Supporting Information, Journal of Materials Chemistry, 2012.

Efficient Orange Light-Emitting Electrochemical Cells

Daniel Tordera,[a] Antonio Pertegás,[a] Nail M. Shavaleev,*[b] Rosario Scopelliti,[b] Enrique Ortí,[a] Henk J. Bolink,*[a] Etienne Baranoff,[b] Michael Grätzel[b] and Mohammad K. Nazeeruddin*[b]

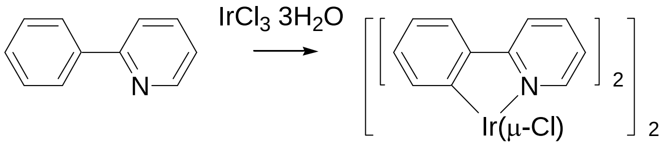
[a] Instituto de Ciencia Molecular, Universidad de Valencia, ES-46980 Paterna (Valencia), Spain. E-mail: henk.bolink@uv.es

[b] Laboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland. Fax: +41 21 693 4111. Tel: +41 21 693 6124. E-mail: nail.shavaleev@epfl.ch, mdkhaja.nazeeruddin@epfl.ch

Contents

1. Synthesis

Complex [(*N*,$C^{2'}$-2-phenylpyridyl)$_2$Ir(*μ*-Cl)]$_2$



The reaction was performed under argon. The solvents were deoxygenated by bubbling with Ar, but they were not dried. $IrCl_3 \cdot 3H_2O$ (500 mg, 1.42 mmol; W. C. Heraeus GmbH) was dissolved in 2-ethoxyethanol/water (12/4 mL) to give purple solution. It was warmed to 60°C. 2-Phenylpyridine (484 mg, 0.45 mL, 3.12 mmol, excess; Aldrich) was added. The reaction mixture was stirred overnight at 120°C to give yellow suspension. It was cooled to room temperature. Water (8 mL) was slowly added to precipitate the product. The suspension was stirred for 30 min and filtered. The solid was washed with ethanol/water (1/1), water, ethanol/water (1/1) again, and ether. Yellow solid: 548 mg (0.51 mmol, 72%; $C_{44}H_{32}Cl_2Ir_2N_4$; MW 1072.09). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 9.28$ (d, $J = 5.6$ Hz, 4H), 7.97 (d, $J = 7.6$ Hz, 4H), 7.82 (td, $J = 8.0, 1.2$ Hz, 4H), 7.58 (dd, $J = 8.0, 1.2$ Hz, 4H), 6.89–6.80 (m, 8H), 6.63 (td, $J = 8.0, 1.2$ Hz, 4H), 5.90 (dd, $J = 8.0, 1.2$ Hz, 4H) ppm.

2. X-Ray Crystallography

Single crystals of **1** for X-ray analysis were grown by slow evaporation of a mixed CH_2Cl_2/hexane solution. The data collection was performed at low temperature [100(2) K] using Mo K_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The data were reduced by EvalCCD[1] and then corrected for absorption.[2] The solution and refinement was performed by SHELX.[3] The structure was refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

Table S1. Crystal Data and Structure Refinement for Complex **1**.

CCDC	876632
empirical formula	$C_{48}H_{35}F_6IrN_6O_{0.50}P$
fw	1040.99
temp [K]	100(2)
wavelength [Å]	0.71073
cryst syst	Orthorhombic
space group	*Pbca*
unit cell dimensions	a = 10.7181(13) Å
	b = 17.865(3) Å
	c = 41.906(4) Å
	α = 90°
	β = 90°
	γ = 90°
vol [Å]^3	8024.3(19)
Z	8
ρ (calc) [Mg/m^3]	1.723
μ [mm^{-1}]	3.442
F(000)	4120
cryst size [mm^3]	0.21 × 0.18 × 0.12
θ range	3.01 – 27.50°
index ranges	$-13 \leq h \leq 13$
	$-23 \leq k \leq 22$
	$-54 \leq l \leq 54$
reflns collected	123459
independent reflns	9194 [R(int) = 0.0540]
completeness to θ	27.50° – 99.8%
absorption correction	Semi-empirical from equivalents
max/min transm	0.7456 / 0.5998
refinement method	Full-matrix least-squares on F^2
data/restraints/params	9194 / 3 / 574
GOF on F^2	1.174
final R indices [$I > 2\sigma(I)$]	R1 = 0.0441, wR2 = 0.0777
R indices (all data)	R1 = 0.0552, wR2 = 0.0814
largest diff. peak/hole [e/Å^3]	2.442 / −1.121

Table S2. Selected Bond Lengths (Å) in Complex **1**[a]

C^N		N^N	
Ir–C	Ir–N	Ir–N	Ir–N
2.012(5)	2.042(4)	2.126(4)	2.143(3)
2.013(4)	2.050(3)		

[a] Each row corresponds to one ligand in the complex.

3. Electrochemistry

Electrochemical experiments were conducted in DMF (99.8%, Extra Dry, over Molecular Sieves, AcroSeal®, Acros) or acetonitrile (99.9%, Extra Dry, over Molecular Sieves, AcroSeal®, Acros), with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Fluka, electrochemical grade) as the supporting electrolyte, with a PC controlled AutoLab PSTAT10 electrochemical workstation. The experiments were carried out under argon in an electrochemical cell through which a stream of Ar was passed (during the measurement, the flow of Ar was stopped to prevent stirring of the solution). Glassy carbon, platinum spiral, and platinum wire served as working, counter, and quasi-reference electrodes. Ferrocene was added as an internal reference at the end of each experiment. Estimated error: ±50 mV. The anodic/cathodic peak separation for the standard (Fc^+/Fc couple) at 100 mV/s was 78 mV. Cyclic voltammetry was performed at scan rates of 1 and 0.1 V/s.

4. Absorption and Emission Spectroscopy

Electronic absorption spectra were recorded with an HP/Agilent 8453 Diode Array UV/VIS spectrophotometer under air in optical cells of 2 or 10 mm path length. The solutions in CH_2Cl_2 (Sigma-Aldrich, puriss p.a., ACS reagent) were freshly prepared before experiment.

Table S3. UV-Vis Absorption Maxima[a]

	λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1})
imp	273 (40), 365 (1.7, sh), 401 (0.1, sh)
1	274 (84), 299 (54, sh), 388 (10), 405 (9.5, sh), 467 (1.4, sh)

[a] In CH_2Cl_2, at room temperature, in the range 250–600 nm. Estimated errors: ±2 nm for λ_{abs}; ±5% for ε.

The solutions of Ir(III) complexes for photophysical measurements were degassed by bubbling with argon, and were kept in gas-tight Young-tap-modified fluorescence cells. The corrected luminescence spectra were recorded with a HORIBA Jobin Yvon FluoroLog®-3 spectrofluorometer at 90° optical geometry. The luminescence quantum yields were calculated from the corrected emission spectra at λ_{exc} of 350, 360, and 370 nm by comparison with a standard, a solution of quinine hemisulfate salt monohydrate (BioReagent, suitable for fluorescence, >98.0%, Fluka) in 0.5 M H_2SO_4 (Φ = 54.6%).[4] The following values of the refractive indices were used for the calculations of Φ: 1.333 for 0.5 M H_2SO_4 and 1.4242 for CH_2Cl_2. Excited-state lifetimes were measured on the same spectrofluorometer with a HORIBA NanoLED (406 nm) excitation source.

The photoluminescence spectrum and quantum yield of **1** in a 90-nm thin film [**1** and 1-butyl-3-methylimidazolium hexafluorophosphate (>98.5%, Sigma-Aldrich) in a 4 to 1 molar ratio] were measured with a Hamamatsu C9920-02 Absolute PL Quantum Yield Measurement System (λ_{exc} = 278 nm).

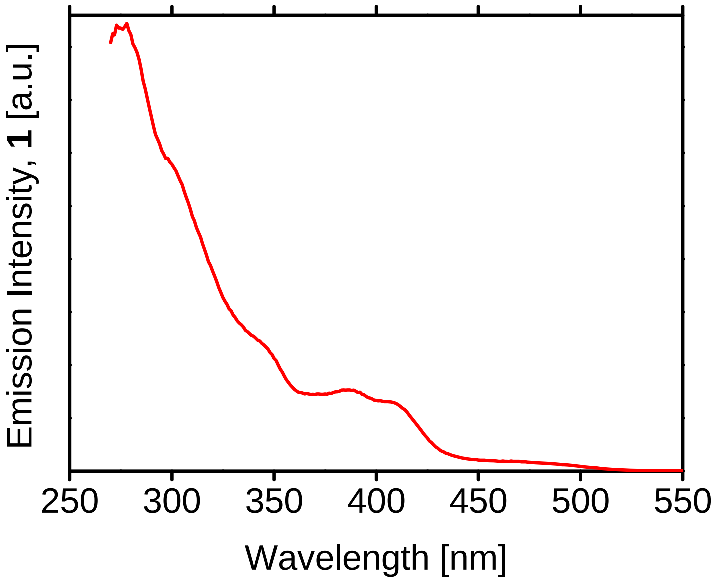


Figure S1. Phosphorescence excitation spectrum of **1** at 10^{-5} M in argon-saturated dichloromethane at room temperature (the emission was monitored at the maximum of the luminescence band; $\Delta\lambda_{exc}$ = 1 nm). The solution was optically dense below 330 nm.

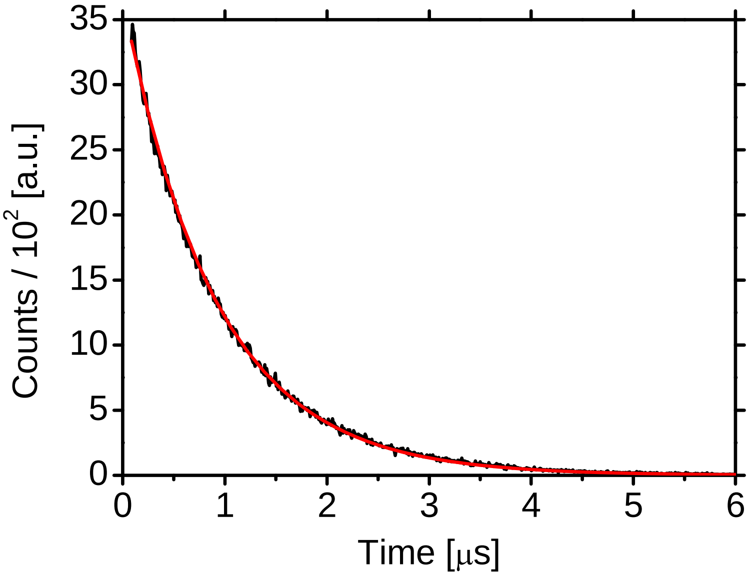


Figure S2. Luminescence decay of **1** at 10^{-5} M in argon-saturated dichloromethane at room temperature (λ_{exc} = 406 nm; λ_{em} = 615 nm; similar decay traces and identical lifetimes were obtained at emission wavelengths of 530, 620, 630, and 640 nm). Black trace represents experimental data; red trace is a single exponential fit to the data.

5. Electroluminescence

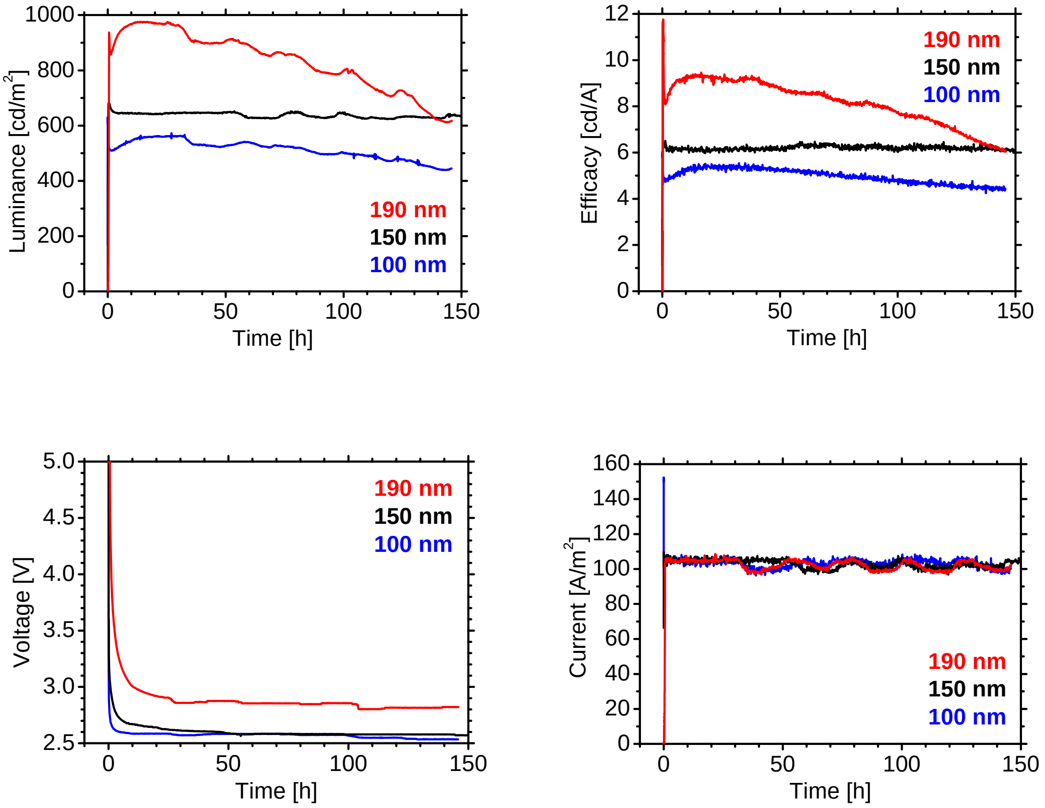
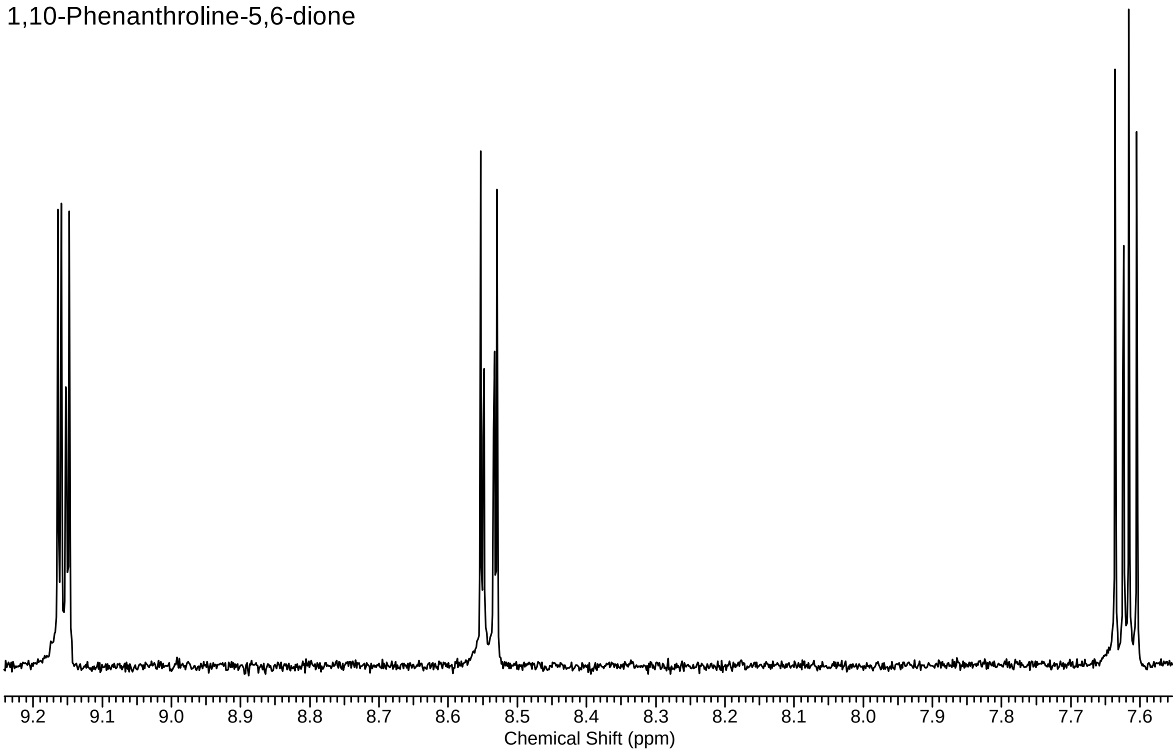


Figure S3. Time-dependence of the luminance, voltage, efficacy and current of a LEC device ITO/PEDOT:PSS/**1**:BMIM–PF$_6$(4:1; 100 nm, 150 nm or 190 nm)/Al. Data for the 150-nm device are taken from Fig. 5 of the main text. The spikes in the luminance and efficacy plots at $t < 1$ h for the 100-nm and 190-nm devices are caused by current fluctuations and are not discussed.

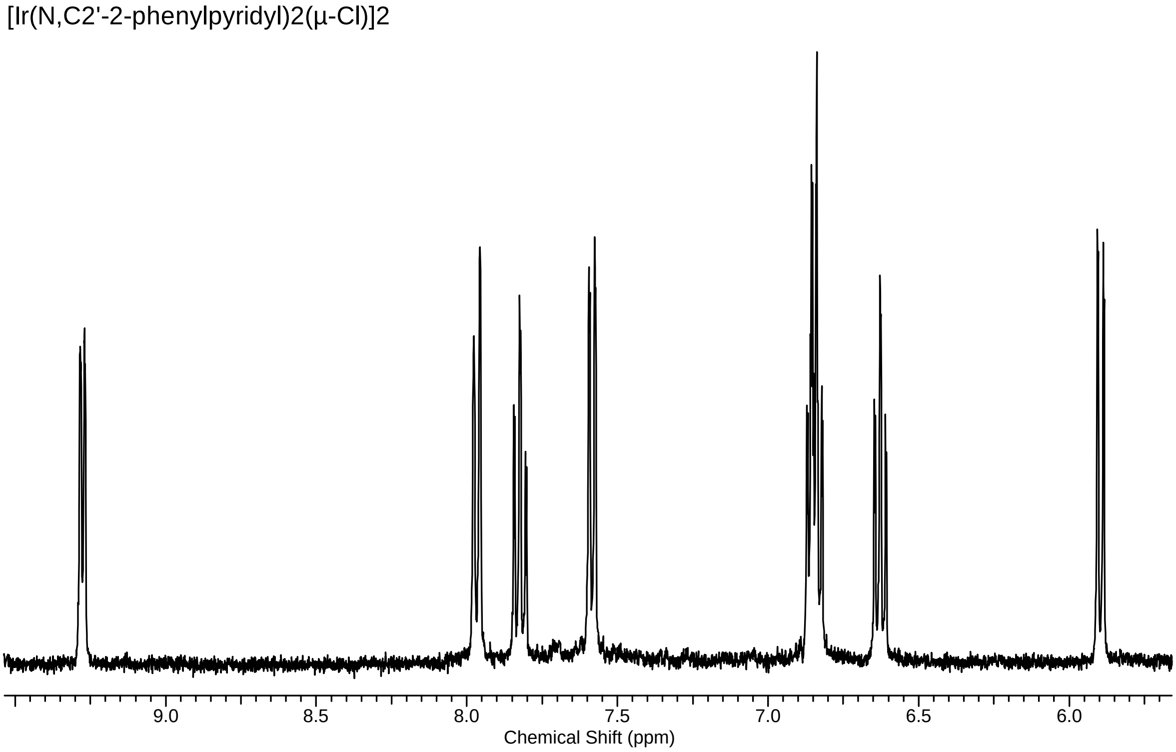
6. References

1. A. J. M. Duisenberg, L. M. J. Kroon-Batenburg and A. M. M. Schreurs, *J. Appl. Cryst.*, 2003, **36**, 220.
2. R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33.
3. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
4. J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

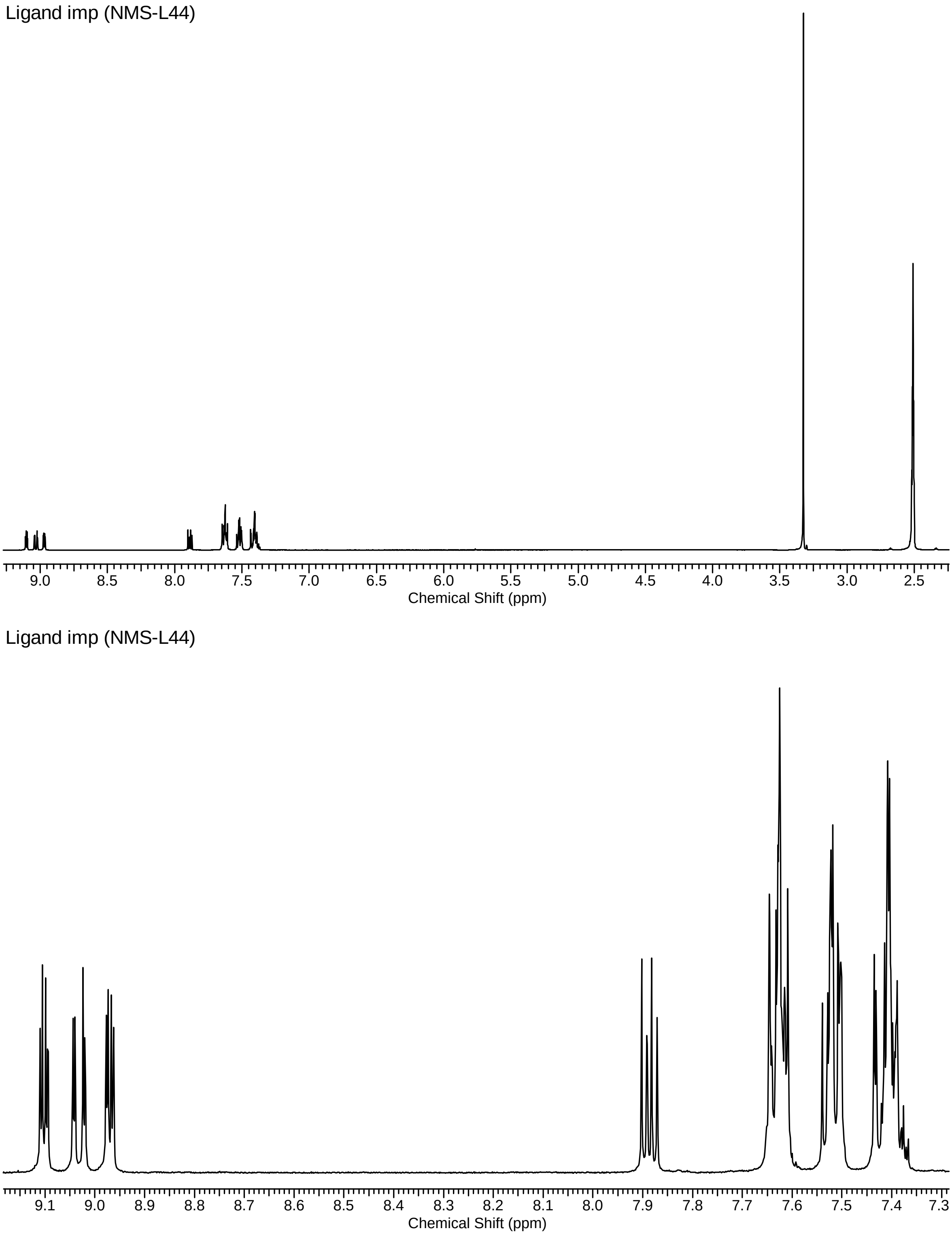
7. NMR Spectra



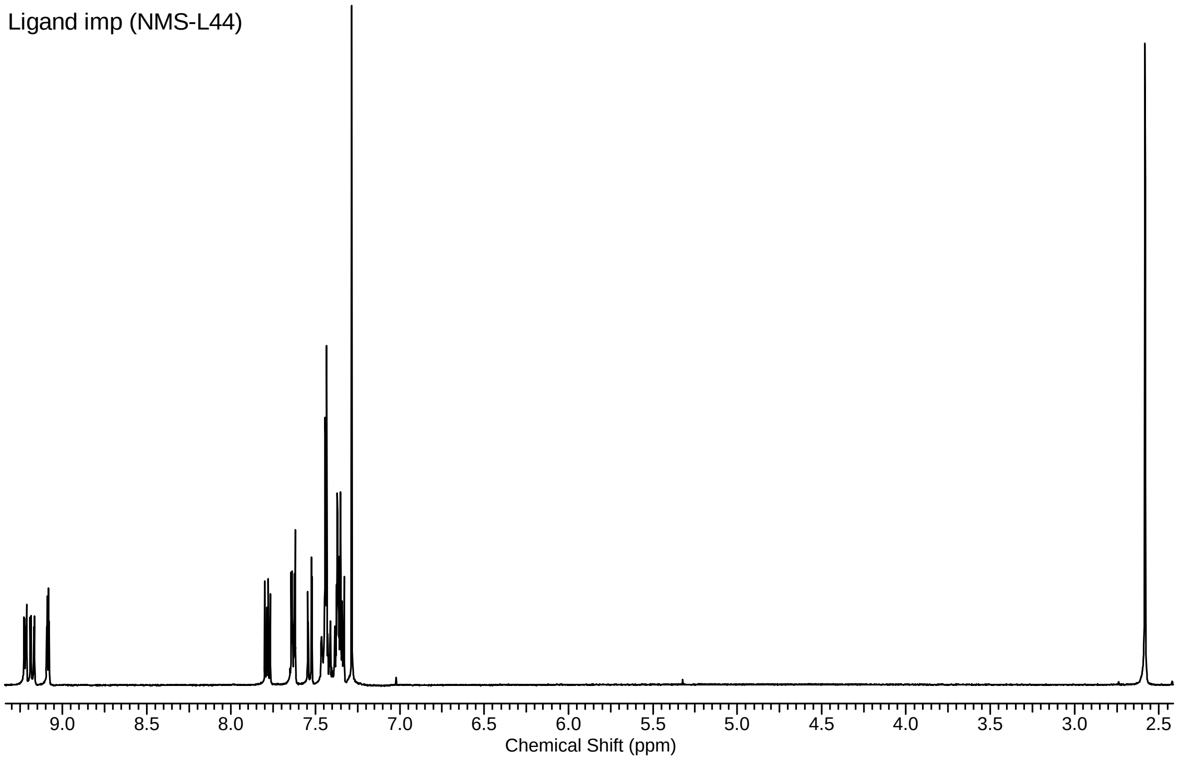
^{1}**H NMR Spectrum** of 1,10-phenanthroline-5,6-dione in $CDCl_3$.

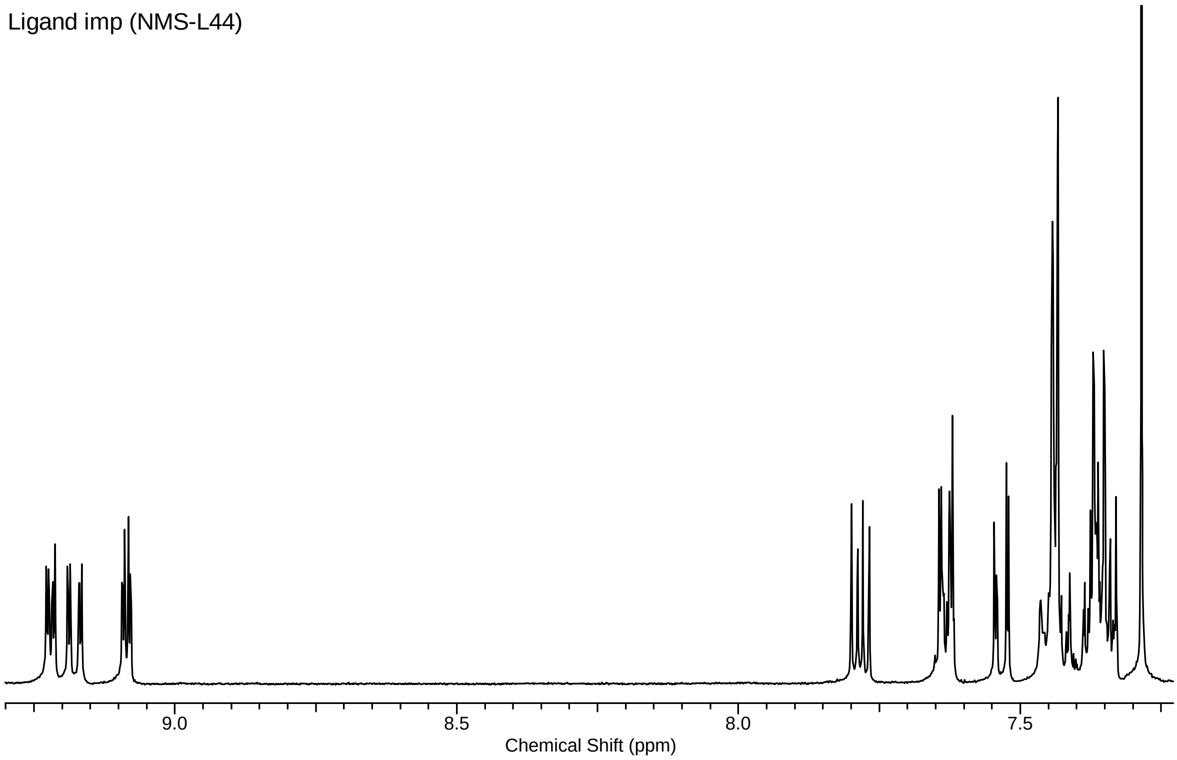


^{1}**H NMR Spectrum** of $[(N,C^{2'}\text{-2-phenylpyridyl})_2\text{Ir}(\mu\text{-Cl})]_2$ in CD_2Cl_2.

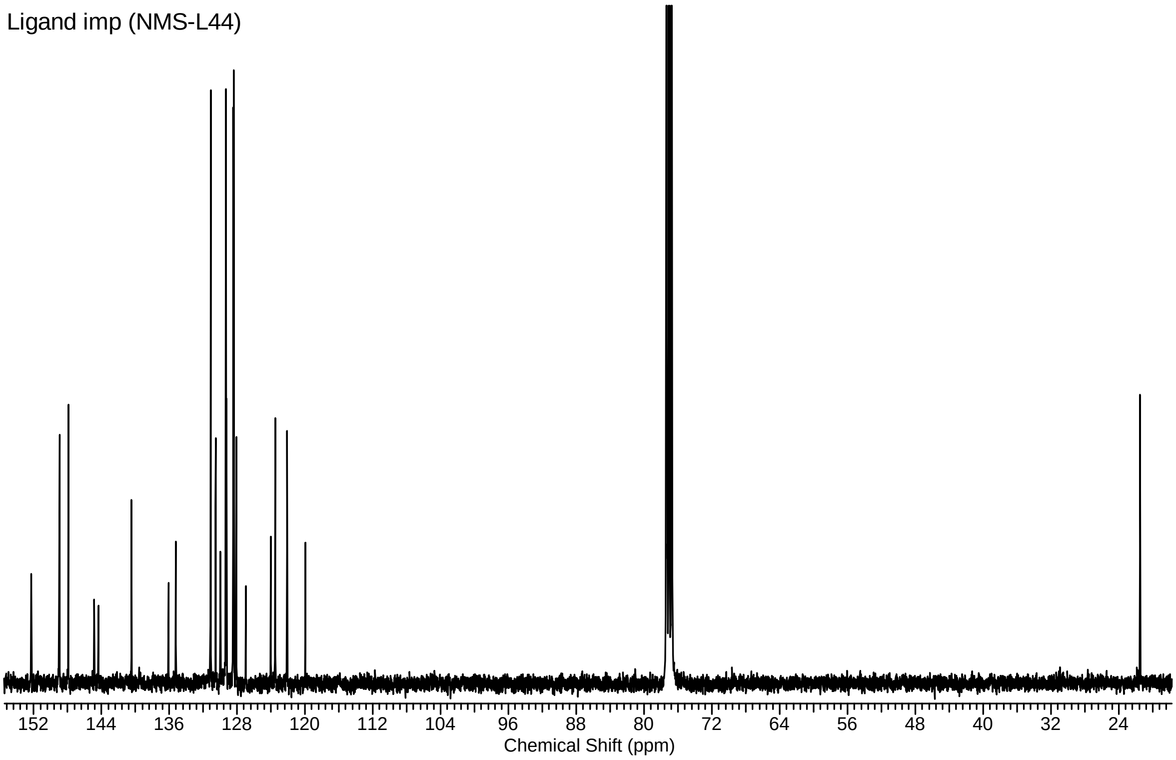


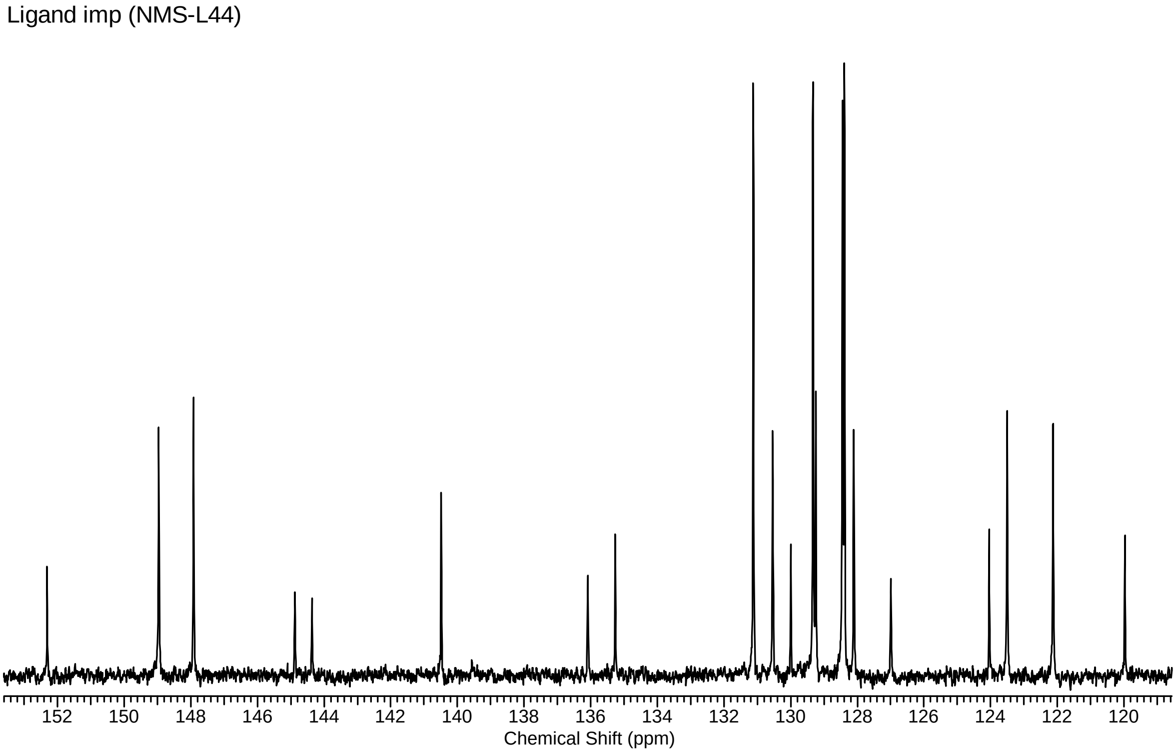
^{1}**H NMR Spectrum** of ligand **imp** in DMSO-d_6 (top, complete; bottom, arom. H).



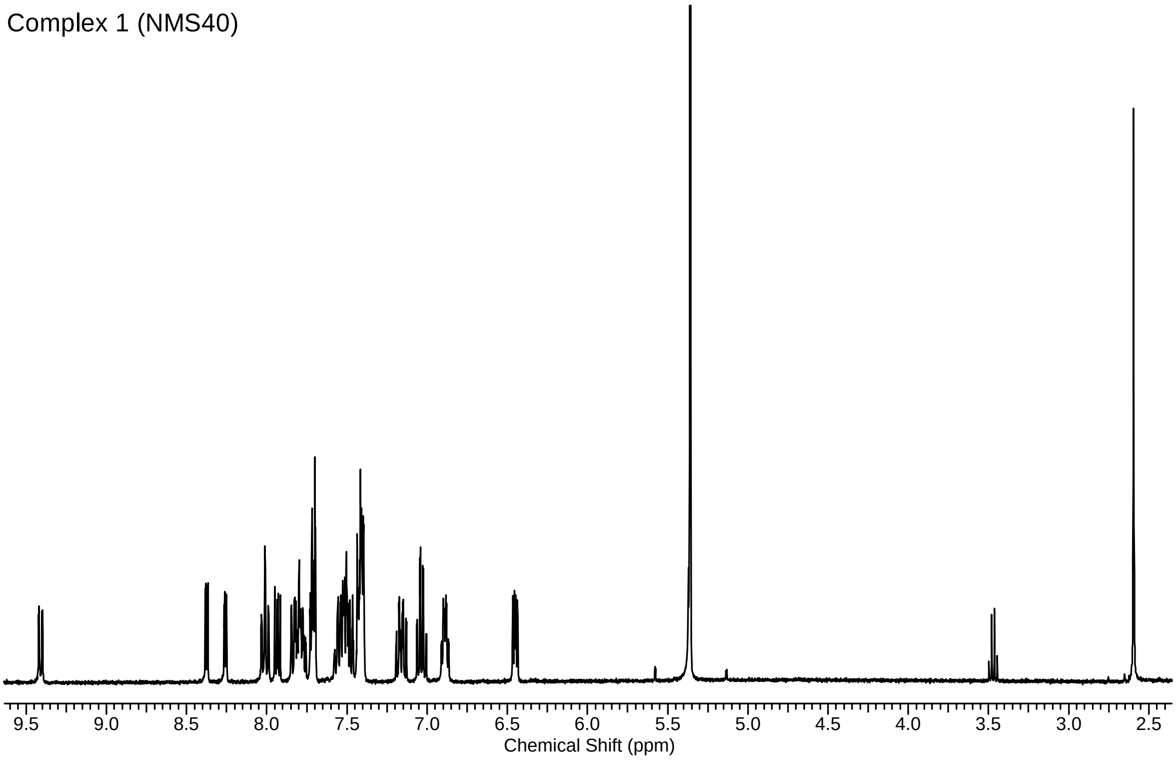


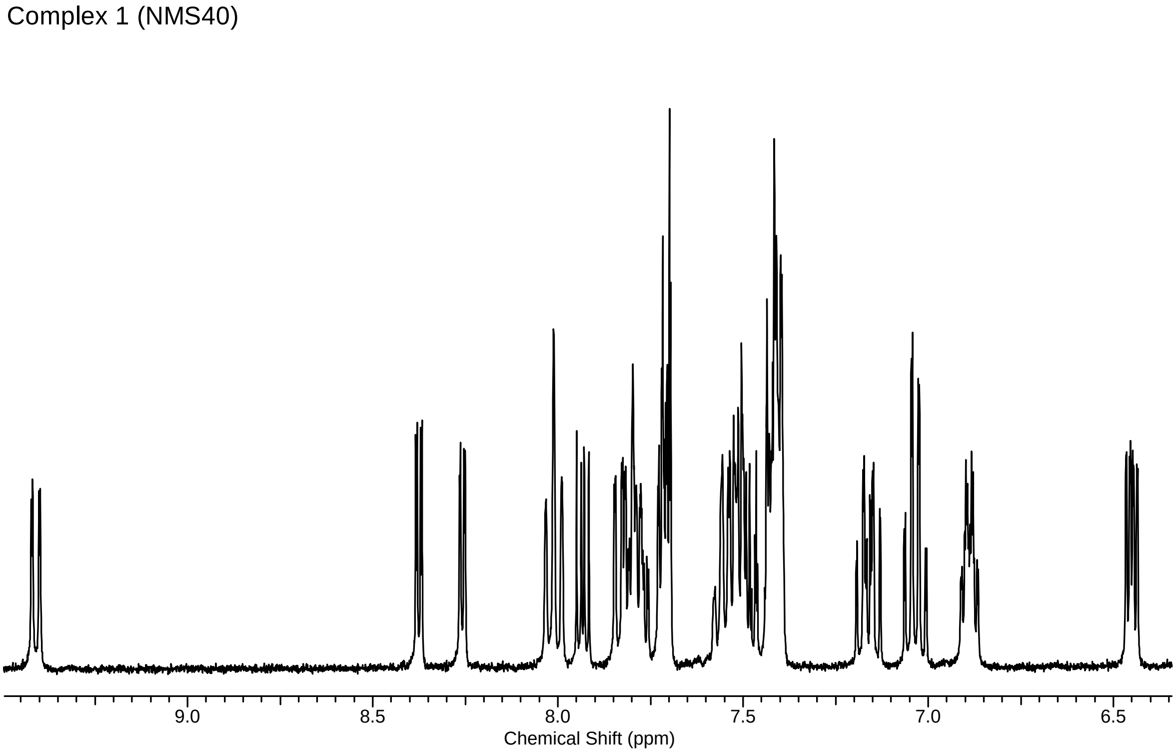
^{1}**H NMR Spectrum** of ligand **imp** in $CDCl_3$ (top, complete; bottom, arom. H).



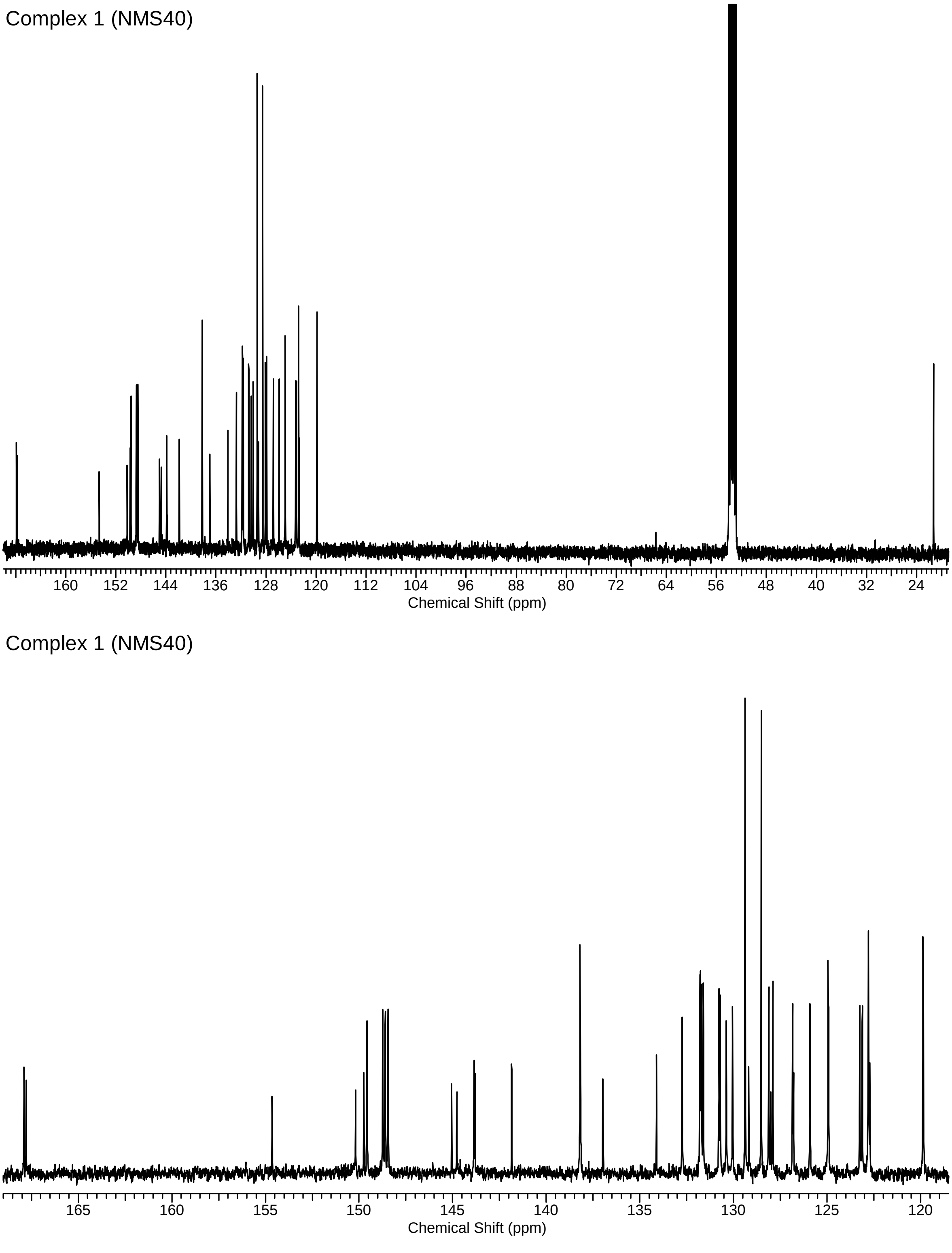


^{13}C NMR Spectrum of ligand **imp** in $CDCl_3$ (top, complete; bottom, arom. C).

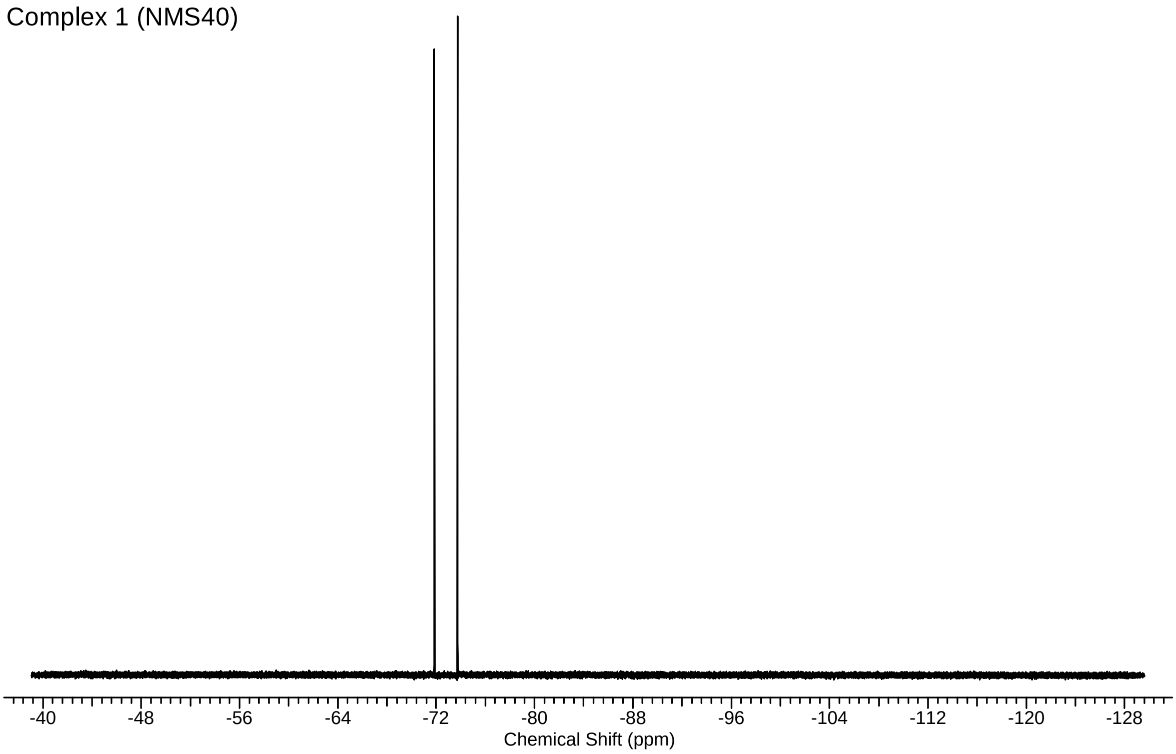




^{1}**H NMR Spectrum** of complex **1** in CD_2Cl_2 (top, complete; bottom, arom. H).



^{13}**C NMR Spectrum** of complex **1** in CD_2Cl_2 (top, complete; bottom, arom. C).



^{19}**F NMR Spectrum** of complex **1** in CD_2Cl_2.