# Function of an *N*-Heterocyclic Carbene Ligand Based on Concept of Chiral Mimetic

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**Function of a new *N*-heterocyclic carbene ligand based on the concept of a chiral mimetic is described. With (4*R*,5*R*)-4,5-diphenyl-1,3-dialkyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborates as *N*-heterocyclic carbene precursors, Rh-catalyzed enantioselective arylation (up to 27% ee) of aromatic aldehydes with arylboronic acids and Pd-catalyzed enantioselective intramolecular $\alpha$-arylation (up to 66% ee) of *N*-(2-bromoaryl)-*N*-alkyl-2-aryl-propanamides are investigated.**

**Key words** optically active *N*-heterocyclic carbene ligand; chiral mimetic; imidazolium salt; asymmetric arylation

We have been developing a novel chiral phosphine ligand **1** mimicking axial chirality, in which a chiral carbon center induces a preferred conformation **2a** by rotation around an N–Ar bond which is fixed by formation of a chelate structure with metal (Fig. 1).[1—6] In order to expand the scope of our chiral mimetic concept, we planned to develop a novel *N*-heterocyclic carbene ligand[7—9] **3**. The substituent R on the $sp^2$ N group in the carbene ligand **3** may be conformationally flexible, but if the complexation of **3** and metal is reflected by the asymmetric center in **3**, a more stable complex **4a**, in which the substituent R on the $sp^2$ N group is fixed, is expected to be selectively formed (Fig. 2).[10] Herein we would like to report our investigations[5] on Rh-catalyzed enantioselective arylation of aromatic aldehydes **5** with arylboronic acids and enantioselective intramolecular $\alpha$-arylation of amides **7** with the novel *N*-heterocyclic carbene (NHC) ligand **3** (Chart 1).

**Rh-Catalyzed Enantioselective Arylation of Aromatic Aldehydes with Arylboronic Acids** Rh-catalyzed arylation of aromatic aldehydes with arylboronic acids was reported by Miyaura in 1998.[11] The corresponding diarylmethanols were obtained in good yields, and with MeO-MOP[12] as a chiral ligand, a product with 41% ee was formed in enantioselective Rh-catalyzed phenylation[4,6,13—17] of 1-naphthaldehyde with $PhB(OH)_2$. A recent attempt by Bolm using planar chiral imidazolium salts as NHC ligand precursors attained moderate enantioselectivity (up to 38% ee).[14] Bolm's results using NHC ligands prompted us to investigate the applicability of NHCs to the rather unexplored enantioselective arylation of aromatic aldehyde with arylboronic acids.

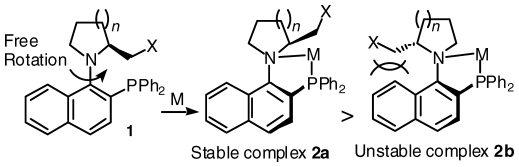



Fig. 1

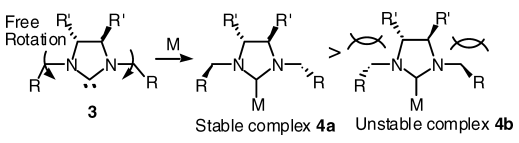



Fig. 2

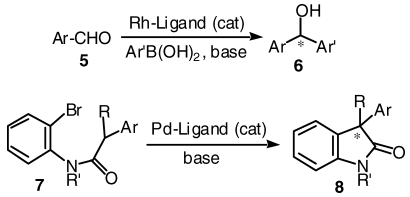
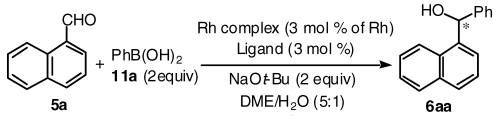



Chart 1. Enantioselective Arylation of Aldehyde and Intramolecular $\alpha$-Arylation of Amide **7**

We began to screen imidazolium salts as NHC ligand precursors **9a**—**d** in enantioselective phenylation of 1-naphthaldehyde (**5a**) with $PhB(OH)_2$ (**14a**). The results are shown in Table 1. At first, reactions were carried out with the use of $RhCl_3 \cdot 3H_2O$ in DME/$H_2O$ (5 : 1) according to Fürstner's procedure[18] (entries 1—4). Among the imidazolium salts screened, **9c** possessing a *t*-butyl group as R substituent gave 20% enantioselectivity. The use of toluene/$H_2O$ (5 : 1) as solvent gave the same results. In place of NaO*t*-Bu, KO*t*-Bu, LiO*t*-Bu and LiOH gave same results, and use of KHMDS and NaHMDS decreased reaction rates but ee's were unaffected. With **9c**, further screening (entries 5, 6) of other rhodium complexes was perforemed, and $[RhCl(CH_2{=}CH_2)_2]_2$ as a Rh source was chosen from the viewpoint of

Table 1. Catalyst Screening[a]




| Entry | Imidazolium salt | Rh complex | Yield (%) of **6aa** | ee[b] (%) of **6aa** |
|---|---|---|---|---|
| 1 | **9a** | $RhCl_3 \cdot 3H_2O$ | 77 | 3 (S) |
| 2 | **9b** | $RhCl_3 \cdot 3H_2O$ | 10[c] | 7 (S) |
| 3 | **9c** | $RhCl_3 \cdot 3H_2O$ | 80 | 20 (S) |
| 4 | **9d** | $RhCl_3 \cdot 3H_2O$ | 81 | 11 (S) |
| 5 | **9c** | $[RhCl(coe)_2]_2$[d] | 59[c] | 20 (S) |
| 6 | **9c** | $[RhCl(CH_2{=}CH_2)_2]_2$ | 93 | 21 (S) |
| 7[e] | **9c** | $[RhCl(CH_2{=}CH_2)_2]_2$ | 81 | 21 (S) |

*a*) For detailed reaction conditions, see experimental section. *b*) Determined by HPLC analysis (Daicel Chiralcel OD-H). *c*) Remainder of mass balance was the unreacted 1-naphthaldehyde **5a**. *d*) coe=cyclooctene. *e*) 6 mol% of **9c** was used.

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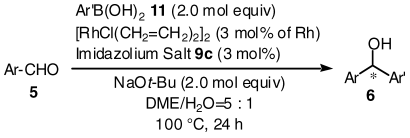
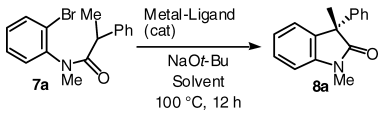
Table 2. Arylation of Aromatic Aldehydes with Ar'B(OH)$_2$[a]




| Entry | Aromatic aldehyde | Ar'B(OH)$_2$ | Yield (%) of **6** | ee[b] (%) of **6** |
|---|---|---|---|---|
| 1 | 1-Naphthaldehyde (**5a**) | 4-F–$C_6H_4$–B(OH)$_2$ (**11b**) | 90 (**6ab**) | 20 (ND[c]) |
| 2 | 1-Naphthaldehyde (**5a**) | 2-Me–$C_6H_4$B(OH)$_2$ (**11c**) | 91 (**6ac**) | 18 (ND[c]) |
| 3 | 2-Naphthaldehyde (**5b**) | PhB(OH)$_2$ (**11a**) | 66[d] (**6ba**) | 10 (S) |
| 4 | 4-$CF_3$–$C_6H_4$–CHO (**5c**) | PhB(OH)$_2$ (**11a**) | 80 (**6ca**) | 11 (S) |
| 5 | 2-Me–$C_6H_4$–CHO (**5d**) | PhB(OH)$_2$ (**11a**) | 61[d] (**6da**) | 27 (S) |
| 6 | 2-MeO–$C_6H_4$–CHO (**5e**) | PhB(OH)$_2$ (**11a**) | 82 (**6ea**) | 23 (S) |

*a*) The reactions were performed using aromatic aldehyde **5**, 1.5 mol% of [RhCl($CH_2$=$CH_2$)$_2$]$_2$, 3 mol% of imidazolium salt **9c**, and 2 mol equiv of Ar'B(OH)$_2$ **11** and NaO*t*-Bu in DME/$H_2O$ (5 : 1) at 100 °C for 24 h. *b*) Determined by HPLC analysis. For detailed conditions, see experimental section. *c*) Not determined. *d*) Remainder of mass balance was the unreacted aromatic aldehyde **5**.

Table 3. Effects of Metal Sources, Ligands and Solvents[a]




| Entry | Metal sources | Ligand | Solvent | Yield of **8a** (%) | ee[b] of **8a** (%) |
|---|---|---|---|---|---|
| 1 | Pd(OAc)$_2$[c] | **9a** | DME | 14[d] | 67 (S) |
| 2 | Pd(OAc)$_2$ | **9b** | DME | 16[d] | 45 (S) |
| 3 | Pd(OAc)$_2$ | **9c** | DME | 8[d] | 41 (S) |
| 4 | Pd(OAc)$_2$ | **9d** | DME | 13[d] | 36 (S) |
| 5 | Pd(OAc)$_2$ | **10** | DME | 7[d] | 23 (S) |
| 6 | $NiCl_2$ | **9a** | DME | NR[e] | — |
| 7 | $RhCl_3$ | **9a** | DME | NR[e] | — |
| 8 | [RhCl(coe)$_2$]$_2$ | **9a** | DME | NR[e] | — |
| 9 | Pd(OAc)$_2$ | **9a** | 1,4-Dioxane | 17[d] | 50 (S) |
| 10 | Pd(OAc)$_2$ | **9a** | Toluene | 8[d] | 46 (S) |
| 11 | Pd(OAc)$_2$ | **9a** | DMF | 0[f] | — |

*a*) The reactions of **7a** were performed using 10 mol% of metal, 20 mol% of the imidazolium salts and 2 mol equiv of NaO*t*-Bu in the shown solvent at 100 °C for 12 h. *b*) Determined by HPLC analysis. *c*) The use of $Pd_2(dba)_3 \cdot CHCl_3$ gave less satisfactory results. *d*) Remainder of mass balance was the unreacted starting amide **5a**. *e*) No reaction occurred. *f*) The debrominated product, *N*-methyl-2,*N*-diphenyl-propionamide, was obtained in 90% yield.

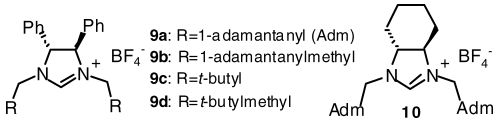



Fig. 3

Table 4. Effects of Bases[a]

| Entry | Base | Yield of **8a** (%) | ee[b] of **8a** (%) |
|---|---|---|---|
| 1 | NaO*t*-Bu | 14[c] | 67 (S) |
| 2 | LiO*t*-Bu | 62[c] | 61 (S) |
| 3[d] | LiO*t*-Bu | 19[c] | 61 (S) |
| 4 | LHMDS | 14[c] | 6 (S) |
| 5 | LiOH | NR[e] | — |
| 6 | KO*t*-Bu | 5[c] | 41 (S) |
| 7 | KOH | 25[c] | 51 (S) |
| 8 | NaOH | 16[c] | 62 (S) |

*a*) The reactions of **7a** were performed using 10 mol% of Pd(OAc)$_2$, 20 mol% of imidazolium salt **9a** and 2 mol equiv of the shown base in DME at 100 °C for 12 h. *b*) Determined by HPLC analysis. *c*) Remainder of mass balance was the unreacted starting amide **7a**. *d*) The reaction was performed at 80 °C. *e*) No reaction occurred.

chemical yield. When compared to Bolm's data (38% ee), we considered that our results (21% ee) might be promising. Hence, we tested the ability of imidazolium salt **9c** to serve as ligand precursor in enantioselective arylation of aromatic aldehydes with arylboronic acids. The results are shown in Table 2. As can be seen, the presence of an *ortho*-substituent in aromatic aldehydes resulted in slightly better asymmetric induction, and the best enantioselectivity was obtained starting from 2-tolualdehyde (**5d**) (27% ee, entry 5).

**Enantioselective Intramolecular $\alpha$-Arylation of *N*-(2-Bromophenyl)-*N*-alkyl-2-arylpropanamides** We chose **7a** as a substrate and screened imidazolium salts **9a**—**d** and **10** as an NHC ligand precursor (Table 3), because Hartwig[19] and Glorius[20] have reported the enantioselective $\alpha$-arylation[21—24] of amide **7a** using carbene ligands, giving oxindole **8a** in 57% ee and 43% ee, respectively. As shown in entries 1—5, reactions were carried out with amide **7a** as a substrate, 10 mol% of Pd(OAc)$_2$, 20 mol% of imidazolium salts **9a**—**d** and **10**, and 2 mol equiv of NaO*t*-Bu in DME at 100 °C for 12 h. Among the imidazolium salts screened, **9a** possessing a 1-adamantanyl group as R substituent gave better asymmetric induction (67% ee, entry 1), although reaction conversion was quite low. Other metal sources such as Ni and Rh resulted in no reaction (entries 6—8). With **9a** as an NHC ligand precursor, the use of other solvents such as 1,4-dioxane, toluene and DMF gave less satisfactory results (entries 9—11).

Using the best Pd(OAc)$_2$-**9a** catalyst in DME, we screened various bases as shown in Table 4. As can be seen, the choice of base played an important role in the reaction conversion. The use of LiO*t*-Bu gave the best reaction conversion with 61% enantioselectivity (entry 2). Lowering the temperature from 100 °C to 80 °C decreased reaction rate (yield 19%), and ee was unaffected (entry 3).

Finally, we examined the enantioselective $\alpha$-arylation with several amides **7b**—**j** under the optimized conditions as shown in Fig. 4. Amides **7b**—**f** possessing various substituents on the Ar group were found to be employable, exhibiting 53—66% enantioselectivity. The substituents on the N group and $\alpha$-position of carbonyl group affected somewhat enantioselectivity (**7a** *vs.* **7g**, **7h**). The substraes **7i** and

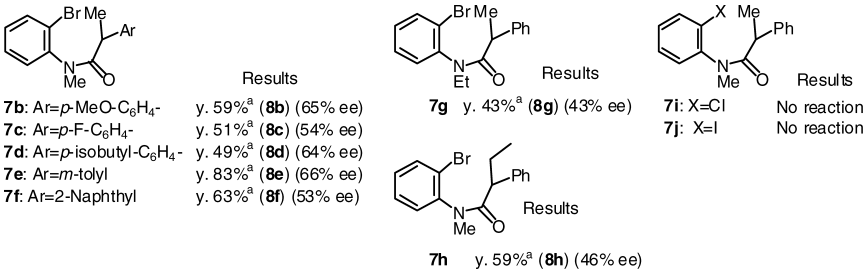



Fig. 4. Enantioselective Intramolecular $\alpha$-Arylation of Several Amides **7b**—**j**

**7j** bearing chloro and iodo groups in place of bromo group resulted in no reaction.

## Conclusion

In summary, we have reported development of a new ligand based on the concept of a chiral mimetic, which opens the possibility of synthesizing a new class of *N*-heterocyclic carbenes for asymmetric catalysis. Currently, we are investigating structural modifications of the imidazolum salts in order to improve the catalyst performance in terms of activity and enantioselectivity.

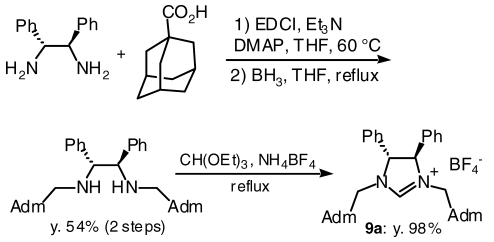



Chart 2. Representative Synthesis of Imidazolium Salt **9a**

### Experimental

**General** IR spectra were measured on a SHIMADZU FTIR-8100 diffraction grating IR spectrophotometer. $^1$H- and $^{13}$C-NMR spectra were measured on a JEOL JNM-EX-270 NMR spectrometer, operating at 270 MHz for $^1$H-NMR and at 68 MHz for $^{13}$C-NMR. $^1$H- and $^{13}$C-NMR spectra were reported in $\delta$ units, parts per million (ppm) downfield from tetramethylsilane ($\delta$=0). EI- and FAB-MS spectra were measured on a JEOL JMS-SX-102A instrument. Specific rotations (in deg cm$^3$ g$^{-1}$ l$^{-1}$) were determined on a JASCO DIP-1000 digital polarimeter.

All aromatic aldehydes, arylboronic acids, and reagents were available from commercial sources and used without further purification. In general, all reactions were performed under an argon atmosphere. $H_2O$ was used without purification. DME, 1,4-dioxane and toluene were distilled from Na/benzophenone ketyl under a nitrogen atmosphere. DMF was distilled from $CaH_2$. Silica gel column chromatography was performed on Fuji silysia BW200.

**Representative Procedure for the Synthesis of (1*R*,2*R*)-*N*,*N*′-bis-(1-Adamantanylmethyl)-1,2-diphenylethane-1,2-diamine (Chart 2)** To a stirred solution of (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediamine (1.50 g, 7.07 mmol) in THF (30.0 ml) were added 1-adamantanecarboxylic acid (3.18 g, 17.7 mmol), DMAP (173 mg, 1.41 mmol), $Et_3N$ (2.46 ml, 1.79 g, 17.7 mmol) and EDCI (3.39 g, 17.7 mmol) at 0 °C. The reaction mixture was stirred for 2 h at 60 °C, diluted with water, and extracted with EtOAc. The organic extracts were successively washed with 10% HCl, water, saturated aq. $NaHCO_3$, water and brine, dried ($Na_2SO_4$) and concentrated. Purification by silica gel column ($CHCl_3$/hexane, 1 : 2) gave a mixture (2.86 g) of coupling product and small amounts of impurities. This mixture was used for the next step without further separation. This mixture was dissolved in THF (20.0 ml), and to this mixture $BH_3$ (26.7 ml, 26.7 mmol, 1.0 M solution in THF) was added at 0 °C. The reaction mixture was heated under reflux for 4 h. After being cooled to 0 °C, MeOH was carefully poured into the reaction mixture. The whole mixture was heated under reflux over night and concentrated. The residue was dissolved in water and extracted with EtOAc. The organic extracts were washed with brine, dried ($Na_2SO_4$) and concentrated. Purification by silica gel column ($CHCl_3$) gave (1*R*,2*R*)-*N*,*N*′-bis-(1-adamantanylmethyl)-1,2-diphenylethane-1,2-diamine (1.96 g, 54% in 2 steps) as colorless needles of mp 146 °C ($CHCl_3$–hexane). $[\alpha]_D^{23}=-5°$ ($c$=3.30, THF). IR (nujol): $\nu$=3315 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.44—2.16 (m, 36H), 3.47 (s, 2H), 6.92—7.02 (m, 4H), 7.04—7.16 (m, 6H). $^{13}$C-NMR ($CDCl_3$): $\delta$=28.64, 33.85, 37.40, 40.95, 60.44, 70.67, 126.39, 127.53, 127.75, 142.03. EI-MS $m/z$=508 ($M^+$), 373, 254 (bp). *Anal.* Calcd for $C_{36}H_{48}N_2$: C, 84.98, H, 9.51, N, 5.51, Found: C, 85.05, H, 9.50, N, 5.26.

**(1*R*,2*R*)-*N*,*N*′-Bis-(1-adamantanylethyl)-1,2-diphenylethane-1,2-diamine** Representative procedure afforded the title compound in 66% yield (2 steps). colorless plates of mp 105 °C ($CHCl_3$–hexane). $[\alpha]_D^{24}=-13°$ ($c$=1.25, THF). IR (nujol): $\nu$=3369 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.10—1.43 (m, 16H), 1.46—1.71 (m, 12H), 1.78—1.92 (br, 8H), 2.25—2.50 (m, 4H), 3.59 (s, 2H), 6.95—7.04 (m, 4H), 7.05—7.18 (m, 6H). $^{13}$C-NMR ($CDCl_3$): $\delta$=28.73, 31.95, 31.78, 42.15, 42.66, 44.89, 69.58, 126.51, 127.66, 127.72, 141.53. FAB-MS: $m/z$=537 ($M^+$+1). *Anal.* Calcd for $C_{38}H_{52}N_2$: C, 85.02, H, 9.76, N, 5.22, Found: C, 84.80, H, 9.74, N, 5.22.

**(1*R*,2*R*)-*N*,*N*′-Bis-(3,3-dimethylbutyl)-1,2-diphenylethane-1,2-diamine** Representative procedure afforded the title compound in 84% yield (2 steps). A colorless oil. $[\alpha]_D^{24}=+4.0°$ ($c$=1.13, THF). IR (neat): $\nu$=3312 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=0.81 (s, 18H), 1.24—1.48 (m, 4H), 2.01 (br s, 2H), 2.29—2.49 (m, 4H), 3.61 (s, 2H), 6.93—7.04 (m, 4H), 7.06—7.17 (m, 6H). $^{13}$C-NMR ($CDCl_3$): $\delta$=29.68, 29.93, 43.91, 44.28, 69.51, 126.57, 127.69, 127.74, 141.46. FAB-MS: $m/z$=381 ($M^+$+1). *Anal.* Calcd for $C_{26}H_{40}N_2$: C, 82.05, H, 10.59, N, 7.36, Found: C, 82.23, H, 10.65, N, 7.01.

**(1*R*,2*R*)-*N*,*N*′-Bis-(1-adamantanylmethyl)-cyclohexane-1,2-diamine** Representative procedure afforded the title compound in 29% yield (2 steps). A white solid of mp 151 °C ($CHCl_3$–hexane). $[\alpha]_D^{25}=+74°$ ($c$=1.05, THF). IR (nujol): $\nu$=3313 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=0.81—1.06 (m, 2H), 1.08—1.32 (m, 2H), 1.36—1.80 (m, 28H), 1.87—2.14 (m, 12H), 2.46 (d, $J$=11.3 Hz, 2H). $^{13}$C-NMR ($CDCl_3$): $\delta$=25.19, 28.50, 32.08, 33.70, 37.28, 40.91, 60.28, 63.43. EI-MS: $m/z$=410 ($M^+$), 275 (bp). *Anal.* Calcd for $C_{28}H_{46}N_2$: C, 81.89, H, 11.29, N, 6.82, Found: C, 81.66, H, 11.54, N, 6.83.

**Representative Procedure for the Synthesis of (4*R*,5*R*)-4,5-Diphenyl-1,3-bis-(1-adamantanylmethyl)-4,5-dihydro-3*H*-imidazol-1-ium Tetrafluoroborate (9a) (Chart 2)** A suspension of (1*R*,2*R*)-*N*,*N*′-di-(1-adamantanylmethyl)-1,2-diphenylethane-1,2-diamine (965 mg, 1.90 mmol) and $NH_4BF_4$ (239 mg, 2.28 mmol) in $(EtO)_3CH$ (2.0 ml) was refluxed over night. The suspension was cooled to rt and concentrated. Purification by silica gel column (MeOH/$CHCl_3$, 1 : 30) gave (4*R*,5*R*)-4,5-diphenyl-1,3-bis-(1-adamantanylmethyl)-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate (**9a**) (1.13 g, 98%) as a white amorphous solid. $[\alpha]_D^{24}=+127°$ ($c$=1.21, THF). IR (nujol): $\nu$=1634 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.42—1.84 (m, 12H), 1.58 (d, $J$=12.7 Hz, 6H), 1.70 (d, $J$=12.7 Hz, 6H), 1.99 (s, 6H), 2.78 (d, $J$=14.7 Hz, 2H), 3.54 (d, $J$=14.7 Hz, 2H), 5.02 (s, 2H), 7.23—7.32 (m, 4H), 7.48—7.58 (m, 6H), 8.86 (s, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta$=27.96, 34.98, 36.41, 40.25, 57.53, 75.90, 126.2, 130.1, 130.2, 135.1, 160.1. FAB-MS: $m/z$=520 ($M^+-BF_4^-$+1). *Anal.* Calcd for $C_{37}H_{47}N_2BF_4$: C, 73.26, H, 7.81, N, 4.62, Found: C, 73.31, H, 7.56, N, 4.51.

**(4*R*,5*R*)-1,3-Bis-(1-adamantanylethyl)-4,5-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium Tetrafluoroborate (9b)** Representative procedure afforded **9b** in 94% yield. Colorless needles of mp 189 °C ($CHCl_3$–hexane). $[\alpha]_D^{24}=+115°$ ($c$=1.26, THF). IR (nujol) $\nu$=1651, 1645 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$=1.33—1.69 (m, 28H), 1.82—1.94 (br, 6H), 3.09—3.23 (m, 2H),

3.61—3.76 (m, 2H), 4.93 (s, 2H), 7.21—7.32 (m, 4H), 7.46—7.53 (m, 6H), 8.69 (s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$=28.38, 31.72, 36.78, 41.03, 41.80, 42.01, 73.11, 127.02, 129.85, 130.04, 134.64, 157.57. FAB-MS $m/z$=548 ($M^+-BF_4^-+1$). *Anal.* Calcd for $C_{39}H_{51}N_2BF_4$: C, 73.81, H, 8.10, N, 4.41, Found: C, 73.70, H, 8.16, N, 4.18.

**(4*R*,5*R*)-1,3-Bis-(2,2-dimethylpropyl)-4,5-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium Tetrafluoroborate (9c)** To a stirred solution of (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediamine (1.50 g, 7.07 mmol) in THF (24.0 ml) were added $Et_3N$ (2.46 ml, 17.7 mmol), DMAP (173 mg, 1.41 mmol) and pivaloyl chloride (7.03 ml, 56.5 mmol) at 0 °C. The reaction mixture was stirred for 3 h at rt, diluted with water, and extracted with EtOAc. The organic extracts were successively washed with 10% NaOH aq., 10% HCl aq. and brine, dried ($Na_2SO_4$) and concentrated. Purification by silica gel column (hexane/EtOAc/$CHCl_3$, 3 : 1 : 1) gave (1*R*,2*R*)-*N*,*N*′-bis-(2,2-dimethylpropionyl)-1,2-diphenylethane-1,2-diamine (2.51 g, 70%) as a white solid. $[\alpha]_D^{24}$=−30° ($c$=1.15, THF). IR (nujol): $\nu$=3391, 1651, 1643, 1634 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.17 (s, 18H), 5.10—5.19 (m, 2H), 6.97 (br s, 2H), 7.04—7.17 (m, 10H). $^{13}$C-NMR ($CDCl_3$): $\delta$=27.42, 38.61, 59.79, 127.01, 127.39, 128.27, 138.99, 179.04. EI-MS: $m/z$=380 ($M^+$), 190 (bp), 57. *Anal.* Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75, H, 8.48, N, 7.36, Found: C, 75.52, H, 8.42, N, 7.11.

(1*R*,2*R*)-*N*,*N*′-Bis-(2,2-dimethylpropionyl)-1,2-diphenylethane-1,2-diamine (1.83 g, 4.82 mmol) was dissolved in THF (12.0 ml), and to this mixture $BH_3$ (19.3 ml, 19.3 mmol, 1.0 M solution in THF) was added at 0 °C. The reaction mixture was heated under reflux for 1.5 h. And to the reaction mixture $BH_3$ (9.65 ml, 9.65 mmol, 1.0 M solution in THF) was added at 0 °C. The reaction mixture was heated under reflux for 14 h. MeOH was carefully added to the reaction mixture at 0 °C. The whole mixture was heated under reflux and concentrated. The residue was dissolved in water and extracted with EtOAc. The organic extracts were washed with brine, dried ($Na_2SO_4$) and concentrated. Purification by silica gel column (hexane/EtOAc, 4 : 1) gave a mixture (800 mg) of diamine and small amounts of impurities. This mixture was used for the next step without further separation. A suspension of this mixture and $NH_4BF_4$ (286 mg, 2.72 mmol) in $(EtO)_3CH$ (1.13 ml) was stirred for 5 h at 120 °C. The suspension was cooled to rt and concentrated. Purification by silica gel column (MeOH/$CHCl_3$, 5 : 95) gave (4*R*,5*R*)-1,3-bis-(2,2-dimethylpropyl)-4,5-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate (**9c**) (561 mg, 26% in 2 steps) as colorless plates of mp 152 °C (MeOH–hexane). $[\alpha]_D^{23}$=+188° ($c$=2.22, THF). IR (nujol) $\nu$=1651, 1643, 1634, 1626, 1620, 1614, 1601, 1583 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$=0.98 (s, 18H), 2.93 (d, $J$=14.5 Hz, 2H), 3.67 (d, $J$=14.5 Hz, 2H), 5.06 (s, 2H), 7.21—7.29 (m, 5H), 7.49—7.58 (m, 5H), 8.99 (s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$=27.70, 33.02, 57.17, 75.37, 126.21, 130.14, 130.18, 134.94, 160.42. EI-MS $m/z$=363 ($M^+-BF_4^-$), 180 (bp), 57 (*t*-Bu). *Anal.* Calcd for $C_{25}H_{35}N_2BF_4$: C, 66.67, H, 7.83, N, 6.22, Found: C, 66.42, H, 7.87, N, 5.95.

**(4*R*,5*R*)-1,3-Bis-(3,3-dimethylbutyl)-4,5-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium Tetrafluoroborate (9d)** Representative procedure afforded **9d** in 82% yield. Colorless plates of mp 166—167 °C ($CHCl_3$–hexane). $[\alpha]_D^{24}$=+186° ($c$=1.20, THF). IR (nujol) $\nu$=1659, 1651, 1643 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$=0.81 (s, 18H), 1.54 (dd, $J$=9.4, 7.7 Hz, 4H), 3.11—3.23 (m, 2H), 3.61—3.75 (m, 2H), 4.95 (s, 2H), 7.24—7.30 (m, 4H), 7.44—7.53 (m, 6H), 8.72 (s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$=29.00, 29.71, 40.48, 43.42, 73.21, 127.13, 129.82, 130.02, 134.56, 134.58, 157.69. EI-MS $m/z$=391 ($M^+-BF_4^-$), 180 (bp), 57 (*t*-Bu). *Anal.* Calcd for $C_{27}H_{39}N_2BF_4$: C, 67.78, H, 8.22, N, 5.86, Found: C, 67.63, H, 8.11, N, 5.88.

**(3a*R*,7a*R*)-1,3-Bis-(1-adamantanylmethyl)-3a,4,5,6,7,7a-hexahydro-3*H*-benzoimidazol-1-ium Tetrafluoroborate (10)** Representative procedure afforded **10** in 92% yield. Colorless plates of mp 248—250 °C ($CHCl_3$–hexane). $[\alpha]_D^{24}$=+4.7° ($c$=0.987, THF). IR (nujol) $\nu$=1608 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$=1.21—1.80 (m, 5H), 1.50 (s, 12H), 1.63 (d, $J$=12.2 Hz, 6H), 1.73 (d, $J$=12.2 Hz, 6H), 1.91—2.09 (m, 2H), 2.03 (br s, 6H), 2.28 (d, $J$=11.1 Hz, 2H), 3.11 (d, $J$=14.6 Hz, 2H), 3.33 (d, $J$=14.6 Hz, 2H), 3.45—3.54 (m, 2H), 8.06 (s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$=23.65, 27.65, 27.91, 34.02, 36.36, 40.12, 57.38, 69.83, 161.99. FAB-MS $m/z$=422 ($M^+$+1−$BF_4^-$). *Anal.* Calcd for $C_{29}H_{45}N_2BF_4$: C, 68.50, H, 8.92, N, 5.51, Found: C, 68.62, H, 8.92, N, 5.34.

**Representative Procedure for the Rh(I)-Catalyzed Asymmetric Arylation of 1-Naphthaldehyde (5a) with Phenylboronic Acid (11a)** To a stirred solution of [RhCl($CH_2$=$CH_2$)$_2$]$_2$ (1.1 mg, 0.027 mmol) in DME (0.30 ml) and $H_2O$ (0.060 ml) were added imidazolium salt **9c** (2.5 mg, 0.0055 mmol), NaO*t*-Bu (35.4 mg, 0.368 mmol), PhB(OH)$_2$ (**11a**) (44.9 mg, 0.368 mmol), and 1-naphthaldehyde (**5a**) (28.8 mg, 0.184 mmol). The reaction mixture was stirred for 8 h at 100 °C and allowed to cool. After usual work-up, purification by silica gel column (hexane : EtOAc=19/1 to 9/1) afforded (1*S*)-(1-naphthyl)phenylmethanol (**6aa**) (40.1 mg, 93%, 21% ee) as a colorless oil. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 ml/min). The physical data were comparable to those reported.[13] The absolute configuration was determined by comparison of the reported specific rotation.[4]

**(−)-4-Fluorophenyl-(1-naphthyl)methanol (6ab)** A white solid of mp 127 °C. $[\alpha]_D^{24}$=−13° ($c$=1.39, THF). IR (nujol): $\nu$=3290 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=2.53 (s, 1H), 6.43 (s, 1H), 6.95 (d, $J$=8.6 Hz, 1H), 6.98 (d, $J$=8.6 Hz, 1H), 7.30 (d, $J$=5.4 Hz, 1H), 7.33 (d, $J$=5.4 Hz, 1H), 7.36—7.52 (m, 3H), 7.57 (d, $J$=6.9 Hz, 1H), 7.73—7.89 (m, 2H), 7.89—7.99 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta$=72.98, 115.23 (d, $J$=21.2 Hz), 123.72, 124.39, 124.85, 125.19, 125.57, 126.10, 128.51, 128.61 (d, $J$=7.8 Hz), 128.70, 130.36, 133.79, 138.40, 138.66 (d, $J$=3.4 Hz), 161.97 (d, $J$=245.4 Hz). EI-MS: $m/z$=252 ($M^+$), 129 (base peak), 123. *Anal.* Calcd for $C_{17}H_{13}FO$: C, 80.93, H, 5.19, Found: C, 81.17, H, 5.49. The ee was determined by HPLC analysis with Daicel chiral OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 ml/min).

**(+)-1-Naphthyl-(2-tolyl)methanol (6ac)** A white solid of mp 119 °C. $[\alpha]_D^{24}$=+1.2° ($c$=1.40, THF). IR (nujol): $\nu$=3272 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=2.22 (s, 3H), 2.46 (s, 1H), 6.58 (s, 1H), 7.08—7.25 (m, 3H), 7.25—7.40 (m, 3H), 7.40—7.56 (m, 2H), 7.76 (d, $J$=7.9 Hz, 1H), 7.80—7.90 (m, 1H), 7.90—8.00 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta$=19.21, 69.78, 123.45, 124.42, 125.19, 125.50, 125.97, 126.19, 126.56, 127.51, 128.31, 128.62, 130.34, 130.95, 133.66, 135.62, 138.03, 140.72. EI-MS: $m/z$=248 ($M^+$), 128, 119 (base peak). *Anal.* Calcd for $C_{18}H_{16}O$: C, 87.06, H, 6.49, Found: C, 86.94, H, 6.48. The ee was determined by HPLC analysis with Daicel chiral OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 ml/min).

**(1*S*)-(2-Naphthyl)phenylmethanol (6ba)** The spectral data were comparable to those reported.[25] The ee was determined by HPLC analysis with Daicel chiralcel OD-H (eluent: hexane/*i*-PrOH, flow: 1.0 ml/min). The absolute configuration was determined by comparison of the reported specific rotation.[26]

**(1*S*)-Phenyl-(4-trifluoromethylphenyl)methanol (6ca)** The physical data were comparable to those reported.[27] The ee was determined by HPLC analysis with Daicel Chiralcel OB-H (eluent: hexane/*i*-PrOH, flow: 0.5 ml/min). The absolute configuration was determined by comparison of the reported specific rotation.[27]

**(1*S*)-Phenyl-2-tolylmethanol (6da)** The physical data were comparable to those reported.[25] The ee was determined by HPLC analysis with Daicel Chiralcel OB-H (eluent: hexane/*i*-PrOH, flow: 1.0 ml/min). The absolute configuration was determined by comparison of the reported specific rotation.[27]

**(1*S*)-(2-Methoxyphenyl)phenylmethanol (6ea)** The physical data were comparable to those reported.[28] The ee was determined by HPLC analysis with Daicel Chiralcel OB-H (eluent: hexane/*i*-PrOH, flow: 1.0 ml/min). The absolute configuration was determined by comparison of the reported specific rotation.[27]

New *N*-(bromophenyl)-*N*-methyl-2-arylpropanamides **7b**, **7c**, and **7e**—**h** were prepared according to the same procedure reported.[19]

***N*-(2-Bromophenyl)-*N*-methyl-2-(4-methoxyphenyl)propanamide (7b)** A colorless oil. IR (neat): $\nu$=1667 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.38 (d, $J$=6.8 Hz, 0.9H), 1.40 (d, $J$=6.8 Hz, 2.1H), 3.16 (s, 2.1H), 3.18 (s, 0.9H), 3.29 (q, $J$=6.8 Hz, 0.7H), 3.46 (q, $J$=6.8 Hz, 0.3H), 3.77 (s, 3H), 6.69—6.78 (m, 2.7H), 6.84—6.97 (m, 2H), 7.13—7.46 (m, 2.3H), 7.59 (dd, $J$=7.9, 1.3 Hz, 0.3H), 7.67—7.73 (m, 0.7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=20.22 (m=minor isomer), 20.74 (M=Major isomer), 36.13 (m), 36.17 (M), 42.40 (m), 43.19 (M), 55.22 (M), 55.24 (m), 113.54 (m), 113.68 (M), 123.59 (M), 124.11 (m), 128.30 (m), 128.34 (M), 128.52 (m), 128.88 (M), 129.50 (M), 129.54 (m), 129.94 (m), 130.78 (M), 132.76 (m), 133.41 (M), 133.72 (M), 133.89 (m), 142.24 (M), 142.51 (m), 158.22 (M), 158.32 (m), 173.83 (M), 174.06 (m). EI-MS $m/z$=347 ($M^+$), 268, 145, 135 (bp). *Anal.* Calcd for $C_{17}H_{18}BrNO_2$: C, 58.63, H, 5.21, N, 4.02, Found: C, 58.93, H, 5.38, N, 3.71.

***N*-(2-Bromophenyl)-*N*-methyl-2-(4-fluorophenyl)propanamide (7c)** A colorless oil. IR (neat): $\nu$=1666 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.38 (d, $J$=7.0 Hz, 0.9H), 1.41 (d, $J$=7.0 Hz, 2.1H), 3.16 (s, 2.1H), 3.18 (s, 0.9H), 3.34 (q, $J$=7.0 Hz, 2.1H), 3.50 (q, $J$=7.0 Hz, 0.9H), 6.69—6.75 (m, 0.7H), 6.83—7.01 (m, 4H), 7.15—7.46 (m, 2.3H), 7.60 (dd, $J$=8.1, 1.4 Hz, 0.3H), 7.69—7.74 (m, 0.7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=20.30 (m=minor isomer), 20.79 (M=Major isomer), 36.20 (m), 36.24 (M), 42.54 (m), 43.31 (M), 114.69 (m), 114.92 (M), 115.00 (m), 115.23 (M), 128.38 (M), 128.63 (m), 128.78 (M), 128.89 (M), 129.34 (m), 129.46 (m), 129.65 (M), 129.70 (m), 129.95 (m), 130.61 (M), 133.55 (M), 133.95 (m), 136.28 (d, $J$=2.7 Hz) (m), 137.29 (d, $J$=3.4 Hz) (M), 142.12 (M), 142.36 (m), 159.75 (M), 159.89 (m), 163.36 (M), 163.49 (m), 173.41 (M), 173.58 (m). FAB-MS $m/z$=336 ($M^+$+1). *Anal.* Calcd for $C_{16}H_{15}BrFNO$: C, 57.16, H, 4.50, N, 4.17, Found:

C, 56.89, H, 4.73, N, 3.91.

***N*-(2-Bromophenyl)-*N*-methyl-2-(3-tolyl)propanamide (7e)** A yellow oil. IR (neat): $\nu$=1666, 1661 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.40 (d, $J$=6.9 Hz, 0.9H), 1.42 (d, $J$=6.9 Hz, 2.1H), 2.25 (s, 3H), 3.16 (s, 2.1H), 3.18 (s, 0.9H), 3.30 (q, $J$=6.9 Hz, 0.7H), 3.50 (q, $J$=6.9 Hz, 0.3H), 6.61—6.83 (m, 2.7H), 6.91—7.46 (m, 4.3H), 7.56 (br d, $J$=7.9 Hz, 0.3H), 7.70 (dd, $J$=1.6, 7.7 Hz, 0.7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=19.91, 20.52, 21.32, 21.34, 36.10, 36.13, 43.21, 44.00, 123.48, 124.06, 124.33, 124.81, 127.19, 127.23, 127.82, 127.92, 127.97, 128.07, 128.38, 128.53, 129.38, 129.40, 129.89, 130.80, 133.27, 133.72, 137.40, 137.70, 140.15, 141.33, 142.04, 142.31, 173.49, 173.69. EI-MS: $m/z$=252 ($M^+-$Br), 119 (bp). FAB-MS: $m/z$=334 ($M^+$+1), 332 ($M^+$+1). HR-MS ($M^+-$Br) Calcd for $C_{17}H_{18}NO$: 252.1388, Found: 252.1384.

***N*-(2-Bromophenyl)-*N*-methyl-2-(2-naphthyl)propanamide (7f)** A yellow oil. IR (neat): $\nu$=1666, 1661 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.49 (d, $J$=6.9 Hz, 0.9H), 1.51 (d, $J$=6.9 Hz, 0.9H), 3.16 (s, 2.1H), 3.18 (s, 0.9H), 3.51 (q, $J$=6.9 Hz, 0.7H), 3.70 (q, $J$=6.9 Hz, 0.3H), 6.59 (dd, $J$=1.6, 7.7 Hz, 0.7H), 7.03 (ddd, $J$=1.3, 7.6, 7.6 Hz, 0.7H), 7.09—7.29 (m, 2H), 7.30—7.55 (m, 3.8H), 7.60—7.88 (m, 3.8H). $^{13}$C-NMR ($CDCl_3$): $\delta$=19.98, 20.54, 36.08, 36.10, 43.33, 44.16, 123.42, 124.05, 125.14, 125.32, 125.44, 125.55, 125.68, 125.81, 126.00, 126.54, 127.23, 127.28, 127.42, 127.46, 127.56, 127.83, 128.11, 128.45, 129.46, 129.84, 130.68, 132.12, 132.24, 133.11, 133.30, 133.70, 137.75, 138.84, 141.92, 142.22, 173.25, 173.45. EI-MS: $m/z$=369 ($M^+$), 367 ($M^+$), 288, 155 (bp). HR-MS ($M^+$) Calcd for $C_{20}H_{18}{}^{79}BrNO$: 367.0572, Found 367.0576, Calcd for $C_{20}H_{18}{}^{81}BrNO$: 369.0551, Found: 369.0590.

***N*-(2-Bromophenyl)-*N*-ethtyl-2-phenylpropanamide (7g)** A yellow oil. IR (neat): $\nu$=1664 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.06 (t, $J$=7.2 Hz, 2.1H), 1.10 (t, $J$=7.2 Hz, 0.9H), 3.30 (q, $J$=6.9 Hz, 1.4H), 3.46 (q, $J$=6.9 Hz, 0.6H), 4.04 (q, $J$=6.9 Hz, 0.7H), 4.27 (q, $J$=6.9 Hz, 0.3H), 6.60 (dd, $J$=1.7, 7.7 Hz, 0.7H), 6.89—7.46 (m, 7.3H), 7.59 (dd, $J$=1.4, 7.9 Hz, 0.3H), 7.71 (dd, $J$=1.4, 7.9 Hz, 0.7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=12.70, 12.80, 20.21, 20.64, 42.92, 43.39, 43.50, 44.43, 124.23, 124.62, 126.37, 126.48, 127.17, 127.76, 127.86, 127.93, 127.96, 128.15, 129.28, 129.40, 131.27, 131.69, 133.31, 133.84, 140.43, 141.49, 141.62, 172.90, 173.11. EI-MS: $m/z$=252 ($M^+-$Br), 105 (bp). FAB-MS: $m/z$=334 ($M^+$+1), 332 ($M^+$+1). HR-MS ($M^+-$Br) Calcd for $C_{17}H_{18}NO$: 252.1388, Found: 252.1386.

***N*-(2-Bromophenyl)-*N*-methyl-2-phenylbutanamide (7h)** A yellow oil. IR (neat): $\nu$=1666 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=0.78 (t, $J$=7.3 Hz, 0.9H), 0.82 (t, $J$=7.3 Hz, 2.1H), 1.67 (dq, $J$=7.4, 28.7 Hz, 1.4H), 2.09 (dq, $J$=7.4, 28.7 Hz, 0.6H), 3.02 (t, $J$=7.4 Hz, 0.7H), 3.15 (s, 2.1H), 3.18 (s, 0.9H), 3.23 (t, $J$=7.4 Hz, 0.3H), 6.59 (dd, $J$=1.7, 7.8 Hz, 0.7H), 6.90—7.46 (m, 7.3H), 7.57 (dd, $J$=1.5, 8.0 Hz, 0.3H), 7.70 (dd, $J$=1.5, 8.0 Hz, 0.7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=12.43, 12.66, 28.23, 28.47, 36.07, 36.08, 51.04, 52.05, 123.33, 124.29, 126.55, 126.60, 127.82, 127.98, 128.14, 128.16, 128.32, 128.46, 129.54, 130.33, 131.00, 133.39, 133.85, 138.97, 140.08, 141.99, 142.39, 172.79, 172.97. EI-MS: $m/z$=252 ($M^+-$Br, bp). FAB-MS: $m/z$=334 ($M^+$+1), 332 ($M^+$+1). HR-MS ($M^+-$Br) Calcd for $C_{17}H_{18}NO$: 252.1388, Found: 252.1366.

**Reresentative Procedure for the Enantioselective Intramolecular $\alpha$-Arylation of Amide 7a with Imidazolium Salt 9a (Entry 2, Table 4)** To a stirred solution of *N*-(2-bromophenyl)-*N*-methyl-2-phenylpropanamide[19] (**7a**) (63.6 mg, 0.200 mmol) in DME (1.0 ml) were added imidazolium salts **9a** (24.3 mg, 0.0400 mmol), $Pd(OAc)_2$ (4.5 mg, 0.0200 mmol) and LiO*t*-Bu (48.0 mg, 0.600 mmol) at rt and the mixture was stirred for 12 h at 100 °C. After being cooled to rt, the mixture was filtered through a layer of silica gel and evaporated. Purification by silica gel column (EtOAc/hexane, 1 : 8) gave (3*S*)-1,3-dimethyl-3-phenyl-1,3-dihydro-indol-2-one (**8a**) (29.3 mg, 62%, 61% ee). The spectral data of **8a** were comparable to those reported.[19]

The spectral data of the oxindole **8d** were comparable to those reported.[19] The physical data of new oxindoles **8b**, **8c** and **8e—h** were shown as follows.

**(3*S*)-3-(4-Methoxyphenyl)-1,3-dimethyl-1,3-dihydro-indol-2-one (8b)** A colorless oil. $[\alpha]_D^{24}$=+57° ($c$=0.83, THF). IR (neat): $\nu$=1717 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.75 (s, 3H), 3.23 (s, 3H), 3.76 (s, 3H), 6.81 (d, $J$=8.6 Hz, 2H), 6.90 (d, $J$=8.1 Hz, 1H), 7.43—7.37 (m, 5H). $^{13}$C-NMR ($CDCl_3$): $\delta$=23.97, 26.50, 51.49, 55.25, 108.17, 113.78, 122.61, 124.02, 127.64, 127.91, 132.73, 134.81, 143.06, 158.54, 179.48. EI-MS $m/z$=267 ($M^+$), 252 (bp). HR-MS (EI): Calcd for $C_{17}H_{17}NO_2$, [$M^+$]: 267.1259. Found: 267.1260.

**(3*S*)-3-(4-Fluorophenyl)-1,3-dimethyl-1,3-dihydro-indol-2-one (8c)** A colorless oil. $[\alpha]_D^{24}$ +68° ($c$=1.30, THF). IR (neat): $\nu$=1717 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.76 (s, 3H), 3.24 (s, 3H), 6.89—7.02 (m, 1H), 6.93 (dd, $J$=7.5, 8.6 Hz, 1H), 6.96 (dd, $J$=8.4, 8.6 Hz, 1H), 7.10 (dd, $J$=7.3, 7.6 Hz, 1H), 7.16 (dd, $J$=7.3, 8.9 Hz, 1H), 7.22—7.38 (m, 3H). $^{13}$C-NMR ($CDCl_3$): $\delta$=24.15, 26.57, 51.59, 108.36, 115.04, 115.35, 122.77, 128.17, 128.23, 128.35, 134.35, 136.38 (d, $J$=3.3 Hz), 143.03, 160.03, 163.64, 179.06. EI-MS $m/z$=255 ($M^+$), 240 (bp). HR-MS (EI): Calcd for $C_{16}H_{14}FNO$, [$M^+$]: 255.1059. Found: 255.10559.

**(3*S*)-1,3-Dimethyl-3-(3-tolyl)-1,3-dihydro-indol-2-one (8e)** A colorless oil. $[\alpha]_D^{29}$=+68° ($c$=1.19, THF). IR (neat): $\nu$=1720, 1715 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.77 (s, 3H), 2.30 (s, 3H), 3.24 (s, 3H), 6.90 (d, $J$=7.6 Hz, 1H), 7.00—7.20 (m, 6H), 7.31 (ddd, $J$=1.3, 7.6, 7.6 Hz, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta$=21.64, 23.78, 26.53, 52.11, 108.17, 122.65, 123.54, 124.04, 127.16, 127.90, 128.26, 134.91, 137.98, 140.56, 143.07, 179.36. EI-MS: $m/z$=251 ($M^+$), 236 (bp, $M^+-$Me). HR-MS ($M^+$) Calcd for $C_{17}H_{17}NO$: 251.1310, Found: 251.1312.

**(3*S*)-1,3-Dimethyl-3-(2-naphthyl)-1,3-dihydro-indol-2-one (8f)** A colorless solid of mp 125 °C. $[\alpha]_D^{29}$=+37° ($c$=0.91, THF). IR (neat): $\nu$=1728, 1715, 1693, 1682 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.89 (s, 3H), 3.27 (s, 3H), 6.94 (d, $J$=7.7 Hz, 1H), 7.10 (ddd, $J$=0.8, 7.4, 7.4 Hz, 1H), 7.20 (dd, $J$=0.8, 7.4 Hz, 1H), 7.30—7.38 (m, 2H), 7.38—7.48 (m, 2H), 7.70—7.83 (m, 4H). $^{13}$C-NMR ($CDCl_3$): $\delta$=23.69, 26.58, 52.33, 108.28, 122.75, 124.14, 124.78, 125.19, 125.86, 125.95, 127.30, 127.96, 128.09, 128.20, 132.37, 133.09, 134.75, 138.01, 143.15, 179.20. EI-MS: $m/z$=287 ($M^+$), 272 (bp, $M^+-$Me). HR-MS ($M^+$) Calcd for $C_{17}H_{17}NO$: 287.1310, Found: 251.1308.

**(3*S*)-1-Ethyl-3-methyl-3-phenyl-1,3-dihydro-indol-2-one (8g)** A yellow oil. $[\alpha]_D^{29}$=+34° ($c$=0.60, THF). IR (neat): $\nu$=1713 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=1.28 (dd, $J$=7.1, 7.3 Hz, 3H), 1.78 (s, 3H), 3.76 (dq, $J$=7.1, 14.2 Hz, 1H), 3.82 (dq, $J$=7.3, 14.2 Hz, 1H), 6.93 (d, $J$=7.7 Hz, 1H), 7.06 (ddd, $J$=0.8, 7.4, 7.4 Hz, 1H), 7.14—7.35 (m, 7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=12.76, 23.67, 34.87, 52.08, 108.36, 122.43, 124.21, 126.45, 127.04, 127.88, 128.42, 135.16, 140.76, 142.13, 178.85. EI-MS: $m/z$=251 (bp, $M^+$), 236 ($M^+-$Me). HR-MS ($M^+$) Calcd for $C_{17}H_{17}NO$: 251.1310, Found: 251.1313.

**(3*S*)-3-Ethyl-1-methyl-3-phenyl-1,3-dihydro-indol-2-one (8h)** A colorless solid of mp 82 °C. $[\alpha]_D^{29}$=+55° ($c$=0.75, THF). IR (nujol): $\nu$=1711 cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$=0.68 (dd, $J$=7.3, 7.4 Hz, 3H), 2.23 (dq, $J$=7.4, 13.5 Hz, 1H), 2.43 (dq, $J$=7.3, 13.5 Hz, 1H), 6.90 (d, $J$=7.7 Hz, 1H), 7.11 (ddd, $J$=1.0, 7.4, 7.4 Hz, 1H), 7.16—7.40 (m, 7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=9.12, 26.37, 30.93, 57.32, 108.08, 122.44, 124.66, 126.84, 127.07, 127.95, 127.98, 128.35, 131.95, 140.11, 143.98, 178.37. EI-MS: $m/z$=251 ($M^+$), 222 (bp, $M^+-$Et). HR-MS ($M^+$) Calcd for $C_{17}H_{17}NO$: 251.1310, Found: 251.1310.

**(3*S*)-1,3-Dimethyl-3-propyl-1,3-dihydro-indol-2-one (13)** A solution of 10% Pd/C (10 mg) and (3*S*)-3-allyl-1,3-dimethyl-1,3-dihydro-indol-2-one (**12**) (95.6 mg, 0.363 mmol) was stirred at rt for 3 h under $H_2$ atmosphere. The mixture was filtered and evaporated. Purification by silica gel column (EtOAc/hexane, 1 : 8) gave (3*S*)-1,3-dimethyl-3-phenyl-1,3-dihydro-indol-2-one (**13**) (64.3 mg, 67%) as a colorless oil. $[\alpha]_D^{19}$=+153° ($c$=1.56, THF). IR (neat): $\nu$=1720, 1717, 1714 cm$^{-1}$. $^1$H-NMR ($CDCl_3$, 50 °C): $\delta$=0.75—1.02 (m, 1H), 0.84 (t, $J$=6.6 Hz, 3H), 1.04—1.22 (m, 1H), 2.04—2.22 (m, 1H), 2.24—2.42 (m, 1H), 3.21 (s, 3H), 6.88 (d, $J$=7.6 Hz, 1H), 7.09 (dd, $J$=7.6, 7.6 Hz, 1H), 7.16—7.39 (m, 7H). $^{13}$C-NMR ($CDCl_3$): $\delta$=14.27, 18.06, 26.39, 40.23, 56.85, 108.08, 122.43, 124.67, 126.77, 127.07, 127.95, 128.36, 132.37, 140.30, 143.86, 178.51. EI-MS $m/z$=265 ($M^+$), 222 (bp). *Anal.* Calcd for $C_{18}H_{19}NO$: C, 81.47, H, 7.22, N, 5.28, Found: C, 81.33, H, 7.25, N, 5.32.

The absolute configurations of oxindoles **8a**—**h** were determined by comparison with the CD spectrum of **13** (Chart 3), whose absolute configuration was known.[29]

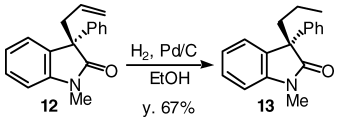



Chart 3

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