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Room-Temperature Rh-Catalyzed Asymmetric 1,4-Addition of Arylboronic Acids to Maleimides and Enones in the Presence of CF_3-Substituted MeOBIPHEP Analogues

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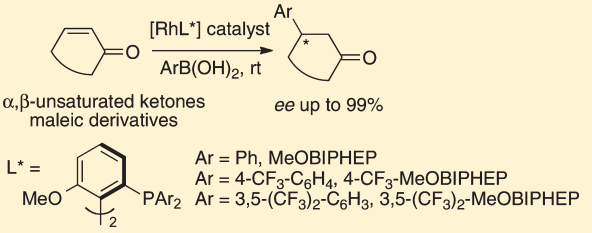
Supporting Information

ABSTRACT: A Rh-based catalytic system implying electron-poor MeOBIPHEP analogues has been developed for the 1,4-addition of boronic acids to maleimides and enones under mild conditions at room temperature and led to succinimide derivatives and arylated cyclic ketones in good to excellent yields and ee. We uncovered the crucial role of the electronic and steric properties of diphosphine ligand and observed a strong boronic acid/ligand dependency in the case of maleimide derivatives and substrate/ligand matching in the case of cyclic enones.



The twentieth century has seen an influx of chiral atropisomeric ligands, the first milestone representative being Noyori's Binap ligand.[1] The performance of Binap has been outstanding in several transformations including C−H and C−C bond formations. Nevertheless, the need for specificity and stereoselectivity in asymmetric processes prompted several academic and industrial groups to design novel atropisomeric backbones and thus novel chiral diphosphines.[2−5] We[6−11] and others[12−17] have been interested in the synthesis of MeOBIPHEP analogues. We have recently described a practical and efficient preparation of analogues *via* a Pd-catalyzed P−C coupling, which allowed an access to several electron-poor diphosphine ligands.[6] We turned our attention to the asymmetric Rh-catalyzed 1,4-addition reactions of boronic acids to Michael acceptors[18−20] and decided to evaluate the unprecedented activity of our new ligands **B**−**G** compared to the parent one **A**.[21,22] Some recent studies[23,24,16,17] comforted us on the ability to perform such Rh-catalyzed processes under mild conditions. We wish therefore to report herein the catalytic efficiency of the fluorinated analogues of the MeOBIPHEP ligand in 1,4-addition reactions of arylboronic acids to maleic derivatives and α,β-unsaturated cyclic ketones.

The addition of boronic acids to maleimides derivatives has been pioneered by Hayashi's group,[25−28] and the best results have been obtained in the presence of chiral dienes as ligands.[29] The resulting α-substituted succinimides are of potential interest for pharmaceutical applications.[30−32] In this context, we studied the addition of phenylboronic acid to benzylmaleimide in the presence of a rhodium catalyst consisting of $[RhCl(C_2H_4)]_2$ dimer, a chiral diphosphine, and KOH[33] as a base (Table 1). A previous report had shown that the use of (*R*)-BINAP allowed the formation of the desired product **2** in a moderate enantiomeric excess (Table 1, entry 1).[25] The use of MeOBIPHEP **A** or 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP **B**, the latter being recently a leader for Au-catalyzed C−C formations,[34−36] led to very disappointing results as no or very low conversions were observed, respectively (Table 1, entries 3 and 4). No reaction was observed without additional phosphorus ligand (Table 1, entry 2). In contrast, the reaction proceeded cleanly in the presence of electron-poor MeOBIPHEP analogues, bearing alkoxycarbonyl (ligands **E**, **F**) or trifluoromethyl groups (ligands **G**, **H**) on the aromatic ring of the phosphine (Table 1, entries 7−11). The reactivity was nevertheless not similar for all ligands as only traces (1−2%) of the desired product **2** were detected by ^{1}H NMR in the presence of (*R*)-4-CO_2*t*-Bu-MeOBIPHEP **C** or (*R*)-3-CO_2*t*-Bu-MeOBIPHEP **D** (Table 1, entries 5−6).

In the case of ligands **E**, **F**, **G**, and **H**, the enantiomeric excesses varied from 75% to 94% (Table 1, entries 7−11).[37] The best result was obtained when the 3,5-$(CF_3)_2$-substituted ligand **H** was used (Table 1, entry 10). This result is very close to the highest enantiomeric excess (95%) achieved using a chiral diene.[29,38] The importance of the amount of base (presumably to generate the active L*Rh-OH species)[18−20,23−29] was demonstrated by conducting the reaction in the presence of 10 mol % KOH instead of 50 mol %. The yield and the reaction stereoselectivity of the reaction dropped to 54% and 88%, respectively (Table 1, entry 11).

Interestingly the observed enantiomeric excesses could be correlated with the σ-donor properties of the ligands **A**−**H** (Table 2). General and simple methods have indeed been

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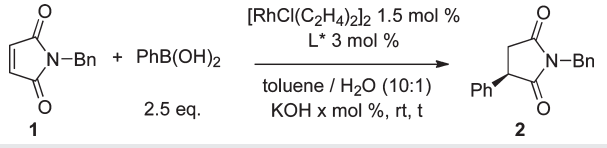
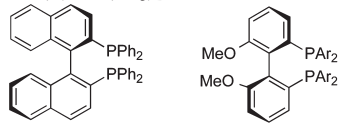
Table 1. Screening of Ligands



1 2

entry	L*	x (%)	t (h)	yield (%)[a]	ee (%)[b]
1[c]	(*R*)-BINAP	50	3	70	58
2		50	24	nr	
3	(*R*)-MeOBIPHEP **A**	50	24	0	
4	(*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP **B**	50	24	0[d]	
5	(*R*)-4-CO$_2$*t*-Bu-MeOBIPHEP **C**	50	24	0[d]	
6	(*R*)-3-CO$_2$*t*-Bu-MeOBIPHEP **D**	50	24	0[d]	
7	(*R*)-4-CO$_2$Bn-MeOBIPHEP **E**	50	24	50	80
8	(*R*)-3,5-(CO$_2$*t*-Bu)$_2$-MeOBIPHEP **F**	50	24	82	75
9	(*R*)-4-CF$_3$-MeOBIPHEP **G**	50	12	72	80
10	(*R*)-3,5-(CF$_3$)$_2$-MeOBIPHEP **H**	50	12	86	94
11	(*R*)-3,5-(CF$_3$)$_2$-MeOBIPHEP **H**	10	24	54	88



(*R*)-BINAP

(*R*)-MeOBIPHEP, Ar = C$_6$H$_5$ **A**
(*R*)-4-MeO-3,5-(*t*-Bu)$_2$MeOBIPHEP
Ar = 4-MeO-3,5-(*t*-Bu)$_2$C$_6$H$_2$ **B**
(*R*)-4-CO$_2$*t*-Bu-MeOBIPHEP, Ar = 4-CO$_2$*t*-Bu-C$_6$H$_4$ **C**
(*R*)-3-CO$_2$*t*-Bu-MeOBIPHEP, Ar = 3-CO$_2$*t*-Bu-C$_6$H$_4$ **D**
(*R*)-4-CO$_2$Bn-MeOBIPHEP, Ar = 4-CO$_2$Bn-C$_6$H$_4$ **E**
(*R*)-3,5-(CO$_2$*t*-Bu)$_2$-MeOBIPHEP, Ar = 3,5-(CO$_2$*t*-Bu)$_2$-C$_6$H$_3$ **F**
(*R*)-4-CF$_3$-MeOBIPHEP, Ar = 4-CF$_3$-C$_6$H$_4$ **G**
(*R*)-3,5-(CF$_3$)$_2$-MeOBIPHEP, Ar = 3,5-(CF$_3$)$_2$-C$_6$H$_3$ **H**

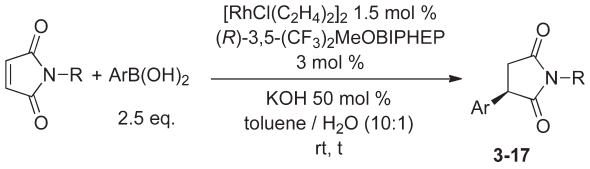
[a] Isolated yield, nr: no reaction. [b] Determined by HPLC analysis (Chiralcel ODH). [c] 50 °C, dioxane/H$_2$O, ref 25. [d] Traces (1−2%) of the desired product were detected by ^{1}H NMR.

Table 2. Electronic Properties of MeOBIPHEP Ligands

L*	^1J (^{77}Se−^{31}P) (Hz)	ν_{CO} (cm^{-1})
(*R*)-MeOBIPHEP **A**	743	2003
(*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP **B**	737	2002
(*R*)-4-CO$_2$*t*-Bu-MeOBIPHEP **C**	755	2012
(*R*)-3-CO$_2$*t*-Bu-MeOBIPHEP **D**	747	2009
(*R*)-4-CO$_2$Bn-MeOBIPHEP **E**	757	2011
(*R*)-3,5-(CO$_2$*t*-Bu)$_2$-MeOBIPHEP **F**	757	2015
(*R*)-4-CF$_3$-MeOBIPHEP **G**	760	2012
(*R*)-3,5-(CF$_3$)$_2$-MeOBIPHEP **H**	782	2040

described in the literature to quantify the σ-donor/π-acceptor character of a phosphine.[39,40] The magnitude of ^1J (^{77}Se−^{31}P) in phosphine selenide obtained from the reaction of a tertiary phosphine and selenium is dependent upon the nature of the organic groups bound to phosphorus.[41−46] Electron-withdrawing groups on phosphorus should cause the coupling constant to increase, whereas electron-donating groups and bulky groups will cause it to decrease.[47] As expected, the electron-withdrawing character of the trifluoromethyl-substituted ligands **G** and **H** induced higher coupling constants than those observed for parent MeOBIPHEP **A** and hindered 4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP **B** ligands (Table 2). It is noteworthy that a fine correlation between the strength of the electron-withdrawing group on the phosphine ligand (resulting from the substitution position and the nature of the group) and the reactivity of the corresponding Rh complex toward 1,4-addition (Table 2 and Table 1 entries 5 and 6 compared to entries 7−11) was observed. Indeed, the 4-CF$_3$-, 4-CO$_2$Bn-, and 3,5-(CO$_2$*t*-Bu)$_2$-substituted selenide derivatives present similar and ≥757 Hz ^1J values, which may be correlated to the observed enantiomeric excesses (Table 1). The same trend was observed when measuring the ν_{CO} stretching frequency by infrared spectroscopy of the complexes [Rh(CO)Cl(L*)].

Table 3. Substrate Scope of the [Rh]/(*R*)-3,5-(CF$_3$)$_2$-MeO-BIPHEP H System



3-17

entry	R	Ar	t (h)	yield (%)[a]		ee (%)[b]
1	Bn	4-Me-C$_6$H$_4$	12	80	**3**	92
2	Bn	4-MeO-C$_6$H$_4$	12	76	**4**	85
3	Bn	4-Br-C$_6$H$_4$	15	71	**5**	70
4	Bn	4-F-C$_6$H$_4$	15	74	**6**	80
5	Bn	4-CF$_3$-C$_6$H$_4$	24	52	**7**	82
6	Bn	3-MeO-C$_6$H$_4$	20	89	**8**	88
7	Bn	3-Cl-C$_6$H$_4$	24	56	**9**	74
8	Bn	3-CF$_3$-C$_6$H$_4$	12	73	**10**	70
9	Bn	3,5-(CF$_3$)$_2$-C$_6$H$_3$	24	55	**11**	37
10	Bn	3,5-Me$_2$-C$_6$H$_3$	24	83	**12**	58
11	Bn	2-Me-C$_6$H$_4$	24	81	**13**	40
12	Bn	2-naphthyl	24	69	**14**	80
13	Me	C$_6$H$_5$	24	68	**15**	83
14	Cy	C$_6$H$_5$	15	88	**16**	91
15	Cy	4-Me-C$_6$H$_4$	15	71	**17**	84

[a] Isolated yield. [b] Determined by HPLC analysis (Chiralcel ODH; see Supporting Information).

We then evaluated the efficiency of the [RhCl(C$_2$H$_4$)$_2$]$_2$/(*R*)-3,5-(CF$_3$)$_2$-MeOBIPHEP **H** catalytic system on 1,4-addition reactions of various boronic acids to maleimides (Table 3). In the case of the benzyl-substituted maleimide, good enantiomeric excesses (80−92%) were obtained when electron-donating or electron-withdrawing groups were placed in the *para* position of the boronic acid (Table 3, entries 1−5). The use of 4-bromo-substituted boronic acid afforded surprisingly the desired product **5** in a lower enantiomeric excess (Table 3, entry 3). The reaction was much more sensitive to the *meta* substitution of the boronic acid. Indeed, succinimides **8**, **9**, and **10** were obtained in 88%, 74%, and 70% enantiomeric excesses, respectively (Table 3, entries 6−8). In order to confirm the electronic versus steric influence on the reaction stereoselectivity, we conducted the 1,4-addition reaction in the presence of 3,5-dimethyl- and 3,5-ditrifluoromethyl-substituted boronic acids (Table 3, entries 9 and 10). As anticipated, when the reaction was conducted in the presence of the 3,5-ditrifluoromethylboronic acid, a low enantiomeric excess of 37% was measured (Table 3, entry 9). The electron-richer 3,5-dimethylboronic acid allowed the formation of the corresponding derivative **12** in a higher yield and

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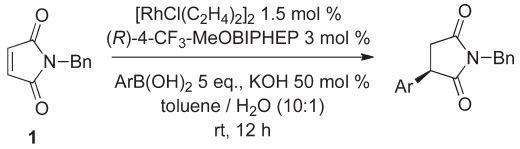
Scheme 1. 1,4-Addition Reactions in the Presence of the [Rh]/(*R*)-4-CF_3-MeOBIPHEP System



Ar = 4-$MeOC_6H_4$	**4**	95 %, 77 % *ee*
Ar = 3-$MeOC_6H_4$	**8**	86 %, 78 % *ee*
Ar = 3,5-$Me_2C_6H_3$	**12**	88 %, 75 % *ee*
Ar = 2-MeC_6H_4	**13**	99 %, 70 % *ee*
Ar = 2-naphthyl	**14**	82 %, 85 % *ee*

enantiomeric excess (58%) (Table 3, entry 10). The *ortho* substitution of the boronic acid induced a drop of the stereoselectivity of the reaction, as the succinimide **13** was isolated in 40% ee (Table 3, entry 11). The reaction of 2-naphthylboronic acid allowed the formation of **14** in 69% yield and 80% ee. The catalytic system was still active when methyl or cyclohexyl maleimides were engaged in the reaction (Table 3, entries 13−15). The addition of phenylboronic acid led to the arylated succinimides **15** and **16** in 83% and 91% enantiomeric excesses, respectively. The use of 4-methyl-substituted boronic acid led this time to a slight decrease of the enantiomeric excess (Table 3, entry 15), compared to the case implying the benzylmaleimide (Table 3, entry 1).

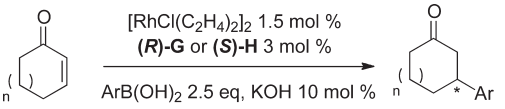
Considering that the stereoselectivity of the reaction of the maleimides showed a higher dependence on the boronic acid's structure than other 1,4-addition to Michael acceptors,[18−20] we decided to employ the less hindered but still electron-poor atropisomeric 4-CF_3-MeOBIPHEP ligand **G** in selected examples (Scheme 1).

Whereas lower enantiomeric excesses were observed in the case of MeO-substituted boronic acids (*para* and *meta* positions), we were pleased to observe higher enantiomeric excesses when 3,5-dimethyl-, 2-methyl-, and 2-naphtylphenylboronic acids were used. Gratifyingly the corresponding derivatives **12**, **13**, and **14** were obtained in good yields and in 75%, 70%, and 85% ee, respectively, which correspond to a substantial gap compared to 58%, 40%, and 80% previously observed (Table 3, entries 10 and 12).

The efficiency of the Rh/MeOBIPHEP analogues was finally studied with more classical substrates such as cyclic enones, having in mind that cyclopentenone was the most challenging substrate.[18−20] The reaction conditions were similar to those used in the case of maleimides, except that a lower amount of base was sufficient to perform the reaction at room temperature.[18−20,23,24] As anticipated, in the presence of 3,5-$(CF_3)_2$-MeOBIPHEP **H** ligand as the chiral inducer, the addition of electron-rich and electron-poor boronic acids afforded the corresponding arylated cyclohexanones **18**−**23** in good yields and excellent enantiomeric excesses (Table 4, entries 1−6). The lower yields obtained in the case of 4-methyl- and 4-methoxyphenylboronic acids (Table 4, entries 3 and 4) compared to literature[16,17,24] may be due to fast protodeboronation of boronic acid as a smaller amount of KOH (10 mol % instead of 20 or 50 mol %) was used.

The 1,4-addition of phenylboronic acid to cycloheptenone afforded the ketone **24** in high enantiomeric excess also (Table 4, entry 7). The reaction of cyclopentenone was much more interesting as, surprisingly, a moderate enantiomeric excess was

Table 4. 1,4-Addition of Boronic Acids to Cyclic Enones



entry	*n*	Ar	L*	*t* (h)	yield (%)		ee (%) (config)[b]
1	1	C_6H_5	(*S*)-**H**	2	92	**18**	99 (*S*)
2	1	4-Br-C_6H_4	(*S*)-**H**	15	96	**19**	98 (*S*)
3	1	4-Me-C_6H_4	(*S*)-**H**	6.5	55	**20**	97 (*S*)
4	1	4-MeO-C_6H_4	(*S*)-**H**	15	58	**21**	97 (*S*)
5	1	4-CF_3-C_6H_4	(*S*)-**H**	15	94	**22**	96 (*S*)
6	1	2-naphthyl	(*S*)-**H**	6.5	82	**23**	97 (*S*)
7	2	C_6H_5	(*S*)-**H**	7	99	**24**	98 (*S*)
8	0	4-Br-C_6H_4	(*S*)-**H**	6.5	89	**25**	72 (*S*)
9	0	4-Br-C_6H_4	(*R*)-**G**	6.5	70	**25**	94 (*R*)
10	0	4-F-3-Cl-C_6H_3	(*S*)-**H**	6.5	82	**26**	84 (*S*)
11	0	4-F-3-Cl-C_6H_3	(*R*)-**G**	6.5	40	**26**	93 (*R*)
12	0	C_6H_5	(*R*)-**G**	2.5	69	**27**	96 (*R*)
13	0	2-naphthyl	(*R*)-**G**	6.5	86	**28**	94 (*R*)
14	0	4-MeO-C_6H_4	(*R*)-**G**	6.5	96	**29**	92 (*R*)

[a] Isolated yield. [b] Determined by HPLC analysis (Chiralcel ADH, ASH; see Supporting Information).

obtained in the presence of the 3,5-$(CF_3)_2$-MeOBIPHEP **H** (Table 3, entry 8). Suspecting a substrate/ligand mismatch, we performed the same reaction with the less hindered 4-CF_3-MeOBIPHEP ligand **G**. The corresponding bromo adduct **25** was this time isolated in 94% enantiomeric excess instead of 72% (table 4, entry 9). This superiority of the 4-CF_3-MeOBIPHEP ligand **G** was confirmed by reacting the 4-fluoro-3-chloroboronic acid (Table 4, entries 10 and 11). The arylated ketone **26** was isolated in modest to good yields but 84% and 93% ee, respectively. Other boronic acids reacted smoothly under the same conditions with cyclopentenone substrate and led to the corresponding ketones with enantiomeric excesses superior to 90% (Table 4, entries 12−14).

In summary, we have extended the methodology of Rh-catalyzed 1,4-addition of boronic acids to Michael acceptors such as challenging maleimides and cyclic enones. We showed that a Rh-based catalytic system imploying electron-poor MeO-BIPHEP analogues allowed very clean reactions under mild conditions at room temperature and led to the succinimide derivatives and arylated cyclic ketones in good to excellent yields and ee. We uncovered the crucial role of the electronic and steric properties of diphosphine ligand and observed a strong boronic acid/ligand dependency in the case of maleimide derivatives and substrate/ligand matching in the case of cyclic enones. Further studies will be dedicated to the study of other catalytic applications of trifluoromethyl-substituted ligands based on the MeO-BIPHEP skeleton.

EXPERIMENTAL SECTION

General Information. Reactions were carried out in dried glassware under argon atmosphere, with degassed solvents. Toluene was distilled from calcium hydride. Solvents used in silica gel chromatographies were "analytical grade" and those used for extractions were

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"synthesis grade". ^{1}H and ^{13}C NMR data for compounds **2**, **4**, **6**, **12**, **13**, **15**, **16**, **18**−**25**, and **27**−**29** were identical to those described in the literature.[25−29,33] Flash chromatography separations were made on silica gel 0.040−0.063 mm, Art. 11567. ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance spectra were recorded at 300 MHz (or 400 MHz), 75 MHz (or 100 MHz), and 121 MHz respectively. High pressure liquid chromatography analyses (HPLC) equipped with a UV detector were performed on instruments equipped with Daicel Chiralcel OA, OB, OD, OD-H, OJ and Chiralpak AD and AS-H. Supercritical fluid chromatography analyses (SFC) were performed on instruments (equipped with Daicel Chiralcel OD-H, OJ and Chiralpak AD and AS-H).

Experimental Details for selected (P−P)Se_2 and Rh Complexes

Diphosphine Diselenide Formation. A solution of diphosphine (1 equiv) and 50 mg of selenium powder (excess) in degassed $CHCl_3$ (or MeOH) (0.015 M) under argon was stirred during 15 h at reflux temperature. The reaction mixture was brought to room temperature, and the black suspension was filtered through a short pad of Celite (CH_2Cl_2). The filtrate was concentrated under reduced pressure, and the solid obtained was used for NMR spectroscopy without further purification.

Synthesis of [RhCl(CO)(P*P)] Complexes. A solution of $[Rh(CO)_2Cl]_2$ (0.5 equiv, M = 388.80) and diphosphine (1 equiv) in dry and degassed CH_2Cl_2 (0.1 M) was degassed and stirred at room temperature under argon during 3 h. The reaction mixture was then concentrated, and the solid obtained was dried under vacuo and directly used for IR ν_{CO} determination without purification.

(4-CO_2t-Bu-MeOBIPHEP)Se_2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (s, 18H), 1.60 (s, 18H), 2.90 (s, 6H), 6.70 (d, ^{3}J = 8.0 Hz, 2H), 6.87 (dd, ^{3}J = 7.9, $^{3}J_{H-P}$ = 13.9 Hz, 2H), 7.19 (app td, ^{3}J = 8.0, $^{4}J_{H-P}$ = 3.1 Hz, 2H), 7.71 (dd, ^{3}J = 8.4, $^{3}J_{H-P}$ = 12.9 Hz, 4H), 7.88−8.02 (m, 12H). ^{31}P NMR ($CHCl_3$, 121 MHz): δ 31.7 ($^{1}J_{P-Se}$ = 755 Hz). [Rh(*p*CO_2*t*-Bu-MeOBIPHEP)(CO)Cl] ^{31}P NMR ($CHCl_3$, 121 MHz): δ 22.7 (dd, $^{2}J_{P-P}$ = 46 Hz, $^{1}J_{P-Rh}$ = 129 Hz), 43.4 (dd, $^{2}J_{P-P}$ = 46 Hz, $^{1}J_{P-Rh}$ = 162 Hz). IR ($CHCl_3$): ν_{CO} = 2012 cm^{-1}.

(3-CO_2t-Bu-MeOBIPHEP)Se_2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.50 (s, 18H), 1.51 (s, 18H), 3.07 (s, 6H), 6.55 (d, ^{3}J = 8.3 Hz, 2H), 6.99 (dd, ^{3}J = 8.1, $^{3}J_{H-P}$ = 14.3 Hz, 2H), 7.13 (app td, ^{3}J = 8.3, $^{4}J_{H-P}$ = 3.4 Hz, 2H), 7.44 (app dtd, ^{3}J = 8.2, $^{4}J_{H-P}$ = 2.6 Hz, 4H), 7.96−8.17 (m, 10H), 8.45 (m, 2H). ^{31}P NMR ($CHCl_3$, 121 MHz): δ 33.3 ($^{1}J_{P-Se}$ = 747 Hz). [Rh(3-CO_2*t*-Bu-MeOBIPHEP)(CO)Cl] ^{31}P NMR ($CHCl_3$, 121 MHz): δ 23.8 (dd, $^{2}J_{P-P}$ = 44 Hz, $^{1}J_{P-Rh}$ = 132 Hz), 43.9 (dd, $^{2}J_{P-P}$ = 44 Hz, $^{1}J_{P-Rh}$ = 159 Hz). IR ($CHCl_3$): ν_{CO} = 2007 cm^{-1}.

(4-CO_2Bn-MeOBIPHEP)Se_2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.87 (s, 6H), 5.34 (s, 4H), 5.39 (s, 4H), 6.68 (d, ^{3}J = 8.4 Hz, 2H), 6.85 (dd, ^{3}J = 8.2, $^{3}J_{H-P}$ = 14.0 Hz, 2H), 7.19 (app td, ^{3}J = 8.3, $^{4}J_{H-P}$ = 2.9 Hz, 2H), 7.34−7.44 (m, 20H, H_{ar}), 7.74 (dd, ^{3}J = 8.4, $^{3}J_{H-P}$ = 13.4 Hz, 4H), 7.91−8.02 (m, 8H), 8.11 (dd, ^{3}J = 8.7, $^{4}J_{H-P}$ = 2.7 Hz, 4H). ^{31}P NMR ($CHCl_3$, 121 MHz): δ 31.6 ($^{1}J_{P-Se}$ = 757 Hz). [Rh(4-CO_2Bn-MeOBIPHEP)(CO)Cl] ^{31}P NMR ($CHCl_3$, 121 MHz): δ 23.1 (dd, $^{2}J_{P-P}$ = 46 Hz, $^{1}J_{P-Rh}$ = 128 Hz), 43.4 (dd, $^{2}J_{P-P}$ = 46 Hz, $^{1}J_{P-Rh}$ = 159 Hz). IR ($CHCl_3$): ν_{CO} = 2011 cm^{-1}.

(3,5-(CO_2t-Bu)$_2$-MeOBIPHEP)Se_2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (s, 36H), 1.57 (s, 36H), 3.24 (s, 6H), 6.70 (d, ^{3}J = 8.3 Hz, 2H), 7.07 (dd, ^{3}J = 8.1 Hz, $^{3}J_{H-P}$ = 14.0 Hz, 2H), 7.31 (m, 2H), 7.76 (d, ^{3}J = 1.6 Hz, 2H), 7.78 (d, ^{3}J = 1.6 Hz, 2H), 7.95 (dd, ^{3}J = 1.6 Hz, $^{4}J_{H-P}$ = 13.7 Hz, 4H, H_5), 8.75 (dd, ^{3}J = 1.6 Hz, $^{4}J_{5-P}$ = 13.5 Hz, 4H, $H_{5'}$). ^{31}P NMR ($CHCl_3$, 121 MHz): δ 33.0 ($^{1}J_{P-Se}$ = 757 Hz). [Rh(3,5-(CO_2t-Bu)$_2$-MeOBIPHEP)(CO)Cl] ^{31}P NMR ($CHCl_3$, 121 MHz): δ 22.9 (dd, $^{2}J_{P-P}$ = 46 Hz, $^{1}J_{P-Rh}$ = 129 Hz), 43.9 (dd, $^{2}J_{P-P}$ = 46 Hz, $^{1}J_{P-Rh}$ = 161 Hz). IR ($CHCl_3$): ν_{CO} = 2015 cm^{-1}.

(4-CF_3-MeOBIPHEP)Se_2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.94 (s, 6H), 6.69 (d, ^{3}J = 8.4 Hz, 2H), 6.85 (dd, ^{3}J = 7.2, $^{3}J_{H-P}$ = 14.0 Hz, 2H), 7.26 (m, 2H), 7.62 (dd, ^{3}J = 8.5, $^{4}J_{H-P}$ = 2.2 Hz, 4H), 7.67 (dd, ^{3}J = 8.4, $^{4}J_{H-P}$ = 2.1 Hz, 4H), 7.82 (dd, ^{3}J = 8.1, $^{3}J_{H-P}$ = 12.9 Hz, 4H), 8.01 (dd, ^{3}J = 8.1, $^{3}J_{H-P}$ = 13.2 Hz, 4H). NMR ^{31}P ($CHCl_3$, 121 MHz): δ 31.6 ($^{1}J_{P-Se}$ = 760 Hz). [Rh(4-CF_3-MeOBIPHEP)(CO)Cl] ^{31}P NMR ($CHCl_3$, 121 MHz): δ 24.6 (dd, $^{2}J_{P-P}$ = 47 Hz, $^{1}J_{P-Rh}$ = 130 Hz), 44.5 (dd, $^{2}J_{P-P}$ = 47 Hz, $^{1}J_{P-Rh}$ = 163 Hz). IR ($CHCl_3$): ν_{CO} = 2012 cm^{-1}.

(3,5-(CF_3)$_2$-MeOBIPHEP)Se_2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.44 (s, 6H), 6.66 (d, J = 9 Hz, 2H), 6.94 (d, J = 9 Hz, 2H), 7.41 (t, J = 9 Hz, 2H), 7.57 (d, J = 36 Hz, 8H), 7.81 (d, J = 30 Hz, 4H).^{31}P NMR ($CHCl_3$, 121 MHz, d ppm): 32.1 ($^{1}J_{P-Se}$ = 782 Hz). [Rh(3,5-(CF_3)$_2$-MeOBIPHEP)-(CO)Cl] ^{31}P NMR ($CHCl_3$, 121 MHz): δ 25.3 (dd, $^{2}J_{P-P}$ = 49 Hz, $^{1}J_{P-Rh}$ = 132 Hz) IR ($CHCl_3$): ν_{CO} = 2040 cm^{-1}.

General Procedure for the 1,4-Addition Reactions. In a Schlenk tube, a solution of 2.9 mg of $[RhCl(C_2H_4)_2]_2$ (0.0075 mmol, 1.5 mol %, M = 388.93) and diphosphine[6] (3 mol %) in a mixture of toluene (1 mL) and KOH (0.10 mL, 0.25 mmol; 2.5 M aqueous) or KOH (0.10 mL, 0.05 mmol; 0.5 M aqueous) was stirred 20 min at room temperature. This mixture was transferred to a vessel containing maleimide (0.50 mmol) or α,β-unsaturated ketone (0.50 mmol) and arylboronic acid (2.5 equiv or 5 equiv) and stirred at room temperature. After completion of the reaction, dichloromethane was added, and the solution was washed twice with an aqueous saturated solution of $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. Crude product was purified by flash chromatography (PE/EtOAc 98/2). Proton and carbon nuclear magnetic resonance spectra were recorded at 300 MHz (or 400 MHz) and 75 MHz (or 100 MHz), respectively.

Compound ***3***. White solid, 112 mg, 80% yield. Mp 98 °C. ^{1}H NMR ($CDCl_3$): δ 7.43−7.40 (m, 2H), 7.34−7.26 (m, 3H), 7.15 (d, *J* = 9 Hz, 2H), 7.05 (d, *J* = 9 Hz), 4.76 (d, *J* = 13.8 Hz, 1H), 4.69 (d, *J* = 13.8 Hz, 1H), 3.96 (dd, *J* = 9 Hz, 6 Hz, 1H), 3.16 (dd, *J* = 19 Hz, *J* = 9 Hz, 1H), 2.79 (dd, *J* = 19 Hz, *J* = 5 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 176.6, 174.9, 136.6, 134.8, 133.1, 128.8, 127.8, 127.6, 126.9, 126.1, 44.5, 41.6, 36.1, 20.0. The ee was determined on a Daicel Chiralcel OD-H column with hexane/isopyl alcohol = 90:10, flow = 1.0 mL/min, 92% ee. $[\alpha]^{25}_{D}$ = +29.4 (*c* 1, $CHCl_3$) (*R*). HRMS calculated for $C_{18}H_{17}O_2NNa$ 302.01001, found 302.01024.

Compound ***5***. Yellow oil, 99 mg, 71% yield. ^{1}H NMR ($CDCl_3$): δ 7.43−7.17 (m, 7H), 6.94 (d, *J* = 12 Hz, 2H), 4.64 (d, *J* = 13.8 Hz, 1H), 4.58 (d, *J* = 13.8 Hz, 1H), 3.87 (dd, *J* = 9.2, 5.1 Hz, 1H), 3.09 (dd, *J* = 18 Hz, *J* = 9.6 Hz, 1H), 2.66 (dd, *J* = 18 Hz, *J* = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 176.9, 175.4, 136.0, 135.6, 132.3, 129.1, 128.8, 128.7, 128.1, 122.0, 45.3, 42.8, 36.8. The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, 70% ee. $[\alpha]^{25}_{D}$ = +39.4 (*c* 1, $CHCl_3$) (*R*). HRMS calculated for $C_{17}H_{14}O_2N$-BrNa 366.01022, found 366.01024.

Compound ***7***. Colorless oil, 87 mg, 52% yield. ^{1}H NMR ($CDCl_3$): δ 7.60 (d, *J* = 9 Hz, 2H), 7.42−7.26 (m, 7H), 4.77 (d, *J* = 14.1 Hz, 1H), 4.06 (d, *J* = 14.1 Hz, 1H), 4.07 (dd, *J* = 9.3, 5.1 Hz, 1H), 3.22 (dd, *J* = 18.1 Hz, *J* = 9.6 Hz, 1H), 2.80 (dd, *J* = 18.1 Hz, *J* = 5.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 177.3, 175.2, 135.6, 128.8, 128.7, 128.1, 127.8, 126.1, 126.0, 64.2, 45.6, 42.8, 36.7, 31.6, 25.2, 22.6, 14.0. The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, 82% ee. $[\alpha]^{25}_{D}$ = +11.1 (*c* 1, $CHCl_3$) (*R*). HRMS calculated for $C_{18}H_{14}O_2NF_3Na$ 356.08688, found 356.08705.

Compound ***8***. Pale yellow oil, 127 mg, 86% yield. ^{1}H NMR ($CDCl_3$): δ 7.43−7.23 (m, 6H), 6.73 (d, J = 7.2 Hz, 1H), 6.68 (m, 2H), 4.75 (d, *J* = 13.8 Hz, 1H), 4.69 (d, *J* = 13.8 Hz, 1H), 3.95 (dd, *J* = 10.5 Hz, 4.5 Hz, 1H), 3.73 (s, 3H), 3.17 (dd, *J* = 18.4 Hz, *J* = 9.5 Hz, 1H), 2.88 (dd, *J* = 18.4 Hz, *J* = 4.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 177.3, 175.8, 160.1, 138.8, 135.8, 130.2, 129.5, 128.8, 128.7, 128.0, 120.7, 119.5, 113.9, 113.4, 113.1, 55.2, 55.1, 45.9, 42.7, 37.2. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, 78% ee. $[\alpha]^{25}_{D}$ = +38.4 (*c* 1, $CHCl_3$) (*R*). HRMS calculated for $C_{18}H_{17}O_3NNa$ 318.11006, found 318.10998.

Compound **9**. Pale yellow oil, 84 mg, 56% yield. ^{1}H NMR ($CDCl_3$): δ 7.33−7.15 (m, 6H), 7.08−6.92 (m, 3H), 4.63 (d, J = 14.1 Hz, 1H), 4.60 (d, J = 14.1 Hz, 1H), 3.88 (dd, J = 12 Hz, 4.8 Hz, 1H), 3.11 (dd, J = 16.5 Hz, J = 9.6 Hz, 1H), 2.78 (dd, J = 16.5 Hz, J = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 176.8, 175.3, 139.0, 135.6, 135.0, 130.4, 128.8, 128.7, 128.2, 128.1, 127.7, 125.6, 45.4, 42.8, 36.9. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, 74% ee. $[\alpha]^{25}_D$ = +26.2 (c 1, $CHCl_3$) (R). HRMS calculated for $C_{17}H_{14}O_2NClNa$ 322.06053, found 322.06056.

Compound **10**. Pale yellow oil, 87 mg, 52% yield. ^{1}H NMR ($CDCl_3$): δ 7.33−7.15 (m, 6H), 7.08−6.92 (m, 3H), 4.63 (d, J = 14.1 Hz, 1H), 4.60 (d, J = 14.1 Hz, 1H), 3.88 (dd, J = 12 Hz, 4.8 Hz, 1H), 3.11 (dd, J = 16.5 Hz, J = 9.6 Hz, 1H), 2.78 (dd, J = 16.5 Hz, J = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 176.6, 175.1, 138.0, 135.6, 131.7, 131.3, 130.8, 129.7, 128.8, 128.2, 124.9, 124.8, 124.4, 124.3, 45.6, 42.9, 36.8, 25.3. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, 82% ee. $[\alpha]^{25}_D$ = +3.2 (c 1, $CHCl_3$) (R). HRMS calculated for $C_{18}H_{14}O_2NF_3Na$ 356.08688, found 356.08705.

Compound **11**. Yellow oil, 111 mg, 55% yield. ^{1}H NMR ($CDCl_3$): δ 7.75 (s, 1H), 7.56 (s, 2H), 7.33−7.18 (m, 5H), 4.79 (d, J = 14.1 Hz, 1H), 4.63 (d, J = 14.1 Hz, 1H), 4.05 (dd, J = 9, 6 Hz, 1H), 3.19 (dd, J = 18 Hz, J = 9.6 Hz, 1H), 2.74 (dd, J = 18 Hz, J = 5.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 175.8, 174.4, 139.3, 135.3, 133.2, 132.7, 132.3, 132.1, 128.8, 128.7, 128.3, 127.8,124.7, 122.1, 121.1, 45.2, 43.0, 36.4. The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, 37% ee. $[\alpha]^{25}_D$ = +4.8 (c 1, $CHCl_3$) (R). HRMS calculated for $C_{19}H_{13}O_2NF_6Na$ 424.07427, found 424.07415.

Compound **14**. Brown solid, 130 mg, 82% yield. mp 130 °C, ^{1}H NMR ($CDCl_3$): δ 7.63−7.50 (m, 3H), 7.63 (s, 1H), 7.50−7.32 (m, 7H), 7.23 (dd, J = 6.9 Hz, J = 9 Hz, 2H), 4.77 (d, J = 14.1 Hz, 1H), 4.73 (d, J = 14.1 Hz, 1H), 4.18 (dd, J = 11.7 Hz, 4.5 Hz, 1H), 3.26 (dd, J = 18.5 Hz, J = 9.3 Hz, 1H), 2.91 (dd, J = 18.5 Hz, J = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 177.3, 175.8, 160.1, 138.8, 135.8, 130.2, 129.5, 128.8, 128.7, 128.0, 120.7, 119.5, 113.9, 113.4, 113.1, 55.2, 55.1, 45.9, 42.7, 37.2. The ee was determined on a Daicel Chiralcel OD-H column with hexane/isoprpyl alcohol = 90:10, flow = 1.0 mL/min, 85% ee. $[\alpha]^{25}_D$ = +31.2 (c 1, $CHCl_3$) (R). HRMS calculated for $C_{21}H_{17}O_2NNa$ 338.11515, found 338.11512.

Compound **17**. White solid. 97 mg, 71% yield. mp 106 °C, ^{1}H NMR ($CDCl_3$): δ 7.16 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 4.05 (tt, J = 12.7 Hz, 3.7 Hz, 1H), 3.93 (dd, J = 9.7 Hz, 4.5 Hz, 1H), 3.11 (dd, J = 18.1 Hz, J = 9.6 Hz, 1H), 2.72 (dd, J = 18.1 Hz, J = 4.5 Hz, 1H), 2.24−2.13 (m, 2H), 1.88−1.79 (m, 2H), 1.70−1.58 (m, 3H), 1.41−1.15 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 177.8, 176.3, 138.0, 129.1, 127.8, 127.2, 52.0, 48.3, 45.6, 37.1, 28.9, 28.7, 25.84, 25.82, 25.0. The ee was determined on a Daicel Chiralcel OD-H column with hexane/isoprpyl alcohol = 90:10, flow = 1.0 mL/min, 84% ee. $[\alpha]^{25}_D$ = +22.9 (c 1, $CHCl_3$) (R).

Compound **26**. Brown oil, 45 mg, 40% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32−7.40 (m, 2H), 7.22−7.30 (m, 3H), 3.40−3.50 (m, 1H), 2.70 (dd, J = 18 Hz, 7.8 Hz, 1H), 2.25−2.55 (m, 4H), 1.95−2.10 (m, 1H). NMR ^{13}C ($CDCl_3$, 75 MHz): δ 158.5, 155.2, 128.9, 126.4, 121.0, 116.7, 45.6, 41.3, 38.7, 31.1. The ee was determined on a Daicel Chiralcel AS-H column with hexane/isopropyl alcohol = 99,5: 0,5, flow = 0.8 mL/min, 93% ee. $[\alpha]^{25}_D$ = +0.33 (c 0,33 $CHCl_3$) (R). HRMS calculated for $C_{11}H_9OFClNa$ 234.01241, found 234.01249.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H, ^{13}C NMR, HPLC spectra of new compounds and HPLC spectra of known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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