

Supporting Information

One Scaffold, Three Chelation Modes: 2-(1*H*-Tetrazol-1-yl)pyridine as Dynamic Ligand for Cationic and Neutral Cyclometalated Iridium(III) Complexes

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Table of Contents	Pages
NMR spectra of ligands L1 and L2	S2 – S5
HRMS spectrum of ligands L1 and L2	S6
Characterization of L3	S7
NMR spectra of complex A	S8 – S9
NMR spectrum of ligand L1 deprotonated	S10
NMR spectra of complexes B and D	S11 – S16
HRMS spectrum of complexes A - D	S17 – S18
Stability studies for complex D	S19
TD-DFT vertical excitations	S20 – S23
DFT and stability studies for complex A	S24
Spin-density distributions of axial ³ MC states	S25

NI-leg-conc2_H_CDCl3
Std Proton parameters

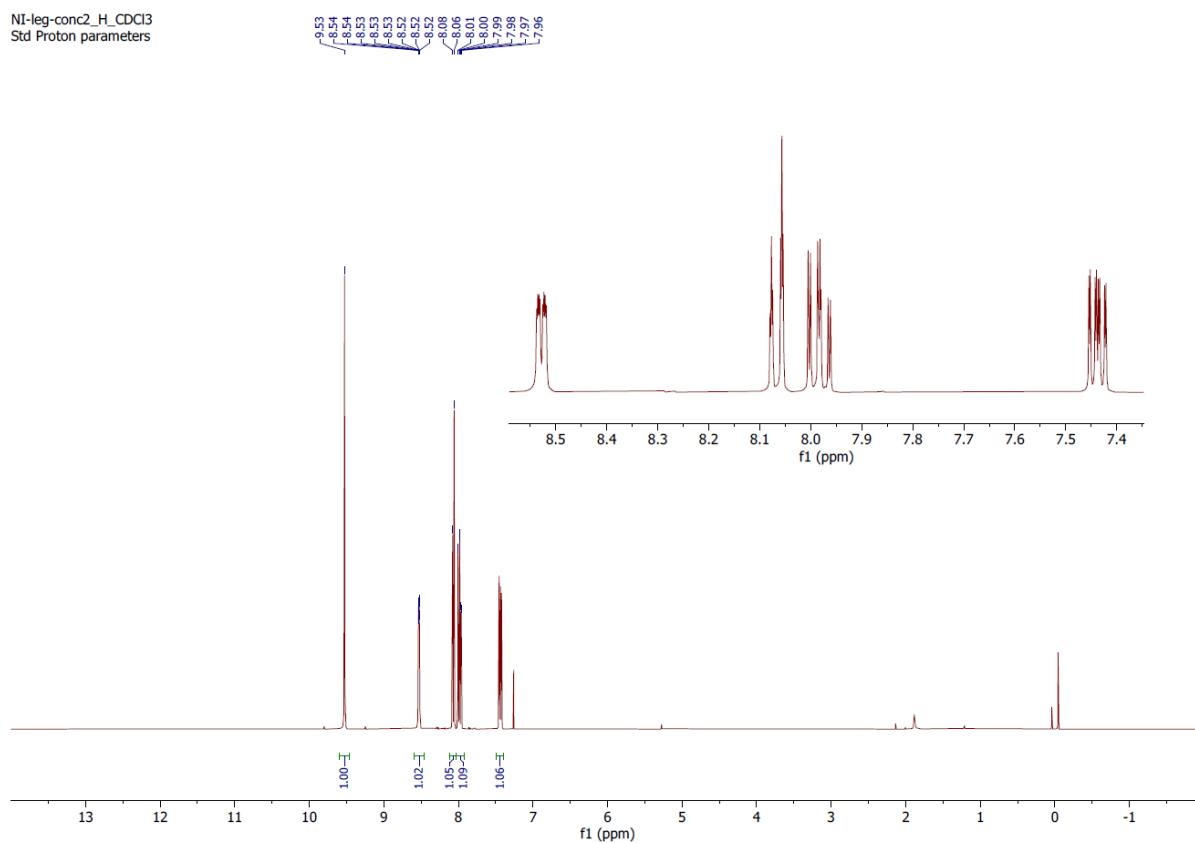


Figure S1. ^1H NMR spectrum of ligand **L1**.

NI-leg-conc2_C_CDCl3
Std Carbon experiment

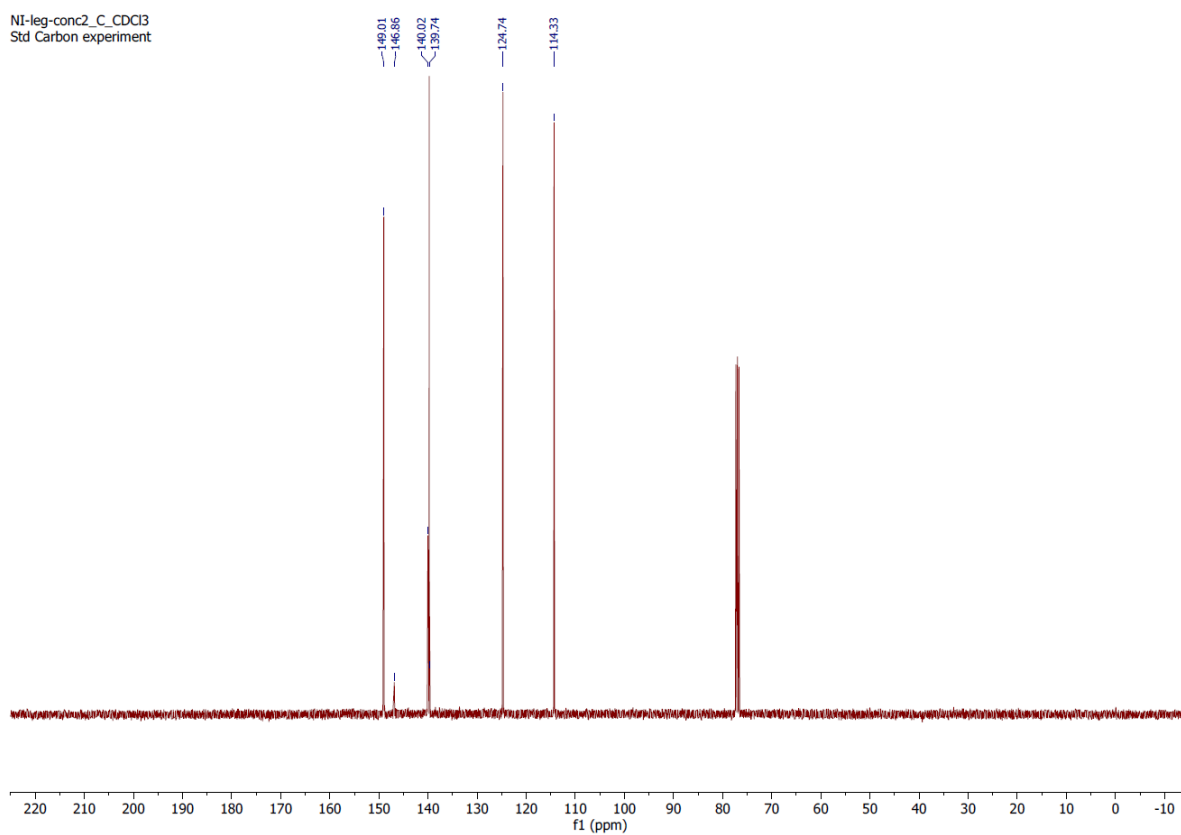


Figure S2. ^{13}C NMR spectrum of ligand **L1**.

NI-leg-conc2_DEPT_CDCl3
Heteronuclear polarization transfer experiment

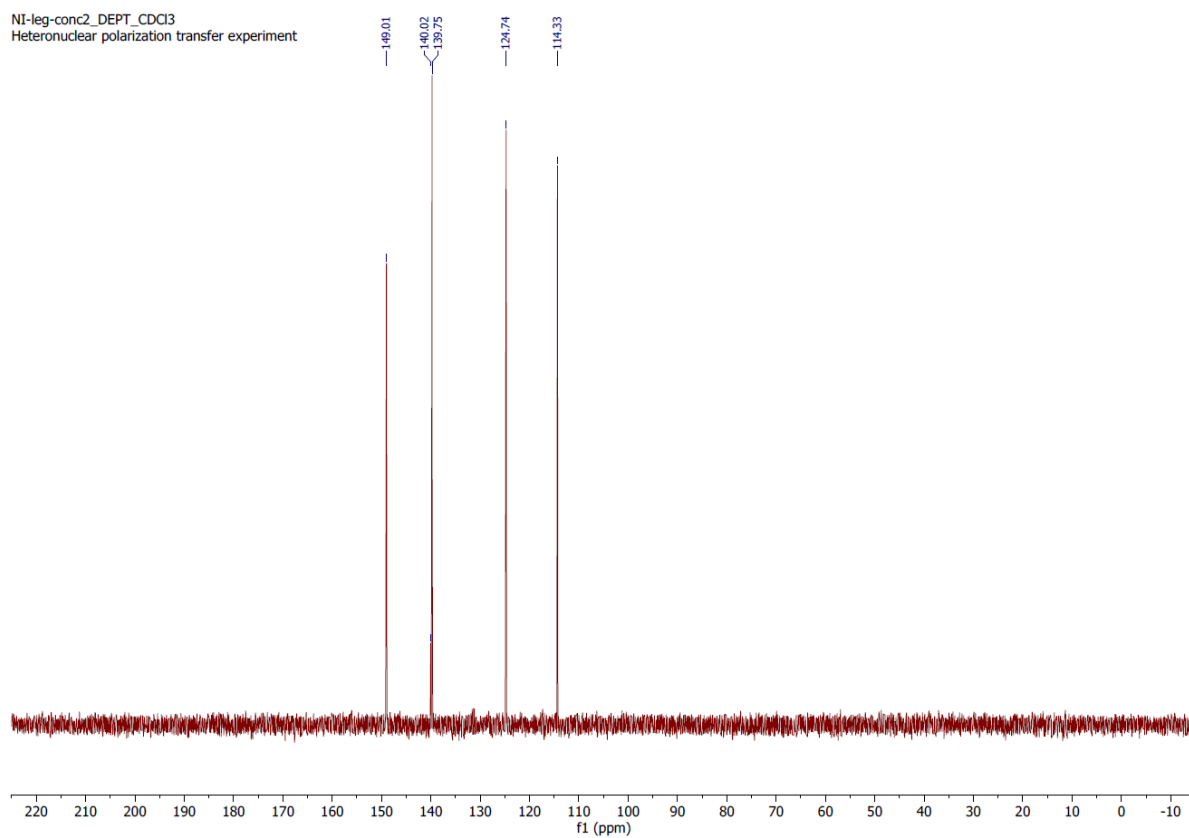


Figure S3. DEPT 135 NMR spectrum of ligand **L1**.

1H_ME537_lavDCM_CD3CN

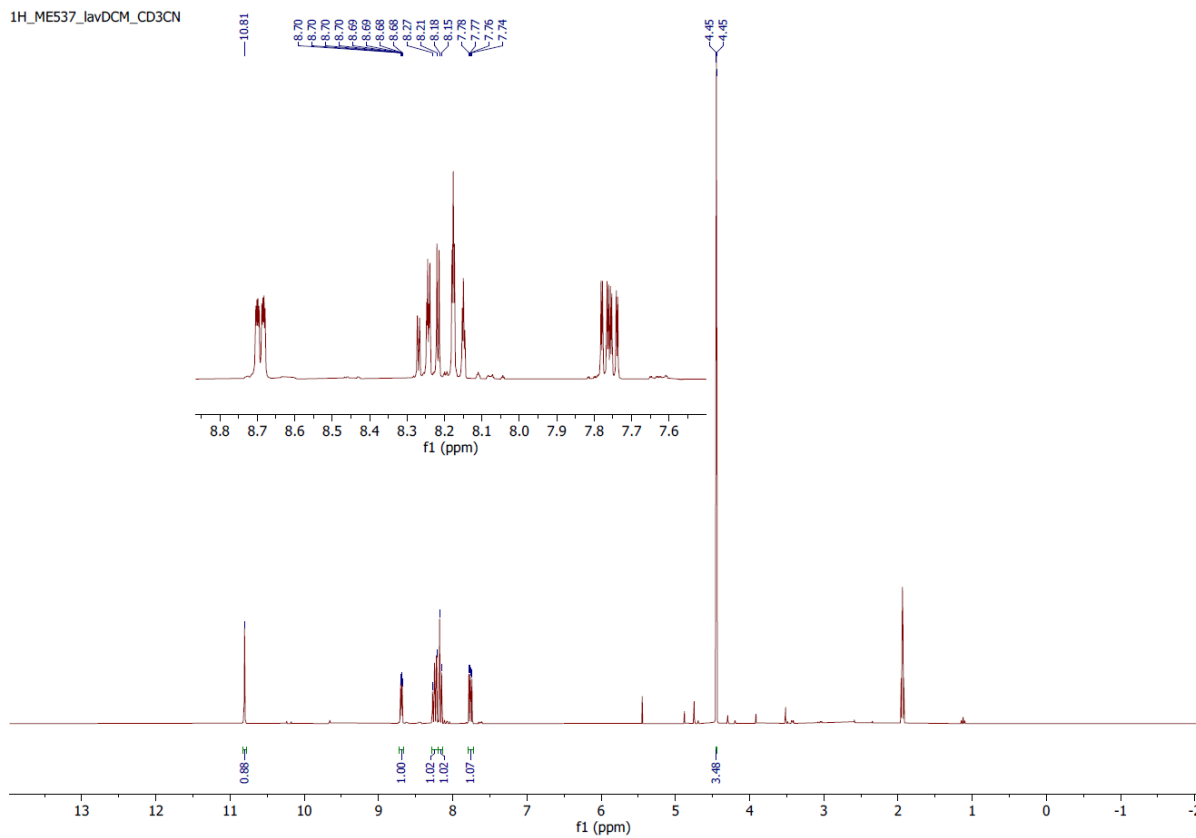


Figure S4. ^1H NMR spectrum of ligand **L2**.

NI3conc_C_CD3CN
Std Carbon experiment

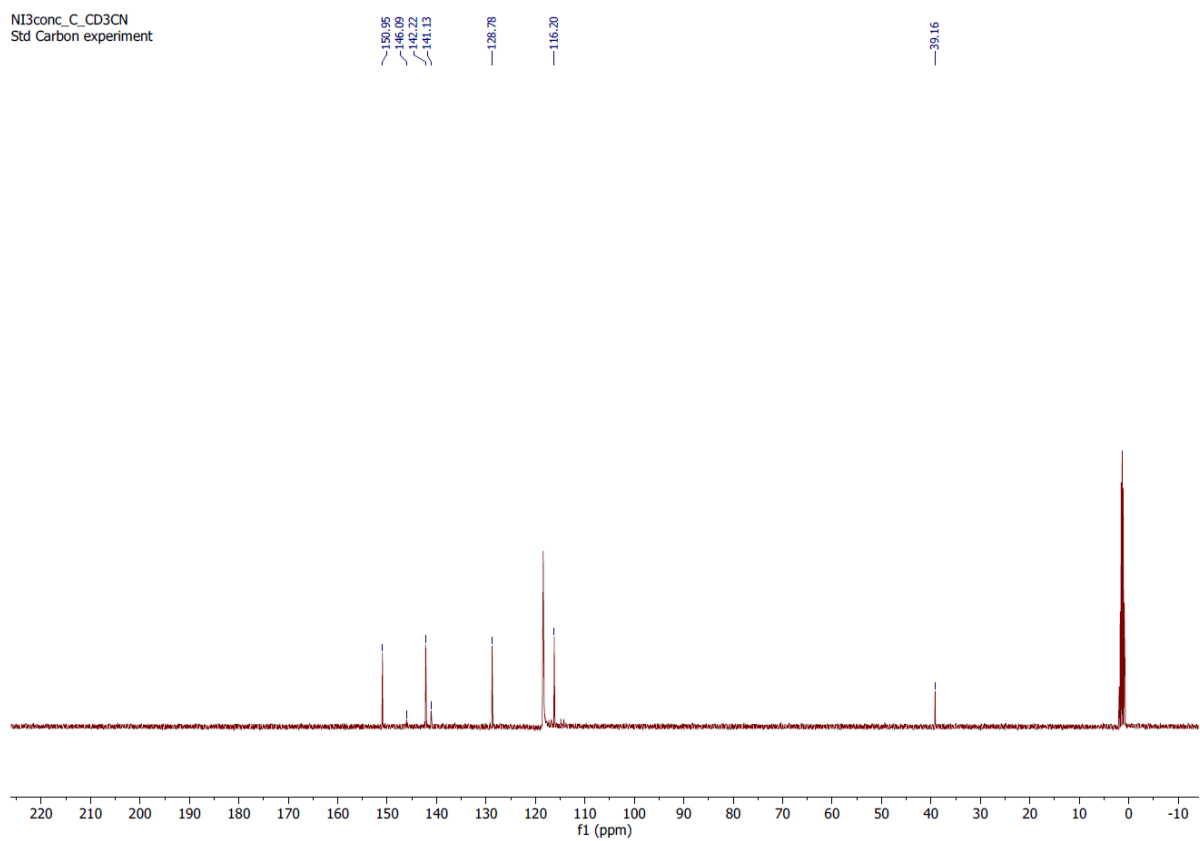


Figure S5. ^{13}C NMR spectrum of ligand **L2**.

NI3conc_DEPT_CD3CN
Heteronuclear polarization transfer experiment

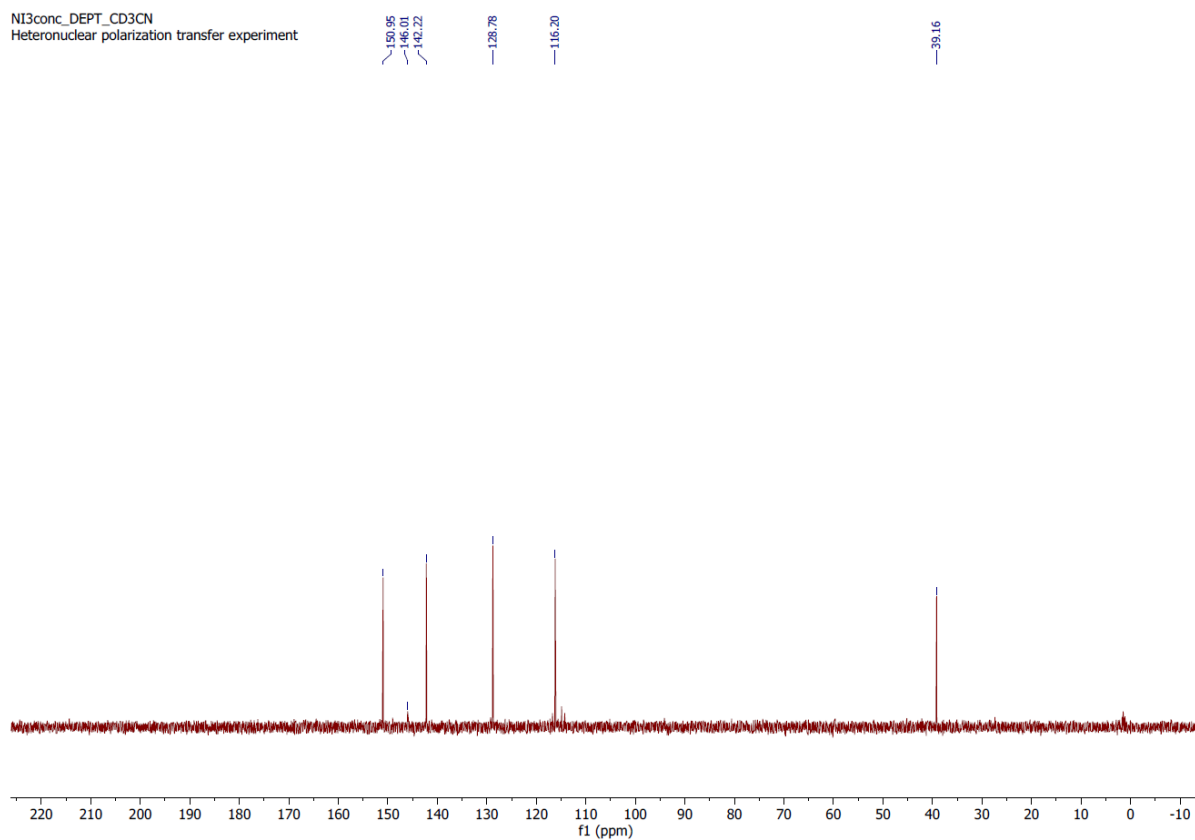


Figure S6. DEPT 135 NMR spectrum of ligand **L2**.

19F_ME537_lavDCM_CD3CN
Std Fluorine

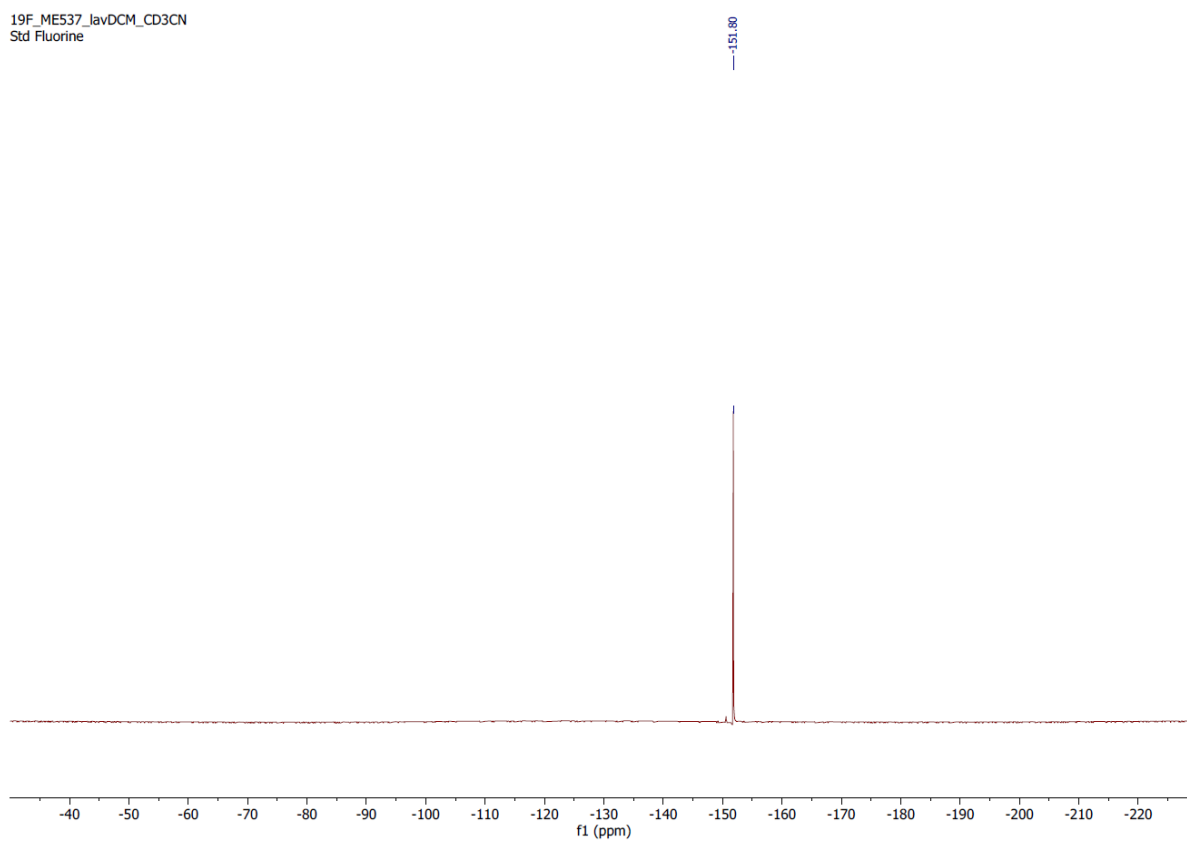


Figure S7. ¹⁹F NMR spectrum of ligand **L2**.

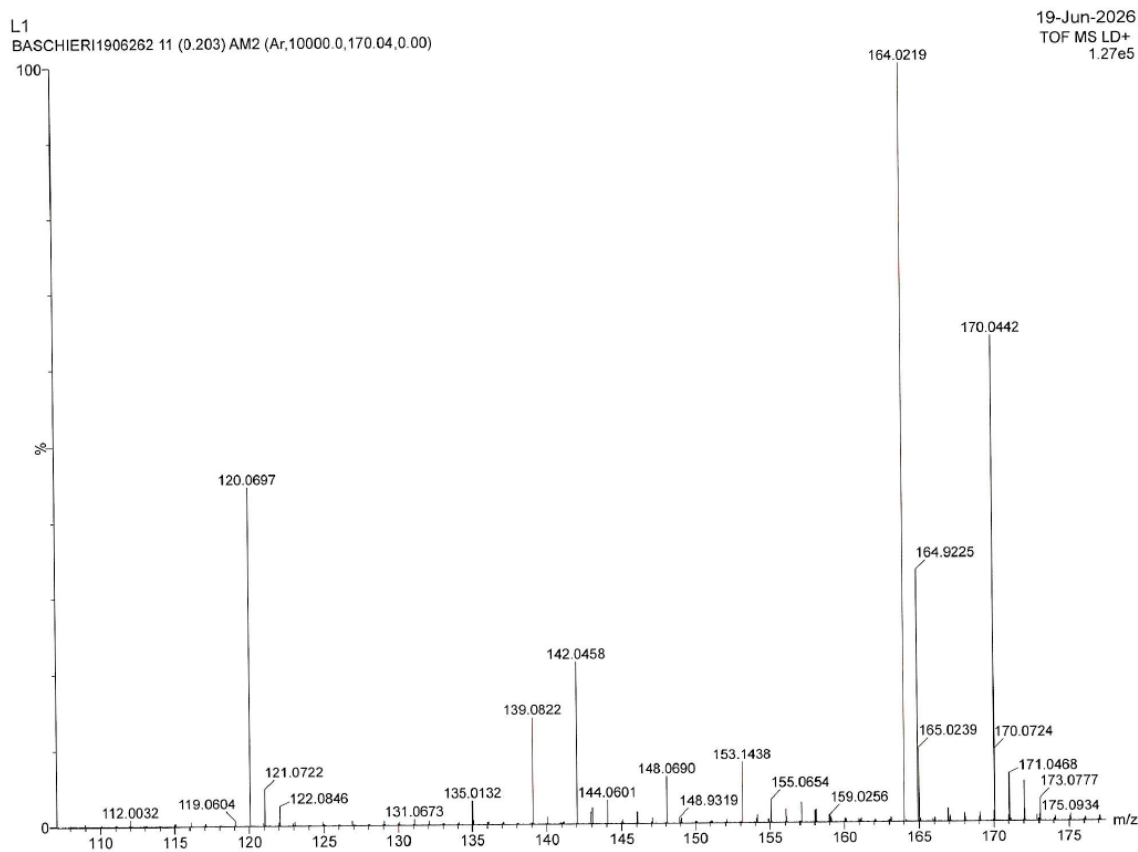


Figure S8. High-resolution mass spectrum of ligand **L1**.

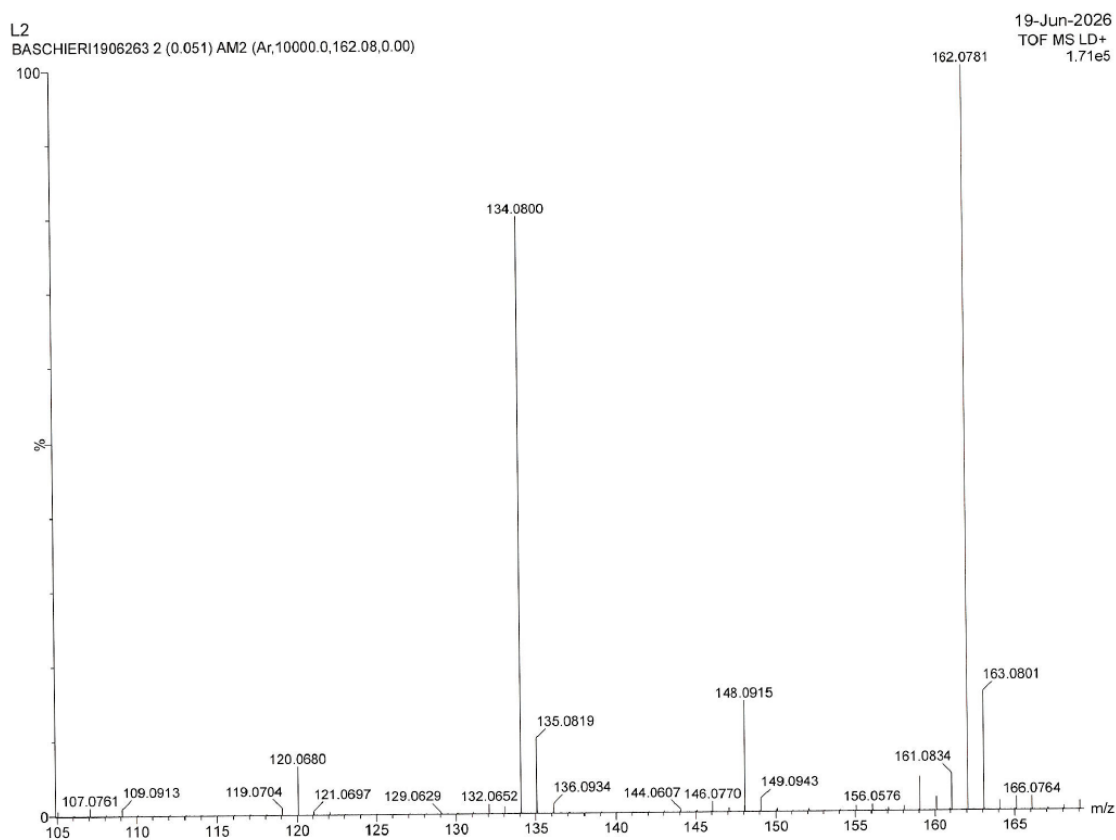


Figure S9. High-resolution mass spectrum of ligand **L2**.

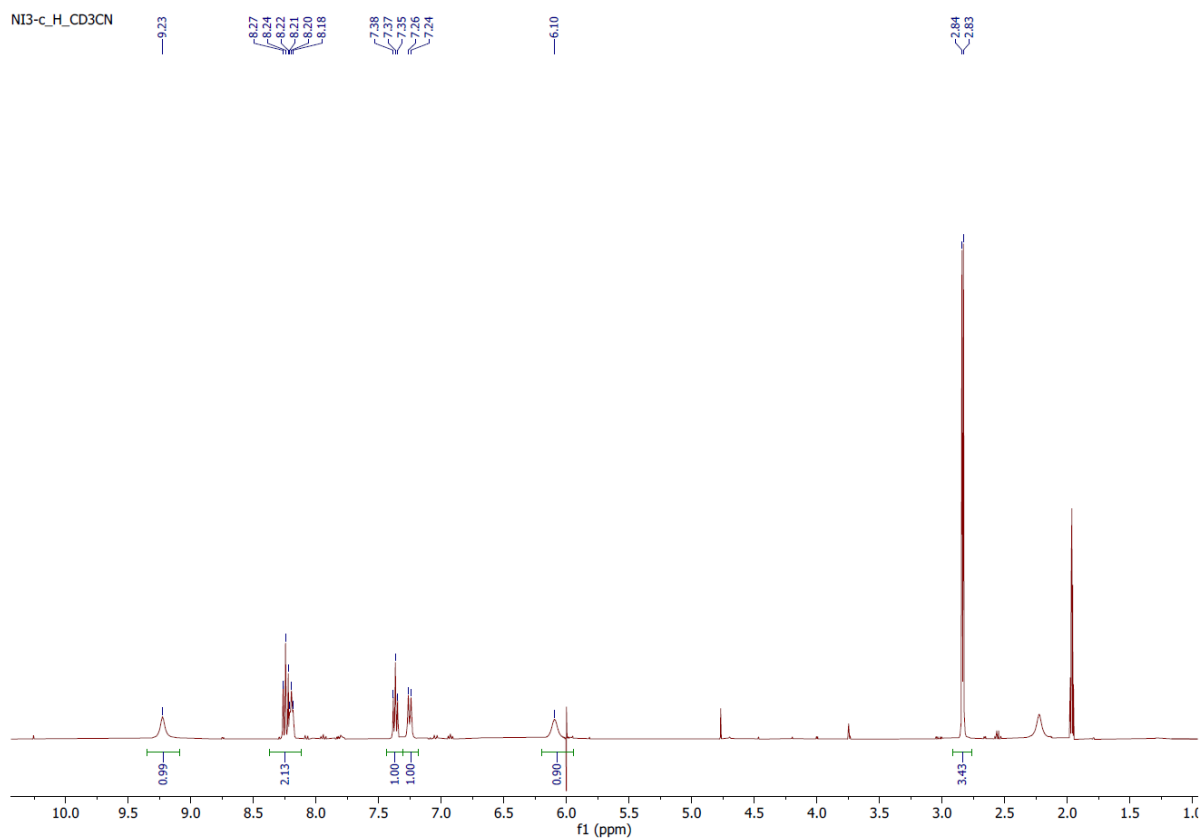


Figure S10. ^1H NMR spectrum of decomposed ligand **L3**.

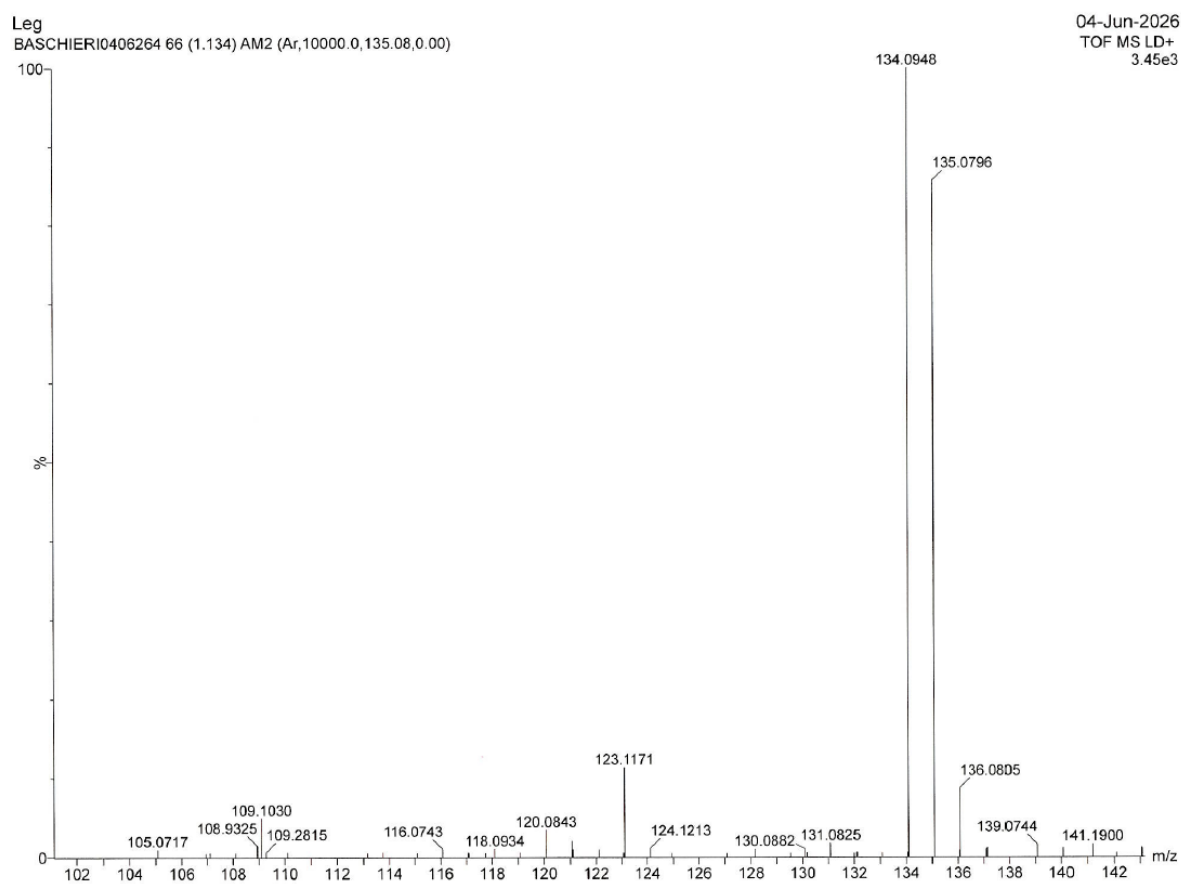


Figure S11. High-resolution mass spectrum of ligand **L3**.

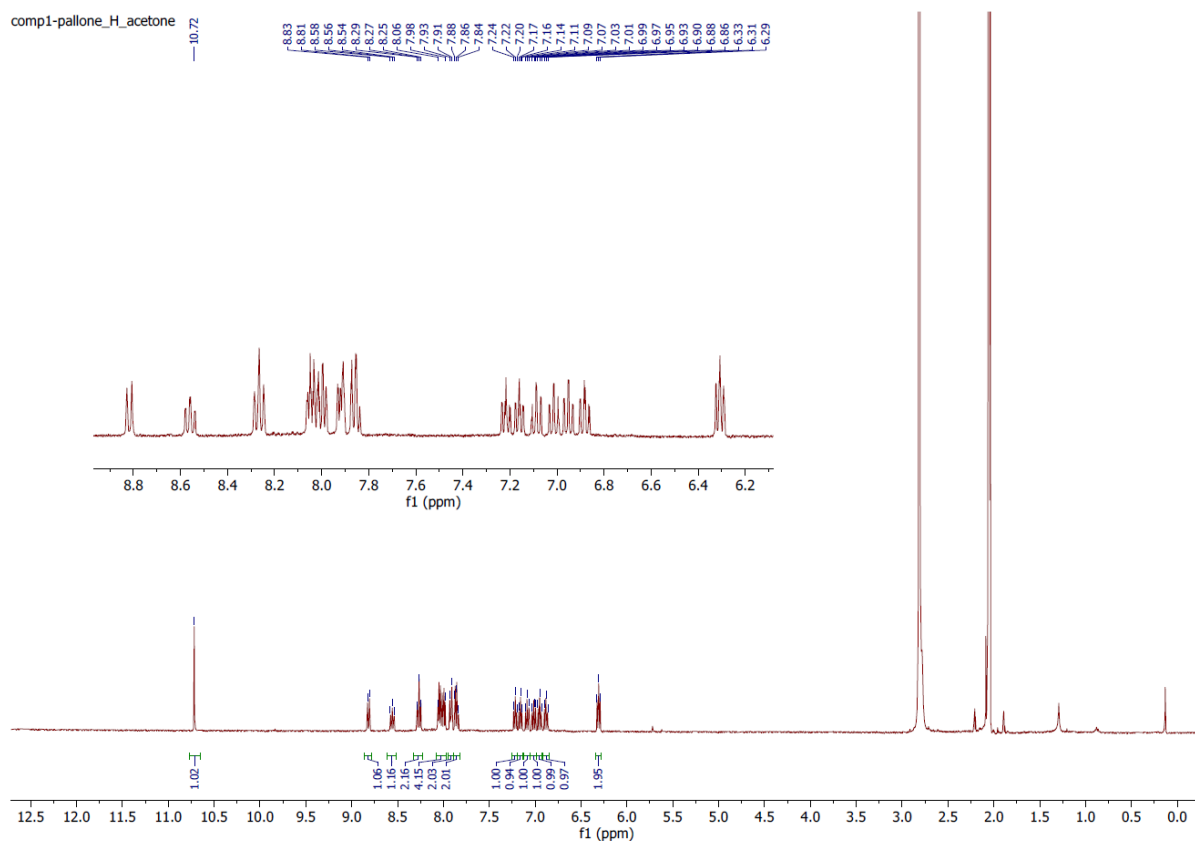


Figure S12. ^1H NMR spectrum of complex A.

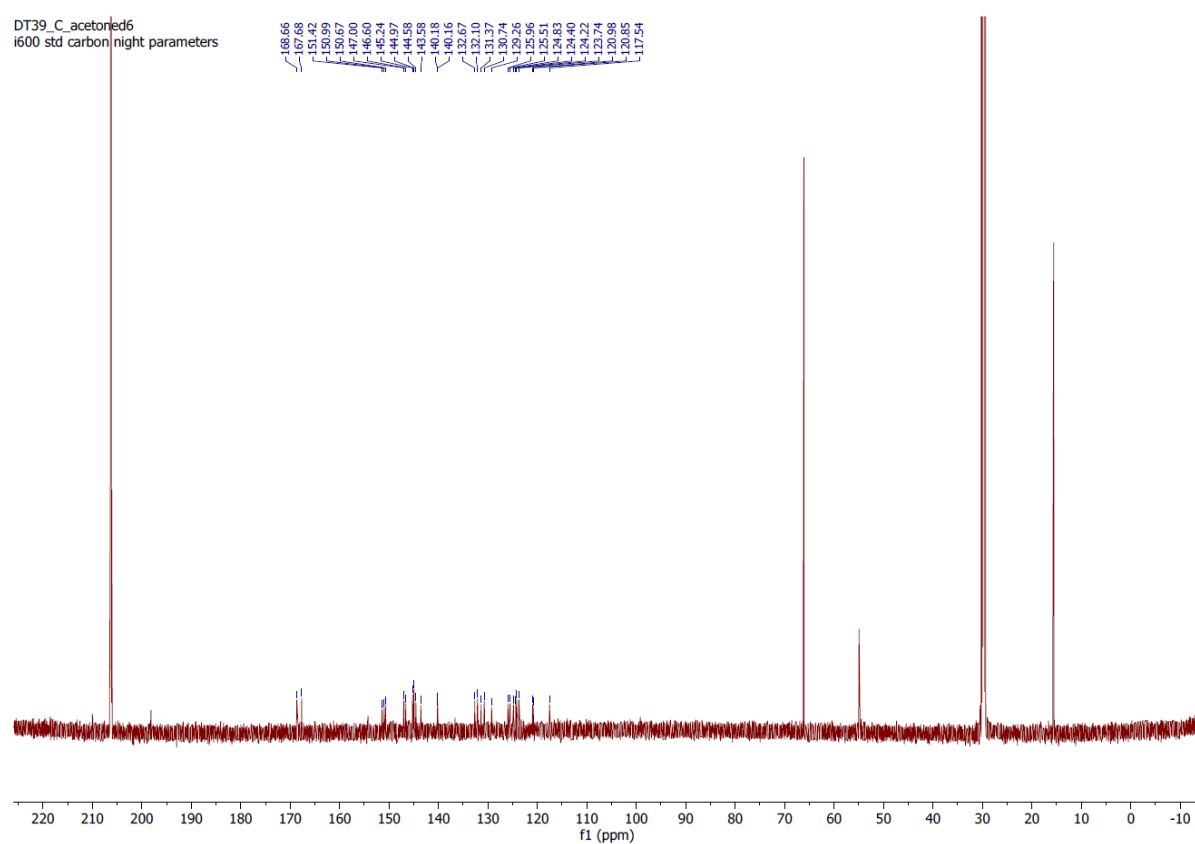


Figure S13. ^{13}C NMR spectrum of complex A.

DT39_Dept_acetone-d6
Heteronuclear polarization transfer experiment

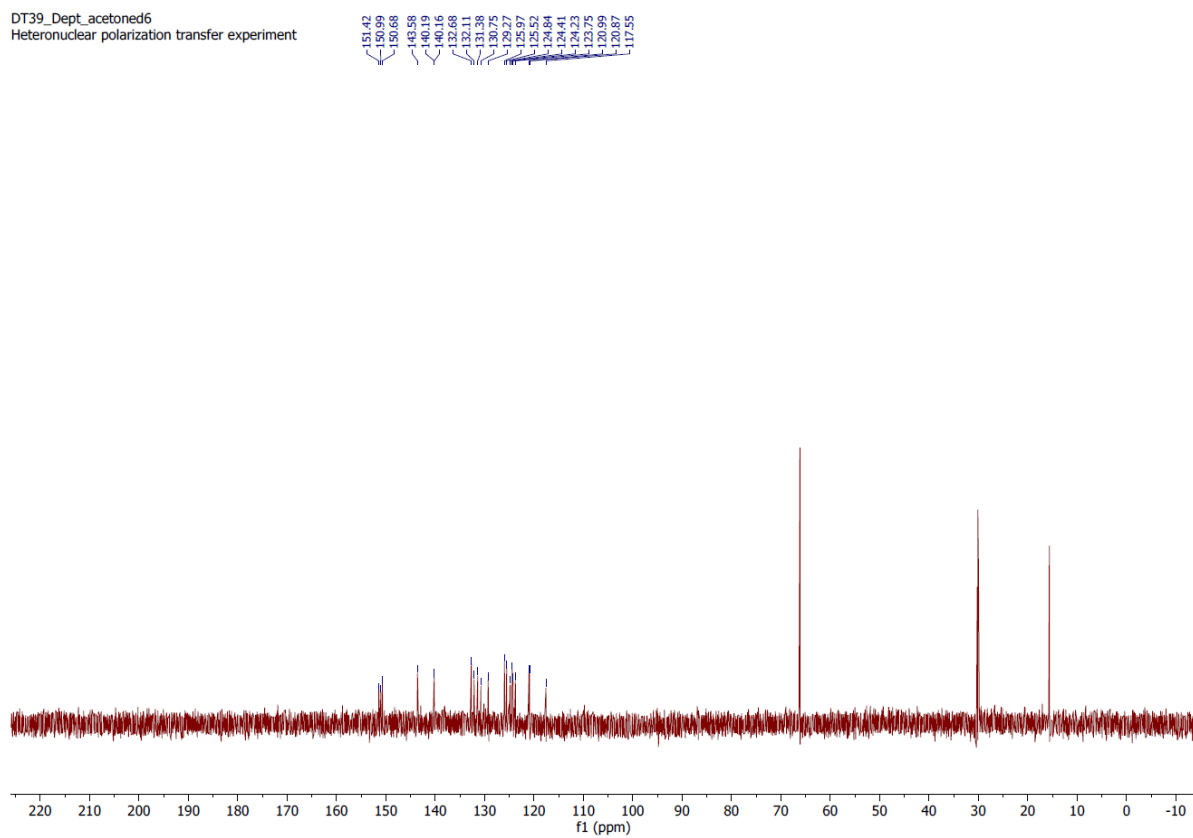


Figure S14. DEPT 135 NMR spectrum of complex A.

19F_ME394_precipitato_Acetone-d6
Std Fluorine experiment

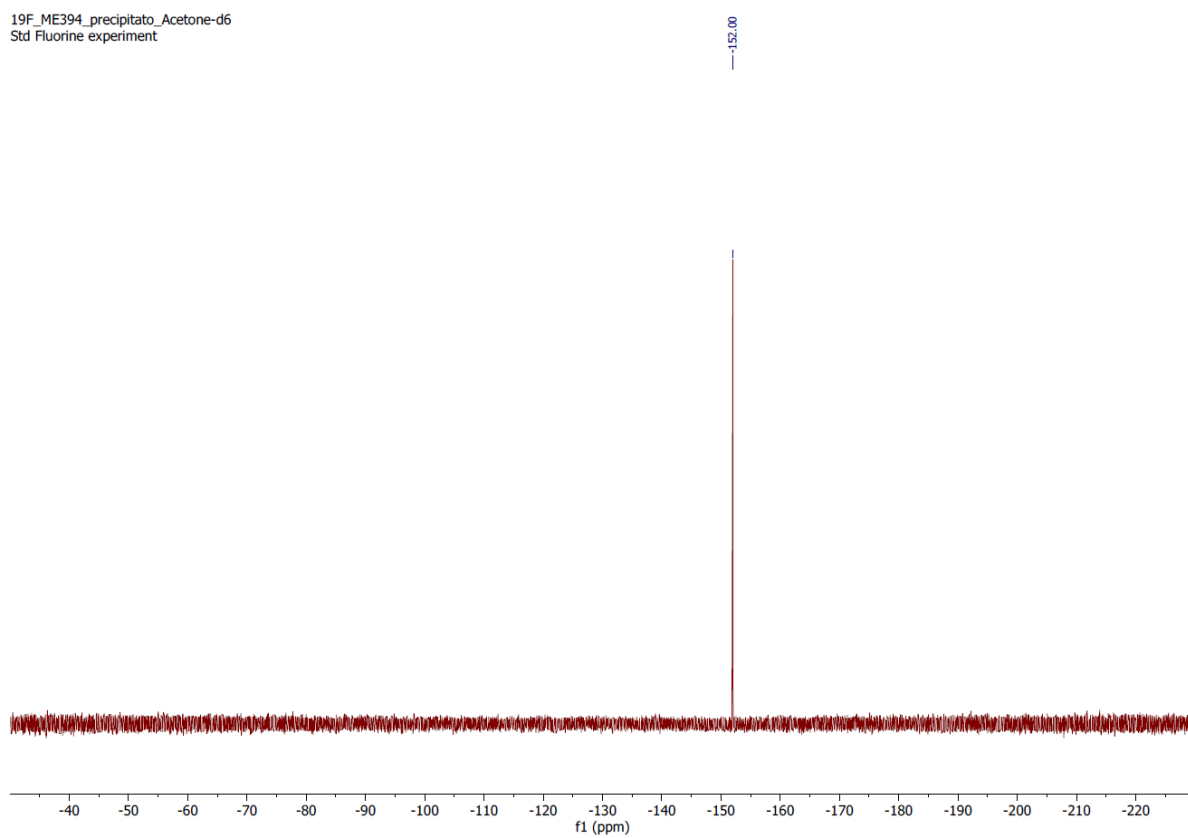


Figure S15. ^{19}F NMR spectrum of complex A.

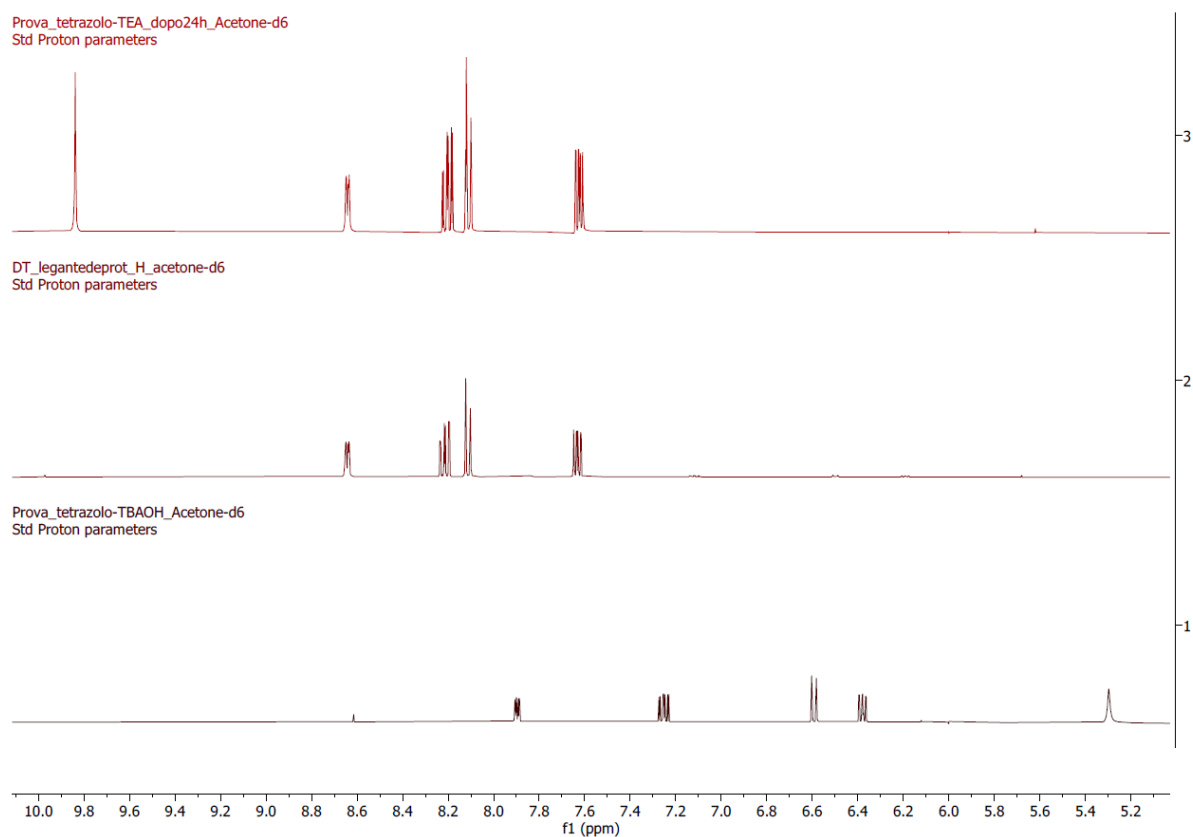


Figure S16. ^1H NMR spectrum shows the deprotonation effect of TEA, DBU or TBAOH on ligand L1.

DT40_lavHex3_H_CDCl3
Std Proton parameters

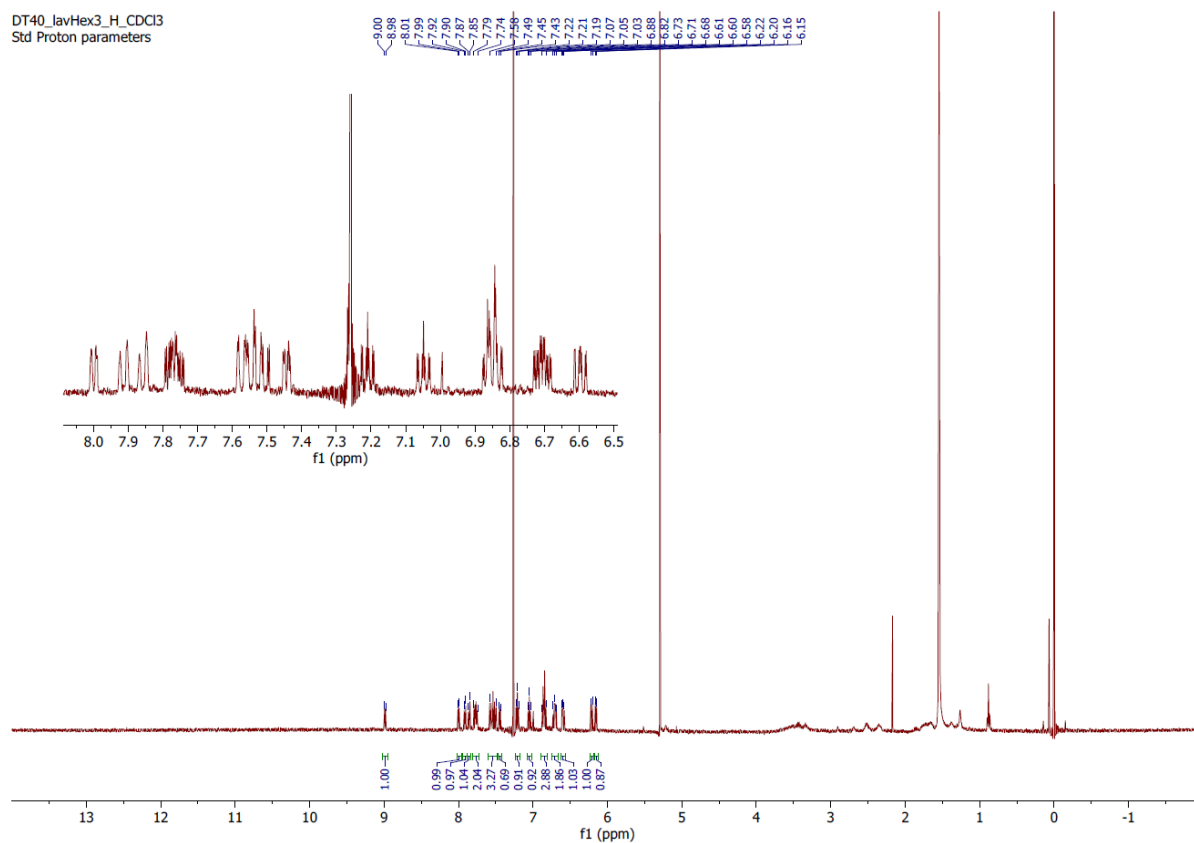


Figure S17. ^1H NMR spectrum of complex **B**.

DT40_C_CDCl3
i600 std carbon night parameters

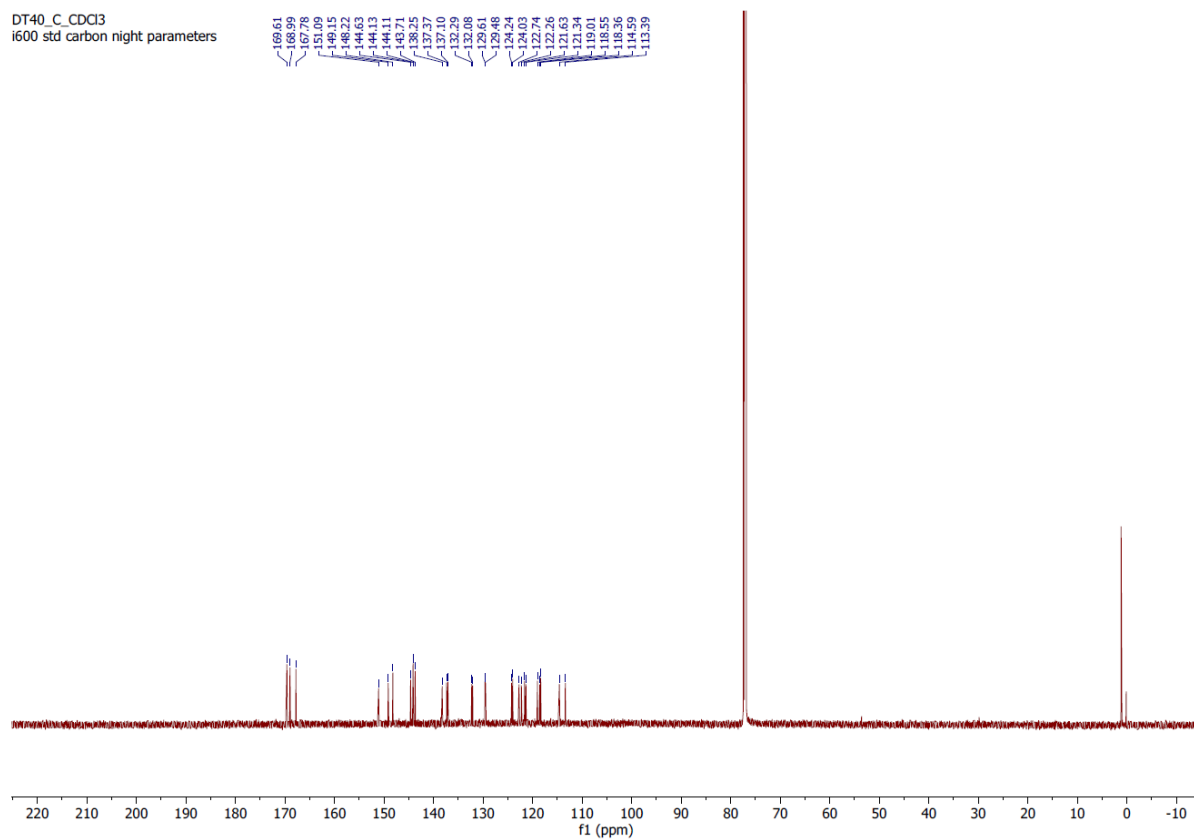


Figure S18. ^{13}C NMR spectrum of complex **B**.

DT40_Dept_CDCl3
Heteronuclear polarization transfer experiment

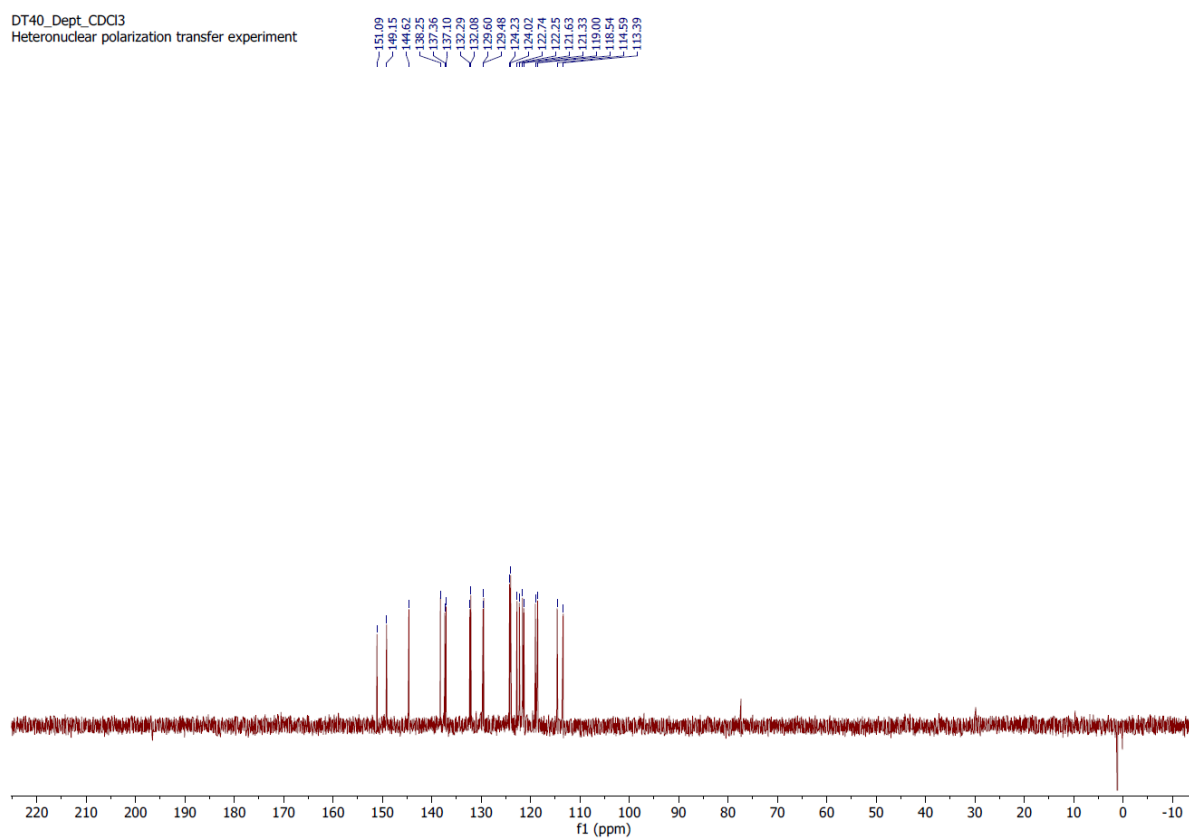


Figure S19. DEPT 135 NMR spectrum of complex **B**.

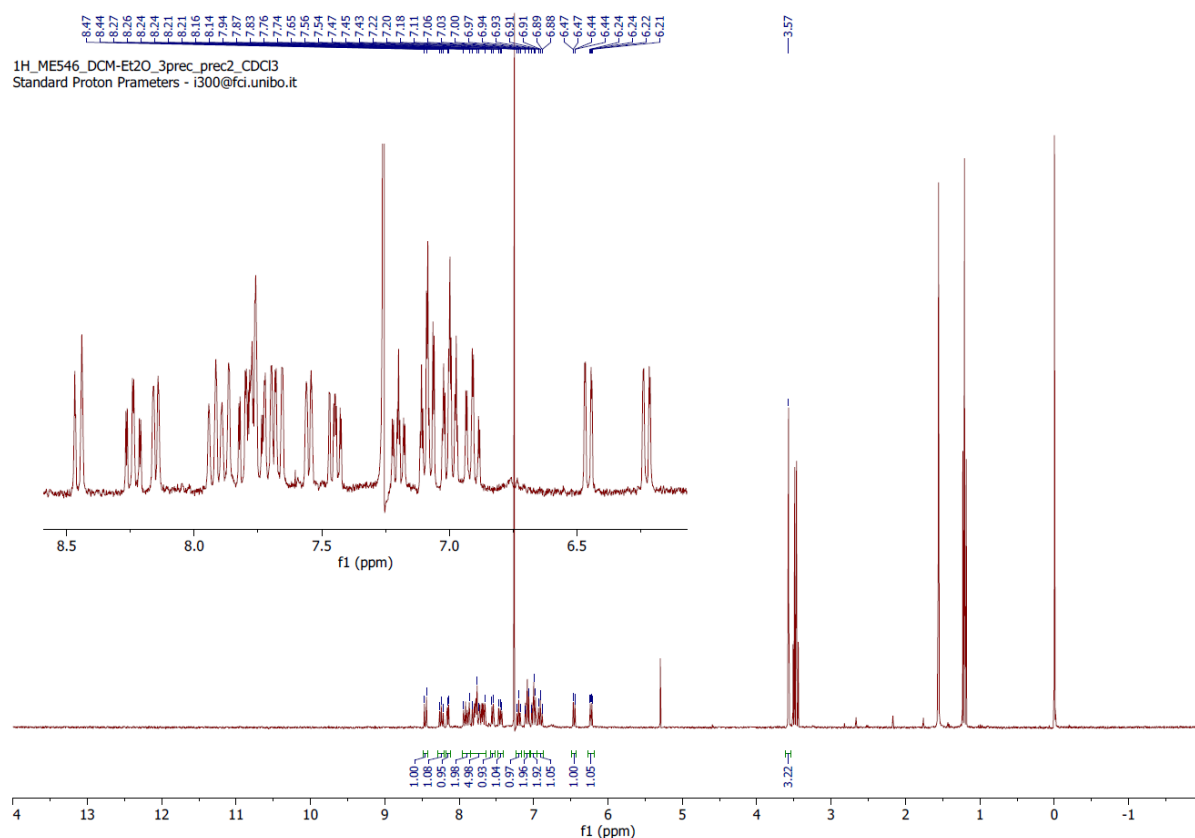


Figure S20. ^1H NMR spectrum of complex **C**.

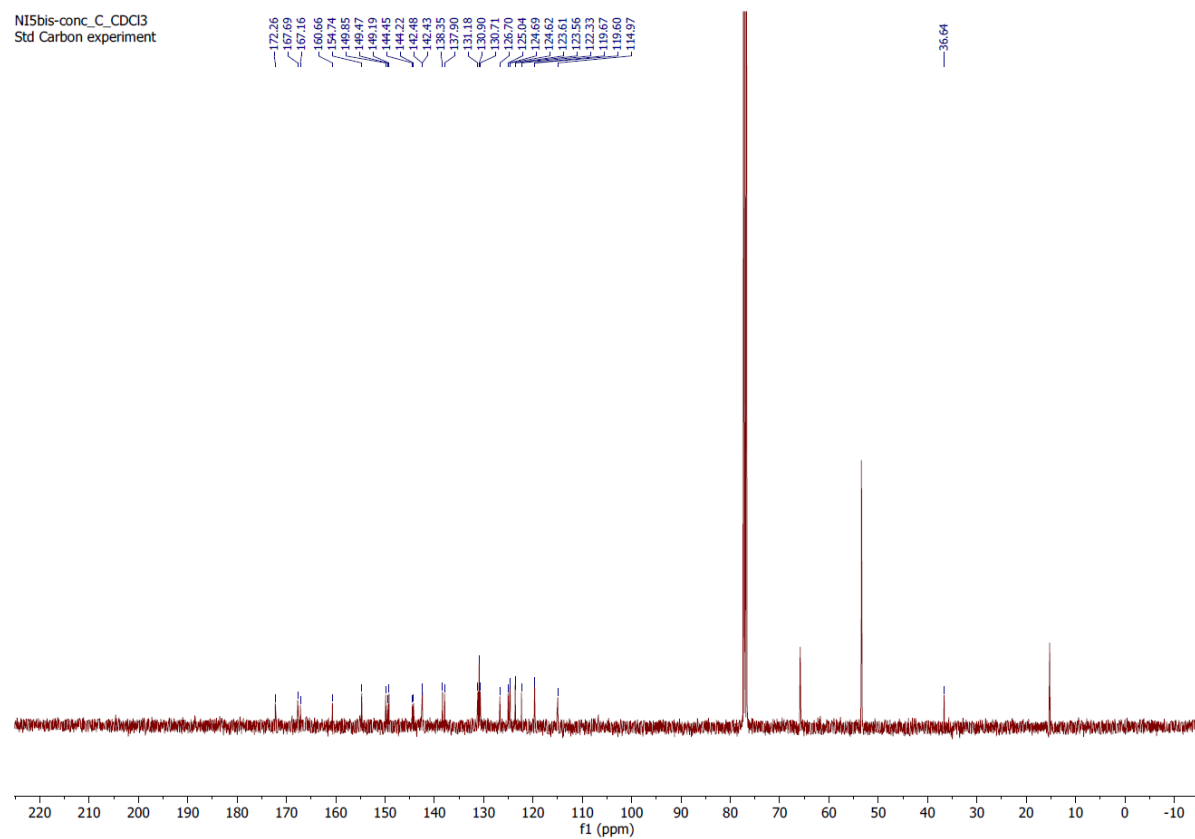


Figure S21. ^{13}C NMR spectrum of complex **C**.

N15bis-conc_DEPT_CDCI3
Heteronuclear polarization transfer experiment

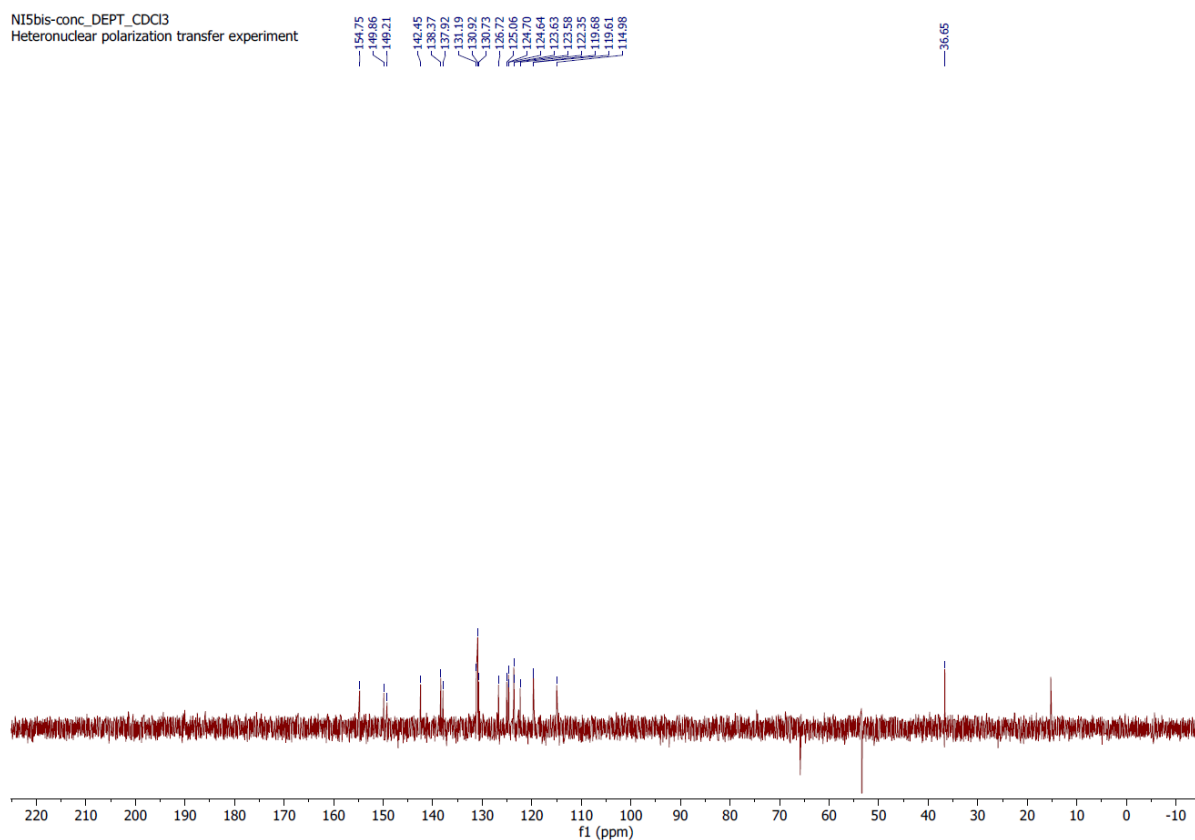


Figure S22. DEPT 135 NMR spectrum of complex **C**.

19F_ME546_DCM-Et2O_3prec_prec2_CDCI3
Std Fluorine

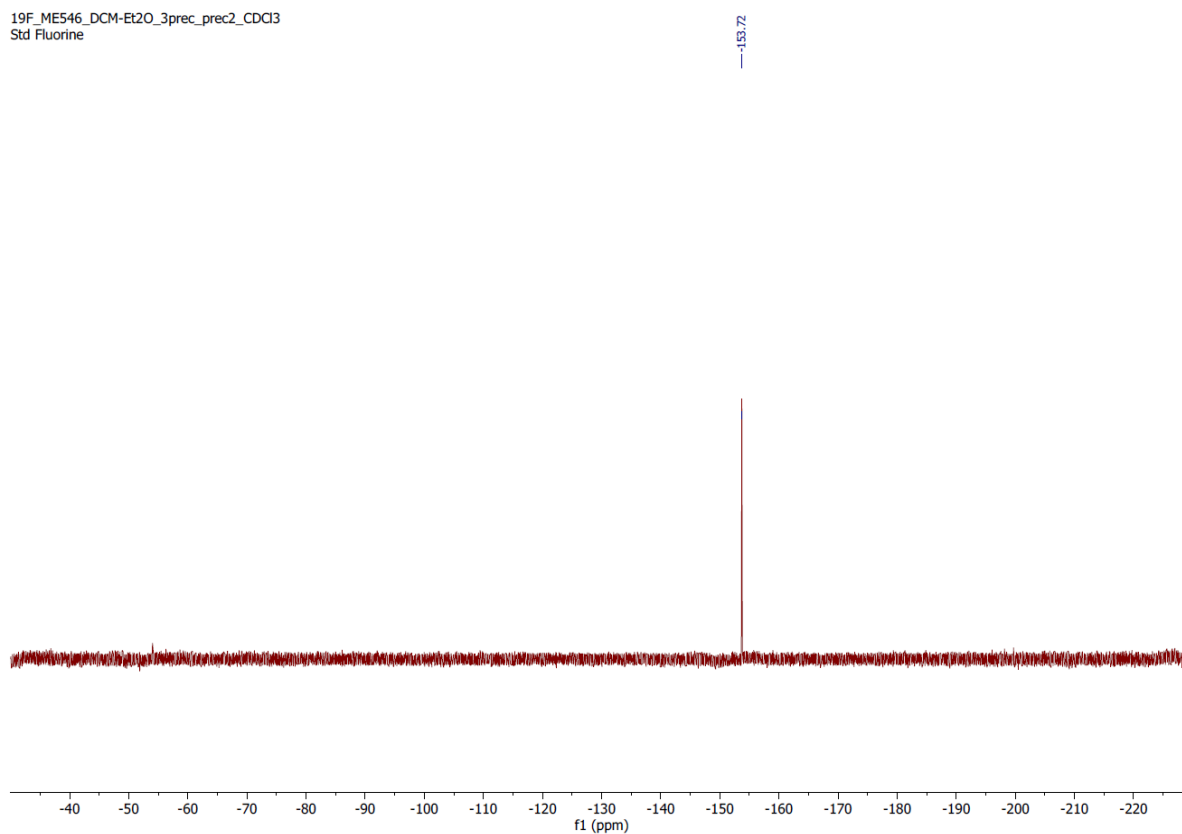


Figure S23. ^{19}F NMR spectrum of complex **C**.

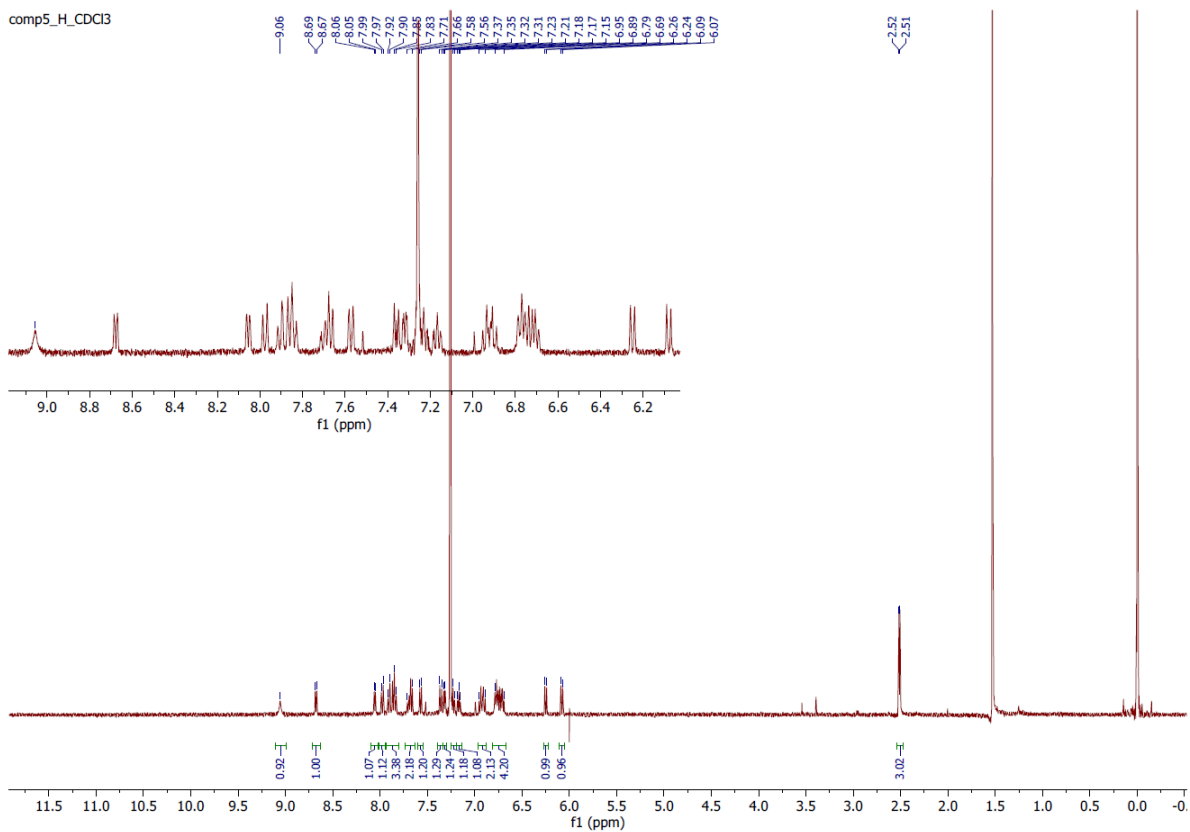


Figure S24. ^1H NMR spectrum of complex **D**.

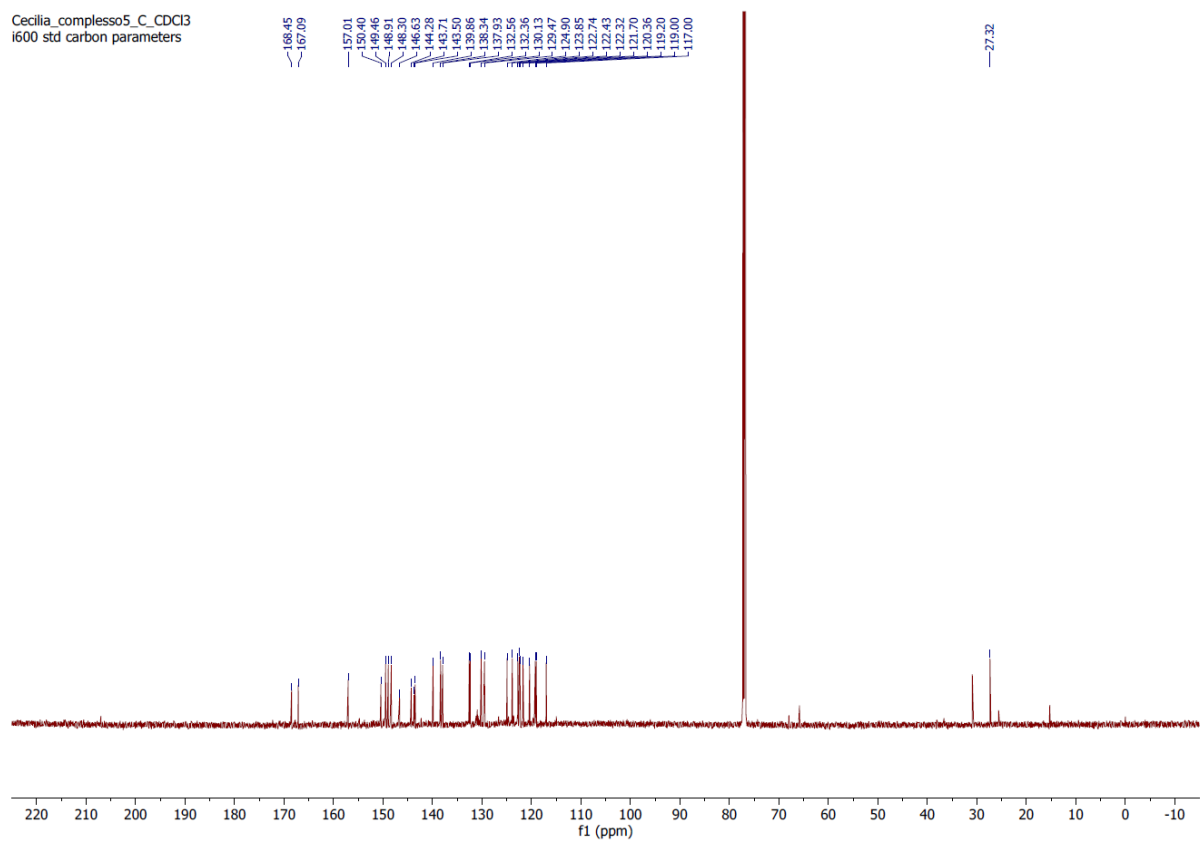


Figure S25. ^{13}C NMR spectrum of complex **D**.

Cecilia_complexo5_Dept1-5_CDCl3
i600 std parameters

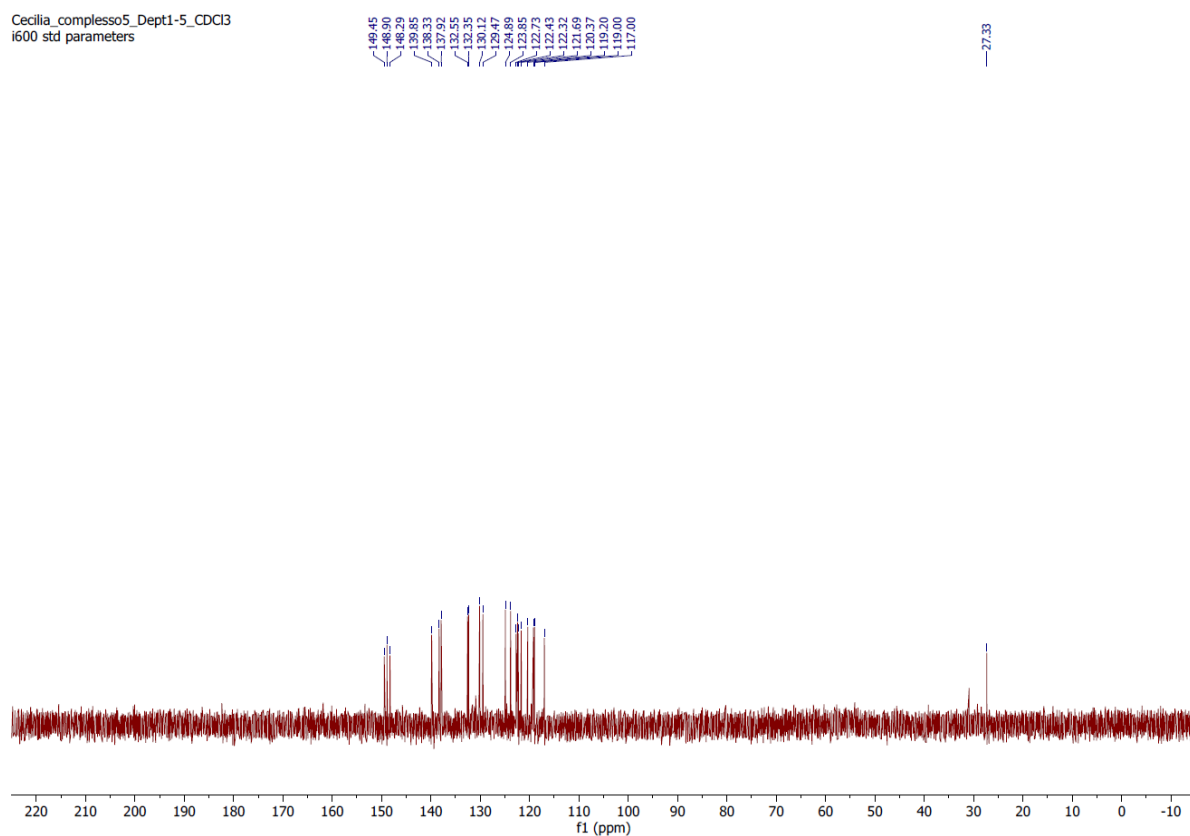


Figure S26. DEPT 135 NMR spectrum of complex **D**.

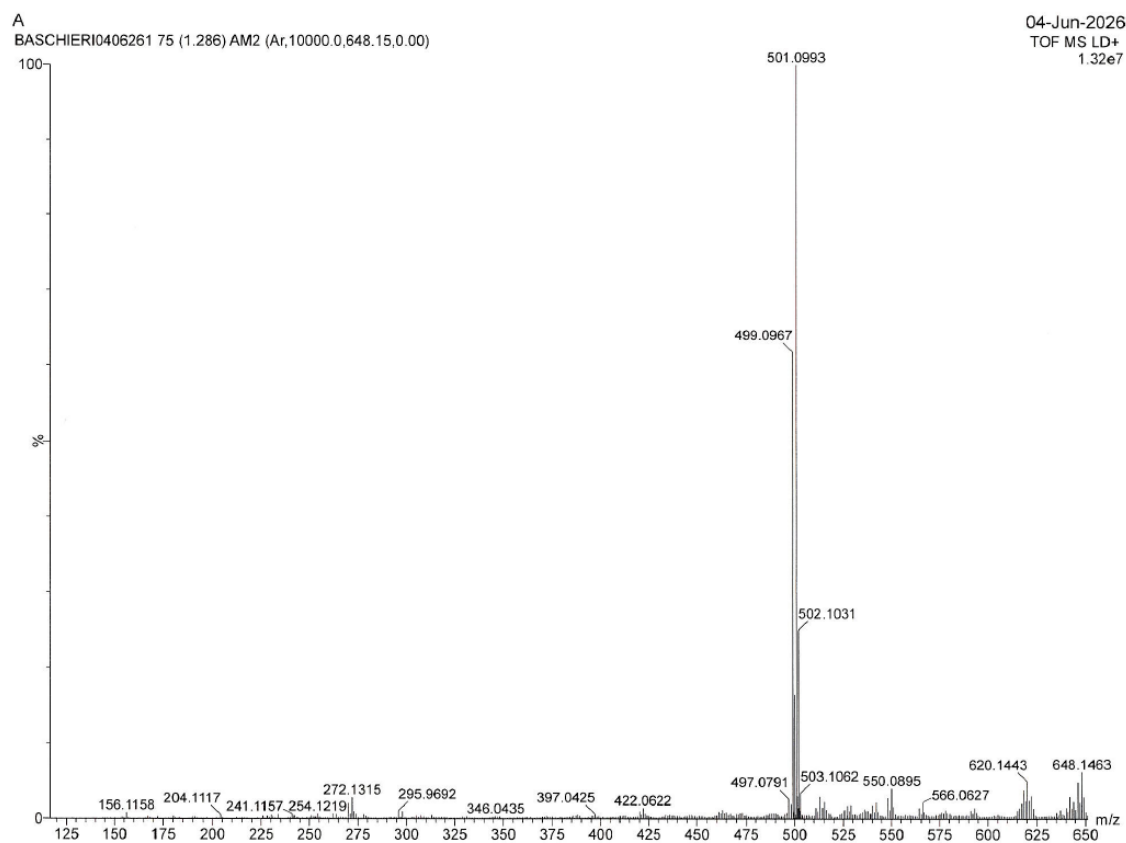


Figure S27. High-resolution mass spectrum of complex A.

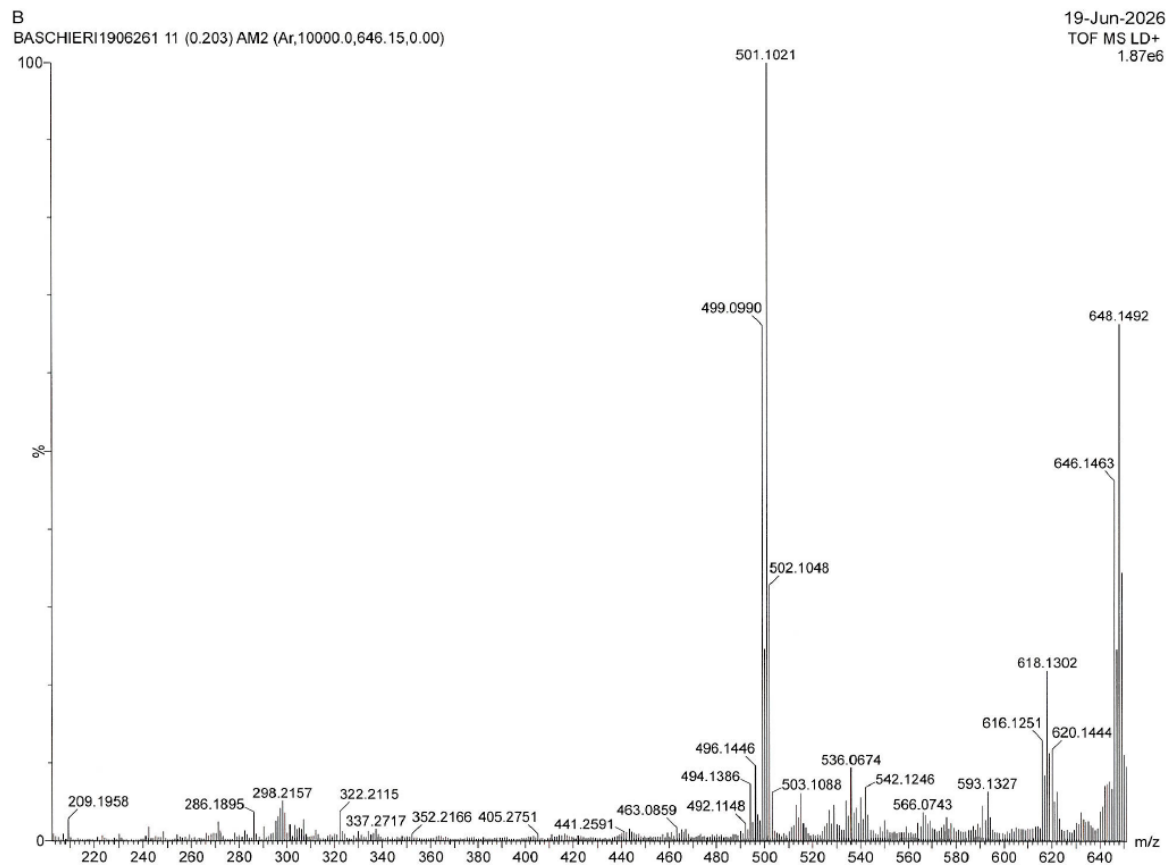


Figure S28. High-resolution mass spectrum of complex B.

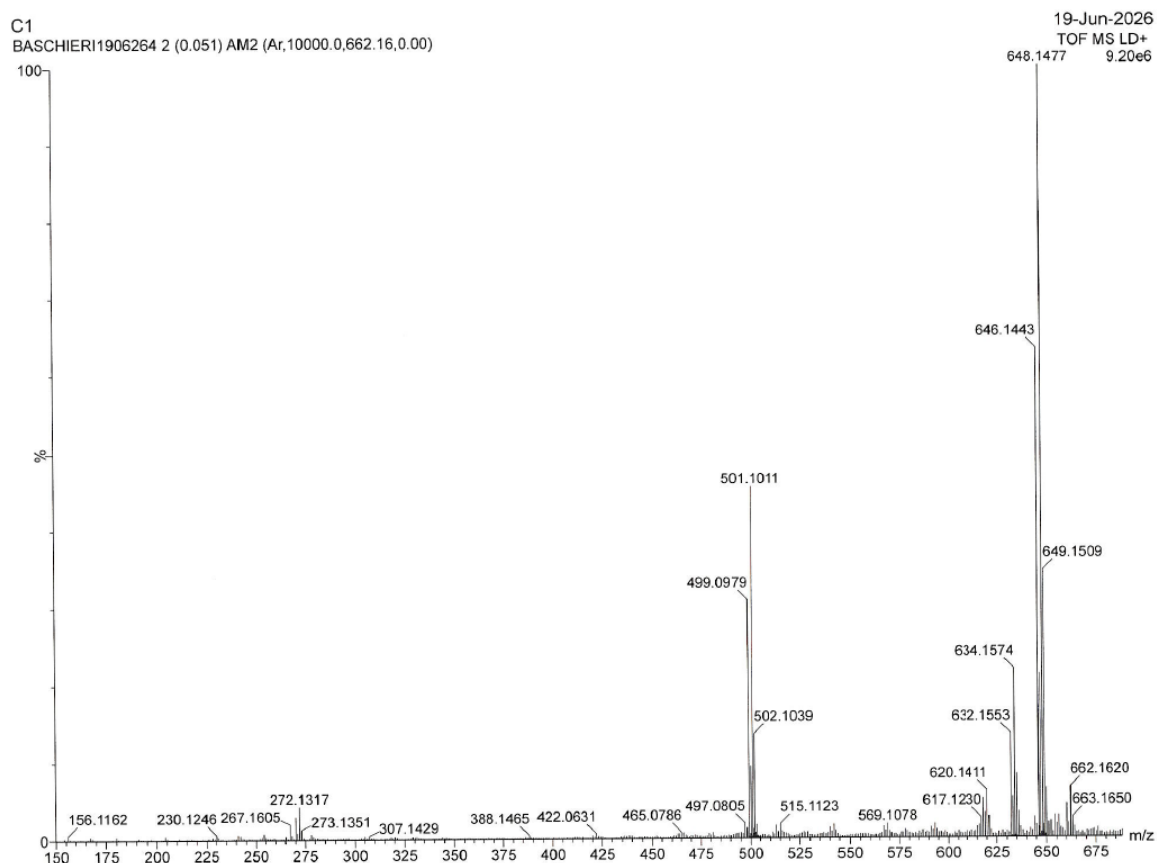


Figure S29. High-resolution mass spectrum of complex C.

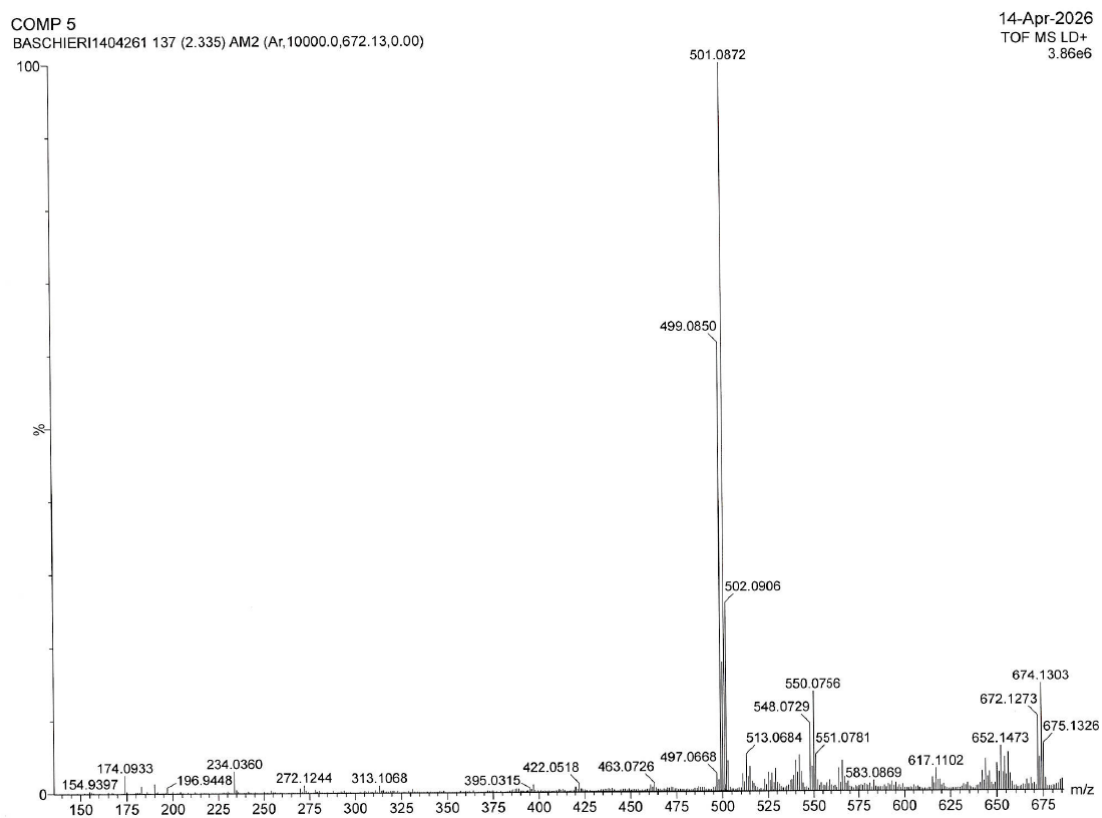


Figure S30. High-resolution mass spectrum of complex D.

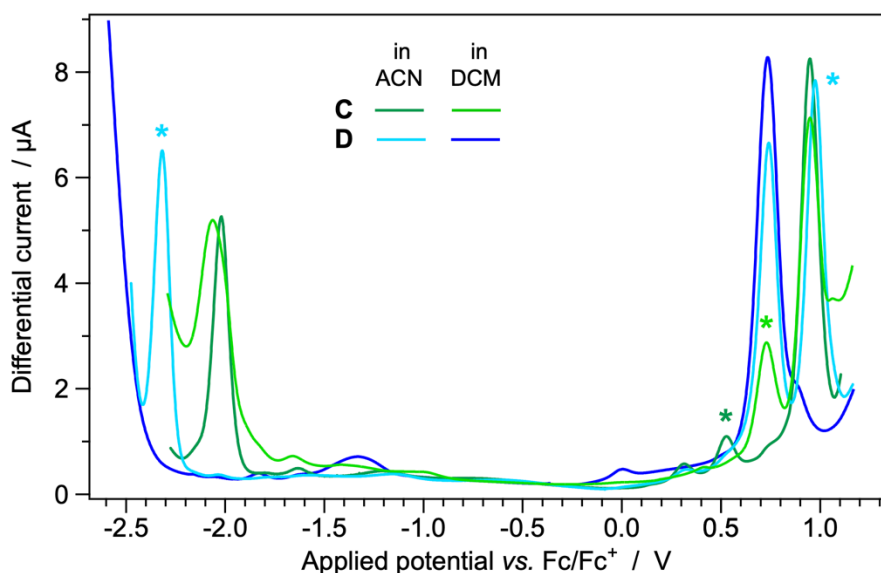


Figure S31. Square-wave voltammograms of complexes **C** and **D** (0.5 mM) recorded in acetonitrile and dichloromethane solution at 298 K. Complex **C** shows minor signs of degradations in both solvents, particularly at positive potentials (marked with green asterisks); conversely, complex **D** shows a clean voltammogram in dichloromethane solution, while additional peaks are observed in acetonitrile due to complex instability in the highly coordinative acetonitrile solution (cyan asterisks).

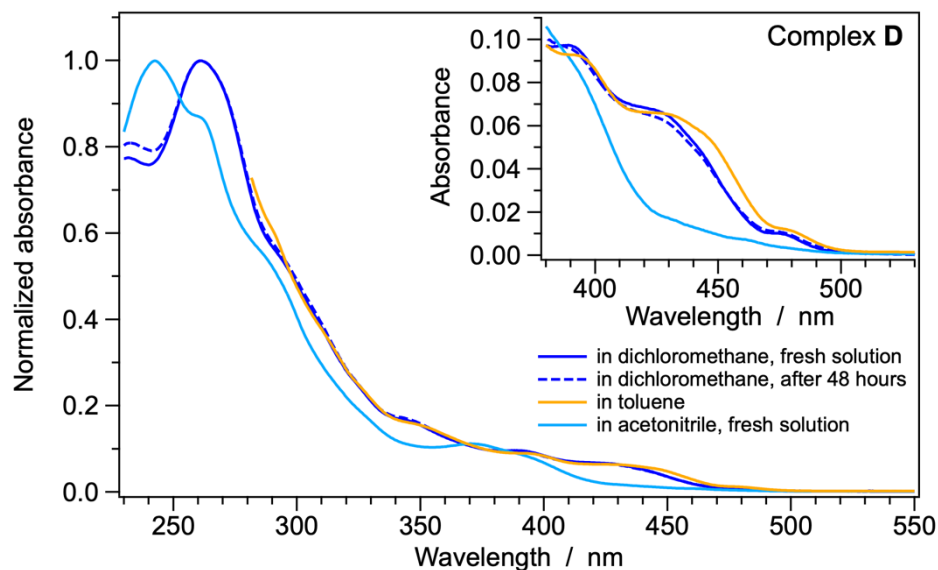


Figure S32. Normalized absorption spectra of complex **D** in different solvents. The absorption spectrum of **D** in acetonitrile lacks absorption features at longer wavelengths (see inset), suggesting possible dissociation of the ancillary ligand due to the coordinating ability of such solvent. On the contrary the spectrum of **D** in dichloromethane is fundamentally superimposable to the one recorded in toluene (an apolar, non-coordinating and acid-free solvent).

Table S1. Calculated NTOs couples describing the triplet excitations below 3.20 eV for **A** in acetonitrile (see Experimental Section for details). The λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: $0.04 \text{ e}^{-1/2} \text{ bohr}^{-3/2}$.

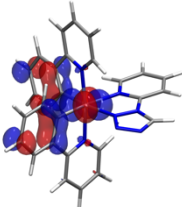
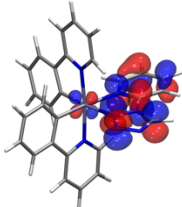
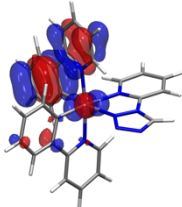
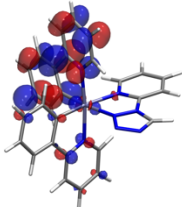
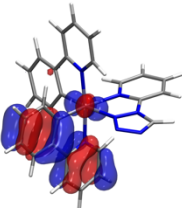
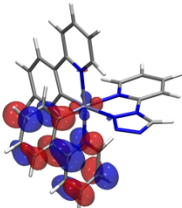
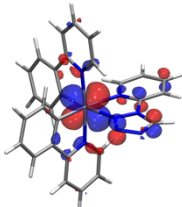
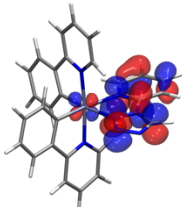
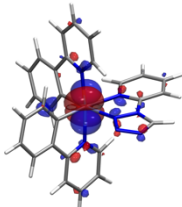
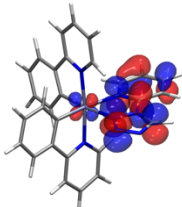
	Transition energy [eV (nm)]	NTO couple hole $\rightarrow$ electron (λ)		Nature
$S_0 \rightarrow T_1$	2.53 (490)		 (99.8%)	Mainly MLCT from the iridium center to the ancillary ligand
$S_0 \rightarrow T_2$	2.76 (449)		 (70.4%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_3$	2.79 (444)		 (65.3%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_4$	3.00 (414)		 (96.7%)	MLCT from the iridium center to the ancillary ligand
$S_0 \rightarrow T_5$	3.07 (404)		 (97.6%)	MLCT from the iridium center to the ancillary ligand

Table S2. Calculated NTOs couples describing the triplet excitations below 3.20 eV for **B** in acetonitrile (see Experimental Section for details). The λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: $0.04 \text{ e}^{-1/2} \text{ bohr}^{-3/2}$.

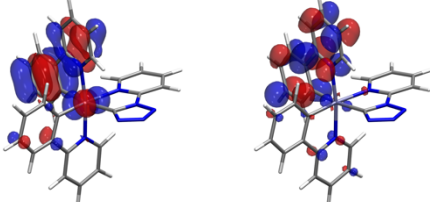
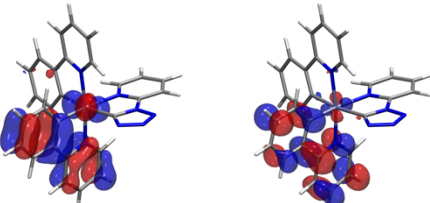
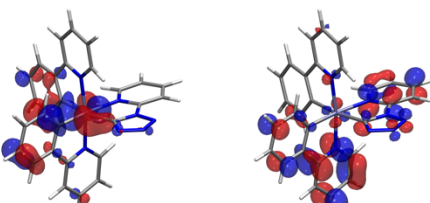
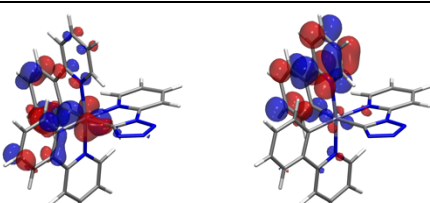
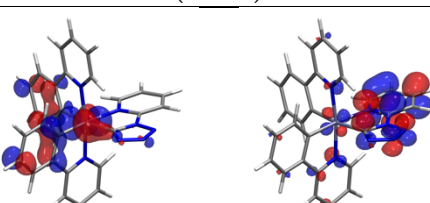
	Transition energy [eV (nm)]	NTO couple hole $\rightarrow$ electron (λ)		Nature
$S_0 \rightarrow T_1$	2.73 (454)		(79.4%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_2$	2.77 (447)		(74.8%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_3$	3.10 (400)		(69.0%)	Mixed LC/LLCT/MLCT character involving both the ppy and the ancillary ligand
$S_0 \rightarrow T_4$	3.12 (398)		(72.3%)	Mixed LC/LLCT/MLCT character involving the ppy ligands
$S_0 \rightarrow T_5$	3.13 (397)		(83.0%)	Mixed MLCT/LLCT character involving the ancillary ligand

Table S3. Calculated NTOs couples describing the triplet excitations below 3.20 eV for **C** in acetonitrile (see Experimental Section for details). The λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: $0.04 \text{ e}^{-1/2} \text{ bohr}^{-3/2}$.

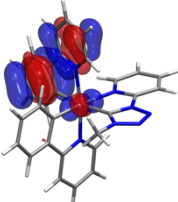
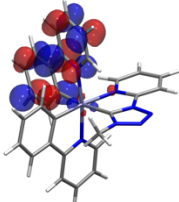
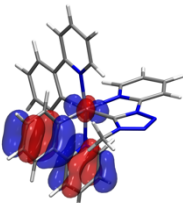
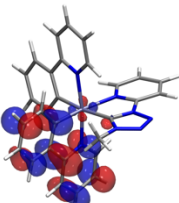
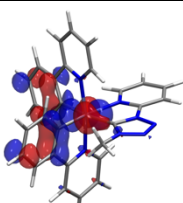
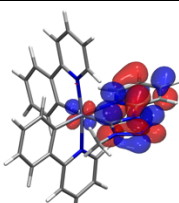
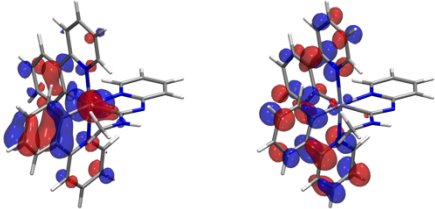
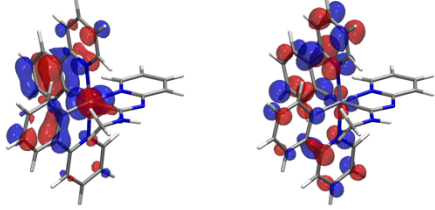
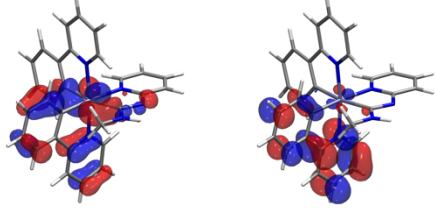
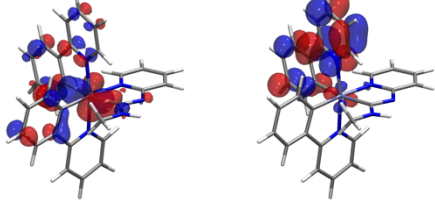
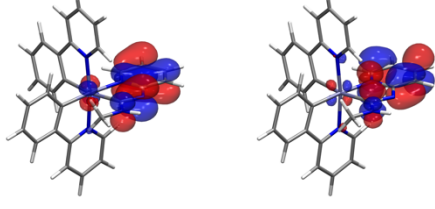
	Transition energy [eV (nm)]	NTO couple hole $\rightarrow$ electron (λ)		Nature
$S_0 \rightarrow T_1$	2.78 (446)		 (82.3%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_2$	2.82 (440)		 (80.1%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_3$	2.91 (426)		 (95.3%)	Mainly MLCT from the iridium center to the ancillary ligand

Table S4. Calculated NTOs couples describing the triplet excitations below 3.20 eV for **D** in acetonitrile (see Experimental Section for details). The λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: $0.04 \text{ e}^{-1/2} \text{ bohr}^{-3/2}$.

	Transition energy [eV (nm)]	NTO couple hole $\rightarrow$ electron (λ)		Nature
$S_0 \rightarrow T_1$	2.68 (462)		(79.1%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_2$	2.73 (455)		(68.6%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_3$	2.96 (418)		(78.3%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_4$	3.02 (411)		(86.0%)	Mainly LC on the cyclometallating ppy ligands
$S_0 \rightarrow T_5$	3.13 (396)		(97.0%)	LC on the ancillary ligand

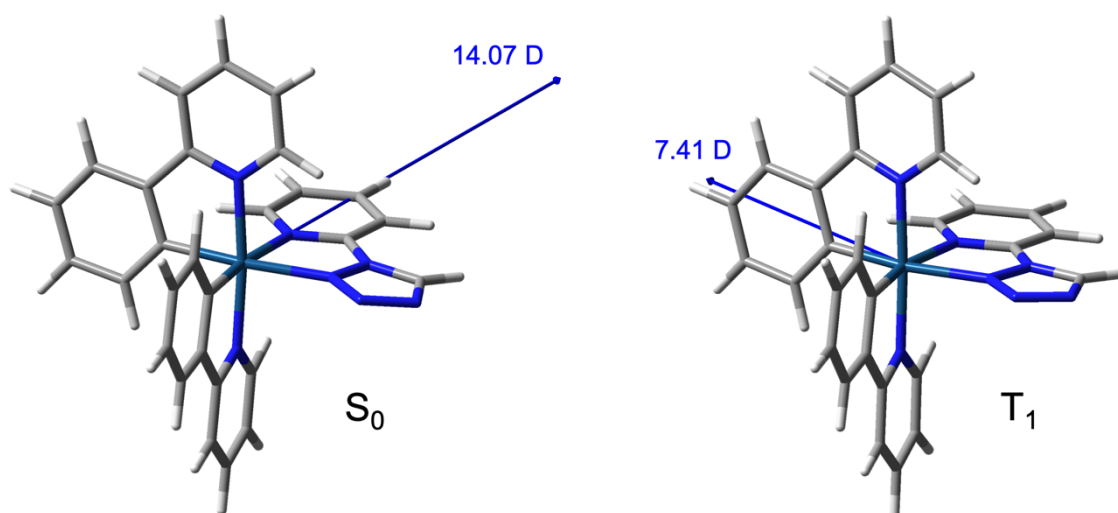


Figure S33. Permanent molecular dipole moment calculated at the M06 level of theory in acetonitrile (using PCM) for complex **A** in its ground-state minimum-energy geometry (S_0 , left) or in the lowest triplet-state minimum (T_1 , right). The excited state is less polar than the ground state. The depicted molecular dipole moment vectors follow the physics convention (*i.e.*, they point from negative to positive charge regions).

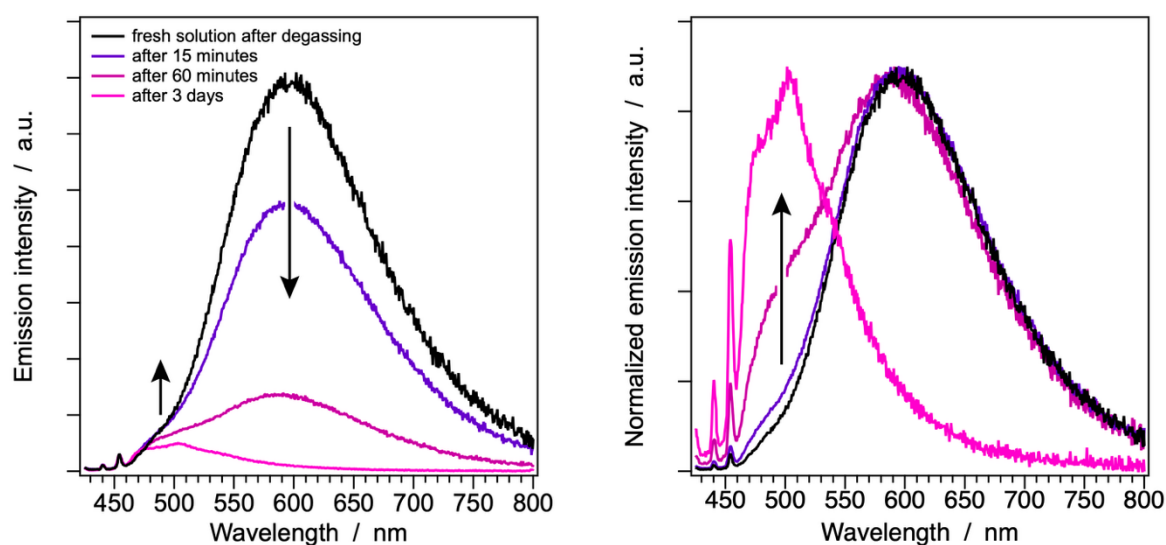


Figure S34. Time evolution of the emission spectra of complex **A** ($\lambda_{\text{exc}} = 400 \text{ nm}$) in oxygen-free acetonitrile solution at room temperature (left); the same spectra are also normalized to compensate for the remarkable intensity reduction over time (right). The characteristic $^3\text{MLCT}$ emission band of complex **A**, peaking at approx. 600 nm, disappears over time and a very weakly emissive structured band appears at approx. 500 nm, probably due to the decoordination of the $\text{N}^{\wedge}\text{N}$ ancillary ligand, leading to a residual ^3LC emission centered on the ppy cyclometallating ligands. Accordingly, a reliable determination of the photoluminescence quantum yield of complex **A** in acetonitrile solution is prevented.

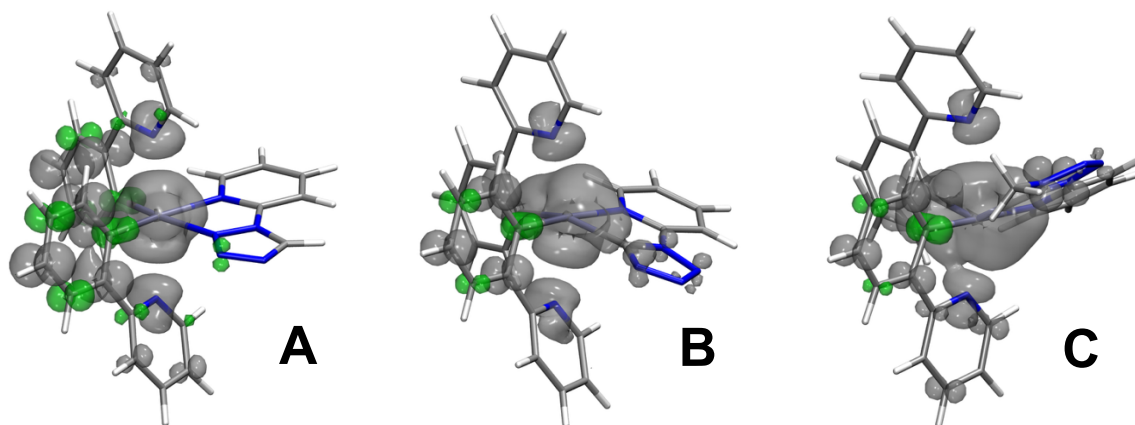


Figure S35. Spin-density distribution of the fully optimized axial ^3MC states in complexes **A–C**, involving the elongation of the axial Ir–N(ppy) bonds (isovalues: $0.002 \text{ e bohr}^{-3}$). In each complex, such axial ^3MC state is found approx. 0.5 eV above the highest lying equatorial ^3MC state (Figure 6). All data are computed in acetonitrile using PCM at the M06 level of theory.