

## Supporting Information

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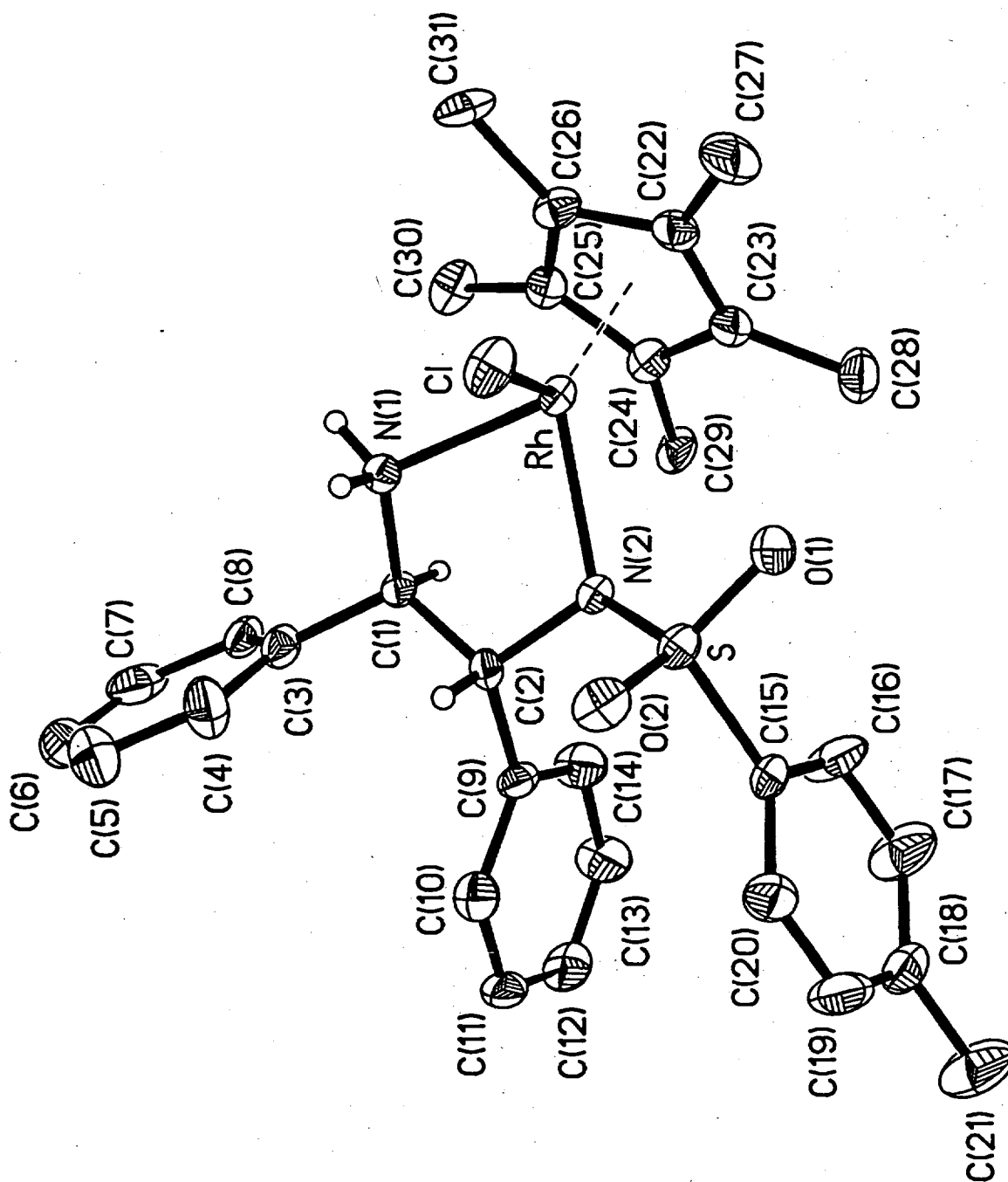


Table 1. Crystal data and structure refinement for 1b.

Identification code	1b	S-4
Empirical formula	$C_{31}H_{36}ClN_2O_2RhS$	
Formula weight	639.04	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	$a = 8.350(3) \text{ \AA}$ $\alpha = 90^\circ$ $b = 16.272(5) \text{ \AA}$ $\beta = 90^\circ$ $c = 21.510(6) \text{ \AA}$ $\gamma = 90^\circ$	
Volume, Z	$2923(2) \text{ \AA}^3$ , 4	
Density (calculated)	$1.452 \text{ Mg/m}^3$	
Absorption coefficient	$0.778 \text{ mm}^{-1}$	
F(000)	1320	
Crystal size	0.44 x 0.30 x 0.16 mm	
$\theta$ range for data collection	1.57 to $22.54^\circ$	
Limiting indices	$0 \leq h \leq 9$ , $0 \leq k \leq 17$ , $0 \leq l \leq 23$	
Reflections collected	2215	
Independent reflections	2215 ( $R_{int} = 0.0000$ )	
Absorption correction	Semi-empirical from psi-scans	
Max. and min. transmission	0.9939 and 0.9190	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	2215 / 0 / 344	
Goodness-of-fit on $F^2$	1.187	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0292$ , $wR2 = 0.0800$	
R indices (all data)	$R1 = 0.0371$ , $wR2 = 0.0946$	
Absolute structure parameter	-0.03(7)	
Largest diff. peak and hole	0.558 and $-0.463 \text{ e\AA}^{-3}$	

Table 2. Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic S-5 displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for 1.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Rh	2779(1)	1579(1)	8935(1)	17(1)
S	-55(2)	2084(1)	7973(1)	21(1)
Cl	539(2)	1896(1)	9601(1)	28(1)
O(1)	-419(7)	1244(3)	8117(3)	27(1)
O(2)	-1111(6)	2715(3)	8209(3)	28(1)
N(1)	3460(8)	2799(4)	9117(3)	21(2)
N(2)	1800(7)	2244(4)	8138(3)	16(2)
C(1)	3785(10)	3216(4)	8518(3)	18(2)
C(2)	2283(11)	3114(4)	8117(3)	20(2)
C(3)	4309(11)	4100(5)	8610(4)	25(2)
C(4)	3240(11)	4715(5)	8779(4)	38(2)
C(5)	3771(13)	5509(6)	8882(5)	46(3)
C(6)	5369(13)	5703(6)	8809(4)	39(3)
C(7)	6442(13)	5101(6)	8641(4)	40(3)
C(8)	5894(11)	4295(5)	8544(4)	25(2)
C(9)	2591(9)	3435(5)	7464(3)	21(2)
C(10)	1866(10)	4153(5)	7245(4)	31(2)
C(11)	2172(12)	4443(5)	6657(4)	32(2)
C(12)	3257(11)	4042(5)	6274(4)	32(2)
C(13)	4011(12)	3343(6)	6482(4)	39(2)
C(14)	3688(11)	3042(5)	7076(4)	33(2)
C(15)	-237(9)	2156(5)	7142(4)	21(2)
C(16)	750(12)	1703(6)	6757(4)	41(2)
C(17)	570(13)	1740(6)	6123(4)	51(3)
C(18)	-538(11)	2259(6)	5856(4)	30(2)
C(19)	-1498(12)	2705(6)	6237(4)	41(2)
C(20)	-1361(11)	2663(5)	6879(4)	33(2)
C(21)	-701(14)	2308(7)	5157(4)	56(3)
C(22)	2829(12)	287(5)	9197(4)	24(2)
C(23)	3138(10)	348(5)	8556(4)	23(2)
C(24)	4551(10)	849(5)	8477(4)	23(2)
C(25)	5131(9)	1077(5)	9078(4)	22(2)
C(26)	4039(10)	752(5)	9523(4)	23(2)
C(27)	1458(12)	-156(6)	9502(4)	39(2)
C(28)	2261(12)	-87(5)	8042(4)	31(2)
C(29)	5301(11)	1031(5)	7857(4)	29(2)
C(30)	6611(9)	1531(6)	9209(4)	31(2)
C(31)	4202(12)	833(6)	10217(4)	36(2)

Table 3. Bond lengths [Å] and angles [°] for 1b.

S-6

Rh-N(1)	2.103(6)	Rh-C(26)	2.126(8)
Rh-C(24)	2.138(8)	Rh-C(25)	2.150(8)
Rh-C(22)	2.176(8)	Rh-C(23)	2.183(8)
Rh-N(2)	2.184(6)	Rh-Cl	2.411(2)
S-O(1)	1.434(6)	S-O(2)	1.446(6)
S-N(2)	1.611(6)	S-C(15)	1.796(8)
N(1)-C(1)	1.481(9)	N(2)-C(2)	1.473(9)
C(1)-C(3)	1.516(11)	C(1)-C(2)	1.531(11)
C(2)-C(9)	1.520(10)	C(3)-C(8)	1.368(13)
C(3)-C(4)	1.390(12)	C(4)-C(5)	1.384(12)
C(5)-C(6)	1.381(14)	C(6)-C(7)	1.377(14)
C(7)-C(8)	1.405(12)	C(9)-C(14)	1.394(11)
C(9)-C(10)	1.399(11)	C(10)-C(11)	1.374(11)
C(11)-C(12)	1.387(12)	C(12)-C(13)	1.375(12)
C(13)-C(14)	1.394(12)	C(15)-C(20)	1.372(11)
C(15)-C(16)	1.381(12)	C(16)-C(17)	1.374(12)
C(17)-C(18)	1.379(13)	C(18)-C(19)	1.357(13)
C(18)-C(21)	1.511(12)	C(19)-C(20)	1.388(12)
C(22)-C(23)	1.406(11)	C(22)-C(26)	1.444(12)
C(22)-C(27)	1.503(12)	C(23)-C(24)	1.445(12)
C(23)-C(28)	1.503(11)	C(24)-C(25)	1.429(11)
C(24)-C(29)	1.503(11)	C(25)-C(26)	1.423(11)
C(25)-C(30)	1.467(11)	C(26)-C(31)	1.504(11)
N(1)-Rh-C(26)	110.6(3)	N(1)-Rh-C(24)	115.0(3)
C(26)-Rh-C(24)	65.1(3)	N(1)-Rh-C(25)	94.9(3)
C(26)-Rh-C(25)	38.9(3)	C(24)-Rh-C(25)	38.9(3)
N(1)-Rh-C(22)	149.1(3)	C(26)-Rh-C(22)	39.2(3)
C(24)-Rh-C(22)	64.5(3)	C(25)-Rh-C(22)	65.1(3)
N(1)-Rh-C(23)	154.0(3)	C(26)-Rh-C(23)	64.7(3)
C(24)-Rh-C(23)	39.0(3)	C(25)-Rh-C(23)	65.1(3)
C(22)-Rh-C(23)	37.6(3)	N(1)-Rh-N(2)	77.3(2)
C(26)-Rh-N(2)	164.9(3)	C(24)-Rh-N(2)	100.0(3)
C(25)-Rh-N(2)	130.0(3)	C(22)-Rh-N(2)	133.5(3)
C(23)-Rh-N(2)	102.3(3)	N(1)-Rh-Cl	84.1(2)
C(26)-Rh-Cl	99.6(2)	C(24)-Rh-Cl	158.3(2)
C(25)-Rh-Cl	134.8(2)	C(22)-Rh-Cl	93.9(2)
C(23)-Rh-Cl	121.6(2)	N(2)-Rh-Cl	94.0(2)
O(1)-S-O(2)	118.2(4)	O(1)-S-N(2)	108.0(4)
O(2)-S-N(2)	113.2(3)	O(1)-S-C(15)	105.0(4)
O(2)-S-C(15)	104.6(4)	N(2)-S-C(15)	106.9(4)
C(1)-N(1)-Rh	108.6(4)	C(2)-N(2)-S	114.3(5)
C(2)-N(2)-Rh	113.5(5)	S-N(2)-Rh	117.0(3)
N(1)-C(1)-C(3)	111.9(6)	N(1)-C(1)-C(2)	106.9(6)
C(3)-C(1)-C(2)	114.4(6)	N(2)-C(2)-C(9)	113.9(6)
N(2)-C(2)-C(1)	108.1(6)	C(9)-C(2)-C(1)	110.1(6)
C(8)-C(3)-C(4)	118.8(8)	C(8)-C(3)-C(1)	119.1(8)
C(4)-C(3)-C(1)	122.1(8)	C(5)-C(4)-C(3)	120.6(9)
C(6)-C(5)-C(4)	120.4(9)	C(7)-C(6)-C(5)	119.7(9)
C(6)-C(7)-C(8)	119.5(9)	C(3)-C(8)-C(7)	121.1(9)
C(14)-C(9)-C(10)	117.7(7)	C(14)-C(9)-C(2)	120.5(7)
C(10)-C(9)-C(2)	121.7(7)	C(11)-C(10)-C(9)	121.2(8)
C(10)-C(11)-C(12)	120.3(8)	C(13)-C(12)-C(11)	119.7(7)
C(12)-C(13)-C(14)	120.0(8)	C(13)-C(14)-C(9)	121.0(8)
C(20)-C(15)-C(16)	118.8(8)	C(20)-C(15)-S	120.4(8)

C(16)-C(15)-S	120.8(6)	C(17)-C(16)-C(15)	120.5(8)	S-7
C(16)-C(17)-C(18)	121.0(9)	C(19)-C(18)-C(17)	118.1(8)	
C(19)-C(18)-C(21)	121.3(9)	C(17)-C(18)-C(21)	120.6(9)	
C(18)-C(19)-C(20)	121.9(9)	C(15)-C(20)-C(19)	119.7(9)	
C(23)-C(22)-C(26)	108.1(8)	C(23)-C(22)-C(27)	127.0(8)	
C(26)-C(22)-C(27)	124.8(7)	C(23)-C(22)-Rh	71.5(5)	
C(26)-C(22)-Rh	68.5(4)	C(27)-C(22)-Rh	124.2(6)	
C(22)-C(23)-C(24)	107.7(8)	C(22)-C(23)-C(28)	126.8(8)	
C(24)-C(23)-C(28)	125.3(7)	C(22)-C(23)-Rh	70.9(5)	
C(24)-C(23)-Rh	68.8(4)	C(28)-C(23)-Rh	129.7(6)	
C(25)-C(24)-C(23)	108.5(7)	C(25)-C(24)-C(29)	127.6(7)	
C(23)-C(24)-C(29)	123.8(7)	C(25)-C(24)-Rh	71.0(5)	
C(23)-C(24)-Rh	72.2(5)	C(29)-C(24)-Rh	126.0(6)	
C(26)-C(25)-C(24)	107.1(7)	C(26)-C(25)-C(30)	126.7(7)	
C(24)-C(25)-C(30)	126.1(7)	C(26)-C(25)-Rh	69.6(5)	
C(24)-C(25)-Rh	70.1(5)	C(30)-C(25)-Rh	127.3(6)	
C(25)-C(26)-C(22)	108.4(7)	C(25)-C(26)-C(31)	125.2(8)	
C(22)-C(26)-C(31)	126.2(8)	C(25)-C(26)-Rh	71.5(4)	
C(22)-C(26)-Rh	72.3(5)	C(31)-C(26)-Rh	125.5(6)	

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for lb.

S-8

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [ (ha^*)^2 U_{11} + \dots + 2hka^* b^* U_{12} ]$$

	U11	U22	U33	U23	U13	U12
Rh	16(1)	21(1)	14(1)	-1(1)	0(1)	-1(1)
S	17(1)	26(1)	19(1)	-2(1)	-1(1)	-1(1)
Cl	24(1)	40(1)	21(1)	-6(1)	5(1)	-2(1)
O(1)	27(3)	25(3)	30(3)	1(3)	-5(3)	-6(3)
O(2)	21(3)	38(3)	25(3)	-1(3)	3(3)	7(3)
N(1)	24(4)	19(3)	19(4)	1(3)	-3(3)	-3(3)
N(2)	14(4)	21(3)	14(3)	-1(3)	1(3)	-2(3)
C(1)	24(4)	18(4)	11(4)	1(3)	3(3)	-4(3)
C(2)	26(4)	16(4)	19(4)	-2(3)	-2(4)	-4(4)
C(3)	29(5)	25(5)	20(4)	1(4)	-2(4)	-10(4)
C(4)	40(6)	29(5)	43(6)	-12(4)	-1(4)	0(4)
C(5)	55(7)	32(5)	49(6)	-8(5)	-7(6)	3(5)
C(6)	60(7)	27(5)	30(6)	6(4)	-10(5)	-18(5)
C(7)	43(6)	46(6)	32(5)	19(5)	-14(5)	-16(5)
C(8)	29(5)	28(5)	19(4)	1(4)	-5(4)	-11(4)
C(9)	23(4)	24(4)	17(4)	4(3)	-4(3)	-5(4)
C(10)	33(6)	28(5)	32(5)	-1(4)	-5(4)	-5(4)
C(11)	42(5)	25(4)	30(5)	11(4)	-14(5)	-9(5)
C(12)	42(6)	39(5)	16(4)	4(4)	5(4)	-10(5)
C(13)	61(6)	39(5)	18(4)	1(4)	13(4)	10(6)
C(14)	43(6)	35(5)	22(5)	0(4)	6(4)	12(5)
C(15)	17(4)	24(4)	21(4)	-2(4)	-4(4)	-3(4)
C(16)	47(6)	56(6)	21(4)	-4(5)	-12(4)	26(6)
C(17)	60(6)	69(7)	23(5)	-11(5)	-4(5)	21(6)
C(18)	28(5)	38(5)	26(5)	0(4)	-7(4)	-6(4)
C(19)	44(6)	45(6)	33(5)	10(4)	-12(5)	9(5)
C(20)	34(5)	30(5)	35(6)	-1(4)	-6(4)	8(5)
C(21)	65(8)	81(8)	20(5)	1(5)	-6(5)	13(7)
C(22)	24(4)	19(4)	29(4)	3(3)	-4(4)	6(4)
C(23)	28(5)	21(4)	21(4)	2(3)	1(4)	-1(4)
C(24)	22(5)	27(5)	22(4)	-4(4)	0(4)	7(4)
C(25)	17(4)	23(4)	25(5)	-3(4)	-3(4)	6(4)
C(26)	24(5)	28(5)	16(4)	0(4)	4(4)	6(4)
C(27)	49(6)	32(5)	36(5)	10(5)	7(5)	-10(5)
C(28)	33(5)	27(4)	32(5)	-8(4)	-5(5)	0(4)
C(29)	37(5)	34(5)	15(4)	-6(4)	3(4)	-2(4)
C(30)	19(4)	43(5)	31(4)	-10(5)	-2(4)	8(5)
C(31)	45(6)	45(6)	17(5)	12(4)	-5(4)	1(5)



Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic S-9 displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 1b.

	x	y	z	U(eq)
H(1B)	2654(8)	3068(4)	9326(3)	80
H(1C)	4364(8)	2807(4)	9362(3)	80
H(1A)	4680(10)	2916(4)	8308(3)	80
H(2A)	1405(11)	3450(4)	8306(3)	80
H(4A)	2135(11)	4589(5)	8825(4)	80
H(5A)	3031(13)	5923(6)	9003(5)	80
H(6A)	5727(13)	6251(6)	8875(4)	80
H(7A)	7544(13)	5229(6)	8590(4)	80
H(8A)	6636(11)	3878(5)	8430(4)	80
H(10A)	1150(10)	4446(5)	7507(4)	80
H(11A)	1636(12)	4921(5)	6511(4)	80
H(12A)	3479(11)	4249(5)	5870(4)	80
H(13A)	4752(12)	3065(6)	6222(4)	80
H(14A)	4223(11)	2563(5)	7219(4)	80
H(16A)	1560(12)	1364(6)	6932(4)	80
H(17A)	1219(13)	1403(6)	5865(4)	80
H(19A)	-2285(12)	3055(6)	6060(4)	80
H(20A)	-2043(11)	2985(5)	7136(4)	80
H(21A)	89(14)	1945(7)	4962(4)	80
H(21B)	-517(14)	2875(7)	5021(4)	80
H(21C)	-1782(14)	2137(7)	5035(4)	80
H(27A)	1541(12)	-97(6)	9954(4)	80
H(27B)	1498(12)	-740(6)	9392(4)	80
H(27C)	443(12)	81(6)	9359(4)	80
H(28A)	2727(12)	68(5)	7641(4)	80
H(28B)	1128(12)	70(5)	8051(4)	80
H(28C)	2356(12)	-683(5)	8099(4)	80
H(29A)	4636(11)	799(5)	7526(4)	80
H(29B)	6373(11)	786(5)	7840(4)	80
H(29C)	5384(11)	1627(5)	7802(4)	80
H(30A)	7130(9)	1681(6)	8816(4)	80
H(30B)	7336(9)	1184(6)	9453(4)	80
H(30C)	6357(9)	2030(6)	9444(4)	80
H(31A)	3300(12)	557(6)	10420(4)	80
H(31B)	4207(12)	1416(6)	10331(4)	80
H(31C)	5207(12)	577(6)	10351(4)	80

## B. Preparation of the Chiral Rhodium Complexes

### 1. (*S*)-Cp\*RhCl[(1*R*,2*R*)-*p*-TsNCH(C<sub>6</sub>H<sub>5</sub>)CH(C<sub>6</sub>H<sub>5</sub>)NH<sub>2</sub>] (1b).

To a solution of [RhCl<sub>2</sub>Cp\*]<sub>2</sub> (309 mg, 0.5 mmol) and (1*R*,2*R*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethylenediamine [(*R,R*)-TsDPEN] (366 mg, 1 mmol) in dichloromethane (10 mL), triethylamine (202 mg, 2 mmol) was added under nitrogen. The solution was stirred for 20 min at 20 °C, washed with water (5 mL), and dried over MgSO<sub>4</sub>. Removal of solvents gave the crude product. Recrystallization from chloroform–hexanes afforded red crystals (575 mg, 91%): mp 221–224 °C (dec); [α]<sub>D</sub><sup>20</sup> –224° (c 0.3, CHCl<sub>3</sub>); IR (KBr): 3449 (H-N, br), 3281, 3209 (H-N, M) cm<sup>-1</sup>; ESIMS: *m/z* (%) 639 (1) [M<sup>+</sup> + 1], 603 [M<sup>+</sup> + 1 - HCl], 367 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.86 (s, 15H; CH<sub>3</sub> in Cp\*), 2.22 (s, 3H; CH<sub>3</sub> in *p*-Ts), 3.32 (m, 1H; *NHH*), 3.71 (m, 1H; *HCNH*<sub>2</sub>), 3.97 (d, *J* = 11 Hz, 1H; *HCN-p*-Ts), 4.03 (m, 1H; *NHH*), 6.64–7.61 (m, 14H; ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 9.65 (CH<sub>3</sub> in Cp\*); 21.2 (CH<sub>3</sub> in *p*-Ts), 69.4 (CNH<sub>2</sub>), 71.8 (CN-*p*-Ts), 93.9, 94.0, 126.4, 126.7, 127.0, 127.7, 126.2, 128.4, 128.6, 139.2, 139.3, 139.7, 140.6. Anal. Calcd for C<sub>31</sub>H<sub>36</sub>ClN<sub>2</sub>O<sub>2</sub>RhS: C, 58.26; H, 5.68; Cl, 5.55; N, 4.38; S, 5.02. Found: C, 58.18; H, 5.67; Cl, 5.69; N, 4.29; S, 4.92.

2. (*R*)-Cp\*RhCl[(1*S*,2*S*)-*p*-TsNCH(C<sub>6</sub>H<sub>5</sub>)CH(C<sub>6</sub>H<sub>5</sub>)NH<sub>2</sub>] (1a). mp 221–224 °C (dec); [α]<sub>D</sub><sup>20</sup> +222° (c 0.3, CHCl<sub>3</sub>). The IR and NMR data were identical with those for the (*S*)-catalyst in part 1, above.

## II. Experimental Procedure for Transfer Hydrogenation

**Method 1: Reduction using Preformed Catalyst.** To a solution of the appropriate imine (4 mmol) and the preformed catalyst (0.02 mmol)\* in dry dichloromethane (or other solvent) (20 mL) was added at 20 °C, under nitrogen, an azeotropic mixture of 5:2 formic acid–triethylamine (2 mL). The mixture was stirred until the substrate disappeared as determined by TLC. Na<sub>2</sub>CO<sub>3</sub> (0.5 M) was added to render the mixture basic, and the mixture was extracted with dichloromethane. The combined organic phase was washed with brine, dried over MgSO<sub>4</sub>, and concentrated to give a crude product that was purified by column chromatography on silica gel. (\*Some experiments were conducted with 0.04 and 0.004 mmol of the Rh-catalyst. See Table 1 in text of paper.)

**Method 2: Reduction using Catalyst Generated *in situ*.\*** A solution of [RhCl<sub>2</sub>Cp\*]<sub>2</sub> (0.01 mmol), (*R,R*)-TsDPEN (0.022 mmol, 1.1 equiv) and triethylamine (0.048 mmol, 2.4 equiv) in dry dichloromethane (or other solvent) (2 mL) was stirred for 20 min under nitrogen at 20 °C. A solution of the appropriate imine (4 mmol) in dichloromethane (18 mL) and an azeotropic mixture of 5:2 formic acid–triethylamine (2 mL) were added to the mixture with continued stirring. The mixture was stirred until the substrate disappeared as determined by TLC. Workup and purification of the product were carried out as described in Method 1. (\*One experiment used 0.04 mmol of the Ru-based catalyst. See Table 1 and refs 2c and 2f in text of paper.)

### C. HPLC analysis, optical rotation data and NMR data of hydrogenation products

HPLC column: Chiralcel OD (25 × 1 cm).

Solvents: A: 2-propanol, B: hexanes–diethylamine (1000:1), C: hexanes.

Flow rate: 3 mL/min.

Temperature: 20 °C

**General.** Optical rotations are quoted for the unpurified reduction mixtures, except for **7d**, which was the pure enantiomer. All physicochemical and spectral data for known compounds matched those reported in the cited references.

**(S)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline [(S)-3a].**  $[\alpha]_D^{20} -41^\circ$  (*c* 0.8, ethanol) (lit. S-isomer,  $[\alpha]_D^{21} -59.5^\circ$  (*c* 4.39, ethanol), Battersby, A.R.; Edwards, T. *P. J. Chem. Soc.* **1960**, 1214–1221), 90% ee by HPLC (A:B = 30:70, S isomer 14.9 min, R isomer 18.4);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.44 (d, 3H,  $J = 6.7$  Hz,  $\text{CH}_3$ ), 2.03 (br; 1H, NH), 2.62–3.30 (m, 4H,  $\text{CH}_2$ ), 3.850, 3.854 (2s, 6H,  $\text{OCH}_3$ ), 4.05 (m, 1H, CH), 6.57, 6.63 (2s, 2H, ArH).

**(R)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline [(R)-3a].**  $[\alpha]_D^{20} +40^\circ$  (*c* 0.5, ethanol) (lit. S-isomer,  $[\alpha]_D^{21} -59.5^\circ$  (*c* 4.39, ethanol), Battersby, A.R.; Edwards, T. *P. J. Chem. Soc.* **1960**, 1214–1221), 89% ee.

**(R)-6,7-Dimethoxy-1-ethyl-1,2,3,4-tetrahydroisoquinoline [(R)-3b].**  $[\alpha]_D^{20} +44^\circ$  (*c* 0.3, dichloromethane) (lit. S-isomer,  $[\alpha]_D^{20} -51.9^\circ$  (*c* 2.1, dichloromethane), Polniaszek, R. P.; Kaufman, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4859–4863), 83% ee by HPLC (A:B = 20:80, S isomer 9.2 min, R isomer 10.3 min);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.01 (t, 3H,  $J = 6.4$  Hz,  $\text{CH}_3$ ), 1.69–1.89 (m; 3H, NH,  $\text{CH}_2$ ), 2.65–3.23 (m, 4H,  $\text{CH}_2$ ), 3.833, 3.837 (2s, 6H,  $\text{OCH}_3$ ), 3.83 (m, 1H, CH), 6.56; 6.62 (2s, 2H; ArH).

**(R)-6,7-Dimethoxy-1-isopropyl-1,2,3,4-tetrahydroisoquinoline [(R)-3c].**  $[\alpha]_D^{20} +106^\circ$  (*c* 0.93, dichloromethane) (lit. S-isomer,  $[\alpha]_D -104.3^\circ$  (*c* 0.9, dichloromethane), Polniaszek, R. P.; Kaufman, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4859–4863), 99% ee by HPLC (A:B = 10:90, S isomer 9.8 min, R isomer 10.5);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.74 (d, 3H,  $J = 6.8$  Hz,  $\text{CH}_3$ ), 1.12 (d, 3H,  $J = 6.9$  Hz,  $\text{CH}_3$ ), 1.69 (br; 1H, NH), 2.26–3.29 (m, 5H, CH,  $\text{CH}_2$ ), 3.84 (s, 6H;  $\text{OCH}_3$ ), 3.87 (m, 1H, CH), 6.56, 6.65 (2s, 2H; ArH).

**(+)-6,7-Dimethoxy-1-cyclohexyl-1,2,3,4-tetrahydroisoquinoline [(+)-3d].**  $[\alpha]_D^{20} +84^\circ$  (*c* 0.46, chloroform), 97% ee by HPLC (A:B = 10:90, minor isomer, 11.4 min, major isomer 12.4 min).  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.03–1.85 (m, 12H, cyclohexyl, NH), 2.54–3.30 (m, 4H,  $\text{CH}_2$ ), 3.848, 3.853 (2s, 6H,  $\text{OCH}_3$ ), 3.85 (m, 1H, CH), 6.56, 6.65 (2s, 2H,

ArH). Lit. (racemic) St. Georgiev, V.; Carlson, R. P.; Van Inwegen, R. G.; Khandwala, A. *J. Med. Chem.* **1979**, *22*, 348–352.

**(R)-6,7-Dimethoxy-1-phenyl-1,2,3,4-tetrahydroisoquinoline [(R)-3e]**.  $[\alpha]_D^{20} +2.3^\circ$  (c 0.53, chloroform) (lit. R-isomer,  $[\alpha]_D^{23} +16.3^\circ$  (c 1.04, chloroform), Uematsu, N; Fujii, Akio.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917), 4.4% ee by HPLC (A:B = 10:90, S isomer 19.2 min, R isomer 25.6 min);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.08 (br, 1H; NH), 2.71–3.24 (m, 4H,  $\text{CH}_2$ ), 3.63, 3.87 (2s, 6H,  $\text{OCH}_3$ ), 5.05 (s, 1H, CH), 6.24, 6.63 (2s, 2H, ArH), 7.24–7.35 (m, 5H, ArH).

**(R)-6,7-Dimethoxy-1-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydroisoquinoline [(R)-3f]**.  $[\alpha]_D^{20} +2.7^\circ$  (c 0.53, chloroform) (lit. S-isomer,  $[\alpha]_D^{25} -34.0^\circ$  (c 1.0, chloroform), Brossi, A.; Teitel, S. *Helv. Chim. Acta* **1971**, *54*, 1564–71), 3.2% ee by HPLC (A:B = 40:60, S isomer 14.7 min, R isomer 20.2 min);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.46 (br, 1H, NH), 2.71–3.26 (m, 4H,  $\text{CH}_2$ ), 3.65, 3.83, (2s, 6H,  $\text{OCH}_3$ ), 3.87 (s, 6H,  $\text{OCH}_3$ ), 4.99 (s, 1H, CH), 6.27, 6.63 (2s, 2H, ArH), 6.78–6.82 (m, 3H, ArH).

**(S)-N-Benzyl-1-phenylethylamine [(S)-5a]**.  $[\alpha]_D^{20} -3.3^\circ$  (c 1.0, ethanol) (lit. S-isomer,  $[\alpha]_D^{21} -53.6^\circ$  (c 3.8, ethanol), Cain, C. M.; Cousins, R. P. C.; Coumbarides, G.; Simpkins, N. S. *Tetrahedron* **1990**, *46*, 523–544), 8.4% ee by HPLC (A:B = 0.2:99.8, S isomer 15.7 min, R isomer 13.5 min).  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.37 (d, 3H,  $J = 6.6$  Hz,  $\text{CH}_3$ ), 1.73 (br, 1H, NH), 3.58, 3.66 (AB, 2H,  $\text{NCH}_2$ ), 3.81 (q, 1H,  $J = 6.6$  Hz, CH), 7.21–7.36 (m, 10H, ArH).

**(-)-N-Benzyl-1-(2-naphthyl)ethylamine [(-)-5b]**.  $[\alpha]_D^{20} -2.0^\circ$  (c 1.0,  $\text{CHCl}_3$ ), 8.4% ee by HPLC (A:B = 1:99, major isomer 11.9 min, minor isomer 10.5 min).  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.43 (d, 3H,  $J = 6.5$  Hz,  $\text{CH}_3$ ), 1.77 (br, 1H, NH), 3.60, 3.68 (AB, 2H,  $\text{NCH}_2$ ), 3.97 (q, 1H,  $J = 6.5$  Hz, CH), 7.19–7.85 (m, 12H, ArH). (+)-Isomer: Lit. ref 2c in text of the paper.

**(R)-3-Methyl-2,3-dihydrobenzo[d]isothiazoline 1,1-Dioxide [(R)-7a]**.  $[\alpha]_D^{20} +20^\circ$  (c 0.88, chloroform) (lit. S-isomer,  $[\alpha]_D^{20} -30^\circ$  (c 1.21, chloroform), Oppolzer, W.; Wills, M.; Starkeman, C.; Bernardinelli, G. *Tetrahedron Lett.* **1990**, *29*, 4117–4120), 68% ee by HPLC (A:C = 20:80, S isomer 14.8 min, R isomer 17.4 min);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.60 (d, 3H,  $J = 6.8$  Hz,  $\text{CH}_3$ ), 4.78 (q, 1H,  $J = 6.7$  Hz, CH), 5.11 (br, 1H, NH), 7.37–7.76 (m, 4H, ArH).

**(+)-3-Butyl-2,3-dihydrobenzo[d]isothiazoline 1,1-Dioxide [(+)-7b]**.  $[\alpha]_D^{20} +37^\circ$  (c 1.13, chloroform), 67% ee by HPLC (A:C = 20:80, minor isomer 11.0 min, major isomer 17.6 min); (racemic lit.: Teeninga, H.; Engberts, J. B. F. N. *J. Org. Chem.* **1983**, *48*, 537–542.);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.92 (d, 3H,  $J = 6.9$  Hz,  $\text{CH}_3$ ), 1.32–1.48 (m, 4H;  $\text{CH}_2$ ), 1.72–1.81 (m, 1H, CHH), 1.91–2.01 (m, 1H, CHH), 4.67–4.71 (m, 1H, CH), 5.03 (br, 1H, NH), 7.37–7.77 (m, 4H, ArH).

**(S)-3-Benzyl-2,3-dihydrobenzo[d]isothiazoline 1,1-Dioxide [(S)-7c].**  $[\alpha]_D^{20} -43.8^\circ$  (c 0.89, chloroform) (lit. S-isomer,  $[\alpha]_D^{23} -64.4^\circ$  (c 1.0, chloroform), Ahn, K. H.; Ham, C.; Kim, S. -K.; Cho, C. -W. *J. Org. Chem.* 1997, 62, 7047–7048), 68% ee by HPLC (A:C = 20:80, S isomer 17.3 min, R isomer 21.8 min);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.01 (dd, 1H,  $J = 9.3, 13.7$  Hz, CHH), 3.26 (dd, 1H,  $J = 4.9, 13.7$  Hz, CHH), 4.76 (br, 1H, NH), 4.88 (m, 1H, CH), 7.26–7.78 (m, 9H, ArH).

**(S)-3-(3-Chlorophenyl)-2,3-dihydrobenzo[d]isothiazoline 1,1-Dioxide [(S)-7d].** Using Method 1, the reaction was carried out at 20 °C for 30 min: yield, 96%; ee 81% by HPLC (A:C 25:75, S-isomer 19.58 min; R-isomer 23.35 min); mp 162 °C (ethyl acetate–hexanes); lit. mp 137–138 °C for the racemic compound [Guerny, C.; Malleron, J. L.; Mignani, S.; Eur. Pat. Appl. EP 429341 A2 910529, 1991];  $[\alpha]_D^{20} +121^\circ$  (c 0.29,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.25 (1H, br, NH), 5.70 (1H, d,  $J = 4.1$  Hz, CHN), 7.13–7.84 (8H, m, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  60.54 (C–N), 121.21, 125.25, 125.67, 127.58, 129.17, 129.70, 130.49, 133.44, 133.47, 135.02, 138.70, 140.80 (Ar). Anal. Calcd for  $\text{C}_{13}\text{H}_{10}\text{ClNO}_2\text{S}$ : C, 55.82; H, 3.60; Cl, 12.67; N, 5.01; S, 11.46. Found: C, 55.70; H, 3.56; Cl, 12.62; N, 4.94; S, 11.39.

**Table 6.** Optimization of Catalytic Conditions for Transfer Hydrogenation of Imines **2c** by **1a**<sup>a</sup>

Entry	solvents	T/°C	time(min)	yield(%) <sup>b</sup>	ee(%) <sup>c</sup>
1	CH <sub>2</sub> Cl <sub>2</sub>	-20	720	96	99
2	CH <sub>2</sub> Cl <sub>2</sub>	0	60	97	99
3	CH <sub>2</sub> Cl <sub>2</sub>	20	10	96	99
4 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	20	10	95	99
5	CH <sub>3</sub> CN	40	5	93	98
6	toluene	20	20	93	94
7	ClCH <sub>2</sub> CH <sub>2</sub> Cl	20	10	95	96
8	THF	20	20	90	98
9	CH <sub>3</sub> COCH <sub>3</sub>	20	10	91	99
10	CH <sub>3</sub> CN	20	10	97	99
11	EtOH	20	40	91	99

<sup>a</sup>Reactions were conducted with a substrate:catalyst molar ratio (S/C) of 200:1 using a 5:2 formic acid-triethylamine azeotrope as hydrogen source (Method 1). All of the reactions gave the R amine. The configurations were determined from the sign of the rotation of the isolated products. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by HPLC analysis (Chiralcel OD column) on the products that were purified by silica gel column chromatography. <sup>d</sup>Catalyst was generated *in situ*.

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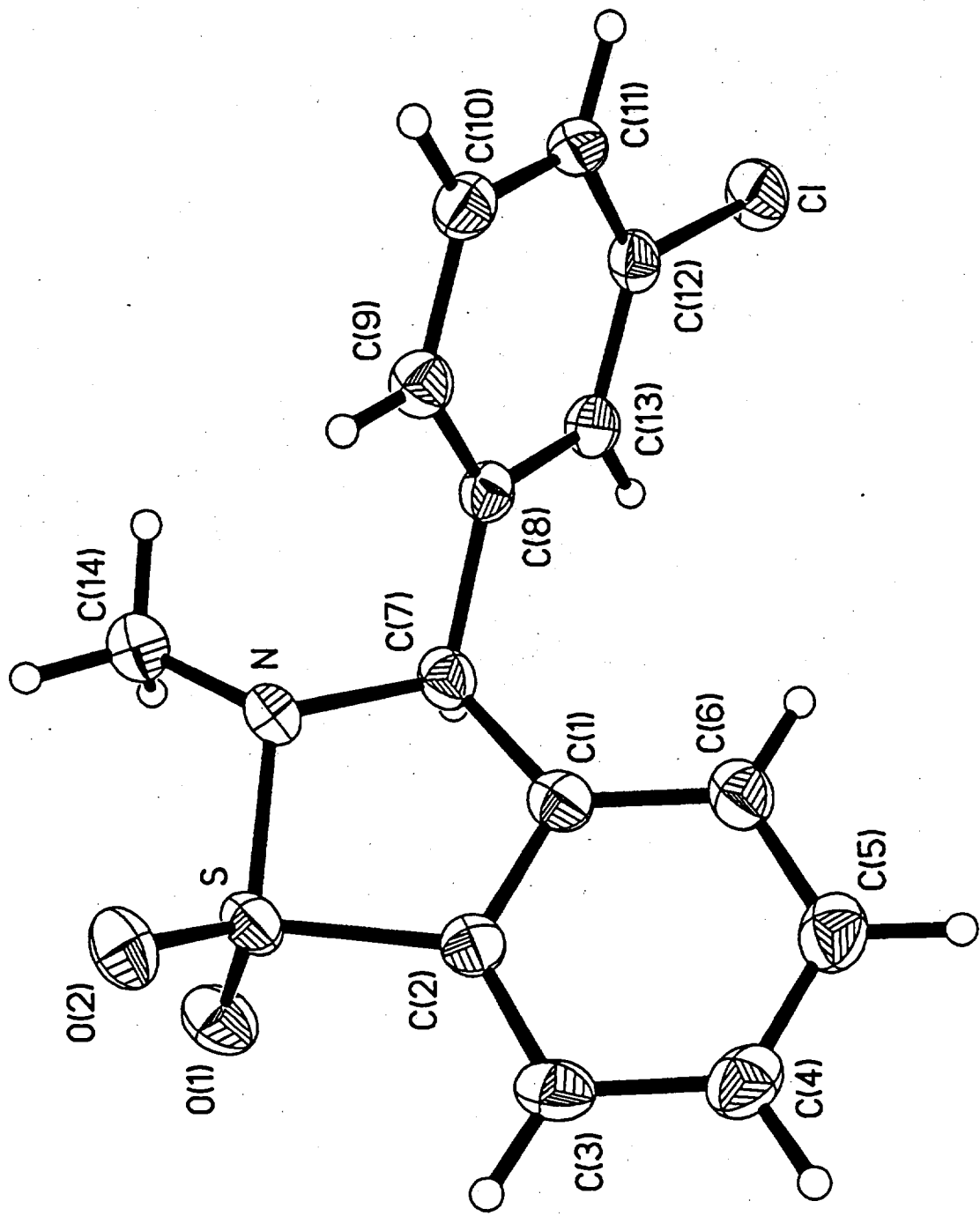


Table 7 Crystal data and structure refinement for 2-Me-7d.

Identification code	2-Me-7d	S-16
Empirical formula	$C_{14}H_{12}ClNO_2S$	
Formula weight	293.76	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_1^2 2_1^2 1$	
Unit cell dimensions	$a = 9.435(2)$ Å $\alpha = 90^\circ$ $b = 9.901(2)$ Å $\beta = 90^\circ$ $c = 13.844(4)$ Å $\gamma = 90^\circ$	
Volume, Z	$1293.3(5)$ Å <sup>3</sup> , 4	
Density (calculated)	$1.509$ Mg/m <sup>3</sup>	
Absorption coefficient	$0.453$ mm <sup>-1</sup>	
F(000)	608	
Crystal size	$0.45 \times 0.40 \times 0.35$ mm	
$\theta$ range for data collection	$2.53$ to $25.05^\circ$	
Limiting indices	$-1 \leq h \leq 11, -1 \leq k \leq 11, -1 \leq l \leq 16$	
Reflections collected	1816	
Independent reflections	1661 ( $R_{int} = 0.0199$ )	
Absorption correction	None	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	1660 / 0 / 172	
Goodness-of-fit on $F^2$	1.063	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0327, wR2 = 0.0780$	
R indices (all data)	$R1 = 0.0388, wR2 = 0.0837$	
Absolute structure parameter	$0.06(11)$	
Largest diff. peak and hole	$0.211$ and $-0.261$ eÅ <sup>-3</sup>	



Table 8 Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for 1.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

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	x	y	z	U(eq)
S	7809(1)	5236(1)	7855(1)	26(1)
C1	7196(1)	492(1)	12294(1)	35(1)
O(1)	6575(3)	6087(2)	7818(2)	35(1)
O(2)	8540(3)	5056(3)	6954(1)	34(1)
N	7476(3)	3742(3)	8336(2)	26(1)
C(1)	8696(3)	4872(3)	9588(2)	24(1)
C(2)	8929(4)	5715(3)	8808(2)	24(1)
C(3)	9881(4)	6781(4)	8807(3)	30(1)
C(4)	10637(4)	6994(4)	9659(3)	33(1)
C(5)	10424(4)	6170(4)	10461(3)	34(1)
C(6)	9459(4)	5111(4)	10440(2)	29(1)
C(7)	7586(4)	3810(3)	9409(2)	24(1)
C(8)	7939(3)	2424(3)	9812(2)	22(1)
C(9)	8751(4)	1498(3)	9310(2)	25(1)
C(10)	9056(3)	251(3)	9714(2)	27(1)
C(11)	8591(4)	-72(3)	10640(2)	27(1)
C(12)	7789(4)	862(3)	11130(2)	24(1)
C(13)	7440(3)	2108(3)	10735(2)	23(1)
C(14)	6256(4)	3026(4)	7926(2)	33(1)

Table 9. Bond lengths [Å] and angles [°] for 2-Me-7d.

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S-O(2)	1.436(2)	S-O(1)	1.438(3)
S-N	1.652(3)	S-C(2)	1.756(3)
C1-C(12)	1.744(3)	N-C(14)	1.466(4)
N-C(7)	1.491(4)	C(1)-C(2)	1.383(4)
C(1)-C(6)	1.402(4)	C(1)-C(7)	1.505(4)
C(2)-C(3)	1.386(5)	C(3)-C(4)	1.394(5)
C(4)-C(5)	1.392(5)	C(5)-C(6)	1.389(5)
C(7)-C(8)	1.518(4)	C(8)-C(9)	1.383(4)
C(8)-C(13)	1.397(4)	C(9)-C(10)	1.385(5)
C(10)-C(11)	1.392(4)	C(11)-C(12)	1.374(5)
C(12)-C(13)	1.389(4)		
O(2)-S-O(1)	115.46(14)	O(2)-S-N	109.31(14)
O(1)-S-N	112.66(14)	O(2)-S-C(2)	113.4(2)
O(1)-S-C(2)	110.8(2)	N-S-C(2)	93.07(14)
C(14)-N-C(7)	117.6(3)	C(14)-N-S	115.2(2)
C(7)-N-S	110.4(2)	C(2)-C(1)-C(6)	118.3(3)
C(2)-C(1)-C(7)	113.8(3)	C(6)-C(1)-C(7)	127.9(3)
C(1)-C(2)-C(3)	124.3(3)	C(1)-C(2)-S	109.1(2)
C(3)-C(2)-S	126.6(3)	C(2)-C(3)-C(4)	116.5(3)
C(5)-C(4)-C(3)	120.8(3)	C(6)-C(5)-C(4)	121.4(3)
C(5)-C(6)-C(1)	118.8(3)	N-C(7)-C(1)	104.1(3)
N-C(7)-C(8)	110.0(3)	C(1)-C(7)-C(8)	114.7(3)
C(9)-C(8)-C(13)	119.8(3)	C(9)-C(8)-C(7)	122.4(3)
C(13)-C(8)-C(7)	117.7(3)	C(8)-C(9)-C(10)	120.2(3)
C(9)-C(10)-C(11)	120.7(3)	C(12)-C(11)-C(10)	118.3(3)
C(11)-C(12)-C(13)	122.2(3)	C(11)-C(12)-C1	119.5(2)
C(13)-C(12)-C1	118.3(2)	C(12)-C(13)-C(8)	118.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for 2-Me-7d.

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The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [ (ha^*)^2 U_{11} + \dots + 2hka^* b^* U_{12} ]$$

	U11	U22	U33	U23	U13	U12
S	31(1)	26(1)	20(1)	4(1)	1(1)	4(1)
Cl	47(1)	38(1)	21(1)	7(1)	3(1)	-9(1)
O(1)	34(1)	35(1)	37(1)	7(1)	-1(1)	10(1)
O(2)	39(1)	42(1)	20(1)	3(1)	4(1)	1(1)
N	31(2)	25(1)	20(1)	3(1)	-4(1)	1(1)
C(1)	29(2)	22(2)	21(1)	-1(1)	5(1)	7(2)
C(2)	27(2)	21(2)	24(2)	-3(1)	0(1)	8(2)
C(3)	34(2)	21(2)	34(2)	3(2)	3(2)	-5(2)
C(4)	33(2)	25(2)	40(2)	-8(2)	-3(2)	4(2)
C(5)	37(2)	32(2)	31(2)	-9(2)	-4(2)	6(2)
C(6)	35(2)	30(2)	22(1)	-2(2)	1(1)	6(2)
C(7)	28(2)	26(2)	20(1)	0(1)	1(1)	4(2)
C(8)	21(2)	24(2)	23(1)	-1(1)	-3(2)	-2(2)
C(9)	26(2)	27(2)	23(2)	-1(1)	2(2)	-1(2)
C(10)	27(2)	26(2)	28(2)	-4(2)	-2(1)	-2(2)
C(11)	31(2)	20(2)	29(2)	2(1)	-7(1)	-3(2)
C(12)	26(2)	27(2)	19(1)	4(1)	-2(2)	-8(2)
C(13)	22(2)	27(2)	20(1)	-2(1)	2(1)	0(2)
C(14)	37(2)	33(2)	29(2)	1(2)	-7(2)	0(2)

Table 11. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2-Me-7d.

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	x	y	z	U(eq)
H(3A)	10012(4)	7337(4)	8255(3)	80
H(4A)	11304(4)	7711(4)	9693(3)	80
H(5A)	10951(4)	6334(4)	11034(3)	80
H(6A)	9318(4)	4560(4)	10993(2)	80
H(7A)	6661(4)	4120(3)	9683(2)	80
H(9A)	9102(4)	1717(3)	8686(2)	80
H(10A)	9589(3)	-390(3)	9355(2)	80
H(11A)	8822(4)	-916(3)	10925(2)	80
H(13A)	6874(3)	2732(3)	11085(2)	80
H(14A)	6308(4)	3055(4)	7219(2)	80
H(14B)	5378(4)	3461(4)	8141(2)	80
H(14C)	6266(4)	2084(4)	8143(2)	80