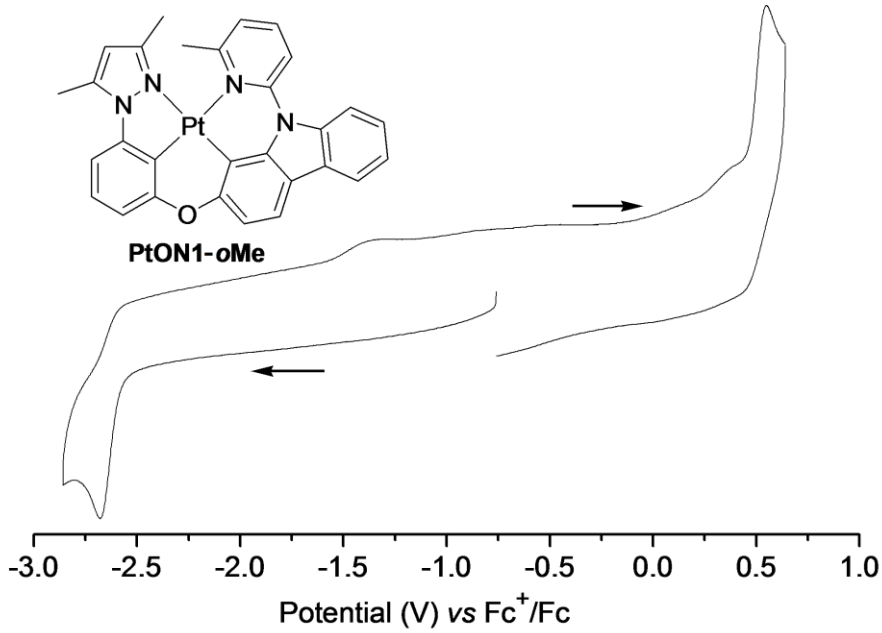


***Figure S15*:** The cyclic voltammogram for **PtON1-*o*Me** with the molecular structure inset in the plot.

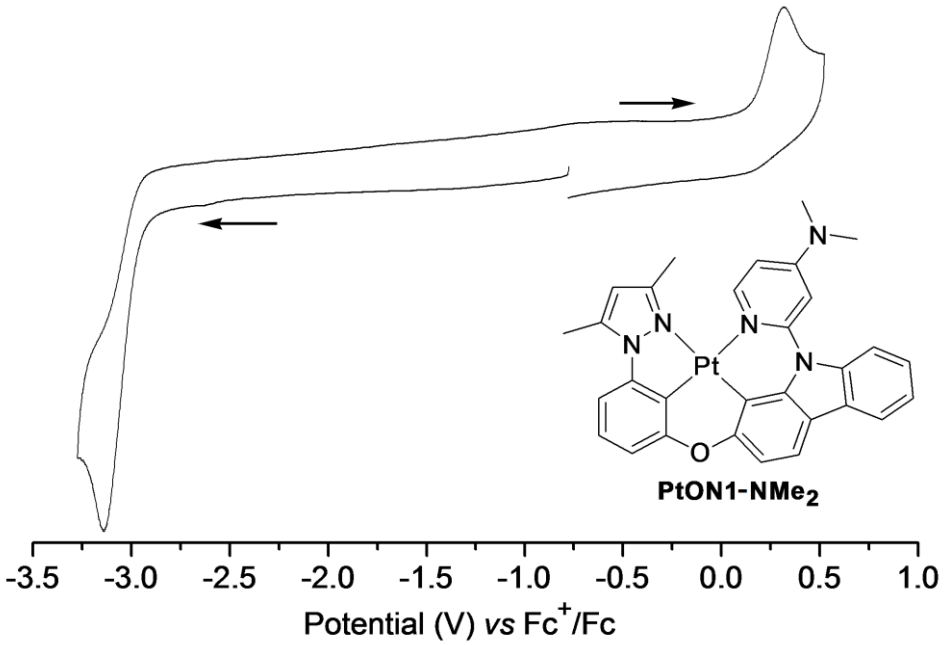


***Figure S16*:** The cyclic voltammogram for **PtON1-NMe$_2$** with the molecular structure inset in the plot.

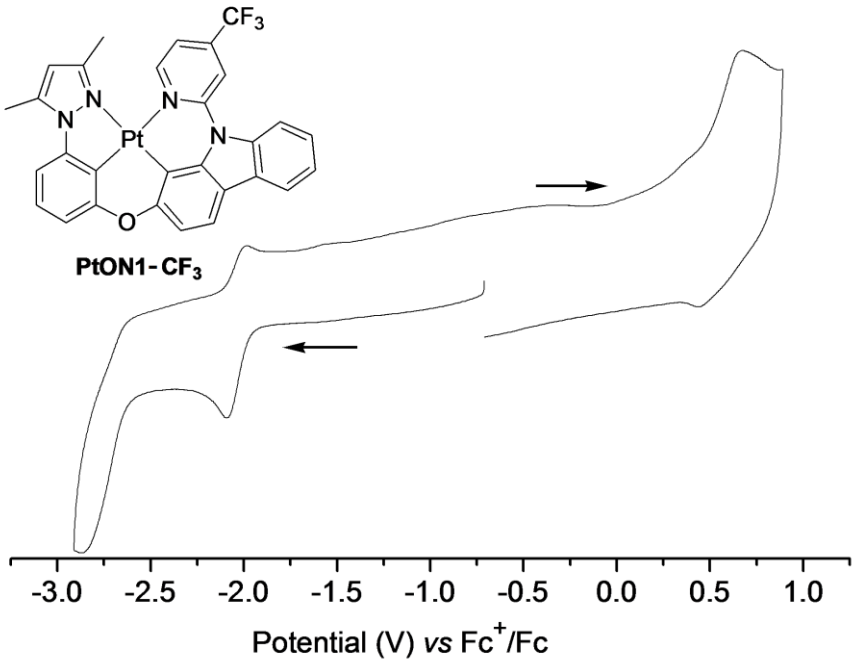


***Figure S17*:** The cyclic voltammogram for **PtON1-CF$_3$** with the molecular structure inset in the plot.

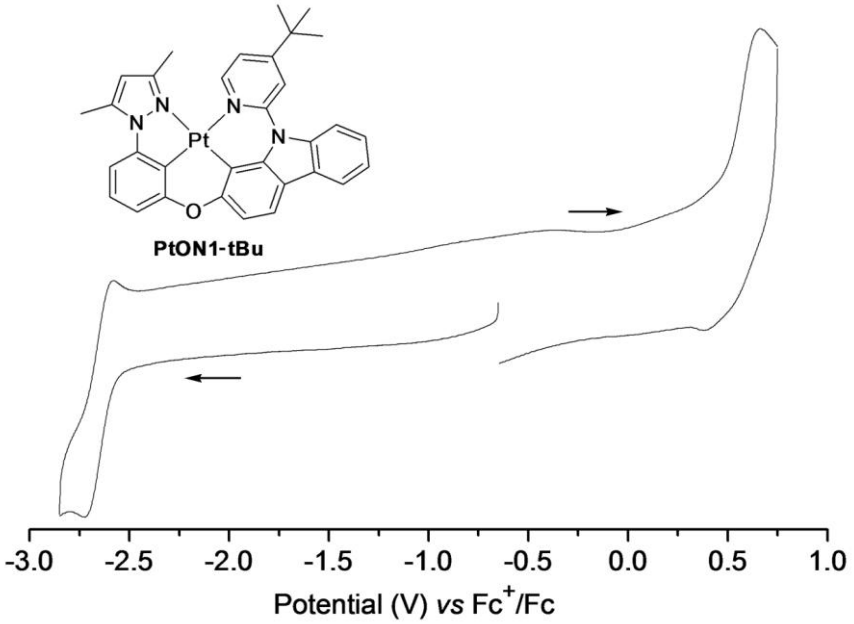


***Figure S18*:** The cyclic voltammogram for **PtON1-tBu** with the molecular structure inset in the plot.

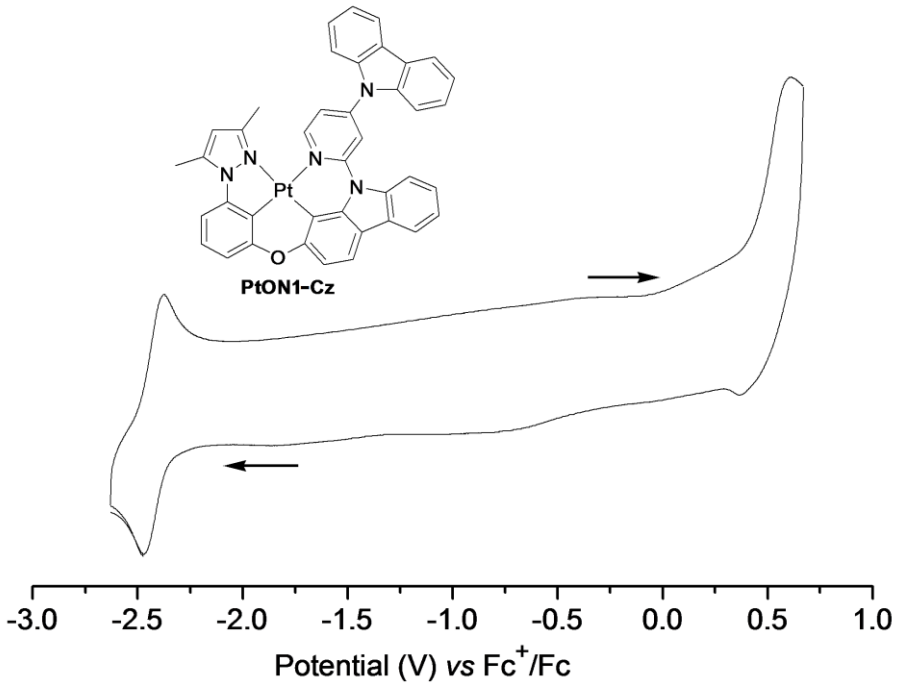


***Figure S19*:** The cyclic voltammogram for **PtON1-Cz** with the molecular structure inset in the plot.

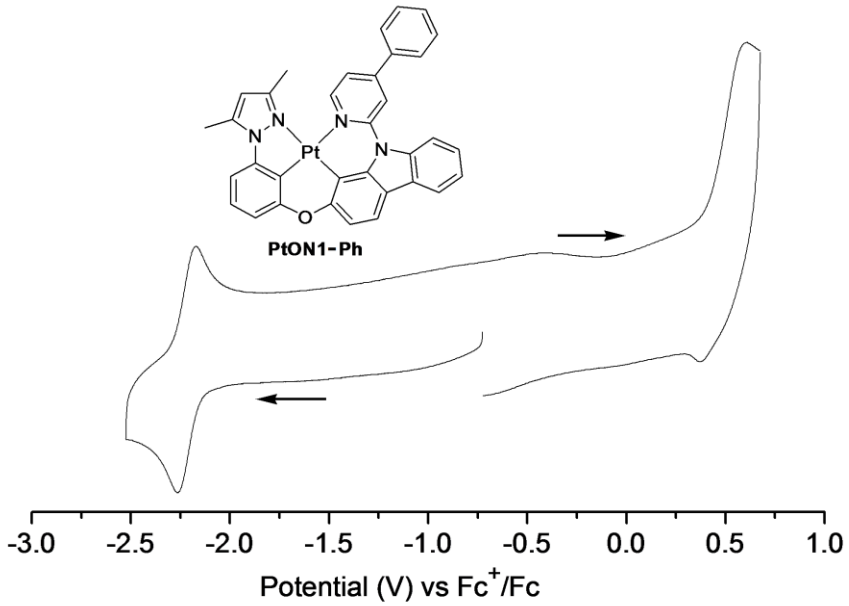


***Figure S20*:** The cyclic voltammogram for **PtON1-Ph** with the molecular structure inset in the plot.

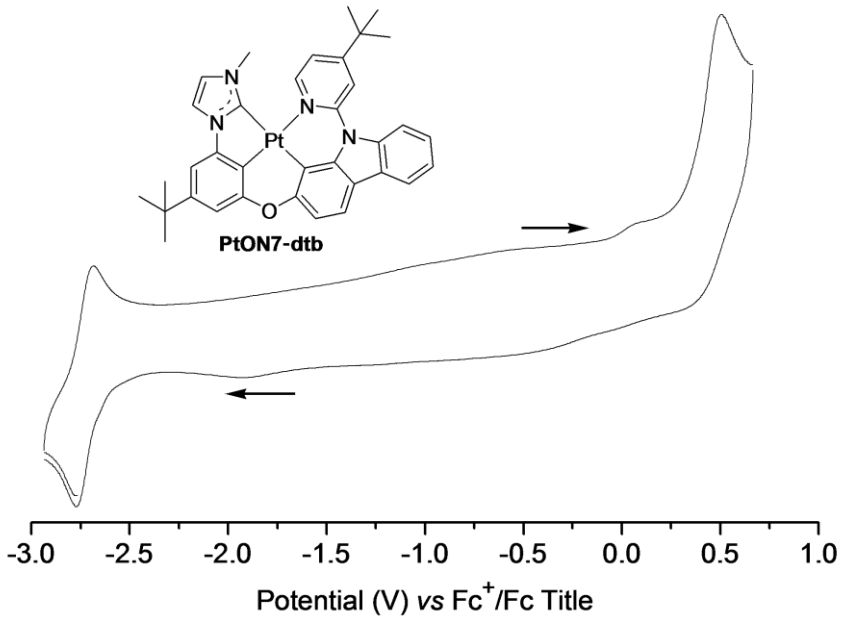


***Figure S21*:** The cyclic voltammogram for **PtON7-dtb** with the molecular structure inset in the plot.

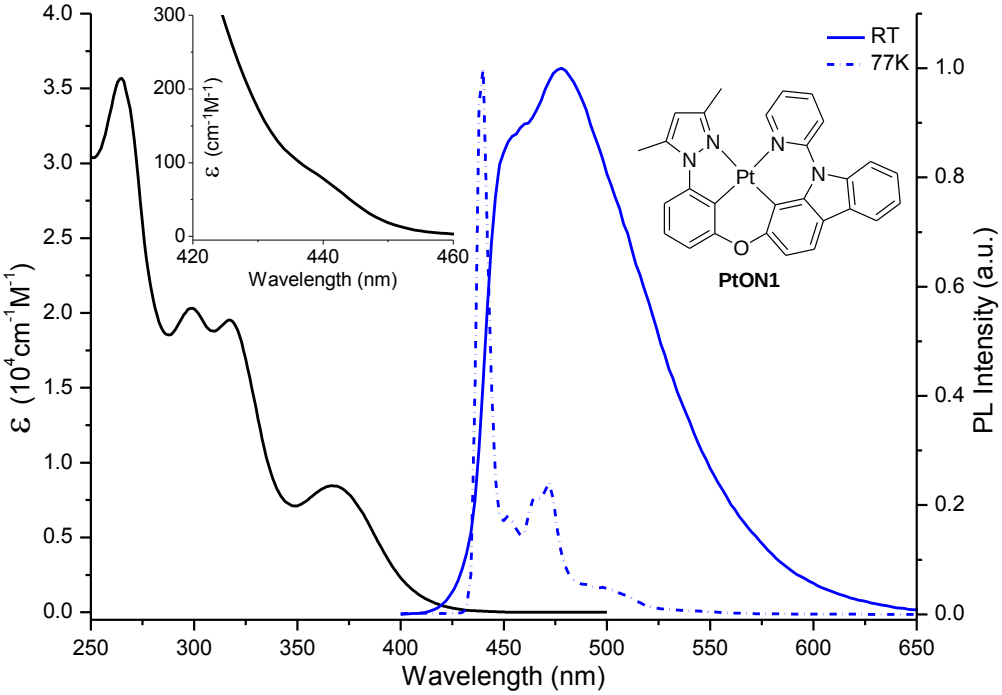


Figure S22: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1**. The T_1 absorption transition and the chemical structure of **PtON1** are shown in the inset.[3]

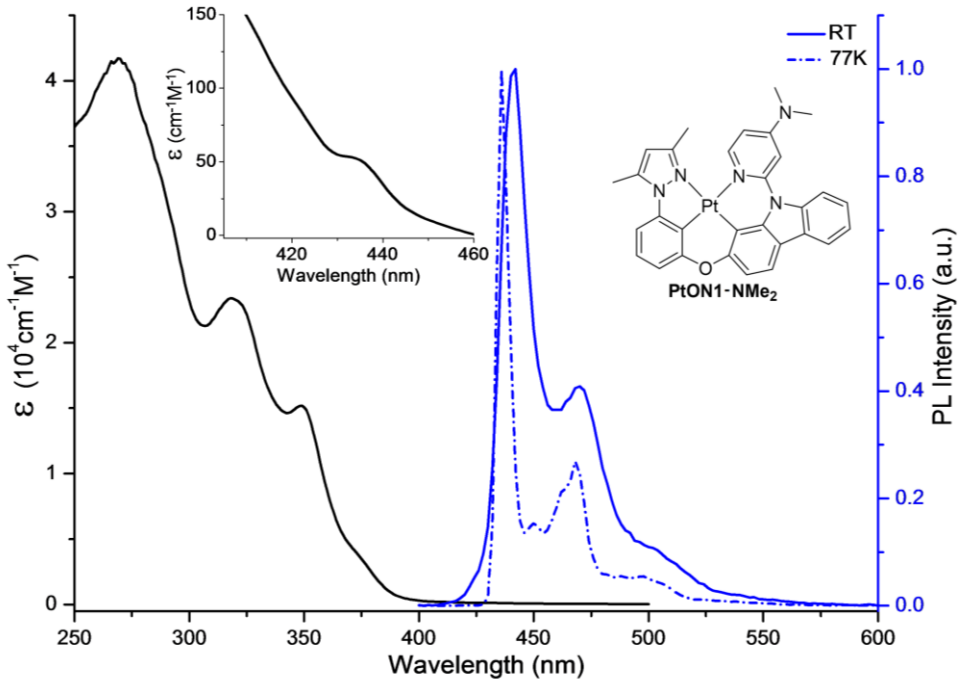


Figure S23: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-NMe$_2$**. The T_1 absorption transition and the chemical structure of **PtON1-NMe$_2$** are shown in the inset.

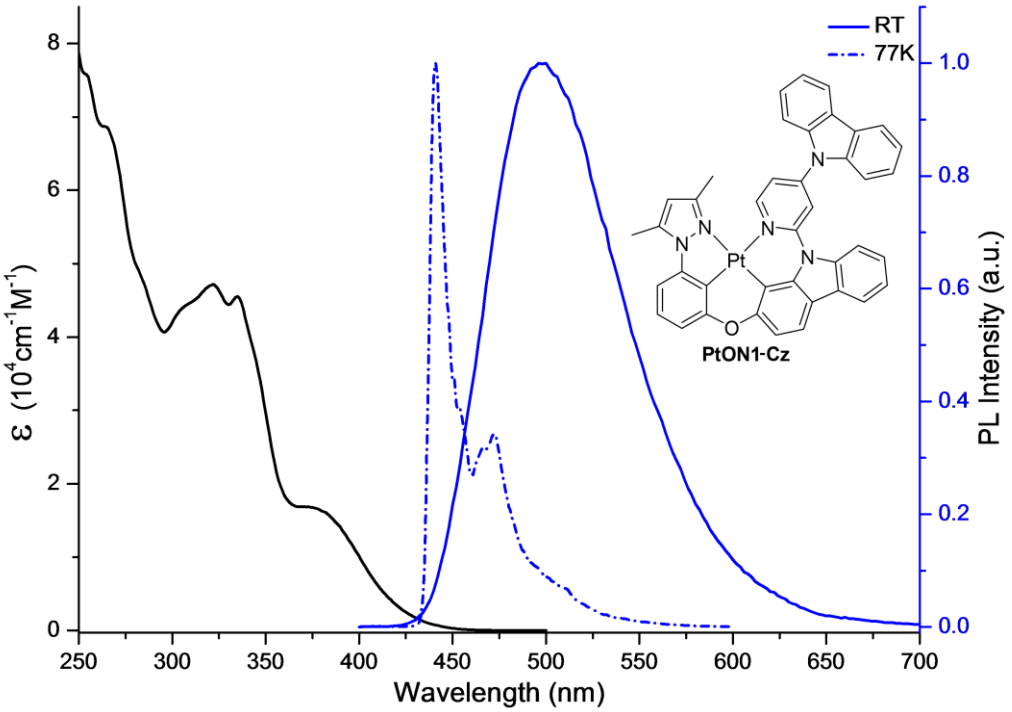


Figure S24: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-Cz**. The T_1 absorption transition and the chemical structure of **PtON1-Cz** are shown in the inset.

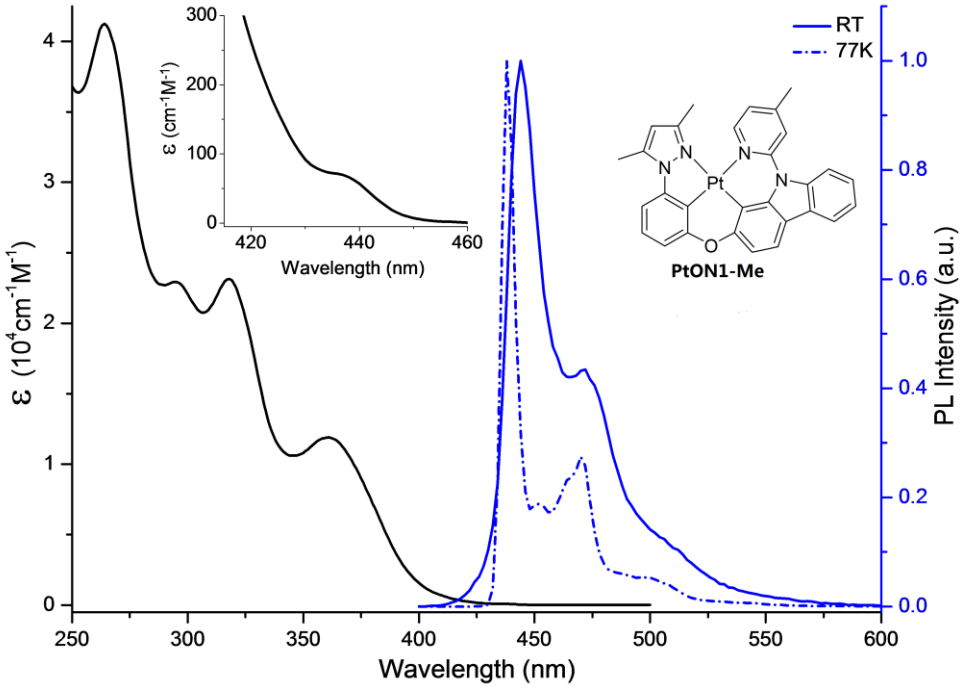


Figure S25: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-Me**. The T_1 absorption transition and the chemical structure of **PtON1-Me** are shown in the inset.

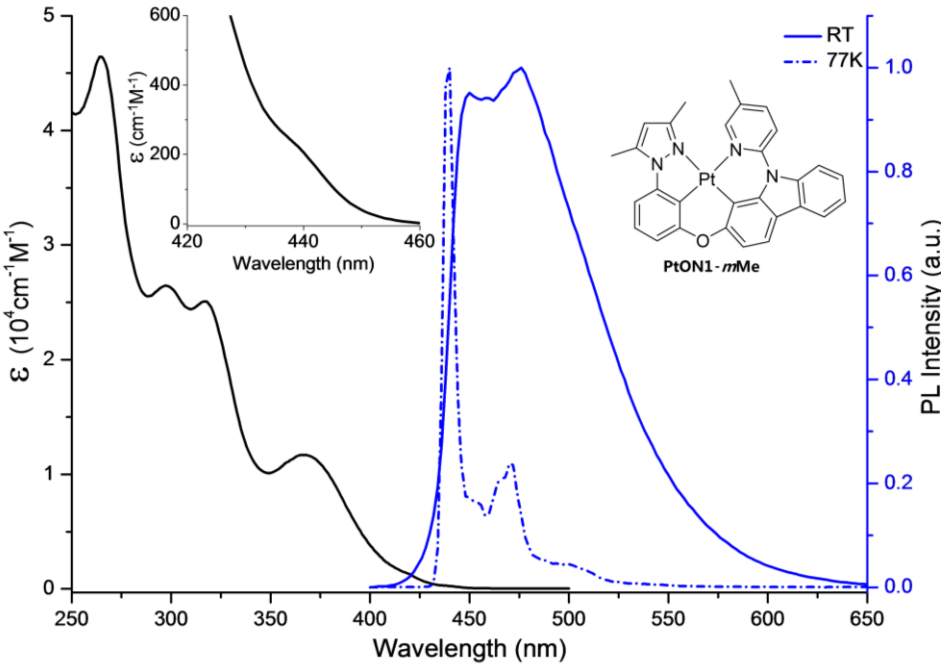


Figure S26: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-*m*Me**. The T_1 absorption transition and the chemical structure of **PtON1-*m*Me** are shown in the inset.

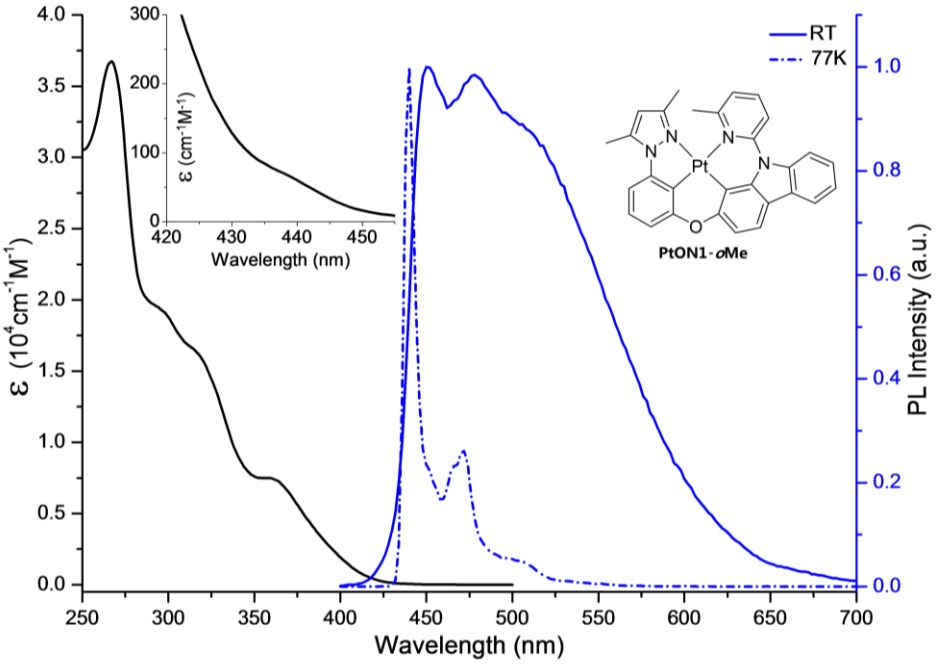


Figure S27: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-*o*Me**. The T_1 absorption transition and the chemical structure of **PtON1-*o*Me** are shown in the inset.

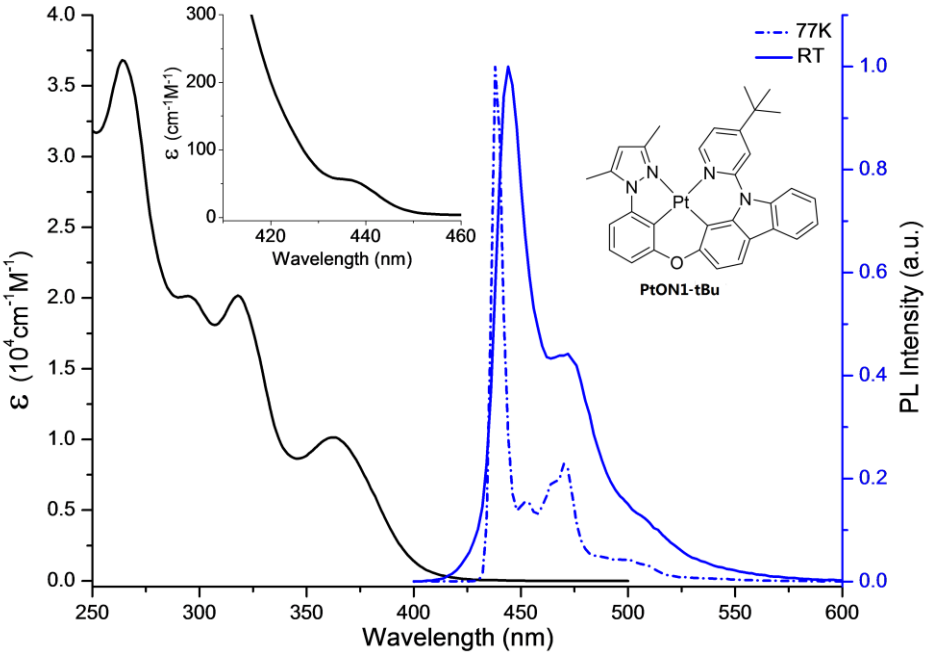


Figure S28: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-tBu**. The T_1 absorption transition and the chemical structure of **PtON1-tBu** are shown in the inset.[3]

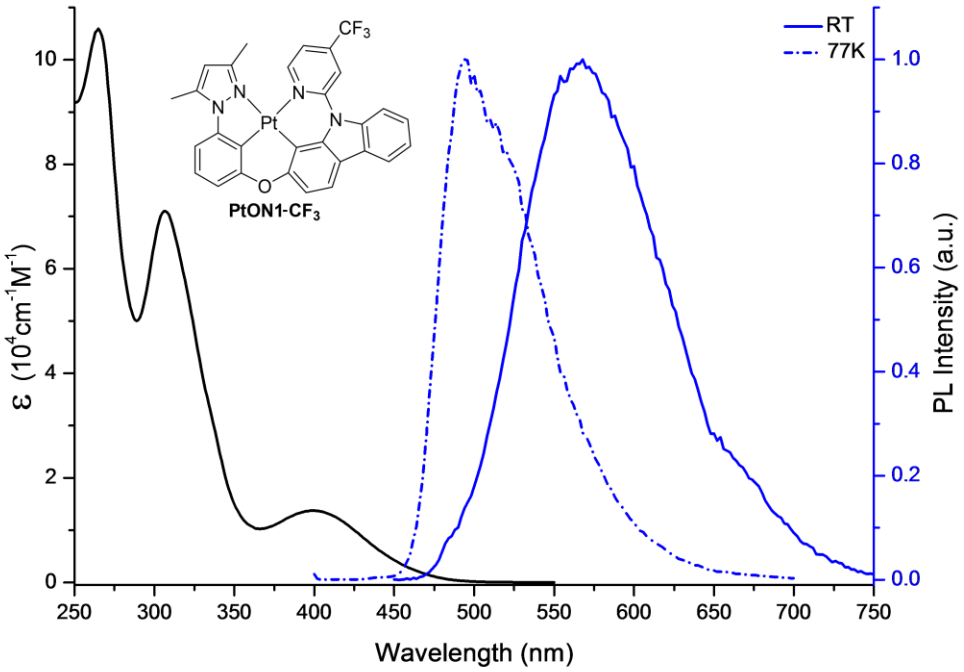


Figure S29: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-CF$_3$**. The T_1 absorption transition and the chemical structure of **PtON1-CF$_3$** are shown in the inset.

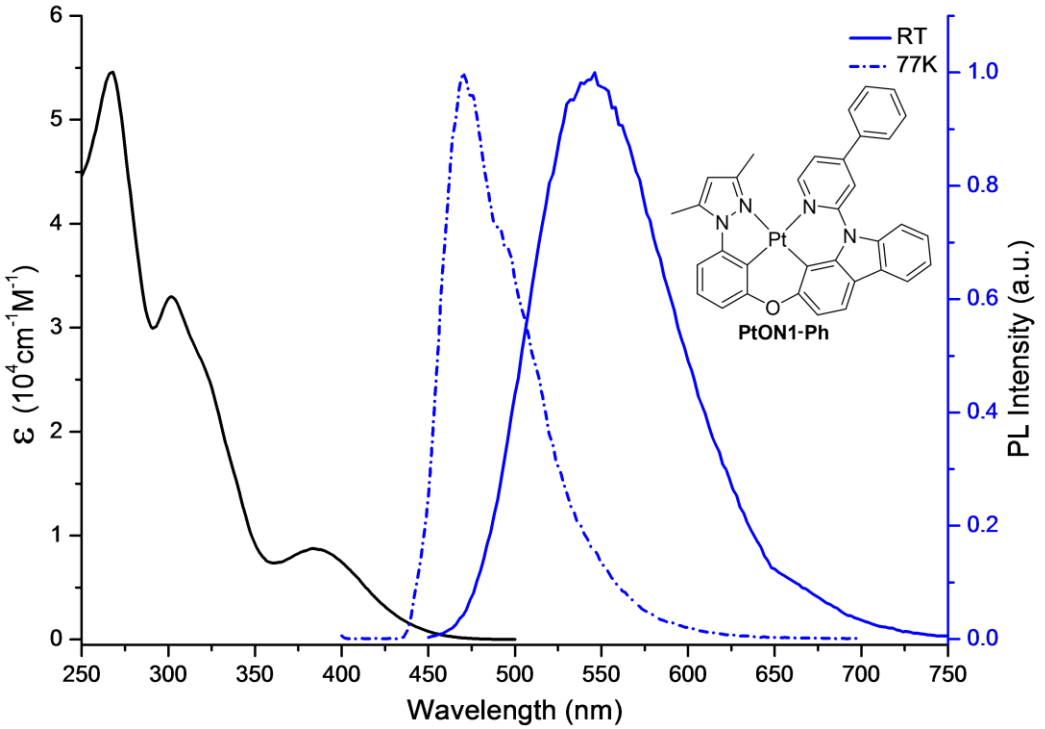


Figure S30: Absorption spectra (in CH_2Cl_2) and emission spectra (room temperature in CH_2Cl_2, 77K in 2-methyl THF) of **PtON1-Ph**. The T_1 absorption transition and the chemical structure of **PtON1-Ph** are shown in the inset.

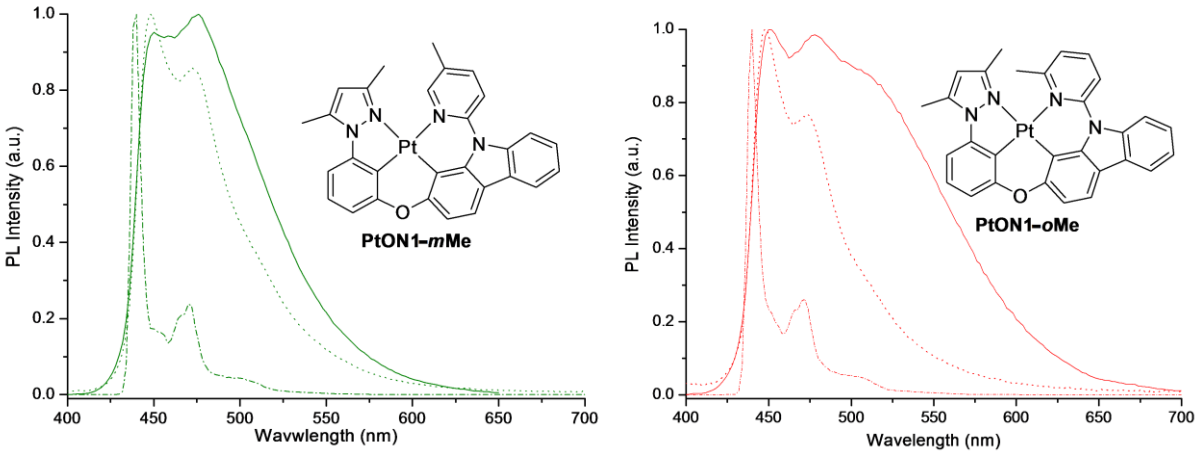


Figure S31: Photoluminescence spectra of **PtON1-*m*Me** (left) and **PtON1-*o*Me** (right) at room temperature in CH_2Cl_2 (solid lines), doped in PMMA (dotted lines) and 77K in 2-Me-THF (dash-dotted lines) with the molecular structure of each emitter inset.

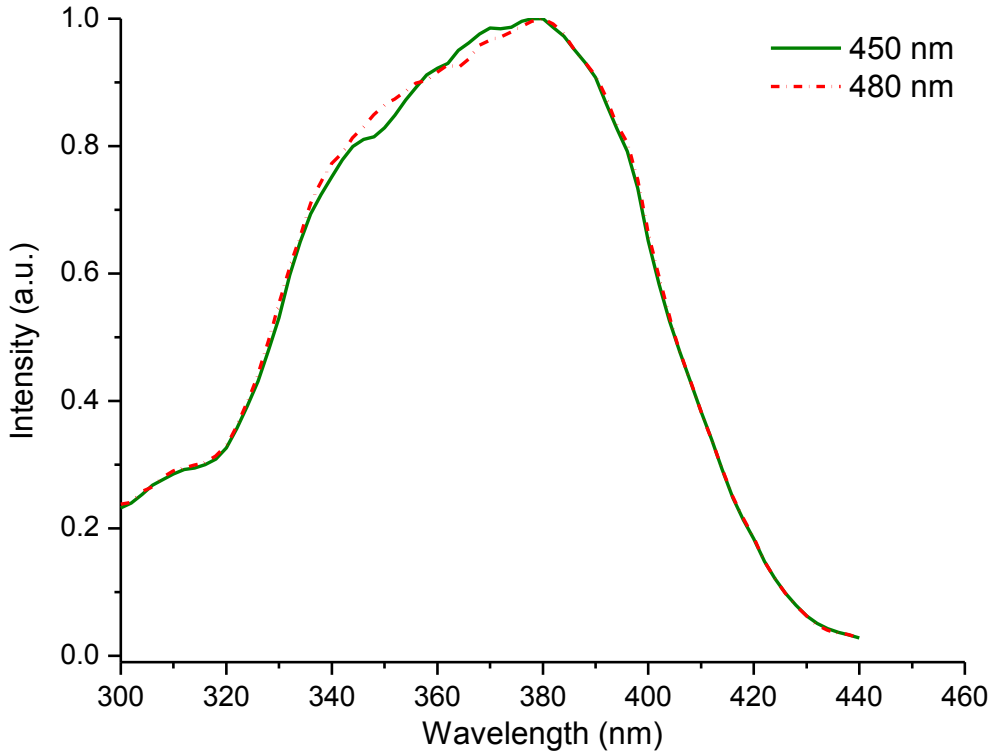


Figure S32: Excitation spectra of **PtON1**(monitored at 450 nm and 480 nm respectively)

References:

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