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Synthesis of [2.2]paracyclophane-based bidentate oxazoline–carbene ligands for the asymmetric 1,2-silylation of *N*-tosylaldimines

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ABSTRACT

A series of novel oxazoline-substituted imidazolium salts with planar and central chirality has been successfully synthesized and applied to copper-catalyzed enantioselective 1,2-silylation of *N*-tosylaldimines. The oxazoline–carbene copper complex generated in situ by the reaction of the oxazoline-substituted imidazolium and Cu_2O demonstrated an exceptionally high catalytic activity in the asymmetric 1,2-silylation of *N*-tosylaldimines, affording chiral α-amino silanes with excellent yields and enantioselectivities.

1. Introduction

Organosilicons are versatile building blocks in organic chemistry. The C—Si bond, once formed, can be converted into various functional groups.[1] A convenient synthetic approach to this class of compounds employs the catalytic addition of Si nucleophiles, generated from reactive silyl-boronate reagents, such as $PhMe_2$-Si-Bpin and $PhCl_2Si$-$SiMe_3$,[2] to unsaturated acceptors. While enantioselective 1,4-silylations of α,β-unsaturated carbonyl and carboxyl compounds have already been widely studied,[3] asymmetric 1,2-silylations of imines have attracted increasing attention in recent years, particularly due to the potential application of the resultant chiral α-amino silanes in silicon-containing peptide isosteres and α-amino acids.[4] In 2011, a catalytic system of CuCN/NaOMe/MeOH was applied to catalyze the racemic 1,2-silylation of aldimines and ketimines using $PhMe_2Si$-Bpin as the silylation reagent.[5] Since then, investigations have been focused on the asymmetric version. In 2014, Oestreich et al. disclosed the first enantioselective 1,2-silylation of various protected imines catalyzed by a chiral six-membered carbene–Cu(I) complex.[6] Then He et al. reported the Cu(I)-catalyzed asymmetric 1,2-silylation of *N*-tosylaldimine by utilizing Hoveyda's chiral imidazolinium salts as ligands.[7] Very recently, our group synthesized a series of novel chiral bicyclic 1,2,4-triazolium salts and applied an optimal carbene precursor as an organocatalyst and a ligand for copper catalyst in the same reaction.[8] Mita and Sato reported on the enantioselective silylation of *N*-*tert*-butylsulfonylimines using a Cu–secondary diamine complex.[9] Despite many excellent results being achieved, the design of novel chiral ligands to enhance the enantioselectivity remains a major focus.

Planar chiral [2,2]paracyclophane-based ligands have received much attention over the past few decades due to their utility in asymmetric catalysis.[10] Since Bolm et al. reported on the first carbene precursors derived from [2.2]paracyclophane,[11] much progress has been made with respect to the synthesis and the catalytic applications of planar chiral [2.2]paracyclophane-based carbene precursors and their metal complexes. In 2011, our group successfully synthesized a planar chiral pseudo-*ortho*-disubstituted [2.2]paracyclophanyl bidentate oxazoline–carbene ligand (S,S_P)-**1** (Fig. 1) and applied it to the Cu-catalyzed asymmetric β-boration of α,β-unsaturated ketones, although the enantioselectivities of the addition products were only moderate.[12] Subsequently, we prepared L-*tert*-leucinol derived oxazoline–carbene precursors (S,S_P)-**2** and (S,S_P)-**3** for the Cu(I)-catalyzed asymmetric β-boration of α,β-unsaturated esters, noting the important influence of the substituents on both the pyridinium and the oxazoline ring on the enantioselectivity of the reaction.[13] Based on these observations, we wanted to further modify the structure of [2.2]paracyclophanyl oxazoline–carbene ligand by introducing a range of substituents at either the pyridinium or the oxazoline ring exhibiting different steric effects in order to evaluate the effect of substituents on the catalytic behavior of the relevant complex. To examine the effects of such a modulation on the catalytic performances of the resulting complex, we herein report the synthesis of three novel oxazoline-substituted [2.2]paracyclophane-based imidazolium salts with planar and central chirality and their

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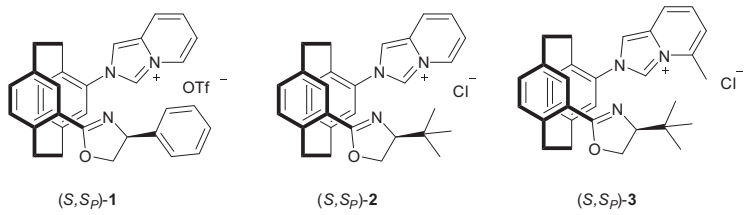


Figure 1. Structures of the reported bidentate oxazoline–carbene precursors.

application in the Cu(I)-catalyzed enantioselective 1,2-silylation of *N*-tosylaldimines.

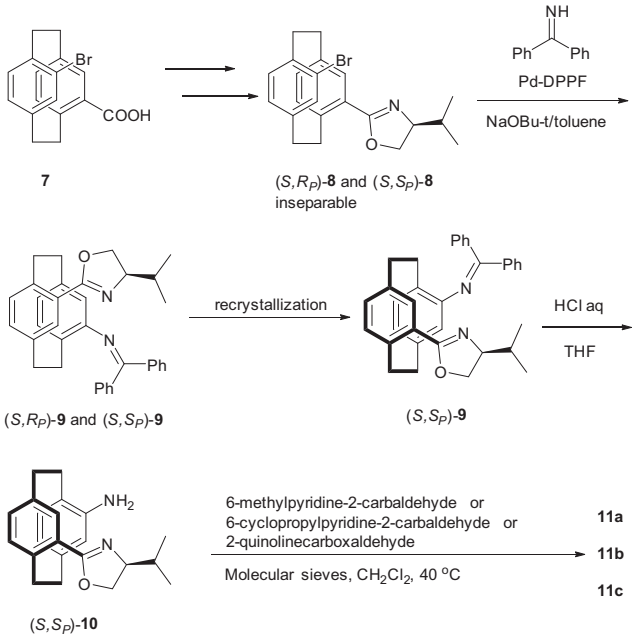
2. Results and discussion

On the basis of our previously reported L-*tert*-leucinol derived oxazoline–carbene precursors (S,S_P)-**3**, we designed and synthesized three new [2.2]paracyclophanyl oxazoline–carbene precursors derived from L-valinol (Fig. 2). The *iso*-propyl group was selected as the substituent on the oxazoline ring because L-valinol is less expensive than L-*tert*-leucinol and the size of the *iso*-propyl group is large enough for resolution and construction of an effective chiral environment. On the other hand, we anticipated that the simple introduction of a range of substituents at pyridine ring might allow for rapid and effective fine-tuning of the steric properties of the carbene center to enhance its chiral recognition ability.

As shown in Scheme 1, the synthesis of the imidazolium salts started from 4-bromo-12-oxazolinyl[2.2]paracyclophane **8**, which can be obtained from racemic 4-bromo-12-carboxyl [2.2]paracyclophane **7** following the literature reported by Bolm et al.[14] However, the two diastereoisomers could not be separated at this step. The reaction of **8** with benzhydrylideneamine under Pd-catalyzed amination, afforded the corresponding imines (S,R_P)-**9** and (S,S_P)-**9** in an overall yield of 85%.[15] The desired enantiopure (S,S_P)-**9** was easily separated from the mixture of diastereoisomers by double recrystallization with ethanol rather than repeated column chromatography on silica gel. 4-Amino-12-oxazolinyl[2.2]paracyclophane (S,S_P)-**10** was then obtained through acid hydrolysis of (S,S_P)-**9** with aqueous HCl under mild conditions in 88% yield.

Treatment of (S,S_P)-**9** with 6-methylpyridine-2-carbaldehyde in dichloromethane, using 4 Å molecular sieves as the dehydrating agent, afforded the corresponding imine **11a**, which was not stable enough for further purification and used directly. Imine **11a** was then reacted with a reagent formed from silver trifluoromethanesulfonate and chloromethyl pivalate, resulted in the formation of the imidazolium triflate. Finally, the desired imidazolium chloride (S,S_P)-**4** was obtained by anion exchange of its analogue triflate with an ion-exchange resin according to the same method reported by McQuade et al.[16] Following the same procedure as above, (S,S_P)-**5** and (S,S_P)-**6** were obtained from 6-cyclopropylpyridine-2-carbaldehyde and quinoline-2-carbaldehyde, respectively (Scheme 2).

The absolute configuration of these imidazolium chlorides was determined by comparing the specific rotation of **12** prepared by



Scheme 1. Synthesis of enantiopure imines **11a–c**.

acid hydrolysis of (S,S_P)-**10** with the reported literature value (Scheme 3).[17]

With these NHC precursors in hand, the corresponding [2.2]-paracyclophanyl oxazoline–carbene copper(I) complexes were generated in situ by the reaction of the imidazolium salts and Cu_2O in THF at 60 °C overnight. According to our previously reported procedure,[8] their catalytic performances were screened using *N*-tosylaldimine **13a** as model substrate and Me_2PhSi-B(pin) as a silylation reagent in toluene at 0 °C for 15 min. As shown in Table 1, all carbene–Cu complexes exhibited good catalytic activity, affording the addition product in yields of 90–95%. Notably, changing the substituent on the oxazoline ring from *tert*-butyl to less bulkier *iso*-propyl did not affect the enantioselectivity (Table 1, entries 1–2), but the yield had a slight increase (from 90% to 94%). Then, the effect of substituent at the α-position of pyridinium on enantioselectivity was also examined. Unfortunately, increasing the steric hindrance resulted in a large decrease in enantioselectivity (Table 1, entries 3–4). We ascribe the lower ee

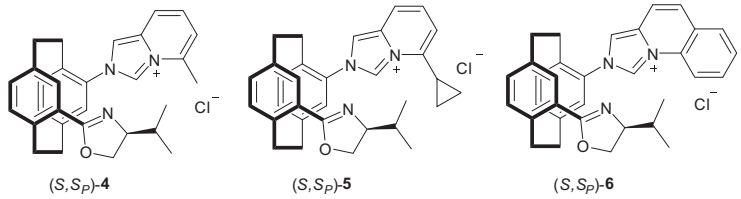
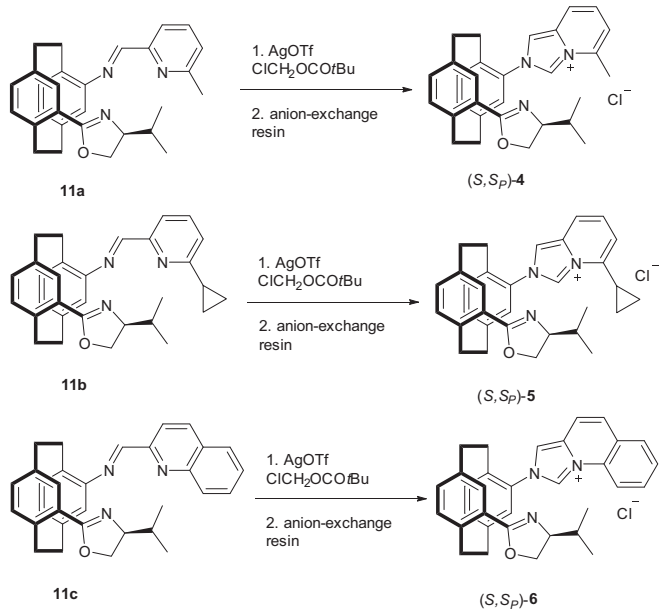
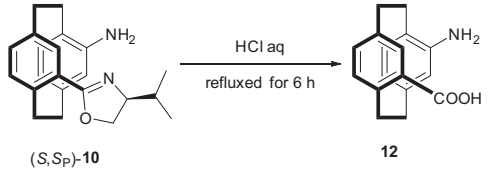


Figure 2. Structures of new bidentate oxazoline–carbene precursors.



Scheme 2. Synthesis of the imidazolium chlorides.



Scheme 3. Synthesis of enantiopure pseudo-*ortho* amino acid.

values obtained from the (S,S_P)-**5** and (S,S_P)-**6** to their structures, in which the substituents are so bulky as to inhibit the construction of an effective chiral environment. Furthermore, it revealed that the size of the substituent at pyridine ring plays a key role in the asymmetric catalysis. On the other hand, in order to study the role of the oxazoline unit at [2.2]paracyclophane backbone, we synthesized unsubstituted [2.2]paracyclophane-based carbene precursor (S_P)-**16** (Scheme 4). This monodentate carbene ligand showed good catalytic activity but lower enantioselectivity, indicating that the oxazoline unit is vital to create an excellent chiral environment (Table 1, entry 5). Based on these results, (S,S_P)-**4** was selected as a suitable ligand for further investigation.

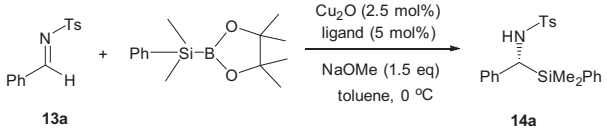
In an attempt to improve the catalytic enantioselectivity, we therefore examined several reaction conditions (Table 2). The reaction did not proceed well in MTBE and DCE (Table 2, entries 1–2), and a sharp decrease in the enantioselectivity was observed (Table 2, entry 2). The use of DME or EA did not affect the reaction rate, but the ee values were not improved (Table 2, entries 3–4). Among the solvents screened, toluene was still the optimal solvent in terms of yield and stereoselectivity (Table 1, entry 2). The impact of temperature on the silylation reaction was evaluated. When the reaction temperature was increased from 0 to 20 °C, both the yield and enantioselectivity were decreased (Table 2, entry 5). However, lowering the reaction temperature from 0 to −20 °C did not alter the enantiomeric excess of **14a** by any appreciable amount (Table 2, entry 6). The effect of the base was also tested (Table 2, entries 7–8). The enantioselectivity was not enhanced by using NaOBu-*t* instead of NaOMe (Table 2, entry 7). The desired silylation did not occur when LiOMe was used as the base (Table 2, entry 8).

Under the optimal reaction conditions, the substrate scope was investigated with a variety of *N*-tosylaldimines. It was found that substituents at the *ortho*- or *para*-position in the benzene ring of *N*-tosylaldimines had little effect on the yield or enantioselectivity, regardless of whether it is an electron-donating substituent or an electron-withdrawing one, providing the corresponding addition products with excellent yields and enantioselectivities (Table 3, entries 2–7 and 11–13). Moreover, the substrates bearing a substituent at the *meta*-position in the phenyl ring, no matter whether it was an electron-donating substituent or an electron-withdrawing one, gave the desired products in excellent yields albeit the ee values were somewhat lower (Table 3, entries 8–10). Furthermore, 1- and 2-naphthyl substituted *N*-tosylaldimines were also compatible with the reaction conditions and afforded the corresponding adducts in good yields and with high enantiomeric excesses (Table 3, entries 14–15). However, a heteroaromatic thiophene-substituted *N*-tosylaldimine was not a good substrate, and a lower enantioselectivity was observed (Table 3, entry 16). The same protocol also allowed for the enantioselective 1,2-silylation of aliphatic *N*-tosylaldimines, high yield and enantioselectivity could be obtained (Table 3, entry 17).

3. Conclusions

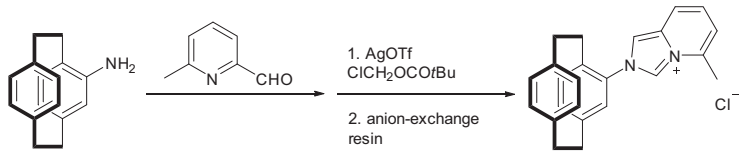
In conclusion, a series of new [2.2]paracyclophanyl oxazoline–carbene precursors derived from L-valinol were synthesized and successfully applied to Cu-catalyzed asymmetric 1,2-silylations of *N*-tosylaldimines. It was found that changing the substituent at the oxazoline ring on the [2.2]paracyclophanyl oxazoline–carbene backbone from *tert*-butyl to less bulkier *iso*-propyl did not affect

Table 1
Evaluation of different NHC ligands[a]



Entry	Ligand	Time (min)	Yield (%)[b]	ee (%)[c]
1	(S,S_P)-**3**	15	90	96
2	(S,S_P)-**4**	15	95	96
3	(S,S_P)-**5**	15	92	88
4	(S,S_P)-**6**	15	95	82
5	(S_P)-**16**	15	90	83

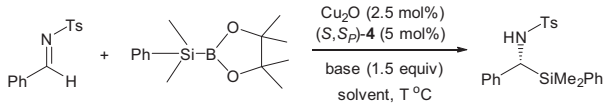
[a] The reaction was carried out with ligand (5 mol %), Cu_2O (2.5 mol %), base (1.5 equiv), $PhMe_2Si$-Bpin (1.5 equiv) and **13a** (0.1 mmol) in toluene (2.0 mL) at 0 °C for 15 min.
[b] Yield of the isolated product.
[c] Determined by chiral HPLC (CHIRALPAK IA) analysis.



(S_P)-**15** (S_P)-**16**

Scheme 4. Synthesis of monodentate carbene ligand.

Table 2
Optimization of reaction conditions[a]

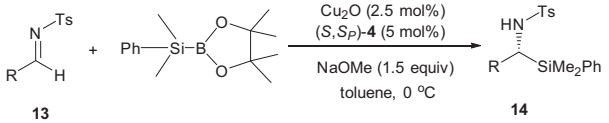


13a **14a**

Entry	Solvent	T (°C)	Base	Yield (%)[b]	ee (%)[c]
1	MTBE	0	NaOMe	76	94
2	DCE	0	NaOMe	85	32
3	DME	0	NaOMe	92	93
4	EA	0	NaOMe	90	82
5	Toluene	25	NaOMe	88	93
6	Toluene	−20	NaOMe	92	96
7	Toluene	0	NaOtBu	90	90
8	Toluene	0	LiOMe	<5	n.d.

[a] The reaction was carried out with (S,S_P)-**4** (5 mol %), Cu_2O (2.5 mol %), base (1.5 equiv), $PhMe_2Si$-Bpin (1.5 equiv) and **13a** (0.1 mmol) in solvent (2.0 mL) at indicated temperature for 15 min.
[b] Yield of the isolated product.
[c] Determined by chiral HPLC (CHIRALPAK IB) analysis.

Table 3
Scope of the methodology[a]



13 **14**

Entry	Aldimines	R	Yield (%)[b]	ee (%)[c]
1	**13a**	Ph	95 **14a**	96
2	**13b**	*p*-MeC_6H_4	90 **14b**	95
3	**13c**	*p*-$MeOC_6H_4$	93 **14c**	95
4	**13d**	*p*-$CF_3C_6H_4$	96 **14d**	96
5	**13e**	*p*-FC_6H_4	98 **14e**	97
6	**13f**	*p*-ClC_6H_4	98 **14f**	95
7[d]	**13g**	*p*-BrC_6H_4	97 **14g**	94
8	**13h**	*m*-MeC_6H_4	97 **14h**	86
9	**13i**	*m*-$MeOC_6H_4$	96 **14i**	87
10	**13j**	*m*-$CF_3C_6H_4$	97 **14j**	91
11	**13k**	*o*-MeC_6H_4	96 **14k**	95
12	**13l**	*o*-$MeOC_6H_4$	94 **14l**	95
13	**13m**	*o*-$CF_3C_6H_4$	96 **14m**	92
14	**13n**	1-Naphthyl	94 **14n**	94
15	**13o**	2-Naphthyl	95 **14o**	94
16	**13p**	2-Thienyl	90 **14p**	86
17	**13q**	Cyclohexyl	90 **14q**	94

[a] The reaction was carried out with (S,S_P)-**4** (5 mol %), Cu_2O (2.5 mol %), NaOMe (1.5 equiv), $PhMe_2Si$-Bpin (1.5 equiv) and **13** (0.1 mmol) in toluene (2.0 mL) at 0 °C for 15 min.
[b] Yield of the isolated product.
[c] Determined by chiral HPLC (CHIRALPAK IB) analysis.
[d] Toluene (3.0 mL) was used as solvent.

the catalytic behavior of relevant complex. In contrast, the size of the substituent at pyridine ring on the carbene skeleton had a significant influence on the catalytic performances of the resulting complex. Moreover, due to inhibit the free rotation about C—N bond connecting the carbene ring and [2.2]paracyclophane moiety, the conformation of copper complex with oxazoline–carbene bidentate ligand (S,S_P)-**4** is more stable than that with monodentate carbene ligand.[8] Thus, the coordination of the oxazoline sidearm to the metal center improves the stability, activity, and chiral environment of the catalyst. Furthermore, the screening of ligands

reveals that (S,S_P)-**4** was the optimal ligand in terms of enantioselectivity and yield. The corresponding chiral α-amino silanes could be obtained in excellent yields (up to 98%) with high enantioselectivities (up to 97% ee).

4. Experimental

4.1. General

Commercially available reagents were used without further purification unless otherwise noted. Solvents were reagent grade and purified by standard techniques. Melting points were recorded on a melting point apparatus and were uncorrected. Optical rotations were taken on a polarimeter with a wavelength of 589 nm. Mass The concentration 'c' has units of g/100 ml (or 10 mg/ml) unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE-300 and AVANCE-400 spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to the internal solvent for ^{1}H NMR and ^{13}C NMR spectra. Mass spectra were recorded on an Agilent Technologies 6510 Q-Tof LC/MS. Enantiomeric excess was determined by HPLC on a Chiralpak IB chiral column.

4.2. General procedures for the synthesis of imidazolium chlorides (S,S_P)-4, (S,S_P)-5 and (S,S_P)-6

4.2.1. (S,S_P)-4-Benzhydrylideneamino-12-(4-*iso*propyloxazolin-2-yl)[2.2]paracyclophane (S,S_P)-9

Under nitrogen, an oven-dried schlenk flask was charged with diastereomeric mixture of 4-bromo-12-(4-isopropyloxazolin-2-yl) [2.2]paracyclophane (2.0 g, 5 mmol), Pd-DPPF (122 mg, 0.15 mmol), benzhydrylideneamine (1.3 ml, 7.5 mmol), NaO^{t}Bu (720 mg, 7.5 mmol) and toluene (10.0 mL). The resulting mixture was heated at reflux for 16 h. After completion of the reaction (monitored by TLC), the solution was allowed to cool to room temperature and then quenched with H_2O (10.0 ml). The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 10.0 ml). The combined organic layers evaporated to dryness under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to afford the (S,R_P)-**9** and (S,S_P)-**9** in an overall yield of 85% (2.12 g). Enantiomerically pure (S,S_P)-**9** was easily separated from the mixture of diastereoisomers by double recrystallization with ethanol as a yellow solid. Yield: 800 mg (64% yield); mp: 168–170 °C; $[\alpha]_D^{20}$ = −742.8 (c 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.93–7.87 (m, 2H), 7.59–7.38 (m, 3H), 7.20–7.10 (m, 3H), 7.03–6.93 (m, 2H), 6.62–6.57 (m, 1H), 6.27–6.40 (m, 2H), 5.29–5.27 (m, 1H), 4.43–4.16 (m, 2H), 4.12–3.90 (m, 2H), 3.57–3.32 (m, 2H), 3.18–3.00 (m, 1H), 2.94–2.67 (m, 3H), 2.50–2.62 (m, 1H), 1.96–1.71 (m, 1H), 1.04 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 163.2, 148.5, 140.7, 140.6, 140.3, 140.0, 136.7, 135.3, 135.0, 133.9, 132.8, 131.0, 130.2, 129.6, 129.5, 128.3, 128.1, 128.0, 127.7, 127.6, 124.2, 73.3, 69.0, 35.3, 33.7, 33.4, 33.2, 32.9, 19.2, 18.8. HRMS (ESI) m/z calcd for $[M+H]^+$ ($C_{35}H_{34}N_2O$): 499.2749, found: 499.2750.

4.2.2. (S,S_P)-4-Amino-12-(4-isopropyloxazolin-2-yl)[2.2]*para*-cyclophane (S,S_P)-10

To a solution of (S,S_p)-4-benzhydrylideneamino-12-(4-isopropyloxazolin-2-yl)[2.2]paracyclophane (S,S_p)-**9** (800 mg, 1.6 mmol) in THF (8 ml), 2 M HCl aq (2.5 mL) was slowly added, and the resulting solution was stirred at room temperature for 2 h. After completion of the reaction (monitored by TLC), 1 M NaOH was added dropwise into the solution until the pH reached 9–11. The mixture was then extracted with CH_2Cl_2 (3 × 5.0 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to afford (S,S_P)-**10** as a white solid. Yield: 475 mg (89% yield); mp: 136–138 °C; $[\alpha]_D^{20}$ = −1.5 (c 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06–7.53 (m, 1H), 7.26 (s, 1H), 6.72–6.41 (m, 2H), 6.39–6.02 (m, 2H), 5.62–5.39 (m, 1H), 4.45–4.26 (m, 1H), 4.21–3.97 (m, 3H), 3.50 (s, 2H), 3.25–3.00 (m, 3H), 3.00–2.74 (m, 3H), 2.75–2.56 (m, 1H), 2.11–1.74 (m, 1H), 1.12 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 145.6, 141.5, 140.0, 138.8, 135.4, 135.1, 135.0, 128.2, 128.2, 124.3, 122.7, 120.5, 72.8, 69.6, 34.9, 34.2, 33.3, 32.4, 32.1, 19.1, 18.6. HRMS (ESI) m/z calcd for $[M+H]^+$ ($C_{22}H_{26}N_2O$): 335.2123, found: 335.2122.

4.2.3. Imidazolium salt (S,S_P)-4

An oven-dried schlenk flask was charged with (S,S_P)-**10** (120 mg, 0.36 mmol), 6-methyl-2-pyridine aldehyde (43.6 mg, 0.36 mmol) and 4 Å molecular sieves (500 mg) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred vigorously at 40 °C for 48 h. After filtration over Celite, the collected organic layers were evaporated under reduced pressure to afford the corresponding imine **11a**, which was used directly without further purification. To a solution of AgOTf (149 mg, 0.58 mmol) in THF (0.5 mL) was added chloromethyl pivalate (77.8 μL, 0.54 mmol) and the mixture was stirred in a sealed tube in the dark at room temperature for 10 min, during which time, a white precipitate appeared. The suspension was filtered over Celite and washed with dry CH_2Cl_2 (2.0 ml). The filtrate was then added to the imine **11a**, and the mixture was stirred in a sealed tube in the dark at 40 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was allowed to cool to room temperature, and ethanol (2.0 ml) was added. After filtration over Celite, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2/ethanol = 30:1) to afford the desired imidazo[1,5-*a*]pyridinium triflate as a white solid. The corresponding imidazo[1,5-*a*]pyridinium chloride (S,S_P)-**4** was prepared by anion exchange of its triflate analogue with an ion-exchange resin (chloride form), following the protocol developed by McQuade.[16] (S,S_P)-**4** was obtained as a white solid. Yield: 90 mg (51%); mp: 246–248 °C; $[\alpha]_D^{20}$ = −225.6 (c 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.01 (s, 1H), 9.16 (s, 1H), 7.98–7.44 (m, 1H), 7.20–6.99 (m, 3H), 6.86 6.91–6.82 (m, 1H), 6.79–6.59 (m, 4H), 4.74–4.56 (m, 1H), 4.53–4.37 (m, 1H), 4.37–4.12 (m, 1H), 4.12–3.94 (m, 1H), 3.65–3.46 (m, 1H), 3.30–2.62 (m, 8H), 2.42–2.13 (m, 1H), 2.02–1.81 (m, 1H), 1.06 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 142.5, 140.9, 139.4, 137.5, 136.2, 135.0, 134.3, 134.0, 133.1, 130.9, 130.2, 128.3, 126.5, 125.8, 125.2, 116.7, 116.3, 114.6, 71.4, 70.6, 35.9, 34.0, 33.6, 33.3, 32.8, 19.6, 18.9. HRMS (ESI) m/z calcd for $[M-Cl]^+$ ($C_{30}H_{32}N_3O$): 450.2545, found: 450.2539.

4.2.4. Imidazolium salt (S,S_P)-5

(S,S_P)-**5** was prepared by the same procedure as for (S,S_P)-**4**, using 6-cyclopropylpyridine-2-carbaldehyde instead of 6-methylpyridine-2-carbaldehyde. The title compound was obtained as a white solid. Yield: 83 mg (45%); mp: 246–248 °C; $[\alpha]_D^{20}$ = −225.6 (c 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.47 (s, 1H), 9.76 (s, 1H), 7.78–7.60 (m, 1H), 7.22–7.11 (m, 2H), 6.96–6.65 (m, 7H), 4.61–4.48 (m, 1H), 4.44–4.17 (m, 2H), 4.10–3.89 (m, 1H), 3.86–3.66 (m, 1H), 3.37–2.98 (m, 5H), 3.03–2.66 (m, 3H), 2.48–2.21 (m, 1H), 2.03–1.68 (m, 2H), 1.16 (d, J = 6.6 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 141.8, 140.6, 139.9, 139.7, 137.9, 136.2, 135.2, 135.1, 134.1, 133.8, 131.0, 130.4, 128.3, 126.4, 125.9, 125.3, 115.9, 114.7, 112.9, 72.0, 70.8,

35.7, 34.1, 33.7, 33.3, 18.9, 18.7, 12.7, 8.2, 7.3. MS (ESI) *m*/*z* calcd for $[M-Cl]^+$ ($C_{32}H_{34}N_3O$): 476.2702, found: 476.2695.

4.2.5. Imidazolium salt (S,S_P)-6

(S,S_P)-**6** was prepared by the same procedure as for (S,S_P)-**4**, using 2-quinolinecarboxaldehyde instead of 6-methylpyridine-2-carbaldehyde. The title compound was obtained as a white solid. Yield: 75 mg (40%); mp: 200 –202 °C; $[\alpha]_D^{20} = -213.5$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.31 (s, 1H), 9.69 (s, 1H), 7.96–7.73 (m, 2H), 7.69–7.54 (m, 1H), 7.59–7.39 (m, 1H), 7.21–7.08 (m, 1H), 6.97–6.86 (m, 1H), 6.83–6.68 (m, 3H), 6.66–6.57 (m, 1H), 4.72–4.57 (m, 1H), 4.51–4.40 (m, 1H), 4.35–4.15 (m, 1H), 4.08–3.86 (m, 1H), 3.86–3.67 (m, 1H), 3.24–2.94 (m, 4H), 2.91–2.67 (m, 2H), 2.37–2.17 (m, 1H), 2.03–1.85 (m, 1H), 1.89–1.72 (m, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 142.1, 140.6, 139.5, 137.7, 136.1, 135.1, 134.7, 133.7, 133.3, 131.1, 130.3, 129.7, 129.1, 128.9, 128.3, 126.9, 125.7, 124.3, 119.5, 115.8, 114.8, 71.7, 70.9, 65.3, 35.7, 34.0, 33.6, 33.0, 18.4, 18.6. MS (ESI) *m*/*z* calcd for $[M-Cl]^+$ ($C_{33}H_{32}N_3O$): 486.2545, found: 486.2555.

4.2.6. Imidazolium salt (S_P)-16

(S_P)-**16** was prepared by the same procedure as for (S,S_P)-**4**, using enantiopure (S_P)-4-amino[2.2]paracyclophane (100 mg, 0.45 mmol) as the starting material. The title compound was obtained as a white solid. Yield: 97 mg (58%); mp: 228–230 °C; $[\alpha]_D^{20} = -10.3$ (*c* 0.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.03 (s, 1H), 8.37–8.02 (m, 1H), 7.67–7.62 (m, 1H), 7.57–7.51 (m, 1H), 7.24–7.12 (m, 2H), 6.87–6.78 (m, 1H), 6.62–6.53 (m, 2H), 6.52–6.47 (m, 1H), 6.45–6.39 (m, 2H), 3.52–3.30 (m, 4H), 3.12–3.04 (m, 2H), 3.02 (s, 3H), 2.96–2.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 140.5, 138.4, 136.8, 135.3, 134.8, 134.3, 133.5, 133.0, 132.7, 132.2, 130.7, 128.5, 127.4, 125.5, 125.2, 116.6, 115.9, 113.9, 35.0, 34.7, 34.43, 32.4, 19.8. HRMS (ESI) *m*/*z* calcd for $[M-Cl]^+$ ($C_{24}H_{23}N_2$): 339.1861, found: 339.1852.

4.3. General procedure for the copper(I)-catalyzed enantioselective 1,2-silylation of *N*-tosylaldimines

Imidazolium salt (S,S_P)-**4** (2.4 mg, 5×10^{-3} mmol) and Cu_2O (0.35 mg, 2.5×10^{-3} mmol) were added to 1.0 mL of anhydrous THF in an oven-dried Schlenk flask under nitrogen. The mixture was stirred at 60 °C overnight to give a brown solution of the Cu complex. The solvent was then evaporated under nitrogen at 80 °C, after which NaOMe (8.1 mg, 0.15 mmol, 1.5 equiv) was added at room temperature, followed by 1.0 mL of anhydrous toluene. The reaction mixture was stirred at room temperature for 1 h, and then cooled to 0 °C. At this temperature, $PhMe_2Si$-Bpin (39 mg, 0.15 mmol, 1.5 equiv) was added via syringe, followed by a solution of the indicated imine (0.1 mmol, 1.0 equiv) in toluene (1.0 mL). the reaction was subsequently maintained at 0 °C for 15 min. The reaction mixture was filtered through a small pad of silica gel and washed with CH_2Cl_2 (5.0 mL). Evaporation of the solvents under reduced pressure and purification of the residue by flash column chromatography afforded the corresponding product **14**.

4.3.1. (*R*)-*N*-{[Dimethyl(phenyl)silyl](phenyl)methyl}-4-toluenesulfonamide 14a

Following the general procedure described above, compound **14a** was obtained as a white solid: 37.5 mg, 95% yield, 96% ee; $[\alpha]_D^{20} = +65$ (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IA column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (15: 1), flow rate = 1.0 mL/min; $t_R = 11.0$ min (*S*, minor), $t_R = 13.7$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.2. (*R*)-*N*-{[Dimethyl(phenyl)silyl](4-tolyl)methyl}-4-toluenesulfonamide 14b

Following the general procedure described above, compound **14b** was obtained as a white solid: 36.8 mg, 90% yield, 95% ee; $[\alpha]_D^{20} = +75$ (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; $t_R = 11.3$ min (*S*, minor), $t_R = 17.3$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.3. (*R*)-*N*-{[Dimethyl(phenyl)silyl](4-methoxyphenyl)-methyl}-4-toluenesulfonamide 14c

Following the general procedure described above, compound **14c** was obtained as a white solid: 39.5 mg, 93% yield, 95% ee; $[\alpha]_D^{20} = +95$ (*c* 0.15, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; $t_R = 12.9$ min (*S*, minor), $t_R = 22.4$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.4. (*R*)-*N*-{[Dimethyl(phenyl)silyl](4-trifluoromethylphenyl) methyl}-4-toluenesulfonamide 14d

Following the general procedure described above, compound **14d** was obtained as a white solid: 44.4 mg, 96% yield, 96% ee; $[\alpha]_D^{20} = +81$ (*c* 0.15, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; $t_R = 11.3$ min (*S*, minor), $t_R = 23.4$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.5. (*R*)-*N*-{[Dimethyl(phenyl)silyl](4-fluorophenyl)-methyl}-4-toluenesulfonamide 14e

Following the general procedure described above, compound **14e** was obtained as a white solid: 40.5 mg, 98% yield, 97% ee; $[\alpha]_D^{20} = +84$ (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; $t_R = 11.4$ min (*S*, minor), $t_R = 18.9$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.6. (*R*)-*N*-{[Dimethyl(phenyl)silyl](4-chlorophenyl)-methyl}-4-toluenesulfonamide 14f

Following the general procedure described above, compound **14f** was obtained as a white solid: 42.2 mg, 98% yield, 95% ee; $[\alpha]_D^{20} = +95.0$ (*c* 0.15, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; $t_R = 11.6$ min (*S*, minor), $t_R = 20.5$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.7. (*R*)-*N*-{[Dimethyl(phenyl)silyl](4-bromophenyl)-methyl}-4-toluenesulfonamide 14g

Following the general procedure described above, compound **14g** was obtained as a white solid: 46.0 mg, 97% yield, 94% ee; $[\alpha]_D^{20} = +84$ (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; $t_R = 11.6$ min (*S*, minor), $t_R = 20.5$ min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.8. (*R*)-*N*-{[Dimethyl(phenyl)silyl](3-tolyl)methyl}-4-toluenesulfonamide 14h

Following the general procedure described above, compound **14h** was obtained as a white solid: 39.6 mg, 97% yield, 86% ee; $[\alpha]_D^{20} = +28$ (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: $\lambda = 220$ nm, solvent:

hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 11.2 min (*S*, minor), t_R = 18.1 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.9. (*R*)-*N*-{[Dimethyl(phenyl)silyl](3-methoxyphenyl)-methyl}-4-toluenesulfonamide 14i

Following the general procedure described above, compound **14i** was obtained as a white solid: 40.8 mg, 96% yield, 87% ee; $[\alpha]_D^{20}$ = +88 (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 12.8 min (*S*, minor), t_R = 17.0 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.10. (*R*)-*N*-{[Dimethyl(phenyl)silyl](3-trifluoromethyl-phenyl) methyl}-4-toluenesulfonamide 14j

Following the general procedure described above, compound **14j** was obtained as a white solid: 45.0 mg, 97% yield, 91% ee; $[\alpha]_D^{20}$ = +62 (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 10.5 min (*S*, minor), t_R = 13.2 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.11. (*R*)-*N*-{[Dimethyl(phenyl)silyl](2-tolyl)methyl}-4-toluenesulfonamide 14k

Following the general procedure described above, compound **14k** was obtained as a white solid: 39.5 mg, 96% yield, 95% ee; $[\alpha]_D^{20}$ = +68 (*c* 0.15, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 10.0 min (*S*, minor), t_R = 13.5 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.12. (*R*)-*N*-{[Dimethyl(phenyl)silyl](2-methoxyphenyl)-methyl}-4-toluenesulfonamide 14l

Following the general procedure described above, compound **14l** was obtained as a white solid: 40.0 mg, 94% yield, 95% ee; $[\alpha]_D^{20}$ = +68 (*c* 0.2, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 11.4 min (*S*, minor), t_R = 14.3 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.13. (*R*)-*N*-{[Dimethyl(phenyl)silyl](2-trifluoromethylphenyl) methyl}-4-toluenesulfonamide 14m

Following the general procedure described above, compound **14m** was obtained as a white solid: 44.5 mg, 96% yield, 92% ee; $[\alpha]_D^{20}$ = +106 (*c* 0.2, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 12.1 min (*S*, minor), t_R = 20.9 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.14. (*R*)-*N*-{[Dimethyl(phenyl)silyl](naphthalen-1-yl)-methyl}-4-toluenesulfonamide 14n

Following the general procedure described above, compound **14n** was obtained as a white solid: 42.0 mg, 94% yield, 94% ee; $[\alpha]_D^{20}$ = +17 (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4:1), flow rate = 0.5 mL/min; t_R = 11.5 min (*S*, minor), t_R = 18.4 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.15. (*R*)-*N*-{[Dimethyl(phenyl)silyl](naphthalen-2-yl)-methyl}-4-toluenesulfonamide 14o

Following the general procedure described above, compound **14o** was obtained as a white solid: 42.5 mg, 95% yield, 94% ee; $[\alpha]_D^{20}$ = +175 (*c* 0.2, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4: 1), flow rate = 0.5 mL/min; t_R = 12.2 min (*S*, minor), t_R = 19.0 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.16. (*R*)-*N*-{[Dimethyl(phenyl)silyl](thiophen-2-yl)-methyl}-4-toluenesulfonamide 14p

Following the general procedure described above, compound **14p** was obtained as a white solid: 36.0 mg, 90% yield, 86% ee; $[\alpha]_D^{20}$ = +66 (*c* 0.1, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (4:1), flow rate = 0.5 mL/min; t_R = 12.0 min (*S*, minor), t_R = 20.6 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

4.3.17. (*R*)-*N*-{[Dimethyl(phenyl)silyl](cyclohexyl)methyl}-4-toluenesulfonamide 14q

Following the general procedure described above, compound **14q** was obtained as a colorless oil: 36.0 mg, 90% yield, 94% ee; $[\alpha]_D^{20}$ = −5 (*c* 0.2, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IB column: λ = 220 nm, solvent: hexane/i-PrOH (25:1), flow rate = 0.5 mL/min; t_R = 18.4 min (*S*, minor), t_R = 20.2 min (*R*, major); other spectral and property data matched those reported in the literature.[8]

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