Supporting Information

Bright Blue Phosphorescence from Cationic Bis-Cyclometalated Iridium(III) Isocyanide Complexes

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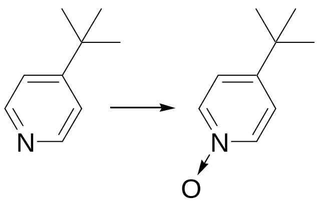
1. General Information

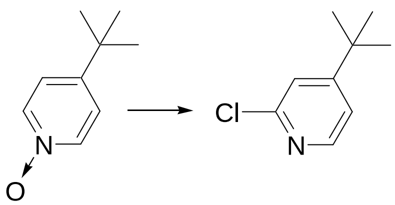
Elemental analyses were performed by Dr. E. Solari, Service for Elemental Analysis, Institute of Chemical Sciences and Engineering (ISIC EPFL). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV400 (400 MHz) spectrometer; ^{19}F NMR spectra, with a Bruker AV200 (200 MHz) or a Bruker AVIII-400 (400 MHz) spectrometers. ESI^{+} and GC-EI^{+} mass spectra were recorded with a Q-TOF Ultima (Waters) or TSQ7000 (Thermo Fisher) spectrometer (Mass-Spectroscopy Service, ISIC EPFL).

Purification, crystal growth, and handling of all compounds were carried out under air. All products were stored in the dark. Chemicals from commercial suppliers were used without purification. Chromatography was performed on a column with an i.d. of 30 mm on silica gel 60 (Fluka, Nr 60752). The progress of reactions and the elution of products were followed on TLC plates (silica gel 60 F_{254} on aluminum sheets, Merck).

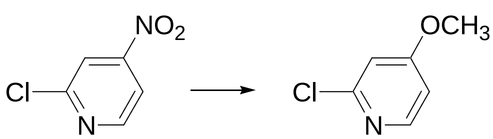
2. Synthesis of 2-Chloropyridines



4-tert-Butylpyridine-N-oxide.[1] The reaction was performed under air. 4-tert-Butylpyridine (5.5 mL, 5.08 g, 37.5 mmol, Aldrich) was dissolved in acetic acid (30 mL, Fluka) at RT. Hydrogen peroxide was added (30% solution in water, 11.5 mL, contains 3.83 g of H_2O_2, 113 mmol, excess, Fluka). The reaction mixture was stirred at 80 °C overnight. It was rotor-evaporated to 1/3 of its volume, neutralized with aqueous solution of Na_2CO_3, and extracted several times with CH_2Cl_2. Organic layers were evaporated to dryness. Purification by chromatography (run twice; silica, 2×25 g) removed the starting material (0.2–1.0% CH_3OH in CH_2Cl_2) and recovered the product (5–7% CH_3OH in CH_2Cl_2). White crystalline solid: 4.94 g (32.7 mmol, 87%; $C_9H_{13}NO$; MW 151.21). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (m, 2H), 7.28 (m, 2H), 1.33 (s, 9H) ppm.

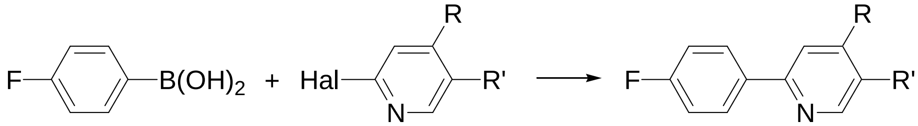


2-Chloro-4-tert-butylpyridine.[2] The reaction was performed under air while protected from the moisture with a ‘dry finger’ ($CaCl_2$). Phosphorus oxychloride ($POCl_3$; 10 mL, 16.5 g, 107 mmol, excess, Riedel-de Haën, used without purification) was added to 4-tert-butylpyridine-N-oxide (2 g, 13.2 mmol) at RT. Reaction mixture was stirred at 130 °C for 5 h to give pale orange solution. It was cooled in an ice bath, carefully diluted with large volume of ice (**CAUTION:** highly exothermic process), and slowly neutralized with a cold solution of NaOH (**CAUTION:** highly exothermic process) while being kept in an ice bath. Extraction with CH_2Cl_2 and purification by chromatography (silica, 20 g; CH_2Cl_2) gave pale yellow oil: 1.54 g (9.1 mmol, 69%; $C_9H_{12}ClN$; MW 169.65). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (dd, J = 5.6, 0.4 Hz, 1H), 7.31 (dd, J = 1.6, 0.8 Hz, 1H), 7.21 (dd, J = 5.6, 1.6 Hz, 1H), 1.32 (s, 9H) ppm.

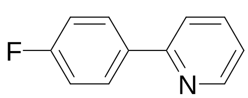


2-Chloro-4-methoxypyridine.[3] The reaction was performed under argon in dry DMF. Sodium methoxide (190 mg, 3.52 mmol, excess, Fluka) was added to a solution of 2-chloro-4-nitropyridine (500 mg, 3.15 mmol, Aldrich) in DMF (4 mL, Acros, 99.8%, ExtraDry, over Molecular Sieves, AcroSeal®) at RT. An exothermic reaction occurred instantly, and the colour of the mixture changed from pale yellow to dark red. It was stirred at RT for 3 h to give brown suspension that was extracted with water and ether. Organic layer was washed with water to remove DMF. Purification by chromatography (silica, 10 g; CH_2Cl_2) gave the product as colourless oil: 393 mg (2.74 mmol, 87%; C_6H_6ClNO; MW 143.57). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, J = 6.0 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 6.77 (dd, J = 5.6, 2.0 Hz, 1H), 3.87 (s, 3H) ppm.

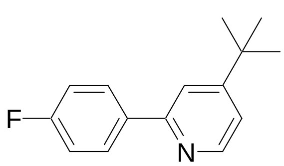
3. Synthesis of 2-Phenylpyridines by Suzuki-Miyaura Reaction



General procedure: The reactions were performed under argon. The solvents were deoxygenated by bubbling with Ar, but they were not dried. 2-Halopyridine, 4-fluorophenylboronic acid (excess, Aldrich or Acros), and K_2CO_3 (excess, Fluka) were dissolved in THF/water (30/10 mL) at RT, followed by addition of $Pd(PPh_3)_4$ (catalyst, Strem). The reaction mixture was stirred at 85 °C for 48 h to give yellow solution. The organic solvent was rotor-evaporated, and the residue was extracted with ether and water. The organic layer was washed with aqueous solution of Na_2CO_3 to remove boronic acid, and then washed with water. It was evaporated to give red residue that was purified by column chromatography. The main problem in the purification is the removal of 2-halopyridine, which precedes the product fraction. In some cases, the product still contained an unidentified impurity (probably originating from boronic acid/anhydride) after chromatography. This impurity was not detected by TLC UV-test, but it was observed in ^1H NMR as two doublets in the aromatic region. In order to remove the impurity, the neat product was sonicated in aq. sol. of Na_2CO_3, and extracted with hexane or a mixture of hexane/ether (3/1 to 1/2, depending on solubility). The organic layer was extracted again with aq. sol. of Na_2CO_3, washed with water, and evaporated to give pure product. The details are provided below.

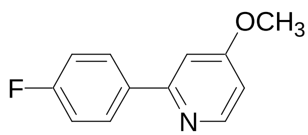


2-(4′-Fluorophenyl)pyridine. The reaction was performed with 2-bromopyridine (0.80 mL, 1.31 g, 8.3 mmol, Fluka), 4-fluorophenylboronic acid (1.74 g, 12.4 mmol), K_2CO_3 (3.92 g, 28 mmol), and $Pd(PPh_3)_4$ (305 mg, 0.26 mmol). Chromatography was run twice (silica, 2×15 g) with hexane/CH_2Cl_2 (1/1 to 1/3). Pale yellow oil that crystallizes to white solid: 976 mg (5.64 mmol, 68%; $C_{11}H_8FN$; MW 173.19). ^1H NMR (400 MHz, DMSO-d_6): δ = 8.67–8.63 (m, 1H), 8.17–8.10 (m, 2H), 7.98–7.93 (m, 1H), 7.91–7.84 (m, 1H), 7.38–7.27 (m, 3H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): 13 signals were observed because each phenyl carbon was coupled to fluorine to give a doublet; the multiplet assignment has not been performed: δ = 164.96, 162.51, 156.28, 149.86, 136.97, 135.87, 135.84, 128.93, 128.85, 122.31, 120.17, 115.80, 115.59 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -113.2$ (Ph–*F*) ppm. GC-EI$^+$ MS: *m/z* 173 (M^+, 100%).

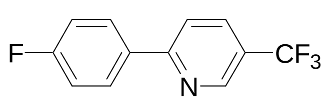


2-(4′-Fluorophenyl)-4-(tert-butyl)pyridine. The reaction was performed with 2-chloro-4-tert-butylpyridine (1.0 g, 6.3 mmol), 4-fluorophenylboronic acid (1.4 g, 10 mmol), K_2CO_3 (2.5 g, 18 mmol), and $Pd(PPh_3)_4$ (350 mg, 0.30 mmol). Chromatography was run twice (silica, 2×30 g) with hexane/CH_2Cl_2 (2.5/1, to remove impurities; 1/1 to 1/1.5, to recover the product). Pale yellow oil: 939 mg (4.1 mmol, 65%; $C_{15}H_{16}FN$; MW 229.29). ^1H NMR (400

MHz, DMSO-d_6): δ = 8.55 (d, J = 5.2 Hz, 1H), 8.19–8.11 (m, 2H), 7.88 (s, 1H), 7.35 (d, J = 5.2 Hz, 1H), 7.34–7.26 (m, 2H), 1.34 (s, 9H, Py–tert-C_4H_9) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 13 signals were observed in the aromatic region because each phenyl carbon was coupled to fluorine to give a doublet; the multiplet assignment has not been performed: δ = 164.67, 162.22, 161.19, 155.80, 150.06, 136.31, 136.29, 129.54, 129.46, 120.08, 117.60, 116.16, 115.95, 35.28 (*C*, Py–tert-C_4H_9), 30.85 (*C*H_3, Py–tert-C_4H_9) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −113.6 (Ph–*F*) ppm. GC-EI$^+$ MS: *m/z* 229 (M^+, 75%), 214 ($\{M - CH_3\}^+$, 100%).

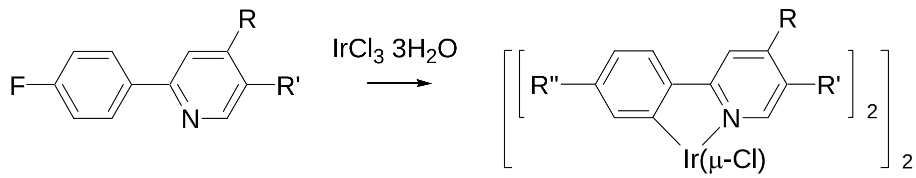


2-(4′-Fluorophenyl)-4-(methoxy)pyridine. The reaction was performed with 2-chloro-4-methoxypyridine (863 mg, 6.0 mmol), 4-fluorophenylboronic acid (1.45 g, 10 mmol), K_2CO_3 (2.7 g, 19.5 mmol), and $Pd(PPh_3)_4$ (300 mg, 0.26 mmol). Chromatography was done on silica (20 g) with hexane/CH_2Cl_2 (1/1.5) to remove impurities, and with 0.2–0.4% CH_3OH in CH_2Cl_2 to recover the product. White crystalline solid: 0.93 g (4.57 mmol, 76%; $C_{12}H_{10}FNO$; MW 203.21). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.46 (d, J = 5.6 Hz, 1H), 8.19–8.10 (m, 2H), 7.48 (d, J = 2.4 Hz, 1H), 7.34–7.25 (m, 2H), 6.94 (dd, J = 5.6, 2.4 Hz, 1H), 3.90 (s, 3H, Py–OCH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2-d_6): 13 aromatic signals were observed because each phenyl carbon was coupled to fluorine to give a doublet; partial multiplet assignment has been performed; δ = 166.71, 164.94, 162.49, 157.94, 151.10, 135.85 (d, $J_{C–F}$ = 3.4 Hz), 128.93 (d, $J_{C–F}$ = 8.1 Hz), 115.58 (d, $J_{C–F}$ = 21 Hz), 108.19, 106.55, 55.42 (Py–O*C*H_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −113.1 (Ph–*F*) ppm. GC-EI$^+$ MS: *m/z* 203 (M^+, 100%).

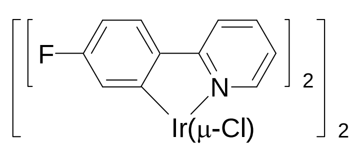


2-(4′-Fluorophenyl)-5-(trifluoromethyl)pyridine. The reaction was performed with 2-bromo-5-(trifluoromethyl)pyridine (1.5 g, 6.64 mmol, Maybridge), 4-fluorophenylboronic acid (1.44 g, 10 mmol), K_2CO_3 (3.0 g, 22 mmol), and $Pd(PPh_3)_4$ (153 mg, 0.13 mmol). Filtration through silica (20 g) by eluting with hexane/CH_2Cl_2 (2/1) left dark red impurity at the top of the column and provided crude product as a white solid. Chromatography was done on silica (30 g) with hexane/CH_2Cl_2 (4/1, to remove impurities; 2/1, to recover the product). White crystalline solid: 1.36 g (5.64 mmol, 85%; $C_{12}H_7F_4N$; MW 241.18). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.95 (s, br, 1H), 8.15–8.08 (m, 2H), 8.03 (dd, J = 8.0, 2.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.28–7.19 (m, 2H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): 26 signals were observed because each phenyl carbon was coupled to fluorine to give a doublet, while CF_3 carbon and 4, 5, 6-carbons of the pyridyl were coupled to three F-atoms to give a quartet each; partial multiplet assignment has been performed; δ = 165.60, 163.12, 159.56, 146.72 (q, $J_{C–F}$ = 4.1 Hz), 134.32 (d, $J_{C–F}$ = 3.2 Hz), 134.17 (q, $J_{C–F}$ = 3.4 Hz), 129.42 (d, $J_{C–F}$ = 8.3 Hz), 124.74 (q, $J_{C–F}$ = 33 Hz), 124.13 (q, $J_{C–F}$ = 270 Hz), 119.68, 115.98 (d, $J_{C–F}$ = 21 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.2 (3F, Py–C*F*$_3$), −111.1 (1F, Ph–*F*) ppm. GC-EI$^+$ MS: *m/z* 241 (M^+, 100%).

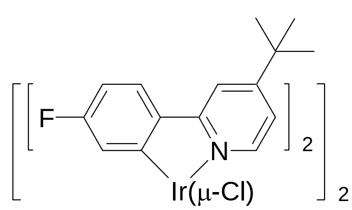
4. Synthesis of Cyclometalated Ir(III) Complexes $[(C^\wedge N)_2Ir(\mu\text{-}Cl)]_2$



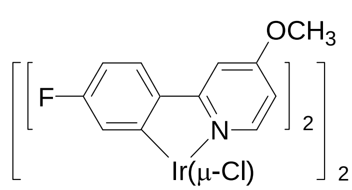
General procedure:[4] The reactions were performed under argon and in the absence of light. The solvents were de-oxygenated by bubbling with Ar, but they were not dried. $IrCl_3{\cdot}3H_2O$ (150 mg, 0.43 mmol, W. C. Heraeus GmbH) was dissolved in 2-ethoxyethanol/water (3/1 ratio; 6/2 mL) at 60 °C to give purple solution. An excess of the ligand (about 1 mmol) was added. The reaction mixture was stirred at 120 °C overnight to give yellow suspension (via intermediate formation of brown suspension and orange solution). It was cooled to RT and filtered. The product was washed with a number of solvents (specified below), dried, and used without purification. The details are provided below.



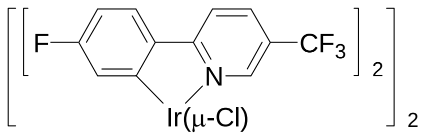
$IrCl_3{\cdot}3H_2O$ (150 mg, 0.43 mmol) and 2-(4′-fluorophenyl)pyridine (166 mg, 0.96 mmol) gave bright yellow solid that was washed with ethanol, water, ethanol again, and ether: 136 mg (0.12 mmol, 55%; $C_{44}H_{28}Cl_2F_4Ir_2N_4$; MW 1144.05). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.19–9.13 (m, 4H), 7.92 (d, J = 8.4 Hz, 4H), 7.85 (td, J = 7.6, 1.6 Hz, 4H), 7.60 (dd, J = 8.4, 6.0 Hz, 4H), 6.91–6.83 (m, 4H), 6.59 (td, J = 8.8, 2.8 Hz, 4H), 5.52 (dd, J = 10, 2.8 Hz, 4H) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −110.8 (Ph–*F*) ppm.



$IrCl_3{\cdot}3H_2O$ (150 mg, 0.43 mmol) and 2-(4′-fluorophenyl)-4-(tert-butyl)pyridine (230 mg, 1.00 mmol) gave bright yellow solid that was washed with ethanol/water (1/1), water, ethanol/water (1/1) again, ether/hexane (1/1), and hexane: 192 mg (0.14 mmol, 65%; $C_{60}H_{60}Cl_2F_4Ir_2N_4$; MW 1368.48). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.08 (d, J = 6.0 Hz, 4H), 7.91 (d, J = 2.0 Hz, 4H), 7.61 (dd, J = 8.8, 6.0 Hz, 4H), 6.92 (dd, J = 6.0, 2.0 Hz, 4H), 6.57 (td, J = 8.8, 2.4 Hz, 4H), 5.40 (dd, J = 10, 2.4 Hz, 4H), 1.55 (s, 36H, Py–tert-C_4H_9) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −111.1 (Ph–*F*) ppm.



$IrCl_3{\cdot}3H_2O$ (150 mg, 0.43 mmol) and 2-(4′-fluorophenyl)-4-(methoxy)pyridine (195 mg, 0.96 mmol, excess) gave yellow solid that was washed with ethanol/water (1/1), water, ethanol/water (1/1) again, hexane, and small volume of ether/hexane (1/1): 96 mg (0.076 mmol, 35%; $C_{48}H_{36}Cl_2F_4Ir_2N_4O_4$; MW 1264.16). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.98 (d, J = 6.8 Hz, 4H), 7.55 (dd, J = 8.8, 6.0 Hz, 4H), 7.39 (d, J = 2.8 Hz, 4H), 6.57 (td, J = 8.8, 2.4 Hz, 4H), 6.50 (dd, J = 6.4, 2.8 Hz, 4H), 5.60 (dd, J = 10.0, 2.4 Hz, 4H), 4.10 (s, 12H, Py–OCH_3) ppm.



$IrCl_3·3H_2O$ (150 mg, 0.43 mmol) and 2-(4′-fluorophenyl)-5-(trifluoromethyl)pyridine (231 mg, 0.96 mmol) gave bright yellow solid that was washed with ethanol/water (1/1), water, ethanol/water (1/1) again, and hexane: 152 mg (0.11 mmol, 50%; $C_{48}H_{24}Cl_2F_{16}Ir_2N_4$; MW 1416.05). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.57 (s, 4H), 8.09–8.05 (m, 8H), 7.71 (dd, J = 8.8, 5.6 Hz, 4H), 6.69 (td, J = 8.4, 2.4 Hz, 4H), 5.40–5.30 (dd, 4H, obscured by solvent signal) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −62.3 (3F, Py–CF_3), −107.0 (1F, Ph–F) ppm.

5. X-Ray Crystallography

Single crystals of **4** for X-ray analysis were grown by slow evaporation of a mixed CH_2Cl_2/hexane solution. The data collection was performed at 100 K using Mo K_α radiation with a Bruker APEX II CCD, having kappa geometry. The raw data were reduced by means of EvalCCD,[5] and then corrected for absorption.[6] The crystal structure solution and refinement were performed by SHELX.[7] 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. Disorder shown by the two tert-butyl groups was modelled using the split model and applying restraints (SIMU and DFIX cards).

Table S1. Crystal Data and Structure Refinement for Complex **4**.

CCDC	857727
empirical formula	$C_{35}H_{36}F_5IrN_4O_5S$
fw	911.94
temp [K]	100(2)
wavelength [Å]	0.71073
cryst syst	triclinic
space group	*P*-1
unit cell dimensions	a = 12.184(2) Å
	b = 16.143(2) Å
	c = 19.756(3) Å
	α = 90.603(9)°
	β = 105.358(12)°
	γ = 101.288(11)°
vol [Å]^3	3666.6(10)
Z	4
ρ (calc) [Mg/m^3]	1.652
μ [mm^{-1}]	3.770
F(000)	1808
cryst size [mm^3]	0.41 × 0.21 × 0.16
θ range	3.12 – 27.50°
index ranges	$-15 \leq h \leq 15$
	$-20 \leq k \leq 20$
	$-25 \leq l \leq 25$
reflns collected	64156
independent reflns	16628 [R(int) = 0.0707]
completeness to θ	27.50° – 98.7 %
absorption correction	semi-empirical from equivalents
max/min transm	0.7456 / 0.3678
refinement method	full-matrix least-squares on F^2
data/restraints/params	16628 / 138 / 975
GOF on F^2	1.131
final R indices [$I > 2\sigma(I)$]	R1 = 0.0524, wR2 = 0.1196
R indices (all data)	R1 = 0.0706, wR2 = 0.1314
largest diff. peak/hole [e/Å^3]	4.360 / -3.319

6. Electrochemistry

Electrochemical experiments were conducted in DMF (99.8%, Extra Dry, over Molecular Sieve, AcroSeal®, Acros) or acetonitrile (99.9%, Extra Dry, over Molecular Sieve, AcroSeal®, Acros), with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Fluka, electrochemical grade) as a 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 stream of Ar was stopped to prevent stirring of solution). Glassy carbon, platinum spiral, and platinum wire served as working, counter, and quasi-reference electrodes. At the end of each experiment, ferrocene was added as an internal reference. Estimated error: ±50 mV. The anodic/cathodic peak separation for the standard (Fc^+/Fc couple) at 100 mV/s was 68–93 mV in CH_3CN and 78–93 mV in DMF.

Cyclic Voltammetry was performed at a scan rate of 1 or 0.1 V/s. Differential Pulse Voltammetry was recorded at a modulation potential of 50 mV, a step potential of 10 mV, a modulation time of 50 ms, and an interval time of 100 ms.

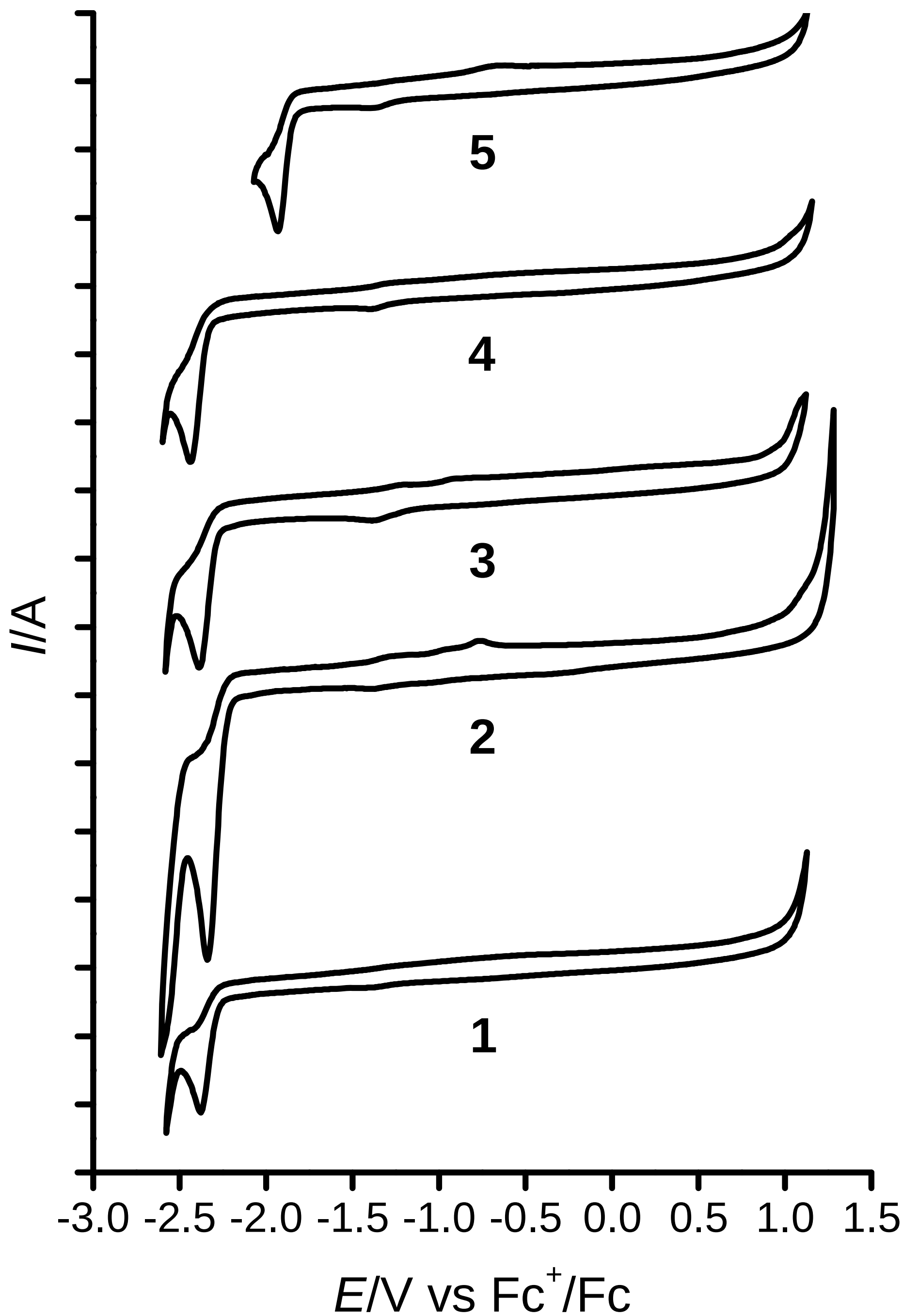


Figure S1. Cyclic voltammograms of **1–5** in DMF (0.1 M NBu_4PF_6, 100 mV/s). The unit on the vertical axis is 10 μA.

7. Infrared Spectroscopy

Infrared absorption spectra of solid films of the complexes were recorded with a Digilab FTS 7000 FT-IR Spectrometer in reflectance mode with background subtraction at atmospheric pressure and at room temperature. The films were formed by evaporation of dichloromethane solution of the complex on a diamond window. The thickness of the films was not controlled. When necessary, the higher absorbance was achieved by evaporating more of the solution of the complex on top of the existing film.

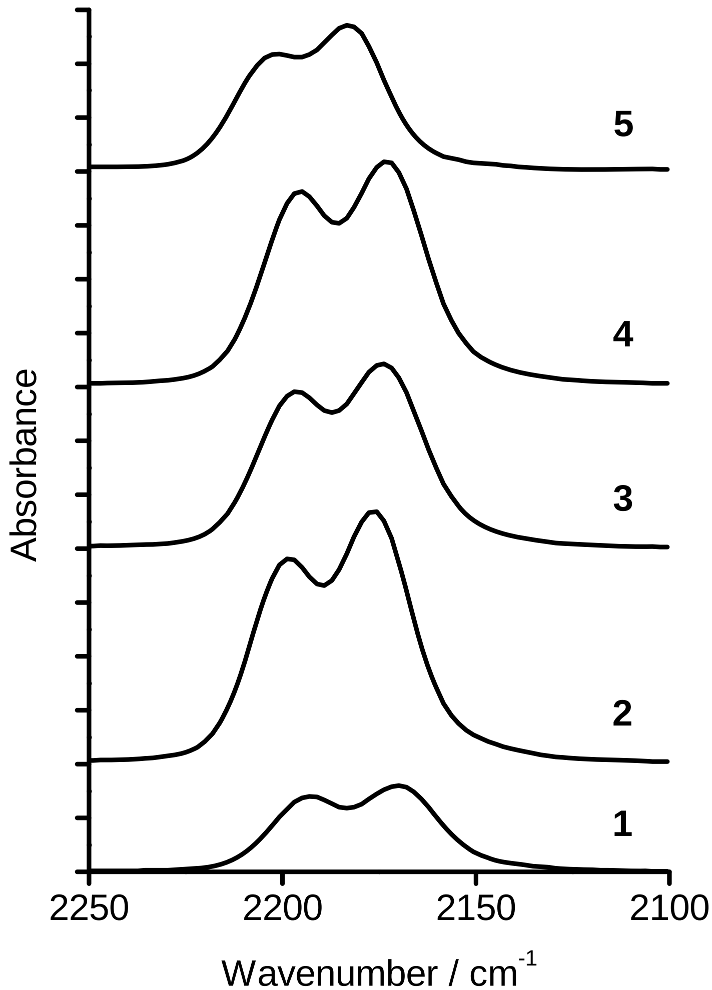


Figure S2. Infrared absorption of solid films of neat complexes **1**–**5** in the range of transitions associated with the stretching vibrations of C≡N bond. The unit on the vertical axis is 0.05. The spectra are shifted with respect to one another along the vertical axis.

8. Photophysical Measurements

Absorption spectra were recorded with a Perkin-Elmer LAMBDA 950 spectrophotometer. The luminescence measurements were conducted in fluorescence cuvettes of 1 cm path length. The samples were purged from oxygen by bubbling with argon. The uncorrected emission spectra were recorded with an Edinburgh Instruments FLS920 spectrometer with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). An Edinburgh Instruments Xe900 450 W xenon arc lamp was a source of excitation light. The corrected emission spectra were calculated by applying a calibration curve supplied with the instrument. Luminescence quantum yields (Φ) in solution were calculated by the method of Demas and Crosby[8] from the corrected spectra on a wavelength scale (nm) using an air-equilibrated solution of quinine sulfate in 1 N H_2SO_4 (Φ = 54.6%).[9]

Emission lifetimes in the nanosecond to microsecond range were measured by a single photon counting technique with the same Edinburgh Instruments FLS920 spectrometer, a laser diode as an excitation source (1 MHz; λ_{exc} = 407 nm; 200 ps time resolution after de-convolution), and the above-mentioned PMT as a detector. Alternatively, the lifetimes were measured with an IBH single photon counting spectrometer equipped either with a thyratron gated nitrogen lamp (2 to 40 kHz; λ_{exc} = 337 nm; 0.5 ns time resolution), or pulsed NanoLED excitation sources (λ_{exc} at 278, 331, 465, and 560 nm; pulse width ≤ 0.3 ns); the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237-01 PMT. Analysis of the luminescence decay profiles was accomplished with the DAS6 Decay Analysis Software provided by the manufacturer.

The luminescence lifetimes in the microsecond to millisecond range were measured with a Perkin-Elmer LS-50 spectrofluorimeter having a pulsed xenon lamp with a variable repetition rate, and were calculated with standard software. The luminescence spectra at 77 K were recorded in a glass tube (2 mm in diameter) placed in a quartz Dewar flask filled with liquid nitrogen. For solid samples, the luminescence quantum yields were calculated by the method of De Mello *et al*.[10] from the corrected emission spectra recorded in a barium sulphate coated integrating sphere (6 inch in diameter), using He-Cd laser as a light source (λ_{exc} = 325 nm; 5 mW), and a CCD AVA-Spec2048 or R928 PMT, as a detector.

The PMMA films containing 1% wt. of the complex were drop-cast from dichloromethane solutions. The neat films of the complexes were spin coated from acetonitrile solutions. The thickness of the films was not controlled.

Experimental errors are estimated to be ±8% for lifetime determinations; ±20% for emission quantum yields; ±2 nm and ±5 nm for absorption and emission maxima.

Table S2. Optical Absorption of Ir(III) Complexes[a]

complex	solvent	λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1})
1	CH_2Cl_2	347 (7.9), 300 (13), 310 (13), 257 (29), 234 (34)
	CH_3CN	341 (7.5), 297 (13), 253 (29), 233 (34)
2	CH_2Cl_2	332 (11), 308 (11), 253 (32), 237 (35)
	CH_3CN	327 (10), 248 (33, sh), 236 (35)
3	CH_2Cl_2	328 (13), 253 (40), 237 (40)
	CH_3CN	326 (12), 250 (41), 238 (40)
4	CH_2Cl_2	322 (14), 252 (51), 236 (55)
	CH_3CN	318 (13), 250 (53), 235 (55)
5	CH_2Cl_2	354 (12), 284 (19), 263 (27), 240 (30)
	CH_3CN	348 (11), 259 (26), 238 (30)

[a]In dichloromethane or acetonitrile, under air, at room temperature. In the range: 220–500 nm. Estimated errors: ±2 nm for λ_{abs}; ±5% for ε.

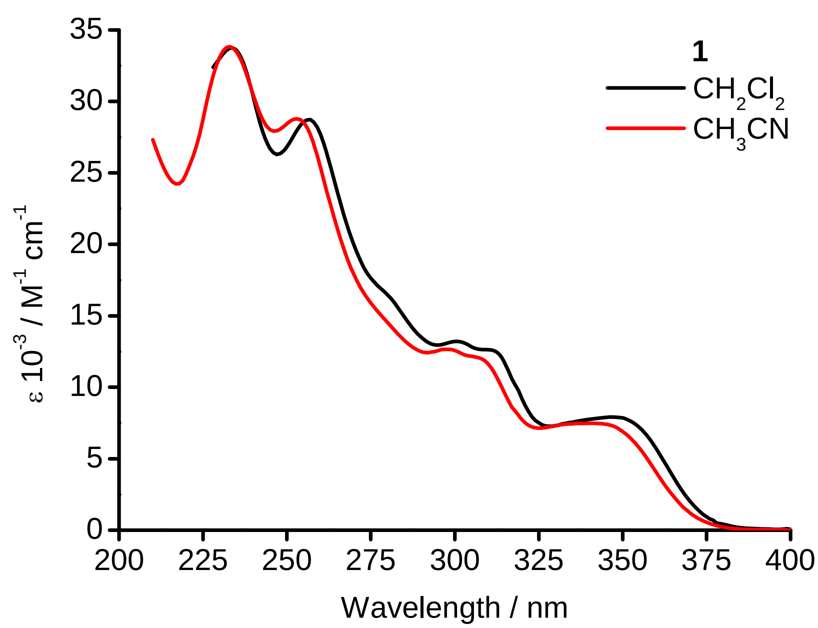


Figure S3. Absorption spectra of **1**.

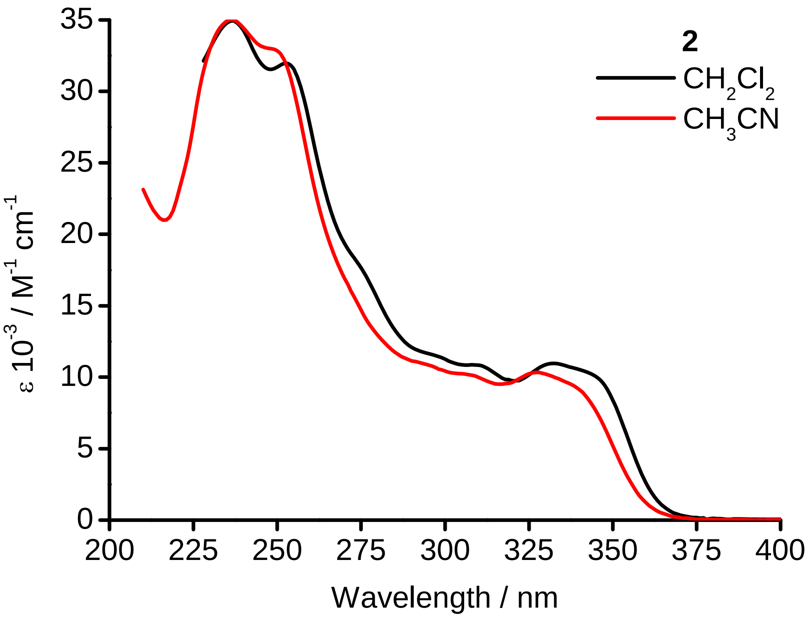


Figure S4. Absorption spectra of **2**.

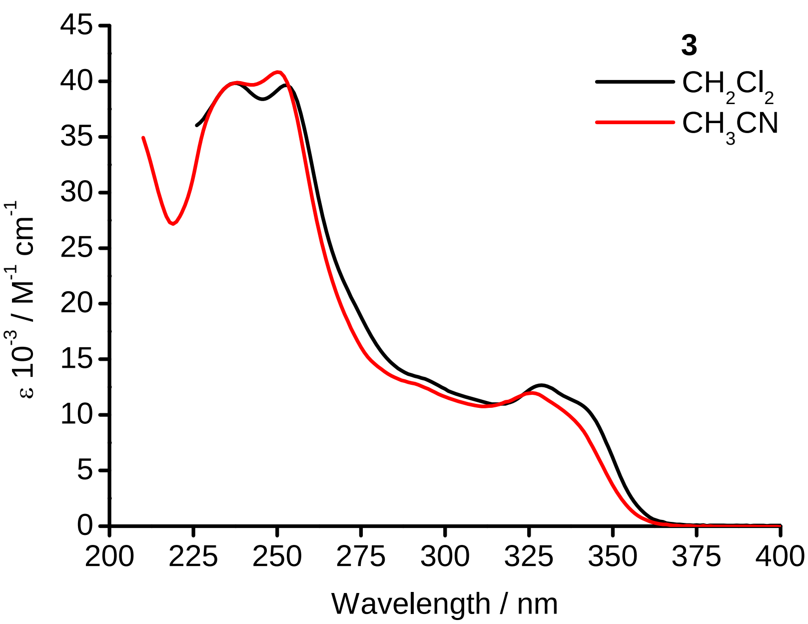


Figure S5. Absorption spectra of **3**.

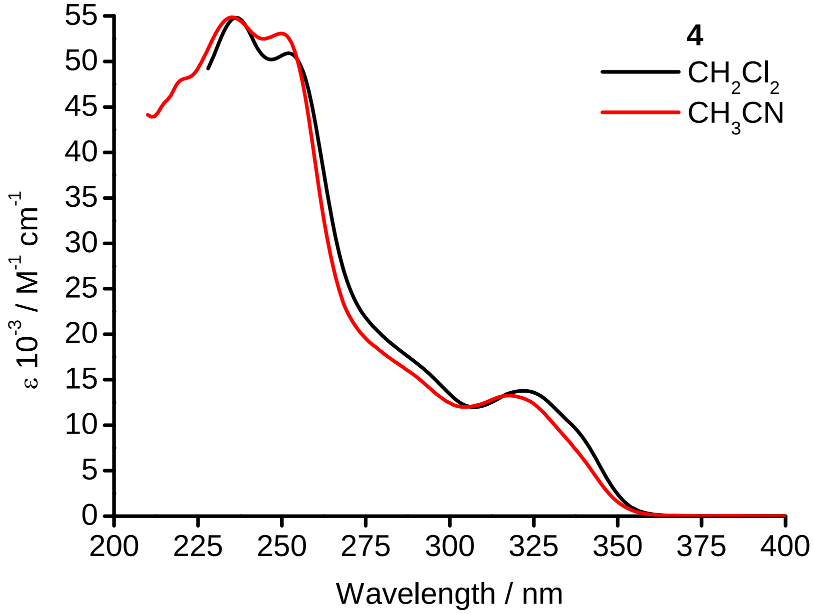


Figure S6. Absorption spectra of **4**.

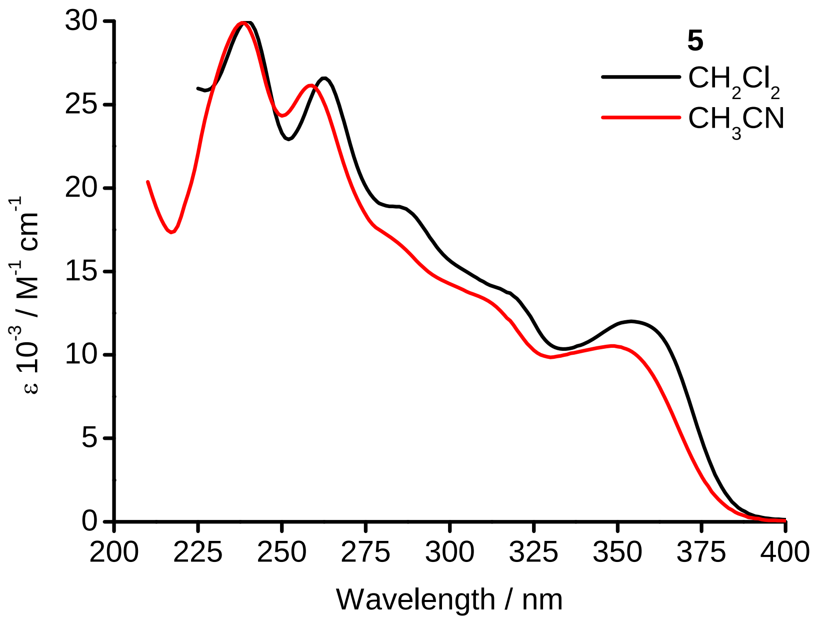


Figure S7. Absorption spectra of **5**.

Table S3. Main Luminescence Maxima of Ir(III) Complexes[a,b,c]

complex	medium	λ_{em}/nm
1	CH_3CN	453, 485, 509
	CH_2Cl_2	455, 486, 513
	CH_2Cl_2, 77K	452, 485, 512
	PMMA	455, 487, 512
	solid	456, 516
2	CH_3CN	447, 478, 502
	CH_2Cl_2	449, 480, 505
	CH_2Cl_2, 77 K	447, 478, 508
	PMMA	449, 478, 503
	solid	456, 484, 510
3	CH_3CN	447, 477, 503
	CH_2Cl_2	449, 478, 505
	CH_2Cl_2, 77 K	445, 477, 502, 541
	PMMA	448, 477, 504
	solid	451, 478, 507
4	CH_3CN	440, 469, 494
	CH_2Cl_2	440, 470, 495
	CH_2Cl_2, 77 K	436, 468, 492
	PMMA	440, 469, 493
	solid	444, 473, 499
5	CH_3CN	458, 487
	CH_2Cl_2	459, 491
	CH_2Cl_2, 77 K	455, 489, 512
	PMMA	458, 486
	solid	463, 490

[a]Acetonitrile or dichloromethane solutions (10^{-5} M), at room temperature, under argon.
[b]Frozen dichloromethane solution at 77 K.
[c]PMMA film (1 wt. % of the complex) or neat solid complex; at room temperature; under air.

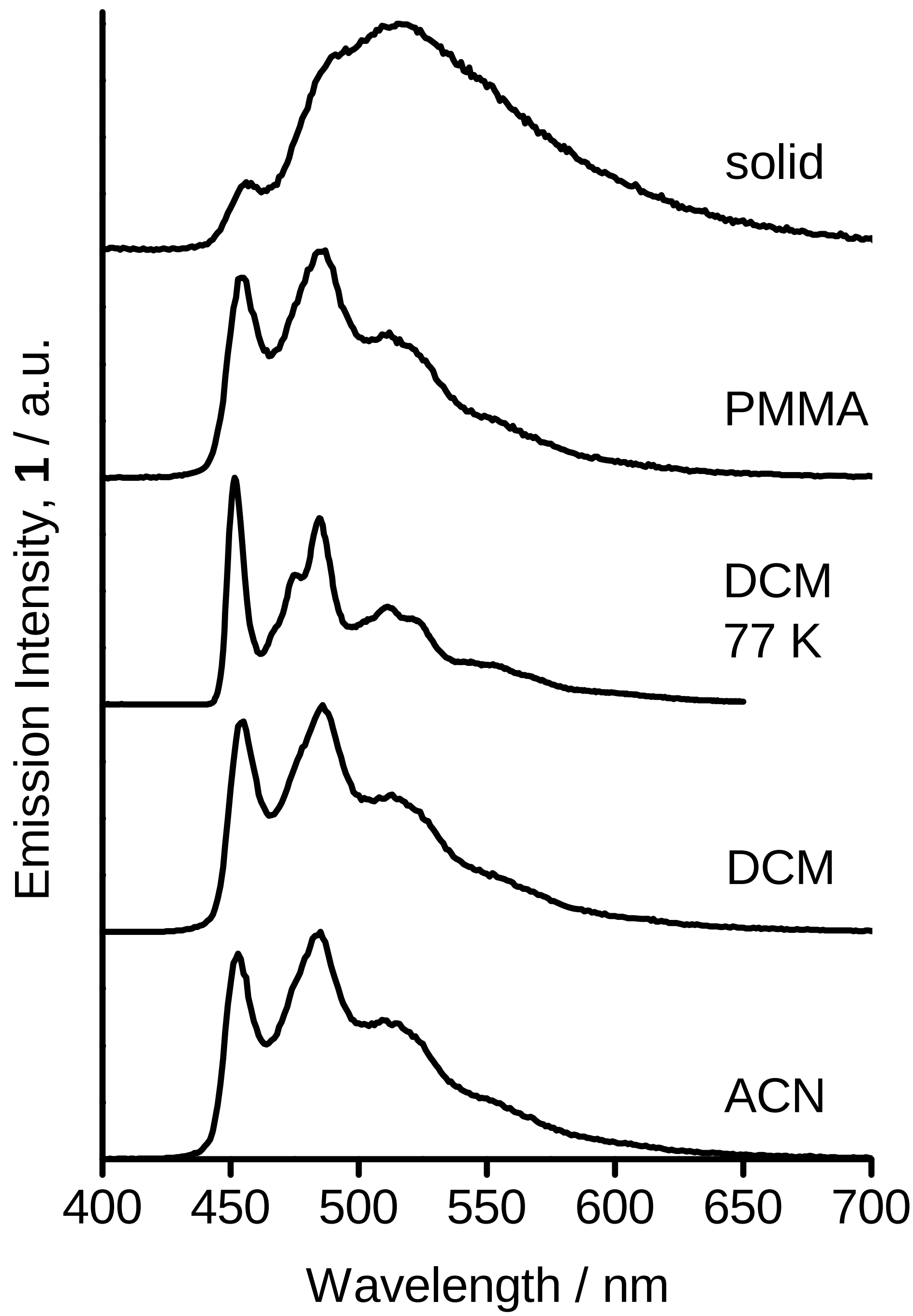


Figure S8. Corrected and normalized room-temperature luminescence spectra of **1** in acetonitrile (ACN), dichloromethane (DCM; also shown at 77 K), PMMA, and as a solid neat film.

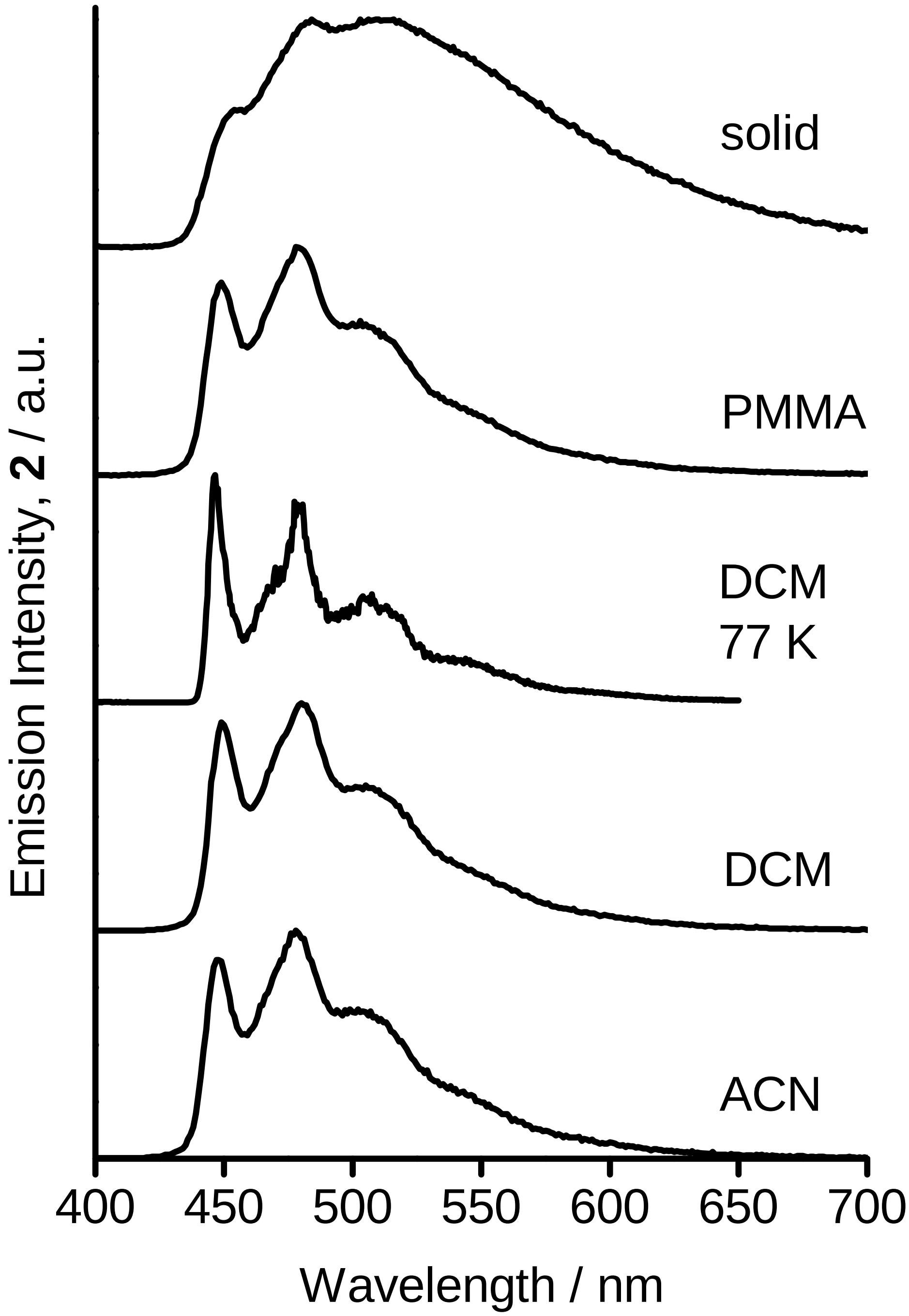


Figure S9. Corrected and normalized room-temperature luminescence spectra of **2** in acetonitrile (ACN), dichloromethane (DCM; also shown at 77 K), PMMA, and as a solid neat film.

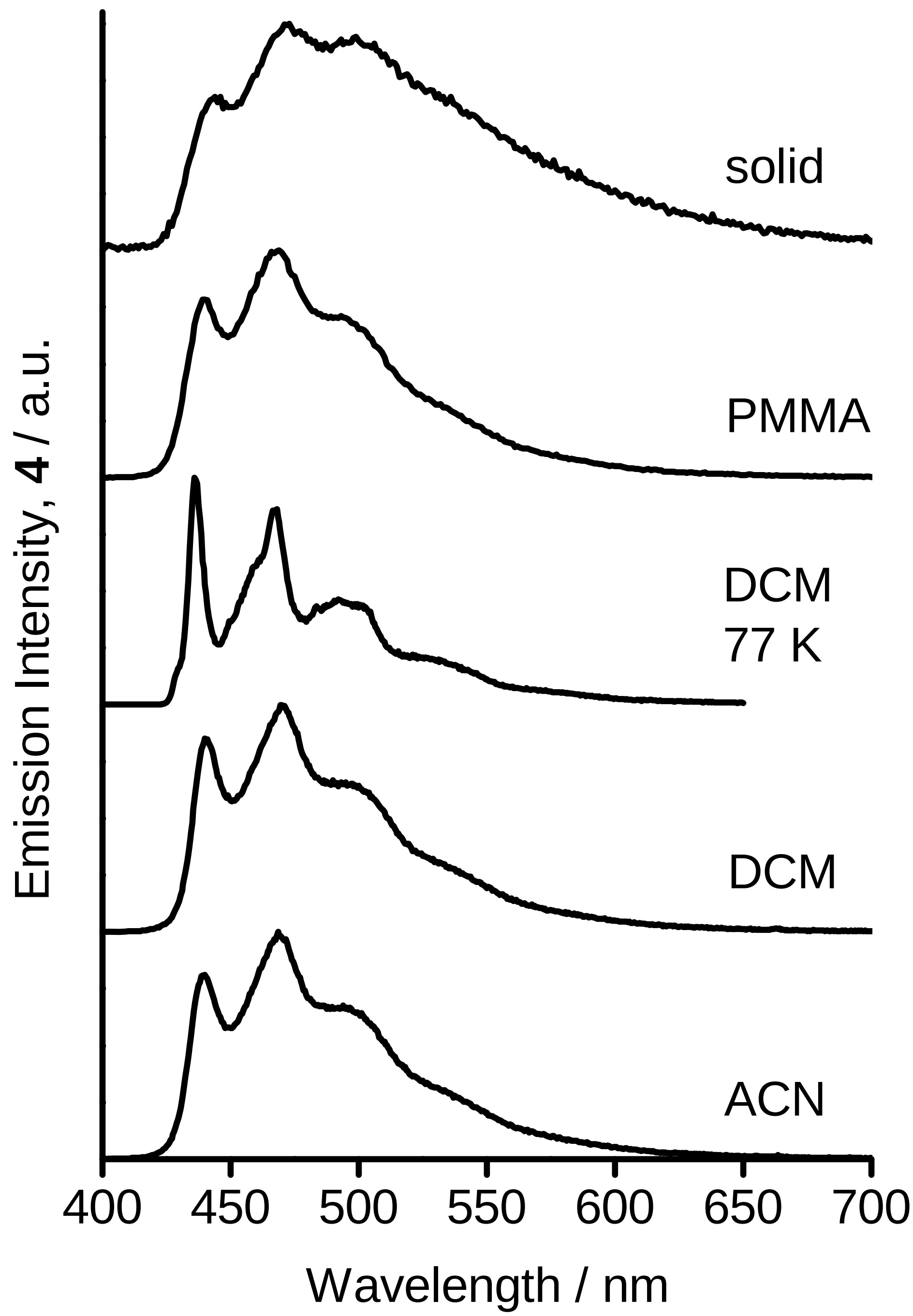


Figure S10. Corrected and normalized room-temperature luminescence spectra of **4** in acetonitrile (ACN), dichloromethane (DCM; also shown at 77 K), PMMA, and as a solid neat film.

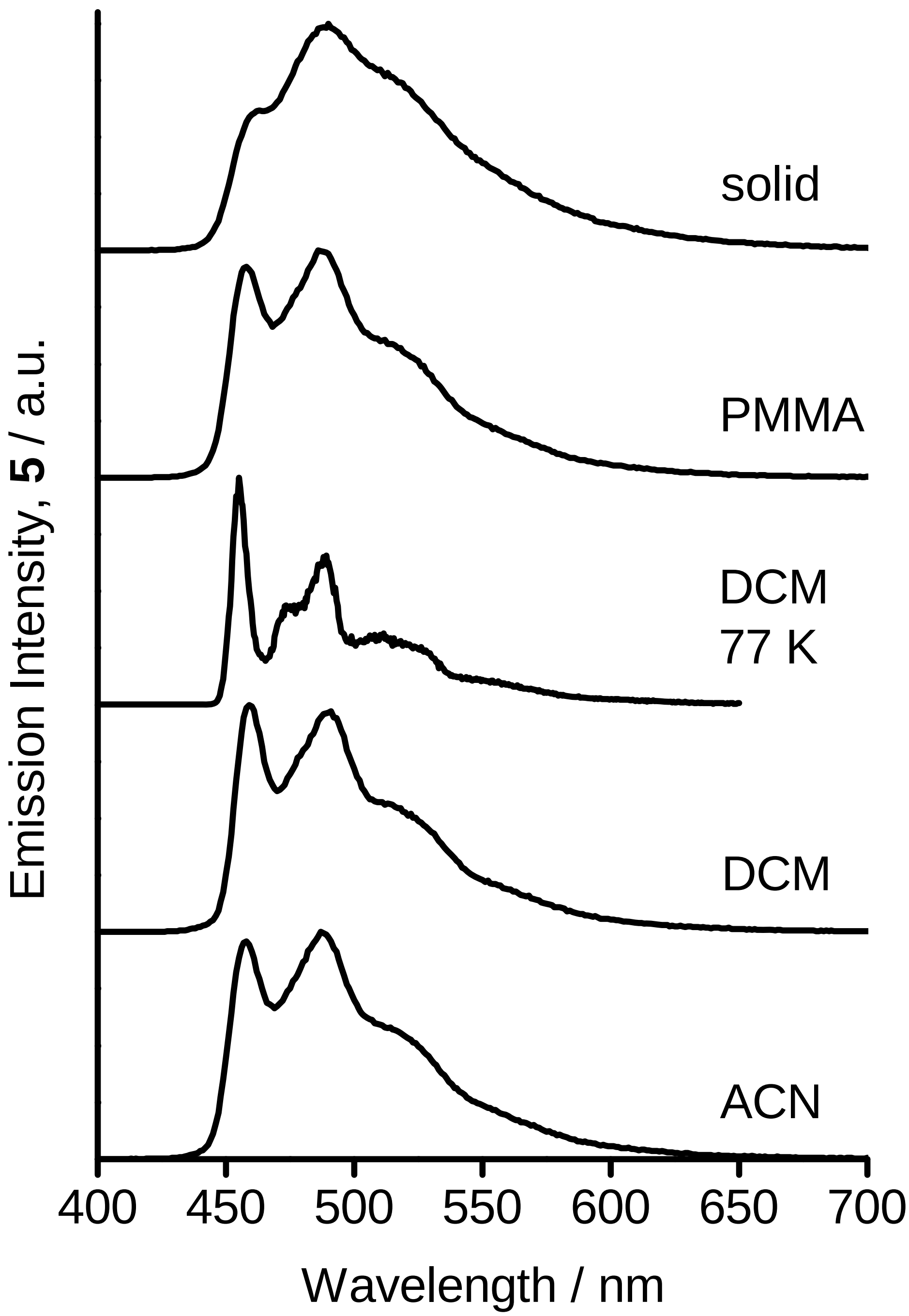


Figure S11. Corrected and normalized room-temperature luminescence spectra of **5** in acetonitrile (ACN), dichloromethane (DCM; also shown at 77 K), PMMA, and as a solid neat film.

9. Theoretical Calculations

Density Functional Theory (DFT) calculations were carried out with the D.02 revision of the Gaussian 03 program package,[11] using Becke's three-parameter B3LYP exchange-correlation functional[12,13] together with the 6-31G** basis set for C, H, O, F, and N atoms,[14] and the "double- ζ" quality LANL2DZ basis set for the Ir.[15] An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core $[(5s)^2(5p)^6]$ electrons and the $(5d)^6$ valence electrons of Ir(III). The geometries of the singlet ground state (S_0) and of the lowest triplet excited state (T_1) were fully optimized in gas phase with symmetry restrictions (C_2). Triplet states were calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of 3. The expected values calculated for S^2 were always smaller than 2.05. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM) approach to model the interaction with the solvent.[16,17] Molecular orbitals were calculated in acetonitrile using gas-phase optimized geometries.

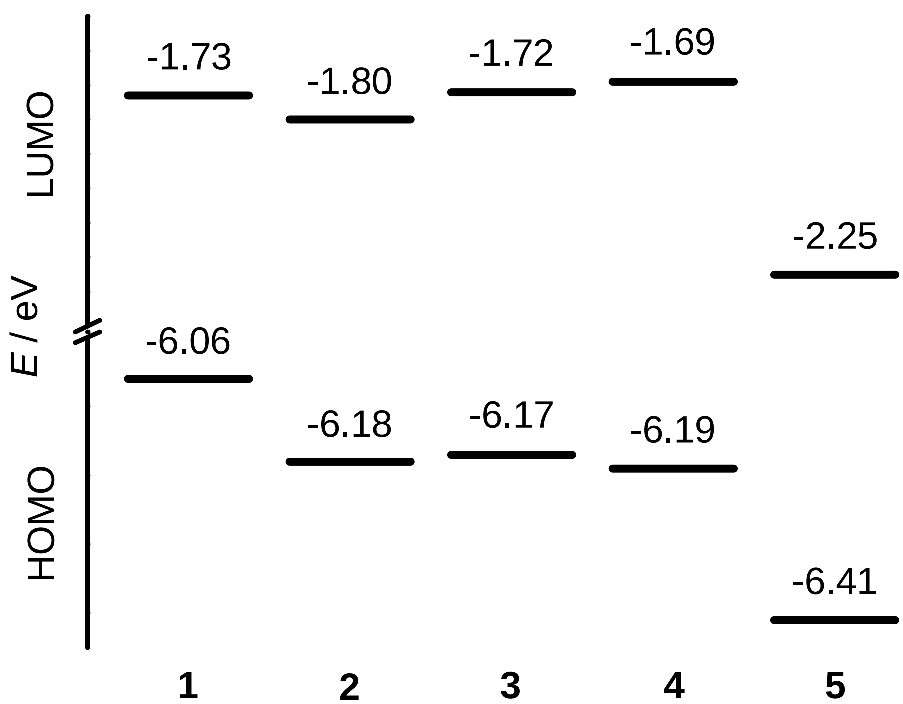


Figure S12. Frontier molecular orbitals of the complexes (HOMO and LUMO; from DFT calculations).

10. References

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11. Cartesian Coordinates of the Computed Species

Complex **1**

S_0				**T_1**			
77	0	0	0.052897	77	0	0	0.135224
6	−1.509244	−0.13327	−1.315664	6	0.343253	1.457287	−1.335306
6	1.509244	0.13327	−1.315664	6	−0.343253	−1.457287	−1.335306
7	0	2.090255	0.238551	7	1.967752	−0.692159	0.295419
7	0	−2.090255	0.238551	7	−1.967752	0.692159	0.295419
6	0.757544	−2.924932	−0.502574	6	−3.020646	0.293542	−0.448679
6	−0.757544	2.924932	−0.502574	6	3.020646	−0.293542	−0.448679
6	−0.824345	−2.593075	1.208284	6	−2.157452	1.635589	1.300627
6	0.824345	2.593075	1.208284	6	2.157452	−1.635589	1.300627
6	0.751577	−4.297624	−0.322571	6	−4.306841	0.753042	−0.238519
6	−0.751577	4.297624	−0.322571	6	4.306841	−0.753042	−0.238519
6	−0.861341	−3.98027	1.426574	6	−3.46021	2.112182	1.556533
6	0.861341	3.98027	1.426574	6	3.46021	−2.112182	1.556533
6	−0.076497	−4.833758	0.668098	6	−4.533842	1.680332	0.804091
6	0.076497	4.833758	0.668098	6	4.533842	−1.680332	0.804091
1	−1.382148	2.457876	−1.252519	1	2.805179	0.431583	−1.224159
1	1.382148	−2.457876	−1.252519	1	−2.805179	−0.431583	−1.224159
1	−1.508755	−4.378054	2.19779	1	−3.610012	2.830392	2.354173
1	1.508755	4.378054	2.19779	1	3.610012	−2.830392	2.354173
1	−1.381461	4.9255	−0.941709	1	5.115052	−0.391302	−0.862951
1	1.381461	−4.9255	−0.941709	1	−5.115052	0.391302	−0.862951
1	−0.106905	−5.904399	0.84303	1	−5.533056	2.049572	1.007221
1	0.106905	5.904399	0.84303	1	5.533056	−2.049572	1.007221
6	−1.407194	−0.25108	1.557295	6	0.276141	1.452477	1.515322
6	1.407194	0.25108	1.557295	6	−0.276141	−1.452477	1.515322
6	−2.148029	0.730009	2.224642	6	1.487756	1.882916	2.083367
6	2.148029	−0.730009	2.224642	6	−1.487756	−1.882916	2.083367
6	−1.610192	−1.600254	1.937243	6	−0.954227	2.068293	1.961558
6	1.610192	1.600254	1.937243	6	0.954227	−2.068293	1.961558
6	−3.052275	0.39268	3.234165	6	1.509133	2.840629	3.089737
6	3.052275	−0.39268	3.234165	6	−1.509133	−2.840629	3.089737
6	−2.520777	−1.938434	2.954159	6	−0.915247	3.032556	2.990889
6	2.520777	1.938434	2.954159	6	0.915247	−3.032556	2.990889
6	−3.240381	−0.94287	3.602324	6	0.297971	3.411337	3.54309
6	3.240381	0.94287	3.602324	6	−0.297971	−3.411337	3.54309
1	−3.612222	1.174776	3.739507	1	2.449495	3.146008	3.536925
1	3.612222	−1.174776	3.739507	1	−2.449495	−3.146008	3.536925
1	−2.671638	−2.973328	3.245719	1	−1.828875	3.490609	3.355162
1	2.671638	2.973328	3.245719	1	1.828875	−3.490609	3.355162
1	−2.023846	1.777368	1.966867	1	2.422454	1.444141	1.750595
1	2.023846	−1.777368	1.966867	1	−2.422454	−1.444141	1.750595
1	3.941605	1.20187	4.388835	1	−0.318439	−4.160788	4.328495
1	−3.941605	−1.20187	4.388835	1	0.318439	4.160788	4.328495
7	−2.417007	−0.23144	−2.046055	7	0.508691	2.321065	−2.101546
7	2.417007	0.23144	−2.046055	7	−0.508691	−2.321065	−2.101546
6	−3.586197	−0.3841	−2.896165	6	0.695903	3.445318	−3.007135
6	3.586197	0.3841	−2.896165	6	−0.695903	−3.445318	−3.007135
6	−4.233957	1.00257	−3.057819	6	2.209303	3.681372	−3.153684
1	−5.122191	0.913865	−3.68858	1	2.376322	4.526964	−3.825832

1	−4.538747	1.4072	−2.089028	1	2.664731	3.914021	−2.187584
1	−3.544216	1.70445	−3.535148	1	2.704908	2.803671	−3.57767
6	−3.1172	−0.937078	−4.252985	6	0.057635	3.071991	−4.356419
1	−2.634897	−1.910773	−4.132961	1	−1.01265	2.879808	−4.243998
1	−3.981902	−1.059155	−4.910392	1	0.186661	3.902177	−5.055615
1	−2.413163	−0.2523	−4.733563	1	0.533169	2.185221	−4.784123
6	−4.54517	−1.364038	−2.196704	6	0	4.665754	−2.378805
1	−4.845815	−0.984305	−1.216879	1	0.436802	4.907426	−1.40655
1	−5.441009	−1.491	−2.810292	1	0.124917	5.52789	−3.039166
1	−4.075464	−2.342249	−2.064509	1	−1.069503	4.481905	−2.24814
6	3.1172	0.937078	−4.252985	6	−0.057635	−3.071991	−4.356419
1	3.981902	1.059155	−4.910392	1	−0.186661	−3.902177	−5.055615
1	2.413163	0.2523	−4.733563	1	−0.533169	−2.185221	−4.784123
1	2.634897	1.910773	−4.132961	1	1.01265	−2.879808	−4.243998
6	4.233957	−1.00257	−3.057819	6	−2.209303	−3.681372	−3.153684
1	5.122191	−0.913865	−3.68858	1	−2.376322	−4.526964	−3.825832
1	4.538747	−1.4072	−2.089028	1	−2.664731	−3.914021	−2.187584
1	3.544216	−1.70445	−3.535148	1	−2.704908	−2.803671	−3.57767
6	4.54517	1.364038	−2.196704	6	0	−4.665754	−2.378805
1	4.075464	2.342249	−2.064509	1	1.069503	−4.481905	−2.24814
1	4.845815	0.984305	−1.216879	1	−0.436802	−4.907426	−1.40655
1	5.441009	1.491	−2.810292	1	−0.124917	−5.52789	−3.039166

Complex **2**

S_0				**T_1**			
77	0	0	0.119129	77	0	0	0.078543
6	1.504439	−0.129397	1.492749	6	1.49761	−0.142627	1.50702
6	−1.504439	0.129397	1.492749	6	−1.49761	0.142627	1.50702
7	0	2.090948	−0.070109	7	0	2.081903	−0.089024
7	0	−2.090948	−0.070109	7	0	−2.081903	−0.089024
6	−0.758088	−2.927828	0.668679	6	−0.697318	−2.944592	0.676091
6	0.758088	2.927828	0.668679	6	0.697318	2.944592	0.676091
6	0.821514	−2.590823	−1.044456	6	0.801742	−2.576892	−1.119973
6	−0.821514	2.590823	−1.044456	6	−0.801742	2.576892	−1.119973
6	−0.755726	−4.299281	0.481924	6	−0.696024	−4.312227	0.465549
6	0.755726	4.299281	0.481924	6	0.696024	4.312227	0.465549
6	0.854311	−3.977467	−1.269712	6	0.807724	−3.966526	−1.37765
6	−0.854311	3.977467	−1.269712	6	−0.807724	3.966526	−1.37765
6	0.068975	−4.832216	−0.513825	6	0.067848	−4.835606	−0.603206
6	−0.068975	4.832216	−0.513825	6	−0.067848	4.835606	−0.603206
1	1.380269	2.463192	1.42214	1	1.285774	2.503306	1.471476
1	−1.380269	−2.463192	1.42214	1	−1.285774	−2.503306	1.471476
1	1.497903	−4.373902	−2.044887	1	1.40703	−4.346458	−2.196604
1	−1.497903	4.373902	−2.044887	1	−1.40703	4.346458	−2.196604
1	1.386063	4.928909	1.098696	1	1.285885	4.953805	1.109233
1	−1.386063	−4.928909	1.098696	1	−1.285885	−4.953805	1.109233
1	0.095606	−5.901874	−0.694964	1	0.074803	−5.900258	−0.808522
1	−0.095606	5.901874	−0.694964	1	−0.074803	5.900258	−0.808522
6	1.4066	−0.247546	−1.383127	6	1.429183	−0.223269	−1.359555
6	−1.4066	0.247546	−1.383127	6	−1.429183	0.223269	−1.359555
6	2.144178	0.740275	−2.03791	6	2.199076	0.769667	−1.962741
6	−2.144178	−0.740275	−2.03791	6	−2.199076	−0.769667	−1.962741
6	1.606705	−1.597415	−1.769237	6	1.593821	−1.593405	−1.799875
6	−1.606705	1.597415	−1.769237	6	−1.593821	1.593405	−1.799875

6	3.03849	0.383015	−3.042285	6	3.082162	0.431764	−2.98093
6	−3.03849	−0.383015	−3.042285	6	−3.082162	−0.431764	−2.98093
6	2.516762	−1.928805	−2.789541	6	2.507061	−1.895861	−2.845509
6	−2.516762	1.928805	−2.789541	6	−2.507061	1.895861	−2.845509
6	3.241587	−0.937827	−3.436304	6	3.247058	−0.892721	−3.434877
6	−3.241587	0.937827	−3.436304	6	−3.247058	0.892721	−3.434877
9	3.737877	1.353017	−3.657451	9	3.80712	1.395688	−3.569498
9	−3.737877	−1.353017	−3.657451	9	−3.80712	−1.395688	−3.569498
1	2.668088	−2.960732	−3.089805	1	2.640673	−2.916402	−3.186823
1	−2.668088	2.960732	−3.089805	1	−2.640673	2.916402	−3.186823
1	2.042924	1.792488	−1.795792	1	2.113111	1.812132	−1.678068
1	−2.042924	−1.792488	−1.795792	1	−2.113111	−1.812132	−1.678068
1	−3.947823	1.164025	−4.22648	1	−3.954686	1.095024	−4.23116
1	3.947823	−1.164025	−4.22648	1	3.954686	−1.095024	−4.23116
7	2.405683	−0.22278	2.231031	7	2.382038	−0.247146	2.261357
7	−2.405683	0.22278	2.231031	7	−2.382038	0.247146	2.261357
6	3.565008	−0.366211	3.097435	6	3.522375	−0.399632	3.152781
6	−3.565008	0.366211	3.097435	6	−3.522375	0.399632	3.152781
6	4.201543	1.025177	3.26391	6	4.150181	0.991238	3.351856
1	5.081681	0.943512	3.906841	1	5.015258	0.902483	4.013954
1	4.517427	1.429146	2.298429	1	4.487145	1.408942	2.399514
1	3.501258	1.72386	3.73028	1	3.437442	1.682082	3.810663
6	3.080481	−0.918929	4.448981	6	3.005698	−0.972121	4.484085
1	2.606435	−1.896142	4.325011	1	2.537497	−1.948639	4.335319
1	3.937024	−1.033793	5.118236	1	3.846492	−1.094126	5.171678
1	2.365933	−0.237381	4.91835	1	2.278879	−0.298266	4.945582
6	4.539177	−1.341979	2.413328	6	4.513032	−1.364775	2.47753
1	4.854108	−0.961238	1.438427	1	4.853847	−0.967928	1.517864
1	5.425806	−1.463925	3.041121	1	5.382856	−1.496585	3.126393
1	4.07674	−2.322737	2.27487	1	4.054546	−2.342961	2.311181
6	−3.080481	0.918929	4.448981	6	−3.005698	0.972121	4.484085
1	−3.937024	1.033793	5.118236	1	−3.846492	1.094126	5.171678
1	−2.365933	0.237381	4.91835	1	−2.278879	0.298266	4.945582
1	−2.606435	1.896142	4.325011	1	−2.537497	1.948639	4.335319
6	−4.201543	−1.025177	3.26391	6	−4.150181	−0.991238	3.351856
1	−5.081681	−0.943512	3.906841	1	−5.015258	−0.902483	4.013954
1	−4.517427	−1.429146	2.298429	1	−4.487145	−1.408942	2.399514
1	−3.501258	−1.72386	3.73028	1	−3.437442	−1.682082	3.810663
6	−4.539177	1.341979	2.413328	6	−4.513032	1.364775	2.47753
1	−4.07674	2.322737	2.27487	1	−4.054546	2.342961	2.311181
1	−4.854108	0.961238	1.438427	1	−4.853847	0.967928	1.517864
1	−5.425806	1.463925	3.041121	1	−5.382856	1.496585	3.126393

Complex **3**

S_0				T_1			
77	0	0	0.253845	77	0	0	0.240737
6	1.503647	−0.129456	1.62361	6	1.497825	−0.142376	1.661045
6	−1.503647	0.129456	1.62361	6	−1.497825	0.142376	1.661045
7	0	2.089145	0.06059	7	0	2.080559	0.066026
7	0	−2.089145	0.06059	7	0	−2.080559	0.066026
6	−0.754869	−2.938127	0.789662	6	−0.695492	−2.953298	0.817201
6	0.754869	2.938127	0.789662	6	0.695492	2.953298	0.817201
6	0.815945	−2.59308	−0.911002	6	0.796337	−2.575872	−0.963541
6	−0.815945	2.59308	−0.911002	6	−0.796337	2.575872	−0.963541

6	−0.749061	−4.303777	0.5907	6	−0.691074	−4.317459	0.594311
6	0.749061	4.303777	0.5907	6	0.691074	4.317459	0.594311
6	0.847485	−3.977963	−1.143031	6	0.801639	−3.966593	−1.229414
6	−0.847485	3.977963	−1.143031	6	−0.801639	3.966593	−1.229414
6	0.069993	−4.868487	−0.407804	6	0.069704	−4.868847	−0.477092
6	−0.069993	4.868487	−0.407804	6	−0.069704	4.868847	−0.477092
1	1.379809	2.485688	1.548705	1	1.287494	2.525052	1.617563
1	−1.379809	−2.485688	1.548705	1	−1.287494	−2.525052	1.617563
1	1.49783	−4.345656	−1.923769	1	1.406992	−4.316949	−2.054083
1	−1.49783	4.345656	−1.923769	1	−1.406992	4.316949	−2.054083
1	1.38636	4.920734	1.212637	1	1.288803	4.947285	1.241848
1	−1.38636	−4.920734	1.212637	1	−1.288803	−4.947285	1.241848
6	1.407111	−0.249874	−1.248727	6	1.426047	−0.223433	−1.204181
6	−1.407111	0.249874	−1.248727	6	−1.426047	0.223433	−1.204181
6	2.146468	0.738426	−1.901295	6	2.191225	0.768724	−1.811659
6	−2.146468	−0.738426	−1.901295	6	−2.191225	−0.768724	−1.811659
6	1.605768	−1.59979	−1.635863	6	1.589641	−1.59471	−1.643471
6	−1.605768	1.59979	−1.635863	6	−1.589641	1.59471	−1.643471
6	3.041737	0.382074	−2.904728	6	3.074194	0.429934	−2.831563
6	−3.041737	−0.382074	−2.904728	6	−3.074194	−0.429934	−2.831563
6	2.516941	−1.929496	−2.654917	6	2.505211	−1.897881	−2.689101
6	−2.516941	1.929496	−2.654917	6	−2.505211	1.897881	−2.689101
6	3.244061	−0.938092	−3.299683	6	3.242454	−0.89478	−3.2815
6	−3.244061	0.938092	−3.299683	6	−3.242454	0.89478	−3.2815
9	3.743541	1.353066	−3.51834	9	3.795765	1.395974	−3.423648
9	−3.743541	−1.353066	−3.51834	9	−3.795765	−1.395974	−3.423648
1	2.668387	−2.961052	−2.956406	1	2.641695	−2.919024	−3.027193
1	−2.668387	2.961052	−2.956406	1	−2.641695	2.919024	−3.027193
1	2.044459	1.790124	−1.657057	1	2.103447	1.811782	−1.529393
1	−2.044459	−1.790124	−1.657057	1	−2.103447	−1.811782	−1.529393
1	−3.951404	1.164389	−4.088918	1	−3.950181	1.097858	−4.07755
1	3.951404	−1.164389	−4.088918	1	3.950181	−1.097858	−4.07755
7	2.406402	−0.223589	2.360557	7	2.384322	−0.251614	2.412987
7	−2.406402	0.223589	2.360557	7	−2.384322	0.251614	2.412987
6	3.5664	−0.374941	3.222888	6	3.527777	−0.417856	3.296357
6	−3.5664	0.374941	3.222888	6	−3.527777	0.417856	3.296357
6	3.987302	1.026983	3.698166	6	3.944374	0.977209	3.794438
1	4.860658	0.939409	4.34966	1	4.805118	0.878426	4.46089
1	4.254584	1.663268	2.85015	1	4.229539	1.622055	2.958888
1	3.184188	1.507242	4.263954	1	3.132844	1.454374	4.350599
6	3.158343	−1.262213	4.412044	6	3.091254	−1.317319	4.465967
1	2.835176	−2.24909	4.070491	1	2.77007	−2.298329	4.10631
1	4.016779	−1.391301	5.076318	1	3.936197	−1.458523	5.14485
1	2.346414	−0.80359	4.982775	1	2.271149	−0.860962	5.026683
6	4.681375	−1.035982	2.392785	6	4.654078	−1.075034	2.478671
1	4.950556	−0.415825	1.533954	1	4.943503	−0.445229	1.633544
1	5.568331	−1.165432	3.018787	1	5.52786	−1.216699	3.120256
1	4.367272	−2.018191	2.030235	1	4.341962	−2.051077	2.098303
6	−3.158343	1.262213	4.412044	6	−3.091254	1.317319	4.465967
1	−4.016779	1.391301	5.076318	1	−3.936197	1.458523	5.14485
1	−2.346414	0.80359	4.982775	1	−2.271149	0.860962	5.026683
1	−2.835176	2.24909	4.070491	1	−2.77007	2.298329	4.10631
6	−3.987302	−1.026983	3.698166	6	−3.944374	−0.977209	3.794438
1	−4.860658	−0.939409	4.34966	1	−4.805118	−0.878426	4.46089
1	−4.254584	−1.663268	2.85015	1	−4.229539	−1.622055	2.958888

1	−3.184188	−1.507242	4.263954	1	−3.132844	−1.454374	4.350599
6	−4.681375	1.035982	2.392785	6	−4.654078	1.075034	2.478671
1	−4.367272	2.018191	2.030235	1	−4.341962	2.051077	2.098303
1	−4.950556	0.415825	1.533954	1	−4.943503	0.445229	1.633544
1	−5.568331	1.165432	3.018787	1	−5.52786	1.216699	3.120256
6	−0.079413	6.384808	−0.640525	6	−0.049874	6.377712	−0.7422
6	1.354196	6.852153	−0.989834	6	1.404812	6.82479	−1.028776
1	1.714902	6.371917	−1.904808	1	1.802847	6.3269	−1.918232
1	−0.72469	6.344827	−2.741034	1	−0.592558	6.295631	−2.869007
1	1.361394	7.93448	−1.151302	1	1.437179	7.905374	−1.200092
6	−1.020604	6.794303	−1.787797	6	−0.930041	6.770247	−1.941562
1	−2.061221	6.521789	−1.582446	1	−1.981781	6.509071	−1.780208
1	−1.564948	6.776261	0.929122	1	−1.603168	6.830868	0.744573
1	−0.988187	7.879788	−1.915511	1	−0.88485	7.852633	−2.091045
6	−0.550907	7.087455	0.657439	6	−0.571769	7.117853	0.51564
1	0.107688	6.873234	1.504318	1	0.039564	6.907802	1.398264
1	2.066478	6.63365	−0.188932	1	2.072639	6.604423	−0.190844
1	−0.5584	8.171867	0.510527	1	−0.550325	8.199473	0.349053
6	0.079413	−6.384808	−0.640525	6	0.049874	−6.377712	−0.7422
6	1.020604	−6.794303	−1.787797	6	0.930041	−6.770247	−1.941562
1	2.061221	−6.521789	−1.582446	1	1.981781	−6.509071	−1.780208
1	0.988187	−7.879788	−1.915511	1	0.88485	−7.852633	−2.091045
1	0.72469	−6.344827	−2.741034	1	0.592558	−6.295631	−2.869007
6	0.550907	−7.087455	0.657439	6	0.571769	−7.117853	0.51564
1	−0.107688	−6.873234	1.504318	1	−0.039564	−6.907802	1.398264
1	0.5584	−8.171867	0.510527	1	0.550325	−8.199473	0.349053
1	1.564948	−6.776261	0.929122	1	1.603168	−6.830868	0.744573
6	−1.354196	−6.852153	−0.989834	6	−1.404812	−6.82479	−1.028776
1	−1.714902	−6.371917	−1.904808	1	−1.802847	−6.3269	−1.918232
1	−1.361394	−7.93448	−1.151302	1	−1.437179	−7.905374	−1.200092
1	−2.066478	−6.63365	−0.188932	1	−2.072639	−6.604423	−0.190844

Complex **4**

S_0				T_1			
77	0	0	0.230184	77	0	0	0.210771
6	1.500673	−0.12943	1.602178	6	1.499097	−0.137675	1.631437
6	−1.500673	0.12943	1.602178	6	−1.499097	0.137675	1.631437
7	0	2.091203	0.037328	7	0	2.083015	0.034463
7	0	−2.091203	0.037328	7	0	−2.083015	0.034463
6	−0.754469	−2.938653	0.773663	6	−0.705136	−2.947061	0.785641
6	0.754469	2.938653	0.773663	6	0.705136	2.947061	0.785641
6	0.81353	−2.596401	−0.938005	6	0.795305	−2.574262	−0.99546
6	−0.81353	2.596401	−0.938005	6	−0.795305	2.574262	−0.99546
6	−0.757515	−4.301427	0.586289	6	−0.71356	−4.31123	0.573389
6	0.757515	4.301427	0.586289	6	0.71356	4.31123	0.573389
6	0.85212	−3.976789	−1.178658	6	0.805751	−3.966281	−1.271412
6	−0.85212	3.976789	−1.178658	6	−0.805751	3.966281	−1.271412
6	0.064438	−4.844036	−0.421202	6	0.055345	−4.837308	−0.498317
6	−0.064438	4.844036	−0.421202	6	−0.055345	4.837308	−0.498317
1	1.375307	2.48264	1.53351	1	1.295789	2.512103	1.582711
1	−1.375307	−2.48264	1.53351	1	−1.295789	−2.512103	1.582711
1	1.4961	−4.35401	−1.959752	1	1.406472	−4.329741	−2.092896
1	−1.4961	4.35401	−1.959752	1	−1.406472	4.329741	−2.092896
1	1.377313	4.951462	1.191174	1	1.302716	4.973066	1.195024

1	−1.377313	−4.951462	1.191174	1	−1.302716	−4.973066	1.195024
6	1.404748	−0.251999	−1.273407	6	1.425496	−0.219888	−1.233035
6	−1.404748	0.251999	−1.273407	6	−1.425496	0.219888	−1.233035
6	2.143795	0.736469	−1.926797	6	2.187705	0.77183	−1.842278
6	−2.143795	−0.736469	−1.926797	6	−2.187705	−0.77183	−1.842278
6	1.60178	−1.601331	−1.66355	6	1.588307	−1.592995	−1.672453
6	−1.60178	1.601331	−1.66355	6	−1.588307	1.592995	−1.672453
6	3.036101	0.381433	−2.932975	6	3.070437	0.433233	−2.864192
6	−3.036101	−0.381433	−2.932975	6	−3.070437	−0.433233	−2.864192
6	2.510057	−1.929716	−2.685439	6	2.505451	−1.896314	−2.718627
6	−2.510057	1.929716	−2.685439	6	−2.505451	1.896314	−2.718627
6	3.236396	−0.938425	−3.330779	6	3.24055	−0.892209	−3.311843
6	−3.236396	0.938425	−3.330779	6	−3.24055	0.892209	−3.311843
9	3.737027	1.352313	−3.547206	9	3.789399	1.399986	−3.458824
9	−3.737027	−1.352313	−3.547206	9	−3.789399	−1.399986	−3.458824
1	2.660675	−2.960794	−2.989649	1	2.644507	−2.917448	−3.055767
1	−2.660675	2.960794	−2.989649	1	−2.644507	2.917448	−3.055767
1	2.043468	1.787625	−1.67971	1	2.099577	1.814892	−1.56039
1	−2.043468	−1.787625	−1.67971	1	−2.099577	−1.814892	−1.56039
1	−3.941571	1.163949	−4.122157	1	−3.948887	1.094646	−4.107609
1	3.941571	−1.163949	−4.122157	1	3.948887	−1.094646	−4.107609
7	2.400427	−0.217758	2.343589	7	2.385527	−0.237525	2.384732
7	−2.400427	0.217758	2.343589	7	−2.385527	0.237525	2.384732
6	3.557006	−0.355983	3.213004	6	3.529711	−0.382177	3.271162
6	−3.557006	0.355983	3.213004	6	−3.529711	0.382177	3.271162
6	4.20291	1.033216	3.36086	6	4.143853	1.014055	3.475619
1	5.08196	0.955269	4.005846	1	5.011809	0.931372	4.134789
1	4.521735	1.421799	2.390052	1	4.473347	1.439967	2.524313
1	3.506557	1.742979	3.81631	1	3.425124	1.695092	3.939632
6	3.067885	−0.886109	4.571961	6	3.024423	−0.966876	4.601554
1	2.58642	−1.861336	4.461242	1	2.56621	−1.947578	4.449398
1	3.922865	−0.997853	5.243853	1	3.868763	−1.082991	5.285878
1	2.357732	−0.192863	5.030819	1	2.291658	−0.303412	5.068595
6	4.526236	−1.347767	2.545137	6	4.528771	−1.333133	2.588164
1	4.844191	−0.983511	1.564877	1	4.860961	−0.928211	1.628882
1	5.411633	−1.465849	3.175509	1	5.402602	−1.458409	3.232991
1	4.05764	−2.327534	2.420639	1	4.080132	−2.315376	2.418963
6	−3.067885	0.886109	4.571961	6	−3.024423	0.966876	4.601554
1	−3.922865	0.997853	5.243853	1	−3.868763	1.082991	5.285878
1	−2.357732	0.192863	5.030819	1	−2.291658	0.303412	5.068595
1	−2.58642	1.861336	4.461242	1	−2.56621	1.947578	4.449398
6	−4.20291	−1.033216	3.36086	6	−4.143853	−1.014055	3.475619
1	−5.08196	−0.955269	4.005846	1	−5.011809	−0.931372	4.134789
1	−4.521735	−1.421799	2.390052	1	−4.473347	−1.439967	2.524313
1	−3.506557	−1.742979	3.81631	1	−3.425124	−1.695092	3.939632
6	−4.526236	1.347767	2.545137	6	−4.528771	1.333133	2.588164
1	−4.05764	2.327534	2.420639	1	−4.080132	2.315376	2.418963
1	−4.844191	0.983511	1.564877	1	−4.860961	0.928211	1.628882
1	−5.411633	1.465849	3.175509	1	−5.402602	1.458409	3.232991
8	0.018232	−6.17693	−0.566266	8	−0.018566	−6.171314	−0.663556
6	0.815233	−6.797049	−1.580334	6	0.715374	−6.773224	−1.73094
1	0.533121	−6.438975	−2.576144	1	0.388419	−6.385019	−2.702047
1	1.881935	−6.618433	−1.407443	1	1.79235	−6.609855	−1.610569
1	0.60769	−7.863463	−1.504166	1	0.50041	−7.839554	−1.673529
8	−0.018232	6.17693	−0.566266	8	0.018566	6.171314	−0.663556

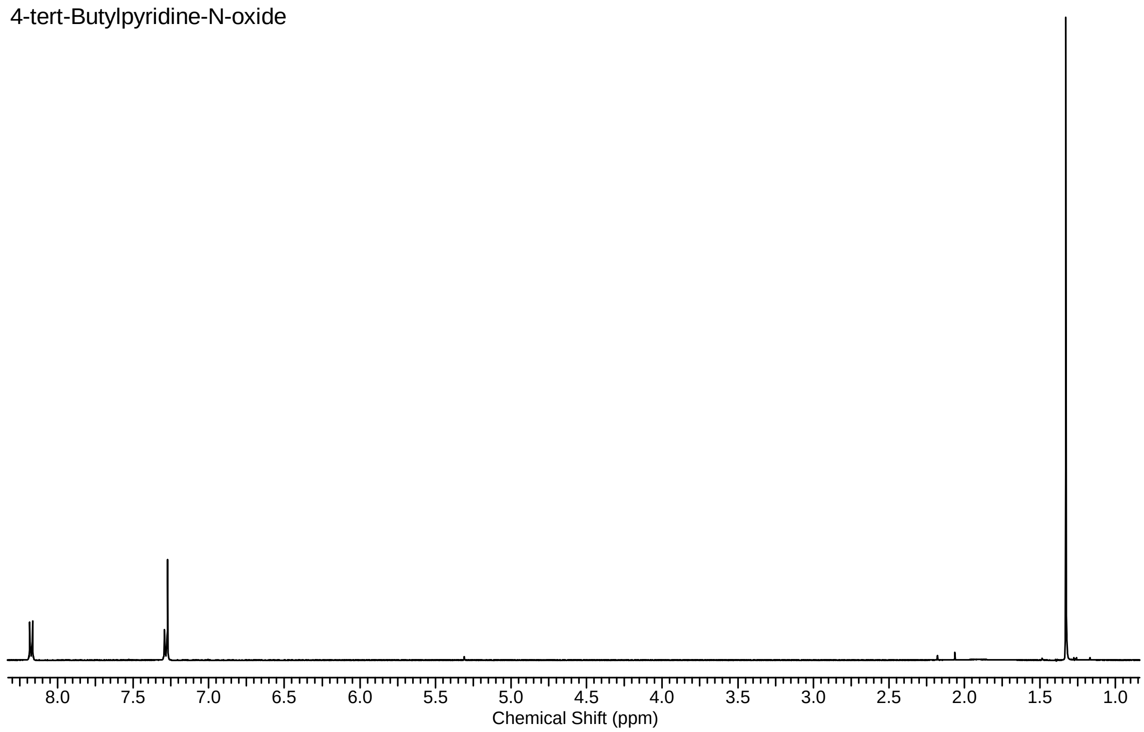
6	−0.815233	6.797049	−1.580334	6	−0.715374	6.773224	−1.73094
1	−0.533121	6.438975	−2.576144	1	−0.388419	6.385019	−2.702047
1	−1.881935	6.618433	−1.407443	1	−1.79235	6.609855	−1.610569
1	−0.60769	7.863463	−1.504166	1	−0.50041	7.839554	−1.673529

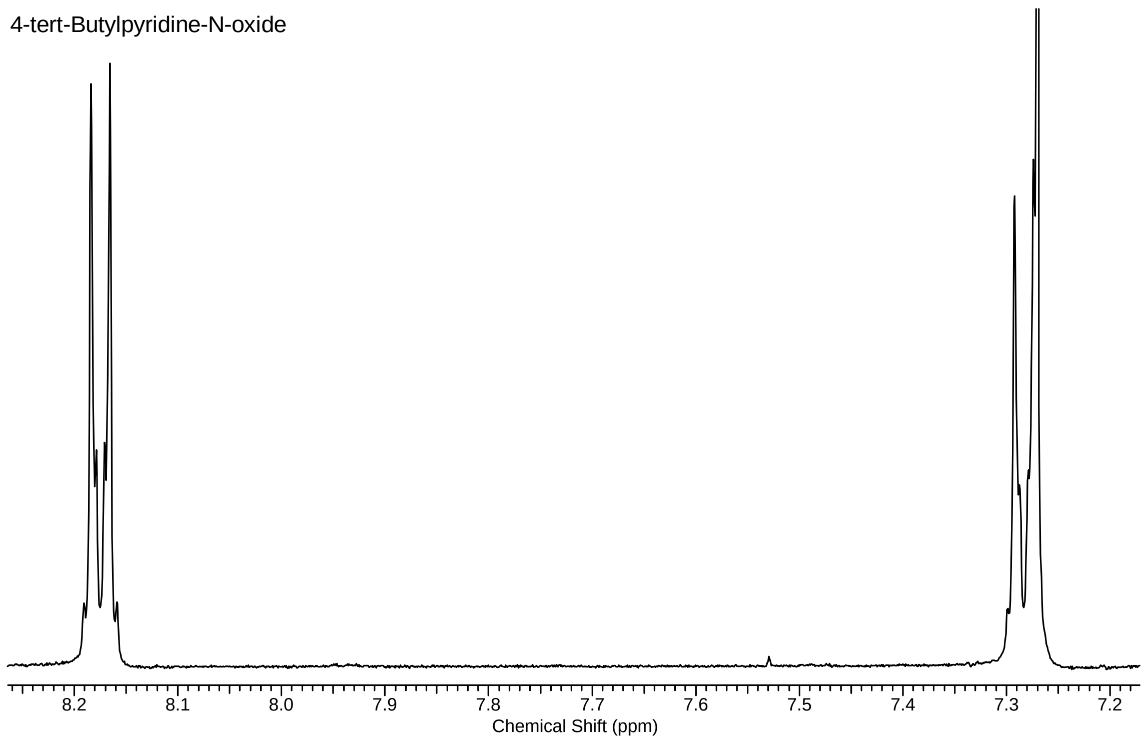
Complex **5**

S_0				**T_1**			
77	0	0	0.140597	77	0	0	0.198396
6	1.49405	−0.192598	−1.243306	6	1.487406	−0.171712	−1.250309
6	−1.49405	0.192598	−1.243306	6	−1.487406	0.171712	−1.250309
7	−0.367229	−2.053998	0.318498	7	−0.346329	−2.051215	0.352444
7	0.367229	2.053998	0.318498	7	0.346329	2.051215	0.352444
6	−0.240611	2.997276	−0.423755	6	−0.221814	3.000728	−0.406921
6	0.240611	−2.997276	−0.423755	6	0.221814	−3.000728	−0.406921
6	1.269955	2.413036	1.284065	6	1.236094	2.416771	1.362453
6	−1.269955	−2.413036	1.284065	6	−1.236094	−2.416771	1.362453
6	0	4.348851	−0.254442	6	0	4.352419	−0.213404
6	0	−4.348851	−0.254442	6	0	−4.352419	−0.213404
6	1.547133	3.778515	1.486845	6	1.472968	3.789839	1.599944
6	−1.547133	−3.778515	1.486845	6	−1.472968	−3.789839	1.599944
6	0.917787	4.746878	0.727337	6	0.865766	4.760264	0.83324
6	−0.917787	−4.746878	0.727337	6	−0.865766	−4.760264	0.83324
1	0.935345	−2.649432	−1.173725	1	0.887643	−2.662445	−1.187873
1	−0.935345	2.649432	−1.173725	1	−0.887643	2.662445	−1.187873
1	2.260163	4.068935	2.247852	1	2.144607	4.078864	2.399489
1	−2.260163	−4.068935	2.247852	1	−2.144607	−4.078864	2.399489
1	1.133696	5.798718	0.882272	1	1.046366	5.812791	1.019312
1	−1.133696	−5.798718	0.882272	1	−1.046366	−5.812791	1.019312
6	1.429016	0.008188	1.640754	6	1.454965	−0.009022	1.621346
6	−1.429016	−0.008188	1.640754	6	−1.454965	0.009022	1.621346
6	1.980461	−1.087068	2.306396	6	2.053057	−1.115016	2.226614
6	−1.980461	1.087068	2.306396	6	−2.053057	1.115016	2.226614
6	1.867522	1.306116	2.015135	6	1.859622	1.316969	2.043669
6	−1.867522	−1.306116	2.015135	6	−1.859622	−1.316969	2.043669
6	2.925054	−0.883718	3.308284	6	2.992172	−0.924231	3.230497
6	−2.925054	0.883718	3.308284	6	−2.992172	0.924231	3.230497
6	2.824203	1.481454	3.033192	6	2.821773	1.468493	3.073653
6	−2.824203	−1.481454	3.033192	6	−2.821773	−1.468493	3.073653
6	3.361159	0.384549	3.689664	6	3.387131	0.357521	3.666317
6	−3.361159	−0.384549	3.689664	6	−3.387131	−0.357521	3.666317
9	3.439277	−1.95453	3.933955	9	3.548387	−1.990006	3.822867
9	−3.439277	1.95453	3.933955	9	−3.548387	1.990006	3.822867
1	3.156866	2.47322	3.322242	1	3.132062	2.454038	3.402675
1	−3.156866	−2.47322	3.322242	1	−3.132062	−2.454038	3.402675
1	1.694178	−2.107457	2.076379	1	1.787604	−2.129796	1.953292
1	−1.694178	2.107457	2.076379	1	−1.787604	2.129796	1.953292
1	−4.097418	−0.488367	4.477892	1	−4.129279	−0.443315	4.45217
1	4.097418	0.488367	4.477892	1	4.129279	0.443315	4.45217
7	2.376275	−0.366738	−1.988589	7	2.347716	−0.338013	−2.019569
7	−2.376275	0.366738	−1.988589	7	−2.347716	0.338013	−2.019569
6	3.495597	−0.627902	−2.882979	6	3.446761	−0.599761	−2.941106
6	−3.495597	0.627902	−2.882979	6	−3.446761	0.599761	−2.941106
6	4.054785	−2.018712	−2.530274	6	4.06526	−1.9535	−2.546283
1	4.895458	−2.244217	−3.191556	1	4.889044	−2.180439	−3.227954

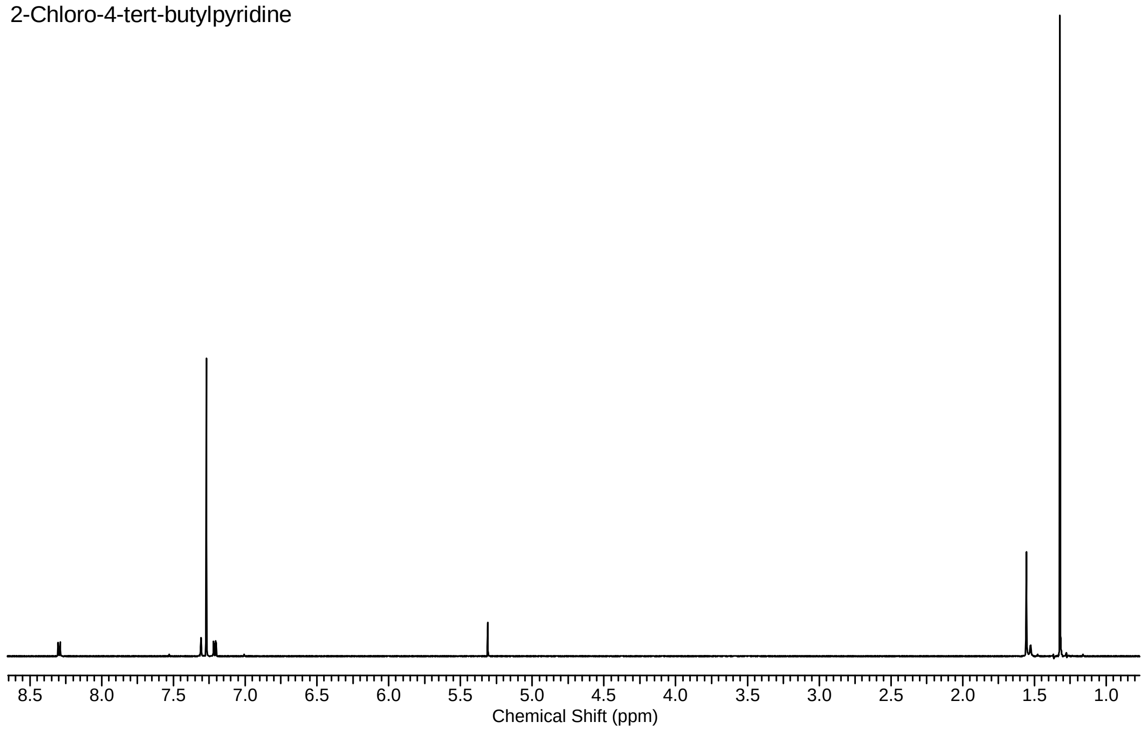
1	4.413019	−2.045394	−1.497816	1	4.461	−1.920428	−1.527817
1	3.298818	−2.798003	−2.661809	1	3.332418	−2.762337	−2.613833
6	2.964745	−0.590114	−4.326351	6	2.863167	−0.645506	−4.363854
1	2.540492	0.389145	−4.563284	1	2.395256	0.306633	−4.627655
1	3.790167	−0.783279	−5.016296	1	3.671068	−0.83989	−5.073751
1	2.199567	−1.354897	−4.483948	1	2.122673	−1.444054	−4.459816
6	4.54726	0.470123	−2.646793	6	4.4634	0.545006	−2.790461
1	4.89608	0.461646	−1.611021	1	4.851141	0.593149	−1.769658
1	5.403994	0.291648	−3.301696	1	5.301059	0.368924	−3.470103
1	4.13975	1.458626	−2.87446	1	4.011496	1.507917	−3.042504
6	−2.964745	0.590114	−4.326351	6	−2.863167	0.645506	−4.363854
1	−3.790167	0.783279	−5.016296	1	−3.671068	0.83989	−5.073751
1	−2.199567	1.354897	−4.483948	1	−2.122673	1.444054	−4.459816
1	−2.540492	−0.389145	−4.563284	1	−2.395256	−0.306633	−4.627655
6	−4.054785	2.018712	−2.530274	6	−4.06526	1.9535	−2.546283
1	−4.895458	2.244217	−3.191556	1	−4.889044	2.180439	−3.227954
1	−4.413019	2.045394	−1.497816	1	−4.461	1.920428	−1.527817
1	−3.298818	2.798003	−2.661809	1	−3.332418	2.762337	−2.613833
6	−4.54726	−0.470123	−2.646793	6	−4.4634	−0.545006	−2.790461
1	−4.13975	−1.458626	−2.87446	1	−4.011496	−1.507917	−3.042504
1	−4.89608	−0.461646	−1.611021	1	−4.851141	−0.593149	−1.769658
1	−5.403994	−0.291648	−3.301696	1	−5.301059	−0.368924	−3.470103
6	−0.749058	5.360976	−1.079349	6	−0.681204	5.366802	−1.08266
9	−1.318609	4.786459	−2.166629	9	−1.4411	4.778258	−2.040586
9	−1.734616	5.940982	−0.367765	9	−1.488705	6.171374	−0.362005
9	0.069301	6.338816	−1.50844	9	0.213447	6.160473	−1.705915
6	0.749058	−5.360976	−1.079349	6	0.681204	−5.366802	−1.08266
9	1.734616	−5.940982	−0.367765	9	1.488705	−6.171374	−0.362005
9	−0.069301	−6.338816	−1.50844	9	−0.213447	−6.160473	−1.705915
9	1.318609	−4.786459	−2.166629	9	1.4411	−4.778258	−2.040586

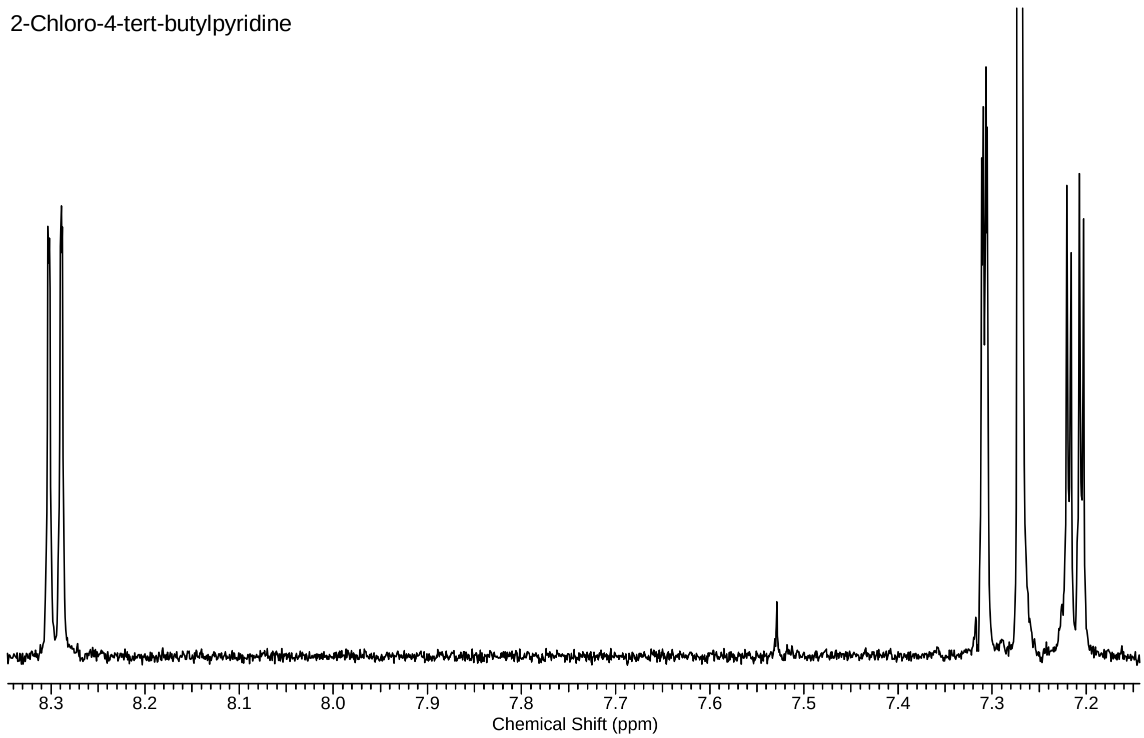
12. NMR Spectra: 2-Chloropyridines (^{1}H)



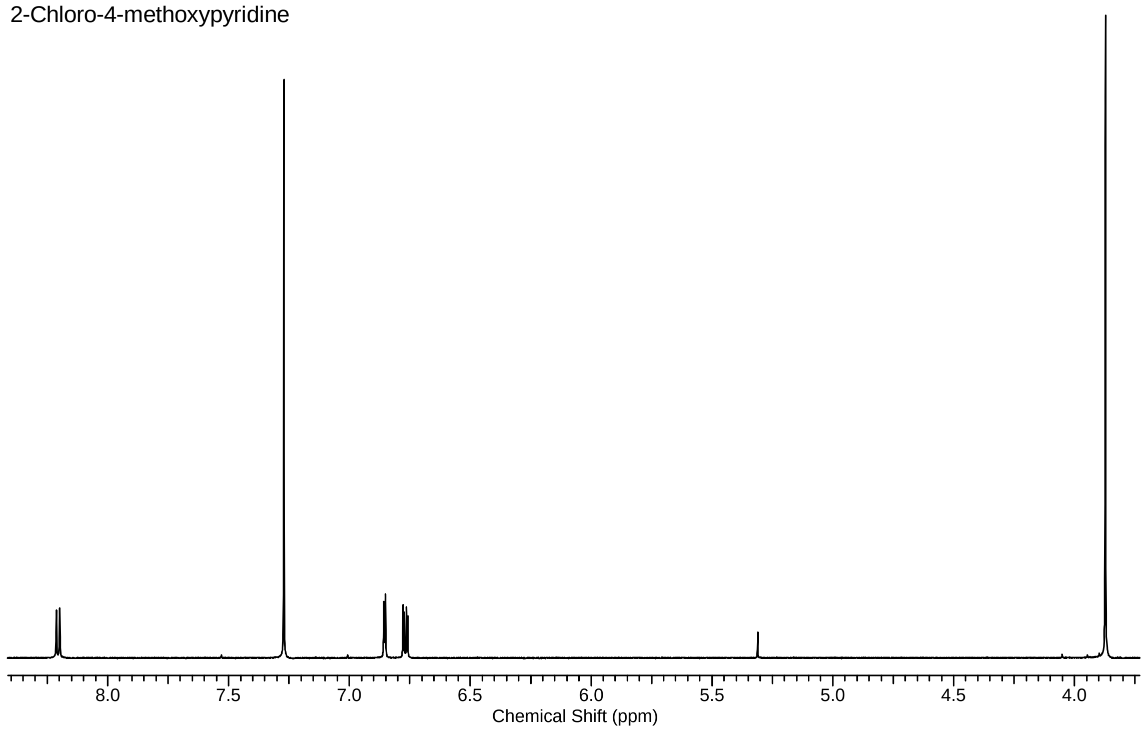


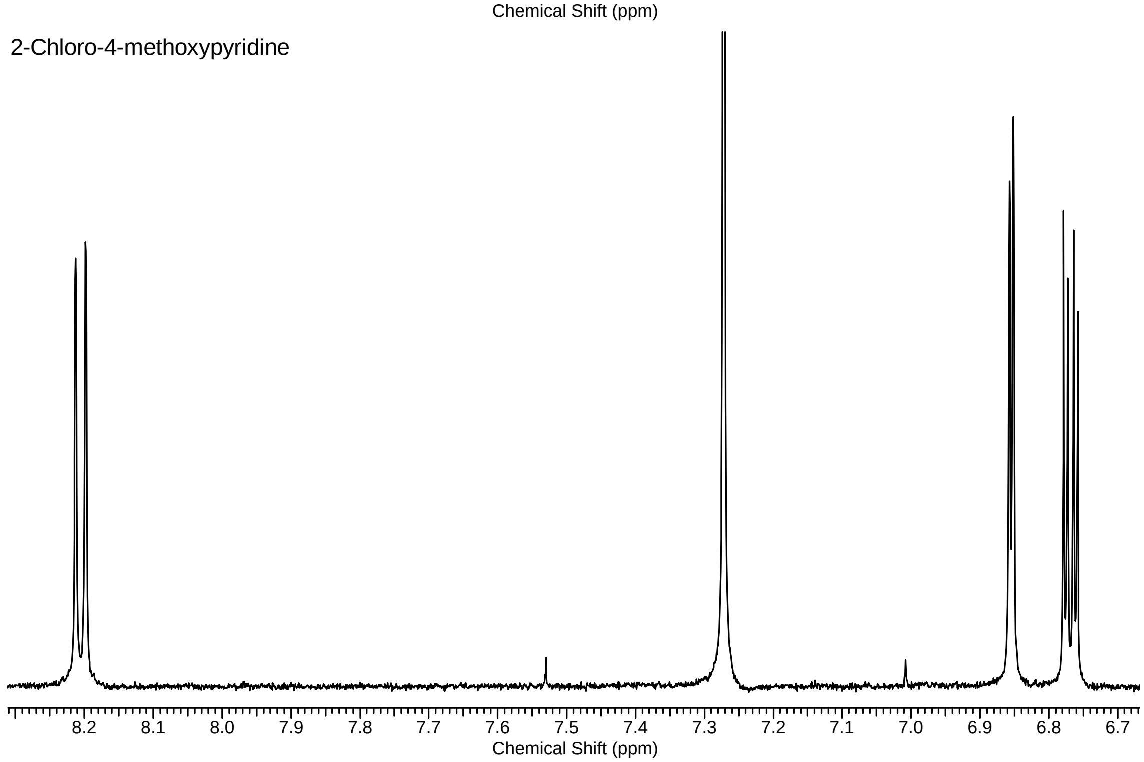
^{1}H NMR Spectrum of 4-*tert*-butylpyridine-N-oxide in $CDCl_3$ (top, complete; bottom, arom. H).





^{1}H NMR Spectrum of 2-chloro-4-*tert*-butylpyridine in $CDCl_3$ (top, complete; bottom, arom. H).

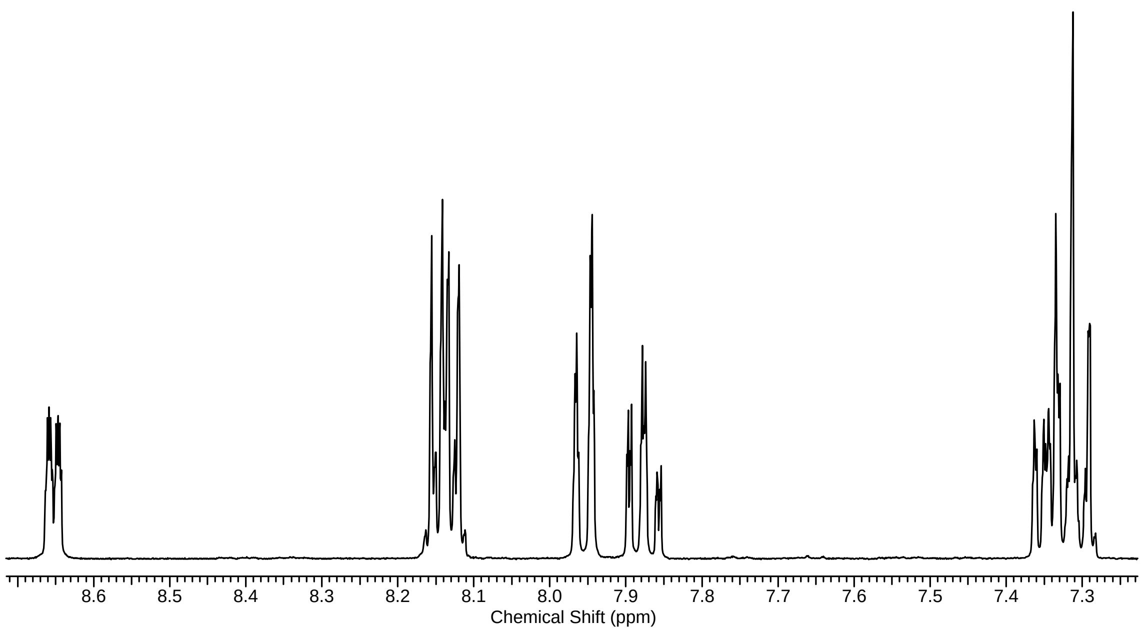




^{1}**H NMR Spectrum** of 2-chloro-4-methoxypyridine in $CDCl_3$ (top, complete; bottom, arom. H).

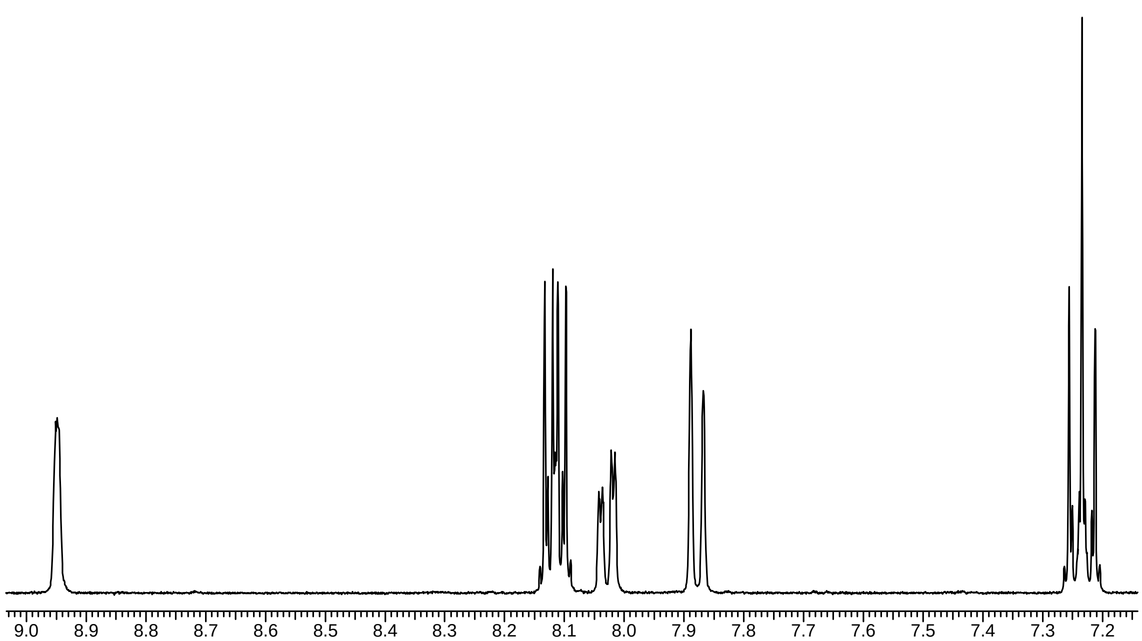
13. NMR Spectra: 2-Phenylpyridines (^{1}H, ^{13}C, ^{19}F)

2-(4-Fluorophenyl)pyridine

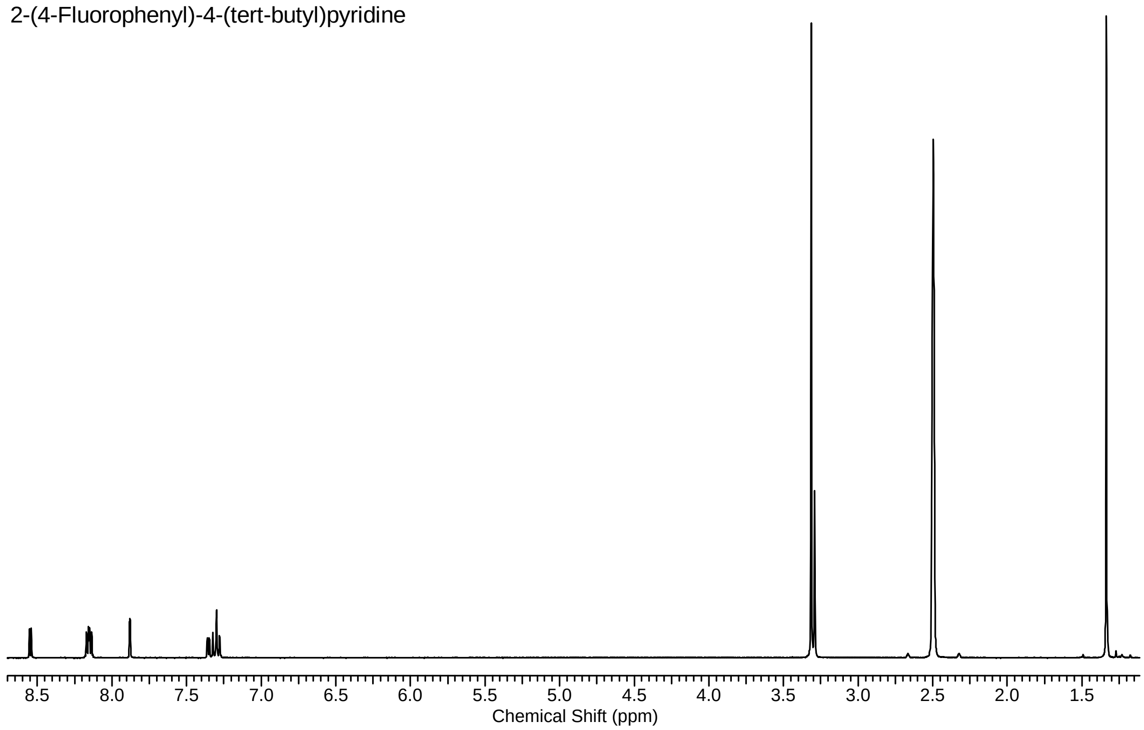


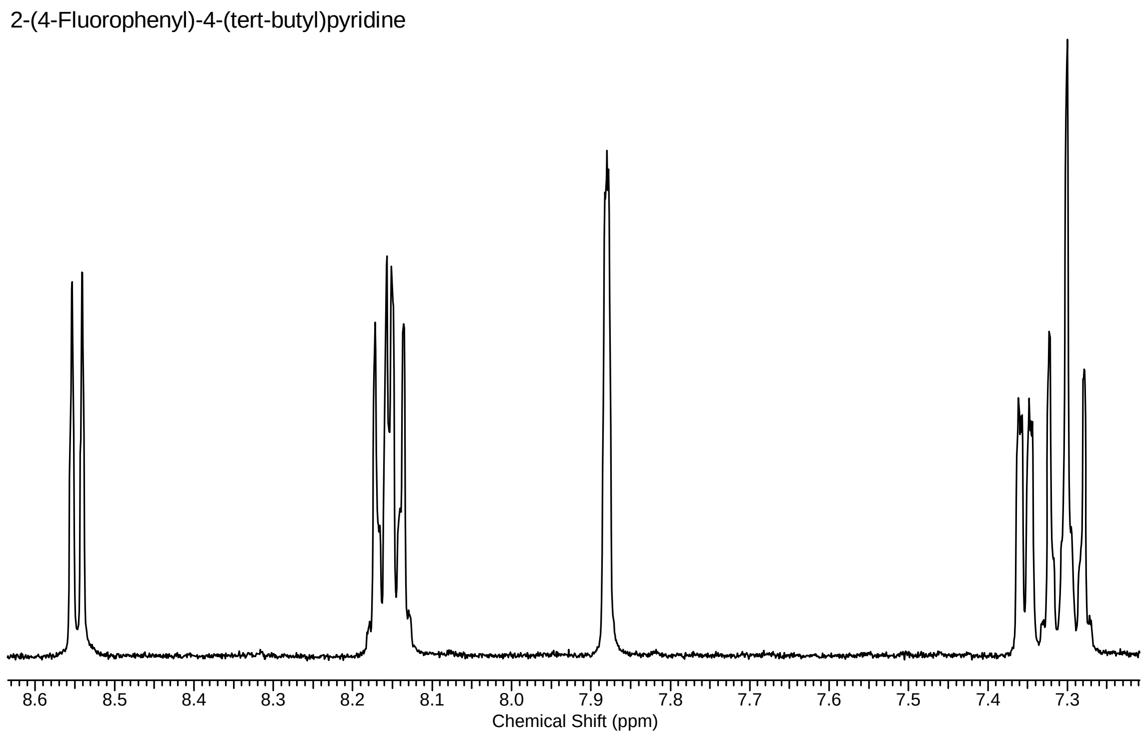
^{1}H NMR Spectrum of 2-(4′-fluorophenyl)pyridine in DMSO-d_6.

2-(4-Fluorophenyl)-5-(trifluoromethyl)pyridine

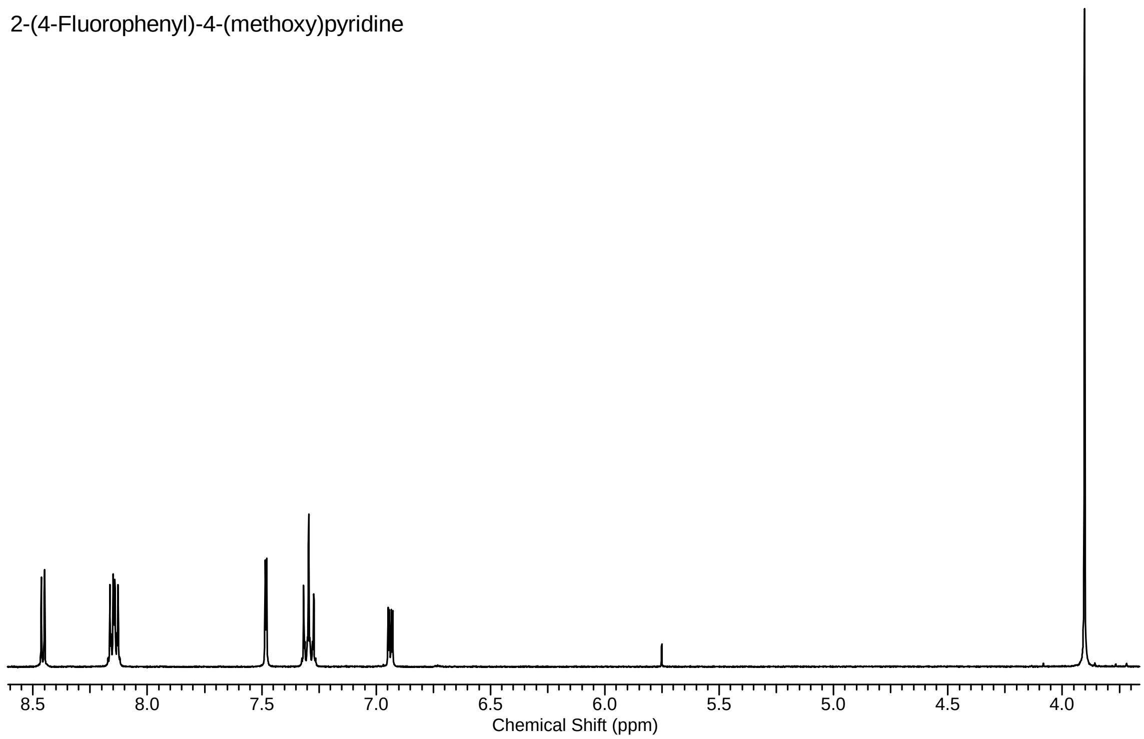


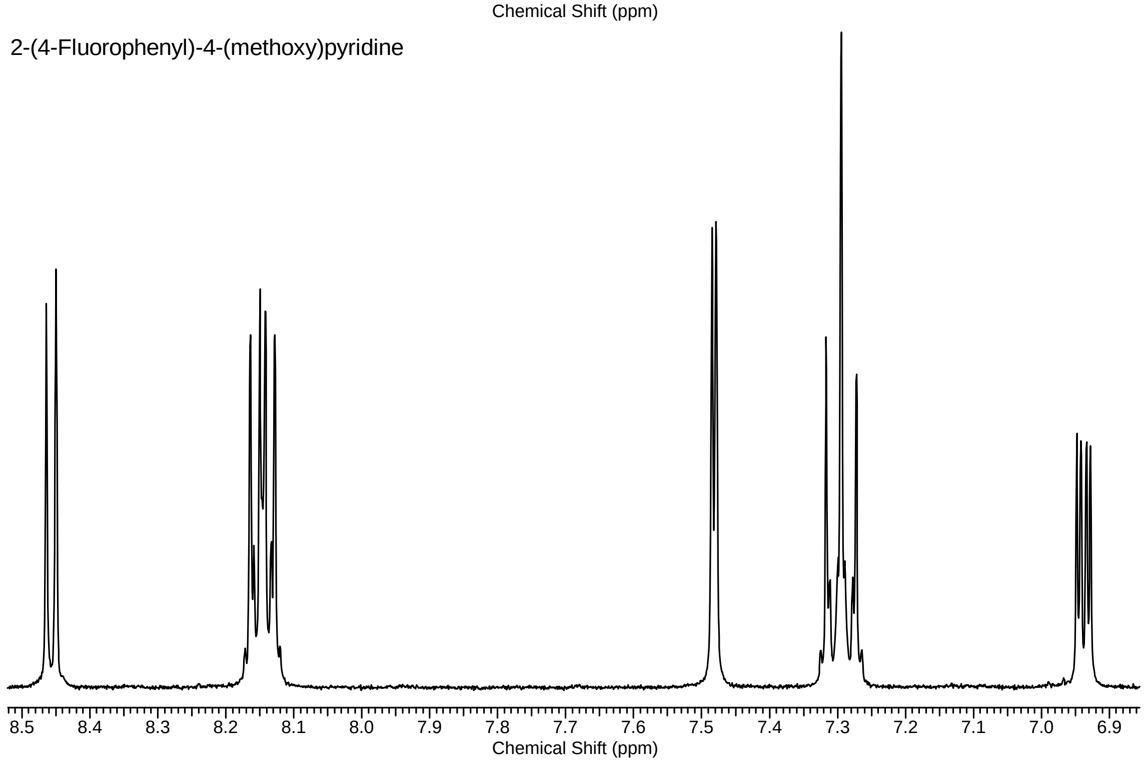
^{1}H NMR Spectrum of 2-(4′-fluorophenyl)-5-(trifluoromethyl)pyridine in CD_2Cl_2.



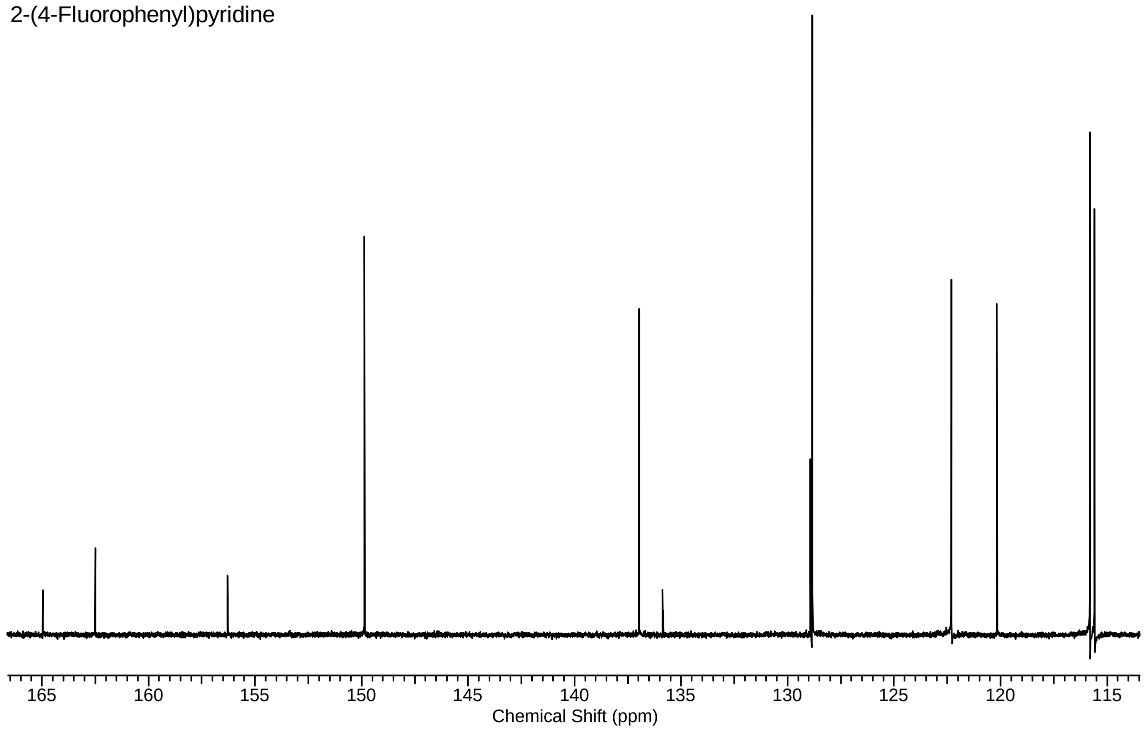


^{1}H NMR Spectrum of 2-(4′-fluorophenyl)-4-(*tert*-butyl)pyridine in DMSO-d_6 (top, complete; bottom, arom. H).

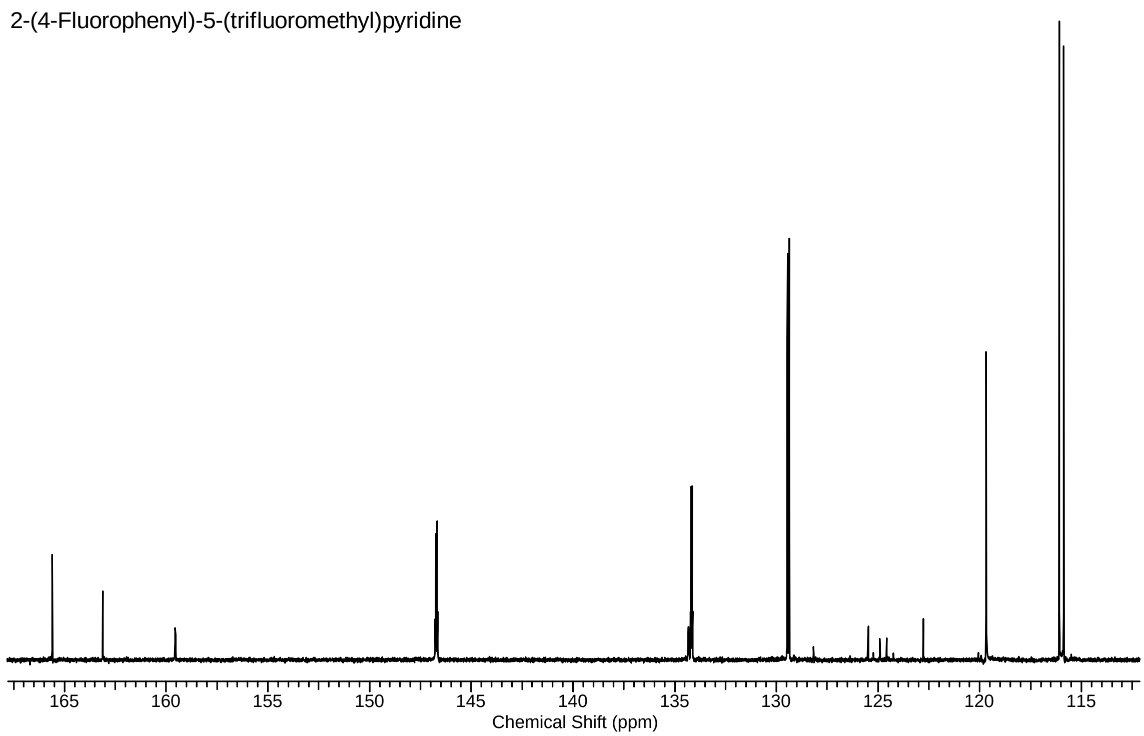




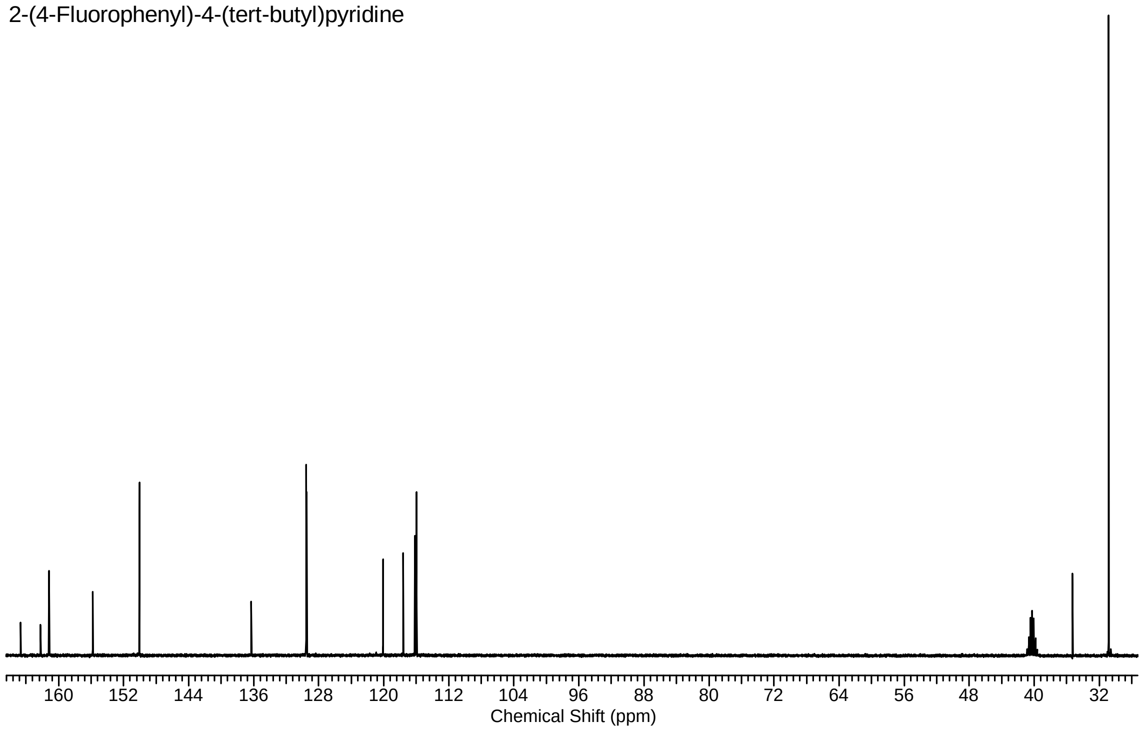
^{1}H NMR Spectrum of 2-(4′-fluorophenyl)-4-(methoxy)pyridine in DMSO-d_6 (top, complete; bottom, arom. H).

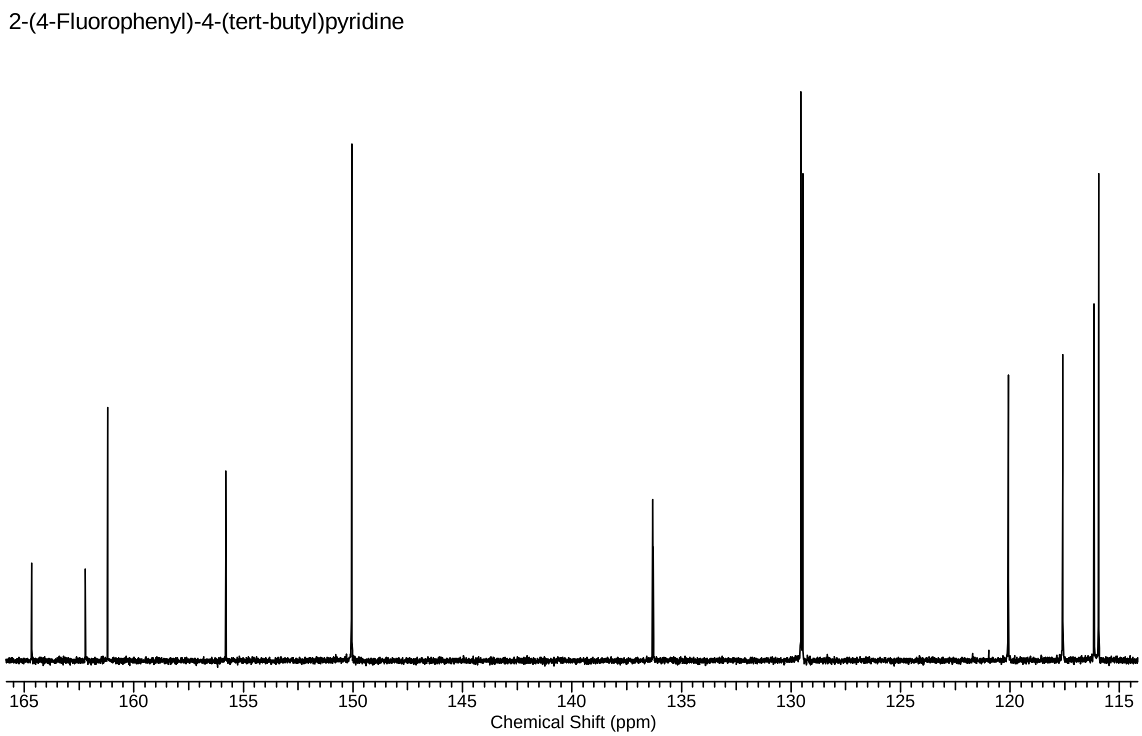


^{13}C NMR Spectrum of 2-(4′-fluorophenyl)pyridine in CD_2Cl_2.

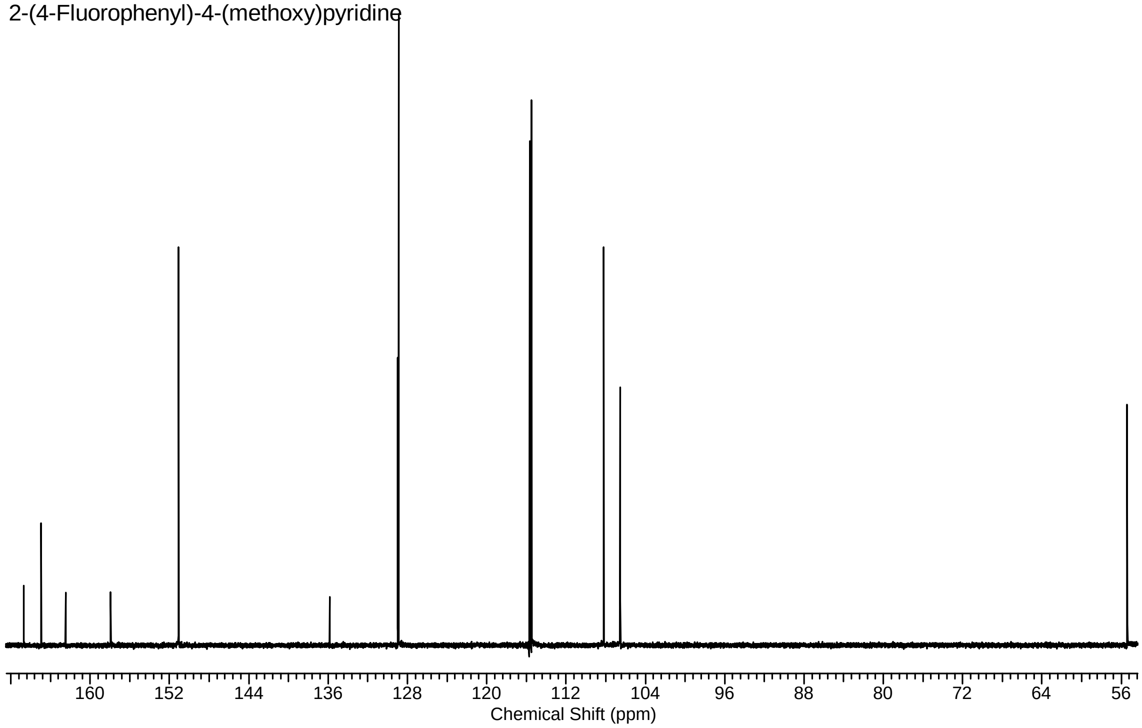


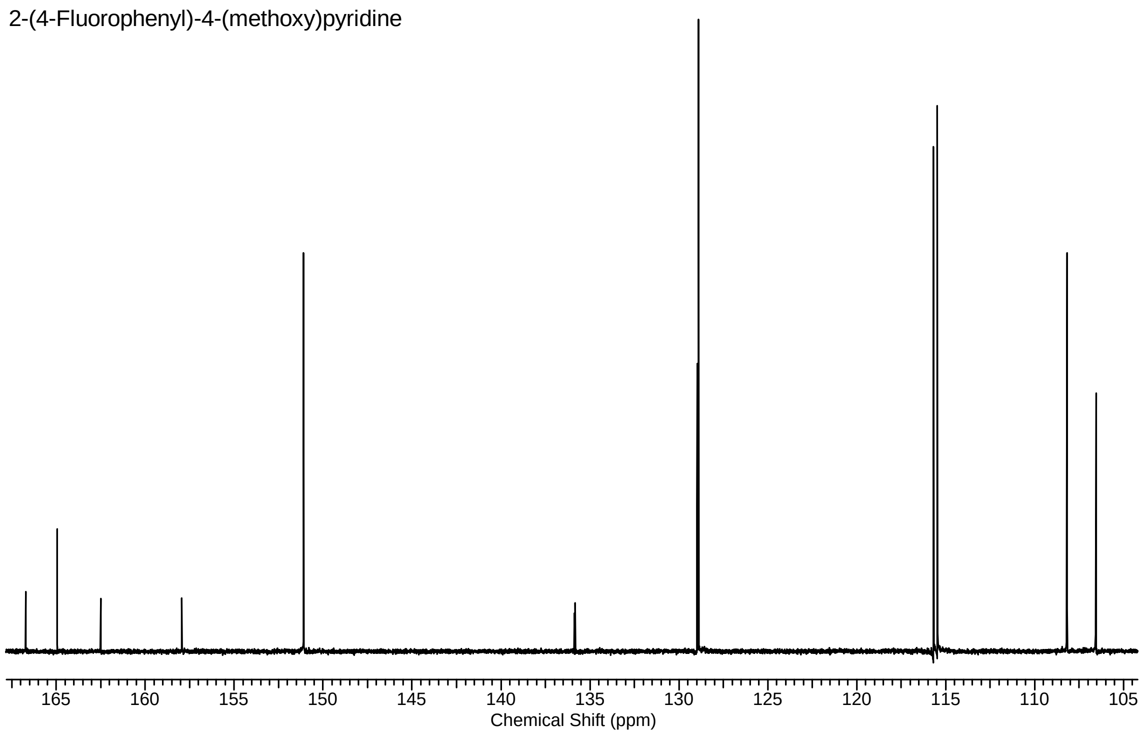
^{13}C NMR Spectrum of 2-(4′-fluorophenyl)-5-(trifluoromethyl)pyridine in CD_2Cl_2.



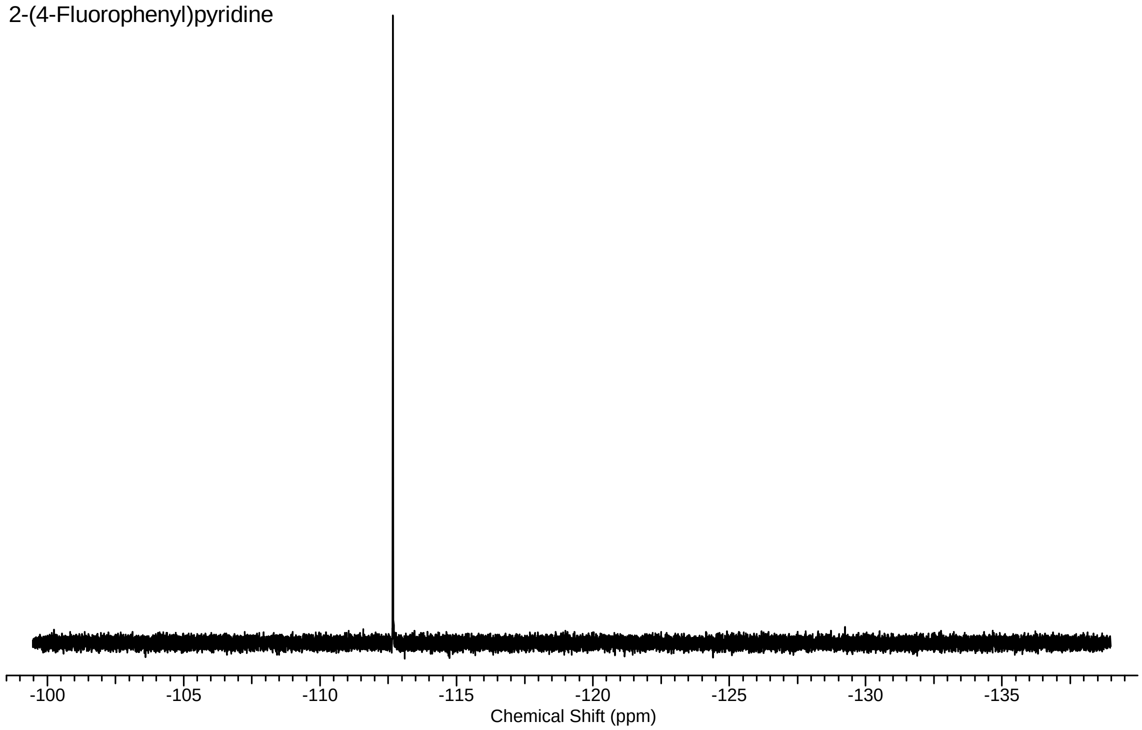


^{13}C NMR Spectrum of 2-(4′-fluorophenyl)-4-(*tert*-butyl)pyridine in DMSO-d_6 (top, complete; bottom, arom.).

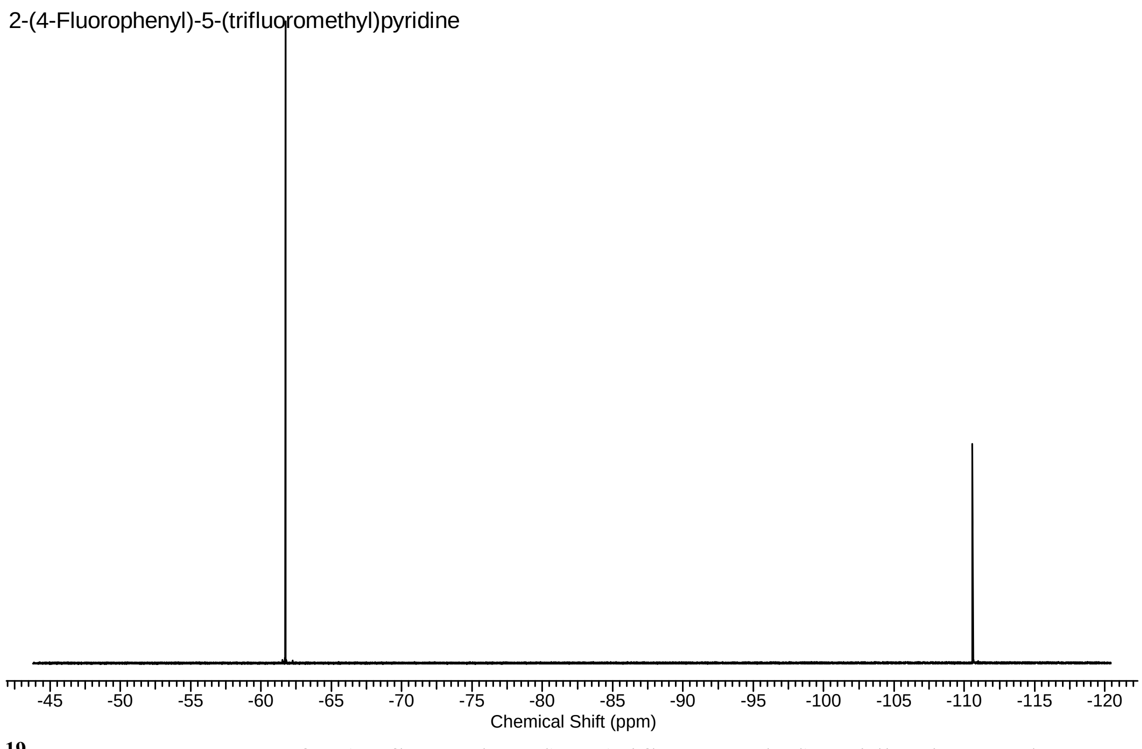




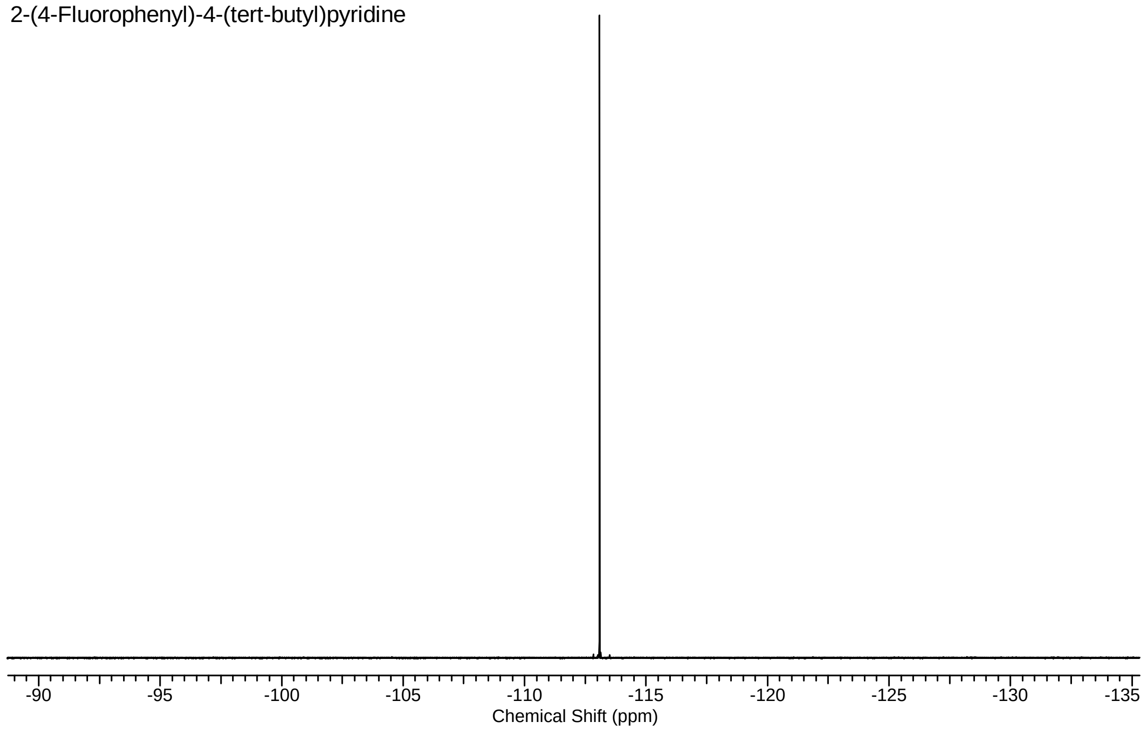
^{13}**C NMR Spectrum** of 2-(4′-fluorophenyl)-4-(methoxy)pyridine in CD_2Cl_2 (top, complete; bottom, arom.).



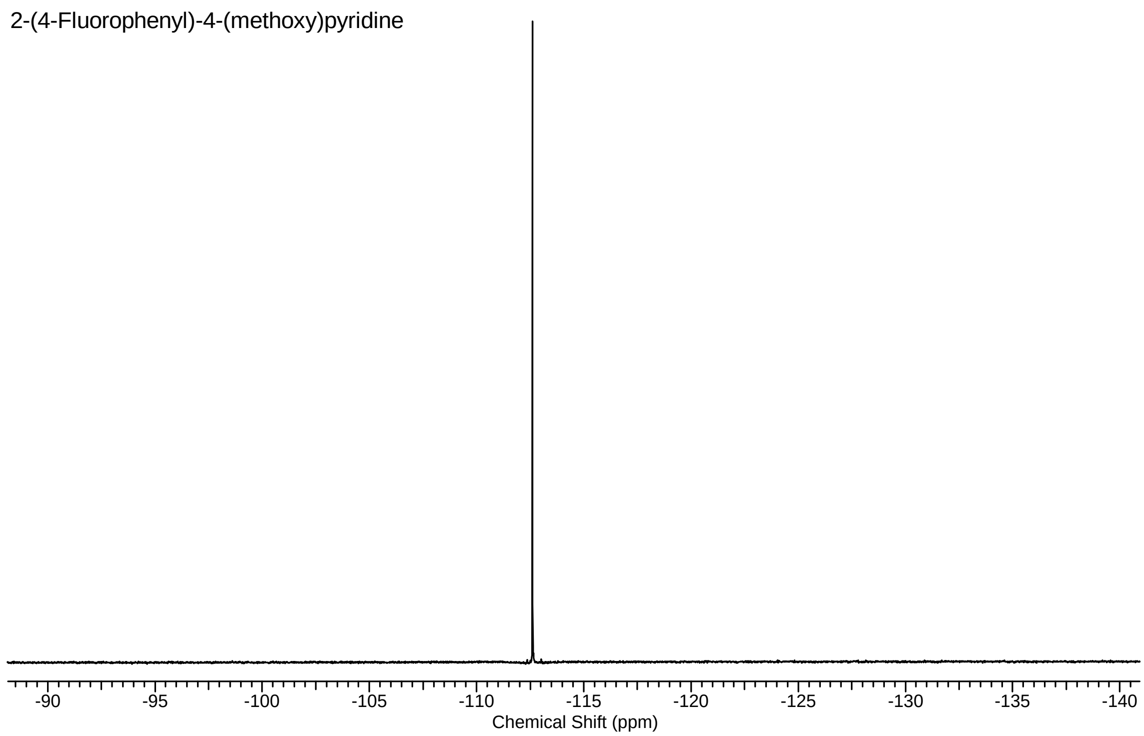
^{19}F NMR Spectrum of 2-(4′-fluorophenyl)pyridine in $CDCl_3$.



^{19}F NMR Spectrum of 2-(4′-fluorophenyl)-5-(trifluoromethyl)pyridine in $CDCl_3$.



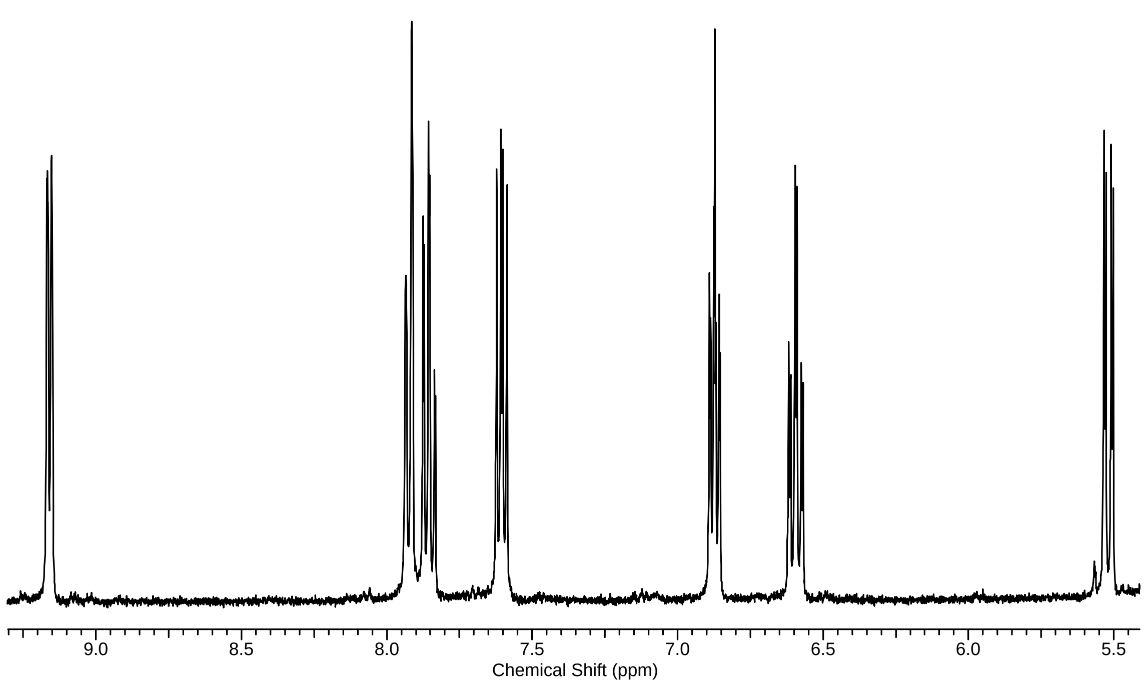
^{19}F NMR Spectrum of 2-(4′-fluorophenyl)-4-(*tert*-butyl)pyridine in $CDCl_3$.



^{19}F NMR Spectrum of 2-(4′-fluorophenyl)-4-(methoxy)pyridine in $CDCl_3$.

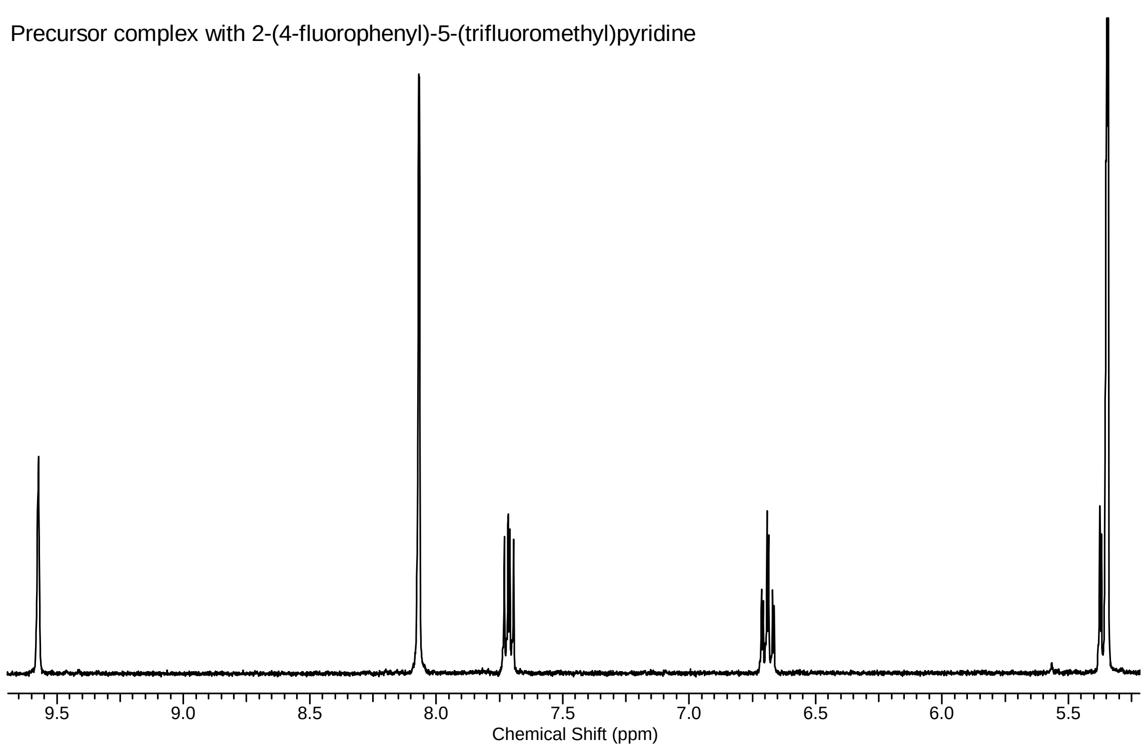
14. NMR Spectra: Cyclometalated Ir(III) Complexes $[(C^{\wedge}N)_2Ir(\mu\text{-}Cl)]_2$ (^1H, ^{19}F)

Precursor complex with 2-(4-fluorophenyl)pyridine

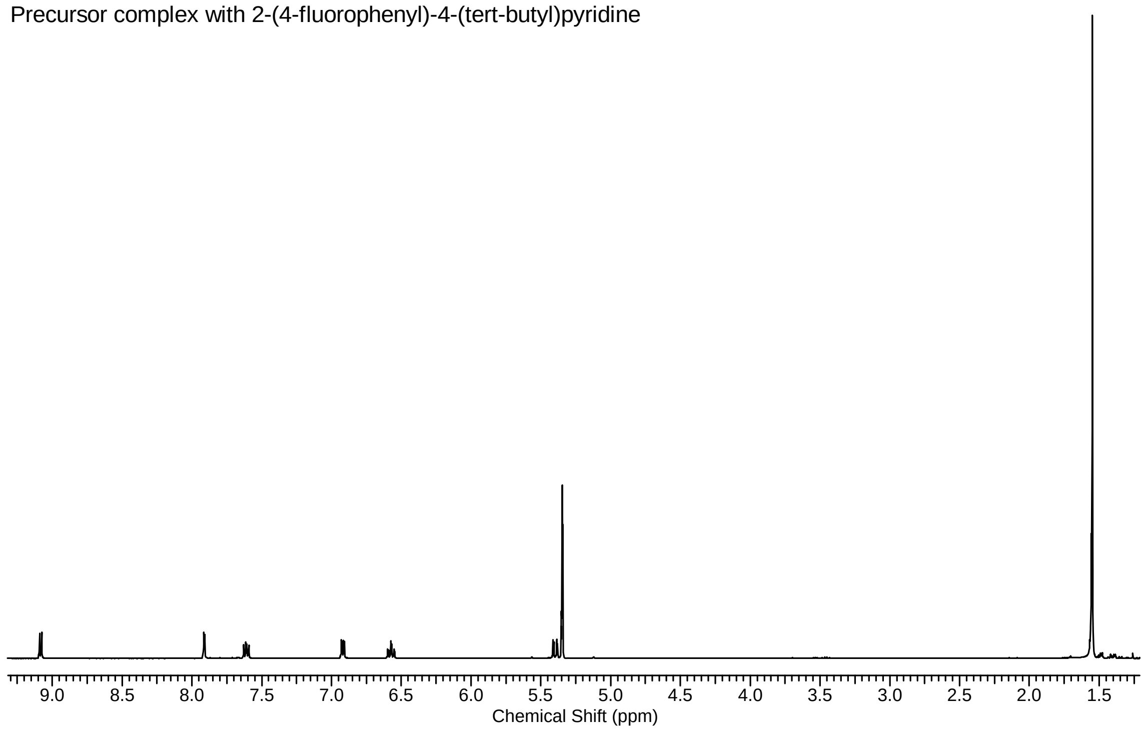


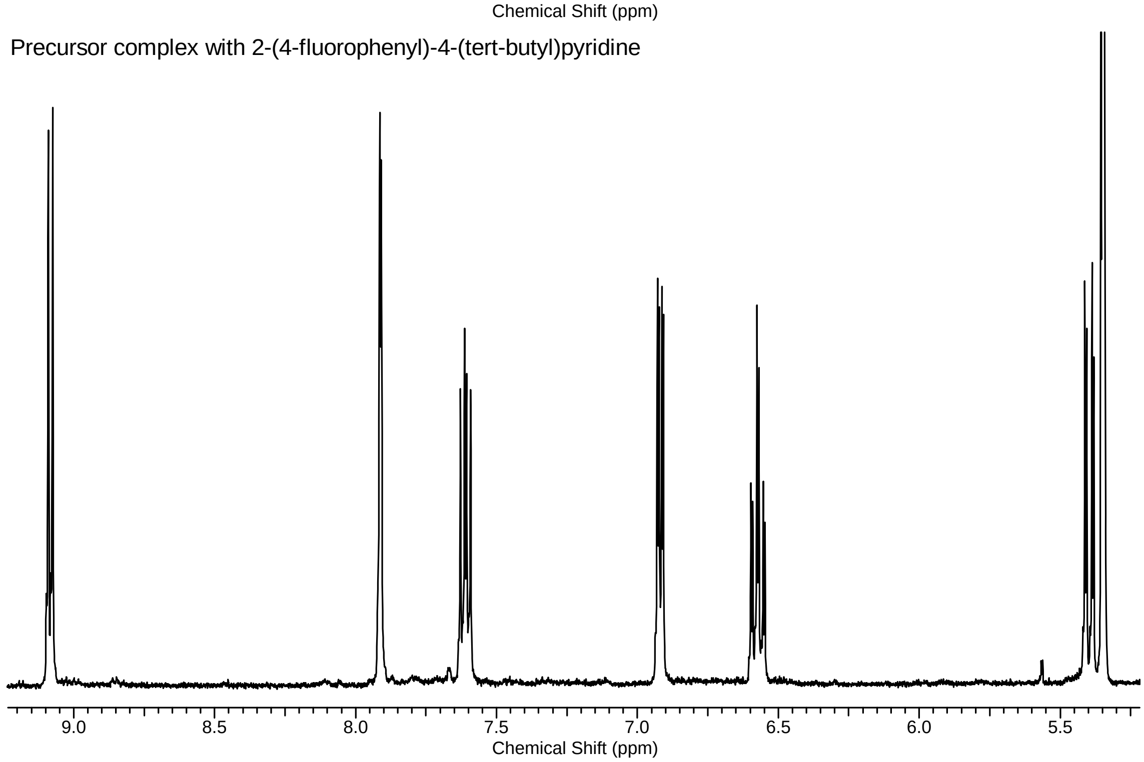
^{1}H NMR Spectrum of complex $[(C^{\wedge}N)_2Ir(\mu\text{-}Cl)]_2$ with 2-(4′-fluorophenyl)pyridine in CD_2Cl_2.

Precursor complex with 2-(4-fluorophenyl)-5-(trifluoromethyl)pyridine

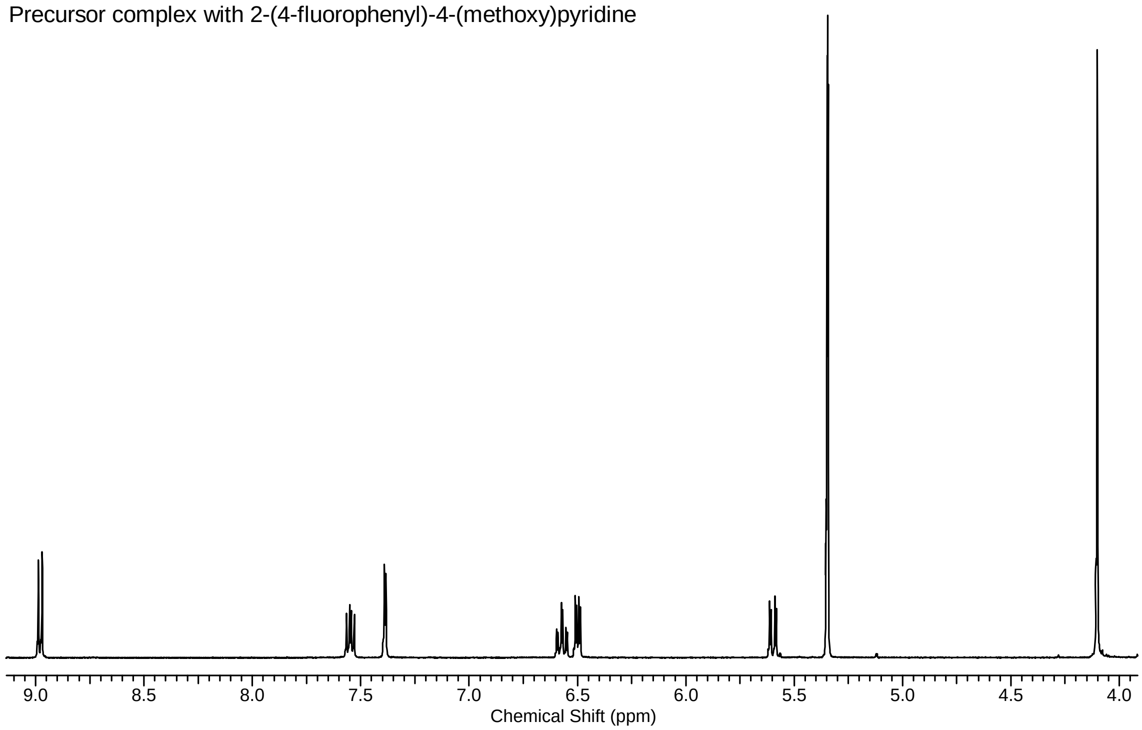


^{1}H NMR Spectrum of complex $[(C^{\wedge}N)_2Ir(\mu\text{-}Cl)]_2$ with 2-(4′-fluorophenyl)-5-(trifluoromethyl)pyridine in CD_2Cl_2.

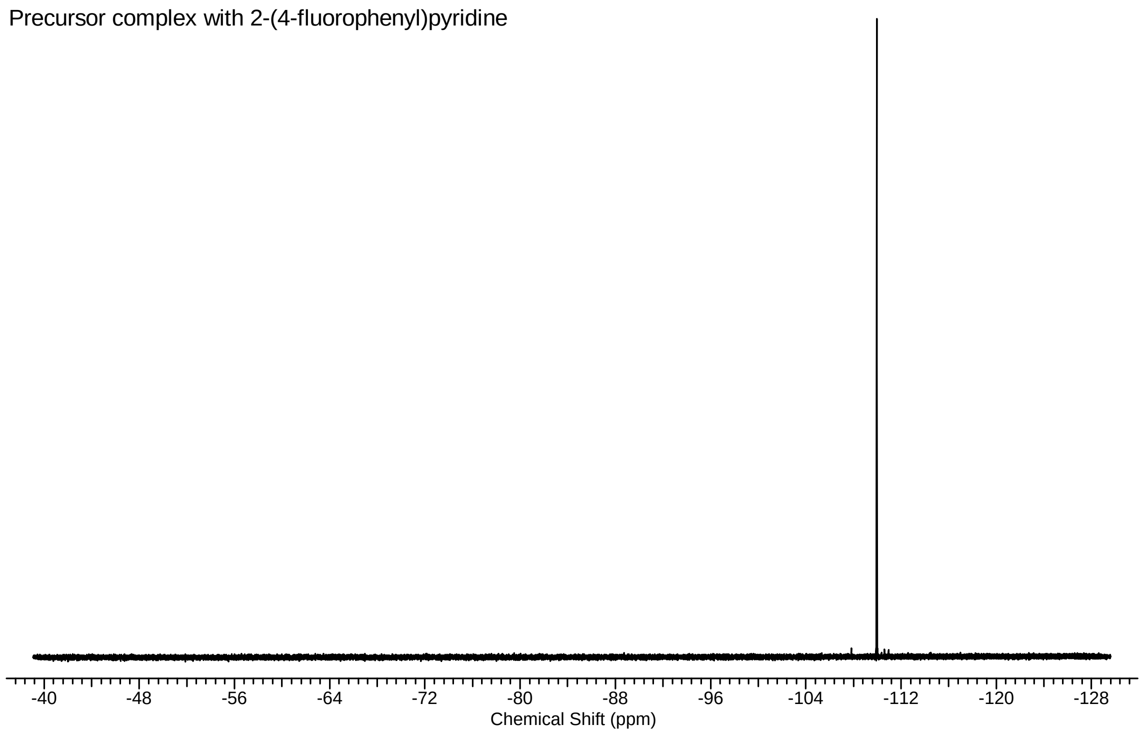




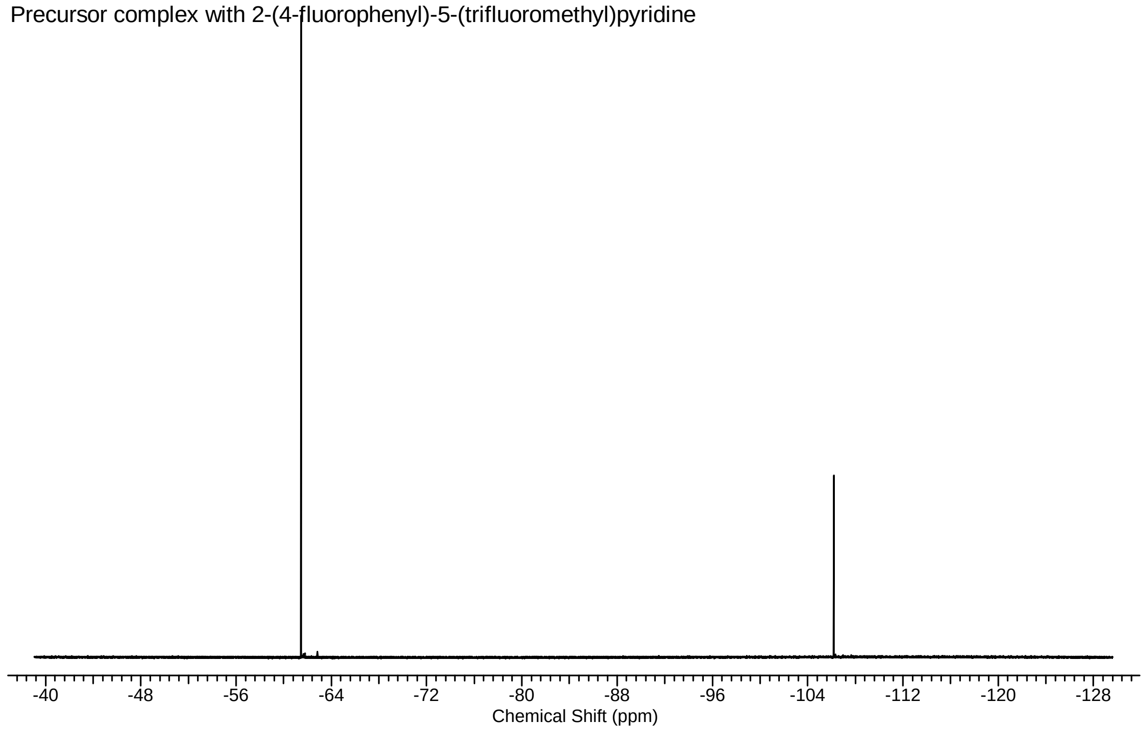
^{1}H NMR Spectrum of complex $[(C^\wedge N)_2Ir(\mu\text{-}Cl)]_2$ with 2-(4′-fluorophenyl)-4-(*tert*-butyl)pyridine in CD_2Cl_2 (top, complete; bottom, arom. H).



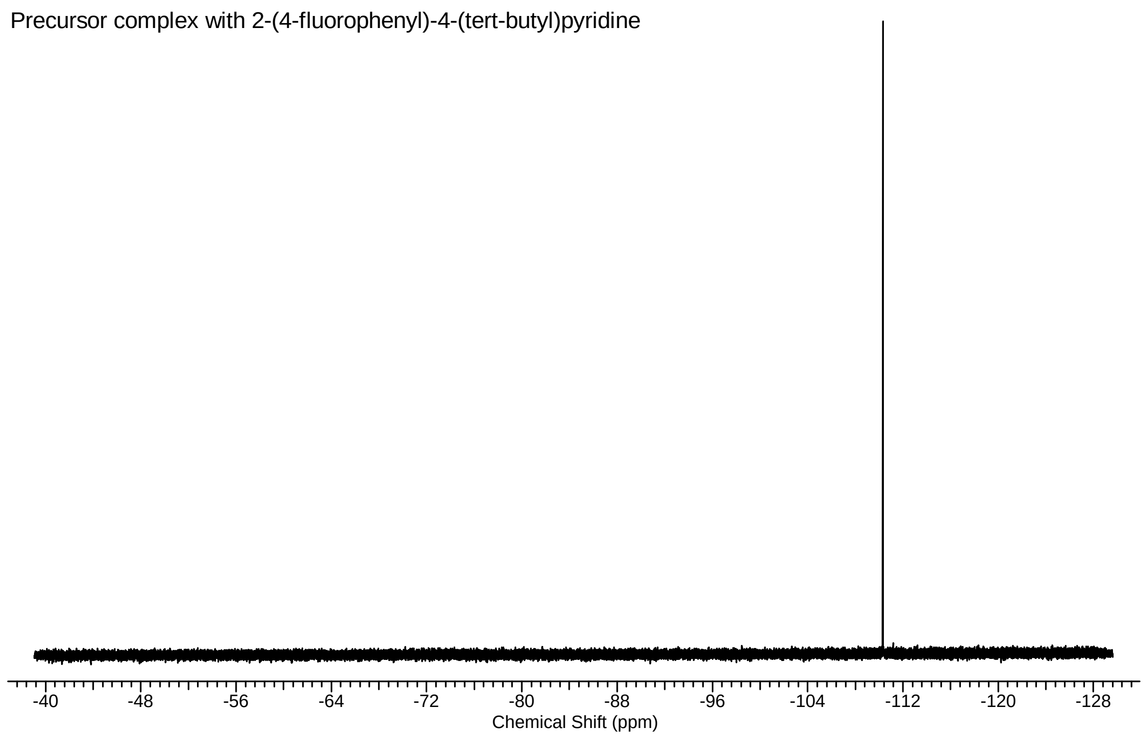
^{1}H NMR Spectrum of complex [(C^N)$_2$Ir(μ-Cl)]$_2$ with 2-(4′-fluorophenyl)-4-(methoxy)pyridine in CD_2Cl_2.



^{19}F NMR Spectrum of complex [(C^N)$_2$Ir(μ-Cl)]$_2$ with 2-(4′-fluorophenyl)pyridine in CD_2Cl_2.

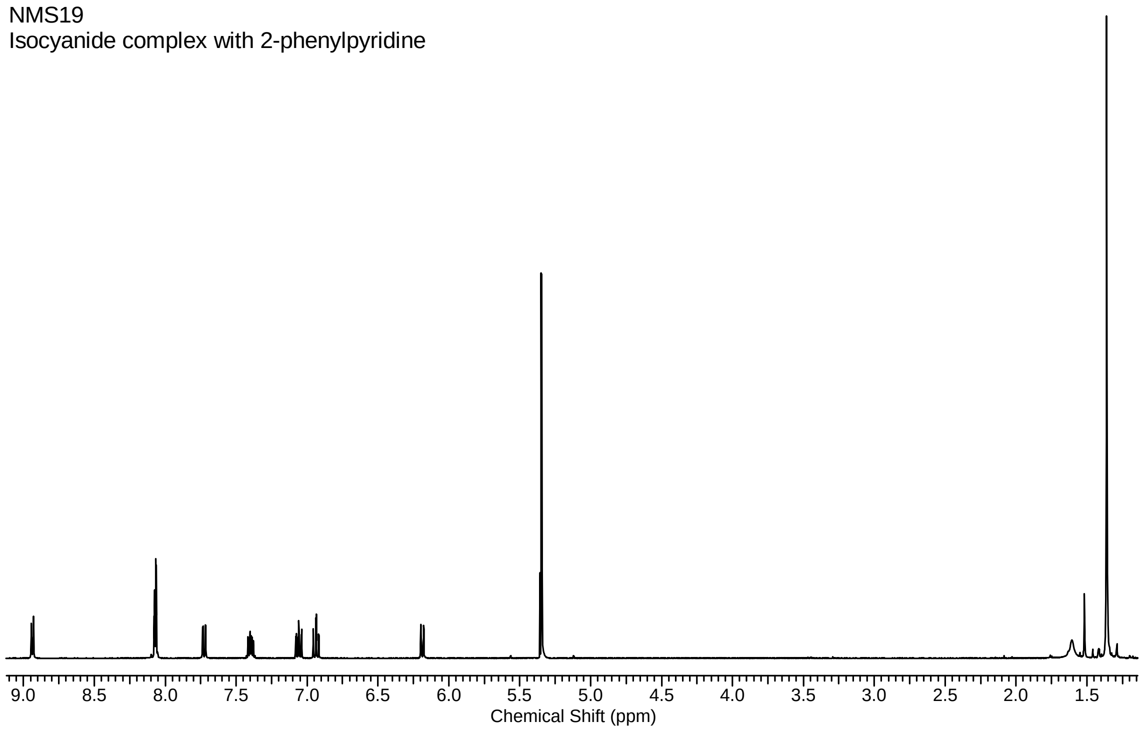


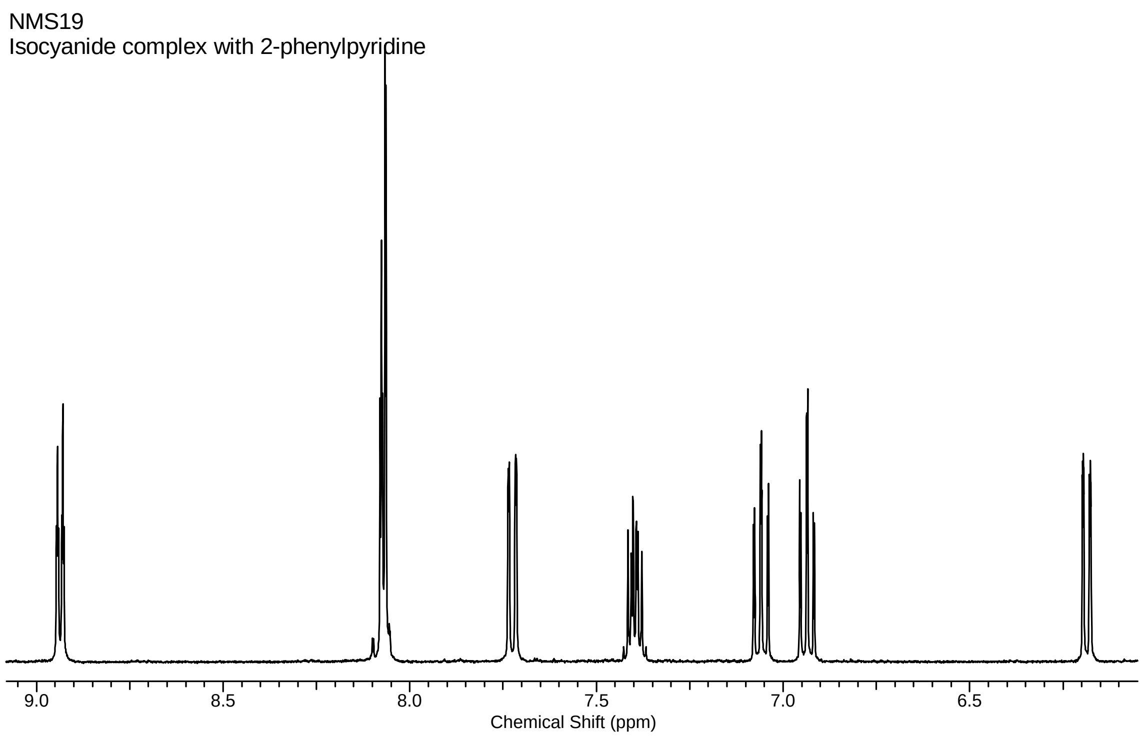
^{19}F NMR Spectrum of complex $[(C^\wedge N)_2Ir(\mu\text{-}Cl)]_2$ with 2-(4′-fluorophenyl)-5-(trifluoromethyl)pyridine in CD_2Cl_2.



^{19}F NMR Spectrum of complex $[(C^\wedge N)_2Ir(\mu\text{-}Cl)]_2$ with 2-(4′-fluorophenyl)-4-(*tert*-butyl)pyridine in CD_2Cl_2.

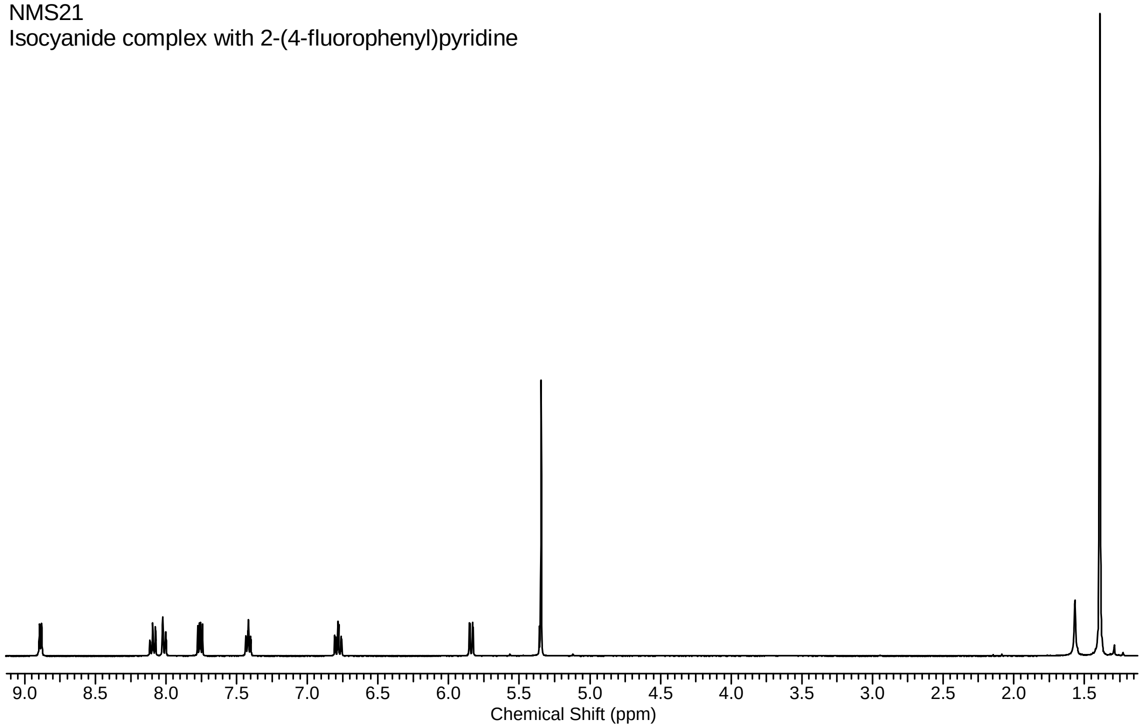
15. NMR Spectra: Ir(III) Isocyanide Complexes (^{1}H, ^{19}F)



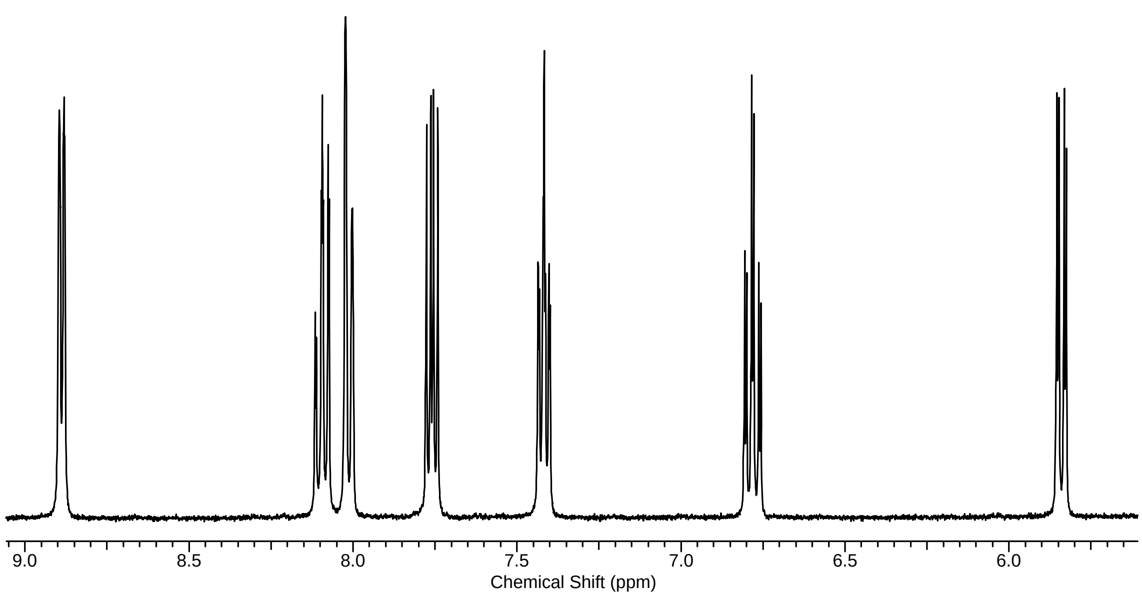


^{1}H NMR Spectrum of complex **1** in CD_2Cl_2 (top, complete; bottom, arom. H).

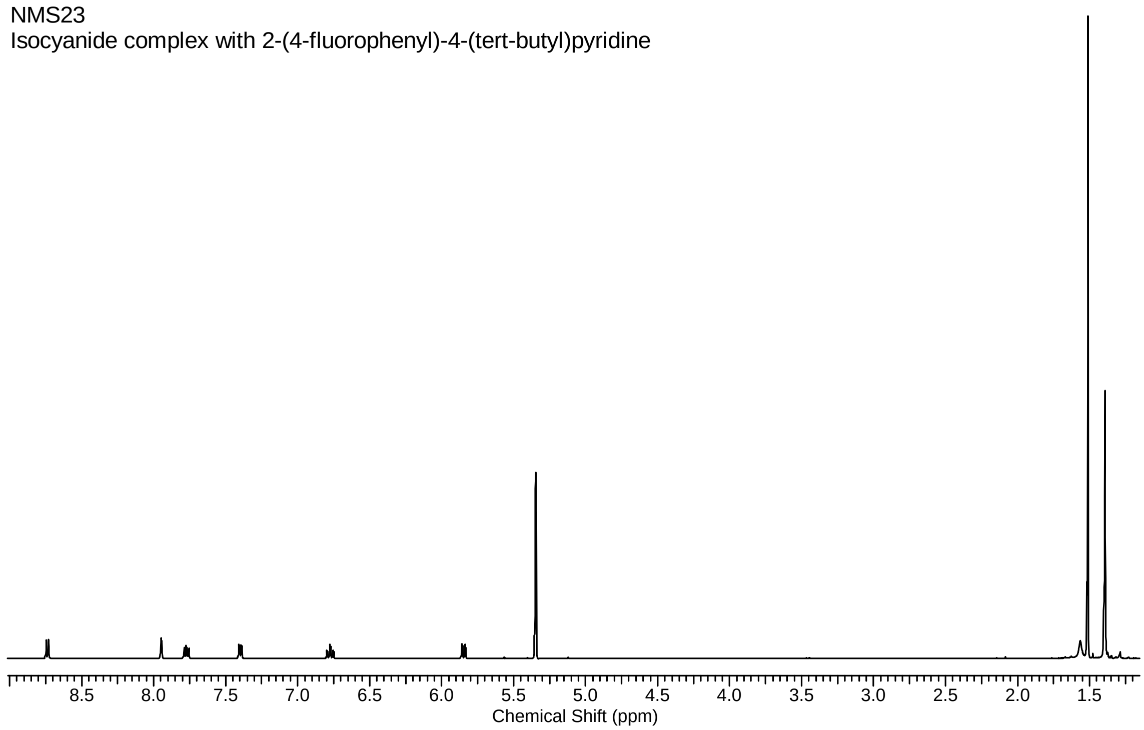
NMS21
Isocyanide complex with 2-(4-fluorophenyl)pyridine

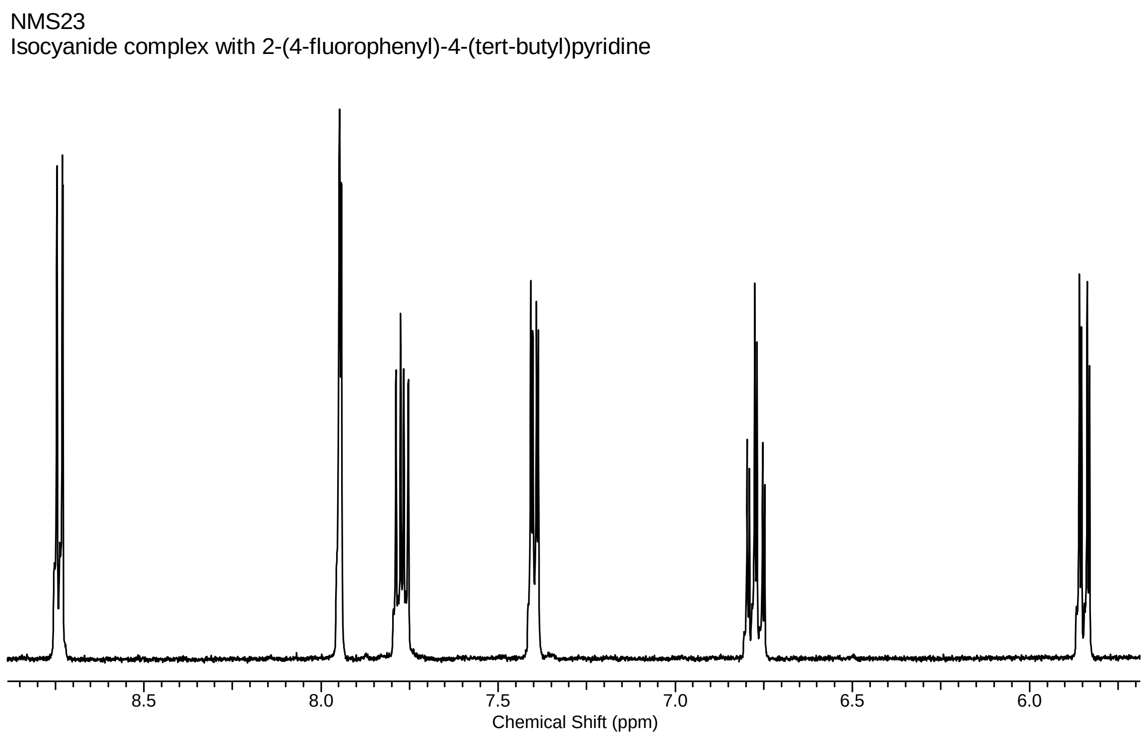


NMS21
Isocyanide complex with 2-(4-fluorophenyl)pyridine

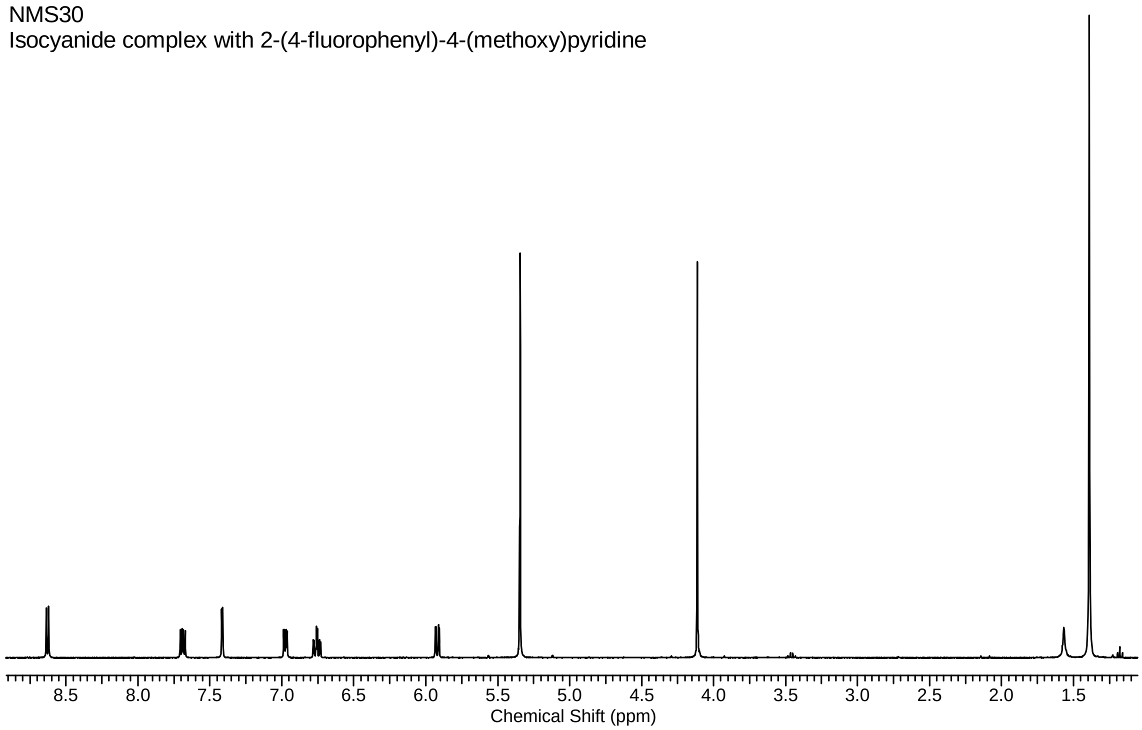


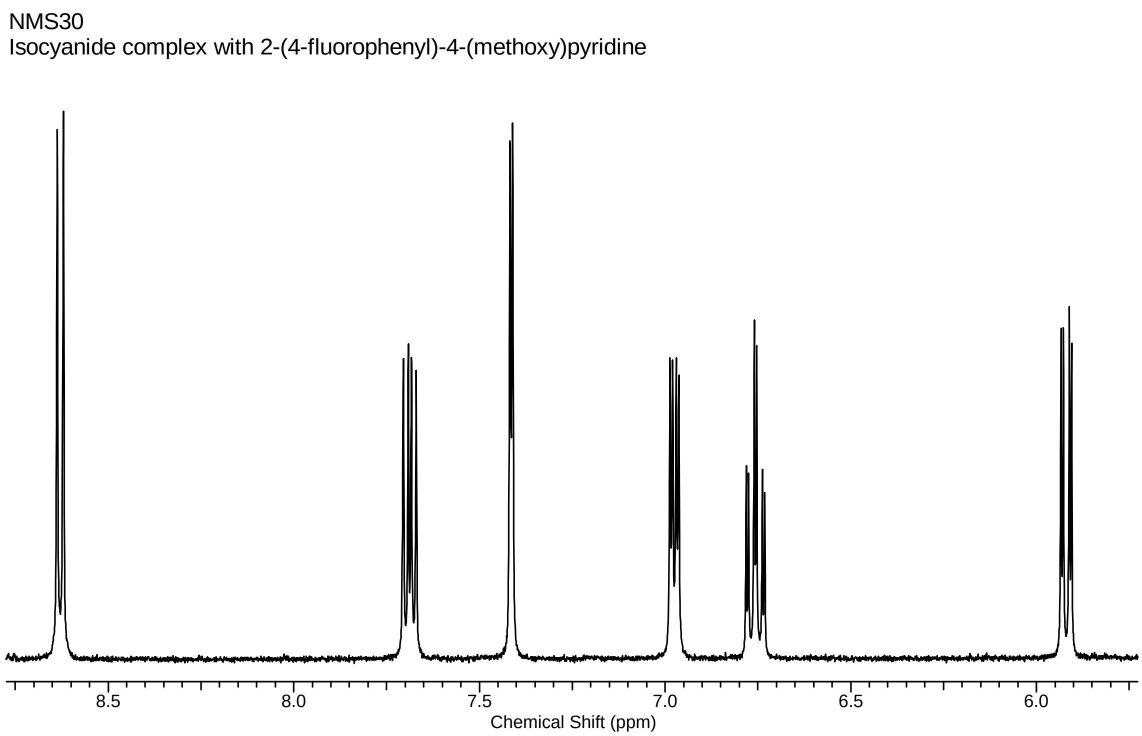
^{1}H NMR Spectrum of complex **2** in CD_2Cl_2 (top, complete; bottom, arom. H).



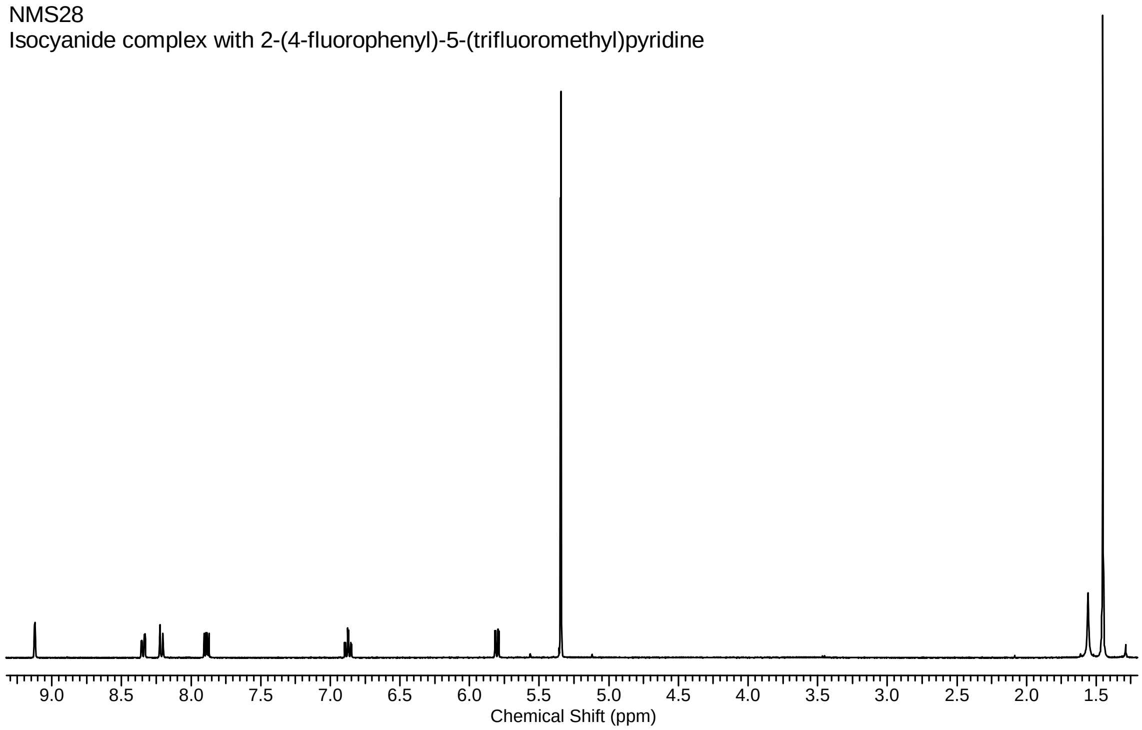


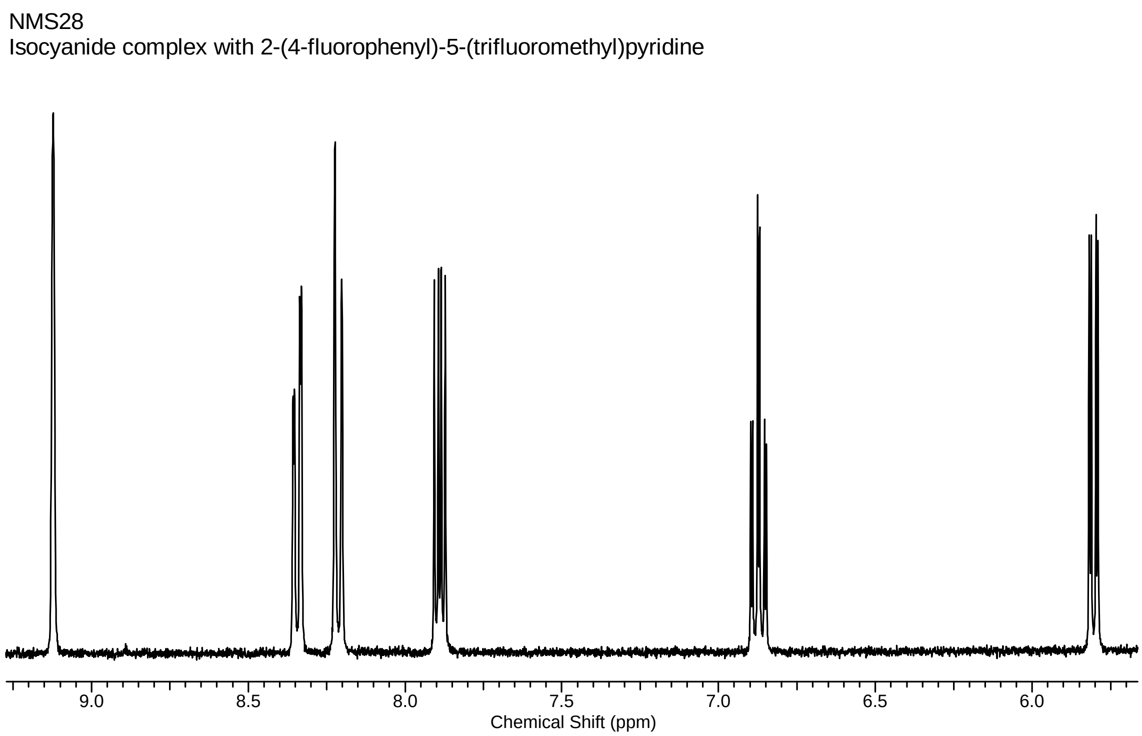
^{1}H NMR Spectrum of complex **3** in CD_2Cl_2 (top, complete; bottom, arom. H).



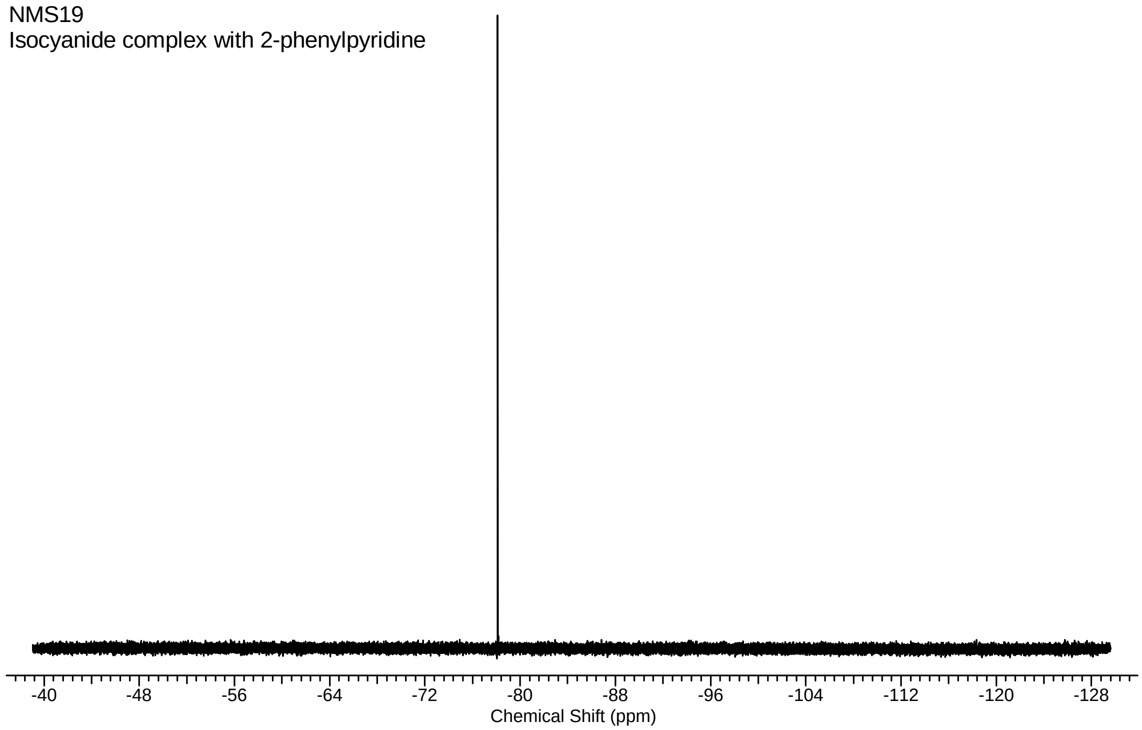


^{1}H NMR Spectrum of complex **4** in CD_2Cl_2 (top, complete; bottom, arom. H).

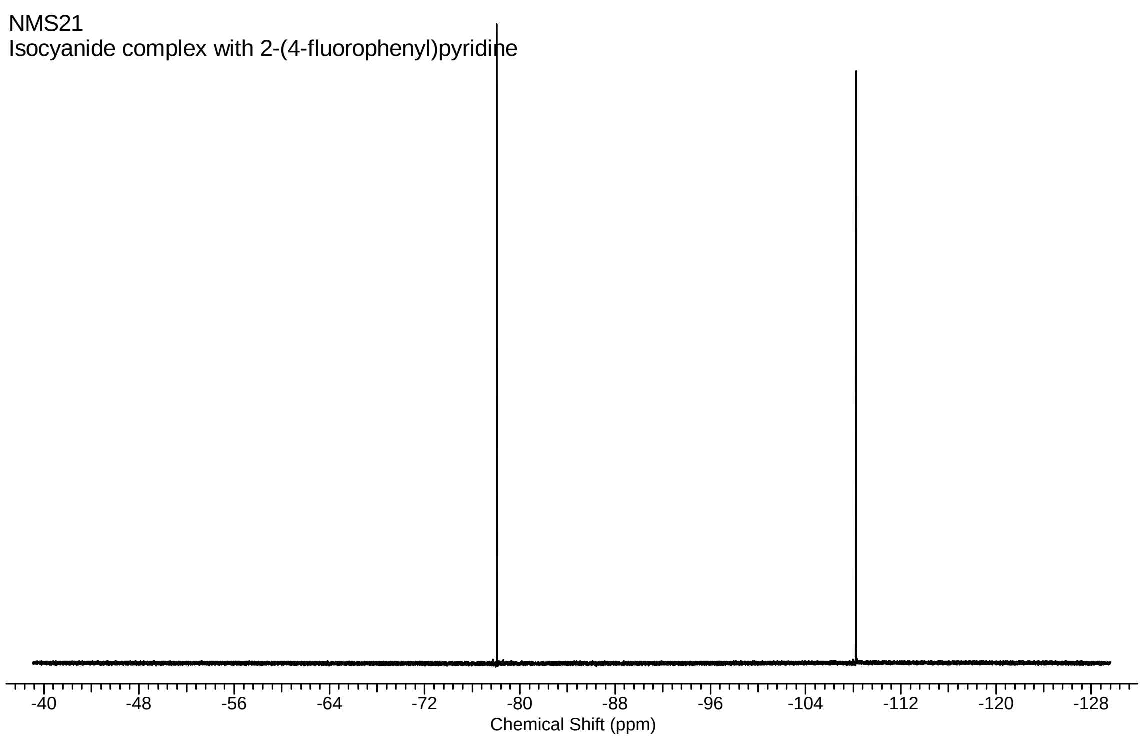




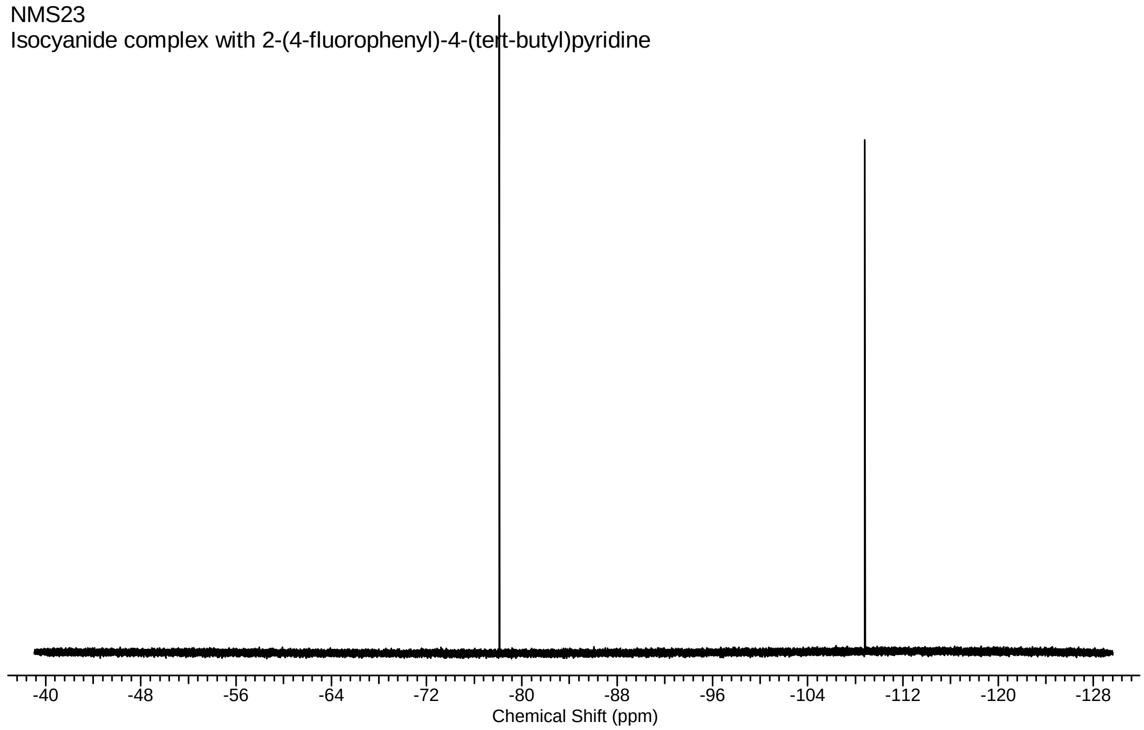
^{1}H NMR Spectrum of complex **5** in CD_2Cl_2 (top, complete; bottom, arom. H).



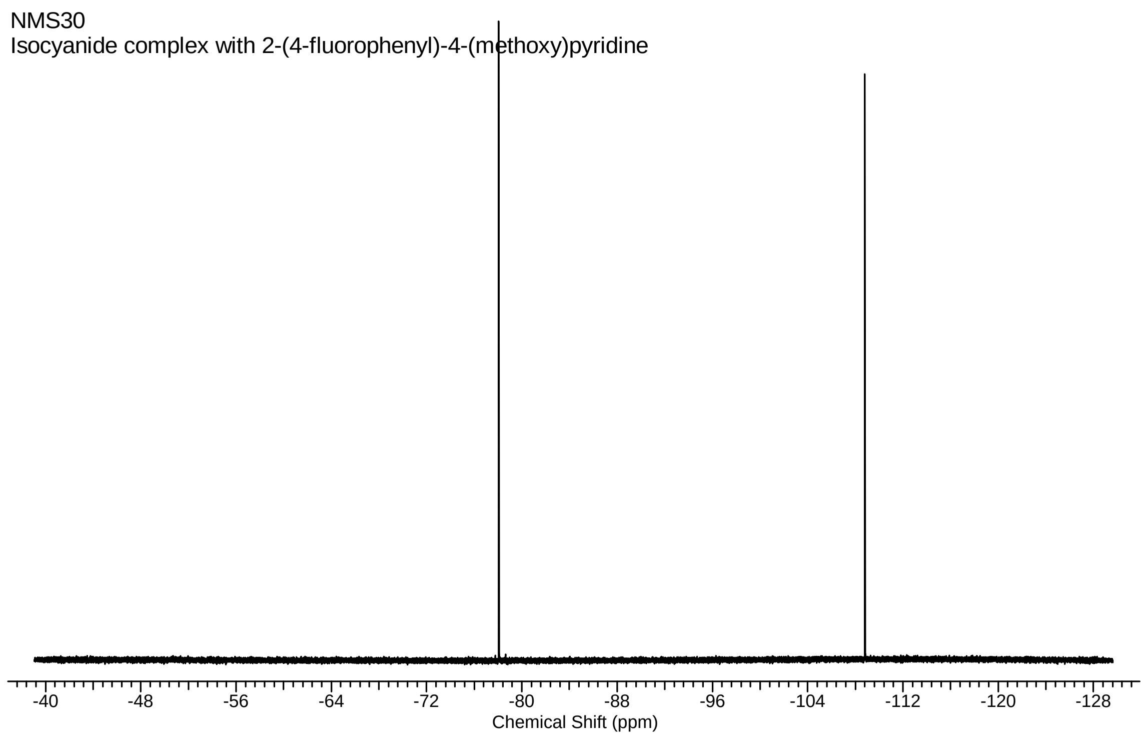
^{19}F NMR Spectrum of complex **1** in CD_2Cl_2.



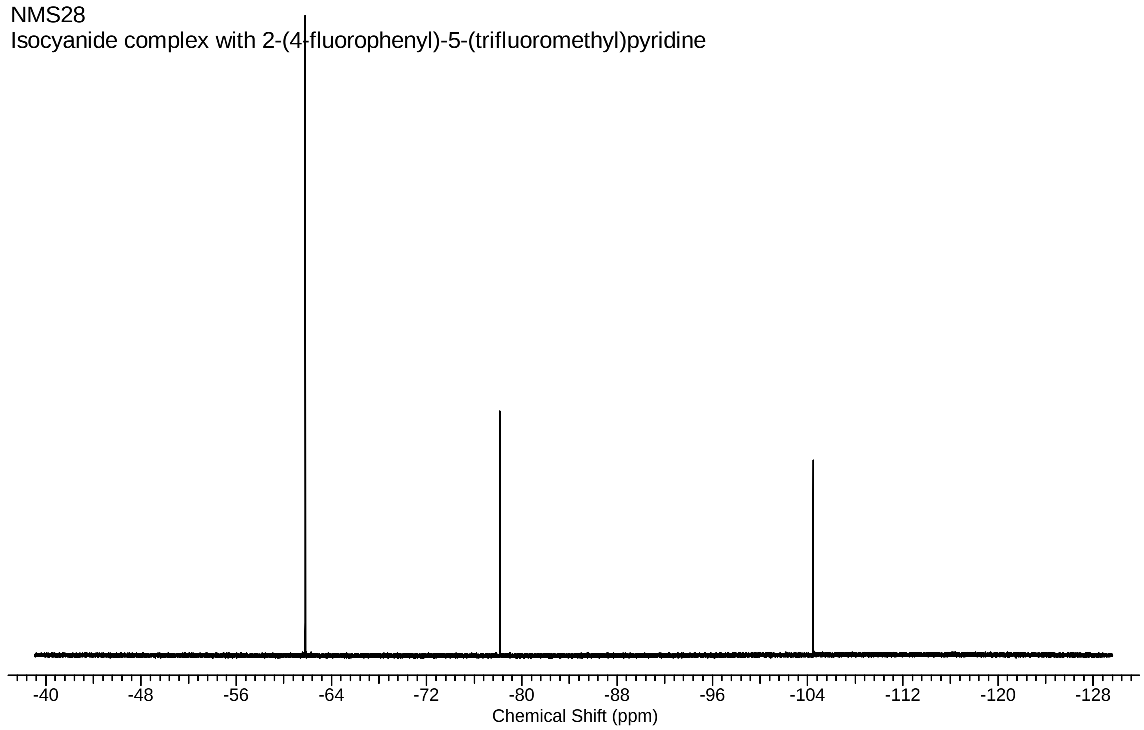
^{19}F NMR Spectrum of complex **2** in CD_2Cl_2.



^{19}F NMR Spectrum of complex **3** in CD_2Cl_2.



^{19}F NMR Spectrum of complex **4** in CD_2Cl_2.



^{19}**F NMR Spectrum** of complex **5** in CD_2Cl_2.