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# Catalytic Asymmetric Insertion of Diazoesters into Aryl-CHO Bonds: Highly Enantioselective Construction of Chiral All-Carbon Quaternary Centers

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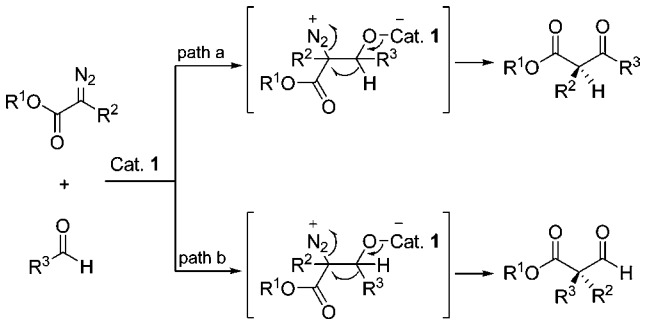
Supporting Information

**ABSTRACT:** This paper describes a catalytic enantioselective route to synthesize functionalized all-carbon quaternary acyclic systems via a boron Lewis acid-promoted formal C−C insertion of diazoesters into aryl-CHO bonds. In the presence of chiral (*S*)-oxazaborolidinium cation **1d** as a catalyst, the reaction proceeded in good yield (up to 83%) with good regioselectivity (up to 88:12) and excellent enantioselectivity (up to 99% ee). The synthetic potential of this method was illustrated by conversion of the products to both $\alpha$- and $\beta$-amino esters.

Mild and selective C−C bond insertion reactions provide potential advantages for synthetic strategies to make useful molecules.[1,2] Among developments in this area, the formal diazo carbon insertion into C−C bonds is a powerful tool for the homologation of aldehydes and ketones (Scheme 1).[2] In this type of reaction, the formal C−H bond insertion

**Scheme 1. Asymmetric Formal Insertion of a Diazoester into the Carbon-CHO Bond**




reaction of aldehydes via a 1,2-hydride shift, namely, the Roskamp reaction, has been well established,[3] and asymmetric methods providing chiral $\beta$-keto esters have recently been achieved (path a).[4] However, the corresponding formal C−C bond insertion to provide one-carbon homologated aldehydes is more challenging due to the difficulty of promoting the selective 1,2-shift of the $R^3$ group in preference to the hydride (path b).

To date, Hossain,[2a−d] Kanemasa,[2e] Kirchner,[2f,g] and other groups[2h,i] have independently reported catalytic variants of the insertion reaction, which can allow the 1,2-shift of an $R^3$ group in preference to a hydride, using simple ethyl diazoacetates ($R^2$ = H) and aryl aldehydes. In 2008, the Maruoka group presented a chiral auxiliary-based approach to formal C−C insertion of aryl diazoacetates into aldehydes.[2j] To the best of our knowledge, no catalytic asymmetric example of this reaction has been reported to date. In connection with our work on asymmetric Roskamp reactions,[4c] herein, we describe the first example of the catalytic asymmetric formal carbon insertion of alkyldiazoesters into aryl-CHO bonds. This methodology is highly valuable since it leads to the enantioselective construction of all-carbon quaternary stereogenic centers in acyclic systems, which is one of the most challenging topics in current synthetic organic chemistry.[5]

Initially, an asymmetric formal C−C insertion reaction between ethyl $\alpha$-benzyl diazoester and benzaldehyde was examined in the presence of 20 mol % oxazaborolidinium ion **1a**[6] activated by triflic imide. When the reaction was carried out at −78 °C in toluene, the $\alpha$-benzyl-$\beta$-ketoester **3** was obtained as the major product via a selective 1,2-hydride shift (Table 1, entry 1). Use of the polar solvent propionitrile led to an increased ratio of the quaternary aldehyde in 96% ee (Table 1, entry 2).[2f,g] Since partial decomposition of the quaternary aldehyde was observed during purification on a silica gel column,[7] product **2** was isolated by silica gel chromatography at −40 °C. Replacement of the ethyl group of the diazoester with a less sterically hindered methyl group afforded the quaternary aldehyde **2b** as the major product in 55% yield in 95% ee (entry 3). We then investigated the effect of changing boracycle catalyst substituents and found that the best boron aryl substituent was the 2,4-dimethyl derivative (entries 3−6). To further improve the regioselectivity and yield, the reaction was performed at −95 °C. The yield of **2** was enhanced to 72%, with a **2**:**3** ratio of 74:26 and in 97% ee (entry 7).

With optimized reaction conditions for the catalytic asymmetric formal C−C insertion reaction in hand, we evaluated this methodology with a range of substituted diazoesters. As summarized in Table 2, catalytic formal C−C insertion reactions were favored when the diazoester $R^2$ group had a $\pi$ bond, especially a phenyl group (Table 2, entries 1 and 2). In the absence of a $\pi$ bond in the $R^2$ group, the formal C−H insertion reaction was preferred (entry 3). Regardless of the electronic properties of the $R^2$ group in the diazoester, the reaction proceeded with good regioselectivity, and the corresponding products were obtained in good yields and

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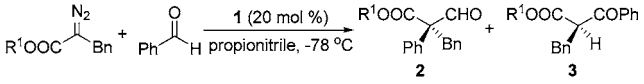
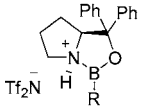
**Table 1. Optimization of Asymmetric Formal Insertion of α-Benzyl Diazoester into Ph−CHO Bond**[a]



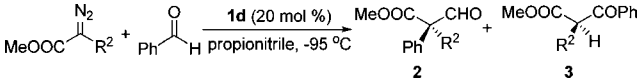
**1a:** R = 1-naphthyl
**1b:** = phenyl
**1c:** = *o*-tolyl
**1d:** = 2,4-dimethylphenyl

**Catalyst**

| entry | 2 | cat. | $R^1$ | *t* | 2:3[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|---|---|---|
| 1[e] | **2a** | **1a** | Et | 1.5 h | 9:91 | 7 | |
| 2 | **2a** | **1a** | Et | 1 h | 33:67 | 30 | 96 |
| 3 | **2b** | **1a** | Me | 30 min | 60:40 | 55 | 95 |
| 4 | **2b** | **1b** | Me | 40 min | 49:51 | 47 | 83 |
| 5 | **2b** | **1c** | Me | 30 min | 59:41 | 56 | 97 |
| 6 | **2b** | **1d** | Me | 40 min | 70:30 | 67 | 97 |
| 7[f] | **2b** | **1d** | Me | 1 h | 74:26 | 72 | 97 |

[a]The reaction of diazoester (0.27 mmol) with benzaldehyde (0.32 mmol) was performed in the presence of **1** (20 mol %), in 1.0 mL of solvent at −78 °C for the time indicated. [b]Determined by $^1$H NMR analysis of the crude reaction mixture. [c]Isolated yield of **2**. [d]The ee of **2** was determined by chiral HPLC. [e]The reaction was performed in toluene. [f]The reaction was performed at −95 °C.

**Table 2. Asymmetric Formal Insertion of Various α-Alkyl Diazoesters into the Ph−CHO Bond**[a]




| entry | 2 | $R^2$ | *t* | 2:3[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|---|---|
| 1 | **2b** | Bn | 1 h | 74:26 | 72 | 97 |
| 2 | **2c** | Allyl | 40 min | 64:36 | 62 | 92 |
| 3 | **2d** | Me | 5 min | 33:67 | 29 | 77 |
| 4 | **2e** | 4-BrBn | 40 min | 80:20 | 75 | 98 |
| 5 | **2f** | 4-MeOBn | 1 h | 73:27 | 70 | 99 |
| 6 | **2g** | 4-$NO_2$Bn | 3 h | 82:18 | 78 | 99 |
| 7 | **2h** | 4-$CF_3$Bn | 1.5 h | 81:19 | 78 | 99 |
| 8 | **2i** | 4-MeBn | 1 h | 73:27 | 69 | 94 |
| 9 | **2j** | 3-BrBn | 40 min | 79:21 | 76 | 99 |
| 10[e] | **2k** | 1-Np$CH_2$ | 2 h | 62:38 | 55 | 94 |

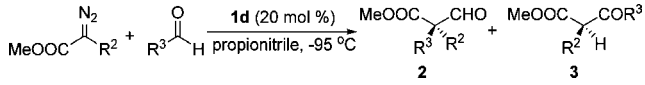
[a]The reaction of diazoester (0.27 mmol) with benzaldehyde (0.32 mmol) was performed in the presence of **1d** (20 mol %), in propionitrile (1.0 mL) at −95 °C for the time indicated. [b]Determined by $^1$H NMR analysis of the crude reaction mixture. [c]Isolated yield of **2** after silica gel chromatography at −40 °C. [d]The ee of **2** was determined by chiral HPLC. [e]The reaction was performed at −95 °C for 1 h and at −78 °C for 1 h.

excellent enantioselectivities (entries 1, 2, and 4−9). As the 1-naphthylmethyl group (1-Np$CH_2$) in the diazoester was sterically hindered, preferential migration of the phenyl group over hydride led to the desired product in moderate yield with consistently high enantioselectivity (entry 10).

Encouraged by the good results illustrated in Table 2, we applied this catalytic methodology to formal C−C insertion reactions with a range of substituted benzaldehydes. Since the 4-bromo group in the product of entry 4 in Table 2 is easily replaced by a large variety of other substituents using Pd(0) catalysis, methyl α-4-bromobenzyl diazoester was selected as the coupling partner.

As summarized in Table 3, although the electronic properties of the aryl aldehydes varied significantly, the reactions produced

**Table 3. Asymmetric Formal Insertion of Diazoesters into Various Aryl-CHO Bonds**[a]




| entry | 2 | $R^2$ | $R^3$ | 2:3[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|---|---|
| 1 | **2e** | 4-BrBn | Ph | 80:20 | 75 | 97 |
| 2 | **2l** | 4-BrBn | 4-BrPh | 88:12 | 82 | 97 |
| 3[e] | **2m** | 4-BrBn | 4-MeOPh | 70:30 | 65 | 95 |
| 4 | **2n** | 4-BrBn | 4-MePh | 86:14 | 82 | 98[f] |
| 5 | **2o** | 4-BrBn | 3-MePh | 83:17 | 80 | 98 |
| 6 | **2p** | 4-BrBn | 4-$CF_3$Ph | 72:28 | 55 | 92 |
| 7[e] | **2q** | 4-BrBn | 2-Furyl | 69:31 | 64 | 94 |
| 8[e] | **2r** | 4-BrBn | 2-Thienyl | 70:30 | 67 | 98 |
| 9 | **2s** | 4-BrBn | 1-Naph | 84:16 | 80 | 99 |
| 10 | **2t** | 4-BrBn | 2-Naph | 87:13 | 83 | 98 |
| 11 | **2u** | Bn | 4-BrPh | 81:19 | 78 | 97 |
| 12 | **2v** | Allyl | 3-MeOPh | 66:34 | 63 | 94[g] |

[a]The reaction of diazoester (0.27 mmol) with aldehyde (0.32 mmol) was performed in the presence of **1d** (20 mol %), in propionitrile (1.0 mL) at −95 °C. [b]Determined by $^1$H NMR analysis of the crude reaction mixture. [c]Isolated yield of **2** after silica gel chromatography at −40 °C. [d]The ee of **2** was determined by chiral HPLC. [e]The reaction was performed at −50 °C. [f]The absolute configuration was assigned as *R* by conversion to the hydrazone and X-ray analysis. [g]The absolute configuration was assigned as *R* by conversion to the known carboxylic acid. For details see the Supporting Information.

the corresponding quaternary aldehydes **2** in good yields and regioselectivities with excellent enantioselectivities (entries 1−8, 11, and 12). It is notable that large naphthyl rings can effectively migrate in the selective formal C−C insertion process to give good results (entries 9 and 10). Reaction of an allyl substituted diazoester with *meta*-anisaldehyde provided **2v**, an important intermediate in the synthesis of bioactive pyrrolidinones, in moderate yield and excellent enantioselectivity (entry 12).[8] The absolute configuration of the newly generated all-carbon quaternary stereocenter was confirmed unambiguously by X-ray crystallographic analysis after transformation of **2n** to the corresponding hydrazone.

The observed stereochemistry for the asymmetric formal C−C insertion reaction using oxazaborolidinium ion catalyst **1d** can be rationalized using the transition state model shown in Figure 1. The mode of coordination of benzaldehyde to **1d** is the same as has been previously observed in enantioselective

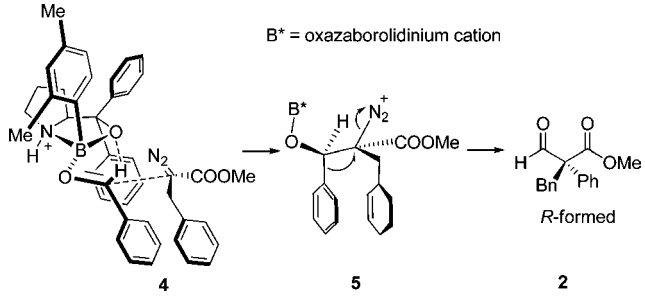



**Figure 1.** Transition state model for the asymmetric formal C−C insertion of α-benzyl diazoester into Ph−CHO catalyzed by **1d**.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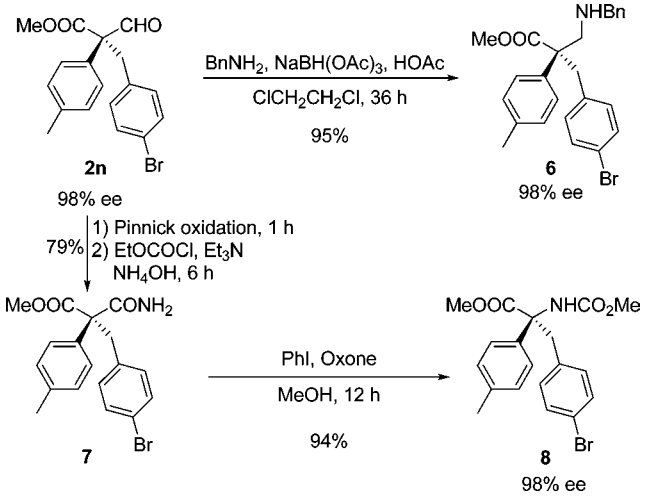
cyanosilylation,[9a] 1,3-dipolar cycloaddition,[9b] cyclopropanation,[9c] and Roskamp reactions.[4c] In the pre-transition-state assembly **4**, shown in Figure 1, the aldehyde group is situated above the phenyl group, which effectively shields the *re* face (back) from attack by the diazoester. Because of the dipole−dipole interaction between the two carbonyl groups, the diazoester approaches the aldehyde group for nucleophilic addition with the ester group situated away from the aldehyde group. Meanwhile, an apparent $\pi-\pi$ interaction between the aryl ring of the aldehyde with the diazoester aryl group holds the two aryl rings together.[10,11] Thus, nucleophilic addition of the diazoester from the *si* face (front) of the aldehyde is facilitated, leading to intermediate **5**. Chemoselective phenyl ring migration with loss of nitrogen provides the quaternary aldehyde *R*-**2** as the major enantiomer.[12]

Further chemical transformations of the resulting optically active all-carbon quaternary aldehyde are illustrated in Scheme 2. Reductive amination of **2n** with sodium triacetoxyborohydride[13] led to the highly optically enriched $\beta$-benzyl amino ester **6** that bears an all-carbon quaternary center.[14] Similarly, oxidation of **2n** with buffered $NaClO_2$[15] followed by amidation[16] gave methyl amide-ester **7**. Hoffmann rearrangement[17] of **7** provided the $\alpha$-quaternary amino acid precursor **8** with retention of ee.[18]

**Scheme 2. Application of Oxazaborolidinium Ion Catalyzed Asymmetric Formal Insertion of Diazoesters into Aryl-CHO Bond**




In summary, the first example of a highly enantiocontrolled catalytic formal C−C insertion of diazoesters into aromatic aldehydes was developed to give functionalized acyclic all-carbon $\alpha$-quaternary aldehydes in good yields and excellent enantioselectivities. The resulting aldehydes can easily be converted into optically active $\alpha$- and $\beta$-amino esters without loss of optical purity. The absolute configuration of the product was the same as predicted by the transition state model in Figure 1. We believe the resulting densely functionalized optically active quaternary stereogenic carbon center bearing compounds could be highly valuable and versatile intermediates for further transformations.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, full analytical data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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