Supporting Information

Cyclometalated luminescent platinum(II) complexes of dissymmetrical 2,2':4',2''-terpyridine and its self-assembled dimer presenting Pt-Ag dative bonds

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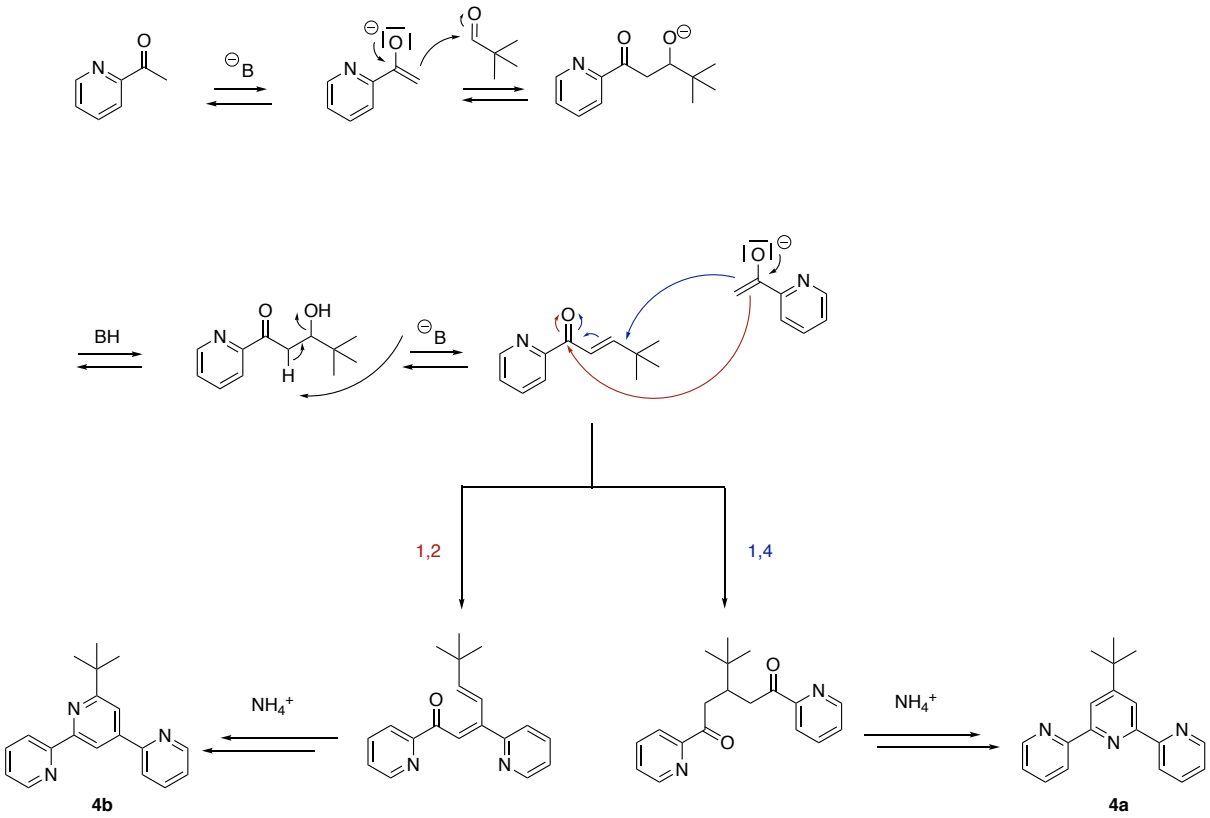
X-ray crystallography data

Identification code	**3**	5
Empirical formula	$C_{87.5}H_{97.5}AgCl_{7.5}F_9N_{10}O_9Pt_2S_3$	$C_{21}H_{21}N_4ClPt$
Formula weight	2464.35	559.96
Temperature/K	200	200(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/m$
a/Å	15.4562(9)	12.6144(9)
b/Å	42.508(3)	6.7077(4)
c/Å	15.6202(12)	12.6960(8)
α/°	90	90
β/°	105.542(4)	106.728(4)
γ/°	90	90
Volume/Å^3	9887.5(12)	1028.79(12)
Z	4	2
ρ_{calc}g/cm^3	1.655	1.808
μ/mm^{-1}	9.854	6.962
F(000)	4896.0	540.0
Crystal size/mm^3	0.15 × 0.02 × 0.02	0.45 × 0.15 × 0.02
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.198 to 94.526	5.394 to 61.116
Index ranges	-14 ≤ h ≤ 14, -40 ≤ k ≤ 40, -14 ≤ l ≤ 12	-17 ≤ h ≤ 17, -9 ≤ k ≤ 9, -18 ≤ l ≤ 18
Reflections collected	36015	29225
Independent reflections	8823 [R_{int} = 0.1455, R_{sigma} = 0.1398]	29225 [R_{int} = 0.0560, R_{sigma} = 0.0751]
Data/restraints/parameters	8823/53/600	29225/0/161
Goodness-of-fit on F^2	1.052	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.1270, wR_2 = 0.2911	R_1 = 0.0558, wR_2 = 0.1227
Final R indexes [all data]	R_1 = 0.1900, wR_2 = 0.3264	R_1 = 0.0706, wR_2 = 0.1294
Largest diff. peak/hole/e Å^{-3}	2.22/-1.79	5.35/-3.75
CCDC number	2339432	2339433

Supplementary Scheme



Scheme S1. Proposed mechanism for the formation of terpyridine **4a** and **4b**.

Supplementary Figures

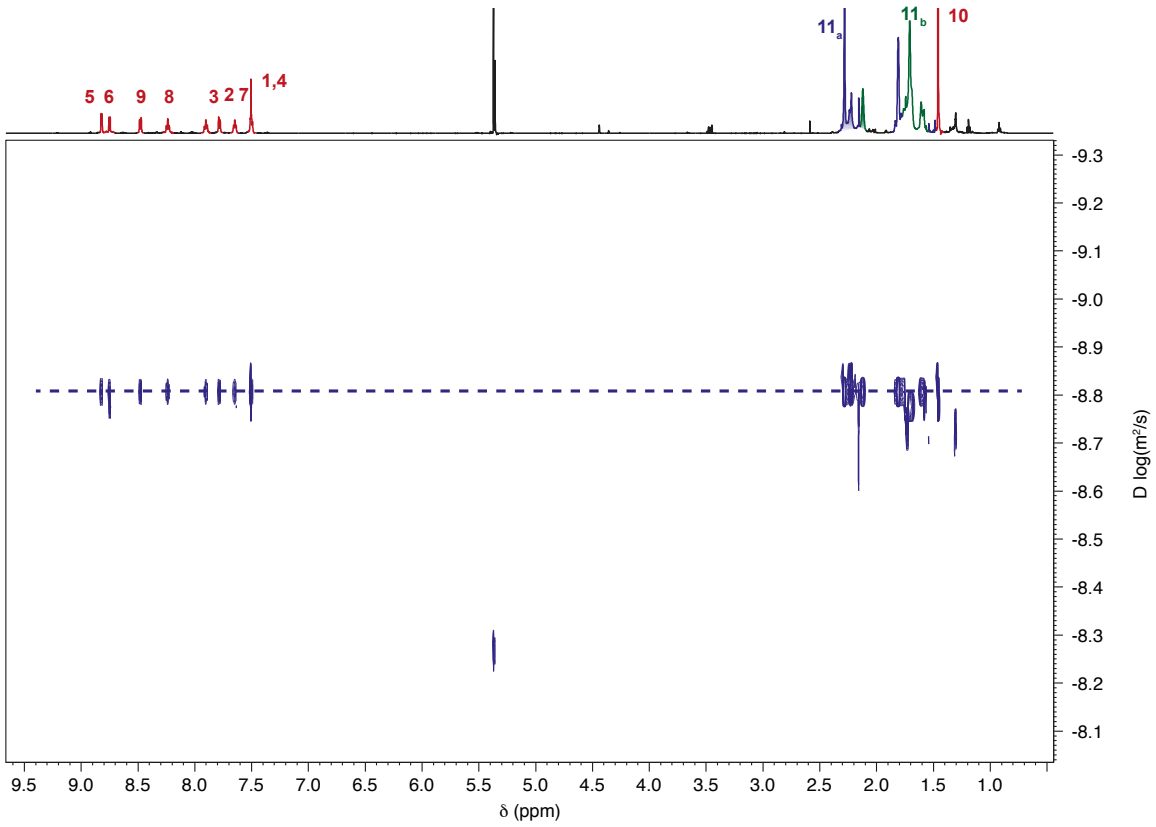


Figure S1. ^{1}H NMR DOSY Spectra (600 MHz, CD_2Cl_2, 300K) of complex **2**.

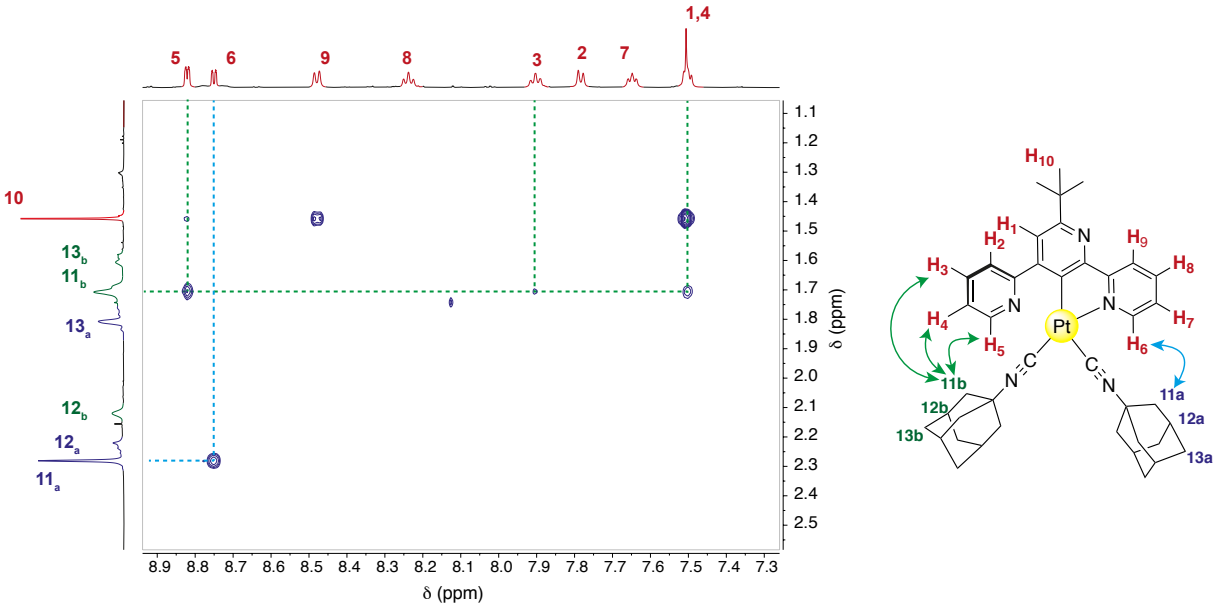


Figure S2. Partial ^{1}H NMR NOESY Spectra (600 MHz, CD_2Cl_2, 300K) of complex **2** showing the regioselectivity of the pyridine decoordination.

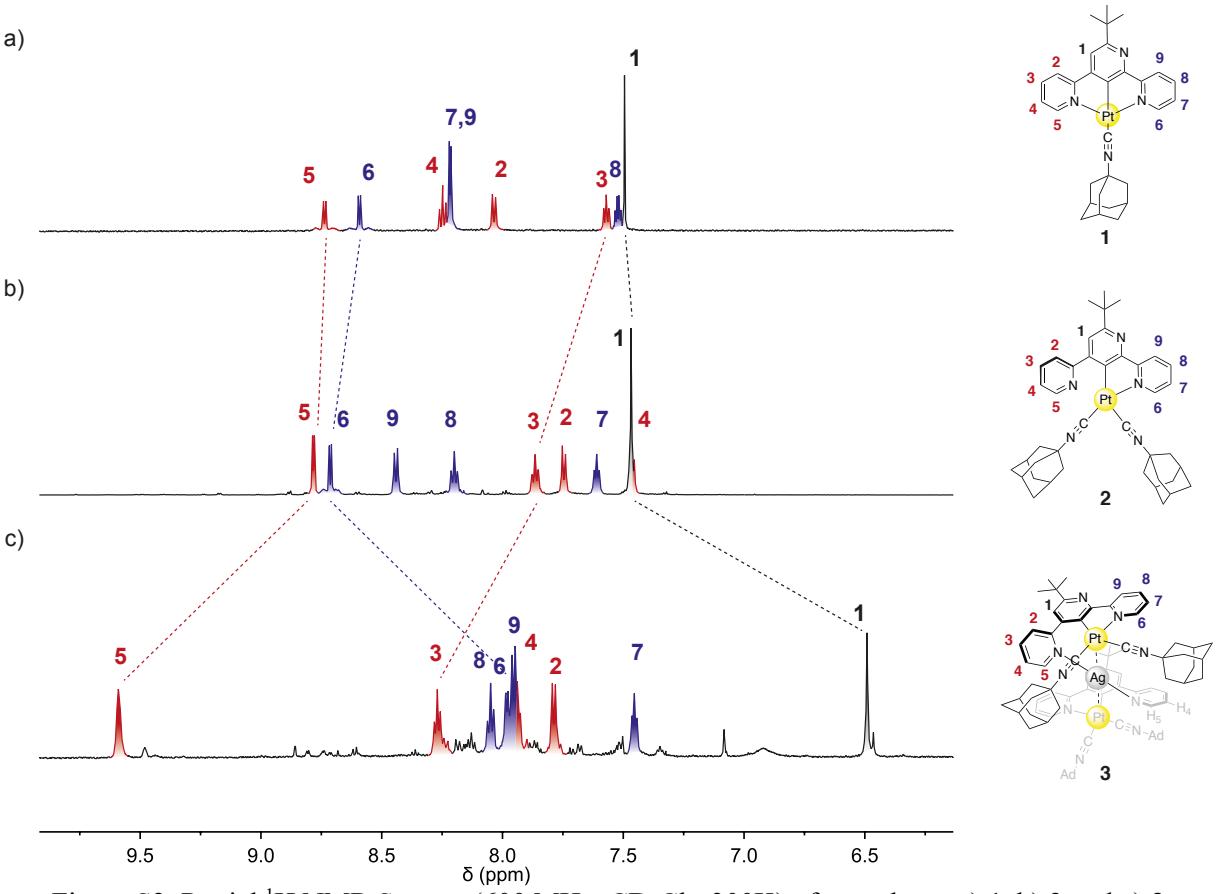


Figure S3. Partial ^{1}H NMR Spectra (600 MHz, CD_2Cl_2, 300K) of complexes a) **1**, b) **2** and c) **3** showing the effect of the different coordination modes on the terpy protons.

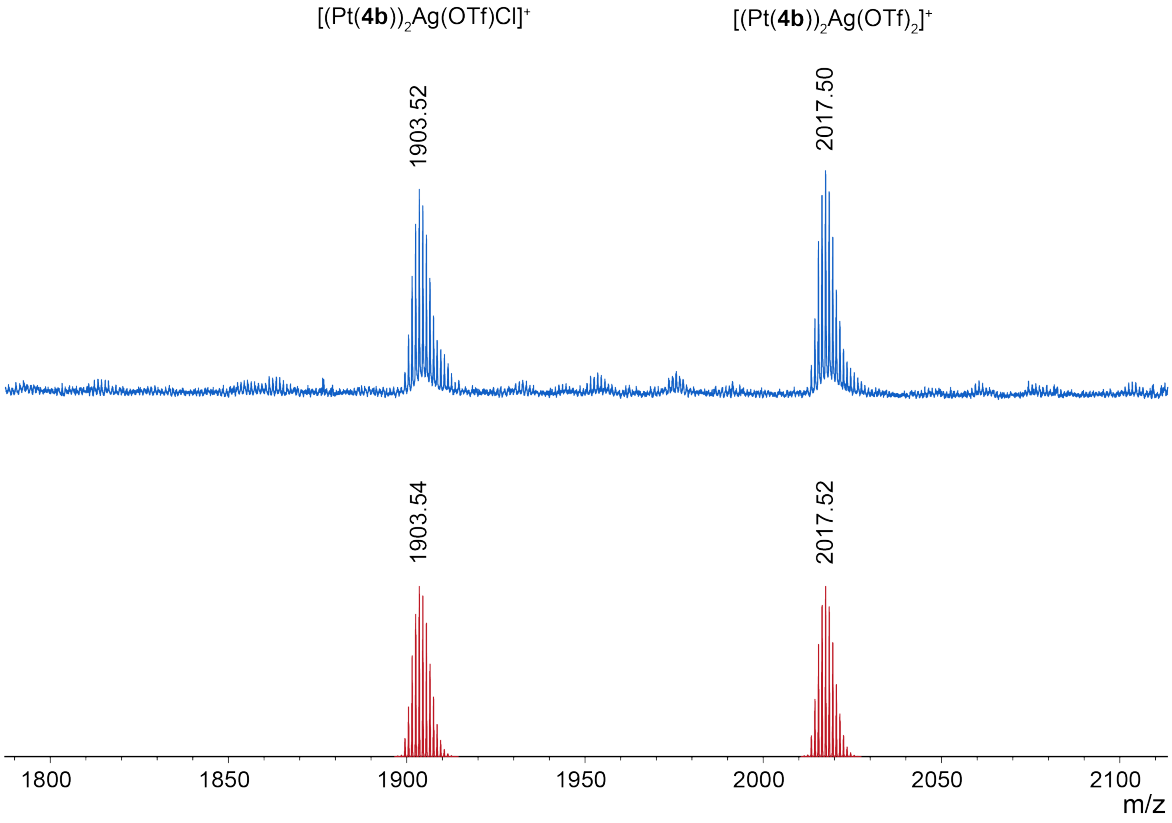


Figure S4. ESI-Tof mass spectra of dimer **3** experimental (top) and calculated (bottom).

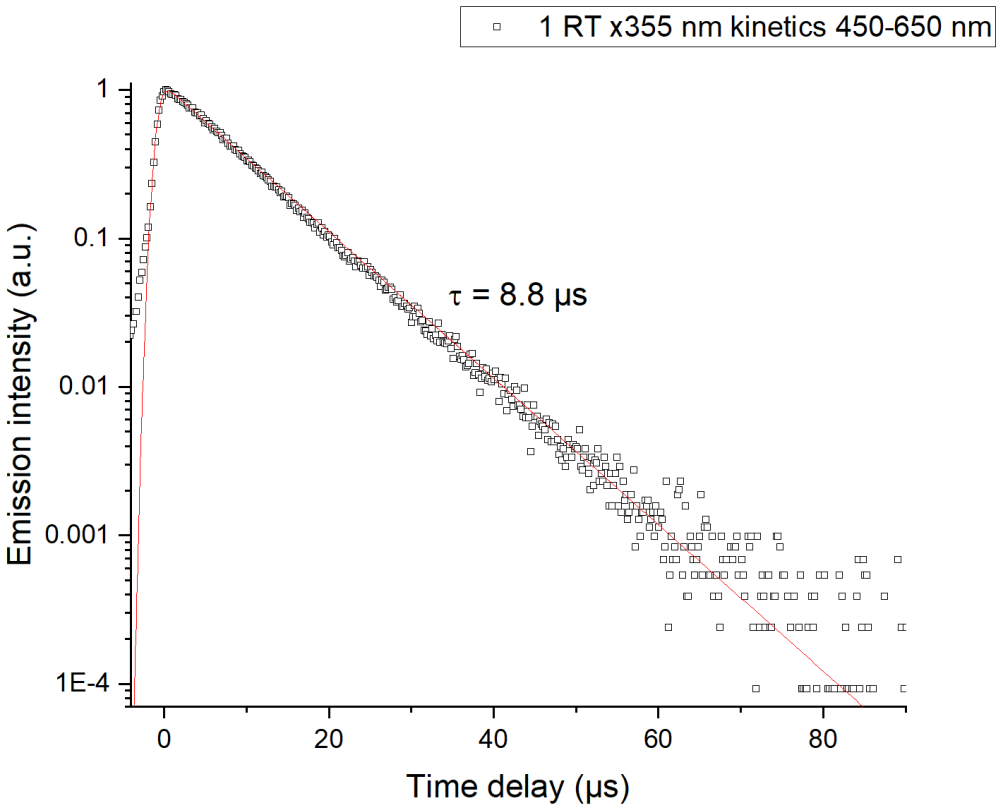


Figure S5. Luminescence decay for **1** in degassed dry $CHCl_3$ at 293 K (λ_{ex}=355 nm).

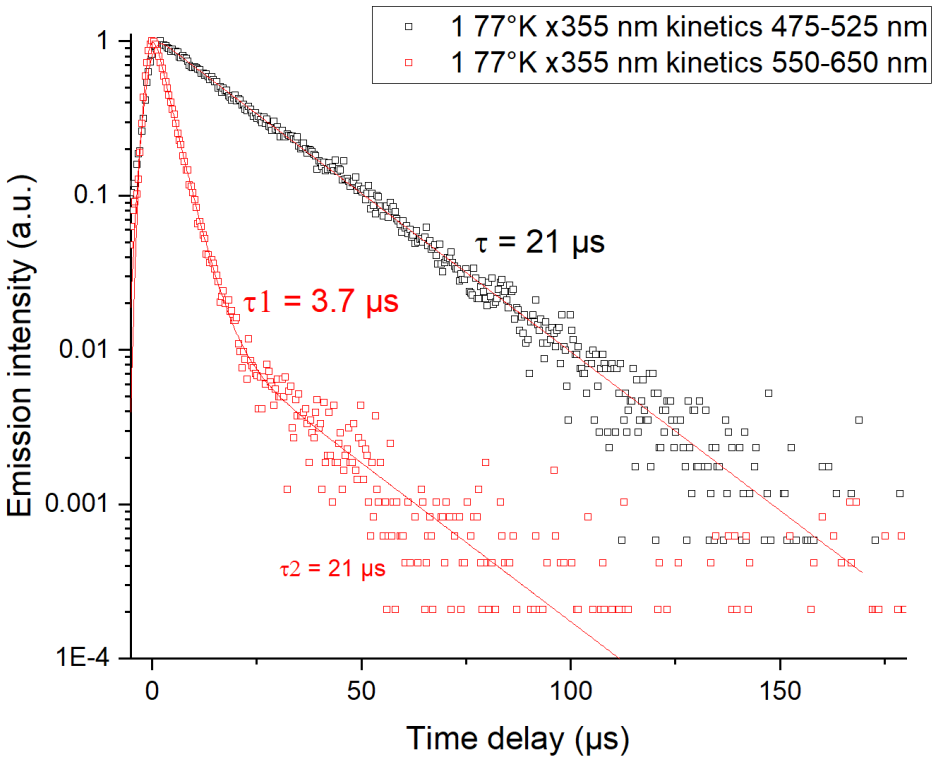


Figure S6. Luminescence decay for **1** in degassed dry $CHCl_3$ at 77 K (λ_{ex}=355 nm).

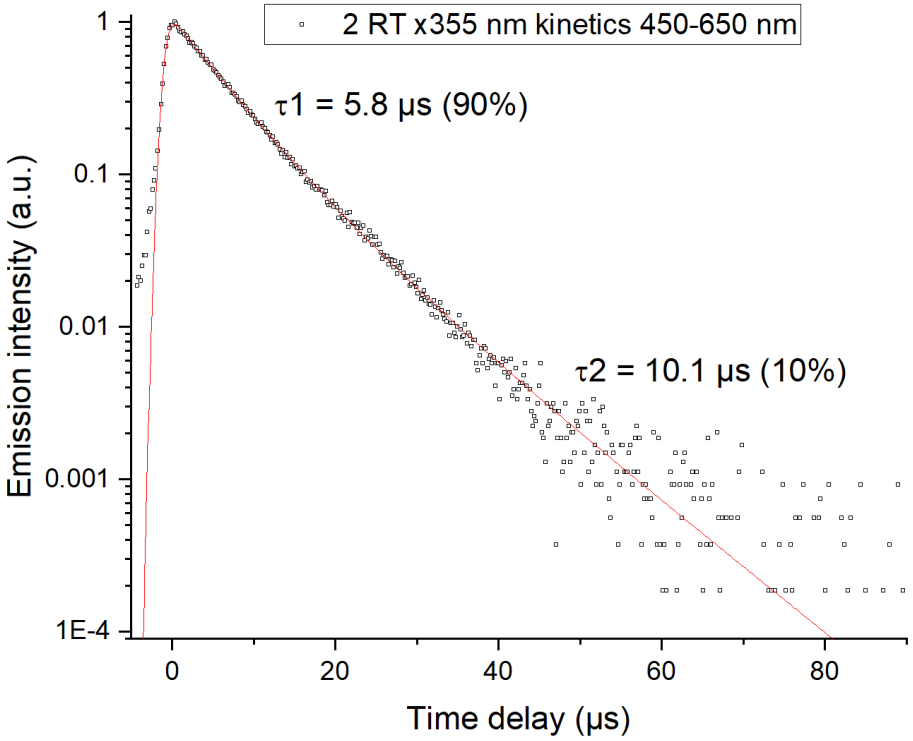


Figure S7. Luminescence decay for **2** in degassed dry $CHCl_3$ at 293 K (λ_{ex}=355 nm).

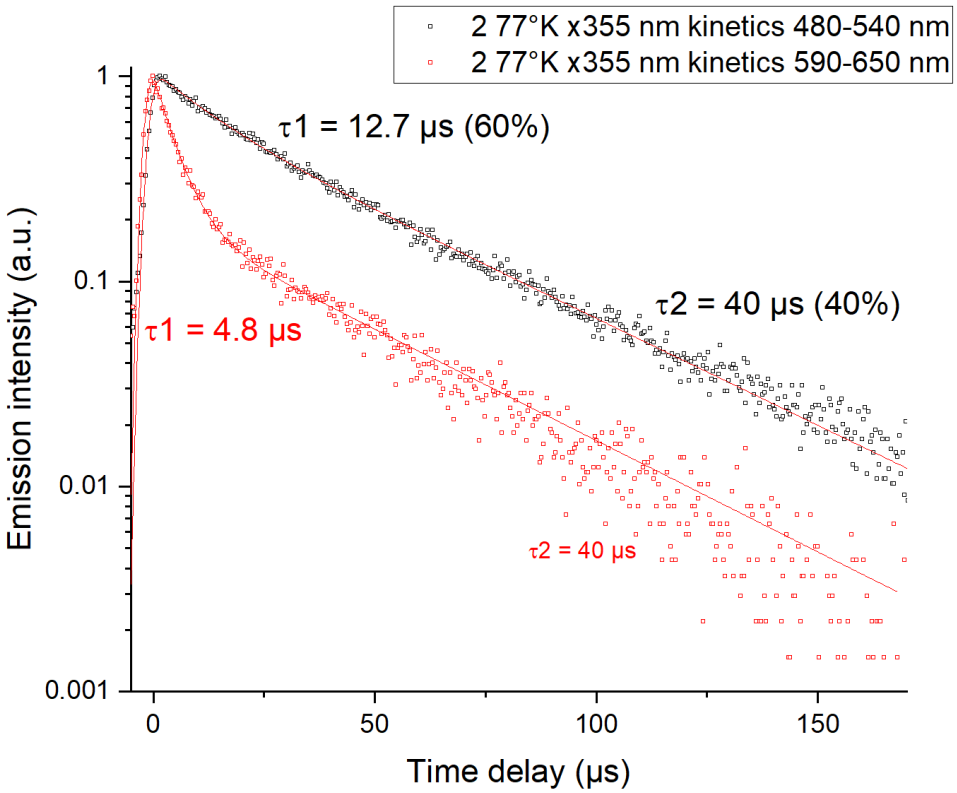


Figure S8. Luminescence decay for **2** in degassed dry $CHCl_3$ at 77 K (λ_{ex}=355 nm).

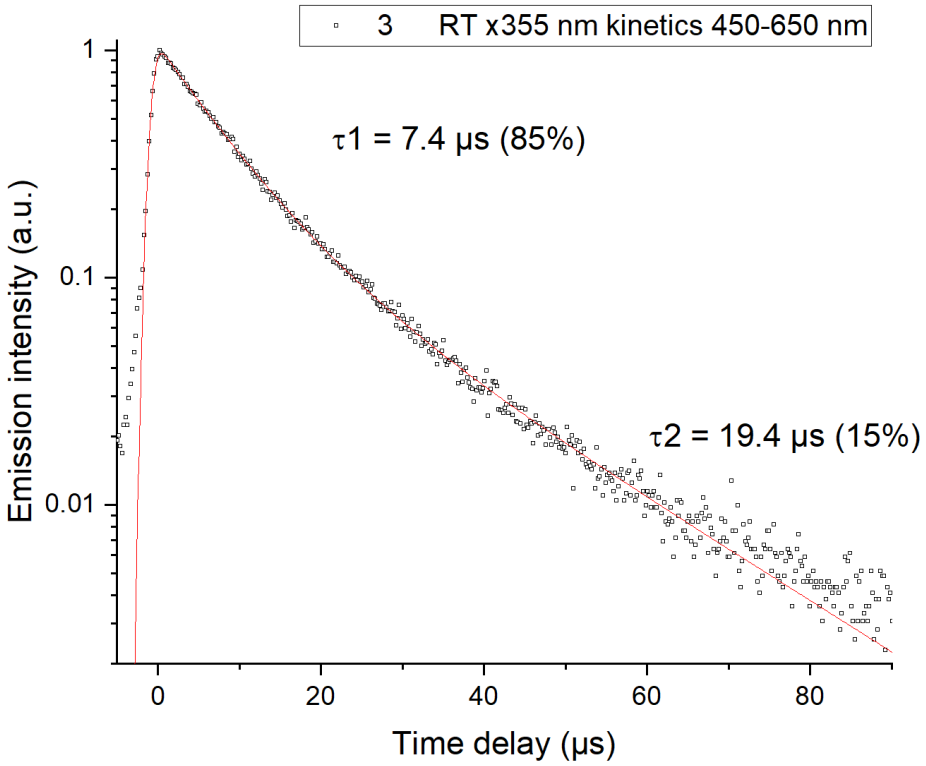


Figure S9. Luminescence decay for **3** in degassed dry $CHCl_3$ at 293 K (λ_{ex}=355 nm).

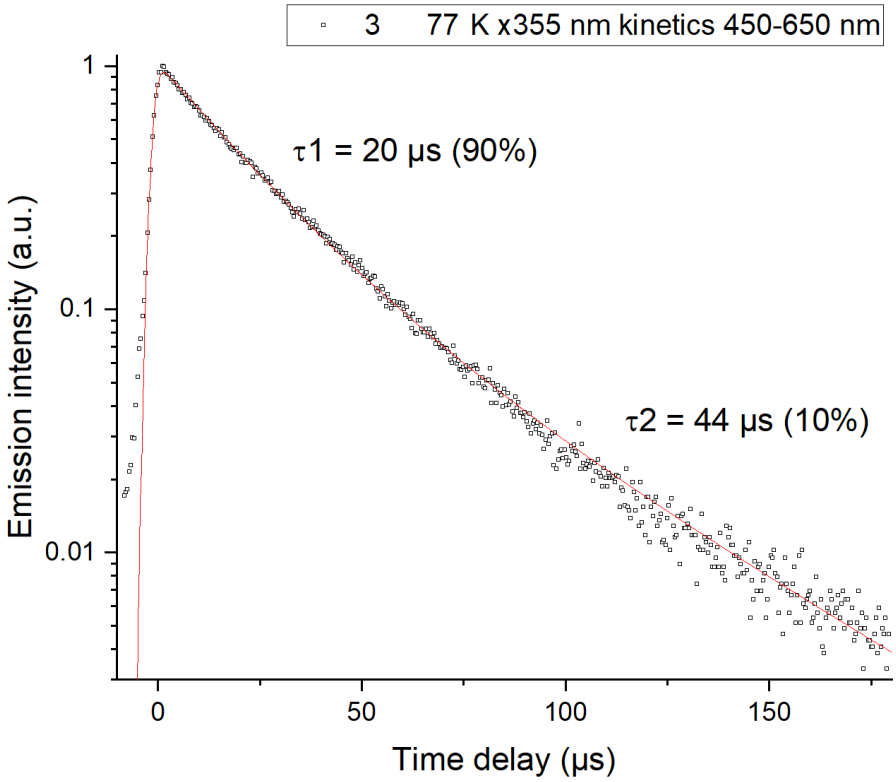


Figure S10. Luminescence decay for **3** in degassed dry $CHCl_3$ at 77 K (λ_{ex}=355 nm).

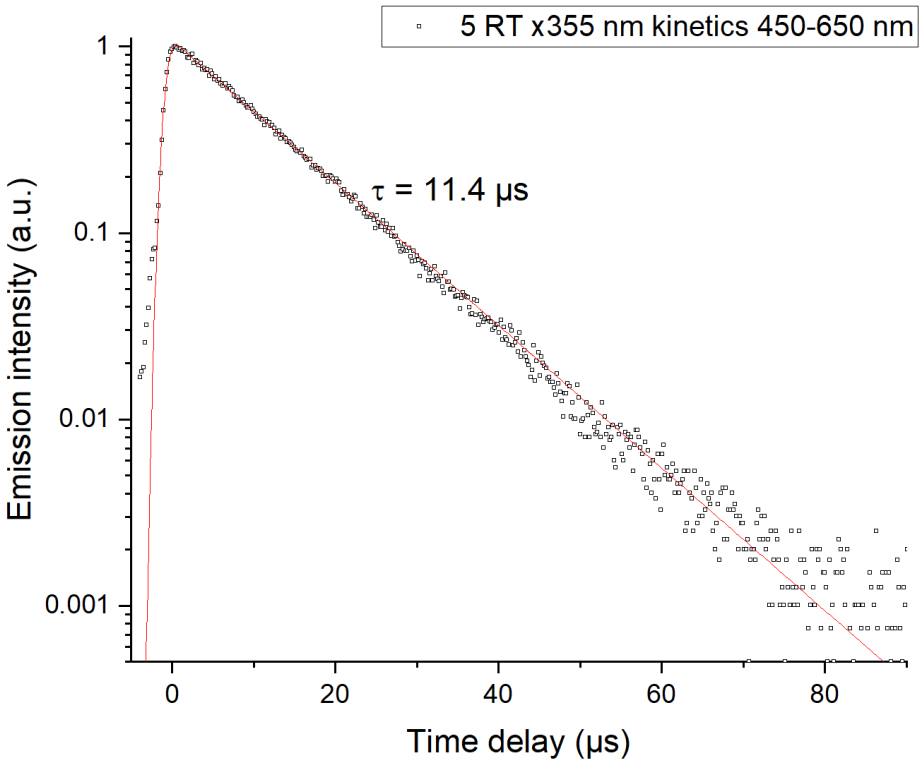


Figure S11. Luminescence decay for **5** in degassed dry $CHCl_3$ at 293 K (λ_{ex}=355 nm).

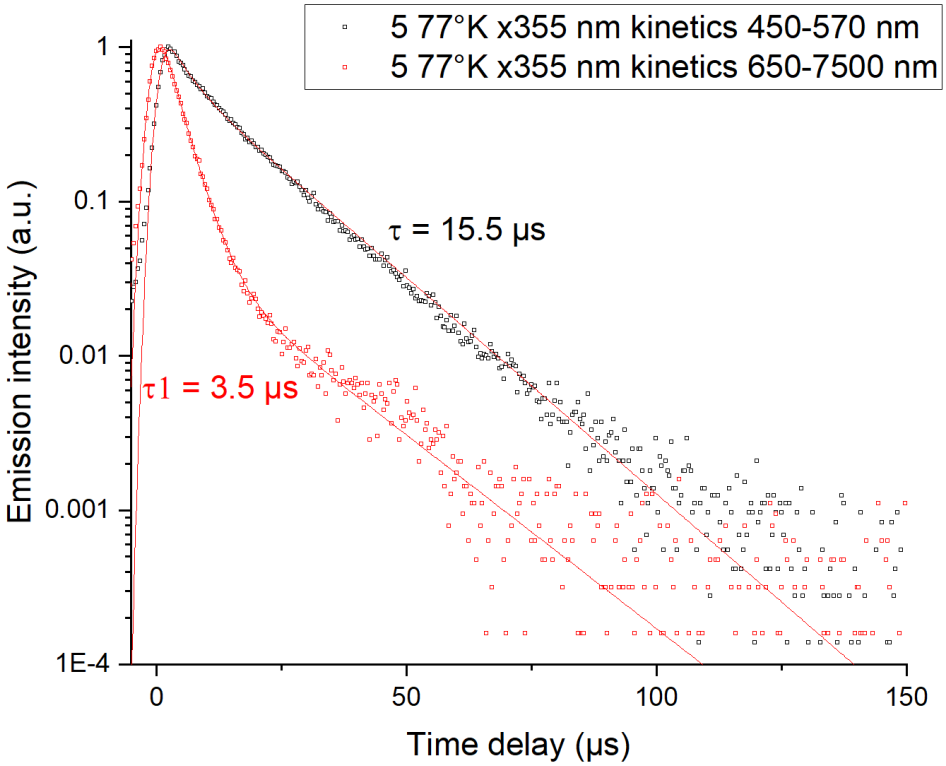


Figure S12. Luminescence decay for **5** in degassed dry $CHCl_3$ at 77 K (λ_{ex}=355 nm).

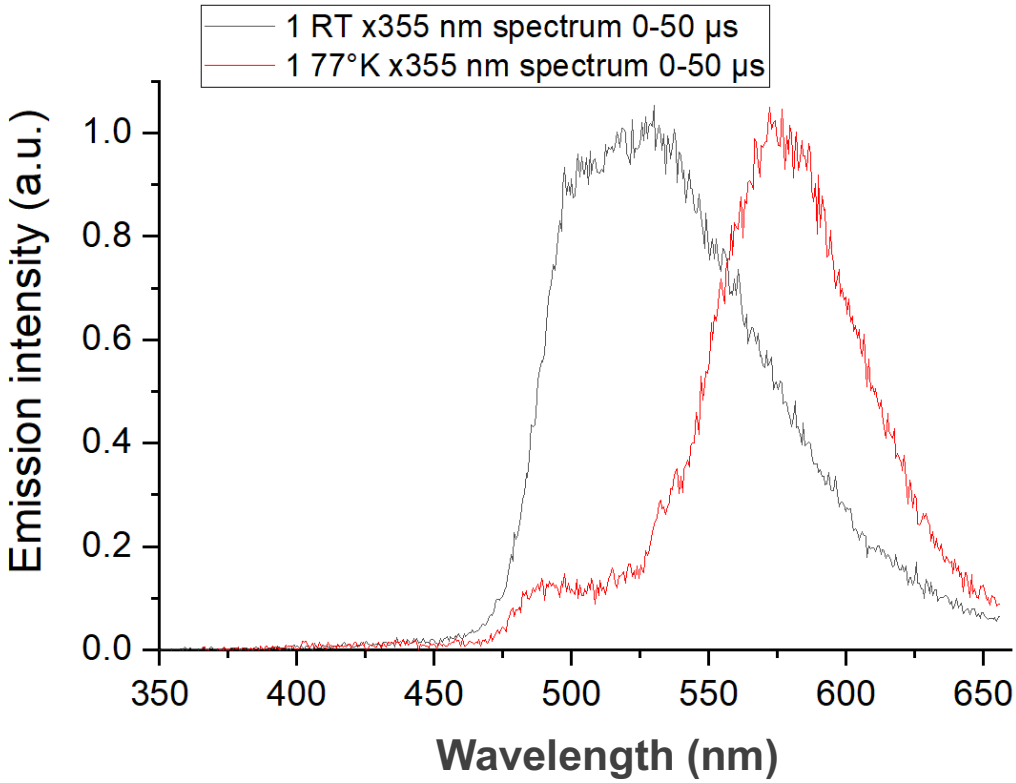


Figure S13. Emission of degassed solutions of **1** in $CHCl_3$ at 293 and 77 K.

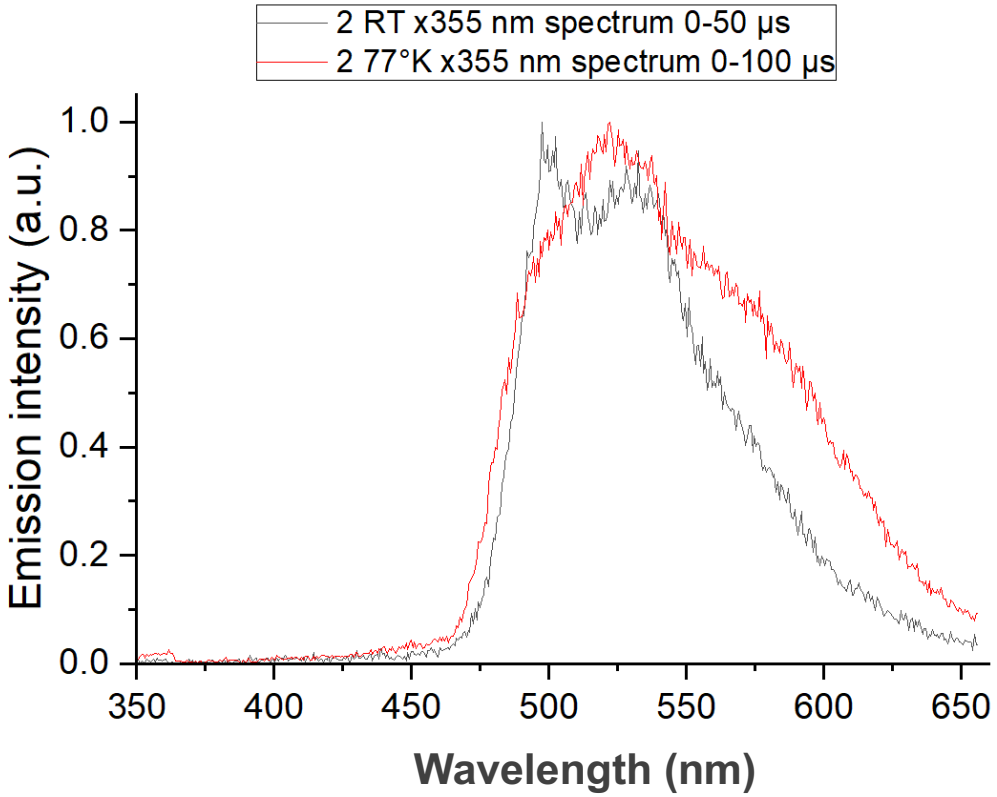


Figure S14. Emission of degassed solutions of **2** in $CHCl_3$ at 293 and 77 K.

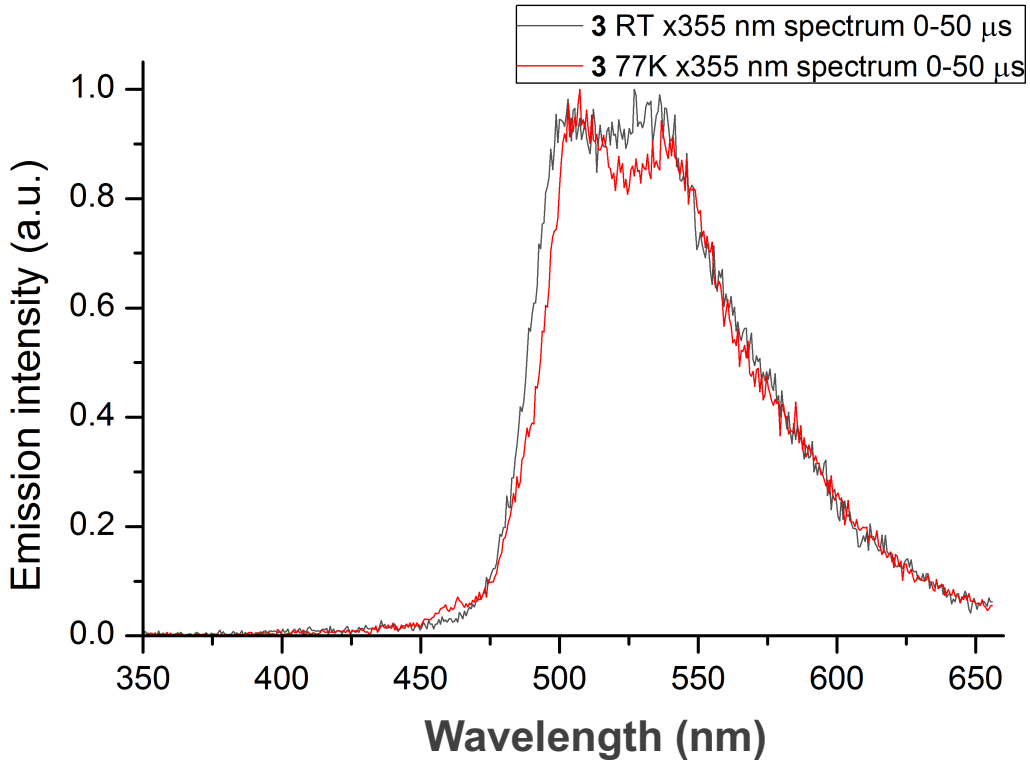


Figure S15. Emission of degassed solutions of **3** in $CHCl_3$ at 293 and 77 K.

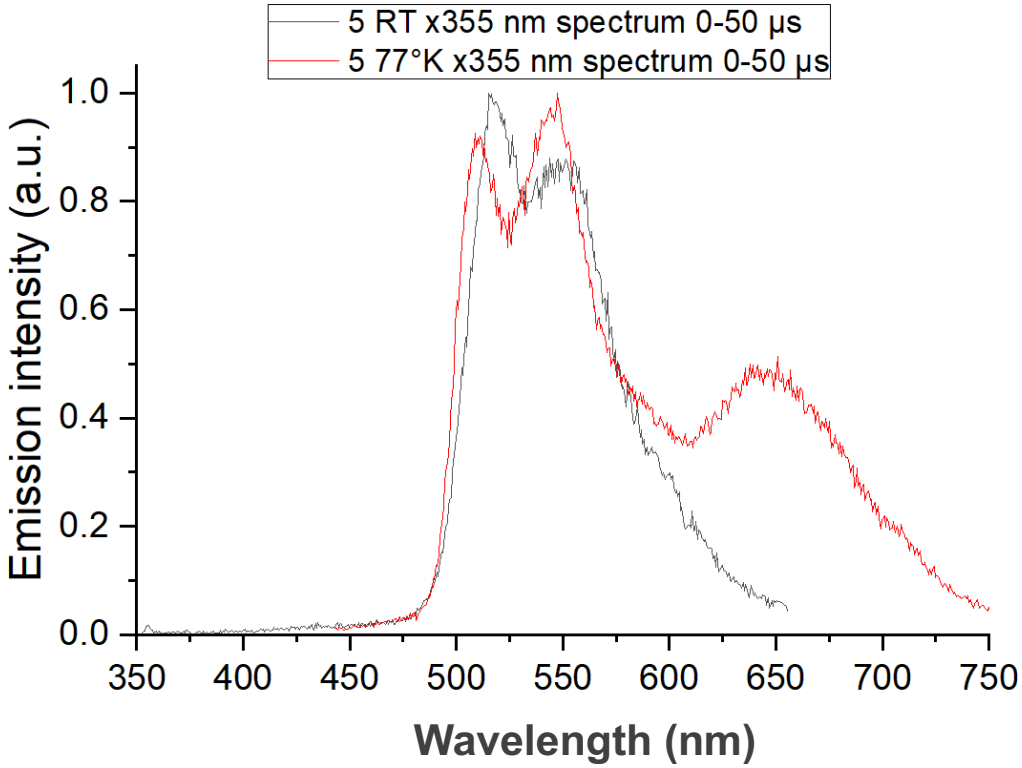


Figure S16. Emission of degassed solutions of **5** in $CHCl_3$ at 293 and 77 K.

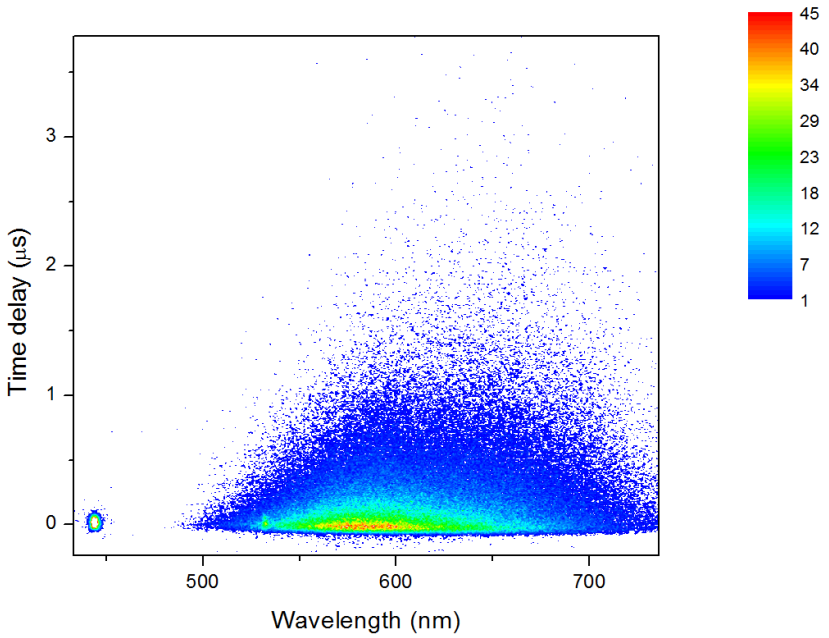


Figure S17. Emission of **1** in the solid state (λ_{ex} = 440 nm). Coloured scale bar corresponds to emission intensity (arbitrary units).

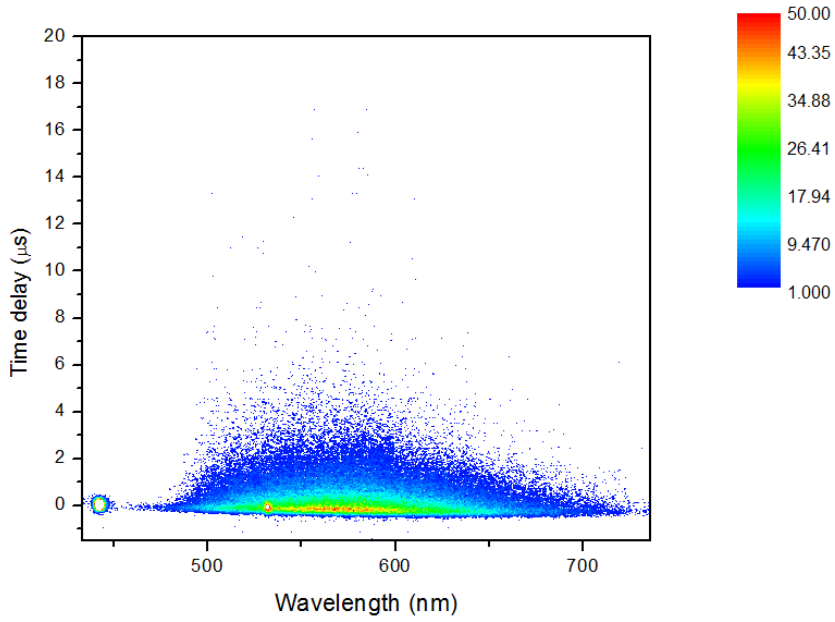


Figure S18. Emission of **2** in the solid state (λ_{ex} = 440 nm). Coloured scale bar corresponds to emission intensity (arbitrary units).

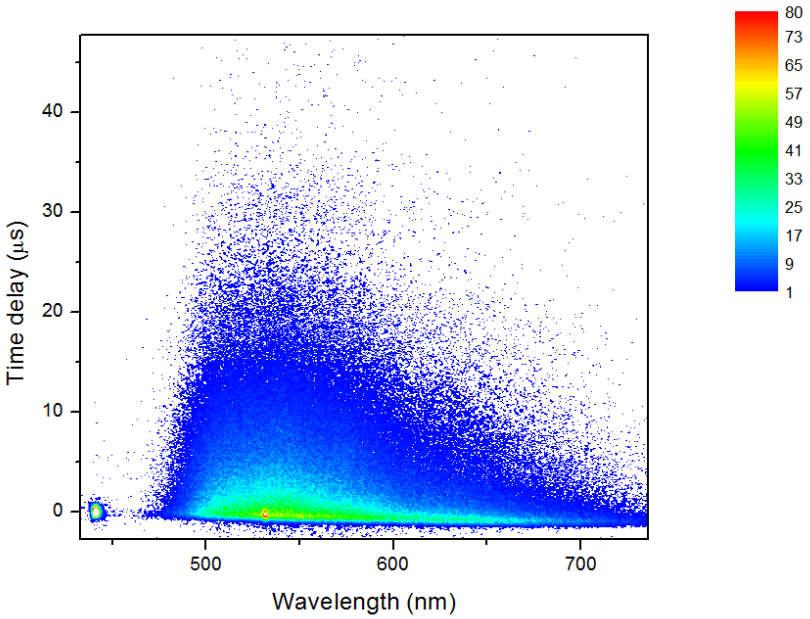


Figure S19. Emission of **3** in the solid state (λ_{ex} = 440 nm). Coloured scale bar corresponds to emission intensity (arbitrary units).

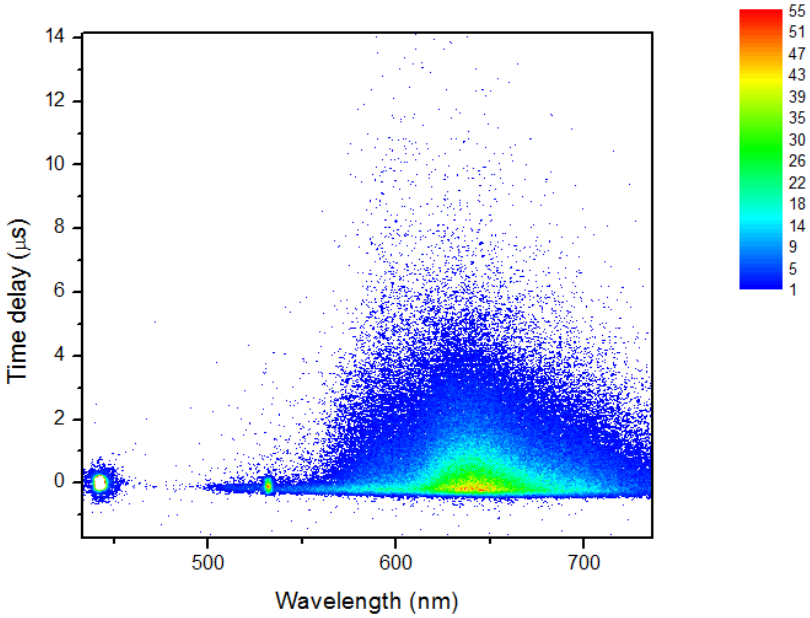


Figure S20. Emission of **5** in the solid state (λ_{ex} = 440 nm). Coloured scale bar corresponds to emission intensity (arbitrary units).

NMR spectra of the compounds

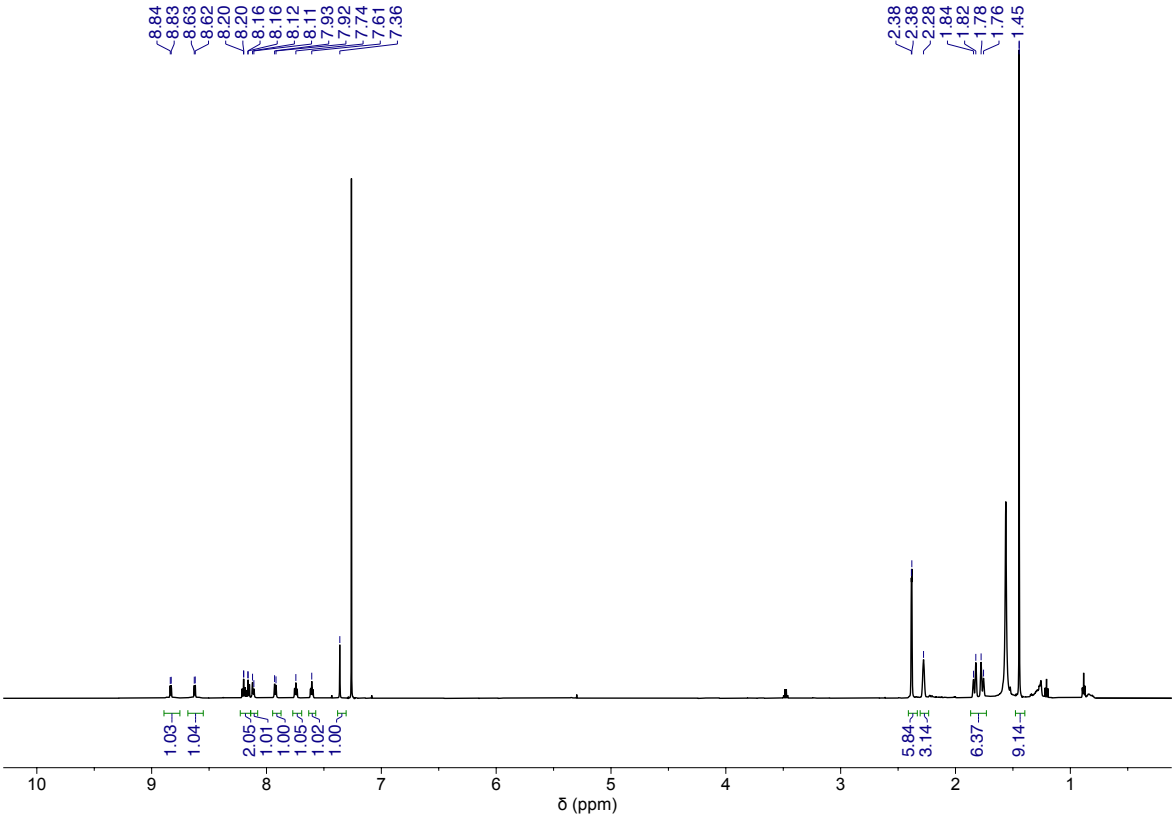


Figure S21. ^{1}H NMR (400 MHz, 300 K) spectrum of complex **1** in $CDCl_3$

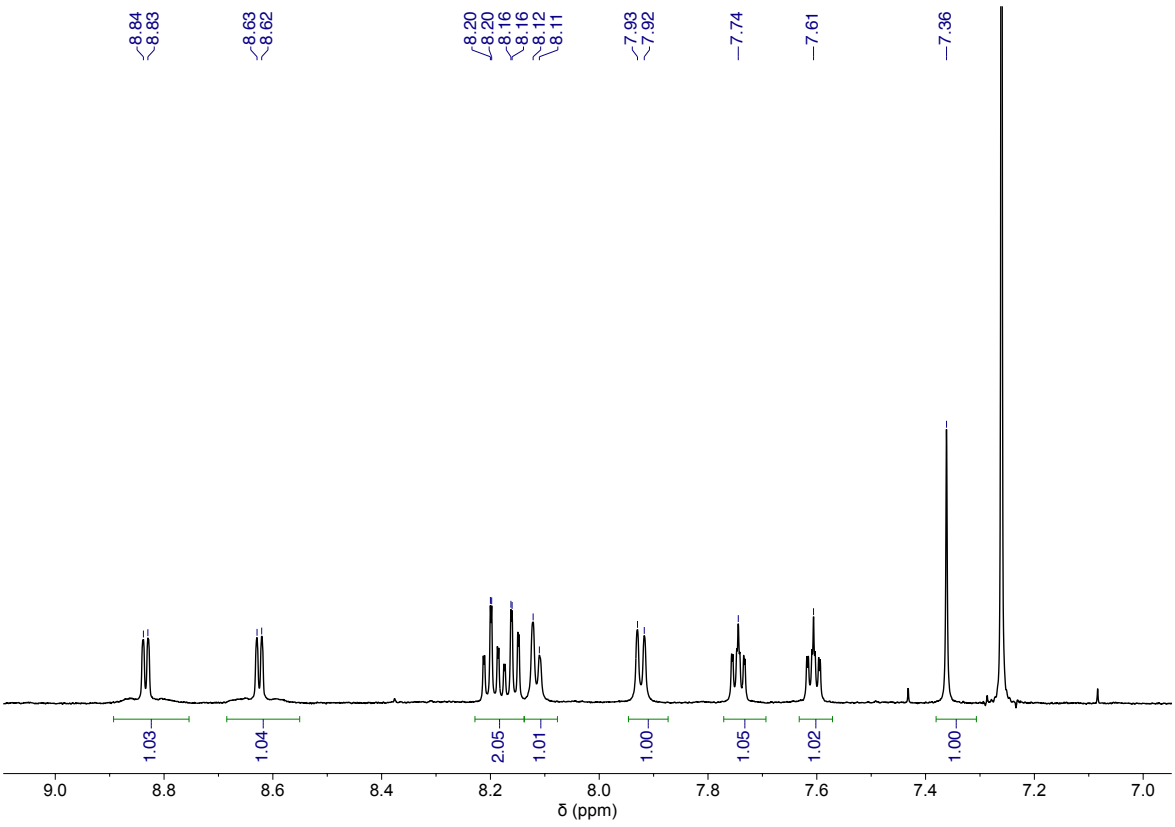


Figure S22. Aromatic region of ^{1}H NMR (400 MHz, 300 K) spectrum of complex **1** in $CDCl_3$

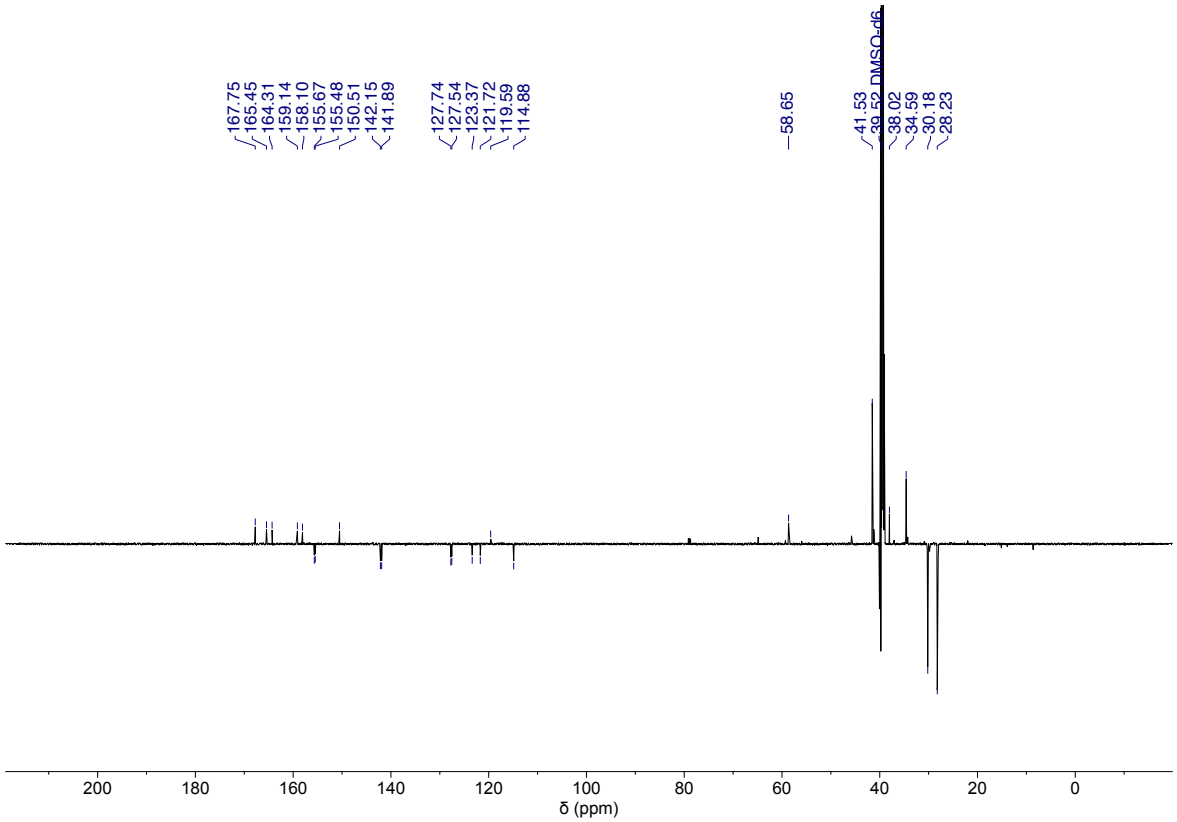


Figure S23. ^{13}C Jmod NMR (151 MHz, 300 K) spectrum of complex **1** in DMSO-d_6

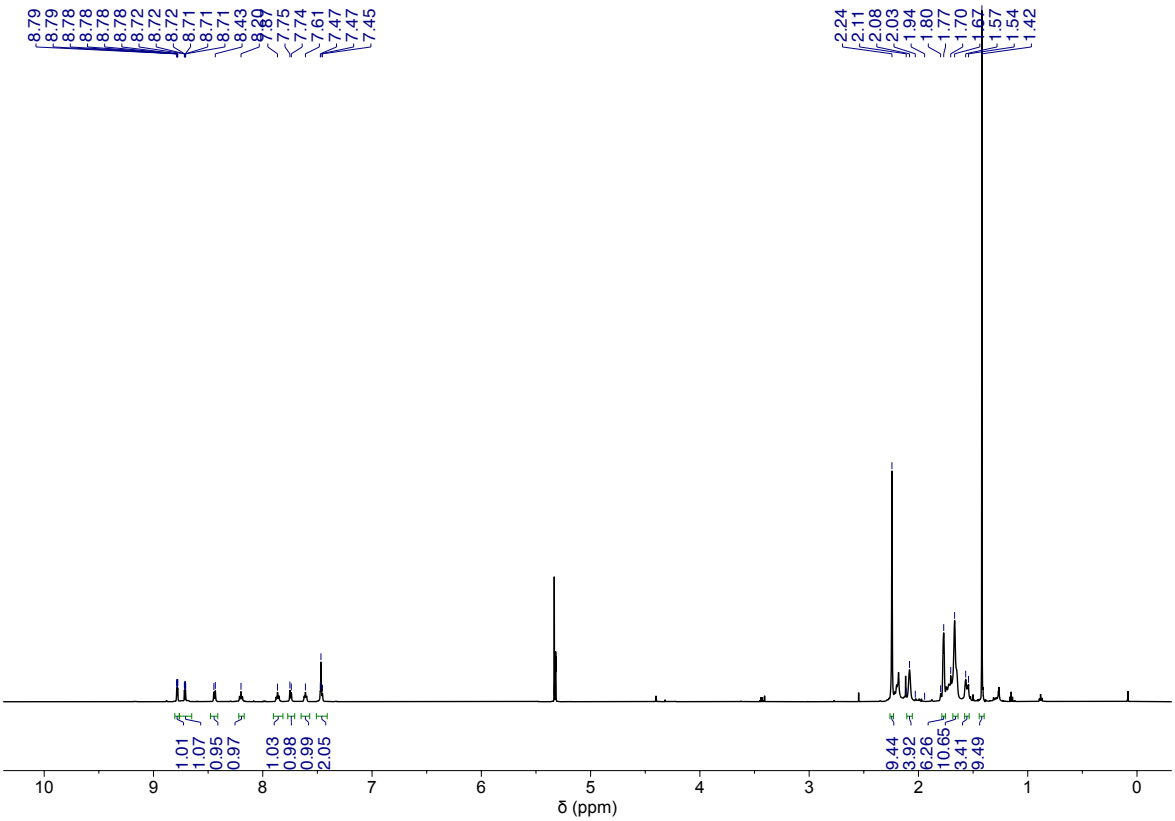


Figure S24. ^{1}H NMR (600 MHz, 300 K) spectrum of complex **2** in CD_2Cl_2

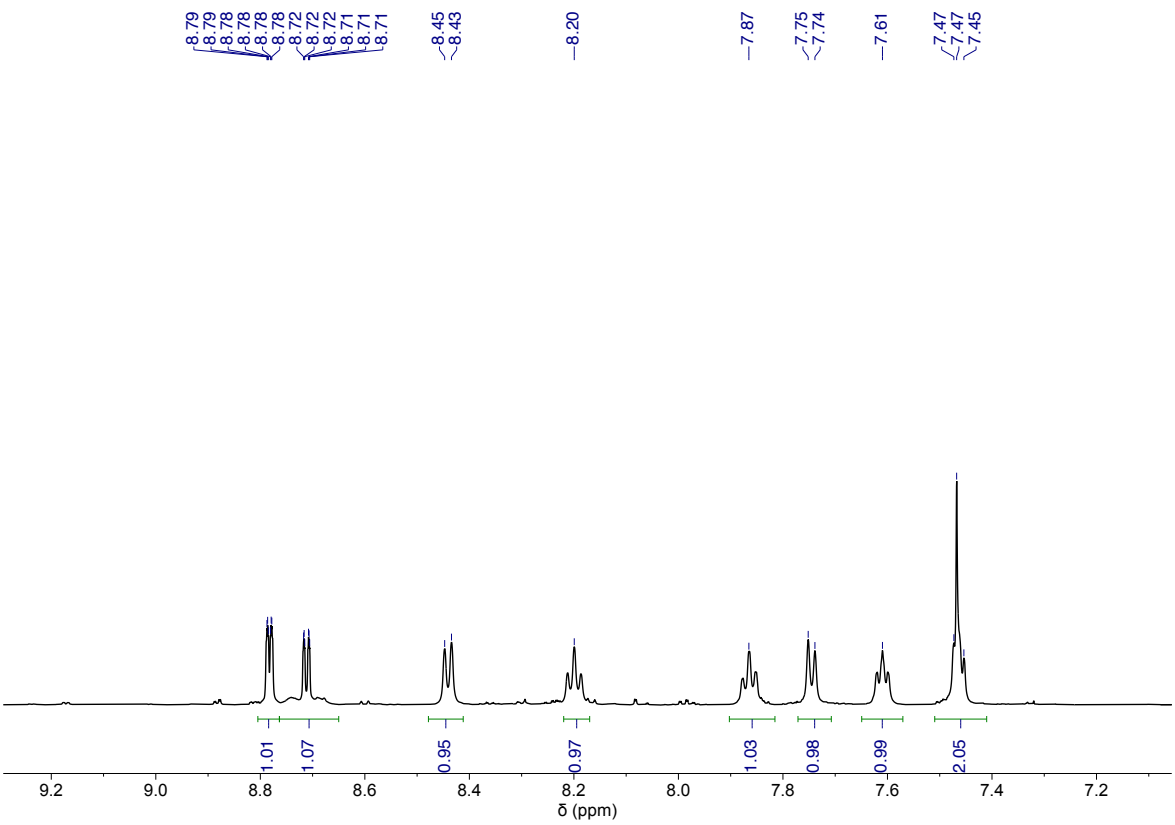


Figure S25. Aromatic region of ^{1}H NMR (600 MHz, 300 K) spectrum of complex **2** in CD_2Cl_2

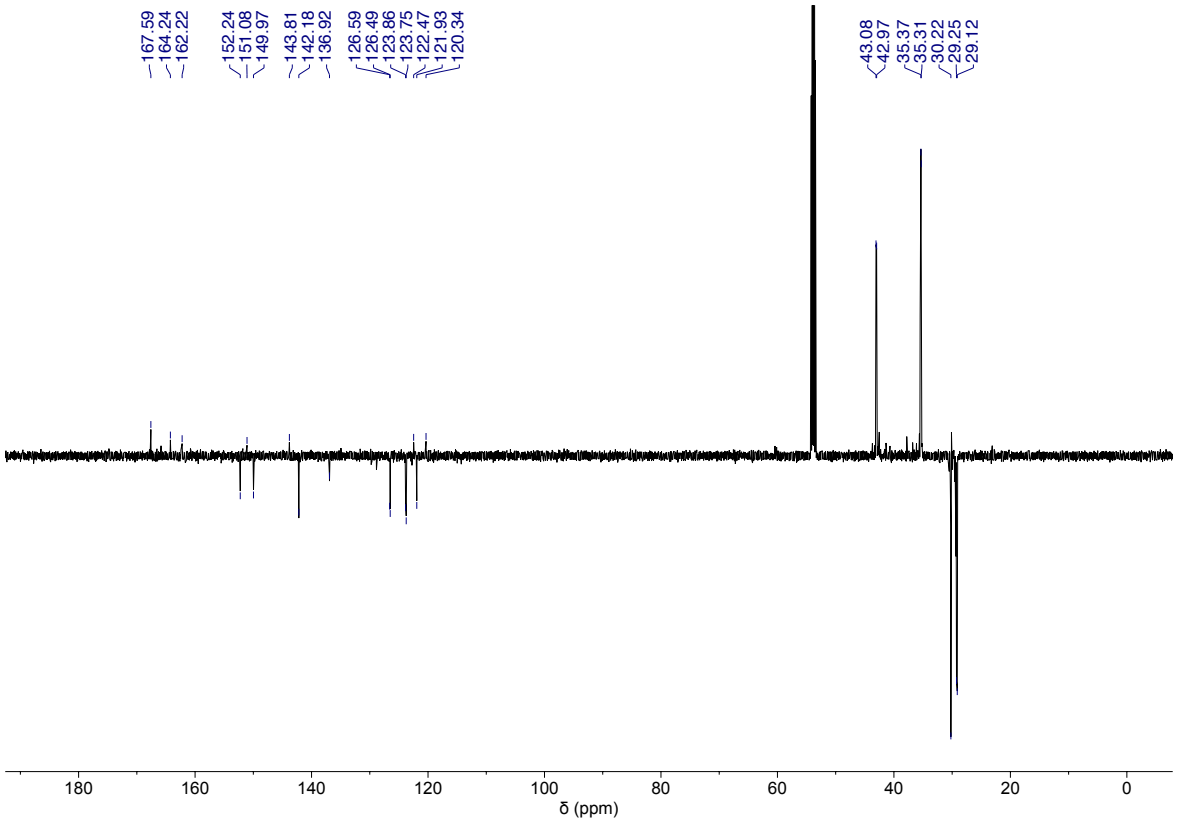


Figure S26. ^{13}C Jmod NMR (151 MHz, 300 K) spectrum of complex **2** in CD_2Cl_2

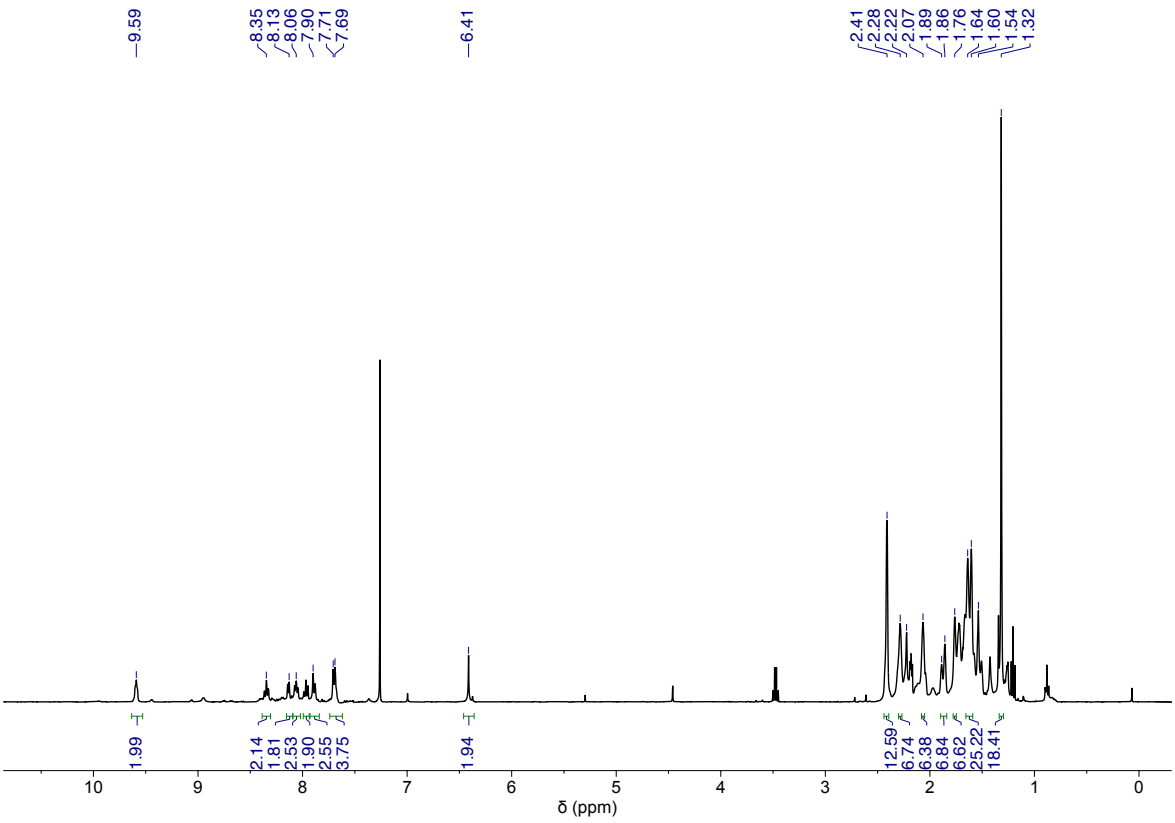


Figure S27. ^{1}H NMR (400 MHz, 300 K) spectrum of complex **3** in $CDCl_3$

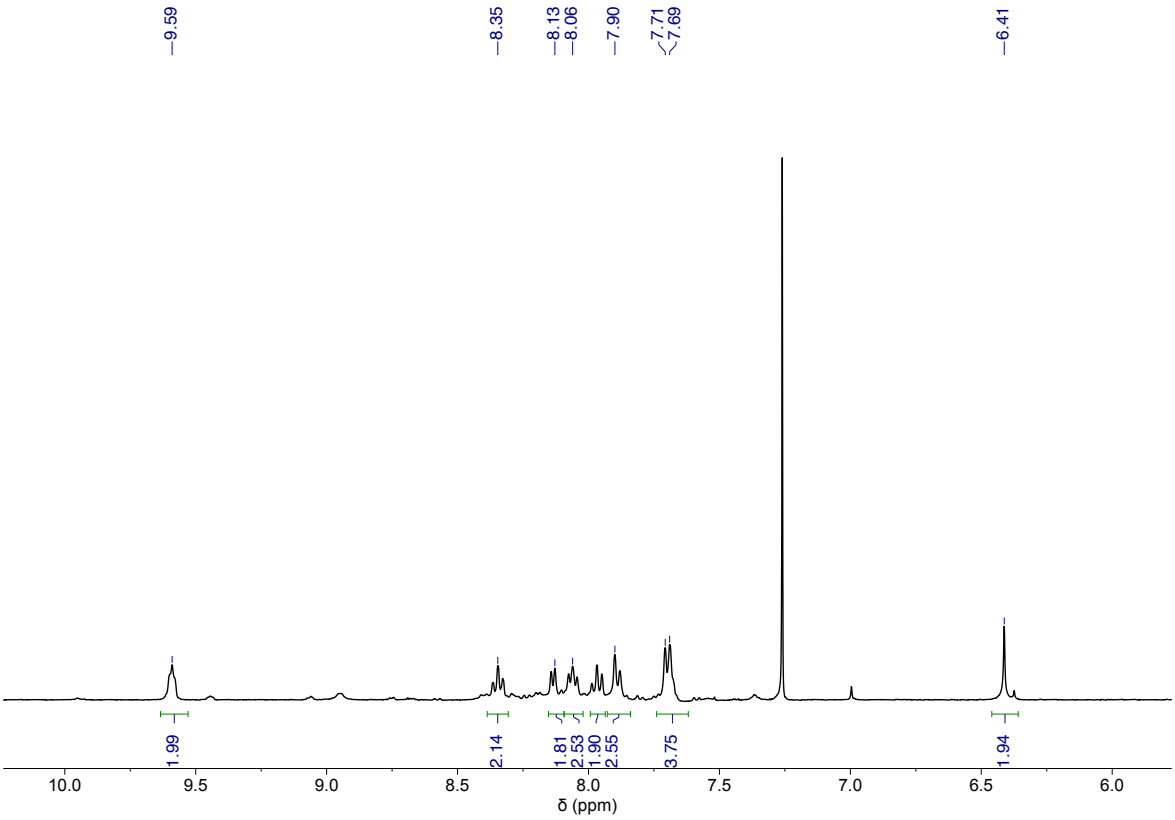


Figure S28. Aromatic region of ^{1}H NMR (400 MHz, 300 K) spectrum of complex **3** in $CDCl_3$

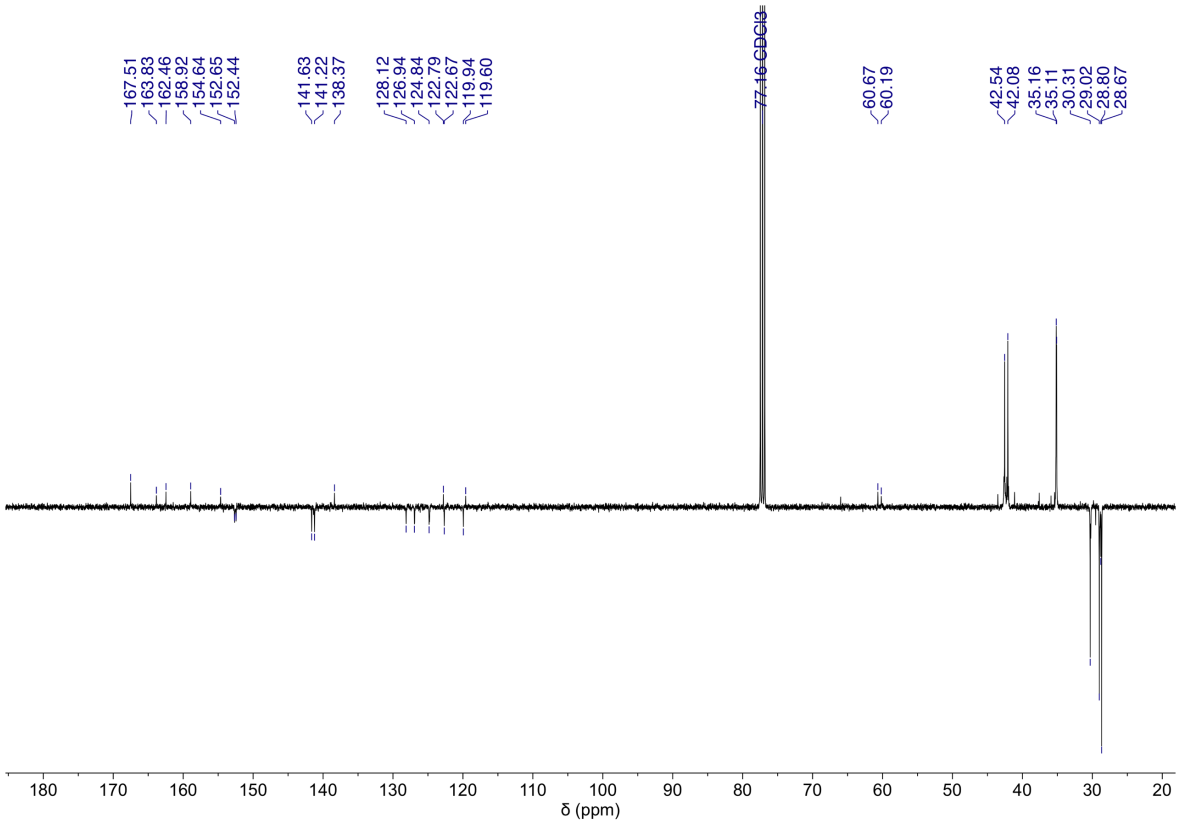


Figure S29. ^{13}C Jmod NMR (100 MHz, 300 K) spectrum of complex **3** in $CDCl_3$

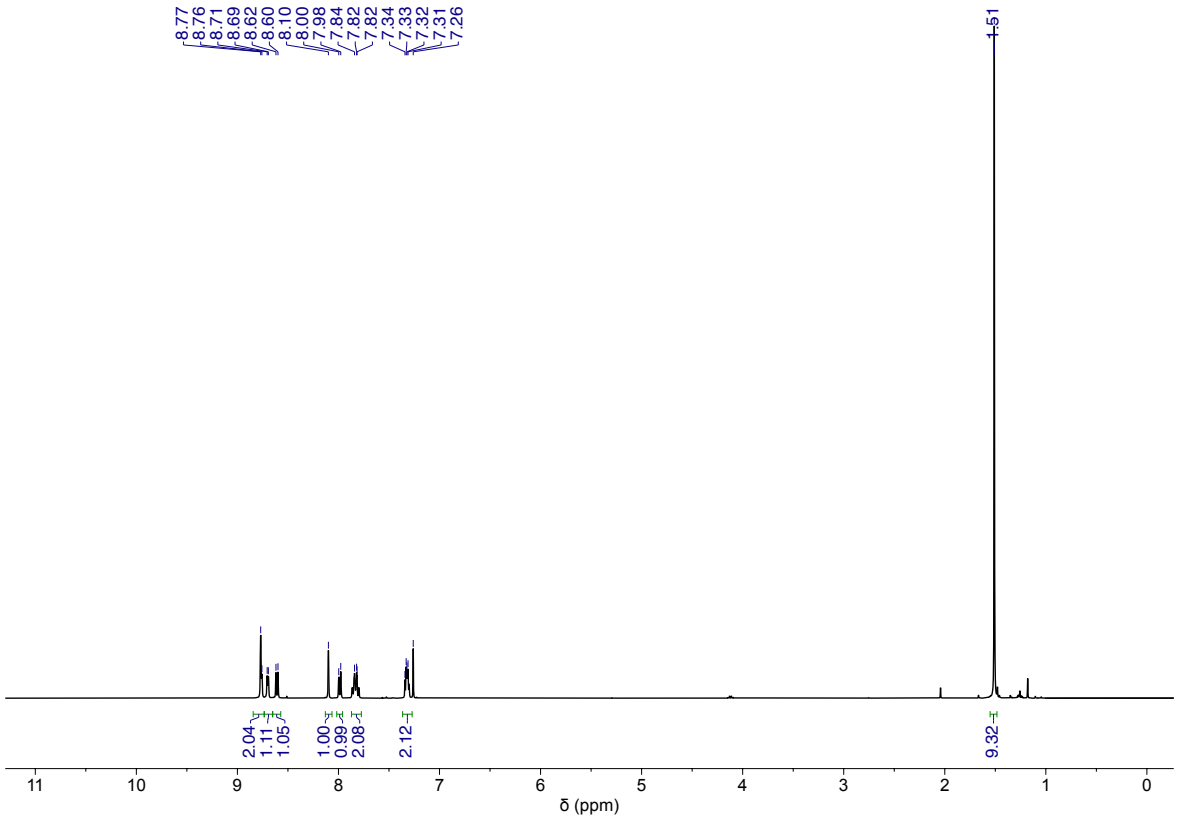


Figure S30. ^{1}H NMR (400 MHz, 300 K) spectrum of ligand **4b** in $CDCl_3$

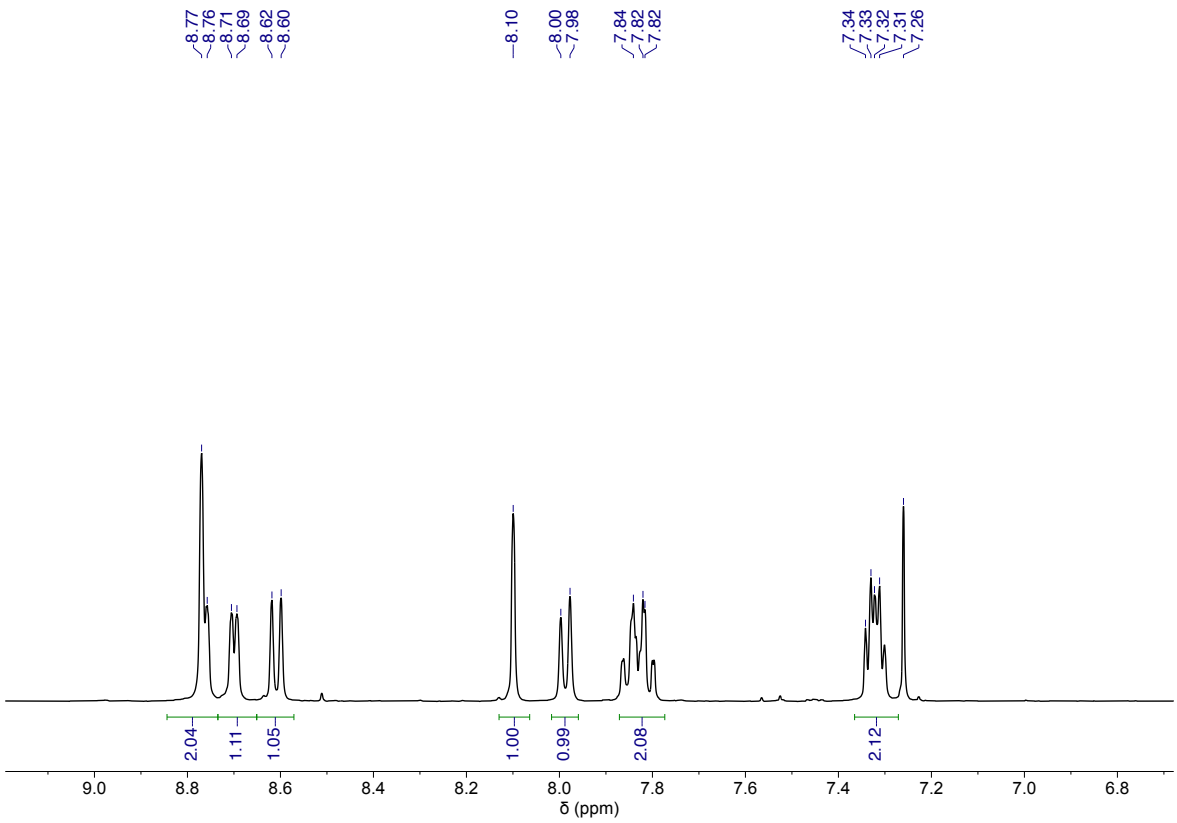


Figure S31. Aromatic region of ^{1}H NMR (400 MHz, 300 K) spectrum of ligand **4b** in $CDCl_3$

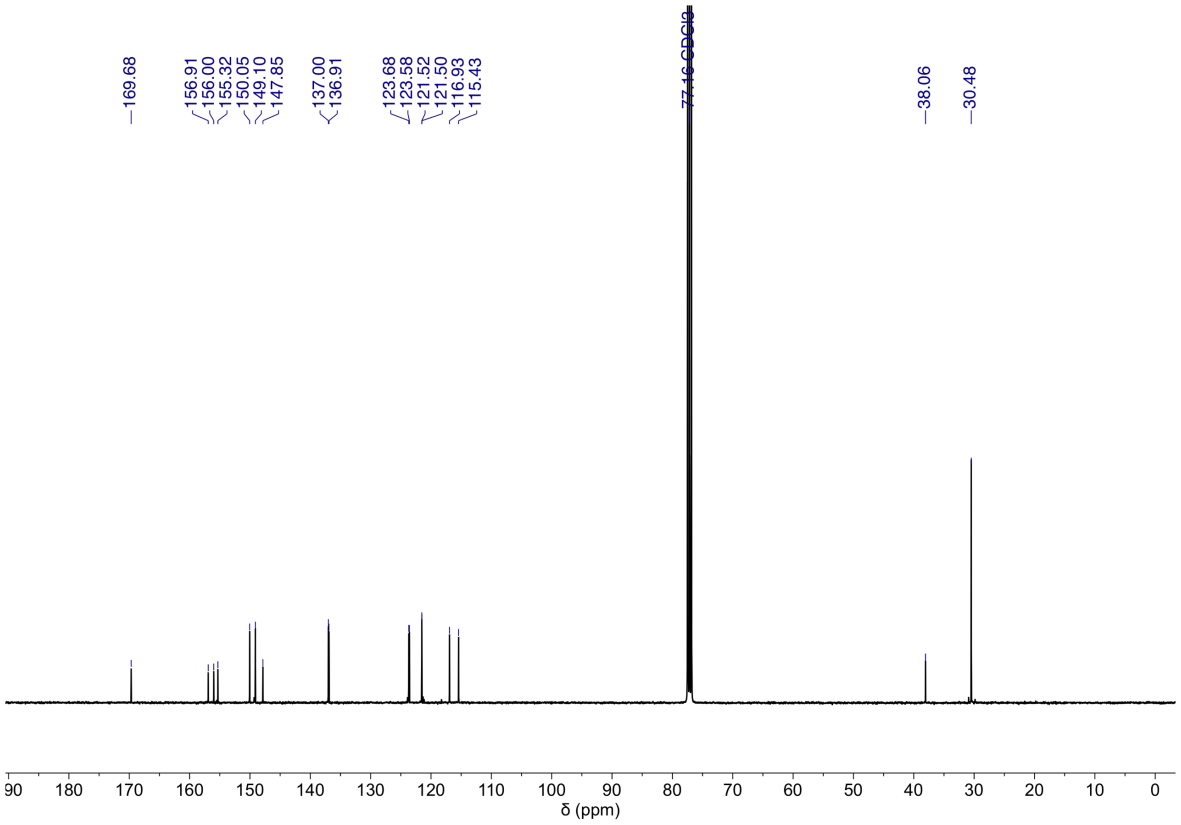


Figure S32. ^{13}C NMR (100 MHz, 300 K) spectrum of ligand **4b** in $CDCl_3$

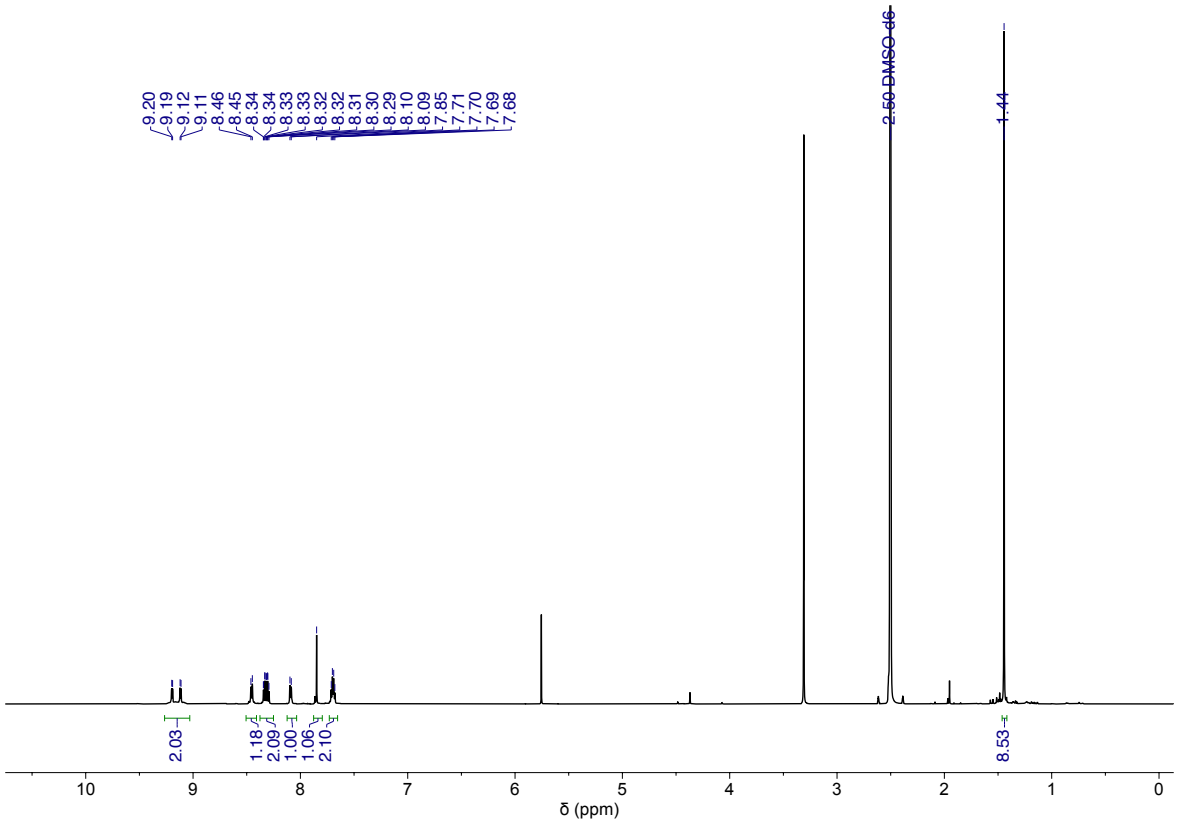


Figure S33. ^{1}H NMR (400 MHz, 300 K) spectrum of complex **5** in DMSO-d_6

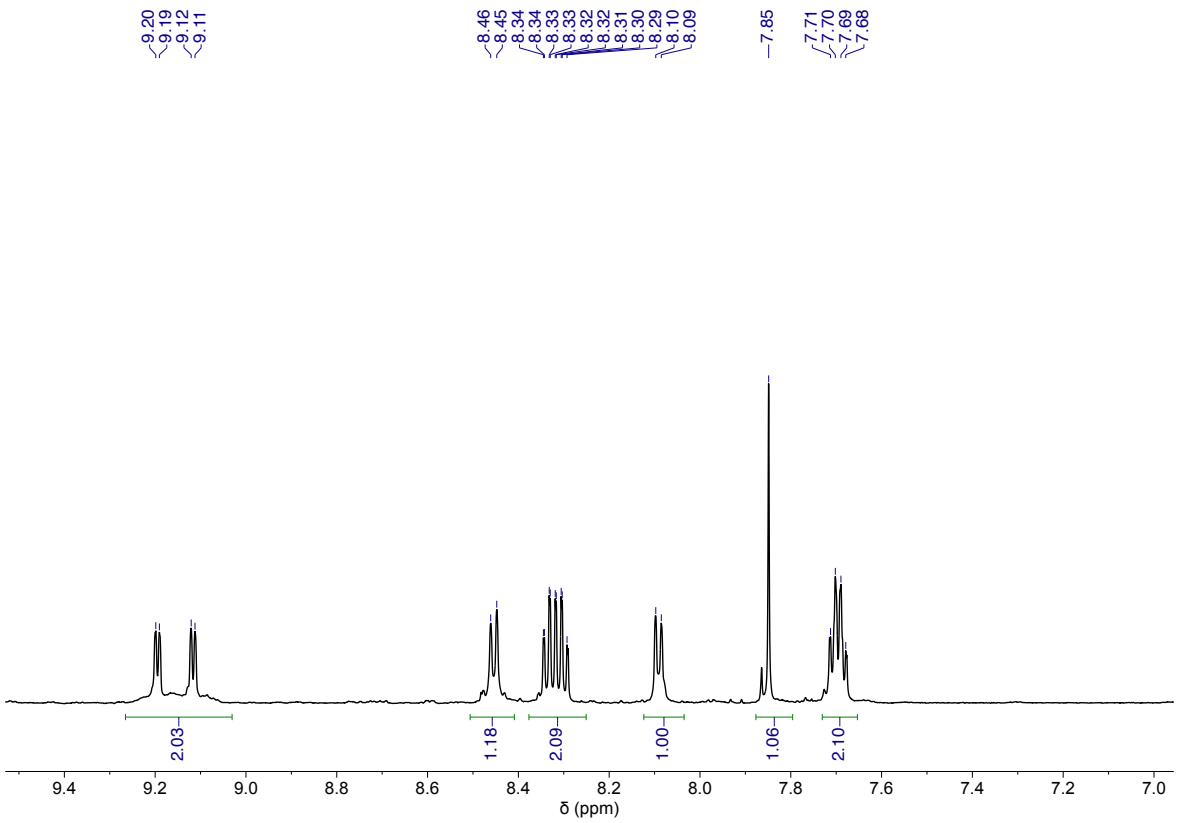


Figure S34. Aromatic region of ^{1}H NMR (400 MHz, 300 K) spectrum of complex **5** in DMSO-d_6

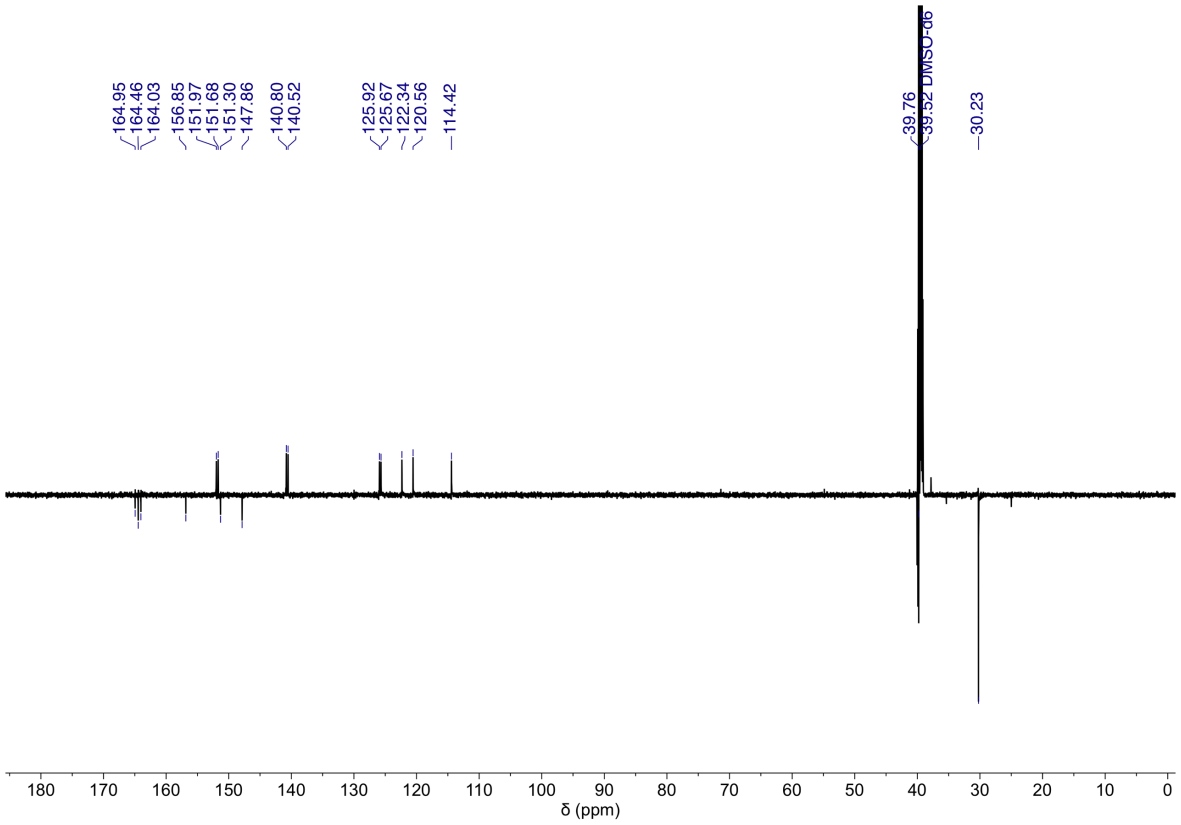


Figure S35. ^{13}C NMR (100 MHz, 300 K) spectrum of ligand **5** in DMSO-d_6