Electronic Supporting Information for

A Mesoionic Nitrogen-Donor Ligand: Structure, Iridium Coordination, and Catalytic Effects

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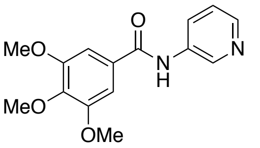
1. Synthetic procedures

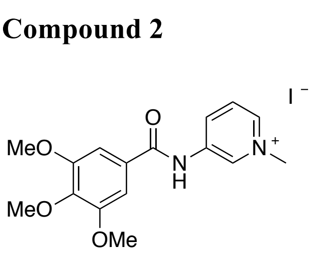
General. The metal precursor salt $[Ir(Cp^*)Cl_2]_2$ was synthesized as reported in the literature.[S1] All other reagents were commercially available and used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C on Bruker spectrometers operating at 300 or 400 MHz (^1H NMR), and 100 MHz (^{13}C NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent signals (^1H, ^{13}C). Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Purity of bulk samples of the complexes has been established by NMR spectroscopy, and by elemental analysis, which were performed at the Microanalytical Laboratory of the University of Bern using a Thermo Scientific Flash 2000 CHNS-O elemental analyser. High-resolution mass spectrometry was carried out with a Thermo Scientific LTQ Orbitrap XL (ESI-TOF).

Compound 1



A solution of 3,4,5-trimethoxybenzoyl chloride (2.54 g, 11 mmol) in THF (10 mL) was added dropwise to a solution of 3-aminopyridine (1.19 mL, 10 mmol) and NEt_3 (1.50 mL, 11 mmol) in THF (30 mL) at 66 °C. The reaction was slowly warmed to rt and stirred for 18 h. The formed precipitate was removed by filtration and washed with THF (50 mL). All filtrates were collected and volatiles were removed in vacuo to give a white solid, which was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH 95:5). All solvents were removed to yield compound **1** as white solids (2.46 g, 85%). ^1H NMR (400 MHz, d_6-DMSO): δ 10.32 (s, 1H, NH), 8.90 (d, $^4J_{HH}$ = 2.6 Hz, 1H, CH_{pyr}), 8.32 (dd, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 1.5 Hz, 1H, CH_{pyr}), 8.15 (ddd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.6, 1.5 Hz, 1H, CH_{pyr}), 7.41 (dd, $^3J_{HH}$ = 8.3, 4.7 Hz, 1H, CH_{pyr}), 7.30 (s, 2H, CH_{Ph}), 3.88 (s, 6H, OCH_3), 3.74 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, d_6-DMSO): δ 166.2 (CO), 152.6 (C_{Ph}), 144.6 (CH_{pyr}), 142.2 (CH_{pyr}), 140.6 (C_{Ph}), 135.6 (C_{pyr}), 129.4 (C_{Ph}), 127.6 (CH_{pyr}), 123.5 (CH_{pyr}), 105.4 (CH_{Ph}), 60.1 (OCH_3), 56.1 (OCH_3). HR-MS: m/z calculated for $C_{15}H_{17}N_2O_4$ $[M+H]^+$ = 289.1188; found, 289.1185.

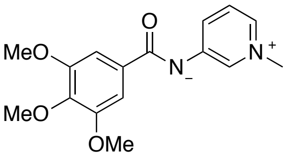
Compound 2



Compound **1** (576 mg, 2.00 mmol) was dissolved in MeCN (15 mL) in a pressure tube. MeI (187 µL, 3.0 mmol) was added and the reaction was stirred for 18 h at 80 °C. The solution was cooled to rt and concentrated to 5 mL. Et_2O (50 mL) was added, which induced formation of a precipitate, which was collected by filtration to yield **2** as a yellow solid (712 mg, 83%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of Et_2O into a MeCN solution of compound **2**. ^1H NMR (300 MHz, d_6-DMSO): δ 11.02 (s, 1H, NH), 9.46 (s, 1H, CH_{pyr}), 8.75 (d, $^3J_{HH}$ = 5.9 Hz, 1H,

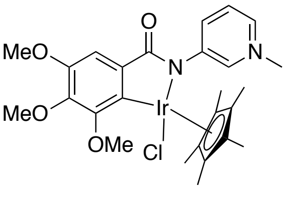
$\mathrm{CH_{pyr}}$), 8.64 (d, $^3J_{\mathrm{HH}}$ = 8.7 Hz, 1H, $\mathrm{CH_{pyr}}$) 8.14 (dd, $^3J_{\mathrm{HH}}$ = 8.7, 5.9 Hz, 1H, $\mathrm{CH_{pyr}}$), 7.33 (s, 2H, $\mathrm{CH_{Ph}}$), 4.41 (s, 3H, $\mathrm{NCH_3}$), 3.89 (s, 6H, $\mathrm{OCH_3}$), 3.76 (s, 3H, $\mathrm{OCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, d_6-DMSO): δ 165.6 (CO), 152.8 ($\mathrm{C_{Ph}}$), 141.3 ($\mathrm{C_{Ph}}$), 140.3 ($\mathrm{CH_{pyr}}$), 138.9 ($\mathrm{C_{pyr}}$), 136.6 ($\mathrm{CH_{pyr}}$), 134.8 ($\mathrm{CH_{pyr}}$), 128.0 ($\mathrm{C_{Ph}}$), 127.8 ($\mathrm{CH_{pyr}}$), 105.7 ($\mathrm{CH_{Ph}}$), 60.2 ($\mathrm{OCH_3}$), 56.2 ($\mathrm{OCH_3}$), 48.5 ($\mathrm{NCH_3}$). HR-MS: m/z calculated for $\mathrm{C_{16}H_{19}N_2O_4}$ $[\mathrm{M{-}I}]^+$ = 303.1339; found, 303.1329. Elem. Anal. Calcd. for $\mathrm{C_{16}H_{19}IN_2O_4}$: C, 44.67; H, 4.45; N, 6.51; Found: C 44.60; H, 4.57; N, 6.57%.

Compound 3



A suspension of the pyridinium salt **2** (320 mg, 1.00 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was placed into a separation funnel. Aqueous NaOH (2 M, 15 mL) was added. After vigorous mixing, the organic phase was collected. The aqueous layer was extracted with $\mathrm{CH_2Cl_2}$ (3 x 15 mL). The combined organic layers were dried over anhydrous $\mathrm{Na_2SO_4}$ and filtered. All volatiles were removed to give compound **3** as a yellowish solid (182 mg, 60%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a $\mathrm{CH_2Cl_2}$ solution of compound **3**. ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.11 (s, 1H, $\mathrm{CH_{pyr}}$), 8.38 (d, $^3J_{\mathrm{HH}}$ = 8.7 Hz, 1H, $\mathrm{CH_{pyr}}$), 8.01 (d, $^3J_{\mathrm{HH}}$ = 5.8 Hz, 1H, $\mathrm{CH_{pyr}}$) 7.62 (dd, $^3J_{\mathrm{HH}}$ = 8.7, 5.8 Hz, 1H, $\mathrm{CH_{pyr}}$), 7.48 (s, 2H, $\mathrm{CH_{Ph}}$), 4.19 (s, 3H, $\mathrm{NCH_3}$), 3.80 (s, 6H, $\mathrm{OCH_3}$), 3.68 (s, 3H, $\mathrm{OCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, d_6-DMSO): δ 169.9 (CO), 153.8 ($\mathrm{C_{pyr}}$), 151.8 ($\mathrm{C_{Ph}}$), 138.8 ($\mathrm{CH_{pyr}}$), 138.5 ($\mathrm{C_{Ph}}$), 136.9 ($\mathrm{C_{Ph}}$), 136.3 ($\mathrm{CH_{pyr}}$), 131.5 ($\mathrm{CH_{pyr}}$), 126.3 ($\mathrm{CH_{pyr}}$), 105.5 ($\mathrm{CH_{Ph}}$), 60.0 ($\mathrm{OCH_3}$), 55.6 ($\mathrm{OCH_3}$), 47.3 ($\mathrm{NCH_3}$). HR-MS: m/z calculated for $\mathrm{C_{16}H_{19}N_2O_4}$ $[\mathrm{M{+}H}]^+$ = 303.1339; found, 303.1332. Elem. Anal. Calcd. for $\mathrm{C_{16}H_{18}N_2O_4}$: C, 63.56; H, 6.00; N, 9.27; Found: C 63.57; H, 6.23; N, 9.42%.

Compound 4



Compound **3** (120 mg, 0.40 mmol), NaOAc (33 mg, 0.40 mol) and $[\mathrm{Ir(Cp^*)Cl_2}]_2$ (120 mg, 0.15 mmol) were dissolved in $\mathrm{CH_2Cl_2}$ and stirred at rt for 18 h. All volatiles were removed under reduced pressure and the crude solid was purified by column chromatography ($\mathrm{SiO_2}$; $\mathrm{CH_2Cl_2}$/MeOH 98:2) to yield complex **4** as an orange solid (153 mg, 77%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of pentane into an acetone solution of complex **4**. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 9.74 (s, 1H, $\mathrm{CH_{pyr}}$), 9.08 (d, $^3J_{\mathrm{HH}}$ = 8.7 Hz, 1H, $\mathrm{CH_{pyr}}$), 7.65 (d, $^3J_{\mathrm{HH}}$ = 5.7 Hz, 1H, $\mathrm{CH_{pyr}}$) 7.43 (dd, $^3J_{\mathrm{HH}}$ = 8.7, 5.7 Hz, 1H, $\mathrm{CH_{pyr}}$), 7.07 (s, 1H, $\mathrm{CH_{Ph}}$), 4.10 (s, 3H, $\mathrm{NCH_3}$), 3.91 (s, 3H, $\mathrm{OCH_3}$), 3.83 (s, 3H, $\mathrm{OCH_3}$), 3.79 (s, 3H, $\mathrm{OCH_3}$), 1.46 (s, 15H, Cp–$\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100 MHz, d_6-DMSO): δ 180.9 (CO), 156.6 ($\mathrm{C_{Ph}}$–Ir), 152.7 ($\mathrm{C_{pyr}}$), 150.0 ($\mathrm{C_{Ph}}$), 146.6 ($\mathrm{C_{Ph}}$), 143.1 ($\mathrm{C_{Ph}}$), 141.3 ($\mathrm{CH_{pyr}}$), 140.5 ($\mathrm{CH_{pyr}}$), 136.9 ($\mathrm{C_{Ph}}$), 132.8 ($\mathrm{CH_{pyr}}$), 126.8 ($\mathrm{CH_{pyr}}$), 108.9 ($\mathrm{CH_{Ph}}$), 87.6 ($\mathrm{C_{Cp}}$), 61.8 ($\mathrm{OCH_3}$), 61.0 ($\mathrm{OCH_3}$), 56.6 ($\mathrm{OCH_3}$), 48.7 ($\mathrm{NCH_3}$), 9.5 (Cp–$\mathrm{CH_3}$). HR-MS: m/z calculated for $\mathrm{C_{26}H_{32}IrN_2O_4}$ $[\mathrm{M{-}Cl}]^+$ =

629.1962; found, 629.1966. Elem. Anal. Calcd. for $C_{26}H_{32}ClIrN_2O_4$: C, 47.02; H, 4.86; N, 4.22; Found: C 46.43; H, 4.88; N, 4.11%.

2. General procedure for catalytic water oxidation

Dynamic Oxygen Evolution Measurements. For oxygen evolution measurements, a solution of the iridium complex **4** (1 mL, concentration as specified in Table 1) was injected into a sealed 40 mL EPA vial containing 10 mL CAN solution (~ 0.4 M) buffered in 1 M HNO_3. The generated oxygen leads to an increase in gas phase pressure, which was dynamically monitored *via* differential digital manometry as described previously.[S2] End points of the reactions were verified by gas chromatography and corrected for nitrogen contamination.

3. Crystallographic details

Crystal structure determinations. Suitable crystals of **2**, **3** and **4** were mounted in air at ambient conditions and measured on an Oxford Diffraction SuperNova area-detector diffractometer at T = 173(2) K using mirror optics monochromated Mo *K*α radiation (λ = 0.71073 Å) and Al filtered.[S3] Data reduction was performed using the CrysAlisPro program.[S4] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in CrysAlisPro was applied. The structures were solved by direct methods using SHELXT,[S5] and all non-hydrogen atoms were refined anisotropically. All H-atoms were placed in geometrically calculated positions and refined using a riding model with each H-atom assigned a fixed isotropic displacement parameter (1.2Ueq of its parent atom, 1.5Ueq for the methyl groups). Structures were refined on F^2 using full-matrix least-squares procedures.[S3] The weighting schemes were based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the SHELXL-2014 program.[S5]

For compound **3**, there are two solvent molecules in the unit cell/asymmetric unit. Position of water molecule was refined without doubts, but the second one was assumed a CH_2Cl_2 molecule as it was used for crystallization. The molecule is highly disordered and no hydrogen atoms were assigned. Chlorine and carbon atoms were assigned according to the donor-acceptor adjacent of the molecule.

Table S1. Crystal data and structure refinement for compound **2**.

CCDC No.	1582052
Empirical formula	$C_{16}H_{19}IN_2O_4$ x CH_3CN
Formula weight	471.28
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 9.76540(10) Å α = 90°
	b = 8.66930(10) Å β = 101.6120(10)°
	c = 23.9759(3) Å γ = 90°
Volume	1988.24(4) Å^3
Z	4
Density (calculated)	14574 Mg/m^3
Absorption coefficient	1.638 mm^{-1}
F(000)	944
Crystal size	0.293 x 0.261 x 0.099 mm^3
Theta range for data collection	1.734 to 224°.
Index ranges	-12<=h<=12, -10<=k<=11, -31<=l<=31
Reflections collected	20170
Independent reflections	4565 [R(int) = 0.0259]
Completeness to theta = 25.242°	100%
Absorption correction	Semi-empirical from equivalents
Max. and min. transimission	0.76671 and 0.75905
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4565 / 0 / 243
Goodness-of-fit on F2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0465
R indices (all data)	R1 = 0.0242, wR2 = 0.0481
Largest diff. peak and hole	0.476 and -0.3 e.Å^{-3}

Table S2. Crystal data and structure refinement for compound **3**.

CCDC No.	1582053
Empirical formula	$C_{16}H_{18}N_2O_4$ x H_2O x $0.5CH_2Cl_2$
Formula weight	367.80
Temperature	173.01(10) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P\ 2_1/n$
Unit cell dimensions	a = 11.6020(2) Å α = 90°
	b = 13.05540(10) Å β = 107.969(2)°
	c = 12.1795(2) Å γ = 90°
Volume	107.969(2) $Å^3$
Z	4
Density (calculated)	1754.83 Mg/m^3
Absorption coefficient	0.247 mm^{-1}
F(000)	764
Crystal size	0.3 x 0.3 x 0.3mm^3
Theta range for data collection	4.24 to 49.978°.
Index ranges	-13<=h<=13, -15<=k<=15, -14<=l<=14
Reflections collected	25283
Independent reflections	3089 [R(int) = 0.0304]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3089 / 0 / 276
Goodness-of-fit on F2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0846
R indices (all data)	R1 = 0.0399, wR2 = 0.0910
Largest diff. peak and hole	0.18 and –0.18 e.$Å^{-3}$

Table S3. Crystal data and structure refinement for compound **4**.

CCDC No.	1582054
Empirical formula	$C_{26}H_{32}ClIrN_2O_4$
Formula weight	664.18
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Orthorombic
Space group	P b c a
Unit cell dimensions	a = 15.5088(3) Å α = 90°
	b = 13.34471(14) Å β = 90°
	c = 24.9142(5) Å γ = 90°
Volume	5156.26(14) Å^3
Z	8
Density (calculated)	1711 Mg/m^3
Absorption coefficient	5.316 mm^{-1}
F(000)	2624
Crystal size	0.305 x 0.044 x 0.026 mm^3
Theta range for data collection	1.635 to 28.107°.
Index ranges	-19<=h<=17, -12<=k<=17, -29<=l<=32
Reflections collected	28230
Independent reflections	5788 [R(int) = 0.0415]
Completeness to theta = 25.242°	100 %
Absorption correction	Gaussian
Max. and min. transmission	1 and 0.482
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5778 / 0 / 316
Goodness-of-fit on F2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0441
R indices (all data)	R1 = 0.063, wR2 = 0.0508
Largest diff. peak and hole	0.83 and -0.725 e.Å^{-3}

4. NMR spectra of all new compounds

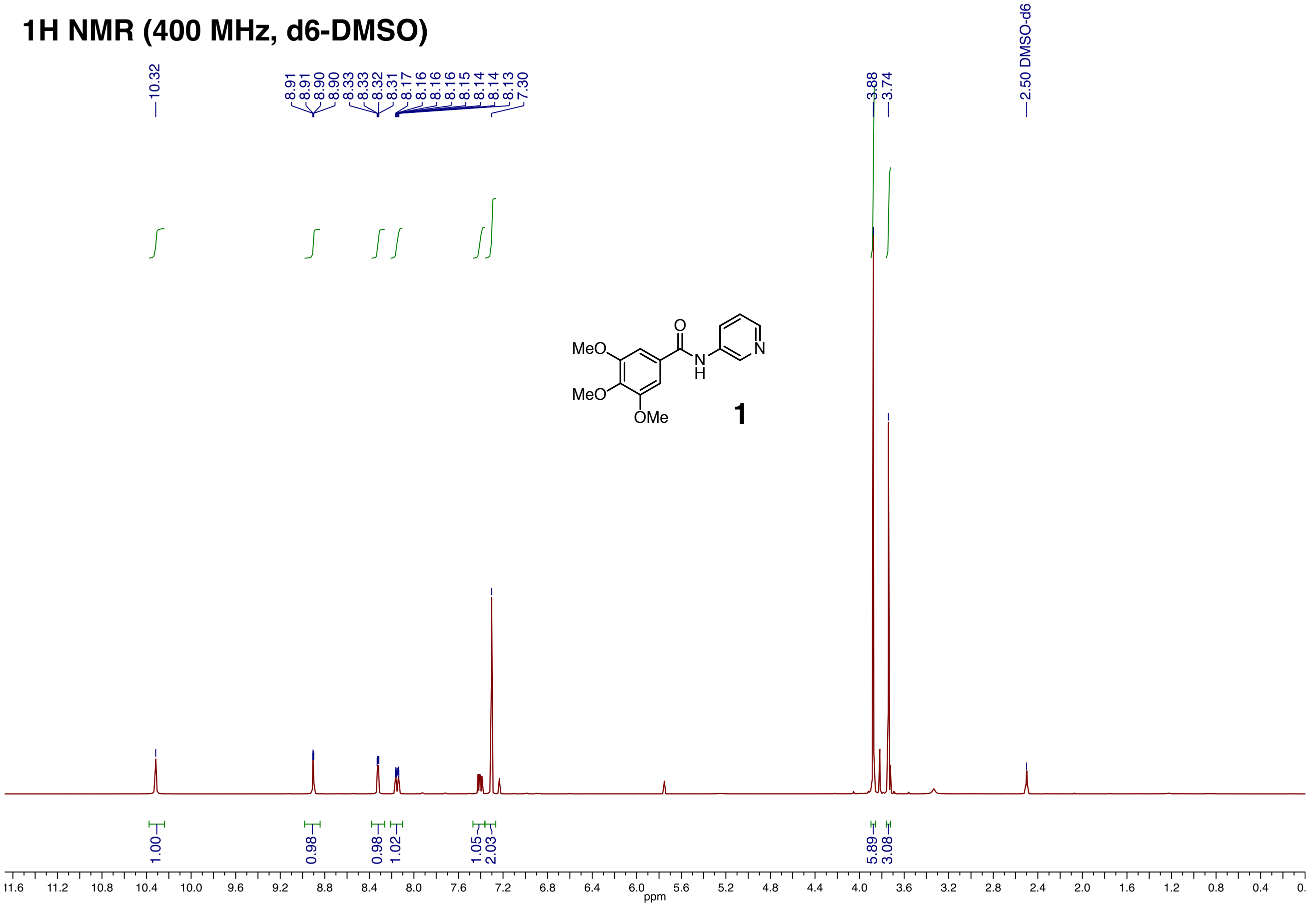


Figure S1. ^{1}H NMR spectrum of compound **1**.

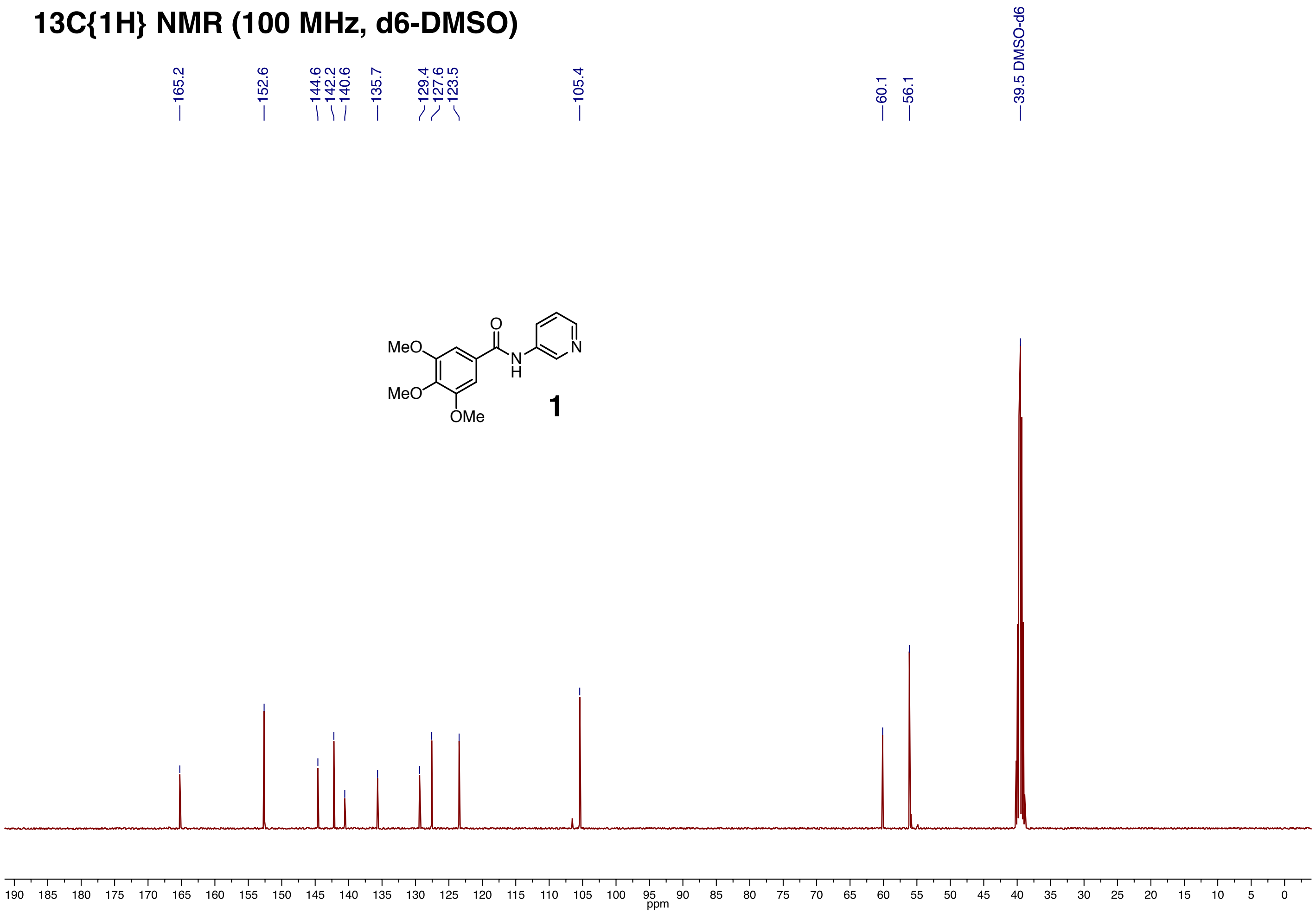


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1**.

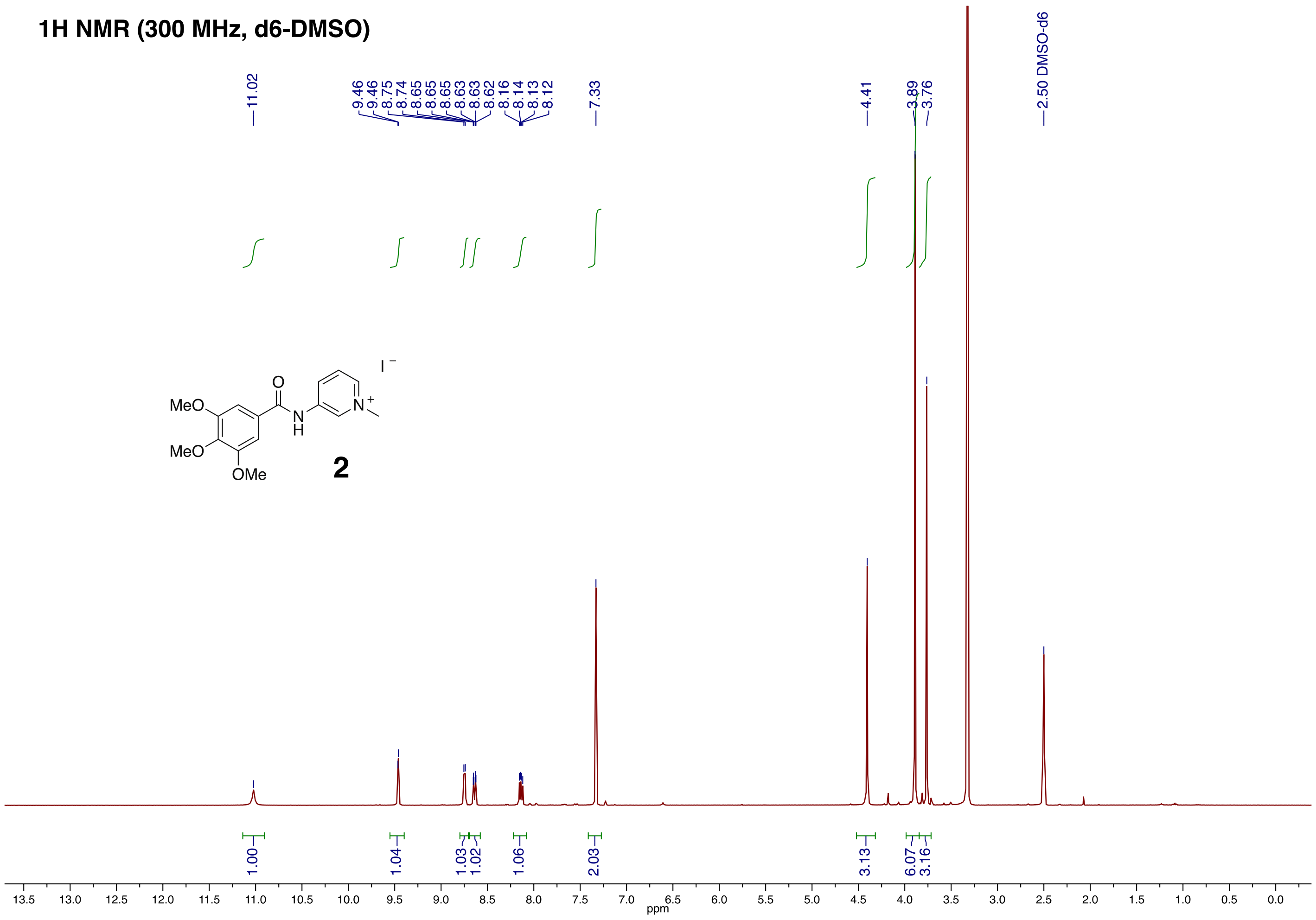


Figure S3. ^{1}H NMR spectrum of compound **2**.

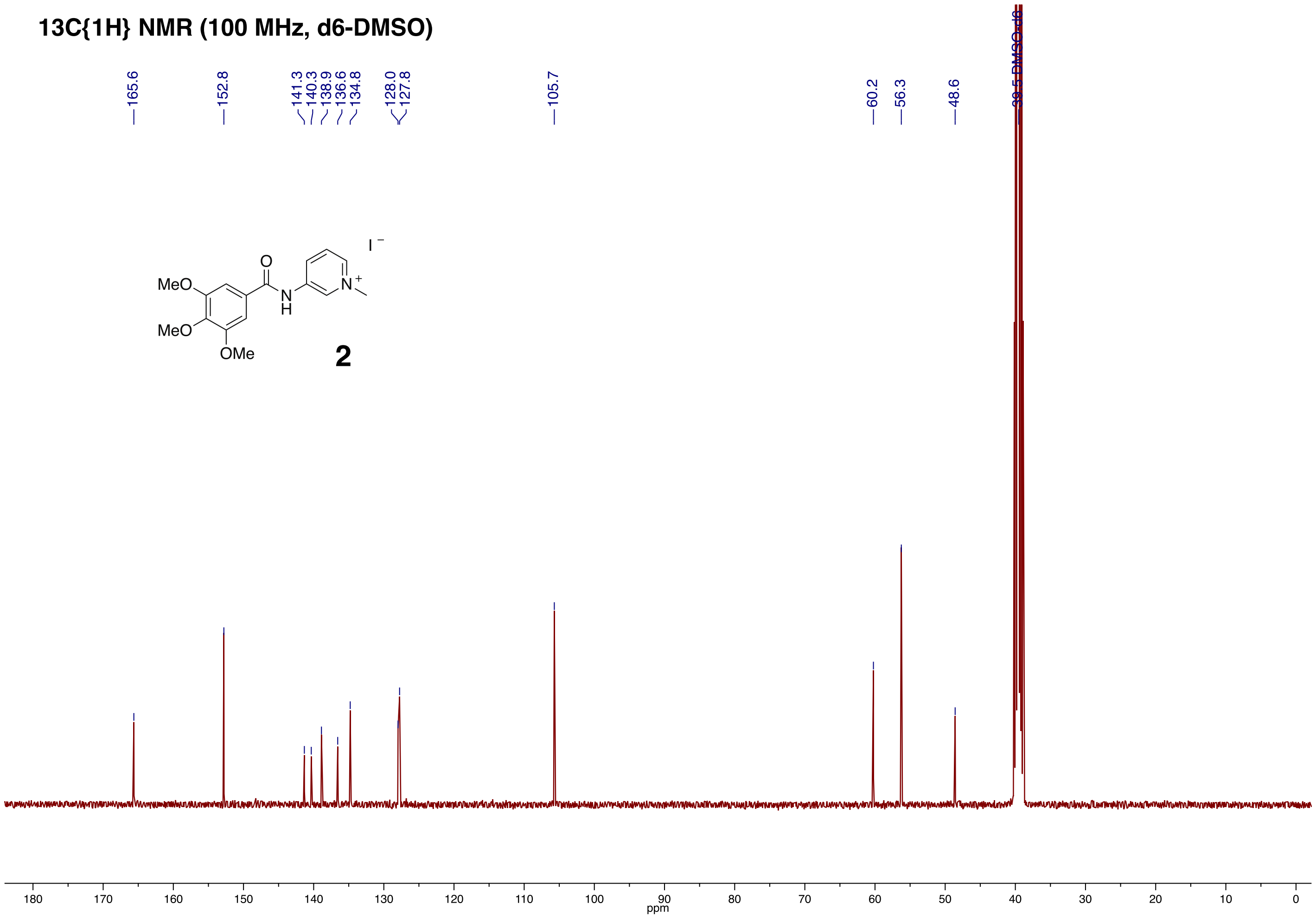


Figure S4. ^{13}C{^{1}H} NMR spectrum of compound **2**.

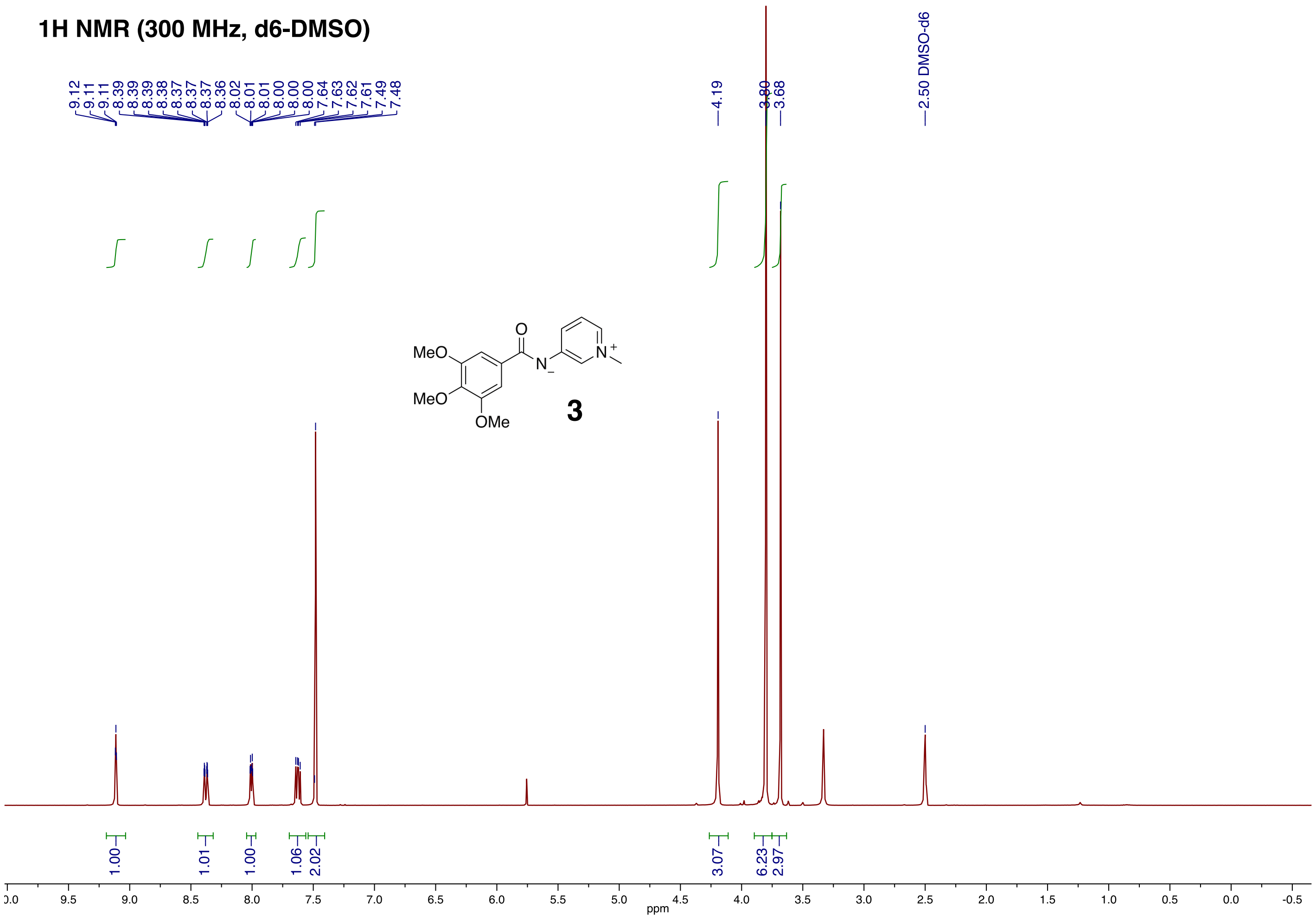


Figure S5. ^{1}H NMR spectrum of compound **3**.

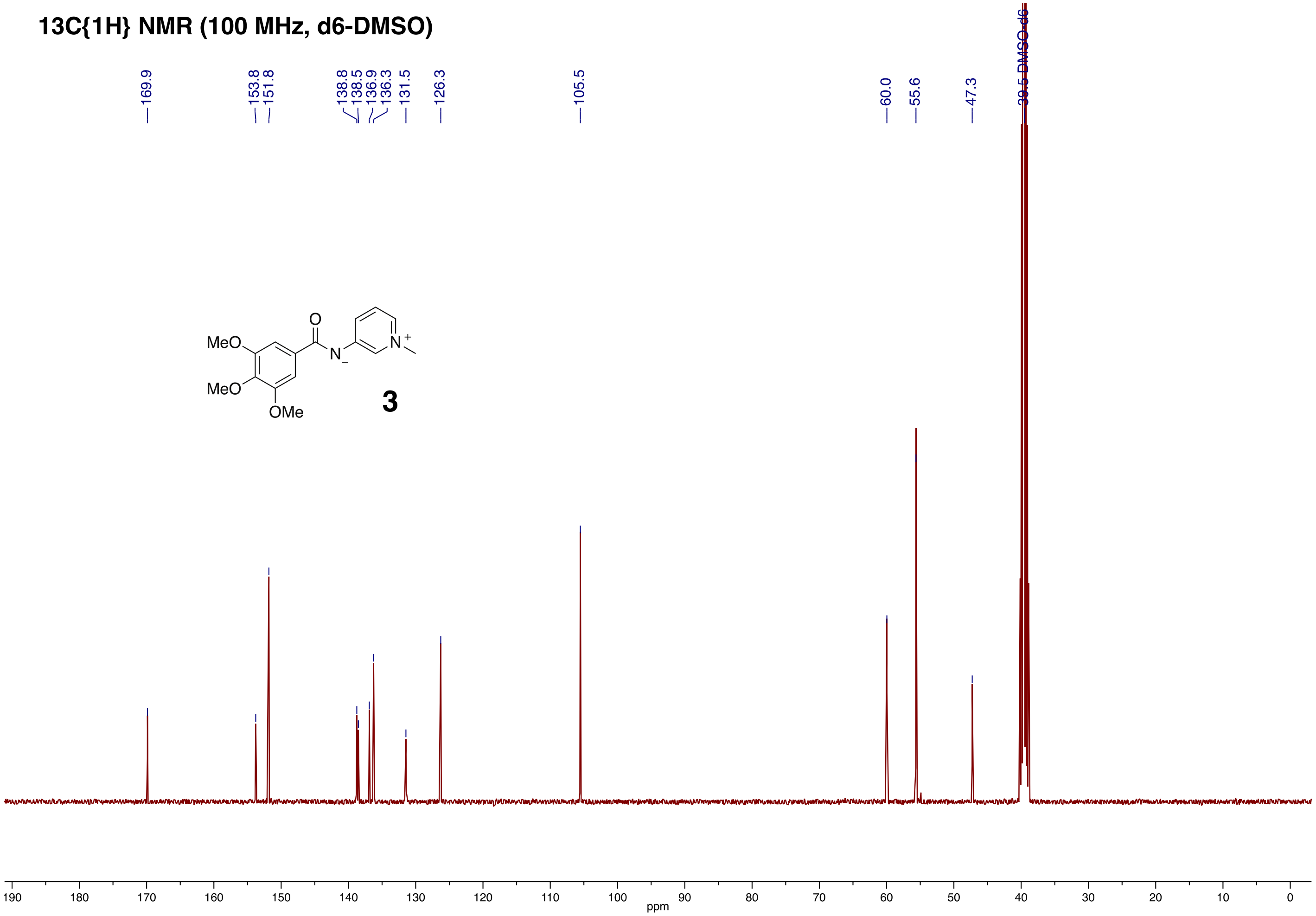


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3**.

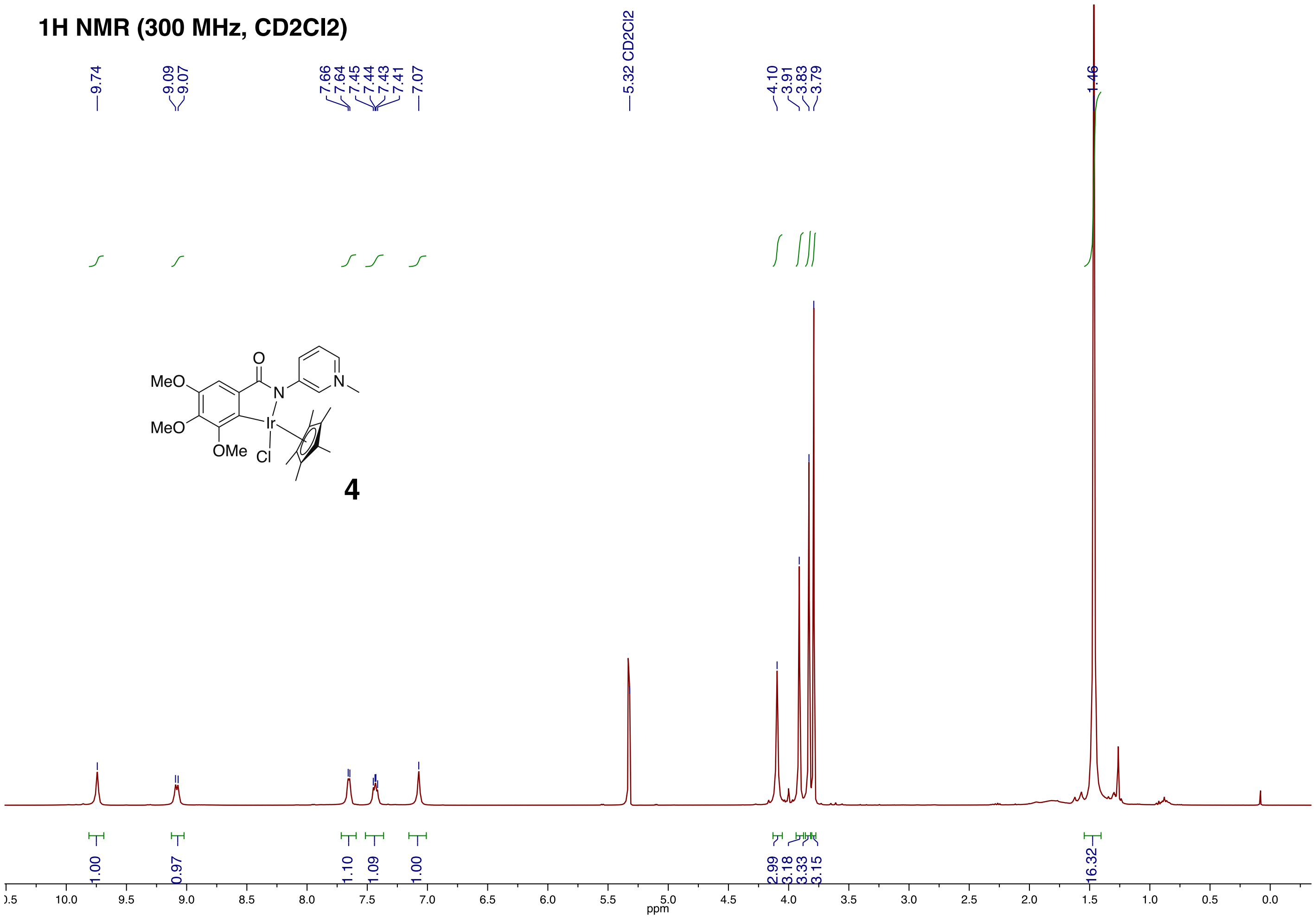


Figure S7. ^{1}H NMR spectrum of compound **4**.

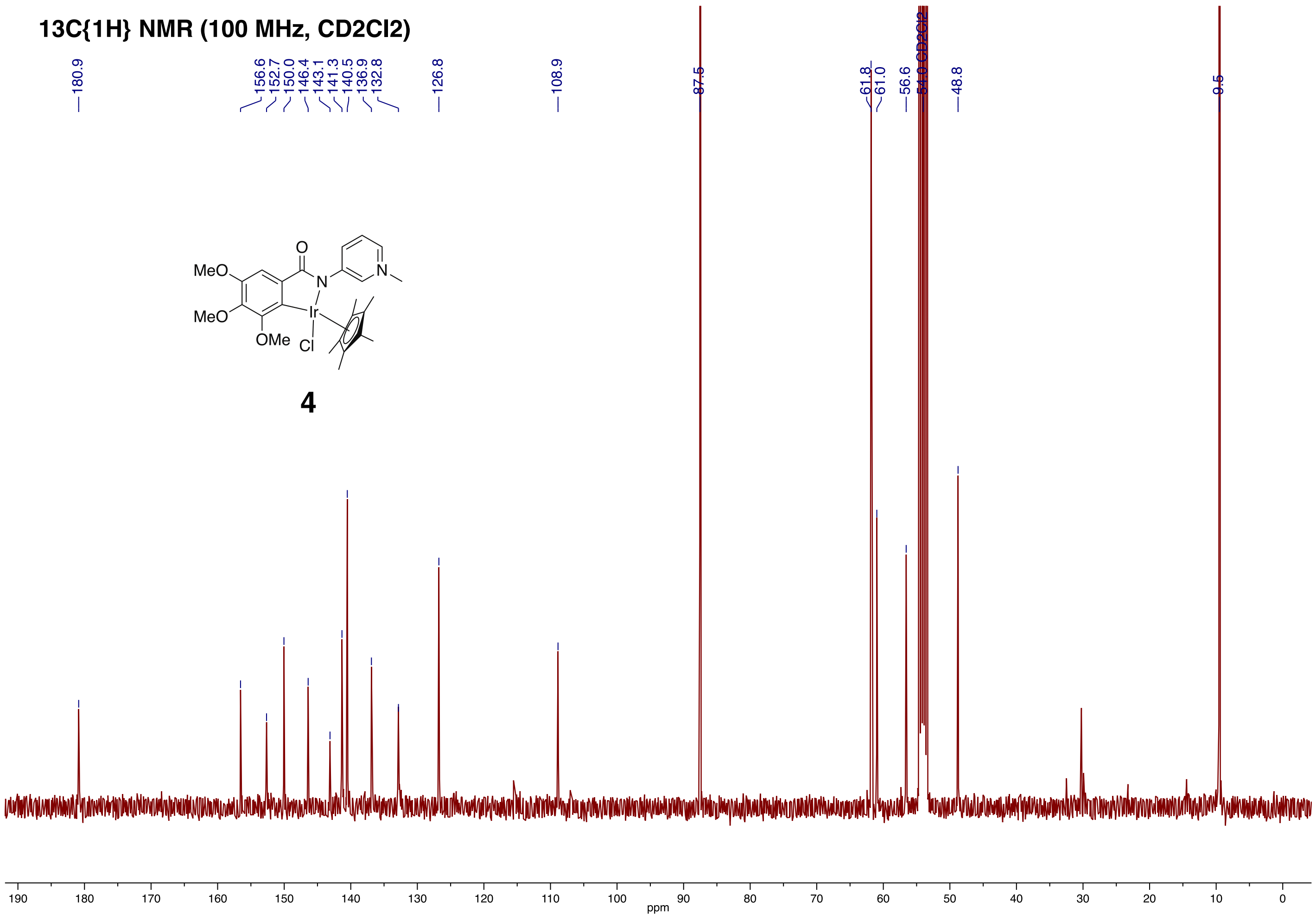


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of compound **4**.

5. IR spectra of compounds 2–4

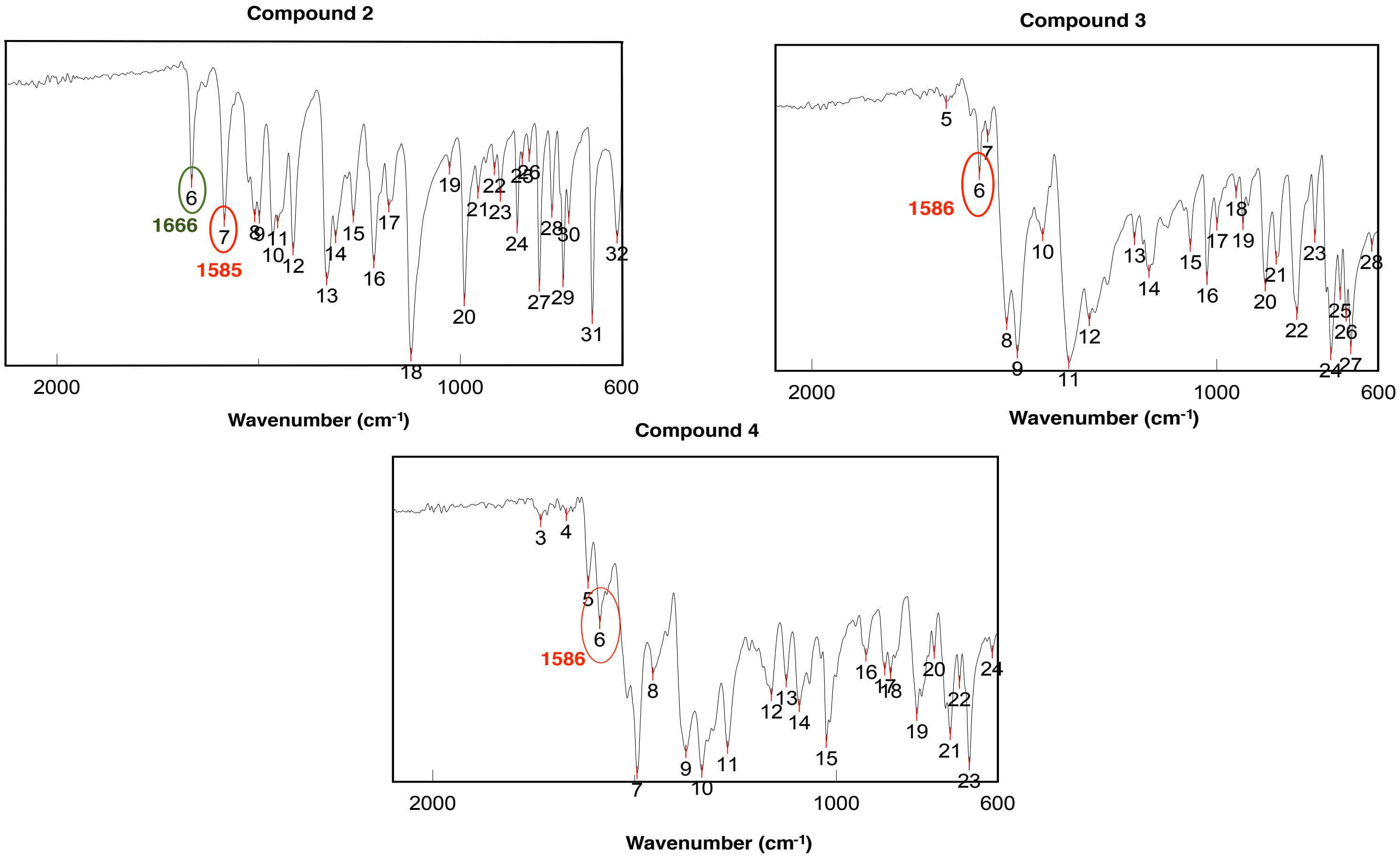


Figure S9. IR spectra of compounds **2**–**4** (assigned amide N–H bend in green, C=O stretch in red).

6. References

[S1] R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. J. Hoyano, A. D. McMaster, B. M. Mattson and S. T. Michel, *Inorg. Chem.* 1990, **29**, 2023.

[S2] N. D. McDaniel, F. J. Coughlin, L. L. Tinker and S. Bernhard, *J. Am. Chem. Soc.* 2008, **130**, 210.

[S3] P. Macchi, H. B. Bürgi, A. S. Chimpri, J. Hauser and Z. Gal, *J. Appl. Cryst*. 2011, **44**, 763.

[S4] CrysAlisPro, version 1.171.34.44; Oxford Diffraction Ltd.: Yarnton, Oxfordshire, U.K., 2010.

[S5] G. M. Sheldrick, *Acta Cryst. Sect. A. Found. Adv.* 2015, **71**, 3.