

Photocatalytic deracemisation of cobalt(III) complexes with fourfold stereogenicity

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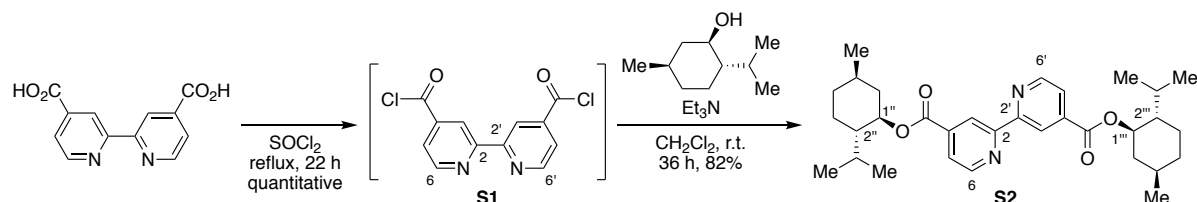
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1. General Information

All chemicals were purchased in reagent grade from several commercial suppliers (Acros Organics, Alfa Aesar, Apollo, Fluka, Fluorochem, Riedel-de Hën, Sigma-Aldrich, TCI) and used without further purification. All solvents except cyclohexane were purchased in HPLC grade, cyclohexane was obtained in CP grade and distilled before use. Dry solvents were obtained from Acros Organics or Sigma-Aldrich. All reactions were carried out in oven-dried glass ware, and when necessary, under an inert atmosphere of dry argon in heat-dried glassware using standard Schlenk technique. If necessary for required precision, reagents and catalysts were introduced as stock solutions in the respective reaction solvent(s) or in a transfer solvent which was subsequently removed *in vacuo*. Flash column chromatography was carried out using Silicycle SiliaFlash P60 (230–400 mesh) silica gel as stationary phase with the indicated solvent systems either under manual elution or using an automated flash purification system Biotage Selekt with UV-detection. Analytical thin-layer chromatography (TLC) was run on aluminum plates pre-coated with silica gel Merck 60. The plates were analyzed under UV light (254 or 366 nm) or stained with a KMnO₄ solution. Preparative TLC was performed on glass plates pre-coated with silica gel Merck 60 F254 (layer thickness: 0.25 mm). NMR spectra were acquired on a Bruker Avance III (400 or 500 MHz) spectrometer at 298 K in deuterated solvents supplied by Fluorochem. Chemical shifts (δ) in ppm are referenced to tetramethylsilane as primary reference in the unified scale. Multiplets are reported with the following designations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a Varian Scimitar 800 FTIR spectrometer, equipped with an ATR module. Absorption bands are reported in wave numbers ($\tilde{\nu}$) in cm⁻¹. Melting points (m.p.) were determined using a Büchi B-545 melting point meter (heating rate: 2 °C/min). High resolution (HR) ESI mass spectra were recorded on a Bruker maXis 4G Q-TOF-instrument by the staff of the mass spectrometry facility at the University of Basel. UV/Vis absorption and circular dichroism (CD) spectra were acquired in acetonitrile solution on a Jasco V-770 UV/Vis spectrometer and a Jasco J-1500 CD spectrometer respectively using a 10 mm quartz cuvette at 20 °C. Enantiomeric ratios were determined by HPLC on a chiral stationary phase using various analytical columns and solvent systems (detection at 225 or 275 nm) with the retention times (Rt) being reported in minutes.

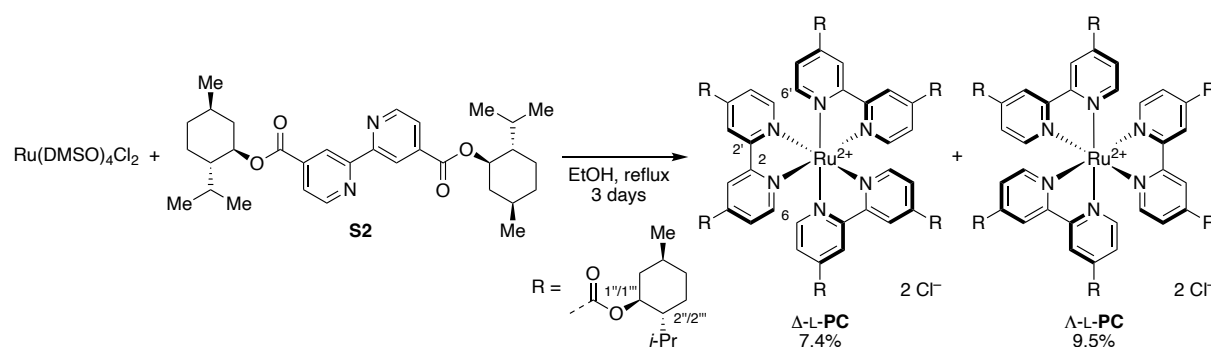
2. Catalyst Synthesis

Bis((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) [2,2'-bipyridine]-4,4'-dicarboxylate (L-menbpy, **S2**)



Adapting a literature procedure,^[1] a mixture of [2,2'-bipyridine]-4,4'-dicarboxylic acid (977 mg, 4.00 mmol, 1.0 equiv.) and SOCl₂ (16 mL, 220 mmol, 55.0 equiv.) was heated to reflux for 22 h until a yellow solution had formed. Excess SOCl₂ was removed by normal pressure distillation and the residue was dried *in vacuo*. [2,2'-Bipyridine]-4,4'-dicarbonyl dichloride (**S3**) was obtained in quantitative yield as a yellow solid and directly used without purification: ¹H NMR (400.1 MHz, CDCl₃): δ 9.07 (2H, s, C3*H*, C3'*H*), 8.96 (2H, d, *J* = 5.0 Hz, C6*H*, C6'*H*), 7.97 (2H, dd, *J* = 5.0, 1.2 Hz, C5*H*, C5'*H*); ¹³C{¹H} NMR (100.0 MHz, CDCl₃): δ 167.9 (COCl), 156.4 (C2, C2'), 150.8 (C6, C6'), 141.6 (C4, C4'), 123.9 (C5, C5'), 121.4 (C3, C3'). Et₃N (309 μL, 2.20 mmol, 2.2 equiv.) was added to a solution of **S1** (281 mg, 1.00 mmol, 1.0 equiv.) and L-(–)-menthol (313 mg, 2.00 mmol, 2.0 equiv.) in CH₂Cl₂ (10 mL). The reaction mixture was stirred at room temperature for 36 h and then filtered through a pad of celite, which was washed with CH₂Cl₂. The filtrate was evaporated under reduced pressure, and diester **S2** was isolated by flash column chromatography on silica gel (cyclohexane/ethyl acetate 98:2→80:20) providing it as a colorless solid (427 mg, 820 μmol, 82%): m.p. 166–168 °C; *R*_f 0.35 (cyclohexane/ethyl acetate 9:1); ¹H NMR (500.1 MHz, CDCl₃): δ 8.93 (2H, dd, *J* = 1.6, 0.8 Hz, C3*H*, C3'*H*), 8.87 (2H, dd, *J* = 5.0, 0.8 Hz, C6*H*, C6'*H*), 7.91 (2H, dd, *J* = 5.0, 1.6 Hz, C5*H*, C5'*H*), 5.03 (2H, ddd, *J* = 10.9, 10.9, 4.5 Hz, C1''*H*, C1'''*H*), 2.16–2.11 (2H, m, C6''*H*_{eq}, C6'''*H*_{eq}), 2.00–1.89 (2H, m, C2''*CH*, C2'''*CH*), 1.79–1.70 (4H, m, C3''*H*_{eq}, C4''*H*_{eq}, C3'''*H*_{eq}, C4'''*H*_{eq}), 1.66–1.53 (4H, m, C2''*H*_{ax}, C5''*H*_{ax}, C2'''*H*_{ax}, C5'''*H*_{ax}), 1.23–1.10 (4H, m, C3''*H*_{ax}, C6''*H*_{ax}, C3'''*H*_{ax}, C6'''*H*_{ax}), 1.00–0.91 (14H, m, C5''*H*, C5'''*H*, C5''*CH*₃, C5'''*CH*₃, CHCH₃), 0.81 (6H, d, *J* = 7.0 Hz, CHCH₃); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 164.7 (CO), 156.6 (C4, C4'), 150.1 (C6, C6'), 139.3 (C2, C2'), 123.2 (C5, C5'), 120.6 (C3, C3'), 76.0 (C1'', C1'''), 47.1 (C2'', C2'''), 40.8 (C6'', C6'''), 34.2 (C4'', C4'''), 31.5 (C5'', C5'''), 26.5 (CH(CH₃)₂), 23.5 (C3'', C3'''), 22.0 (C5''*CH*₃, C5'''*CH*₃), 20.8 (CHCH₃), 16.4 (CHCH₃); IR (ATR): $\tilde{\nu}$ 2953m, 2923m, 2871w, 1719s, 1557w, 1453w, 1366s, 1285s, 1250s, 1128s, 955m, 914m, 764m, 692m; HRMS (ESI⁺): *m/z* calcd. for C₃₂H₄₅N₂O₄⁺ ([M+H]⁺) 521.3374, found 521.3381.

[Ru(L-menbpy)₃Cl₂] (L-PC)

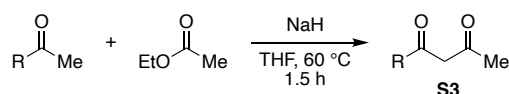


Combining two literature procedures,^[2] a mixture of Ru(DMSO)₄Cl₂ (48.4 mg, 100 μmol, 1.0 equiv.) and L-menbpy (**S2**, 156 mg, 300 μmol, 3.0 equiv.) in ethanol (10 mL) was heated to reflux under argon for three days. The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel (CHCl₃/MeOH 95:5) to provide a diastereomeric mixture of the Δ- and Λ-isomers. Repeated column chromatography on silica gel (two times with CHCl₃/MeOH 95:5, three times with CH₂Cl₂/*i*-PrOH 9:1) provided diastereomerically pure Δ-L-PC (12.8 mg, 7.38 μmol, 7.4%) and Λ-L-PC (16.4 mg, 9.46 μmol, 9.5%) as red

solids. Analytical data for Δ -[Ru(L-menbpy)₃]Cl₂ (Δ -L-**PC**): *R*_f 0.36 (CHCl₃/MeOH 9:1); ¹H NMR (500.1 MHz, CDCl₃): δ 8.82 (6H, s, C3*H*, C3'*H*), 8.57 (6H, br, C6*H*, C6'*H*), 8.10 (6H, d, *J* = 5.6 Hz, C5*H*, C5'*H*), 4.99 (6H, ddd, *J* = 10.9, 10.9, 4.4 Hz, C1''*H*_{ax}, C1'''*H*_{ax}), 2.14–2.07 (6H, m, C6''*H*_{eq}, C6'''*H*_{eq}), 1.86–1.77 (6H, m, C2''*CH*, C2'''*CH*), 1.77–1.69 (12H, m, C3''*H*_{eq}, C4''*H*_{eq}, C3'''*H*_{eq}, C4'''*H*_{eq}), 1.58–1.50 (12H, m, C2''*H*_{ax}, C5''*H*_{ax}, C2'''*H*_{ax}, C5'''*H*_{ax}), 1.21–1.06 (12H, m, C3''*H*_{ax}, C6''*H*_{ax}, C3'''*H*_{ax}, C6'''*H*_{ax}), 0.98–0.85 (42H, m, C4''*H*_{ax}, C5''*CH*₃, C4'''*H*_{ax}, C5'''*CH*₃, CHCH₃), 0.76 (18H, d, *J* = 6.9 Hz, CHCH₃); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 162.7 (CO), 155.9 (C6, C6'), 155.7 (HMBC, C4, C4'), 139.6 (C2, C2'), 127.8 (C5, C5'), 122.1 (C3, C3'), 77.5 (C1'', C1'''), 46.9 (C2'', C2'''), 40.6 (C6'', C6'''), 34.0 (C4'', C4'''), 31.5 (C5'', C5'''), 26.4 (CH(CH₃)₂), 23.4 (C3'', C3'''), 21.9 (C5''*CH*₃, C5'''*CH*₃), 20.7 (CHCH₃), 16.4 (CHCH₃); IR (ATR): $\tilde{\nu}$ 2954m, 2870m, 1719s, 1456w, 1408w, 1237s, 1128s, 954m, 845w, 764m; HRMS (ESI⁺): *m/z* calcd. for C₉₆H₁₃₂N₆O₁₂Ru²⁺ (M²⁺) 831.4470, found 831.4480. Analytical data for Λ -[Ru(L-menbpy)₃]Cl₂ (Λ -L-**PC**): *R*_f 0.25 (CHCl₃/MeOH 9:1); ¹H NMR (500.1 MHz, CDCl₃): δ 8.80 (6H, d, *J* = 1.1 Hz, C3*H*, C3'*H*), 8.63 (6H, d, *J* = 5.5 Hz, C6*H*, C6'*H*), 8.05 (6H, dd, *J* = 5.5, 1.6 Hz, C5*H*, C5'*H*), 5.02 (6H, ddd, *J* = 10.9, 10.9, 4.4 Hz, C1''*H*_{ax}, C1'''*H*_{ax}), 2.09–2.02 (6H, m, C6''*H*_{eq}, C6'''*H*_{eq}), 1.98–1.89 (6H, m, C2''*CH*, C2'''*CH*), 1.79–1.69 (12H, m, C3''*H*_{eq}, C4''*H*_{eq}, C3'''*H*_{eq}, C4'''*H*_{eq}), 1.60–1.51 (12H, m, C2''*H*_{ax}, C5''*H*_{ax}, C2'''*H*_{ax}, C5'''*H*_{ax}), 1.17–1.04 (12H, m, C3''*H*_{ax}, C6''*H*_{ax}, C3'''*H*_{ax}, C6'''*H*_{ax}), 0.96–0.87 (42H, m, C4''*H*_{ax}, C5''*CH*₃, C4'''*H*_{ax}, C5'''*CH*₃, CHCH₃), 0.80 (18H, d, *J* = 6.9 Hz, CHCH₃); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 162.7 (CO), 156.0 (C6, C6'), 155.9 (C4, C4'), 139.6 (C2, C2'), 127.5 (C5, C5'), 122.1 (C3, C3'), 77.4 (C1'', C1'''), 47.0 (C2'', C2'''), 40.7 (C6'', C6'''), 34.0 (C4'', C4'''), 31.5 (C5'', C5'''), 26.1 (CH(CH₃)₂), 23.1 (C3'', C3'''), 22.0 (C5''*CH*₃, C5'''*CH*₃), 20.9 (CHCH₃), 16.1 (CHCH₃); IR (ATR): $\tilde{\nu}$ 2928m, 2869m, 1719s, 1456w, 1407m, 1245s, 1128s, 955m, 845w, 764m; HRMS (ESI⁺): *m/z* calcd. for C₉₆H₁₃₂N₆O₁₂Ru²⁺ (M²⁺) 831.4470, found 831.4484.

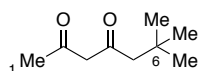
3. Substrate Synthesis

General Procedure A: Claisen Condensation to 1,3-Diketones



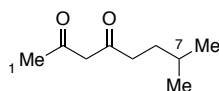
Following an adapted literature procedure,^[3] the respective ketone (50.0 mmol, 1.0 equiv.) was added to a mixture of NaH (60% in mineral oil, 6.00 g, 150 mmol, 3.0 equiv.) in THF (100 mL). The reaction mixture was stirred at room temperature for 15 min before ethyl acetate (8.79 mL, 90.0 mmol, 1.8 equiv.) was added. After stirring under reflux for 1 h (gas evolution!), the reaction mixture was cooled to 0 °C, and sat. aq. NH₄Cl solution (50 mL) was added. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3x50 mL). The combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, filtered and evaporated under reduced pressure, and the diketone **S3** was purified by column chromatography on silica gel.

6,6-Dimethylheptane-2,4-dione (**S3a**)



Following the general procedure **A**, the reaction of 4,4-dimethyl-2-pentanone (3.55 mL, 25.0 mmol, 1.0 equiv.), NaH (60% in mineral oil, 3.00 g, 75.0 mmol, 3.0 equiv.) and ethyl acetate (4.40 mL, 45.0 mmol, 1.8 equiv.) in THF (50 mL) provided the title compound after filtration through silica gel (cyclohexane/ethyl acetate 95:5) as a yellow liquid (3.86 g, 24.7 mmol, 99%). In CDCl₃ solution, **S3a** exists as a 15.8:1 mixture of the enol and keto form, only the NMR signals of the enol form are given: *R*_f 0.30 (cyclohexane/ethyl acetate 95:5); ¹H NMR (500.1 MHz, CDCl₃): δ 15.63 (1H, s, OH), 5.44 (1H, s, C3H), 2.12 (2H, s, C5H), 2.07 (3H, s, C1H), 1.01 (1H, m, C6(CH₃)₃); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 193.7 (C2), 190.8 (C4), 102.0 (C3), 51.3 (C5), 31.7 (C6), 29.9 (C6(CH₃)₃), 25.8 (C1); IR (ATR): ν̄ 3422br, 2594m, 2870m, 1709m, 1588s, 1527s, 1466m, 1365s, 1232m, 1023w, 970w, 772w, 669w; HRMS (ESI⁺): *m/z* calcd. for C₉H₁₆NaO₂⁺ ([M+Na]⁺) 179.1043, found 179.1039.

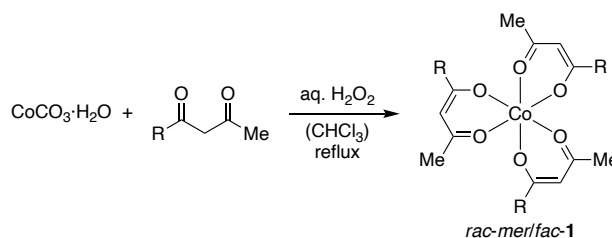
7-Methyloctane-2,4-dione (**S3b**)



Following the general procedure **A**, the reaction of 5-methyl-2-hexanone (7.04 mL, 50.0 mmol, 1.0 equiv.), NaH (60% in mineral oil, 6.00 g, 150 mmol, 3.0 equiv.) and ethyl acetate (8.79 mL, 90.0 mmol, 1.8 equiv.) in THF (100 mL) provided the title compound after flash column chromatography on silica gel (cyclohexane/ethyl acetate 98:2→93:7) as a pale yellow liquid (5.12 g, 32.8 mmol, 66%). In CDCl₃ solution, **S3b** exists as a 6.2:1 mixture of the enol and keto form, only the NMR signals of the enol form are given: *R*_f 0.28 (cyclohexane/ethyl acetate 95:5); ¹H NMR (500.1 MHz, CDCl₃): δ 15.51 (1H, s, OH), 5.50 (1H, s, C3H), 2.29–2.23 (2H, m, C5H), 2.05 (3H, s, C1H), 1.63–1.52 (1H, m, C7H), 1.52–1.45 (2H, m, C6H), 0.91 (6H, d, *J* = 6.6 Hz, C7(CH₃)₂); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 194.7 (C4), 191.3 (C2), 99.7 (C3), 36.3 (C5), 34.6 (C6), 27.7 (C7), 24.9 (C1), 22.3 (C7(CH₃)₂); IR (ATR): ν̄ 2958m, 1506s, 1466m, 1238m, 1101w, 922m, 782m; HRMS (ESI⁺): *m/z* calcd. for C₉H₁₆NaO₂⁺ ([M+Na]⁺) 179.1043, found 179.1042.

1-Cyclohexylbutane-1,3-dione was prepared according to a literature procedure.^[3]

General Procedure B: Preparation of Cobalt(III) Diketonates



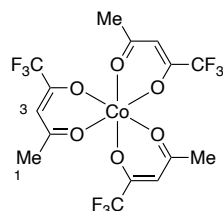
General Procedure B1: Neat Reaction

35% Aq. H_2O_2 (1.61 mL, 20.0 mmol, 20.0 equiv.) was added dropwise to a stirred mixture of $\text{CoCO}_3 \cdot \text{H}_2\text{O}$ (137 mg, 1.00 mmol, 1.0 equiv.) and the respective diketone (3.00 mmol, 3.0 equiv.) at room temperature. After complete addition, the resulting mixture was heated to 100 °C over night, before it was cooled to room temperature, diluted with ethanol (10 mL) and filtered through celite. Water (20 mL) was added and the resulting mixture was extracted with CHCl_3 (5x10 mL). The combined extracts were dried over Na_2SO_4 , filtered and evaporated under reduced pressure. Column chromatography on silica gel provided the respective cobalt(III) diketonate **1** as a mixture of the *mer*- and *fac*-diastereomers, which were separated by preparative TLC on silica gel.

General Procedure B2: Reaction in CHCl_3

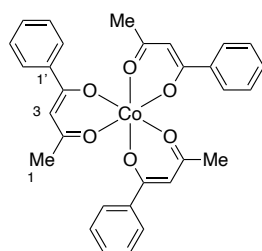
35% Aq. H_2O_2 (1.61 mL, 20.0 mmol, 20.0 equiv.) was added dropwise to a stirred mixture of $\text{CoCO}_3 \cdot \text{H}_2\text{O}$ (137 mg, 1.00 mmol, 1.0 equiv.) and the respective diketone (3.00 mmol, 3.0 equiv.) in CHCl_3 (5 mL) at room temperature. After complete addition, the resulting mixture was heated to reflux over night, before it was cooled to room temperature and washed with water (3x2 mL). The organic layer was dried over Na_2SO_4 , filtered and evaporated under reduced pressure. Column chromatography on silica gel provided the respective cobalt(III) diketonate **1** as a mixture of the *mer*- and *fac*-diastereomers, which were separated by preparative TLC on silica gel.

$\text{Co}(\text{tfac})_3$ (**1a**)



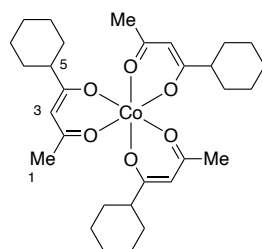
Following a modified general procedure **B1**, the reaction of $\text{Co}(\text{CO}_3) \cdot \text{H}_2\text{O}$ (137 mg, 1.00 mmol, 1.0 equiv.) with 1,1,1-trifluoropentane-2,4-dione (1.46 mL, 12.0 mmol, 12.0 equiv.) and 10% aq. H_2O_2 (283 μL , 10.0 mmol, 10.0 equiv.) provided the title compound after column chromatography on silica gel (toluene) as a green solid (366 mg, 706 μmol , 71%, 12.7:1 d.r. (*mer*/*fac*)). The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene). Analytical data for *mer*-**1a**: R_f 0.33 (cyclohexane/toluene 2:5); ^1H NMR (500.1 MHz, CDCl_3): δ 6.07 (1H, s, C3H), 6.05 (1H, s, C3H), 6.01 (1H, s, C3H), 2.45 (1H, s, C1H), 2.44 (1H, s, C1H), 2.40 (1H, s, C1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 199.4 (C2), 199.0 (C2), 198.8 (C2), 172.2–168.9 (C4), 177.7–111.0 (HMBC, m, C5), 94.3 (C3), 94.1 (C3), 94.0 (C3), 27.8 (C1), 27.8 (C1), 27.5 (C1); $^{19}\text{F}\{^1\text{H}\}$ NMR (470.6 MHz, CDCl_3): δ -73.5, -73.6, -73.7; IR (ATR): $\tilde{\nu}$ 1600s, 1524m, 1449w, 1363w, 1288s, 1193s, 1132s, 1012w, 954w, 872m, 791m, 738m, 655m; HRMS (ESI⁺): m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{CoF}_9\text{NaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 540.9714, found 540.9712; HPLC (Chiralpak IA (5 μm , 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 10 °C): Rt 11.2 (Δ), 13.6 (Δ). Analytical data for *fac*-**1a**: R_f 0.22 (cyclohexane/toluene 2:5); ^1H NMR (500.1 MHz, CDCl_3): δ 6.03 (3H, s, C3H), 2.41 (9H, s, C1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 198.4 (C2), 171.2 (q, J = 35.1 Hz, C4), 114.1 (HMBC, q, J = 283.1 Hz, C5), 94.0 (C3), 27. (C1); $^{19}\text{F}\{^1\text{H}\}$ NMR (376.5 MHz, CDCl_3): δ -73.5; IR (ATR): $\tilde{\nu}$ 1600s, 1525m, 1443m, 1366w, 1283s, 1192s, 1127s, 1025w, 957w, 873m, 786m, 739m, 655m; HRMS (ESI⁺): m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{CoF}_9\text{NaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 540.9714, found 540.9718; HPLC (Chiralpak IA (5 μm , 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 10 °C): Rt 10.1 (Δ), 12.3 (Δ).

Co(bzac)₃ (**1b**)



Following the general procedure **B2**, the reaction of Co(CO₃)·H₂O (137 mg, 1.00 mmol, 1.0 equiv.) with 1-phenylbutane-1,3-dione (446 μ L, 3.00 mmol, 3.0 equiv.) and 35% aq. H₂O₂ (1.62 mL, 20.0 mmol, 20.0 equiv.) in CHCl₃ (5 mL) provided the title compound after column chromatography on silica gel (toluene/*i*-PrOH 100:0→100:2) as a green solid (119 mg, 219 μ mol, 22%, 7.5:1 d.r. (*mer/fac*)). The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene/*i*-PrOH 50:1). Analytical data for *mer*-**1b**: *R*_f 0.33 (toluene/*i*-PrOH 50:1); ¹H NMR (500.1 MHz, CDCl₃): δ 7.88–7.83 (6H, m, C2'*H*, C6'*H*), 7.44–7.38 (3H, m, C4'*H*), 7.35–7.29 (m, C3'*H*, C5'*H*), 6.24 (1H, s, C3*H*), 6.23 (1H, s, C3*H*), 6.21 (1H, s, C3*H*), 2.38 (3H, s, C1*H*), 2.37 (3H, s, C1*H*), 2.35 (3H, s, C1*H*); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 191.8 (C2), 191.7 (C2), 191.5 (C2), 182.7 (C4), 182.5 (C4), 182.3 (C4), 137.1 (C4'), 137.0 (C4'), 136.9 (C4'), 131.1 (C1'), 131.0 (C1'), 131.0 (C1'), 128.1 (C3', C5'), 128.0 (C3', C5'), 128.0 (C3', C5'), 127.6 (C2', C6'), 127.5 (C2', C6'), 127.5 (C2', C6'), 94.7 (C3), 94.5 (C3), 94.2 (C3), 27.0 (C1), 27.0 (C1), 26.8 (C1); IR (ATR): $\tilde{\nu}$ 3062w, 2923w, 1587m, 1551s, 1512s, 1450m, 1376s, 1305m, 1028w, 910w, 860w, 715m; HRMS (ESI⁺): *m/z* calcd. for C₃₀H₂₇CoNaO₆⁺ ([M+Na]⁺) 565.1032, found 565.1033; HPLC (Chiralpak IC-3 (3 μ m, 250x4.6 mm), heptane/*i*-PrOH 95:5, 1.0 mL/min, 40 °C): *R*_t 10.5, 13.1. Analytical data for *fac*-**1b**: *R*_f 0.21 (toluene/*i*-PrOH 50:1); ¹H NMR (500.1 MHz, CDCl₃): δ 7.90–7.87 (6H, m, C2'*H*, C6'*H*), 7.45–7.40 (m, 3H, C4'*H*), 7.36–7.31 (6H, m, C3'*H*, C5'*H*), 6.23 (3H, s, C3*H*), 2.33 (9H, s, C1*H*); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 191.3 (C2), 182.6 (C4), 137.0 (C1'), 131.0 (C4'), 128.1 (C3', C5'), 127.5 (C2', C6'), 94.4 (C3), 26.8 (C1); IR (ATR): $\tilde{\nu}$ 3063w, 2923w, 1588m, 1553s, 1516s, 1450m, 1378s, 1305m, 1028w, 909w, 860w, 714m; HRMS (ESI⁺): *m/z* calcd. for C₃₀H₂₇CoNaO₆⁺ ([M+Na]⁺) 565.1032, found 565.1041; HPLC (Chiralpak IC-3 (3 μ m, 250x4.6 mm), heptane/*i*-PrOH 95:5, 1.0 mL/min, 40 °C): *R*_t 9.0, 11.5.

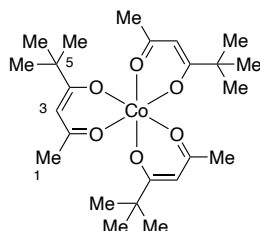
Co(cycac)₃ (**1c**)



Following the general procedure **B2**, the reaction of Co(CO₃)·H₂O (34.2 mg, 250 μ mol, 1.0 equiv.) with 1-cyclohexylbutane-1,3-dione (126 mg, 750 μ mol, 3.0 equiv.) and 35% aq. H₂O₂ (404 μ L, 5.00 mmol, 20.0 equiv.) in CHCl₃ (1.3 mL) provided the title compound after column chromatography on silica gel (toluene/*i*-PrOH 100:0→100:4) as a green oil (35.2 mg, 63.0 μ mol, 25%, 8.2:1 d.r. (*mer/fac*)). The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene/*i*-PrOH 25:1). Analytical data for *mer*-**1c**: *R*_f 0.48 (toluene/*i*-PrOH 25:1); ¹H NMR (500.1 MHz, CDCl₃): δ 5.50 (1H, s, C3*H*), 5.49 (1H, s, C3*H*), 5.41 (1H, s, C3*H*), 2.40–2.32 (3H, m), 2.20 (6H, s, C1*H*), 2.13 (3H, s, C1*H*), 1.85–1.58 (15H, m), 1.44–1.11 (15H, m); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 195.9 (C4), 195.8 (C4), 195.5 (C4), 189.9 (C2), 189.8 (C2), 189.1 (C2), 94.5 (C3), 94.2 (C3), 93.5 (C3), 48.1 (C5), 48.1 (C5), 48.0 (C5), 31.4 (CH₂), 31.3 (CH₂), 31.0 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 30.1 (CH₂), 26.5 (C1), 26.5 (C1), 26.3 (CH₂), 26.20 (CH₂), 26.1 (CH₂), 26.1 (CH₂), 26.0 (C1, CH₂), 26.0 (CH₂), 25.9 (CH₂), 25.9 (CH₂); IR (ATR): $\tilde{\nu}$ 2923m, 2853m, 1570s, 1515s, 1397s, 1174w, 1027w, 728w; HRMS (ESI⁺): *m/z* calcd. for C₃₀H₄₅CoNaO₆⁺ ([M+Na]⁺) 583.2440, found 583.2444; HPLC (Chiralpak IC-3 (3 μ m, 250x4.6 mm), heptane/*i*-PrOH 99:1, 1.0 mL/min, 40 °C): *R*_t 5.8 (Λ), 8.4 (Δ). Analytical data for *fac*-**1c**: *R*_f 0.26 (toluene/*i*-PrOH 25:1); ¹H NMR (500.1 MHz, CDCl₃): δ 5.46 (3H, s, C3*H*), 2.37–2.30 (3H, m, C5*H*), 2.14 (9H, s, C1*H*), 1.80–1.70

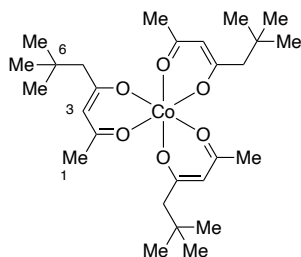
(12H, m), 1.65–1.62 (3H, m), 1.43–1.34 (6H, m), 1.31–1.13 (10H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 196.2 (C4), 189.1 (C2), 94.4 (C3), 47.9 (C5), 30.9 (CH_2), 30.2 (CH_2), 26.1 (CH_2), 26.0 (C1), 26.0 (CH_2), 25.8 (CH_2); IR (ATR): $\tilde{\nu}$ 2928m, 2853m, 1572s, 1517s, 1400s, 1174w, 1026w, 761w; HRMS (ESI^+): m/z calcd. for $\text{C}_{30}\text{H}_{45}\text{CoNaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 583.2440, found 583.2449; HPLC (Chiralpak IC-3 (3 μm , 250x4.6 mm), heptane/*i*-PrOH 99:1, 1.0 mL/min, 40 $^\circ\text{C}$): Rt 7.1 (Δ), 8.6 (Λ).

Co(pivac)₃ (1d)



Following the general procedure **B2**, the reaction of $\text{Co}(\text{CO}_3)\cdot\text{H}_2\text{O}$ (137 mg, 1.00 mmol, 1.0 equiv.) with 5,5-dimethylhexane-2,4-dione (391 μL , 3.00 mmol, 3.0 equiv.) and 35% aq. H_2O_2 (1.62 mL, 20.0 mmol, 20.0 equiv.) in CHCl_3 (5 mL) provided the title compound after column chromatography on silica gel (toluene/*i*-PrOH 100:0 $\rightarrow$ 100:3) as a green oil (40.8 mg, 85.0 μmol , 8.5%, 2.6:1 d.r. (*mer/fac*)). The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene/*i*-PrOH 25:1). Analytical data for *mer*-**1d**: R_f 0.26 (toluene/*i*-PrOH 50:1); ^1H NMR (500.1 MHz, CDCl_3): δ 5.64 (1H, s, C3H), 5.62 (1H, s, C3H), 5.50 (1H, s, C3H), 2.24 (3H, s, C1H), 2.17 (3H, s, C1H), 2.12 (3H, s, C1H), 1.11 (9H, s, C5(CH_3)₃), 1.11 (9H, s, C5(CH_3)₃), 1.09 (9H, s, C5(CH_3)₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 198.5 (C4), 198.3 (C4), 190.4 (C2), 189.0 (C2), 189.0 (C2), 93.2 (C3), 92.3 (C3), 91.2 (C3), 40.2 (C5), 40.1 (C5), 28.5 (C5(CH_3)₃), 28.4 (C5(CH_3)₃), 28.2 (C5(CH_3)₃), 26.7 (C1), 26.4 (C1), 26.0 (C1); IR (ATR): $\tilde{\nu}$ 2962m, 2870w, 1569s, 1507s, 1386s, 1284w, 1232w, 1168w, 1021w, 898w, 767w, 664w; HRMS (ESI^+): m/z calcd. for $\text{C}_{24}\text{H}_{39}\text{CoNaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 505.1971, found 505.1976; HPLC (Chiralpak IC-3 (3 μm , 250x4.6 mm), heptane/*i*-PrOH 99:1, 1.0 mL/min, 5 $^\circ\text{C}$): Rt 9.0 (Δ), 9.6 (Λ). Analytical data for *fac*-**1d**: R_f 0.13 (toluene/*i*-PrOH 50:1); ^1H NMR (500.1 MHz, CDCl_3): δ 5.57 (3H, s, C3H), 2.15 (9H, s, C1H), 1.11 (27H, s, C5(CH_3)₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 198.6 (C4), 189.4 (C2), 92.0 (C3), 40.2 (C5), 28.3 (C5(CH_3)₃), 26.3 (C1); IR (ATR): $\tilde{\nu}$ 2962m, 2870w, 1568s, 1506s, 1385s, 1285w, 1233m, 1168m, 1021w, 898m, 767m, 664m; HRMS (ESI^+): m/z calcd. for $\text{C}_{24}\text{H}_{39}\text{CoNaO}_6^+$ ($[\text{M}+\text{Na}]^+$) 505.1971, found 505.1979; HPLC (Chiralpak IC-3 (3 μm , 250x4.6 mm), heptane/*i*-PrOH 99:1, 1.0 mL/min, 5 $^\circ\text{C}$): Rt 12.3 (Δ), 13.7 (Λ).

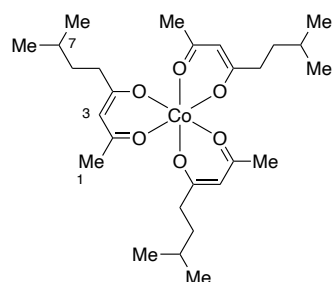
Co(dmbac)₃ (1e)



Following the general procedure **B1**, the reaction of $\text{Co}(\text{CO}_3)\cdot\text{H}_2\text{O}$ (137 mg, 1.00 mmol, 1.0 equiv.) with 6,6-dimethylheptane-2,4-dione (469 mg, 3.00 mmol, 3.0 equiv.) and 35% aq. H_2O_2 (1.62 mL, 20.0 mmol, 20.0 equiv.) provided the title compound after column chromatography on silica gel (toluene/*i*-PrOH 100:0 $\rightarrow$ 100:2) as a green oil (201 mg, 383 μmol , 38%, 2.0:1 d.r. (*mer/fac*)). The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene/*i*-PrOH 25:1). Analytical data for *mer*-**1e**: R_f 0.34 (toluene/*i*-PrOH 50:1); ^1H NMR (500.1 MHz, CDCl_3): δ 5.43 (1H, s, C1H), 5.43 (1H, s, C1H), 5.42 (1H, s, C1H), 2.39 (1H, d, J = 11.8 Hz, C5H), 2.34 (1H, d, J = 12.1 Hz, C5H), 2.23 (1H, d, J = 12.4 Hz, C5H), 2.17 (3H, s, C1H), 2.16–2.10 (5H, m, C1H, C5H), 2.10 (3H, s, C1H), 0.95 (9H, s, C6(CH_3)₃), 0.93 (9H, s, C6(CH_3)₃), 0.90 (9H, s, C6(CH_3)₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 191.5 (C4), 191.3 (C4), 191.2 (C4), 188.9 (C2), 188.8 (C2), 188.5 (C2), 98.7 (C3), 98.6 (C3), 98.6 (C3), 53.0 (C5), 52.7 (C5), 52.7 (C5), 32.1 (C6), 32.0 (C6), 32.0 (C6), 29.9 (C6(CH_3)₃), 29.9 (C6(CH_3)₃), 26.2 (C1), 26.0 (C1), 25.8 (C1); IR (ATR): $\tilde{\nu}$ 2952m, 2867w, 1569s, 1514s, 1387s, 1281w, 1232w,

1137w, 1024w, 911m, 727m, 640m; HRMS (ESI⁺): m/z calcd. for C₂₇H₄₅CoNaO₆⁺ ([M+Na]⁺) 547.2440, found 547.2446; HPLC (Chiralpak IG-3 (3 μm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 40 °C): Rt 7.0 (Δ), 7.3 (Δ). Analytical data for *fac*-**1e**: R_f 0.11 (toluene/*i*-PrOH 50:1); ¹H NMR (500.1 MHz, CDCl₃): δ 5.42 (3H, s, C3H), 2.37 (3H, d, J = 11.9 Hz, C5H), 2.12 (9H, s, C1H), 2.12 (3H, d, J = 11.9 Hz, C5H), 0.90 (27H, s, C6(CH₃)₃); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 191.4 (C4), 188.5 (C2), 98.4 (C3), 52.9 (C5), 32.0 (C6), 29.9 (C6(CH₃)₃), 25.9 (C1); IR (ATR): $\tilde{\nu}$ 2953m, 2867w, 1570s, 1515s, 1389s, 1281w, 1232w, 1138w, 1024w, 909m, 726m, 641m; HRMS (ESI⁺): m/z calcd. for C₂₇H₄₅CoNaO₆⁺ ([M+Na]⁺) 547.2440, found 547.2449; HPLC (Chiralpak IG-3 (3 μm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 40 °C): Rt 7.3 (Δ), 7.8 (Δ).

Co(mpac)₃ (**1f**)



Following the general procedure **B1**, the reaction of Co(CO₃)·H₂O (137 mg, 1.00 mmol, 1.0 equiv.) with 7-methyloctane-2,4-dione (469 mg, 3.00 mmol, 3.0 equiv.) and 35% aq. H₂O₂ (1.62 mL, 20.0 mmol, 20.0 equiv.) provided the title compound after column chromatography on silica gel (toluene/*i*-PrOH 100:0→100:2) as a green oil (280 mg, 534 μmol, 53%, 2.2:1 d.r. (*mer*/*fac*)). The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene/*i*-PrOH 20:1). Analytical data for *mer*-**1f**: R_f 0.37 (toluene/*i*-PrOH 25:1); ¹H NMR (500.1 MHz, CDCl₃): δ 5.52 (1H, s, C3H), 5.52 (1H, s, C3H), 5.46 (1H, s, C3H), 2.54–2.42 (3H, m, C5H), 2.36–2.27 (3H, m, C5H), 2.20 (6H, s, C1H), 2.14 (3H, s, C1H), 1.55–1.38 (9H, m, C6H, C7H), 0.87–0.83 (18H, m, C7(CH₃)₂); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 193.0 (C4), 192.8 (C4), 189.6 (C2), 189.6 (C2), 189.1 (C2), 96.5 (C3), 96.2 (C3), 95.8 (C3), 37.8 (C5), 37.8 (C5), 37.7 (C5), 6.3 (C6), 36.3 (C6), 36.1 (C6), 27.7 (C7), 27.7 (C7), 27.4 (C7), 26.3 (C1), 26.3 (C1), 25.9 (C1), 22.5 (C7CH₃), 22.4 (C7CH₃), 22.4 (C7CH₃), 22.3 (C7CH₃); IR (ATR): $\tilde{\nu}$ 2955m, 2869w, 1572s, 1516s, 1396s, 1277w, 1177w, 1102w, 1020w, 762w, 637w; HRMS (ESI⁺): m/z calcd. for C₂₇H₄₅CoNaO₆⁺ ([M+Na]⁺) 547.2440, found 547.2447; HPLC (Chiralpak IG-3 (3 μm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 40 °C): Rt 8.4 (Δ), 10.3 (Δ). Analytical data for *fac*-**1f**: R_f 0.21 (toluene/*i*-PrOH 25:1); ¹H NMR (500.1 MHz, CDCl₃): δ 5.49 (3H, s, C3H), 2.53–2.44 (3H, m, C5H), 2.38–2.30 (3H, m, C5H), 2.15 (9H, s, C1H), 1.53–1.38 (9H, m, C6H, C7H), 0.85 (18H, t, J = 5.9 Hz, C7(CH₃)₂); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 193.2 (C4), 189.1 (C2), 96.2 (C3), 37.7 (C5), 36.2 (C6), 27.4 (C7), 26.0 (C1), 22.5 (C7CH₃), 22.4 (C7CH₃); IR (ATR): $\tilde{\nu}$ 2955m, 2869w, 1572s, 1516s, 1396s, 1277w, 1178w, 1102w, 1020w, 762w, 637w; HRMS (ESI⁺): m/z calcd. for C₂₇H₄₅CoNaO₆⁺ ([M+Na]⁺) 547.2440, found 547.2444; HPLC (Chiralpak IG-3 (3 μm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 40 °C): Rt 8.8 (Δ), 10.5 (Δ).

4. Configurational Stability Evaluation

Thermodynamic Equilibrium between *mer*- and *fac*-Diastereomers

Samples of the cobalt(III) complexes **1a–f** in acetonitrile were heated to 80 °C until HPLC or NMR analysis showed a constant diastereomeric ratio (Table S1).

Table S1. Diastereomeric ratios in the thermodynamic equilibrium (MeCN, 80 °C).

Entry	Complex	d.r. (<i>mer/fac</i>)	Analysis method
1	1a	80:20	HPLC
2	1b	82:18	¹ H NMR
3	1c	78:22	HPLC
4	1d	58:42	HPLC
5	1e	66:34	HPLC
6	1f	70:30	HPLC

Configurational Stability of **1a**

A solution of *rac-mer-1a* (98:2 d.r., 518 µg, 1.00 µmol, 1.0 equiv.), Et₃N (0 or 3.0 equiv.) and tfacH (0 or 3.0 equiv.) in acetonitrile or CHCl₃ (0.2 mL) was irradiated with a Kessil PR160L-467nm lamp (40 W, 100% intensity, 10 cm distance) or stirred in the dark under air for 12 h. An aliquot was withdrawn from the reaction mixture, diluted with acetonitrile/water 3:1 and analyzed by HPLC (Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 50:50, 0.5 mL/min, 40 °C) to determine the diastereomeric ratio (Table S2).

Table S2. Evaluation of the configurational stability of **1a** under various conditions.

Entry ^a	Light	Solvent	Time [h]	Et ₃ N	tfacH	d.r. ^b (<i>mer/fac</i>)
1	Darkness	MeCN	12	0 equiv.	0 equiv.	100:0
2	Darkness	MeCN	12	3 equiv.	3 equiv.	— ^c
3	Darkness	MeCN	12	3 equiv.	0 equiv.	— ^c
4	Darkness	MeCN	12	0 equiv.	3 equiv.	100:0
5	Blue LED	MeCN	12	0 equiv.	0 equiv.	— ^c
6	Blue LED	MeCN	12	3 equiv.	3 equiv.	— ^c
7	Blue LED	MeCN	12	3 equiv.	0 equiv.	— ^c
8	Blue LED	MeCN	12	0 equiv.	3 equiv.	— ^c
9	Darkness	CHCl ₃	24	0 equiv.	0 equiv.	100:0
10	Darkness	CHCl ₃	24	3 equiv.	3 equiv.	99:1
11	Darkness	CHCl ₃	24	3 equiv.	0 equiv.	100:0
12	Darkness	CHCl ₃	24	0 equiv.	3 equiv.	99:1
13	Blue LED	CHCl ₃	6	0 equiv.	0 equiv.	95:5
14	Blue LED	CHCl ₃	6	3 equiv.	3 equiv.	83:17
15	Blue LED	CHCl ₃	6	3 equiv.	0 equiv.	81:19
16	Blue LED	CHCl ₃	6	0 equiv.	3 equiv.	93:7
17	Blue LED	CHCl ₃	10	0 equiv.	0 equiv.	93:7
18	Blue LED	CHCl ₃	10	3 equiv.	3 equiv.	58:42
19	Blue LED	CHCl ₃	10	3 equiv.	0 equiv.	62:38
20	Blue LED	CHCl ₃	10	0 equiv.	3 equiv.	91:9

^a Reaction conditions: *rac-mer-1a* (1.00 µmol, 1.0 equiv.), Et₃N (0 or 3.0 equiv.), tfacH (0 or 3.0 equiv.), MeCN or CHCl₃ (5 mmol/L), blue LED (467 nm) or darkness, r.t., 6–12 h. ^b Determined by HPLC. ^c Complete decomposition.

Preparation of Enantiomerically Highly Enriched **1a**

Stereoisomerically highly enriched samples (>99:1 d.r., >99:1 e.r.) of Λ -*mer*-**1a** and Λ -*fac*-**1a** (absolute configurations assigned by CD spectroscopy) were obtained by HPLC separation of the isolated diastereomers on a chiral stationary phase (Chiralpak IA (5 μ m, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 10 °C).

Thermal Stereoisomerization of **1a** at 90 °C

A stirred solution of Λ -*mer*-**1a** (>99:1 d.r., >99:1 e.r.) in heptane was heated to 90 °C. Aliquots were withdrawn in regular time intervals and analyzed by HPLC on a chiral stationary phase (Chiralpak IA (5 μ m, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 10 °C).

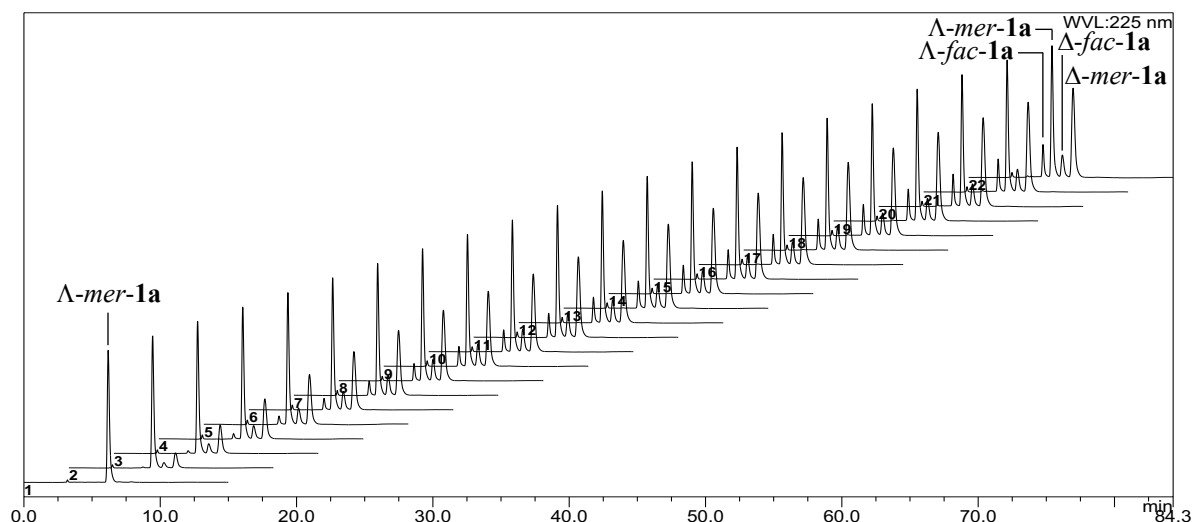


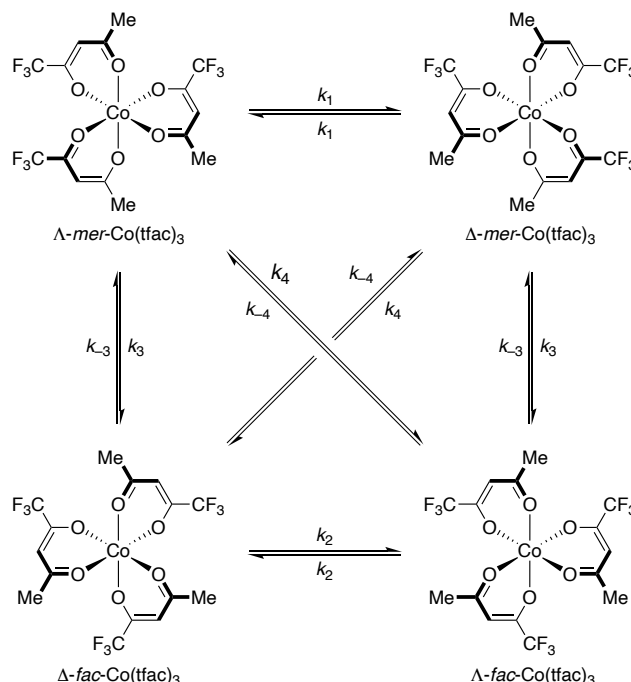
Figure S1. Overlay of the normalized HPLC traces of the thermal isomerization of **1a** at 90 °C in heptane.

Table S3. Uncorrected HPLC data of the thermal isomerization of **1a** at 90 °C in heptane.

Entry	Time [min]	Rel. Area [%]			
		Λ - <i>fac</i>	Λ - <i>mer</i>	Δ - <i>fac</i>	Δ - <i>mer</i>
1	0	0.08	98.99	0.47	0.45
2	10	0.40	81.80	4.21	13.58
3	20	1.10	70.28	6.55	22.07
4	30	2.02	62.29	7.95	27.74
5	40	2.88	56.78	8.77	31.56
6	50	3.69	52.93	9.18	34.20
7	60	4.42	50.59	9.31	35.68
8	70	5.13	48.06	9.50	37.30
9	80	5.77	46.52	9.46	38.25
10	90	6.23	45.40	9.46	38.91
11	100	6.67	44.53	9.43	39.37
12	110	7.02	43.91	9.31	39.76
13	120	7.33	43.34	9.25	40.08
14	130	7.56	42.94	9.16	40.33
15	140	7.78	42.67	9.06	40.49
16	150	7.94	42.39	8.95	40.71
17	160	8.08	42.22	8.89	40.82
18	170	8.17	42.03	8.85	40.95
19	180	8.26	41.90	8.81	41.03
20	190	8.32	41.83	8.74	41.11
21	200	8.35	41.70	8.75	41.20
22	210	8.41	41.63	8.68	41.27

Determination of the Thermal Isomerization Barriers at 90 °C

The stereoisomerization in **1a** can be described as an equilibrium between its four stereoisomers (Scheme S1). As an intramolecular mechanism is presumed, all reactions are expected to follow first-order kinetics.



Scheme S1. Possible macroscopically observable stereoisomerization reactions of **1a** with rate constants.

The kinetic situation is described by the following set of four differential equations:

$$\frac{d[\Lambda\text{-mer}]}{dt} = -(k_1 + k_3 + k_4)[\Lambda\text{-mer}] + k_1[\Delta\text{-mer}] + k_{-3}[\Delta\text{-fac}] + k_{-4}[\Delta\text{-fac}]$$

$$\frac{d[\Delta\text{-mer}]}{dt} = -(k_1 + k_3 + k_4)[\Delta\text{-mer}] + k_1[\Lambda\text{-mer}] + k_{-3}[\Lambda\text{-fac}] + k_{-4}[\Delta\text{-fac}]$$

$$\frac{d[\Lambda\text{-fac}]}{dt} = -(k_2 + k_{-3} + k_{-4})[\Lambda\text{-fac}] + k_2[\Delta\text{-fac}] + k_3[\Delta\text{-mer}] + k_4[\Lambda\text{-mer}]$$

$$\frac{d[\Delta\text{-fac}]}{dt} = -(k_2 + k_{-3} + k_{-4})[\Delta\text{-fac}] + k_2[\Lambda\text{-fac}] + k_3[\Lambda\text{-mer}] + k_4[\Delta\text{-mer}]$$

For the determination of the thermal isomerization barriers, the relative HPLC areas (Table S3) were corrected for differing absorption coefficients of the *mer*- and *fac*-diastereomers. Solving the set of differential equations given above by numeric integration/non-linear regression provided the rate constants k , from which the activation free energies $\Delta G^\ddagger$ were obtained using the Eyring equation

$$\Delta G^\ddagger = -RT \ln \left(\frac{kh}{k_B T} \right)$$

with the gas constant $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$, the temperature $T = 363.15 \text{ K}$ (90 °C), the Planck constant $h = 6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}$ and the Boltzmann constant $k_B = 1.381 \cdot 10^{-23} \text{ J/K}$. Corrected HPLC data, the result of the regression analysis, the rate constants and activation free energies for the stereoisomerization processes in **1a** are shown in Figure S2.

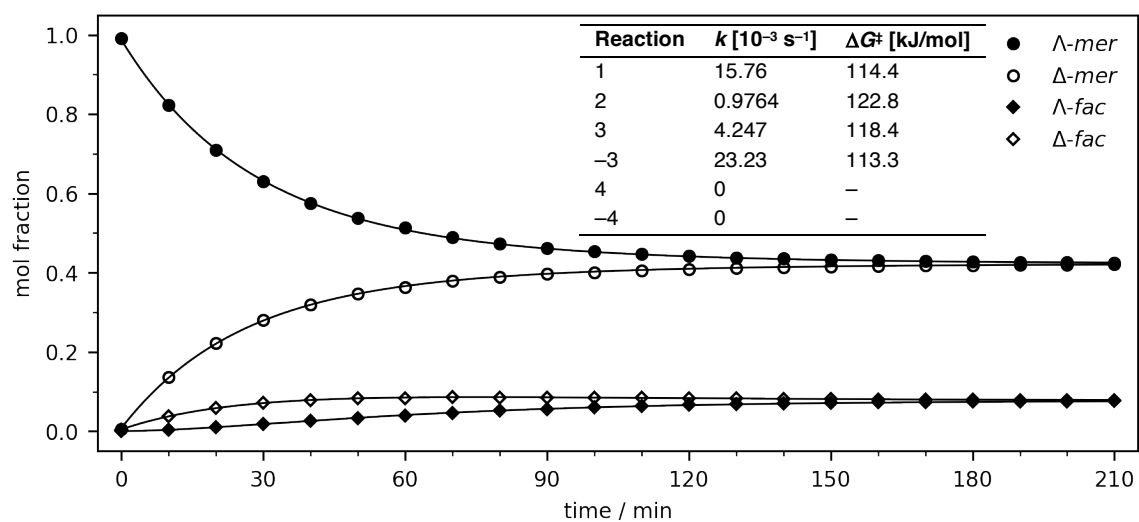


Figure S2. Thermal isomerization data of **1a** at 90 °C in heptane (markers) and solution of the rate equations obtained by numeric integration/non-linear regression (solid lines).

5. Acridinium Catalyzed Photostereoisomerization

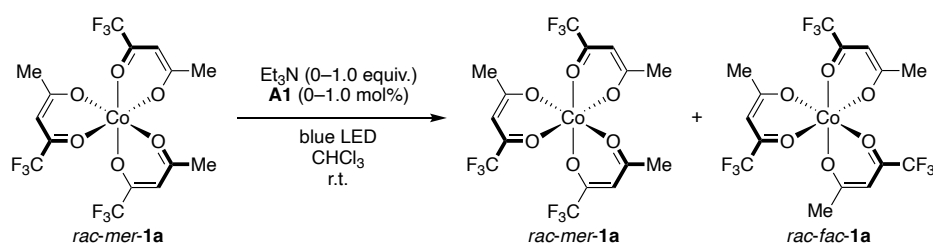
To probe the feasibility to photostereoisomerize fourfold stereogenic cobalt(III) complexes, solutions of *rac-mer-1a* were irradiated in the presence of acridinium photocatalysts.^[4] In an initial reaction progress analysis under air, in which the d.r. was measured over time, only small amounts of *fac-1a* formed in the presence of acridinium photocatalyst **A1** (1.0 mol%) within 4 h (Table S4, Figure S3). A slightly faster isomerization was observed in the presence of one equivalent of Et₃N in the absence of **A1**. Conversely, when both Et₃N and acridinium **A1** were present, a fast diastereomerization reaction was observed. Under air, the amount of the amine had no visible effect on the initial rate of the photoisomerization. However, the isomerization stopped after ca. 90 min at ca. 90:10 d.r. when substoichiometric 0.1 equiv. of Et₃N were employed, whereas the reaction in presence of 1.0 equiv. Et₃N stopped after 3 h at a d.r. of 82:18. As the amine was suspected to be oxidized in the photocatalytic diastereomerization under air and that the reaction stops before reaching the photostationary state (PSS), a subsequent conditions screening was performed under argon (Table S5).

Performing the photodiastereomerization of **1a** with **A1** (1.0 mol%) in the presence of Et₃N (1.0 equiv.) yielded a d.r. of 73:27 after 3.5 h of irradiation (entry 1). Variation of the photocatalyst to **A2** resulted in the progression to a diastereomeric ratio of 64:36 (*mer/fac*) within 3.5 h (entry 2). A screening of various acridinium, Ru- and Ir-based photocatalysts revealed only slight variation of the diastereomeric ratio after 3.5 h (entries 3–12). The investigations on the photocatalytic diastereomerization of **1a** were continued with **A2**, and the progression to the PSS was confirmed by subjecting *rac-fac-1a* to the reaction conditions giving rise to a diastereomeric mixture of *mer-* and *fac-1a* in similar yield and d.r. after 3.5 h (entry 13). Remarkably, the 64:36 d.r. (*mer/fac*) in the PSS of the photocatalytic diastereomerization of **1a** differs significantly from the diastereomeric ratio of 80:20 (*mer/fac*) in acetonitrile (Table S1, entry 1). Assaying the influence of the base, its variation showed a minor influence on the outcome of the diastereomerization process. While the aliphatic bases diisopropylethylamine (DIPEA), *N*-methylmorpholine (NMM) and 1,4-diazabicyclo[2.2.2]octane (DABCO) provided similar d.r.'s and slightly increased yields compared to Et₃N, the reaction in the presence of aromatic amine lutidine yielded a d.r. of 70:30 after 3.5 h of irradiation (entries 14–17). Decreasing the amount of Et₃N to 0.1 equiv. resulted in an incomplete conversion to 68:32 d.r. but slightly increased yield under argon (entry 18). Decreasing the loading of the photocatalyst led to a reduced yield (entries 19 and 20).

As it was already observed in the reaction progress analysis under air, the diastereomerization was slow in the absence of a base giving rise to a d.r. of 92:8 after 3.5 h of irradiation (entry 21). Conversely, the presence of the acridinium photocatalyst was not required when the reaction was performed under argon although the yield was significantly reduced to 42% (entry 21). In the absence of both **A2** and Et₃N, decomposition and only slight diastereomerization (95:5 d.r.) was found (entry 22). In order to study the effect of oxygen on the photocatalytic diastereomerization, the control experiments (entries 21–23) were repeated under air. In the presence of **A1** and Et₃N (1.0 equiv.), only a slight difference in yield was observed (54% under argon, 69% under air, entry 24). While the presence of the acridinium photocatalyst had only a minor effect on the yield under argon, the absence of the photocatalyst gave rise to a d.r. of 92:8 after 3.5 h of irradiation under air (67:33 d.r. under argon) and only 35% yield (42% yield under argon, entry 25).

Attempts to render the acridinium photocatalyzed stereoisomerization of Co(tfac)₃ (**1a**) in CHCl₃ enantioselective by using enantioenriched (84:16–93:7 e.r.) atropisomeric acridinium photocatalysts **A10–19**^[4a] only yielded racemic product (Table S6, entries 1–10). Neither varying the solvent to toluene, THF or ethanol (entries 11–13) nor adding Et₃N or diketone ligand were able to induce enantioselectivity in the photostereoisomerization of **1a** (entries 14–16).

Reaction Progress Analysis of Photocatalytic Diastereomerization of Co(tfac)₃ (**1a**) under Air



A solution of *rac-mer-1a* (518 μg , 1.00 μmol , 1.0 equiv.), Et₃N (0 or 10 mol%) and **A1** (0 or 1.0 mol%), in CHCl₃ (0.2 mL) was irradiated with a Kessil PR160L-467nm lamp (44 W, 100% intensity, 10 cm distance). In regular time intervals, aliquots were withdrawn from the reaction mixture, diluted with acetonitrile/water 3:1 and analyzed by HPLC (Supelco Ascentis Express C18 (2.7 μm , 100x2.1 mm), H₂O/MeCN 50:50, 0.5 mL/min, 40 °C).

Table S4. Reaction progress analysis of the photoisomerization of **1a** under air.

Entry ^a	Time [min]	d.r. ^b (<i>mer/fac</i>)			
		A1, no base	A1, Et ₃ N (0.1 equiv.)	A1, Et ₃ N (1.0 equiv.)	No photocatalyst, Et ₃ N (1.0 equiv.)
1	0	99.6:0.4	99.7:0.3	99.7:0.3	99.3:0.7
2	15	99.3:0.7	96.3:3.7	96.5:3.5	99.3:0.7
3	30	99.0:1.0	94.5:5.5	93.4:6.6	98.9:1.1
4	45	98.8:1.2	91.6:8.4	91.5:8.5	98.1:1.9
5	60	98.5:1.5	91.2:8.8	89.4:10.6	98.0:2.0
6	90	98.1:1.9	90.2:9.8	85.3:14.7	96.4:3.6
7	120	97.6:2.4	90.1:9.9	83.4:16.6	95.3:4.7
8	180	96.9:3.1	89.7:10.3	81.1:18.9	92.8:7.2
9	240	96.8:3.2	Not determined	81.3:18.7	90.8:9.2

^a Reaction conditions: *rac-mer-1a* (1.00 μmol , 1.0 equiv.), **A1** (0–1.0 mol%), Et₃N (0–1.0 equiv.), CHCl₃ (5 mmol/L), blue LED (467 nm, 44 W), r.t. ^b Determined by HPLC.

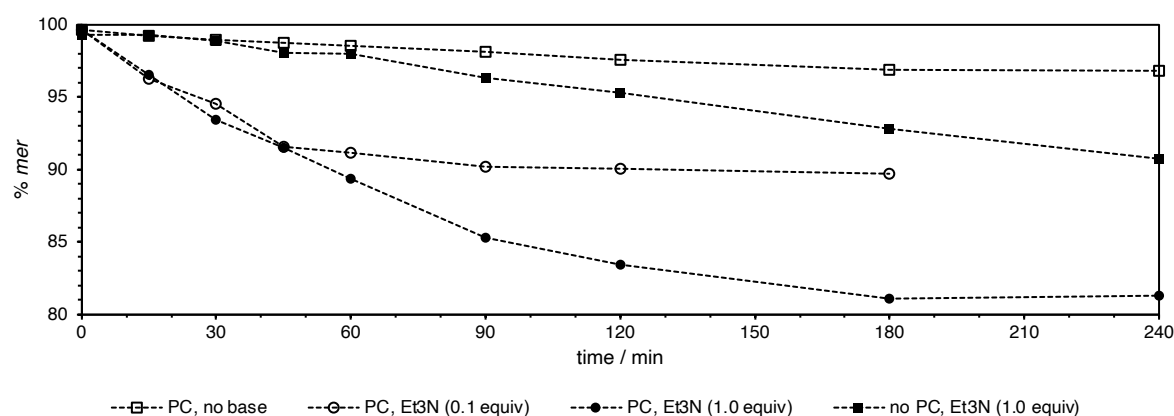
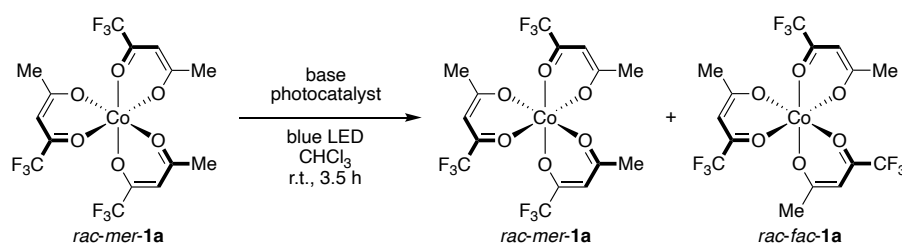


Figure S3. Reaction progress analysis of the photocatalytic diastereomerization of **1a** under air.

Photocatalytic Diastereomerization of Co(tfac)₃ (**1a**)

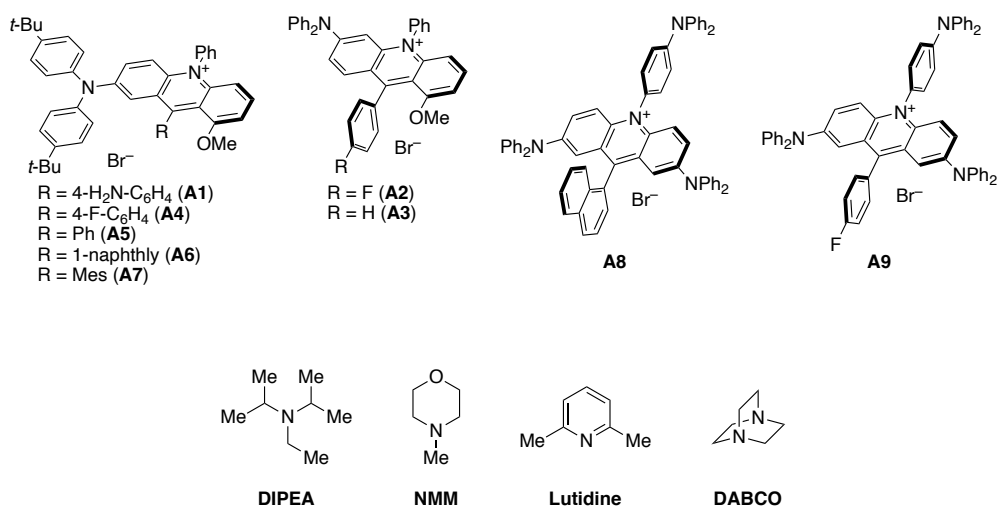


A solution of *rac-mer-1a* (518 µg, 1.00 µmol, 1.0 equiv.), Et₃N (0–1.0 equiv.) and the respective photocatalyst^[4b,c] (0–1.0 mol%), in CHCl₃ (0.2 mL) under argon or air was irradiated with a Kessil PR160L-456nm lamp (44 W, 100% intensity, 10 cm distance) for 3.5 h. A durene stock solution in acetonitrile was added to the reaction mixture, an aliquot of it was diluted with acetonitrile/water 3:1 and analyzed by HPLC (Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 50:50, 0.5 mL/min, 40 °C).

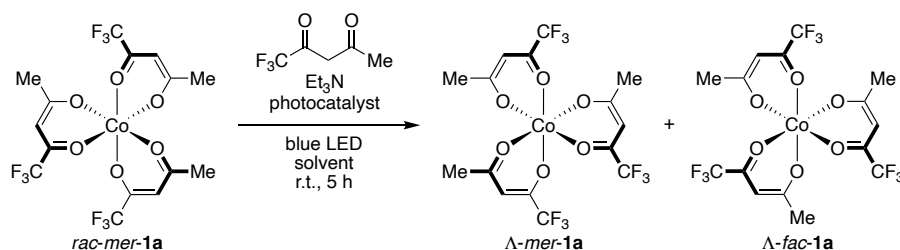
Table S5. Conditions screening for the photoisomerization of **1a** following the general procedure C.

Entry ^a	Photocatalyst (mol%)	Base (equiv.)	Deviation from Std. Conditions	Yield ^b [%]	d.r. ^b (<i>mer/fac</i>)
1	A1 (1)	Et ₃ N (1)	—	46	73:27
2	A2 (1)	Et ₃ N (1)	—	54	64:36
3	A3 (1)	Et ₃ N (1)	—	56	68:32
4	A4 (1)	Et ₃ N (1)	—	46	76:24
5	A5 (1)	Et ₃ N (1)	—	51	74:26
6	A6 (1)	Et ₃ N (1)	—	50	69:31
7	A7 (1)	Et ₃ N (1)	—	55	69:31
8	A8 (1)	Et ₃ N (1)	—	55	75:25
9	A9 (1)	Et ₃ N (1)	—	39	78:22
10	[Ru(bpy) ₃](PF ₆) ₂ (1)	Et ₃ N (1)	—	48	77:23
11	[Ru(bpz) ₃](PF ₆) ₂ (1)	Et ₃ N (1)	—	42	59:41
12	Ir(ppy) ₃ (1)	Et ₃ N (1)	—	68	84:16
13	A2 (1)	DIPEA (1)	—	61	65:35
14	A2 (1)	2,6-lutidine (1)	—	69	70:30
15	A2 (1)	NMM (1)	—	63	66:34
16	A2 (1)	DABCO (1)	—	70	66:34
17	A2 (1)	Et ₃ N (0.1)	—	67	68:32
18	A2 (0.5)	Et ₃ N (1)	—	64	65:35
19	A2 (0.1)	Et ₃ N (1)	—	48	66:34
20	A2 (1)	Et ₃ N (1)	Starting from <i>rac-fac-1a</i>	54	65:35
21	A2 (1)	—	—	58	92:8
22	—	Et ₃ N (1)	—	42	67:33
23	—	—	—	77	95:5
24	A2 (1)	Et ₃ N (1)	Under air	69	66:34
25	A2 (1)	—	Under air	58	94:6
26	—	Et ₃ N (1)	Under air	35	92:8
27	—	—	Under air	48	97:3

^a Reaction conditions: *rac-mer-1a* (1.00 µmol, 1.0 equiv.), photocatalyst (0–1.0 mol%), Et₃N (0–1.0 equiv.), CHCl₃ (5 mmol/L), Ar, blue LED (467 nm, 44 W), r.t., 3.5 h. ^b Determined by HPLC using durene as internal standard.



Attempted Photoderacemization of $\text{Co}(\text{tfac})_3$ (**1a**) with Acridinium Photocatalysts

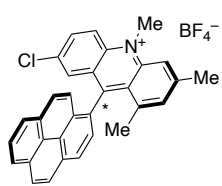


A solution of *rac-mer-1a* (1.30 mg, 2.50 μmol , 1.0 equiv.), Et_3N (0 or 3.0 equiv.) and the respective photocatalyst^[4a] (1.0 mol%), in CHCl_3 (1 mL) was irradiated with a Kessil PR160L-456nm lamp (11 W, 25% intensity, 15 cm distance) for 5 h. The reaction mixture was by HPLC on a chiral stationary phase (Chiralpak IA (5 μm , 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 10 $^\circ\text{C}$)

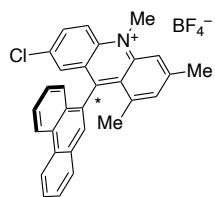
Table S6. Attempted Photoderacemization of **1f** with non-racemic atropisomeric acridinium photocatalysts.

Entry ^a	Photocatalyst	Solvent	Et_3N	tfacH	Outcome
1	A10	CHCl_3	0 equiv.	0 equiv.	Racemic
2	A11	CHCl_3	0 equiv.	0 equiv.	Racemic
3	A12	CHCl_3	0 equiv.	0 equiv.	Racemic
4	A13	CHCl_3	0 equiv.	0 equiv.	Racemic
5	A14	CHCl_3	0 equiv.	0 equiv.	Racemic
6	A15	CHCl_3	0 equiv.	0 equiv.	Racemic
7	A16	CHCl_3	0 equiv.	0 equiv.	Racemic
8	A17	CHCl_3	0 equiv.	0 equiv.	Racemic
9	A18	CHCl_3	0 equiv.	0 equiv.	Racemic
10	A19	CHCl_3	0 equiv.	0 equiv.	Racemic
11	A20	CHCl_3	0 equiv.	0 equiv.	Racemic
12	A21	CHCl_3	0 equiv.	0 equiv.	Racemic
13	A10	Toluene	0 equiv.	0 equiv.	Racemic
14	A10	THF	0 equiv.	0 equiv.	Racemic
15	A10	EtOH	0 equiv.	0 equiv.	Racemic
16	A10	CHCl_3	3 equiv.	0 equiv.	Racemic, decomposition
17	A10	CHCl_3	3 equiv.	3 equiv.	Complete decomposition
18	A10	CHCl_3	0 equiv.	3 equiv.	Racemic

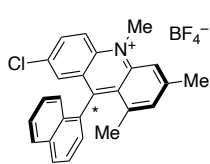
^a Reaction conditions: *rac-mer-1a* (2.50 μmol , 1.0 equiv.), photocatalyst (1.0 mol%), Et_3N (0–3.0 equiv.), solvent (2.5 mmol/L), blue LED (467 nm, 11 W), r.t., 5 h.



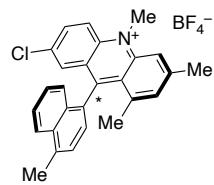
A10 (91:9 e.r.)



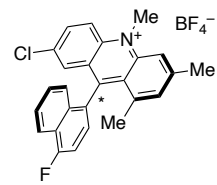
A11 (90:10 e.r.)



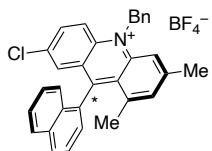
A12 (91:9 e.r.)



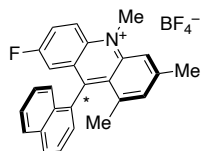
A13 (89:11 e.r.)



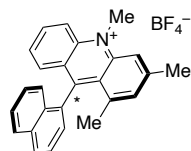
A14 (90:10 e.r.)



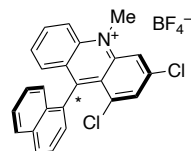
A15 (93:7 e.r.)



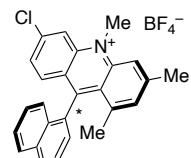
A16 (90:10 e.r.)



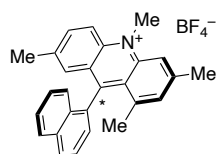
A17 (88:12 e.r.)



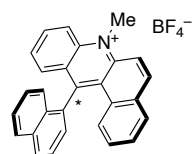
A18 (89:11 e.r.)



A19 (84:16 e.r.)



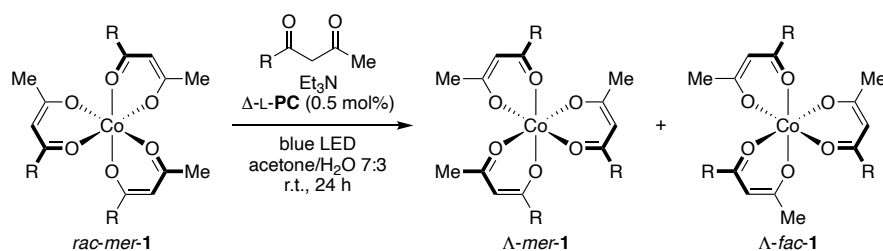
A20 (90:10 e.r.)



A21 (90:10 e.r.)

6. Photoderacemization

General Procedure C: Photoderacemization of Cobalt(III) Diketonates



A solution of the respective cobalt(III) complex *rac-mer-1* (10.0 μmol , 1.0 equiv.), the respective diketone (100 μmol , 10.0 equiv.), Et_3N (141 nL, 1.00 μmol , 10 mol%) and $\Delta\text{-[Ru(L-menbpy)}_3\text{]Cl}_2$ ($\Delta\text{-L-PC}$, 86.7 μg , 50.0 nmol, 0.5 mol%) in acetone/water 3:1 (1.0 mL) under argon was irradiated with a Kessil PR160L-456nm lamp (50 W, 25% intensity, 10 cm distance) for 24 h. An aliquot (10.0 μL) was withdrawn from the reaction mixture, combined with a durene stock solution in acetonitrile, diluted with acetonitrile/water 3:1 and analyzed by HPLC to determine the yield and the diastereomeric ratio. The reaction mixture was then concentrated under reduced pressure and extracted with CHCl_3 . The *mer*- and *fac*-diastereomers were separated by preparative TLC on silica gel (toluene/*i*-PrOH 25:1) and analyzed by HPLC on a chiral stationary phase.

Substrate Screening

The substrate screening (Table S7) was performed according to the general procedure C starting from *rac-mer-1* (10.0 μmol , 1.0 equiv.).

Control Experiments

The control experiments (Table S8) were performed according to the general procedure C starting from *rac-mer-1f* (2.50 μmol , 1.0 equiv.).

Solvent Screening

The solvent screening (Table S9, Figures S4 and S5) was performed according to the general procedure C starting from a diastereomeric mixture (69:31 *mer/fac*) of *rac-1f* (2.50 μmol , 1.0 equiv.).

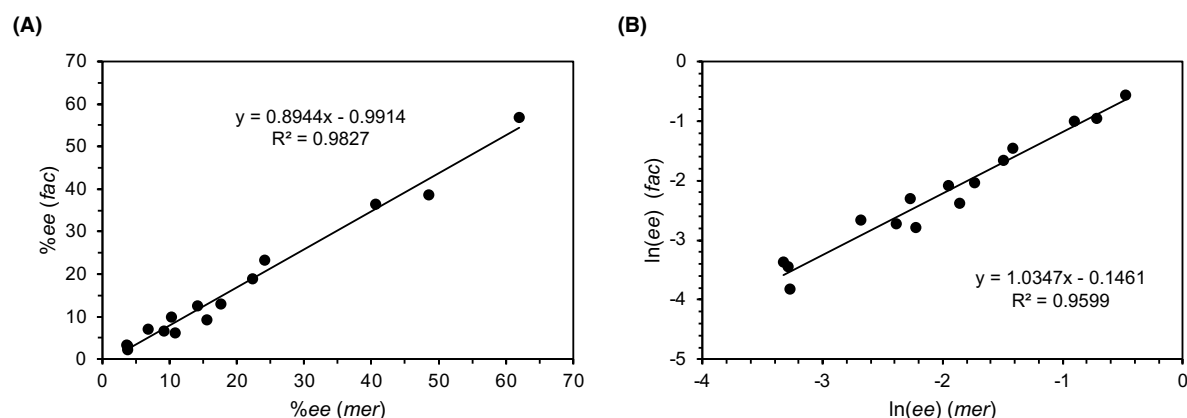


Figure S4. Correlation between the (A) *ee* and (B) $\ln(ee)$ of *mer*- and *fac-1f*.

Table S7. Substrate screening under standard reaction conditions (general procedure C).

Entry ^a	Complex	Deviation from Std. Conditions	Yield ^b [%]	d.r. ^b (<i>mer/fac</i>)	e.r. ^c (<i>mer</i>)	e.r. ^c (<i>fac</i>)
1	1a	—	0	—	—	—
2	1b	—	0	—	—	—
3	1c	—	84	79:21	84:16	69:31
4	1d	—	88	78:22	44:56	71:29
5	1d	48 h, starting from <i>rac-fac-1d</i>	52	71:29	50:50	68:32
6	1e	2.5 mmol/L	94	68:32	73:27	74:26
7	1f	—	72	70:30	88:12	82:18

^a Reaction conditions: *rac-mer-1* (10.0 μ mol, 1.0 equiv.), diketone (10 equiv.), Et₃N (10 mol%), Δ -L-PC (0.5 mol%), acetone/H₂O 7:3 (5 mmol/L), Ar, blue LED (456 nm, 13 W), r.t., 24 h. ^b Determined by HPLC using durene as internal standard. ^c Determined by HPLC on a chiral stationary phase after isolation, given as Λ : Δ .

Table S8. Control experiments for the photoderacemization of *rac-mer-1f* (general procedure C).

Entry ^a	Deviation from Std. Conditions	Yield ^b [%]	d.r. ^b (<i>mer/fac</i>)	e.r. ^c (<i>mer</i>)	e.r. ^c (<i>fac</i>)
1	In the dark	100	100:0	50:50	—
2	Without photocatalyst	77	76:24	50:50	50:50
3	Without Et ₃ N	75	68:32	84:16	78:12
4	Without additional diketone ligand	44	70:30	80:20	74:26
5	Using <i>rac</i> -[Ru(bpy) ₃]Cl ₂	62	66:34	50:50	50:50
6	Using Δ -L-PC	79	67:33	33:67	36:64

^a Reaction conditions: *rac-mer-1f* (2.50 μ mol, 1.0 equiv.), **S3b** (10 equiv.), Et₃N (10 mol%), Δ -L-PC (0.5 mol%), acetone/H₂O 7:3 (5 mmol/L), Ar, blue LED (456 nm, 13 W), r.t., 24 h. ^b Determined by HPLC using durene as internal standard. ^c Determined by HPLC on a chiral stationary phase after isolation, given as Λ : Δ .

Table S9. Solvent screening for the Δ -L-PC catalyzed photoderacemization of **1f**.

Entry ^a	Solvent	d.r. ^b (<i>mer/fac</i>)	e.r. ^c (<i>mer</i>)	e.r. ^c (<i>fac</i>)
1	EtOH	68:32	59:41	57:43
2	<i>i</i> -PrOH	68:32	55:47	53:47
3	CF ₃ CH ₂ OH	68:32	52:48	52:48
4	(CF ₃) ₂ CHOH	68:32	52:48	51:49
5	MeCN	70:30	70:30	68:32
6	DMSO	69:31	74:26	69:31
7	DMF	68:32	61:39	59:41
8	NMP	72:28	81:19	78:20
9	EtOAc	68:32	53:47	53:47
10	Dioxane	68:32	55:45	55:45
11	Acetone	68:32	62:38	62:38
12	THF	69:31	57:43	56:44
13	CH ₂ Cl ₂	68:32	55:45	53:47
14	CHCl ₃	68:32	52:48	52:48
15	Toluene	68:32	58:42	55:45

^a Reaction conditions: *rac-mer/fac-1a* (2.50 μ mol, 1.0 equiv.), **S3b** (10 equiv.), Et₃N (10 mol%), Δ -L-PC (0.5 mol%), solvent (5 mmol/L), Ar, blue LED (456 nm, 13 W), r.t., 24 h. ^b Determined by HPLC of the crude product. ^c Determined by HPLC on a chiral stationary phase after isolation, given as Λ : Δ .

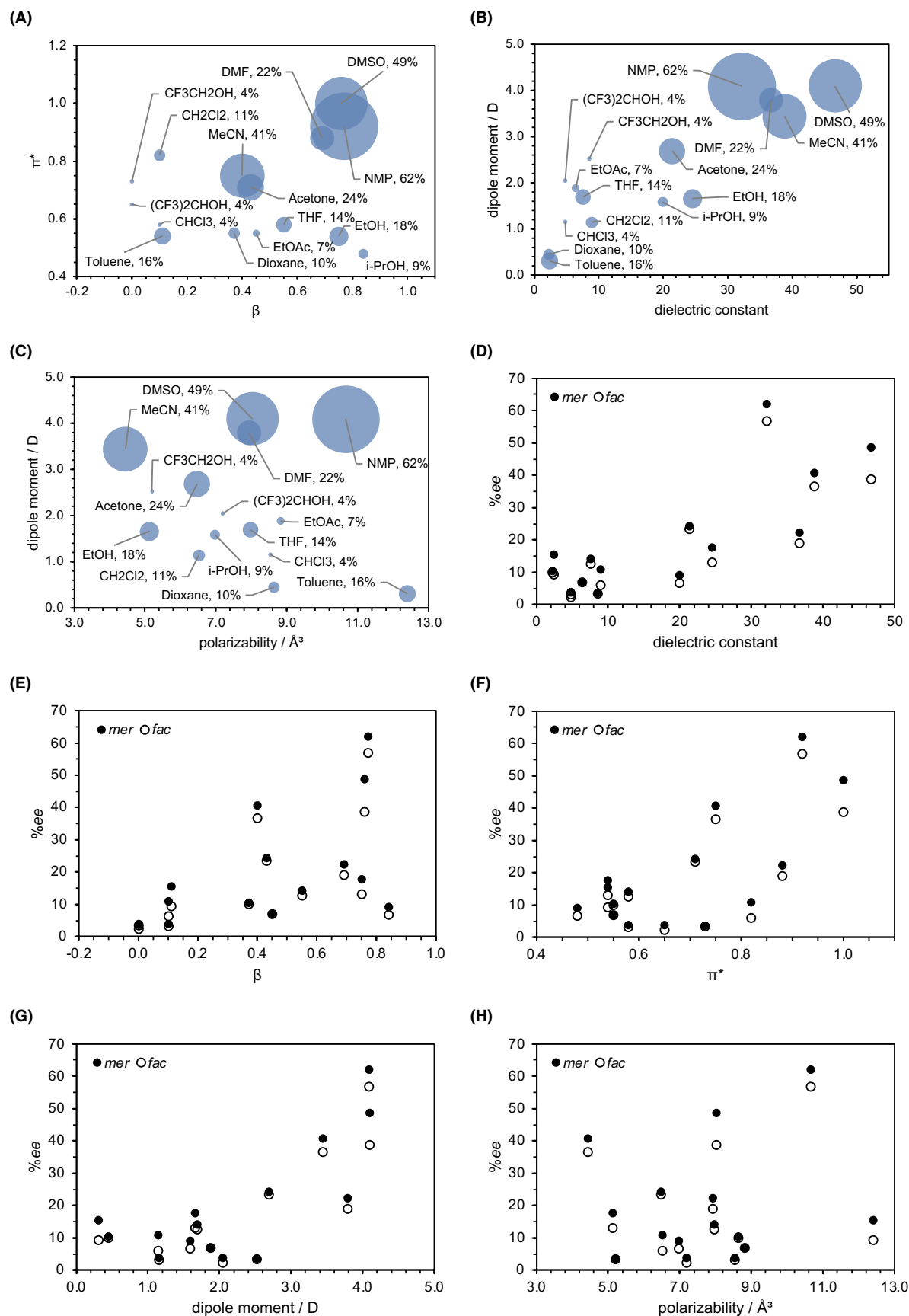
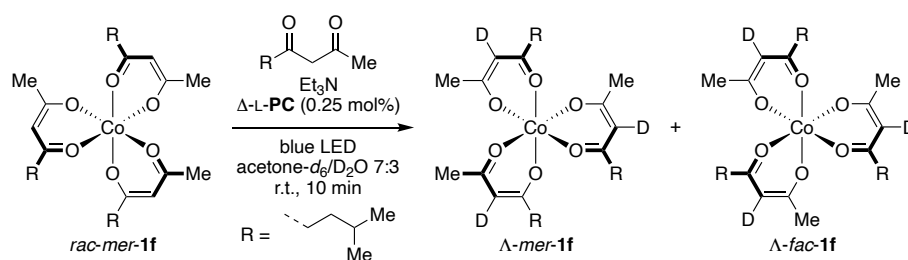


Figure S5. Correlation between the enantiomeric excess of **1f** and the Kamlet–Taft parameters β and π^* (A, E, F), the dipole moment and the dielectric constant (B, D, G) and the dipole moment and the polarizability (C, G, H) of different solvents. The diameters of the bubbles in A–C correspond to the ee of *mer*-**1f**.

Deuteration Study



A solution of *rac-mer-1f* (2.62 mg, 5.00 μmol , 1.0 equiv.), **S3b** (7.81 mg, 50.0 μmol , 10.0 equiv.), $\Delta\text{-L-PC}$ (21.7 μg , 12.5 nmol, 0.25 mol%), Et_3N (70 nL, 500 nmol, 0.1 equiv.) and anisole as internal standard (1.64 μL , 15.0 μmol , 3.0 equiv.) in acetone- d_6 / D_2O 7:3 (1.0 ml) was irradiated in an NMR tube with a Kessil lamp (456 nm, 13 W) at room temperature for 10 min.

Et_3N catalyzed H/D exchange between D_2O and free diketone ligand **S3b** led to virtually complete deuteration of its most acidic C3 position, and no corresponding signal could be observed in the ^1H NMR spectrum before and after the irradiation. In contrast, before the reaction mixture was irradiated with blue light, the three C3H signals of *mer-1f* were observed. After 10 min of irradiation, a singlet corresponding to C1H of *fac-1f* appeared (confirmed by HPLC) while the C3H signals of *mer-1f* disappeared completely.

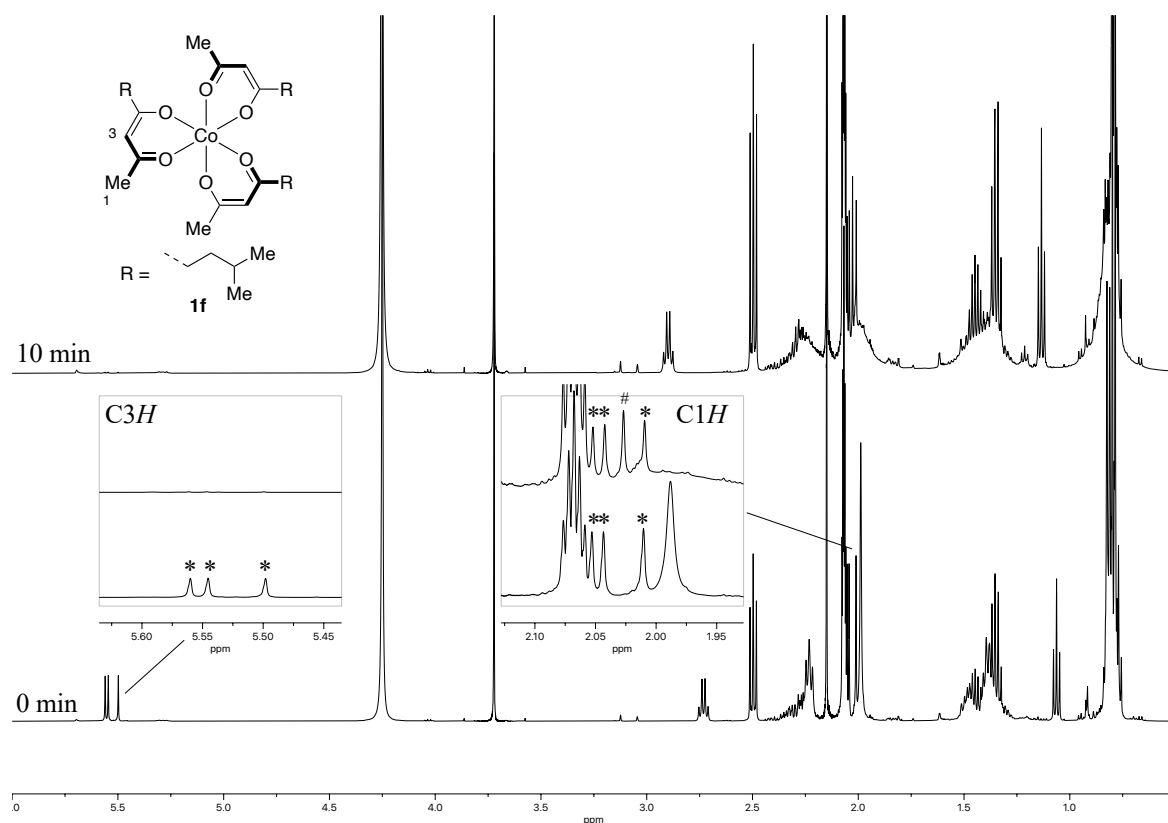


Figure S6. ^1H NMR spectrum (500.1 MHz, acetone- d_6 / D_2O 7:3) of the photoderacemization of *mer-1f* after 0 and 10 min of irradiation (* = *mer-1f*, # = *fac-1f*).

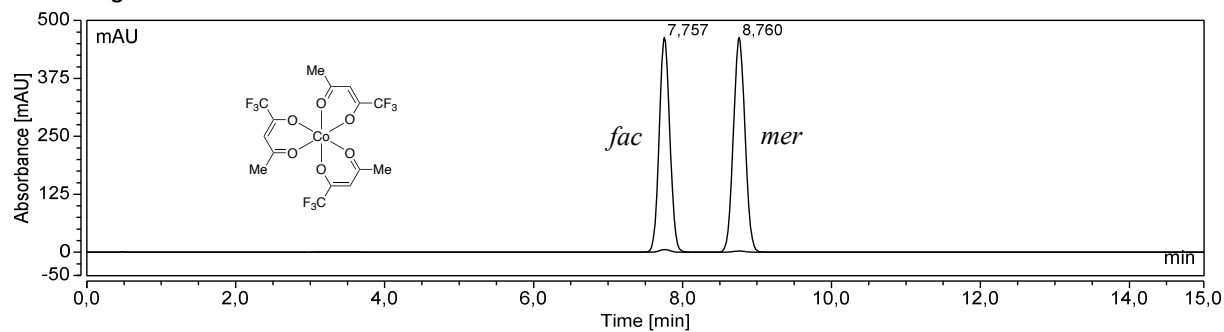
Chromatogram and Results

7. HPLC Data

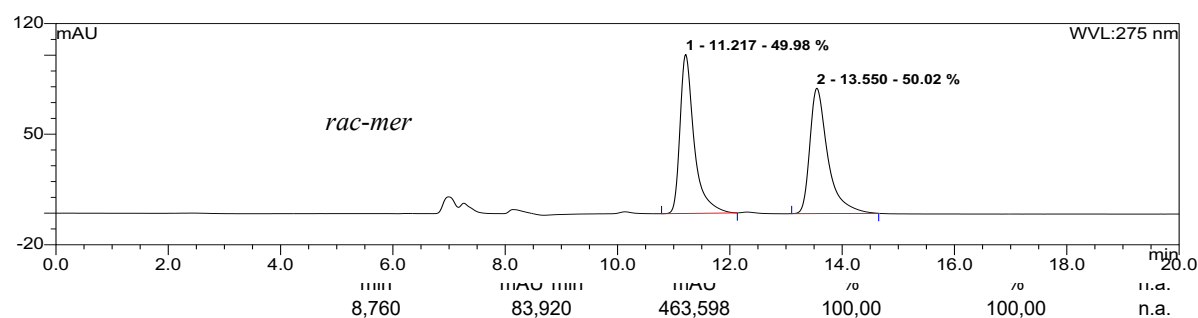
Co(tfac)₃ (1a)

HPLC Conditions: Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 50:50, 0.5 mL/min, 40 °C

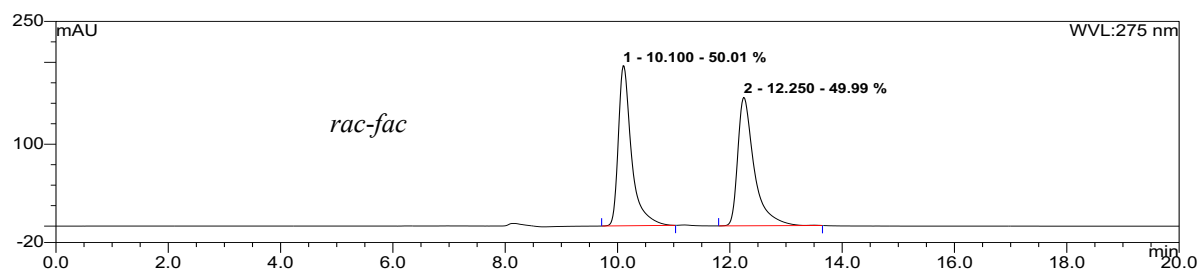
Chromatogram



HPLC Conditions: Chiralpak IA (5 µm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 10 °C



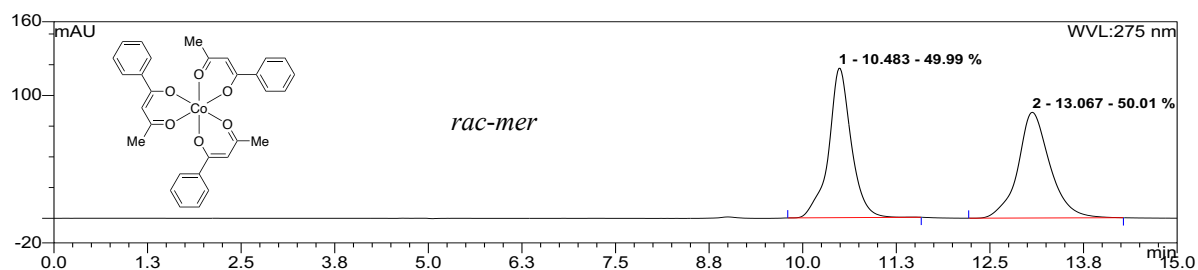
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	11.22	100.693	29.385	49.98
2	13.55	79.401	29.410	50.02
Total:		180.094	58.795	100.00



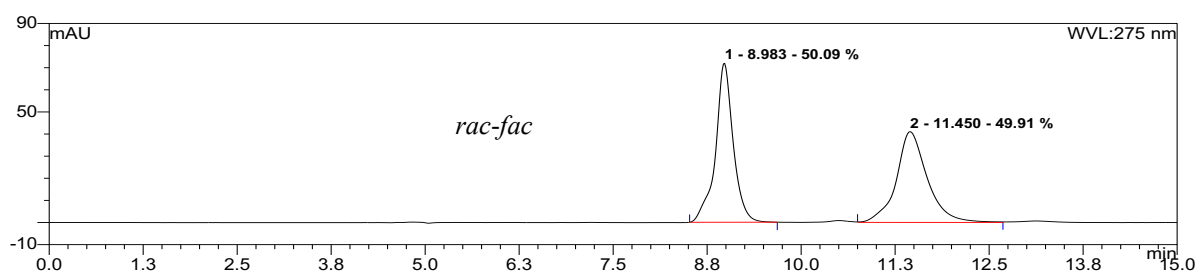
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	10.10	195.626	53.147	50.01
2	12.25	156.859	53.123	49.99
Total:		352.485	106.270	100.00

Co(bzac)₃ (1b)

HPLC Conditions: Chiralpak IC-3 (3 μm, 250x4.6 mm), heptane/*i*-PrOH 95:5, 1.0 mL/min, 40 °C



No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	10.48	121.664	42.572	49.99
2	13.07	86.080	42.592	50.01
Total:		207.744	85.164	100.00



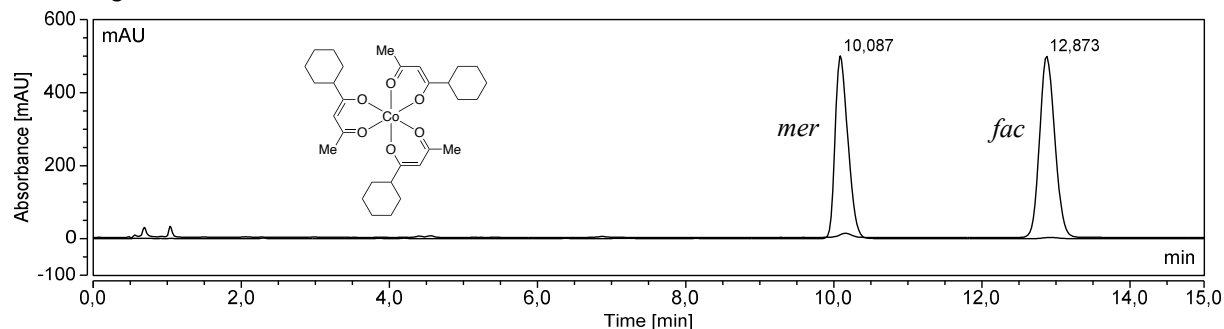
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.98	71.871	19.668	50.09
2	11.45	41.033	19.594	49.91
Total:		112.904	39.262	100.00

Injection Details

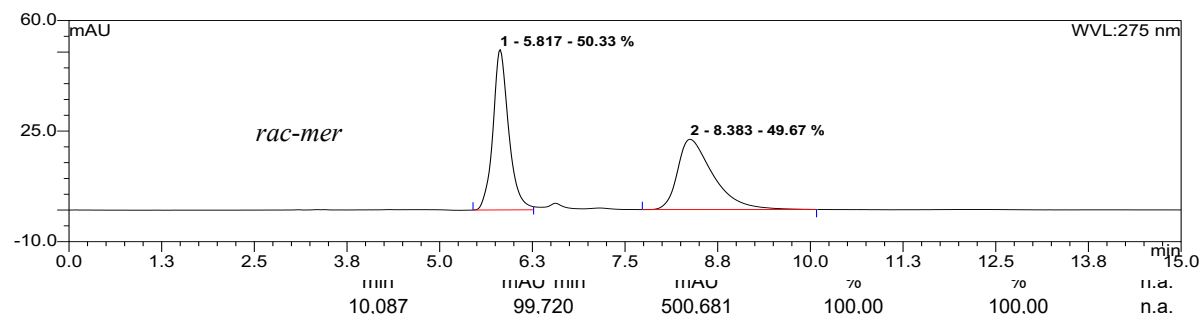
Co(cycac)₃ (1c)

HPLC Conditions: Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 75:25, 0.5 mL/min, 40 °C

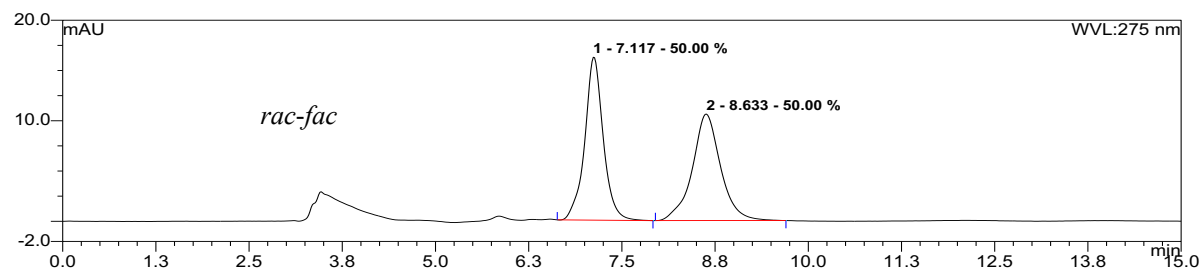
Chromatogram



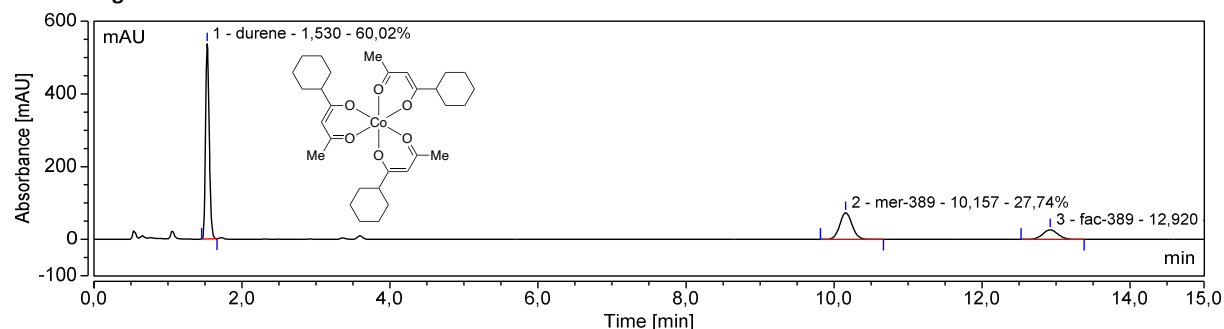
HPLC Conditions: Chiralpak IC-3 (3 µm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 1.0 mL/min, 40 °C



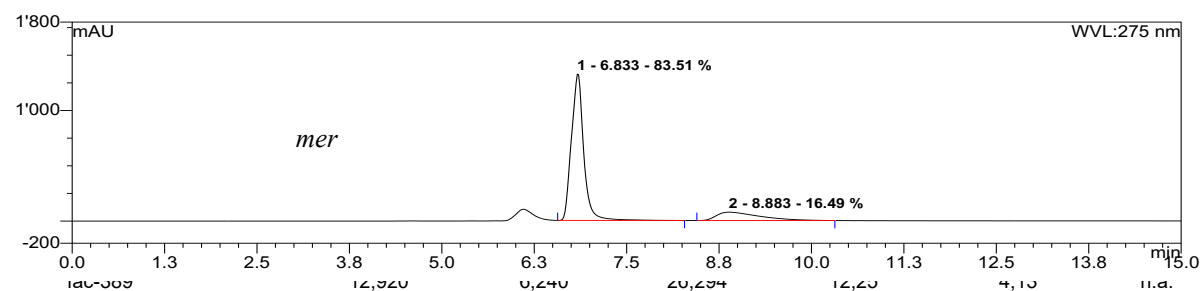
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	5.82	50.751	12.505	50.33
2	8.38	22.233	12.340	49.67
Total:		72.984	24.845	100.00



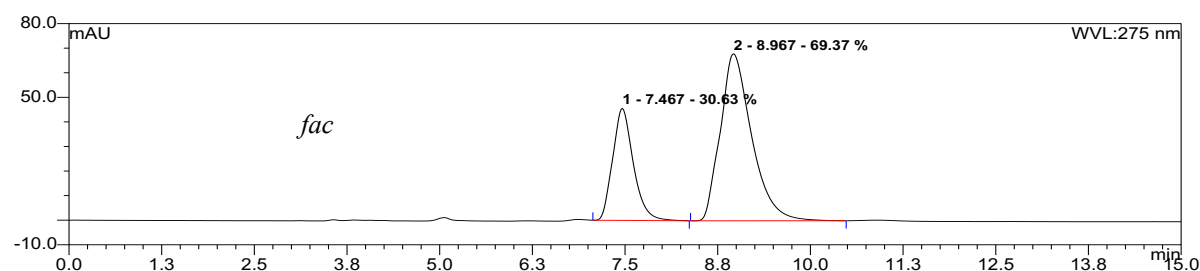
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	7.12	16.210	4.665	50.00
2	8.63	10.599	4.665	50.00
Total:		26.808	9.330	100.00

**Photoderacemization:
Chromatogram**


No.	Peak Name	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	durene	1.530	537.032	30.583	60.02
2	mer	10.157	73.447	14.134	27.74
3	fac	12.920	26.294	6.240	12.25
Total:			636.772	50.956	100.00



No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	6.83	1323.961	254.273	83.51
2	8.88	75.067	50.200	16.49
Total:		1399.027	304.472	100.00



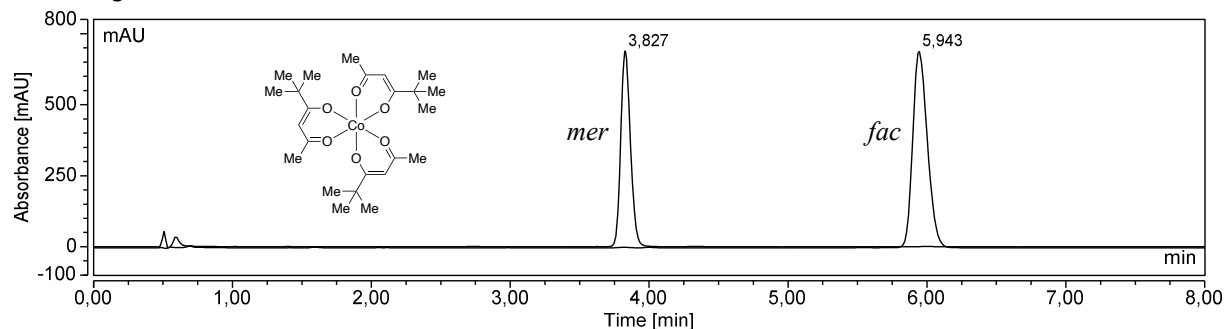
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	7.47	45.542	14.720	30.63
2	8.97	67.970	33.333	69.37
Total:		113.512	48.054	100.00

Injection Details

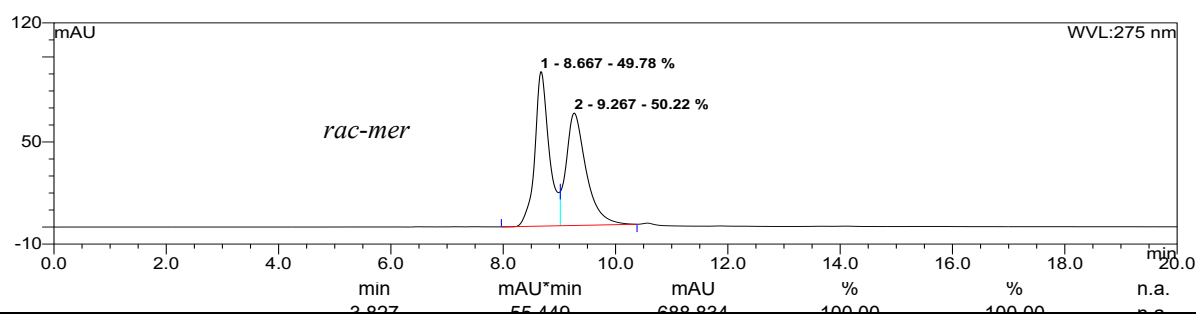
Co(pivac)₃ (1d)

HPLC Conditions: Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 75:25, 0.5 mL/min, 40 °C

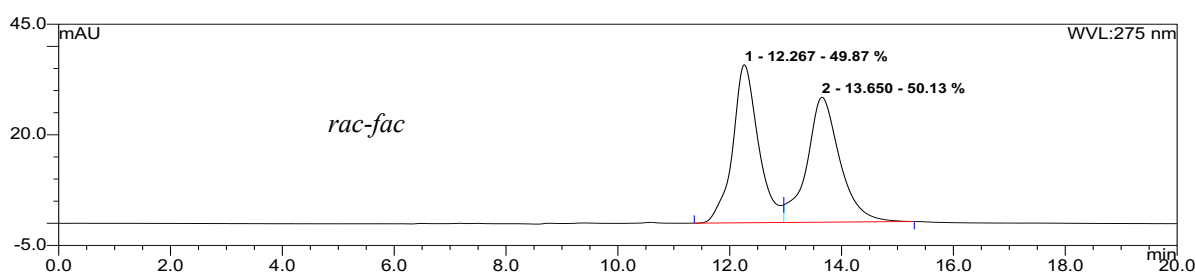
Chromatogram



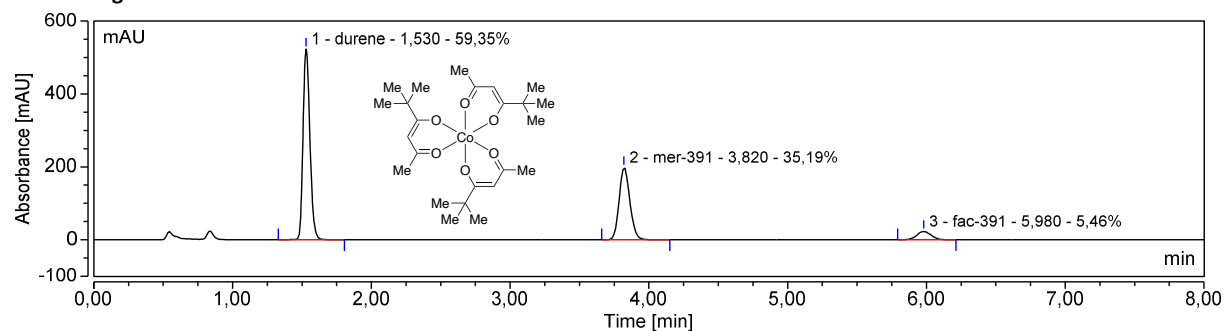
HPLC Conditions: Chiralpak IC-3 (3 µm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 5 °C



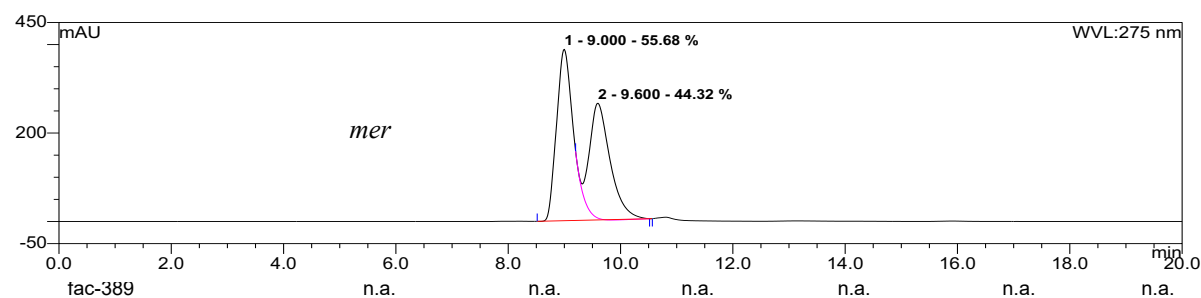
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.67	90.737	26.991	49.78
2	9.27	66.115	27.229	50.22
Total:		156.851	54.220	100.00



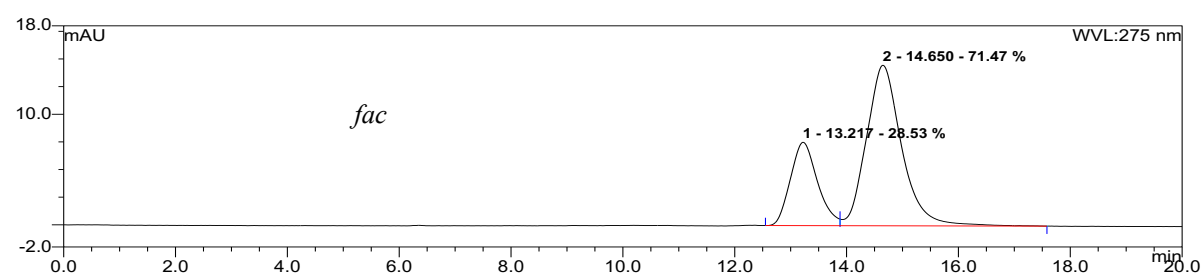
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	12.27	35.731	19.162	49.87
2	13.65	28.245	19.260	50.13
Total:		63.976	38.422	100.00

**Photoderacemization:
Chromatogram**


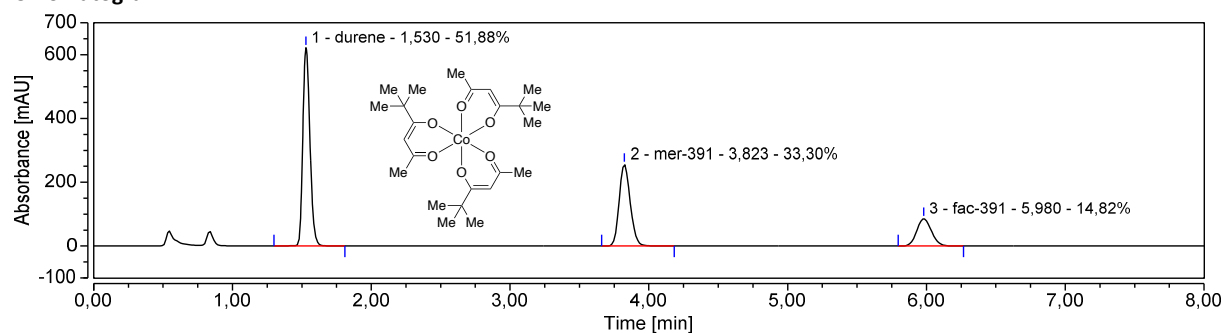
No.	Peak Name	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	durene	1.530	523.053	29.826	59.35
2	mer	3.820	198.091	17.687	35.19
3	fac	5.980	22.877	2.742	5.46
Total:			744.021	50.255	100.00



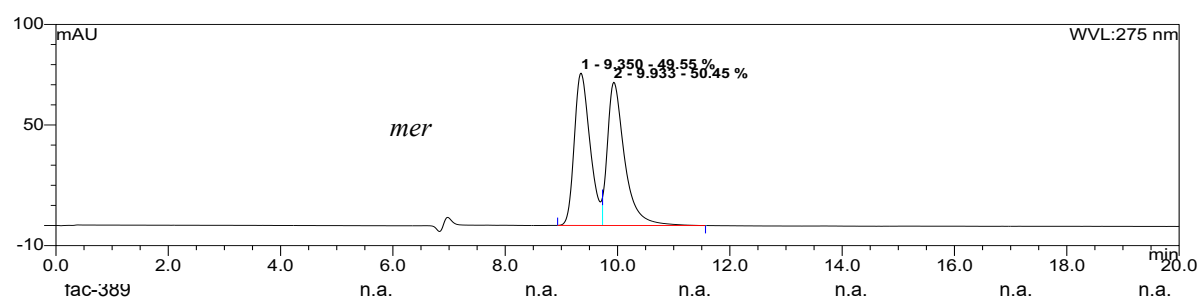
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	9.00	387.599	137.257	55.68
2	9.60	259.786	109.247	44.32
Total:		647.385	246.505	100.00



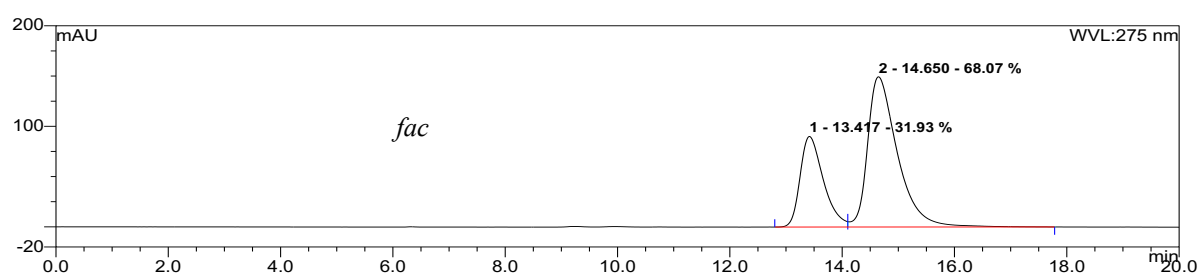
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	13.22	7.535	4.225	28.53
2	14.65	14.519	10.587	71.47
Total:		22.054	14.812	100.00

Photoderacemization (after 48 h):
Chromatogram


No.	Peak Name	Rt.Time min	Height mAU	Area mAU*min	Rel.Area %
1	durene	1.530	621.829	36.802	51.88
2	mer	3.823	255.979	23.619	33.30
3	fac	5.980	85.509	10.514	14.82
Total:			963.318	70.935	100.00



No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	9.35	75.774	24.793	49.55
2	9.93	71.253	25.243	50.45
Total:		147.026	50.035	100.00



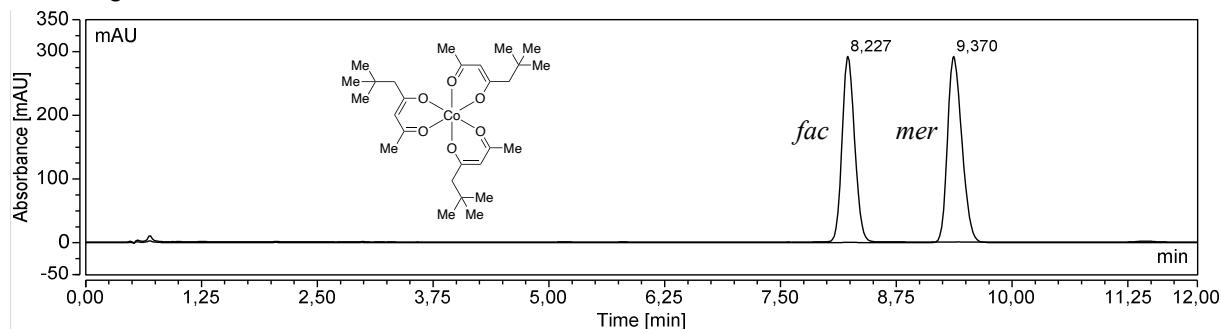
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	13.42	90.124	43.175	31.93
2	14.65	149.473	92.043	68.07
Total:		239.597	135.218	100.00

Injection Details

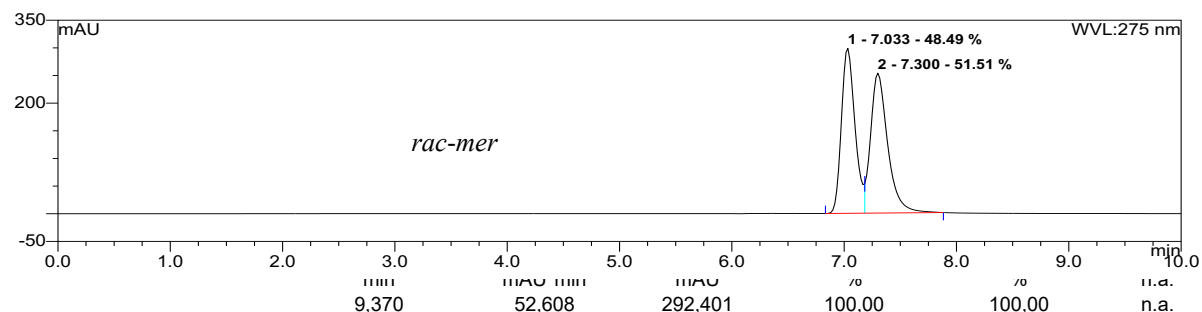
Co(dmbac)₃ (1e)

HPLC Conditions: Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 75:25, 0.5 mL/min, 40 °C

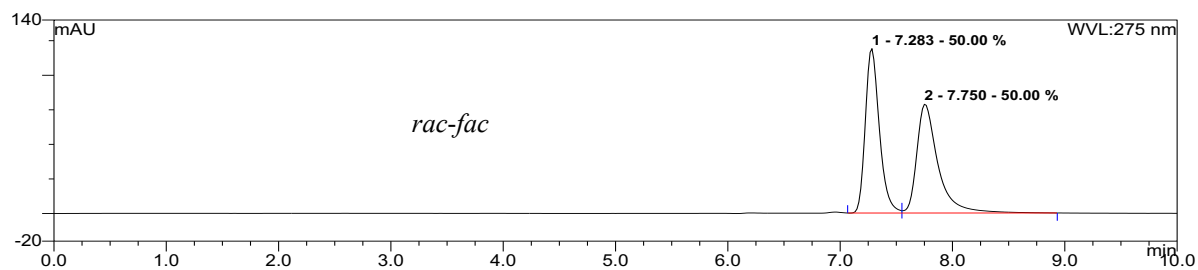
Chromatogram



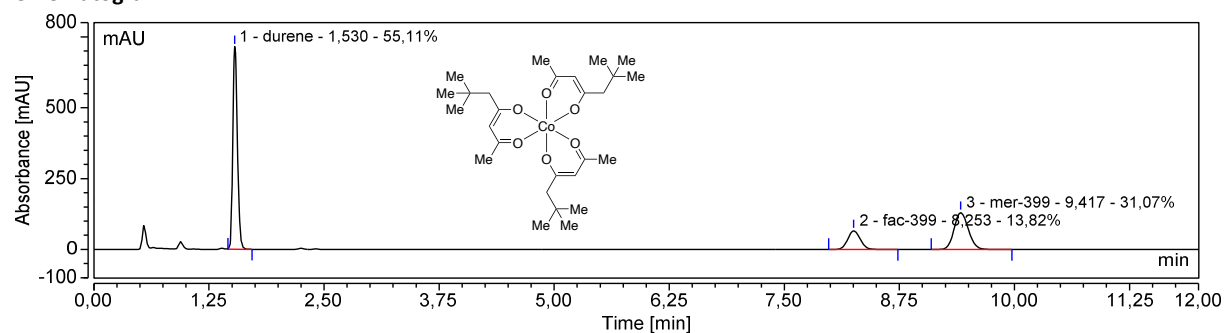
HPLC Conditions: Chiralpak IG-3 (3 µm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 40 °C



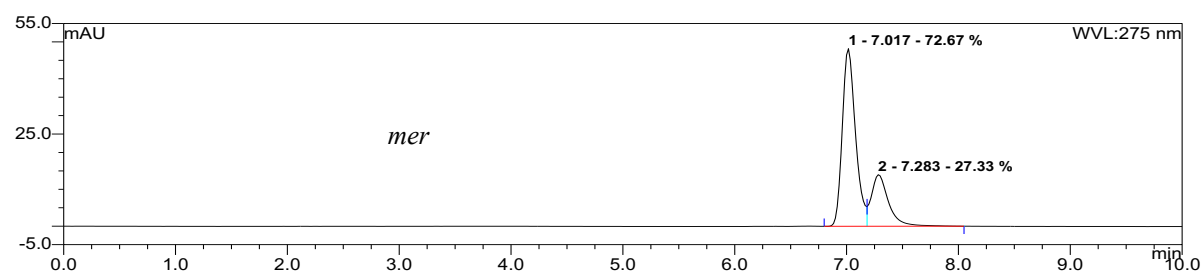
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	7.03	298.363	41.924	48.49
2	7.30	253.201	44.543	51.51
Total:		551.564	86.467	100.00



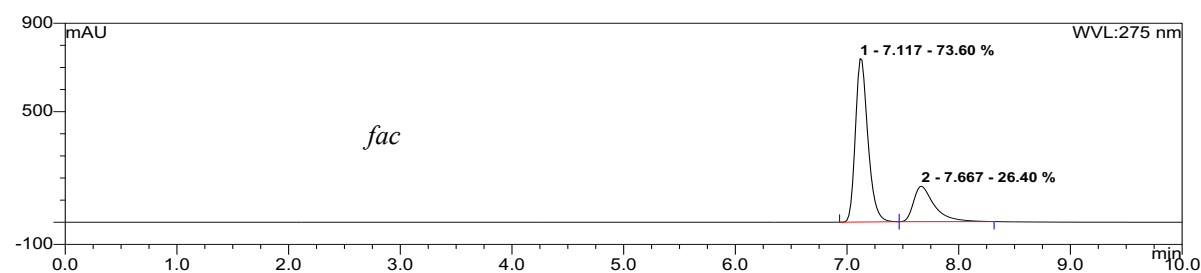
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	7.28	118.941	17.258	50.00
2	7.75	78.697	17.256	50.00
Total:		197.638	34.513	100.00

**Photoderacemization:
Chromatogram**


No.	Peak Name	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	durene	1.530	714.669	41.283	55.11
2	fac	8.253	65.915	10.351	13.82
3	mer	9.417	130.304	23.277	31.07
Total:			910.889	74.910	100.00



No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	7.02	48.175	6.608	72.67
2	7.28	14.000	2.485	27.33
Total:		62.175	9.094	100.00



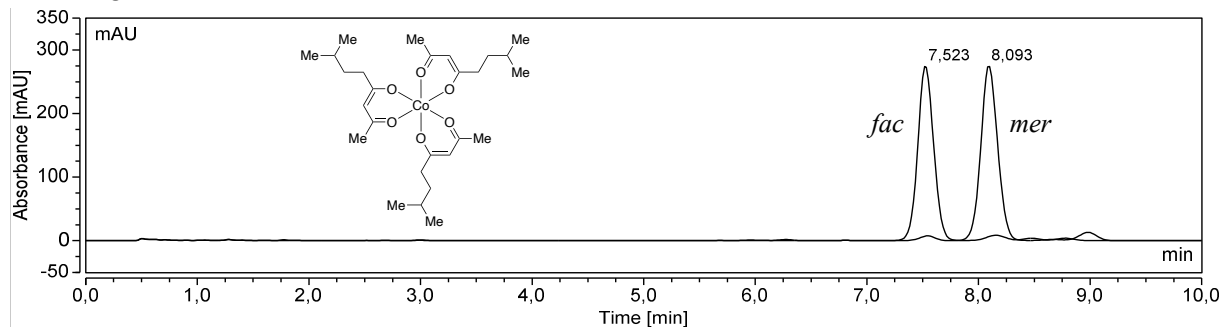
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	7.12	738.940	96.013	73.60
2	7.67	160.460	34.446	26.40
Total:		899.401	130.459	100.00

Injection Details

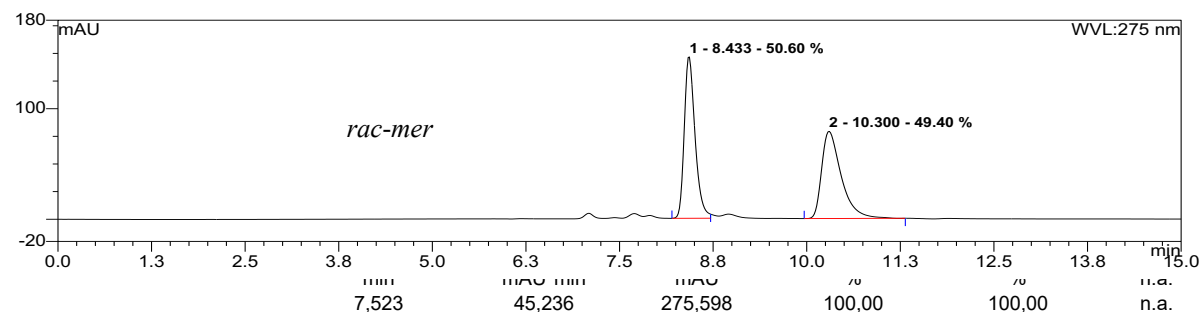
Co(mpac)₃ (1f)

HPLC Conditions: Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H₂O/MeCN 75:25, 0.5 mL/min, 30 °C

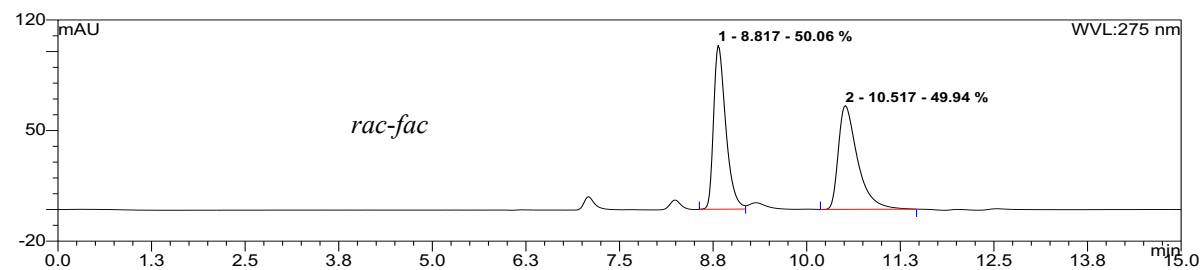
Chromatogram



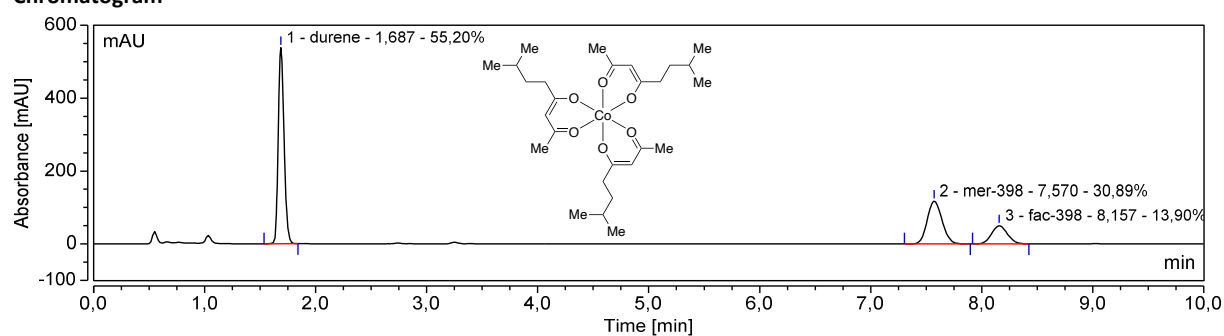
HPLC Conditions: Chiralpak IG-3 (3 µm, 250x4.6 mm), heptane/*i*-PrOH 99:1, 0.5 mL/min, 40 °C



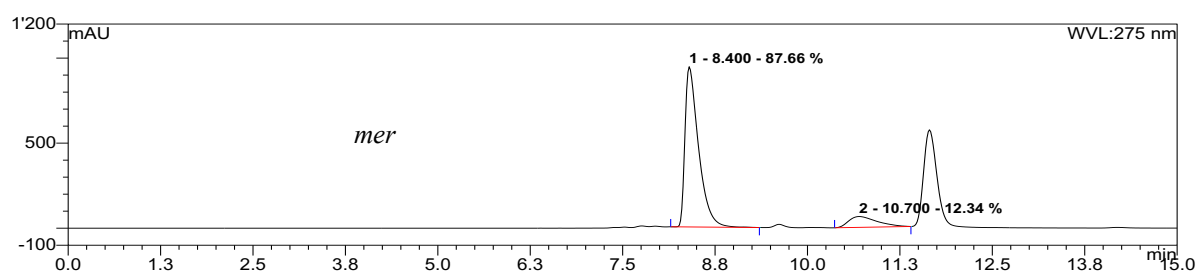
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.43	145.935	24.372	50.60
2	10.30	78.841	23.789	49.40
Total:		224.776	48.161	100.00



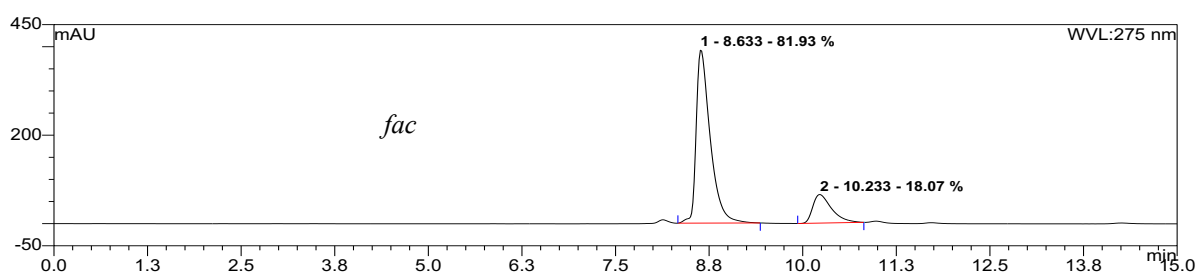
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.82	103.689	19.569	50.06
2	10.52	65.676	19.519	49.94
Total:		169.365	39.087	100.00

**Photoderacemization:
Chromatogram**


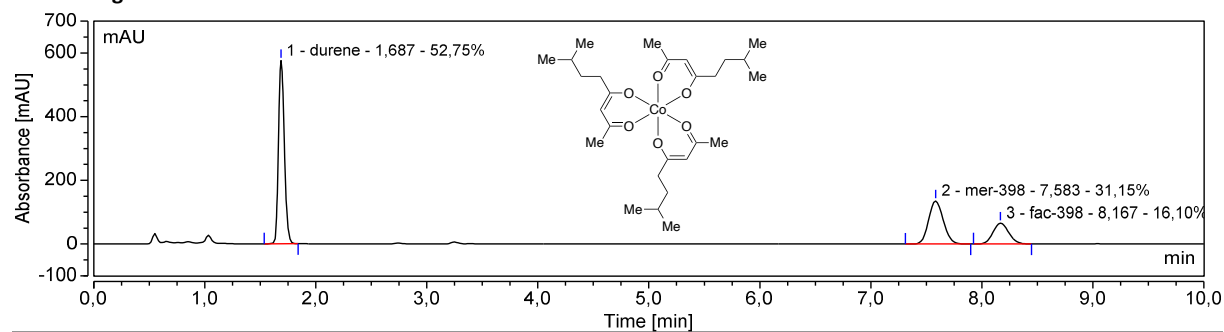
No.	Peak Name	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	durene	1.687	32.656	538.298	55.20
2	mer	7.570	18.274	117.705	30.89
3	fac	8.157	8.224	49.807	13.90
Total:			59.154	705.810	100.00



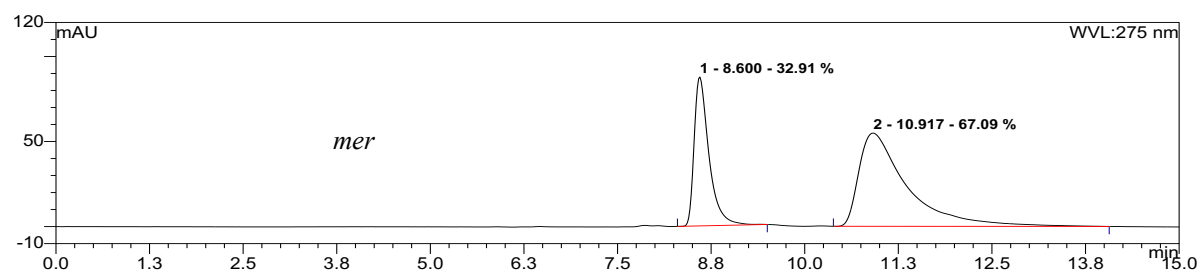
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.40	941.839	200.454	87.66
2	10.70	63.629	28.220	12.34
Total:		1005.469	228.674	100.00



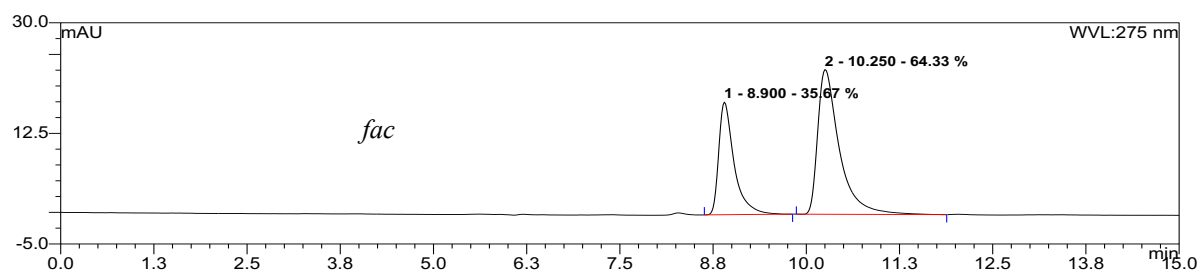
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.63	390.856	85.246	81.93
2	10.23	64.508	18.799	18.07
Total:		455.364	104.045	100.00

Photoderacemization (with A-L-PC):
Chromatogram


No.	Peak Name	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	durene	1.687	35.129	575.438	52.75
2	mer	7.583	20.743	135.204	31.15
3	fac	8.167	10.720	65.597	16.10
Total:			66.591	776.239	100.00



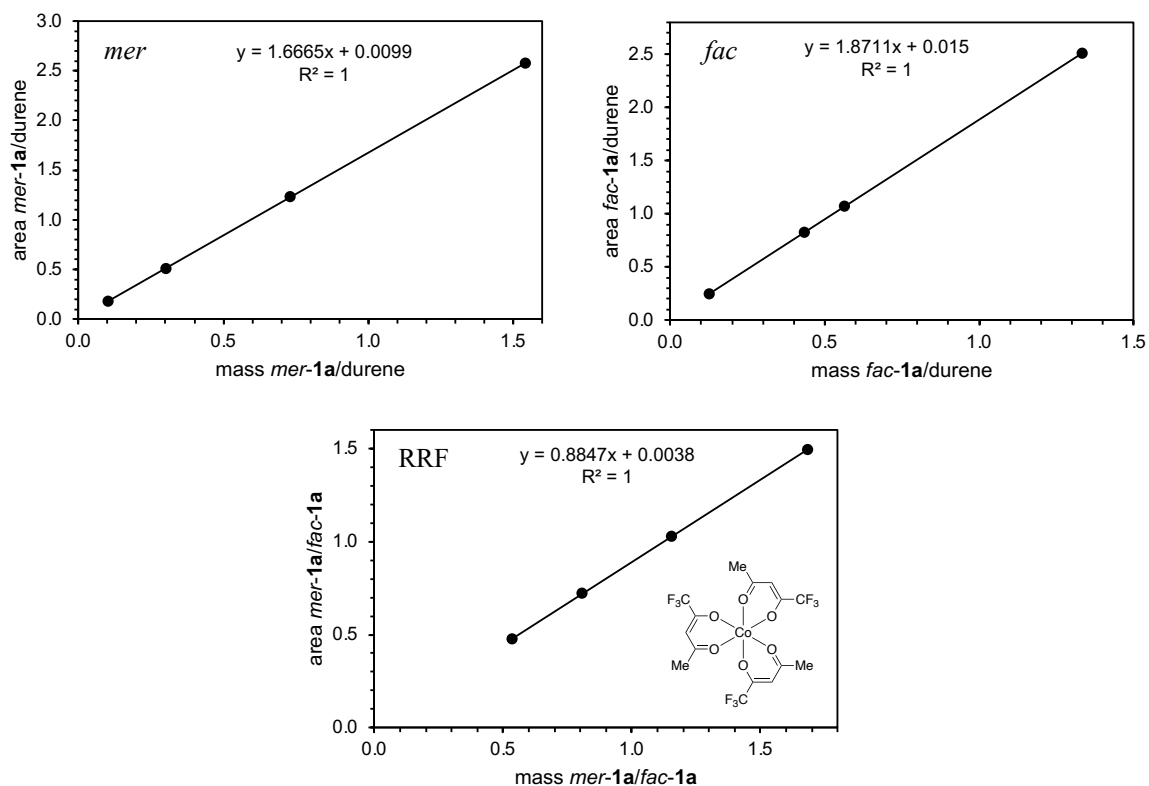
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.60	87.547	20.028	32.91
2	10.92	54.805	40.821	67.09
Total:		142.352	60.849	100.00



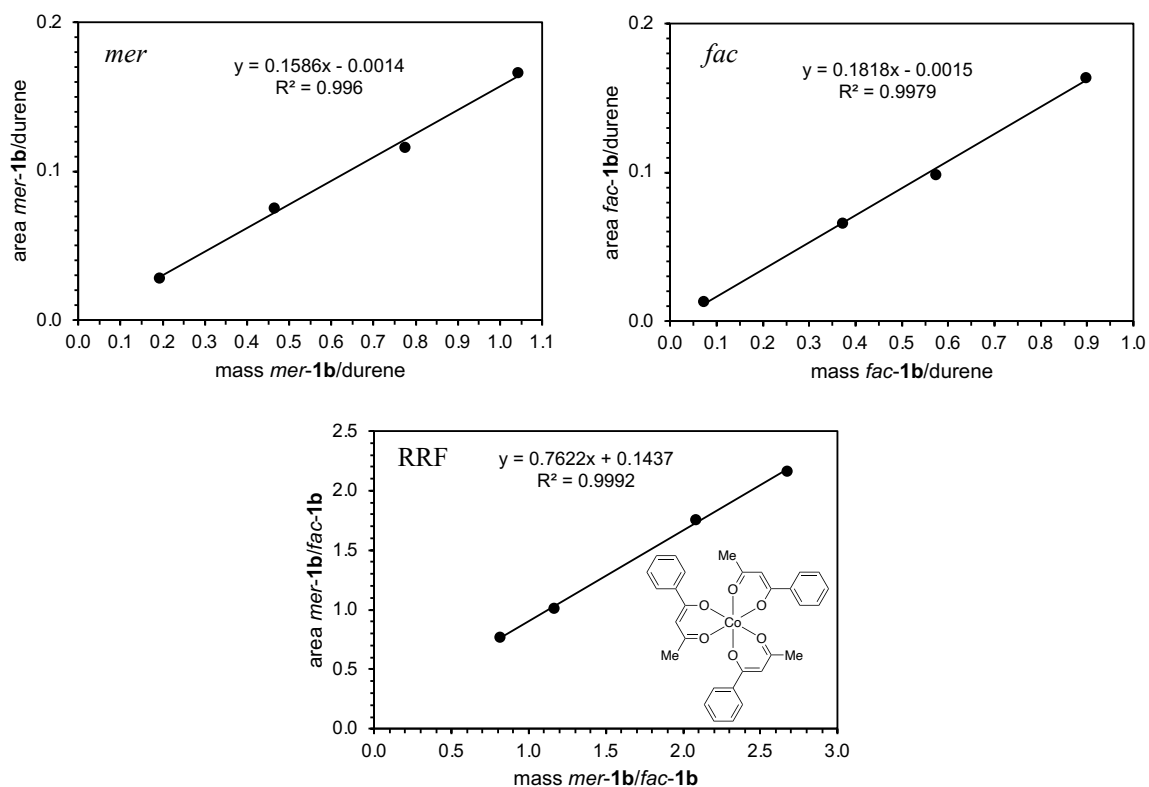
No.	Ret.Time min	Height mAU	Area mAU*min	Rel.Area %
1	8.90	17.825	4.263	35.67
2	10.25	22.897	7.688	64.33
Total:		40.722	11.951	100.00

8. Calibration Data

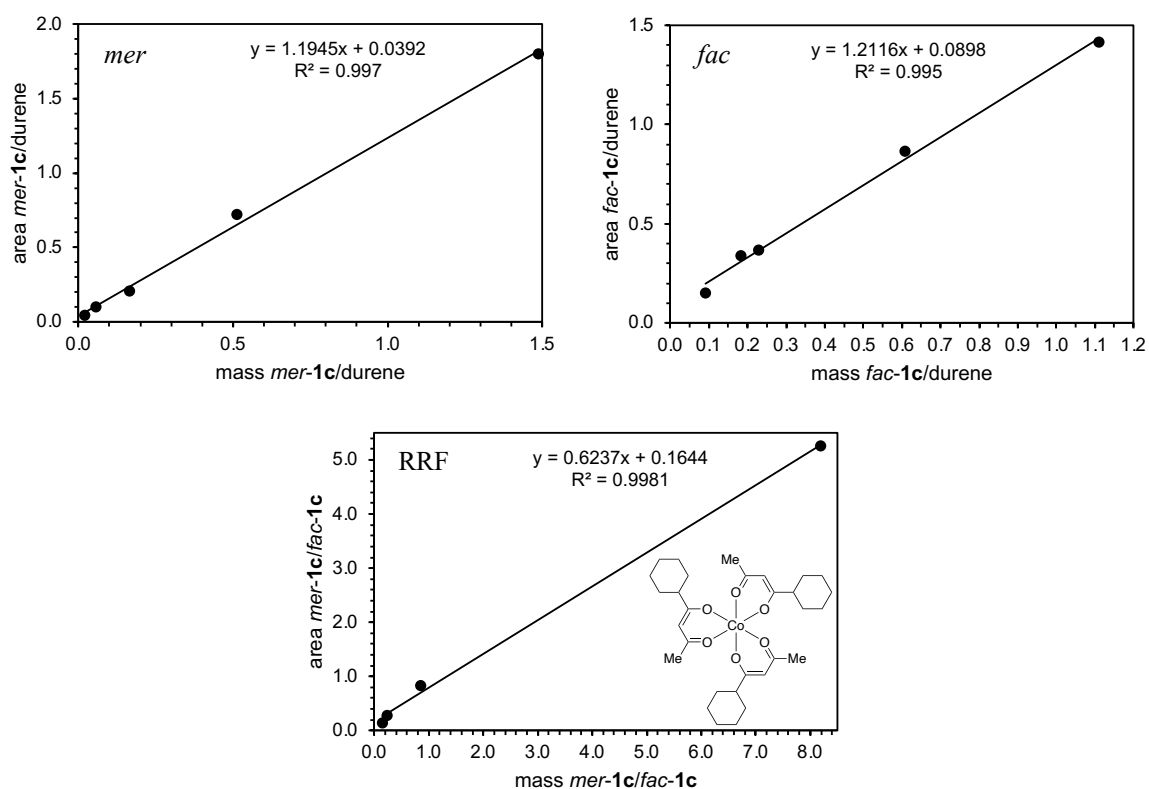
Co(tfac)₃ (1a): HPLC-DAD (225 nm)



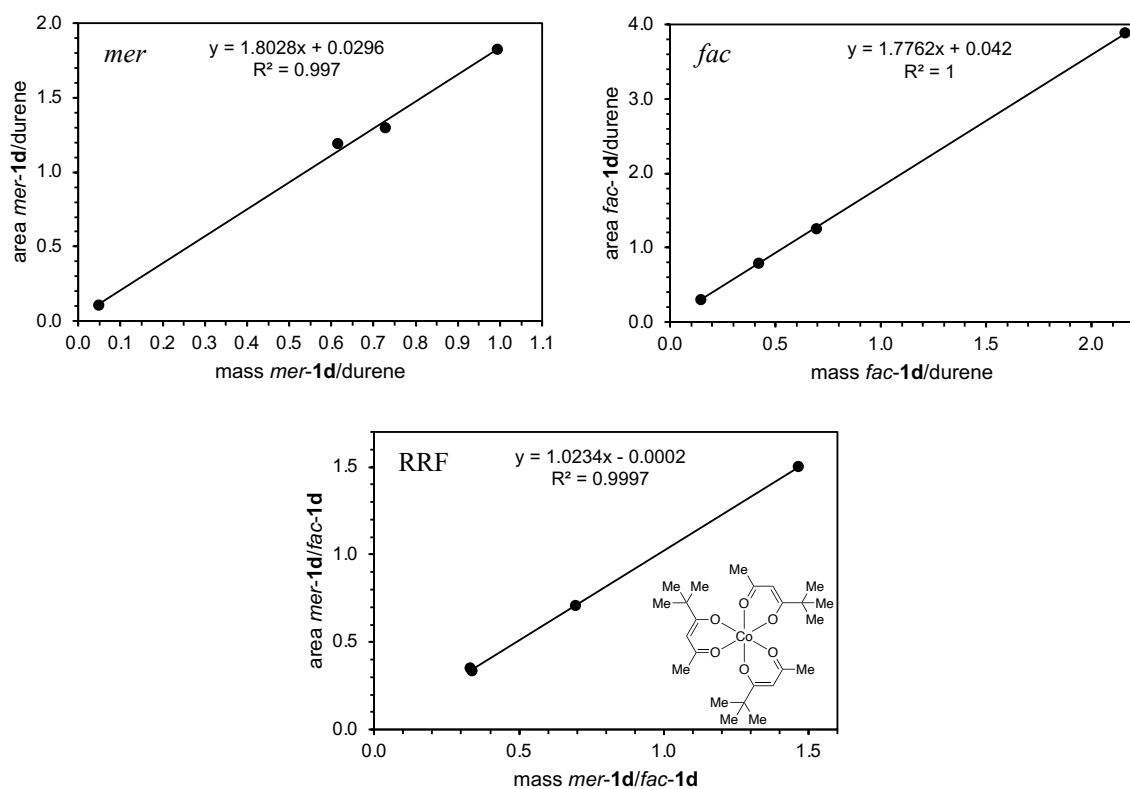
Co(bzac)₃ (1b): ¹H NMR (500.1 MHz, CD₂Cl₂), CH₃ signals



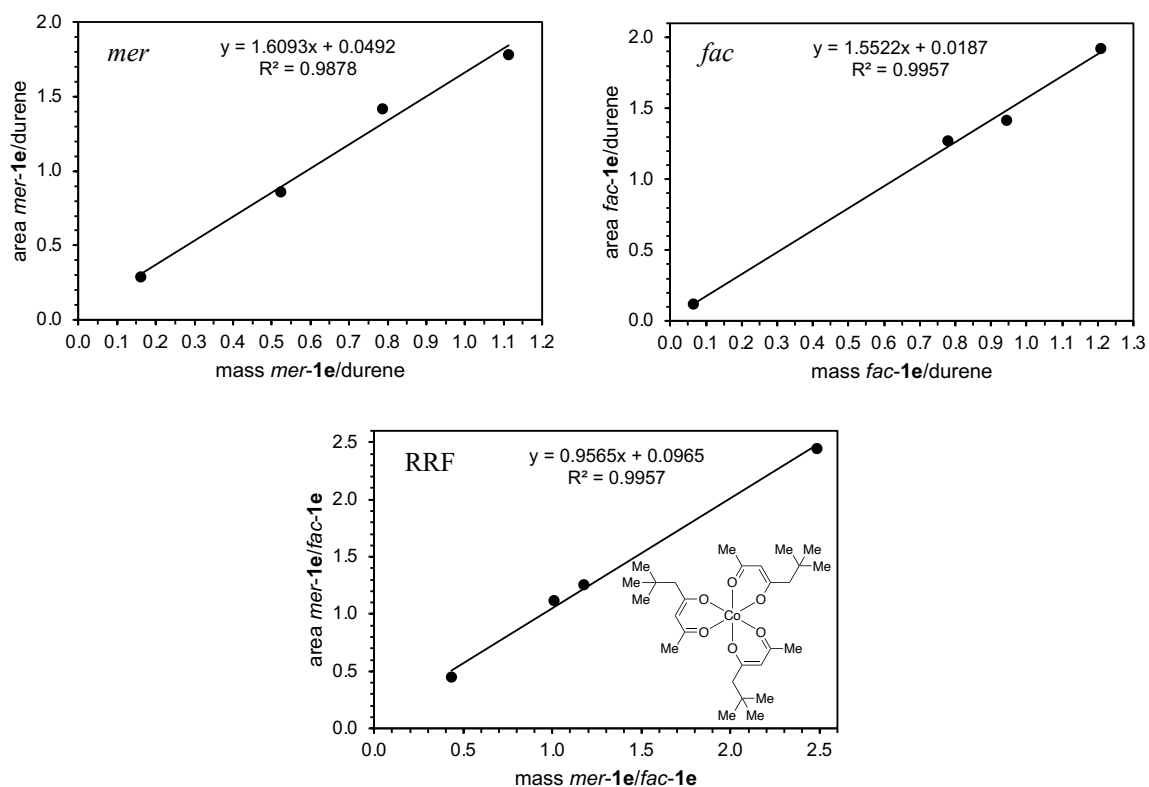
Co(cycac)₃ (1c): HPLC-DAD (225 nm)



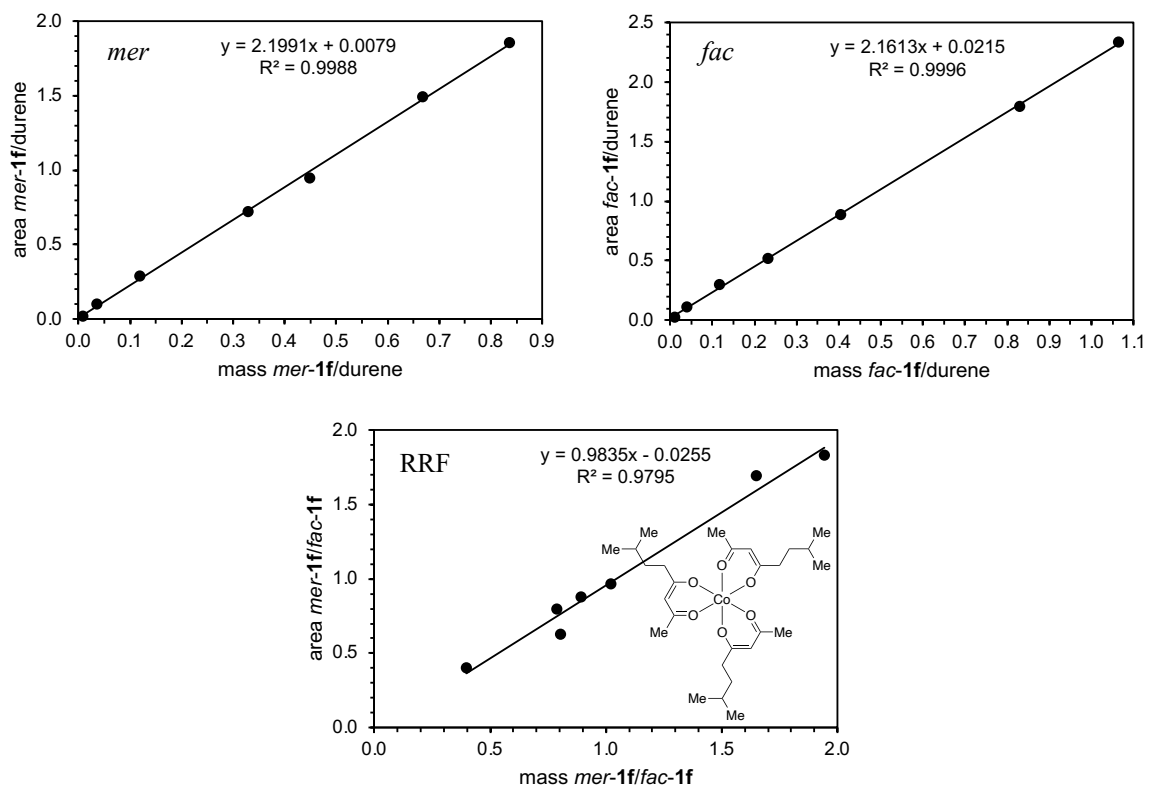
Co(pivac)₃ (1d): HPLC-DAD (225 nm)



Co(dmbac)₃ (1e): HPLC-DAD (225 nm)

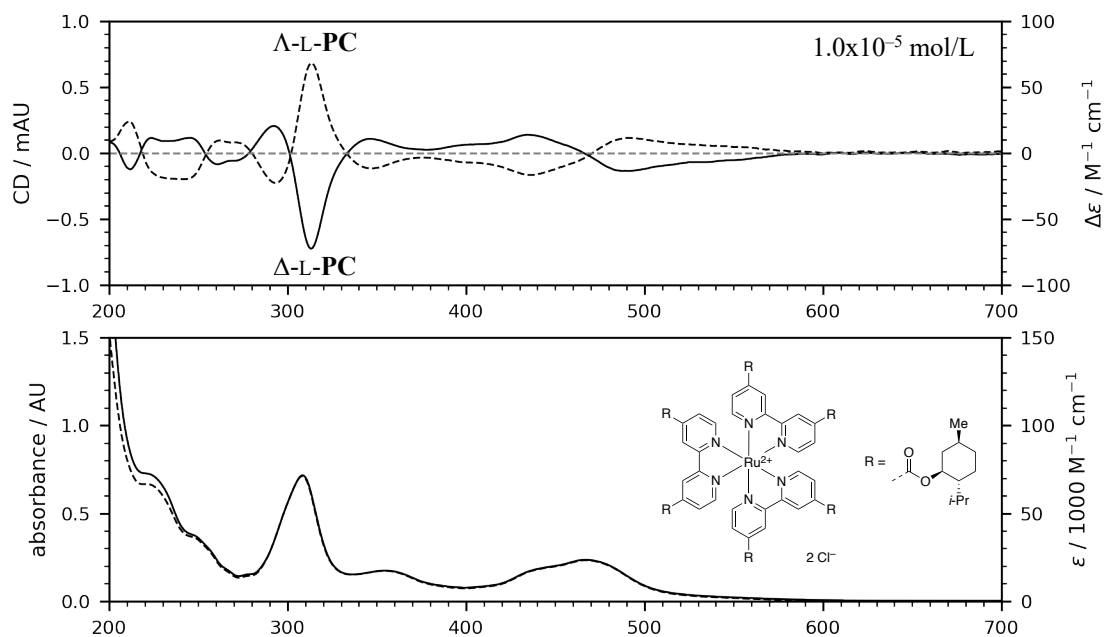


Co(mpac)₃ (1f): HPLC-DAD (225 nm)



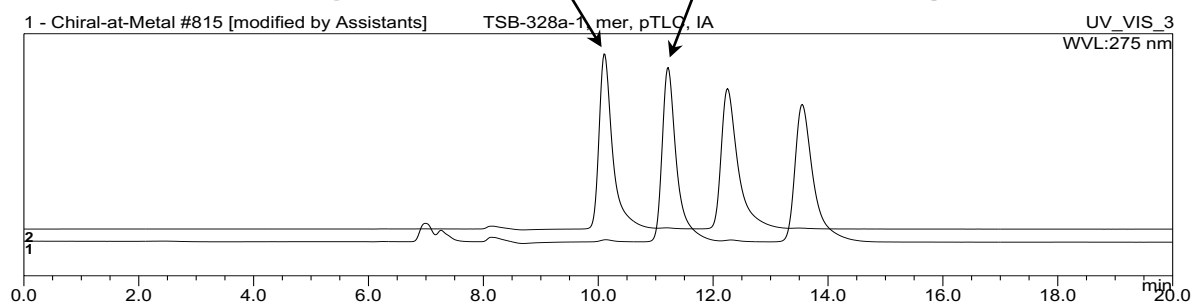
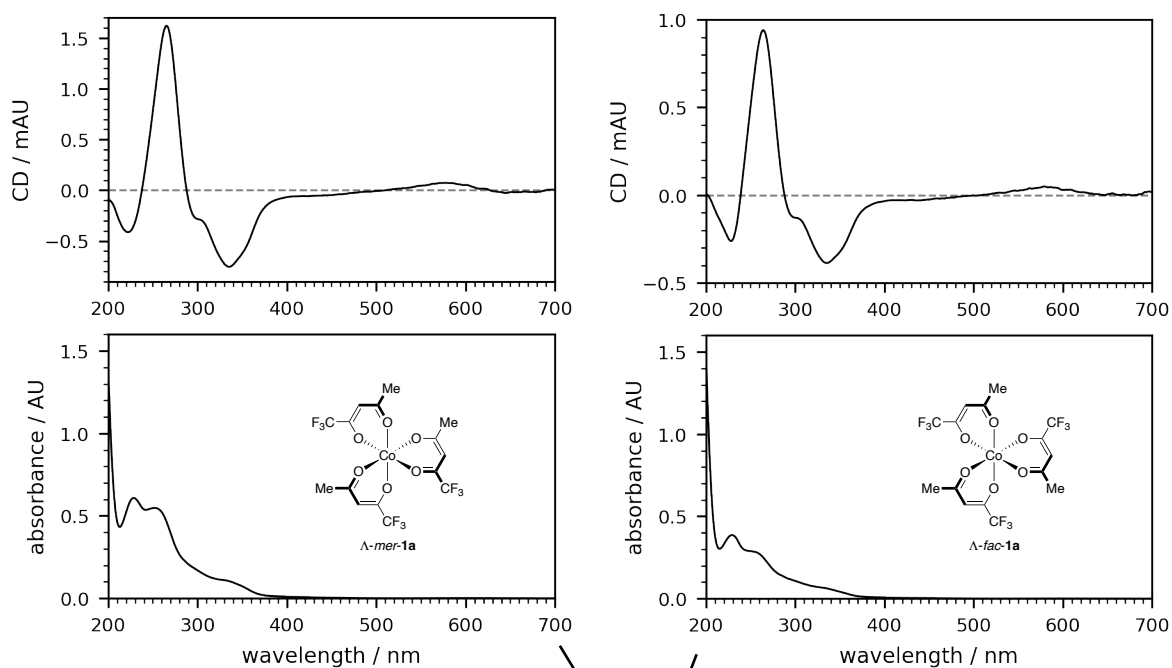
9. CD and UV/Vis Spectra

Chiral Photocatalysts^[2b]

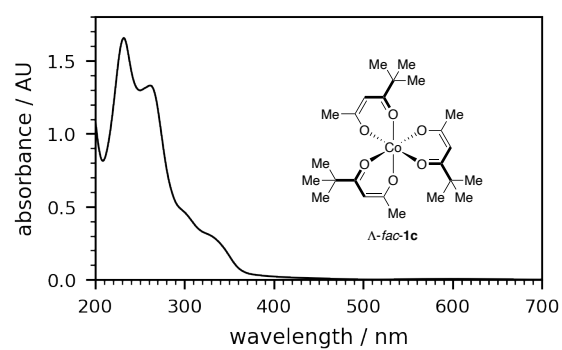
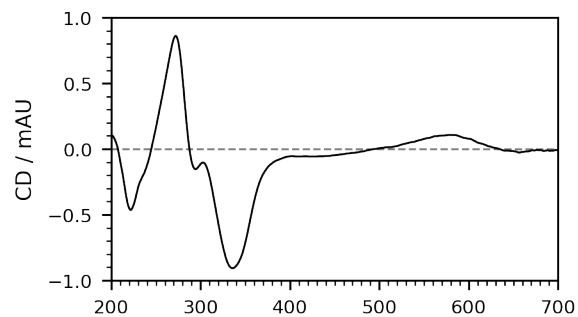
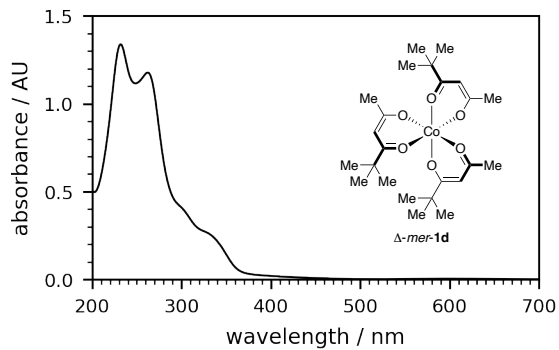
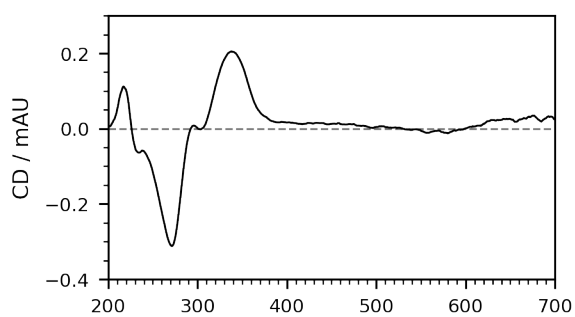
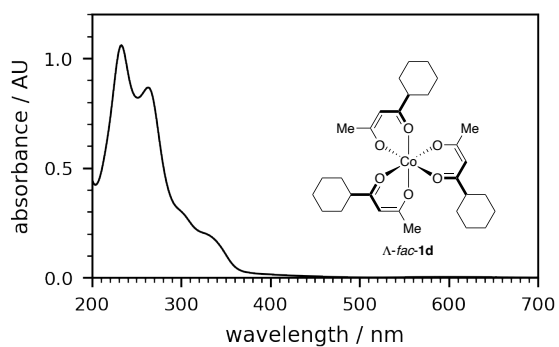
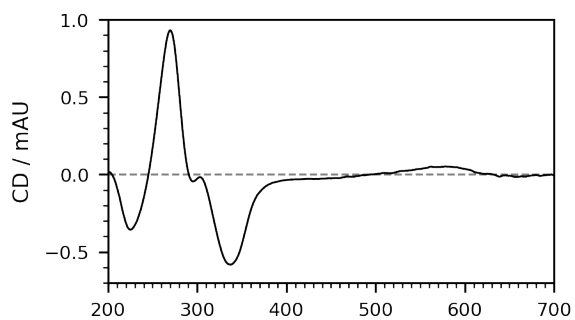
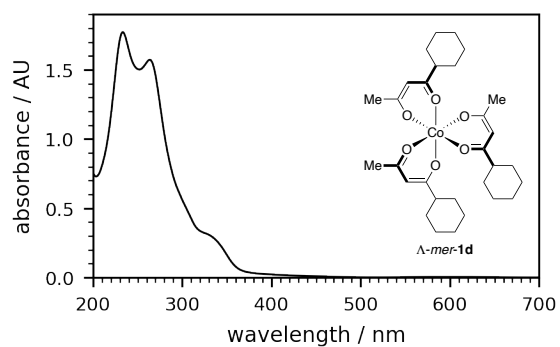
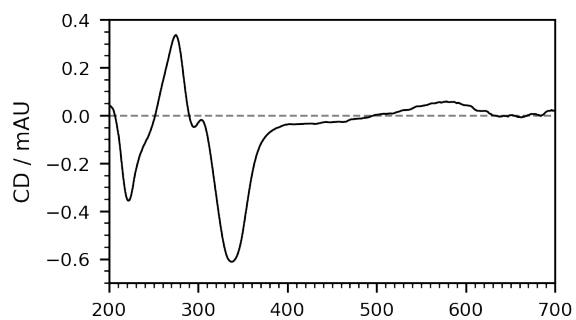


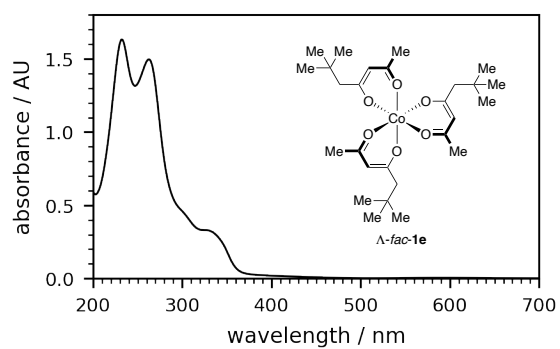
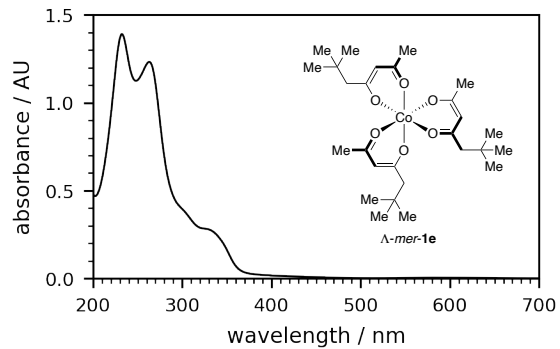
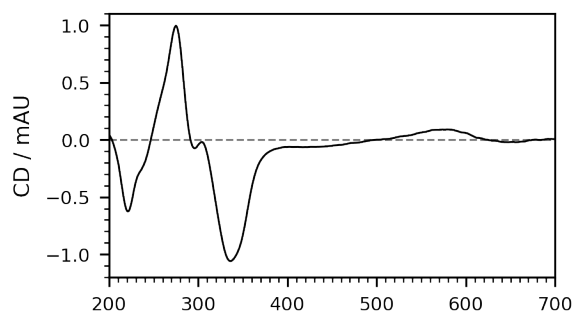
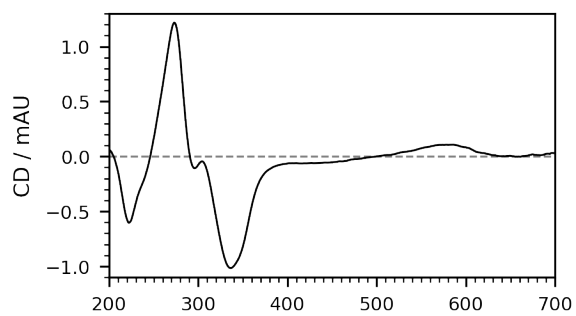
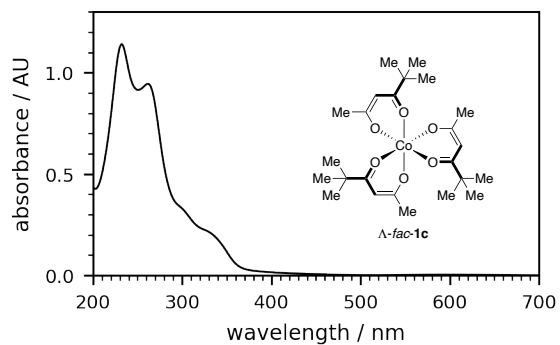
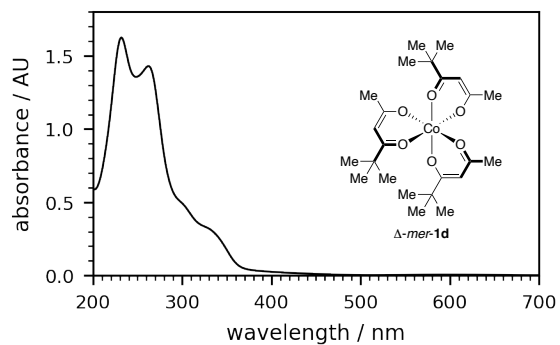
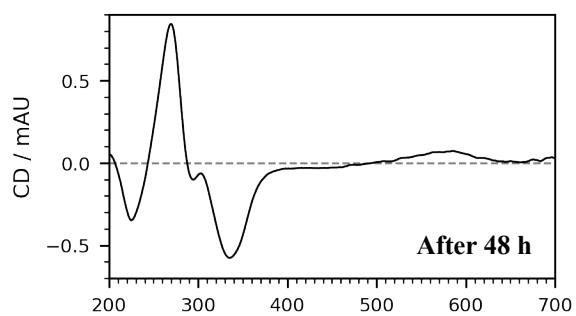
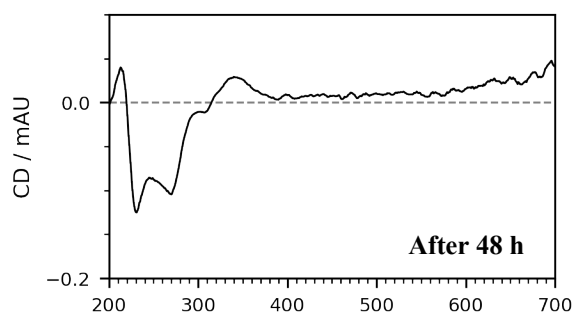
Co(tfac)₃ (**1a**)^[5]

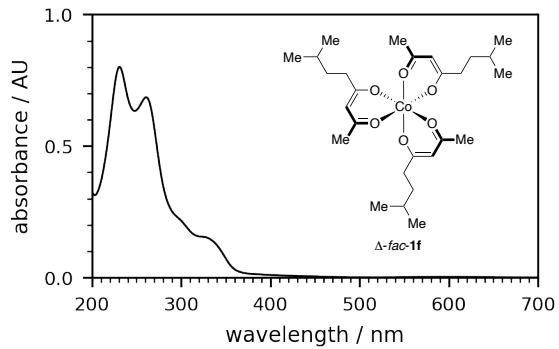
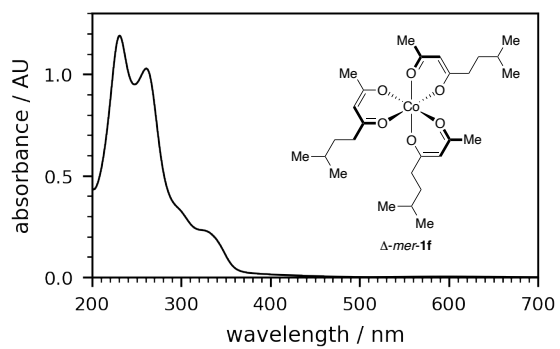
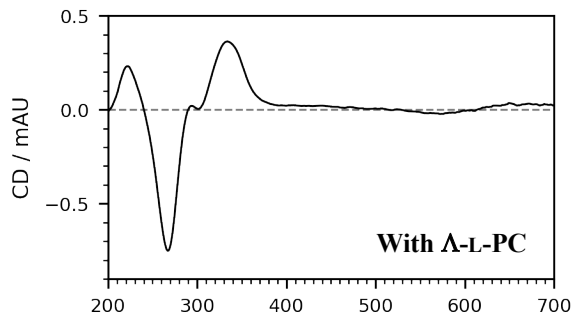
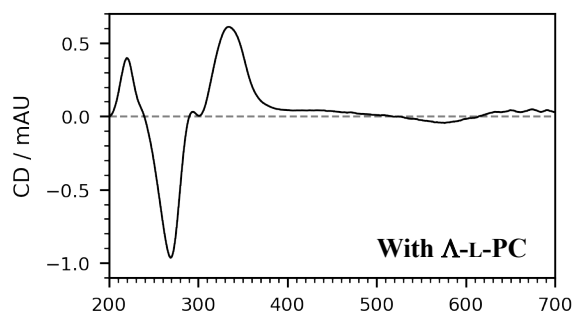
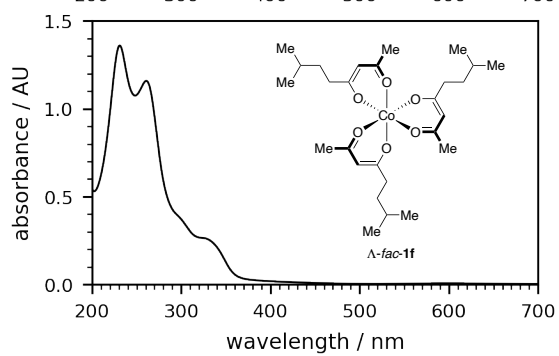
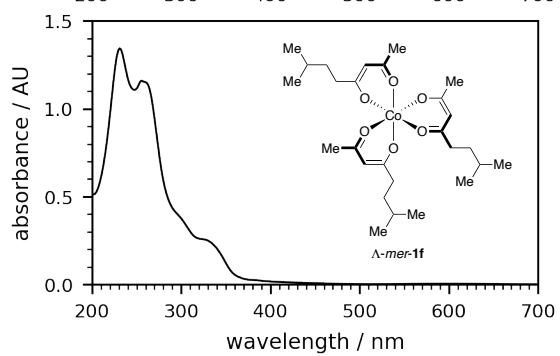
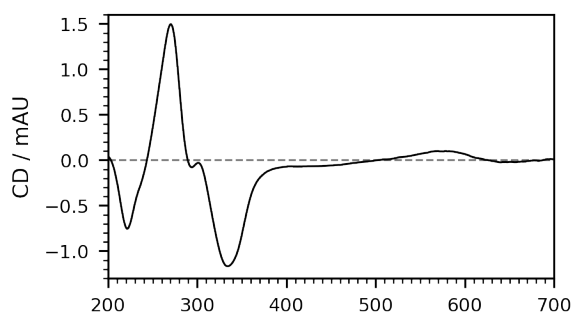
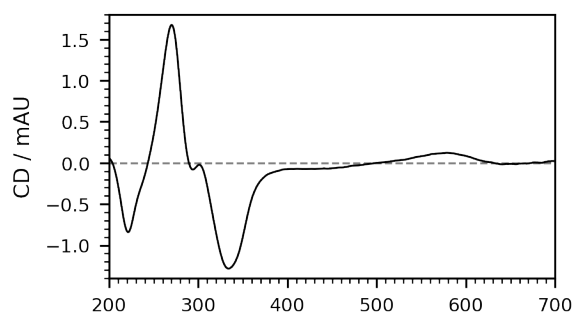
$\Lambda\text{-mer-1a}$ and $\Lambda\text{-fac-1a}$ were isolated by HPLC on a chiral stationary phase (see above).



Photoderacemization Products

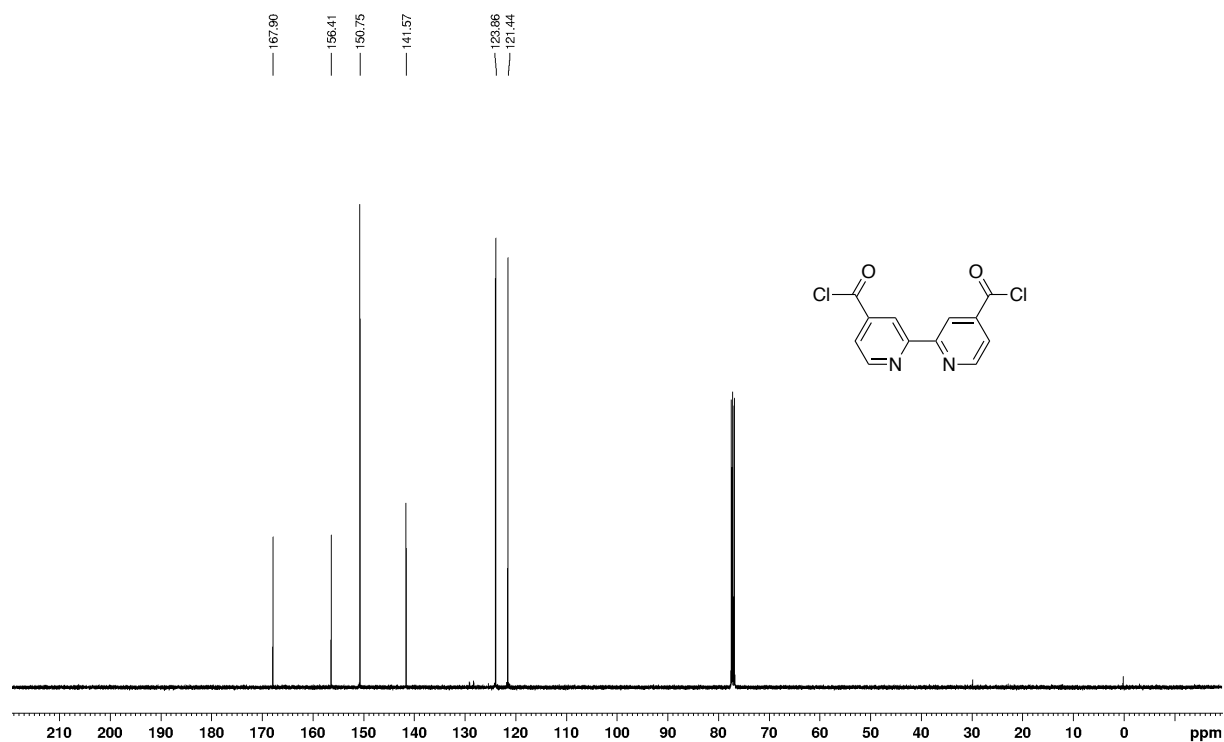
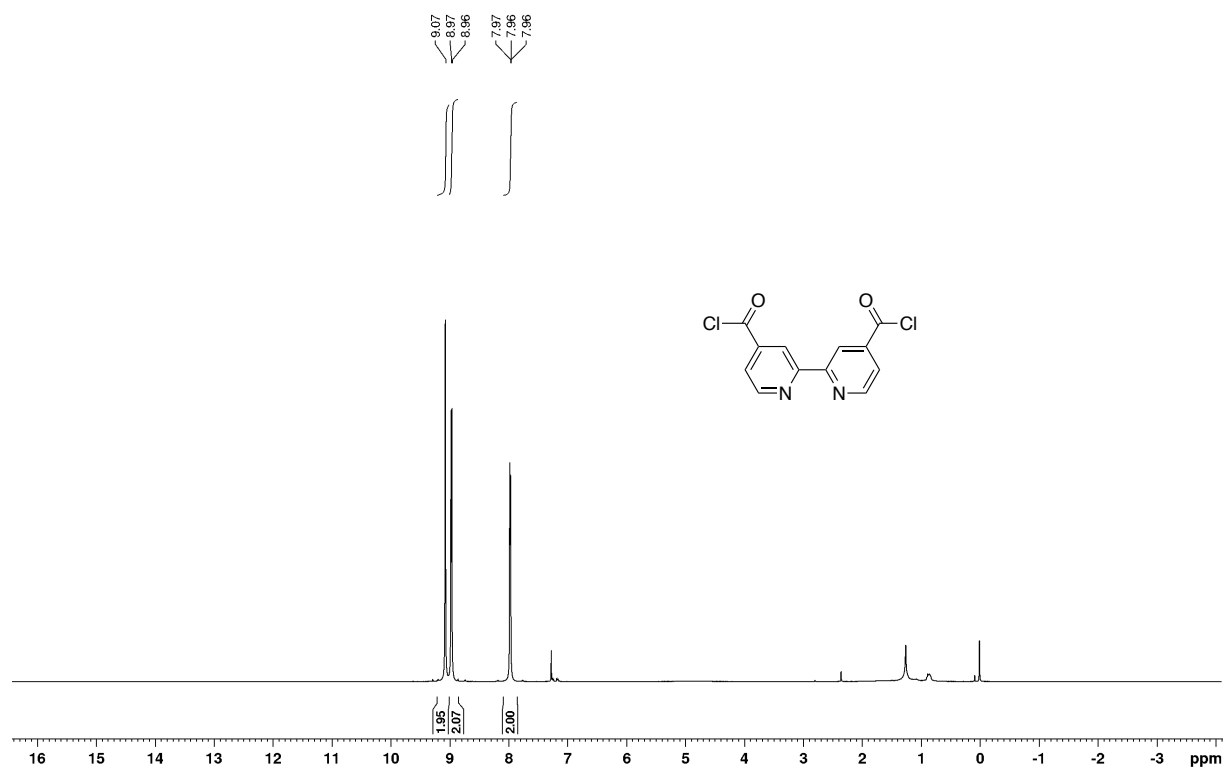




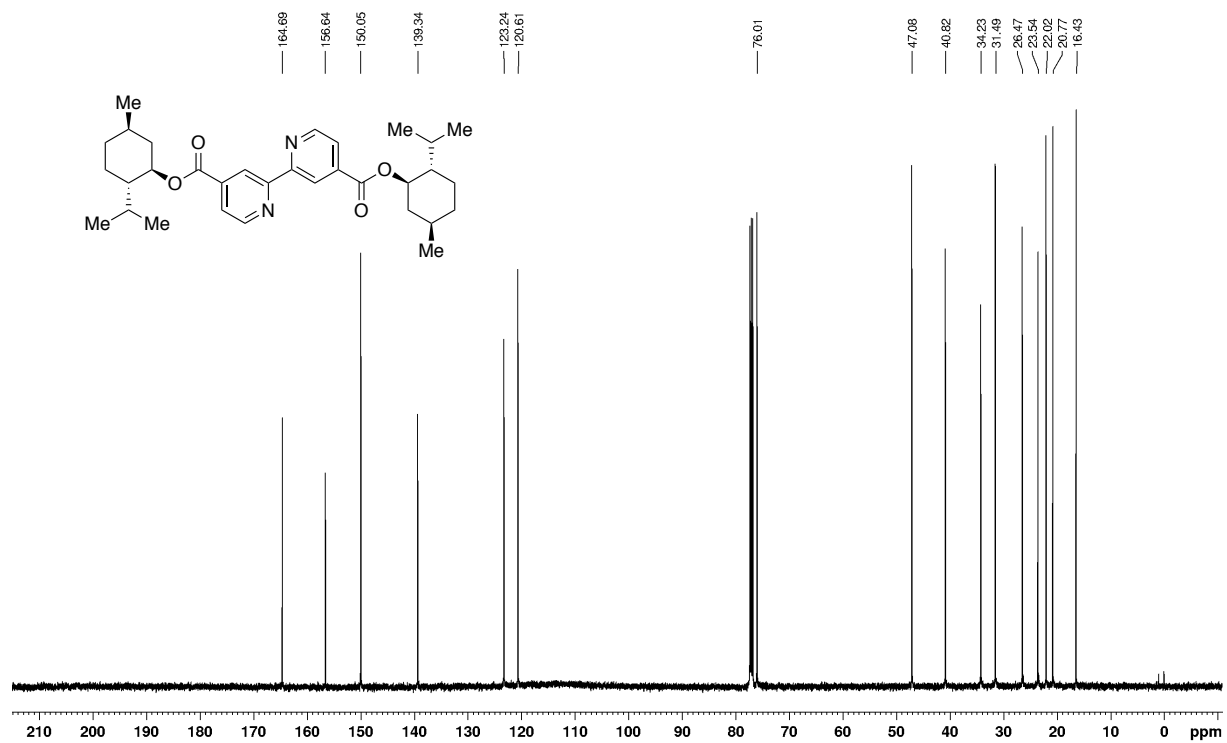
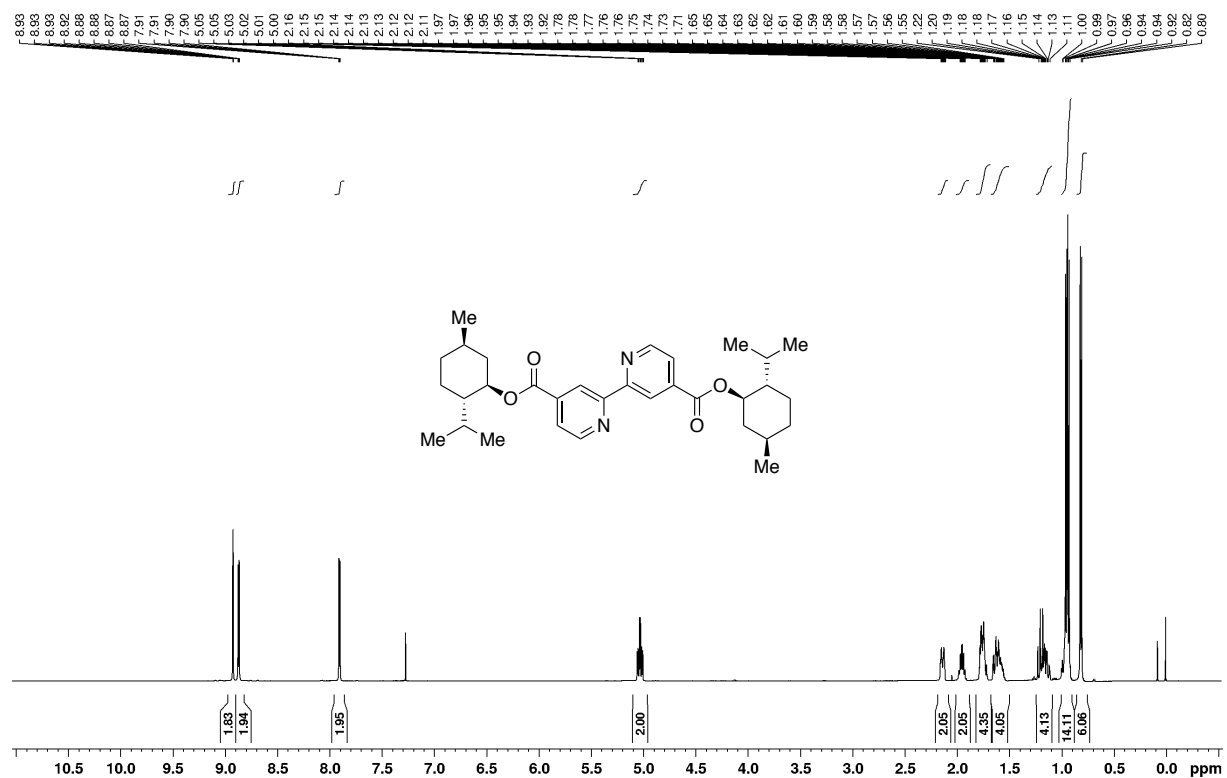


10. NMR Spectra

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of [2,2'-Bipyridine]-4,4'-dicarbonyl dichloride (S1)



^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of Bis((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) [2,2'-bipyridine]-4,4'-dicarboxylate (L-menbpy, S2)



¹H NMR spectrum (CDCl₃) of the Ru(II) complex.

Chemical structure: A Ru(II) complex with four 2,6-disubstituted pyridine ligands and two chloride ions. The R group is defined as a 4-methyl-2-(prop-1-en-1-yl)pyrrolidine ring.

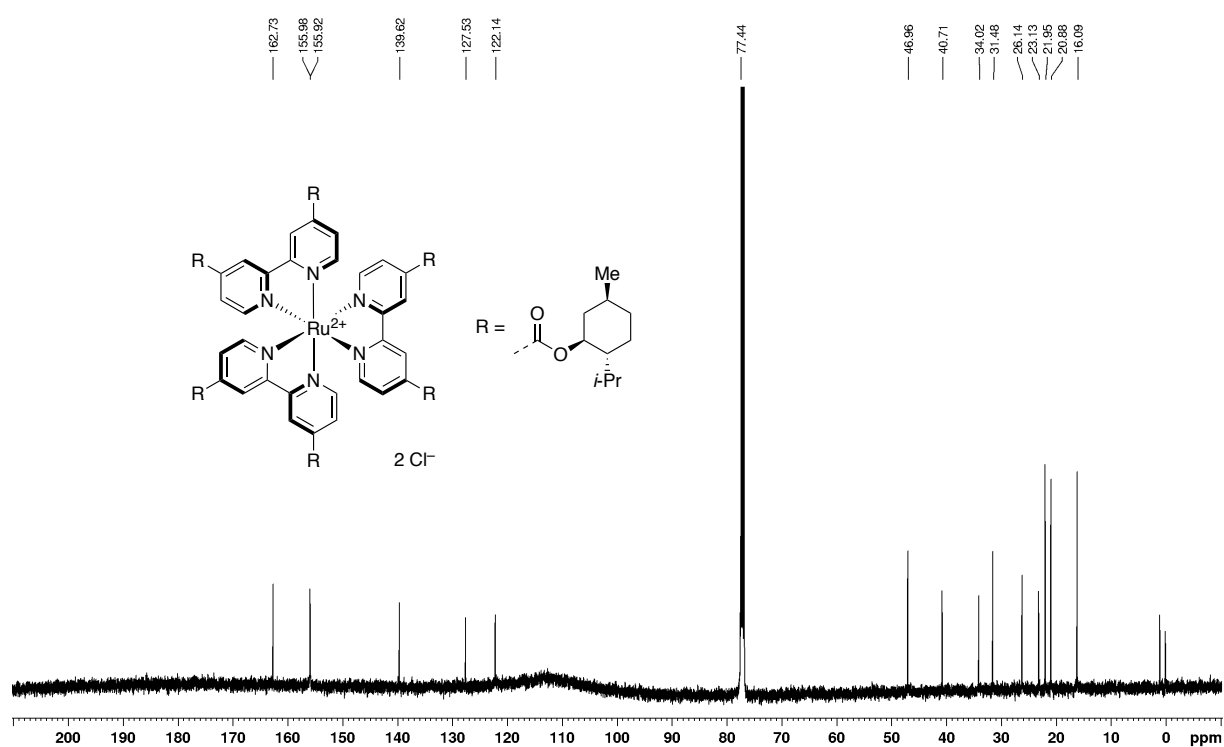
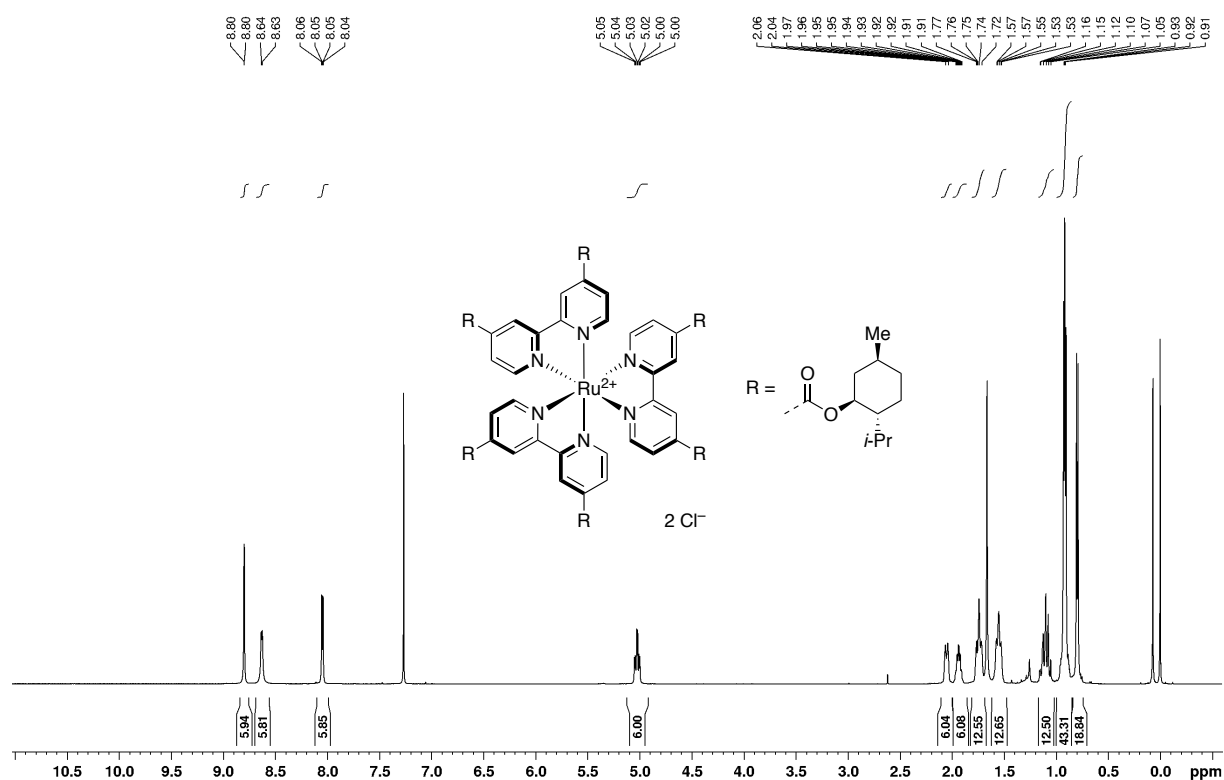
Integration values (from left to right): 6.21, 5.96, 5.91, 5.91, 6.00, 6.08, 12.03, 12.09, 12.37, 42.51, 17.75.

Peak assignments (from left to right):

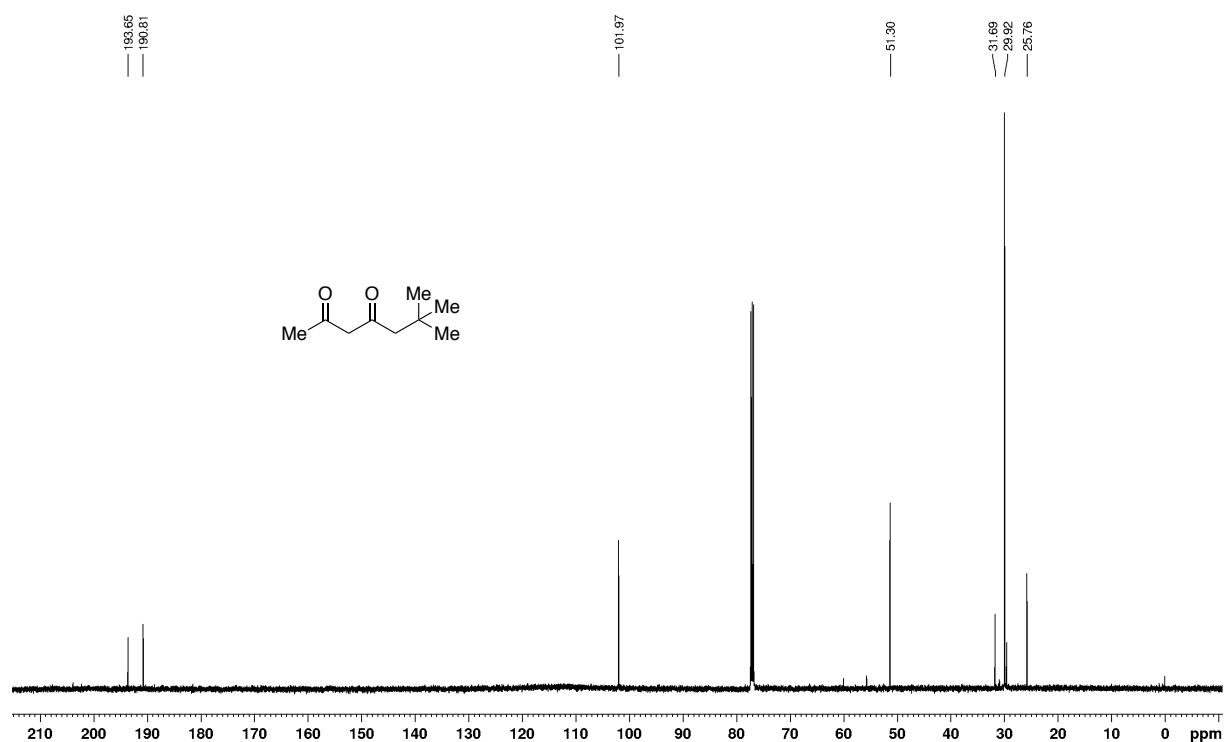
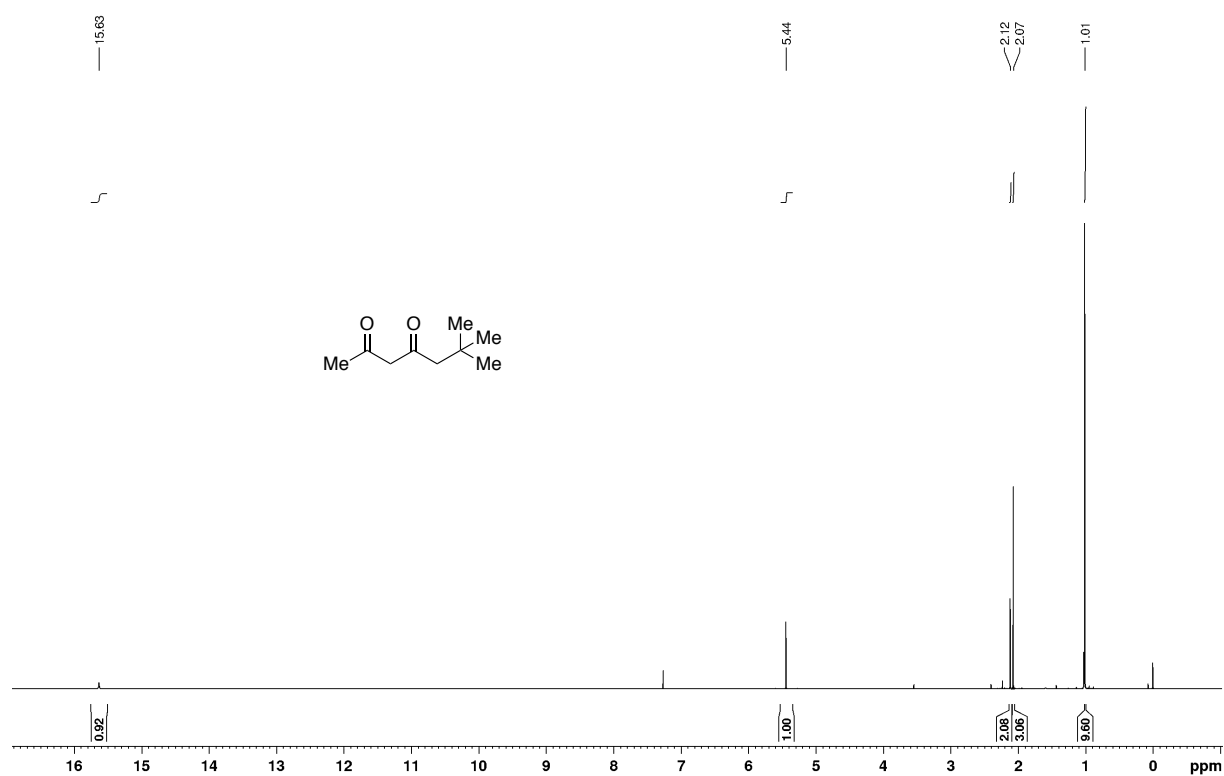
- 8.82, 8.57, 8.11, 8.10 (aromatic protons, integration 6.21, 5.96, 5.91)
- 7.20 (solvent peak, integration 5.91)
- 5.02, 5.01, 4.99, 4.98, 4.97, 4.96 (aromatic protons, integration 5.91)
- 2.12, 2.10, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.74, 1.72, 1.56, 1.55, 1.54, 1.52, 1.20, 1.18, 1.16, 1.12, 1.10, 1.09, 1.07, 0.97, 0.95 (aliphatic protons, integration 6.00, 6.08, 12.03, 12.09, 12.37, 42.51, 17.75)



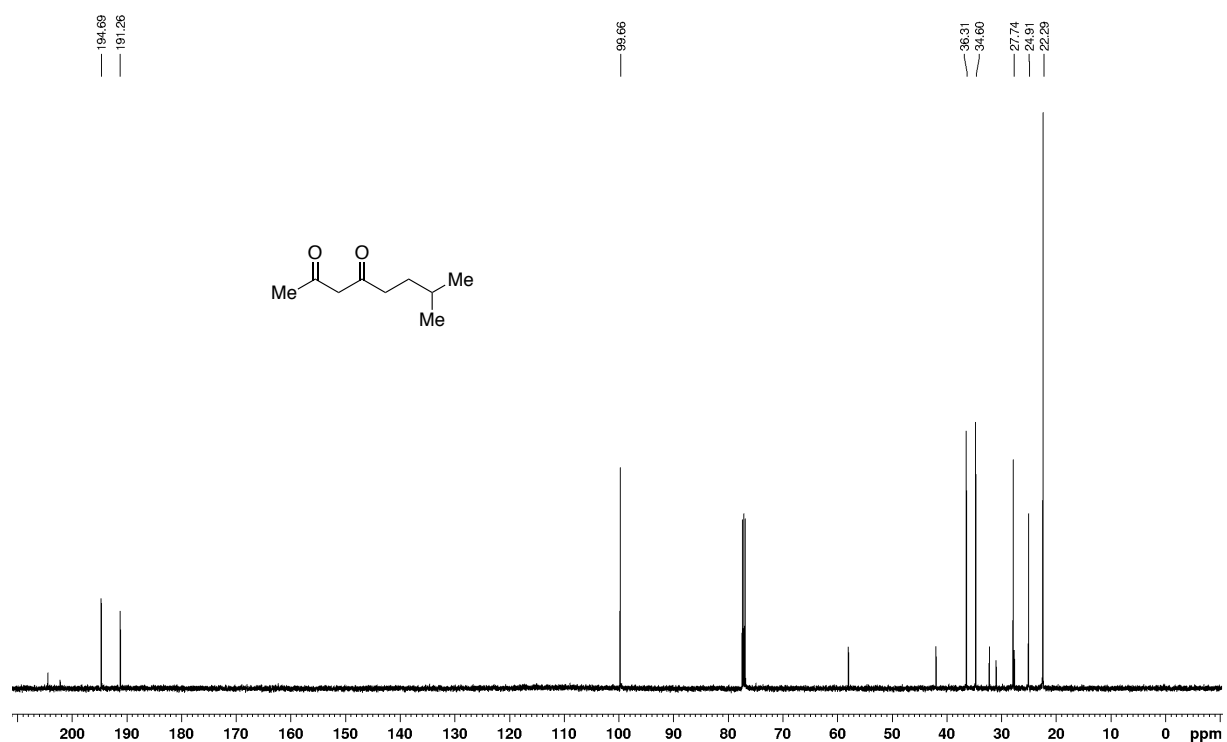
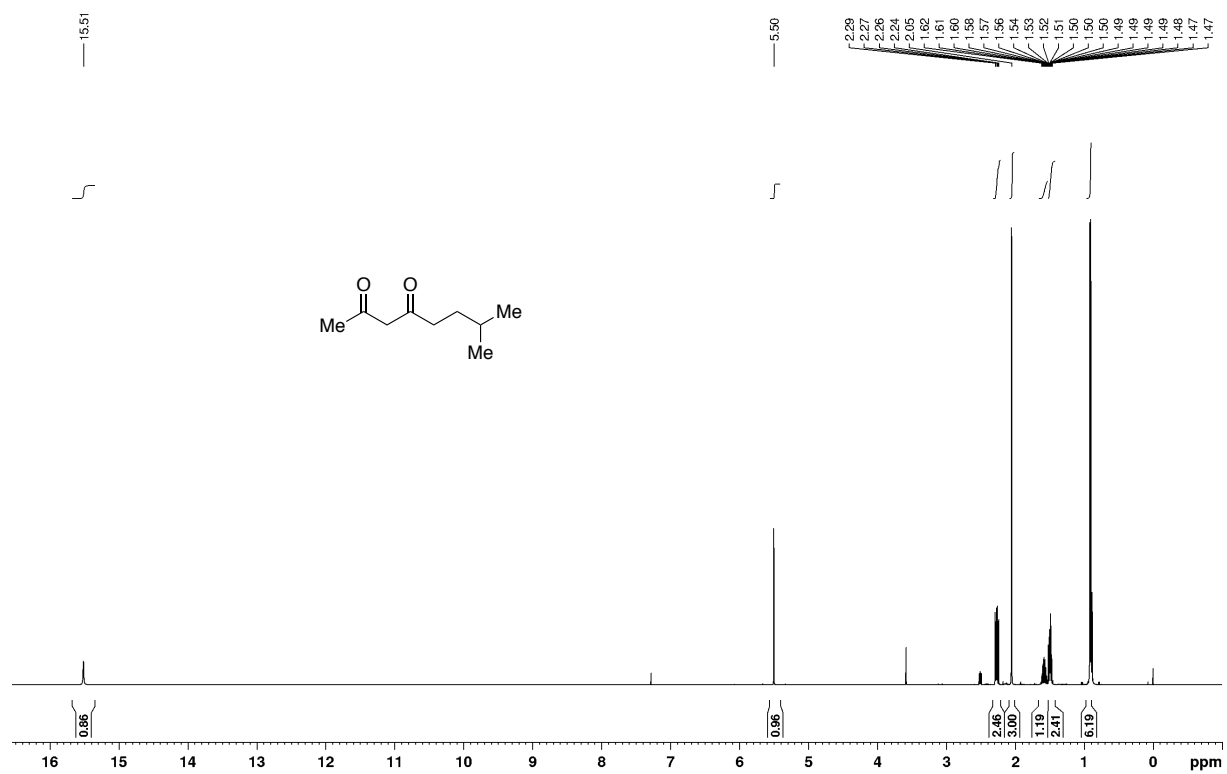
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of Λ -[Ru(L-menbpy) $_3$]Cl $_2$ (Λ -L-PC)



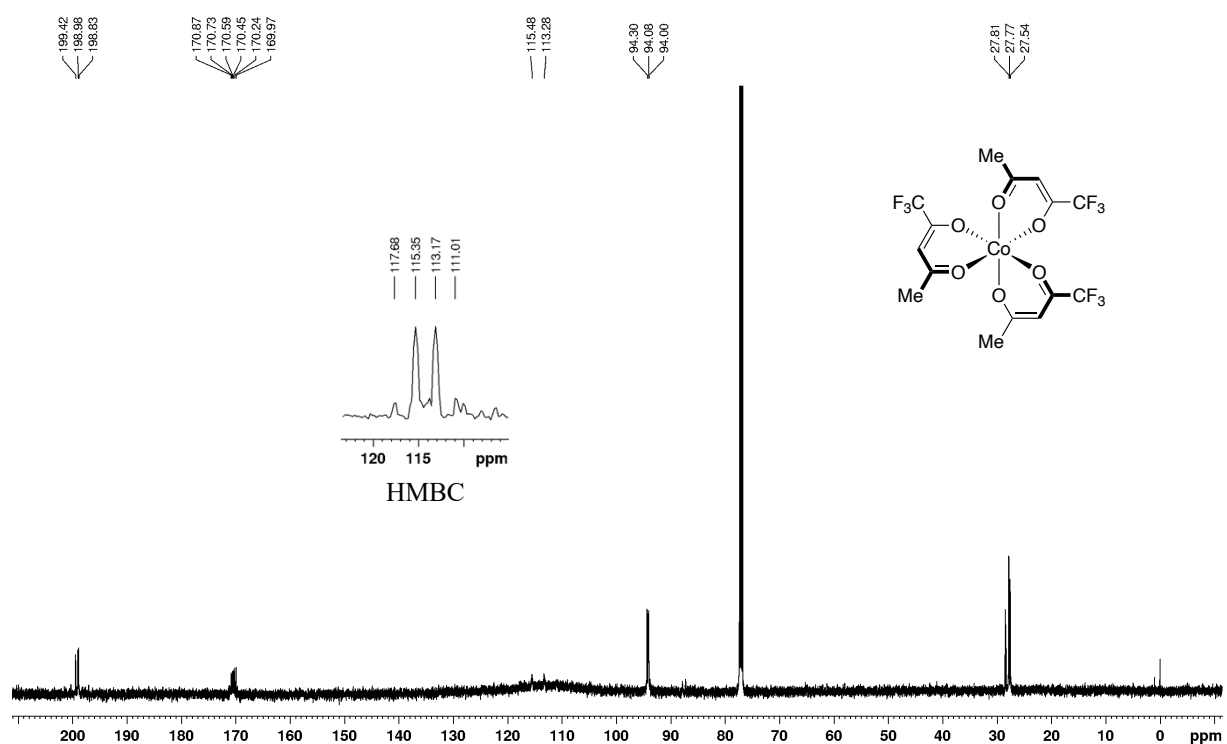
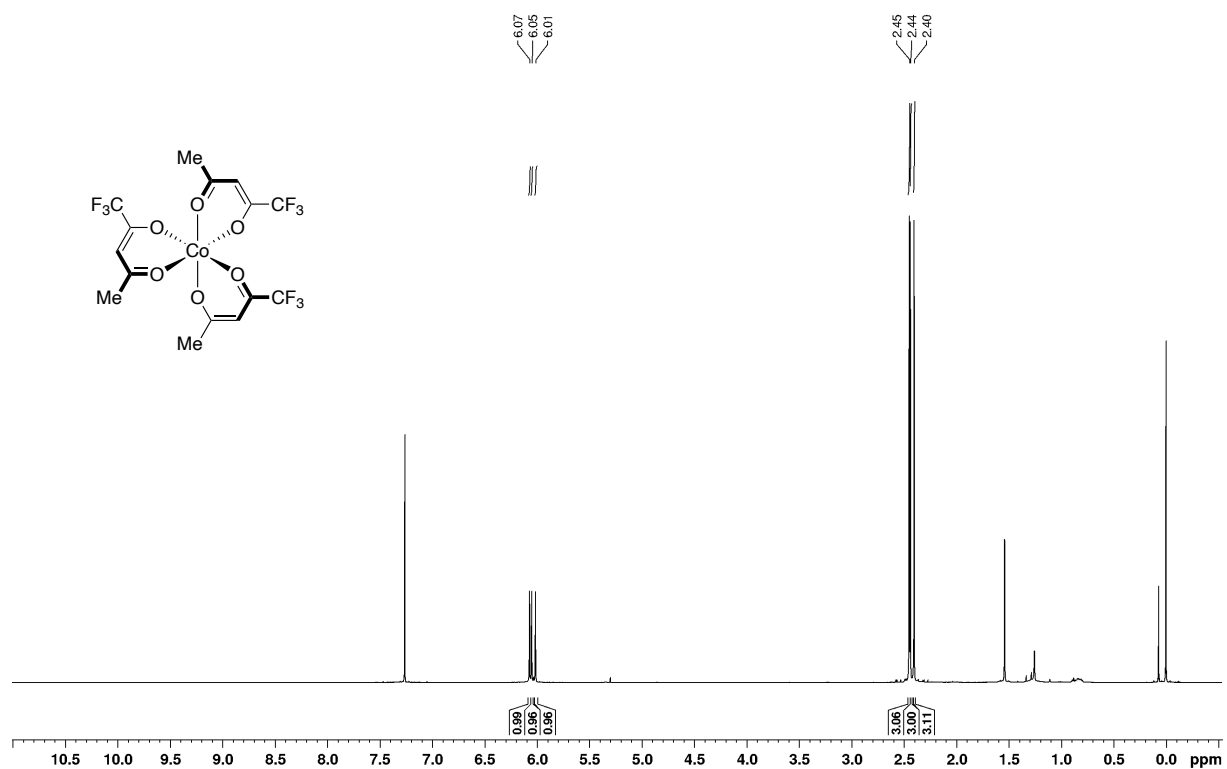
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 6,6-Dimethylheptane-2,4-dione (S3a)

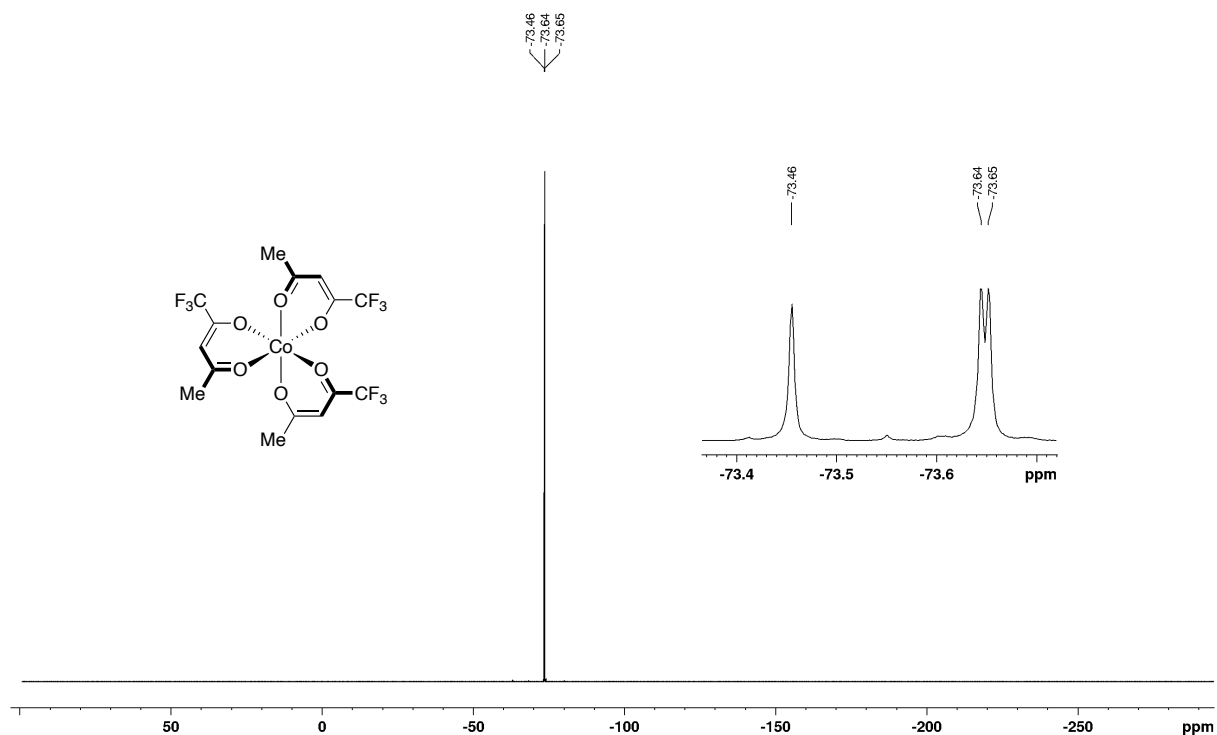


^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 7-Methyloctane-2,4-dione (S3b)

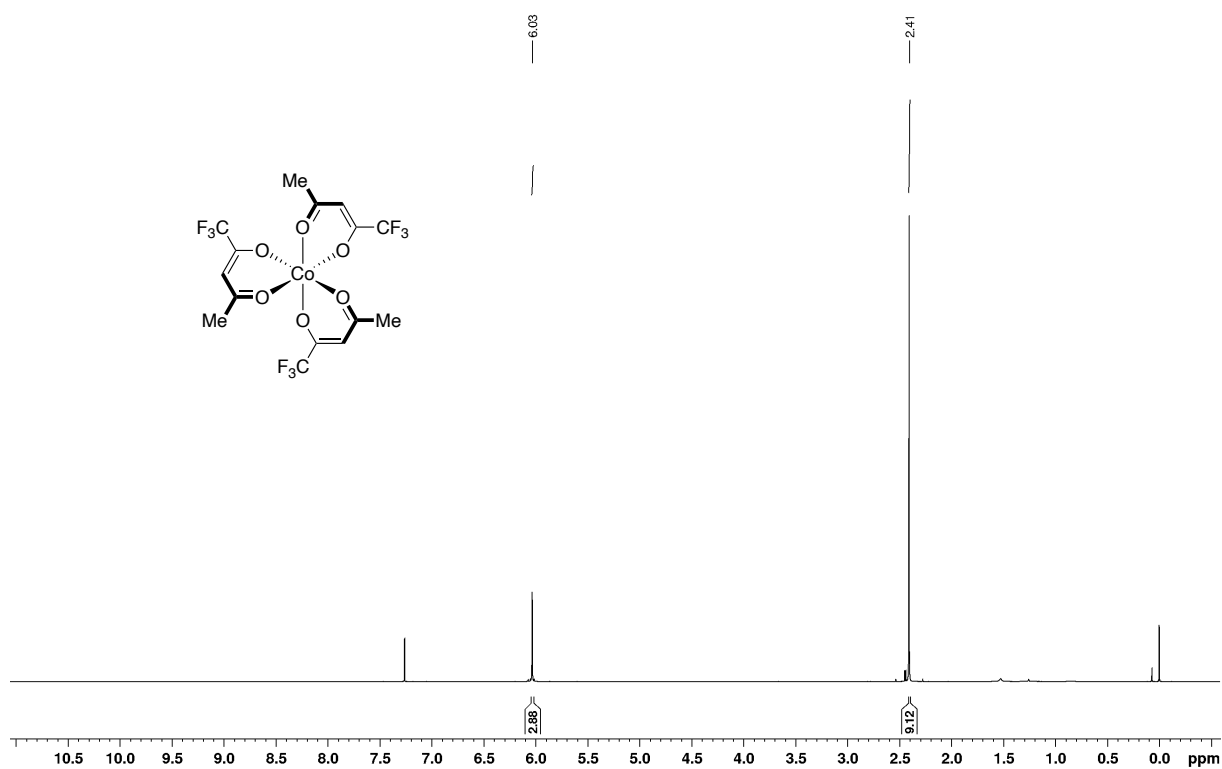


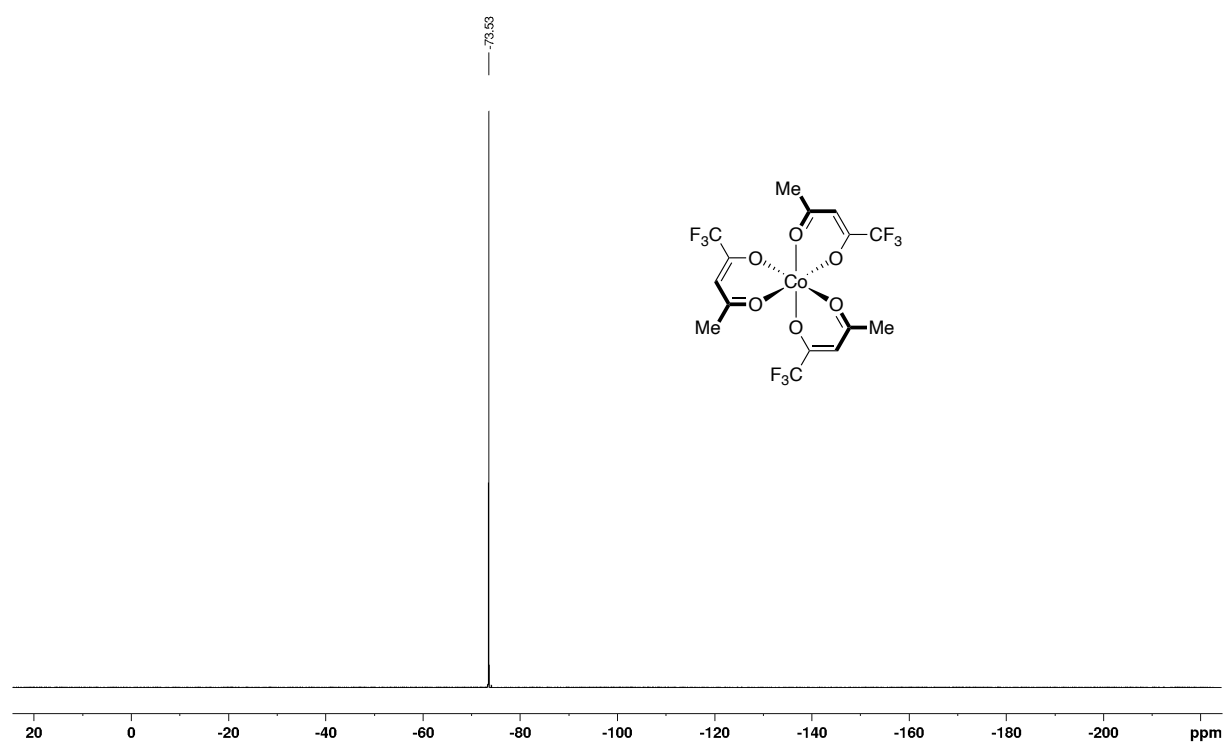
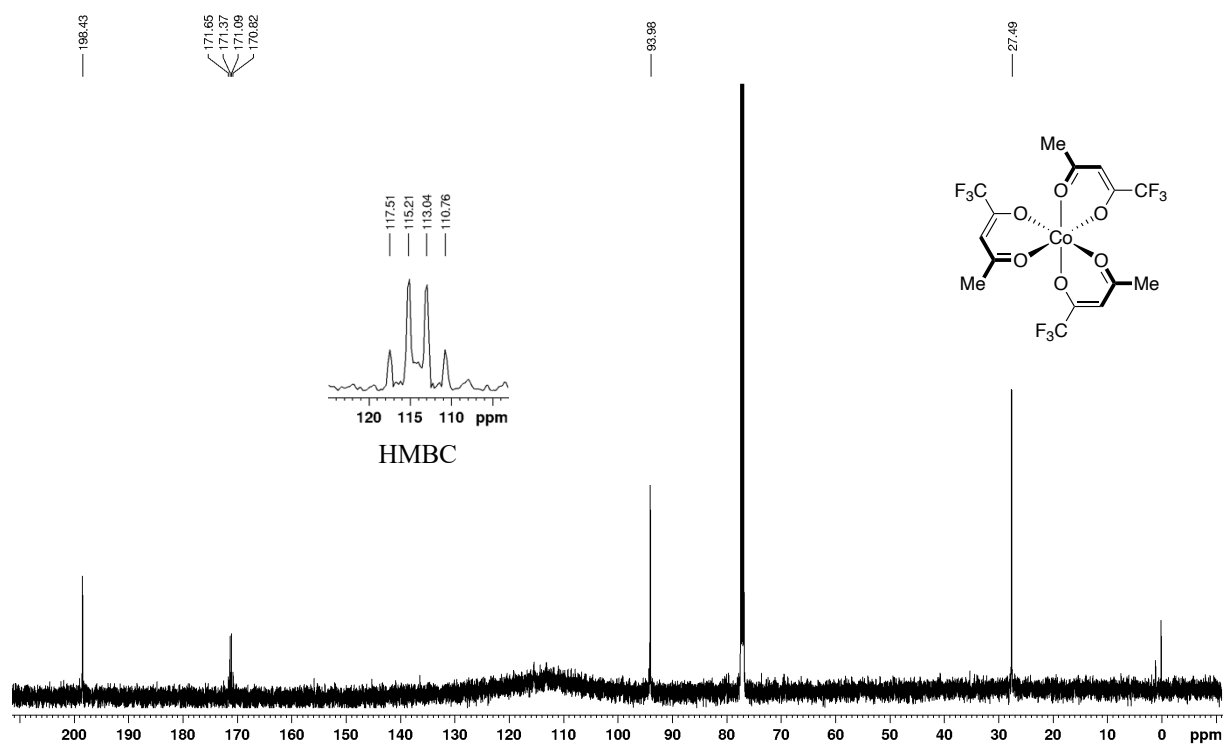
^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR of *mer*-Co(tfac)₃ (*mer*-1a)





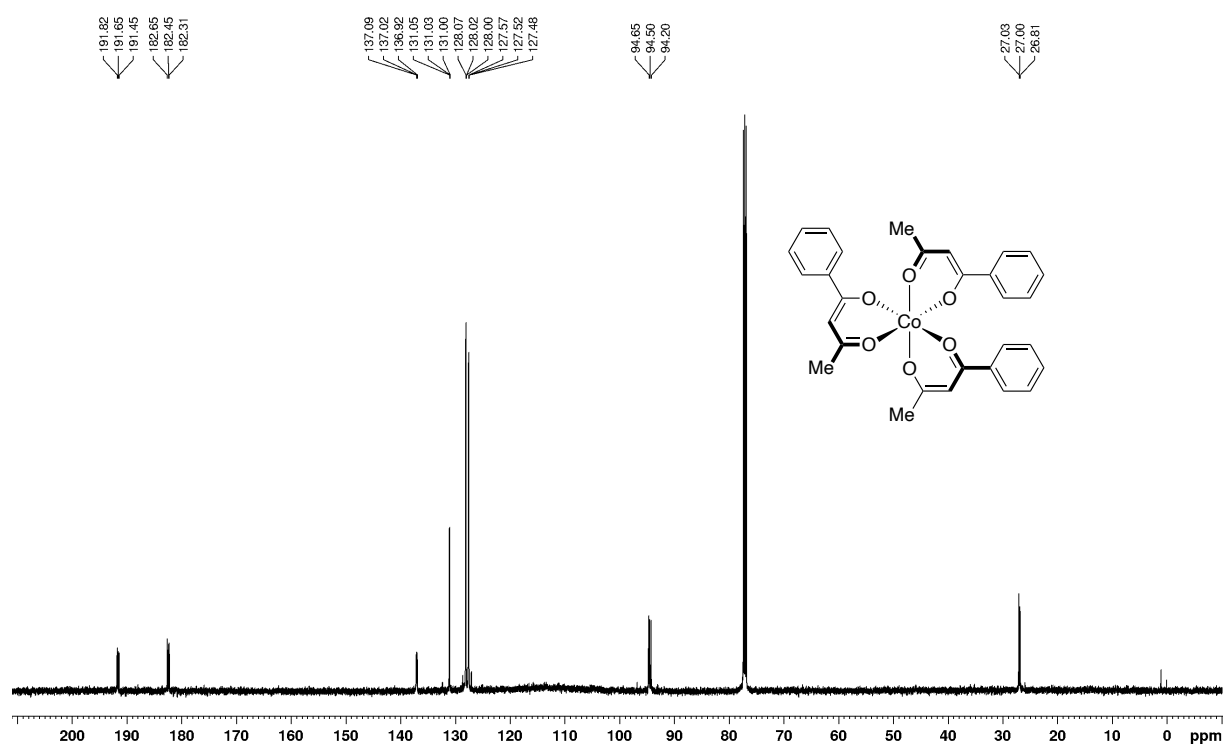
¹H, ¹³C{¹H} and ¹⁹F{¹H} NMR of *fac*-Co(tfac)₃ (*fac*-1a)



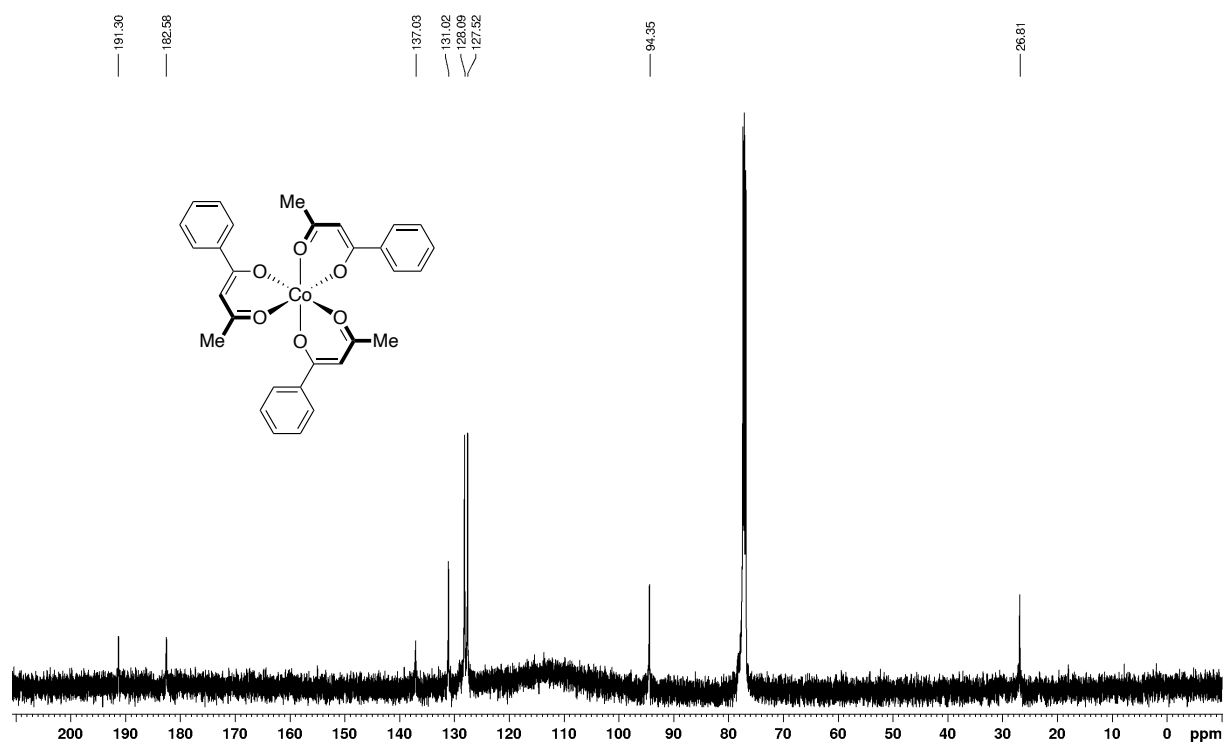
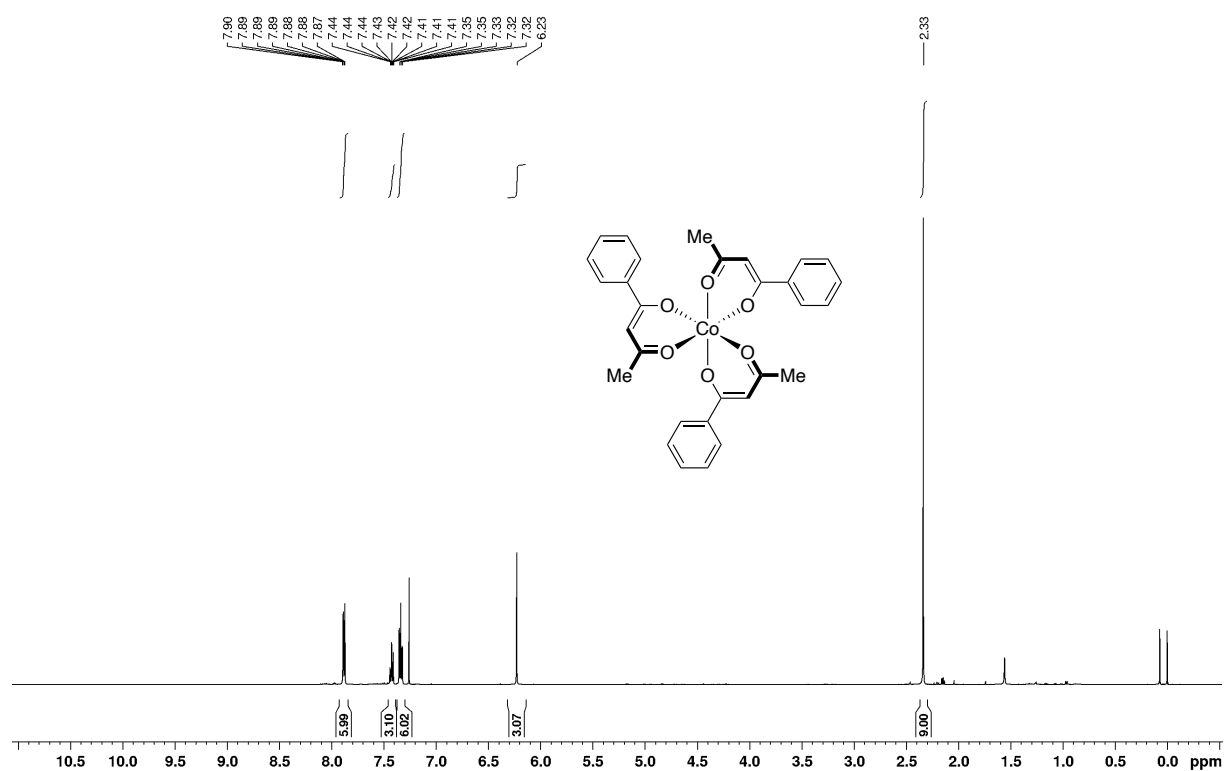


Chemical structure of compound 10 is shown above the spectrum. The structure is a cobalt(II) complex with two 2-methyl-5-phenyl-2,5-dihydroxy-1,4-benzodioxin-6-yl ligands and two 2-phenyl-3-methyl-2,5-dihydroxy-1,4-benzodioxin-6-yl ligands.

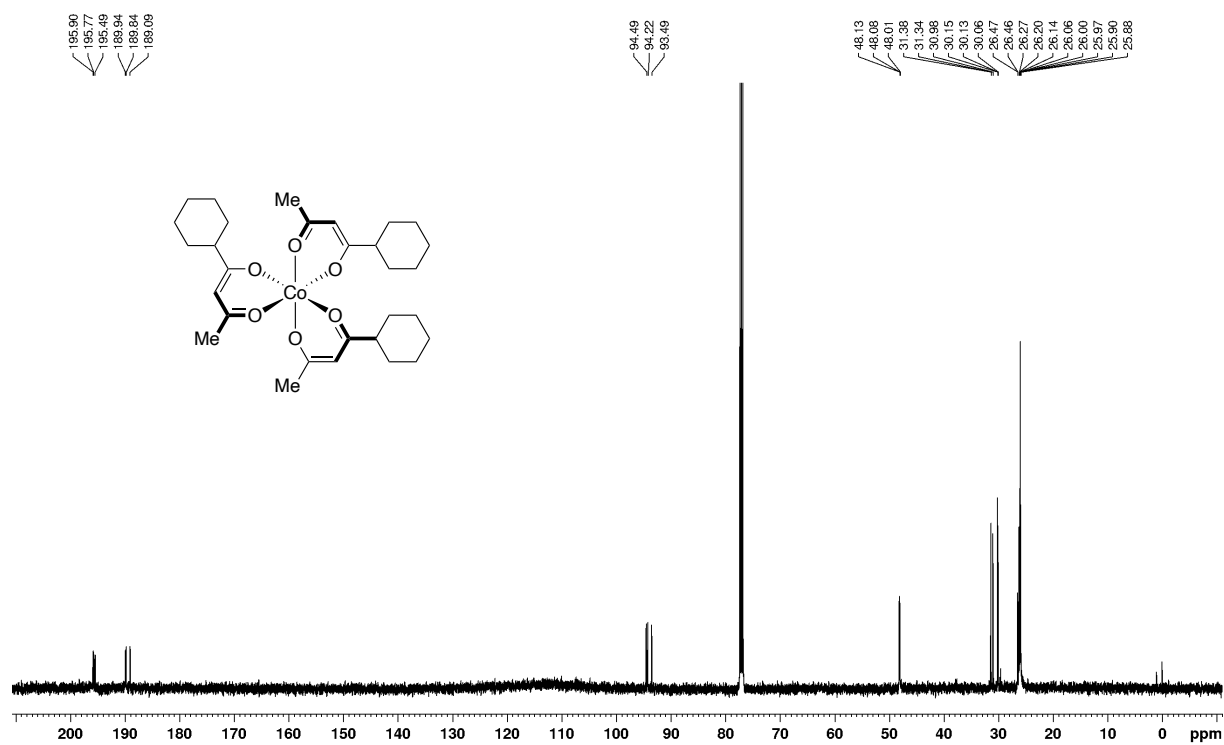
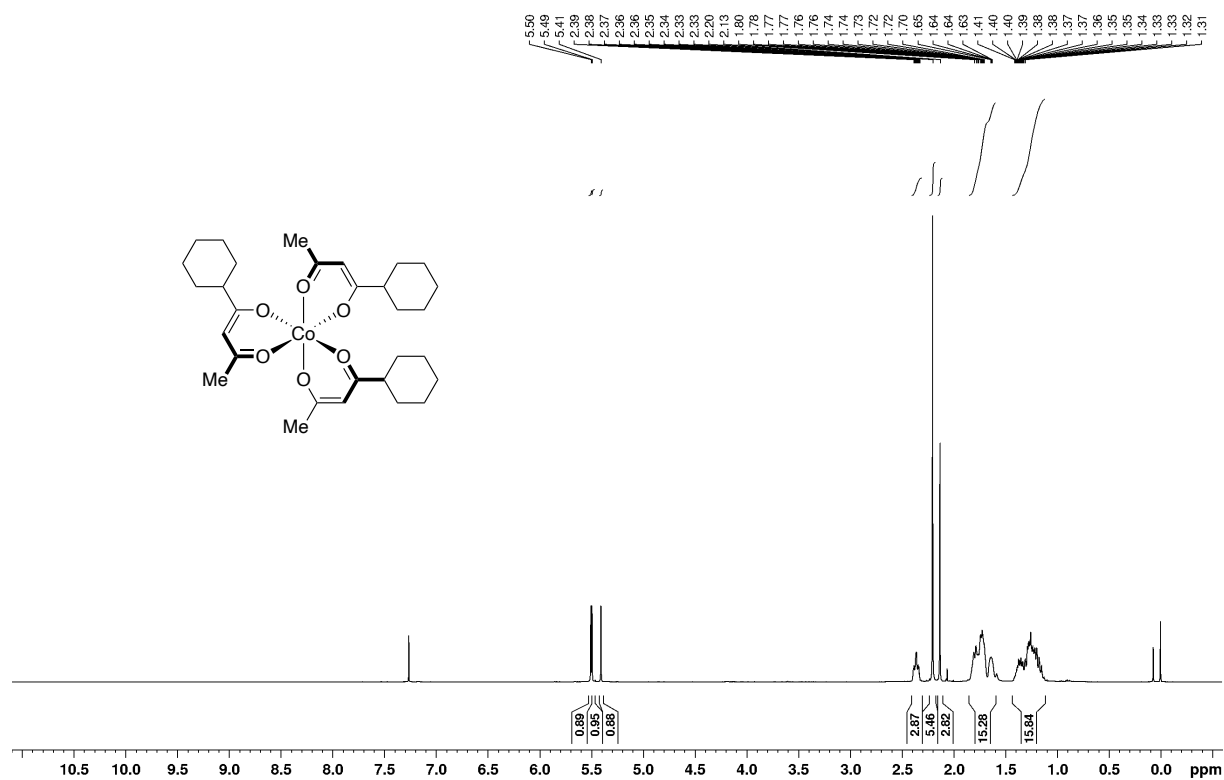
¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents chemical shift in ppm, ranging from 0.0 to 10.5. The spectrum shows several peaks, with integration values provided below the baseline: 3.03, 2.98, 2.99, 1.00, 1.00, 0.96, 5.08, 2.98, 3.98. A list of chemical shifts (δ) is provided at the top of the spectrum: 7.87, 7.87, 7.87, 7.86, 7.85, 7.85, 7.85, 7.83, 7.83, 7.43, 7.43, 7.43, 7.42, 7.42, 7.42, 7.41, 7.41, 7.40, 7.40, 7.39, 7.39, 7.39, 7.38, 7.38, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.31, 7.31, 7.30, 7.30, 7.30, 7.30, 6.24, 6.23, 6.21. A list of integration values is provided at the bottom: 2.38, 2.37, 2.35.



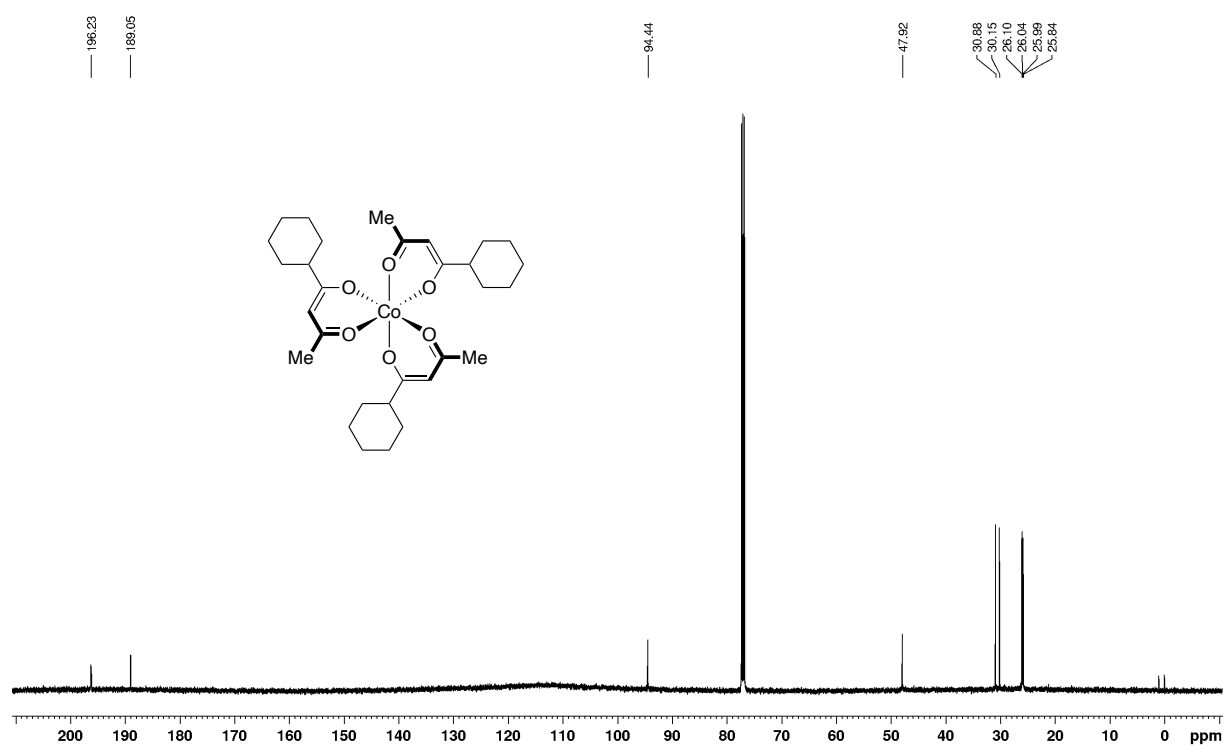
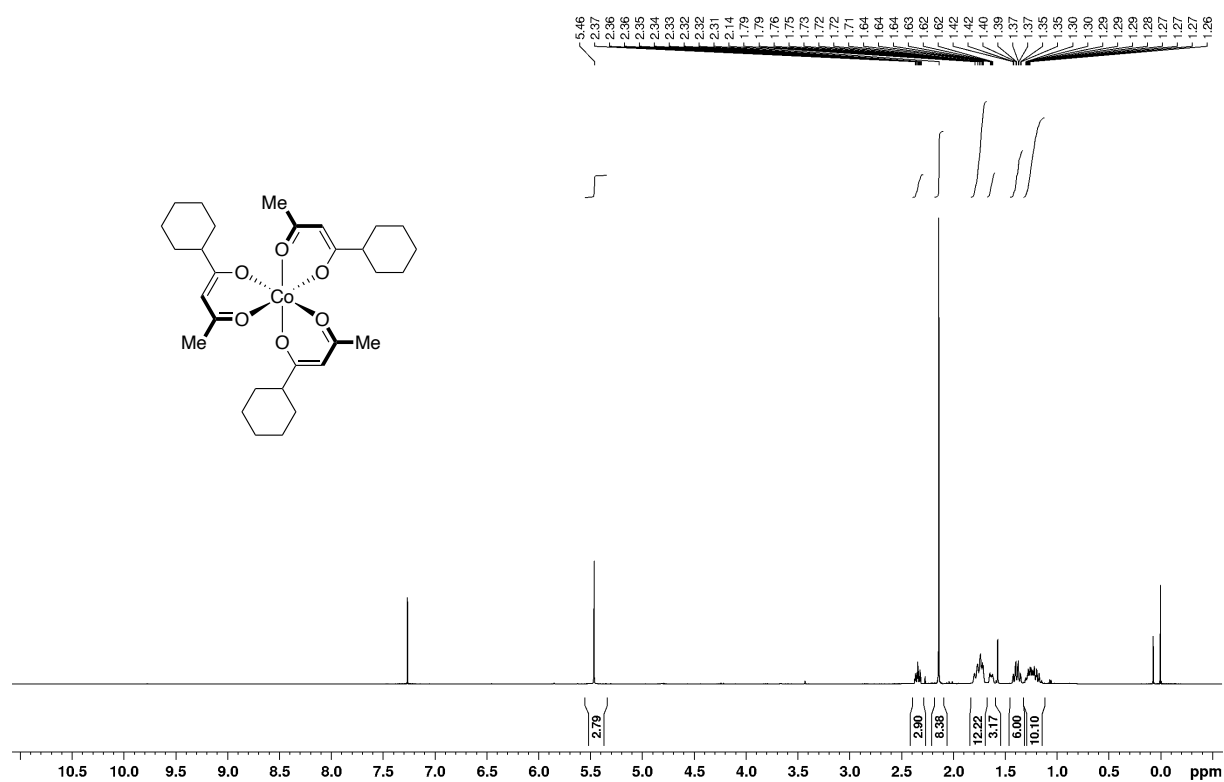
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of *fac*-Co(bzac)₃ (*fac*-1b)



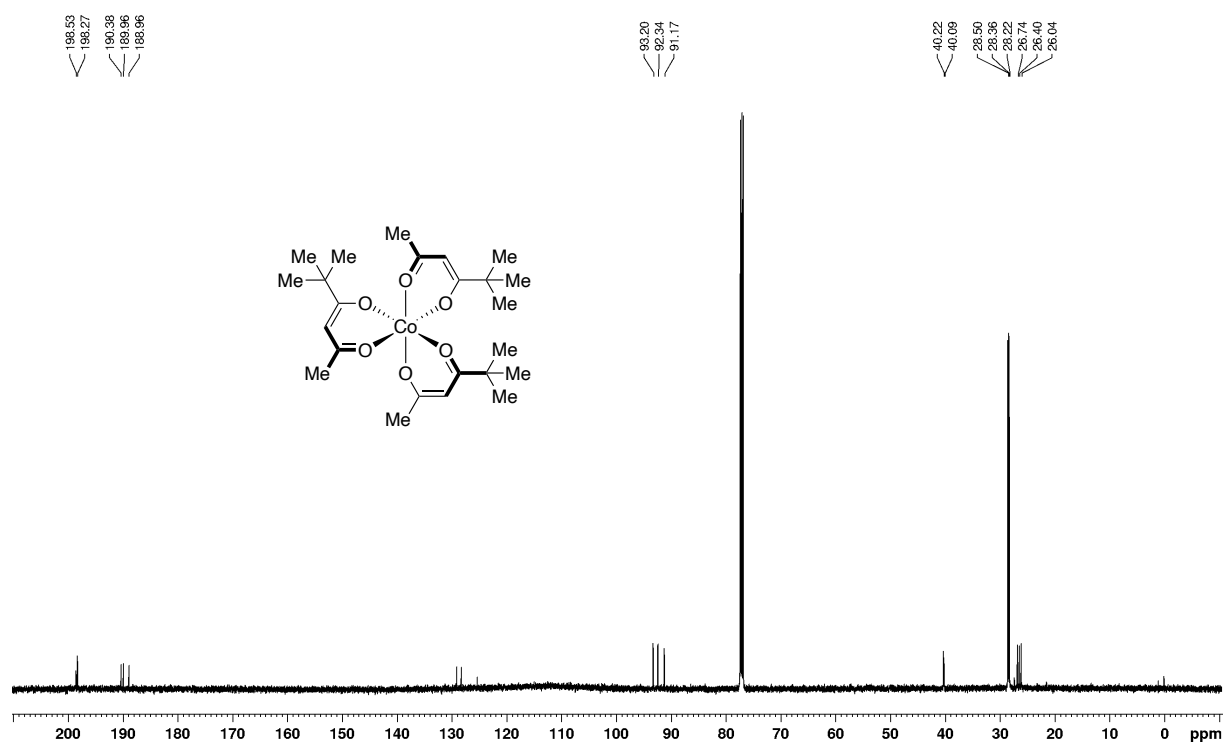
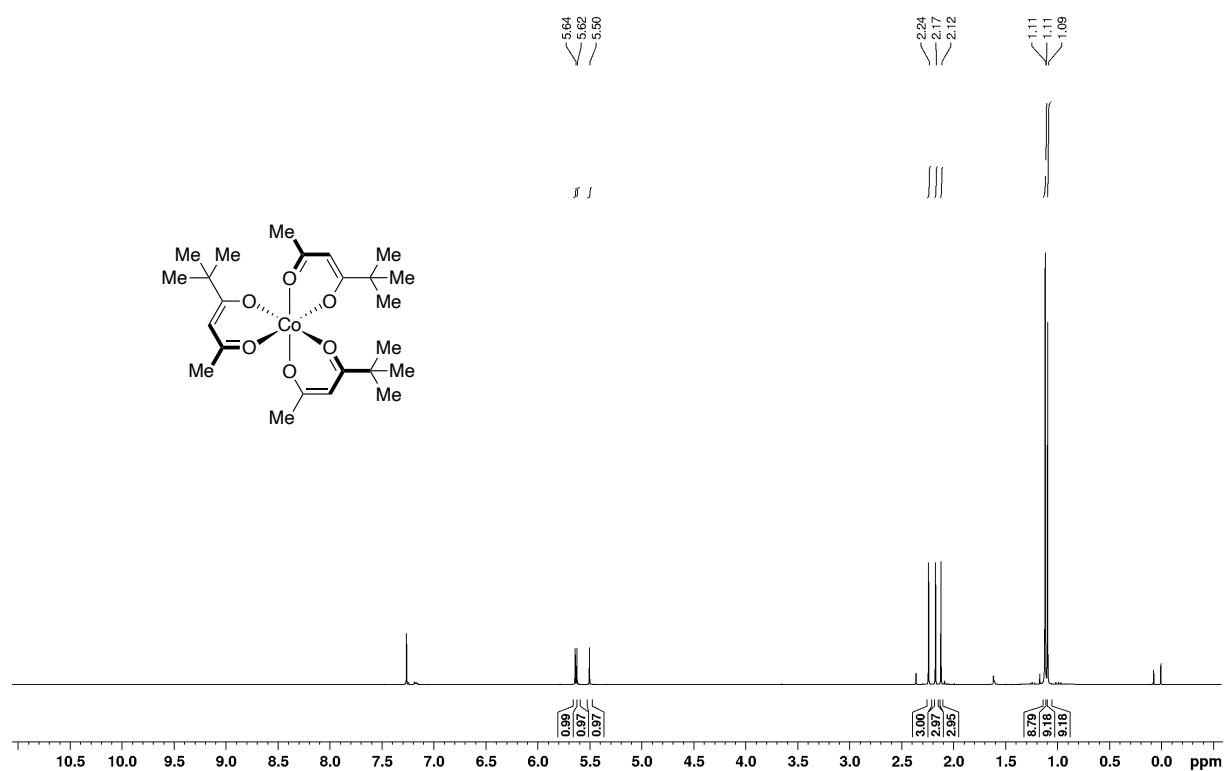
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of *fac*-Co(cycac)₃ (*fac*-1c)



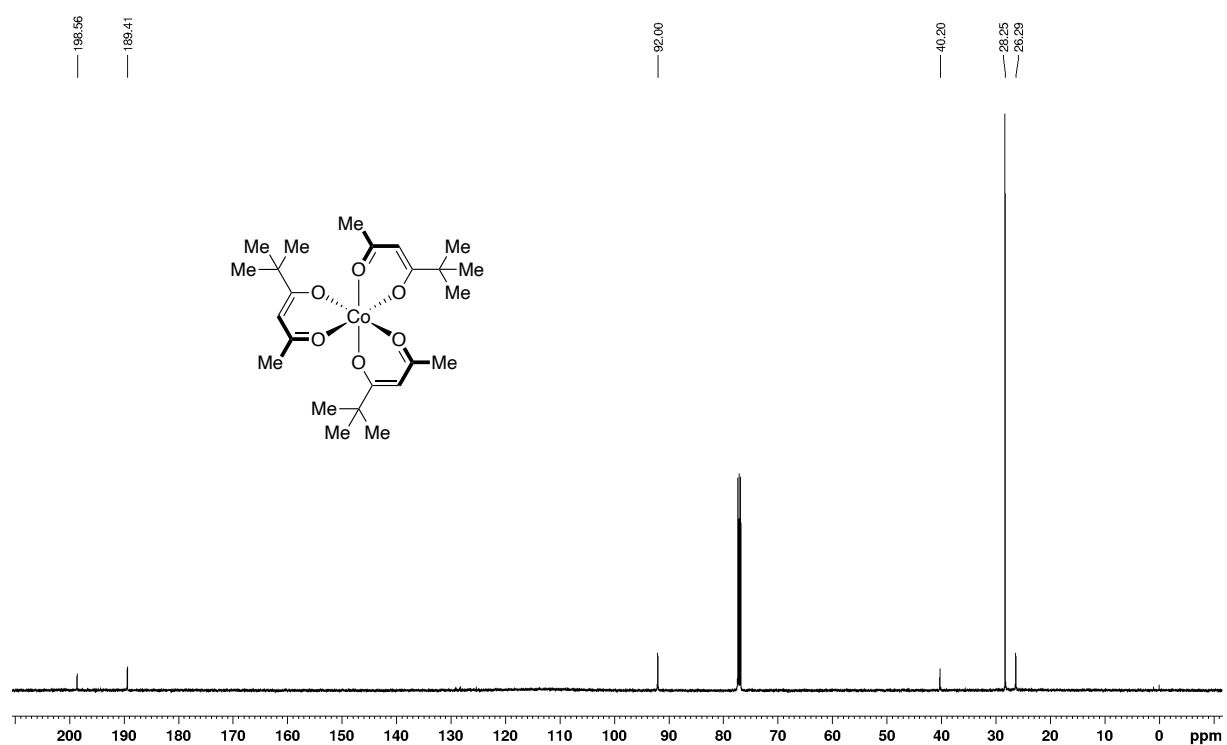
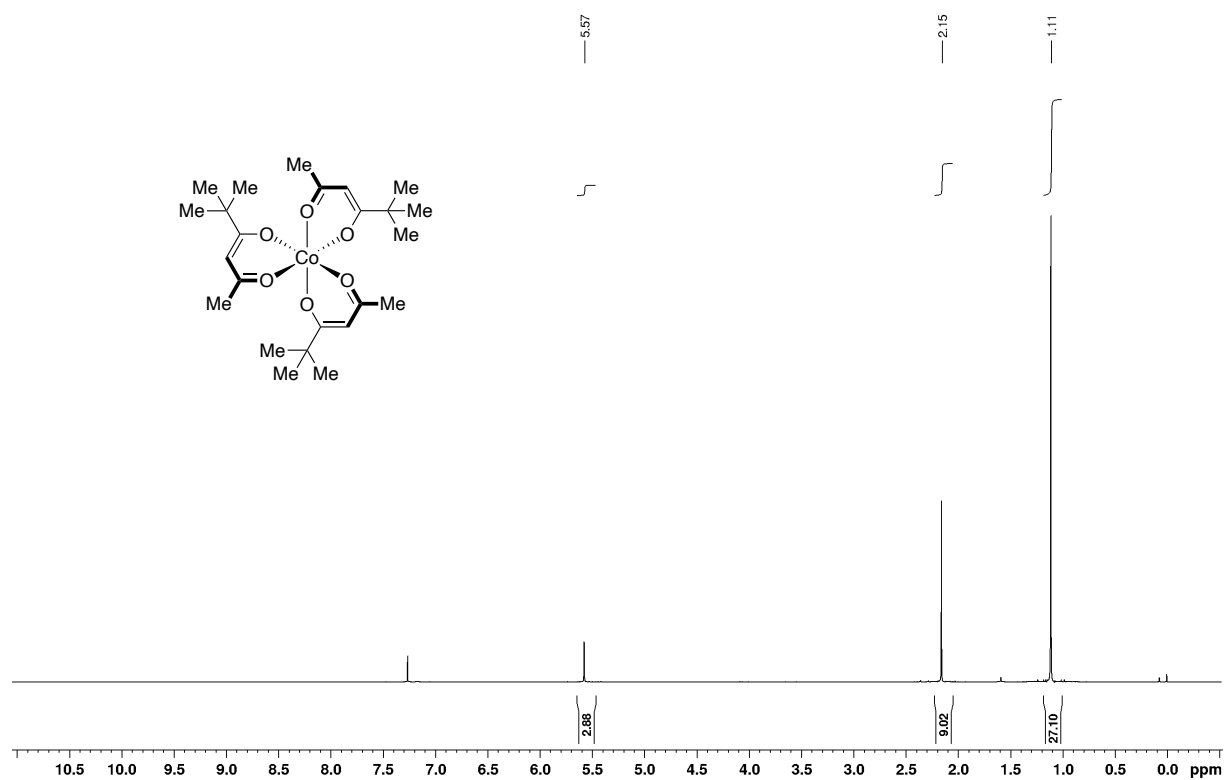
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of *mer*-Co(cycac)₃ (*mer*-1c)



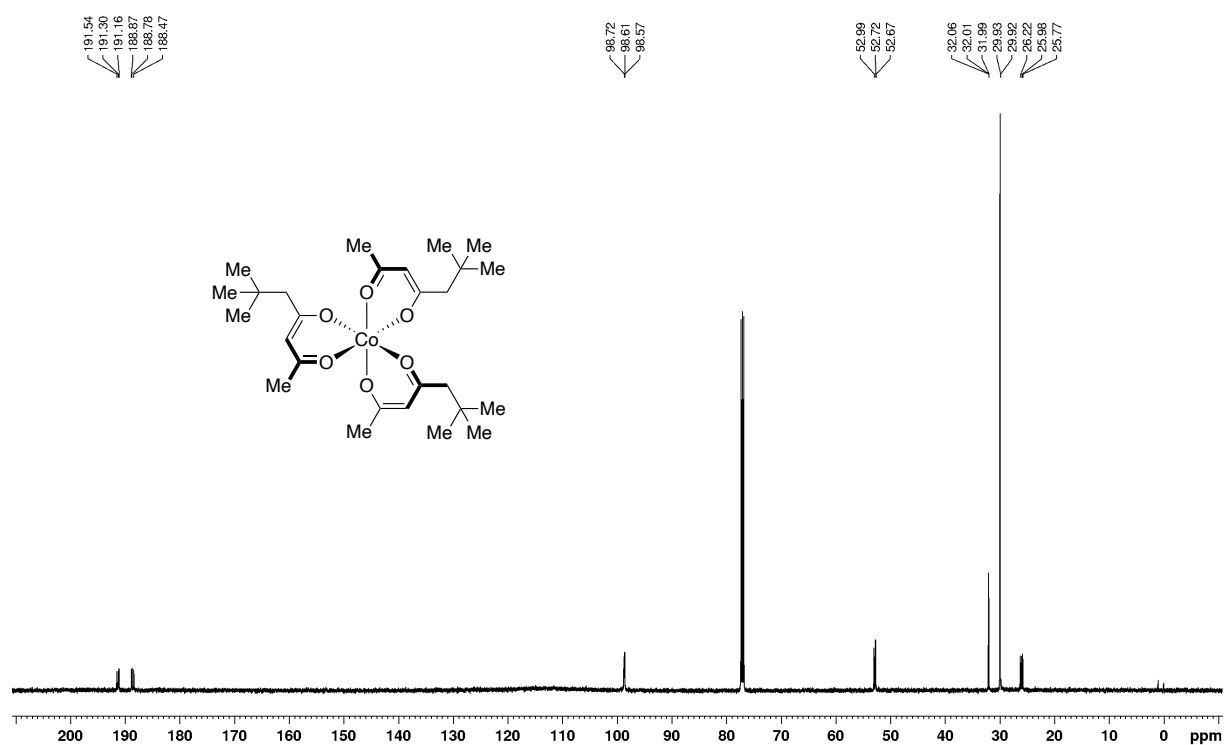
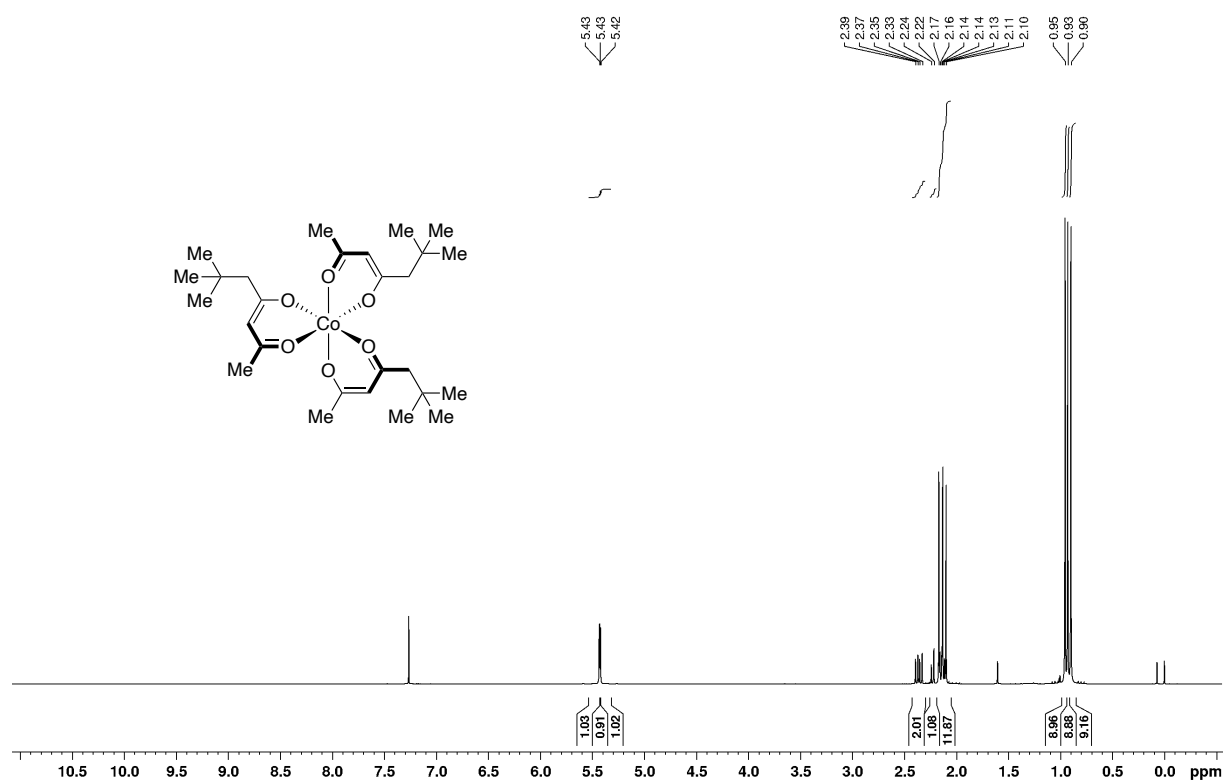
***mer*-Co(pivac)₃ (*mer*-1d)**



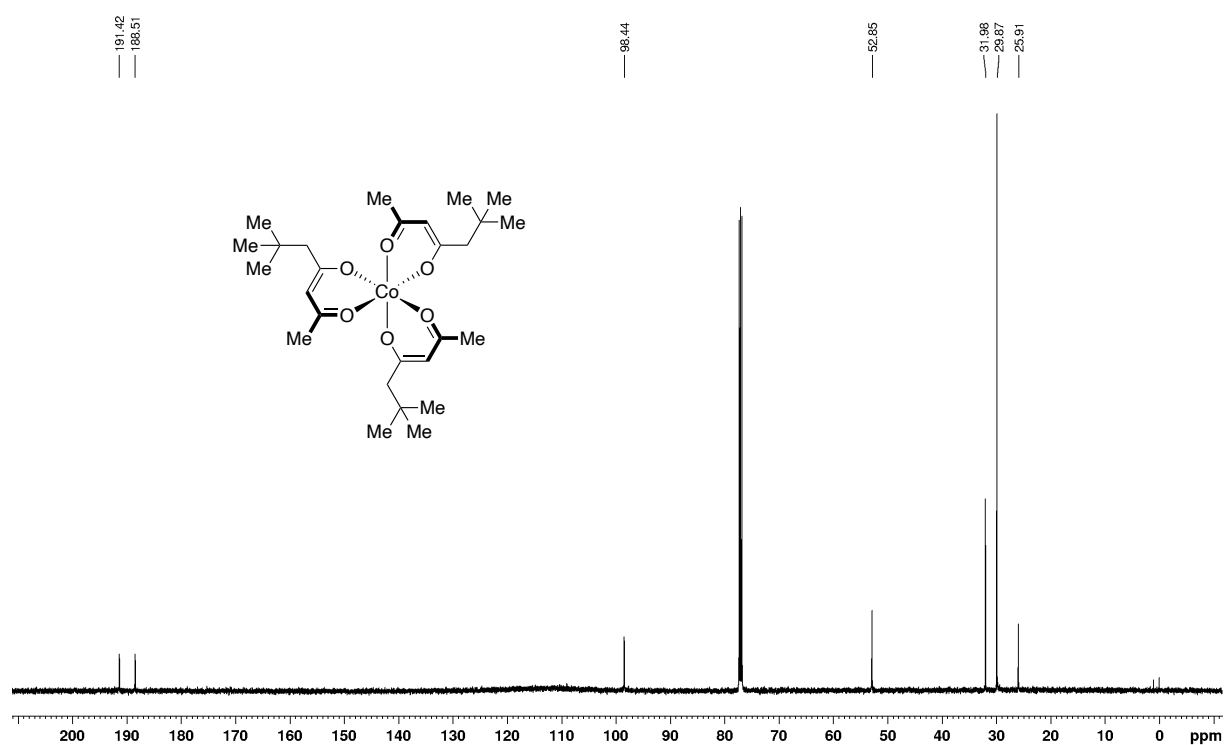
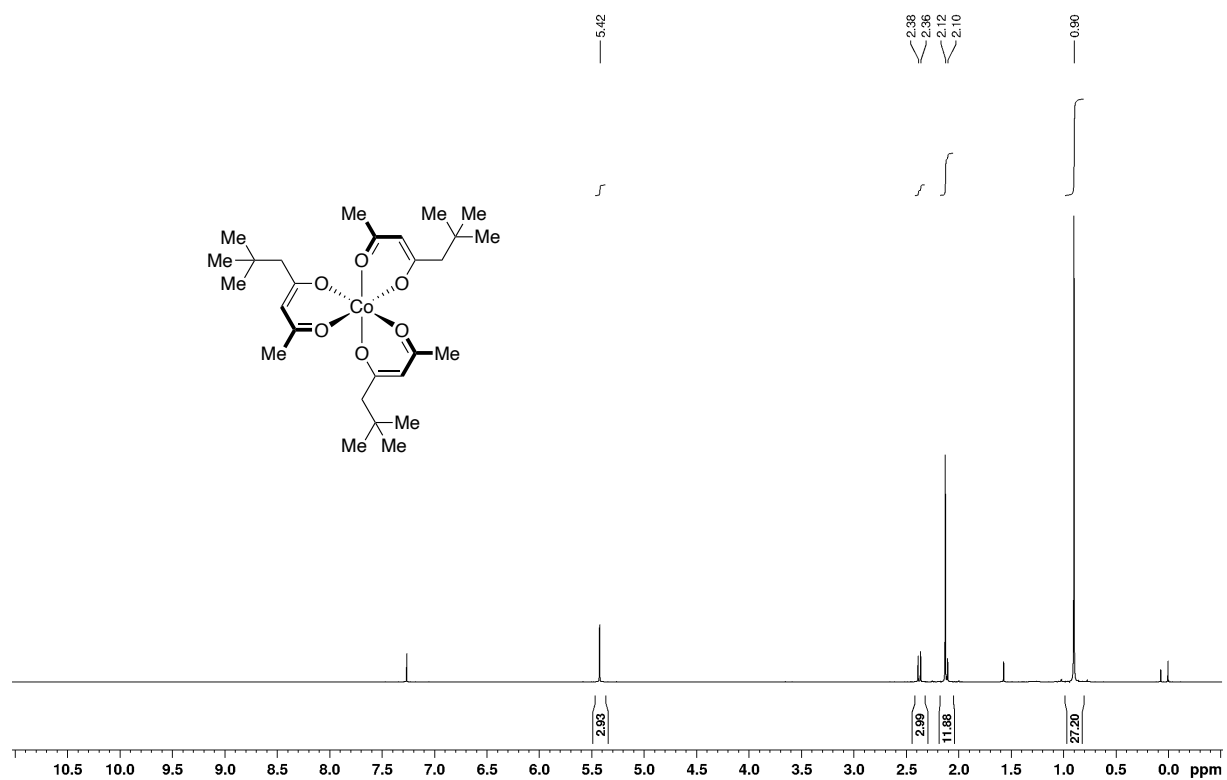
fac-Co(pivac)₃ (*fac*-1d)



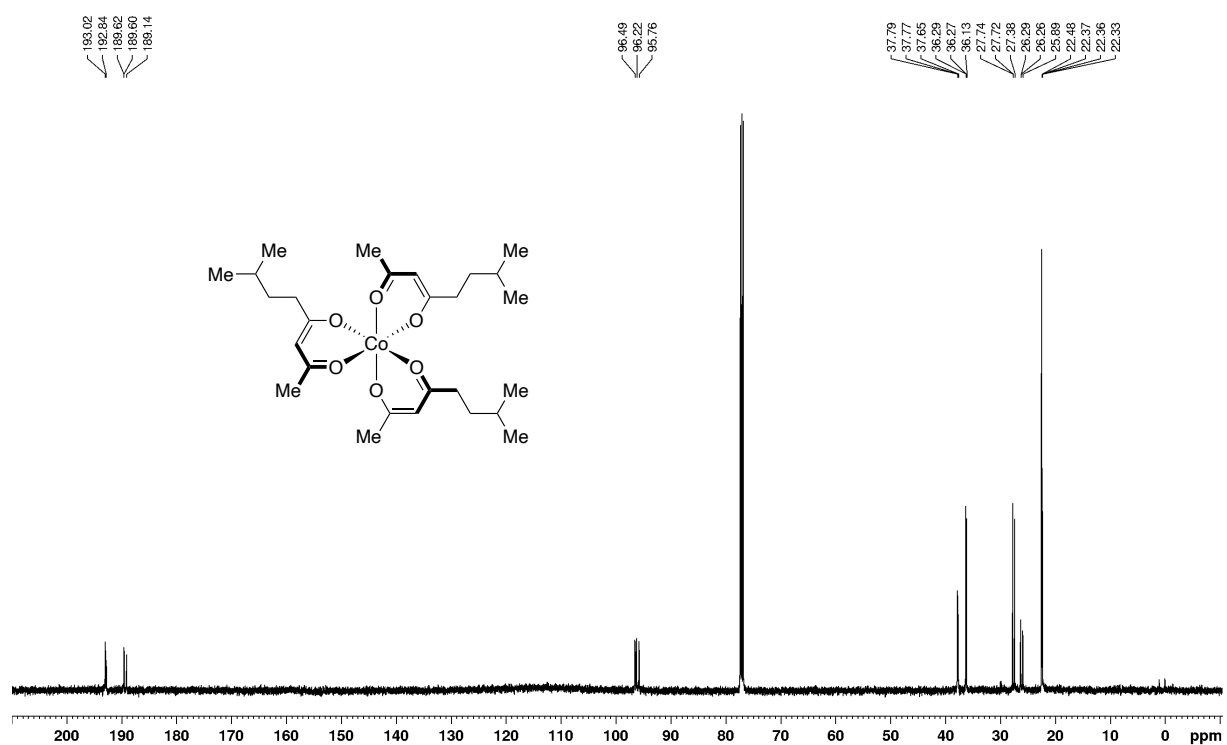
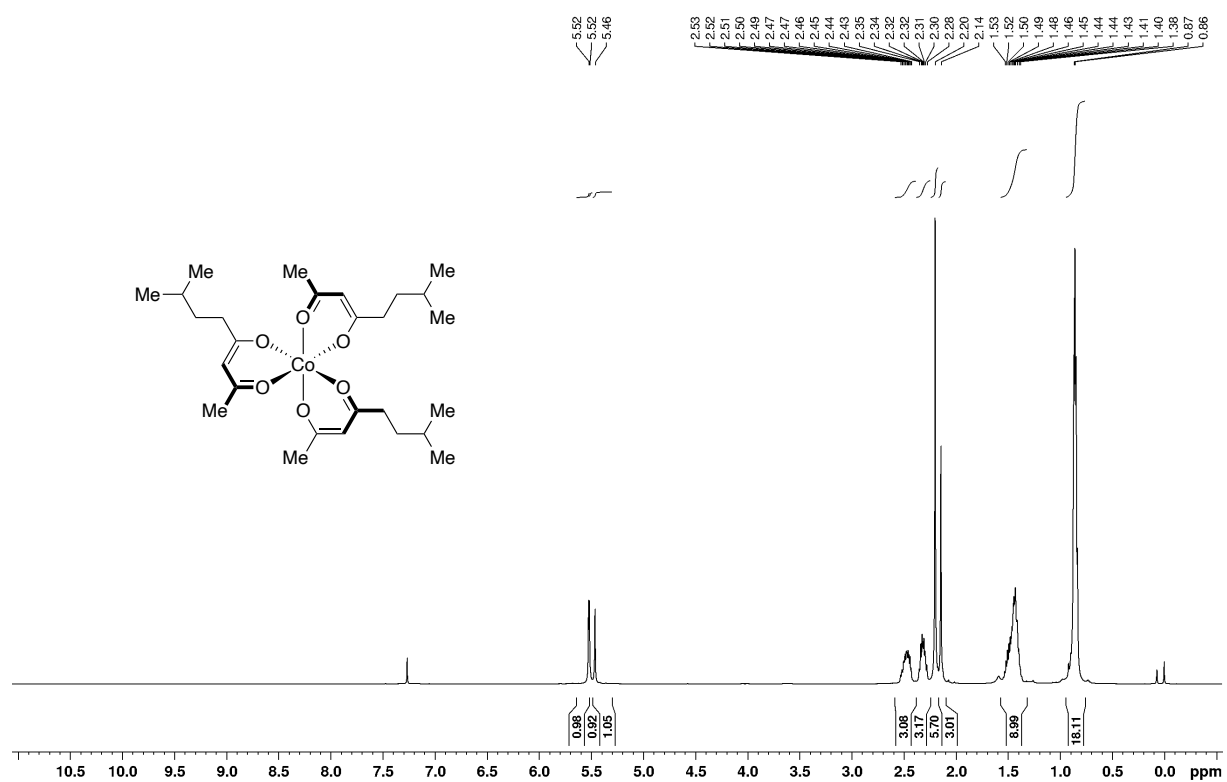
***mer*-Co(dmbac)₃ (*mer*-1e)**



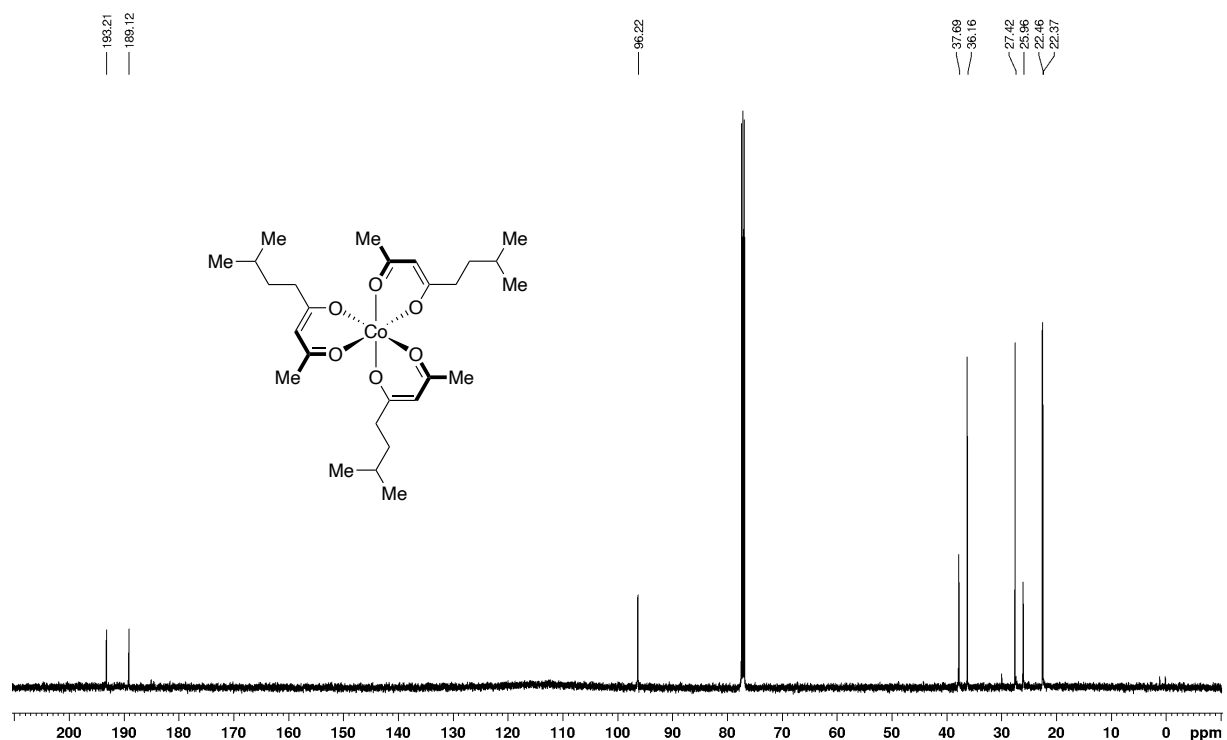
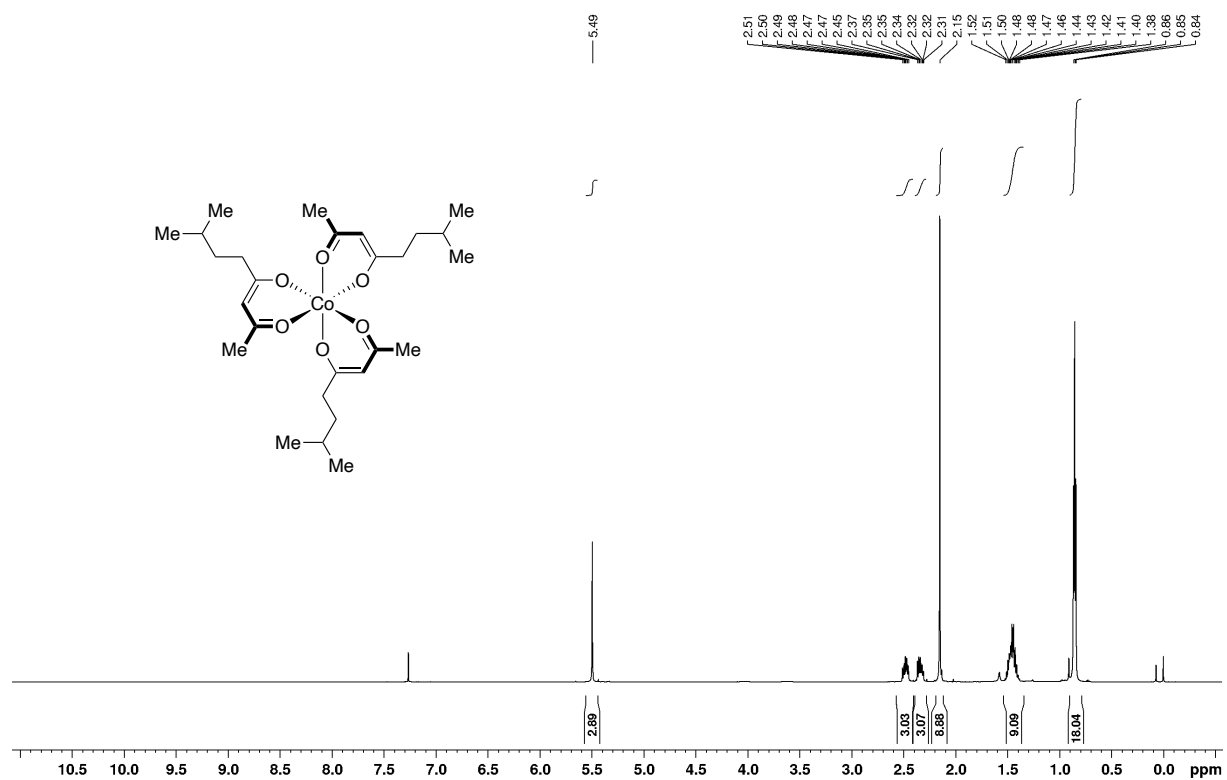
fac-Co(dmbac)₃ (*fac*-1e)



***mer*-Co(mpac)₃ (*mer*-1f)**



fac-Co(mpac)₃ (*fac*-1f)



11. References

- [1] Y. Shigeta, A. Kobayashi, M. Yoshida, M. Kato, *Inorg. Chem.* **2019**, *58*, 7385–7392.
- [2] a) A. Schramm, C. Stroh, K. Dössel, M. Lukas, O. Fuhr, H. v. Löhneysen, M. Mayor, *Chem. Commun.* **2013**, *49*, 1076–1078; b) T. Hamada, B. S. Brunschwig, K. Eifuku, E. Fujita, M. Körner, S. Sakaki, R. van Eldik, J. F. Wishart, *J. Phys. Chem. A* **1999**, *103*, 5645–5654.
- [3] M. Roudier, T. Constantieux, A. Quintard, J. Rodriguez, *Org. Lett.* **2014**, *16*, 2802–2805.
- [4] a) X. Wu, C. Sparr, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201424. b) M. Jakobi, C. Sparr, *Org. Process Res. Dev.* **2022**, *26*, doi: 10.1021/acs.oprd.2c00209; c) M. Jakobi, B. Zilate, C. Sparr, *Adv. Synth. Catal.* **2022**, *364*, doi: 10.1002/adsc.202200819; We thank Dr. Xingxing Wu and Markus Jakobi for providing the acridinium photocatalysts.
- [5] H. Sato, H. Unoa, H. Nakanob, *Dalton Trans.* **2011**, *40*, 1332–1337.