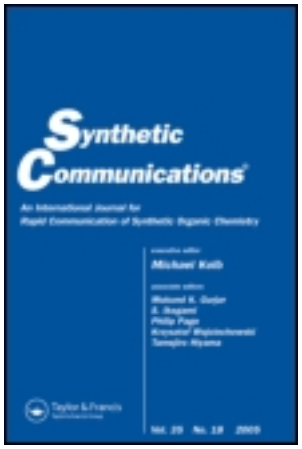

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Novel Chiral Bisformamide-Promoted Asymmetric Allylation of Benzaldehyde with Allyltrichlorosilane

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Accepted author version posted online: 30 Jun 2011.Published online: 08 Jun 2011.

To cite this article: Kaori Ishimaru , Kaori Ono , Yuya Tanimura & Takakazu Kojima (2011) Novel Chiral Bisformamide-Promoted Asymmetric Allylation of Benzaldehyde with Allyltrichlorosilane, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:24, 3627-3634, DOI: 10.1080/00397911.2010.519841

To link to this article: http://dx.doi.org/10.1080/00397911.2010.519841

Synthetic Communications®, 41: 3627–3634, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.519841

NOVEL CHIRAL BISFORMAMIDE-PROMOTED ASYMMETRIC ALLYLATION OF BENZALDEHYDE WITH ALLYLTRICHLOROSILANE

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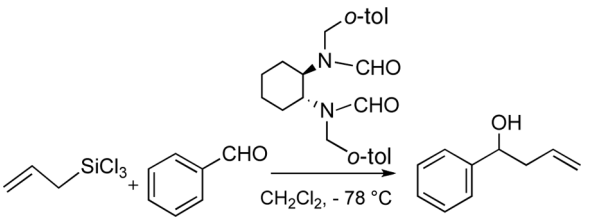
GRAPHICAL ABSTRACT



Abstract *Novel chiral bisformamides have been prepared from (*R,R*)-1,2-cyclohexanediamine and utilized as Lewis bases in the asymmetric allylation of benzaldehyde with allyltrichlorosilane. The reaction in the presence of Lewis base* ***1i*** *gave an 83:17 enantiomeric ratio (*R/S*) of the products in 90% isolated yield.*

Keywords Aldehyde; allylation; bisformamide; Lewis base

INTRODUCTION

The asymmetric allylation of aldehydes with allylsilanes is one of the most important carbon–carbon bond-formation reactions in organic synthesis.[1] In particular, allylation promoted by Lewis bases without the presence of metals has been an attractive synthetic approach.[2,3] Recently, allylations of aldehydes using chiral *N*-oxide,[4] bis-*N*-oxide,[5] tri-*N*-oxide,[6] phosphoramide,[7] bisphosphoramide,[8] phosphine oxide,[9] formamide,[10] diamine,[11] and proline catalysts[12] have been demonstrated to furnish the products in excellent yields and enantioselectivities. This is the first report of allylation using chiral C_2-symmetric bisformamides to investigate their Lewis basicity and applications. During the course of our studies, Feng et al. reported an asymmetric one-pot, three-component Strecker reaction using chiral bisformamides;[13] however, the catalysts had four chiral centers, and two formyl

Received September 7, 2010.

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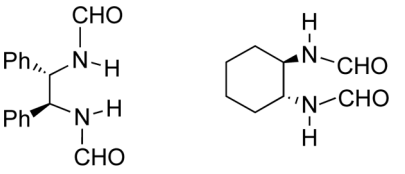


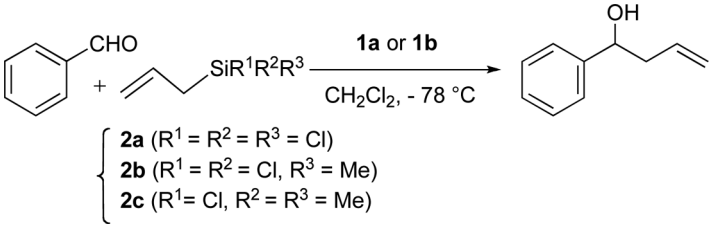
1a **1b**

Scheme 1. Lewis bases **la** and **lb**.

and two amide moieties were necessary to control the reactivities and the enantioselectivities of the products. In this communication, we describe the preparation of novel chiral bisformamides and their first application to the asymmetric allylation reaction.

First, we prepared chiral bisformamides **1a**[7e] and **1b** from (*S*,*S*)-1,2-diphenylethylenediamine and (*R*,*R*)-1,2-cyclohexanediamine, respectively (Scheme 1). The ^{1}H NMR spectra of the chiral bisformamides show the mixture of rotamers; see supporting information in Ref. 7e. Asymmetric allylations of benzaldehyde with allylsilane **2a**–**2c** in the presence of **1a** or **1b** were investigated to study the influence of the various allylsilane reagents (Table 1). The reactions were conducted using a stoichiometric amount of the Lewis base in dichloromethane at −78°C for 3 days. After workup, the corresponding homoallylic alcohol was obtained only in the case of entry 2. The product was purified by flash column chromatography (*n*-hexane/dichloromethane 2/1), and the Lewis base was recovered nearly quantitatively by changing the eluent to CH_3COOEt on the same column. The enantiomeric ratios were determined by chiral high-performance liquid chromatographic (HPLC) analysis.

Table 1. Asymmetric allylation of benzaldehyde with allylsilanes **2a**–**2c** in the presence of Lewis bases[a]

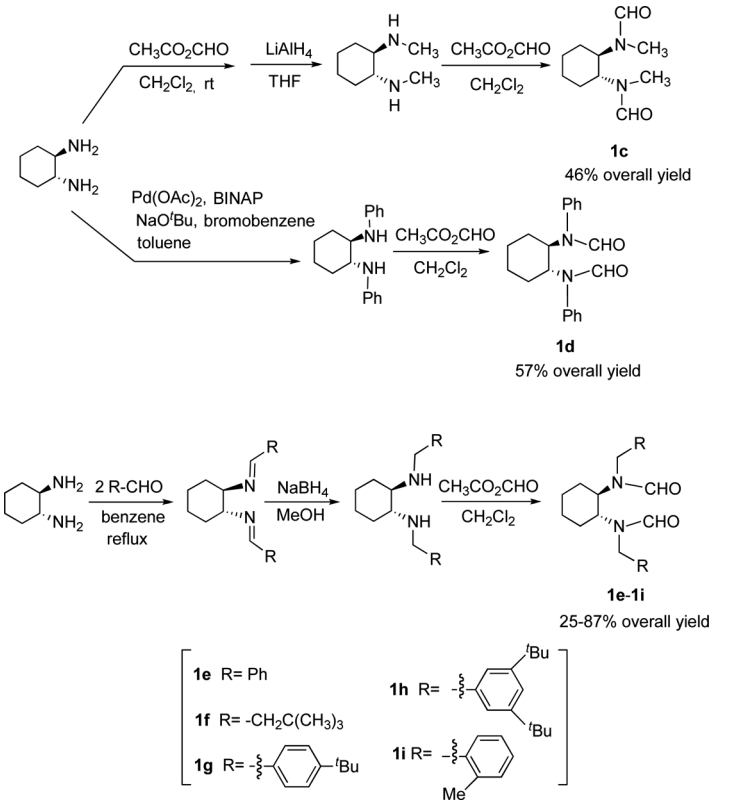


Entry	Lewis base	Allylsilane	Er (*R*/*S*)[b]	Yield (%)[c]
1	**1a**	**2a**	—	0
2	**1b**	**2a**	36:64	63
3	**1b**	**2b**	—	0
4	**1b**	**2c**	—	0

[a]Reaction performed with 0.5 mmol of Lewis base, 0.5 mmol of benzaldehyde, and 1.5 mmol of allylsilane in dichloromethane (2 mL) at −78 °C for 3 days.

[b]Determined by Daicel Chiralcel OD (*n*-hexane/*i*-PrOH = 19/1).

[c]Isolated yields after column chromatography.

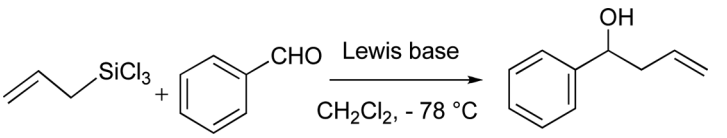


Scheme 2. Preparation of Lewis bases **1c**–**1i**.

To improve the enantioselectivities, we next prepared various Lewis bases **1c**–**1i** having substituents on the nitrogen atoms (Scheme 2). Bisformylation of (*R*,*R*)-1,2-cyclohexanediamine with acetic formic anhydride followed by reduction with lithium aluminum hydride gave (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane by a method similar to that in Ref. 7e. Again, bisformylation of the resulting diamine with acetic formic anhydride afforded the Lewis base **1c** in 46% overall yield. The coupling reaction of 1,2-cyclohexanediamine with bromobenzene followed by bisformylation provided the corresponding Lewis base **1d**. Lewis bases **1e**–**1i** were obtained in 25–87% overall yields by formation of imines, reduction with $NaBH_4$,[7c] and bisformylation as in the method of **1c** and **1d**.

Allylations with **1c**–**1i** were conducted using a method similar to that used in Table 1 except for the amount of Lewis bases (Table 2). Interestingly, the major enantiomer in all cases was *R*, which was opposite that of entry 2 in Table 1. The reason for this is not clear; however, the chirality on the nitrogen atoms by chirality transfer[15] in the transition state would be different from the case in Table 1. From optimization of the reaction conditions, it was found that 5 equiv. of Lewis base to aldehyde was necessary for greater yields of the product (entries 2 and 4–9 in Table 2). Although allylation with Lewis base **1c** having methyl groups on the

Table 2. Asymmetric allylation of benzaldehyde with allyltrichlorosilane in the presence of Lewis base[a]



Entry	Lewis base (equiv. to aldehyde)	Er (R/S)[b]	Yield (%)[c]
1	**1c** (1)	58:42	14
2	**1c** (5)	58:42	75
3	**1d** (1)	79:21	19
4	**1d** (5)	79:21	80
5	**1e** (5)	60:40	91
6	**1f** (5)	67:33	81
7	**1g** (5)	70:30	71
8	**1h** (5)	44:56	88
9	**1i** (5)	83:17	90

[a]Reaction performed with Lewis base (0.5 mmol or 2.5 mmol), 0.5 mmol of benzaldehyde, and 1.5 mmol of allyltrichlorosilane in dichloromethane (2 mL) at −78 °C for 3 days.
[b]Determined by Daicel Chiralcel OD (*n*-hexane/*i*-PrOH = 19/1).
[c]Isolated yields after column chromatography (*n*-hexane/dichloromethane = 2/1).

nitrogen atoms gave a 58:42 (R/S) ratio of the product, the use of **1d** having benzyl substituents afforded a greater enantiomeric ratio (R/S 79:21, 80% yield in entry 4). The best result was obtained with Lewis base **1i** ($R/S = 83:17$, 90% yield in entry 9). Allylations with Lewis bases having bulky substituents on the benzyl groups did not give good results (entries 7 and 8). We also explored the influence of various additives such as molecular sieves, Na_2SO_4, hexamethyl phosphoramide (HMPA), or diisopropylethylamine; however, the enantiomeric ratios were nearly the same, and the yields were poor, showing these additives did not accelerate the reaction. We also conducted the reaction of *m*-tolualdehyde in the presence of Lewis base **1i**, and high enantiomeric ratio was obtained ($R/S = 92:8$,[15] 100% isolated yield). The reaction of *o*-tolualdehyde using **1i** gave a 57:43 (R/S) ratio of the product in quantitative yield. Absolute configuration of the major enantiomer was assigned by comparing the retention time as in Ref. 5a.

In conclusion, we have first prepared the novel chiral C_2-symmetric bisformamides and explored their use in the allylation of benzaldehydes with allyltrichlorosilane. Further studies to investigate the reaction mechanism and applications are now in progress.

EXPERIMENTAL

All reactions were performed under an argon atmosphere in dried flasks, and the components were added by means of syringes. All solvents were dried by standard methods. ^{1}H NMR spectra were recorded at 300 MHz (JEOL JNM-AL300 BK1) in $CDCl_3$. Compound **1a** and (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine were prepared according to the method in Ref. 7e (supporting information), and the spectral data were identical with those in Refs. 7e and 7c, respectively.

Typical Experimental Procedure for Reaction of Benzaldehyde with Allyltrichlorosilane in the Presence of Lewis Base 1

Benzaldehyde (0.051 mL, 0.5 mmol) at room temperature was added to a stirred solution of Lewis base **1** (2.5 mmol) in dry dichloromethane (2 mL). The solution was cooled to −78 °C, and then allylsilane (1.5 mmol) was slowly added. The reaction mixture was stirred at −78 °C for 3 days and quenched with 2 mL of aqueous saturated $NaHCO_3$. The mixture was extracted with dichloromethane (10 mL × 3), and the combined organic layers were dried over Na_2SO_4. The precipitates were filtered off, and the solvent was evaporated to give the crude product. The crude product was purified by flash column chromatography on SiO_2(*n*-hexane/dichloromethane = 2/1), and isolated yields were measured. The spectral data of the homoallylic alcohol was consistent with the data in Ref. 5a (supporting information). The enantiomeric ratio was determined by a chiral column (Daicel Chiralcel OD, *n*-hexane/*i*-PrOH 19/1).

Data

Compound 1b. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31–1.50 (m, 4H), 1.65–1.92 (m, 2H), 2.04–2.08 (m, 2H), 3.75–3.88 (m, 2H), 5.95–6.20 (m, 2H), 8.15 (brs, 2H). HRMS-FAB(M^+): Obsd. m/z 170.1063. Calcd. for $C_8H_{14}N_2O_2$: 170.1055.

Compound 1c. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20–1.50 (m, 2H), 1.51–2.06 (m, 6H), 2.81 (s, 3H), 2.85 (s, 3H), 4.40–4.52 (m, 2H), 7.93–8.17 (m, 2H). HRMS-FAB(M^+): Obsd. m/z 198.1375. Calcd. for $C_{10}H_{18}O_2N_2$: 198.1368.

(1*R*,2*R*)-*N*,*N*′-Diphenyl-1,2-cyclohexanediamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10–1.25 (m, 2H), 1.35–1.50 (m, 2H), 1.73–1.79 (m, 2H), 2.33–2.37 (m, 2H), 3.12–3.25 (m, 2H), 3.75–3.88 (m, 2H), 6.61–6.75 (m, 5H), 7.14–7.28 (m, 5H). HRMS-FAB(M^+): Obsd. m/z 266.1771. Calcd. for $C_{18}H_{22}N_2$: 266.1783.

Compound 1d. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20–1.45 (m, 4H), 1.50–1.65 (m, 2H), 1.91–2.08 (m, 2H), 4.52–4.75 (m, 2H), 7.21–7.44 (m, 10H), 8.21 (s, 2H) (8.42, s, rotamer). HRMS-FAB(M^+): Obsd. m/z 322.1680. Calcd. for $C_{20}H_{22}O_2N_2$: 322.1681.

(1*R*,2*R*)-*N*,*N*′-Dibenzyl-1,2-cyclohexanediamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10–1.25 (m, 4H), 1.73–1.79 (m, 2H), 2.13–2.25 (m, 2H), 2.33–2.40 (m, 2H), 2.50–2.85 (brm, 2H), 3.67 (d, 2H, J = 9.7 Hz), 3.97 (d, 2H, J = 9.7 Hz), 7.28–7.32 (m, 10H). HRMS-FAB(M^+): Obsd. m/z 294.2082. Calcd. for $C_{20}H_{26}N_2$: 294.2096.

Compound 1e. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06–1.35 (m, 4H), 1.45–1.79 (m, 6H), 4.18–4.26 (m, 2H), 4.28–4.40 (m, 2H), 7.17–7.35 (m, 10H), 8.16–8.31 (m, 2H). HRMS-FAB(M^+): Obsd. m/z 350.2001. Calcd. for $C_{22}H_{26}O_2N_2$: 350.1994.

(1*R*,2*R*)-*N*,*N*′-Bis(3,3-dimethylbutyl)-1,2-cyclohexanediamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (s, 18H), 1.21–1.34 (m, 2H), 1.42–1.60 (m, 6H), 1.76–1.91 (m, 2H), 2.22–2.31 (m, 2H), 2.55–2.80 (m, 4H), 2.93–3.06 (m, 2H), 3.70–4.05 (brs, 2H). HRMS-FAB(M^+): Obsd. m/z 282.3029. Calcd. for $C_{18}H_{38}N_2$: 282.3035.

Compound 1f. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (s, 18H), 1.15–1.50 (m, 6H), 1.62–2.08 (m, 8H), 2.80–3.24 (m, 2H), 3.26–3.52 (m, 2H), 7.99–8.07 (m, 2H). HRMS-FAB(M^+): Obsd. m/z 338.2929. Calcd. for $C_{20}H_{38}O_2N_2$: 338.2933.

(1*R*,2*R*)-*N*,*N*′-Bis[(4-*t*-butylphenyl)methyl]-1,2-cyclohexanediamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 18H), 1.25–1.35 (m, 4H), 1.73–1.82 (m, 2H), 2.13–2.27 (m, 2H), 2.45–2.55 (m, 2H), 3.68 (d, 2H, $J = 13.0$ Hz), 3.96 (d, 2H, $J = 13.0$ Hz), 7.23 (d, 4H, $J = 8.1$ Hz), 7.36 (d, 4H, $J = 8.1$ Hz). HRMS-FAB(M^+): Obsd. m/z 406.3355. Calcd. for $C_{28}H_{42}N_2$: 406.3348.

Compound 1g. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (s, 18H), 1.15–1.32 (m, 4H), 1.51–1.92 (m, 6H), 4.35–4.42 (m, 2H), 4.60–4.66 (m, 2H), 7.09–7.36 (m, 8H), 8.15–8.26 (m, 2H). HRMS-FAB(M^+): Obsd. m/z 462.3252. Calcd. for $C_{30}H_{42}O_2N_2$: 462.3246.

(1*R*,2*R*)-*N*,*N*′-Bis[(3,5-di-*t*-butylphenyl)methyl]-1,2-cyclohexanediamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 36H), 1.22–1.32 (m, 2H), 1.47–1.58 (m, 2H), 1.82–1.85 (m, 2H), 2.25–2.29 (m, 2H), 2.65–2.68 (m, 2H), 3.80 (d, 2H, $J = 12.8$ Hz), 4.10 (d, 2H, $J = 12.8$ Hz), 7.11–7.35 (m, 6H). HRMS-FAB(M^+): Obsd. m/z 518.4611. Calcd. for $C_{36}H_{58}N_2$: 518.4600.

Compound 1h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 18H), 1.32 (s, 18H), 1.48–1.80 (m, 10H), 3.72–3.75 (m, 2H), 4.41–4.46 (m, 2H), 6.92–7.42 (m, 6H), 8.25–8.30 (m, 2H). HRMS-FAB(M^+): Obsd. m/z 574.4493. Calcd. for $C_{38}H_{58}O_2N_2$: 574.4498.

(1*R*,2*R*)-*N*,*N*′-Bis[(2-methylphenyl)methyl]-1,2-cyclohexanediamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12–1.35 (m, 4H), 1.73–1.85 (m, 2H), 2.30 (s, 6H), 2.29–2.42 (m, 4H), 2.80 (brs, 2H), 3.65 (d, 2H, $J = 13.1$ Hz), 3.93 (d, 2H, $J = 13.1$ Hz), 7.14–7.26 (m, 8H). HRMS-FAB(M^+): Obsd. m/z 322.2417. Calcd. for $C_{22}H_{30}N_2$: 322.2409.

Compound 1i. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18–1.38 (m, 6H), 1.26 (s, 6H), 1.50–1.75 (m, 4H), 4.40–4.47 (m, 2H), 4.63–4.75 (m, 2H), 6.85–7.40 (m, 8H), 8.20–8.32 (m, 2H). HRMS-FAB(M^+): Obsd. m/z 378.2300. Calcd. for $C_{24}H_{30}O_2N_2$: 378.2307.

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