Supplementary material

Palladium-Catalysed Direct Arylation of a Tris-Cyclometallated Ir(III) Complex Bearing 2,2'-Thienylpyridine Ligands: A Powerful Tool for the Tuning of Luminescence Properties

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General procedure

As a typical experiment, the reaction of the aryl bromide (2 or 3 mmol), iridium complex **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) at 130-150 °C during 24-48 h in DMAc (5 mL) in the presence of $Pd(OAc)_2$ (0.005 g, 0.025 mmol), under argon affords the coupling product after evaporation of the solvent and filtration on silica gel (pentane/ether) or (pentane/dichloromethane/methanol).

Monoarylation of 1 with 4-bromobenzonitrile (2a)

The reaction of 4-bromobenzonitrile (0.364 g, 2 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 3 h affords the product **2a** in 12% (0.046 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.45 (m, 13H), 7.27 (d, *J* = 4.6 Hz, 1H), 7.25 (d, *J* = 4.6 Hz, 1H), 6.84-6.74 (m, 4H), 6.54 (d, *J* = 4.6 Hz, 1H), 6.46 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 162.5, 162.4, 161.7, 161.0, 158.7, 158.6, 148.2, 147.9, 144.6, 139.1, 137.7, 136.9, 136.8, 135.4, 135.2,

135.1, 135.0, 134.9, 133.8, 132.4, 128.2, 128.0, 120.1, 119.4, 119.3, 118.9, 117.9, 117.6, 117.5, 109.9. HRMS calcd for M^+ $C_{34}H_{21}F_9IrN_4S_3$ 774.0552, found 774.0551.

Diarylation of 1 with 4-bromobenzonitrile (2b)

The reaction of 4-bromobenzonitrile (0.364 g, 2 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 3 h affords the product **2b** in 38% (0.057 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66-7.47 (m, 17H), 7.29 (d, *J* = 4.6 Hz, 1H), 6.88 (s, 1H), 6.84-6.79 (m, 3H), 6.78 (s, 1H), 6.56 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 162.4, 161.7, 161.6, 160.4, 160.3, 158.1, 148.2, 147.9, 144.8, 139.0, 138.9, 137.9, 137.8, 137.2, 137.1, 135.3, 133.8, 133.6, 132.5, 128.3, 126.0, 120.2, 119.5, 119.0, 118.9, 118.1, 118.0, 117.7, 109.9. HRMS calcd for M^+ $C_{41}H_{24}F_9IrN_5S_3$ 875.0818, found 875.0814.

Triarylation of 1 with 4-bromobenzonitrile (2c)

The reaction of 4-bromobenzonitrile (0.546 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 150 °C during 48 h affords the product **2c** in 64% (0. 280 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, DMSO): δ 7.80 (t, *J* = 7.8 Hz, 3H), 7.76 (d, *J* = 8.2 Hz, 6H), 7.71 (d, *J* = 7.8 Hz, 3H), 7.65 (d, *J* = 8.2 Hz, 6H), 7.55 (d, *J* = 6.2 Hz, 3H), 7.10 (t, *J* = 6.5 Hz, 3H), 6.84 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 161.3, 160.0, 148.9, 144.9, 139.1, 139.0, 138.5, 134.0, 133.9, 126.8, 122.3, 119.8, 119.1, 110.1. HRMS calcd for M^+ $C_{48}H_{27}F_9IrN_6S_3$ 976.1083, found 976.1082.

Diarylation of 1 with 4-nitrobromobenzene (3b)

The reaction of 4-bromonitrobenzene (0.606 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 24 h affords the

product **3b** in 50% (0.225 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.18 (d, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.76-7.55 (m, 13H), 7.33 (d, *J* = 4.5 Hz, 1H), 6.99 (s, 1H), 6.92 (t, *J* = 6.7 Hz, 2H), 6.88 (s, 1H), 6.87 (t, *J* = 6.4 Hz, 1H), 6.56 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 162.2, 161.4, 161.3, 160.2, 160.0, 157.7, 148.0, 147.8, 146.0, 144.1, 144.0, 140.9, 140.8, 138.7, 138.6, 137.0, 136.9, 135.2, 135.0, 134.5, 134.3, 134.2, 130.7, 128.6, 128.5, 128.4, 125.7, 124.0, 123.9, 120.3, 119.4, 118.1, 118.0, 117.6, 104.9. HRMS calcd for M^+ $C_{39}H_{24}IrN_5S_3$ 915.0614, found 915.0613.

Triarylation of 1 with 4-trifluoromethylbromobenzene (4c)

The reaction of 4-bromotrifluoromethylbromobenzene (0.675 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 48 h affords the product **4c** in 48% (0.258 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.9 Hz, 6H), 7.62-7.75 (m, 15H), 6.90 (s, 3H), 6.87 (t, *J* = 5.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 160.4, 148.0, 145.4, 138.2, 136.9, 136.8, 133.2, 128.6 (q, *J* = 33.4 Hz), 125.9, 125.6 (q, *J* = 3.7 Hz), 121.4 (q, *J* = 271.7 Hz), 119.7, 117.9. HRMS calcd for M^+ $C_{48}H_{27}F_9IrN_3S_3$ 1105.0847, found 1105.0846.

Triarylation of 1 with 3,5-bis(trifluoromethyl)bromobenzene (5c)

The reaction of 3,5-bis(trifluoromethyl)bromobenzene (0.879 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 150 °C during 48 h affords the product **5c** in 63% (0.415 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 6H), 7.70 (s, 3H), 7.67-7.754 (m, 9H), 6.89 (s, 3H), 6.87 (t, *J*=6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.7, 159.8, 148.0, 143.9, 137.6, 137.2, 136.9, 133.6, 131.8 (q, *J*=33.2 Hz), 125.7 (m), 123.2, (q, *J*=272.8 Hz), 120.30 (m), 120.1, 118.1. HRMS calcd for M^+ $C_{51}H_{24}F_{18}IrN_3S_3$ 1309.0469, found 1309.0469.

Triarylation of 1 with 2-bromonaphthalene (6c)

The reaction of 2-bromonaphthalene (0.621 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 48 h affords the product **6c** in 20% (0.105 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 3H), 7.82 (d, *J* = 7.7 Hz, 3H), 7.78-7.73 (m, 9H), 7.60 (d, *J* = 5.4 Hz, 3H), 7.55-7.50 (m, 6H), 7.44-7.38 (m, 6H), 7.07 (s, 3H), 6.78 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.3, 161.4, 147.9, 147.4, 136.7, 135.6, 133.7, 132.7, 132.6, 132.4, 128.1, 128.1, 127.6, 126.2, 125.6, 124.8, 124.1, 119.1, 117.6.

Triarylation of 1 with 1-bromonaphthalene (7c)

The reaction of 1-bromonaphthalene (0.621 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 48 h affords the product **7c** in 26% (0.130 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.5 Hz, 3H), 7.82 (d, *J* = 8.1 Hz, 3H), 7.77 (d, *J* = 8.1 Hz, 3H), 7.74 (d, *J* = 5.5 Hz, 3H), 7.57 (d, *J* = 6.5 Hz, 3H), 7.55-7.49 (m, 6H), 7.43-7.38 (m, 6H), 7.14 (t, *J*=7.7 Hz, 3H), 6.94 (s, 3H), 6.83 (t, *J* = 6.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6, 160.9, 148.1, 145.1, 136.8, 136.6, 135.7, 133.8, 133. 3, 131.90, 128.1, 127.9, 127.6, 126.3, 126.1, 125.7, 125.1, 119.1, 117.5.

Triarylation of 1 with 3-bromopyridine (8c)

The reaction of 3-bromopyridine (0.474 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 150 °C during 48 h affords the product **8c** in 52% (0.230 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.84 (s, 3H), 8.43 (d, *J* = 4.3 Hz, 3H), 7.84 (d, *J* = 8.0 Hz, 3H), 7.65-

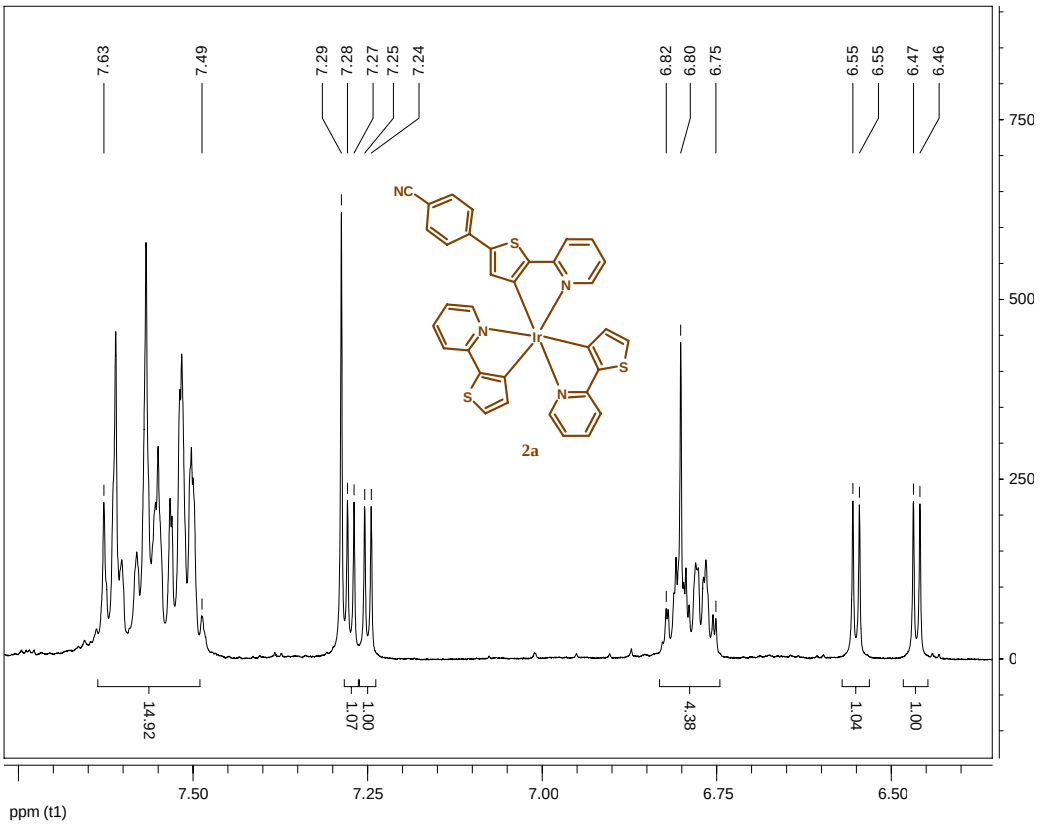
7.45 (m, 9H), 7.23 (dd, *J* = 7.8, 4.6 Hz, 3H), 6.86 (s, 3H), 6.82 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 160.4, 148.0, 147.9, 147.0, 143.2, 136.9, 136.4, 132.9, 132.8, 130.9, 123.5, 119.7, 117.9. HRMS calcd for M^+ $C_{42}H_{27}IrN_6S_3$ 904.1083, found 904.1085.

Triarylation of 1 with 5-bromopyrimidine (9c)

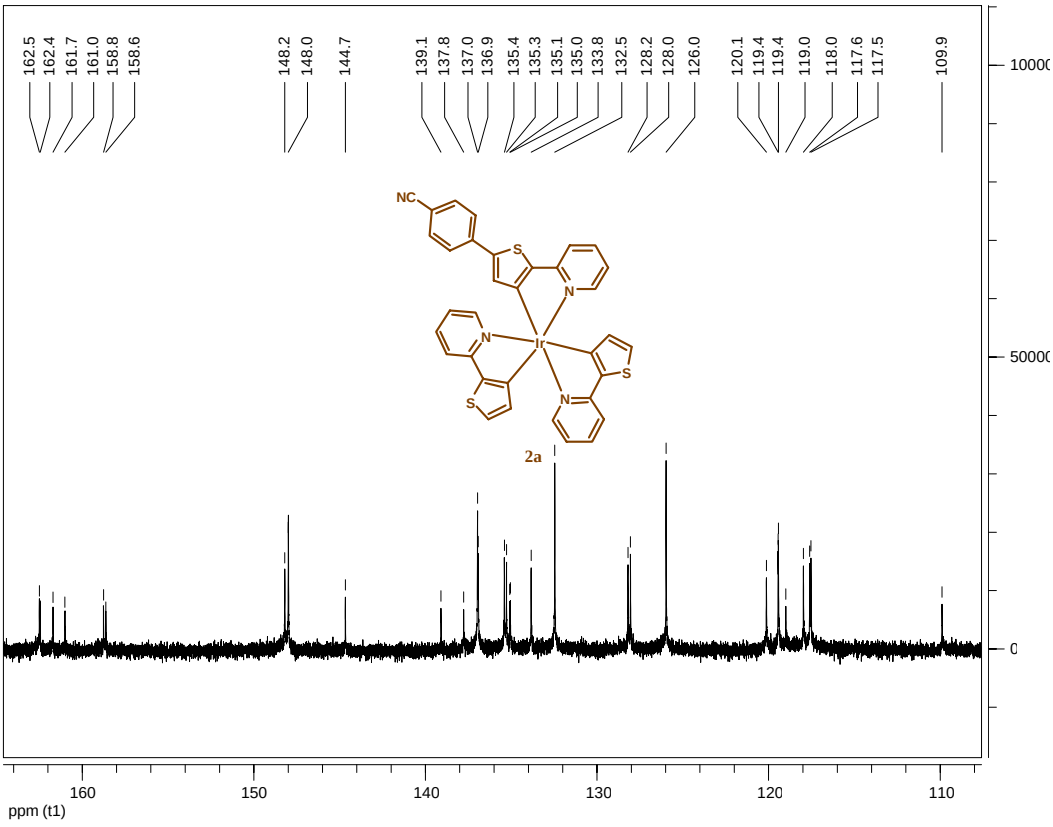
The reaction of 5-bromopyrimidine (0.476 g, 3 mmol), **1** (0.336 g, 0.5 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (0.005 g, 0.025 mmol) in DMAc (5 mL) at 130 °C during 48 h affords the product **9c** in 56% (0.252 g) isolated yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.02 (s, 3H), 8.89 (s, 6H), 7.65-7.55 (m, 9H), 6.86 (t, *J* = 5.9 Hz, 3H), 6.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6, 159.5, 156.8, 153.3, 148.0, 139.1, 137.7, 137.2, 133.5, 128.9, 120.3, 118.2. HRMS calcd for M^+ $C_{39}H_{24}IrN_9S_3$ 907.0941, found 907.9042.

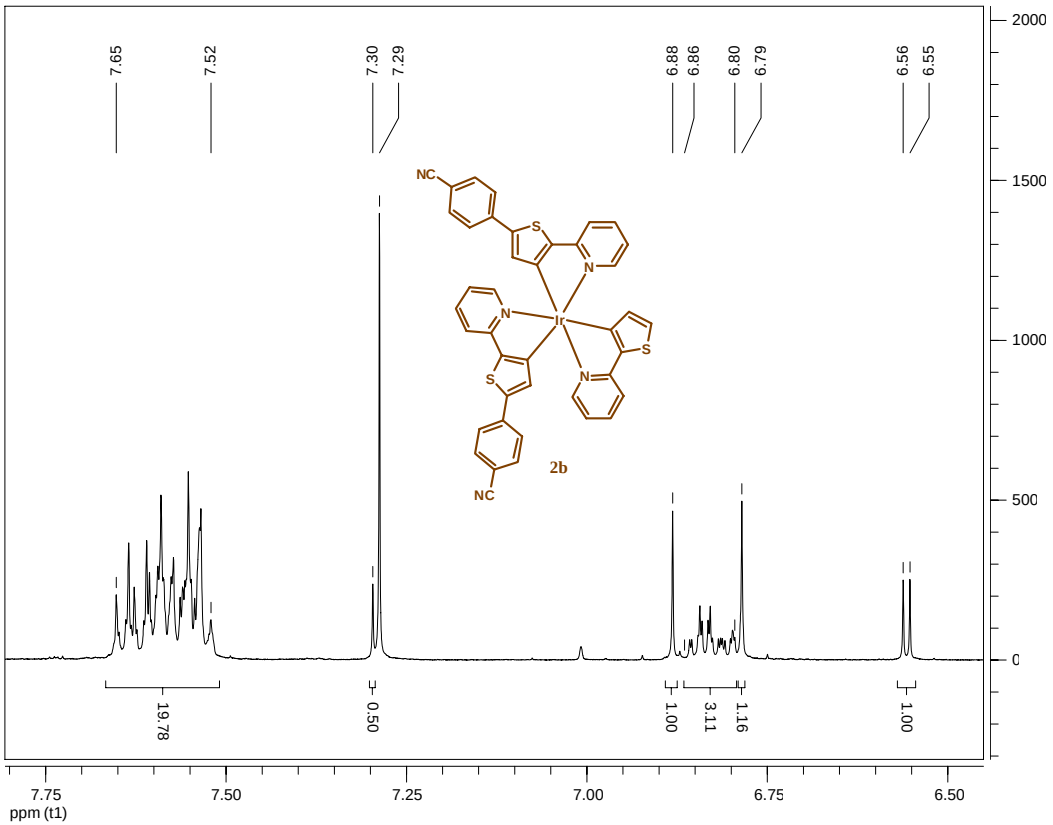
2a ^{1}H, NMR (500MHz, $CDCl_3$)



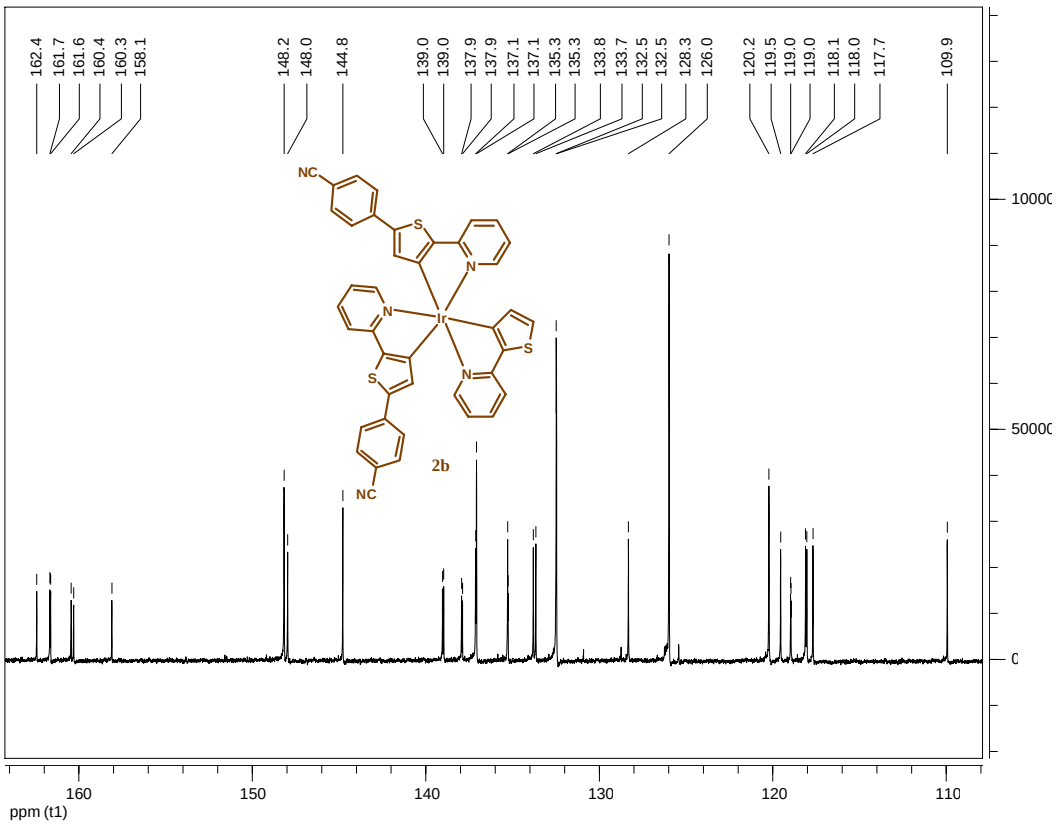
2a ^{13}C, NMR (125MHz, CD_2Cl_2)



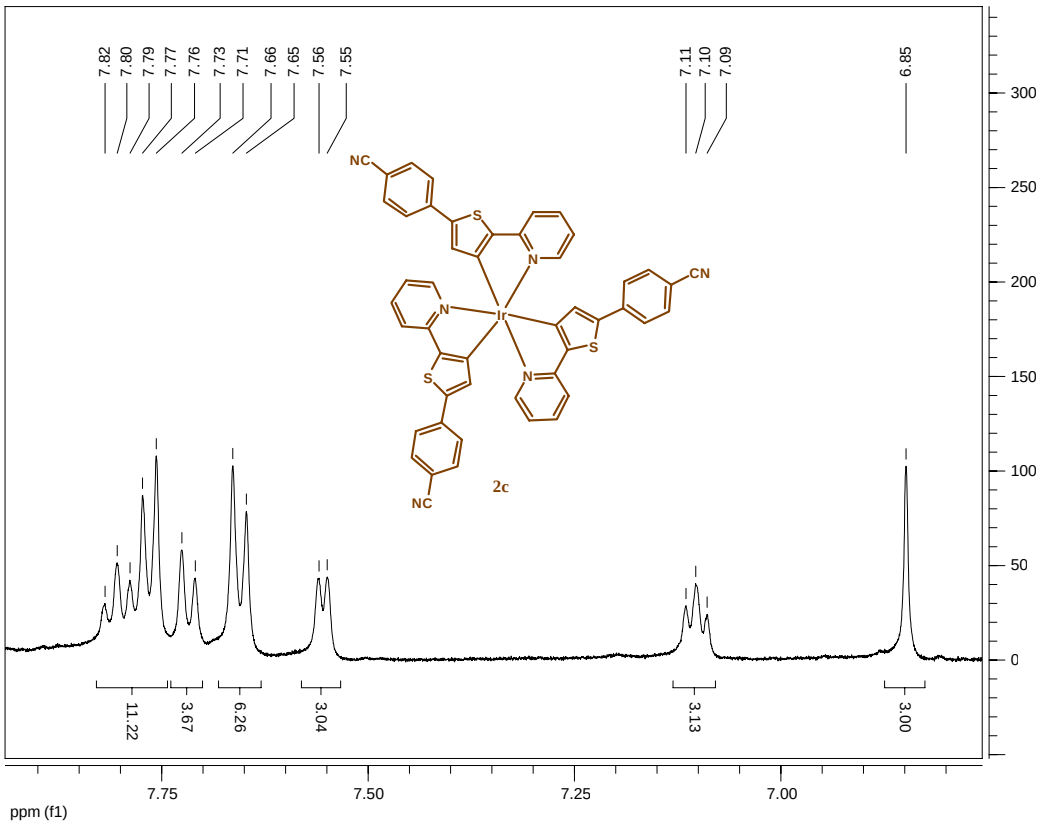
2b ^{1}H, NMR (500MHz, $CDCl_3$)



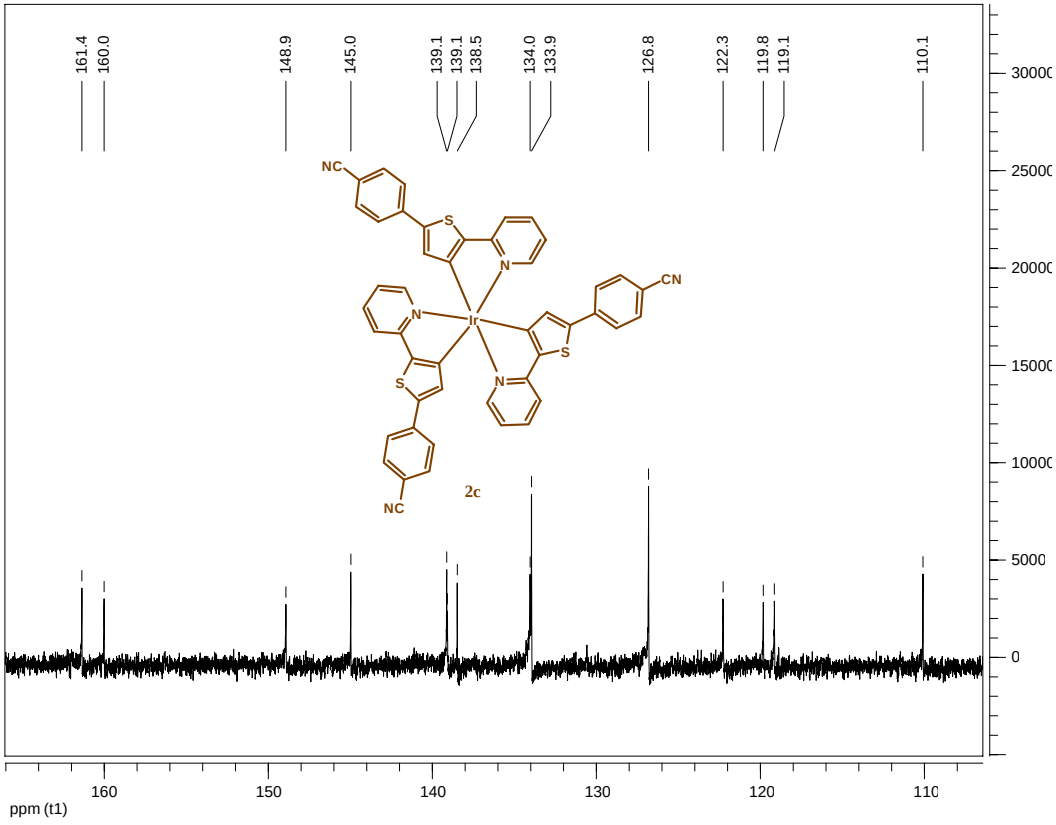
2b ^{13}C, NMR (125MHz, CD_2Cl_2)



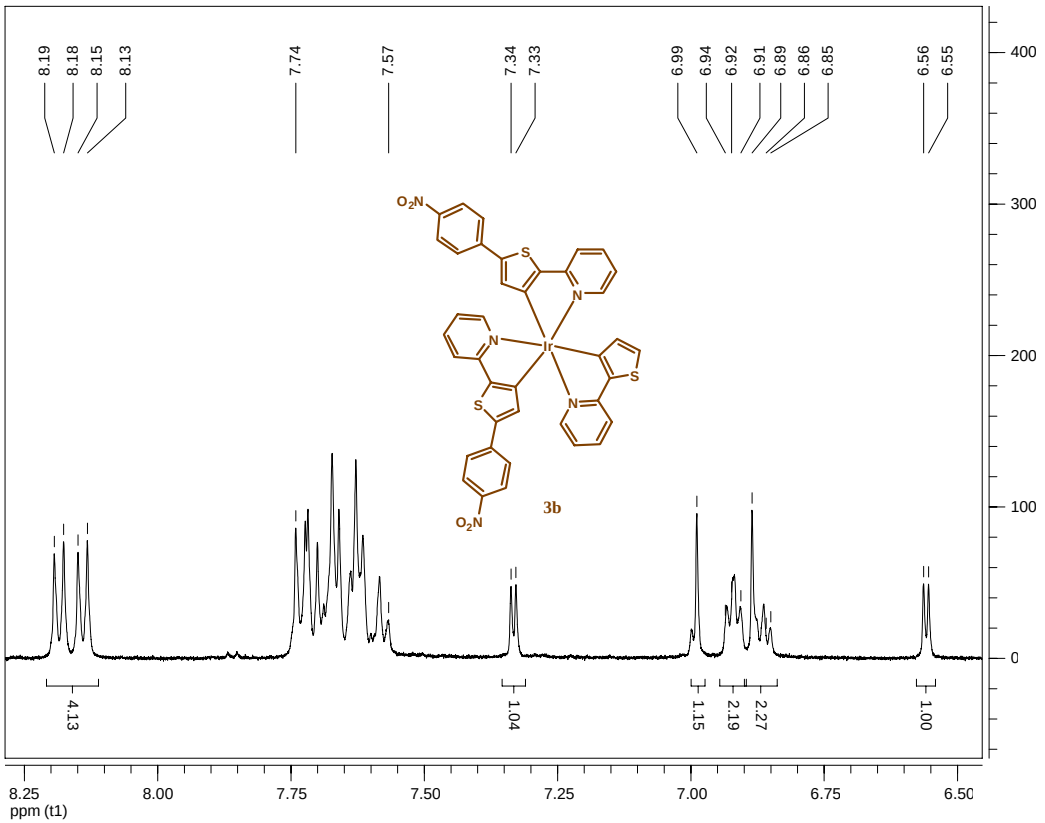
2c ^{1}H, NMR (500MHz, DMSO)



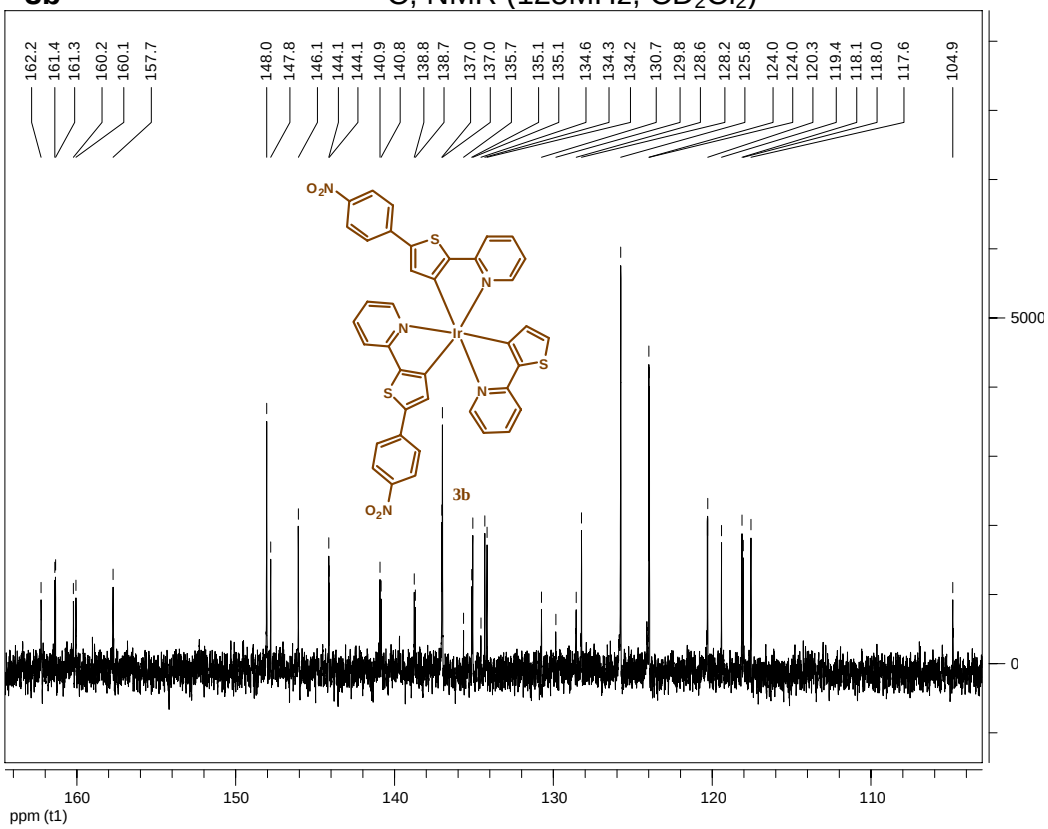
2c ^{13}C, NMR (125MHz, DMSO)



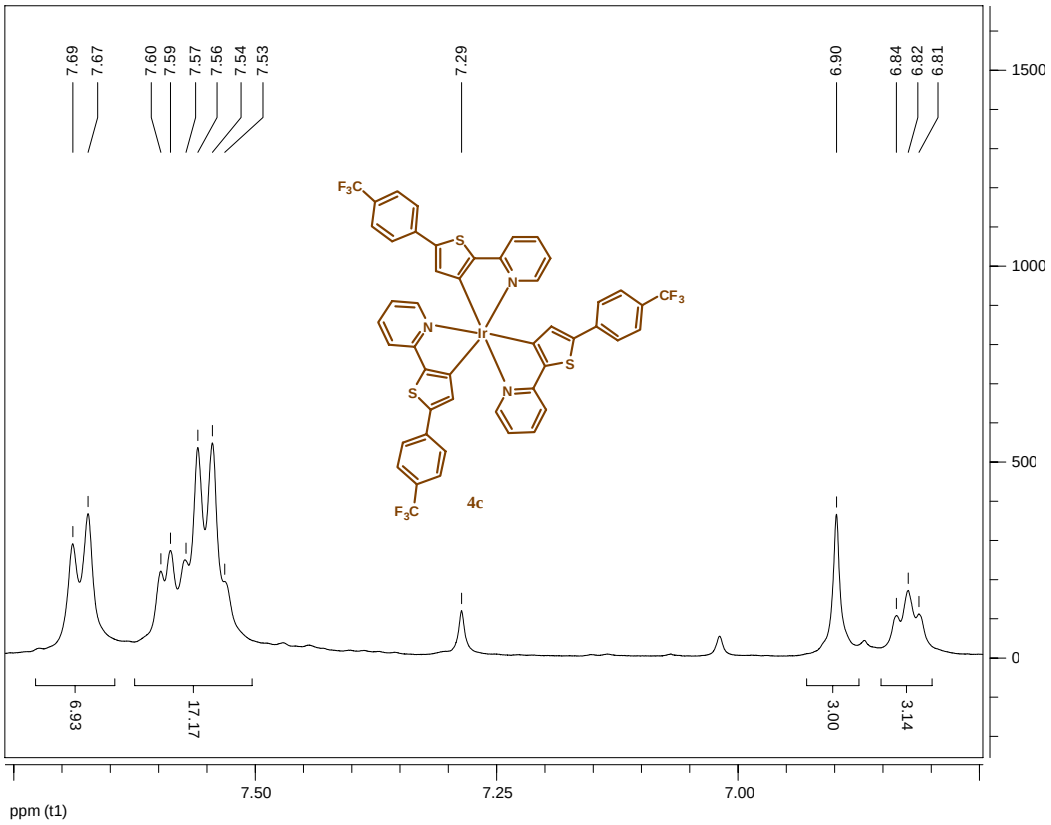
3b ^{1}H, NMR (500MHz, CD_2Cl_2)



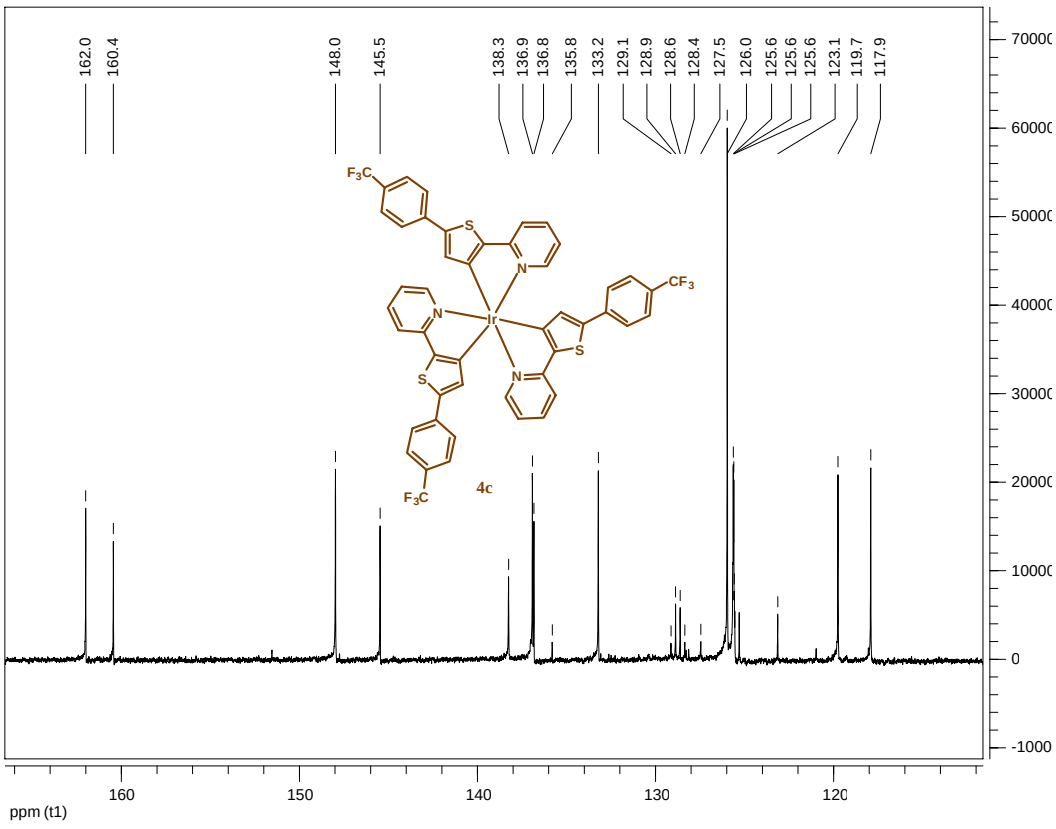
3b ^{13}C, NMR (125MHz, CD_2Cl_2)



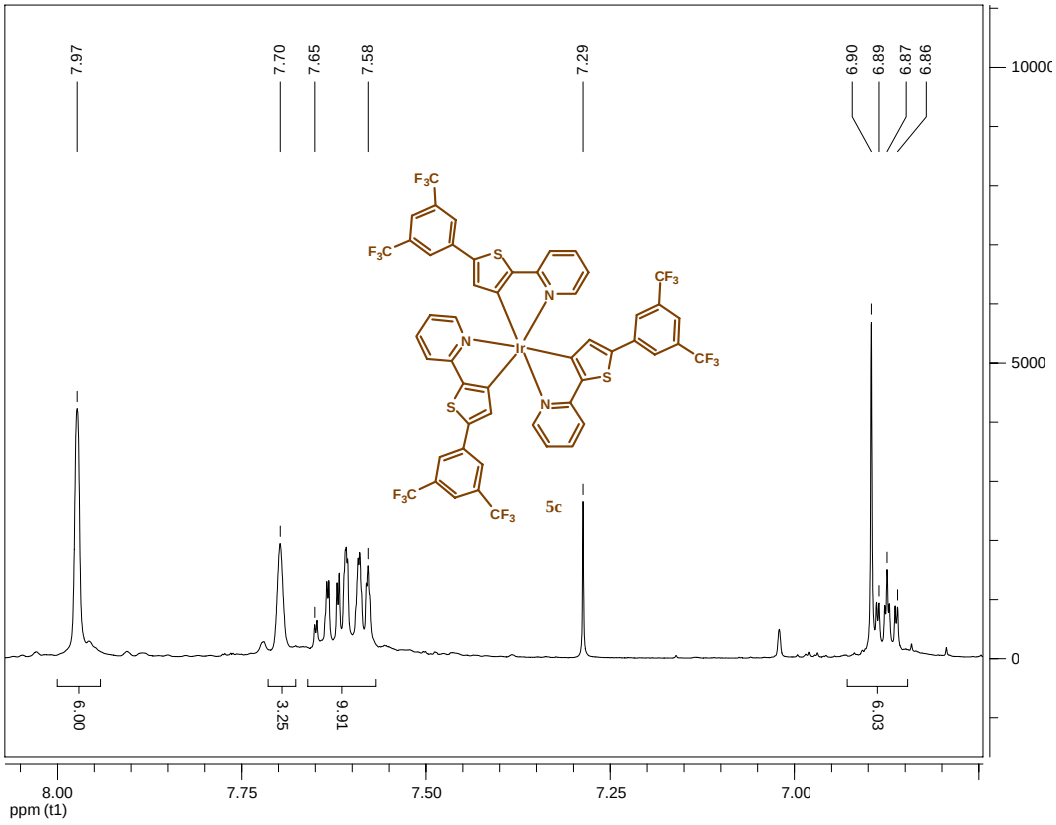
4c ^{1}H, NMR (500MHz, $CDCl_3$)



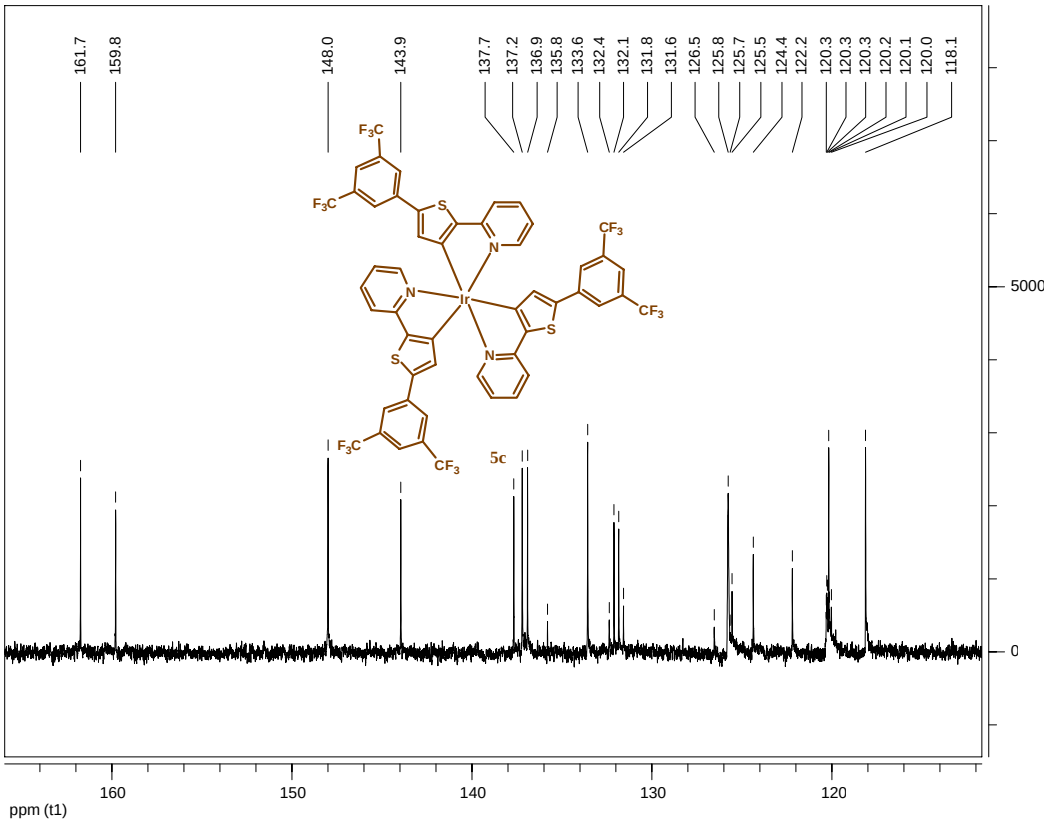
4c ^{13}C, NMR (125MHz, $CDCl_3$)



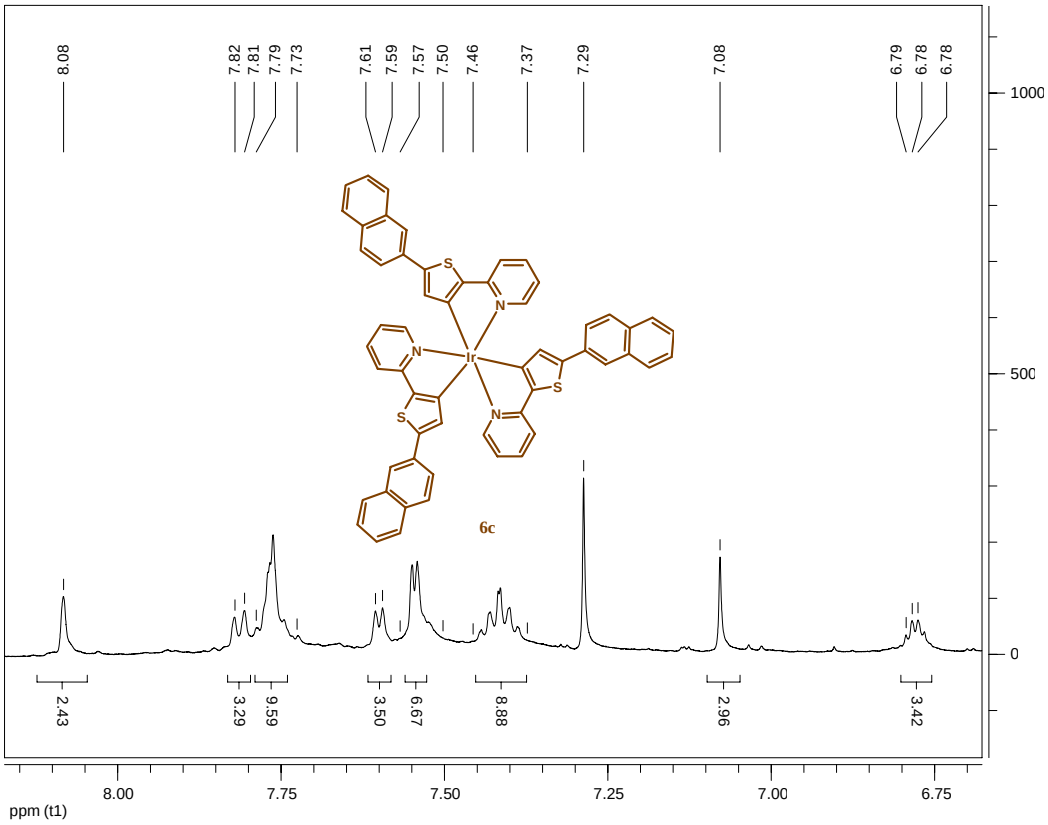
5c ^{1}H, NMR (500MHz, $CDCl_3$)



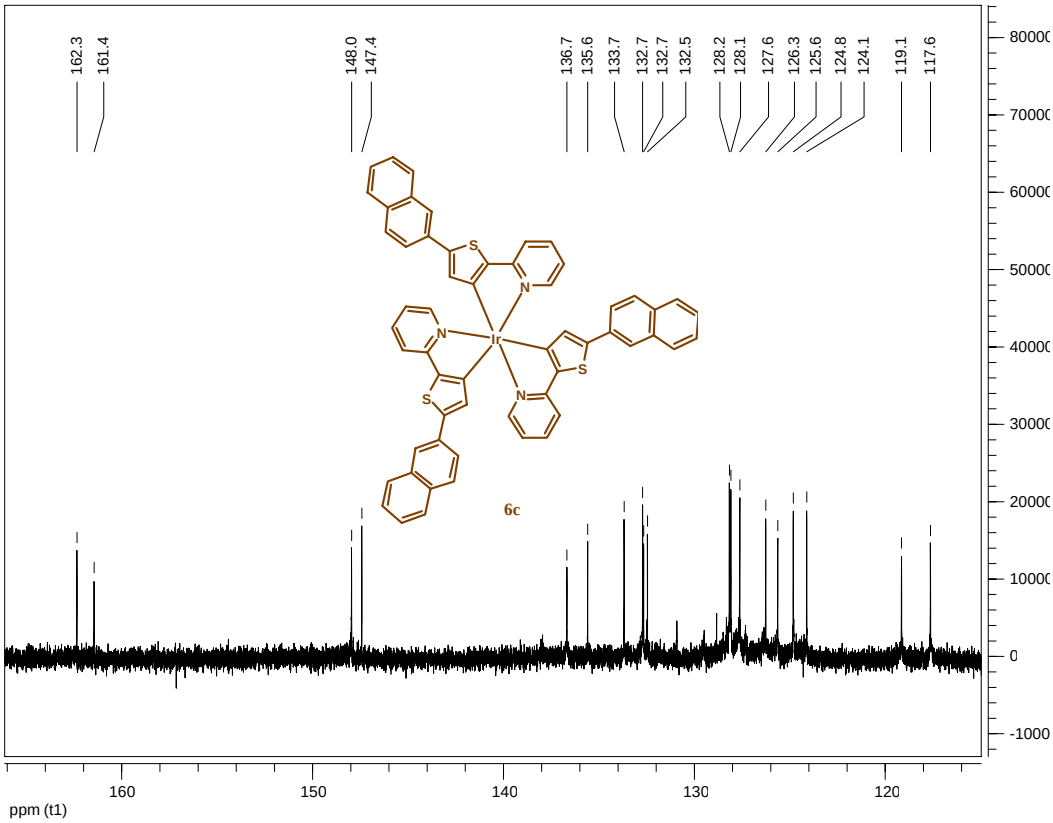
5c ^{13}C, NMR (125MHz, $CDCl_3$)



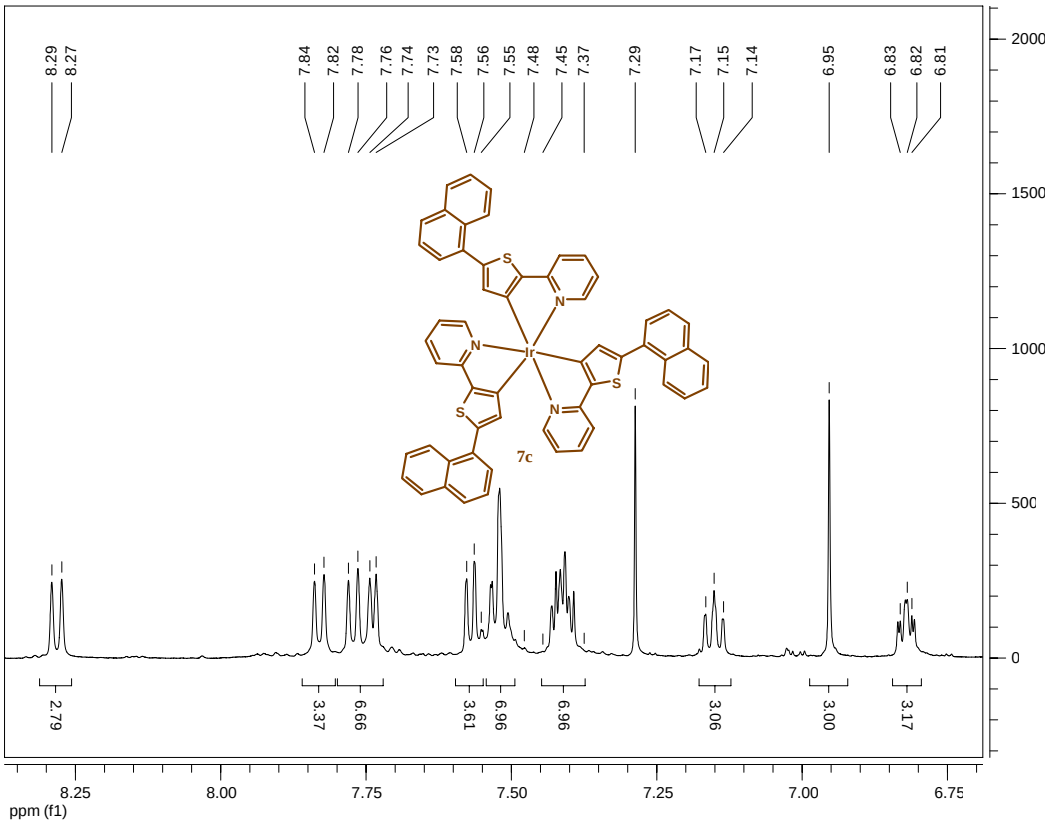
6c ^{1}H, NMR (500MHz, $CDCl_3$)



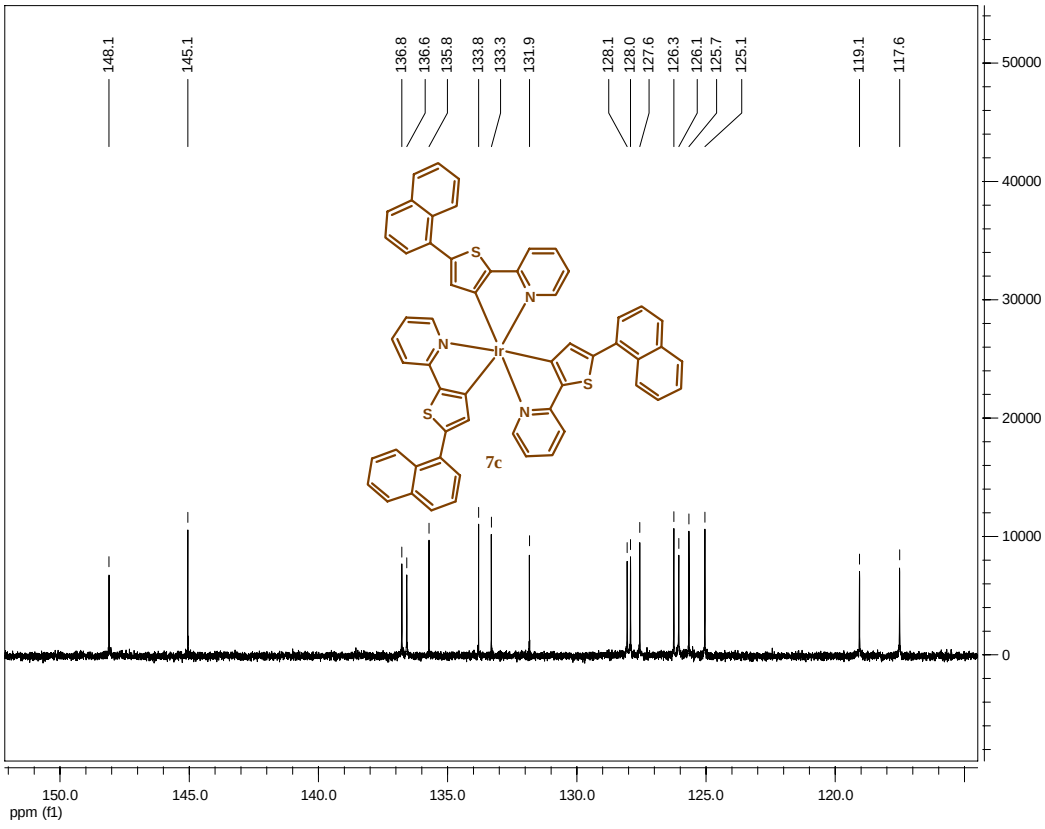
6c ^{13}C, NMR (125MHz, $CDCl_3$)



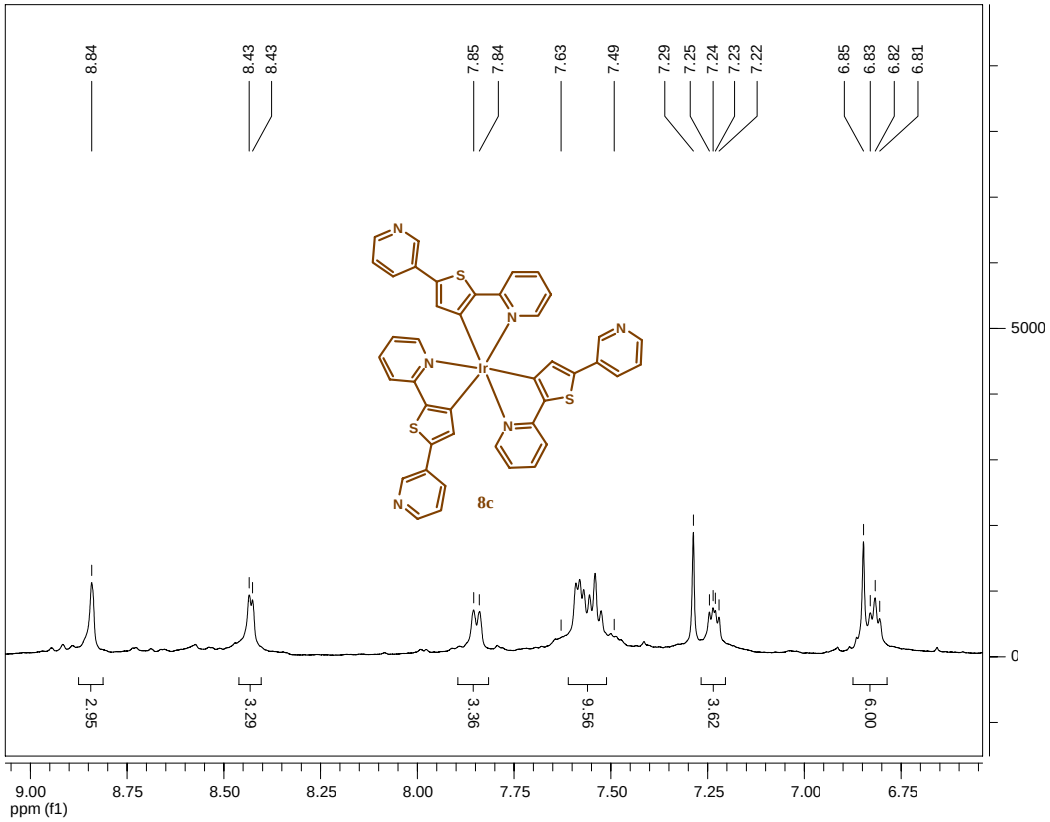
7c ^{1}H, NMR (500MHz, $CDCl_3$)



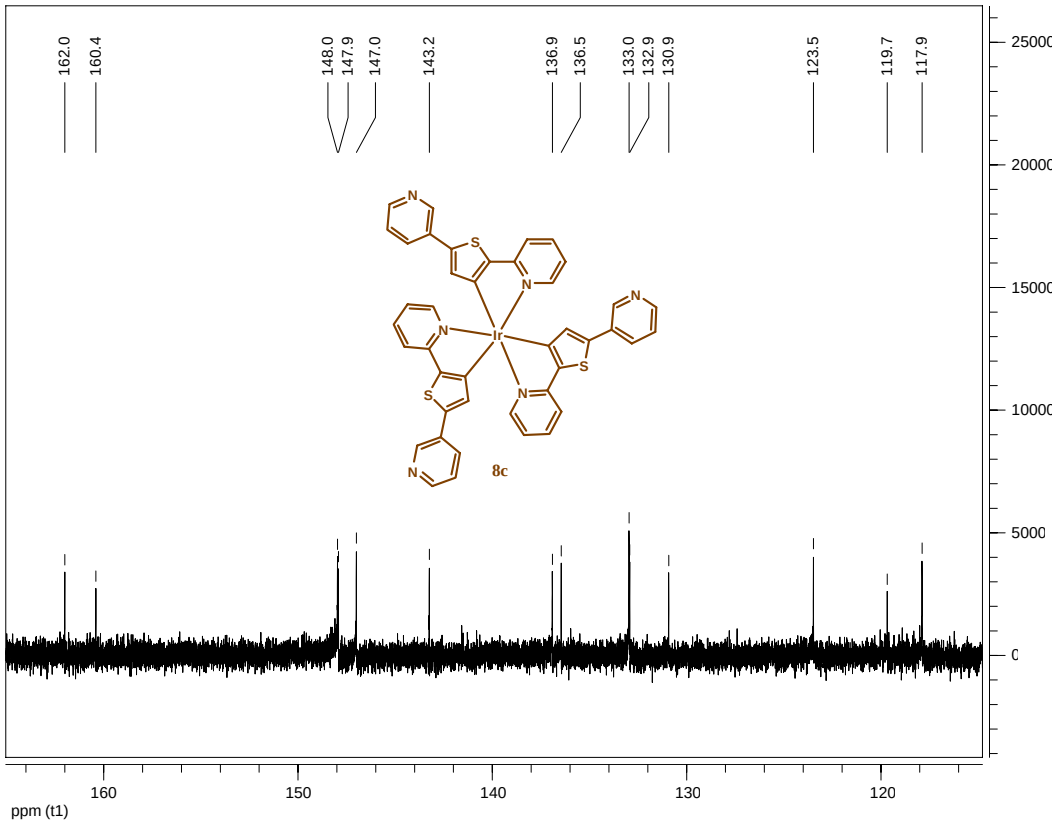
7c ^{13}C, NMR (125MHz, $CDCl_3$)



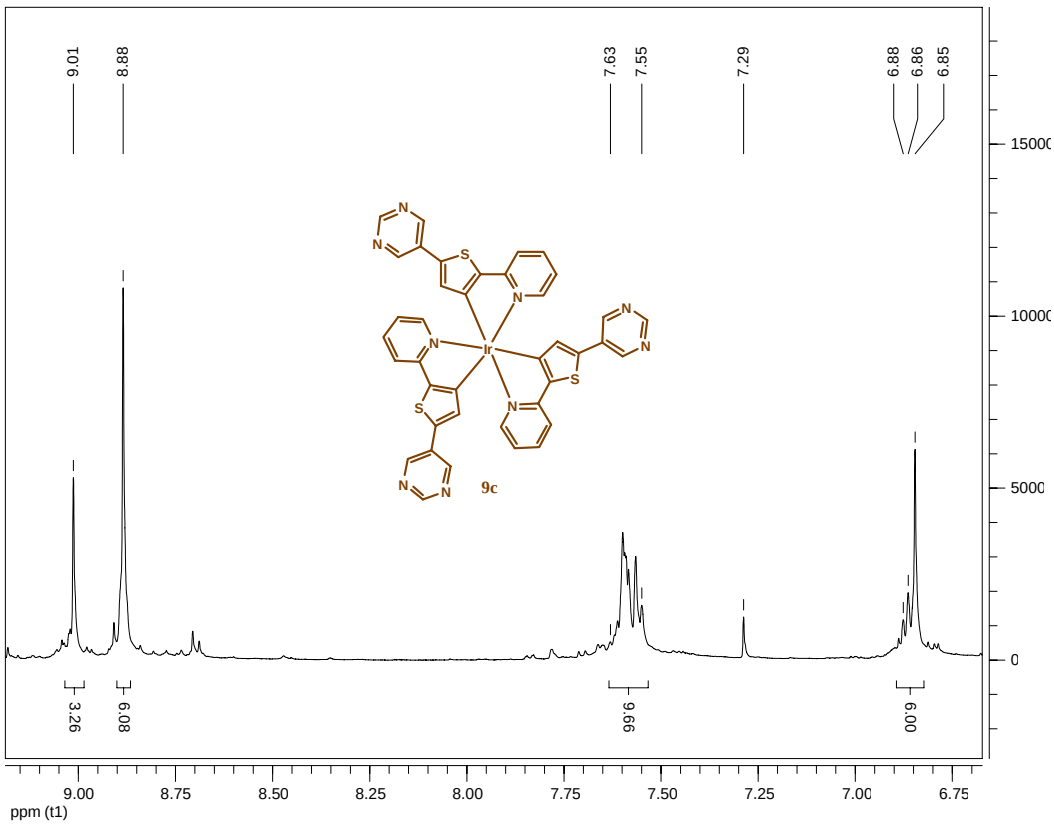
8c ^{1}H, NMR (500MHz, $CDCl_3$)



8c ^{13}C, NMR (125MHz, $CDCl_3$)



9c ^{1}H, NMR (500MHz, $CDCl_3$)



9c ^{13}C, NMR (125MHz, $CDCl_3$)

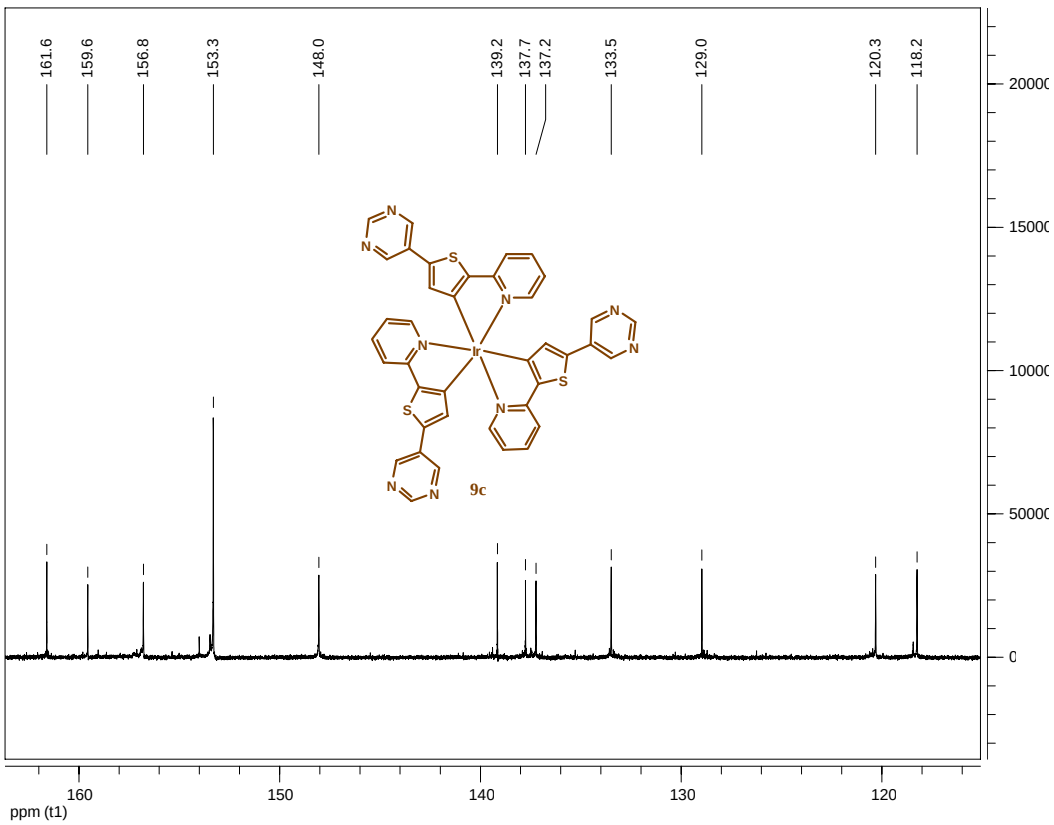


Table S1 Full luminescence data for the complexes investigated.[(a)]

	λ_{max} / nm [(b)]	Φ_{lum} $\times 10^2$	τ / ns degassed [aerated]	k_Q^{O2} / 10^8 $M^{-1}s^{-1}$ [(c)]	k_r / 10^3 s^{-1} [(d)]	Σk_r / 10^4 s^{-1} [(d)]	λ_{max} (77 K) / nm [(e)]	τ (77 K) / μs [(e)]
1 $Ir(thpy)_3$	548, 592, 643(sh)	40	7100 [87]	52	56	8.5	542, 563, 588, 612, 640	9.2
2a mono-CN	677, 742, 812(sh)	0.84	1100 [370]	8.2	7.6	90	667, 699, 736, 777	1.1
2b bis-CN	676, 740, 813(sh)	0.81	1300 [380]	8.5	6.2	76	668, 698, 737, 776	1.3
2c tris-CN	673, 738	1.1	1500 [420]	7.8	7.3	66	667, 698, 734, 774	1.8
4c CF_3	652, 712, 795(sh)	2.0	2400 [370]	10	8.3	41	647, 678, 712, 747, 789	2.6
5c $(CF_3)_2$	654, 714, 798(sh)	1.7	2100 [350]	11	8.1	47	653, 682, 718, 756, 798	2.2
8c m-pyr	645, 703, 784(sh)	1.9	2800 [390]	10	6.8	35	649, 669, 704, 736, 779	3.1

(a) Values refer to solutions in CH_2Cl_2 at 298 K, except where indicated otherwise. *(b)* $\lambda_{excitation}$ = 455 nm. *(c)* k_Q^{O2} is the biomolecular rate constant for quenching by dissolved molecular oxygen, estimated on the basis of the liftetimes in degassed and air-equilibrated solutions. *(d)* k_r and Σk_{nr} are the estimated radiative and non-radiative rate constants estimated from the Φ_{lum} and τ values, assuming that formation of the emitting state occurs with unitary efficiency. (e) In diethyl ether / isopentane / ethanol (2:2:1 v/v).

Figure S1 Overlay of the absorption spectra of **2a**, **2b** and **2c** in CH_2Cl_2 at 298 K.

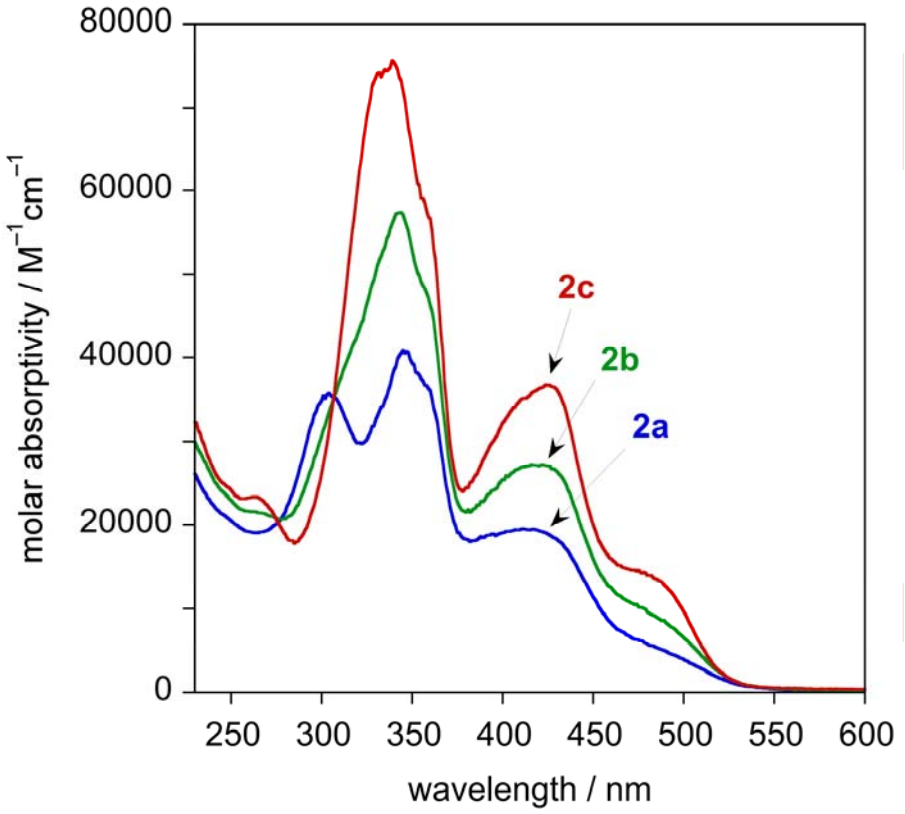
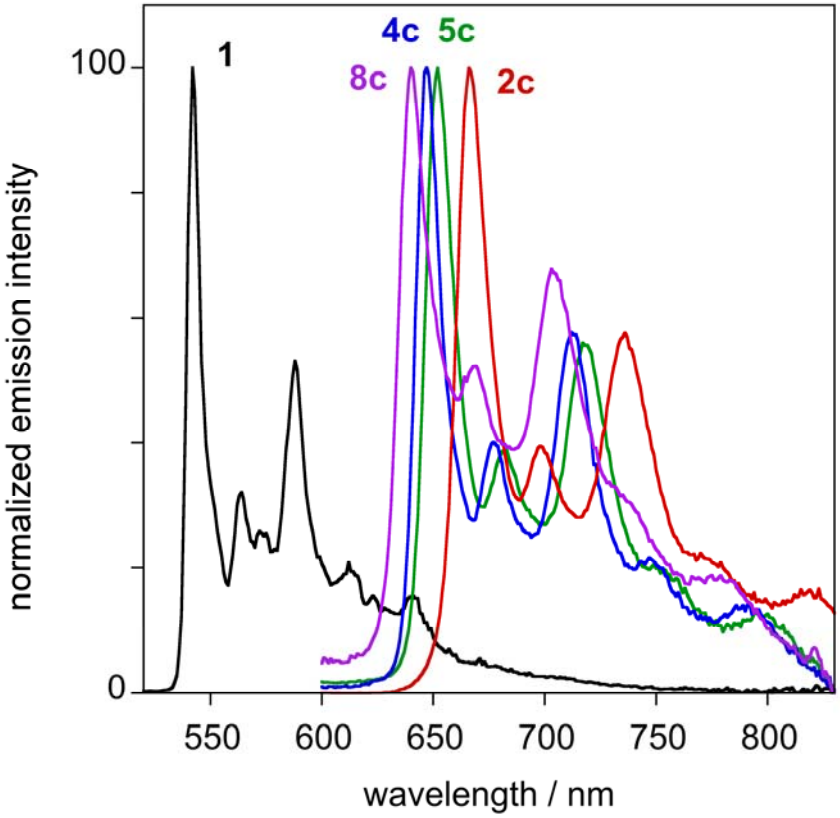


Figure S2 Overlay of the emission spectra recorded in EPA at 77 K {EPA = diethyl ether / isopentane / ethanol, 2:2:1 v/v}



Instrumentation for luminescence measurements

UV-vis absorption spectra were recorded using analytikjena SPECORD 205 spectrometer using quartz cuvettes of 1 cm path length. Steady state emission spectra were measured using a JobinYvon FluoroMax 2 spectrometer. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Luminescence quantum yields were determined using $[Ru(bpy)_3]Cl_2$ in air-equilibrated water as the standard, for which Φ_{lum} = 0.028 [K. Nakamaru, *Bull. Chem. Soc. Jpn*, 1982, **55**, 2697]. Estimated uncertainty in Φ_{lum} is ± 20% or better.

The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting (TCSPC), following excitation at 374 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is ± 10% or better.