A New Class of 'Tethered' Ruthenium (II) Catalyst for Asymmetric Transfer Hydrogenation Reactions.

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A) General:

All reactions, unless otherwise stated, were run under an atmosphere of nitrogen in flame or oven dried glassware (round bottomed flasks or Schlenk tubes). Room temperature refers to ambient room temperature (20-22 °C), 0 °C refers to an ice slush bath and -78°C refer to a dry-ice acetone bath. Heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by Thin Layer Chromatography (TLC) using aluminium backed silica gel 60 (F₂₅₄) plates, visualised using UV_{254 nm} and PMA, potassium permanganate or ninhydrin dips as appropriate. Flash column chromatography was carried out routinely using 60 Å silica gel (Merck). NMR spectra were recorded on Bruker DPX-300 (300Mhz) or DXP 400 (400 Mhz) spectrometer. Chemical shifts are reported in δ units, parts per million downfield from (CH₃)₄Si. Coupling constants (J) are measured in hertz. IR spectra were recorded on a Nicolet Model Avatar 320 FTIR instrument. Mass spectra were recorded on a 7070E VG mass spectrometer. Determination of enantiomeric excesses by HPLC analysis (using a Merck-Hitachi L-6200 A intelligent pump, Merck-Hitachi L-4000 UV detector, Axxiom chromatography data system and controller model 727 and a Daicel Chiralcel OD 4.6 x 250 mm column) or GC analysis (Hewlett Packard 5890A gas chromatography, Hewlett Packard 3396A integrator and Supelco BETA DexTM 120 fused silica capillary column 30m x 0.25 mm x 0.25 μ m film thickness) as stated. Elemental analyses were performed using the Exeter Analytical Model CE440. Melting points were recorded on a Stuart Scientific SMP1 instrument and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

B) Materials:

Commercially available reagents were used without purification: 3-phenyl-propan-1-ol (Aldrich), oxalylchloride (Aldrich), dimethylsulfoxide (Lancaster), L-(-)-norephedrine (Fluka), benzenethanethiol (Aldrich), (*R,R*)-1,2-diphenylethylene-diamine (Fluka), hydrate ruthenium (III) trichloride (Apollo), peracetic acid (36-40% solution in acetic acid) (Aldrich), triethylamine (99%) (Lancaster), thionyl chloride (Aldrich), hydrochloric acid (2M solution in diethyl ether) (Aldrich), sodium (stick in paraffin) (BDH) and ammonia (BOC). All anhydrous solvents were used as supplied by Romil in HyDryTM, except dimethylformamide and propan-2-ol, which were supplied by Aldrich. Formic acid: triethylamine mixture (5:2 molar) is a commercially available azeotrope (Fluka).

C) Synthesis of (*R,R*)-(N-2-cyclohexa-1,4-dienyl-ethanesulfonyl)-1,2-diphenylethylene-diamine 6

a) CH₃CO₃H (36-40% in acetic acid) (3 eq), DCM, rt, 2h; b) Na, NH₃, EtOH, -78°C, 3h; c) SOCl₂ (20 eq), DMF (2 eq), DCM, 35°C, 16h; d) Et₃N (2 eq), DCM, rt, o/n.

1) Synthesis of 2-phenyl-ethanesulfonic acid A¹

To a stirred solution of benzenethanethiol (9 g, 65 mmol) in dichloromethane (285 mL) was dropwise added peracetic acid (36.5 mL, 195 mmol) at 0°C. The reaction mixture was warmed to room temperature and stirred for 2h. Then the solution was concentrated under high-reduced pressure at 40°C to afford a viscous yellow oil (12 g, 100% yield) that turns red after few hours. IR $\nu_{\max}$ (cm⁻¹) 3368, 3026, 1682, 1105 and 1016; ¹H NMR (400 MHz, CDCl₃) δ_{H} (ppm) 11.00 (br s, 2H), 7.27-7.14 (m, 5H), 3.33-

3.11 (m, 2H) and 3.10-3.07 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} (ppm) 137.9, 129.2, 128.8, 127.3, 53.3 and 30.3; MS (EI) m/z 186 ($[\text{M}]^+$, 12), 169 (5), 104 (100), 91 (26) and 77 (25%); HRMS (EI) m/z calculated for $\text{C}_8\text{H}_{10}\text{O}_3\text{S}$ $[\text{M}]^+$ 186.0350. Found 186.0358.

2) Synthesis of 2-cyclohexa-1,4-dienyl-ethanesulfonyl chloride **B**

To a refluxing solution of ammonia² (177 mL) was slowly added a solution of 2-phenyl-ethanesulfonic acid **A** (5.0 g, 26 mmol) in ethanol (9 mL) at -78°C while stirring. Small pieces of cleaned sodium were added to the reaction mixture until the blue coloured persisted. During the addition of sodium, a small amount of ethanol was several times added to facilitate stirring. After the addition of sodium over the course of 3h, the ammonia was allowed to evaporate at room temperature overnight. The solution was filtered off and the residue was washed several times with ethanol (10 mL) to afford a slight orange solid. To a stirred suspension of the solid in anhydrous dichloromethane (350 mL) was added thionyl chloride (37 mL, 520 mmol), followed by anhydrous dimethylformamide (4 mL, 52 mmol) at 0°C . The mixture was heated at 35°C for 16h and filtered off. The filtrate was concentrated under reduced pressure to give an orange oil which was purified by flash chromatography (10 $\rightarrow$ 20% v/v ethyl acetate: hexane) to afford 2-cyclohexa-1,4-dienyl-ethanesulfonyl chloride **B** as a colourless oil (3.9 g, 73% yield). IR ν_{max} (cm^{-1}) 3029, 2921, 2854, 2820, 1367 and 1164; ^1H NMR (400 MHz, CDCl_3) δ_{H} (ppm) 5.71 (br s, 2H), 5.58 (br s, 1H), 3.78-3.74 (m, 2H) and 2.74-2.61 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} (ppm) 129.8, 124.5, 123.7, 122.8, 64.2, 32.1, 29.2 and 27.10; MS (EI) m/z 208 ($[\text{M}(^{37}\text{Cl})]^+$, 15), 206 ($[\text{M}(^{35}\text{Cl})]^+$, 42), 171 (8%), 153 (14%), 105 (100%), 91 (99%) and 79 (83%); Anal. Calculated for $\text{C}_8\text{H}_{11}\text{ClO}_2\text{S}$: C, 46.49; H, 5.36; Cl, 17.15; S, 15.51. Found: C, 46.22; H, 5.22; Cl, 17.12; S, 15.32.

3) Synthesis of (*R,R*)-(N-2-cyclohexa-1,4-dienyl-ethanesulfonyl)-1,2-diphenylethylene-diamine **6**³

To a stirred solution of (*R,R*)-1,2-diphenylethylene-diamine (1.00 g, 4.7 mmol) in anhydrous dichloromethane (20 mL) was added triethylamine (1.3 mL, 9.4 mmol), followed by 2-cyclohexa-1,4-dienyl-ethanesulfonyl chloride **B** (0.97 g, 4.7 mmol) at room temperature. The reaction mixture was stirred overnight at room temperature and concentrated to give a yellow oil which was purified by flash chromatography (10 $\rightarrow$ 80% v/v ethyl acetate: hexane) to afford a white solid (1.08 g, 60% yield). mp $123-124^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} +20.4$ (c 1.00, CHCl_3); IR ν_{max} (cm^{-1}) 3343, 3290, 3143, 3025, 2870, 2816, 1599, 1451, 1313 and 1129; ^1H NMR (400 MHz, CDCl_3) δ_{H} (ppm) 7.32-7.24 (m, 10H); 5.86 (br s, 1H), 5.64 (br s, 2H), 5.18 (br s, 1H), 4.56 (d, $J = 5.5$ Hz, 1H), 4.24 (d, $J = 5.5$ Hz, 1H), 2.62-2.58 (m, 2H), 2.55-2.47 (m, 1H), 2.45-2.37 (m, 1H), 2.32-2.28 (m, 2H), 2.17-2.13 (m, 2H) and 1.53 (br s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} (ppm) 142.3, 140.3, 131.6, 129.1, 129.0, 128.3, 128.2, 127.4, 127.2, 124.4, 124.1 and 120.5; MS (EI) m/z 381 ($[\text{M}-\text{H}]^+$, 6), 211 (4), 196 (7), 106 (100) and 79 (26%); Anal. Calculated for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$: C, 69.08; H, 6.85; N, 7.32. Found: C, 68.79; H, 6.80; N, 7.14.

D) Synthesis of ruthenium (II) dimer **4**⁴

To a stirred solution of (*R,R*)-(N-2-cyclohexa-1,4-dienyl-ethanesulfonyl)-1,2-diphenylethylene-diamine **6** (1.08 g, 2.8 mmol) in anhydrous dichloromethane (20 mL) was added a 2M solution of hydrochloric acid in diethyl ether (4.2 mL, 8.5 mmol) at 0°C . The reaction mixture was stirred 5 minutes at room temperature and concentrated under reduced pressure to give a white residue. To a suspension of the residue in ethanol (50 mL) was added hydrate ruthenium (III) trichloride (0.46 g, 1.8 mmol). The reaction mixture was stirred at reflux for 21h and concentrated until dryness. The residue was washed several times with anhydrous dichloromethane to afford a khaki solid (0.70 g, 66% yield). mp $240-241^\circ\text{C}$ (dec.); IR ν_{max} (cm^{-1}) 3057, 2916, 2361, 2339, 1494, 1455, 1318 and 1143; ^1H NMR (300 MHz, DMSO) δ_{H} (ppm) 8.78 (br s, 3H), 8.53 (d, $J = 9.6$ Hz, 1H), 7.29-7.15 (m, 10H), 5.99-5.94 (m, 2H), 5.79-5.73 (m, 2H), 5.44 (d, $J = 5.8$ Hz, 1H), 4.74 (dd, $J = 9, 9$ Hz, 1H), 4.53 (br s, 1H), 3.33-3.24 (m, 1H), 2.83-2.71 (m, 2H), 2.62-2.54 (m, 1H, slight overlap with DMSO peak); ^{13}C NMR (100 MHz, DMSO) δ_{C} (ppm) 138.1, 134.4, 128.7, 128.4, 127.9, 127.8, 102.9, 88.0, 86.1, 85.9, 84.2, 61.0, 58.2, 51.5 and 26.7; HRMS (LSIMS) m/z calculated for $^{102}\text{RuC}_{22}\text{H}_{24}\text{N}_2\text{O}_2\text{SCl}$ 517.0290. Found 517.0299. This result corresponds to direct conversion to compound **3** in the mass spectrometer; the dimer could not be observed by LSIMS or ESIMS due to this facile rearrangement. A detailed ESIMS analysis by the EPSRC MS service identified ions corresponding to M-3HCl-Cl for the dimer.

E) Synthesis of ruthenium(II) catalyst **2**⁵

To a suspension of ruthenium (II) dimer **4** (0.200 g, 0.17 mmol) in propan-2-ol (10 mL) was added triethylamine (0.19 mL, 1.4 mmol) at room temperature. The reaction mixture was refluxed for 1h and concentrated under reduced pressure to give a brown residue, which was washed several times with anhydrous dichloromethane and dried *in vacuo* to afford a dark brown powder (0.101 g, 57% yield). mp $258-260^\circ\text{C}$ (dec.); HRMS (LSIMS) m/z calculated for $\text{RuC}_{22}\text{H}_{24}\text{N}_2\text{O}_2\text{SCl}$ $[\text{M}+\text{H}]^+$ 517.0290. Found 517.0289. Recrystallisation from acetonitrile afford orange crystals which the molecular structure was determined by single crystal X-ray analysis (see section H).

F) General experimental procedure for the asymmetric transfer hydrogenation catalysed by ruthenium (II) dimer **4** and **2**

A solution of ruthenium (II) dimer **2** (0.010 g, 8.3×10^{-3} mmol) in formic acid/ triethylamine (5:2) mixture (1.5 mL) was stirred at 28°C for 10 minutes then ketone (3.3 mmol) was added. The reaction mixture was stirred at 28°C until completion and filtered through a pad of silica gel. The pad was washed with a 40 % solution of ethyl acetate in hexane (100 mL). The filtrate was concentrated under reduced pressure to afford the reduction product. The same procedure was employed for the reduction using **2**.

G) HPLC, GC analysis and optical rotation data of the reduction products

(R)-1-phenylethanol: $[\alpha]_D^{27} +54.9$ (c 1.00, CHCl_3) (lit.⁶ $[\alpha]_D^{23} +48.6$ (c 1.0, CH_2Cl_2), 96 % e.e. (*R*)), 96 % e.e. (*R*) by GC (Chiracel β -DEX 120, T = 115°C, P = 11 psi, *R* isomer 8.7 min, *S* isomer 9.2 min).

(R)-1-indanol: $[\alpha]_D^{27} -30.5$ (c 1.00, CHCl_3) (lit.⁷ $[\alpha]_D^{23} +30.9$ (c 1.99, CHCl_3), 92 % e.e. (*S*)), 84 % e.e. (*R*) by HPLC (chiralcel OD column, propan-2-ol:hexane = 2:98 (1 mL/min), *S* isomer 13.8 min, *R* isomer 15.8 min).

(R)-1-tetralol: $[\alpha]_D^{27} -32.3$ (c 1.00, CHCl_3) (lit.⁸ $[\alpha]_D +34.4$ (c 1.01, CHCl_3), 98 % e.e. (*S*)), 98 % e.e. (*R*) by HPLC (chiralcel OD column, propan-2-ol:hexane = 2:98 (1 mL/min), *S* isomer 10.7 min, *R* isomer 11.7 min).

(R)-1-(2'-naphthyl)ethanol: $[\alpha]_D^{27} +45.4$ (c 1.00, CHCl_3) (lit.⁸ $[\alpha]_D -34.3$ (c 1.10, EtOH)), 86 % e.e. (*S*)), 90 % e.e. (*R*) by HPLC (chiralcel OD column, ethanol:hexane = 5:95 (1 mL/min), *S* isomer 14.7 min, *R* isomer 16.4 min).

(R)-1-(*p*-chlorophenyl)ethanol: $[\alpha]_D^{27} +44.2$ (c 1.00, ether) (lit.⁹ $[\alpha]_D^{21} +46.1$ (c 0.9-1.1, ether), 91 % e.e. (*R*)), 92 % e.e. (*R*) by GC (Chiracel β -DEX 120, T = 140°C, P = 11 psi, *R* isomer 11.1 min, *S* isomer 11.8 min).

(R)-1-(*p*-methoxyphenyl)ethanol: $[\alpha]_D^{27} +32.3$ (c 1.00, CHCl_3) (lit.⁷ $[\alpha]_D^{23} -51.9$ (c 1.04, CHCl_3), 97 % e.e. (*S*)), 90 % e.e. (*R*) by GC (Chiracel β -DEX 120, T = 125°C, P = 11 psi, *R* isomer 24.2 min, *S* isomer 25.2 min).

H) Synthesis of (1*R*,2*S*)-(N-3-cyclohexa-1,4-dienyl-propyl)-norephedrine **5**

(i) Na, NH_3 , EtOH, -78°C, 3h; (ii) $(\text{ClCO})_2$ (1.2 eq), DMSO (2.5 eq), Et_3N (5.5 eq), DCM, -78°C, 80 min; (iii) (a) 4 Å molecular sieves, L-(-)-norephedrine (1 eq), DCM, rt, o/n, (b) NaBH_4 (3 eq), MeOH, rt, o/n; EtOH: ethanol; DMSO: dimethylsulfoxide; rt: room temperature; o/n: overnight.

1) Synthesis of 3-cyclohexa-1,4-dienyl-propan-1-ol **C**

To a refluxing solution of ammonia² (350 mL) was slowly added a solution of 3-phenyl-propan-1-ol (10 g, 73 mmol) in ethanol (24 mL) at -78°C while stirring. Small pieces of cleaned sodium were added to the reaction mixture until the blue colour persisted. During the addition of sodium, a small amount of ethanol was several times added to facilitate stirring. After the addition of sodium over the course of 3h, the reaction mixture was carefully poured into an ice-cooled solution of ammonium chloride. 3-cyclohexa-1,4-dienyl-propan-1-ol **C** was then extracted with dichloromethane (3 x 25 mL) and the combined organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford a colourless oil. The oil was purified by bulb-to-bulb distillation under reduced pressure (5.10^{-2} - 3.10^{-2} mm Hg, 100-105 °C) (10 g, 100% yield). IR ν_{max} (cm^{-1}) 3309, 3024, 2936, 2850, 2818, 1428 and 1057; ^1H NMR (400 MHz, CDCl_3) δ_{H} (ppm) 5.71 (br s, 2H), 5.45 (br s, 1H), 3.65-3.62 (m, 2H) and 2.68-2.66 (m, 2H), 2.62-2.58 (m, 2H), 2.04 (t, $J = 7.6$ Hz, 2H), 1.88 (br s, 1H) and 1.73-1.66 (m, 2H); ^{13}C NMR (100

MHz, CDCl₃) δ_C (ppm) 134.9, 124.65, 124.6, 119.1, 63.1, 34.1, 30.6, 29.3 and 27.1; MS (EI) m/z 138 ([M]⁺, 17), 120 (18), 105 (16), 91 (100), 79 (61) and 67 (7); HRMS (EI) m/z calculated for C₉H₁₄O 138.1044. Found 138.1042.

2) Synthesis of 3-cyclohexa-1,4-dienyl-propionaldehyde D

To a solution of oxalylchloride at -78°C (0.75 mL, 8.7 mmol) in dichloromethane (9 mL) was added dropwise a solution of dimethylsulfoxide (1.3 mL, 18 mmol) in dichloromethane (9 mL). The solution was stirred 15 minutes at -78°C then a solution of 3-cyclohexa-1,4-dienyl-propan-1-ol **C** (1 g, 7 mmol) in dichloromethane (18 mL) was slowly added at the same temperature. After 50 minutes of stirring at -78°C, triethylamine (5.5 mL, 40 mmol) was added and the reaction mixture was allowed to warm up to room temperature. After 15 minutes, water (20 mL) was added and the aldehyde was extracted with dichloromethane (3 x 15 mL). The combined organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure to give slightly clear green oil. The oil was purified by bulb-to-bulb distillation under reduced pressure (5.10⁻²-3.10⁻² mm Hg, 70-80 °C) to afford a colourless oil (0.9 g, 97% yield). IR $\nu_{\max}$ (cm⁻¹) 3026, 2881, 2850, 2818, 2718, 1720 and 1428; ¹H NMR (300 MHz, CDCl₃) δ_H (ppm) 9.78 (s, 1H), 5.70 (br s, 2H), 5.44 (br s, 1H), 2.72-2.62 (m, 2H), 2.62-2.54 (m, 4H) and 2.31 (t, J = 7.4 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ_C (ppm) 202.2, 132.8, 124.0, 123.6, 119.0, 41.3, 29.25, 28.85 and 26.4; MS (EI) m/z 136 ([M]⁺, 8), 134(22), 118 (78), 91 (100), 79 (70) and 65 (24); HRMS (EI) m/z calculated for C₉H₁₂O 136.0888. Found 136.0888.

3) Synthesis of (1R,2S)-(N-3-cyclohexa-1,4-dienyl-propyl)-norephedrine 5

To a suspension of powdered 4 Å molecular sieves (2.8 g) in dichloromethane (40 mL) was added 3-cyclohexa-1,4-dienyl-propionaldehyde **D** (2.0 g, 15 mmol), followed by L-(-)-norephedrine (2.2 g, 15 mmol) at room temperature. The reaction mixture was stirred overnight at room temperature, filtered and concentrated under reduced pressure. The colourless oily residue was dissolved in methanol and sodium borohydride (1.7 g, 45 mmol) was added at room temperature. The reaction mixture was stirred overnight and water (20 mL) was added. The product was extracted with dichloromethane (3 x 20 mL) and the combined organic layer dried over magnesium sulfate and filtered. After concentration under reduced pressure, a colourless oil was obtained and was purified by flash chromatography (20→80% v/v ethyl acetate: hexane) to afford a white solid (2.6 g, 65% yield). mp 59-60 °C; $[\alpha]_D^{20}$ -5.6 (c 0.9, CHCl₃); IR $\nu_{\max}$ (cm⁻¹) 3082, 3023, 2970, 2879, 2853, 2818 and 1426; ¹H NMR (400 MHz, CDCl₃) δ_H (ppm) 7.33-7.23 (m, 5H), 5.71 (br s, 2H), 5.44 (br s, 1H), 4.77-7.76 (m, 1H), 2.98-2.92 (m, 1H), 2.79-2.58 (m, 6H), 2.34 (br s, 1H), 2.05-2.01 (m, 2H), 1.68-1.61 (m, 2H) and 0.83 (d, J = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ_C (ppm) 141.7, 134.8, 128.5, 127.5, 126.5, 124.7, 124.6, 119.2, 73.4, 58.9, 47.2, 35.5, 29.3, 28.0, 27.2 and 14.8; MS (EI) m/z 272 ([M+H]⁺, 3), 252 (48), 164 (100), 91(55), 79 (22) and 58 (17); Anal. Calculated for C₁₈H₂₅NO: C, 79.66; H, 9.28; N, 5.16. Found: C, 79.82; H, 9.40; N, 5.26.

I) Synthesis of the chloro-bridged η^6 -arene ruthenium (II) dimer 3⁴

To a stirred solution of (1R,2S)-(N-3-cyclohexa-1,4-dienyl-propyl)-norephedrine **5** (1.709 g, 6.3 mmol) in diethyl ether (20 mL) was added a 2 M solution of hydrochloric acid in diethyl ether (9 mL, 19 mmol) at room temperature. The reaction mixture was stirred 5 minutes at room temperature and concentrated under reduced pressure to give a white residue. To a suspension of the residue in ethanol (50 mL) was added hydrate ruthenium (III) trichloride (1.089 g, 5.2 mmol). The reaction mixture was stirred at reflux for 14h and filtered to give green solid residue. The residue was washed with anhydrous dichloromethane to afford a green/khaki solid (1.358 g, 55% yield). mp 239-240 °C (dec.); IR $\nu_{\max}$ (cm⁻¹) 3291, 3042, 2980, 2788, 1448 and 1410; ¹H NMR (400 MHz, DMSO) δ_H (ppm) 8.71 (br s, 2H), 7.40-7.25 (m, 5H), 6.11 (d, J = 4.0 Hz, 1H), 6.04 (t, J = 5, 9 Hz, 2H), 5.84 (d, J = 5.5 Hz, 3H), 5.16 (br s, 1H), 3.45 (br s, 1H), 3.14 (br s, 2H), 2.64-2.60 (m, 2H), 2.09-2.02 (m, 2H) and 0.94 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, DMSO) δ_C (ppm) 141.2, 128.15, 127.25, 125.8, 106.1, 88.8, 85.4, 83.7, 69.3, 58.3, 44.1, 29.5, 25.0 and 9.3; HRMS (LSIMS) m/z calculated for ¹⁰²RuC₁₈H₂₄NOCl₂ 442.0278. Found 442.0290. Dimer was not observed by LSIMS or ESIMS.

J) General experimental procedure for the asymmetric transfer hydrogenation catalysed by ruthenium (II) dimer **3**

To a stirred suspension of ruthenium (II) dimer **3** (0.004 g, $4.2 \cdot 10^{-3}$ mmol) in dry and degassed propan-2-ol (15 mL) was added a 0.1 M solution of KOH (0.84 mL, $8.5 \cdot 10^{-2}$ mmol), followed by ketone (1.7 mmol) at 28°C. The reaction mixture was stirred at 28°C until completion and hexane was added (30 mL). The mixture was filtered through a pad of silica gel and the pad was washed with a 40 % solution of ethyl acetate in hexane (150 mL). The filtrate was concentrated under reduced pressure to afford the reduction product. Purification by flash chromatography was applied when appropriate.

K) HPLC, GC analysis and optical rotation data of the reduction products

(R)-1-phenylethanol: $[\alpha]_D^{28} +25.8$ (*c* 1.00, CHCl₃) (lit.⁹ $[\alpha]_D^{23} +48.6$ (*c* 1.0, CH₂Cl₂), 96 % e.e. (*R*)), 66 % e.e. (*R*) by GC (Chiracel β-DEX 120, T = 115°C, P = 11 psi, *R* isomer 9.0 min, *S* isomer 9.5 min).

(R)-1-(4'-methylphenyl)ethanol: $[\alpha]_D^{28} +31.8$ (*c* 1.00, CHCl₃) (lit.¹⁰ $[\alpha]_D -54.1$ (*c* 0.0532, CHCl₃), 96 % e.e. (*S*)), 57 % e.e. (*R*) by GC (Chiracel β-DEX 120, T = 115°C, P = 11 psi, *R* isomer 13.2 min, *S* isomer 14.1 min).

(R)-1-(4'-chlorophenyl)ethanol: $[\alpha]_D^{28} +24.8$ (*c* 1.00, CHCl₃) (lit.⁹ $[\alpha]_D^{21} +46.1$ (*c* 0.9-1.1, ether), 91 % e.e. (*R*)), 54 % e.e. (*R*) by GC (Chiracel β-DEX 120, T = 140°C, P = 11 psi, *R* isomer 11.1 min, *S* isomer 11.7 min).

(R)-1-(4'-methoxyphenyl)ethanol: $[\alpha]_D^{28} +28.0$ (*c* 1.00, CHCl₃) (lit.⁷ $[\alpha]_D^{23} -51.9$ (*c* 1.04, CHCl₃), 97 % e.e. (*S*)), 52 % e.e. (*R*) by GC (Chiracel β-DEX 120, T = 125°C, P = 11 psi, *R* isomer 25.1 min, *S* isomer 25.9 min).

(R)-1-(4'-fluorophenyl)ethanol: $[\alpha]_D^{28} +26.4$ (*c* 1.00, CHCl₃) (lit.¹⁰ $[\alpha]_D -47.5$ (*c* 0.0576, CHCl₃), 97 % e.e. (*S*)), 55 % e.e. (*R*) by GC (Chiracel β-DEX 120, T = 115°C, P = 11 psi, *R* isomer 10.1 min, *S* isomer 10.8 min).

(R)-1-(4'-nitrophenyl)ethanol: $[\alpha]_D^{28} +13.5$ (*c* 1.00, CHCl₃) (lit.¹¹ $[\alpha]_D^{25} -30.5$ (*c* 4, CHCl₃), 96 % e.e. (*S*)), 36 % e.e. (*R*) by GC (Chiracel β-DEX 120, T = 170°C, P = 11 psi, *R* isomer 18.7 min, *S* isomer 19.4 min).

(R)-1-indanol: $[\alpha]_D^{28} -21.8$ (*c* 1.00, CHCl₃) (lit.⁷ $[\alpha]_D^{23} +30.9$ (*c* 1.99, CHCl₃), 92 % e.e. (*S*)), 66 % e.e. (*R*) by HPLC (chiralcel OD column, propan-2-ol:hexane = 2:98 (1 mL/min), *S* isomer 12.1 min, *R* isomer 13.7 min).

(R)-1-(2'-naphthyl)ethanol: $[\alpha]_D^{28} +28.8$ (*c* 1.00, CHCl₃) (lit.⁸ $[\alpha]_D -34.3$ (*c* 1.10, EtOH)), 86 % e.e. (*S*)), 58 % e.e. (*R*) by HPLC (chiralcel OD column, propan-2-ol:hexane = 2:98 (1 mL/min), *S* isomer 21.7 min, *R* isomer 23.6 min).

L) ^1H and ^{13}C NMR spectra

1) ^1H and ^{13}C NMR spectra of 2-phenyl-ethanesulfonic acid A

Parameters: Proton with CDCl_3 SF=400.03 SW=8223.68 AQ=3.98 TD=65536 Units=ppm

Parameters: C13pend.with CDCl_3 SF=100.59 SW=25125.63 AQ=1.30 TD=131072 Units=ppm

2) ^1H and ^{13}C NMR spectra of 2-cyclohexa-1,4-dienyl-ethanesulfonyl chloride **B**

3) ^1H and ^{13}C NMR spectra of (*R,R*)-(N-2-cyclohexa-1,4-dienyl-ethanesulfonyl)-1,2-diphenylethylene-diamine **6**

Parameters: Proton with CDCl₃ SF=400.03 SW=8223.68 AQ=1.99 TD=65536 Units=ppm

Parameters: C13pend.with CDCl₃ SF=100.59 SW=25125.63 AQ=1.30 TD=131072 Units=ppm

4) ^1H and ^{13}C NMR spectra of Ruthenium (II) dimer 4

Parameters: Proton with DMSO SF=300.13 SW=6172.84 AQ=2.65 TD=65536 Units=ppm

Parameters: C13pend.with DMSO SF=100.59 SW=25125.63 AQ=1.30 TD=131072 Units=ppm

5) ^1H and ^{13}C NMR spectra of 3-cyclohexa-1,4-dienyl-propan-1-ol C

Parameters: Proton with CDCl_3 SF=400.03 SW=8223.68 AQ=1.99 TD=65536 Units=ppm

Parameters: C13 pend.with CDCl_3 SF=100.59 SW=25125.63 AQ=1.30 TD=131072 Units=ppm

6) ^1H and ^{13}C NMR spectra of 3-cyclohexa-1,4-dienyl-propionaldehyde **D**

Parameters: Proton with CDCl_3 SF=300.13 SW=6172.84 AQ=2.65 TD=65536 Units=ppm

Parameters: $\text{C}13\text{pend. with } \text{CDCl}_3$ SF=75.47 SW=18832.39 AQ=1.74 TD=131072 Units=ppm

7) ^1H and ^{13}C NMR spectra of (1*R*,2*S*)-(N-3-cyclohexa-1,4-dienyl-propyl)-norephedrine **5**

Parameters: Proton with CDCl₃ SF=400.03 SW=8223.68 AQ=1.99 TD=65536 Units=ppm

Parameters: C13pend.with CDCl₃ SF=100.59 SW=25125.63 AQ=1.30 TD=131072 Units=ppm

8) ^1H and ^{13}C NMR spectra of chloro-bridged η^6 -arene ruthenium (II) dimer **3**

M) Single X-ray data analysis data of 2

1) ORTEP plot of the molecular structure

2) Experimental Details

The asymmetric unit contains one complex. There are two complexes in the unit cell. There are several traditional and no traditional hydrogen bonds in the structure. The amine hydrogens were found and are involved in hydrogen bonding to the Cl and sulphonamide oxygen of neighbouring molecules. There is no intermolecular H bonding.

Each complex forms three contacts with its neighbour. Receiving two H bonds *via* the sulphonamide oxygens and donating the third *via* the alpha carbon of the sulphonamide (see structure at the end of the document). This motif is replicated forming a helix that travels along the "b" axis of the crystal. Additionally, the chlorine forms further contacts in the "a" direction that link the helices together. These contacts are listed below

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.851(19)	2.04(2)	2.888(4)	176(4)	N1-H1A...O5A
1.00	2.26	3.220(6)	159.7	C11-H11A...O5B
0.85(4)	2.67(4)	3.504(4)	168(4)	N1-H1B...Cl1
1.00	2.50	3.402(4)	149.7	C13-H13A...Cl1
0.99	2.91	3.712(5)	138.4	C6-H6B...Cl1

Least-squares planes (x,y,z in crystal coordinates) and deviations from them

(* indicates atom used to define plane)

- * 0.0012 (0.0031) C8
- * 0.0008 (0.0032) C9
- * -0.0046 (0.0028) C10
- * 0.0064 (0.0033) C11
- * -0.0045 (0.0033) C12
- * 0.0007 (0.0027) C13
- 1.6596 (0.0015) Ru1

Deviation of least squares plane through the benzene ring (C8 to C13) from ruthenium ion (1.6596(0.0015) Å from ring).

Crystal Data

C22 H23 Cl N2 O2 Ru S, M = 516.00,

Monoclinic, space group P2(1)
a = 6.4552(8), b = 14.6777(18), c = 11.1916(14) Å,
alpha = 90 deg., beta = 102.127(3) deg., gamma = 90 deg.,
U = 1036.7(2) Å³ (by least squares refinement on 4991 reflection positions),
T = 180(2) K, lambda = 0.71073 Å, Z = 2,
D(cal) = 1.653 Mg/m³, F(000) = 524.
mu(MoK-alpha) = 1.007 mm⁻¹.
Crystal character: orange block.
Crystal dimensions 0.22 x 0.16 x 0.10 mm,

Data Collection and Processing

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 180(2) K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986).
Maximum theta was 29.15 deg.
The hkl ranges were -8/ 8, -18/ 19, -6/ 15.
6730 reflections measured, 4663 unique [R(int) = 0.0257].
Absorption correction by Semi-empirical from equivalents;
minimum and maximum transmission factors: 0.68; 0.91.

No crystal decay

Structure Analysis and Refinement

Systematic absences indicated either space group P2 (1) or P2 (1)/m.
The former was chosen because of the known chirality of the system and shown to be correct by successful refinement.

The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods.

Hydrogen atoms were added at calculated positions and refined using a riding Model except the hydrogens on the amine, which were found in a difference synthesis. Anisotropic displacement parameters were used for all non-H atoms;
H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for the amine hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The chirality was checked by refinement of a delta-f'' multiplier. Absolute structure parameter x = 0.01(3).

Floating origin constraints were generated automatically.

The weighting scheme was calc $w = 1/[\sigma^2(F_o^2) + (0.0234P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.
Goodness-of-fit on F² was 0.945,
R1[for 3972 reflections with
 $I > 2\sigma(I)$] = 0.0326, wR2 = 0.0628.
Data / restraints / parameters 4663/ 2/ 269.
Extinction coefficient 0.0163(11).
Largest difference Fourier peak and hole 0.412 and -0.763 e.Å⁻³.

Refinement used SHELXTL (Sheldrick, 1997).

We thank EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

References

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3) Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U (eq)
Ru1	5428.6(4)	-4147.1(2)	5593.2(2)	18(1)
Cl1	1773.3(14)	-4684.5(7)	4822.7(9)	27(1)
N1	6278(6)	-5013(2)	4267(3)	17(1)
C2	5014(6)	-4805(3)	3020(4)	14(1)
C3	4980(6)	-3775(3)	2830(4)	16(1)
O5B	5792(5)	-1936.4(18)	2926(3)	35(1)
O5A	4366(5)	-1800(2)	4796(3)	38(1)
N4	5011(5)	-3329(2)	4021(3)	21(1)
S5	5683.7(17)	-2288.1(7)	4122.8(9)	26(1)
C6	8294(7)	-2210(4)	5021(4)	40(1)
C7	8334(8)	-2282(4)	6381(4)	44(1)
C8	7457(7)	-3160(3)	6752(4)	27(1)
C9	5466(7)	-3197(3)	7110(4)	28(1)
C10	4653(6)	-4027(4)	7394(3)	34(1)
C11	5769(10)	-4849(4)	7351(4)	39(1)
C12	7721(9)	-4812(4)	6988(4)	40(2)
C13	8571(6)	-3978(4)	6698(4)	32(1)
C14	5826(6)	-5320(2)	2019(3)	17(1)
C15	7811(6)	-5151(3)	1787(4)	24(1)
C16	8461(7)	-5552(3)	818(4)	30(1)
C17	7125(7)	-6148(3)	58(4)	31(1)
C18	5172(7)	-6333(3)	292(4)	35(1)
C19	4515(6)	-5923(3)	1260(4)	24(1)
C20	3047(6)	-3500(2)	1858(3)	18(1)
C21	3037(6)	-3645(3)	635(4)	28(1)
C22	1239(7)	-3423(3)	-247(4)	37(1)
C23	-508(7)	-3052(3)	74(4)	33(1)
C24	-470(7)	-2879(3)	1286(4)	29(1)
C25	1284(6)	-3109(3)	2176(4)	24(1)

4) Table 2. Bond lengths [Å] and angles [deg].

Ru1-N4	2.100(3)
Ru1-N1	2.112(3)
Ru1-C12	2.147(5)
Ru1-C13	2.156(4)
Ru1-C10	2.183(4)
Ru1-C8	2.187(4)
Ru1-C11	2.191(5)
Ru1-C9	2.193(5)
Ru1-Cl1	2.4655(10)
N1-C2	1.492(5)
N1-H1A	0.851(19)
N1-H1B	0.85(4)
C2-C3	1.526(5)
C2-C14	1.532(5)
C2-H2A	1.0000
C3-N4	1.482(5)
C3-C20	1.528(5)
C3-H3A	1.0000
O5B-S5	1.450(3)
O5A-S5	1.440(3)
N4-S5	1.586(3)
S5-C6	1.775(4)
C6-C7	1.520(6)
C6-H6A	0.9900
C6-H6B	0.9900
C7-C8	1.501(7)
C7-H7A	0.9900
C7-H7B	0.9900
C8-C13	1.407(6)
C8-C9	1.425(6)
C9-C10	1.389(8)
C9-H9A	1.0000
C10-C11	1.412(8)
C10-H10A	1.0000
C11-C12	1.404(8)
C11-H11A	1.0000
C12-C13	1.407(7)
C12-H12A	1.0000
C13-H13A	1.0000
C14-C15	1.382(5)
C14-C19	1.385(5)
C15-C16	1.375(6)
C15-H15A	0.9500
C16-C17	1.387(6)
C16-H16A	0.9500
C17-C18	1.367(6)
C17-H17A	0.9500
C18-C19	1.382(6)
C18-H18A	0.9500
C19-H19A	0.9500
C20-C21	1.384(5)
C20-C25	1.386(5)
C21-C22	1.395(6)
C21-H21A	0.9500
C22-C23	1.367(6)
C22-H22A	0.9500
C23-C24	1.374(6)
C23-H23A	0.9500

C24-C25	1.384(5)
C24-H24A	0.9500
C25-H25A	0.9500

N4-Ru1-N1	6.22(12)
N4-Ru1-C12	144.8(2)
N1-Ru1-C12	89.81(17)
N4-Ru1-C13	110.73(16)
N1-Ru1-C13	96.91(15)
C12-Ru1-C13	38.17(19)
N4-Ru1-C10	135.48(19)
N1-Ru1-C10	147.3(2)
C12-Ru1-C10	67.8(2)
C13-Ru1-C10	80.34(15)
N4-Ru1-C8	94.22(15)
N1-Ru1-C8	127.16(15)
C12-Ru1-C8	68.6(2)
C13-Ru1-C8	37.80(17)
C10-Ru1-C8	67.90(18)
N4-Ru1-C11	172.88(18)
N1-Ru1-C11	110.88(18)
C12-Ru1-C11	37.8(2)
C13-Ru1-C11	68.57(19)
C10-Ru1-C11	37.7(2)
C8-Ru1-C11	81.04(18)
N4-Ru1-C9	105.28(17)
N1-Ru1-C9	164.64(14)
C12-Ru1-C9	80.34(17)
C13-Ru1-C9	68.10(16)
C10-Ru1-C9	37.0(2)
C8-Ru1-C9	37.97(17)
C11-Ru1-C9	67.74(19)
N4-Ru1-Cl1	86.85(9)
N1-Ru1-Cl1	86.12(10)
C12-Ru1-Cl1	124.87(16)
C13-Ru1-Cl1	162.40(13)
C10-Ru1-Cl1	87.73(11)
C8-Ru1-Cl1	146.02(13)
C11-Ru1-Cl1	94.11(15)
C9-Ru1-Cl1	109.17(12)
C2-N1-Ru1	111.3(2)
C2-N1-H1A	117(3)
Ru1-N1-H1A	104(3)
C2-N1-H1B	109(3)
Ru1-N1-H1B	104(3)
H1A-N1-H1B	111(4)
N1-C2-C3	108.8(3)
N1-C2-C14	112.3(3)
C3-C2-C14	112.5(4)
N1-C2-H2A	107.7
C3-C2-H2A	107.7
C14-C2-H2A	107.7
N4-C3-C2	108.4(4)
N4-C3-C20	112.2(3)
C2-C3-C20	110.3(3)
N4-C3-H3A	108.6
C2-C3-H3A	108.6
C20-C3-H3A	108.6
C3-N4-S5	116.2(3)
C3-N4-Ru1	118.4(2)

S5-N4-Ru1	120.39(19)
O5A-S5-O5B	117.02(19)
O5A-S5-N4	109.50(19)
O5B-S5-N4	110.02(17)
O5A-S5-C6	105.4(2)
O5B-S5-C6	106.01(19)
N4-S5-C6	108.4(2)
C7-C6-S5	112.1(3)
C7-C6-H6A	109.2
S5-C6-H6A	109.2
C7-C6-H6B	109.2
S5-C6-H6B	109.2
H6A-C6-H6B	107.9
C8-C7-C6	114.1(4)
C8-C7-H7A	108.7
C6-C7-H7A	108.7
C8-C7-H7B	108.7
C6-C7-H7B	108.7
H7A-C7-H7B	107.6
C13-C8-C9	118.6(4)
C13-C8-C7	119.6(4)
C9-C8-C7	121.7(5)
C13-C8-Ru1	69.9(2)
C9-C8-Ru1	71.3(3)
C7-C8-Ru1	128.2(3)
C10-C9-C8	120.3(4)
C10-C9-Ru1	71.1(3)
C8-C9-Ru1	70.8(3)
C10-C9-H9A	119.2
C8-C9-H9A	119.2
Ru1-C9-H9A	119.2
C9-C10-C11	121.5(4)
C9-C10-Ru1	71.9(3)
C11-C10-Ru1	71.5(3)
C9-C10-H10A	118.6
C11-C10-H10A	118.6
Ru1-C10-H10A	118.6
C12-C11-C10	118.2(5)
C12-C11-Ru1	69.4(3)
C10-C11-Ru1	70.9(3)
C12-C11-H11A	120.3
C10-C11-H11A	120.3
Ru1-C11-H11A	120.3
C11-C12-C13	121.2(5)
C11-C12-Ru1	72.8(3)
C13-C12-Ru1	71.3(3)
C11-C12-H12A	118.9
C13-C12-H12A	118.9
Ru1-C12-H12A	118.9
C8-C13-C12	120.3(4)
C8-C13-Ru1	72.3(2)
C12-C13-Ru1	70.5(3)
C8-C13-H13A	119.3
C12-C13-H13A	119.3
Ru1-C13-H13A	119.3
C15-C14-C19	118.1(3)
C15-C14-C2	121.5(3)
C19-C14-C2	120.3(3)
C16-C15-C14	121.3(4)
C16-C15-H15A	119.3
C14-C15-H15A	119.3
C15-C16-C17	120.0(4)

C15-C16-H16A	120.0
C17-C16-H16A	120.0
C18-C17-C16	119.1(4)
C18-C17-H17A	120.5
C16-C17-H17A	120.5
C17-C18-C19	120.8(4)
C17-C18-H18A	119.6
C19-C18-H18A	119.6
C18-C19-C14	120.6(4)
C18-C19-H19A	119.7
C14-C19-H19A	119.7
C21-C20-C25	119.0(3)
C21-C20-C3	119.8(3)
C25-C20-C3	121.2(3)
C20-C21-C22	119.6(4)
C20-C21-H21A	120.2
C22-C21-H21A	120.2
C23-C22-C21	121.1(4)
C23-C22-H22A	119.4
C21-C22-H22A	119.4
C22-C23-C24	119.2(4)
C22-C23-H23A	120.4
C24-C23-H23A	120.4
C23-C24-C25	120.5(4)
C23-C24-H24A	119.7
C25-C24-H24A	119.7
C24-C25-C20	120.5(4)
C24-C25-H25A	119.7
C20-C25-H25A	119.7

Symmetry transformations used to generate equivalent atoms.

5) Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hk a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru1	19(1)	21(1)	11(1)	-3(1)	-1(1)	3(1)
Cl1	19(1)	39(1)	22(1)	-4(1)	4(1)	0(1)
N1	16(2)	18(2)	14(2)	1(1)	0(1)	-3(1)
C2	16(2)	11(2)	15(2)	0(2)	0(2)	3(2)
C3	19(2)	15(2)	13(2)	-4(2)	1(2)	2(2)
O5B	56(2)	21(2)	25(2)	3(1)	4(2)	-7(1)
O5A	57(2)	19(2)	38(2)	-15(1)	12(2)	5(1)
N4	31(2)	15(2)	17(2)	-2(1)	1(2)	4(2)
S5	38(1)	16(1)	22(1)	-5(1)	3(1)	-1(1)
C6	43(3)	41(3)	32(3)	-3(2)	2(2)	-21(2)
C7	51(3)	51(3)	26(2)	-3(2)	-2(2)	-22(2)
C8	28(2)	38(3)	14(2)	-9(2)	-2(2)	-7(2)
C9	22(2)	40(3)	20(2)	-9(2)	-2(2)	13(2)
C10	31(2)	57(4)	15(2)	-8(3)	5(2)	-4(3)
C11	64(4)	36(3)	10(2)	5(2)	-8(2)	-11(3)
C12	56(4)	37(3)	17(2)	-9(2)	-16(2)	23(3)
C13	26(2)	49(4)	15(2)	-14(2)	-6(2)	7(2)
C14	27(2)	14(2)	9(2)	0(2)	-1(2)	-1(2)
C15	20(2)	26(2)	23(2)	-5(2)	1(2)	1(2)
C16	28(2)	31(2)	34(3)	3(2)	13(2)	9(2)
C17	52(3)	27(2)	18(2)	-2(2)	14(2)	12(2)
C18	45(3)	35(3)	23(2)	-16(2)	3(2)	-6(2)
C19	27(2)	21(2)	23(2)	-7(2)	5(2)	-8(2)
C20	20(2)	18(2)	15(2)	1(2)	-2(2)	-1(2)
C21	33(2)	29(2)	20(2)	-1(2)	4(2)	6(2)
C22	51(3)	38(3)	17(2)	1(2)	-4(2)	4(2)
C23	26(2)	39(3)	28(2)	2(2)	-8(2)	4(2)
C24	24(2)	31(2)	29(2)	15(2)	2(2)	4(2)
C25	27(2)	24(2)	19(2)	5(2)	3(2)	3(2)

6) Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

	x	y	z	U (eq)
H1A	6150(60)	-5546(17)	4540(40)	25
H1B	7580(60)	-4880(30)	4290(40)	25
H2A	3525	-5007	2990	17
H3A	6288	-3594	2543	19
H6A	9171	-2704	4783	47
H6B	8925	-1621	4854	47
H7A	9816	-2216	6838	53
H7B	7508	-1770	6620	53
H9A	4519	-2651	6978	34
H10A	3131	-4058	7456	41
H11A	5053	-5448	7402	47
H12A	8381	-5392	6785	48
H13A	9815	-3981	6295	38
H15A	8745	-4750	2308	28
H16A	9825	-5421	669	36
H17A	7561	-6425	-617	38
H18A	4257	-6747	-217	42
H19A	3150	-6056	1408	29
H21A	4248	-3895	397	33
H22A	1228	-3532	-1085	44
H23A	-1735	-2915	-533	40
H24A	-1656	-2598	1513	34
H25A	1279	-2999	3012	28

Structure showing the interactions between 2 molecules

Interaction between two molecules with amine sulphonamide H bonding (NH1a ... O5a) and CH hydrogen bonds between the sulphonamide and aromatic H (C11-H11a ... O5a) and the chlorine and an alpha proton of the sulphonamide (C6-H6a ... C11).

N) References

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