Photocatalytic deracemisation of cobalt(III) complexes with fourfold stereogenicity

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Table of Contents

1. General Information ........................................................................................................ 2
2. Catalyst Synthesis......................................................................................................... 3
3. Substrate Synthesis....................................................................................................... 5
4. Configurational Stability Evaluation .............................................................................. 10
5. Acridinium Catalyzed Photostereoisomerization .......................................................... 14
6. Photoderacemization ..................................................................................................... 19
7. HPLC Data ................................................................................................................... 23
8. Calibration Data ............................................................................................................ 35
9. CD and UV/Vis Spectra ............................................................................................... 38
10. NMR Spectra ............................................................................................................... 42
11. References ................................................................................................................... 61
1. General Information

All chemicals were purchased in reagent grade from several commercial suppliers (Acros Organics, Alfa Aesar, Apollo, Fluka, Fluorochem, Riedel-de Häen, 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 glassware, 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 (ν) 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((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) [2,2'-bipyridine]-4,4'-dicarboxylate (t-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'-dicarboxyl 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, C3H, C3'H), 8.96 (2H, d, J = 5.0 Hz, C6H, C6'H), 7.97 (2H, dd, J = 5.0, 1.2 Hz, C5H, 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'). EtN₃ (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; Rf 0.35 (cyclohexane/ethyl acetate 9:1); 1H NMR (500.1 MHz, CDCl₃): δ 8.93 (2H, dd, J = 1.6, 0.8 Hz, C3H, C3'H), 8.87 (2H, dd, J = 5.0, 0.8 Hz, C6H, C6'H), 7.91 (2H, dd, J = 10.9, 10.9, 4.5 Hz, C1''H, C1'''H), 2.16–2.11 (2H, m, C6''H₃, C6'''H₃), 2.00–1.89 (2H, m, C2''CH₂, C2'''CH₂), 1.79–1.70 (4H, m, C3''H₃, C4''H₃, C3'''H₃, C4'''H₃), 1.66–1.53 (4H, m, C2''H₃, C5''H₃, C2'''H₃, C5'''H₃), 1.23–1.10 (4H, m, C3''H₅, C6''H₅, C3'''H₅, C6'''H₅), 1.00–0.91 (14H, m, C5''''H₃, C5'''''H₃, C5''''CH₃, C5'''''CH₃, 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''CH₃, C5'''CH₃), 20.8 (CHCH₃), 16.4 (CHCH₃); IR (ATR): v 2953m, 2923m, 2871w, 1719s, 1557w, 1453w, 1366s, 1285s, 1250s, 1128s, 955m, 914m, 764m, 692m; HRMS (ESI⁺): m/z calcd. for C₃₂H₃₂N₂O₄⁺ ([M+H]⁺) 521.3374, found 521.3381.

[Ru(t-menbpy)₂]Cl₂ (t-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-PC (12.8 mg, 7.38 µmol, 7.4%) and Λ-PC (16.4 mg, 9.46 µmol, 9.5%) as red
solids. Analytical data for Δ-[Ru(1-menbpy)]Cl₂ (Δ-1-PC): R: 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''Hax, C1'''Hax), 2.14–2.07 (6H, m, C6''Heq, C6'''Heq), 1.86–1.77 (6H, m, C2''CH, C2'''CH), 1.77–1.69 (12H, m, C3''Heq, C4''Heq, C3'''Heq, C4'''Heq), 1.58–1.50 (12H, m, C2''Has, C5''Has, C2'''Has, C5'''Has), 1.21–1.06 (12H, m, C3''Has, C6''Has, C3'''Has, C6'''Has), 0.98–0.85 (42H, m, C4''Has, C5''Has, C4'''Has, C5'''Has, CH₂CH₃), 0.76 (18H, d, J = 6.9 Hz, CH₂CH₃); 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 (CH₃(CH₃)) 23.4 (C3'', C3''''), 21.9 (C5''CH₃, C5'''CH₃), 20.7 (CH₂CH₃), 16.4 (CH₂CH₃); IR (ATR): ν 2954m, 2870m, 1719s, 1456w, 1408w, 1237s, 1128s, 954m, 845w, 764m; HRMS (ESI⁺): m/z calc. for C₉₀H₁₃₂N₂₀₂Ru²⁺ (M²⁺) 831.4470, found 831.4480. Analytical data for Α-[Ru(1-menbpy)]Cl₂ (Α-1-PC): R: 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, ddd, J = 5.5, 5.5, 1.6 Hz, C5'H, C5''H), 5.02 (6H, ddd, J = 10.9, 10.9, 4.4 Hz, C1''Hax, C1'''Hax), 2.09–2.02 (6H, m, C6''Heq, C6'''Heq), 1.98-1.89 (6H, m, C2''CH, C2'''CH), 1.79–1.69 (12H, m, C3''Heq, C4''Heq, C3'''Heq, C4'''Heq), 1.60–1.51 (12H, m, C2''Has, C5''Has, C2'''Has, C5'''Has), 1.17–1.04 (12H, m, C3''Has, C6''Has, C3'''Has, C6'''Has), 0.96–0.87 (42H, m, C4''Has, C5''CH₃, C4'''Has, C5'''CH₃, CH₂CH₃), 0.80 (18H, d, J = 6.9 Hz, CH₂CH₃); 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 (CH₂CH₃), 23.1 (C3'', C3''''), 22.0 (C5''CH₃, C5'''CH₃), 20.9 (CH₂CH₃), 16.1 (CH₂CH₃); IR (ATR): ν 2928m, 2869m, 1719s, 1456w, 1407m, 1245s, 1128s, 955m, 845w, 764m; HRMS (ESI⁺): m/z calc. for C₉₀H₁₃₂N₂₀₂Ru²⁺ (M²⁺) 831.4470, found 831.4484.
3. Substrate Synthesis

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

Following an adapted literature procedure, 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). The reaction mixture was filtered through silica gel 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: 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)); 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)), 25.8 (C1); IR (ATR): v = 3422br, 2954m, 2870m, 1709m, 1588s, 1527s, 1466m, 1365s, 1232m, 1023w, 922m, 782m; HRMS (ESI⁺): m/z calcd. for C₁₀H₁₀NaO₂⁺ ([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: 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)); IR (ATR): v = 2958m, 1506s, 1466m, 1238m, 1101w, 922m, 782m; HRMS (ESI⁺): m/z calcd. for C₁₀H₁₁NaO₂⁺ ([M+Na]⁺) 179.1043, found 179.1042.

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

S5
General Procedure B: Preparation of Cobalt(III) Diketonates

\[ \text{CoCO}_3 \cdot \text{H}_2\text{O} + \text{aq. H}_2\text{O} \overset{\text{reflux}}{\rightarrow} \text{Co}(\text{fac})_2\text{R} \]

**General Procedure B1: Neat Reaction**

35% Aq. H\(_2\)O (1.61 mL, 20.0 mmol, 20.0 equiv.) was added dropwise to a stirred mixture of CoCO\(_3\)·H\(_2\)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\(_2\)SO\(_4\), filtered and evaporated under reduced pressure. Column chromatography on silica gel provided the respective cobalt(III) diketone \(\text{I}\) 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\(_2\)O (1.61 mL, 20.0 mmol, 20.0 equiv.) was added dropwise to a stirred mixture of CoCO\(_3\)·H\(_2\)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\(_2\)SO\(_4\), filtered and evaporated under reduced pressure. Column chromatography on silica gel provided the respective cobalt(III) diketone \(\text{I}\) as a mixture of the mer- and fac-diastereomers, which were separated by preparative TLC on silica gel.

\(\text{Co(fac)}_2\) (\(\text{Ia}\))

Following a modified general procedure \(\text{B1}\), the reaction of Co(\(\text{CO}_3\))·H\(_2\)O (137 mg, 1.00 mmol, 1.0 equiv.) with 1,1,1-trifluorooctane-2,4-dione (1.46 mL, 12.0 mmol, 12.0 equiv.) and 10% aq. H\(_2\)O (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-\(\text{Ia}\): \(R_f\) 0.33 (cyclohexane/toluene 2:5); \(^1\)H NMR (500.1 MHz, CDCl\(_3\)): \(\delta\) 6.07 (1H, s, C\(_3\)H), 6.05 (1H, s, C\(_3\)H), 6.01 (1H, s, C\(_3\)H), 2.45 (1H, s, C\(_1\)H), 2.44 (1H, s, C\(_1\)H), 2.40 (1H, s, C\(_1\)H); \(^{13}\)C {\(^1\)H} NMR (125.8 MHz, CDCl\(_3\)): \(\delta\) 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); \(^{19}\)F {\(^1\)H} NMR (470.6 MHz, CDCl\(_3\)): \(\delta\) –73.5, –73.6, –73.7; IR (ATR): \(\nu\) 1600s, 1524m, 1449w, 1363w, 1288s, 1193s, 1132s, 1012w, 954w, 872m, 791m, 738m, 655m; HRMS (ESI\(^+\)): \(m/z\) calcd. for \(\text{C}_{13}\text{H}_{12}\text{CoF}_3\text{NaO}_6^+\) ([M+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 (A), 13.6 (A). Analytical data for fac-\(\text{Ia}\): \(R_f\) 0.22 (cyclohexane/toluene 2:5); \(^1\)H NMR (500.1 MHz, CDCl\(_3\)): \(\delta\) 6.03 (3H, s, C\(_3\)H), 2.41 (9H, s, C\(_1\)H); \(^{13}\)C {\(^1\)H} NMR (125.8 MHz, CDCl\(_3\)): \(\delta\) 198.4 (C2), 171.2 (q, \(J = 35.1 \text{ Hz}, \text{C4}\), 114.1 (HMBC, q, \(J = 231.1 \text{ Hz}, \text{C5}\), 94.0 (C3), 27. (C1); \(^{19}\)F {\(^1\)H} NMR (376.5 MHz, CDCl\(_3\)): \(\delta\) –73.5; IR (ATR): \(\nu\) 1600s, 1525m, 1443m, 1366w, 1283s, 1192s, 1127s, 1025w, 957w, 873m, 786m, 739m, 655m; HRMS (ESI\(^+\)): \(m/z\) calcd. for \(\text{C}_{13}\text{H}_{12}\text{CoF}_3\text{NaO}_6^+\) ([M+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 (A), 12.3 (A).
Following the general procedure B2, the reaction of Co(CO)_5H_2O (137 mg, 1.00 mmol, 1.0 equiv.) with 1-phenylbutane-1,3-dione (446 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:→100:2) as a green solid (119 mg, 219 µmol, 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: Rf 0.33 (toluene/i-PrOH 50:1); ^1H NMR (500.1 MHz, CDCl_3): 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, C3H), 6.23 (1H, s, C3H), 6.21 (1H, s, C3H), 2.38 (3H, s, C1H), 2.37 (3H, s, C1H); ^13C[^1H] NMR (125.8 MHz, CDCl_3): 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): ν 3062w, 2923w, 1587m, 1551s, 1512s, 1450m, 1376s, 1305m, 1028w, 910w, 860w, 715m; HRMS (ESI\^+): m/z calcld. for Co_6H_2CoNaO_6^- ([M+Na^-]^-) 565.1032, found 565.1033; HPLC (Chiralpak IC-3 (3 µm, 250x4.6 mm), heptane/i-PrOH 95:5, 1.0 mL/min, 40 °C): Rt 10.5, 13.1. Analytical data for fac-1b: Rf 0.21 (toluene/i-PrOH 50:1); ^1H NMR (500.1 MHz, CDCl_3): 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, C3H), 2.33 (3H, s, C1H); ^13C[^1H] NMR (125.8 MHz, CDCl_3): 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): ν 3063w, 2923w, 1588m, 1553s, 1516s, 1450m, 1378s, 1305m, 1028w, 909w, 860w, 714m; HRMS (ESI\^+): m/z calcld. for Co_6H_2CoNaO_6^- ([M+Na^-]^-) 565.1032, found 565.1041; HPLC (Chiralpak IC-3 (3 µm, 250x4.6 mm), heptane/i-PrOH 95:5, 1.0 mL/min, 40 °C): Rt 9.0, 11.5.

**Co(cycac)_3 (1c)**

Following the general procedure B2, the reaction of Co(CO)_5H_2O (34.2 mg, 250 µmol, 1.0 equiv.) with 1-cyclohexylbutane-1,3-dione (126 mg, 750 µmol, 3.0 equiv.) and 35% aq. H_2O_2 (404 µL, 5.00 mmol, 20.0 equiv.) in CHCl_3 (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 µmol, 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: Rf 0.28 (toluene/i-PrOH 25:1); ^1H NMR (500.1 MHz, CDCl_3): δ 5.50 (1H, s, C3H), 5.49 (1H, s, C3H), 5.41 (1H, s, C3H), 2.40–2.32 (3H, m), 2.20 (6H, s, C1H), 2.13 (3H, s, C1H), 1.85–1.58 (15H, m), 1.44–1.11 (15H, m); ^13C[^1H] NMR (125.8 MHz, CDCl_3): 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 (CH_2), 31.3 (CH_2), 31.0 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 26.5 (C1), 26.5 (C1), 26.3 (CH_3), 26.2 (CH_2), 26.1 (CH_3), 26.1 (CH_3), 26.0 (C1, CH_3), 26.0 (C1, CH_3), 25.9 (CH_3), 25.9 (CH_3); IR (ATR): ν 2923m, 2853m, 1570s, 1515s, 1397s, 1174w, 1027w, 728w; HRMS (ESI\^+): m/z calcld. for Co_6H_2CoNaO_6^- ([M+Na^-]^-) 583.2440, found 583.2444; HPLC (Chiralpak IC-3 (3 µm, 250x4.6 mm), heptane/i-PrOH 99:1, 1.0 mL/min, 40 °C): Rt 5.8 (A), 8.4 (A). Analytical data for fac-1c: Rf 0.26 (toluene/i-PrOH 25:1); ^1H NMR (500.1 MHz, CDCl_3): δ 5.46 (3H, s, C3H), 2.37–2.30 (3H, m, C5H), 2.14 (9H, s, C1H), 1.80–1.70
(12H, m), 1.65–1.62 (3H, m), 1.43–1.34 (6H, m), 1.31–1.13 (10H, m); $^{13}$C($^1$H) NMR (125.8 MHz, CDCl$_3$): $\delta$ 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): $\nu$ 2928m, 2853m, 1572s, 1517s, 1400s, 1174w, 1026w, 761w; HRMS (ESI$^+$): $m/z$ calcd. for $\text{C}_{24}\text{H}_{26}\text{CONaO}_3^+$ ([M+Na$^+$]) 583.2440, found 583.2449; HPLC (Chiralpak IC-3 (3 $\mu$m, 250x4.6 mm), heptane/i-ProOH 99:1, 1.0 mL/min, 40 °C): Rt 7.1 ($\Delta$), 8.6 ($\Delta$).

Co(pivac) (1d)

Following the general procedure B2, the reaction of Co(CO)$_3$-H$_2$O (137 mg, 1.00 mmol, 1.0 equiv.) with 5,5-dimethylhexane-2,4-dione (391 $\mu$L, 3.00 mmol, 3.0 equiv.) and 35%aq. H$_2$O$_2$ (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-ProOH 100:0→100:3) as a green oil (40.8 mg, 85.0 $\mu$mol, 8.5%, 2.61 d.r. (mer/fac)). The mer- and fac-diastereomers were separated by preparative TLC on silica gel (toluene/i-ProOH 25:1). Analytical data for mer-1d: Rt 0.26 (toluene/i-ProOH 50:1); $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta$ 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$_3$)$_3$), 1.09 (9H, s, C5(CH$_3$)$_3$); $^{13}$C($^1$H) NMR (125.8 MHz, CDCl$_3$): $\delta$ 198.5 (C4), 198.3 (C4), 194.0 (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): $\nu$ 2962m, 2870w, 1569s, 1507s, 1386s, 1284w, 1232w, 1168w, 898w, 767w, 664w; HRMS (ESI$^+$): $m/z$ calcd. for $\text{C}_{24}\text{H}_{22}\text{CoNaO}_3^+$ ([M+Na$^+$]) 505.1971, found 505.1976; HPLC (Chiralpak IC-3 (3 $\mu$m, 250x4.6 mm), heptane/i-ProOH 99:1, 1.0 mL/min, 5 °C): Rt 9.0 ($\Delta$), 9.6 ($\Delta$). Analytical data for fac-1d: Rt 0.13 (toluene/i-ProOH 50:1); $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta$ 5.57 (3H, s, C3H), 2.15 (9H, s, C1H), 1.11 (27H, s, C5(CH$_3$)$_3$); $^{13}$C($^1$H) NMR (125.8 MHz, CDCl$_3$): $\delta$ 198.6 (C4), 189.4 (C2), 92.0 (C3), 40.2 (C5), 28.3 (C5(CH$_3$)$_3$), 26.3 (C1); IR (ATR): $\nu$ 2962m, 2870w, 1569s, 1506s, 1385s, 1285w, 1233m, 1186m, 1021w, 898m, 767m, 664m; HRMS (ESI$^+$): $m/z$ calcd. for $\text{C}_{24}\text{H}_{22}\text{CoNaO}_3^+$ ([M+Na$^+$]) 505.1971, found 505.1979; HPLC (Chiralpak IC-3 (3 $\mu$m, 250x4.6 mm), heptane/i-ProOH 99:1, 1.0 mL/min, 5 °C): Rt 12.3 ($\Delta$), 13.7 ($\Delta$).

Co(dmbac) (1e)

Following the general procedure B1, the reaction of Co(CO)$_3$-H$_2$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$_2$O$_2$ (1.62 mL, 20.0 mmol, 20.0 equiv.) provided the title compound after column chromatography on silica gel (toluene/i-ProOH 100:0→100:2) as a green oil (201 mg, 383 $\mu$mol, 38%, 2.01 d.r. (mer/fac)). The mer- and fac-diastereomers were separated by preparative TLC on silica gel (toluene/i-ProOH 25:1). Analytical data for mer-1e: Rt 0.34 (toluene/i-ProOH 50:1); $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta$ 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$_3$)$_3$); $^{13}$C($^1$H) NMR (125.8 MHz, CDCl$_3$): $\delta$ 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): $\nu$ 2952m, 2867w, 1569s, 1514s, 1387s, 1281w, 1232w,
Following the general procedure B1, the reaction of Co(CO$_3$)$_2$·H$_2$O (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. H$_2$O$_2$ (1.62 mL, 20.0 mmol, 20.0 equiv.) provided the title compound after column chromatography on silica gel (toluene/i-PrOH 100:0→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$_t$ 0.37 (toluene/i-PrOH 25:1); $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta$ 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(CH$_3$)$_3$); $^{13}$C [$^1$H] NMR (125.8 MHz, CDCl$_3$): $\delta$ 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 (C7CH$_3$), 22.4 (C7CH$_3$), 22.3 (C7CH$_3$); IR (ATR): $\nu$ 2953m, 2869w, 1572s, 1516s, 1396s, 1277w, 1177w, 1102w, 1020w, 762w, 637w; HRMS (ESI$^+$): m/z calcd. for C$_{27}$H$_{40}$CoNaO$_6^+$ ([M+Na$^+$]) 547.2440, found 547.2447; HPLC (Chiralpak IG-3 (3 µm, 250×4.6 mm), heptane/i-PrOH 99:1, 0.5 mL/min, 40 °C): Rt 8.4 (A), 10.3 (Δ). Analytical data for fac-1f: R$_t$ 0.21 (toluene/i-PrOH 25:1); $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta$ 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(CH$_3$)$_3$); $^{13}$C [$^1$H] NMR (125.8 MHz, CDCl$_3$): $\delta$ 193.2 (C4), 189.1 (C2), 96.2 (C3), 37.7 (C5), 36.2 (C6), 27.4 (C7), 26.0 (C1), 22.5 (C7CH$_3$), 22.4 (C7CH$_3$); IR (ATR): $\nu$ 2955m, 2869w, 1572s, 1516s, 1396s, 1277w, 1178w, 1102w, 1020w, 762w, 637w; HRMS (ESI$^+$): m/z calcd. for C$_{27}$H$_{40}$CoNaO$_6^+$ ([M+Na$^+$]) 547.2440, found 547.2444; HPLC (Chiralpak IG-3 (3 µm, 250×4.6 mm), heptane/i-PrOH 99:1, 0.5 mL/min, 40 °C): Rt 8.8 (A), 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).

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

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

| Entry  | Light     | Solvent | Time [h] | Et₃N | tfacH | d.r. b (mer/fac) |
|--------|-----------|---------|----------|------|-------|-----------------|
| 1      | Darkness  | MeCN    | 12       | 0    | 0     | 100:0           |
| 2      | Darkness  | MeCN    | 12       | 3    | 3     | ~               |
| 3      | Darkness  | MeCN    | 12       | 3    | 0     | ~               |
| 4      | Darkness  | MeCN    | 12       | 0    | 3     | 100:0           |
| 5      | Blue LED  | MeCN    | 12       | 0    | 3     | ~               |
| 6      | Blue LED  | MeCN    | 12       | 3    | 3     | ~               |
| 7      | Blue LED  | MeCN    | 12       | 3    | 3     | ~               |
| 8      | Blue LED  | MeCN    | 12       | 3    | 3     | ~               |
| 9      | Darkness  | CHCl₃   | 24       | 0    | 0     | 100:0           |
| 10     | Darkness  | CHCl₃   | 24       | 3    | 3     | 99:1            |
| 11     | Darkness  | CHCl₃   | 24       | 3    | 0     | 100:0           |
| 12     | Darkness  | CHCl₃   | 24       | 0    | 3     | 99:1            |
| 13     | Blue LED  | CHCl₃   | 6        | 0    | 0     | 95:5            |
| 14     | Blue LED  | CHCl₃   | 6        | 3    | 3     | 83:17           |
| 15     | Blue LED  | CHCl₃   | 6        | 3    | 0     | 81:19           |
| 16     | Blue LED  | CHCl₃   | 6        | 3    | 0     | 93:7            |
| 17     | Blue LED  | CHCl₃   | 10       | 0    | 3     | 93:7            |
| 18     | Blue LED  | CHCl₃   | 10       | 3    | 3     | 58:42           |
| 19     | Blue LED  | CHCl₃   | 10       | 3    | 3     | 62:38           |
| 20     | Blue LED  | CHCl₃   | 10       | 3    | 3     | 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 \( \Lambda\)-mer-1a and \( \Lambda\)-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 \( \mu \)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 \( \Lambda\)-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 \( \mu \)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] | \( \Lambda\)-fac | \( \Lambda\)-mer | \( \Delta\)-fac | \( \Delta\)-mer |
|-------|------------|----------------|---------------|---------------|---------------|
| 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.

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

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

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

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

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

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 \(R = 8.314 \text{ J/(mol} \cdot \text{K)\), 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 \(k_B = 1.381 \cdot 10^{-23} \text{ J/K. Corrected HPLC data, the result of the regression analysis, the rate constants and activation free energies for the stereoisomerization processes in 1a are shown in Figure S2.\)}}

Scheme S1. Possible macroscopically observable stereoisomerization reactions of 1a with rate constants.
**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 \(^{[3]}\). 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 acidinium, 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(fac)-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.), Et$_3$N (0 or 10 mol%) and A1 (0 or 1.0 mol%), in CHCl$_3$ (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), H$_2$O/MeCN 50:50, 0.5 mL/min, 40 °C).

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

| Entry | Time [min] | 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%), Et$_3$N (0–1.0 equiv.), CHCl$_3$ (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 Diastereomeration of Co(tfac)$_3$ (1a)

A solution of rac-mer-1a (518 µg, 1.00 µmol, 1.0 equiv.), Et$_3$N (0–1.0 equiv.) and the respective photocatalyst[^4b,c] (0–1.0 mol%), in CHCl$_3$ (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), H$_2$O/MeCN 50:50, 0.5 mL/min, 40 °C).

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

| Entry | Photocatalyst (mol%) | Base (equiv.) | Deviation from Std. Conditions | Yield[^d] | d.r.[^b] (mer/fac) |
|-------|----------------------|--------------|-------------------------------|-----------|-------------------|
| 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 rac-fac-1a      | 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%), Et$_3$N (0–1.0 equiv.), CHCl$_3$ (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 Co(tfac)₂ (1a) with Acridinium Photocatalysts

A solution of rac-mer-1a (1.30 mg, 2.50 µmol, 1.0 equiv.), Et₃N (0 or 3.0 equiv.) and the respective photocatalyst[3a] (1.0 mol%), in CHCl₃ (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/t-PrOH 99:1, 0.5 mL/min, 10 °C)

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

| Entry | Photocatalyst | Solvent  | Et₃N   | tfacH  | Outcome          |
|-------|---------------|----------|--------|--------|------------------|
| 1     | A10           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 2     | A11           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 3     | A12           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 4     | A13           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 5     | A14           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 6     | A15           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 7     | A16           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 8     | A17           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 9     | A18           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 10    | A19           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 11    | A20           | CHCl₃    | 0 equiv. | 0 equiv. | Racemic          |
| 12    | A21           | CHCl₃    | 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           | CHCl₃    | 3 equiv. | 0 equiv. | Racemic, decomposition |
| 17    | A10           | CHCl₃    | 3 equiv. | 3 equiv. | Complete decomposition |
| 18    | A10           | CHCl₃    | 3 equiv. | 3 equiv. | Racemic          |

*a Reaction conditions: rac-mer-1a (2.50 µmol, 1.0 equiv.), photocatalyst (1.0 mol%), Et₃N (0–3.0 equiv.), solvent (2.5 mmol/L), blue LED (467 nm, 11 W), r.t., 5 h*
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$_3$N (141 nL, 1.00 µmol, 10 mol%) and Δ-[Ru(1,10-phen)]$_2$Cl$_2$ (Δ-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 | Complex | Deviation from Std. Conditions | Yield [\%] | d.r. a (mer/fac) | e.r. c (mer) | e.r. c (fac) |
|-------|---------|-------------------------------|------------|------------------|-------------|-------------|
| 1     | 1a      | –                             | 0          | –                | –           | –           |
| 2     | 1b      | –                             | 0          | –                | –           | –           |
| 3     | 1c      | –                             | 84         | 79.21 \(94\)    | 69.31       | –           |
| 4     | 1d      | –                             | 88         | 78.22 \(44\)    | 71.29       | –           |
| 5     | 1d      | 48 h, starting from rac-fac-1d| 52         | 71.29 \(50\)    | 68.32       | –           |
| 6     | 1e      | 2.5 mmol/L                    | 94         | 68.32 \(73\)    | 74.26       | –           |
| 7     | 1f      | –                             | 72         | 70.30 \(88\)    | 82.18       | –           |

* Reaction conditions: rac-mer-1 \((10.0 \text{ mmol, 1.0 equiv.)}, \text{ diketone (10 equiv.), EtN (10 mol\%), }\)\(\Delta\)-l-PC \((0.5 \text{ mol\%)}, \text{ acetone/H}_2\text{O 7:3 (5 mmol/L), Ar, blue LED (456 nm, 13 W), r.t., 24 h.}^b \) Determined by HPLC using durene as internal standard. \(^c \) Determined by HPLC on a chiral stationary phase after isolation, given as \(\Lambda:\Delta.\)

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

| Entry | Deviation from Std. Conditions | Yield [\%] | d.r. a (mer/fac) | e.r. c (mer) | e.r. c (fac) |
|-------|-------------------------------|------------|------------------|-------------|-------------|
| 1     | In the dark                    | 100        | 100:0            | 50:50       | –           |
| 2     | Without photocatalyst          | 77         | 76:24            | 50:50       | 50:50       |
| 3     | Without EtN                    | 75         | 68:32            | 84:16       | 78:12       |
| 4     | Without additional diketone ligand | 44       | 70:30            | 80:20       | 74:26       |
| 5     | Using rac-[Ru(bpy)\_3]Cl\_2     | 62         | 66:34            | 50:50       | 50:50       |
| 6     | Using \(\Delta\)-l-PC          | 79         | 67:33            | 33:67       | 36:64       |

* Reaction conditions: rac-mer-1f \((2.50 \text{ mmol, 1.0 equiv.)}, \text{ S3b (10 equiv.), EtN (10 mol\%), }\)\(\Delta\)-l-PC \((0.5 \text{ mol\%)}, \text{ acetone/H}_2\text{O 7:3 (5 mmol/L), Ar, blue LED (456 nm, 13 W), r.t., 24 h.}^b \) Determined by HPLC using durene as internal standard. \(^c \) Determined by HPLC on a chiral stationary phase after isolation, given as \(\Lambda:\Delta.\)

**Table S9.** Solvent screening for the \(\Delta\)-l-PC catalyzed photoderacemization of 1f.

| Entry | Solvent | d.r. a (mer/fac) | e.r. c (mer) | e.r. c (fac) |
|-------|---------|------------------|-------------|-------------|
| 1     | EtOH    | 68:32            | 59:41       | 57:43       |
| 2     | \(t\)-PrOH | 68:32           | 55:47       | 53:47       |
| 3     | CF\_3CH\_2OH | 68:32         | 52:48       | 52:48       |
| 4     | (CF\_3)\_2CHOH | 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\_2Cl\_2 | 68:32         | 55:45       | 53:47       |
| 14    | CHCl\_3 | 68:32            | 52:48       | 52:48       |
| 15    | Toluene | 68:32            | 58:42       | 55:45       |

* Reaction conditions: rac-mer/fac-1a \((2.50 \text{ mmol, 1.0 equiv.)}, \text{ S3b (10 equiv.), EtN (10 mol\%), }\)\(\Delta\)-l-PC \((0.5 \text{ mol\%)}, \text{ solvent (5 mmol/L), Ar, blue LED (456 nm, 13 W), r.t., 24 h.}^b \) Determined by HPLC of the crude product. \(^c \) Determined by HPLC on a chiral stationary phase after isolation, given as \(\Lambda:\Delta.\)
Figure S5. Correlation between the enantiomeric excess of 1f and the Kamlet–Taft parameters $\beta$ and $\pi^*$ (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.), Δ-l-PC (21.7 µg, 12.5 nmol, 0.25 mol%), Et₃N (70 nL, 500 nmol, 0.1 equiv.) and anisole as internal standard (1.64 µL, 15.0 µmol, 3.0 equiv.) in acetone-d₆/D₂O 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.

Et₃N catalyzed H/D exchange between D₂O 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-d₆/D₂O 7:3) of the photoderacemization of mer-1f after 0 and 10 min of irradiation (* = mer-1f, # = fac-1f).](image-url)
7. HPLC Data

Co(tfac)$_3$ (1a)

**HPLC Conditions:** Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H$_2$O/MeCN 50:50, 0.5 mL/min, 40 °C

![HPLC Chromatogram](image)

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

![HPLC Chromatogram](image)

| 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 |

**WVL: 275 nm**

**rac-mer**

| 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 |

**WVL: 275 nm**

**rac-fac**
Co(cycac)$_3$ (1c)

**HPLC Conditions:** Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H$_2$O/MeCN 75:25, 0.5 mL/min, 40 °C

![HPLC chromatogram for Co(cycac)$_3$ (1c)](chart1)

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

![HPLC chromatogram for Chiralpak IC-3](chart2)

| 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 and Retention time](image)

| 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     |

![Chromatogram and Retention time](image)

| 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       | 100.00     |

![Chromatogram and Retention time](image)

| 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        | 100.00     |
Co(pivac)$_3$ (1d)

**HPLC Conditions**: Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H$_2$O/MeCN 75:25, 0.5 mL/min, 40 °C

![HPLC Chromatogram](image1)

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

![HPLC Chromatogram](image2)

| No. | Ret.Time | Height  | Area     | Rel.Area |
|-----|----------|---------|----------|----------|
|     | min      | mAU     | mAU*min  | %        |
| 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 | Height  | Area     | Rel.Area |
|-----|----------|---------|----------|----------|
|     | min      | mAU     | mAU*min  | %        |
| 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:

| 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**   |

WVL:275 nm

| 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**   |

WVL:275 nm

| 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):

| 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      |
Co(dmbac)$_3$ (1e)

**HPLC Conditions:** Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H$_2$O/MeCN 75:25, 0.5 mL/min, 40 °C

![HPLC Chromatogram](image)

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

![HPLC Chromatogram](image)

| 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 and Retention Data](chart)

| 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** |

![Chromatogram and Retention Data](chart)

| 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** |

![Chromatogram and Retention Data](chart)

| 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** |
Co(mpac)$_3$ (1f)

**HPLC Conditions:** Supelco Ascentis Express C18 (2.7 µm, 100x2.1 mm), H$_2$O/MeCN 75:25, 0.5 mL/min, 30 °C

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

### Integration Results

| 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     |

### Integration Results

| 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:

| 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**   |

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![Chromatogram](image1)

| 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**   | **100.00**   |

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![Chromatogram](image2)

| 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**    | **100.00**   |
Photoderacemization (with L-PC):  

| No. | Peak Name | Ret. Time | Area | Height | 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 | Height | Area | 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 | Height | Area | 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(fac)$_3$ (1a): HPLC-DAD (225 nm)

Co(bzac)$_3$ (1b): $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$), CH$_3$ 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)

\[ y = 1.6093x + 0.0492 \quad R^2 = 0.9878 \]

\[ y = 1.5522x + 0.0187 \quad R^2 = 0.9957 \]

\[ y = 2.1991x + 0.0079 \quad R^2 = 0.9988 \]

\[ y = 2.1613x + 0.0215 \quad R^2 = 0.9996 \]

Co(mpac)$_3$ (1f): HPLC-DAD (225 nm)

\[ y = 0.9565x + 0.0965 \quad R^2 = 0.9957 \]

\[ y = 2.1613x + 0.0215 \quad R^2 = 0.9996 \]

\[ y = 0.9835x - 0.0255 \quad R^2 = 0.9795 \]
9. CD and UV/Vis Spectra

Chiral Photocatalysts\textsuperscript{2b}

\textbf{Co(tfac)}\textsubscript{3} (1a)\textsuperscript{5}

\( \Lambda\text{-}mer\text{-}1a \) and \( \Lambda\text{-}fac\text{-}1a \) were isolated by HPLC on a chiral stationary phase (see above).
Photoderacemization Products
After 48 h
10. NMR Spectra

$^1$H and $^{13}$C($^1$H) NMR of [2,2'-Bipyridine]-4,4'-dicarbonyl dichloride (S1)
$^{1}$H and $^{13}$C{$^1$H} NMR of Bis((1$R$,2$S$,5$R$)-2-isopropyl-5-methylcyclohexyl) [2,2'-bipyridine]-4,4'-dicarboxylate (L-menbpy, S2)
$^1$H and $^{13}$C$^1$H NMR of $\Delta$-[Ru(L-menbpy)$_3$]Cl$_2$ ($\Delta$-l-PC)
$^1$H and $^{13}$C$^1$H NMR of $\Lambda$-[Ru($\mu$-menbpy)$_3$]Cl$_2$ ($\Lambda$-l-PC)
$^1$H and $^{13}$C$[^1]$H NMR of 6,6-Dimethylheptane-2,4-dione (S3a)
$^1$H and $^{13}$C$^{[1]H}$ NMR of 7-Methyloctane-2,4-dione (S3b)
$^1$H, $^{13}$C$[^1]$H and $^{19}$F$[^1]$H NMR of mer-Co(tfac)$_3$ (mer-1a)
$^{1}\text{H}, ^{13}\text{C}(^1\text{H})$ and $^{19}\text{F}(^1\text{H})$ NMR of fac-Co(fac)$_3$ (fac-1a)
$^1$H and $^{13}$C($^1$H) NMR of mer-Co(bzac)$_3$ (mer-1b)
$^1$H and $^{13}$C [$^1$H] NMR of fac-Co(bzac)$_3$ (fac-1b)
$^1$H and $^{13}$C\(^{1}{H}\) NMR of \textit{fac-Co(cycac)$_3$} (\textit{fac-1c})
$^1$H and $^{13}$C$^1$H NMR of mer-Co(cycac)$_3$ (mer-1c)
mer-Co(pivac)_3 (mer-1d)
$\text{fac-Co(pivac)}_3$ (fac-1d)
mer-Co(dmbac)$_3$ (mer-1e)
**fac-Co(dmbac)$_3$ (fac-1e)**

[Chemical structure of fac-Co(dmbac)$_3$ (fac-1e)]

[Chemical shift graph for fac-Co(dmbac)$_3$ (fac-1e)]

[S58]
mer-Co(mpac)$_3$ (mer-1f)
$\text{fac-Co(mpac)}_3$ (fac-1f)
11. References

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