Supporting Information

trans-Diastereoselective Ru(II)-Catalyzed Asymmetric Transfer Hydrogenation of α-Aacetamido Benzocyclic Ketones via Dynamic Kinetic Resolution

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1 Materials and Methods

General. Reactions were conducted under an inert atmosphere using anhydrous solvents when required. Analytical thin layer chromatography (TLC) was performed on Silica Gel 60F254 plates. Flash column chromatography was performed using Silica Gel 60 (40–63 μm). Melting points were determined on a Kofler apparatus and are uncorrected. The enantiomeric excess (ee) of reduced products was determined by HPLC (Knauer UV detector K-2501) or by GC (Varian 3900 instrument) using chiral columns. 1H (299.9 MHz; internal MeSi) and 13C NMR (75.4 MHz; internal CDCl3, δ 77.00) spectra were recorded for solutions in CDCl3 if not stated otherwise. HRMS measurements were obtained on Agilent 6224 Accurate Mass TOF LC/MS System.

Catalysts. 3C-[Teth-(R,R)-TsDPEN-RuCl] (C1) and (R,R)-TsDENE® (C2) are commercially available (as their dichlorido Ru(II) dimers). 

Reagents. HCO3H/Et3N 3:2 was prepared by adding Et3N (280 mL, 2 mol) to HCO3H (113 mL, 3 mol).

2 Synthesis of Ru(II) Catalyst Active-C4

syn-(3R)-3-[(S)-α-[3-(Cyclohexa-1,4-dienyl)propyl]amino]benzyl]-1,1-dioxo-1,2-benzothiazolidine hydrochloride ruthenium(II) dichloride dimer (2). The above prepared preligand 1 (1.09 g, 2.76 mmol) was dissolved in absolute EtOH (83 mL), treated with 37% HCl (230 μL, 2.76 mmol, 1eq) and stirred at rt for 15 min. To the orange colored solution was added RuCl3·3H2O (656 mg, 2.51 mmol, 0.91 eq) in one portion then the mixture warmed to 65 °C under stirring. After stirring 2 h, the reaction mixture was concentrated and the residual water eliminated by coevaporation with toluene under
reduced pressure. The dark green solid gum was triturated with cold MeOH (10 mL), and the precipitate collected and washed with MeOH to obtain the title compound as a green powder (1.24 g, 75%).\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 9.63–9.29 (m, 2H, NH\(_2\)), 8.40 (s, 1H, NH), 7.90 (s, 1H, Ar-H, o- to SO\(_2\)), 7.70 (s, 1H, Ar-H), 7.60 (d, \(J = 7\) Hz, 1H, Ar-H), 7.49 (app t, \(J = 7\) Hz, 1H, Ar-H), 7.38 (d, \(J = 6\) Hz, 2H, Ar-H), 7.23–7.14 (m, 3H, Ar-H), 6.02 (s, 1H, Ru-Ar-H), 5.85–5.72 (m, 2H, Ru-Ar-H + CH), 5.67 (s, 1H, Ru-Ar-H), 5.65–5.56 (m, 1H, Ru-Ar-H), 5.39 (s, 1H, CH), 5.05 (s, 1H, Ru-Ar-H), 3.27–1.73 (6H, (CH\(_2\))\(_3\)). HRMS (ESI) calculated for C\(_{23}\)H\(_{23}\)N\(_2\)O\(_2\)RuS \([\text{M–Cl}]^+\) 493.0524, found 493.0517.

Note that this di-μ-chlorido Ru(II) dimer \(2\) is not stable on prolonged standing in DMSO; solvolysis and formation of crystalline RuCl\(_2\)(DMSO)\(_4\) occurs as determined by single-crystal X-ray diffraction analysis (single crystals grown from DMSO overlaying with Et\(_2\)O).

**ansa-RuCl\([\text{syn-(3R,1'S)}]\)-ULTAM-(CH\(_2\))\(_3\)Ph \((C4)\).**

![ansa-RuCl\([\text{syn-(3R,1'S)}]\)-ULTAM-(CH\(_2\))\(_3\)Ph \((C4)\)](image)

To a cold (0 °C) suspension of the above prepared, shelf-stable Ru(II)–Cl dimer \(2\) (54 mg, 89.8 µmol Ru atom) in CH\(_2\)Cl\(_2\) (1.3 mL) was added \(N, N\)-disopropylethylamine (92 µL, 0.53 mmol) and the mixture stirred at rt (23 °C) for 1 h. Water (10 mL) and CH\(_2\)Cl\(_2\) (10 mL) were added, and the organic layer was separated, dried (Na\(_2\)SO\(_4\)), filtered and concentrated. To the solid residue was added iPrOH, the undissolved material filtered off, and the filtrate concentrated and purified by column chromatography eluting with CH\(_2\)Cl\(_2\)/MeOH (20:1) to obtain the title compound as an orange solid (>95% pure by \(^1\)H NMR) (20 mg, 43%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.65 (d, \(J = 7.7\) Hz, 2H, Ar-H), 7.23–7.10 (m, 4H, Ar-H), 7.05 (app td, \(J = 7.5\) and 1.1 Hz, 2H, Ar-H), 6.80 (d, \(J = 7.6\) Hz, 1H, Ar-H), 6.65 (app t, \(J = 5.4\) Hz, 1H, Ru-Ar-H), 6.39 (app t, \(J = 5.5\) Hz, 1H, Ru-Ar-H), 5.97 (app t, \(J = 5.7\) Hz, 1H, Ru-Ar-H), 5.33 (d, \(J = 5.5\) Hz, 1H, Ru-Ar-H), 5.00–4.87 (m, 1H, NH), 4.73 (d, \(J = 4.8\) Hz, 1H, CH-NSO\(_2\)), 4.68 (d, \(J = 5.7\) Hz, 1H, Ru-Ar-H), 4.14–4.06 (m, 1H, CH-NH), 3.14–3.03 (m, 1H), 2.65–2.51 (m, 1H), 2.33–1.93 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.3, 137.9, 132.8, 132.1, 130.2, 129.1, 128.9, 127.9, 123.5, 120.6, 98.2, 90.9, 84.9, 82.1, 77.5, 76.0, 67.5, 66.1, 49.3, 30.4, 29.0. HRMS (ESI) calculated for C\(_{23}\)H\(_{23}\)N\(_2\)O\(_2\)RuS \([\text{M–Cl}]^+\) 493.0524, found 493.0519.

Its structure was determined by X-ray crystallography (a monocrystal in needle form grown from MeOH/CH\(_2\)Cl\(_2\)).
3 Synthesis of Keton Substrates S1–S10

2-Acetamido-indones S1–S5 were prepared according to the literature procedure.\(^3\) α-Acetamidoacetone is commercially available.

2-Acetamido-3-phenyl-1-indene (S6)

\[
\begin{align*}
\text{AcHN} & \quad \text{CO}_2\text{H} \\
\xrightarrow{\text{CICO}_2\text{Et}, \text{Et}_3\text{N}} & \quad \text{Me} \\
\text{Ph}_2\text{C} & \quad \text{H} \\
\xrightarrow{\text{NMe}} & \quad \text{NHAc}
\end{align*}
\]

**STEPS 1 and 2: Synthesis of 4-(diphenylmethylidene)-2-methylazol-5-one.** To a solution of N-acetylglucine (7.75 g, 66.2 mmol) and Et\(_3\)N (9.2 g, 66.5 mmol) in toluene (80 mL) was added ethyl chloroformate (6.3 mL, 66 mmol) dropwise over 50 min and the mixture left stirring at rt for 4 h. The reaction mixture was filtered directly into a solution of benzophenone imine (6.00 g, 33.1 mmol) in toluene (15 mL) and the resulting mixture was stirred at 50 °C for 2 days. After concentration, the residue was triturated with Et\(_2\)O/hexane 5:1 to afford a light yellow powder (3.84 g). The mother liquor was concentrated and the residue recrystallized from toluene/hexane to yield another crop of yellow crystals (1.03 g). Total yield: 4.87 g, 56% (ca 90% purity by \(^1\)H NMR). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.71–7.21\) (m, 10H), 2.35 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 165.6, 164.5, 150.1, 138.4, 136.6, 132.0, 130.3, 130.2, 130.0, 129.6, 128.1, 127.9, 15.5.

**STEP 3:** The above oxazolone (4.57 g, 17.4 mmol) was added portionwise to a suspension of AlCl\(_3\) (6.94 g, 52.1 mmol) in tetrachloroethylene (75 mL) and the mixture stirred at rt for 2 h. The green-colored mixture was poured onto ice (150 mL) and the product extracted with CH\(_2\)Cl\(_2\) (2×30 mL). The combined organic layers were washed with saturated NaHCO\(_3\)(aq), dried (Na\(_2\)SO\(_4\)) and concentrated to dryness. All the solvents were removed, and some toluene was added and the resulting orange precipitate collected by filtration (3.78 g, 83% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.56 – 7.41\) (m, 6H), 7.32 (app dd, \(J = 7.7\) and 1.1 Hz, 1H), 7.19 (app t, \(J = 7.3\) Hz, 1H), 7.12 (d, \(J = 7.2\) Hz, 1H), 6.98 (s, 1H), 2.05 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 193.2, 167.9, 144.7, 133.9, 132.5, 129.3, 128.5, 128.4, 128.2, 127.7, 127.5, 123.0, 121.4, 23.2.

**rac-2-Acetamido-1-acenaphthenone (rac-S7)**

\[
\begin{align*}
\text{NH}_2\text{OH} & \quad \text{HCl} \\
\xrightarrow{\text{Na}_2\text{CO}_3} & \quad \text{EtOH, reflux} \\
\text{Pd/C, H}_2, \text{Ac}_2\text{O} & \quad \text{THF, 25 °C} \\
\text{C}_1\text{H}_5\text{H}_5\text{O}_2 & \quad \text{fw 225.24}
\end{align*}
\]

**STEP 1. Synthesis of acenaphthoquinone mono-oxide.** A suspension of acenaphthoquinone (9.11 g, 50 mmol), hydroxylamine hydrochloride (3.47 g, 50 mmol) and anhydrous Na\(_2\)CO\(_3\) (5.30 g, 50 mmol) in 96% ethanol was heated at reflux for 45 min then cooled to rt. The precipitate was filtered, washed with water, and dried under vacuo over P\(_2\)O\(_5\) to afford a fine brown powder (7.13 g, 72% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)+drop DMSO-d\(_6\)) \(\delta 8.43\) (dd, \(J = 7.0\) and 0.5 Hz, 1H), 8.14 (dd, \(J = 8.2\) and 0.5 Hz, 1H), 8.06–7.96 (m, 2H), 7.78–7.67 (m, 2H). NMR data is in accordance with the literature.\(^4\)

**STEP 2.** A mixture of the above oxime (5.00 g, 25.4 mmol), Ac\(_2\)O (15.0 mL) and 10% Pd/C (250 mg) in THF (25 mL) was hydrogenated (40 psi H\(_2\)) for 3 h, then filtered through Celite\textsuperscript{TM} and concentrated. The title compound was obtained after trituration with Et\(_2\)O as white crystals (4.98 g, 87% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.14\) (d, \(J = 8.1\) Hz, 1H), 7.99 (d, \(J = 7.0\) Hz, 1H), 7.92−7.84 (m, 1H), 7.74 (dd, \(J = 8.0\) and 7.2 Hz, 1H), 7.68−7.61 (m, 2H), 6.12 (d, \(J = 7.5\) Hz, 1H), 5.75 (d, \(J = 7.5\) Hz, 1H), 2.15 (s, 3H). NMR data is in accordance with the literature.\(^5\)

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**rac-2-Acetamido-1-tetralone (rac-S8)**

**STEP 1: Synthesis of 2-hydroxylimino-1-tetralone.** To a suspension of KOtBu (5.39 g, 48.0 mmol) in Et₂O (50 mL), were added tBuOH (50 mL) and isoamyl nitrite (7.0 mL, 52 mmol), then 1-tetralone (5.85 g, 40.0 mmol) dropwise over 30 min. The resulting brown suspension was stirred at rt for 4 h and the precipitate filtered. This potassium salt of the oxime was added to cold (0 °C) 1M HCl (100 mL). The neutralized product was extracted with CH₂Cl₂ (100 mL), dried (MgSO₄), and concentrated to afford an oil. After recrystallization from EtOAc, green-tinted crystals were obtained (3.34 g, 50% yield). ¹H NMR (300 MHz, CDCl₃) δ 10.51 (br s, 1H), 8.12 (dd, J = 7.8 and 1.2 Hz, 1H), 7.54 (app td, J = 7.5 and 1.4 Hz, 1H), 7.38 (ddd, J = 7.8, 1.1 and 0.6 Hz, 1H), 7.33–7.27 (m, 1H), 3.19 (ddd, J = 7.1, 6.0 and 1.2 Hz, 2H), 3.11–3.04 (m, 2H). NMR data is in accordance with the literature.⁶

**STEP 2:** To the above oxime (3.34 g, 19 mmol) were successively added AcOH (30 mL), Ac₂O (23 mL) and Zn powder (3.73 g, 57 mmol). The resulting slurry was stirred at rt for 30 h, then the mixture was filtered through Celite™ and concentrated on Kugel-Rohr. The oil was recrystallized from EtOAc to yield the title compound as white crystals (1.57 g, 41% yield). Mp 123 °C (lit: 123–124 °C); ¹H NMR (300 MHz, CDCl₃) δ 8.01 (dd, J = 7.8 and 1.2 Hz, 1H), 7.52 (td, J = 7.5 and 1.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 7.7 Hz, 1H), 6.65 (s, 1H), 4.65 (dt, J = 13.5 and 5.0 Hz, 1H), 3.28 (ddd, J = 17.4, 12.9 and 4.6 Hz, 1H), 3.00 (ddd, J = 17.3, 4.3 and 2.4 Hz, 1H), 2.81 (ddd, J = 12.4, 4.6 and 2.4 Hz, 1H), 2.09 (s, 3H), 1.89 (ddd, J = 26.2, 12.9 and 4.5 Hz, 1H).

**rac-6-Methoxy-2-acetamido-1-tetralone (rac-S9)**

**STEP 1: Synthesis of 2-hydroxylimino-6-methoxy-1-tetralone.** A solution of 6-methoxy-1-tetralone (7.05 g, 40.0 mmol) in tBuOH (25 mL) and Et₂O (25 mL) was added via cannula during 30 min to a mixture of KOtBu (5.39 g, 48 mmol), tBuOH (25 mL), Et₂O (25 mL) and isoamyl nitrite (7.0 mL, 52 mmol), then the mixture stirred at rt for additional 3.5 h. The precipitate was collected and washed with Et₂O to afford a purple powder (potassium salt of the oxime). This salt was added portionwise to cold (0 °C) 1 M HCl(aq) (150 mL), and the precipitate collected and air-dried overnight to obtain a grey-tinted powder (7.49 g, 91% for 2 steps). ¹H NMR displayed the mono-oxime as a 9:1 isomeric mixture. The major isomer: ¹H NMR (300 MHz, CDCl₃) δ 8.10 (d, J = 8.7 Hz, 1H), 6.89 (dd, J = 8.7, 2.5 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H), 3.89 (s, 3H), 3.18–3.11 (m, 2H), 3.07–2.99 (m, 2H). NMR data is in accordance with the literature.⁸

**STEP 2:** A suspension of the above oxime (3.70 g, 18.0 mmol) and 10% Pd/C (185 mg) in Ac₂O (10 mL) and THF (20 mL) was hydrogenated (30 psi of H₂) until the consumption of hydrogen ceased (2 h). The reaction mixture was filtered through Celite™ and concentrated on Kugel-Rohr. The oil was recrystallized from EtOAc to yield the title compound as white crystals (1.47 g, 35% yield). ¹H NMR (303 MHz, CDCl₃) δ 7.99 (d, J = 8.8 Hz, 1H), 6.85 (dd, J = 8.8, 2.3 Hz, 1H), 6.71 (d, J = 2.2 Hz, 2H), 6.68 – 6.59 (m, 2H), 4.57 (dt, J = 13.4, 4.9 Hz, 1H), 3.87 (s, 3H), 3.24 (ddd, J = 17.4, 13.0, 4.6 Hz, 1H), 2.95 (ddd, J = 17.2, 4.4, 2.5 Hz, 1H), 2.80 (ddt, J = 12.0, 4.6, 2.5 Hz, 1H), 1.85 (app qd, J = 13.0, 4.4 Hz, 1H). NMR data is in accordance with the literature.⁹

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**rac-2-Phthalimido-1-Indanone** (*rac*-S10). A slurry of 2-phthalimido-3-phenylpropanoic acid\(^{10}\) (8.95 g, 30.3 mmol), \(\text{CH}_2\text{Cl}_2\) (50 mL), pyridine (50 µL) and \(\text{SOCl}_2\) (2.3 mL, 31.8 mmol) was stirred at 50 °C for 1.5 h. The resulting solution was cooled to rt, diluted with tetrachloroethylene (30 mL), and treated portionwise with \(\text{AlCl}_3\) (8.08 g, 60.6 mmol). After heating at 70 °C for 3 h, then at rt overnight, the reaction mixture was poured onto ice-water (300 mL), and the product extracted with \(\text{CH}_2\text{Cl}_2\) (2x 100 mL). The combined organic layers were dried (\(\text{MgSO}_4\)) and filtered through a pad of silica gel (50 g) eluting with \(\text{CH}_2\text{Cl}_2\). After partial concentration, hexane was added and the white precipitate collected (3.18 g, 38%); mp 191–192 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.90–7.65 (m, 6H), 7.55–7.41 (m, 2H), 5.10 (dd, \(J = 8.5\) and 5.8 Hz, 1H), 3.61 (dd, \(J = 16.5\) and 8.5 Hz, 1H), 3.43 (dd, \(J = 16.5\) and 5.8 Hz, 1H). NMR data is in accordance with the literature.\(^{11}\)

### 4 ATH of 1-Indanone and α-Tetralone

**(*R*)-1-Indanol.** To a solution of active \(\text{ansa-RuH}\{\text{syn-}(3R,1'S)\text{-ULTAM}\}(\text{CH}_3)_2\text{Ph}\) cat. (active-C4) (1.0 \(\mu\)mol), prepared from the corresponding \(\mu\)-chlorido Ru(II) dimer 2 (0.601 mg) in HCO\(_2\)H/\(\text{Et}_3\text{N}\) 3:2 (0.50 mL), was added 1-indanone (132 mg, 1.0 mmol). The reaction was stirred at 60 °C for 4.5 h (full conversion by TLC) with gentle N\(_2\) sweeping then it was partitioned between EtOAc and water, the organic layer dried (\(\text{Na}_2\text{SO}_4\)), filtered through a short plug of silica gel and concentrated to afford the title compound in quantitative yield as a thick oil which solidified upon standing; 98% ee. Ee was determined by chiral HPLC analysis on Chiralcel OD column (25 cm); eluent hexane/2-PrOH 98:2, flow rate 1 mL/min, \(\lambda = 254\) nm, \(t_R\): 22.3 min (S), 26.0 min (R).

**(*R*)-1-Tetralol.** Prepared from α-tetralone (146 mg, 1.0 mmol) following a similar procedure as for 1-indanol; 98% ee. Ee was determined by chiral GC analysis on CP-Chirasil-Dex CB column (25 m); 130 °C, \(t_R\): 11.3 min (S), 11.4 min (R).

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\(^{10}\) Prepared from \(\text{rac}\)-phenylalanine and phthalic anhydride.

\(^{11}\) (a) Takemura, S.; Matsumoto, Y.; Terauchi, H.; Miki, Y. *Yakugaku Zasshi* 1979, 99, 1111–1115. (b) Rouf, A.; Gupta, P.; Aga, M. A.; Kumar, B.; Parshad, R.; Taneja, S. C. *Tetrahedron: Asymmetry* 2011, 22, 2134–2143.
5 AT$_{H}$ of $\alpha$-Acetamido Benzocyclic Ketones S1–S10

(1S,2S)-2-Acetamido-1-indanone (P1). To a solution of the Ru(II)–H cat. active-C4 (2.0 μmol), prepared from the corresponding $\mu$-chlorido Ru(II) dimer 2 (1.20 mg, 1 μmol) in HCO$_2$H/Et$_3$N 3:2 (0.50 mL) was added 2-acetamido-1-indenone (S1) (187 mg, 1.0 mmol) and chlorobenzene (1.3 mL). The reaction mixture was stirred at 60 °C for 3 h with continuous mild N$_2$ sweeping. An aliquot of the reaction mixture was diluted with CDCl$_3$ and analyzed by $^1$H NMR (300 MHz, CDCl$_3$) revealing 100% conversion and trans/cis = 91:9; diagnostic peaks: 4.62 (ddd, $J = 14.5, 7.2$ and 5.6 Hz, 1H, cis-P1), 4.30–4.19 (m, 1H, trans-P1). For ee determination (>99.5%), an aliquot of the reaction mixture was dried under high vacuum and analyzed by chiral HPLC (see below). The reaction mixture was concentrated and the solid residue was triturated with cold CH$_2$CN to yield the pure P1 as white crystals; dr $>$99:1, >99% ee. (159 mg, 83% yield). $^1$H NMR (303 MHz, CD$_2$OD) δ 7.40–7.31 (m, 1H), 7.29–7.15 (m, 3H), 4.98 (d, $J = 6.4$ Hz, 1H), 4.30 (app td, $J = 7.9$ and 6.6 Hz, 1H), 3.37–3.23 (m, 1H), 2.69 (dd, $J = 15.6$ and 7.9 Hz, 1H), 1.99 (s, 3H). NMR data is in accordance with the literature.\textsuperscript{12}

Ee was determined by chiral HPLC analysis on Chiralcel OJ-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, $t_b$: 15.1 min (1S,2R), 16.5 min (1R,2S), 17.9 min (1R,2R), 41.3 min (1S,2S; major). The absolute configuration was assigned by comparing the HPLC retention times with the literature data.\textsuperscript{12}

Note that the intermediary 2-acetamido-1-indanone (S1') is racemic. This product was isolated carrying out the same reaction as above at 50 °C for 3 h (S1.S1':P1 = 2:90:8 by $^1$H NMR (CDCl$_3$); characteristic peak for S1' is 2.09 ppm (s, 3H). Workup: The mixture was partitioned between water (10 mL) and EtOAc (10 mL), and the organic layer concentrated to yield a colorless oil; racemic by chiral HPLC analysis: Chiralpak IA column (25 cm), eluent hexane/2-PrOH 90:10, flow rate 1 mL/min, λ = 254 nm, $t_b$: 24.1 min and 26.1 min.

(1S,2S)-2-Acetamido-4-methyl-1-indanone (P2). Prepared from S2 (201 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: dr = 93:7 by $^1$H NMR (300 MHz, CDCl$_3$), diagnostic peaks δ 4.62–4.52 (m, 1H; cis-P2), 4.23 (tdd, $J = 8.7, 6.7$ and 4.8 Hz, 1H; trans-P2); >99.9% ee by HPLC. Stereopure product as white powder was obtained after trituration with MeCN (164 mg, 80% yield); dr $>$99:1, >99.9% ee. $^1$H NMR (303 MHz, CD$_2$OD) δ 7.26–7.02 (m, 3H), 4.96 (d, $J = 6.3$ Hz, 1H), 4.29 (td, $J = 7.5$ and 6.3 Hz, 1H), 3.41–3.21 (m, 1H), 2.57 (dd, $J = 15.8$ and 7.5 Hz, 1H), 2.24 (s, 3H), 1.98 (s, 3H). NMR data is in accordance with the literature.\textsuperscript{12}

Ee was determined by chiral HPLC analysis on Chiralcel OD-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, $t_b$: 20.2 min (S,S), 36.1 min (R,R). The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

(1S,2S)-2-Acetamido-4-bromo-1-indanone (P3). Prepared from S3 (266 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: dr = 87:13 by $^1$H NMR (300 MHz, CDCl$_3$); diagnostic peaks: δ 4.66–4.53 (m, 1H; cis-P3), 4.23 (tdd, $J = 8.9, 6.9$ and 4.7 Hz, 2H; trans-P3), 99.8% ee by HPLC. After trituration with MeCN, stereopure product was obtained as a white powder (213 mg, 79% yield); dr $>$99:1, >99.9% ee. $^1$H NMR (300 MHz, CD$_2$OD) δ 7.43 (dt, $J = 8.0$ and 0.9 Hz, 1H), 7.38–7.28 (m, 1H), 7.24–7.11 (m, 1H), 5.03 (d, $J = 6.5$ Hz, 1H), 4.30 (td, $J = 7.8$ and 6.5 Hz, 1H), 3.41–3.29 (m, 1H), 2.66 (dd, $J = 16.3$ and 7.6 Hz, 1H), 1.99 (s, 3H). NMR data is in accordance with the literature.\textsuperscript{12}

\textsuperscript{12} Hu, Q.; Chen, J.; Zhang, Z.; Liu, Y.; Zhang, W. Org. Lett. 2016, 18, 1290–1293.
Ee was determined by chiral HPLC analysis on Chiralpak AD-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, tR: 17.8 min (R), 27.8 min (S). The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

(1S,2S)-2-Acetamido-6-methyl-1-indanol (P4). Prepared from S4 (201 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: dr = 92:8 by 1H NMR (300 MHz, CDCl3); diagnostic peaks: δ 4.57 (dd, J = 14.2, 7.1 and 5.9 Hz, 1H; cis-P4), 4.27–4.15 (m, 1H; trans-P4); 99.9% ee by HPLC. Stereopure product as white powder was obtained after trituration with MeCN (168 mg, 82% yield); dr >99:1, >99.9% ee. 1H NMR (300 MHz, CD2OD) δ 7.16 (s, 1H), 7.12–7.00 (m, 2H), 4.93 (d, J = 6.5 Hz, 1H), 4.28 (td, J = 7.9 and 6.5 Hz, 1H), 3.24 (dd, J = 15.5 and 7.9 Hz, 1H), 2.62 (dd, J = 15.5 and 7.9 Hz, 1H), 2.32 (s, 3H), 1.98 (s, 3H). NMR data is in accordance with the literature.12

Ee was determined by chiral HPLC analysis on Chiralcel OD-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, tR: 21.5 min (S), 30.9 min (R). The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

(1S,2S)-2-Acetamido-6-fluoro-1-indanol (PS). Prepared from S5 (205 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: dr = 87:13 by 1H NMR (300 MHz, CDCl3), diagnostic peaks: δ 4.66–4.54 (m, 1H; cis-PS), 4.30–4.16 (m, 1H; trans-PS), 99.6% ee by HPLC. After trituration with MeCN, stereopure product was obtained as white powder (167 mg, 80% yield); dr >99:1, >99.9% ee. 1H NMR (300 MHz, CD2OD) δ 7.19 (ddq, J = 8.2, 4.6 and 0.7 Hz, 1H), 7.07–7.01 (m, 1H), 6.96 (dd, J = 9.2, 8.2, 2.6 and 0.8 Hz, 1H), 4.96 (d, J = 6.8 Hz, 1H), 4.31 (app td, J = 8.1 and 6.8 Hz, 1H), 3.25 (dd, J = 15.6 and 7.9 Hz, 2H), 2.64 (dd, J = 15.4 and 8.3 Hz, 1H), 1.99 (s, 3H). NMR data is in accordance with the literature.12

Ee was determined by chiral HPLC analysis on Chiralpak AD-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, tR: 16.0 min (R,R), 22.9 min (S,S). The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

(1S,2S,3R)-2-Acetamido-3-phenyl-1-indanol (P6). Prepared from S6 (263 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: dr = 81:3:4:12 by 1H NMR (300 MHz, DMSO-d6), diagnostic peaks: δ 5.67 (d, J = 6.6 Hz, 1H), 5.58 (d, J = 5.1 Hz, 1H), 5.55 (d, J = 7.2 Hz, 1H), 5.31 (d, J = 4.7 Hz, 1H); >99% ee. After crystallization from EtOAc, stereopure product was obtained (152 mg, 57% yield); >99.5% ee, dr >99:1. 1H NMR (300 MHz, DMSO-d6) δ 8.26 (d, J = 8.0 Hz, 1H), 7.40–7.13 (m, 8H), 6.72 (d, J = 7.4 Hz, 1H), 5.67 (s, 1H), 4.97 (d, J = 7.1 Hz, 1H), 4.27–4.08 (m, 2H), 1.80 (s, 3H). 13C NMR (75 MHz, DMSO-d6) δ 169.3, 143.6, 142.1, 141.6, 128.4, 127.7, 127.0, 126.6, 124.0, 123.7, 76.9, 67.6, 52.1, 22.9.

Ee was determined by chiral HPLC analysis on Chiralpak OJ-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 240 nm, tR: 11.9 min [[1S,2S,3R]-P6], 15.6 min [[1R,2R,3S]-P6]. The absolute configuration was determined by X-ray analysis (monocrystal grown from MeOH/EtOAc).

(1S,2S)-2-Acetamido-1-acenaphthlen (P7). Prepared from S7 (263 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: >98% ee; dr = 84:16 by 1H NMR (300 MHz, CDCl3); diagnostic peaks: δ 2.14 (s, 3H), 2.12 (s, 3H). After trituration with MeCN, stereopure product was isolated as a 1:1 solvate with formic acid (186 mg, 68% yield); dr >99:1, >99% ee. 1H NMR (300 MHz, DMSO-d6) δ 8.59 (d, J = 8.2 Hz, 1H), 8.51 (s, 1H, HCO2H), 7.77 (t, J = 7.8 Hz, 2H), 7.63–7.43 (m, 3H), 7.29 (d, J = 6.9 Hz, 1H), 6.03 (s, 1H), 5.41 (dd, J = 8.2 and 3 Hz, 1H), 5.31 (d, J = 2 Hz, 1H), 1.93 (s, 3H). 13C NMR (75 MHz, DMSO-d6) δ 169.3, 165.9 (HCO2H), 144.1, 142.5, 135.5, 130.3, 128.2, 123.9, 123.6, 120.0, 119.5, 80.1, 62.2, 22.7.
Ee was determined by chiral HPLC analysis on Chiralcel OJ-H column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, ts: 16.9 min (S,R)-P7, 40.5 min (R,R)-P7, 56.1 min (S,S)-P7, 66.2 min (R,S)-P7.

The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

**cis-**15,2S)-2-Acetamido-1-tetralol (P8). Prepared from rac-S8 (203 mg, 1.0 mmol) following a similar procedure as for P1. Crude product: dr = 79:21 by 1H NMR (300 MHz, CDCl3); diagnostic peaks: δ 4.69 (d, J = 3.6 Hz, 1H; cis-P8), 4.63 (d, J = 8.2 Hz, 1H, trans-P8); 99.9% ee (HPLC). After recrystallization from MeCN, stereopure product was isolated as white thin needles (102 g, 50% yield); dr > 99:1; >99% ee. 1H NMR (300 MHz, CDCl3) δ 7.60–7.73 (m, 1H), 7.30–7.17 (m, 2H), 7.13–7.06 (m, 1H), 5.65 (s, 1H), 4.60 (dd, J = 7.6 and 5.0 Hz, 1H), 4.16–4.04 (m, 1H), 3.65 (d, J = 5.1 Hz, 1H), 3.00 (ddd, J = 16.3, 10.4, and 5.6 Hz, 1H), 2.84 (dt, J = 17.1 and 5.0 Hz, 1H), 2.20–2.10 (m, 1H), 2.06 (s, 3H), 1.80 (dtd, J = 12.9, 10.6, and 5.6 Hz, 1H). NMR data is in accordance with the literature data for the racemic compound.13

Ee was determined by chiral HPLC analysis on Chiralpak IA column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, ts: 18.0 min (R,R), 34.9 min (S,S).

The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

**cis-**15,2S)-2-Acetamido-6-methoxy-1-tetralol (P9). Prepared from rac-S9 (117 mg, 0.5 mmol) following a similar procedure as for P1. Crude product: dr = 77:23 by 1H NMR (300 MHz, CDCl3); diagnostic peaks: δ 4.19–4.08 (m, 1H; cis-P9), 4.02 (ddt, J = 14.2, 7.3, and 3.3, 1H; trans-P9); 99.9% ee (HPLC). Stereopure compound was obtained after trituration with MeCN (104 mg, 44% yield); dr > 99:1 (by 1H NMR), >99% ee. Mp 159–160 °C (lit14 158–160 °C). 1H NMR (300 MHz, CD3OD) δ 7.36 (d, J = 8.5 Hz, 1H), 6.77 (dd, J = 8.5 and 2.6 Hz, 1H), 6.64 (d, J = 2.6 Hz, 1H), 4.48 (d, J = 7.3 Hz, 1H), 4.00 (dd, J = 10.4, 7.4, and 3.3 Hz, 1H), 3.75 (s, 3H), 3.30 (app d, J = 1.7 Hz, 2H), 2.98–2.72 (m, 2H), 2.09 (dd, J = 13.1, 5.6 and 3.3 Hz, 1H), 1.97 (s, 3H), 1.75 (ddt, J = 13.2, 9.2 and 5.9 Hz, 1H).13 C NMR (75 MHz, CD3OD) δ 173.4, 160.4, 138.6, 131.0, 130.9, 113.7, 113.6, 72.2, 55.6, 54.0, 28.3, 27.2, 22.8.

Ee was determined by chiral HPLC analysis on Chiralpak IA column (25 cm); eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm, ts: 34.5 min (R,R), 55.7 min (S,S).

The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

**cis-**(15,2R)-2-Phthalimido-1-indanol (P10).15 Prepared from racemic 2-phthalimido-1-indanone (rac-S10) (139 mg, 0.5 mol) following a similar procedure as for S1.

The reaction was carried out using:

(a) ansa-Ru(II)–H cat. active-C4 of syn-(3R,1’S)-ULTAM ligand: cis/trans = 97:3; 94% ee (cis), 13% ee (trans). Recrystallization from EtOAc afforded stereopure cis-(15,2R)-P10 (103 g, 74% yield); or (b) ansa-Ru[(R,R)-PipSO2DENP-(CH2)]Ph (active-C3): cis/trans = 97:3; 98% ee (cis), 8% ee (trans). Recrystallization from EtOAc afforded stereopure cis-(15,2R)-P10 (113 g, 81% yield); mp 201–202 °C (lit16 201.5–202.5 °C). 1H NMR (300 MHz, CDCl3) δ 7.92–7.80 (m, 2H), 7.79–7.67 (m, 2H), 7.56–7.46 (m, 1H), 7.42–7.24 (m, 3H), 5.23–5.06 (m, 2H), 4.02 (dd, J = 16.1 and 8.3 Hz, 1H), 3.18 (dd, J = 16.1 and 8.6 Hz, 1H), 2.52 (d, J = 10.4 Hz, 1H).

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(13) Hirata, Y.; Yanagisawa, I.; Mase, T.; Kubo, K.; Takahashi, K.; Murakami, M. J. Pharm. Soc. Jpn. 1977, 97, 1091–1100.
(14) Chiemprasert, T.; Riemek, H. J.; Zymalkowski, F. Liebig’s Ann. 1965, 685, 141–148.
(15) For the preparation of stereopure trans-(−)-2-phthalimido-1-indanol via lipase-catalyzed kinetic resolution of the racemic trans-alcohol, see ref 11b.
(16) Dornhege, E. Liebig’s Ann. Chem. 1971, 743, 42–49.
Ee was determined by chiral HPLC analysis on Chiralpak IA column (25 cm); eluent hexane/2-PrOH 80:20, flow rate 1 mL/min, λ = 220 nm, \( t_R \): 15.6 min (1S,2R), 17.3 min (1R,2S), 18.5 min (trans), 23.4 min (ent-trans).

The absolute configuration was assigned on the basis of the generally observed trend of enantioselectivity.

cis-(1S,2R)-β-amino-1-indanol. To a suspension of cis-(1S,2R)-P10 (70 mg, 0.25 mmol) in EtOH (1 mL)/H₂O (1 mL) was added hydrazine hydrate (30 μL, 0.75 mmol), then stirred at 60 °C for 2 h to obtain complete deprotection. The mixture was partitioned between EtOAc (5 mL) and brine (2 mL), and the organic layer dried (Na₂SO₄) and concentrated affording a pure title compound (31 mg, 84% yield). \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 7.50–7.39 (m, 1H), 7.30–7.17 (m, 3H), 4.86 (d, \( J = 5.4 \) Hz, 1H), 3.80–3.66 (m, 1H), 3.13 (dd, \( J = 15.7, 6.5 \) Hz, 1H), 2.77 (dd, \( J = 15.7, 5.0 \) Hz, 1H).

Enantioenriched 1-acetamido-2-propanol. Prepared from α-acetamidoacetone (25 mg, 0.22 mmol) following a similar procedure as for 1-indanone (S/C = 1000). After complete conversion (1 h), the volatiles were removed under high vacuo to afford >95% pure product by \(^1\)H NMR. \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 5.92 (br s, 1H), 3.93 (dqd, \( J = 12.8, 6.4, \) and 3.0 Hz, 1H), 3.45 (ddd, \( J = 14.0, 6.6, \) and 3.0 Hz, 1H), 3.11 (ddd, \( J = 14.0, 7.7, \) and 5.2 Hz, 1H), 2.46 (br s, 1H), 2.02 (s, 3H), 1.20 (d, \( J = 6.0 \) Hz, 3H). NMR data is in accordance with the literature.\(^{17}\) Enrac = 85:15 was determined by \(^1\)H NMR in the presence of 30 mol% Eu(hfc)₃. Diagnostic peaks in \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 2.25 (d, \( J = 6.5 \) Hz, 1H; major), 2.22 (d, \( J = 6.0 \) Hz, 1H; minor).

\(^{17}\) Satam, J. R.; Gawande, M. B.; Deshpande, S. S.; Jayaram, R. V. Synth. Commun. 2007, 37, 3011–3020.
6 HPLC and GC Chromatograms

1-Indanol. HPLC: Chiralcel OD column (25 cm), eluent hexane/2-PrOH 98:2, flow rate 1 mL/min, λ = 254 nm. Conditions adopted from ref 1.

Crude ATH product using RuH[(3R,1’S)-ULTAM-(CH₂)₃Ph] (active-C4):

![HPLC Chromatogram](image)

| Peak ID       | Retention Time | Area    | Area % | Height | Height % |
|---------------|----------------|---------|--------|--------|----------|
| (S)-enantiomer| 22.333         | 4040    | 0.77   | 109    | 1.05     |
| (R)-enantiomer| 25.967         | 522482  | 99.23  | 10276  | 98.95    |

1-Tetralol. GC: CP-Chirasil-Dex CB column (25 m), 130 °C. Conditions adopted from ref 1.

Crude ATH product using RuH[(3R, 1’S)-ULTAM-(CH₂)₃Ph] (active-C4):

![GC Chromatogram](image)

| Peak ID   | Time [Min] | Height [uV] | Area [uV.Min] | Area [%] |
|-----------|------------|-------------|---------------|----------|
| (S)-1-tetralol | 11.27     | 535.9       | 32.1          | 0.805    |
| (R)-1-tetralol | 11.37     | 15322       | 3959.9        | 99.195   |
2-Acetamido-1-indanol (P1). HPLC: Chiralcel OJ-H column (25 cm), eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm.

Racemate prepared via NaBH₄ reduction:

| Peak ID      | Retention Time | Area   | Area % | Height | Height % |
|--------------|----------------|--------|--------|--------|----------|
| cis-(15,2R)-P1 | 15.050         | 20855  | 6.89   | 5279   | 12.93    |
| cis-(1R,2S)-P1 | 16.500         | 19876  | 6.56   | 4541   | 11.12    |
| trans-(1R,2R)-P1 | 17.867        | 13195  | 43.55  | 23675  | 57.97    |
| trans-(1S,2S)-P1 | 41.267        | 13028  | 43.00  | 7342   | 17.98    |

Crude ATH product using RuH[(3R,1'S)-ULTAM-(CH₂)₃Ph] (active-C4) with a cosolvent (PhCl); detection at λ = 260 nm:

| Peak ID      | Retention Time | Area   | Area % | Height | Height % |
|--------------|----------------|--------|--------|--------|----------|
| cis-(15,2R)-P1 | 15.400         | 28639  | 5.34   | 630    | 16.41    |
| impurity     | 26.450         | 44599  | 8.31   | 609    | 15.86    |
| trans-(15,2S)-P1 | 40.833        | 463193 | 86.35  | 2600   | 67.73    |
The product using RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4) after trituration with CH$_3$CN:

| Peak ID     | Retention Time | Area  | Area % | Height | Height % |
|-------------|----------------|-------|--------|--------|----------|
| cis-(15,2R)-P1 | 15.167         | 3067  | 0.07   | 101    | 0.45     |
| trans-(15,2S)-P1 | 40.400         | 4164114 | 99.93  | 22319  | 99.55    |
2-Acetamido-1-indanon (S1'). HPLC: Chiralpak IA column (25 cm), eluent hexane/2-PrOH 90:10, flow rate 1 mL/min, $\lambda = 254$ nm.

The reference mixture prepared by mixing the ATH products from runs with RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4) and RuH[(S,S)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph] (active-C3), respectively:

Crude ATH product, derived from a run with RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4):
2-Acetamido-4-methyl-1-indanol (P2). HPLC: Chiralcel OD-H column (25 cm), eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm

Racemate prepared via NaBH₄ reduction:

| Peak ID | Retention Time | Area     | Area % | Height | Height % |
|---------|----------------|----------|--------|--------|----------|
| trans-(S,S) | 20.217    | 2247341 | 50.29  | 34096  | 61.58    |
| trans-(R,R) | 36.117    | 2221450 | 49.71  | 21275  | 38.42    |

Crude ATH product using Ru[(3R, 1'S)-ULTAM(CH₂)₂Ph] (C4):
2-Acetamido-4-bromo-1-indanol (P3). Chiralpak AD-H, eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm.

The reference mixture prepared by mixing the ATH products from runs with RuH[(3R,1'S)-ULTAM-(CH₂)₃Ph] (active-C4) and RuH[(S,S)-PipSO₂DPEN-(CH₂)₃Ph] (active-C3), respectively.
2-Acetamido-6-methyl-1-indanol (P4). HPLC: Chiralcel OD-H, eluent hexane/2-ProH 95:5, flow rate 1 mL/min, \( \lambda = 220 \) nm.

Racemate prepared via NaBH\(_4\) reduction:

| Peak ID     | Retention Time | Area   | Area % | Height | Height % |
|-------------|----------------|--------|--------|--------|----------|
| trans-(S,S)| 21.500         | 2305103| 52.50  | 30573  | 56.28    |
| unknown     | 28.633         | 70001  | 1.59   | 1060   | 1.95     |
| trans-(R,R)| 30.867         | 2015454| 45.90  | 22694  | 41.77    |

Crude ATH product using RuH\([(3R,1'S)-ULTAM-(CH\(_2\)_3)Ph]\) (active-C4):

| Peak ID     | Retention Time | Area   | Area % | Height | Height % |
|-------------|----------------|--------|--------|--------|----------|
| trans-(S,S)| 21.200         | 6046125| 100.00 | 87663  | 100.00   |
2-Acetamido-6-fluoro-1-indanol (P5). HPLC: Chiralpak AD-H, eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm.

The reference mixture prepared by mixing the ATH products derived from runs with RuH[(3R,1'S)-ULTAM-(CH₂)₃Ph] (active-C4) and RuH[(S,S)-PipSO₂DPEN-(CH₂)₃Ph] (active-C3), respectively.

| Peak ID    | Retention Time | Area    | Area % | Height | Height % |
|------------|----------------|---------|--------|--------|----------|
| cis-(15,2'R) | 12.750         | 14127   | 2.49   | 395    | 3.99     |
| trans-(1'R,2'R) | 15.983         | 222186  | 39.20  | 4418   | 44.68    |
| cis-(1'R,25)  | 18.567         | 36456   | 6.43   | 682    | 6.90     |
| trans-(15,25) | 22.850         | 293984  | 51.87  | 4393   | 44.43    |

Crude ATH product using RuH[(3R,1'S)-ULTAM-(CH₂)₃Ph] (active-C4):

| Peak ID    | Retention Time | Area    | Area % | Height | Height % |
|------------|----------------|---------|--------|--------|----------|
| cis-(15,2'R) | 12.617         | 26151   | 5.03   | 742    | 9.21     |
| trans-(1'R,2'R) | 15.833         | 1088    | 0.21   | 26     | 0.32     |
| trans-(15,25) | 22.733         | 492268  | 94.76  | 7285   | 90.46    |
2-Acetamido-3-phenyl-1-indanol (P6). HPLC: Chiralcel OJ-H column (25 cm), eluent hexane/2-PrOH 95:5, flow rate 1mL/min, \( \lambda = 240 \) nm.

Racemate prepared via NaBH₄ reduction:

| Peak ID      | Retention Time | Area    | Area %  | Height  | Height % |
|--------------|----------------|---------|---------|---------|----------|
| (1S,2S,3R)   | 11.883         | 449083  | 54.56   | 56453   | 59.98    |
| (1R,2R,3S)   | 15.650         | 374020  | 45.44   | 37670   | 40.02    |

Crude ATH product using RuH[(3R,1′S)-ULTAM-(CH₂)$_3$Ph] (active-C4):

| Peak ID              | Retention Time | Area    | Area %  | Height  | Height % |
|----------------------|----------------|---------|---------|---------|----------|
| unindent. diastereomer | 11.083         | 4204    | 2.95    | 201     | 9.02     |
| (1S,2S,3R)           | 11.983         | 138161  | 97.01   | 2023    | 90.76    |
| (1R,2R,3S)           | 15.617         | 54      | 0.04    | 5       | 0.22     |
2-Acetamido-1-acenaphthenol (P7). HPLC: Chiralcel OD-H, eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm.

The reference mixture prepared by mixing the ATH products from runs with RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4) and RuH[(S,S)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph] (active-C3), respectively.

| Peak ID                  | Retention Time | Area     | Area %  | Height | Height % |
|--------------------------|----------------|----------|---------|--------|----------|
| unknown                  | 16.883         | 2022844  | 12.55   | 44018  | 29.29    |
| trans-(1R,2R) + cis-(15,2R) | 40.517         | 7264696  | 45.09   | 66424  | 44.19    |
| trans-(15,2S)            | 56.100         | 4886116  | 30.32   | 30281  | 20.15    |
| cis-(1R,2S)              | 66.150         | 1939288  | 12.04   | 9577   | 6.37     |

Crude ATH product using RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4): >98% ee

Note that ee was calculated based on dr = 84:16 which was determined by $^1$H NMR.
Crude ATH product using Ru([(S,S)-PipSO$_2$DPEN(CH$_2$)$_3$Ph]) (C3): 98% ee

| Peak ID  | Retention Time | Area    | Area % | Height | Height % |
|----------|----------------|---------|--------|--------|----------|
| unknown  | 16.933         | 1288481 | 8.58   | 25530  | 18.73    |
| trans-(1R,2R) | 40.383     | 10468900 | 69.69  | 94797  | 69.53    |
| trans-(1S,2S) | 57.317     | 111478  | 0.74   | 671    | 0.49     |
| cis-(1R,2S)  | 65.750        | 3153125 | 20.99  | 15339  | 11.25    |

Triturated ATH product from run with Ru([(3R,1'S)-ULTAM(CH$_2$)$_3$Ph]) (C4): >99% ee

| Peak ID  | Retention Time | Area    | Area % | Height | Height % |
|----------|----------------|---------|--------|--------|----------|
| unknown  | 17.633         | 4559844 | 19.65  | 87651  | 46.66    |
| trans-(R,R) | 42.600       | 73612   | 0.32   | 600    | 0.32     |
| cis-(S,S)  | 55.233         | 18569075 | 80.03  | 99594  | 53.02    |
2-Acetamido-1-tetralol (P8). HPLC: Chiralpak IA, eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm.

The reference mixture prepared by mixing the ATH products from runs with RuH[(3R,1’S)-ULTAM-(CH₂)₃Ph] (active-C4) and RuH[(S,S)-PipSO₂DPEN-(CH₂)₃Ph] (active-C3), respectively.

| Peak ID      | Retention Time | Area   | Area % | Height | Height % |
|--------------|----------------|--------|--------|--------|----------|
| trans-(1R,2R) | 18.017         | 549127 | 47.00  | 11333  | 60.49    |
| cis-(1R,2S)  | 19.950         | 62871  | 5.38   | 1018   | 5.43     |
| cis-(1S,2R)  | 30.367         | 89662  | 7.67   | 1404   | 7.49     |
| trans-(1S,2S)| 34.883         | 466575 | 39.94  | 4981   | 26.59    |

Crude ATH product using RuH[(3R,1’S)-ULTAM-(CH₂)₃Ph] (active-C4):

| Peak ID      | Retention Time | Area   | Area % | Height | Height % |
|--------------|----------------|--------|--------|--------|----------|
| trans-(1R,2R) | 18.833         | 651    | 0.05   | 22     | 0.16     |
| cis-(1S,2R)  | 30.400         | 120590 | 8.83   | 1710   | 12.23    |
| trans-(1S,2S)| 33.683         | 1244069| 91.12  | 12248  | 87.61    |
2-Acetamido-6-methoxy-1-tetralol (P9). HPLC: Chiralpak IA, eluent hexane/2-PrOH 95:5, flow rate 1 mL/min, λ = 220 nm.

The reference mixture prepared by mixing the ATH products from runs with RuH[(3R,1'S)-ULTAM-(CH₂)₃Ph] (active-C4) and RuH[(S,S)-PipSO₂DPEN(CH₂)₃Ph] (active-C3).

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Crude ATH product using RuH[(3R,1'S)-ULTAM-(CH₂)₃Ph] (active-C4):

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| Peak ID  | Retention Time | Area  | Area % | Height | Height % |
|----------|----------------|-------|--------|--------|----------|
| (1R,2R)+(1R,2S) | 34.175 | 3268510 | 49.79 | 30420 | 58.09 |
| (15,2S) | 55.667 | 3233830 | 49.26 | 21455 | 40.97 |
| (15,2R) | 65.950 | 62355 | 0.95 | 492 | 0.94 |

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| Peak ID  | Retention Time | Area  | Area % | Height | Height % |
|----------|----------------|-------|--------|--------|----------|
| trans-(1R,2R) | 33.083 | 7892  | 0.07 | 112 | 0.17 |
| cis-(15,2R) | 36.600 | 83678 | 0.79 | 807 | 1.25 |
| trans-(15,2S) | 54.683 | 10519830 | 99.14 | 63633 | 98.58 |
## Triturated ATH product P9:

| Peak ID | Retention Time | Area   | Area % | Height | Height % |
|---------|----------------|--------|--------|--------|----------|
| trans-(S,S) | 55.000        | 5216202 | 100.00 | 34830  | 100.00   |

## 2-Pthalimido-1-indanol (P10).

HPLC: Chiralpak IA, eluent hexane/2-PrOH 80:20, flow rate 1 mL/min, $\lambda = 220$ nm.

The reference mixture prepared by mixing the ATH products from runs with RuH[(3$R$,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4) and RuH[(S,S)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph] (active-C3).
Crude ATH product using RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4):

![Graph showing retention times and areas for Crude ATH product]

| Peak ID         | Retention Time | Area     | Area %  | Height   | Height % |
|-----------------|----------------|----------|---------|----------|----------|
| cis-(1R,2S)     | 15.400         | 602955   | 2.92    | 24418    | 3.37     |
| cis-(15,2R)     | 17.150         | 19179548 | 92.86   | 673232   | 92.84    |
| trans           | 18.117         | 493215   | 2.39    | 17301    | 2.39     |
| ent-trans       | 23.183         | 378654   | 1.83    | 10235    | 1.41     |

Crude product using RuH[(S,S)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph] (active-C3):

![Graph showing retention times and areas for Crude product using RuH[(S,S)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph]]

| Peak ID | Retention Time | Area     | Area %  | Height   | Height % |
|---------|----------------|----------|---------|----------|----------|
| (R,S)   | 15.283         | 16162995 | 95.77   | 612710   | 96.24    |
| (S,R)   | 17.183         | 153539   | 0.91    | 6213     | 0.98     |
| trans   | 18.117         | 303088   | 1.80    | 10804    | 1.70     |
| ent-trans | 23.117     | 257822   | 1.53    | 6907     | 1.08     |
1-Acetamido-2-propanol. $^1$H NMR spectra were recorded in the presence of 30 mol% Eu(hfc)$_3$ in CDCl$_3$.

The quasi-racemate was prepared by running ATH using a ≈1:1 mixture of RuH[(R,R)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph] (active-C3) and RuH[(S,S)-PipSO$_2$DPEN-(CH$_2$)$_3$Ph] (ent-active-C3):

![NMR spectrum of quasi-racemate](image1)

Crude ATH product using RuH[(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (active-C4):

![NMR spectrum of crude product](image2)
7 ¹H and ¹³C NMR Spectra
$^{1}H$ NMR (300 MHz, CD$_3$OD)
contains a trace of Et$_3$N
8 Computational Analysis

Figure S1. Optimized TS structures in the gas phase: a) “cis-TS” leading to the cis-configured product P1 and b) “trans-TS” leading to the trans-configured product P1.

Figure S2. Optimized TS structures in chlorobenzene: a) “cis-TS” leading to the cis-configured product P1 and b) “trans-TS” leading to the trans-configured product P1.

Computational Methods

All calculations were executed using Gaussian 09, Revision E.01. The geometries of reactants, catalyst and transition states were optimized at M06-2x/6-31G(d, p) level in gas phase and in chlorobenzene.

(18) Frisch, M.J.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foreman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox. D.J. Gaussian 09 (Revision E.01). Gaussian, Inc., Wallingford, CT (2009).
using Tomasi’s Polarized Continuum Model (PCM) corrections. To include the relativistic effect of heavy atoms, core electrons of ruthenium atom were treated by using effective core potential with def2-TZVP basis set. The calculated energies (\(\Delta E\), 298.15 K, 1.0 atm) result from the sum of the Gibbs free energies as obtained from the frequency analysis at M06-2x/6-31G(d, p) level and PCM corrections. Energy values are given in kcal mol\(^{-1}\). Frequency calculations for all stationary points were carried out to describe them either as minima \((i = 0)\) or as first-order transition states \((i = 1)\). For all transition structures, visualization of the imaginary frequencies corresponded to the expected normal mode for the elementary step under investigation. Intrinsic reaction coordinate calculations (IRC) were performed from the transition states in forward and reverse directions to confirm the lowest energy reaction pathways that connect the corresponding minima.

### Table S1. Calculated Energy for the “trans-TS” Structure in a Gas Phase and in Chlorobenzene Leading to the trans-Configured Product P1

| Structure | Energy (Hartree) | \(\Delta G_{298}\) (kcal mol\(^{-1}\)) | Imaginary \(\nu\) (cm\(^{-1}\)) | Energy (Hartree) | \(\Delta G_{298}\) (kcal mol\(^{-1}\)) | Imaginary \(\nu\) (cm\(^{-1}\)) |
|-----------|-----------------|-------------------------------|-------------------|-----------------|-------------------------------|-------------------|
| Reactant  | -630.607021     | n.a.                          | n.a.              | -630.616074     | n.a.                          | n.a.              |
| Catalyst  | -1642.924929    | n.a.                          | n.a.              | -1642.945912    | n.a.                          | n.a.              |
| TS        | -2273.514203    | 11.14                         | -508.45           | -2273.536555    | 15.96                         | -192.20           |

### Table S2. Calculated Energy for the “cis-TS” Structure in a Gas Phase and in Chlorobenzene Leading to the cis-Configured Product P1

| Structure | Energy (Hartree) | \(\Delta G_{298}\) (kcal mol\(^{-1}\)) | Imaginary \(\nu\) (cm\(^{-1}\)) | Energy (Hartree) | \(\Delta G_{298}\) (kcal mol\(^{-1}\)) | Imaginary \(\nu\) (cm\(^{-1}\)) |
|-----------|-----------------|-------------------------------|-------------------|-----------------|-------------------------------|-------------------|
| Reactant  | -630.603393     | n.a.                          | n.a.              | -630.615678     | n.a.                          | n.a.              |
| Catalyst  | -1642.924929    | n.a.                          | n.a.              | -1642.945912    | n.a.                          | n.a.              |
| TS        | -2273.499085    | 18.35                         | -617.78           | -2273.522039    | 24.82                         | -107.45           |

Coordinates of the reactant in “cis-TS”:

| in gas phase | in chlorobenzene |
|--------------|------------------|
| O 0.67347900 2.04390700 0.60736400 | O -0.61976000 2.08815200 -0.59305000 |
| C 0.173206000.94593700 0.61138000 | C -0.15132200 0.97271200 -0.60581800 |
| C 0.86438200 -0.33610500 1.13738900 | C -0.86845700 -0.28619600 -1.14516500 |
| C -1.18575700 0.55064300 0.18528900 | C 1.19703000 0.54754900 -0.17899400 |
| C -1.30463500 -0.83752200 0.22470100 | C 1.29186100 -0.84248100 -0.23723800 |
| C -0.00863000 -1.50252800 0.62464700 | C -0.01570600 -1.47647400 -0.65146500 |
| C -2.23858500 1.37569000 -0.20070500 | C 2.26374700 1.34905700 0.22275400 |
| C -3.44495300 0.77907200 -0.54221200 | C 3.45775600 0.72602100 0.56218800 |
| C -3.57793500 -0.61420100 -0.49623300 | C 3.56614800 -0.66951400 0.49702800 |

(19) (a) Tomasi, J.; Persico, M. Chem. Rev. 1994, 94, 2027–2094. (b) Tomasi, J.; Bonaccorsi, R.; Cami, R.; de Valle, F. J. O. J. Mol. Struct. 1991, 234, 401–424.
(20) (a) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297–3305. (b) Weigend, F. Phys. Chem. Chem. Phys. 2006, 8, 1057–1065
Coordinates of the reactant in “trans-T5”:

|                         | in gas phase        | in chlorobenzene |
|-------------------------|---------------------|------------------|
| O                       | -0.08521800 2.39702000 0.06651700 | O 0.08742500 2.39172900 -0.08168100 |
| C                       | 0.19461500 1.22510800 0.18423800 | C -0.19434200 1.21682700 -0.18794200 |
| C                       | -0.82402900 0.10935100 0.43934500 | C 0.82301200 0.09811400 -0.43294700 |
| C                       | 1.51620500 0.57472400 0.06894500 | C -1.51650800 0.57331700 -0.07030500 |
| C                       | 1.33599500 -0.80423400 -0.05127800 | C -1.34102600 -0.06011300 0.05658800 |
| C                       | -0.13373400 -1.17271700 -0.06459800 | C 0.12547500 -1.18103200 0.07065000 |
| C                       | 2.77567200 1.16816500 0.04510700 | C -2.77513100 1.17143600 -0.05142800 |
| C                       | 3.88253800 0.33897500 -0.07729100 | C -3.88465800 0.34624700 0.07456500 |
| C                       | 3.71459600 -1.04755700 -0.18177400 | C -3.72117100 -1.04110700 0.18690800 |
| C                       | 2.44909800 -1.62968300 -0.17308300 | C -2.45745800 -1.16212700 0.18168900 |
| H                       | -0.46590600 -1.38780900 -1.08623500 | H 0.45419400 -1.39958900 1.09252000 |
| H                       | -0.37712700 -2.04068900 0.54945500 | H 0.35591100 -2.05092100 -0.54569800 |
| H                       | 2.87105900 2.24635500 0.12848500 | H -2.87180900 2.24887100 -0.14268100 |
| H                       | 4.88226600 0.76013800 -0.09007200 | H -4.88286300 0.77070400 0.08377000 |
| H                       | 4.59146600 -1.68143100 -0.27296100 | H -4.60024200 -1.67120900 0.28097000 |
| H                       | 2.33657200 -2.70592400 -0.26372700 | H -2.34864700 -2.70410700 0.27730800 |
| N                       | -2.08025100 0.45561000 -0.16988400 | N 2.08072800 0.44025100 0.17778400 |
| H                       | -2.18597000 1.42277300 -0.44824700 | H 2.17582600 1.38733700 0.52086000 |
| C                       | -3.16682400 -0.34662100 0.01311800 | C 3.17564400 -0.33792900 -0.01805200 |
| C                       | -4.47909300 0.18081800 -0.52834500 | C 4.47376500 0.18337500 0.55681600 |
| H                       | -4.38373800 1.14547800 -1.02957900 | H 4.36411800 1.14031100 1.06843600 |
| H                       | -4.88931200 -0.55198900 -1.22841400 | H 4.86626800 -0.55670000 1.25672600 |
| H                       | -5.18446900 0.27031700 0.30011400 | H 5.19596200 0.28769600 -0.25525500 |
| O                       | -3.07521300 -1.43059800 0.56505600 | O 3.10479400 -1.40653500 -0.61296100 |
| H                       | -0.93988000 0.02387000 1.53147900 | H 0.94283700 0.01424600 -1.52412400 |
Coordinates of the Ru(II) catalyst active-\textbf{C4}:

|                       | in gas phase   | in chlorobenzene |
|-----------------------|----------------|------------------|
| N                     | -0.19158800    | 1.09886800       | -1.42423200 |
| N                     | 0.36756200     | -1.06691400      | -0.54900800 |
| C                     | 0.57515500     | 1.22815700       | -1.29899400 |
| C                     | 1.12722800     | -0.21080300      | -1.42812300 |
| C                     | -1.65216700    | 2.35531500       | -1.17779900 |
| C                     | -3.16832300    | 2.71524000       | -1.29354500 |
| C                     | -3.83726700    | 1.68263600       | 0.00038000  |
| N                     | -2.12178500    | -2.10377300      | 0.12143100  |
| C                     | -3.81512000    | -0.84736000      | -0.19873500 |
| C                     | -1.91743700    | -1.01589500      | 1.91776700  |
| C                     | -2.21626700    | -2.17107000      | 1.11110000  |
| C                     | -3.36178400    | 0.32174700       | 0.46292200  |
| C                     | -2.49713800    | 0.20443400       | 1.61484500  |
| Ru                    | -1.66777000    | -0.69674100      | -0.40063000 |
| H                     | -1.09224500    | 0.83404600       | -2.39320300 |
| H                     | 0.93396300     | 1.81794300       | -2.15600700 |
| H                     | 0.99146900     | -0.50869900      | -2.48473600 |
| H                     | -1.30563300    | 3.12370000       | -1.88348800 |
| H                     | -1.93925400    | 2.70178700       | -0.17297000 |
| H                     | -3.39702000    | 1.48691100       | -2.11723900 |
| H                     | -1.70240300    | -1.26703200      | -1.85071500 |
| H                     | -3.60923200    | 3.14153400       | -1.55983700 |
| H                     | -4.92183000    | 1.65387100       | -0.14952400 |
| H                     | -3.64945500    | 2.41587500       | 0.79261100  |
| H                     | -3.46580300    | -2.98502000      | -0.45737800 |
| H                     | -4.53564100    | -0.76899600      | -1.00535600 |
| H                     | -1.14782500    | -1.09834600      | 2.67639200  |
| H                     | -1.67851300    | -3.09561400      | 1.28659800  |
| H                     | -2.21048400    | 1.09859700       | 2.16057300  |
| C                     | 0.98579800     | 1.97320300       | -0.04694900 |
| C                     | 2.79805700     | -1.32713600      | -0.09750600 |
| C                     | 2.58988500     | -0.34995400      | -1.05829900 |
| C                     | 4.05638300     | -1.64042100      | 0.39465800  |
| C                     | 5.14024300     | -0.92378800      | -0.10393000 |
| C                     | 4.94986900     | 0.06647000       | 0.91751800  |
| C                     | 3.67788300     | 0.35868700       | -1.55819400 |
| C                     | 1.24303000     | -2.07963000      | 0.34696900  |
| C                     | 0.95441600     | -1.89547700      | 1.77918800  |
| C                     | 1.21649000     | -3.47099400      | -0.10331200 |
| C                     | 1.48517200     | 3.27108300       | -0.18934700 |
| C                     | 1.86645500     | 4.02285300       | 0.91816000  |
| C                     | 1.75580600     | 3.47808100       | 2.19353600  |
| C                     | 1.26984500     | 2.18188300       | 2.34636500  |
| C                     | 0.88306200     | 1.42903000       | 1.23988700  |
| H                     | 4.18141100     | -2.41420200      | 1.14494000  |
| H                     | 6.14042100     | -1.13413800      | 0.26033800  |
Coordinates of “cis-TS”:

|        | in gas phase                     | in chlorobenzene                  |
|--------|----------------------------------|-----------------------------------|
| N      | -0.08830800 -1.09279600 -1.31809400 | N -0.09275100 -1.1108000 -1.31496800 |
| O      | 1.62852400 0.68016200 -1.77616100  | O 1.65481900 0.73050200 -1.78182700  |
| C      | 2.24477800 0.73637600 -0.62760600  | C 2.26243900 0.74610800 -0.62759800  |
| C      | 2.04526000 2.04289300 0.26469800  | C 2.25259400 2.04558780 0.27479700  |
| N      | -0.74515200 0.47804300 0.64420600  | N -0.75704500 0.48486000 0.64707800  |
| C      | -1.36392500 -0.34302500 -1.54445900 | C -1.36583000 -0.35415900 -1.54553700 |
| C      | 3.72226100 0.36588500 -0.56781700  | C 3.74232000 0.36652200 -0.58062000  |
| C      | 4.48204100 1.44769700 -0.10488000  | C 4.51559400 1.45334600 -0.16831200  |
| N      | -1.23915100 0.90797600 -0.66566400  | N -1.24357800 0.90112500 -0.67265500  |
| C      | 3.61800400 2.65513100 0.14510800  | C 3.65873700 2.65896200 0.11744300  |
| C      | 4.34000600 -0.82309400 -0.39691900  | C 4.34971000 -0.83059100 -0.94506100  |
| C      | 5.72342300 -0.94018500 -0.82539500  | C 5.73664200 -0.94594800 -0.86695500  |
| C      | -0.02585800 -2.30540200 -2.15237400 | C -0.04841300 -2.34862900 -2.12054500 |
| C      | 6.48129300 0.13460000 -0.36576300  | C 6.50819300 0.13746300 -0.44020200  |
| C      | 5.86533300 1.34579000 -0.00943000  | C 5.90184700 1.34338600 -0.09371500  |
| C      | 1.20824700 -3.16584000 -1.89612200 | C 1.19884300 -3.19246100 -1.87712700 |
| C      | 1.09016400 -4.08771700 -0.67045000 | C 1.11639900 -4.09756000 -0.63656700 |
| C      | 1.78680700 -1.79704600 2.34793700 | C 1.80886600 -1.77954800 2.36020600 |
| C      | 1.98858000 -2.65651000 1.22029100 | C 2.00940200 -2.64478000 1.23840400 |
| C      | -0.60386200 -2.30342500 2.28767000 | C -0.57894300 -2.29110200 2.30743300 |
| C      | 0.50280600 -1.62031500 2.88404800 | C 0.52613800 -1.60416100 2.89946400 |
| C      | 0.98229500 3.74100400 -1.07588200 | C 0.96397200 3.75531400 -0.99831000 |
| C      | 0.18193270 3.84335600 -1.95661100 | C 0.17754020 3.90462700 -1.90495000 |
| C      | 0.90262100 -3.33643500 0.62669900 | C 0.92617700 -3.33136800 0.65025800 |
| C      | -0.40538000 -3.16174100 1.18817400 | C -0.38097400 -3.15334400 1.21072100 |
| N      | 1.11079300 2.94161700 0.01854800  | N 1.14604500 2.94479700 0.07183400  |
| C      | -2.61339700 -1.17803400 -1.31329900 | C -2.61618100 -1.18619800 -1.33201600 |
| C      | -2.74550000 1.94939400 0.90902200  | C -2.78278000 1.93120100 0.87549100  |
| C      | -2.50799100 1.69371500 -0.43629200 | C -2.52089500 1.67820200 -0.46231500 |
| C      | -3.82570600 2.69132400 1.36165100 | C -3.88185500 2.66031900 1.31127600 |
| C      | -4.70811100 3.18466300 0.40608000 | C -4.75718600 3.13576100 0.39957800 |
| C      | -4.48976200 2.93880000 -0.95338800 | C -4.51325000 2.89011200 -1.01626000 |
| C      | -3.39140500 2.19971400 -1.38411600 | C -3.39657900 2.16727800 -1.42894600 |
| S      | -1.43545400 1.24261100 1.88242900 | S -1.47206300 1.25287500 1.86114600 |
| C      | -1.93033800 0.29149300 2.88895300 | C -1.95579000 0.32186700 2.89367500 |
| C      | -0.61093900 2.33729100 2.42197900 | C -0.66591400 2.36995800 2.40048600 |
| C      | -3.29087700 -1.66488900 -2.45250800 | C -3.30798000 -1.64772300 -2.45554900 |
| C      | -4.43633300 -2.44634600 -2.32290800 | C -4.45593700 -2.42593200 -2.32655100 |
Coordinates of "trans-TS":

|                  | in gas phase                  | in chlorobenzene                  |
|------------------|-------------------------------|-----------------------------------|
| N                | 0.04590300 -1.22070800 -1.26602000 | 0.04600000 -1.19890000 -1.27200000 |
| N                | 0.71307400 3.00688100 -0.28981000 | 0.74610000 3.05210000 -0.24890000 |
| N                | -0.85846600 0.38249700 0.57547200 | -0.85100000 0.38620000 0.59750000 |
| C                | -1.34505100 -0.72324400 -1.50565400 | -1.34500000 -0.69390000 -1.49820000 |
| C                | -1.40807400 0.61434900 -0.75616500 | -1.40820000 0.62810000 -0.73300000 |
| C                | 2.04908500 1.01847100 -1.16740400 | 2.05890000 1.04790000 -1.12210000 |
|        | x         | y         | z         |        | x         | y         | z         |        | x         | y         | z         |
|--------|-----------|-----------|-----------|--------|-----------|-----------|-----------|--------|-----------|-----------|-----------|
| C      | -4.888063 | 2.187342  | -1.163915 | C      | -4.899600 | 2.178900  | -1.123700 | O      | -2.028090 | 0.171559  | 2.831987  |
|        | 1.545325  | 1.545124  |           |        | 1.547400  | 2.868300  |           |        | -0.952828 | 2.320864  | 2.251897  |
| C      | -1.163915 | 2.187342  | -1.123700 | C      | -1.123700 | 2.184920  | -1.123700 | O      | -0.952828 | 2.320864  | 2.251897  |
|        | -1.163915 | 2.184920  | -1.123700 |        | -1.163915 | 2.184920  | -1.123700 |        | -0.952828 | 2.320864  | 2.251897  |
| S      | -3.712743 | 1.770039  |          | S      | -3.712743 | 1.770039  |          | O      | -3.712743 | 1.770039  |          |
|        | 1.113953  | 1.786300  |          |        | 1.113953  | 1.786300  |          |        | 1.113953  | 1.786300  |          |
| O      | -2.028090 | 0.171559  | 2.831987  | O      | -2.028090 | 0.171559  | 2.831987  | O      | -2.028090 | 0.171559  | 2.831987  |
|        | 0.171559  | 2.831987  |          |        | 0.171559  | 2.831987  |          |        | 0.171559  | 2.831987  |          |
| S      | -1.649182 | 1.118700  |          | S      | -1.649182 | 1.118700  |          | O      | -3.756321 | 0.435137  | 2.184920  |
|        | 1.118700  | 1.786300  |          |        | 1.118700  | 1.786300  |          |        | 0.435137  | 2.184920  |          |
| O      | -2.028090 | 0.171559  | 2.831987  | O      | -2.028090 | 0.171559  | 2.831987  | O      | -3.756321 | 0.435137  | 2.184920  |
|        | 0.171559  | 2.831987  |          |        | 0.171559  | 2.831987  |          |        | 0.435137  | 2.184920  |          |
| S      | -3.712743 | 1.770039  |          | S      | -3.712743 | 1.770039  |          | O      | -3.712743 | 1.770039  |          |
|        | 1.113953  | 1.786300  |          |        | 1.113953  | 1.786300  |          |        | 1.113953  | 1.786300  |          |
| O      | -2.028090 | 0.171559  | 2.831987  | O      | -2.028090 | 0.171559  | 2.831987  | O      | -3.712743 | 1.770039  |          |
|        | 0.171559  | 2.831987  |          |        | 0.171559  | 2.831987  |          |        | 1.113953  | 1.786300  |          |
| S      | -1.649182 | 1.118700  |          | S      | -1.649182 | 1.118700  |          | O      | -3.712743 | 1.770039  |          |
|        | 1.118700  | 1.786300  |          |        | 1.118700  | 1.786300  |          |        | 1.113953  | 1.786300  |          |
| O      | -2.028090 | 0.171559  | 2.831987  | O      | -2.028090 | 0.171559  | 2.831987  | O      | -3.712743 | 1.770039  |          |
|        | 0.171559  | 2.831987  |          |        | 0.171559  | 2.831987  |          |        | 1.113953  | 1.786300  |          |
9 Single-Crystal X-Ray Diffraction of C4

Single-crystal X-ray diffraction of C4

Obtaining a single crystal of RuCl[syn-(3R,1’S)-ULTAM-(CH2)3Ph] (C4) was challenging. Several crystallization attempts have failed. A small single crystal (0.130 × 0.049 × 0.031 mm) of rather poor quality was finally discovered in powdered material obtained from MeOH/CH₂Cl₂ solution. This crystal was attached to a MiTeGen MicroMount™ (100 μm aperture size) (Figure S3) with silicone grease (Merck) and transferred onto the magnetic base of the goniometer head. Single-crystal X-ray diffraction data were collected on an Agilent SuperNova Dual diffractometer equipped with an Atlas CCD area detector using micro-focus sealed X-ray tube with mirror monochromator. Crystal was measured with Cu Kα radiation in cold nitrogen stream at 150 K. CrysAlisPro software package¹ was used for data processing, including an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, and a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Crystal structure was solved and refined within OLEX2 (v. 1.2) program² by the SHELXT structure solution program³ and full-matrix least-squares minimization with SHELXL (v. 2018/3),⁴ respectively. Final difference Fourier map displays highest peak and deepest hole (0.443/−0.529 eÅ⁻³) located 0.74 Å from C18 and 0.75 Å from Ru, respectively (Table S3). Molecular graphics were prepared using the Diamond software.⁵

Figure S3. Single crystal of RuCl[syn-(3R,1’S)-ULTAM-(CH2)3Ph] (C4) mounted on a MiTeGen MicroMount™ (100 μm aperture size) that was used for single-crystal X-ray diffraction. Crystal in the second (middle) and third (right) photo is rotated by 84° and 126°, respectively, with respect to the orientation in the first photo (left).

The aforementioned poor quality of the measured small single crystal is reflected in the low C–C bond precision (0.012 Å). However, the anisotropic refinement of the crystal structure model including all non-hydrogen atoms resulted in the difference electron density map where residual electron density maxima for all hydrogen atoms could be located at the expected positions. The sole exception was the phenyl hydrogen atom H21 attached to C21, where several Fourier peaks could be observed in the vicinity of the carbon atom. The refinement of the crystal structure with all carbon-bonded hydrogen atoms included in calculated positions using a riding model yielded the strongest residual electron density peak (0.52 eÅ⁻³) located 0.87 Å from N1, as expected for the R₂N–H amine moiety. Hydrogen atom bonded to N1 was thus placed in the aforementioned position. Free refinement of this acidic H1-atom resulted in short H1–N1 distance (0.73(7) Å) and in unrealistically small Uiso (0.003(15) Å²).

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¹ CrysAlisPro Software System, version 1.171.39.46; Rigaku Oxford Diffraction, Rigaku Corporation, Oxford, UK, 2018.
² Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Cryst. 2009, 42, 339–341.
³ Sheldrick, G. M. Acta Crystallogr. 2015, A71, 3–8.
⁴ Sheldrick, G. M. Acta Crystallogr. 2015, C71, 3–8.
⁵ Brandenburg, K. Diamond - Crystal and Molecular Structure Visualization, version 3.1; Crystal Impact GbR: Bonn, Germany, 1997–2005.
The N1–H1 bond distance was therefore restrained (DFIX 0.88 0.02) to the default effective N–H distance of 0.88 Å for $T = 150 \text{ K}$ and the isotropic thermal displacement parameter of H1 was fixed at 1.2U$_{eq}$ value of N1.

Table S3. Summary of Crystal Data and Structure Refinement for the Crystal Structure of RuCl[\text{syn-(3R,1'S)-ULTAM-(CH}_2)_3Ph] (C4)

| Compound | RuCl[\text{syn-(3R,1'S)-ULTAM-(CH}_2)_3Ph] |
|----------|------------------------------------------|
| Formula  | C$_{23}$H$_{23}$ClN$_2$O$_2$RuS           |
| $F_w$    | 528.01                                   |
| $T$ [K]  | 150                                      |
| Crystal system | trigonal                            |
| Space group | $P3_1$                                    |
| $a$ [Å]  | 9.2850(2)                                |
| $b$ [Å]  | 9.2850(2)                                |
| $c$ [Å]  | 20.8483(4)                               |
| $\alpha$ ['] | 90                                     |
| $\beta$ ['] | 90                                    |
| $\gamma$ ['] | 120                                   |
| $V$ [Å$^3$] | 1556.56(7)                              |
| $Z$      | 3                                        |
| $\rho_{calc}$ [g/cm$^3$] | 1.690                             |
| Crystal size [mm] | 0.130 x 0.049 x 0.031 | |
| Radiation type | Cu Kα                                  |
| $\lambda$ [Å] | 1.54184                                |
| $\mu$ [mm$^{-1}$] | 8.431                         |
| $F$(000) | 804                                      |
| $2\theta_{max}$ ['] | 145.786                              |
| Index ranges | $-10 \leq h \leq 11$ | $-11 \leq k \leq 7$ | $-25 \leq l \leq 25$ |
| Reflections collected | 8988                                  |
| Independent reflections | 4024                                 |
| Reflections with $|I > 2\sigma(I)$ | 3795                                |
| $R_{int}$ | 0.0381                                   |
| $R_{free}$ | 0.0494                                 |
| Data/restraints/parameters | 4024/2/274                        |
| $S$ $^a$ | 1.036                                    |
| $R_1, wR_2$ $^b$ $|I > 2\sigma(I)$ | 0.0324, 0.0795               |
| $R_1, wR_2$ $^b$ [all data] | 0.0358, 0.0818               |
| $\Delta \rho_{min}, \Delta \rho_{max}$ [eÅ$^{-3}$] | -0.529, 0.443          |
| Flack $x$ $^d$ | -0.010(11)                            |

$^a$ $S = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}$/$N_w - N_p$

$^b$ $R_1 = \frac{1}{N} \sum | F_o | - |F_c | / \sum |F_o |

$^c wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}$/$N_w - N_p$

$^d$ From 1742 selected quotients (Parsons' method)

CCDC 1905532 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/structures.
Figure S4. The asymmetric unit and the atom numbering scheme in the crystal structure of RuCl[syn-(3R,1'S)-ULTAM-(CH$_2$)$_3$Ph] (C4). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted as small spheres of arbitrary radius.
Table S4. Interatomic Distances in RuCl[syn-(3R,1’S)-ULTAM-(CH₂)₃Ph] (C4)

| Bond Lengths [Å] |
|------------------|
| Ru–Cl            | Ru–C21          | S–C1          |
| 2.4361 (16)      | 2.177 (7)       | 1.755 (8)     |
| Ru–N1            | Ru–C22          | N1–H1         |
| 2.164 (6)        | 2.169 (7)       | 0.87 (3)      |
| Ru–N2            | Ru–C23          | N1–C8         |
| 2.059 (5)        | 2.188 (7)       | 1.509 (9)     |
| Ru–C18           | S–O1            | N1–C15        |
| 2.174 (7)        | 1.450 (5)       | 1.487 (9)     |
| Ru–C19           | S–O2            | N2–C7         |
| 2.188 (7)        | 1.439 (5)       | 1.455 (9)     |
| Ru–C20           | S–N2            |               |
| 2.177 (8)        | 1.584 (5)       |               |

| Bond Angles [°] |
|-----------------|
| N1–Ru–N2        | C8–N1–Ru       | C9–C8–N1     |
| 77.7 (2)        | 113.8 (4)      | 113.5 (5)    |
| N1–Ru–Cl        | C15–N1–Ru      | C9–C8–C7     |
| 80.79 (15)      | 118.6 (5)      | 116.1 (6)    |
| N2–Ru–Cl        | C15–N1–C8      | C9–C8–H8     |
| 88.40 (16)      | 113.6 (5)      | 107.4        |

The RuCl[syn-(3R,1’S)-ULTAM-(CH₂)₃Ph] (C4) compound crystallises in the trigonal space group P3₁ with three molecules in the unit cell. The asymmetric unit is comprised of a single molecule of complex [RuCl(C₂₃H₉₃N₅SO₂)] (Figure S4). The absolute configuration established by anomalous dispersion (Flack x = -0.010(11), Hooft y = -0.007(8)) is R, S, S for C7, C8, and N1, respectively. A typical piano-stool coordination environment is observed for the ruthenium metal with η⁶-phenyl ring (Ru–C 2.169(7)–2.188(7) Å), sultam nitrogen (Ru–N2 2.059(5) Å), amine nitrogen (Ru–N1 2.164(6) Å), and chlorido...
ligand (Ru–Cl 2.436(2) Å) (Table S4). The η^6-coordinated phenyl ring C18–C23 is slightly expanded (C–C 1.40(1)–1.44(1) Å) in comparison to the non-coordinated phenyl moiety C9–C14 (C–C 1.38(1)–1.40(1) Å). The bite angle N1–Ru–N2 is 77.7(2)° (Table S5). The molecular geometry around N2 atom is practically trigonal planar, the N2-atom is displaced from the mean plane Ru-C7-S only by −0.058(6) Å. The distance between Ru atom and the mean plane C18–C23 (η^6-phenyl ring) or the plane centroid is 1.653(3) Å. The angles (centroid-Ru-X) subtended at atom Ru by plane centroid and atoms Cl, N1, and N2 are 126.7(1)^°, 132.0(2)^°, and 132.8(2)^°, respectively.

The amine hydrogen atom is in close proximity to the Ru-bonded chloride ligand (H1∙∙∙Cl 2.40(8) Å) (Table S6, Figure S5). Metal-bound chloride often accepts hydrogen bonds,^26 so this could be an intramolecular N1–H1∙∙∙Cl hydrogen bond. However, the sterically imposed H1–Cl–Ru angle of 59(2)^° deviates significantly from 90° favorized for the involvement of the p-type lone pairs on chlorine.\textsuperscript{27} Moreover, a potential weak intramolecular Cphenyl–H∙∙∙N hydrogen bond can be identified between the H14-atom of the C9–C14 phenyl ring and the sultam N2-atom. Similarly, a weak intramolecular Cphenyl–H∙∙∙O hydrogen bond could involve H22-atom bonded to C18–C23 η^6-phenyl ring and the O2-atom of the sultam O=S=O moiety.

![Figure S5](image.png)

**Figure S5.** Potential weak intramolecular N1–H1∙∙∙Cl, C14–H14∙∙∙N2, and C22–H22∙∙∙O2 hydrogen-bonding interactions. Other hydrogen atoms have been omitted for clarity.

Intermolecular interactions in the crystal structure include weak Cphenyl–H∙∙∙O=S hydrogen bonds connecting molecules of the complex along the c-crystallographic axis (Table S6, Figure S6). Several potential weak intermolecular Caryl–H∙∙∙Cl–M interactions can also be observed (H2′∙∙∙Cl 2.89 Å, H13′∙∙∙Cl 2.91 Å, H22′∙∙∙Cl 3.02 Å, H23′∙∙∙Cl 3.03 Å).

All calculations involving mean planes, centroids, and distances not included in CIF have been performed in the OLEX2 program using SHELXL matrix.

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(26) Aullón, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, *653–654.*
(27) Yap, G. P. A.; Rheingold, A. L.; Das, P.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 3474–3476.
Table S6. Possible Weak Intra- and Intermolecular Hydrogen Bonds in C4

|                  | D−H  | H⋅⋅⋅A | D⋅⋅⋅A   | D−H⋅⋅⋅A |
|------------------|------|------|---------|---------|
| N1−H1⋅⋅⋅Cl       | 0.87 (3) | 2.40 (8) | 2.988 (6) | 125 (7) |
| C14−H14⋅⋅⋅N2     | 0.95  | 2.57  | 3.176 (8) | 121.5   |
| C22−H22⋅⋅⋅O2     | 0.95  | 2.46  | 3.046 (10)| 119.9   |
| C12−H12⋅⋅⋅O1<sup>i</sup> | 0.95  | 2.52  | 3.200 (9)  | 128.9   |
| C20−H20⋅⋅⋅O2<sup>ii</sup>| 0.95  | 2.49  | 3.238 (9)  | 135.6   |

<sup>a</sup> Symmetry transformations for the generation of equivalent atoms:

(i) −x+y+1, −x+1, z−1/3; (ii) −y+1, x−y, z+1/3.

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Figure S6. Hydrogen-bonded chain that runs parallel to the c-crystallographic axis (3<sub>1</sub> screw axis). Dashed lines indicate potential C<sub>phenyl</sub>−H⋅⋅⋅O=S hydrogen bonding and all remaining hydrogen atoms have been omitted for clarity.
Figure S7. The crystal packing and the unit cell of RuCl[syn-{3R,1'S}-ULTAM-(CH$_2$)$_3$Ph] (C4) viewed along the $b$-crystallographic axis. Hydrogen atoms have been omitted for clarity.
Figure S8. The comparison of steric around the Ru center in RuCl\(\text{syn-} (3R,1'S) - \text{ULTAM-} (\text{CH}_2)_2 \text{Ph}) \ (\text{C4}) \) (left) and Wills’ tethered ruthenium diamine chiral complex\(^{28}\) (right). Only amine hydrogen is depicted, all other hydrogen atoms have been omitted for clarity.

\(^{28}\) Hayes, A. M.; Morris, D. J.; Clarkson, G. J.; Wills, M. J. Am. Chem. Soc. \textbf{2005}, \textit{127}, 7318–7319.
Single-crystal X-ray diffraction of P6

A selected needle-shaped colorless crystal was mounted on a glass fiber (Figure S9). Single-crystal X-ray diffraction data were collected on an Agilent SuperNova Dual diffractometer equipped with an Atlas CCD area detector using micro-focus sealed X-ray tube with mirror monochromator. Crystal was measured with Cu Kα radiation in cold nitrogen stream at 150 K. CrysAlisPro software package\textsuperscript{21} was used for data processing, including an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, and a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Crystal structure was solved and refined within OLEX2 (v. 1.2) program\textsuperscript{22} by the SHELXT structure solution program\textsuperscript{23} and full-matrix least-squares minimization with SHELXL (v. 2018/3),\textsuperscript{24} respectively. Final difference Fourier map displays highest peak and deepest hole (0.182/−0.140 eÅ\textsuperscript{−3}) located 0.77 Å from C3 and 0.99 Å from C8, respectively (Table S7). Molecular graphics were prepared using the Diamond software.\textsuperscript{25}

![Figure S9. Single crystal of P6 mounted on a glass fiber.](image)

Residual electron density maxima for all hydrogen atoms could be located in the difference electron density map. The hydrogen atoms located on heteroatoms (O1, N1) and chiral centers (C1, C2, C3) were freely isotropically refined. All other carbon-bonded hydrogen atoms were included in calculated positions using a riding model. Three Fourier peaks, including the strongest residual electron density peak (0.25, 0.14, 0.12 eÅ\textsuperscript{−3}), could be observed in between the hydrogen atoms of the C17 methyl group (AFIX 137). This group was therefore modelled with hydrogen atoms disordered over the two positions rotated from one another by 56.1(3)°. The refinement of the second free variable yielded equal occupancies (0.50(3)). Disordered model has lower residual factors (R\textsubscript{1}[I > 2σ(I)] and wR\textsubscript{2}[all data] decreased from 3.23% and 8.63% to 3.00% and 7.57%, respectively) and a smoother difference electron density map (−0.219/0.253 versus −0.140/0.182 eÅ\textsuperscript{−3}).
**Table S7. Summary of Crystal Data and Structure Refinement for the Crystal Structure of P6**

| Compound | P6 |
|----------|----|
| Formula  | C₁₇H₁₇NO₂ |
| Fₑ [K]   | 267.31 |
| Crystal system | monoclinic |
| Space group | P₂₁ |
| a [Å]    | 5.04590(10) |
| b [Å]    | 9.5181(2) |
| c [Å]    | 14.8677(4) |
| α [°]    | 90 |
| β [°]    | 96.042(2) |
| γ [°]    | 90 |
| V [Å³]   | 710.09(3) |
| Z        | 2 |
| ρ calc [g/cm³] | 1.250 |
| Crystal size [mm] | 1.162 × 0.058 × 0.047 |
| Radiation type | Cu Kα |
| λ [Å]    | 1.54184 |
| μ [mm⁻¹] | 0.654 |
| F(000)   | 284 |
| 2θ max ['] | 149.292 |
| Index ranges | −5 ≤ h ≤ 6 |
|          | −11 ≤ k ≤ 11 |
|          | −18 ≤ l ≤ 15 |
| Reflections collected | 7334 |
| Independent reflections | 2902 |
| Reflections with | 2817 |
| | [I > 2σ(I)] |
| Rint      | 0.0286 |
| Rsigma    | 0.0290 |
| Data/restraints/parameters | 2902/1/204 |
| S a | 1.050 |
| R₁,wick [I > 2σ(I)] | 0.0300, 0.0746 |
| R₁,all [all data] | 0.0313, 0.0757 |
| δρmin, δρmax (eÅ⁻³) | −0.140, 0.182 |
| Flack x d | −0.12(9) |

*a S = [ΣΣw(Fo²−Fc²)/ΣΣw(Fo²)]²/(Np−Sr)
*b R₁ = Σ ||Fo||−|Fc||/Σ||Fo||
*c wR² = [ΣΣw(Fo²−Fc²)²]/[ΣΣw(Fo²)]²
*d from 1273 selected quotients (Parsons' method)

CCDC 1905533 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).
**Figure S10.** The asymmetric unit and the atom numbering scheme in the crystal structure of P6. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted as small spheres of arbitrary radius. The methyl group H-atoms are disordered over two positions with equal occupancies (0.50(3)).

The P6 compound crystallises in the monoclinic space group P2₁ with two molecules in the unit cell. The asymmetric unit is comprised of a single molecule (Figure S10, Table S8, Table S9). The absolute configuration established by anomalous dispersion (Flack \( x = -0.12(9) \), Hooft \( y = -0.10(9) \)) is S, S, R for C1, C2, and C3, respectively.

Each molecule is hydrogen-bonded to four other molecules by donating two (via O–H and N–H) and accepting two hydrogen bonds (via O=C and O(H)). Thus, hydrogen-bonded layers are formed parallel to \( ab \)-crystallographic plane. Molecules are interconnected along the \( a \)-crystallographic axis by the N–H···O(H) hydrogen bonds, whereas the O–H···O=C hydrogen bonds are running in zig-zag fashion along the \( b \)-crystallographic axis (Figure S11). A potential weak C–H···O=C hydrogen bond, involving the disordered methyl group as donor and carbonyl oxygen as a bifurcated acceptor, can be observed between the neighboring molecules linked by N–H···O(H) hydrogen bonds (Table S10).
Table S8. Interatomic Distances in P6

| Bond Lengths [Å] |
|------------------|
|                  |
| O1–H1O           | 0.91 (3) |
| O1–C1            | 1.418 (2) |
| O2–C16           | 1.241 (2) |
| N1–H1N           | 0.90 (3) |
| N1–C2            | 1.454 (2) |
| N1–C16           | 1.340 (2) |
| C1–H1            | 1.01 (2) |
| C1–C2            | 1.546 (2) |
| C1–C9            | 1.504 (2) |
| C2–H2            | 0.98 (2) |
| C2–C3            | 1.548 (2) |
| C3–H3            | 0.98 (2) |
| C3–C4            | 1.523 (2) |
| C3–C10           | 1.514 (2) |
| C4–C5            | 1.390 (3) |
| C4–C9            | 1.385 (3) |
| C5–C6            | 1.395 (3) |
| C5–H5            | 0.95 |
| C6–H6            | 0.95 |
| C7–H7            | 0.95 |
| C7–C8            | 1.390 (3) |
| C8–H8            | 0.95 |
| C9–C10           | 1.391 (3) |
| C10–C11          | 1.391 (3) |
| C11–H11          | 0.95 |
| C11–C12          | 1.391 (3) |
| C12–H12          | 0.95 |
| C12–C13          | 1.371 (3) |
| C13–H13          | 0.95 |
| C13–C14          | 1.382 (3) |
| C14–H14          | 0.95 |
| C14–C15          | 1.386 (3) |
| C15–H15          | 0.95 |
| C16–C17          | 1.508 (3) |
| C17–H17A         | 0.98 |
| C17–H17B         | 0.98 |
| C17–H17C         | 0.98 |
| C17–H17D         | 0.98 |
| C17–H17E         | 0.98 |
| C17–H17F         | 0.98 |

Table S9. Selected Bond Angles in P6

| Angles [°] |
|------------|
|            |
| C1–O1–H1O | 112 (2) |
| O1–C1–H1  | 109.7 (13) |
| O1–C1–C2  | 113.18 (14) |
| O1–C1–C9  | 110.87 (14) |
| C2–C1–H1  | 109.5 (14) |
| C9–C1–H1  | 111.1 (13) |
| O2–C16–N1 | 122.33 (17) |
| O2–C16–C17| 122.30 (17) |
| N1–C16–C17| 115.37 (17) |
| C2–N1–H1N | 119.3 (15) |
| C16–N1–H1N| 117.6 (15) |
| C16–N1–C2 | 123.10 (16) |
| N1–C2–C1  | 112.46 (14) |
| N1–C2–H2  | 108.5 (12) |
| N1–C2–C3  | 114.30 (14) |
| C1–C2–H2  | 107.1 (13) |
| C1–C2–C3  | 105.49 (13) |
| C3–C2–H2  | 108.6 (12) |
| C3–C2–C3  | 107.7 (13) |
| C2–C3–C4  | 101.42 (14) |
| C4–C3–H3  | 108.3 (13) |
| C10–C3–C2 | 117.43 (15) |
| C10–C3–H3 | 108.4 (13) |
| C10–C15   | 119.41 (18) |
| C3–C4–C2  | 108.6 (12) |
| C9–C4–C5  | 121.22 (17) |
| C9–C4–C5  | 120.40 (17) |
| C10–C11   | 120.8 (2) |
| C10–C12   | 120.7 (2) |
| C11–C12   | 121.52 (19) |
| C15–C10   | 117.55 (17) |
| C15–C10   | 117.55 (17) |

Table S10. Intermolecular Hydrogen Bonds in P6

| D–H···A | D–H | H···A | D···A | D–H···A |
|---------|-----|------|------|---------|
| O1–H1O–O2i | 0.91 (3) | 1.73 (3) | 2.6253 (19) | 171 (3) |
| N1–H1N–O1ii | 0.90 (3) | 2.00 (3) | 2.906 (2) | 179 (2) |
| C17–H17C–O2ii | 0.98 | 2.36 | 3.280 (3) | 156.2 |

*a Symmetry transformations for the generation of equivalent atoms:
(i) −x+1, y+1/2, −z+1; (ii) x−1, y, z.
Figure S11. Hydrogen-bonded layer parallel to the $ab$-crystallographic plane. Dashed lines indicate hydrogen bonding. Except for the H-bond donor groups ($O$–H and $N$–H) all other hydrogen atoms have been omitted for clarity.
Figure S12. The crystal packing and the unit cell of P6 viewed along the α-crystallographic axis. Only one set of hydrogen atoms is depicted for the disordered methyl groups.