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# Approaches towards the enantioselective recognition of anionic guest species using chiral receptors based on rhenium(I) and ruthenium(II) with amide bipyridine ligands

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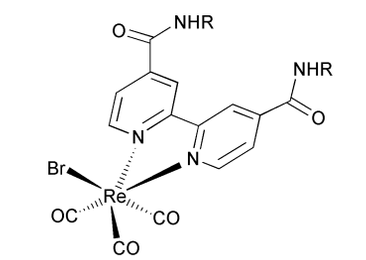
The syntheses of chiral anion receptors based on rhenium(I) and ruthenium(II) with amide bipyridine ligands are reported. The rhenium(I) hosts were prepared in moderate to high yields by co-ordinating chiral bipyridine ligands to a $Re(CO)_3Br$ centre. The ruthenium(II) receptors were synthesised *via* the chiral building blocks *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$ or by chromatographic resolution on a SP Sephadex C-25 cation exchanger. Chiral purity was determined by $^1$H NMR and circular dichroism spectroscopy and lanthanide shift experiments. $^1$H NMR titration studies showed that these receptors bind chiral carboxylate anions in DMSO-$d_6$, although significant chiral discrimination was not observed.

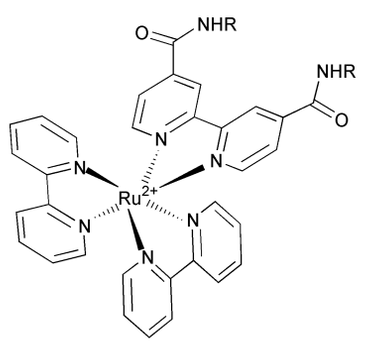
## Introduction

The search for enantioselective abiotic receptors is a key objective in supramolecular chemistry.[1] This is not surprising, given the potential applications for chiral recognition across a broad scientific area. For example, numerous chiral receptors have been shown to bind biologically important molecules such as amino acid derivatives, with a view towards stereoselective recognition and enzyme mimicry.[2] Enantiomeric resolution has been achieved using chiral host molecules as chiral stationary phases in column chromatography.[3] Stereoselective receptors have also been employed in asymmetric synthesis and catalysis,[4] transport and extraction of optically active guests[5] and the development of sensory agents.[6]

A wide range of chiral hosts has appeared in the literature, including binaphthalene systems,[4b,5a,b,6,7] aryl cages,[2a,f] urea-based receptors,[8] cyclophanes,[9] porphyrins[10] and sapphyrins.[11] These receptors generally recognise chiral neutral or cationic guests such as amino acids and peptides, but few address the problem of chiral *anion* co-ordination.[2h,8,10b,11] We have previously prepared anion receptors which incorporate amide bipyridine ligands co-ordinated to transition metal centres.[12] In an effort to develop enantioselective anion receptors, we have therefore designed three chiral hosts based on (2,2'-bipyridine)-ruthenium(II) or -rhenium(I) architectures (Fig. 1). Receptors of type 1 incorporate a 4,4'-diamide-2,2'-bipyridine ligand co-ordinated to rhenium(I), where the amide and 3,3'-bipyridine protons form a hydrogen bonding site for the anionic guest and the chirality stems from two asymmetric centres (R) on the bipyridine backbone. Chiral recognition is expected to result from steric interactions between the R substituents and the enantiomeric guests. Type 2 receptors are based on a 4,4'-diamide-2,2'-bipyridine ligand co-ordinated to ruthenium(II), where the amide substituents (R) are both achiral. The chirality of this system originates from the *Λ*- or *Δ*-helical configuration of ligands at the metal centre. Enantioselective binding would require the guest to interact more favourably with one helical array than the other. Type 3 receptors are analogous to type 2, but contain additional chiral centres (R) on the 4,4'-diamide-2,2'-bipyridine ligand. Thus, chiral recognition could arise from interactions with the metal helicity and/or the asymmetric functionality R.




Type 1 (R = chiral group)




Type 2 (R = achiral group)

Type 3 (R = chiral group)

**Fig. 1** Types of chiral host based on rhenium(I) and ruthenium(II) with amide bipyridine ligands.

These receptors have the potential to recognise chiral anions by multipoint interactions, involving electrostatic forces, hydrogen bonding, π-stacking if the guest has an aromatic surface, and steric interactions. We report here the synthetic approach towards each type of receptor and the preliminary binding studies with chiral anionic guests.

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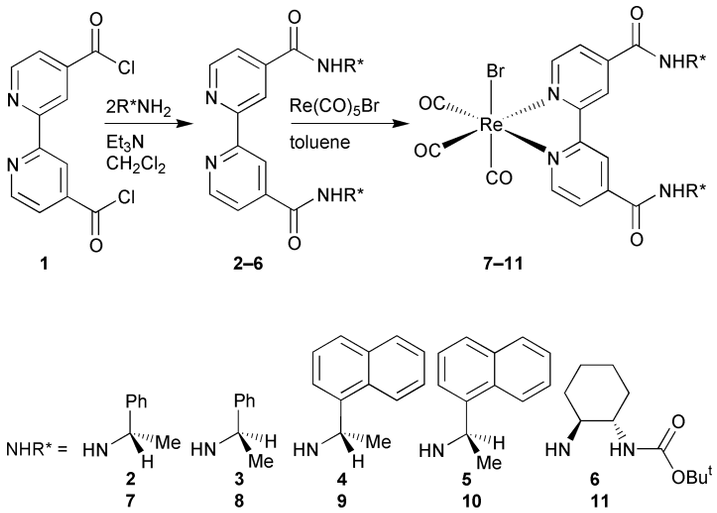



**Scheme 1**

## Results and discussion

### Synthesis of chiral rhenium(I) receptors

The chiral rhenium(I) receptors **7–11** were prepared according to Scheme 1. Condensation of 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine **1**[13] with *S*-/*R*-α-methylbenzylamine and *S*-/*R*-1-(1-naphthyl)ethylamine gave ligands **2**–**5** respectively in 72–87% yield. Ligand **6** was synthesised from *tert*-butoxycarbonyl-*S*,*S*-1,2-diaminocyclohexane and acid chloride **1** in 71% yield. Monoprotection of *S*,*S*-1,2-diaminocyclohexane was achieved by an adaptation of a literature method using di-*tert*-butyldicarbonate.[14] Complexation reactions were performed with ligands **2–6** and bromopentacarbonylrhenium(I) in refluxing toluene. This gave the chiral rhenium(I) receptors **7–11** as orange solids in 63–93% yield.

Co-ordination to rhenium(I) was confirmed by NMR spectroscopy, elemental analysis and FAB mass spectrometry (see Experimental section). For example, $^1$H NMR spectroscopy showed the bpyH6,6', bpyH3,3', bpyH5,5' and bpyNH resonances shift significantly downfield on metal complexation ($0.18 \leq \Delta\delta \leq 0.38$ ppm). This is consistent with ligand-to-metal σ-donation in the rhenium(I) complexes.[15] Interestingly, the two halves of the bipyridine ring are equivalent in the NMR spectra of ligands **2–6**, but not in the metal complexes **7–11**. This is illustrated by comparing the $^1$H NMR spectra of ligand **2** and its rhenium(I) complex **7** (Fig. 2). The observed disparity between the two pyridine rings in **7–11** is not caused by a *meridional* geometry of the carbonyl groups, since *facial* substitution is predicted due to CO labilisation *cis* to Br.[16] The preference for *facial* co-ordination in $[Re(CO)_3XL]$ molecules (X = halide, L = polypyridyl) is well-established in the literature.[15,17] The lack of magnetic equivalence is therefore due to the position of the chiral substituents relative to the *facial* $Re(CO)_3Br$ centre. Since there is no symmetry element which interconverts the two halves of the bipyridine ring for the *facial* receptors **7–11** (Scheme 1), the two halves can exhibit different chemical shifts. In contrast, the two pyridine rings are related by a $C_2$ axis in the free ligands **2–6** and no peak splitting is observed.

### Synthesis of chiral ruthenium(II) receptors from *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$

The synthesis and reactivity of the chiral building blocks *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$ has been reported by Hua and von Zelewsky.[18] The chiral ruthenium(II) receptors *Λ*- and *Δ*-**12** were prepared by reacting *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$ with ligand **3** in ethylene glycol solvent mixtures (Scheme 2).[19] A chemically pure ruthenium complex was only obtained after three days in 90% ethylene glycol–10% water, but addition of glacial acetic acid to the mixture considerably reduced the reaction time. It is postulated that the acetic acid protonates the pyridine rings in *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$, which facilitates the substitution process.

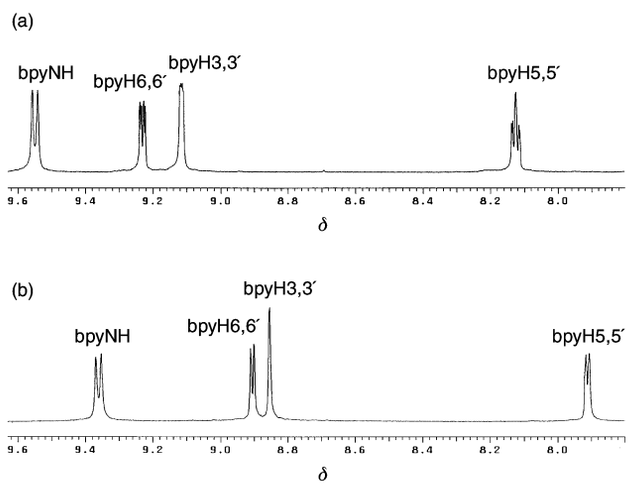



**Fig. 2** $^1$H NMR spectra (500 MHz, DMSO-$d_6$, low field region) of (a) receptor **7**; (b) ligand **2**. In (a), bpyH6,6' appear as two overlapping doublets coupling to bpyH5,5'; bpyH5,5' are two overlapping double doublets coupling to bpyH3,3' and bpyH6,6'; and bpyH3,3' occur as a multiplet comprised of two overlapping doublets coupling to bpyH5,5'. In (b), bpyH6,6', bpyH3,3' and bpyH5,5' form a doublet, singlet and doublet respectively.

Receptors *Λ*- and *Δ*-**12** possess chirality at the metal centre and on the bipyridine backbone and are therefore diastereomeric. Fig. 3 compares the $^1$H NMR spectra of *Λ*- and *Δ*-**12** with the 1 : 1 mixture of both diastereomers. This mixture was obtained by refluxing *rac*,*cis*-$[Ru(bpy)_2Cl_2]$[20] with ligand **3** in aqueous ethanol, followed by column chromatography on Sephadex LH-20. Each isomer of receptor **12** contains eleven magnetically distinct bipyridine protons. The two halves of the *substituted* bipyridine ligand are related by a $C_2$ axis and therefore account for three signals (bpyH3,3', bpyH5,5' and bpyH6,6'), while the remaining eight resonances are assigned to the *unsubstituted* bipyridine rings. The important point to note from Fig. 3 is the position of the bpyH3,3' singlet. Fig. 3a shows that this peak occurs at different chemical shifts for the two diastereomers. The bpyH3,3' signal appears further downfield in the *Λ*-isomer (Fig. 3b) compared to the *Δ*-form (Fig. 3c), and this can be used to assess diastereomeric purity. The $^1$H NMR spectra of *Λ*- and *Δ*-**12** both show a small peak adjacent to the main bpyH3,3' singlet, which indicates the presence of the other diastereomer. The

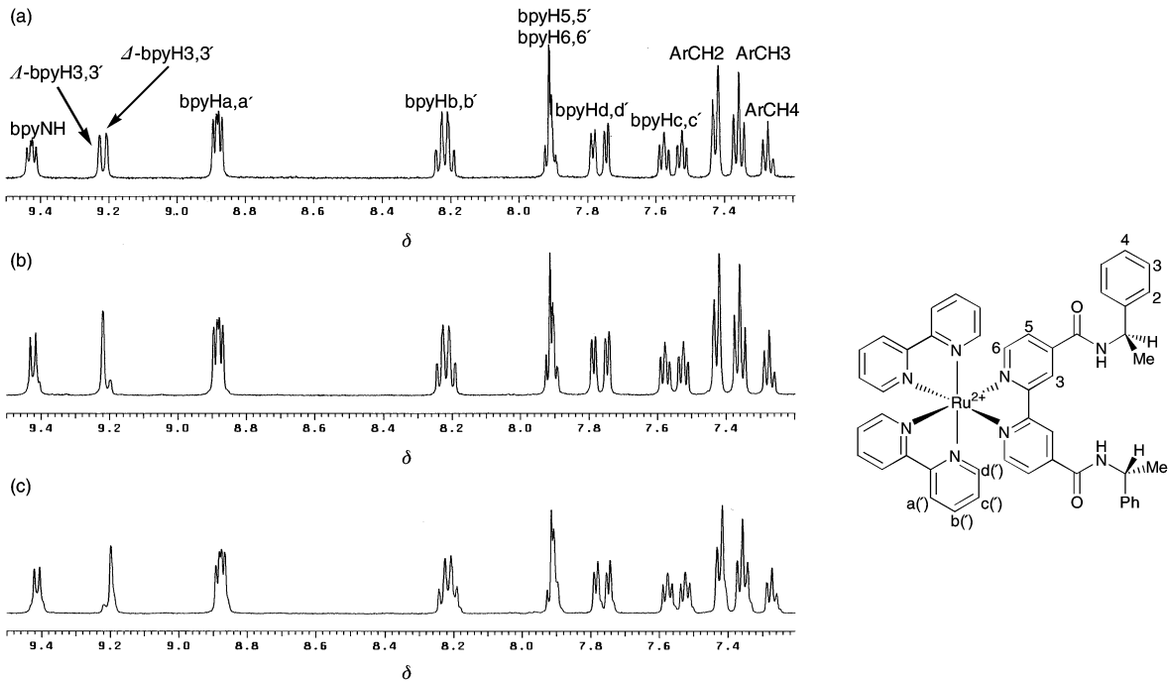
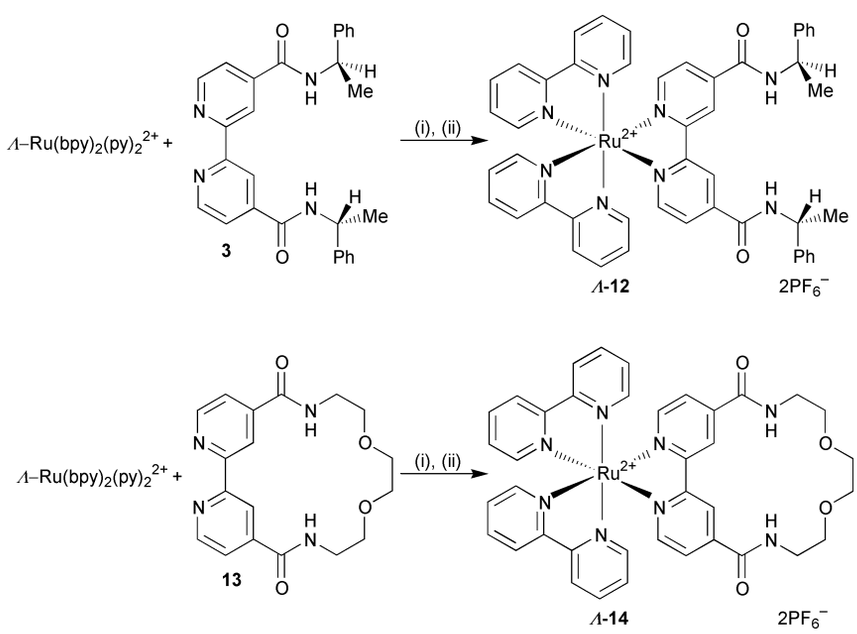



**Fig. 3** $^1$H NMR spectra (500 MHz, DMSO-$d_6$) of (a) the 1 : 1 diastereomeric mixture of *Λ*- and *Δ*-**12** synthesised from *rac*,*cis*-[Ru(bpy)$_2$Cl$_2$]; (b) *Λ*-**12**; (c) *Δ*-**12**. The protons on the substituted bipyridine ring are labelled by numbers. The protons on the unsubstituted rings are represented by letters.




**Scheme 2** Synthesis of ruthenium(II) receptors **12** and **14** from *Λ*- and *Δ*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ chiral building blocks (shown for the *Λ*-isomeric forms). *Λ*-**12**: (i) Ethylene glycol : water (90 : 10 v/v), 3 days; (ii) $NH_4PF_6$ (aq). *Δ*-**12**/*Λ*-**14**/*Δ*-**14**: (i) Ethylene glycol : water : acetic acid (90 : 5 : 5 v/v), 4 h; (ii) $NH_4PF_6$ (aq).

diastereomeric excess is calculated to be approximately 70% in both cases.

From the above discussion, it is clear that the reaction between ligand **3** and *Λ*- or *Δ*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ does not proceed with complete stereoretention. This result may be due to the limited solubility of compound **3** and/or steric factors hindering co-ordination to the metal centre. In the free bipyridine ligand, the nitrogen atoms on the ring are *anti* and the amide groups are oriented away from each other. However, the nitrogen atoms must adopt a *cis* disposition in the complexed form, which inevitably introduces steric interactions between the 4,4'-substituents. It is likely that the metal centre can rearrange before both nitrogen atoms of ligand **3** are co-ordinated.

With the above discussion in mind, the macrocyclic ligand **13** was synthesised according to a literature procedure (Scheme 2).[12b] This molecule has the nitrogen atoms predisposed for *cis* co-ordination and contains solubilising groups to promote dissolution in an ethylene glycol medium. Ligand **13** was reacted with *Λ*- and *Δ*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in an ethylene glycol–water–acetic acid mixture to give macrocyclic receptors *Λ*- and *Δ*-**14**, which were recrystallised from acetonitrile–water. The racemic version of macrocycle **14** was synthesised from [Ru(bpy)$_2$Cl$_2$] and ligand **13** using microwave heating, followed by purification on SP Sephadex C-25 as the support. This is an alternative method to the literature preparation of racemic **14**.[12b]

Receptors *Λ*- and *Δ*-**14** are enantiomeric and therefore possess the same $^1$H NMR spectrum. However, the enantiomeric purity can be analysed by $^1$H NMR spectroscopy when a chiral lanthanide shift reagent (LSR) is present.[21] Research by Barton and Nowick suggests that the LSR co-ordinates to the counter

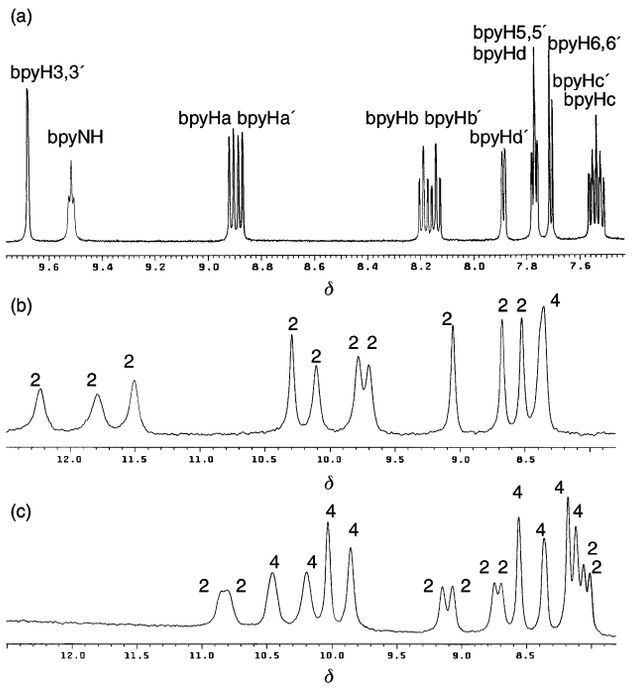



**Fig. 4** $^1$H NMR spectra (500 MHz, $CD_2Cl_2$) for the chloride salts of (a) racemic **14** in the absence of shift reagent (see Fig. 3 for the proton labelling system); (b) *Δ*-**14** with added Eu(tfc)$_3$; (c) racemic **14** with added Eu(tfc)$_3$. The number of protons contributing to each peak is shown for (b) and (c).

anion of the receptor and the resultant anionic complex interacts with the *Λ*- or *Δ*-ruthenium(II) cation to give two diastereomeric species.[21b] The degree of lanthanide induced shift ($\Delta\delta$) and the difference in shift between the two diastereomers ($\Delta\Delta\delta$) are maximised with small counter anions and non-polar solvents.[21b] For these reasons, the LSR studies were performed on the chloride salts of the *Δ*-, *Λ*- and racemic macrocycles (prepared by ion exchange on the hexafluorophosphate salts), in dichloromethane-$d_2$ solutions.

The $^1$H NMR spectrum of racemic **14** in the absence of shift reagent is shown in Fig. 4a. Four resonances are attributed to the bpyH3,3', bpyH5,5', bpyH6,6' and bpyNH protons on the substituted bipyridine ligand. The remaining signals are assigned to the eight magnetically nonequivalent protons on the unsubstituted bipyridine rings. The $^1$H NMR spectra for *Δ*- and racemic-**14** in the presence of tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) {Eu(tfc)$_3$} are shown in Figs. 4b and 4c respectively. The low field region of *Λ*- or *Δ*-**14** with Eu(tfc)$_3$ is comprised of eleven peaks from the twelve bipyridine and NH protons, giving a total integration of 24H.[22] As seen from Fig. 4b, each peak appears as just a singlet in the *Δ* (or *Λ*) $^1$H NMR spectrum. This contrasts with the racemic host in the presence of Eu(tfc)$_3$ (Fig. 4c). This spectrum is comprised of sixteen signals, since some peaks are split into two as consequence of two diastereomeric species in solution. The LSR experiment therefore demonstrates the optical purity of *Λ*- and *Δ*-**14**.

The absolute configurations of *Λ*- and *Δ*-**14** were assigned using circular dichroism spectroscopy.[23] According to exciton theory,[24] (polypyridine)ruthenium(II) complexes with a *Λ* configuration (with respect to a $C_3$ or pseudo $C_3$ axis) will give a *negative* CD band to *higher* energy and a *positive* CD band to *lower* energy in the region of the ligand-centred (LC) long-axis polarised transitions (*ca.* 285 nm for [Ru(bpy)$_3^{2+}$][25]). The CD spectra of *Λ*- and *Δ*-**14** are shown in Fig. 5 and reveal the typical mirror image relationship for enantiomeric molecules. Since *Λ*- and *Δ*-**14** are synthesised from *Λ*- and *Δ*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ respectively, the two pyridine groups are substituted with retention of configuration. Hua and von Zelewsky previously

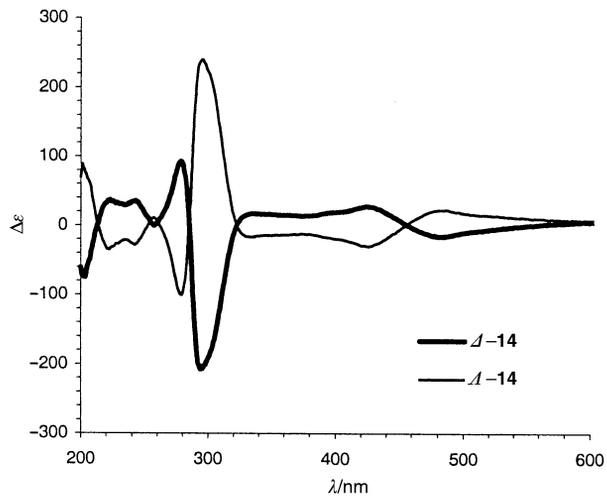



**Fig. 5** CD spectra of receptors of *Λ*- and *Δ*-**14** recorded in MeCN.

reported stereoretention for the reaction between *Δ*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ and 1,10-phenanthroline.[18]

### Chromatographic separations of chiral ruthenium(II) receptors

The second approach towards chiral ruthenium(II) receptors was chromatographic separation on SP Sephadex C-25.[21a,26] In this technique, the resolution of the *Λ*- and *Δ*-isomers depends on their differential association with the counter anion of the eluent and/or the chiral support. Chromatography offers two major advantages in the synthesis of chiral ruthenium(II) systems. Firstly, the use of chiral building blocks (as exemplified by the von Zelewsky method[18]) requires subsequent reactions to proceed with stereoretention. The preparation of *Λ*- and *Δ*-**12** (Scheme 2) shows this is not always the case, since *Δ*-/*Λ*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ can lose some of their stereochemical integrity upon ligand substitution. Chromatography circumvents this problem by employing resolution as the final stage in the synthesis. Secondly, diastereomeric salt formation results in the selective crystallisation of one ruthenium enantiomer for a given chiral counter anion. In contrast, chromatography allows both enantiomers to be obtained in a single experiment.

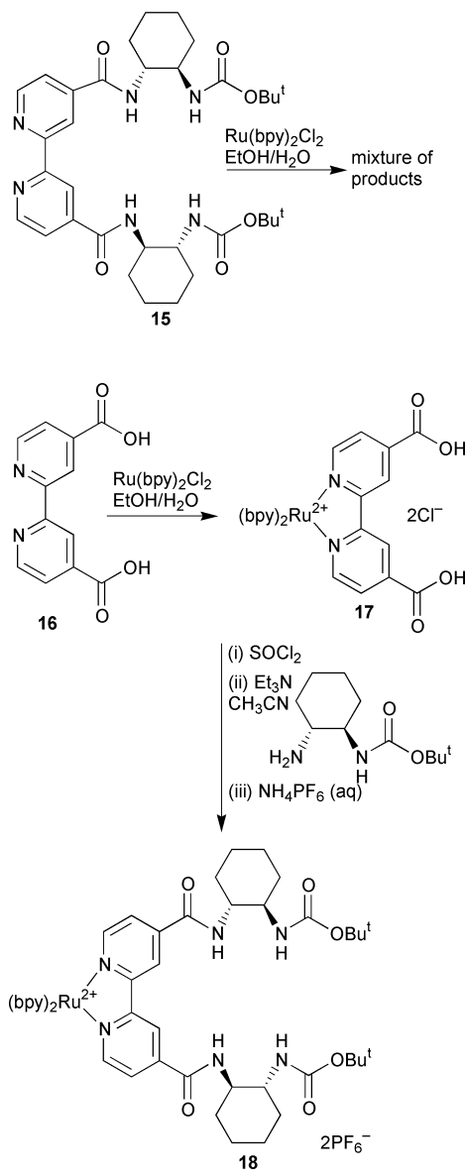
Receptors **12** and **18** (Schemes 2 and 3 respectively) were prepared, and chromatographic separation attempted using SP Sephadex C-25 as the support. The two possible synthetic routes to receptor **18** are detailed in Scheme 3. The reaction between ligand **15** (preparation as for the enantiomer **6**, Scheme 1) and [Ru(bpy)$_2$Cl$_2$] gave an intractable mixture of products. Consequently, receptor **18** was prepared *via* [4,4'-dicarboxy-2,2'-bipyridine]bis(2,2'-bipyridine)ruthenium(II) dichoride (**17**). Compound **17** was synthesised in near quantitative yield from ligand **16** and [Ru(bpy)$_2$Cl$_2$] by an alternative method to the literature procedure.[12c] Thionyl chloride was used to convert compound **17** to the bis(acid chloride), which was then condensed with *tert*-butoxycarbonyl-*R*,*R*-diaminocyclohexane. Addition of ammonium hexafluorophosphate gave the target receptor **18** in high yield.

Receptors **12** and **18** both exist as pairs of diastereomers due to the chirality at the metal centre and on the bipyridine backbone. This diastereomeric relationship suggests that an achiral eluent could be used to effect separation. Each receptor was therefore eluted with aqueous sodium 4-tosylate on an SP Sephadex C-25 cation exchanger. Table 1 shows the distance required to achieve band separation (the 'effective column length', ECL) was six metres for host **18**, but the isomers of **12** could not be separated with 4-tosylate as the anion. However, receptor **12** was separated (ECL = 15 m) using the chiral eluent sodium *O*,*O*'-dibenzoyl-L-tartrate. Toluoyl-L-tartrate reduced the separation distance to seven metres, but the receptor proved

**Table 1** Summary of chiral chromatography results for receptors **12** and **18**

| Receptor | Eluent[a] | ECL[b]/m | Band 1 helicity[c] | Band 2 helicity |
|---|---|---|---|---|
| **12** | (−)-*O*,*O*'-Dibenzoyl-L-tartrate | 15 | [d] | [d] |
| **12** | (−)-Di-*O*,*O*'-4-toluoyl-L-tartrate | 7 | *Δ*[e] | *Λ*[e] |
| **18** | 4-Tosylate | 6 | *Λ* | *Δ* |

[a] As the aqueous sodium salt. [b] Effective column length (distance required to separate the isomers). [c] Band 1 is the band eluted first. [d] Helicity not determined. [e] Helicity recorded in sodium (−)-di-*O*,*O*'-4-toluoyl-L-tartrate solution.




**Scheme 3**

too insoluble under the chromatographic conditions to work on a preparative scale.

Circular dichroism spectroscopy was used to determine absolute configurations for the isomers of **18**. The signs of the LC long-axis polarised transitions around 300 nm showed band 1 was *Λ* and band 2 was *Δ* (Table 1). The CD spectra of bands 1 and 2 were mirror images, due to the mirror image *Λ*- and *Δ*-arrangements at the metal centre.

The $^1$H NMR spectrum of receptor **18** prior to separation was compared with the spectra for bands 1 and 2 (Fig. 6). This gave a diagnostic test of diastereomeric purity, since the bpyH3,3' singlet occurs at different chemical shifts for the *Λ*- and *Δ*-isomers. Receptor **18** before separation shows two singlets for the bpyH3,3' resonance (Fig. 6a). However, *Λ*- and *Δ*-**18** are characterised by just one bpyH3,3' singlet each; these occur at *δ* 9.25 for *Λ*-**18** (Fig. 6b) and 9.22 for *Δ*-**18** (Fig. 6c). This proves that both bands are diastereomerically pure.

**Table 2** Stability constants for chiral rhenium(I) and ruthenium(II) receptors with optically active guests in DMSO-$d_6$[a]

| Receptor | *N*-Cbz-L-Glu[b] | *N*-Cbz-D-Glu[b] | L-Lac[c] | D-Lac[c] |
|---|---|---|---|---|
| **7** | 134(4) | 140(3) | — | — |
| **8** | — | 140(4) | — | — |
| **9** | 160(4) | 128(4) | — | — |
| **10** | — | — | 31(5) | 35(7) |
| **11** | 26(3) | 22(3) | — | — |
| *Λ*-**14** | $>10^3$ | — | — | 103(5) |
| *Δ*-**14** | $>10^3$ | — | — | 101(7) |
| *Λ*-**18** | 200(14) | 250(21) | — | — |
| *Δ*-**18** | — | 254(22) | [d] | — |

[a] Determined at 298 K; ± errors in parentheses. [b] $NMe_4^+$ salt. [c] $Na^+$ salt. [d] No binding.

## Preliminary binding studies with chiral anionic guests

Preliminary $^1$H NMR binding studies were performed with receptors **7–11**, **14** and **18** and the chiral anions *N*-Cbz-L(D)-glutamate (Cbz = carbobenzyloxy) and L(D)-lactate in DMSO-$d_6$ solution. Significant downfield shifts of the bpyH3,3' and amide protons were observed on addition of anions, which suggests that these protons form hydrogen bonds with the carboxylate functionality of the guests. Stability constants were determined by EQNMR [27] analysis of the $^1$H NMR titration curves and the results are presented in Table 2. The first point to note from the table is the behaviour of rhenium(I) receptors **7–11** with chiral anionic guests. The phenyl-based hosts **7** and **8** are enantiomeric, as are the naphthyl receptors **9** and **10**. The association of *N*-Cbz-L-glutamate with host **7** should therefore be the same as *N*-Cbz-D-glutamate with **8**, since there is an enantiomeric relationship between these complexes. This is indeed the case (within experimental error), which shows that $^1$H NMR spectroscopy is an accurate technique for determining relative stability constants. Glutamate binding by receptors **7–9** is *ca.* $10^2$ $M^{-1}$ and surprisingly strong for electroneutral hosts in a competitive DMSO-$d_6$ solvent system. In contrast, receptor **11** possesses a low affinity for the glutamate anion (*K ca.* 20–30 $M^{-1}$). This is possibly due to the large cyclohexyl groups in **11**, which may sterically block approach of guests towards the amide bipyridine binding site. Complexation of the lactate anion by host **10** is also relatively weak. This contrasts with the larger stability constants obtained for the enantiomeric receptor **9** and *N*-Cbz-glutamate. The disparity in binding strength between glutamate and lactate partly reflects the different geometries and charges (−2 and −1 respectively) of these guests. In addition, the smaller counter cation for lactate ($Na^+$) compared to glutamate ($NMe_4^+$) will attenuate binding by strongly associating with the negative charge. The most important point to note from Table 2 is the degree of enantioselection exhibited by hosts **7–11**. Disappointingly, each receptor shows little difference in binding strength between the D- and L-forms of a particular guest, except for receptor **9** which displays a small stereogenic preference for *N*-Cbz-L-Glu (160 $M^{-1}$) over *N*-Cbz-D-Glu (128 $M^{-1}$). This lack of enantioselectivity

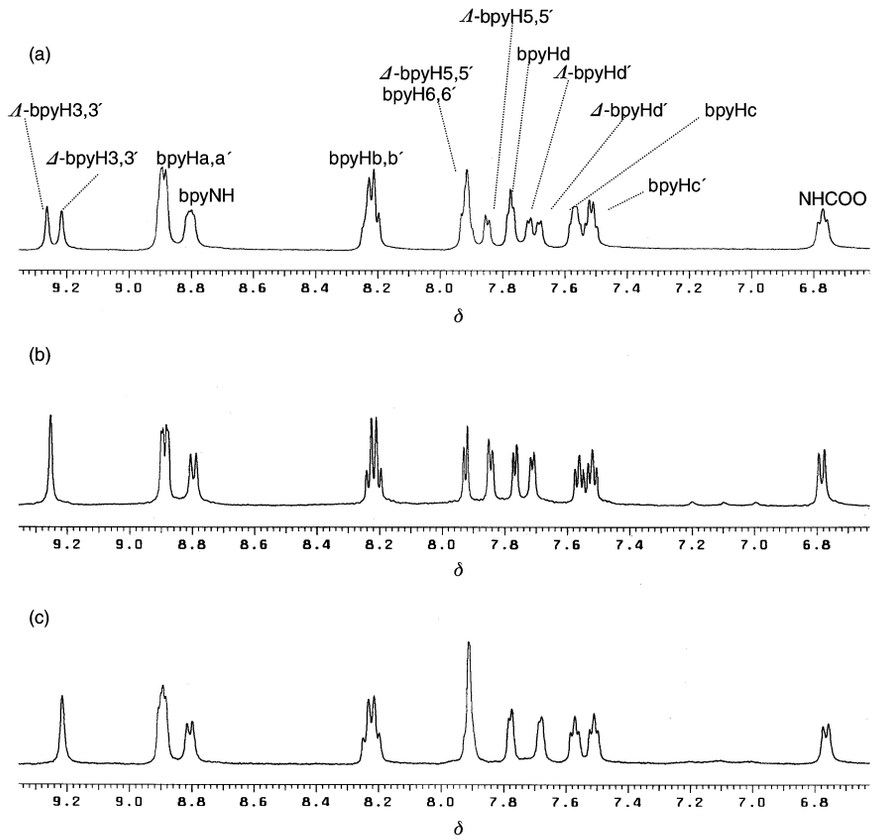



**Fig. 6** $^1$H NMR spectra (500 MHz, DMSO-$d_6$) of (a) receptor **18** as the 1 : 1 mix of diastereomers; (b) *Λ*-**18** (band 1); (c) *Δ*-**18** (band 2). (See Fig. 3 for the proton labelling system.)

probably reflects conformational flexibility in the host structure, which accommodates both configurations of the guest equally well.

The effect of metal helicity on anion binding was examined with the ruthenium(II)-based receptors **14** and **18**. Unfortunately, no enantio-discrimination was observed between the *Λ*- and *Δ*-isomers (Table 2). For example, the stability constants for D-lactate are the same for *Λ*- and *Δ*-**14**, as are the binding constants for *Λ*- and *Δ*-**18** with *N*-Cbz-D-Glu. This implies that the amide binding site is too far removed from the unsubstituted bipyridine rings to be affected by the metal helicity. The chiral guest probably approaches from the side opposite to the $Ru(bpy)_2^{2+}$ moiety, and therefore only encounters an achiral planar binding surface. Table 2 also shows the *R*,*R*,*R*,*R* cyclohexyl functionality in *Λ*-**18** does not display a significant stereogenic preference for *N*-Cbz-L- or -D-Glu. This finding is important and demonstrates that *R*,*R*,*R*,*R* cyclohexyl groups are not appropriate substituents for chiral host–guest recognition in this case.

Receptors *Λ*- and *Δ*-**18** possess low affinities for glutamate and lactate compared to hosts *Λ*- and *Δ*-**14**. For example, the stability constant for *Λ*-/*Δ*-**14** and lactate is *ca.* 100 $M^{-1}$, whereas *Δ*-**18** does not co-ordinate this anion in DMSO-$d_6$. This is a consequence of the large cyclohexyl groups in **18**, which probably block the anion binding site (*cf.* host **11** above). However, the association between glutamate and *Λ*-/*Δ*-**18** is still an order of magnitude larger than the rhenium(I) analogue **11**, due to the electrostatic interaction between the dipositive charge in *Λ*-/*Δ*-**18** and the anionic guest.

## Conclusion

A new series of chiral rhenium(I) and ruthenium(II) receptors has been synthesised and their anion recognition properties examined. The neutral hosts **7–11** were prepared by co-ordinating chiral bipyridine ligands to a bromotricarbonyl-rhenium(I) centre. Stability constants were evaluated for chiral carboxylate anions in DMSO-$d_6$, but there was generally no evidence for enantioselective complexation. The exception was receptor **9** with *N*-Cbz-glutamate, which did exhibit a small stereogenic preference for the L-isomer over the D-form. Although the degree of chiral discrimination was disappointing, these neutral rhenium hosts bind biologically important anions with moderate strength, even in the competitive solvent DMSO-$d_6$.

The ruthenium(II) receptors **12** and **14** were synthesised from the chiral building blocks *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$.[18] The pyridine groups in *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$ could be substituted by functionalised bipyridine ligands, but the reaction did not proceed with complete stereoretention for host **12**. The macrocyclic receptors *Λ*- and *Λ*-**14** were synthesised from *Λ*- and *Δ*-$[Ru(bpy)_2(py)_2]^{2+}$ respectively in high optical purity. However, *N*-Cbz-L-glutamate and D-lactate did not differentiate between the *Λ*- and *Δ*-helical arrays.

The ruthenium(II) receptors **12** and **18** were separated on a SP Sephadex C-25 cation exchanger. The isomer configurations were then empirically assigned using circular dichroism spectroscopy. The $^1$H NMR spectra of receptors *Λ*- and *Δ*-**18** demonstrated that both molecules were diastereomerically pure. Preliminary binding studies with host **18** and chiral carboxylate anions did not reveal any enantioselective recognition. However, this work has served to establish a variety of stereoselective synthetic approaches to (2,2'-bipyridine)-ruthenium(II) and -rhenium(I) receptors.

## Experimental

### Instrumentation

NMR spectra were recorded on Varian or Bruker 300 MHz and Varian 500 MHz spectrometers. Mass spectrometry was carried out at the SERC Mass Spectrometry Service, Swansea.

Elemental analysis was performed at the Inorganic Chemistry Laboratory, University of Oxford. Electronic spectra were measured on a Varian CARY 5E UV-VIS-NIR spectrophotometer, and circular dichroism (CD) using a JASCO J-715 spectropolarimeter.

### Reagent and solvent pre-treatment

Commercially available materials were used without further purification unless otherwise stated. Acetonitrile and dichloromethane were distilled from calcium hydride and calcium chloride respectively and toluene was dried over sodium. Thionyl chloride was distilled from triphenylphosphite and used immediately in subsequent reactions. 4,4'-Dicarboxy-2,2'-bipyridine,[13] *Λ*-[Ru(bpy)$_2$(py)$_2$]{(−)-*O*,*O*'-dibenzoyl-L-tartrate}·12H$_2$O,[18] *Δ*-[Ru(bpy)$_2$(py)$_2$]{(+)-*O*,*O*'-dibenzoyl-D-tartrate}·12H$_2$O,[18] *rac,cis*-[Ru(bpy)$_2$Cl$_2$][20] and 4,4'-[1,12-dioxo-5,8-dioxa-2,11-diaza(12)carbamoyl]-2,2'-bipyridinophane **13**[12b] were synthesised according to literature procedures.

### Protocol for the NMR titrations

Aliquots of anionic guest (250 μmol in 0.5 ml of deuterated solvent) were added to a solution of the host (5 μmol in 0.5 ml) and the chemical shift of a specific nucleus on the host was monitored for each addition from 0 to 5 equivalents of guest. The resulting titrations were analysed by the EQNMR program.[27]

### Protocol for the lanthanide shift experiments

Solid tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) {Eu(tfc)$_3$} (1.8 mg, 2.0 μmol) was added to a solution of racemic, *Λ*- or *Δ*-**14** (1.7 mg, 2.0 μmol) in $CD_2Cl_2$ (1 ml). The mixture was stirred for 5 min and then filtered. The $^1$H NMR spectrum of the filtrate was recorded.

### Syntheses

**4,4'-Bis(chlorocarbonyl)-2,2'-bipyridine.** *Typical preparation*. 4,4'-Dicarboxy-2,2'-bipyridine (0.869 g, 3.56 mmol) was refluxed in thionyl chloride (25 ml) for 16 h under nitrogen. The excess thionyl chloride was then removed by distillation and the yellow residues dried under vacuum (4 h). The acid chloride was assumed to form in quantitative yield and was used immediately in subsequent reactions.

**4,4'-Bis(*S*-α-methylbenzylcarbamoyl)-2,2'-bipyridine 2.** A solution of 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine (1.00 g, 3.56 mmol) in dry $CH_2Cl_2$ (30 ml) was added dropwise to a stirred solution of *S*-α-methylbenzylamine (1.72 g, 14.2 mmol) and triethylamine (2.02 g, 0.020 mol) in dry $CH_2Cl_2$ (30 ml). This gave a pink precipitate, which was stirred at room temperature under nitrogen for 1 h and then refluxed for 1.5 h. The precipitate was removed by filtration and washed with $CH_2Cl_2$ (3 × 50 ml), aqueous ammonia solution (1 M, 100 ml) and then water until the washings ran at neutral pH. The pink solid was dried in an oven at 40 °C (1.15 g, 72%). $^1$H NMR (500 MHz, DMSO-d$_6$) *δ*: 9.36 (2H, d, *J* = 5 Hz, NH), 8.91 (2H, d, *J* = 5 Hz, bpyH6,6'), 8.85 (2H, s, bpyH3,3'), 7.91 (2H, d, *J* = 5 Hz, bpyH5,5'), 7.45 (4H, d, *J* = 8 Hz, ArCH2), 7.37 (4H, t, *J* = 7.8 Hz, ArCH3), 7.26 (2H, t, *J* = 7.5 Hz, ArCH4), 5.22 (2H, quint, *J* = 7.5 Hz, CH), 1.50 (6H, d, *J* = 7.5 Hz, Me). $^{13}$C NMR (125 MHz, DMSO-d$_6$) *δ*: 164.25 (CONH), 155.74, 150.15, 144.59, 143.18, 128.49, 126.94, 126.34, 122.40, 118.62, 49.01 (CH), 22.19 ($CH_3$). Found: C, 73.2; H, 6.0; N, 12.0. Calc. for $C_{28}H_{26}N_4O_2$·0.5H$_2$O: C, 73.2; H, 5.9; N, 12.2%. FAB-MS: *m*/*z* 473 (M + Na)$^+$, 451 (M + H)$^+$.

**4,4'-Bis(*R*-α-methylbenzylcarbamoyl)-2,2'-bipyridine 3.** Synthesis and characterisation as for ligand **2**, using *R*-α-methylbenzylamine instead of the *S*-isomer (1.39 g, 87%).

**4,4'-Bis[*S*-1-(1-naphthyl)ethylcarbamoyl]-2,2'-bipyridine 4.** 4,4'-Bis(chlorocarbonyl)-2,2'-bipyridine (0.230 g, 0.819 mmol) was dissolved in dry $CH_2Cl_2$ (20 ml) and added dropwise to a stirred solution of *S*-1-(1-naphthyl)ethylamine (0.561 g, 3.28 mmol) and triethylamine (0.464 g, 4.59 mmol) in dry $CH_2Cl_2$ (30 ml) under nitrogen. The mixture was stirred for 1 h at room temperature and then refluxed for a further 16 h. The precipitate was removed by filtration and purified as for ligand **2**. This afforded the product as a pink solid (0.333 g, 74%). $^1$H NMR (300 MHz, DMSO-d$_6$) *δ*: 9.48 (2H, d, *J* = 7.7 Hz, NH), 8.86 (2H, d, *J* = 4.9 Hz, bpyH6,6'), 8.82 (2H, s, bpyH3,3'), 8.22 (2H, d, *J* = 8.2 Hz, ArH), 7.96 (2H, d, *J* = 7.7 Hz, ArH), 7.89 (2H, d, *J* = 4.9 Hz, bpyH5,5'), 7.86 (2H, d, *J* = 7.8 Hz, ArH), 7.67 (2H, d, *J* = 7.1 Hz, ArH), 7.53–7.62 (6H, m, ArH), 6.00 (2H, quint, CH), 1.66 (6H, d, *J* = 6.7 Hz, Me). $^{13}$C NMR (125 MHz, DMSO-d$_6$) *δ*: 164.11 (CONH), 155.67, 150.15, 143.04, 139.96, 133.57, 130.64, 128.88, 127.59, 126.45, 125.79, 125.66, 123.23, 122.88, 122.40, 118.58, 45.19 (CH), 21.39 (Me). Found: C, 77.2; H, 5.4; N, 10.0. Calc. for $C_{36}H_{30}N_4O_2$·0.5H$_2$O: C, 77.3; H, 5.6; N, 10.0%. FAB-MS *m*/*z* 573 (M + Na)$^+$, 551 (M + H)$^+$.

**4,4'-Bis[*R*-1-(1-naphthyl)ethylcarbamoyl]-2,2'-bipyridine 5.** Synthesis and characterisation as for ligand **4**, using *R*-1-(1-naphthyl)ethylamine instead of the *S*-isomer (0.356 g, 79%).

***tert*-Butoxycarbonyl-*S*,*S*-1,2-diaminocyclohexane.** A solution of di-*tert*-butyldicarbonate (1.03 g, 4.70 mmol) in dioxane (30 ml) was added dropwise to a stirred solution of *S*,*S*-1,2-diaminocyclohexane (4.29 g, 0.0376 mol) in dioxane (80 ml). The mixture was stirred for 22 h and the solvent was then evaporated to give a yellow solid. This was suspended in $H_2O$ (50 ml) and the insoluble bis substituted product removed by filtration. The filtrate was extracted with $CH_2Cl_2$ (3 × 50 ml) and the organic fractions were washed with $H_2O$ (3 × 30 ml). The organic layer was dried over $MgSO_4$ and the solvent was then removed to give a yellow solid, which was dried under vacuum (0.814 g, 81%). In the following NMR, cy indicates the protons on the cyclohexyl ring. $^1$H NMR (300 MHz, $CDCl_3$) *δ*: 4.44 (1H, s, br, NHCO), 3.13 (1H, m, br, C*H*NHCO), 2.31 (1H, td, *J* = 10 Hz, *J'* = 4 Hz, C*H*NH$_2$), 1.97 (2H, m, cy), 1.70 (2H, m, cy), 1.42 (11H, s, $OCMe_3$, NH$_2$), 1.02–1.32 (4H, m, cy). Found: C, 61.5; H, 10.2; N, 13.0. Calc. for $C_{11}H_{22}N_2O_2$: C, 61.7; H, 10.4; N, 13.1%.

***tert*-Butoxycarbonyl-*R*,*R*-1,2-diaminocyclohexane.** Synthesis and characterisation as for the *S*,*S*-enantiomer, using di-*tert*-butyldicarbonate (1.62 g, 7.40 mmol) and *R*,*R*-1,2-diaminocyclohexane (6.76 g, 0.0592 mol). This afforded the product as a yellow solid (1.49 g, 94%).

**4,4'-Bis(1-carbonyl-2-*tert*-butoxycarbonyl-*S*,*S*-1,2-diaminocyclohexyl)-2,2'-bipyridine 6.** A solution of 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine (0.388 g, 1.38 mmol) in dry $CH_2Cl_2$ (20 ml) was added dropwise to a stirred solution of *tert*-butoxycarbonyl-*S*,*S*-1,2-diaminocyclohexane (0.610 g, 2.85 mmol) and triethylamine (0.783 g, 7.74 mmol) in dry $CH_2Cl_2$ (20 ml) under nitrogen. The mixture was stirred at room temperature for 1 h, refluxed for 2 h and then stirred at room temperature for a further 15 h. The precipitate was removed by filtration and purified as for ligand **2**. This afforded the product as a white solid (0.621 g, 71%). $^1$H NMR (500 MHz, DMSO-d$_6$) *δ*: 8.85 (2H, d, *J* = 4.5 Hz, bpyH6,6'), 8.77 (2H, s, bpyH3,3'), 8.62 (2H, d, *J* = 9 Hz, bpyNH), 7.82 (2H, d, *J* = 4.5 Hz, bpyH5,5'), 6.72 (2H, d, *J* = 9.5 Hz, NHCOO), 3.75 (2H, m, C*H*NH), 3.39 (2H, m, C*H*NH), 1.80 (4H, m, cy), 1.67 (4H, m, cy), 1.30–1.45 (4H, m, cy), 1.17 (18H, s, $OCMe_3$), 1.14–1.22 (4H, m, cy). Found: C, 63.0; H, 7.5; N, 12.9. Calc. for $C_{34}H_{48}N_6O_6$·0.5H$_2$0: C, 63.2; H, 7.7; N, 13.0%. FAB-MS *m*/*z* 660 (M + Na)$^+$, 638 (M + H)$^+$.

**4,4'-Bis(1-carbonyl-2-*tert*-butoxycarbonyl-*R*,*R*-1,2-diaminocyclohexyl)-2,2'-bipyridine.** Synthesis and characterisation as for the *S*,*S*-ligand **6**, using 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine (0.882 g, 3.14 mmol), *tert*-butoxycarbonyl-*R*,*R*-1,2-diaminocyclohexane (1.39 g, 6.46 mmol) and triethylamine (1.78 g, 0.0176 mol). This afforded the product as a pink solid (1.74 g, 87%).

**General procedure for the synthesis of rhenium(I) receptors 7–11.** Bromopentacarbonylrhenium(I) (1.14 equiv.) was suspended in dry toluene (50 ml) and refluxed under nitrogen until it dissolved. The appropriate 4,4'-diamide-2,2'-bipyridine ligand (1 equiv.) was then added and the orange mixture refluxed for 15 h. The mixture was cooled to room temperature, filtered and the solvent evaporated from the filtrate to yield an orange solid. This was dissolved in $CH_2Cl_2$ (30 ml), stirred and the solvent then evaporated (repeated twice). The receptor was obtained as an orange solid, which was dried under vacuum.

**Bromotricarbonyl[4,4'-bis(*S*-α-methylbenzylcarbamoyl)-2,2'-bipyridine]rhenium(I) 7.** Synthesised from $[Re(CO)_5Br]$ (0.108 g, 0.265 mmol) and ligand **2** (0.105 g, 0.233 mmol); yield 0.162 g, 87%. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.55 (2H, d, $J$ = 8 Hz, NH), 9.23 (2H, 2 overlapping d, $J$ = 5.5 Hz/5 Hz, bpyH6/6'), 9.12 (2H, m, bpyH3,3'), 8.12 (2H, 2 overlapping dd, $J$ = 5 Hz, $J'$ = 1.5 Hz, bpyH5,5'), 7.46 (4H, d, $J$ = 7 Hz, ArCH2), 7.37 (4H, t, $J$ = 7.5 Hz, ArCH3), 7.28 (2H, t, $J$ = 7.5 Hz, ArCH4), 5.24 (2H, quint, $J$ = 7 Hz, CH), 1.54 (6H, d, $J$ = 6.5 Hz, Me). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 197.21 (ReCO *cis* to Br), 189.10 (ReCO *trans* to Br), 162.64 (CONH), 155.76, 153.98, 144.79, 144.02, 128.58, 127.11, 126.32, 125.94, 122.54, 49.32 (CH), 22.25 (Me). Found: C, 45.3; H, 3.8; N, 6.4. Calc. for $ReC_{31}H_{26}N_4O_5Br\cdot H_2O$: C, 45.5; H, 3.5; N, 6.8%. FAB-MS *m*/*z* 823 $(M + Na)^+$, 800 $(M)^+$, 721 $(M - Br)^+$.

**Bromotricarbonyl[4,4'-bis(*R*-α-methylbenzylcarbamoyl)-2,2'-bipyridine]rhenium(I) 8.** Synthesised from $[Re(CO)_5Br]$ (0.108 g, 0.265 mmol) and ligand **3** (0.105 g, 0.233 mmol); yield 0.174 g, 93%. Characterisation as for receptor **7**.

**Bromotricarbonyl[4,4'-bis{*S*-1-(1-naphthyl)ethylcarbamoyl}-2,2'-bipyridine]rhenium(I) 9.** Synthesised from $[Re(CO)_5Br]$ (0.108 g, 0.265 mmol) and ligand **4** (0.128 g, 0.233 mmol); yield 0.132 g, 63%. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.71 (2H, d, $J$ = 8 Hz, NH), 9.22 (2H, 2 overlapping d, $J$ = 4.8 Hz, bpyH6,6'), 9.12 (2H, s, bpyH3,3'), 8.23 (2H, d, $J$ = 8 Hz, ArH), 8.14 (2 overlapping d, $J$ = 6 Hz, bpyH5,5'), 7.99 (2H, d, $J$ = 8.5 Hz, ArH), 7.89 (2H, d, $J$ = 8 Hz, ArH), 7.71 (2H, t, $J$ = 6 Hz, ArH), 7.52–7.63 (6H, m, ArH), 6.02 (2H, m, CH), 1.67 (6H, d, $J$ = 7 Hz, Me). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 197.24 (ReCO *cis* to Br), 189.13 (ReCO *trans* to Br), 162.58 (CONH), 155.83, 154.06, 144.63, 139.58, 139.54, 133.63, 130.61, 130.57, 129.00, 127.86, 126.64, 125.96, 125.78, 123.17, 123.00, 122.65, 122.60, 45.75 (CH), 21.57 (Me), 21.52 (Me). Found: C, 50.8; H, 3.8; N, 5.7. Calc. for $ReC_{39}H_{30}N_4O_5Br\cdot H_2O$: C, 51.0; H, 3.5; N, 6.1%. FAB-MS *m*/*z* 923 $(M + Na)^+$, 900 $(M)^+$, 821 $(M - Br)^+$.

**Bromotricarbonyl[4,4'-bis{*R*-1-(1-naphthyl)ethylcarbamoyl}-2,2'-bipyridine]rhenium(I) 10.** Synthesised from $[Re(CO)_5Br]$ (0.108 g, 0.265 mmol) and ligand **5** (0.128 g, 0.233 mmol); yield 0.151 g, 72%. Characterisation as for receptor **9**.

**Bromotricarbonyl[4,4'-bis(1-carbonyl-2-*tert*-butoxycarbonyl-*S*,*S*-1,2-diaminocyclohexyl)-2,2'-bipyridine]rhenium(I) 11.** Synthesised from $[Re(CO)_5Br]$ (0.149 g, 0.368 mmol) and ligand **6** (0.205 g, 0.323 mmol); yield 0.249 g, 74%. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.23 (2H, 2 overlapping d, $J$ = 6 Hz/5.5 Hz, bpyH6/6'), 9.10 (2H, s, bpyH3,3'), 8.96 (1H, d, $J$ = 9 Hz, bpyNH), 8.93 (1H, d, $J$ = 9 Hz, bpyNH), 8.09 (2H, d, $J$ = 5.5 Hz, bpyH5,5'), 6.80 (2H, d, $J$ = 9 Hz, NHCOO), 3.81 (2H, m, C*H*NH), 3.44 (2H, m, C*H*NH), 1.82 (4H, m, cy), 1.71 (4H, m, cy), 1.36–1.45 (4H, m, cy), 1.23 (4H, m, cy), 1.13 (9H, s, $OCMe_3$), 1.12 (9H, s, $OCMe_3$). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 197.13 (ReCO *cis* to Br), 189.11 (ReCO *trans* to Br), 162.33/162.25 (CONH), 155.83/155.73/155.68 (CONH/bpy), 154.00/153.96 (bpy), 145.17/145.13 (bpy), 125.81/125.65 (bpy), 122.27/122.06 (bpy), 77.62 ($OC(CH_3)_3$), 54.47 (CHNH), 53.28 (CHNH), 31.78 (cy), 31.74 (cy), 28.27 ($OC(CH_3)_3$), 28.23 ($OC(CH_3)_3$), 24.93 (cy), 24.70 (cy). Found: C, 42.4; H, 4.9; N, 7.7. Calc. for $ReC_{37}H_{48}N_6O_9Br\cdot 3H_2O$: C, 42.7; H, 5.2; N, 8.1%. FAB-MS *m*/*z* 1009 $(M + Na)^+$, 986 $(M)^+$, 907 $(M - Br)^+$, 851 $(M - Br - 2CO)^+$.

**Diastereomeric [4,4'-bis(*R*-α-methylbenzylcarbamoyl)-2,2'-bipyridine]bis(2,2'-bipyridine)ruthenium(II) dichloride.** $[Ru(bpy)_2Cl_2]$ (0.260 g, 0.518 mmol) and ligand **3** (0.188 g, 0.416 mmol) were refluxed in 9 : 1 EtOH : $H_2O$ (30 ml) under nitrogen for 16 h. The solvent was then removed under vacuum to give a crude dark brown solid. This was loaded onto a Sephadex LH-20 column and eluted with MeCN and then 20 : 1 v/v MeCN : MeOH. The last (red) fraction was collected and the solvent evaporated to yield the product as a dark red solid (0.361 g, 85%).

This molecule exists in two diastereomeric forms due to the chirality at the metal centre and at the substituted bipyridyl. Diastereomer 1(2) is labelled as dst1(2) in the following NMR. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 10.10 (2H, s, bpyH3,3' dst1), 10.07 (2H, s, bpyH3,3' dst2), 9.85 (4H, d, $J$ = 8 Hz, NH), 8.88 (8H, m, bpyHa,a'), 8.20 (8H, m bpyHb,b'), 7.92 (4H, d, $J$ = 6.5 Hz, bpyH6,6'), 7.90 (4H, d, $J$ = 6.5 Hz, bpyH5,5'), 7.80 (4H, m, bpyHd), 7.73 (4H, m, bpyHd'), 7.48–7.58 (16H, m, ArCH2, bpyHc,c'), 7.35 (4H, t, $J$ = 7.8 Hz, ArCH3 dst1), 7.33 (4H, t, $J$ = 7.8 Hz, ArCH3 dst2), 7.25 (4H, m, ArCH4), 5.24 (4H, m, CH), 1.61 (12H, d, $J$ = 7.5 Hz, Me). Found: C, 56.3; H, 5.3; N, 11.1. Calc. for $RuC_{48}H_{42}N_8O_2Cl_2\cdot 5H_2O$: C, 56.3; H, 5.1; N, 10.9%. FAB *m*/*z* cluster at 899–901 $(M - Cl)^+$, 864 $(M - 2Cl)^+$.

**Diastereomeric [4,4'-bis(*R*-α-methylbenzylcarbamoyl)-2,2'-bipyridine]bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate 12.** An aqueous solution of the chloride salt of compound **12** was converted to the hexafluorophosphate salt by adding a saturated solution of $NH_4PF_6$ (aq). The hexafluorophosphate salt of compound **12** was precipitated as an orange solid, which was removed by filtration and washed with cold water before being dried under vacuum (0.394 g, 79% from ligand **3**). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.44 (4H, 2 overlapping d, $J$ = 7.5 Hz, 8 Hz, NH dst1,dst2), 9.24 (2H, s, bpyH3,3' dst1), 9.22 (2H, s, bpyH3,3' dst2), 8.88 (8H, 2 overlapping d, $J$ = 7.5 Hz/8.5 Hz, bpyHa/a'), 8.22 (8H, m, bpyHb,b'), 7.91 (8H, m, bpyH5,5', bpyH6,6'), 7.79 (4H, d, $J$ = 5.5 Hz, bpyHd), 7.75 (4H, d, $J$ = 5.5 Hz, bpyHd'), 7.58 (4H, t, $J$ = 6.5 Hz, bpyHc), 7.52 (4H, t, $J$ = 6.8 Hz, bpyHc'), 7.43 (8H, d, $J$ = 8 Hz, ArCH2), 7.36 (8H, t, $J$ = 7.5 Hz, ArCH3), 7.27 (4H, t, $J$ = 7.3 Hz, ArCH4), 5.22 (4H, m, CH), 1.51 (12H, d, $J$ = 7 Hz, Me). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 162.61 (CONH), 157.18, 156.55, 156.50, 151.98, 151.67, 151.31, 143.99, 143.96, 142.23, 138.41, 128.53, 128.19, 128.12, 127.13, 126.33, 126.29, 125.94, 124.71, 124.68, 122.33, 49.21 (CH dst1), 49.14 (CH dst2), 22.08 (Me). Found: C, 48.7; H, 3.7; N, 9.2. Calc. for $RuC_{48}H_{42}N_8O_2P_2F_{12}\cdot 2H_2O$: C, 48.5; H, 3.9; N, 9.4%. FAB-MS *m*/*z* 1009 $(M - PF_6)^+$, 864 $(M - 2PF_6)^+$.

***Λ*-[4,4'-Bis(*R*-α-methylbenzylcarbamoyl)-2,2'-bipyridine]-bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate *Λ*-12.** *Λ*-$[Ru(bpy)_2(py)_2]\{(-)$-*O*,*O*'-dibenzoyl-L-tartrate$\}\cdot 12H_2O$ (0.163 g, 0.143 mmol) and ligand **3** (0.161 g, 0.357 mmol) were refluxed in 9 : 1 ethylene glycol : $H_2O$ (25 ml) in the dark and under nitrogen for 3 days. The mixture was then cooled, diluted with water (10 ml) and filtered. A saturated solution of $NH_4PF_6$ (aq) was added to the filtrate to yield an orange precipitate,

which was removed by filtration and recrystallised from MeCN–$H_2O$ to give the product as a brown solid (0.0544 g, 33%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.42 (2H, d, $J$ = 8.5 Hz, NH), 9.22 (2H, s, bpyH3,3')*, 8.89 (4H, 2 overlapping d, $J$ = 8 Hz/8.5 Hz, bpyHa/a'), 8.21 (4H, m, bpyHb,b'), 7.91 (4H, m, bpyH5,5', bpyH6,6'), 7.79 (2H, d, $J$ = 5 Hz, bpyHd), 7.75 (2H, d, $J$ = 5.5 Hz, bpyHd'), 7.58 (2H, t, $J$ = 6.5 Hz, bpyHc), 7.52 (2H, t, $J$ = 6.8 Hz, bpyHc'), 7.43 (4H, d, $J$ = 7.5 Hz, ArCH2), 7.36 (4H, t, $J$ = 7.5 Hz, ArCH3), 7.27 (2H, t, $J$ = 7.3 Hz, ArCH4), 5.23 (2H, quint, $J$ = 7 Hz, CH), 1.51 (6H, d, $J$ = 7 Hz, Me). *Small side peak at $\delta$ 9.20 due to bpyH3,3' from *Δ*-**12**. Found: C, 48.9; H, 4.1; N, 9.6. Calc. for $RuC_{48}H_{42}N_8O_2P_2F_{12}\cdot 2H_2O$: C, 48.5; H, 3.9; N, 9.4%.

***Δ*-[4,4'-Bis(*R*-α-methylbenzylcarbamoyl)-2,2'-bipyridine]-bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate *Δ*-12.** *Δ*-[$Ru(bpy)_2(py)_2$]{(+)-*O*,*O*'-dibenzoyl-D-tartrate}·$12H_2O$ (50 mg, 0.044 mmol) and ligand **3** (50 mg, 0.011 mmol) were refluxed in ethylene glycol (4 ml) containing water (5 drops) and glacial acetic acid (5 drops) in the dark and under nitrogen for 4 h. Work up as for *Λ*-**12** gave the product as a dark red solid (0.0276 g, 55%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.41 (2H, d, $J$ = 8 Hz, NH), 9.20 (2H, s, bpyH3,3')*, 8.88 (4H, 2 overlapping d, $J$ = 7.5 Hz/8 Hz, bpyHa/a'), 8.22 (4H, m, bpyHb,b'), 7.92 (4H, m, bpyH5,5', bpyH6,6'), 7.78 (2H, d, $J$ = 5.5 Hz, bpyHd), 7.75 (2H, d, $J$ = 5 Hz, bpyHd'), 7.57 (2H, t, $J$ = 6.8 Hz, bpyHc), 7.52 (2H, t, $J$ = 6.8 Hz, bpyHc'), 7.42 (4H, d, $J$ = 8 Hz, ArCH2), 7.36 (4H, t, $J$ = 7.5 Hz, ArCH3), 7.28 (2H, t, $J$ = 7 Hz, ArCH4), 5.22 (2H, quint, $J$ = 7 Hz, CH), 1.51 (6H, d, $J$ = 7 Hz, Me). *Small side peak at $\delta$ 9.22 due to bpyH3,3' from *Λ*-**12**. Found: C, 48.9; H, 4.4; N, 9.3. Calc. for $RuC_{48}H_{42}N_8O_2P_2F_{12}\cdot 2H_2O$: C, 48.5; H, 3.9; N, 9.4%.

**Chromatographic separation of receptor 12.** The chloride salt of receptor **12** (5.0 mg, 5.3 μmol) in water (50 ml) was loaded onto a SP Sephadex C-25 cation exchange column (1.6 cm × 1 m). Elution with sodium (−)-*O*,*O*'-dibenzoyl-L-tartrate (0.075 M) resulted in band separation after 15 m. Elution with sodium (−)-di-*O*,*O*'-4-toluoyl-L-tartrate (0.075 M) reduced the band separation distance to 7 m. However, the receptor was too insoluble under the chromatographic conditions to work on a preparative scale.

**Racemic [1,12-dioxo-5,8-dioxa-2,11-diaza(12)carbamoyl-2,2'-bipyridinophane]bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate 14 (see ref. 12*b*).** [$Ru(bpy)_2Cl_2$] (0.0979 g, 0.195 mmol) and ligand **13** (0.0559 g, 0.157 mmol) in 9 : 1 ethylene glycol : $H_2O$ (25 ml) were heated in a microwave oven on medium high power for 1.5 min. TLC (silica; 1 : 1 v/v 10% NaCl (aq) : EtOH) of the resulting red solution showed the formation of the product at $R_f$ = 0.17. This solution was diluted to 100 ml with water and purified by cation exchange chromatography on SP Sephadex C-25, using NaCl (aq) (0.2 M) as the eluent. The second band (dark red) was collected and a saturated solution of $NH_4PF_6$ (aq) added to precipitate the product as an orange solid. This was removed by filtration, washed with cold water and then dried under vacuum (0.116 g, 70%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 8.97 (2H, t, br, $J$ = 5 Hz, NH), 8.89 (4H, 2 overlapping d, $J$ = 7.5 Hz, bpyHa,a'), 8.80 (2H, s, bpyH3,3'), 8.23 (4H, m, bpyHb,b'), 7.87 (2H, d, $J$ = 5.5 Hz, bpyH6,6'), 7.78 (6H, m, bpyHd,d', bpyH5,5'), 7.58 (4H, m, bpyHc,c'), 3.76 (4H, s, $OCH_2CH_2O$), 3.59 (4H, m, $OCH_2CH_2NH$), 3.39 (4H, m, $OCH_2CH_2NH$). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 164.11 (CONH), 156.75, 156.69, 155.90, 152.30, 151.53, 151.42, 142.66, 138.48, 138.44, 128.19, 128.09, 125.88, 124.78, 123.73, 71.04 ($OCH_2CH_2O$), 69.47 ($OCH_2CH_2NH$). Found: C, 40.2; H, 4.2; N, 9.7. Calc. for $RuC_{38}H_{36}N_8O_4P_2F_{12}\cdot 4H_2O$: C, 40.3; H, 3.9; N, 9.9%. ES-MS *m*/*z* 915 $(M - PF_6)^+$, 385 $(M - 2PF_6)^{2+}$.

***Λ*-[1,12-Dioxo-5,8-dioxa-2,11-diaza(12)carbamoyl-2,2'-bipyridinophane]bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate *Λ*-14.** *Λ*-[$Ru(bpy)_2(py)_2$]{(−)-*O*,*O*'-dibenzoyl-L-tartrate}·$12H_2O$ (0.050 g, 43.7 μmol) and ligand **13** (0.0389 g, 0.109 mmol) were refluxed in ethylene glycol (4 ml) containing water (5 drops) and glacial acetic acid (5 drops) in the dark and under nitrogen for 4 h. Work up as for *Λ*-**12** afforded the product as a red solid (0.0189 g, 41%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 8.97 (2H, t, br, NH), 8.89 (4H, d, $J$ = 8 Hz, bpyHa,a'), 8.79 (2H, s, bpyH3,3'), 8.23 (4H, m, bpyHb,b'), 7.87 (2H, d, $J$ = 5.5 Hz, bpyH6,6'), 7.78 (6H, m, bpyHd,d', bpyH5,5'), 7.58 (4H, m, bpyHc,c'), 3.75 (4H, s, $OCH_2CH_2O$), 3.59 (4H, m, $OCH_2CH_2NH$), 3.39 (4H, m, $OCH_2CH_2NH$). Found: C, 42.2; H, 3.3; N, 10.1. Calc. for $RuC_{38}H_{36}N_8O_4P_2F_{12}\cdot H_2O$: C, 42.4; H, 3.6; N, 10.4%. UV-VIS $\lambda_{max}$/nm (MeCN): 470 ($\varepsilon$/$10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$ 13.5), 354 (9.5), 287 (65.8), 254 (27.6), 246 (28.5). CD $\lambda_{max}$/nm (MeCN): 480 ($\Delta\varepsilon$ +15), 425 (−21), 296 (+162), 279 (−68), 245 (−16), 202 (+58).

***Δ*-[1,12-Dioxo-5,8-dioxa-2,11-diaza(12)carbamoyl-2,2'-bipyridinophane]bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate *Δ*-14.** Synthesis as for *Λ*-**14**, using *Δ*-[$Ru(bpy)_2(py)_2$[{(+)-*O*,*O*'-dibenzoyl-D-tartrate}·$12H_2O$. The product was obtained as a red solid (0.0233 g, 50%). Characterisation as for *Λ*-**14**, except for the CD spectrum: $\lambda$/nm (MeCN): 480 ($\Delta\varepsilon$ −12), 425 (+21), 296 (−160), 279 (+71), 245 (+26), 202 (−56).

**Racemic, *Λ*- and *Δ*-[1,12-dioxo-5,8-dioxa-2,11-diaza(12)-carbamoyl-2,2'-bipyridinophane]bis(2,2'-bipyridine)ruthenium(II) dichloride.** *Racemic macrocycle*. The hexafluorophosphate salt of racemic **14** (86.3 mg, 81.4 μmol) was dissolved in the minimum amount of acetone and loaded onto an Amberlite IRA 400(Cl) ion exchange column. Elution with water gave an aqueous solution of the chloride salt; the solvent was evaporated from this solution to yield the chloride salt of racemic **14** as a dark red solid (0.0681 g, quantitative). $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$: 9.68 (2H, d, $J$ = 1.5 Hz, bpyH3,3'), 9.51 (2H, t, $J$ = 4.5 Hz, NH), 8.91 (2H, d, $J$ = 8 Hz, bpyHa), 8.88 (2H, d, $J$ = 8 Hz, bpyHa'), 8.19 (2H, td, $J$ = 8.1 Hz, $J'$ = 1.2 Hz, bpyHb), 8.14 (2H, td, $J$ = 8.1 Hz, $J'$ = 1.3 Hz, bpyHb'), 7.88 (2H, d, $J$ = 5 Hz, bpyHd'), 7.77 (4H, m, bpyH5,5', bpyHd), 7.70 (2H, d, $J$ = 5.5 Hz, bpyH6,6'), 7.54 (4H, m, bpyHc,c'), 3.84 (4H, s, $OCH_2CH_2O$), 3.78 (4H, m, $OCH_2CH_2NH$), 3.62 (4H, m, $OCH_2CH_2NH$). Found: C, 46.6; H, 5.1; N, 11.3; P, <0.05. Calc. for $RuC_{38}H_{36}N_8O_4Cl_2\cdot 8H_2O$: C, 46.3; H, 5.3; N, 11.4; P, 0.0%. ES-MS *m*/*z* 805 $(M - Cl)^+$, 385 $(M - 2Cl)^{2+}$. *Λ*- and *Δ*-**14** (11.2 mg, 10.6 μmol and 7.5 mg, 7.1 μmol respectively) were converted to the dark red chloride salts (1.7 mg, 29% and 2.6 mg, 29% respectively) in the same way as the racemic macrocycle.

**[4,4'-Dicarboxy-2,2'-bipyridine]bis(2,2'-bipyridine)-ruthenium(II) dichloride 17 (see ref. 12*c*).** A solution of [$Ru(bpy)_2Cl_2$] (0.659 g, 1.31 mmol) in 1 : 1 EtOH : $H_2O$ (130 ml) was added to a suspension of 4,4'-dicarboxy-2,2'-bipyridine (0.340 g, 1.39 mmol) in 1 : 1 EtOH : $H_2O$ (650 ml). The mixture was refluxed for 3 days under nitrogen and was then cooled and filtered to remove unreacted 4,4'-dicarboxy-2,2'-bipyridine. The solvent was evaporated from the red filtrate to give the product as a brown solid, which was dried under vacuum (1.01 g, 96%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.27 (2H, s, bpyH3,3'), 8.93 (4H, 2 overlapping d, $J$ = 7.5 Hz/8 Hz, bpyHa/a'), 8.22 (4H, m, bpyHb,b'), 7.97 (2H, d, $J$ = 6 Hz, bpyH6,6'), 7.90 (2H, d, $J$ = 6 Hz, bpyH5,5'), 7.78 (2H, d, $J$ = 6 Hz, bpyHd), 7.73 (2H, d, $J$ = 5.5 Hz, bpyHd'), 7.59 (2H, t, $J$ = 6.8 Hz, bpyHc), 7.53 (2H, t, $J$ = 6.5 Hz, bpyHc'). Found: C, 48.2; H, 4.1; N, 10.4. Calc. for $RuC_{32}H_{24}N_6O_4Cl_2\cdot 4H_2O$: C, 48.0; H, 4.0; N, 10.5%.

**Diastereomeric [4,4'-bis(1-carbonyl-2-*tert*-butoxycarbonyl-*R*,*R*-1,2-diaminocyclohexyl)-2,2'-bipyridine]bis(2,2'-bipyridine)-ruthenium(II) hexafluorophosphate 18.** Compound **17** (0.150 g, 0.187 mmol) was refluxed in thionyl chloride (30 ml) for 15 h under nitrogen. The excess thionyl chloride was then removed by distillation and the brown residue dried under vacuum for 2 h, then heated under vacuum (60–70 °C) for a further 45 min. The residue was dissolved in dry $CH_3CN$ (40 ml) and added dropwise to a stirred solution of *tert*-butoxycarbonyl-*R*,*R*-1,2-diaminocyclohexane (0.147 g, 0.687 mmol) and triethylamine (0.20 g, 1.96 mmol) in dry $CH_3CN$ (40 ml) under nitrogen. The resulting red solution was refluxed for 2 h and the solvent was then evaporated to yield a red solid. This was dissolved in water (20 ml) and a saturated solution of $NH_4PF_6$ (aq) added. The resulting precipitate was removed by filtration and washed with water (50 ml). This gave the product as an orange solid, which was dried under vacuum (0.236 g, 92%).

This molecule exists as two diastereomers due to the chirality at the metal centre (*Δ* or *Λ*) and at the substituted bipyridyl (*R*,*R*,*R*,*R*). These diastereomers are labelled as band 1 (*Λ*,*R*,*R*,*R*,*R*) and band 2 (*Δ*,*R*,*R*,*R*,*R*) in the following $^1$H NMR spectrum. $^1$H NMR (500 MHz, DMSO-$d_6$) *δ*: 9.26 (2H, s, bpyH3,3' band 1), 9.21 (2H, s, bpyH3,3' band 2), 8.89 (8H, m, bpyHa,a'), 8.80 (4H, m, bpyNH), 8.21 (8H, m, bpyHb,b'), 7.92 (6H, m, bpyH6,6' band 1, bpyH6,6' band 2, bpyH5,5' band 2), 7.85 (2H, d, *J* = 6 Hz, bpyH5,5' band 1), 7.77 (4H, m, bpyHd), 7.71 (2H, d, *J* = 5.5 Hz, bpyHd' band 1), 7.68 (2H, d, *J* = 5 Hz, bpyHd' band 2), 7.56 (4H, m, bpyHc), 7.51 (4H, m, bpyHc'), 6.77 (4H, m, NHCOO), 3.78 (4H, m, CHNH), 3.39 (4H, m, CHNH), 1.77 (8H, m, cy), 1.68 (8H, m, cy), 1.34–1.45 (8H, m, cy), 1.21 (8H, m, cy), 1.02 (18H, s, $OCMe_3$ band 1), 1.00 (18H, s, $OCMe_3$ band 2). Found: C, 46.8; H, 5.1; N, 9.8. Calc. for $RuC_{54}H_{64}N_{10}O_6P_2F_{12}\cdot 2H_2O$: C, 47.1; H, 5.0; N, 10.2%. ES–MS *m*/*z* 1195 $(M - PF_6)^+$.

**Chromatographic separation of receptor 18.** Receptor **18** (0.100 g, 0.073 mmol) was loaded onto a SP Sephadex C-25 column (1 m × 5 cm) as a solution in water : acetone (200 ml, 95 : 5 v/v). Elution with sodium 4-tosylate (0.125 M) gave observable diastereomer separation after *ca*. 6 m. The two bands were collected and the water evaporated under vacuum. The orange residues were suspended in MeCN (150 ml) and stirred at room temperature overnight before filtration to remove insoluble sodium 4-tosylate. The solvent was evaporated and the solids dissolved in the minimum amount of water. Elution with water on Amberlite IRA 400(Cl) ion exchange resin gave the receptors as their chloride salts; these were converted to the hexafluorophosphate salts by adding a saturated solution of $NH_4PF_6$ (aq). The precipitates were allowed to stand for 2 h before filtration. The orange solids were washed with cold water and dried under vacuum (0.064 g, 64% combined yield of both diastereomers). Band 1 $^1$H NMR (500 MHz, DMSO-$d_6$) *δ*: 9.25 (2H, s, bpyH3,3'), 8.89 (4H, m, bpyHa,a'), 8.80 (2H, d, *J* = 8.5 Hz, bpyNH), 8.22 (4H, m, bpyHb,b'), 7.92 (2H, d, *J* = 6 Hz, bpyH6,6'), 7.84 (2H, d, *J* = 6 Hz, bpyH5,5'), 7.77 (2H, d, *J* = 6 Hz, bpyHd), 7.71 (2H, d, *J* = 6 Hz, bpyHd'), 7.56 (2H, t, *J* = 6.5 Hz, bpyHc), 7.52 (2H, t, *J* = 7 Hz, bpyHc'), 6.78 (2H, d, *J* = 9 Hz, NHCOO), 3.77 (2H, m, CHNH), 3.39 (2H, m, CHNH), 1.77 (4H, m, cy), 1.69 (4H, m, cy), 1.34–1.44 (4H, m, cy), 1.21 (4H, m, cy), 1.02 (18H, s, $OCMe_3$). Band 2 $^1$H NMR (500 MHz, DMSO-$d_6$) *δ*: 9.22 (2H, s, bpyH3,3'), 8.89 (4H, m, bpyHa,a'), 8.81 (2H, d, *J* = 8.5 Hz, bpyNH), 8.22 (4H, m, bpyHb,b'), 7.91 (4H, m, bpyH6,6', bpyH5,5'), 7.78 (2H, d, *J* = 5 Hz, bpyHd), 7.68 (2H, d, br, bpyHd'), 7.57 (2H, t, *J* = 6.5 Hz, bpyHc), 7.51 (2H, t, *J* = 7 Hz, bpyHc'), 6.76 (2H, d, *J* = 9 Hz, NHCOO), 3.77 (2H, m, CHNH), 3.39 (2H, m, CHNH), 1.78 (4H, m, cy), 1.69 (4H, m, cy), 1.34–1.46 (4H, m, cy), 1.21 (4H, m, cy), 1.00 (18H, s, $OCMe_3$). Band 1 UV-VIS $\lambda_{max}$/nm (MeCN): 467 ($\varepsilon/10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ 14.0), 356 (9.7), 288 (65.4), 254 (29.2), 246 (30.4). Band 2 UV-VIS $\lambda_{max}$/nm (MeCN): 467 ($\varepsilon/10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ 14.7), 356 (10.3), 287 (69.5), 254 (32.3), 247 (34.3). Band 1 CD $\lambda$/nm (MeCN): 479 ($\Delta\varepsilon$ +14), 425 (−20), 296 (+171), 280 (−77), 245 (−19), 222 (−27). Band 2 CD $\lambda$/nm (MeCN): 479 ($\Delta\varepsilon$ −12), 425 (+20), 296 (−163), 280 (+80), 245 (+24), 222 (+21).

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