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# Planar chiral imidazolium salts based on [2.2]paracyclophane in the asymmetric rhodium-catalyzed 1,2-addition of arylboronic acids to aldehydes

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ABSTRACT

A series of planar chiral imidazolium salts derived from [2.2]paracyclophane have been synthesized and characterized. By using these imidazolium salts as carbene precursors, the Rh-catalyzed 1,2-addition of arylboronic acids to aldehydes proceeded readily with low catalyst loadings (0.03–0.3 mol %) and gave a variety of chiral diarylmethanols in excellent yields and moderate enantioselectivities.



## 1. Introduction

The asymmetric arylation of aldehydes has recently received considerable attention since chiral diarylmethanols are key structural elements in an array of pharmacologically active compounds and are, for that reason, important synthetic targets.[1] The asymmetric Rh-catalyzed addition of organoboronic acids to aldehydes is a general method for the synthesis of optically active diarylmethanols which have attracted much attention since Miyaura et al. first reported in 1998.[2] Due to the advantageous features of organoboronic acids, such as low toxicity and easy manipulation, considerable efforts have been made in this type of reaction.[3]

Complexes with *N*-heterocyclic carbenes (NHCs)[4] have, during recent years, gathered considerable interest from the organic chemistry community and have been widely used in homogeneous metal catalysis.[5] Impressive progress has been made with regard to their synthesis and application.[5,6] The Rh-NHC-catalyzed addition of arylboronic acid derivatives to aldehydes deserves particular mention because these methods present high efficiency with a reasonable tolerance towards polar substituents in the substrates.[7] In 2005, Bolm reported the synthesis of a variety of chiral imidazolium salts and their application in the asymmetric arylation of aldehydes.[8] The protocol they reported can afford optically active diarylmethanols in good yield. In spite of these efforts, examples of the catalyzed addition with chiral *N*-heterocyclic carbene ligands remain scarce. Thus, it is still desirable to develop or find more active chiral catalysts and efficient catalytic systems for 1,2-addition of organoboronic acids to aldehydes.

The element of planar chirality plays an increasingly important role in modern organometallic chemistry.[9] The field of [2.2]paracyclophane chemistry has expanded considerably since these compounds first attracted the interest of chemists in the middle of the last century.[10] Recently, there has been notable progress, especially with regard to the synthesis of new derivatives and their applications in asymmetric catalysis.[11,12] A series of planar chiral imidazoliniums derived from [2.2]paracyclophane have been prepared by this group and their applications as rhodium or ruthenium complexes in highly enantioselective transformations have also been demonstrated.[12] The above-mentioned findings and our interests in NHCs and C–C forming reactions triggered our efforts to develop new planar chiral imidazolium salts as NHC precursors for application in homogeneous catalysis. We herein report the synthesis of a new family of planar chiral imidazolium salts based on [2.2]paracyclophane and their application in the asymmetric rhodium-catalyzed 1,2-addition of arylboronic acids to aldehydes.

## 2. Results and discussion

Our straightforward synthetic pathway to the planar chiral imidazolium salts is shown in Schemes 1 and 2. The synthesis of new planar chiral imidazolium salts began with the known compounds ($S_p$)-4-amino-12-bromo[2.2]paracyclophane **1a** and ($4R_p$,$13S_p$)-4-amino-13-bromo[2.2]paracyclophane **2a** (Schemes 1 and 2).[12] One of the important characteristics of **1a** and **2a** is the fact that they are easily tunable in their steric profile.

Suzuki–Miyaura coupling with arylboronic acids under Pd-DPPF catalysis gave the sterically hindered amino [2.2]paracyclophanes in good to excellent yields (85–99%).[12] Treatment of the substituted amino [2.2]paracyclophanes with aqueous glyoxal in THF at room temperature gave the corresponding diimines in essentially quantitative yield. In analogy to procedures for the transformation of glyoxal-derived diimines into imidazolium salts,[13] we treated diimines with chloromethyl ethyl ether in THF at 40 °C. However, all imidazolium chlorides could not be purified by chromatography and recrystallization except for **3a** (54% yield). Following another literature method,[14] the treatment of diimines with paraformaldehyde and hydrogen chloride in toluene gave very similar results. We were pleased to find that a reagent formed from

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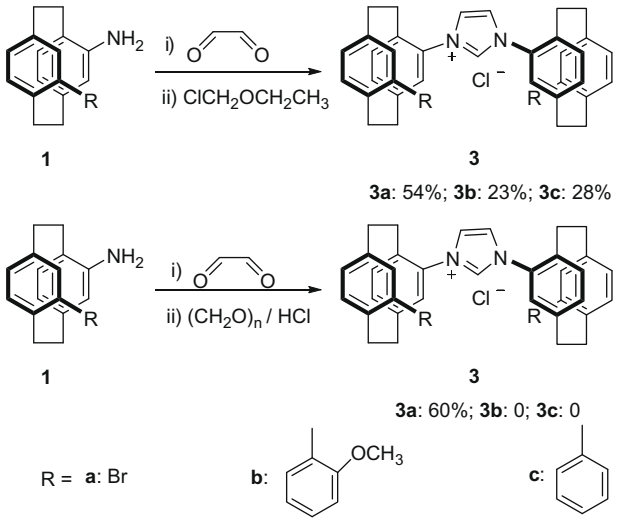
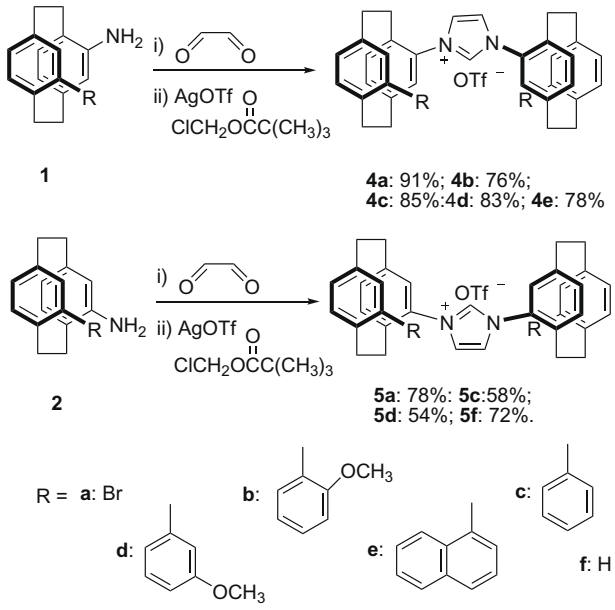



**Scheme 1.** Synthesis of the imidazolium chlorides.




**Scheme 2.** Synthesis of the imidazolium triflates.

equal amounts of silver triflate and chloromethyl pivalate[15] resulted in the formation of the desired imidazolium triflates in moderate to good yields (54–91%). The imidazolium salts **3a**, **4a**–**e** and **5a**–**f** were purified, and fully characterized by NMR, mass spectrometry, and, in the case of **4a**, single-crystal X-ray diffraction analysis (Fig. 1).

The imidazolium salts **3a**, **4a**–**e** and **5a**–**f** thus obtained were then used as precursors for rhodium–NHC complexes, which were applied in the catalytic addition of arylboronic acids to aromatic aldehydes.

We began by optimizing the reaction conditions using **4a** as ligand, a number of parameters were varied using phenylboronic acid and 1-naphthaldehyde as model substrates.

The reaction conditions were evaluated with a particular emphasis on solvent effects. The 1,2-addition of phenylboronic acid to 1-naphthaldehyde with 3.0 mol % of catalyst generated in situ from imidazolium salt **4a** and $[Rh(OAc)_2]_2$ in the presence

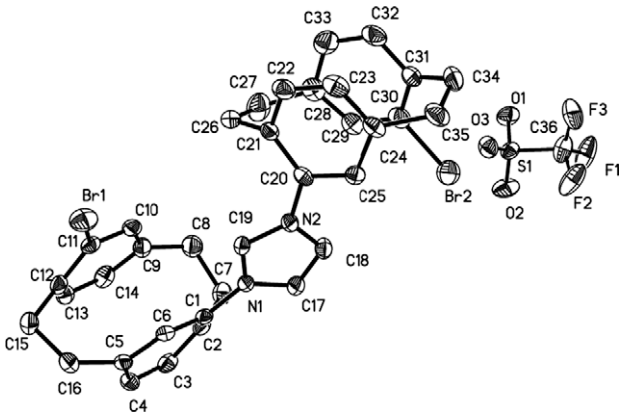
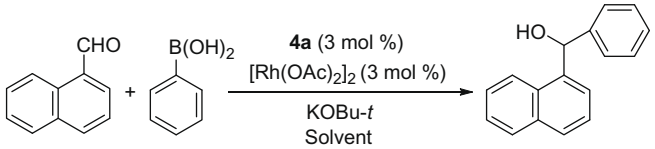



**Figure 1.** ORTEP diagram of the molecular structure of **4a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

of potassium *tert*-butoxide/phenylboronic acid (1:2) was examined in different solvents at 80 °C for 2 h. As can be seen from Table 1, no products were obtained in dioxane or DME if no water was involved. The rate and enantioselectivity of the reaction was influenced by the amount of water in the DME/water system (Table 1, entries 2–5). In DME/water (5:1), the ligand showed good activity (64% yield) and moderate enantioselectivity (36% ee). However, the complexes were unstable in this solvent system and this cause led to relatively low yield. Our efforts indicated that MeOH/DME (5:1) was the most suitable, affording the desired product in 99% yield and 41% ee (Table 1, entry 7). Therefore, MeOH/DME (5:1) was selected as the reaction solvent in the following reactions. Different rhodium sources were also investigated with ligand **4a** (Table 1, entries 9–11); $[Rh(OAc)_2]_2$ emerged as the best choice of catalyst precursors.

We chose MeOH/DME (5:1) as the solvent system and other ligands were screened in the arylation of aldehydes (Table 2). Diarylmethanol **8ab** was obtained in high yield (95–99%) with each of the imidazolium salts **3a**, **4a**–**e** and **5a**–**f**. The ligands **4a** and **5a**

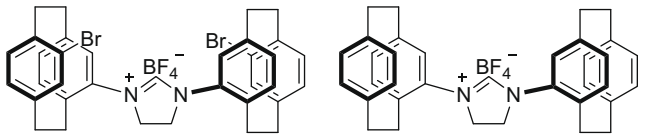
**Table 1**
Optimization of the reaction conditions[a]




| Entry | Solvent | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | Dioxane | 0 | — |
| 2 | DME | 0 | — |
| 3 | DME/$H_2O$ (10:1) | 58 | 36 (*R*) |
| 4 | DME/$H_2O$ (5:1) | 64 | 36 (*R*) |
| 5 | DME/$H_2O$ (3:1) | 70 | 0 |
| 6 | MeOH | 99 | 30 (*R*) |
| 7 | MeOH/DME (5:1) | 99 | 41 (*R*) |
| 8 | Ethanol/DME (5:1) | 99 | 37 (*R*) |
| 9[d] | MeOH/DME (5:1) | 90 | 34 (*R*) |
| 10[e] | MeOH/DME (5:1) | 89 | 11 (*R*) |
| 11[f] | MeOH/DME (5:1) | 83 | 30 (*R*) |

[a] Reaction conditions: $[Rh(OAc)_2]_2$ (3 mol %), **4a** (3 mol %), KOBu-*t* (1 equiv), arylboronic acids (2 equiv), $N_2$, 80 °C, 2 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Column) analysis.
[d] $[Rh(nbd)Cl]_2$ was used as the rhodium source.
[e] $[Rh(cod)Cl]_2$ was used as the rhodium source.
[f] $RhCl_3$ was used as the rhodium source.

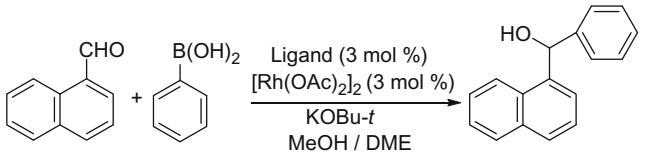
gave the product with 41% and 31% ee, respectively (Table 2, entries 2 and 7). It is well-known that an increase in the bulkiness of chiral groups may lead to increased enantiocontrol in asymmetric reactions. In the hope of increasing the enantioselectivity to appreciable levels, steric bulk was introduced to the ligands **4a** and **5a**. These sterically hindered ligands **4b**–**e**, **5c**, and **5d** gave inferior enantioselectivities in contrast to ligands **4a** and **5a**. Imidazolium chloride **3a** gave almost the same activity with the corresponding imidazolium triflate **4a** and a slightly inferior enantioselectivity. Better results were obtained with imidazolium salts **4a** and **5f** as ligands, however, the analogous imidazolinium tetrafluoroborate **L1** and **L2** exhibited very poor catalytic abilities (Scheme 3, Table 2, entries 11 and 12).




L1 L2

**Scheme 3.** Imidazolinium salts **L1** and **L2**.

**Table 2**
Ligand evaluation study[a]




6a 7b 8ab

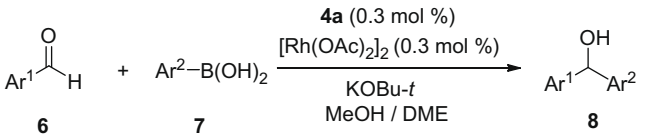
| Entry | Ligand | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|
| 1 | **3a** | 99 | 37 (*R*) |
| 2 | **4a** | 99 | 41 (*R*) |
| 3 | **4b** | 95 | 10 (*R*) |
| 4 | **4c** | 95 | 3 (*R*) |
| 5 | **4d** | 99 | 14 (*R*) |
| 6 | **4e** | 97 | 30 (*R*) |
| 7 | **5a** | 99 | 31 (*S*) |
| 8 | **5c** | 95 | 3 (*S*) |
| 9 | **5d** | 99 | 7 (*S*) |
| 10 | **5f** | 99 | 40 (*S*) |
| 11 | **L1** | 9 | 13 (*S*) |
| 12 | **L2** | 14 | 5 (*S*) |

[a] Reaction conditions: $[Rh(OAc)_2]_2$ (3 mol %), ligand (3 mol %), KOBu-*t* (1 equiv), arylboronic acids (2 equiv), $N_2$, MeOH/DME (5:1), reflux, 2 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Columns) analysis.

In view of the high activity of these ligands, the low catalyst loading conditions were carried out with **4a** as the carbene precursor. The 1,2-addition of phenylboronic acid to 1-naphthaldehyde with 0.3 and 0.1 mol % of the catalyst, under our optimized reaction conditions, led to product **8ab** in 98% yield/41% ee and in 94% yield/32% ee, respectively. In contrast to the 3 mol % catalyst loading, the reaction rate was slower but the enantioselectivity did not diminish with 0.3 mol % catalyst. Even with 0.03 mol % of the catalyst, the reaction proceeded readily and gave the desired product in 91% yield and 21% ee after 12 h.

As shown in Table 3, the optimized protocol was tested in the asymmetric arylation of aldehydes with different steric and electronic properties. In most cases, the reaction proceeded with notable efficiency (up to 99% isolated yield) and moderate

**Table 3**
Scope of the methodology[a]




6 7 8

| Entry | $Ar^1$ | $Ar^2$ | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|
| 1 | 1-Naphthyl **6a** | Phenyl **7b** | 94 **8ab** | 41 (*R*) |
| 2 | 1-Naphthyl **6a** | 2-$MeOC_6H_4$ **7c** | 97 **8ac** | 52 (−) |
| 3 | 1-Naphthyl **6a** | 3-$MeOC_6H_4$ **7d** | 97 **8ad** | 34 (+) |
| 4 | Phenyl **6b** | 1-Naphthy **7a** | 94 **8ba** | 41 (*S*) |
| 5 | Phenyl **6b** | 2-$MeOC_6H_4$ **7c** | 97 **8bc** | 46 (*S*) |
| 6 | Phenyl **6b** | 3-$MeOC_6H_4$ **7d** | 97 **8bd** | 28 (*S*) |
| 7 | 2-$MeOC_6H_4$ **6c** | 1-Naphthy **7a** | 96 **8ca** | 52 (+) |
| 8 | 2-$MeOC_6H_4$ **6c** | Phenyl **7b** | 95 **8cb** | 46 (*R*) |
| 9 | 2-$MeOC_6H_4$ **6c** | 3-$MeOC_6H_4$ **7d** | 99 **8cd** | 40 (+) |
| 10 | 4-$ClC_6H_4$ **6d** | 1-Naphthyl **7a** | 92 **8da** | 45 (*R*) |
| 11 | 4-$ClC_6H_4$ **6d** | 2-$MeOC_6H_4$ **7c** | 95 **8db** | 42 (−) |
| 12 | 4-$ClC_6H_4$ **6d** | 3-$MeOC_6H_4$ **7d** | 93 **8dd** | 38 (*R*) |

[a] Reaction conditions: $[Rh(OAc)_2]_2$ (0.3 mol %), **4a** (0.3 mol %), KOBu-*t* (1 equiv), arylboronic acids (2 equiv), $N_2$, MeOH/DME (5:1), reflux, 6 h.
[b] Isolated yields.
[c] Determined by chiral HPLC (CHIRALPAK IA Column) analysis.

enantioselectivity (up to 52%) with only 0.3 mol % catalyst. The substitution pattern of the substrates had an important effect on the enantioselectivity of the products. The aromatic aldehyde or arylboronic acid bearing an *ortho*-substituent afforded the chiral diarylmethanols with higher enantiomeric excess. An interesting feature of this methodology is that both enantiomers of a given diarylmethanol can be easily prepared with the same chiral ligand, just by the appropriate choice of the reaction partners: arylboronic acid or aldehyde.

## 3. Conclusion

In conclusion, a series of planar chiral imidazolium salts based on [2.2]paracyclophane have been prepared. Their applicability in rhodium-catalyzed asymmetric additions of arylboronic acids to aromatic aldehydes has been demonstrated. Even with 0.03 mol % of the catalyst, the reactions could be carried out quickly and gave the chiral diarylmethanols in excellent yields.

## 4. Experimental

### 4.1. General remarks

Commercially available reagents were used without further purification unless otherwise noted. Solvents were reagent grade and purified by standard techniques. ($S_p$)-4-Amino-12-bromo[2.2] paracyclophane **1a**, $S_p$-4-amino-12-(2-methoxyphenyl)[2.2]paracyclophane **1b**, $S_p$-4-amino-12-phenyl[2.2] paracyclophane **1c**, ($4R_p$,$13S_p$)-4-amino-13-bromo[2.2]paracyclophane **2a**, ($4R_p$,$13S_p$)-4-amino-13-phenyl[2.2] paracyclophane **2c**, ($4R_p$,$13S_p$)-4-amino-13-(3-methoxyphenyl)[2.2]paracyclophane **2d**, ($R_p$)-4-amino [2.2]paracyclophane **2f,** *N*,*N*′-Bis[$R_p$-(−)-12-bromo-4-[2.2]paracyclophanyl] imidazolinium Tetrafluoroborate **L1** and *N*,*N*′-bis [($R_p$-(−)-4-[2.2]paracyclophanyl] imidazolinium tetrafluoroborate **L2** were prepared according to published procedures. Melting points were recorded on a melting point apparatus and are uncorrected. $^1H$ and $^{13}C$ spectra were recorded on 400 and 300 MHz spectrometers. Mass spectra were recorded on an Agilent 100 ABI-API14000 spectrometer. Optical rotations were taken on a polarimeter with a wavelength of 589 nm. The concentration '*c*' has units of g/100 mL (or 10 mg/mL) unless otherwise noted.

### 4.2. General procedures for the synthesis of ($S_p$)-4-amino-12-aryl[2.2]paracyclophane 1

($S_p$)-4-Amino-12-bromo [2.2]paracyclophane **1a** (501.3 mg, 1.66 mmol), arylboronic acid (2.49 mmol), KF (289.7 mg, 4.98 mmol) and Pd-DPPF (13.6 mg, $1.66 \times 10^{-2}$ mmol) in 1,4-dioxane (5.0 mL) were stirred at 80 °C for about 4 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 filtered. The solution was extracted by dichloromethane (10.0 mL × 3), and the solvent was removed on a rotary evaporator. The residue was purified by chromatography on silica gel (hexanes/ethyl acetate = 20:1), and pure product was isolated.

($S_p$)-4-Amino-12-(3-methoxyphenyl) [2.2]paracyclophane **1d** was obtained as a crystalline white solid (99% yield). Mp 100–101 °C; $R_f$ 0.54 (hexanes/ethyl acetate = 5:1); $[\alpha]_D^{20} = -62$ (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$, rt): $\delta$ 7.30–7.27 (m, 1H), 7.20 (d, *J* = 1.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.56 Hz, 2H), 6.23 (s, 1H), 5.67 (s, 1H), 3.86 (s, 3H), 3.64–3.45 (m, 2H),3.13–3.11 (m, 3H), 2.89–2.74 (m, 3H), 2.45–2.38 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 159.1, 142.5, 140.9, 140.2, 138.5, 135.8, 134.5, 134.4, 131.8, 128.9, 127.3, 121.5, 115.0, 111.2, 54.8, 33.7, 33.5, 31.9, 31.7. HRMS (ESI): calcd for $C_{23}H_{24}NO$ $(M+H)^+$ 330.1858, found 330.1868.

($S_p$)-4-Amino-12-(1-naphthyl) [2.2]paracyclophane **1e** was obtained as a crystalline white solid (98% yield). Mp 185–187 °C, $R_f$ 0.58 (hexanes/ethyl acetate = 5:1); $[\alpha]_D^{20} = -333.5$ (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$, rt): $\delta$ 7.92 (d, *J* = 8.5 Hz, 1H), 7.85 (t, *J* = 7.4 Hz, 2H), 7.77–7.75 (m, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.36 (d, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 1.6, Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.59–6.29 (m, 2H), 6.28 (s, 1H), 5.86 (s, 1H), 3.21–3.16 (m, 3H), 2.82–2.77 (m, 2H), 2.69–2.65 (m, 2H), 2.42–2.32 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 141.6, 139.9, 139.1, 138.9, 137.2, 134.9, 133.6, 133.6, 133.0, 131.8, 129.3, 128.1, 127.4, 126.6, 126.0, 125.9, 125.6, 125.6, 34.3, 34.0, 32.58, 32.2. HRMS (ESI): calcd for $C_{26}H_{24}N$ $(M+H)^+$ 350.1909, found 350.1907.

### 4.3. General procedures for the synthesis of imidazolium chloride 2

#### 4.3.1. Method A

Compound **1a** (604.4 mg, 2.0 mmol) and 40% glyoxal (348.0 mg, 2.4 mmol) in 2.0 mL THF were stirred at room temperature for 5 h, during which time the color 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 yellow solid (594.8 mg, 95% yield).

A 5 mL single-necked flask was charged with 90.0 mg (0.91 mmol) of chloromethylethyl ether (95%) in 0.30 ml THF. To this colorless solution was added a solution of 575 mg (0.91 mmol), of the above diimine in 2.0 ml THF and two drops of water. The flask was sealed under nitrogen with a septum and the mixture stirred at 40 °C. A solid began to appear after 1 h of stirring. Stirring at 40 °C was continued for 16 h and then the mixture was allowed to cool to 23 °C and the precipitated solids were collected by filtration. The off-white precipitate was collected by filtration and washed with THF. Then the resulting solid was chromatographed on silica gel ($CH_2Cl_2$/MeOH 50:1–10:1) and pure product was isolated (387.0 mg, 54% yield).

#### 4.3.2. Method B

Compound **1a** (604.4 mg, 2.0 mmol) and 40% glyoxal (348.0 mg, 2.4 mmol) in 2.0 mL THF was stirred at room temperature for 5 h, during which time the color 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 (594.8 mg, 95% yield).

To a solution of diimine (413 mg, 0.66 mmol) in toluene (5.0 ml) was added 20.0 mg (0.66 mmol) of paraformaldehyde in solid form. The reaction mixture was heated to 100 °C until most of paraformaldehyde was dissolved. It was then cooled to 40 °C and 0.17 ml of HCl (0.66 mmol, 4 M in dioxane) was syringed in. The reaction mixture was heated to 70 °C for 5 h during which time the color of the reaction mixture turned brown and a white precipitate appeared. It was then allowed to stir at rt for 36 h. The off-white precipitate was collected by filtration and washed with THF. Then the resulting solid was chromatographed on silica gel ($CH_2Cl_2$/MeOH 50:1–10:1) and the pure product was isolated (312.0 mg, 60% yield).

*N*,*N*′-Bis[($S_p$)-(+)-12-bromo-4-[2.2]paracyclophanyl]imidazolium chloride **3a** was obtained as a solid; Mp >260 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 15:1); $[\alpha]_D^{20} = +26.7$ (c 0.50, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 11.36 (s, 1H), 8.38 (s, 2H), 7.20 (s, 2H), 6.88 (d, *J* = 3.9 Hz, 2H), 6.71 (s, 6H), 6.60 (s, 2H), 3.58–3.55 (m, 4H), 3.22–3.19 (m, 6H), 2.99–2.91 (m, 4H), 2.64–2.57 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 141.4, 141.0, 138.3, 137.5, 135.3, 135.0, 132.8, 132.8, 131.8, 125.6, 122.2, 122.1, 35.0, 33.4, 32.4, 31.8. HRMS (ESI): calcd for $C_{35}H_{31}Br_2N_2$ $(M-Cl)^+$ 639.0834, found 639.0851.

### 4.4. General procedures for the synthesis of imidazolium triflates 4 and 5

Compound **1** or **2** (1.0 mmol) and 40% glyoxal (174.0 mg, 1.2 mmol) in 1.0 mL THF was stirred at room temperature for 5 h, during which time the color 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 yellow solid.

To a suspension of AgOTf (0.33 g, 1.3 mmol) in $CH_2Cl_2$ (2.0 mL) was added chloromethyl pivalate (0.16 ml, 1.1 mmol) and the resulting suspension was stirred for 45 min. After filtration the filtrate was added to the above diimine (1.0 mmol) and 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 MeOH (1.0 mL) was added, the solvent was removed in vacuo and the resulting oil was chromatographed on silica gel ($CH_2Cl_2$/MeOH 50:1–10:1) and pure product was isolated.

#### 4.4.1. *N*,*N*′-Bis[($S_p$)-(+)-12-bromo-4-[2.2]paracyclophanyl]imidazolium trifluoromethanesulfonate 4a

Compound **4a** was obtained as a white solid (91% yield). Mp >260 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +18$ (*c* 1.3, $CHCl_3$); $^1$H NMR (300 MHz, DMSO, rt): $\delta$ 9.50 (s, 1H), 8.31 (d, *J* = 1.5 Hz, 2H), 7.40 (d, *J* = 1.5 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.89–6.83 (m, 6H), 6.78 (s, 2H), 3.42–2.96 (m, 14H), 2.77–2.50 (m, 2H); $^{13}$C NMR (75 MHz, DMSO, rt): $\delta$ 147.1, 146.6, 143.7, 142.5, 140.9, 140.7, 140.0, 138.5, 137.9, 137.7, 137.6, 130.9, 128.5, 128.1, 39.9, 38.1, 36.7, 36.5, 35.8. HRMS (ESI): calcd for $C_{35}H_{31}Br_2N_2$ $(M-OTf)^+$ 639.0834, found 639.0939.

#### 4.4.2. *N*,*N*′-Bis[($S_p$)-(+)-12-(2-methoxyphenyl)-4-[2.2]paracyclophanyl]imidazolium trifluoromethanesulfonate 4b

Compound **4b** was obtained as a slight yellow solid (76% yield). Mp 168–170 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +83.2$ (*c*

0.50, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.73 (s, 1H), 7.92 (d, $J$ = 1.4 Hz, 2H), 7.28–7.26 (m, 2H), 7.08–7.07 (m, 4H), 6.98–6.95 (m, 8H), 6.73 (d, $J$ = 7.5 Hz, 2H), 6.62–6.57 (m, 4H), 3.69 (s, 6H), 3.50–3.29 (m, 4H), 3.23–3.15 (m, 4H), 3.10–2.88 (m, 6H), 2.65–2.49 (m, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 156.3, 143.2, 138.8, 137.4, 137.2, 135.8, 135.8, 135.1, 134.1, 133.0, 132.7, 132.5, 130.4, 129.4, 129.2, 128.6, 126.3, 123.7, 120.9, 111.7, 65.8, 55.4, 34.2, 34.0, 33.6, 32.6. HRMS (ESI): calcd for $C_{49}H_{45}N_2O_2$ $(M-OTf)^+$ 693.3481, found 693.3607.

#### 4.4.3. *N,N′*-Bis[($S_p$)-(+)-12-phenyl-4-[2.2]paracyclophanyl]-imidazolium trifluoromethanesulfonate 4c

Compound **4c** was obtained as a white solid (85% yield). Mp 156–158 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +64.7$ ($c$ 0.50, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.92 (s, 1H), 7.45 (t, $J$ = 7.5 Hz, 5H), 7.35–7.26 (m, 7H), 6.90–6.65 (m, 10H), 6.46 (s, 2H), 3.56–3.48 (m, 2H), 3.25–3.06 (m, 12H), 2.82–2.75 (m, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 142.6, 140.1, 139.8, 139.7, 139.1, 137.4, 137.1, 136.1, 135.6, 134.1, 132.9, 132.9, 132.6, 130.0, 129.1, 128.3, 127.4, 124.54, 124.5, 123.3, 122.8, 34.3, 34.2, 33.4, 31.8. HRMS (ESI): calcd for $C_{47}H_{41}N_2$ $(M-OTf)^+$ 633.3270, found 633.3241.

#### 4.4.4. *N,N′*-Bis[($S_p$)-(+)-12-(3-methoxyphenyl)-4-[2.2]paracyclophanyl]imidazolium Trifluoromethanesulfonate 4d

Compound **4d** was obtained as a white solid (83% yield). Mp 170–172 °C, $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +78.5$ ($c$ 0.50, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.96 (s, 1H), 7.50 (d, $J$ = 1.2 Hz, 2H), 7.39–7.34 (t, $J$ = 7.8 Hz, 2H), 6.97 (d, $J$ = 7.5 Hz, 2H), 6.87–6.83 (m, 6H), 6.77–6.45 (m, 8H), 6.47 (s, 2H), 3.77 (s, 6H), 3.59–3.51 (m, 2H), 3.30–3.02 (m, 14H), 2.87–2.80 (m, 2H): $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 159.9, 142.5, 141.5, 139.6, 139.3, 137.4, 137.1, 136.1, 135.7, 133.8, 133.0, 132.8, 130.0, 129.8, 124.4, 123.6, 120.4, 114.9, 112.3, 55.2, 34.3, 34.2, 33.5, 31.8. HRMS (ESI): calcd for $C_{49}H_{45}N_2O_2$ $(M-OTf)^+$ 693.3481, found 693.3453.

#### 4.4.5. *N,N′*-Bis[($S_p$)-(+)-12-(1-Naphthyl)-4-[2.2]paracyclophanyl]imidazolium trifluoromethanesulfonate 4e

Compound **4e** was obtained as a white solid (78% yield). Mp 192–194 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +121.3$ ($c$ 0.50, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.33 (s, 1H), 7.84–7.80 (m, 4H), 7.66–7.60 (m, 3H), 7.43–7.37 (m, 3H), 7.25–7.22 (m, 2H), 7.20–7.14 (m, 7H), 6.93 (d, $J$ = 7.8 Hz, 2H), 6.86–6.80 (m, 4H), 6.68 (d, $J$ = 6.3 Hz, 2H), 6.43 (d, $J$ = 1.5 Hz, 2H), 3.23–2.94 (m, 12H), 2.78–2.48 (m, 2H), 2.46–2.41 (m, 12H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 143.1, 139.0, 137.9, 137.4, 136.2, 136.0, 135.4, 134.3, 134.1, 133.2, 132.8, 132.5, 132.3, 130.3, 128.2, 128.1, 125.9, 125.8, 125.4, 124.0, 123.4, 34.4, 34.0, 33.3, 31.9. HRMS (ESI): calcd for $C_{55}H_{45}N_2$ $(M-OTf)^+$ 733.3583, found 733.3564.

#### 4.4.6. *N,N′*-Bis[($4R_p$,$13S_p$)-13-bromo-4-[2.2]paracyclophanyl]-imidazolium trifluoromethanesulfonate 5a

Compound **5a** was obtained as a white solid (78% yield). Mp >260 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +151.0$ ($c$ 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 10.08–10.01 (s, 1H), 7.64 (s, 2H), 7.10 (s, 2H), 6.99 (s, 2H), 6.70 (s, 6H), 6.47 (d, $J$ = 7.8 Hz, 2H), 3.69–3.59 (m, 2H), 3.47–3.24 (m, 8H), 3.13–3.05 (m, 2H), 2.94–2.86 (m, 4H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 142.6, 142.4, 137.7, 136.6, 135.9, 135.8, 135.1, 133.8, 135.1, 133.8, 131.3, 130.5, 125.6, 123.8, 123.1, 37.10, 34.5, 34.1, 29.0. HRMS (ESI): calcd for $C_{35}H_{31}Br_2N_2$ $(M-OTf)^+$ 639.0834, found 639.0908.

#### 4.4.7. *N,N′*-Bis[($4R_p$,$13S_p$)-13-phenyl-4-[2.2]paracyclophanyl]-imidazolium Trifluoromethanesulfonate 5c

Compound **5c** was obtained as a white solid (58% yield). Mp 178–180 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +172.8$ ($c$ 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.93 (s, 1H), 7.37 (s, 2H), 7.31(d, $J$ = 7.5 Hz, 4H), 7.01–6.85 (m, 8H), 6.81–6.69 (m, 8H), 6.67 (d, $J$ = 6.3 Hz, 2H), 3.50–3.36 (m, 6H), 3.29–2.99 (m, 8H), 2.83–2.74 (m, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 144.1, 140.7, 140.2, 138.6, 137.5, 136.0, 135.2, 134.8, 133.6, 132.7, 132.4, 131.0, 129.7, 128.7, 128.3, 127.1, 125.4, 122.2, 34.7, 34.6, 34.4, 32.8. HRMS (ESI): calcd for $C_{47}H_{41}N_2$ $(M-OTf)^+$ 633.3270, found 633.3241.

#### 4.4.8. *N,N′*-Bis[($4R_p$,$13S_p$)-13-(3-methoxyphenyl)-4-[2.2]-paracyclophanyl]imidazolium trifluoromethanesulfonate 5d

Compound **5d** was obtained as a slight yellow solid (54% yield). Mp 196–198 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = +210.3$ ($c$ 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.69 (s, 1H), 7.36 (s, 2H), 7.14 (d, $J$ = 7.8 Hz, 4H), 6.99 (s, 2H), 6.92–6.80 (m, 6H), 6.70 (d, $J$ = 7.5 Hz, 2H), 6.65–6.6.56 (m, 4H), 6.50 (d, $J$ = 8.1 Hz, 2H), 3.59 (s, 6H), 3.33–3.22 (m, 8H), 3.14–3.04 (m, 2H), 2.97–2.72 (m, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$ 155.6, 144.2, 139.3, 137.5, 136.6, 136.3, 134.7, 134.3, 132.8, 132.4, 131.2, 130.1, 128.8, 127.6, 127.0, 123.1, 122.2, 121.0, 111.8, 55.6, 35.0, 34.6, 34.1, 33.6. HRMS (ESI): calcd for $C_{49}H_{45}N_2O_2$ $(M-OTf)^+$ 693.3481, found 693.3452.

#### 4.4.9. *N,N′*-Bis[($R_p$)-(−)-4-[2.2]paracyclophanyl]imidazolium trifluoromethanesulfonate 5f

Compound **5f** was obtained as a white solid (72% yield). Mp138–141 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = -26.4$ ($c$ 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, rt): $\delta$ 9.30 (s, 1H), 7.93 (s, 2H), 6.78 (d, $J$ = 7.5 Hz, 2H), 6.68–6.51 (m, 13H), 3.51–2.66 (m, 16H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rt): $\delta$143.5, 140.3, 138.3, 137.4, 135.6, 134.7, 133.5, 133.3, 133.2, 132.6, 132.0, 128.4, 126.9, 123.7, 65.8, 34.9, 34.4, 32.5, 15.2. HRMS (ESI): calcd for $C_{35}H_{33}N_2$ $(M-OTf)^+$ 481.2644, found 481.2660.

#### 4.4.10. *N,N′*-Bis[($R_p$)-(−)-12-bromo-4-[2.2]paracyclophanyl]imidazolinium tetrafluoroborate L1

Compound **L1** was obtained as a white solid (80% yield). Mp >260 °C; $R_f$ 0.4 ($CH_2Cl_2$/ethanol = 20:1); $[\alpha]_D^{20} = -52.0$ ($c$ 0.12, $CHCl_3$); $^1H$ NMR (300 MHz, DMSO, rt): $\delta$ 8.93 (s, 1H), 7.08 (s, 2H), 6.89 (s, 2H), 6.84–6.79 (m, 6H), 5.06–5.04 (m, 2H), 4.56 (m,2H), 3.37–2.99 (m, 16H); $^{13}C$ NMR (75 MHz, DMSO, rt): $\delta$156.1, 141.9, 140.7, 138.2, 137.2, 135.4, 134.7, 133.6, 133.5, 132.1, 131.3, 125.6, 120.3, 49.5, 34.7, 32.9, 32.3, 31.7. HRMS (ESI): calcd for $C_{35}H_{33}Br_2N_2$ $(M-BF_4)^+$ 641.0990, found 641.0982.

### 4.5. General procedure for the solvent effect over the arylation of aldehyde (Table 1)

At first, $Rh_2(OAc)_4$ (3.3 mg, $7.5 \times 10^{-3}$ mmol, 3 mol %) was weighed into a flamed dried tube equipped with a condenser and under an argon atmosphere. The solvent (0.50 mL) was added and the suspension was stirred at room temperature for 5 min. Then, NHC ligand **4a** (5.9 mg, $7.5 \times 10^{-3}$ mmol, 3 mol %) phenylboronic acid (61.0 mg, 0.50 mmol), KOBu-*t* (28.0 mg, 0.25 mmol), and 1-naphthaldehyde (34.0 mg, 0.25 mmol) were added successively. The resulting mixture was stirred at 80 °C for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which crystallized upon standing at low temperature (fridge).

### 4.6. General procedure for the ligand evaluation (Table 2)

At first, $Rh_2(OAc)_4$ (3.3 mg, $7.5 \times 10^{-3}$ mmol, 3 mol %) was weighed into a flamed dried tube equipped with a condenser and under an argon atmosphere. Next, MeOH/DME (5:1) (0.50 mL)

was added and the suspension was stirred at room temperature for 5 min. Then, NHC ligand ($7.5 \times 10^{-3}$ mmol, 3 mol %) phenylboronic acid (61.0 mg, 0.50 mmol), KOBu-*t* (28.0 mg, 0.25 mmol), and 1-naphthaldehyde (34.0 mg, 0.25 mmol) were added successively. The resulting mixture was stirred at reflux for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which crystallized upon standing at low temperature (fridge).

### 4.7. General procedure for the evaluation of the in situ methodology (Table 3)

At first, $Rh_2(OAc)_4$ (1.7 mg, $2.5 \times 10^{-3}$ mmol, 0.3 mol %) was weighted into a flamed dried tube equipped with a condenser and under argon atmosphere. MeOH/DME (5:1) (0.5 mL) was added and the suspension was stirred at room temperature for 5 min. Then, NHC ligand **4a** (3.0 mg, $2.5 \times 10^{-3}$ mmol, 0.3 mol %) arylboronic acid (305.0 mg, 2.5 mmol), KOBu-*t* (140.0 mg, 1.25 mmol), and aryl aldehyde (170.0 mg, 1.25 mmol) were added successively. The resulting mixture was stirred at reflux for 6 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which crystallized upon standing at low temperature (fridge).

#### 4.7.1. (1-Naphthyl)phenylmethanols 8ab and 8ba

(*R*)-(+)-**8ab**: 94% yield; $[\alpha]_D^{20} = +10.5$ (*c* 0.4, $CHCl_3$) with 41% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 18.0 min (minor) and 19.1 min (major).

(*S*)-(−)-**8ba:** 94% yield; $[\alpha]_D^{20} = -10.5$ (*c* 0.4, $CHCl_3$) with 41% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 17.8 min (major) and 19.0 min (minor).

$^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.03 (d, $J$ = 3.3 Hz, 1H), 8.01–7.80 (m, 2H), 7.64 (d, $J$ = 6.9 Hz, 1H), 7.50–7.35 (m, 5H) 7.34–7.24 (m, 3H), 6.53 (s, 1H), 2.35 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 143.1, 138.7, 133.9, 130.7, 128.8, 128.6, 128.5, 127.7, 127.06, 126.1, 125.6, 125.3, 124.6, 123.9, 73.6. HRMS (ESI): calcd for $C_{17}H_{13}$ $(M-OH)^+$ 217.1017, found 217.1022.

#### 4.7.2. (1-Naphthyl) (2-methoxyphenyl)methanols 8ac and 8ca

(−)-**8ac**: 97% yield; $[\alpha]_D^{20} = -28.3$ (*c* 0.4, $CHCl_3$) with 52% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 13.6 min (minor) and 14.5 min (major).

(+)-**8ca**: 96% yield; $[\alpha]_D^{20} = +28.3$ (*c* 0.4, $CHCl_3$) with 52% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 13.7 min (major) and 14.7 min (minor).

$^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.00 (d, $J$ = 7.8 Hz 1H), 7.86–7.78 (m, 2H), 7.65 (d, $J$ = 7.2 Hz, 1H), 7.50–7.38 (m, 3H) 7.28–7.23 (m, 1H), 6.96–6.78 (m, 4H), 3.89 (s, 3H), 3.05 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 156.9, 138.0, 133.7, 131.3, 131.0, 129.0, 128.6, 128.4, 125.9, 125.5, 125.4, 124.3, 124.2, 120.8, 110.5, 101.1, 72.6, 68.4, 55.5. HRMS (ESI): calcd for $C_{18}H_{15}O$ $(M-OH)^+$ 247.1123, found 247.1116.

#### 4.7.3. (1-Naphthyl) (3-Methoxyphenyl)methanol 8ad

(+)-**8ad**: 97% yield; $[\alpha]_D^{20} = +20.5$ (*c* 0.4, $CHCl_3$) with 34% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 24.9 min (minor) and 27.0 min (major). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 8.06–8.03 (m, 1H), 7.86–7.78 (m, 2H), 7.60 (d, $J$ = 7.2 Hz, 1H), 7.48–7.40 (m, 3H), 7.25–7.20 (m, 1H), 6.98–6.98 (m, 1H), 6.80 (d, $J$ = 8.1 Hz, 1H), 6.49 (s, 1H), 3.75 (s, 3H), 2.36 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 159.8, 144.8, 138.7, 133.9, 130.7, 129.5, 128.8, 128.5, 126.2, 125.6, 125.3, 124.7, 123.9, 119.4, 113.0, 112.7, 73.5, 55.2. HRMS (ESI): calcd for $C_{18}H_{15}O$ $(M-OH)^+$ 247.1123, found 247.1118.

#### 4.7.4. (2-Methoxyphenyl)phenylmethanol (8bc and 8cb)

(*S*)-(−)-**8bc**: 97% yield; $[\alpha]_D^{20} = -17.8$ (*c* 0.4, $CHCl_3$) with 46% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 13.7 min (major) and 14.7 min (minor).

(*R*)-(+)-**8cb**: 95% yield; $[\alpha]_D^{20} = +17.8$ (*c* 0.4, $CHCl_3$) with 46% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 13.6 min (minor) and 14.5 min (major). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.39–7.26 (m, 7H), 6.95–6.85 (m, 2H), 6.04 (d, $J$ = 4.5 Hz, 1H), 3.78 (s, 3H), 3.05 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 156.7, 143.3, 132.0, 128.7, 128.1, 127.8, 127.1, 126.6, 120.8, 110.8, 72.1, 55.4. HRMS (ESI): calcd for $C_{14}H_{13}O$ $(M-OH)^+$ 197.0966, found 197.0960.

#### 4.7.5. (3-Methoxyphenyl)phenylmethanol 8bd

(*S*)-(−)-**8bd**: 97% yield; $[\alpha]_D^{20} = -7.8$ (*c* 0.4, $CHCl_3$) with 28% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 19.9 min (major) and 20.9 min (minor). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.36–7.19 (m, 6H), 6.93–6.90 (m, 2H), 6.79–6.76 (m, 1H), 5.74 (s, 1H), 3.75 (s, 3H), 2.4 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 159.7, 145.5, 143.7, 129.5, 128.5, 127.6, 126.5, 118.9, 113.0, 112.1, 72.1, 55.2. HRMS (ESI): calcd for $C_{14}H_{13}O$ $(M-OH)^+$ 197.0966, found 197.0962.

#### 4.7.6. (2-Methoxyphenyl) (3-methoxyphenyl)methanol 8cd

(+)-**8cd**: 99% yield; $[\alpha]_D^{20} = +26.7$ (*c* 0.4, $CHCl_3$) with 40% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 15.7 min (minor) and 17.1 min (major). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.27–7.18 (m, 3H), 6.97–6.75 (m, 5H), 6.02 (d, $J$ = 3.6 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.07–3.06 (d, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 159.5, 156.7, 145.0, 131.9, 129.1, 128.7, 127.9, 120.8, 118.9, 112.6, 112.1, 110.8, 72.0, 55.4, 55.1. HRMS (ESI): calcd for $C_{15}H_{15}O_2$ $(M-OH)^+$ 227.1072, found 227.1065.

#### 4.7.7. (4-Chlorophenyl) (1-naphthyl)methanol 8da

(*R*)-(−)-**8da**: 92% yield; $[\alpha]_D^{20} = -35.2$ (*c* 0.4, $CHCl_3$) with 45% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm); retention times 25.3 min (major) and 26.6 min (minor). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.85–7.76 (m, 3H), 7.51–7.20 (m, 8H), 6.37 (s, 1H), 2.56 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 141.6, 138.4, 134.0, 133.3, 130.6, 128.8, 128.7, 128.6, 128.3, 126.3, 125.7, 125.3, 124.8, 123.8, 73.0. HRMS (ESI): calcd for $C_{17}H_{12}Cl$ $(M-OH)^+$ 2251.0628, found 251.0622.

#### 4.7.8. (4-Chlorophenyl)(2-methoxyphenyl)methanol 8db

(−)-**8db**: 95% yield; $[\alpha]_D^{20} = -15.6$ (*c* 0.7, $CHCl_3$) with 42% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 13.0 min (major)

and 13.9 min (minor). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.32–7.19 (m, 6H), 6.96–6.85 (m, 2H), 6.00 (s, 1H), 3.79 (s, 3H), 3.03 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 156.6, 141.9, 132.8, 131.5, 128.9, 128.2, 127.9, 127.7, 120.9, 110.8, 71.6, 55.4. HRMS (ESI): calcd for $C_{14}H_{12}ClO$ $(M-OH)^+$ 231.0577, found 231.0573.

### 4.7.9. (4-Chlorophenyl)(3-methoxyphenyl)methanol 8dd

(*R*)-(−)-**8dd**: 93% yield; $[\alpha]_D^{20} = -2.7$ (*c* 1.2, $CHCl_3$) with 38% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 3:1, flow 1.0 ml/min, detection at 254 nm), retention times 28.2 min (major) and 29.7 min (minor). $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 7.33–7.21 (m, 5H), 6.91–6.79 (m, 3H), 5.76 (s, 1H), 3.77 (s, 3H), 2.27 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$, rt): $\delta$ 159.8, 145.0, 142.1, 133.3, 129.6, 127.8, 118.8, 113.1, 112.1, 75.5, 55.2. HRMS (ESI): calcd for $C_{14}H_{12}ClO$ $(M-OH)^+$ 231.0577, found 231.0579.

## 4.8. Crystallographic analysis of 4a

Colorless, needle-like crystals were grown from hexane–$CH_2Cl_2$ (10:1), $C_{36}H_{31}Br_2F_3N_2O_3S$, $M$ = 788.50, $a$ = 9.7672(9) Å, $b$ = 16.2570(15) Å, $c$ = 20.1385(18) Å, $v$ = 3197.7(5) Å$^3$, $T$ = 273(2) K, $Z$ = 35, $D_{calcd}$ = 3.922 Mg/m$^3$. Final $R$ indices [$I > 2\sigma(I)$], $R_1$ = 0.0459, $wR_2$ = 0.0769; $R$ indices (all data), $R_1$ = 0.1023, $wR_2$ = 0.0932.

Crystallographic data (excluding structure factors) for **4a** have been deposited with the CambridgeCrystallographic Data Centre as supplementary publication number CCDC 753625. Copies of the data can be obtained, free of charge, on application to CCDC, 12Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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