Catalyst Controlled Site- and Stereoselective Rhodium(II) Carbene C(sp^3)-H Functionalization of Allyl Boronates.

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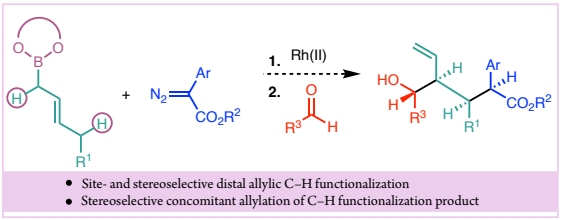


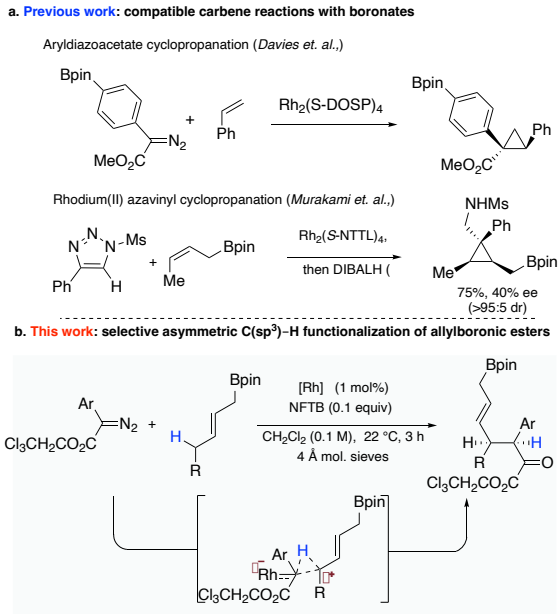
ABSTRACT: Rhodium(II) catalyst-controlled site- and stereoselective carbene insertion into the distal allylic C(sp^3)–H bond of allyl boronates is reported. The optimum chiral catalyst for this reaction is Rh$_2$(*S*-TPPTTL)$_4$. The fidelity and asymmetric induction of this catalytic transformation allows for a highly diastereoselective and enantioselective C–C bond formation without interference from the allyl boronate functionality. The resulting functionalized allyl boronates are susceptible to stereoselective allylations, generating products with control of stereochemistry at four contiguous stereogenic centers.

Allylboronic acid derivatives are useful allylation reagents, capable of reacting with a variety of electrophilic substrates in a stereoselective manner.[1] One of the most significant of these transformations is the allylation of aldehydes, which can be used to generate products with two new stereocenters in a highly diastereoselective manner.[2-7] Either chiral auxiliaries[8-13] or chiral catalysts[14-21] can achieve high levels of asymmetric induction. We have recently examined various substrates for enantioselective catalyst-controlled intermolecular C–H functionalization by means of donor/acceptor carbene-induced C–H insertion.[22-31] In this study we examined the use of allylboronates as substrates for the carbene C–H functionalization and determined whether the resulting elaborate allyl boronates can then be used in stereoselective allylation reactions.

Many synthetically useful reactions have been developed involving the reactions of transient metal carbenes with boron compounds. Representative examples include rhodium-catalyzed α-arylation and α-vinylation of rhodium(II) azavinyl carbenes derived from *N*-sulfonylimines,[32] copper-catalyzed cross-coupling reactions between allylboronic acids and α-diazo carbonyls,[33] and B–H insertion reactions.[34, 35] In contrast, there are relatively few examples in which the boron functionality is compatible in the carbene chemistry and remains unchanged.[36] Davies and co-workers showed pinacolborane-functionalized aryldiazoacetates are viable substrates for carbene reactions (Scheme 1).[37] Murakami and coworkers reported a highly efficient and stereoselective cyclopropanation of allyl pinacolboranes using *N*-mesyltriazoles as carbene precursors.[38] In this study we describe the stereoselective and site-selective carbene insertion into C(sp^3)–H bonds of allyl boronic esters and demonstrate that the highly functionalized allylboronates can be employed in a subsequent allylation reaction.

The first stage of the study explored whether allylboronic acid derivatives were viable substrates for C–H functionalization with rhodium carbene intermediates. A catalyst screen using the pinacoloboron derivative **1** as substrate with the standard trichloroethyl aryldiazoacetate **2**[23] was conducted (Table 1). All the standard chiral catalysts resulted in site selective reactions at the distal allylic position to the boron functionality to form **3**. Presumably, the electron-withdrawing nature of the boronate group blocks C–H functionalization at the proximal allylic position.

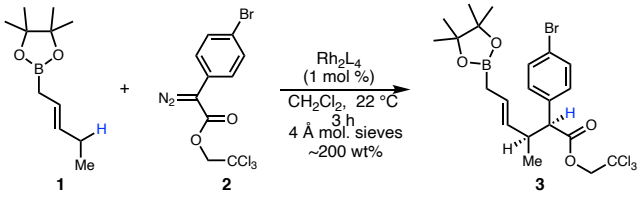
Scheme 1. Carbene reactions with boron compounds



The diastereoselectivity of the reaction was dependent on the catalyst. Our original chiral catalyst, Rh_2(*R*-DOSP)$_4$ gave a 3.6:1 d.r. and many of the newer catalysts gave even worse results (entries 1-5). Rh_2(*S*-TPPTTL)$_4$ was the only catalyst that gave a good diastereomeric ratio of **3** (9.6:1 d.r.) and it also resulted in reasonable levels of enantioinduction (80% ee) (entry 6).[39] Recently, Rh_2(*S*-TPPTTL)$_4$ has been shown to give enhanced enantioselectivity when HFIP or NFTB was used as an additive.[28, 40, 41] Conducting the reaction with either additive (0.1 equiv) increased the enantioselectivity to 92-93% ee (entries 7 and 8). Modifying the temperature of the reaction was not beneficial as the yield dropped at lower temperatures and the stereoselectivity dropped at higher temperatures (see SI for complete details).

With the optimized catalyst in hand, we set to investigate the asymmetric Rh_2(*S*-TPPTTL)$_4$ catalyzed carbene C(sp^3)–H functionalization with a range of allyl boronic esters **4-8** (Scheme 2). In addition to the reactions at 2° sites, the reactions could be conducted at 1° sites, as illustrated in the formation of **9** and **10**, and tertiary allylic sites as seen with **11**. In each case, the enantioselectivity was relatively constant, between 93-95% ee. The formation of **10** illustrates the influence of steric control because the substrate has two allylic methyl groups but only the trans methyl group is functionalized.

Table 1. Catalyst optimization studies



Entry	L	% yield[b]	r.r.[c]	d.r.[c]	% ee[d]
1	*R*-DOSP	89	>98:2	3.6:1	---
2	S-*p*-BrTPCP	76	>98:2	2.7:1	---
3	*S*-2-Cl-5-BrTPCP	82	>98:2	1.5:1	---
4	*R*-PTAD	65	>98:2	1:1	---
5	*R*-TCPTAD	74	>98:2	3:1	---
6	*S*-TPPTTL	95	>98:2	9:1	80
7[e]	*S*-TPPTTL	62[g]	>98:2	8:1	92
8[f]	*S*-TPPTTL	54[g]	>98:2	9:1	93

[(a)]Reaction conditions: **1** (0.6 mmol), **2** (0.2 mmol), [Rh] catalyst (1 mol %), 3 h reaction time. [(b)]combined NMR yield of **3** and its diastereomer. [(c)]determined by crude NMR analysis. [(d)]determined by chiral HPLC analysis of the isolated major product **3**. [(e)]0.1 equiv of HFIP (hexafluoro isopropanol). [(f)]0.1 equiv of NFTB (nonafluoro-*tert*-butyl alcohol). [(g)]*Isolated* yield of the major diastereomer **3**.

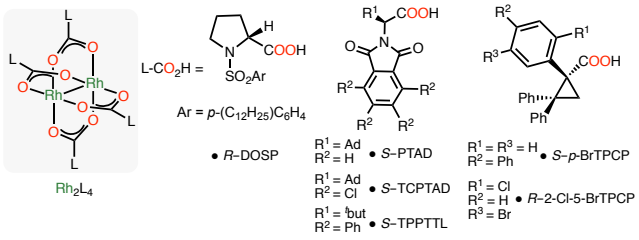
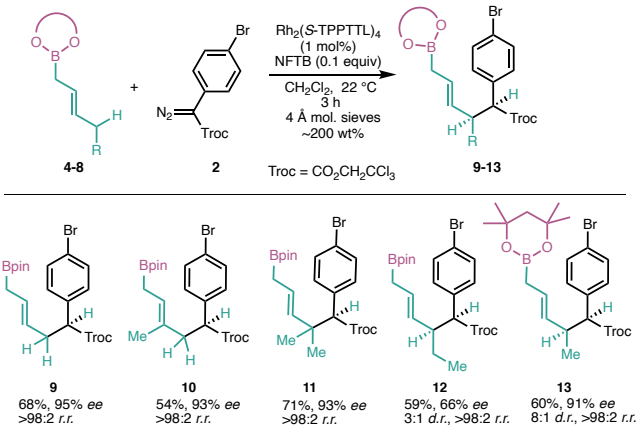


Figure 1. Selected catalysts for optimization

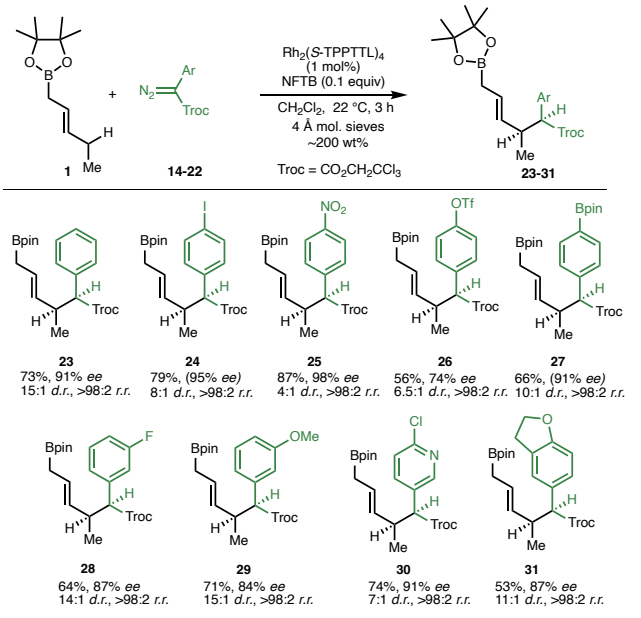
Scheme 2. Scope of allyl boronic esters[a]



Allyl boronates with a longer alkyl chain generate the desired product **12** but the enantioselectivity (66% ee) and diastereoselectivity (3:1 d.r.) are considerably inferior. A brief study was also conducted to examine the influence of the boronate. As the boronate is well away from the site of C–H functionalization, it should have limited influence on the stereochemical outcome of the reaction and indeed **13** was formed with similar stereocontrol as was seen for the pinacolonate **3**. Catecholborane, however, was not an effective substrate for this reaction because the monosubstituted aryl ring in catechol borane is prone to cyclopropanation.

The study to date has been conducted on *p*-bromophenyldiazoacetate **2** but the reaction can be extended to a range of other aryldiazoacetates (**14-22**) as illustrated in the formation of **23-31** (Scheme 3). In most instances, the enantioselectivity of the reaction was >85% ee. However, there were some distinctive trends in the diastereoselectivity. Electron deficient substituents at the para position caused a drop in diastereoselectivity, as seen in the formation of the nitro derivative **26**, (4:1 d.r.) but it was formed with highest level of enantioselectivity (98% ee). Aryldiazoacetates with meta-substituents enhance the diastereoselectivity, with the methoxy derivative

Scheme 3. Scope of aryldiazoacetates[a]

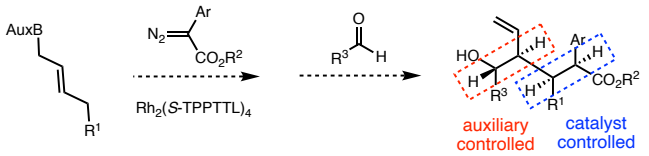


For **24** and **27**, the ee values should be considered as estimates because the signals were not fully resolved by chiral HPLC

29 giving the best result (15:1 d.r.). The compatibility of the current approach with heteroaryldiazoacetates was tested with carbene precursors containing pyridine functionality as well as dihydrobenzofuran. In both cases, the products **30** and **31**, were formed uneventfully with respectable levels of stereocontrol.

One of the most useful applications of allyl boronates is in stereoselective allylations of aldehydes. Typically, the reaction proceeds through a chair-like transition state leading to excellent diastereocontrol.[9] When chiral allylboronates are used, highly enantioselective reactions can be achieved.[11, 12] Therefore, we decided to explore whether the two stereogenic centers generated in the C–H functionalization steps can be followed by a stereoselective allylation to generate products with four contiguous stereogenic centers (Scheme 4). Also, we wished to determine whether the two chiral influences would operate independently of each other, in which case, the chiral catalyst would control two stereogenic centers and the chiral auxiliary on the boronate would control the other stereogenic centers.

Scheme 4. Proposed synthesis of four stereogenic centers



The α-pinene-derived auxiliary developed by Brown[13, 42-47] and others[7, 48, 49] was used in the study because it has been shown to cause high asymmetric induction in the allylation step and was expected to be compatible with the rhodium(II) carbene reaction. The asymmetric induction in Rh_2(TPPTTL)$_4$-catalyzed C–H functionalization of **32** was controlled by the catalyst (Scheme 5). Both Rh_2(*S*-TPPTTL)$_4$ and the Rh_2(*R*-TPPTTL)$_4$-catalyzed reactions were highly stereoselective. In the Rh_2(*S*-TPPTTL)$_4$-catalyzed reactions, the isomer ratio for the two newly generated stereogenic centers was 9:76:3:12 d.r. and the asymmetric induction was 88:12 (peaks 2 and 4 versus peaks 1 and 3). Very similar stereochemical results were obtained in the Rh_2(*R*-TPPTTL)$_4$-catalyzed reaction to form **36** (76:12:10:2 d.r.) with an asymmetric induction of 86:14 (peaks 1 and 3 versus peaks 2 and 4). Thus, the chiral auxiliary has little influence on the asymmetric induction generated by the catalyst during the C–H functionalization.

The allyl boronate **33** was then applied to the allylation of benzaldehyde to form the homoallylic alcohol **34** which has four contiguous stereogenic centers in 53% isolated yield and excellent enantioselectivity (91% ee). The ratio of the two major diastereomers in **34** was 24:1 d.r. The shielding effect of the phenyl rings in the NMR allowed a tentative assignment of the major diastereomer as drawn. (see supporting information for details) Confirmation of this assignment was made by conversion of the major diastereomer of **34** to lactone **35** (75% yield), which generated suitable single crystals for an X-ray crystallographic determination of the relative and absolute stereochemistry. A similar allylation with **36** was expected to generate a different major diastereomer to **34**. The NMR of the resulting product **37**, however, was identical to **34**, leading to an initial tentative assignment of **37** as the enantiomer of **34**. This was subsequently confirmed by converting the major diastereomer of **37** to lactone **38**, which was shown by single crystal X-ray crystallography to be the lactone enantiomer of **35**.

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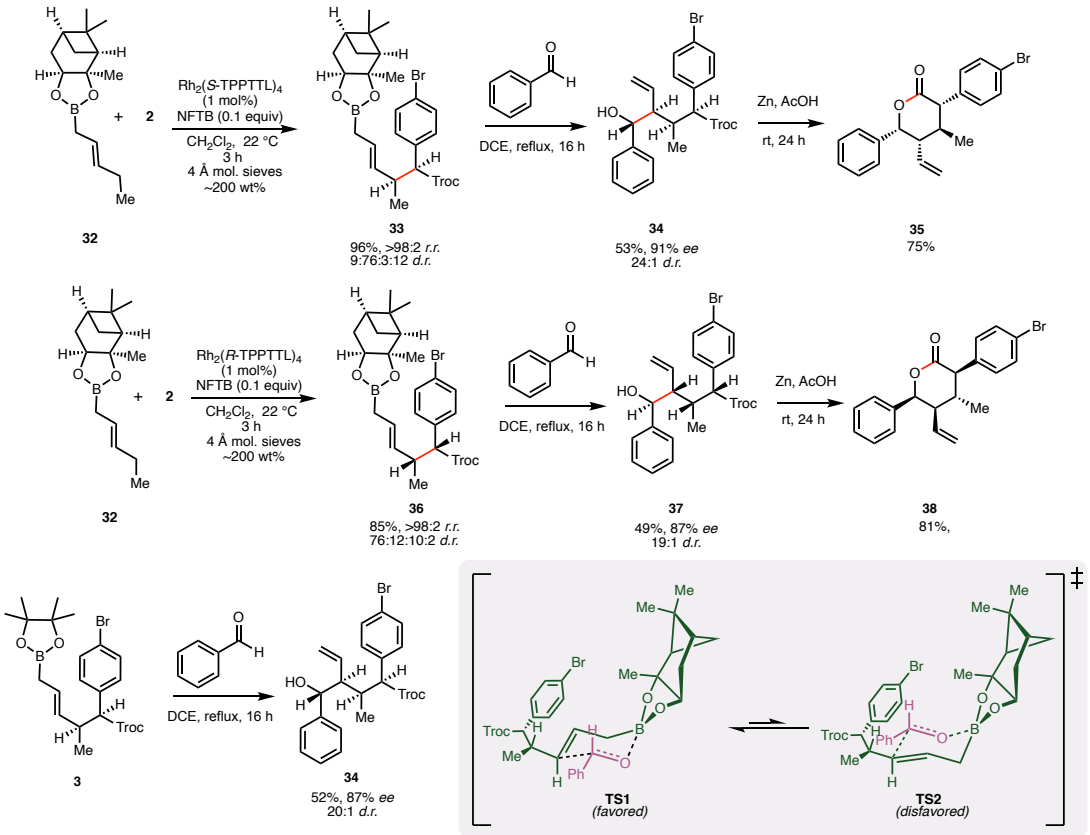
Scheme 5. Allylation of C–H functionalization product



These results indicate that the stereochemistry of the two newly formed stereogenic centers during allylation was controlled by the configuration of the two stereogenic centers generated by the C–H functionalization. The boron chiral auxiliary played virtually no role in the stereochemical outcome of the allylation. To test this hypothesis, the allylation of benzaldehyde was conducted on the pinacolone boronate **3**, lacking a chiral auxiliary. The reaction gave rise to **34** with control of the relative stereochemistry at the four stereogenic centers in a similar way to the outcome with the chiral auxiliary

These results demonstrate that stereogenic centers at the distal allylic position in allyl boronic esters are able to exert excellent stereocontrol on the allylation. Even though extensive studies on the stereoselectivity of allylation with allyl boronates have been conducted,[50, 51] relatively few examples have been reported with stereogenic centers adjacent to the distal allyl group relative to the boron functionality,[52] presumably because such chiral allyl boronates would not be readily accessible. A reasonable explanation for the stereocontrol is illustrated in the presumed chair-like transition state of the allylation.[1, 53] The bulky group would be aligned *anti-* to the allyl group and then there is competition for attack on the side of the methyl group or the hydrogen. A chair transition state with the benzaldehyde approaching on the side of the hydrogen (**TS1**) is consistent with the observed stereochemical outcome.

In conclusion these studies demonstrate that allylic C–H functionalization of allyl boronates with aryldiazoacetates at the distal allylic position to the boronate is a favorable process. The optimized catalyst, Rh_2(*S*-TPPTTL)$_4$ is capable of functionalizing 1°, 2° and 3° C–H bonds with good enantiocontrol. Furthermore, in the case of 2° C–H functionalization, good diastereocontrol is also possible. The resulting chiral allylboronates can undergo allylation of benzaldehyde to generate a product with four contiguous stereogenic centers. The asymmetric induction in the allylation is controlled by the two stereogenic centers generated in the C–H functionalization step. These studies further demonstrate the versatility of the dirhodium-catalyzed C–H functionalization by donor/acceptor carbenes and illustrate how the corresponding products can be applied to even more elaborate synthetically useful products.

ASSOCIATED CONTENT

Accession Codes

The following crystal structures have been deposited in the Cambridge Crystallographic Data Centre: **35** (CCDC 2206542), **38** (CCDC 2204183). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 902 1223 336033.

Data Availability: The data underlying this study are available in the published article and its online supplementary material.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Complete experimental procedures and compound characterization are available in the Supporting Information. (PDF).

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Notes

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