

Bridging and Axial Carbene Binding Modes in Cobalt Corrole Complexes: Effect on Carbene Transfer

^aBradley W. Musselman and ^aNicolai Lehnert*

^aDepartment of Chemistry and Department of Biophysics, University of Michigan, 930 N. University, Ann Arbor, MI, USA 48109

Email: lehnertn@umich.edu

Supplementary Information

Table of Contents

1. General Procedures.....	S2-3
2. Proposed cyclopropanation mechanistic cycles for Fe- and Co-porphyrins.....	S4
3. TOF-MS of 2a	S5
4. NMR Spectra of 2a	S6-7
5. NMR Spectra of 1a + EDA.....	S8-16
6. TOF-MS of 1a + EDA.....	S17
7. ¹ H NMR spectrum of 2b	S18
8. ¹ H NMR spectrum of 2b + EDA.....	S19
9. UV-Vis Spectra of 1a and 2a with EDA.....	S20-21
10. ¹ H-NMR of Cyclopropanation Reactions.....	S22-S28
11. EPR of 1b and 1b + EDA.....	S29
12. Cyclic Voltammetry of 2a	S30
13. Structures of N-bridging carbene modes.....	S31
14. Spin Density Plots.....	S32
15. DFT optimized structures of [Co ^{III} (tpc)(CHCO ₂ Me)]	S33
16. DFT optimized coordinates.....	S34-S43
17. References.....	S44

General Procedures

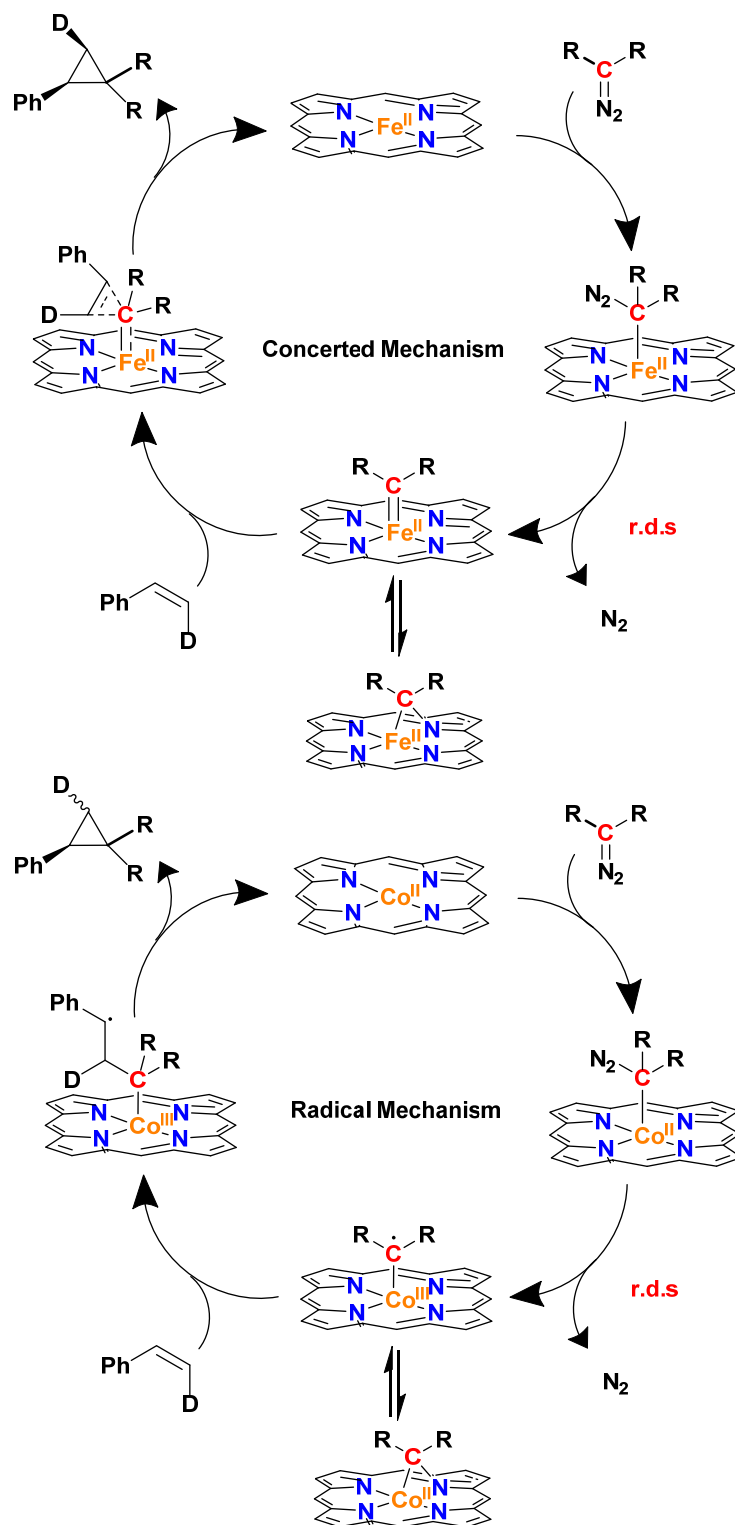
Materials. All chemicals and reagents were purchased from commercial suppliers (Sigma Aldrich, Fisher Scientific, Acros, Frontier Scientific, and Cambridge Isotope Laboratories) and used without further purification unless otherwise noted. Reactions involving inert atmospheres were performed under an Ar atmosphere using standard Schlenk techniques or in a N₂-filled dry box. Toluene, dichloromethane (DCM), 2-methyltetrahydrofuran (2-MeTHF), acetonitrile (CH₃CN), 1,2-dichloroethane (DCE), dimethylsulfoxide (DMSO), and tetrahydrofuran (THF) were dried over CaH₂, distilled, and degassed via repeated freeze-pump-thaw cycles. Dry, degassed solvents were stored over 4Å molecular sieves, except CH₃CN, which was stored over 3Å molecular sieves. H₃tpc,¹ H₃tppc,^{2, 3} and [Co(tpc)(PPh₃)]⁴ were synthesized according to reported procedures. 2-¹³C-glycine (99%) was purchased from Cambridge Isotope Laboratories. 2-¹³C-ethyl diazoacetate was synthesized according to a published procedure.⁵

Instrumentation. ¹H-NMR spectra were measured on either a Varian MR400 (operating at 400 MHz), a Varian Inova 500 (operating at 500 MHz), or a Varian VNMR 500 (operating at 500 MHz). All NMR measurements were referenced with either TMS or residual, internal solvent peaks. UV-Visible spectra were recorded on an Analytic Jena Specord S600 UV-Vis spectrometer. Cyclic voltammograms (CVs) were obtained on a CH instruments CHI660C electrochemical workstation using a three-component cell, consisting of a glassy carbon working electrode, a platinum auxiliary electrode, and a Ag wire pseudoreference electrode. CVs were recorded in 0.1 M tetrabutylammonium hexafluorophosphate in CH₂Cl₂. Potentials were corrected to the Fc⁺/Fc standard by independently measuring the ferrocenium/ferrocene couple under the same conditions (Fc⁺/Fc = 624 mV vs. SHE). Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker X-band EMX spectrometer equipped with an Oxford Instruments liquid helium cryostat. EPR spectra were obtained on frozen solutions (~5 mM) in 2-MeTHF.

General Procedure for Cyclopropanation Reactions. Reactions were performed on a 0.25 mmol scale unless otherwise specified. To a flame-dried Schlenk tube was added catalyst (5 μmol), styrene (30 μL), EDA (30 μL) and dry toluene (5 mL) in a nitrogen-filled dry box. The reaction vessels were then brought outside of the

drybox and kept under a nitrogen atmosphere on a Schlenk line. The mixtures were stirred for up to 16 hours at 80 °C unless otherwise specified. The crude product was dried *in vacuo* and 1,3,5-trimethoxybenzene was added as an internal standard as specified below (~7-10mg). Yields were determined *in situ* from the crude product mixture via ¹H-NMR spectroscopy in CDCl₃ using the integrations of the multiplet signals at δ 2.53 ppm (trans isomer) and 2.09 ppm (cis isomer).⁶

Synthesis of [Co^{III}(tppc)(P(OEt)₃)] (2a). In a N₂-filled dry box, to a flame-dried flask was added H₃tppc (101 mg, 83.4 μmol) and Co(OAc)₂·4H₂O (102 mg, 412 μmol, ~5 equiv) which was dissolved in 15mL of DMSO giving a dark green solution. The vessel was removed from the dry box and opened to air and P(OEt)₃ (144 mg, 867 μmol, ~10 equiv) was added. The solution was heated to 100 °C for 1 hr, resulting in a dark red solution. The solution was cooled to rt and the product was precipitated over water (~50mL) to give a crude, dark red powder. The crude solid was washed with water (3x50mL) and redissolved in DCM. The organic layer was dried over Na₂SO₄, filtered, and dried *in vacuo*. The product was purified by column chromatography on silica gel (1:1 Hexanes/DCM) and eluted as a red band. Yield: 98.9 mg (82%). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 8.58 (d, 2H), 8.27 (m, 6H), 7.88 (m, 13H), 7.78 (d, 1H), 7.75 (d, 2H), 7.66 (d, 1H), 7.53 (m, 8H), 7.43 (m, 3H), 6.89 (m, 6H), 6.73 (m, 3H), 6.13 (m, 5H), 6.01 (t, 2H), 5.81 (m, 4H), 5.75 (t, 3H), 0.26 (p, 6H), -0.55 (t, 9H). ¹³C-NMR (CDCl₃, 176 MHz) δ (ppm) 207.08, 146.73, 146.53, 143.76, 143.74, 143.67, 143.45, 143.38, 143.36, 143.13, 143.12, 142.81, 142.44, 142.16, 141.88, 140.81, 140.61, 140.32, 139.96, 137.60, 137.00, 136.08, 130.22, 129.59, 129.07, 129.05, 128.58, 128.44, 128.14, 127.75, 127.70, 127.67, 127.54, 127.42, 127.37, 127.28, 126.36, 126.29, 126.00, 125.91, 125.70, 125.47, 124.89, 124.55, 117.84, 117.82, 117.53, 114.99, 59.14, 31.08, 15.67. ³¹P-NMR (CDCl₃, 400 MHz) δ (ppm): 265.40. UV-Vis (DCM) λ_{max} (nm): 423 (58.3 mM⁻¹ cm⁻¹), 571 (17.6 mM⁻¹ cm⁻¹). TOF-MS [C₉₇H₇₄CoN₄O₃P]; calcd. 1433.4864 m/z [M⁺], found 1433.4865 m/z.



Scheme S1. Proposed catalytic cycles for cyclopropanation showcased by Fe- and Co-porphyrins.⁷

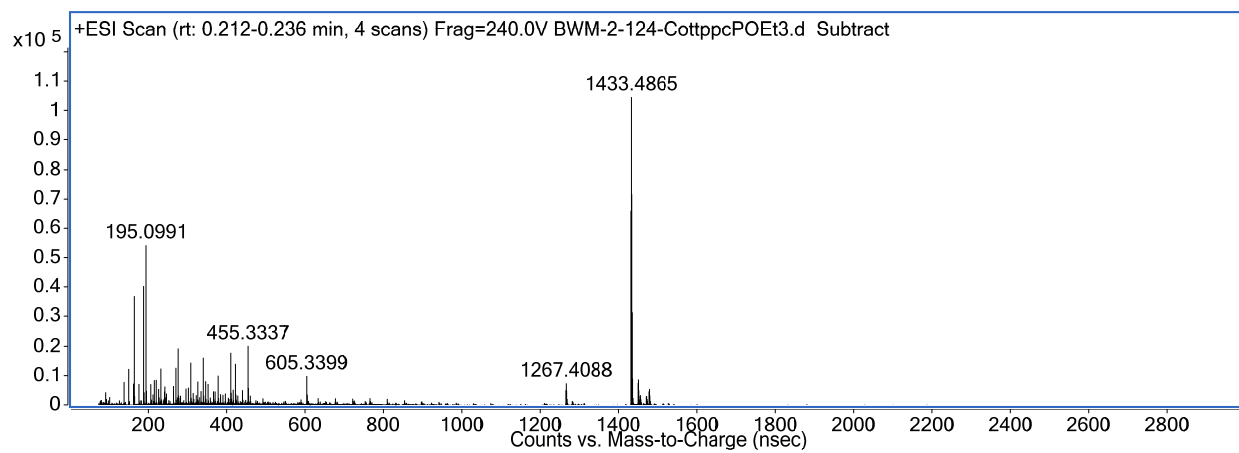


Figure S1. TOF-MS of $[\text{Co}^{\text{III}}(\text{ttppc})(\text{P}(\text{OEt})_3)]$ (**2a**). Calcd for $[\text{C}_{97}\text{H}_{74}\text{CoN}_4\text{O}_3\text{P}]$, 1433.4864 m/z $[\text{M}^+]$; found 1433.4865 m/z.

NMR spectra of $[\text{Co}^{\text{III}}(\text{tppc})(\text{P}(\text{OEt})_3)]$ (2a)

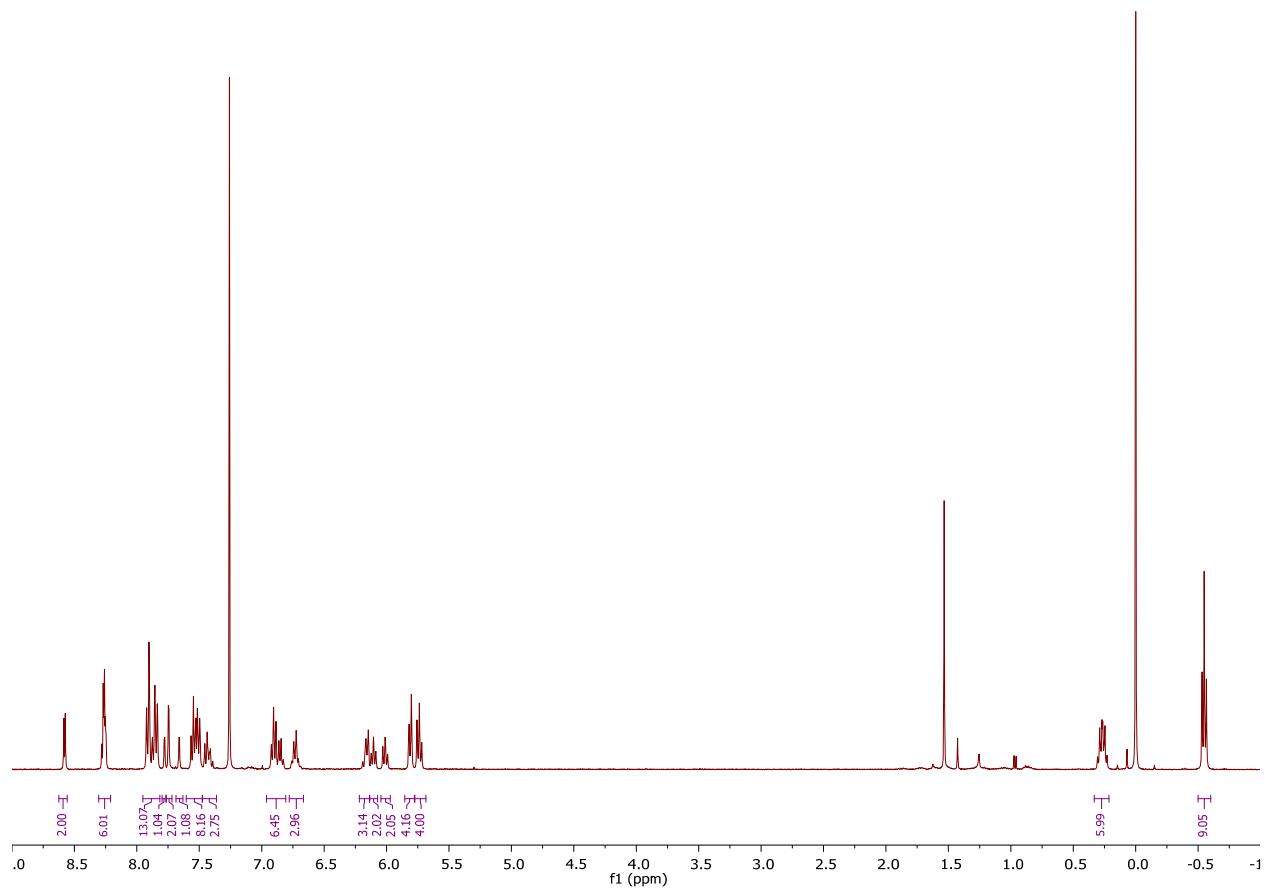


Figure S2. $^1\text{H-NMR}$ spectrum of $[\text{Co}^{\text{III}}(\text{tppc})(\text{P}(\text{OEt})_3)]$ in CDCl_3 at room temperature.

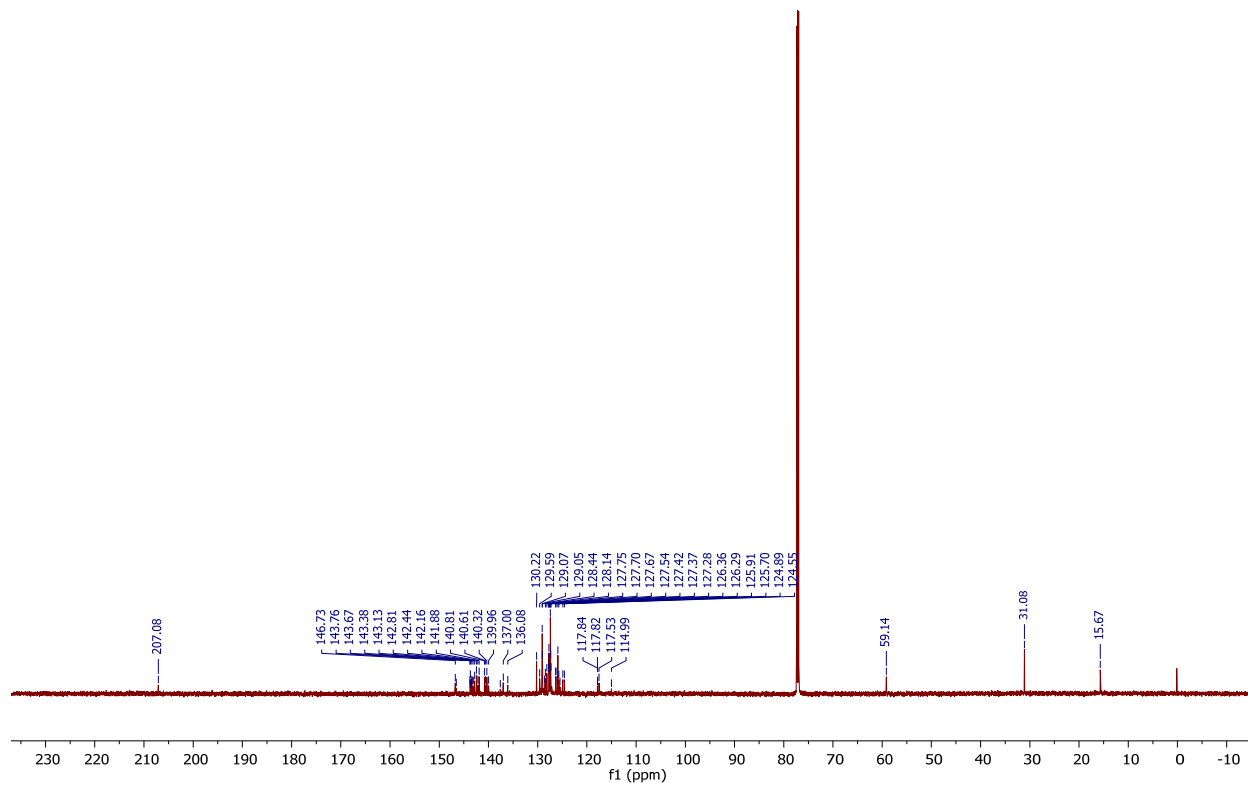


Figure S3. ^{13}C -NMR spectrum of $[\text{Co}^{\text{III}}(\text{tppc})(\text{P}(\text{OEt})_3)]$ in CDCl_3 at room temperature.

NMR spectra of 1a + EDA

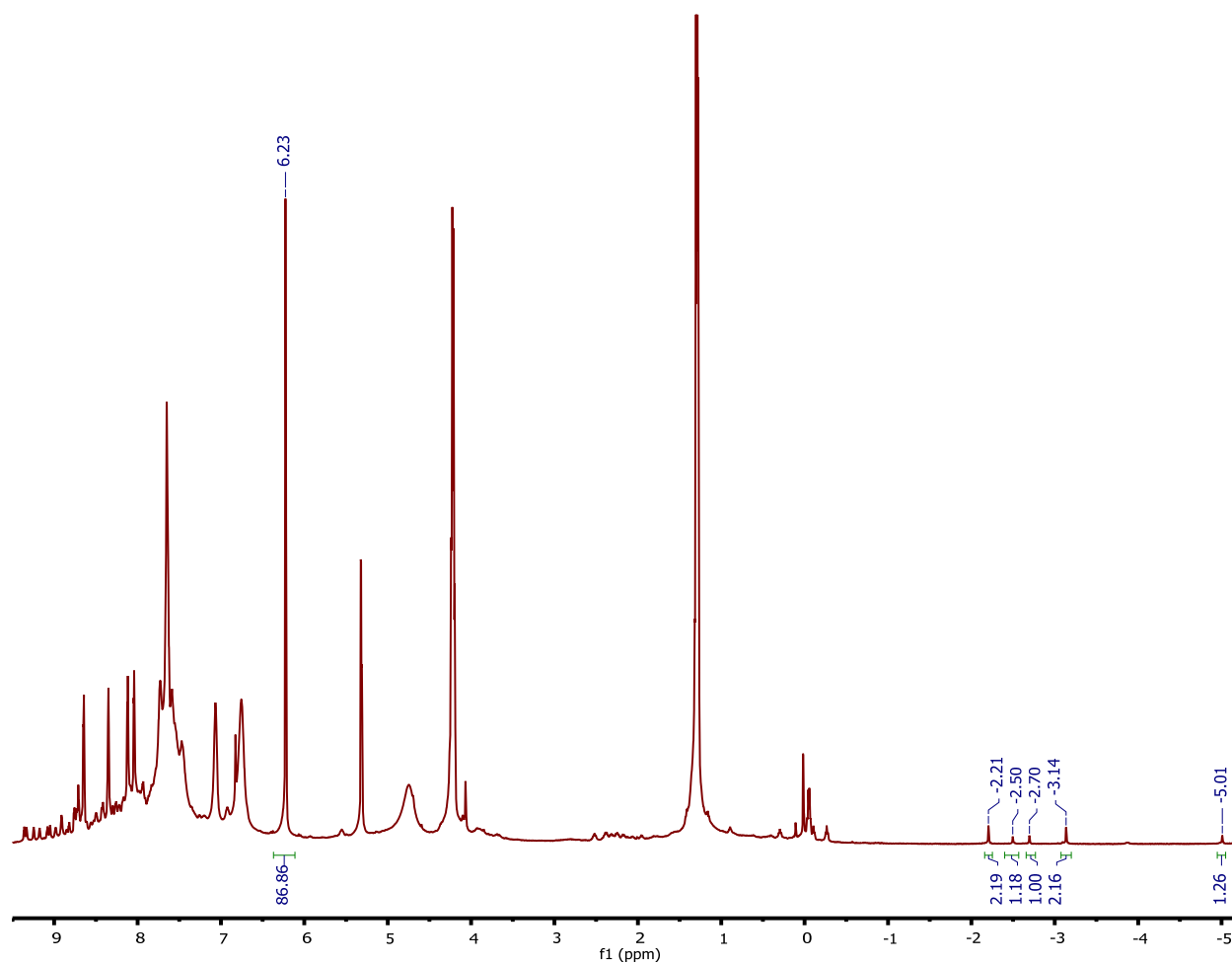


Figure S4. ¹H-NMR spectrum of [Co^{III}(tpc)(PPh₃)] (**1a**) + EDA (5 equiv) in CD₂Cl₂ at room temperature. The peak at 6.23 ppm corresponds to the diethyl maleate byproduct from carbene dimerization.

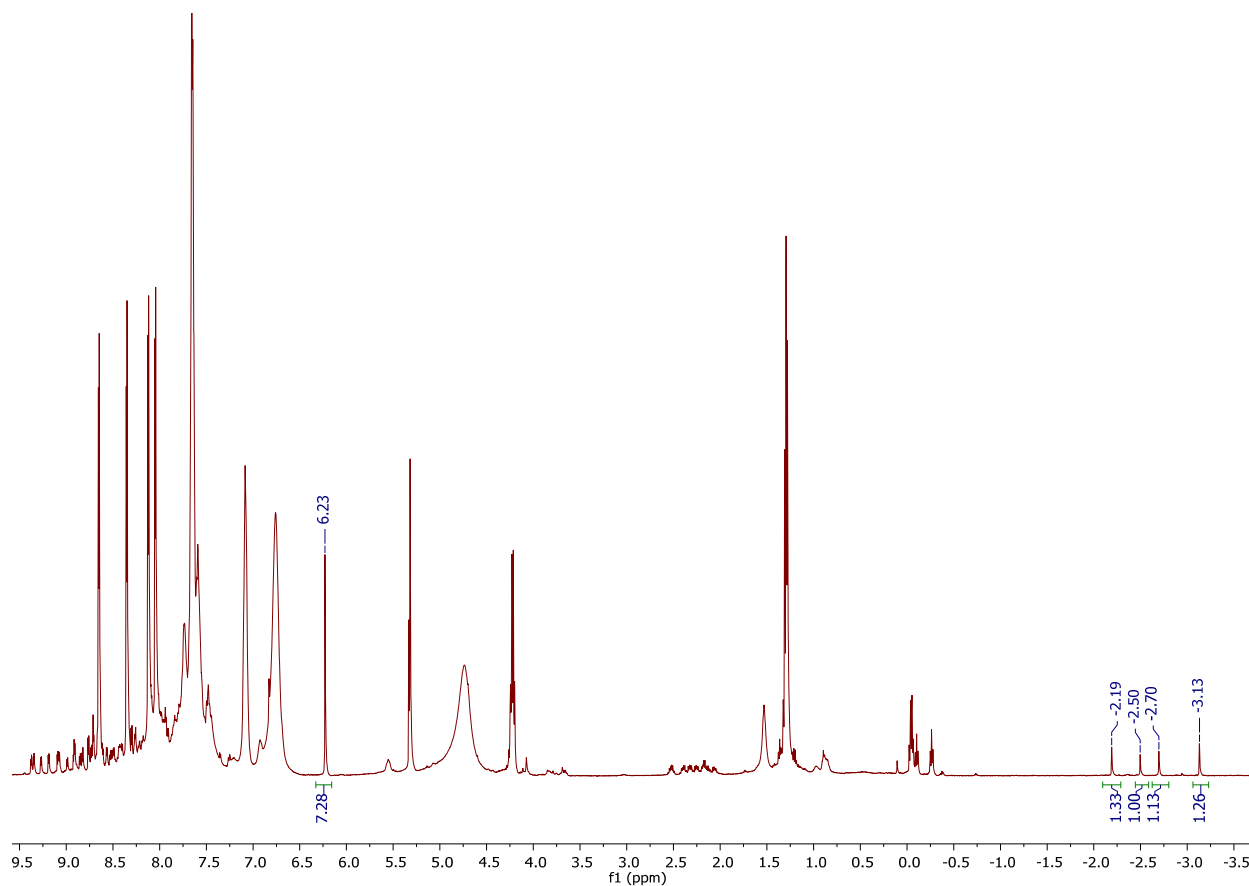


Figure S5. ¹H-NMR spectrum of [Co^{III}(tpc)(PPh₃)] (**1a**) + EDA (1 equiv) in CD₂Cl₂ at room temperature.

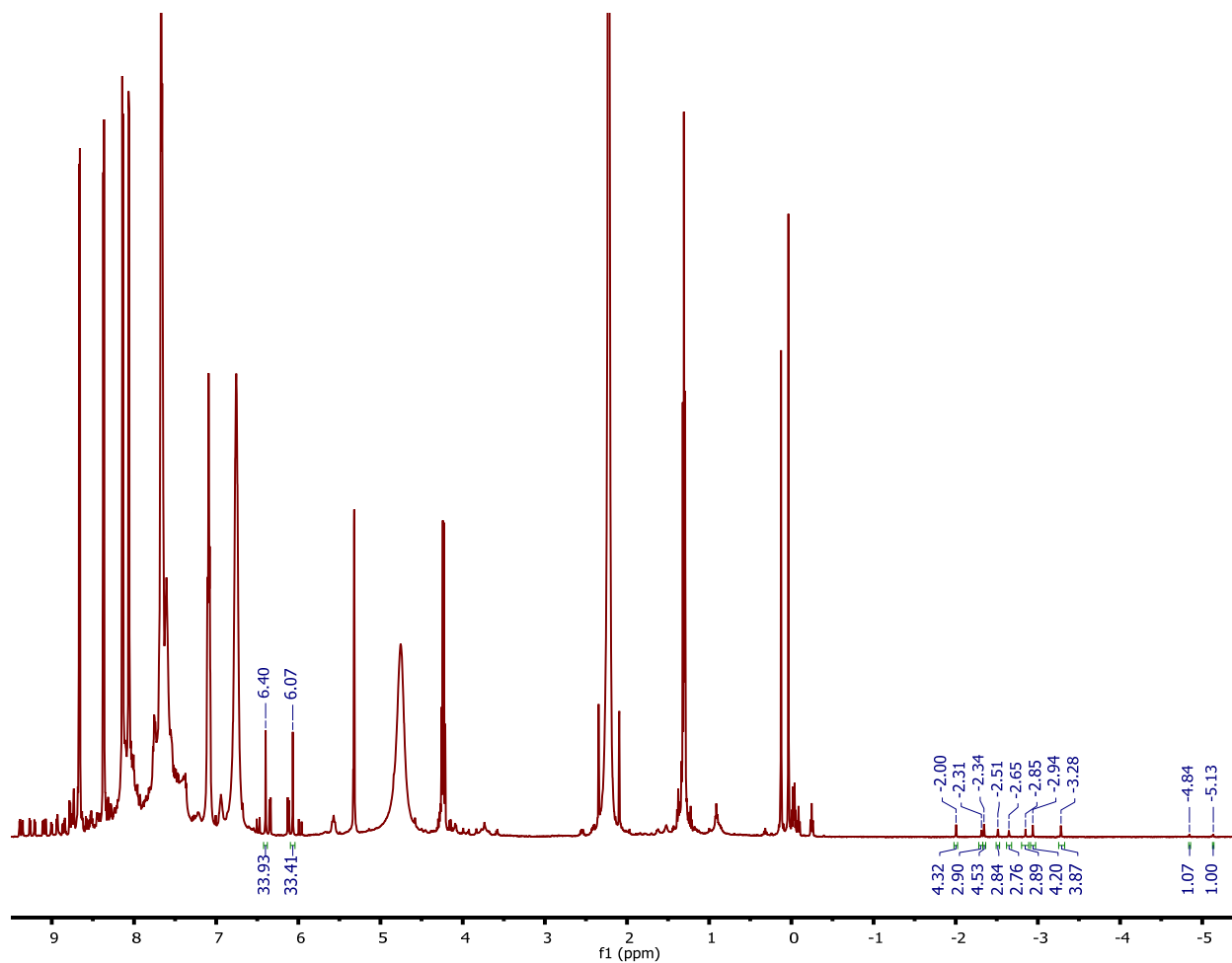


Figure S6. $^1\text{H-NMR}$ spectrum of $[\text{Co}^{\text{III}}(\text{tpc})(\text{PPh}_3)]$ (**1a**) + $2\text{-}^{13}\text{C-EDA}$ (5 equiv) in CD_2Cl_2 at room temperature. The peak at 2.22 ppm corresponds to hexamethylbenzene which was used as an internal standard.

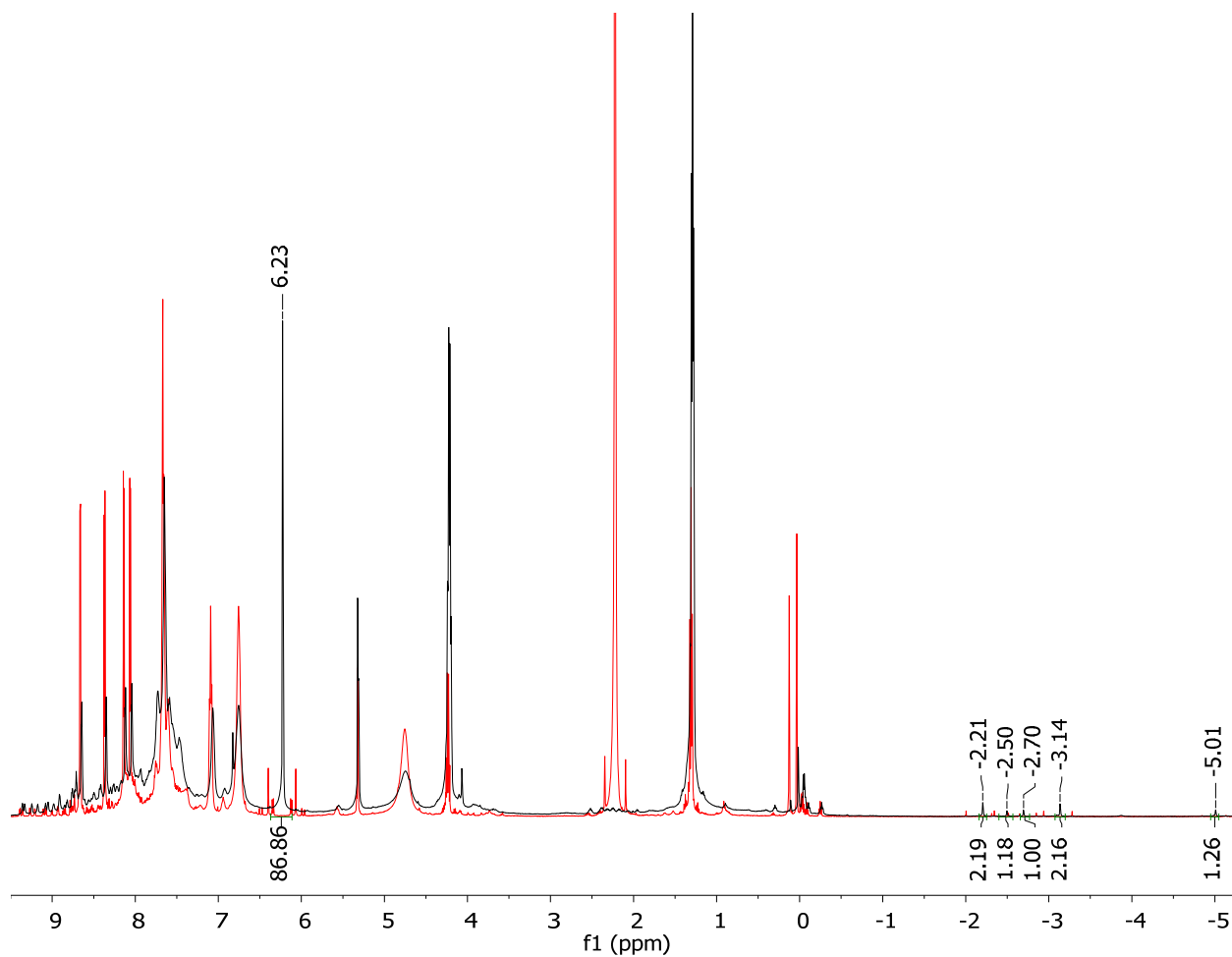


Figure S7. Overlay of the ¹H-NMR spectra of **1a** + EDA (black) and **1a** + 2-¹³C-EDA (red) in CD₂Cl₂ at room temperature. The peak at 6.23 ppm corresponds to the EDA dimerization byproduct, diethyl maleate. The peak at 2.22 ppm in the red trace corresponds to hexamethylbenzene which was used as an internal standard.



Figure S8. ^1H - ^{13}C HSQC spectrum of **1a** + 2- ^{13}C -EDA (5 equiv) in CD_2Cl_2 at room temperature.

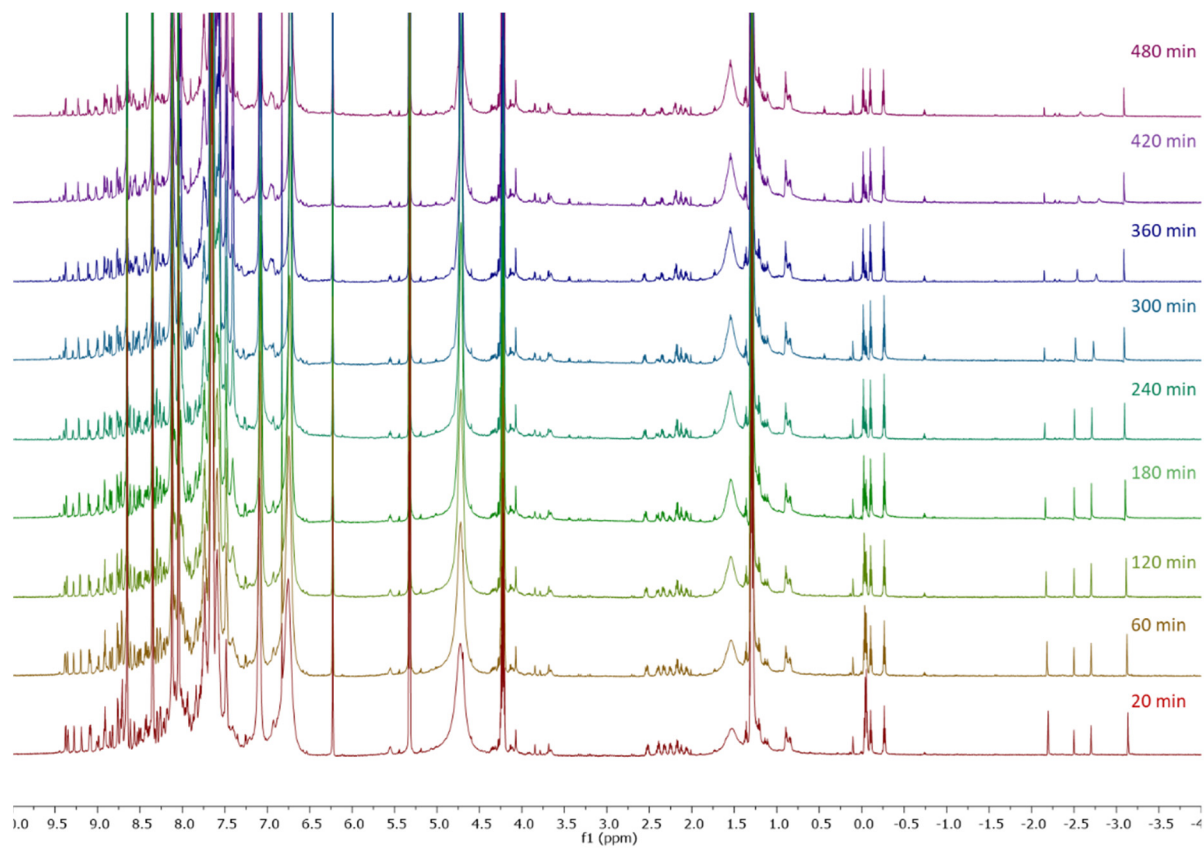


Figure S9a. Time-course ¹H-NMR spectra of the *in situ* reaction of **1a** with EDA (1.2 equiv) in CD₂Cl₂ at room temperature at various time-points.

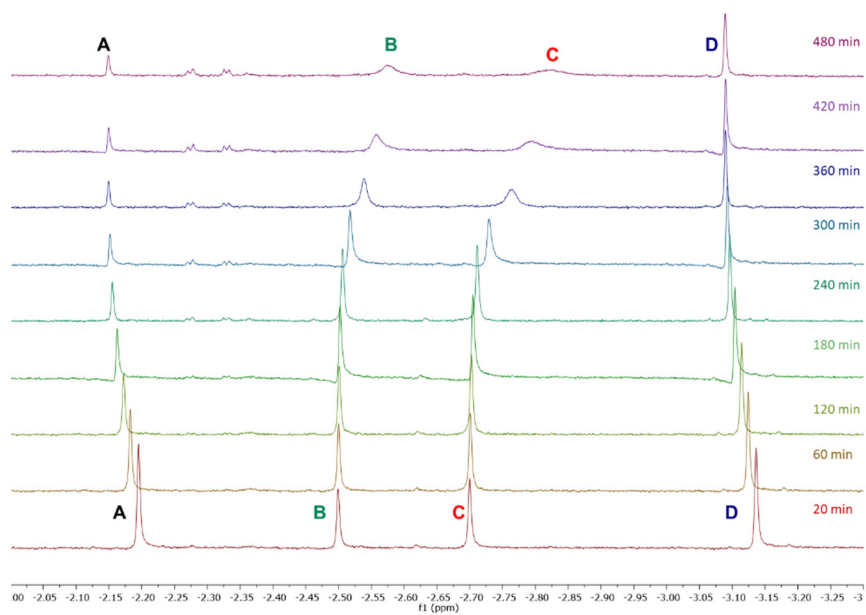


Figure S9b. Time-course ^1H -NMR spectra of the *in situ* reaction of **1a** with EDA (1.2 equiv) in CD_2Cl_2 at room temperature at various time-points, zoomed into the $\delta = -2$ to -3.3 ppm window to show the evolution of the four carbenoid proton signals, assigned to the N-bridging carbene complex of $[\text{Co}^{\text{III}}(\text{tpc})(\text{CHCO}_2\text{Et})]$, over time.

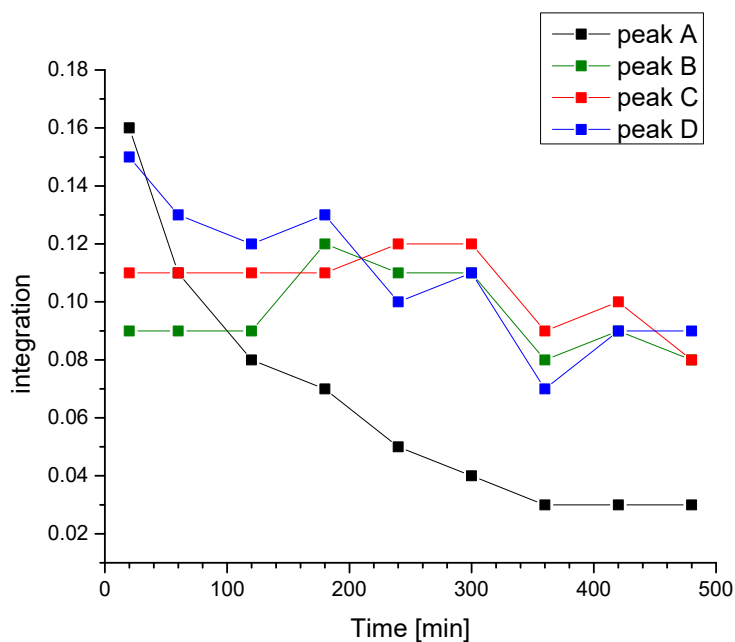


Figure S9c. Plot of the relative integrations of the carbenoid protons vs time. Integrations were normalized to the residual solvent peak (see Figure S9b).

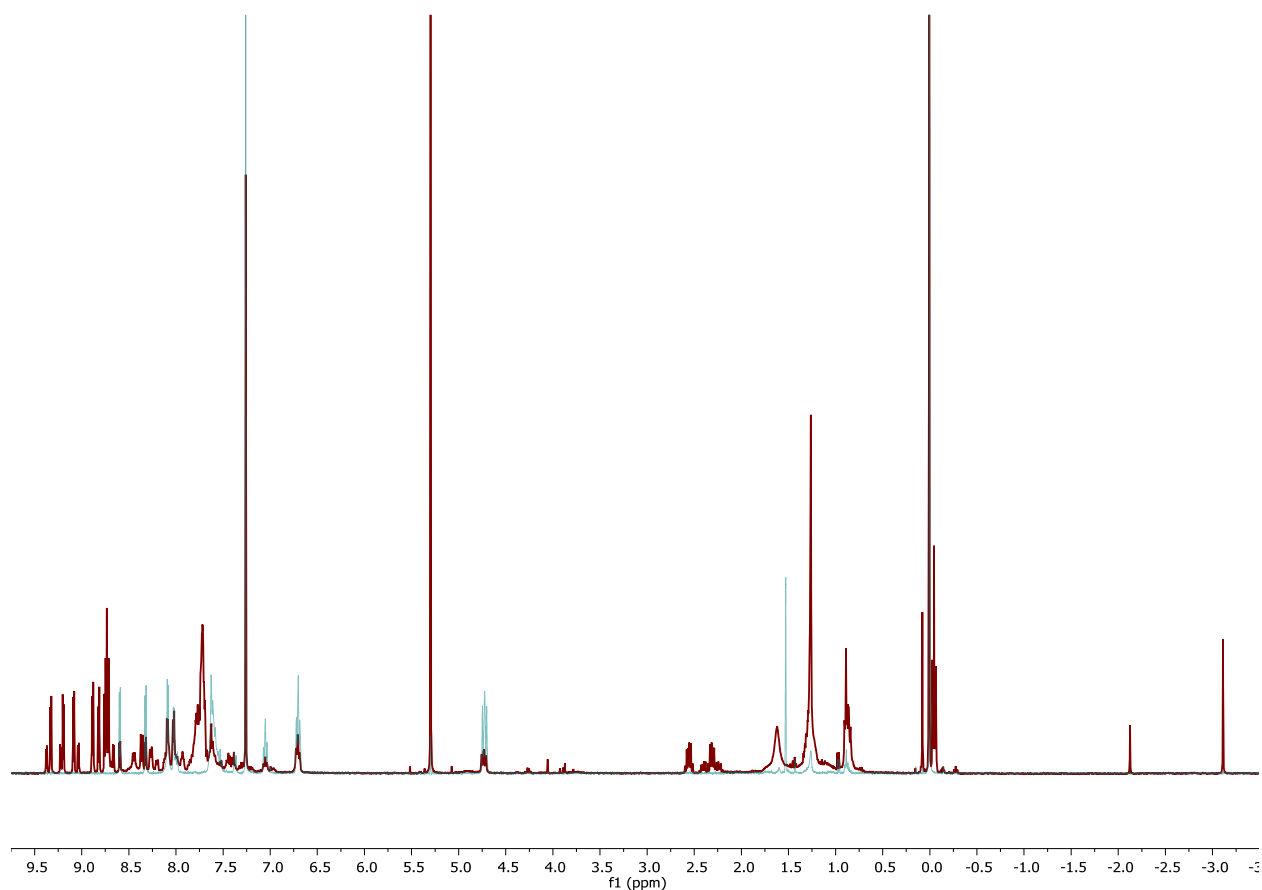


Figure S10a. ^1H -NMR spectrum of **1a** + EDA (2 equiv) after separation via column chromatography (silica, 1:1 DCM/Hexanes). The spectrum was collected in CDCl_3 and referenced to the residual solvent peak. The spectrum in red corresponds to the product of **1a** + EDA and the spectrum in blue corresponds to **1a**. The former spectrum contains a mixture of 2 diastereomers of $[\text{Co}^{\text{III}}(\text{tpc})(\text{CHCO}_2\text{Et})]$ and **1a**.

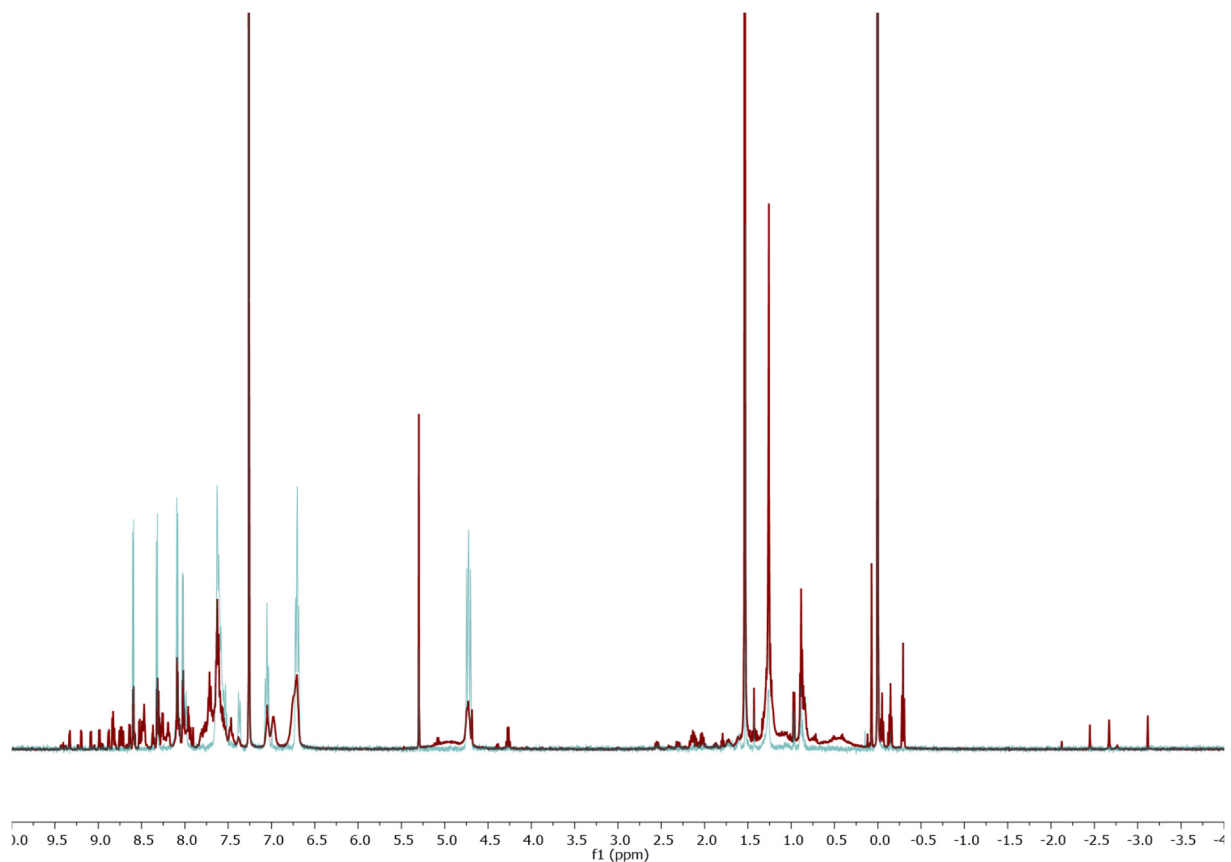


Figure S10b. ^1H -NMR spectrum of **1a** + EDA (2 equiv) after separation via column chromatography (silica, 1:1 DCM/Hexanes). The spectrum was collected in CDCl_3 and referenced to the residual solvent peak. The spectrum in red corresponds to the product of **1a** + EDA and the spectrum in blue corresponds to **1a**. The former spectrum contains a mixture of the four diastereomers of $[\text{Co}^{\text{III}}(\text{tpc})(\text{CHCO}_2\text{Et})]$ and **1a**.

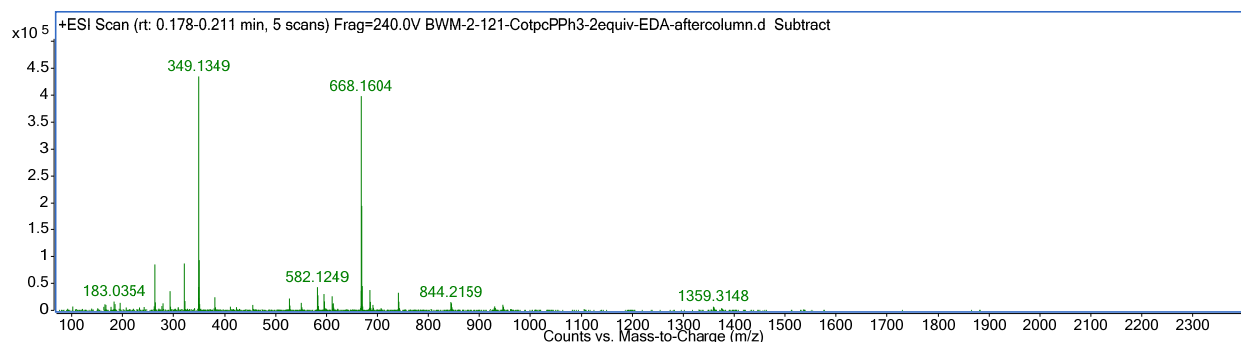


Figure 10c. TOF-MS of the product of the reaction of **1a** + EDA (2 equiv) after separation by column chromatography on silica (1:1 DCM/Hexanes; see Figure S10a). Calcd for $[\text{C}_{41}\text{H}_{29}\text{CoN}_4\text{O}_2]$ 668.1623 m/z $[\text{M}^+]$; found 668.1604 m/z.

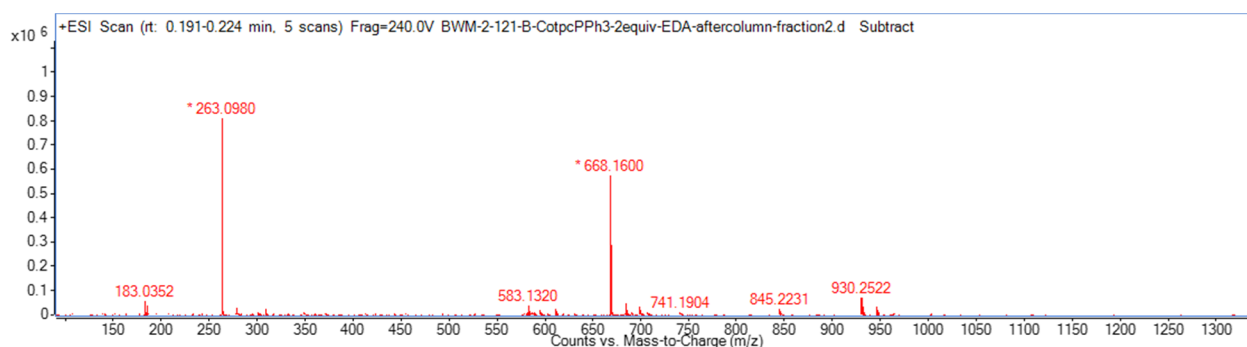


Figure 10d. TOF-MS of the product of the reaction of **1a** + EDA (2 equiv) after separation by column chromatography on silica (1:1 DCM/Hexanes; see Figure S10b). The spectrum contains a mixture of two species $[\text{Co}^{\text{III}}(\text{tpc})(\text{CHCO}_2\text{Et})]$ and $[\text{Co}^{\text{III}}(\text{tpc})(\text{PPh}_3)(\text{CHCO}_2\text{Et})]$. Calcd for $[\text{C}_{41}\text{H}_{29}\text{CoN}_4\text{O}_2]$ 668.1623 m/z $[\text{M}^+]$; found 668.1604 m/z. Calcd for $[\text{C}_{59}\text{H}_{44}\text{CoN}_4\text{O}_2\text{P}]$ 930.2534 m/z $[\text{M}^+]$; found 930.2522 m/z.

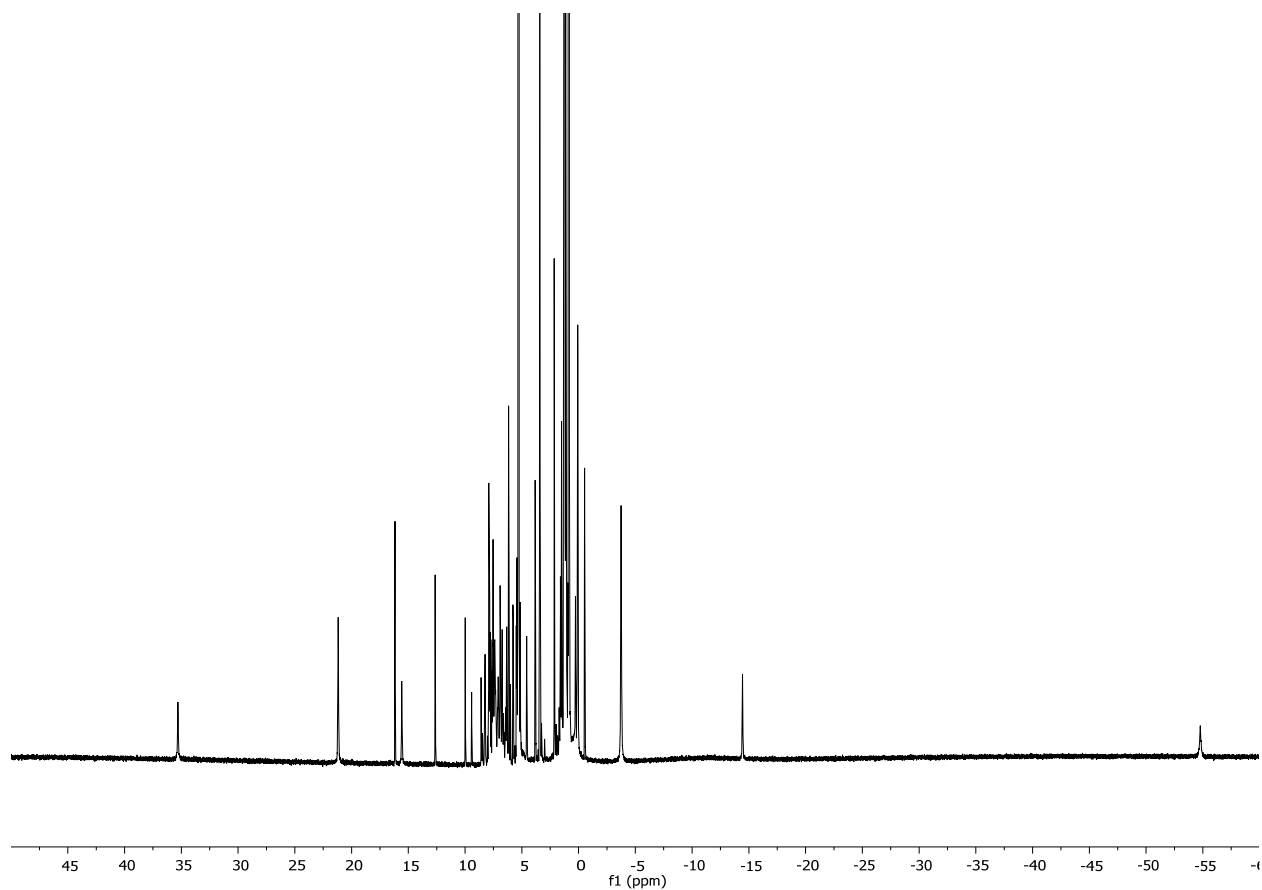


Figure S11. ¹H-NMR spectrum of **2b**, [CoCp₂][Co^{II}(tppc)], in CD₂Cl₂ at room temperature. The sample was prepared in a N₂-filled dry box and the sample was sealed with a screw cap NMR tube for the measurement.

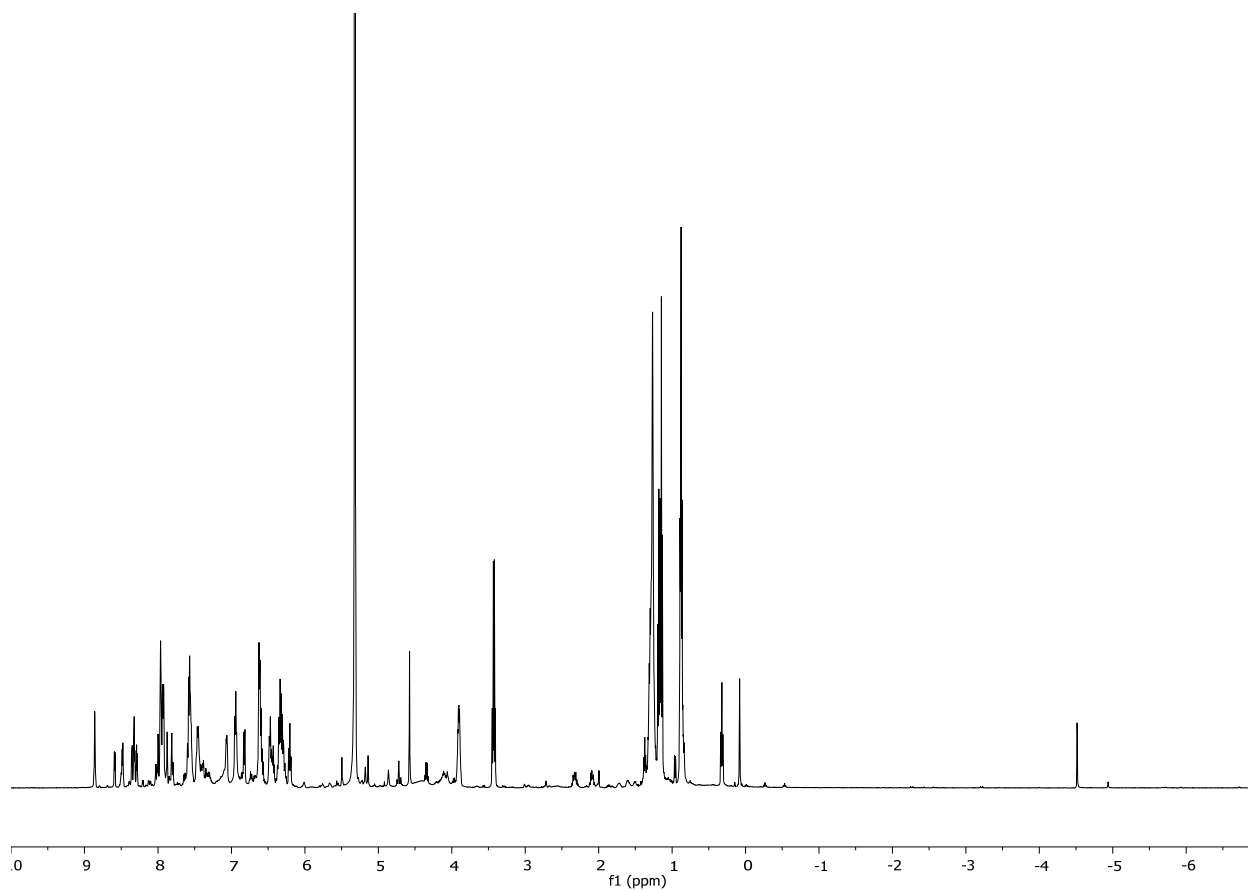


Figure S12. ^1H -NMR spectrum of the *in situ* reaction of **2b** with EDA (2 equiv) in CD_2Cl_2 at room temperature. The sample was prepared in a N_2 -filled dry box and the sample was sealed with a screw cap NMR tube for the measurement.

UV-Vis Spectra of 1a and 2a with EDA

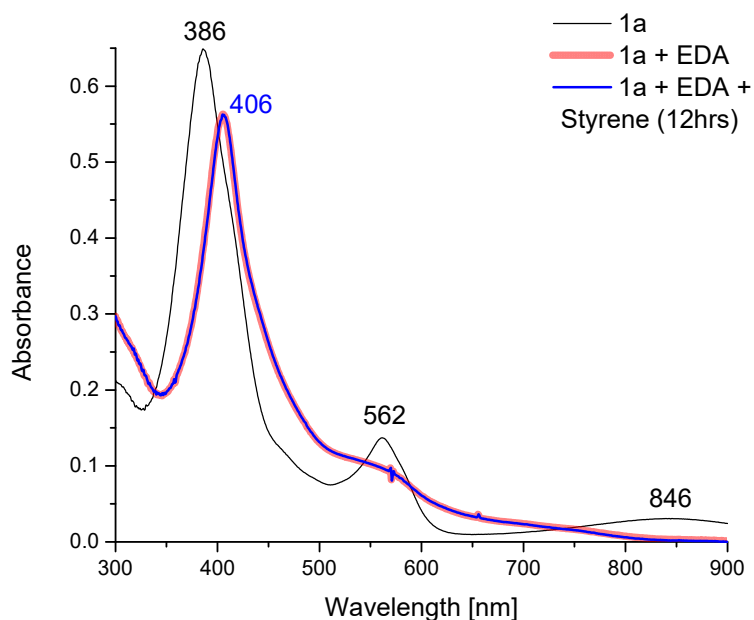


Figure S13a. UV-Vis spectra of **1a** (black) and **1a** + EDA (1 equiv; red) in CH_2Cl_2 at room temperature. After incubation with EDA for 5 minutes, styrene (5 equiv) was added and a UV-vis spectrum was collected after 12 hours (blue, overlays with red).

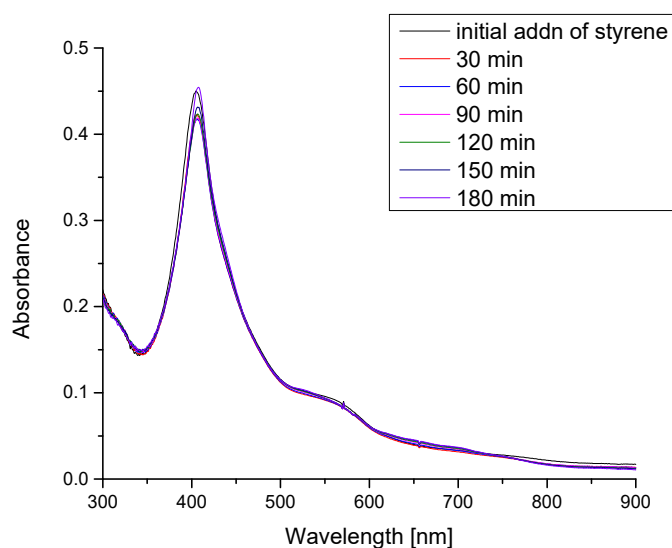


Figure S13b. Time-course UV-Vis spectra of **1a** + EDA (1 equiv), following the addition of styrene (5 equiv) in CH_2Cl_2 at room temperature. Spectra were collected every 30 min for 3 hours.

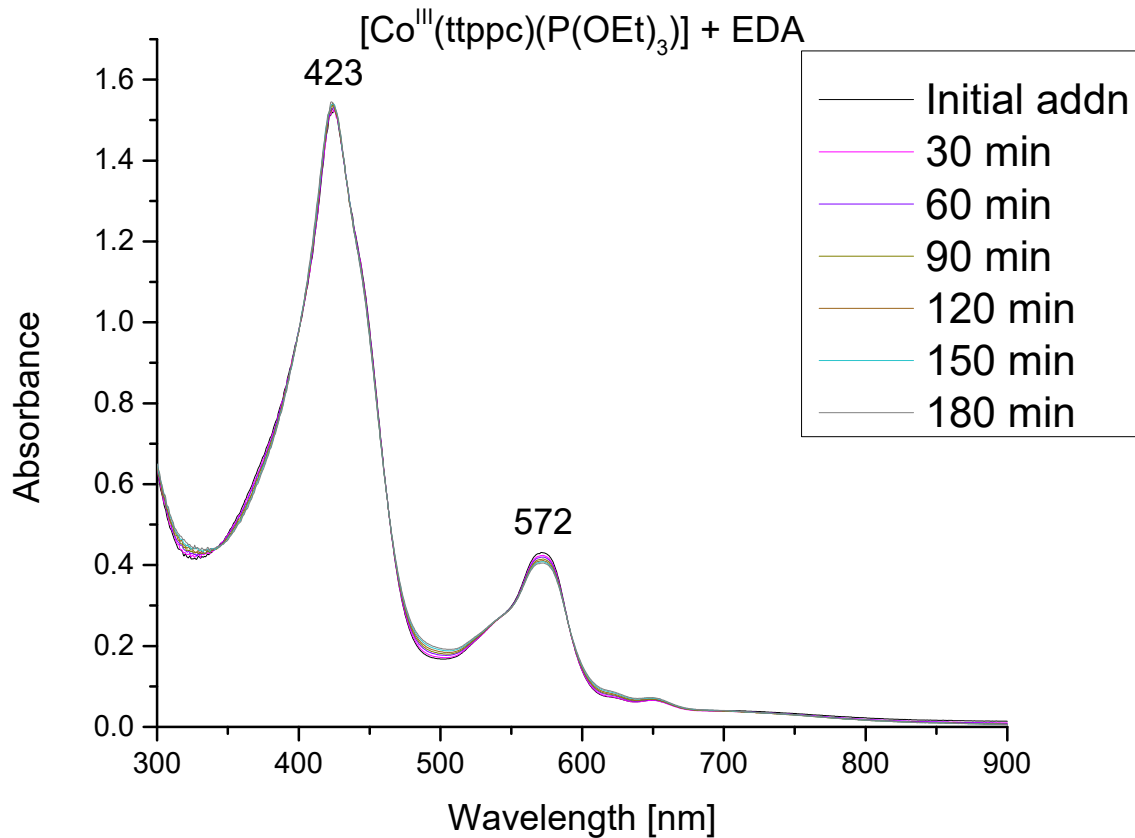


Figure S14. Time-course UV-Vis spectra of $[\text{Co}^{\text{III}}(\text{tppc})(\text{P}(\text{OEt})_3)]$ (**2a**) with EDA (10 equiv) in CH_2Cl_2 at room temperature. Spectra were collected every 30 mins for 3 hours.

¹H-NMR of Cyclopropanation Reactions

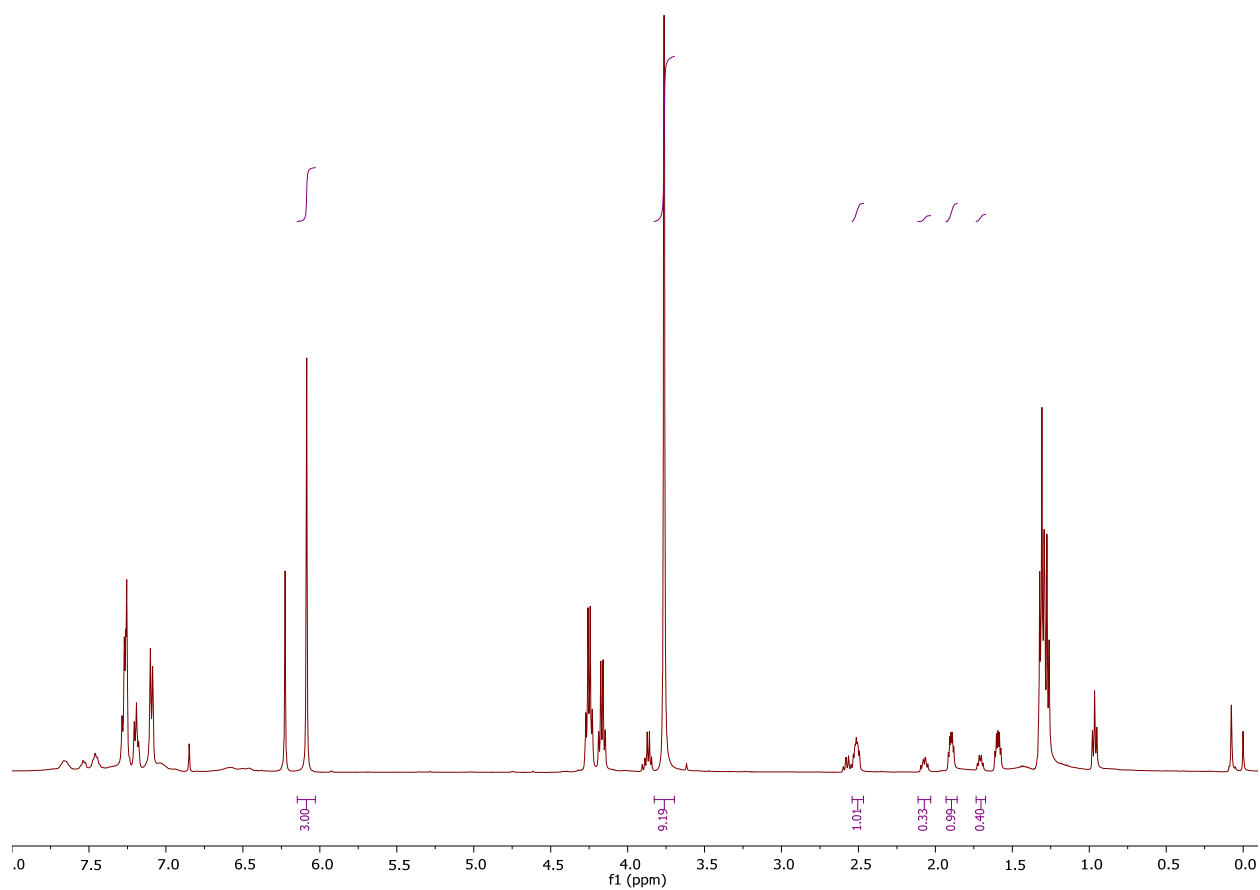


Figure S15. ¹H-NMR spectra for the cyclopropanation of styrene and EDA with **1a** (2 mol%) at 80 °C in toluene for 1h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (8.3 mg). 27% yield.

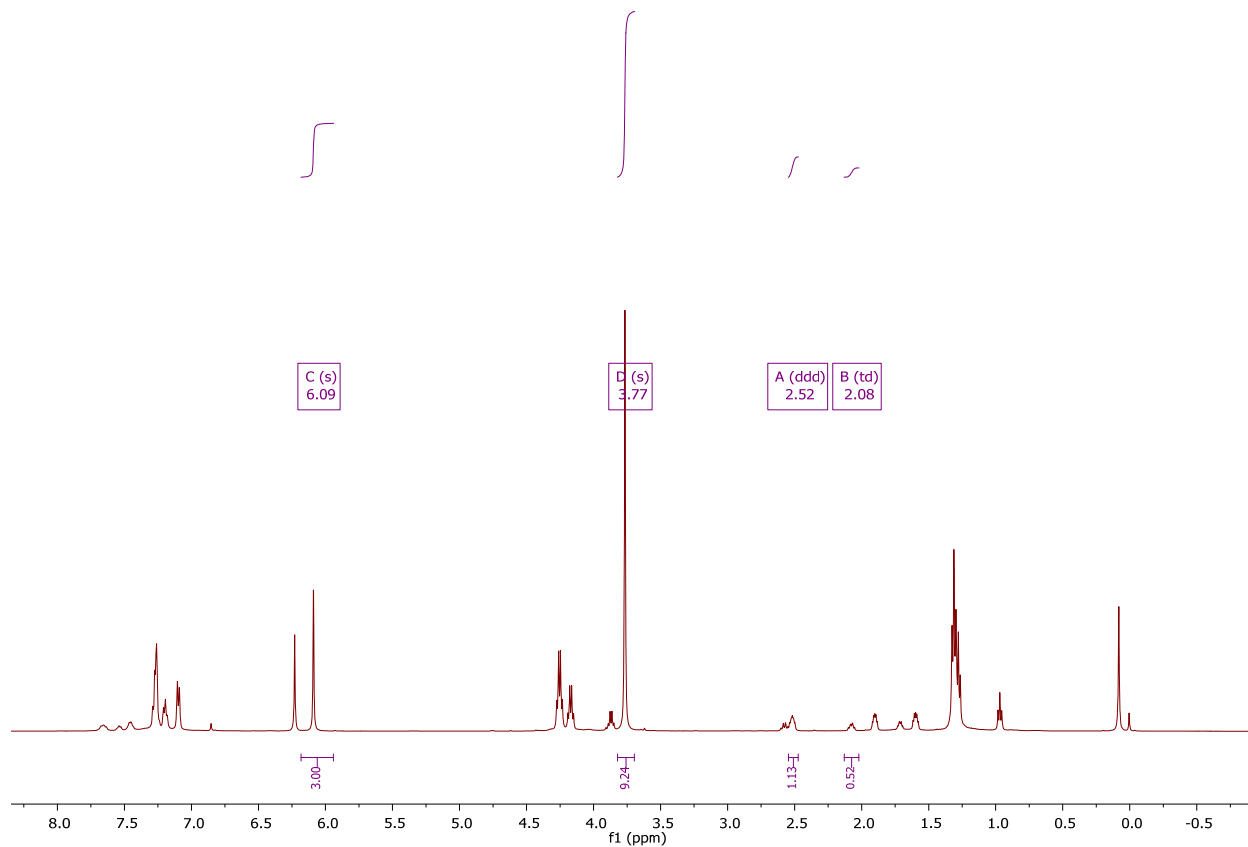


Figure S16. $^1\text{H-NMR}$ spectra for the cyclopropanation of styrene and EDA with **1a** (2 mol%) at 80 °C in toluene for 16h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (6.9 mg). 27% yield.

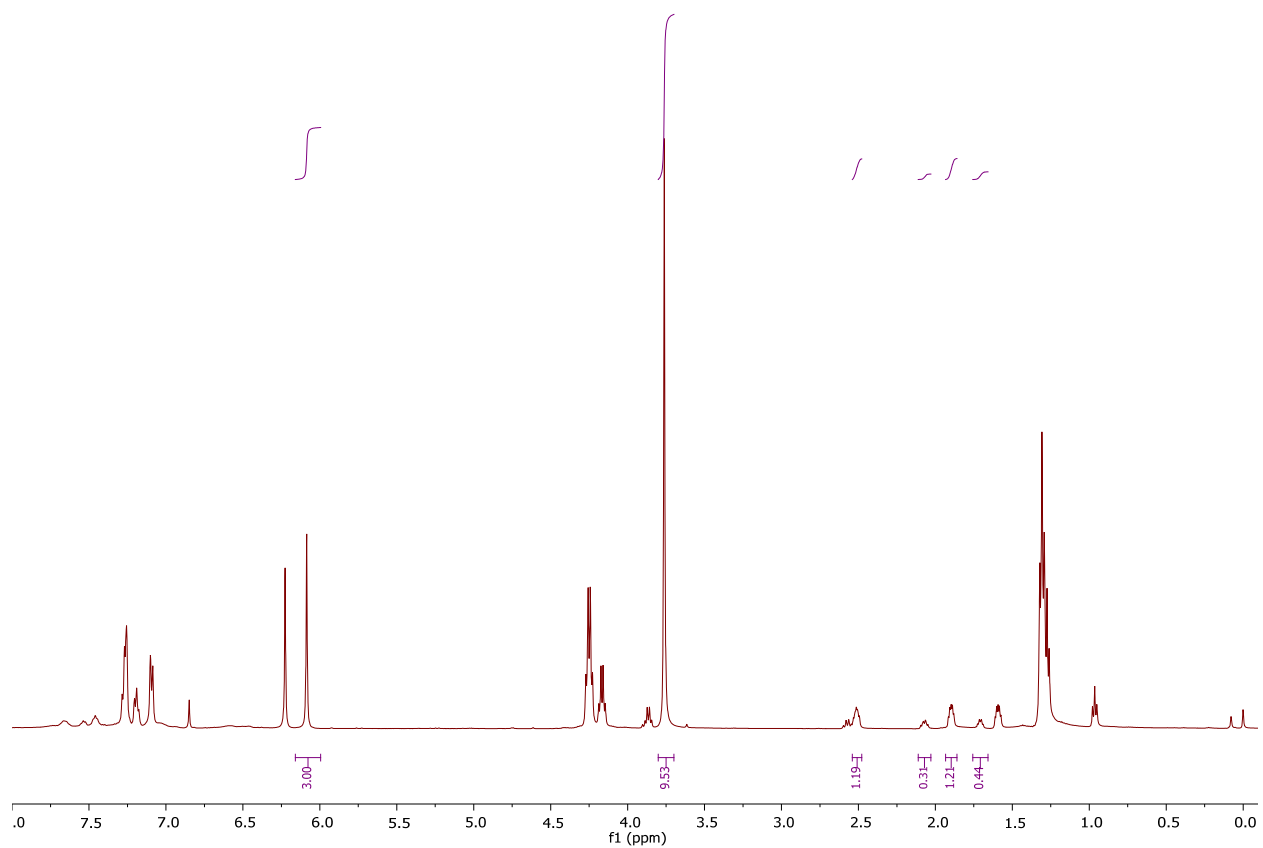


Figure S17. $^1\text{H-NMR}$ spectra for the cyclopropanation of styrene and EDA with **1a** (2 mol%) at r.t. in toluene for 1h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (7.3 mg). 26% yield.

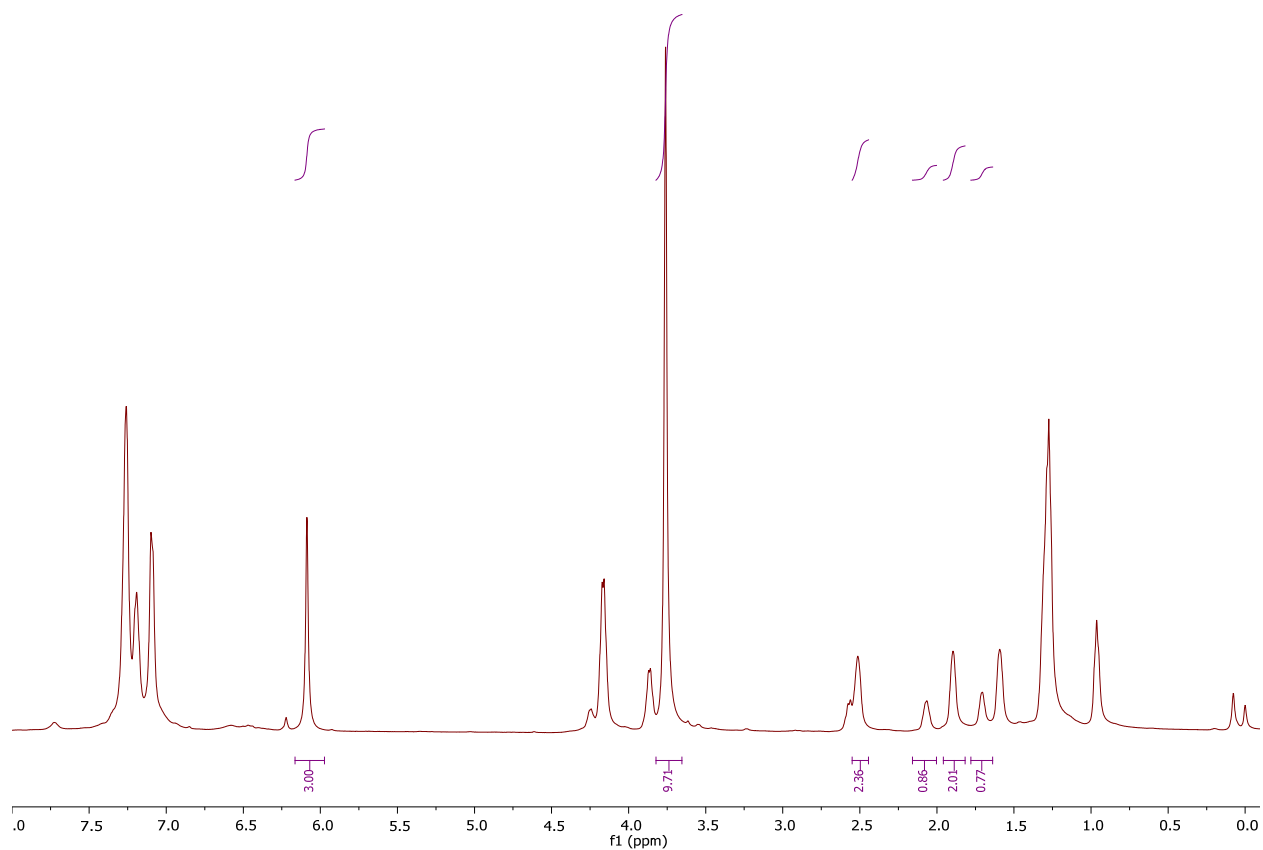


Figure S18. $^1\text{H-NMR}$ spectra for the cyclopropanation of styrene and EDA with $[\text{Co}^{\text{II}}(\text{TPP})]$ (2 mol%) at 80 °C in toluene for 1h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (8.1 mg). 62% yield.

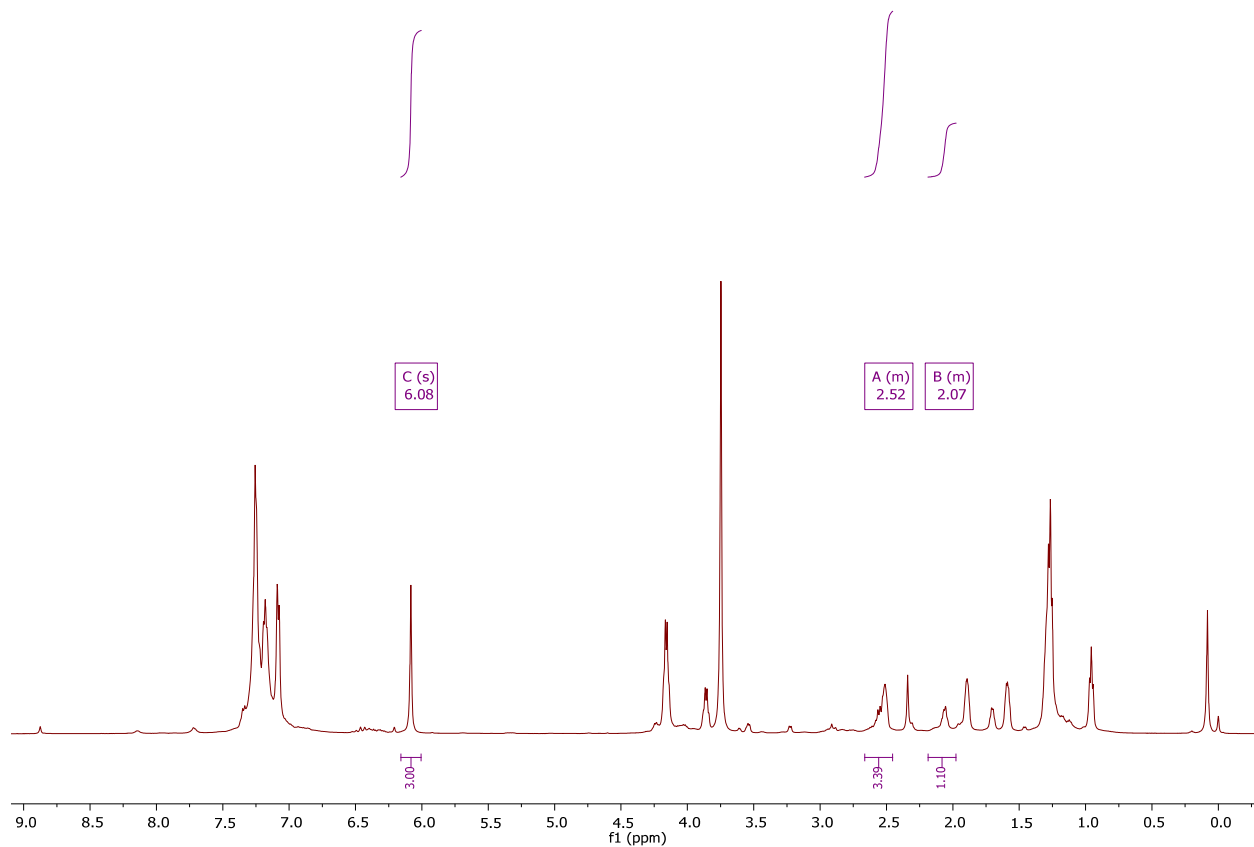


Figure S19. ¹H-NMR spectra for the cyclopropanation of styrene and EDA with [Co^{II}(TPP)] (2 mol%) at 80 °C in toluene for 16h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (7.3 mg). 78% yield.

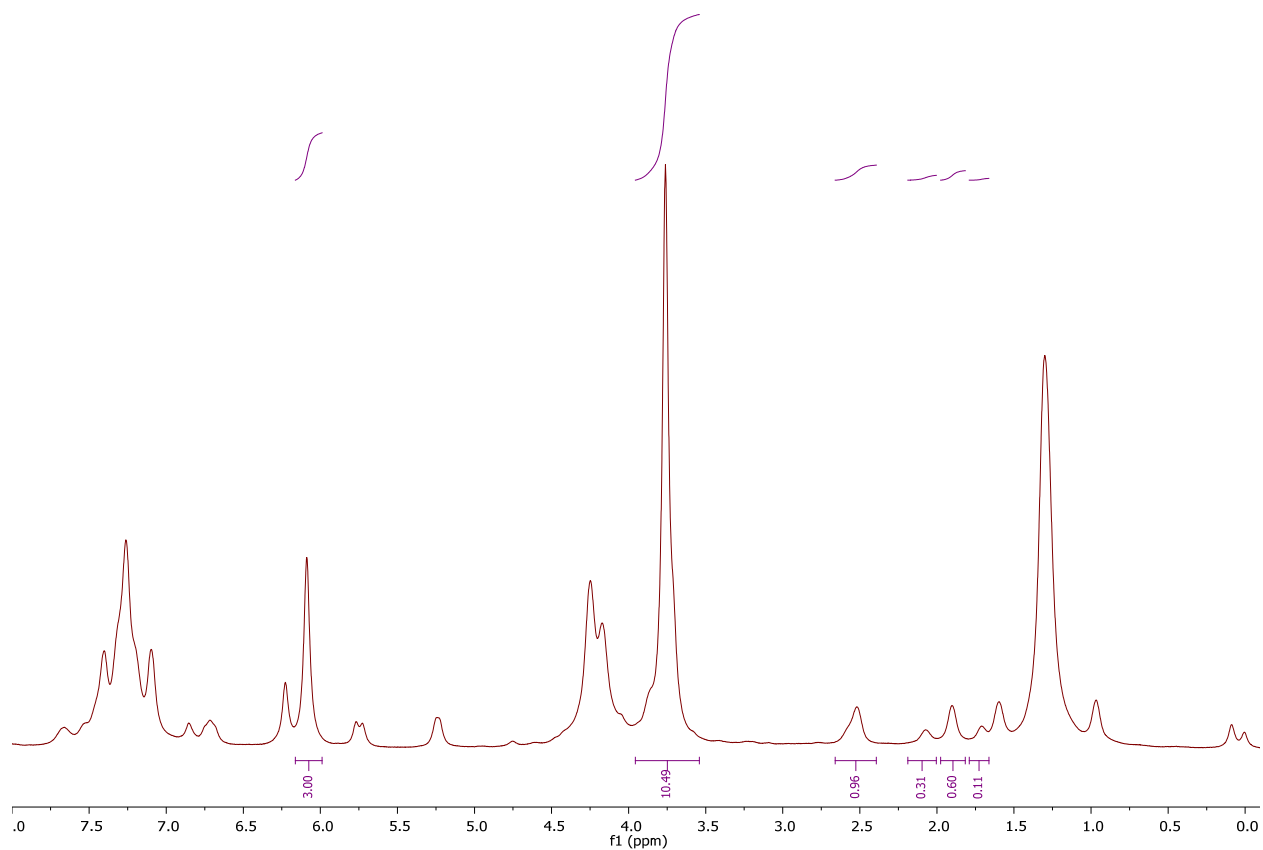


Figure S20. $^1\text{H-NMR}$ spectra for the cyclopropanation of styrene and EDA with **1a** (2 mol%) and CoCp_2 (2 mol%) at 80 °C in dichloroethane for 16h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (9.6 mg). 30% yield.

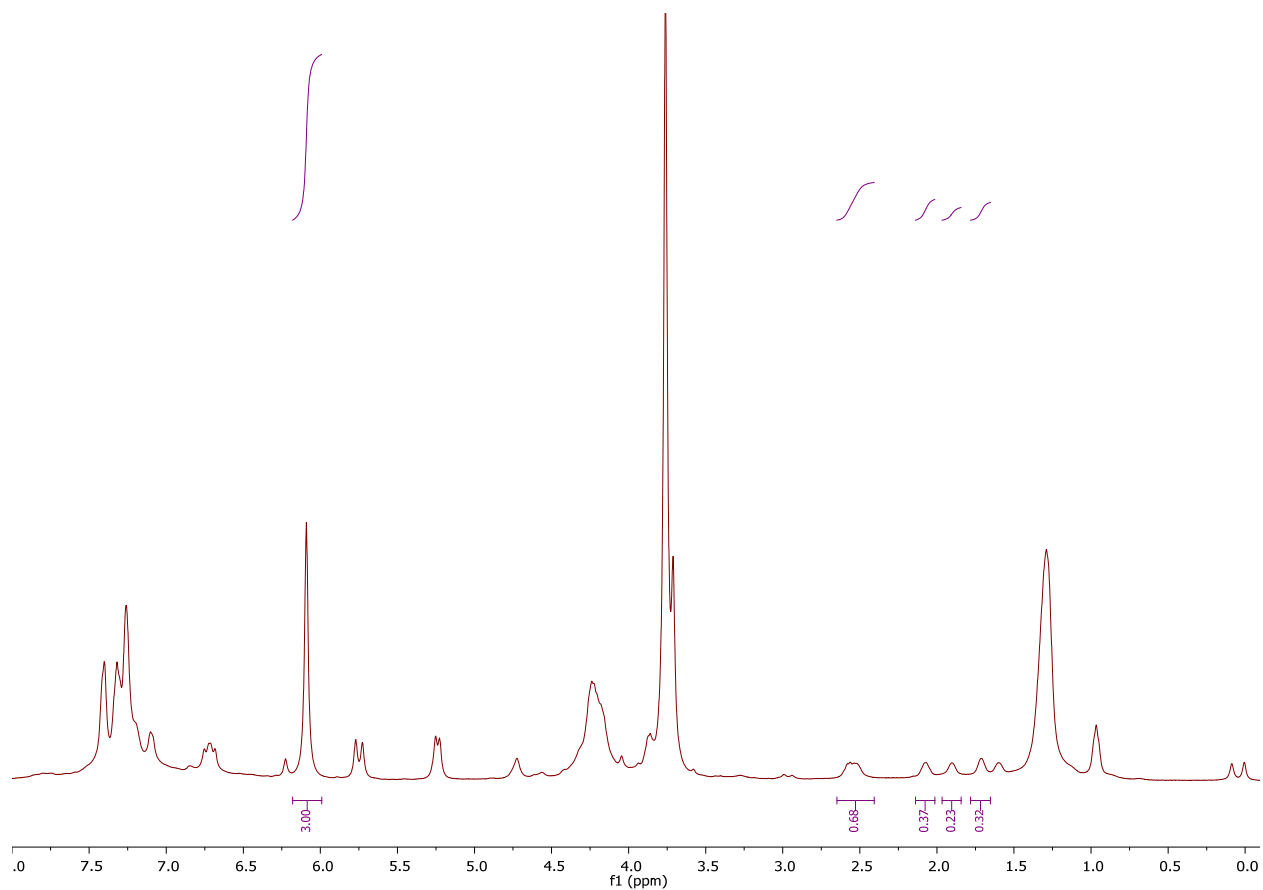


Figure S21. $^1\text{H-NMR}$ spectra for the cyclopropanation of styrene and EDA with **2a** (2 mol%) and CoCp_2 (2 mol%) at 80 °C in dichloroethane for 16h. The yield was determined using 1,3,5-trimethoxybenzene as an internal standard (11.5 mg). 29% yield.

EPR Spectrum of 1b

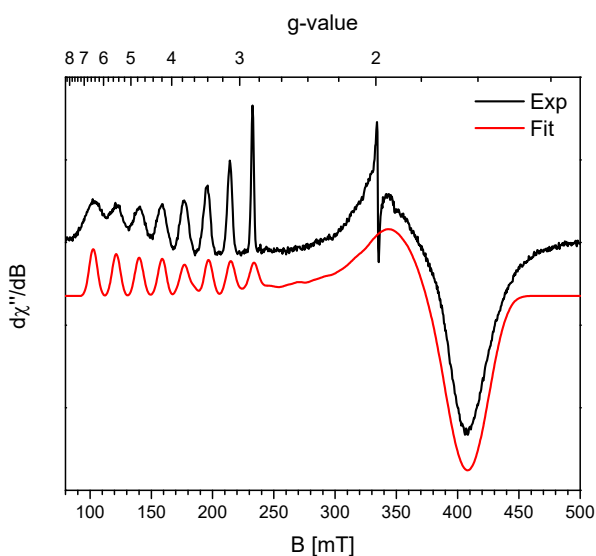


Figure S22. EPR spectrum of **1a** (5.5mM) reduced with KC_8 (1.3 equiv) in 2-MeTHF at 20K. Microwave power = 20 mW, microwave frequency = 9.316 GHz, modulation amplitude = 5 G, $g_z = 3.96$, $g_x = 1.87$, $g_y = 1.655$, $sg_z = 0.075$, $sg_x = 0.1$, $sg_y = 0.06$, $A_z = 1036$ MHz.

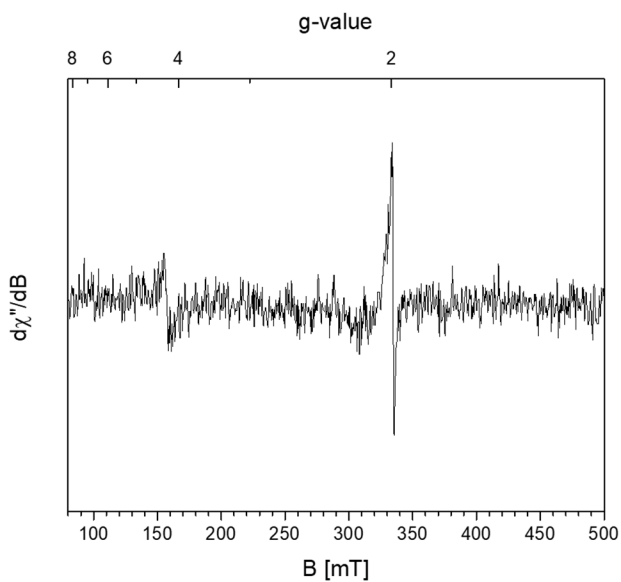
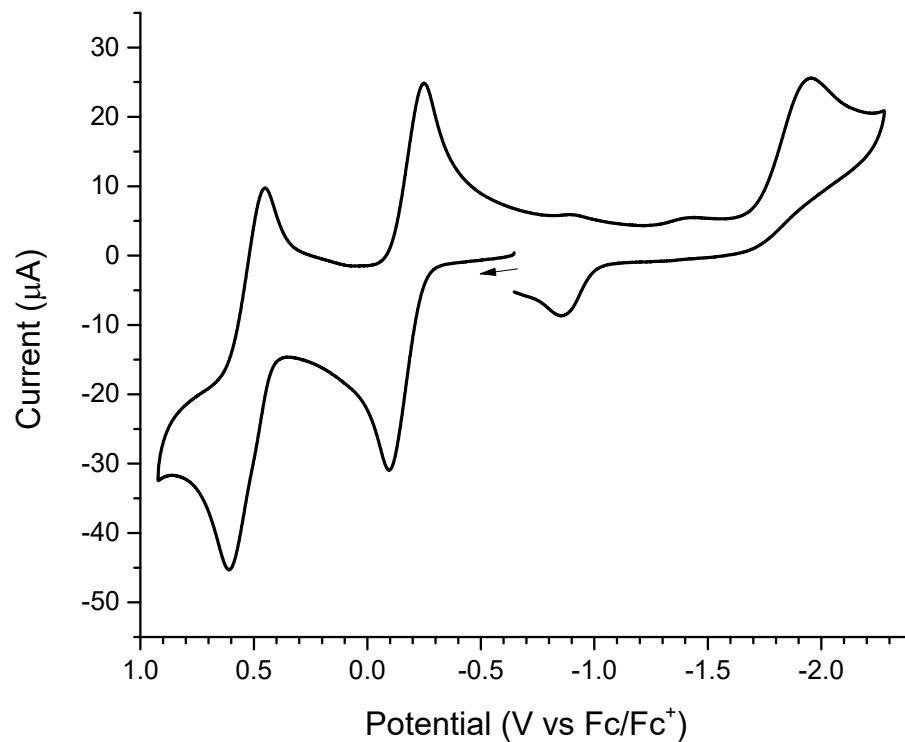


Figure S23. EPR spectrum of **1a** (5.5mM) reduced with KC_8 (1.3 equiv) followed by addition of EDA (20 μ L; \sim 30 equiv) in 2-MeTHF at 20K. Microwave power = 2 mW, microwave frequency = 9.331 GHz, modulation amplitude = 5 G. No signal is observed, other than the cavity background.

Cyclic Voltammogram of 2a



Event	$E_{1/2, \text{ox2}}$	$E_{1/2, \text{ox1}}$	$E_{\text{p, irrev-ox1}}$	$E_{\text{p, irrev-red1}}$
E (V)	0.531	-0.175	-0.846	-1.959

Figure S24. Cyclic voltammogram of **2a** in CH_2Cl_2 at r.t. with 0.1 M $[\text{TBA}](\text{PF}_6)$ supporting electrolyte. The data are referenced against Fc^+/Fc and measured at a scan rate of 100 mV s^{-1} .

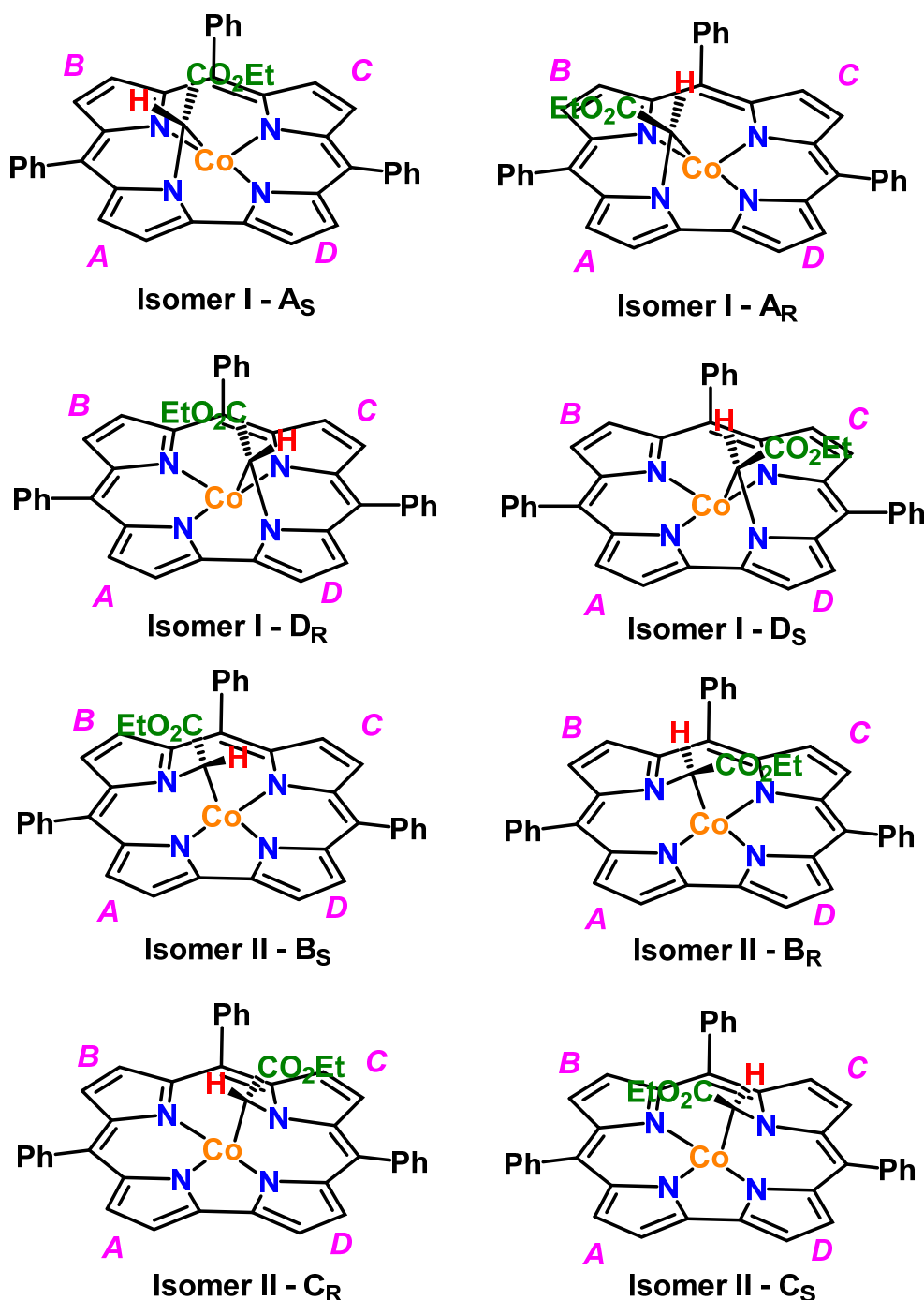


Figure S25. All possible structures for the N-bridged carbene adduct of **1a** + EDA leading to eight possible stereoisomers. Pyrrole rings are coded A-D where Isomer I corresponds to the carbene bridging between symmetrical pyrroles A and D and Isomer II corresponds to the carbene bridging between symmetrical pyrroles B and C. Depending on the two possible orientations of the carbene (labeled “R” and “S”), each isomer gives rise to two different signals, leading to a total of four ¹H-NMR signals for the H-atom of the bridging carbene intermediate.⁸

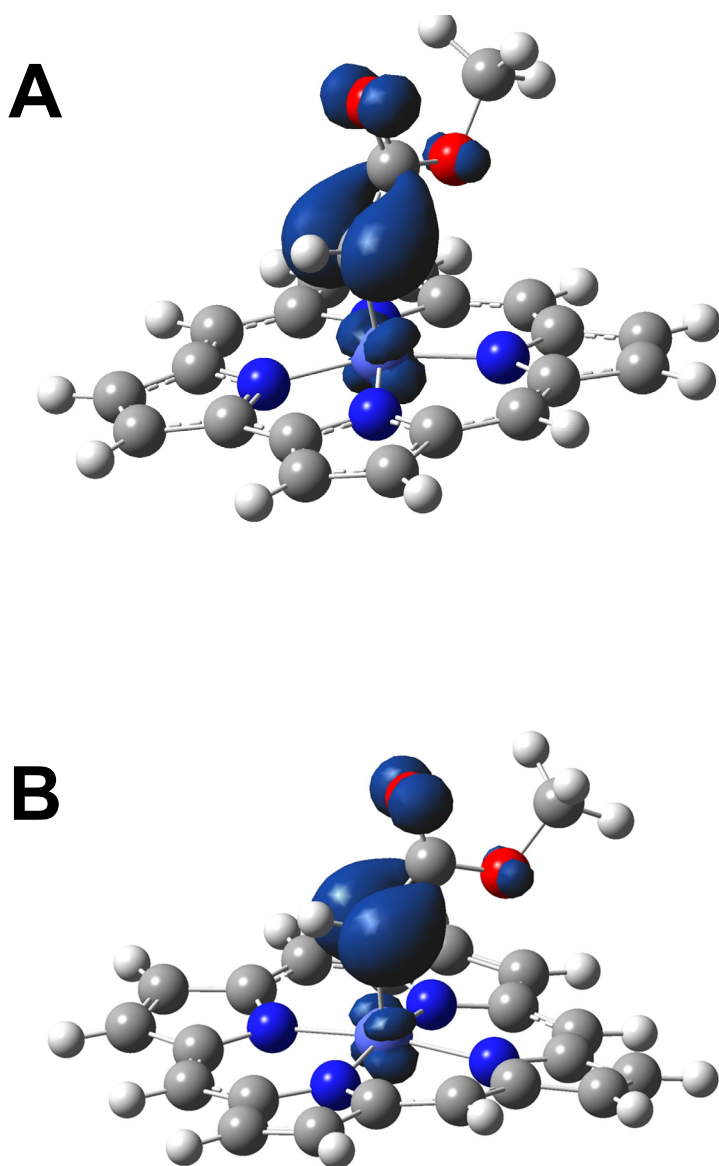


Figure S26. A) Spin density plot of the DFT-optimized structure of the Co^{III}-corrole-carbene radical with an isovalue of 0.005. Spin densities are calculated at 61% for the carbenoid carbon and at 20% for the cobalt center. B) Spin density plot of the DFT-optimized structure of the Co^{III}-porphyrin carbene radical with an isovalue of 0.005. Spin densities are calculated at 61% for the carbenoid carbon and at 10% for the cobalt center. Geometry optimizations were performed using the BP86 functional with the def2-TZVP basis set. Calculations were performed using Gaussian 16.⁹

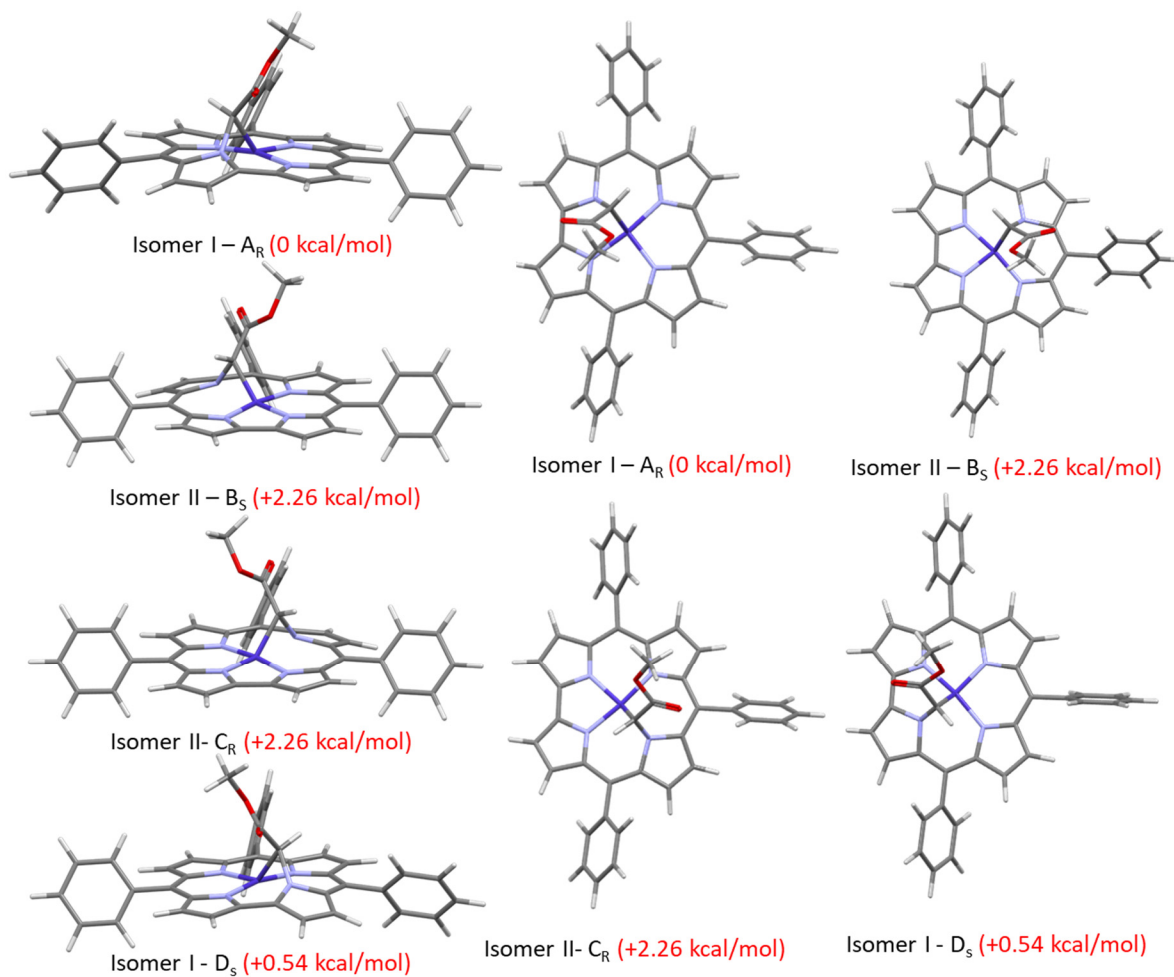


Figure S27. DFT optimized structures of Isomers I - A_R , Isomer II - B_S , Isomer II - C_R , and Isomer I - D_S of $[\text{Co}^{\text{III}}(\text{tpc})(\text{CHCO}_2\text{Me})]$, using the BP86 functional and TZVP basis set (left: side view; right: top view). Relative energies are reported in red. For simplification, the ethyl group of the carbene ester was replaced with a methyl group for the calculations. All calculations were performed using Gaussian 16.⁹

Table S1. DFT optimized coordinates for the Co^{III}-corrole carbene radical using BP86/def2-TZVP.⁹

CoCor_MDA			
-1 2			
N	-1.71213900	-1.21624700	-0.21682400
N	0.91283100	-1.39704800	-0.76711100
N	0.91450000	1.39539000	-0.76741600
N	-1.71074500	1.21786600	-0.21727800
C	-2.97004200	-0.70995600	-0.00675900
C	-3.87777700	-1.80379000	0.13749300
H	-4.95172800	-1.72796900	0.29536900
C	-3.12976200	-2.97208700	0.01864100
H	-3.49920000	-3.99505900	0.06325000
C	-1.76062300	-2.58916600	-0.20032100
C	-0.59798700	-3.33662500	-0.42457500
C	0.64810400	-2.76246600	-0.71236300
C	1.84906800	-3.47469100	-1.06941500
H	1.93100300	-4.55939000	-1.12077000
C	2.82005900	-2.54268000	-1.34843200
H	3.84625200	-2.71975000	-1.66602100
C	2.23065000	-1.24163700	-1.15500800
C	2.84965600	-0.00204400	-1.33697700
C	2.23188800	1.23831400	-1.15605900
C	2.82263300	2.53859900	-1.35054200
H	3.84879700	2.71435800	-1.66895200
C	1.85295400	3.47184900	-1.07109800
H	1.93609900	4.55643200	-1.12293300
C	0.65135700	2.76115600	-0.71311500
C	-0.59400300	3.33684300	-0.42520300
C	-1.75756300	2.59083700	-0.20080400
C	-3.12617800	2.97543100	0.01839400
H	-3.49438000	3.99885200	0.06291900
C	-3.87560200	1.80802900	0.13737800
H	-4.94963200	1.73351100	0.29534400
C	-2.96923700	0.71309300	-0.00695500
H	3.89599800	-0.00273600	-1.65035300
H	-0.65610700	4.42706100	-0.41743300
H	-0.66141400	-4.42676300	-0.41672300
Co	-0.28136100	0.00000600	-0.28443900
C	-0.10772000	-0.00028800	1.55681600
H	-1.05674800	-0.00007300	2.10522000
C	1.03689300	0.00015600	2.41697100
O	0.96511700	0.00020400	3.65903600
O	2.26276200	0.00039900	1.77872900
C	3.38910100	0.00039200	2.65673100
H	3.39373900	0.89260800	3.30331600
H	3.39330000	-0.89142200	3.30385000
H	4.27140400	0.00002900	2.00326000

Table S2. DFT optimized coordinates for the Co^{III}-porphyrin-carbene radical using BP86/def2-TZVP.⁹

CoPor-MDA

0 2			
Co	-0.29689800	0.00004600	-0.34778800
N	1.03769900	-1.39342300	-0.76006000
N	1.03685800	1.39440200	-0.75954000
N	-1.69725400	1.39887000	-0.25415900
N	-1.69637500	-1.39970100	-0.25410300
C	0.89822300	-2.76102600	-0.59116200
C	2.34364900	-1.21962900	-1.18253900
C	2.12705900	-3.44377500	-0.90710000
C	3.01781200	-2.48797400	-1.29664700
C	2.34295800	1.22150700	-1.18187800
C	0.89659700	2.76186900	-0.59009200
C	3.01647200	2.49026700	-1.29527000
C	2.12515400	3.44541000	-0.90541100
C	-1.50385900	2.76523300	-0.14310200
C	-3.06470400	1.22236000	-0.13050300
C	-2.76035600	3.44707400	0.03461800
C	-3.73185600	2.49033200	0.02453200
C	-3.06388900	-1.22408900	-0.13011800
C	-1.50204800	-2.76594200	-0.14308600
C	-3.73017200	-2.49247900	0.02523300
C	-2.75804100	-3.44858200	0.03513100
C	2.95082300	0.00117300	-1.41683900
C	-0.28242200	3.40652200	-0.25859200
C	-3.71223400	-0.00107300	-0.09834500
C	-0.28027500	-3.40645100	-0.25928700
H	2.26267200	-4.52155700	-0.85700300
H	4.04639900	-2.61032300	-1.62778400
H	4.04505600	2.61330600	-1.62616100
H	2.26017800	4.52324000	-0.85476300
H	-2.86719900	4.52463200	0.13416400
H	-4.80813400	2.61143900	0.12164600
H	-4.80633900	-2.61427800	0.12270500
H	-2.86414900	-4.52619900	0.13483500
H	-0.25810100	-4.49158800	-0.15233100
H	-4.79796400	-0.00141400	0.00557900
H	-0.26095200	4.49164500	-0.15137100
H	3.98735700	0.00156900	-1.75627100
C	-0.10881200	-0.00044200	1.49907000
C	1.04214400	-0.00022700	2.36288800
O	0.91950900	-0.00051800	3.59458200
O	2.26669100	0.00011300	1.75133000
C	3.38343700	-0.00005100	2.65934800
H	3.36691800	-0.89324900	3.30060400
H	4.27696000	0.00002100	2.02427300
H	3.36698400	0.89298000	3.30084600
H	-1.06349500	0.00070800	2.03395000

Table S3. DFT optimized coordinates for [Co^{III}(tpc)(CHCO₂Me)] Isomer I – A_R using BP86/TZVP.⁹

Cotpc-MDA-bridge-pyrrole-A-R

0 1			
Co	-0.01274400	-0.44753600	-0.22513200
N	1.20693900	-1.82822900	-0.51777300
N	1.36008200	0.82113700	-0.20407200
N	-1.43571600	0.81037100	-0.22921900
N	-1.25426000	-1.94796400	-0.00447200
C	0.71632700	-3.12319000	-0.61708300
C	1.81345000	-4.02139100	-0.79979500
H	1.74413900	-5.10119400	-0.90196300
C	2.96373900	-3.25405100	-0.77726100
H	3.98740300	-3.60827400	-0.86499000
C	2.57350000	-1.87201100	-0.59923300
C	3.33864100	-0.69058000	-0.51537400
C	4.82171100	-0.78131100	-0.62424500
C	5.65175000	-0.33298000	0.42144300
H	5.19402200	0.08261100	1.32179700
C	7.04281400	-0.43072300	0.32289500
H	7.66936900	-0.08353900	1.14783000
C	7.63145600	-0.97809000	-0.82268100
H	8.71833500	-1.05355100	-0.89977200
C	6.81824900	-1.42652600	-1.86950400
H	7.26901700	-1.84664200	-2.77166800
C	5.42690400	-1.33079300	-1.77105500
H	4.79571400	-1.66521100	-2.59729100
C	2.72977200	0.57546500	-0.36262000
C	3.41126000	1.84215000	-0.42074900
H	4.47931200	1.96249400	-0.57805200
C	2.47026400	2.83232500	-0.29007200
H	2.62951100	3.90622100	-0.32780400
C	1.18581700	2.19639700	-0.15385300
C	-0.05912800	2.85246100	-0.04558500
C	-0.06305300	4.34103300	0.07899100
C	0.52151600	4.97106900	1.19380700
H	0.97118500	4.35572400	1.97628700
C	0.51689600	6.36432900	1.31233200
H	0.96878600	6.83458500	2.18887200
C	-0.07022600	7.15393000	0.31716700
H	-0.07296300	8.24230500	0.40932700
C	-0.65273600	6.54013500	-0.79736300
H	-1.10630900	7.14878400	-1.58315900
C	-0.64983500	5.14668500	-0.91496900
H	-1.09393000	4.66988900	-1.79166800
C	-1.29438700	2.17846500	-0.06189000
C	-2.59883900	2.76897800	0.12414100
H	-2.78601600	3.82557100	0.29292500
C	-3.51884800	1.75538700	0.07348000
H	-4.59526100	1.83423600	0.19704100
C	-2.80395700	0.51972700	-0.14413600
C	-3.40564900	-0.76085900	-0.26333500
C	-4.88428400	-0.87438200	-0.40137600

C	-5.62000800	-1.72475100	0.44764300
H	-5.09579100	-2.27710000	1.23092700
C	-7.00528100	-1.84999300	0.31099900
H	-7.55881600	-2.50571700	0.98711400
C	-7.68278300	-1.13158200	-0.68084400
H	-8.76524800	-1.22961000	-0.78819900
C	-6.96346900	-0.28894700	-1.53621400
H	-7.48234600	0.26641100	-2.32097700
C	-5.57842000	-0.16189800	-1.39948300
H	-5.01754300	0.48202700	-2.08003200
C	-2.65898700	-1.95062800	-0.33330800
C	-2.93639200	-3.24411300	-0.80749000
H	-3.91558700	-3.57255600	-1.14705300
C	-1.74415500	-3.99647300	-0.88994000
H	-1.65143100	-4.98902000	-1.32370400
C	-0.67706300	-3.20484000	-0.47398700
C	-0.80519800	-1.34656900	1.23880600
H	-1.58440600	-0.73159500	1.70167800
C	-0.04416900	-2.14244200	2.26021100
O	0.01597200	-3.35459700	2.35552800
O	0.52434400	-1.27617100	3.14124200
C	1.23852800	-1.90047800	4.23687700
H	2.06963100	-2.50915500	3.85514200
H	1.61347200	-1.07001800	4.84423500
H	0.56364300	-2.53885000	4.82423800

Table S4. DFT optimized coordinates for [Co^{III}(tpc)(CHCO₂Me)] Isomer II – B_s using BP86/TZVP.⁹

Cotpc-MDA-bridge-pyrrole-B-S

0 1			
Co	0.00594200	-0.77019700	-0.28092800
N	1.20065500	-2.17517300	-0.32058600
N	1.40793400	0.48824100	-0.35921500
N	-1.45364800	0.54246500	0.05590400
N	-1.25121900	-2.17660500	-0.35384600
C	0.67901500	-3.45327600	-0.33429500
C	1.75928400	-4.38237300	-0.33969000
H	1.67308700	-5.46604000	-0.35155100
C	2.93318600	-3.63661000	-0.31912900
H	3.95001100	-4.02033500	-0.32493000
C	2.57273800	-2.24178000	-0.31873100
C	3.35968400	-1.07232100	-0.31349800
C	4.84409700	-1.20408600	-0.29470300
C	5.60383200	-0.69981300	0.77830400
H	5.09031400	-0.21158000	1.60933000
C	6.99500100	-0.83662500	0.79667700
H	7.56612300	-0.44495800	1.64171700
C	7.65390100	-1.48022400	-0.25698500
H	8.74086000	-1.58640400	-0.24263700
C	6.91072400	-1.98663900	-1.32895700
H	7.41677900	-2.48415800	-2.15962200
C	5.51917100	-1.85117200	-1.34756300
H	4.94291900	-2.23251700	-2.19336300
C	2.77456800	0.21770500	-0.33331800
C	3.48432100	1.47103900	-0.37276400
H	4.56603200	1.57075000	-0.39330600
C	2.55472400	2.48275800	-0.39141600
H	2.73966200	3.55277800	-0.40696100
C	1.25328400	1.86862300	-0.38075000
C	0.01041700	2.54951600	-0.40753000
C	0.01537600	4.03278800	-0.58948400
C	-0.51501800	4.86987700	0.41019400
H	-0.90468600	4.41616100	1.32396800
C	-0.51767000	6.25847700	0.24563700
H	-0.92354000	6.89603100	1.03464300
C	0.00469300	6.83165900	-0.91965100
H	0.00102700	7.91647100	-1.04767900
C	0.53227600	6.00761000	-1.92051600
H	0.93556500	6.44703600	-2.83585800
C	0.53895300	4.61884300	-1.75691300
H	0.94246300	3.97553500	-2.54211500
C	-1.24334500	1.93791700	-0.29878700
C	-2.51299400	2.45872100	-0.62148800
H	-2.67846700	3.48056900	-0.95185200
C	-3.47473200	1.45475700	-0.54964500
H	-4.52378500	1.55406800	-0.81618000
C	-2.87277600	0.23337100	-0.19241100
C	-3.41938500	-1.06086900	-0.17257000
C	-4.90271400	-1.18850500	-0.19935700
C	-5.70066500	-0.54363900	0.76622500

H	-5.21690700	0.04440100	1.54948100
C	-7.09250300	-0.66672400	0.74243100
H	-7.69313100	-0.16746300	1.50624700
C	-7.71465300	-1.43493900	-0.24843100
H	-8.80243200	-1.53101900	-0.26719100
C	-6.93403000	-2.07751100	-1.21617100
H	-7.41191700	-2.67049900	-1.99939200
C	-5.54178600	-1.95672200	-1.19269700
H	-4.93628600	-2.44513500	-1.95890600
C	-2.61792100	-2.23461500	-0.20335600
C	-2.98864900	-3.62346000	-0.09374000
H	-4.00029200	-3.99727000	0.03730300
C	-1.82094200	-4.37381400	-0.16409700
H	-1.73666100	-5.45664000	-0.10951400
C	-0.74173000	-3.45075700	-0.30834600
C	-0.85693900	-0.06218600	1.23868500
H	-1.51580400	-0.81444800	1.68827700
C	-0.22597700	0.78605300	2.30773700
O	-0.49022700	1.94922700	2.55854200
O	0.62119600	0.02008000	3.03826900
C	1.21780800	0.68335400	4.18134200
H	0.43943000	1.04258500	4.86903200
H	1.83894600	-0.07959100	4.66186600
H	1.83070000	1.53358200	3.85250700

Table S5. DFT optimized coordinates for [Co^{III}(tpc)(CHCO₂Me)] Isomer II – C_R using BP86/TZVP.⁹

Cotpc-MDA-bridge-pyrroleC-R

0 1			
Co	-0.00594000	-0.77000400	-0.28166000
N	1.25136800	-2.17644100	-0.35513200
N	1.45357600	0.54252300	0.05576300
N	-1.40796500	0.48824200	-0.35975200
N	-1.20054200	-2.17507400	-0.32238700
C	0.74186200	-3.45057800	-0.30975000
C	1.82098500	-4.37366800	-0.16505200
H	1.73665700	-5.45648800	-0.11040100
C	2.98868600	-3.62332800	-0.09430100
H	4.00027300	-3.99717500	0.03708300
C	2.61799300	-2.23448600	-0.20393900
C	3.41944700	-1.06073900	-0.17261600
C	4.90277100	-1.18831700	-0.19889000
C	5.70038300	-0.54346600	0.76698800
H	5.21634700	0.04449600	1.55013300
C	7.09223400	-0.66648900	0.74365400
H	7.69257900	-0.16723100	1.50769700
C	7.71475200	-1.43462800	-0.24703500
H	8.80254200	-1.53066100	-0.26543800
C	6.93447500	-2.07718400	-1.21506600
H	7.41264700	-2.67012000	-1.99815600
C	5.54222300	-1.95645200	-1.19205700
H	4.93700700	-2.44483800	-1.95850800
C	2.87279700	0.23349100	-0.19224000
C	3.47481100	1.45502300	-0.54890500
H	4.52397000	1.55446000	-0.81498100
C	2.51305200	2.45896500	-0.62072800
H	2.67856200	3.48089000	-0.95082800
C	1.24333000	1.93796600	-0.29849800
C	-0.01041400	2.54957700	-0.40763700
C	-0.01546500	4.03282600	-0.58951900
C	0.51480400	4.86999100	0.41018300
H	0.90445700	4.41631400	1.32398600
C	0.51730800	6.25858000	0.24565000
H	0.92308000	6.89617200	1.03467600
C	-0.00512200	6.83173000	-0.91963500
H	-0.00160100	7.91654700	-1.04763600
C	-0.53262100	6.00763300	-1.92049700
H	-0.93597600	6.44702000	-2.83583100
C	-0.53913800	4.61886200	-1.75691500
H	-0.94257400	3.97553600	-2.54214300
C	-1.25327900	1.86866600	-0.38112400
C	-2.55471800	2.48278900	-0.39167500
H	-2.73969300	3.55280800	-0.40704600
C	-3.48432800	1.47108400	-0.37284300
H	-4.56604600	1.57080600	-0.39313900
C	-2.77460700	0.21774800	-0.33357300
C	-3.35962600	-1.07231800	-0.31371800
C	-4.84404600	-1.20413000	-0.29423300
C	-5.60326800	-0.69975800	0.77908300

H	-5.08936200	-0.21142300	1.60980900
C	-6.99443500	-0.83657800	0.79811400
H	-7.56517600	-0.44484300	1.64338200
C	-7.65380700	-1.48026600	-0.25519100
H	-8.74076200	-1.58644600	-0.24034100
C	-6.91113000	-1.98677500	-1.32746900
H	-7.41758500	-2.48436200	-2.15785000
C	-5.51958600	-1.85130700	-1.34672900
H	-4.94370300	-2.23274900	-2.19273800
C	-2.57263600	-2.24172500	-0.31940200
C	-2.93302500	-3.63656300	-0.31946200
H	-3.94984600	-4.02031900	-0.32456100
C	-1.75910900	-4.38229900	-0.34041900
H	-1.67286100	-5.46596300	-0.35222300
C	-0.67887900	-3.45314700	-0.33595700
C	0.85687200	-0.06257600	1.23844600
H	1.51565700	-0.81504400	1.68779300
C	0.22576300	0.78539300	2.30757700
O	0.48926800	1.94879400	2.55816700
O	-0.62058200	0.01888500	3.03848000
C	-1.21764400	0.68210200	4.18138200
H	-1.82814500	1.53406100	3.85264500
H	-1.84107500	-0.08015600	4.66002200
H	-0.43955500	1.03874400	4.87076600

Table S6. DFT optimized coordinates for [Co^{III}(tpc)(CHCO₂Me)] Isomer I – D_s using BP86/TZVP.⁹

Cotpc-MDA-bridge-pyrroleD-S

0 1			
Co	0.01171700	-0.44633800	-0.22202600
N	1.25025500	-1.94736600	-0.00867300
N	1.43498100	0.80806500	-0.21322800
N	-1.35845400	0.82538500	-0.21753900
N	-1.21051600	-1.82232000	-0.51963400
C	0.67074200	-3.20296900	-0.48260100
C	1.73735800	-3.99627500	-0.89618400
H	1.64411500	-4.98864400	-1.33023700
C	2.93069000	-3.24564400	-0.81177200
H	3.91001900	-3.57615200	-1.14901800
C	2.65506100	-1.95114000	-0.33925200
C	3.40307200	-0.76161200	-0.27979700
C	4.88043800	-0.87969200	-0.43439400
C	5.62582900	-1.70997300	0.42561500
H	5.11089200	-2.24267000	1.22845400
C	7.00915600	-1.84074000	0.27405600
H	7.57071600	-2.48060200	0.95869600
C	7.67432800	-1.14817700	-0.74411500
H	8.75517900	-1.25047300	-0.86317300
C	6.94485900	-0.32632800	-1.61099600
H	7.45401800	0.20842400	-2.41616300
C	5.56177500	-0.19378900	-1.45932900
H	4.99277300	0.43375600	-2.14840500
C	2.80471600	0.52037600	-0.16266000
C	3.52388900	1.76311700	-0.00023600
H	4.60420300	1.84746700	0.07608700
C	2.60430900	2.77725100	0.04697300
H	2.79418300	3.84143000	0.15555400
C	1.29551100	2.17810800	-0.06656100
C	0.06205000	2.85144800	-0.04401500
C	0.07307000	4.34419800	0.08001400
C	0.36345100	4.95847900	1.31113800
H	0.57315700	4.33250800	2.18155800
C	0.37806100	6.35250900	1.42791000
H	0.60253400	6.81296800	2.39292700
C	0.10082000	7.15455000	0.31536000
H	0.11158900	8.24299800	0.40643600
C	-0.18981400	6.55424800	-0.91479800
H	-0.40284300	7.17306000	-1.78963700
C	-0.20269200	5.16025700	-1.03159800
H	-0.42190000	4.69245500	-1.99421000
C	-1.18366100	2.19982200	-0.14489300
C	-2.47363900	2.83613400	-0.20281800
H	-2.63725400	3.90985800	-0.17853500
C	-3.41668700	1.84793000	-0.33491000
H	-4.49087900	1.96982900	-0.44076200
C	-2.73199700	0.58115400	-0.33662400
C	-3.34197400	-0.68309200	-0.49608100
C	-4.82658000	-0.77547500	-0.58688700
C	-5.64387400	-0.35791600	0.48117700

H	-5.17570600	0.03529300	1.38621800
C	-7.03589800	-0.45757000	0.39824700
H	-7.65252500	-0.13409100	1.24012300
C	-7.63796200	-0.97678400	-0.75342100
H	-8.72552700	-1.05392100	-0.81815000
C	-6.83728000	-1.39541100	-1.82199200
H	-7.29858100	-1.79407100	-2.72856200
C	-5.44501300	-1.29725700	-1.73938700
H	-4.82363500	-1.60882400	-2.58188400
C	-2.57700300	-1.86325700	-0.60033700
C	-2.96934500	-3.24337100	-0.78992900
H	-3.99365100	-3.59493800	-0.88088400
C	-1.82047900	-4.01239500	-0.81865100
H	-1.75298700	-5.09143400	-0.92967300
C	-0.72169500	-3.11753000	-0.62872700
C	0.80471900	-1.35263700	1.23893800
H	1.58497000	-0.74040500	1.70316200
C	0.04136700	-2.14993800	2.25697300
O	-0.03159400	-3.36207900	2.34269400
O	-0.51447400	-1.28471100	3.14750300
C	-1.23317000	-1.91010100	4.23949400
H	-0.56378800	-2.55962700	4.82092400
H	-1.59893000	-1.08055500	4.85366300
H	-2.07087400	-2.50760200	3.85455600

References

1. B. Koszarna and D. T. Gryko, *The Journal of Organic Chemistry*, 2006, **71**, 3707-3717.
2. J. P. T. Zaragoza, T. H. Yosca, M. A. Siegler, P. Moënne-Loccoz, M. T. Green and D. P. Goldberg, *J. Am. Chem. Soc.*, 2017, **139**, 13640-13643.
3. H.-Y. Liu, F. Yam, Y.-T. Xie, X.-Y. Li and C. K. Chang, *Journal of the American Chemical Society*, 2009, **131**, 12890-12891.
4. M. Goswami, P. Geuijen, J. N. H. Reek and B. de Bruin, *Eur. J. Inorg. Chem.*, 2018, **2018**, 617-626.
5. J. Egloff, M. Ranocchiari, A. Schira, C. Schotes and A. Mezzetti, *Organometallics*, 2013, **32**, 4690-4701.
6. L. Huang, Y. Chen, G. Y. Gao and X. P. Zhang, *J Org Chem*, 2003, **68**, 8179-8184.
7. Y. Wei, A. Tinoco, V. Steck, R. Fasan and Y. Zhang, *J. Am. Chem. Soc.*, 2018, **140**, 1649-1662.
8. P. Chattopadhyay, T. Matsuo, T. Tsuji, J. Ohbayashi and T. Hayashi, *Organometallics*, 2011, **30**, 1869-1873.
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.