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Design and synthesis of a novel chiral triptycene-based imine ligand for enantioselective epoxide ring-opening reactions

Mamta Guleria, Manpreet Kaur, Divya Tagra and Jyoti Agarwal *

A novel chiral triptycene-based imine ligand has been designed, synthesized and then characterized using various spectroscopic techniques, including FT-IR, ^1H NMR, ^{13}C NMR, and HRMS. It was first coordinated with cobalt to form a cobalt(II) complex, followed by combination with various axial ligands, such as acetate, tosylate, triflate, α,α,α -trifluoro-*p*-toluate and chloride, to generate the corresponding cobalt(III) complexes. These complexes were further analysed using EDS to confirm the coordination with cobalt. All the triptycene-based cobalt complexes demonstrated high catalytic efficiency towards the ring-opening reaction of epoxides with aniline derivatives, yielding β -amino alcohols in very high yields (up to >99%) with appreciable enantiomeric ratios (up to 81 : 19).

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Introduction

The three-dimensional arrangement of atoms in a molecule, that is, its stereochemistry, dictates its properties and interactions, especially in biological systems. The profound challenges in organic synthesis are defined by the hindrances in creating new stereocenters with precise control over their handedness.^{1–3} Chiral catalysts, particularly those based on transition metals, offer a powerful solution to this obstacle, enabling the efficient and cost-effective synthesis of enantiomerically pure compounds through asymmetric reactions.^{4–6} As a result, significant progress has been made in recent years for developing various transition metal catalysts, particularly those incorporating privileged ligands, such as Jacobsen,^{7–9} BINOL (1,1'-bi-2-naphthol),¹⁰ and BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)¹¹ ligands.

Over the past few years, triptycene has attracted growing interest as a ligand framework in catalysis. It features a rigid, three-dimensional structure with a well-defined geometry and excellent thermal stability. Combined with its ease of functionalization, triptycene offers a stable platform that can support well-positioned catalytic sites. These structural features may help to maintain the spatial arrangement around the metal center and enable selective binding of substrates.^{12–16} Several non-chiral P-functionalized and carbene-based triptycene metal complexes have been reported to incorporate diverse transition metals, like iridium, palladium, platinum, ruthenium, nickel, and zinc, for non-asymmetric catalytic transformations, such as Suzuki cross-coupling,¹⁷ cyanation of aryl halides,¹⁸

hydrocyanation of butadiene,¹⁹ hydrogenation of ketones,²⁰ isomerization reactions,²¹ CO_2 cycloaddition to 1,2-epoxyhexane,²² hydrosilylation of styrene,²³ borylation of α,β -unsaturated esters,²⁴ and hydrogenation of enones.²⁵

The applications of triptycene-based ligands in asymmetric catalysis remain relatively underexplored, despite their promising structural advantages and high rigidity. Only a few research groups have used the triptycene ligands in asymmetric catalysis, and those studies have primarily relied on expensive and less abundant 4d and 5d transition metals. For example, Leung *et al.* designed a (P-Functionalised) monophosphinotriptycene ligand and employed it in a Pd-catalyzed Suzuki–Miyaura cross-coupling reaction between 2-methylphenylboronic acid and 1-bromo-2-methylnaphthalene, resulting in a racemic mixture. Later, the same ligand was used in the enantioselective hydrosilylation of styrene, achieving a low yield (52%) and moderate enantiomeric excess (58%) with limited substrate scope.²³ Similarly, Savka *et al.* designed a carbene-based triptycene complex and applied it in the enantioselective borylation of α,β -unsaturated esters, resulting in good enantioselectivity but in a dearth in substrate generality.²⁴ Also, Wirth *et al.* synthesized chiral iodotriptycene ligands and tested them in the enantioselective α -oxytosylation of propiophenone, but both the yield and enantioselectivity were remarkably low.²⁵ Recently, our research group has also developed cobalt-coordinated triptycene oligomers as catalysts for the stereoselective aldol reaction of isatin and ketones to afford high yields of the oxindole product.²⁶

Collectively, these studies highlight a persistent limitation of triptycene-based chiral ligands, *i.e.* The difficulty in achieving high stereoselectivity and maintaining a broad substrate scope. This has created a clear impetus for the structural modification of the triptycene scaffold and the development of new

Department of Chemistry and Centre of Advanced Studies, Panjab University, Sector-14, Chandigarh 160014, India. E-mail: jyotiagarwa@gmail.com; jagarwal@pu.ac.in



transition-metal-based chiral triptycene catalysts capable of achieving improved performance in asymmetric synthesis.

Thus, in line with designing triptycene derivatives for diverse applications,^{26–28} we have designed a novel imine-based chiral triptycene ligand bearing multiple functional groups for metal complexation and evaluated its catalytic potential for asymmetric C–N bond-forming reactions, *i.e.*, enantioselective epoxide ring-opening reaction affording β -amino alcohols. β -Amino alcohols serve as crucial building blocks for the production of various important drugs, including β -blockers, and they also act as chiral auxiliaries in asymmetric synthesis.^{29–33}

Results and discussion

Synthesis of the chiral triptycene-based ligand (8)

A novel triptycene-based chiral ligand was synthesized through the condensation of 2-formyl-1-hydroxytriptycene (6) with (*R,R*)-1,2-cyclohexanediamine (7), as shown in Scheme 1.

The triptycene precursor (6) was obtained *via* a four-step synthetic route starting from 1-hydroxyanthraquinone (1), following a previously reported literature.³⁴ The synthesis of 2-formyl-1-hydroxy triptycene began with the methylation of 1-hydroxyanthraquinone (1) using anhydrous potassium carbonate (K_2CO_3) in dimethylformamide (DMF), followed by the addition of iodomethane (MeI) at 50 °C to yield 1-methoxyanthraquinone (2) in >99% yield. The carbonyl groups were then reduced using zinc dust, and the resulting product was refluxed with a 10% aqueous NaOH solution to produce 1-methoxyanthracene (3) in 80% yield. A [4 + 2] Diels–Alder reaction between compound (3) and the benzyne intermediate, generated *in situ* from anthranilic acid and isopentyl nitrite, afforded 1-methoxytriptycene (4) in 81% yield. The methoxy group on the triptycene core was subsequently demethylated using BBr_3 in dry dichloromethane (DCM) to yield 1-hydroxytriptycene (5) in 94% yield. The formylation of compound (5) using hexamethylenetetramine (HMTA) and trifluoroacetic acid (TFA) produced the precursor, 2-formyl-1-hydroxytriptycene (6), in 70% yield. Each intermediate product was characterized

using 1H NMR, ^{13}C NMR, and IR spectroscopy. All the experimental details with spectral data have been provided in the experimental section.

Coordination with cobalt metal

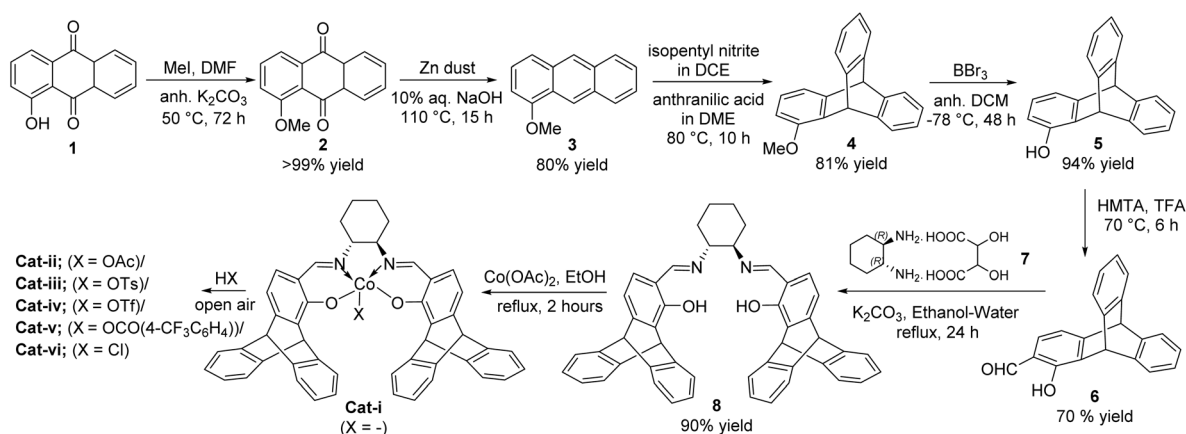
The cobalt(II) complex of triptycene TpCo(II) (**Cat-i**) was synthesized in over 99% yield by coordinating the chiral triptycene-based ligand (8) with cobalt(II) acetate. Subsequently, a series of cobalt(III) complexes (**Cat-ii** to **Cat-vi**) bearing different axial ligands were generated from the reaction of **Cat-i** with various acids, including acetic acid (**Cat-ii**), *p*-toluenesulfonic acid (**Cat-iii**), trifluoroacetic acid (**Cat-iv**), and α,α,α -trifluoro-*p*-toluic acid (**Cat-v**), as well as with chloride ion (**Cat-vi**). Detailed experimental procedures and characterization data for these transformations have been provided in the experimental section.

Catalytic applications

To evaluate the catalytic activity of the triptycene catalysts, initially, **Cat-ii** bearing –OAc group as the axial ligand was chosen as a catalyst for the reaction of cyclohexene oxide (9) with aniline (10a), and various reaction parameters, such as solvents, temperature and catalyst loading, were screened to achieve the optimal reaction conditions.

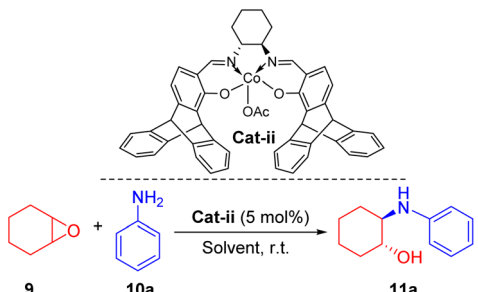
All the results are summarised in Table 1. At the onset, the reaction was conducted in dichloromethane (DCM) using 5 mol% of the **Cat-ii** at room temperature. The reaction proceeded to completion within 1.5 hours to afford an excellent yield (>99%) of product **11a**, although a moderate enantiomeric ratio (62 : 38) was observed (Table 1, entry 1). Previously reported studies confirmed that solvent polarity played a key role in determining the catalytic efficacy of catalysts.^{35–37} Therefore, a series of polar/non-polar and protic/aprotic solvents was tested. Polar aprotic solvents, such as acetonitrile (ACN) and dichloroethane (DCE), favoured the formation of product **11a** in high yields of >99% and 76%, with enantiomeric ratios of 72 : 28 and 62 : 38, respectively (Table 1, entries 2 and 3).

Ethereal solvents tetrahydrofuran (THF) and *tert*-butyl methyl ether (*t*BuOMe) also delivered excellent yields of >99% and 71%, respectively, with slightly ameliorated



Scheme 1 Synthesis of 2-formyl-1-hydroxytriptycene (6) and triptycene ligand (8), followed by Co(II) and Co(III) complex formation.



Table 1 Solvent and temperature screening for the enantioselective epoxide ring-opening reaction^a


S. no.	Solvent	Temp. (°C)	Time (h)	Yield ^b (%)	er ^c (%)
1	DCM	RT	1.5	>99	62 : 38
2	ACN	RT	1.5	>99	72 : 28
3	DCE	RT	1.5	76	62 : 38
4	THF	RT	1.5	71	68 : 32
5	^t BuOMe	RT	1.5	>99	74 : 26
6	Toluene	RT	1.5	65	60 : 40
7	EtOH	RT	1.5	>99	71 : 29
8	HFIP	RT	1.5	>99	56 : 44
9	^t BuOH	RT	1.5	80	64 : 36
10	H ₂ O	RT	1.5	>99	67 : 33
11 ^d	NaCl solution	RT	1.5	>99	70 : 30
12	Neat	RT	1.5	>99	55 : 45
13	ACN	0	24	50	61 : 39
14	^t BuOMe	0	24	66	56 : 44
15 ^e	DCM	RT	24	Trace	—

^a Reaction was performed by stirring the solution of cyclohexene oxide (0.4 mmol) and aniline (0.4 mmol) in 1 mL of the solvent in the presence of 5 mol% of TpCo(III) catalyst (**Cat-ii**). ^b Isolated yields. ^c The enantiomeric ratios (er) were determined by HPLC using the Chiralpak IA column. ^d NaCl solution was made by dissolving 2.5 g of NaCl in 10 mL of water. ^e Reaction was performed by stirring the solution of cyclohexene oxide (0.4 mmol) and aniline (0.4 mmol) in 1 mL of solvent without any catalyst.

enantioselectivities (68 : 32 and 74 : 26 er) (Table 1, entries 4 and 5). Toluene provided a lower yield (65%) with an enantiomeric ratio of 60 : 40 (Table 1, entry 6), which may be attributed to the low solubility of the catalyst in the solvent. Next, protic solvents, such as ethanol and hexafluoroisopropanol (HFIP), were used, affording the complete conversion of the substrate into product **11a** in near quantitative yield, with 71 : 29 and 56 : 44 enantiomeric ratios, respectively (Table 1, entries 7 and 8). However, in the case of ^tBuOH, the yield of the product was reduced to 80%, with an enantiomeric ratio of 64 : 36 (Table 1, entry 9).

In addition to this, convincing results were established using water and NaCl solution as solvents, with an excellent yield (>99%) and moderate enantioselectivities (67 : 33 and 70 : 30, respectively) (Table 1, entries 10 and 11). One reaction was also tested under the neat condition, without using any solvent. The efficacy of **Cat-ii** remained ineffective, affording product **11a** in near quantitative yield; however, the enantioselectivity of the product was reduced to give an almost racemic mixture (Table 1, entry 12).

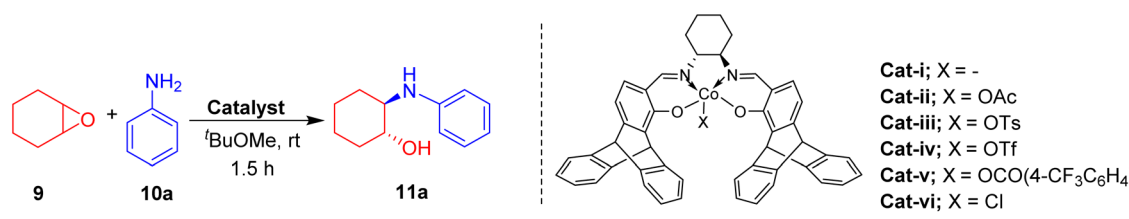
Thus, among the tested solvents, ^tBuOMe was observed as the most efficient solvent, affording >99% yield of product **11a** with 74 : 26 er at room temperature. Next, the effect of temperature on the reaction outcome was studied, and the reaction was conducted at 0 °C in ACN and ^tBuOMe (Table 1, entries 13 and 14). Unfortunately, both reactions afforded low yields and enantiomeric ratios. In ACN, the yield dropped to 50% with 61 : 39 er, while in ^tBuOMe, the yield decreased to 66% with 56 : 44 er. Moreover, the reaction time greatly increased (24 hours). A blank reaction without any catalyst was performed between cyclohexene oxide (**9**) and aniline (**10a**) in DCM as a solvent, and only a trace amount of the product was formed even after 24 hours. This confirmed the catalytic role of the triptycene-cobalt metal complex in the studied reaction (Table 1, entry 15).

Next, the influence of other Co(III) complexes bearing diverse axial ligands on the reaction outcome was investigated, as shown in Table 2. **Cat-i**, devoid of an axial ligand and featuring cobalt in the +2 oxidation state, resulted in product **11a** in 90% yield and with 65 : 35 er within 3 hours (Table 2, entry 1). Other Co(III) complexes bearing axial ligands, like acetate, tosylate, triflate and α,α,α -trifluoro-*p*-toluate, afforded product **11a** in quantitative yield, with enantiomeric ratios ranging from 60 : 40 to 74 : 26, as given in Table 2 (entries 3–6). Further, **Cat-vi**, containing a small anionic axial ligand, *i.e.* Chloride ion, was also tested as a catalyst, providing product **11a** in 95% yield with a 71 : 29 enantiomeric ratio in 3 hours.

The potential of various basic additives, such as triethylamine, pyridine, pyridine *N*-oxide, and 4-(phenylpropyl)pyridine, triphenylphosphane, is well known for the asymmetric ring-opening reactions to improve the enantioselectivities of β -amino alcohols.^{38,39} Therefore, we also investigated the effect of various additives, including both (*R*)- and (*S*)- enantiomers of *N*-(2-methoxybenzylidene)-1-phenylethanamine (**A** and **B** respectively), triethylamine (**C**), diisopropylethylamine (**D**), triphenylphosphine (**F**), alkaloid-like cinchonine (**G**) and quinine (**E**), pivalic acid (**H**) and (*R*)-(-)-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate (**I**) on the reaction outcome. When (*R*)-*N*-(2-methoxybenzylidene)-1-phenylethanamine (**A**) was employed with 5 mol% of **Cat-ii**, the yield and reaction time remained unaffected, but the enantiomeric ratio decreased from 74 : 26 to 64 : 36 (Table 3, entry 1). Similarly, on using (*S*)-*N*-(2-methoxybenzylidene)-1-phenylethanamine (**B**), product **11a** was formed in 95% yield with a decreased enantiomeric ratio of 55 : 45 (Table 3, entry 2). However, when additive **A** was tested with 5 mol% of **Cat-i**, the enantiomeric ratio was improved to 75 : 25, albeit with a slight downfall in the yield to 90% in 3 hours (Table 3, entry 3). The use of **B** with **Cat-i** further upsurged the enantiomeric ratio to 76 : 24, with approximately 92% yield (Table 3, entry 4). Other tested additives (**C**, **D**, **E**, **F**, **G**, **H**, **I**) were observed to be less important when it came to surpassing the performance of (*S*)-*N*-(2-methoxybenzylidene)-1-phenylethanamine (**B**) (Table 3, entries 5–11).

Thereafter, we varied the catalyst loading to 2 mol% and 10 mol% with additive **B**, which resulted in a decrease in the yield to 60% with a 62 : 38 enantiomeric ratio observed for the 2 mol% loading and a yield of 90% with a 74 : 26 enantiomeric

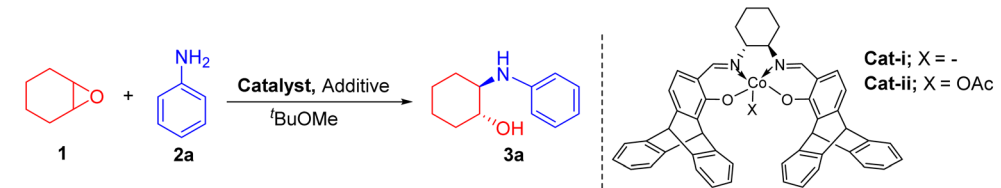


Table 2 Screening of different catalysts for the enantioselective epoxide ring-opening reaction^a


Cat-i; X = -
Cat-ii; X = OAc
Cat-iii; X = OTs
Cat-iv; X = OTf
Cat-v; X = OCO(4-CF₃C₆H₄)
Cat-vi; X = Cl

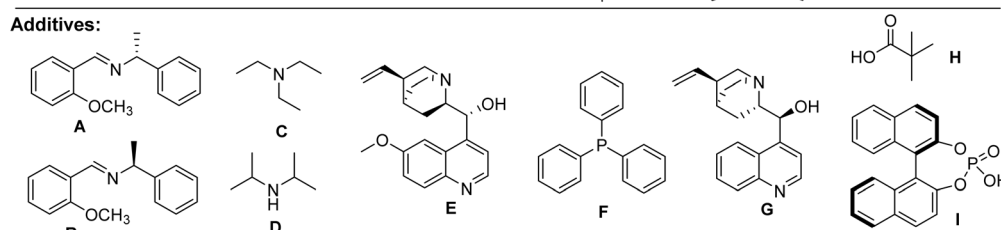
S. no.	Catalyst	Ligand (X)	Time (h)	Yield ^b (%)	er ^c (%)
1	Cat-i	—	3	90	65 : 35
2	Cat-ii	OAc	1.5	>99	74 : 26
3	Cat-iii	OTs	1.5	>99	55 : 45
4	Cat-iv	OTf	1.5	>99	64 : 36
5	Cat-v	OCO(4-CF ₃ C ₆ H ₄)	1.5	>99	61 : 39
6	Cat-vi	Cl	3	95	71 : 29

^a Reaction was performed by stirring the solution of cyclohexene oxide (0.4 mmol) and aniline (0.4 mmol) in 1 mL of ^tBuOMe in the presence of 5 mol% of different catalysts. ^b Isolated yield. ^c The enantiomeric ratios (er) were determined by HPLC using the Chiralpak IA column.

Table 3 Screening of various reaction parameters for the enantioselective epoxide ring-opening reaction^a


Cat-i; X = -
Cat-ii; X = OAc

Additives:



S. no.	Catalyst	Cat. loading (mol%)	Temp. (°C)	Additive	Time (h)	Yield ^b (%)	er ^c
1	Cat-ii	5	RT	A	1.5	99	64 : 36
2	Cat-ii	5	RT	B	2.5	95	55 : 45
3	Cat-i	5	RT	A	3	90	75 : 25
4	Cat-i	5	RT	B	3	92	76 : 24
5	Cat-i	5	RT	F	3	90	61 : 39
6	Cat-i	5	RT	C	3	84	63 : 37
7	Cat-i	5	RT	D	3	86	62 : 38
8	Cat-i	5	RT	E	3	89	70 : 30
9	Cat-i	5	RT	G	3	85	70 : 30
10	Cat-i	5	RT	H	3	87	68 : 32
11	Cat-i	5	RT	I	3	85	68 : 32
12	Cat-i	2	RT	B	3	60	62 : 38
13	Cat-i	10	RT	B	3	90	74 : 26
14	Cat-i	5	0	B	48	50	74 : 26
15	Cat-i	5	10	B	48	54	71 : 29
16	Cat-i	5	50	B	3	92	70 : 30

^a Reaction was performed by stirring the solution of cyclohexene oxide (0.4 mmol) and aniline (0.4 mmol) in 1 mL of ^tBuOMe in the presence of 5 mol% of TpCo catalyst with 5 mol% of different additives at room temperature. ^b Isolated yield. ^c The enantiomeric ratios (er) were determined by HPLC using the Chiralpak IA column.



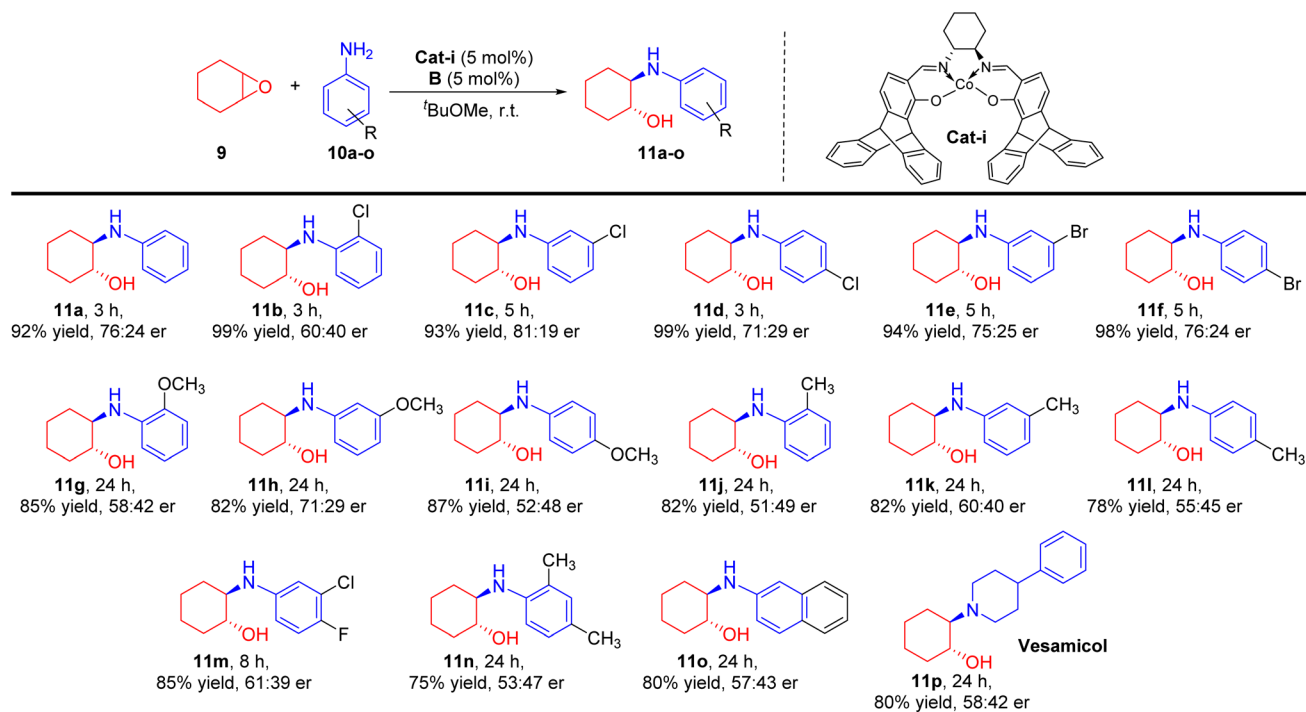
ratio for the 10 mol% loading (Table 3, entries 12 and 13). The effect of different temperatures (0 °C, 10 °C, and 50 °C) was also investigated; however, no enhancement in either the yield or the enantiomeric excess of product **11a** was observed (Table 3, entries 14–16). At 0 °C and 10 °C, product **11a** was obtained in reduced yields of 50% and 54%, with enantiomeric ratios of 74 : 26 and 71 : 29, respectively. In both cases, the reaction time was extended to 48 hours. In contrast, on increasing the temperature to 50 °C, product **11a** was formed in 92% yield, with a slightly lower enantiomeric ratio of 70 : 30.

Based on the above analysis results, the optimized reaction conditions were determined to be 5 mol% of **Cat-i** in combination with 5 mol% of (*S*)-*N*-(2-methoxybenzylidene)-1-phenylethanamine (**B**) as the additive in *tert*-butyl methyl ether as the solvent at room temperature, as summarized in Table 3 (entry 4). With these reaction conditions established, the substrate scope of the reaction was investigated. A vast array of aromatic amines with both cyclic and acyclic epoxides was reacted to produce the corresponding β -amino alcohols. For instance, aniline reacted with cyclohexene oxide to excellently furnish the desired product **11a** in 92% yield and 76:24 er within 3 hours (Table 4, entry 1). In case of the chloroaniline derivatives, when the reaction of *ortho*-chloroaniline with compound **9** was conducted, product **11b** was afforded in 99% yield, but with a low er of 60:40, likely due to the steric hindrance at the *ortho*-position. However, the use of *meta*- and

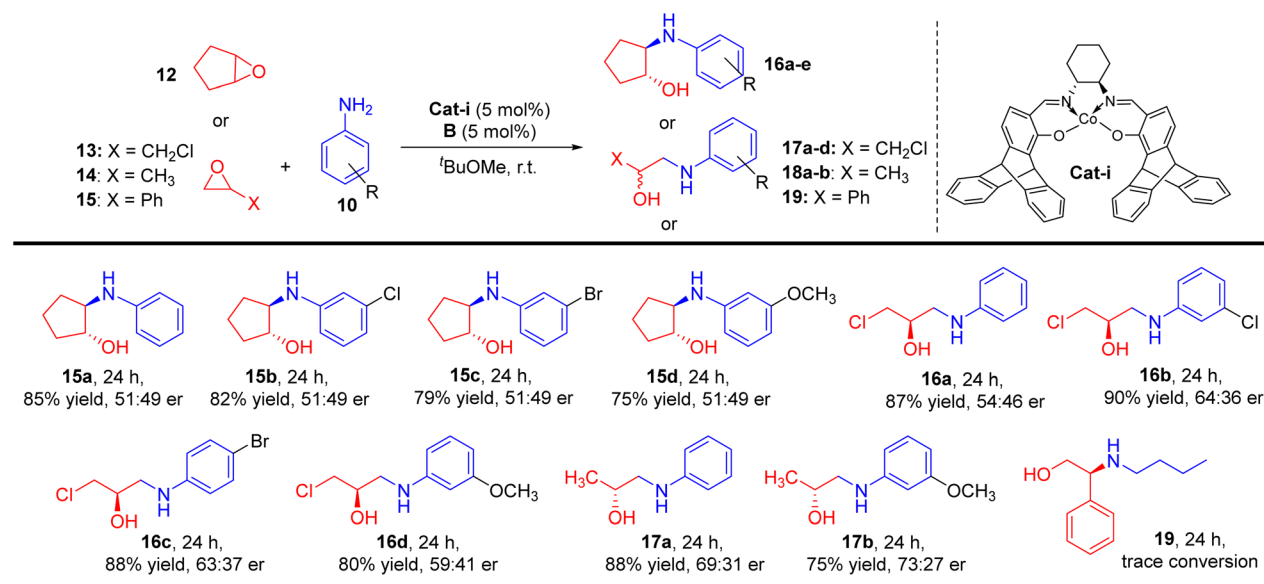
para-chloroanilines (**10c** and **10d**) led to products **11c** and **11d** in comparable yields (93–99%), with significantly higher enantiomeric ratios of 81:19 and 71:29, respectively (Table 4, entries 2–4). Bromoaniline derivatives also afforded excellent yields (94–98%) and moderate enantiomeric ratios of 75:25 (**11e**) and 76:24 (**11f**) (Table 4, entries 5–6).

In contrast, electron-rich anilines, such as anisidines and toluidines, showed markedly reduced reactivity, requiring extended reaction times of 24 hours (Table 4, entries 7–12). For example, *ortho*- and *para*-methoxyanilines gave 85% (58:42 er) and 87% (52:48 er) yields, respectively. However, *meta*-methoxyaniline gave an 82% yield with slightly better enantiomeric ratio of 71:29. On the other hand, *ortho*, *meta* and *para*-methyl anilines provided their corresponding products in yields ranging from 78% to 82%, with enantiomeric ratios ranging from 51:49 to 60:40. Thus, halogenated anilines were unanimously one step ahead of electron-rich amines, such as anisidines and toluidines, as far as reactivity and enantioselectivity were concerned. Indistinguishably, bulky anilines, including 3-chloro-4-fluoroaniline, 2,4-xylidene, and 2-naphthylamine, also indicated moderate yields (75–85%) with low enantiomeric ratios (61:39–53:47) (Table 4, entries 13–15). Then, the reaction of secondary aliphatic amine 4-phenylpiperidine with cyclohexene oxide was conducted to generate vesamicol (**11p**), a key pharmacological tool for studying the function of the vesicular acetylcholine transporter (VACHT).^{9,32} This reaction

Table 4 Reaction of cyclohexene oxide with different substituted anilines^{a,b,c}



^a Reaction was performed by stirring the solution of cyclohexene oxide (0.4 mmol) and different substituted anilines (0.4 mmol) in 1 mL of *t*-BuOMe in the presence of 5 mol% of **Cat-i** and 5 mol% of additive **B** at room temperature. ^b Isolated yield. ^c The enantiomeric ratios (er) were determined by HPLC using a chiral stationary phase.

Table 5 Reaction of cyclopentene oxide (4), epichlorohydrin (5) and propylene oxide (6) with different substituted anilines^{a,b,c}

^a Reaction was performed by stirring the solution of cyclopentene oxide (12), epichlorohydrin (13) and propylene oxide (14) (0.4 mmol) and substituted anilines (0.4 mmol) in 1 mL of *t*BuOMe in the presence of 5 mol% of Cat-i and 5 mol% of additive B at room temperature.

^b Isolated yield. ^c The enantiomeric ratios (er) were determined by HPLC using the chiral stationary phase.

produced the corresponding product, **11p**, in 80% yield with a 58 : 42 enantiomeric ratio (Table 4, entry 16).

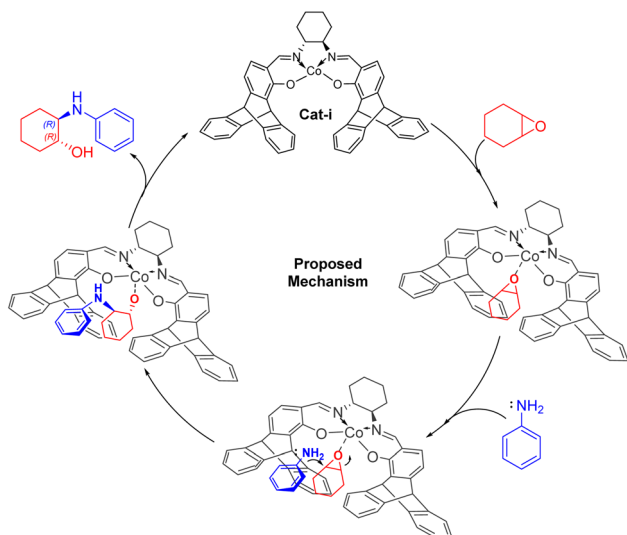
Following this, the reaction was conducted with cyclopentene oxide and aniline, yielding product **15a** in 85% yield (Table 5, entry 1). *Meta*-chloroaniline and *meta*-bromoaniline resulted in the formation of corresponding products **15b** and **15c** in 82% and 79% yields, respectively (Table 5, entries 2 and 3). Furthermore, product **15d** was produced in 75% yield with *meta*-methoxyaniline (Table 5, entry 4). Unfortunately, all

reactions involving cyclopentene oxide produced almost racemic products.

Further investigations were carried out with terminal epoxides, such as epichlorohydrin **13** and propylene oxide **14**, which exclusively yielded a single regioisomer in high chemical yields (90–75%), but with moderate optical selectivity ranging from 73 : 27 er to 54 : 46 er, as depicted in Table 5 (entries 5–10). Further, the reaction of styrene oxide with primary aliphatic amine (*n*-butylamine) was tested. Unfortunately, no product formation occurred even after 24 hours of stirring (Table 5, entry 11). The absolute configuration of the major isomer was determined to be (*R,R*) in the case of cyclic epoxide and *R* in the case of terminal epoxides, by comparing their HPLC chromatograms (τ_R) with those reported in the literature.²⁹

Proposed mechanism

The plausible reaction mechanism is depicted in Scheme 2. In this catalytic cycle, the triptycene-based cobalt complex coordinates with the epoxide, enhancing its electrophilic character, and the bulky triptycene moiety creates a chiral environment, inducing asymmetry in the reaction pathway. The aniline is positioned within this chiral pocket (may be through hydrogen bonding) with the catalyst framework. Due to the spatial shielding provided by the bulky triptycene unit, one face of the coordinated epoxide becomes less accessible, directing the nucleophilic aniline to preferably attack the less-hindered side. This nucleophilic substitution proceeds *via* a backside S_N2-type mechanism, yielding the *trans*- β -amino alcohol as the product. The triptycene-cobalt catalyst is then regenerated to participate in subsequent reaction cycles.



Scheme 2 Proposed mechanism of the epoxide ring-opening reaction.



Conclusions

In this study, we have designed and synthesized a novel triptycene-based chiral ligand, which was coordinated to cobalt to generate a series of novel cobalt complexes bearing different axial ligands. These cobalt catalysts were effectively employed in the asymmetric ring-opening of epoxides, affording β -amino alcohols in near quantitative yields, and in the case of terminal epoxides, complete regioselectivity was achieved. Although good yields and regioselectivity were obtained, the stereoselectivity was modest. Currently, our lab is focused on the structural modifications of the triptycene skeleton to enhance the results in terms of stereoselectivity and expand its applicability to a broader range of asymmetric reactions.

Experimental section

All the solvents and reagents were purchased at the highest commercial quality and used without further purification. Melting points were obtained on a Thomas-Hoover apparatus with open capillaries and are uncorrected. FTIR spectra were recorded using a Bruker alpha Eco-ATR spectrometer in the spectral region of 4000–650 cm^{-1} . ^1H -NMR spectra were recorded on a Bruker Avance Neo 500 MHz spectrometer in the CDCl_3 solvent. Spectroscopic data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad singlet, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, td = triplet of doublet, dt = doublet of triplet, qd = quartet of doublet), integration, and coupling constants in Hertz (Hz). The ^{13}C NMR spectra were recorded at 125 MHz in CDCl_3 , relative to trimethylsilane as the internal standard. Powder X-ray diffraction (PXRD) spectra were recorded using Panalytical's X'Pert Pro X-ray diffractometer. Field-emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDS) data were obtained (HITACHI Japan SU8010 series). Crude products were isolated and purified by column chromatography over 60–120-mesh silica gel using hexanes and ethyl acetate as eluents. The progress of the reaction was monitored by thin-layer chromatography (TLC) on silica-coated aluminum plates F_{254} and visualized in a UV chamber.

General procedure for the epoxide ring-opening reaction

In a 25-mL round-bottom flask, epoxide (0.4 mmol, 1 equiv.) and 5 mol% of the triptycene-based catalyst (0.02 mmol) were dissolved in 1 mL of *tert*-butyl methyl ether. Subsequently, 5 mol% of an additive (0.02 mmol) was added to the reaction mixture. The mixture was stirred at room temperature, followed by the addition of aniline (0.4 mmol, 1 equiv.) or its derivatives. The reaction was allowed to proceed for the optimized reaction time, and progress was monitored by TLC. Upon completion, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography using a gradient of ethyl acetate and hexane (10 : 90 to 20 : 80) as the eluents to afford the pure product. The enantiomeric excess was

determined by HPLC analysis using chiral columns Chiralpak IA, IB, AS-H and phenomenex amylose-1 ($\lambda = 254$ nm, IPA/hexanes used as the eluent).

Synthesis of triptycene-based chiral ligand (8). Chiral ligand **8** was synthesized in multi-steps (A–G) using the following procedures.

(A) Synthesis of 1-methoxyanthraquinone (2). To a mixture of 1-hydroxyanthraquinone (**1**) (5 g, 22.3 mmol, 1.0 equiv.) in DMF (40 mL), anhydrous K_2CO_3 (12.3 g, 89.2 mmol, 4 equiv.) was added at 50 $^\circ\text{C}$, followed by iodomethane (1.7 mL, 22.3 mmol, 1 equiv.) added dropwise into the stirring mixture. The reaction mixture was stirred for 24 hours. After 24 hours, the second portion of iodomethane (1.7 mL, 22.3 mmol, 1 equiv.) was added dropwise into the stirring mixture, and the reaction was allowed to progress for an additional 48 hours. Once the reaction was completed, the solvent was evaporated under reduced pressure. Water was added, and the product was separated by adding ethyl acetate. The organic layers were collected, evaporated, and dried over anhydrous Na_2SO_4 . The pure product (1-methoxyanthraquinone (**2**)) was obtained using column chromatography with hexane and ethyl acetate (90 : 10) as the eluting solvent. Results: >99% yield, 5.3 g as orange solid. IR (KBr): ν_{max} 2967, 1674, 1583, 1456, 1263, 966, 799 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.31–8.26 (m, 1H), 8.25–8.22 (m, 1H), 7.98 (dd, $J_1 = 1$ Hz, $J_2 = 7.5$ Hz, 1H), 7.82–7.70 (m, 3H), 7.36 (dd, $J_1 = 0.5$ Hz, $J_2 = 8.5$ Hz, 1H), 4.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 183.7, 160.6, 135.9, 135.2, 134.4, 133.4, 132.7, 127.4, 126.7, 119.9, 118.1, 56.7 ppm.

(B) Synthesis of 1-methoxyanthracene (3). A mixture of 1-methoxyanthraquinone (**2**) (5 g, 21 mmol, 1 equiv.) and Zn dust (8.2 g, 126 mmol, 6 equiv.) in 117 mL of 10% aqueous NaOH was added. The reaction mixture was stirred for 15 hours at 110 $^\circ\text{C}$. The progress of the reaction was checked by TLC. When the reaction was completed, the reaction mixture turned red. After cooling, the reaction mixture was filtered with the help of a sintered funnel using vacuum filtration. The precipitate was washed with water, followed by dichloromethane (DCM). The crude product was purified by column chromatography in pure *n*-hexane, affording pure 1-methoxyanthracene (**3**). Results: 80% yield, 3.5 g as green crystalline solid. IR (KBr): ν_{max} 2923, 1624, 1578, 1261, 1145, 851, 749 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.85 (s, 1H), 8.37 (s, 1H), 8.08–8.02 (m, 1H), 8.02–7.95 (d, $J = 8.5$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.50–7.43 (m, 1H), 7.40–7.34 (m, 1H), 6.74 (d, $J = 7.5$), 4.08 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 155.6, 132.8, 132.1, 131.4, 128.9, 128.0, 125.8, 125.4, 125.2, 121.2, 120.7, 101.8, 55.7.

(C) Synthesis of 1-methoxytriptycene (4). To a refluxing solution of 1-methoxyanthracene (**3**) (3 g, 11.8 mmol, 1 equiv.) in anhydrous dichloroethane (38 mL), a solution of anthranilic acid (3.2 g, 23.6 mmol, 2 equiv.) in anhydrous 1,2-dimethoxyethane (9 mL) was added *via* a syringe over a period of 1.5 hours. Also, a solution of (3.2 mL, 27.1 mmol, 2.3 equiv.) of isopentyl nitrite in dichloroethane (13 mL) was added to the reaction mixture in such a way that there was slightly more isopentyl nitrite than anthranilic acid in the reaction mixture. After the addition, the resultant mixture was refluxed, and the progress of the reaction was monitored by thin-layer



chromatography (TLC). After the completion of the reaction, the crude product was passed through a silica pad using *n*-hexane to obtain the pale-yellow-coloured 1-methoxytriptycene (4). Results: 81% yield, 2.7 g as a yellow solid. IR (KBr): $\nu_{\max}$ 2925, 2855, 1594, 1501, 1456, 1378, 1261, 1071, 749, 719 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): 7.44 (dd, $J_1 = 4$ Hz, $J_2 = 6.5$ Hz, 2H), 7.40 (dd, $J_1 = 2$ Hz, $J_2 = 4.5$ Hz, 2H), 7.06 (d, $J = 7.5$ Hz, 1H), 7.02–6.98 (m, 4H), 6.98–6.94 (m, 1H), 6.61 (dd, $J_1 = 0.5$, $J_2 = 8$ Hz, 1H), 5.93 (s, 1H), 5.44 (s, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 154.5, 147.7, 145.9, 145.4, 133.1, 125.2, 125.1, 123.9, 123.7, 116.6, 108.5, 55.8, 54.4, 46.9 ppm.

(D) Synthesis of 1-hydroxytriptycene (5). To a solution of 1-methoxytriptycene (4) (2.5 g, 8.8 mmol, 1 equiv.), we added BBr_3 (1 M solution in DCM, 22 mL) in dichloromethane at -78°C under a nitrogen atmosphere. The resulting solution was stirred at ambient temperature for 48 hours. It was then transferred to a beaker containing 20 g of ice. The aqueous layer was extracted with dichloromethane. The combined organic phase was washed with brine and water, dried over anhydrous Na_2SO_4 , filtered, and concentrated. The pure product was extracted using column chromatography, with a mixture of hexane and ethyl acetate in a ratio of 98 : 2 and 95 : 5 as eluting solvents to give an off-white solid of 1-hydroxytriptycene (5). Results: 94% yield, 2.26 g as a yellow solid. IR (KBr): $\nu_{\max}$ 3386, 2982, 1647, 1457, 1308, 1276, 1033, 750, 710 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.42 (dd, $J_1 = 3.5$ Hz, $J_2 = 6.5$ Hz, 2H), 7.39 (dd, $J_1 = 2.5$ Hz, $J_2 = 5$ Hz, 2H), 7.02 (d, $J = 7$ Hz, 1H), 7.01–6.98 (m, 4H), 6.86–6.81 (m, 1H), 6.45 (dd, $J_1 = 1$ Hz, $J_2 = 8$ Hz, 1H), 5.84 (s, 1H), 5.42 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.3, 148.1, 145.7, 145.2, 131.2, 126.1, 125.3, 125.2, 123.8, 123.7, 116.8, 113.1, 54.4, 47.1 ppm.

(E) Synthesis of 2-formyl-1-hydroxytriptycene (6). To a mixture of 1-hydroxytriptycene (5) (2.2 g, 8.1 mmol, 1 equiv.) and HMTA (1.4 g, 9.8 mmol, 1.2 equiv.), trifluoroacetic acid (TFA) (48 mL) was added with continuous stirring. The mixture was then refluxed at a temperature of 70°C , under a nitrogen atmosphere, for 6 hours. Once the reaction had proceeded for the required amount of time, a 4 M hydrochloric acid (HCl) solution was added to the mixture and stirred for an additional 30 minutes. The resulting compound was then extracted using dichloromethane. The pure product was then isolated using column chromatography in pure *n*-hexane to afford the pure 2-formyl-1-hydroxytriptycene (6). Results: 70% yield, 1.7 g as a yellow solid. IR (KBr): $\nu_{\max}$ 3345, 2961, 1646, 1457, 1260, 1033, 764, 521 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 11.10 (s, 1H), 9.77 (s, 1H), 7.49–7.43 (m, 2H), 7.42–7.36 (m, 2H), 7.24 (d, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.06–6.98 (m, 4H), 5.98 (s, 1H), 5.47 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 196.3, 156.2, 155.9, 144.7, 144.4, 133.2, 132.4, 125.8, 125.5, 124.1, 124.0, 119.3, 116.1, 55.0, 46.3.

(F) Resolution of *cis/trans*-1,2-diaminocyclohexane. Resolution of *cis/trans*-1,2-diaminocyclohexane was done using (+)-tartaric acid to get the (*R,R*)-1,2-diaminocyclohexane monotartrate salt (7) as a white solid in 84% yield. In a 100 mL beaker equipped with an overhead stirrer, L-(+)-tartaric acid (7.5 g, 50 mmol, 0.5 equiv.) was dissolved in distilled water (20 mL) at room temperature under stirring. Once complete dissolution

was achieved, a racemic solution of 1,2-diaminocyclohexane (12 mL, 100 mmol, 1 equiv.) was gradually added, allowing the mixture temperature to rise to 70°C . Subsequently, glacial acetic acid (5 mL, 87.5 mmol, 0.88 equiv.) was added dropwise, with increasing the temperature to a maximum of 90°C . Immediate precipitation of a white solid was observed, and the suspension was stirred vigorously while cooling to room temperature over 2 hours. The mixture was then further cooled in an ice bath ($\leq 5^\circ\text{C}$) for an additional 2 hours. The precipitated solid was collected by vacuum filtration, washed with cold water (5°C), and rinsed with methanol. The filter cake was left under an air stream for 1 hour to remove residual solvent, followed by analysis of enantiomeric purity through conversion into the bis-*m*-toluoyl amide derivative. Finally, the material was dried to yield the tartrate salt of (1*R*,2*R*)-cyclohexane-1,2-diamine (7) as a white crystalline solid in 84% yield and with $\geq 99\%$ enantiomeric excess.⁴⁰

(G) Synthesis of triptycene-based chiral ligand (8). In a round-bottom flask (*R,R*)-1,2-cyclohexanediamine (7) (0.4 g, 3.4 mmol, 1 equiv.) was dissolved in ethanol (8 mL), followed by the addition of K_2CO_3 (0.94 g, 6.8 mmol, 2 equiv.) in water. The reaction mixture was stirred for 15–20 minutes until a homogeneous solution was obtained. Subsequently, 2-formyl-1-hydroxytriptycene (6) (1 g, 3.4 mmol, 1 equiv.) was added, and the mixture was refluxed for 24 hours. Upon completion of the reaction, the resulting yellow precipitate was filtered, washed with cold water, and dried. The pure product (9) (chiral triptycene-based ligand) was isolated in 90% yield (Scheme 2). Results: 90% yield, 2.1 g as a yellow solid. IR (KBr): $\nu_{\max}$ 1629, 1458, 1303, 1276, 1045, 765, 747, 722, 638 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 8.39 (s, 2H), 7.43–7.35 (m, 9H), 6.99–6.93 (m, 11H), 6.90 (d, $J = 7.6$ Hz, 2H), 5.83 (s, 2H), 5.57 (s, 2H), 1.81 (d, $J = 12.1$ Hz, 2H), 1.74 (d, $J = 5.8$ Hz, 2H), 1.55 (d, $J = 8.5$ Hz, 2H), 1.47–1.34 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 164.9, 155.5, 150.8, 145.3, 129.3, 125.3, 125.1, 123.8, 123.7, 116.9, 114.5, 72.5, 54.7, 46.6, 33.3, 24.3. HRMS (ESI) calcd for $[\text{M} + \text{H}]^+$: 675.3003, found: 675.2928.

Synthesis of cobalt complexes. Co(II) (Cat-i) and Co(III) complexes (Cat-i–Cat-vi) were synthesized using the following procedures, and the presence of cobalt was confirmed by the EDS spectra given in SI.

Synthesis of (1*R*,2*R*)-TpCo(II)–(Cat-i). To synthesize the cobalt complex, a warm ethanolic solution of the chiral triptycene-based ligand (9) (1 g, 1.5 mmol, 1 equiv.) was added dropwise to a nitrogen-purged solution of cobalt(II) acetate tetrahydrate (0.37 g, 1.5 mmol, 1 equiv.). The reaction mixture was refluxed for 2 hours, after which the solvent was removed under reduced pressure, followed by recrystallisation in ethanol to afford pure cobalt complex TpCo(II) (Cat-i). Results: 99% yield, 1.08 g as reddish-orange solid. IR (KBr): $\nu_{\max}$ 1599, 1583, 1458, 1326, 1234, 774, 730, 666, 640, 614, 530, 442 cm^{-1} .

Synthesis of (1*R*,2*R*)-TpCo(III)–OAc (Cat-ii). A solution of the Co(II) complex (Cat i) (0.5 g, 0.68 mmol) in toluene (1 mL) was treated with acetic acid (0.5 g, 1.36 mmol) and stirred under aerobic conditions at room temperature for 30 minutes, during which the color of the mixture changed from orange to brown. Thereafter, all the volatile components were removed under



reduced pressure to afford pure **Cat-ii** as a brown solid, which was then recrystallised using ethanol as the solvent. Results: 99% yield, 0.53 g as brown solid. IR (KBr): ν_{max} 2963, 1260, 1095, 1016, 797, 765, 750 cm^{-1} .

Synthesis of (1R, 2R)-TpCo(III)-OTs (Cat-iii). To a solution of Co(II) complex (**Cat i**) (0.2 g, 0.27 mmol) in dichloromethane (4 mL), *p*-toluenesulfonic acid monohydrate (0.05 g, 0.29 mmol) was added. The resulting reaction mixture was stirred in air at room temperature for 60 minutes. All the volatile materials were removed in a rotary evaporator to afford **Cat-iii**, which was further purified using the recrystallisation method in ethanol. Results: 95% yield, 0.23 g as green solid. IR (KBr): ν_{max} 2956, 1721, 1625, 1522, 1434, 1275, 1169, 750, 681 cm^{-1} .

Synthesis of (1R, 2R)-TpCo(III)-OTf (Cat-iv). A solution of the Co(II) complex (**Cat i**) (0.2 g, 0.27 mmol) in toluene (1 mL) was treated with trifluoroacetic acid (0.06 g, 0.54 mmol) and stirred under air at room temperature for 30 minutes. Subsequently, all volatile components were removed under reduced pressure, followed by recrystallisation in ethanol to yield pure **Cat-iv**. Results: 99% yield, 0.22 g as brown solid. IR (KBr): ν_{max} 2962, 1684, 1583, 1429, 1317, 1260, 1098, 1016, 764, 750 cm^{-1} .

Synthesis of (1R, 2R)-TpCo(III)- α,α,α -trifluoro-*p*-toluate (Cat-v). To a solution of the Co(II) complex (**Cat i**) (0.1 g, 0.12 mmol), α,α,α -trifluoro-*p*-toluic acid (0.04 g, 0.24 mmol) in dichloromethane (2 mL) was added. The resulting reaction mixture was stirred in air at room temperature for 60 minutes. All the volatile materials were removed *in vacuo*, and the obtained compound was recrystallised in ethanol to afford **Cat v**. Results: 95% yield, 0.11 g as a brown solid. IR (KBr): ν_{max} 2923, 2849, 1695, 1583, 1457, 1430, 1318, 1260, 1099, 1017, 1062, 862, 747 cm^{-1} .

Synthesis of (1R, 2R)-TpCo(III)-Cl (Cat-vi). To a solution of Co(III) complex (**Cat iii**) (0.2 g) in a 60-mL separatory funnel, dichloromethane (8 mL) was added and agitated until all the solid particles dissolved. The organic layer was washed with brine and further dried over anhydrous Na_2SO_4 , followed by solvent evaporation on a rotary evaporator to obtain a green solid. The obtained green solid was washed with pentane, followed by recrystallisation in ethanol to obtain the final product, **Cat-vi**. Results: 95% yield, 0.18 g as a green solid. IR (KBr): ν_{max} 2928, 2844, 1698, 1580, 1430, 1320, 1269, 1017, 1060, 863, 747 cm^{-1} .

Author contributions

Mamta Guleria: formal analysis, investigation, methodology, data curation, validation, writing – original draft. Manpreet Kaur: methodology, validation, writing – review & editing. Divya Tagra: validation, writing – review & editing. Jyoti Agarwal: conceptualization, methodology, formal analysis, writing – review & editing, visualization, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information (SI): the information about materials and measurements used to carry out the experimental work, the characterization data, copies of ^1H , ^{13}C spectra and HPLC chromatograms of amino alcohols are available in supporting information. Also, the copies of ^1H , ^{13}C spectra of triptycene ligand and its intermediates with the copies EDS spectra, PXRD graphs and FESEM images of all triptycene-cobalt complexes have been provided in the supplementary information. See DOI: <https://doi.org/10.1039/d5ra07454a>.

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