Potent New Heterogeneous Asymmetric Catalysts

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Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

A set of new, air-stable, Rh^{I}-based heterogeneous asymmetric hydrogenation catalysts have been synthesised, characterised, and tested. Individual members of this new family all exhibit good enantioselectivity.

Introduction. – Even though enzymes are currently more extensively used [1] industrially than asymmetric transition-metal complexes for enantiselective catalytic conversions involving pharmaceuticals and agrochemicals, the latter are of growing importance [2–6]. Such complexes have, however, overwhelmingly been utilized homogeneously, and their heterogeneous asymmetric counterparts have hitherto performed disappointingly [7], so far as their enantiselectivity is concerned, largely because they contained a range of different kinds of active centres, each with its own catalytic selectivity. Earlier, we have shown [8–11] that, provided the active organometallic moiety is heterogenised in a single-site fashion, superior catalytic performance may be achieved. Such asymmetric heterogeneous catalysts are intrinsically more convenient than their homogeneous precursors since they provide an expedient, inexpensive route to introducing chiral centres without recourse to costly separations or use of expensive solvents (such as supercritical CO_2 or ionic liquids) [12].

Results and Discussion. – The ligands employed in this study are (*S*,*S*,*S*)-[2-(4,5-dihydro-4′,5′-diphenyloxazol-2′-yl)ferrocenyl]phosphine ((*S*,*S*,*S*)-dipof; **1a**), L-tryptophan benzyl ester (**1b**), (−)-(*S*)-2-(aminomethyl)-1-ethylpyrrolidine (**1c**), and (+)-(1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (**1d**) (*Fig. 1*).

Reaction of 1 mol-equiv. of each of these ligands with the rhodium cation $[Rh(cod)(THF)_2]^+$ (cod = cycloocta-1,5-diene), previously obtained from the reaction between $[RhCl(cod)]_2$ and $AgCF_3SO_3$, produced the homogeneous catalyst designated **2a**–**2d**, respectively (see also the *Table*) $[Rh(cod)L\text{-}L]CF_3SO_3$ in near quantitative yield. The final compounds are air-stable and easily handled. In all cases, the new compounds were characterised by ^1H-, ^{13}C-, and ^{31}P- (where appropriate) NMR, by

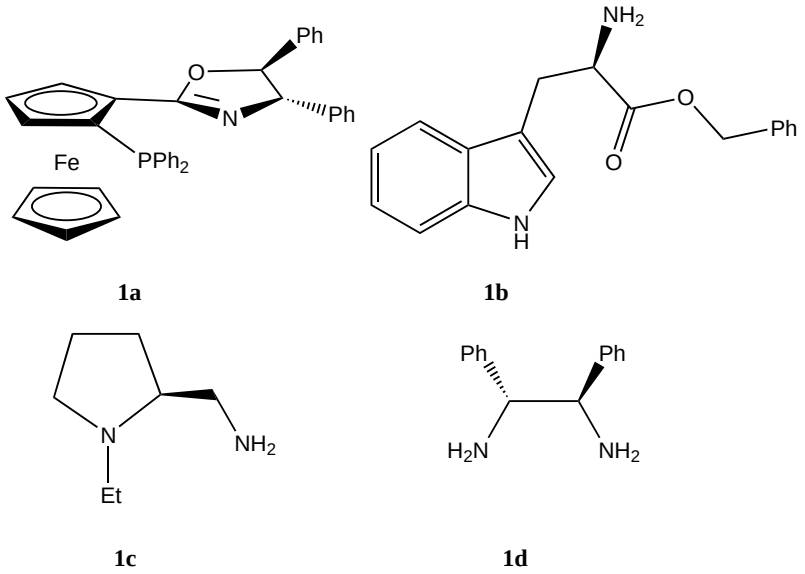

Fig. 1. *The chiral ligands employed in this study.* The atoms in bold are those that ligand to the Rh(I) centre.

mass spectrometry and single-crystal X-ray diffraction. A segment of the crystal structure of **2b** is shown in *Fig. 2*.

It is noteworthy that the metal is coordinated to the O-atom of the C=O group and to one of the N moieties, which is a relatively rare occurrence in organometallic chemistry. It is also noteworthy that the tryptophan ring is tilted towards the Rh centre, affording a high degree of steric hindrance conducive for asymmetric catalysis. The crystal structure of catalyst **2c** was also determined, and the key feature is presented in *Fig. 3*. The structure of **2d** is shown in *Fig. 4*.

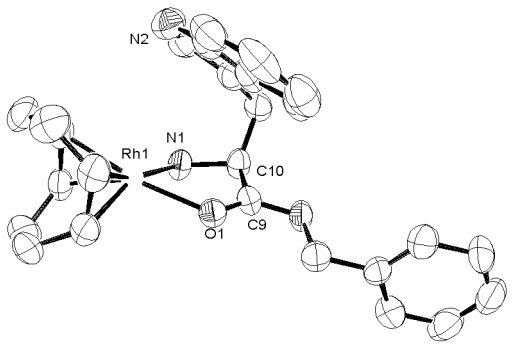

Fig. 2. *A fragment of the crystal structure for the homogeneous catalyst* **2b** (the triflate anion is omitted for clarity). The ellipsoids are at the 50% probability level. Rh(1)–N(1): 2.119(5) Å, Rh(1)–O(1): 2.144(5) Å, C(9)–O(1): 1.233(8) Å, N(1)–Rh(1)–O(1): 78.30(9)°, C(10)–N(1)–Rh(1): 110.3(4)°, Rh(1)–O(1)–C(9): 113.4(4)°.

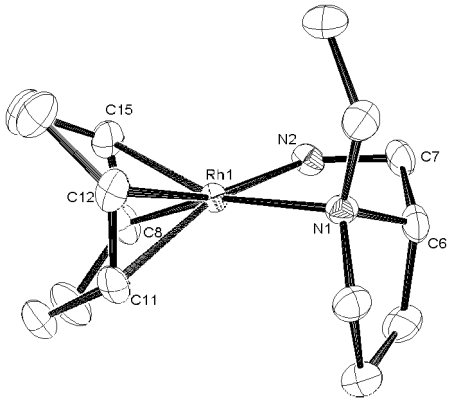

Fig. 3. *A fragment of the crystal structure for the homogeneous catalyst* **2c** (the triflate anion is omitted for clarity). The ellipsoids are at the 50% probability level. Rh(1)–N(1): 2.178(3) Å, Rh(1)–N(2): 2.112(3) Å, C(8)–Rh(1): 2.126(3) Å, C(11)–Rh(1): 2.124(4) Å, C(12)–Rh(1): 2.129(3) Å, C(15)–Rh(1): 2.146(3) Å, N(1)–Rh(1)–N(2): 91.26(15)°.

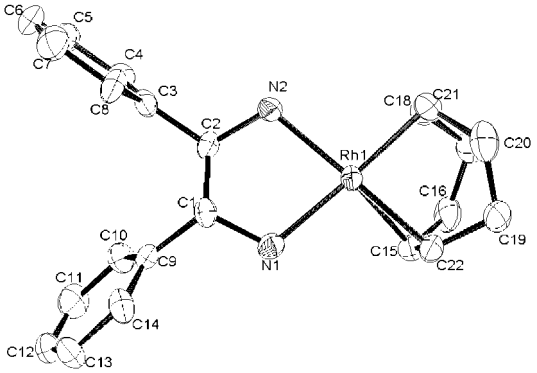

Fig. 4. *A fragment of the crystal structure for the homogeneous catalyst* **2d** (the triflate anion is omitted for clarity). The ellipsoids are at the 50% probability level. Rh(1)–N(1): 2.105(5) Å, Rh(1)–N(2): 2.128(5) Å, C(18)–Rh(1): 2.146(7) Å, C(15)–Rh(1): 2.121(7) Å, C(21)–Rh(1): 2.116(7) Å, C(22)–Rh(1): 2.126(7) Å, N(1)–Rh(1)–N(2): 80.16(19)°.

A number of organometallic homogeneous catalysts may be heterogenised in a single-site fashion onto the inner walls of high-area, mesoporous silica supports (using an appropriate alkyl bromide tether). But, recently, an even more straightforward method of anchoring an asymmetric organometallic catalyst has emerged, entailing tethering *via* a noncovalent interaction [4]. This involves the use of the polar counter-ion, $CF_3SO_3^-$, which, through quite strong H-bonding, is 'anchored' to the pendant silanol groups of the mesoporous silica [13]. One of the principal purposes of this paper is to demonstrate the advantages of the simple triflate anion method (devised recently by *Rege et al.* [4]) in heterogenising viable precursor homogeneous asymmetric catalysts. For this purpose, we have taken two entirely new ligands, **1a** and **1b**, and two

others, **1c** and **1d**, that we have already used for the preparation of heterogeneous catalysts by our earlier [10] anchoring method.

Our heterogeneous chiral catalysts were easily prepared by simple sorption of the homogeneous catalysts from a CH_2Cl_2 slurry onto the surface of the mesoporous silica. The presence of the chiral catalyst inside the mesopore was established by elemental analysis and, for catalyst **3a** (where **3a** is the heterogeneous analogue of **2a**), by ^{31}P-CP/MAS (cross-polarization magic angle spinning) NMR. (The spectrum shows a broad signal centred at δ 22.9 ppm, which is comparable to that observed with the homogeneous precursor (δ 23.9 ppm (CD_2Cl_2)).

To investigate the asymmetric catalytic performance of the heterogenised catalysts, their efficiency in the hydrogenation of the C=C bond was studied, the conversion of (*E*)-α-phenylcinnamic acid to 2,3-diphenylpropanoic acid being our test reaction (*Table*).

Table 1. *The Activities, Selectivity* (for 2,3-diphenylpropionic acid) *and Enantiomeric Excess* (ee) *for the Various Homogeneous and Heterogeneous Catalysts for the Hydrogenation of* (E)-α-*Phenylcinnamic acid*

Form of the Rh^I catalyst		Ligand	Conversion [%]	Selectivity [%]	ee [%]
Homogeneous	**2a**	(*S*,*S*,*S*)-dipof (**1a**)	65	70	73
	2b	L-Tryptophan benzyl ester (**1b**)	88	59	67
	2c	(−)-(*S*)-2-(Aminomethyl)-1-ethylpyrrolidine (**1c**)	86	84	83
	2d	(+)-(1*R*,2*R*)-1,2-Diphenylethane-1,2-diamine (**1d**)	64	84	66
Heterogeneous	**3a**	(*S*,*S*,*S*)-dipof (**1a**)	79	64	94
	3a*	(*S*,*S*,*S*)-dipof [a]) (**1a**)	85	62	88
	3a	(*S*,*S*,*S*)-dipof recycled	79	67	91
	3b	L-Tryptophan benzyl ester (**1b**)	81	47	69
	3c	(−)-(*S*)-2-(Aminomethyl)-1-ethylpyrrolidine (**1c**)	90	84	97
	3d	(+)-(1*R*,2*R*)-1,2-Diphenylethane-1,2-diamine (**1d**)	70	91	90

[a]) Catalyst **3a*** is catalyst **3a** after being stored for 6 months. Reaction conditions: substrate, *ca.* 0.5 g; solvent (MeOH), *ca.* 30 ml; homogeneous catalyst, *ca.* 10 mg; heterogeneous catalyst, *ca.* 50 mg; pressure, 20 bar; temperature, 313 K; time 24 h.

The results show a marked increase in the enantiomeric excess once the catalyst is anchored onto the mesoporous material. The change in stereoselectivity confirms the importance of confinement in chiral catalysis and the role mesoporous silica plays in these systems [8–12][14]. We have demonstrated that prolonged storage of the catalyst **3a**, under normal conditions, does not alter the catalytic performance. The recycling test of **3a** shows little change in enantioselectivity and conversion, thus confirming that, despite a relatively low-energy bonding of the homogeneous catalyst onto the mesoporous silica surface, the system is not readily susceptible to leaching. In summary, we have illustrated the ease of synthesis of several stable new asymmetric homogeneous catalysts, as well as the ease of producing potent heterogeneous analogues.

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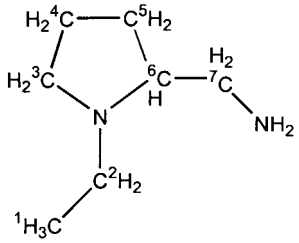
Experimental Part

1. *Synthesis and Characterisation of Homogeneous Catalysts.* All compounds were purchased from *Aldrich*, unless otherwise stated. The solvents were all predried by standard methods. The reactions were carried out under a N_2 atmosphere by standard *Schlenk* line techniques. The NMR measurements were performed on a *Bruker DPX* (500 MHz) employing cryo-probe technology or a *Bruker* 400-MHz spectrometer.

*[Rh(Cycloocta-1,5-diene){(*S,S,S*)-dipof}]CF$_3$SO$_3$* (**2a**). $[RhCl(cod)]_2$ (46 mg, 0.09 mmol) was dissolved in THF (5 ml), to which $AgCF_3SO_3$ (37 mg, 0.19 mmol) was added, and this soln. was stirred for 1 h at r.t. The soln. was then filtered (to remove AgCl), and to the filtrate (*S*,*S*,*S*)-dipof (**1a**; 110 mg, 0.19 mmol) was added, and the soln. left to stir for 1 h. Then, the soln. was slightly concentrated *in vacuo*, and hexane (25 ml) was added to precipitate the required product. The soln. was filtered and the product washed with hexane (2 × 20 ml) and Et_2O (2 × 20 ml), and dried *in vacuo:* **2a** (100 mg, 55%). Orange powder. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.79–2.72 (*m*, 8 H); 3.40 (*m*, 1 H); 3.65 (*m*, 1 H); 3.74 (*m*, 1 H); 4.77 (*s*, 5 H); 4.80 (*m*, 1 H); 5.05 (*m*, 1 H); 5.15 (*m*, 1 H); 5.18 (*m*, 1 H); 5.28 (*m*, 1 H); 5.45 (*m*, 1 H); 6.64–7.73 (*m*, 20 H). ^{31}P-NMR ($CDCl_3$): 23.9 (*d*, ^1J(P,Rh) = 149.8). ESI-MS (pos.): 803 (100).

*[Rh(Cycloocta-1,5-diene)(*L*-tryptophan Benzyl Ester)]CF$_3$SO$_3$* (**2b**). $[RhCl(cod)]_2$ (60 mg, 0.12 mmol) was dissolved in THF (5 ml) to which $AgCF_3SO_3$ (62 mg, 0.24 mmol) was added and the soln. was stirred for 1 h at r.t. The soln. was then filtered (to remove AgCl) and to the filtrate L-*tryptophan benzyl ester* (**1b**; 72 mg, 0.24 mmol) was added, and the soln. was left to stir for 1 h. Then, the soln. was slightly concentrated *in vacuo*, and hexane (25 ml) was added to precipitate the required product. The soln. was filtered, and the product was washed with hexane (2 × 20 ml) and dried *in vacuo*. The residue was recrystallized in CH_2Cl_2 to give **2b** (121 mg, 77%). Yellow crystals. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 1.50–1.69 (*m*, 4 H, cod); 2.09–2.30 (*m*, 4 H, cod); 3.25 (*d*, ^3J = 6.0, C*H*$_2$CH); 3.58 (*m*, 4 H, cod); 4.15 (*t*, ^3J = 6.0, CH$_2$C*H*); 5.26 (*s*, CH_2O); 7.16–7.72 (*m*, 10 H, Ph, C_8H_6N); 9.28 (*s*, NH). ^{13}C-NMR (CD_2Cl_2): 29.5, 30.8 (CH_2, cod); 30.1 (*C*H$_2$CH); 56.3 (CH$_2$*C*H); 69.9 (CH_2O); 82.9 (*d*, *J*(Rh,C) = 63, CH, cod); 103.2, 112.5, 119.0, 119.6, 120.4, 121.2, 122.2, 124.5, 129.0, 129.3, 129.4, 134.3, 138.0 (Ph and C_8H_6N); 179.3 (C=O). ESI-MS (pos.): 505 (85%). Anal. calc. for $C_{27}H_{30}F_3N_2O_5RhS$: C 49.55, H 4.62, N 4.28; found C 48.42, H 4.57, N 4.05.

*[Rh{(−)-(*S*)-2-(Aminomethyl)-1-ethylpyrrolidine}(cycloocta-1,5-diene)]CF$_3$SO$_3$* (**2c**). $[RhCl(cod)]_2$ (100 mg, 0.20 mmol) was dissolved in THF (10 ml), to which $AgCF_3SO_3$ (104 mg, 0.40 mmol) was added, and this soln. was stirred for 1 h at r.t. The soln. was then filtered (to remove AgCl) and to the filtrate *(−)-(*S*)-2-(aminomethyl)-1-ethylpyrrolidine* (**1c**; 52 mg, 0.40 mmol) was added, and the soln. was left to stir for 1 h. Then, the soln. was slightly concentrated *in vacuo*, and hexane (25 ml) was added to precipitate the required product. The soln. was filtered, and the product was washed with hexane (2 × 20 ml) and Et_2O (2 × 20 ml), and dried *in vacuo:* **2c** (172 mg, 88%). Yellow powder.



^{1}H-NMR ($CDCl_3$): 1.54 (*t*, *J* = 7, Me(1)); 1.74 (br. *s*, 2 CH_2 (cod)); 1.80–2.09 (*m*, CH_2(4), CH_2(5)); 2.30 (br. *s*, 2 CH_2 (cod)); 2.45–2.70 (*m*, CH_2(2), CH_2(3)); 2.90 (*m*, CH(6)); 3.10 (*m*, CH_2(7)); 3.57 (*d*, ^1J(Rh,H) = 37, 2 CH (cod)); 3.75 (*d*, ^1J(Rh,H) = 74, 2 CH (cod)). ^{13}C-NMR ($CDCl_3$): 12.2 (C(1)); 21.7 (C(4)); 24.4 (C(5)); 29.6 (*d*, *J*(Rh,C) = 12, CH_2 (cod)); 30.5 (*d*, *J*(Rh,C) = 36, CH_2 (cod)); 45.5 (C(7)); 50.9 (C(2)); 56.5 (C(3)); 67.1 (C(6)); 79.6 (*d*, *J*(Rh,C) = 65, CH (cod)); 83.6 (*d*, *J*(Rh,C) = 240, CH (cod)). ESI-MS (pos.): 339 (M^+), 231 ([M − cod]$^+$). Anal. calc. for $C_{16}H_{28}F_3N_2RhSO_3$: C 39.34, H 5.74, N 5.74; found: C 39.84, H 5.54, N 5.69. Crystals suitable for X-ray diffraction were obtained by recrystallisation in CH_2Cl_2/Et_2O.

*[Rh(Cycloocta-1,5-diene){(+)-(1*R,2R*)-1,2-diphenylethan-1,2-diamine}]CF$_3$SO$_3$* (**2d**). $[RhCl(cod)]_2$ (100 mg, 0.20 mmol) was dissolved in THF (10 ml), to which $AgCF_3SO_3$ (104 mg, 0.40 mmol) was added, and this soln. was stirred for 1 h at r.t. The soln. was then filtered (to remove AgCl) and to the filtrate *(+)-(1*R,2R*)-1,2-diphenylethane-1,2-diamine* (**1d**; 83 mg, 0.40 mmol) was added, and the soln. was left to stir for 1 h. Then, the

soln. was slightly concentrated *in vacuo*, and hexane (25 ml) was added to precipitate the required product. The soln. was filtered, and the product was washed with hexane (2 × 20 ml) and Et_2O (2 × 20 ml) and dried *in vacuo:* **2d** (195 mg, 86%). Yellow powder. ^{1}H-NMR (CD_3OD): 1.95 (br. *m*, 2 CH_2); 2.46 (br. *m*, 2 CH_2); 4.01 (*s*, 2 NCH); 4.24 (*m*, 2 CH); 4.35 (*m*, 2 CH); 7.1–7.3 (*m*, 10 arom. H). ^{13}C-NMR (CD_3OD); 31.5 (CH_2); 66.3 (NCH); 81.4 (CH); 128.4, 129.2, 129.6, 140.5 (Ph). ESI-MS (pos.): 423 (M^+). Anal. calc. for $C_{23}H_{28}F_3N_2RhSO_3$: C 48.25, H 4.90, N 4.90; found C 47.95, H 4.83, N 4.60. Crystals suitable for X-ray diffraction were obtained from a MeOH/Et_2O soln.

2. *Synthesis and Characterisation of Heterogeneous Catalysts.* The triflate salt (50 mg) was dissolved in CH_2Cl_2 (20 ml), to which dry calcined *MCM-41* (500 mg) was added to form a slurry. This was left stirring at r.t. for 3 h; during this time the solid took on the colour of the Rh complex, and the soln. became pale. The soln. was filtered and the *MCM-41* was washed with copious amounts of CH_2Cl_2 until the washings were colourless. The catalyst was then dried *in vacuo* and isolated as a pale yellow solid. Elemental analysis: **3c**: C 3.77, H 0.83, N 0.42; **3d**: C 3.76, H 0.72, N 0.39. ^{19}F-MAS Measurements of catalyst **3d**, of the homogeneous catalyst and the heterogeneous catalyst were identical. ^{31}P-CP/MAS (spinning 6 kHz, contact time 5 ms, recycle delay 5 s) of catalyst **3a** is given, the isotropic chemical shift (22.9 ppm) is consistent with that of its homogeneous counterpart in solution.

3. *Description of the Hydrogenation Experiment and Analytical Methods.* The catalytic reactions (enantioselective hydrogenations) were carried out in a high-pressure stainless-steel catalytic reactor (100 ml) lined with Poly Ether Ether Ketone (PEEK). The homogeneous catalyst (10 mg; or 50 mg of the mesoporous silica anchored heterogeneous catalyst), which was previously evacuated and stored under inert conditions (N_2 or Ar), was transferred under an inert atmosphere to the catalyst-delivery unit, which was subsequently sealed and introduced to the high-pressure reactor (using dry He).

The substrate ((*E*)-α-phenylcinnamic acid; 0.5 g), solvent (MeOH; 30 g) and a suitable internal standard (cyclododecane) were then introduced into the reactor, and the reactor was sealed. The reactor as well as the inlet and outlet ports were inertized with dry N_2 (thrice) prior to the introduction of H_2 (5 bar). A leak test was carried out, and the reactor was then pressurized to 20 bar with H_2. The reactor was then heated to the desired temp. (313 K), and the contents were stirred using a mechanical stirrer at 400 rpm. (Where kinetic and rate effects were studied, a mini-robot liquid-sampling valve was employed to remove small aliquots of the sample without perturbing the pressure in the reactor.)

At the end of the reaction, the heating was turned off, and the contents of the reactor were cooled (quenched). The reactor was then depressurised. A mass-balance calculation was made at this stage to check for handling and weight losses. The products were analysed (using a suitable internal standard) by GC (*Varian*, model *3400 CX*) employing a *HP-1* capillary column (25 m × 0.32 mm) and flame ionisation detector with a variable-ramp-temperature program from 433 to 493 K. The identities of the products were first confirmed using authenticated standards, and their individual response factors were determined using a suitable internal standard (calibration method). The conversions and selectivities were determined as defined by the following equations, and the yields were normalised with respect to the response factors obtained as above:

Conversion [%] = [(moles of initial substrate – moles of residual substrate)/(moles of initial substrate)] × 100

Selectivity [%] = [(moles of individual product)/(moles of total products)] × 100

The products were further identified by NMR spectroscopy (^{1}H and ^{13}C in CD_3OD), which showed loss of the C=C and gain of a C–C moiety. The enantioselectivities (ee's) were first determined by GC (*Hewlett-Packard*, *HP 5890*) using a chiral column (γ-cyclodextrin dialkyl (*Chiraldex*), 20 m × 0.25 mm), and the identities of the chiral products were further confirmed by LCMS (*Shimadzu LCMS-QP8000*) equipped with a chiral detector (*OR-990, JASCO*), again, using a chiral column (*CHIRALCEL OJ-R*, *DAICEL*). ee Values were calculated from the peak areas of the enantiomers using the following formula:

$$ee = ([R] - [S]) \times 100/([R] + [S])$$

Finally, as a further confirmation, the products were isolated from the reaction mixture and esterified to the methyl ester by the following procedure: 300 µl of the sample was taken in a glass vial, 2 ml of 14% BF_3 in MeOH was added to the glass vial, which was sealed with a *Teflon*-lined stopper and heated for 1 h at 353 K. The sample was cooled to r.t. and 2 ml of *Milli-Q* reagent water was added with mild shaking. HPLC-Grade CH_2Cl_2 (2 ml) was added before the analysis, which was again performed on the LCMS (*Shimadzu LCMS-QP8000*) using the same chiral column (*CHIRALCEL OJ-R*, *DAICEL*).

Crystal Data of **2b**: $C_{28}H_{32}Cl_2F_3N_2O_5RhS$, 739.43 g mol^{-1}, monoclinic, space group $P2(1)$, $a = 10.3924(3)$, $b = 11.2263(4)$, $c = 13.8107(4)$ Å, $\beta = 102.276(2)^\circ$, $V = 1574.43(9)$ Å^3, $T = 180(2)$ K, $Z = 2$, $\mu = 0.835$ mm^{-1}, 9885 reflections measured 6122 independent, $R_1[I > 2\sigma(I)] = 0.0492$ $R_2[I > 2\sigma(I)] = 0.1162$, R_1(all data) = 0.0795, R_2(all data) = 0.1543. *CCDC* Ref. No. 199872.

Crystal Data of **2c**: $C_{20}H_{28}F_3N_2O_3RhS$, 488.37 g mol^{-1}, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 9.3462(2)$, $b = 13.2369(3)$, $c = 15.8161(4)$ Å, $\beta = 90^\circ$, $V = 1956.68(8)$ Å^3, $T = 180(2)$ K, $Z = 4$, $\mu = 1.025$ mm^{-1}, 18061 reflections measured 4471 independent, $R_1[I > 2\sigma(I)] = 0.0350$ $R_2[I > 2\sigma(I)] = 0.0633$, R_1(all data) = 0.0499, R_2(all data) = 0.0676. CCDC Ref. No. 199871.

Crystal data of **2d**: $C_{24}H_{30}Cl_2F_3N_2O_5RhS$, 657.37 g mol^{-1}, monoclinic, space group $P2(1)$, $a = 12.9486(3)$, $b = 9.9939(2)$, $c = 21.3221(6)$ Å, $\beta = 98.4060(10)^\circ$, $V = 2729.59(11)$ Å^3, $T = 180(2)$ K, $Z = 4$, $\mu = 0.947$ mm^{-1}, 16134 reflections measured 8957 independent, $R_1[I > 2\sigma(I)] = 0.0450$, $R_2[I > 2\sigma(I)] = 0.1122$, R_1(all data) = 0.0552, R_2(all data) = 0.1186. CCDC Ref. No. 199870. Single-crystal data were collected using a *Nonius CCD* diffractometer with a sealed-tube MoK_α source. All structures were solved with SHELXS-97 and refined using full-matrix least-squares on F^2 using SHELXS-97 software. The *CCDC* contains supplementary crystallographic data for this paper. This data maybe obtained, free of charge, *via* http:/www.ccdc.cam.ac.uk/conts/retrieving.html (or free from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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