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Synthesis of new alkoxy/sulfonate-substituted carbene precursors derived from [2.2]paracyclophane and their application in the asymmetric arylation of aldehydes

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ABSTRACT

A series of novel planar chiral alkoxy/sulfonate-substituted carbene precursors have been designed and synthesized. They were used as *N*-heterocyclic carbene ligands in the Rh-catalyzed asymmetric addition of arylboronic acids to aromatic aldehydes, affording chiral diarylmethanols with high yields and moderate enantioselectivities.

1. Introduction

Over the last decade, much attention has been paid to the asymmetric arylation of aldehydes because the chiral diarylmethanol products are key intermediates for the synthesis of pharmaceutically and biologically active compounds.[1] The rhodium-catalyzed addition of arylboronic acids to aromatic aldehydes was first reported by Miyaura in 1998.[2] Due to the low toxicity and easy manipulation of organoboronic acids, the asymmetric addition of organoboronic acids to aldehydes and ketones attracted great interest. Recently, excellent results on the enantioselective carbonyl addition reactions of arylboronic reagents have been reported by several groups.[3,4] In 2006, Hayashi reported that a catalytic system based on the chiral methoxy-substituted phosphine ligand (MeO–MOP) derived from a binaphthyl backbone afforded excellent enantioselectivity (up to 93% ee).[4] It was suggested that the methoxy group on the ligand backbone could play an important role in the Rh-catalyzed asymmetric carbonyl addition of organoboronic reagents. For the investigation of novel catalyst systems, the design of new chiral ligands is a key strategy to achieve highly stereocontrolled reaction.

Since the end of the last century, *N*-heterocyclic carbenes (NHCs) have been successfully employed in various homogeneous metal-catalyzed reactions.[5] Among them, NHC ligands have showed good ability in asymmetric transition metal catalysis since they are neutral, σ-donating ligands with negligible π backbonding.[6] Recently, Tomioka and co-workers[7] and Alexakis and co-workers[8] introduced a new class of NHC precursors based on the concept of chiral alkoxy-substituted NHC ligands. These ligands were efficient in the enantioselective conjugate addition of Grignard reagents to cyclic enones (up to 96% ee). Kündig et al. designed and synthesized a series of chiral alkoxy-substituted NHC precursors, and applied them in Pd-catalyzed asymmetric intramolecular α-arylation of amides with excellent yields and enantioselectivities.[9] The importance of the alkoxy-substituted ligands led us to investigate a series of other alkoxy-substituted NHC ligands, such as planar chiral [2.2]paracyclophane-based NHC precursors. Since [2.2]paracyclophane is regarded as a very good backbone for chiral ligands,[10] Bolm had already developed the methoxy-substituted NHC precursor derived from [2.2]paracyclophane in 2005.[11a] However, due to the flexibility of the methylene which linked the imidazolium salt to the [2.2]paracyclophane backbone, the ligand did not show satisfactory efficiency in the asymmetric arylation of aldehydes (38% ee). On the other hand, there are a few reports concerning the carbene-metal catalyzed asymmetric addition of arylboronic acids to aldehydes.[11] Herein, we report the synthesis of a new family of alkoxy- and sulfonate-substituted NHC precursors based on a [2.2]paracyclophane backbone **6**–**8**, and **10** (Fig. 1) and their application in the enantioselective rhodium-catalyzed addition of arylboronic acids to aromatic aldehydes.

2. Results and discussion

We designed and synthesized five new planar chiral imidazolium salts and one imidazolinium salt based on the [2.2]paracyclophane skeleton. Our synthetic route to the new alkoxy- and sulfonate-substituted planar chiral imidazolium salts is shown in Schemes 1 and 2. The synthetic pathway started with enantiomerically pure *pseudo-ortho*-disubstituted [2.2]paracyclophanyl amines **1a**, **1b**, **1c**, and **4**, *pseudo-gem*-disubstituted [2.2]paracyclophanyl amine **5**. The planar chiral amines **1a**, **1b**, **1c**, and **5** can be obtained following the previous literature.[12,13] (R_p)-4-Mesylate-substituted [2.2]paracyclophanyl amine **4** was easily prepared in high yield from (R_p)-

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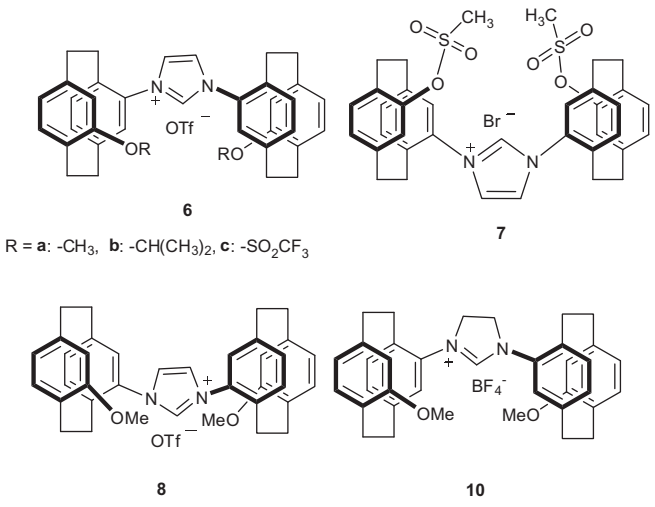
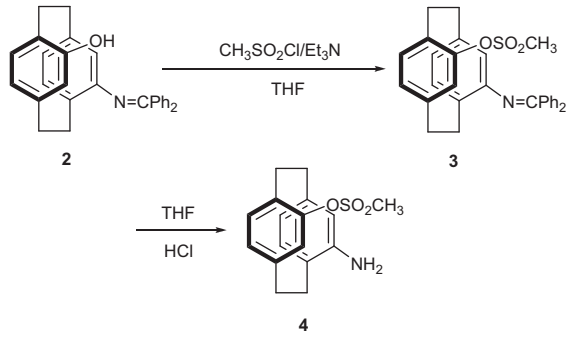
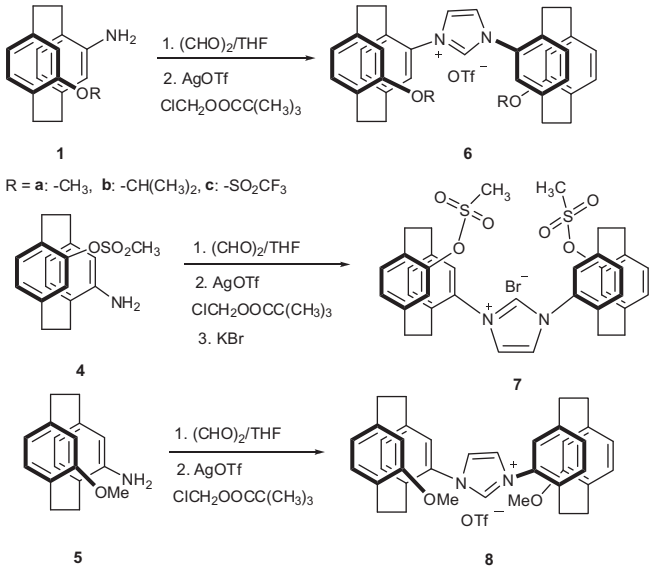


Figure 1. Novel chiral imidazolium and imidazolinium salts.

4-hydroxy-12-benzhydrylideneamino [2.2]paracyclophane **2** by mesylation with methanesulfonyl chloride, followed by imine **3** hydrolysis under acidic conditions (Scheme 1).

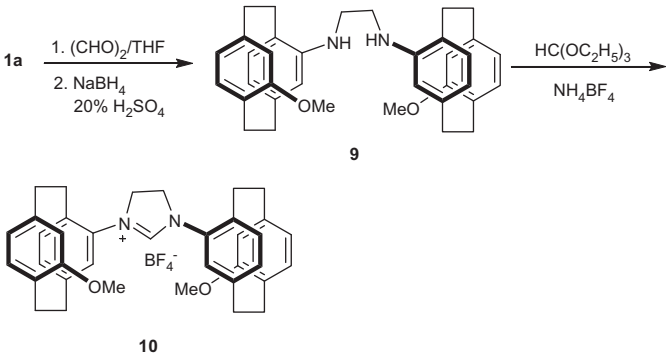


Scheme 1. Synthesis of (R_p)-4-amino-12-methanesulfonyloxy[2.2]paracyclophane.



Scheme 2. Synthesis of imidazolium triflates.

Amines **1a**, **1b**, **1c**, **4**, and **5** reacted with aqueous glyoxal in THF to furnish the corresponding diimines in essentially quantitative yield. The diimines were treated with a solution of silver triflate and chloromethyl pivalate in dark conditions at 40 °C to form imidazolium trifluoromethanesulfonates.[11d,14] The mesylate-substituted imidazolium bromide **7** was obtained from its triflate analogue by anion exchange with a saturated KBr aqueous solution. In addition, the methoxy-substituted imidazolinium tetrafluoroborate **10** was synthesized by converting **1a** into the corresponding dimine (Scheme 3), subsequent reduction with $NaBH_4$/20% H_2SO_4, and ring-closing with triethyl orthoformate in the presence of a catalytic amount of formic acid.[15] All the imidazolium and imidazolinium salts were purified, and fully characterized by NMR and mass spectrometry.



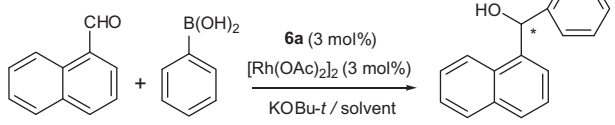
Scheme 3. Synthesis of imidazolinium tetrafluoroborate.

With the novel imidazolium salts **6a**, **6b**, **6c**, **7**, **8**, and imidazolinium salts **10** in hand, we turned our attention to their application in Rh-catalyzed asymmetric additions of arylboronic acids to aromatic aldehydes.

We began our experiment under the identical conditions used in our previous study on the rhodium-catalyzed asymmetric arylation of aromatic aldehydes.[11d] The reaction of phenylboronic acid and 1-naphthaldehyde was performed with 3.0 mol % of catalyst generated in situ from imidazolium salt **6a** and $[Rh(OAc)_2]_2$ in MeOH/DME (5:1) at 80 °C for 7 h. Compared to our previous work, the enantioselectivity of the reaction was improved.[11d] With this promising result, various aliphatic alcohols were screened as solvents (Table 1), and it was found that in *t*-BuOH, ligand **6a** showed good enantioselectivity (48% ee). It was suggested that the polarity of solvent was the crucial factor in this reaction. Thus we mixed *t*-BuOH with MeOH, EtOH, and water to adjust the polarity. Among these mixed solvents, *t*-BuOH/MeOH (5:1) emerged as the best choice, affording the addition product in good enantioselectivity (52% ee).

In *t*-BuOH/MeOH (5:1), we evaluated the rhodium sources and ligands (Table 2). No enantioselectivity was observed with $[Rh(COD)Cl]_2$ as the rhodium source. The asymmetric reaction employing $[Rh(TFA)_2]_2$, $RhCl_3$, $[Rh(NBD)Cl]_2$, $Rh(CO)_2(acac)$, and $[Rh(C_2H_4)_2Cl]_2$ as rhodium sources afforded product **c12** in lower yields (40–60%) and enantioselectivities (23–46% ee) (Table 2, entries 2–6). From the initial range of rhodium sources tested, $[Rh(OAc)_2]_2$ proved to be the best. Next, we examined different planar chiral carbene precursors shown in Figures 1 and 2. From our predictions, imidazolium salt **6b** and imidazolinium salt **10** were ineffective ligands. The carbene precursor **6c**, possessing an electron-deficient moiety, resulted in high yield (93%) and low enantioselectivity (24% ee). Ligand **7** was found to be less efficient in this reaction in terms of reactivity (30% yield) or enantioselectivity (31% ee). Ligand **8**, bearing a methoxy substituent at the 13-position of the [2.2]paracyclophane, led to the formation of diarylmethanol with similar enantioselectivity to ligand **6a**, but a significant decrease in reactivity was observed (Table 2, entry 13). Our former ligand **11** (Fig. 2) which showed good catalytic

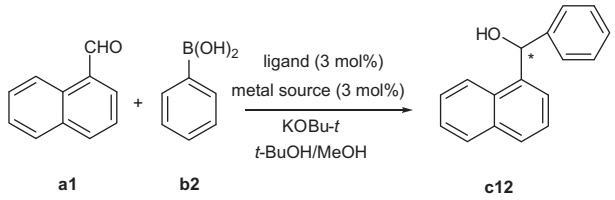
Table 1
Evaluation of the solvent[a]



Entry	Solvent	Yield[b] (%)	ee[c] (%)
1	MeOH/DME	90	46 (*S*)
2	MeOH	72	38 (*S*)
3	EtOH	80	32 (*S*)
4	*n*-PrOH	48	18 (*S*)
5	*i*-PrOH	88	33 (*S*)
6	*t*-BuOH	64	48 (*S*)
7	*t*-Amyl alcohol	0	—
8	*t*-BuOH/MeOH (10:1)	76	49 (*S*)
9	*t*-BuOH/MeOH (5:1)	76	52 (*S*)
10	*t*-BuOH/EtOH (10:1)	88	47 (*S*)
11	*t*-BuOH/H_2O (10:1)	36	47 (*S*)
12	*t*-BuOH/EtOH (3:1)	88	42 (*S*)
13	*t*-BuOH/EtOH (1:1)	88	41 (*S*)
14	*t*-BuOH/EtOH (1:3)	76	30 (*S*)

[a] Reaction conditions: $[Rh(OAc)_2]_2$ (3 mol %), **6a** (3 mol %), KOBu-*t* (1 equiv), arylboronic acids (2 equiv), N_2, 80 °C, 7 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Columns) analysis.

Table 2
Evaluation of rhodium source and ligand[a]

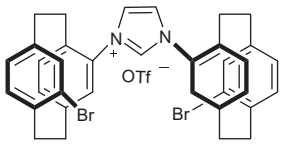


Entry	Metal source	Ligand	Yield[b] (%)	ee[c] (%)
1[d]	$[Rh(COD)Cl]_2$	**6a**	78	0
2	$[Rh(TFA)_2]_2$	**6a**	52	37 (*S*)
3	$RhCl_3$	**6a**	33	46 (*R*)
4[d]	$[Rh(NBD)Cl]_2$	**6a**	60	46 (*S*)
5	$Rh(CO)_2(acac)$	**6a**	52	23 (*S*)
6[d]	$[Rh(C_2H_4)_2Cl]_2$	**6a**	40	42 (*S*)
7[e]	$[Rh(OAc)_2]_2$	**6a**	73	40 (*S*)
8[f]	$[Rh(OAc)_2]_2$	**6a**	71	38 (*S*)
9[g]	$[Rh(OAc)_2]_2$	**6a**	67	37 (*S*)
10	$[Rh(OAc)_2]_2$	**6b**	0	—
11	$[Rh(OAc)_2]_2$	**6c**	93	24 (*S*)
12	$[Rh(OAc)_2]_2$	**7**	30	31 (*R*)
13	$[Rh(OAc)_2]_2$	**8**	40	48 (*S*)
14	$[Rh(OAc)_2]_2$	**10**	0	—
15	$[Rh(OAc)_2]_2$	**11**	36	23 (*R*)

[a] Reaction conditions: metal source (3 mol %), ligand (3 mol %), KOBu-*t* (1 equiv), arylboronic acids (2 equiv), N_2, 80 °C, 7 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Columns) analysis.
[d] Metal source: 1.5 mol %.
[e] $[Rh(OAc)_2]_2$ (4.5 mol %).
[f] $[Rh(OAc)_2]_2$ (2.25 mol %).
[g] $[Rh(OAc)_2]_2$ (1.5 mol %).

abilities in the MeOH/DME system[11d] was also used in *t*-BuOH/MeOH, and exhibited low activity (36% yield) and enantioselectivity (23% ee). So these results indicate that the methoxy group on the [2.2]paracyclophanyl ligand backbone plays an important role in the catalytic process.

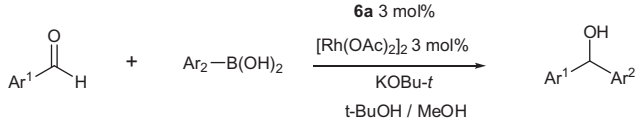
As shown in Table 3, various substrates with different steric and electronic properties were examined in the asymmetric arylation



11

Figure 2. Imidazolium salt **11.**

Table 3
Scope of the methodology[a]



a b c

Entry	Ar^1	Ar^2	Yield[b] (%)	ee[c] (%)
1	1-Naphthyl **a1**	Phenyl **b2**	76 **c12**	52 (*S*)
2	1-Naphthyl **a1**	2-$MeOC_6H_4$ **b3**	52 **c13**	44 (+)
3	1-Naphthyl **a1**	3-$MeOC_6H_4$ **b4**	95 **c14**	42 (−)
4	Phenyl **a2**	1-Naphthyl **b1**	99 **c21**	46 (*R*)
5	Phenyl **a2**	2-$MeOC_6H_4$ **b3**	94 **c23**	36 (*R*)
6	Phenyl **a2**	3-$MeOC_6H_4$ **b4**	99 **c24**	48 (*S*)
7	4-ClC_6H_4 **a3**	1-Naphthyl **b1**	99 **c31**	54 (*S*)
8	4-ClC_6H_4 **a3**	Phenyl **b2**	93 **c32**	52 (*S*)
9	4-ClC_6H_4 **a3**	2-$MeOC_6H_4$ **b3**	93 **c33**	22 (+)
10	4-ClC_6H_4 **a3**	3-$MeOC_6H_4$ **b4**	99 **c34**	54 (*S*)
11	4-$MeOOCC_6H_4$ **a4**	1-Naphthyl **b1**	99 **c41**	54 (+)
12	4-$MeOOCC_6H_4$ **a4**	Phenyl **b2**	99 **c42**	53 (*R*)
13	4-$MeOOCC_6H_4$ **a4**	2-$MeOC_6H_4$ **b3**	93 **c43**	48 (−)
14	4-$MeOOCC_6H_4$ **a4**	3-$MeOC_6H_4$ **b4**	81 **c44**	54 (+)

[a] Reaction conditions: metal source (3 mol %), ligand (3 mol %), KOBu-*t* (1 equiv), arylboronic acids (2 equiv), N_2, 80 °C, 7 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Columns) analysis.

of aromatic aldehydes under our optimized conditions. In most cases, the asymmetric reactions gave the desired products in excellent yields (up to 99%). With the electron-deficient arylaldehydes, the catalyst was more enantioselective (Table 3, entries 7, 10, 11 and 14). However, the *ortho*-methoxy substituent on the arylboronic acid **b3** reacted with aromatic aldehydes to produce the chiral diarylmethanols with lower enantiomeric excess (Table 3, entries 2, 5, 9 and 13).

3. Conclusion

In conclusion, a series of alkoxy- and sulfonate-substituted planar chiral carbene precursors based on the [2.2]paracyclophane skeleton have been prepared and applied in asymmetric additions of arylboronic acids to aromatic aldehydes. Among the new ligands screened, the methoxy-substituted ligand **6a** gave the best enantioselectivity. This shows that the methoxy substituent on the ligand backbone plays an important role in the catalytic process. Studies on further modifications of [2.2]paracyclophane-based carbene precursors as well as applications in asymmetric catalysis are currently in progress.

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. (S_p)-4-amino-12-

methoxy[2.2]paracyclophane **1a**, (S_p)-4-amino-12-*i*-propoxy [2.2]paracyclophane **1b**, (S_p)-4-amino-12-trifluoromethanesulfonyloxy[2.2]paracyclophane **1c**, (R_p)-4-benzhydrylideneamino-12-hydroxy[2.2]paracyclophane **2**, (S_p)-4-amino-13-methoxy[2.2] paracyclophane **5**, and *N*,*N*′-bis[(S_p)-12-bromo-4-[2.2]paracyclophanyl]imidazolium triflate **11** were prepared according to published procedures.[11d,13] Melting points were recorded on a melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 300 MHz spectrometers. HRMS spectra were recorded on an Agilent 100 ABI-API4000 spectrometer. Enantiomeric excess was determined using HPLC on a Chiralpak IA chiral column 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. Synthesis of (R_p)-4-amino-12-methanesulfonyloxy[2.2]paracyclophane 4

In an oven-dried Schlenk flask, (R_p)-4-benzhydrylideneamino-12-hydroxy[2.2]paracyclophane (320 mg, 0.8 mmol) and anhydrous Et_3N (0.222 mL, 1.6 mmol) were dissolved in anhydrous THF (4.0 mL). Under 0 °C, methanesulfonyl chloride (0.0624 mL, 0.8 mmol) in anhydrous THF (2.0 mL) was added dropwise to the stirred mixture over 20 min. The mixture was then stirred at room temperature for 6 h. After the reaction was complete, hydrochloric acid (12.0 M, 0.4 mL) was added to the mixture. Stirring was continued for 4 h. After the yellow mixture faded, the white precipitate formed was filtered, washed with ether (3 × 5.0 mL), and dried in vacuo. The remaining solid was dissolved in ethanol (4.0 mL), and saturated NaOH was added dropwise until the stirred mixture tested basic (pH 9). The solvent was removed, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). Target compound **4** was obtained as a white solid (221 mg, 88% yield). Mp 220–222 °C; R_f 0.4 (CH_2Cl_2/$CH_3COOC_2H_5$ = 10:1); $[\alpha]_D^{20} = +15.5$ (*c* 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.08 (d, *J* = 1.7 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.44 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 6.10 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.86 (s, 1H), 3.75 (s, 2H), 3.45–3.30 (m, 1H), 3.20–3.07 (m, 2H), 3.02 (d, *J* = 5.2 Hz, 4H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.67 (d, *J* = 13.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 147.2, 144.1, 141.8, 140.8, 134.9, 134.7, 131.5, 131.0, 123.9, 122.5, 121.8, 118.2, 36.3, 33.1, 31.7, 31.5, 30.9. HRMS (ESI) Calcd for $C_{17}H_{19}NO_3S$ $(M+H)^+$ 318.1158. Found: 318.1187.

4.3. General procedures for the synthesis of imidazolium triflates 6, 7 and 8

Compound **1**, **4** or **5** (1.0 mmol), and 40% glyoxal (145 mg, 1.0 mmol) in 0.5 mL of THF was stirred at room temperature for 5–8 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, to the mixture was added water (2.0 mL) and then extracted with CH_2Cl_2 (3 × 5.0 ml). The solvent was removed on a rotary evaporator, and the desired diimine was obtained as a yellow solid.

A solution of AgOTf (0.66 mg, 0.26 mmol) and chloromethyl pivalate (0.035 ml, 0.24 mmol) in THF was stirred in a sealed tube in the dark at room temperature for 10 min, until a white precipitate appeared. Next, a solution of diimine (104.8 mg, 0.2 mmol) in CH_2Cl_2 (2.0 ml) was added to the above suspension, and the mixture was sequentially stirred at 40 °C for 24 h. After the solvent was removed in vacuo, the resulting oil was chromatographed on silica gel (CH_2Cl_2/EtOH = 100:1–20:1) to give the crude product. After recrystallization in THF, the pure product was obtained.

4.3.1. *N*,*N*′-Bis[(S_p)-(+)-12-methoxy-4-[2.2]paracyclophanyl]-imidazolium triflate 6a

Compound **6a** was obtained as a white solid (68% yield). Mp >260 °C; R_f 0.6 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = +20.9$ (*c* 0.36, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 8.97 (s, 1H), 8.10 (s, 2H), 7.02 (s, 2H), 6.80 (d, J = 7.9 Hz, 2H), 6.69–6.64 (m, 4H), 6.48 (d, J = 7.8 Hz, 2H), 6.01 (s, 2H), 3.83 (s, 6H), 3.45–3.41 (m, 2H), 3.30–2.68 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 158.4, 143.0, 142.0, 136.6, 136.2, 135.3, 133.9, 133.7, 132.0, 130.0, 128.1, 124.6, 123.5, 119.6, 59.9, 34.4, 33.6, 31.1, 30.3. HRMS (ESI): calcd for $C_{37}H_{37}O_2N_2$ $(M\text{-}OTf)^+$ 541.2855. Found: 541.2860.

4.3.2. *N*,*N*′-Bis[(S_p)-(−)-12-isopropoxy-4-[2.2]paracyclophanyl]-imidazolium triflate 6b

Compound **6b** was obtained as a yellow solid (45% yield). Mp 115–118 °C; R_f 0.6 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = -74.4$ (*c* 0.68, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 9.10 (s, 1H), 8.21 (s, 2H), 6.99 (s, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.71–6.65 (m, 4H), 6.51(d, *J* = 7.5 Hz, 2H), 6.10 (s, 2H), 4.20–4.11 (m, 2H), 3.41–3.32 (m, 2H), 3.18–2.77 (m, 14H), 1.30–1.23 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 155.7, 143.0, 141.6, 136.3, 135.3, 134.9, 133.9, 132.5, 129.1, 124.5, 124.3, 123.3, 34.4, 33.7, 31.1, 30.5, 29.7, 22.7, 22.5. HRMS (ESI): Calcd for $C_{41}H_{45}O_2N_2$ $(M\text{-}OTf)^+$ 597.3476. Found: 597.3481.

4.3.3. *N*,*N*′-Bis[(S_p)-(+)-12-trifluoromethanesulfonyloxy-4-[2.2]-paracyclophanyl]-imidazolium triflate 6c

Compound **6c** was obtained as a white solid (82% yield). Mp >260 °C; R_f 0.6 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = +146.3$ (*c* 0.36, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 9.35 (s, 1H), 7.91 (s, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.91–6.80 (m, 6H), 6.70–6.72 (d, 2H), 6.29 (s, 2H), 3.55–3.45 (m, 2H), 3.36–3.10 (m, 8H), 3.03–2.95 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 147.3, 143.1, 141.4, 137.0, 136.1, 135.5, 134.7, 133.2, 132.5, 131.1, 123.3, 122.9, 122.6, 120.4(d, *J* = 319.5 Hz), 116.1, 33.6, 32.6, 30.6, 30.1. HRMS (ESI): Calcd for $C_{37}H_{31}F_6N_2O_6S_2$ $(M\text{-}OTf)^+$ 777.1522. Found: 777.1567.

4.3.4. *N*,*N*′-Bis[(R_p)-(+)-12-methanesulfonyloxy-4-[2.2]paracyclophanyl] -imidazolium bromide 7[16]

The pure product *N*,*N*′-bis[(R_p)-(+)-12-methanesulfonyloxy-4-[2.2]paracyclophanyl]-imidazolium triflate (240 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (10.0 mL), saturated KBr aqueous solution (10.0 mL) was added and the mixture was stirred. After 12 h, saturated KBr aqueous solution was removed. The products were collected by filtration. Compound **7** was obtained as a white solid (42% yield). Mp >240 °C (decomposition); R_f 0.4 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = +82.6$ (*c* 0.2, CH_3CN); ^{1}H NMR (300 MHz, DMSO-d_6, rt): δ 9.35 (s, 1H), 8.17 (s, 2H), 7.27 (s, 2H), 6.93 (t, *J* = 8.0 Hz, 4H), 6.82 (t, *J* = 6.8 Hz, 4H), 6.42 (s, 2H), 3.31 (s, 8H), 3.25–3.06 (m, 8H), 2.97 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.8, 143.5, 142.9, 137.7, 136.8, 136.6, 134.8, 133.5, 133.2, 125.9, 124.6, 124.4, 56.9, 38.5, 34.3, 33.5, 31.8, 31.1, 19.5. HRMS (ESI): Calcd for $C_{37}H_{37}BrN_2O_6S_2$ $(M\text{-}Br)^+$ 669.2099. Found: 669.2148.

4.3.5. *N*,*N*′-Bis[(S_p)-(+)-13-methoxy-4-[2.2]paracyclophanyl]-imidazolium triflate 8

Compound **8** was obtained as a white solid (45% yield). Mp >245 °C (decomposition); R_f 0.6 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = +81.7$ (*c* 0.17, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 9.32 (s, 1H), 7.86 (d, J = 1.5 Hz, 2H), 7.16 (s, 2H), 6.66 (dd, J = 7.8, 1.2 Hz, 2H), 6.58 (dd, J = 7.8, 2.9 Hz, 4H), 6.45 (dd, J = 7.7, 1.5 Hz, 2H), 6.29 (d, J = 1.5 Hz, 2H), 3.60 (s, 6H), 3.42–3.00 (m, 14H), 2.79–2.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 159.3, 142.9, 142.4, 137.2, 135.2, 134.6, 133.3, 131.3, 126.9, 125.6, 125.2,

123.7, 120.7, 57.5, 34.5, 34.4, 31.8 29.8. HRMS (ESI): Calcd for $C_{37}H_{37}O_2N_2$ (M-OTf)$^+$ 541.285. Found: 541.2853.

4.4. Synthesis of *N,N′*-bis[(S_p)-(−)-12-methoxy-4-[2.2]paracyclophanyl]- imidazolinium tetrafluoroborate 10

To a suspension of the diimine obtained from **1a** (326 mg, 0.6 mmol) in THF (9.0 mL) at 0 °C was added $NaBH_4$ (331.2 mg, 8.4 mmol) in 20 mg portions. H_2SO_4 (20%, 1.2 mL) in THF (5.0 mL) was added dropwise for 1 h. After being stirred at room temperature for another 2 h, to the mixture were added 5.0 ml of water and then 3.0 ml of 3.0 M hydrochloric acid. A colorless solid precipitated and saturated NaOH was added dropwise until the stirred mixture tested basic (pH 9). The solution was extracted with dichloromethane (3 × 10.0 mL). The solvent was removed on a rotary evaporator and the crude product was subjected to chromatography on silica gel with hexanes/ethyl acetate (5:1) to give the desired glyoxal diamine **9** as a white solid (272 mg, 83%). Mp 185–190 °C; R_f 0.4 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = +21.6$ (*c* 0.81, CH_2Cl_2) ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 6.40 (d, *J* = 7.5 Hz, 2H) 6.23(d, J = 7.8 Hz, 2H), 6.19 (s, 2H), 6.08 (d, *J* = 7.5 Hz, 2H), 5.94 (d, *J* = 7.5 Hz, 2H), 5.23 (s, 4H), 3.69–3.60(m, 2H), 3.56 (d, *J* = 4.5 Hz, 2H), 3.49 (s, 4H), 3.3–3.16 (m, 4H), 2.98–2.78 (m, 8H), 2.62–2.45 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 157.7, 146.1, 142.4, 141.7, 135.2, 134.9, 126.9, 124.5, 123.7, 122.0, 113.6, 112.5, 58.5, 43.1, 33.9, 33.2, 32.2, 31.3. HRMS (ESI): Calcd for $C_{37}H_{38}O_2N_2$ (M+H)$^+$ 533.3168. Found: 533.3196.

A mixture of diamine **9** (105.2 mg, 0.2 mmol), triethylorthoformate (1.0 mL), one drop of formic acid, and ammonium tetrafluoroborate (31.4 mg, 0.3 mmol) was stirred at 120 °C for 8 h. After completion of the reaction as indicated by TLC, the solvent was removed on a rotary evaporator. The crude product was subjected to chromatography on silica gel (dichloromethane/ethanol = 50:1), and the target compoud **10** was obtained as a green solid (102 mg, 82% yield). Mp >180 °C (decomposition); R_f 0.6 (CH_2Cl_2/ethanol = 20:1); $[\alpha]_D^{20} = -58.8$ (*c* 0.4, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 8.44 (s, 1H), 6.69 (d, J = 8.1 Hz, 2H), 6.80 (s, 2H), 6.59 (d, J = 7.8 Hz, 2H), 6.52 (d, J = 7.8 Hz, 2H), 6.45 (d, J = 7.8 Hz, 2H), 6.33 (s, 2H), 4.99 (m, 2H), 4.51 (m, 2H), 3.75 (s, 6H), 3.12–2.94 (m, 13H), 2.80–2.76 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 157.2, 141.8, 141.3, 135.5, 134.1, 133.8, 133.6, 131.4, 128.0, 126.6, 120.1, 118.8, 58.1, 50.3, 33.7, 32.7, 30.4, 29.2, 28.7. HRMS (ESI): Calcd for $C_{37}H_{39}O_2N_2$ (M-BF_4)$^+$ 543.3006. Found: 543.3001.

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

At first, $Rh_2(OAc)_4$ (1.7 mg, 3.8×10^{-3} mmol, 3 mol %) was weighed into a dried tube equipped with a condenser under a nitrogen atmosphere. The solvent (1.0 mL) was added and the suspension was stirred at room temperature for 5 min. Next, ligand **3a** (2.6 mg, 3.8×10^{-3} mmol, 3 mol %), phenylboronic acid (30.5 mg, 0.25 mmol), KOBu-*t* (14.0 mg, 0.125 mmol), and 1-naphthaldehyde (19.5 mg, 0.125 mmol) were added successively. The resulting mixture was stirred at 80 °C for 7 h. The reaction mixture was concentrated in vacuo and the residue was purified by chromatography (hexanes/ethyl acetate = 10:1), giving the desired diarylmethanols as a slightly yellow oil at room temperature.

4.6. General procedure for the rhodium source evaluation (Table 2)

At first, the metal source (3.8×10^{-3} mmol, 3 mol %) was weighed into a dried tube equipped with a condenser under a nitrogen atmosphere. Next, *t*-BuOH/MeOH (5:1) (1.2 mL) was added and the suspension was stirred at room temperature for 5 min. Next, NHC ligand **6a** (2.6 mg, 3.8×10^{-3} mmol, 3 mol %) phenylboronic acid (30.5 mg, 0.25 mmol), KOBu-*t* (14.0 mg, 0.125 mmol), and 1-naphthaldehyde (19.5 mg, 0.125 mmol) were added successively. The resulting mixture was stirred at 80 °C for 7 h. The reaction mixture was concentrated in vacuo and the residue was purified by chromatography (hexanes/ethyl acetate = 10:1), to give the desired diarylmethanols as a slightly yellow oil at room temperature.

4.7. General procedure for the ligand evaluation (Table 2)

At first, $Rh_2(OAc)_4$ (1.7 mg, 3.8×10^{-3} mmol, 3 mol %) was weighed into a dried tube equipped with a condenser under a nitrogen atmosphere. Next, *t*-BuOH/MeOH (5:1) (1.2 mL) was added and the suspension was stirred at room temperature for 5 min. Then, the NHC ligand (3.8×10^{-3} mmol, 3 mol %) phenylboronic acid (30.5 mg, 0.25 mmol), KOBu-*t* (14.0 mg, 0.125 mmol), and 1-naphthaldehyde (19.5 mg, 0.125 mmol) were added successively. The resulting mixture was stirred at 80 °C for 7 h. The reaction mixture was concentrated in vacuo and the residue was purified by chromatography (hexanes/ethyl acetate = 10:1), giving the desired diarylmethanols as a slightly yellow oil at room temperature.

4.8. General procedure for the evaluation of the methodology

At first, $Rh_2(OAc)_4$ (1.7 mg, 3.8×10^{-3} mmol, 3 mol %) was weighed into a dried tube equipped with a condenser under a nitrogen atmosphere. Next, *t*-BuOH/MeOH (5:1) (1.2 mL) was added and the suspension was stirred at room temperature for 5 min. Then, NHC ligand **6a** (2.6 mg, 3.8×10^{-3} mmol, 3 mol %) arylboronic acid (0.25 mmol), KOBu-*t* (14.0 mg, 0.125 mmol), and aryl aldehyde (0.125 mmol) were added successively. The resulting mixture was stirred at 80 °C for 7 h. The reaction mixture was concentrated in vacuo and the residue was purified by chromatography (hexanes/ethyl acetate = 10:1), giving the desired diarylmethanols as a slightly yellow oil at room temperature.

4.8.1. (1-Naphthyl) phenylmethanols c12 and c21

(*S*)-(−)-**c12**: 76% yield; $[\alpha]_D^{20} = -23.6$ (*c* 0.16, CH_2Cl_2) 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 17.3 min (major) and 18.4 min (minor).

(*R*)-(+)-**c21**: 76% yield; $[\alpha]_D^{20} = +15.7$ (*c* 0.11, CH_2Cl_2) 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 21.5 min (minor) and 23.0 min (major).

^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.2. (1-Naphthyl) (2-methoxyphenyl) methanol c13

(+)-**c13**: 52% yield; $[\alpha]_D^{20} = +27.1$ (*c* 0.14, CH_2Cl_2) with 44% 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 21.2 min (major) and 25.4 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.3. (1-Naphthyl) (3-methoxyphenyl)methanol c14

(−)-**c14**: 95% yield; $[\alpha]_D^{20} = -34.5$ (*c* 0.12, CH_2Cl_2) 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 34.2 min (major) and 37.4 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.4. (2-Methoxyphenyl)phenylmethanol c23

(*R*)-(+)-**c23**: 94% yield; $[\alpha]_D^{20} = +10.9$ (*c* 0.10, CH_2Cl_2) with 36% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 10:1, flow 1.0 ml/min, detection at 254 nm), retention times 16.4 min (minor) and 17.3 min (major). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.5. (3-Methoxyphenyl)phenylmethanol c24

(*S*)-(+)-**c24**: 99% yield; $[\alpha]_D^{20} = +13.8$ (*c* 0.22, CH_2Cl_2) with 48% 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 30.2 min (major) and 34.7 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.6. (4-Chlorophenyl) (1-naphthyl)methanol c31

(*S*)-(−)-**c31**: 99% yield; $[\alpha]_D^{20} = -48.4$ (*c* 0.10, CH_2Cl_2) with 54% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 10:1, flow 1.0 ml/min, detection at 254 nm), retention times 8.5 min (major) and 9.1 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.7. (4-Chlorophenyl) phenylmethanol c32

(*S*)-(+)-**c32**: 93% yield; $[\alpha]_D^{20} = +25.0$ (*c* 0.1, CH_2Cl_2) with 52% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 10:1, flow 1.0 ml/min, detection at 254 nm), retention times 18.0 min (major) and 19.1 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.35–7.25 (m, 9H), 5.81 (s, 1H), 2.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 143.4, 142.2, 133.3, 128.7, 128.6, 127.9, 127.86, 126.5, 75.6. HRMS (ESI): Calcd for $C_{13}H_{10}Cl$ $(M-OH)^+$ 219.0285. Found: 219.0249.

4.8.8. (4-Chlorophenyl)(2-methoxyphenyl)methanol c33

(+)-**c33**: 93% yield; $[\alpha]_D^{20} = +26.8$ (*c* 0.11, CH_2Cl_2) with 22% 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 (major) and 19.1 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 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): δ 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.

4.8.9. (4-Chlorophenyl)(3-methoxyphenyl)methanol c34

(*S*)-(+)-**c34**: 99% yield; $[\alpha]_D^{20} = +25.0$ (*c* 0.12, CH_2Cl_2) with 54% 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 39.0 min (minor) and 42.8 min (major) ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.33–7.21 (m, 5H), 6.9–6.79 (m, 3H), 5.76 (s, 1H), 3.77 (s, 3H), 2.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 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.

4.8.10. (1-Naphthyl) [4-(methoxycarbonyl)phenyl] methanol c41

(+)-**c41**: 99% yield; $[\alpha]_D^{20} = +34.8$ (*c* 0.23, CH_2Cl_2) with 54% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 4:1, flow 1.0 ml/min, detection at 254 nm), retention times 17.7 min (major) and 21.3 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): 8.01 (d, J = 6.0 Hz, 1H), 7.99 (t, J =8.4 Hz, 2H), 7.87–7.80 (m, 2H), 7.53–7.40 (m, 6H), 6.53 (s, 1H), 3.87 (s, 3H), 2.55 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 166.9, 148.2, 138.3, 134.1, 130.6, 129.8, 129.3, 128.9, 128.8, 126.8, 126.3, 125.8, 125.3, 125.2, 123.9, 73.5, 52.1. HRMS (ESI): Calcd for $C_{19}H_{15}O_2$ $(M-OH)^+$ 275.1072. Found: 275.1079.

4.8.11. [4-(Methoxycarbonyl)phenyl]phenylmethanol c42

(*R*)-(−)-**c42**: 99% yield; $[\alpha]_D^{20} = -14.4$ (*c* 0.21, CH_2Cl_2) with 53% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 2:1, flow 1.0 ml/min, detection at 254 nm), retention times 23.7 min (major) and 29.2 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 8.05–7.97 (m, 3H), 7.54–7.40 (m, 6H), 6.55 (s, 1H), 3.88 (s, 3H), 2.50 (d, J =3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 166.9, 148.1, 138.3, 129.8, 128.9, 126.8, 126.4, 125.8, 125.2, 73.6, 52.1. HRMS (ESI): Calcd for $C_{15}H_{13}O_2$ $(M-OH)^+$ 225.0916. Found: 225.0910.

4.8.12. (2-Methoxyphenyl)[4-(methoxycarbonyl)phenyl]methanol c43

(−)-**c43**: 93% yield; $[\alpha]_D^{20} = -20.0$ (*c* 0.25, CH_2Cl_2) with 48% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/chloroform = 2:1, flow 1.0 ml/min, detection at 254 nm), retention times 14.7 min (major) and 16.7 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 8.00–7.97 (d, J =8.1 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H), 7.31–7.20 (m, 2H), 6.97-6.88 (m, 2H), 6.08 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 156.7, 148.5, 131.4, 129.5, 129.1, 128.9, 127.9, 126.4, 120.9, 110.9, 72.1, 55.4, 52.0. HRMS (ESI): Calcd for $C_{16}H_{15}O_3$ $(M-OH)^+$ 255.1021. Found: 255.1010.

4.8.13. (3-Methoxyphenyl)[4-(methoxycarbonyl)phenyl]-methanol c44

(+)-**c44**: 81% yield; $[\alpha]_D^{20} = +36.9$ (*c* 0.23, CH_2Cl_2) with 54% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 4:1, flow 1.0 ml/min, detection at 254 nm), retention times 16.4 min (major) and 20.0 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.99 (d, *J* = 6.0 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 2H), 7.28–7.22 (m, 1H), 6.92 (d, *J* = 6.0 Hz, 2H), 6.83–6.79 (m, 1H), 5.84 (s, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 166.9, 159.9, 148.5, 144.9, 129.8, 129.7, 129.3, 126.3, 118.9, 113.3, 112.2, 75.8, 55.2, 52.1. HRMS (ESI): Calcd for $C_{16}H_{15}O_3$ $(M-OH)^+$ 255.1021. Found: 255.1031.

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