Asymmetric Catalysis

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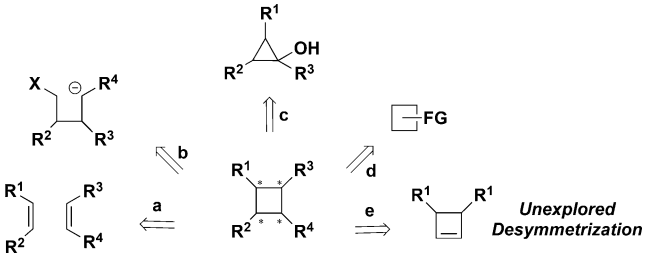
# Enantioselective Synthesis of Cyclobutylboronates via a Copper-Catalyzed Desymmetrization Approach

*Manuel Guisán-Ceinos[+], Alejandro Parra[+], Víctor Martín-Heras, and Mariola Tortosa**

***Abstract:*** *The first catalytic enantioselective synthesis of cyclobutylboronates, by using a chiral copper(I) complex, is reported. A broad variety of cyclobutanes have been prepared with consistently high levels of diastereo- and enantiocontrol. Moreover, this method constitutes the first report of an enantioselective desymmetrization of meso-cyclobutenes to prepare chiral cyclobutanes.*

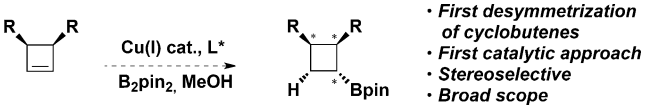
Cyclobutanes are prevalent structures in a large number of natural products, and important synthetic intermediates due to their rich chemistry.[1] Additionally, they have attracted considerable attention in drug discovery mostly due to their structural rigidity.[2] Consequently, the development of asymmetric methods for the preparation of chiral cyclobutanes has become an important goal in chemical synthesis. A number of catalytic enantioselective approaches have been developed toward this aim (Scheme 1) including [2+2] cycloadditions




***Scheme 1.*** General approaches for the catalytic enantioselective formation of cyclobutanes.

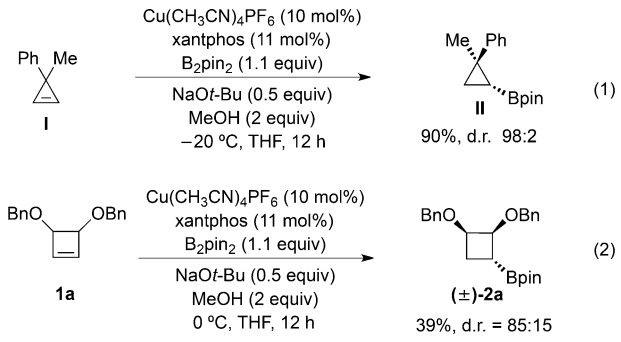
(approach a),[3] acyclic ring closures (approach b),[4] catalytic Wagner–Meerwein shifts of cyclopropanols[5] (approach c) and direct functionalization of cyclobutanes or activated cyclobutenes (approach d).[6] In this context, the enantioselective functionalization of the double bond in prochiral *meso*-cyclobutenes (approach e) could provide a direct way to prepare chiral cyclobutanes with up to four contiguous stereocenters. Surprisingly, this approach remains almost entirely unexplored.[7]

As part of our interest in unconventional C–B bond formation,[8] we intended to accomplish this novel desymmetrization (approach e, Scheme 1) in the context of an unmet challenge in chemical synthesis: the preparation of non-racemic cyclobutylboronates (Scheme 2). Despite their synthetic versatility, there are no examples of enantioselective catalytic methods for their preparation in the literature.[9] The only two examples reported for the synthesis of enantiomerically enriched cyclobutyl boronic esters require the use of stoichiometric amounts of a chiral inductor and are structurally limited.[10] Therefore, the development of a general catalytic enantioselective method is highly desirable. We envisioned using a cyclobutene, a chiral copper(I) complex and a diboron compound to accomplish this goal.[11]




***Scheme 2.*** Copper-catalyzed enantioselective synthesis of cyclobutylboronates.

At the outset of the project, we were encouraged by the excellent results previously observed in the desymmetrization of cyclopropenes [Scheme 3, Eq. (1)].[8c] However, the difference in ring strain and the presence of two prochiral stereocenters instead of one, made it non-obvious that we could achieve similar results in the case of cyclobutenes. Indeed, clear differences in reactivity and stereoselectivity were observed when cyclopropene **I** and cyclobutene **1a** were treated under similar copper-catalyzed borylation conditions using a non-chiral ligand (Scheme 3). Although far from optimal, this preliminary result showed the feasibility of the borylation in cyclobutenes (not previously reported) and encouraged us to pursue an enantioselective version.




***Scheme 3.*** Preliminary results using a non-chiral ligand.

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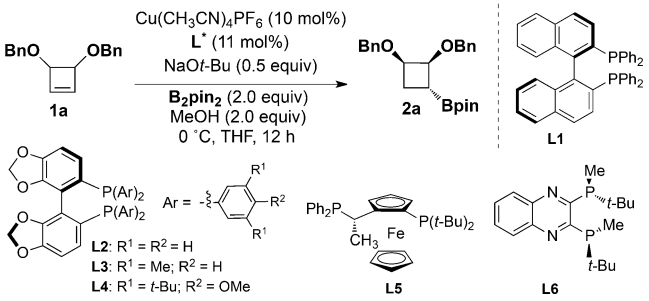
We next examined the copper-catalyzed borylation of cyclobutene **1a** in the presence of a variety of chiral phosphines (Table 1). Cyclobutene **1a** was treated in THF,

***Table 1:*** Reaction optimization.[a]



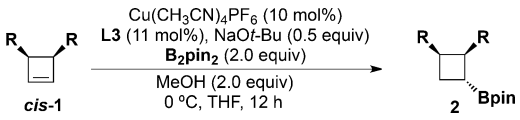

| Entry | L* | Change in other parameters | d.r.[b] | e.r.[c] | Yield [%][d] |
|---|---|---|---|---|---|
| 1[a] | **L1** | – | 93:7 | 96:4 | 76 |
| 2[a] | **L2** | – | >98:2 | 94:6 | 93 |
| ***3***[a] | ***L3*** | **–** | ***>98:2*** | ***99:1*** | ***96*** |
| 4[a] | **L4** | – | >98:2 | 96:4 | 90 |
| 5[a] | **L5** | – | 95:5 | 15:85 | 84 |
| 6[a] | **L6** | – | 90:10 | 82:18 | 81 |
| 7 | **L3** | using KO*t*-Bu | 80:20 | 99:1 | 81 |
| 8 | **L3** | using NaOMe | 80:20 | 98:2 | 44 |
| 9 | **L3** | using CuCl | 94:6 | 98:2 | 90 |
| 10 | **L3** | 5 mol% $Cu^{I}$ | 90:10 | 95:5 | 70 |
| 11 | **L3** | 1.1 equiv $B_2pin_2$ | >98:2 | 99:1 | 60 |

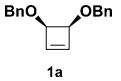
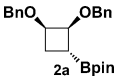
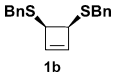
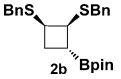
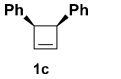
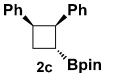
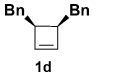
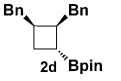
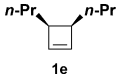
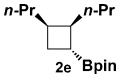
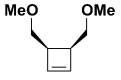
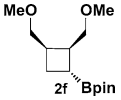
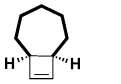
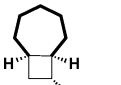
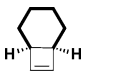
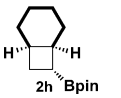
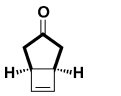
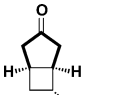
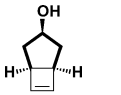
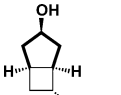
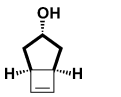
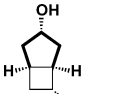
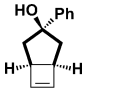
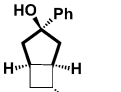
[a] Reaction conditions: **1** (0.1 mmol), $B_2pin_2$ (0.20 mmol), NaO*t*-Bu (50 mol%), $Cu(CH_3CN)_4PF_6$ (10 mol%), **L** (11 mol%), MeOH (0.2 mmol), THF (0.2 M). [b] d.r. determined by $^1$H-NMR analysis. [c] e.r. determined by chiral SFC. [d] Yield of isolated **2a**.

at 0 °C, with $Cu(CH_3CN)_4PF_6$ (10 mol%), $B_2pin_2$ (2 equiv), NaO*t*-Bu (0.5 equiv), MeOH (2 equiv) and 10 mol% of a chiral ligand (Table 1, entries 1–6). Segphos derivatives **L2**–**L4** were identified as the optimal ligands to obtain the best balance between diastereo- and enantiocontrol. For cyclobutane **1a**, (*R*)-DM-Segphos was the ligand of choice, providing cyclobutylboronate **2a** in 96% isolated yield and with almost perfect stereocontrol (Table 1, entry 3, d.r. ≥ 98:2, e.r. = 99:1). With KO*t*-Bu or NaOMe the diastereoselectivities and yields were significantly reduced (Table 1, entries 7 and 8). CuCl provided comparable results although the diastereomeric ratio was slightly lower than using $Cu(CH_3CN)_4PF_6$ (Table 1, entry 9). When the reaction was carried out in the presence of 5 mol% of copper salt, we observed the formation of **2a** with inferior results (Table 1, entry 10). Finally, using 1.1 equivalents of $B_2pin_2$, compound **2a** was obtained with excellent stereocontrol but in only 60% yield (Table 1, entry 11).

With the optimal conditions in hand, we next explored the scope of the method (Table 2). When we applied the optimal conditions (Table 1, entry 3) to cyclobutane **1b** (R = SBn) we observed the formation of **2b** with excellent stereocontrol (d.r. ≥ 98:2, e.r. = 99:1) but low yield (22%, not shown in Table 2). We reasoned that the low yield could be due to coordination of the copper catalyst to the sulfur atoms and

***Table 2:*** Substrate scope.




| Entry[a] | 1 | 2 | d.r.[c] | e.r. | Yield [%][b] |
|---|---|---|---|---|---|
| 1 |  |  | ≥98:2 | 99:1[d] | 96 |
| 2[g] |  |  | ≥98:2 | 99:1[d] | 52 |
| 3 |  |  | ≥98:2 | 97:3[d] | 70 |
| 4[h] |  |  | ≥98:2 | 96:4[e] | 91 |
| 5[h] |  |  | ≥98:2 | 97:3[e] | 85 |
| 6[h] |  |  | ≥98:2 | 97:3[e] | 93 |
| 7[h] |  |  | ≥98:2 | 97:3[e] | 78 |
| 8[h] |  |  | ≥98:2 | 96:4[e] | 95 |
| 9 |  |  | ≥98:2 | 96:4[e] | 91 |
| 10[h] |  |  | ≥98:2 | 97:3[f] | 73 |
| 11[h] |  |  | ≥98:2 | 97:3[f] | 76 |
| 12 |  |  | ≥98:2 | 98:2 | 91 |

[a] Reaction conditions: **1** (0.2 mmol), $B_2pin_2$ (0.4 mmol), NaO*t*-Bu (50 mol%), $Cu(CH_3CN)_4PF_6$ (10 mol%), **L** (11 mol%), MeOH (0.4 mmol), THF (0.2 M). [b] Yield of isolated **2**. [c] d.r. determined by $^1$H NMR analysis. [d] e.r. determined by chiral SFC or HPLC. [e] e.r. determined by chiral SFC or HPLC previous oxidation of the C–B bond. [f] e.r. determined by SFC or HPLC previous benzoylation of the alcohol. [g] **L4** was used instead of **L3**. [h] The reaction was carried out at −20 °C.

that this coordination could be minimized with a bulkier ligand. In fact, when we used (*R*)-DTBM-Segphos (**L4**) instead of **L3**, compound **2b** was obtained with an improved 52% yield (Table 2, entry 2), maintaining the diastero- and enantioselective ratios. Compound **2c**, with two aromatic

susbtituents, was also prepared in high yield and excellent stereoselectivity (Table 2, entry 3, d.r. ≥ 98:2, e.r. = 99:1). Cyclobutenes **1d** (R = Bn) and **1e** (R = *n*-Pr), bearing alkyl groups with different steric hindrance, afforded cyclobutanes **2d** and **2e** as single diastereomers with 96:4 (entry 4) and 97:3 (entry 5) e.r. values, respectively. We were also pleased to find that alkyl substituents with coordinating alkoxy groups did not alter the yield or the stereoselectivity of the reaction (Table 2, entry 6, d.r. ≥ 98:2, e.r. = 97:3).

We were then interested in testing the copper-catalyzed desymmetrization in bicyclic cyclobutenes (Table 2, **1g**–**1l**). The catalytic system was robust for the preparation of [5.2.0] (compound **2g**), [4.2.0] (compound **2h**) and [3.2.0] bicycles (compounds **2i**–**2l**). For all cases we observed high yields and nearly perfect diastereo- and enantioselectivities. Remarkably, the conditions are compatible with the presence of an unprotected ketone (compound **2i**) that could also react under copper-catalyzed borylation conditions.[13] Diastereomeric cyclobutenes **1j** and **1k** afforded the desired boronic esters **2j** and **2k** with similar levels of stereocontrol. Additionally, the presence of a tertiary stereocenter (compound **2l**) affected neither the diastereo- nor enantioselectivity. In these last three examples (**2j**–**2l**), enantiomerically enriched compounds with four stereocenters were obtained in a single step starting from *meso* precursors (**1j**–**1l**).

The absolute configuration of the products was established from single-crystal X-ray crystallography of *p*-bromobenzoates **3** and **4**, prepared from **2c** and **2l** by C–B bond oxidation followed by benzoylation (Figure 1).[14] The X-ray structures indicate that the C–B bond formation always takes place *anti* to the substituents in the cyclobutene ring and selectively through the *re*-face.

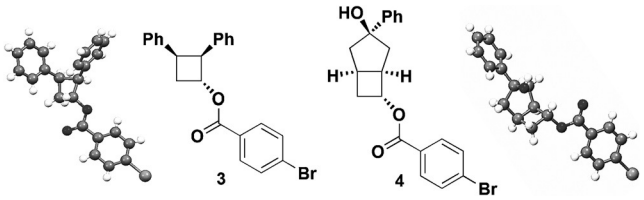
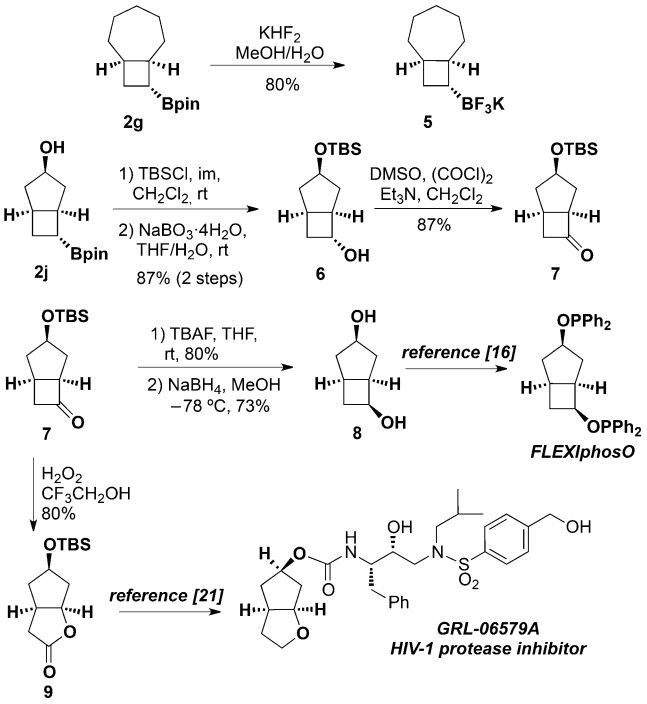



***Figure 1.*** Determination of the absolute configuration.

To demonstrate the synthetic versatility of the products, we have converted them into a variety of useful intermediates (Scheme 4). First, we were interested in the transformation of the pinacol ester moiety into trifluoroborate salts, which have been successfully used as partners in cross-coupling reactions.[15] Gratifyingly, boronic ester **2g** was smoothly transformed into trifluoroborate salt **5** in good yield. We have also prepared enantiomerically enriched cyclobutanone **7** in three steps (protection-double oxidation) from boronic ester **2j**. As shown is Scheme 4, bicycle [3.2.0] ketones such as **7** are versatile intermediates for the preparation of valuable compounds. Deprotection of the hydroxy group in **7**, followed by diastereoselective reduction of the carbonyl group afforded diol **8**. Compound **8** is the precursor of chiral ligand FlexiphosO,[16] which has been reported as a useful ligand in




***Scheme 4.*** C–B bond functionalization.

rhodium-catalyzed asymmetric hydrogenations[17] and palladium 1,6-diene cycloisomerizations.[18] It should be pointed out that our approach represents the first catalytic enantioselective synthesis of diol **8**.[17a,18a] Additionally, ketone **7** can be transformed into Corey's lactone[19] derivative **9** through a regioselective Baeyer–Villiger oxidation.[20] The sequence described in Scheme 3 represents a novel approach for the enantioselective synthesis of compound **9**, which is an intermediate in the preparation of the HIV-1 protease inhibitor GRL-06579A.[21]

In summary, we have developed the first catalytic enantioselective synthesis of cyclobutylboronates, catalyzed by a chiral phosphine-copper(I) complex. The method provides access to a wide range of cyclobutylboronates, with three stereogenic centers, in high yields and with excellent stereocontrol. Functionalization of the C–B bond provides valuable synthetic intermediates. Moreover, this method constitutes the first report of an enantioselective desymmetrization of *meso*-cyclobutenes to prepare chiral cyclobutanes.

## Acknowledgements

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**Keywords:** asymmetric catalysis · boron · copper · cyclobutanes · cyclobutenes

  

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