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New C_2-symmetric six-membered carbene ligands for asymmetric diethylzinc addition of arylaldehydes

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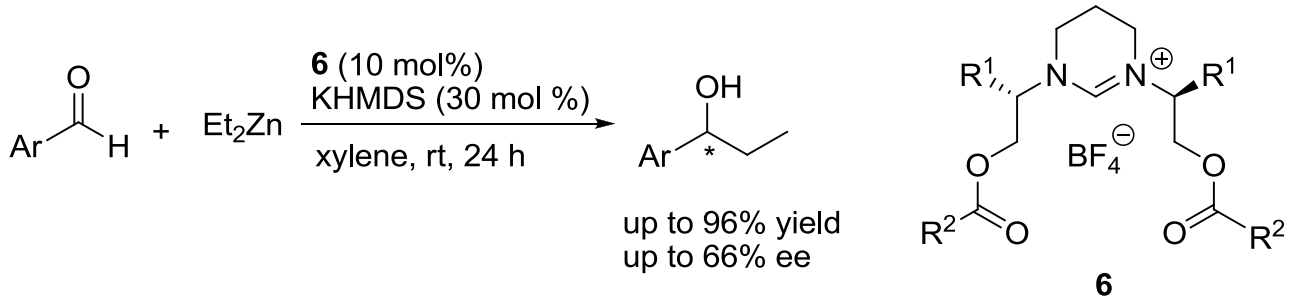
Abstract

A series of new six-membered NHC precursors were prepared by simply esterification of their parent compounds. Their applicability in asymmetric diethylzinc addition of arylaldehydes has been demonstrated and the corresponding secondary alcohol was obtained with good yields and moderate enantioselectivities.



Keywords: N-Heterocyclic carbene, tetrahydropyrimidinium, amino alcohols, asymmetric diethylzinc addition, chiral secondary alcohols

Introduction

Since the first isolation of free N-heterocyclic carbene (NHC) by Arduengo's group in 1991,[1] these types of ligands have gathered considerable interests because of their attractive properties such as higher stability to air, thermal and moisture than phosphane ligands, and NHCs are now ubiquitous in modern synthetic chemistry.[2-12] As an extension, the development of new chiral NHC precursors for catalysis has become an important issue and an enormous number of new chiral carbenes emerged, some of which have shown excellent enantioselectivity in asymmetric catalysis.[13-18] However, among the chiral NHCs synthesized, examples of chiral hydroxyalkyl NHC ligands are still rare. In 2004, Arnold and co-workers reported the synthesis of salt **1** (Figure 1),[19] the Cu^{I} complex of this ligand was used as a catalyst in diethylzinc conjugated addition to cyclohexenone, affording the desired product in up to 51% *ee*. Almost at the same time, another type of hydroxy-bearing NHC salt **2** derived from (L)-valine was prepared by Mauduit's group and this compound showed high efficiency in chiral molecular recognition.[20] Furthermore, the same group designed and synthesized a series of new bidentate NHC precursors **3** based on commercial available amino alcohols,[21-23] which were successfully applied in Cu^{II}-catalyzed asymmetric addition of diethylzinc to cyclohexanone, as well as asymmetric allylic substitution of allyl phosphates with Grignard reagents. Moreover, the same ligand **3** was proved to be an excellent ligand in multicomponent catalytic enantioselective transformations.[24] With similar starting materials, Wilhelm's group prepared several new tridentate NHC precursors **4** as ionic liquids,[25-26] and these salts were also used as catalyst in asymmetric diethylzinc addition to arylaldehydes, giving the corresponding secondary alcohols in good yields and moderate *ees* (up to 66%).

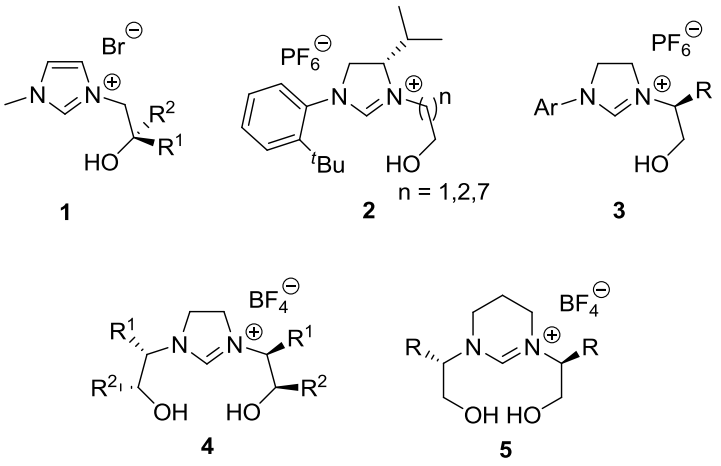
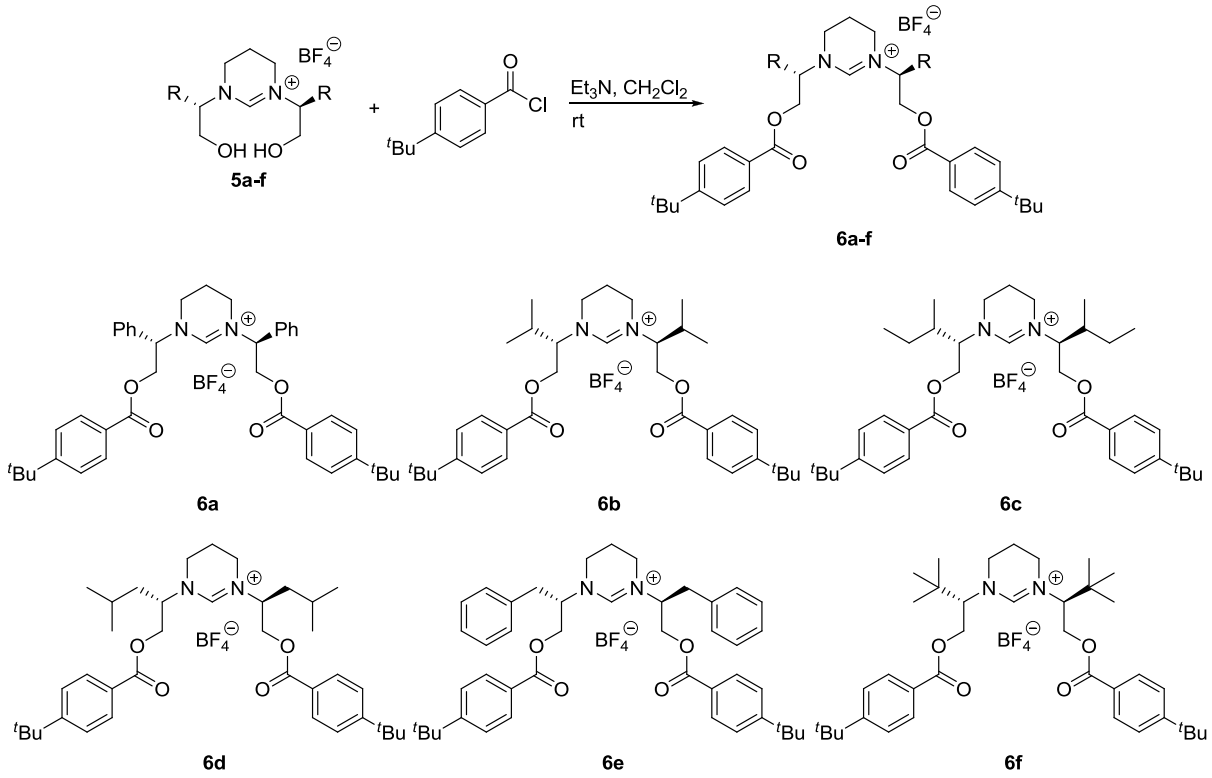


Figure 1. Representative chiral hydroxyalkyl NHC ligands.

Results and Discussion

Very recently, we reported the synthesis of several enantiopure 3,4,5,6-tetrahydropyrimidinium salts **5** incorporating two hydroxyl groups as effective ligands in Pd-catalyzed deprotonative cross-coupling process (DCCP).[27] Next, we examined the activity of these ligands in asymmetric diethylzinc addition to aldehydes. The yields are good but the *ee* values are rather low (Table 1, entries 1–6). Usually, the hydroxy group in the N-substituent of the NHC ligand was introduced as a coordination group to block the rotation of *N*-substituent which subsequently elevates the enantioselectivity in catalytic transformations. On the other hand, little

attention was paid to modifications the OH group with a steric functional group, which may result in an elevated chiral environment around the carbene center. With this expectation in mind, a series of derivatives of salts **5** are therefore prepared in this paper with the aim to improve their performance in asymmetric catalysis. As shown in Scheme 1, simple treatment of compounds **5a–f** with 4-(*tert*-butyl)benzoyl chloride provided esterification product **6a–f** in good yields (76–92%). Luckily, single crystals of **6f** were obtained from CH_2Cl_2, and the ORTEP view of this compound was obtained (Figure 2).



Scheme 1. Synthesis of NHC precursors **6a–f**.

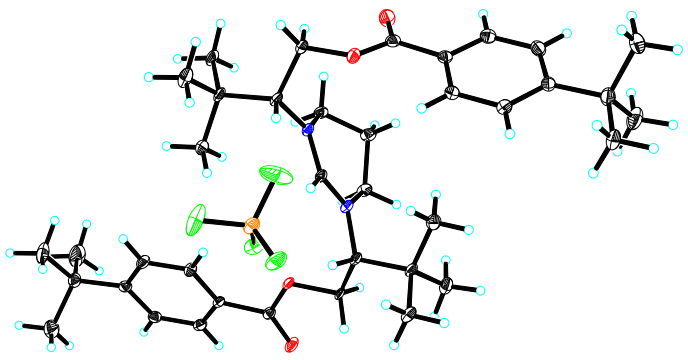
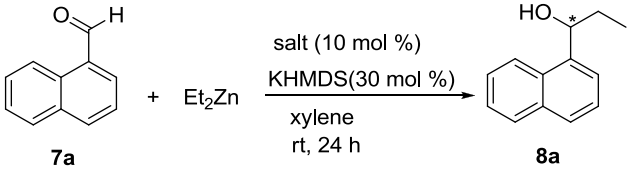


Figure 2. Crystal structure of **6f.**

Table 1. Comparison of NHC precursors

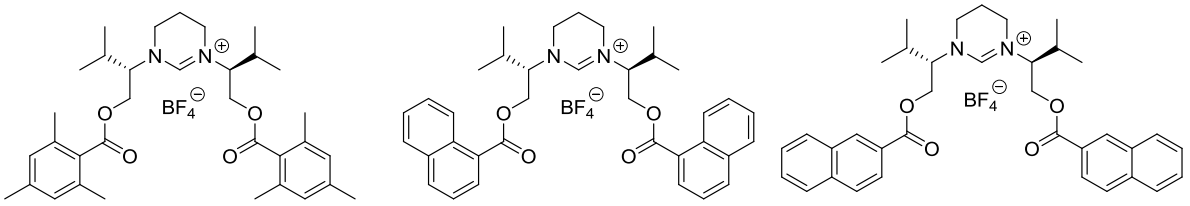


7a **8a**

Entry[a]	Catalyst	Yield (%)[b]	ee (%)[c]
1	**5a**	89	4
2	**5b**	92	21
3	**5c**	81	9
4	**5d**	90	5
5	**5e**	86	13
6	**5f**	77	1
7	**6a**	73	7
8	**6b**	93	58
9	**6c**	80	20
10	**6d**	83	8
11	**6e**	81	41
12	**6f**	95	7
13	**6g**	90	9
14	**6h**	83	11
15	**6i**	92	23

[a] Reaction condition: salt (10 mol %), KHMDS (30 mol %), Et_2Zn (2 equiv), N_2, xylene, rt, 24 h. [b] Isolated yield. [c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

The synthesized tetrahydropyrimidinium salts **6** were tested in asymmetric diethylzinc addition of 1-naphthaldehyde (**7a**) according to our procedure in the same transformation with pyrimidone salts as catalysts.[28] As presented in Table 1, all derivatives **6a–f** showed better enantioselectivities than their parent compounds **5a–f**, and **6b** gave the best result (93% yield, 58% *ee*). We then tried various conditions of different bases and solvents. Unfortunately, all combinations didn't improve the enantioselectivity (see Supporting information for details). Futhermore, three new salts **6g–6i** (Figure 3), derived from the same parent compound as **6b**, were also prepared and tested in the same reaction, no improvement of *ee* value was observed as well (entries 13–15).



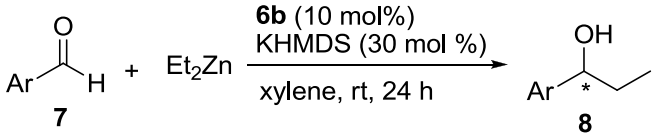
6g **6h** **6i**

Figure 3. The structures of **6g–6i**.

Using **6b** as catalyst, various arylaldehydes with different substituents were examined in this transformation. As summarized in Table 2, the reaction proceeded well in most cases (73–96% yield). Arylaldehydes bearing electron-donating (entries 3–7) and electron-withdrawing (entries 8–11) groups, as well

as heterocyclic sustrates (entries 13–15), were all well-tolerated, giving the corresponding adducts **8b–8p** in good yields and moderate enantiomeric excesses. The best enantioselectivity was obtained starting from 2-quinolinecarbaldehyde (66% *ee*, entry 15).

Table 2. Scope of methodology



Entry[a]	Ar	Product	Yield (%)[b]	ee (%)[c]
1	2-Naphthyl	**8b**	83	34
2	Ph	**8c**	91	37
3	2-MePh	**8d**	74	43
4	3-MePh	**8e**	79	50
5	3,4-diMePh	**8f**	86	44
6	2-MeOPh	**8g**	88	45
7	4-MeOPh	**8h**	75	36
8	2-FPh	**8i**	84	35
9	4-FPh	**8j**	80	45
10	4-BrPh	**8k**	90	36
11	4-CF_3Ph	**8l**	96	40
12	Cinnamyl	**8m**	87	60
13	3-Pyridine	**8n**	73	45
14	2-Thienyl	**8o**	88	38
15	2-Quinolyl	**8p**	76	66

[a] Reaction condition: **6b** (10 mol %), KHMDS (30 mol %), Et_2Zn (2 equiv), N_2, xylene, rt, 24 h.
[b] Isolated yields. [c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

Conclusions

In summary, a series of new six-membered NHC precursors (**6a–6i**) have been prepared and the single-crystal X-ray diffraction further confirmed the structure of compound **6f**. The catalytical activity of these ligands in

asymmetric diethylzinc addition to arylaldehydes was tested and the corresponding secondary alcohols were obtained with excellent yields and moderate *ees* (up to 66%). Further work is currently underway to prepare more chiral six-membered NHC ligands, as catalysts in other asymmetric transformation, by modification the hydroxyl group in *N*-substituent.

Experimental Section

General. MS spectra were measured on a Finnigan LCQDECA XP instrument and a Agilent Q-TOF 1290 LC/6224 MS system; ^{1}H and ^{13}C NMR spectra were obtained on Bruker AVANCE III 500 MHz and 600 MHz spectrometers (Bruker Co., Switzerland) with TMS as the internal standard; silica gel GF_{254} and H (10−40 mm, Qingdao Marine Chemical Factory, China) were used for TLC and CC. Unless otherwise noted, all reactions were carried out under an atmosphere of argon or nitrogen.

General procedure for the synthesis of compounds 6. To a mixture of salt **5** (2 mmol) and Et_3N (9.6 mmol) in dry dichloromethane (10 mL) was added 4-*tert*-butylbenzoyl chloride (8 mmol) at 0 ^{o}C. After stiring at room temperature for 12 h, the mixture was poured into water (25 mL) and extracted with dichloromethane (3 × 10 mL). The organic fractions were combined, washed with brine and dried over Na_2SO_4. The solvent was then removed under reduced pressure and the residue was purified by column chromatography (silica gel, CH_2Cl_2/MeOH) to afford the corresponding products **6**.

6a. White powder; yield 1.31 g (89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.19 (d, *J* 8.6 Hz, 4H), 7.60 (d, *J* 8.6 Hz, 4H), 7.29 (d, *J* 7.5 Hz, 2H), 7.13 (t, *J* 7.8 Hz, 4H), 6.99 (d, *J* 7.5 Hz, 4H), 5.61 (dd, *J* 10.7, 3.5 Hz, 2H), 5.46 – 5.35 (m, 2H), 4.47 (m, 2H), 3.35 – 3.21 (m, 2H), 2.89 – 2.76 (m, 2H), 1.80 – 1.73 (m, 2H), 1.38 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.44, 157.70, 131.59, 131.58, 130.14, 129.48, 129.32, 127.57, 125.95, 125.85, 65.75, 60.10, 38.75, 35.27, 31.16, 18.65; ESIMS *m/z* 645.3.

6b. 81% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.99 (d, *J* 8.6 Hz, 4H), 7.46 (d, *J* 8.6 Hz, 4H), 4.78 (dd, *J* 12.4, 10.4 Hz, 2H), 4.27 (dd, *J* 12.4, 3.4 Hz, 2H), 3.95 (m, 2H), 3.47 – 3.37 (m, 2H), 3.20 – 3.09 (m, 2H), 2.03 – 1.94 (m, 2H), 1.82 (dd, *J* 6.5, 4.0 Hz, 2H), 1.33 (s, 18H), 1.02 (d, *J* 6.6 Hz, 6H), 0.52 (d, *J* 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.35, 157.56, 155.43, 129.90, 125.88, 125.71, 70.31, 60.73, 38.82, 35.17, 31.06, 26.80, 19.10, 18.98; HR-ESIMS: *m/z* 578.4090 $[M–BF_4+H]^+$ (calcd for $C_{36}H_{54}N_2O_4^+$, 578.4078).

6c. 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.02 (d, *J* 8.6 Hz, 4H), 7.49 (d, *J* 8.7 Hz, 4H), 4.80 (dd, *J* 12.3, 10.5 Hz, 2H), 4.25 (dd, *J* 12.4, 3.4 Hz, 2H), 4.03 (m, 2H), 3.43 (dd, *J* 12.7, 6.2 Hz, 2H), 3.16 – 3.07 (m, 2H), 2.02 – 1.98 (m, 2H), 1.57 – 1.52 (m, 2H), 1.33 (s, 18H), 0.97 (d, *J* 6.6 Hz, 6H), 0.87 – 0.81 (m, 2H), 0.75 (m, 2H), 0.50 (t, *J* 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.37, 157.42, 155.34, 129.82, 126.01, 125.72, 69.17, 61.05, 39.06, 35.14, 32.99, 31.05, 25.10, 18.74, 14.98, 10.69; HR-ESIMS: *m/z* 605.4395 $[M–BF_4]^+$ (calcd for $C_{38}H_{57}N_2O_4^+$, 605.4313).

6d. 92% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.02 (d, *J* 8.6 Hz, 4H), 7.49 (d, *J* 8.6 Hz, 4H), 4.75 (m, 2H), 4.35 (dd, *J* 9.3, 4.6 Hz, 2H), 4.02 (dd, *J* 12.4, 3.4 Hz, 2H), 3.53 – 3.42 (m, 2H), 3.27 – 3.16 (m, 2H), 2.05 (dd, *J* 7.3, 4.2 Hz, 2H), 1.43 (m, 2H), 1.33 (s, 18H), 1.31 – 1.27 (m, 2H), 1.17 – 1.10 (m, 2H), 0.72 (d, *J* 6.6 Hz, 6H), 0.63 (d, *J* 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.46, 157.52, 154.79, 129.92, 125.89, 125.77, 62.60, 62.31, 38.47, 36.24, 35.18, 31.08, 29.70, 24.61, 22.82, 21.46; HR-ESIMS: *m/z* 605.4410 $[M–BF_4]^+$ (calcd for $C_{38}H_{57}N_2O_4^+$, 605.4313).

6e. 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.96 – 7.89 (m, 4H), 7.46 – 7.41 (m, 4H), 7.25 – 7.13 (m, 10H), 4.68 (dd, *m*, 2H), 4.54 (d, *J* 9.8 Hz, 2H), 4.24 (dd, *J* 12.4, 3.5 Hz, 2H), 3.14 (m, 4H), 2.99 (dd, *J* m, 2H), 2.79

(m, 2H), 1.74 – 1.66 (m, 2H), 1.25 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.04, 157.52, 154.32, 134.83, 129.71, 129.11, 128.88, 127.42, 125.99, 125.72, 65.24, 62.84, 41.03, 35.11, 34.99, 30.98, 18.66; HR-ESIMS: *m/z* 673.4094 $[M–BF_4]^+$ (calcd for $C_{44}H_{53}N_2O_4^+$, 673.4000).

6f. 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.99 (d, *J* 7.3 Hz, 4H), 7.45 (d, *J* 8.1 Hz, 4H), 4.98 (t, *J* 11.5 Hz, 2H), 4.23 (m, 4H), 3.50 (dd, *J* 12.8, 6.1 Hz, 2H), 3.35 – 3.26 (m, 2H), 2.01 – 1.93 (m, 2H), 1.33 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.32, 157.36, 129.81, 126.03, 125.56, 72.41, 58.69, 40.65, 35.11, 33.98, 31.05, 29.67, 27.37, 18.81; HR-ESIMS: *m/z* 605.4412 $[M–BF_4]^+$ (calcd for $C_{38}H_{57}N_2O_4^+$, 605.4313).

6g. 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 6.83 (s, 4H), 4.52 (m, 4H), 3.89 – 3.80 (m, 2H), 3.38 (dd, *J* 12.8, 6.5 Hz, 2H), 3.28 (dd, *J* 12.7, 6.6 Hz, 2H), 2.28 (s, 6H), 2.26 (s, 12H), 2.04 – 1.98 (m, 2H), 1.96 – 1.88 (m, 2H), 1.04 (d, *J* 6.6 Hz, 6H), 0.70 (d, *J* 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.16, 154.83, 139.75, 135.27, 129.79, 128.52, 69.83, 62.17, 39.85, 29.68, 27.04, 21.07, 19.93, 18.96, 18.88; HR-ESIMS: *m/z* 549.3754 $[M–BF_4]^+$ (calcd for $C_{34}H_{49}N_2O_4^+$, 549.3687).

6h. 73% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* 8.7 Hz, 2H), 8.62 (s, 1H), 8.38 (dd, *J* 7.3, 1.1 Hz, 2H), 8.03 (d, *J* 8.2 Hz, 2H), 7.88 (d, *J* 8.1 Hz, 2H), 7.64 (m, 2H), 7.58 – 7.51 (m, 4H), 4.75 (dd, *J* 12.5, 10.4 Hz, 2H), 4.39 (dd, *J* 12.5, 3.4 Hz, 2H), 4.00 (m, 2H), 3.49 – 3.40 (m, 2H), 3.16 – 3.09 (m, 2H), 2.02 – 1.95 (m, 2H), 1.83 – 1.74 (m, 2H), 1.00 (d, *J* 6.6 Hz, 6H), 0.40 (d, *J* 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.64, 155.07, 134.12, 133.77, 131.43, 128.68, 128.11, 126.27, 125.39, 125.11, 124.97, 124.54, 70.28, 61.16, 39.07, 29.68, 19.03, 18.88; HR-ESIMS: *m/z* 565.3186 $[M–BF_4]^+$ (calcd for $C_{36}H_{41}N_2O_4^+$, 565.3061).

6i. 86% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 2H), 8.67 (s, 1H), 8.08 (d, *J* 8.0 Hz, 2H), 8.02 (dd, *J* 8.6, 1.6 Hz, 2H), 7.86 (dd, *J* 8.3, 3.1 Hz, 4H), 7.64 – 7.54 (m, 4H), 4.84 (dd, *J* 12.3, 10.6 Hz, 2H), 4.30 (dd, *J* 12.4, 3.4 Hz, 2H), 4.03 (m, 2H), 3.50 – 3.39 (m, 2H), 3.21 – 3.09 (m, 2H), 2.05 – 1.97 (m, 2H), 1.86 – 1.72 (m, 2H), 0.96 (d, *J* 6.6 Hz, 6H), 0.42 (d, *J* 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.33, 155.02, 135.70, 132.48, 131.77, 129.73, 128.60, 128.37, 127.58, 126.79, 125.98, 124.96, 70.38, 61.26, 39.21, 26.79, 19.03, 18.98; HR-ESIMS: m/z 565.3191 $[M–BF_4]^+$ (calcd for $C_{36}H_{41}N_2O_4^+$, 565.3061).

Representative procedure for the asymmetric addition of diethylzinc to aldehyde. Under argon atmosphere, a mixture of salt **6b** (0.01 mmol) and KHMDS (0.03 mmol) in xylene (1 mL) was stirred for 5 min at room temperature. Then diethylzinc (0.2 mmol) was added dropwise, followed by addition of aldehdye **7** (0.1 mmol). Upon stirring for 24 h at room temperature, the reaction was quenched by HCl (1 M, 1.0 mL), and extracted with Et_2O (3 × 2 mL). The combined organic phases were washed with water and dried over Na_2SO_4 and concentrated under vacuum. The residue was further purified by column chromatography (silica gel, hexane/AcOEt) to give product **8**.

8a. 93% yield, 58% ee ; the spectral data were comparable to those reported.[29] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (minor) = 15.7 min, t_r (major) = 28.6 min).

8b. 83% yield, 34% ee; The spectral data were comparable to those reported.[30] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (minor) = 19.2 min, t_r (major) = 22.5 min). **8c**. 91% yield, 37% ee; The spectral data were comparable to those reported.[31] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (major) = 10.6 min, t_r (minor) = 12.2 min). **8d**. 74% yield, 43% ee; The spectral data were comparable to those reported.[31] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (major) = 12.7 min, t_r (minor) = 15.4 min). **8e**. 79% yield, 50% ee; The spectral data were comparable to those reported.[29] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (minor) = 18.3 min, t_r (major) = 20.5 min). **8f**. 92% yield, 20% ee; The spectral data were comparable to those reported.[28] The ee was determined by HPLC analysis with

Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.4 mL/min, t_r (minor) = 8.9 min, t_r (major) = 9.7 min).

8g. 63% yield, 24% ee; The spectral data were comparable to those reported.[29] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (minor) = 18.5 min, t_r (major) = 21.9 min).

8h. 75% yield, 36% ee; The spectral data were comparable to those reported.[30] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (major) = 10.6 min, t_r (minor) = 12.2 min).

8i. 84% yield, 35% ee; The spectral data were comparable to those reported.[32] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (major) = 11.9 min, t_r (minor) = 15.3 min).

8j. 80% yield, 45% ee; The spectral data were comparable to those reported.[29] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 93/7, flow rate = 0.5 mL/min, t_r (major) = 11.6 min, t_r (minor) = 13.6 min).

8k. 90% yield, 36% ee; The spectral data were comparable to those reported.[32] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 93/7, flow rate = 0.5 mL/min, t_r (minor) = 11.9 min, t_r (major) = 12.8 min).

8l. 83% yield, 28% ee; The spectral data were comparable to those reported.[28] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 93/7, flow rate = 0.5 mL/min, t_r (major) = 11.2 min, t_r (minor) = 13.1 min).

8m. 87% yield, 60% ee; The spectral data were comparable to those reported.[29] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 93/7, flow rate = 0.5 mL/min, t_r (minor) = 14.1 min, t_r (major) = 15.8 min).

8n. 73% yield, 45% ee; The spectral data were comparable to those reported.[33] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 93/7, flow rate = 0.5 mL/min, t_r (minor) = 13.6 min, t_r (major) = 14.6 min).

8o. 88% yield, 38% ee; The spectral data were comparable to those reported.[30] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 93/7, flow rate = 0.5 mL/min, t_r (major) = 9.4 min, t_r (minor) = 10.7 min).

8p. 76% yield, 66% ee; The spectral data were comparable to those reported.[34] The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL/min, t_r (minor) = 14.1 min, t_r (major) = 30.2 min.

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Supplementary Material

^{1}H and ^{13}C NMR spectra of new compounds and crystallographic data of **6f**.

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