Electronic Supplementary Information

Expanding the Family of Bis-Cyclometalated Chiral-at-Metal Rhodium(III) Catalysts with a Benzothiazole Derivative

Jiajia Ma, Xiaodong Shen, Klaus Harms and Eric Meggers*

*Email: meggers@chemie.uni-marburg.de

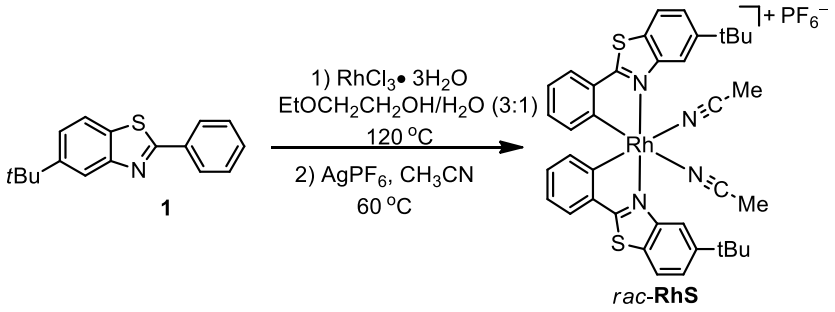
Contents:

1. General Information

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. Catalytic reactions were performed by using standard Schlenk glassware techniques. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2), sodium/benzophenone (THF, Et_2O). Column chromatography was performed with silica gel 60 M from Macherey–Nagel (irregular shaped, 230–400 mesh, pH 6.8, pore volume: 0.81 $mL \times g^{-1}$, mean pore size: 66 Å, specific surface: 492 $m^2 \times g^{-1}$, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^1H NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^1H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), δ = 5.32 ppm (CD_2Cl_2). $^{13}C\{^1H\}$ NMR spectroscopy: δ = 77.1 ppm ($CDCl_3$), δ = 53.8 ppm (CD_2Cl_2). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer or on a Nicolet Avatar 330 FT-IR spectrophotometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (600-200 nm, 1 nm band width, 50 nm/min scanning speed, accumulation of 3 scans). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI technique. Chiral HPLC chromatography was performed with an Agilent 1200, 1260 or Shimadzu Lc-2030c HPLC system. Optical rotations were measured with a Perkin-Elmer 241 or 341 polarimeter at concentrations of 1.0 g/100 mL. (*S*)-3-fluoro-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol {(*S*)-**3**} was prepared according to the published procedure.[1] All other reagents were commercially available and used without further purification.

2. Synthesis of Rhodium Catalysts Λ-RhS and Δ-RhS

Racemic Rhodium Catalyst:



The racemic rhodium catalyst *rac*-**RhS** was synthesized according to a route reported by us with some modifications.[2] Accordingly, 5-(*tert*-butyl)-2-phenylbenzo[*d*]thiazole **1** (268 mg, 1.0 mmol) was added to $RhCl_3$•$3H_2O$ (131 mg, 0.50 mmol) in a mixture of 2-ethoxyethanol and water (v/v = 3:1, 10 mL). The reaction mixture was heated at 120 °C for 4 h under an atmosphere of nitrogen, then poured into water (50 mL). The resulting precipitate was collected by centrifugation, washed with water and dried to obtain a brown solid. To the brown solid in CH_3CN (10 mL) was added $AgPF_6$ (160 mg, 0.60 mmol) in one portion, then stirred at 60 °C overnight. After cooled to room temperature, the mixture was filtered. The filtrate was collected, evaporated to dryness and purified by column chromatograph on silica gel (100% CH_2Cl_2 to CH_2Cl_2/CH_3CN = 20:1) to give *rac*-**RhS** (315 mg, 0.365 mmol, 73% yield for two steps) as a pale yellow solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.50 (d, J = 1.6 Hz, 2H), 8.05 (d, J = 8.6 Hz, 2H), 7.73 (dd, J = 8.6, 1.8 Hz, 2H), 7.67 (dd, J = 7.6, 1.2 Hz, 2H), 7.03 (td, J = 7.4, 1.1 Hz, 2H), 6.83 (td, J = 7.7, 1.4 Hz, 2H), 6.22 (d, J = 7.8 Hz, 2H), 2.18 (s, 6H), 1.47 (s, 18H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 176.9, 176.8, 160.9, 160.5, 152.8 (2C), 150.0 (2C), 140.3 (2C), 133.3 (2C), 131.2 (2C), 129.1 (2C), 126.2 (2C), 125.5 (2C), 124.5 (2C), 123.0 (2C), 122.1 (2C), 116.7 (2C), 35.6 (2C), 31.6 (2C), 3.5 (2C).

HRMS (ESI, *m*/*z*) calcd for $C_{38}H_{38}N_4RhS_2^+$ $[M\text{-}PF_6]^+$: 717.1587, found: 717.1596.

IR (film): *v* (cm^{-1}) 3118, 2961, 2868, 2282, 1579, 1556, 1477, 1441, 1416, 1364, 1318, 1296, 1281, 1266, 1254, 994, 836, 784, 757, 730, 700, 668, 556, 460.

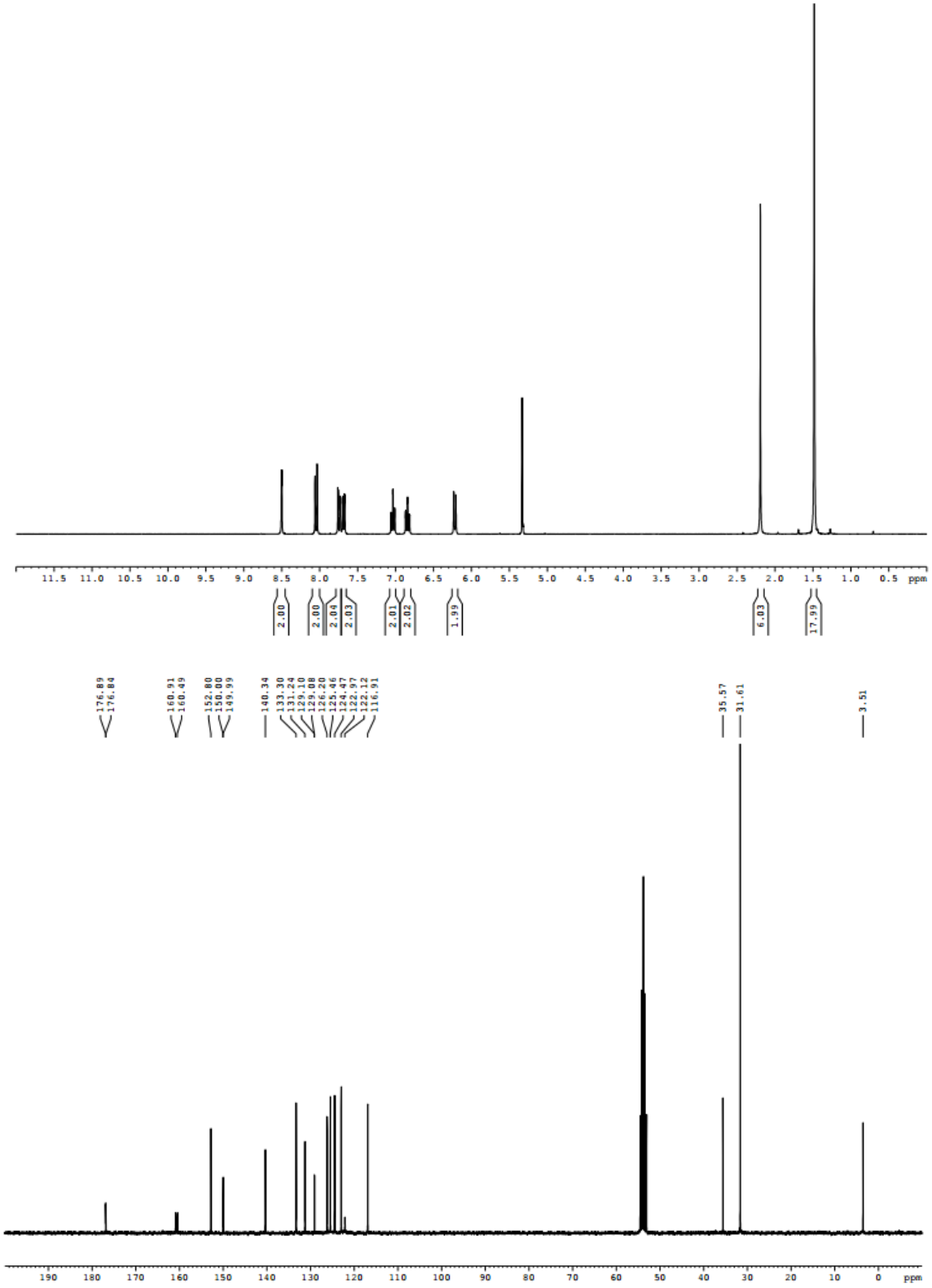
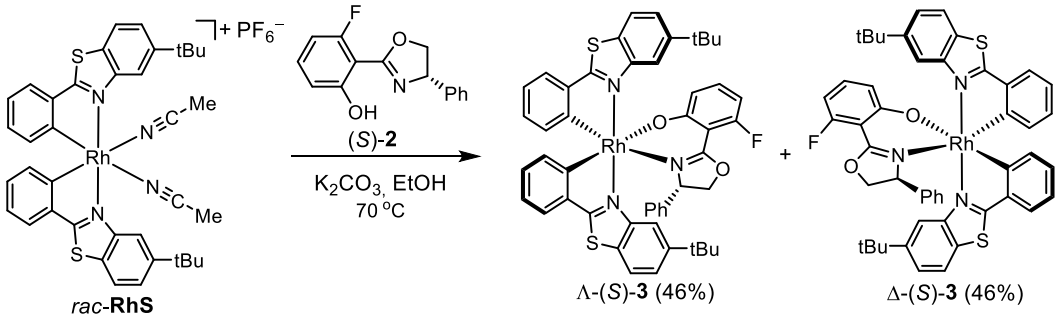


Figure S1. ^{1}H and ^{13}C NMR spectra of complex *rac*-**RhS**.

Intermediate Rhodium Auxiliary Complexes Λ-(*S*)-4 and Δ-(*S*)-4:



To the racemic rhodium catalyst *rac*-**RhS** (254 mg, 0.3 mmol) and K_2CO_3 (124 mg, 0.9 mmol) in absolute ethanol (6.0 mL) was added (*S*)-3-fluoro-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol {(*S*)-**2**} (91 mg, 0.33 mmol) in one portion, and then heated at 70 °C overnight. Afterwards, the reaction mixture was cooled to room temperature and concentrated to dryness. The residue was filtered by a thin pad of silica gel, and the filtrate was evaporated to give the mixture of two diastereoisomers, which was then washed by EtOH (5 × 8 mL) to give Λ-(*S*)-**3** (122 mg, 0.137 mmol, 46% yield) as a yellow solid. The filtrate was concentrated and subjected to a flash chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1:10) to give Δ-(*S*)-**3** (123 mg, 0.139 mmol, 46% yield) as a yellow solid. For larger scales, a modified resolution procedure is recommended in which the mixture of diastereoisomers of *rac*-**RhS** (680 mg, 0.8 mmol) are directly subjected to silica gel chromatography (*n*-hexane/CH_2Cl_2 = 1:10) without any decrease of the yields. Λ-(*S*)-**3** elutes firstly (329 mg, 0.369 mmol, 46% yield) and Δ-(*S*)-**3** afterwards (326 mg, 0.367 mmol, 46% yield)}. The assigned configurations were confirmed by the crystal structure of Λ-(*S*)-**3** (see below).

Λ-(*S*)-**3**:

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.90 (d, *J* = 1.6 Hz, 1H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.80 (d, *J* = 5.1 Hz, 1H), 7.62-7.59 (m, 2H), 7.53 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.46 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.98 (td, *J* = 7.3, 1.0 Hz, 1H), 6.92 (td, *J* = 7.4, 1.0 Hz, 1H), 6.86-6.70 (m, 6H), 6.36-6.15 (m, 4H), 5.88 (d, *J* = 7.9 Hz, 1H), 5.81 (qd, *J* = 7.8, 1.1 Hz, 1H), 4.89-4.84 (m, 2H), 4.02-3.97 (m, 1H), 1.45 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 177.3 (2C), 175.7 (2C), 175.1 (2C), 170.4, 170.1, 168.2, 168.0, 165.9 (2C), 163.6 (d, *J* = 257.2 Hz), 151.5, 151.4, 151.3, 141.7, 141.4, 141.2, 135.3, 133.2, 132.9,

132.8, 129.9, 129.6, 129.4 (2C), 128.8 (2C), 127.9, 127.6, 125.9 (2C), 123.9, 123.0, 122.4, 122.3, 121.3, 120.4 (2C), 119.6, 116.5, 101.2 (d, J = 6.3 Hz), 98.5 (d, J = 24.0 Hz), 75.7, 69.4, 35.3, 35.2, 31.7, 31.6.

HRMS (ESI, *m*/*z*) calcd for $C_{49}H_{43}FN_3O_2RhS_2Na^+$ $[M+Na]^+$: 914.1728, found: 914.1731.

IR (film): ν (cm^{-1}) 2956, 2927, 1617, 1591, 1578, 1526, 1474, 1458, 1438, 1414, 1391, 1376, 1292, 1245, 1156, 1092, 1015, 988, 924, 814, 791, 752, 719, 689, 668, 462.

CD {CH_3OH/DCM (4:1)} for Λ-(*S*)-**3**: λ, nm (Δε, $M^{-1}cm^{-1}$) 425 (+25), 380 (–10), 362 (–6), 339 (–21), 318 (–2), 299 (+41), 278 (–21), 266 (–15), 254 (–29), 234 (+18), 221 (–30).

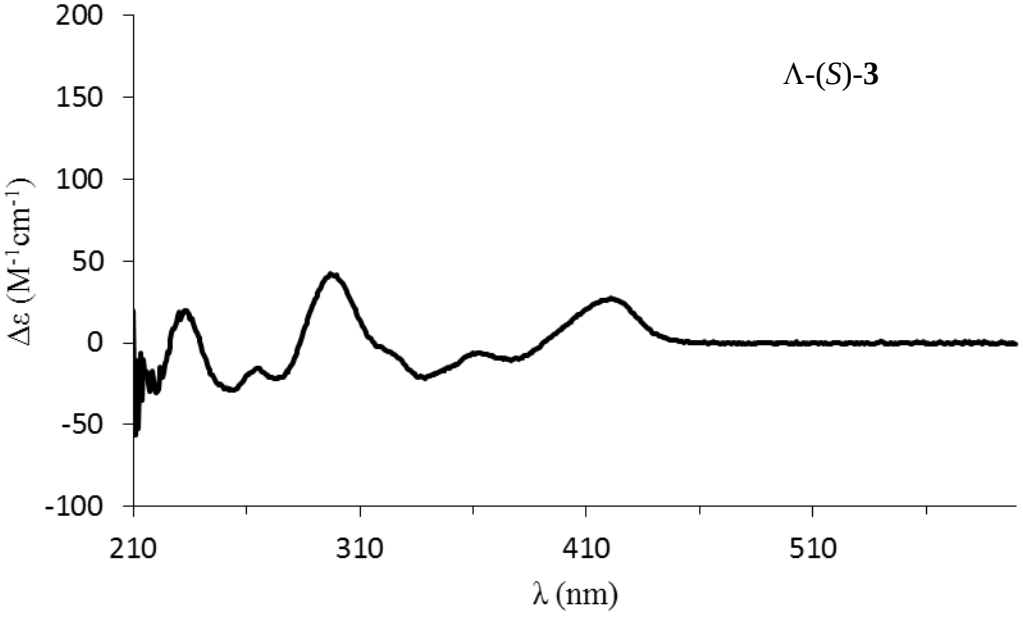


Figure S2. CD spectrum of complex Λ-(*S*)-**3**. Recorded in CH_3OH/DCM (v/v = 4:1, 0.2 mM).

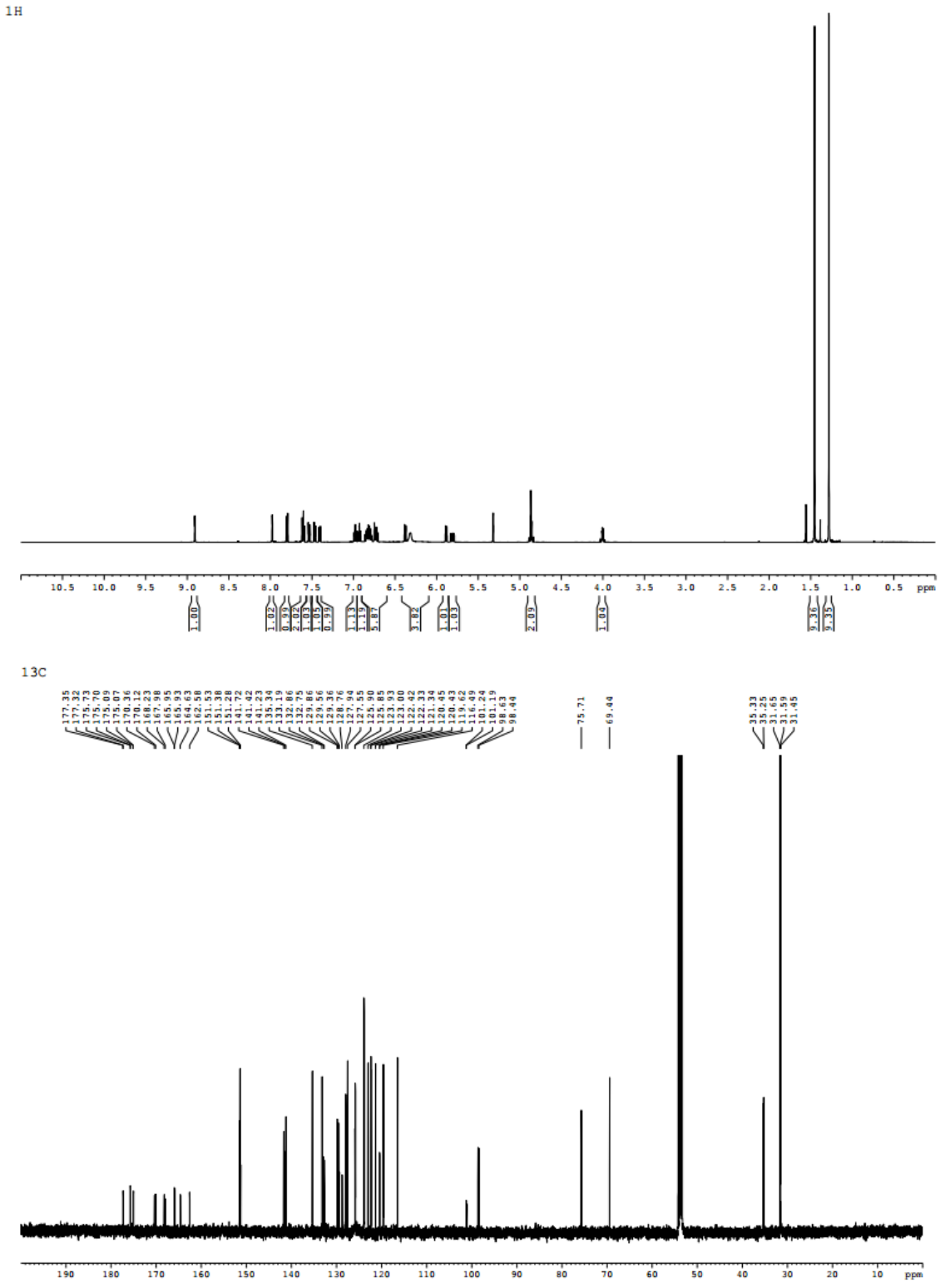


Figure S3. ^{1}H and ^{13}C NMR spectra of complex Λ-(*S*)-**3**.

Δ-(*S*)-**3**:

^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.06 (d, *J* = 1.8 Hz, 1H), 8.37 (d, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.51 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.95 (td, *J* = 7.4, 1.1 Hz, 1H), 6.92-6.80 (m, 5H), 6.80-6.73 (m, 2H), 6.57 (td, *J* = 7.4, 1.0 Hz, 1H), 6.40 (td, *J* = 7.8, 1.4 Hz, 1H), 6.28 (d, *J* = 7.8 Hz, 1H), 6.24 (d, *J* = 8.6 Hz, 1H), 6.14 (d, *J* = 7.8 Hz, 1H), 5.81 (dd, *J* = 11.5, 7.9 Hz, 1H), 4.30 (t, *J* = 9.3 Hz, 1H), 4.03 (dd, *J* = 12.0, 9.4 Hz, 1H), 3.92 (dd, *J* = 12.0, 8.5 Hz, 1H), 1.37 (s, 9H), 1.23 (s, 9H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.5, 176.4 (2C), 174.9 (2C), 169.3, 169.1, 168.7, 168.5, 167.0, 163.0 (d, *J* = 254.6 Hz), 152.5, 151.2, 151.0, 141.0, 140.5, 138.7, 135.2, 133.4, 132.8, 132.7, 130.1, 129.5, 128.7, 128.5, 128.2, 127.6, 127.3, 125.9, 125.6, 124.5, 124.4, 123.0, 122.2, 122.0, 121.9, 119.3 (2C), 118.8, 117.3, 103.7 (d, *J* = 8.1 Hz), 98.4 (d, *J* = 22.2 Hz), 74.9, 70.2, 35.5, 35.4, 31.5, 31.4.

IR (film): *v* (cm^{-1}) 2959, 2900, 1618, 1577, 1553, 1530, 1473, 1458, 1436, 1415, 1374, 1292, 1246, 1156, 1092, 1028, 988, 930, 814, 788, 752, 719, 695, 668, 460.

HRMS (ESI, *m*/*z*) calcd for $C_{49}H_{44}FN_3O_2RhS_2^+$[M+H]$^+$: 892.1909, found: 892.1910.

CD {CH_3OH/DCM (4:1)} for Δ-(*S*)-**3**: λ, nm (Δε, $M^{-1}cm^{-1}$) 417 (–35), 379 (+33), 362 (+31), 344 (+54), 299 (–58), 274 (+21), 263 (+6), 244 (+36), 233 (–5), 220 (+65).

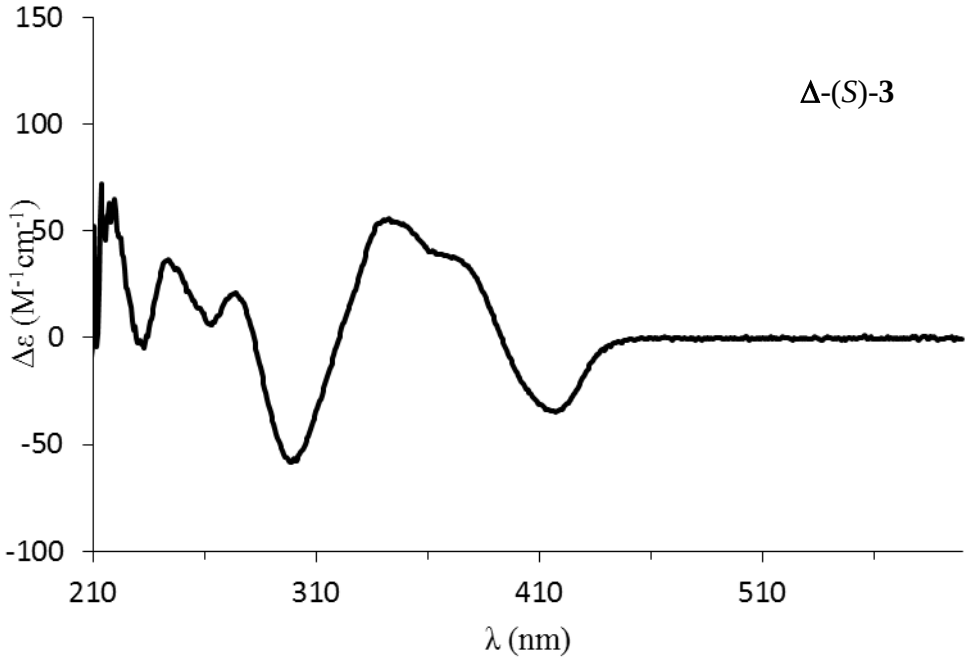


Figure S4. CD spectrum of Δ-(*S*)-**3**. Recorded in CH_3OH/DCM (v/v = 4:1, 0.2 mM).

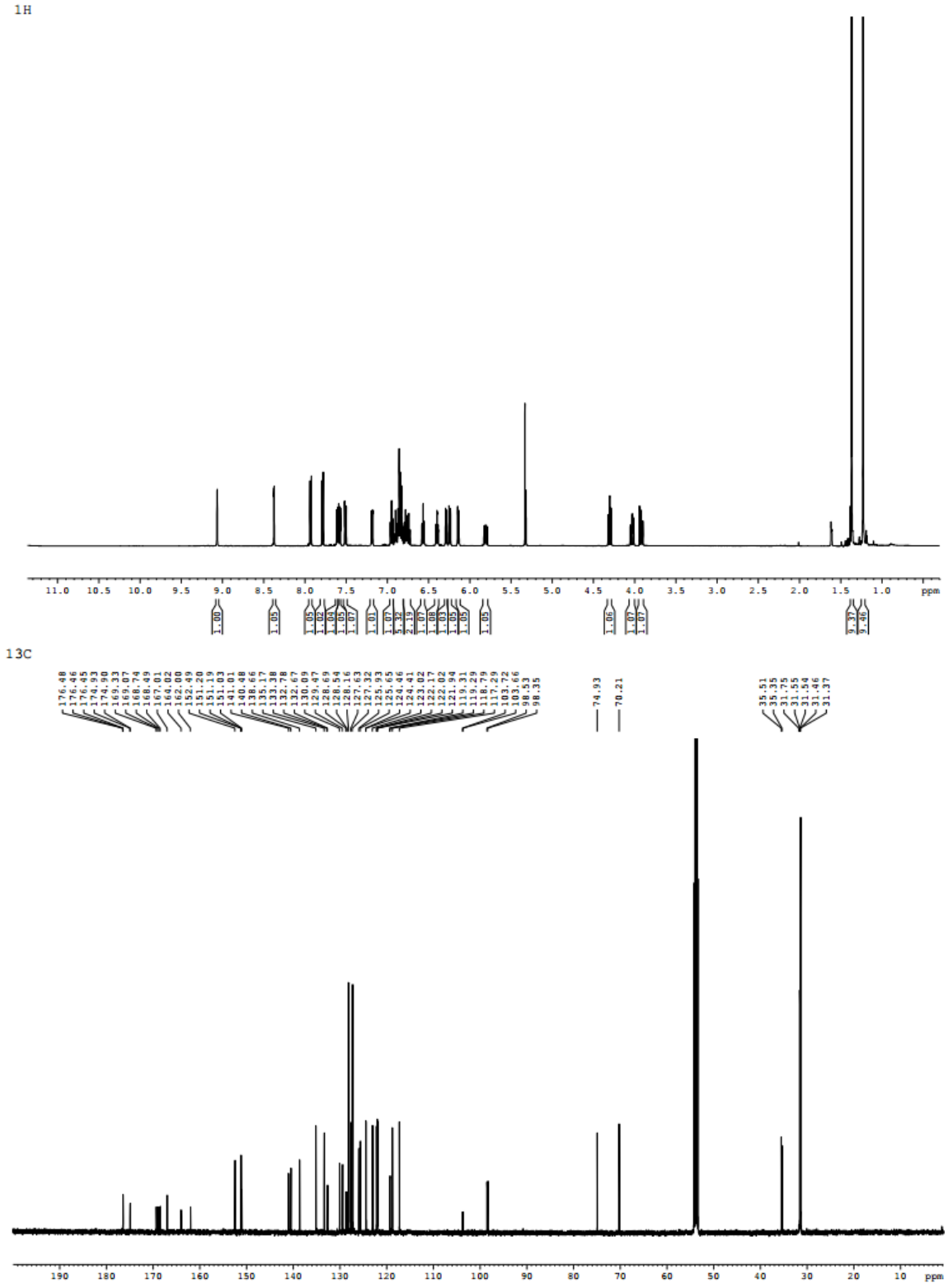
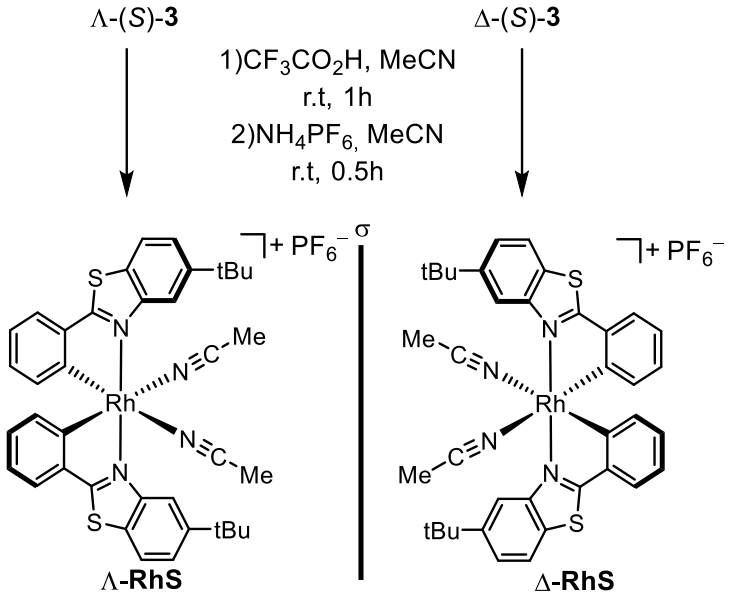


Figure S5. ^{1}H and ^{13}C NMR spectra of complex Δ-(*S*)-**3**.

Enantiopure Rhodium Catalysts:

To a suspension of Λ-(*S*)-**3** (122 mg, 0.137 mmol) or Δ-(*S*)-**3** (123 mg, 0.139 mmol) in CH_3CN (5 mL) was added TFA (62 μL, 0.84 mmol) in one portion, then stirred at room temperature for 1 h in the dark. The reaction mixture was evaporated to dryness, redissolved in CH_3CN, followed by the addition of excess NH_4PF_6, then stirred at room temperature for another 0.5 h. The mixture was filtered by a thin pad of silica gel, and the pale yellow filtrate was concentrated, then subjected to the column chromatography on silica gel (100% CH_2Cl_2 to CH_2Cl_2/CH_3CN = 20:1) to give the enantiopure catalysts Λ-**RhS** (100 mg, 0.116 mmol, 85% yield) or Δ-**RhS** (96.0 mg, 0.111 mmol, 80% yield) as yellow solids.



CD (CH_3OH) for Λ-**RhS**: λ, nm (Δε, $M^{-1}cm^{-1}$) 408 (–45), 368 (+77), 357 (+66), 347 (+65), 300 (–99), 265 (+36), 253 (+36), 240 (+60).

CD (CH_3OH) for Δ-**RhS**: λ, nm (Δε, $M^{-1}cm^{-1}$) 407 (+51), 367 (–79), 360 (–71), 348 (–67), 301 (–107), 262 (–32), 253 (–35), 242 (–68).

All other spectroscopic data of Λ-**RhS** and Δ-**RhS** were in agreement with the *rac*-**RhS**.

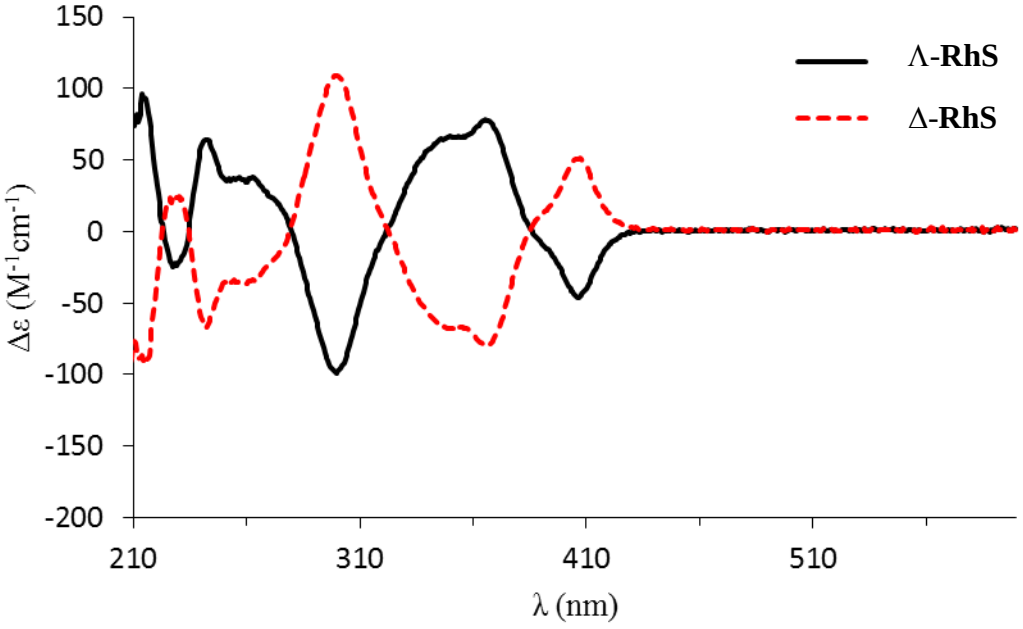
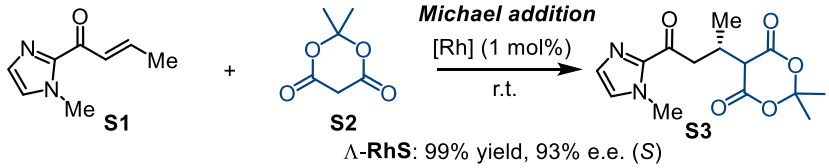


Figure S6. CD spectra of Λ-**RhS** and Δ-**RhS**. Recorded in CH_3OH (0.2 mM).

3. Rhodium-Catalyzed Asymmetric Reactions

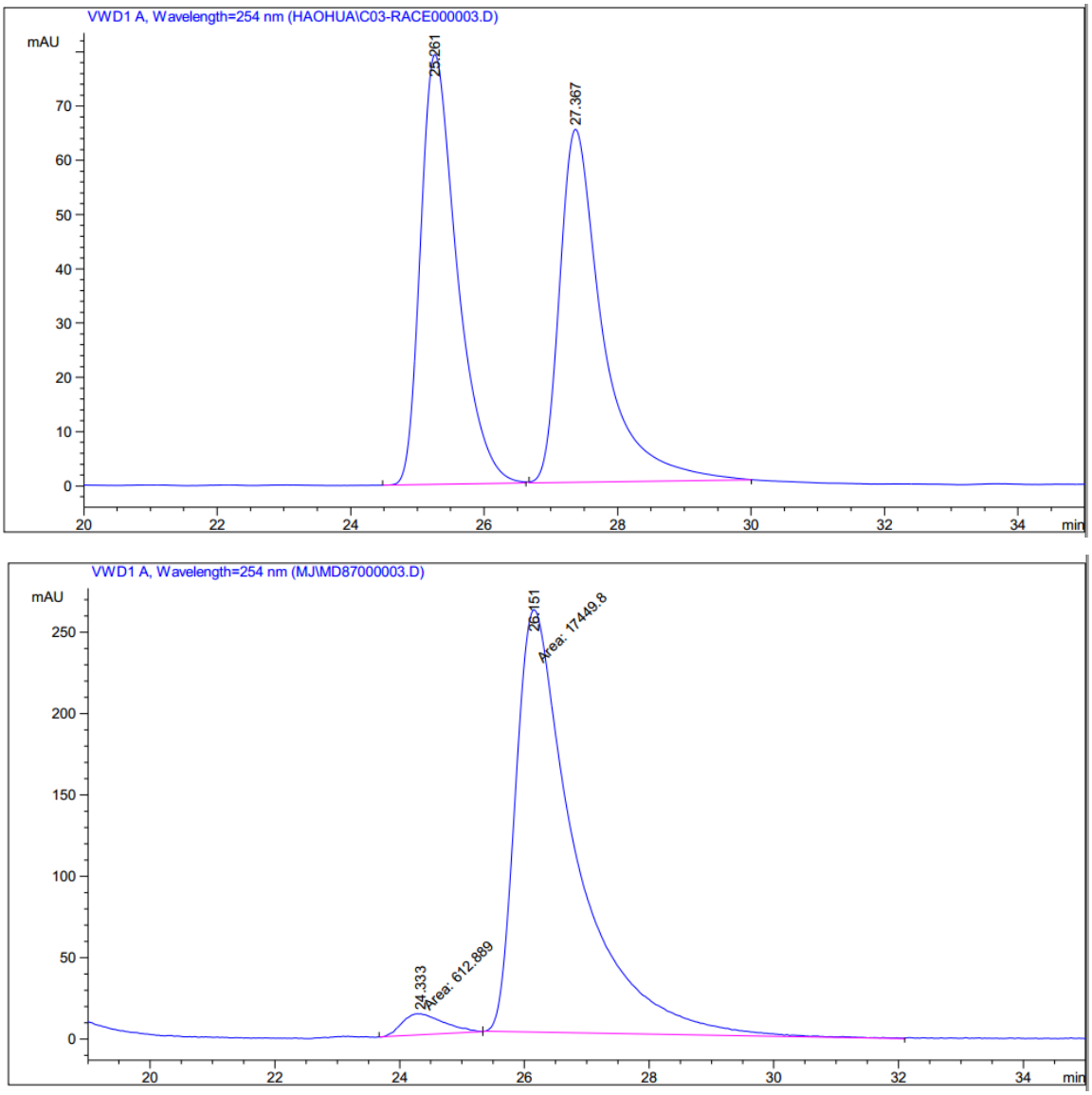
Michael addition reaction:



To a solution of catalyst Λ-**RhS** (1.7 mg, 0.002 mmol, 1 mol%) in distilled, anhydrous THF (0.20 mL, 1.0 M) was added the acylimidazole **S1** (30.2 mg, 0.20 mmol) in a Schlenk tube. After being stirred at room temperature for 20 min, the nucleophile **S2** (86.5 mg, 0.60 mmol) was added at room temperature. The reaction was stirred at room temperature for 16 h under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:2 to 2:1) to afford the product **S3** (58.0 mg, 99% yield, 93% e.e.). Enantiomeric excess established by HPLC analysis by using a Chiralpak AD-H column, e.e. = 93% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate = 0.8 mL/min, 40 °C, t_r (minor) = 24.3 min, t_r (major) = 26.1 min), $[\alpha]_D^{20}$ = +4.1° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, *J* = 0.9 Hz, 1H), 7.03 (s, 1H), 4.22-4.16 (m, 1H), 3.98 (s, 3H), 3.56 (dd, *J* = 7.2, 5.0 Hz, 2H), 3.24-3.10 (m, 1H), 1.77 (d, *J* = 5.8 Hz, 6H), 1.21 (d, *J* = 7.0 Hz, 3H).

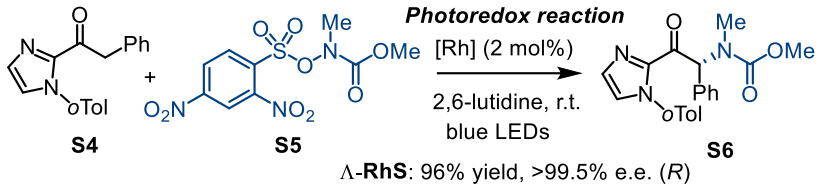
All other spectroscopic data were in agreement with the literature.[2]



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.333	MM	0.7839	612.88879	13.03154	3.3931
2	26.151	MM	1.1195	1.74498e4	259.77649	96.6069

Figure S7. HPLC traces of *rac*-**S3** (reference) and (*S*)-**S3**. Area integration = 96.6:3.4 (93.2% e.e.).

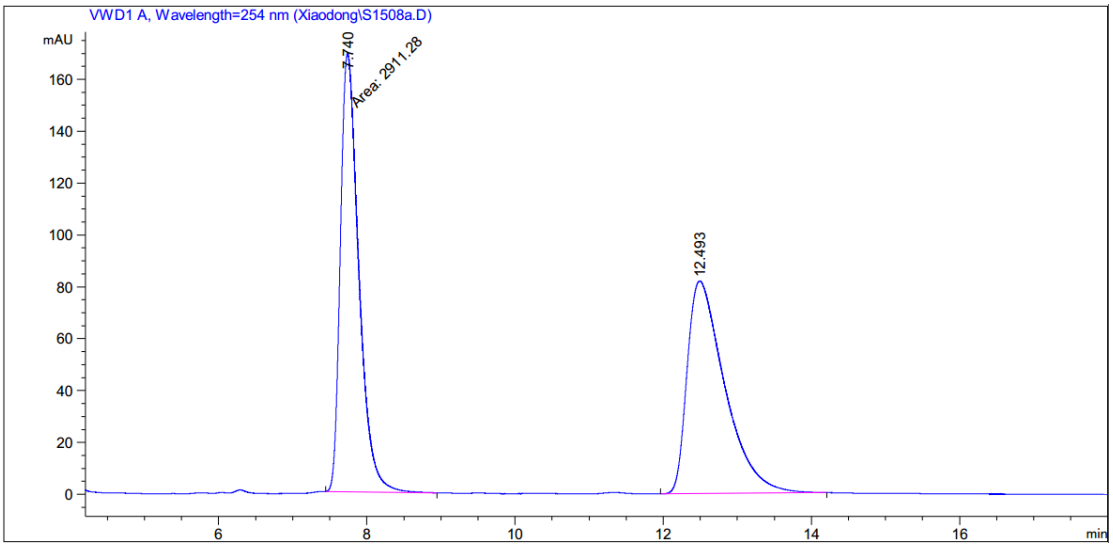
Photoredox reaction:

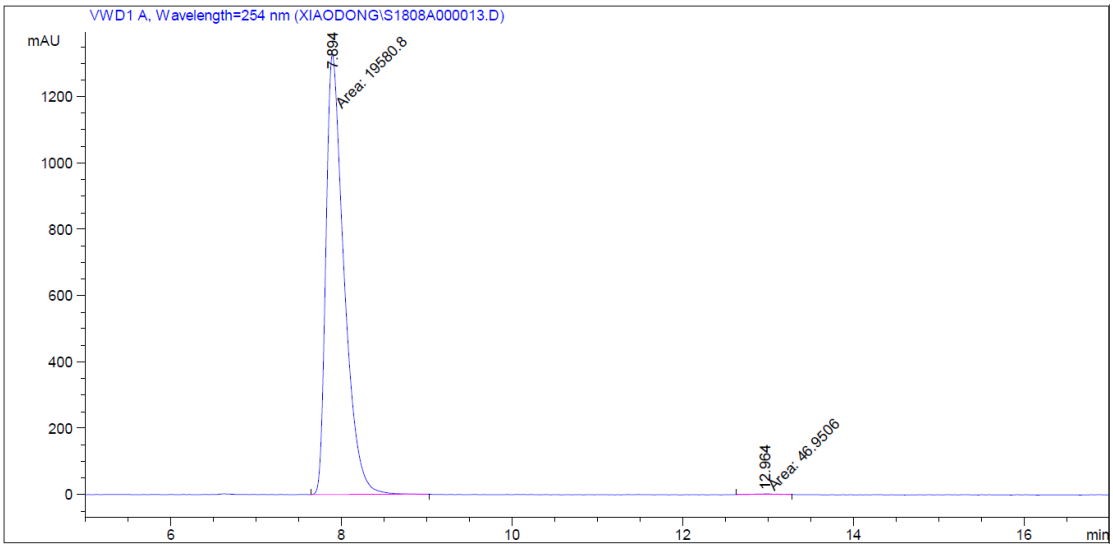


To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Λ-**RhS** (3.5 mg, 0.004 mmol, 2 mol%), 2-acyl imidazoles **S4** (104.8 mg, 0.4 mmol, 2.0 equiv), and the nitrogen reagent **S5** (67.0 mg, 0.20 mmol, 1.0 equiv). The Schlenk tube was then degassed by alternative evacuation and back filling with nitrogen. DMSO (0.25 mL), CH_3CN (0.75 mL), and 2,6-lutidine (36.4 mg, 40 µL, 0.34 mmol, 1.7 equiv) were then added to the Schlenk tube via syringe addition. The resulting clear solution was degassed for 5 min by bubbling nitrogen through the reaction medium. The reaction mixture was stirred at room temperature and positioned approximately 10 cm from 24 W blue LEDs. 2 hours later, the reaction mixture was concentrated in *vacuo*. The resulting crude oil was purified by flash chromatography on silica gel (EtOAc/ *n*-hexane = 1:4 to 1:2) to provide the target compound **S6** (2 hours, 69.7 mg, 0.192 mmol, 96% yield). Enantiomeric excess established by HPLC analysis using a Chiralpak OD-H column, e.e. = 99.5% (HPLC: OD-H, 254 nm, *n*-hexane /isopropanol = 85:15, flow rate 1.0 mL/min, 25 ^{o}C), t_r (major) = 7.9 min, t_r (minor) = 13.0 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 -7.17 (m, 10H), 7.17-6.97 (m, 2H), 3.70 (s, 3H), 2.73 and 2.69 (s and s, 3H, contained the rotamer), 2.04 and 1.97 (s and s, 3H, contained the rotamer).

All other spectroscopic data were in agreement with the literature.[3]





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.894	MM	0.2456	1.95808e4	1328.85364	99.7608
2	12.964	MM	0.3345	46.95055	2.33945	0.2392

Figure S8. HPLC traces of *rac*-**S6** (reference) and (*R*)-**S6**. Area integration = 99.8:0.2 (99.6% e.e.).

4. Enantiomeric Purities of the Rhodium Catalysts

The analysis was performed with a Daicel Chiralpak IB (250 × 4.6 mm) HPLC column on a Shimadzu Lc-2030c HPLC system. The column temperature was 25 °C and UV-absorption was measured at 254 nm. Solvent A = 0.1% TFA in H_2O, solvent B = MeCN.

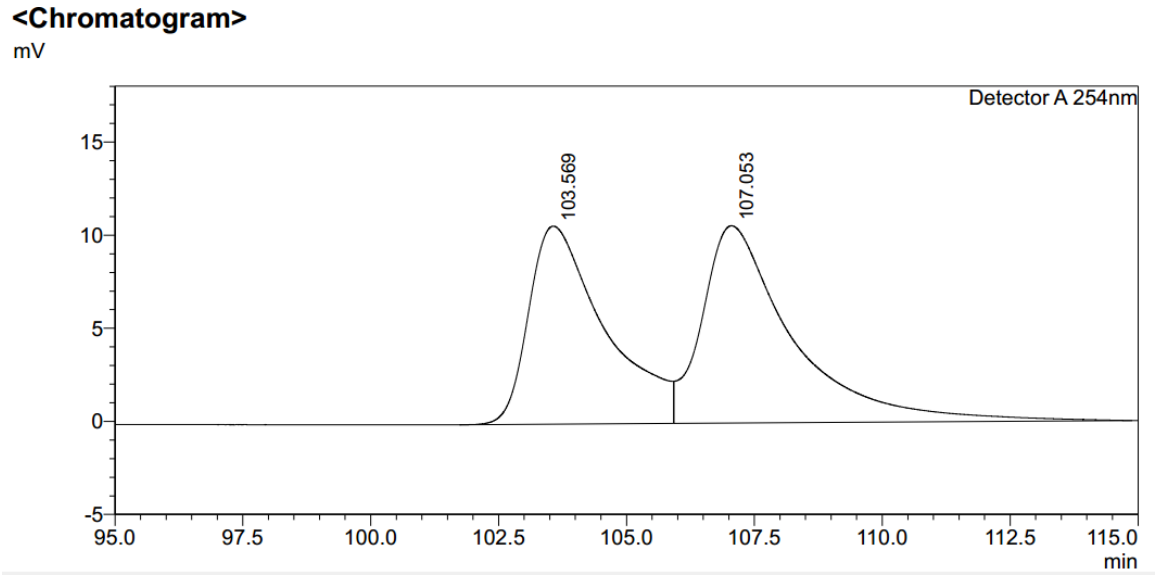


Figure S9. HPLC trace for the racemic reference complexes Δ/Λ-**RhS**. (Daicel Chiralpak IB, with a linear gradient of 40% to 50% B in 180 min, flow rate = 0. 6 mL/min).

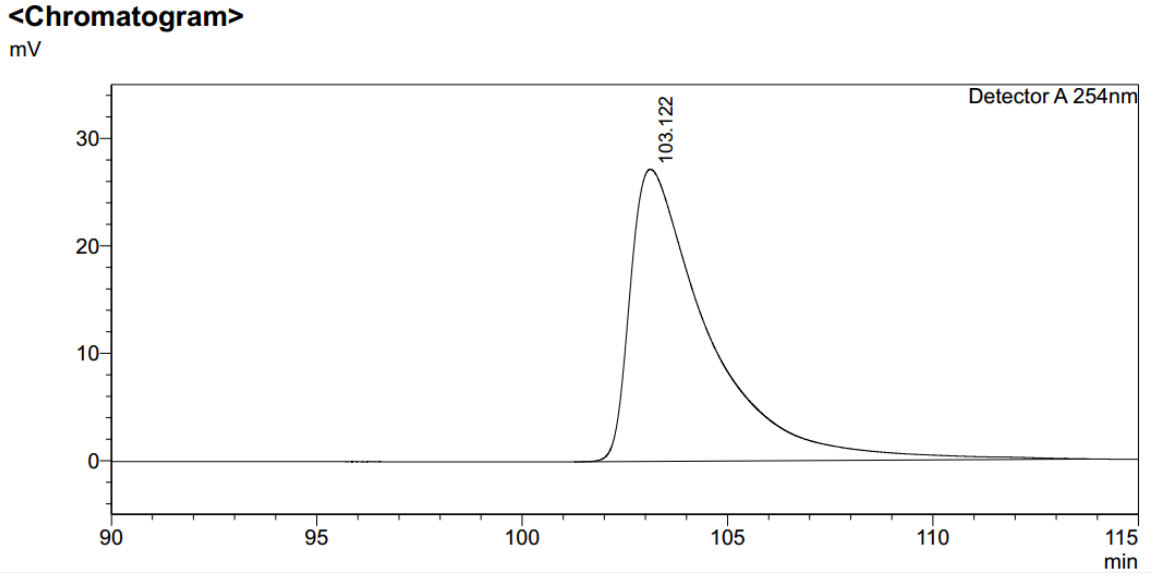
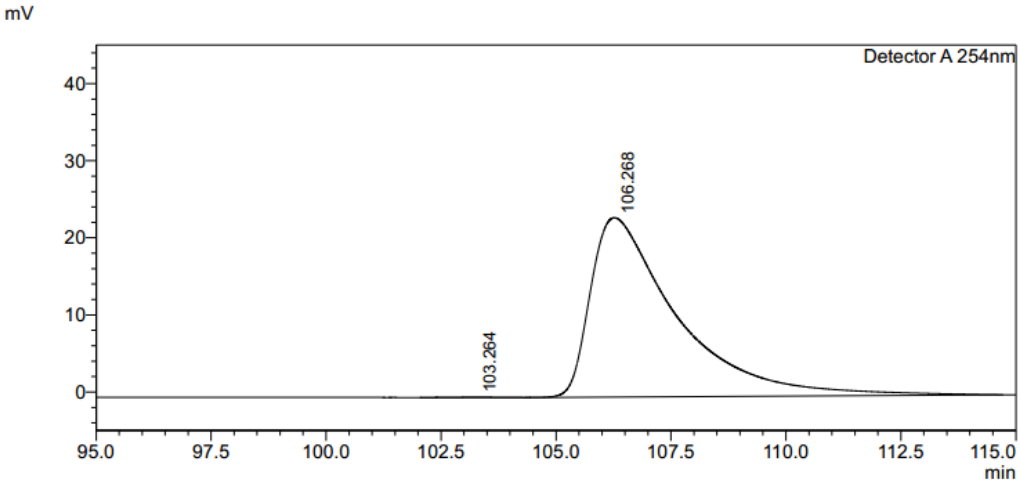


Figure S10. HPLC trace for the complex Δ-**RhS**. Integration of peak areas > 99% e.e.

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	103.264	2809	47	0.092
2	106.268	3037937	23259	99.908
Total		3040746	23306	100.000

Figure S11. HPLC trace for the complex Λ-**RhS**. Integration of peak areas = 99.8% e.e.

5. Investigation of the Configurational Stability of the Rhodium Catalyst

5.1. Catalyst Stability Investigated by ^{1}H NMR

The rhodium complex Λ-**RhS** (20.0 mg) was stored in a brown glass vial and kept on the bench at room temperature. ^{1}H NMR spectras were recorded after 2, 4, 6, and 8 days.

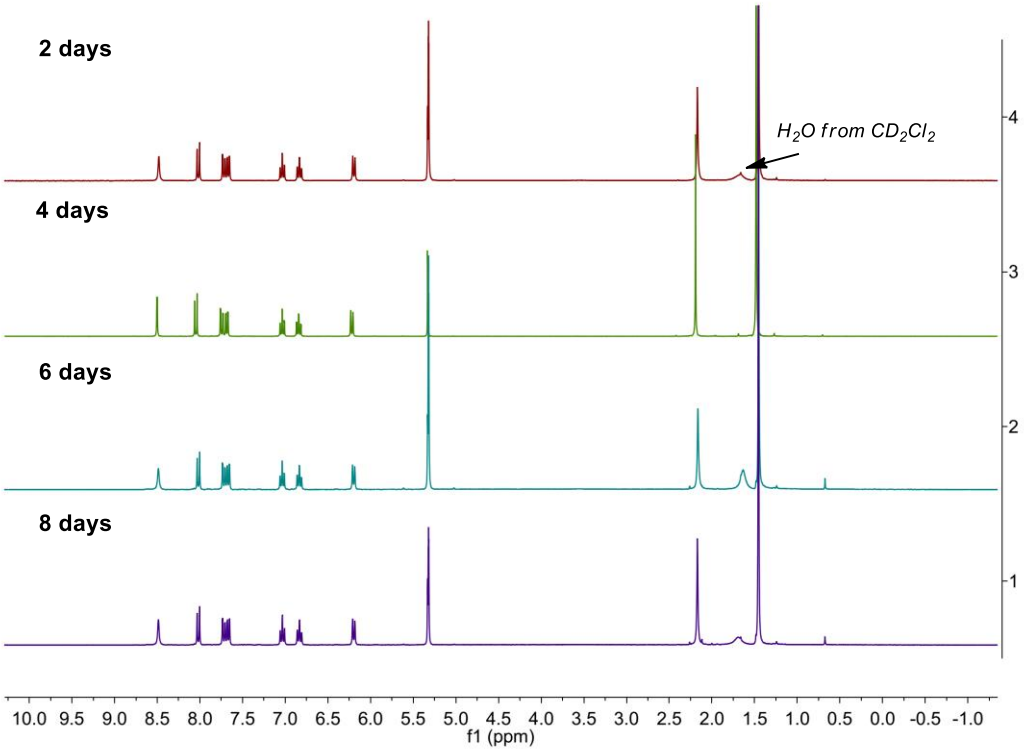


Figure S12. ^{1}H NMR of Λ-**RhS** recorded in CD_2Cl_2 over 8 days.

5.2. Catalyst Stability Investigated by HPLC on Chiral Stationary Phase

Enantiopure rhodium complex Λ-**RhS** (20.0 mg) was stored in a brown vial and kept on the bench at room temperature. The HPLC traces were collected after 2, 4, 6 and 8 days. HPLC conditions: Daicel Chiralpak IB (250 × 4.6 mm) column, the column temperature was 25 °C and UV-absorption was measured at 254 nm. Solvent A = 0.1% TFA, solvent B = MeCN with a linear gradient of 40% to 50% B in 180 min with a flow rate = 0.6 mL/min.

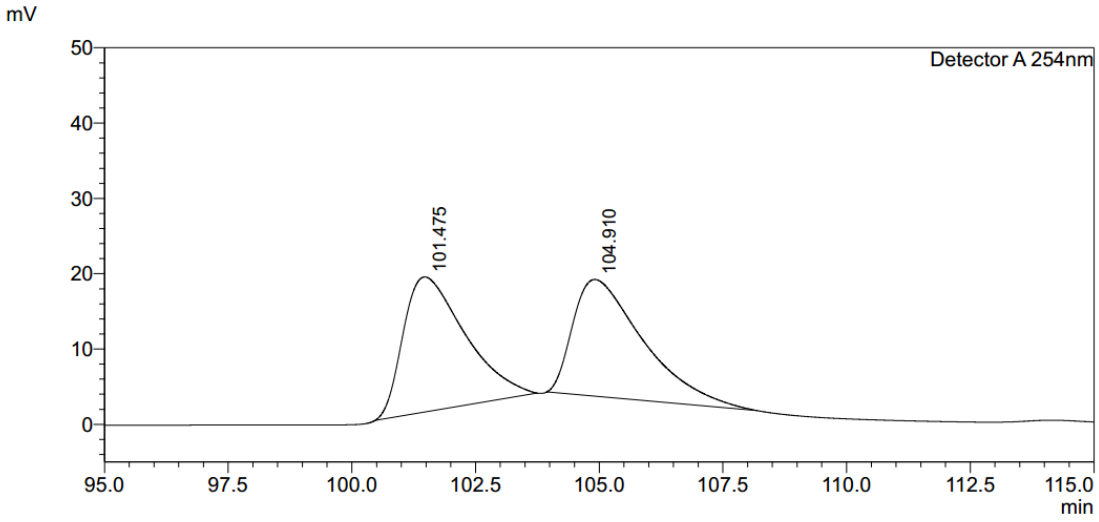
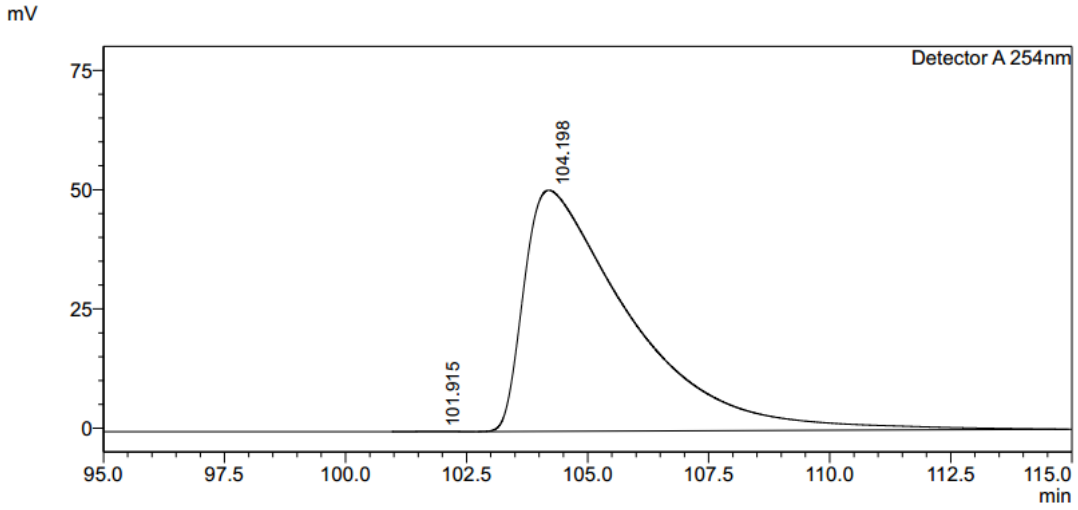


Figure S13. HPLC trace for the racemic reference complexes Δ/Λ-**RhS**. (Daicel Chiralpak IB, with a linear gradient of 40% to 50% B in 180 min, flow rate = 0. 6 mL/min), (the retention time changed compared with former when the HPLC conditions were reproduced).

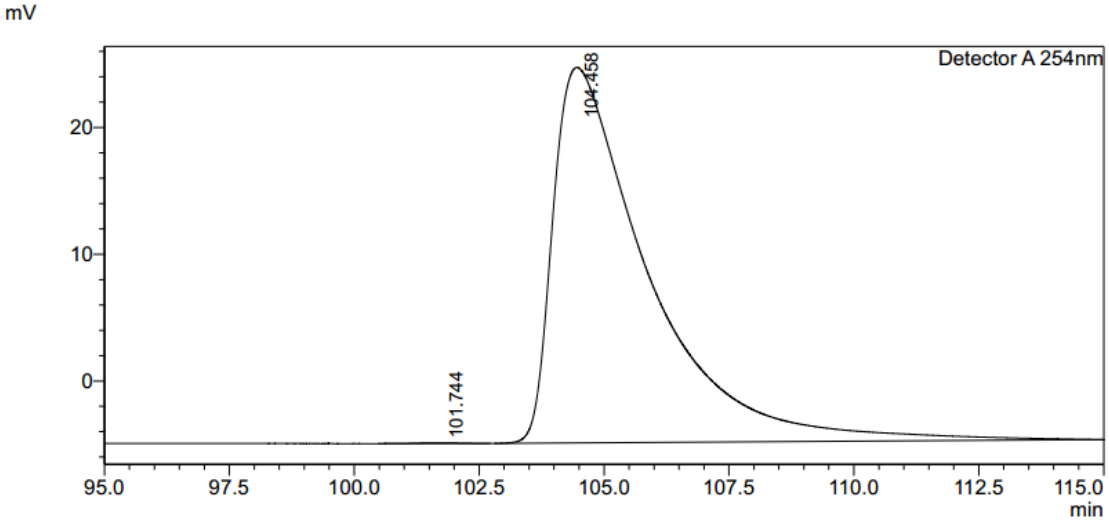


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	101.915	3119	0.040
2	104.198	7720649	99.960
Total		7723768	100.000

Figure S14. HPLC trace of the freshly prepared Λ-**RhS** (99.9% e.e.).

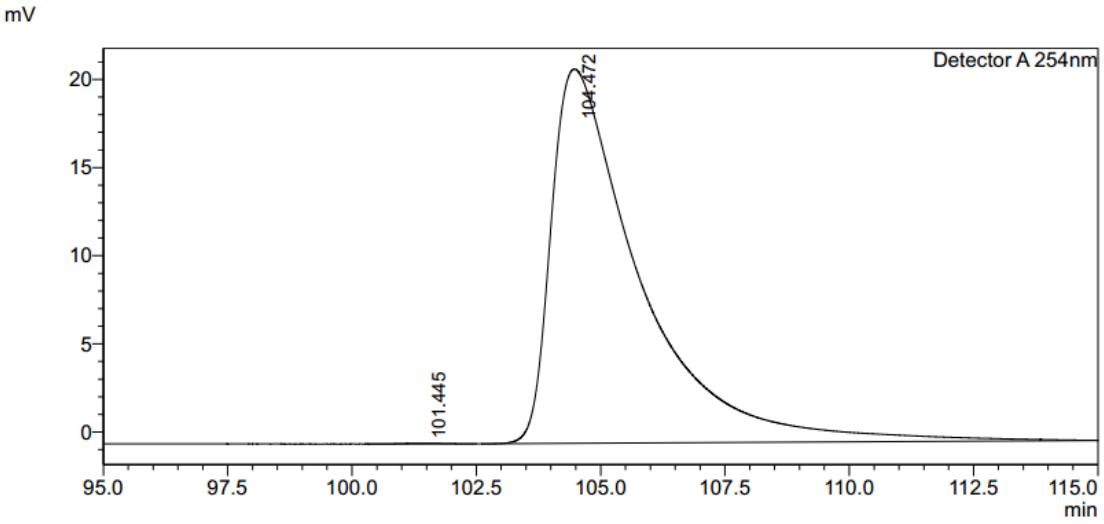


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	101.744	3485	0.088
2	104.458	3943796	99.912
Total		3947282	100.000

Figure S15. HPLC trace of the Λ-**RhS** after 2 days (99.8% e.e.).

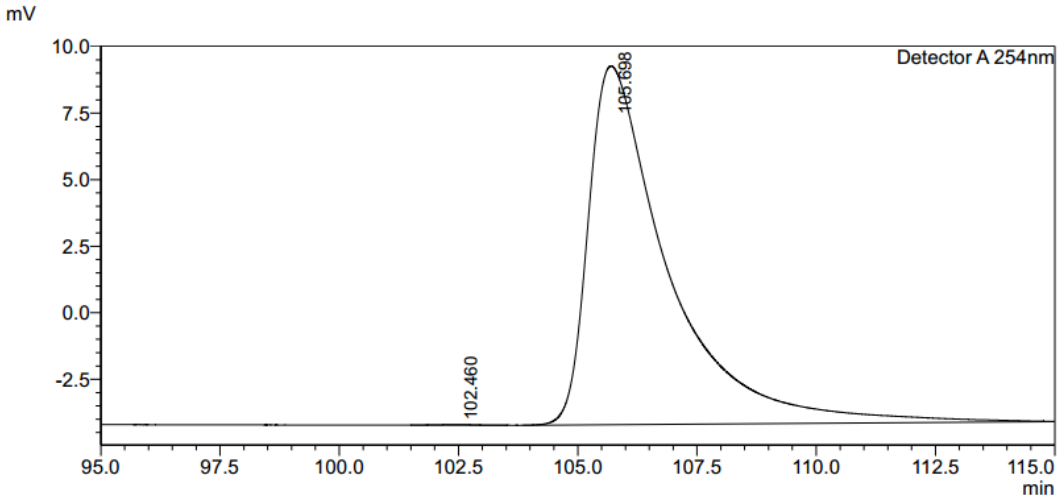


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	101.445	2766	0.104
2	104.472	2650355	99.896
Total		2653121	100.000

Figure S16. HPLC trace of the Λ-**RhS** after 4 days (99.8% e.e.).

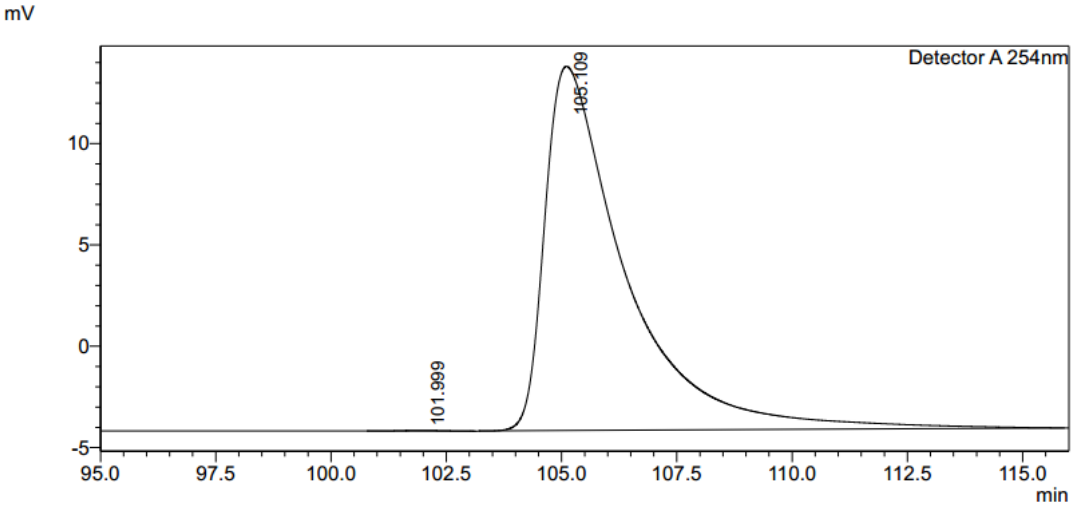


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	102.460	1399	0.089
2	105.698	1576676	99.911
Total		1578075	100.000

Figure S17. HPLC trace of the Λ-**RhS** after 6 days (99.8% e.e.).



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	101.999	2206	0.101
2	105.109	2191386	99.899
Total		2193592	100.000

Figure S18. HPLC trace of the Λ-**RhS** after 8 days (99.8% e.e.).

6. Single Crystal X-Ray Diffraction Studies

Crystals of Λ-(*S*)-**3** and Λ-**RhS** were obtained by slow diffusion from a solution of the compounds in CH_2Cl_2 layered with *n*-hexane at room temperature for several days.

Crystal data and details of the structure determination are presented in Table S1. X-ray data were collected with a Bruker 3 circuit D8 Quest diffractometer with MoKa radiation (microfocus tube with multilayer optics) and Photon 100 CMOS detector at 115 K. Scaling and absorption correction was performed by using the SADABS[4] software package of Bruker. Structures were solved using direct methods in SHELXS or SHELXT[5] and refined using the full matrix least squares procedure in SHELXL-2014[6]. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C atom, and Uiso(H) was set at 1.2 Ueq(Csp^2) and 1.5 Ueq(Csp^3). Disorder of PF_6 ions, solvent molecules or phenyl and *tert*-butyl groups was refined using restraints for both the geometry and the anisotropic displacement factors.

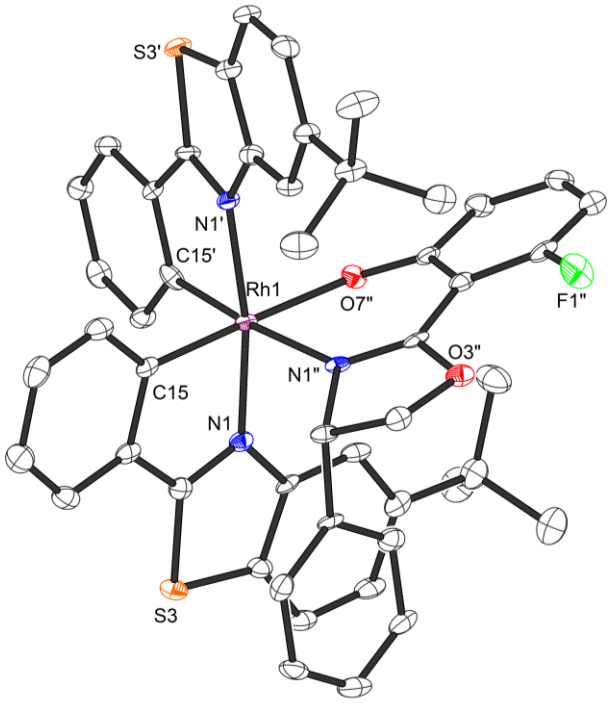


Figure S19. Crystal structure of Λ-(*S*)-**3**. ORTEP drawing with 50 % probability thermal ellipsoids.

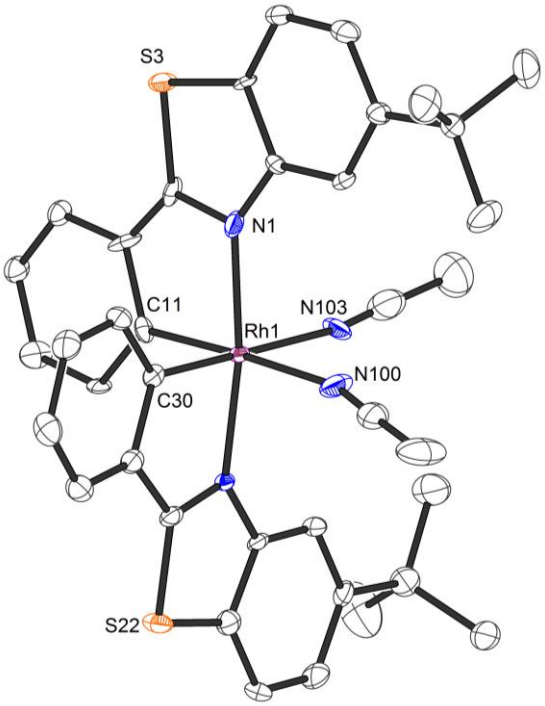


Figure S20. Crystal structure of Λ-**RhS**. The hexafluorophosphate counteranion and the solvent molecules are omitted for clarity. ORTEP drawing with 50 % probability thermal ellipsoids.

Table S1. Crystal data and details of the structure determination.

	Λ-(*S*)-**3**	Λ-**RhS**
Empiric formula	C_{49} H_{43} F N_3 O_2 Rh S_2	C_{40} H_{42} Cl_4 F_6 N_4 P Rh S_2
Formula weight	891.89	1032.57
Crystal system, space group	Monoclinic, $P2_1$	Triclinic, P1
a, *b*, *c* (Å)	9.9533(7), 13.4582(10), 12.1722(7)	12.3943(5), 13.2600(6), 14.1991(6)
α, β, γ (°)	90, 102.666(2), 90	102.772(2), 104.015(2), 90.825(2)
V (Å^3)	2068.3(3)	2202.41(16)
Z	2	2
μ (mm^{-1})	0.563	0.822
Crystal size (mm)	0.15 x 0.13 x 0.06	0.43 x 0.18 x 0.03
T_{min}, T_{max}	0.79, 0.97	0.77, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11397, 7003, 6335	87967, 15931, 15144
R_{int}	0.0335	0.0483
Goodness-of-fit on F^2	1.035	1.070
R index (all data)	wR2 = 0.0938	wR2 = 0.0915
R index conventional [I>2sigma(I)]	R1 = 0.0406	R1 = 0.0371
No. of reflections	7003	15931
No. of parameters	529	1133

No. of restraints	1	417
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.556, -0.668	2.017, -0.659
Absolute structure parameter	-0.02(2)	0.010(7)
CCDC	1455732	1455731

7. References

1) E. Marchi, R. Sinisi, G. Bergamini, M. Tragni, M. Monari, M. Bandini and P. Ceroni, *Chem. Eur. J.*, 2012, **18**, 8765–8773.
2) C. Wang, L.-A. Chen, H. Huo, X. Shen, K. Harms, L. Gong and E. Meggers, *Chem. Sci.*, 2015, **6**, 1094–1100.
3) X. Shen, K. Harms, M. Marsch and E. Meggers, submitted for publication.
4) *SADABS. Bruker AXS area detector scaling and absorption correction*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.
5) G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122.
6) G. M. Sheldrick, *SHELXT*, Universität Göttingen, Göttingen, Germany, 2014.