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Directed Rh(I)-Catalyzed Asymmetric Hydroboration of Prochiral 1-Arylcycloprop-2-ene-1-carboxylic Acid Derivatives

Andrew Edwards,[a] Marina Rubina,[a,b] and Michael Rubin*[a,c]

Abstract A full account on rhodium-catalyzed asymmetric, directed hydroboration of functionalized prochiral cyclopropenes affording enantiomerically enriched cyclopropylboronates is reported. The scope and limitations of two alternate directing groups, ester and carboxamide, are evaluated. It was found that hydroboration of esters appeared to be more sensitive to substitution in the aromatic ring of the substrates. Specifically, *ortho*-halogens were detrimental for diastereo- and enantioselectivity, potentially, due to additional coordination with rhodium. In contrast, more Lewis-basic amide directing groups allowed for stronger chelation to the transition metal, leading to consistently high diastereo- and enantioselectivity in hydroboration across a broader range of substrates.

Introduction

Chiral cyclopropanes are found in a variety of natural products[1,2] and medicinal agents,[3] and are also highly sought-after synthons and ligands for organic synthesis[4] and asymmetric catalysis.[5] Such scaffolds are typically assembled via diastereoselective 1,3-ring closures[6] or asymmetric cyclopropanation reactions.[7,8] Another less established, but potent method involves a chemo- and diastereoselective installation of additional substituents into a pre-formed chiral or prochiral cyclopropane.[9] The strain release-driven addition of different entities to cyclopropenes has emerged as a unique tool that allows for assembly of chiral cyclopropane scaffolds with complementary substitution patterns.[10] Several research groups contributed their work to the development of synthetic methodologies exploiting ring-retentive, metal-catalyzed[11] and organocatalytic[12] stereoselective additions of various reagents to cyclopropenes en route to chiral cyclopropanes. We previously communicated a first example of the carboxylate-directed asymmetric Rh-catalyzed hydroboration of prochiral 3,3-disubstituted cyclopropenes to produce enantiomerically enriched cyclopropylboronic esters.[13] Herein, we demonstrate the use of a carboxamide function as an alternative, superior directing group and provide insight into the origins of diastereo- and enantioselectivity of this transformation.

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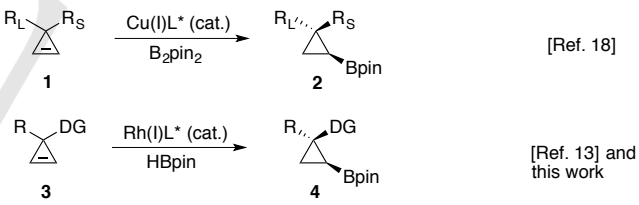
Results and Discussion

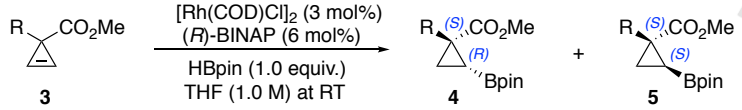
Cyclopropylboronic acid derivatives are primarily employed as stable, but reactive surrogates of cyclopropyl nucleophile. Cyclopropylboronates are normally obtained via a reaction of trialkylborates with cyclopropylmetal derivatives,[14] 1,3-cyclization of acyclic boronate precursors,[15] or [1+2]-cycloaddition of carbenoid species to vinylboronates.[16] There are only a handful of examples exploiting non-catalyzed hydroboration of the smallest cyclic olefins to obtain these useful synthons.[17] Two reports, succeeding our communication,[13] were published independently by the Tian and Lin, and Tortosa groups, showcasing copper-catalyzed formal hydroboration of cyclopropenes **1**.[18] This reaction was reported as a non-directed process, in which the facial selectivity was governed by a steric effect to install the boronate moiety *trans* to the largest substituent R_L (Scheme 1). This was in contrast to our Rh-catalyzed methodology that utilized a directing group (DG, typically an ester function) in substrate **3**, to furnish sterically hindered *cis*-substituted cyclopropyl boronates **4** (Scheme 1). A strong directing effect was also required, although not sufficient, to obtain high degrees of enantioselectivity in this reaction.[13]



Scheme 1.

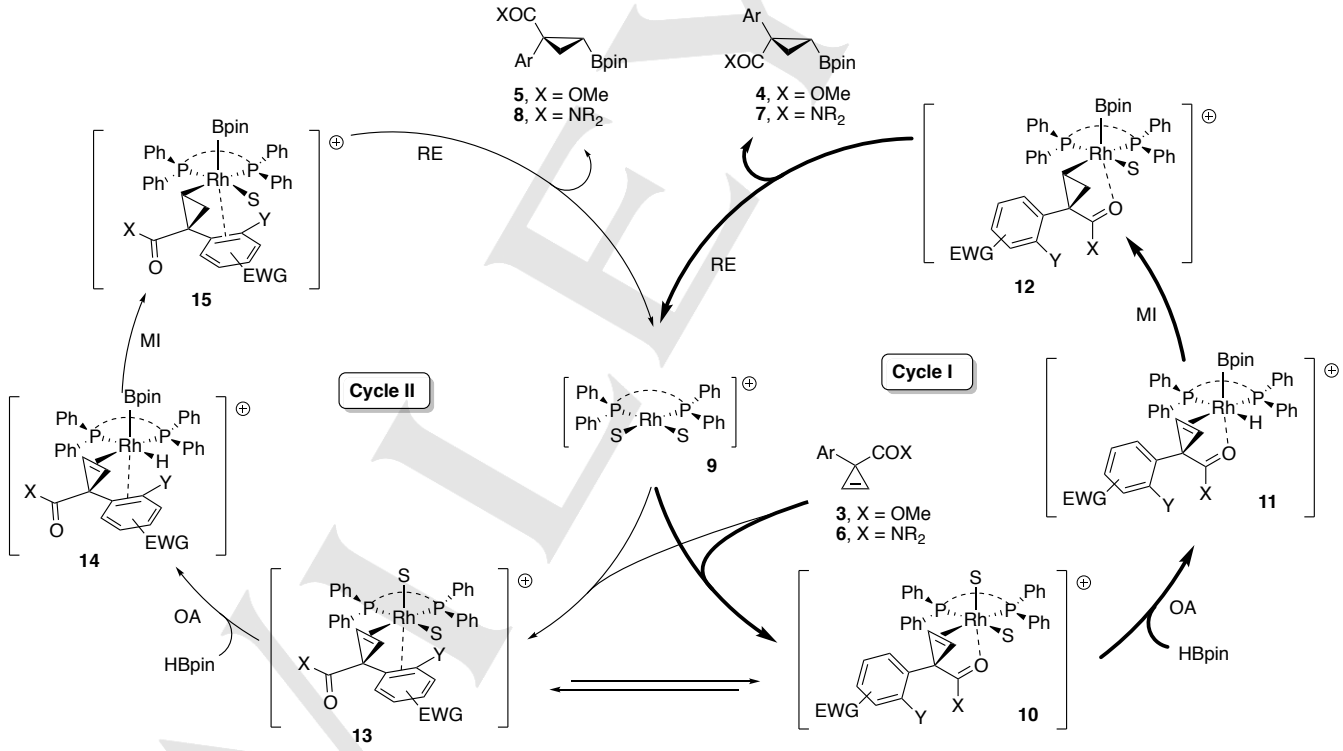
We have recently reported an improved protocol for catalytic cyclopropenation of trimethylsilylacetylene,[19] which streamlined access to esters **3** (DG = CO_2Me). This allowed us to perform an in-depth study of the asymmetric hydroboration reaction with respect to substrate scope and limitations. Previously, we have shown a single example of a 1-aryl-substituted ester (methyl 1-phenylcycloprop-2-ene-1-carboxylate **3a**) employed in this transformation.[13] This result was now reproduced by treating cyclopropene **3a** with pinacolborane (Bpin) in the presence of rhodium catalyst and (*R*)-BINAP (Method A, Table 1, entry 1). 1-Naphthylcyclopropene carboxylate (**3b**, entry 2) was slightly less efficient than the benchmark example in terms of selectivity (Method B). All cyclopropenes possessing *para*-substituted phenyl groups (**3c**-**e**) at C-1 provided the corresponding cyclopropylboronates **4c**-**e** with similar diastereo- and enantioselectivity (entries 3-5). The stereochemical outcome in

Table 1. Catalytic Asymmetric Hydroboration of 1-Arylcycloprop-2-ene-1-carboxylates **3**



					major	minor	
	3	R	**4**	yield, %[a]	dr (**4**:**5**)[b]	er[c]	$[\alpha]_D^{20}$ (c)[d]
1	**3a**	Ph	**4a**	99 (A)	99:1	99:1	-57.9 (4.07)
2	**3b**	1-naphthyl	**4b**	99 (B)	97:3	97:3	-40.6 (2.27)
3	**3c**	4-MeC_6H_4	**4c**	94 (A)	99:1	98:2	-62.4 (2.30)
4	**3d**	4-FC_6H_4	**4d**	80 (A)	98:2	96:4	-40.6 (0.90)
5	**3e**	4-BrC_6H_4	**4e**	89 (B)	98:2	97:3	-51.9 (1.17)
6	**3f**	3-BrC_6H_4	**4f**	90 (B)	85:15	99:1	-35.5 (1.30)
7	**3g**	3-$CF_3C_6H_4$	**4g**	75 (B)	96:4	96:4	-39.1 (1.33)
8	**3h**	2-ClC_6H_4	**4h**	91 (B)	89:11	97:3	-53.5 (1.20)
9	**3i**	2,3-$F_2C_6H_3$	**4i**	55(85) (A)	54:46	90:10 88:12	-49.2 (0.77)
10	**3j**	2,4-$F_2C_6H_3$	**4j**	60(87) (B)	57:43	90:10 68:32	-48.5 (0.87)
11	**3k**	2-Cl-4-FC_6H_3	**4k**	92 (B)	94:6	83:17	-47.8 (2.37)
12	**3l**	2-Cl-4,5-$F_2C_6H_2$	**4l**	83 (B)	75:25	93:7	-38.7 (1.43)
13	**3m**	2,4-$Cl_2C_6H_3$	**4m**	83 (B)	84:16	83:17	-54.5 (1.63)
14	**3n**	2-Br-4-FC_6H_3	**4n**	81 (B)	97:3	94:6	-38.2 (1.67)

[a] Isolated yield of purified products (NMR yields are provided in parentheses for compounds **4i** and **4j**). Methods (A) and (B) correspond to addition of cyclopropene as neat oil or as a solution in THF, respectively. [b] Diastereomeric ratios were determined by ^{1}H NMR or HPLC analyses of crude reaction mixtures. [c] Enantiomeric ratios were determined by chiral HPLC analyses of purified products (see Experimental Part for details) [d] Concentrations are provided in g/100 mL of dichloromethane.



Scheme 2. Proposed mechanism for directed asymmetric hydroboration of cyclopropenes. Structure of the ligand chiral backbone is omitted for clarity and substituted with a curved dashed line.

hydroboration of *meta*-substituted substrates was not that straightforward. Thus, facial selectivity in the reaction of *meta*-trifluoromethyl-substituted derivative (**3f**) was very high (entry 7), while *meta*-bromosubstituted boronate **4f** was obtained as a

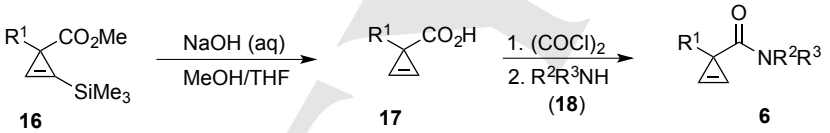
mixture with a notable amount of diastereomeric product **5f** (entry 6). The enantioselectivity of hydroboration in both cases remained high.

ortho-Halogenated 1-arylcyclopropene carboxylates were generally less selective than *para*- and *meta*-analogs (entries 8-14). All difluoro-substituted substrates, particularly those possessing a fluorine atom in the 2-position, afforded lower yields and poor diastereomeric ratios, with an average *er* near 9:1 for the main diastereomer (entries 9, 10, and 12). The lowest enantioselectivity for the major product was obtained for cyclopropenes **3k** and **3m**, both bearing an *ortho*-chlorophenyl group at C-1 and an additional halogen in the 4-position (entries 11 and 13). For all fluoro-substituted analogs, the placement of fluorine in any position other than para- (entries 4, 11, 14) resulted in deterioration of diastereoselectivity (entries 9, 10, 12).

Based on the observations described above, we propose the following mechanistic rationale (Scheme 2). The catalytic cycle begins with coordination of cyclopropene **3** to chiral rhodium(I) species **9**, which can be achieved in two different ways, leading to complementary facial selectivity. In the preferred pathway, coordination of the cyclopropene double bond with simultaneous chelation through the carbonyl moiety would produce cationic η^2-species **10**[20] (Scheme 2, Cycle I). Oxidative addition of rhodium into the H-B bond of pinacolborane provides Rh(III)-complex **11**, which undergoes subsequent stereochemistry defining, irreversible migratory insertion producing chiral cyclopropyl rhodium(III) complex **12**. Finally, reductive elimination affords *cis*-cyclopropyl boronate **4** and regenerates the catalytically active species **9** (Cycle I). It is believed that catalytic Cycle II (Scheme 2) may account for poor facial selectivity observed in hydroboration of several *ortho*-halogenated substrates. The complementary complex **13** produced via η^2-coordination of the aromatic ring to the metal must experience a significant back-donation component, since it is most efficiently realized for more electron-deficient aryl rings. Furthermore, fluorophilic interaction[21] could play an important role in stabilization of such complexes with *ortho*-fluorosubstituted aryl rings. Subsequent steps, including oxidative addition into B-H bond to form Rh(III)-complex **14**, followed by *syn*-specific concerted hydrorhodation of cyclopropene and reductive elimination, affords *trans*-cyclopropyl boronate **5** (Scheme 2, Cycle II).

An important implication of the proposed mechanistic rationale was a potential possibility to address poor diastereoselectivity by employing a directing group capable of stronger binding to the transition metal. Such modification would help shift the equilibrium between species **10** and **13** towards the former and deter the catalytic Cycle II (Scheme 2).

Table 2. Preparation of 1-arylcycloprop-2-ene-1-carboxamides **6**

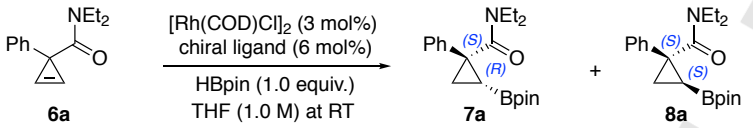


16 **17** **6**

	16	R^1	17	Yield, %[a]	R2	R3	6	Yield, %[a]
1	**16a**	Ph	**17a**	88 [23]	Et	Et	**6a**	89 [23]
2	**16b**	1-Naphthyl	**17b**	91 [23]	Et	Et	**6b**	92 [23]
3	**16c**	4-MeC_6H_4	**17c**	95	Et	Et	**6c**	86
4	**16d**	4-FC_6H_4	**17d**	96	Et	Et	**6d**	78
5	**16e**	4-BrC_6H_4	**17e**	92	Et	Et	**6e**	89
6	**16g**	3-$CF_3C_6H_4$	**17g**	88	Et	Et	**6g**	84
7	**16h**	2-ClC_6H_4	**17h**	84	Et	Et	**6h**	93
8	**16i**	2,3-$F_2C_6H_3$	**17i**	94	Et	Et	**6i**	85
9	**16j**	2,4-$F_2C_6H_3$	**17j**	86 [23]	Et	Et	**6j**	85 [23]
10	**16k**	2-Cl-4-FC_6H_3	**17k**	82 [23]	Et	Et	**6k**	83 [23]
11	**16l**	2-Cl-4,5-FC_6H_2	**17l**	84	Et	Et	**6l**	89
12	**16m**	2,4-$Cl_2C_6H_3$	**17m**	93	Et	Et	**6m**	94
13	**16n**	2-Br-4-FC_6H_3	**17n**	97	Et	Et	**6n**	82
14	**16a**	Ph	**17a**		Bn	Bn	**6o**	76 [23]
15			**17a**		*i*-Pr	*i*-Pr	**6p**	59 [23]
16			**17a**		-$(CH_2)_5$-		**6q**	83 [23]
17			**17a**		-$(CH_2)_2O(CH_2)_2$-		**6r**	95 [23]
18			**17a**		Me	Bn	**6s**	88 [23]
19			**17a**		*i*-Pr	Bn	**6t**	80 [23]
20			**17a**		Me	OMe	**6u**	83 [23]
21			**17a**		Bu	H	**6v**	85 [23]
22			**17a**		*c*-C_7H_{13}	H	**6w**	81 [23]
23			**17a**		2-$FuCH_2$	H	**6x**	77 [23]
24			**17a**		$CH_2CH{=}CH_2$	H	**6y**	92 [23]
25		Me			Et	Et	**6z**	95 [22][b]

[a] Isolated yields of purified products. References for previously reported compounds are given in brackets. Experimental details for preparation of newly synthesized compounds are provided in the Supporting Information section. [b] Prepared via a base-assisted 1,2-elimination of 2-bromo-*N*,*N*-diethyl-1-methylcyclopropanecarboxamide.

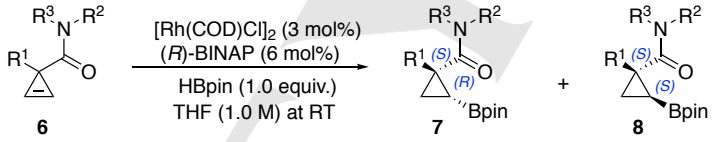
Table 3. Optimization of the chiral phosphine ligand for asymmetric hydroboration of carboxamide **6a**



	Ligand (CAS Number)	Price[a]	Time[b]	Yield, %[c]	dr (7:8 ratio)[d]	er[e]
1	(*R*)-BINAP (*76189-55-4*)		30 min	66	>98:2	ND
2	(*R*)-BINAP		4 h	77	>98:2	ND
3	(*R*)-BINAP		4 h	81	>98:2	ND
4	**(*R*)-BINAP**	**72.60**	**18 h**	**97**	**>98:2**	**96:4**
5	(*R*)-Tol-BINAP (*99646-28-3*)	76.80	30 min	89	>98:2	97:3
6	(*R*)-DM-BINAP (*137219-86-4*)	252.07	4 h	90	>98:2	98:2
7	(*R*,*R*)-Norphos (*71042-55-2*)	1322.78	2 h	96	>98:2	97:3
8	(*S*)-Phanephos (*192463-40-4*)	432.49	1 h	86	>98:2	98:2
9	(*S*)-BINAPINE (*528854-26-4*)	1113.36	30 min	99	>98:2	>99:1
10	(*R*)-BINAM-P (*74974-14-4*)	387.70	8 h	81	97:3	34:66
11	(*S*,*S*)-Chiraphos (*64896-28-2*)	175.71	30 min	99	>98:2	3:97
12	(*S*,*S*)-Me-Duphos (*136735-95-0*)	159.92	2 h	80	98:2	82:18
13	(*R*,*R*,*S*,*S*)-Duanphos (*528814-26-8*)	417.65	18 h	73	>98:2	81:19
14	Taniaphos SL-T001-1 (*1003012-96-1*)	484.05	42 h	27	95:5	ND
15	Josiphos SL-J008-1 (*166172-63-0*)	556.33	42 h	55	93:7	7:93

[a] Relative prices for ligands are given in USD/mmol, as listed in Sigma-Aldrich on-line product catalog for the United States, as of summer 2017. [b] Time required for the reactions to achieve maximum conversion. [c] NMR yields measured for crude reaction mixtures using *p*-xylene as the internal standard. [d] Measured by NMR or HPLC of crude mixtures. Notation >98:2 indicates that minor isomer **8a** could not be observed by these methods. [e] Enantiomeric ratios (1*S*,2*R*)-**7a**:(1*R*:2*S*)-**7a** were determined by chiral HPLC analyses of crude mixtures.

Table 4. Catalytic Asymmetric hydroboration of 1-arylcycloprop-2-ene-1-carboxamides **6**



						major		minor	
	6	R^1	R^2	R^3	**7**	yield, %[a]	dr (**7**:**8**)[b]	er[c]	$[\alpha]_D^{20}$ (c)[d]
1	**6a**	Ph	Et	Et	**7a**	92	>98:2	96:4	+43.2 (1.13)
2	**6b**	1-Naphthyl	Et	Et	**7b**	88	>98:2	95:5	+151.8 (1.87)
3	**6c**	4-MeC_6H_4	Et	Et	**7c**	92	>98:2	91:9	+44.6 (1.30)
4	**6d**	4-FC_6H_4	Et	Et	**7d**	88	>98:2	90:10	+38.8 (1.53)
5	**6e**	4-BrC_6H_4	Et	Et	**7e**	85	>98:2	87:13	+21.3 (1.60)[e]
6	**6g**	3-CF3C_6H_4	Et	Et	**7g**	87	>98:2	92:8	+9.6 (1.10)[e]
7	**6h**	2-ClC_6H_4	Et	Et	**7h**	96	>98:2	88:12	+140.6 (2.23)[e]
8	**6i**	2,3-$F_2C_6H_3$	Et	Et	**7i**	91	>98:2	92:8	+103.5 (1.30)
9	**6j**	2,4-$F_2C_6H_3$	Et	Et	**7j**	96	>98:2	96:4	+104.6 (1.90)
10	**6k**	2-Cl-4-FC_6H_3	Et	Et	**7k**	85	>98:2	97:3	+139.1 (1.67)
11	**6l**	2-Cl-4,5-FC_6H_2	Et	Et	**7l**	91	>98:2	97:3	+121.8 (2.30)[e]
12	**6m**	2,4-$Cl_2C_6H_3$	Et	Et	**7m**	98	>98:2	98:2	+132.1 (2.43)[e]
13	**6n**	2-Br-4-FC_6H_3	Et	Et	**7n**	98	>98:2	95:5	+105.2 (2.77)[e]
14	**6o**	Ph	Bn	Bn	**7o**	98	>98:2	97:3	+9.7 (0.90)
15	**6p**	Ph	*i*-Pr	*i*-Pr	**7p**	83	>98:2	83:17	+52.0 (1.33)
16	**6q**	Ph	-$(CH_2)_5$-		**7q**	69	>98:2	98:2	+7.8 (0.73)
17	**6r**	Ph	-$(CH_2)_2O(CH_2)_2$-		**7r**	48	>98:2	96:4	-59.2 (0.83)
18	**6s**	Ph	Me	Bn	**7s**	73	>98:2	96:4	-8.8 (1.83)
19	**6t**	Ph	*i*-Pr	Bn	**7t**	82	>98:2	92:8	+33.1 (1.47)
20	**6u**	Ph	Me	OMe	**7u**	68	97:3	95:5	-64.6 (0.73)
21	**6v**	Ph	Bu	H	**7v**	81	>98:2	92:8	-30.6 (1.10)
22	**6w**	Ph	*c*-C_7H_{13}	H	**7w**	94	>98:2	91:9	-23.8 (1.23)
22	**6x**	Ph	2-FuCH_2	H	**7x**	34	>98:2	94:6	-35.8 (0.57)
24	**6y**[f]	Ph	CH=CHMe	H	**7y**	58	>98:2 (E)	94:6	-35.7 (0.37)
						E:Z = 1:2	>98:2 (Z)	94:6	
25	**6z**	Me	Et	Et	**7z**	92	>98:2	92:8	+49.5 (0.80)[e]

[a] Isolated yields of purified products. [b] Diastereomeric ratios were determined by ^{1}H NMR or HPLC analyses of crude reaction mixtures. [c] Enantiomeric ratios were determined by chiral HPLC analyses of purified products (see Experimental Part for details) [d] Concentrations are provided in g/100 mL of dichloromethane. [e] Measured in chloroform. [f] N-allylamide (R^2 = allyl) was used as starting material in this reaction.

Our previous experience with alkali metal-assisted nucleophilic additions to cyclopropenes directed by a carboxamide function at C-3[23] prompted us to probe this directing group in the transition metal-catalyzed hydroboration. Substrates required for this investigation, prochiral 1-arylcycloprop-2-ene-1-carboxamides **6**, are now easily available from acyl chlorides generated in situ from the corresponding 1-arylcycloprop-2-ene-1-carboxylic acids **17**.[24] The acids, in turn, can be prepared by hydrolysis of esters **16**[19,25] accompanied by desilylation of the cyclopropene double bond. This two-step protocol was employed for preparation of *N*,*N*-diethylcycloprop-2-ene-1-carboxamides **6a-n**, bearing various aryl substituents at C-1 (Table 2, entries 1-13). Also, employing 1-phenylcycloprop-2-ene-1-carboxylic acid **17a** and different amines **18**, we have synthesized a series of secondary (**6v-y**, entries 21-24) and tertiary amides **6o-t** (entries 14-19), including Weinreb amide **6u** (entry 20).[23]

To test the efficiency of cyclopropene carboxamides in the directed asymmetric hydroboration we subjected compound **6a** to standard reaction conditions with pinacolborane in the presence of $[Rh(COD)Cl]_2$ (3 mol%) and chiral diphosphine ligand (6 mol%). A series of chiral ligands were screened, which have previously demonstrated promising results in the reaction with esters.[13] Our main goal for this optimization was to maximize conversion and the enantioselectivity, as high diastereoselectivity has been routinely observed in reactions of carboxamides. Striving to develop an economically-viable method, we also took into consideration the relative cost of chiral diphosphine ligands. Our results showed that the most affordable (*R*)-BINAP was superior or on par with many of the more expensive ligands tested (Table 3). (*R*,*R*)-Norphos and (*S*)-BINAPINE outperformed (*R*)-BINAP (Table 3, entries 7, 9), but were cost-prohibitive for the preparative method development. Furthermore, the reactivity and selectivity of (*R*,*R*)-Norphos and (*S*,*S*)-Chiraphos appeared to be specific to substrate **6a**. Reactions with other cyclopropenes provided variable selectivities in the presence of these ligands, while hydroboration catalyzed by (*R*)-BINAP complex afforded consistently good results for all carboxamides tested (Table 4). Indeed, all *N*,*N*-diethylamides **6b-h** derived from cycloprop-2-enecarboxylic acids bearing various mono-substituted aryl groups at C-1, reacted smoothly affording (+)-(1*S*,2*R*)-boronates **7b-h** (Table 4, entries 2-7) in high yields as single diastereomers, although optical purity of the products was generally somewhat lower than that of the corresponding ester analogs **4b-h** (Table 1, entries 2-8). However, amides **6i-n** displayed greater diastereo- and enantioselectivity (Table 4, entries 8-13), as compared to parent poly-halogenated arylcyclopropyl esters **3i-n** (Table 1, entries 9-14).

With these results in hand, we examined the compatibility of this reaction with various substituents at the nitrogen atom in the amide moiety. In spite of increased steric hindrance around the directing group, *N*,*N*-dibenzylamide **6o** afforded the corresponding *cis*-cyclopropyl boronate **7o** very selectively (Table 3, entry 14). The relative and absolute configuration of this product was unambiguously assigned by X-ray crystallography (Figure 1). An excessive steric hindrance at nitrogen atom in *N*,*N*-diisopropylamide **6p** lowered the overall yield of product **7p**, as well as the enantioselectivity, although *cis*-diastereoselectivity remained high (entry 15). Likewise, hydroboration of amide **6t** bearing an isopropyl and a benzyl group at nitrogen atom displayed, but less dramatic, reduction of enantioselectivity **7t** (entry 19). An attempt to employ derivatives

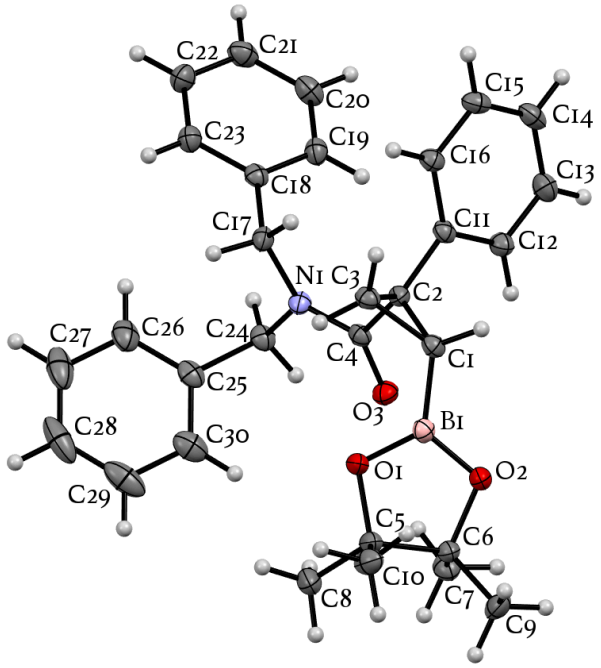


Figure 1. ORTEP drawing of (1*S*,2*R*)-(+)-*N*,*N*-Dibenzyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (**7o**) showing 50% probability amplitude displacement ellipsoids.

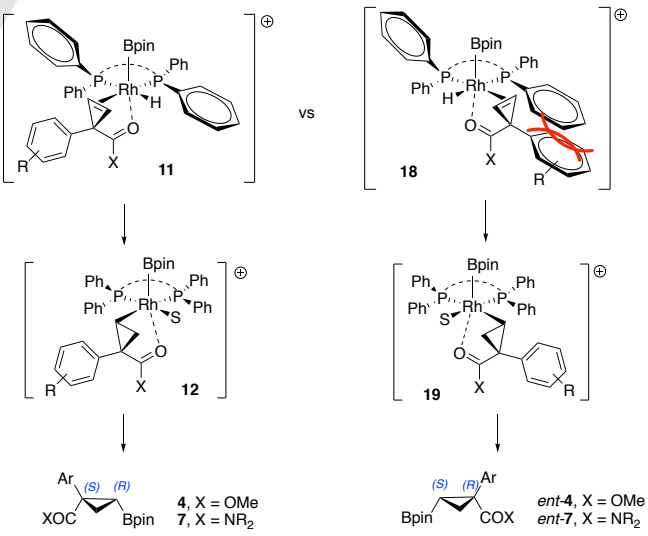
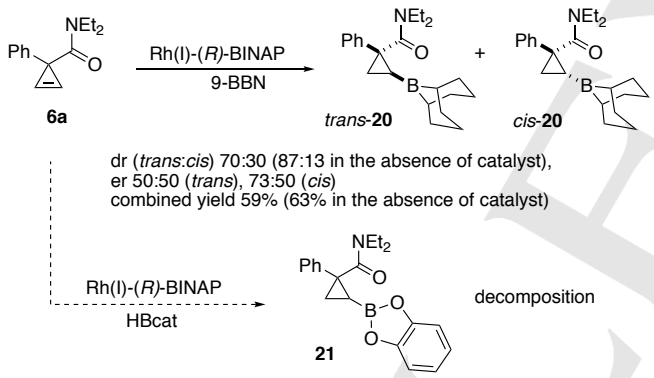


Figure 2. Proposed rationale for the origins of enantioselectivity in the Rh-catalyzed hydroboration of cyclopropenyl esters and amides.

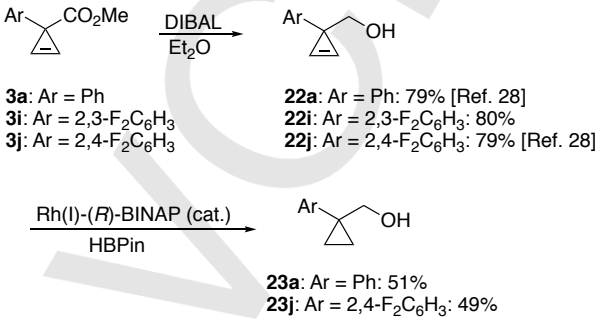
of cyclic amines (**6q**,**r**) led to a notable decrease of chemical yield; however, provided consistently high diastereo- and enantiopurity of the resulting boronates **7q**,**r** (entries 16, 17). Finally, Weinreb amide **6u**, amenable for subsequent functionalization,[26] reacted smoothly to provide *cis*-boronate **7u** (entry 20). Hydroboration of secondary amides bearing either a primary (**6v**) or a secondary (**6w**) alkyl group at nitrogen atom proved very efficient and highly selective (entries 21-22). *N*-(furan-2-ylmethyl)-substituted analog **7x** was also obtained very selectively, although chemical yield in this reaction was rather poor (entry 22). Interestingly, hydroboration of allylamide **6y** was accompanied by the Rh-catalyzed 1,2-migration of the double bond to afford a thermodynamically more stable *N*-prop-2-enyl amide **7y** as a mixture of *E*- and *Z*-isomers (entry 24). We have also evaluated the catalytic hydroboration of 3-methyl-cyclopropene-3-carboxamide **6z**. The corresponding boronate **7z** was obtained in high yield and reasonably high enantioselectivity, as a sole diastereomer (entry 25).

The observed enantioselectivity can be attributed to the predominant formation of the octahedral Rh(III)-complex **11** with a left-handed chelation of cyclopropenyl carboxylate (or carboxamide) (Figure 2). This orientation, as opposed to the alternate arrangement in complex **18**, allows for minimal steric interaction between the phenyl rings of the ligand and the substrate, leading to the formation of cyclopropylrhodium complex **12** and, ultimately, products **4** and **7** (Figure 2).

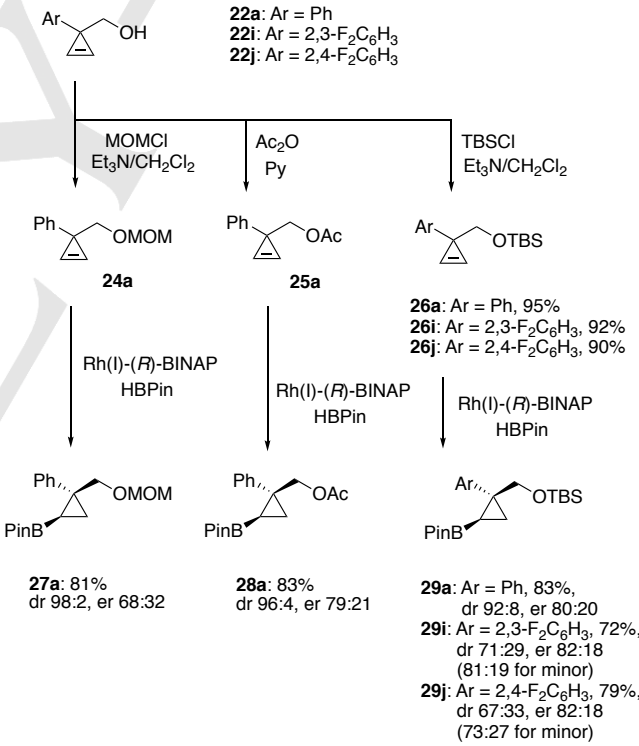


Scheme 3.

A scale up hydroboration using standard reaction conditions and 2 mmols of **6a** was also performed to obtain product **7a** in excellent yield (96%) and high diastereo- and enantioselectivity (dr >99:1, er 94:6). We also tested the possibility to employ different hydroborating agents in this transformation. Hydroboration or **6a** with 9-BBN carried out in the presence of Rh(I) complex with chiral BINAP ligand afforded a mixture of racemic cyclopropropylboranes *trans*-**20** (major product, resulting from non-directed process) and partially enriched *cis*-**20** (minor product) (Scheme 3). Very similar diastereoselectivity and yield were obtained upon hydroboration of **6a** with 9-BBN in the absence of Rh-catalyst, which suggests significant contribution of a background, non-catalytic hydroboration process. This observation is in accord with numerous literature reports on non-catalyzed reactions of cyclopropenes with BH_3 complexes and alkylboranes, affording racemic cyclopropylboranes[27] or products of their thermal rearrangements.[28] We also examined the possibility to employ catecholborane as a hydroborating agent in the Rh(I)-catalyzed reaction of cyclopropene **6a**. Fast and complete conversion of the starting material was observed, however, the obtained cyclopropylboronates **21** were hydrolytically unstable and readily decomposed during isolation attempts.



Scheme 4.



Scheme 5.

On an earlier submission of this manuscript, a reviewer suggested the possibility to flip the diastereoselectivity of the reaction by accentuating the "*ortho*-fluoro" effect described above. To test this idea, we synthesized cyclopropenes **22, 24-26**, bearing weakly-directing[29] alkoxymethyl substituents. We first probed alcohols **22a** and **22j**, obtained by reduction of the corresponding esters **3a** and **3j** with DIBAL.[30] The hydroxymethyl group appeared to be incompatible with the reaction

conditions, potentially, due to rapid protonolysis of the intermediate cyclopropyl rhodium species. As a result, cyclopropanes **23**[31] and **23j** were the only products isolated from these reactions. Next, MOM ether **24a,** acetate **25a**, and silyl ethers **26a**,**i**,**j** were subjected to the catalytic hydroboration reaction under the standard reaction conditions. The parent substrates bearing an unsubstituted phenyl ring (**24a**, **25a**, **26a**) reacted selectively *cis*- to the protected primary alcohol function. The diastereoselectivity in the series **27a**, **28a**, **29a** decreased only slightly with increase of the protecting group size (Scheme 5). In sharp contrast, the facial selectivity in hydroboration of *ortho*-fluorinated substrates **26i**,**j** was significantly lower (Scheme 5), manifesting the contribution of the "*ortho*-fluoro" effect into stabilization of reactive intermediates **13**-**15** (Scheme 2). However, gain in thermodynamic stability appears to be insufficient to outweigh the input of other effects (primarily the significant sterics of the aryl ring) and allow for a complete switch of the selectivity in the hydroboration reaction.

Conclusions

We have evaluated the scope and limitations of two alternate directing groups, ester and carboxamide, in the metal-catalyzed, asymmetric hydroboration of prochiral cyclopropenes. Hydroboration of esters appeared to be more sensitive to substitution in the aromatic ring of the substrates. *ortho*-Halogens have been particularly detrimental for diastereo- and enantioselectivity, potentially, due to complementary coordination with rhodium. This effect was also observed in the hydroboration of alkoxymethyl-substituted analogs. In contrast, a more Lewis-basic amide directing groups allowed for stronger chelation to the transition metal, leading to consistently high diastereo- and enantioselectivity in hydroboration across a large variety of substrates.

Experimental Section

General Information. NMR spectra were recorded on a 400 MHz NMR instrument equipped with BBO probe or 500 MHz NMR instrument, equipped with dual carbon/proton (CPDUL) cryoprobe at room temperature. ^{13}C NMR spectra were registered with broad – band decoupling. Signs (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT – 135 experiments. Column chromatography was carried out employing silica gel with particle size 63-200 μm). Anhydrous tetrahydrofuran was obtained by passing degassed HPLC – grade commercially available stabilizer-free solvent consecutively through two columns with activated alumina (Innovative Technology). Anhydrous DMSO was obtained by distilling degassed HPLC-grade solvent over calcium hydride. Starting materials, cyclopropene esters **3a**-**n** and **16a**-**n** were prepared according to our earlier published report.[19] Carboxylic acids **17a**, **17b**, **17j**, and **17k** and carboxamides **6a**,**b**, **6j**,**k**, and **6o**-**y** were also synthesized according to the previously published procedures.[23] Preparation of carboxylic acids **17c**-**e**, **17g-i**, and **17l**-**n** as well as amides **6c**-**e**, **6g**-**i**, **6l**-**n**, is detailed in the Supporting Information. All other solvents and reagents were purchased from commercial vendors and used as received. All manipulations with transition metal complexes and chiral ligands were conducted under inert atmosphere (<8 ppm residual oxygen and moisture) using a combination of glovebox and standard Schlenk techniques. After quench the reaction mixtures and compounds were treated on air. All the obtained materials were moisture and oxygen stable at ambient temperatures. Representative procedures are provided below. See Supporting Information for the full account.

Hydroboration of Esters

(-)-Methyl (1*S*,2*R*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (**4a**), Typical Procedure **A**: A 1 mL reaction vial was charged in a glove box with $[Rh(COD)Cl]_2$ (7.4 mg, 0.015 mmol, 3 mol%) and (*R*)-BINAP (19.9 mg, 0.03 mmol, 6 mol%). Freshly distilled anhydrous tetrahydrofuran (500 μL) was then added to the vial via syringe and the mixture was stirred until homogenous. Pinacol borane (73 μL, 0.50 mmol, 1.0 equiv.) was added via syringe followed by methyl 1-phenylcycloprop-2-ene-1-carboxylate (**3a**)[32] (87 mg, 0.50 mmol, 1.0 equiv.). The reaction was then stirred for 30 min at room temperature. The product was purified by column chromatography on Silica gel eluting with a mixture hexane/EtOAc (3:1). The titled compound was obtained as pale-yellow oil, R_f 0.52. Yield 149 mg (0.493 mmol, 99%), dr >99:1, er 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.27 – 7.18 (m, 3H), 3.56 (s, 3H), 1.62 (dd, *J* = 8.4, 3.5 Hz, 1H), 1.30 (dd, *J* = 10.2, 3.5 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.71 (dd, *J* = 10.2, 8.4 Hz, 1H).; ^{13}C (126 MHz, $CDCl_3$): δ 174.5, 140.4, 130.3 (+, 2C), 128.2 (+, 2C), 127.3 (+), 83.7 (2C), 52.5 (+), 34.5, 25.1 (+, 4C), 19.1 (-), 11.9; FT IR (KBr, cm^{-1}): 3052, 3026, 2978, 2949, 2932, 1718, 1435, 1410, 1391, 1371, 1313, 1292, 1215, 1198, 1167, 1144, 1107, 972, 858, 768, 752, 700, 667; HRMS (TOF ES): HRMS (TOF ES): Found 302.1685, calculated for $C_{17}H_{23}BO_4$ (M+) 302.1689 (1.3 ppm); $[\alpha]_D^{20}$ -57.9° (c 4.07, CH_2Cl_2).

(-)-Methyl (1*S*,2*R*)-1-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (**4b**), Typical Procedure **B**: A 1 mL reaction vial was charged in a glove box with $[Rh(COD)Cl]_2$ (3.8 mg, 7.50 μmol, 3 mol%.) and (*R*)-BINAP (10 mg, 0.015 mmol, 6 mol%.). Freshly distilled anhydrous tetrahydrofuran (500 μl) was then added to the vial via syringe and the mixture was stirred until homogenous. Pinacol borane (37.0 μL, 0.25 mmol, 1.0 equiv.) was added via syringe followed by solution of methyl 1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (**3b**)[19] (56 mg, 0.25 mmol, 1.0 equiv.) in a minimal amount of tetrahydrofuran (about 100 μL). The reaction mixture was stirred for 30 min at room temperature. The product was purified by column chromatography on Silica gel eluting with a mixture hexane/EtOAc (3:1). The titled compound was obtained as a colorless solid, mp 122.3-124.7 °C, R_f 0.52. Yield 87.2 mg (0.248 mmol, 99%), dr 97:3; er 97:3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.81 – 7.75 (m, 1H), 7.60 – 7.44 (m, 3H), 7.45 – 7.37 (m, 1H), 3.53 (s, 3H), 1.98 – 1.85 (m, 1H), 1.54 – 1.43 (m, 1H), 1.35 (s, 6H), 1.34 (s, 6H), 0.95 – 0.80 (m, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 174.9, 136.9, 133.7, 133.3, 128.6 (+), 128.2 (+), 127.9 (+), 126.4 (+), 125.7 (+), 125.3 (+), 125.1 (+), 83.8 (2C), 52.6 (+), 32.1, 25.2 (+, 2C), 25.1 (+, 2C), 20.2 (-), 13.4; FT IR (KBr, cm^{-1}): 3045, 2976, 2949, 2930, 1717, 1437, 1414, 1391, 1312, 1288, 1223, 1202, 1165, 1144, 970, 858, 800, 779, 736, 685; HRMS (TOF ES): HRMS (TOF ES): Found 352.1844, calculated for $C_{21}H_{25}BO_4$ (M+) 352.1846 (0.6 ppm); $[\alpha]_D^{20}$ -40.6° (c 2.27, CH_2Cl_2).

Hydroboration of Amides

(1*S*,2*R*)-(+)-*N*,*N*-Diethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (**7a**): This compound was obtained via typical procedure **B** using *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**6a**)[24] (54 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane/EtOAc (2:1). The titled compound

was obtained as a pale-yellow oil, R_f 0.37. Yield 79 mg (0.229 mmol, 92%), dr >98:2, er 96:4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.23 (m, 4H), 7.21 – 7.13 (m, 1H), 3.50 – 3.29 (m, 2H), 3.27 – 3.14 (m, 2H), 1.65 (dd, *J* = 9.8, 3.9 Hz, 1H), 1.41 (dd, *J* = 7.5, 3.9 Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H), 0.65 (dd, *J* = 9.8, 7.5 Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 175.5, 140.1, 128.7 (+, 2C), 127.7 (+, 2C), 126.8 (+), 81.4 (2C), 43.1 (-), 42.1 (-), 36.0, 25.2 (+, 2C), 25.1 (+, 2C), 19.5 (-), 18.7, 12.6 (+), 12.6 (+); FT IR (KBr, cm^{-1}): 3061, 2976, 2935, 2876, 1643, 1634, 1601, 1470, 1454, 1404, 1381, 1325, 1211, 1142, 1115, 953, 860, 760, 700; HRMS (TOF ES): HRMS (TOF ES): Found 366.2214, calculated for $C_{20}H_{30}BNO_3Na$ (M+Na) 366.2216 (0.5 ppm); $[\alpha]_D^{20}$ +43.2° (c 1.13, CH_2Cl_2).

The same reaction was performed in the presence of cationic Rh species. To this end (procedure **C**), the reaction vessel was charged $[Rh(CO)Cl]_2$ (6.1 mg, 12 µmol, 4 mol%), AgOTf (6.6 mg, 26 µmol, 8.5 mol%), and (*R*)-BINAP (15 mg, 24 µmol, 8.0 mol%). Anhydrous THF was added and the mixture was stirred at room temperature for 30 min. Then pinacolborane (76 mg, 0.30 mmol, 1.0 equiv.) was added, immediately followed with *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**6a**) (65 mg, 0.30 mmol, 1.0 equiv.). Alternatively (procedure **D**) the reaction vessel was loaded with Bis(norbornadiene)rhodium(I) tetrafluoroborate $(Rh(nbd)BF_4$, 9.0 mg, 24 µmol, 8.0 mol%), and (*R*)-BINAP (15 mg, 24 µmol, 8.0 mol%). Anhydrous THF was added and the mixture was stirred at room temperature for 30 min. Then pinacolborane (76 mg, 0.30 mmol, 1.0 equiv.) was added, immediately followed with *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**6a**) (65 mg, 0.30 mmol, 1.0 equiv.). The resulting reaction mixtures were stirred at room temperature for 18 hr and then worked up in the same manner as described above for procedures **A** and **B**. In both cases compound **7a** was obtained as sole product as pale-yellow oil. Yields 99 mg (0.288 mmol, 96%), dr >98:2, er 95:5 for procedure **C** and 95 mg (0.276 mmol, 92%), dr >98:2, er 95:5, for procedure **D**, respectively. Chromatographic and spectral properties of these samples were identical to those for material **7a** described above.

Hydroboration of Other Substrates

2-(9-Borabicyclo[3.3.1]nonan-9-yl)-N,N-diethyl-1-phenylcycloprop-ane-1-carboxamide (**20**): This compound was obtained via typical procedure **B** using *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**6a**) (108 mg, 0.50 mmol, 1.0 equiv.) and 9-borabicyclo[3.3.1]nonane dimer (1.0 ml, 0.5M in THF, 0.50 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane:EtOAc (3:1). The titled compound was obtained as a colorless solid, R_f 0.31. Yield 89.6 mg yield (0.266 mmol, 53%), dr: 70:30. ^{1}H NMR (500 MHz, $CDCl_3$): **Major** (*trans*): δ 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 3.48 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.35 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.26 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.07 (dq, *J* = 14.2, 7.1 Hz, 1H), 1.99 – 1.88 (m, 2H), 1.86 – 1.80 (m, 3H), 1.76 – 1.66 (m, 5H), 1.54 (s, 2H), 1.46 – 1.40 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.00 – 0.93 (m, 2H), 0.73 (t, *J* = 7.1 Hz, 3H), 0.69 – 0.64 (m, 1H), 0.50 – 0.42 (m, 1H). **Minor** (*cis*): δ 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 2H), 7.11 – 7.06 (m, 1H), 3.74 – 3.38 (m, 4H), 1.95 (dd, *J* = 8.4, 2.8 Hz, 1H), 1.92 – 1.82 (m, 3H), 1.82 – 1.73 (m, 1H), 1.71 – 1.61 (m, 3H), 1.54 (s, 2H), 1.45 (dd, *J* = 8.4, 2.7 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.26 – 1.23 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.22 – 1.16 (m, 1H), 1.13 – 1.05 (m, 1H), 0.77 – 0.71 (m, 1H), 0.71 – 0.61 (m, 1H), 0.59 – 0.53 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): **Major** (*trans*): δ 179.8, 140.8, 129.0 (+, 2C), 128.9 (+, 2C), 126.7 (+), 44.4 (-), 43.7 (-), 36.1, 33.6 (-), 32.7 (-), 32.4 (-), 31.8 (-), 28.0 (+), 27.9 (+), 25.9 (-), 25.5 (-), 18.8 (-), 12.6 (+), 12.5(+), 12.2 (+). **Minor** (*cis*): δ 178.9, 148.3, 129.8 (+, 2C), 127.8 (+, 2C), 124.8 (+), 44.8 (-), 43.0 (-), 33.0 (-), 32.7 (-), 32.5 (-), 31.0 (-), 27.1, 27.0 (+), 26.9 (+), 25.6 (-), 25.0 (-), 21.5 (-), 14.3 (+), 13.0 (+), 12.9 (+); FT IR (KBr, cm^{-1}): 2978, 2914, 2869, 2835, 1600, 1488, 1314, 1212, 968, 759, 726, 700; HRMS (TOF ES): Found 338.2650, calculated for $C_{22}H_{33}BNO$ (M+H) 338.2655 (1.5 ppm).

(1-(2,4-Difluorophenyl)cyclopropyl)methanol (**23j**): This compound was obtained via under condition of typical procedure **B** employing (1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methanol (**22j**)[30] (91.0 mg, 0.50 mmol, 1.00 equiv.). The product was purified by column chromatography eluting with a mixture hexane:EtOAc (3:1). The titled compound was obtained as a pale yellow oil, R_f 0.22. Yield 45.1 mg (0.244 mmol, 49%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 1H), 6.90 – 6.73 (m, 2H), 3.60 (d, *J* = 6.1 Hz, 2H), 1.47 (t, *J* = 6.2 Hz, 1H), 0.92 – 0.76 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.6 (dd, *J* = 249.5, 11.8 Hz), 162.1 (dd, *J* = 247.7, 12.0 Hz), 133.2 (+, dd, *J* = 9.6, 6.0 Hz), 125.6 (dd, *J* = 14.1, 3.7 Hz), 111.1 (+, dd, *J* = 20.9, 3.6 Hz), 105.5 – 101.5 (+, m), 70.4 (-), 23.6, 10.3 (-, d, *J* = 1.7 Hz, 2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.5 (d, *J* = 7.5 Hz), -112.0 (d, *J* = 7.5 Hz); FT IR (KBr, cm^{-1}): 3354, 3082, 3007, 2928, 2872, 1614, 1601, 1506, 1466, 1421, 1267, 1138, 1117, 1084, 1036, 968, 849, 816, 734; HRMS (TOF ES): HRMS (TOF ES): Found 235.0558, calculated for $C_{11}H_{10}F_2O_2Na$ (M+Na) 235.0547 (4.7 ppm).

(+)-2-((1*R*,2*S*)-2-((Methoxymethoxy)methyl)-2-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**27a**): This compound was obtained via typical procedure **B** employing (1-((methoxymethoxy)methyl)cycloprop-2-en-1-yl)benzene (**24a**)[11a] (95.2 mg, 0.50 mmol, 1.0 equiv.), $[Rh(COD)Cl]_2$ (14.8 mg, 0.03 µmol, 0.06 equiv.) and (*R*)-BINAP (37.4 mg, 0.06 mmol, 0.12 equiv.), pinacol borane (148.0 µl, 1.0 mmol, 2.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane:EtOAc (20:1). The titled compound was obtained as a colorless oil, R_f 0.31. Yield 128.2 mg (0.402 mmol, 81%), dr: 98:2, er: 68:32 (Column IC, IPA 3%, Flow rate 1 mL/min). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.31 – 7.25 (m, 2H), 7.21 – 7.16 (m, 1H), 4.53 (s, 2H), 3.96 (d, *J* = 10.1 Hz, 1H), 3.70 (d, *J* = 10.1 Hz, 1H), 3.14 (s, 3H), 1.29 (s, 6H), 1.28 (s, 6H), 1.22 (dd, *J* = 9.5, 3.8 Hz, 1H), 1.12 (dd, *J* = 7.3, 3.8 Hz, 1H), 0.47 (dd, *J* = 9.5, 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 128.9 (+, 2C), 128.1 (+, 2C), 126.3 (+), 96.3 (-), 83.4 (2C), 72.8 (-), 55.1 (+), 32.3, 25.1 (+, 2C), 24.8 (+, 2C), 17.6 (-), 7.3 (+); FT IR (KBr, cm^{-1}): 2978, 2929, 2882, 1415, 1371, 1323, 1215, 1147, 1106, 1053, 966, 859, 700; HRMS (TOF ES): Found 337.2322, calculated for $C_{20}H_{31}BO_2Na$ (M+Na) 337.2315 (2.1 ppm); $[\alpha]_D^{20}$ +10.5° (c 1.04, $CHCl_3$).

(-)-(1*S*,2*R*)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-cyclopropyl)methyl acetate (**28a**): This compound was obtained via typical procedure **B** employing (1-phenylcycloprop-2-en-1-yl)methyl acetate (**25a**)[11a] (94.2 mg, 0.50 mmol, 1.00 equiv.) and allowing the reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane:EtOAc (3:1). The titled compound was obtained as a pale-yellow oil, R_f 0.29. Yield 130.0 mg (0.412 mmol, 83%), dr 96:4, er 79:21 (Column IC, IPA 3%, Flow Rate 1.0mL/min). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.32 (m, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 4.51 (d, *J* = 11.41 Hz, 1H), 4.19 (d, *J* = 11.4 Hz, 1H), 1.97 (s, 3H), 1.27 (s, 6H), 1.24 (s, 6H), 1.24 – 1.19 (m, 1H), 1.15 (dd, *J* = 7.3, 3.9 Hz, 1H), 0.51 (dd, *J* = 9.6, 7.3 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3): δ 171.1, 143.8, 129.0 (+, 2C), 128.2 (+, 2C), 126.7 (+), 83.5 (2C), 70.2 (-), 31.1, 25.1 (+, 2C), 24.6 (+, 2C), 21.2 (+), 17.9 (-), 7.3; FT IR (KBr, cm^{-1}): 3059, 2978, 2934, 1742, 1732, 1416, 1371, 1362, 1327, 1248, 1215, 1167, 1144, 1028, 976, 858, 729, 700, 671; HRMS (TOF ES): HRMS (TOF ES): Found 339.1745, calculated for $C_{18}H_{25}BO_4Na$ (M+Na) 339.1744 (0.3 ppm); $[\alpha]_D^{20}$ -35.6° (c 1.25, $CHCl_3$).

(-)-*tert*-Butyldimethyl(((1*S*,2*R*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methoxy)silane (**29a**): This compound was obtained via typical procedure **B** employing *tert*-butyldimethyl((1-phenylcycloprop-2-en-1-yl)methoxy)silane (**26a**) (130.2 mg, 0.50 mmol,

1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane:EtOAc (20:1). The titled compound was obtained as a colorless oil, R_f 0.47. Yield 154.6 mg (0.398 mmol, 80%), dr 92:8, er 80:20 (Column IC, IPA 0.4%, Flow Rate 1.0mL/min). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 3.85 (d, *J* = 10.5 Hz, 1H), 3.74 (d, *J* = 10.4 Hz, 1H), 1.29 (s, 6H), 1.27 (s, 6H), 1.10 – 1.06 (m, 1H), 1.04 (dd, *J* = 7.1, 3.7 Hz, 1H), 0.77 (s, 9H), 0.39 (dd, *J* = 9.2, 7.2 Hz, 1H), -0.25 (s, 3H), -0.27 (s, 3H); ^{13}C NMR (126 MHz, CDCl3): δ 145.0, 130.3 (+, 2C), 127.7 (+, 2C), 126.3 (+), 83.3 (2C), 68.7 (-), 35.4, 26.1 (+, 3C), 25.2 (+, 2C), 24.8 (+, 2C), 18.5, 16.4 (-), 6.1, -5.5 (+), -5.6 (+); FT IR (KBr, cm-1): 3059, 2978, 2955, 2928, 2885, 2856, 1472, 1416, 1379, 1321, 1252, 1213, 1146, 1088, 1076, 837, 773, 700; HRMS (TOF ES): HRMS (TOF ES): Found 411.2523, calculated for $C_{22}H_{37}BO_3SiNa$ (M+Na) 411.2503 (4.9 ppm); $[\alpha]_D^{20}$ -23.39 (c 1.24, $CHCl_3$).

(-)-*tert*-Butyl(((1*S*,2*R*)- and (-)-*tert*-Butyl(((1*S*,2*S*)-1-(2,3-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methoxy)dimethylsilane (*cis*-**29i** and *trans*-**29i**): This compound was obtained via typical procedure **B** employing *tert*-butyl((1-(2,3-difluorophenyl)cycloprop-2-en-1-yl)methoxy)dimethylsilane (**26i**) (148.0 mg, 0.50 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane:EtOAc (20:1). The titled compound was obtained as a colorless oil, R_f 0.35 (major), 0.30 (minor). Yield 152.2 mg (0.358 mmol, 72%), dr 2.5:1, dr: 2.5:1, er: **Major (*cis*)**: 82:18 (Column IB, IPA 0.4%, Flow Rate 1.0mL/min) **Minor (*trans*)**: 73:27 (Column IB, IPA 0.4%, Flow Rate 1.0mL/min); ^{1}H NMR (500 MHz, $CDCl_3$): **Major (*cis*)**: δ 7.16 – 7.07 (m, 1H), 7.04 – 6.89 (m, 2H), 3.88 (d, *J* = 10.7 Hz, 1H), 3.71 (d, *J* = 10.7 Hz, 1H), 1.28 (s, 6H), 1.26 (s, 6H), 1.11 – 1.09 (m, 1H), 1.09 – 1.07 (m, 1H), 0.75 (s, 9H), 0.35 (t, *J* = 8.4 Hz, 1H), -0.23 (s, 3H), -0.27 (s, 3H). **Minor (*trans*)**: δ 7.10 – 7.04 (m, 1H), 7.04 – 6.91 (m, 2H), 3.86 (d, *J* = 10.1 Hz, 1H), 3.44 (d, *J* = 10.2 Hz, 1H), 1.16 (dd, *J* = 9.6, 3.7 Hz, 1H), 1.11 – 1.09 (m, 1H), 1.10 (s, 6H), 0.96 (s, 6H), 0.80 (s, 9H), 0.48 (dd, *J* = 9.6, 7.0 Hz, 1H), -0.10 (s, 3H), -0.14 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): **Major (*cis*)**: δ 150.6 (dd, *J* = 247.0, 12.8 Hz), 150.2 (dd, *J* = 248.6, 12.3 Hz), 134.2 (d, *J* = 10.8 Hz), 128.2 (+, t, *J* = 3.1 Hz), 123.0 (+, dd, *J* = 7.2, 4.6 Hz), 115.4 (+, d, *J* = 17.2 Hz), 83.4 (2C), 67.4 (-), 30.4 (d, *J* = 2.7 Hz), 26.0 (+, 3C), 25.2 (+, 2C), 24.7 (+, 2C), 18.4, 15.8 (-), 5.6 (+), -5.6 (+), -5.7 (+). **Minor (*trans*)**: δ 151.7 (dd, *J* = 249.5, 13.8 Hz), 151.6 (dd, *J* = 249.5, 16.4 Hz), 131.6 (d, *J* = 10.1 Hz), 128.1 (+, t, *J* = 3.2 Hz), 123.2 (+, dd, *J* = 6.6, 4.9 Hz), 115.3 (+, d, *J* = 16.8 Hz), 83.0 (2C), 68.9 (-), 29.8, 25.9 (+, 3C), 24.9 (+, 2C), 24.5 (+, 2C), 18.4, 14.4 (-), 4.1 (+), -5.5 (+), -5.5 (+); ^{19}F NMR (376 MHz, $CDCl_3$) **Major (*cis*)**: δ -140.0 (d, *J* = 20.8 Hz), -141.2 (d, *J* = 20.5 Hz). **Minor (*trans*)**: δ -140.3 (d, *J* = 21.0 Hz), -140.5 (d, *J* = 20.8 Hz); FT IR (KBr, cm^{-1}): 2978, 2956, 2929, 2885, 2857, 1372, 1324, 1255, 1213, 1146, 1090, 836, 780, 729; HRMS (TOF ES): Found 421.2893, calculated for $C_{24}H_{40}BF_2OSi$ (M+H) 421.2910 (4.0 ppm); $[\alpha]_D^{20}$ **Major (*cis*)**: -30.7° (c 1.88, $CHCl_3$), **Minor (*trans*)**: -14.8° (c 0.88, $CHCl_3$).

(-)-*tert*-Butyl(((1*S*,2*R*)- and (-)-*tert*-Butyl(((1*S*,2*S*)-1-(2,4-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methoxy)dimethylsilanes (*cis*-**29j** and *trans*-**29j**): This compound was obtained via typical procedure **B** employing *tert*-butyl((1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methoxy)dimethylsilane (**26j**) (148.0 mg, 0.50 mmol, 1.00 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography eluting with a mixture hexane:EtOAc (20:1). The titled compound was obtained as a colorless oil, R_f 0.30 (major), 0.25 (minor). Yield 167.2 mg (0.394 mmol, 79%), dr 2:1, er: **Major (*cis*)**: 82:18 (Column IB, IPA 0.2%, Flow Rate 1.0mL/min) **Minor (*trans*)**: 81:19 (Column IB, IPA 0.4%, Flow Rate 1.0mL/min). ^{1}H NMR (500 MHz, $CDCl_3$): **Major (*cis*)**: δ 7.35 – 7.28 (m, 1H), 6.77 – 6.67 (m, 2H), 3.84 (d, *J* = 10.6 Hz, 1H), 3.66 (d, *J* = 10.6 Hz, 1H), 1.28 (s, 6H), 1.26 (s, 6H), 1.11 – 1.02 (m, 2H), 0.75 (s, 9H), 0.30 (dd, *J* = 9.2, 7.4 Hz, 1H), -0.24 (s, 3H), -0.27 (s, 3H). **Minor (*trans*)**: δ 7.32 – 7.21 (m, 1H), 6.81 – 6.73 (m, 1H), 6.74 – 6.64 (m, 1H), 3.83 (d, *J* = 10.1 Hz, 1H), 3.39 (d, *J* = 10.1 Hz, 1H), 1.13 (dd, *J* = 9.5, 3.7 Hz, 1H), 1.10 (s, 6H), 1.07 (dd, *J* = 7.1, 3.7 Hz, 1H), 0.96 (s, 6H), 0.79 (s, 9H), 0.43 (dd, *J* = 9.6, 7.0 Hz, 1H), -0.11 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): **Major (*cis*)**: δ 163.0 (dd, *J* = 249.5, 12.6 Hz), 162.9 (dd, *J* = 248.2, 12.5 Hz), 134.4 (+, dd, *J* = 9.5, 5.9 Hz), 127.7 (dd, *J* = 13.6, 3.6 Hz), 110.3 (+, dd, *J* = 20.8, 3.6 Hz), 103.3 (+, t, *J* = 25.5 Hz), 83.4 (2C), 67.4 (-), 30.1, 26.0 (+, 3C), 25.2 (+, 2C), 24.7 (+, 2C), 18.4, 15.9 (-), 5.5 (+), -5.5 (+), -5.7 (+). **Minor (*trans*)**: δ 162.6 (dd, *J* = 249.2, 12.0 Hz), 162.0 (dd, *J* = 246.5, 12.0 Hz), 134.2 (+, dd, *J* = 9.8, 6.3 Hz), 125.0 (dd, *J* = 13.7, 3.6 Hz), 110.4 (+, dd, *J* = 20.6, 3.3 Hz), 103.3 (+, t, *J* = 25.5 Hz), 83.0 (2C), 69.1 (-), 29.4, 25.9 (+, 3C), 24.9 (+, 2C), 24.6 (+, 2C), 18.4, 14.4 (-), 4.1 (+), -5.5 (+), -5.5 (+); ^{19}F NMR (376 MHz, $CDCl_3$) **Major (*cis*)**: δ -111.8 (d, *J* = 7.4 Hz), -113.0 (d, *J* = 6.9 Hz). **Minor (*trans*)**: δ -111.0 (d, *J* = 7.5 Hz), -113.3 (d, *J* = 7.3 Hz); FT IR (KBr, cm-1): 2979, 2952, 2929, 2887, 2858, 1598, 1504, 1446, 1415, 1371, 1359, 1325, 1257, 1083, 968, 837, 775; HRMS (TOF ES): HRMS (TOF ES): Found 447.2299, calculated for $C_{22}H_{35}BF_2O_3SiNa$ (M+Na) 447.2314 (3.4 ppm); $[\alpha]_D^{20}$ **Major (*cis*)**: -31.1° (c 2.04, $CHCl_3$) **Minor (*trans*)**: -18.9° (c 1.44, $CHCl_3$).

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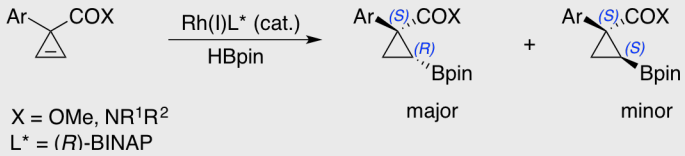

Directed enantioselective Rh(I)-catalyzed hydroboration of cyclopropenes

*Andrew Edwards, Marina Rubina, and Michael Rubin**

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Directed Rh(I)-Catalyzed Asymmetric Hydroboration of Prochiral 1-Arylcycloprop-2-ene-1-carboxylic Acid Derivatives