Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

M-CPOnes: Transition Metal Complexes with Cyclopropenone-Based Ligands for Light-Triggered Carbon Monoxide Release

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1 Materials and Methods

Solvents and reagents were commercially obtained and used without further purification and distilled water was used. Pressure tubes (15 mL) were purchased from FengTecEx GmbH and as a precaution, the reactions using pressure tubes were performed behind a blast shield.

For thin-layer chromatography Macherey Nagel plates (Polygram®SIL G/UV_{254}, coating thickness 0.2 mm) equipped with a fluorescence indicator were used. Silica gel with a pore diameter of 0.040-0.063 mm was purchased from Merck. For flash chromatography Biotage® SNAP Ultra columns (10 g, 25 g, 50 g) and Biotage® Sfär Silica HC D columns (10 g, 25 g) were used on an Isolera One from Biotage®.

Centrifugation of the complexes was performed using a Grant-Bio LMC-3000.

1.1 Light Sources

For irradiation experiments, a custom-built light source was used consisting of five 365 nm Nichia NCSU275 UV SMD-LEDs (148 nW).

1.2 NMR Spectroscopy

NMR spectra were recorded on a Bruker Avance 200, a Bruker AvanceNeo 500, or a Bruker Avance 600 spectrometer, the latter being equipped with a cryogenically cooled triple-resonance probe head. Chemical shifts for ^{1}H, ^{13}C, and ^{19}F spectra are expressed in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). ^{1}H and ^{13}C spectra were referenced to either TMS at 0.0 ppm or $CDCl_3$ (δ_H = 7.62 ppm, δ_C = 77.16 ppm), CD_3CN (δ_H = 1.94 ppm, δ_C = 1.32 ppm), toluene-d_8 (δ_H = 7.09 ppm). Furthermore, ^{19}F spectra of the *in situ* cycloaddition experiments were referenced to C_6F_6 (δ_F = -164.9 ppm). All measurements were carried out at 298 K unless reported otherwise. The following abbreviations are used to describe signal multiplicity for ^{1}H, ^{13}C and ^{19}F NMR spectra: s: singlet, d: doublet, t: triplet, m: multiplet, br: broad.

1.3 Mass Spectrometry

Mass spectra using electron ionization (EI-MS) were recorded on a Jeol AccuTOF. High resolution electrospray ionisation mass spectrometry (ESI-MS) was carried out on a Thermo Scientific Q Exactive Plus (spray voltage 3-4 eV, capillary temperature 40-50 °C) infused from a Harvard syringe pump at a rate of 5-10 µL per minute.

1.4 Infrared Spectroscopy

Infrared spectra were recorded on a 1600 series FT-IR spectrometer from Perkin Elmer, equipped with an A531-G Golden-Gate-Diamond-ATR-Unit. For analysis, the intensities were classified as weak (w), medium (m) and strong (s).

1.5 UV/vis Spectroscopy

UV/vis spectra were recorded on a Perkin Elmer UV Lambda 650 using Hellma Macro quartz cuvettes with a pathlength of 10 mm.

1.6 Fluorescence Spectroscopy

Fluorescence spectra were recorded on a Perkin Fluorescence Spectrometer LS55 using Hellma Micro quartz cuvettes for fluorescence with a pathlength of 25 mm.

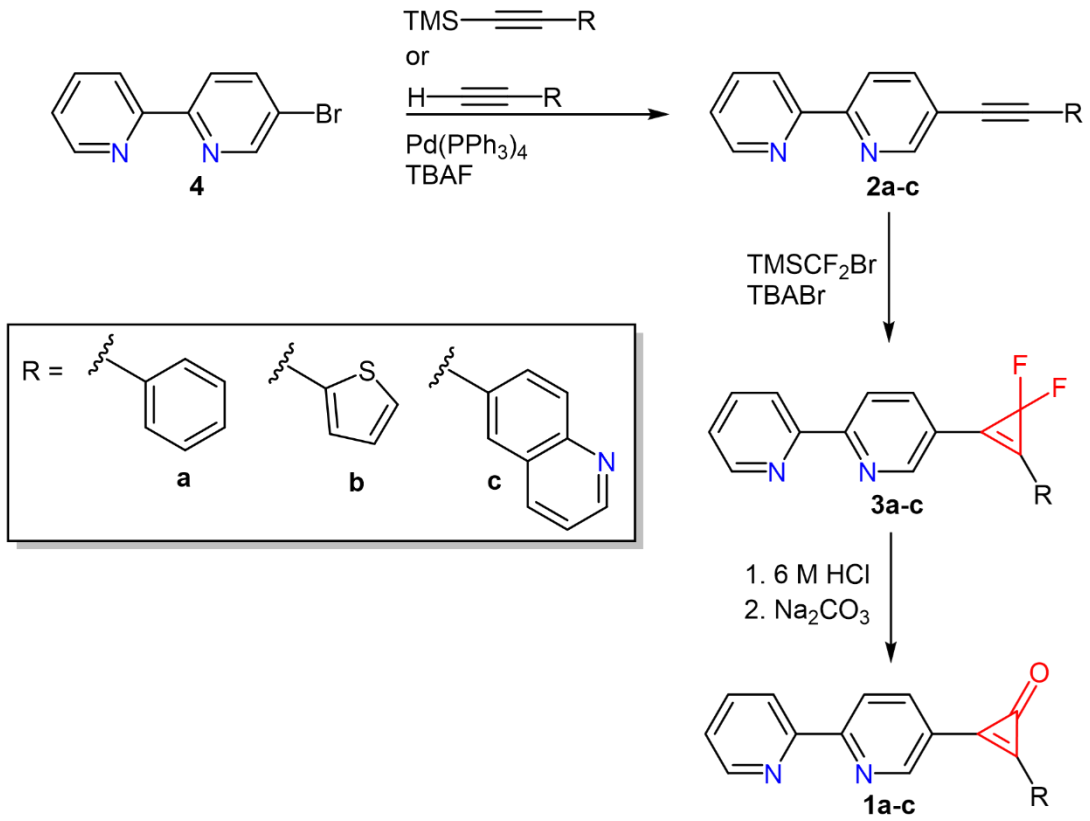
1.7 X-Ray Crystallography

A suitable crystal was selected and mounted on a XtaLAB Synergy, Dualflex, HyPix diffractometer. Using Olex2,[1] the structure was solved with SHELXT[2] and refined with the SHELXL[3] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropic. The C-H H atoms were positioned with idealised geometry and were refined isotropic with Uiso(H) = 1.2 Ueq(C) using a riding model.

CCDC 2142653 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

2 Ligand Synthesis

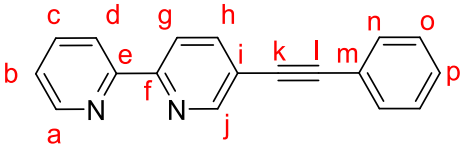
Bipyridine-based ligands **1a-c** and **2a-c** were prepared according to Scheme S1. The precursor 5-bromo-2,2'-bipyridine (**4**) was prepared according to a literature-known procedure.[4] Alkyne derivatives **2a-c** were obtained after Sonogashira-type cross-coupling with either the TMS-protected or deprotected alkyne precursor adapting a copper-free Sonogashira cross-coupling procedure.[5] Compounds **3a-c** were synthesised adapting a procedure from the literature.[6] Cyclopropenones **1a-c** were obtained after hydrolysis of difluorocyclopropenes **3a-c** with hydrochloric acid followed by precipitation under basic conditions.



Scheme S1. Synthesis of the bipyridine-based ligands **2a-c** and **1a-c**.

2.1 Phenyl-Substituted Bipyridine Ligands

2.1.1 5-(Phenylethynyl)-2,2'-bipyridine (**2a**)



5-Bromo-2,2'-bipyridine (**4**) (1.87 g, 7.95 mmol) and $Pd(PPh_3)_4$ (459 mg, 5 mol%) were added under a nitrogen atmosphere to a three necked flask. Phenylacetylene (0.96 mL, 8.75 mmol)

and tetrabutylammonium fluoride (1 M in tetrahydrofuran, 47.7 mL, 47.7 mmol) were added and the reaction mixture was heated at 70 °C for 3 h. After cooling to room temperature, 50 mL water and 30 mL dichloromethane were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was dry loaded onto silica gel and purified by flash column chromatography (silica gel, 5% ethyl acetate/cyclohexane) and the product was obtained as a colourless crystalline solid.

Yield: 1.42 g (70%, 5.54 mmol)

The analytical data is consistent with the literature data.[7]

^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 8.85 (dd, ^4J = 2.2 Hz, ^5J = 0.8 Hz, 2H, H_j) 8.71 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 2H, H_a), 8.43 (dt, ^3J = 7.9 Hz, ^4J = 1.1 Hz, 1H, H_d), 8.42 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1H, H_g), 7.99 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 2H, H_h), 7.85 (td, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 2H, H_c), 7.59-7.53 (m, 2H, H_n), 7.40-7.36 (m, 3H, $H_{o,p}$), 7.34 (ddd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, ^4J = 1.1 Hz, 2H, H_b).

^{13}C NMR (151 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 155.5 (C_e), 154.8 (C_f), 151.7 (C_j), 149.3 (C_a), 139.4 (C_h), 137.0 (C_c), 131.7 (C_n), 128.8 (C_p), 128.5 (C_o), 123.9 (C_b), 122.6 (C_m), 121.4 (C_d), 120.3 ($C_{g,i}$), 93.4 (C_l), 86.4 (C_k).

HRMS (EI, 70 eV) *m/z*: 256.09987 $[M]^+$ (calculated: 256.10005 for $C_{18}H_{12}N_2$, difference: -0.7 ppm).

FT-IR: ṽ = 3052.9 (w), 3005.7 (w), 2216.7 (w), 1586.4 (m), 1570.7 (w), 1539.9 (m), 1492.0 (m), 1454.6 (s), 1432.3 (m), 1368.7 (m), 1243.2 (m), 1143.4 (w), 1121.4 (w), 1090.8 (w), 1039.1 (w), 1020 (w), 914.9 (w), 862.5 (m), 795.9 (s), 753.3 (s), 745,5 (s), 686.6 (s), 647.4 (m), 619.3 (m), 562.9 (w), 540.8 8m), 540.4 (m) cm^{-1}.

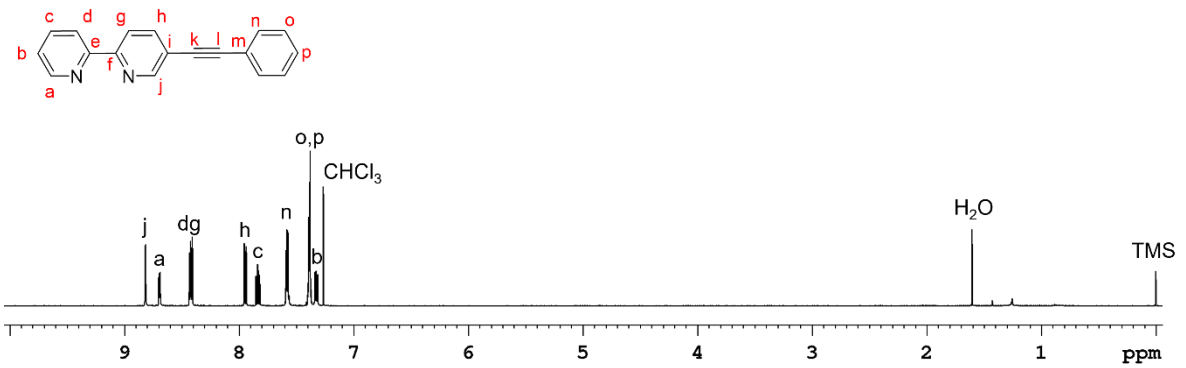


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(phenylethynyl)-2,2'-bipyridine (5-(phenylethynyl)-2,2'-bipyridine (**2a**).

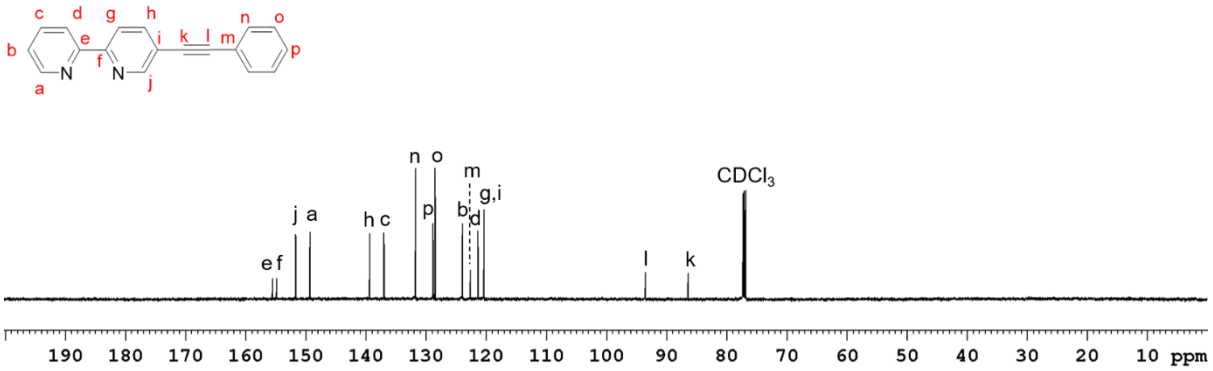


Figure S2. ^{13}C NMR spectrum (151 MHz, $CDCl_3$, 298 K, TMS) of 5-(phenylethynyl)-2,2'-bipyridine (**2a**).

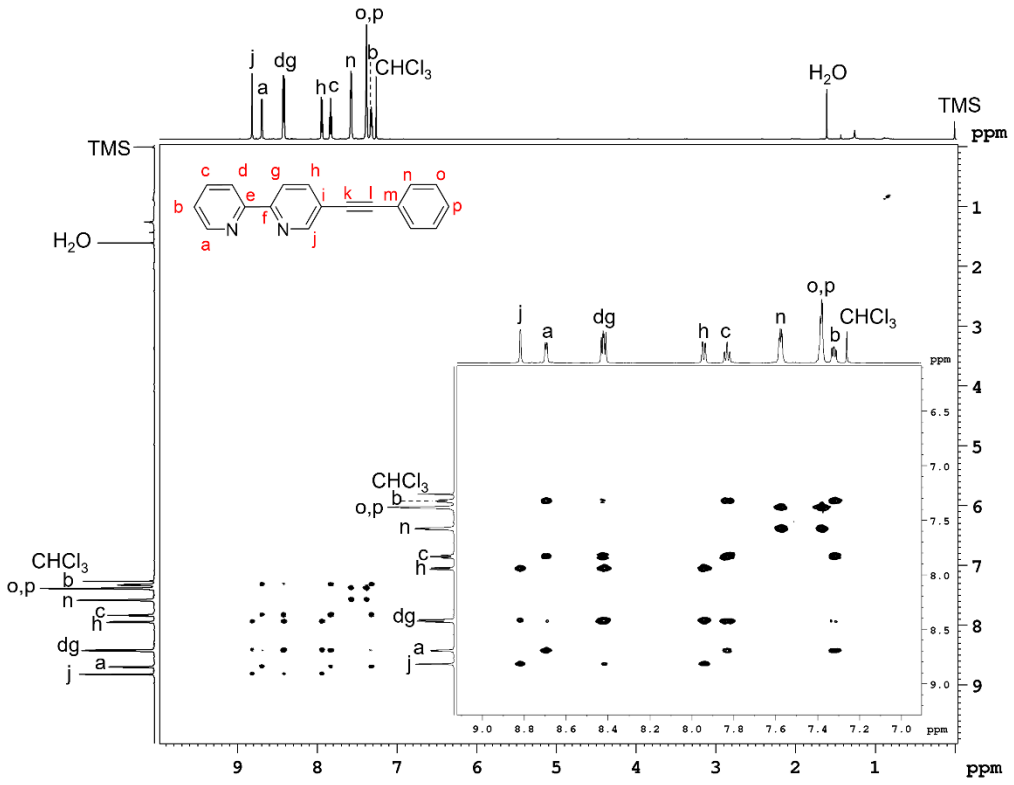


Figure S3. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, $CDCl_3$, 298 K, TMS) of 5-(phenylethynyl)-2,2'-bipyridine (**2a**).

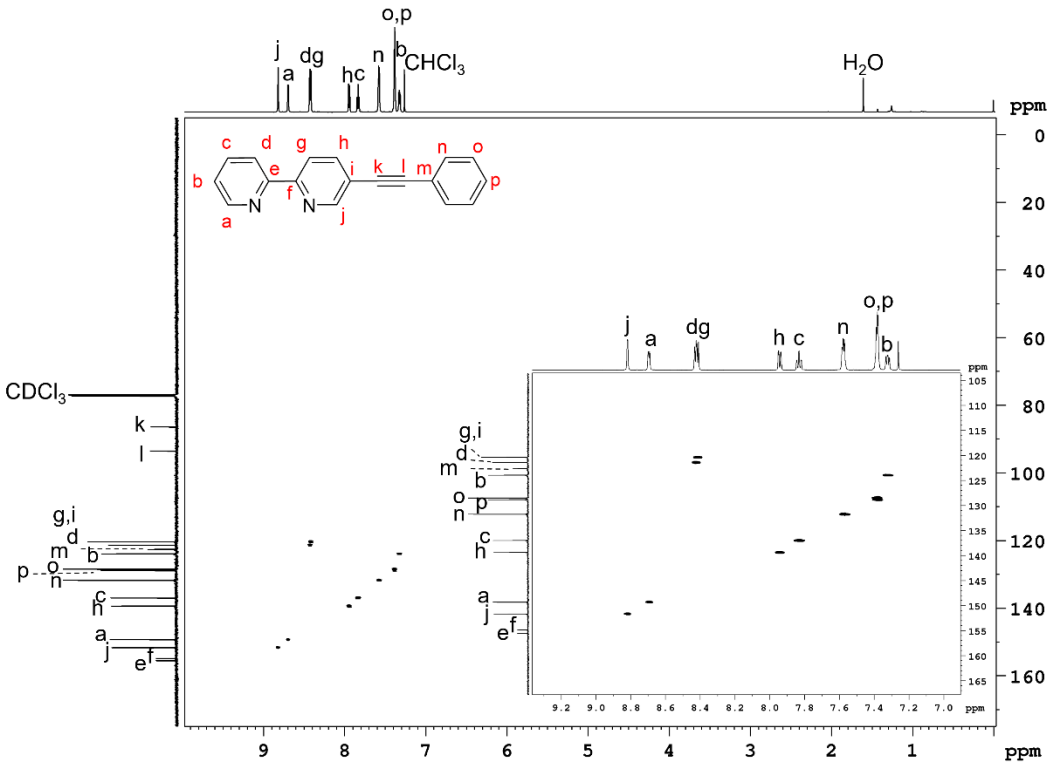


Figure S4. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K, TMS) of 5-(phenylethynyl)-2,2'-bipyridine (**2a**).

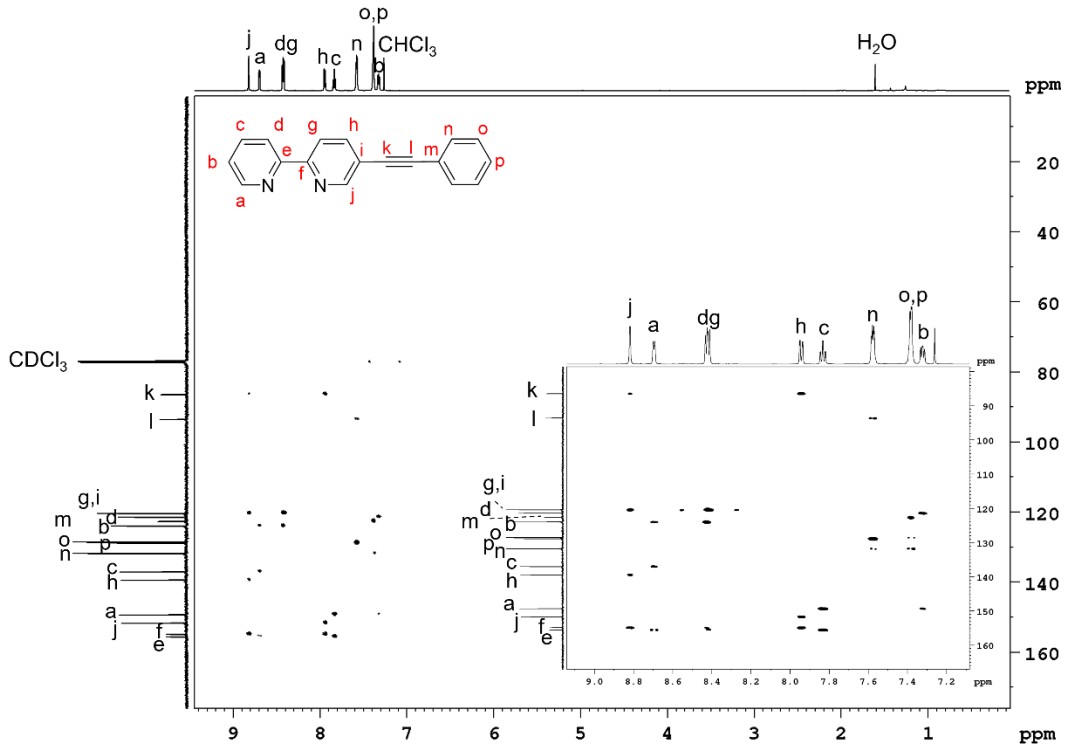
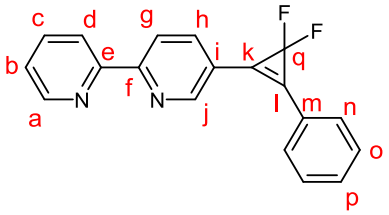


Figure S5. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K, TMS) of 5-(phenylethynyl)-2,2'-bipyridine (**2a**).

2.1.2 5-(3,3-Difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**)



5-(Phenylethynyl)-2,2'-bipyridine (**2a**) (500 mg, 1.95 mmol) and TBABr (18.9 mg, 58.5 µmol) were added under a nitrogen atmosphere to a pressure tube. 6 mL Dry toluene and (bromodifluoromethyl)trimethylsilane (422 µL, 2.92 mmol) were added. The pressure tube was immediately closed and the reaction mixture was heated at 120 °C for 2 hours. After cooling to room temperature, addition of 10 mL dichloromethane caused partial precipitation of the product from the reaction mixture. The solid was filtered, washed with DCM and afterwards added to 20 mL sat. aqueous Na_2CO_3 solution. The aqueous layer was extracted with dichloromethane (3 x 10 mL) and the combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo* giving the product as a powdered brownish solid (40 mg, 131 µmol). Furthermore, the filtrate of the crude reaction mixture was also added to 50 mL sat. aqueous Na_2CO_3 solution. The aqueous layer was extracted with dichloromethane (3 x 15 mL) and the organic extracted were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (silica gel, 5%-10% ethyl acetate/cyclohexane) to obtain the product as a powdered white solid (152 mg, 496 µmol).

Yield: 192 mg (32%, 627 µmol)

^{1}H NMR (600 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 9.10 (d, ^4J = 1.7 Hz, 1H, H_j), 8.73 (d, ^3J = 4.8 Hz, 1H, H_a), 8.61 (d, ^3J = 8.2 Hz, 1H, H_g), 8.50 (d, ^3J = 7.9 Hz, 1H, H_d), 8.17 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, H_h), 7.87 (td, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H, H_c), 7.82 (dd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 2H, H_n), 7.60-7.51 (m, 3H, $H_{o,p}$), 7.37 (ddd, ^3J = 7.4 Hz, ^3J = 4.8 Hz, 1H, H_b).

^{13}C NMR (151 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 157.6 (C_f), 155.0 (C_e), 150.4 (C_j), 149.4 (C_a), 137.9 (C_h), 137.1 (C_c), 131.6 (C_p), 130.5 (C_n), 129.4 (C_o), 125.3 (t, $^2J_{CF}$ = 11 Hz, C_l), 124.5 (C_b), 124.2 (C_m), 121.7 (C_d), 121.2 (C_g), 120.9 (C_i), 120.1 (t, $^2J_{CF}$ = 11 Hz, C_k), 101.6 (t, $^1J_{CF}$ = 272 Hz, C_q).

^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ (ppm): -112.4 (s, C-F_2) ppm.

MS (EI, 70 eV) *m/z*: 306.09 $[M]^+$, 256.09 $[M\text{-}CF_2]^+$.

HRMS (EI, 70 eV) *m/z*: 306.09663 $[M]^+$ (calculated: 306.09685 for $C_{19}H_{12}N_2F_2$, difference: -0.73 ppm).

FT-IR: $\tilde{\nu}$ = 1782.6 (w), 1588.1 (m), 1571.7 (w), 1547.5 (w), 1497.7 (w), 1458.3 (m), 1437.1 (w), 1363.0 (m), 1266.1 (s), 1266.1 (s), 1156.9 (w), 1091.5 (w), 1019.5 (w), 993.31 (s), 831.3 (s), 800.8 (s), 768.8 (w), 754.5 (s), 737.0 (s), 689.1 (s), 636.3 (m), 618.7 (w), 574.7 (w), 538.8 (w) cm^{-1}.

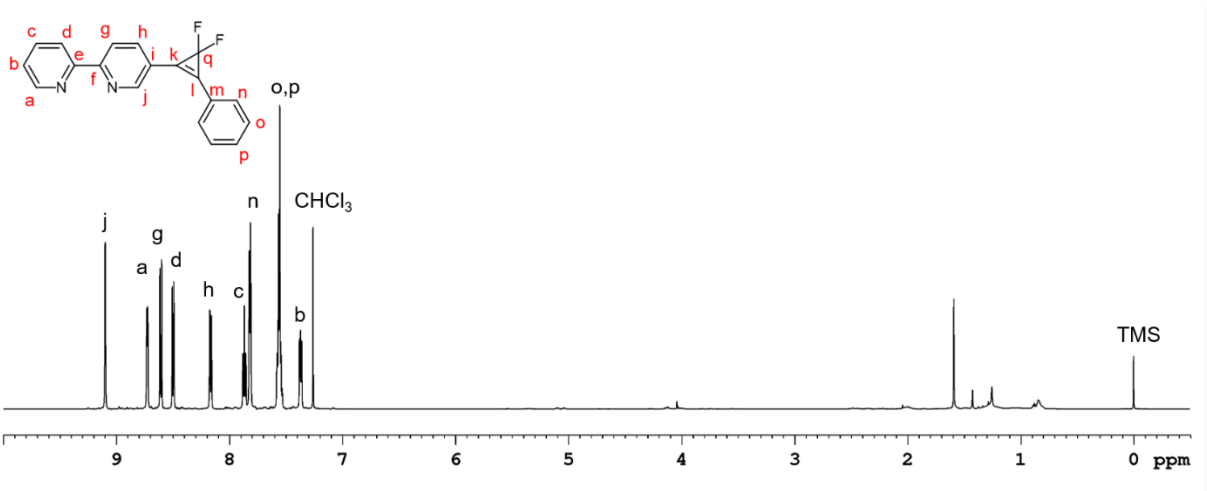


Figure S6. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K, TMS) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

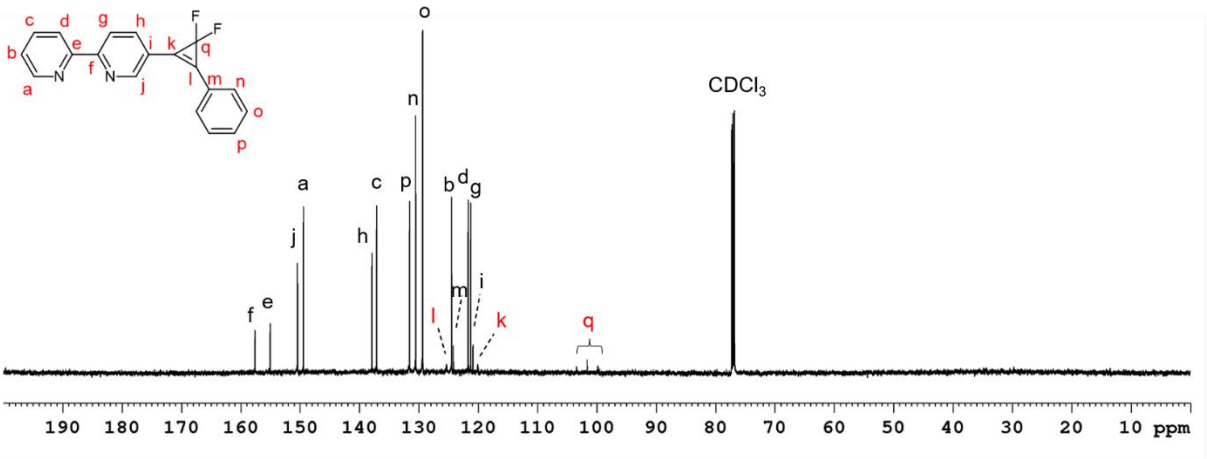


Figure S7. ^{13}C NMR spectrum (151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

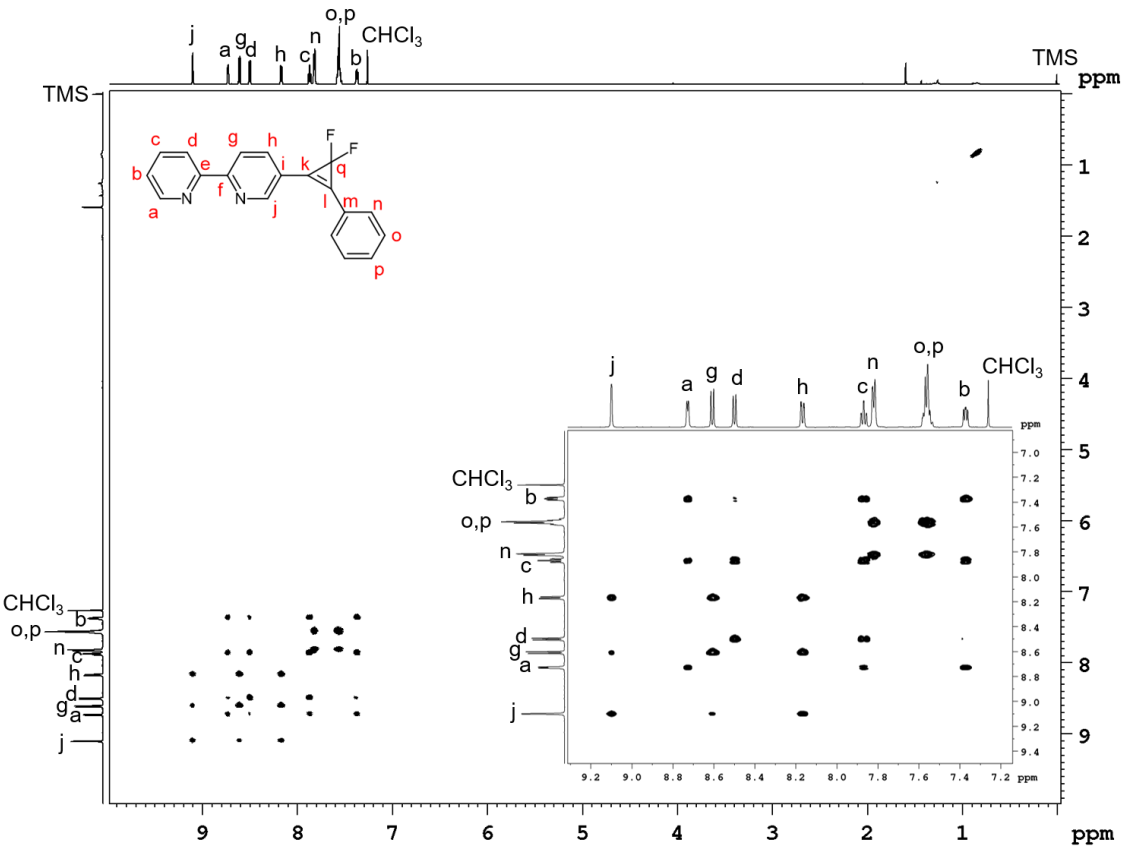


Figure S8. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, $CDCl_3$, 298 K, TMS) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

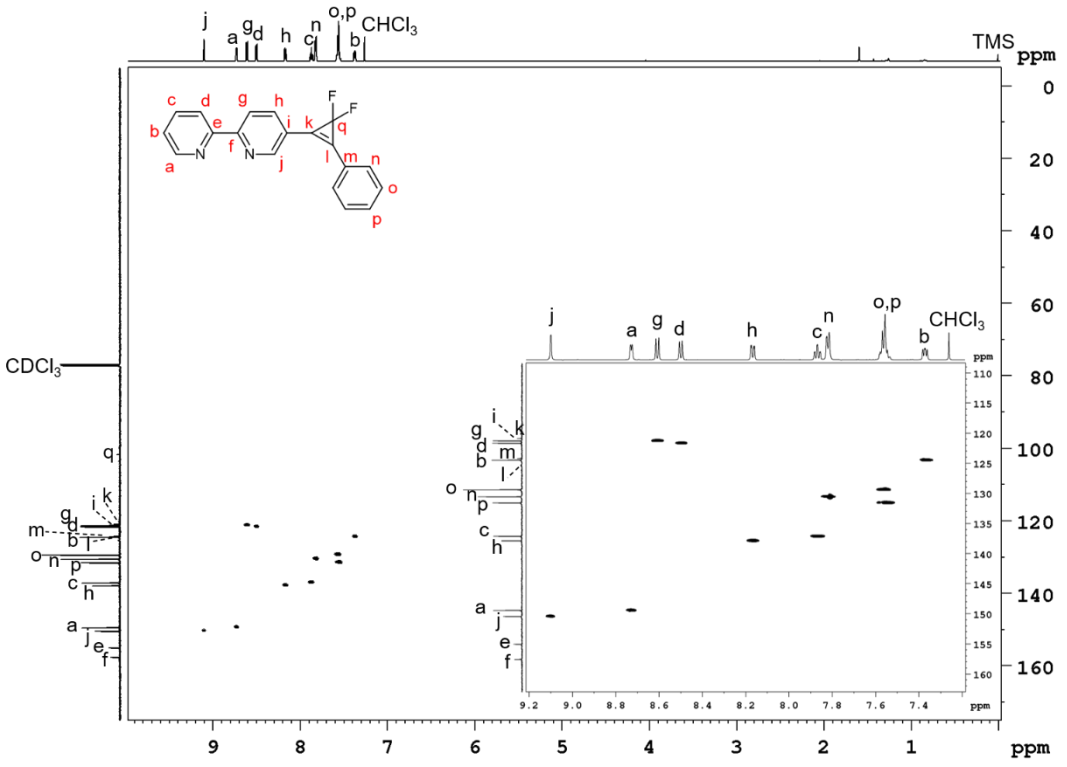


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K, TMS) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

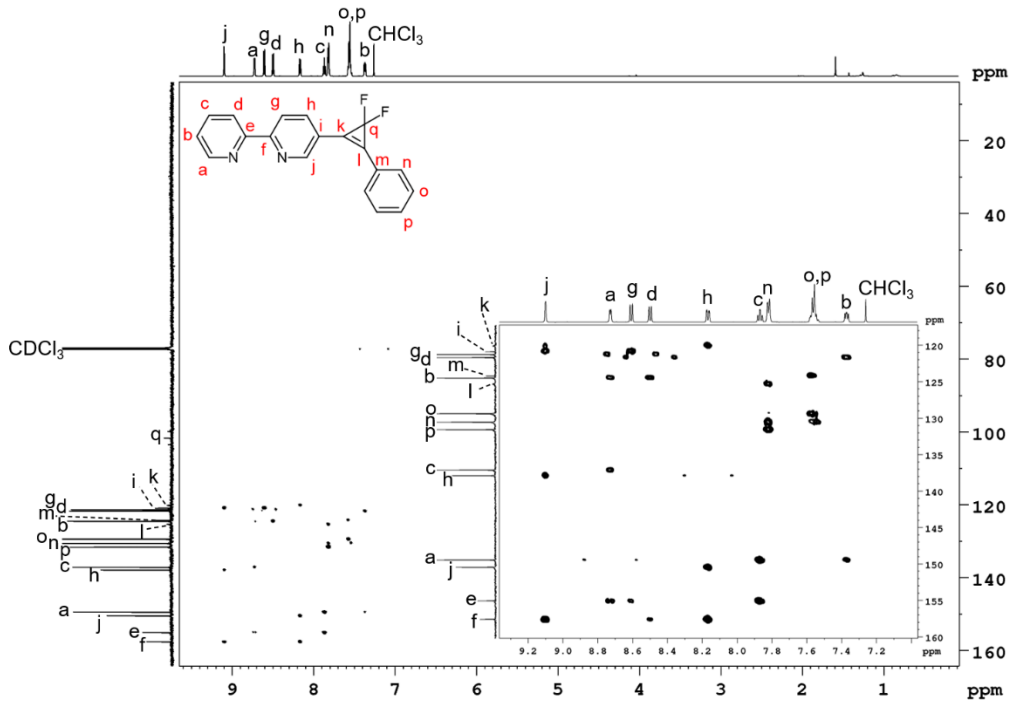


Figure S10. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K, TMS) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

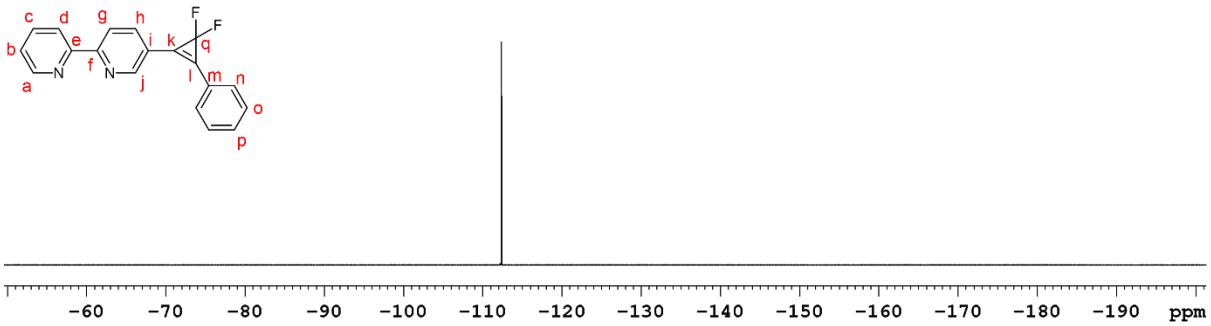


Figure S11. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

2.1.2.1 X-Ray Crystal Structure of **3a**

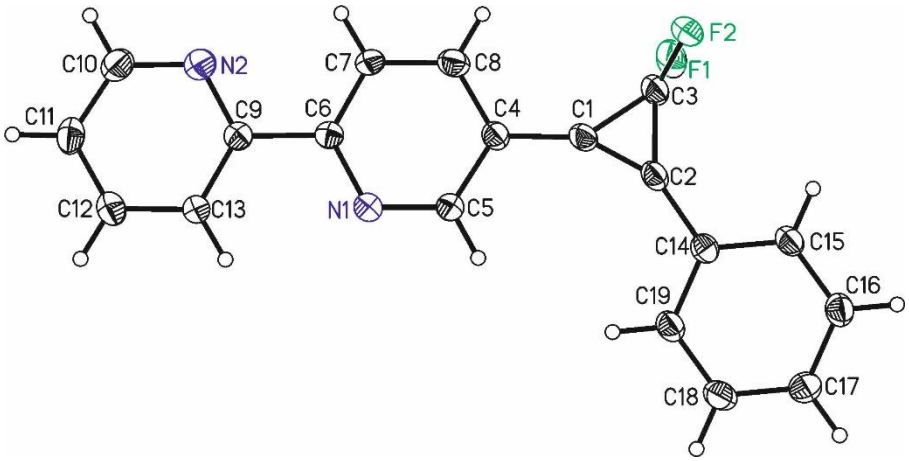
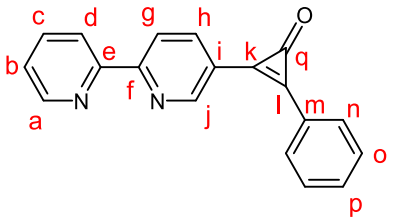


Figure S12. Crystal structure of **3a** with labelling and displacement ellipsoids drawn at the 50% probability level.

Table S1. Selected crystal data and details of the structure refinement for 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**).

Empirical formula	$C_{19}H_{12}F_2N_2$	F(000)	316.0
Formula weight	306.31	Crystal size/mm^3	0.08 × 0.05 × 0.02
Temperature/K	100.01(10)	Radiation	Cu Kα (λ = 1.54184)
Crystal system	triclinic	2Θ range /°	6.668 to 156.094
Space group	P-1	Reflections collected	18340
a/Å	6.91900(10)	Independent refl.	3042
b/Å	8.13080(10)	Refl. with [I>=2σ (I)]	2870
c/Å	13.4122(2)	R_{int}	0.0171
α/°	82.2840(10)	Parameters	208
β/°	84.2680(10)	GoF on F^2	1.097
γ/°	77.2190(10)	R_1 for [I>=2σ (I)]	0.0388
Volume/Å^3	727.248(18)	R_1 for all data	0.0404
Z	2	wR_2 for [I>=2σ (I)]	0.1142
ρ_{calc}g/cm^3	1.399	wR_2 for all data	0.1156
μ/mm^{-1}	0.841	Largest diff. peak/hole / e Å^{-3}	0.26/-0.27

2.1.3 5-(2-Cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**)



5-(3,3-Difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**) (100 mg, 327 μmol) was dissolved in 9 mL 6 M hydrochloric acid. The clear brown solution was left standing at room

temperature in the dark for 15 min. After this, the solution was added dropwise to 50 mL sat. aqueous Na_2CO_3 solution which was cooled to 0 °C. The precipitate was filtered, washed with water and dried under air at room temperature giving the product as a colourless powdered solid.

In the case of unreacted starting material, it is possible to repeat this procedure in order to ensure complete hydrolysis.

Yield: 85 mg (91%, 299 µmol)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 9.29 (dd, ^4J = 2.1 Hz, ^5J = 0.8 Hz, 1H, H_j), 8.74 (ddd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, ^5J = 1.0 Hz, 1H, H_a), 8.68 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1H, H_g), 8.53 (dt, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, H_d), 8.37 (dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1H, H_h), 8.04-7.99 (m, 2H, H_n), 7.89 (td, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, H_c), 7.68-7.59 (m, 3H, $H_{o,p}$), 7.40 (ddd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, ^4J = 1.0 Hz, 1H, H_b).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 158.9 (C_f), 155.2 (C_q), 154.7 (C_e), 151.3 (C_j), 150.0 (C_l), 149.5 (C_a), 145.5 (C_k), 139.1 (C_h), 137.2 (C_c), 133.2 (C_p), 131.6 (C_n), 129.5 (C_o), 124.8 (C_b), 123.8 (C_m), 122.0 (C_d), 121.4 (C_g), 120.0 (C_i).

HRMS (ESI) *m/z*: 285.10201 $[M+H]^+$ (calculated: 285.10224 for $C_{19}H_{13}N_2O$, difference: -0.81 ppm), 257.10710 $[M-CO+H]^+$.

FT-IR: ṽ = 3051.9 (w), 1850.47 (s), 1780.9 (m), 1623.37 (s), 1595.7 (m), 1586.8 (s), 1546.9 (m), 1456.7 (m), 1444.4 (m), 1435.0 (m), 1372.2 (m), 1341.0 (s), 1310.7 (w), 1246.2 (w), 1153.4 (w), 1138.8 (w), 1092.8 (w), 1073.8 (w), 1015.2 (m), 992.5 (w), 958.2 (m), 942.0 (w), 801.8 (m), 796.5 (s), 749.7 (s), 728.0 (m), 683.5 (s), 639.6 (m), 621.7 (m), 551.1 (w), 541.1 (m) cm^{-1}.

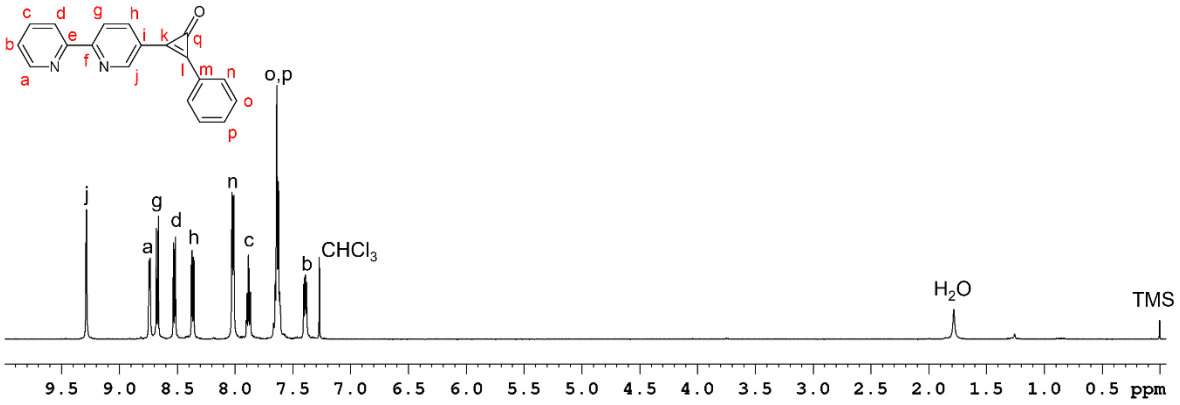


Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**).

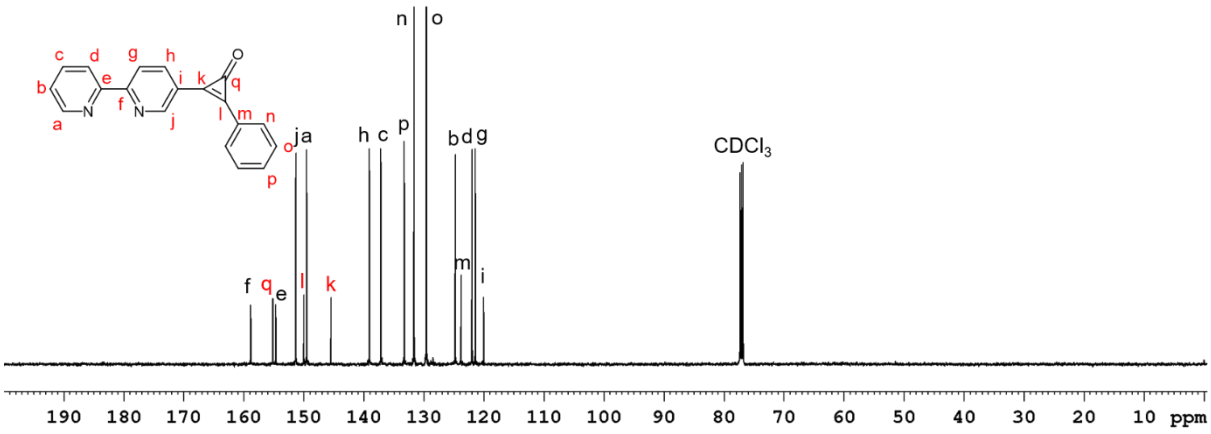


Figure S14. ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**).

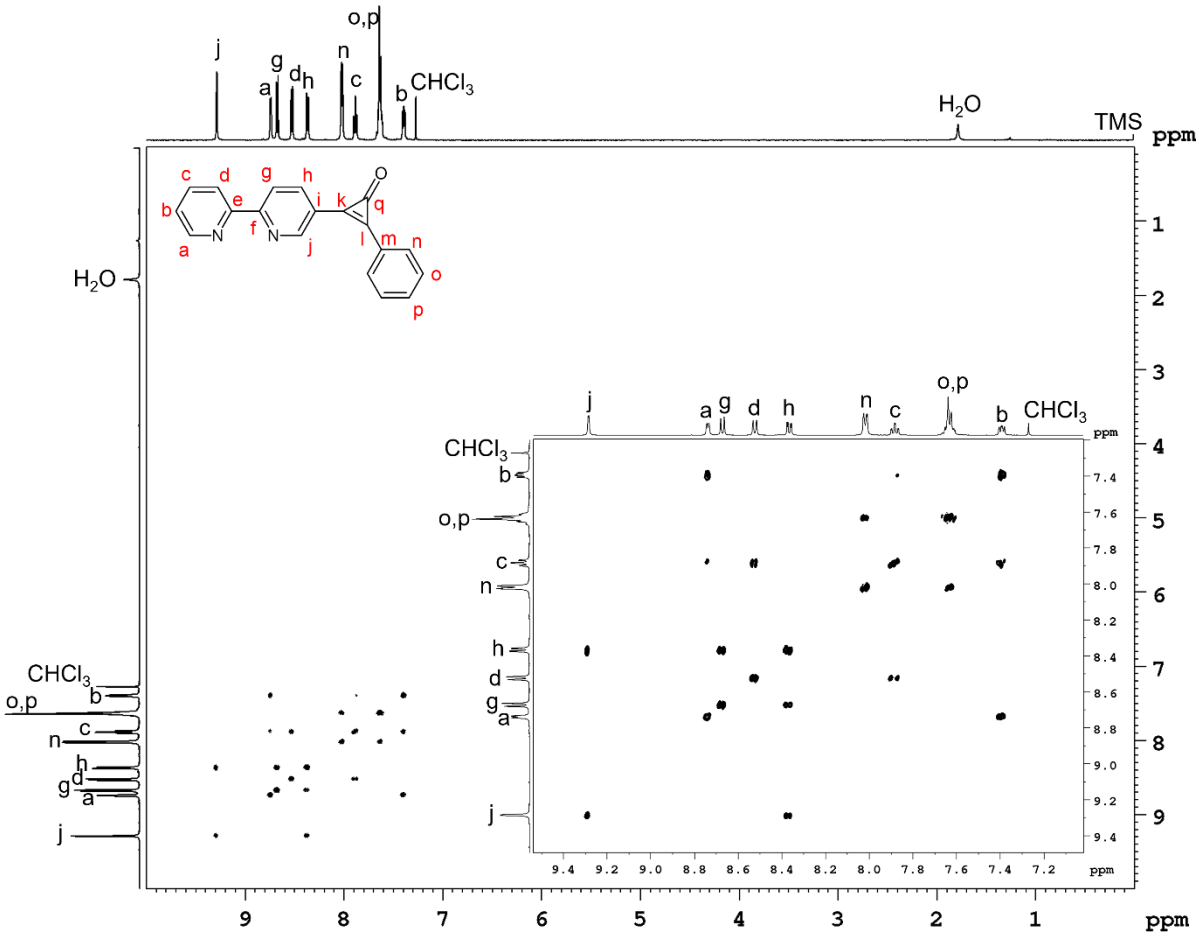


Figure S15. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**).

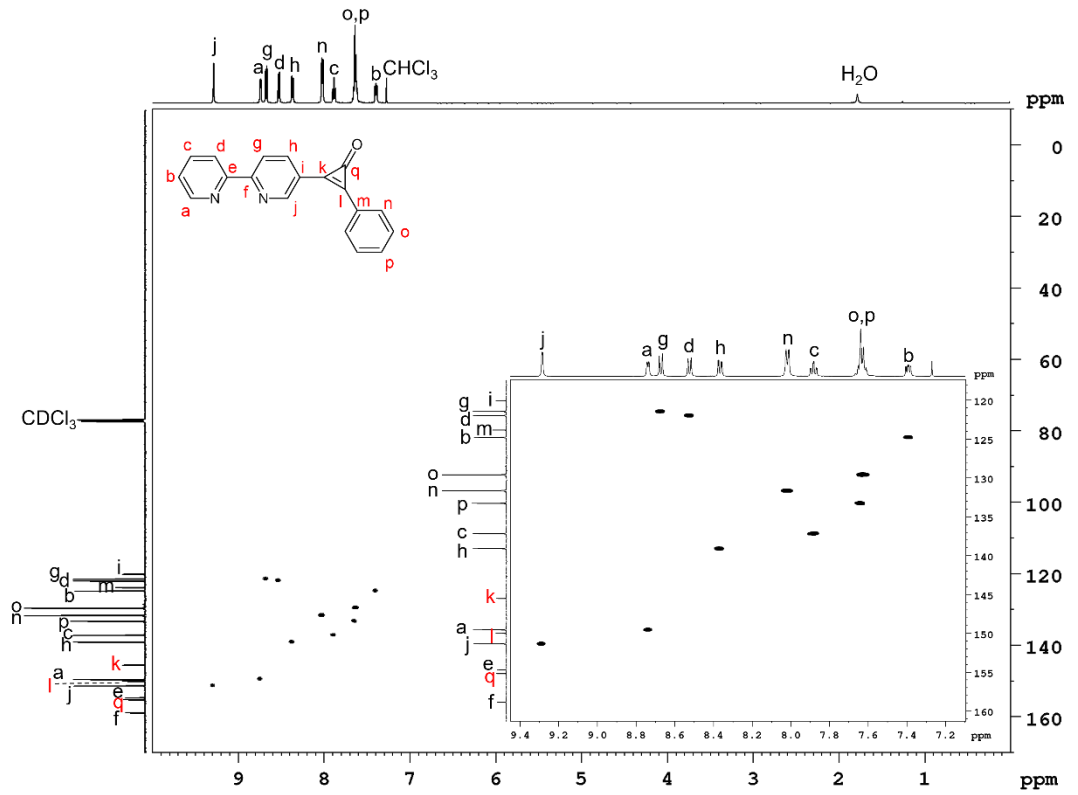


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**).

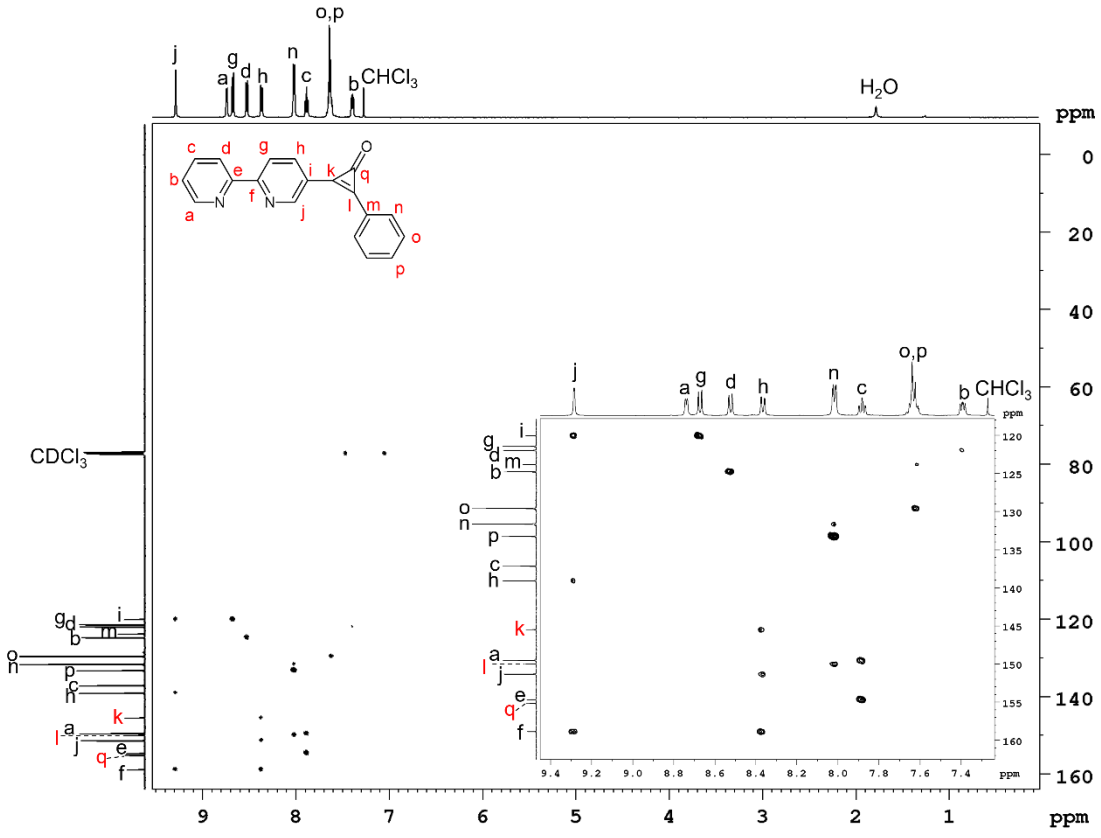
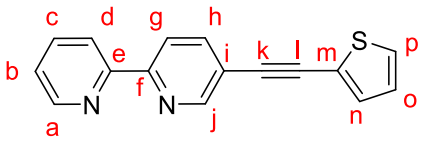


Figure S17. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**).

2.2 Thiophene-Substituted Bipyridine Ligands

2.2.1 5-(Thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**)



5-Bromo-2,2'-bipyridine (**4**) (1.0 g, 4.25 mmol) and $Pd(PPh_3)_4$ (245 mg, 5 mol%) were added under a nitrogen atmosphere to a three necked flask. 2-Ethynylthiophene (444 µL, 4.68 mmol) and tetrabutylammonium fluoride (1 M in tetrahydrofuran, 25.5 mL, 25.5 mmol) were added and the reaction mixture was heated at 70 °C for 2 h. After cooling to room temperature, 50 mL water and 30 mL dichloromethane were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was dry loaded onto silica gel and purified by flash column chromatography (silica gel, 2%-15% ethyl acetate/cyclohexane) and the product was obtained as a yellow crystalline solid.

Yield: 658 mg (58%, 2.51 mmol)

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ (ppm): 8.80 (dd, ^4J = 2.1 Hz, ^5J = 0.8 Hz, 1H, H_j), 8.69 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 1H, H_a), 8.42 (dt, ^3J = 7.9 Hz, ^4J = 1.1 Hz, 1H, H_d), 8.41 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1H, H_g), 7.92 (dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1H, H_h), 7.83 (td, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, H_c), 7.36-7.34 (m, 2H, $H_{n,p}$), 7.32 (ddd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, J = 1.1 Hz, 1H, H_b) 7.06-7.03 (m, 1 H, H_o).

^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ (ppm): 155.5 (C_e), 154.9 (C_f), 151.4 (C_j), 149.3 (C_a), 139.1 (C_h), 137.0 (C_c), 132.6 ($C_{n/p}$), 128.1 ($C_{n/p}$), 127.3 (C_o), 124.0 (C_b), 122.6 (C_m), 121.4 (C_d), 120.4 (C_g), 120.0 (C_i) 90.1 (C_k), 86.8 (C_l).

HRMS (EI, 70 eV) *m/z*: 262.05615 $[M]^+$ (calculated: 262.05647 for $C_{16}H_{10}N_2S_1$, difference: -1.22 ppm).

FT-IR: ṽ = 3052.4 (w), 2203.1 (m), 1954.7 (w), 1798.68 (w), 1655.2 (w), 1587.0 (m), 1570.1 (w), 1541.4 (w), 1518.9 (w), 1455.8 (s), 1431.6 (m), 1424.1 (m), 1369.7 (m), 1357.7 (w), 1300.9 (w), 1242.0 (w), 1215.2 (m), 1141.3 (w), 1117.2 (w), 1090.3 (w), 1075.7 (w), 1059.2 (w), 1040.7 (w), 1018.9 (m), 993.1 (w), 901.1 (w), 850.6 (m), 830.5 (m), 794.7 (s), 744.4 (s), 722.1 (m), 697.4 (s), 607.0 (m), 646.2 (m) cm^{-1}.

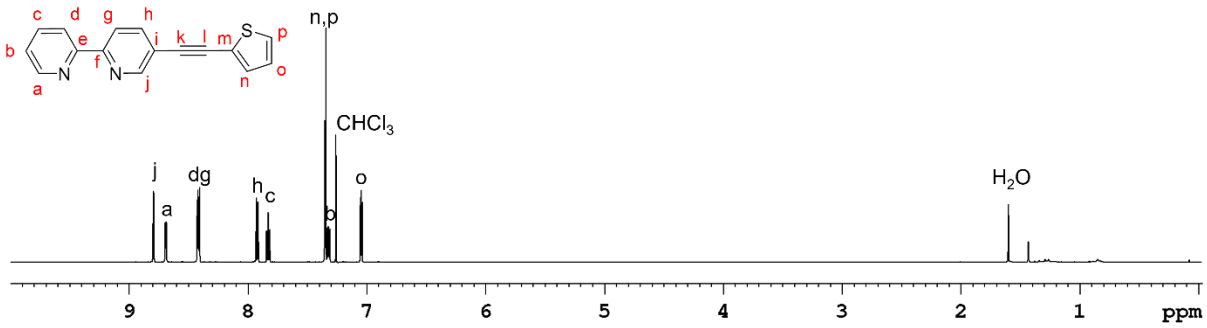


Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**).

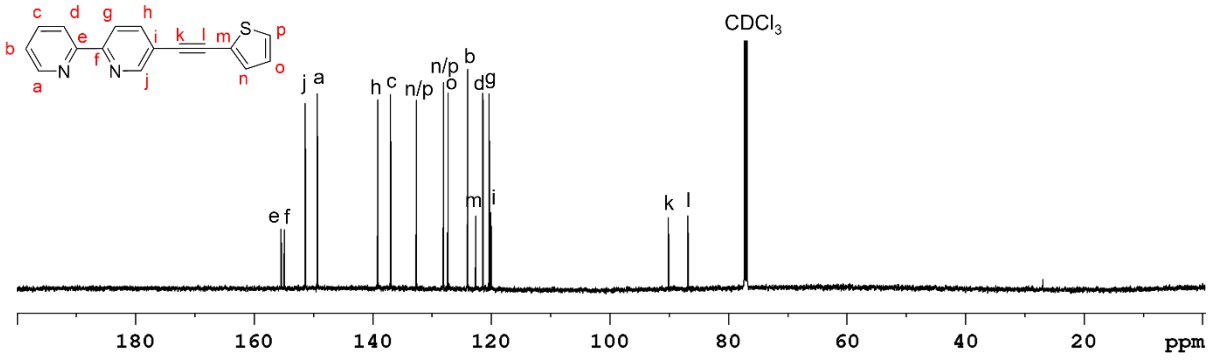


Figure S19. ^{13}C NMR spectrum (151 MHz, $CDCl_3$, 298 K) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**).

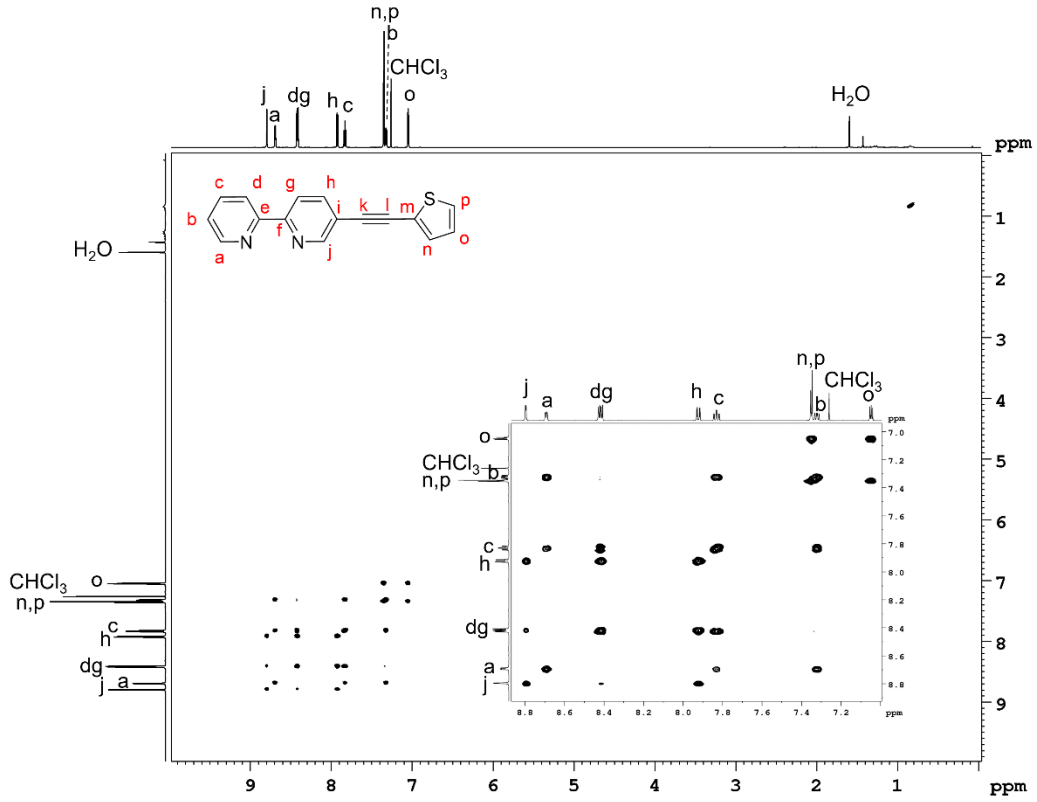


Figure S20. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**).

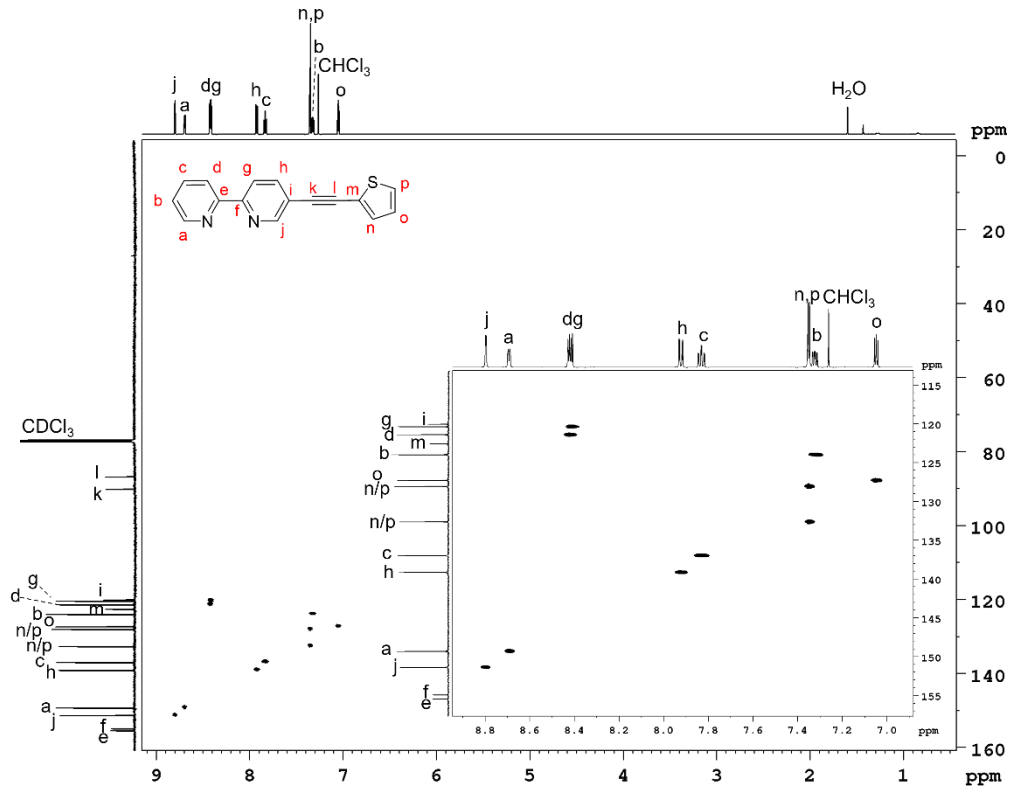


Figure S21. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**).

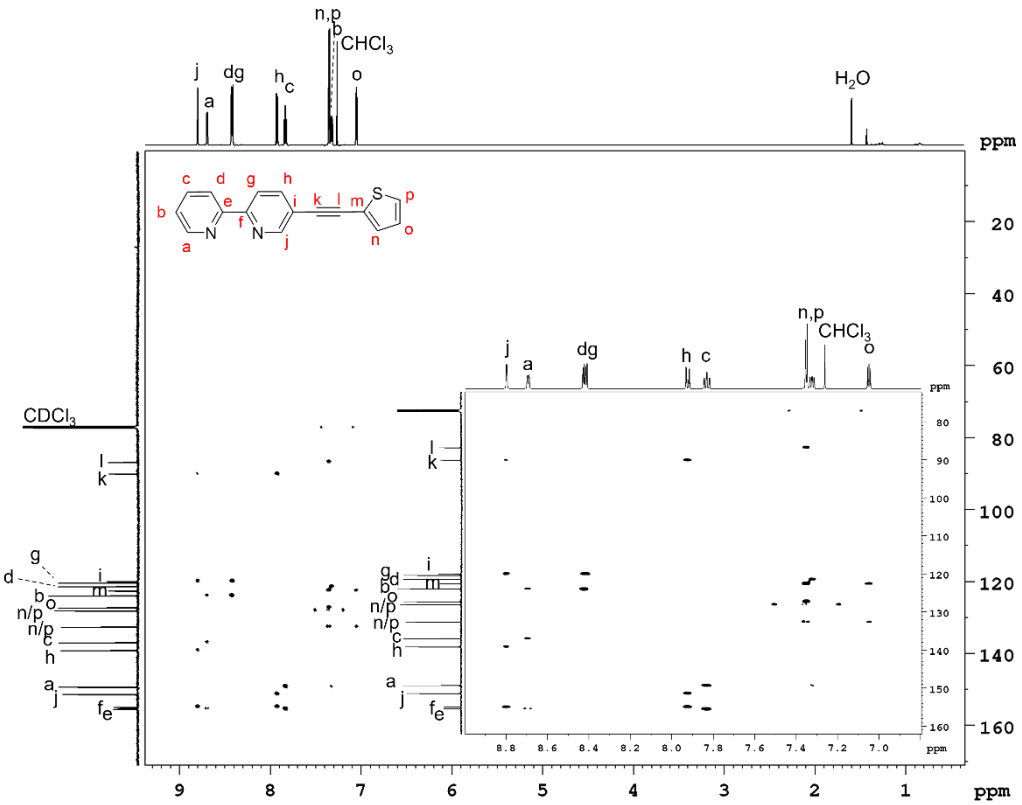
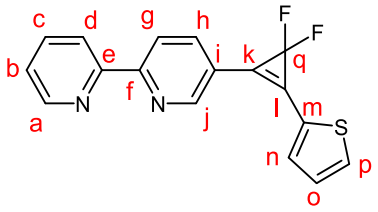


Figure S22. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**).

2.2.2 5-(3,3-Difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**)



5-(Thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (500 mg, 1.61 mmol) and TBABr (18.4 mg, 57.2 µmol) were added under a nitrogen atmosphere to a pressure tube. 10 mL Dry toluene and (bromodifluoromethyl)trimethylsilane (444 µL, 2.86 mmol) were added. The pressure tube was immediately closed and the reaction mixture was heated at 120 °C for 2 hours. After cooling to room temperature, the reaction mixture was added to 50 mL sat. aqueous Na_2CO_3 solution. The aqueous layer was extracted with dichloromethane (3 x 35 mL), the combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo.* The residue was dry loaded onto silica gel and purified by flash column chromatography (silica gel, 5%-20% ethyl acetate/cyclohexane) and the product was obtained as a colourless crystalline solid.

Yield: 297 mg (50%, 951 µmol)

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ (ppm): 9.06 (dd, ^4J = 2.2 Hz, ^5J = 0.8 Hz, 1H, H_j), 8.72 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 1H, H_a), 8.60 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1H, H_g), 8.49 (dt, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 1H, H_d), 8.13 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1H, H_h), 7.86 (td, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, H_c), 7.73 (dd, ^3J = 5.1 Hz, ^4J = 0.9 Hz, 1H, H_n), 7.61 (dd, ^3J = 3.6 Hz, ^4J = 0.9 Hz, 1H, H_p), 7.37 (ddd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, ^4J = 1.1 Hz, 1H, H_b), 7.25 (dd, ^3J = 5.1 Hz, ^3J = 3.6 Hz, 1H, H_o).

^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ (ppm): 157.3 (C_f), 155.0 (C_e), 150.1 (C_j), 149.4 (C_a), 137.5 (C_h), 137.2 (C_c), 132.8 (C_p), 132.2 (C_n), 128.7 (C_o), 125.7 (C_m), 124.4 (C_b), 121.7 (C_d), 121.3 (C_g), 120.7 (C_i), 118.3 (t, $^2J_{CF}$ = 12 Hz, C_l), 116.0 (t, $^2J_{CF}$ = 12 Hz, C_k), 100.4 (t, $^1J_{CF}$ = 274 Hz, C_q).

^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ (ppm): -111.0 (s, C-F_2) ppm.

MS (EI, 70 eV) *m/z*: 312.05 $[M]^+$, 262.06 $[M\text{-}CF_2]^+$.

HRMS (EI, 70 eV) *m/z*: 312.05317 $[M]^+$ (calculated: 312.05328 for $C_{17}H_{10}N_2S_1F_2$, difference: -0.34 ppm).

FT-IR: ṽ = 3075.4 (w), 3057.5 (w), 1777.9 (m), 1591.3 (m), 1548.9 (w), 1515.0 (w), 1461.7 (m), 1434.9 (w), 1417.9 (m), 1370.6 (m), 1334.6 (w), 1284.0 (s), 1224.8 (m), 1149.2 (w), 1130.6 (w), 1092.1 (w), 1066.9 (w), 1040.5 (w), 994.3 (s), 920.6 (w), 860.1 (w), 827.5 (s), 795.9 (m), 783.1 (m), 762.9 (w), 743.8 (s), 725.2 (s), 709.5 (m), 658.8 (w), 637.6 (m), 619.1 (m), 577.8 (w), 551.9 (m) cm^{-1}.

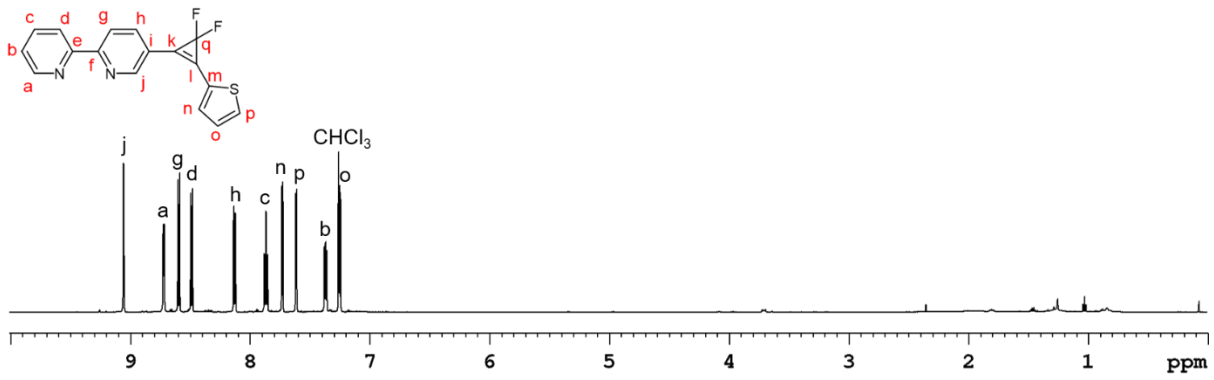


Figure S23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**).

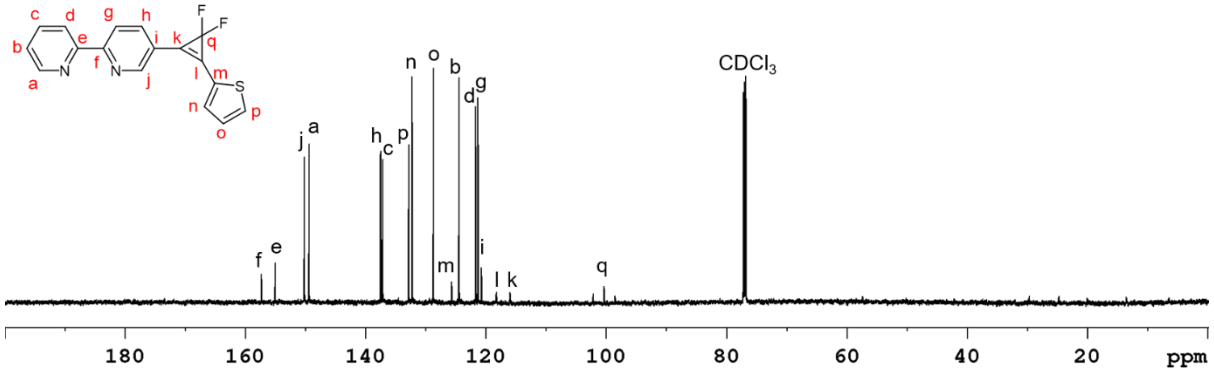


Figure S24. ^{13}C NMR spectrum (151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**).

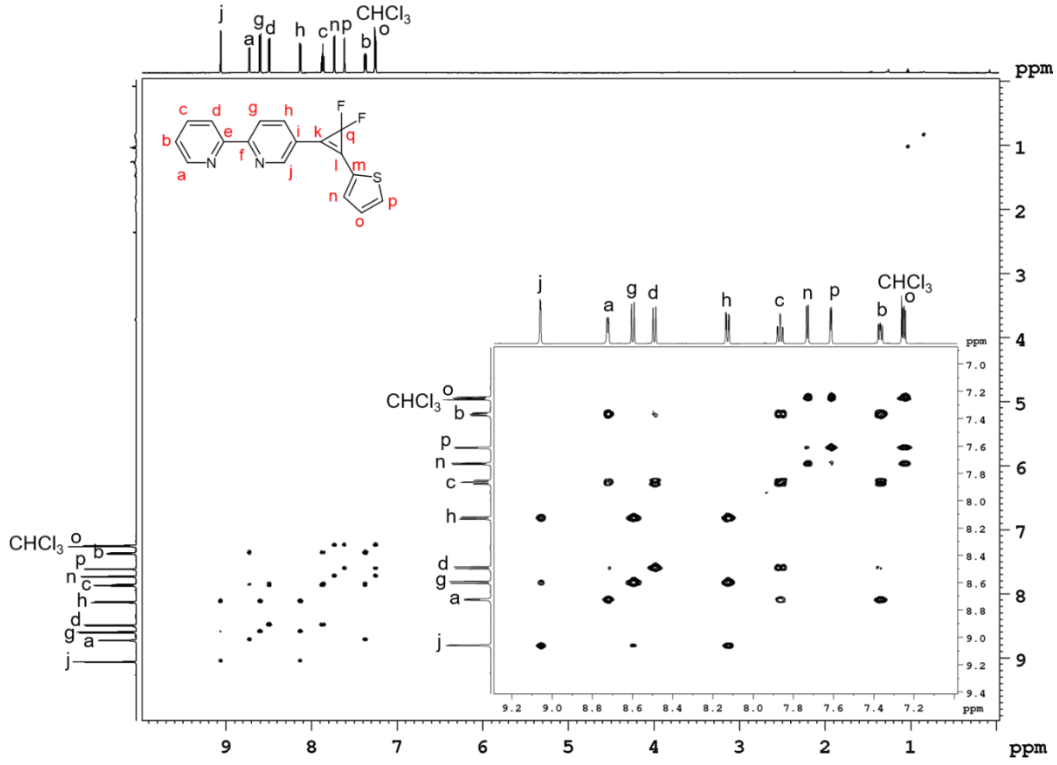


Figure S25. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**).

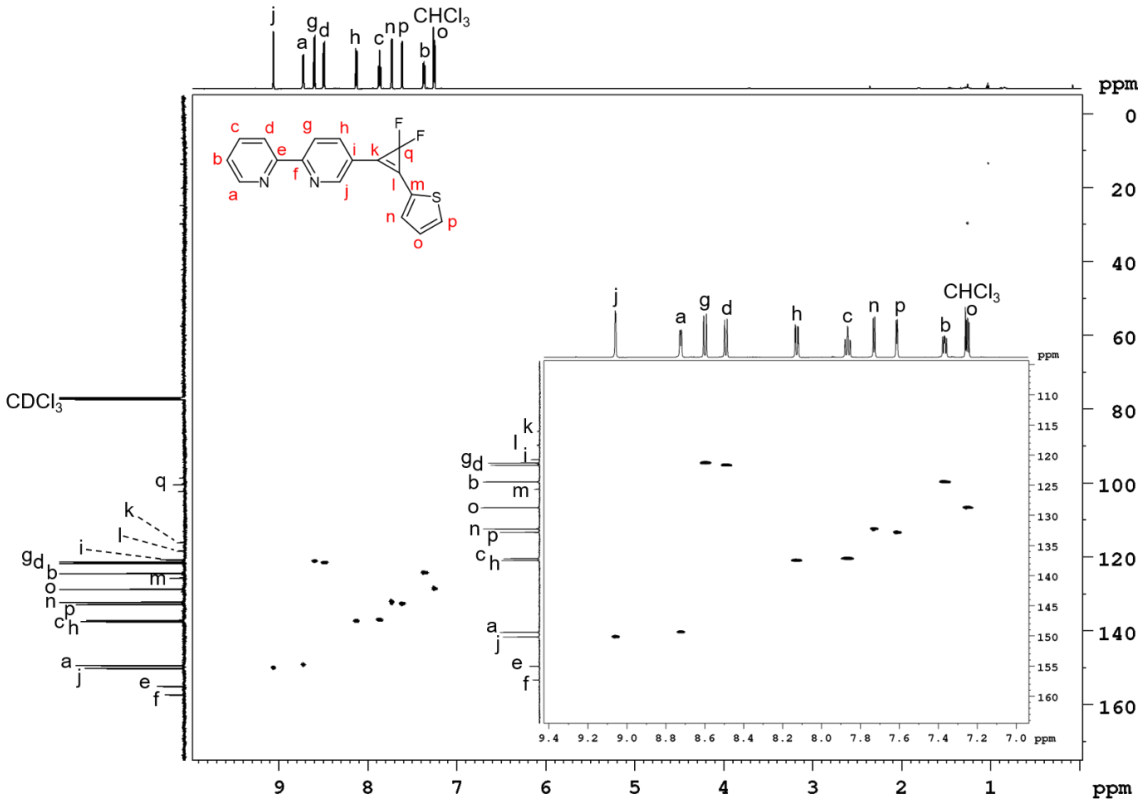


Figure S26. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**).

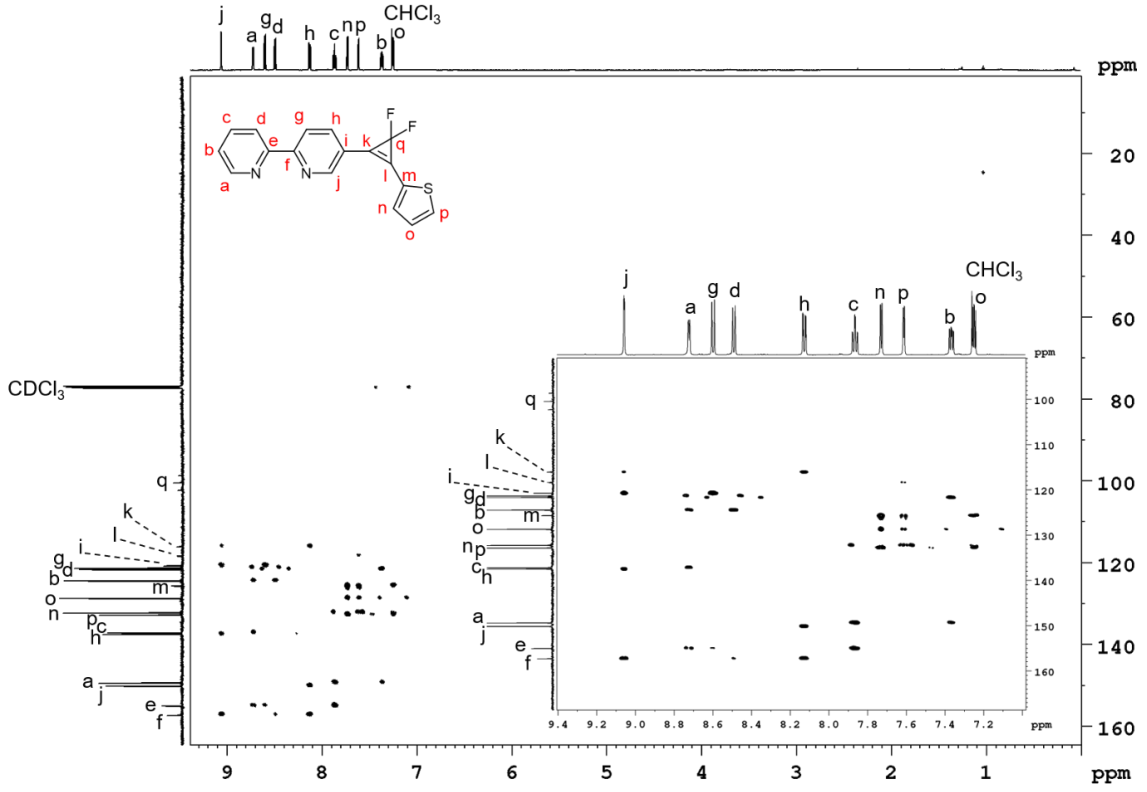


Figure S27. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**).

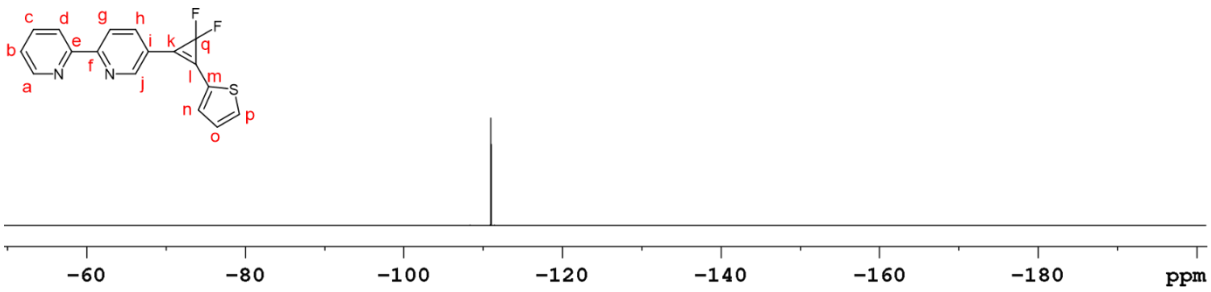
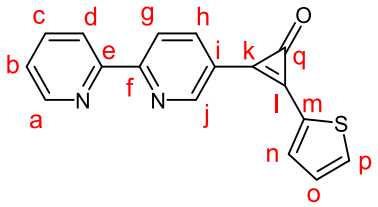


Figure S28. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**).

2.2.3 5-(2-Cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**)



5-(3,3-Difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**) (113 mg, 362 µmol) was suspended in 5 mL 6 M hydrochloric acid and addition of 0.5 mL conc. hydrochloric acid was necessary to dissolve **3b**. The clear yellow solution was left standing at room temperature in the dark for 15 min. After this, the solution was added dropwise to 50 mL sat. aqueous Na_2CO_3 solution which was cooled to 0 °C. The precipitate was filtered, washed with water and dried under air at room temperature giving the product as a brownish powdered solid.

In the case of unreacted starting material, it is possible to repeat this procedure in order to ensure complete hydrolysis.

Yield: 82 mg (78%, 282 µmol)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 9.25 (d, ^4J = 1.7 Hz, 1H, H_j), 8.72 (d, ^3J = 4.5 Hz, 1H, H_a), 8.65 (d, ^3J = 8.2 Hz, 1H, H_g), 8.51 (d, ^3J = 7.9 Hz, 1H, H_d), 8.34 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, H_h), 7.93 (d, ^3J = 3.6 Hz, 1H, H_n), 7.89-7.84 (m, 2H, $H_{c,p}$), 7.38 (dd, ^3J = 6.7 Hz, ^3J = 4.5 Hz, 1H, H_b), 7.32 (dd, ^3J = 4.7 Hz, ^3J = 3.6 Hz, 1H, H_o).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ (ppm): 158.6 (C_f), 154.7 (C_e), 151.9 (C_q), 151.2 (C_j), 149.5 (C_a), 14189 (C_l), 138.7 (C_h), 137.9 (C_k), 137.1 (C_c), 137.1 (C_n), 134.5 (C_p), 129.33 (C_o), 125.3 (C_m), 124.7 (C_b), 121.9 (C_d), 121.4 (C_g), 119.8 (C_i).

HRMS (ESI) *m/z*: 291.05843 $[M+H]^+$ (calculated: 291.05866 for $C_{17}H_{11}N_2OS$, difference: -0.78 ppm), 263.06360 $[M-CO+H]^+$.

FT-IR: $\tilde{\nu}$ = 3057.6 (w), 1839.6 (s), 1621.4 (s), 1586.9 (m), 1543.4 (m), 1483.4 (w), 1459.1 (m), 1433.6 (w), 1409.0 (m), 1380.3 (w), 1360.9 (m), 1320.5 (m), 1230.0 (w), 1134.6 (w), 1087.8 (w), 1063.3 (w), 1030.6 (w), 1010.0 (w), 991.6 (w), 866.6 (m), 853.3 (w), 797.8 (m), 748.5 (m), 731.2 (s), 701.2 (m), 655.9 (w), 635.4 (m), 616.3 (w), 547.9 (w) cm^{-1}.

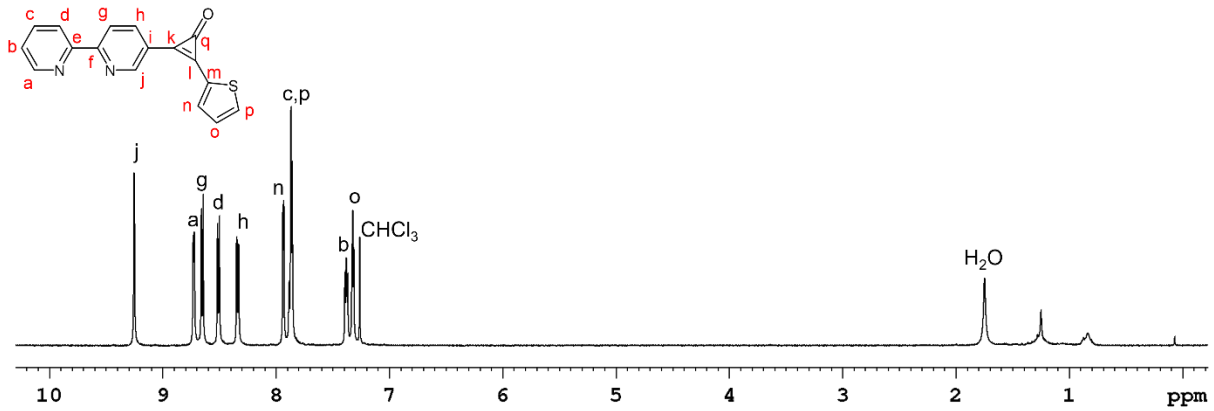


Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**).

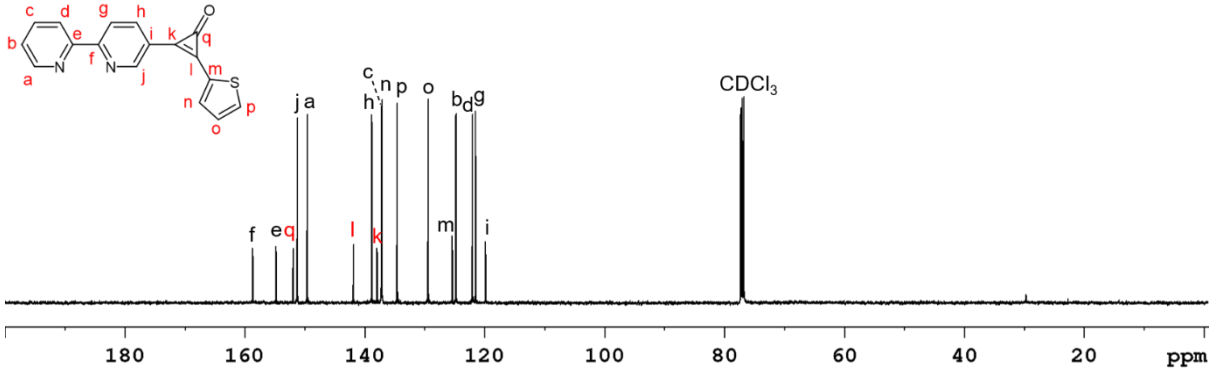


Figure S30. ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**).

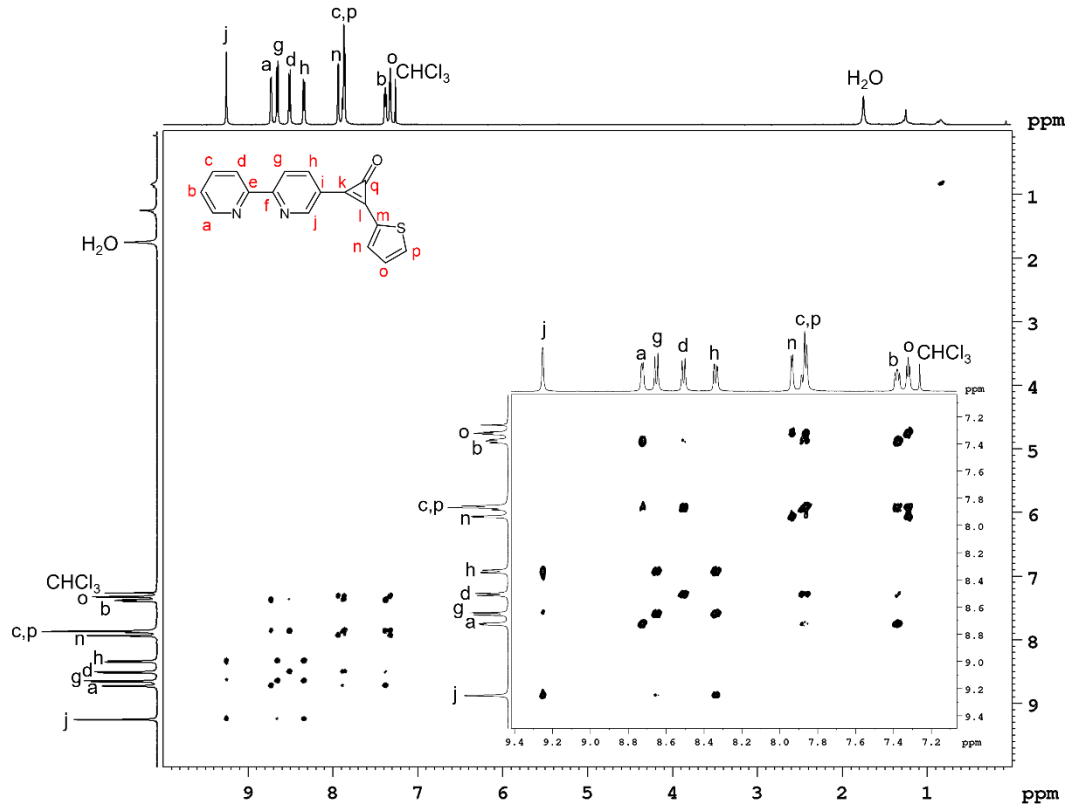


Figure S31. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**).

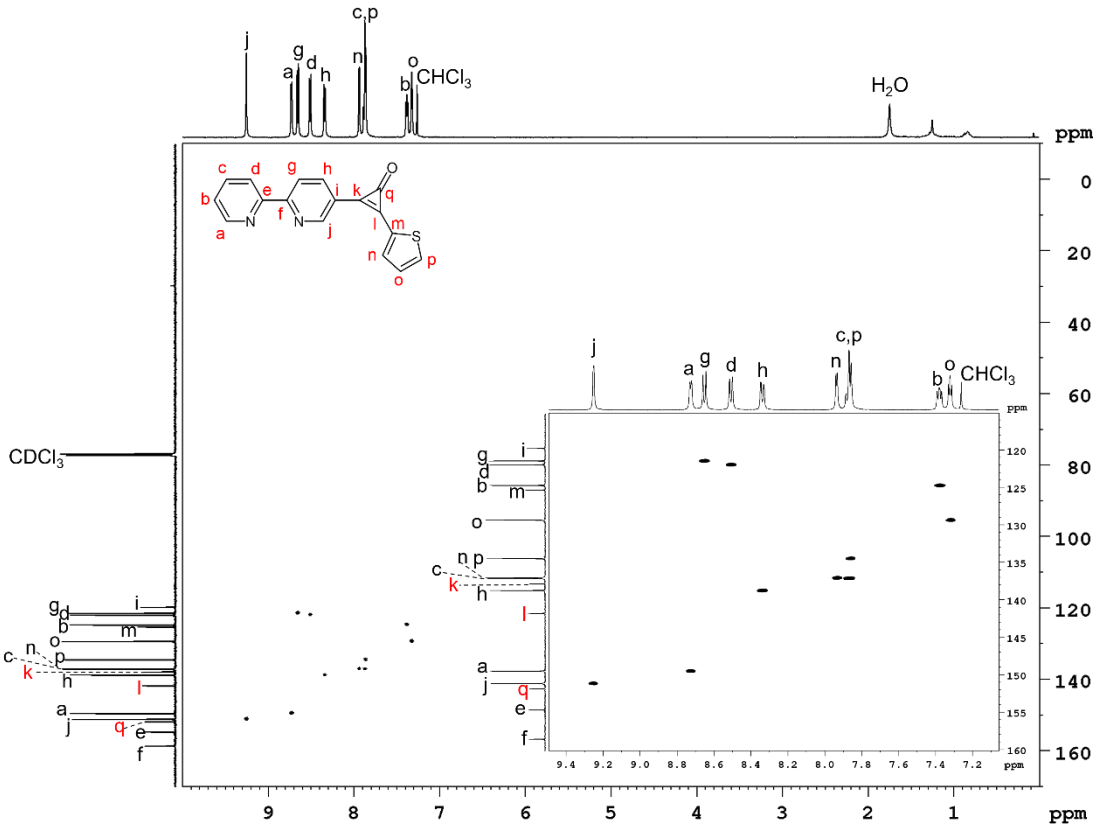


Figure S32. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**).

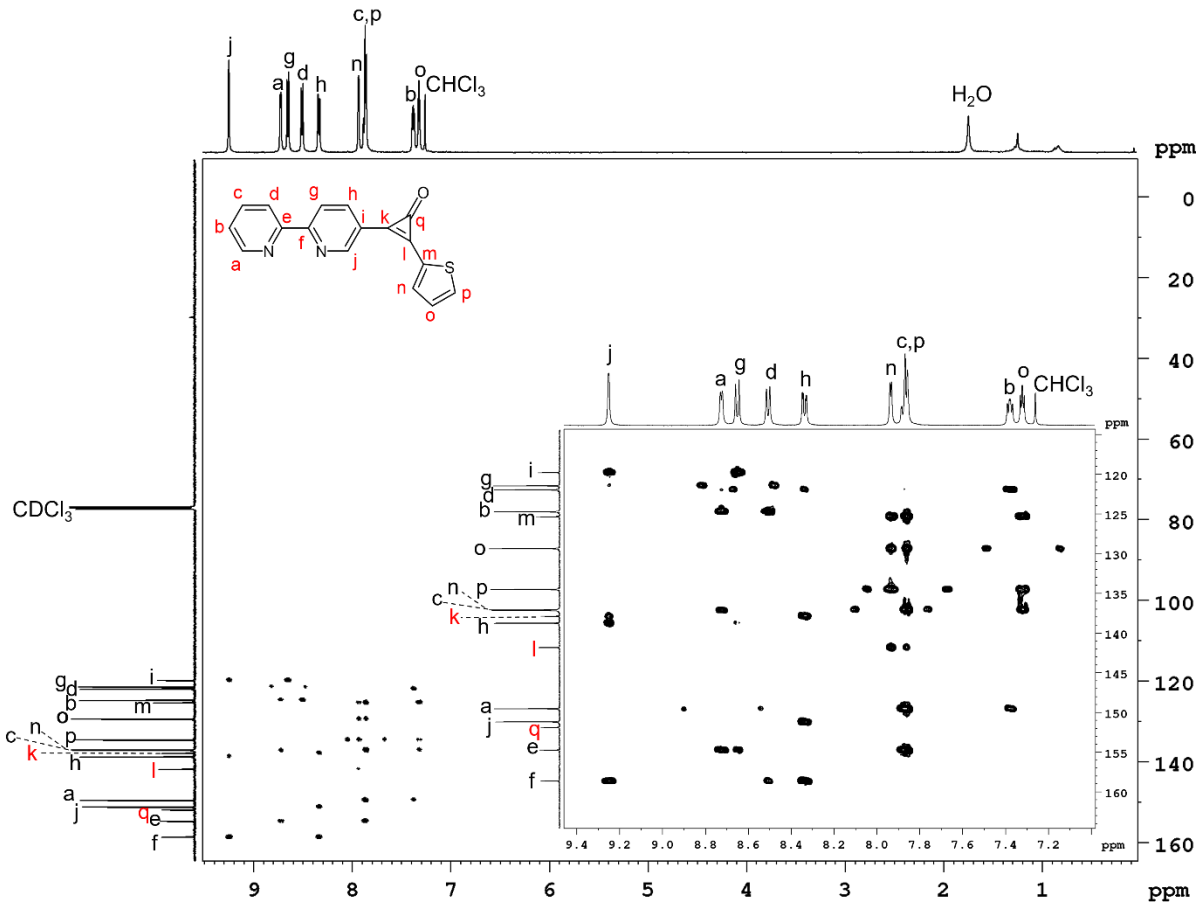
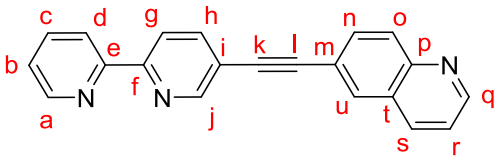


Figure S33. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**).

2.3 6-Quinoline-Substituted Bipyridine Ligands

2.3.1 5-(Quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**)



5-Bromo-2,2'-bipyridine (**4**) (1.20 g, 5.10 mmol) and $Pd(PPh_3)_4$ (294 mg, 5 mol%) were added under a nitrogen atmosphere to a three necked flask. 6-((Trimethylsilyl)ethynyl)quinoline (1.38 g, 6.12 mmol) and tetrabutylammonium fluoride (1 M in tetrahydrofuran, 30.6 mL, 30.6 mmol) were added and the reaction mixture was heated at 70 °C for 20 h. After cooling to room temperature, 50 mL water and 25 mL dichloromethane were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was dry loaded onto silica gel and purified by flash column chromatography (silica gel, 5%-80% ethyl acetate/cyclohexane). The solvent of product-containing fractions was removed *in vacuo* and the residue was dissolved in 10 mL conc. hydrochloric acid and washed with dichloromethane (3x10 mL). The layers were separated and the aqueous layer was

basified with conc. sodium hydroxide solution. The precipitated colourless product was collected and dried *in vacuo*.

***R*f** (1:4, ethyl acetate/cyclohexane) = 0.10

Yield: 1.12 g (66%, 3.64 mmol)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 8.94 (dd, ^{3}J = 4.2 Hz, ^{4}J = 1.5 Hz, 1H, H_q), 8.87 (dd, ^{4}J = 2.1 Hz, ^{5}J = 0.8 Hz, 1H, H_j), 8.71 (ddd, ^{3}J = 4.8 Hz, ^{4}J = 1.8 Hz, ^{5}J = 1.1 Hz, 1H, H_a), 8.45 (dd, ^{3}J = 8.2 Hz, ^{5}J = 0.8 Hz, 1H, H_g), 8.44 (dt, ^{3}J = 8.0 Hz, ^{5}J = 1.1 Hz, 1H, H_d), 8.17 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.5 Hz, 1H, H_s), 8.11 (d, ^{3}J = 8.7 Hz, 1H, H_o), 8.08 (d, ^{4}J = 1.7 Hz, 1H, H_u), 7.99 (dd, ^{3}J = 8.3 Hz, ^{4}J = 2.1 Hz, 1H, H_h), 7.87-7.83 (m, 2H, $H_{c,n}$), 7.45 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.2 Hz, 1H, H_r), 7.34 (ddd, ^{3}J = 7.5 Hz, ^{3}J = 4.8 Hz, ^{4}J = 1.1 Hz, 1H, H_b).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 155.4 (C_e), 155.1 (C_f), 151.7 (C_j), 151.2 (C_q), 149.3 (C_a), 147.9 (C_p), 139.5 (C_h), 137.0 (C_c), 135.9 (C_s), 132.0 (C_n), 131.5 (C_u), 129.8 (C_o), 128.0 (C_t), 124.0 (C_b), 121.9 (C_r), 121.4 (C_d), 121.1 (C_m), 120.4 (C_g), 120.0 (C_i), 93.1 (C_l), 87.6 (C_k).

HRMS (EI, 70 eV) *m/z*: 307.11059 $[M]^+$ (calculated: 307.11095 for $C_{21}H_{13}N_3$, difference: -1.18 ppm).

FT-IR: ṽ = 3044.3 (w), 1586.4 (m), 1569.8 (m), 1542.3 (m), 1495.2 (m), 1453.9 (s), 1430.9 (m), 1368.9 (w), 1337.5 (w), 1288.4 (w), 1241.5 (w), 1130.1 (w), 1088.8 (w), 1063.7 (w), 1040.0 (w), 1021.5 (m), 993.2 (w), 956.3 (w), 925.0 (w), 906.1 (w), 882.6 (m), 849.1 (m), 831.1 (s), 792.1 (s), 768.6 (w), 744.4 (s), 837.3 (s), 645.9 (m), 617.32 (s), 561.7 (w), 543.5 (w) cm^{-1}.

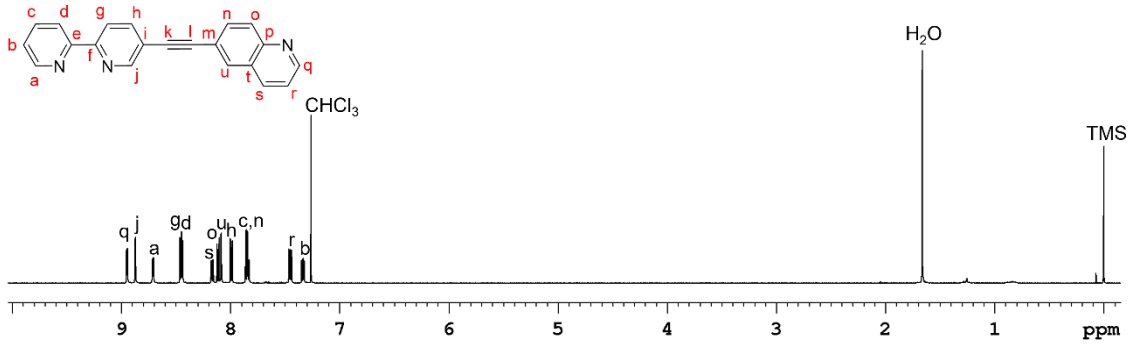


Figure S34. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**).

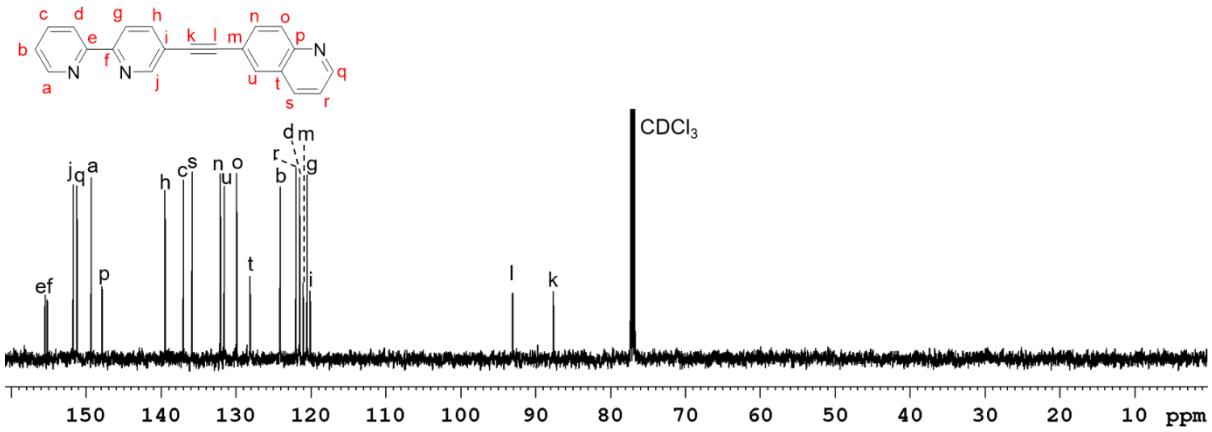


Figure S35. ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K, TMS) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**).

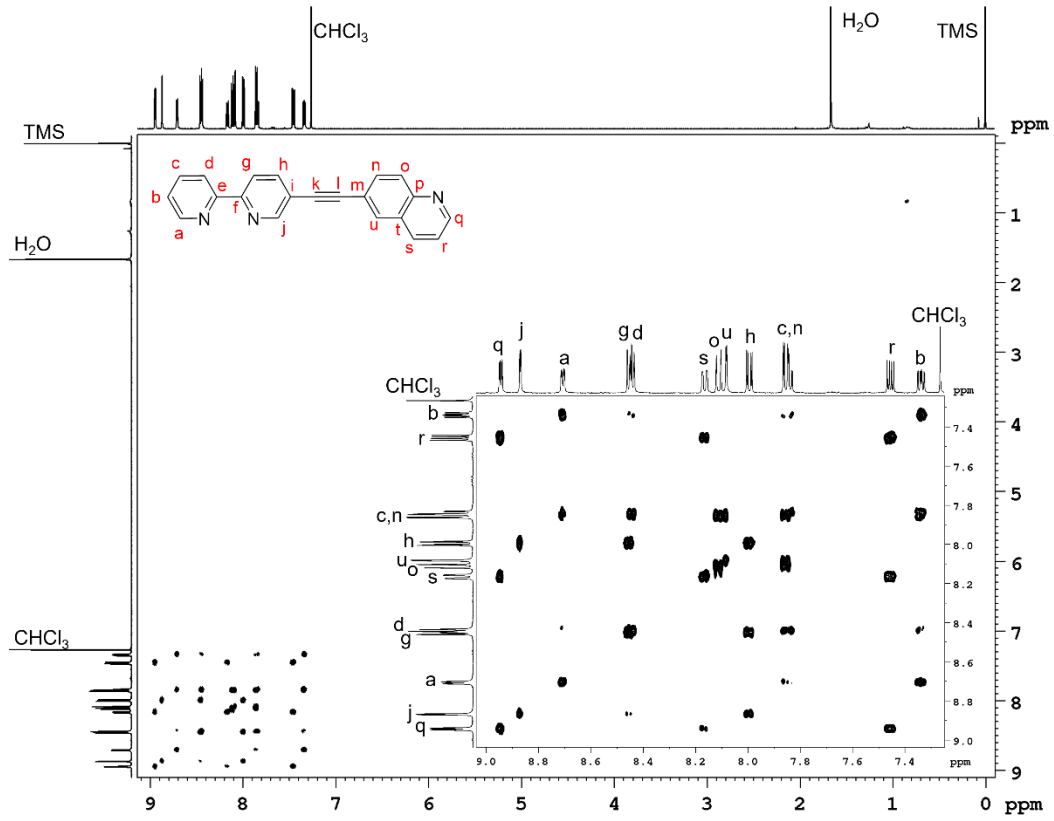


Figure S36. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**).

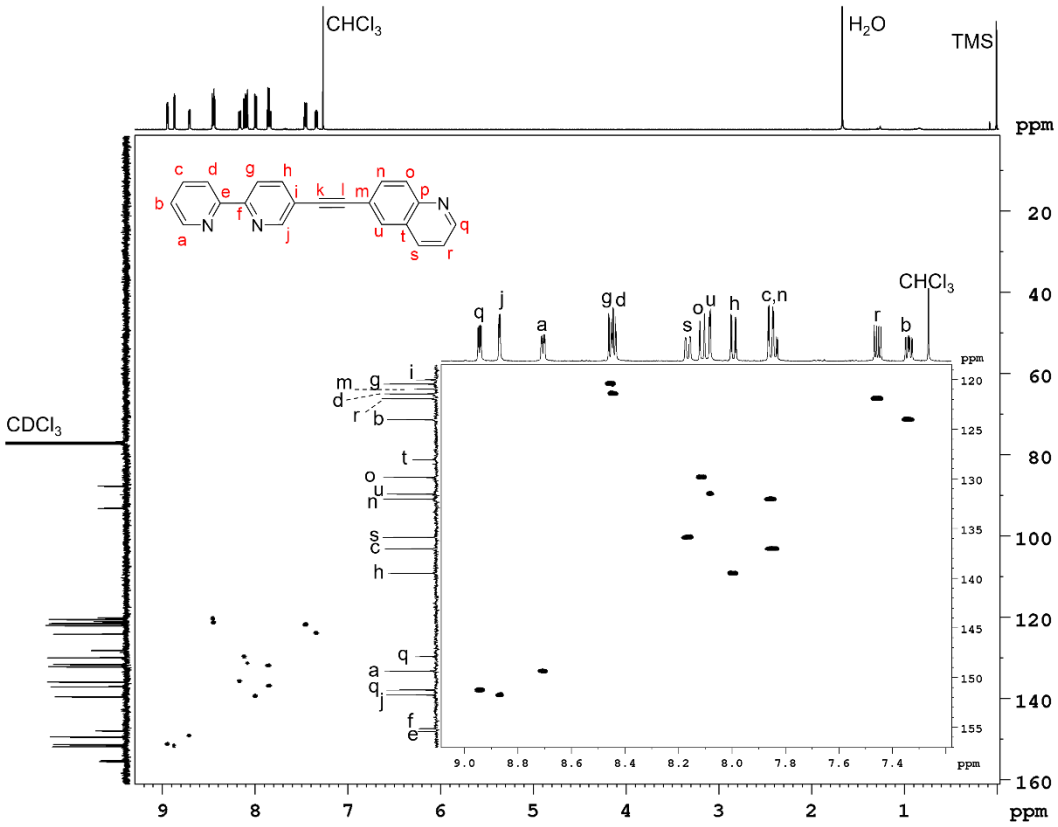


Figure S37. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K, TMS) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**).

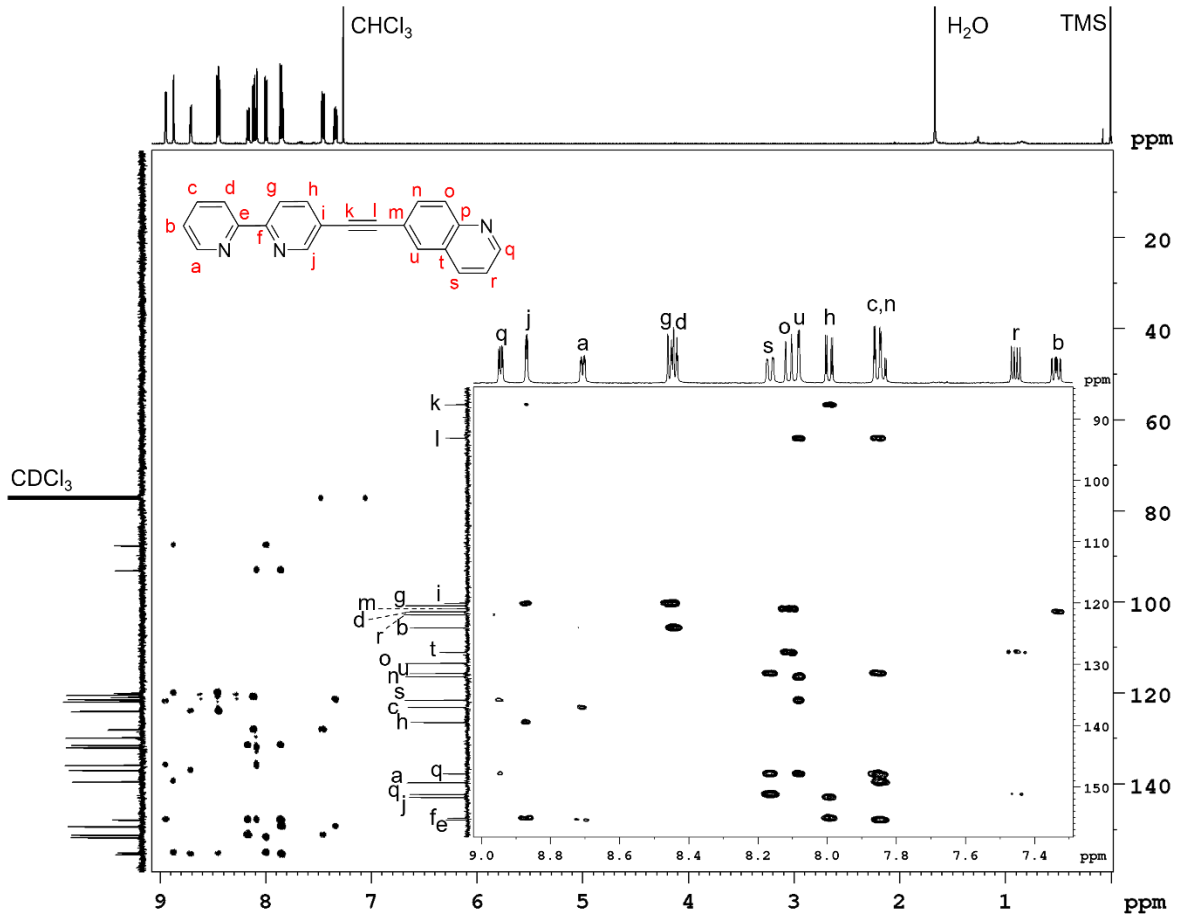
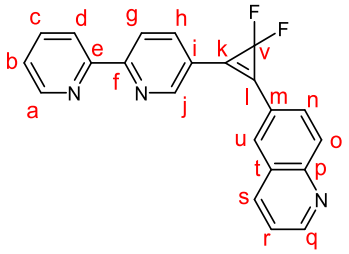


Figure S38. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K, TMS) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**).

2.3.2 5-(3,3-Difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**)



5-(Quinolin-2-ylethynyl)-2,2'-bipyridine (**2c**) (614 mg, 2.0 mmol) and TBABr (19.3 mg, 60 µmol) were added under a nitrogen atmosphere to a pressure tube. 6 mL Dry toluene and (bromodifluoromethyl)trimethylsilane (466 µL, 1.5 mmol) were added. The pressure tube was immediately closed and the reaction mixture was heated at 120 °C for 2 hours. After cooling to room temperature, 10 mL dichloromethane was added and the crude reaction mixture was added to 25 mL sat. aqueous Na_2CO_3 solution. The phases were separated and the aqueous layer was extracted with dichloromethane (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo.* The crude product was purified by flash chromatography (silica gel, 50%-80% ethyl acetate/cyclohexane) to obtain the product as a powdered yellowish solid.

R_f (2:1, ethyl acetate/cyclohexane) = 0.27

Yield: 150 mg (21%, 0.42 mmol)

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ (ppm): 9.16 (dd, ^{4}J = 2.2 Hz, ^{5}J = 0.8 Hz, 1H, H_j), 9.03 (dd, ^{3}J = 4.2 Hz, ^{4}J =1.7 Hz, 1H, H_q), 8.74 (ddd, ^{3}J = 4.7 Hz, ^{4}J = 1.8 Hz, ^{5}J = 0.9 Hz, 1H, H_a), 8.64 (d, ^{3}J = 8.2 Hz, 1H, H_g), 8.51 (d, ^{3}J = 7.7 Hz, 1H, H_d), 8.31-8.26 (m, 3H, $H_{o,s,u}$), 8.22 (dd, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, 1H, H_h), 8.10 (dd, ^{3}J = 8.6 Hz, ^{4}J = 1.8 Hz, 1H, H_n), 7.87 (td, ^{3}J = 7.7 Hz, ^{4}J = 1.8 Hz, 1H, H_c), 7.53 (dd, ^{3}J = 8.2 Hz, ^{3}J = 4.2 Hz, 1H, H_r), 7.38 (ddd, ^{3}J = 7.7 Hz, ^{3}J = 4.7 Hz, ^{4}J = 1.1 Hz, 1H, H_b).

^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ (ppm): 157.9 (C_f), 154.9 (C_e), 152.4 (C_q), 150.5 (C_j), 149.5 (C_a), 149.0 (C_p), 138.0 (C_h), 137.1 (C_c), 136.7 (C_s), 131.1 ($C_{o/u}$), 131.1 ($C_{o/u}$), 130.0 (C_n), 128.2 (C_t), 124.5 ($C_{b,l}$), 122.4 (C_r), 122.3 (C_m), 121.7 (C_d), 121.3 (C_g),121.2 (C_k), 120.7 (C_i), 101.4 ($^{1}J_{CF}$ = 272 Hz, C_v).

^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ (ppm): -112.5 (s, C-F_2) ppm.

MS (EI, 70 eV) *m/z*: 357.11 $[M]^+$, 307.11 $[M\text{-}CF_2]^+$.

HRMS (EI, 70 eV) *m/z*: 357.10753 $[M]^+$ (calculated: 357.10775 for $C_{22}H_{13}N_3F_2$, difference: -0.62 ppm).

FT-IR: $\tilde{\nu}$ = 3054.7 (w), 1774.1 (w), 1662.6 (w), 1588.1 (m), 1571.7 (w), 1546.3 (w), 1501.1 (w), 1454.1 (m), 1435.7 (w), 1371.1 (m), 1313.9 (m), 1277.2 (s), 1192.3 (w), 1147.6 (w), 1115.5 (w), 1092.3 (w), 1060.3 (w), 1040.2 (w), 1003.0 (s), 990.4 (m), 949.6 (m), 927.1 (w), 890.5 (w), 855.8 (m), 827.8 (s), 797.9 (s), 783.2 (w), 745.7 (s), 710.9 (w), 668.5 (w), 635.3 (w), 611.7 (w), 576.6 (w), 560.8 (w) cm^{-1}.

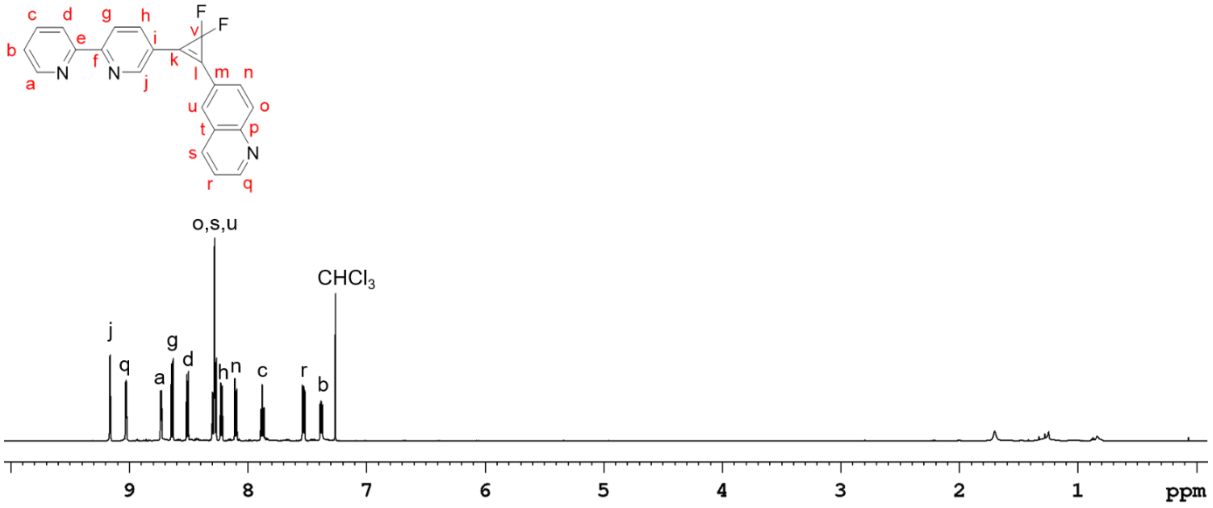


Figure S39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**).

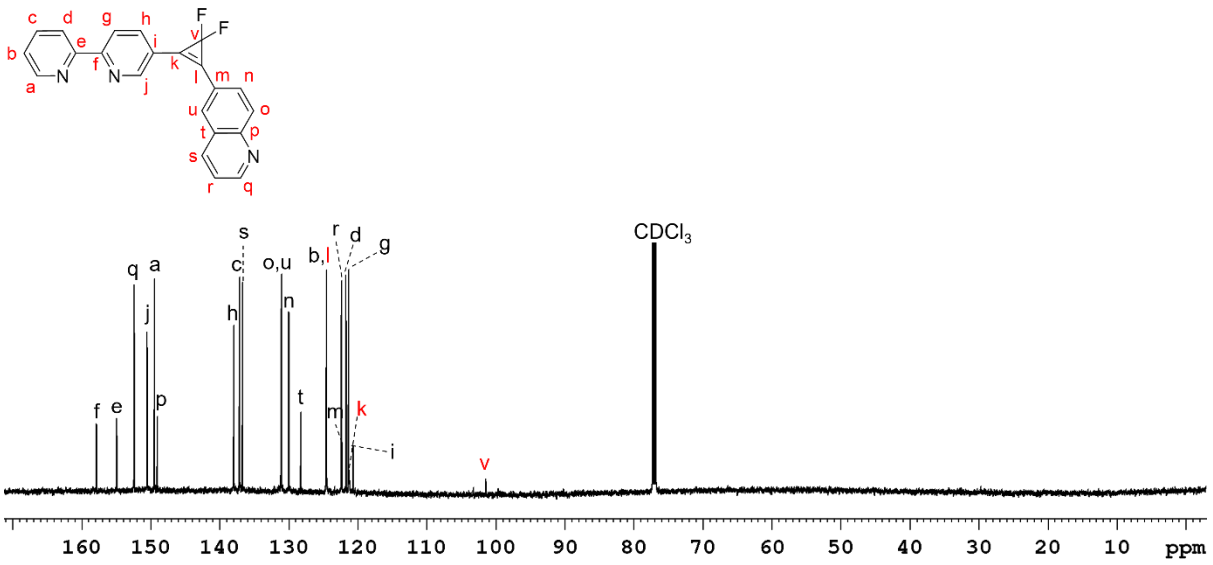


Figure S40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**).

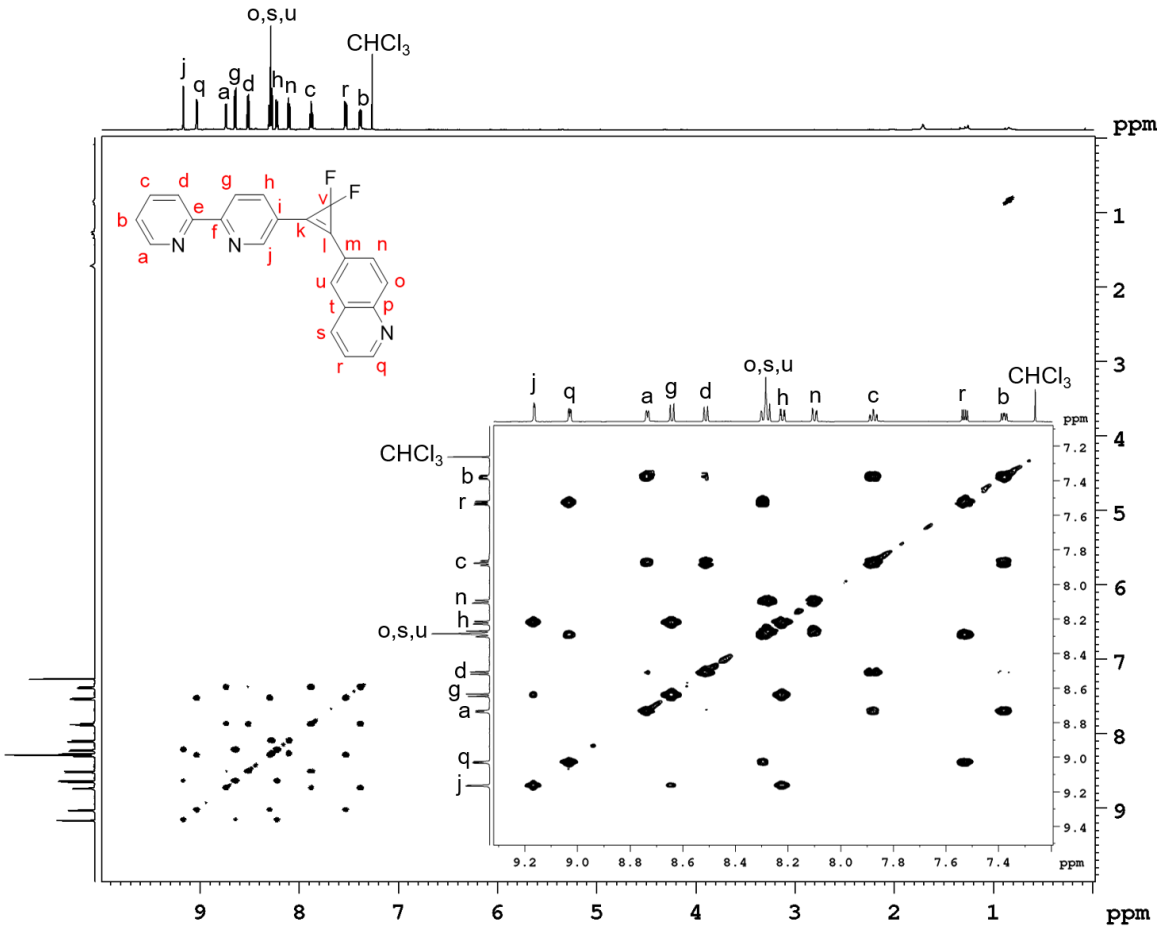


Figure S41. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**).

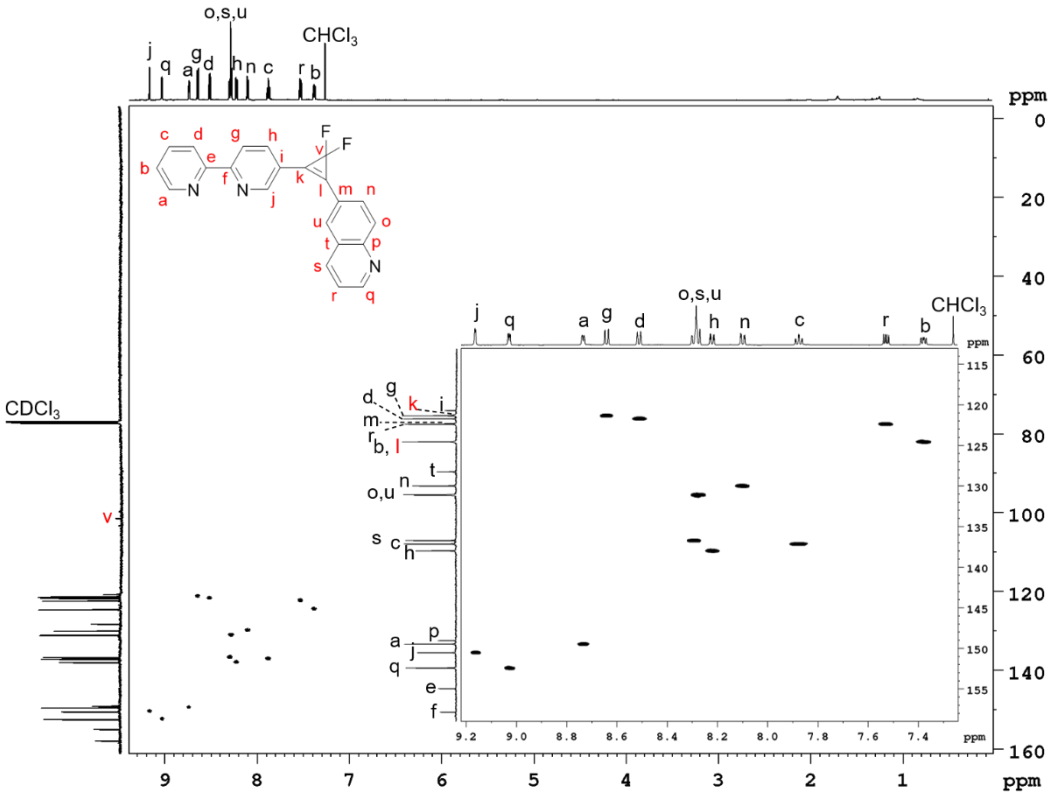


Figure S42. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**).

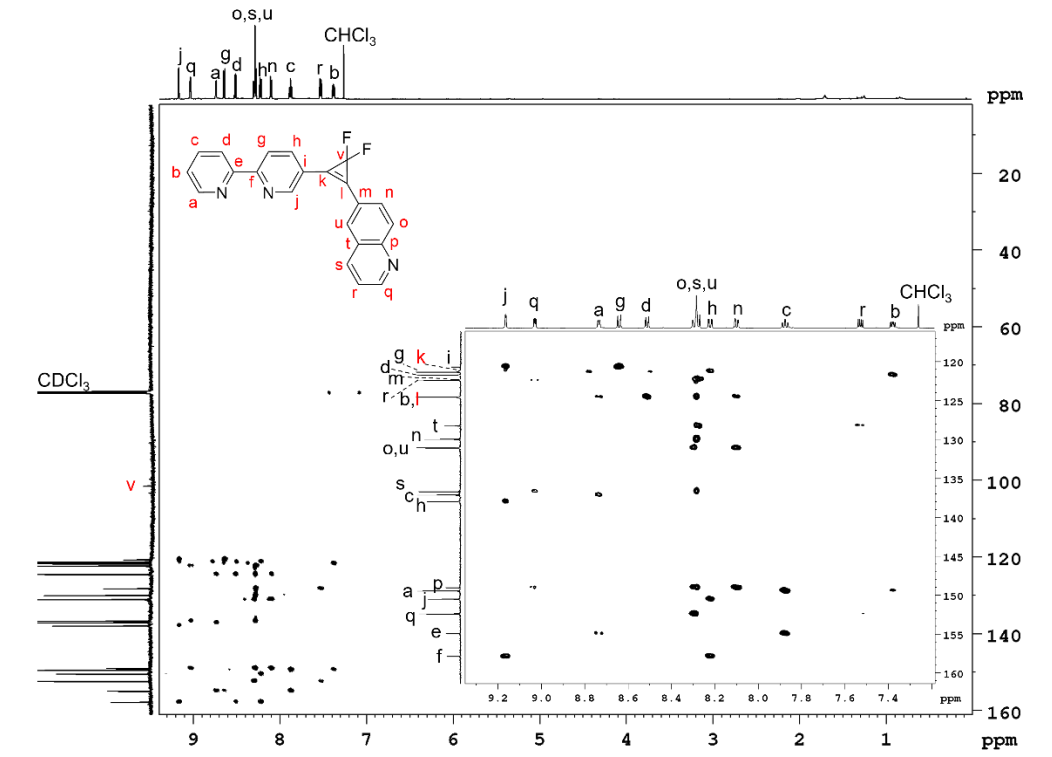


Figure S43. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**).

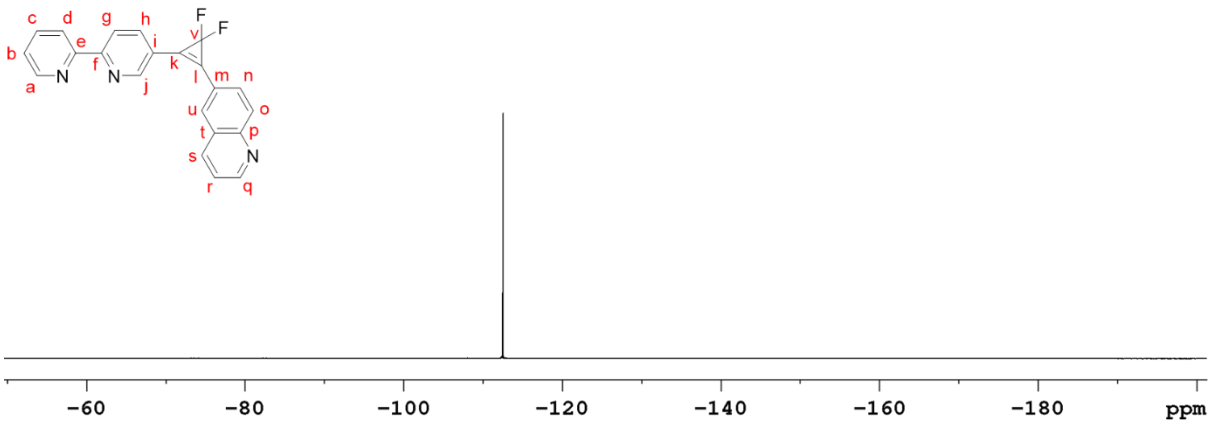
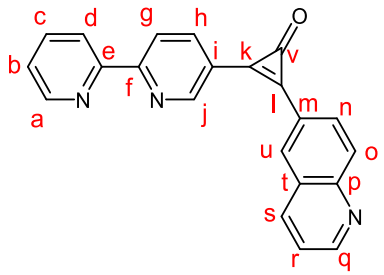


Figure S44. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**).

2.3.3 5-(2-Cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**)



5-(3,3-Difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**) (50 mg, 140 µmol) was suspended in 2.5 mL 6 M hydrochloric acid. The clear orange solution was left standing at room temperature in the dark for 1 h. After this, the solution was added dropwise to 20 mL sat. aqueous Na_2CO_3 solution which was cooled to 0 °C. The precipitate was filtered and washed with water. The residue was dissolved in dichloromethane, dried over $MgSO_4$ and the solvent was removed under nitrogen flow and further dried under air at room temperature giving the product as a yellow powdered solid.

In the case of unreacted starting material, it is possible to repeat this procedure in order to ensure complete hydrolysis.

Yield: 32 mg (68%, 95 µmol)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 9.36 (dd, ^4J = 2.2 Hz, ^5J = 0.8 Hz, 1H, H_j), 9.08 (dd, ^3J = 4.2 Hz, ^4J = 1.7 Hz, 1H, H_q), 8.75 (ddd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, ^5J = 1.1 Hz, 1H, H_a), 8.71 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1H, H_g), 8.57 (d, ^4J = 1.8 Hz, 1H, H_u), 8.54 (dt, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, H_d), 8.43 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1H, H_h), 8.36-8.32 (m, 2H, $H_{o,s}$), 8.25 (dd, ^3J = 8.7 Hz, ^4J = 1.8 Hz, 1H, H_n), 7.89 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_c), 7.57 (dd, ^3J = 8.3 Hz, ^3J = 4.2 Hz, 1H, H_r), 7.40 (ddd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, ^4J = 1.1 Hz, 1H, H_b).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K, TMS) δ (ppm): 159.1 (C_f), 155.2 (C_v), 154.6 (C_e), 153.2 (C_q), 151.4 (C_j), 149.6 ($C_{a,p}$), 149.1 (C_l), 146.4 (C_k), 139.2 (C_h), 137.2 (C_c), 137.2 (C_s), 133.8 (C_u), 131.3 (C_o), 129.8 (C_n), 128.2 (C_t), 124.9 (C_b), 122.6 (C_r), 122.0 (C_d), 121.6 (C_m), 121.5 (C_g), 119.9 (C_i).

HRMS (ESI) *m/z*: 336.1124 $[M+H]^+$ (calculated: 336.11314 for $C_{22}H_{14}N_3O_1$, difference: -2.11 ppm) 308.1176 $[M-CO+H]^+$.

FT-IR: $\tilde{\nu}$ = 3241.4 (w), 3056.9 (w), 2195.7 (w), 1933.0 (w), 1836.3 (s), 1621.2 (s), 1584.7 (s), 1545.7 (m), 1498.2 (w), 1455.6 (m), 1433.5 (m), 1371.6 (m), 1343.4 (m), 1310.0 (m), 1247.5 (w), 1192.4 (w), 1146.0 (w), 1113.7 (w), 1090.4 (w), 1037.8 (w), 1017.5 (w), 992.9 (w), 951.8 (w), 890.1 (w), 835.8 (s), 795.6 (s), 740.2 (s), 706.5 (m), 649.1 (m), 637.9 (m), 608.8 (m) cm^{-1}.

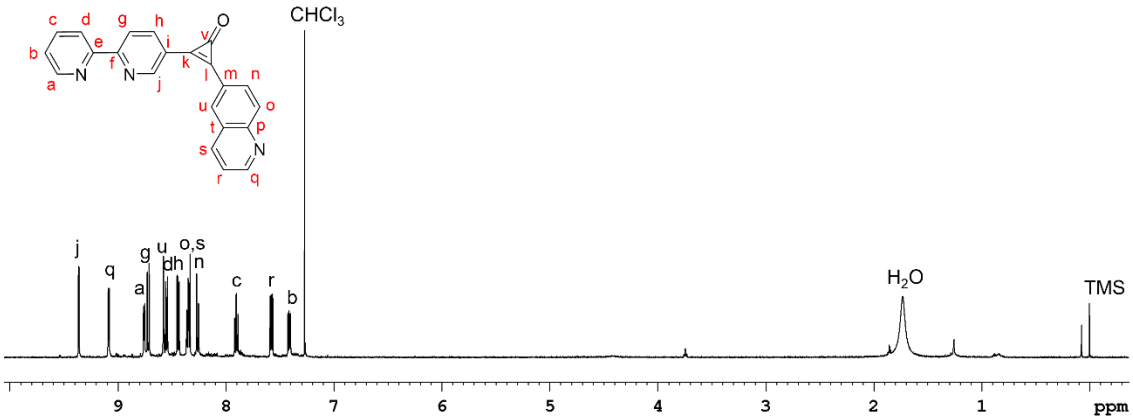


Figure S45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**).

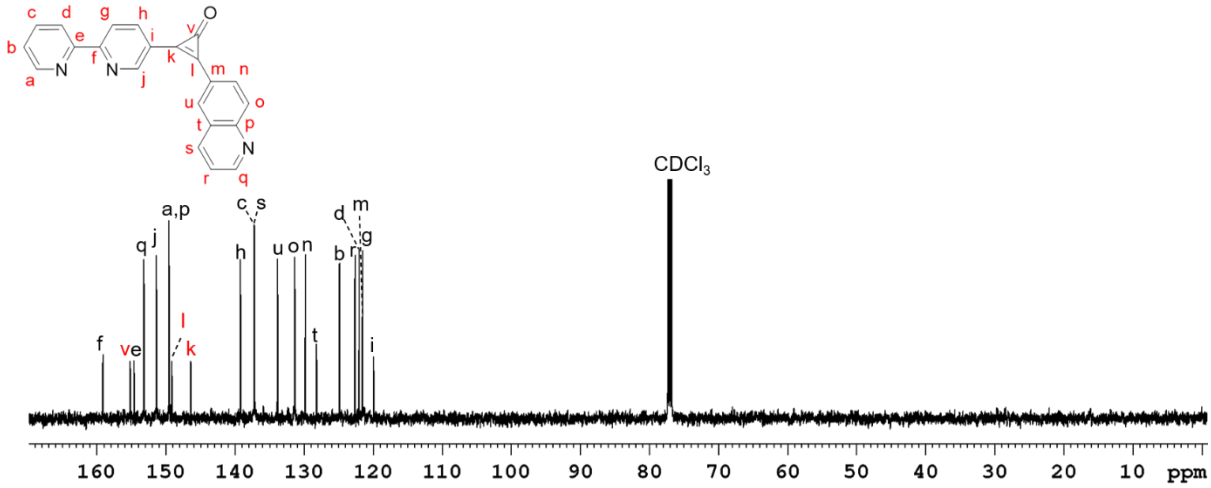


Figure S46. ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**).

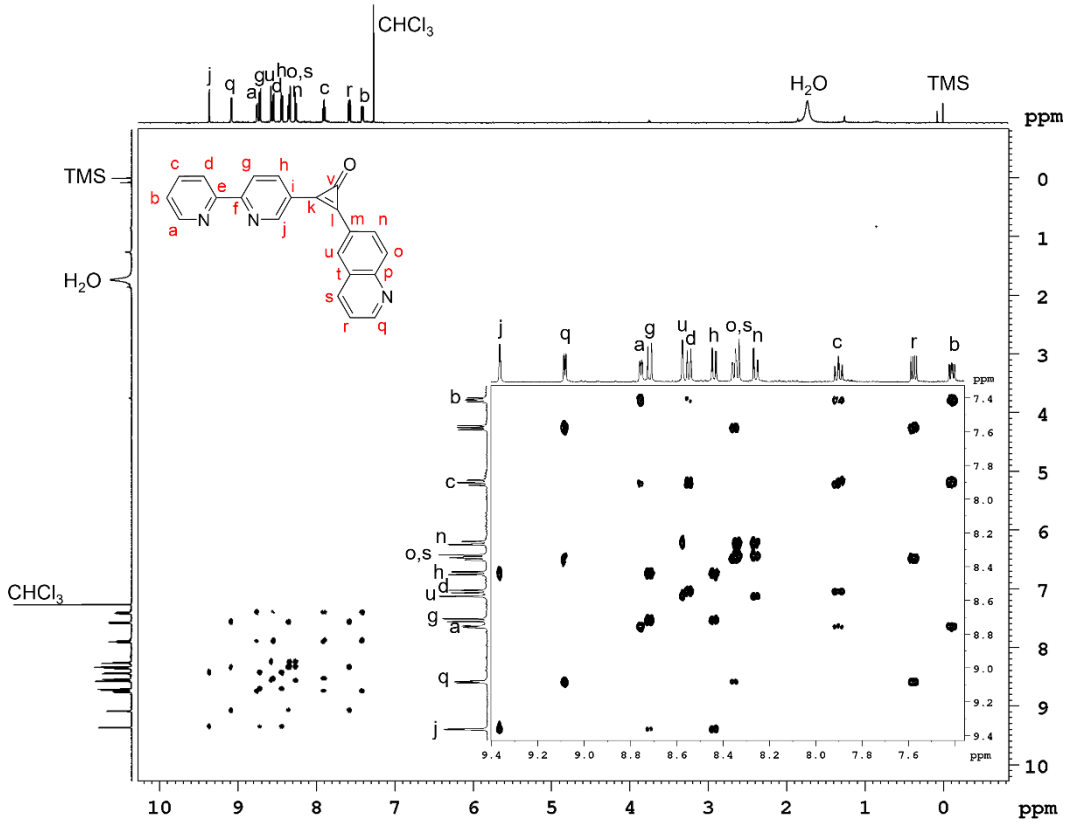


Figure S47. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**).

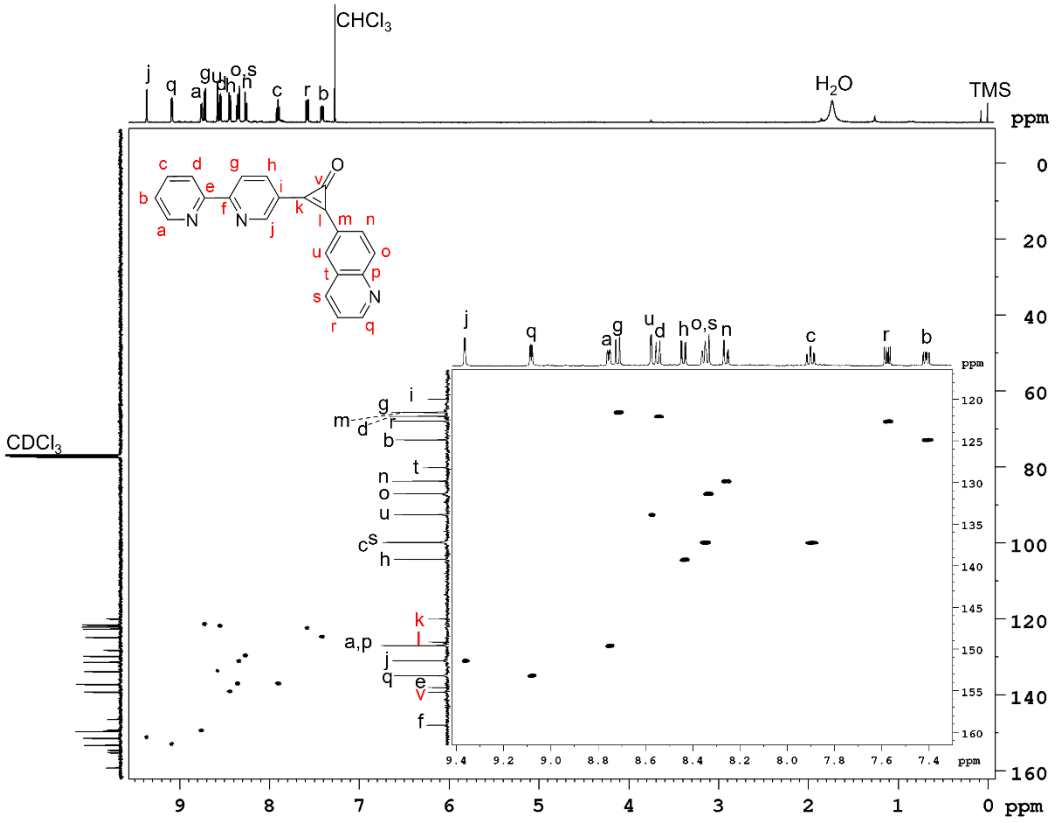


Figure S48. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**).

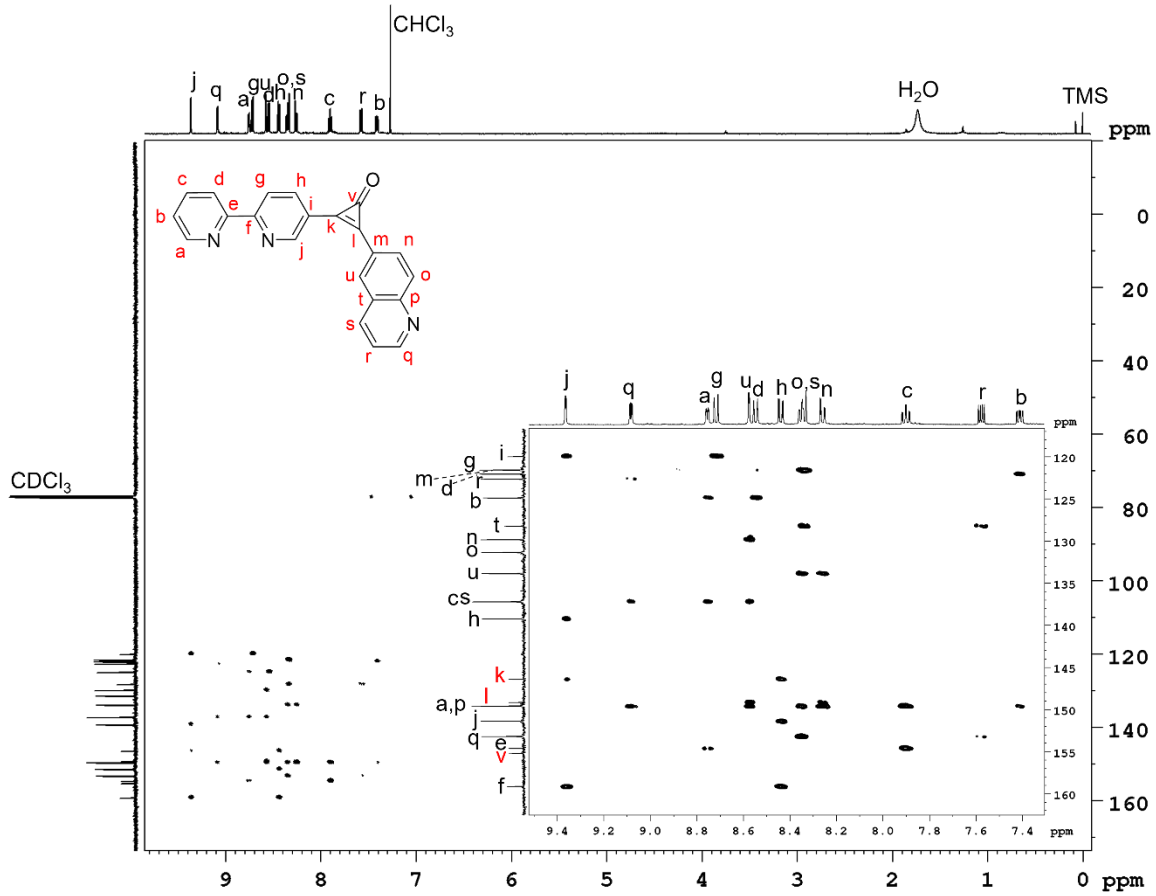
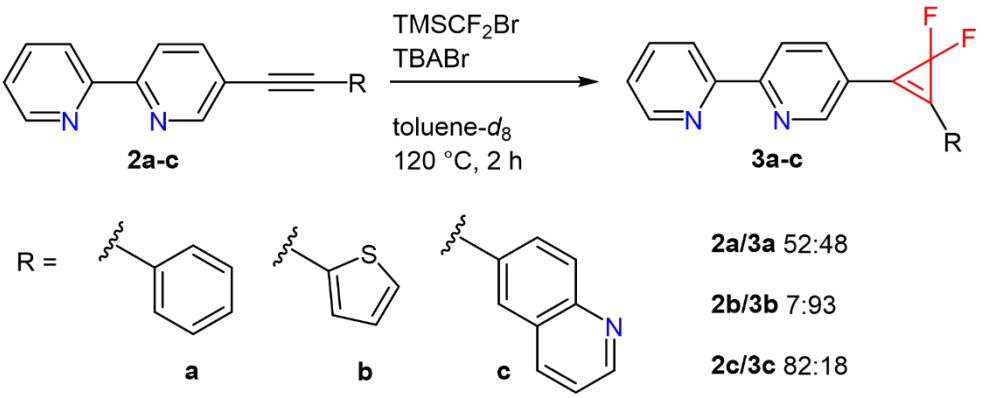


Figure S49. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz/126 MHz, $CDCl_3$, 298 K, TMS) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**).

3 *In situ* Cycloaddition Experiments



Scheme S2. *In situ* synthesis of difluorocyclopropenes **3a-c** through a [2+1] cycloaddition reaction of alkyne derivatives **2a-c** and :CF_2.

General procedure: Under a nitrogen flow, 0.1 mml of the respective alkyne derivative **2a-c**, 0.97 mg (3.0 µmol) TBABr and 23.4 µL (0.15 mmol) $TMSCF_2Br$ were added to 0.6 mL toluene-d_8 (containing hexafluorobenzene as an internal ^{19}F standard) in an NMR tube. The NMR tube was sealed and ^{1}H NMR and ^{19}F NMR spectra were measured. The reaction mixture was heated for 2 h at 120 °C and after cooling to room temperature, ^{1}H NMR and ^{19}F

NMR spectra were measured. $TMSCF_2Br$, HCF_2Br and Me_3SiF were tentatively assigned based on their shifts reported in the literature.[8-10]

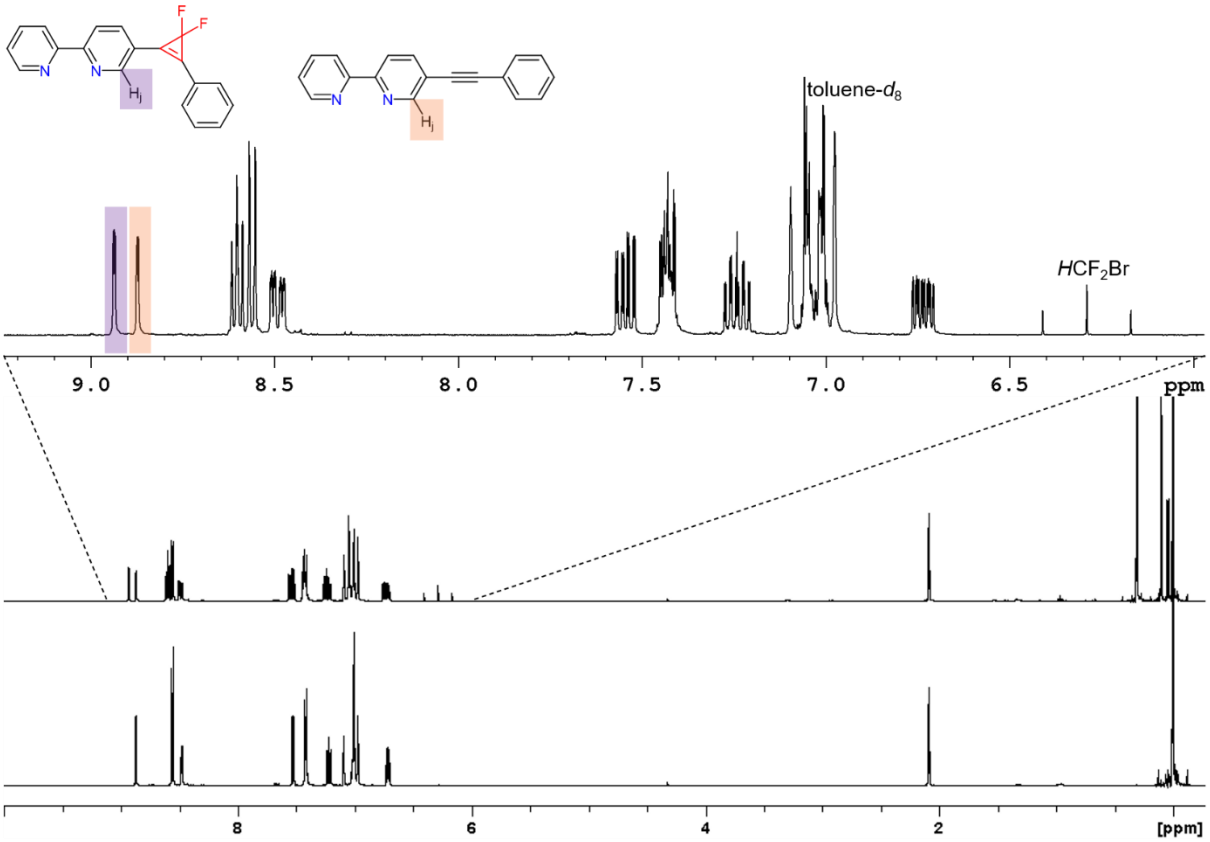


Figure S50. ^1H NMR spectrum (500 MHz, toluene-d_8, 298 K, C_6F_6) of 5-(phenylethynyl)-2,2'-bipyridine (**2a**), $TMSCF_2Br$ and TBABr before (bottom) and after heating for 2 h at 120 °C (top).

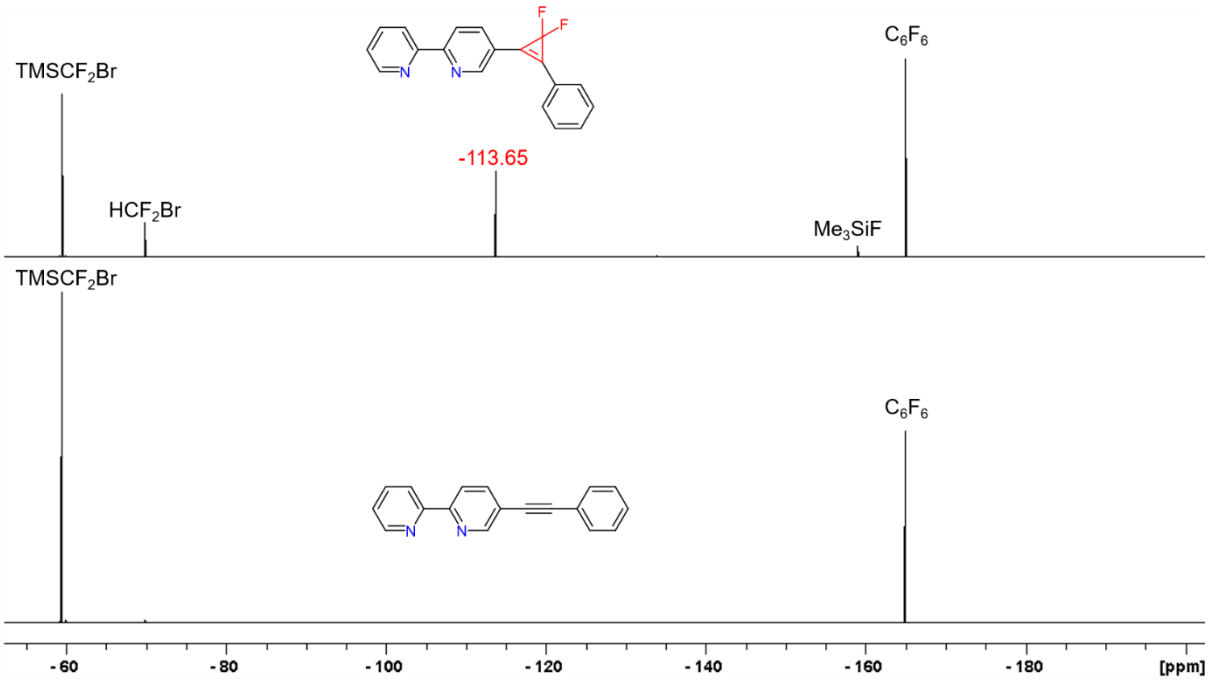


Figure S51. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K, C_6F_6) of 5-(phenylethynyl)-2,2'-bipyridine (**2a**), $TMSCF_2Br$ and TBABr before (bottom) and after heating for 2 h at 120 °C (top).

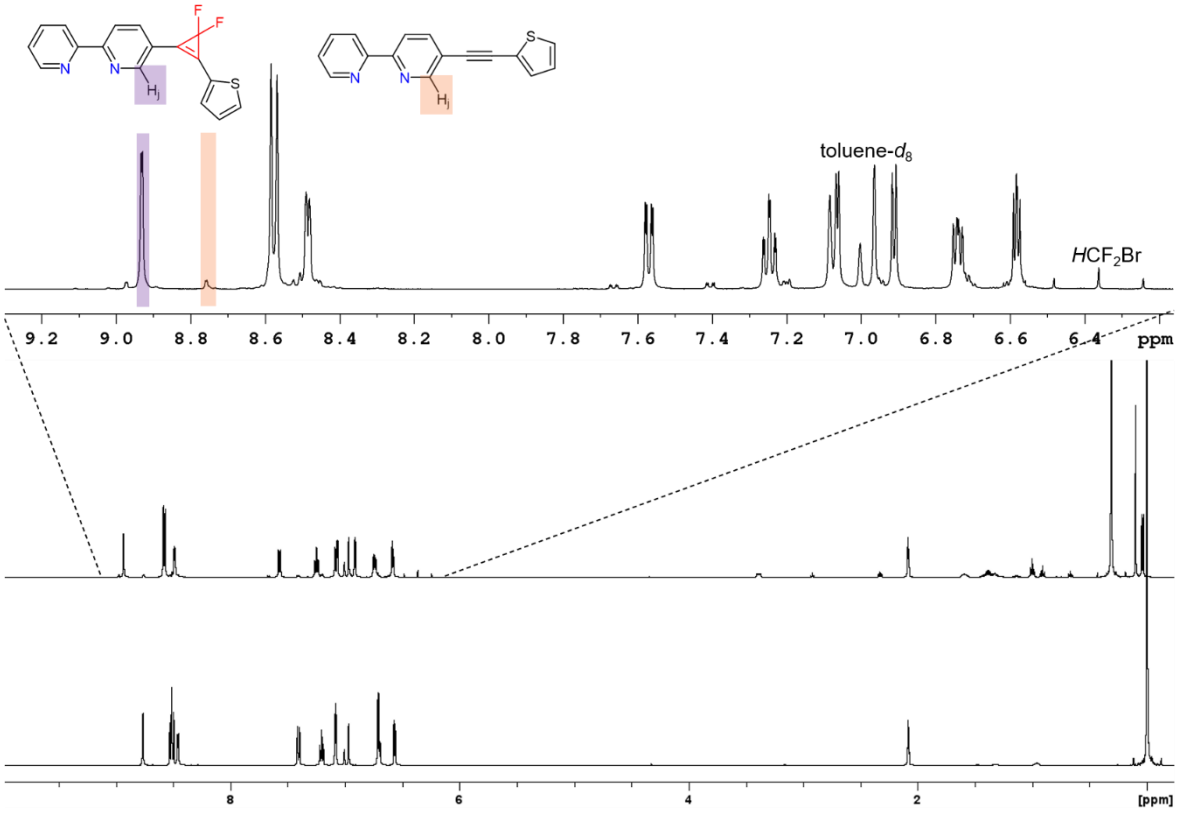


Figure S52. ^{1}H NMR spectrum (500 MHz, toluene-d_8, 298 K, C_6F_6) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**), $TMSCF_2Br$ and TBABr before (bottom) and after heating for 2 h at 120 °C (top).

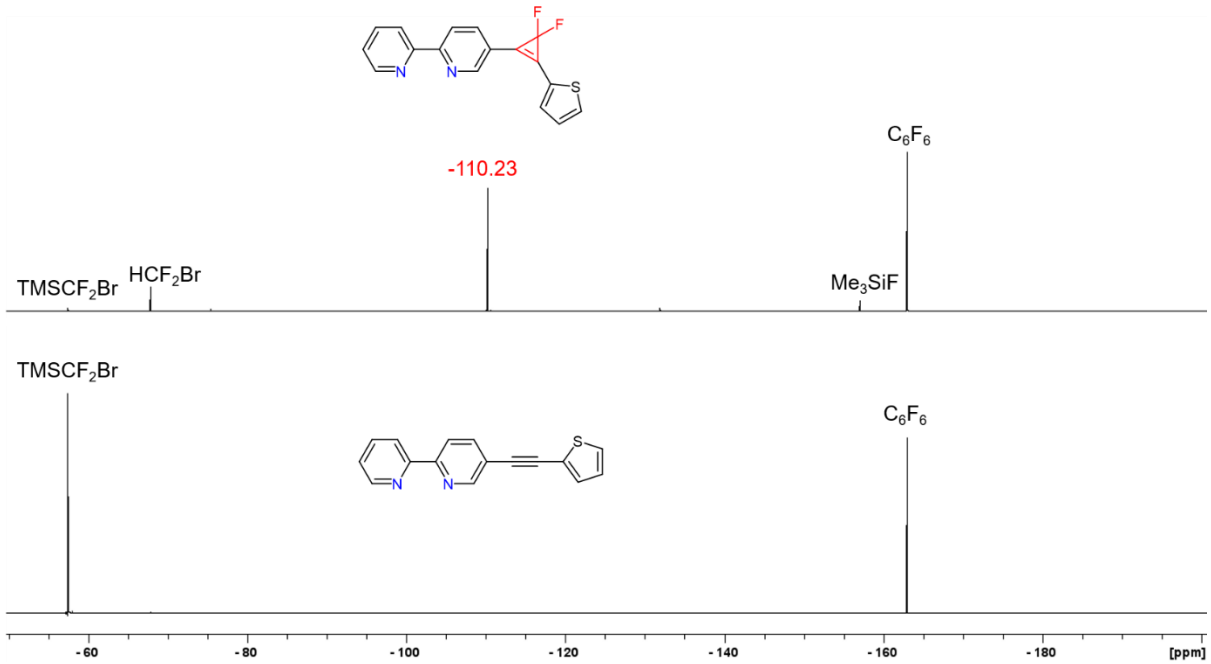


Figure S53. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K, C_6F_6) of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**), $TMSCF_2Br$ and TBABr before (bottom) and after heating for 2 h at 120 °C (top).

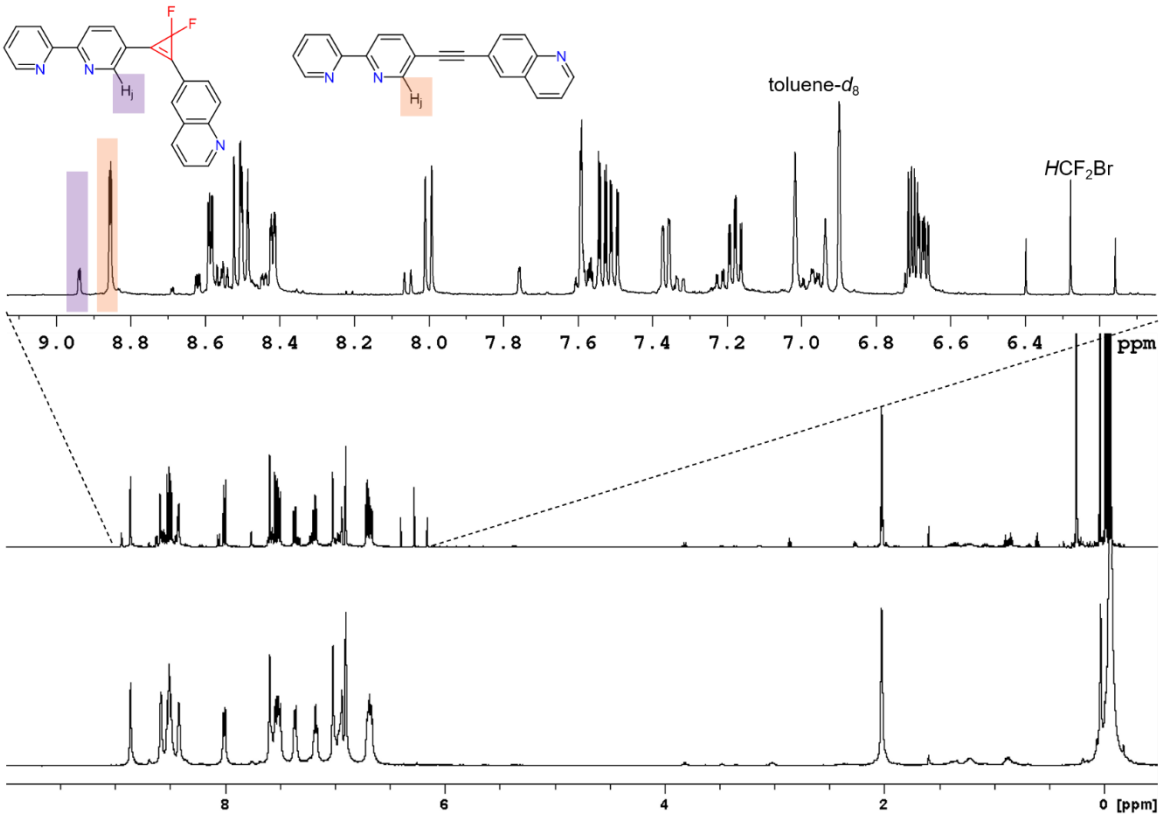


Figure S54. ^{1}H NMR spectrum (500 MHz, toluene-d_8, 298 K, C_6F_6) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**), $TMSCF_2Br$ and TBABr before (bottom) and after heating for 2 h at 120 °C (top).

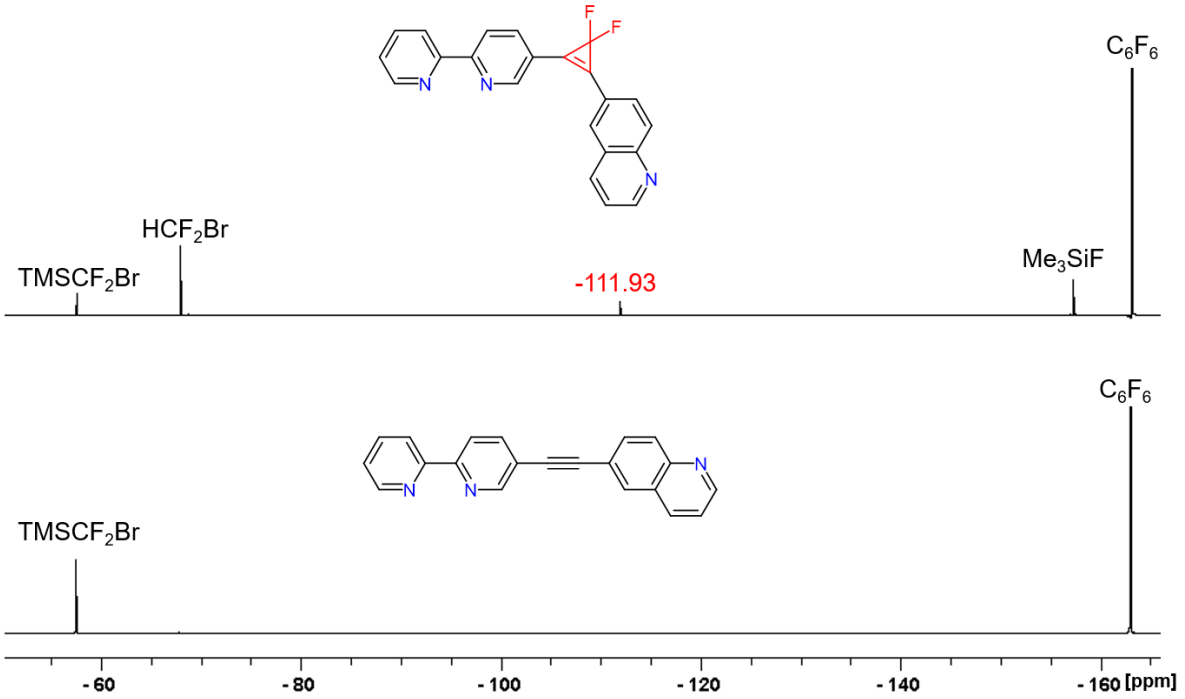
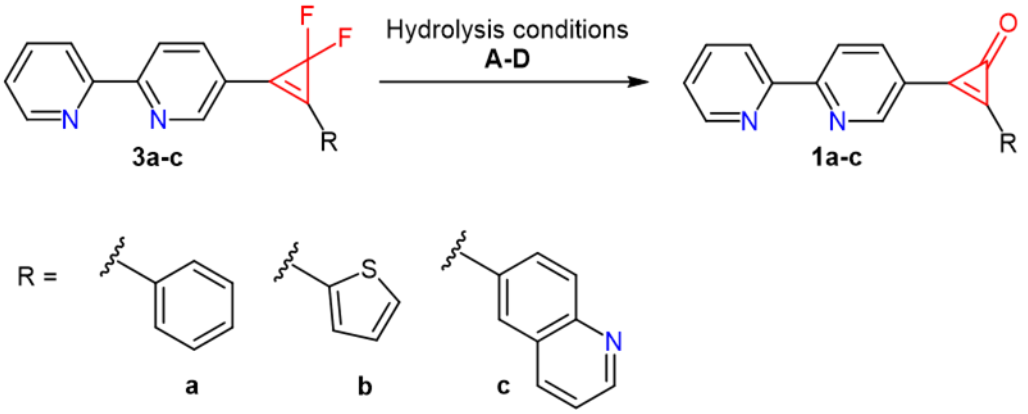


Figure S55. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K, C_6F_6) of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**), $TMSCF_2Br$ and TBABr before (bottom) and after heating for 2 h at 120 °C (top).

4 Hydrolysis



Scheme S3. Hydrolysis of difluorocyclopropenes **3a-c** to cyclopropenones **1a-c** under different conditions.

General hydrolysis conditions A-D: 5 mg of the respective difluorocyclopropene **3a-c** was used for each hydrolysis attempt and the samples were left standing for 24 hours at room temperature in the dark.

Hydrolysis **A**: **3** was dissolved in 0.5 mL lab stock $CDCl_3$.

Hydrolysis **B**: **3** was dissolved in 0.7 mL lab stock $CDCl_3$ and 20 mg silica gel was added. After standing, the silica gel was filtered off.

Hydrolysis **C**: **3** was dissolved in 0.5 mL lab stock $CDCl_3$ and 20 mg Amberlyst®15 was added. After standing, the Amberlyst®15 was filtered off.

Hydrolysis **D**: **3** was dissolved in 1 mL 6 M HCl. After standing for 24 h, the acidic solution was added dropwise at 0 °C to 5 mL sat. Na_2CO_3 solution. The precipitate was extracted with 0.7 mL $CDCl_3$ and dried over $MgSO_4$.

As a by-product was observed following hydrolysis of **3c** with hydrolysis condition **D** (Figure S58, D), the hydrolysis conditions were optimised (hydrolysis **D.1**)

Hydrolysis **D.1**: 50 mg of **3c** was dissolved in 2.5 mL 6 M HCl. After standing for 1 h, the acidic solution was added dropwise to 5 mL sat. Na_2CO_3 solution at 0 °C. The precipitate was extracted with dichloromethane, dried over $MgSO_4$ and the solvent was removed under a N_2 stream.

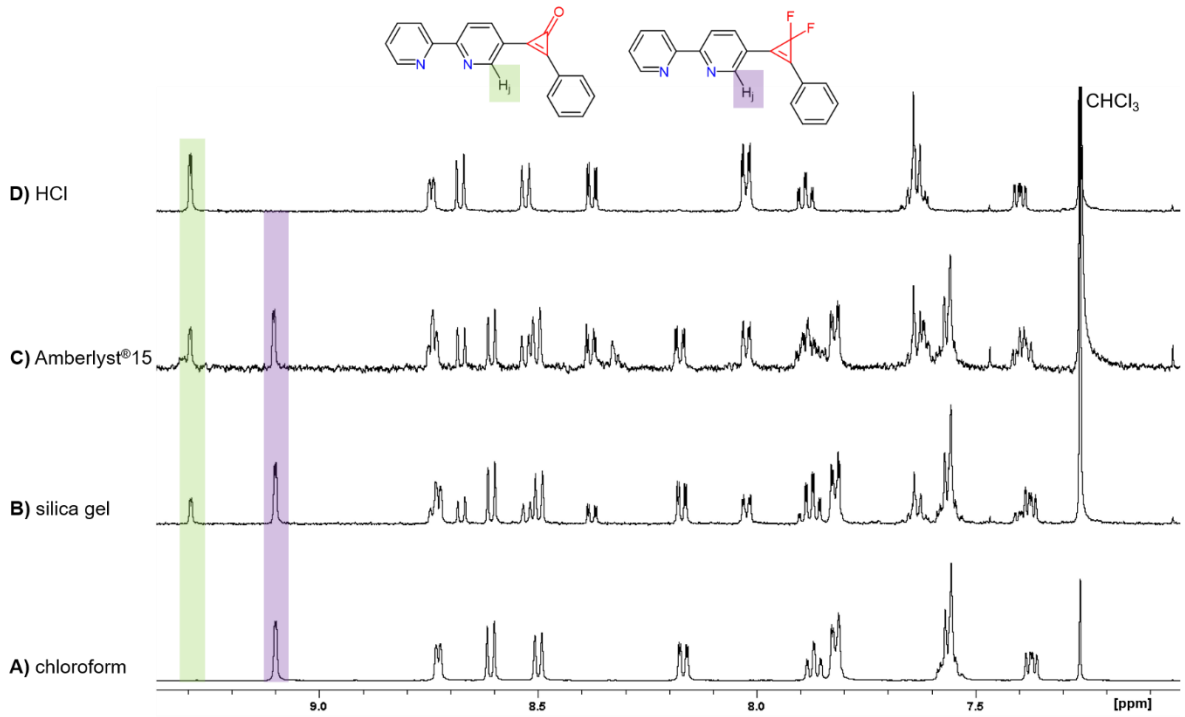


Figure S56. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**) under hydrolysis conditions **A**-**D**. Additional signals to the difluorocyclopropene and cyclopropenone were observed under hydrolysis condition **C**.

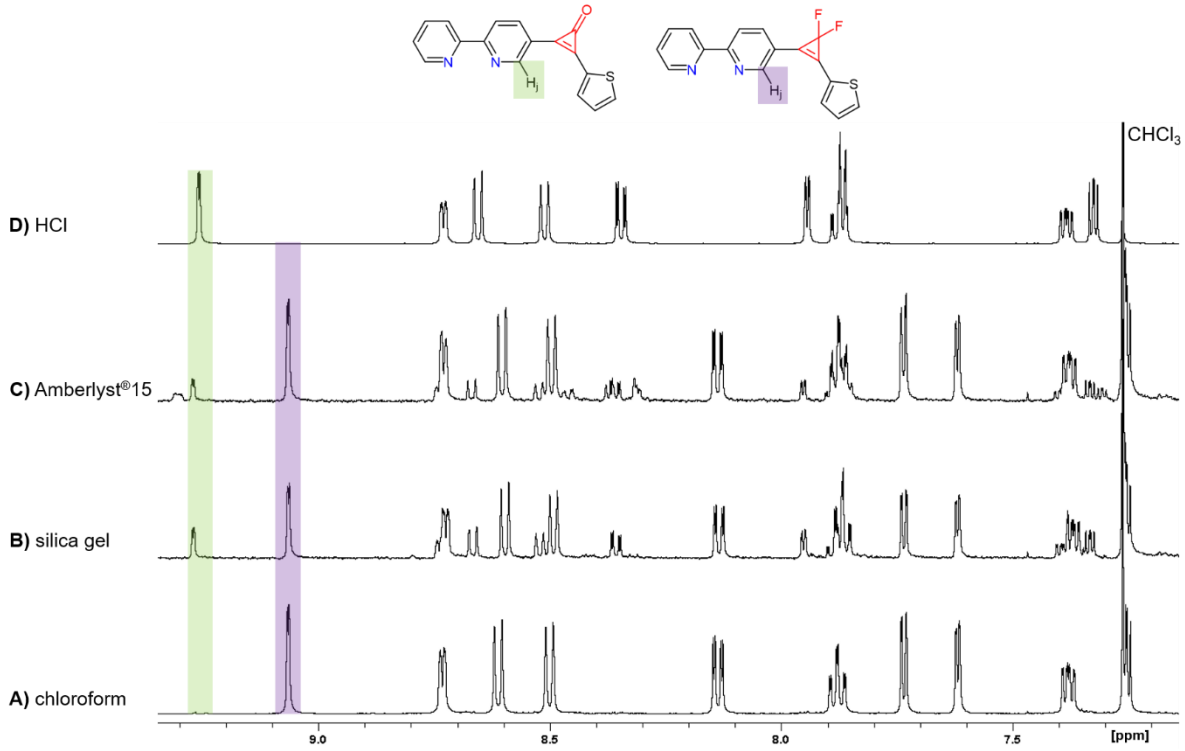


Figure S57. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**) under hydrolysis conditions **A**-**D**. Additional signals to the difluorocyclopropene and cyclopropenone were observed under hydrolysis condition **C**.

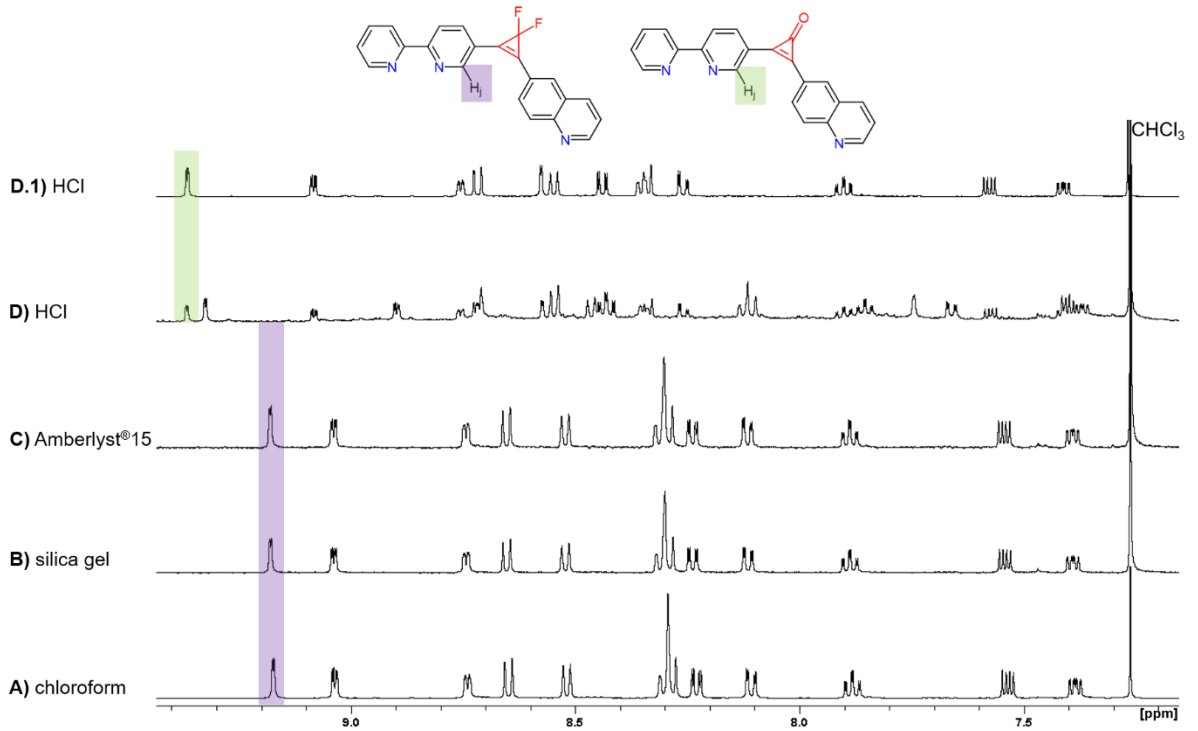


Figure S58. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**) under hydrolysis conditions **A**-**D.1**.

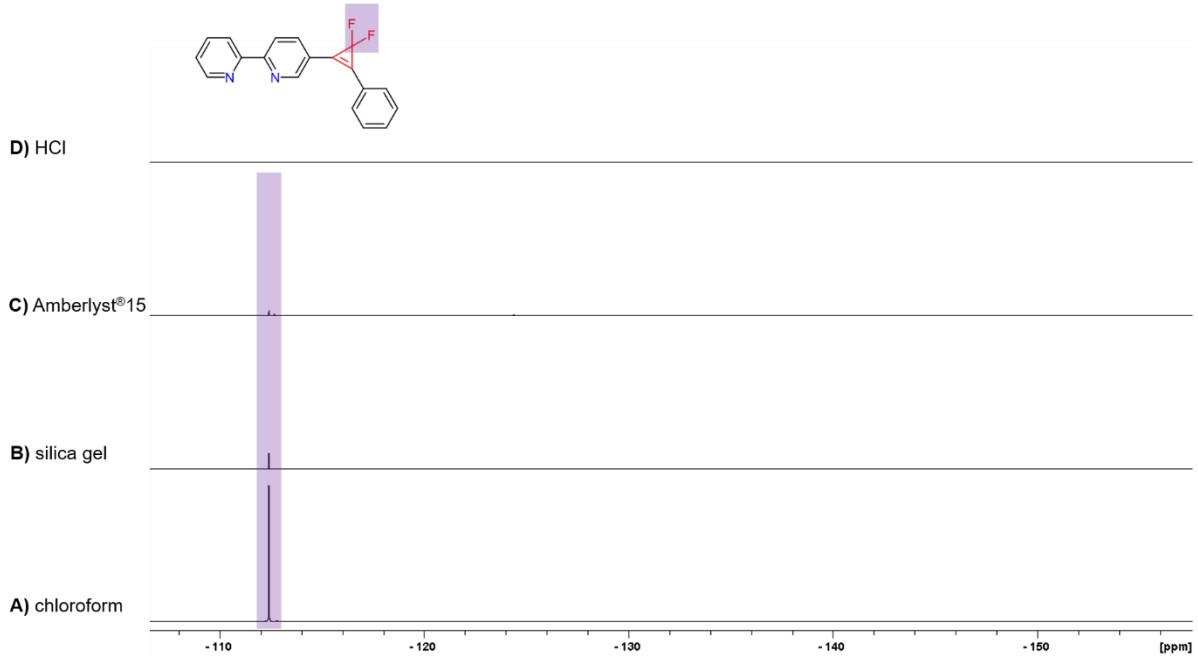


Figure S59. ^{19}F NMR spectra (471 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)-2,2'-bipyridine (**3a**) under hydrolysis conditions **A**-**D**.

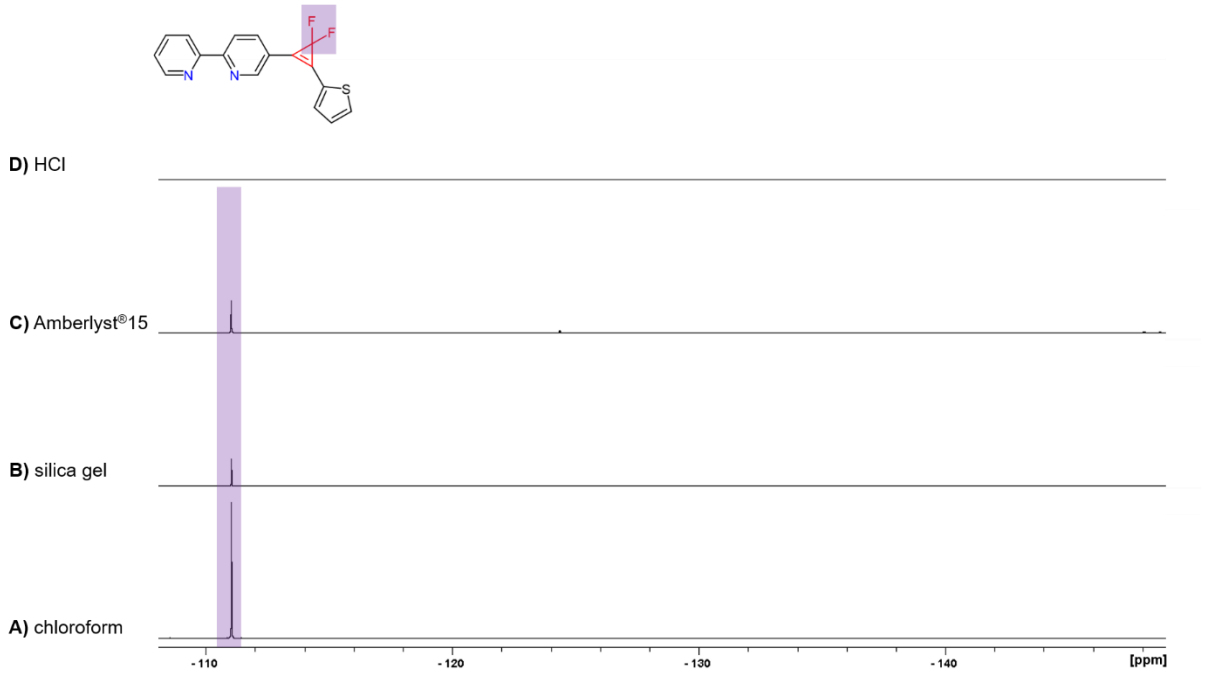


Figure S60. ^{19}F NMR spectra (471 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-2-(thiophen-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3b**) under hydrolysis conditions **A**-**D**. Under conditions **C**, additional signals were observed at -124.3, -148.7 and -148.0 ppm.

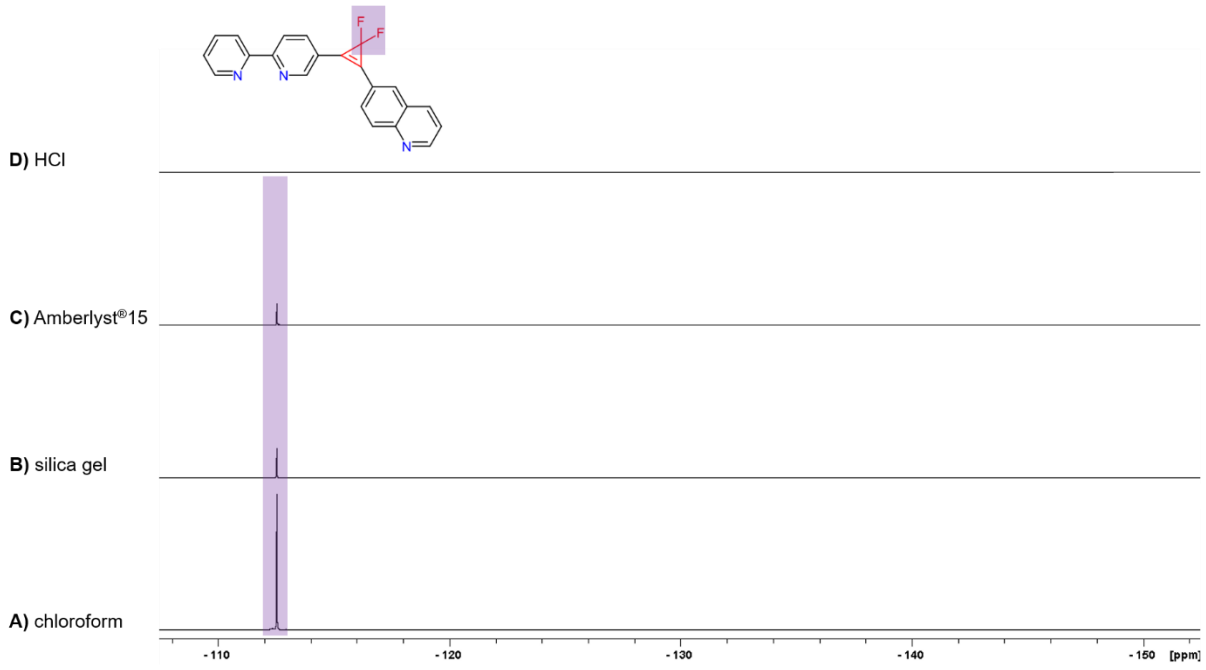


Figure S61. ^{19}F NMR spectra (471 MHz, $CDCl_3$, 298 K) of 5-(3,3-difluoro-6-(quinolin-2-yl)cycloprop-1-en-1-yl)-2,2'-bipyridine (**3c**) under hydrolysis conditions **A**-**D**.

5 Stability

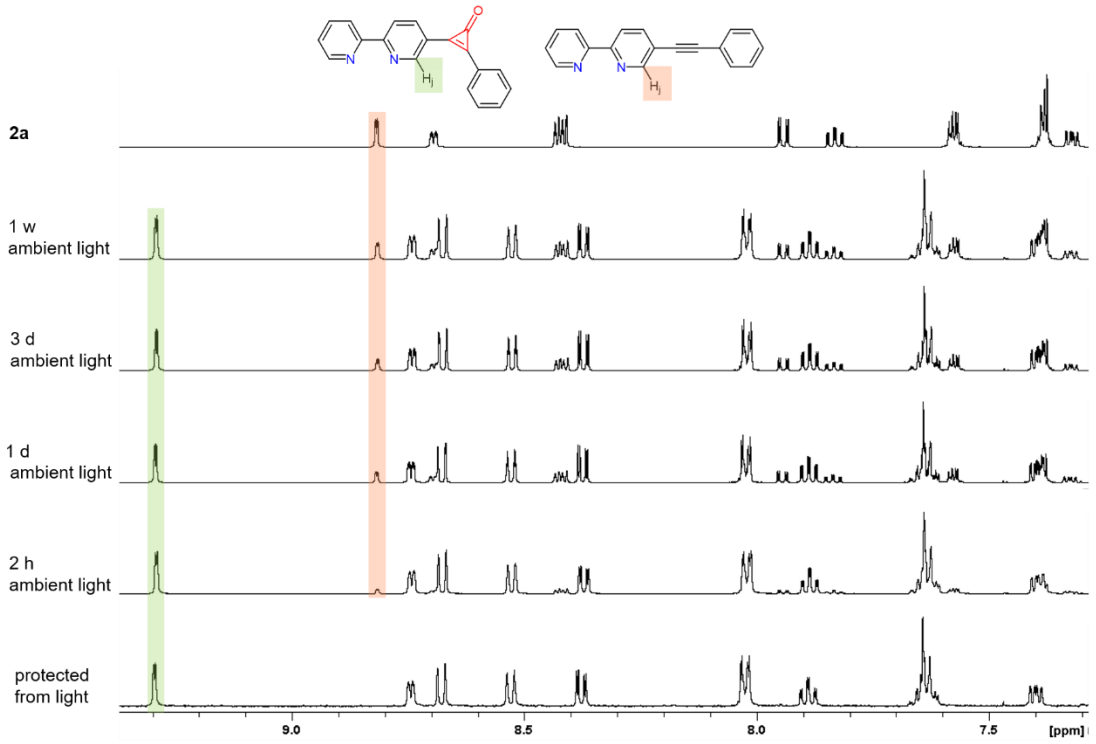


Figure S62. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) protected from light (bottom), under ambient light over one week (**1a**/**2a** 69:31) and reference 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (top).

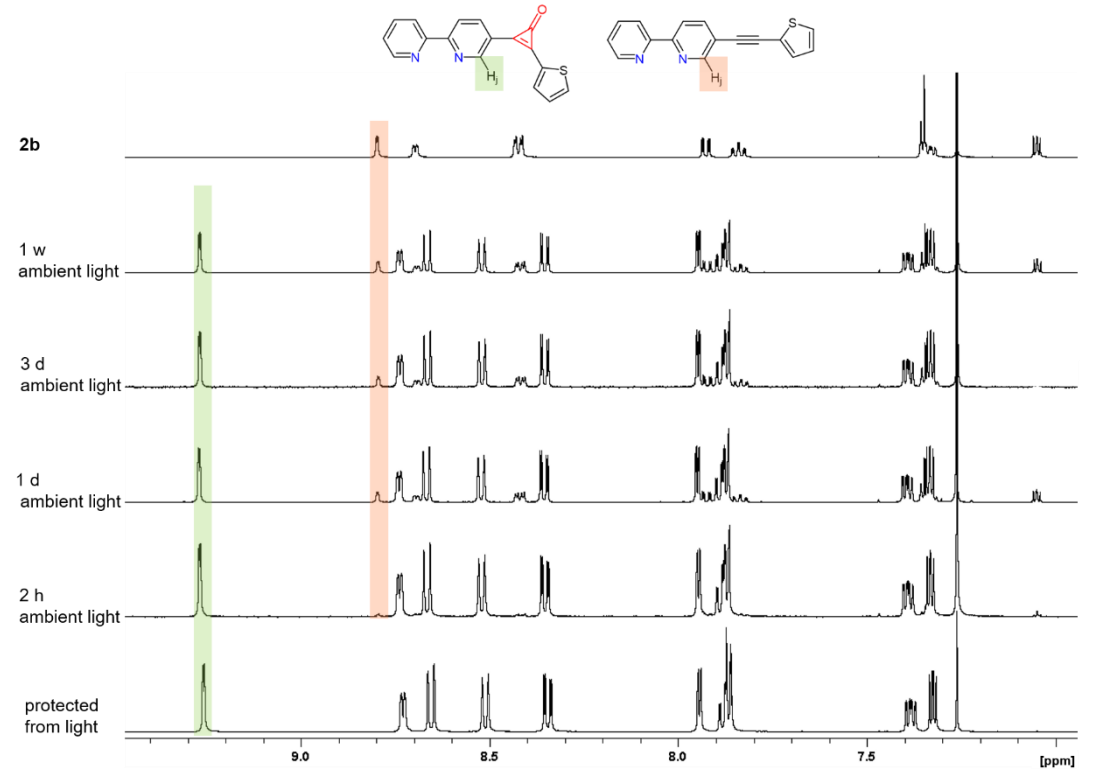


Figure S63. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**) protected from light (bottom), under ambient light over one week (**1b**/**2b** 75:25) and reference 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (top).

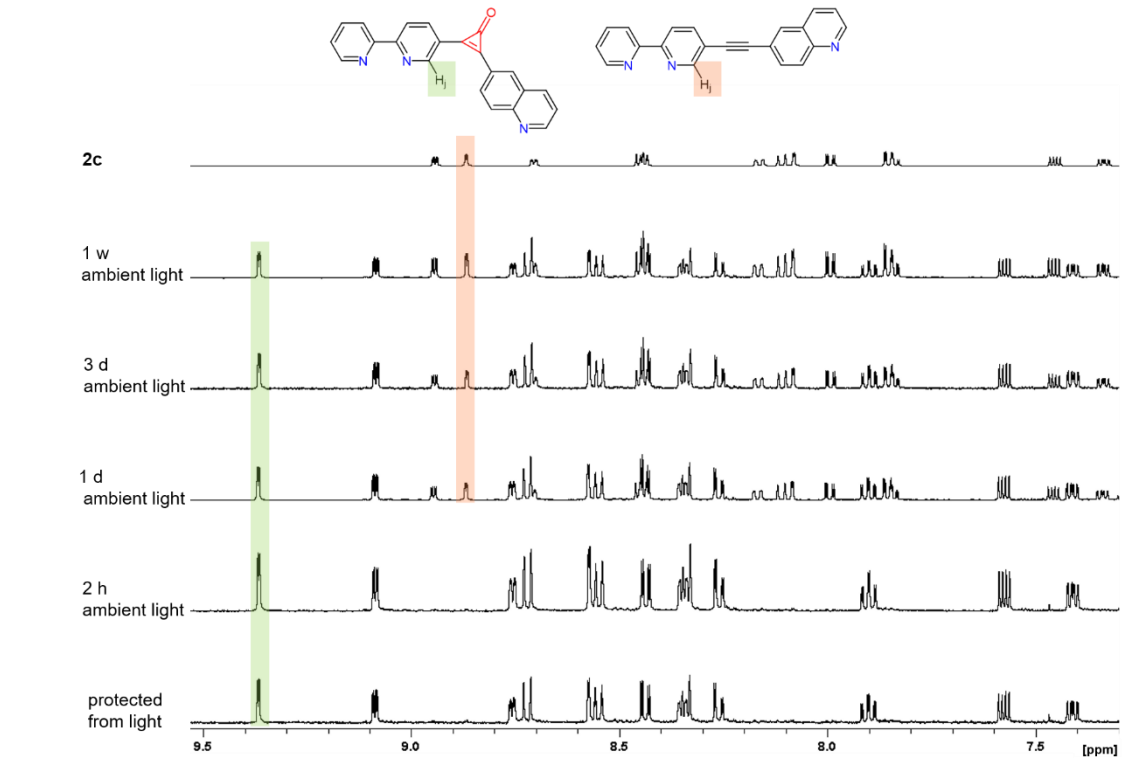


Figure S64. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**) protected from light (bottom), under ambient light over one week (**1c/2c** 49:51) and reference 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**) (top).

6 Ligand Irradiation

6.1 5-(2-Cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**)

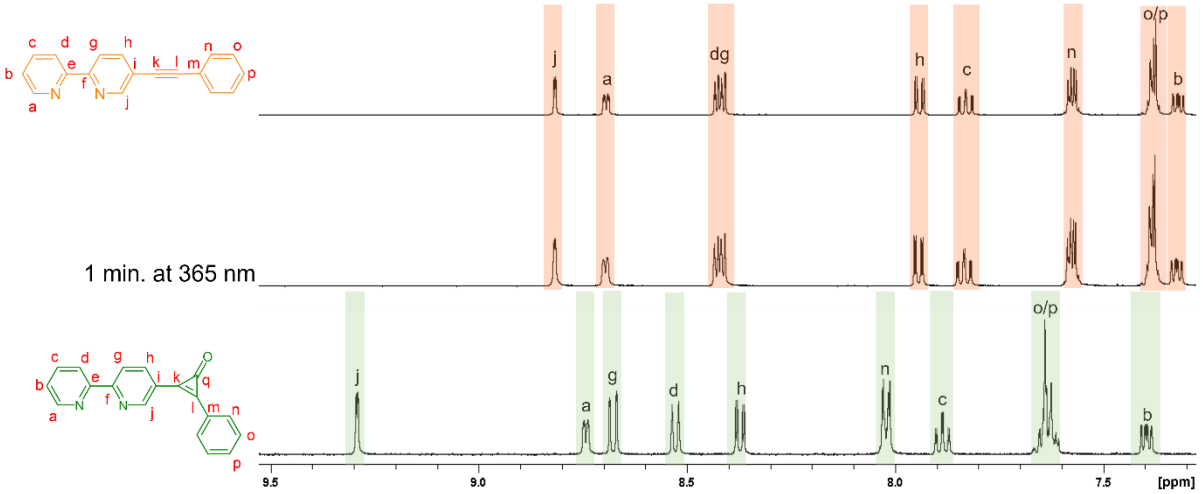


Figure S65. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) without irradiation (bottom) and after irradiation with 365 nm for 1 minute as well as the reference spectrum of 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (top).

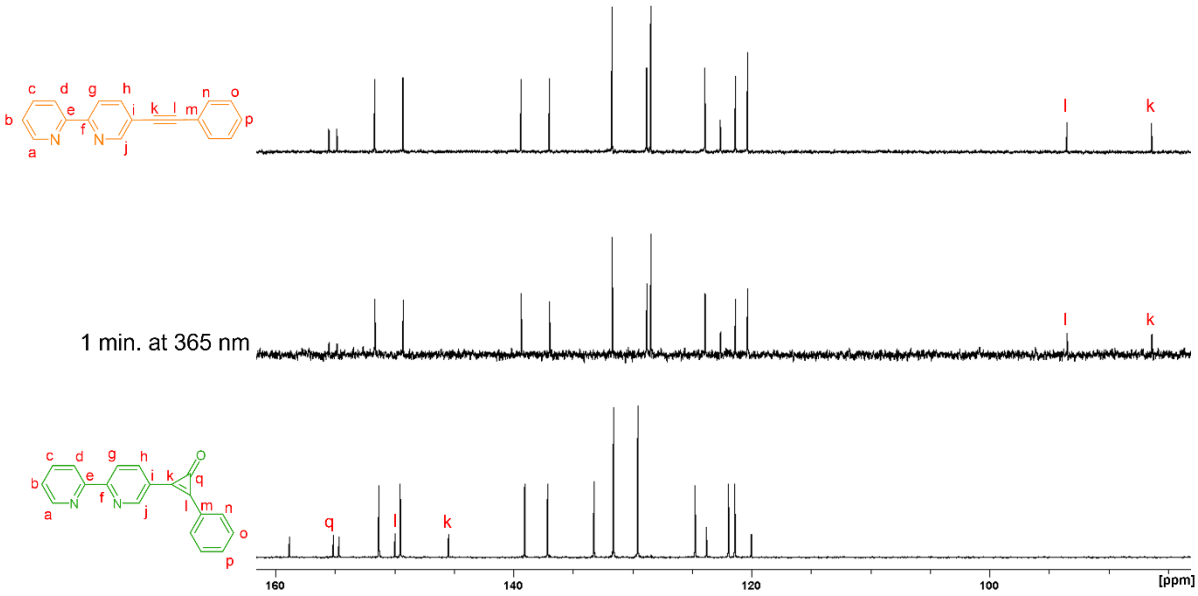


Figure S66. ^{13}C NMR spectra (126/151 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) without irradiation (bottom) and after irradiation with 365 nm for 1 minute as well as the reference spectrum of 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (top).

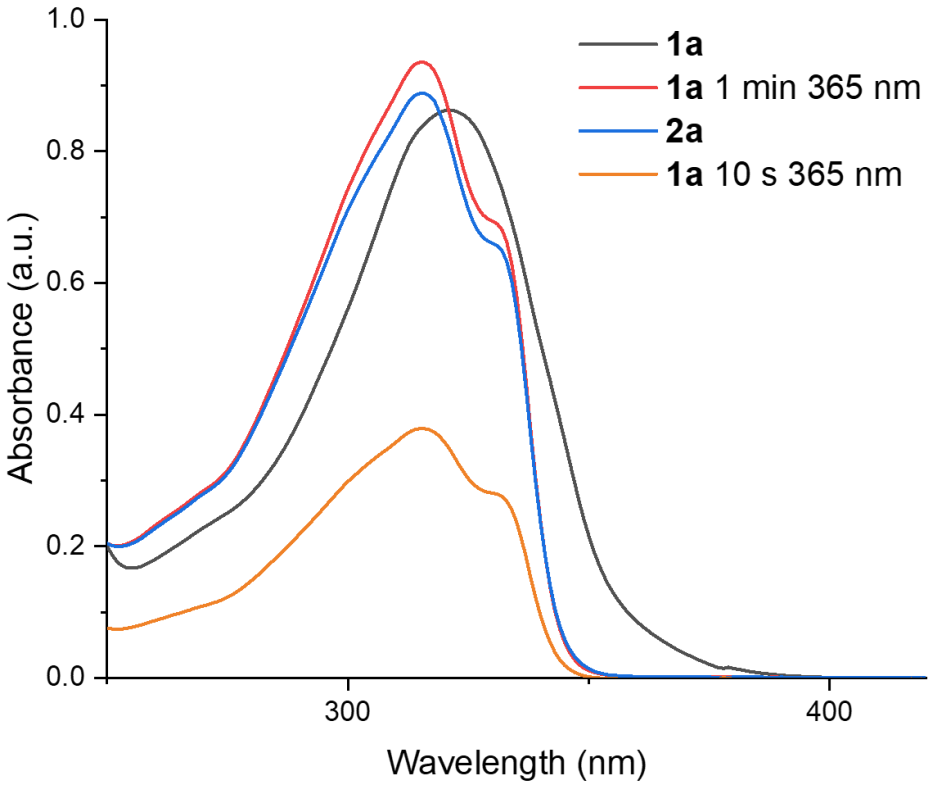


Figure S67. UV/vis spectra (CH_3CN, 298 K) of 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (4.40 µM) without irradiation (black) and after irradiation with 365 nm for 1 minute (red) as well as the reference spectrum of 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (blue, 4.40 µM) and the UV/vis spectrum of a different sample of **1a** (2.20 µM) following irradiation for 10 s (orange).

6.2 5-(2-Cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**)

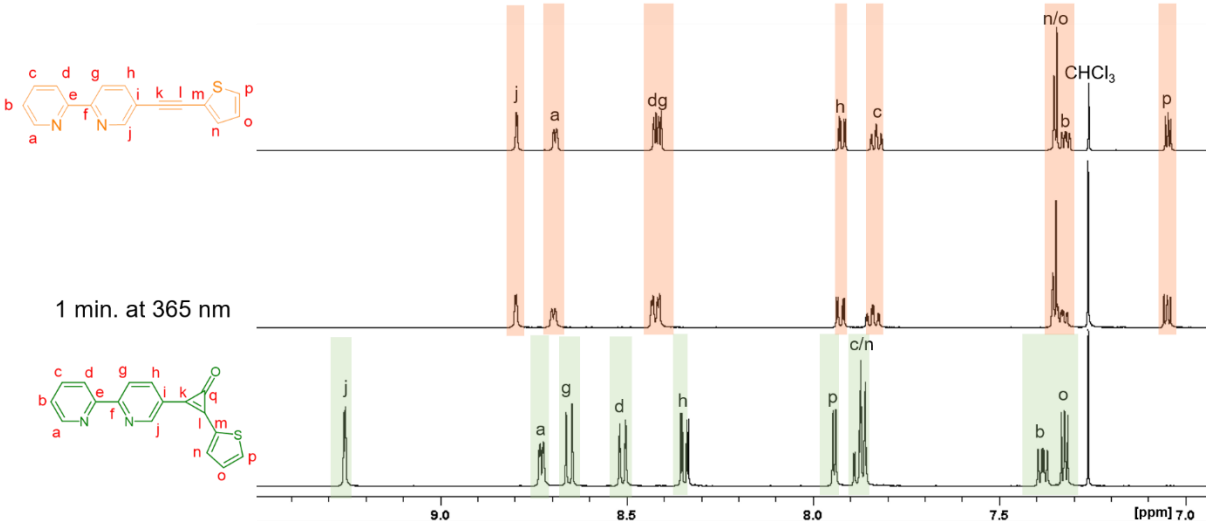


Figure S68. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**) without irradiation (bottom) and after irradiation with 365 nm for 1 minute of as well as reference spectrum of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (top).

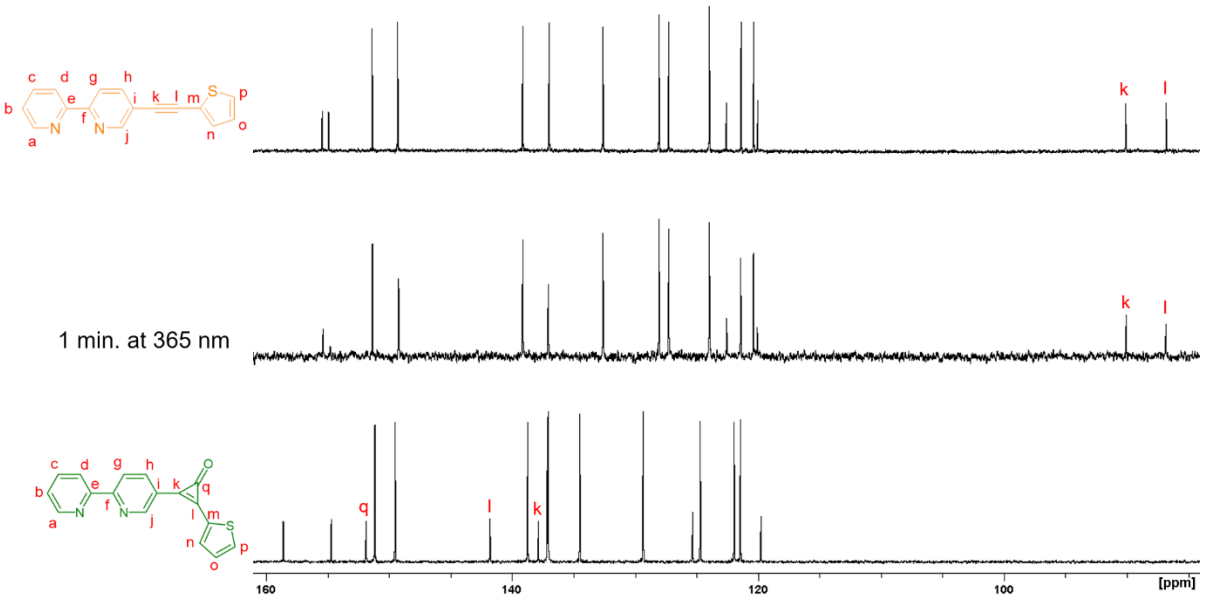


Figure S69. ^{13}C NMR spectra (126/151 MHz, $CDCl_3$, 298 K) 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**) without irradiation (bottom) and after irradiation with 365 nm for 1 minute as well as the reference spectrum of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (top).

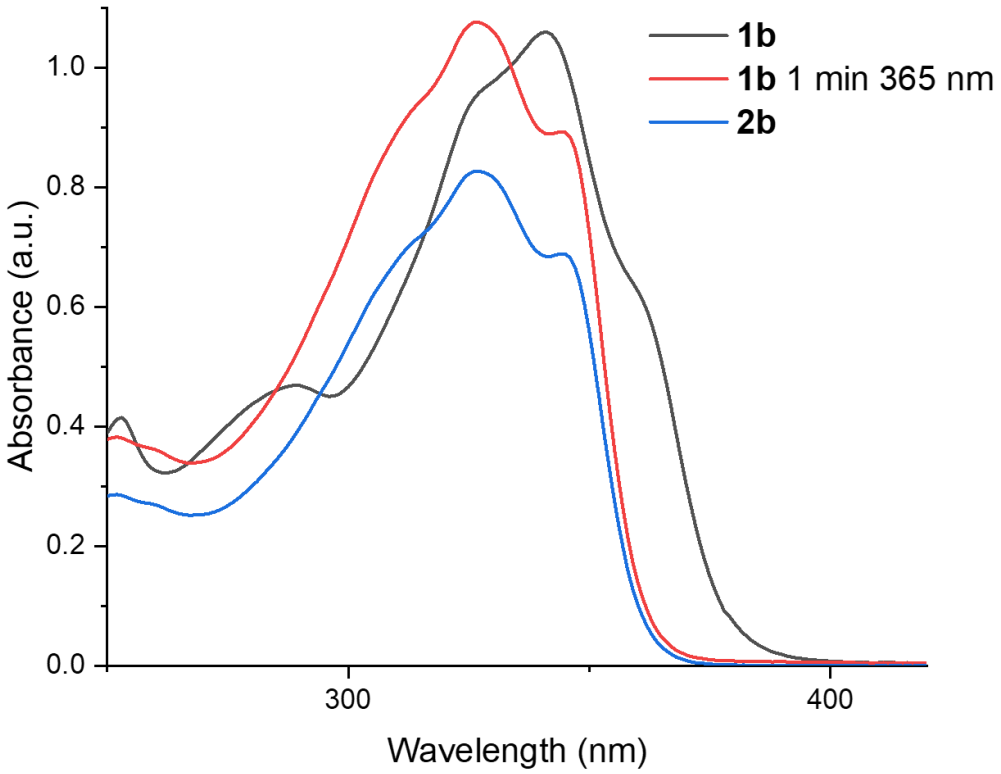


Figure S70. UV/vis spectra (CH_3CN, 298 K) of 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**) (3.15 µM) without irradiation (black) and after irradiation with 365 nm for 1 minute (red) as well as the reference spectrum of 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (blue, 3.15 µM).

6.3 5-(2-Cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**)

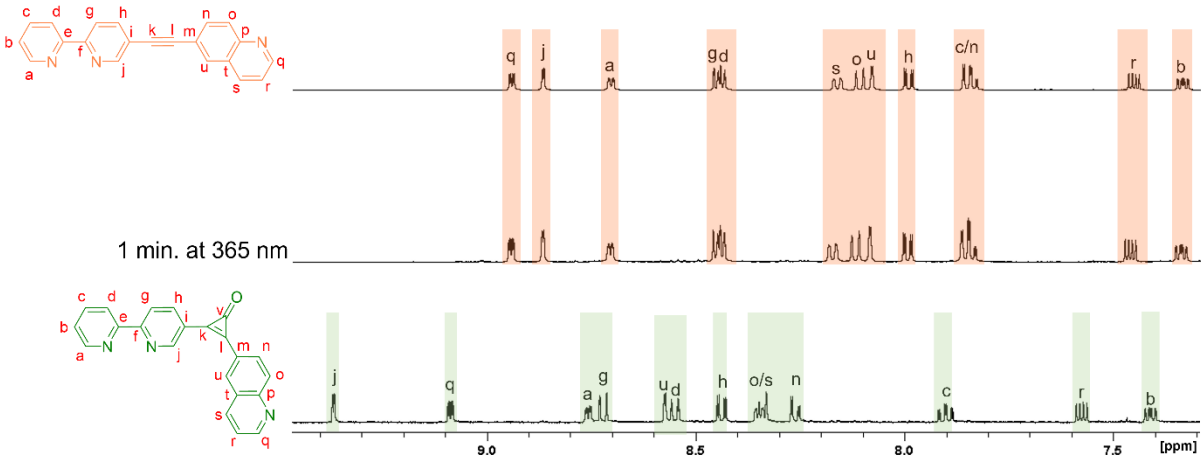


Figure S71. ^1H NMR spectra (500 MHz, $CDCl_3$, 298 K) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**) without irradiation (bottom) and after irradiation with 365 nm for 1 minute as well as the reference spectrum of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**) (top).

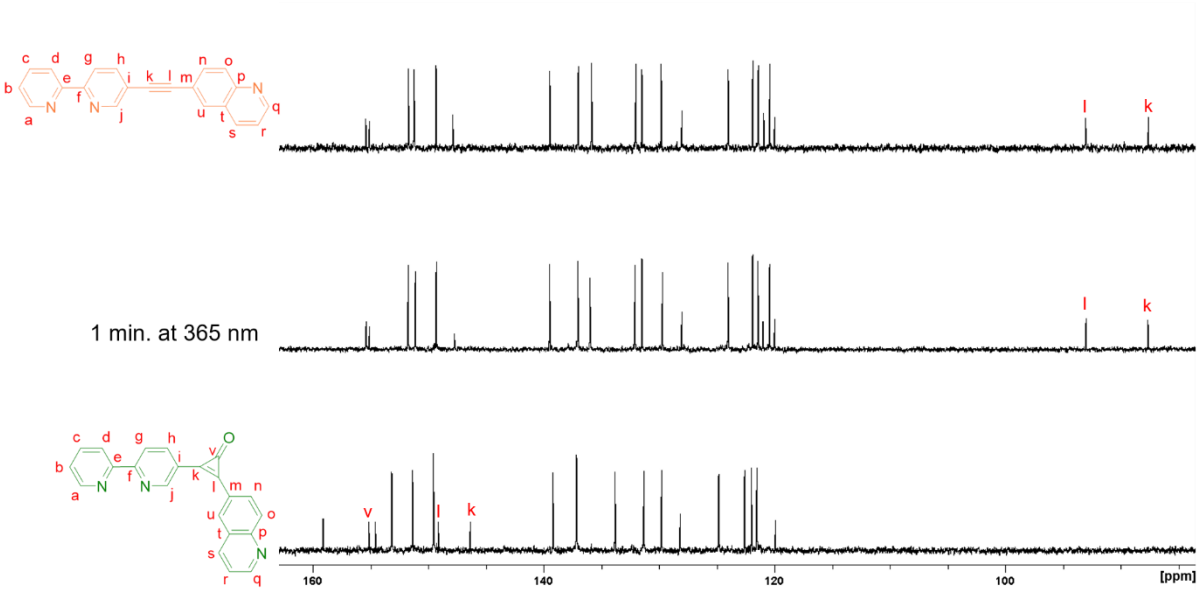


Figure S72. ^{13}C NMR spectra (126/151 MHz, $CDCl_3$, 298 K) 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**) without irradiation (bottom) and after irradiation with 365 nm for 1 minute as well as the reference spectrum of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**) (top).

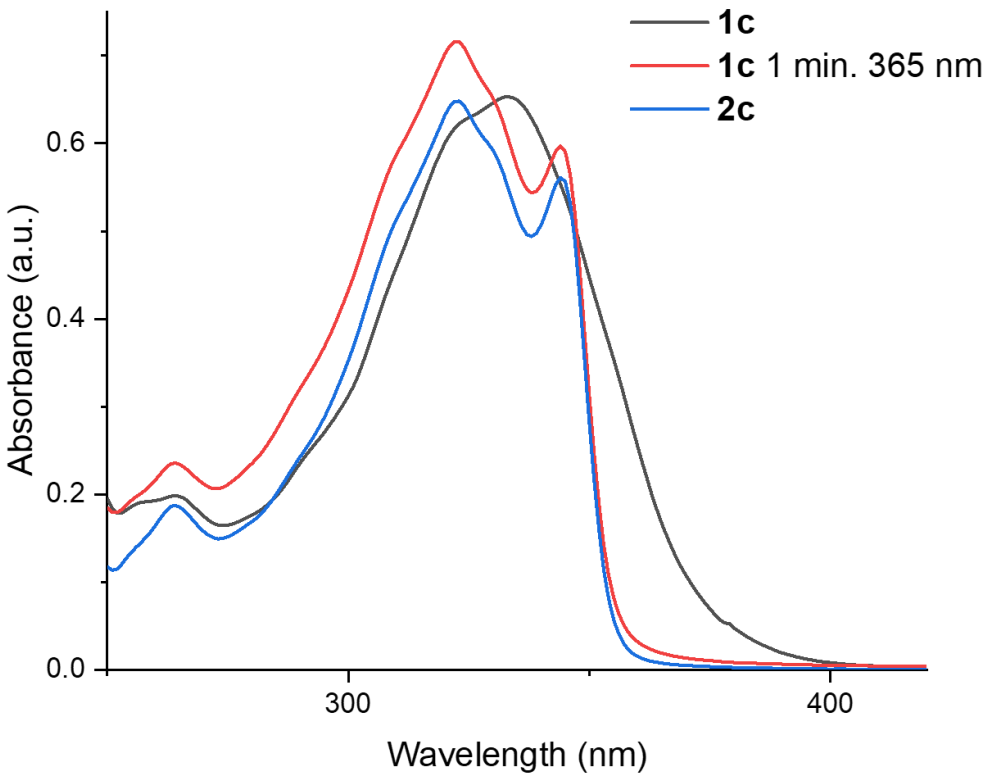
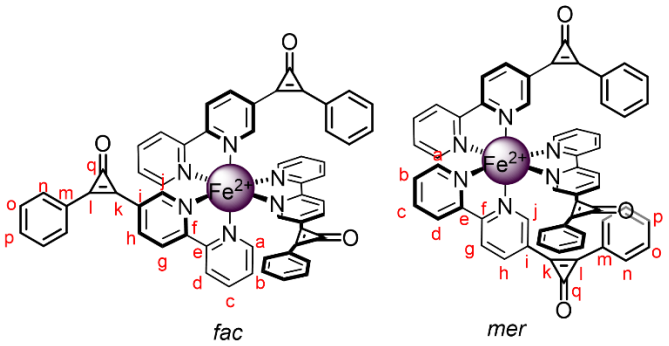


Figure S73. UV/vis spectra (CH_3CN, 298 K) of 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**) (1.86 µM) without irradiation (black) and after irradiation with 365 nm for 1 minute (red) as well as the reference spectrum of 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**) (blue, 2.44 µM).

7 M-CPOnes 1a-1c

7.1 Fe-CPOne-**1a**



Iron tetrafluoroborate hexahydrate (3.36 mg, 10.0 µmol) and 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (8.5 mg, 30.0 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 8.83-8.78 (t, ^3J = 8.2 Hz, 2H, $H_{d,g}$), 8.77-8.65 (m, 8H, $H_{d,g,h}$), 8.59 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 2H, H_h), 8.29-8.23 (m, 2H, H_c), 8.23-8.18 (m, 2H, H_c), 8.00 (d, ^4J = 0.7 Hz, 1H, H_j), 7.95 (d, ^4J = 1.0 Hz, 1H, H_j), 7.89 (d, ^4J = 0.9 Hz, 1H, H_j), 7.79 (d, ^4J = 1.0 Hz, 1H, H_j), 7.72-7.67 (m, 2H, $H_{a,p}$), 7.63-7.46 (m, 24H, $H_{a,b,n,o,p}$), 7.40 (d, ^3J = 5.5 Hz, 1H, H_a).

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 162.4 (C_f), 162.3 (C_f), 162.0 (C_f), 161.9 (C_f),159.5 (C_e), 159.4 (C_e), 159.2 (C_e), 158.9 (C_e), 157.3 (C_j), 157.1 (C_j), 156.7 (C_j), 156.5 (C_a), 156.3 (C_j), 156.0 (C_a), 155.5 (C_a), 154.8 (C_q), 154.7 (C_q), 154.6 (C_q), 154.2 (C_l), 154.0 (C_l), 154.0 (C_l), 144.3 (C_k), 144.2 (C_k), 144.1 (C_k), 144.0 (C_k), 141.7 (C_h),141.5 (C_h), 141.4 (C_h), 141.3 (C_h), 140.2 (C_c), 140.2 (C_c), 140.1 (C_c), 134.9 (C_p), 134.8 (C_p), 134.7 (C_p), 132.6 ($C_{n/o}$), 132.6 ($C_{n/o}$), 132.5 ($C_{n/o}$), 132.5 ($C_{n/o}$), 130.6 ($C_{n/o}$), 130.4 ($C_{n/o}$), 130.4 ($C_{n/o}$), 129.6 (C_b), 129.4 (C_b), 129.3 (C_b), 129.1 (C_b), 127.0 ($C_{d/g}$), 126.5 ($C_{d/g}$), 125.8 ($C_{d/g}$), 125.8 ($C_{d/g}$), 125.4 ($C_{d/g}$), 125.4 ($C_{d/g}$), 124.1 (C_m), 124.1 (C_m), 124.1 (C_i), 124.0 (C_m), 124.0 (C_m), 123.9 (C_i), 123.7 (C_i), 123.5 (C_i).

HRMS (ESI, CH_3CN) *m/z*: 454.1092 [Fe-CPOne-**1a**]$^{2+}$, 440.1118 [Fe-CPOne-**1a** -CO]$^{2+}$, 426.1142 [Fe-CPOne-**1a** -2(CO)]$^{2+}$, 412.1169 [Fe-CPOne-**1a** -3(CO)]$^{2+}$.

FT-IR: ṽ = 3598.7 (w), 3088.7 (w), 1842.7 (s), 1626.9 (s), 1487.5 (w), 1466.9 (m), 1447.2 (m), 1385.4 (w), 1341.8 (m), 1277.74 (w), 1243.3 (w), 1050.7 (s), 852.5 (m), 792.6 (m), 768.6 (m), 732.4 (m), 687.3 (s), 543.5 (w), 519.8 (m) cm^{-1}.

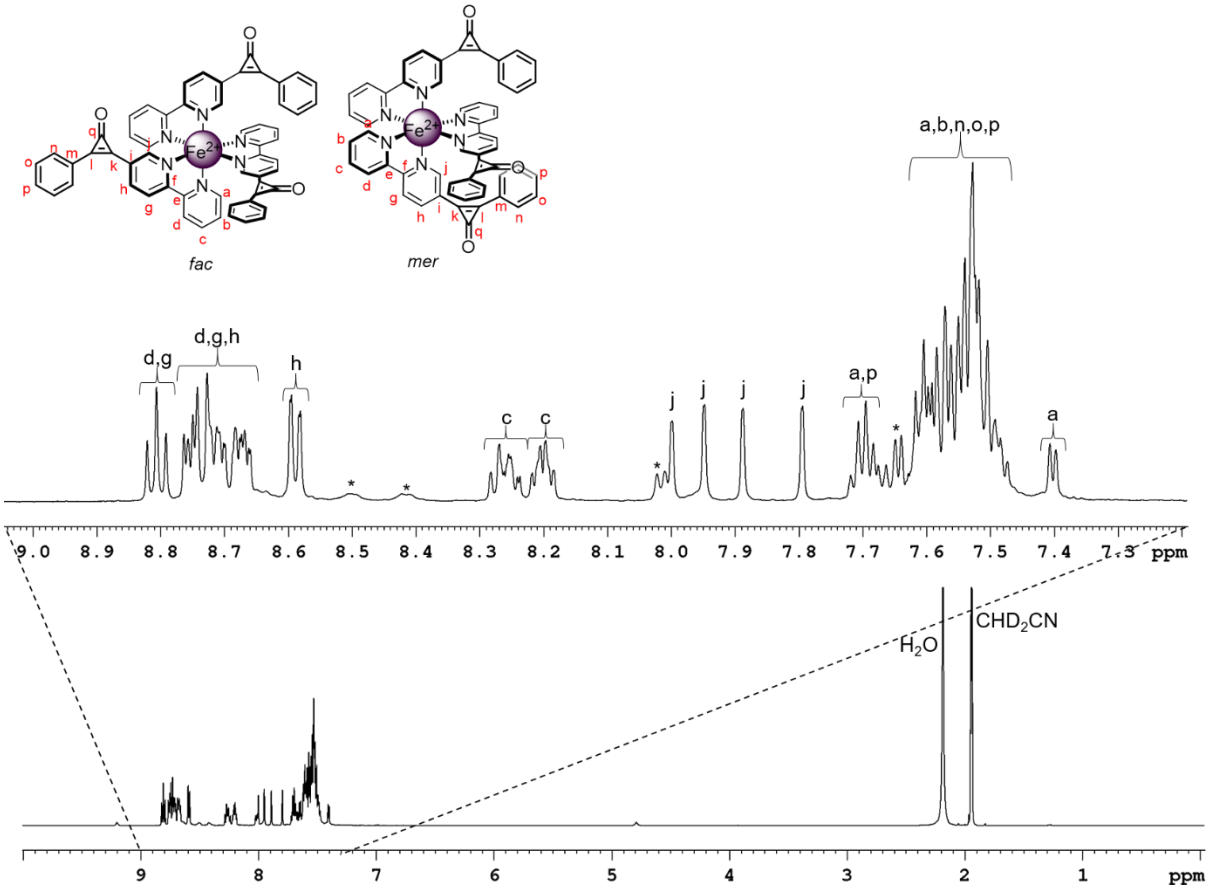


Figure S74. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Fe-CPOne-**1a**. Note: Signals labelled with * are attributed to free ligand.

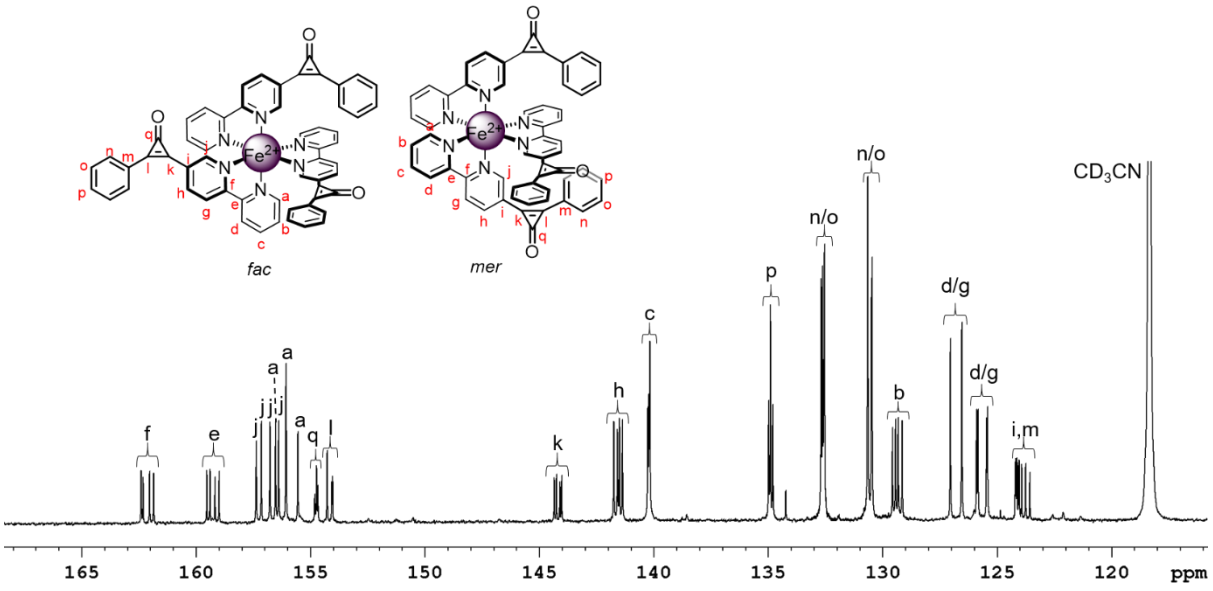


Figure S75. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Fe-CPOne-**1a**.

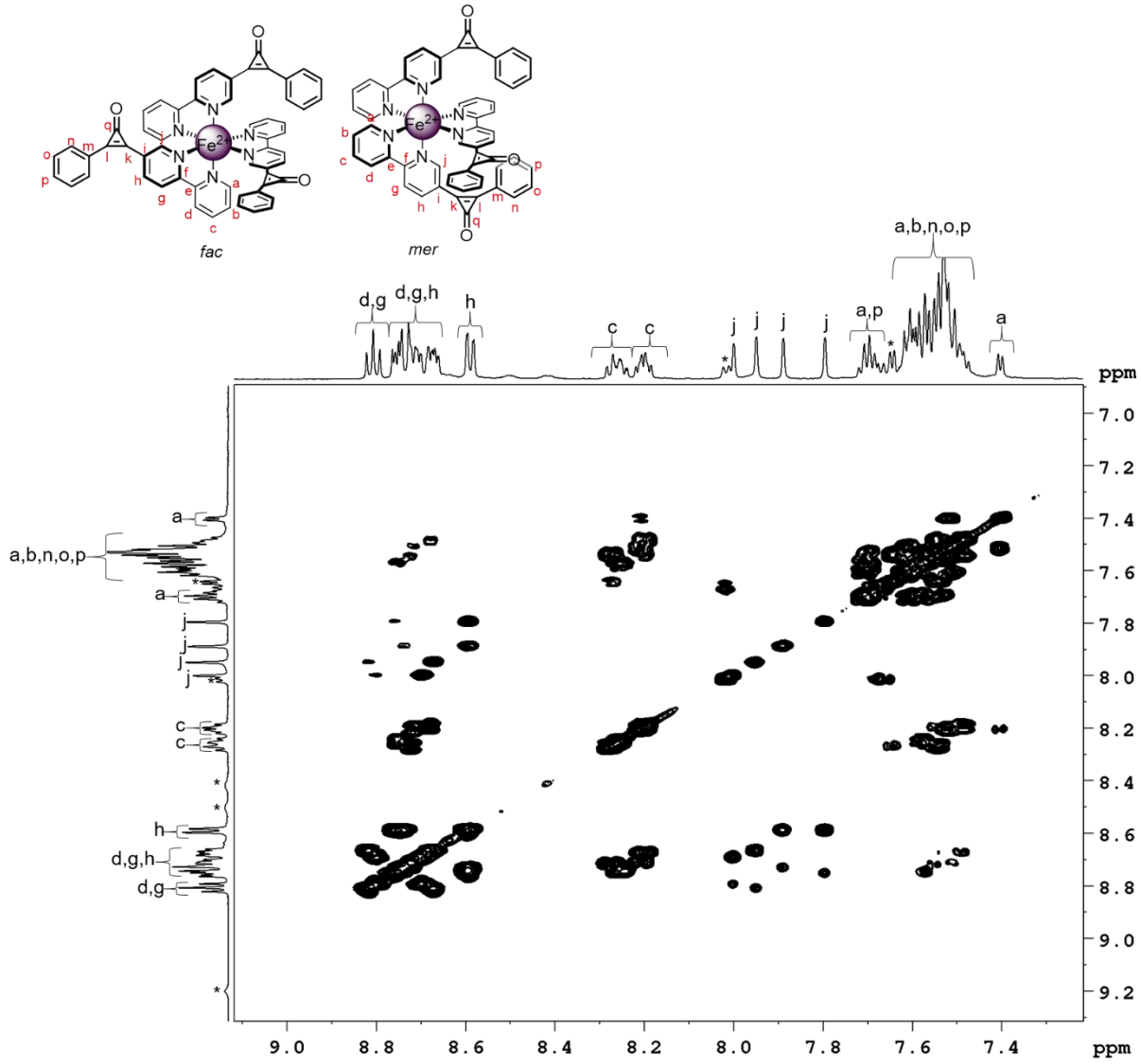


Figure S76. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Fe-CPOne-**1a**. Note: Signals labelled with * are attributed to free ligand.

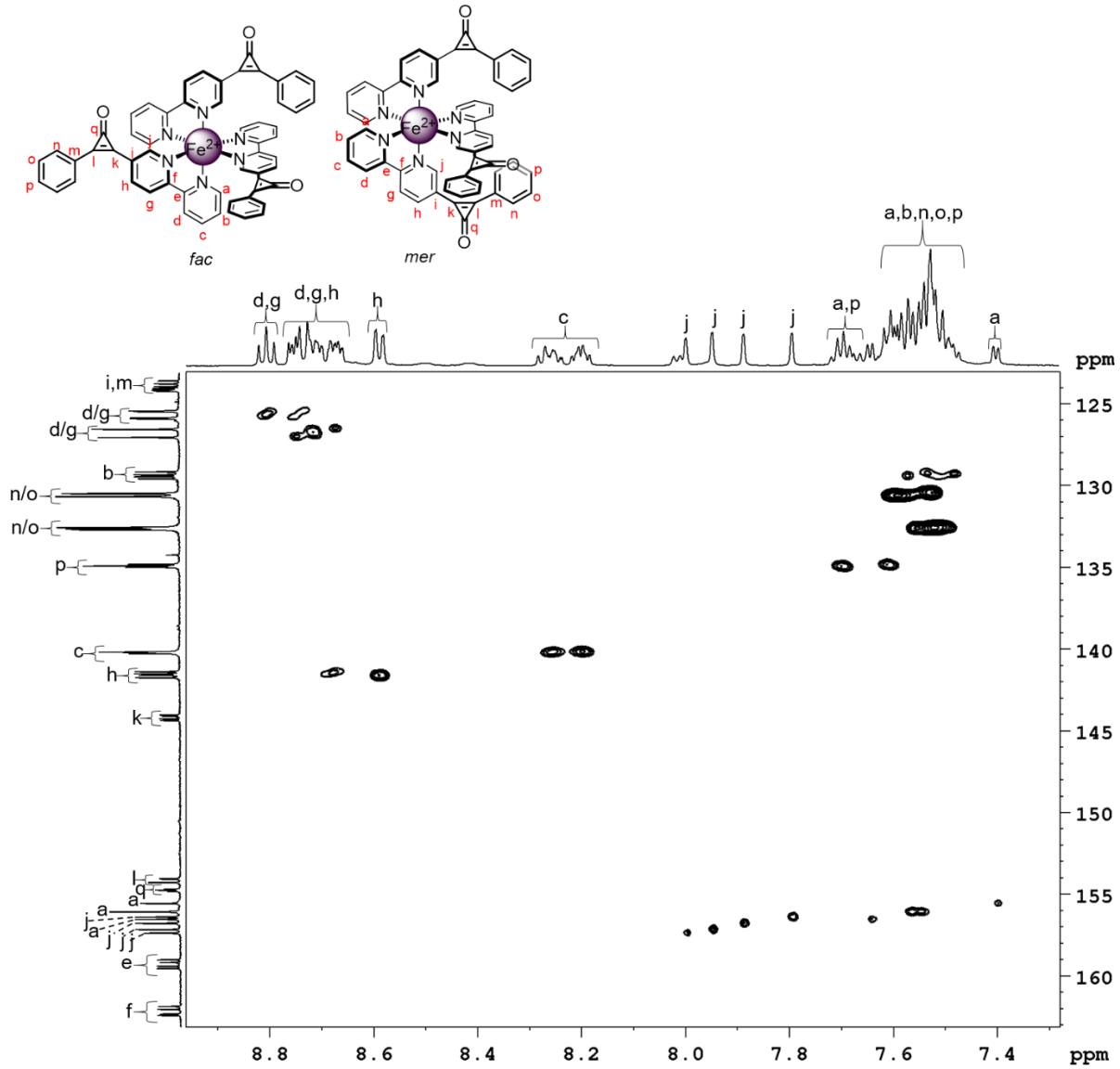


Figure S77. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Fe-CPOne-**1a**.

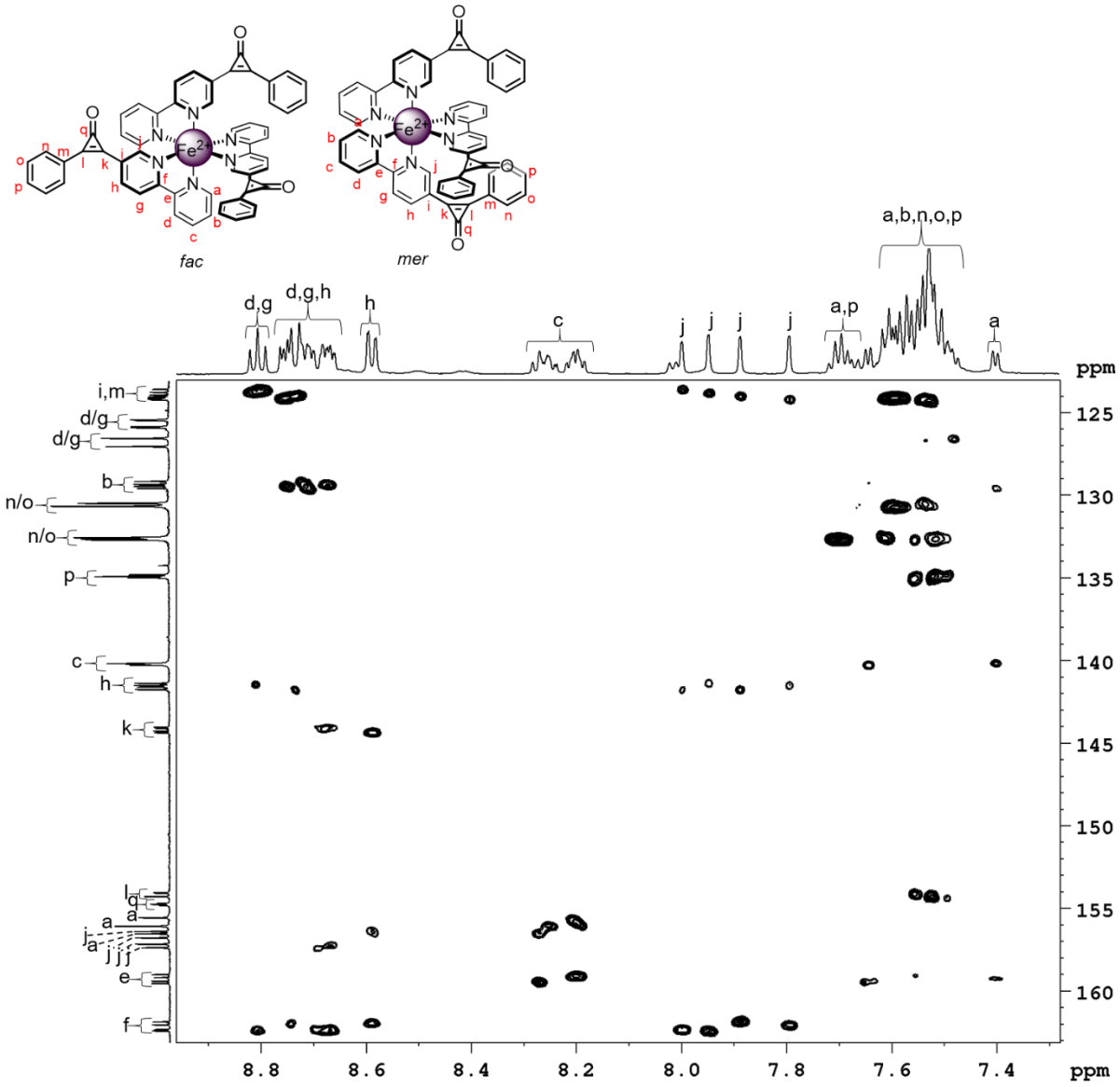


Figure S78. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Fe-CPOne-**1a**.

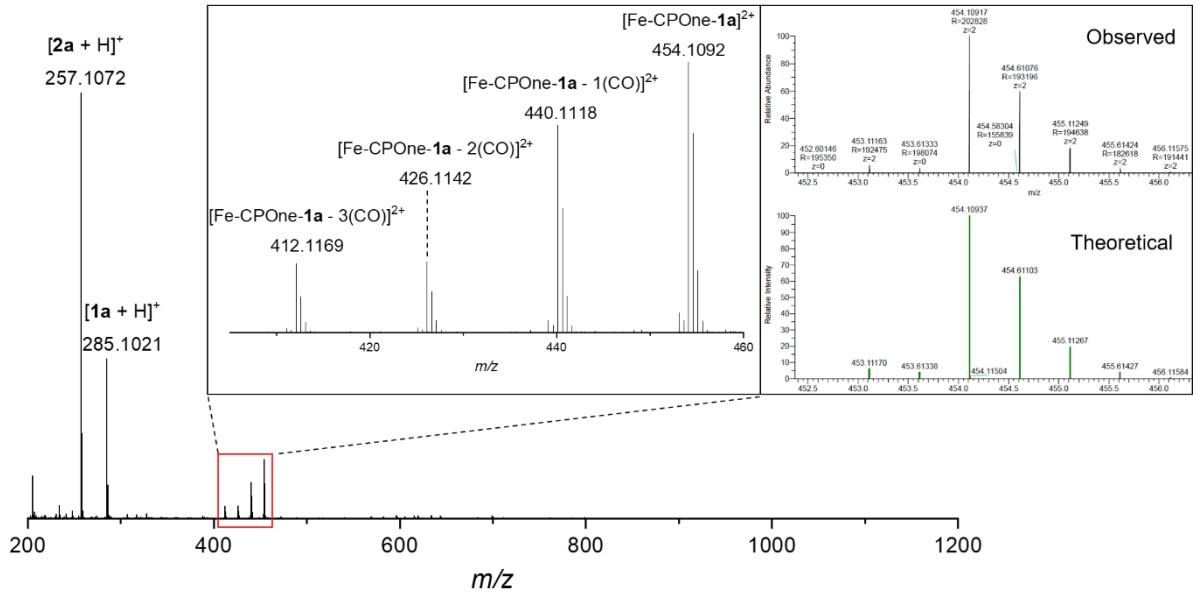
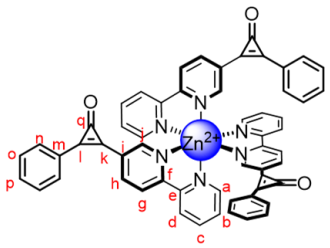


Figure S79. High resolution ESI mass spectrum of Fe-CPOne-**1a** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

7.2 Zn-CPOne-**1a**



Zinc trifluoromethanesulfonate (2.94 mg, 8.1 µmol) and 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (6.9 mg, 24.3 µmol) were dissolved in CD_3CN (0.5 mL).

Note: Because of the broadness of the signals, unambiguous assignment of the ^{1}H and ^{13}C NMR spectra was not possible and *fac/mer* isomers could not be distinguished.

HRMS (ESI, CH_3CN) *m/z*: 1065.1632 [Zn-CPOne-**1a** +OTf]$^{1+}$, 458.1054 [Zn-CPOne-**1a**]$^{2+}$, 444.1080 [Zn-CPOne-**1a** -CO]$^{2+}$, 430.1106 [Zn-CPOne-**1a** -2(CO)]$^{2+}$.

FT-IR: $\tilde{\nu}$ = 3084.5 (w), 2251.6 (w), 2079.5 (w), 1846.5 (s), 1630.1 (m), 1603.3 (m), 1561.3 (w), 1473.3 (m), 1440.9 (m), 1381.3 (w), 1342.3 (w), 1317.7 (w), 1274.8 (s), 1258.5 (s), 1222.9 (s), 1148.1 (s), 1028.4 (s), 925.0 (w), 858.6 (w), 799.1 (m), 767.1 (s), 751.0 (s), 736.3 (m), 688.2 (m), 658.0 (w), 635.0 (s), 572.6 (m), 542.9 (w), 516.2 (m) cm^{-1}.

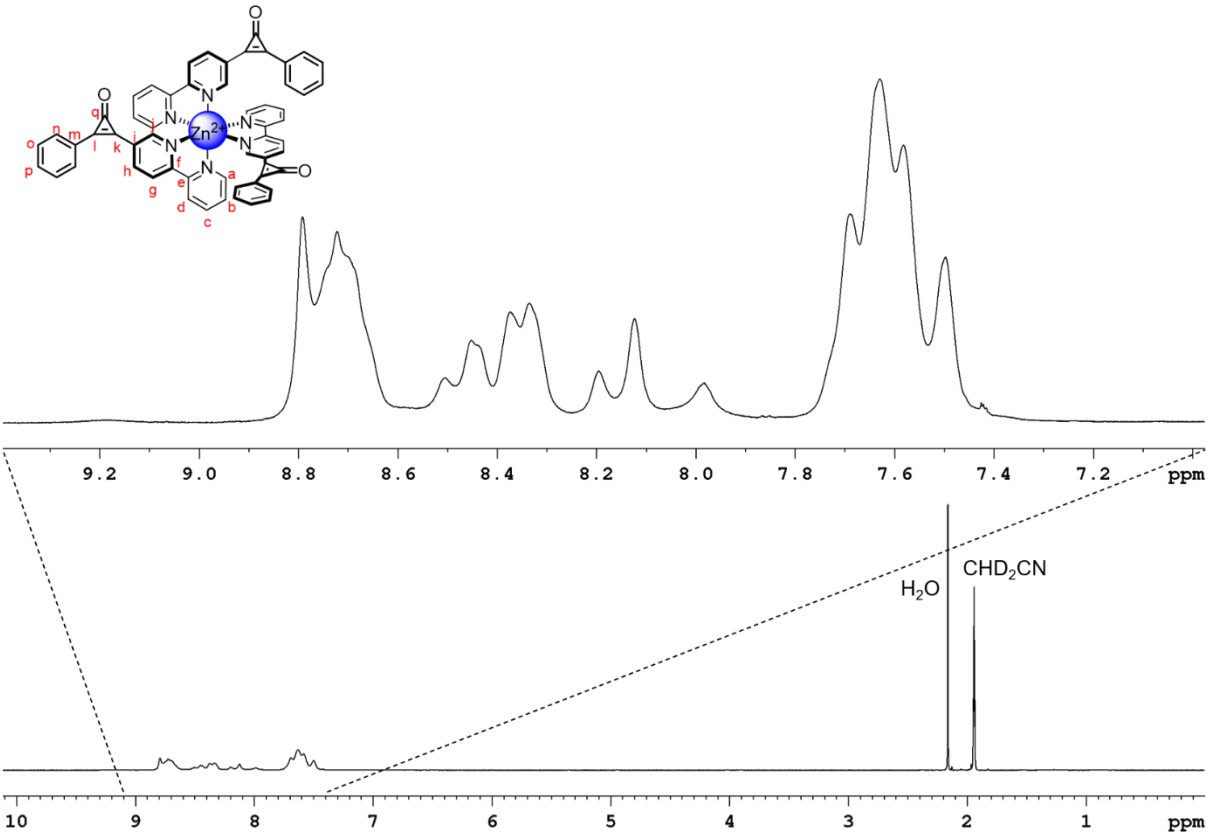


Figure S80. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Zn-CPOne-**1a**.

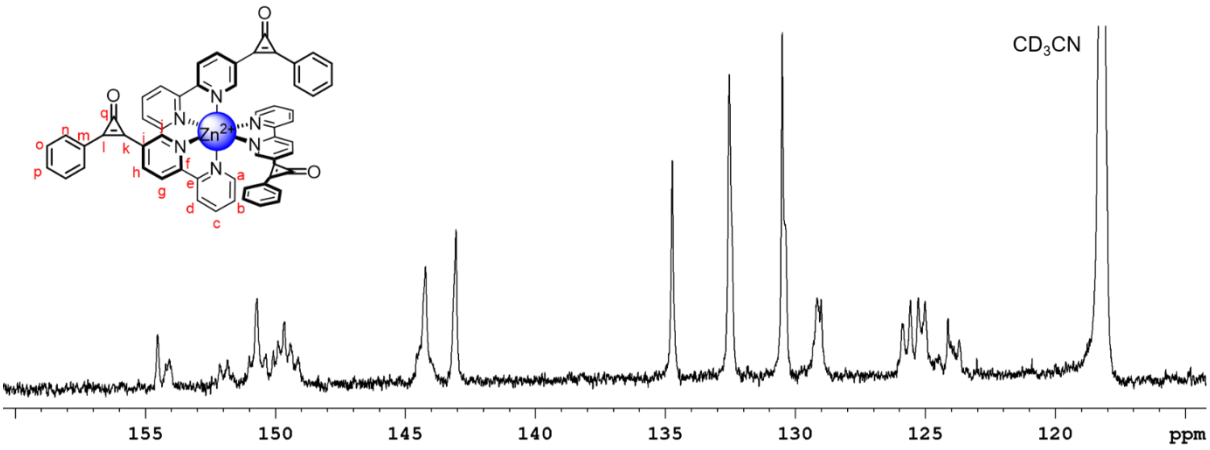


Figure S81. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Zn-CPOne-**1a**.

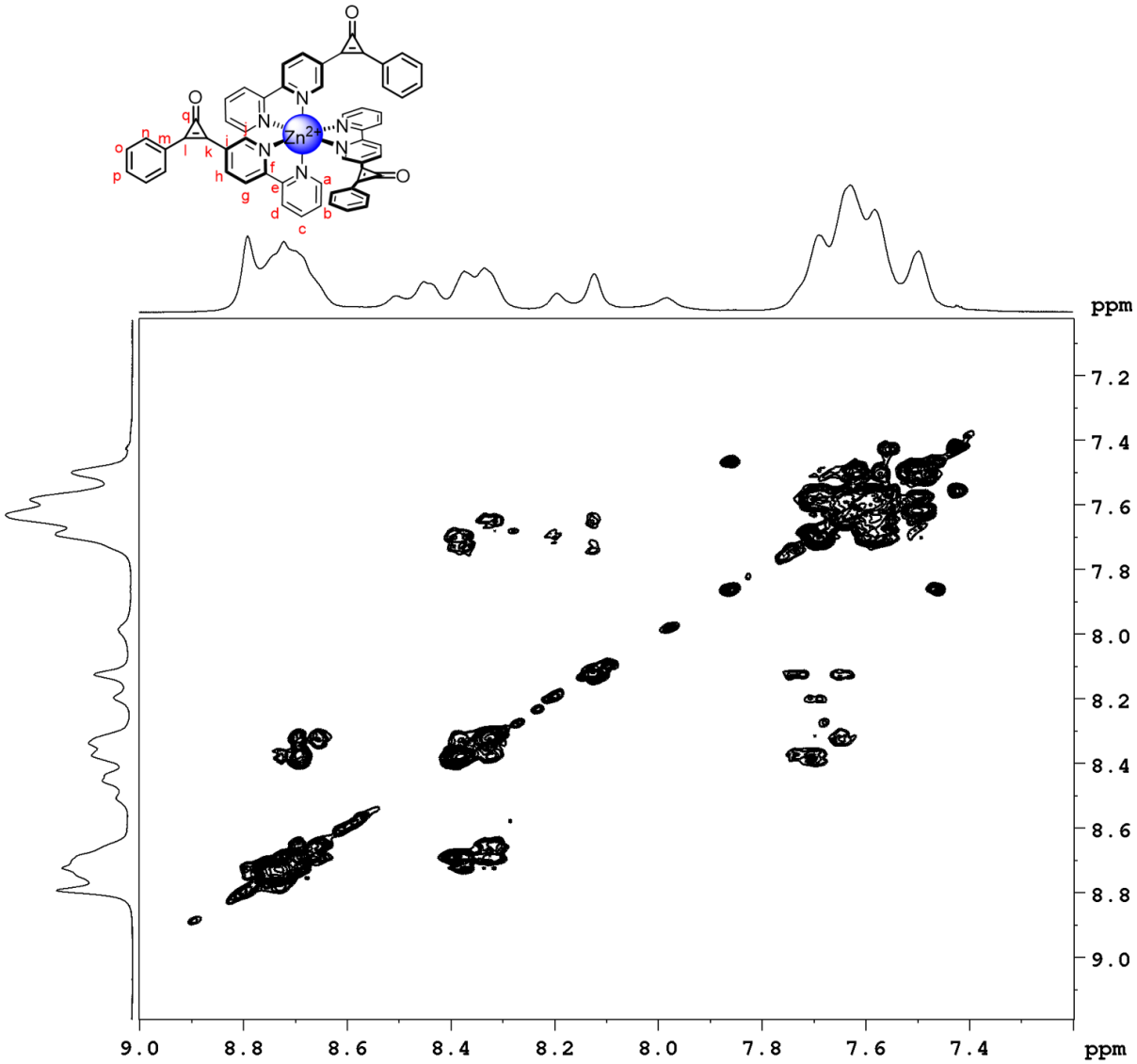


Figure S82. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Zn-CPOne-**1a**.

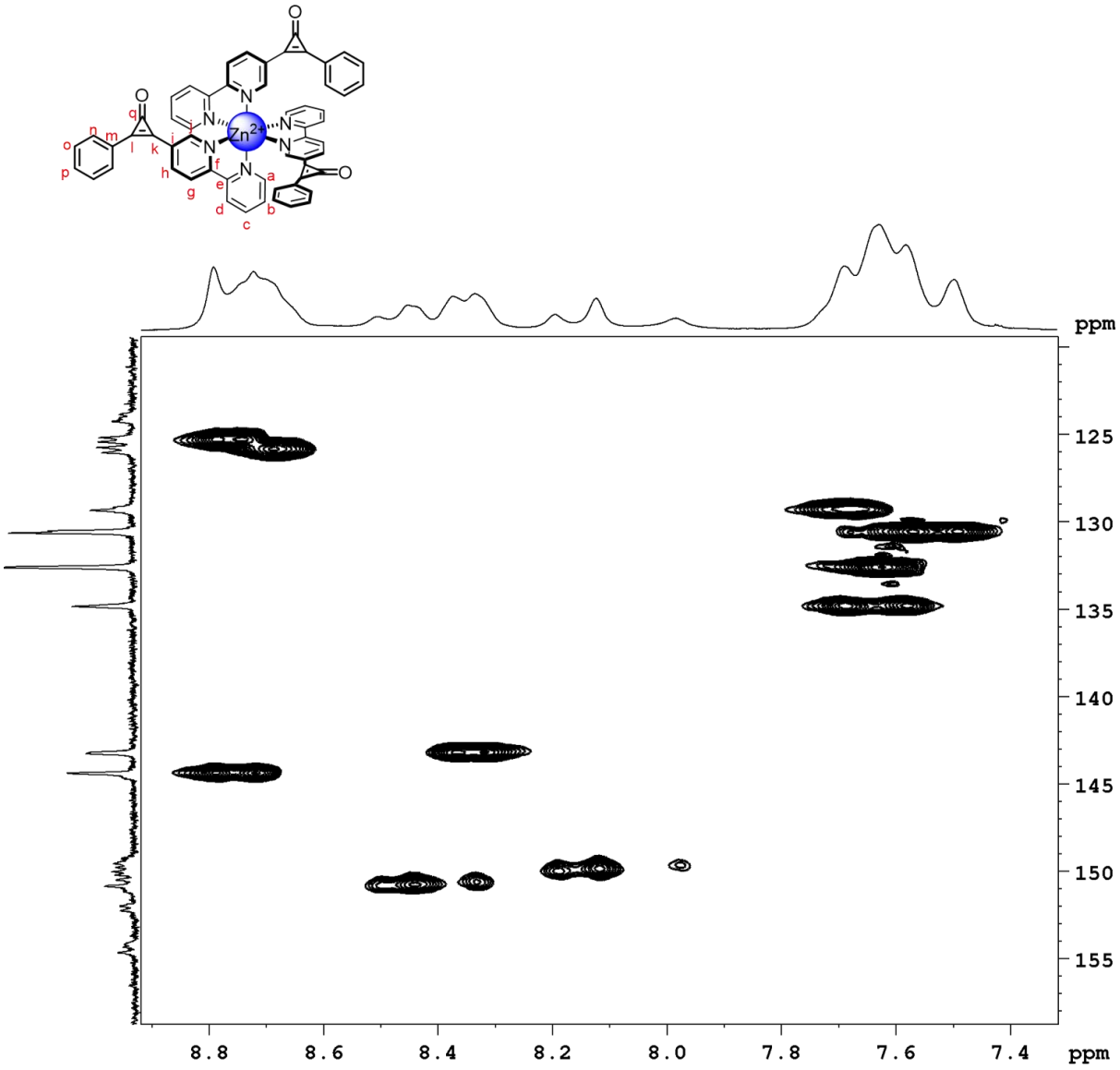


Figure S83. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Zn-CPOne-**1a**.

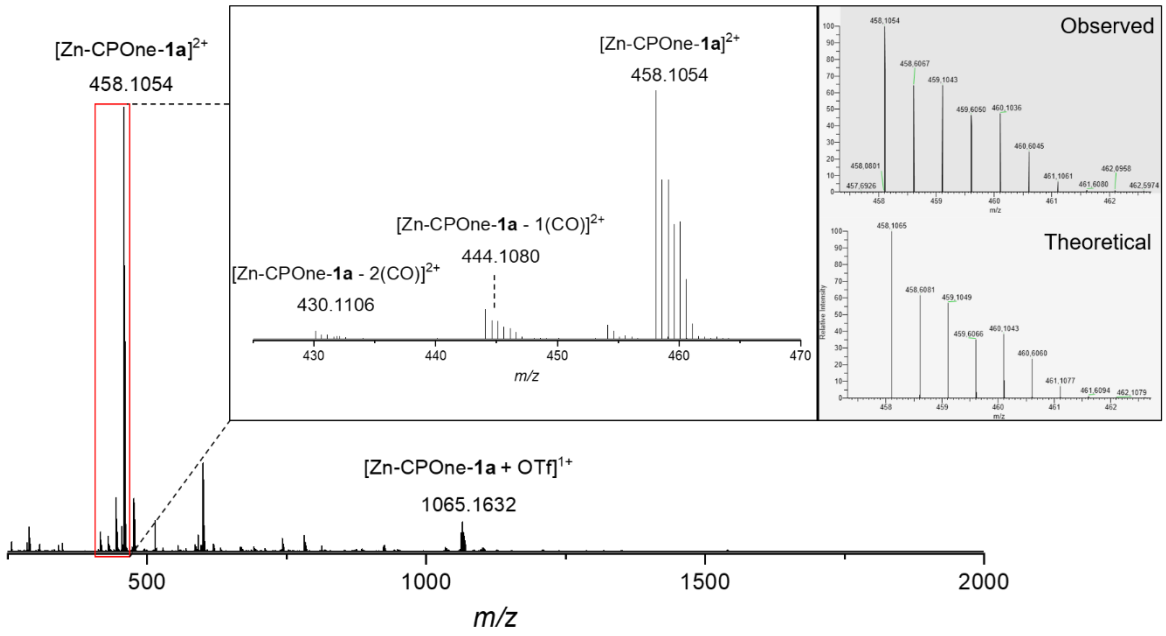


Figure S84. High resolution ESI mass spectrum of Zn-CPOne-**1a** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

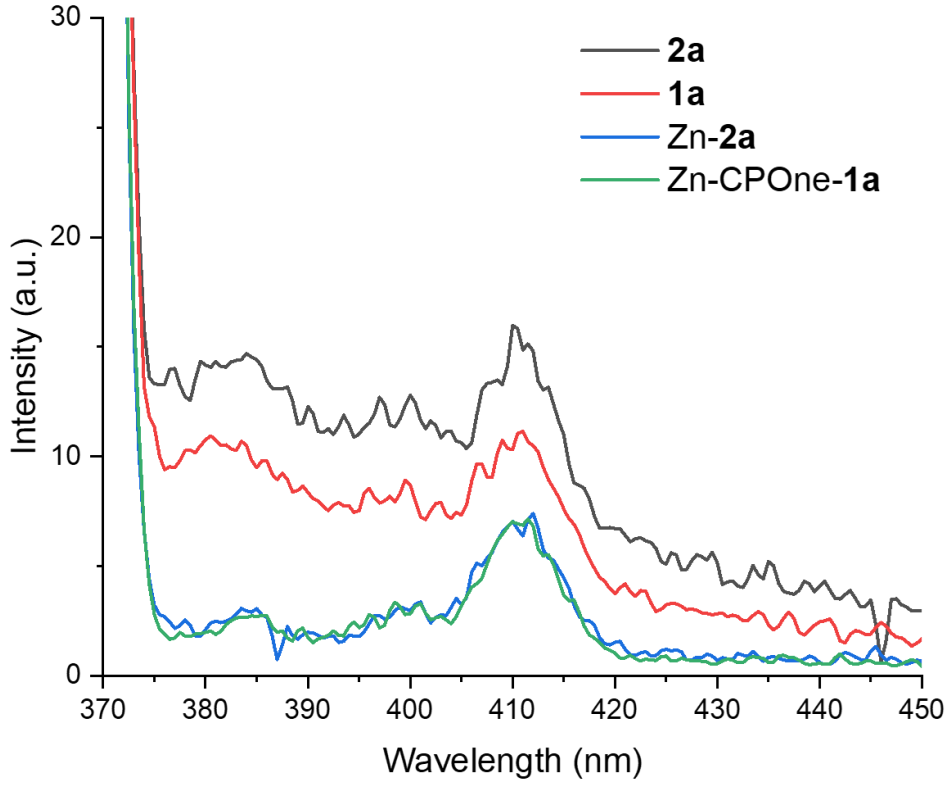


Figure S85. Emission spectra (CH_3CN, 298 K) with excitation at 365 nm of 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (black, 0.20 μM), 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (red, 0.20 μM), Zn-**2a** (blue, 0.02 μM) and Zn-CPOne-**1a** (green, 0.02 μM).

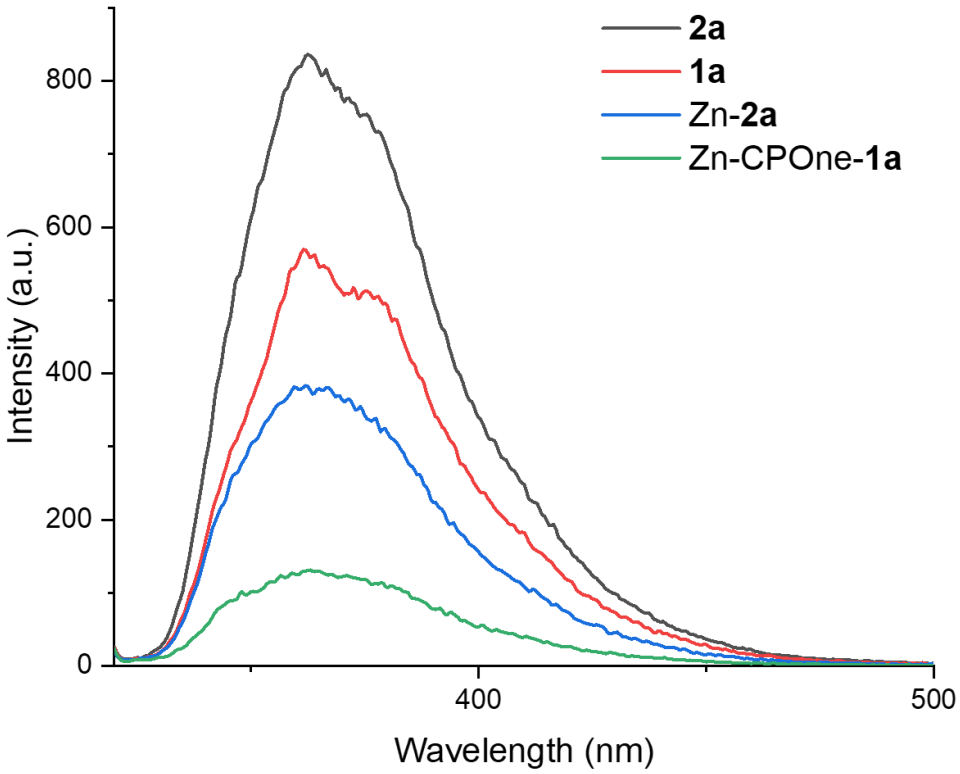
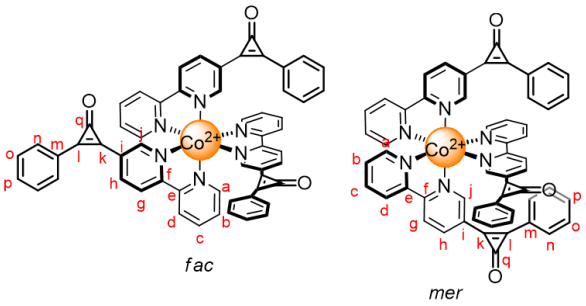


Figure S86. Emission spectra (CH_3CN, 298 K) with excitation at 312 nm of 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (black, 0.20 µM), 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (red, 0.20 µM), Zn-**2a** (blue, 0.02 µM) and Zn-CPOne-**1a** (green, 0.02 µM).

7.3 Co-CPOne-**1a**



Cobalt bis(trifluoromethylsulfonyl)imide (6.46 mg, 10.4 µmol) and 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (8.9 mg, 31.3 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 103.4 (br, 1H, $H_{a/j}$), 98.2 (br, 1H, $H_{a/j}$), 96.3 (br, 1H, $H_{a/j}$), 92.0 (s, 1H, H_{d1}), 91.0 (br, 1H, $H_{a/j}$), 88.1 (s, 1H, H_{d2}), 85.8 (s, 1H, H_{g1}), 85.7 (s, 1H, H_{dfac}), 85.2 (br, 1H, $H_{a/j}$), 82.3 (s, 1H, H_{gfac}), 81.6 (br, 1H, $H_{a/j}$), 81.4 (s, 1H, H_{d3}), 79.1 (s, 1H, H_{g2}), 75.1 (s, 1H, H_{g3}), 52.3 (s, 1H, H_{b2}), 51.6 (s, 1H, H_{b1}), 46.8 (s, 1H, H_{b3}), 45.9 (s, 1H, H_{bfac}), 19.6 (s, 1H, H_{c1}), 17.7 (s, 1H, H_{c2}), 16.6 (s, 1H, H_{h1}), 15.0 (s, 1H, H_{hfac}), 14.6 (s, 1H, H_{cfac}), 12.8 (s, 1H, H_{c3}), 11.5 (s, 1H, H_{h2}), 10.0 (s, 1H, H_{h3}), 6.8 (s, 1H, H_p), 6.5 (s, 1H, H_n), 6.5 (s, 1H, H_p), 6.3 (s, 1H, H_p), 6.2 (s, 1H, H_p), 6.1 (s, 1H, H_n), 6.0 (s, 1H, H_n), 5.8 (s, 1H, H_n), 2.9 (s, 1H, H_o), 2.8 (s, 1H, H_{ofac}), 1.7 (s, 1H, H_o), 1.3 (s, 1H, H_o).

Note: While it was possible to assign the proton signals within one spin system (indicated by numbers) based on the COSY spectrum, the different spin systems within each ligand could not be correlated to a particular ligand environment. For the signals of the bipyridine, the fac isomer was, therefore, tentatively assigned based on the integral of the signals. The three remaining sets of signals corresponding to the mer isomer were arbitrarily labelled with black, red, and blue labels according to their decreasing chemical shift. Protons corresponding to the R substituent were tentatively assigned in grey due to the signal overlap in the diamagnetic region of the spectra.[11] *Protons a and j are assigned in grey based on related complexes.*[11]

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 652.2 (s), 649.5 (s), 648.1 (s), 644.4 (s), 642.9 (s), 609.9 (d, $^1J_{CH}$ = 182 Hz, C_{b1}), 605.9 (d, $^1J_{CH}$ = 179 Hz, C_{bfac}), 603.1 (d, $^1J_{CH}$ = 175 Hz, C_{b2}), 597.6 (d, $^1J_{CH}$ = 171 Hz, C_{b3}), 429.9 (d, $^1J_{CH}$ = 163 Hz, C_{d1}), 428.9 (d, $^1J_{CH}$ = 163 Hz, C_{g1}), 424.6 (d, $^1J_{CH}$ = 160 Hz, C_{dfac}), 423.6 (d, $^1J_{CH}$ = 158 Hz, C_{g2}), 416.7 (d, $^1J_{CH}$ = 193 Hz, C_{gfac}), 415.4 (d, $^1J_{CH}$ = 172 Hz, C_{d2}), 410.0 (d, $^1J_{CH}$ = 137 Hz, C_{g3}), 408.9 (d, $^1J_{CH}$ = 138 Hz, C_{d3}), 223.7 (s), 222.3 (s), 219.3 (s), 217.7 (s), 197.0 (d, $^1J_{CH}$ = 164 Hz, C_{c2}), 188.8 (d, $^1J_{CH}$ = 164 Hz, C_{c1}), 184.6 (d, $^1J_{CH}$ = 168 Hz, C_{c3}), 176.6 (d, $^1J_{CH}$ = 167 Hz, C_{cfac}), 172.3 (d, $^1J_{CH}$ = 172 Hz, C_{hfac}), 171.1-167.1 (overlapping signals), 166.6 (d, $^1J_{CH}$ = 167 Hz, C_{h1}), 159.46 (d, $^1J_{CH}$ = 166 Hz, C_{h3}), 158.4-153.9 (overlapping signals), 153.71 (d, $^1J_{CH}$ = 173 Hz, C_{h2}), 149.8-135.7 (overlapping signals), 134.3-130.5 (overlapping signals, C_p), 130.4-128.1 (overlapping signals, C_o), 127.2-125.0 (overlapping signals, C_n), 126.2-119.4 (overlapping signals), 68.3 (unresolved d, $C_{a/j}$), 66.0 (unresolved d, $C_{a/j}$), 52.0 (unresolved d, $C_{a/j}$), 50.1 (unresolved d, $C_{a/j}$), 26.1 (unresolved d, $C_{a/j}$), 10.0 (unresolved d, $C_{a/j}$), 6.1 (unresolved d, $C_{a/j}$), -103.0 (s, $C_{e/f}$), -109.5 (s, $C_{e/f}$), -127.3, (s, $C_{e/f}$), -135.1, (s, $C_{e/f}$), -146.3, (s, $C_{e/f}$), -151.0, (s, $C_{e/f}$), -170.7, (s, $C_{e/f}$), -176.7 (s, $C_{e/f}$).

Note: Quaternary carbons and carbons close to the paramagnetic centre (a and j) could not be unambiguously assigned due to the lack of HMBC equivalent in the paramagnetic NMR toolbox. Carbons a, j, e and f are assigned based on related complexes.[11]

HRMS (ESI, CH_3CN) *m/z*: 455.6076 [Co-CPOne-**1a**]$^{2+}$, 441.6102 [Co-CPOne-**1a** -CO]$^{2+}$, 427.6130 [Co-CPOne-**1a** -2(CO)]$^{2+}$, 413.6152 [Co-CPOne-**1a** -3(CO)]$^{2+}$.

FT-IR: $\tilde{\nu}$ = 3080.0 (w), 1848.1 (s), 1633.6 (m), 1601.7 (m), 1562.6 (w), 1471.4 (m), 1441.6 (m), 1382.1 (w), 1345.5 (s), 1471.4 (m), 1175.3 (s), 1131.1 (s), 1051.3 (s), 925.2 (w), 855.4 (w), 795.4 (m), 767.6 (s), 748.8 (s), 736.1 (s), 686.9 (m), 651.5 (m), 598.0 (s), 569.1 (s), 509.7 (s) cm^{-1}.

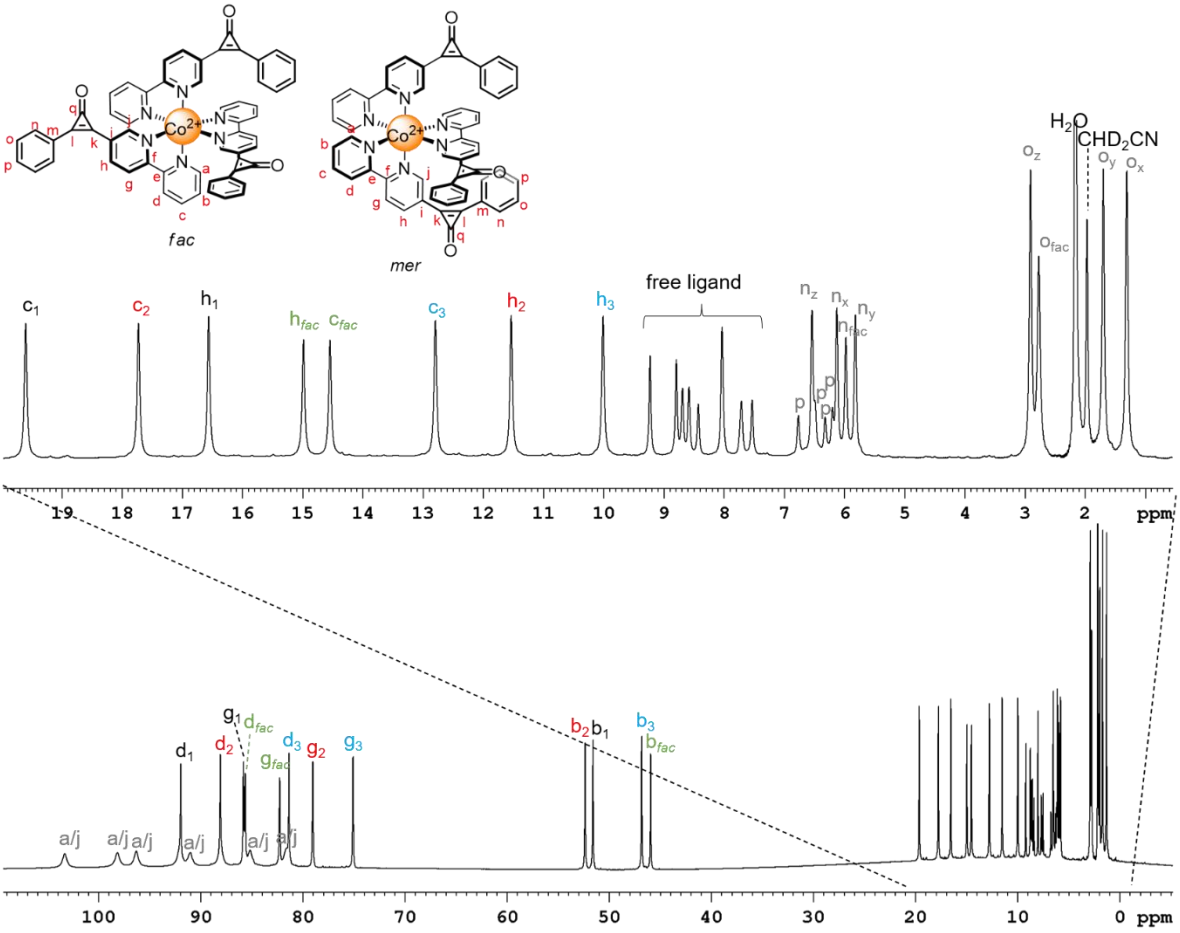


Figure S87. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

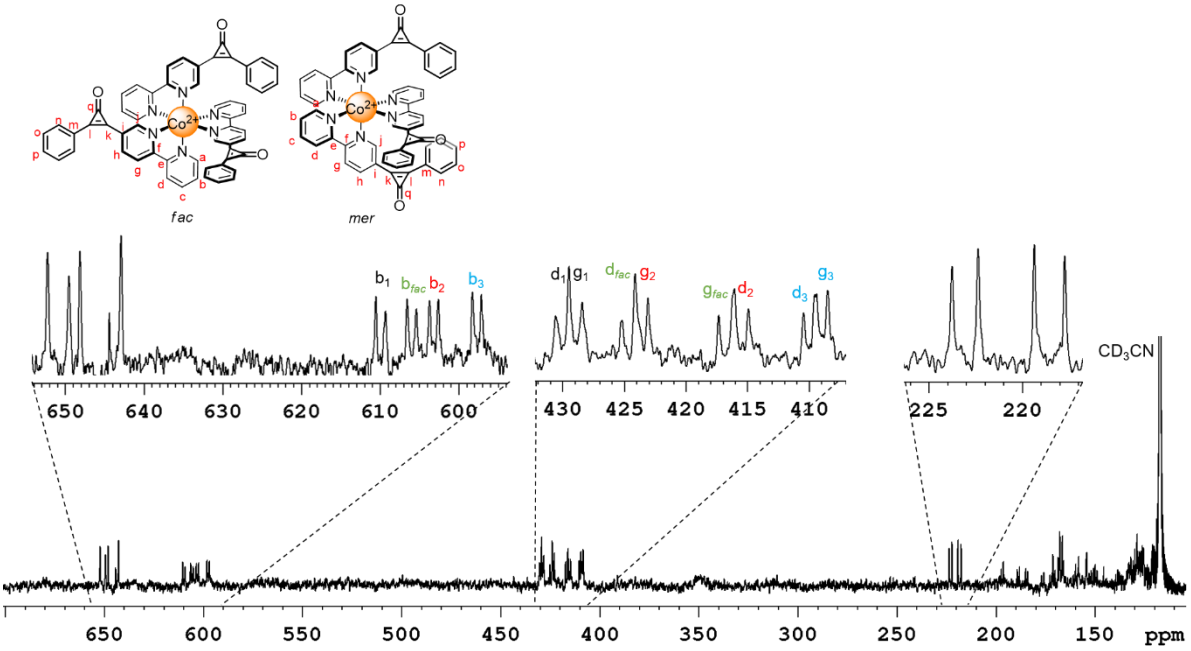


Figure S88. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

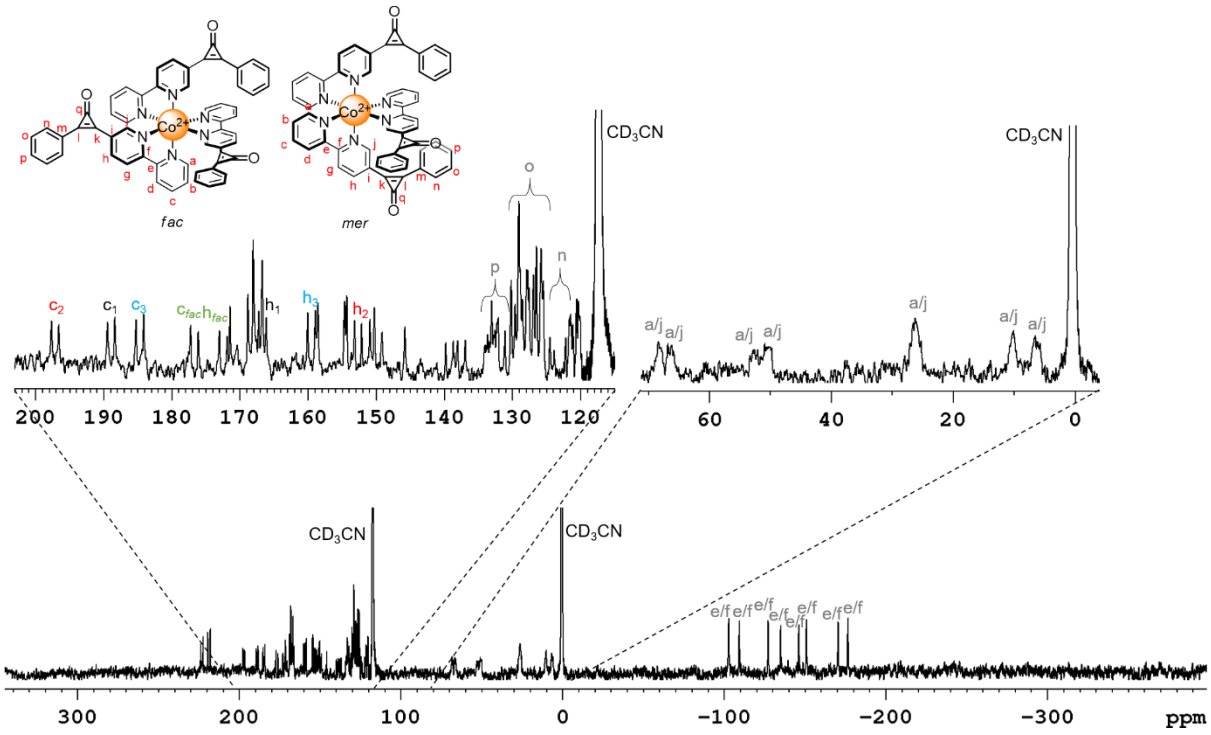


Figure S89. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

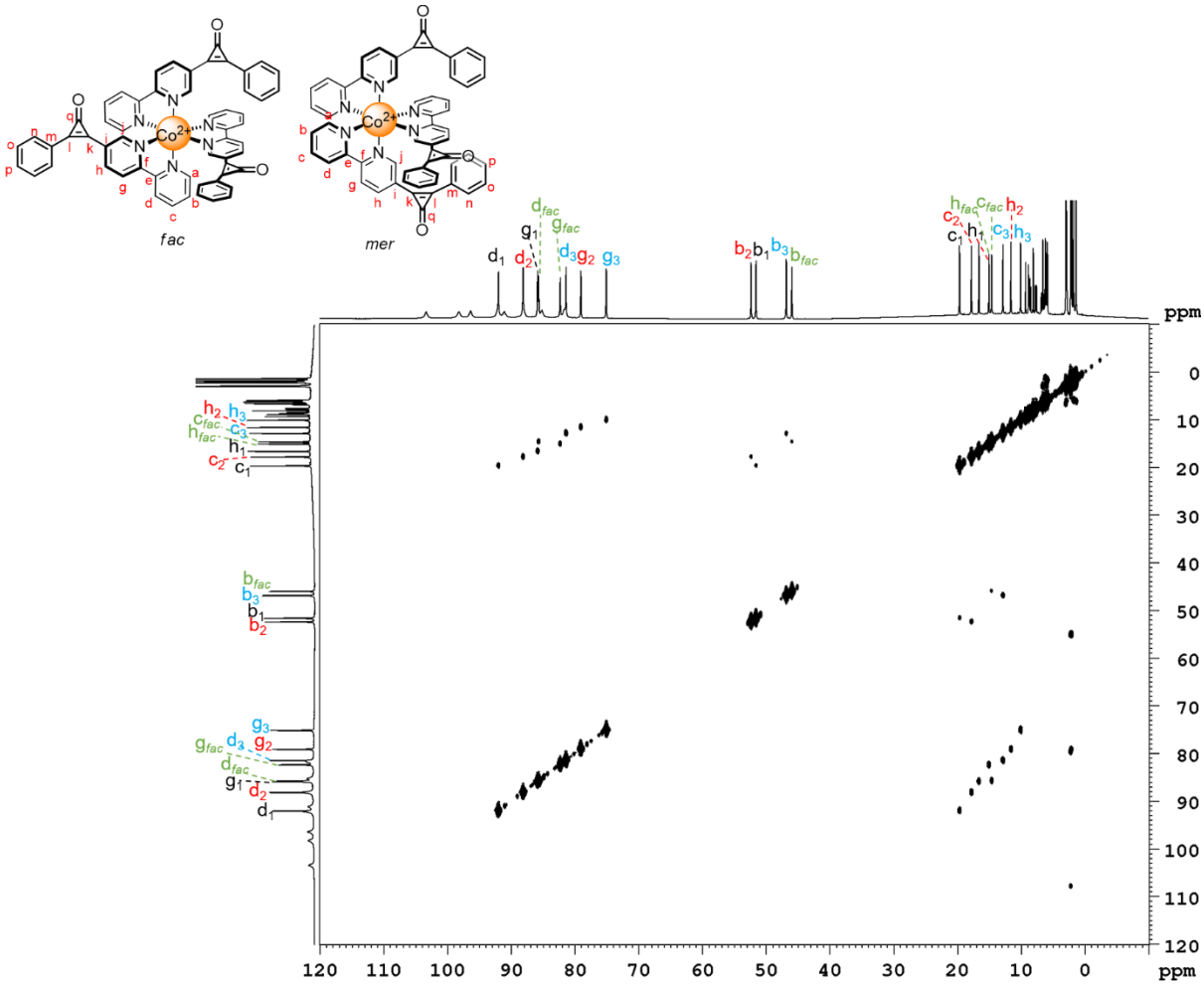


Figure S90. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

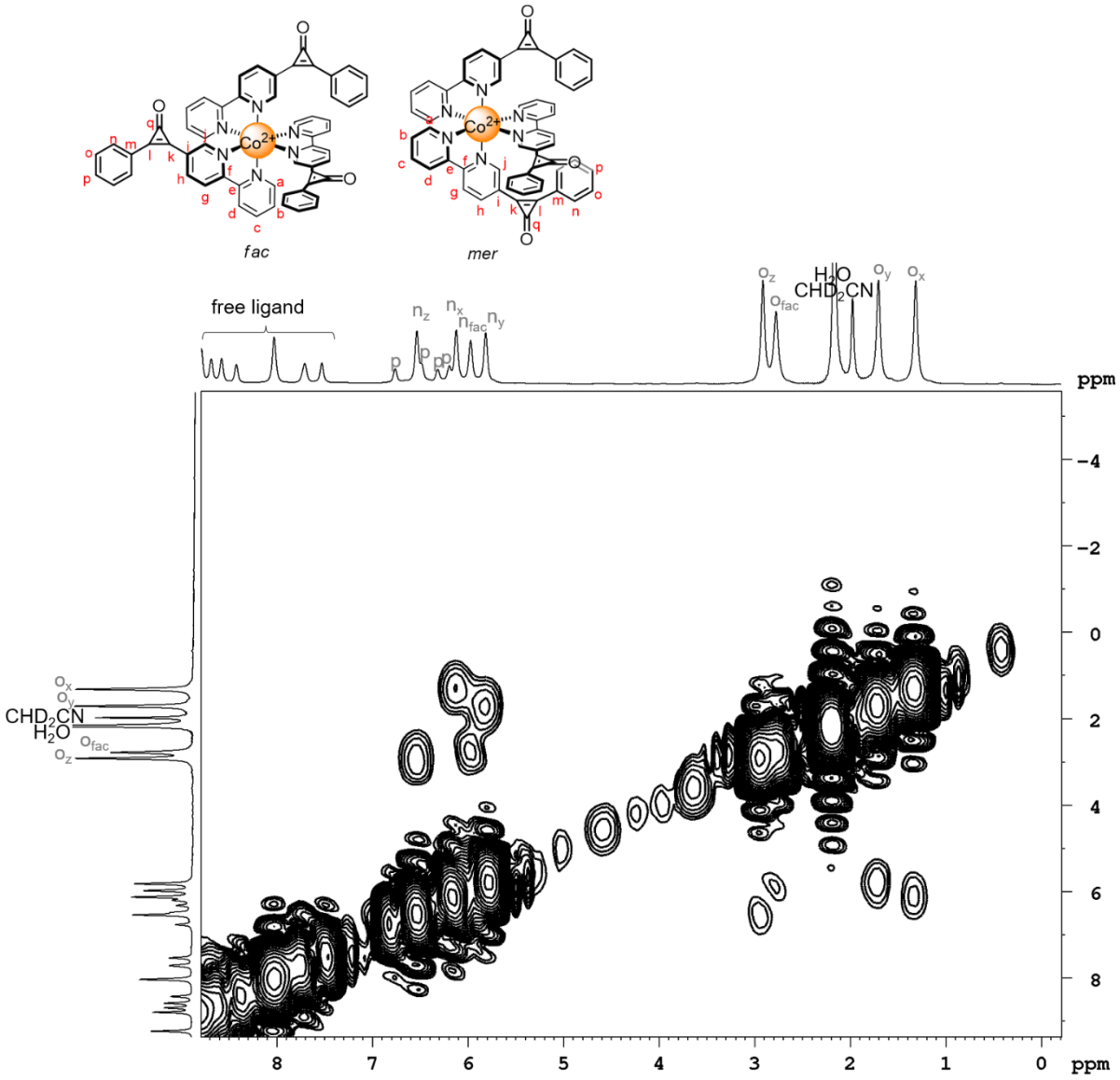


Figure S91. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

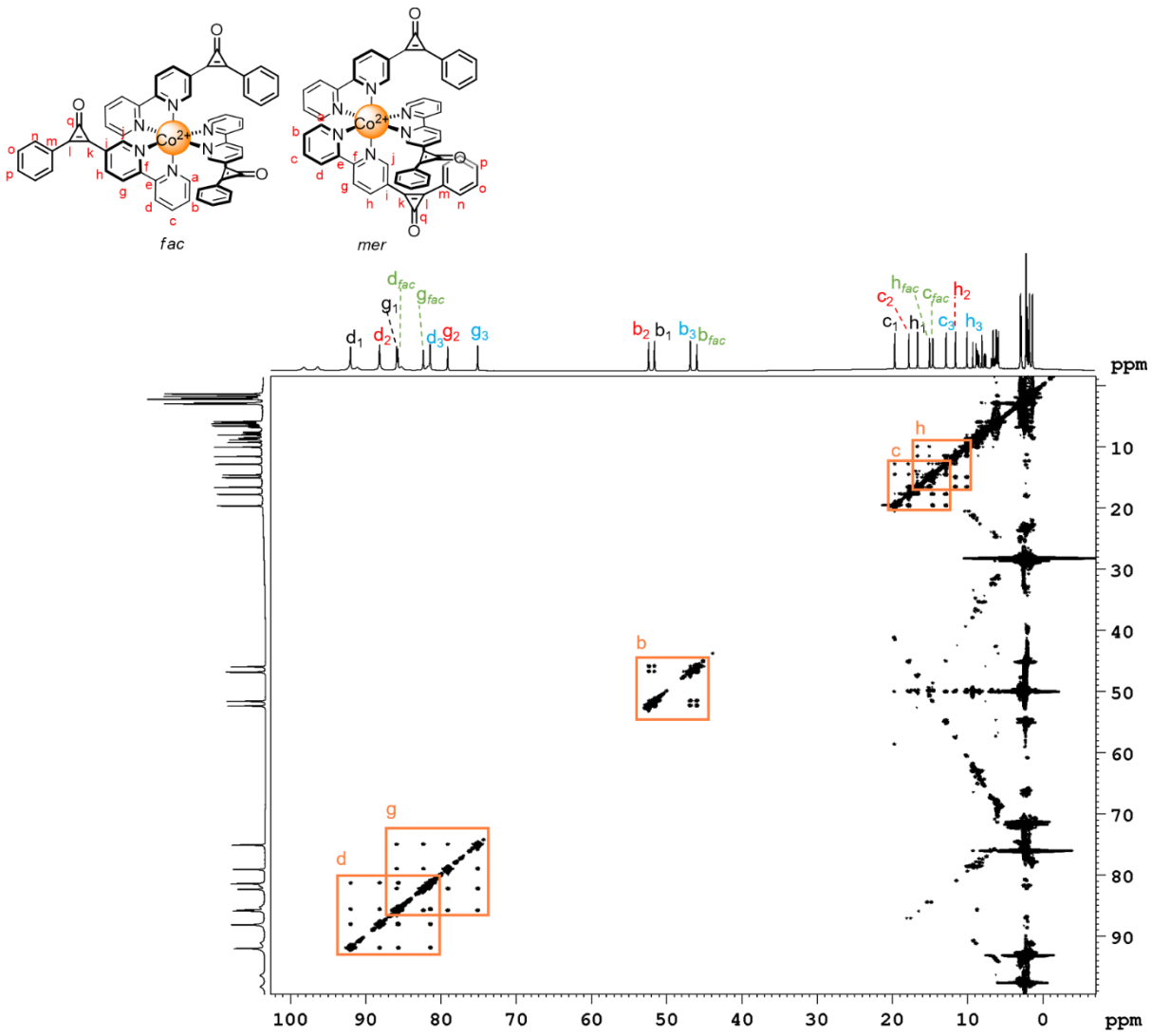


Figure S92. ^{1}H-^{1}H NOESY NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

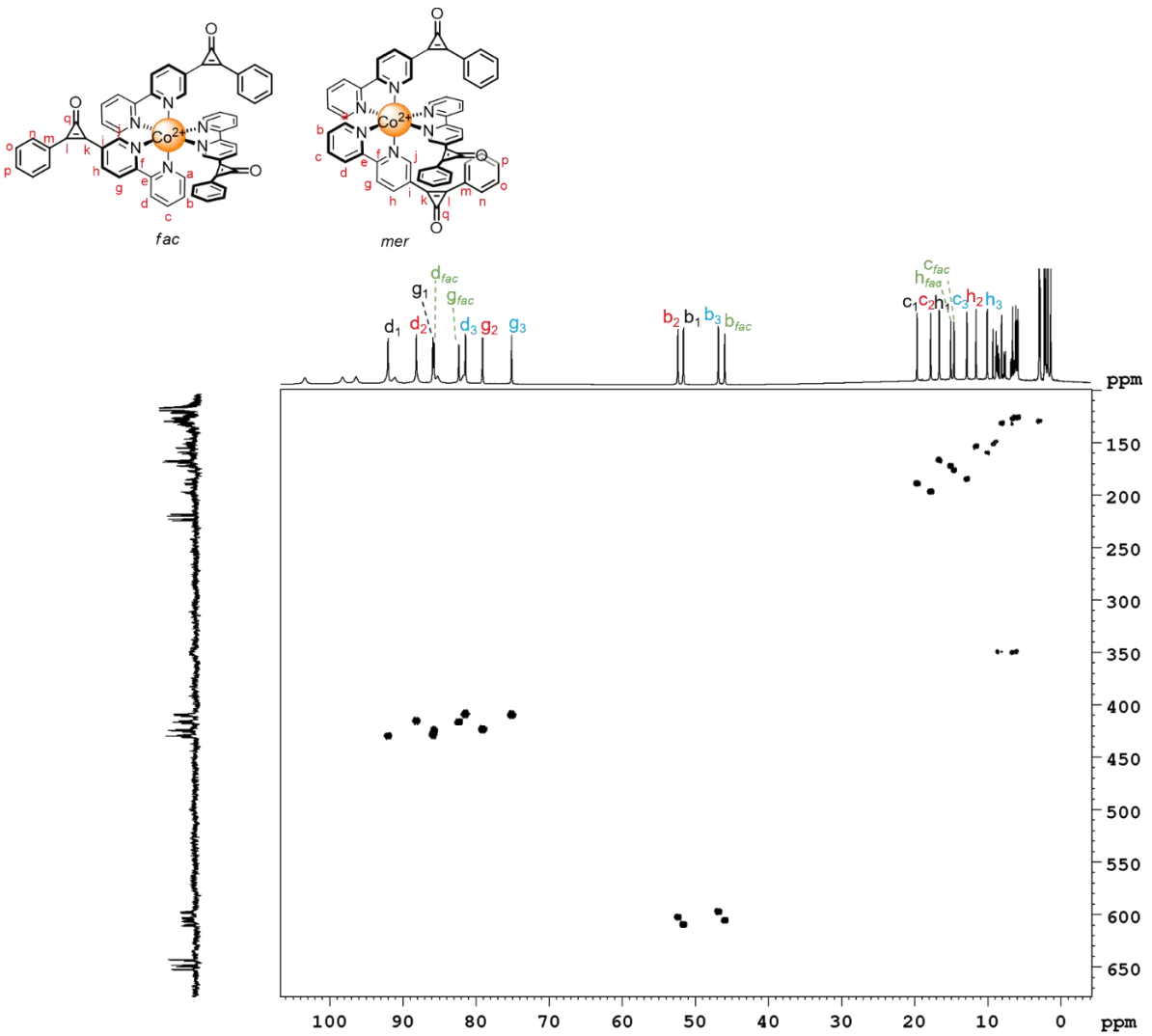


Figure S93. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-CPOne-**1a**.

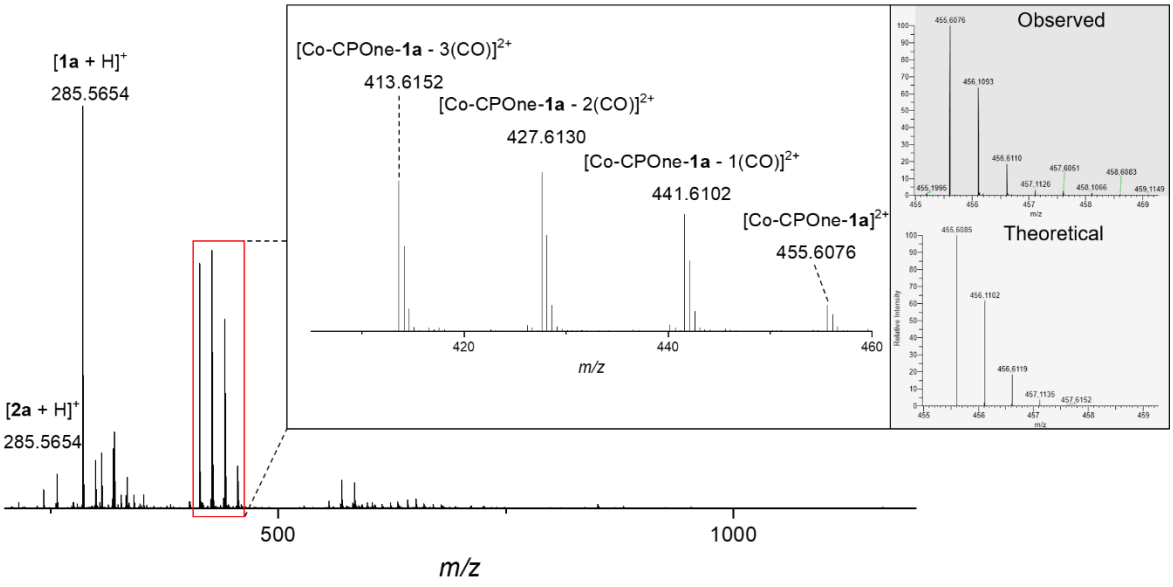
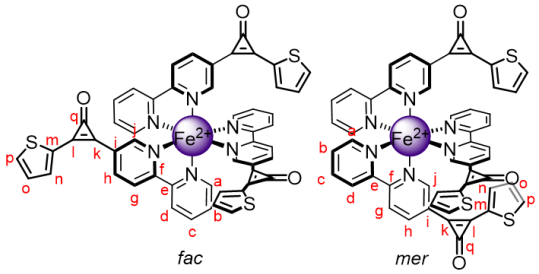


Figure S94. High resolution ESI mass spectrum of Co-CPOne-**1a** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

7.4 Fe-CPOne-**1b**



Iron tetrafluoroborate hexahydrate (3.80 mg, 11.3 µmol) and 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**) (9.80 mg, 33.8 µmol) were dissolved in CD_3CN (0.5 mL). After standing at room temperature over night the solution was added dropwise to diethyl ether (6 mL) and was centrifuged. The organic layer was decanted and the residue washed twice with diethyl ether (10 mL) to obtain the product as a purple powdery solid.

^{1}H NMR (500 MHz, CD_3CN, 298 K) δ (ppm): 8.82 (d, ^3J = 8.4 Hz, 1H, H_g), 8.79 (d, ^3J = 8.7 Hz, 1H, H_g), 8.76-8.73 (m, 2H, H_g), 8.73-8.67 (m, 3H, $H_{d,h}$), 8.66-8.61 (m, 3H, $H_{d,h}$), 8.54 (overlapping dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 2H, H_h), 8.27-8.23 (m, 2H, H_c), 8.21-8.16 (m, 2H, H_c), 8.08 (d, ^4J = 1.5 Hz, 1H, H_j), 8.06 (d, ^4J = 1.2 Hz, 1H, H_j), 8.04-8.02 (m, 2H, $H_{n/p}$), 7.99 (dd, ^3J = 5.0 Hz, ^4J = 0.9 Hz, 1H, $H_{n/p}$), 7.97 (dd, ^3J = 5.1 Hz, ^4J = 0.8 Hz, 1H, $H_{n/p}$), 7.95 (d, ^4J = 1.3 Hz, 1H, H_j), 7.89 (d, ^4J = 1.4 Hz, 1H, H_j), 7.66 (dd, ^3J = 3.9, ^4J = 0.9 Hz, 1H, $H_{n/p}$), 7.65-7.62 (m, 2H, $H_{n/p}$), 7.62-7.58 (m, 2H, $H_{a,n/p}$), 7.57-7.44 (m, 6H, $H_{a,b}$), 7.36 (d, ^3J = 5.4 Hz, 1H, H_a), 7.35-7.31 (m, 2H, H_o), 7.30-7.26 (m, 2H, H_o).

^{13}C NMR (126 MHz, CD_3CN, 298 K) δ (ppm): 162.0 (C_f),161.9 (C_f), 161.5 (C_f), 161.4 (C_f), 159.4 (C_e), 159.3 (C_e), 159.0 (C_e), 158.8 (C_e), 156.5 (C_j), 156.3 (C_a), 156.0 (C_j), 156.0 (C_a), 155.9 (C_j), 155.7 (C_a), 155.3 (C_a), 151.4 (C_q), 151.4 (C_q), 151.2 (C_q), 145.9 (C_l), 145.8 (C_l), 145.7 (C_l), 145.6 (C_l), 141.4 (C_h), 141.0 (C_h), 141.0 (C_h), 140.1 (C_c), 140.1 (C_c), 140.0 (C_c), 140.0 (C_c), 138.7 ($C_{n/p}$), 138.6 ($C_{n/p}$), 138.6 ($C_{n/p}$), 138.4 ($C_{n/p}$), 137.3 ($C_{n/p}$), 137.1 ($C_{n/p}$), 136.9 ($C_{n/p}$), 136.1 (C_k), 136.1 (C_k), 135.9 (C_k), 130.6 (C_o), 130.6 (C_o), 130.5 (C_o), 130.5 (C_o), 129.4 (C_b), 129.3 (C_b), 129.1 (C_b), 129.1(C_b), 126.9 (C_d), 126.7 (C_d), 126.4 (C_d), 126.3 (C_d), 125.9 (C_g), 125.7 (C_g), 125.5 (C_g), 125.3(C_m), 125.3 (C_g), 125.2 (C_m), 125.2 (C_m), 125.1 (C_m), 123.8 (C_i), 123.7(C_i), 123.6 (C_i), 123.5 (C_i).

HRMS (ESI, CH_3CN) *m/z*: 463.0440 [Fe-CPOne-**1b**]$^{2+}$, 449.0466 [Fe-CPOne-**1b** -CO]$^{2+}$, 435.0493 [Fe-CPOne-**1b** -2(CO)]$^{2+}$, 421.0517 [Fe-CPOne-**1b** -3(CO)]$^{2+}$.

FT-IR: $\tilde{\nu}$ = 3443.9 (w), 3110.8 (w), 1842.4 (s), 1619.9 (s), 1487.4 (w), 1466.0 (m), 1440.3 (w), 1406.9 (m), 1384.9 (w), 1361.0 (m), 1315.5 (w), 1279.6 (w), 1243.1 (w), 1033.5 (s), 852.9 (m), 791.1 (m), 749.8 (m), 728.8 (m), 666.3 (w) cm^{-1}.

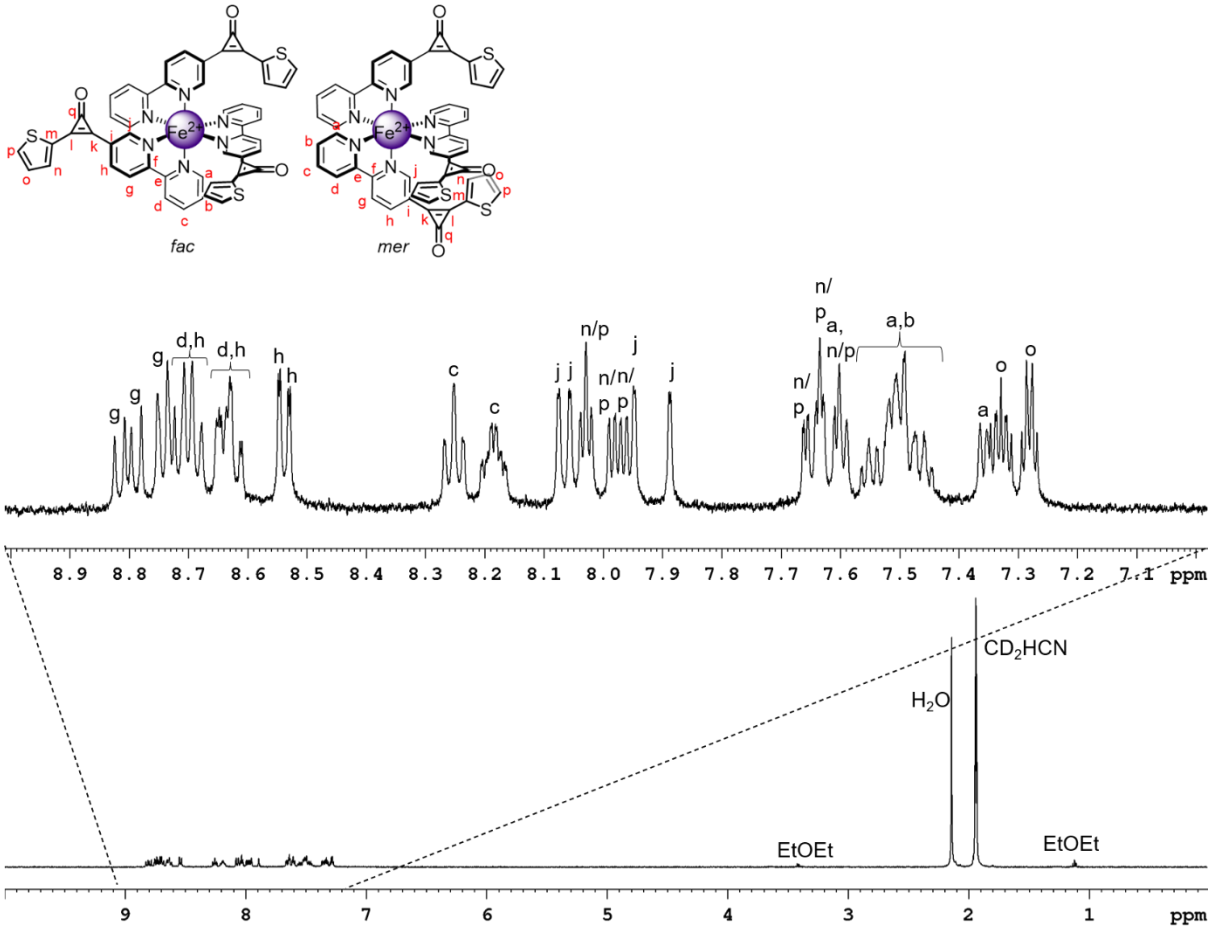


Figure S95. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-CPOne-**1b**.

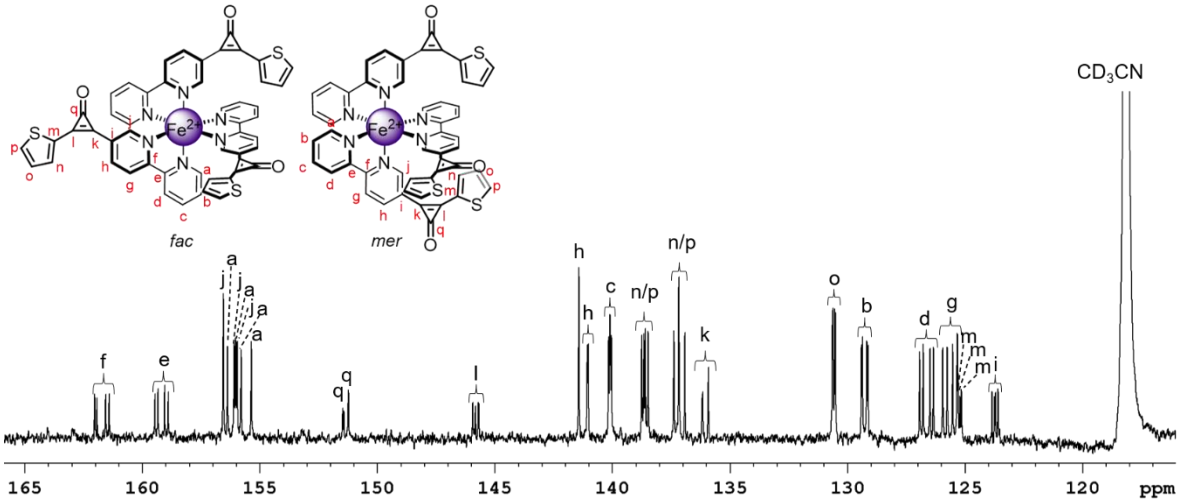


Figure S96. ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of Fe-CPOne-**1b**.

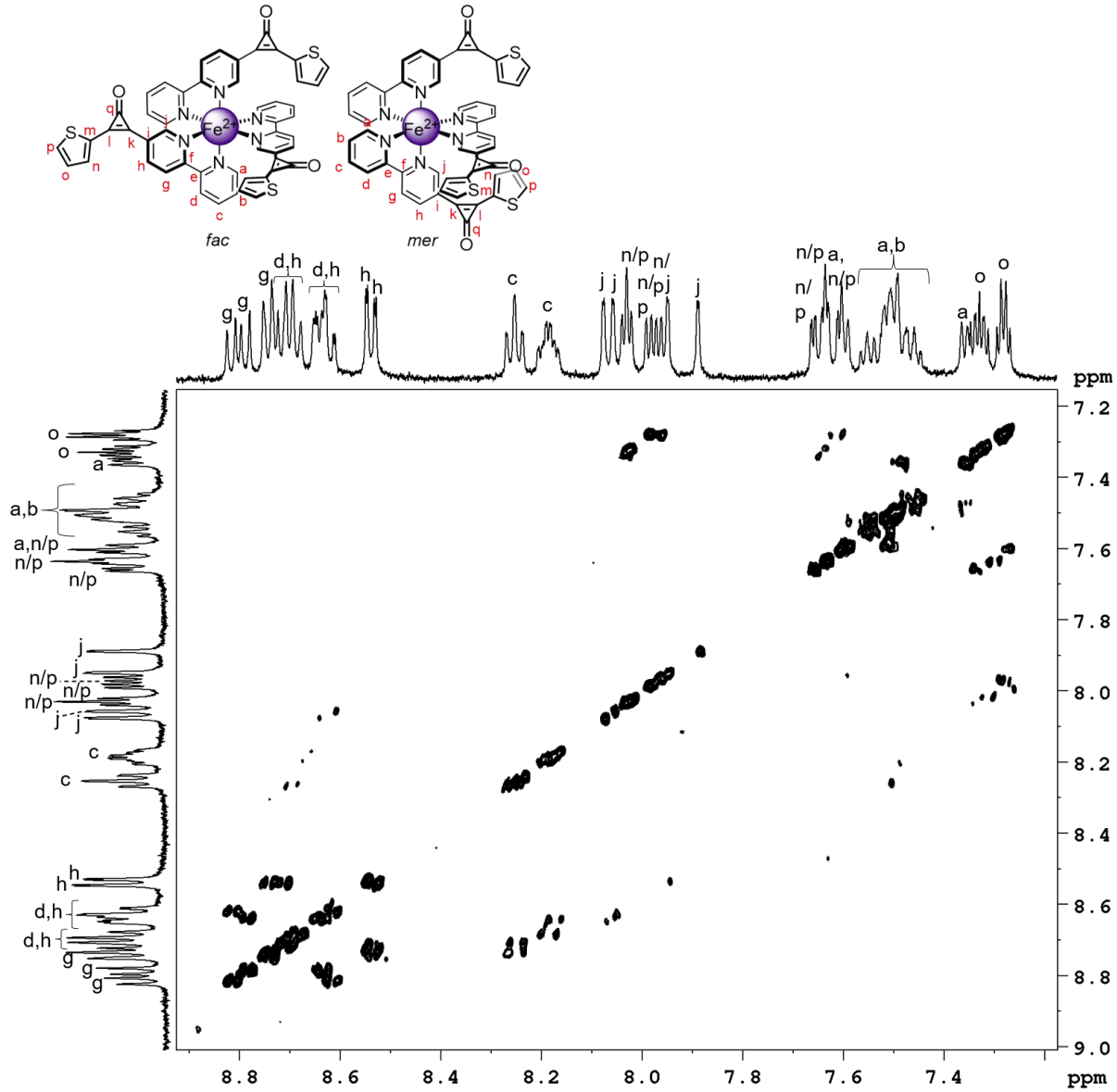


Figure S97. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-CPOne-**1b**.

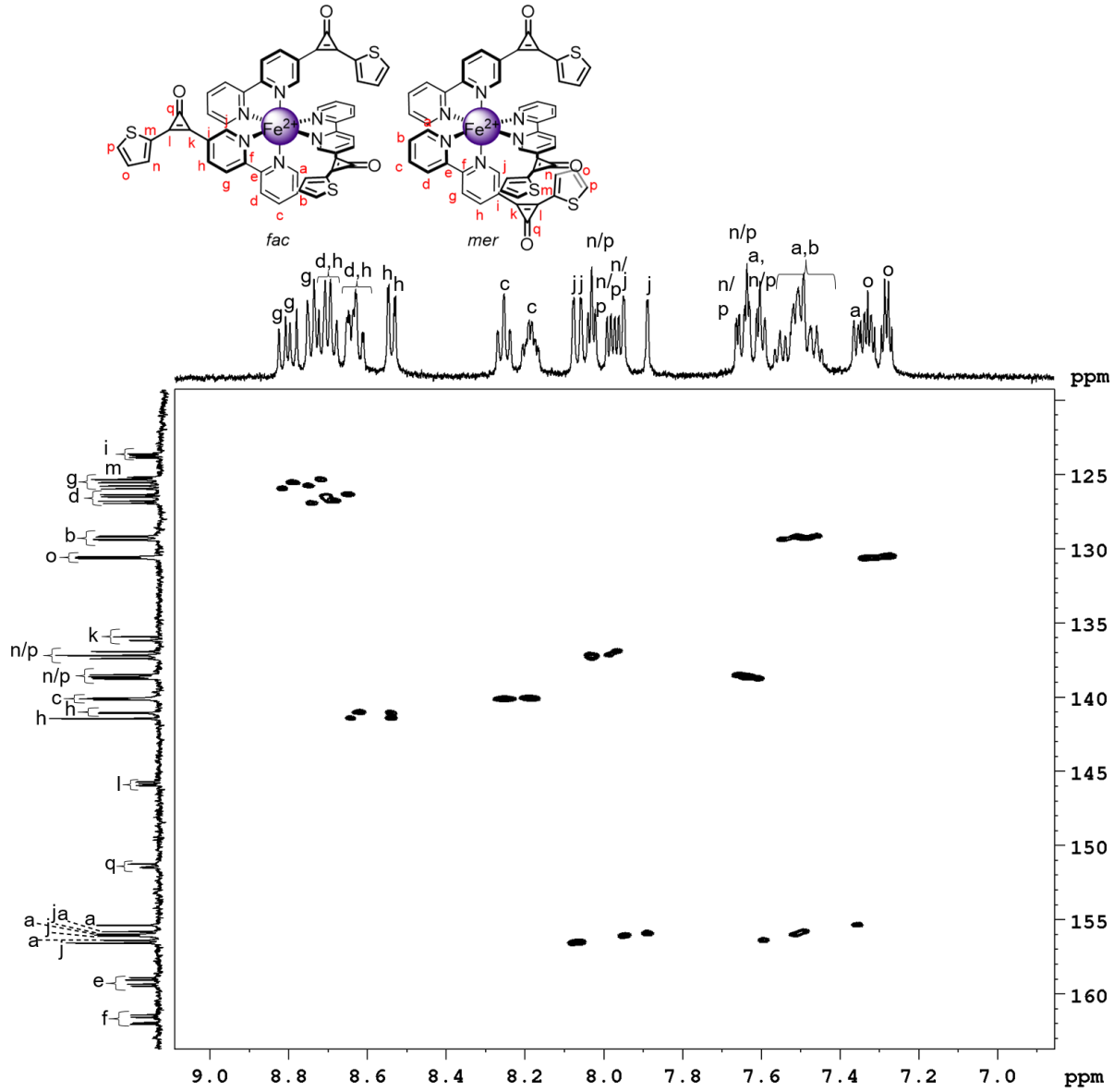


Figure S98. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Fe-CPOne-**1b**.

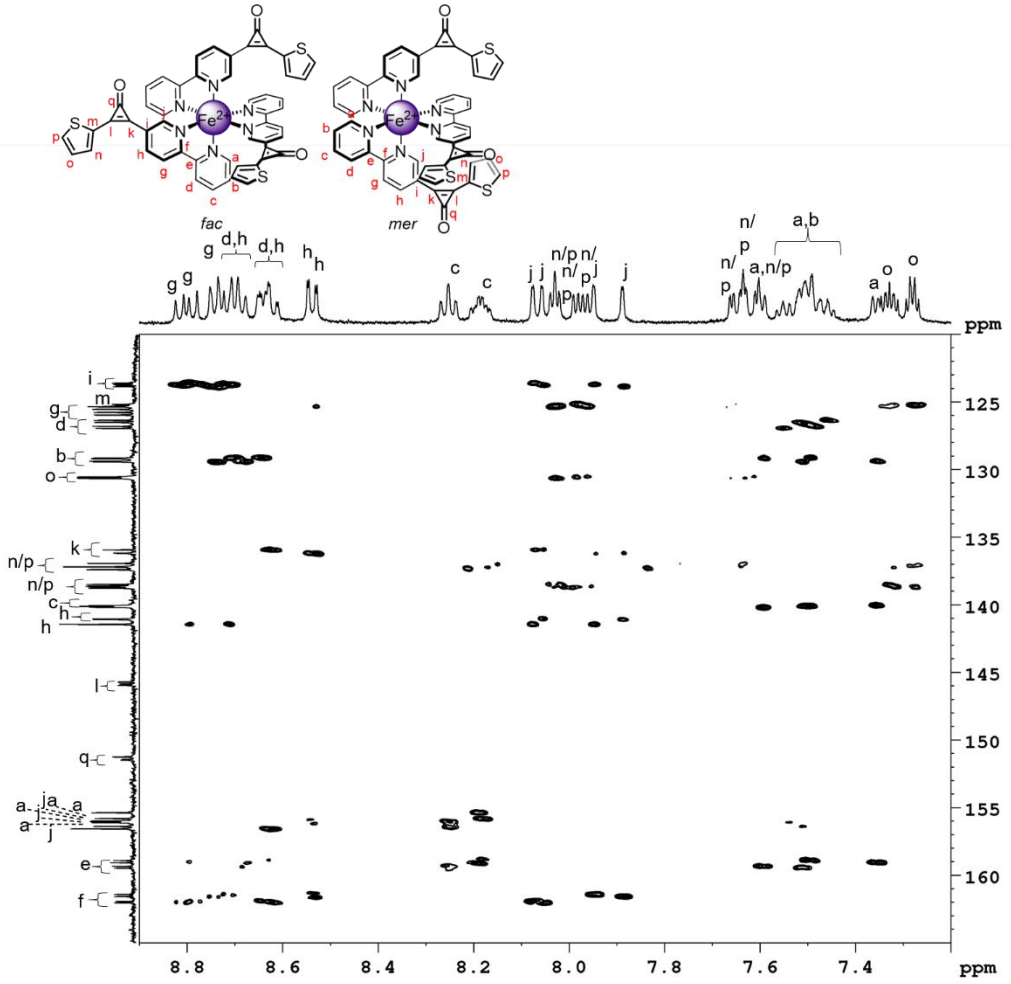


Figure S99. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Fe-CPOne-**1b**.

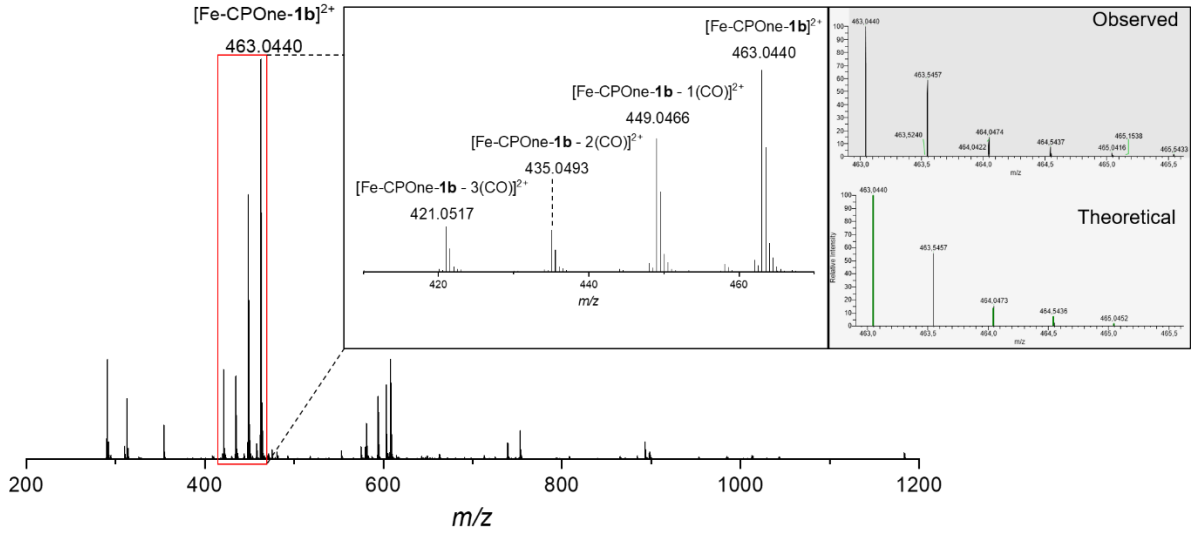
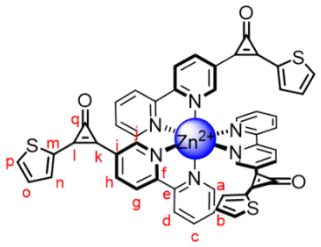


Figure S100. High resolution ESI mass spectrum of Fe-CPOne-**1b** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

7.5 Zn-CPOne-**1b**



Zinc trifluoromethanesulfonate (2.94 mg, 8.1 µmol) and 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (6.9 mg, 24.3 µmol) were dissolved in CD_3CN (0.5 mL).

Note: Because of the broadness of the signals, unambiguous assignment of the ^{1}H and ^{13}C NMR spectra was not possible and *fac/mer* isomers could not be distinguished.

HRMS (ESI, CH_3CN) *m/z*: 1083.0349 [Zn-CPOne-**1b** + OTf]$^{1+}$, 467.0413 [Zn-CPOne-**1b**]$^{2+}$, 453.0437 [Zn-CPOne-**1b** -CO]$^{2+}$, 439.0463 [Zn-CPOne-**1b** -2(CO)]$^{2+}$, 425.0463 [Zn-CPOne-**1b** -3(CO)]$^{2+}$.

FT-IR: $\tilde{\nu}$ = 3085.7 (w), 2366.0 (w), 2252.3 (w), 2162.0 (w), 1844.03 (s), 1602.9 (s), 1561.5 (m), 1472.6 (m), 1440.6 (w), 1407.5 (m), 1362.6 (w), 1317.0 (w), 1246.9 (s), 1222.2 (s), 1150.8 (s), 1059.4 (w), 1027.3 (s), 855.7 (w), 798.1 (w) cm^{-1}.

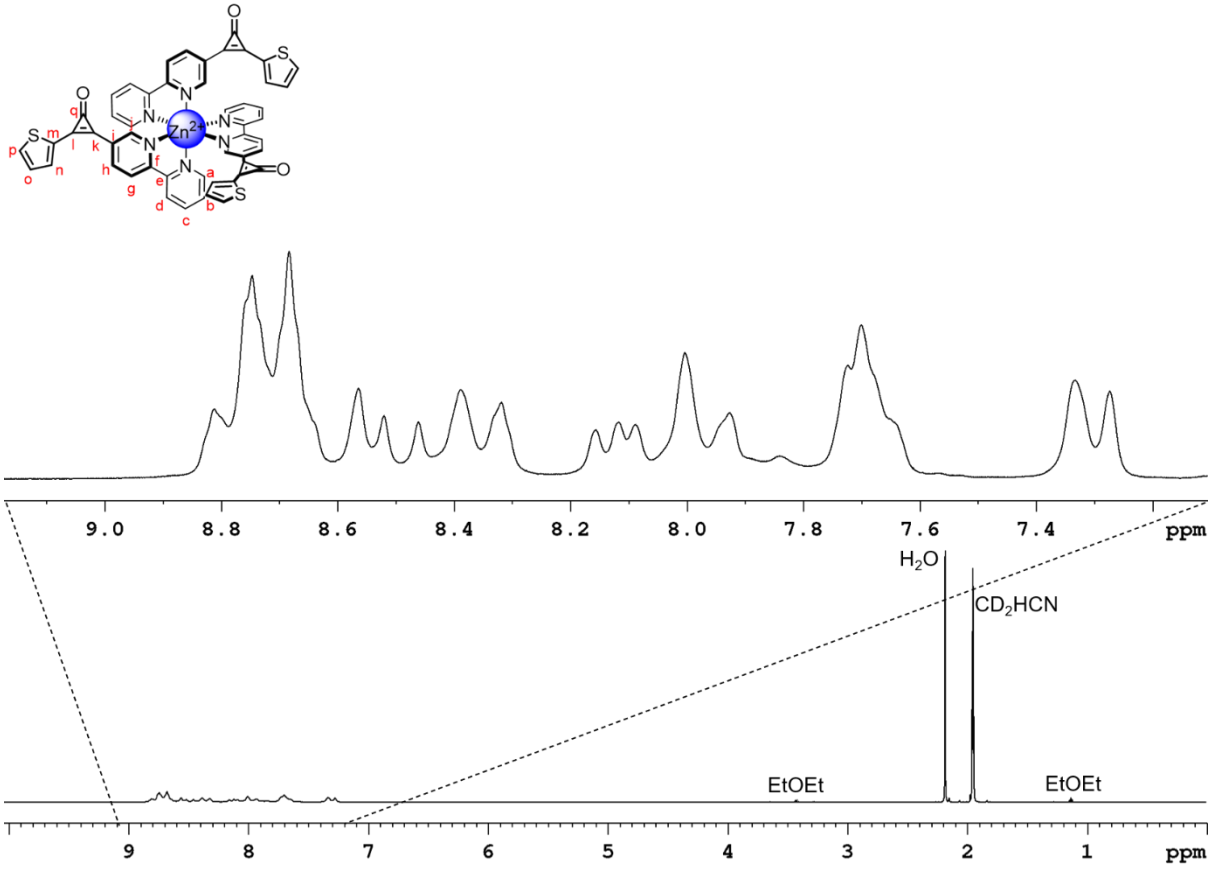


Figure S101. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Zn-CPOne-**1b**.

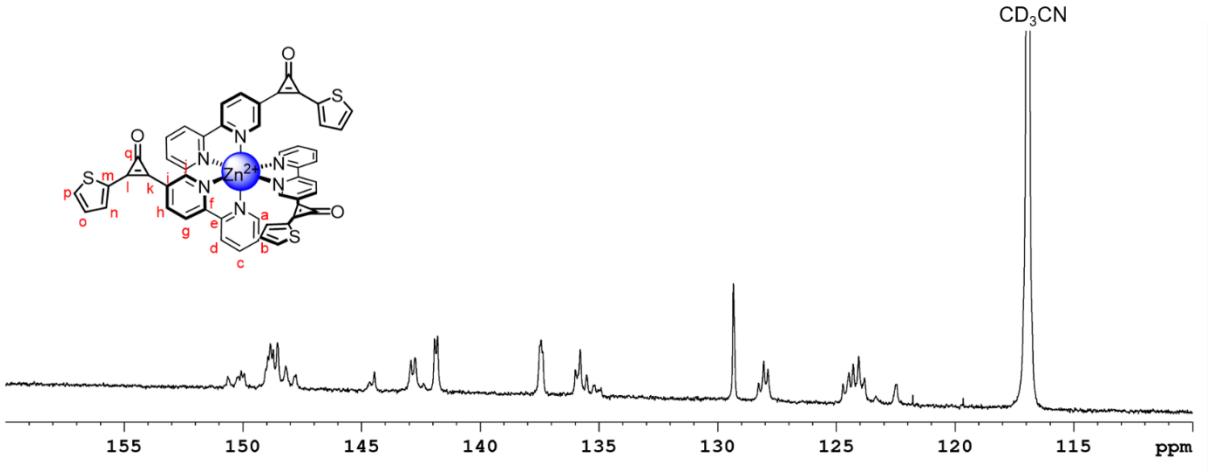


Figure S102. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Zn-CPOne-**1b**.

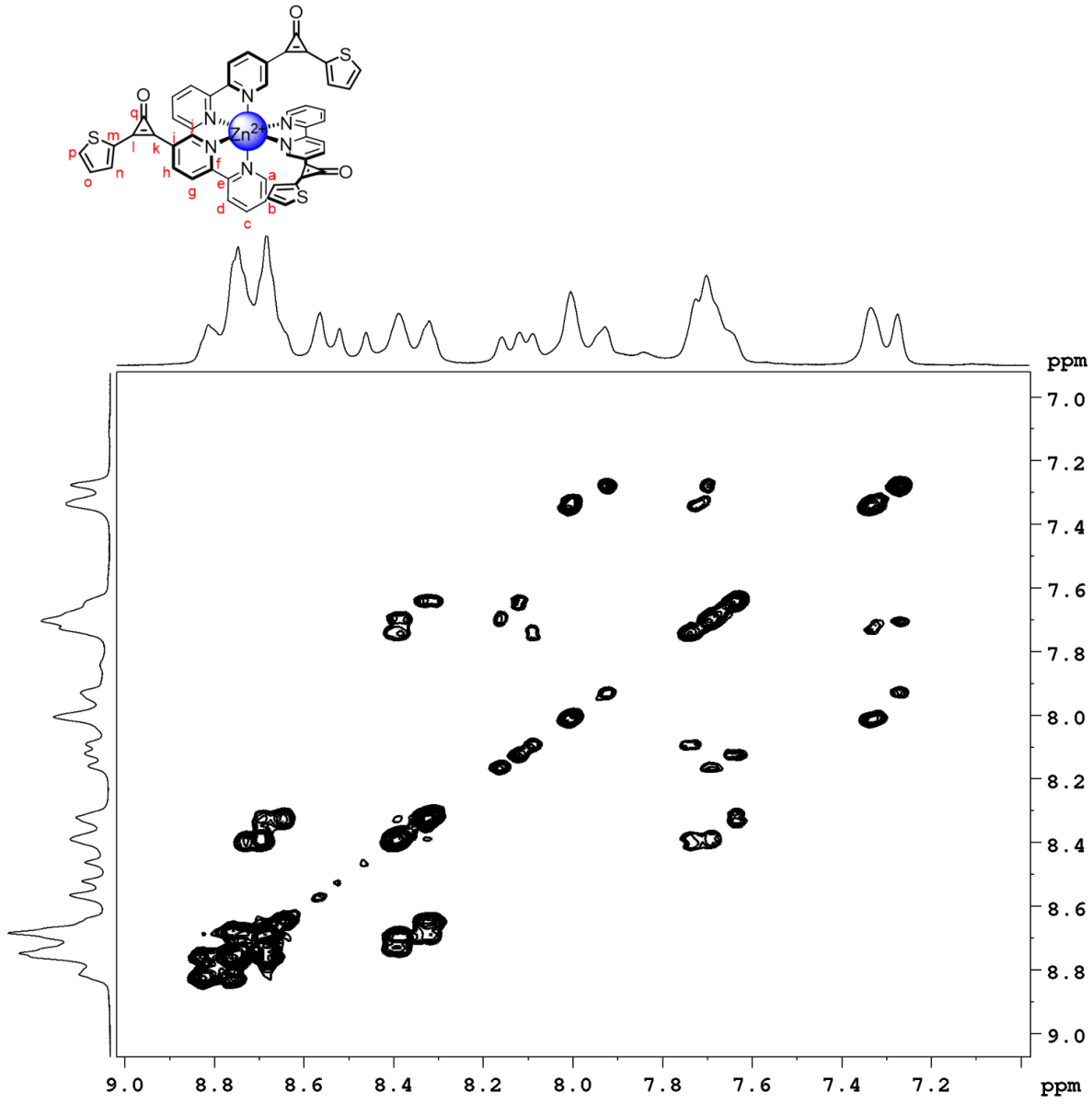


Figure S103. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Zn-CPOne-**1b**.

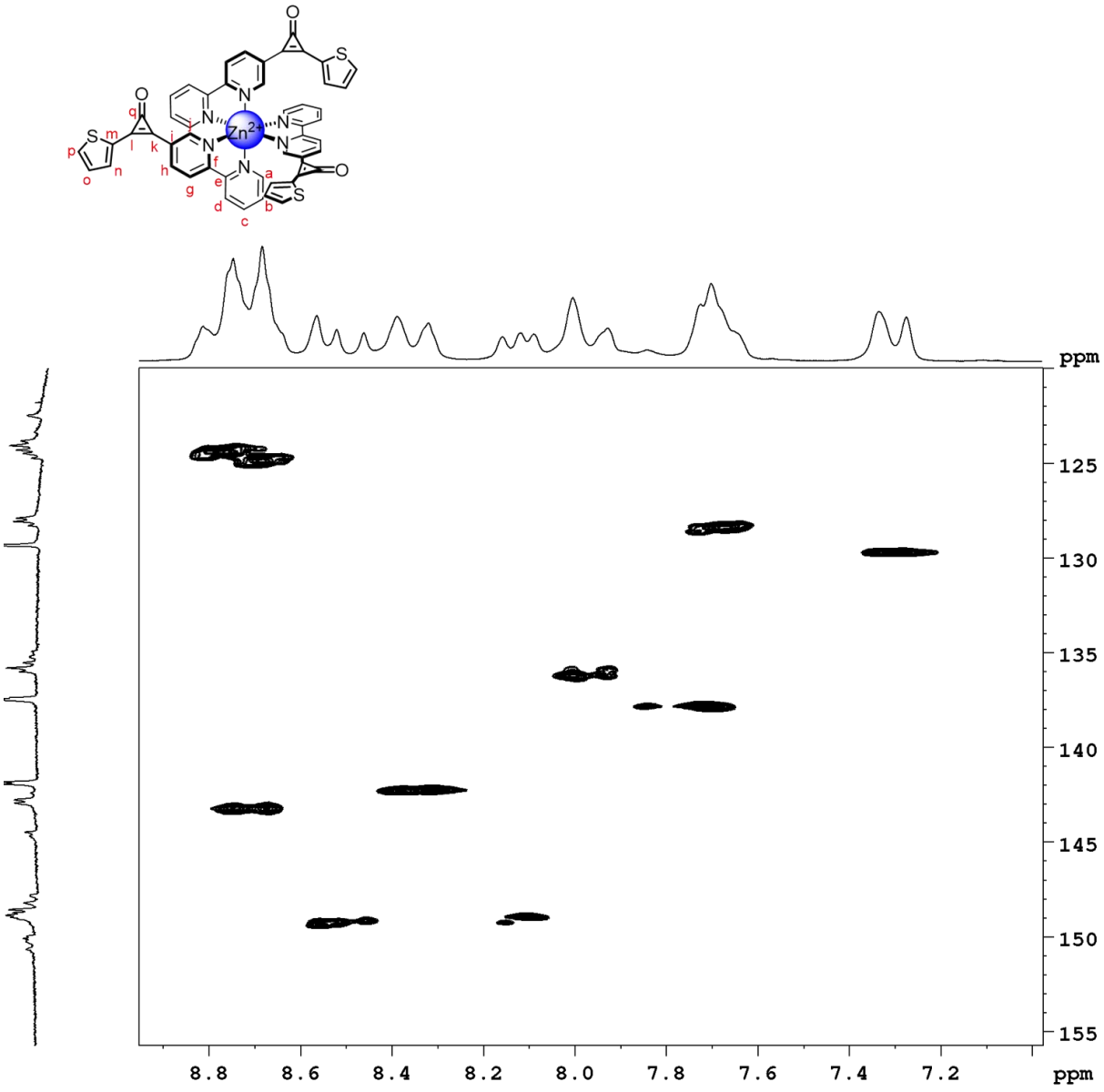


Figure S104. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Zn-CPOne-**1b**.

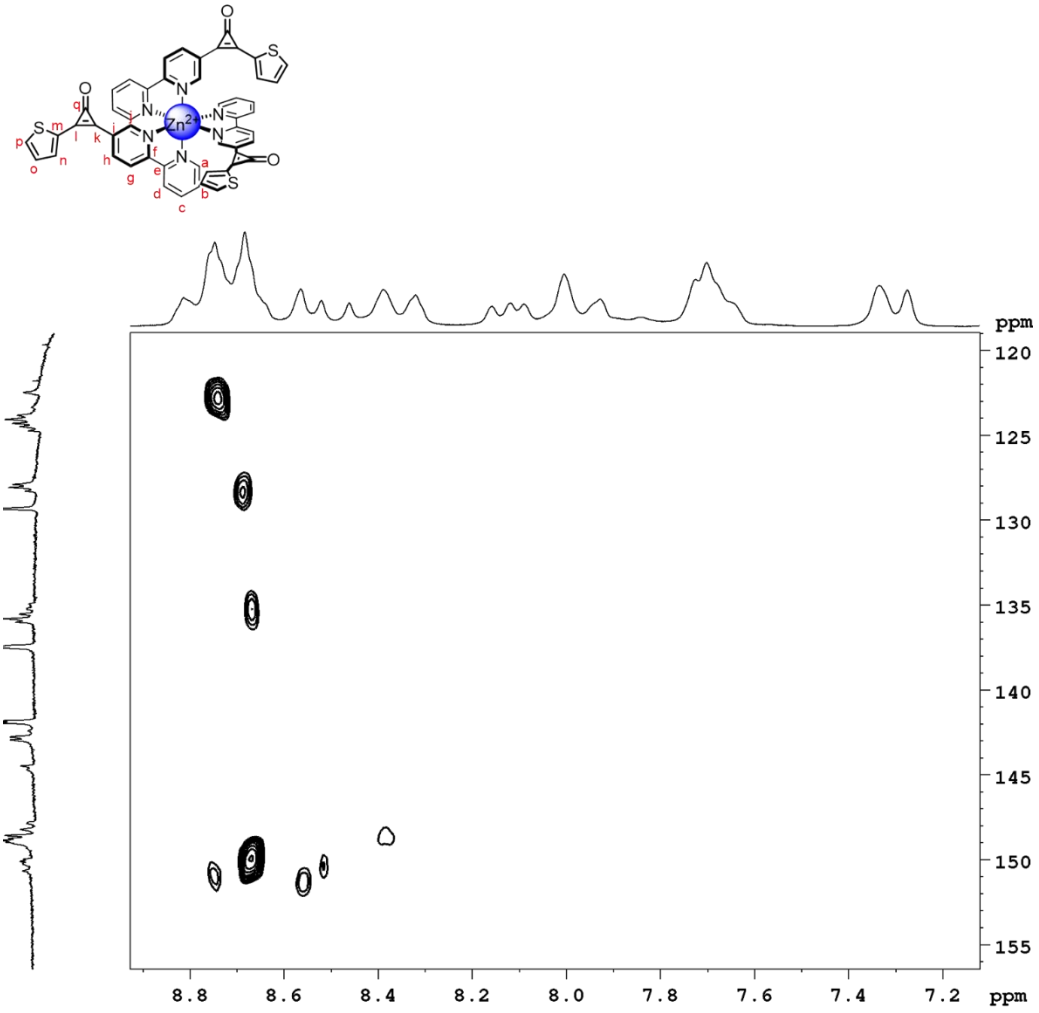


Figure S105. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Zn-CPOne-**1b**.

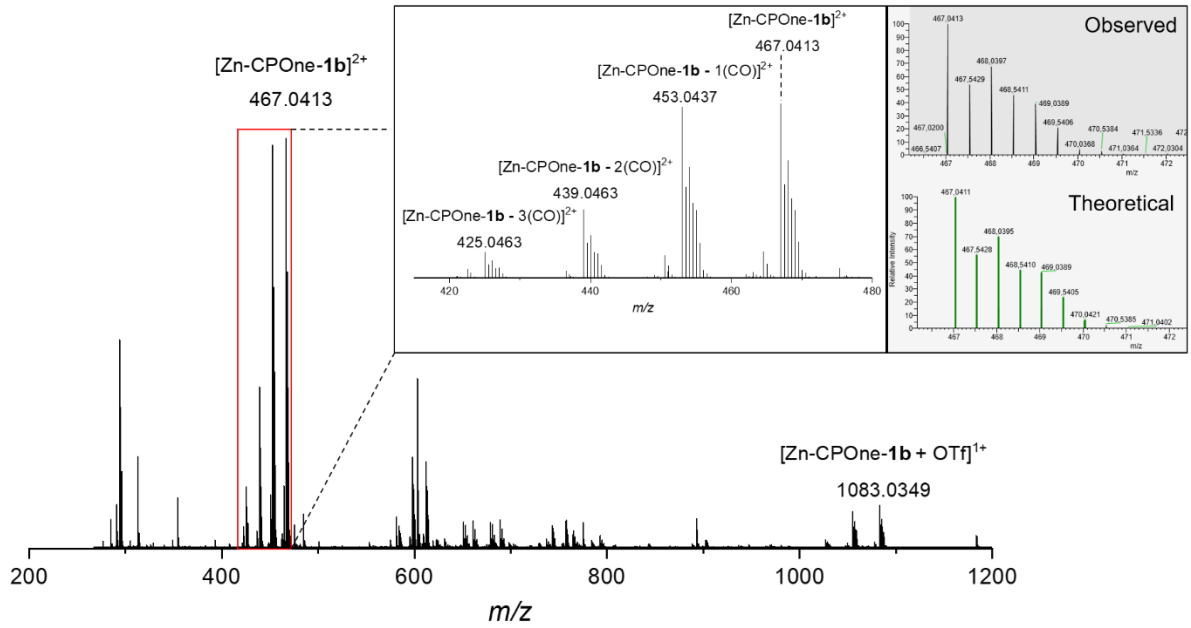
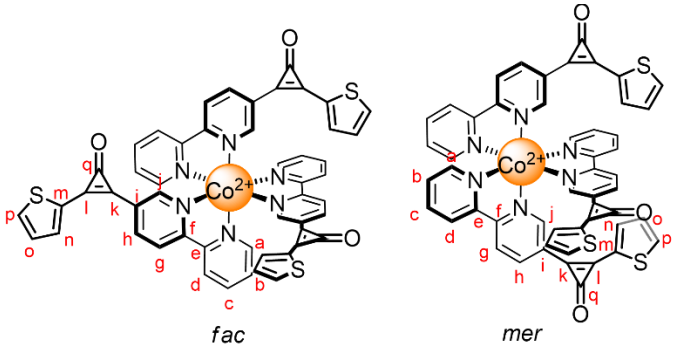


Figure S106. High resolution ESI mass spectrum of Zn-CPOne-**1b** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

7.6 Co-CPOne-**1b**



Cobalt bis(trifluoromethylsulfonyl)imide (7.25 mg, 11.7 µmol) and 5-(2-cycloprop-2-enone-3-(thiophen-2-yl))-2,2'-bipyridine (**1b**) (10.2 mg, 35.2 µmol) were dissolved in CD_3CN (0.5 mL). After standing at room temperature over night the solution was added dropwise to diethyl ether (6 mL) and was centrifuged. The organic layer was decanted and the residue washed twice with diethyl ether (10 mL) to obtain the product as a yellow powdery solid.

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 102.3 (br, 1H, $H_{a/j}$), 98.2 (br, 1H, $H_{a/j}$), 95.5 (br, 1H, $H_{a/j}$), 91.6 (s, 1H, H_{d1}), 90.9 (br, 1H, $H_{a/j}$), 89.9 (br, 1H, $H_{a/j}$), 87.8 (s, 1H, H_{d2}), 86.1 (s, 1H, H_{dfac}), 86.0 (s, 1H, H_{g1}), 82.9 (s, 1H, H_{d3}), 82.4 (s, 1H, H_{gfac}), 79.9 (s, 1H, H_{g2}), 78.3 (br, 1H, $H_{a/j}$), 76.9 (s, 1H, H_{g3}), 52.3 (s, 1H, H_{b2}), 51.9 (s, 1H, H_{b1}), 46.1 (s, 1H, H_{b3}), 45.9 (s, 1H, H_{bfac}), 19.2 (s, 1H, H_{c1}), 17.5 (s, 1H, H_{c2}), 16.6 (s, 1H, H_{h1}), 15.1 (s, 1H, H_{hfac}), 14.7 (s, 1H, H_{cfac}), 13.4 (s, 1H, H_{c3}), 11.8 (s, 1H, H_{h2}), 10.6 (s, 1H, H_{h3}), 7.0 (s, 1H, $H_{n/o/p}$), 6.8 (s, 1H, $H_{n/o/p}$), 6.3 (s, 1H, $H_{n/o/p}$), 6.1 (s, 1H, $H_{n/o/p}$), 6.0 (s, 1H, $H_{n/o/p}$), 5.9 (s, 1H, $H_{n/o/p}$), 5.6 (s, 1H, $H_{n/o/p}$), 5.4 (s, 1H, $H_{n/o/p}$), 4.1 (s, 1H, $H_{n/o/p}$), 3.5 (s, 1H, $H_{n/o/p}$), 3.2 (s, 1H, $H_{n/o/p}$), 2.6 (s, 1H, $H_{n/o/p}$).

Note: While it was possible to assign the proton signals within one spin system (indicated by numbers) based on the COSY spectrum, the different spin systems within each ligand could not be correlated to a particular ligand environment. For the signals of the bipyridine, the fac isomer was, therefore, tentatively assigned based on the integral of the signals. The three remaining sets of signals corresponding to the mer isomer were arbitrarily labelled with black, red, and blue labels according to their decreasing chemical shift. Protons corresponding to the R substituent were tentatively assigned in grey due to the signal overlap in the diamagnetic region of the spectra.[11] *Protons a and j are assigned in grey based on related complexes.*[11]

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 649.1 (s), 648.2 (s), 643.2 (s), 642.9 (s), 608.1 (d, $^1J_{CH}$ = 179 Hz, C_{b1}), 605.1 (d, $^1J_{CH}$ = 135 Hz, C_{b2}), 604.0 (d, $^1J_{CH}$ = 138 Hz, C_{bfac}), 601.5 (d, $^1J_{CH}$ = 165 Hz, C_{b3}), 430.2 (d, $^1J_{CH}$ = 167 Hz, C_{g1}), 427.1 (d, $^1J_{CH}$ = 112 Hz, C_{d1}), 426.0 (d, $^1J_{CH}$ = 120 Hz, C_{g2}), 424.5 (d, $^1J_{CH}$ = 170 Hz, C_{dfac}), 417.3 (d, $^1J_{CH}$ = 172 Hz, C_{gfac}), 413.8 (d, $^1J_{CH}$ = 89 Hz, C_{g3}), 412.7 (d, $^1J_{CH}$ = 116 Hz, C_{d2}), 411.6 (d, $^1J_{CH}$ = 176 Hz, C_{d3}), 214.1 (s), 213.0 (s), 209.9 (s), 209.1 (s), 197.9 (d, $^1J_{CH}$ = 166 Hz, C_{c2}), 191.4 (d, ^1J = 164.Hz, C_{c1}), 183.3 (d, ^1J = 167 Hz, C_{c3}), 176.9 (d, ^1J = 166 Hz, C_{cfac}), 173.0 (d, ^1J = 168 Hz, C_{hfac}), 171.9 (s), 169.5 (s), 168.7 (d, ^1J = 169 Hz, C_{h1}), 160.5 (s), 158.5 (d, ^1J = 171 Hz, C_{h3}), 158.4 (s), 154.2 (d, ^1J = 169 Hz, C_{h2}), 137.2-132.1 (overlapping signals, $C_{n/o/p}$), 128.1-122.9 (overlapping signals, $C_{n/o/p}$), 68.7 (unresolved d, $C_{a/j}$), 67.8 (unresolved d, $C_{a/j}$), 62.4 (unresolved d, $C_{a/j}$), 39.3 (unresolved d, $C_{a/j}$), 29.5 (unresolved d, $C_{a/j}$), 24.0 (unresolved d, $C_{a/j}$), 6.8 (unresolved d, $C_{a/j}$), -104.0 (s, $C_{e/f}$), -110.9 (s, $C_{e/f}$), -125.1 (s, $C_{e/f}$), -133.6 (s, $C_{e/f}$), -143.6 (s, $C_{e/f}$), -148.6 (s, $C_{e/f}$), -165.9 (s, $C_{e/f}$), -172.5 (s, $C_{e/f}$).

Note: Quaternary carbons and carbons close to the paramagnetic centre (a and j) could not be unambiguously assigned due to the lack of HMBC equivalent in the paramagnetic NMR toolbox. Carbons a, j, e and f are assigned based on related complexes.[11]

HRMS (ESI, CH_3CN) *m/z*: 1209.0049 [Co-CPOne-**1b** + NTf_2]$^{1+}$, 464.5433 [Co-CPOne-**1b**]$^{2+}$, 450.5458 [Co-CPOne-**1b** -CO]$^{2+}$, 436.5484 [Co-CPOne-**1b** -2(CO)]$^{2+}$, 422.5509 [Co-CPOne-**1b** -3(CO)]$^{2+}$.

FT-IR: ṽ = 3089.7 (w), 1842.7 (s), 1623.0 (s), 1602.7 (m), 1561.7 (w), 1470.7 (m), 1440.9 (w), 1408.3 (m), 1346.9 (s), 1329.1 (s), 1225.1 (m), 1177.3 (s), 1131.6 (s), 1051.8 (s), 854.5 (m), 795.7 (m), 733.5 (s) cm^{-1}.

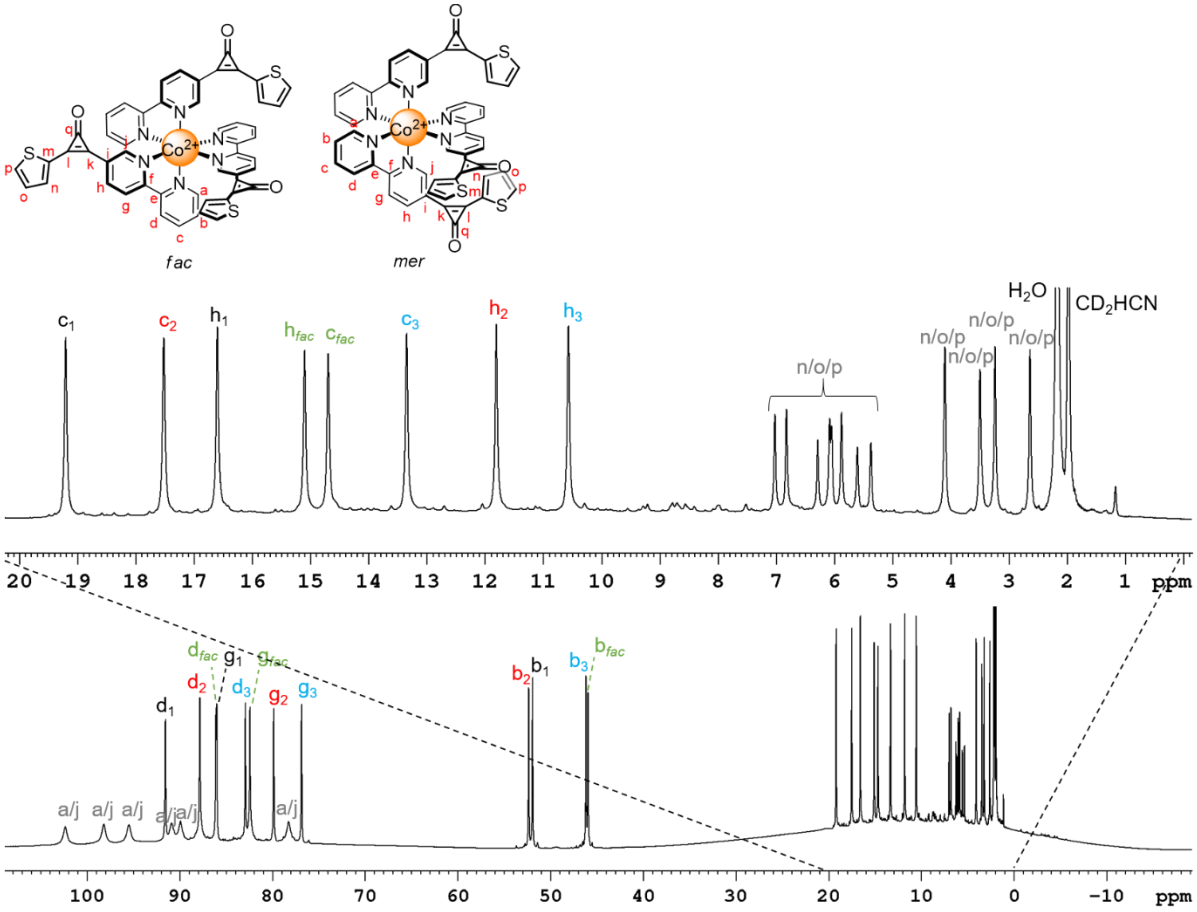


Figure S107. ^{1}H NMR spectrum (600 MHz, CD_3CN $_3$, 298 K) of Co-CPOne-**1b**.

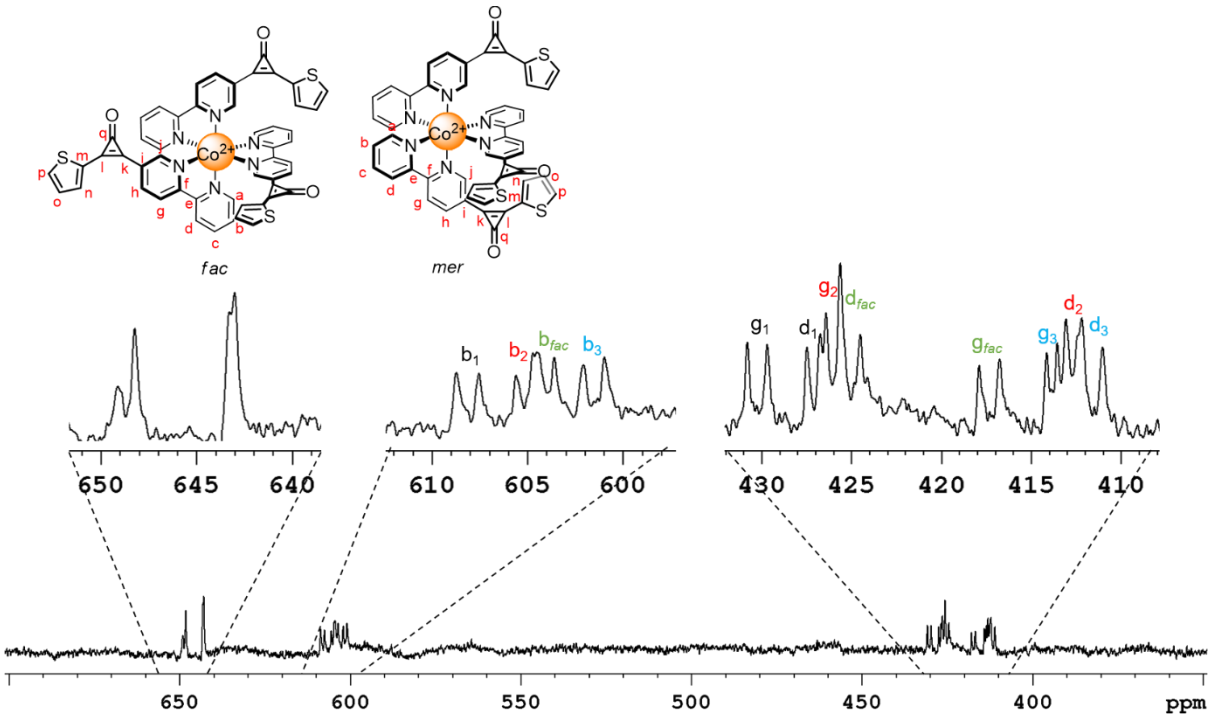


Figure S108. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Co-CPOne-**1b**.

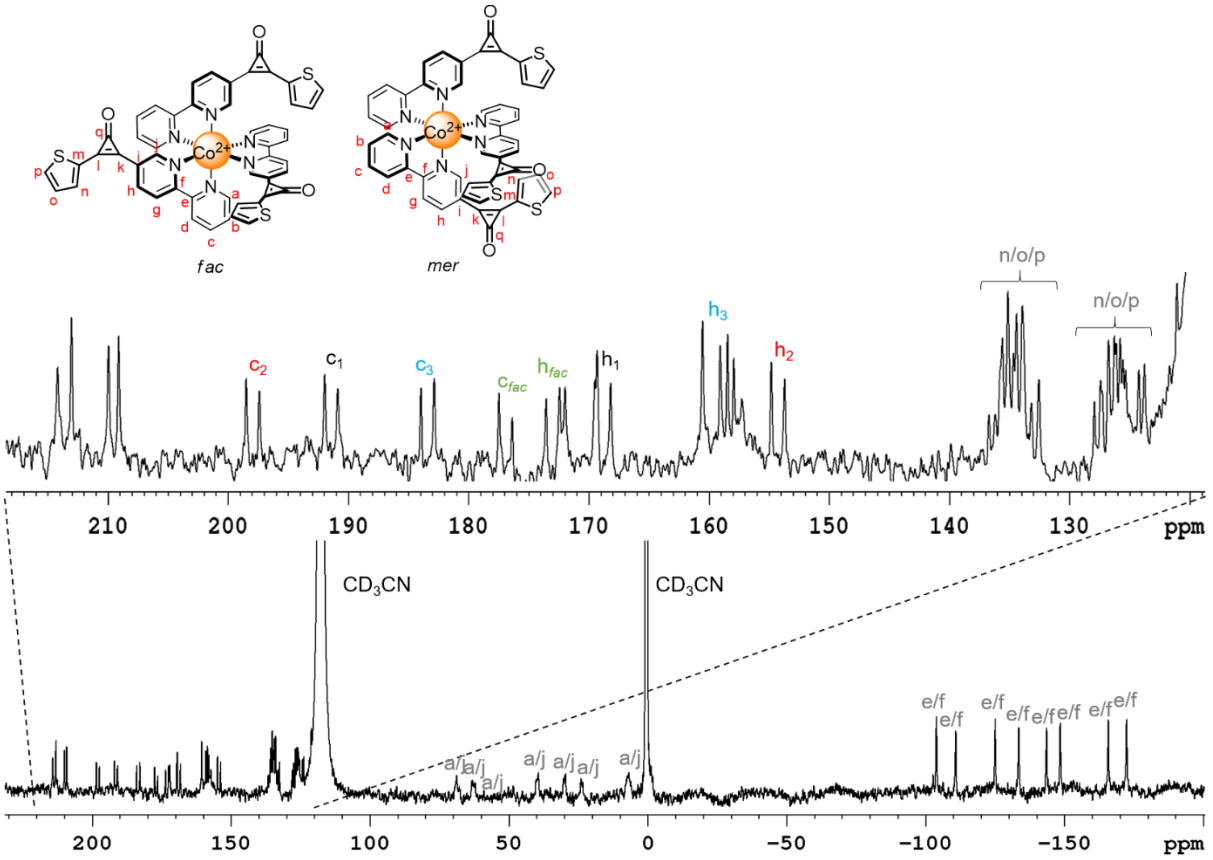


Figure S109. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Co-CPOne-**1b**.

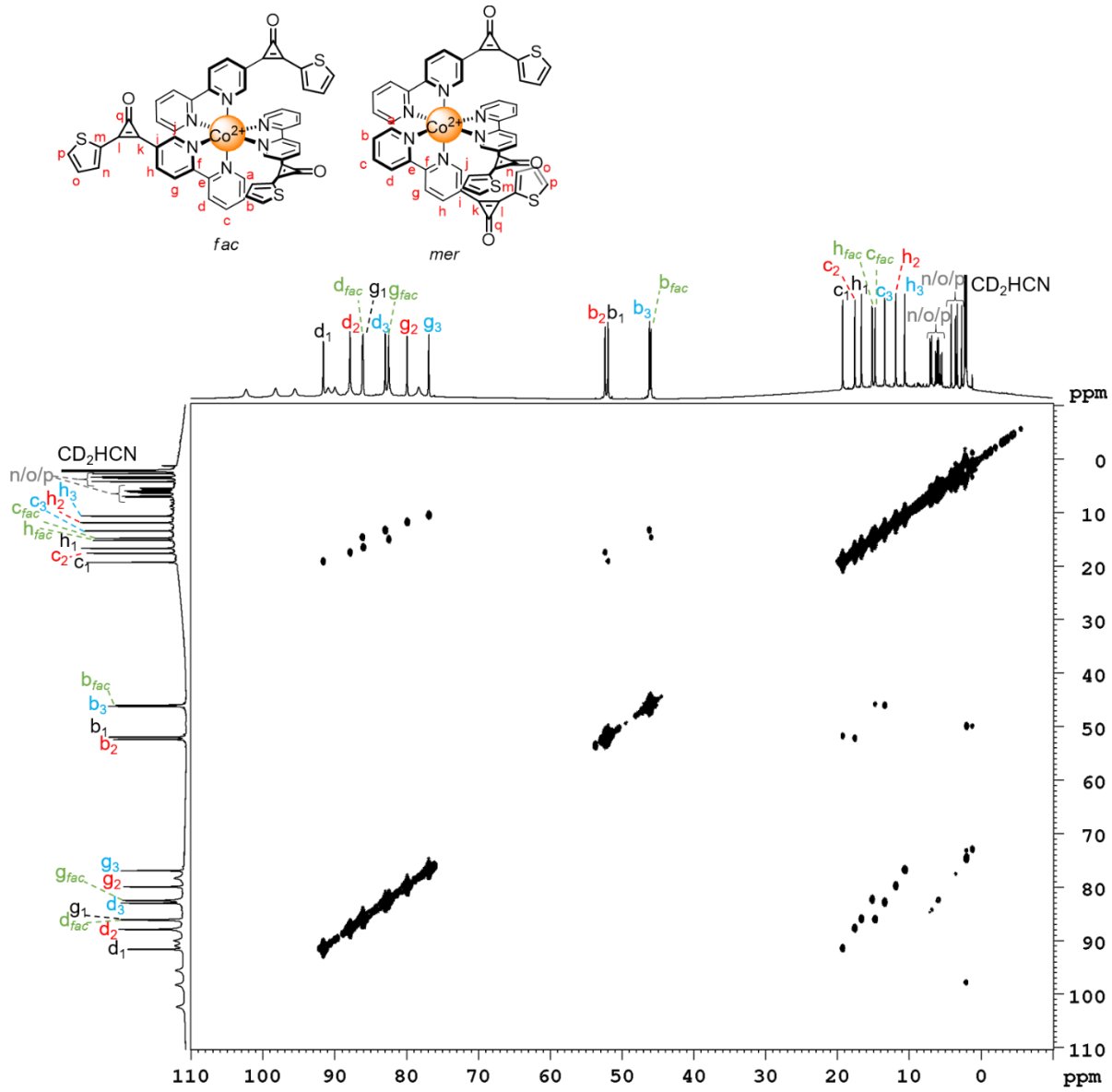


Figure S110. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1b**.

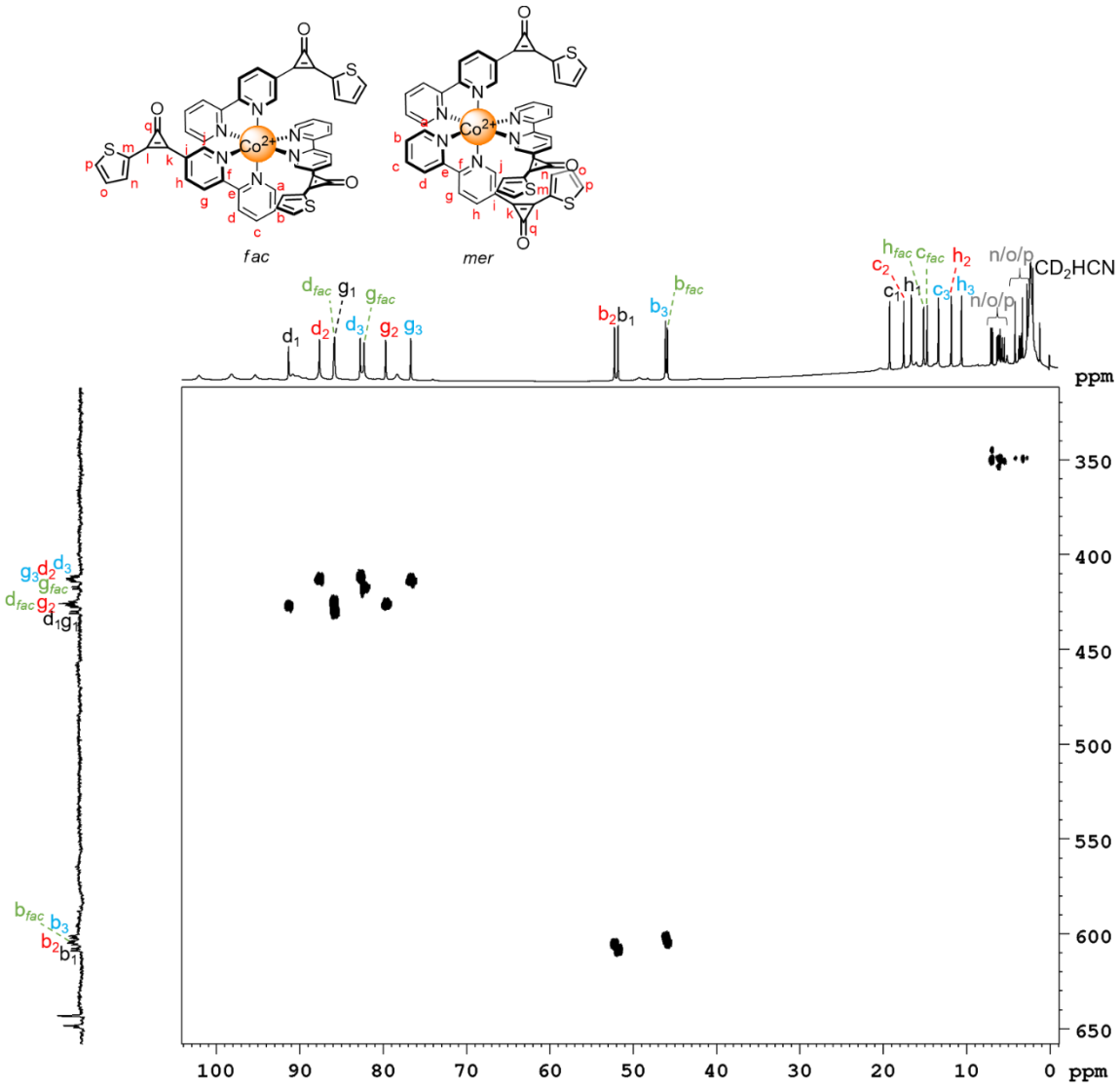


Figure S111. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-CPOne-**1b**.

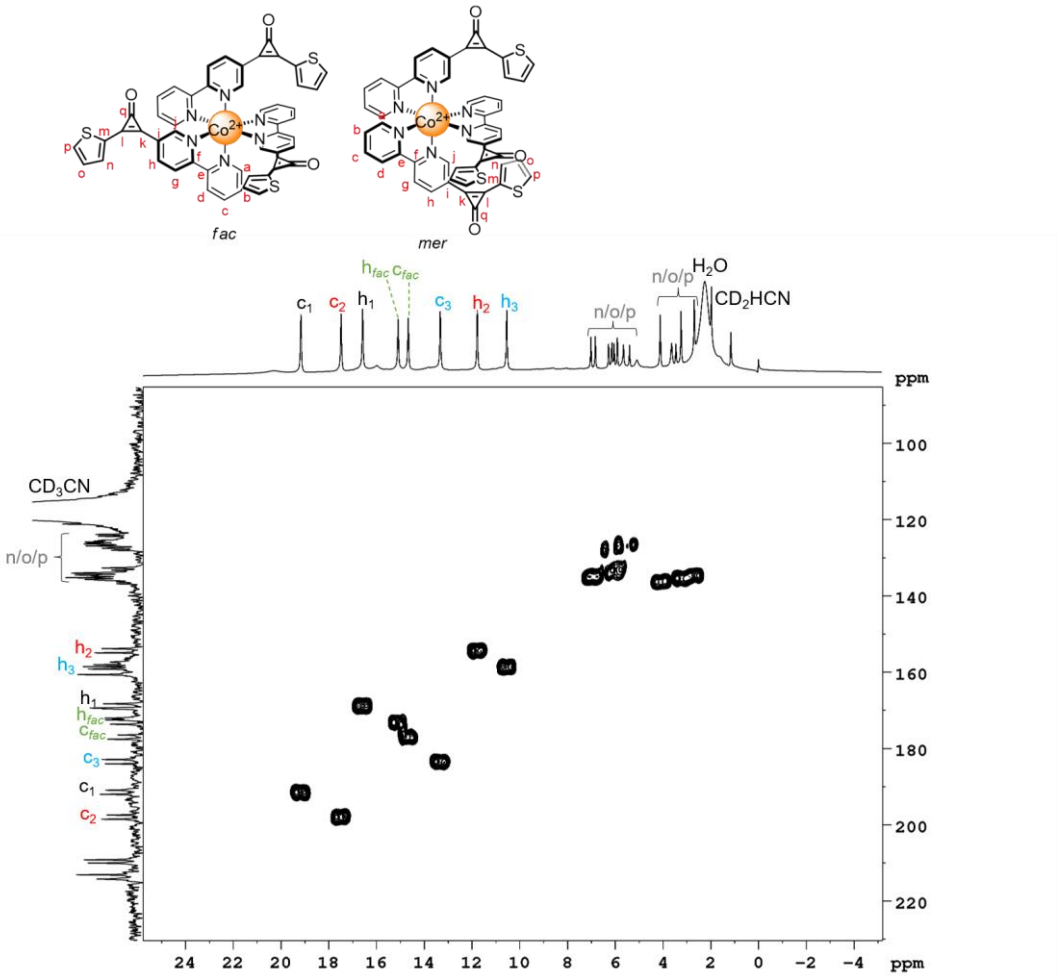


Figure S112. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-CPOne-**1b**.

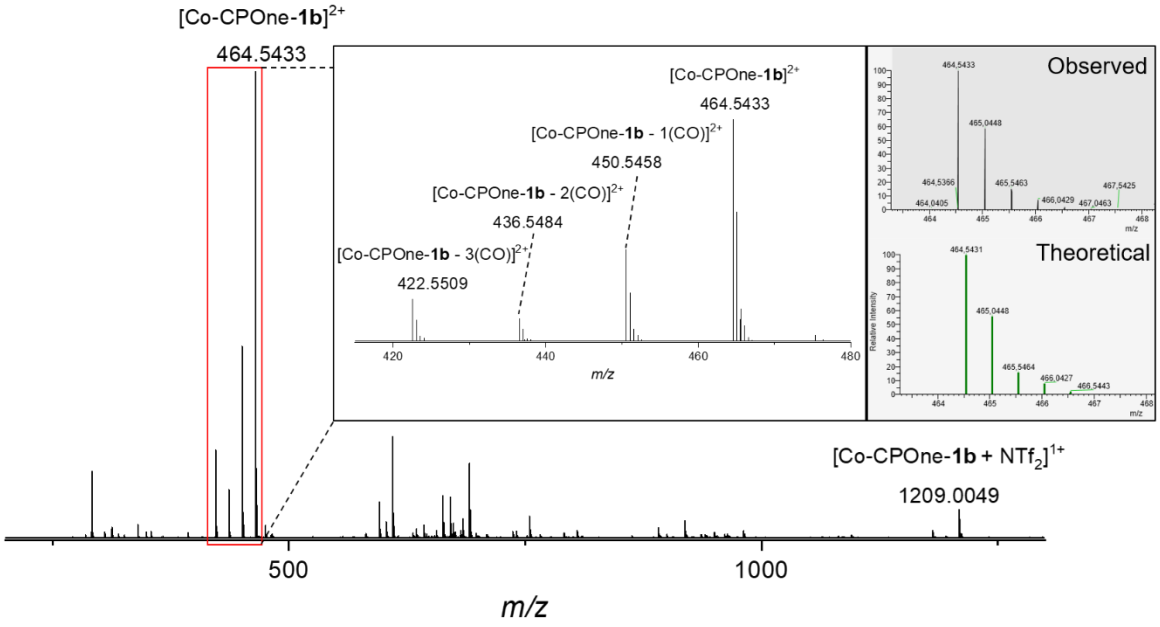
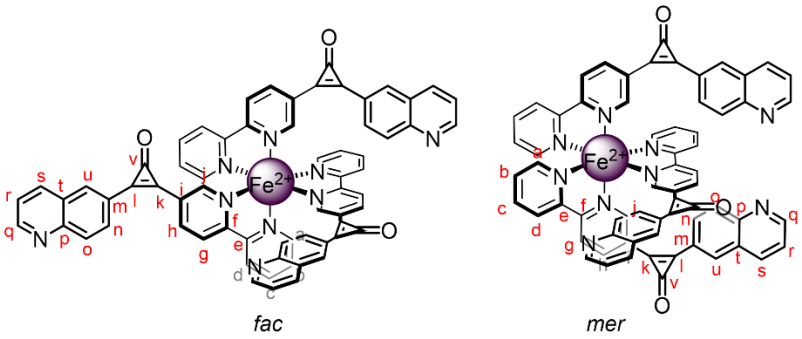


Figure S113. High resolution ESI mass spectrum of Co-CPOne-**1b** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

7.7 Fe-CPOne-**1c**



Iron tetrafluoroborate hexahydrate (0.53 mg, 1.57 µmol) and 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**) (1.60 mg, 4.77 µmol) were dissolved in CD_3CN (0.5 mL) and all characterisation was carried out immediately.

Note: The complex interconverts into a dynamic combinatorial library (DCL) within hours as evidenced by the loss of signals over time (Figure S115). Acquisition of NMR data of sufficient quality for analysis was not possible because of the interconversion as well as the overlap and broadness of the signals.

HRMS (ESI, CH_3CN,) *m/z*: 530.6253 [Fe-CPOne-**1c**]$^{2+}$, 516.6279 [Fe-CPOne-**1c** -CO]$^{2+}$, 502.6303 [Fe-CPOne-**1c** -2(CO)]$^{2+}$, 488.6328 [Fe-CPOne-**1c** -3(CO)]$^{2+}$.

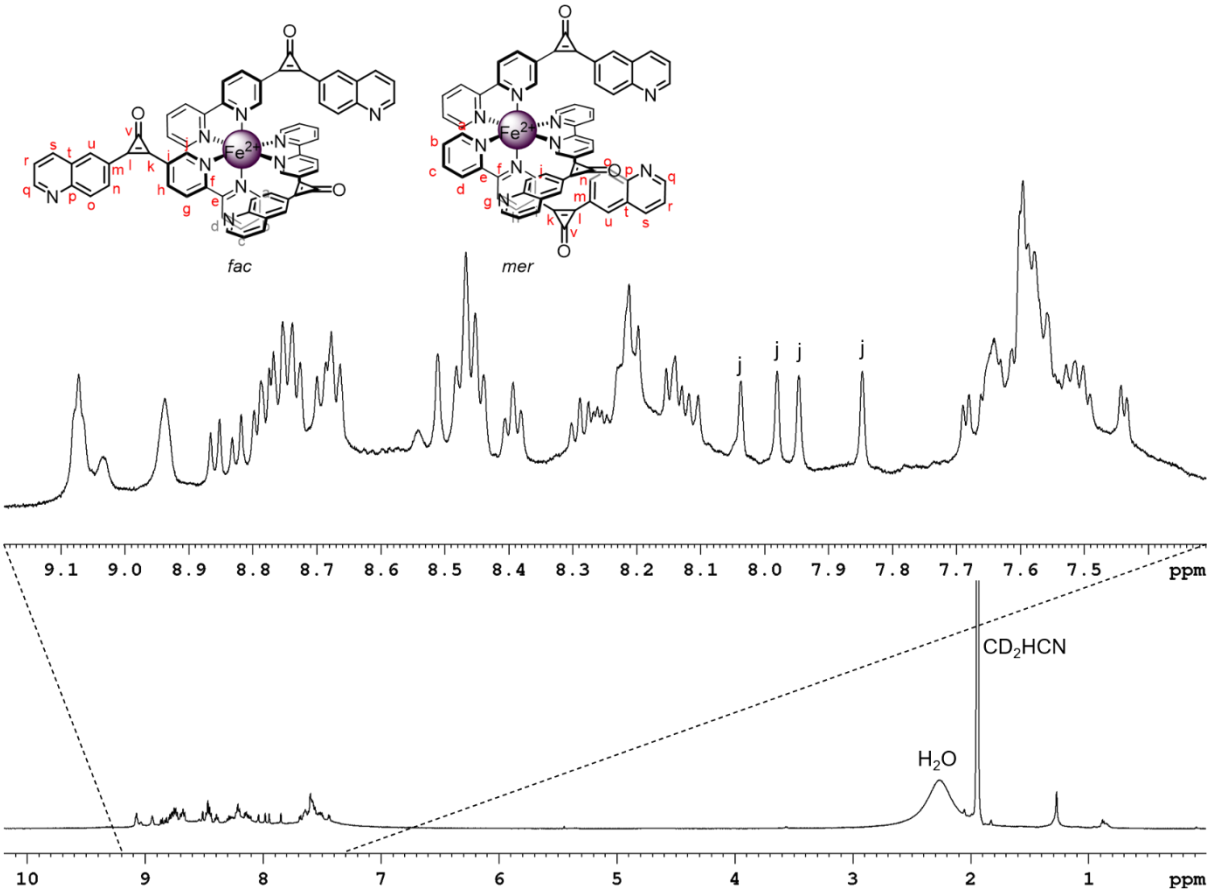


Figure S114. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Fe-CPOne-**1c**. Protons j are tentatively assigned.

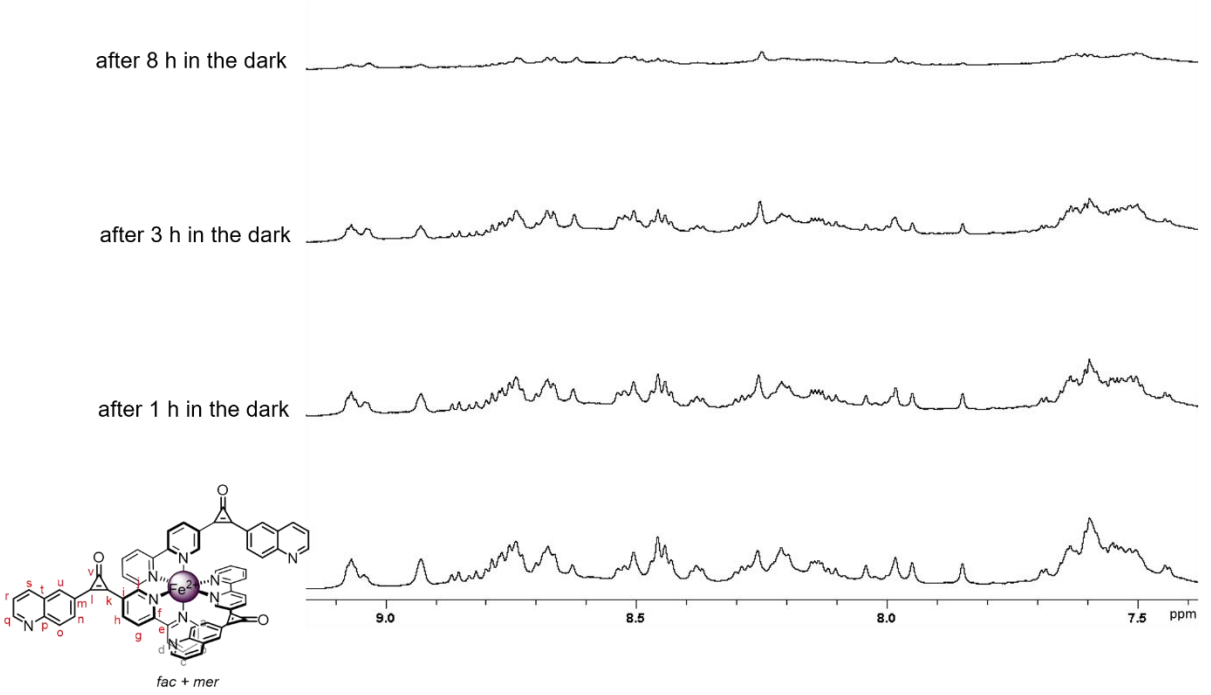


Figure S115. ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of Fe-CPOne-**1c** directly after preparation (bottom) and after 1 h, 3 h and 8 h in the dark.

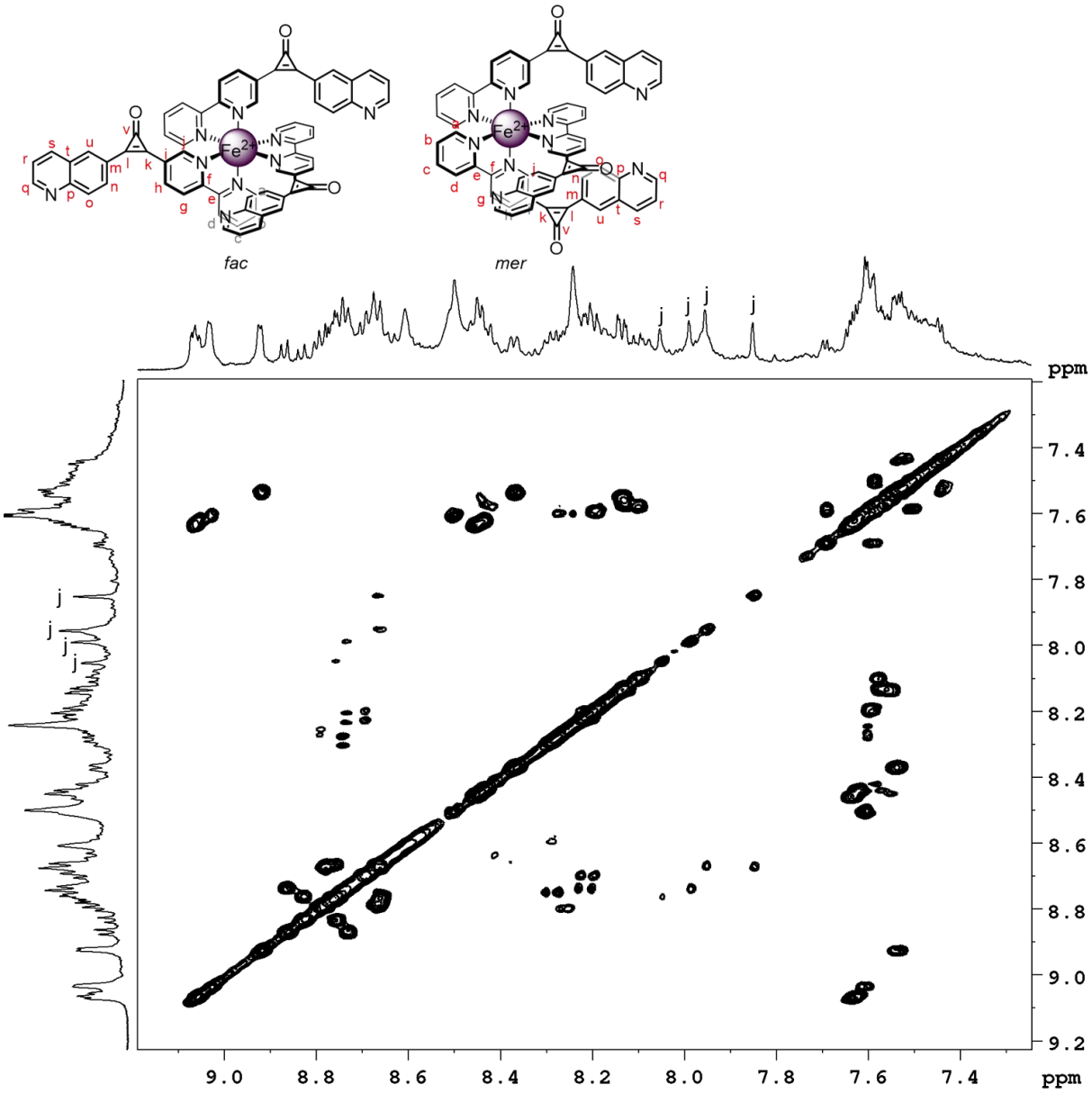


Figure S116. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Fe-CPOne-**1c**. Note: this complex was prepared using iron trifluoromethanesulfonate rather than iron tetrafluoroborate.

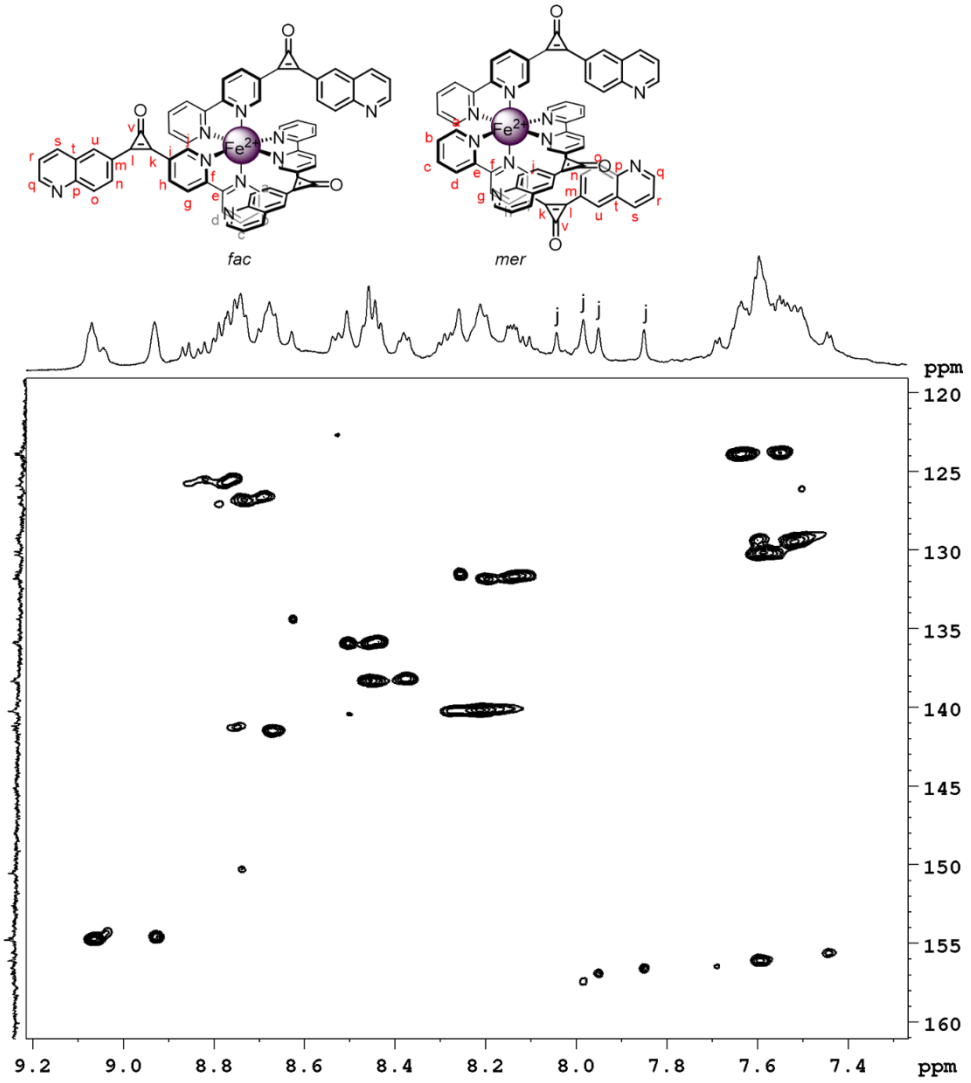


Figure S117. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Fe-CPOne-**1c**.

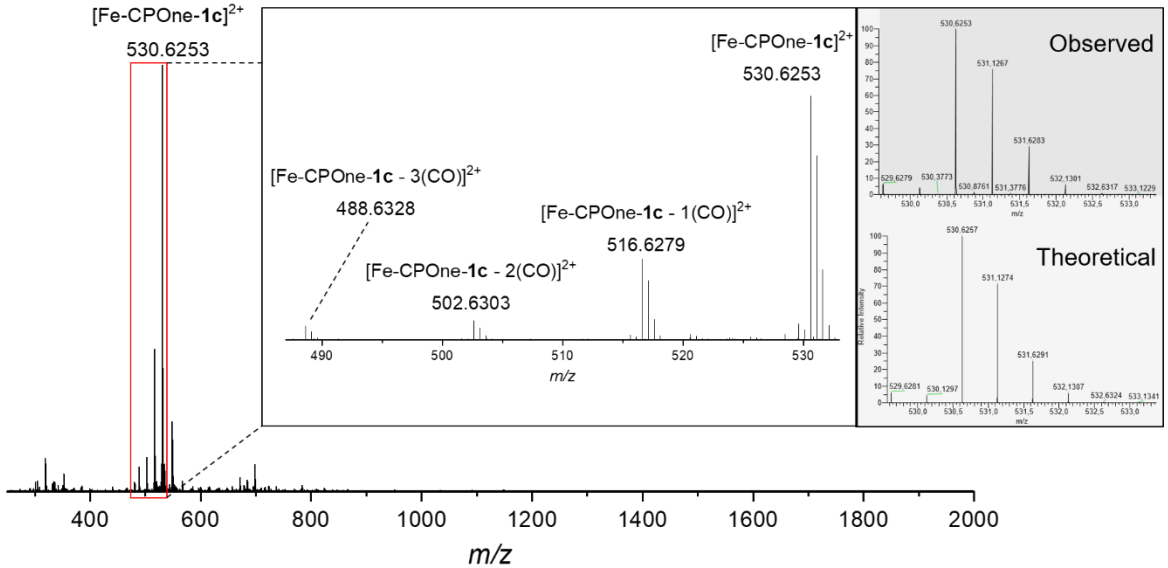
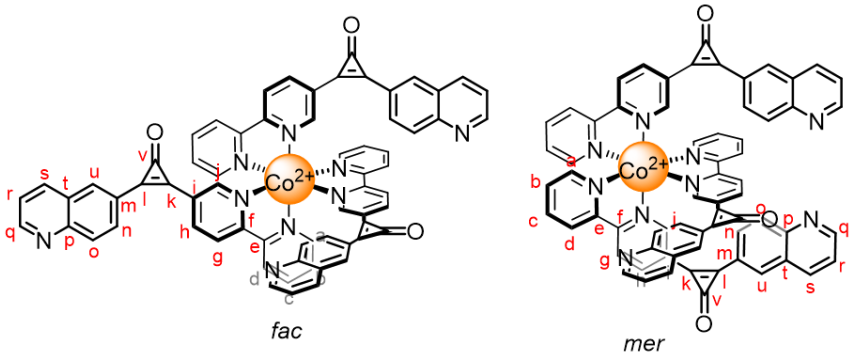


Figure S118. High resolution ESI mass spectrum of freshly prepared Fe-CPOne-**1c** showing in the insets the distinct fragment pattern upon CO loss as well as the observed and theoretical isotope patterns.

7.8 Co-CPOne-**1c**



Cobalt bis(trifluoromethylsulfonyl)imide (4.68 mg, 7.55 µmol) and 5-(2-cycloprop-2-enone-6-(quinolin-2-yl))-2,2'-bipyridine (**1c**) (7.6 mg, 22.7 µmol) were dissolved in CD_3CN (0.5 mL) and all characterisation was carried out immediately.

Note: The complex interconverts into a dynamic combinatorial library (DCL) within hours (Figure S120).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 104.6 (br, 1H, $H_{a/j}$), 99.5 (br, 1H, $H_{a/j}$), 97.2 (br, 1H, $H_{a/j}$), 92.7 (br, 1H, $H_{a/j}$), 92.1 (s, 1H, H_{d1}), 91.5 (br, 1H, $H_{a/j}$), 88.1 (s, 1H, H_{d2}), 87.1 (br, 1H, $H_{a/j}$), 85.7 (s, 2H, $H_{g1,d3}$), 82.3 (s, 1H, H_{g2}), 81.5 (s, 1H, H_{dfac}), 80.3 (br, 1H, $H_{a/j}$), 78.8 (s, 1H, H_{g3}), 75.0 (s, 1H, H_{gfac}), 52.9 (s, 1H, H_{b2}), 52.0 (s, 1H, H_{b1}), 46.6 (s, 1H, H_{bfac}), 46.1 (s, 1H, H_{b3}), 19.6 (s, 1H, H_{c1}), 17.7 (s, 1H, H_{c2}), 16.5 (s, 1H, H_{h1}), 14.9 (s, 1H, H_{h2}), 14.5 (s, 1H, H_{c3}), 12.8 (s, 1H, H_{cfac}), 11.5 (s, 1H, H_{h3}), 10.0 (s, 1H, H_{hfac}), 7.5-7.1 (m, 13H, $H_{n,s-q}$), 6.9 (s, 1H, H_n), 6.5 (s, 1H, H_n), 6.3 (s, 1H, H_n), 5.8 (s, 1H, H_u), 5.7 (s, 1H, H_u), 4.5 (s, 1H, H_u), 4.5 (s, 1H, H_u), 2.0 (s, 3H, H_o), 0.2 (s, 1H, H_o).

Note: While it was possible to assign the proton signals within one spin system (indicated by numbers) based on the COSY spectrum, the different spin systems within each ligand could not be correlated to a particular ligand environment. For the signals of the bipyridine, the fac isomer was, therefore, tentatively assigned based on the integral of the signals. The three remaining sets of signals corresponding to the mer isomer were arbitrarily labelled with black, red, and blue labels according to their decreasing chemical shift. Protons corresponding to the R substituent were tentatively assigned in grey due to the signal overlap in the diamagnetic region of the spectra.[11] *Protons a and j are assigned in grey based on related complexes.*[11]

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 609.9 (C_{b1}), 606.6 (C_{b3}), 601.9 (C_{b2}), 597.7 (C_{fac}), 428.7 (C_{d1}), 426.7 (C_{g1}), 423.8 (C_{d3}), 422.4 (C_{g3}), 415.1 (C_{g2}), 413.9 (C_{d2}), 409.7 (C_{gfac}), 409.5 (C_{dfac}), 197.8 (C_{c2}), 189.5 (C_{c1}), 184.5 (C_{fac}), 176.4 (C_{c3}), 173.2 (C_{h2}), 167.5 (C_{h1}), 159.7 (C_{hfac}), 153.8 (C_{h3}), 133.2 (C_u), 132.7 (C_o), 127.0 (C_o), 125.2 (C_o), 136.9-121.9 ($C_{n,q-u}$).

Note: Because of the interconversion, overlap and broadness of the signals, acquisition of ^{13}C NMR data of sufficient quality for assignment was not possible. Therefore, the carbons reported above were assigned through the cross-peaks in the HMQC spectrum (Figure S123).

HRMS (ESI, CH_3CN) *m/z*: 532.1244 [Co-CPOne-**1c**]$^{2+}$, 518.1270 [Co-CPOne-**1c** -CO]$^{2+}$, 504.1294 [Co-CPOne-**1c** -2(CO)]$^{2+}$.

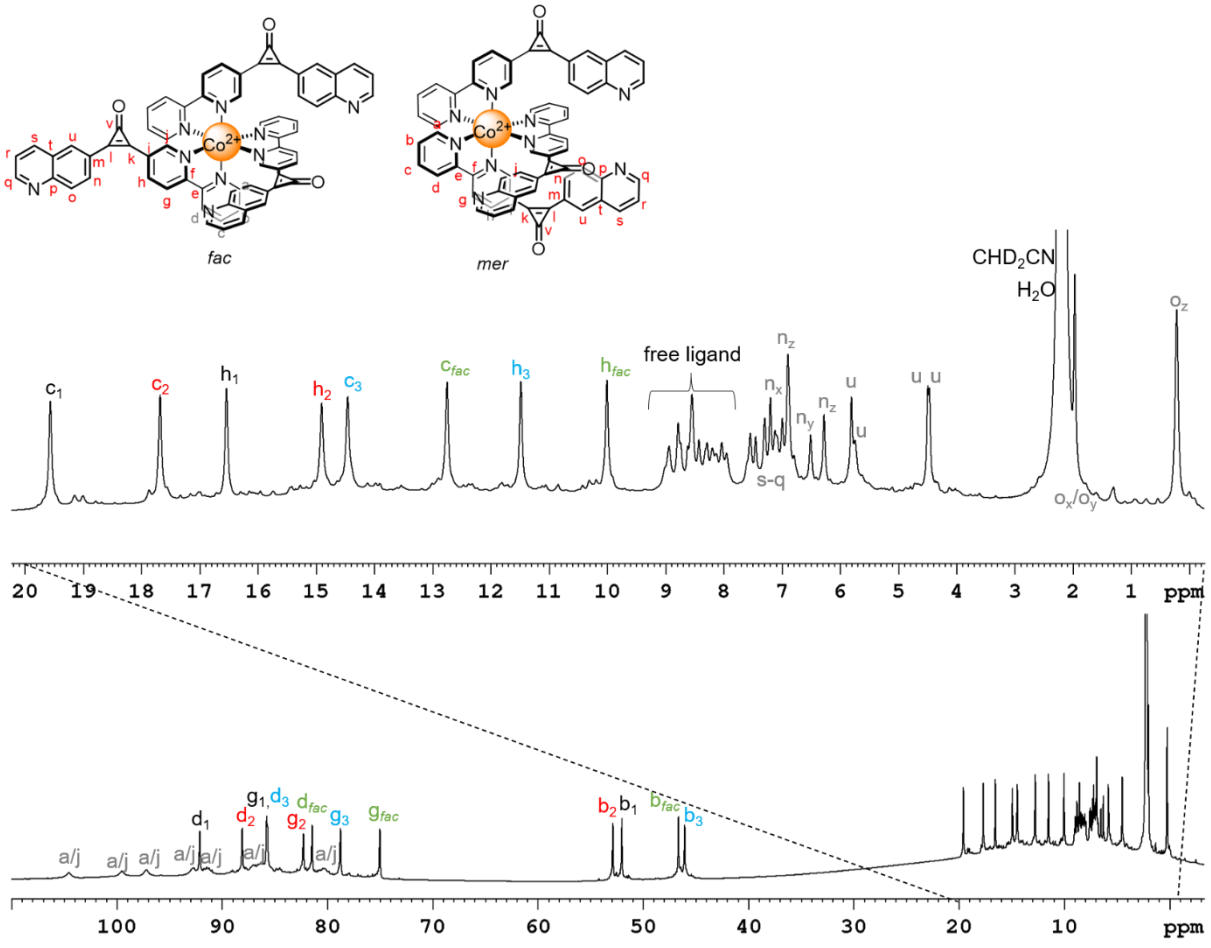


Figure S119. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1c**.

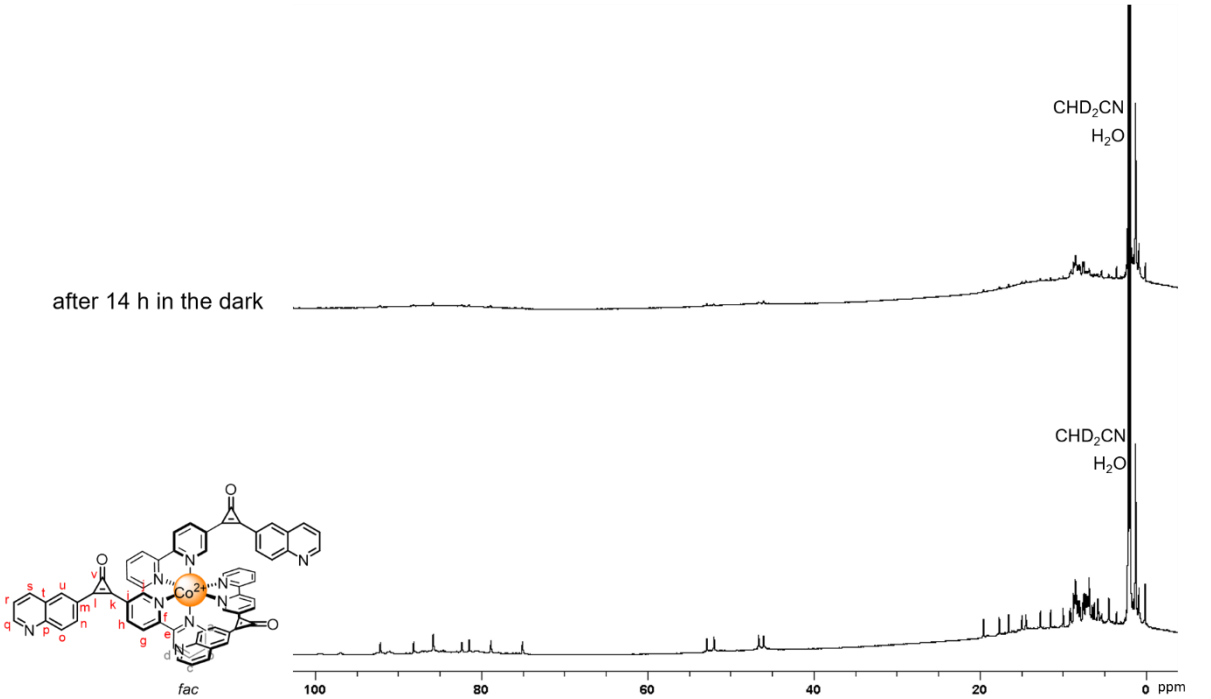


Figure S120. ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1c** directly after preparation (bottom) and after 12 h in the dark.

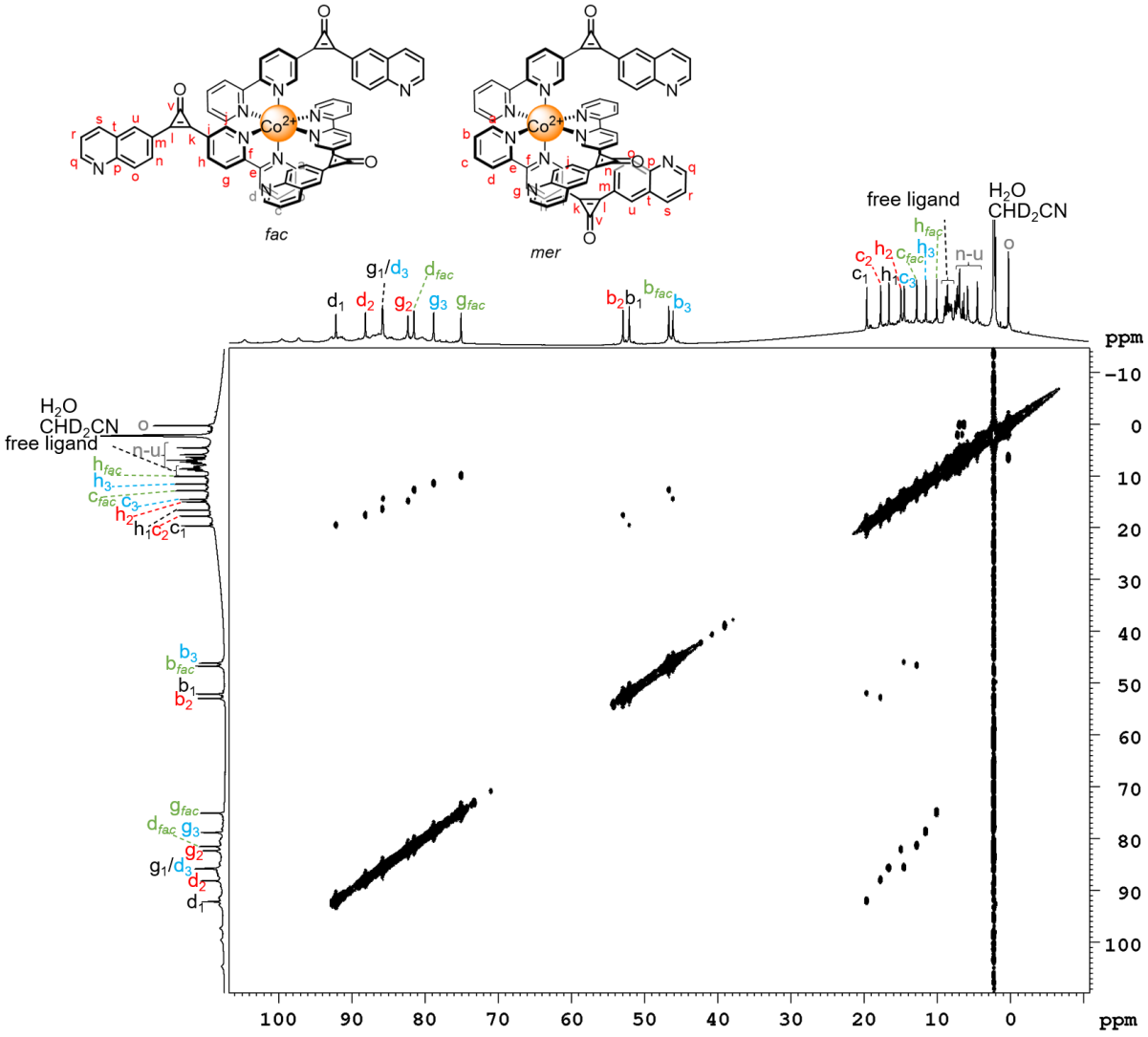


Figure S121. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Co-CPOne-**1c**.

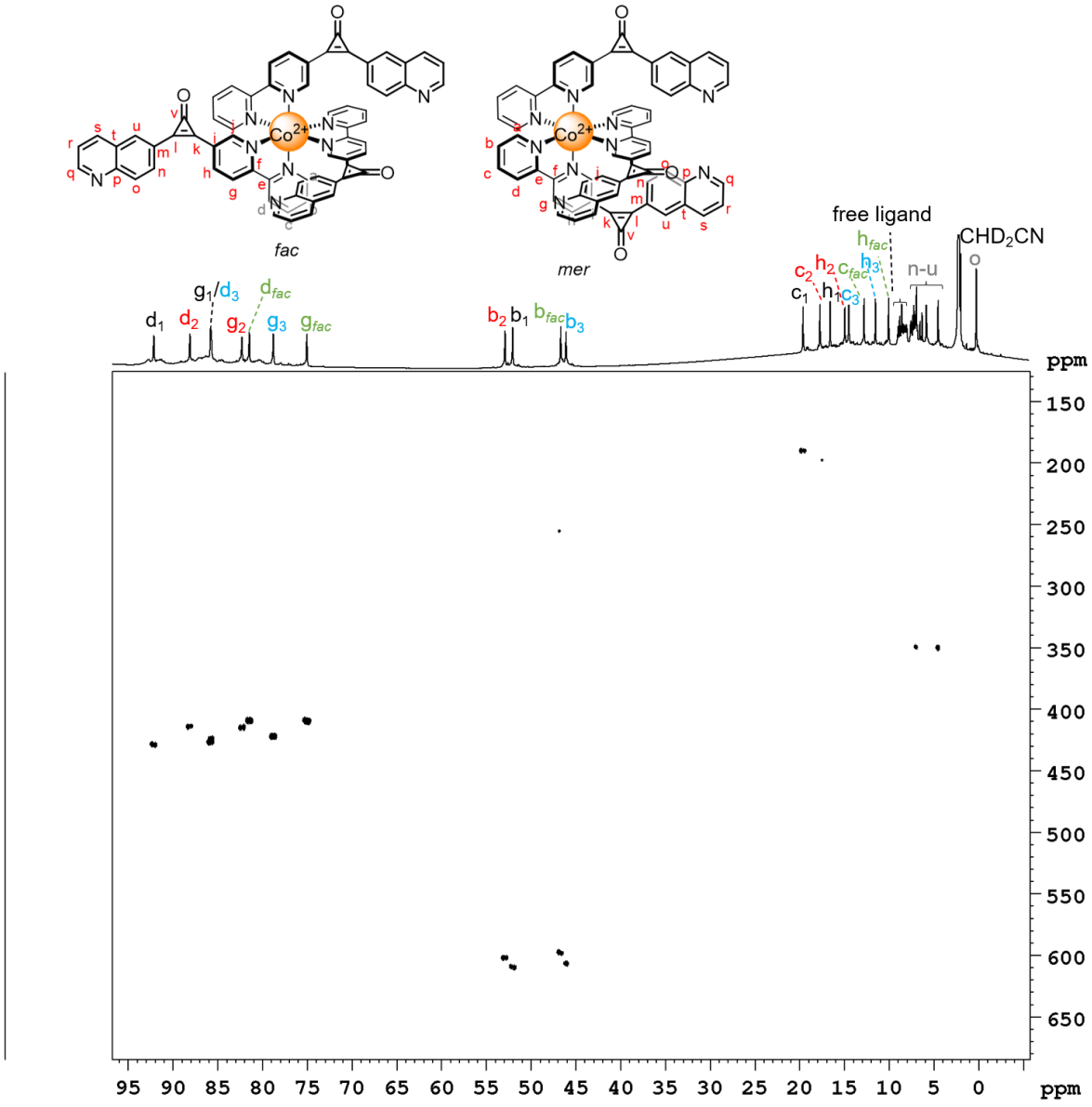


Figure S122. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-CPOne-**1c**.

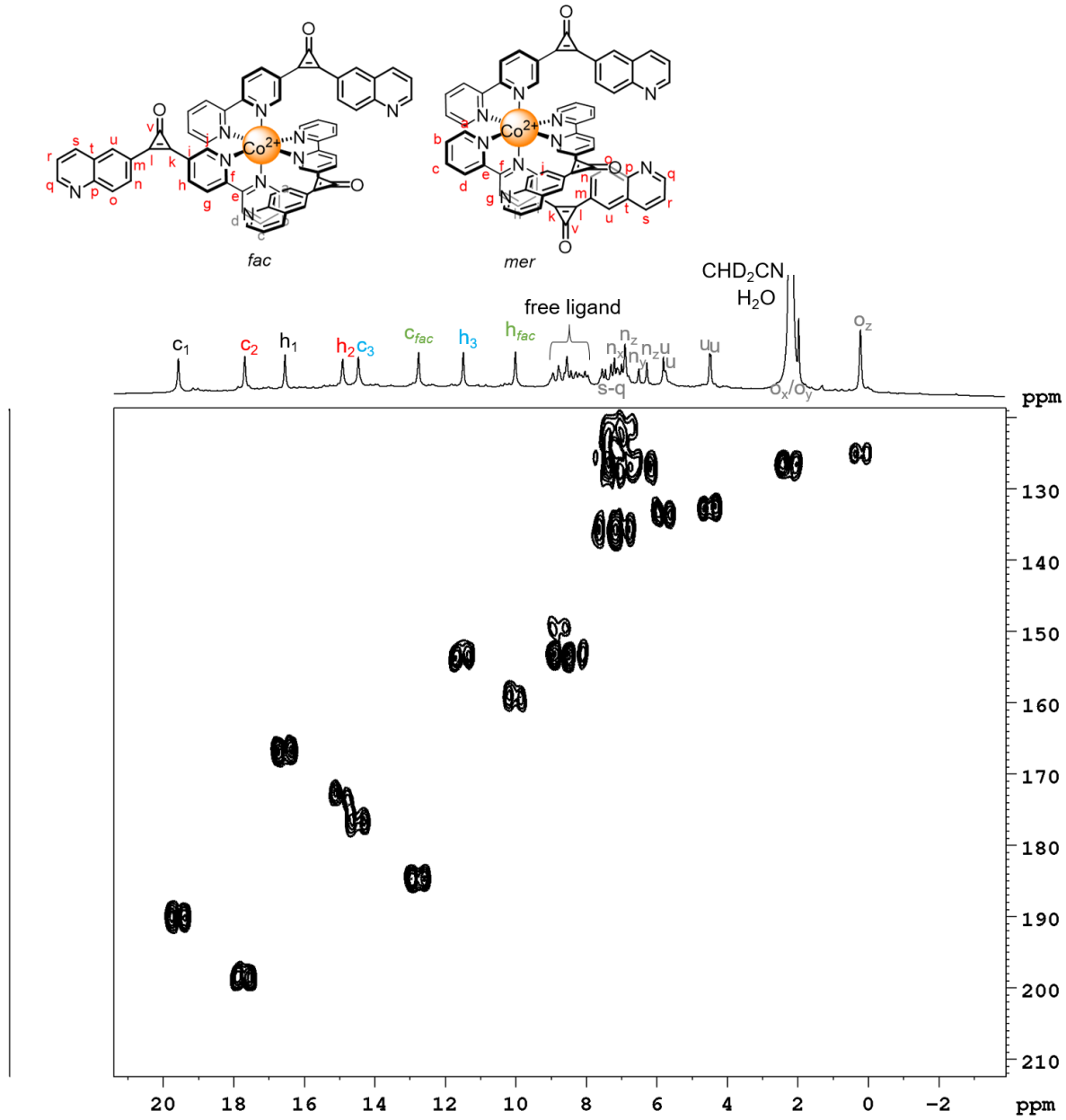


Figure S123. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-CPOne-**1c**.

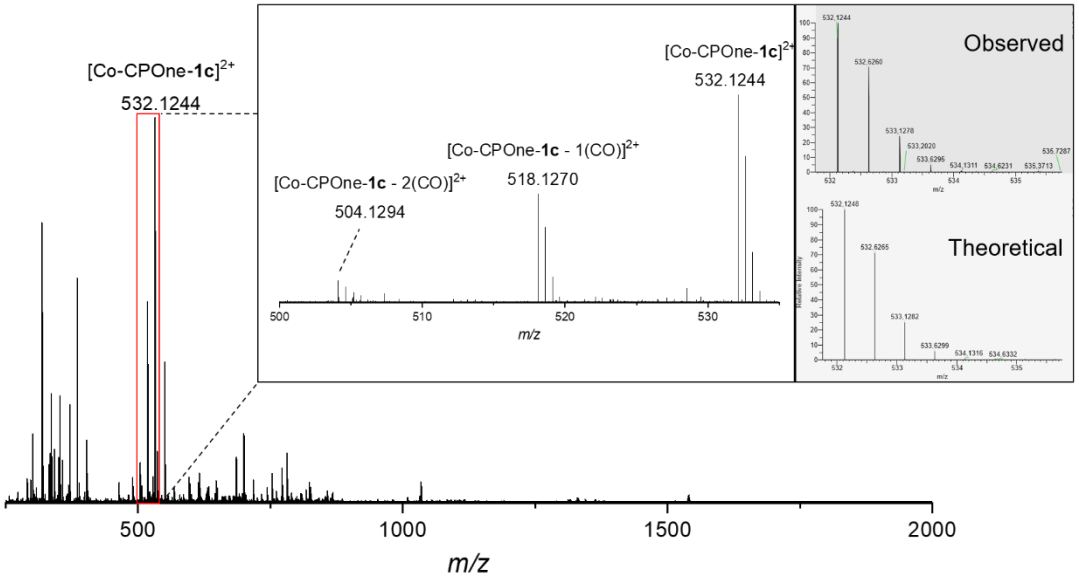
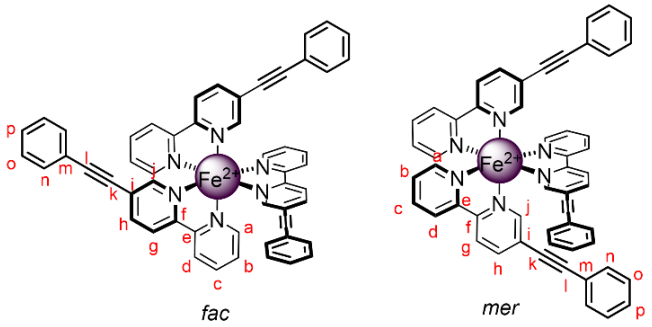


Figure S124. High resolution ESI mass spectrum of freshly prepared Co-CPOne-**1c** showing in the insets the distinct fragmenting pattern upon CO loss as well as the observed and theoretical isotope patterns.

8 Complexes M-2a-2c

8.1 Complex Fe-**2a**



Iron tetrafluoroborate hexahydrate (3.95 mg, 11.7 µmol) and 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (9.9 mg, 3.9 µmol) were dissolved in CD_3CN (0.5 mL). After standing at room temperature overnight the solution was added dropwise to diethyl ether (6 mL) and centrifuged. The organic layer was decanted and the residue washed twice with diethyl ether (10 mL) to obtain the product as a red powdery solid.

^{1}H NMR (500 MHz, CD_3CN, 298 K) δ (ppm): 8.59-8.51 (m, 8H, $H_{d,g}$), 8.24-8.20 (m, 4H, H_h), 8.18-8.11 (m, 4H, H_c), 7.64 (dd, ^4J = 1.2 Hz, ^5J = 0.6 Hz, 1H, H_j), 7.57 (dd, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H, H_j), 7.54 (ddd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H, H_a), 7.51-7.38 (m, 28H, $H_{a,b,j,n,o,p}$), 7.33 (ddd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H, H_a).

^{13}C NMR (126 MHz, CD_3CN, 298 K) δ (ppm): 159.8 (C_e), 159.7 (C_e), 159.7 (C_e), 159.6 (C_e), 159.1 (C_f), 159.0 (C_f), 158.9 (C_f), 158.9 (C_f), 157.2 (C_j), 157.0 (C_j), 156.9 (C_j), 156.6 (C_j), 155.9 (C_a), 155.6 (C_a), 155.3 (C_a), 141.9 (C_h), 141.9 (C_h), 141.9 (C_h), 141.8 (C_h), 140.0 (C_c), 139.9 (C_c), 132.7 ($C_{n/o}$), 130.9 (C_p), 129.9 ($C_{n/o}$), 128.8 (C_b), 128.7 (C_b), 128.7 (C_b), 128.6 (C_b), 125.8 (C_d), 125.6 (C_d), 125.6 (C_d), 125.5 (C_d), 124.9 (C_g), 124.8 (C_i), 124.8 (C_i, C_g), 124.8 (C_i), 124.7 (C_i, C_g), 124.6 (C_g), 122.3 (C_m), 122.3 (C_m), 122.2 (C_m), 97.4 (C_l), 97.3 (C_l), 97.3 (C_l), 97.2 (C_l), 85.2 (C_k), 85.1 (C_k), 85.1 (C_k), 85.0 (C_k).

HRMS (ESI, CH_3CN) *m*/z: 412.1168 [Fe-**2a**]$^{2+}$, 284.0668 [Fe-**2a** -1(**2a**)]$^{2+}$, 257.1071 [**2a** +H]$^{+}$.

FT-IR: $\tilde{\nu}$ = 3630.9 (w), 3080.6 (w), 2222.6 (w), 1601.3 (w), 1557.6 (w), 1494.7 (w), 1465.7 (m), 1439.0 (m), 1376.1 (w), 1313.5 (w), 1278.1 (w), 1237.9 (w), 1056.1 (s), 911.8 (w), 853.8 (w), 788.3 (m), 753.2 (s), 730.9 (m), 691.8 (m), 671.9 (w), 573.5 (w), 546.7 (w), 519.8 (m) cm^{-1}.

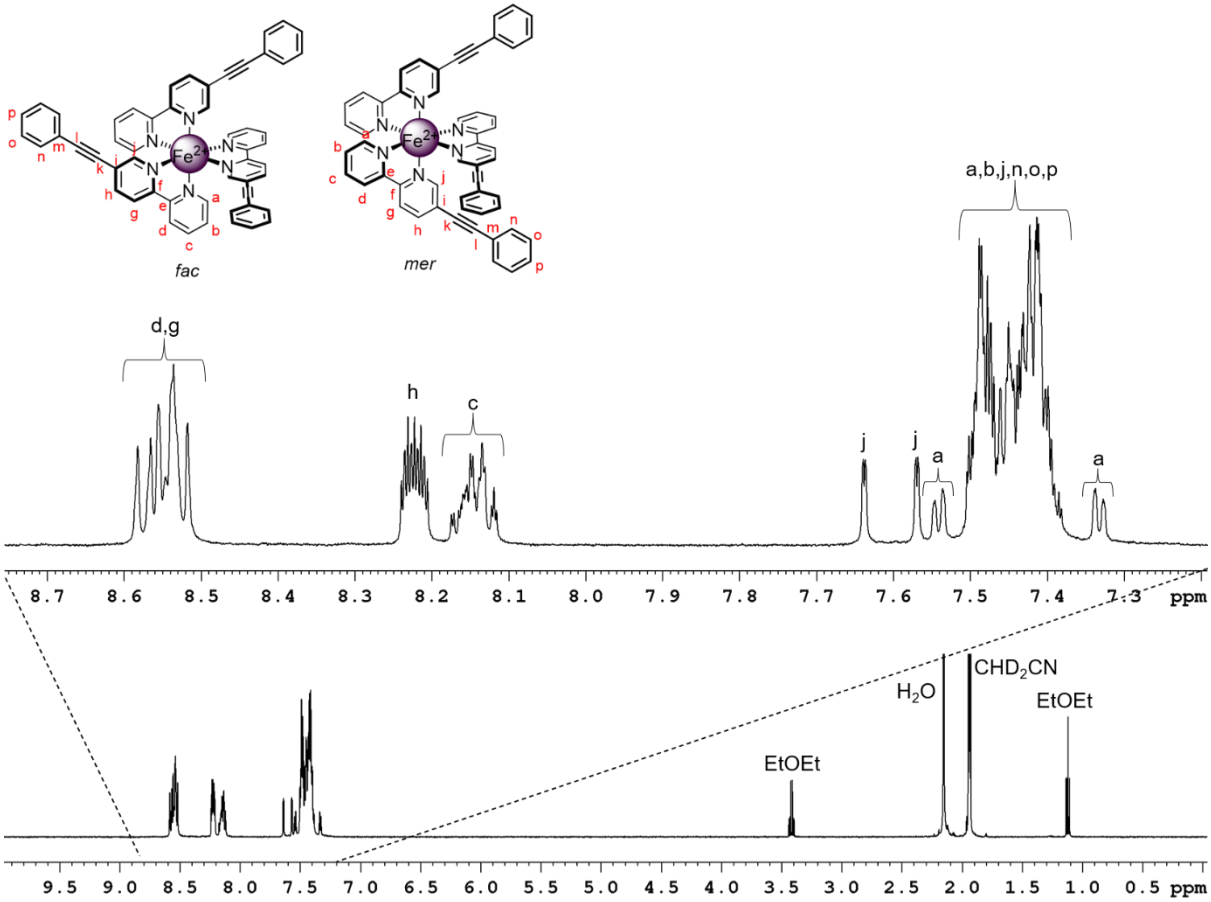


Figure S125. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-**2a**.

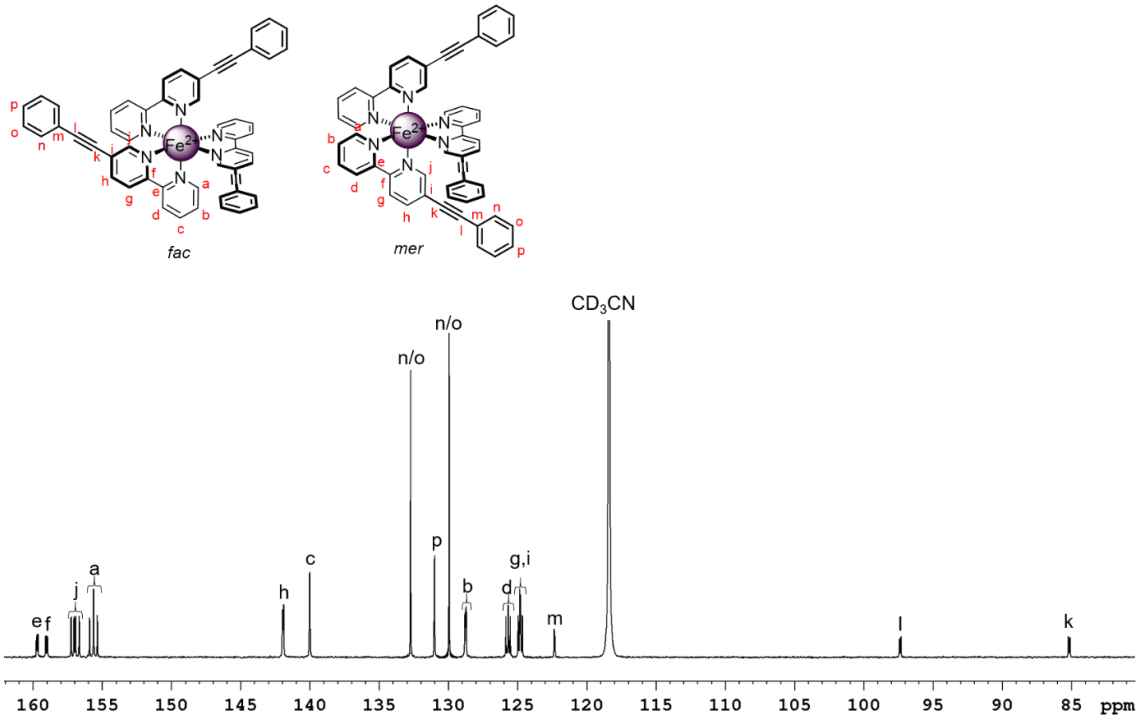


Figure S126. ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of Fe-**2a**.

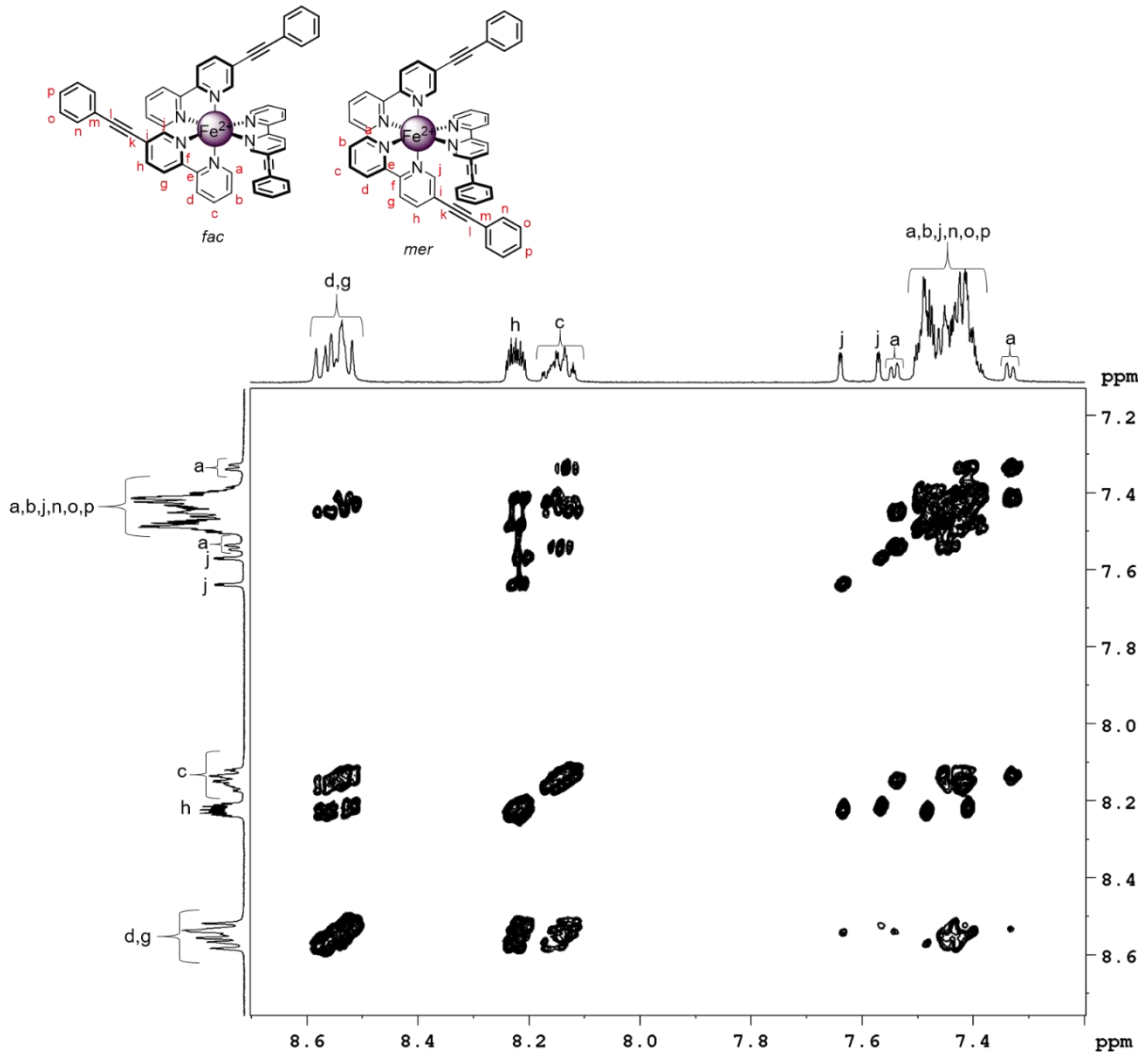


Figure S127. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-**2a**.

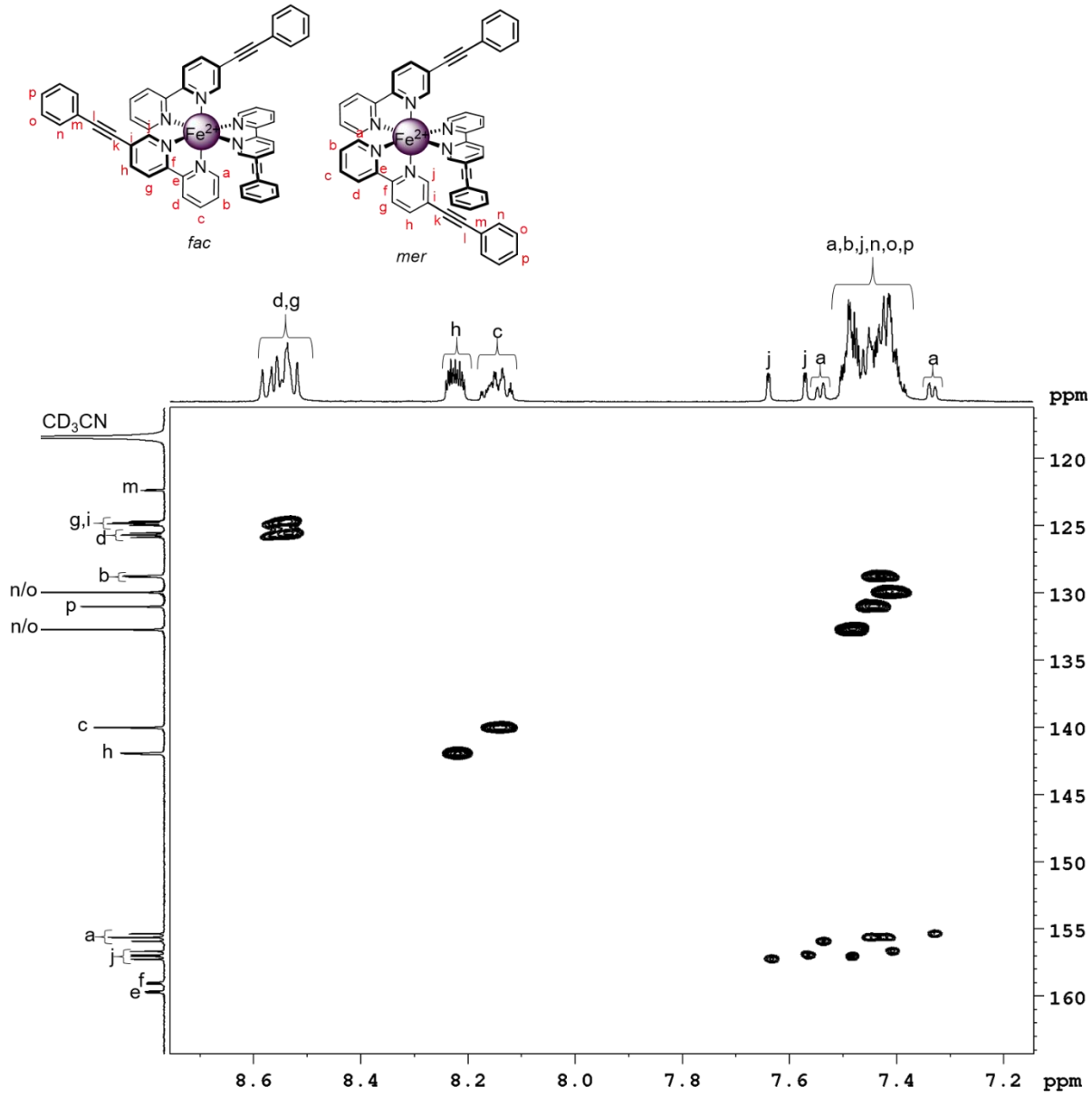


Figure S128. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Fe-**2a**.

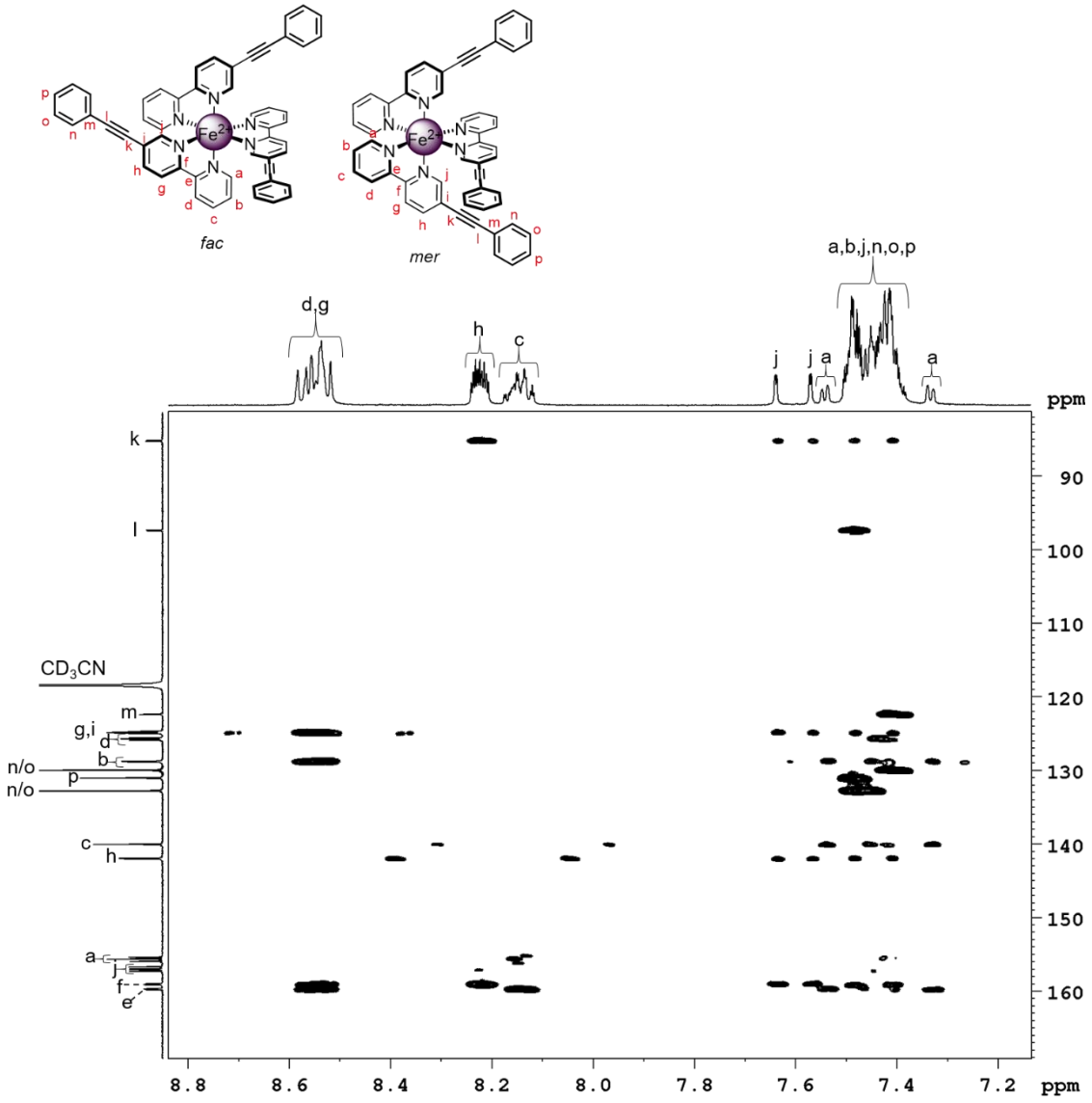


Figure S129. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/126 MHz, CD_3CN, 298 K) of Fe-**2a**.

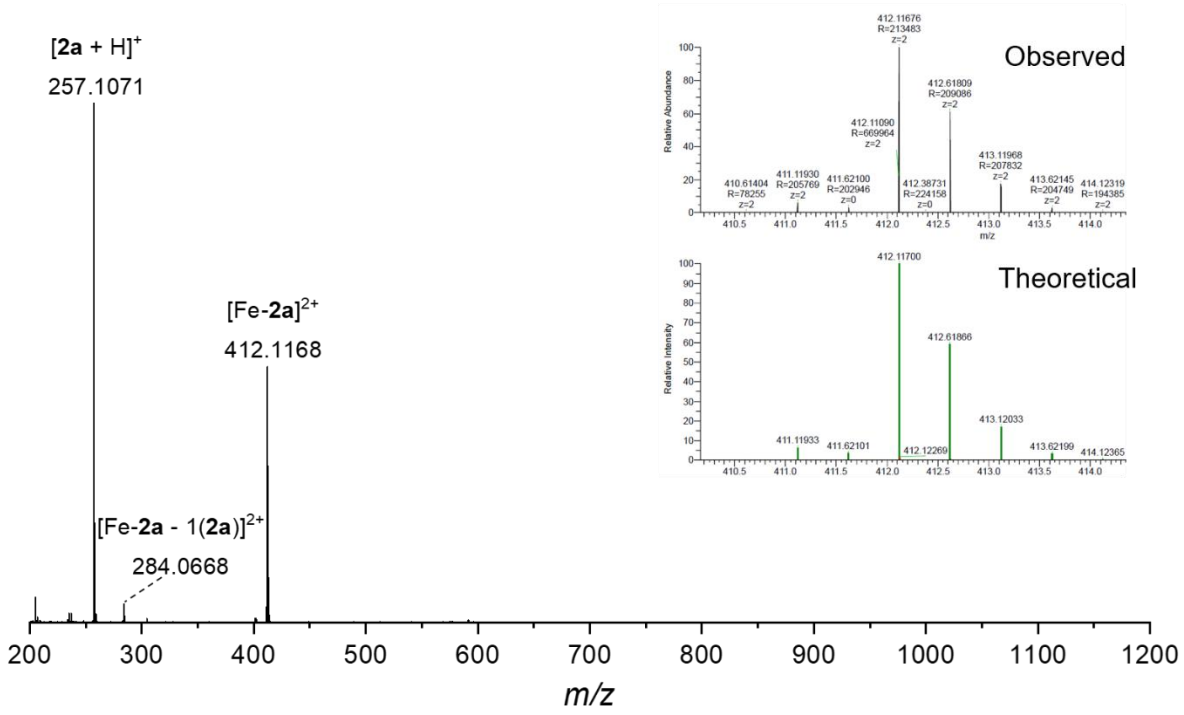
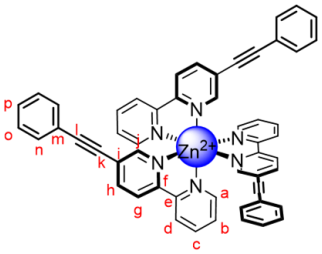


Figure S130. High resolution ESI mass spectrum of Fe-**2a** showing in the insets the observed and theoretical isotope patterns.

8.2 Complex Zn-**2a**



Zinc trifluoromethanesulfonate (3.93 mg, 10.8 µmol) and 5-(2-cycloprop-2-enone-3-phenyl)-2,2'-bipyridine (**1a**) (9.20 mg, 32.4 µmol) were dissolved in CD_3CN (0.5 mL).

Note: Because of the broadness of the signals, complete and unambiguous assignment of the ^{1}H and ^{13}C NMR spectra was not possible and *fac/mer* isomers could not be distinguished.

HRMS (ESI, CH_3CN) *m/z*: 416.1138 [Zn-**2a**]$^{2+}$, 288.0639 [Zn-**2a** -1(**2a**)]$^{2+}$, 257.1071 [**2a** +H]$^{+}$.

FT-IR: $\tilde{\nu}$ = 3064.9 (w), 2221.6 (w), 1600.1 (w), 1561.1 (w), 1498.1 (w), 1487.4 (w), 1472.0 (m), 1438.8 (m), 1376.1 (w), 1315.0 (w), 1265.5 (s), 1223.9 (m), 1149.9 (s), 1070.9 (w), 1049.5 (w), 1029.1 (s), 925.7 (w), 856.2 (w), 794.1 (m), 751.3 (s), 734.2 (m), 692.6 (m), 665.3 (w), 633.6 (s), 572.1 (m), 543.3 (w), 532.5 (w), 516.1 (m) cm^{-1}.

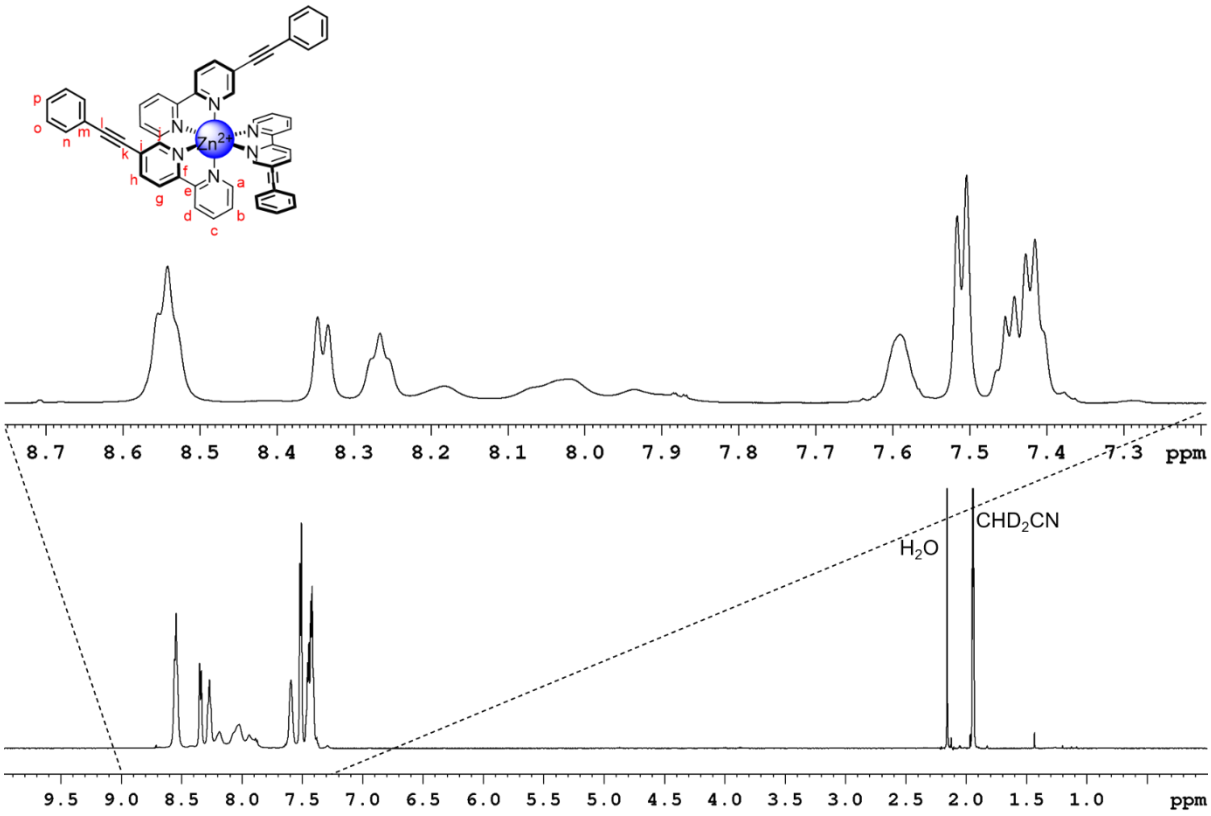


Figure S131. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of Zn-**2a**.

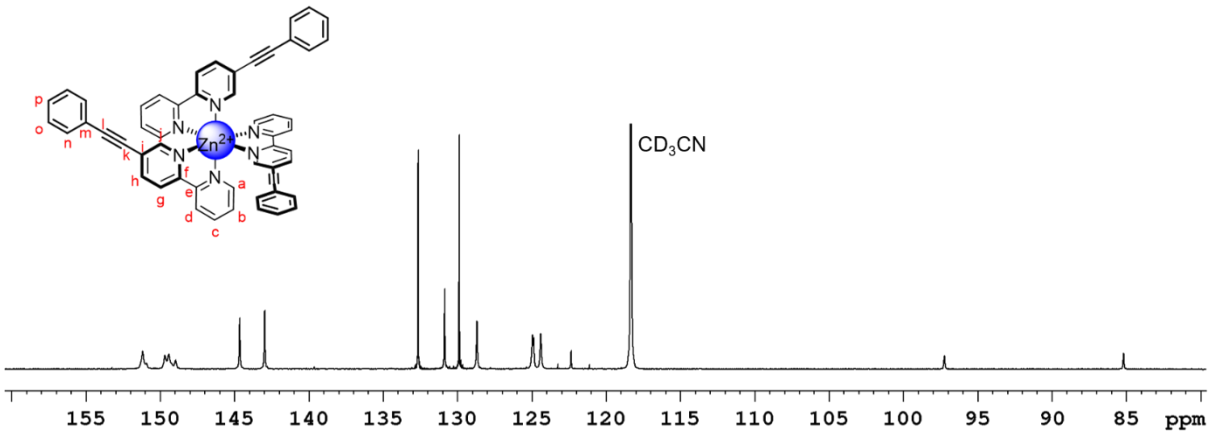


Figure S132. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of Zn-**2a**.

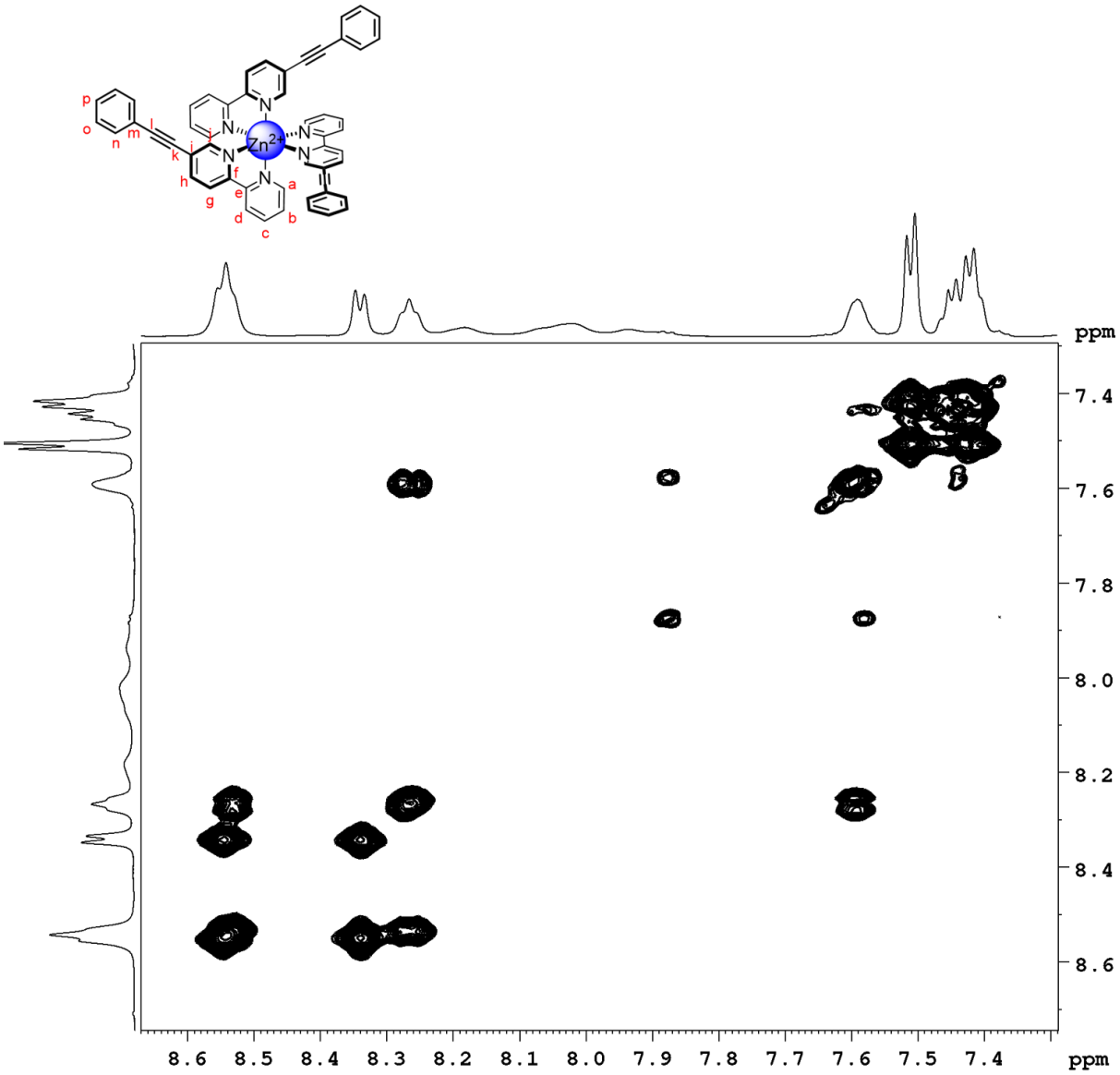


Figure S133. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of Zn-**2a**.

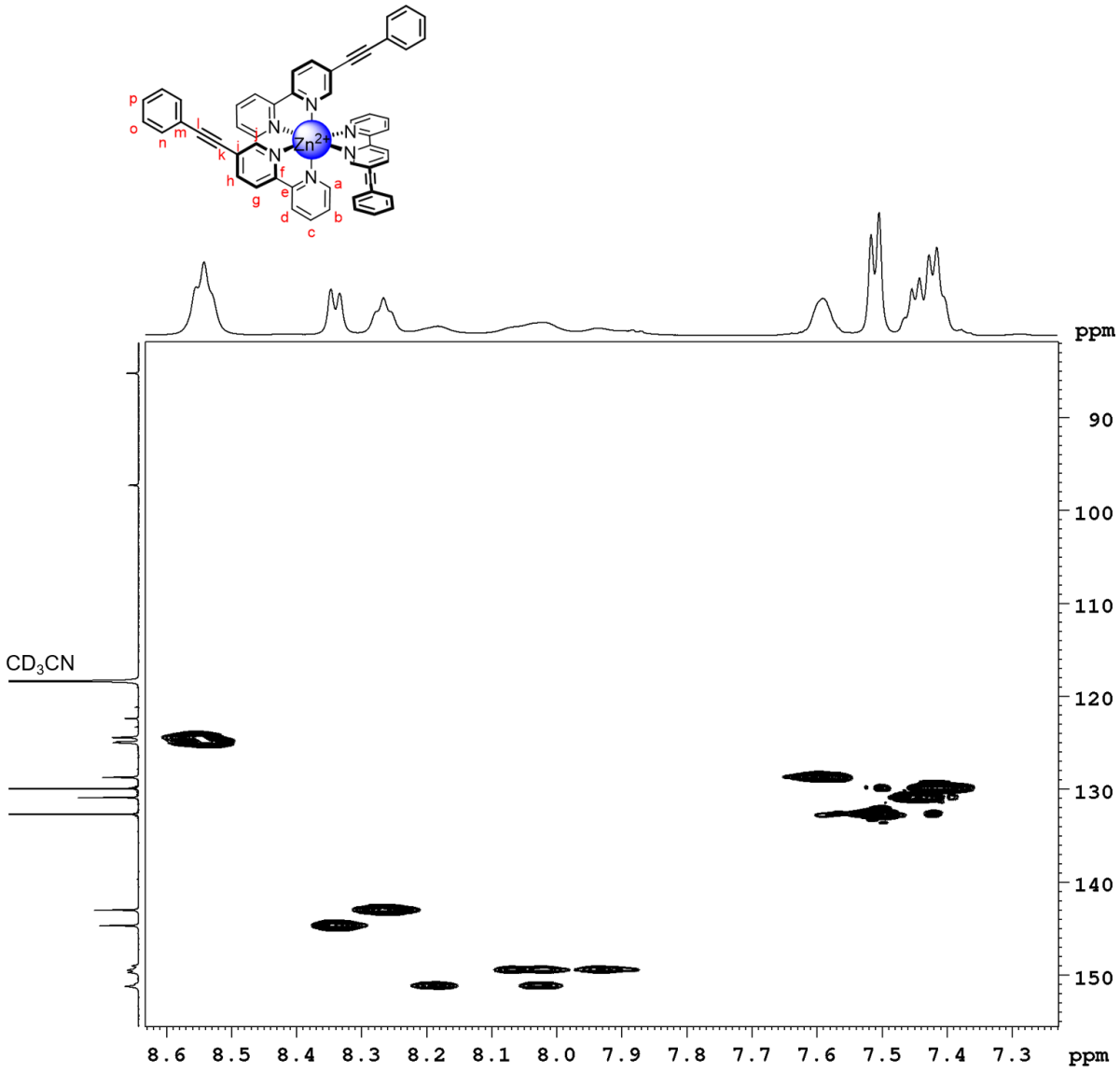


Figure S134. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Zn-**2a**.

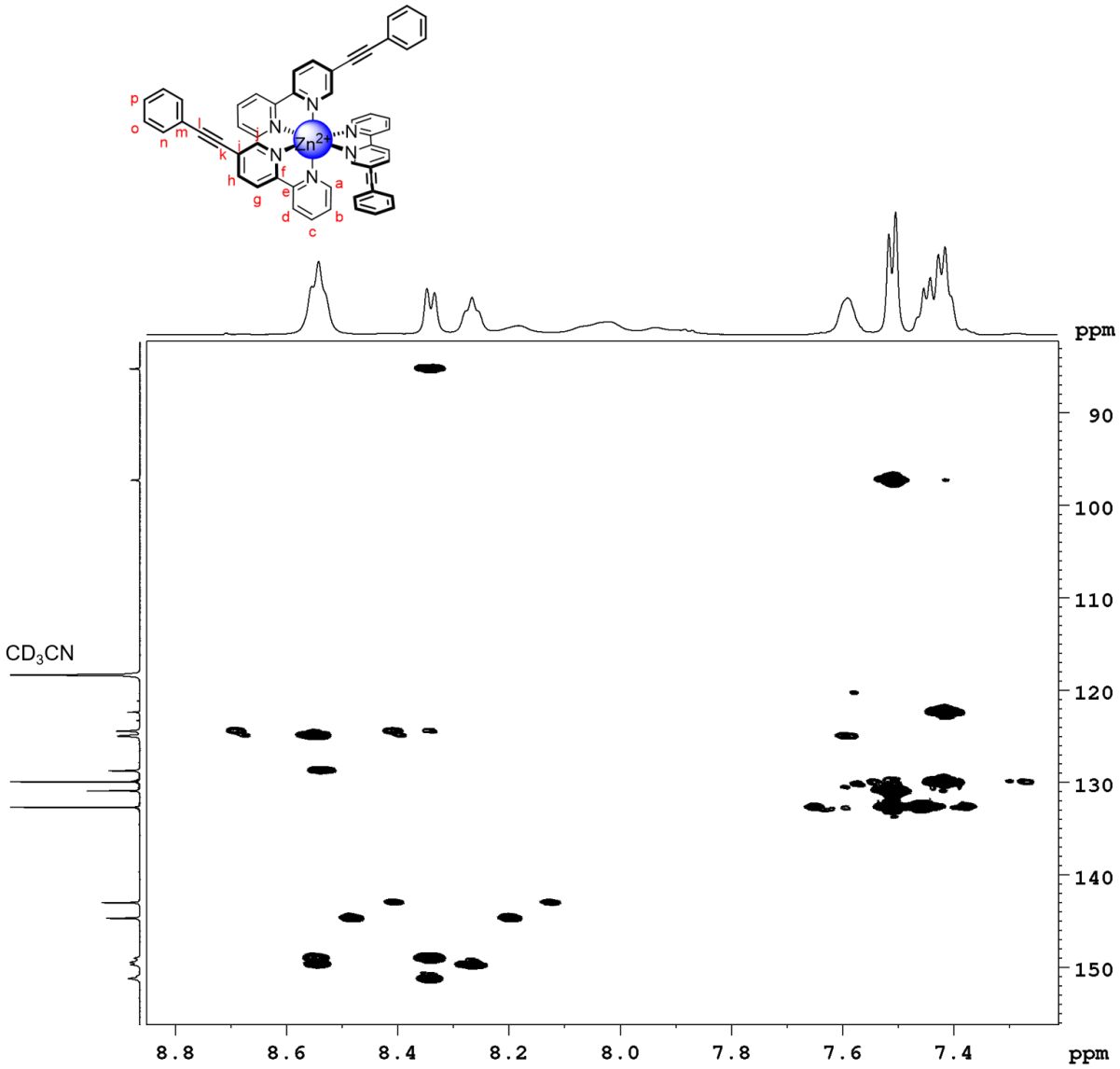


Figure S135. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Zn-**2a**.

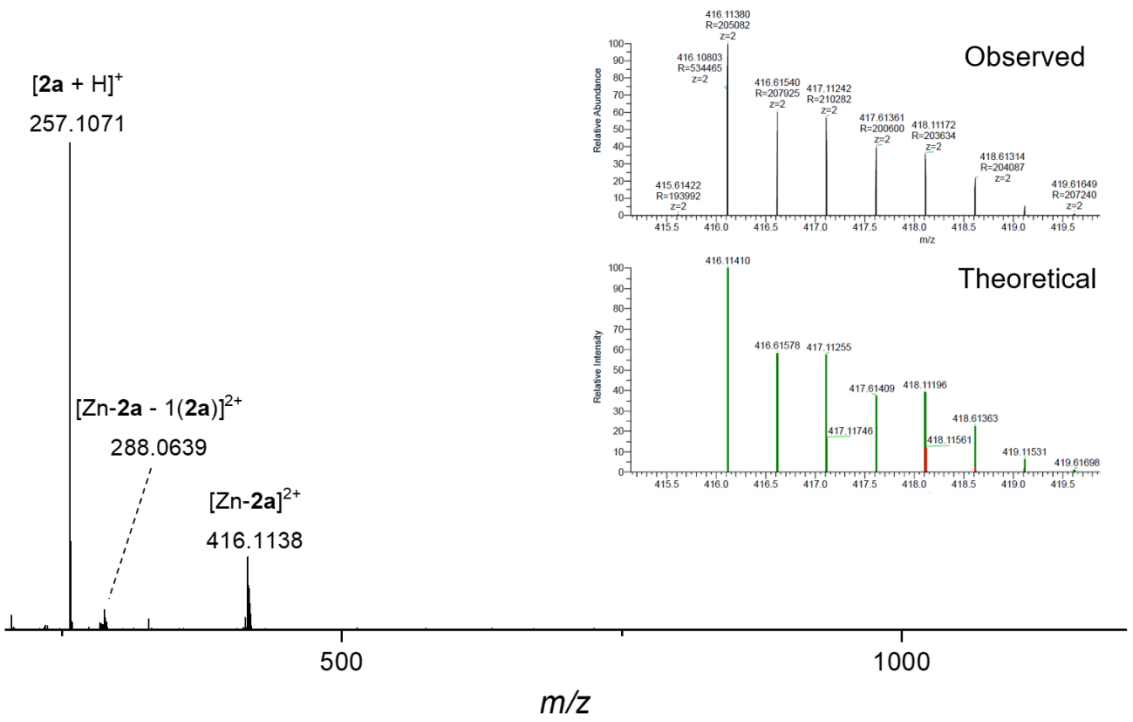
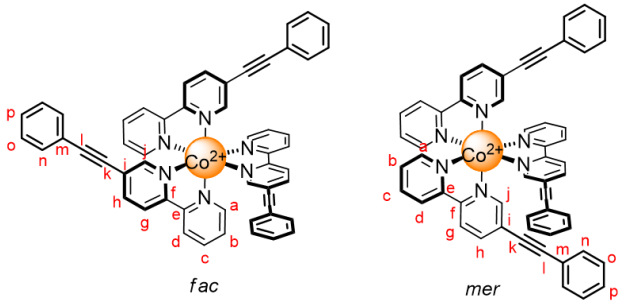


Figure S136. High resolution ESI mass spectrum of Zn-**2a** showing in the insets the observed and theoretical isotope patterns.

8.3 Complex Co-**2a**



Cobalt bis(trifluoromethylsulfonyl)imide (7.89 mg, 12.7 µmol) and 5-(phenylethynyl)-2,2'-bipyridine (**2a**) (9.8 mg, 38.2 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 104.1 (br, 1H, $H_{a/j}$), 100.7 (br, 1H, $H_{a/j}$), 92.5 (br, 1H, $H_{a/j}$), 90.1 (br, 1H, $H_{a/j}$), 89.7 (s, 1H, H_{d1}), 89.5 (br, 1H, $H_{a/j}$), 87.7 (s, 1H, H_{d2}), 85.9 (s, 1H, $H_{a/j}$), 85.7 (s, 1H, H_{g1}), 85.6 (s, 1H, H_{dfac}), 83.9 (s, 1H, H_{g2}), 82.9 (s, 1H, H_{d3}), 81.5 (s, 1H, H_{gfac}), 80.5 (s, 1H, $H_{a/j}$), 79.1 (s, 1H, H_{g3}), 78.5 (s, 1H, $H_{a/j}$), 51.9 (s, 1H, H_{b1}), 51.2 (s, 1H, H_{b2}), 46.2 (s, 1H, H_{bfac}), 45.8 (s, 1H, H_{b3}), 18.0 (s, 1H, H_{c1}), 17.0 (s, 1H, H_{c2}), 15.7 (s, 1H, H_{h1}), 14.9 (s, 1H, H_{h2}), 14.5 (s, 1H, H_{cfac}), 13.4 (s, 1H, H_{c3}), 12.4 (s, 1H, H_{hfac}), 11.4 (s, 1H, H_{h3}), 6.4 (s, 1H, H_p), 6.2 (s, 1H, H_p), 5.9 (s, 1H, H_p), 5.7 (s, 1H, H_p), 5.0 (s, 4H, $H_{n/o}$), 4.7 (s, 4H, $H_{n/o}$), 3.8 (s, 4H, $H_{n/o}$), 3.5 (s, 4H, $H_{n/o}$).

Note: While it was possible to assign the proton signals within one spin system (indicated by numbers) based on the COSY spectrum, the different spin systems within each ligand could not be correlated to a particular ligand environment. For the signals of the bipyridine, the fac isomer was, therefore, tentatively assigned based on the integral of the signals. The three remaining sets of signals corresponding to the mer isomer were arbitrarily labelled with black, red, and blue labels according to their decreasing chemical shift. Protons corresponding to the

R substituent were tentatively assigned in grey due to the signal overlap in the diamagnetic region of the spectra.[11] *Protons a and j are assigned in grey based on related complexes.*[11]

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 694.9 (s), 693.0 (s), 689.7 (s), 607.2 (d, $^1J_{CH}$ = 177 Hz, C_{b1}), 605.3 (overlapping d, C_{bfac}), 604.5 (overlapping d, C_{b2}), 601.2 (d, $^1J_{CH}$ = 170 Hz, C_{b3}), 424.2 (d, $^1J_{CH}$ = 167 Hz, C_{gfac}), 421.6 (overlapping d, C_{g1}/C_{dfac}), 420.3 (overlapping d, C_{d1}), 417.6 (overlapping d, C_{g3}), 416.2 (overlapping d, C_{g2}), 413.6 (d, $^1J_{CH}$ = 164 Hz, C_{d2}) 413.4 (d, $^1J_{CH}$ = 164 Hz, C_{d3}), 195.8 (d, $^1J_{CH}$ = 165 Hz, C_{c2}), 190.8 (d, $^1J_{CH}$ = 167 Hz, C_{c1}), 182.9 (overlapping d, $^1J_{CH}$ = 167. Hz, C_{c3}), 182.4 (s), 178.5 (d, $^1J_{CH}$ = 123 Hz, C_{fac}), 174.0 (d, $^1J_{CH}$ = 167 Hz, C_{h2}), 170.0 (d, $^1J_{CH}$ = 165 Hz, C_{h1}), 159.9 (d, $^1J_{CH}$ = 173 Hz, C_{h3}), 156.2 (d, $^1J_{CH}$ = 170 Hz, C_{hfac}), 135.4-134.2 (overlapping signals, $C_{n/o}$), 130.5-125.5 (overlapping signals, C_p), 73.0 (unresolved d, $C_{a/j}$), 65.6 (unresolved d, $C_{a/j}$), 35.3 (unresolved d, 2C, $C_{a/j}$), 28.73 (unresolved d, 2C, $C_{a/j}$), -114.2 (s, 1C, $C_{e/f}$), -115.59 (s, $C_{e/f}$), -139.8 (s, $C_{e/f}$), -140.2 (s, $C_{e/f}$), -146.0 (s, $C_{e/f}$), -169.0 (s, $C_{e/f}$), -169.5 (s, $C_{e/f}$).

Note: Quaternary carbons and carbons close to the paramagnetic center (a and j) could not be unambiguously assigned due to the lack of HMBC equivalent in the paramagnetic NMR toolbox. Carbons a, j, e and f are assigned based on related complexes.[11]

HRMS (ESI, CH_3CN) *m/z*: 413.6158 [Co-**2a**]$^{2+}$, 285.5659 [Co-**2a** -1(**2a**)]$^{2+}$.

FT-IR: ṽ = 3079.2 (w), 2217.4 (w), 2175.7 (w), 1600.2 (w), 1558.5 (w), 1498.7 (w), 1487.9 (w), 1469.7 (m), 1440.7 (m), 1352.6 (s), 1334.1 (s), 1173.6 (s), 1134.6 (s), 1048.8 (s), 919.2 (w), 850.9 (w), 791.7 (m), 747.9 (m), 733.2 (m), 687.6 (m), 665.8 (w), 639.2 (w), 606.0 (s), 569.1 (s), 543.4 (w), 532.1 (w), 511.0 (s) cm^{-1}.

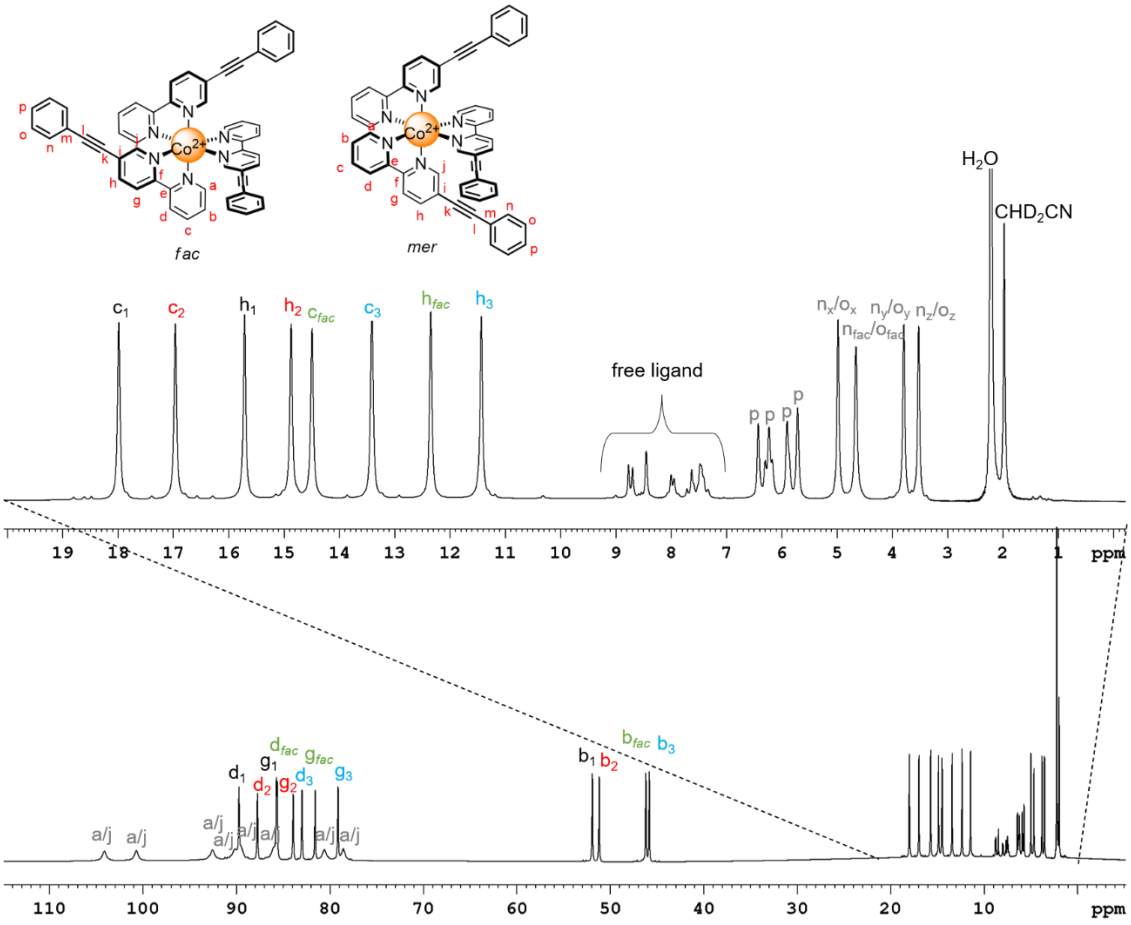


Figure S137. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of complex Co-**2a**.

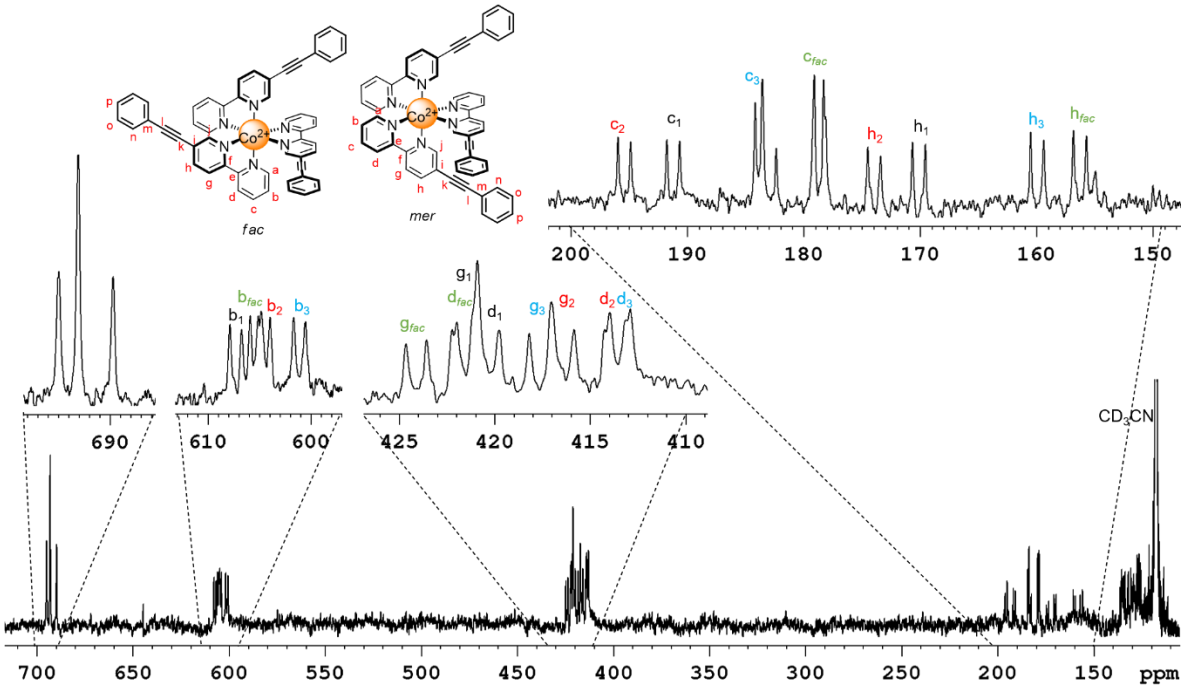


Figure S138. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of complex **Co-2a**.

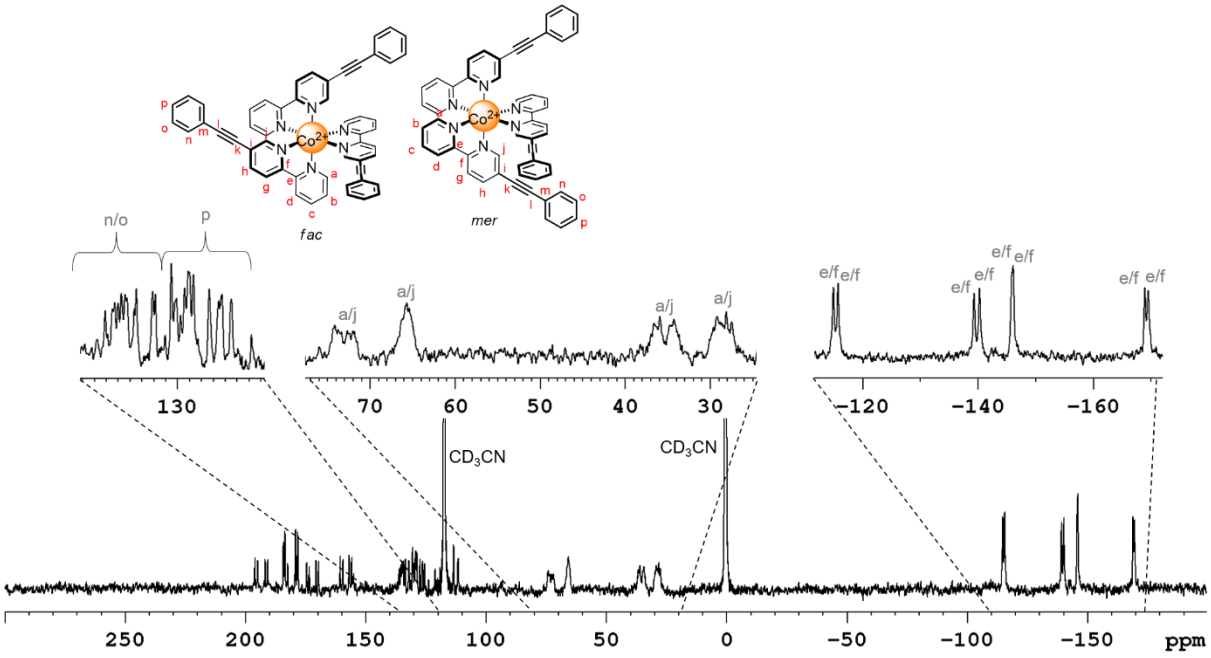


Figure S139. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of complex **Co-2a**.

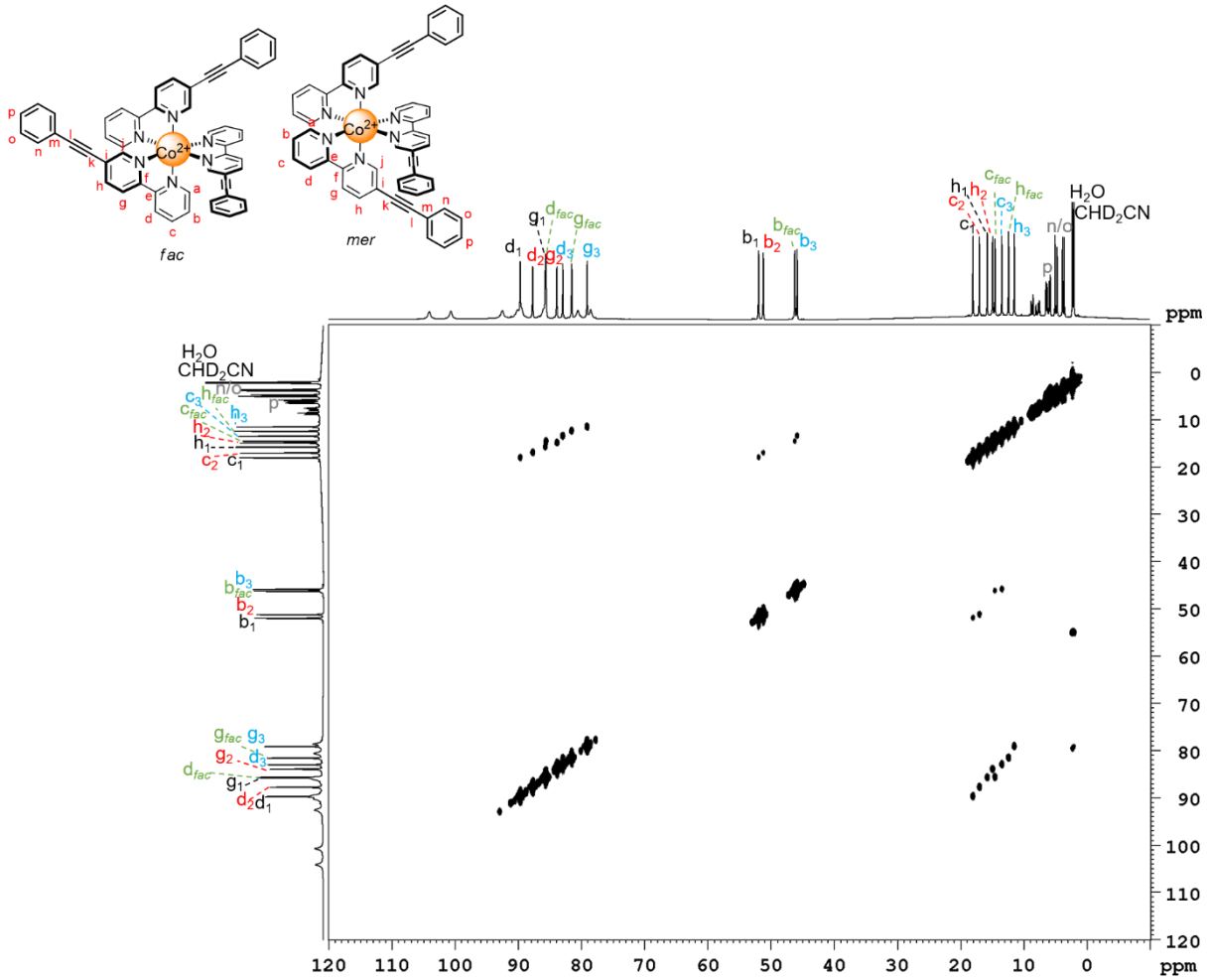


Figure S140. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of complex Co-**2a**.

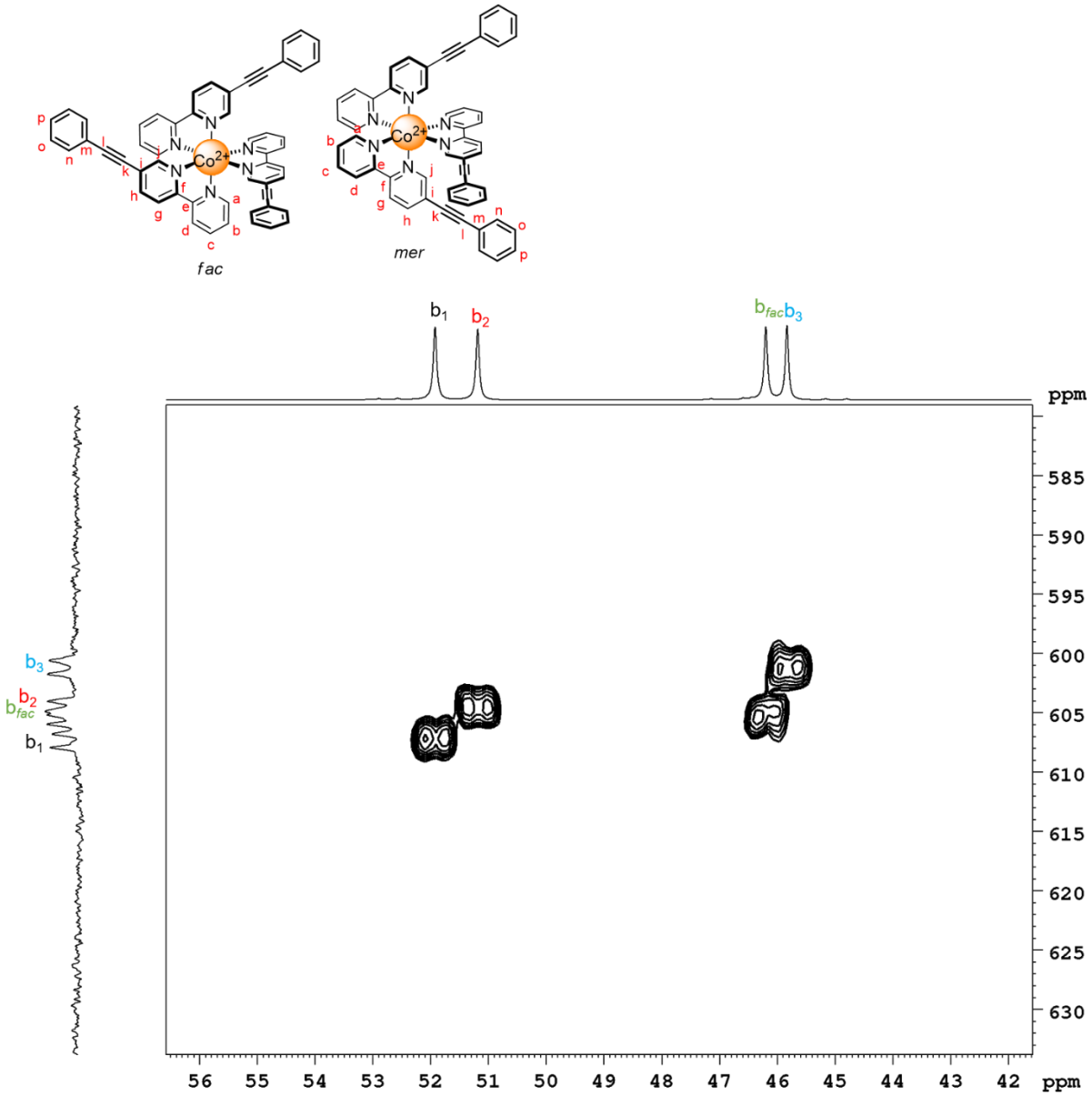


Figure S141. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-**2a**.

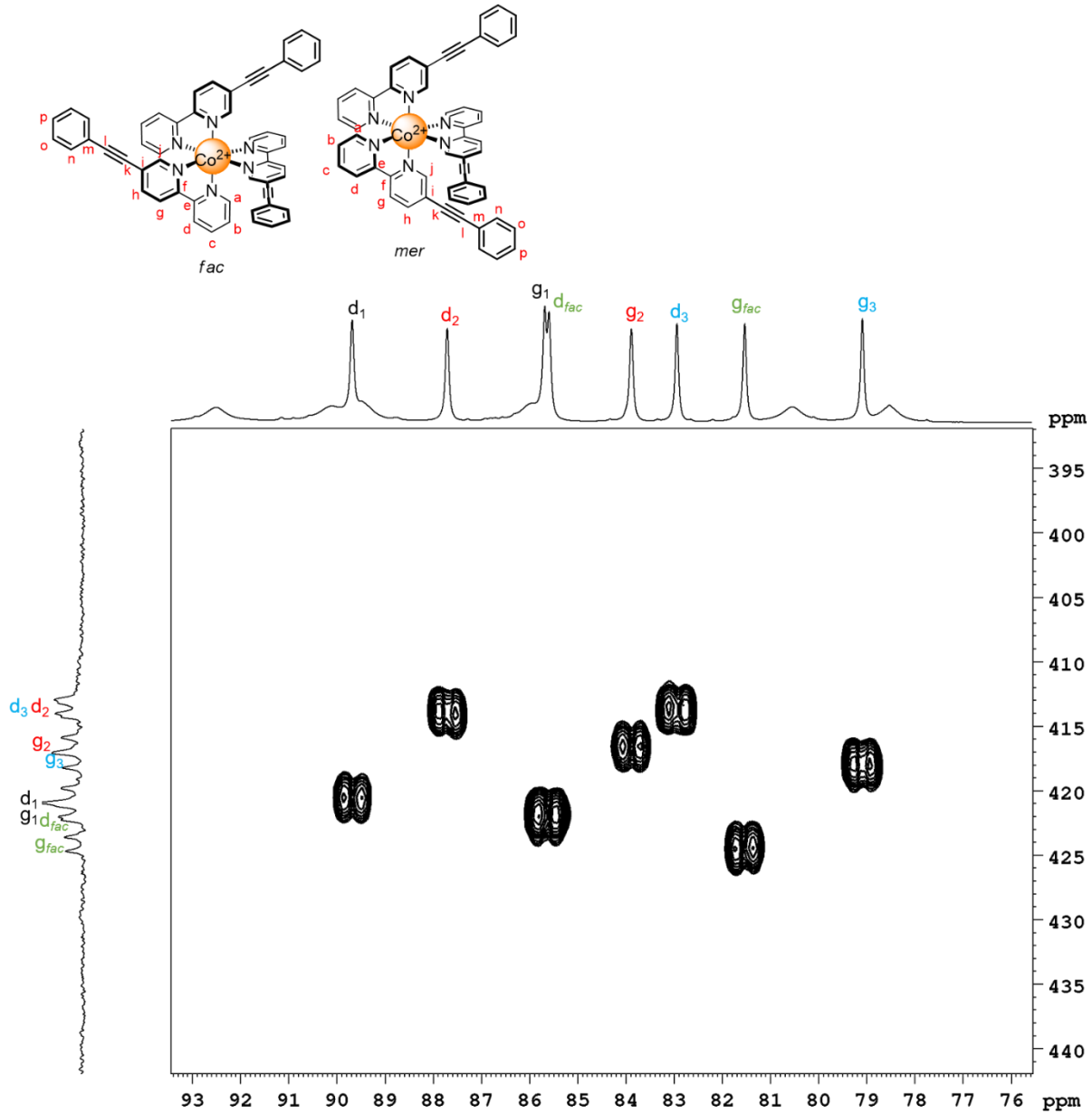


Figure S142. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-**2a**.

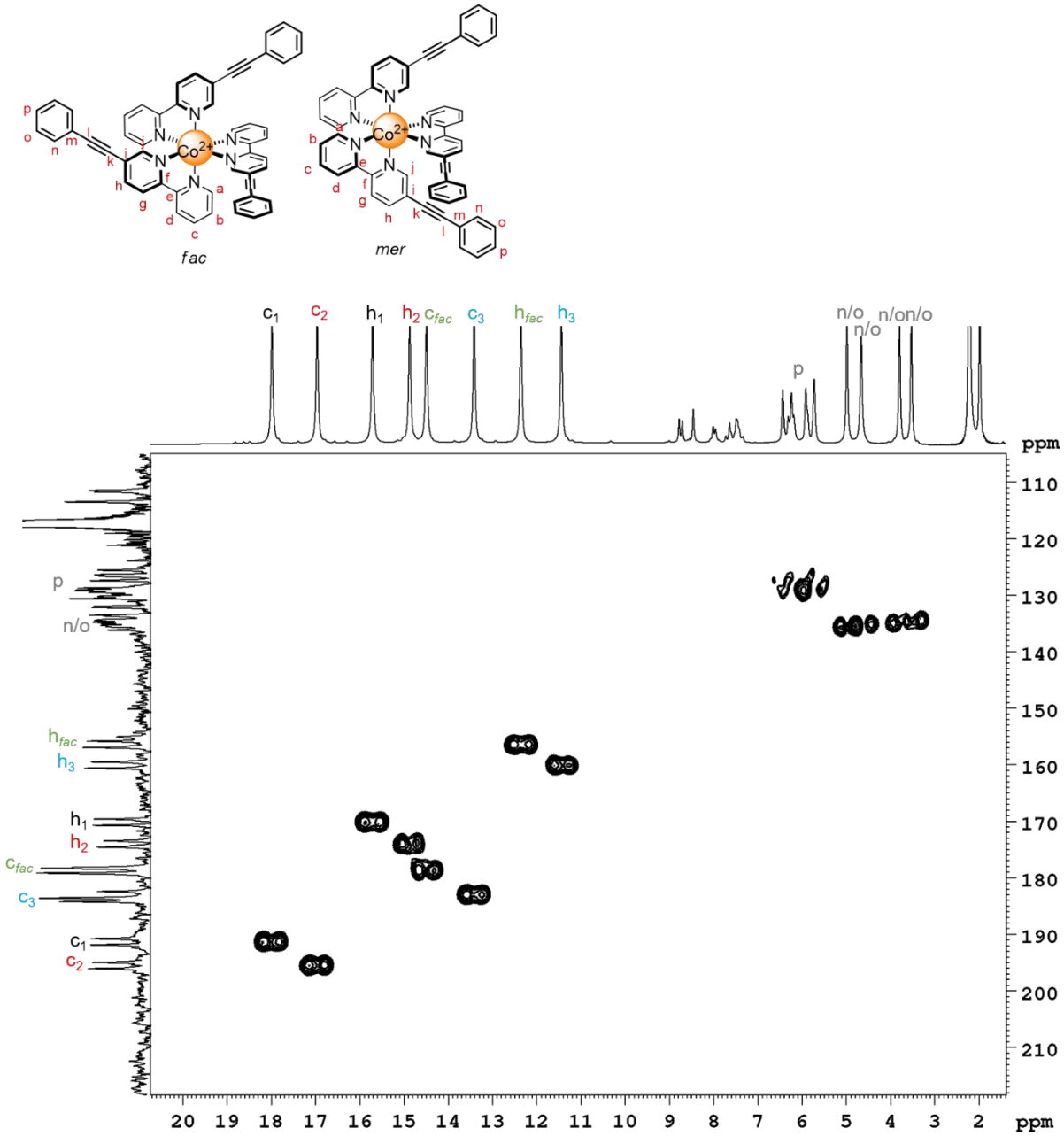


Figure S143. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-**2a**.

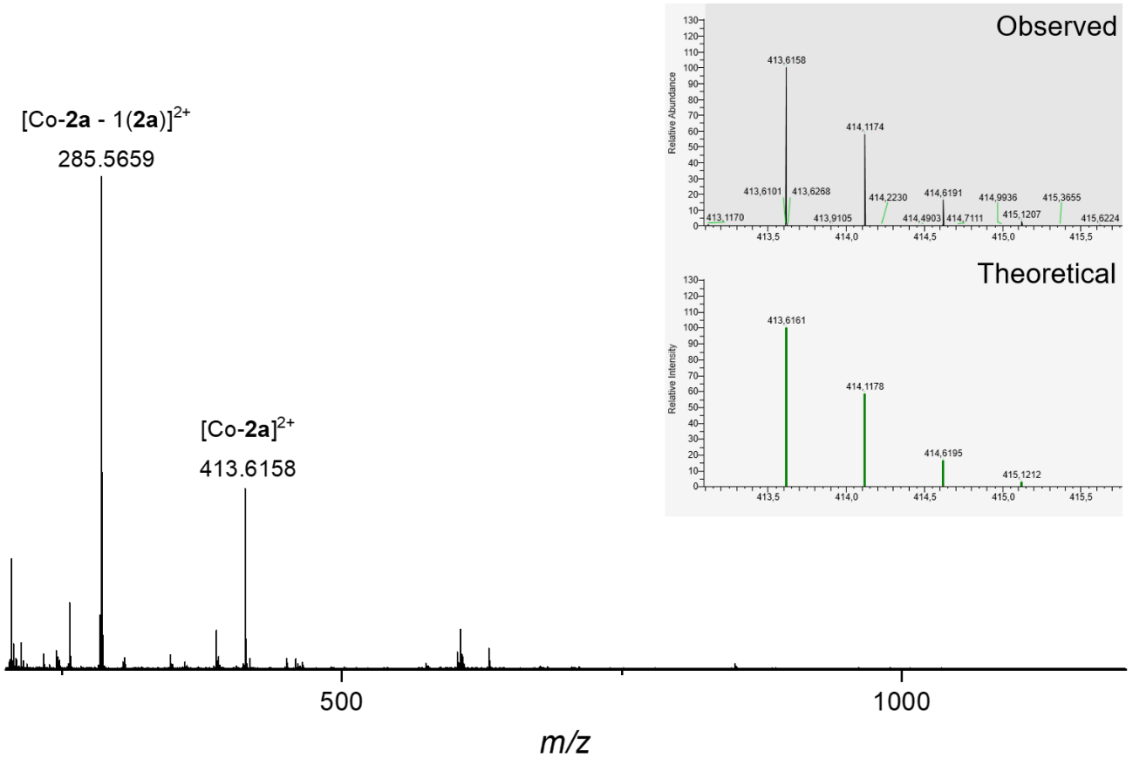
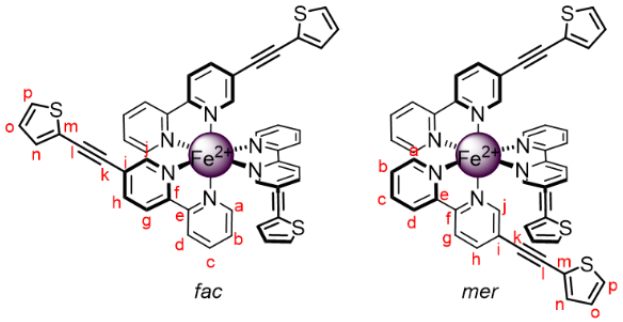


Figure S144. High resolution ESI mass spectrum of Co-**2a** showing in the insets the observed and theoretical isotope patterns.

8.4 Complex Fe-2b



Iron tetrafluoroborate hexahydrate (4.58 mg, 13.7 µmol) and 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (10.6 mg, 40.2 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (500 MHz, CD_3CN, 298 K) δ (ppm): 8.58-8.47 (m, 8H, $H_{d,g}$), 8.30-8.08 (m, 7H, $H_{h,c}$), 8.01(t, ^3J = 7.4 Hz, 1H, H_c), 7.66 (s, 1H, H_j), 7.57-7.29 (m, 18H, $H_{a,b,j,n,p}$), 7.16 (br, 1H, H_a), 7.11-7.03 (m, 4H, H_o).

^{13}C NMR (126 MHz, CD_3CN, 298 K) δ (ppm): 159.5 (C_e), 159.4 (C_e), 159.3 (C_e), 158.8 (C_f), 158.7 (C_f), 158.7 (C_f), 158.6 (C_f), 156.4 (C_j), 156.3 (C_j), 156.1 (C_j), 155.5 (C_a), 155.3 (C_a), 155.3 (C_a), 154.9 (C_a), 141.8 (C_h), 141.4 (C_h), 141.3 (C_h), 139.7 (C_c), 135.5 ($C_{n/p}$), 135.0 ($C_{n/p}$), 131.6 ($C_{n/p}$), 131.1 ($C_{n/p}$), 128.9 (C_o), 128.7 (C_o), 128.5 (C_b), 128.5 (C_b), 128.4 (C_b), 128.4 (C_b), 125.6 (C_d), 125.4 (C_d), 125.2 (C_d), 124.9 (C_g), 124.7 (C_g), 124.5 (C_g), 124.5 (C_i), 124.3-124.2 ($C_{i,g}$), 121.6 (C_m), 121.5 (C_m), 121.3 (C_m), 121.3 (C_m).

HRMS (ESI, CH_3CN) *m/z*: 929.1058 [Fe-**2b** -1(**2b**) +BF_4]$^{1+}$, 421.0515 [Fe-**2b**]$^{2+}$.

FT-IR: ṽ = 3622.9 (w), 3109.4 (w), 2923.9 (w), 2203.1 (m), 1595.1 (w), 1557.7 (w), 1465.9 (m), 1438.3 (w), 1420.1 (m), 1375.3 (w), 1312.4 (w), 1288.5 (w), 1237.9 (w), 1218.4 (w), 1170.8

(w), 1050.7 (s), 1030.8 (s), 909.6 (w), 852.5 (m), 786.3 (m), 747.4 (m), 725.6 (s), 679.8 (w), 570.2 (w), 543.9 (w), 520.2 (m), 505.8 (w) cm^{-1}.

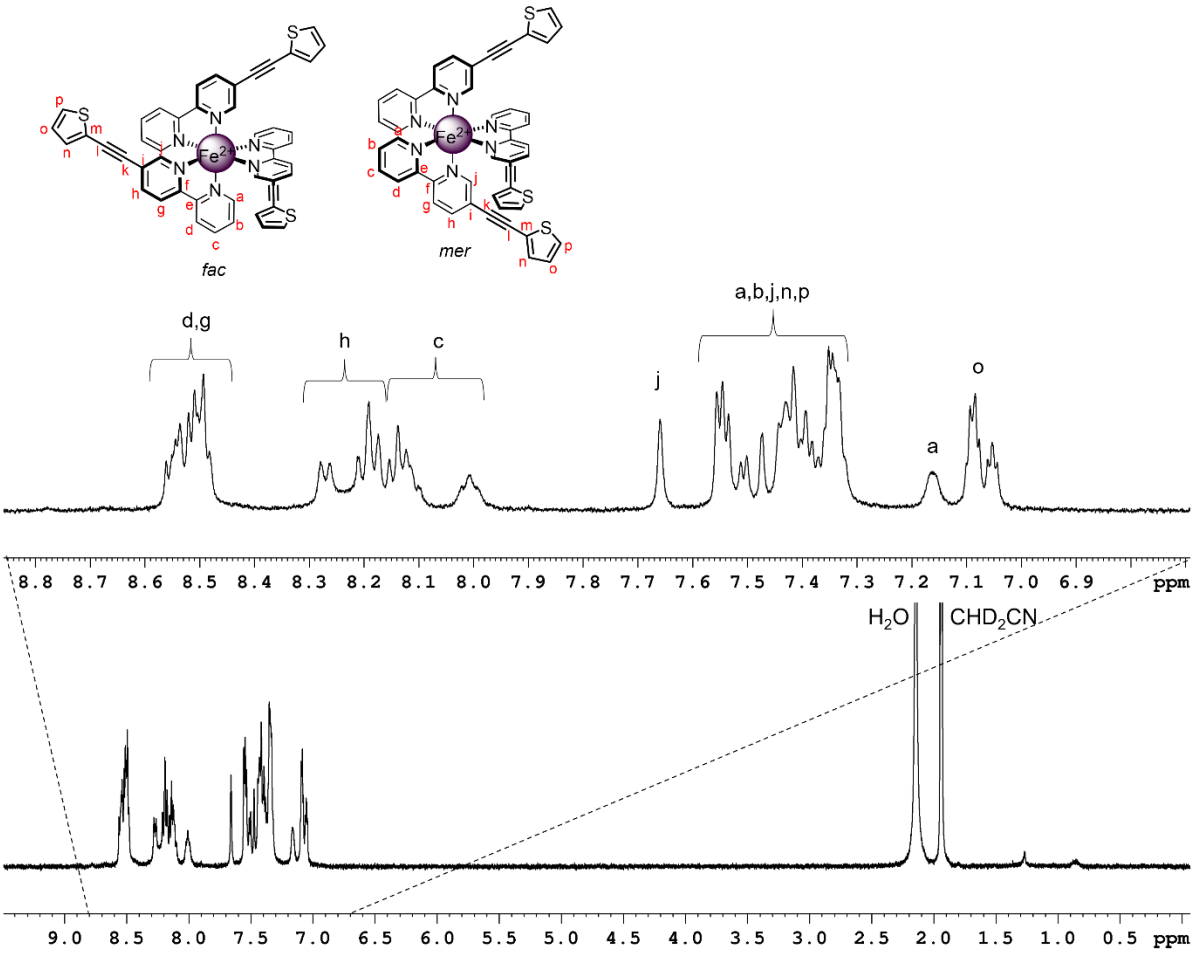


Figure S145. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-**2b**.

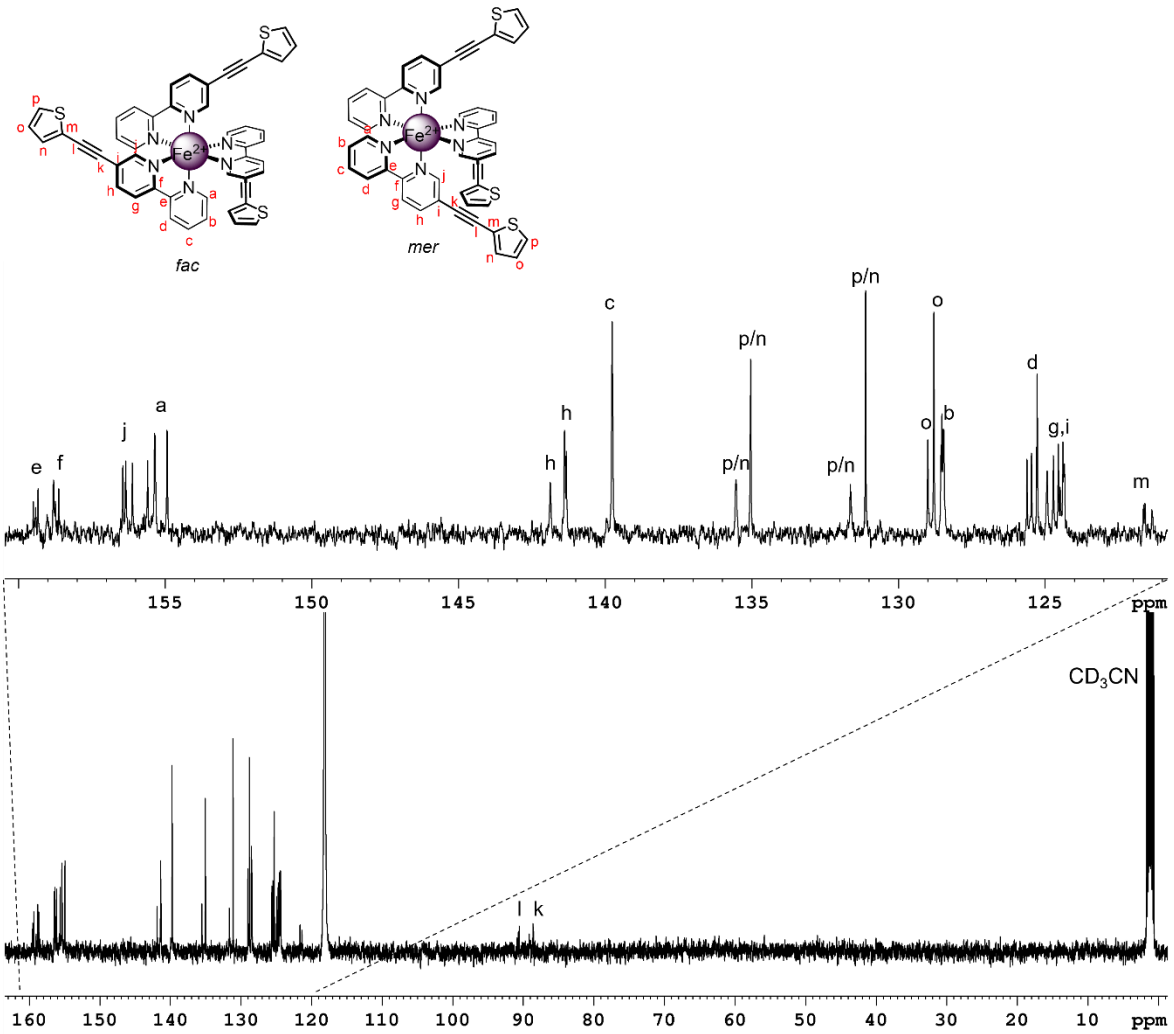


Figure S146. ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of Fe-**2b**.

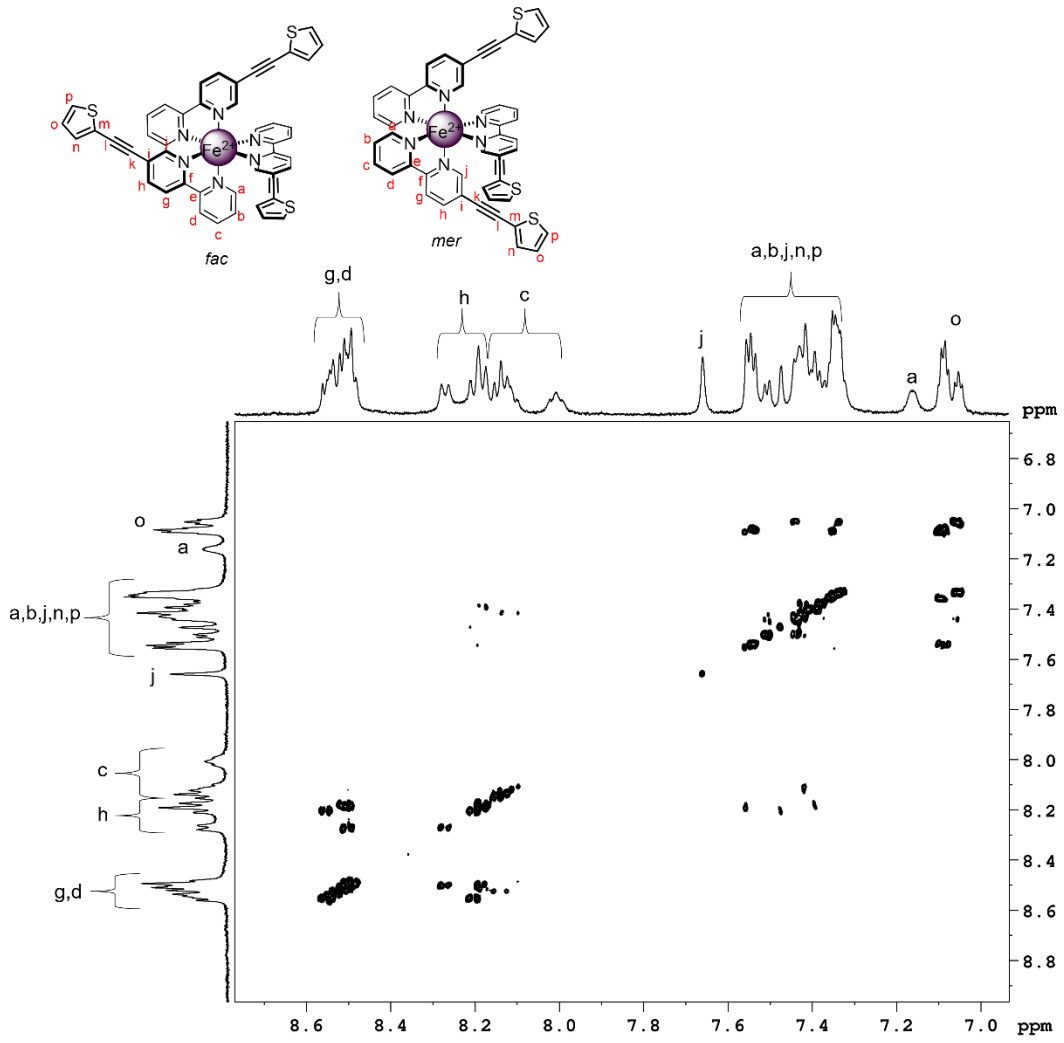


Figure S147. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-**2b**.

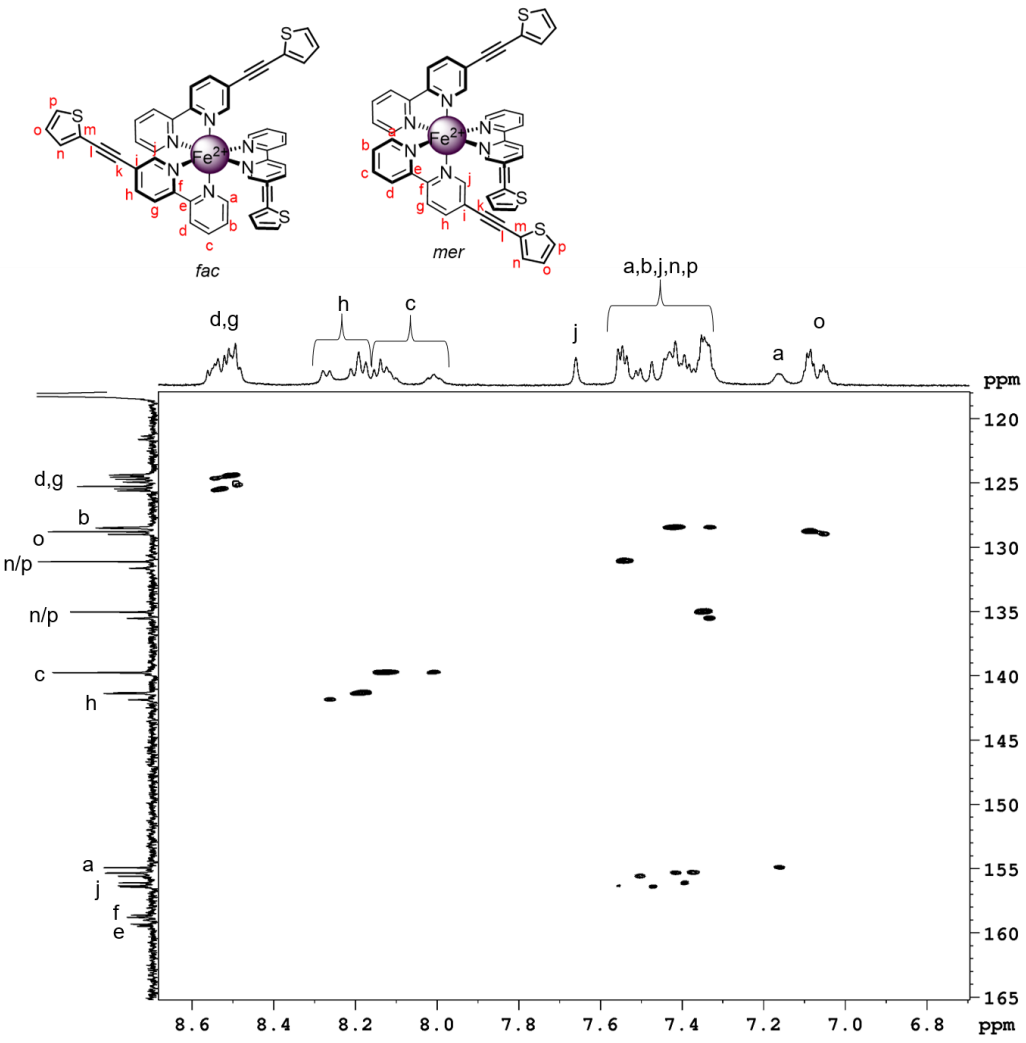


Figure S148. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Fe-**2b**.

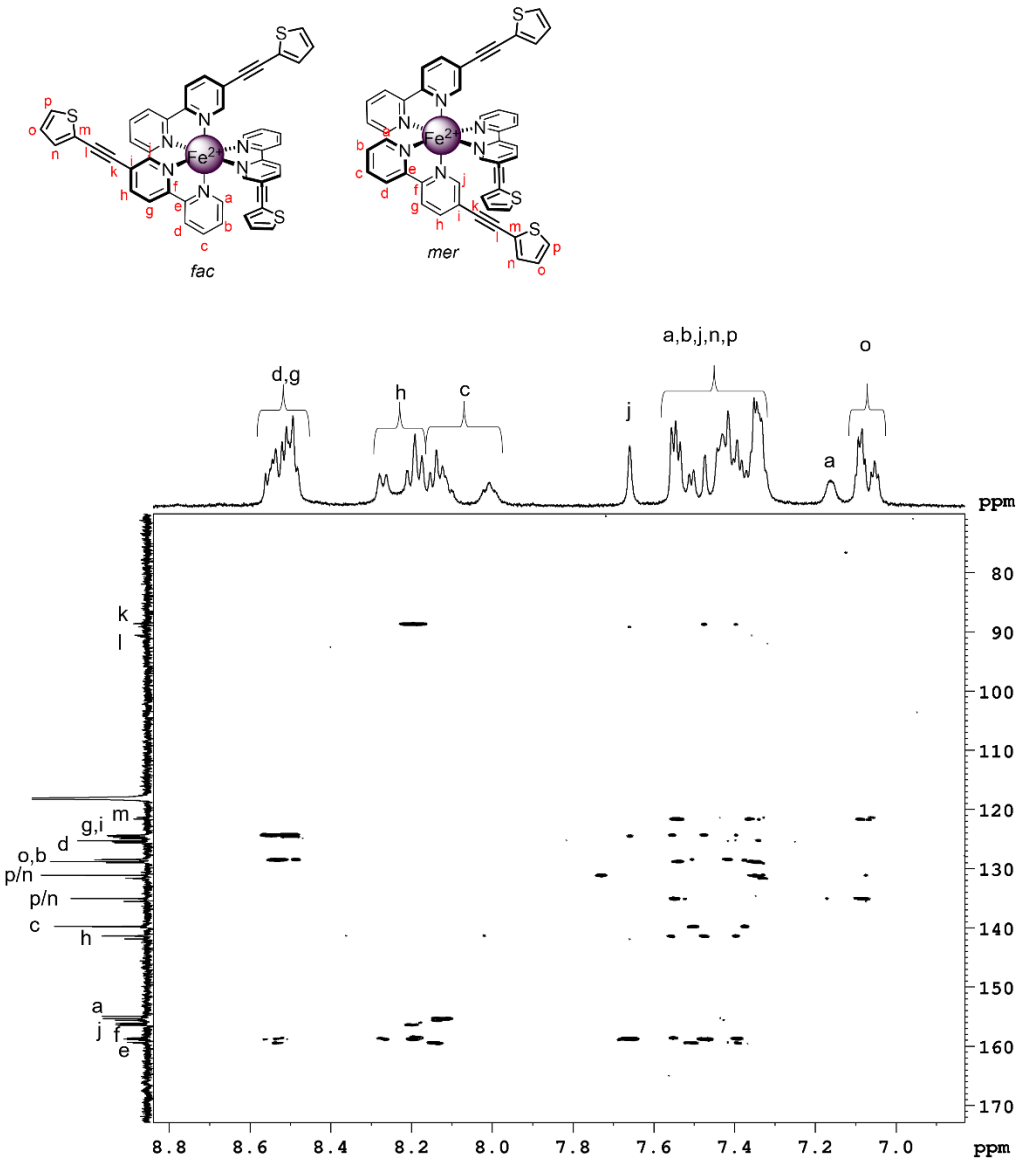


Figure S149. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Fe-**2b**.

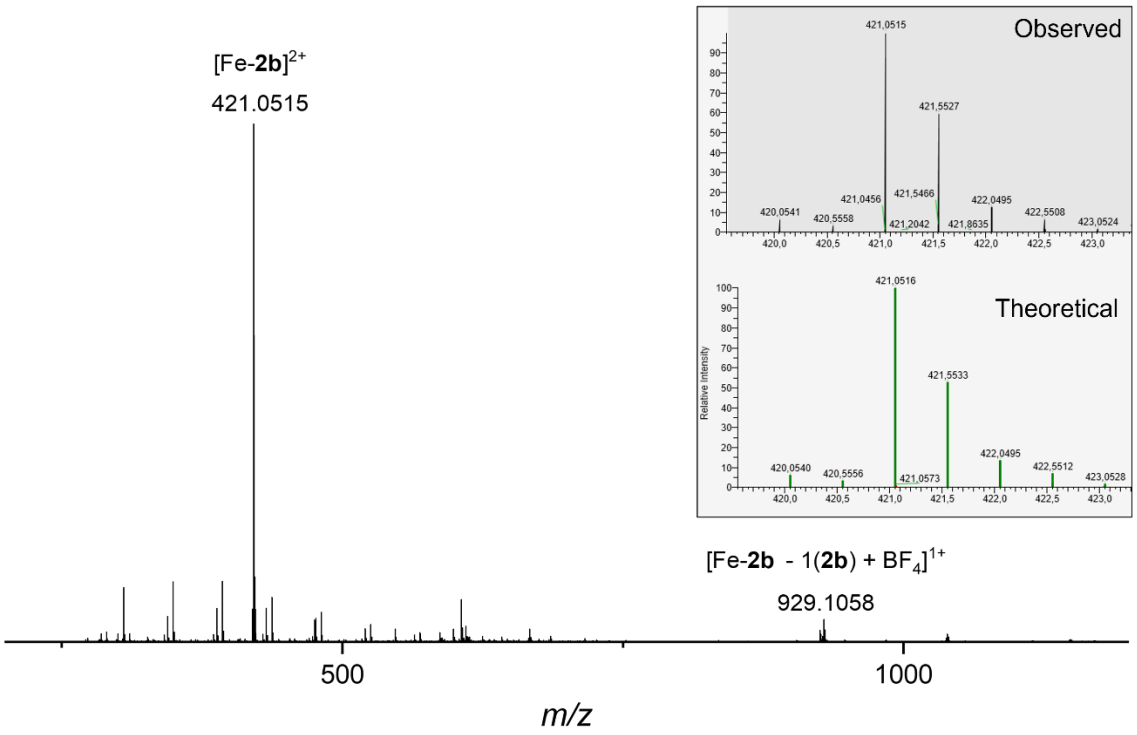
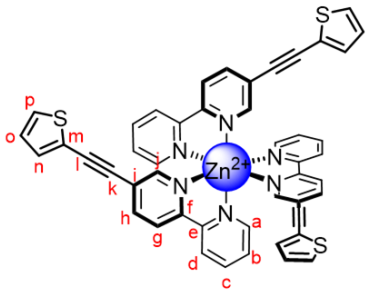


Figure S150. High resolution ESI mass spectrum of Fe-**2b** showing in the insets the observed and theoretical isotope patterns.

8.5 Complex Zn-2b



Zinc trifluoromethanesulfonate (4.71 mg, 13.0 µmol) and 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (10.2 mg, 39.2 µmol) were dissolved in CD_3CN (0.5 mL).

Note: Because of the broadness of the signals, unambiguous assignment of the ^{1}H and ^{13}C NMR spectra was not possible and *fac/mer* isomers could not be distinguished.

HRMS (ESI, CH_3CN) *m/z*: 736.9937 [Zn-**2b** -1(**2b**) +OTf]$^{1+}$, 425.0489 [Zn-**2b**]$^{2+}$, 294.0207 [Zn-**2b** -1(**2b**)]$^{2+}$.

FT-IR: ṽ = 3489.8 (w), 3104.8 (w), 2201.4 (m), 1594.9 (m), 1556.8 (w), 1517.3 (w), 1471.9 (m), 1439.3 (m), 1420.0 (m), 1374.6 (w), 1313.9 (w), 1253.4 (s), 1219.8 (s), 1151.1 (s), 1027.3 (s), 854.1 (m), 793.5 (m), 730.8 (m), 665.2 (w), 636.9 (s), 619.8 (m), 573.3 (m) cm^{-1}.

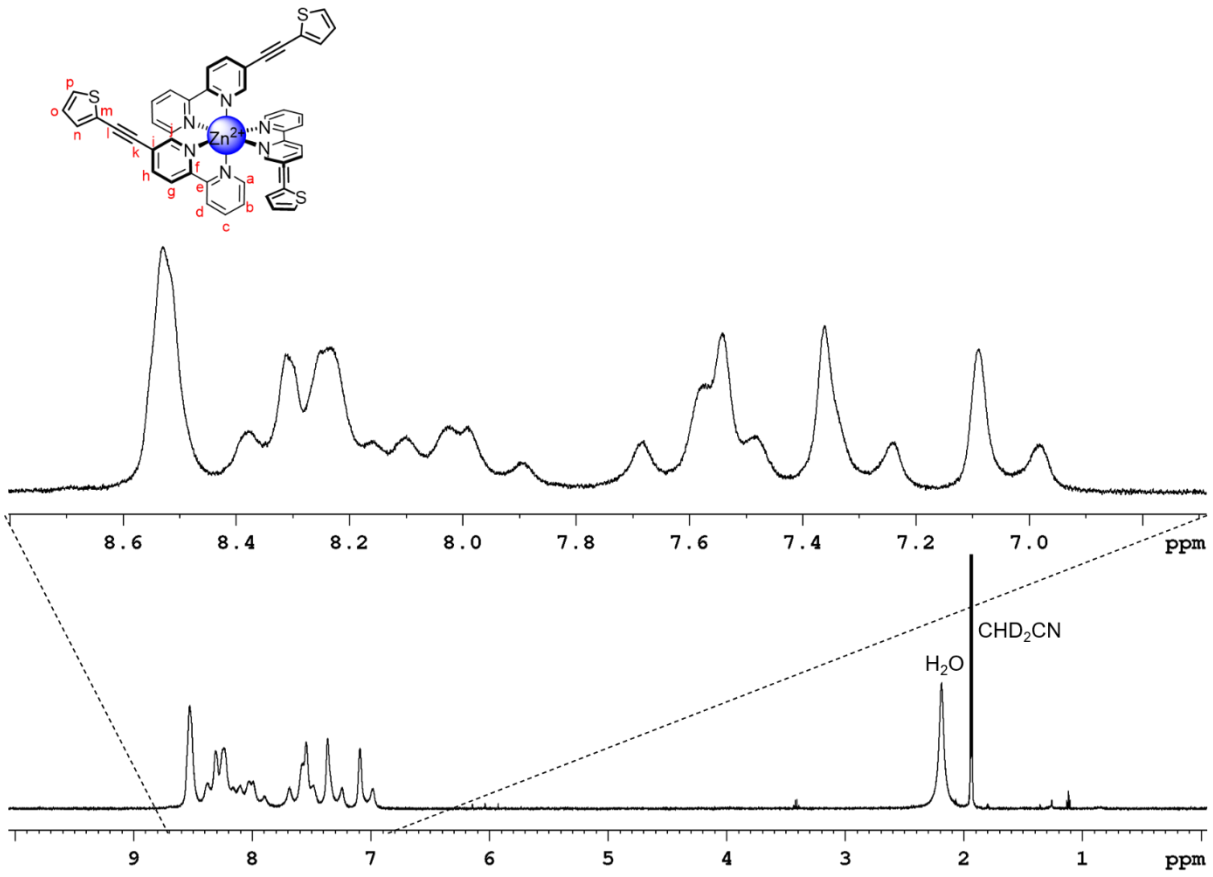


Figure S151. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of Zn-**2b**.

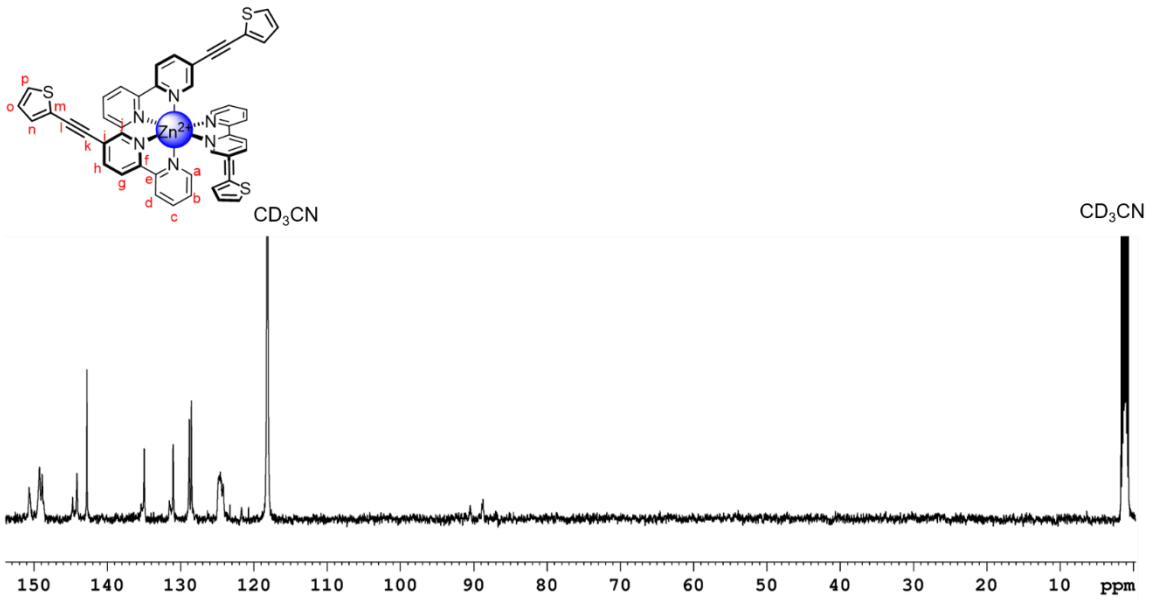


Figure S152. ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of Zn-**2b**.

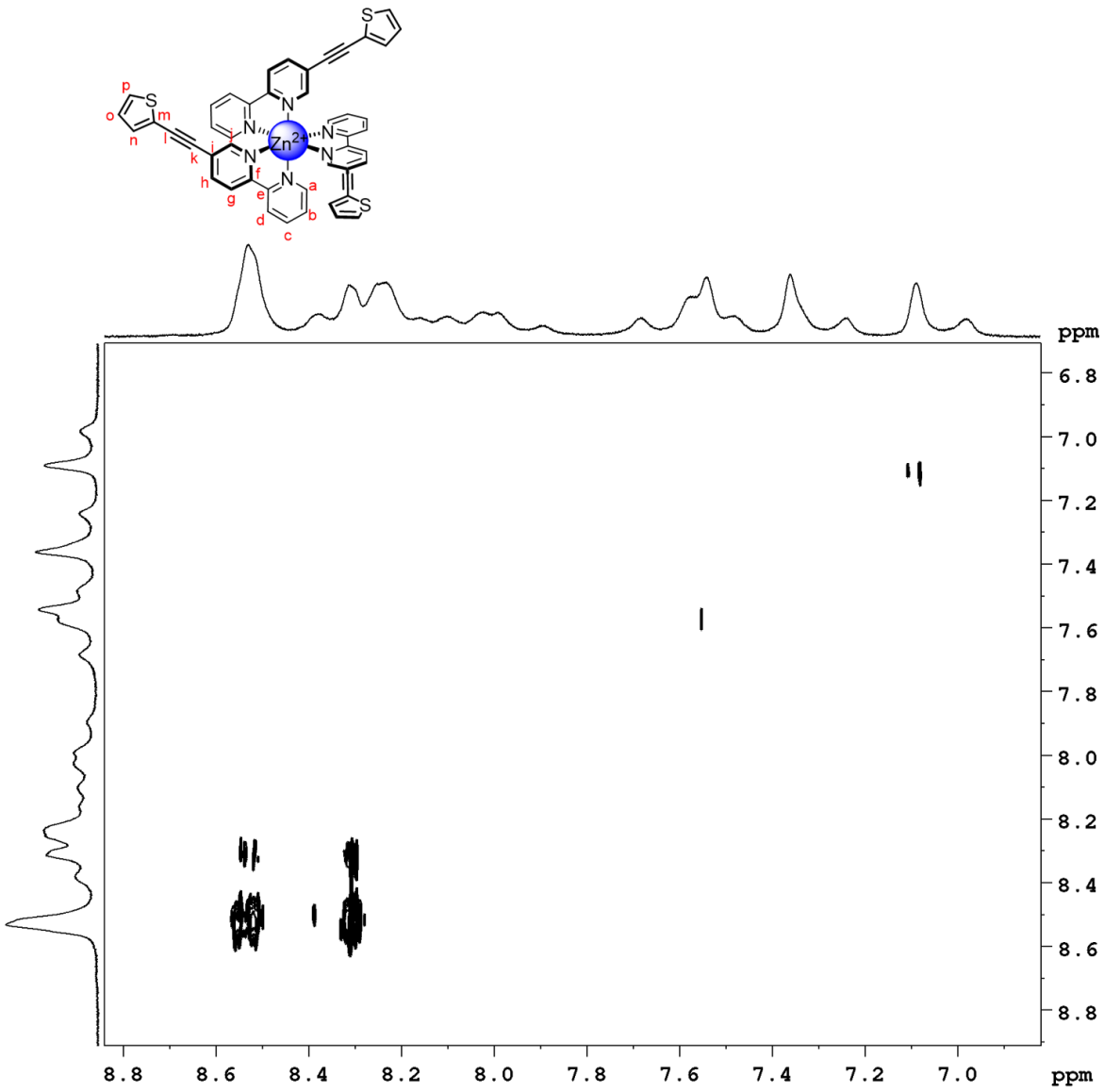


Figure S153. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of Zn-**2b**.

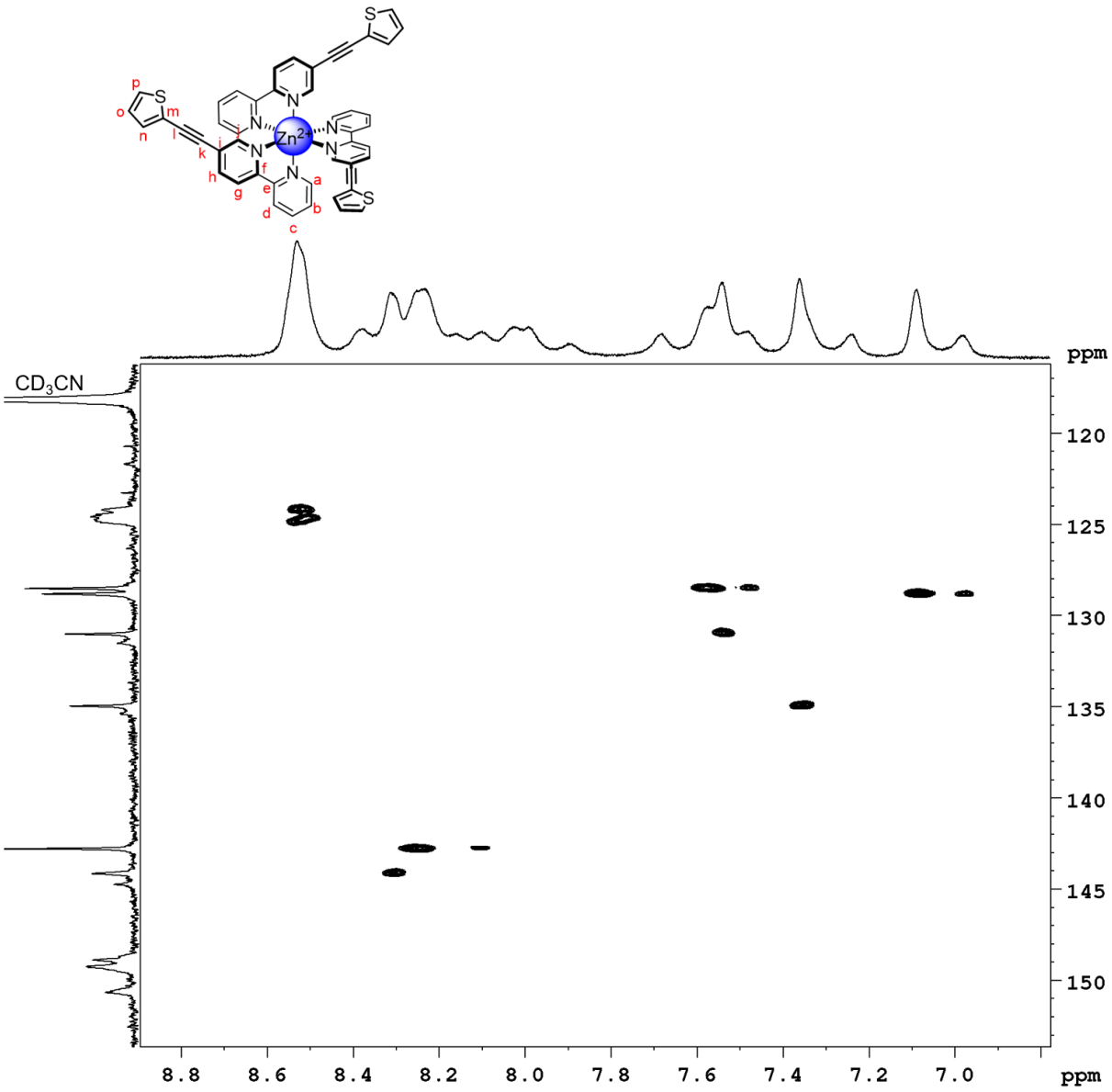


Figure S154. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Zn-**2b**.

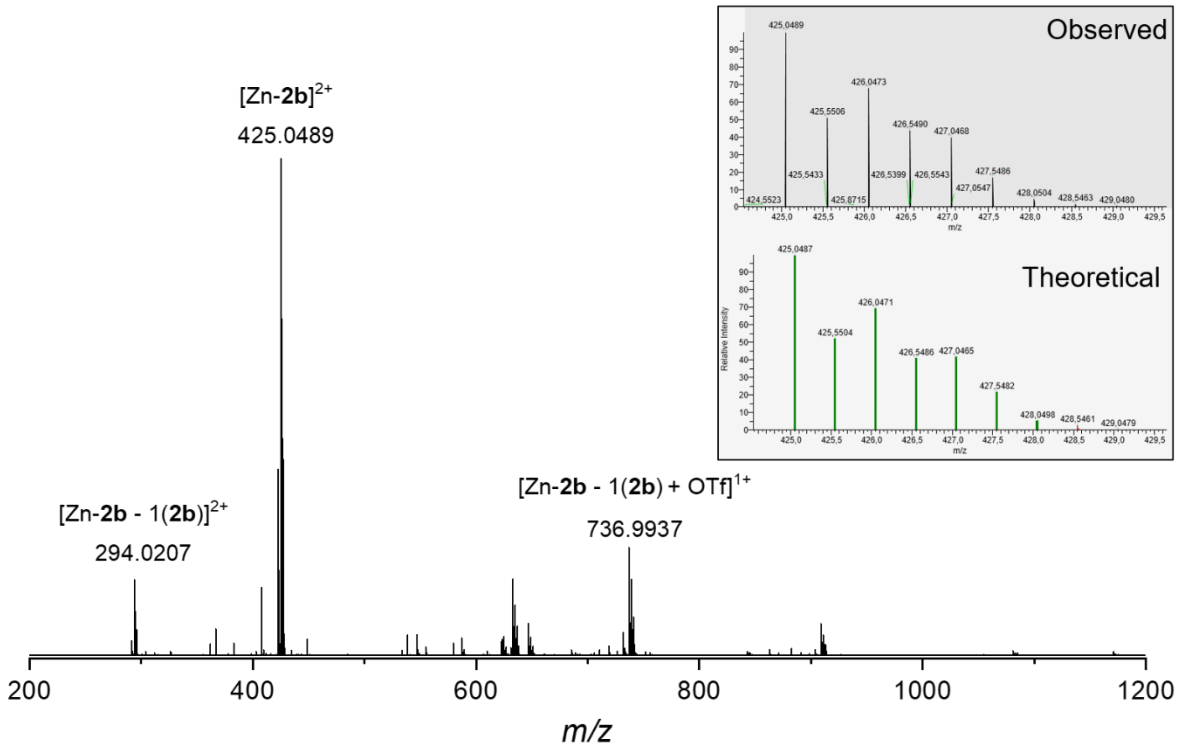
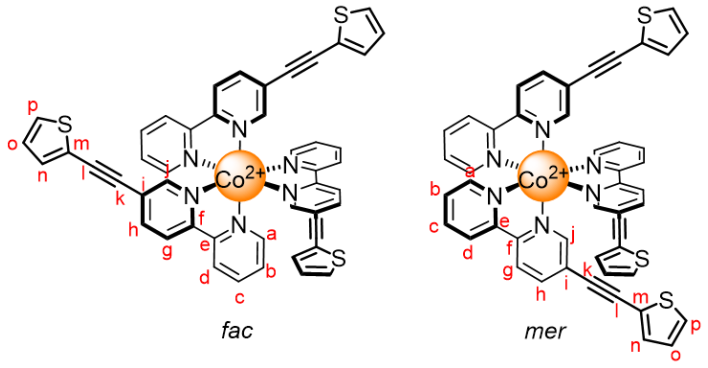


Figure S155. High resolution ESI mass spectrum of Zn-**2b** showing in the insets the observed and theoretical isotope patterns.

8.6 Complex Co-2b



Cobalt bis(trifluoromethylsulfonyl)imide (8.01 mg, 12.9 µmol) and 5-(thiophen-2-ylethynyl)-2,2'-bipyridine (**2b**) (10.1 mg, 38.5 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 104.5 (br, 1H, $H_{a/j}$), 101.6 (br, 1H, $H_{a/j}$), 91.7 (br, 1H, $H_{a/j}$), 89.5 (s, 1H, H_{d1}), 89.3 (br, 1H, $H_{a/j}$), 87.6 (s, 1H, H_{d2}), 86.6 (br, 1H, $H_{a/j}$), 85.4 (s, 1H, H_{g1}), 85.0 (brs, 2H, $H_{dfac/gfac}$), 82.9 (s, 1H, H_{d3}), 82.5 (br, 1H, $H_{a/j}$), 81.3 (s, 1H, H_{g2}), 79.3 (br, 1H, $H_{a/j}$), 78.8 (s, 1H, H_{g3}), 77.5 (br, 1H, $H_{a/j}$), 52.1 (s, 1H, H_{b1}), 51.2 (s, 1H, H_{b2}), 45.6 (s, 1H, H_{b3}), 45.4 (br, 1H, H_{bfac}), 17.9 (s, 1H, H_{c1}), 16.9 (s, 1H, H_{c2}), 15.6 (s, 1H, H_{h1}), 14.3 (s, 1H, $H_{cfac/hfac}$), 13.8 (s, 1H, $H_{cfac/hfac}$), 13.3 (s, 1H, H_{c3}), 12.2 (s, 1H, H_{h2}), 11.3 (s, 1H, H_{h3}), 6.5 (s, 1H, $H_{n/p}$), 6.2 (s, 1H, $H_{n/p}$), 5.9 (s, 1H, $H_{n/p}$), 5.8 (s, 1H, $H_{n/p}$), 5.6 (s, 1H, $H_{n/p}$), 5.5 (s, 1H, $H_{n/p}$), 5.0 (s, 1H, H_o), 3.8 (s, 1H, H_o), 3.6 (s, 1H, H_o).

Note: While it was possible to assign the proton signals within one spin system (indicated by numbers) based on the COSY spectrum, the different spin systems within each ligand could not be correlated to a particular ligand environment. For the signals of the bipyridine, the fac isomer was, therefore, tentatively assigned based on the integral of the signals. However,

unambiguous assignment of some signals was not possible due to the absence of COSY cross-peaks, most likely due to the broadness of the signals. The three remaining sets of signals corresponding to the mer isomer were arbitrarily labelled with black, red, and blue labels according to their decreasing chemical shift. Protons corresponding to the R substituent were tentatively assigned in grey due to the signal overlap in the diamagnetic region of the spectra.[11] *Protons a and j are assigned in grey based on related complexes.*[11]

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 607.6 (d, $^1J_{CH}$ = 169 Hz, C_{b1}), 605.2 (d, $^1J_{CH}$ = 171 Hz, $C_{b2/bfac}$), 601.4 (d, $^1J_{CH}$ = 172 Hz, C_{b3}), 423.9 (d, $^1J_{CH}$ = 158 Hz, C_{g2}), 421.9 (d, $^1J_{CH}$ = 165 Hz, C_{g1}), 419.9 (d, $^1J_{CH}$ = 168 Hz, C_{d1}), 417.3 (d, $^1J_{CH}$ = 161 Hz, C_{g3}), 414.04 (overlapping d, $^1J_{CH}$ = 114 Hz, C_{d3}), 412.9 (overlapping d, $^1J_{CH}$ = 114 Hz, C_{d2}), 195.9 (d, $^1J_{CH}$ = 169 Hz, C_{c2}), 191.8 (d, $^1J_{CH}$ = 169 Hz, C_{c1}), 188.8 (s), 188.4 (s), 183.9 (s), 183.4 (s), 182.5 (overlapping d, $^1J_{CH}$ = 161 Hz, C_{c3}), 174.8 (d, $^1J_{CH}$ = 165 Hz, $C_{cfac/hfac}$), 171.0 (d, $^1J_{CH}$ = 171 Hz, C_{h1}), 159.9 (d, $^1J_{CH}$ = 173 Hz, C_{h3}), 156.6 (d, $^1J_{CH}$ = 170 Hz, C_{h2}), 140.4-135.7 (overlapping signals, C_o) 130.9-123.2 (overlapping signals, C_n, $C_{p,}$), 74.4 (unresolved d, $C_{a/j}$), 65.5 (unresolved d, $C_{a/j}$), 38.6 (unresolved d, $C_{a/j}$), 35.3 (unresolved d, $C_{a/j}$), 29.6 (unresolved d, $C_{a/j}$), -114.7 (s, $C_{e/f}$), -115.7 (s, $C_{e/f}$), -139.3 (s, $C_{e/f}$), -140.0 (s, $C_{e/f}$), -146.1 (s, $C_{e/f}$), -168.9 (s, $C_{e/f}$), -169.5 (s, $C_{e/f}$).

Note: Quaternary carbons and carbons close to the paramagnetic center (a and j) could not be unambiguously assigned due to the lack of HMBC equivalent in the paramagnetic NMR toolbox. Carbons a, j, e and f are assigned based on related complexes.[11] *The carbon signals for the fac isomer could not be assigned due to the absence of HMQC cross-peaks, attributed to the broadness of the signals.*

HRMS (ESI, CH_3CN) *m/z*: 862.9632 [Co-**2b** -1(**2b**) +NTf_2]$^{1+}$, 422.5511 [Co-**2b**]$^{2+}$, 291.5228 [Co-**2b** -1(**2b**)]$^{2+}$.

FT-IR: $\tilde{\nu}$ = 3109.1 (w), 2201.6 (m), 1595.4 (w), 1557.8 (w), 1517.3 (w), 1470.5 (w), 1440.6 (w), 1420.1 (w), 1347.1 (s), 1330.1 (s), 1280.5 (w), 1172.1 (s), 1130.8 (s), 1050.6 (s), 1015.5 (m), 920.1 (w), 853.9 (m), 789.4 (m), 761.6 (w), 730.5 (s), 651.7 (m), 611.5 (m), 597.9 (s), 568.8 (s), 534.7 (w), 506.6 (s), 469.6 (w), 418.8 (m), 411.6 (m), 405.9 (m) cm^{-1}.

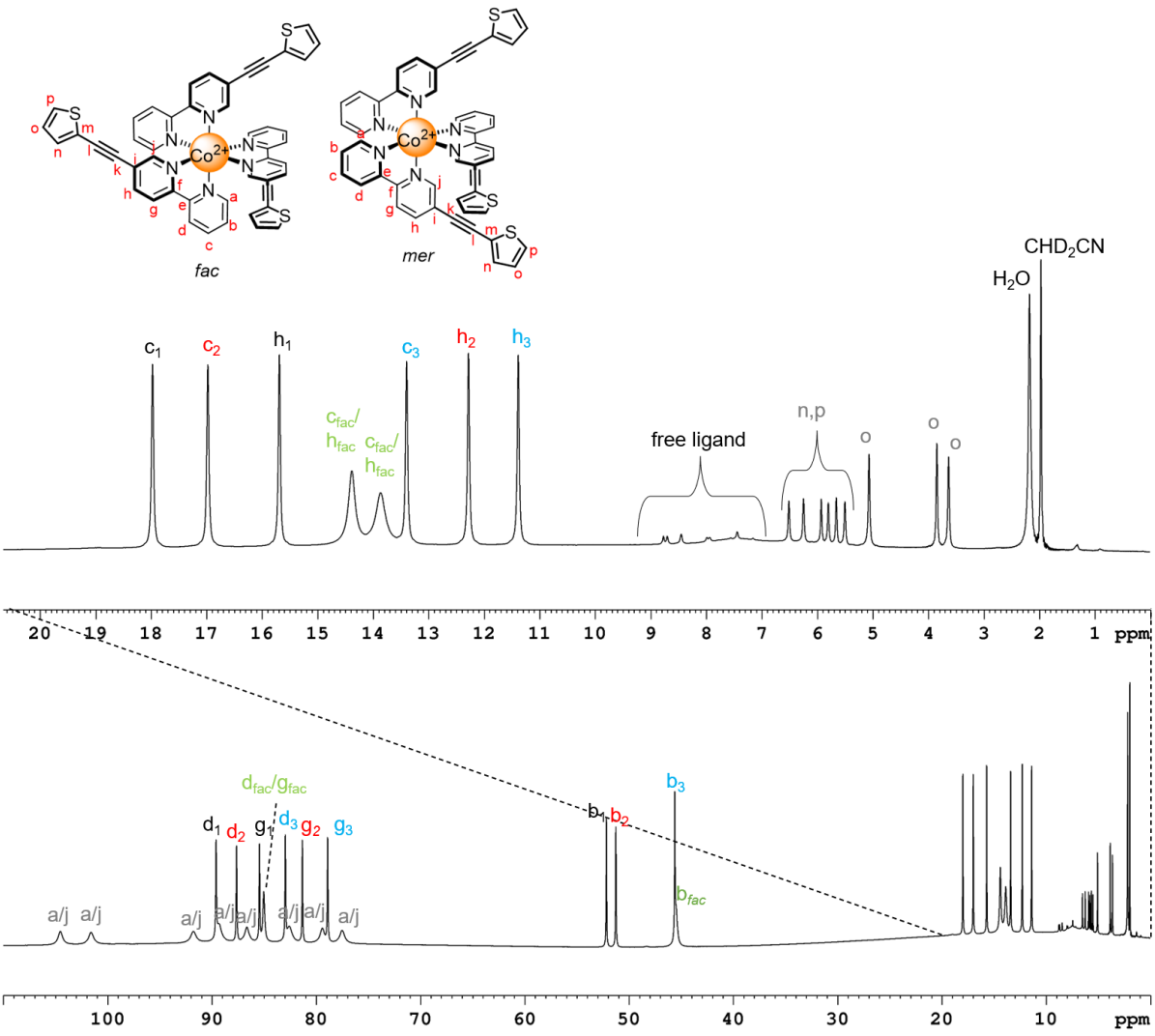


Figure S156. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of complex Co-**2b**.

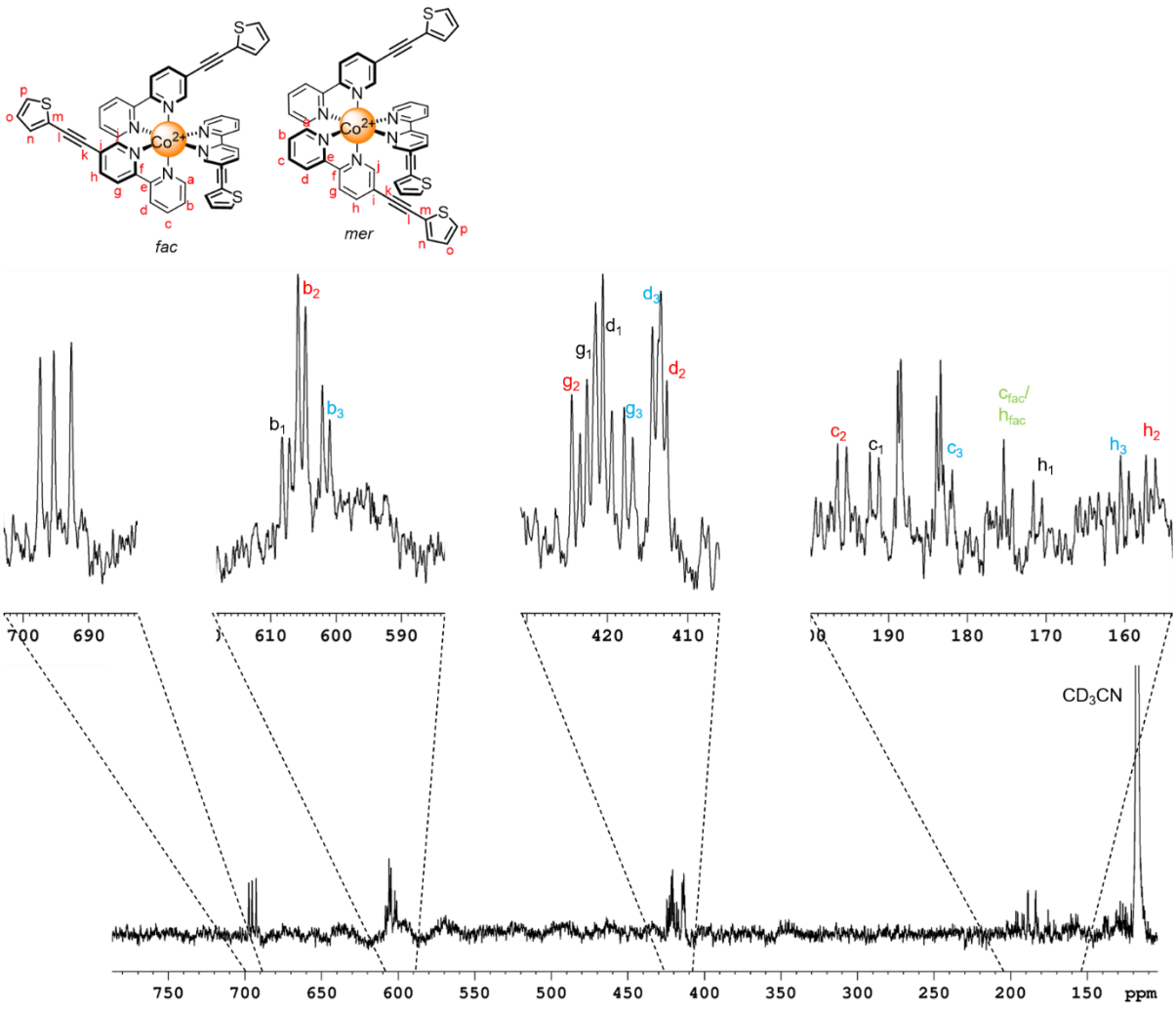


Figure S157. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of complex **Co-2b**.

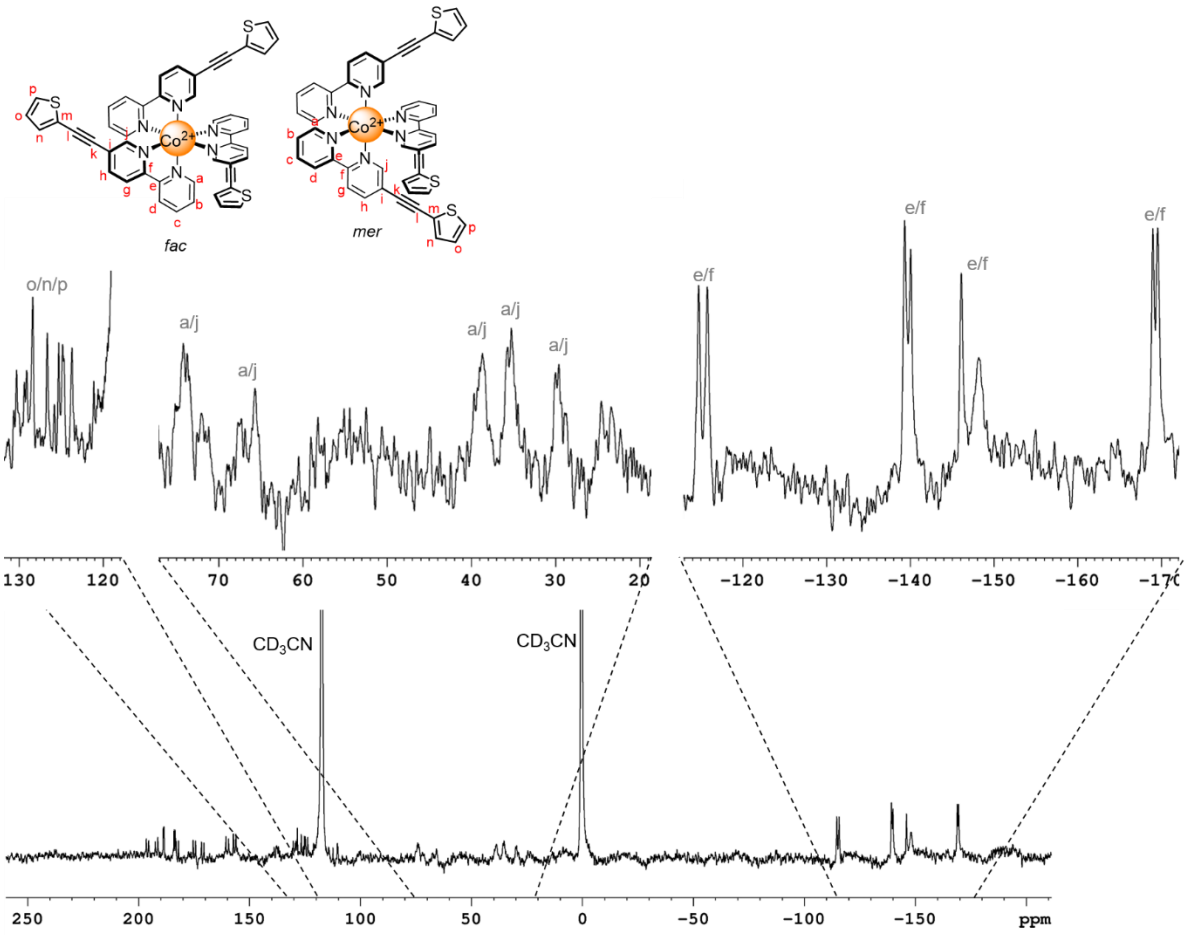


Figure S158. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of complex **Co-2b**.

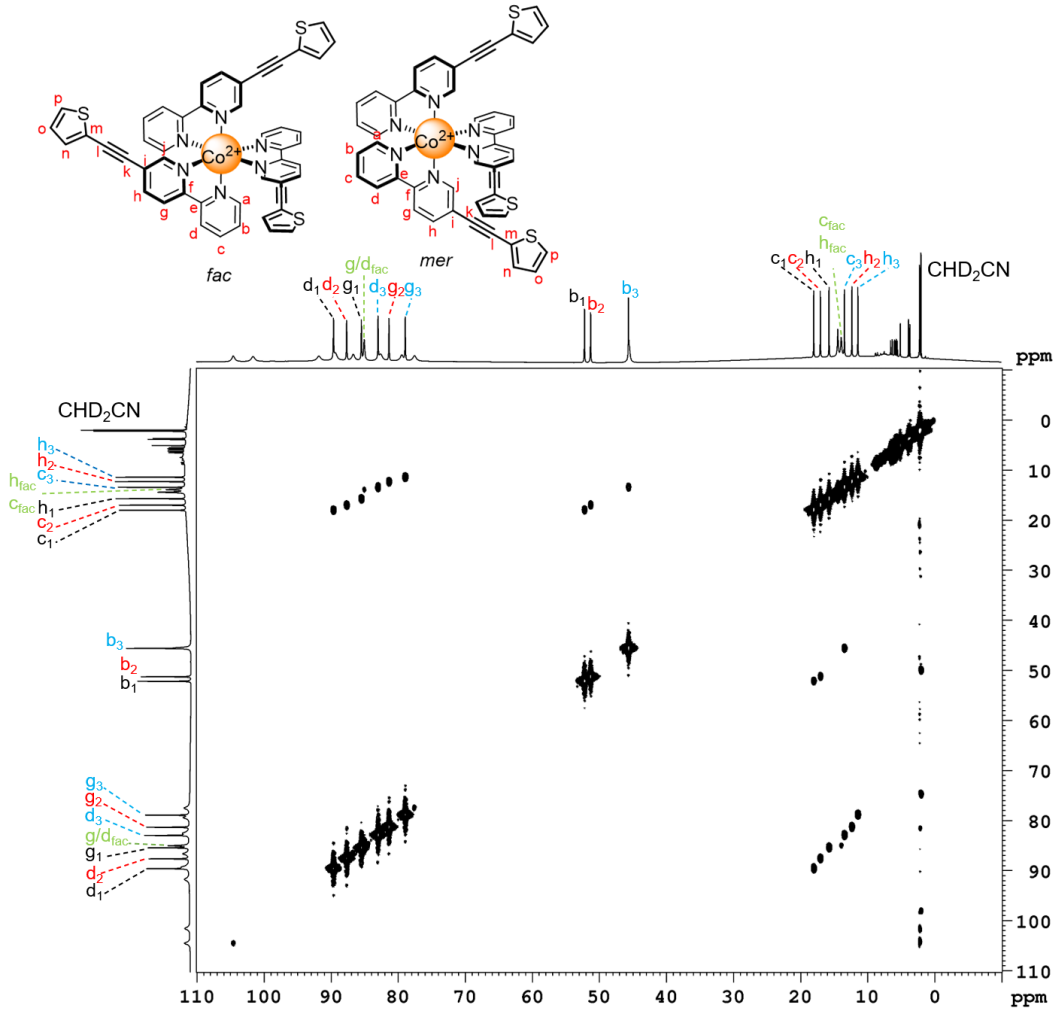


Figure S159. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of complex Co-**2b**.

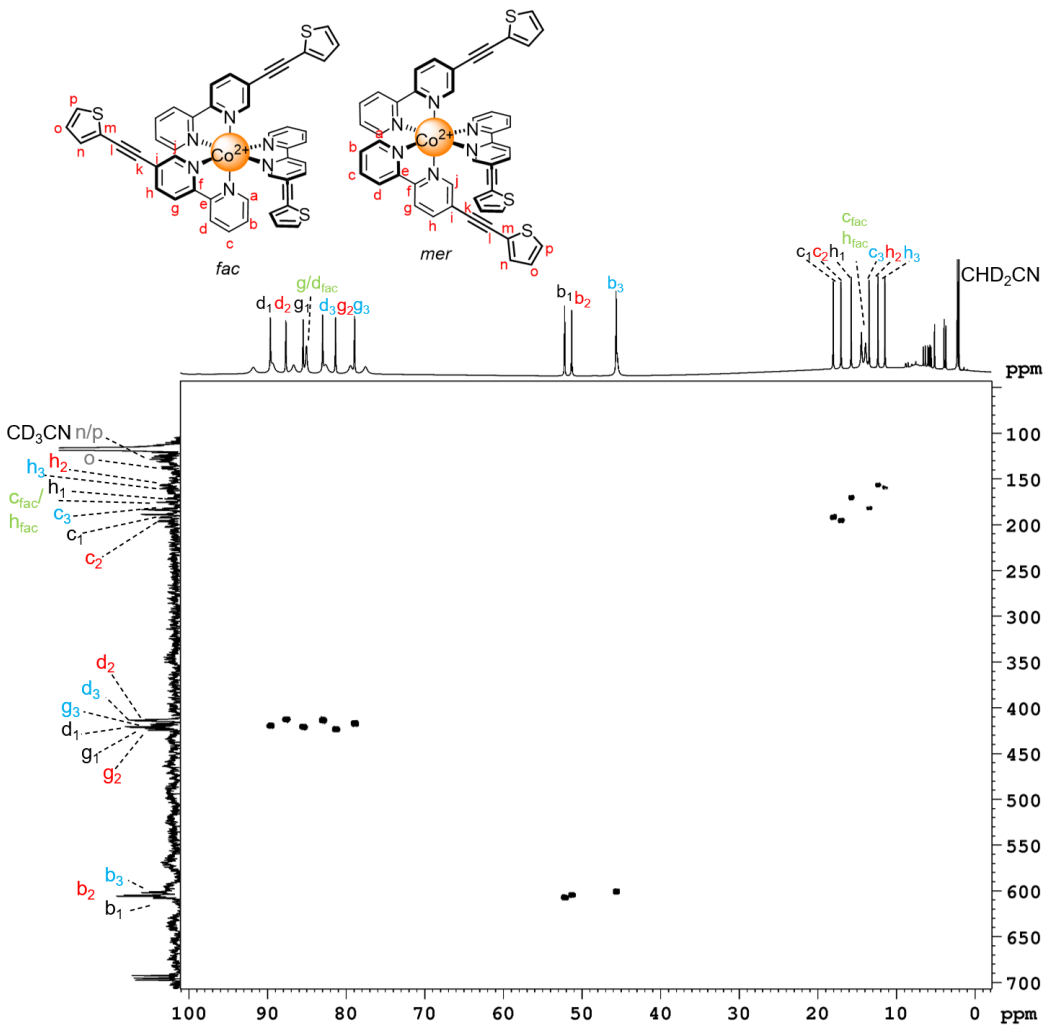


Figure S160. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-**2b**.

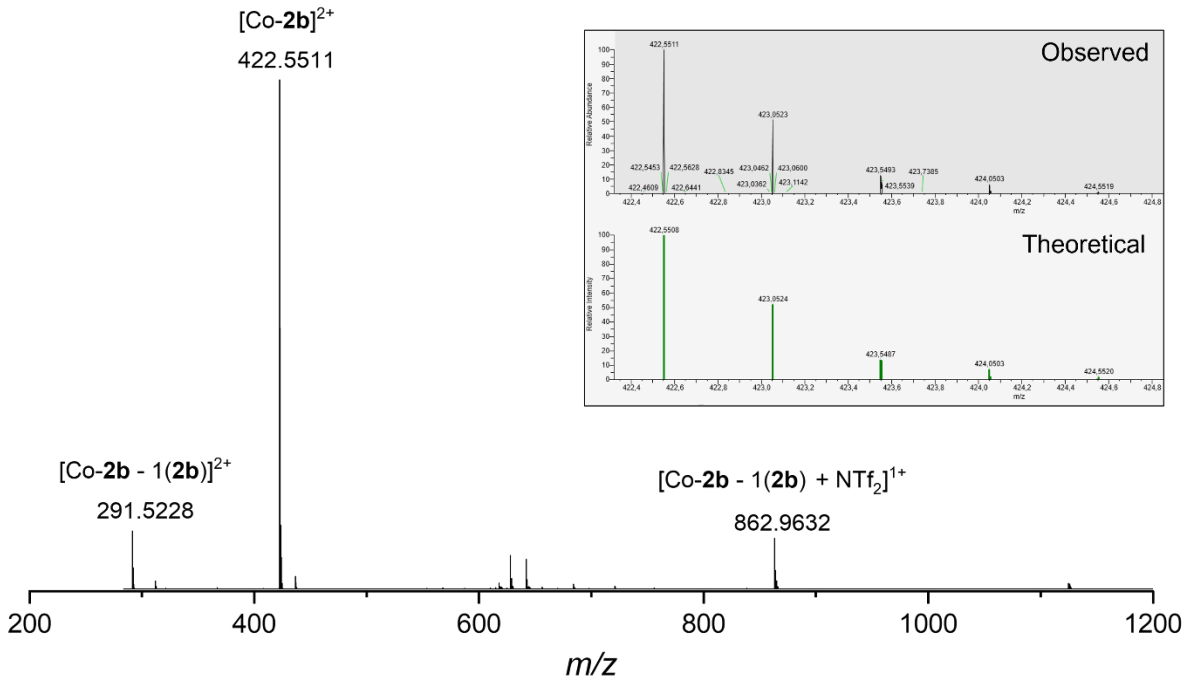
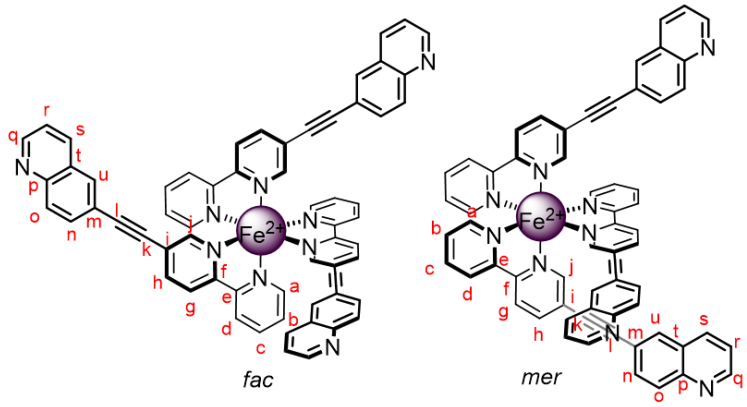


Figure S161. High resolution ESI mass spectrum of Co-**2b** showing in the insets the observed and theoretical isotope patterns.

8.7 Complex Fe-2c



Iron tetrafluoroborate hexahydrate (1.99 mg, 5.91 µmol) and 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**) (5.45 mg, 17.7 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (500 MHz, CD_3CN, 298 K) δ (ppm): 8.90 (br, 4H, H_q), 8.66-8.54 (m, 8H, $H_{d,g}$), 8.34-8.23 (m, 8H, $H_{h,r}$), 8.22-8.13 (m, 4H, H_c), 8.10-8.07 (m, 4H, H_u), 8.05-8.01 (m, 4H, H_o), 7.79-7.71 (m, 5H, $H_{n,j}$), 7.66 (s, 1H, H_j), 7.60-7.41 (m, 13H, $H_{a,b,j,\ s}$), 7.36 (d, ^3J = 5.1 Hz, 1H, H_a).

^{13}C NMR (126 MHz, CD_3CN, 298 K) δ (ppm): 159.7 (C_e), 159.7 (C_e), 159.6 (C_e), 159.6 (C_e), 159.3 (C_f), 159.3 (C_f), 159.2 (C_f), 159.1 (C_f), 157.4 (C_j), 157.2 (C_j), 157.1 (C_j), 156.8 (C_j), 155.9 (C_a), 155.7 (C_a), 155.4 (C_a), 152.9 (C_q), 148.7 (C_p), 142.2 (C_h), 142.1 (C_h), 142.0 (C_h), 140.1 (C_c), 140.0 (C_c), 137.4 (C_r),133.3 (C_u), 132.5 (C_n), 130.8 (C_o), 129.1, (C_t), 128.9 (C_b), 128.8 (C_b), 128.8 (C_b), 128.8 (C_b), 125.9 (C_d), 125.8 (C_d), 125.6 (C_d), 125.0 (C_g), 124.9 (C_g), 124.8 (C_g), 124.7 (C_g), 124.6 (C_i), 124.6 (C_i), 123.5 (C_s), 120.6 (C_m), 120.5 (C_m), 96.9 (C_l), 96.8 (C_l), 96.8 (C_l), 96.7 (C_l), 86.2 (C_k), 86.2 (C_k), 86.1 (C_k), 86.1 (C_k).

HRMS (ESI, CH_3CN) *m*/z: 488.6327 $[Fe\text{-}\mathbf{2c}]^{2+}$.

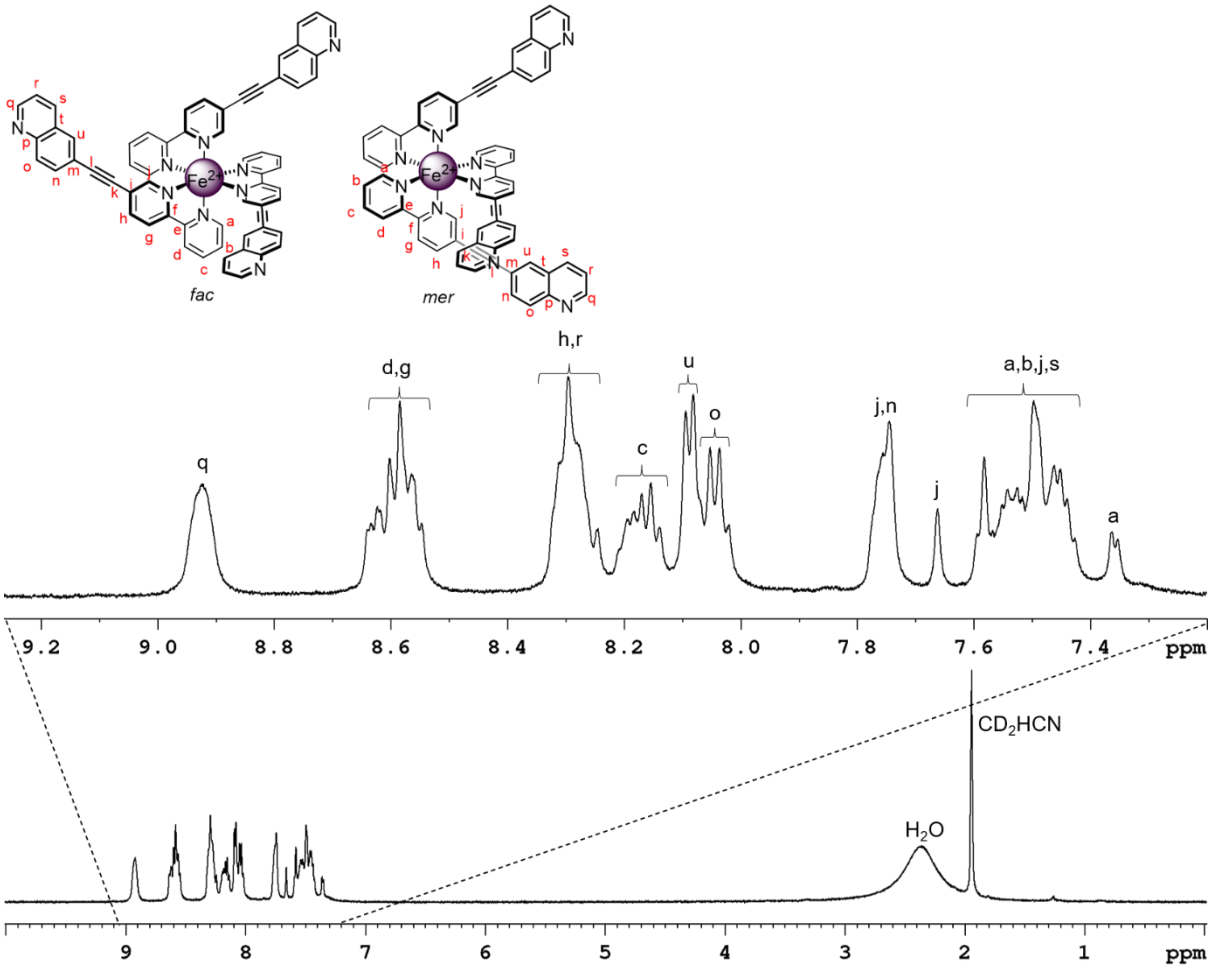


Figure S162. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-**2c**.

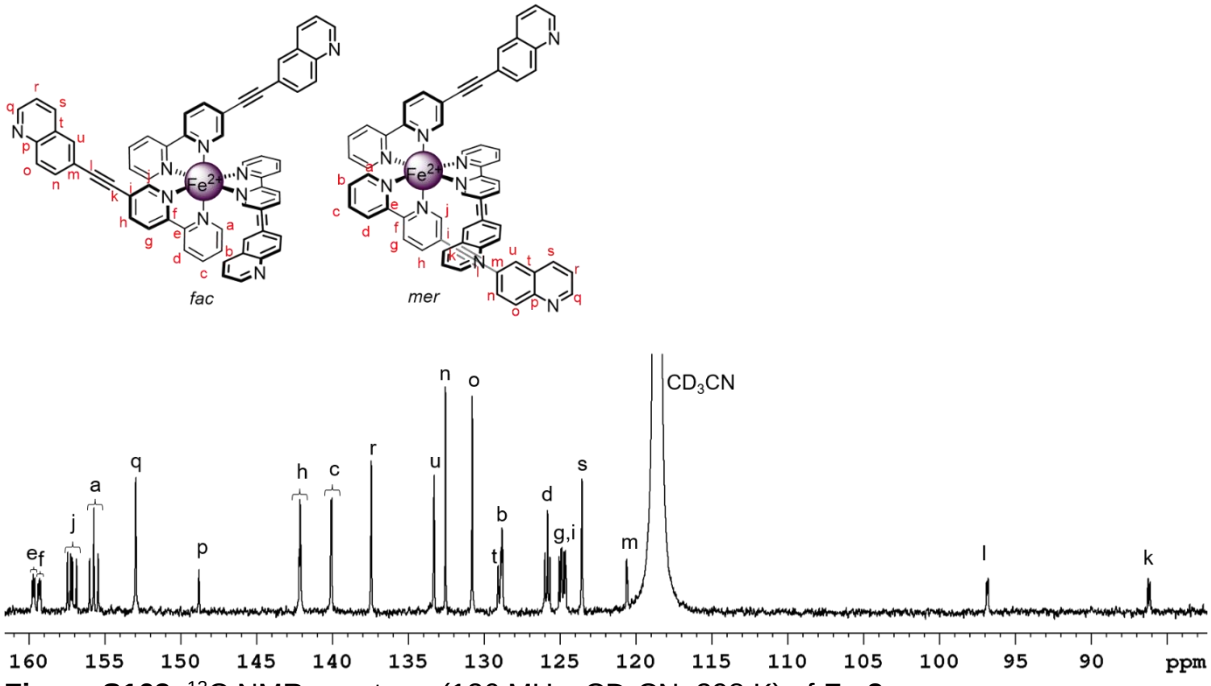


Figure S163. ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of Fe-**2c**.

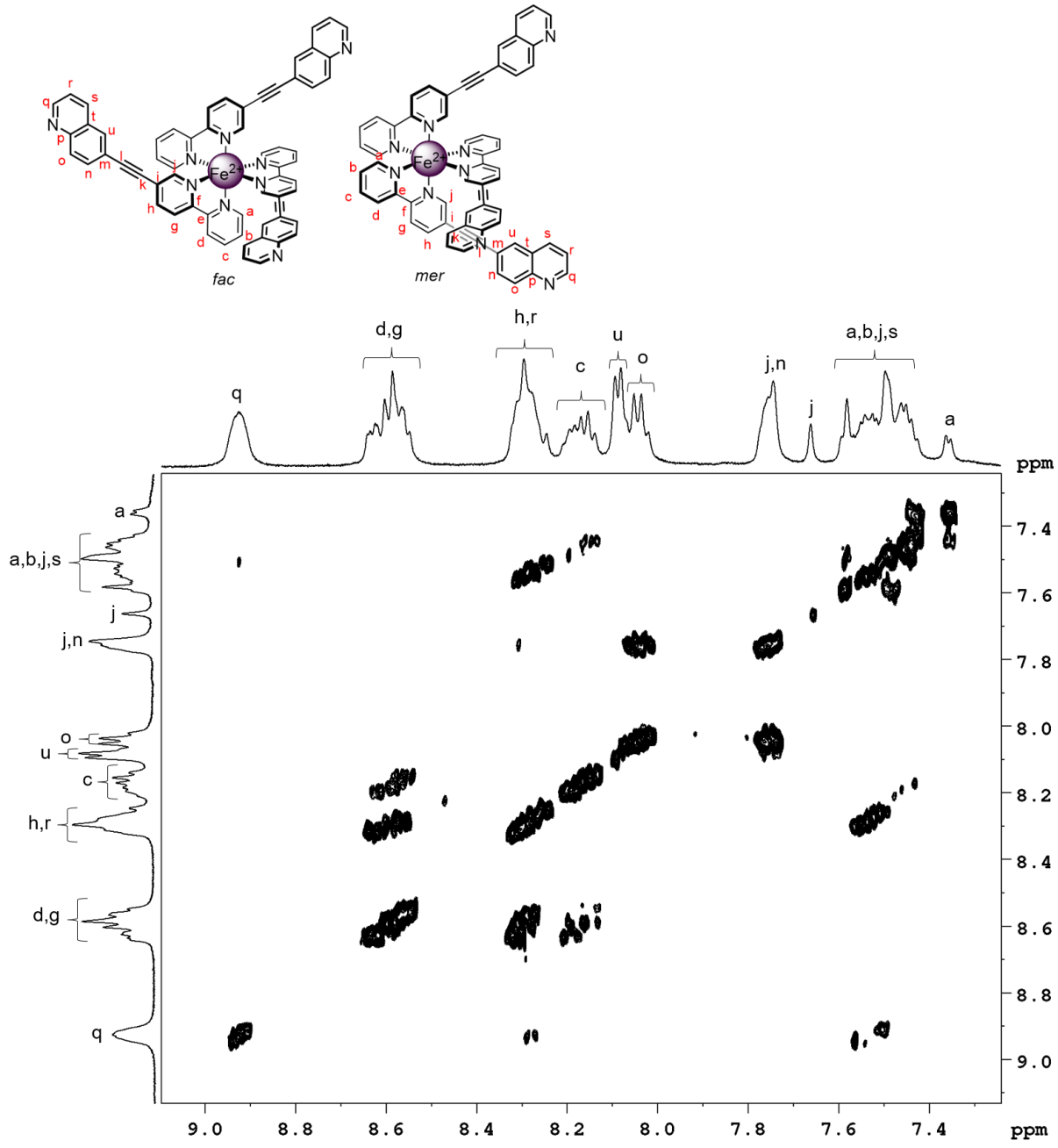


Figure S164. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_3CN, 298 K) of Fe-**2c**.

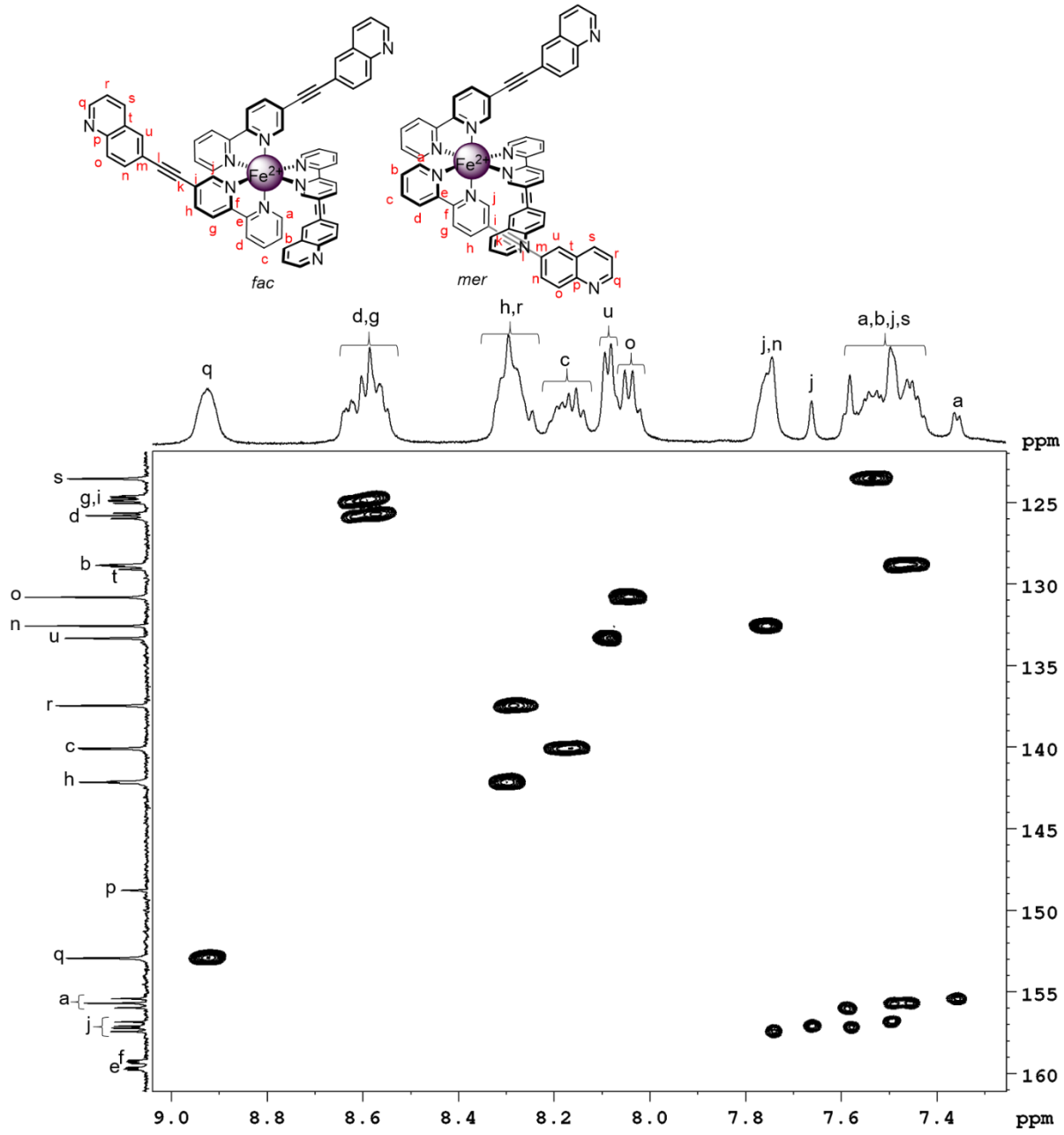


Figure S165. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz/126 MHz, CD_3CN, 298 K) of Fe-**2c**.

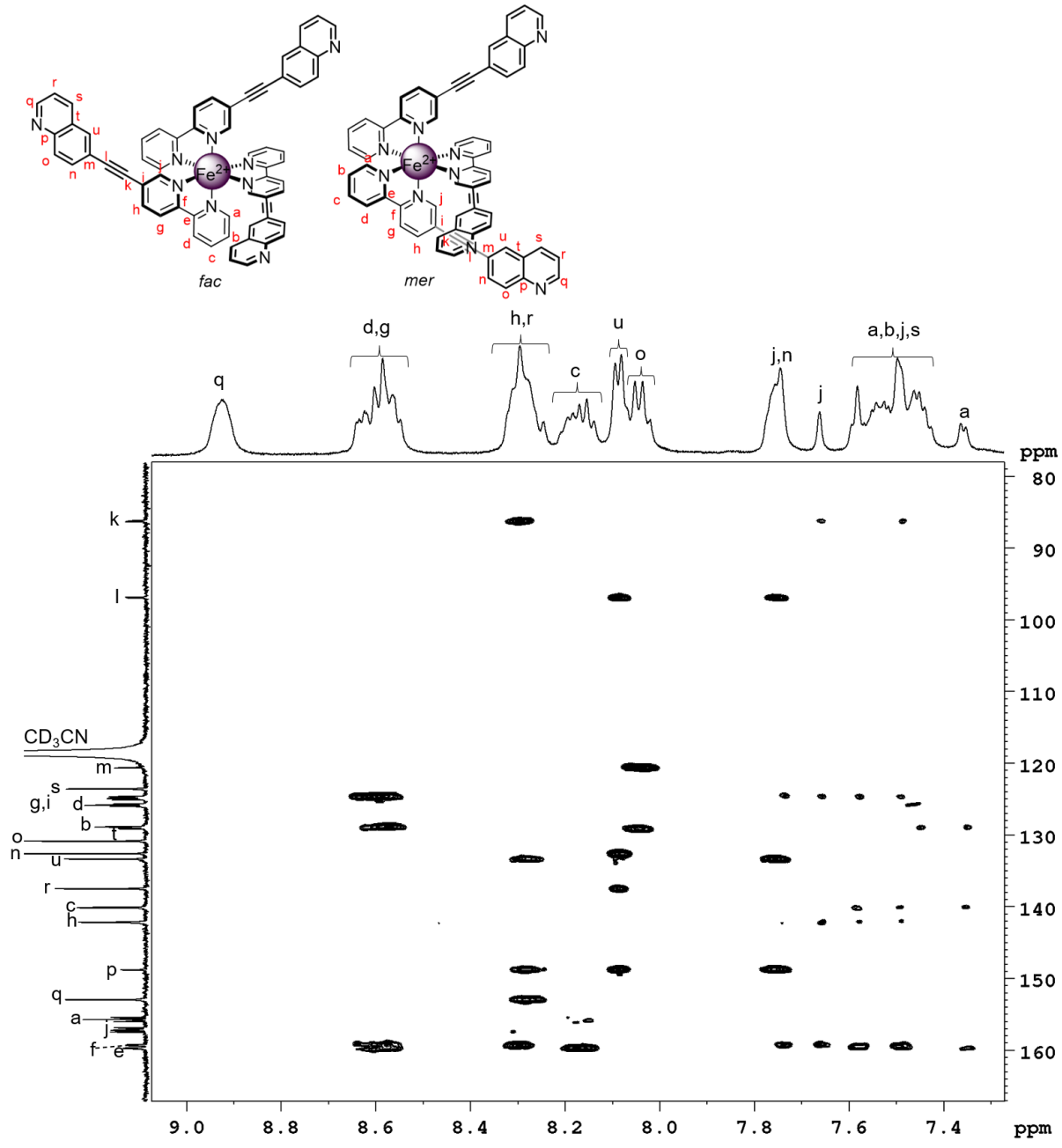


Figure S166. ^{1}H-^{13}C HMBC NMR spectrum (600 MHz/126 MHz, CD_3CN, 298 K) of Fe-**2c**.

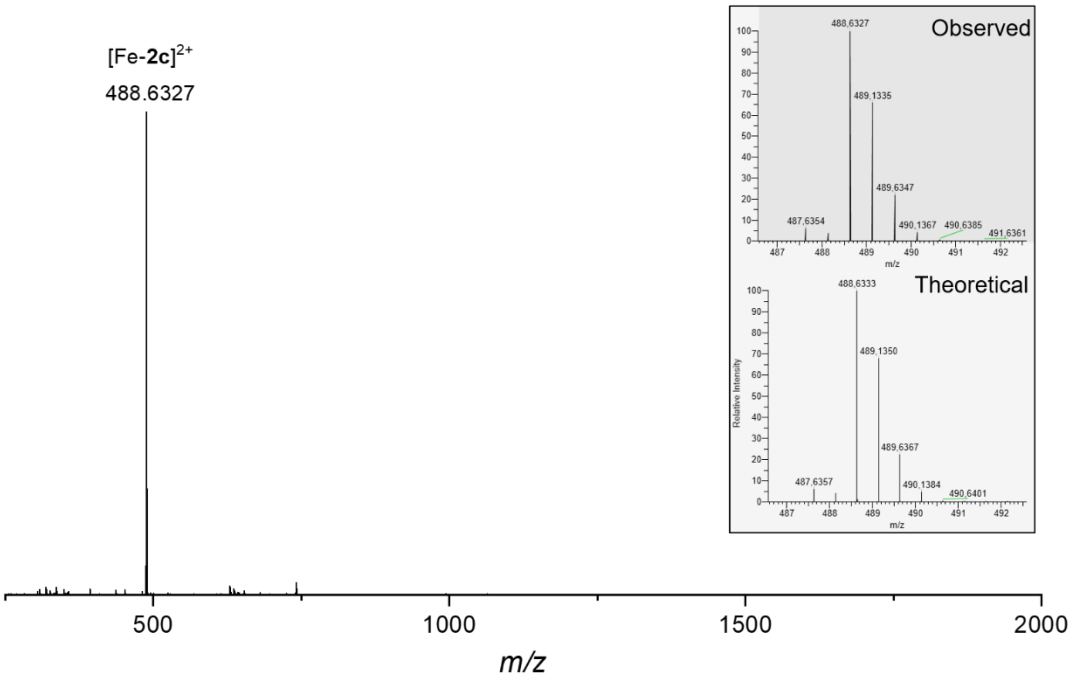
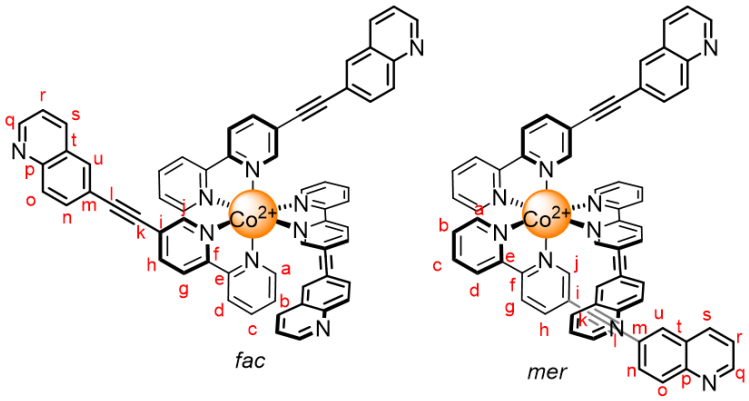


Figure S167. High resolution ESI mass spectrum of Fe-**2c** showing in the insets the observed and theoretical isotope patterns.

8.8 Complex Co-2c



Cobalt bis(trifluoromethylsulfonyl)imide (3.58 mg, 5.18 µmol) and 5-(quinolin-6-ylethynyl)-2,2'-bipyridine (**2c**) (5.21 mg, 15.5 µmol) were dissolved in CD_3CN (0.5 mL).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 104.6 (br, 1H, $H_{a/j}$), 101.1 (br, 1H, $H_{a/j}$), 92.8 (br, 1H, $H_{a/j}$), 90.3 (br, 1H, $H_{a/j}$), 89.9 (s, 1H, H_{d1}), 87.8 (s, 1H, H_{d2}), 86.3 (br, 1H, $H_{a/j}$), 85.6 (s, 2H, $H_{g1/d3}$), 83.7 (s, 1H, H_{g2}), 82.9 (s, 1H, H_{dfac}), 81.3 (s, 1H, H_{g3}), 80.3 (br, 1H, $H_{a/j}$), 78.8 (s, 1H, H_{gfac}), 78.1 (br, 1H, $H_{a/j}$), 52.2 (s, 1H, H_{d1}), 51.5 (s, 1H, H_{d2}), 46.2 (s, 1H, H_{d3}), 45.8 (s, 1H, H_{bfac}), 18.1 (s, 1H, H_{c1}), 17.1 (s, 1H, H_{c2}), 15.8 (s, 1H, H_{h1}), 14.9 (s, 1H, H_{h2}), 14.5 (s, 1H, H_{c3}), 13.4 (s, 1H, H_{cfac}), 12.3 (s, 1H, H_{h3}), 11.4 (s, 1H, H_{hfac}), 7.2-6.2 (m, 2H, H_{n-u}), 5.4 (d, 1H, H_{n-u}), 5.0 (d, 1H, H_{n-u}), 4.2 (d, 1H, H_{n-u}), 3.9 (d, 1H, H_{n-u}).

Note: While it was possible to assign the proton signals within one spin system (indicated by numbers) based on the COSY spectrum, the different spin systems within each ligand could not be correlated to a particular ligand environment. For the signals of the bipyridine, the fac isomer was, therefore, tentatively assigned based on the integral of the signals. The three

remaining sets of signals corresponding to the mer isomer were arbitrarily labelled with black, red, and blue labels according to their decreasing chemical shift. Protons corresponding to the R substituent were tentatively assigned in grey due to the signal overlap in the diamagnetic region of the spectra.[11]

^{13}C NMR (151 MHz, CD_3CN, 298 K) δ (ppm): 696.1 (s), 694.4 (s), 694.1 (s), 690.8, 607.6 (s) (unresolved d, C_{b1}), 605.6 (unresolved d, C_{b3}), 604.9 (unresolved d, C_{b2}), 601.5 (unresolved d, C_{bfac}) 424.1 (d, ^1J = 167 Hz, C_{g3}), 421.6 (overlapping d, $C_{g1,d3}$), 420.3 (overlapping d, C_{d1}), 417.4 (overlapping d, C_{gfac}), 415.6 (overlapping d, C_{g2}), 413.4 (overlapping d, $C_{d2,dfac}$), 196.3 (d, ^1J = 165 Hz, C_{c2}), 191.2 (d, ^1J = 161 Hz, C_{c2}), 185.2 (s), 184.3 (s), 182.6 (d, ^1J = 164 Hz, C_{cfac}), 180.1 (s), 179.5 (s), 178.2 (unresolved d, C_{c3}), 174.5 (unresolved d, C_{h2}), 170.5 (unresolved d, C_{h1}), 160.2 (d, ^1J = 163 Hz, C_{hfac}), 156.4 (d, ^1J = 169 Hz, C_{h3}), 154.5-142.7 (overlapping signals), 153.2-147.8 (overlapping signals), 131.8-138.4 (overlapping signals, C_{n-u}), 135.3-120.4 (overlapping signals, C_{n-u}), 74.4 (unresolved d, $C_{a/j}$), 67.0 (unresolved d, $C_{a/j}$), 35.9 (unresolved d, $C_{a/j}$), 28.3 (unresolved d,$C_{a/j}$), -114.1 (s, $C_{e/f}$), -114.7 (s, $C_{e/f}$), -139.0 (s, $C_{e/f}$), -139.6 (s, $C_{e/f}$), -146.1 (s, $C_{e/f}$), -169.6 (s, $C_{e/f}$), -170.1 (s, $C_{e/f}$).

Note: Quaternary carbons and carbons close to the paramagnetic center (a and j) could not be unambiguously assigned due to the lack of HMBC equivalent in the paramagnetic NMR toolbox. Carbons a, j, e and f are assigned based on related complexes.[11]

HRMS (ESI, CH_3CN) *m/z*: 1261.1841 [Co-**2c** +NTf_2]$^{1+}$, 953.0696 [Co-**2c** -1(**2c**) +NTf_2]$^{1+}$, 490.1316 [Co-**2c**]$^{2+}$, 336.5760 [Co-**2c** -1(**2c**)]$^{2+}$.

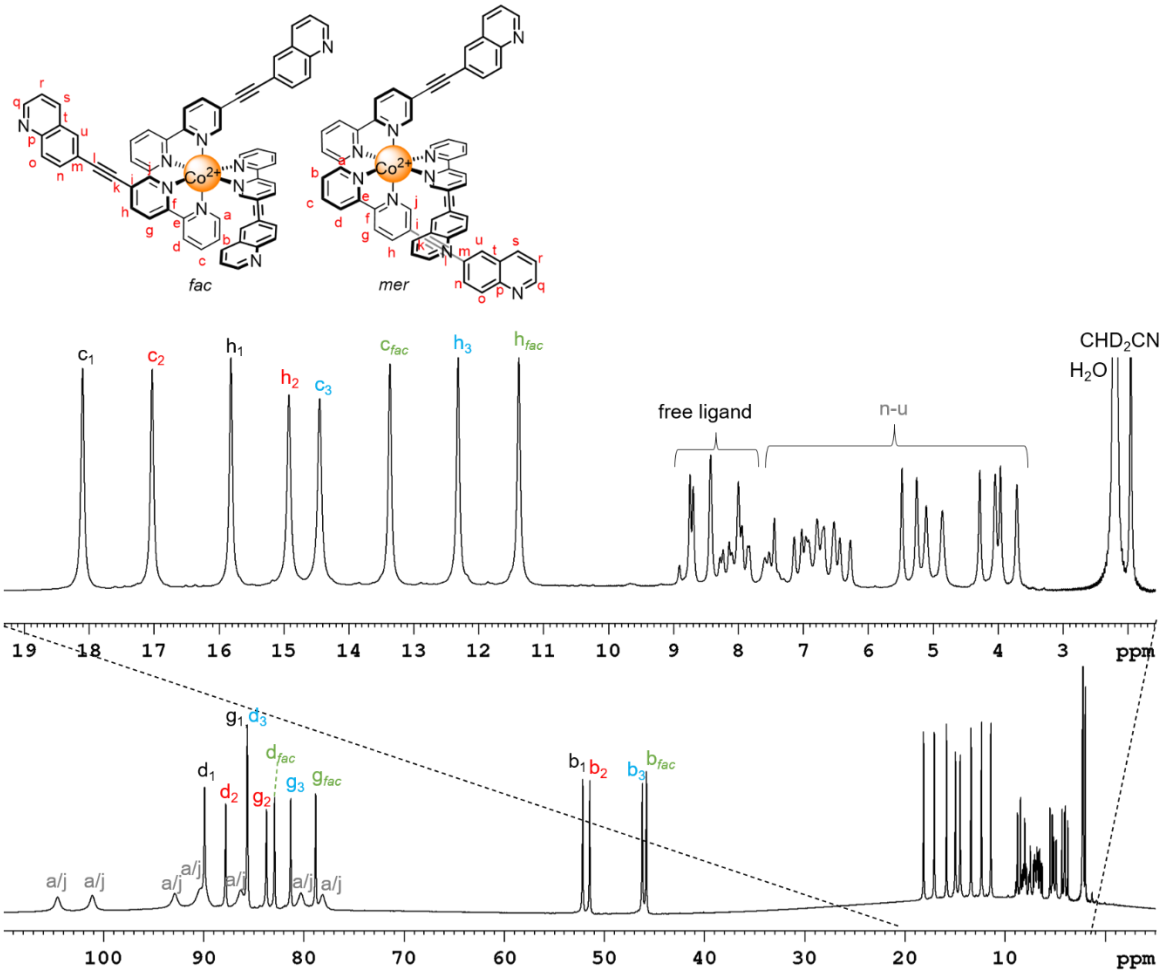


Figure S168. ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of complex Co-**2c**.

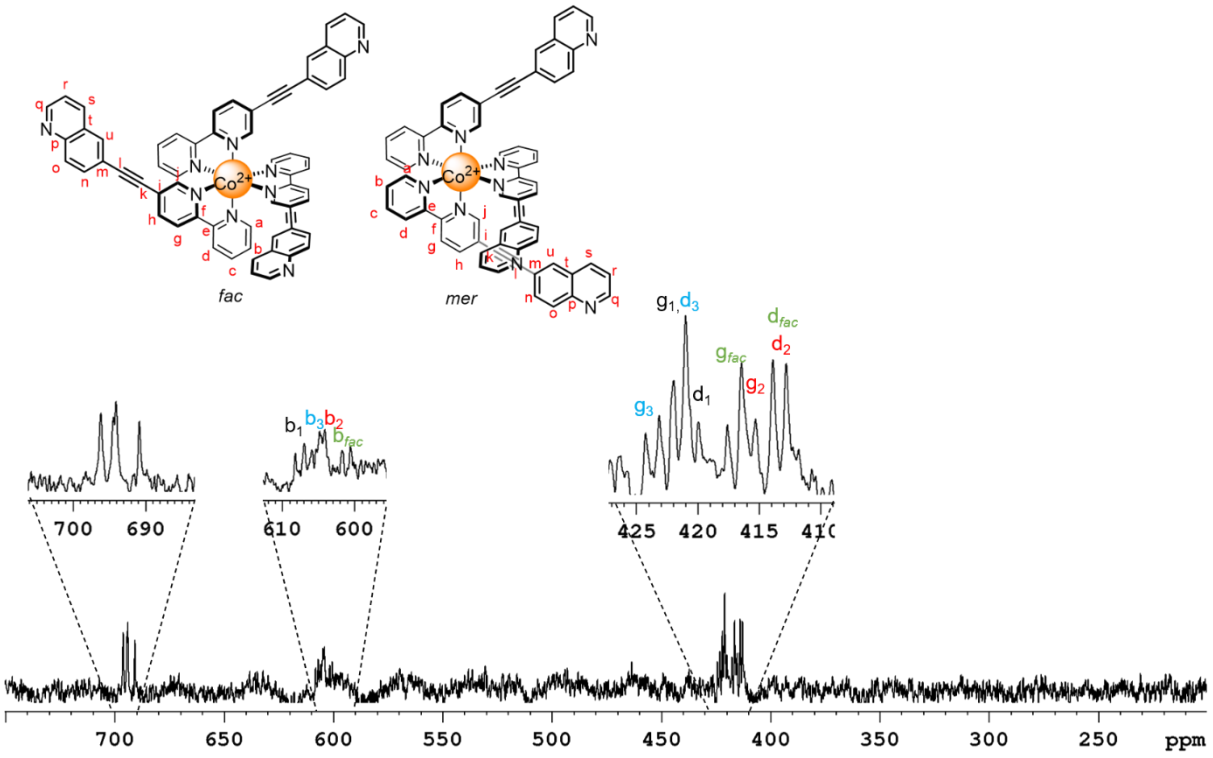


Figure S169. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of complex **Co-2c**.

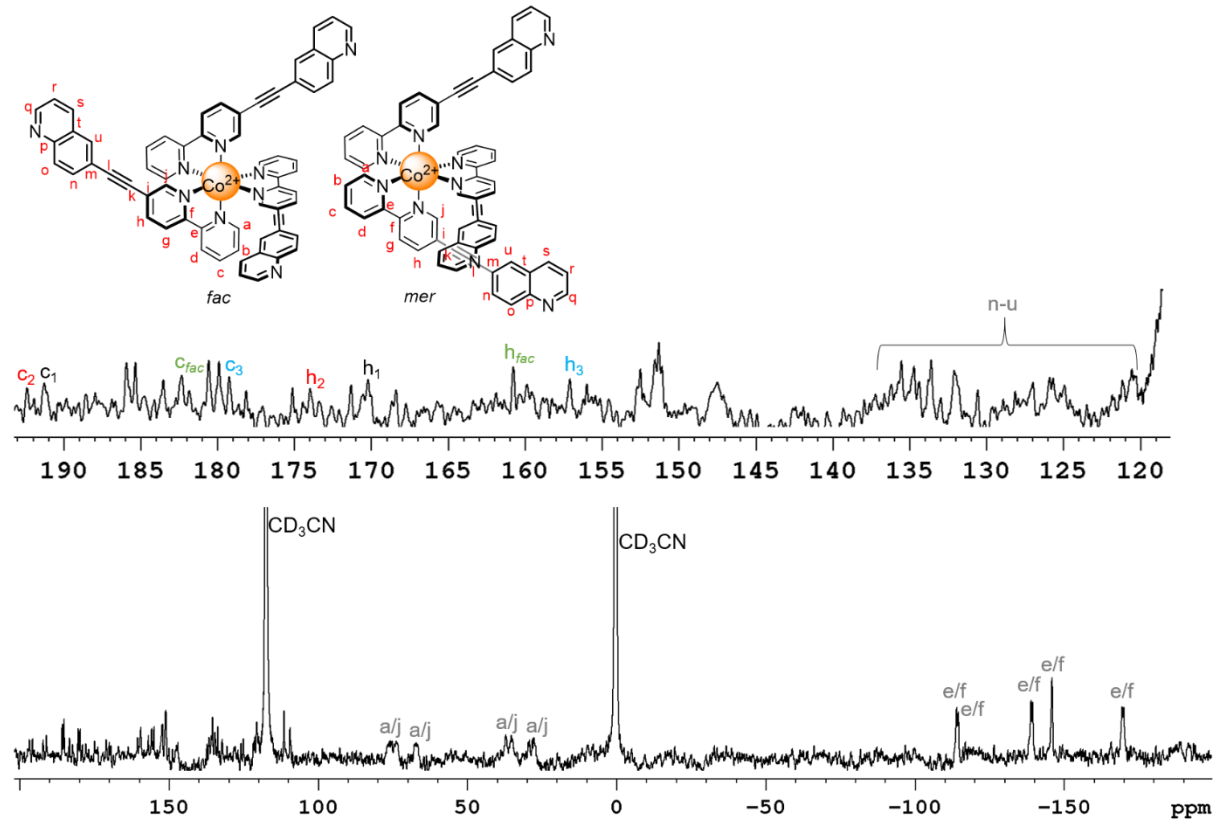


Figure S170. ^{13}C NMR spectrum (151 MHz, CD_3CN, 298 K) of complex **Co-2c**.

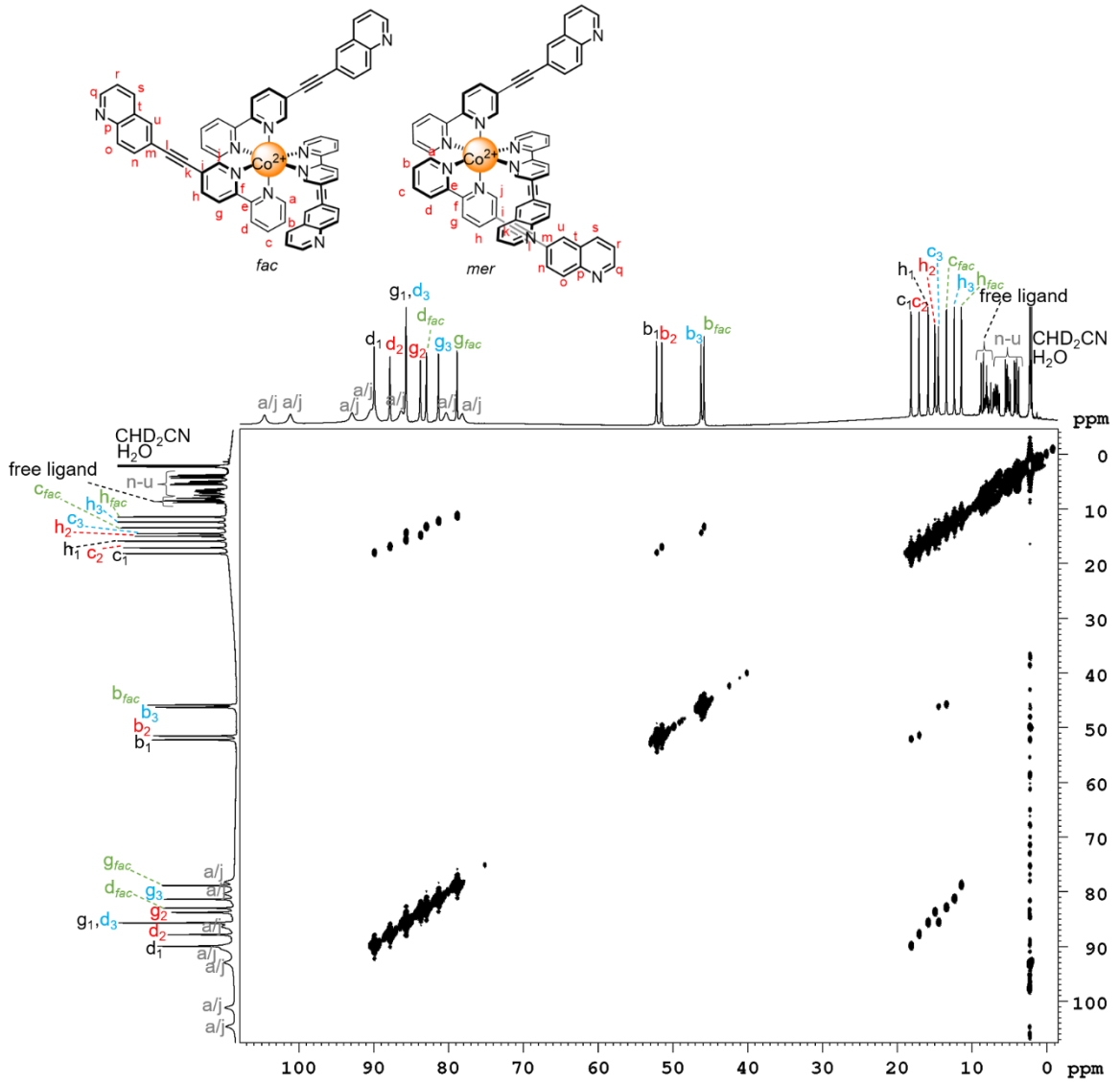


Figure S171. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_3CN, 298 K) of complex Co-**2c**.

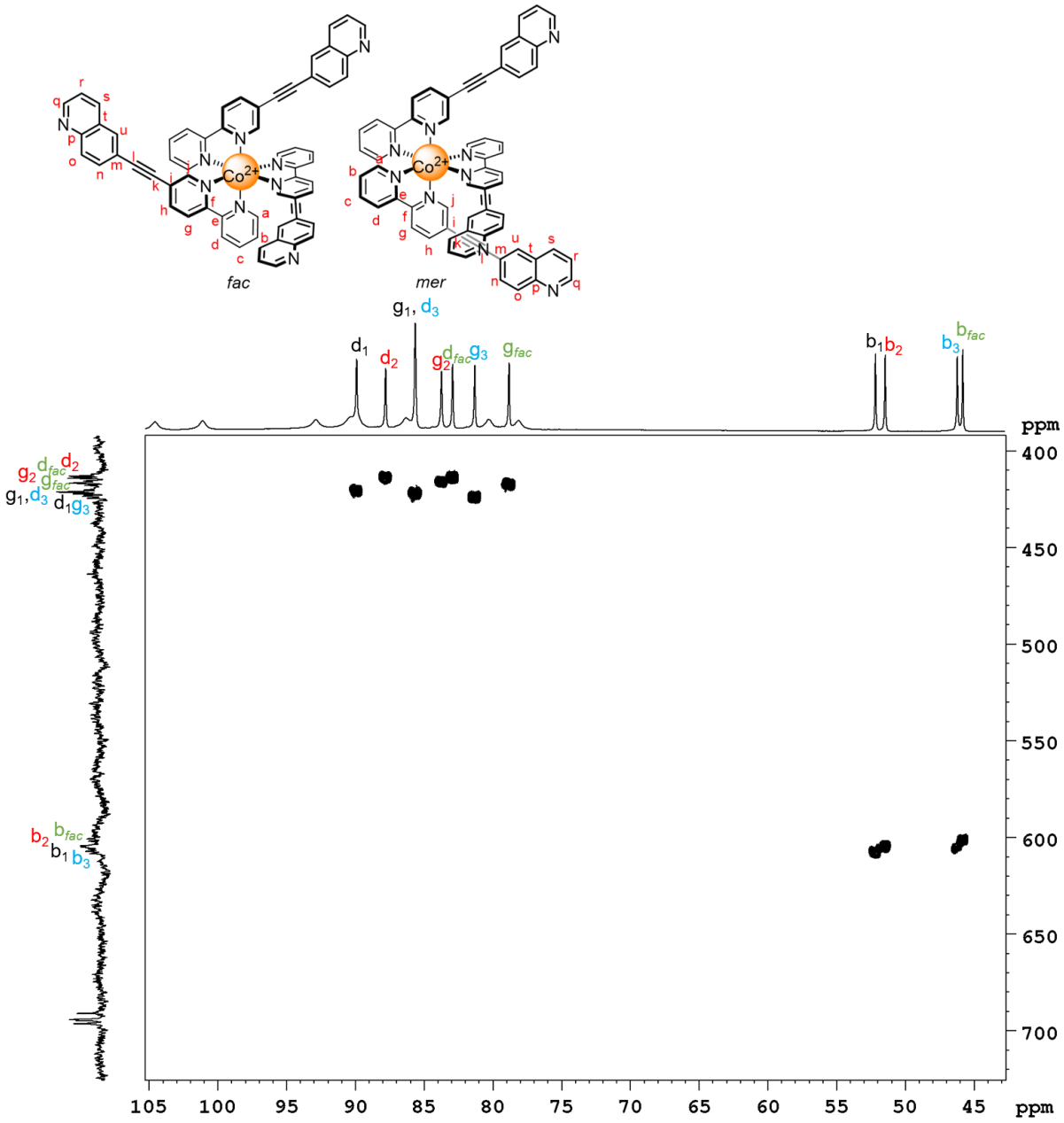


Figure S172. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-**2c**.

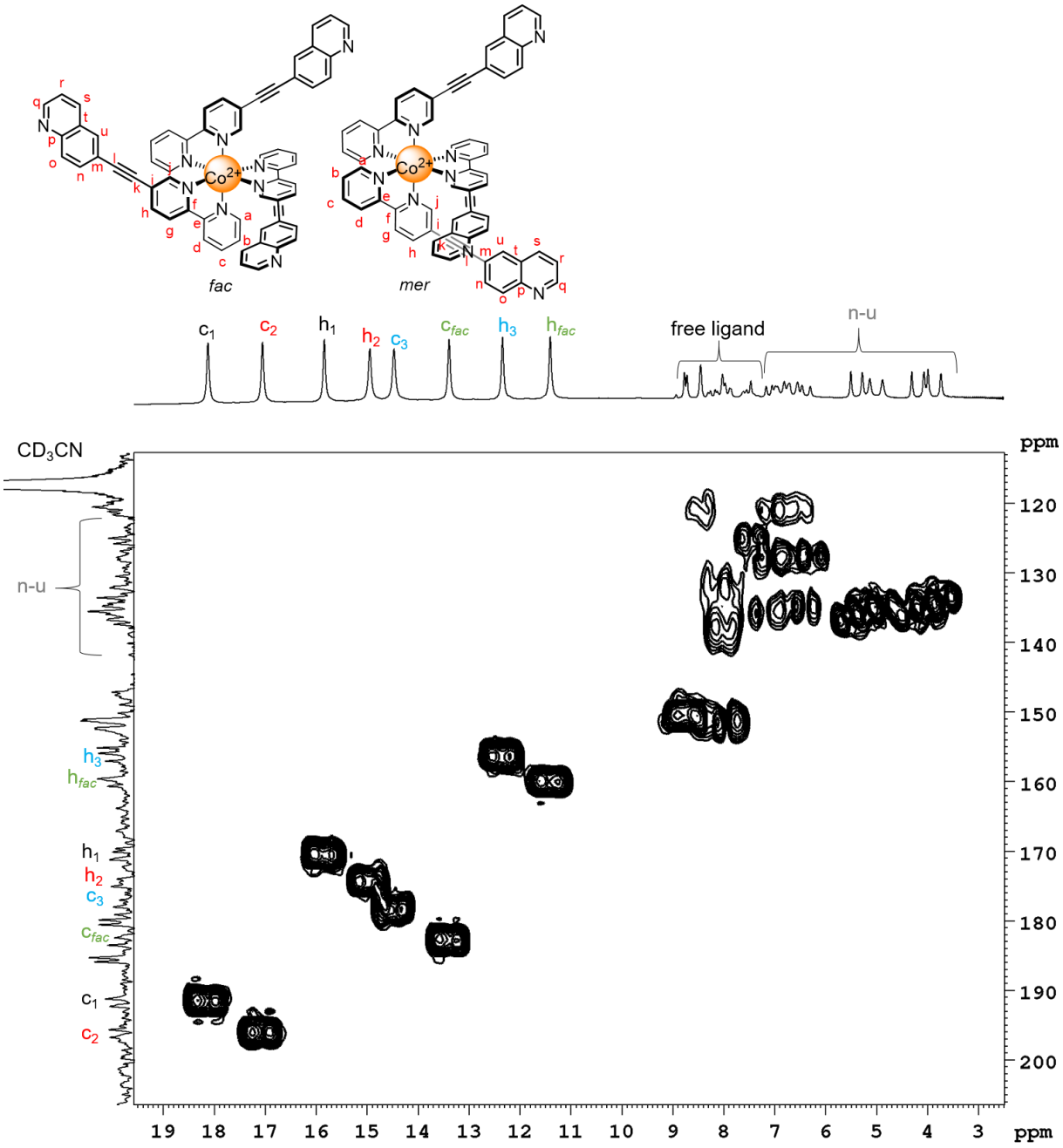


Figure S173. ^{1}H-^{13}C HMQC NMR spectrum (600 MHz/151 MHz, CD_3CN, 298 K) of Co-**2c**.

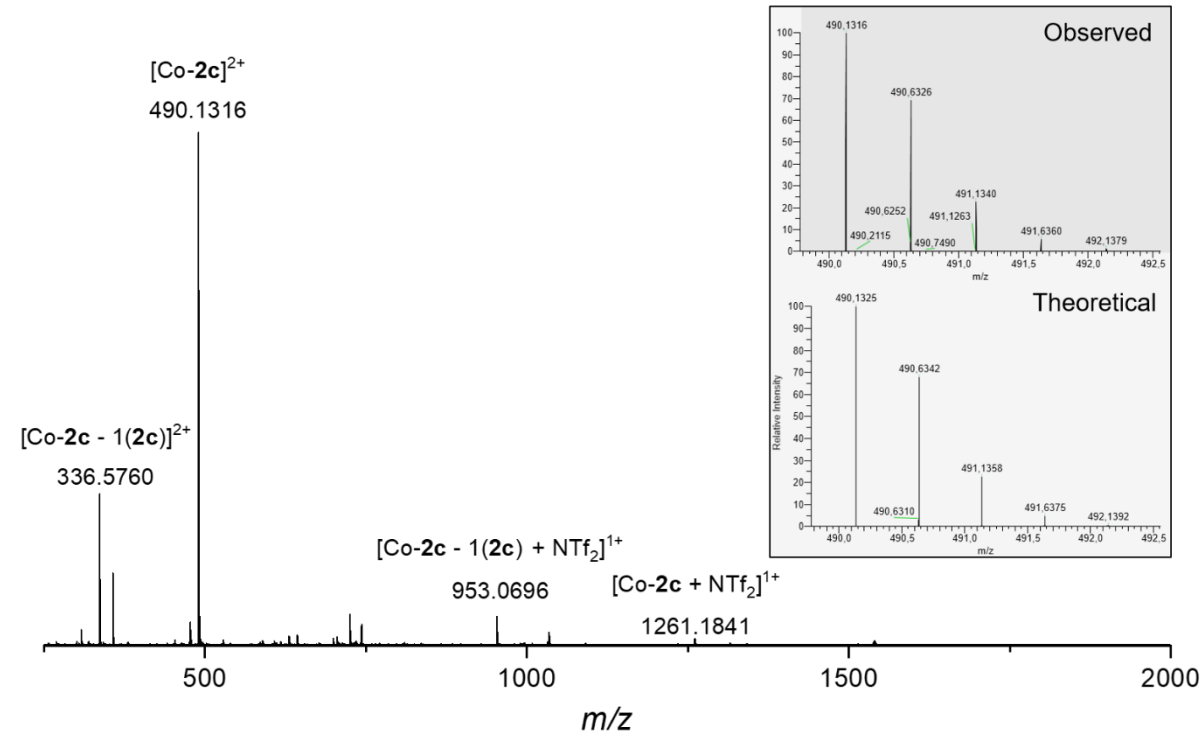


Figure S174. High resolution ESI mass spectrum of Co-**2c** showing in the insets the observed and theoretical isotope patterns.

9 M-CPOne Irradiation

9.1 Zn-CPOne-**1a**

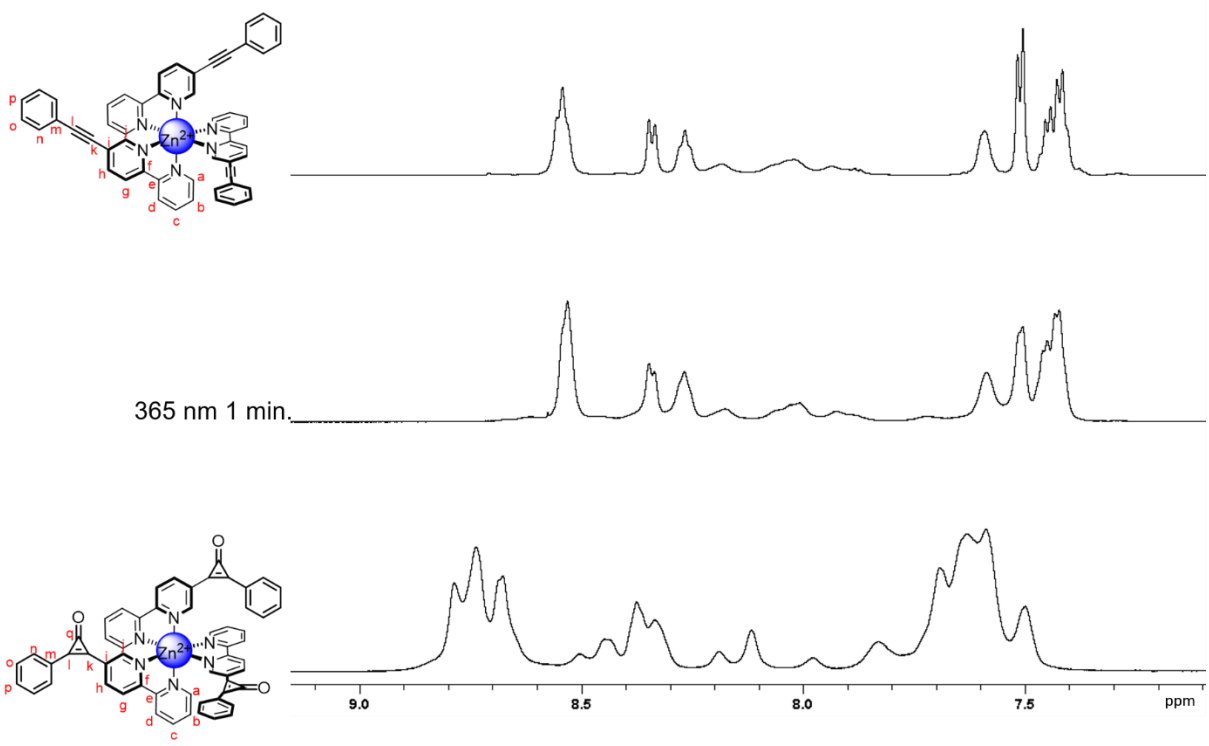


Figure S175. ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of: Zn-CPOne-**1a** before (bottom) and after irradiation with 365 nm for 1 minute (middle); the reference complex Zn-**2a** (top).

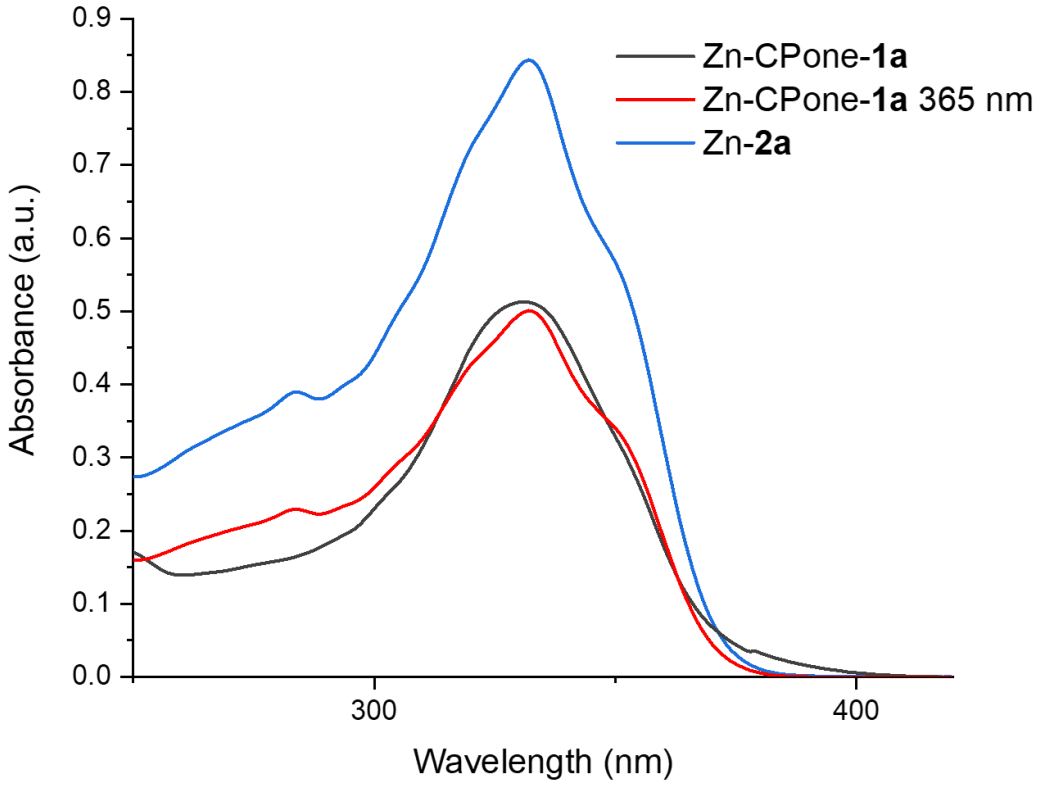


Figure S176. UV/vis spectra (CH_3CN, 298 K) of: Zn-CPOne-**1a** (2.47 μM) before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Zn-**2a** (blue, 8.28 μM).

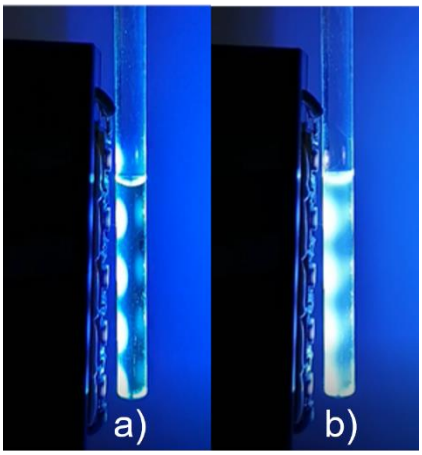


Figure S177. NMR sample of Zn-CPOne-**1a**: a) at the start of and b) after irradiation with 365 nm for 1 min showing the change in fluorescence following irradiation.

9.2 Zn-CPOne-**1b**

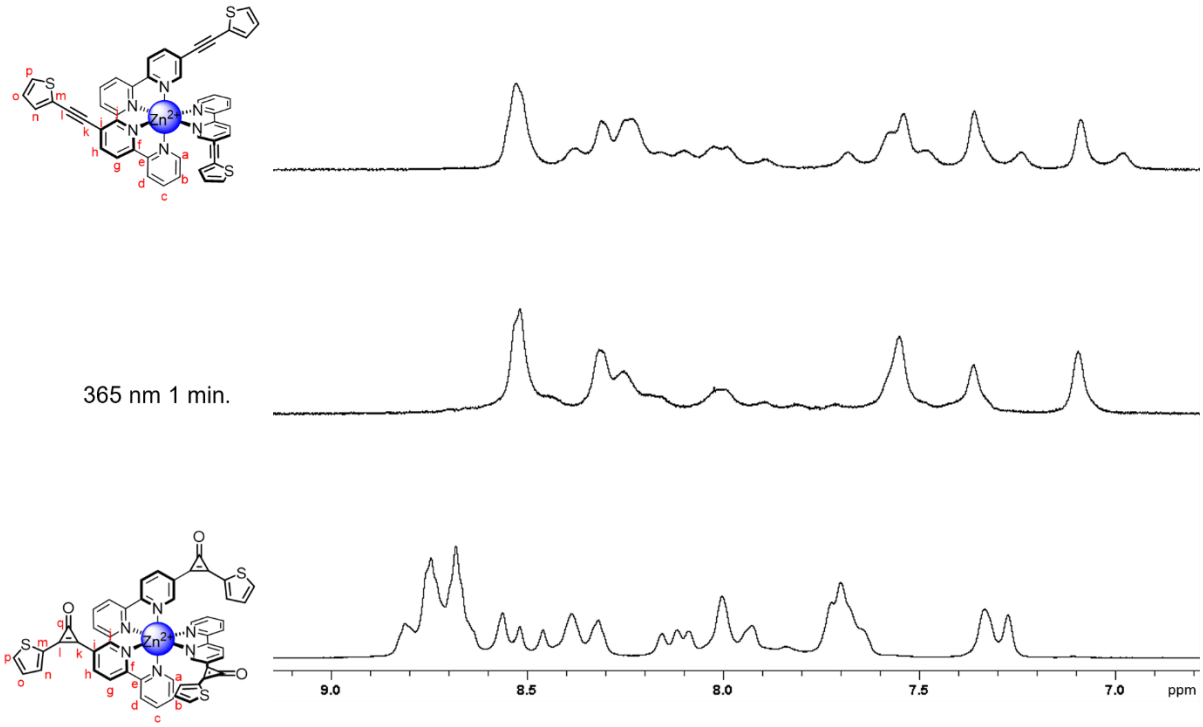


Figure S178. ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of: Zn-CPOne-**1b** before (bottom) and after irradiation with 365 nm for 1 minute (middle); reference complex Zn-**2b** (top).

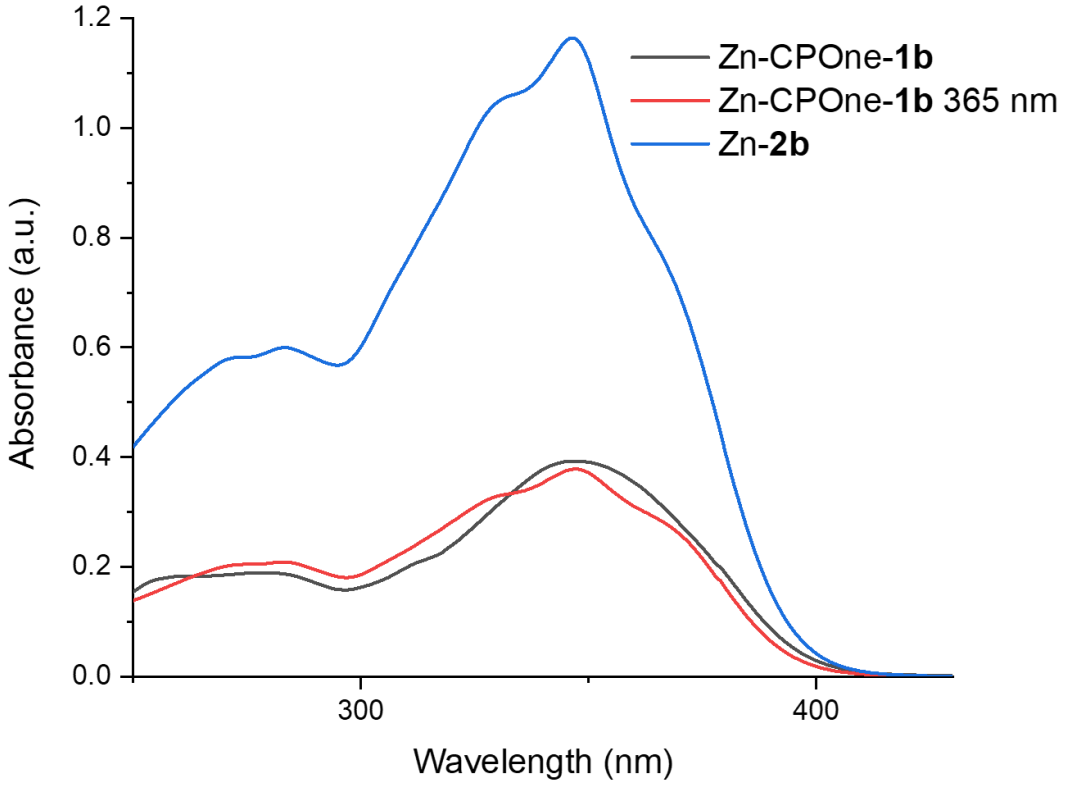


Figure S179. UV/vis spectra (CH_3CN, 298 K) of: Zn-CPOne-**1b** (1.62 μM) before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Zn-**2b** (blue, 5.43 μM).

9.3 Fe-CPOne-**1a**

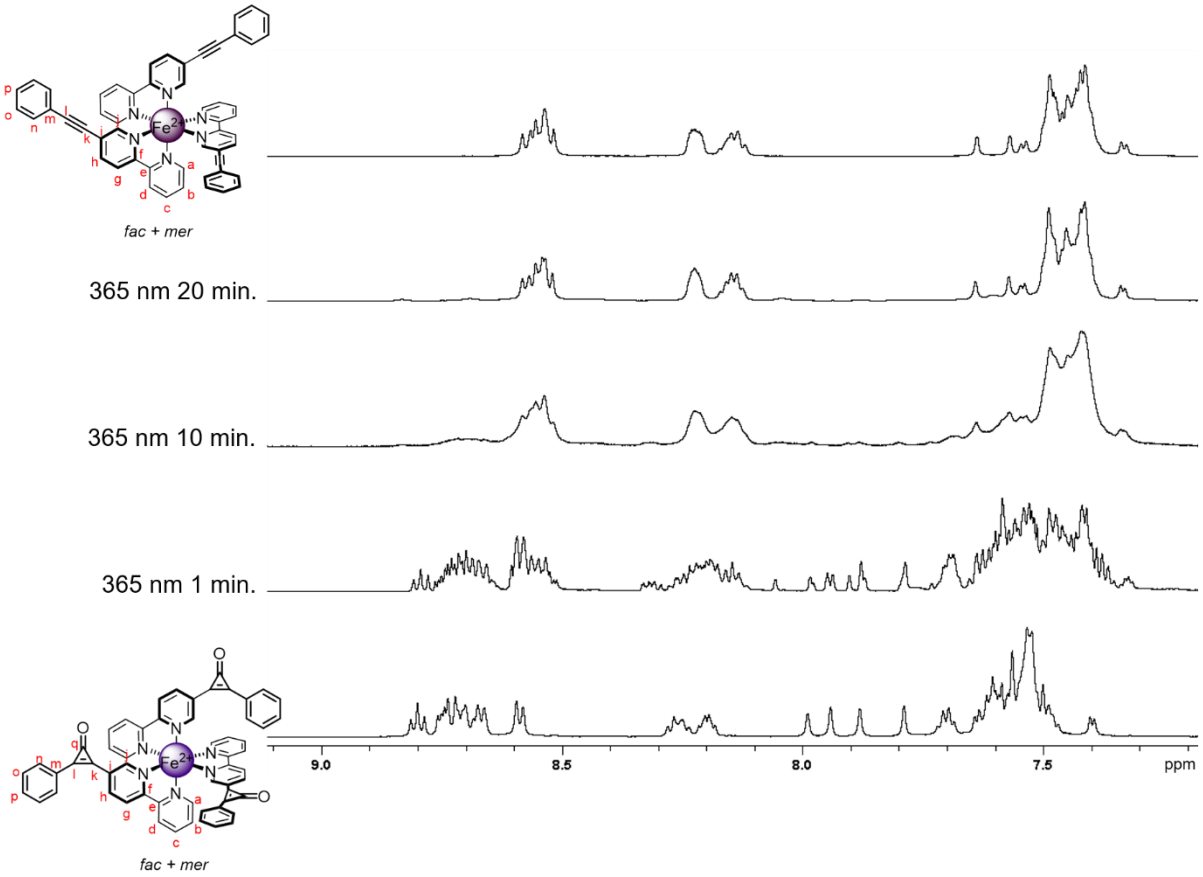


Figure S180. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Fe-CPOne-**1a** before (bottom) and after irradiation with 365 nm for 1-20 minutes; reference complex Fe-**2a** (top).

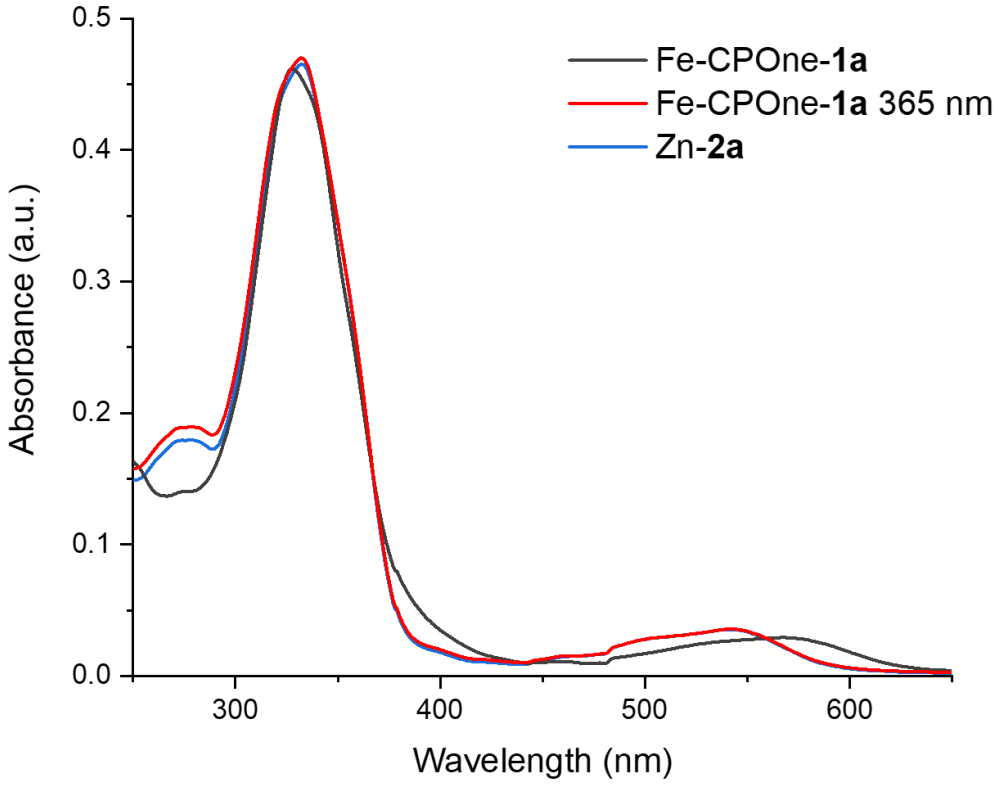


Figure S181. UV/vis spectra (CH_3CN, 298 K) of: Fe-CPOne-**1a** (2.10 μM) before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Fe-**2a** (blue, 5.65 μM).

Figure S182. NMR sample of Fe-CPOne-**1a**: a) before and b) after irradiation at 365 nm for 20 minutes.

9.4 Fe-CPOne-**1b**

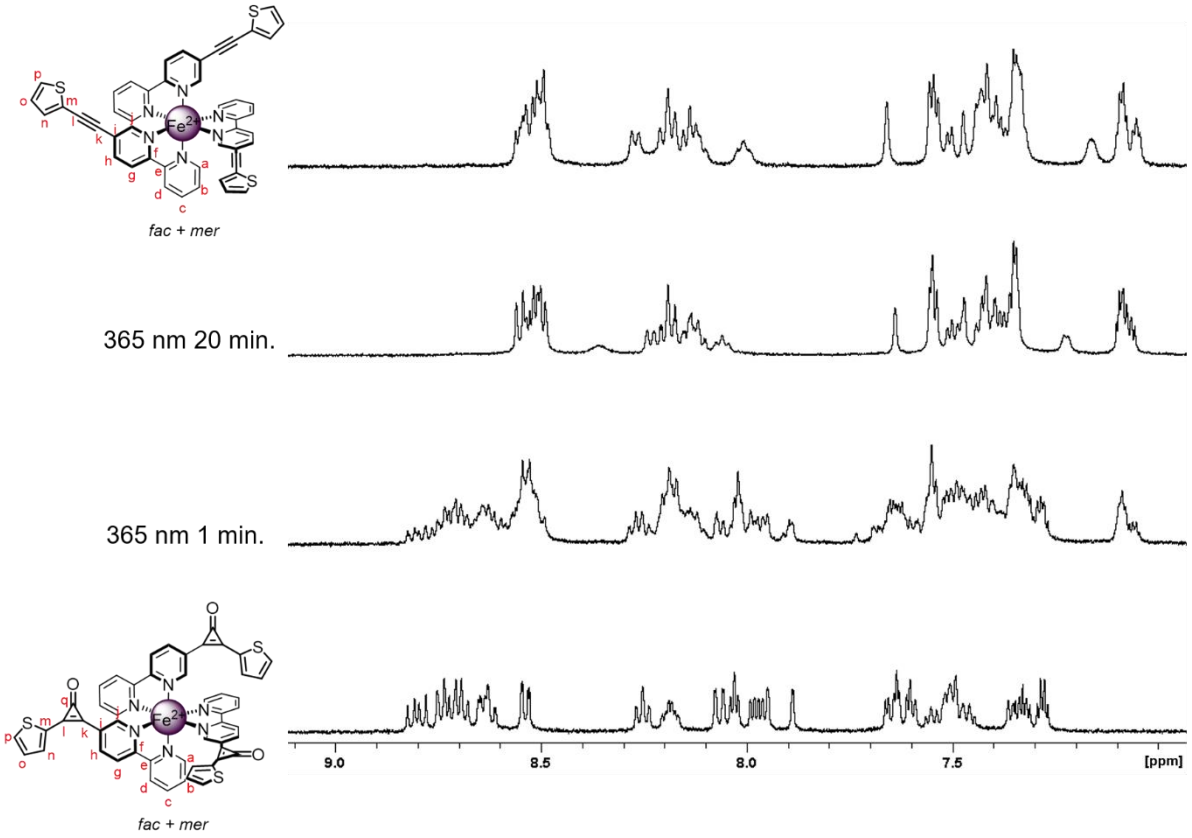


Figure S183. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Fe-CPOne-**1b** before (bottom) and after irradiation with 365 nm for 1 and 20 minutes; reference complex Fe-**2b** (top).

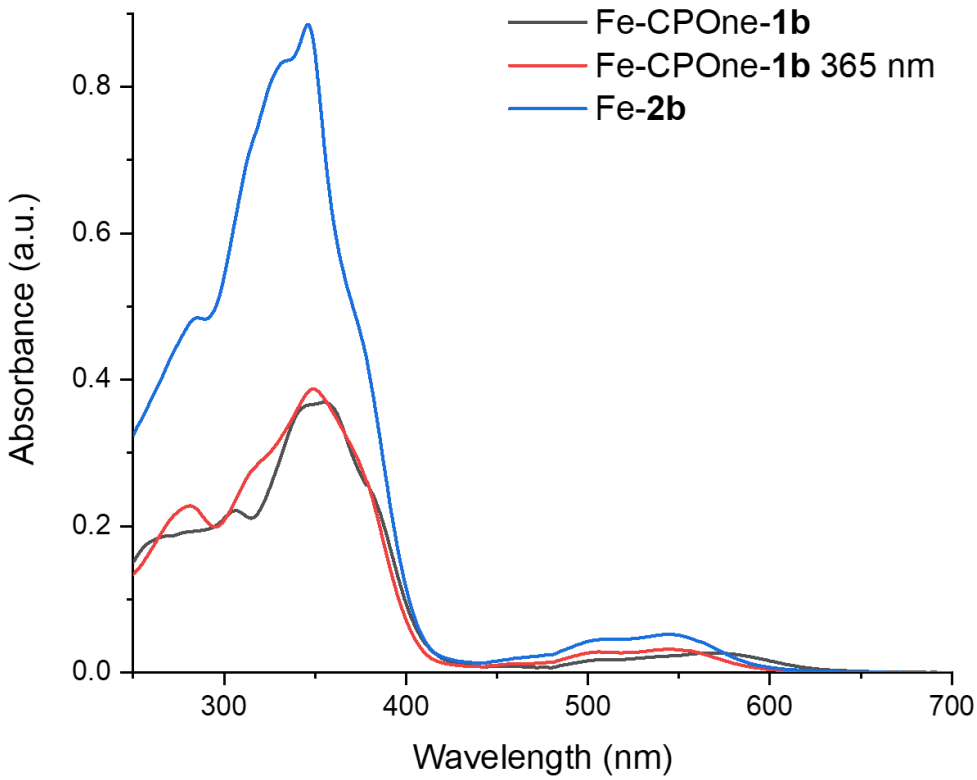


Figure S184. UV/vis spectra (CH_3CN, 298 K) of: Fe-CPOne-**1b** (1.66 µM) before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Fe-**2b** (blue, 3.89 µM).

9.5 Fe-CPOne-**1c**

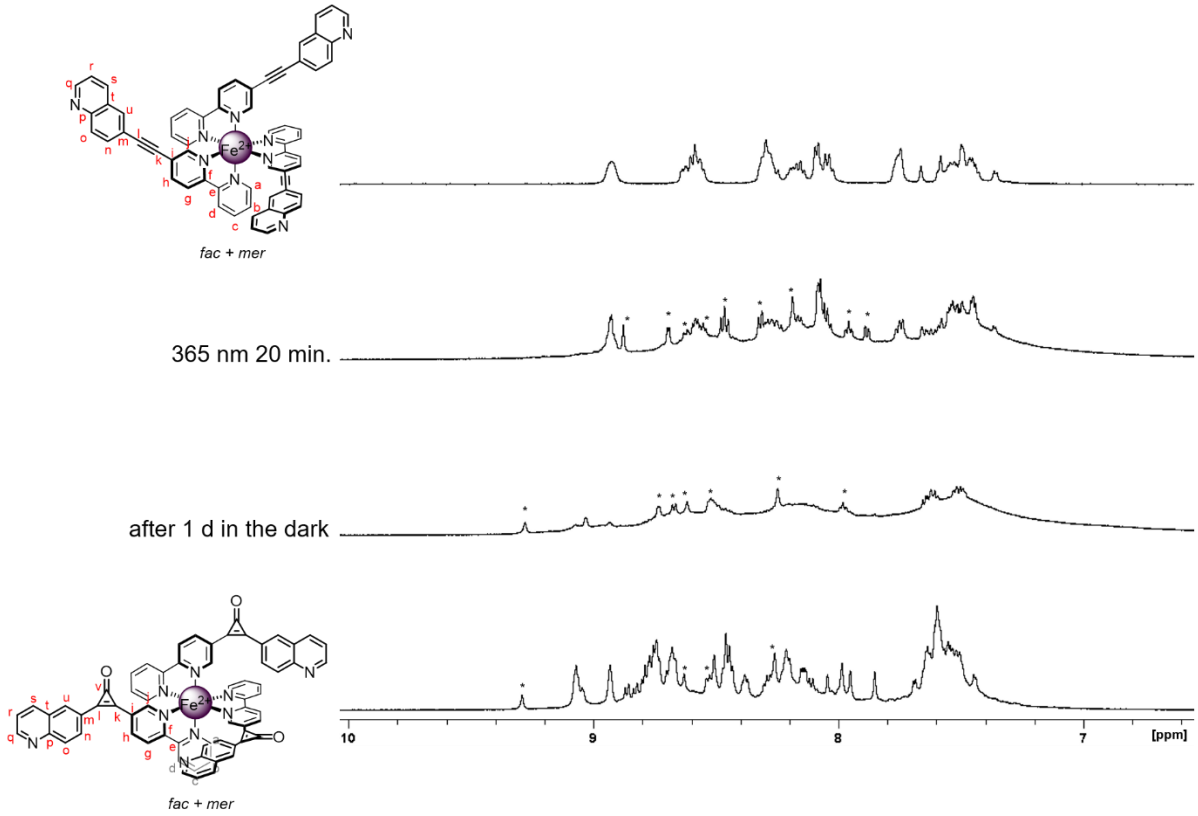


Figure S185. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Fe-CPOne-**1c** measured immediately after preparation without irradiation (bottom), after standing for 1 d in the dark before and after irradiation with 365 nm for 20 min (middle spectra); reference complex Fe-**2c** (top). *Note: Signals marked with * have been tentatively assigned as free ligand.*

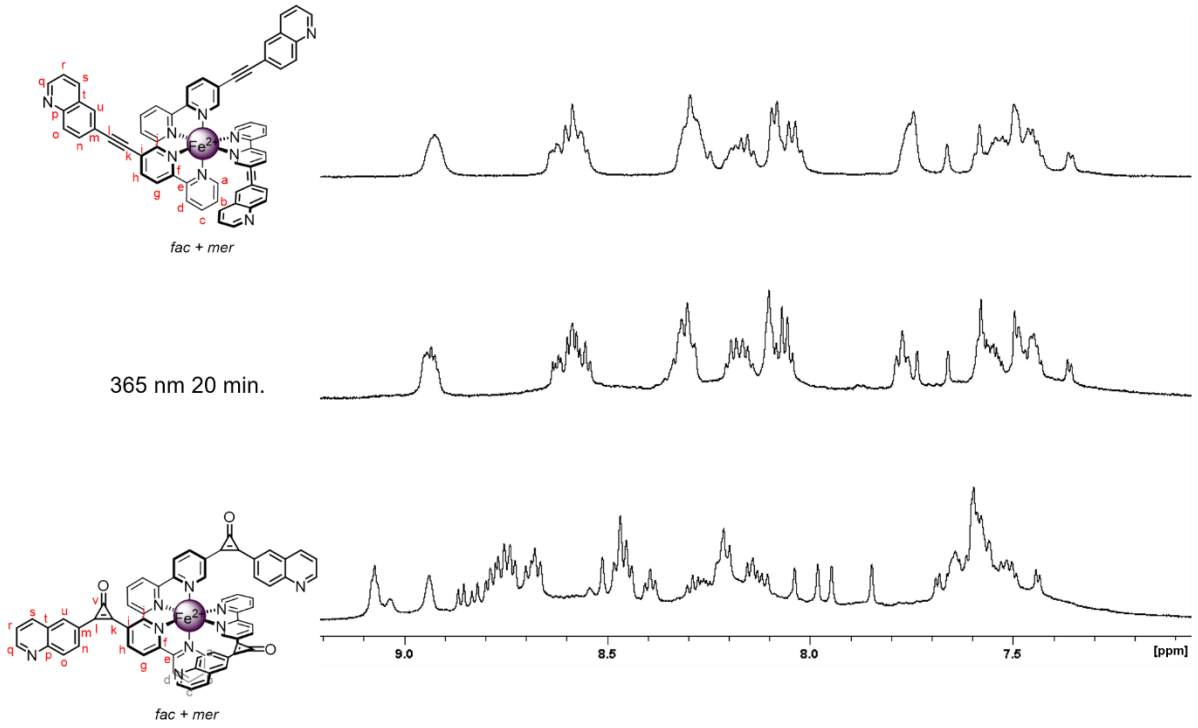


Figure S186. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Fe-CPOne-**1c** measured immediately after preparation before (bottom) and after irradiation with 365 nm for 20 min (middle); reference complex Fe-**2c** (top).

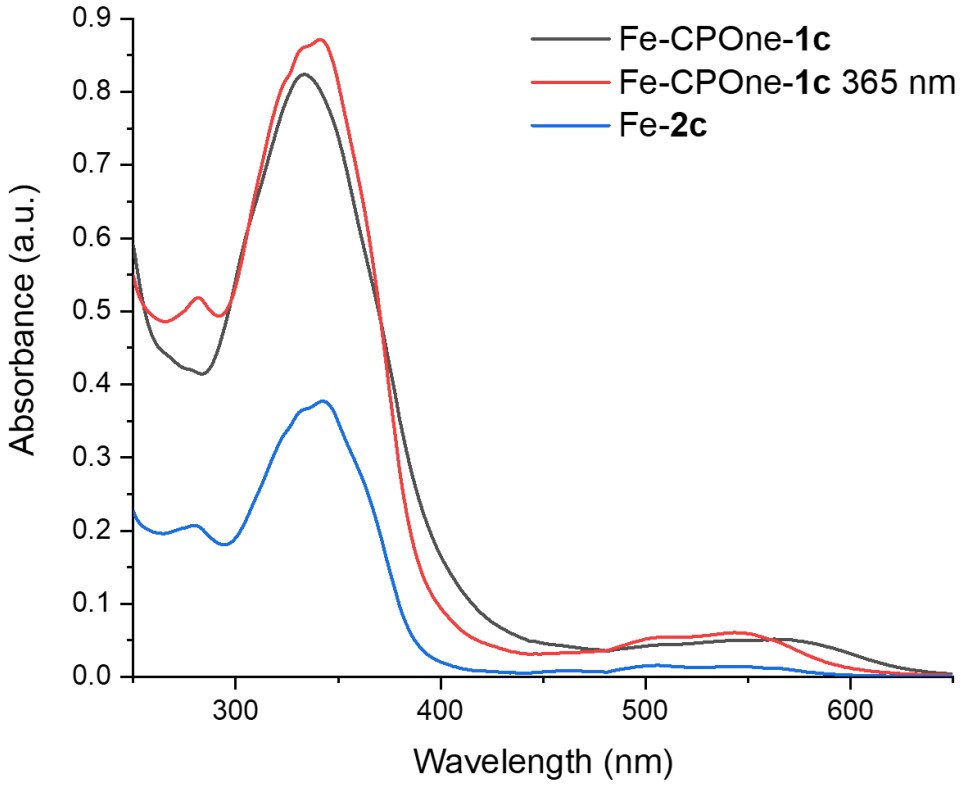


Figure S187. UV/vis spectra (CH_3CN, 298 K) of: Fe-CPOne-**1c** (7.97 μM) measured immediately after preparation before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Fe-**2c** (blue, 3.12 μM).

9.6 Co-CPOne-**1a**

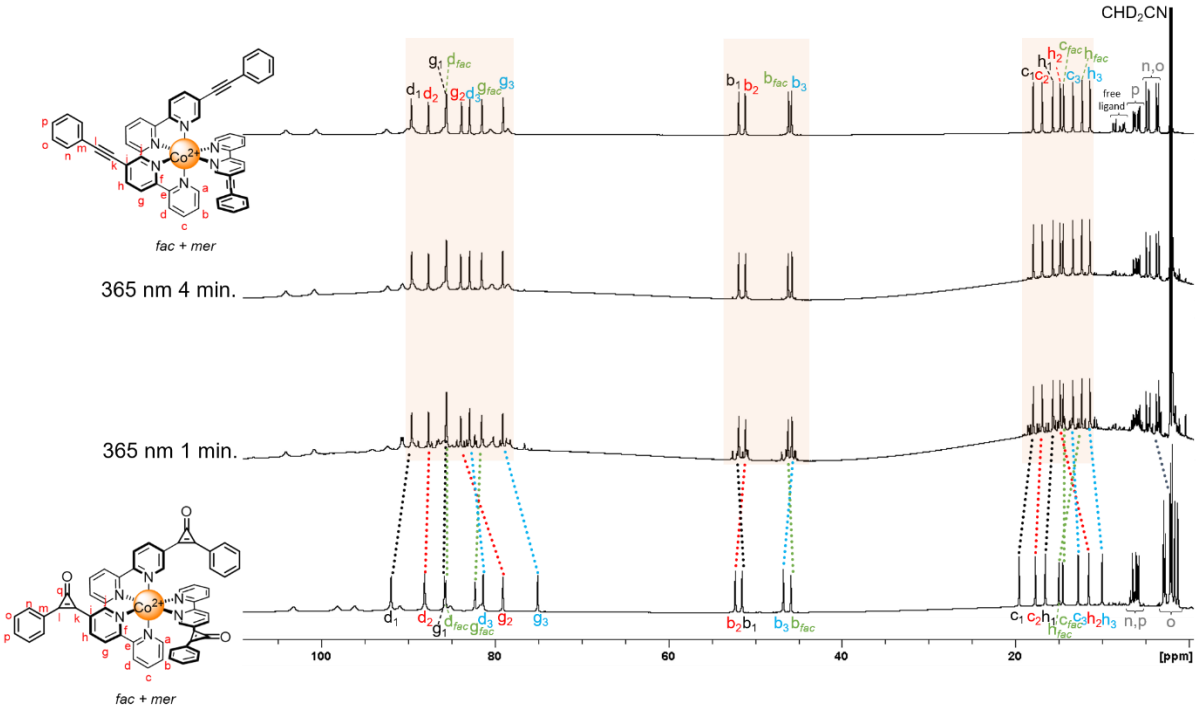


Figure S188. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Co-CPOne-**1a** before (bottom) and after irradiation 365 nm for 1 and 4 minutes; reference complex Co-**2a** (top).

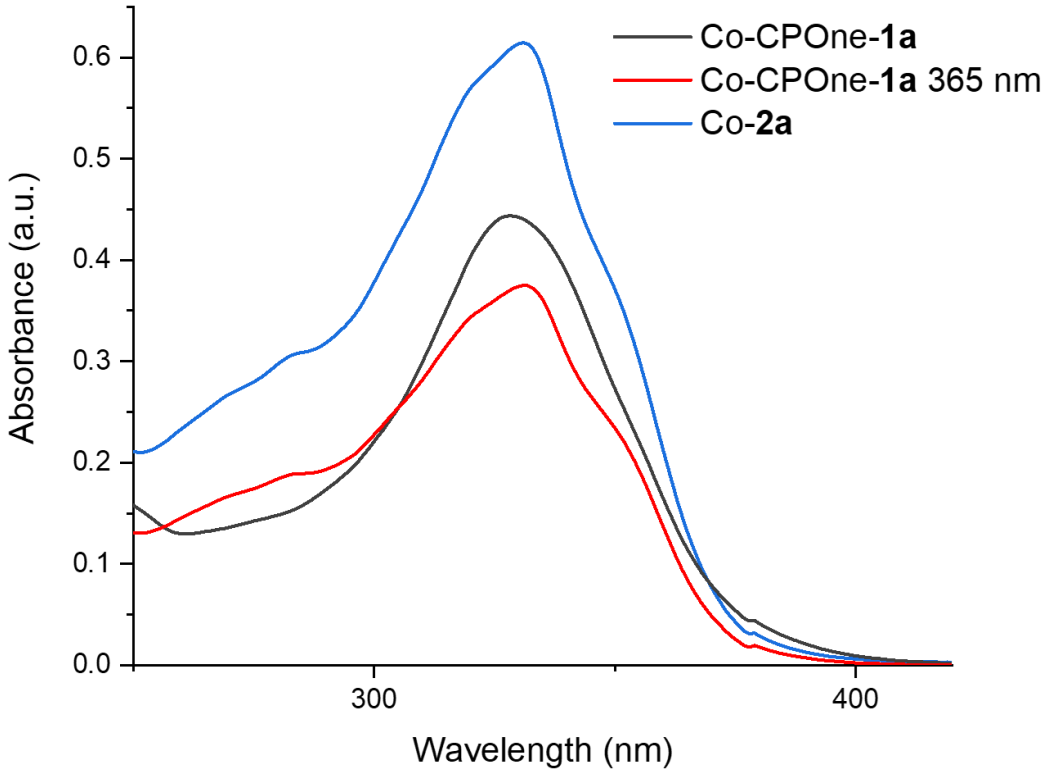


Figure S189. UV/vis spectra (CH_3CN, 298 K) of: Co-CPOne-**1a** (0.74 µM) measured immediately after preparation before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Co-**2a** (blue, 4.50 µM).

9.7 Co-CPOne-**1b**

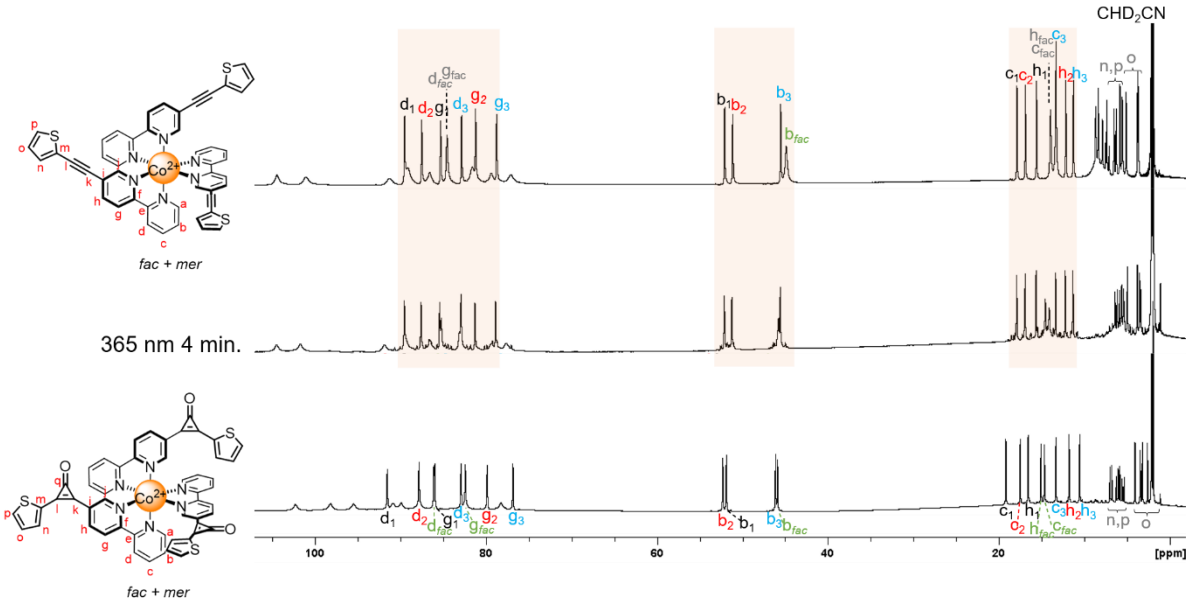


Figure S190. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Co-CPOne-**1b** before (bottom) and after irradiation 365 nm for 4 minutes (middle); reference complex Co-**2b** (top).

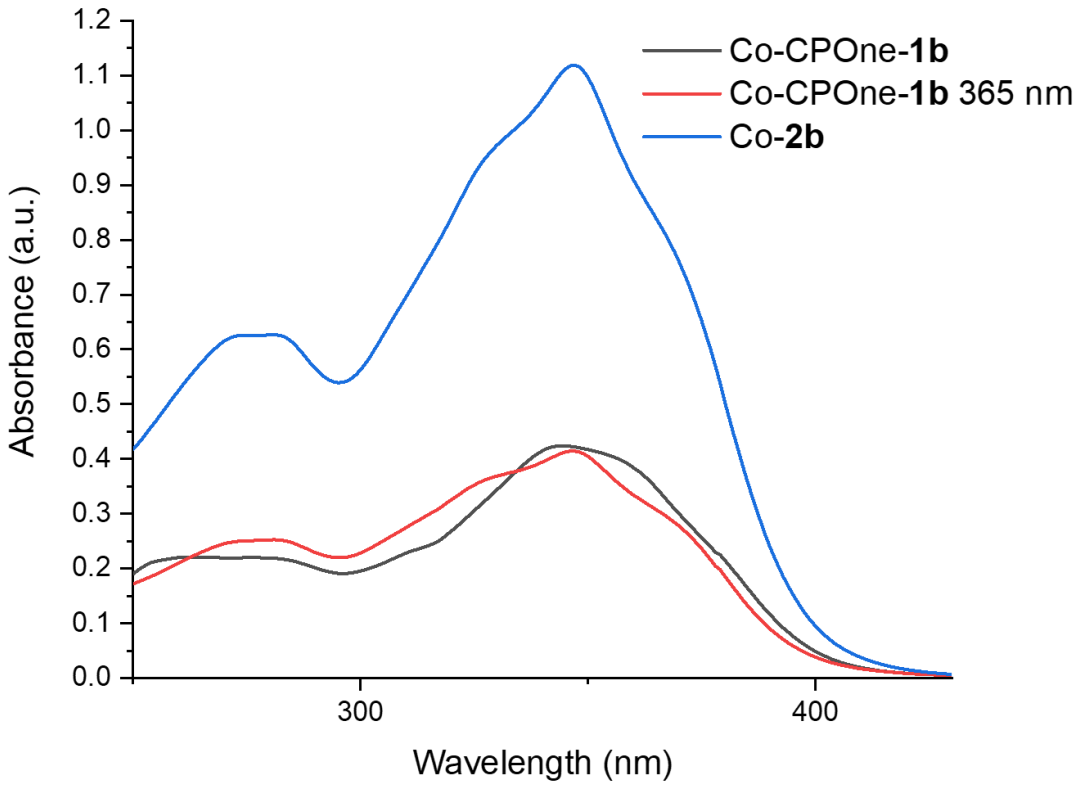


Figure S191. UV/vis spectra (CH_3CN, 298 K) of: Co-CPOne-**1b** (3.36 µM) measured immediately after preparation before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Co-**2b** (blue, 3.36 µM).

9.8 Co-CPOne-**1c**

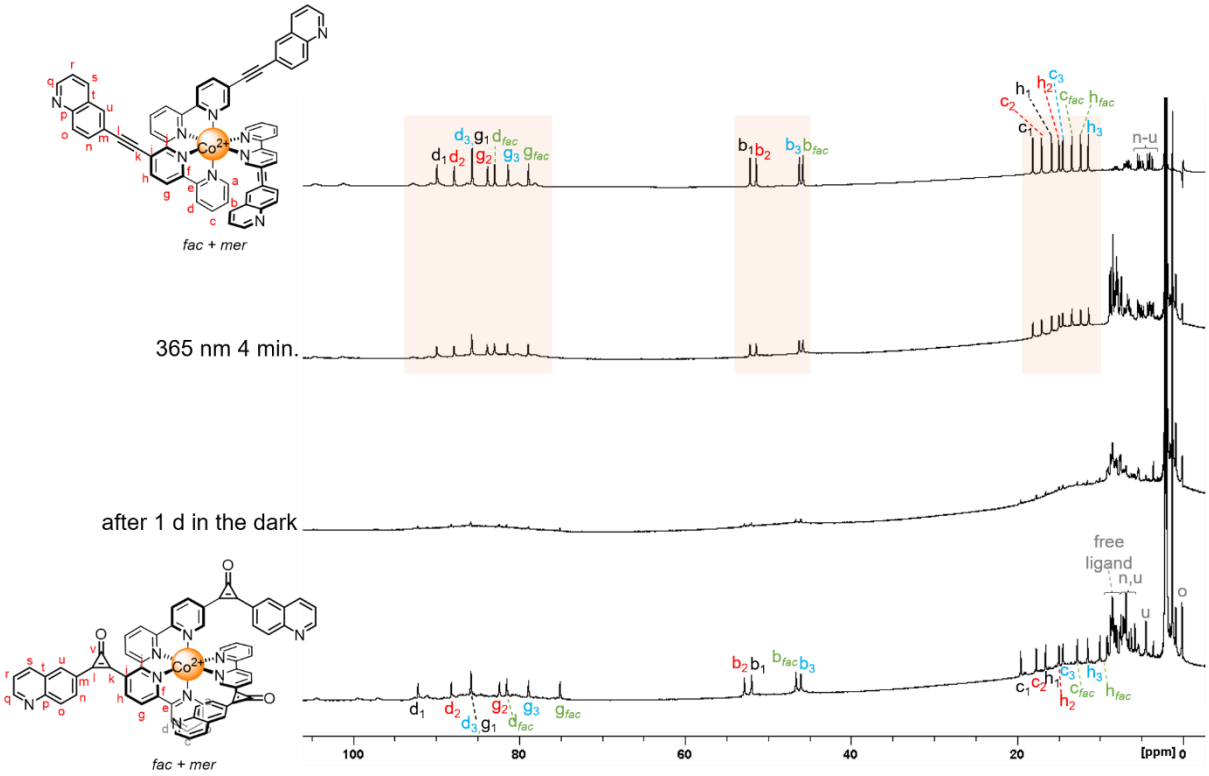


Figure S192. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Co-CPOne-**1c** measured immediately after preparation without irradiation (bottom), after standing for 1 d in the dark before and after irradiation with 365 nm for 4 min. (middle); reference complex Co-**2c** (top).

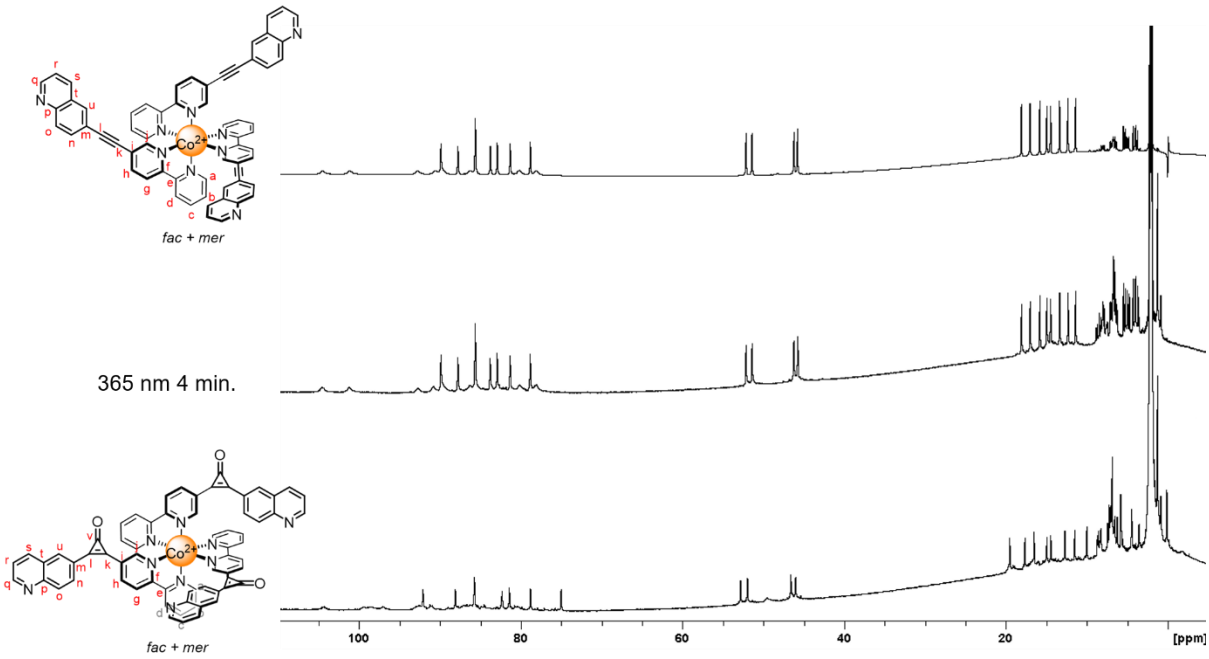


Figure S193. ^{1}H NMR spectra (500/600 MHz, CD_3CN, 298 K) of: Co-CPOne-**1c** measured immediately after preparation before (bottom) and after irradiation 365 nm for 4 min. (middle); reference complex Co-**2c** (top).

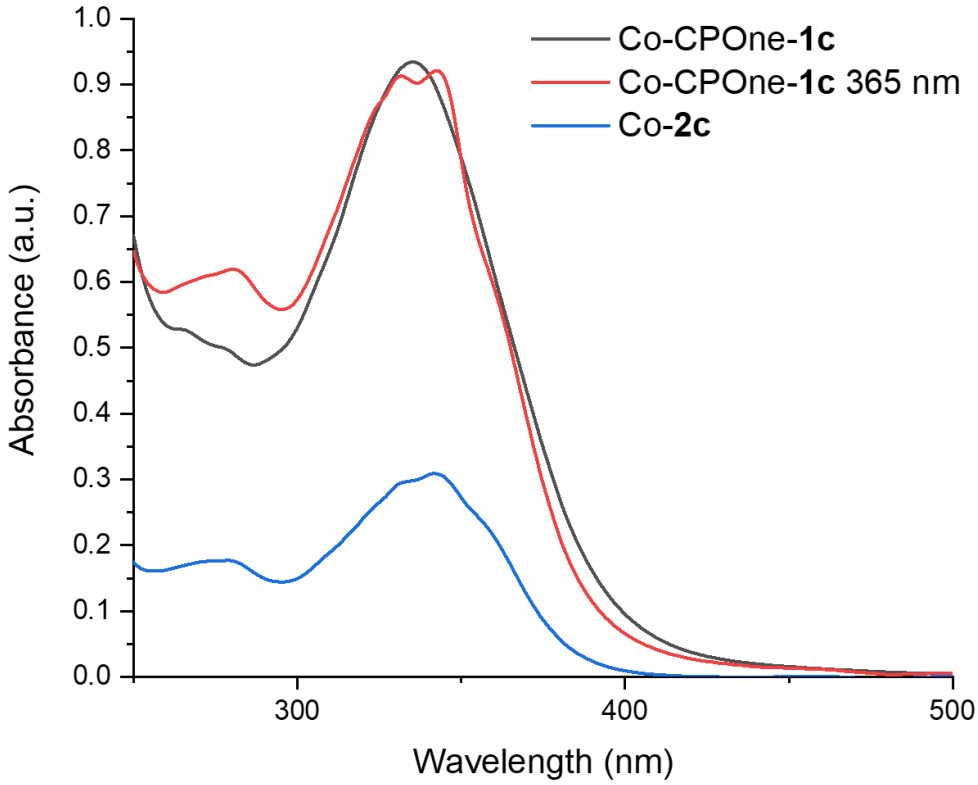


Figure S194. UV/vis spectra (CH_3CN, 298 K) of: Co-CPOne-**1c** (7.45 µM) measured immediately after preparation before (black) and after irradiation with 365 nm for 1 minute (red); reference complex Co-**2c** (blue, 2.14 µM).

10 References

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