Supporting Information

Class-II-Aldolase-Mimicking Polyfunctional Lewis Acid / Azolium-Aryloxide Catalysts in Direct Enantioselective Nitroaldol Additions

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1. General Remarks

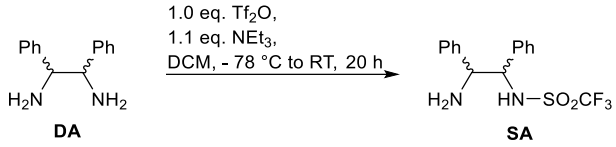
All air- and moisture-sensitive reactions were conducted in oven-dried glassware (150 °C) that was further heated to 630 °C for several min under high vacuum. Reactions were carried out under a positive pressure of nitrogen (ca. 0.2 bar). Liquids were added via syringe, and solids were introduced neat against a flow of nitrogen. Solvents were removed using a rotary evaporator equipped with a 40 °C water bath. Non-volatile compounds were dried under vacuum (0.03 mbar) and, when required, freeze-dried using liquid nitrogen. Technical-grade solvents (dichloromethane, petroleum ether, diethyl ether, tetrahydrofuran, *n*-pentane, and toluene) were distilled prior to use. Anhydrous solvents (acetonitrile, tetrahydrofuran, toluene, dichloromethane) were purified using a solvent purification system (MBraun MB SPS800). Aldehydes used for nitroaldol reaction were purified by distillation or column chromatography. Nitromethane and 1-nitropropane were stirred over calcium hydride for 2 h and subsequently distilled. Catalytic enantioselective reactions were performed in a parallel synthesizer (Heidolph Synthesis 1) with shaking at 250 rpm for nitromethane and in Schlenk flask using bath cryostat for cooling for nitropropane. $Ni(acac)_2$ was dried in a Kugelrohr distillation apparatus under reduced pressure (0.01 mbar) at 100 °C for 1 h. Unless otherwise noted, reactions were magnetically stirred and monitored by ^{1}H NMR spectroscopy or thin-layer chromatography (TLC, silica gel 60 F254). TLC spots were visualized by UV fluorescence quenching and/or $KMnO_4$/NaOH staining. column chromatography was performed on silica gel 60 (40–63 µm particle size) under forced flow at 0.2–0.4 bar overpressure. **Analytical Methods, NMR Spectroscopy:** NMR spectra were recorded at room temperature on Bruker Avance spectrometers operating at 700, 500, 400, or 300 MHz (^{1}H), 176, 125, 100, or 75 MHz (^{13}C), 376 MHz (^{19}F) and 162 MHz (^{31}P). For catalytic reaction monitoring, spectra were recorded at 45° (optimized catalytic condition). Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet (complex pattern), dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, br = broad signal. **Infrared Spectroscopy:** IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with ATR unit. Absorption bands are reported in wavenumbers (cm^{-1}). **Optical Rotation:** Measurements were carried out on a polarimeter at the sodium D line using a 100 mm path length cell. **Melting Points:** Melting points were determined in open glass capillaries using a Stuart SMP40 automatic melting point apparatus and are uncorrected. Mass Spectrometry: Mass spectra were obtained from the MS service of the University of Stuttgart using a Finnigan MAT95 (EI or CI) or a Bruker Daltonics micrOTOF-Q (ESI). Ionization methods are indicated in parentheses. **UV–Vis Spectroscopy:** UV–Vis spectra were recorded on a PerkinElmer Lambda 365 spectrometer. **Chiral HPLC:** Enantiomeric excesses (*ee*) were determined by HPLC (Elite LaChrom system with HITACHI modules) using chiral stationary phase columns (Daicel Chiralpak AS-H, AD-H or Daicel Chiralcel OD-H, IJ-H). **Computational Details:** The conformational space of all geometries was explored using the Conformer and Rotamer Ensemble Sampling Tool (CREST).[1] Stationary points were preoptimized using GFN2-xTB.[2] All electronic structure calculations were carried out using density functional theory (DFT) with Turbomole V7.7.1.[3] Geometry optimizations and frequency calculations were conducted using the PBEh-3c composite method with the def2-mSVP basis set,[4] including DFT-D3[5] dispersion corrections and Becke-Johnson damping.[6] All transition states exhibited exactly one imaginary frequency. Their intrinsic reaction coordinate (IRC) paths connected to the appropriate minima. Gibbs free energies were computed at 318.15 K within the rigid-rotor-harmonic-oscillator approximation, assuming a reference concentration of 1 mol/L. Single-point energies were computed at the B3LYP-D3(BJ)/def2-TZVP[7, 8] level, where implicit solvent effects were considered via COSMO[9] (ε = 35.87 for nitromethane). All geometry optimizations and free energy calculations

were performed within the ChemShell framework[10] via DL-FIND.[11] For the microkinetic modelling, the Julia packages Catalyst[12] and PEtab[13] were used

2. Experimental Procedure

2.1 General Procedure (GP)

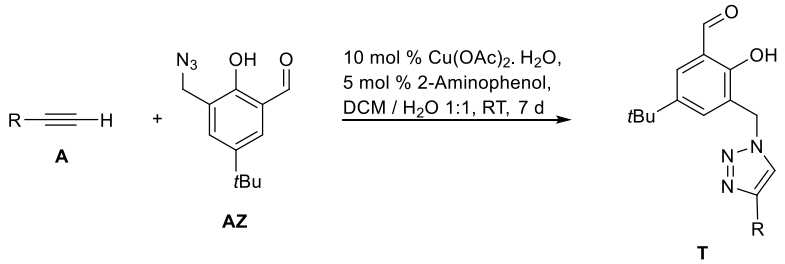
2.1.1 General Procedure for Synthesis of Sulfonamides (SA1-RR and SA1-SS) (GP 1)



DA **SA**

Following a literature procedure,[14] to a solution of the corresponding chiral diamine (**DA**, 1.0 eq.) in dry dichloromethane (DCM, 4 mL/mmol) under nitrogen atmosphere trifluoromethanesulfonic anhydride (1.0 eq., 1 M in DCM) was added dropwise over a period of 2 hours using a syringe pump at -78 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred overnight. Upon completion, demineralized water (4 mL/mmol) was added to the mixture, followed by the addition of triethylamine (1.1 eq.). The aqueous and organic phases were separated, and the aqueous phase was extracted twice with dichloromethane (2 × 25 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography using a solvent mixture of dichloromethane and methanol (DCM: MeOH, 30:1 to 15:1) to yield the desired sulfonamides (**SA**) as white solids.

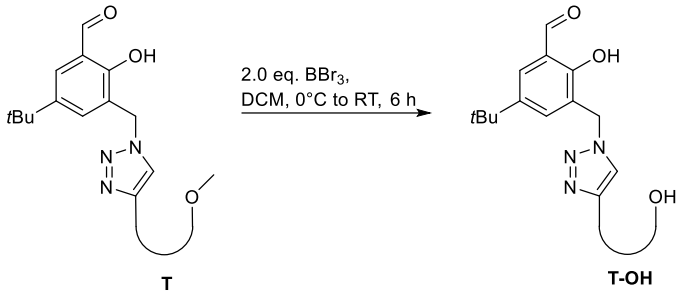
2.1.2 General Procedure for the Click Reactions (GP2)



A **AZ** **T**

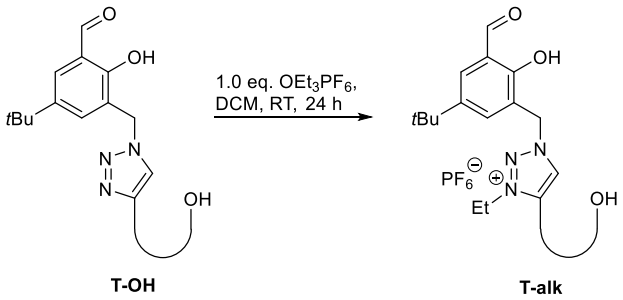
The alkyne-azide cycloaddition was carried out according to a literature procedure.[15] Alkyne **A** (1.0 eq.), azide **AZ** (1.0 eq.), copper(II) acetate monohydrate (10 mol%), and 2-aminophenol (5 mol%) were dissolved in a mixture of DCM and water (1:1, 0.2 mL/mmol) and stirred at room temperature until complete conversion of the starting material (alkyne) was observed (5-7 days). Upon completion, the phases were separated, and the aqueous layer was extracted twice with DCM (2 × 10 mL). The combined organic layers were dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:ethyl acetate) to afford the desired triazoles.

2.1.3 General Procedure for Methyl Deprotection (GP3)



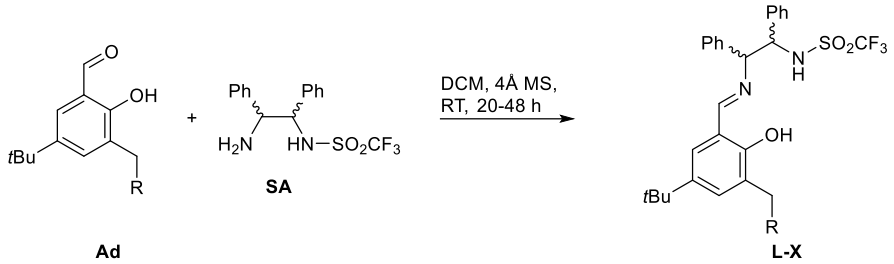
The deprotection of methyl group was done using a literature known procedure.[16] The methyl-protected alcohol (1.0 eq.) was dissolved in dry DCM (1 mL/mmol) under nitrogen atmosphere. The solution was cooled to 0 °C and BBr_3 (2.0 eq., 1.0 M in DCM) was then added dropwise. After complete addition, the reaction mixture was allowed to warm to room temperature and stir for 6 hours. The reaction was quenched by addition of demineralized water (5 mL) and stirred for an additional 30 min under air. The phases were separated, and the organic layer was washed with demineralized water (2 × 5 mL), extracted with DCM, and dried over sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:ethyl acetate) to isolate the deprotected triazoles.

2.1.4 General Procedure for Alkylation of Triazoles (GP4)



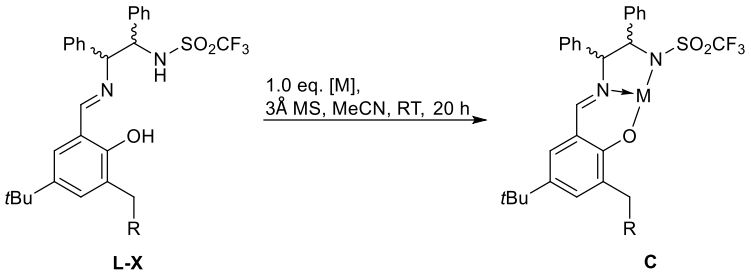
The alkylation of triazoles was done using a known literature procedure.[15] The corresponding aldehyde (1.0 eq.) and OEt_3PF_6 (1.0 eq.) were dissolved in anhydrous DCM (5 mL/mmol) under nitrogen atmosphere in the presence of molecular sieves (4Å). The reaction mixture was stirred for 24 h at room temperature. Afterwards the reaction mixture was quenched with MeOH (1 ml/mmol) and stirred for another 30 min. Demineralized water (5 mL) was added and the phases were separated, the organic phase was washed with demineralized water (2 x 5 mL), extracted with DCM and dried over sodium sulphate. The solvent was removed under reduced pressure. The residue was dissolved in DCM (0.1 mL/mmol) and the product was precipitated by adding this solution to pentane (100 mL/g crude product). The solid was filtered off, washed with pentane and dried in vacuum to yield a white solid, which was used in the following steps without further purification.

2.1.5 General Procedure for the Imine-Synthesis (GP5)



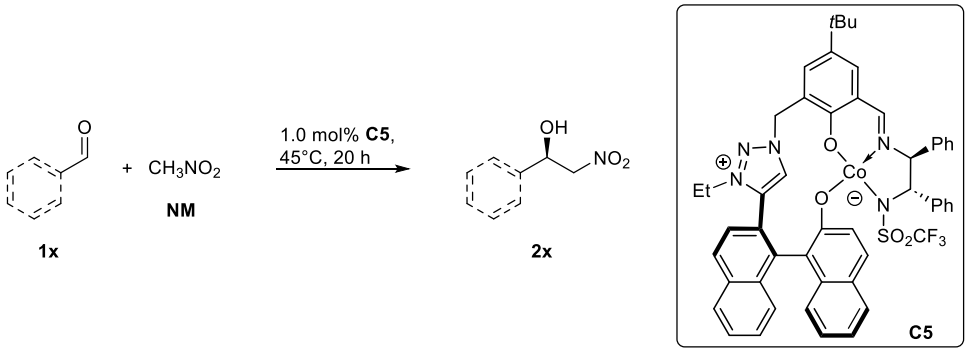
Following a literature procedure [14] the corresponding aldehyde (1.0 eq.) and amine **SA1-SS** or **SA1-RR** (1.05 eq.) was dissolved in anhydrous DCM (0.1 mL/mmol) under a nitrogen atmosphere in the presence of molecular sieves (4Å). The reaction mixture was stirred at room temperature for 24 to 48 hours. The reaction progress was monitored by ^{1}H-NMR spectroscopy to ensure complete consumption of the aldehyde. Upon completion, the molecular sieves were removed by filtration through a pad of Celite®, which was subsequently washed with DCM. The combined filtrate was concentrated under reduced pressure. The residue was dissolved in DCM (0.1 mL/mmol) and the product was precipitated by slowly adding this solution to a mixture of diethyl ether and *n*-pentane (1:10). The solvent was decanted and the precipitated yellow solid dried under vacuum. The imine was used directly in subsequent steps without further purification.

2.1.6 General Procedure for the Complexation (GP6)



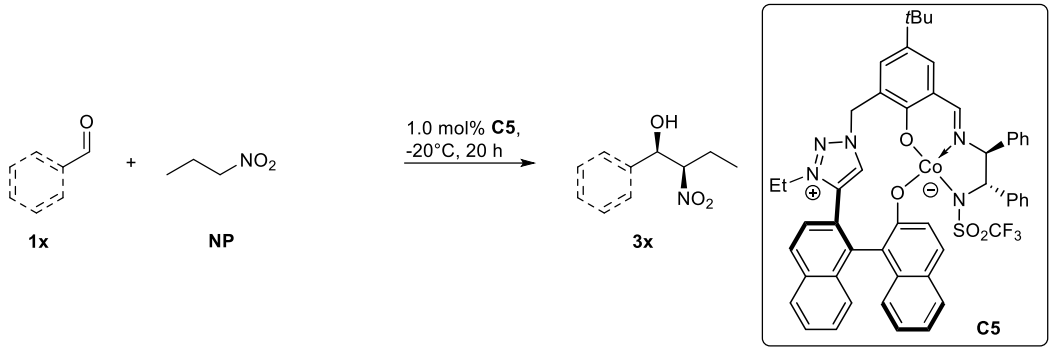
Following a literature procedure [14], the corresponding imine (1.0 eq.) and metal source (1.0 eq.) were dissolved in anhydrous acetonitrile (0.1 mL/mmol) under nitrogen atmosphere in the presence of molecular sieves (3Å). The reaction mixture was stirred at room temperature for 20 hours. After completion, the solution was filtered through a pad of Celite® and eluted with DCM. The solvent was removed under reduced pressure. The residue was dissolved in DCM (0.1 mL/mmol), and the product was precipitated by adding this solution to a mixture of diethyl ether and *n*-pentane (1:10 v/v). After the solvent was decanted, the precipitated solid was collected and dried under vacuum.

2.1.7 General Procedure for the Catalytic Asymmetric Nitroaldol Addition of Aldehydes to Nitromethane (GP 7)



The activated catalyst **C5** (1.0 mol%) was added to a vial in a parallel synthesizer system (*Heidolph Synthesis 1*) and evacuated for 20 min. Dry nitromethane (**NM**, 6.0 eq.) was then added, and the mixture was stirred for 15 min. Subsequently, a stock solution of aldehyde (**1x**, 1.0 eq.) in nitromethane (**NM**, 6.0 eq.) was added to the vial. The catalytic reaction was carried out at 45°C under a nitrogen atmosphere with shaking at 250 rpm for 20 hours. After completion, the reaction mixture was diluted with PE:ethyl acetate (1:1, 2 mL), filtered through a short pad of silica gel, and eluted with additional PE:ethyl acetate (1:1, 10 mL). The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (PE:ethyl acetate), yielding the desired product (**2x**) as a white solid.

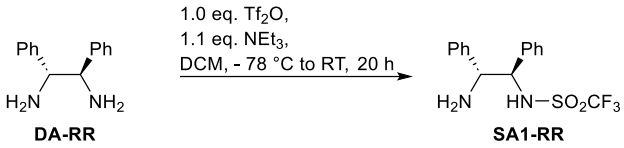
2.1.8 General Procedure for the Catalytic Asymmetric Nitroaldol Addition of Aldehydes to Nitropropane (GP 8)



The activated catalyst **C5** (1.0 mol%) was added to a Schlenk flask under nitrogen and evacuated for 20 min. Dry nitropropane (**NP**, 6.0 eq.) was then added, and the mixture was stirred for 15 min. Subsequently, a stock solution of aldehyde (**1x**, 1.0 eq.) in nitropropane (**NP**, 6.0 eq.) was added to the schlenk flask. The catalytic reaction was carried out at -10 or -20°C (depending on the substrate) under a nitrogen atmosphere for 20 hours. After completion, the reaction mixture was diluted with petroleum ether and ethyl acetate (1:1, 2 mL), filtered through a short silica gel pad, and washed with additional (PE: ethyl acetate, 1:1, 10 mL). The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (PE: ethyl acetate), affording the desired product (**3x**) as a white solid. In the case of 4-bromo benzaldehyde and 4-iodo benzaldehyde 1M THF were used.

2.2 Synthesis of Sulfonamides SA1-RR and SA1-SS

2.2.1 Synthesis of *N*-((1*R*,2*R*)-2-Amino-1,2-diphenylethyl)-1,1,1-trifluormethane sulfonamide (SA1-RR) [14, 17]

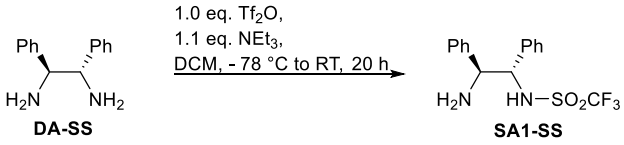


Sulfonamide **SA1-RR** was prepared according to the general procedure **GP 1** using (1*R*,2*R*)-1,2-diphenylethylenediamine **DA-RR** (800 mg, 3.76 mmol, 1.0 eq.) and trifluoromethanesulfonic anhydride (1 M in DCM, 3.7 mL, 3.70 mmol, 1.0 eq.) and triethylamine (574 µL, 4.14 mmol, 1.1 eq.). The crude product was purified by column chromatography (DCM:MeOH, 30:1 to 15:1) and **SA1-RR** was isolated as a white solid (1093.7 mg, 3.17 mmol, 84%).

$C_{15}H_{15}F_3N_2O_2S$, MW: 334.35 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.30 (*m*, 10H, Ar-*H*), 4.70 (*d*, *J* = 2.7 Hz, 1H, C*H*), 4.48 (*d*, *J* = 2.8 Hz, 1H, C*H*), 3.73-2.86 (*br*, 2H, NH_2). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -77.90.

The analytical data of **SA1-RR** agrees with the literature.[17]

2.2.2 Synthesis of *N*-((1*S*,2*S*)-2-Amino-1,2-diphenylethyl)-1,1,1-trifluormethane sulfonamide (SA1-SS) [14, 17]



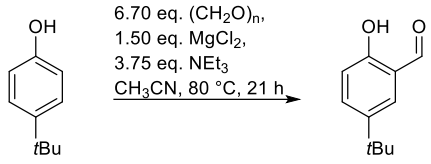
Sulfonamide **SA1-SS** was prepared according to the general procedure **GP 1** using (1*S*,2*S*)-1,2-diphenylethylenediamine **DA-SS** (1.0 g, 4.71 mmol, 1.0 eq.) and trifluoromethanesulfonic anhydride (1 M in DCM, 4.7 mL, 4.71 mmol, 1.0 eq.) and triethylamine (718 µL, 5.18, mmol, 1.1 eq.). The crude product was purified by column chromatography (DCM: MeOH, 30:1 to15:1) and **SA1-SS** was isolated as a white solid (1.3 g, 3.85 mmol, 81%).

$C_{15}H_{15}F_3N_2O_2S$, MW: 334.35 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.30 (*m*, 10H, Ar-*H*), 4.70 (*d*, *J* = 2.7 Hz, 1H, C*H*), 4.48 (*d*, *J* = 2.8 Hz, 1H, C*H*), 3.73-2.86 (*br*, 2H, NH_2). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -77.90.

The analytical data of **SA1-SS** agrees with the literature.[17]

2.3 Synthesis of Triazol(ium) or Imidazolium based Aldehydes

2.3.1 Synthesis of 4-*tert*-Butyl-2-hydroxy-benzaldehyde (S-2) [14]



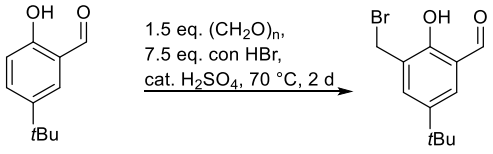
S-1 **S-2**

4-*tert*-Butyl-2-hydroxybenzaldehyde (**S-2**) was synthesized according to the procedure reported by *Bhatt et al*.[17] 4-*tert*-Butylphenol **S-1** (8.0 g, 53.36 mmol, 1.0 eq.), paraformaldehyde (10.7 g, 356.81 mmol, 6.7 eq.), and magnesium chloride (7.6 g, 79.88 mmol, 1.5 eq.) were added to a 250 mL round-bottom flask. Acetonitrile (3 mL/mmol) was then added, followed by the slow addition of triethylamine (27.8 mL, 199.81 mmol, 3.75 eq.). The resulting reaction mixture was stirred at 80 °C for 21 hours. After cooling to room temperature, 1 M hydrochloric acid was added to the mixture until all solids were dissolved. The aqueous layer was separated and extracted with diethyl ether (3 × 100 mL). The combined organic phases were dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (PE:ethyl acetate, 10:1) to yield 4-*tert*-butyl-2-hydroxybenzaldehyde **S-2** as a yellow oil (9.1 g, 50.77mmol, 95%).

$C_{11}H_{14}O_2$, MW: 178.23 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 10.89 (*s*, 1H, Ar-O*H*), 9.87 (*s*, 1H, Ar-C*H*O), 7.60 (*dd*, *J* = 8.7 Hz, *J* = 2.6 Hz, 1H, Ar-*H*), 7.50 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 6.93 (*d*, J = 8.7 Hz, 1H, Ar-*H*), 1.34 (*s*, 9H, Ar-C(CH_3)$_3$ ppm.

The analytical data for **S-2** agrees with the literature. [17]

2.3.3 Synthesis of 3-(Bromomethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde (S-3) [17]



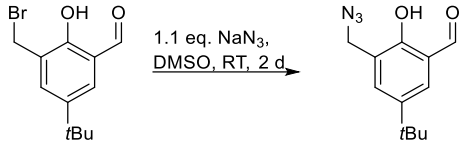
S-2 **S-3**

The synthesis of Bromo-methylated aldehyde **S-3** was done according to literature from *Bhatt et al*. [17] 4-*tert*-butyl-2-hydroxy-benzaldehyde **S-2** (7.0 g, 39.30 mmol, 1.0 eq.) and paraformaldehyde (1.8 g, 58.90 mmol, 1.5 eq.) were added into a round bottom flask (100 ml). and were suspended in concentrated hydrobromic acid (48%, 33.3 mL, 613.7 mmol, 7.5 eq.). A catalytic amount of concentrated sulfuric acid (10 drops) was then added, and the reaction mixture was stirred at 70 °C for 48 h. Upon completion, the mixture was cooled to room temperature and quenched with 60 mL of water. The aqueous and organic phases were separated, and the aqueous layer was extracted with DCM (2 x 50 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. The product 3-(Bromomethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **S-3** was isolated without further purification as brownish oily liquid (10.2 g, 37.54 mmol, 96%).

$C_{12}H_{15}BrO_2$, MW: 271.15 g/mol; **^{1}H-NMR ($CDCl_3$, 400 MHz):** δ = 11.34 (*s*, 1H, Ar-O*H*), 9.89 (*s*, 1H, Ar-C*H*O), 7.64 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 7.51 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 4.59 (*s*, 2H, Ar-CH_2-Br), 1.34 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-3** agrees with the literature.[15]

2.3.4 Synthesis of 3-(Azidomethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde (S-4) [15, 31]



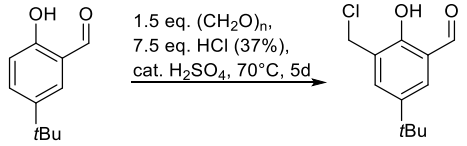
S-3 **S-4**

The synthesis of azide **S-4** was prepared according to a literature procedure.[15] Sodium azide (0.8 g, 12.20 mmol, 1.1 eq.) was added to a round-bottom flask and dissolved in dry DMSO (2 mL/mmol). Once the NaN_3 had fully dissolved, a solution of 3-(bromomethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **S-3** (3.0 g, 11.10 mmol, 1.0 eq) in dry DMSO (11 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was diluted by addition of demineralized water (20 mL) and extracted three times with DCM (each 25 mL). The combined organic layers were dried over sodium sulphate, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (PE:ethyl acetate, 4:1) to obtain the product (2.4 g, 10.28 mmol, 93%) as yellow solid.

$C_{12}H_{15}N_3O_2$, MW: 233.27 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 11.19 (*s*, 1H, Ar-O*H*), 9.93 (*s*, 1H, Ar-C*H*O), 7.56 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 7.53 (*d*, *J* = 2.4 Hz, 1H, Ar-C*H*), 4.44 (*s*, 2H, Ar-CH_2-N_3), 1.32 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-4** agrees with the literature.[18]

2.3.5 Synthesis of 3-(Chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde (S-5) [17]



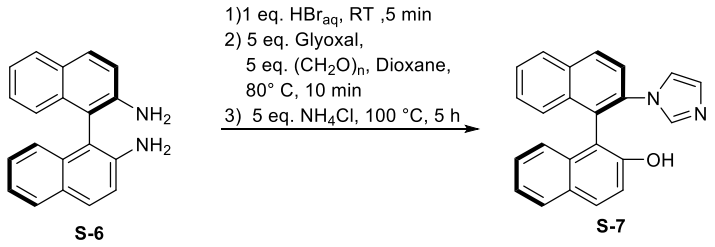
S-2 **S-5**

3-(Chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **S-5** was synthesized according to the method described by Bhatt *et al*.[17] 4-*tert*-butyl-2-hydroxybenzaldehyde **S-2** (8.0 g, 44.90 mmol, 1.0 eq.) and paraformaldehyde (2.0 g, 67.30 mmol, 1.5 eq.) were added to a round-bottom flask and suspended in concentrated hydrochloric acid (37%, 27.3 mL, 332.20 mmol, 7.5 eq.). A catalytic amount of sulfuric acid (10 drops) was added, and the reaction mixture was stirred at 70 °C for 5 days. Upon completion, the reaction mixture was cooled to room temperature and demineralized water (40 mL) was added. The layers were separated, and the aqueous phase was extracted with DCM (2 × 30 mL). The combined organic layers were dried over sodium sulfate, and the solvent was removed under reduced pressure. The product, 3-(chloromethyl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde **S-5**, was obtained as brownish oil (9.4 g, 41.42 mmol, 92%) and used without further purification.

$C_{12}H_{15}ClO_2$, MW: 226.70 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 11.27 (*s*, 1 H, Ar-O*H*), 9.90 (*s*, 1 H, Ar-C*H*O), 7.68 (*d*, *J* = 2.4 Hz, 1 H, Ar-*H*), 7.52 (*d*, *J* = 2.5 Hz, 1 H, Ar-*H*), 4.70 (*s*, 2 H, Cl-CH_2-Ar), 1.34 (*s*, 9 H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-5** agrees with the literature.[17]

2.3.6 Synthesis of (*R*)-2-(Imidazol-1-yl)-2′-hydroxy-1, 1′-binaphthyl (S-7) [15, 16]



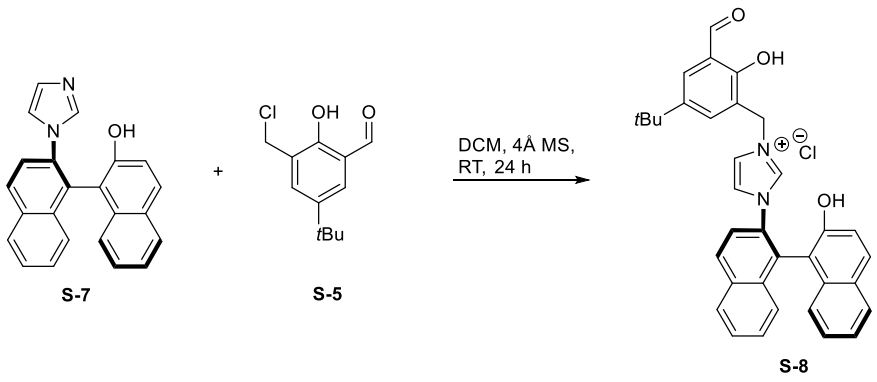
S-6 **S-7**

The synthesis of monoimidazole **S-7** was performed according to a modified literature [18] from *Chianese* and *Crabtree.*[19] *(R)*-2,2'-Diamino-1,1'-binapthyl **S-6** (250.0 mg, 0.87 mmol, 1.0 eq.) was suspended in demineralized water (10 mL/mmol) and concentrated hydrobromic acid (47%, 0.2 mL, 4.39 mmol, 5.0 eq.) was added slowly. The reaction mixture was stirred for 5 min at room temperature. Afterwards aqueous glyoxal solution (40%, 0.2 mL, 4.39 mmol, 5.0 eq.), paraformaldehyde (132.1 mg, 4.39 mmol, 5.0 eq.) were added to the reaction mixture and then the reaction mixture was stirred for 10 min at 80°C. Then ammonium chloride (235.1 mg, 4.39 mmol, 5.0 eq.) was added and the mixture was stirred for 5 h at 100°C. Afterwards, the reaction mixture was cooled down to room temperature and quenched with saturated sodium carbonate solution (1 mL/mmol) The aqueous phase was extracted three times with DCM (each 20 mL), dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (acetone: MeOH, 10:1) to give **S-7** (271.4 mg, 0.80 mmol, 92%) as a yellow solid.

$C_{23}H_{16}N_2O$, MW: 336.39 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.44-9.87 (*br*, 1H, C-O*H*), 8.06 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.97 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.83 (*d*, *J* = 8.1 Hz, 1H, Ar-*H*), 7.74 (*t*, *J* = 1.1 Hz,1H, N-C*H*-N), 7.64-7.50 (*m*, 3H, Ar-*H*), 7.41-7.33 (*m*, 2H, Ar-*H*), 7.32-7-26 (*m*, 1H, Ar-*H*), 7.24-7.17 (*m*, 1H, Ar-*H*), 6.90 (*d*, *J* = 8.4 Hz,1H, Ar-*H*), 6.83 (*t*, *J* = 1.4 Hz, 1H, N-C*H*-CH-N), 6.83-6.78 (*m*, 2H, Ar-*H*, N-C*H*-CH-N) ppm.

The analytical data for **S-7** agrees with the literature.[19]

2.3.7 Synthesis of (*R*)-3-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-1-(2'-hydroxy-(1,1'-binaphthalene)-2-yl)-1*H*-imidazol-3-ium chloride (S-8) [14]



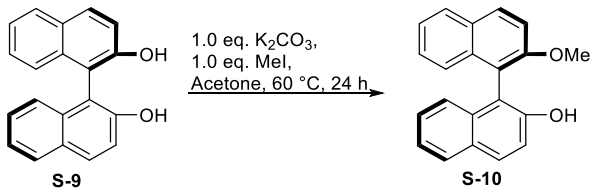
S-7 **S-5** **S-8**

The aldehyde **S-8** was synthesized according to a literature procedure.[14] Imidazole **S-7** (30.0 mg, 0.089 mmol, 1.0 eq.) and chloro-methylated aldehyde **S-5** (20.2 mg, 0.089 mmol, 1.0 eq.) were dissolved in anhydrous DCM (*c* = 0.02-0.05 mol/L) under nitrogen atmosphere. The reaction mixture was stirred for 24 h at room temperature. Afterwards the solvent was evaporated under reduced pressure. The residue was dissolved in DCM (1 2 mL/mmol), and the product was precipitated by adding this solution to *n*-pentane. The solvent was decanted, the product was dried *in vacuo* to yield a brownish solid (50.2 mg, 0.089 mmol, >99%), which was used in the following steps without further purification.

$C_{35}H_{31}ClN_2O_3$, MW: 563.09 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 11.25 (*s*, 1H, Ar-O*H*), 10.08 (*s*, 1H, Ar-O*H*), 9.91 (*s*, 1H, Ar-C*H*O), 9.82 (*s*, 1H, N-C*H*-N), 8.35 (*d*, *J* = 2.2 Hz, 1H, Ar-*H*), 8.10 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.99 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.80-7.69 (*m*, 3H, Ar-*H*), 7.68-7.60 (*m*, 1H, Ar-*H*), 7.58 (*d*, *J* = 2.5 Hz,1H, Ar-*H*), 7.49 (*d*, *J* = 8.8 Hz,1H, Ar-*H*), 7.48-7.40 (*m*, 2H, Ar-*H*), 7.25-7.14 (*m*, 1H, Ar-*H*), 7.10 (*t*, 1H, N-C*H*-C-N), 7.09-6.98 (*m*, 1H, Ar-*H*), 6.84 (*t*, *J* = 1.9 Hz, 1H, N-C-C*H*-N), 6.80 (*d*, J = 8.3 Hz, 1H, Ar-*H*), 5.73 (*d*, *J* = 14.4 Hz, 1H, Ar-CH_2-N), 5.64 (*d*, *J* = 14.3 Hz,1H, Ar-CH_2-N),1.40 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-8** agrees with the literature. [14]

2.3.8 Synthesis of (*R*)-2-Hydroxy-2'-methoxy-1,1' binaphthyl (S-10) [17]



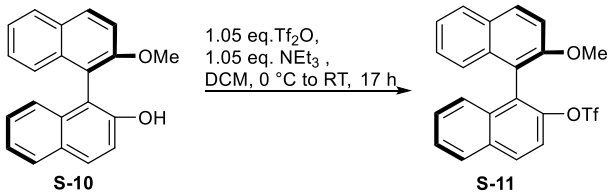
S-9 **S-10**

The synthesis of (*R*)-2-Hydroxy-2′-methoxy-1,1′-binaphthyl **S-10** was performed according to a literature procedure.[8] (*R*)-BINOL **S-9** (2.0 g, 7.0 mmol, 1.0 eq.) and anhydrous K_2CO_3 (0.9 g, 7.0 mmol, 1.0 eq.) were added to a 250 mL round-bottom flask. Dry acetone (150 mL) was then added to form a suspension, followed by the dropwise addition of methyl iodide (0.9 g, 0.4 mL, 7.00 mmol, 1.0 eq.). The reaction mixture was refluxed for 6 hours under nitrogen atmosphere. After completion, the reaction was cooled to room temperature and quenched with water (60 mL). Acetone was removed under reduced pressure, the phases were separated and the aqueous layer was extracted with DCM (3 × 40 mL). The combined organic extracts were washed with brine (40 mL), dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (DCM: PE, 3:2) to afford (*R*)-2-hydroxy-2′-methoxy-1,1′-binaphthyl **S-10** as a white foam (1.8 g, 6.09 mmol, 87%).

$C_{21}H_{16}O_2$, MW: 300.36 g/mol. **^{1}H NMR (400 MHz, $CDCl_3$):** $\boldsymbol{\delta}$ = 8.08 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.93-7.81 (*m,* 3H, Ar-*H*), 7.51 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.41-7.36 (*m*, 2H, Ar-*H*), 7.35-7.28 (*m*, 2H, Ar-*H*), 7.26-7.20 (*m*, 1H, Ar-*H*), 7.19 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.07 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 4.91 (*s*, 1H, Ar-O*H*), 3.82 (*s*, 3H, Ar-OCH_3) ppm.

The analytical data for **S-10** agrees with the literature. [20]

2.3.9 Synthesis of (*R*)-(1-(2-Methoxy-1-naphthyl)-2-naphthyl)-trifluoromethansulfonic acid (S-11) [18]



S-10 **S-11**

The synthesis of (*R*)-(1-(2-Methoxy-1-naphthyl)-2-naphthyl)-trifluoromethanesulfonic acid **S-11** was performed according to a literature procedure.[21] (*R*)-2-Hydroxy-2′-methoxy-1,1′-binaphthyl **S-10** (1.83 g, 6.1 mmol, 1.00 eq.) was dissolved in dry DCM (4 mL/mmol) under nitrogen atmosphere and cooled to 0 °C. Afterwards, triethylamine (890 µL, 6.4 mmol, 1.05 eq.) was added, followed by trifluoromethanesulfonic anhydride (1 M in

DCM, 6.4 mL, 6.4 mmol, 1.05 eq.). After complete addition, the reaction mixture was warmed to room temperature and stirred for an additional 17 h. Next, the reaction mixture was quenched with water, and the phases were separated. The aqueous phase was extracted three times with DCM (each 20 mL). The combined organic layers were washed with brine (30 mL), dried over sodium sulphate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:ethyl acetate, 4:1) to yield **S-11** (2.54 g, 6.40 mmol, 97%) as a white foam.

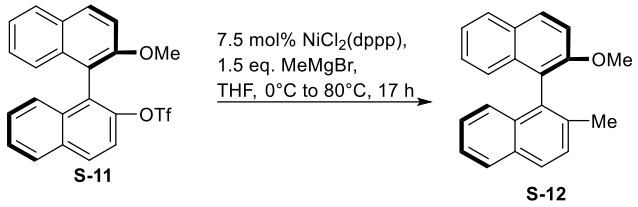
$C_{22}H_{15}F_3O_4S$, MW: 432.41 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 8.10-8.04 (*m*, 2H, Ar-*H*), 7.99 (*d*, *J* = 6.4 Hz, 1H, Ar-*H*),7.91 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.61-7.53 (*m*, 2H, Ar-*H*), 7.48 (*d*, *J* = 8.1 Hz, 1H, Ar-*H*), 7.36 (*m*, 3H, Ar-*H*), 7.22-7.26 (*m*, 1H, Ar-*H*), 6.03 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 3.81 (*s,* 3H, R-O-C*H*$_3$) ppm.

The analytical data for **S-11** agrees with the literature. [21]

2.3.10 Synthesis of Dichloro(1,3-bis(diphenylphosphino)propane)nickel(II) ($NiCl_2$(dppp)) [19]

According to a modified literature procedure,[22] nickel(II) chloride hexahydrate (1.0 g, 4.21 mmol, 1.0 eq.) was dissolved in dry ethanol (5 mL/mmol) at room temperature. 1,3-Bis(diphenylphosphino)propane (dppp) (1.7 g, 4.21 mmol, 1.0 eq.) was then added to the solution, and the mixture was stirred for 4 hours. The resulting red precipitate was collected by filtration and washed with cold ethanol (0 °C, 2 × 10 mL). The solid was dried under high vacuum for 24 hours and used in the subsequent step without further purification or characterization.

2.3.11 Synthesis of (*R*)-2-Methoxy-2´-methyl-1,1´-binaphthyl (S-12) [20]



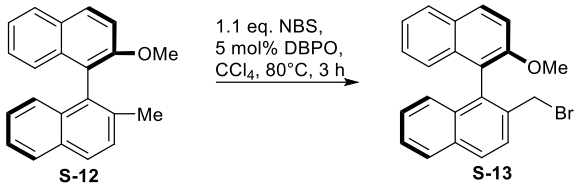
S-11 **S-12**

The Kumada coupling was performed according to a literature procedure.[23] $NiCl_2$(dppp) (238.8 mg, 0.44 mmol, 7.5 mol%) and (*R*)-(1-(2-Methoxy-1-naphthyl)-2-naphthyl)-trifluoromethansulfonic acid **S-11** (2.5 g, 5.87 mmol, 1.0 eq.) was added in a round bottom flask (100 ml) under nitrogen atmosphere. Dry THF (5ml/mol) was added, and the resulting mixture was cooled to 0 °C. Methyl magnesium bromide (3 M in Diethyl ether, 2.94 mL, 8.81 mmol, 1.5 eq.) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 5 min and for 20 h at 80 °C. After cooling to room temperature, the reaction was quenched with demineralized water (50 mL). The aqueous layer was extracted with DCM (3 × 30 mL), and the combined organic layers were sequentially washed with 1 M hydrochloric acid (80 mL) and saturated sodium bicarbonate solution (80 mL), then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:ethyl acetate, 50:1) to give pure product **S-12** (1.52g, 5.09 mmol, 89%) as a white foam.

$C_{22}H_{18}O$, MW: 298.39 g/mol.**^{1}H- NMR (400 MHz, $CDCl_3$):** δ= 7.98 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*),7.91-7.85 (*m*, 3H, Ar-*H*), 7.54-7.50 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.49-7.44 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.42-7.31 (*m*, 2H, Ar-*H*), 7.24-7.17 (*m*, 2H, Ar-*H*), 7.14 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.01 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 3.78 (*s,* 3H, R-O-C*H*$_3$), 2.11 (*s,* 3H, -C*H*$_3$)ppm.

The analytical data for **S-12** agrees with the literature.[23]

2.3.12 Synthesis of (*R*)-2-(Bromomethyl)-2´-methoxy-1,1´-binaphthyl (S-13) [21]



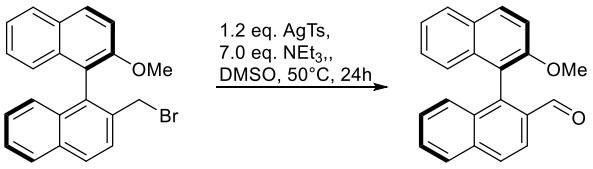
S-12 S-13

The bromination of compound **S-13** was performed according to literature procedure.[24] **S-12** (1.52 g, 5.09 mmol, 1.0 eq.), crystallized NBS (0.91 g, 5.09 mmol, 1.0 eq.) and DBPO (61.70 mg, 0.25 mmol, 5 mol%) was added to a round bottom flask (100 ml) under nitrogen atmosphere. Dry tetrachloromethane (CCl_4) was added to the flask (5 mL/mmol) and the reaction mixture was stirred at 80 °C for 3-6 h (until the reaction complete). After completion, the reaction mixture was cooled down to room temperature and diluted with demineralized water (20 mL). The phases were separated, and the aqueous phase was extracted three times with DCM (each 20 mL), dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:EE, 20:1) to give **S-13** (1.67g, 4.42 mmol, 87%) as a white foam.

$C_{22}H_{17}BrO$, MW: 377.28 g/mol **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.95 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*),7.88 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*),7.84-7.76(*m*, 2H, Ar-*H*), 7.65 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.38(*m*, 2H, Ar-*H*), 7.28-7.21 (*m*, 1H, Ar-*H*), 7.17-7.11 (*m*, 2H, Ar-*H*), 7.01 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 6.89 (*d*, *J* = 8.6 Hz, 1H, Ar-*H*), 4.29-4.17(*q*, 2H, Ar-CH_2-Br) 3.70 (*s,* 3H, R-O-CH_3) ppm.

The analytical data for **S-13** agrees with the literature.[24]

2.3.13 Synthesis of (*R*)-2-Formyl-2´-methoxy-1,1´-binaphthyl (S-14) [22]



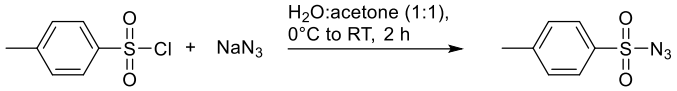
S-13 S-14

The synthesis of aldehyde **S-14** was performed according to a literature procedure [25] The bromide **S-13** (2.00 g, 5.3 mmol, 1.0 eq), silver tosylate (AgTs) (1.77 g, 6.36 mmol, 1.2 eq), and triethylamine (5.65 ml, 40.81 mmol, 7.7 eq) were dissolved in DMSO (5 mL/mmol) and the reaction mixture was stirred at 50 °C for 24 hours. Upon completion, the reaction was cooled to room temperature, and demineralized water (20 mL) was added. The resulting mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with saturated aqueous sodium thiosulfate solution (2 × 50 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified through column chromatography (PE:ethyl acetate, 10:1), yielding product **S-14** (1.27 g, 4.02 mmol, 79%) as a white solid.

$C_{22}H_{16}O_2$, MW: 312.37 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** *δ* = 9.68 (*s*, 1H, Ar-C*H*O), 8.16 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 8.07 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 8.02 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.96 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.90 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.62-7.56 (*m*, 1H, Ar-*H*), 7.49-7.44 (*m*, 1H, Ar-*H*), 7.38-7.28 (*m*, 3H, Ar-*H*), 7.24-7.17 (*m*, 1H, Ar-*H*), 6.96 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 3.77 (*s*, 3H, Ar-O-CH_3) ppm.

The analytical data for **S-14** agrees with the literature. [25]

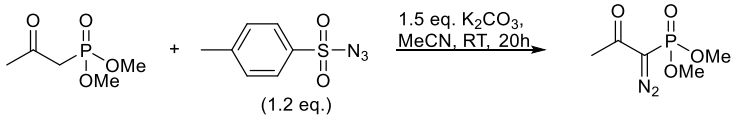
2.3.14 Synthesis of Tosyl azide (⚠ *Caution: Potentially explosive*) (S-16) [23]



S-15 S-16

Tosyl azide **S-16** was synthesized according to a reported procedure. [26] Tosyl chloride **S-15** (4.00 g, 21.05 mmol, 1.0 eq.) was dissolved in water:acetone (1:1, 5 mL/mmol) and cooled to 0 °C. To the chilled solution, sodium azide (1.37 g, 21.05 mmol, 1.0 eq.) was added and the reaction mixture was stirred at room temperature for 2 h. Upon completion, acetone was removed under reduced pressure, and the aqueous phase was extracted with DCM (3 × 30 mL). The combined organic layers were dried over anhydrous magnesium sulphate and concentrated under reduced pressure. The resulting tosyl azide **S-16** was obtained as a white solid (4.15 g, 21.05 mmol, 99%) and was used in the subsequent step without further purification.

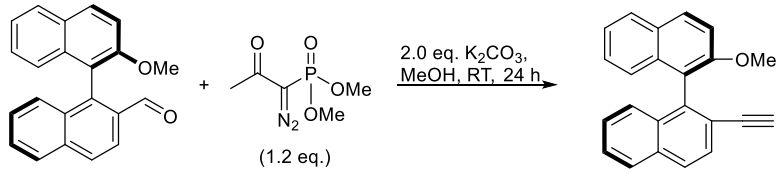
2.3.15 Synthesis of Dimethyl-(1-diazo-2-oxopropyl)-phosphonate (S-17) [24]



S-16 S-17

According to a slightly modified literature procedure, [27] tosyl azide **S-16** (⚠ Caution: potentially explosive, 2.84 g, 14.45 mmol, 1.2 eq.) and potassium carbonate (2.49 g, 18.07 mmol, 1.5 eq.) were suspended in dry acetonitrile (3 mL/mmol) under nitrogen atmosphere. To this suspension, dimethyl (2-oxopropyl) phosphonate (2.0 ml, 12.04 mmol, 1.0 eq.) was added dropwise. The reaction mixture was stirred at room temperature for 20 h. After completion, the resulting solid was filtered off and washed twice with DCM (2 × 10 mL). The combined organic phases were concentrated under reduced pressure. The crude residue was purified by flash chromatography (ethyl acetate as eluent) to afford the Bestmann-Ohira reagent **S-17** as a yellow liquid (2.1 g, 10.08 mmol, 90%).
$C_5H_9N_2O_4P$, MW: 192.11 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 3.84 (*s*, 3H, P-O-C*H*$_3$), 3.81 (*s*, 3H, P-O-C*H*$_3$), 2.23 (*s*, 3H, C-C*H*$_3$). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = 14.61-13.97 (*m*) ppm.
The analytical data for **S-17** agrees with the literature. [27]

2.3.16 Synthesis of (*R*)-2-Ethynyl-2´-methoxy-1,1´-binaphthyl (S-18) [25]



S-14 S-17 S-18

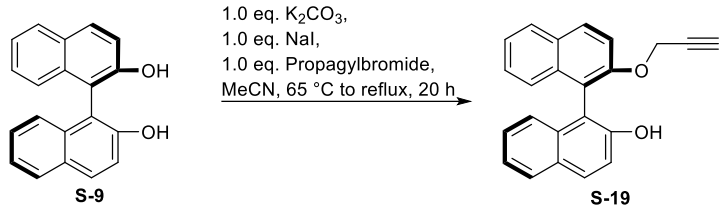
The synthesis of the alkyne **S-18** was carried out following a literature-reported procedure. [16] To a round-bottom flask (50 mL) under a nitrogen atmosphere, aldehyde **S-14** (400.0 mg, 1.28 mmol, 1.0 eq.), and potassium carbonate (359.9 mg, 2.56 mmol, 2.0 eq.) were added. Dry methanol (8 mL/mmol) was added to the round-bottom flask, maintaining a nitrogen atmosphere. Subsequently, the Bestmann-Ohira reagent **S-17** (295.2 mg, 245 µl, 1.53 mmol, 1.2 eq.) was added, and the reaction mixture was stirred at room temperature for 24 h. After completion, the reaction was diluted with diethyl ether (10 mL) and demineralized water (10 mL). The phases were separated, and the aqueous phase was extracted with diethyl ether (3 x 25 mL). The combined organic layers were dried over

anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (PE: DCM, 3:1) to give product **S-18** (367.3mg, 1.19 mmol, 93%) as a white solid.

$C_{23}H_{16}O$, MW: 308.38 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.02 (*d*, *J* = 9.1 Hz, 1H, *Ar-H*), 7.95-7.85 (*m*, 3H, Ar-*H*), 7.73 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.50-7.41 (*m*, 2H, Ar-*H*), 7.37-7.18 (*m*, 4H, Ar-*H*), 7.05 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 3.81 (*s*, 3H, Ar-O-CH_3), 2.77 (*s*, 1H, Ar-CC*H*) ppm.

The analytical data for **S-18** agrees with the literature. [28]

2.3.17 Synthesis of (*R*)-2'-(Prop-2-yn-1-yloxy)-[1,1´-binaphthalene]-2-ol (S-19) [26]

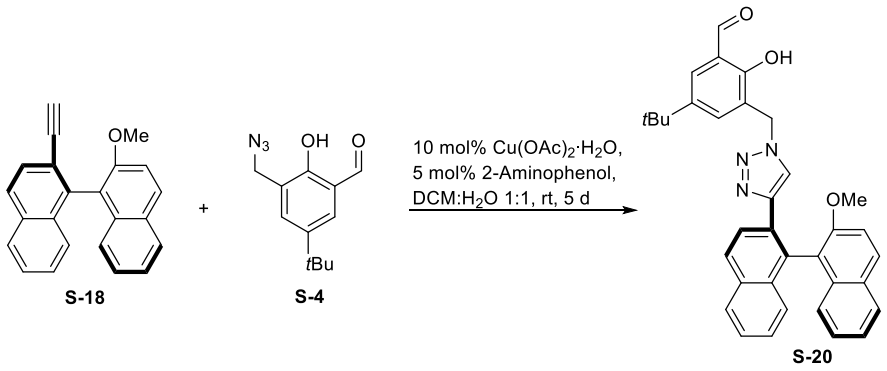


The synthesis of corresponding alkyne **S-19** was performed according to the literature procedure. [17] (*R*)-1,1´-Bi-2-naphthol **S-9** (500.0 mg, 1.74 mmol, 1.0 eq.), potassium carbonate (241.4 mg, 1.74 mmol, 1.0 eq.) and sodium iodide (261.7 mg, 1.74 mmol, 1.0 eq.) were dissolved in dry acetonitrile (20 mL/mmol) under nitrogen atmosphere. Propargyl bromide (188.1 µL, 1.74 mmol, 1.0 eq.) was added dropwise to the reaction mixture and stirred at 65 C for 2 hours, then heated to reflux for an additional 18 hours. After cooling down to room temperature, the precipitated solid was filtered off and washed three times with DCM (each 25 mL). After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography using DCM to get the pure product **S-19** as orange oil (446.6 mg, 1.36 mmol, 79%).

$C_{23}H_{16}O_2$, MW: 328.37 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.08 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.99-7.90 (*m*, 2H, Ar-*H*), 7.87 (*d*, *J* = 8.3 Hz, 1H, Ar-*H*), 7.60 (*d*, *J* = 9.2 Hz, 1H, Ar-*H*), 7.46-7.28 (*m*, 4H, Ar-*H*), 7.25-7.11 (*m*, 2H, Ar-*H*), 7.10 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 4.98 (*s*, 1H, Ar-O*H*), 4.73-4.58 (*m*, 2H, Ar-O-CH_2-C), 2.40 (*t*, *J* = 2.2 Hz, 1H, CC*H*) ppm.

The analytical data for **S-19** agrees with the literature. [29]

2.3.18 Synthesis of (*R*)-5-*tert*-Butyl-2-hydroxy-3-((4-(1-(2-hydroxy-1-naphthyl)-2-naphthyl)-1*H*-1,2,3-triazol-1-yl)-methyl)-benzaldehyde (S-20) [15, 27]



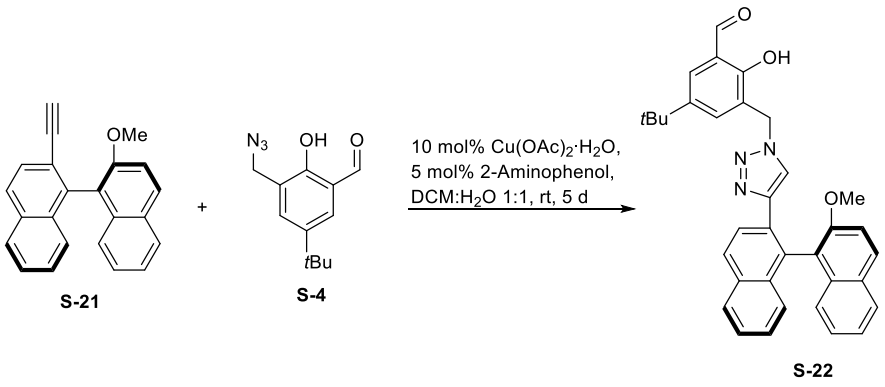
The synthesis of **S-20** was performed according to **GP 2**. For that 3-(Azidomethyl-5-(*tert*-butyl)-2-hydroxybenzaldehyd **S-4** (227.1 mg, 0.97 mmol, 1.0 eq.), (*R*)-2-Ethinyl-2′-hydroxy-1,1′-binaphthyl **S-18** (300 mg, 0.97 mmol, 1.0 eq.), copper (II)acetate monohydrate (19.4 mg, 0.097 mmol, 10 mol%) and 2-Aminophenol

(5.31 mg, 0.048 mmol, 5 mol%) were used. Purification was done by column chromatography (PE: ethyl acetate, 4:1) and product **S-20** was isolated as a yellowish solid (480.6 mg, 0.88 mmol, 90%).

$C_{35}H_{31}N_3O_3$, MW: 541.65 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.76 (*s*, 1H, Ar-O*H*), 9.92 (*s*, 1H, Ar-C*H*O), 8.61 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 8.04 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.96 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.91 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.81 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.48 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.46-7.42 (*td*, 2H, Ar-*H*), 7.32 (*d*, *J* = 2.3 Hz, 1H, Ar-*H*), 7.28 (*d*, *J* = 2.0 Hz, 1H, Ar-*H*), 7.25-7.15 (*m*, 2H, Ar-*H*), 7.05 (*t*, *J* = 7.6 Hz, 1H, Ar-*H*), 6.96 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 6.13 (*s*, 1H, N-C*H*), 5.19 (*dd*, *J* = 14.6, 18.5 Hz, 2H, N-CH_2-C), 3.52 (*s*, 3H, Ar-OCH_3), 1.23 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-20** agrees with the literature. [30]

2.3.19 Synthesis of (*S*)-5-*tert*-Butyl-2-hydroxy-3-((4-(1-(2-hydroxy-1-naphthyl)-2-naphthyl)-1H-1,2,3-triazol-1-yl)-methyl)-benzaldehyde (S-22) [15, 30]

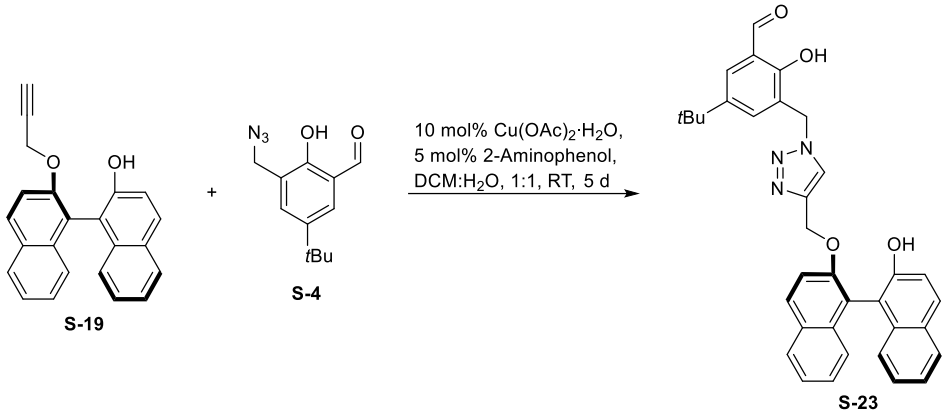


The synthesis of **S-22** was performed according to the general procedure **GP 2**. For that 3-(Azidomethyl-5-(*tert*-butyl)-2-hydroxybenzaldehyd **S-4** (75.71mg, 0.32 mmol, 1.0 eq.), (*S*)-2-Ethinyl-2′-hydroxy-1,1′-binaphthyl **S-21** (100 mg, 0.32 mmol, 1.0 eq.), copper (II)acetate monohydrate (6.48 mg, 0.032 mmol, 10 mol%) and 2-Aminophenol (1.77 mg, 0.016 mmol, 5 mol%) were used. Purification was done by column chromatography (PE:ethyl acetate, 4:1) and product **S-22** was isolated as yellowish solid (152.7 mg, 0.28 mmol, 84%).

$C_{35}H_{31}N_3O_3$, MW: 541.65 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.67 (*s*, 1H, Ar-O*H*), 9.79 (*s*, 1H, Ar-C*H*O), 8.64 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 8.02 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.90 (*d*, *J* = 8.7 Hz, 1H, Ar-*H*), 7.81 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.77 (*d*, *J* = 8.1 Hz, 1H, Ar-*H*), 7.42 (*t*, *J* = 7.6 Hz, 2H, Ar-*H*), 7.39 (*d*, *J* = 2.3 Hz, 1H, Ar-*H*), 7.33 (*d*, *J* = 1.9 Hz, 1H, Ar-*H*), 7.20 (*m*, 1H, Ar-*H*), 7.15 (*d*, *J* = 9.1 Hz, 1H, Ar-*H*), 7.07 (*t*, *J* = 7.6 Hz, 1H, Ar-*H*), 6.89 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 6.10 (*s*, 1H, N-C*H*), 5.18 (*dd*, *J* = 14.5, 18.6 Hz, 2H, N-CH_2-C), 3.50 (*s*, 3H, Ar-OCH_3), 1.21 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-22** agrees with the literature. [30]

2.3.20 Synthesis of (*R*)-5-(*tert*-Butyl)-2-hydroxy-3-((4-(((2´-hydroxy-(1,1´-binaphthalene)-2-yl)-oxy)-methyl)-1*H*-1,2,3-triazol-1-yl)-methyl-benzaldehyde (S-23) [15, 30]

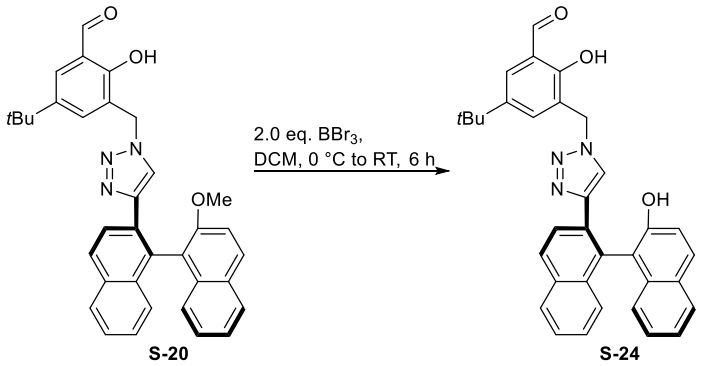


The synthesis of **S-23** was performed according to the general procedure **GP 2**. For that 3-(azidomethyl-5-(*tert*-butyl)-2-hydroxybenzaldehyd **S-4** (75.16 mg, 0.32 mmol, 1.0 eq.), (*R*)-2-hydroxy-2′-propargyloxy-1,1′-binaphthyl **S-19** (100 mg, 0.32 mmol, 1.0 eq.), copper(II)acetate monohydrate (6.43 mg, 0.097 mmol, 10 mol%) and 2-aminophenol (1.76 mg, 0.016 mmol, 5 mol%) were used. Purification was done by column chromatography (PE: ethyl acetate, 4:1), and product **S-23** was isolated as a brown solid (164.40 mg, 0.29 mmol, 91%).

$C_{35}H_{31}N_3O_4$, MW: 557.65 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 11.21 (*s*, 1H, Ar-O*H*), 9.91 (*s*, 1H, Ar-C*H*O), 8.07 (*d*, *J* = 8.6 Hz, 1H, Ar-*H*), 7.97-7.88 (*m*, 3H, 2-Ar-C*H*, 1-C=C*H*-N), 7.58-7.52 (*m*, 2H, Ar-*H*), 7.49 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 7.47-7.38 (*m*, 1H, Ar-*H*), 7.34-7.26 (*m*, 3H, Ar-*H*), 7.18 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.17-7.11 (*m*, 1H, Ar-*H*), 7.08-6.98 (*m*, 2H, Ar-*H*), 5.44-5.36 (*m*, 2H, Ar-CH_2-N), 5.26 (*br*, 1H, Ar-O*H*), 5.26-5.13 (*dd*, *J* = 13.5, 21.0 Hz, 2H, Ar-O-CH_2-C), 1.26 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-23** agrees with the literature.[30]

2.3.21 Synthesis of (*R*)-(5-*tert*-Butyl-2-hydroxy-3-((4-(1-(2-hydroxy-1-naphthyl)-2-naphthyl)-triazol-1-yl)-methyl)-benzaldehyde (S-24) [16, 30]



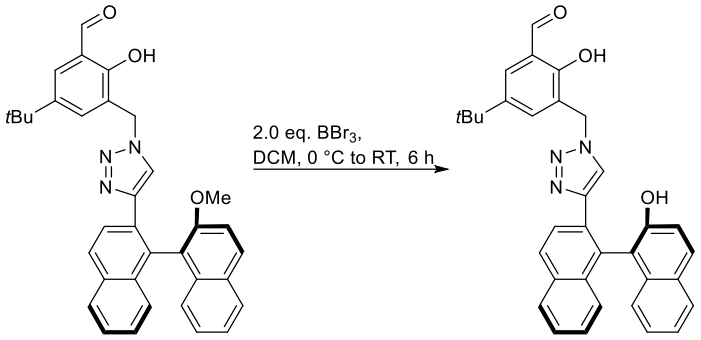
The deprotection of the methyl group of the aldehyde **S-24** was performed according to **GP 3**. For that, the aldehyde **S-20** (150.0 mg, 0.27 mmol, 1.0 eq.) and boron tribromide solution (553.8 µL, 0.55 mmol, 2.0 eq., 1 M in DCM) were used. Purification was done by column chromatography (PE: ethyl acetate, 4:1), and product **S-24** was isolated as a colorless solid (134.7 mg, 0.25 mmol, 92%).

$C_{34}H_{29}N_3O_3$, MW: 527.62 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.61 (*s*, 1H, Ar-O*H*), 9.88 (*s*, 1H, Ar-C*H*O), 8.67 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 8.10 (*d*, *J* = 8.7 Hz, 1H, Ar-*H*), 7.91 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.90 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.84 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.43 (*t*, *J* = 7.5 Hz, 2H, Ar-*H*), 7.41 (*d*, *J* = 2.2 Hz, 1H, Ar-*H*), 7.31 (*d*, *J* = 2.1 Hz, 1H, Ar-*H*), 7.22 (*m*, 2H, Ar-*H*), 7.16 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.05 (*t*, *J* = 7.5 Hz, 1H, Ar-*H*), 6.86 (*d*,

J = 8.4 Hz, 1H, Ar-*H*), 6.23 (*s*, 1H, N-C*H*), 5.14 (*dd*, *J* = 14.5, 18.7 Hz, 2H, N-CH_2-C), 4.80-4.60 (*br*, 1H, Ar-O*H*), 1.04 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-24** agrees with the literature.[30]

2.3.22 Synthesis of (*S*)-(5-tert-Butyl-2-hydroxy-3-((4-(1-(2-hydroxy-1-naphthyl)-2-naphthyl)-triazol-1-yl)-methyl)-benzaldehyde (S-25) [16, 30]



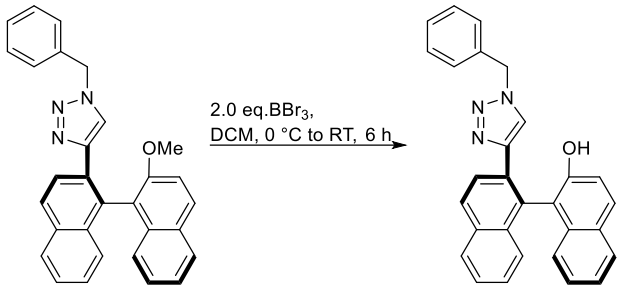
S-22 **S-25**

The deprotection of the methyl group from aldehyde **S-25** was performed according to the general procedure **GP 3**. For this, the aldehyde **S-22** (50.0 mg, 0.092 mmol, 1.0 eq.) and boron tribromide solution (184 µL, 0.18 mmol, 2.0 eq., 1 M in DCM) were used. Purification was carried out by column chromatography (PE:EE, 4:1), and product **S-25** was isolated as a colorless solid (47.4 mg, 0.089 mmol, 97%).

$C_{34}H_{29}N_3O_3$, MW: 527.62 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.60 (*s*, 1H, Ar-O*H*), 9.88 (*s*, 1H, Ar-C*H*O), 8.68 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 8.11 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.91 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.89 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.84 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.44 (*t*, *J* = 7.6 Hz, 2H, Ar-*H*), 7.41 (*d*, *J* = 2.1 Hz, 1H, Ar-*H*), 7.34 (*d*, *J* = 2.0 Hz, 1H, Ar-*H*), 7.22 (*m*, 2H, Ar-*H*), 7.17 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.05 (*t*, *J* = 7.6 Hz, 1H, Ar-*H*), 6.86 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 6.17 (*s*, 1H, N-C*H*), 5.14 (*dd*, *J* = 14.5, 18.7 Hz, 2H, N-CH_2-C), 4.82-4.61 (*br*, 1H, Ar-O*H*), 1.09 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

The analytical data for **S-25** agrees with the literature.[30]

2.3.23 Synthesis of (*R*)-2'-(1-Benzyl-1H-1,2,3-triazol-4-yl) -(1,1'-binaphthalene)-2-ol (S-27) [16, 30]



S-26 **S-27**

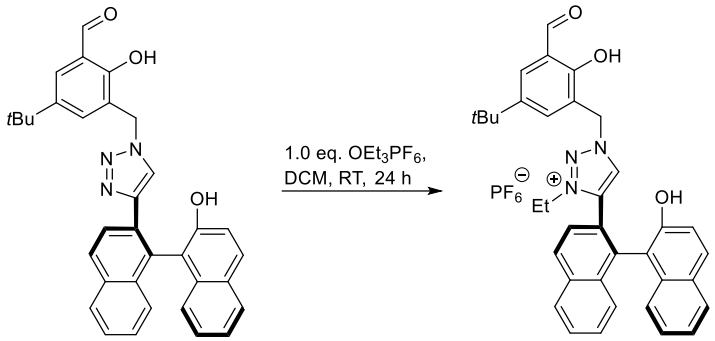
The deprotection of the methyl group of aldehyde **S-27** was performed according to the general procedure **GP 3**. For that, the aldehyde **S-26** (30.0 mg, 0.067 mmol, 1.0 eq.) and boron tribromide solution (135.8 µL, 0.13 mmol, 2.0 eq., 1 M in DCM) were used. Purification was done by column chromatography (PE: ethyl acetate, 4:1), and product **S-27** was isolated as a colorless solid (28.8 mg, 0.067 mmol, 99%).

$C_{29}H_{21}N_3O$, MW: 427.20 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.64 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 8.11 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.96 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.79 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.50 (*m*, 1H, Ar-*H*), 7.37-

7.26 (*m*, 5H, Ar-*H*), 7.24-7.10 (*m*, 4H, Ar-*H*), 6.97 (*d*, *J* = 8.6 Hz, 1H, Ar-*H*), 6.84-6.78 (*m*, 2H, Ar-*H*), 5.94 (*s*, 1H, C=C*H*-N), 5.20 (*s*, 2H, Ar-CH_2), 4.79 (*br*, 1H, Ar-O*H*) ppm.

The analytical data for **S-27** agrees with the literature.[30]

2.3.24 Synthesis of (*R*)-5-*tert*-Butyl-3-((3-ethyl-4-(1-(2-hydroxy-1-naphthyl)-2-naphthyl)-triazol-3-ium-1-yl)-methyl)-2-hydroxy-benzaldehyde hexafluorophosphate (S-28) [15, 30]



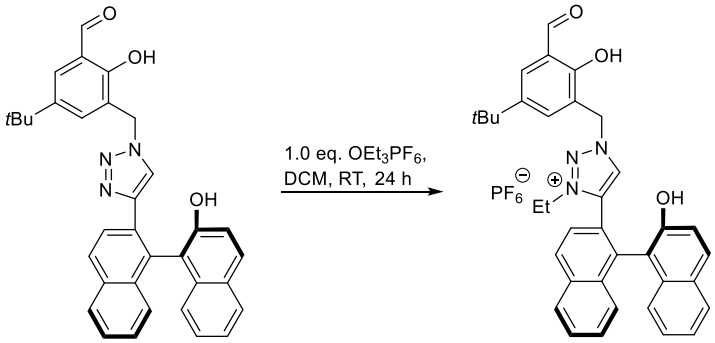
S-20 **S-28**

The alkylation of the triazole **S-20** was performed according to the general procedure **GP 4**. For that, triazole **S-20** (100.0 mg, 0.189 mmol, 1.0 eq.) and triethyloxonium hexafluorophosphate (47.0 mg, 0.0189 mmol, 1.0 eq.) were used. After precipitation, the alkylated triazolium **S-28** (127.3 mg, 0.18 mmol, 96%) was isolated as a white solid.

$C_{36}H_{34}F_6N_3O_3P$, MW: 701.65 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.72 (*s*, 1H, Ar-O*H*), 9.90 (*s*, 1H, Ar-C*H*O), 8.10 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.99 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.72 (*m*, 3H, Ar-*H*), 7.62 (*m*, 4H, Ar-*H*, C-C*H*-N), 7.37 (*m*, 2H, Ar-*H*), 7.24 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.17 (*m*, 2H, Ar-*H*), 6.84 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 6.26-5.75 (*br*, 1H, Ar-O*H*), 5.49 (*s*, 2H, Ar-CH_2-N), 4.29 (*m*, 1H, N-CH_2-CH_3), 4.17 (*m*, 1H, N-CH_2-CH_3), 1.33 (*s*, 9H, Ar-C(CH_3)$_3$), 1.31 (*t*, *J* = 7.0 Hz, 3H, N-CH_2-CH_3). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -73.5, -71.6 (*d*, *J* = 713.6 Hz, PF_6^-). **^{31}P-NMR (376 MHz, $CDCl_3$):** δ = -157.6 to -131.2 (*sept*, *J* = 712.7 Hz, *P*F_6^-) ppm.

The analytical data for **S-28** agrees with the literature.[30]

2.3.25 Synthesis of (*S*)-5-*tert*-Butyl-3-((3-ethyl-4-(1-(2-hydroxy-1-naphthyl)-2-naphthyl)-triazol-3-ium-1-yl)-methyl)-2-hydroxy-benzaldehyde hexafluorophosphate (S-29) [15, 30]



S-21 **S-29**

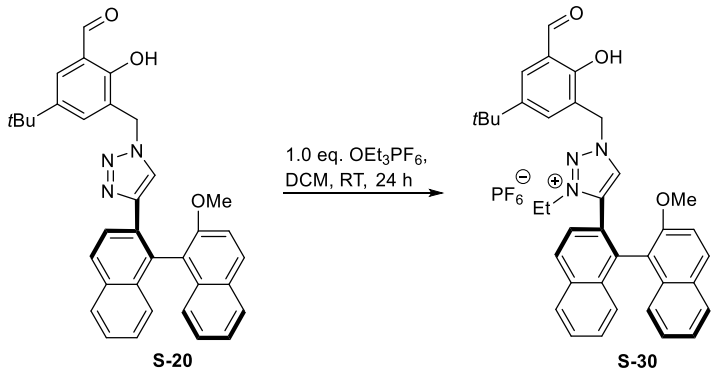
The alkylation of triazole **S-21** was performed according to the general procedure **GP 4**. For that, triazole **S-21** (50.0 mg, 0.094 mmol, 1.0 eq.) and triethyloxonium hexafluorophosphate (23.5 mg, 0.094 mmol, 1.0 eq.) were used. After precipitation, the alkylated triazolium **S-29** (66.3 mg, 0.094 mmol, 99%) was isolated as a white solid.

$C_{36}H_{34}F_6N_3O_3P$, MW: 701.65 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 10.74 (*s*, 1H, Ar-O*H*), 9.89 (*s*, 1H, Ar-C*H*O), 8.10 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.98 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.72 (*m*, 3H, Ar-*H*), 7.63 (*m*, 4H, Ar-*H*, C-

C*H*-N), 7.36 (*m*, 2H, Ar-*H*), 7.24 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.17 (*m*, 2H, Ar-*H*), 6.83 (*d*, *J* = 8.3 Hz, 1H, Ar-*H*), 6.28-5.73 (*br*, 1H, Ar-O*H*), 5.51 (*s*, 2H, Ar-CH_2-N), 4.27 (*m*, 1H, N-CH_2-CH_3), 4.16 (*m*, 1H, N-CH_2-CH_3), 1.34 (*s*, 9H, Ar-C(CH_3)$_3$), 1.29 (*t*, *J* = 7.1 Hz, 3H, N-CH_2-CH_3). **^{19}F-NMR (376 MHz, CDCl$_3$):** δ = -73.4, -71.6 (*d*, *J* = 713.2 Hz, PF_6^-). **^{31}P-NMR (376 MHz, CDCl$_3$):** δ = -157.6 to -131.4 (*sept*, *J* = 712.7 Hz, PF_6^-) ppm.

The analytical data for **S-29** agrees with the literature.[30]

2.3.26 Synthesis of (*R*)-5-*tert*-Butyl-3-((3-ethyl-4-(-1-(2-methoxy-1-naphthyl)-2-naphthyl)-triazol-3-ium-1-yl)-methyl)-2-hydroxy-benzaldehyde hexafluorophosphate(S-30) [15, 30]

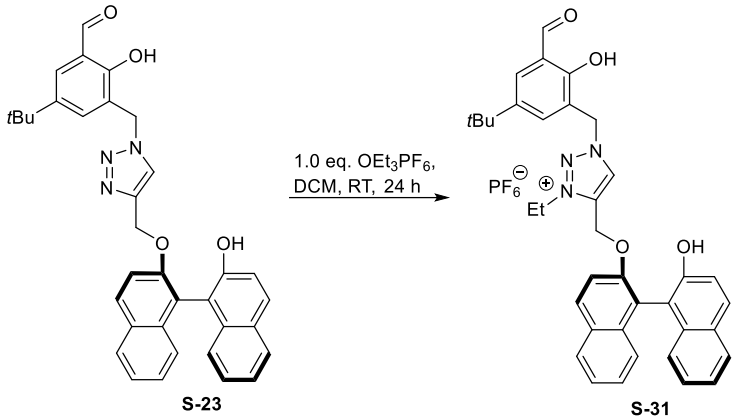


The alkylation of the triazole **S-20** was performed according to the general procedure **GP 4**. For that, triazole **S-20 (**25.0 mg, 0.046 mmol, 1.0 eq.) and triethyloxonium hexafluorophosphate (11.45 mg, 0.046 mmol, 1.0 eq.) were used. After precipitation, the alkylated triazolium **S-30** (31.6 mg, 0.045 mmol, 98%) was isolated as a white solid.

$C_{37}H_{36}F_6N_3O_3P$, MW: 715.68 g/mol. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ =10.58 (*s*, 1H, Ar-O*H*), 9.97 (*s*, 1H, Ar-C*H*O), 8.15 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 8.04 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.84 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.82-7.72 (*m*, 3H, Ar-*H*), 7.72 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.66-7.59 (*m*, 2H, Ar-*H*), 7.41-7.29 (*m*, 2H, Ar-*H*), 7.26-7.15 (*m*, 3H, C-C*H*-N), 6.87 (*d*, *J* = 8.6 Hz, 1H, Ar-*H*), 5.60-5.42 (*dd*, *J* = 14.5, 68.0 Hz, 2H, N-CH_2-C), 4.34-4.25 (*m*, 2H, N-CH_2-CH_3), 3.62 (*s*, 3H, Ar-O-CH_3), 1.45 (*t*, *J* = 7.4 Hz, 3H, N-CH_2-CH_3), 1.32 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, CDCl$_3$):** δ = -74.8, -72.9 (*d*, *J* = 712.4 Hz, PF_6^-). **^{31}P-NMR (162 MHz, CDCl$_3$):** δ = -159.9 to -131.4 (*sept*, *J* = 712.4 Hz, PF_6^-) ppm.

The analytical data for **S-30** agrees with the literature. [30]

2.3.27 Synthesis of (*R*)-1-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-3-ethyl-4-(((2'hydroxy-(1,1´-bianphthalene)-2-yl)-oxy)-methyl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (S-31) [15, 30]



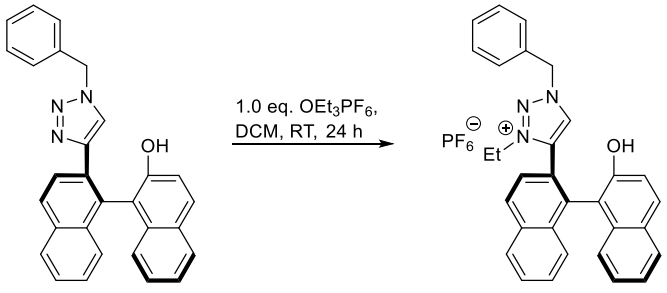
S-23 S-31

The alkylation of the triazole **S-23** was performed according to the general procedure **GP 4**. For this, triazole **S-23** (100.0 mg, 0.179 mmol, 1.0 eq.) and triethyloxonium hexafluorophosphate (44.5 mg, 0.179 mmol, 1.0 eq.) were used. After precipitation, the alkylated triazolium **S-31** (123.7 mg, 0.175 mmol 98%) was isolated as a brownish solid.

$C_{37}H_{36}F_6N_3O_4P$, MW: 731.68 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 11.40-11.0 (*br*, 1H, Ar-O*H*), 9.87 (*s*, 1H, Ar-C*H*O), 8.09 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 8.04 (*s*, 1H, C=C*H*-N), 7.92 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.89-7.81 (*m*, 2H, Ar-*H*), 7.73 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 7.65 (*d*, *J* = 2.1 Hz, 1H, Ar-*H*), 7.58 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.44 (*t*, *J* = 7.3 Hz, 1H, Ar-*H*), 7.34-7.28 (*m*, 2H, Ar-*H*), 7.25-7.15 (*m*, 3H, Ar-*H*), 6.93 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 5.60-5.50 (*m*, 2H, Ar-CH_2-N), 5.30 (*d*, *J* = 13.8 Hz, 1H, Ar-O-CH_2-C), 5.16 (*d*, *J* = 13.6 Hz, 1H, Ar-O-CH_2-C), 3.72-3.60 (*m*, 2H, N-CH_2-CH_3), 1.34 (*s*, 9H, Ar-C(CH_3)$_3$), 1.05 (*t*, *J* = 7.3 Hz, 3H, N-CH_2-CH_3) ppm. **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -73.8, -71.9 (*d*, *J* = 712.8 Hz, PF_6^-). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -153.5 to-135.8 (*sept*, *J* = 702.5 Hz, *P*F_6^-) ppm.

The analytical data for **S-31** agrees with the literature. [30]

2.3.28 Synthesis of (*R*)-1-benzyl-3-ethyl-4-(2´-hydroxy-(1,1'-binaphthalen)-2-yl)-1*H*-1,2,3-triazol-3-ium Hexafluorophosphate (S-32) [15, 30]



S-27 S-32

The alkylation of triazole **S-27** was performed according to the general procedure **GP 4**. For this, triazole **S-27** (28.00 mg, 0.06 mmol, 1.0 eq.) and triethyloxonium hexafluorophosphate (15.55 mg, 0.06 mmol, 1.0 eq.) were used. After precipitation, the alkylated triazolium **S-32** (36.09 mg, 0.06 mmol, 99%) was isolated as a brownish solid.

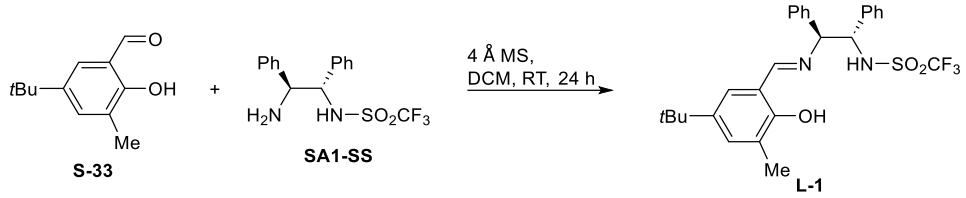
$C_{31}H_{26}F_6N_3OP$, **MW:** 601.53 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.47 (*br*, 1H, Ar-O*H*), 8.10 (*d*, *J* = 8.6 Hz, H, Ar-*H*), 7.99 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.95 (*s*, 1H, C=C*H*-N), 7.70 (*d*, *J* = 8.1 Hz, 1H, Ar-*H*), 7.68-7.57

(*m*, 3H, Ar-*H*), 7.42-7.37 (*m*, 2H, Ar-*H*), 7.36 (*t*, *J* = 7.7 Hz, 1H, Ar-*H*), 7.26 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.21 (*t*, *J* = 7.6 Hz, 2H, Ar-*H*), 7.09 (*t*, *J* = 7.6 Hz, 1H, Ar-*H*), 6.86 (*d*, *J* = 7.6 Hz, 2H, Ar-*H*), 6.75 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 5.24 (*dd*, *J* = 14.7, 19.6 Hz, 2H, N-CH_2-Ar), 4.36-4.26 (*m*, 1H, N-CH_2-CH_3), 4.10- 4.07 (*m*, 1H, N-CH_2-CH_3), 1.26 (*t*, *J* = 7.5 Hz, 3H, N-CH_2-CH_3)ppm.

The analytical data for **S-32** agrees with the literature. [30]

2.4 Ligand Synthesis

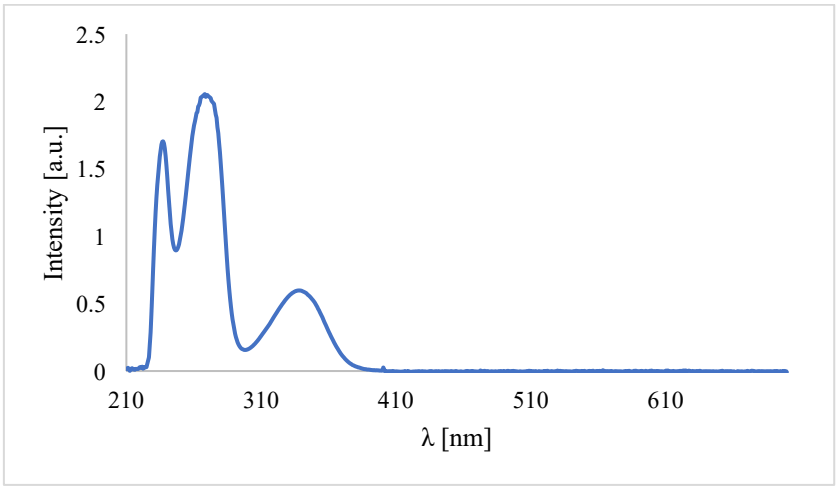
2.4.1 Synthesis of Imine N-((1*S*,2*S*)-2-((-5-(*tert*-Butyl)-2-hydroxy-3-methylbenzylidene) amino)-1,2-diphenylethyl)-1,1,1-trifluoromethanesulfonamide (L-1) [30]



Imine **L-1** was synthesized according to the general procedure **GP 5**. The aldehyde **S-33** (20 mg, 0.104 mmol, 1.0 eq.) and sulfonamide **SA1-SS** (35.81 mg, 0.104 mmol, 1.0 eq.) were used. The imine **L-1** was isolated as yellowish solid (52.19 mg, 0.100 mmol, 96.7%).

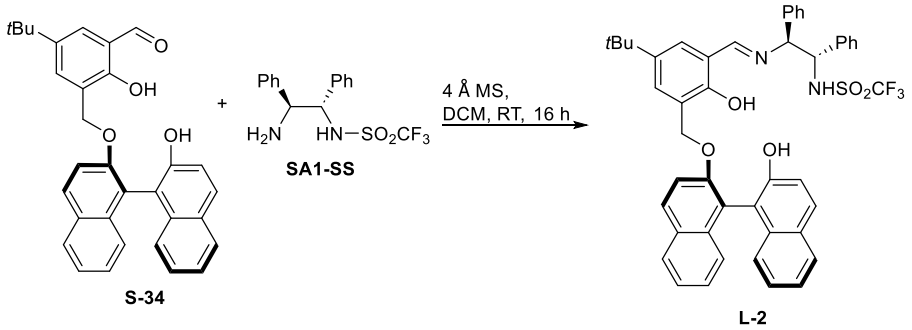
$C_{27}H_{29}F_3N_2O_3S$, MW: 518.60 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.10 (*s*, 1H, *H*C=N), 7.37-7.34 (*m*, 2H, Ar-*H*), 7.33-7.27 (*m*, 8H, Ar-*H*), 7.12-7.05 (*m*, 2H, Ar-*H*), 6.89 (*d*, *J* = 2.5 Hz, 1H, Ar-*H*), 6.02 (*br*, 1H, Ar-O*H*), 5.06 (*d*, *J* = 4.3 Hz, 1H, C*H*-N-SO_2), 4.61 (*d*, *J* = 4.4 Hz, 1H, C=N-C*H*), 2.27 (*s*, 3H, Ar-CH_3), 1.20 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (400 MHz, $CDCl_3$):** δ = -77.5 (*s*, CF_3) ppm.

UV/Vis (DCM, 2 x 10^{-4} M):



The analytical data for **L-1** agrees with the literature. [30]

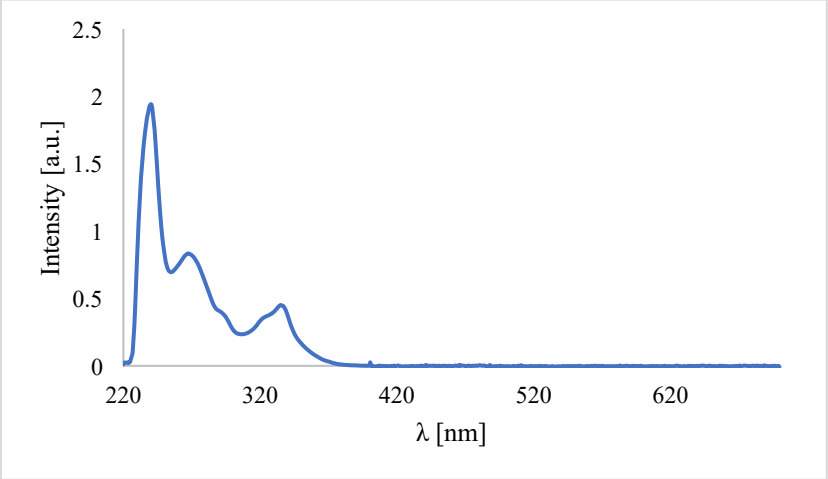
2.4.2 Synthesis of Imine N-((1*S*,2*S*)-2-((-5-(*tert*-Butyl)-2-hydroxy-3-((((*R*)-2´-hydroxy-(1,1´-binaphthalen)-2-yl)oxy)methyl)benzylidene)amino)-1,2-diphenylethyl)-1,1,1-trifluoromethanesulfonamide (L-2) [14]



Imine **L-2** was synthesized according to the general procedure **GP 5**. Therefore, aldehyde **S-34** (25.0 mg, 0.05 mmol, 1.0 eq.) and sulfonamide **SA1-SS** (18.1 mg, 0.05 mmol, 1.0 eq.) were used. The imine **L-2** was isolated as yellowish solid (41.1 mg, 0.05 mmol, 98%).

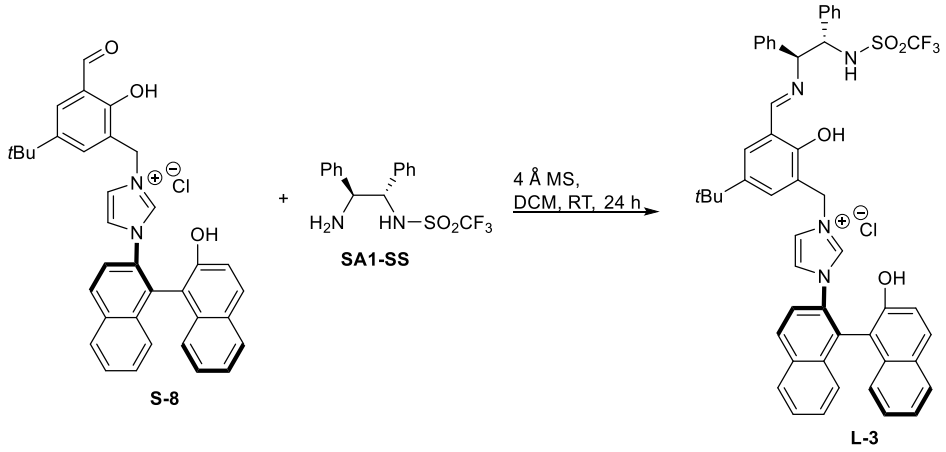
$C_{47}H_{41}F_3N_2O_4S$, MW: 802.91 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 12.67 (*br*, 1H, Ar-O*H*), 8.10 (*s*, 1H, *H*C=N), 8.06 (*d*, *J* = 9.1 Hz, 1H, Ar-*H*), 7.92 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.88 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.83 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.67 (*d*, *J* = 7.6 Hz, 1H, Ar-*H*), 7.34-7.26 (*m*, 10H, Ar-*H*), 7.25-7.10 (*m*, 4H, Ar-*H*), 7.11 (*d*, 1H, Ar-*H*), 7.08-7.04 (*m*, 2H, Ar-*H*), 6.99 (*s*, 1H, Ar-*H*), 6.90 (*s*, 1H, Ar-*H*), 5.95 (*br*, 1H, Ar-O*H*), 5.26 (*dd*, *J* = 12.8, 27.5 Hz, 2H, O-CH_2-Ar), 5.04 (*d*, *J* = 3.6 Hz, 1H, C*H*-N-SO_2), 4.65 (*d*, *J* = 3.6 Hz, 1H, C=N-C*H*), 0.97 (*s*, 9H, Ar-C(CH_3)$_3$) ppm.

UV/Vis (DCM, 2 x 10^{-4} M):



The analytical data for **L-2** agrees with the literature. [14]

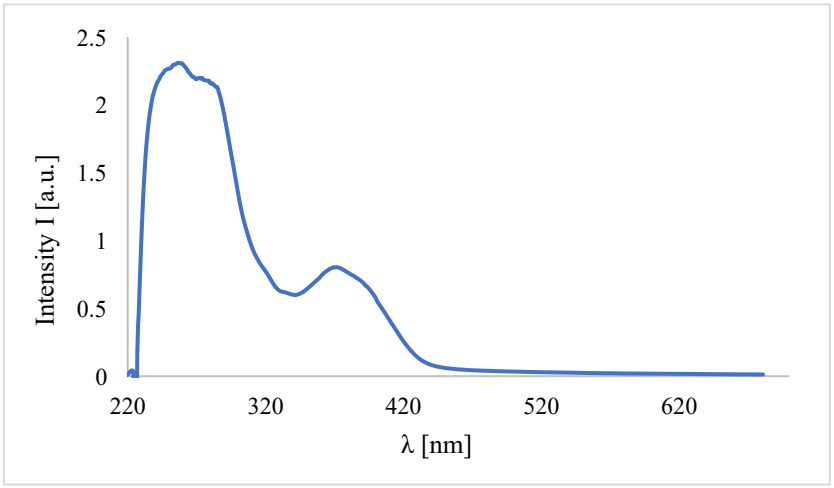
2.4.3 Synthesis of Imine 3-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-1-((*R*)-2´-hydroxy-[1,1´-binaphthalene]-2-yl)-1*H*-imidazol-3-ium chloride (L-3) [14]



Imine **L-3** was synthesized according to the general procedure **GP 5**. For that, the aldehyde **S-8** (50.0 mg, 0.088 mmol, 1.0 eq.) and sulfonamide **SA1-SS** (30.6 mg, 0.088 mmol, 1.0 eq.) were used. The imine **L-3** was isolated as a yellowish solid (78.2 mg, 0.088 mmol, 99%).

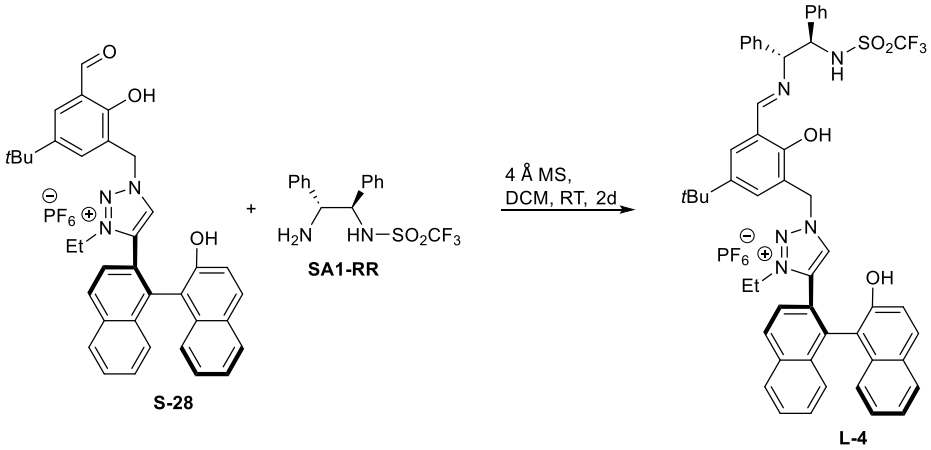
$C_{50}H_{44}ClF_3N_4O_4S$, MW: 889.43 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 14.11-14.04 (*br*, 1H, Ar-O*H*), 9.37 (*s*, 1H, C*H*N), 8.21 (*s*, 1H, Ar-*H*), 8.07 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.79 (*d*, *J* = 8.1 Hz, 1H, Ar-H), 7.85 (*s*, 1H, Ar-*H*), 7.66-7.49 (*m*, 5H, Ar-*H*), 7.43-7.29 (*m*, 5H, Ar-*H*), 7.20-7.04 (*m*, 9H, Ar-*H*), 7.02-6.96 (*m*, 2H, Ar-*H*), 6.86 (*s*, 1H, N-C*H*-N), 6.81 (*s*. 1H, N-C*H*), 6.78 (*s*, 1H, N-C*H*), 5.67 (*d*, *J* = 13.5 Hz, 1H, C*H*-N-SO2), 5.41 (*d*, *J* = 10.3 Hz, 1H, N-CH_2), 5.26 (*d*, 1H, N-CH_2), 4.93 (*d*, *J* = 9.7 Hz, 1H, CHN-C*H*), 1.17 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -78.0 (*s*, CF_3) ppm.

UV/Vis (DCM, 2 x 10^{-4} M):



The analytical data for **L-3** agrees with the literature. [14]

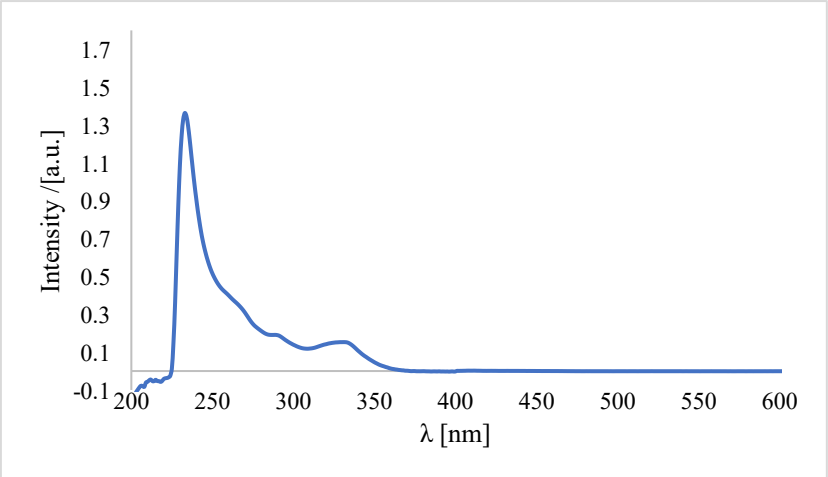
2.4.4 Synthesis of Imine 1-(5-(*tert*-Butyl)-3-(-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-((*R*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (L-4)[14, 30]



Imine **L-4** was synthesized according to the general procedure **GP 5**. Therefore, the aldehyde **S-28** (50.0 mg, 0.071 mmol, 1.0 eq.) and sulfonamide **SA1-RR** (25.7 mg, 0.074 mmol, 1.05 eq.) were used. The imine **L-4** was isolated as yellow solid (59.7 mg, 0.058 mmol, 95%).

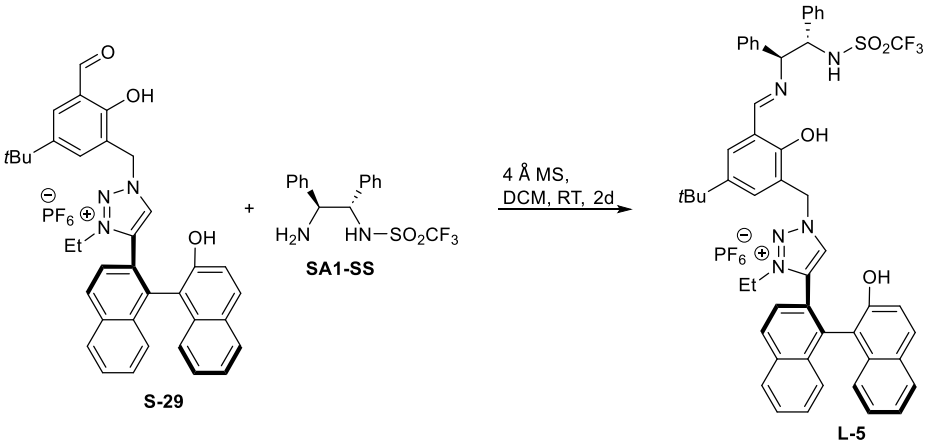
$C_{51}H_{47}F_9N_5O_4PS$, MW: 1027.98 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 13.58 (*br*, 1H, Ar-O*H*), 8.50 (*s*, 1H, Ar-*H*), 8.09 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.89 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.59 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 7.56-7.45 (*m*, 3H, Ar-*H*), 7.44 (*d*, J = 9.0 Hz, 1H, Ar-*H*), 7.38-7-17 (*m*, 6H, Ar-*H*), 7.05-6.94 (*m*, 12H, Ar-*H*), 6.68 (*d*, 1H, Ar-*H*), 5.52 (*d*, *J* = 13.9 Hz, 1H, N-CH_2-Ar), 5.30 (*d*, 1H, N-CH_2-Ar), 4.93 (*d*, *J* = 8.8 Hz, 1H, C*H*-N-SO_2), 4.47 (*d*, *J* = 9.1 Hz, 1H, C=N-C*H*), 4.34-4.04 (*m*, 2H, N-CH_2-C), 1.25 (*t*, *J* = 7.6 Hz, 3H, N-C-CH_3), 1.19 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -70.38, -72.28 (*d*, *J* = 714.4 Hz, PF_6^-), -77.78 (*s*, CF_3). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -130.7 to -157.3 (*sept*, *J* = 719.9 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data **L-4** agrees with the literature. [30]

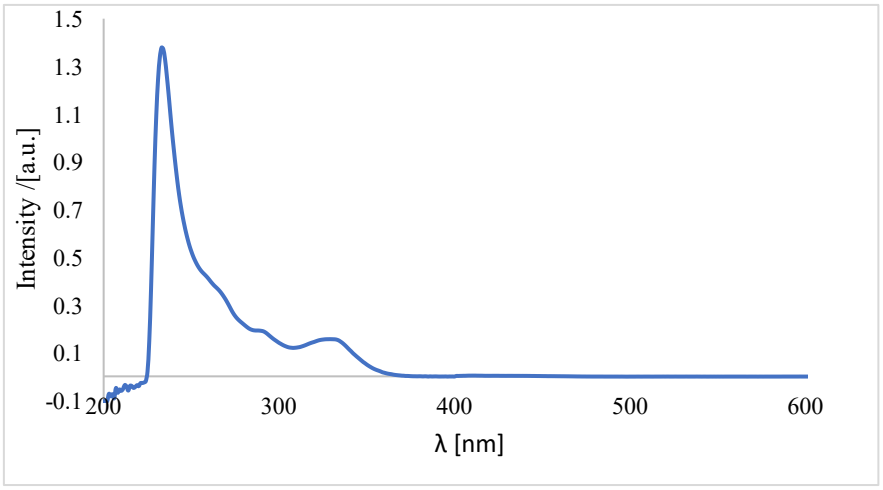
2.4.5 Synthesis of Imine 1-(5-(tert-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-((*R*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium hexafluorophosphate (L-5)[14, 30]



Imine **L-5** was synthesized according to the general procedure **GP 5**. Therefore, the aldehyde **S-29** (50.0 mg, 0.071 mmol, 1.0 eq.) and sulfonamide **SA1-SS** (25.7 mg, 0.074 mmol, 1.05 eq.) were used. The imine **L-5** was isolated as yellow solid (73.1 mg, 0.017 mmol, 99%).

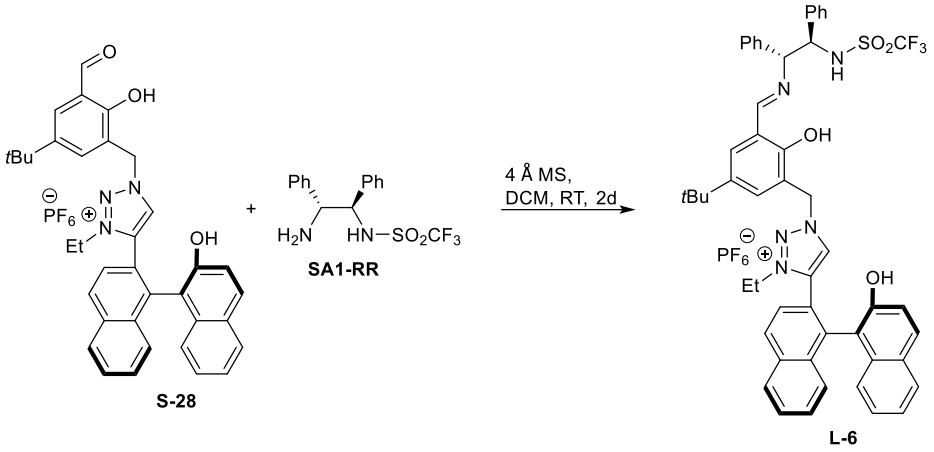
$C_{51}H_{47}F_9N_5O_4PS$, MW: 1027.98 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 13.47 (*br*, 1H, Ar-O*H*), 8.53 (*s*, 1H, Ar-*H*), 8.09 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.99 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.76 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.63-7.58 (*m*, 3H, Ar-*H*), 7.48 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.44-7-30 (*m*, 6H, Ar-*H*), 7.27-7.16 (*m*, 12H, Ar-*H*), 6.85 (*d*, *J* = 8.2Hz, 1H, Ar-*H*), 5.48 (*d*, *J* = 14.5 Hz, 1H, N-C*H*$_2$-Ar), 5.30 (*d*, *J* = 14.4 Hz, 1H, N-C*H*$_2$-Ar), 5.04 (*d*, *J* = 9.1 Hz, 1H, C*H*-N-SO$_2$), 4.47 (*d*, J = 9.1 Hz, 1H, C=N-C*H*), 4.32-4.08 (*m*, 2H, N-C*H*$_2$-C), 1.24 (*t*, *J* = 7.5 Hz, 3H, N-C-C*H*$_3$), 1.19 (*s*, 9H, Ar-C(C*H*$_3$)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -70.37, -72.28 (*d*, *J* = 714.2 Hz P*F*$_6^-$), -77.75 (*s*, CF_3). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -130.8 to -157.20 (*sept*, *J* = 719.8 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **L-5** agrees with the literature. [30]

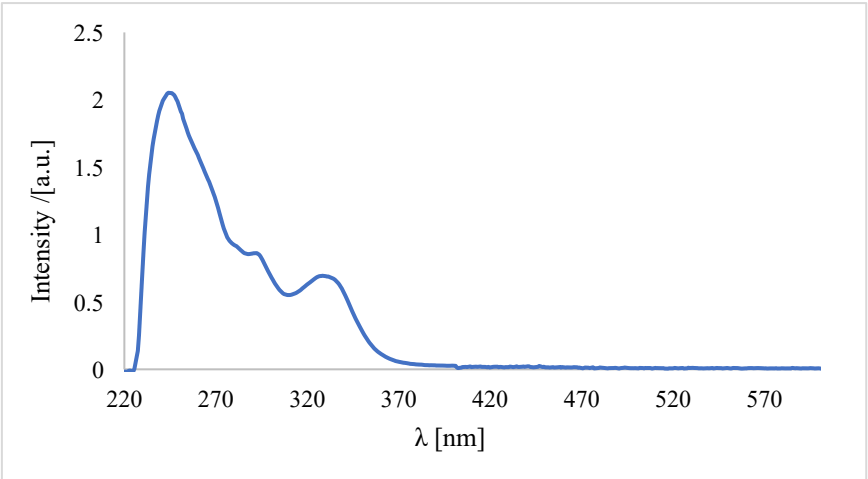
2.4.6 Synthesis of Imine 1-(5-(*tert*-Butyl)-3-(-(((1*R*,2*R*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-((*S*)-2´-hydroxy-(1,1'-binaphthalene)-2-yl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (L-6) [14, 30]



Imine **L-6** was synthesized according to the general procedure **GP 5**. Therefore, the aldehyde **S-28** (40.0 mg, 0.057 mmol, 1.0 eq.) and Sulfonamide **SA1-RR** (20.6 mg, 0.059 mmol, 1.05 eq.) were used. Imine **L-6** was isolated as a yellow solid (57.3 mg, 0.055 mmol, 97%).

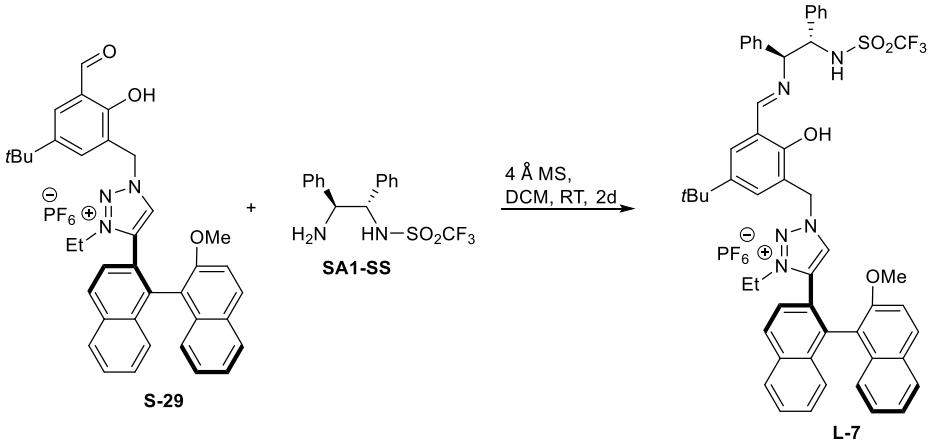
$C_{51}H_{47}F_9N_5O_4PS$, MW: 1027.98 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 13.71 (*br*, 1H, Ar-O*H*), 8.69 (*s*, 1H, Ar-*H*), 8.04 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.96 (*s*, 1H, Ar-*H*), 7.70 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.67-7.55 (*m*, 3H, Ar-*H*), 7.51-7-40 (*m*, 6H, Ar-*H*), 7.39-7.16 (*m*, 14H, Ar-*H*), 6.91 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 5.61 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-Ar), 5.31 (*d*, *J* = 14.4 Hz, 1H, N-CH_2-Ar), 5.05 (*d*, *J* = 9.0 Hz, 1H, C*H*-N-SO_2), 4.95 (*d*, *J* = 9.0 Hz, 1H, C=N-C*H*), 4.39-4.13 (*m*, 2H, N-CH_2-C), 1.25 (*t*, *J* = 7.5 Hz, 3H, N-C-CH_3), 1.1 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -70.91, -72.82 (*d*, *J* = 714.4 Hz PF_6^-), -77.85 (*s*, CF_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ = -130.8 to -157.20 (*sept*, *J* = 719.8 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-4} M):



The analytical data for **L-6** agrees with the literature. [30]

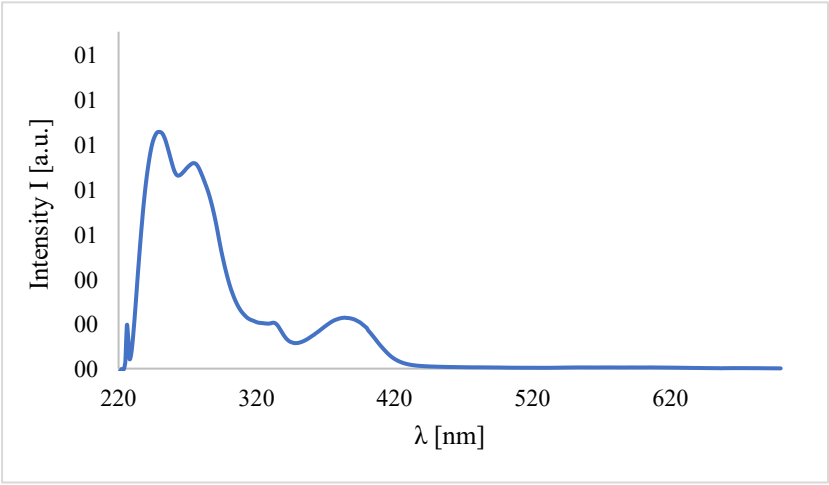
2.4.7 Synthesis of imine 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-((*R*)-2´-methoxy-(1,1´-binaphthalene)-2-yl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (L-7)[14, 30]



Imine **L-7** was synthesized according to the general procedure **GP 5**. Therefore, the aldehyde **S-29** (30 mg, 0.041 mmol, 1.0 eq.) and sulfonamide **SA1-SS** (17.6 mg, 0.05 mmol, 1.0 eq.) were used. The imine **L-7** was isolated as a yellowish solid (52.1 mg, 0.049 mmol, 93%).

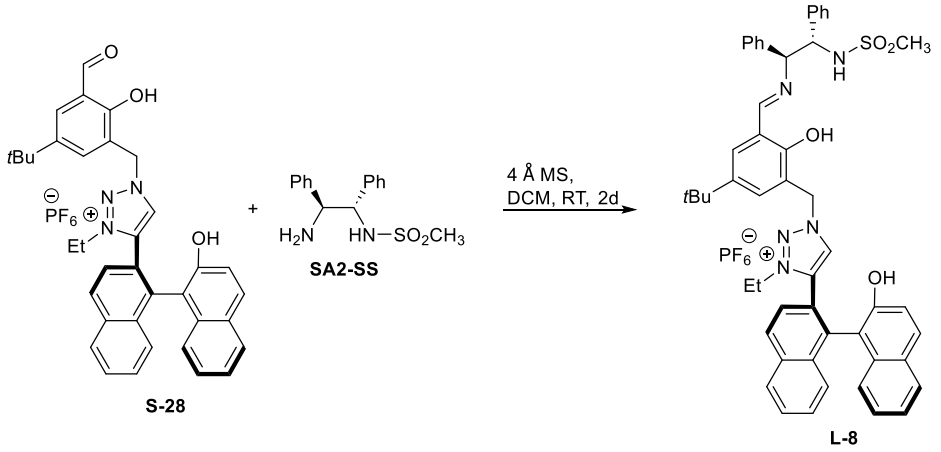
$C_{52}H_{49}F_9N_5O_4PS$, MW: 1042.01 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 13.35 (*br*, 1H, Ar-O*H*), 8.86 (*s*, 1H, Ar-*H*), 8.06 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.96 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.67 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.59-7.48 (*m*, 3H, Ar-*H*), 7.34-7.26 (*m*, 4H, Ar-*H*), 7.25-7.10 (*m*, 13H, Ar-*H*), 7.06(*t*, *J* = 8.2 Hz, 1H, Ar-*H*), 6.72 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 6.59 (*m*, 1H, Ar-*H*), 5.50 (*d*, *J* = 14.1 Hz, 1H, N-CH_2-Ar), 5.20 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-Ar), 5.02 (*d*, *J* = 8.5 Hz, 1H, C*H*-N-SO_2), 4.95 (*d*, *J* = 8.9 Hz, 1H, C=N-C*H*), 4.35-4.17 (*m*, 2H, N-C*H*-C), 3.34 (*s*, 3H, Ar-O-CH_3), 1.39 (*t*, *J* = 7.3 Hz, 3H, N-C-CH_3), 1.19 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -71.66, -73.53, (*d*, *J* = 713.8 Hz, PF_6^-), -77.78 (*s*, CF_3). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -133.7 to -154.1 (*sept*, *J* = 700.2 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **L-7** agrees with the literature. [30]

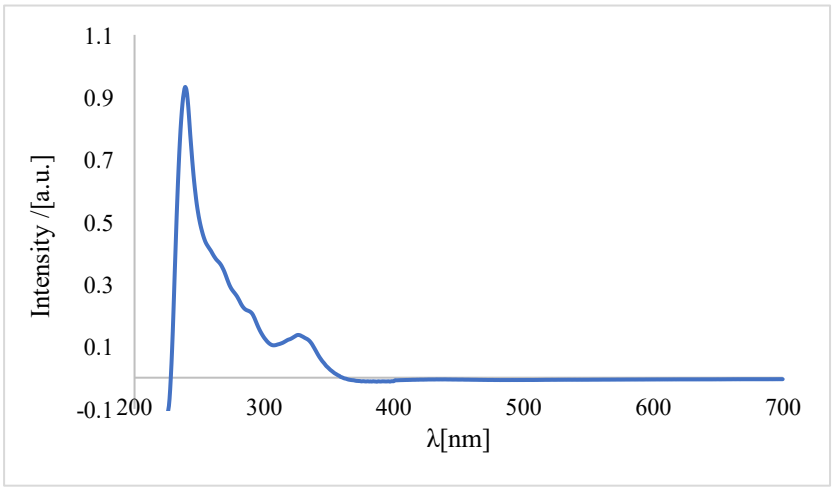
2.4.8 Synthesis of Imine 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((methyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-((*S*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium hexafluorophosphate (L-8)[14, 30]



Imine **L-8** was synthesized according to **GP 5**. For that the aldehyde **S-28** (30.0 mg, 0.042 mmol, 1.0 eq.) and sulfonamide **SA2-SS** (13.1 mg, 0.044 mmol, 1.05 eq.) were used. The imine **L-8** was isolated as yellowish solid (37.3 mg, 0.038 mmol, 90%).

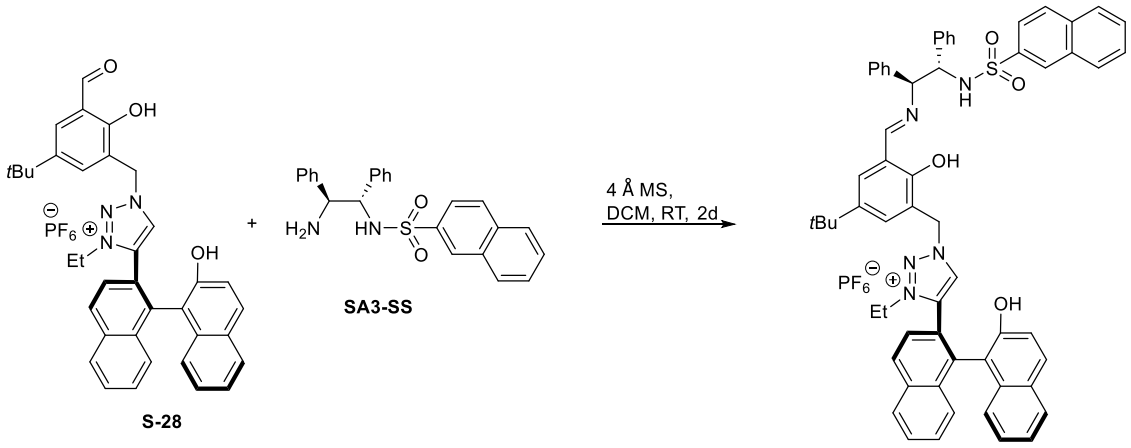
$C_{51}H_{50}F_6N_5O_4PS$, MW: 974.02 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 14.50 (*br*, 1H, Ar-O*H*), 8.50 (*s*, 1H, CHN), 8.10 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.94 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.73 (*s*, 1H, C=C*H*-N), 7.62 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.60-7.52 (*m*, 2H, Ar-*H*), 7.50 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.32-7.22 (*m*, 5H, Ar-*H*), 7.20-7.10 (*m*, 12H, Ar-*H*), 6.81 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 6.08 (*d*, *J* = 8.8 Hz, 1H, Ar-*H*), 5.34(*d*, *J* = 14.2 Hz, 1H, N-CH_2-C), 5.30 (*d*, *J* = 14.1 Hz, 1H, N-CH_2-C), 4.99 (*t*, *J* = 8.8 Hz, 1H, S-NH-C*H*), 4.84 (*d*, *J* = 9.1 Hz, 1H, C=N-C*H*), 4.40-4.22 (*m*, 1H, N-CH_2-CH_3), 4.20-4.04 (*m*, 1H, N-CH_2-CH_3), 2.36 (*s*, 3H, SO_2-CH_3), 1.28 (*t*, *J* = 7.4 Hz, 3H, N-CH_2-CH_3) 1.20 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -71.5 - -73.8 (*d*, *J* = 713.9 Hz, PF_6). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -144.6 (*sept*, *J* = 713.4 Hz, *P*F_6) ppm.

UV/Vis (DCM, 2 x 10-5 M):



The analytical data for **L-8** agrees with the literature. [30]

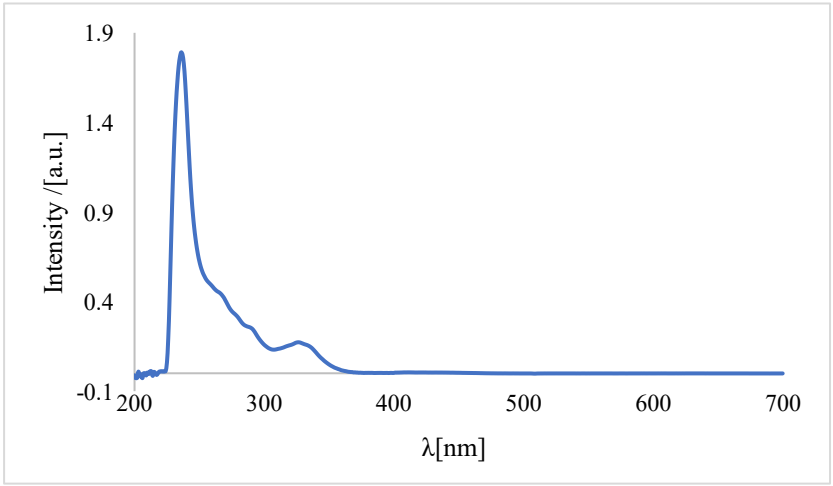
2.4.9 Synthesis of Imine 1-(5-(*tert*-Butyl)-2-hydroxy-3-(-(((1*S*,2*S*)-2-(naphthalene-2-sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2´-hydroxy-(1,1'-binaphthalene)-2-yl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (L-9) [14, 30]



Imine **L-9** was synthesized according to **GP 5**. For that the aldehyde **S-28** (35.0 mg, 0.049 mmol, 1.0 eq.) and sulfonamide **SA3-SS** (21.1 mg, 0.049 mmol, 1.05 eq.) were used. The imine **L-9** was isolated as yellowish solid (51.8 mg, 0.047 mmol, 96%).

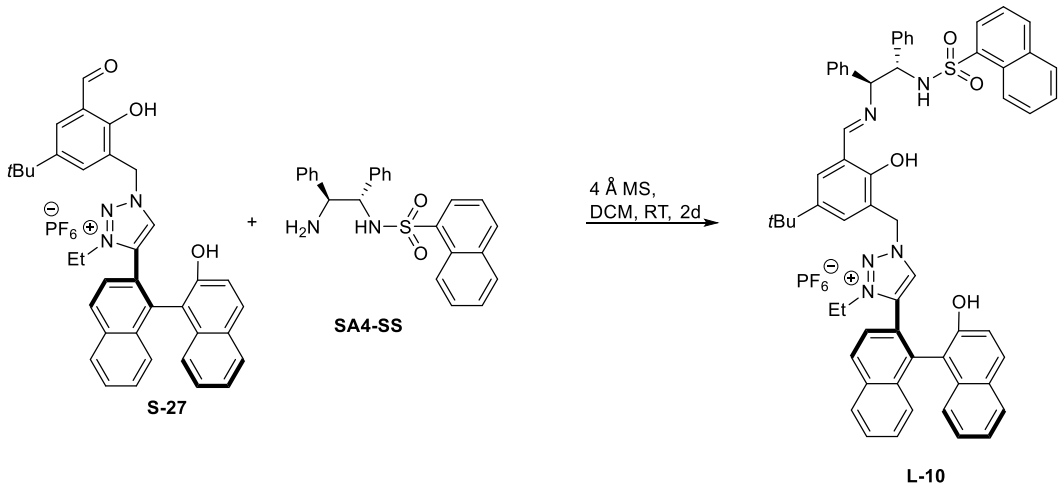
$C_{60}H_{54}F_6N_5O_4PS$, MW: 1086.14 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.54 (*br*, 1H, Ar-O*H*), 8.50 (*s*, 1H, Ar-*H*), 8.01 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.90 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.64 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.57-7.52 (*m*, 3H, Ar-*H*), 7.44 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 7.37-7-20 (*m*, 9H, Ar-*H*), 7.21-6.89 (*m*, 16H, Ar-*H*), 6.75 (*d*, *J* = 7.7 Hz, 1H, Ar-*H*), 5.54 (*d*, *J* = 14.1 Hz, 1H, N-CH_2-Ar), 5.41 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-Ar), 5.01 (*d*, *J* = 8.5 Hz, 1H, C*H*-N-SO_2), 4.59 (*d*, *J* = 8.4 Hz, 1H, C=N-C*H*), 4.44-4.21 (*m*, 2H, N-CH_2-C), 1.25 (*t*, *J* = 7.5 Hz, 3H, N-C-CH_3), 1.18 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -71.5, -73.4 (*d*, *J* = 712.8 Hz, PF_6^-). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -134.8 to -159.6 (*sept*, *J* = 708.0 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10-5 M):



The analytical data for **L-9** agrees with the literature. [30]

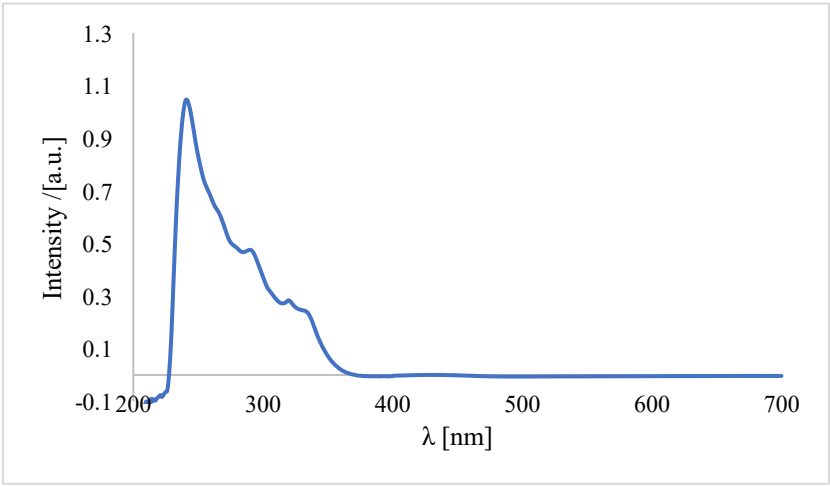
2.4.10 Synthesis of Imine 1-(5-(*tert*-Butyl)-2-hydroxy-3-(-(((1*S*,2*S*)-2-(naphthalene-1-sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2'-hydroxy-(1,1´-binaphthalene)-2-yl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (L-10)[14, 30]



Imine **L-10** was synthesized according to **GP 5**. For that the aldehyde **S-28** (20.0 mg, 0.028 mmol, 1.0 eq.) and sulfonamide **SA4-SS** (12.1 mg, 0.029 mmol, 1.05 eq.) were used. The imine **L-10** was isolated as yellowish solid (28.6 mg, 0.026 mmol, 93%).

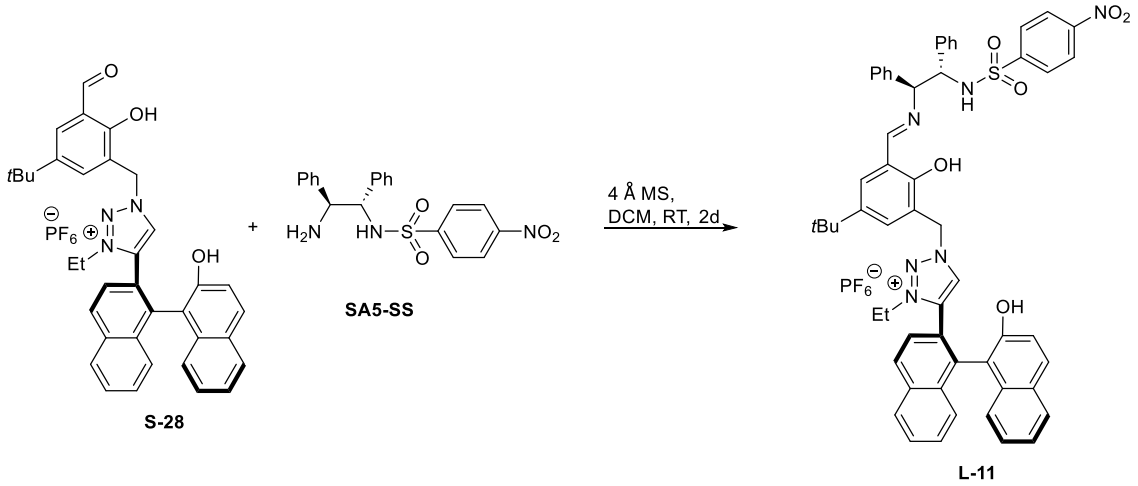
$C_{60}H_{54}F_6N_5O_4PS$, MW: 1086.14 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.44 (*br*, 1H, Ar-O*H*), 8.48-8.40 (*m*, 2H, C*H*N, Ar-*H*), 7.95 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.89 (*t*, *J* = 7.7 Hz, 2H, Ar-*H*), 7.70 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.61 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.58-7.49 (*m*, 3H, Ar-*H*), 7.48-7.39 (*m*, 2H, Ar-*H*), 7.38-7-28 (*m*, 4H, Ar-*H*), 7.24 (*d*, *J* = 8.2 Hz, 2H, Ar-*H*), 7.19-7.13 (*m*, 2H, Ar-*H*), 7.12-7.02 (*m*, 8H, Ar-*H*), 6.80 (*d*, *J* = 8.2 Hz, 1H, Ar-*H*), 6.72-6.65 (*dt*, 1H, Ar-*H*), 6.64-6.56 (*m*, 4H, Ar-*H*), 5.51 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-Ar), 5.32 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-Ar), 4.79 (*d*, *J* = 9.1 Hz, 1H, C*H*-N-SO_2), 4.70 (*d*, *J* = 9.0 Hz, 1H, C=N-C*H*), 4.32-4.07 (*m*, 2H, N-CH_2-C), 1.26 (*t*, *J* = 7.4 Hz, 3H, N-C-CH_3), 1.18 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = -71.38, -73.28 (*d*, *J* = 712.5 Hz, PF_6^-). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -133.6 to -158.1 (*sept*, *J* = 710.1 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10-5 M):



The analytical data for **L-10** agrees with the literature. [30]

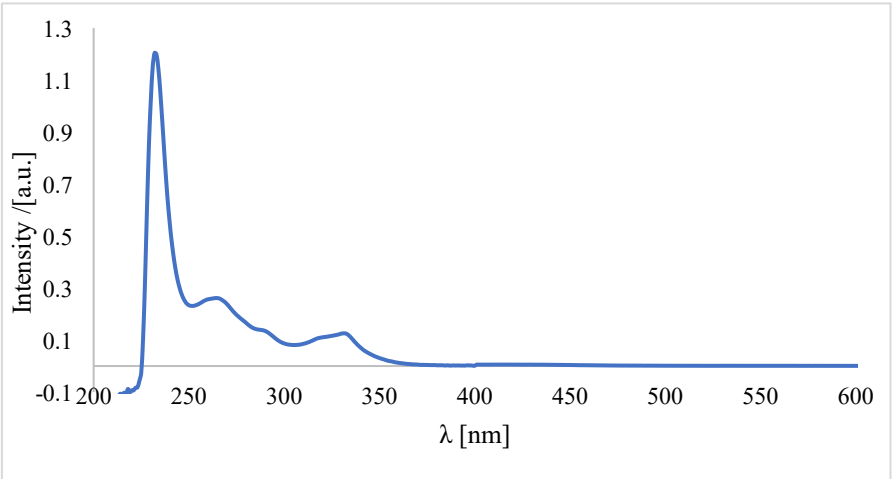
2.4.11 Synthesis of Imine 1-(5-(*tert*-Butyl)-2-hydroxy-3-(-(((1*S*,2*S*)-2-((4-nitrophenyl)sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2'-hydroxy-(1,1'-binaphthalene)-2-yl)-1*H*-1,2,3-triazol-3-ium hexafluorophosphate (L-11)[14, 30]



Imine **L-11** was synthesized according to **GP 5**. For that the aldehyde **S-28** (25.0 mg, 0.035 mmol, 1.0 eq.) and sulfonamide **SA5-SS** (14.8 mg, 0.037 mmol, 1.05 eq.) were used. The imine **L-11** was isolated as yellowish solid (35.2 mg, 0.032 mmol, 94%).

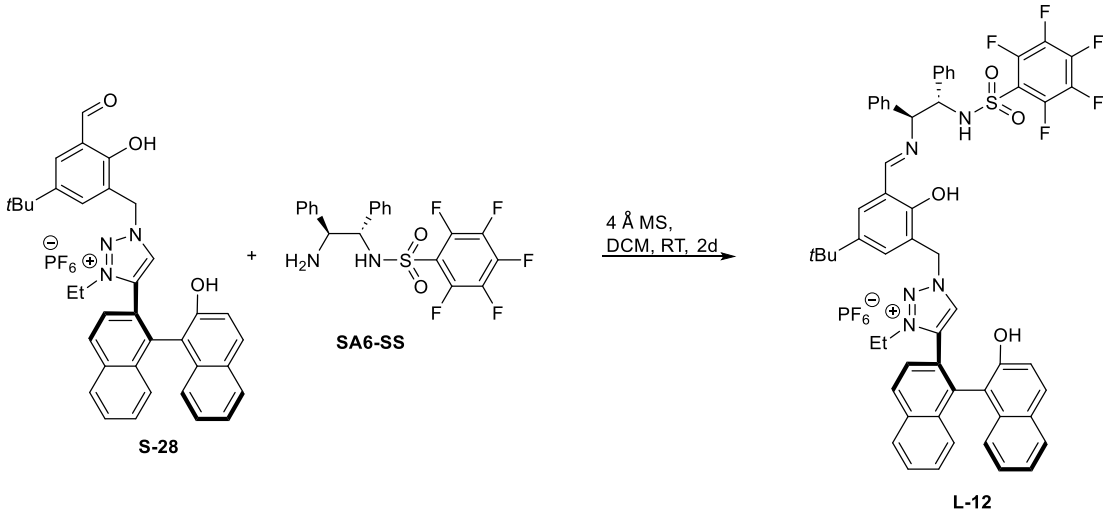
$C_{56}H_{51}F_6N_6O_6PS$, MW: 1081.08 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.73 (*br*, 1H, Ar-O*H*), 8.55 (*s*, 1H, C*H*N), 8.06 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.93 (*d*, *J* = 8.4 Hz, 2H, Ar-*H*), 7.82 (*s*, 1H, C=C*H*-N), 7.77 (*d*, *J* = 8.5 Hz, 2H, Ar-*H*), 7.64 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.59-7.47 (*m*, 5H, Ar-*H*), 7.40-7.27 (*m*, 5H, Ar-*H*), 7.24-7.04 (*m*, 7H, Ar-*H*), 7.02 -6.84 (*m*, 6H, Ar-*H*), 6.78 (*d*, *J* = 8.1 Hz, 2H, Ar-*H*), 5.10 (*d*, *J* = 14.1 Hz, 1H, N-CH_2-C), 4.87 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-C), 4.35-4.24 (*m*, 1H, N-CH_2-CH_3), 4.22-4.12 (*m*, 1H, N-CH_2-CH_3), 1.32 (*t*, *J* = 7.3 Hz, 3H, N-CH_2-CH_3) 1.17(*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** *δ* = -70.65, -72.55 (*d*, *J* = 715.6 Hz, PF_6^-). **^{31}P-NMR (162 MHz, $CDCl_3$):** *δ* = -130.2 to -152.9 (*sept*, *J* = 710.4 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **L-11** agrees with the literature. [30]

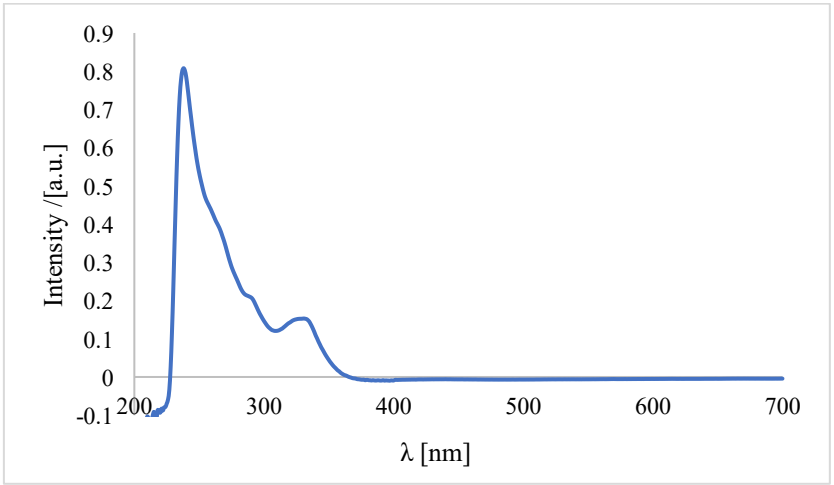
2.4.12 Synthesis of Imine 1-(5-(tert-Butyl)-2-hydroxy-3-(-(((1*S*,2*S*)-2-((perfluorophenyl)sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2´-hydroxy-[1,1´-binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium hexafluorophosphate (L-12)[14, 30]



Imine **L-12** was synthesized according to **GP 5**. For that the aldehyde **S-28** (25.0 mg, 0.035 mmol, 1.0 eq.) and sulfonamide **SA6-SS** (16.5 mg, 0.037 mmol, 1.05 eq.) were used. The imine **L-12** was isolated as yellowish solid (37.4 mg, 0.033 mmol, 93%).

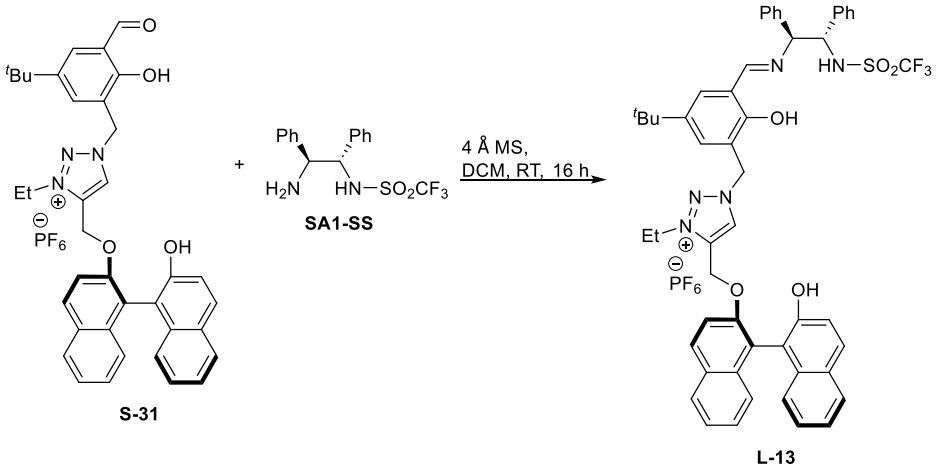
$C_{56}H_{47}F_{11}N_5O_4PS$, MW: 1126.03 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.68 (*br*, 1H, Ar-O*H*), 8.55 (*s*, 1H, C*H*N), 8.01 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 7.94 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.73 (*s*, 1H, C=C*H*-N), 7.57 (*d*, *J* = 8.4 Hz, 1H, Ar-*H*), 7.55-7.51 (*m*, 2H, Ar-*H*), 7.50-7.43 (*m*, 2H, Ar-*H*), 7.32 (*d*, *J* = 9.1 Hz, 1H, Ar-*H*), 7.30-7.26 (*m*, 5H, Ar-*H*), 7.26-6.99 (*m*, 11H, Ar-*H*), 6.87 (*d*, *J* = 7.7 Hz, 1H, Ar-*H*), 5.41 (*d*, *J* = 14.2 Hz, 1H, N-CH_2 C), 5.22 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-C), 5.17 (*d*, *J* = 9.4 Hz, 1H, S-NH-C*H*), 5.01 (*d*, *J* = 9.4 Hz, 1H, C=N-C*H*), 4.41-4.24 (*m*, 1H, N-CH_2-CH_3), 4.22-4.10 (*m*, 1H, N-CH_2-CH_3), 1.32 (*t*, *J* = 7.4 Hz, 3H, N CH_2-CH_3) 1.19 (*s*, 9H, Ar-C(CH_3)$_3$).
^{19}F-NMR (376 MHz, $CDCl_3$): δ = −71.1, −72.6 (d, *J* = 713.9 Hz, PF_6), −135.5 (*d*, *J* = 17.7 Hz, 2F, Ar-F), −147.2 (*t*, *J* = 16.6 Hz, 1F, Ar-F), −160.0 (*t*, *J* = 18.4 Hz, 2F, Ar-F). **^{31}P-NMR (162 MHz, $CDCl_3$):** *δ* = -132.7 - -159.3 (*sept*, *J* = 707.2 Hz, *P*F_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **L-12** agrees with the literature. [30]

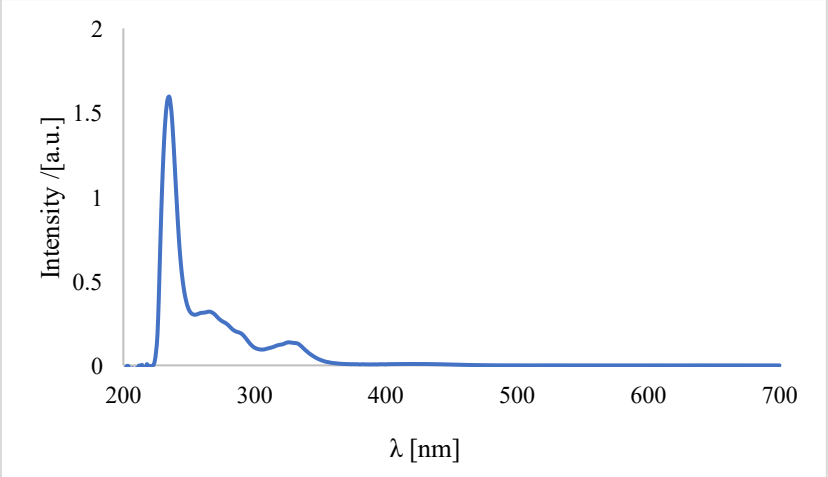
2.4.13 Synthesis of Imine 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-((((*R*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)oxy)methyl)-1H-1,2,3-triazol-3-ium hexafluorophosphate (L-13) [14, 30]



Imine **L-13** was synthesized according to the general procedure **GP 5**. The aldehyde **S-31** (80.0 mg, 0.109 mmol, 1.0 eq.) and sulfonamide **SA1-SS** (39.5 mg, 0.114 mmol, 1.05 eq.) were used. The imine **L-13** was isolated as yellow solid (108.9 mg, 0.107mmol, 94%).

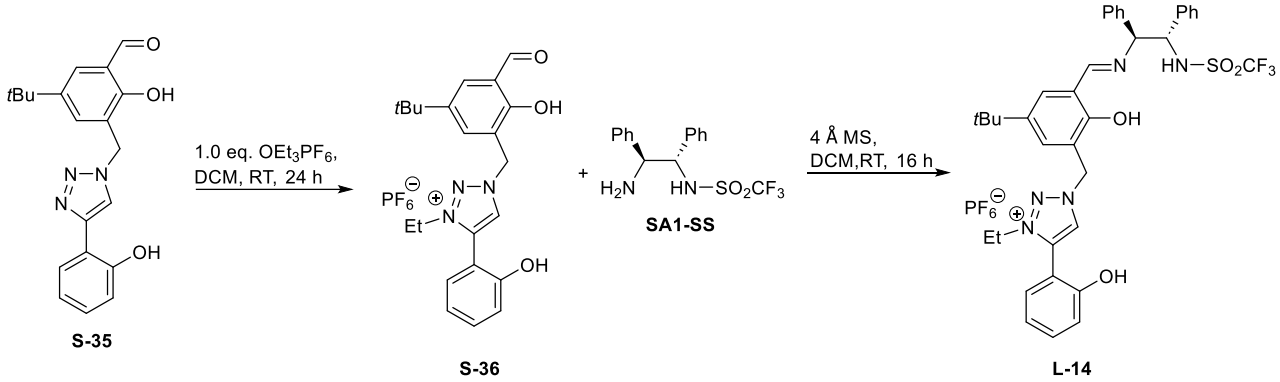
$C_{52}H_{49}F_9N_5O_5PS$, MW: 1058,01 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 14.53 (*s*, 1H, Ar-O*H*), 8.36 (*s*, 1H, C*H*=NR), 8.35 (*s*, 1H, Ar-*H*), 8.07 (*d*, *J* = 8.9 Hz, 1H, Ar-*H*), 7.91 (*d*, *J* = 8.3 Hz, 1H, Ar-*H*), 7.83 (*d*, *J* = 8.4 Hz, 2H, Ar-*H*), 7.59 (*d*, *J* = 9.0 Hz, 1H, Ar-*H*), 7.45 (*t*, *J* = 8.1 Hz, 1H, Ar-*H*), 7.40-7.29 (*m*, 5H, Ar-*H*), 7.27-7.14 (*m*, 9H, Ar-*H*), 7.11-7.01 (*m*, 4H, Ar-*H*), 6.96 (*d*, *J* = 8.5 Hz, 1H, Ar-*H*), 5.75 (*d*, *J* = 14.0 Hz, 1H, Ar-CH_2-N), 5.37-5.24 (*t*, 2H, 1-Ar-C*H*-N, 2-O-C*H*-N), 5.16 (*d*, *J* = 14.0 Hz, 1H, Ar-CH_2-N), 4.94 (*d*, *J* = 9.5 Hz, 1H,O-CH_2), 4.86 (*d*, *J* = 9.6 Hz, 1H, O-CH_2), 3.69-3.49 (*m*, 2H, N-CH_2-C), 1.26 (*s*, 9H, Ar-C((CH_3)$_3$)), 0.99 (t, *J* = 7.1 Hz, 3H, N-C-CH_3) ppm.**^{19}F-NMR (400 MHz, $CDCl_3$):** δ = −71.32, −73.47 (*d*, *J* = 714.4 Hz, PF_6-), -78.0 (*s*, CF_3). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = -144.6 (*sept*, *J* = 703.8 Hz, PF_6^-) ppm.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **L-13** agrees with the literature.[30]

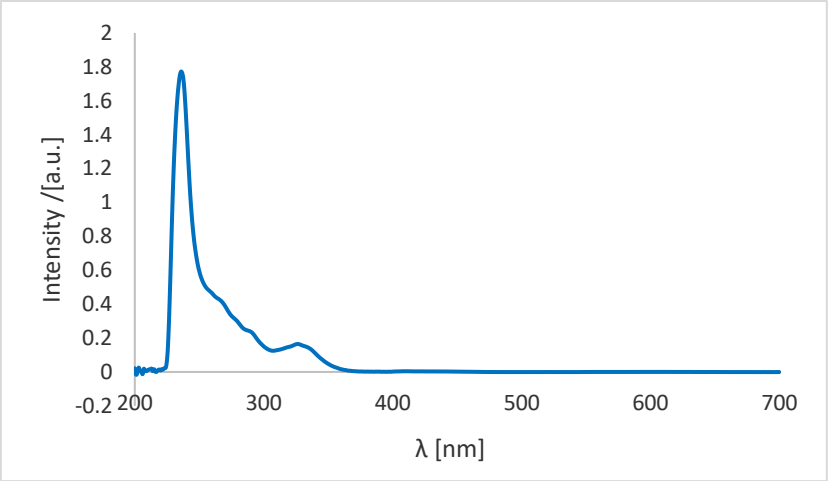
2.4.14 Synthesis of Imine 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-hydroxybenzyl)-3-ethyl-4-(2-hydroxyphenyl)-1H-1,2,3-triazol-3-ium hexafluorophosphate (L-14) [14, 30]



The preparation of imine **L-14** was done using crude **S-36**. The corresponding aldehyde **S-35** (50 mg, 0.142 mmol, 1.0 eq.) and OEt_3PF_6 (35.31 mg, 0.142 mmol, 1.0 eq.) were dissolved in anhydrous DCM (*c* = 3 ml/mmol) under nitrogen atmosphere in the presence of molecular sieves (4Å). The reaction mixture was stirred for 24 h at room temperature. Afterwards the reaction mixture was quenched with MeOH (1 ml/mmol) and stirred for another 30 min. The phases were separated, the organic phase was washed with demineralized water (2 x 5 mL) and extracted with DCM and dried over sodium sulphate. The crude product (**S-35**+**S-36**) was used for the next reaction. For the imine synthesis, a mixture of the crude **S-36** (70 mg, 0.133 mmol, 1.0 eq.) and the amine **SA1-SS** (48.68 mg, 0.141 mmol, 1.05 eq.) were dissolved in anhydrous DCM (*c* = 2 ml/mmol) under nitrogen atmosphere. The reaction mixture was stirred for 12h at room temperature. Afterwards the reaction mixture was purified by column chromatography (DCM:MeOH 50:1) to give the desired product **L-14** (83.74 mg, 74%) as yellowish solid.

$C_{37}H_{39}F_9N_5O_4PS$, MW: 851.76 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.97 (*br*, 1H, Ar-O*H*), 8.32 (*s*, 2H, Ar-*H*), 7.83 (*d*, *J* = 2.3 Hz, 1H, Ar-*H*), 7.66 (*d*, *J* = 2.3 Hz, 1H, Ar-*H*), 7.59 (*d*, *J* = 2.2 Hz, 1H, Ar-*H*), 7.55-7.28 (*m*, 2H, Ar-*H*), 7.34 (*d*, *J* = 2.3 Hz, 4H, Ar-*H*), 7.21-7-10 (*m*, 3H, Ar-*H*), 6.85-6.68 (*m*, 4H, Ar-*H*), 5.76 (*d*, *J* = 14.0 Hz, 1H, N-CH_2-Ar), 5.65 (*d*, *J* = 14.1 Hz, 1H, N-CH_2-Ar), 5.48 (*d*, *J* = 9.4 Hz, 1H, C*H*-N-SO_2), 4.79 (*d*, *J* = 7.5 Hz, 1H, C=N-C*H*), 4.47-4.45 (*m*, 2H, N-CH_2-C), 1.48 (*t*, *J* = 7.3 Hz, 3H, N-C-CH_3), 1.21 (*s*, 9H, Ar-C(CH_3)$_3$). **^{19}F-NMR (376 MHz, $CDCl_3$):** δ = −71.0 - −72.3 (d, *J* = 714.6 Hz, PF_6), −77.8 (s, CF_3). **^{31}P-NMR (162 MHz, $CDCl_3$):** δ = −144.6 (*sept*, *J* = 708.2 Hz, PF_6) ppm.

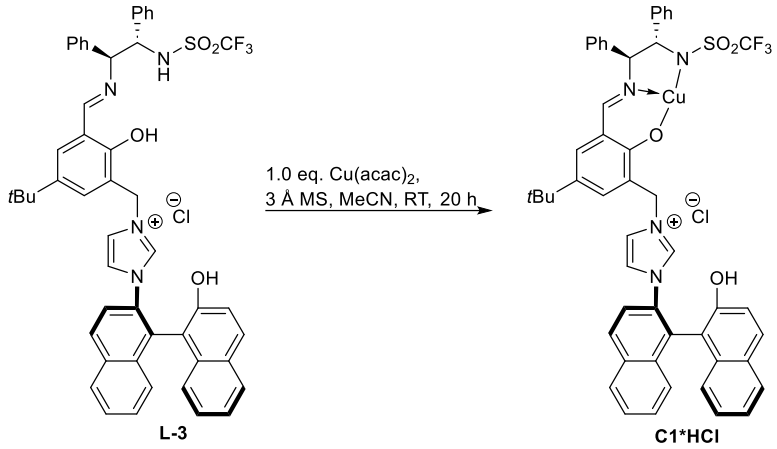
UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **L-14** agrees with the literature.[30]

2.5 Catalyst synthesis

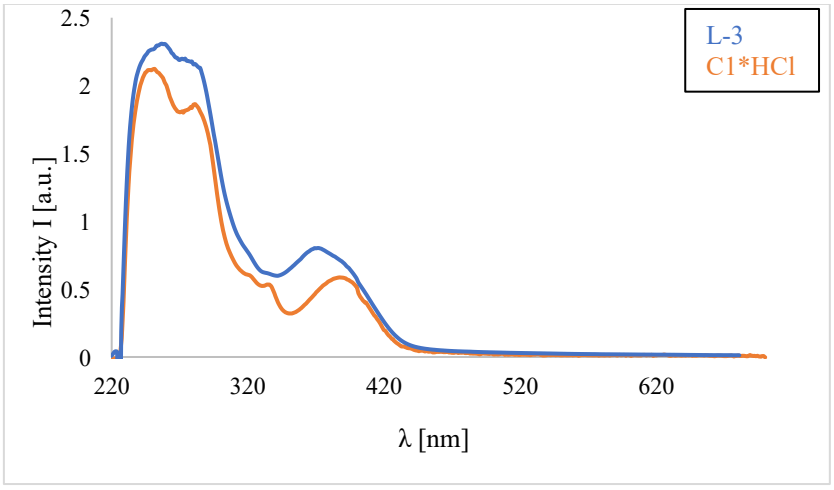
2.5.1 Synthesis of Phenoxyimine-Cu(II) Precatalyst 3-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-1-(2´hydroxy-[1,1´-binaphthalene]-2-yl)-1H-imidazole-3-ium-Cu(II) Chloride (C1*HCl) [14]



The synthesis of the phenoxyimine-Cu(II) complex **C1*HCl** was performed according to **GP 6**. The phenolimine-preligand **L-3** (20.0 mg, 22.5 µmol, 1.0 eq.) and $Cu(acac)_2$ (5.8 mg, 22.5 µmol, 1.0 eq.) were used. The phenoxyimine-Cu(II) complex **C1*HCl** was isolated as green solid (19.4 mg, 22.5 µmol, 99%).

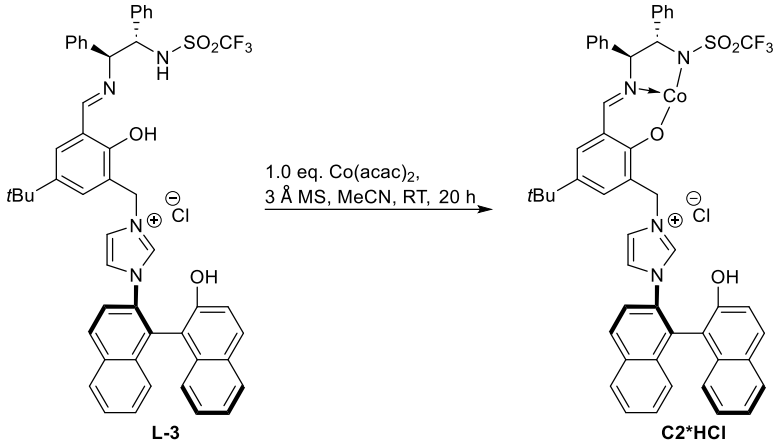
$C_{50}H_{42}ClCuF_3N_4O_4S$, MW: 950.96 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}Cl]^+$ $C_{50}H_{42}CuF_3N_4O_4S^+$: 914.2169. Found: 914.2178.

UV/Vis (DCM, 2 x 10^{-4} M):



The analytical data for **C1*HCl** agrees with the literature. [14]

2.5.2 Synthesis of Phenoxyimine-Co(II) Precatalyst 3-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-1-(2'hydroxy-[1,1´-binaphthalene]-2-yl)-1H-imidazole-3-ium-Co(II) Chloride (C2*HCl) [14]

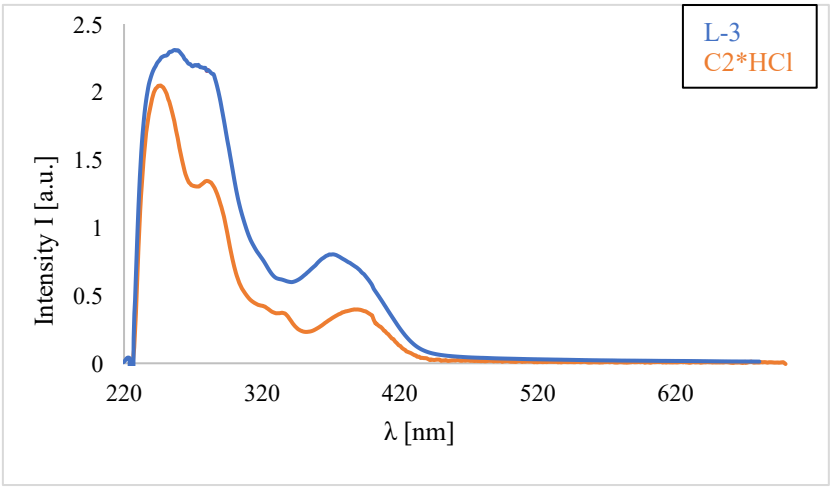


L-3 C2*HCl

The synthesis of phenoxyimine-Co(II) complex **C2*HCl** was performed according to **GP 6**. The phenolimine-preligand **L-3** (25.0 mg, 28.1 µmol, 1.0 eq.) and $Co(acac)_2$ (7.2 mg, 28.1 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C2*HCl** was isolated as green solid (26.5 mg, 28.1 µmol, 99%).

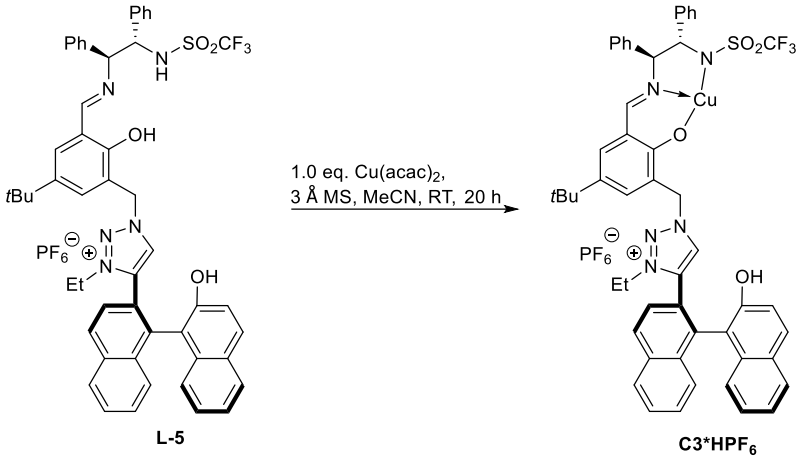
$C_{50}H_{42}ClCoF_3N_4O_4S$, MW: 946.34 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}Cl]^+$ $C_{50}H_{42}CoF_3N_4O_4S^+$: 910.2205. Found: 910.2209.

UV/Vis (DCM, 2 x 10^{-4} M):



The analytical data for **C2*HCl** agrees with the literature. [14]

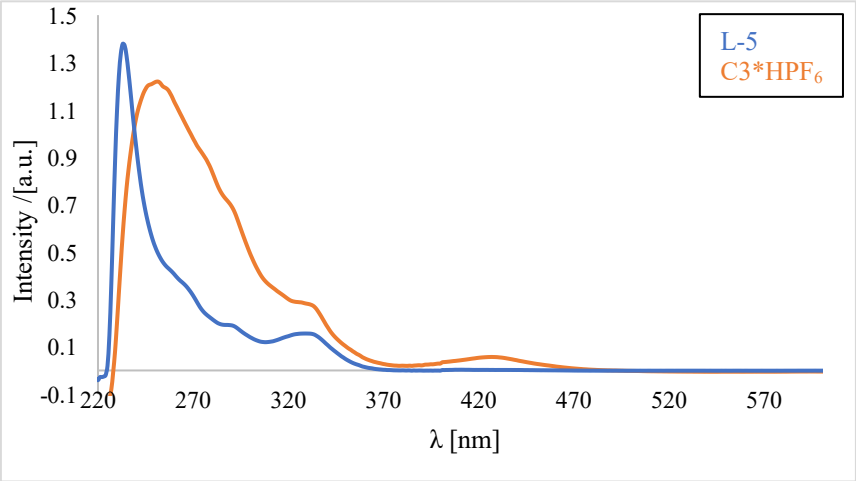
2.5.3 Synthesis of Phenoxyimine-Cu(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3 ethyl-4-((*R*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium-Cu(II) Hexafluorophosphate (C3*HPF$_6$) [14, 30]



The synthesis of phenoxyimine-Cu(II) complex **C3*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-4** (50.0 mg, 48.2 µmol, 1.0 eq.) and $Cu(acac)_2$ (12.7 mg, 48.2 µmol, 1.0 eq.) were used. The phenoxyimine-Cu(II) complex **C3*HPF$_6$** was isolated as green solid (51.6 mg, 47.3 µmol, 98%).

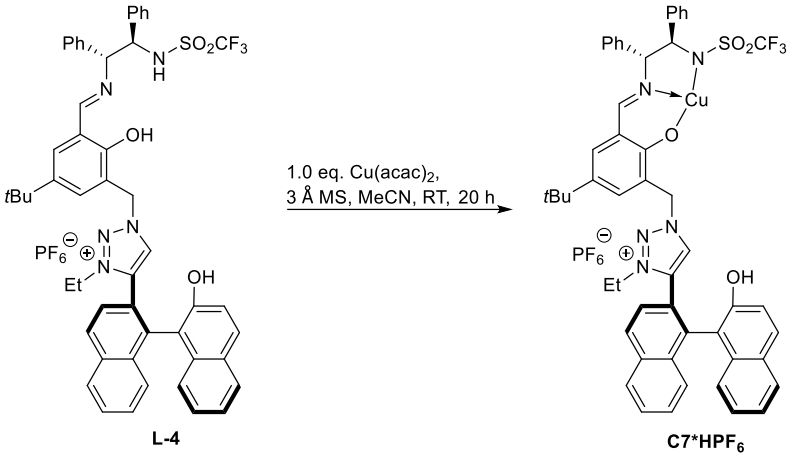
$C_{51}H_{45}CuF_9N_5O_4PS$, MP: 1089.52 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **HRMS (ESI)** ***m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{51}H_{45}CuF_3N_5O_4S^+$: 943.2437. Found: 943.2435 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **C3*HPF$_6$** agrees with the literature. [30]

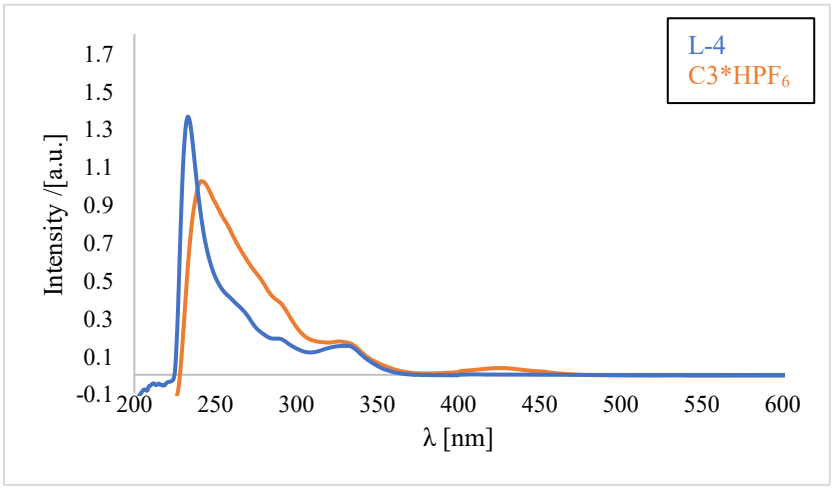
2.5.4 Synthesis of Phenoxyimine-Cu(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*R*,2*R*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3 ethyl-4-((*R*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium-Cu(II) Hexafluorophosphate (C7*HPF$_6$) [14, 30]



The synthesis of phenoxyimine-Cu(II) complex **C7*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-4** (50.0 mg, 48.2 µmol, 1.0 eq.) and $Cu(acac)_2$ (12.7 mg, 48.2 µmol, 1.0 eq.) were used. The phenoxyimine-Cu(II) complex **C7*HPF$_6$** was isolated as green solid (52.4 mg, 48.2 µmol, 99%).

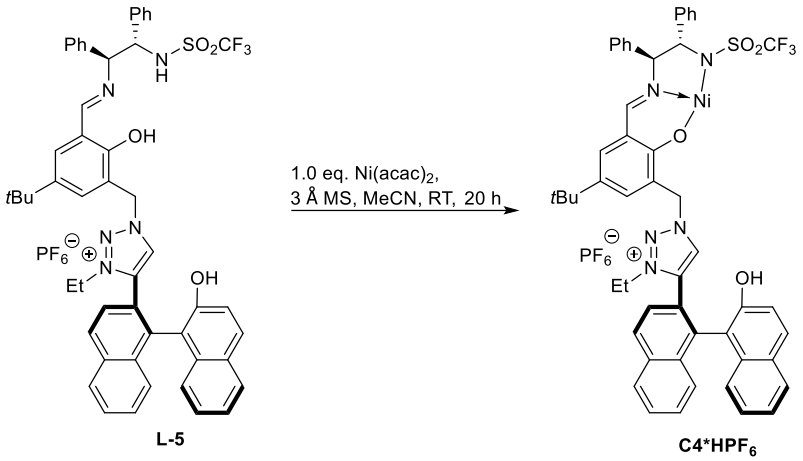
$C_{51}H_{45}CuF_9N_5O_4PS$, MW: 1089.52 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **HRMS (ESI)** ***m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{51}H_{45}CuF_3N_5O_4S^+$: 943.2437. Found: 943.2438. Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



The analytical data for **C7*HPF$_6$** agrees with the literature. [30]

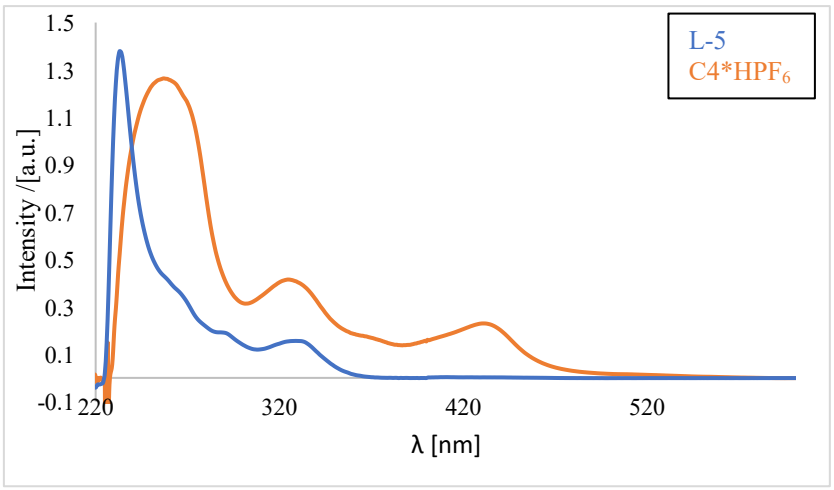
2.5.5 Synthesis of Phenoxyimine-Ni(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3 ethyl-4-((*R*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium-Cu(II) Hexafluorophosphate (C4*HPF$_6$) [14, 28]



The synthesis of phenoxyimine-Ni(II) complex **C4*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-5** (20.0 mg, 20.1µmol, 1.0 eq.) and Ni(acac)$_2$ (5.1 mg, 20.1µmol, 1.0 eq.) were used. The phenoxyimine-Ni(II) complex **C4*HPF$_6$** was isolated as brown solid (21.3 mg, 20.1 µmol, 99%).

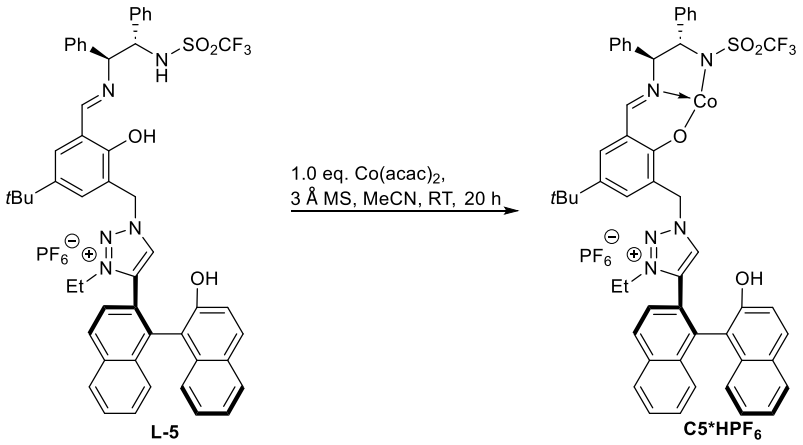
$C_{51}H_{45}NiF_9N_5O_4PS$, MP: 1084.90 g/mol. **^{1}H-NMR:** diamagnetic species but structural analysis by NMR spectroscopy is not possible due to the resulting line broadening caused by the paramagnetic contributions of the complex. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{51}H_{45}NiF_3N_5O_4S^+$: 938.2492. Found: 938.2496 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



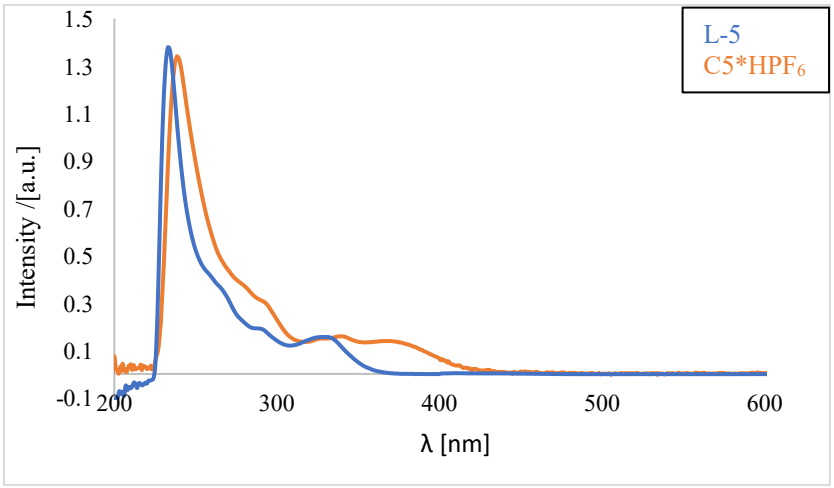
The analytical data for **C4*HPF$_6$** agrees with the literature. [31]

2.5.6 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3 ethyl-4-((*R*)-2'-hydroxy-(1,1'-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium-Co(II) Hexafluorophosphate (C5*HPF$_6$) [14]

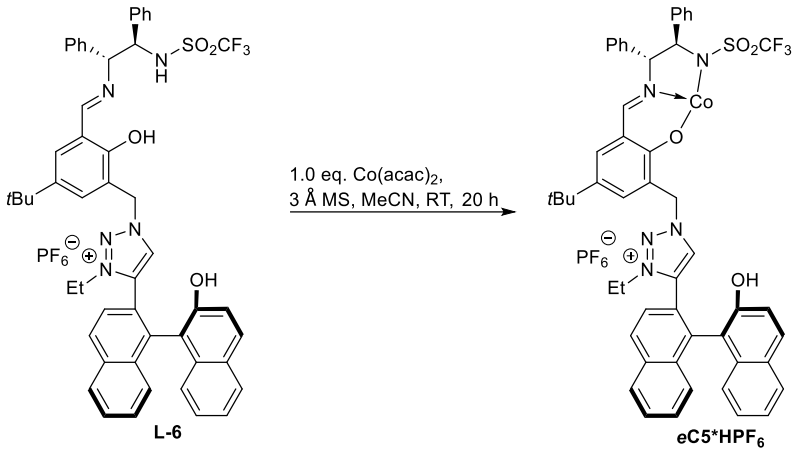


The synthesis of phenoxyimine-Co(II) complex **C5*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-5** (100.0 mg, 0.102 mmol, 1.0 eq.) and Co(acac)$_2$ (26.4 mg, 0.102 mmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C5*HPF$_6$** was isolated as yellowish brown solid (107.3mg, 0.098 mmol, 96%). **C$_{51}$H$_{45}$CoF$_9$N$_5$O$_4$PS, MP:** 1084.90 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP**: 235-248 °C, decomposition. **[α]$^{20}_D$** = +31 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$):** $\tilde{\nu}$ = 3525, 2956, 1627, 1602, 1455, 1377, 1228, 1188, 1145, 1059, 844, 699, 559. **HRMS (ESI)** ***m/z***: Calculated for [M-PF$_6$]$^+$ $C_{51}H_{45}CoF_3N_5O_4S^+$: 939.2471. Found: 939.2473 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):

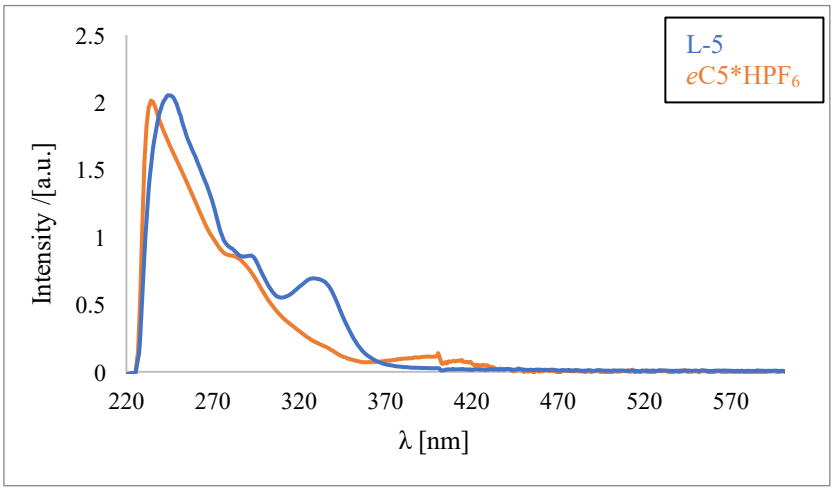


2.5.7 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*R*,2*R*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3 ethyl-4-((*S*)-2´-hydroxy-(1,1´-binaphthalene)-2-yl)-1H-1,2,3-triazol-3-ium-Co(II) Hexafluorophosphate (*e*C5*HPF$_6$) [14]

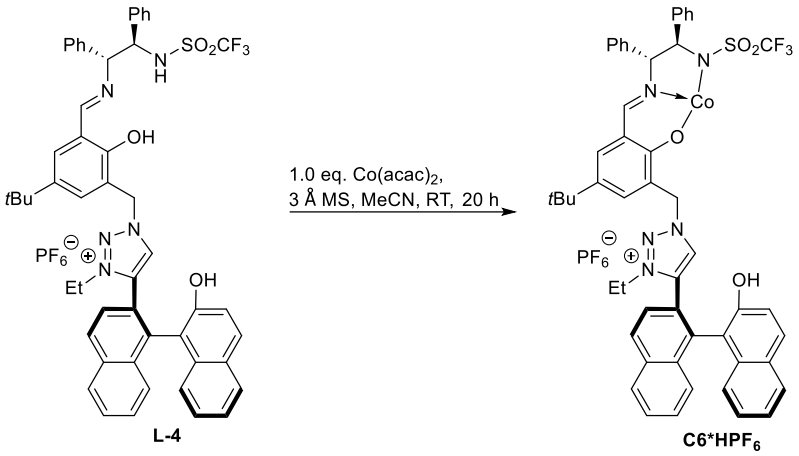


The synthesis of phenoxyimine-Co(II) complex ***e*C5*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-6** (100.0 mg, 0.102 mmol, 1.0 eq.) and Co(acac)$_2$ (26.4 mg, 0.102 mmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex ***e*C5*HPF$_6$** was isolated as yellowish brown solid (110.6 mg, 0.102 mmol, 99%). **$C_{51}H_{45}CoF_9N_5O_4PS$, MP:** 1084.90 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP**: 235-248 °C, decomposition. **$[\alpha]^{20}_D$** = +31 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$): $\tilde{\nu}$** = 3526, 2956, 1625, 1601, 1455, 1380, 1228, 1189, 1145, 1061, 845, 701, 556. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{51}H_{45}CoF_3N_5O_4S^+$: 939.2471. Found: 939.2474 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-4} M):

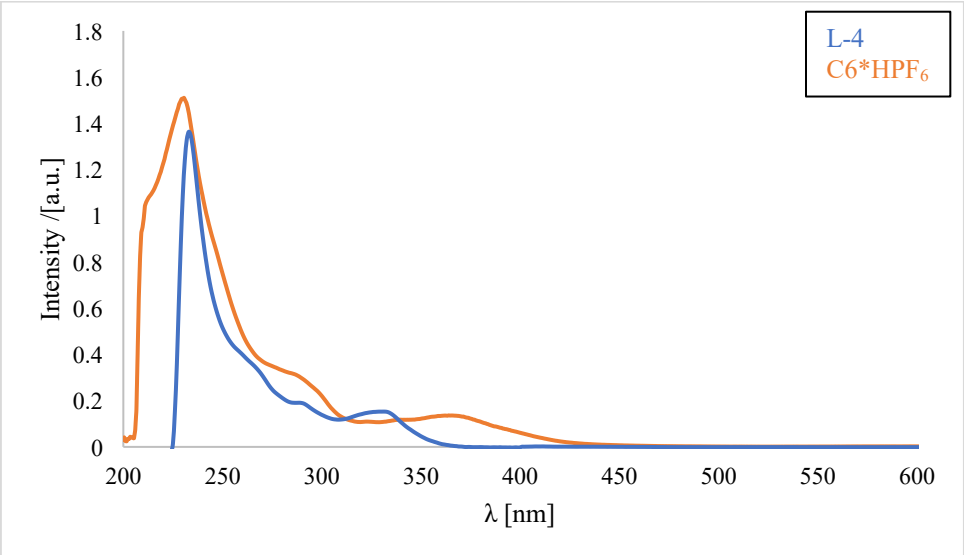


2.5.8 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*R*,2*R*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3 ethyl-4-((*R*)-2'-hydroxy-(1,1'-binaphthalen)-2-yl)-1H-1,2,3-triazol-3-ium-Co(II) Hexafluorophosphate (C6*HPF$_6$) [14]

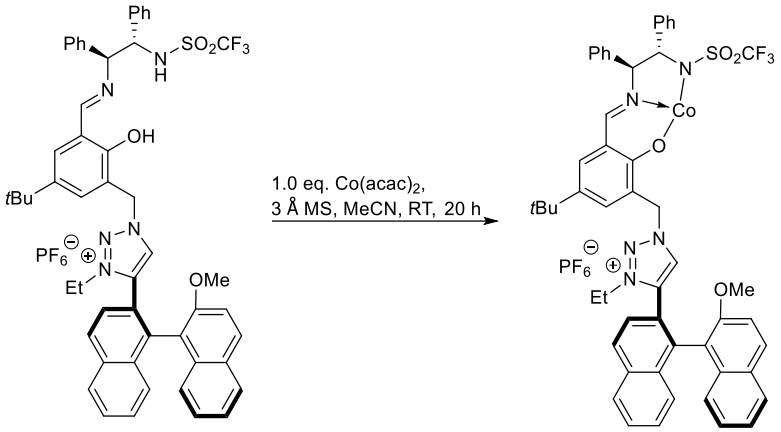


The synthesis of phenoxyimine-Co(II) complex **C6*HPF$_6$** was performed according to **GP 6**. The phenolimine-Preligand **L-4** (100.0 mg, 0.102 mmol, 1.0 eq.) and Co(acac)$_2$ (26.40 mg, 0.102 mmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C6*HPF$_6$** was isolated as yellowish brown solid (110.2mg, 0.102 mmol, 99%). **C$_{51}$H$_{45}$CoF$_9$N$_5$O$_4$PS, MW:** 1084.90 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP**: 197-199 °C, decomposition. **$[\alpha]^{20}_D$** = +63 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$): $\tilde{\nu}$** = 3450, 2955, 2022,1623, 1553, 1452, 1326, 1273, 1185, 1147, 547, 559. **HRMS (ESI) *m/z***: Calculated for [M-PF$_6$]$^+$ $C_{51}H_{45}CoF_3N_5O_4S^+$: 939.2471. Found: 939.2467 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



2.5.9 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-2-oxy-3-(-(((1*S*,2*S*)-2-(naphthalen-2-sulfonamido)-1,2 diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2´-methoxy-[1,1´- binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (CC1) [14]

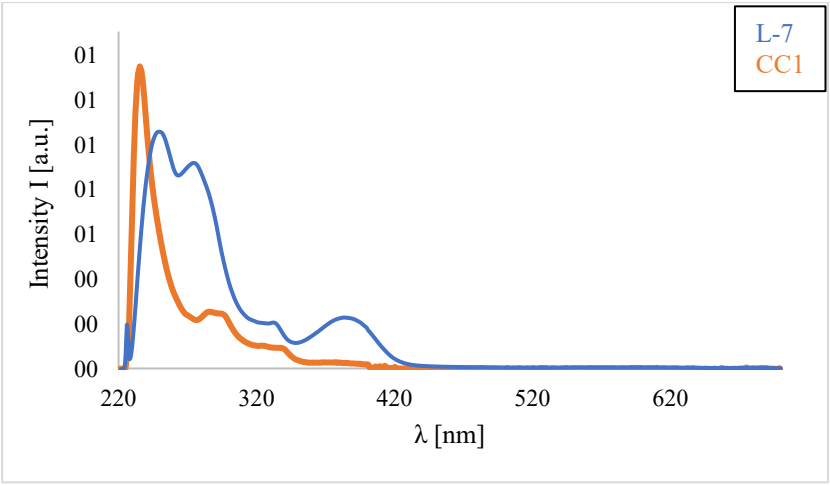


L-7 CC1

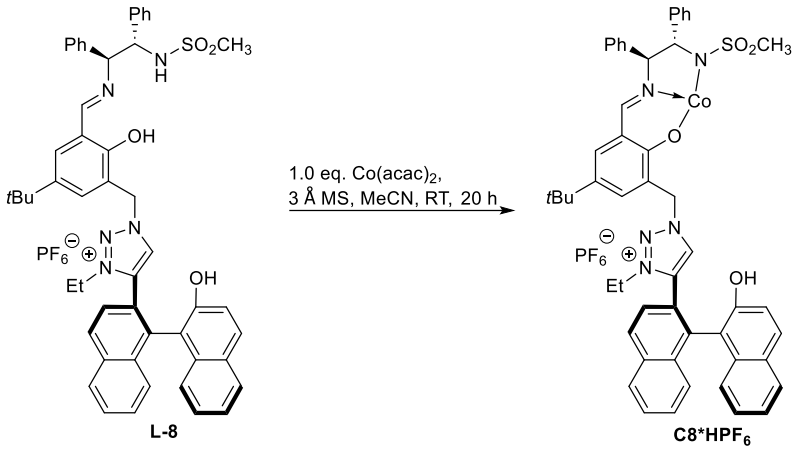
The synthesis of phenoxyimine-Co(II) complex **CC1** was performed according to **GP 6**. The phenolimine-preligand **L-7** (25.0 mg, 0.024 mmol, 1.0 eq.) and $Co(acac)_2$ (6.1 mg, 0.024 mmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **CC1** was isolated as yellowish brown solid (26.1 mg, 0.024 mmol, 99%).

$C_{52}H_{47}CoF_9N_5O_4PS$, MW: 1098.93 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP**: 180-184 °C, decomposition. **$[\alpha]^{20}_D$** = +61 (c = 0.1 g/dl, DCM). **IR ($CDCl_3$): $\tilde{\nu}$** = 3054, 2956, 1625, 1594, 1554, 1329, 1271, 1150, 838, 556. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{52}H_{47}CoF_3N_5O_4S^+$: 953.2627. Found: 953.2424 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):

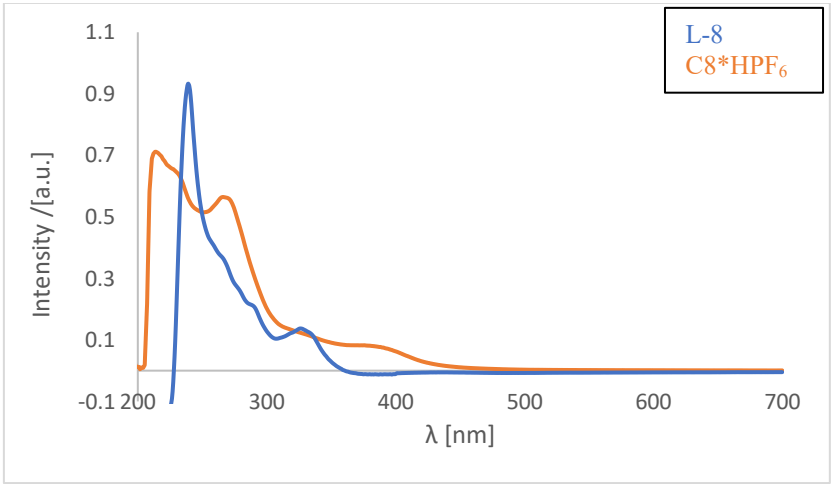


2.5.10 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-2-oxy-3-(-(((1*S*,2*S*)-2-(methylsulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((R)-2´-hydroxy-[1,1´-binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (C8*HPF$_6$) [14]

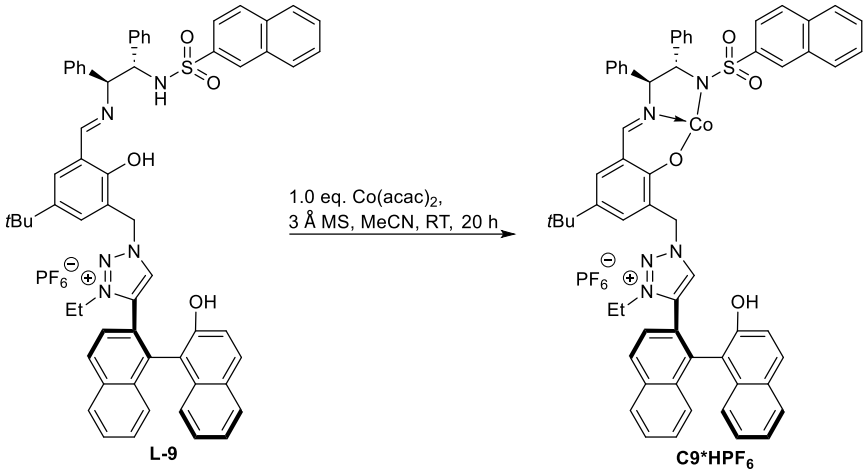


The synthesis of phenoxyimine-Co(II) complex **C8*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-8** (25.0 mg, 25.6 µmol, 1.0 eq.) and $Co(acac)_2$ (6.6 mg, 0.025 mmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C8*HPF$_6$** was isolated as yellowish brown solid (25.1 mg, 24.3 µmol, 95%). **$C_{51}H_{48}CoF_6N_5O_4PS$, MW:** 1030.92 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 193°C, decomposition. **$[\alpha]^{20}_D$** = +30 (c = 0.1 g/dl, DCM). **IR ($CDCl_3$): $\tilde{\nu}$** = 3054, 2959, 2932, 1625, 1584, 1514, 1435,1390, 1345, 1274, 1245, 1220, 1115, 1022, 971, 936, 843, 821, 751, 702, 629, 558. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{51}H_{48}CoN_5O_4S^+$: 855.2753. Found: 844.2750 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



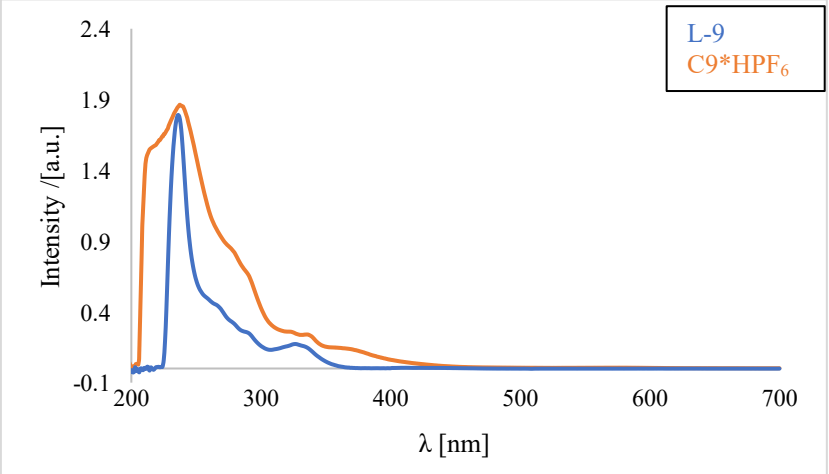
2.5.11 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-2-oxy-3-(-(((1*S*,2*S*)-2-(naphthyl-2-sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((R)-2'-hydroxy-[1,1'-binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (C9*HPF$_6$) [14]



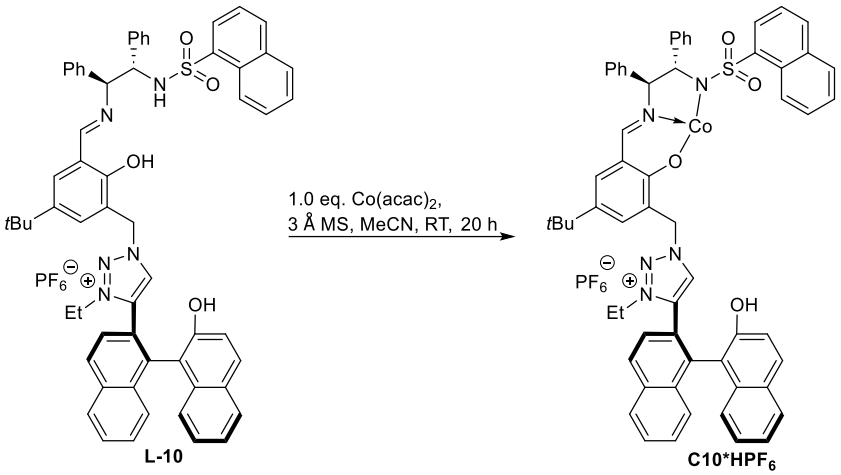
The synthesis of phenoxyimine-Co(II) complex **C9*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-9** (25.0 mg, 23.4 µmol, 1.0 eq.) and Co(acac)$_2$ (5.9 mg, 23.4 µmol, 1.0 eq.) were used. Phenoxyimine-Co(II) complex **C9*HPF$_6$** was isolated as yellowish brown solid (20.5 mg, 17.9 µmol, 78%).

C$_{60}$H$_{52}$CoF$_6$N$_5$O$_4$PS, MW: 1143.06 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 224-230°C, decomposition. **$[\alpha]^{20}_D$** = +71 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$): $\tilde{\nu}$** = 3055, 2961, 2869, 1625, 1587, 1516, 1454, 1434, 1391, 1345, 1273, 1121, 1019, 971, 928, 843, 819, 750, 700, 644, 556. **HRMS (ESI) *m/z***: Calculated for [M-PF$_6$]$^+$ C$_{60}$H$_{52}$CoN$_5$O$_4$S$^+$: 997.3067. Found: 997.3061 Calculated for PF$_6^-$: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-4} M):

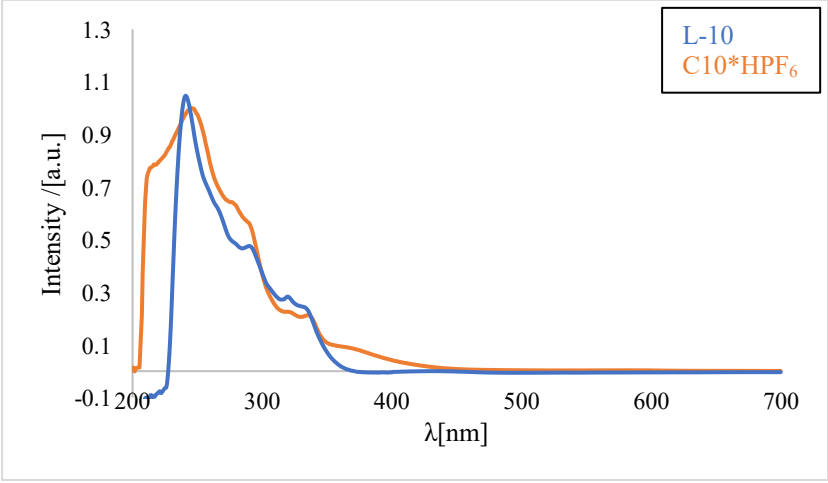


2.5.12 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-2-oxy-3-(-(((1*S*,2*S*)-2-(naphthyl-1-sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2´-hydroxy-[1,1´-binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (C10*HPF$_6$) [14]

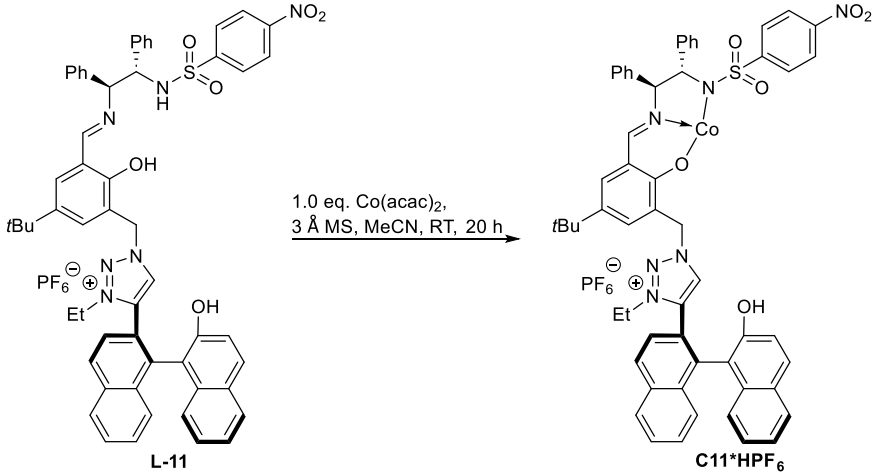


The synthesis of phenoxyimine-Co(II) complex **C10*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-10** (25.0 mg, 23.4 µmol, 1.0 eq.) and $Co(acac)_2$ (5.9 mg, 23.4 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C10*HPF$_6$** was isolated as yellowish brown solid (24.6 mg, 21.5 µmol, 94%). **$C_{60}H_{52}CoF_6N_5O_4PS$, MW:** 1143.06 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 220-230°C, decomposition. **$[\alpha]^{20}_D$** = +35 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$): $\tilde{\nu}$** = 3056, 2959, 2870, 1624, 1585, 1513, 1454, 1434, 1392, 1344, 1273, 1245, 1219, 1118, 1021, 973, 936, 843, 820, 772, 751, 700, 591, 557. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{60}H_{52}CoN_5O_4S^+$: 997.3067. Found: 997.3061 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):

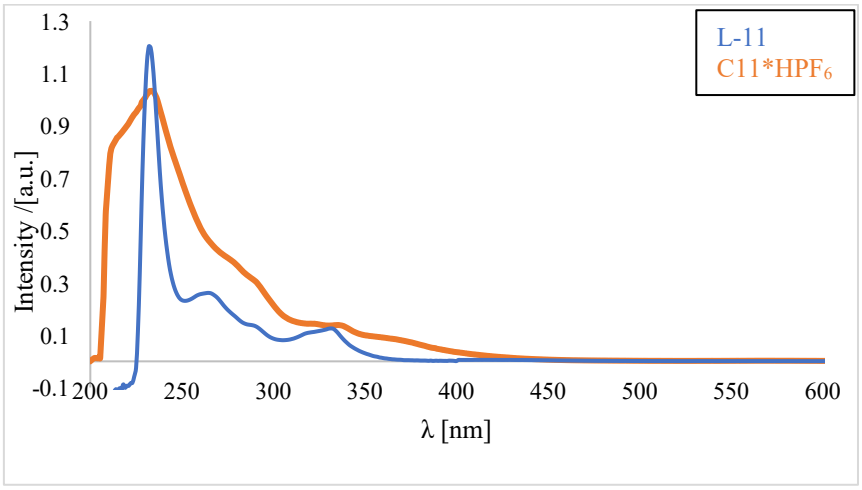


2.5.13 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-2-oxy-3-(-(((1*S*,2*S*)-2-(4-nitrophenyl)sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2´-hydroxy-[1,1´-binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (C11*HPF$_6$) [14]

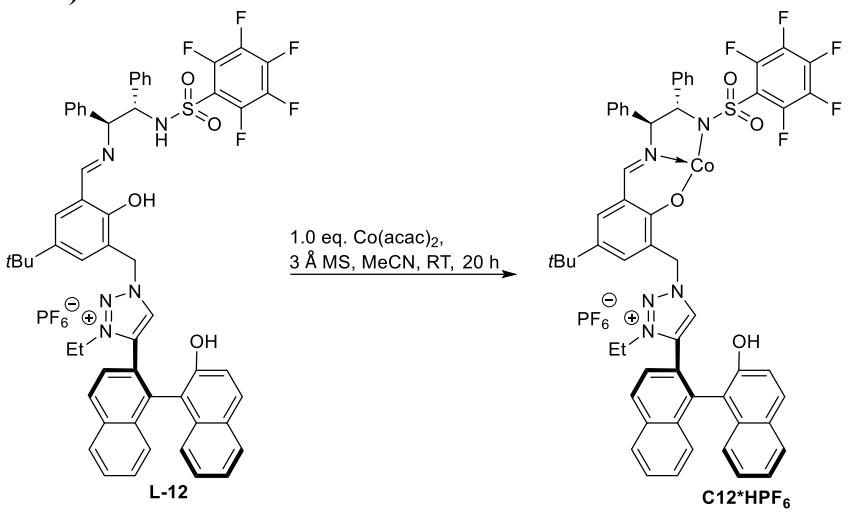


The synthesis of phenoxyimine-Co(II) complex **C11*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-11** (25.0 mg, 23.1 µmol, 1.0 eq.) and Co(acac)$_2$ (5.9 mg, 23.1 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C11*HPF$_6$** was isolated as yellowish brown solid (24.7 mg, 21.7 µmol, 94%). **C$_{56}$H$_{49}$CoF$_6$N$_6$O$_6$PS, MW:** 1137.98 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 248°C, decomposition. **$[\alpha]^{20}_D$** = -112 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$): $\tilde{\nu}$** = 3060, 2958, 2870, 1625, 1586, 1520, 1454, 1434, 1392, 1346, 1273, 1220, 1118, 1136, 1099, 1019, 976, 936, 842, 749, 735, 701, 628, 557. **HRMS (ESI) *m/z***: Calculated for [M-PF$_6$]$^+$ $C_{56}H_{49}CoN_6O_6S^+$: 992.2760. Found: 992.2763 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



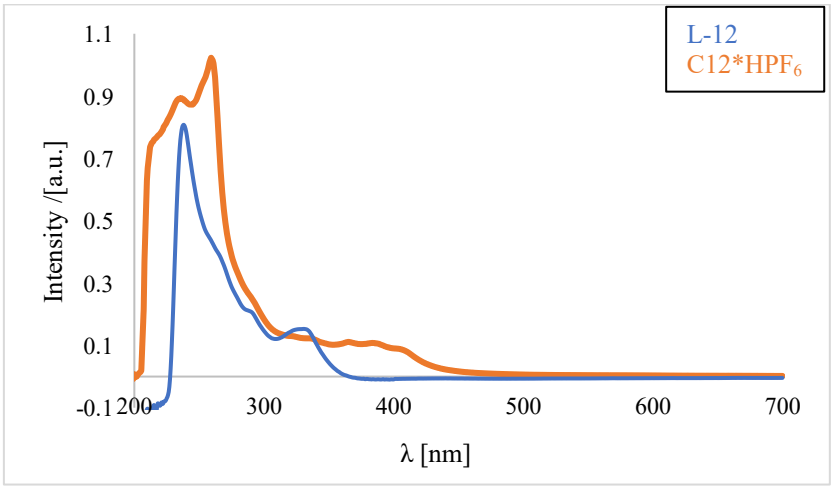
2.5.14 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-2-oxy-3-(-(((1*S*,2*S*)-2-(hexafluorophenyl)sulfonamido)-1,2-diphenylethyl)imino)methyl)benzyl)-3-ethyl-4-((*R*)-2'-hydroxy-[1,1'-binaphthalene]-2-yl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (C12*HPF$_6$) [14]



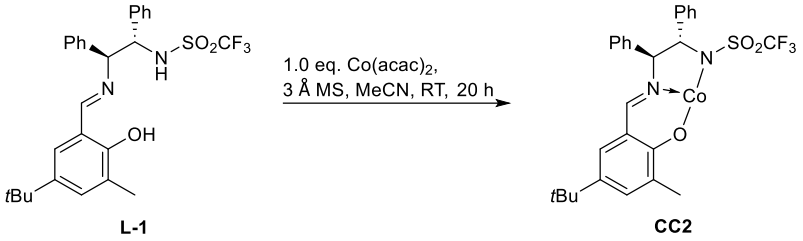
The synthesis of phenoxyimine-Co(II) complex **C12*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-12** (25.0 mg, 22.6 µmol, 1.0 eq.) and Co(acac)$_2$ (5.7 mg, 22.6 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **C12*HPF$_6$** was isolated as yellowish brown solid (25.1mg, 21.2 µmol, 96%).

C$_{56}$H$_{45}$CoF$_{11}$N$_5$O$_4$PS, MW: 1182.94 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 210-215 °C, decomposition. **$[\alpha]^{20}_D$** = +60 (c = 0.1 g/dl, CH_2Cl_2). **IR (CDCl$_3$):** $\tilde{\nu}$ = 3064, 2951, 2869, 1626, 1584, 1521, 1456, 1434, 1394, 1342, 1276, 1221, 1117, 1134, 1106, 1020, 975, 936, 841, 750, 734, 698, 625, 554. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{56}H_{45}CoF_5N_5O_4S^+$: 1037.2438. Found: 1037.2436 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



2.5.15 Synthesis of the Co(II)-Precatalyst ((1*S*,2*S*)-2-((5-(tert-Butyl)-2-oxy-3 methylbenzylidene) amino)-1,2-diphenylethyl)-1,1,1-trifluoromethane sulfonamide-Co(II) (CC2) [14]

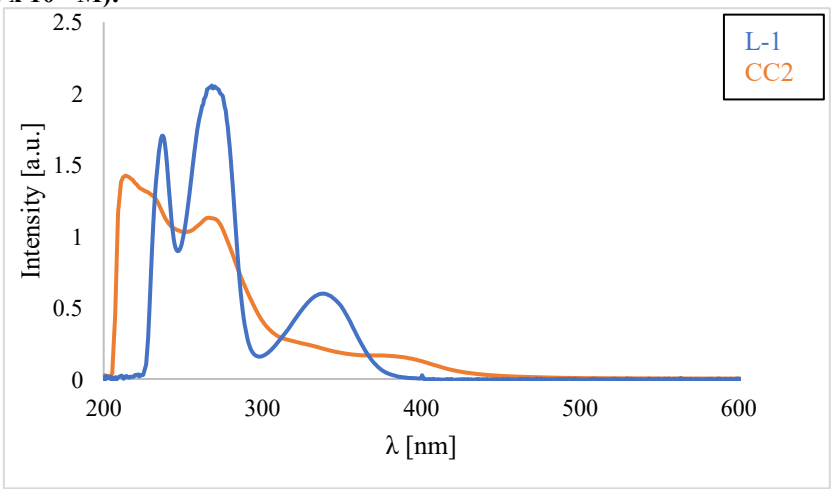


L-1 CC2

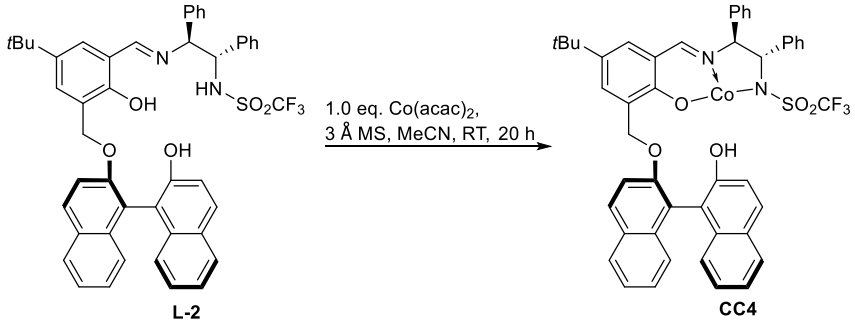
The synthesis of phenoxyimine-Co(II) complex **CC2** was performed according to **GP 6**. The phenolimine-preligand **L-1** (25.0 mg, 48.2 µmol, 1.0 eq.) and $Co(acac)_2$ (12.4 mg, 48.2 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **CC2** was isolated as yellowish brown solid (24.7 mg, 42.9 µmol, >99%).

$C_{27}H_{27}CoF_3N_2O_3S$, MW: 575.51 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **$[\alpha]^{20}_D$** = -39 (c = 0.1 g/dl, CH_2Cl_2). **IR ($CDCl_3$): $\tilde{\nu}$** = 3064, 3031, 2958, 2869, 1622, 1585, 1521, 1454, 1433, 1380, 1302, 1266, 1227, 1186, 1145, 1026, 927, 834, 763, 699, 618, 606, 514, 419. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{27}H_{27}CoF_3N_2O_3S^+$: 575.1026. Found: 575.1017

UV/Vis (DCM, 2 x 10^{-4} M):



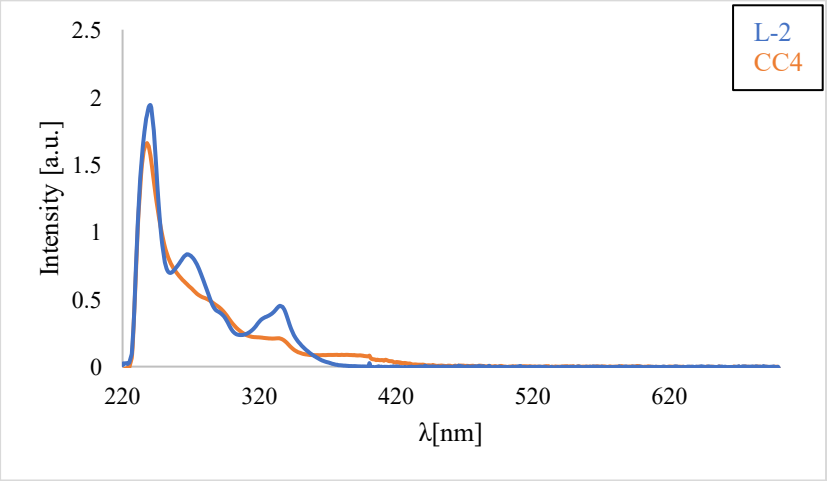
2.5.16 Synthesis of the Co(II)-Precatalyst ((1*S*,2*S*)-2-((-5-(*tert*-Butyl)-2oxy-3-((((*R*)-2´-hydroxy-[1,1´-binaphthalene]-2-yl)oxy)methyl)benzylidene)amino)-1,2-diphenylethyl)-1,1,1-trifluoromethane sulfonamide Co(II) (CC4) [14]



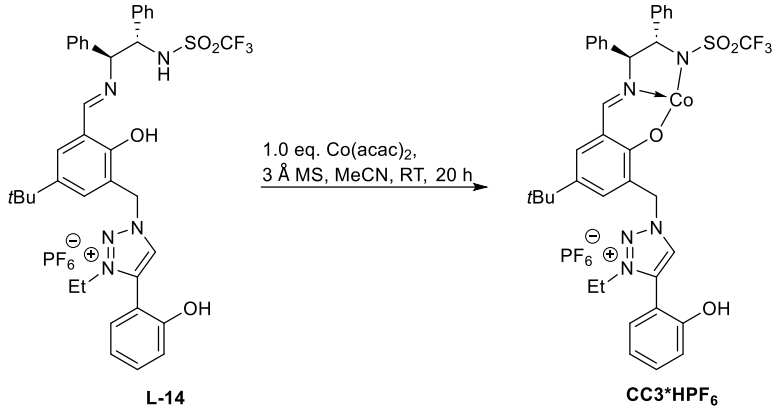
L-2 CC4

The synthesis of phenoxyimine-Co(II) complex **CC4** was performed according to **GP 6**. The phenolimine-Preligand **L-2** (25.0 mg, 31.1 µmol, 1.0 eq.) and $Co(acac)_2$ (12.40 mg, 31.1 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **CC4** was isolated as yellowish brown solid (25.1 mg, 29.1 µmol, 94%).
$C_{47}H_{39}CoF_3N_2O_5S$, MW: 859.82 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP**: 180-182 °C, decomposition. **$[\alpha]^{20}_D$** = +59 (c = 0.1 g/dl, DCM). **IR ($CDCl_3$): $\tilde{\nu}$** = 3538, 2960, 1622, 1591, 1519, 1456, 1380, 1308, 1266, 1188, 1146, 1072, 911, 815, 749, 700, 608, 512. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{47}H_{40}CoF_3N_2O_5S^+$: 860.1936. Found: 860.1937

UV/Vis (DCM, 2 x 10^{-4} M):

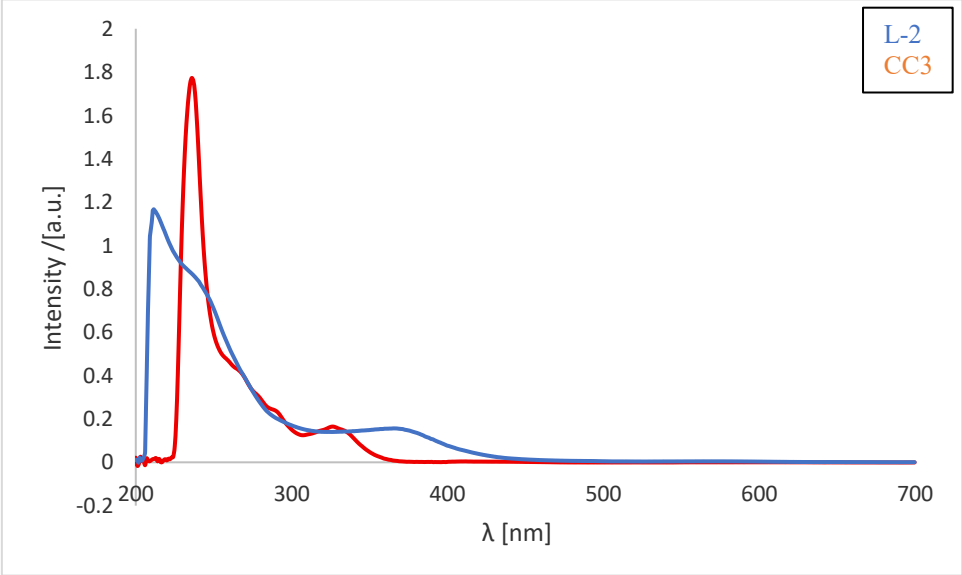


2.5.17 Synthesis of the Co(II)-Precatalyst 1-(5-(*tert*-Butyl)-3-((((1*S*,2*S*)-1,2 diphenyl-2-((trifluoromethyl)sulfonamido)ethyl)imino)methyl)-2 oxybenzyl)-3-ethyl-4-(2-hydroxyphenyl)-1H-1,2,3-triazol-3-ium-Co(II) Hexafluorophosphate (CC3*HPF$_6$) [14]

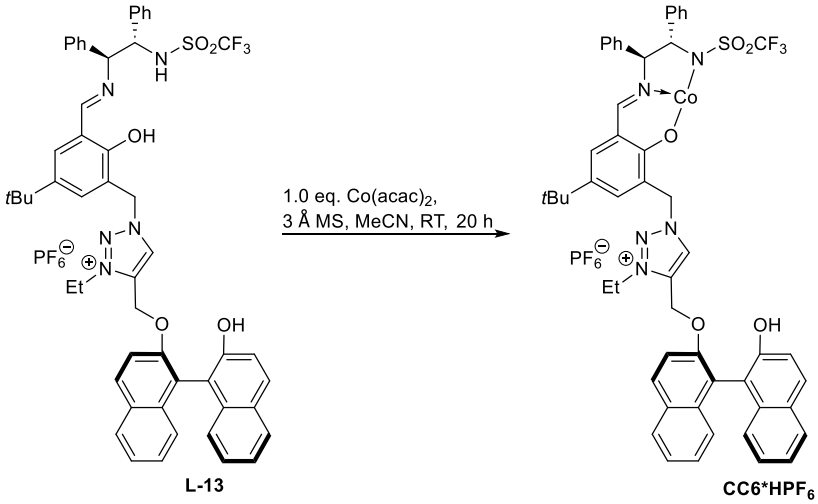


The synthesis of phenoxyimine-Co(II) complex **CC3*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-14** (25 mg, 29.4 µmol, 1.0 eq.) and Co(acac)$_2$ (7.6 mg, 29.4 µmol, 1.0 eq.) were used. The Phenoxyimine-Co(II) complex **CC3*HPF$_3$** was isolated as yellowish brown solid (24.7 mg, 27.0 µmol, 92%). **C$_{37}$H$_{37}$CoF$_9$N$_5$O$_4$PS, MP:** 908.68 g/mol. **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 242-245 °C, decomposition. **$[\alpha]^{20}_D$** = -29 (c = 0.1 g/dl, DCM). **IR (CDCl$_3$):** $\tilde{\nu}$ = 3442, 2960, 2298, 2225, 2183, 2166, 2121, 1992, 1966, 1628, 1547, 1455, 1392, 1312, 1180, 1069, 931, 842, 766, 701, 612, 558, 512, 430. **HRMS (ESI)** ***m/z***: Calculated for [M-PF$_6$]$^+$C$_{37}$H$_{37}$CoF$_3$N$_5$O$_4$S$^+$: 763.1845 Found: 763.1839. Calculated for PF$_6^-$: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



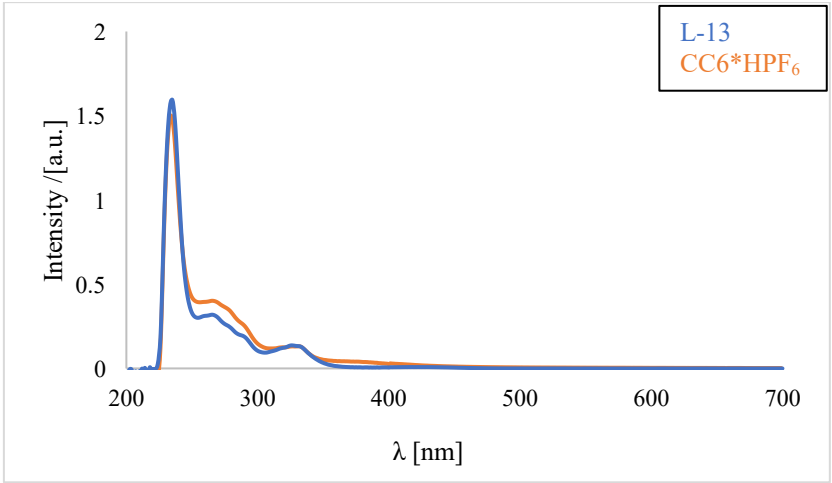
2.5.18 Synthesis of Phenoxyimine-Co(II) Precatalyst 1-(5-(*tert*-Butyl)-3-(-(((1*S*,2*S*)-1,2-diphenyl-2-((trifluoromethyl)-sulfonamido)ethyl)imino)methyl)-2-oxybenzyl)-3-ethyl-4-((((*R*)-2'-hydroxy-[1,1'-binaphthalene]-2-yl)oxy)methyl)-1H-1,2,3-triazol-3-ium Hexafluorophosphate Co(II) (CC6*HPF$_6$) [14]



L-13 CC6*HPF$_6$

The synthesis of phenoxyimine-Co(II) complex **CC6*HPF$_6$** was performed according to **GP 6**. The phenolimine-preligand **L-13** (25.0 mg, 24.0 µmol, 1.0 eq.) and Co(acac)$_2$ (6.1 mg, 24.0 µmol, 1.0 eq.) were used. The phenoxyimine-Co(II) complex **CC6*HPF$_6$** was isolated as yellowish brown solid (26.3 mg, 24.0 µmol, >99%). **C$_{52}$H$_{47}$CoF$_9$N$_5$O$_5$PS, MW:** 1114.93 g/mol **^{1}H-NMR:** paramagnetic species, no NMR spectra recorded. **^{13}C-NMR:** paramagnetic species, no NMR spectra recorded. **MP.:** 182-186 °C, decomposition. **$[\alpha]^{20}_D$** = -26 (c = 0.1 g/dl, CH_2Cl_2). **IR (CDCl$_3$): $\tilde{\nu}$** = 3137, 3061, 3030, 2963, 1642, 1592, 1547, 1509, 1454, 1433, 1381, 1365, 1298, 1271, 1209, 1176, 1145, 1071, 1020, 908, 840, 728, 699, 647, 614, 599, 558, 513, 494. **HRMS (ESI) *m/z***: Calculated for $[M\text{-}PF_6]^+$ $C_{51}H_{45}CoF_3N_5O_4S^+$: 939.2471. Found: 939.2467 Calculated for PF_6^-: 144.96. Found: 144.96.

UV/Vis (DCM, 2 x 10^{-5} M):



2.6 Catalyst and Condition Screening

2.6.1 Metal Screening

To evaluate the influence of different metal centers and different ligand configurations, the catalytic reaction was carried out following general procedure **GP7**. In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (1.02 mmol, 20 eq.), and the corresponding catalyst (5 mol%) were used. The reaction mixtures were stirred under standard conditions, and the results of the screening experiments are summarized in **Table S1**. The activation of the Co, Cu, and Ni catalysts was carried out using the procedure developed by Willig *et al.*[14] The Zn catalyst was prepared in-situ using ligand **L-5** and diethylzinc.

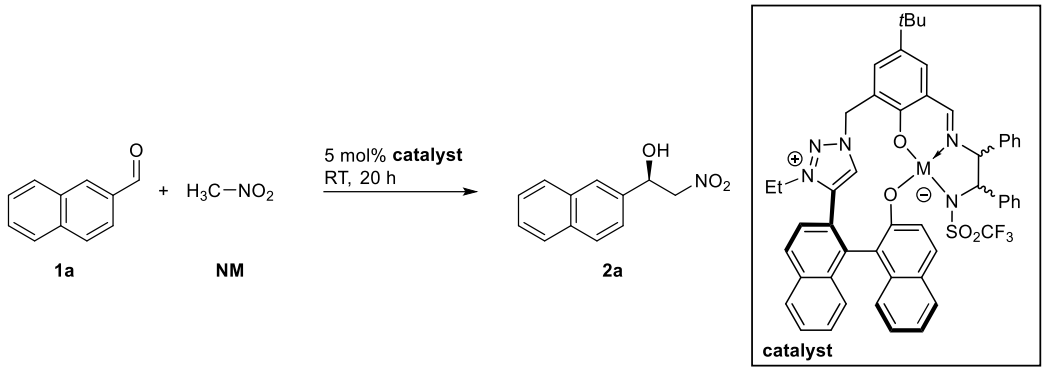


Table S1: Metal screening of the nitroaldol reaction between 2-napthaldehyde **(1a)** and nitromethane (**NM)**

entry	M	configuration	catalyst	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	Cu	(*R, R*)	C7	42	42	80
2	Cu	(*S, S*)	C3	15	15	19
3	Co	(*R, R*)	C6	87	87	35
4	**Co**	**(*S, S*)**	**C5**	**76**	**76**	**73**
5	Ni	(*S, S*)	C4	38	38	40
6	Zn	(*S, S*)	CC10	90	71	11

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.6.2 Activation Method Screening with Co catalyst

To investigate the activation of the Co catalyst using different bases and the effect of various filtration methods, the catalytic reactions were performed according to general procedure **GP7**. In each experiment, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (1.02 mmol, 20 eq.), and the corresponding catalyst (5 mol%) were used (**Table S2**).

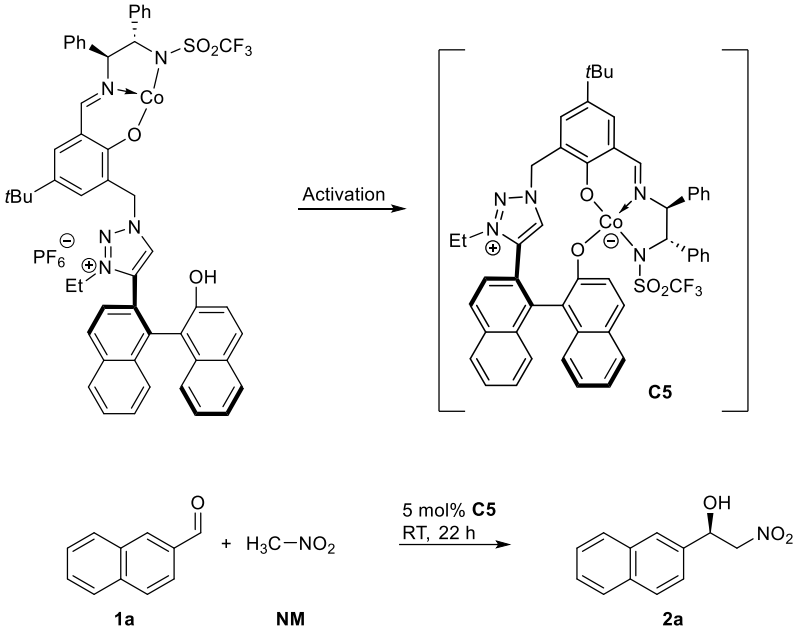


Table S2: activation of the nitroaldol reaction between 2-napthaldehyde **(1A)** and nitromethane (**NM)**

entry	activation	method	conversation [%][1]	yield [%][1]	*ee* [%][2]
1[3]	DCM:THF:NEt_3	Silica gel	76	76	73
2[3]	DCM:THF:NEt_3	Water extraction	75	75	67
3[3]	DCM:THF:NEt_3	Alumina oxide neutral	82	82	*rac*
4[3]	**DCM:THF:DIPEA**	Silica gel	**86**	**86**	**75**
5[3]	DCM:THF:DIPEA	Water extraction	80	80	70
6[3]	DCM:THF:DIPEA	Alumina oxide neutral	85	85	*rac*
7[4]	Cs_2CO_3 (THF)	Silica gel	67	67	*56*
8[4]	K_2CO_3 (THF)	Silica gel	11	10	52
9[5]	K*t*OBu (THF)	Silica gel	93	93	38

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase. [3] activation mixture of 66:33:1 was used. [4]excesses of base used. [5]1.0 eq. used.

2.6.3 Temperature Screening

To investigate the influence of temperature on the nitroaldol reaction, the catalytic reactions were performed according to general procedure **GP7**. In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (1.02 mmol, 20 eq.), and the corresponding catalyst (5 mol%) were used (**Table S3**).

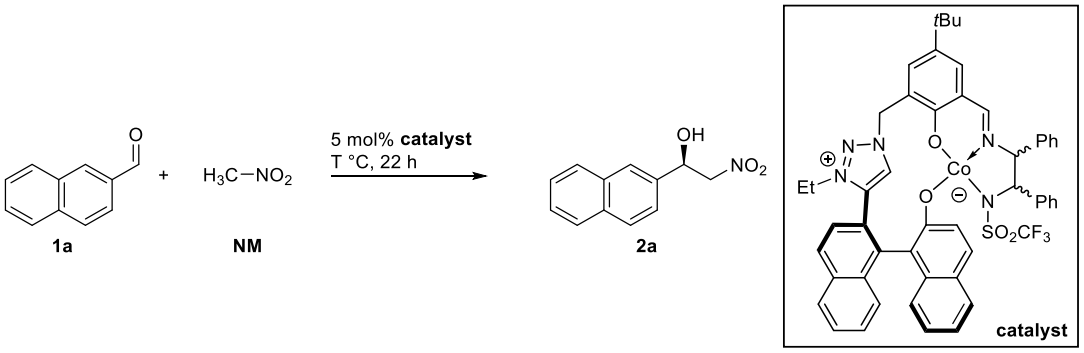


Table 3: Temperature screening of the nitroaldol reaction between 2-napthaldehyde (**1a)** and nitromethane **(NM)**

entry	T	configuration	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	-20	(S, S)	68	68	29
2	-20	(R, R)	63	63	13
3	0	(S, S)	93	93	40
4	0	(R, R)	92	92	18
5	RT	(S, S)	86	86	75
6	RT	(R, R)	87	87	35
7	40	(S, S)	80	80	84
8	40	(R, R)	82	82	70
9	**45**	**(S, S)**	**80**	**80**	**97**
10	50	(S, S)	78	78	91
11	55	(S, S)	72	72	83
12	60	(S, S)	61	60	81

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.6.4 Sulfonamides Screening

For screening the different sulfonamides on the nitroaldol reaction, the catalytic reactions were performed according to general procedure **GP7**. In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (1.02 mmol, 20 eq.), and the corresponding catalyst (5 mol%) were used (**Table S4)**.

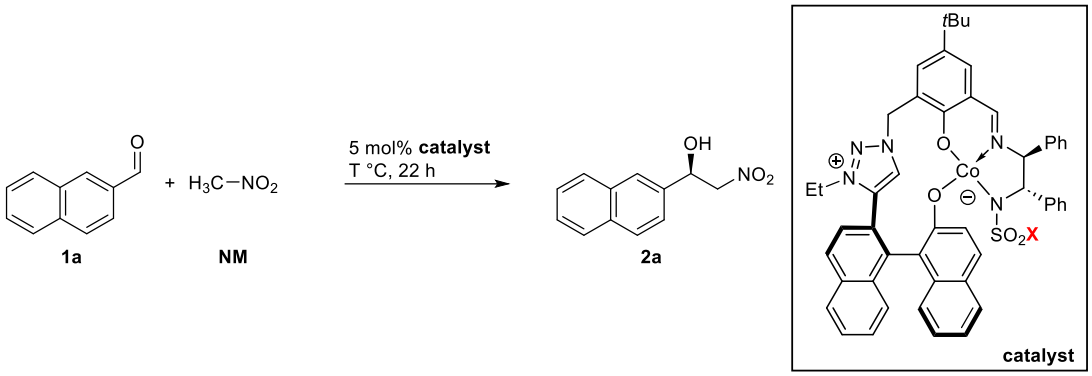


Table S4: sulphonamide screening of the nitroaldol reaction between 2-napthaldehyde (**1a)** and nitromethane **(NM)**

entry	X	catalyst	T (°C)	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	**-CF_3**	**C5**	**45**	**80**	**80**	**97**
2	**-CF_3**	**C5**	50	**78**	**78**	**91**
3	-CH_3	C8	50	40	40	*rac*
4	2-naphthyl	C9	50	71	70	74
5	1-naphthyl	C10	50	68	68	62
6	-nosyl	C11	50	66	66	69
7	-C_6F_6	C12	50	50	50	57

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.6.5 Catalyst Loading Screening

For screening the catalyst loading on the nitroaldol reaction, the catalytic reactions were performed according to general procedure **GP7**. In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (1.02 mmol, 20 eq.), and the corresponding catalyst (5 mol%) were used (**Table S5**).

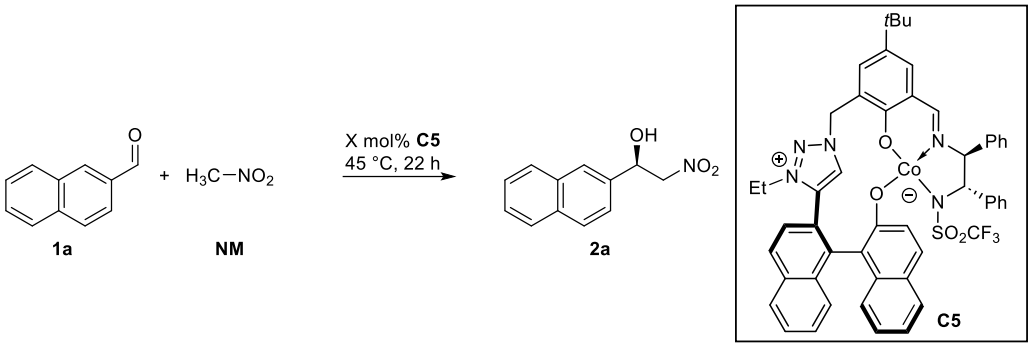


Table S5: catalyst loading screening of the nitroaldol reaction between 2-napthaldehyde (**1a**) and nitromethane **(NM)**

entry	C5 (X mol%)	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	**5.0**	**80**	**80**	**97**
2	4.0	81	81	94
3	3.0	76	76	91
4	2.0	73	73	87
5	**1.0**	**70**	**70**	**86**
6	0.5	56	56	85

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.6.6 Order of Addition of Substrate

For screening the order of addition of substrate on the nitroaldol reaction, the catalytic reactions were performed according to general procedure **GP7** but with the order of addition mentioned in **Table S6.** In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (0.55 mmol, 10 eq.), and the corresponding catalyst (5 mol%) were used.

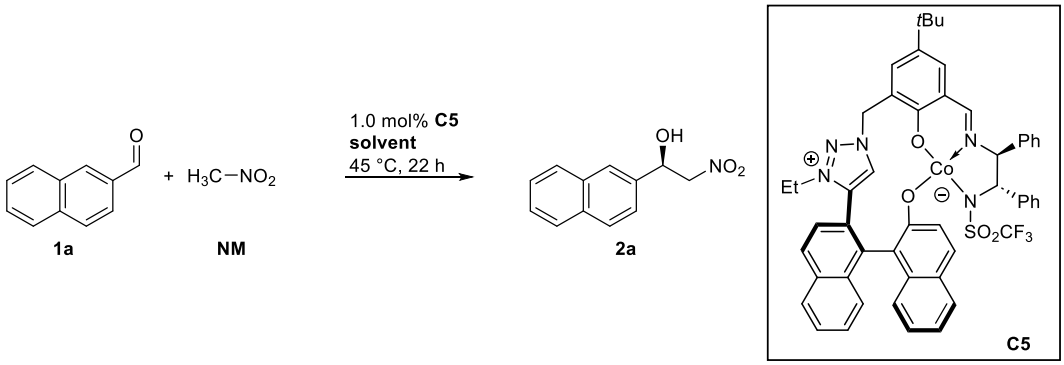


Table S6: Investigation of order of addition of substrate in the nitroaldol reaction between 2-napthaldehyde (**1a)** and nitromethane (**NM)**

entry	Order of addition	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	Stirring **C5** with **NM** for 15 min then addition of **1a** with 1M THF	79	79	86
2	Stirring **C5** with **NM** for 15 min then adding **1a** with **NM**	**74**	**74**	**96**
3	Stirring **C5** with 1M THF and **NM** for 15 min then adding **1a** with **Nm**	80	80	85
4	Stirring **C5** with **1a** in 1M THF for 15 min then adding **NM**	75	74	86

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.6.7 Solvent Screening

For screening the solvent on the nitroaldol reaction, the catalytic reactions were performed according to general procedure **GP7**. In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (0.55 mmol, 10 eq.), and the corresponding catalyst (5 mol%) were used (**Table S7**).

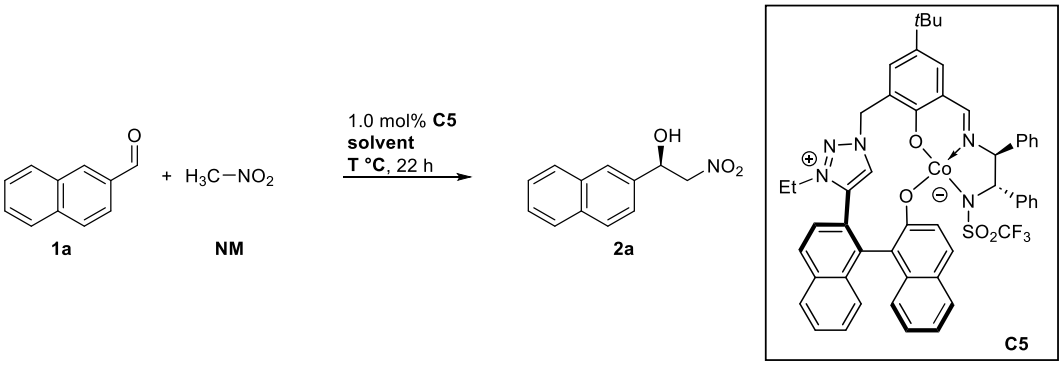


Table 7: solvent screening of the nitroaldol reaction between 2-napthaldehyde (**1a)** and nitromethane (**NM)**

entry	solvent	T (°C)	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	toluene	25	66	66	60
2	MeCN	25	43	43	69
3	DCM	25	25	25	55
4	THF	25	80	80	91
5	**CH_3NO_2**	**25**	**86**	**86**	**93**
6	toluene	50	10	10	54
7	MTBE	50	71	71	22
8	MeCN	50	30	30	71
9	DCE	50	26	26	42
10	$CHCl_3$	50	17	17	56
11	THF	50	76	76	93
12	DME	50	58	58	40
13	CH_3NO_2	50	78	78	91
14	**CH_3NO_2**	**45**	**74**	**74**	**96**
15	DMSO	50	90	90	*rac*

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.6.8 Screening of Additives

For screening the additives on the nitro-aldol reaction using, the catalytic reactions were performed according to general procedure **GP7**. In each case, **1a** (8 mg, 0.05 mmol, 1.0 eq.), **NM** (0.55 mmol, 10 eq.), and the corresponding catalyst (5 mol%) were used (**Table S8**).

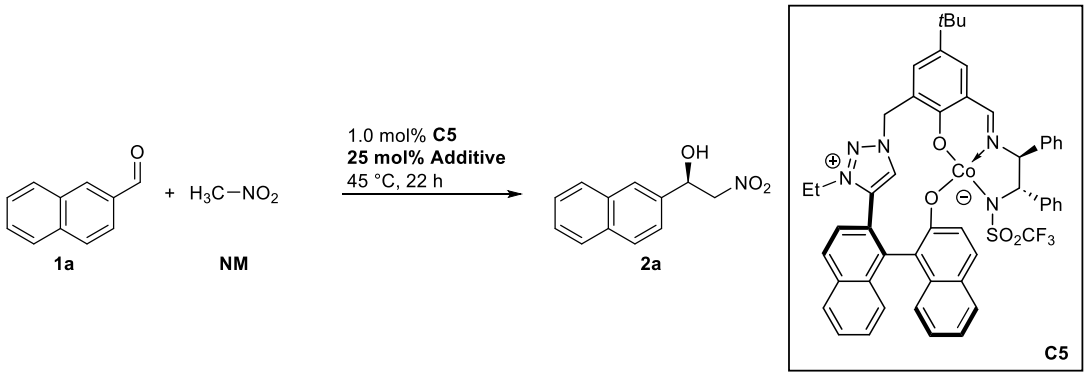


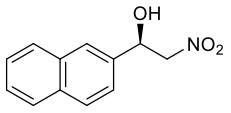
Table S8: Screening of additives in the nitroaldol reaction between 2-napthaldehyde (**1a)** and nitromethane (**NM**)

entry	additive	conversation [%][1]	yield [%][1]	*ee* [%][2]
1	**-**	**74**	**74**	**96**
2	Water	67	67	85
3	HFIP	70	70	86
4	MeOH	62	61	85
5	EtOH	60	60	84
6	*i*-PrOH	61	61	80
7	*n*-BuOH	57	56	81
8	Phenol	64	64	85
9	Acetic Acid	38	38	76
10	DIPEA	84	84	52

[1]Determined by ^{1}H-NMR using Mesitylene as internal standard. [2]Determined by HPLC on chiral, stationary phase.

2.7 Synthesis of Asymmetric Nitroaldol Products

2.7.1 Synthesis of (*R*)-1-(Naphthalen-2-yl)-2-nitroethan-1-ol (2a) [29]



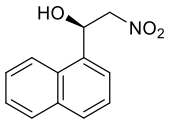
2a

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 2-naphthaldehyde (**1a**, 40.0 mg, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 165 µL, 3.07 mmol, 12 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 5:1), the desired product **2a** was obtained as a white solid (41.2 mg, 0.19 mmol, 74% yield with 96% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of cyclohexane/*i*-PrOH (80:20) at a flow rate of 1.0 mL/min over 30 min. Detection was performed at 211 nm, with retention times of $\mathbf{t}_{maj}$ **(*R*)** = 13.8 min and $\mathbf{t}_{min}$**(*S*)** = 18.8 min.

$C_{12}H_{11}NO_3$, **MW**: 217.22 g/mol. **^{1}H-NMR** (**400 MHz, $CDCl_3$**): δ = 7.92-7.82 (*m*, 4H, Ar-*H*), 7.57-7.45 (*m*, 2H, Ar-*H*), 7.44-7.40 (*m*, 1H, Ar-*H*), 5.64 (*dt*, *J*= 2.9, 9.5 Hz, 1H, C*H*-OH), 4.74-4.66 (*dd*, *J*= 1.5, 8.4 Hz, 1H, CH_2-NO_2), 4.64-4.57 (*dd*, *J*= 9.4, 13.5 Hz, 1H, CH_2-NO_2), 2.88 (br, *s*, 1H, CH-O*H*) ppm.

The analytical data for **2a** agrees with the literature. [32]

2.7.2 Synthesis of (*R*)-1-(Naphthalen-1-yl)-2-nitroethan-1-ol (2b) [32]



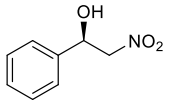
2b

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 1-naphthaldehyde (**1b**, 40.0 mg, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 165 µL, 3.07 mmol, 12 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 5:1), the desired product **2b** was obtained as a white solid (39.7 mg, 0.18 mmol, 71% yield, 89% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 1.0 mL/min over 40 min. Detection was performed at 254 nm, with retention times of $\mathbf{t}_{maj}$**(*R*)** = 19.7 min and $\mathbf{t}_{min}$**(*S*)** = 30.5 min.

$C_{12}H_{11}NO_3$, **MW**: 217.22 g/mol. **^{1}H-NMR** (**400 MHz, $CDCl_3$**): δ = 8.06 (*d*, 1H, Ar-*H*), 7.93-7.77 (*m*, 2H, Ar-*H*), 7.73 (*d*, 1H, Ar-*H*), 7.64-7.50 (m, 3H, Ar-*H*), 6.28 (dd, 1H, C*H*-OH), 4.98-4.88 (*m*, 2H, CH_2-NO_2), 2.88 (*s*, br,1H, CH-O*H*) ppm.

The analytical data for **2b** agrees with the literature. [32]

2.7.3 Synthesis of (*R*)-2-Nitro-1-phenylethan-1-ol (2c) [32]



2c

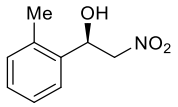
The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, benzaldehyde (**1c**, 38.3 µL, 0.37 mmol, 1.0 eq.), nitromethane (**NM**, 242 µL, 4.52 mmol, 12 eq.), and catalyst **C5** (3.54 mg, 3.8µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2c**

was obtained as a white solid (49.2 mg, 0.29 mmol, 78% yield, 86% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 1.0 mL/min over 40 min. Detection was performed at 211 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 21.4 min and $\mathbf{t_{min}(S)}$ = 26.9 min.

$C_8H_9NO_3$, **MW**: 167.06 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.60 – 7.31 (*m*, 5H, Ar-*H*), 5.46 (*dd*, *J*= 9.4, 13.4 Hz, 1H, C*H*-OH), 4.62 – 4.45 (*m*, 2H, CH_2-NO_2), 2.98 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2c** agrees with the literature. [32]

2.7.4 Synthesis of (*R*)-2-Nitro-1-(*o*-tolyl)-ethan-1-ol (2d) [30]



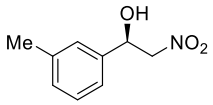
2d

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, o-tolylaldehyde (**1d**, 34.3 µL, 0.32 mmol, 1.0 eq.), nitromethane (**NM**, 212 µL, 3.95 mmol, 12 eq.), and catalyst **C5** (3.10 mg, 3.3µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2d** was obtained as a white solid (50.7 mg, 0.29 mmol, 84% yield, 92% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 1.0 mL/min over 40 min. Detection was performed at 211 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 17.3 min and $\mathbf{t_{min}(S)}$ = 28.2 min.

$C_9H_{11}NO_3$, **MW**: 181.07 g/mol. **^{1}H-NMR (300 MHz, $CDCl_3$)**: δ = 7.56−7.52 (*t*, 1H, Ar-*H*), 7.31−7.26 (*m*, 2H, Ar-*H*), 7.14−7.07 (*d*, 1H, Ar-*H*), 5.71 (dd, *J*= 9.5, 2.7 Hz, 1H, C*H*-OH), 4.62−4.52 (*dd*, *J*= 9.4, 13.5 Hz, 1H, CH_2-NO_2), 4.49−4.42 (*dd*, *J*= 2.6, 13.4 Hz, 1H, CH_2-NO_2), 2.72 (*s*, br, 1H, CH-O*H*), 2.41(s, 3H, Ar-CH_3) ppm.

The analytical data for **2d** agrees with the literature. [33]

2.7.5 Synthesis of (*R*)-2-Nitro-1-(*m*-tolyl) ethan-1-ol (2e) [33]



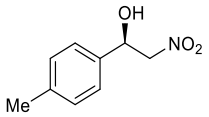
2e

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, m-tolylaldehyde (**1e**, 34.3 µL, 0.32 mmol, 1.0 eq.), nitromethane (**NM**, 212 µL, 3.95 mmol, 12 eq.), and catalyst **C5** (3.10 mg, 3.3µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2e** was obtained as a white solid (54.4 mg, 0.30 mmol, 91% yield, 94% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 23.6min and $\mathbf{t_{min}(S)}$ = 27.7 min.

$C_9H_{11}NO_3$, **MW**: 181.07 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.29–7.24 (*m*, 1H, Ar-*H*), 7.23–7.07 (*m*, 3H, Ar-*H*), 5.41 (dd, *J*= 9.4, 2.9 Hz, 1H, C*H*-OH), 4.65–4.41 (m, 2H, CH_2-NO_2), 2.36 (s, 3H, Ar-CH_3) ppm.

The analytical data for **2e** agrees with the literature. [33]

2.7.6 Synthesis of (*R*)-2-Nitro-1-(*p*-tolyl) ethan-1-ol (2f) [33]



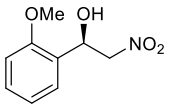
2f

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, *p*-tolylaldehyde (**1f**, 34.3 µL, 0.32 mmol, 1.0 eq.), nitromethane (**NM**, 212 µL, 3.95 mmol, 12 eq.), and catalyst **C5** (3.10 mg, 3.3µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2f** was obtained as a white solid (38.8 mg, 0.21 mmol, 51% yield, 88% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 0.5 mL/min over 60 min. Detection was performed at 220 nm, with retention times of $\mathbf{t}_{maj}(\boldsymbol{R})$ = 38.7 min and $\mathbf{t}_{min}(\boldsymbol{S})$ = 49.1 min.

$C_9H_{11}NO_3$, **MW**: 181.07 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.32–7.27 (*d*, *J*= 8.0 Hz, 2H, Ar-*H*), 7.24–7.19 (*d*, *J*= 7.9 Hz, 2H, Ar-*H*), 5.44 (*dd*, *J*= 9.4, 2.9 Hz, 1H, C*H*-OH), 4.65–4.56 (*m*, 1H, CH_2-NO_2), 4.53 – 4.47 (*m*, 1H, CH_2-NO_2), 2.75 (*s*, br, 1H, CH-O*H*), 2.37(*s*, 3H, Ar-CH_3) ppm.

The analytical data for **2f** agrees with the literature. [33]

2.7.7 Synthesis of (*R*)-1-(2-Methoxyphenyl)-2-nitroethan-1-ol (2g) [33]



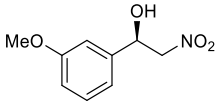
2g

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 2-methoxybenzaldehyde (**1g**, 31.25 µL, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 165 µL, 3.08 mmol, 12 eq.), and catalyst **C5** (2.41 mg, 2.6µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate 10:1), the desired product **2g** was obtained as a white solid (48.4 mg, 0.23 mmol, 92% yield, 94% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 0.5 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t}_{maj}(\boldsymbol{R})$ = 30.4 min and $\mathbf{t}_{min}(\boldsymbol{S})$ = 36.6min.

$C_9H_{11}NO_4$, **MW**: 197.07 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.42–7.37 (*m*, 1H, Ar-*H*), 7.34–7.28 (*m*, 1H, Ar-*H*), 7.00–6.93 (*m*, 1H, Ar-*H*), 6.92–6.88 (*m*, 1H, Ar-*H*), 5.58 *(dd*, *J*= 9.2, 3.2 Hz, 1H, C*H*-OH), 4.57 (*dd*, *J*= 3.4, 13.1 Hz, 1H, CH_2-NO_2), 4.48 (*dd*, *J*= 9.0, 13.2 Hz, 1H, CH_2-NO_2), 3.82 (*s*, 3H, Ar-OCH_3), 3.60 (*d*, 1H, CH-O*H*) ppm.

The analytical data for **2g** agrees with the literature. [33]

2.7.8 Synthesis of (*R*)-1-(3-Methoxyphenyl)-2-nitroethan-1-ol (2h) [33]



2h

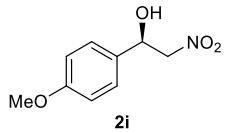
The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 3-methoxybenzaldehyde (**1h**, 31.25 µL, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 165 µL, 3.08 mmol, 12 eq.), and catalyst **C5** (2.41 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2h** was obtained as a white solid (40.9 mg, 0.20 mmol, 80% yield, 90% *ee*). The

enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 0.8mL/min over 60 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 30.6 min and $\mathbf{t_{min}(S)}$ = 40.3min.

$C_9H_{11}NO_4$, **MW**: 197.07 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.24 (*ddd*, 1H, Ar-*H*), 6.98–6.93 (*m*, 2H, Ar-*H*), 6.90–6.86 (*m*, 1H, Ar-*H*), 5.50 (*dd*, *J*= 2.5, 8.2 Hz, 1H, C*H*-OH), 4.23 (*dd*, *J*= 9.4, 13.4 Hz, 1H, CH_2-NO_2), 4.10 (*dd*, *J*= 9.3, 13.2 Hz, 1H, CH_2-NO_2), 3.73 (*s*, 3H, Ar-OCH_3)ppm.

The analytical data for **2h** agrees with the literature. [33]

2.7.9 Synthesis of (*R*)-1-(4-Methoxyphenyl)-2-nitroethan-1-ol (2i) [33]



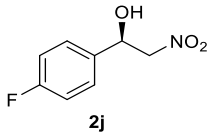
2i

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 4-methoxybenzaldehyde (**1i**, 31.25 µL, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 165 µL, 3.08 mmol, 12 eq.), and catalyst **C5** (2.41 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2i** was obtained as a white solid (32.5 mg, 0.16 mmol, 64% yield, 94% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 25.9 min and $\mathbf{t_{min}(S)}$ = 31.9min.

$C_9H_{11}NO_4$, **MW**: 197.07 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.34 (*d*, *J*= 8.5 Hz, 2H, Ar-*H*), 7.14 (*d*, *J*= 8.5 Hz, 2H, Ar-*H*), 5.44 (*dd*, *J*= 2.9, 9.2 Hz, 1H, C*H*-OH), 4.65.4.57 (*dd*, *J*= 9.4, 13.4 Hz, 1H, CH_2-NO_2), 4.52-4.45 (*dd*, *J*= 2.9, 13.4 Hz, 1H, CH_2-NO_2), 3.82 (*s*, 3H, Ar-OCH_3), 2.77 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2i** agrees with the literature. [33]

2.7.10 Synthesis of (*R*)-1-(4-Fluorophenyl)-2-nitroethan-1-ol (2j) [31]



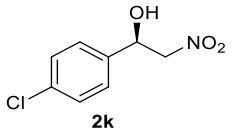
2j

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 4-fluorobenzaldehyde (**1j**, 30.57 µL, 0.32 mmol, 1.0 eq.), nitromethane (**NM**, 173 µL, 3.22 mmol, 12 eq.), and catalyst **C5** (3.02 mg, 3.2 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 5:1), the desired product **2j** was obtained as a white solid (42.6 mg, 0.23 mmol, 71% yield, 87% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 19.3 min and $\mathbf{t_{min}(S)}$ = 34.8min.

$C_8H_8FNO_3$, **MW**: 185.05 g/mol.**^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.45-7.36 (*m*, 2H, Ar-*H*), 7.25-7.17 (*m*, 2H, Ar-*H*), 5.46 (*dd*, *J*= 3.0, 9.4 Hz, 1H, C*H*-OH), 4.64.4.54 (*dd*, *J*= 9.5, 13.4 Hz, 1H, CH_2-NO_2), 4.53-4.45 (*dd*, *J*= 2.9, 13.5 Hz, 1H, CH_2-NO_2), 2.93 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2j** agrees with the literature. [34]

2.7.11 Synthesis of (*R*)-1-(4-Chlorophenyl)-2-nitroethan-1-ol (2k) [34]



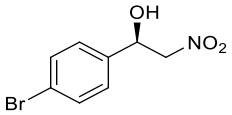
2k

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 4-chlorobenzaldehyde (**1k**, 40 mg, 0.28 mmol, 1.0 eq.), nitromethane (**NM**, 150 µL, 2.84 mmol, 12 eq.), and catalyst **C5** (2.67 mg, 2.8 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 5:1), the desired product **2k** was obtained as a white solid (38.4 mg, 0.19 mmol, 69% yield, 80% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 18.4 min and $\mathbf{t_{min}(S)}$ = 22.7 min.

$C_8H_8ClNO_3$, **MW**: 201.02 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.44-7.34 (*m*, 4H, Ar-*H*), 5.45 (*dd*, *J*= 2.9, 9.6 Hz, 1H, C*H*-OH), 4.62-4.52 (*dd*, *J*= 9.5, 13.4 Hz, 1H, CH_2-NO_2), 4.53-4.45 (*dd*, *J*= 3.0, 13.5 Hz, 1H, CH_2-NO_2), 2.89 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2k** agrees with the literature. [34]

2.7.12 Synthesis of (*R*)-1-(4-Bromophenyl)-2-nitroethan-1-ol (2l) [33]



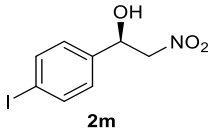
2l

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 4-bromobenzaldehyde (**1l**, 46.5 mg, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 161 µL, 2.84 mmol, 12 eq.), and catalyst **C5** (2.36 mg, 2.5 µmol, 1 mol%) were used. After purification by column chromatography (PE: ethyl acetate, 5:1), the desired product **2l** was obtained as a white solid (53.8 mg, 0.19 mmol, 87% yield, 89% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 21.0 min and $\mathbf{t_{min}(S)}$ = 27.2 min.

$C_8H_8BrNO_3$, **MW**: 246.06 g/mol.**^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.55 (*d*, *J*= 8.5 Hz, 2H, Ar-*H*), 7.25 (*d*, *J*= 8.4 Hz, 2H, Ar-*H*), 5.44 (*m*, 1H, C*H*-OH), 4.61-4.53 (*dd*, *J*= 9.3, 13.4 Hz, 1H, CH_2-NO_2), 4.52-4.46 (*dd*, *J*= 3.0, 9.4 Hz, 1H, CH_2-NO_2), 2.87 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2l** agrees with the literature. [33]

2.7.13 Synthesis of (*R*)-1-(4-Iodophenyl)-2-nitroethan-1-ol (2m) [32]



2m

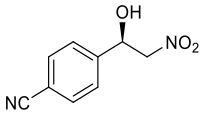
The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 4-iodobenzaldehyde (**1m**, 60 mg, 0.25 mmol, 1.0 eq.), nitromethane (**NM**, 166 µL, 3.1 mmol, 12 eq.), and catalyst **C5** (2.43 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 5:1), the desired product **2m** was obtained as a white solid (69.1 mg, 0.23 mmol, 91% yield, 95% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-

PrOH (85:15) at a flow rate of 0.8 mL/min over 50 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 26.8 min and $\mathbf{t_{min}(S)}$ = 36.6 min.

$C_8H_8INO_3$, **MW**: 292.95 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.16 (*d*, *J*= 8.4 Hz, 2H, Ar-*H*), 6.98 (*d*, *J*= 8.5 Hz, 2H, Ar-*H*), 5.42 (*m*, 1H, C*H*-OH), 4.60-4.52 (*dd*, *J*= 9.4, 13.4 Hz, 1H, CH_2-NO_2), 4.51-4.46 (*dd*, *J*= 2.9, 9.5 Hz, 1H, CH_2-NO_2), 2.84 (*s,* br, 1H, CH-O*H*) ppm.

The analytical data for **2m** agrees with the literature. [35]

2.7.14 Synthesis of (*R*)-4-(1-Hydroxy-2-nitroethyl) benzonitrile (2n) [33]



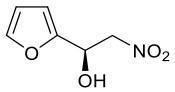
2n

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, 2-formylbenzonitrile (**1n**, 35 mg, 0.26 mmol, 1.0 eq.), nitromethane (**NM**, 143 µL, 2.66 mmol, 12 eq.), and catalyst **C5** (2.5 mg, 2.7 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 5:1), the desired product **2n** was obtained as a white solid (48.3 mg, 0.25 mmol, 94% yield, 70% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (80:20) at a flow rate of 0.8 mL/min over 30 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 15.3 min and $\mathbf{t_{min}(S)}$ = 17.4 min.

$C_9H_8N_2O_3$, **MW**: 192.17 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.73 (*d*, *J*= 8.3 Hz, 2H, Ar-*H*), 7.56 (*d*, *J*= 8.4 Hz, 2H, Ar-*H*), 5.53 (*m*, 1H, C*H*-OH), 4.62-4.49 (*m*, 2H, CH_2-NO_2), 3.17 (*s*, *br*, 1H, CH-O*H*) ppm.

The analytical data for **2n** agrees with the literature. [33]

2.7.15 Synthesis of (*R*)-1-(Furan-2-yl)-2-nitroethan-1-ol (2o) [33]



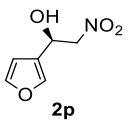
2o

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, furan-2-carbaldehyde (**1o**, 25.86 µL mg, 0.31 mmol, 1.0 eq.), nitromethane (**NM**, 167 µL, 3.12 mmol, 12 eq.), and catalyst **C5** (2.93 mg, 3.1µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2o** was obtained as a white solid (38.6 mg, 0.24 mmol, 79% yield, 90% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel IJ-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 1.0 mL/min over 30 min. Detection was performed at 211 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 19.1 min and $\mathbf{t_{min}(S)}$ = 22.2 min.

$C_6H_7NO_4$, **MW**: 157.13 g/mol.**^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.50 (*d*, *J*= 8.4 Hz, 1H, Ar-*H*), 7.41 (*m*, 1H, Ar-*H*), 6.42 (*d*, *J*= 8.2 Hz, 1H, Ar-*H*), 5.45 (*m*, 1H, C*H*-OH), 4.66-4.60 (*m*, 1H, CH_2-NO_2), 4.57-4.52 (*m*, 1H, CH_2-NO_2), 2.77 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2o** agrees with the literature. [36]

2.7.16 Synthesis of (*R*)-1-(Furan-3-yl)-2-nitroethan-1-ol (2p) [34]



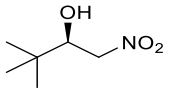
2p

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, furan-3-carbaldehyde (**1p**, 25.86 µL mg, 0.31 mmol, 1.0 eq.), nitromethane (**NM**, 167 µL, 3.12 mmol, 12 eq.), and catalyst **C5** (2.93 mg, 3.1µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2p** was obtained as a white solid (41.2 mg, 0.24 mmol, 83% yield, 93% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel IJ-H) with a mobile phase of *n*-hexane/*i*-PrOH (90:10) at a flow rate of 0.5 mL/min over 65 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 57.1 min and $\mathbf{t_{min}(S)}$ = 61.4 min.

$C_6H_7NO_4$, **MW**: 157.13 g/mol. **^{1}H-NMR** (**400 MHz, $CDCl_3$**): δ = 7.46-7.46 (*m*, 2H, Ar-*H*), 6.40 (*d*, *J*= 8.4 Hz, 1H, Ar-*H*), 5.40 (*dd*, *J*= 3.0, 9.5 Hz, 1H, C*H*-OH), 4.61-4.58 (*dd*, *J*= 9.4, 13.7 Hz 1H, CH_2-NO_2), 4.52-4.48 (*dd*, *J*= 3.2, 13.7 Hz, 1H, CH_2-NO_2), 3.40 (*s*, br, 1H, CH-O*H*) ppm.

The analytical data for **2p** agrees with the literature. [37]

2.7.17 Synthesis of (*R*)-3,3-Dimethyl-1-nitrobutan-2-ol (2q) [35]



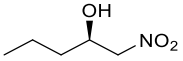
2q

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, pivaldehyde (**1q**, 37.83 µL, 0.34 mmol, 1.0 eq.), nitromethane (**NM**, 224 µL, 4.29 mmol, 12 eq.), and catalyst C1 (3.27 mg, 3.5 µmol, 1 mol%) were used. After purification by (PE: ethyl acetate, 10:1), the desired product **2q** was obtained as a colorless liquid (37.1 mg, 0.25 mmol, 72% yield, 81% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel AD-H) with a mobile phase of cyclohexane/*i*-PrOH (95:05) at a flow rate of 1.0 mL/min over 30 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 14.7 min and $\mathbf{t_{min}(S)}$ = 17.5 min.

$C_6H_{13}NO_3$, **MW**: 147.17 g/mol.**^{1}H-NMR** (**400 MHz, $CDCl_3$**): δ = 4.58-4.52 (*dd*, *J*= 13.0, 9.5 Hz, 1H, CH_2NO_2), 4.35-4.31 (*dd*, *J*= 9.6, 2.0 Hz, 1H, CH_2NO_2), 3.99- 4.96 (*m*, 1H, C*H*-OH), 2.64-2.62 (*d*, *J*= 5.0 Hz, 1H, CH-O*H*), 0.92 (*s*, 9H, C(CH_3)$_3$) ppm.

The analytical data for **2q** agrees with the literature. [38]

2.7.18 Synthesis of (*R*)-1-Nitropentan-2-ol (2r) [27]



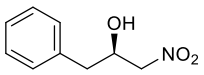
2r

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, *n*-butanal (**1r**, 31.25 µL, 0.34 mmol, 1.0 eq.), nitromethane (**NM**, 223 µL, 4.16 mmol, 12 eq.), and catalyst **C5** (3.25 mg, 3.5µmol, 1 mol%) were used. After purification (PE:ethyl acetate, 10:1), the desired product **2r** was obtained as a colorless liquid (40.2 mg, 0.30 mmol, 87% yield, 83% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (95:05) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(R)}$ = 20.5 min and $\mathbf{t_{min}(S)}$ = 28.6 min.

$C_5H_{11}NO_3$, **MW**: 133.15 g/mol. ^{1}H-NMR (**400 MHz, $CDCl_3$**): δ = 4.54-4.36 (*m*, 2H, CH_2NO_2), 4.34-4.28 (*m*, 1H, C*H*-OH), 2.96-2.71 (*s*, br, 1H, CH-O*H*), 1.66-1.27 (*m*, 4H, alkyl-*H*), 0.94 (*t*, *J*= 6.5 Hz, 3H, CH_3) ppm.

The analytical data for **2r** agrees with the literature. [27]

2.7.19 Synthesis of (*R*)-1-Nitro-3-phenylpropan-2-ol (2s) [36]



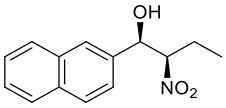
2s

The catalytic reaction was carried out according to the general procedure **GP 7**. Specifically, phenylacetaldehyde (**1s**, 39.85 mg, 0.3512 mmol, 1.0 eq.), nitromethane (**NM**, 230 µL, 4.29 mmol, 12 eq.), and catalyst **C5** (3.36 mg, 3.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **2s** was obtained as a white solid (50.3 mg, 0.33 mmol, 93% yield, 94% *ee*). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel OD-H) with a mobile phase of *n*-hexane/*i*-PrOH (80:20) at a flow rate of 0.8 mL/min over 40 min. Detection was performed at 220 nm, with retention times of $\mathbf{t_{maj}(\boldsymbol{R})}$ = 22.5 min and $\mathbf{t_{min}(\boldsymbol{S})}$ = 31.9 min.

$C_9H_{11}NO_3$, **MW**: 181.19 g/mol. ^{1}H-NMR (**400 MHz, $CDCl_3$**): δ = 7.37-7.19 (*m*, 5H, Ar-*H*), 4.53 (*m,*1H, CH-O*H*), 4.43-4.24 (*m*, 2H, CH_2-NO_2), 3.12 (*s*, br, 1H, CH-O*H*), 3.09-2.80 (*m*, 2H, CH_2-C) ppm.

The analytical data for **2s** agrees with the literature. [39]

2.7.20 Synthesis of (*R*, *R*)-1-(Naphthalene-2-yl)-2-nitrobutan-1-ol (3a) [37]



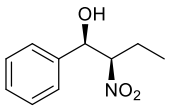
3a

The catalytic reaction was carried out according to **GP 8**. Specifically, 2-naphthaldehyde (40.0 mg, 0.25 mmol, 1.0 eq.), nitropropane (**NP**, 228 µL, 2.56 mmol, 10 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE: ethyl acetate, 10:1), the desired product **3a** was obtained as a white solid (46.4 mg, 0.18 mmol, 74%, dr(*syn*: *anti*) = (69:31), *ee*(*syn*) = 93%) The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralpak AS-H) with a mobile phase of cyclohexane/*i*-PrOH (95:05) at a flow rate of 0.7 mL/min over 40 min. Detection was performed at 216 nm, with retention times of ***anti***-isomer: $\mathbf{t_{min}}$ = 12.2 min and $\mathbf{t_{maj}}$ = 13.6 min and for ***syn***-isomer: $\mathbf{t_{min}}$ = 15.2 min and $\mathbf{t_{maj}}$ = 21.3 min.

$C_{14}H_{15}NO_3$, **MW**: 245.27 g/mol. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.87-7.74 (*m*, 4H$_{anti,\ syn}$, Ar-*H*), 7.51-7.34 (*m*, 3H$_{anti,\ syn}$, Ar-*H*), 5.31 (*m*, 1H$_{anti}$, C*H*-OH), 5.14 (*dd*, *J*= 8.9, 4.2 Hz, 1H$_{syn}$, C*H*-OH), 4.66 (*ddd*, *J*=12.9, 9.2, 3.6 Hz, 1H$_{syn,}$ C*H*-NO_2), 4.62 (*ddd*, *J* =10.9, 4.6, 3.5 Hz, 1H$_{anti}$, C*H*-NO_2), 2.45 (*m*, 1H$_{syn}$, CH_2-CH_3), 2.15 (*ddq*, *J*=14.7, 10.9, 7.4 Hz, 1H$_{anti}$, CH_2-CH_3), 1.86 (*dqd*, *J*=14.0, 7.7, 3.2 Hz, 1H$_{anti}$, CH_2-CH_3), 1.36 (*dqd*, *J*=14.7, 7.5, 3.7 Hz, 1H$_{syn}$, CH_2-CH_3), 0.87 (*t*, *J*=7.5 Hz, 3H$_{anti}$, CH_2-CH_3), 0.82 (*t*, *J*=7.4 Hz, 3H$_{syn}$, CH_2-CH_3) ppm.

The analytical data for **3a** agrees with the literature. [40]

2.7.21 Synthesis of (*R*, *R*)-2-Nitro-1-phenylbutan-1-ol (3c) [32]



3c

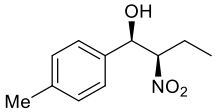
The catalytic reaction was carried out according to **GP 8**. Specifically, benzaldehyde (27.0 mg, 25.8 µL, 0.25 mmol, 1.0 eq.), nitropropane (**NP**, 228 µL, 2.56 mmol, 10 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were

used. After purification by column chromatography (PE: ethyl acetate, 10:1), the desired product **3c** was obtained as a white solid (34.9 mg, 0.17 mmol, 69%, dr(*syn*:*anti*) = (70:30), ee(*syn*) = 80%) The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralpak AS-H) with a mobile phase of cyclohexane/*i*-PrOH (95:05) at a flow rate of 0.7 mL/min over 50 min. Detection was performed at 216 nm, with retention times of ***anti***-isomer: $\mathbf{t}_{min}$ = 14.8 min and $\mathbf{t}_{maj}$ = 16.7 min and for ***syn***-isomer: $\mathbf{t}_{min}$ = 19.1 min and $\mathbf{t}_{maj}$ = 27.6 min.

$C_{10}H_{13}NO_3$, **MW**: 195.21 g/mol.**^{1}H-NMR** (**400 MHz, $CDCl_3$**): δ = 7.87-7.28 (*m*, 5H$_{anti,\ syn}$, Ar-*H*), 5.21 (*m*, 1H$_{anti}$, C*H*-OH), 5.10 (*dd*, *J*=9.2, 4.3 Hz, 1H$_{syn}$, C*H*-OH), 4.68-4.56 (*m*, 1H$_{syn,}$ C*H*-NO_2), 4.52 (*ddd*, *J*=10.7, 4.9, 3.2 Hz, 1H$_{anti}$, C*H*-NO_2), 2.66 (*d*, *J*=2.9 Hz, 1H$_{anti}$, CH-O*H*), 2.52 (*d*, *J*=4.2 Hz, 1H$_{anti}$, CH-O*H*), 2.40 (*m*, 1H$_{syn}$, C*H*$_2$-CH_3), 2.20 (*ddq*, *J*=14.7, 11.0, 7.4 Hz, 1H$_{anti}$, C*H*$_2$-CH_3), 1.90 (*dqd*, J=15.2, 7.8, 3.4 Hz, 1H$_{anti}$, C*H*$_2$-CH_3), 1.38 (*m*, 1H$_{syn}$, C*H*$_2$-CH_3), 0.92 (*t*, *J*=7.4 Hz, 3H$_{anti}$, CH_2-C*H*$_3$), 0.86 (*t*, *J*=7.5 Hz, 3H$_{syn}$, CH_2-C*H*$_3$) ppm.

The analytical data for **3c** agrees with the literature.[32]

2.7.22 Synthesis of (*R*, *R*)- 2-Nitro-1-*p*-tolylbutan-1-ol (3f) [40]



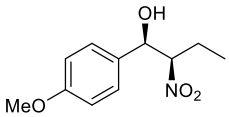
3f

The catalytic reaction was carried out according to **GP 8**. Specifically, *p*-methylbenzaldehyde (30.0 mg, 30.1 µL, 0.25 mmol, 1.0 eq.), nitropropane (**NP**, 267 µL, 2.99 mmol, 10 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE: ethyl acetate, 10:1), the desired product **3f** was obtained as a white solid (42.4 mg, 0.20 mmol, 81%, dr(*syn*:*anti*) = (74:26), ee(*syn*) = 86%) The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralpak AS-H) with a mobile phase of *n*-hexane/*i*-PrOH (95:05) at a flow rate of 0.8 mL/min over 50 min. Detection was performed at 216 nm, with retention times of ***anti***-isomer: $\mathbf{t}_{min}$ = 19.2 min and $\mathbf{t}_{maj}$ = 21.9 min and for ***syn***-isomer: $\mathbf{t}_{min}$ = 26.2 min and $\mathbf{t}_{maj}$ = 39.2 min.

$C_{11}H_{15}NO_3$, **MW**: 209.24 g/mol.**^{1}H-NMR** (**400 MHz, $CDCl_3$**): δ = 7.28 (*d*, *J*=8.3 Hz, 2H$_{anti}$, Ar-*H*), 7.23–7.09 (m, 4H$_{syn}$, Ar-*H*), 7.19 (*d*, *J*=8.1 Hz, 2H$_{anti}$, Ar-*H*), 5.16 (*dd*, *J*=4.9, 3.1 Hz, 1H$_{anti}$, C*H*-OH), 4.99 (*dd*, J=9.1, 4.0 Hz, 1H$_{syn}$, C*H*-OH), 4.59–4.48 (*m*, 1H$_{syn}$, C*H*-NO_2), 4.56 (*ddd*, *J*=11.0, 5.2, 3.2 Hz, 1H$_{anti}$, C*H*-NO_2), 2.57 (*d*, *J*=3.4 Hz, 1H$_{anti}$, CH-O*H*), 2.53 (*d*, *J*=3.7 Hz, 1H$_{syn}$, CH-O*H*), 2.37 (s, 3H$_{syn}$, Ar-C*H*$_3$), 2.35 (s, 3H$_{anti}$, Ar-C*H*$_3$), 2.19 (*ddq*, *J*=14.7, 10.6, 7.4 Hz, 1H$_{anti}$, C*H*$_2$-CH_3), 1.94 (*dqd*, J=14.9, 7.6, 3.5 Hz, 1H$_{anti}$, C*H*$_2$-CH_3), 1.84–1.71 (*m*, 1H$_{syn}$, C*H*$_2$-CH_3), 1.51–1.36 (*m*, 1H$_{syn}$, C*H*$_2$-CH_3), 0.93 (*t*, J=7.6 Hz, 3H$_{anti}$, CH_2-C*H*$_3$), 0.87 (*t*, *J*=7.5 Hz, 3H$_{syn}$, CH_2-C*H*$_3$) ppm.

The analytical data for **3f** agrees with the literature. [40]

2.7.23 Synthesis of (*R*, *R*)-1-(4-Methoxyphenyl) -2-nitrobutan-1-ol (3i) [38]



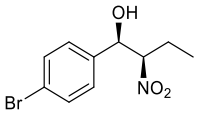
3i

The catalytic reaction was carried out according to **GP 8**. Specifically, 4-methoxybenzaldehyde (31.25 µL, 0.25 mmol, 1.0 eq.), nitropropane (**NP**, 228 µL, 2.56 mmol, 10 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were

used. After purification by column chromatography (PE: ethyl acetate, 10:1), the desired product **3i** was obtained as a white solid (38.5 mg, 0.17 mmol, 67%, dr(*syn*:*anti*) = (75:25), *ee*(*syn*) = 88%). The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralpak AS-H) with a mobile phase of cyclohexane/*i*-PrOH (95:05) at a flow rate of 0.7 mL/min over 50 min. Detection was performed at 216 nm, with retention times of ***anti***-isomer: $\mathbf{t}_{min}$ = 16.2 min and $\mathbf{t}_{maj}$ = 18.6 min and for ***syn***-isomer: $\mathbf{t}_{min}$ = 21.1 min and $\mathbf{t}_{maj}$ = 30.8 min.

$C_{11}H_{15}NO_4$, **MW**: 225.24 g/mol.**^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.35-7.28 (*m*, 2H$_{anti,}$ 2H$_{syn,}$ Ar-*H*), 6.96-6.88 (*m*, 2H$_{syn}$, 2H$_{anti,}$ Ar-*H*), 5.12 (*m*, 1H$_{anti}$, C*H*-OH), 4.97 (*dd*, *J*=9.1, 3.8 Hz, 1H$_{syn}$, C*H*-OH), 4.66-4.58 (*m*, 1H$_{syn}$,1H$_{anti}$, C*H*-NO$_2$), 3.85 (*s*, 3H$_{syn}$, Ar-OC*H*$_3$), 3.82 (*s*, 3H$_{anti}$, Ar-OC*H*$_3$), 2.52 (*d*, *J*=3.1 Hz, 1H$_{anti}$, CH-O*H*), 2.49 (*d*, *J*=4.0 Hz, 1H$_{syn}$, CH-O*H*), 2.41 (*m*, 1H$_{syn}$, C*H*$_2$-CH$_3$), 2.18 (*ddq*, *J*=14.7, 11.0, 7.5 Hz, 1H$_{anti}$, C*H*$_2$-CH$_3$), 1.98 (*dqd*, *J*=4.9, 7.5, 3.6 Hz, 1H$_{anti}$, C*H*$_2$-CH$_3$), 1.88–1.76 (*m*, 1H$_{syn}$, C*H*$_2$-CH$_3$), 0.97 (*t*, *J*=7.4 Hz, 3H$_{anti}$, CH$_2$-C*H*$_3$), 0.87 (*t*, *J*=7.4 Hz, 3H$_{syn}$, CH$_2$-C*H*$_3$) ppm.
The analytical data for **3i** agrees with the literature.[41]

2.7.24 Synthesis of (*R*, *R*)-1-(4-Bromophenyl)-2-nitrobutan-1-ol (3l) [39]



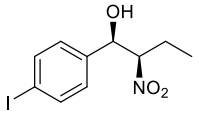
3l

The catalytic reaction was carried out according to **GP 8**. Specifically, 4-bromobenzaldehyde (47 mg, 0.25 mmol, 1.0 eq.), nitropropane (**NP**, 228 µL, 2.56 mmol, 10 eq.), catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE: ethyl acetate, 10:1), the desired product **3l** was obtained as a white solid (58.6 mg, 0.21 mmol, 84%, dr(*syn*:*anti*) = (81:19), ee(*syn*) = 94%) The enantiomeric excess (*ee*) was determined by HPLC using a chiral stationary phase (Chiralcel AD-H) with a mobile phase of *n*-hexane/*i*-PrOH (85:15) at a flow rate of 1.0 mL/min over 30 min. Detection was performed at 220 nm, with retention times of ***anti***-isomer: $\mathbf{t}_{min}$ = 10.3 min and $\mathbf{t}_{maj}$ = 11.0 min and for ***syn***-isomer: $\mathbf{t}_{min}$ = 9.0 min and $\mathbf{t}_{maj}$ = 13.3 min.

$C_{10}H_{12}BrNO_4$, **MW**: 274.11g/mol.**^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.57-7.53 (*d*, *J*=8.1 Hz, 2H$_{syn,}$ Ar-*H*), 7.53-7.50 (*d*, *J*=8.0 Hz, 2H$_{anti,}$ Ar-*H*), 7.28-7.25 (*m*, 2H$_{syn}$, 2H$_{anti,}$ Ar-*H*), 5.15 (*m*, 1H$_{anti}$, C*H*-OH), 5.05 (*dd*, *J*=9.6, 3.3 Hz, 1H$_{syn}$, C*H*-OH), 4.60-4.51 (*m*, 1H$_{syn}$,1H$_{anti}$, C*H*-NO$_2$), 2.70 (*d*, 1H$_{anti}$, CH-O*H*), 2.50 (*d*, 1H$_{syn}$, CH-O*H*), 2.20 (*m*, 1H$_{anti}$, C*H*$_2$-CH$_3$), 1.94-1.80 (*m*, 1H$_{anti}$, 1H$_{syn}$, C*H*$_2$-CH$_3$), 1.48 (*m*, 1H$_{syn}$, C*H*$_2$-CH$_3$), 0.95 (*t*, *J*=7.6 Hz, 3H$_{anti}$, CH$_2$-C*H*$_3$), 0.88 (*t*, *J*=7.5 Hz, 3H$_{syn}$, CH$_2$-C*H*$_3$) ppm.

The analytical data for **3l** agrees with the literature. [42]

2.7.25 Synthesis of (*R*, *R*)-1-(1-(4-Iodophenyl)-2-nitrobutan-1-ol (3m)



3m

The catalytic reaction was carried out according to **GP 8**. Specifically, 4-iodobenzaldehyde (58 mg, 0.25 mmol, 1.0 eq.), nitropropane (**NP**, 228 µL, 2.56 mmol, 10 eq.), and catalyst **C5** (2.4 mg, 2.6 µmol, 1 mol%) were used. After purification by column chromatography (PE:ethyl acetate, 10:1), the desired product **3m** was obtained as a white solid (69.4 mg, 0.21 mmol, 86%, dr(*syn*:*anti*) = (80:20), ee(*syn*) = 91%). The enantiomeric excess (*ee*) was

determined by HPLC using a chiral stationary phase (Chiralcel AD-H) with a mobile phase of cyclohexane/*i*-PrOH (95:05) at a flow rate of 0.7 mL/min over 30 minutes. Detection was performed at 216 nm, with retention times of ***anti***-isomer: $\mathbf{t}_{min}$ = 11.6 min and $\mathbf{t}_{maj}$ = 13.2 min and for ***syn***-isomer: $\mathbf{t}_{min}$ = 10.0 min and $\mathbf{t}_{maj}$ = 15.3 min.

$C_{10}H_{12}INO_3$, **MW**: 321.11g/mol. **MP**= 67-74°C, **$[\alpha]^{20}_D$** = +16(c = 0.1 g/dL, CH_2Cl_2, sample with 91% *ee*). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.59-7.51 (*m*, 2H$_{syn,}$ 2H$_{anti,}$ Ar-*H*), 7.29-7.28 (*m*, 1H$_{syn}$, 1H$_{anti,}$ Ar-*H*), 7.27-7.25 (*m*, 1H$_{syn}$, 1H$_{anti,}$ Ar-*H*), 5.18 (*d*, *J*=5.1 Hz, 1H$_{anti}$, C*H*-OH), 5.03 (*d*, *J*=8.9 Hz, 1H$_{syn}$, C*H*-OH), 4.62-4.51 (*m*, 1H$_{syn}$,1H$_{anti}$, C*H*-NO_2), 2.74 (*s*, *br*, 1H$_{anti}$, CH-O*H*), 2.52 (s, *br*, 1H$_{syn}$, CH-O*H*), 2.23-2.10 (*m*, 1H$_{anti}$, CH_2-CH_3), 1.94-1.80 (*m*, 1H$_{anti}$, 1H$_{syn}$, CH_2-CH_3), 1.51-1.40 (*m*, 1H$_{syn}$, CH_2-CH_3), 0.95 (*t*, *J*=7.4 Hz, 3H$_{anti}$, CH_2-CH_3), 0.91 (*t*, *J*=7.5 Hz, 3H$_{syn}$, CH_2-CH_3) ppm.**^{13}C-NMR (150 MHz, $CDCl_3$)** δ= 137.6, 132.2, 128.5, 123.2, 94.9, 74.8, 23.9, 10.3. **IR ($CDCl_3$):** $\tilde{\nu}$ = 3441, 2976, 2940, 1718, 1595, 1550, 1490, 1461, 1345, 1260, 1091, 1049, 1014, 833, 807, 725. **HRMS (ESI) *m*/*z***: Calculated for $[M]^+$ $C_{10}H_{12}INO_3$: 320.9862 Found: 320.9869.

3 Mechanistic Studies

3.1 Variable Time Normalization Analysis (VTNA)

For kinetic investigations, Visual Kinetic Analysis [40] was used, a method that enables mechanistic insights through the visual comparison of reaction profiles. For that, the Variable Time Normalization Analysis (VTNA) method, developed by *J. Burés* was applied. [41, 42] This approach is based on the principle that concentration profiles obtained from experiments with varying concentrations of a given component can only be superimposed if the time axis is normalized. Specifically, the time axis is replaced by the integral of the concentration of component *A*, raised to the power of its kinetic order $\boldsymbol{\alpha}$, allowing for the determination of reaction orders through visual overlay. [43-45]

$$\sum[A]^{\alpha}\Delta t \; = \sum_{i=1}^{n}\left(\frac{[A]_i + [A]_{i-1}}{2}\right)^{\alpha}(t_i - t_{i-1}) \qquad (1)$$

When all *n* (eq. 1) components that influence the reaction rate are simultaneously accounted for in the normalization of the time scale for each reaction profile, the resulting *n*+1 profiles collapse onto a single straight line. The slope of the straight corresponds to the experimental rate constant k_{obs}.[43-45]

The corresponding experiments **K1-K4** were performed by adding a solution of the catalyst **C5**, mesitylene (internal standard), 2-napthaldehyde (**1a**), nitromethane (**NM**) in tetrahydrofuran-d8 to an NMR sample tube (**Table S9)**. The reaction mixture was analyzed by ^{1}H-NMR spectroscopy at 45°C temperature to monitor the conversion of 2-napthaldehyde (**1a**) and the yield of nitroalcohol (**2a**) dependence of time (**Figure S1**).

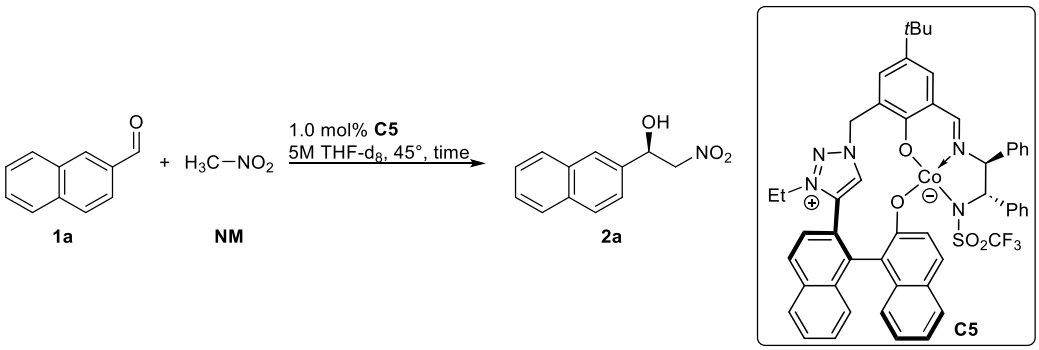


Table S9: Concentrations of the 2-napthaldehyde (**1a**), nitrometahne (**NM**) and catalyst **C5** in the VTNA experiments of the nitroaldol reaction

entry	Nr	[**1a**] mol/L	[**NM**] mol/L	[**C5**] mol/L
1	**K1**	0.2049	5.63	0.01
2	**K2**	**0.3073**	5.63	0.01
3	**K3**	0.2049	**6.55**	0.01
4	**K4**	0.2049	5.63	**0.02**

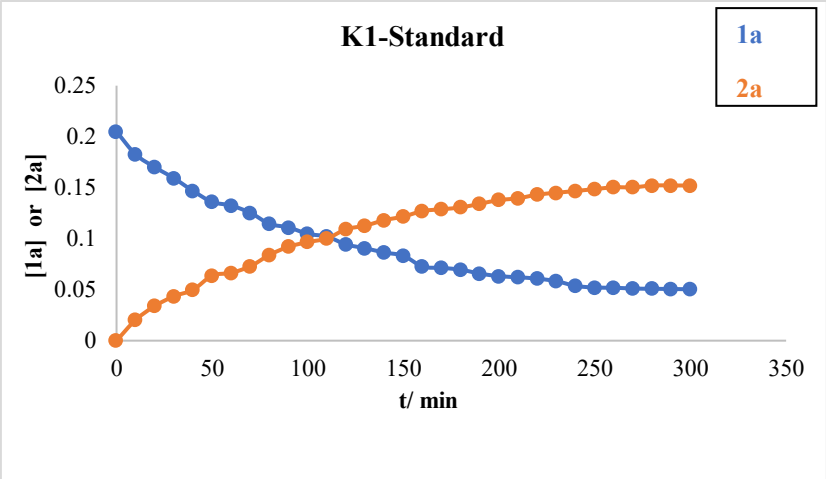


Figure S1. Conversion of (**1a**) and the yield of (**2a**) dependence of time.

The determination of the partial reaction order **α** with respect to 2-naphthaldehyde (**1a**) was exemplified using experiments **K1** and **K2**, in which the initial concentration of 2-naphthaldehyde (**1a**) was systematically varied. For this evaluation, the concentration time profiles of 2-naphthaldehyde (**1a**) were analyzed. As illustrated in **Figure S2**, the time axes were normalized according to Equation **(1)** using different trial values of the partial reaction order **α**. This normalization was performed iteratively until the best overlap of the concentration profiles was achieved. Specifically, normalization was tested for **α** = 0.5, **α** = 1.08, **α** = 1.4 and **α** = 2.0. Among these, the best superposition of the 2-naphthaldehyde (**1a**) concentration curves was obtained for **α** = 1.08, indicating that the partial reaction order of 2-naphthaldehyde in the overall rate law is approximately 1.08.

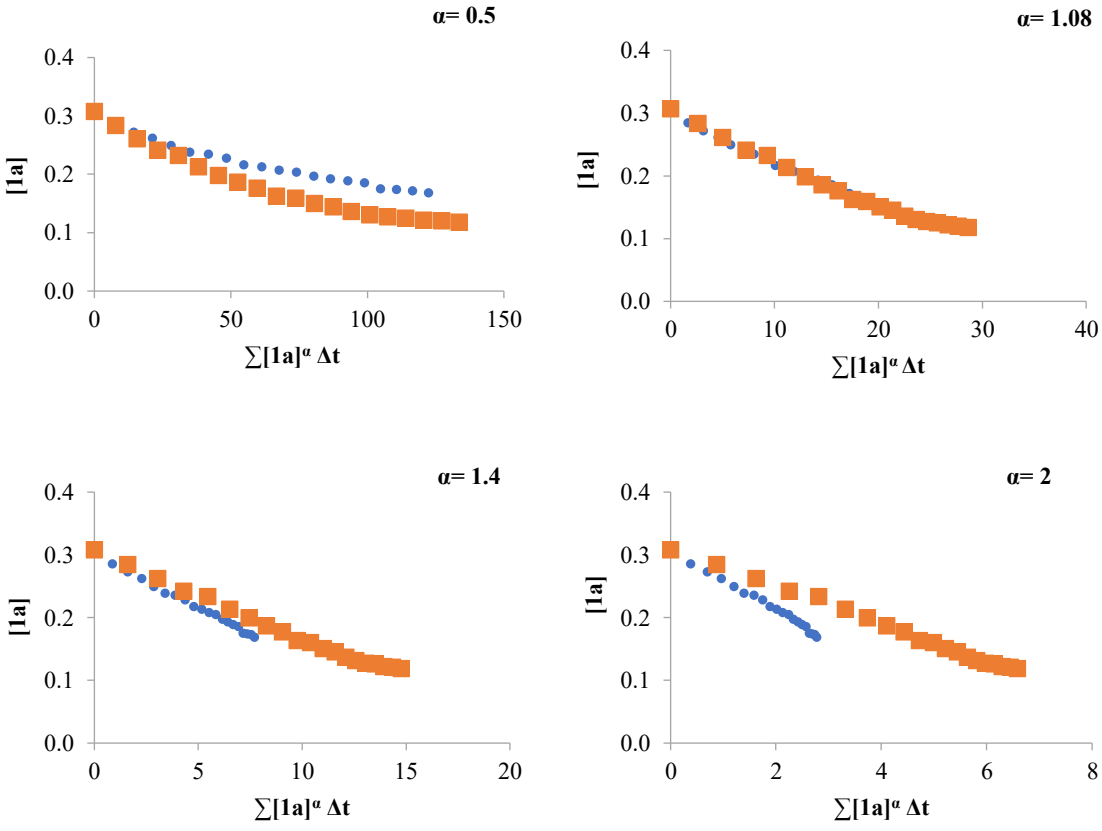


Figure S2: Determination of a partial reaction order **α** for the 2-napthaldehyde (**1a**) using VTNA

Similarly, using the concentration curve of 2-naphthaldehyde (**1a**), the partial order of nitromethane (**NM**) was exemplified using experiments **K1** and **K3**, in which the initial concentration of nitromethane (**NM**) was systematically varied. As illustrated in **Figure S3**, the time axes were normalized according to Equation **(1)** using different trial values of the partial reaction order $\boldsymbol{\beta}$. This normalization was performed iteratively until the best overlap of the concentration profiles was achieved. Specifically, normalization was tested for $\boldsymbol{\beta} = 0.5$ and $\boldsymbol{\beta} = 0.85$. Among these, the best superposition of the 2-naphthaldehyde (**1a**) concentration curves was obtained for $\boldsymbol{\beta} = 0.85$, indicating that the partial reaction order of nitromethane (**NM**) in the overall rate law is approximately 0.85.

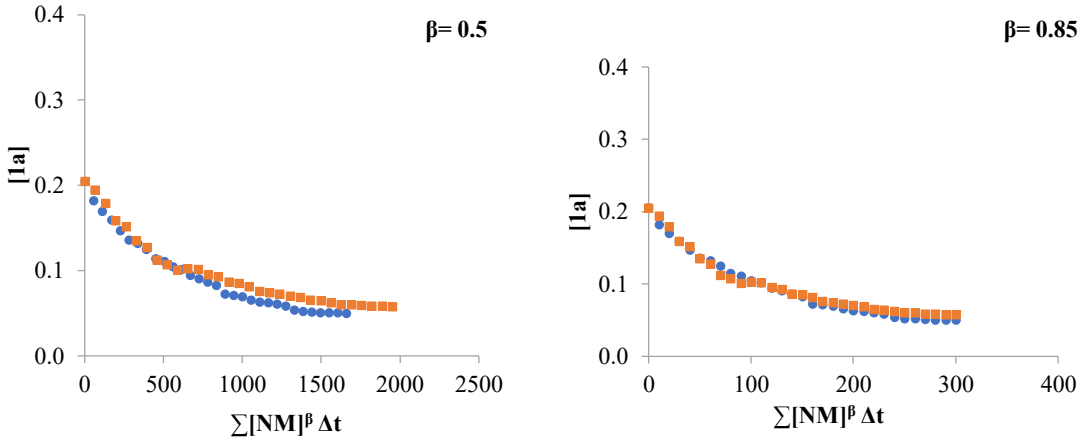
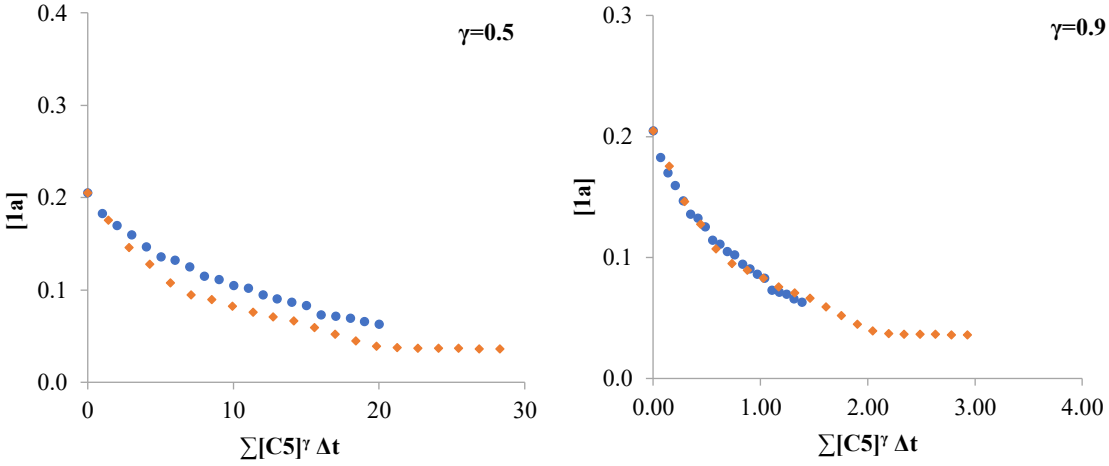


Figure S3: Determination of a partial reaction order $\boldsymbol{\beta}$ for the nitromethane (**NM**) using VTNA

Similarly, using the concentration curve of 2-naphthaldehyde (**1a**), the partial order of catalyst (**C5**) was exemplified using experiments **K1** and **K4**, in which the initial concentration of catalyst (**C5**) was systematically varied. As illustrated in **Figure S4**, the time axes were normalized according to Equation **(1)** using different trial values of the partial reaction order $\boldsymbol{\gamma}$. This normalization was performed iteratively until the best overlap of the concentration profiles was achieved. Specifically, normalization was tested for $\boldsymbol{\gamma} = 0.5$, $\boldsymbol{\gamma} = 0.9$ and $\boldsymbol{\gamma} = 1.3$. Among these, the best superposition of the 2-naphthaldehyde (**1a**) concentration curves was obtained for $\boldsymbol{\gamma} = 0.9$, indicating that the partial reaction order of catalyst (**C5**) in the overall rate law is approximately 0.9.



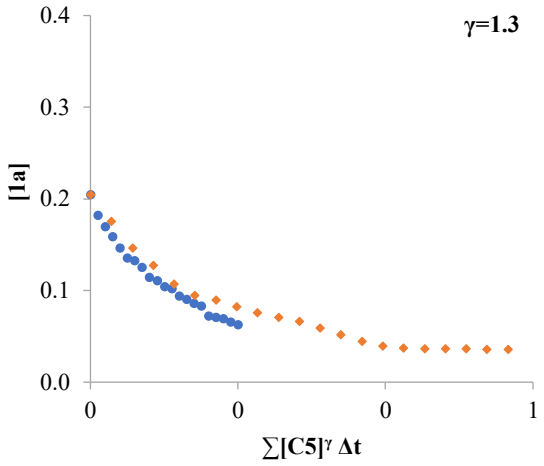
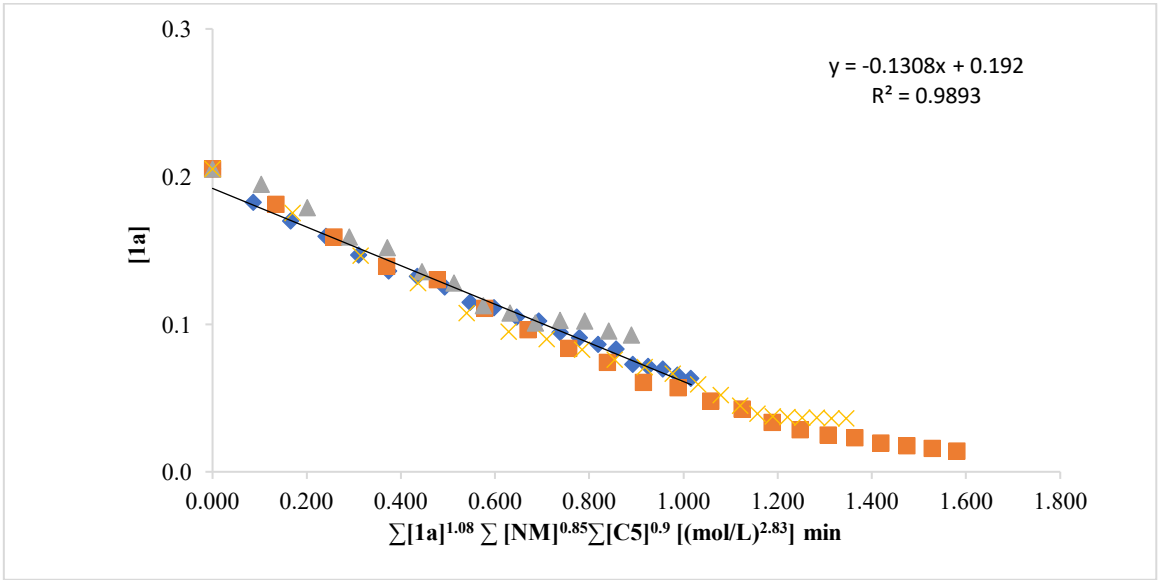


Figure S4: Determination of a partial reaction order γ for the catalyst (**C5**) using VTNA

In the final step of the analysis, the previously determined partial reaction orders were employed to perform the linearization. This evaluation utilized the 2-naphthaldehyde (**1a**) concentration profiles from experiments **K1** to **K4**. As expected, the resulting plots aligned along a straight line, with the slope corresponding to the experimentally determined rate constant, k_{obs}. However, since the Variable Time Normalization Analysis (VTNA) relies on visual curve overlaps, it does not support quantitative error estimation.



The experimental rate law for the nitroaldol reaction using catalyst **C5** can be determined as:

$$r = \quad 0.1308\ [\mathbf{C5}]^{0.9}\ [\mathbf{1a}]^{1.08}\ [\mathbf{NM}]^{0.85}$$

NMR Data for VTNA

Table S10: Standard K1

entry	Time (h)	[1a]	[NM]	[2a]
1	0	0.2049	5.6345	0
2	0.167	0.18258	5.61413	0.02037
3	0.333	0.17005	5.600467	0.034033
4	0.517	0.15931	5.591005	0.043495
5	0.683	0.14678	5.584577	0.049923
6	0.850	0.13604	5.570776	0.063724
7	1.017	0.13246	5.568019	0.066481
8	1.200	0.1253	5.566498	0.068002
9	1.367	0.11456	5.55037	0.08413
10	1.533	0.11098	5.542351	0.092149
11	1.700	0.104751	5.53784	0.09666
12	1.867	0.102012	5.53426	0.10024
13	2.050	0.094369	5.52531	0.10919
14	2.217	0.090592	5.52173	0.11277
15	2.383	0.086457	5.51636	0.11814
16	2.550	0.083163	5.51278	0.12172
17	2.717	0.072728	5.50741	0.12709
18	2.900	0.071278	5.50562	0.12888
19	3.067	0.069595	5.50383	0.13067
20	3.233	0.065729	5.50025	0.13425
21	3.400	0.063241	5.49667	0.13783
22	3.567	0.062167	5.49488	0.13962
23	3.750	0.060788	5.4913	0.1432
24	3.917	0.058336	5.48951	0.14499
25	4.083	0.053682	5.48772	0.14678
26	4.250	0.052089	5.48593	0.14857
27	4.433	0.051892	5.48414	0.15036
28	4.600	0.051122	5.48414	0.15036
29	4.767	0.050854	5.48235	0.15215
30	4.933	0.050693	5.48235	0.15215
31	5.100	0.050317	5.48235	0.15215

Table S11: Difference in 2-napthaldehyde (**1a**) **K2**

entry	Time (h)	[1a]	[NM]	[2a]
1	0	0.3073	5.6345	0
2	0.167	0.28356	5.618157	0.016343
3	0.350	0.26134	5.59154	0.04296
4	0.667	0.24165	5.566659	0.067841
5	0.733	0.2327	5.557262	0.077239
6	0.900	0.21301	5.545072	0.089428
7	1.067	0.19869	5.532739	0.101762
8	1.233	0.18616	5.512905	0.121595
9	1.400	0.176333	5.50562	0.12888
10	1.583	0.16289	5.49488	0.13962
11	1.750	0.15931	5.48951	0.14499
12	0.900	0.15036	5.48056	0.15394
13	2.083	0.14499	5.47698	0.15752
14	2.250	0.13604	5.468805	0.165695
15	2.433	0.13067	5.463487	0.171013
16	2.600	0.12709	5.459341	0.175159
17	2.767	0.1253	5.458049	0.176451
18	2.933	0.12172	5.455724	0.178776
19	3.117	0.11993	5.45192	0.18258
20	3.283	0.11814	5.44655	0.18795
21	3.450	0.11635	5.44476	0.18974
22	3.617	0.11456	5.44297	0.19153
23	3.783	0.11277	5.44118	0.19332
24	3.967	0.115634	5.44118	0.19332
25	4.133	0.114739	5.44118	0.19332
26	4.300	0.114202	5.44118	0.19332
27	4.467	0.113665	5.44297	0.19153

28	4.633	0.112591	5.44297	0.19153
29	4.817	0.111875	5.44297	0.19153
30	5.000	0.111696	5.44297	0.19153

Table S12: Difference in nitromethane (**NM**) **K3**

entry	Time (h)	[1a]	[2]	[3a]
1	0	0.2049	6.557	0
2	0.168	0.194645	6.551809	0.005191
3	0.342	0.179107	6.544271	0.012729
4	0.627	0.158952	6.535037	0.021963
5	0.696	0.151667	6.531278	0.025722
6	0.850	0.135664	6.524154	0.032847
7	1.017	0.127806	6.5166	0.0404
8	1.200	0.112537	6.511373	0.045627
9	1.367	0.107418	6.508044	0.048957
10	1.533	0.100813	6.506791	0.05021
11	1.700	0.102751	6.505663	0.051337
12	1.867	0.102012	6.504338	0.052662
13	2.050	0.095369	6.50339	0.053611
14	2.217	0.09284	6.501832	0.055168
15	2.383	0.086568	6.498589	0.058411
16	2.550	0.08521	6.496874	0.060126
17	2.717	0.081359	6.495943	0.061057
18	2.900	0.076236	6.494117	0.062883
19	3.067	0.074036	6.492309	0.064691
20	3.233	0.072821	6.490502	0.066499
21	3.400	0.070632	6.488729	0.068271
22	3.567	0.068622	6.486152	0.070848
23	3.750	0.065608	6.485418	0.071582
24	3.917	0.064583	6.485185	0.071815
25	4.083	0.062368	6.483628	0.073372
26	4.250	0.060521	6.483565	0.073435
27	4.433	0.060125	6.483389	0.073611
28	4.600	0.059112	6.483194	0.073806
29	4.767	0.058851	6.482593	0.074407
30	4.933	0.058253	6.48244	0.07456

Table S13: Difference in catalyst (**C5**) **K4**

entry	Time (h)	[1a]	[NM]	[2a]
1	0	0.2049	5.6345	0
2	0.167	0.18974	5.620056	0.014444
3	0.283	0.17542	5.60586	0.02864
4	0.383	0.158952	5.590735	0.043766
5	0.467	0.146297	5.57944	0.05506
6	0.567	0.135664	5.567984	0.066516
7	0.667	0.127806	5.561933	0.072567
8	0.767	0.112537	5.545985	0.088516
9	0.848	0.107418	5.540453	0.094047
10	0.960	0.100813	5.534976	0.099524
11	1.103	0.094977	5.531038	0.103462
12	1.139	0.08907	5.523144	0.111356
13	1.242	0.089715	5.520746	0.113755
14	1.337	0.084971	5.518889	0.115611
15	1.433	0.08268	5.517524	0.116977
16	1.521	0.081033	5.515913	0.118588
17	1.619	0.075807	5.512154	0.122347
18	1.781	0.073753	5.507593	0.126907
19	1.826	0.070791	5.506954	0.127546
20	1.918	0.06981	5.50383	0.13067
21	2.011	0.06623	5.50025	0.13425
22	2.109	0.06265	5.49667	0.13783
23	2.212	0.05907	5.49309	0.14141
24	2.314	0.05549	5.48951	0.14499
25	2.312	0.05191	5.48593	0.14857
26	2.416	0.04833	5.48235	0.15215

27	2.519	0.04475	5.47698	0.15752
28	2.627	0.04296	5.47519	0.15931
29	2.744	0.03938	5.47161	0.16289
30	2.949	0.03759	5.470715	0.163785
31	3.150	0.037411	5.470894	0.163606
32	3.325	0.037053	5.471252	0.163248
33	3.501	0.036874	5.471431	0.163069
34	3.651	0.036856	5.471252	0.163248
35	3.848	0.036785	5.47161	0.16289
36	4.011	0.036767	5.471252	0.163248
37	4.123	0.036785	5.471073	0.163427
38	4.341	0.036516	5.470984	0.163517
39	4.529	0.036337	5.470966	0.163534
40	4.676	0.036427	5.470948	0.163552
41	4.841	0.036176	5.47093	0.16357
42	5.030	0.036122	5.470894	0.163606

3.2 Spectroscopy

After complexation and activation, catalyst **C5*HPF$_6$** and **C5** were investigated by ^{1}H and ^{19}F-NMR spectroscopy. In Figure **S5**, the ^{1}H-NMR spectra of the ligand (Figure **S5**, green spectrum), the non-activated Co(II) catalyst **C5*HPF$_6$** (Figure **S5**, red spectrum), and the activated Co(II) catalyst **C5** (Figure **S5**, blue spectrum) are shown.

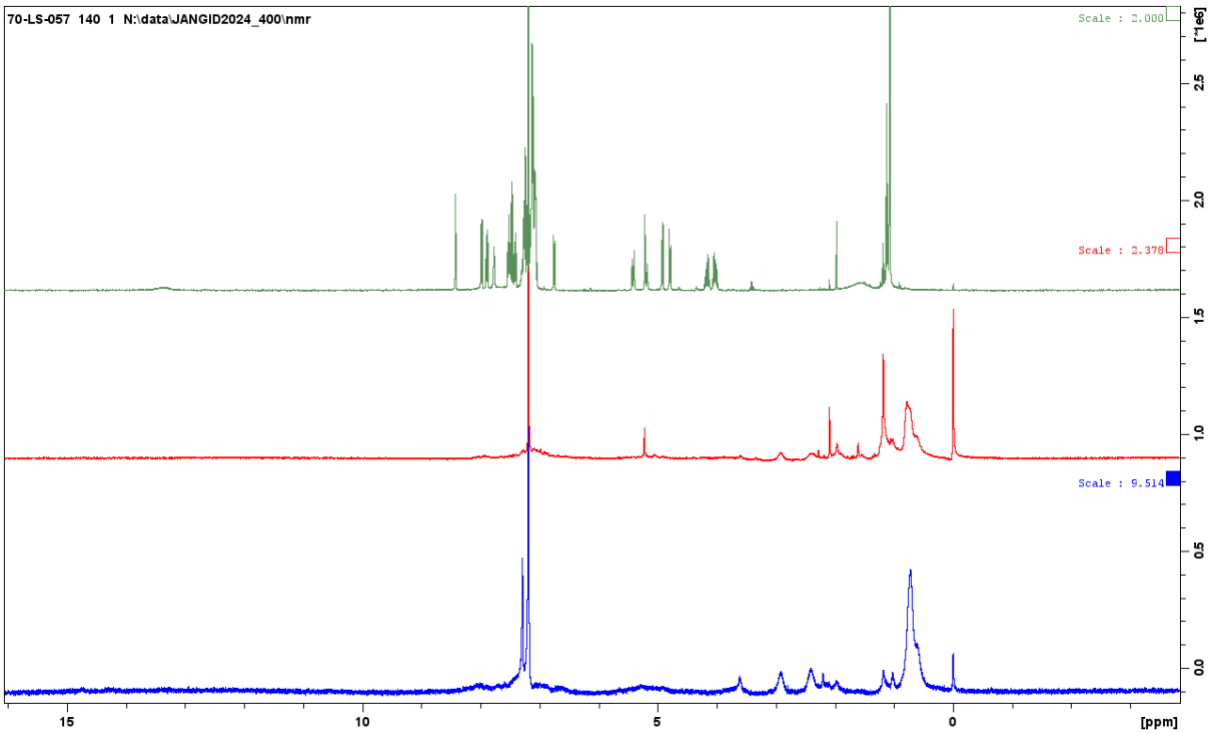


Figure S5: Comparison of the ^{1}H NMR spectra of the ligand (**L-5**, green spectrum) and the complexes **C5*HPF$_6$** and (red spectrum) and **C5** (blue spectrum).

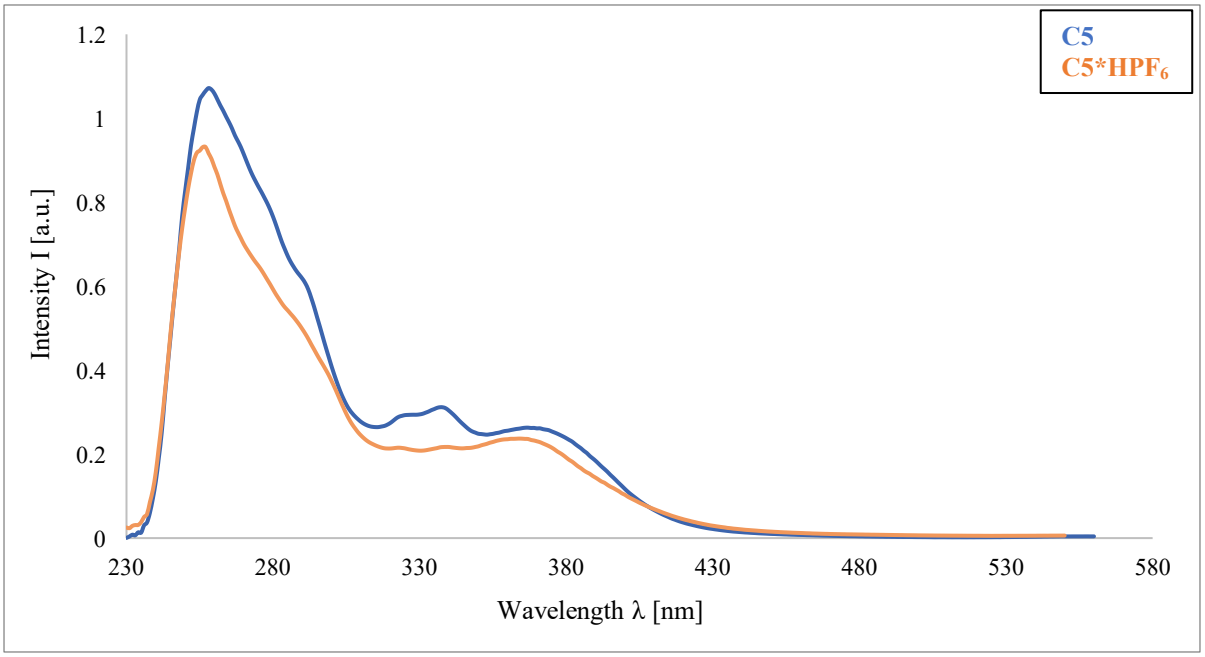


Figure S6: Comparison of the UV-Vis spectra of the complexes **C5*HPF$_6$** and **C5**.

3.3 Studies on the Non-Linear Effect

In the kinetic studies described in Chapters 3.1 to determine the reaction order of the nitro- aldol reaction catalyzed by **C5,** a first-order dependence on the catalyst **C5** was observed. To further investigate and support this interpretation, studies on the non-linear effect (NLE) were conducted. [43, 44] In these experiments, the catalyzed reaction was performed using catalysts of varying enantiomeric purities (see first column in **Table S14**). In this approach, the catalyst was used with varying enantiomeric excesses, ranging from racemic to >99%, and the resulting enantiomeric excess of the product was monitored. When the enantiomeric excess of the catalyst is plotted against that of the product, a linear correlation is expected if only a single catalyst molecule is involved in the enantioselectivity-determining step. However, if the plot shows a non-linear trend, either upwards (positive NLE) or downwards (negative NLE) this suggests a mechanism involving more than one catalyst molecule in the stereoselectivity-determining step (**Figure S7**, **Table S14)**.

As shown in **Figure S7**, a clear linear correlation between the enantiomeric excess of the product nitro alcohols (**3a**) and the complex (**C5** + ***e*C5**) can be observed. This provides strong evidence for a catalytic cycle involving only a single catalyst molecule.

Table S14: Investigations of the nonlinear effect in the nitro-aldol reaction.

#	*ee* (C5 + *e*C5) /%	*ee* (2a) /%
1	0	1
2	20	17
3	40	36
4	60	54
5	80	77
6	100	96

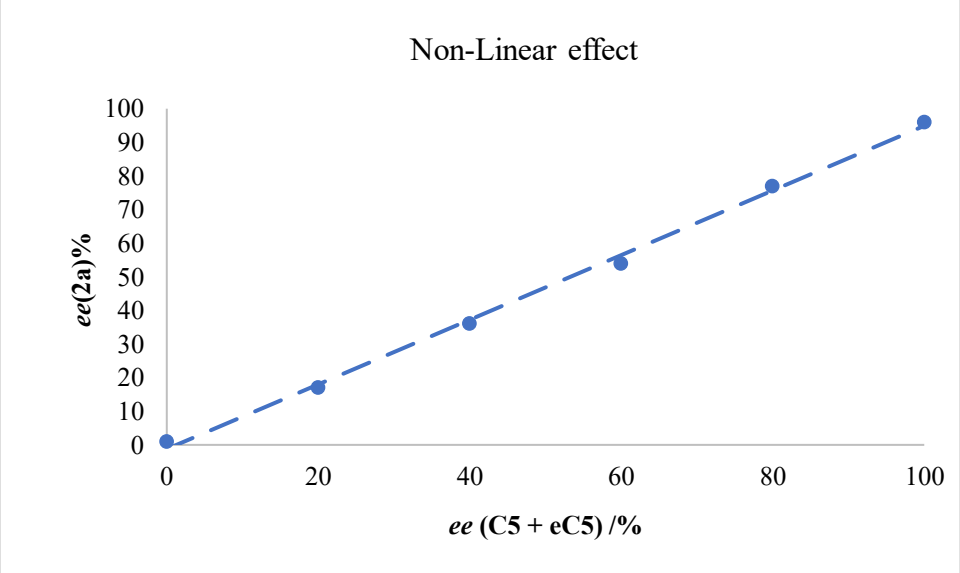


Figure S7: Linear effect plot of the nitro-aldol reaction with different ee-values of the catalyst (**C5** + ***e*C5**) and the product nitro alcohols (**NA-1**)

3.4 UV-Vis Experiments

3.4.1 Beer's Law Plot

To support the investigations showed in **Chapters 3.1** (VTNA) and **3.3** (non-linear effect study), UV-Vis spectroscopy experiments were carried out for the catalysts **C5*HPF$_6$** and **C5**. These experiments aimed to examine the relationship between the absorption intensity of characteristic bands and the catalyst concentration. Plots of absorption intensity versus concentration were generated (**Figure S8)**. Intensity values at the absorption maximum (367 nm) are summarized in **Table S15**, and the corresponding Beer's law plot is shown in **Figure S9**.

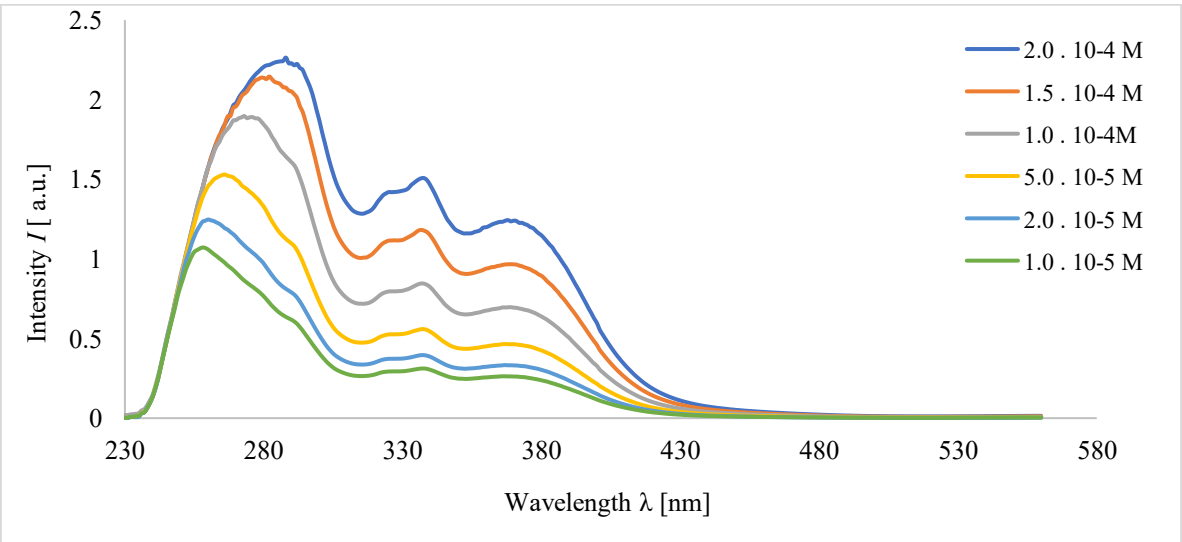


Figure S8: The UV-Vis spectra of the concentration series of **C5*HPF$_6$** in dry THF in a concentration range from $1.0 \cdot 10^{-5}$ M to $2.0 \cdot 10^{-4}$ M.

Table S15: Measured and calculated data for the concentration and UV-Vis absorbance dependence of complex **C5*HPF$_6$** at 367 nm

entry	c [M]. 10^{-4}	Intensity (367nm)
1	2	1.24029
2	1.5	0.96574
3	1	0.69403
4	0.5	0.46445
5	0.2	0.32317
6	0.1	0.26288

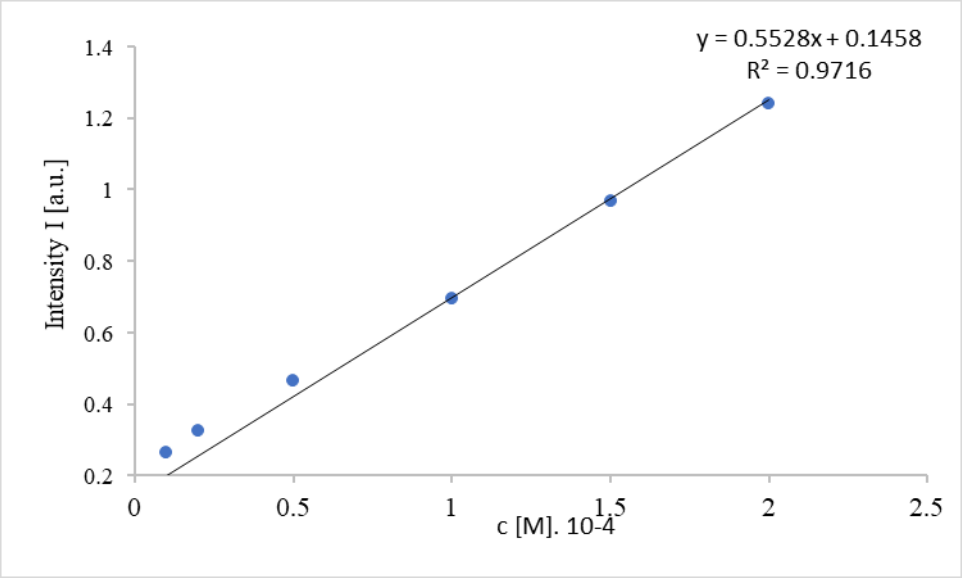


Figure S9: Plot of the intensity of the absorption band at 367nm versus the concentration of **C5*HPF$_6$**.

No deviation from the Lambert-Beer law was observed, supporting the conclusion that no catalyst dimer is present for the Co(II) precatalyst **C5*HPF$_6$**. This result provides additional evidence against dimer or under the conditions investigated.

Identical experiments were also performed for the activated catalyst **C5**. Plots of absorption intensity versus concentration were generated and are shown in **Figure S9**. Intensity values at the absorption maximum (365 nm) are summarized in **Table S16**, and the corresponding Beer's law plot is shown in **Figure S10**.

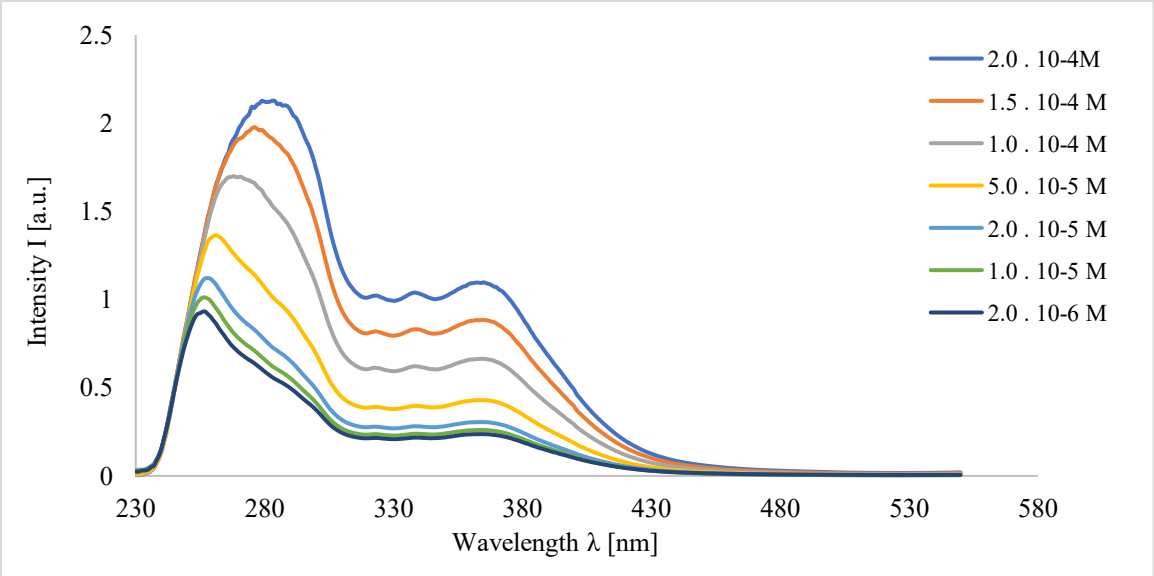


Figure S9: The UV-Vis spectra of the concentration series of **C5** in dry THF in a concentration range from $2.0 \cdot 10^{-6}$ M to $2.0 \cdot 10^{-4}$ M.

Table S16: Measured and calculated data for the concentration and UV-Vis absorbance dependence of catalyst **C5** at 365nm

entry	c [M]. 10^{-4}	Intensity (365nm)
1	2	1.097648648
2	1.5	0.884267021
3	1	0.663719232
4	0.5	0.42904574
5	0.2	0.305018024
6	0.1	0.260387
7	0.02	0.236817034

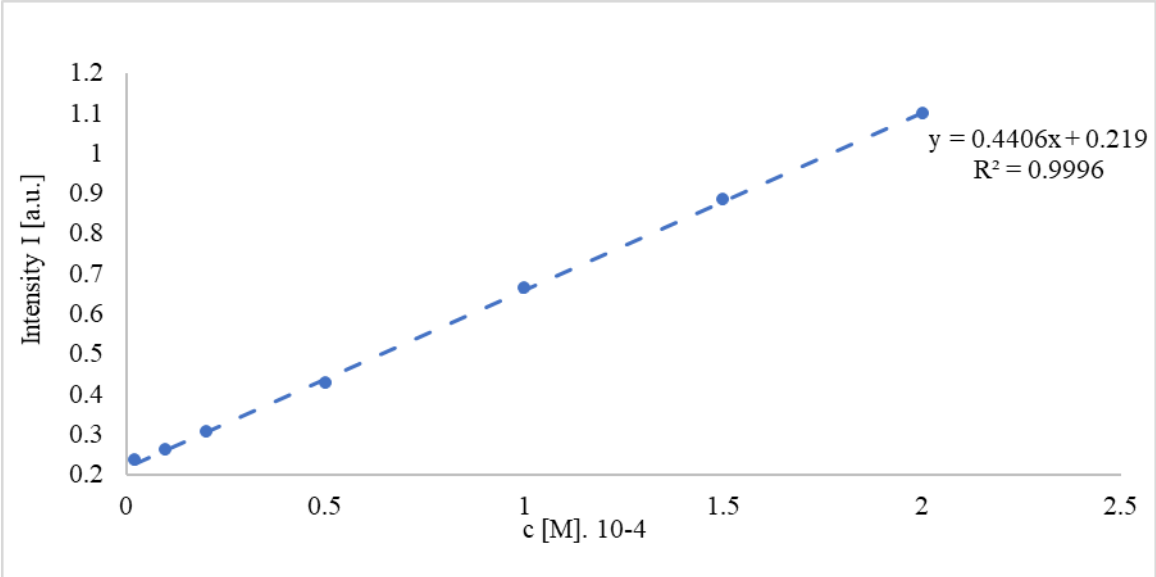


Figure S10: The UV-Vis spectra of the concentration series of **C5** in dry THF in a concentration range from $2.0 \cdot 10^{-6}$ M to $2.0 \cdot 10^{-4}$ M.

UV-Vis measurement at high concentrations was done to investigate the *d-d* transitions of the cobalt center. These mesaurements were conductes in pure $MeNO_2$ and in THF with the addition of $MeNO_2$ and **1a**. The results are shown in **figure S11** and show weak signals at 14000 cm^{-1} and 17000 cm^{-1}.

C5 in $MeNO_2$ (**2**) does show one broad signal at 17000 cm^{-1} and no further signals in the spectral range. **C5** in THF shows a different signature with signals at 14000 cm^{-1} and 17500 cm^{-1}. The addition of **1a** to the THF solution did not change the position and relative intensity of the signals. The change in intensity can be attributed to the change in concentration in the cuvette. However, the addition of $MeNO_2$(**NM**) to the THF solution did change the signal pattern towards the one observed for the pure $MeNO_2$(**NM**) measurement. These results indicate that both $MeNO_2$(**NM**) and THF are coordinating to the Co center and change the ligand field splitting. In a competitive environment $MeNO_2$ (**NM**) is the stronger ligand with respect to THF. The substrate **1a** does not show a change in the ligand field, indicating that it is not coordinating to the metal center under these conditions.

The spectra in pure Solvents are fitted with gaussian bell curves. The parameters of the fits are represented in **Table S17**. Additional bands for the shoulder at high energies are not shown since they are not resolved and do not represent *d-d* transitions.

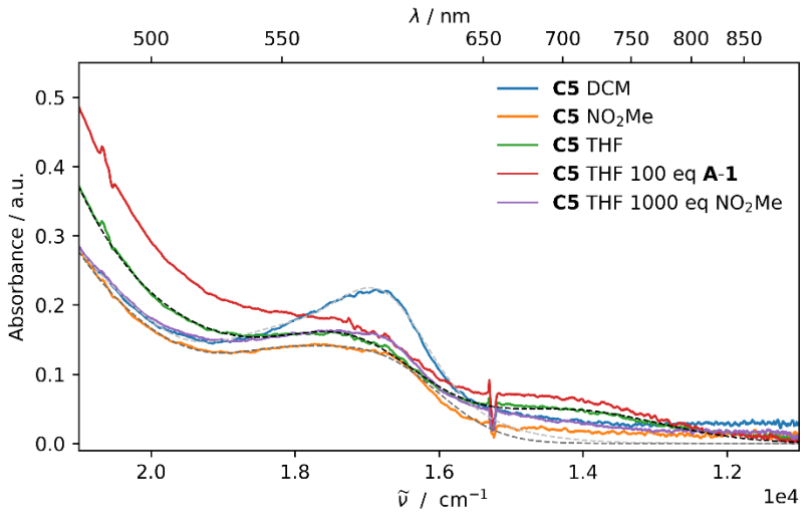


Figure S11: UV-Vis spectra of **C5** in different solvents and with the addition of reactions substrates. The concentration **C5** in solution is 2 mM in a 10 mm cuvette. The Solvent Spectra are fitted with gaussian curves and the parameters in table 16.

Table S17: Fitting parameters for the UV-Vis Spectra of **C5** in different solvents shown in Figure S11. A additional peak at around 22700 cm^{-1} is in all spectra but not discussed further.

Solvent	Center ν / cm^{-1}	Linewidth / cm^{-1}	Intensity / a.u.
DCM	20567(20)	763(30)	0.10(2)
	18000(200)	1500(100)	0.17(2)
	16740(30)	581(30)	0.10(2)
$MeNO_2$	21380(20)	665(30)	0.10(2)
	18000(200)	1500(100)	0.14(2)
	16694(30)	392(20)	0.05(1)
THF	19501(30)	1500(50)	0.13(2)
	17162(30)	988(20)	0.10(2)
	14187(30)	1245(30)	0.05(1)

3.4.2 CD Experiments

In CD Spectroscopy the sample is probed with circular polarized light of different handedness. Molecules with optical active centers interact differently with right- and left-hand polarized light. This difference is probed in the UV-Vis region on **C5**. Not only are the two chiral centers in the backbone of the ligand but also the binaphthol center is optically active. DFT calculations reveal charge transfer transitions between the Cobalt center and the coordinated naphtholate that are optically active. This opens the possibility to probe the coordination of the naphtholate to the Cobalt center by the presence of a CD signal and thereby the interaction between substrates.

The signal at 26300 cm^{-1} was first observed in CD measurements on **C5** and the origin of the signal was confirmed by comparison to the inactive precatalyst **C5*HPF$_6$** and the ligand, which did not show the signal as shown in **Figure S12**. This is the foundation for further measurements where the substrate $MeNO_2$ (**NM**) was added to **C5** in increasing equivalents up to a limit due to the absorption of $MeNO_2$ (**NM**). The results are illustrated in Figure S13 and show a decrease of signal intensity at 26300 cm^{-1} by the addition of $MeNO_2$ (**NM**). Similarly, the second substrate **1a** was added in lower equivalents due to the absorption of the aldehyde. Measurements were possible up to 100 eq and did not show a change in the signal at 26300 cm^{-1} as shown in **Figure S13**. The change in the spectra at higher energies can be attributed to the strong absorption of the aldehyde in the sample and the limitations of the detector.

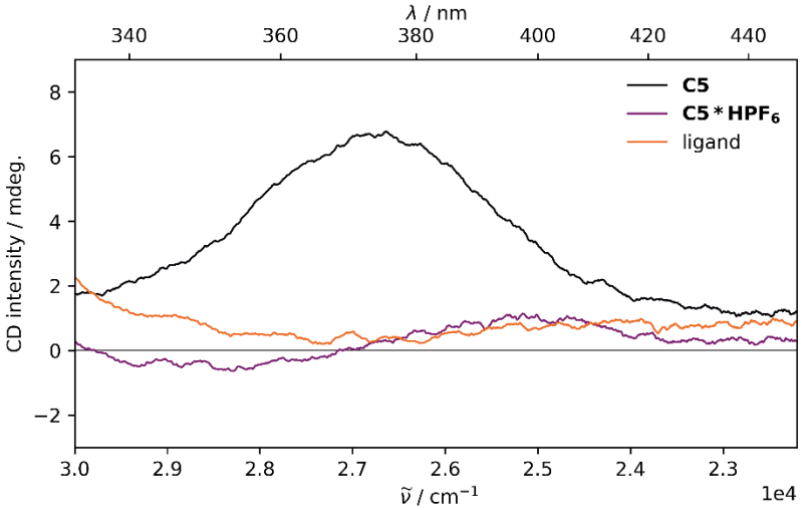


Figure S12: CD Spectra of **C5**, **C5*HPF$_6$** and the ligand in a range between 22200-30000 cm^{-1}. The concentration of the samples was 0.2 mM in a 2 mm cuvette.

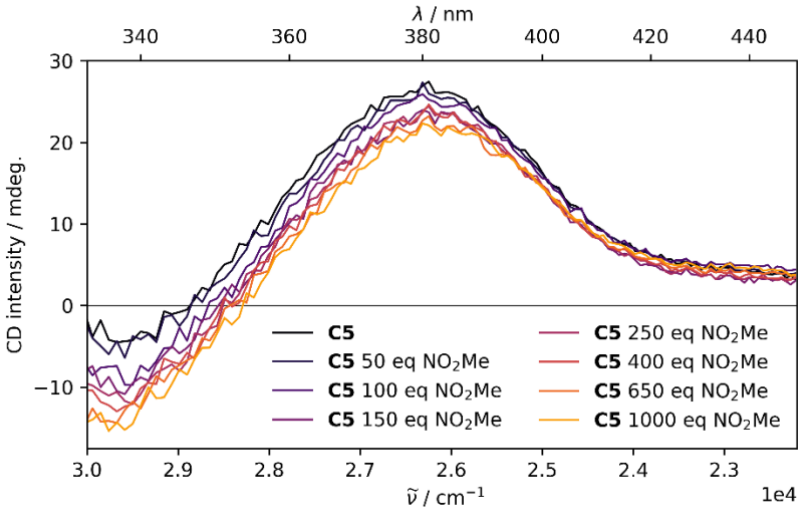


Figure S13: CD spectra of **C5** (0.2 mM in a 10 mm cuvette) in a range between 22200-30000 cm^{-1} with the subsequent addition of $MeNO_2$ (**NM**) to the solution. The intensities were corrected for the small changes in concentration.

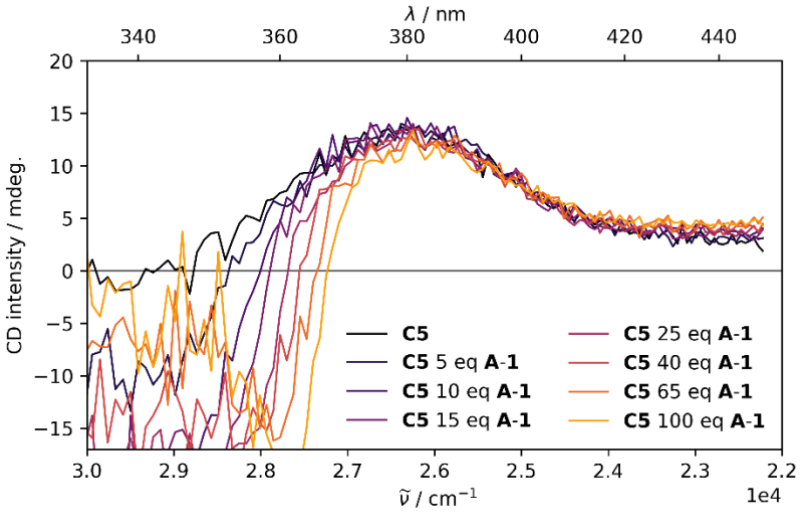


Figure S14: CD spectra of **C5** (0.2 mM in a 10 mm cuvette) in a range between 22200-30000 cm^{-1} with the subsequent addition of **1a** to the solution. The intensities were corrected for the small changes in concentration.

3.5 SQUID and EPR

The magnetic properties of the Co(II)-based d^7 systems, the precatalyst **C5*HPF$_6$** and **C5** were investigated by SQUID magnetometry using pellet samples. The molar magnetic susceptibility, χ_m was measured as a function of temperature, *T*.

The $\chi_m T$ versus *T* plots for the precatalyst **C5*HPF$_6$** and **C5** are shown in Figures **S15** and **S16**, together with magnetisation versus magnetic field data. At 1.8 K the magnetisation approaches saturation, while at 10 K it exhibits a nearly linear response. In both systems, the data are consistent with an S = 3/2 ground state. The corresponding spin Hamiltonian parameters are listed in Table 5. Initial estimates for the fitting parameters were taken from CASSCF calculations based on PBEh-3c/def2-mSVP geometries.

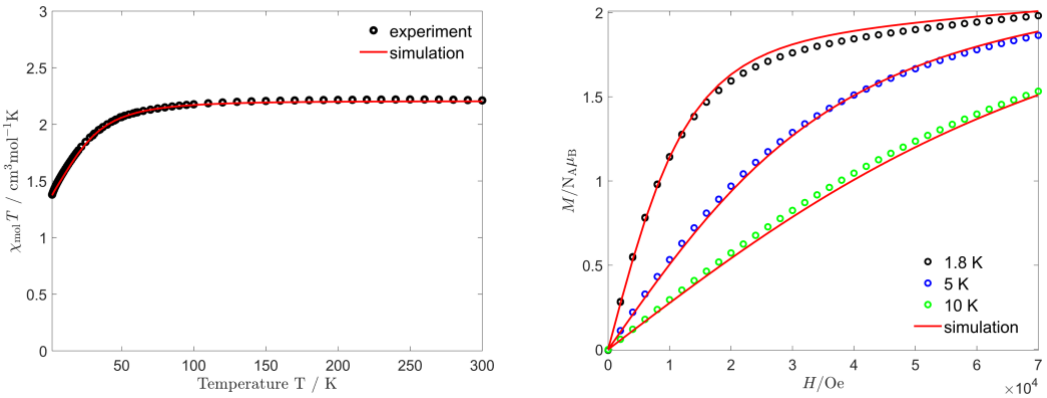


Figure S15. Temperature dependence of the molar magnetic susceptibility-temperature product ($\chi_m T$ vs. *T*, left*)* and field dependence of the magnetisation (*M* vs. *H*, right) measured on the Co(II)-based precatalyst **C5*HPF$_6$**.

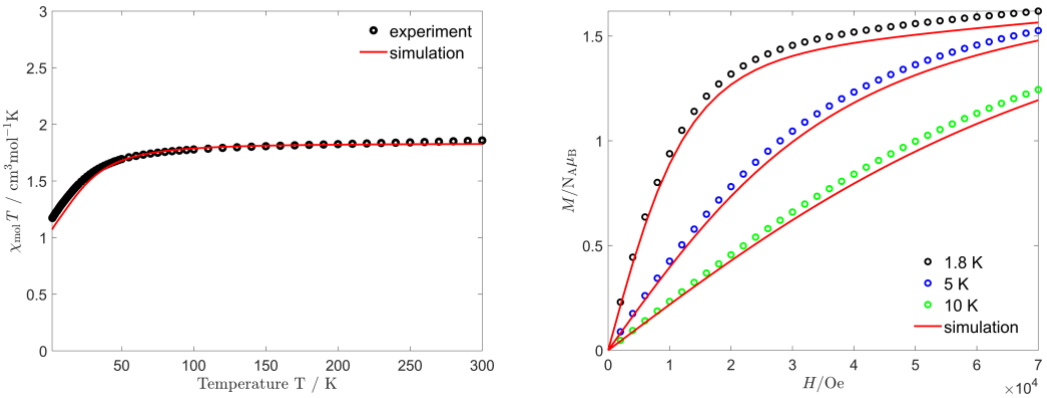


Figure S16. Temperature dependence of the molar magnetic susceptibility-temperature product ($\chi_m T$ vs. T, left) and field dependence of the magnetisation (M vs. H, right) measured on the Co(II)-based activated catalyst (**C5**).

EPR spectroscopy at X-band frequency (9.6 GHz) was also employed. Unlike SQUID magnetometry, which probes bulk magnetic behaviour, EPR selectively detects paramagnetic species here, the Co(II) centre, and provides insight into potential changes in the spin environment upon activation.

Powder EPR spectra of the precatalyst **C5*HPF$_6$** and **C5**, recorded at 4 K (Figures **S17** and **S18**), span a broad magnetic field range and appear qualitatively similar. Both spectra fit well to an S = 3/2 system with g_{iso} = 2.2 and a positive zero-field splitting of D = 28 cm^{-1}. These results indicate that the Co(II) spin environment is unchanged upon activation.

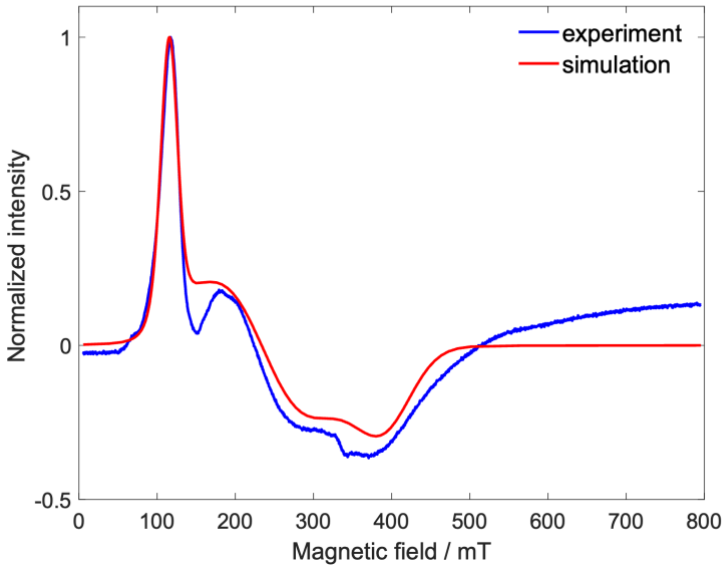


Figure S17. X-band EPR spectrum measured on a powder of the Co(II)-based precatalyst **C5*HPF$_6$** at 4 K.

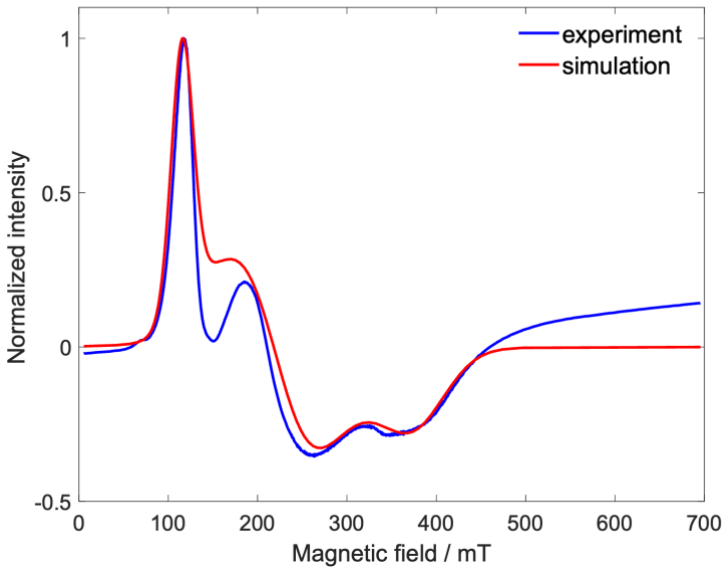


Figure S18: X-band EPR spectrum measured on a powder of the Co(II)-based activated catalyst (**C5**) at 4 K.

3.6 Microkinetic Modelling

Differential Equations of the Kinetic Model

All elementary reactions of the reaction network are listed in Table 6 in the manuscript. Based on these reactions, the corresponding set of ordinary differential equations (ODEs) is derived. The ODEs include rate constants k, where the subscript refers to the elementary reaction, and the symbols + and – indicate the forward and backward reactions. As an example, the rate equation for species **A** is given by:

$$\frac{d[\boldsymbol{A}]}{dt} = -k_{+1}[\boldsymbol{A}] + k_{-1}[\boldsymbol{B1}][ald] + k_{+4}[\boldsymbol{E}][NM] - k_{-4}[\boldsymbol{A}][prod]$$

The rate constants k_i, are connected to the corresponding Gibbs free energy barriers $\Delta G_i^{\ddagger}$ via transition state theory using the Eyring equation:

$$k_i = \frac{k_{\mathrm{B}}T}{h}\exp\left(\frac{-\Delta G_i^{\ddagger}}{RT}\right)$$

where k_{B} is the Boltzmann constant, h the Planck constant, T the temperature and R the gas constant.

Loss Function

The loss function used is the negative log likelihood (NLLH), which is also the default in the PEtab package.[**Error! Bookmark not defined.**] Since the standard deviation σ of the experimental data is unknown, it is treated as a parameter and fitted during optimization. By default, a Gaussian noise model is chosen. [13]

For the model shown in Figures **S19, S20** (SI) and **6** (manuscript), the resulting loss function value is -749.18, which is close to the global minimum of -772.42 obtained (shown in Figure **6** in the manuscript).

Simulation Results

Figure **S19** and **S20** show the measured concentration profiles of the 2-naphthylcarbaldehyde (**1a**) and its product (dots, **2a**) and results from our kinetic model (lines) for different starting conditions.

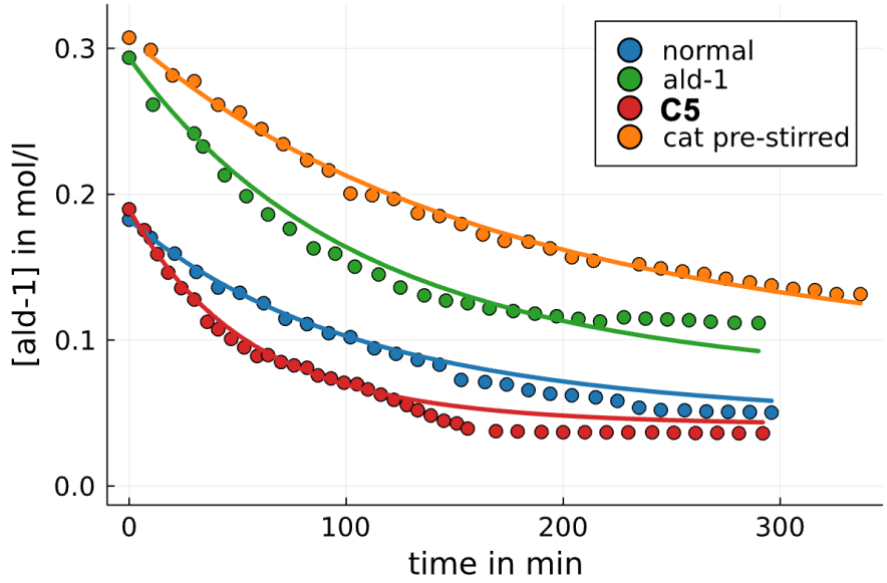


Figure S19. The measured concentration profiles of the product (dots) are compared with the microkinetic model simulations (lines) under the following four starting conditions: the standard conditions of the reaction in Table 1 entry 13 in the manuscript (blue); an increased aldehyde concentration (green); an increased catalyst concentration (red); and a catalyst that was pre-stirred in nitromethane for 5 h before the addition of the aldehyde (orange).

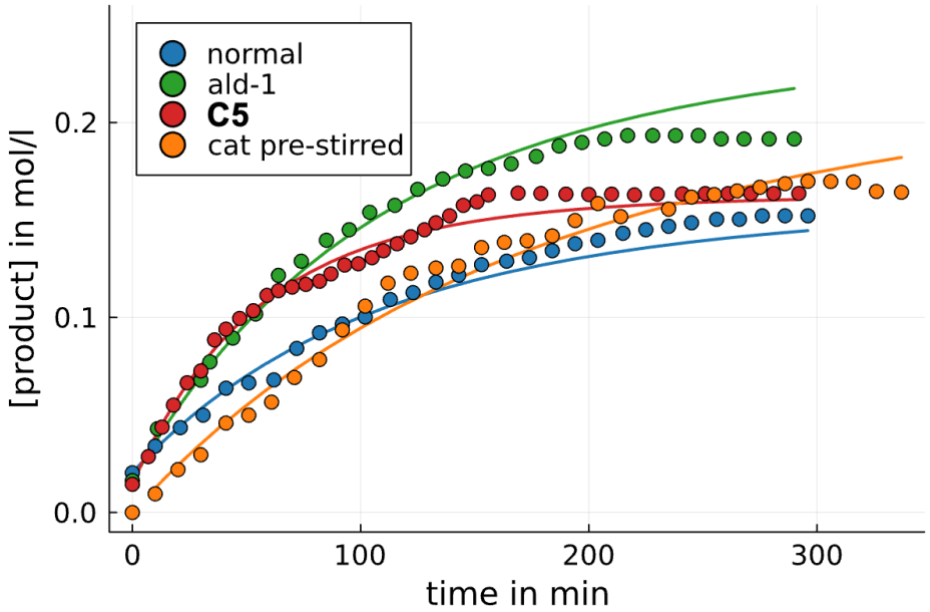


Figure S20: The measured concentration profiles of the product (dots) are compared with the microkinetic model simulations (lines) under the same starting conditions as in Figure S19.

3.7 Molecular Geometries

The following list contains the Cartesian coordinates for all geometries in XYZ format:

Standard Mechanism

Intermediate **I**

116

C	1.176489	-5.400585	-1.828769
C	0.234757	-4.486438	-2.191802
C	-0.385886	-3.666872	-1.219308
C	-1.295909	-2.634941	-1.721565
N	-2.631858	-2.519748	-1.523921
C	-3.514881	-3.391249	-0.750966
C	-4.300339	-2.620165	0.289261
N	-3.143541	-1.500550	-2.143699
N	-2.147396	-0.942681	-2.755766
C	-0.988432	-1.580917	-2.538910
C	-0.069333	-3.772278	0.119359
C	-0.777023	-2.987150	1.154729
C	-0.586302	-1.603345	1.235107
O	0.154137	-0.973772	0.379100
C	-1.238802	-0.908393	2.304545
C	-2.019474	-1.551655	3.209674
C	-2.249221	-2.945419	3.127512
C	-1.614605	-3.668706	2.084497
C	-1.882742	-5.058934	2.001833
C	-2.720495	-5.677810	2.891927
C	-3.338948	-4.953411	3.924865
C	-3.099252	-3.609933	4.032641
C	0.960773	-4.685936	0.498151
C	1.574780	-5.511737	-0.478659
C	2.591313	-6.412130	-0.088420
C	2.996321	-6.483848	1.214006
C	2.405177	-5.650485	2.182454
C	1.413680	-4.776349	1.835457
H	1.638612	-6.034087	-2.574636
H	-0.049980	-4.383647	-3.230733
H	-4.171292	-3.898914	-1.458400
H	-2.879740	-4.140429	-0.287393
H	-4.829610	-3.326899	0.926259
H	-3.638604	-2.033818	0.923530
H	-5.028200	-1.953928	-0.170313
H	-0.041176	-1.261187	-2.935799
H	-1.086434	0.157854	2.408692
H	-2.481614	-0.987077	4.011100
H	-1.417516	-5.650680	1.223999
H	-2.902581	-6.740835	2.798821
H	-3.994007	-5.454215	4.624907
H	-3.568413	-3.033116	4.821341
H	3.052113	-7.037957	-0.842716
H	3.779357	-7.172476	1.502631

H	2.744453	-5.697609	3.208475
H	0.976089	-4.130759	2.583633
C	-2.352699	0.299843	-3.510057
C	-2.711702	1.436635	-2.609036
C	-1.775851	1.785298	-1.607573
O	-0.648447	1.161696	-1.571783
Co	0.421917	0.893277	0.031746
N	2.069963	1.924759	0.519713
S	3.516795	1.284912	0.446104
C	4.318092	2.011553	-1.049321
F	5.477110	1.405792	-1.279976
F	3.537272	1.839292	-2.114060
F	4.539557	3.308200	-0.889165
O	4.389523	1.678824	1.539265
O	3.369132	-0.114533	0.085581
C	1.867427	3.185595	1.217348
C	0.473528	3.120957	1.894178
N	-0.420689	2.554514	0.903988
C	-1.350219	3.255552	0.384225
C	-2.168770	2.830932	-0.725932
C	-3.369671	3.512238	-0.939855
C	-4.269448	3.183257	-1.938404
C	-5.566158	3.968376	-2.104687
C	-6.415731	3.435386	-3.258543
C	-6.396683	3.874199	-0.818149
C	-5.237104	5.438815	-2.394063
C	-3.910108	2.107044	-2.752878
H	2.612052	3.325817	2.008493
H	0.172766	4.148551	2.136753
H	-1.559728	4.250258	0.788948
H	-3.600412	4.331548	-0.265936
H	-6.715056	2.397128	-3.103034
H	-7.329788	4.024066	-3.347532
H	-5.895590	3.501557	-4.215969
H	-5.866875	4.284575	0.042402
H	-7.330515	4.430988	-0.920221
H	-6.646544	2.837895	-0.586477
H	-4.664140	5.896382	-1.586599
H	-4.650889	5.537314	-3.308587
H	-6.151861	6.022717	-2.515869
H	-4.582501	1.777436	-3.535769
C	0.382930	2.299547	3.164191
C	1.380520	1.446090	3.618856
C	-0.797041	2.400433	3.900213
C	1.191847	0.702518	4.776976
C	-0.983804	1.663625	5.056962
C	0.013379	0.803160	5.495957
H	2.314713	1.343868	3.086866
H	-1.584023	3.065145	3.561358
H	1.976251	0.036533	5.110519
H	-1.905394	1.761473	5.616208

H	-0.128147	0.217800	6.394840
C	1.905472	4.407480	0.322395
C	2.328760	5.618924	0.860513
C	1.469619	4.381228	-0.998283
C	2.314320	6.780849	0.105131
C	1.451190	5.543603	-1.755587
C	1.871370	6.746363	-1.208779
H	2.687325	5.651095	1.883468
H	1.152953	3.452172	-1.452562
H	2.658138	7.710436	0.539726
H	1.111599	5.504794	-2.782443
H	1.861963	7.649478	-1.804878
H	-1.418434	0.474183	-4.043369
H	-3.132895	0.109368	-4.246226
O	3.419156	-3.786823	-3.671178
N	2.782980	-2.878872	-3.204275
C	3.067647	-2.462679	-1.814733
H	3.675412	-1.562389	-1.859078
H	3.604844	-3.255256	-1.306617
O	1.936935	-2.255085	-3.809319
H	2.137804	-2.229041	-1.304211

Transition State **I** → **II$_s$**
116

C	-3.615451	-2.889751	2.714301
C	-2.271524	-3.088401	2.804388
C	-1.491186	-3.202351	1.634623
C	-0.034074	-3.326581	1.751302
N	0.699957	-4.435510	1.492767
C	0.217280	-5.788946	1.243191
C	-0.151381	-6.493359	2.534731
N	1.976196	-4.219694	1.562226
N	2.090605	-2.965759	1.876138
C	0.897877	-2.360595	2.017520
C	-2.054261	-3.120305	0.376515
C	-1.219279	-3.333402	-0.830888
C	-0.236585	-2.404433	-1.178269
O	-0.016522	-1.295896	-0.529983
C	0.614797	-2.701046	-2.287851
C	0.475812	-3.842607	-3.007607
C	-0.527240	-4.791265	-2.691395
C	-1.387283	-4.528429	-1.593208
C	-2.361207	-5.510832	-1.279662
C	-2.468924	-6.666313	-2.008871
C	-1.617699	-6.914029	-3.097961
C	-0.667549	-5.984919	-3.426210
C	-3.449951	-2.858065	0.276218
C	-4.234064	-2.751157	1.453203
C	-5.617428	-2.486678	1.337437
C	-6.196198	-2.315920	0.112103

C	-5.415099	-2.403011	-1.056840
C	-4.077547	-2.670992	-0.977405
H	-4.215134	-2.801328	3.611071
H	-1.790639	-3.145938	3.771938
H	-0.633283	-5.715367	0.570917
H	1.011893	-6.304522	0.708876
H	0.699115	-6.563003	3.211949
H	-0.967253	-5.984308	3.046873
H	-0.484079	-7.504702	2.306985
H	0.792864	-1.317501	2.254060
H	1.390041	-1.984115	-2.524576
H	1.138891	-4.041947	-3.842194
H	-3.039406	-5.350696	-0.451781
H	-3.224516	-7.394238	-1.742744
H	-1.715148	-7.827539	-3.669190
H	-0.001086	-6.158689	-4.262833
H	-6.211143	-2.407798	2.239678
H	-7.254648	-2.105009	0.035918
H	-5.877884	-2.252575	-2.023177
H	-3.479587	-2.732145	-1.876528
C	3.414851	-2.330101	1.800159
C	3.628430	-1.787810	0.420083
C	3.031379	-0.540220	0.099749
O	2.455090	0.121660	1.043356
Co	1.288324	1.638166	0.824517
N	1.732367	3.570063	0.700831
S	1.489667	4.539459	1.936075
C	3.161151	5.119973	2.461922
F	3.715686	5.872651	1.519295
F	3.059553	5.838818	3.571834
F	3.957782	4.083072	2.701709
O	0.801261	5.770232	1.581803
O	1.045593	3.718884	3.045832
C	1.935047	4.090976	-0.641053
C	1.270223	3.087826	-1.627047
N	1.657349	1.774043	-1.154971
C	2.539215	1.080167	-1.764242
C	3.148853	-0.121626	-1.253071
C	3.896274	-0.884429	-2.162873
C	4.493964	-2.083999	-1.839856
C	5.293790	-2.926464	-2.824860
C	6.735394	-3.069206	-2.320137
C	4.654089	-4.315424	-2.947560
C	5.335293	-2.296127	-4.216651
C	4.318300	-2.519239	-0.520127
H	1.449341	5.064348	-0.772646
H	1.680441	3.276140	-2.627816
H	2.883341	1.410047	-2.748592
H	3.980652	-0.497958	-3.171612
H	7.215922	-2.094367	-2.227794
H	6.780623	-3.552182	-1.342965

H	7.329420	-3.673089	-3.009381
H	3.620575	-4.242680	-3.289215
H	5.204716	-4.931917	-3.661013
H	4.644570	-4.849993	-1.996812
H	4.338543	-2.191797	-4.649615
H	5.808229	-1.312486	-4.207883
H	5.915921	-2.926606	-4.891527
H	4.741048	-3.470874	-0.214135
C	-0.241502	3.150859	-1.718383
C	-1.037779	3.964679	-0.920971
C	-0.858112	2.327182	-2.659743
C	-2.420077	3.953182	-1.068168
C	-2.234052	2.318117	-2.808682
C	-3.022398	3.133275	-2.007434
H	-0.606385	4.614262	-0.172615
H	-0.253634	1.675748	-3.279886
H	-3.023465	4.588870	-0.434133
H	-2.691860	1.670077	-3.544554
H	-4.099173	3.125626	-2.114003
C	3.389327	4.237540	-1.038955
C	3.728900	5.182286	-2.002712
C	4.387991	3.411558	-0.535402
C	5.031223	5.300035	-2.460510
C	5.692333	3.523615	-0.995283
C	6.019444	4.465444	-1.958324
H	2.963309	5.843922	-2.393100
H	4.158415	2.684761	0.231906
H	5.276293	6.048621	-3.202734
H	6.457307	2.873341	-0.591148
H	7.038853	4.555136	-2.309966
H	3.442880	-1.553369	2.561311
H	4.139743	-3.100159	2.056084
C	-1.793111	0.355087	0.332415
H	-2.820809	0.016413	0.288831
H	-0.943133	-0.613011	-0.157611
H	-1.580030	1.236163	-0.261411
N	-1.362050	0.484783	1.651475
O	-1.915245	-0.082830	2.558149
O	-0.298613	1.121669	1.894833

Intermediate **II$_s$**
116

C	0.975140	-5.263958	-0.549721
C	0.319929	-4.441726	-1.416303
C	-0.793971	-3.697401	-0.976916
C	-1.400714	-2.718028	-1.885180
N	-2.627244	-2.774031	-2.461016
C	-3.570731	-3.890227	-2.459345
C	-4.999996	-3.443775	-2.238335
N	-2.912995	-1.696373	-3.124380

N	-1.873243	-0.931908	-2.997887
C	-0.902927	-1.500770	-2.259955
C	-1.233342	-3.764741	0.328176
C	-2.378632	-2.927548	0.761204
C	-2.222370	-1.555433	0.891881
O	-1.087114	-0.903459	0.716370
C	-3.353207	-0.750125	1.198832
C	-4.570425	-1.309294	1.423426
C	-4.758993	-2.709657	1.347460
C	-3.648442	-3.524858	1.008844
C	-3.863357	-4.920929	0.904694
C	-5.102278	-5.465298	1.116071
C	-6.198430	-4.651077	1.450678
C	-6.020855	-3.299477	1.566285
C	-0.545411	-4.604915	1.243802
C	0.563489	-5.365909	0.796168
C	1.245523	-6.196009	1.712910
C	0.855934	-6.258099	3.020561
C	-0.233352	-5.487728	3.471159
C	-0.917174	-4.681375	2.605434
H	1.831966	-5.834824	-0.884732
H	0.655565	-4.344849	-2.440417
H	-3.457141	-4.414790	-3.409120
H	-3.244840	-4.560837	-1.668681
H	-5.630980	-4.327177	-2.158959
H	-5.098018	-2.884176	-1.310620
H	-5.367891	-2.834088	-3.060946
H	0.032946	-1.032526	-2.004131
H	-3.212778	0.322352	1.248617
H	-5.417899	-0.679378	1.667019
H	-3.032840	-5.572423	0.664053
H	-5.235463	-6.536253	1.033548
H	-7.170941	-5.093189	1.620052
H	-6.855642	-2.659151	1.825902
H	2.090715	-6.776897	1.364766
H	1.387494	-6.893950	3.716068
H	-0.527539	-5.533646	4.511242
H	-1.747913	-4.086489	2.960139
C	-1.945010	0.464586	-3.461488
C	-2.247962	1.367854	-2.305698
C	-1.171386	1.737070	-1.462425
O	0.023433	1.392862	-1.795568
Co	1.533263	1.225613	-0.581942
N	2.972098	2.557534	-0.208148
S	4.483040	2.321715	-0.626131
C	4.800367	3.554164	-1.960092
F	6.025536	3.403714	-2.446508
F	3.929409	3.398886	-2.953172
F	4.680512	4.789153	-1.485048
O	5.442718	2.677514	0.404317
O	4.568637	1.047432	-1.318499

C	2.633517	3.530347	0.814187
C	1.590245	2.844685	1.747423
N	0.592251	2.326258	0.840629
C	-0.560678	2.852398	0.717337
C	-1.519479	2.486453	-0.300368
C	-2.838932	2.898481	-0.105907
C	-3.882789	2.562011	-0.952093
C	-5.299774	3.048339	-0.667231
C	-6.295973	2.560083	-1.718904
C	-5.760086	2.527628	0.700134
C	-5.322394	4.582124	-0.660705
C	-3.546618	1.763215	-2.045382
H	3.507164	3.801175	1.412834
H	1.162684	3.604405	2.415875
H	-0.873676	3.628050	1.422251
H	-3.042336	3.502961	0.772982
H	-6.354881	1.470502	-1.753227
H	-7.294811	2.930135	-1.483364
H	-6.046194	2.920230	-2.718556
H	-5.114074	2.870530	1.509424
H	-6.772376	2.870176	0.924935
H	-5.763037	1.436568	0.718516
H	-4.662855	4.997382	0.102324
H	-5.002641	4.983370	-1.623269
H	-6.329349	4.953382	-0.458481
H	-4.320444	1.434413	-2.728781
C	2.160356	1.707006	2.575157
C	3.456915	1.742080	3.082326
C	1.361059	0.606527	2.873530
C	3.935918	0.706816	3.868707
C	1.842250	-0.433504	3.655008
C	3.131191	-0.385141	4.158651
H	4.120503	2.565692	2.860888
H	0.352698	0.543144	2.487500
H	4.950206	0.750927	4.242825
H	1.209945	-1.289315	3.847957
H	3.511974	-1.197200	4.764555
C	2.031999	4.815766	0.283970
C	2.046758	5.943584	1.100272
C	1.405797	4.901595	-0.953600
C	1.445677	7.126001	0.699957
C	0.798795	6.082899	-1.356259
C	0.813849	7.197692	-0.533173
H	2.545514	5.898848	2.062654
H	1.394645	4.049726	-1.619155
H	1.477848	7.993154	1.346854
H	0.315505	6.129842	-2.323388
H	0.344442	8.118899	-0.852552
H	-0.989997	0.697595	-3.927745
H	-2.724711	0.489272	-4.220062
O	1.162739	-2.075563	0.907704

N	2.104135	-1.439840	0.341707
C	3.337068	-1.519875	0.702593
H	4.077040	-0.955356	0.162109
H	3.573667	-2.135815	1.551920
O	1.768631	-0.686058	-0.682672
H	-0.226709	-1.445844	0.748450

Intermediate **III$_s$**
136

C	-4.084186	-5.150699	-0.779867
C	-3.349246	-4.822250	0.321575
C	-1.998494	-5.218717	0.413164
C	-1.229579	-4.862657	1.612712
N	-0.806500	-5.742926	2.555623
C	-1.087867	-7.171473	2.663561
C	-1.810852	-7.506036	3.953376
N	-0.098213	-5.174503	3.479961
N	-0.063369	-3.919749	3.163807
C	-0.743847	-3.652220	2.030891
C	-1.379289	-5.898063	-0.618589
C	0.071357	-6.189369	-0.499054
C	0.969018	-5.135997	-0.550278
O	0.626520	-3.885444	-0.853849
C	2.329069	-5.346067	-0.212325
C	2.776982	-6.590267	0.104592
C	1.909731	-7.707958	0.086987
C	0.541645	-7.505902	-0.228168
C	-0.311575	-8.635991	-0.234500
C	0.165604	-9.884275	0.061727
C	1.521167	-10.077596	0.383176
C	2.371138	-9.006155	0.391355
C	-2.135123	-6.241284	-1.770567
C	-3.505549	-5.881983	-1.838456
C	-4.255497	-6.234668	-2.982675
C	-3.669748	-6.902655	-4.019869
C	-2.302343	-7.237840	-3.963807
C	-1.552386	-6.912898	-2.869210
H	-5.118783	-4.841234	-0.856150
H	-3.793309	-4.256281	1.130216
H	-1.690993	-7.429573	1.797808
H	-0.143787	-7.706316	2.572773
H	-1.208573	-7.269749	4.828353
H	-2.758656	-6.974194	4.027771
H	-2.023328	-8.573712	3.970862
H	-0.835631	-2.666871	1.595553
H	2.993817	-4.491566	-0.208083
H	3.817382	-6.738526	0.367259
H	-1.357111	-8.514310	-0.487353
H	-0.506449	-10.732375	0.040867
H	1.887107	-11.069044	0.613613

H	3.419158	-9.142482	0.630271
H	-5.300473	-5.954518	-3.028982
H	-4.251428	-7.167904	-4.892730
H	-1.843279	-7.751387	-4.797719
H	-0.500350	-7.162989	-2.837842
C	0.759993	-3.010469	3.981932
C	1.993326	-2.590154	3.249372
C	1.855772	-1.511355	2.331507
O	0.711492	-0.968922	2.194224
Co	0.009427	0.365255	0.871522
N	-0.198785	1.820862	-0.543079
S	-1.521882	2.459282	-1.133503
C	-1.567013	1.928376	-2.911551
F	-1.318312	0.628849	-3.034855
F	-2.769775	2.174526	-3.422034
F	-0.667582	2.593887	-3.631822
O	-2.684350	1.795766	-0.566397
O	-1.485598	3.906906	-1.229154
C	1.059970	2.500065	-0.783934
C	2.112980	1.377523	-0.960447
N	1.975831	0.485519	0.171257
C	3.009831	-0.132604	0.597548
C	3.028464	-1.138185	1.623158
C	4.239259	-1.804460	1.863033
C	4.366488	-2.848527	2.755910
C	5.671862	-3.591829	3.011005
C	5.514160	-5.057821	2.586656
C	6.836728	-2.991801	2.224085
C	6.021845	-3.527689	4.503370
C	3.197927	-3.226019	3.435765
H	1.048977	3.089262	-1.706658
H	3.114240	1.826281	-0.964648
H	3.977075	0.075488	0.128357
H	5.102004	-1.472821	1.296915
H	4.706792	-5.556559	3.124972
H	5.291470	-5.129114	1.520529
H	6.431859	-5.618646	2.776500
H	7.754289	-3.540109	2.442115
H	6.676830	-3.048337	1.145906
H	7.012269	-1.947456	2.487642
H	6.137965	-2.494800	4.833695
H	5.254460	-3.988050	5.127003
H	6.958305	-4.052575	4.703194
H	3.237672	-4.050109	4.141590
C	1.933224	0.639719	-2.272526
C	1.518128	-0.684101	-2.347852
C	2.209297	1.318088	-3.456348
C	1.365939	-1.307090	-3.579187
C	2.058038	0.699860	-4.685292
C	1.630412	-0.618450	-4.750856
H	1.315741	-1.254522	-1.451955

H	2.544165	2.348956	-3.419991
H	1.032377	-2.335670	-3.614799
H	2.272181	1.249067	-5.592751
H	1.506457	-1.104202	-5.709841
C	1.474005	3.438935	0.338424
C	2.682896	4.126321	0.238874
C	0.687010	3.654122	1.462186
C	3.111843	4.976256	1.243812
C	1.117857	4.500904	2.475638
C	2.331177	5.159644	2.376867
H	3.298870	4.009404	-0.646465
H	-0.284529	3.187964	1.549992
H	4.053171	5.500515	1.140494
H	0.488113	4.651449	3.342657
H	2.661543	5.821113	3.167048
H	0.135080	-2.156130	4.236474
H	0.989458	-3.567031	4.888168
H	-7.472266	-1.303791	-5.147893
C	-6.984273	-0.739297	-4.362726
C	-7.537561	0.425768	-3.903376
C	-6.902111	1.175133	-2.894445
C	-5.723819	0.740984	-2.353593
C	-5.139760	-0.465248	-2.800589
C	-5.768801	-1.213550	-3.828076
C	-5.150007	-2.403440	-4.293357
C	-3.967801	-2.830992	-3.770328
C	-3.352272	-2.093063	-2.729770
C	-3.930334	-0.940072	-2.256300
H	-8.468810	0.781873	-4.324275
H	-7.345345	2.101944	-2.556241
H	-5.212732	1.315688	-1.591031
H	-3.451844	-0.375245	-1.464285
H	-3.488387	-3.727756	-4.139833
H	-5.628502	-2.962422	-5.088600
C	-2.091985	-2.502711	-2.129176
H	-1.745918	-1.861511	-1.310019
C	-3.556525	-0.495630	1.797629
H	-4.054852	-1.265582	1.235532
H	-4.058509	0.107249	2.532518
O	-1.448998	-3.481970	-2.474080
H	-0.173606	-3.819758	-1.434682
N	-2.326056	-0.224206	1.515583
O	-1.662957	-0.879969	0.615439
O	-1.649387	0.693168	2.085122

Transition State **III$_s$ → IV$_s$**
136

C	-4.455589	-5.345847	-0.409489
C	-3.739449	-4.952059	0.682239
C	-2.329551	-4.896330	0.617919

C	-1.564329	-4.445623	1.786238
N	-0.945249	-5.260499	2.675358
C	-0.946050	-6.720419	2.714090
C	-1.501775	-7.251398	4.020398
N	-0.276864	-4.603502	3.569820
N	-0.461359	-3.353995	3.280803
C	-1.242683	-3.179461	2.199735
C	-1.647016	-5.233531	-0.532516
C	-0.162498	-5.268011	-0.495956
C	0.579668	-4.098674	-0.426463
O	0.065891	-2.881194	-0.504902
C	1.977562	-4.173287	-0.186270
C	2.604846	-5.369270	-0.048306
C	1.889205	-6.584735	-0.156010
C	0.491730	-6.532978	-0.395768
C	-0.204667	-7.763112	-0.489158
C	0.445515	-8.959971	-0.345642
C	1.828918	-9.002818	-0.100512
C	2.530793	-7.832016	-0.011506
C	-2.388909	-5.591220	-1.690770
C	-3.804121	-5.655451	-1.624092
C	-4.536690	-5.981865	-2.787291
C	-3.893703	-6.220635	-3.966982
C	-2.487803	-6.155039	-4.034552
C	-1.752019	-5.851074	-2.925086
H	-5.536380	-5.398380	-0.363548
H	-4.242321	-4.679058	1.601028
H	-1.543909	-7.046603	1.867105
H	0.074909	-7.055183	2.535497
H	-0.899798	-6.940927	4.872205
H	-2.527902	-6.922062	4.179805
H	-1.500533	-8.339612	3.988025
H	-1.485200	-2.212939	1.784960
H	2.525743	-3.244558	-0.107873
H	3.671226	-5.400721	0.141290
H	-1.268235	-7.763730	-0.688036
H	-0.112782	-9.883362	-0.430071
H	2.331839	-9.954195	0.008829
H	3.598816	-7.847389	0.171172
H	-5.617860	-6.011277	-2.737677
H	-4.464862	-6.445475	-4.857516
H	-1.989994	-6.334852	-4.977996
H	-0.673983	-5.785266	-2.983628
C	0.320979	-2.339848	4.003219
C	1.638350	-2.147950	3.320914
C	1.684375	-1.261353	2.211571
O	0.615575	-0.619717	1.898969
Co	0.307044	0.448930	0.318515
N	0.731919	2.343149	-0.065566
S	-0.314611	3.488475	0.252409
C	-1.083186	3.884631	-1.381126

F	-1.643400	2.814012	-1.924502
F	-2.014818	4.819166	-1.230367
F	-0.159343	4.347992	-2.223818
O	-1.396744	2.879892	1.007950
O	0.284307	4.744579	0.657353
C	2.087167	2.635564	-0.473859
C	2.593425	1.336519	-1.186201
N	2.266209	0.272669	-0.265995
C	3.176698	-0.274269	0.439265
C	2.944555	-1.151756	1.560614
C	4.047442	-1.880898	2.028428
C	3.985929	-2.759580	3.089610
C	5.169973	-3.577678	3.588123
C	4.824058	-5.071325	3.524473
C	6.422933	-3.342495	2.745381
C	5.485970	-3.189974	5.038463
C	2.740857	-2.867835	3.720433
H	2.133287	3.456407	-1.196178
H	3.680780	1.418052	-1.317293
H	4.225571	-0.066827	0.206651
H	4.985272	-1.736416	1.504928
H	3.962896	-5.321187	4.145673
H	4.588163	-5.376929	2.503975
H	5.662943	-5.677140	3.873552
H	7.245559	-3.950399	3.124592
H	6.270872	-3.618708	1.700141
H	6.749506	-2.301676	2.777847
H	5.737548	-2.131464	5.114860
H	4.641968	-3.375940	5.704355
H	6.332673	-3.766087	5.417819
H	2.629210	-3.542762	4.563175
C	1.948979	1.120008	-2.538352
C	1.289421	-0.059356	-2.861775
C	2.039646	2.116969	-3.507180
C	0.695122	-0.220085	-4.105854
C	1.463064	1.952159	-4.754358
C	0.777351	0.783182	-5.055420
H	1.225048	-0.873884	-2.153916
H	2.566493	3.038885	-3.291404
H	0.156788	-1.135332	-4.313878
H	1.541269	2.742470	-5.489333
H	0.311452	0.660201	-6.024424
C	3.035969	2.964651	0.661494
C	4.283639	3.502459	0.356390
C	2.739912	2.690826	1.989977
C	5.219964	3.747515	1.347199
C	3.677578	2.928408	2.985153
C	4.920224	3.453718	2.670039
H	4.524591	3.743103	-0.673983
H	1.768370	2.301182	2.260819
H	6.180156	4.174761	1.088383

H	3.428065	2.707904	4.014820
H	5.646852	3.643765	3.449119
H	-0.273240	-1.428960	4.018753
H	0.434162	-2.707697	5.021143
H	-6.594996	-3.351861	-6.935769
C	-6.882215	-3.308954	-5.892049
C	-8.183918	-3.512203	-5.526451
C	-8.558777	-3.451711	-4.168952
C	-7.623357	-3.187914	-3.208161
C	-6.269311	-2.975622	-3.555837
C	-5.892061	-3.038995	-4.921789
C	-4.534518	-2.839639	-5.262647
C	-3.593614	-2.608778	-4.302044
C	-3.964043	-2.553927	-2.941350
C	-5.276536	-2.725226	-2.588302
H	-8.932975	-3.717705	-6.279615
H	-9.592497	-3.610840	-3.892016
H	-7.911573	-3.133859	-2.164985
H	-5.560466	-2.692394	-1.540919
H	-2.552646	-2.482359	-4.565520
H	-4.245641	-2.884712	-6.305842
C	-2.919904	-2.408682	-1.893233
H	-3.265293	-2.693191	-0.885423
C	-3.305173	-0.389386	-1.407153
H	-3.120852	0.100166	-2.350499
H	-4.306174	-0.394149	-1.004066
O	-1.714511	-2.534002	-2.201228
H	-0.712811	-2.774827	-1.167032
N	-2.326025	-0.253889	-0.484886
O	-1.167709	0.003186	-0.919585
O	-2.500855	-0.510306	0.703510

Intermediate **IV$_s$**
136

C	-4.526688	-5.164009	-0.252941
C	-3.787700	-4.768719	0.824420
C	-2.380809	-4.714086	0.728218
C	-1.574188	-4.319785	1.887337
N	-0.960919	-5.185267	2.732640
C	-1.004059	-6.644800	2.716493
C	-1.520340	-7.209233	4.025082
N	-0.242005	-4.585524	3.627897
N	-0.388394	-3.321048	3.386609
C	-1.192982	-3.084032	2.335410
C	-1.717460	-5.027090	-0.440198
C	-0.237078	-4.977215	-0.453799
C	0.399015	-3.722980	-0.441666
O	-0.236674	-2.604878	-0.503951
C	1.831423	-3.729816	-0.345573
C	2.548343	-4.875839	-0.236554

C	1.916558	-6.144116	-0.251060
C	0.503260	-6.188677	-0.389715
C	-0.105031	-7.469536	-0.434216
C	0.636043	-8.616970	-0.322843
C	2.030706	-8.561361	-0.161731
C	2.650035	-7.339417	-0.133184
C	-2.484846	-5.407951	-1.575360
C	-3.897773	-5.493293	-1.474551
C	-4.649753	-5.869670	-2.610475
C	-4.028086	-6.140495	-3.794785
C	-2.625925	-6.047384	-3.898014
C	-1.872058	-5.687812	-2.817973
H	-5.606174	-5.220324	-0.184125
H	-4.272329	-4.502153	1.755235
H	-1.645737	-6.919261	1.883633
H	-0.002384	-7.000263	2.479696
H	-0.874021	-6.949505	4.861381
H	-2.528673	-6.857553	4.241043
H	-1.553161	-8.295028	3.952293
H	-1.399569	-2.100507	1.958199
H	2.332892	-2.772635	-0.356275
H	3.628344	-4.830166	-0.147402
H	-1.176458	-7.547787	-0.569645
H	0.139490	-9.578143	-0.368239
H	2.606215	-9.473058	-0.074392
H	3.726915	-7.277203	-0.023170
H	-5.728776	-5.920724	-2.535181
H	-4.614570	-6.411094	-4.662499
H	-2.146097	-6.250169	-4.846150
H	-0.797184	-5.601097	-2.899378
C	0.451213	-2.362182	4.115423
C	1.757250	-2.194060	3.404697
C	1.798685	-1.313988	2.293824
O	0.725940	-0.665669	1.983754
Co	0.410463	0.261907	0.333526
N	0.740873	2.170175	-0.084370
S	-0.364066	3.256348	0.237143
C	-1.049714	3.743707	-1.410104
F	-1.557185	2.699383	-2.053858
F	-2.010073	4.645994	-1.251704
F	-0.093276	4.276475	-2.168592
O	-1.466094	2.553445	0.878942
O	0.149464	4.502426	0.766289
C	2.096844	2.524570	-0.441881
C	2.672740	1.246385	-1.139427
N	2.370011	0.169873	-0.225055
C	3.283059	-0.325222	0.516785
C	3.053612	-1.203253	1.636990
C	4.151136	-1.956335	2.077113
C	4.085290	-2.857325	3.117824
C	5.244722	-3.746388	3.546625

C	4.836476	-5.215931	3.373652
C	6.497973	-3.496246	2.708292
C	5.590212	-3.479745	5.016965
C	2.852003	-2.942334	3.774288
H	2.129622	3.342638	-1.167500
H	3.757933	1.371562	-1.247932
H	4.327770	-0.076868	0.309068
H	5.082841	-1.822179	1.540560
H	3.976016	-5.477361	3.991169
H	4.568395	-5.430770	2.338010
H	5.655248	-5.880498	3.657508
H	7.304810	-4.149697	3.042904
H	6.331411	-3.705685	1.649951
H	6.855000	-2.468883	2.800669
H	5.887718	-2.441287	5.168397
H	4.747777	-3.680954	5.680220
H	6.415870	-4.117032	5.340380
H	2.741081	-3.626830	4.609206
C	2.058524	1.022339	-2.503741
C	1.361185	-0.133213	-2.833935
C	2.203152	2.011415	-3.474472
C	0.781715	-0.275303	-4.088362
C	1.642990	1.864025	-4.730839
C	0.918624	0.720504	-5.039293
H	1.254042	-0.946457	-2.128715
H	2.760416	2.913747	-3.250606
H	0.213081	-1.169668	-4.304079
H	1.765309	2.646971	-5.467649
H	0.466354	0.610159	-6.016185
C	2.994029	2.900581	0.718994
C	4.213049	3.514594	0.442939
C	2.685043	2.605383	2.039978
C	5.108452	3.817452	1.455068
C	3.582369	2.901361	3.056564
C	4.795874	3.505334	2.770641
H	4.462723	3.770499	-0.581663
H	1.735506	2.153854	2.291354
H	6.045720	4.304130	1.218414
H	3.323797	2.664072	4.080167
H	5.489656	3.741564	3.566719
H	-0.108048	-1.431441	4.181279
H	0.581146	-2.765528	5.117848
H	-6.685402	-3.746066	-7.005855
C	-6.970915	-3.598670	-5.971226
C	-8.268202	-3.780258	-5.581803
C	-8.639396	-3.584829	-4.235601
C	-7.705009	-3.212576	-3.310611
C	-6.355035	-3.019405	-3.683802
C	-5.981620	-3.217232	-5.036623
C	-4.628803	-3.036994	-5.396753
C	-3.688397	-2.690477	-4.467936

C	-4.053730	-2.498771	-3.119819
C	-5.362567	-2.658833	-2.750018
H	-9.017013	-4.072876	-6.305855
H	-9.669976	-3.728273	-3.938939
H	-7.990982	-3.057856	-2.276909
H	-5.650781	-2.540433	-1.709627
H	-2.652680	-2.582769	-4.755043
H	-4.337089	-3.189404	-6.429032
C	-3.010896	-2.148567	-2.084488
H	-3.219964	-2.741348	-1.181344
C	-3.231728	-0.657761	-1.691592
H	-2.992342	0.000067	-2.523629
H	-4.241394	-0.480115	-1.329900
O	-1.743857	-2.357486	-2.565986
H	-1.115703	-2.489012	-1.794357
N	-2.309363	-0.349932	-0.584560
O	-1.199830	0.042255	-0.912089
O	-2.642459	-0.572880	0.543555

Transition State **IV$_s$ → V**
136

C	-4.518993	-5.137883	-0.234570
C	-3.786540	-4.731592	0.843265
C	-2.381269	-4.644680	0.744566
C	-1.576114	-4.260113	1.908324
N	-0.961404	-5.138592	2.739752
C	-1.015806	-6.597641	2.715196
C	-1.550831	-7.163404	4.015249
N	-0.232306	-4.552949	3.635452
N	-0.371982	-3.285378	3.408995
C	-1.185127	-3.031726	2.367941
C	-1.714191	-4.932260	-0.428502
C	-0.233374	-4.863018	-0.447550
C	0.400528	-3.607985	-0.442671
O	-0.238031	-2.487078	-0.497679
C	1.833437	-3.612775	-0.372146
C	2.555830	-4.755264	-0.265298
C	1.927914	-6.024386	-0.264360
C	0.513711	-6.072451	-0.388720
C	-0.089384	-7.355851	-0.428015
C	0.657029	-8.500555	-0.323728
C	2.052782	-8.440492	-0.174336
C	2.667497	-7.216498	-0.152213
C	-2.475498	-5.326807	-1.563656
C	-3.885623	-5.448690	-1.458943
C	-4.631212	-5.842839	-2.593284
C	-4.006442	-6.096508	-3.779721
C	-2.607534	-5.967030	-3.886702
C	-1.859684	-5.589771	-2.808546
H	-5.596726	-5.219208	-0.163024

H	-4.274867	-4.482639	1.777001
H	-1.650694	-6.863419	1.874487
H	-0.014321	-6.959561	2.488148
H	-0.913810	-6.908524	4.860124
H	-2.560333	-6.808063	4.219258
H	-1.587067	-8.248855	3.939133
H	-1.392803	-2.042972	2.005626
H	2.334710	-2.657071	-0.404635
H	3.636664	-4.704573	-0.191779
H	-1.161387	-7.439584	-0.554348
H	0.162974	-9.463192	-0.365039
H	2.632344	-9.350052	-0.091642
H	3.745084	-7.149667	-0.052701
H	-5.708334	-5.921788	-2.514662
H	-4.588157	-6.381675	-4.645896
H	-2.125668	-6.156542	-4.836557
H	-0.787690	-5.476197	-2.893744
C	0.485486	-2.343556	4.139598
C	1.792191	-2.193474	3.426625
C	1.833525	-1.332800	2.301019
O	0.759191	-0.698418	1.974045
Co	0.412089	0.135384	0.274429
N	0.733273	2.069896	-0.095533
S	-0.373257	3.148330	0.245681
C	-1.049984	3.682759	-1.391433
F	-1.556528	2.660941	-2.070975
F	-2.009816	4.581855	-1.210738
F	-0.089533	4.236823	-2.130166
O	-1.482686	2.438970	0.866368
O	0.139635	4.382178	0.804371
C	2.084823	2.450106	-0.444380
C	2.684741	1.188953	-1.153052
N	2.399468	0.100125	-0.247479
C	3.313959	-0.346927	0.523549
C	3.090888	-1.220542	1.649833
C	4.190087	-1.961994	2.103605
C	4.121286	-2.855298	3.151694
C	5.279932	-3.739969	3.591360
C	4.873111	-5.211111	3.428752
C	6.535012	-3.495894	2.754386
C	5.621130	-3.461438	5.060336
C	2.886712	-2.936538	3.806359
H	2.107835	3.274031	-1.163762
H	3.767589	1.335315	-1.258656
H	4.352833	-0.058780	0.338589
H	5.124501	-1.827902	1.571691
H	4.010080	-5.467751	4.044677
H	4.609625	-5.434091	2.393564
H	5.690867	-5.873190	3.721400
H	7.340940	-4.147314	3.095108
H	6.370495	-3.712298	1.697144

H	6.891833	-2.467945	2.840432
H	5.917527	-2.421581	5.204092
H	4.776878	-3.657707	5.722741
H	6.446140	-4.095451	5.391611
H	2.775510	-3.611791	4.648746
C	2.075367	0.972621	-2.520868
C	1.385779	-0.183318	-2.865510
C	2.211130	1.974369	-3.480092
C	0.803566	-0.313134	-4.120038
C	1.647940	1.839739	-4.736630
C	0.929837	0.695873	-5.058253
H	1.286928	-1.006405	-2.171247
H	2.763170	2.877407	-3.246339
H	0.241496	-1.208970	-4.346764
H	1.763031	2.633196	-5.463377
H	0.474966	0.595406	-6.035041
C	2.974063	2.832465	0.719779
C	4.172058	3.489182	0.450814
C	2.680618	2.500034	2.035567
C	5.063920	3.796324	1.464851
C	3.574792	2.799843	3.053594
C	4.768399	3.445570	2.774613
H	4.407469	3.774798	-0.569298
H	1.746548	2.013657	2.279788
H	5.984973	4.315895	1.234479
H	3.329626	2.532179	4.073019
H	5.460012	3.683980	3.571993
H	-0.058394	-1.403959	4.210653
H	0.611395	-2.753166	5.140022
H	-6.699280	-3.738187	-7.030818
C	-6.988369	-3.604195	-5.995357
C	-8.281840	-3.815316	-5.608160
C	-8.658154	-3.637369	-4.261013
C	-7.732160	-3.253130	-3.332448
C	-6.385919	-3.030538	-3.703049
C	-6.007762	-3.209821	-5.057155
C	-4.658604	-3.000016	-5.415172
C	-3.725291	-2.645565	-4.482409
C	-4.094467	-2.475570	-3.132395
C	-5.400486	-2.661275	-2.765089
H	-9.023842	-4.117992	-6.335047
H	-9.685772	-3.804340	-3.966436
H	-8.022037	-3.112300	-2.297815
H	-5.690870	-2.558710	-1.723584
H	-2.692002	-2.514483	-4.768389
H	-4.364048	-3.135865	-6.448980
C	-3.059211	-2.120916	-2.092313
H	-3.264219	-2.721174	-1.193776
C	-3.293009	-0.636740	-1.686149
H	-3.070989	0.032814	-2.513576
H	-4.299894	-0.474646	-1.309655

O	-1.788469	-2.317535	-2.574209
H	-1.154423	-2.415360	-1.808330
N	-2.354628	-0.340820	-0.590475
O	-1.248640	0.042805	-0.935262
O	-2.669941	-0.577303	0.540240

Intermediate **V**
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C	-3.325209	-3.419340	2.991101
C	-1.969103	-3.387042	2.871822
C	-1.370883	-3.102420	1.624509
C	0.092539	-3.136452	1.539487
N	0.818192	-4.110785	0.933261
C	0.327897	-5.294050	0.230019
C	1.057244	-6.552556	0.652721
N	2.092983	-3.904936	1.009941
N	2.221813	-2.801881	1.675956
C	1.035138	-2.273653	2.031843
C	-2.125917	-2.787450	0.515620
C	-1.495065	-2.564574	-0.805822
C	-0.738583	-1.415981	-1.063769
O	-0.526247	-0.492313	-0.159878
C	-0.199281	-1.273078	-2.379911
C	-0.382088	-2.206846	-3.346286
C	-1.123337	-3.384038	-3.101816
C	-1.699212	-3.552902	-1.817558
C	-2.447032	-4.738657	-1.597839
C	-2.597868	-5.682001	-2.579213
C	-2.018352	-5.504456	-3.847079
C	-1.296760	-4.368975	-4.094776
C	-3.546309	-2.754001	0.649269
C	-4.146744	-3.116026	1.882865
C	-5.556119	-3.136364	1.986239
C	-6.338925	-2.811292	0.913892
C	-5.744902	-2.423793	-0.302572
C	-4.384595	-2.387265	-0.429393
H	-3.781053	-3.648754	3.945110
H	-1.343696	-3.586331	3.731701
H	-0.733535	-5.359623	0.452984
H	0.420093	-5.106533	-0.838879
H	2.116275	-6.512999	0.407031
H	0.952599	-6.736007	1.721506
H	0.622173	-7.398323	0.122993
H	0.916024	-1.350723	2.572934
H	0.351996	-0.379438	-2.625262
H	0.041308	-2.045141	-4.330747
H	-2.916051	-4.910494	-0.638231
H	-3.177980	-6.572749	-2.374586
H	-2.147351	-6.254872	-4.615334
H	-0.844640	-4.209155	-5.066705

H	-6.006696	-3.415110	2.930859
H	-7.417325	-2.839400	1.001370
H	-6.369031	-2.140790	-1.139513
H	-3.935868	-2.071189	-1.360699
C	3.573081	-2.242114	1.835578
C	4.089909	-1.752948	0.518975
C	3.373657	-0.680991	-0.069731
O	2.410043	-0.174635	0.616711
Co	0.940944	0.825544	-0.115643
N	1.147428	2.827557	-0.011365
S	0.512249	3.598668	1.214458
C	1.835684	4.563026	2.072233
F	2.276517	5.556724	1.312841
F	1.328865	5.076887	3.185216
F	2.855929	3.779603	2.395902
O	-0.449462	4.625432	0.839587
O	0.165109	2.582513	2.199946
C	1.538220	3.524407	-1.227779
C	1.485145	2.487024	-2.390023
N	1.986841	1.250140	-1.825045
C	3.159366	0.815744	-2.079070
C	3.804190	-0.256965	-1.354753
C	4.937679	-0.847478	-1.934284
C	5.642961	-1.878678	-1.348991
C	6.866150	-2.533095	-1.979297
C	8.069834	-2.377885	-1.040760
C	6.587317	-4.023973	-2.210746
C	7.225884	-1.901266	-3.323616
C	5.170103	-2.327666	-0.106555
H	0.842769	4.335803	-1.474634
H	2.145676	2.846094	-3.189117
H	3.742563	1.280861	-2.879505
H	5.251003	-0.463131	-2.897651
H	8.293001	-1.325595	-0.859796
H	7.898618	-2.848889	-0.071747
H	8.959138	-2.840923	-1.473438
H	5.737142	-4.164418	-2.879637
H	7.453998	-4.513592	-2.659798
H	6.364447	-4.549331	-1.280969
H	6.421914	-2.006476	-4.054347
H	7.462932	-0.840205	-3.227243
H	8.106457	-2.392305	-3.740085
H	5.670475	-3.154079	0.387830
C	0.114948	2.240392	-2.983219
C	-1.071713	2.401205	-2.274543
C	0.054488	1.752263	-4.286504
C	-2.285616	2.047834	-2.848558
C	-1.156394	1.409671	-4.864186
C	-2.331360	1.546418	-4.138882
H	-1.075616	2.811786	-1.274134
H	0.970802	1.632670	-4.854331

H	-3.195639	2.163081	-2.274228
H	-1.183126	1.032700	-5.878280
H	-3.279264	1.267874	-4.579678
C	2.943069	4.084827	-1.182234
C	3.241803	5.231118	-1.911419
C	3.967652	3.440109	-0.497391
C	4.534982	5.726540	-1.960195
C	5.263839	3.932053	-0.548772
C	5.552951	5.074164	-1.279511
H	2.448657	5.750572	-2.437591
H	3.752375	2.563262	0.098154
H	4.746369	6.627180	-2.521739
H	6.049228	3.421838	-0.006438
H	6.563311	5.460456	-1.310732
H	3.487646	-1.444209	2.571725
H	4.200052	-3.029878	2.251125
H	-5.155394	4.459214	-1.195670
C	-5.591489	3.515504	-0.890684
C	-6.796481	3.114603	-1.397819
C	-7.364806	1.890443	-0.992730
C	-6.712271	1.092425	-0.094429
C	-5.462137	1.475877	0.440727
C	-4.894881	2.711429	0.039484
C	-3.647392	3.093998	0.584161
C	-2.992550	2.283376	1.464766
C	-3.544741	1.044426	1.859765
C	-4.756929	0.659971	1.354833
H	-7.320720	3.739228	-2.109064
H	-8.322382	1.586187	-1.394842
H	-7.147821	0.152538	0.221927
H	-5.190705	-0.290616	1.645073
H	-2.043968	2.591882	1.873829
H	-3.202548	4.039578	0.297686
C	-2.786822	0.141034	2.803101
O	-1.476497	-0.124351	2.399498
H	-3.369688	-0.781809	2.913045
C	-2.679502	0.784170	4.180138
H	-3.667394	1.005374	4.582629
H	-1.426639	-0.307964	1.445084
H	-2.070350	1.685131	4.151952
N	-2.030268	-0.169289	5.129667
O	-2.623523	-1.199544	5.355101
O	-0.970752	0.136018	5.609349

Inverse Mechanism
Intermediate **II$_i$**
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C	-4.116099	-1.540886	3.310372
C	-2.880792	-2.111175	3.403605
C	-2.185036	-2.498303	2.237992

C	-0.825016	-3.034086	2.371590
N	-0.415605	-4.300129	2.100993
C	-1.232391	-5.459475	1.746602
C	-0.623796	-6.270137	0.622223
N	0.864627	-4.450067	2.233112
N	1.304359	-3.287220	2.599199
C	0.325723	-2.378363	2.713845
C	-2.716061	-2.295645	0.978644
C	-1.934659	-2.662622	-0.222437
C	-0.800116	-1.884070	-0.516636
O	-0.494597	-0.864657	0.197377
C	-0.013245	-2.283177	-1.649009
C	-0.362459	-3.337239	-2.429627
C	-1.523832	-4.104631	-2.165811
C	-2.319887	-3.755333	-1.041473
C	-3.464677	-4.551808	-0.781557
C	-3.783710	-5.622059	-1.575787
C	-2.986405	-5.963678	-2.681463
C	-1.879184	-5.208285	-2.963984
C	-3.998747	-1.684511	0.873829
C	-4.704828	-1.311751	2.047668
C	-5.969258	-0.690763	1.926356
C	-6.513226	-0.446524	0.697852
C	-5.814098	-0.814394	-0.468038
C	-4.588534	-1.413042	-0.384042
H	-4.648685	-1.246632	4.205942
H	-2.425580	-2.268186	4.372555
H	-1.359248	-6.057297	2.650254
H	-2.207282	-5.072466	1.464010
H	0.309279	-6.743591	0.920449
H	-1.328739	-7.048171	0.334498
H	-0.442033	-5.650662	-0.253273
H	0.514324	-1.356439	2.983441
H	0.884371	-1.722835	-1.868225
H	0.260842	-3.609927	-3.273917
H	-4.105583	-4.308752	0.057282
H	-4.665763	-6.207893	-1.350071
H	-3.249163	-6.809851	-3.301676
H	-1.252915	-5.456157	-3.813380
H	-6.500308	-0.405883	2.826313
H	-7.478604	0.034506	0.615896
H	-6.254923	-0.621096	-1.437456
H	-4.053990	-1.692222	-1.282190
C	2.750233	-3.029819	2.638799
C	3.278062	-2.833699	1.254732
C	2.914917	-1.639275	0.566663
O	2.193152	-0.763111	1.154013
Co	0.921863	0.596045	0.295055
N	1.830986	2.519087	0.259043
S	1.245167	3.784957	0.998728
C	2.508889	4.249515	2.262230

F	3.628582	4.658955	1.675699
F	2.053481	5.233439	3.030229
F	2.794796	3.209460	3.038643
O	1.150600	4.983993	0.173241
O	0.100584	3.421786	1.820353
C	2.744473	2.763682	-0.846864
C	2.360949	1.796957	-1.998177
N	2.271932	0.505201	-1.359607
C	3.229447	-0.320889	-1.526609
C	3.439342	-1.515562	-0.749380
C	4.257599	-2.511056	-1.294613
C	4.570125	-3.681452	-0.633237
C	5.421114	-4.795495	-1.228867
C	4.592952	-6.085446	-1.301774
C	5.899858	-4.456996	-2.640174
C	6.655965	-5.030579	-0.349295
C	4.050180	-3.806639	0.660806
H	2.660838	3.786275	-1.226280
H	3.182450	1.810052	-2.728934
H	3.975574	-0.118351	-2.302266
H	4.647306	-2.334642	-2.290592
H	5.182462	-6.901596	-1.725272
H	4.251071	-6.408067	-0.317104
H	3.709164	-5.947855	-1.926400
H	6.520475	-3.559281	-2.657235
H	6.503844	-5.275555	-3.034515
H	5.067031	-4.307924	-3.329856
H	7.266409	-4.129178	-0.283345
H	6.386109	-5.319799	0.667395
H	7.277504	-5.829531	-0.759391
H	4.264129	-4.704040	1.233275
C	1.082081	2.117033	-2.743168
C	0.516894	3.387715	-2.773345
C	0.460964	1.099015	-3.462153
C	-0.644406	3.627488	-3.493374
C	-0.705240	1.333611	-4.173619
C	-1.265665	2.603110	-4.189910
H	0.946469	4.202453	-2.208758
H	0.876873	0.099942	-3.453820
H	-1.078065	4.618721	-3.486507
H	-1.174597	0.521678	-4.714414
H	-2.182181	2.791261	-4.733734
C	4.205583	2.541585	-0.510677
C	5.173500	3.159005	-1.298221
C	4.619189	1.699201	0.513841
C	6.523353	2.937006	-1.078434
C	5.970413	1.470029	0.732382
C	6.926826	2.084978	-0.060223
H	4.866186	3.833371	-2.090627
H	3.886240	1.220058	1.146858
H	7.259718	3.434766	-1.696211

H	6.274430	0.806083	1.531215
H	7.979694	1.908016	0.117256
H	2.882757	-2.147085	3.262849
H	3.213845	-3.880699	3.135102
H	-5.914591	6.348257	-0.954327
C	-6.055941	5.348206	-1.345339
C	-7.255003	4.986191	-1.895686
C	-7.444033	3.687247	-2.407208
C	-6.426666	2.776246	-2.355555
C	-5.178260	3.121664	-1.791814
C	-4.986381	4.429938	-1.278238
C	-3.731347	4.774267	-0.715971
C	-2.713760	3.870644	-0.655195
C	-2.909640	2.563319	-1.165299
C	-4.110320	2.205408	-1.721242
H	-8.066048	5.700789	-1.941142
H	-8.396728	3.416107	-2.842122
H	-6.565295	1.777046	-2.750822
H	-4.245832	1.202329	-2.110218
H	-1.757098	4.140802	-0.226099
H	-3.588170	5.775840	-0.329711
C	-1.847803	1.561584	-1.080248
O	-0.794428	1.783530	-0.525531
H	-2.064714	0.578298	-1.526002
C	-2.161415	1.344032	2.359840
H	-1.891514	2.295695	1.912624
H	-2.372230	0.608439	1.587625
H	-2.995849	1.439363	3.043455
N	-0.990045	0.853594	3.110387
O	-1.120475	0.597869	4.277093
O	0.054420	0.698948	2.509007

Transition State **II$_i$ → IIIa$_i$**
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C	-4.196022	-1.799272	3.780257
C	-2.960424	-2.366930	3.695248
C	-2.388963	-2.644536	2.435417
C	-1.008487	-3.141948	2.397720
N	-0.574947	-4.327970	1.902602
C	-1.372287	-5.455311	1.423870
C	-0.819300	-6.041738	0.142036
N	0.716741	-4.437697	1.925146
N	1.140412	-3.326517	2.439838
C	0.142933	-2.492893	2.762985
C	-3.051341	-2.327381	1.263914
C	-2.410241	-2.581524	-0.047894
C	-1.266495	-1.863484	-0.376003
O	-0.748298	-0.943108	0.399462
C	-0.597249	-2.141156	-1.603273
C	-1.091634	-3.056963	-2.477389

C	-2.274906	-3.780171	-2.190787
C	-2.934980	-3.545433	-0.955684
C	-4.085961	-4.319145	-0.667539
C	-4.548442	-5.258052	-1.551117
C	-3.894737	-5.478911	-2.775913
C	-2.779282	-4.748501	-3.082447
C	-4.317394	-1.681201	1.343710
C	-4.899639	-1.432064	2.613199
C	-6.148369	-0.774384	2.684669
C	-6.778624	-0.349156	1.550464
C	-6.186791	-0.563017	0.290803
C	-4.992119	-1.217895	0.189229
H	-4.632930	-1.591845	4.748706
H	-2.404839	-2.601231	4.593060
H	-1.403823	-6.196455	2.223743
H	-2.381629	-5.080509	1.281157
H	0.138080	-6.533486	0.300652
H	-1.526156	-6.776286	-0.240076
H	-0.695123	-5.274155	-0.618495
H	0.304881	-1.525369	3.207119
H	0.316905	-1.599436	-1.816771
H	-0.571744	-3.250323	-3.408272
H	-4.614603	-4.163380	0.264168
H	-5.431536	-5.833043	-1.304357
H	-4.272512	-6.220481	-3.466725
H	-2.260233	-4.911813	-4.019666
H	-6.588582	-0.593809	3.657496
H	-7.726696	0.167497	1.616254
H	-6.676124	-0.191513	-0.599639
H	-4.541684	-1.369780	-0.781803
C	2.582677	-3.043462	2.477195
C	3.123672	-2.825748	1.102082
C	2.844493	-1.586908	0.454724
O	2.148467	-0.700208	1.056581
Co	1.251563	0.976931	0.417382
N	2.111249	2.851592	0.252114
S	1.481216	4.148096	0.909566
C	2.467916	4.427796	2.442401
F	3.730609	4.694812	2.122714
F	1.979072	5.456835	3.125580
F	2.450880	3.354969	3.222755
O	1.721296	5.364783	0.141282
O	0.142316	3.877113	1.402358
C	3.106821	3.014248	-0.789661
C	2.739498	2.044367	-1.939825
N	2.527954	0.764583	-1.296633
C	3.338697	-0.185736	-1.549821
C	3.418899	-1.433704	-0.836196
C	4.186228	-2.455979	-1.407755
C	4.413640	-3.668945	-0.790873
C	5.221829	-4.802259	-1.409209

C	4.332215	-6.044606	-1.550474
C	5.753489	-4.436333	-2.794621
C	6.420651	-5.132716	-0.510602
C	3.858649	-3.814059	0.486195
H	3.107951	4.030846	-1.194370
H	3.603479	1.988592	-2.617367
H	4.072969	-0.055979	-2.352428
H	4.615024	-2.259864	-2.383868
H	4.890937	-6.874373	-1.989081
H	3.948419	-6.383975	-0.587168
H	3.473795	-5.840063	-2.191942
H	6.422589	-3.574734	-2.761276
H	6.322003	-5.271127	-3.207252
H	4.947916	-4.214740	-3.497115
H	7.071687	-4.265576	-0.393019
H	6.111387	-5.448913	0.486610
H	7.013587	-5.944081	-0.938470
H	4.016667	-4.740389	1.029873
C	1.534859	2.417307	-2.780764
C	0.869729	3.633815	-2.685692
C	1.079997	1.483357	-3.709218
C	-0.239514	3.894213	-3.479222
C	-0.027081	1.740483	-4.501404
C	-0.700485	2.949040	-4.380644
H	1.182657	4.389746	-1.980528
H	1.586393	0.530140	-3.806060
H	-0.755510	4.839277	-3.373286
H	-0.364801	0.997757	-5.213229
H	-1.575177	3.151396	-4.984720
C	4.526835	2.709960	-0.353325
C	5.578108	3.214050	-1.114372
C	4.825066	1.899230	0.734381
C	6.894851	2.910407	-0.808755
C	6.142525	1.589510	1.041267
C	7.181545	2.089521	0.272313
H	5.362181	3.864408	-1.955550
H	4.032495	1.511116	1.358298
H	7.696356	3.321723	-1.408748
H	6.355394	0.954920	1.891715
H	8.207831	1.849471	0.517878
H	2.696155	-2.162454	3.106849
H	3.062003	-3.888355	2.969884
H	-6.364508	5.002788	-0.805667
C	-6.270922	4.081140	-1.366485
C	-7.350520	3.563696	-2.028089
C	-7.233521	2.365746	-2.760724
C	-6.035560	1.709784	-2.815345
C	-4.904602	2.219481	-2.138347
C	-5.021354	3.425941	-1.400952
C	-3.887528	3.934291	-0.719297
C	-2.693870	3.279029	-0.749268

C	-2.581787	2.072175	-1.482168
C	-3.658411	1.563511	-2.163930
H	-8.302463	4.076729	-1.992752
H	-8.094824	1.970951	-3.282834
H	-5.939197	0.790709	-3.381239
H	-3.556826	0.638495	-2.722626
H	-1.833118	3.663832	-0.215388
H	-3.982495	4.856770	-0.160274
C	-1.340216	1.307433	-1.476867
O	-0.392917	1.598589	-0.779662
H	-1.314692	0.421002	-2.128738
C	-1.818069	0.778080	2.025122
H	-1.853450	1.650201	1.384920
H	-1.410970	-0.322836	1.085511
H	-2.711869	0.588765	2.604441
N	-0.677154	0.753988	2.809109
O	-0.692608	0.267695	3.928921
O	0.414749	1.118521	2.319052

Intermediate **IIIa**$_{i}$
136

C	-4.064510	-1.512501	3.914296
C	-2.887834	-2.173151	3.729909
C	-2.476786	-2.553179	2.433618
C	-1.129522	-3.120298	2.291186
N	-0.768794	-4.316733	1.763885
C	-1.625732	-5.432710	1.370724
C	-1.209581	-6.035553	0.045731
N	0.519285	-4.465007	1.703611
N	1.008039	-3.369823	2.195126
C	0.061588	-2.507488	2.588076
C	-3.247253	-2.244448	1.326999
C	-2.813692	-2.637137	-0.035332
C	-1.687261	-2.062303	-0.588812
O	-0.948356	-1.132939	0.010934
C	-1.231638	-2.467542	-1.869692
C	-1.934128	-3.375567	-2.598573
C	-3.114665	-3.964310	-2.087091
C	-3.548787	-3.603025	-0.785721
C	-4.696376	-4.250300	-0.268347
C	-5.369852	-5.188496	-1.003781
C	-4.942107	-5.532753	-2.298150
C	-3.833956	-4.928409	-2.823763
C	-4.444389	-1.493390	1.502879
C	-4.862758	-1.140430	2.811523
C	-6.040978	-0.378901	2.979258
C	-6.757543	0.043812	1.896200
C	-6.327484	-0.277329	0.594446
C	-5.205497	-1.032442	0.402856
H	-4.373385	-1.225668	4.911333

H	-2.251971	-2.399290	4.574076
H	-1.588459	-6.169784	2.174018
H	-2.639512	-5.045417	1.327439
H	-0.246082	-6.536187	0.114556
H	-1.957033	-6.766677	-0.257656
H	-1.151073	-5.276115	-0.730561
H	0.253103	-1.542295	3.051121
H	-0.312032	-2.038355	-2.247503
H	-1.581361	-3.670163	-3.579632
H	-5.051867	-3.997856	0.721894
H	-6.244868	-5.667178	-0.584013
H	-5.486387	-6.272388	-2.869545
H	-3.487195	-5.189809	-3.816424
H	-6.355003	-0.117175	3.982048
H	-7.649758	0.639783	2.034487
H	-6.879649	0.086368	-0.261787
H	-4.882768	-1.260282	-0.603103
C	2.460349	-3.143579	2.190194
C	2.990432	-2.854204	0.823527
C	2.807929	-1.545116	0.288570
O	2.133498	-0.682486	0.945249
Co	1.493079	1.168951	0.514055
N	2.291951	3.067271	0.415562
S	1.563094	4.329311	1.038731
C	2.357128	4.562518	2.687158
F	3.640900	4.871828	2.525105
F	1.765210	5.552496	3.346630
F	2.282066	3.460897	3.420008
O	1.880057	5.575771	0.348283
O	0.178303	4.026840	1.348322
C	3.345498	3.266058	-0.557687
C	3.059034	2.320550	-1.748930
N	2.813801	1.020123	-1.161386
C	3.506681	0.019256	-1.533295
C	3.456879	-1.298858	-0.952763
C	4.160394	-2.316791	-1.607721
C	4.270186	-3.601825	-1.116193
C	5.009029	-4.727213	-1.828849
C	4.037573	-5.883500	-2.100433
C	5.592978	-4.271811	-3.165828
C	6.162692	-5.227530	-0.949871
C	3.673888	-3.828421	0.129940
H	3.360874	4.292970	-0.936383
H	3.956027	2.288114	-2.383269
H	4.231736	0.146143	-2.345162
H	4.639876	-2.056737	-2.544615
H	4.546022	-6.706690	-2.607253
H	3.610032	-6.282640	-1.179429
H	3.209872	-5.558671	-2.732654
H	6.324154	-3.471227	-3.041492
H	6.105073	-5.104105	-3.651047

H	4.819480	-3.922498	-3.852207
H	6.871088	-4.425126	-0.740280
H	5.811015	-5.613471	0.007919
H	6.705205	-6.035571	-1.445572
H	3.761711	-4.808735	0.588198
C	1.886152	2.694818	-2.639862
C	1.143388	3.860990	-2.502141
C	1.533304	1.803651	-3.651859
C	0.053558	4.105477	-3.327941
C	0.448574	2.046099	-4.478619
C	-0.309413	3.197145	-4.308010
H	1.385630	4.595301	-1.748950
H	2.102880	0.892192	-3.790940
H	-0.521619	5.011141	-3.187867
H	0.193992	1.336530	-5.255936
H	-1.168908	3.385335	-4.937840
C	4.737493	2.962190	-0.035003
C	5.836765	3.419607	-0.757334
C	4.964661	2.208038	1.108335
C	7.130281	3.123896	-0.359454
C	6.259062	1.907211	1.509148
C	7.345912	2.358946	0.777910
H	5.677755	4.029389	-1.640611
H	4.133282	1.868377	1.709692
H	7.969501	3.498836	-0.931128
H	6.415749	1.320196	2.404822
H	8.353784	2.126947	1.096634
H	2.627748	-2.309574	2.870075
H	2.918457	-4.035841	2.614671
H	-6.624996	3.748111	-1.131937
C	-6.323290	2.859378	-1.672184
C	-7.249263	2.120896	-2.357413
C	-6.861944	0.961488	-3.058780
C	-5.552210	0.568910	-3.064399
C	-4.574262	1.316179	-2.370280
C	-4.964355	2.478500	-1.656791
C	-3.984782	3.218980	-0.948963
C	-2.681183	2.825173	-0.930668
C	-2.295071	1.663261	-1.643033
C	-3.216738	0.936989	-2.353287
H	-8.287363	2.426069	-2.363119
H	-7.604769	0.385441	-3.594201
H	-5.249281	-0.321638	-3.602099
H	-2.908210	0.045858	-2.890859
H	-1.934821	3.386425	-0.380445
H	-4.288414	4.107408	-0.409598
C	-0.924710	1.165716	-1.564670
O	-0.126649	1.589677	-0.758795
H	-0.655428	0.365228	-2.268092
C	-1.665328	0.878491	2.079092
H	-1.701105	1.659752	1.339779

H	-1.386236	-0.648545	0.755661
H	-2.558816	0.573996	2.599359
N	-0.521902	0.720345	2.736183
O	-0.456583	0.052727	3.785089
O	0.564630	1.212696	2.287128

Transition State **IIIa$_i$** → **IIIb$_i$**
136

C	-4.058048	-1.566588	3.951931
C	-2.891071	-2.237474	3.751704
C	-2.486355	-2.596146	2.447918
C	-1.135072	-3.154671	2.289389
N	-0.767747	-4.367458	1.807347
C	-1.619046	-5.492106	1.427802
C	-1.218496	-6.083902	0.092329
N	0.521938	-4.507577	1.748459
N	1.002077	-3.387018	2.192069
C	0.051413	-2.514574	2.548067
C	-3.264724	-2.271565	1.351895
C	-2.837898	-2.653959	-0.015837
C	-1.726030	-2.057402	-0.570306
O	-1.025072	-1.097741	0.041868
C	-1.257029	-2.445769	-1.848353
C	-1.947112	-3.363091	-2.579631
C	-3.120274	-3.970792	-2.073005
C	-3.559511	-3.625076	-0.768754
C	-4.702267	-4.282824	-0.255087
C	-5.367532	-5.220225	-0.997482
C	-4.934710	-5.552960	-2.293633
C	-3.831493	-4.936784	-2.816345
C	-4.454384	-1.511359	1.543845
C	-4.855995	-1.165811	2.859420
C	-6.020873	-0.388249	3.044347
C	-6.741943	0.053558	1.971612
C	-6.331251	-0.265680	0.663025
C	-5.222144	-1.036144	0.455099
H	-4.358741	-1.291459	4.954704
H	-2.249403	-2.479089	4.587388
H	-1.560895	-6.232679	2.226442
H	-2.637409	-5.113520	1.402987
H	-0.241729	-6.560495	0.141515
H	-1.952417	-6.834017	-0.198049
H	-1.194658	-5.321625	-0.683439
H	0.203544	-1.499154	2.919931
H	-0.344219	-2.002550	-2.226894
H	-1.589281	-3.647206	-3.561903
H	-5.060373	-4.037121	0.736234
H	-6.240768	-5.707131	-0.583393
H	-5.472988	-6.294767	-2.867541
H	-3.483934	-5.191173	-3.810622

H	-6.320768	-0.131997	4.053009
H	-7.624789	0.659948	2.124524
H	-6.887478	0.110288	-0.185610
H	-4.913078	-1.262287	-0.555567
C	2.451689	-3.147406	2.185357
C	2.976647	-2.838590	0.821489
C	2.807058	-1.518051	0.306832
O	2.148870	-0.652730	0.974254
Co	1.529530	1.235115	0.594842
N	2.358853	3.135761	0.457065
S	1.693281	4.434081	1.076325
C	2.471400	4.616606	2.738951
F	3.771931	4.860048	2.601754
F	1.920306	5.631806	3.395659
F	2.325675	3.515452	3.462048
O	2.088725	5.662357	0.393991
O	0.287759	4.220888	1.365957
C	3.406419	3.301544	-0.529010
C	3.086305	2.355796	-1.707713
N	2.829295	1.061223	-1.113357
C	3.506410	0.055557	-1.502149
C	3.451316	-1.267269	-0.936412
C	4.140548	-2.283826	-1.608860
C	4.239103	-3.576222	-1.135144
C	4.960952	-4.701925	-1.865330
C	3.973308	-5.843799	-2.140107
C	5.540072	-4.240036	-3.202524
C	6.113882	-5.225570	-0.998791
C	3.645400	-3.810755	0.110642
H	3.439635	4.323944	-0.917624
H	3.973322	2.307281	-2.355139
H	4.222175	0.183190	-2.322239
H	4.618400	-2.016712	-2.544478
H	4.467161	-6.670546	-2.655507
H	3.546934	-6.243202	-1.218675
H	3.145692	-5.503303	-2.764285
H	6.282410	-3.449958	-3.077181
H	6.037572	-5.073037	-3.701709
H	4.765654	-3.873659	-3.878848
H	6.835560	-4.435571	-0.787127
H	5.761781	-5.613285	-0.041919
H	6.641382	-6.038361	-1.502975
H	3.723614	-4.797476	0.556625
C	1.905843	2.743328	-2.582738
C	1.180810	3.920134	-2.441156
C	1.526085	1.851525	-3.584764
C	0.082616	4.174624	-3.252776
C	0.432720	2.103338	-4.396981
C	-0.306940	3.265332	-4.222037
H	1.446531	4.656905	-1.698188
H	2.081634	0.931943	-3.727155

H	-0.478036	5.089174	-3.110796
H	0.156632	1.392094	-5.165698
H	-1.173488	3.460736	-4.839492
C	4.797477	2.980427	-0.016286
C	5.896644	3.430618	-0.742448
C	5.023715	2.228272	1.128406
C	7.189801	3.131448	-0.345941
C	6.317464	1.924125	1.528092
C	7.404611	2.369983	0.793810
H	5.736825	4.041302	-1.624904
H	4.192553	1.896286	1.734142
H	8.029158	3.503278	-0.919101
H	6.473639	1.341433	2.426514
H	8.412281	2.137575	1.112912
H	2.612947	-2.318980	2.873230
H	2.918094	-4.039871	2.600240
H	-6.645313	3.674009	-1.344124
C	-6.309389	2.758490	-1.815150
C	-7.202669	1.944320	-2.456410
C	-6.771179	0.748995	-3.065723
C	-5.450317	0.398632	-3.027270
C	-4.506080	1.223162	-2.376000
C	-4.940624	2.420509	-1.752679
C	-3.993308	3.236702	-1.085172
C	-2.682590	2.874118	-1.007903
C	-2.252747	1.675639	-1.626303
C	-3.139513	0.883682	-2.308929
H	-8.249277	2.216105	-2.496280
H	-7.489351	0.112335	-3.564925
H	-5.112858	-0.519602	-3.493653
H	-2.798614	-0.031065	-2.782946
H	-1.960348	3.492367	-0.490038
H	-4.328713	4.156488	-0.622947
C	-0.876942	1.206900	-1.475460
O	-0.122787	1.661775	-0.645626
H	-0.563873	0.397559	-2.149819
C	-1.656483	1.664002	2.177532
H	-1.457384	2.566536	1.632109
H	-1.480370	-0.751712	0.823458
H	-2.645715	1.377652	2.493230
N	-0.652419	0.966879	2.626449
O	-0.817678	-0.035135	3.376575
O	0.566392	1.278603	2.326479

Intermediate **IIIb$_i$**
136

C	-3.387732	-2.765969	3.033188
C	-2.047103	-3.008377	3.032026
C	-1.369412	-3.226830	1.815262
C	0.097571	-3.296823	1.810450

N	0.860993	-4.391824	1.576021
C	0.428051	-5.779746	1.469040
C	0.071325	-6.360822	2.823645
N	2.125865	-4.111310	1.511832
N	2.198329	-2.831721	1.708151
C	0.995032	-2.266878	1.910491
C	-2.036315	-3.207729	0.608677
C	-1.276871	-3.405307	-0.650661
C	-0.443786	-2.402683	-1.120532
O	-0.318999	-1.206270	-0.572546
C	0.377716	-2.643904	-2.254725
C	0.323300	-3.830183	-2.913262
C	-0.553661	-4.860675	-2.497306
C	-1.366813	-4.640002	-1.356657
C	-2.234544	-5.683723	-0.951112
C	-2.282749	-6.869932	-1.634725
C	-1.469353	-7.084688	-2.760537
C	-0.624487	-6.092721	-3.178553
C	-3.430701	-2.936293	0.597404
C	-4.109152	-2.710207	1.821565
C	-5.489672	-2.412724	1.800295
C	-6.169889	-2.337243	0.618369
C	-5.496658	-2.557290	-0.599056
C	-4.160651	-2.848043	-0.610507
H	-3.907930	-2.588869	3.966153
H	-1.489481	-3.010175	3.959668
H	-0.418044	-5.809515	0.786990
H	1.247434	-6.319079	0.999600
H	0.917633	-6.327799	3.508626
H	-0.767113	-5.832697	3.276311
H	-0.221745	-7.402260	2.699932
H	0.841821	-1.203854	2.058754
H	1.055388	-1.859220	-2.566667
H	0.960263	-3.998630	-3.773386
H	-2.877233	-5.539920	-0.091807
H	-2.959907	-7.647817	-1.306328
H	-1.517119	-8.025188	-3.292550
H	0.005854	-6.242661	-4.047098
H	-6.001869	-2.233347	2.737387
H	-7.225831	-2.101906	0.615471
H	-6.042486	-2.498339	-1.531908
H	-3.647877	-3.011465	-1.549053
C	3.479393	-2.140488	1.495203
C	3.599595	-1.685216	0.074896
C	2.974596	-0.457895	-0.286729
O	2.341668	0.211200	0.598665
Co	0.908136	1.604147	0.397208
N	1.424696	3.596066	0.461777
S	0.838714	4.559933	1.565540
C	2.185982	4.740183	2.812605
F	3.230677	5.367688	2.286147

F	1.759826	5.436142	3.861202
F	2.584380	3.543338	3.237677
O	0.611960	5.923711	1.107077
O	-0.201435	3.872388	2.313949
C	2.059722	4.164217	-0.713950
C	1.606291	3.314195	-1.926729
N	1.811670	1.944130	-1.512088
C	2.682624	1.229016	-2.102409
C	3.147011	-0.057108	-1.639790
C	3.862737	-0.857288	-2.536081
C	4.413536	-2.076897	-2.191382
C	5.164385	-2.975721	-3.165596
C	6.613383	-3.152707	-2.693644
C	4.479566	-4.347131	-3.229692
C	5.190726	-2.392053	-4.577943
C	4.264752	-2.457083	-0.852529
H	1.738371	5.196111	-0.886698
H	2.259403	3.561845	-2.775849
H	3.159879	1.608725	-3.012567
H	3.974260	-0.482740	-3.547314
H	7.128280	-2.192495	-2.644368
H	6.667846	-3.605646	-1.702751
H	7.168526	-3.798461	-3.377636
H	3.444802	-4.252364	-3.562506
H	4.999742	-5.008145	-3.926363
H	4.463791	-4.844256	-2.258980
H	4.186157	-2.257301	-4.983312
H	5.703454	-1.429337	-4.614102
H	5.723973	-3.066488	-5.249551
H	4.695278	-3.395860	-0.517136
C	0.169656	3.509562	-2.373216
C	-0.668304	4.498377	-1.872097
C	-0.335023	2.635386	-3.332836
C	-1.984990	4.590988	-2.302214
C	-1.649237	2.722311	-3.759712
C	-2.485705	3.699159	-3.235698
H	-0.327131	5.193213	-1.118110
H	0.297962	1.853414	-3.734801
H	-2.627399	5.354236	-1.883346
H	-2.022297	2.025691	-4.499730
H	-3.518205	3.763787	-3.552998
C	3.574065	4.175266	-0.667798
C	4.258989	5.126814	-1.417523
C	4.309425	3.237534	0.047675
C	5.644181	5.143283	-1.461082
C	5.695866	3.248777	0.003012
C	6.369075	4.198377	-0.750186
H	3.698829	5.875695	-1.967076
H	3.804514	2.495083	0.649165
H	6.156548	5.899421	-2.041831
H	6.252273	2.510216	0.565537

H	7.450971	4.207618	-0.777087
H	3.504070	-1.305567	2.192777
H	4.258171	-2.851326	1.765248
H	-7.029329	4.432848	1.937302
C	-7.017711	3.535741	1.330577
C	-8.185474	2.887021	1.036977
C	-8.176116	1.719712	0.247609
C	-6.995133	1.226259	-0.230963
C	-5.773355	1.875257	0.056214
C	-5.781506	3.050103	0.851783
C	-4.554035	3.692758	1.148145
C	-3.371452	3.202126	0.681810
C	-3.368447	2.038255	-0.124576
C	-4.539809	1.391203	-0.422096
H	-9.125523	3.270989	1.410783
H	-9.108385	1.219652	0.020669
H	-6.978839	0.330890	-0.840270
H	-4.522016	0.483932	-1.016857
H	-2.433623	3.680045	0.933244
H	-4.564149	4.582792	1.765199
C	-2.114778	1.479940	-0.621673
O	-1.030622	1.943835	-0.333009
H	-2.199750	0.623057	-1.305014
C	-1.945181	1.228314	2.921826
H	-3.007784	1.064851	2.972330
H	-0.929140	-0.974692	0.199545
H	-1.436924	1.970548	3.509857
N	-1.265394	0.535185	2.076055
O	-1.819163	-0.329735	1.309878
O	0.026537	0.675078	1.981725

Transition State **IIIb$_i$ → IV$_i$**
136

C	-3.189346	-4.095086	3.137053
C	-1.834004	-3.962561	3.100176
C	-1.163712	-3.909030	1.861128
C	0.288696	-3.693238	1.828423
N	1.217999	-4.657075	1.613339
C	1.015813	-6.098980	1.541324
C	0.940501	-6.723018	2.921578
N	2.421282	-4.179933	1.538518
N	2.289097	-2.903100	1.707101
C	1.010745	-2.531936	1.901120
C	-1.851250	-3.974472	0.667485
C	-1.104319	-3.917014	-0.614731
C	-0.577489	-2.719207	-1.060724
O	-0.745340	-1.546958	-0.457789
C	0.224379	-2.682968	-2.229626
C	0.462972	-3.816134	-2.938305
C	-0.088391	-5.057982	-2.542035

C	-0.890729	-5.104870	-1.373711
C	-1.449236	-6.352548	-1.004379
C	-1.209380	-7.481637	-1.742235
C	-0.399291	-7.431704	-2.889481
C	0.145011	-6.237807	-3.277222
C	-3.268298	-4.088551	0.694802
C	-3.939449	-4.157721	1.942698
C	-5.347140	-4.274526	1.962610
C	-6.059747	-4.314838	0.798059
C	-5.395270	-4.236991	-0.441243
C	-4.033986	-4.126190	-0.493176
H	-3.706775	-4.133110	4.087343
H	-1.265730	-3.877690	4.017133
H	0.105456	-6.271131	0.973265
H	1.843679	-6.497782	0.959511
H	1.849878	-6.540680	3.492740
H	0.089843	-6.341633	3.485373
H	0.815879	-7.800220	2.822250
H	0.705883	-1.505504	2.036670
H	0.651169	-1.734059	-2.526936
H	1.084349	3.774575	-3.824628
H	-2.090587	-6.414815	-0.133986
H	-1.656083	-8.420627	-1.441925
H	-0.216835	-8.329737	-3.463932
H	0.764848	-6.182434	-4.164235
H	-5.855092	-4.325123	2.917760
H	-7.137791	-4.401750	0.824056
H	-5.968527	-4.262939	-1.358161
H	-3.529341	-4.061736	-1.447791
C	3.443048	-2.024158	1.466120
C	3.466026	-1.585314	0.036734
C	2.697741	-0.443727	-0.322269
O	1.994728	0.143835	0.573108
Co	0.608621	1.563068	0.442559
N	1.279540	3.491214	0.569284
S	0.798922	4.401602	1.763264
C	2.302536	4.721994	2.782383
F	3.187533	5.434565	2.094380
F	1.981287	5.394518	3.881156
F	2.872522	3.575662	3.142797
O	0.367092	5.736821	1.374328
O	-0.03342	3.601880	2.649834
C	1.821747	4.097473	-0.632120
C	1.238300	3.322619	-1.846860
N	1.422719	1.932564	-1.495010
C	2.296784	1.248064	-2.115099
C	2.820729	-0.024724	-1.674616
C	3.586122	-0.763900	-2.582083
C	4.254564	-1.925942	-2.244555
C	5.066624	-2.757620	-3.229360
C	6.544186	-2.746250	-2.815958

C	4.551162	-4.202934	-3.229932
C	4.963908	-2.216747	-4.655203
C	4.185770	-2.297656	-0.898369
H	1.529610	5.147695	-0.722870
H	1.852158	3.577335	-2.723324
H	2.752383	1.657400	-3.023286
H	3.648568	-0.381955	-3.594676
H	6.940960	-1.730293	-2.810916
H	6.691301	-3.161070	-1.817622
H	7.146040	-3.340054	-3.507533
H	3.498549	-4.244630	-3.513708
H	5.116509	-4.814867	-3.936171
H	4.640934	-4.672498	-2.249526
H	3.932504	-2.202425	-5.013023
H	5.366544	-1.206152	-4.741315
H	5.535836	-2.849412	-5.335625
H	4.726450	-3.177138	-0.561588
C	-0.203689	3.620091	-2.207142
C	-0.852546	4.790366	-1.837214
C	-0.885069	2.712422	-3.014912
C	-2.150803	5.043286	-2.260025
C	-2.181199	2.960122	-3.431321
C	-2.823403	4.130510	-3.052424
H	-0.377178	5.512240	-1.187868
H	-0.406385	1.785710	-3.305466
H	-2.643775	5.952655	-1.944035
H	-2.694132	2.233504	-4.048398
H	-3.842301	4.323741	-3.360922
C	3.334182	4.048332	-0.719180
C	3.989911	4.972829	-1.527089
C	4.089277	3.076783	-0.073719
C	5.364527	4.928087	-1.695902
C	5.465248	3.025915	-0.244323
C	6.108576	3.947998	-1.055105
H	3.415592	5.746178	-2.026062
H	3.604859	2.357817	0.571569
H	5.855226	5.662775	-2.321206
H	6.036535	2.259733	0.263618
H	7.182634	3.908910	-1.181524
H	3.348129	-1.182734	2.149523
H	4.325755	-2.601944	1.733554
H	-5.847931	6.933618	0.638033
C	-6.171197	5.947324	0.327643
C	-7.463052	5.738414	-0.069813
C	-7.883631	4.456028	-0.473887
C	-7.002416	3.410663	-0.470186
C	-5.661718	3.597006	-0.065559
C	-5.237575	4.888045	0.338951
C	-3.891483	5.070333	0.734669
C	-3.003614	4.037327	0.709419
C	-3.424599	2.748347	0.314255

C	-4.726530	2.539532	-0.053528
H	-8.168161	6.559190	-0.076189
H	-8.907532	4.302226	-0.787836
H	-7.323624	2.423705	-0.781116
H	-5.049891	1.550471	-0.362424
H	-1.976917	4.200336	0.998140
H	-3.561628	6.053263	1.048847
C	-2.463971	1.614023	0.245154
O	-1.272499	1.816375	-0.099383
H	-2.941314	0.660668	-0.041798
C	-2.453103	1.164221	2.233488
H	-3.458209	0.832676	2.447044
H	-1.262749	-1.574757	0.372944
H	-2.098185	2.091669	2.659190
N	-1.532214	0.176039	2.158054
O	-1.886565	-1.003654	1.972119
O	-0.314889	0.471371	2.124725

Intermediate **IV$_i$**
136

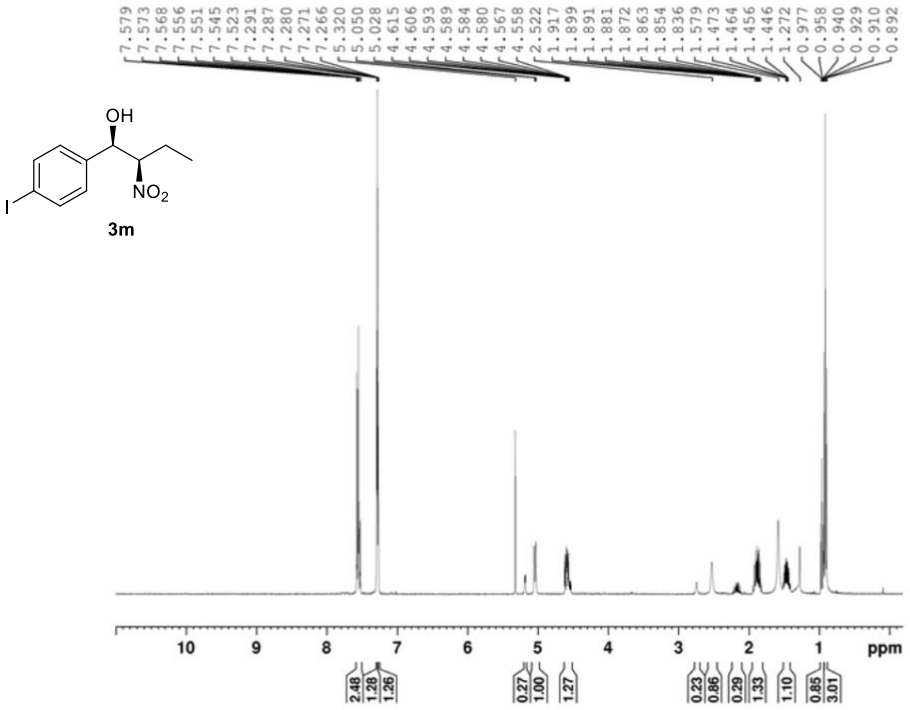
C	-4.083197	-3.130625	2.322821
C	-2.735537	-3.287714	2.454581
C	-1.907891	-3.274962	1.310152
C	-0.454270	-3.385465	1.447798
N	0.234484	-4.452409	1.916738
C	-0.287392	-5.707233	2.442402
C	-0.105886	-5.807055	3.944680
N	1.522319	-4.279355	1.861353
N	1.682088	-3.096172	1.355291
C	0.515636	-2.493037	1.084931
C	-2.435554	-3.094906	0.045240
C	-1.506585	-3.078303	-1.108397
C	-1.179739	-1.870632	-1.695636
O	-1.856161	-0.761590	-1.396756
C	-0.110812	-1.820331	-2.626098
C	0.587587	-2.942239	-2.955048
C	0.238987	-4.200780	-2.413274
C	-0.836124	-4.271849	-1.492005
C	-1.194793	-5.541882	-0.980036
C	-0.507764	-6.669495	-1.341633
C	0.575803	-6.590858	-2.235476
C	0.931227	-5.380064	-2.762399
C	-3.837289	-2.929920	-0.101773
C	-4.667321	-2.950102	1.049257
C	-6.061297	-2.777485	0.897021
C	-6.608035	-2.598846	-0.342211
C	-5.785124	-2.581842	-1.485809
C	-4.433439	-2.742632	-1.369552
H	-4.718052	-3.124699	3.199858
H	-2.290782	-3.377865	3.436704

H	-1.338553	-5.744484	2.164202
H	0.222405	-6.512887	1.917068
H	0.947061	-5.781278	4.219532
H	-0.615039	-4.995187	4.462580
H	-0.524526	-6.747730	4.298847
H	0.429446	-1.501407	0.684176
H	0.151476	-0.862610	-3.057004
H	1.422675	-2.875589	-3.640827
H	-2.049332	-5.624277	-0.319861
H	-0.813035	-7.632978	-0.953457
H	1.112158	-7.487501	-2.515550
H	1.751528	-5.312594	-3.465886
H	-6.690741	-2.786002	1.778118
H	-7.677107	-2.469165	-0.449079
H	-6.228774	-2.435414	-2.461244
H	-3.805766	-2.728204	-2.249447
C	3.043655	-2.562921	1.161225
C	3.236644	-1.935597	-0.185507
C	2.725295	-0.624310	-0.380709
O	2.142614	-0.046680	0.607368
Co	0.852040	1.428798	0.560295
N	1.273376	3.392645	0.786826
S	0.850136	4.317044	2.002880
C	2.395485	4.657076	2.953721
F	3.226292	5.406389	2.239097
F	2.102078	5.302911	4.075190
F	3.010410	3.522148	3.267659
O	0.395099	5.636915	1.604089
O	0.063694	3.531929	2.941746
C	1.790517	4.036428	-0.412465
C	1.221269	3.265449	-1.638107
N	1.506700	1.878125	-1.355303
C	2.405154	1.252780	-2.009612
C	2.916614	-0.054009	-1.665981
C	3.668771	-0.737158	-2.630014
C	4.197506	-1.996843	-2.426721
C	5.067770	-2.723690	-3.446364
C	6.453570	-2.974771	-2.836265
C	4.433345	-4.066859	-3.824937
C	5.251738	-1.909648	-4.726867
C	3.933970	-2.583510	-1.181234
H	1.444232	5.070882	-0.478828
H	1.769652	3.600454	-2.529901
H	2.839822	1.720484	-2.898564
H	3.831233	-0.231311	-3.574622
H	6.930955	-2.036691	-2.550640
H	6.401283	-3.601755	-1.945055
H	7.105194	-3.480655	-3.551873
H	3.471432	-3.918381	-4.318823
H	5.076521	-4.617085	-4.514841
H	4.265044	-4.704678	-2.955954

H	4.301726	-1.708946	-5.225818
H	5.745034	-0.954770	-4.537876
H	5.875573	-2.461434	-5.431370
H	4.310794	-3.580314	-0.974775
C	-0.259509	3.492356	-1.871159
C	-0.803649	4.773862	-1.819527
C	-1.092904	2.437980	-2.223773
C	-2.139080	4.988456	-2.118134
C	-2.435440	2.646436	-2.502597
C	-2.963049	3.924745	-2.456841
H	-0.191065	5.623730	-1.548656
H	-0.702291	1.433800	-2.287914
H	-2.539364	5.993001	-2.071573
H	-3.064593	1.798424	-2.736924
H	-4.011749	4.089998	-2.666266
C	3.302384	4.060924	-0.514490
C	3.899055	5.052609	-1.287996
C	4.117903	3.105679	0.081241
C	5.272087	5.091641	-1.470166
C	5.492874	3.139056	-0.102182
C	6.075899	4.129229	-0.876904
H	3.278912	5.815511	-1.746435
H	3.691332	2.332242	0.704408
H	5.714733	5.879044	-2.066337
H	6.110780	2.387078	0.371017
H	7.149308	4.156606	-1.011276
H	3.209390	-1.840003	1.959982
H	3.708567	-3.411079	1.309211
H	-6.001314	5.144281	-0.141060
C	-6.158181	4.073049	-0.184347
C	-7.352183	3.566980	-0.618950
C	-7.553757	2.173402	-0.675141
C	-6.557920	1.317842	-0.293178
C	-5.315480	1.812985	0.161600
C	-5.110742	3.213433	0.214373
C	-3.856234	3.699721	0.646155
C	-2.858684	2.844467	1.007940
C	-3.067285	1.445814	0.989942
C	-4.269157	0.952411	0.563079
H	-8.147309	4.235620	-0.921998
H	-8.501895	1.784137	-1.022874
H	-6.704647	0.245192	-0.335865
H	-4.430029	-0.119337	0.517228
H	-1.903777	3.251827	1.310058
H	-3.681777	4.767998	0.669867
C	-1.958202	0.498802	1.390410
O	-0.889179	0.545734	0.513141
H	-2.386263	-0.515984	1.402186
C	-1.564274	0.810393	2.847048
H	-2.383314	0.553922	3.514898
H	-1.408167	-0.174856	-0.678985

H	-1.271702	1.848398	2.984346
N	-0.397314	-0.016745	3.217998
O	-0.585006	-1.073118	3.774142
O	0.696584	0.389301	2.891425

4. NMR DATA




```
Current Data Parameters
NAME      70-CS-HN-NP-SCC-008-3
EXPNO                       430
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20251203
Time                      18.05
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894465 sec
RG                        205.35
DW                        62.400 usec
DE                         6.50 usec
TE                       293.0 K
D1                     1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                 400.1024708 MHz
NUC1                         1H
P1                        13.70 usec
PLW1                  12.00000000 W

F2 - Processing parameters
SI                           65536
SF                   400.1000018 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
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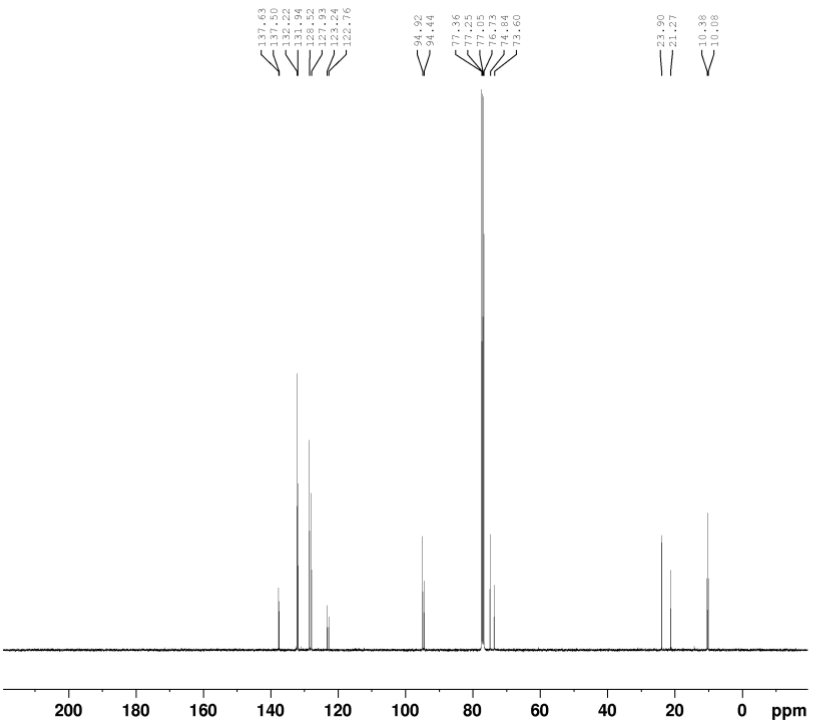


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Current Data Parameters
NAME      70-CS-HN-NP-SCC-008-1
EXPNO                       571
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20251203
Time                       5.15
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        3000
DS                           4
SWH                   24038.461 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631488 sec
RG                        205.35
DW                        20.800 usec
DE                         6.50 usec
TE                       293.0 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                 100.6152851 MHz
NUC1                         13C
P1                        10.00 usec
PLW1                  48.00000000 W

======== CHANNEL f2 ========
SFO2                 400.1016004 MHz
NUC2                         1H
CPDPRG[2                waltz16
PCPD2                     90.00 usec
PLW2                  12.00000000 W
PLW12                  0.27805999 W
PLW13                  0.22522999 W

F2 - Processing parameters
SI                           32768
SF                   100.6052250 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```
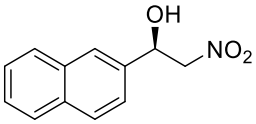
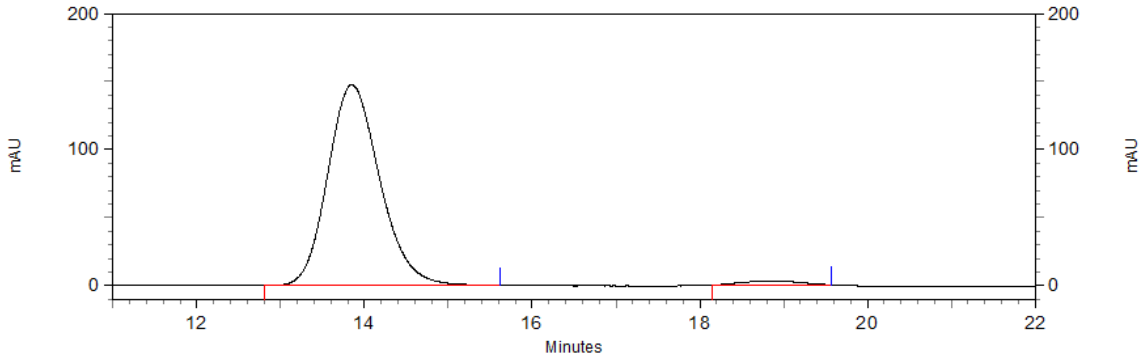

5. HPLC DATA

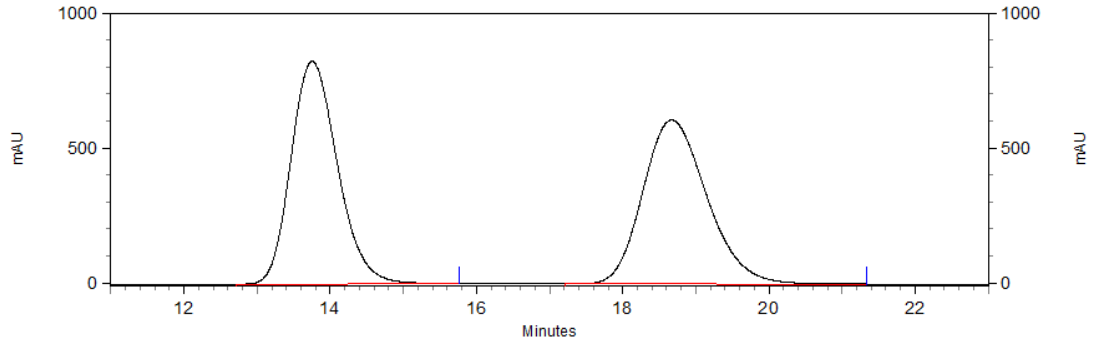


2a, (Chiralcel OD-H, cyclohexane/*i*-PrOH (80:20), 1.0 mL/min, 210 nm)

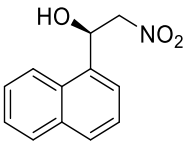


Retention Time	Area	Area %	Height	Height %
13.847	25372240	97.85	589315	98.01
18.857	557685	2.15	11960	1.99
Totals	25929925	100.00	601275	100.00

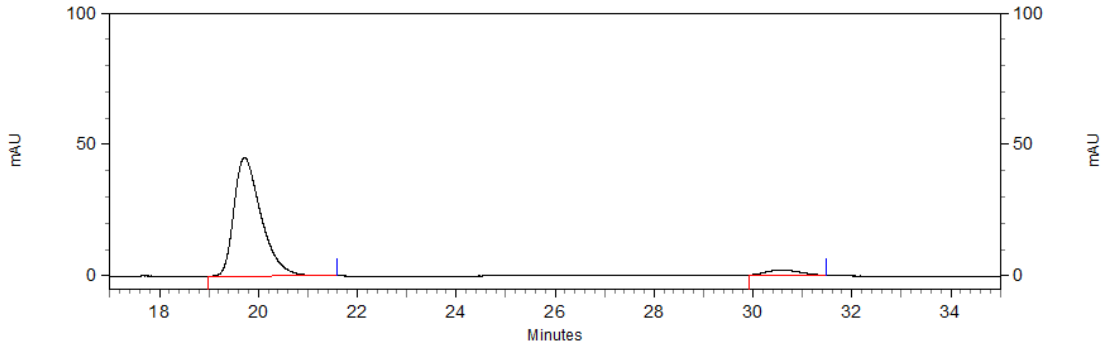
Racemic 2a



Retention Time	Area	Area %	Height	Height %
13.750	145773854	49.64	3297144	57.60
18.670	147902631	50.36	2426719	42.40
Totals	293676485	100.00	5723863	100.00

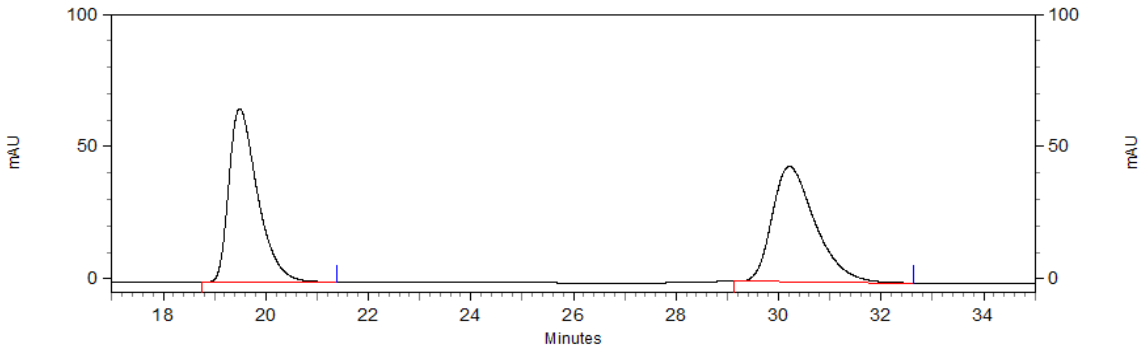


2b, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 1.0 mL/min, 254 nm)

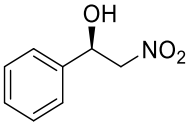


Retention Time	Area	Area %	Height	Height %
19.720	6875191	94.71	180383	95.73
30.557	384068	5.29	8050	4.27
Totals	7259259	100.00	188433	100.00

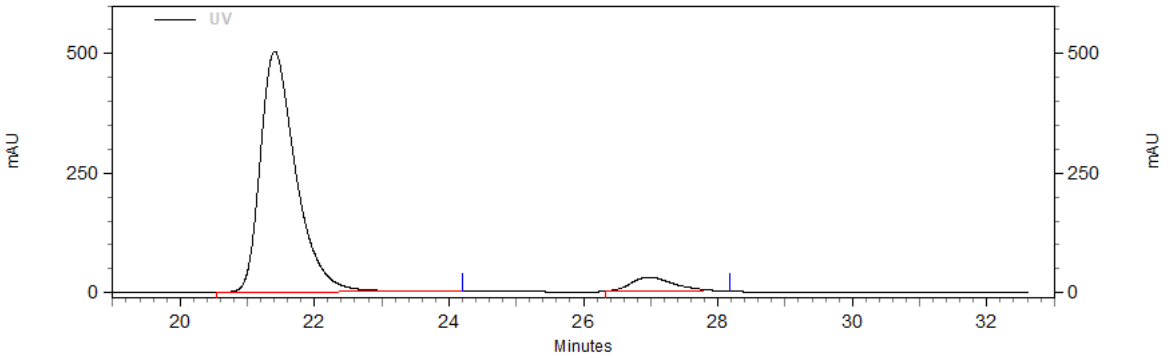
Racemic 2b



Retention Time	Area	Area %	Height	Height %
19.490	10204018	50.11	262533	60.09
30.213	10159055	49.89	174370	39.91
Totals	20363073	100.00	436903	100.00

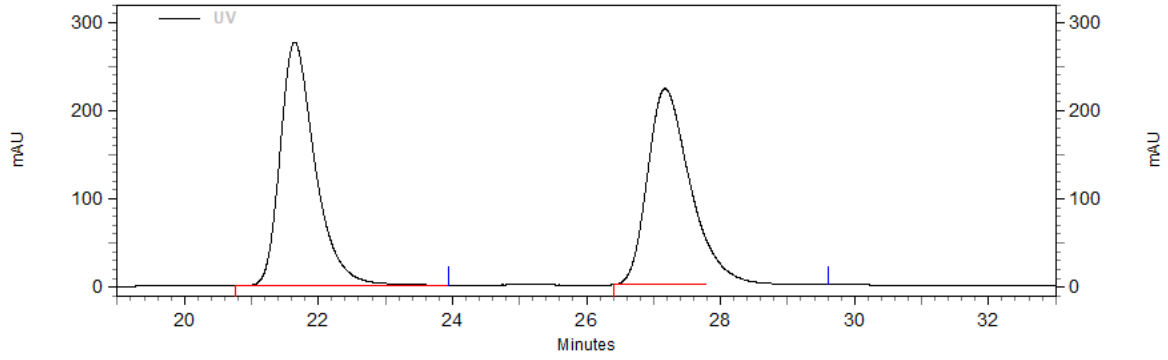


2c, (Chiralcel OD-H, n-hexane/*i*-PrOH (90:10), 1.0 mL/min, 211 nm)

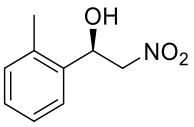


Retention Time	Area	Area %	Height	Height %
21.407	73717686	93.19	2010605	94.41
26.980	5384693	6.81	118971	5.59
Totals	79102379	100.00	2129576	100.00

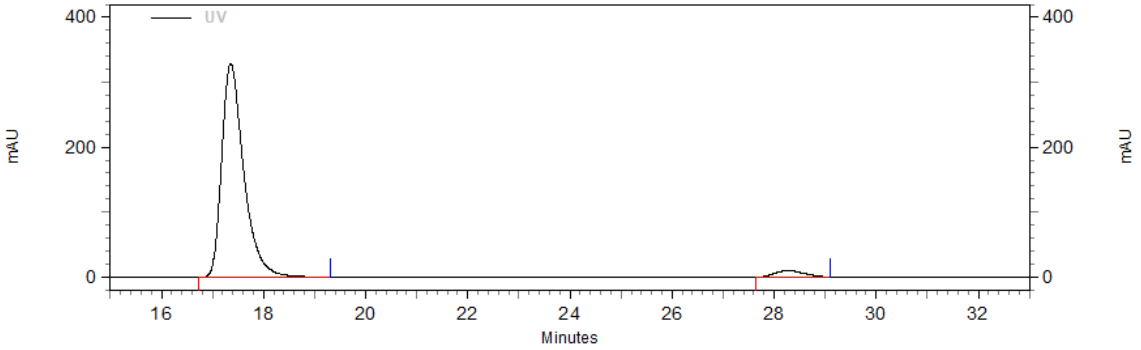
Racemic 2c



Retention Time	Area	Area %	Height	Height %
21.643	39969806	50.24	1103178	55.43
27.173	39582524	49.76	887176	44.57
Totals	79552330	100.00	1990354	100.00

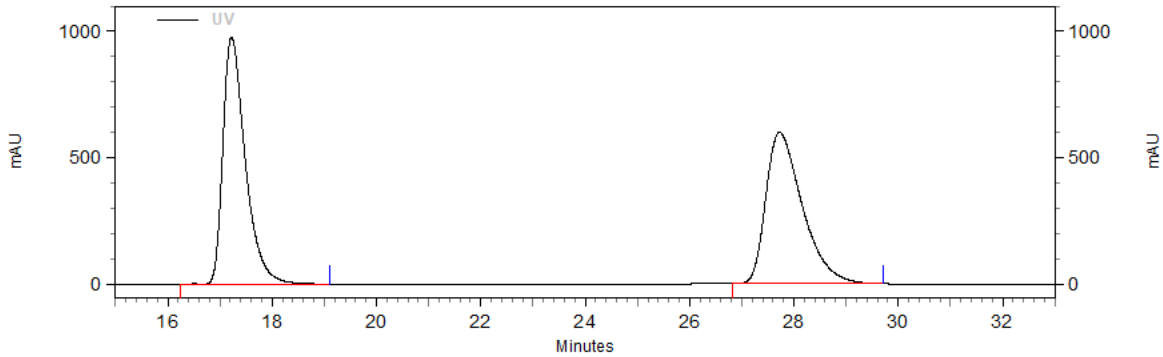


2d, (Chiralcel OD-H, n-hexane/*i*-PrOH (90:10), 1.0 mL/min, 211 nm)

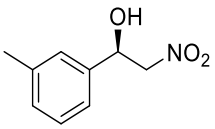


Retention Time	Area	Area %	Height	Height %
17.357	39434151	95.96	1317759	97.05
28.263	1661917	4.04	40047	2.95
Totals	41096068	100.00	1357806	100.00

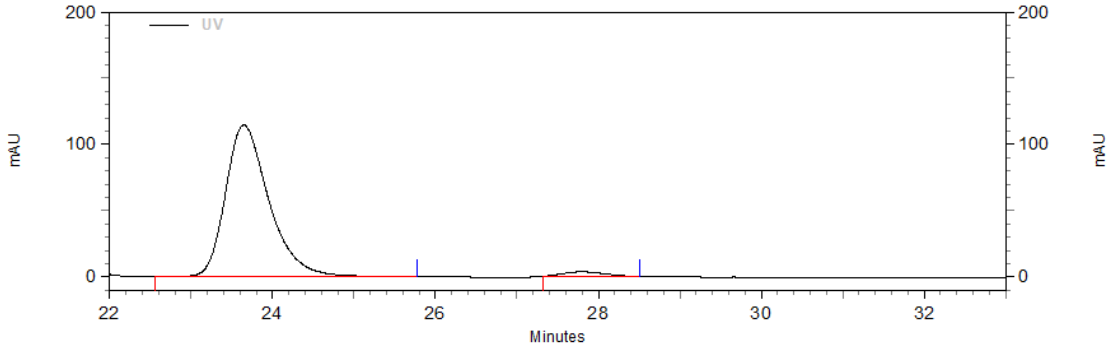
Racemic 2d



Retention Time	Area	Area %	Height	Height %
17.223	116871974	50.12	3905467	62.05
27.727	116300310	49.88	2388192	37.95
Totals	233172284	100.00	6293659	100.00

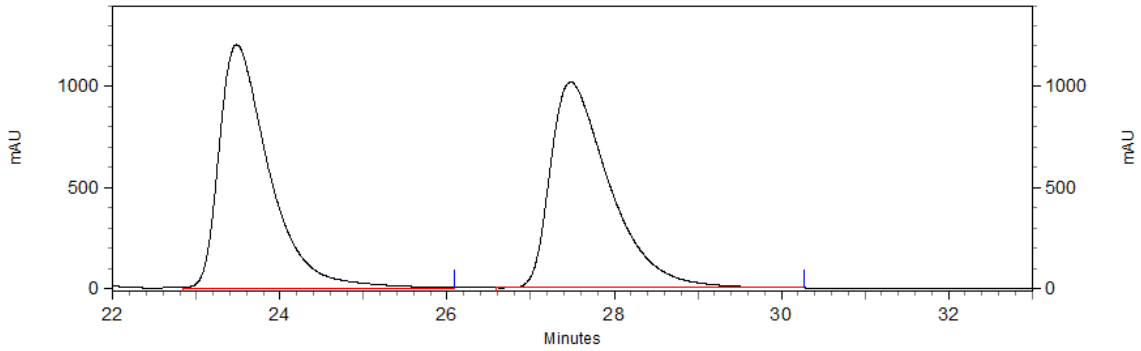


2e, (Chiralcel OD-H, n-hexane/*i*-PrOH (90:10), 0.8 mL/min, 220 nm)

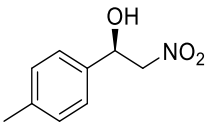


Retention Time	Area	Area %	Height	Height %
23.643	16961368	97.13	457273	97.01
27.790	501406	2.87	14080	2.99
Totals	17462774	100.00	471353	100.00

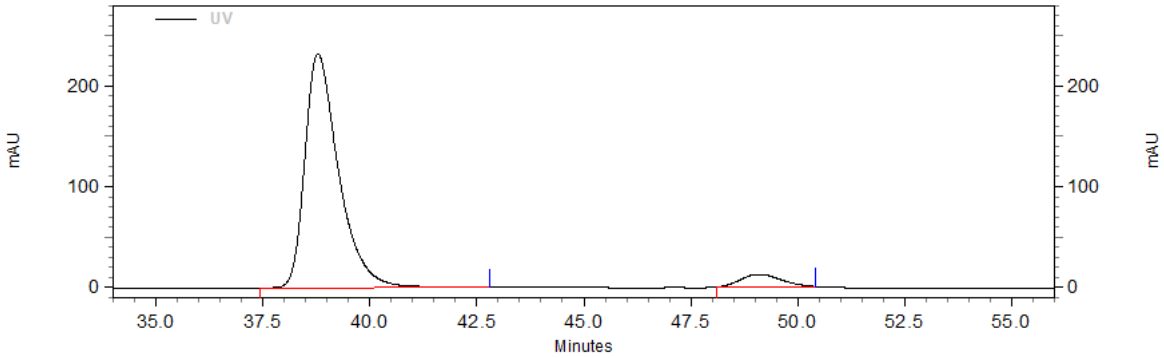
Racemic 2e



Retention Time	Area	Area %	Height	Height %
23.477	202678770	50.28	4827750	54.26
27.477	200396570	49.72	4069525	45.74
Totals	403075340	100.00	8897275	100.00

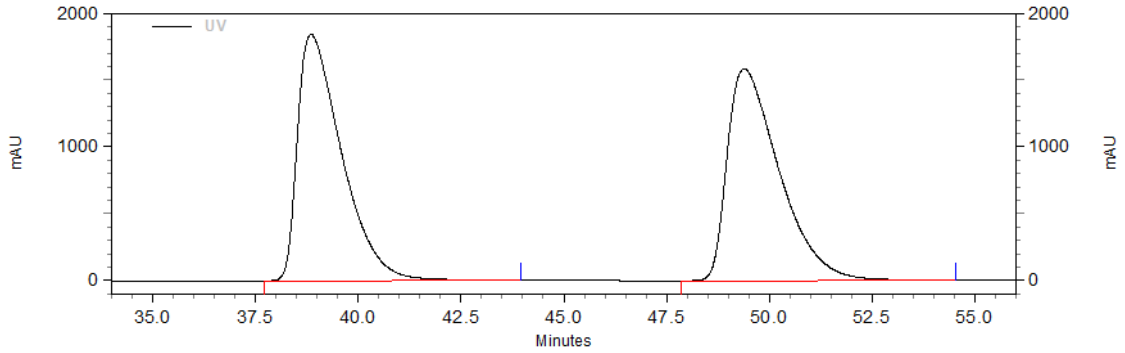


2f, (Chiralcel OD-H, n-hexane/*i*-PrOH (90:10), 0.5 mL/min, 220 nm)

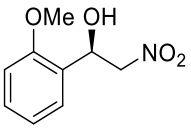


Retention Time	Area	Area %	Height	Height %
38.780	50919656	93.99	927968	94.93
49.103	3256344	6.01	49560	5.07
Totals	54176000	100.00	977528	100.00

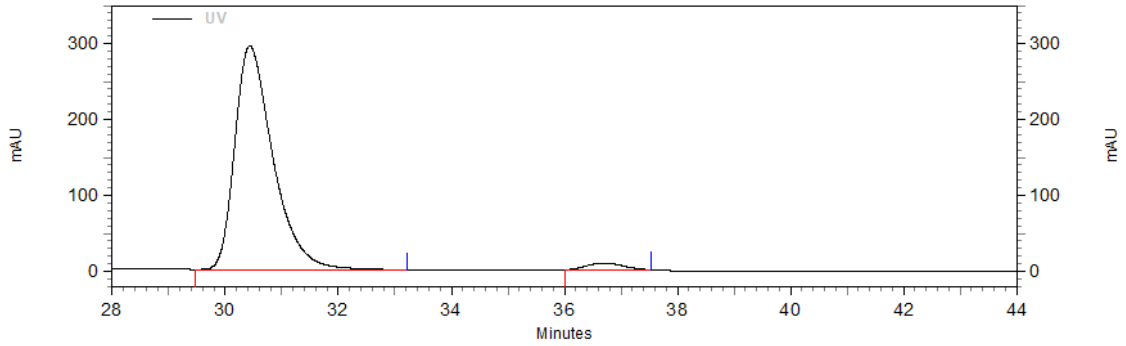
Racemic 2f



Retention Time	Area	Area %	Height	Height %
38.843	550221121	49.64	7367480	53.75
49.393	558112588	50.36	6339785	46.25
Totals	1108333709	100.00	13707265	100.00

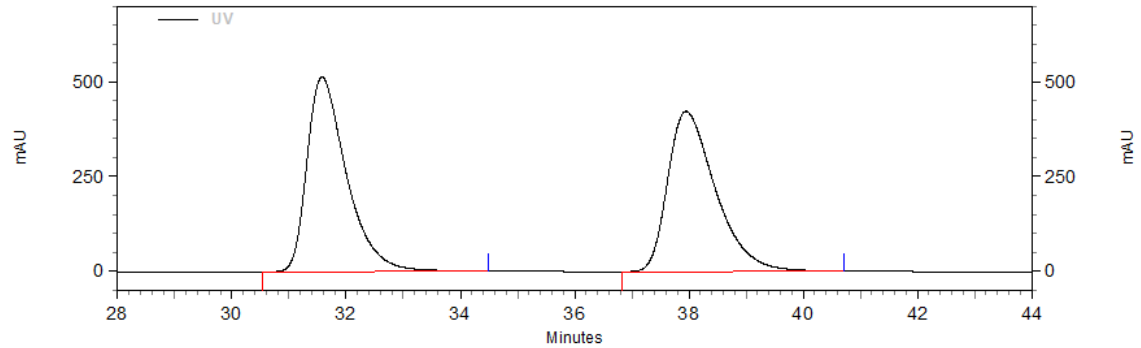


2g, (Chiralcel OD-H, n-hexane/*i*-PrOH (90:10), 0.5 mL/min, 220 nm)

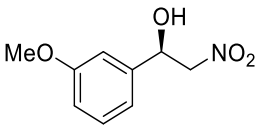


Retention Time	Area	Area %	Height	Height %
30.433	55329178	97.12	1178765	96.98
36.690	1638226	2.88	36652	3.02
Totals	56967404	100.00	1215417	100.00

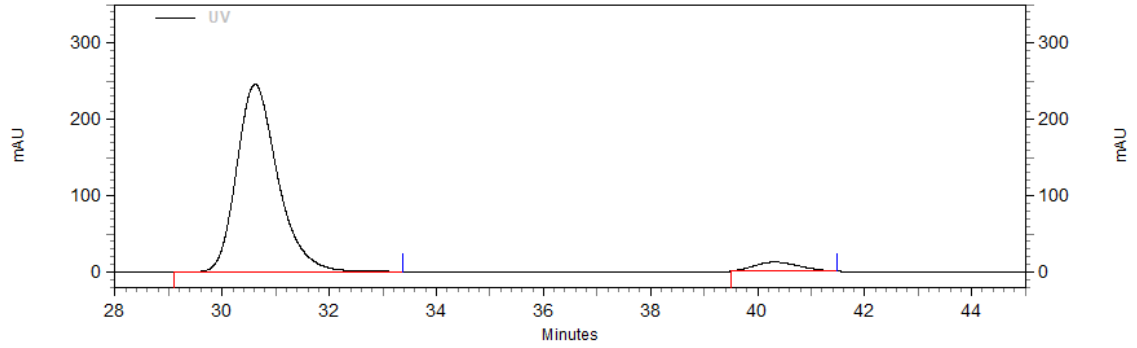
Racemic 2g



Retention Time	Area	Area %	Height	Height %
31.577	98800928	50.08	2055172	54.85
37.950	98468265	49.92	1691385	45.15
Totals	197269193	100.00	3746557	100.00

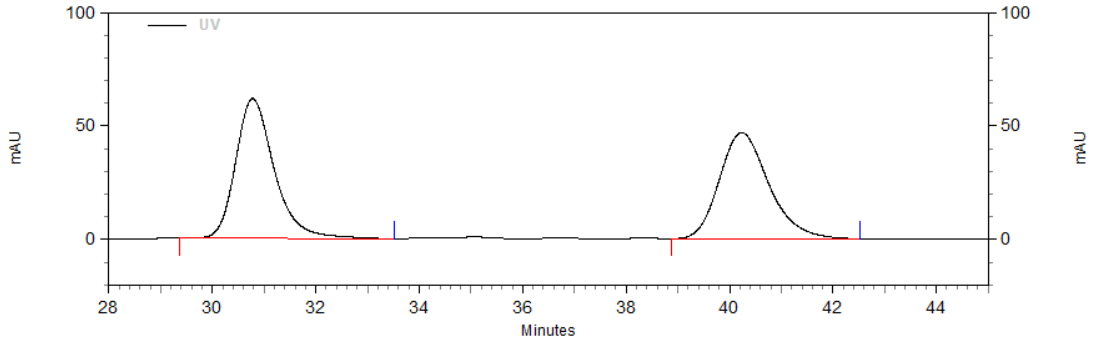


2h, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 0.8 mL/min, 220 nm)

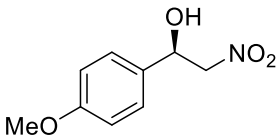


Retention Time	Area	Area %	Height	Height %
30.613	52421501	94.91	981996	95.35
40.317	2811508	5.09	47939	4.65
Totals	55233009	100.00	1029935	100.00

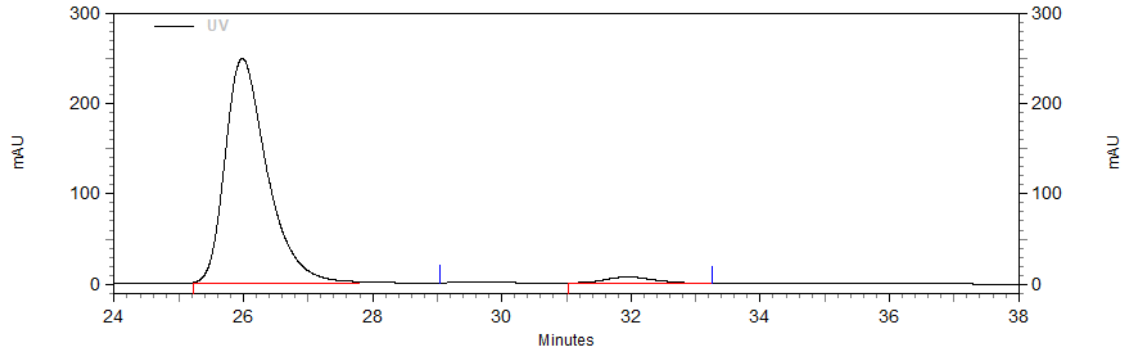
Racemic 2h



Retention Time	Area	Area %	Height	Height %
30.780	12784683	50.78	246329	56.90
40.237	12392135	49.22	186550	43.10
Totals	25176818	100.00	432879	100.00

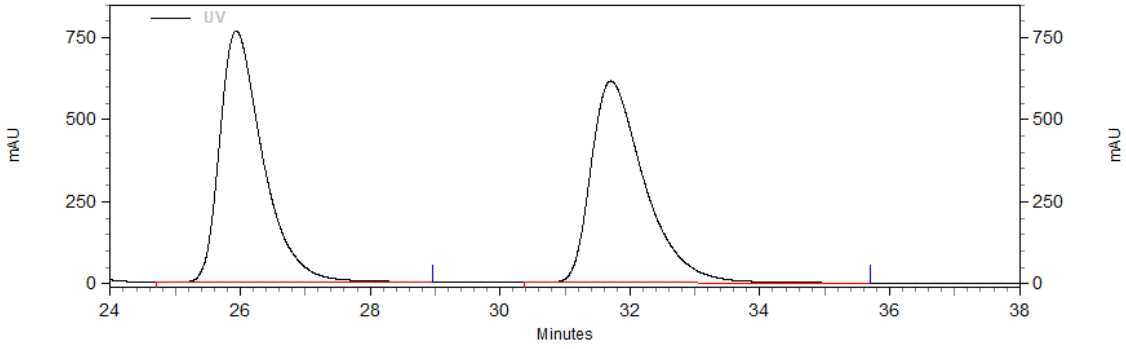


2i, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 0.8 mL/min, 220 nm)

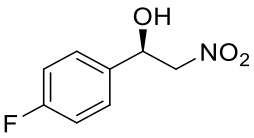


Retention Time	Area	Area %	Height	Height %
25.980	44736387	96.84	992888	97.30
31.947	1459339	3.16	27514	2.70
Totals	46195726	100.00	1020402	100.00

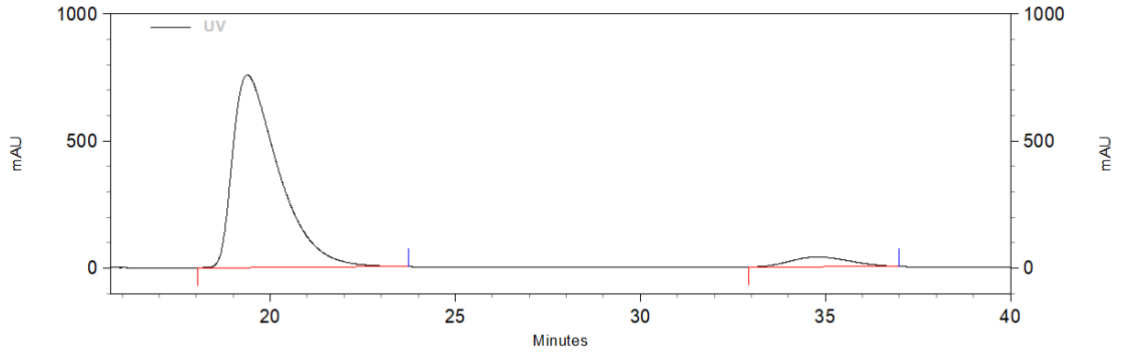
Racemic 2i



Retention Time	Area	Area %	Height	Height %
25.937	140725037	50.02	3062311	55.47
31.707	140635816	49.98	2458649	44.53
Totals	281360853	100.00	5520960	100.00

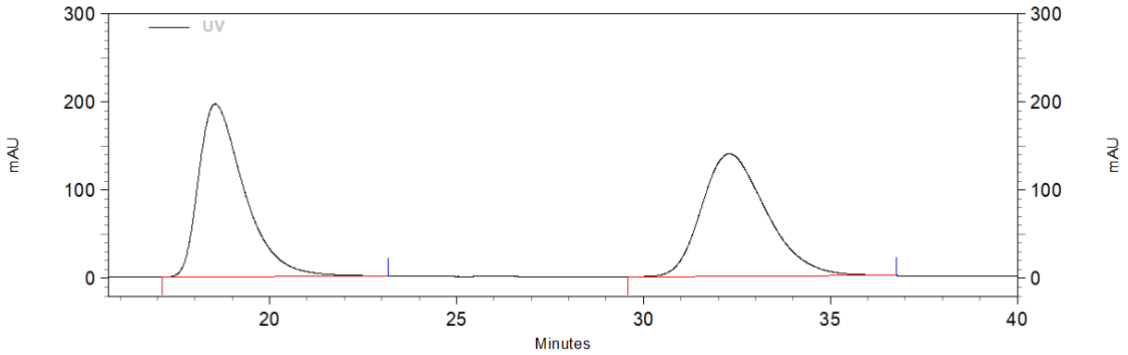


2j, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 0.8 mL/min, 220 nm)

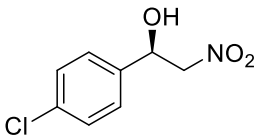


Retention Time	Area	Area %	Height	Height %
19.380	261450816	93.66	3031731	95.08
34.807	17693498	6.34	156983	4.92
Totals	279144314	100.00	3188714	100.00

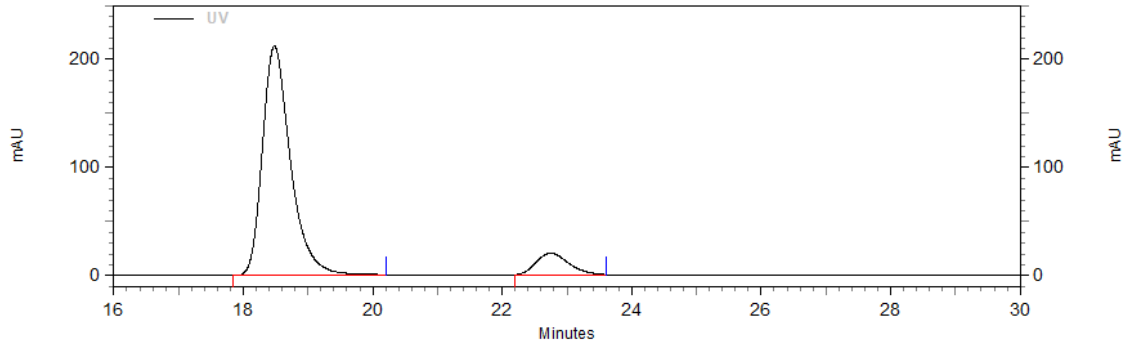
Racemic 2j



Retention Time	Area	Area %	Height	Height %
18.540	66671817	49.84	784558	58.50
32.300	67089095	50.16	556458	41.50
Totals	133760912	100.00	1341016	100.00

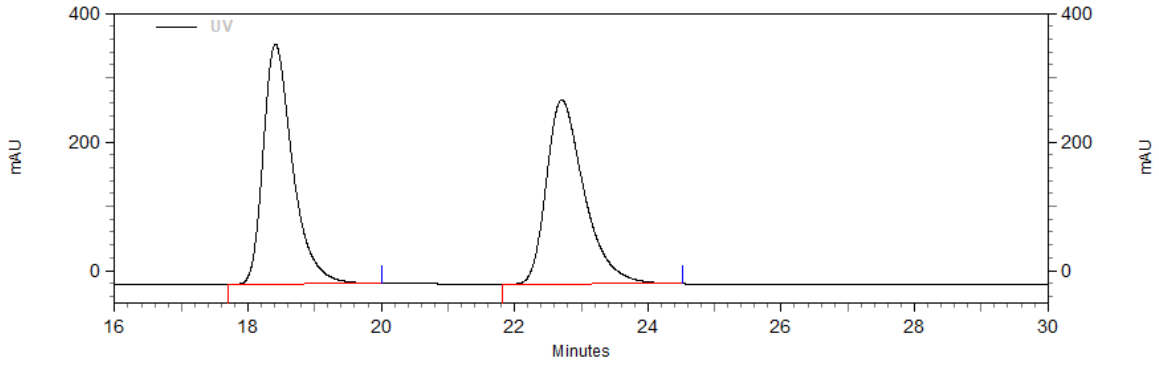


2k, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 0.8 mL/min, 220 nm)

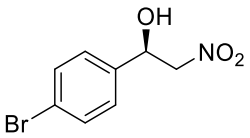


Retention Time	Area	Area %	Height	Height %
18.477	25539795	90.15	848219	91.36
22.750	2791565	9.85	80245	8.64
Totals	28331360	100.00	928464	100.00

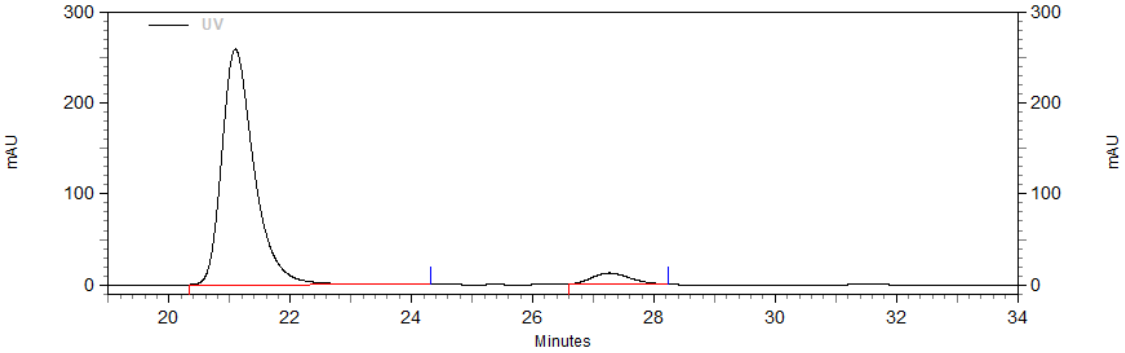
Racemic 2k



Retention Time	Area	Area %	Height	Height %
18.410	45674078	50.24	1493384	56.58
22.707	45235483	49.76	1146154	43.42
Totals	90909561	100.00	2639538	100.00

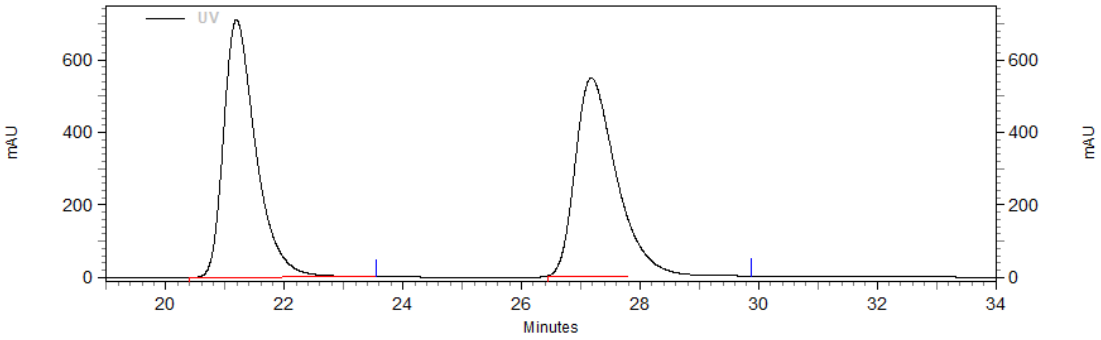


2l, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 0.8 mL/min, 220 nm

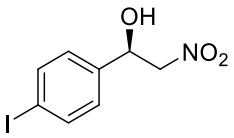


Retention Time	Area	Area %	Height	Height %
21.093	38156471	94.71	1033523	95.47
27.260	2131524	5.29	48987	4.53
Totals	40287995	100.00	1082510	100.00

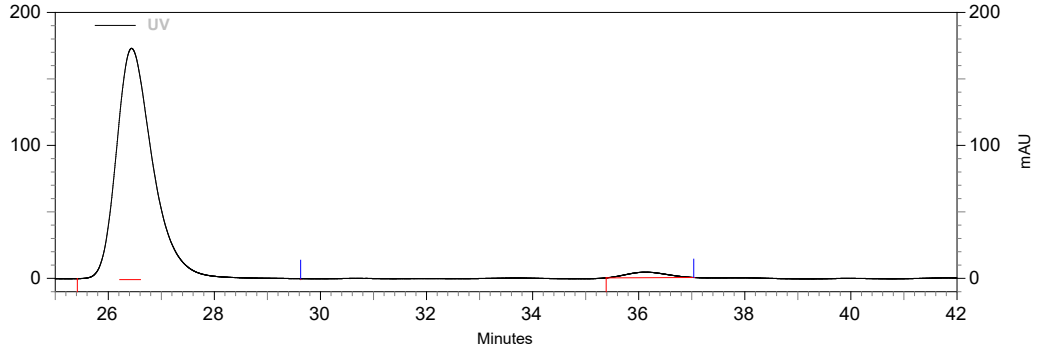
Racemic 2l



Retention Time	Area	Area %	Height	Height %
21.190	107147778	50.36	2838093	56.54
27.177	105625349	49.64	2181488	43.46
Totals	212773127	100.00	5019581	100.00

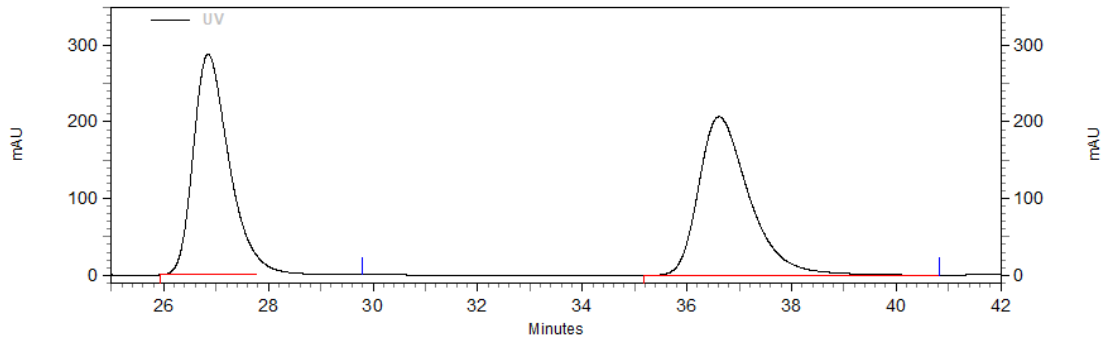


2m, (Chiralcel OD-H, n-hexane/*i*-PrOH (85:15), 0.8 mL/min, 220

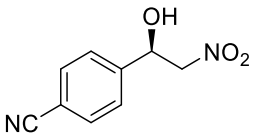


Retention Time	Area	Area %	Height	Height %
26.440	33696609	97.50	695467	97.65
36.130	864954	2.50	16719	2.35
Totals	34561563	100.00	712186	100.00

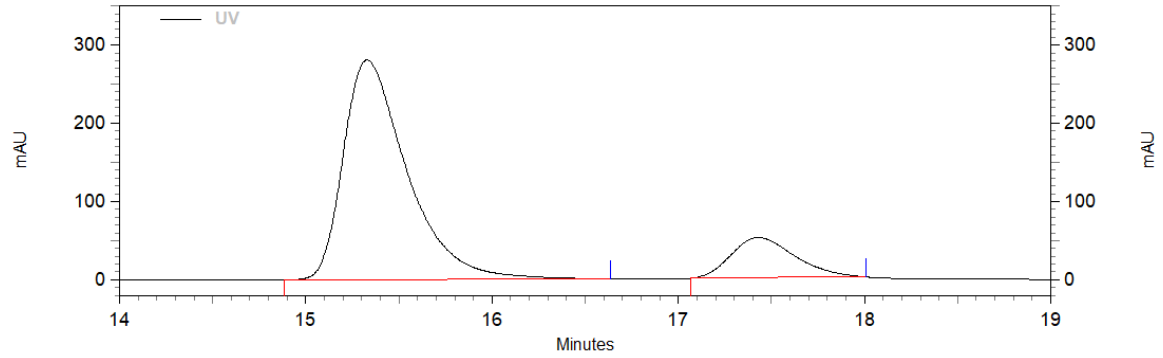
Racemic 2m



Retention Time	Area	Area %	Height	Height %
26.843	55214920	49.88	1151793	58.20
36.617	55474758	50.12	827172	41.80
Totals	110689678	100.00	1978965	100.00

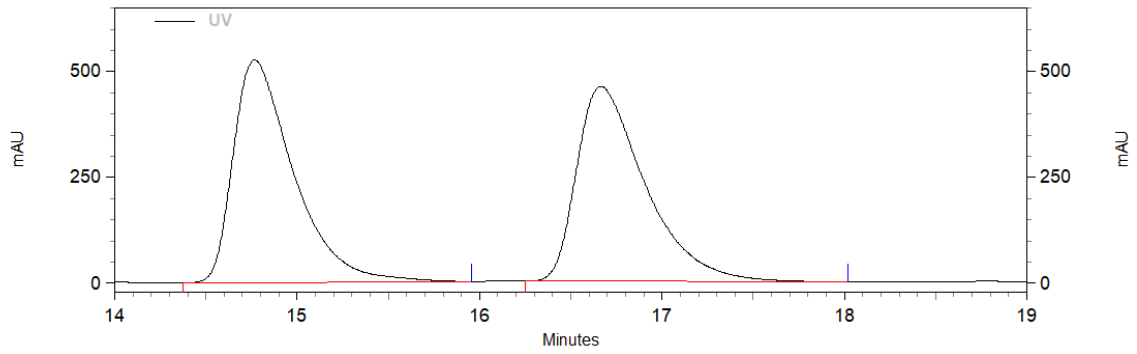


2n, (Chiralcel OD-H, n-hexane/*i*-PrOH (80:20), 0.8 mL/min, 220nm)

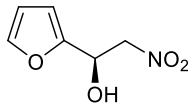


Retention Time	Area	Area %	Height	Height %
15.330	26690859	84.48	1122155	84.49
17.430	4904272	15.52	205970	15.51
Totals	31595131	100.00	1328125	100.00

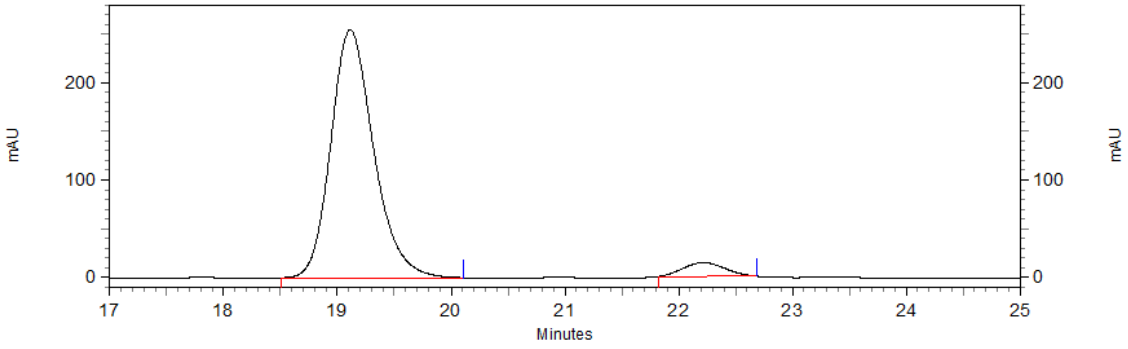
Racemic 2n



Retention Time	Area	Area %	Height	Height %
14.767	48242561	50.09	2100423	53.30
16.667	48063265	49.91	1840491	46.70
Totals	96305826	100.00	3940914	100.00

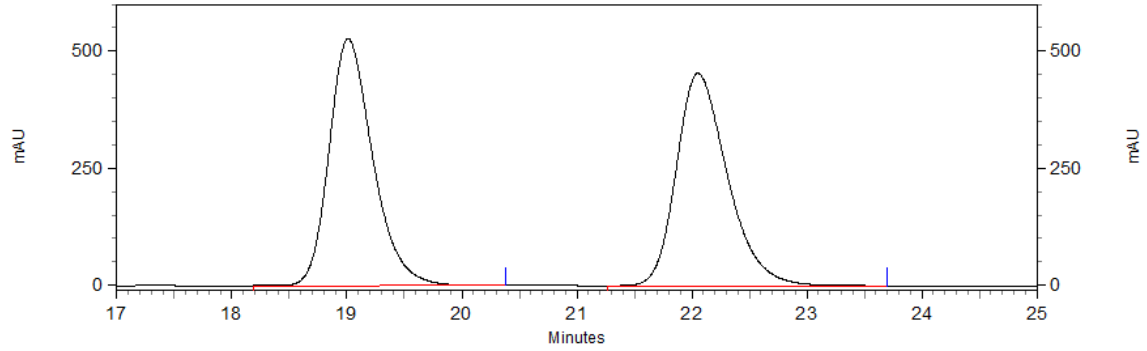


2o, (Chiralcel IJ-H, n-hexane/*i*-PrOH (90:10), 1.0 mL/min, 211nm)

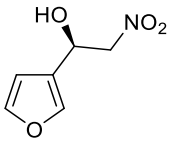


Retention Time	Area	Area %	Height	Height %
19.113	26626180	94.91	1018292	94.77
22.217	1428645	5.09	56235	5.23
Totals	28054825	100.00	1074527	100.00

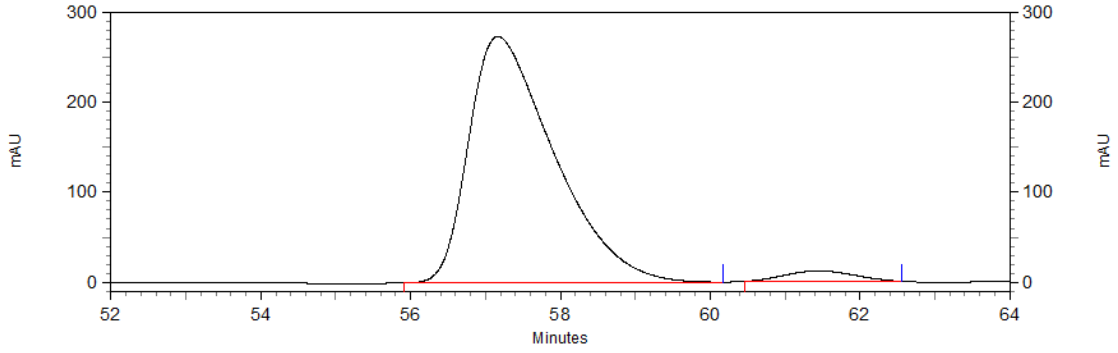
Racemic 2o



Retention Time	Area	Area %	Height	Height %
19.010	55833368	49.93	2108148	53.76
22.053	55983566	50.07	1813598	46.24
Totals	111816934	100.00	3921746	100.00

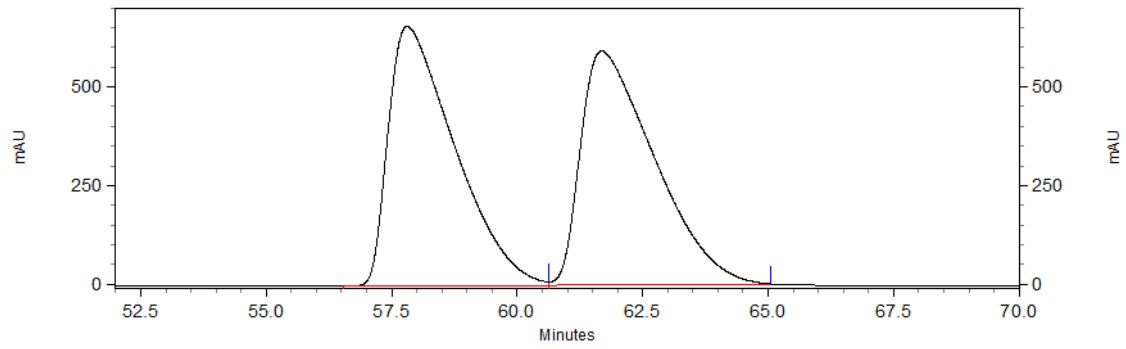


2p, (Chiralcel IJ-H, n-hexane/*i*-PrOH (90:10), 0.5 mL/min, 220nm

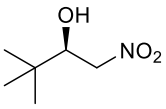


Retention Time	Area	Area %	Height	Height %
57.167	86321845	96.68	1091955	95.95
61.440	2965254	3.32	46057	4.05
Totals	89287099	100.00	1138012	100.00

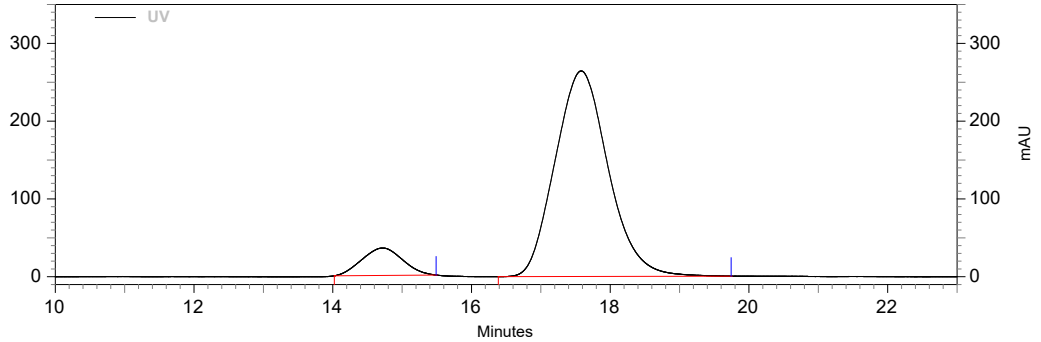
Racemic 2p



Retention Time	Area	Area %	Height	Height %
57.810	240711918	49.94	2623874	52.60
61.687	241276055	50.06	2364907	47.40
Totals	481987973	100.00	4988781	100.00

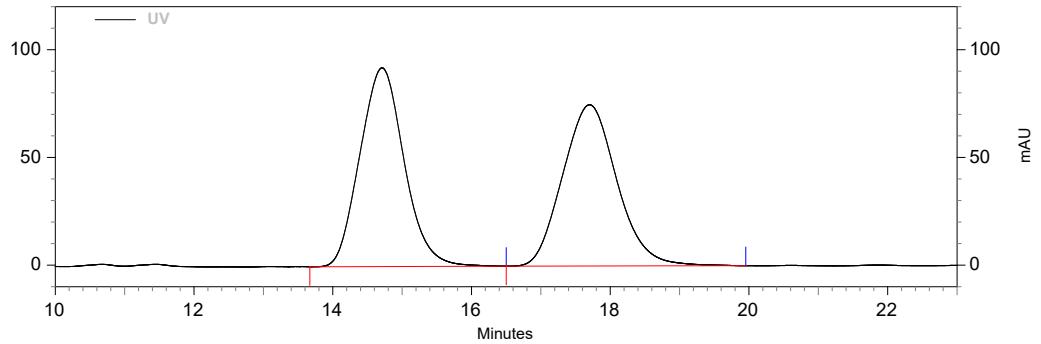


2q, (Chiralcel OD-H, cyclohexane/*i*-PrOH (95:05), 1.0 mL/min, 220nm)

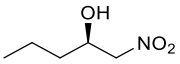


Retention Time	Area	Area %	Height	Height %
14.717	5752963	9.29	140819	11.76
17.583	56175733	90.71	1056640	88.24
Totals	61928696	100.00	1197459	100.00

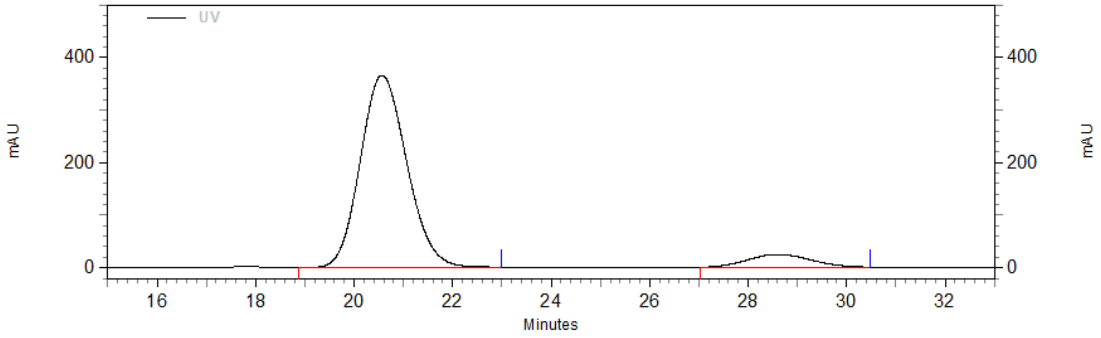
Racemic 2q



Retention Time	Area	Area %	Height	Height %
14.710	16352199	50.11	369044	55.20
17.700	16277476	49.89	299490	44.80
Totals	32629675	100.00	668534	100.00

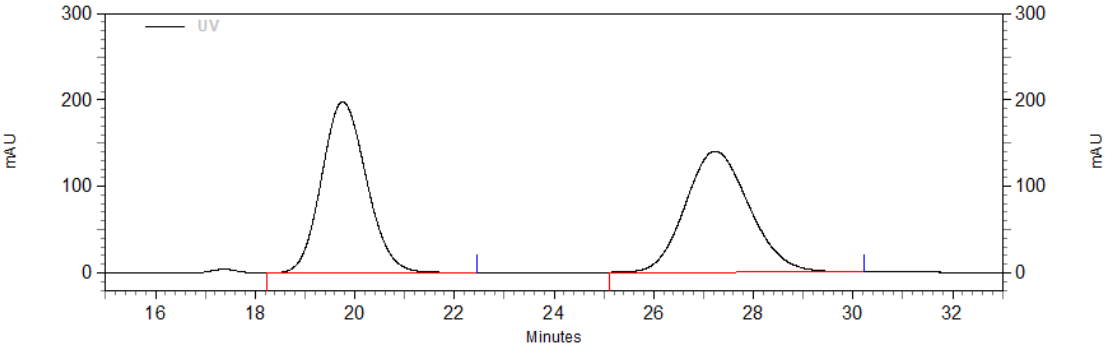


2r, (Chiralcel OD-H, n-hexane/*i*-PrOH (95:05), 0.8 mL/min, 220nm)

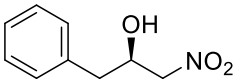


Retention Time	Area	Area %	Height	Height %
20.567	95827776	91.60	1462370	93.73
28.613	8789357	8.40	97791	6.27
Totals	104617133	100.00	1560161	100.00

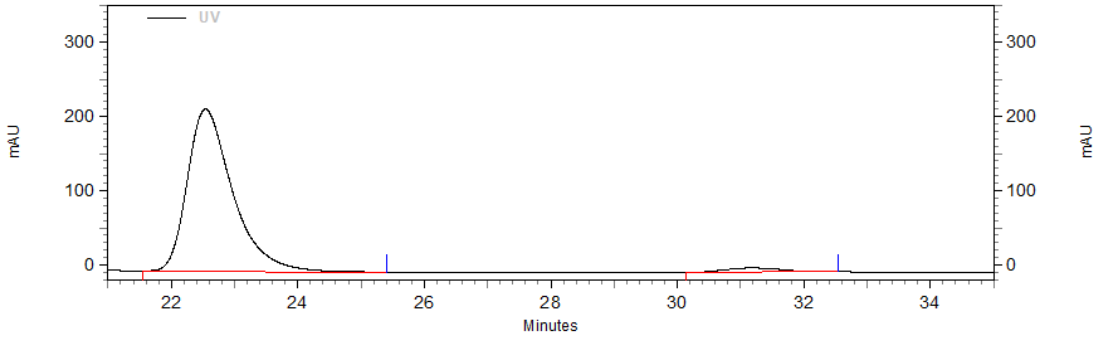
Racemic 2r



Retention Time	Area	Area %	Height	Height %
19.760	49632736	49.91	792538	58.58
27.233	49803615	50.09	560381	41.42
Totals	99436351	100.00	1352919	100.00

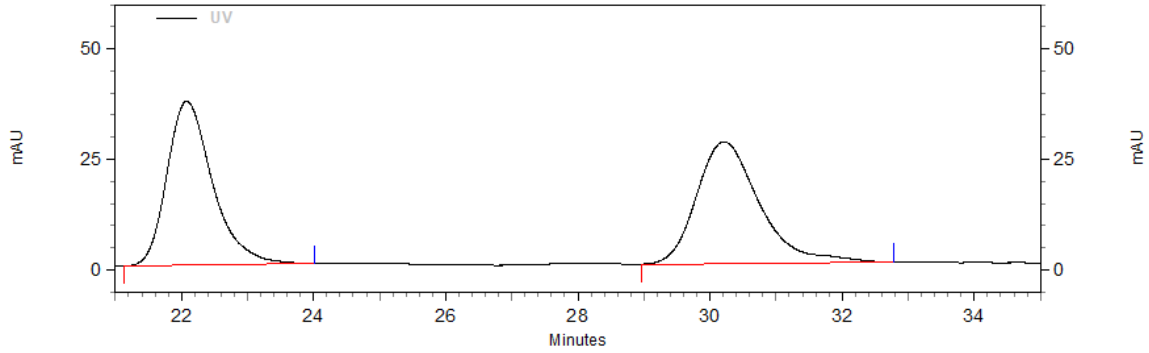


2s, (Chiralcel OD-H, n-hexane/*i*-PrOH (80:20), 0.8 mL/min, 220nm)

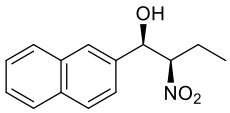


Retention Time	Area	Area %	Height	Height %
22.540	43461766	96.87	872305	97.42
31.193	1403629	3.13	23139	2.58
Totals	44865395	100.00	895444	100.00

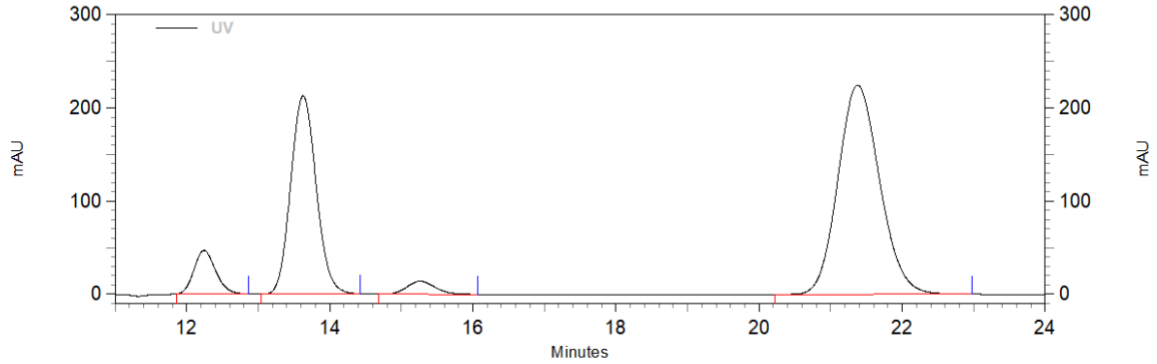
Racemic 2s



Retention Time	Area	Area %	Height	Height %
22.080	7120319	49.59	148493	57.45
30.210	7239500	50.41	109972	42.55
Totals	14359819	100.00	258465	100.00

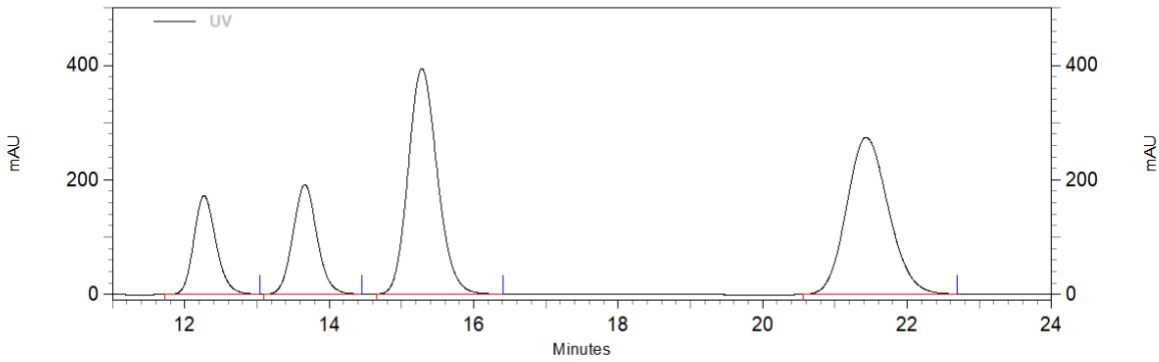


3a, (Chiralpak AS-H, Cyclohexane/*i*-PrOH (95:05), 0.7 mL/min, 216nm)

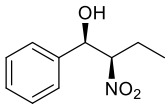


Retention Time	Area	Area %	Height	Height %
12.243	3937535	5.25	187002	9.38
13.627	21117276	32.41	852202	42.73
15.267	1547210	2.02	56001	2.81
21.377	36405469	59.51	898988	45.08
Totals	63007490	100.00	1994193	100.00

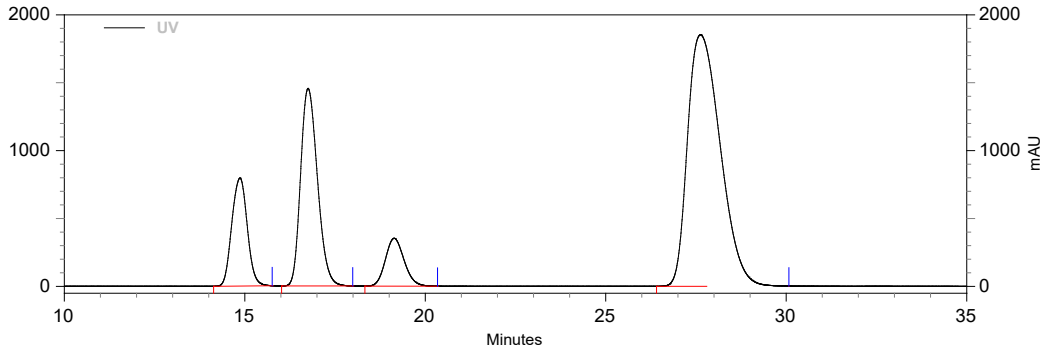
Racemic 3a



Retention Time	Area	Area %	Height	Height %
12.267	14700836	12.17	689569	16.69
13.663	17734559	14.68	765693	18.54
15.283	44152264	36.54	1577896	38.20
21.433	44235945	36.61	1097289	26.57
Totals	120823604	100.00	4130447	100.00

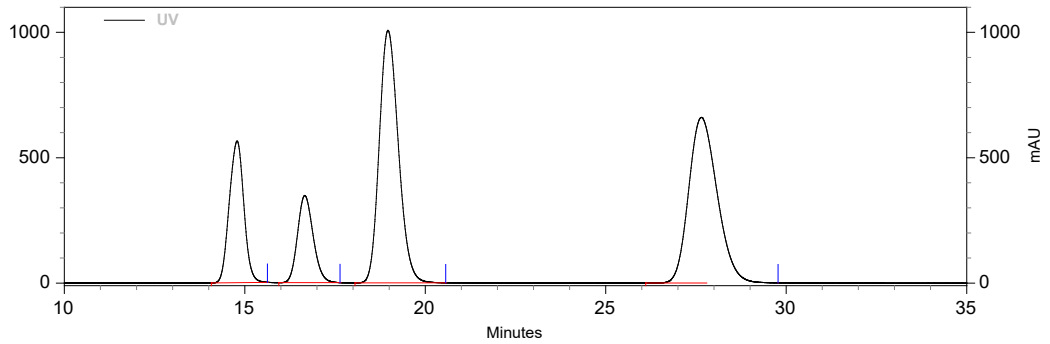


3c, (Chiralpak AS-H, Cyclohexane/*i*-PrOH (95:05), 0.7 mL/min, 216nm)

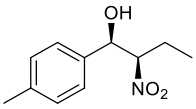


Retention Time	Area	Area %	Height	Height %
14.867	94562946	11.80	3182505	17.86
16.753	188692672	23.55	5818252	32.65
19.137	50780910	6.34	1409607	7.91
27.630	467144764	58.31	7411119	41.59
Totals	801181292	100.00	17821483	100.00

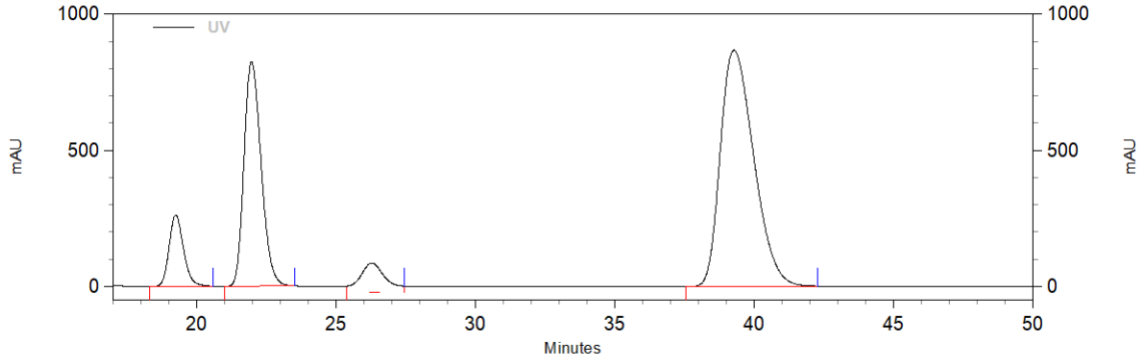
Racemic 3c



Retention Time	Area	Area %	Height	Height %
14.787	53365903	13.90	2258197	21.89
16.663	51907651	12.52	1390385	13.48
18.967	148330612	37.22	4027180	39.03
27.650	144917010	36.36	2641853	25.61
Totals	398521176	100.00	10317615	100.00

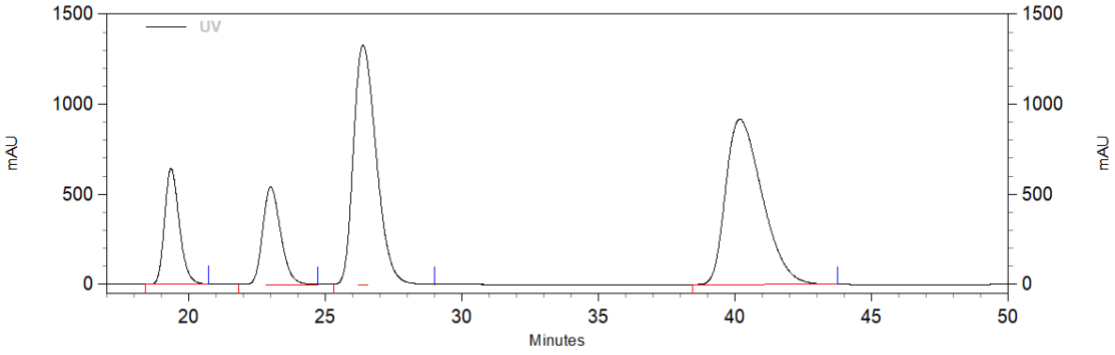


3f, (Chiralpak AS-H, Cyclohexane/*i*-PrOH (95:05), 0.7 mL/min, 216nm)

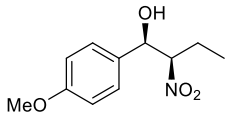


Retention Time	Area	Area %	Height	Height %
19.253	37693193	6.59	1048892	12.70
21.977	141406588	28.46	3301879	39.97
26.277	28303349	4.70	433601	5.25
39.273	289513505	60.26	3475853	42.08
Totals	496916635	100.00	8260225	100.00

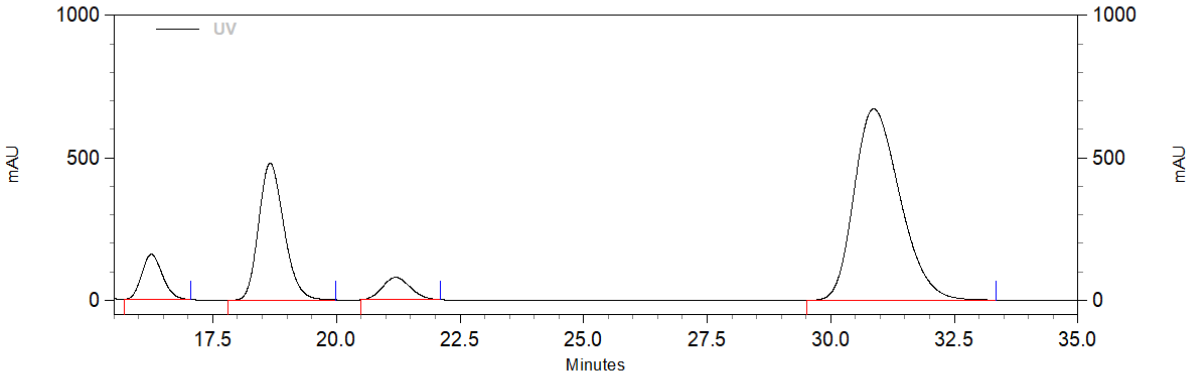
Racemic 3f



Retention Time	Area	Area %	Height	Height %
19.363	96216871	11.39	2569871	18.72
23.007	99521610	11.78	2169071	15.80
26.387	308791931	38.05	5314986	38.72
40.167	340285300	38.78	3671989	26.75
Totals	844815712	100.00	13725917	100.00

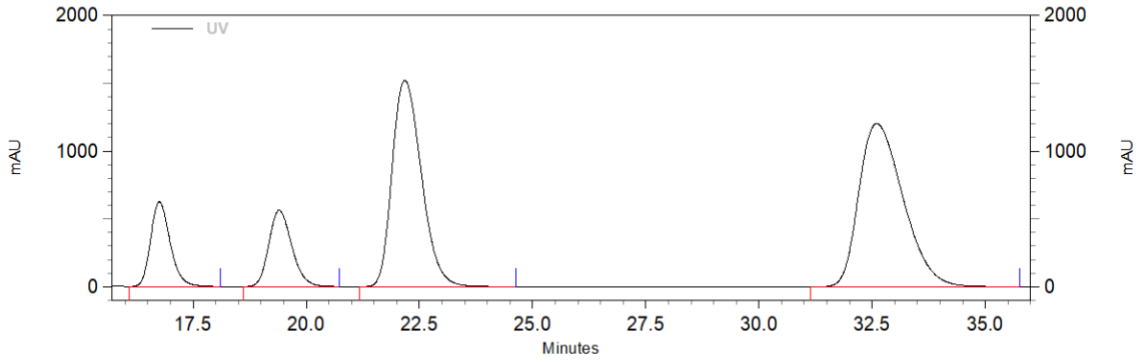


3i, (Chiralpak AS-H, Cyclohexane/*i*-PrOH (95:05), 0.7 mL/min, 216nm)

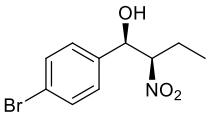


Retention Time	Area	Area %	Height	Height %
16.253	18548245	6.80	634031	11.41
18.653	68430288	25.10	1920474	34.57
21.193	12388755	4.13	313557	5.64
30.867	173312042	63.97	2686915	48.37
Totals	272679330	100.00	5554977	100.00

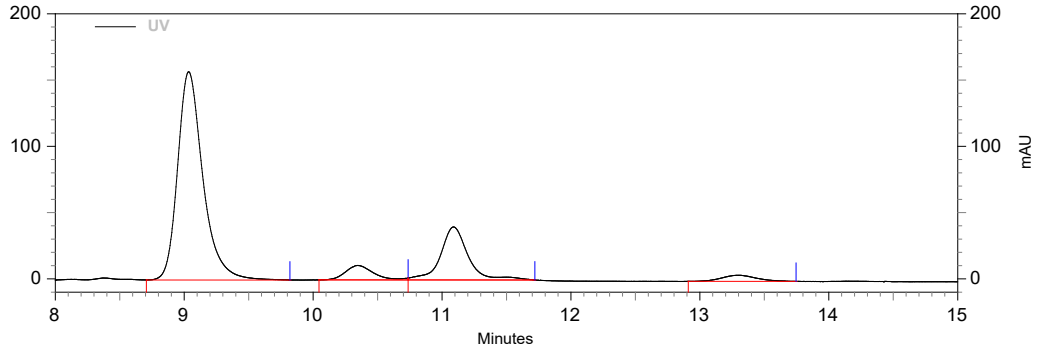
Racemic 3i



Retention Time	Area	Area %	Height	Height %
16.757	74781455	9.91	2501388	15.98
19.400	79258300	10.50	2250153	14.38
22.173	283922286	38.90	6081542	38.86
32.600	316649110	40.69	4815316	30.77
Totals	754611151	100.00	15648399	100.00

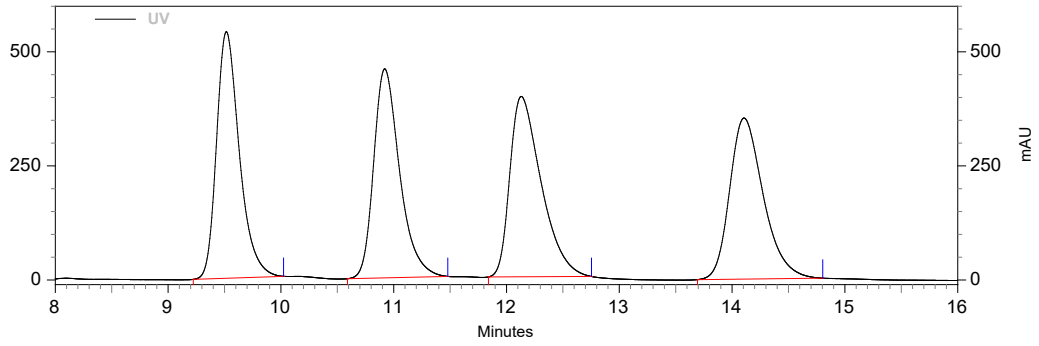


3l, (Chiralcel AD-H, *n*-hexane/*i*-PrOH (85:15), 1.0 mL/min, 220nm)

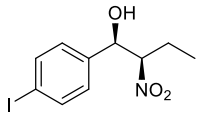


Retention Time	Area	Area %	Height	Height %
9.033	8551554	77.42	628372	73.91
10.347	654628	4.49	43459	5.11
11.090	2369162	14.87	159840	18.80
13.310	346384	2.22	18481	2.17
Totals	11921728	100.00	850152	100.00

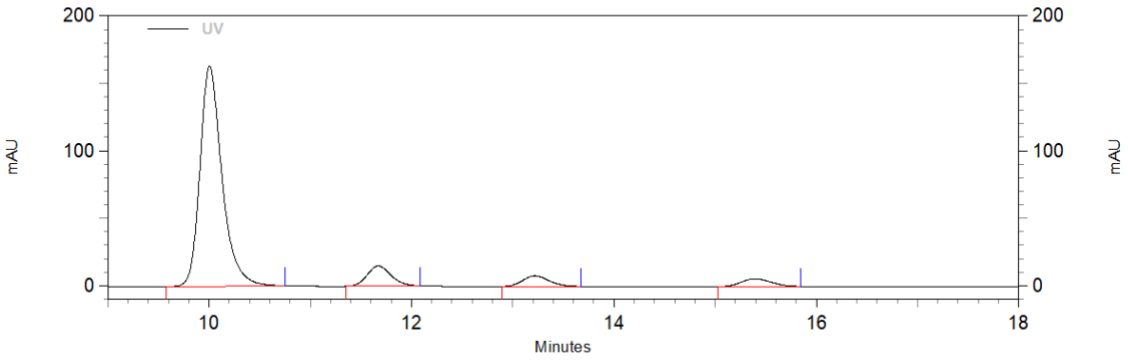
Racemic 2x



Retention Time	Area	Area %	Height	Height %
9.517	30368594	25.69	2161808	30.94
10.920	29248645	24.50	1831908	26.22
12.130	29276968	24.52	1580505	22.62
14.107	30488618	25.29	1411657	20.22
Totals	119382825	100.00	6985878	100.00

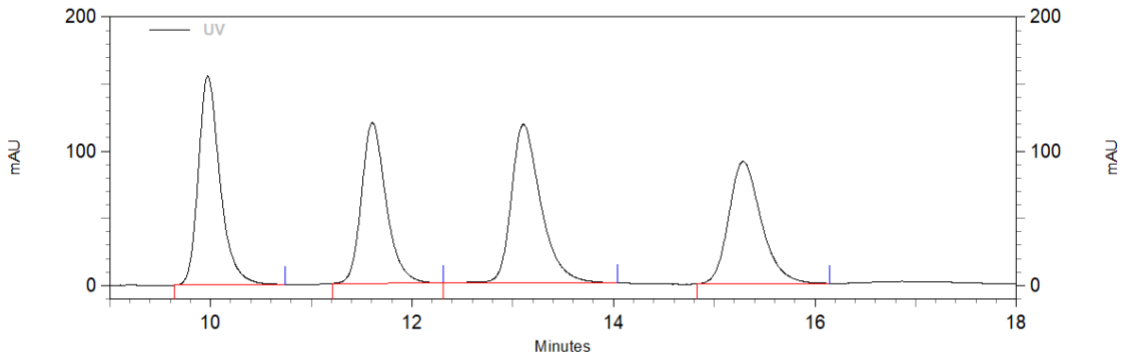


3m, (Chiralcel AD-H, Cyclohexane/*i*-PrOH (85:15), 1.0 mL/min, 220nm)



Retention Time	Area	Area %	Height	Height %
10.007	9899098	83.86	652683	85.01
11.677	971321	8.13	59618	7.77
13.220	582850	4.13	31797	4.14
15.397	493806	3.88	23674	3.08
Totals	11947075	100.00	767772	100.00

Racemic 3m



Retention Time	Area	Area %	Height	Height %
9.973	9684307	27.41	622582	32.12
11.607	8145109	23.05	479088	24.71
13.107	8180874	23.15	472512	24.37
15.287	9326611	26.39	364362	18.80
Totals	35336901	100.00	1938544	100.00

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