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Full Paper

# Crystal Structure Studies towards the Synthesis and Applications of N-heterocyclic Carbene–Metal Complexes Derived from [2.2]Paracyclophane

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The crystal structures of six planar chiral N-heterocyclic carbene (NHC) precursors and one NHC–Rh complex derived from [2.2]paracyclophane were described. The NHC–metal complexes were prepared to examine their catalytic activities toward the Rh-catalyzed asymmetric addition of phenylboronic acid to 1-naphthaldehyde. The results were correlated to the single-crystal crystallographic studies. The novel NHC precursor **5** can achieve high catalytic activity in the asymmetric addition of phenylboronic acid to 1-naphthaldehyde.

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## Introduction

Since chiral N-heterocyclic carbenes (NHCs) were first reported by Herrmann et al. and Enders et al.,[1] much research has focussed on the isolation of novel NHC precursors and their applications as ligands in transition metal catalysis.[2] Planar chiral NHC precursors, such as substituted [2.2]paracyclophane derivatives, play an important role in asymmetric catalysis.[3] These planar chiral NHCs as well as their metal complexes have been prepared and applied in asymmetric catalytic reactions with good yields and enantioselectivities.[4,5] However, there is still a lack of systemic structural studies in this area.

The study of the structures and chemical reactivities of NHCs has become an active research area after Arduengo et al. reported the synthesis and isolation of stable imidazol-2-ylidene carbenes for the firt time in 1991.[6] Despite the isolation and characterization of a vast array of NHC precursors and NHC–metal complexes,[7] there are few reports on the systematic structural studies regarding the stability and reactivity of NHCs in catalysis systems. In the previous studies, our group has employed dozens of planar chiral NHC precursors and their complexes based on optically pure [2.2]paracyclophane. These NHCs demonstrated high catalytic activities toward the 1,2-addition of arylboronic acids to aldehydes and β-boration of acyclic enones,[5] which may be due to the NHC structure and the basicity of the ligands. In this study, we present the single-crystal crystallographic studies of six [2.2]paracyclophanyl NHC precursors and one NHC–Rh complex **1**–**7** (Fig. 1) to explore the relationships between the structure of ligands and their complexes.

## Results and Discussion

We designed and synthesized six planar chiral NHC precursors and one NHC–Rh complex based on the [2.2]paracyclophane skeleton. The NHC precursors **1**, **2**, **3**, **4**, **6**, and NHC–Rh **7** could be obtained following our published procedure.[5] ($R_p$)-12-Amino-4-fluoro[2.2]paracyclophane **10** was readily prepared in high yield from ($R_p$)-4-bromo-12-fluoro[2.2]paracyclophane **8**[8] by amination with benzhydrylideneamine, followed by imine **9** hydrolysis under acidic conditions (Scheme 1). The compound **10** was converted into corresponding diimine by treatment with aqueous glyoxal in THF. Then, the imidazolium triflate was obtained by using Glorius process with silver triflate and chloromethyl pivalate. At last, the reaction of imidazolium triflate and saturated KBr aqueous solution resulted in the formation of *N*,*N*′-bis[($R_p$)-(−)-12-fluoro-4-[2.2]paracyclophanyl] imidazolium bromide **5** in moderate yield (Scheme 2). The structures of these planar chiral NHC precursors **1**–**6** and the NHC–Rh complex 7 were all determined by X-ray diffraction (Fig. 2).

It is known that the free NHCs can be obtained from the imidazolium or imidazolinium salts using standard deprotonating agents such as *t*-BuOK (potassium *tert*-butoxide), KHMDS (potassium bis(trimethylsilyl)amide), or NaH. However, present attempts to prepare the free NHCs from the [2.2]paracyclophanyl-NHC precursors using standard deprotonating agents failed. These results indicate that it may not always be safe to assume carbene-C bonding in the imidazolium and imidazolinium salts when preparing NHC complexes in situ.[9] Deprotonation using silver oxide as base has been widely used to synthesize NHC–Ag complexes that can transfer the carbene ligands to a variety of

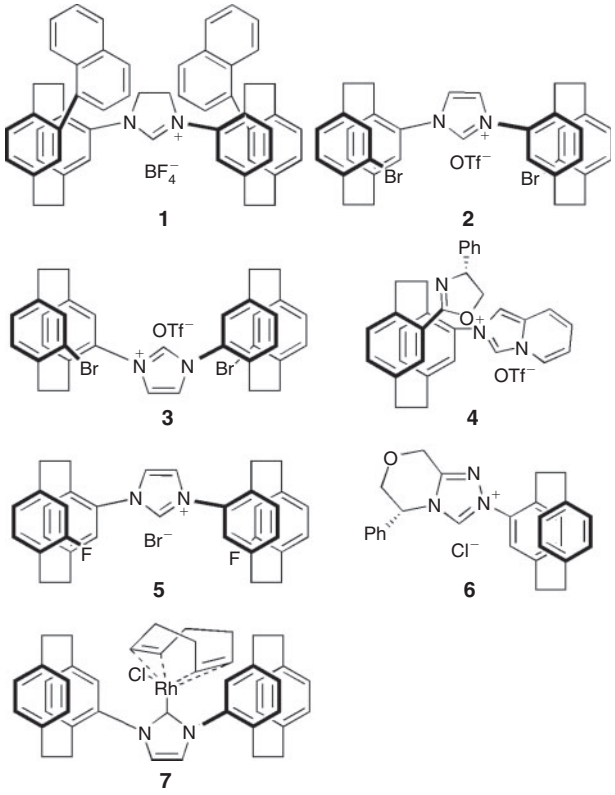
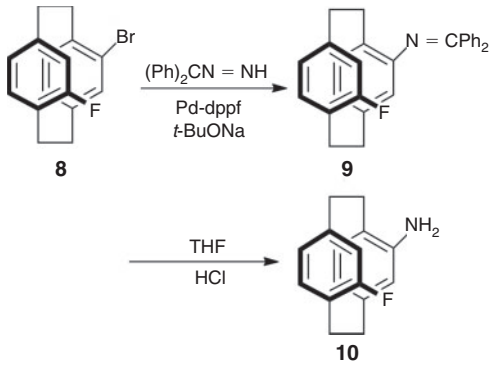
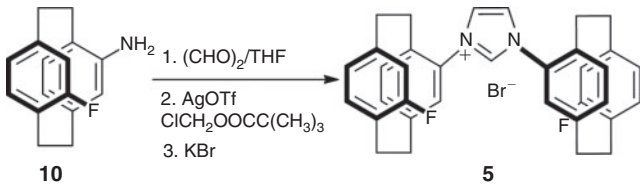



**Fig. 1.** Planar chiral NHC precursors and NHC–Rh complex.




**Scheme 1.** Synthesis of $R_p$-4-amino-12-fluoro[2.2]paracyclophane.




**Scheme 2.** Synthesis of imidazolium bromide.

other metals.[10] Following this strategy, the imidazolinium salt **1** and imidazolium salts **2**–**4** were treated with an excess of $Ag_2O$ in anhydrous $CH_2Cl_2$, but no reaction occurred. The anion exchange of the imidazolinium salt **1** with NaBr in the presence of $Ag_2O$ in anhydrous $CH_2Cl_2$[11] resulted in the hydrolysis of the imidazolinium salt **1** and generated N-formylethylenediamines.[12] It seems to be the effect of the bulky naphthyl group in the imidazolinium **1**. However, when the less bulky imidazolinium salt **11** was used to generate NHC–Ag complexes under the same conditions, the hydrolysis product was also observed (Scheme 3). The hydrolysis reaction of the imidazolinium salts **1** and **11** with $Ag_2O$ may be due to the sensitivity of the structure and high basicity of the NHCs.

Generally, the NCN bond angles of NHC precursors have a dramatic effect on basicity.[13] From the crystal structure data of the imidazolinium salt **1** (Table 1), the NCN bond angle is 114.09(18)° which is quite large compared with other bond angles in the imidazolinium salts.[14] As a result, the p$K_a$ value of this precursor could be higher than that of other ligands.[13] As evidenced, the $^1$H NMR data (298 K, $CDCl_3$, N–CH–N of NHC precursor) are consistent with the basicity of the imidazolinium salt **1**. On the other hand, it is well known that the ring strain results from a combination of angle strain, conformational strain, and transannular strain that can substantially weaken the C–N bonds of the ring. Compared with the crystal structures of 1,3-bis(2-methylnaphthalen-1-yl)-imidazolinium tetrafluoroborate (SI2MeNap·$HBF_4$), 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene (SIMes), SIMesAgCl, 1,3-bis (2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr), and SIPrAgCl (Table 1), the C–N bond lengths of the NCN moiety in compound **1** are shorter.[14] This suggests that the angle strain of the imidazolinium salt **1** should not lead to ring-opening. Günay et al. and Kantchev et al. have concluded that the ring-opening reaction of the imidazolinium salts is attributed to the lower acidity.[15] Therefore, the high basicity of the imidazolinium salt **1** might be the main reason for the hydrolysis.

On the other hand, the conformational environment around the imidazolinium ring may also affect the stability of compound **1**. The conformations of compounds **1**–**7** are dependent on the orientation of the phenyl rings relative to the heterocyclic core, shown in Chart 1 as **A**, **B**, and **C**.[13]

The dihedral angles in Table 2 can predict the conformations of compounds **1**–**7**. For clarity in describing the conformations, structure **A** is the highest energy conformation and structure **C** is the lowest energy one among the three conformations. The conformation of compound **1** resembles that of the *C*2 symmetric structure **C**, in which one phenyl ring is orthogonal to the imidazoline core, while the other phenyl ring and imidazoline ring is twisted, with the dihedral angle being 22.7°. As in other reported imidazolinium salts,[14] the two phenyl rings are almost orthogonal to the imidazoline core that also belong to structure **C**. The structure **C** has the least conformational strain. As such, the conformational strain of imidazolinium salt **1** should not result in the ring-opening reaction. It is worth mentioning that the imidazolium salts **3** and **5** and NHC–Rh **7** all belong to structure **C** with the least conformational strain. The conformation of compound **2** corresponds to the structure **B**, which exhibits a propeller-type arrangement. Compounds **4** and **6** only have one [2.2]paracyclophane, in which the closest phenyl ring of the [2.2] paracyclophane unit is twisted to heterocyclic ring, while the other closest six-membered ring and heterocyclic ring is almost planar. The structures of these NHC precursors **1**–**6** and NHC–Rh **7** are conformationally stable.

These results prompted us to further investigate the reactivity of NHC precursors **2**–**6** with $Ag_2O$. Under the same reaction conditions,[11] imidazolium salts **2** and **3** reacted with $Ag_2O$ and NaBr in anhydrous $CH_2Cl_2$ at room temperature for 3 days; the yields were moderate (37 % and 68 %, respectively). When the reaction was carried out with compound **4**, however, 91 % conversion was observed after ~12 h. In the absence of NaBr,

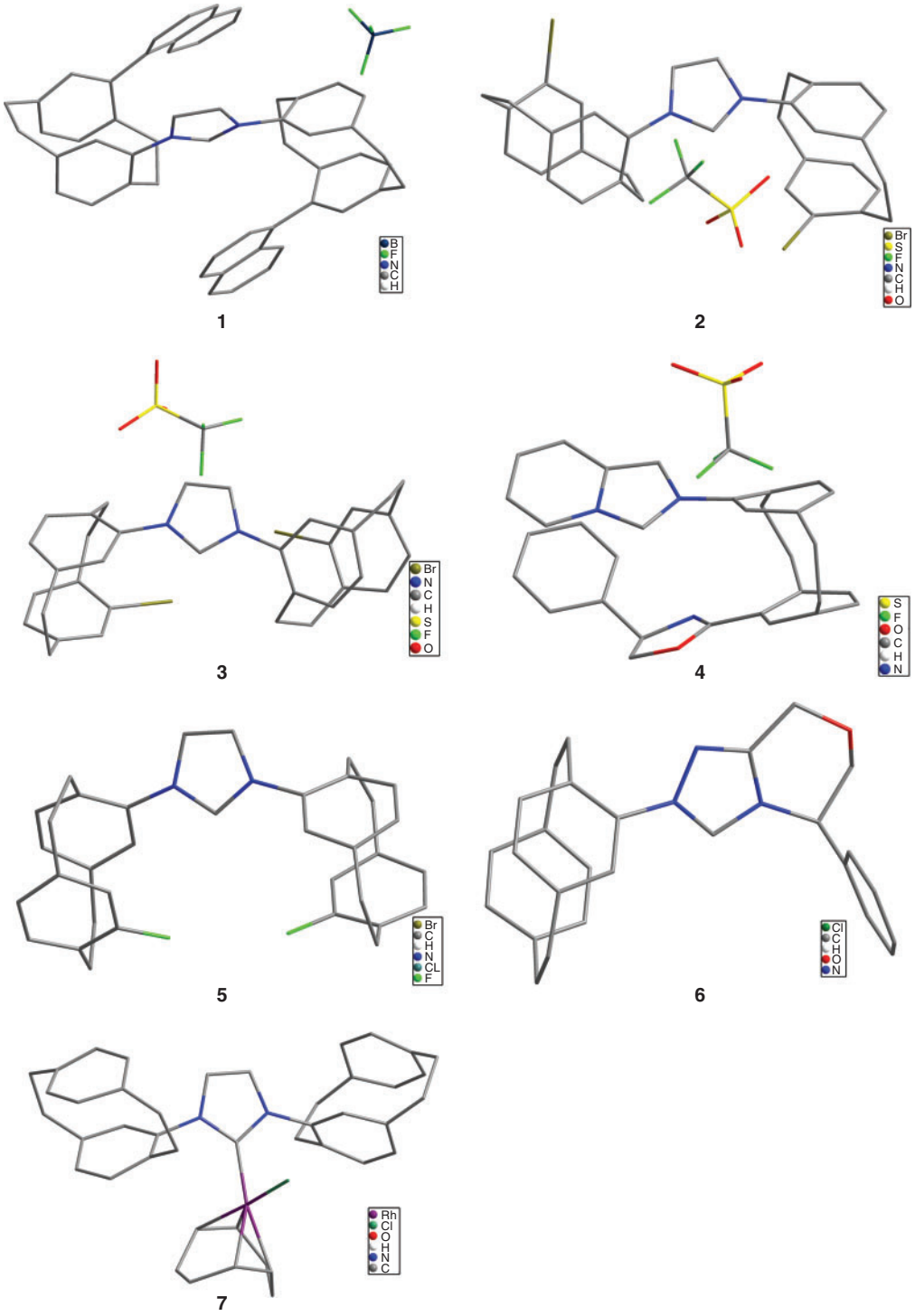
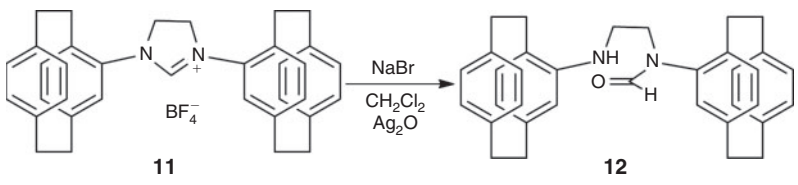



**Fig. 2.** NHC precursors and NHC–Rh crystal structures. Hydrogen atoms and solvent molecules are omitted for clarity.




**Scheme 3.** Hydrolysis of imidazolinium tetrafluoroborate.

**Table 1. NCN bond angles and $^1$H NMR chemical shifts of N–CH–N for NHC precursors and NHC–Rh complex**

| Compound | Bond angles of N–C–N [°] | $^1$H NMR δ of N–CH–N [ppm] | Bond lengths of N–C and C–N in N–C–N [Å] |
|---|---|---|---|
| **1** | 114.09(18) | 8.05–8.06 | 1.291(3) 1.298(3) |
| SIMes | 114.1(3) | – | 1.307(4) 1.309(4) |
| SIPr | 111.3(6) | – | 1.320(7) 1.314(7) |
| SI2MeNap·$HBF_4$ | 113.1(3) | 9.47 | 1.311(3) 1.311(3) |
| SIMesAgCl | 108.51(17) | – | 1.332(16) 1.332(16) |
| SIPrAgCl | 109.6(7) | – | 1.308(12) 1.329(12) |
| **2** | 108.4(4) | 9.50 | 1.317(6) 1.337(6) |
| **3** | 108.6(6) | 10.01–10.08 | 1.326(7) 1.356(7) |
| **4** | 106.8(6) | 9.97 | 1.334(7) 1.366(7) |
| **5** | 108.6(3) | 9.70 | 1.316(5) 1.332(4) |
| **6** | 107.4(3) | 11.14 | 1.318(4) 1.334(5) |
| **7** | 103.7(4) | – | 1.357(6) 1.361(6) |

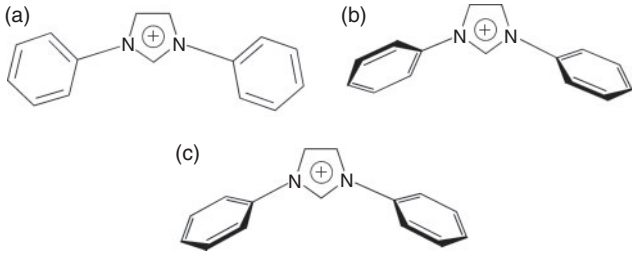



**Chart 1.**

**Table 2. Dihedral angles for compounds 1–7**

| Compound | Angle between heterocyclic ring and closest left-hand phenyl ring [°] | Angle between heterocyclic ring and closest right-hand phenyl ring [°] |
|---|---|---|
| **1** | 87.3 | 22.7 |
| **2** | 142.1 | 35.2 |
| **3** | 34.1 | 32.4 |
| **4** | 178.3 | 37.8 |
| **5** | 126.9 | 133.5 |
| **6** | 41.8 | 3.3 |
| **7** | 52.9 | 72.5 |

the imidazolium salt **5**, as an ion exchange product of its triflate analogue, and the triazolium salt **6** could react with $Ag_2O$ directly to give 91 % and 97 % yields, respectively, after 12 h. It is also observed that the reactions of NHC precursors **2**–**6** with $Ag_2O$ do not lead to ring-opening. These results reveal that the reactivity of NHC precursors with an excess of $Ag_2O$ in anhydrous $CH_2Cl_2$ is related to their structure and acidity. From the crystal structures of the NHC precursors **2**–**6** (Table 1), the NCN bond angles are between 106.8° and 108.6°, and the p$K_a$ value[13] is suitable for reaction with $Ag_2O$. The $^1$H NMR data (298 K, $CDCl_3$, N–CH–N of NHC precursors) are also consistent with the basicity of the NHC precursors. As a rule of thumb, the greater the chemical shift of proton, the higher the acidity of the NHC precursors. Therefore, the acidity is too weak for the imidazolinium salt **1** to form corresponding NHC–Ag complex (Table 1). On the other hand, the mean deviation from plane of the imidazolinium ring is 0.2399 Å in imidazolinium salt **1**. Unlike the imidazolinium salt **1**, the mean deviations from plane of the heterocyclic rings in the imidazolium salts **2**–**5** and the triazolium salt **6** ranged from 0.0031 to 0.0222 Å. In the case of the NHC–Rh complex **7**, the mean deviation from plane of the imidazole ring in NHC–Rh complex is 0.0068 Å. Based on the NCN bond angle (103.7(4)°) and the mean deviation from the plane of NHC–Rh complex, the structures of the imidazolium salts **2**–**5** and the triazolium salt **6** are more suitable for the preparation of NHC–metal complexes.

Because we found that the synthesis of NHC–Ag complexes was affected by the structure of these NHC precursors, we further investigated the impact of structure on catalytic activity.

With the imidazolium salts **2**, **3**, **4**, and **5**, the imidazolinium salt **1,** the triazolium salt **6,** and the NHC–Rh complex **7** in hand, we preliminarily examined their application in Rh-catalyzed asymmetric addition of phenylboronic acid to 1-naphthaldehyde.

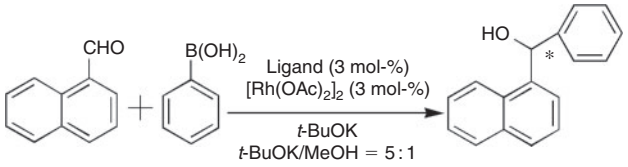
We began our experiment under identical conditions used in our previous study of Rh-catalyzed asymmetric arylation of aromatic aldehydes.[5d] The reaction of phenylboronic acid and 1-naphthaldehyde was performed with 3.0 mol-% of catalyst generated in situ from NHC precursor and $[Rh(OAc)_2]_2$ (rhodium acetate) in *t*-butanol/methanol (*t*-BuOH/MeOH) (5 : 1) at 80°C for 7 h. Compared with our previous work,[5d] the enantioselectivity of the reaction was improved by the use of ligand **5**.

Because of the high basicity and prompt hydrolysis, the imidazolinium salt **1** was almost ineffective as a ligand for the reaction (Table 3, entry 1). The carbene precursors **2** and **3**, possessing electron-deficient substituents, resulted in low yields (36 % and 45 %, respectively) and low enantioselectivities (23 % and 38 % ee, respectively). Ligands **4** and **6** were found to be less efficient in this reaction in terms of either reactivity or enantioselectivity (Table 3, entries 4 and 6). Ligand **5**, bearing a fluoro substituent on the 12-position of the [2.2]paracyclophane, showed good catalytic properties in the reaction (92 % yield, 54 % ee). This result suggested that the fluoro moiety[16] in ligand **5** could play an important role in the Rh-catalyzed asymmetric addition reaction. However, the NHC–Rh complex **7** yielded the desired product with low enantiomeric excess (Table 3, entry 7).

## Conclusions

The crystal structures of six planar chiral NHC precursors and one NHC–Rh complex derived from [2.2]paracyclophane were described. The NHC–metal complexes were prepared and evaluated as ligands in the Rh-catalyzed asymmetric addition of phenyl boronic acid to 1-naphthaldehyde. The results were correlated to the single-crystal crystallographic studies. This work has

**Table 3. Evaluation of ligands and NHC–Rh[A]**




| Entry | Metal source | Ligand | Yield [%][B] | ee [%][C] |
|---|---|---|---|---|
| 1 | $[Rh(OAc)_2]_2$ | **1** | 10 | 3 (*R*) |
| 2 | $[Rh(OAc)_2]_2$ | **2** | 36 | 23 (*S*) |
| 3 | $[Rh(OAc)_2]_2$ | **3** | 45 | 38 (*S*) |
| 4 | $[Rh(OAc)_2]_2$ | **4** | 42 | 7 (*S*) |
| 5 | $[Rh(OAc)_2]_2$ | **5** | 92 | 54 (*S*) |
| 6 | $[Rh(OAc)_2]_2$ | **6** | 47 | 5 (*S*) |
| 7 | – | **7** | 84 | 12 (*R*) |

[A]Reaction conditions: $[Rh(OAc)_2]_2$ (3 mol-%), ligand (3 mol-%), *t*-BuOK (1 equiv.), phenylboronic acid (2 equiv.), 1-naphthaldehyde (1 equiv.), $N_2$, 80°C, 7 h.
[B]Isolated yield.
[C]Determined by chiral HPLC (CHIRALPAK IA Column) analysis.

established that the planar chiral NHC precursors do not always give normal NHCs on metalation, implying that the chemistry of this ligand system can be more complex than currently thought. Further studies to synthesize the [2.2]paracyclophane-based carbene complexes as well as investigating their applications in asymmetric catalysis are in progress in our group.

## Experimental

### *Material*

Commercially available reagents were used without further purification unless otherwise noted. Solvents were reagent grade and purified by standard techniques. *N*,*N*′-bis[(4$S_p$,13$R_p$)-(−)-13-(1-naphthyl)-4-[2.2]paracyclophanyl]-4,5-dihydroimidazolium tetrafluoroborate (**1**), *N*,*N*′-bis[($S_p$)-(+)-12-bromo-4-[2.2]paracyclophanyl]imidazolium triflate (**2**), *N*,*N*′-bis[(4$R_p$,13$S_p$)-13-bromo-4-[2.2]paracyclophanyl]imidazolium triflate (**3**), (*R*,4$S_p$,13$R_p$)-3-{13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane-4-yl}imidazo[1,5-α]pyridinium triflate (**4**), triazolium salt (*R*,$R_p$)-**6**, chloro($\eta^2$,$\eta^2$-1,5-cyclo-octadiene)-[*N*,*N*′-bis[($R_p$)-(+)-4- [2.2]paracyclophanyl]imidazole-2-ylidene]rhodium (**7**), and $R_p$-4-bromo-12-fluoro[2.2]paracyclophane (**8**) were prepared according to published procedures.[5,9] Melting points were recorded on a melting point apparatus and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 MHz and 300 MHz spectrometers. High-Resolution mass spectrometry (HRMS) patterns were recorded on an Agilent Technologies 6510 Q-Tof LC/MS. Enantiomeric excess was determined using HPLC on a Chiralpak IA chiral column. Optical rotations were determined on a polarimeter with a wavelength of 589 nm. The concentration '*c*' has units of g per 100 mL (or 10 mg mL$^{-1}$) unless otherwise noted.

### *Synthesis of* $R_p$*-4-Amino-12-fluoro[2.2]paracyclophane (**10**)*

($R_p$)-4-Bromo-12-fluoro[2.2]paracyclophane (**8**) (418.0 mg, 1.37 mmol), 4,12-bis(benzhydrylideneamino) [2.2]paracyclophane (3.9 mg, 0.0069 mmol), benzhydrylideneamine (372.4 mg, 2.06 mmol), sodium *t*-butoxide (198.0 mg, 2.06 mmol), and Pd(dppf)$Cl_2$ (10.3 mg, 0.014 mmol, where dppf = 1,1′-bis-(dipheny1phosphino) ferrocene) in toluene (2.0 mL) were stirred at 115°C for ~8 h under a slight positive pressure of nitrogen. After completion of the reaction as indicated by TLC, the mixture was cooled to the room temperature; water (5.0 mL) was added and the solution of water and reaction mixture was filtered. The solution was extracted using dichloromethane (5.0 mL × 3), and the solvent was removed using a rotary evaporator. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1), and pure product ($R_p$)-4-benzhydrylideneamino-12-fluoro[2.2]paracyclophane (**9**) was obtained (430 mg, 77.4 %).

To the solution of ($R_p$)-4-benzhydrylideneamino-12-fluoro [2.2]paracyclophane (**9**) (430 mg, 1.06 mmol) in THF (4.0 mL) was added concentrated HCl (12.0 M, 0.25 mL, 3.0 mmol), and the mixture was stirred at room temperature for 4 h. After the yellow colour of the mixture disappeared, the white precipitate was collected by filtration. The precipitate was washed with ether (3 × 5.0 mL), and dried under vacuum. The remaining solid was dissolved in ethanol (4.0 mL), and saturated NaOH was added dropwise until the stirred mixture was basic (pH 9). The solvent was removed, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1). The target compound **10** was obtained as a white solid (243.2 mg, 95.1 %), mp 178–180°C. $[\alpha]_D^{20}$ −167.7° (*c* 0.13 in $CH_2Cl_2$). $\delta_H$ ($CDCl_3$, 300 MHz) 6.78 (1H, dd, *J* 11.8, 1.6), 6.54 (1H, t, *J* 8.1), 6.31 (1H, s), 6.28 (1H, s), 6.04 (1H, dd, *J* 7.7, 1.7), 5.88 (1H, dd, *J* 3.1, 1.8), 3.53 (2H, s), 3.37–3.25 (1H, m), 3.14–2.97 (3H, m), 2.97–2.79 (2H, m), 2.69–2.54 (2H, m). $\delta_C$ ($CDCl_3$,75 MHz) 162.21, 158.98, 144.57, 142.36, 142.26, 141.16, 134.99, 134.89, 134.81, 127.75, 127.71, 124.71, 124.47, 123.47, 122.48, 117.73, 115.47, 115.17, 33.26, 32.03, 32.01, 31.46, 29.54. *m*/*z* (HRMS ESI) 242.1339; $[M + H]^+$ requires 242.1345.

### *General Procedures for the Synthesis of Imidazolium Bromide (**5**)*

$R_p$-4-Amino-12-fluoro[2.2]paracyclophane (**10**) (243 mg, 1.0 mmol) and 40 % glyoxal (174.0 mg, 1.2 mmol) in 1.0 mL THF were stirred at room temperature for 5 h, during which time the colour of the reaction mixture turned yellow and a yellow precipitate appeared. After completion of the reaction, as indicated by TLC, the yellow precipitate was collected by filtration and washed with 2.0 mL water. The desired diimine was isolated as a yellow solid (251 mg, 99.5 %).

A solution of AgOTf (0.165 g, 0.65 mmol, where AgOTf = silver triflate) and chloromethyl pivalate (0.08 mL, 0.55 mmol) in THF was stirred in a sealed tube in the dark at room temperature for 10 min until a white precipitate appeared. Then, a solution of the diimine (251 mg, 0.5 mmol) in $CH_2Cl_2$ (2.0 mL) was added to the above suspension. The solution was stirred in a sealed tube in the dark at 40°C for 8 h. After the solution was cooled to room temperature, the solvent was removed under vacuum. The resulting oil was chromatographed on silica gel ($CH_2Cl_2$/ethanol (EtOH) = 50 : 1–10 : 1) to afford the pure product (186.5 mg, 56 %).

The pure product *N*,*N*′-bis[($R_p$)-(−)-12-fluoro-4-[2.2]paracyclophanyl]-imidazolium triflate (186.5 mg, 0.28 mmol) was dissolved in $CH_2Cl_2$ (5.0 mL), saturated KBr aqueous solution (5.0 mL) was added, and the mixture was stirred vigorously. After 12 h, saturated KBr aqueous solution was removed. The product was collected by filtration. Compound **5** was obtained as a white solid (80.3 mg, 48 %), mp > 250°C. $[\alpha]_D^{20}$ −212.3° (*c* 0.15 in $CH_2Cl_2$). $\delta_H$ ($CDCl_3$, 300 MHz) 9.70 (1H, s),

7.99 (2H, s), 7.17 (2H, s), 6.81 (2H, d, *J* 8.0), 6.70 (2H, t, *J* 7.8), 6.62 (4H, dd, *J* 11.7, 8.3), 6.25 (2H, d, *J* 9.8), 3.46 (2H, ddd, *J* 13.6, 10.0, 4.0), 3.40–3.05 (10H, m), 2.95–2.75 (4H, m). $\delta_C$ ($CDCl_3$, 75 MHz) 161.73, 158.50, 143.34, 143.30, 143.26, 141.80, 136.35, 135.96, 134.66, 134.49, 134.41, 133.69, 132.72, 128.93, 125.41, 125.28, 125.18, 123.77, 123.17, 121.51, 117.18, 116.89, 76.94, 76.72, 76.52, 76.09, 34.05, 33.03, 30.97, 28.43. *m*/*z* (HRMS ESI) 517.2452; $[M - Br]^+$ requires 517.2455.

### *General Procedure for the Synthesis of N-Formylethylenediamine (**12**)*[10]

A dry Schlenk tube was charged with *N*,*N*′-bis[4-[2.2]paracyclophanyl]imidazolinium tetrafluoroborate[2a] (**11**) (57 mg, 0.1 mmol), NaBr (51 mg, 0.5 mmol), $Ag_2O$ (14 mg, 0.06 mmol), and $CH_2Cl_2$ (3.0 mL). The mixture was stirred in the absence of light for 48 h at room temperature. The resulting off-white precipitate was filtered and the solvent was removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$); the target compound **12** was obtained as a white solid (32.5 mg, 65 %). $\delta_H$ ($CDCl_3$, 400 MHz) 8.65 (1H, s), 6.78 (1H, dd, *J* 7.7, 1.7), 6.71–6.46 (7H, m), 6.36–6.26 (4H, m), 6.20 (1H, d, *J* 7.6), 6.02 (1H, d, *J* 7.6), 5.12 (1H, s), 4.59 (1H, ddd, *J* 13.5, 7.8, 5.5), 4.07 (1H, s), 3.46 (1H, dt, *J* 13.6, 5.5), 3.19–2.73 (16H, m), 2.59 (1H, dt, *J* 3.9, 8.1).

### *Details of X-Ray Data Collection and Refinement*

The crystallographic data of **1**–**7** were collected on a Bruker Smart APEX CCD area-detector diffractometer with $Mo_{K\alpha}$ radiation ($\lambda$ 0.71073 Å). The crystal data were solved by the direct method and refined by a full-matrix least-squares method on $F^2$ using the *SHELXL-97* crystallographic software package.[17] The *SQUEEZE*/*PLATON* program[18] was used to model some disordered guest water molecules in compound 4.

## Supplementary Material

The experimental materials details, methods and spectral data for products are available on the Journal's website. Crystallographic data (excluding structure factors) for **1**, **2**, **3**,[19] **4**, **5**,[20] **6**, and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1023337, CCDC 753625, CCDC 1015372, CCDC 821397, CCDC 1017723, CCDC 1017741, and CCDC 903887, respectively. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html; fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk.

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[19] Crystal data for compound **3**: $C_{36}H_{31}Br_2F_3N_2O_3S$, $M$ 788.51, colourless block, orthorhombic, space group $P$ 21 21 21, $a$ 10.932(2), $b$ 12.123(2), $c$ 25.594(5) Å, $\beta$ 90°, $V$ 3391.9(11) Å$^3$, $Z$ 4, $D_c$ 1.544 Mg m$^{-3}$, $F_{000}$ 1592, $Mo_{K\alpha}$ radiation, $\mu$ 2.507 mm$^{-1}$, $T$ 296 K. 16581 data measured, of which 7446 unique ($R_{int}$ 0.0954), $\theta_{max}$ 27.50°, $\theta_{min}$ 1.86°. Refinement of 7446 reflections (424 parameters) with $I > 2\sigma(I)$ converged at final $R_1$ 0.0562 ($R_1$ all data 0.2021), $wR_2$ 0.0973 ($wR_2$ all data 0.1224), GoF 1.001. The structure was solved by the direct method and refined by the full-matrix least-squares method on $F^2$ using the *SHELXTL 97* crystallographic software package.

[20] Crystal data for compound **5**: $C_{36}H_{32}BrCl_3F_2N_2$, $M$ 714.08, colourless block, orthorhombic, space group $P$ 2(1) 2(1) 2(1), $a$ 11.703(5), $b$ 11.958(5), $c$ 23.535(10) Å, $\beta = 90°$, $V = 3294(2)$ Å$^3$, $Z$ 28, $D_c$ 1.446 Mg m$^{-3}$, $F_{000}$ 1464, $Mo_{K\alpha}$ radiation, $\mu$ 1.532 mm$^{-1}$, $T$ 273 K. 16468 data measured, of which 5808 unique ($R_{int}$ 0.0489), $\theta_{max}$ 25.02°, $\theta_{min}$ 1.91°. Refinement of 5808 reflections (397 parameters) with $I > 2\sigma(I)$ converged at final $R_1$ 0.0421 ($R_1$ all data 0.0780), $wR_2$ 0.0843 ($wR_2$ all data 0.0962), GoF 0.990. The structure was solved by the direct method and refined by the full-matrix least-squares method on $F^2$ using the *SHELXTL 97* crystallographic software package.