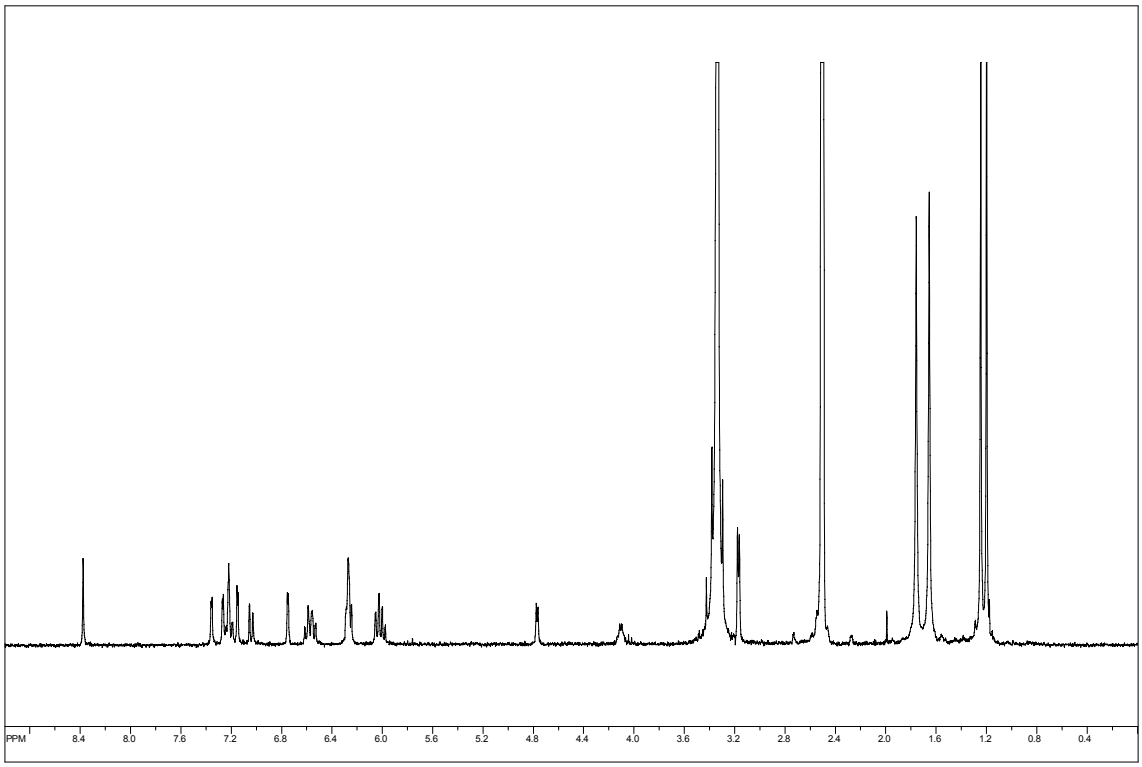
Electronic Supplementary Material for Chemical Communications

Supporting Information

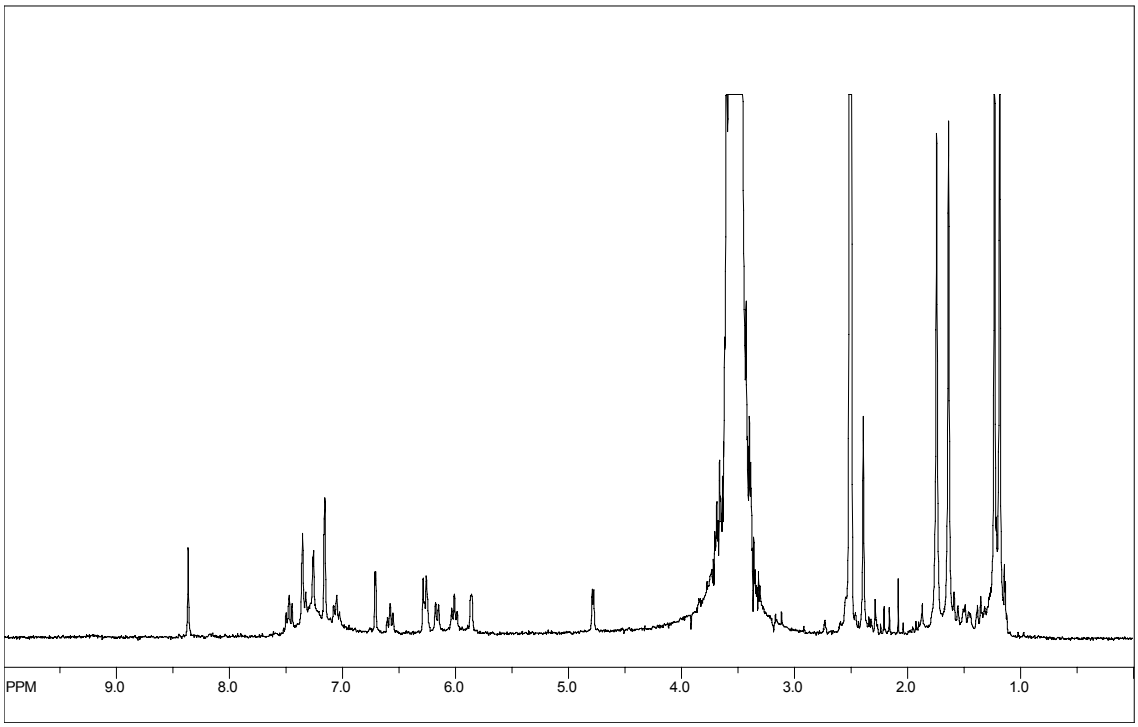
General. ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker 300 MHz NMR spectrometer. High-resolution mass spectroscopy (MALDI-TOF) was performed on a Voyager-DE STR Biospectrometry Workstation. All circular dichroism (CD) experiments were performed on a JASCO J-175 spectrometer in DMSO @ 20 ºC. All reagents were purchased from either Aldrich or TCI and used as received.

Neutral Diimine Ligand. To a stirring solution of *meso*-1,2-bis(2-hydroxyphenyl)-ethylenediamine (1.0 g, 2.4624 mmol) in ethanol (10 ml) was added 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1.154 g, 4.9248 mmol) and allowed to stir at RT for 12 h. The reaction mixture was then filtered to give the title compound as a yellow solid (1.308 g, 79%). The crude product was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.36 (d, J = 2.4 Hz, 2H), 7.31 (dd, J = 1.7 Hz, 7.7 Hz, 2H), 7.13 (t, J = 7.7 Hz, 2H), 6.91 (d, J = 2.3 Hz, 2H), 6.88 (t, J = 7.5 Hz, 2H), 6.82 (dd, J = 1.7 Hz, 8.4 Hz, 2H), 5.23 (s, 2H), 1.46 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 158.0, 153.9, 140.6, 136.9, 129.7, 129.3, 127.9, 127.0, 121.3, 118.2, 116.8, 74.5, 35.4, 34.5, 31.8, 29.7; HRMS (MALDI-TOF; $M + H^+$) calcd for $C_{44}H_{57}N_2O_4$: 677.25, found: 677.3766.

Racemic Cobalt(III) Diimine Complex ±1. To a stirring solution of the neutral diimine ligand (300.0 mg, 0.4432 mmol) in ethanol (10 ml) was added Cobalt(II) acetate tetrahydrate (110.4 mg, 0.4432 mmol) and allowed to reflux for 1.5 h. After cooling the solvent was evaporated under reduced pressure to yield a brown solid. It was then purified through flash chromatography on silica gel (5% methanol/dichloromethane) to yield the title compound as a dark brown solid (222.7 mg, 69%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.17 (bs, 1H), 8.38 (s, 1H), 7.36 (d, J = 2.5 Hz, 1H), 7.27 (d, J = 2.3 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.15 (d, J = 2.3 Hz, 1H), 7.04 (d, J = 7.7 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 6.62 – 6.54 (m, 2H), 6.27 – 6.24 (m, 3H), 6.05 – 5.98 (m, 2H), 4.77 (d, J = 3.9 Hz, 1H), 1.76 (s, 9H), 1.66 (s, 9H), 1.25 (s, 9H), 1.20 (s, 9H); HRMS (MALDI-TOF; M + H^+) calcd for $C_{44}H_{54}CoN_2O_4$: 733.34, found: 733.6638.



Locked Cobalt(III) Diimine Complex ±1. To a stirring solution of Cobalt (III) Diimine Complex **±1** (70 mg, 0.0955 mmol) in DMSO (3.0 ml) was added acetic anhydride (44.1 µl, 0.4776 mmol) and allowed to stir at RT for 30 min. It was then precipitated out of brine, filtered, and dried to yield a brown solid. It was then purified by flash chromatography on silica gel (5% methanol/dichloromethane) to yield the title compound as a dark brown solid (53.6 mg, 72% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (s, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.36 (s, 2H), 7.27 (d, J = 2.4 Hz, 1H), 7.16 (d, J = 2.7 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 2.3 Hz, 1H), 6.58 (t, J = 7.6 Hz, 1H), 6.28 (d, J = 8.3 Hz, 2H), 6.19 (d, J = 7.3 Hz, 1H), 6.01 (t, J = 7.2 Hz, 1H), 5.85 (d, J = 2.2 Hz, 1H), 4.78 (d, J = 3.8 Hz, 1H), 2.40 (s, 3H), 1.75 (s, 9H), 1.65 (s, 9H), 1.24 (s, 9H), 1.19 (s, 9H); HRMS (MALDI-TOF; M + H^+) calcd for $C_{46}H_{56}CoN_2O_5$: 775.35, found: 775.7591.

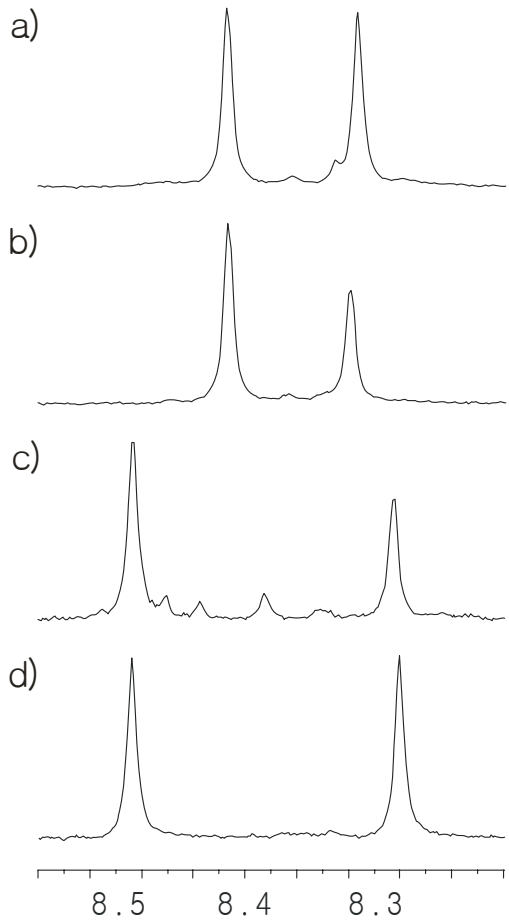


General Procedure for Imprint/Lock/Separation of Cobalt(III) Diimine Ligand ±1. To a stirring solution of Cobalt (III) Diimine Complex **±1** (70 mg, 0.0955 mmol) in DMSO (3.0 ml) was added either chiral phenyl alanine sodium salt (35.8 mg, 0.1910 mmol) or chiral 2-phenyl-3-methylaziridine (25.4 mg, 0.1910 mmol) imprinting agent and allowed to heat to 70 °C for 1.5 h. The reaction mixture then was allowed to cool to ambient temperature and acetic anhydride (44.1 μl, 0.4776 mmol) added and stirred for another 30 min. It was then precipitated out of brine, filtered, and dried to yield a brown solid, which was purified by flash chromatography on silica gel (5% methanol/dichloromethane) to yield the Locked Cobalt (III) Diimine complex **±1** as a dark brown solid (53.6 mg, 72% yield).

General Procedure for Stereoselective Catalysis. To a small round bottom flask containing Locked Cobalt (III) Diimine complex **±1** (56.3 mg, 0.0727 mmol) was added racemic styrene oxide (1.66 ml, 14.5315 mmol) followed by N-methyl aniline (0.86 ml, 7.9923 mmol) and allowed to stir at ambient temperature for 12 h. The reaction mixture was then subjected to high vacuum distillation under gentle heating as enantioenriched styrene oxide was recovered in good yield (0.54 ml, 72%).

We have been able to demonstrate the chiral memory effect purely from ^{1}H NMR without the use of CD. Figure S1 shows that the chiral aziridine can be chased with *R*-phenethylamine instead of benzylamine (Figure 2d). As the chiral aziridine is replaced with *R*-phenethylamine, the two imine peaks due to the aziridine bound complex (Figure S1b) are replaced with two new imine peaks of the amine bound complex (Figure S1c). Interestingly, the integration ratio (2:1) of the two newly formed imine peaks is about the same as that of the two initial imine peaks (Figure S1b and S1c). Finally, heating the *R*-phenethylamine bound complex results in the integration ratio of the two imine signals to change to about 1:1 (Figure S1d). We independently confirmed that *R*-phenethylamine binds to **±1** is no observable stereoselectivity (Addition of two equivalents of *R*-phenethylamine to **±1** results in rapid coordination of the amine forming the diastereomeric complexes in a ratio of about 1:1. Heating the solution does not alter the ratio of the diastereomeric complexes). These results clearly show that chiral memory can be transferred from the aziridine bound complex to the amine bound complex (Figure S1b and S1c).

Figure S1. ^{1}H NMR spectra in DMSO-d_6 of (a) 1:1 ratio of the diastereomeric complexes formed from the addition of 2 equiv. of (2R,3S)-2-phenyl-3-methylaziridine to the Co(III) ligand complex **±1**, (b) stabilization of one diastereomer over the other in a 2:1 ratio after equilibration, (c) displacement of aziridine with chiral *R*-phenethylamine with retention of chiral memory, (d) equilibration of the diastereomers formed between **±1** and *R*-phenethylamine.



Origin of stereoselectivity

To understand the origin of selectivity, it is instructive to compare the binding of the chiral aziridine to **±1** with its binding to (*R,R*)-**2** and (*S,S*)-**2** (Figure S2, the cobalt metal not shown is hidden behind the aziridine nitrogen).[6] Although the two metal complexes (**1** and **2**) may appear quite different at first sight, close examination reveals that the origin of stereoselective recognition of the chiral aziridine may well be related in the two systems. The precise positioning of the aziridine in its complex with (*R,R*)-**2** and (*S,S*)-**2** has been determined by crystallography, ^{1}H NMR and molecular mechanics computation.[6] The ^{1}H NMR signals for the aziridine methyl group in the diastereomeric complex with **±1** are highly split (Figure S2c) as it is with racemic **2**. Indeed, the chemical shifts for the methyl group in the complex with **±1** (δ 0.71 and 0.36) matches closely with those for the methyl group in the complex with racemic **2** (δ 0.64 and 0.33). These results show that the positioning of the coordinated aziridine in the diastereomeric complexes with **1** and **2** is essentially the same. Indeed, molecular mechanics computation confirms that the relative positioning of the aziridine is about the same for all four disastereomeric complexes (Figure S2).

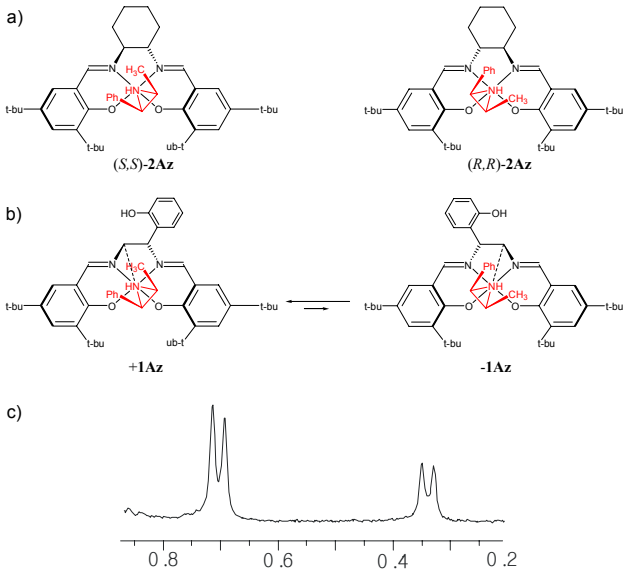


Figure S2. (a) Schematic representation of the chiral aziridine coordinated to (*R*,*R*)-**2** and (*S*,*S*)-**2** based on the X-ray crystal structures of (*R*,*R*)-**2Az** and (*S*,*S*)-**2Az** (Co behind aziridine N not shown). (b) Schematic representation of the chiral aziridine coordinated to **±1** (coordinated phenol is behind N) (c) ^{1}H NMR chemical shifts for the methyl groups **+1Az** (left) and **-1Az** (right).

We propose that the positioning of (2*R*,3*S*)-2-phenyl-3-methylaziridine in the diastereomeric complex with **±1** is as shown in Figure S2b (the metal and the coordinated phenol are behind the aziridine nitrogen) in accordance with the known positioning of the chiral aziridine in the diastereomeric complex with (*R*,*R*)-**2** and (*S*,*S*)-**2** (Figure S2a).[6] The ^{1}H NMR signal for the methyl group in **-1Az** (as in (*R*,*R*)-**2Az**) is upfield shifted because it is positioned directly on top of the aromatic ring. The

integration ratio for the aziridine methyl peaks (2:1 after equilibration of the phenoxy groups by heating) shows that +**1Az** is more stable than –**1Az** (Figure 2c). The greater stability of +**1Az** (and (*S*,*S*)-**2Az**) appears to be due to favorable interaction between the aziridine phenyl group and the di-*tert*-butylphenoxy group of the metal complex.[6]