Journal of Organometallic Chemistry 693 (2008) 3519–3526

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Enantioselective silicon–boron additions to cyclic 1,3-dienes catalyzed by the platinum group metal complexes

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ARTICLE INFO

*Article history:*
Received 2 June 2008
Received in revised form 12 August 2008
Accepted 20 August 2008
Available online 28 August 2008

*Keywords:*
Silaboration
Interelement
Enantioselective
Diastereoselective
Catalysis

ABSTRACT

Silaborations of 1,3-cyclohexadiene and 1,3-cycloheptadiene were achieved using catalysts prepared from different combinations of phosphorus ligands and group 10 metal compounds. For the six-membered compound, 1,4-adducts with up to 82% ee were obtained employing Pt(0) and phosphoramidite ligands. For the seven-membered diene optimal conditions were found using catalysts based on Ni(0), but the highest selectivity observed was merely 22% ee. No improvement of the chiral induction was obtained using chiral silylboranes in combination with chiral phosphoramidite ligands in the additions to 1,3-cyclohexadiene. The adduct obtained from cyclohexadiene was used in allylborations of aldehydes under microwave irradiation to produce homoallylic alcohols with moderate to good diastereoselectivity.


## 1. Introduction

Additions of homo- and heteroelement–element linkages to unsaturated organic compounds catalyzed by the platinum group metals constitute synthetically highly versatile processes providing access to a variety of functionalized species for further transformations [1]. The insertion of 1,3-dienes into interelement σ bonds has emerged as a powerful route for the preparation of compounds containing two equal or different allylic functions in one step. The silaboration of 1,3-dienes, which normally proceeds in a 1,4-fashion, is particularly useful affording compounds containing at the same time allylsilane [2] and allylborane [3] functions [1c,e], which both serve as synthetically versatile structural motifs. The reactions were first studied by Suginome, Ito and coworkers, who found that whereas a Pt(0) catalyst resulted in 1:1 mixtures of E and Z olefins [4], pure Z isomers were obtained using a catalyst generated from $Ni(acac)_2$ and DIBALH [5]. The regioselectivity in reactions with unsymmetrically substituted dienes was poor, however. From cyclic substrates, *cis*-1,4-disubstituted adducts were obtained as the major products. The mechanism involves oxidative addition of the interelement linkage to the metal, insertion of the unsaturated moiety into an element–metal bond, and reductive elimination. The ease of oxidative addition has been shown to be highly dependent on the structure of the phosphine ligand and the silylborane [6]. The π-allyl complex resulting from insertion of the diene was recently detected by NMR spectroscopy [7].

Although conditions were at hand defining the relative configuration of the two new stereocenters formed in additions to cyclic 1,3-dienes, control of the absolute configuration is desirable in order to obtain non-racemic synthetic building blocks. So far this has been achieved in rather few interelement additions. Stereochemical control in silaborations was first achieved with 1,2-dienes as substrates. By using a combination of a chiral catalyst and chiral non-racemic silylboranes, high diastereoselectivities were observed in silaborations of achiral [8] and chiral [9] 1,2-dienes. Later enantioselective silaboration of 1,2-dienes was also achieved employing chiral phosphoramidites [10]. We decided to study the possibility to induce asymmetry in the silaboration of 1,3-dienes. After screening a multitude of metal–ligand combinations, we were able to report that platinum(0) together with chiral phosphoramidites served as useful catalyst precursors for enantioselective additions to 1,3-cyclohexadiene [11].

We have now further optimized this reaction and found conditions to include seven-membered cyclic dienes. The results of this study are presented here together with results from reactions of the adducts from cyclohexadiene with aldehydes.

## 2. Results and discussion

### 2.1. 1,3-Cyclohexadiene

Although it was shown by Ito and Suginome that Ni catalysts were superior to those based on Pt [5], their studies and our previous results indicated that using $Ni(acac)_2$ only a narrow range of electron-rich phosphines are able to provide active catalysts for

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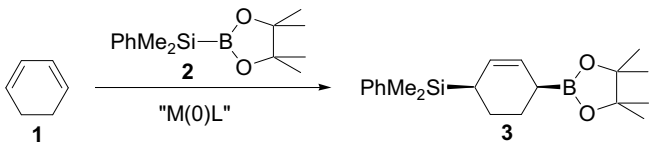
doi:10.1016/j.jorganchem.2008.08.029




**Scheme 1.**

the silaboration of 1,3-cyclohexadiene (Scheme 1). In the search for asymmetric catalysts, we therefore decided to evaluate not only Ni but also Pd and Pt complexes with a wide range of ligands under different conditions (room temperature, 80 °C and 110 °C). Using Ni(0) complexes we could confirm that electron-rich ligands seemed to be required, and with palladium complexes we could never observe any product formation. In contrast, catalysts prepared from $Pt(acac)_2$/DIBALH proved to provide the product using a wide range of ligands [11].

*2.1.1. Phosphoramidite Pt complexes*

In contrast to the situation with Ni, essentially all ligands tested together with $Pt(acac)_2$ provided the desired product, exceptions being *o*-(dicyclohexylphosphino)biphenyl and bidentate ligands, e.g. binap. The product was in fact formed even in the absence of ligand (16% yield, 20 h, 110 °C). The reactions were rather slow at 80 °C and were therefore usually run at 110 °C [11].

In our previous study we found that among the chiral ligands tested, phosphoramidites resulted in highest enantioselectivities [11]. The most interesting results are summarized in Table 1. It was obvious that the structure of the amine part of the ligand as well as the relative configuration of the two parts of the ligand play a major role for both the yield and the enantioselectivity. The highest enantiomeric excess was achieved using ligand **4a** (70% ee and 61% yield, entry 1). Using (*S*)-binaphthyl and chiral (*R*,*R*)- and (*S*,*S*)-bis(2-phenylethyl)amine gave the product with 28 and 69% ee, respectively (entries 2 and 3). The methylbenzyl substituted amidite afforded the product in 84% yield and 69% ee (entry 4). Replacing the binaphthyl part of the ligand with a substituted analogue did not improve the enantioselectivity of the reaction, the best result being a small increase in yield when using 3,3′-dimethyl substituted **5** (entry 5), although at the expense of the enantioselectivity (see Fig. 1).

Considering the promising results obtained using amidites derived from methylbenzylamine and bis(2-phenylethyl)amine (entries 3 and 4, Table 1), we decided to use dibenzylsubstituted ligand **4e**. Gratifyingly, the catalyst prepared with this ligand furnished the product in 84% yield and with the highest ee obtained so far, 77% (entry 1, Table 2).

We then proceeded by modifying the reaction conditions. First the ligand to metal ratio was varied using ligand **4d** at 110 °C. A 2:1 ratio proved to be most beneficial. A lower ligand/Pt ratio resulted in decreased reaction rate, possibly due to catalyst decomposition, while an increased ratio, 3:1, effectively inhibited the reaction (entries 2–4, Table 2). Since the catalysts containing ligand **4e** and **4d** seemed to exhibit higher activity than those with previously used ligands, reactions at lower temperatures were tested. Using ligand **4d** a decrease in reaction temperature to 80 °C evidently resulted in a moderate yield, but an increase in the enantiomeric excess to 78% ee. Encouraged by these results we performed the reaction using **4e** at 80 °C. Gratifyingly, an enantiomeric excess of 82% was recorded without too serious decrease in reactivity (58% yield, entry 6, Table 2). Under these conditions little difference was found between a 1:1 and a 2:1 ligand/Pt ratio, even though the 1:1 ratio gives the most reactive catalyst system (entries 6 and 7, Table 2). It is possible that catalyst decomposition is a less serious problem at 80 °C and that the reaction therefore works satisfactorily using a 1:1 ratio. Increasing the ratio to 3:1 again effectively inhibited the reaction (entry 8). It seems likely that an excess of amidite ligand inhibits the formation of some catalytically active species. On a 1 mmol scale, the conditions of entry 6 (except reaction time: 48 h) gave compound **3** in 73% isolated yield.

In order to further attempt to optimize the phosphoramidite ligand structure, ligands **6,** (*R*,*R*)-**7**, and (*S*,*R*)-**7** (see Fig. 2) were synthesized by a slight modification of the Feringa protocol [12]. During the course of our work the synthesis of **7** was also reported by Eberhartdt et al. [13]. These ligands are structurally similar to **4e**, but have a more rigid amine part. Ligand **6** can exist as two diastereomers due to the tropos nature of the biphenyl moiety.

Once these new amidites were at hand, they were tested in the silaboration of 1,3-cyclohexadiene. The results are summarized in Table 3. To our disappointment, no increase in enantioselectivity was observed and the reactivity was considerably lower than that

**Table 1**
Silaboration with phosphoramidite Pt complexes

| Entry | Ligand | Time (h) | Yield (%)[a] | ee (%) (product) |
|---|---|---|---|---|
| 1 | (*S*)-**4a** | 41 | 61 | 70 (**3**) |
| 2 | (*S*)-**4b** | 30 | 40 | 28 (**3**) |
| 3 | (*S*)-**4c** | 48 | 58 | 69 (**3**) |
| 4 | (*S*)-**4d** | 48 | 84 | 69 (**3**) |
| 5 | (*R*)-**5** | 48 | 92 | 58 (*ent*-**3**) |

Reactions performed in toluene using 5% $Pt(acac)_2$ and 10% of the ligand at 110 °C.
[a] Determined by $^1$H NMR using 1-methoxynaphthalene as internal standard.

**Table 2**
Lowering of reaction temperature and catalyst optimization

| Entry | Ligand | L/Pt ratio | Temperature (°C) | Time (h) | Yield (%)[a] | ee (%) |
|---|---|---|---|---|---|---|
| 1 | **4e** | 2:1 | 110 | 24 | 84 | 77 |
| 2 | **4d** | 1:1 | 110 | 24 | 50 | 69 |
| 3 | **4d** | 2:1 | 110 | 24 | 84 | 69 |
| 4 | **4d** | 3:1 | 110 | 24 | <5 | n.d. |
| 5 | **4d** | 2:1 | 80 | 48 | 69 | 78 |
| 6 | **4e** | 1:1 | 80 | 24 | 58[b] | 82[c] |
| 7 | **4e** | 2:1 | 80 | 48 | 53 | 81 |
| 8 | **4e** | 3:1 | 80 | 48 | <5 | n.d. |

Reactions performed in toluene using 5% $Pt(acac)_2$ (reduced to Pt(0) by DIBALH).
[a] Determined by $^1$H NMR using 1-methoxynaphthalene as internal standard.
[b] Average of three runs.
[c] Average of three runs. Deviation 1%.

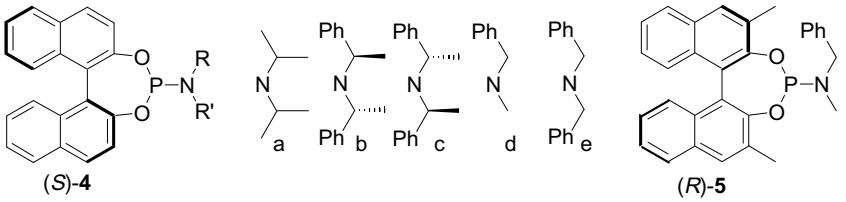



**Fig. 1.** Phosphoramidite ligands.

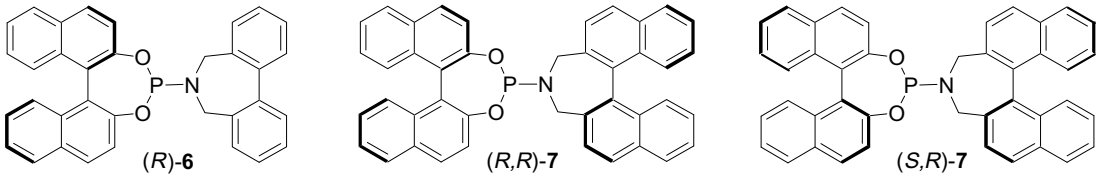



**Fig. 2.** Phosphoramidite ligands.

**Table 3**
Silaboration using phosphoramidite ligands

| Entry | Ligand | Time (h) | Yield (%)[a] | ee (%) (product) |
|---|---|---|---|---|
| 1 | (*R*)-**6** | 48 | 51 | 58 (*ent*-**3**) |
| 2 | (*R*,*R*)-**7** | 48 | 38 | 53 (*ent*-**3**) |
| 3 | (*S*,*R*)-**7** | 48 | 20 | 56 (**3**) |

Reactions performed in toluene using 5% $Pt(acac)_2$, 10% ligand, 80 °C.
[a] Determined by $^1H$ NMR using 1-methoxynaphthalene as internal standard.

**Table 4**
Silaboration using chiral tropos P-ligands

| Entry | Ligand | Time (h) | Yield (%)[a] | ee (%) |
|---|---|---|---|---|
| 1 | **10** | 20 | 60 | 4 |
| 2 | **11** | 16 | <5 | n.d. |

Reactions performed in toluene using 5% $Ni(acac)_2$, 10% ligand, 80 °C.
[a] Determined by $^1H$ NMR using 1-methoxynaphthalene as internal standard.

using **4e**. The biphenyl ligand gave the highest yield, suggesting that the binaphthyl ligands are too sterically hindered for satisfactory performance.

*2.1.2. Nickel complexes*

We decided to also further study catalysts based on Ni. Being limited to electron-rich phosphines when performing the reaction under Ni catalysis, we synthesized tropos ligands **10** and **11**, having electronic properties that were expected to be suitable for the reaction under study. The ligands were then tested in the silaboration of cyclohexadiene. The reaction using **11** gave only trace amounts of products, while **10** gave an appreciable yield, but a disappointingly low ee of merely 4% (see Scheme 2 and Table 4).

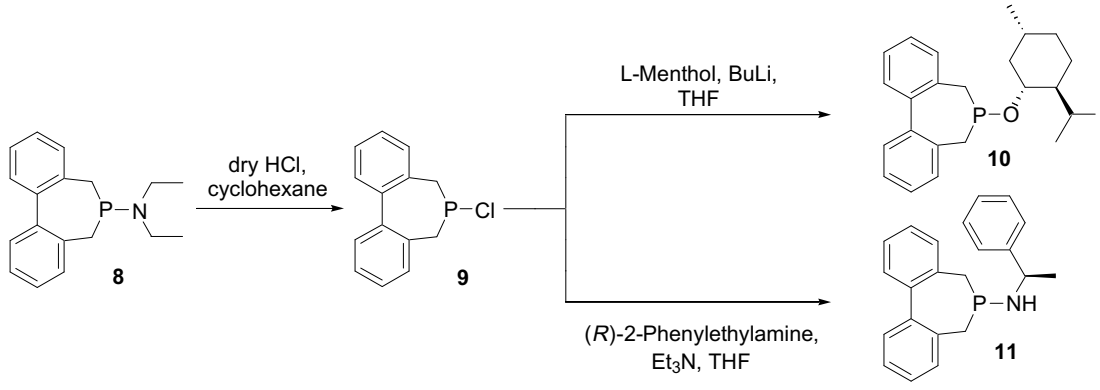
*2.1.3. Ligand mixtures*

Recently mixtures of chiral monodentate P-ligands have emerged as a new principle in asymmetric catalysis [14]. Combinations of chiral and achiral ligands have also been used successfully in rhodium catalyzed asymmetric hydrogenations [15]. Attempts to apply this strategy by mixing **4e** with achiral phosphines and tropoisomeric **8**, obtained as an intermediate in the synthesis of **10** and **11**, proved unsuccessful and never provided enantioselectivities higher than those observed with the chiral ligands alone.

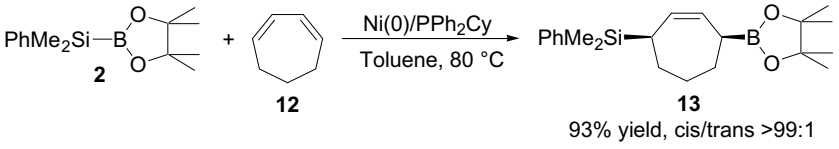
*2.2. 1,3-Cycloheptadiene*

In our effort to widen the scope of the asymmetric reaction we also turned our attention to 1,3-cycloheptadiene, which has previously been successfully silaborated by Ito and Suginome using $Ni(0)/PPh_2Cy$ [5] (see Scheme 3).

We again started our investigation by screening combinations of metals and ligands. To our surprise, using $Pt(acac)_2$ and $Pt_2(dba)_3$ together with $PPh_3$ or $PPh_2Cy$ at 80 °C and 110 °C, the expected product was not obtained. Instead small amounts of some other silaboration product that was not fully characterized were observed. When $Pd(acac)_2$ was tested under the same conditions as the platinum complexes, no product was observed. Finally we fine-tuned the reaction conditions using $Ni(acac)_2$ (Table 5). Triphenylphosphine was found to be a superior ligand to $PPh_2Cy$




**Scheme 2.** Synthesis of tropos ligands.




**Scheme 3.**

**Table 5**
Silaboration of cycloheptadiene using Ni complexes

| Entry | Metal | Ligand | Concentration (M) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | $Ni(acac)_2$ (5%) | $PPh_2Cy$ (10%) | 0.5 | 61 |
| 2 | $Ni(acac)_2$ (5%) | $PPh_2Cy$ (10%) | 0.8 | 50 |
| 3 | $Ni(acac)_2$ (10%) | $PPh_2Cy$ (20%) | 0.8 | 73 |
| 4 | $Ni(acac)_2$ (5%) | $PPh_2Cy$ (20%) | 0.5 | 84 |
| 5 | $Ni(acac)_2$ (5%) | $PPhMe_2$ (10%) | 0.5 | – |
| 6 | $Ni(acac)_2$ (5%) | $PPh_3$ (10%) | 0.5 | 97 |
| 7 | $Ni(acac)_2$ (5%) | $PPh_3$ (20%) | 0.5 | 83 |

Reactions performed in toluene for 24 h at 80 °C.
[a] Determined by $^1H$ NMR using 1-methoxynaphthalene as internal standard.

**Table 6**
Silaboration of cycloheptadiene using chiral Ni complexes

| Entry | Ligand | Yield[a] (%) | ee (%) |
|---|---|---|---|
| 1 | **4f** | 60 | 12 |
| 2 | **4g** | 55 | 22 |
| 3 | **4a** | – | |
| 4 | **4c** | 8 | 10 |
| 5 | **16** | 8 | n.d. |
| 6 | **17** | 17 | n.d. |
| 7 | **18** | 87 | 10 |
| 8 | **19** | 30 | 14 |
| 9 | Binap | 11 | n.d. |

Reactions performed in toluene, 80 °C 5% $Ni(acac)_2$, 2:1 P/Ni ratio, 24 h.
[a] Determined by $^1H$ NMR using 1-methoxy-naphthalene as internal standard.

and the reaction was best performed using a 2:1 $PPh_3/Ni(acac)_2$ ratio. Decreasing the amount of solvent did not increase the reaction rate (entries 1 and 2). Since a complex with triphenylphosphine catalyzed the reaction, we hoped that we could use a variety of monodentate, chiral phosphines as ligands.

In order to determine the enantioselectivity of the reaction, **13** was oxidized to allylic alcohol **14** [16] and then transformed into the (*S*)-Mosher ester. As the $^1H$ NMR spectra of the two diastereomers were very similar and their $^{19}F$ NMR signals overlapped, the enantiomeric excess was assessed by chiral HPLC (see Scheme 4).

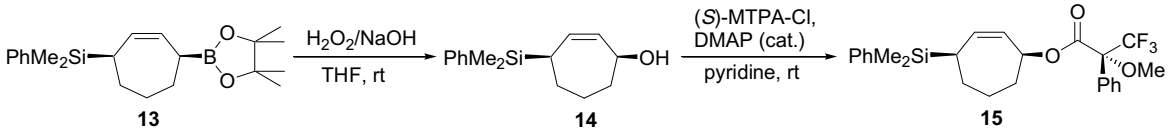
Phosphoramidites were first used as ligands as they gave superior induction in the silaboration of 1,3-cyclohexadiene. As expected, they did indeed give the desired product but, disappointingly, the highest ee observed was 22% (entries 1–4, Table 6). It seems that small substituents on nitrogen are beneficial for the reactivity of the complex. Then a variety of other chiral ligands were examined. The ee values were not higher than 20% and many of the ligands reacted sluggishly, although most of them provided the product (entries 5–9, Table 6 and Fig. 3).

### 2.3. Chiral silylboranes

Chiral analogues of **2** can easily be synthesized by reacting a chiral diol with $PhMe_2SiBCl(NEt_2)$ [8]. Such compounds have successfully been applied in the asymmetric silaboration of allenes [8,9]. Three structurally different silylboranes, **20**–**22**, were synthesized and applied in the silaboration of cyclohexadiene and cycloheptadiene (see Fig. 4).

#### 2.3.1. 1,3-Cyclohexadiene

The three silylboranes **20**, **21**, and **22** were employed in the silaboration of 1,3-cyclohexadiene together with several metal complexes and ligands. $Ni(acac)_2$ and $Pt(acac)_2$ were used in combination with the most reactive achiral ligands. The most interesting results are summarized in Table 7. Under nickel catalysis promising selectivities (up to 58% de) were observed using $PPh_2Cy$ as the ligand. Replacing it by tropos ligand **8** resulted in somewhat lower yields and unaltered or diminished selectivities. Combining platinum and $PPh_3$ as catalyst resulted in a 1:1 mixture of two




**Scheme 4.**

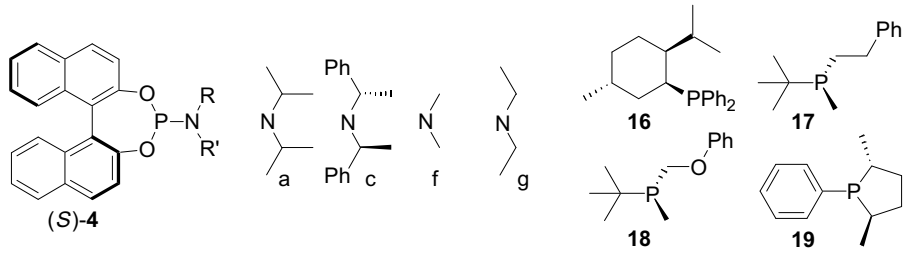



**Fig. 3.** Chiral ligands employed in silaboration of 1,3-cycloheptadiene.

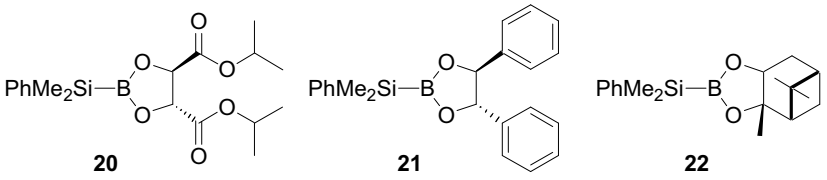



**Fig. 4.** Chiral silylboranes.

**Table 7**
Silaboration of 1,3-cyclohexadiene using **20**, **21**, and **22**

| Entry | Silylborane | Metal | Ligand | Temperature (°C) | Time (h) | Yield (%)[a] | de (%) |
|---|---|---|---|---|---|---|---|
| 1 | **20** | $Ni(acac)_2$ | $PPh_2Cy$ | 80 | 24 | 40 | 58 |
| 2 | **21** | $Ni(acac)_2$ | $PPh_2Cy$ | 80 | 24 | 86 | 44 |
| 3 | **22** | $Ni(acac)_2$ | $PPh_2Cy$ | 80 | 24 | 46 | 19 |
| 4 | **22** | $Pt(acac)_2$ | (*R*)-**4f** | 110 | 48 | 72 | 37 |
| 5 | **22** | $Pt(acac)_2$ | (*S*)-**4f** | 110 | 48 | 62 | 21 |
| 6 | **22** | $Pt(acac)_2$ | (*R*)-**4d** | 110 | 48 | 78 | 59 |
| 7 | **22** | $Pt(acac)_2$ | (*R*)-**4e** | 80 | 48 | 86 | 71 |

Reactions performed in toluene using 5% $M(acac)_2$, 10% ligand.
[a] Determined by $^1H$ NMR using 1-methoxynaphthalene as internal standard.

diastereomers, while combinations with phosphoramidite ligands exclusively resulted in lowered selectivities. Silylborane **22** gave the highest yields and selectivities and it was shown that (*R*)-configuration on the binol gave the matched complex (Table 7, entries 4–5).

### 2.3.2. 1,3-Cycloheptadiene

1,3-Cycloheptadiene was reacted with **20** and **21** using $Ni(acac)_2$ and achiral phosphines. The best results were obtained with **21**, yielding 70% of the desired product, with poor diastereoselectivity (7% de), employing $PPh_2Cy$ as the ligand.

## 2.4. Synthetic applications

We decided to investigate the reactivity of compound **3** in allylboration reactions, as these usually proceed with good to excellent diastereoselectivities, especially when catalyzed by Lewis acids [3,17]. Among the Lewis acids employed, $Sc(OTf)_3$ stands out as being the most efficient [18]. The 1,4-silaboration products of silylborane **2** and butadiene and 2,3-dimethylbutadiene have been subjected to allylboration reactions, and found to give the expected alcohols under mild reaction conditions [5]. The use of cyclic allylboronates in allylboration reactions has also been reported [19] (see Scheme 5).

### 2.4.1. Allylboration of aldehydes

As model substrate benzaldehyde was chosen and the reaction was first tested at room temperature in DCM, although without any noticeable conversion. Changing solvent to toluene and/or increasing the temperature (80 °C, 110 °C) did not result in any conversion of the starting materials. Using $Sc(OTf)_3$ (10 mol%) as Lewis acid in DCM, toluene or hexane at room temperature resulted in decomposition of the starting material, even in the absence of benzaldehyde and no allylboration product was observed. $BF_3 \cdot OEt_2$ was also tested at room temperature and −78 °C but still no product formation was observed. Considering the sterically demanding nature of our substrate, with the bulky dimethylphenylsilyl group blocking the access of the electrophile, we assumed that more forcing reaction conditions were required. Therefore we switched solvent to 1,2-dichlorobenzene, increased the amount of benzaldehyde from a slight excess to 10 equiv. and heated the reaction mixture in a microwave reactor. At 180 °C product started appearing, and after 5 h at 240 °C it could be isolated in 75% yield (sum of isomers). A screening of different aldehydes was then undertaken to investigate the scope and limitations of this reaction. Heating at 240 °C for 2 h was chosen as standard conditions (see Table 8).

**Table 8**
Allylboration of aldehydes

| Entry | Aldehyde | Yield[a] (%) | d.r.[b] | Product |
|---|---|---|---|---|
| 1 | Benzaldehyde | 77 | 72:28 | **23a** |
| 2 | Valeraldehyde | 88 | 71:29 | **23b** |
| 3 | Furfural | 76 | 87:13 | **23c** |
| 4 | Pivalaldehyde | 0 | – | – |
| 5 | *p*-Anisaldehyde | 0 | – | – |
| 6 | 4-Fluorobenzaldehyde | 90 | 65:35 | **23d** |
| 7 | Cyclohexanal | 72 | 90:10 | **23e** |
| 8 | *p*-(Trifluoromethyl)benzaldehyde | 64 | 72:28 | **23f** |

Reaction performed for 2 h in 1,2-dichlorobenzene at 240 °C in a microwave reactor.
[a] Determined by $^1H$ NMR using 1-methoxynaphthalene as internal standard. Sum of the two diastereomers.
[b] Estimated from crude $^1H$ NMR spectrum.

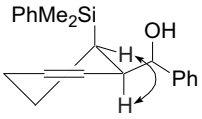
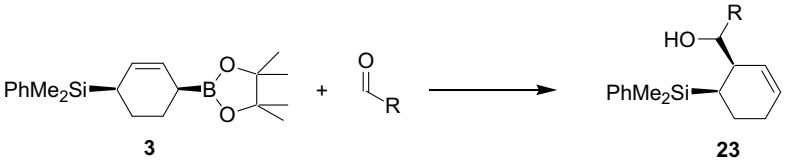



**Fig. 5.** NOESY correlation observed.

We were pleased to find that the reaction proceeded with both aliphatic and aromatic aldehydes, although the sterically demanding pivaldehyde and the electronically deactivated *p*-anisaldehyde failed to react. The diastereoselectivities obtained were good to modest. The yields were generally good. A cis configuration of the $PhMe_2Si$– and Ph(OH)CH-groups was confirmed by a strong NOESY correlation between the corresponding cis protons for both isomers of **23a**. The two diastereomers therefore differ in relative configuration at the hydroxy-substituted carbon atom (see Fig. 5).

## 3. Conclusion

Silaborations of 1,3-cyclohexadiene and 1,3-cycloheptadiene require different types of catalysts, containing Pt and Ni, respectively, in order to proceed efficiently. In contrast to the situation with linear 1,4-disubstituted 1,3-dienes, which provide 1:1 mixtures of dienylboranes and hydrosilylated products [20], only 1,4-silaborated adducts were obtained from the cyclic substrates. The product from addition of 2-(dimethylphenylsilyl)-4,4,5,5-tetrametyl-1,3,2-dioxaborolane to 1,3-cyclohexadiene was formed with 82% ee using a catalyst obtained by reduction of $Pt(acac)_2$ in the presence of a phosphoramidite with (*R*)-binaphthyl and dibenzylamino groups. Attempts to improve the enantioselectivity by using mixtures of phosphoramidites and achiral phosphines were unsuccessful. The conditions employed for reactions of cyclohexadiene did not provide the desired product from




3 23

**Scheme 5.**

1,3-cycloheptadiene. Instead, Ni(0) and phosphoramidites gave the 1,4-*cis* adduct with up to 22% ee. The allylboration of aldehydes using the product from silaboration of 1,3-cyclohexadiene was successfully performed in a microwave reactor at 240 °C.

## 4. Experimental

### 4.1. General remarks

All transition metal catalyzed reactions were prepared inside a nitrogen filled glovebox using oven dried glassware. After the reaction flask had been sealed, heating was performed outside the glovebox. Toluene, THF, $Et_2O$, and hexane were dried using a Glass-contour solvent dispensing system. The microwave heating was performed using a Smith Creator™ single mode cavity from Biotage. Cyclohexane was distilled from $CaH_2$ prior to use. Compounds **2** [21], **4** [12], **5** [11], **8**–**10** [22], **17**–**18** [23], **19** [24], **20**–**22** [8], and (*S*)-MTPA-Cl [25] were synthesized according to literature procedures. $Ni(acac)_2$ was dried in vacuo (1 mm Hg, 110 °C) prior to use. Benzaldehyde, *p*-anisaldehyde, furfural, and cyclohexanal used in allylboration reactions were freshly distilled. All other chemicals were of at least 97% purity and used as received. $^1H$ NMR spectra were recorded at 500 or 400 MHz, $^{13}C$ spectra at 125 MHz, and $^{31}P$ spectra at 202 MHz. The $^1H$ and $^{13}C$ chemical shifts are reported relative to $CHCl_3$; $^{31}P$ chemical shifts were not calibrated.

### 4.2. General procedure for silaboration of 1,3-dienes

Inside a nitrogen filled glovebox: silylborane **2** (52.2 mg, 0.2 mmol) was weighed into a vial. $M(acac)_2$ (0.01 mmol), ligand (0.02 mmol), toluene (0.20 mL), 1-methoxynaphtalene (29 μL, 0.2 mmol), and diene (0.50 mmol) were then added. The resulting mixture was cooled in a freezer at −35 °C for approx 10 min. DIBALH (1 M) in cyclohexane (20 μL, 0.02 mol) was added via a syringe and the solution was allowed to warm to room temperature over 30 min. Heating was then performed outside the glovebox. The yield was monitored by taking out 20 μL samples, evaporating the solvents, recording the $^1H$ NMR spectrum and comparing the integrals from 1-methoxynaphthalene ($\delta$ 4.0, –OMe) and compound **3** ($\delta$ 0.27 and 0.29, $-SiMe_2Ph$). The enantiomeric excess of compound **3** was determined as previously described [11].

### 4.3. Compound ***14***

Compound **13** [5] (crude product [26], maximum 0.2 mmol) was dissolved in THF (15 mL). NaOH (2 M, 1.5 mL, 3 mmol) and $H_2O_2$ (50% w/w, 0.7 mL, 1 mmol) were added via a syringe. The resulting mixture was stirred vigorously for 2.5 h and then diluted with 30 mL of $Et_2O$, washed with brine (2 × 10 mL), dried over $MgSO_4$, filtered, and purified by flash chromatography on silica gel using 5% EtOAc in hexane as eluent, yielding the desired product as a colorless oil in 71% yield (over 2 steps using $PPh_3$ as ligand for formation of **13**); $^1H$ NMR ($CDCl_3$): $\delta$ *7.52–7.50* (m, 2H), 7.37–7.35 (m, 2H), 5.76–5.72 (m, 1H), 5.66–5.62 (m, 1H), 4.40 (s, 1H), 1.9–1.25 (m, 9H), 0.32 (s, 3H), 0.30 (s, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 138.3, 137.7, 134.4, 131.3, 129.6, 128.2, 72.0, 37.2, 29.9, 28.4, 27.7, −3.9, −4.0.

### 4.4. Compound ***15***

Inside a nitrogen filled glovebox compound **14** (6.74 mg, 0.027 mmol) was weighed into a flask. DMAP (1.77 mg, 0.016 mmol) and (*S*)-MTPA-Cl (12 μl, 0.035 mmol) were then added. Pyridine (120 μL) was added via a syringe and the solution was stirred at r.t. for 16 h. The resulting product was taken up in EtOAc (20 mL) and washed with sat. $NaHCO_3$ (2 × 10 mL) and $NH_4Cl$ (2 × 10 mL) solutions and brine (2 × 10 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvents were evaporated in vacuo to yield the title compound. The enantiomeric excess was determined by HPLC [CHIRALCEL OD-H, 0.025% *i*-PrOH/hexane, 1 mL/min]. $^1H$ NMR ($CDCl_3$) $\delta$ *7.52–7.48* (m, 4H), 7.39–7.36 (m, 6H), 5.75–5.67 (m, 2.5H), 5.61–5.55 (m, 0.5H), 0.27 (s, 6H).

### 4.5. Synthesis of phosphoramidite ligands

#### 4.5.1. Synthesis of the chlorophosphite

Under an $N_2$-atmosphere (*R*)- or (*S*)-binol (287 mg, 1 mmol) was suspended in toluene (3 mL) and THF was added until the binol dissolved (0.5 mL). The binol solution was slowly added to a cooled (−60 °C) solution of $Et_3N$ (278 μL, 2 mmol) and $PCl_3$ (87 μL, 1 mmol) and the resulting mixture was stirred at −60 °C for 2 h and then transferred into a nitrogen filled glovebox and filtered through celite to remove $Et_3N{\cdot}HCl$. The solution was diluted to 10.00 mL with toluene to obtain a 0.10 M solution of the chlorophosphite that was stored in the glovebox at −35 °C.

#### 4.5.2. Synthesis of phosphoramidite ligands

Inside a nitrogen filled glovebox a 0.1 M solution of the chlorophosphite (1.76 mL, 0.176 mmol) was added to a solution of amine (52.0 mg, 0.176 mmol) and $Et_3N$ (24.7 μL, 0.176 mmol) in toluene (0.6 mL) at −35 °C. The resulting mixture was stirred at r.t. for 18 h and filtered through celite using toluene as eluent. The resulting mixture was removed from the glovebox and the solvent was removed in vacuo. The crude amidite was purified on deactivated silica gel (prepared by suspending $SiO_2$ (250 g) and $NaHCO_3$ (5 g) in MeOH and then evaporating the solvent until dryness) using a gradient of hexane–DCM mixtures.

#### 4.5.3. (*R*)-***6***

$^1H$ and $^{31}P$ NMR spectra were in accordance with literature data [27].

#### 4.5.4. (*R,R*)-***7***

$^1H$ and $^{31}P$ NMR spectra were in accordance with literature data [13].

#### 4.5.5. (*S,R*)-***7***

$^1H$ and $^{31}P$ NMR spectra were in accordance with literature data [13].

### 4.6. Compound ***11***

$Et_3N$ (50.8 μL, 365 μmol) was added to a solution of **9** (30 mg, 122 μmol) and (*R*)-(+)-1-phenylethylamine (14.7 mg, 122 μmol) in THF (1 mL), and the mixture was stirred at r.t. for 18 h and then filtered through celite. After evaporation of the solvents, **11** (16 mg, 40%) was obtained as a colourless oil. MS (EI, 70 eV): *m/z* 330 [$M^+$−1] (76), 288 (100), 226 (8), 212 (24), 197 (82), 178 (40), 165 (40), 152 (8), 136 (6), 120 (12), 105 (24); $^1H$ NMR ($CDCl_3$) (mixture of two diastereomers) $\delta$ 1.46 (d, $J$ = 6.7 Hz, 3H), 1.49 (d, $J$ = 6.7 Hz, 3H), 1.61 (br t, $J$ = 8.2 Hz, 2 × 1H), 2.36–2.17 (m, 4 × 1H), 2.48–2.58 (m, 2 × 1H), 2.77 (dd, $J_{H-H}$ = 12.4, $J_{P-H}$ = 14.6 Hz, 1H), 2.88 (app t, $J$ = 13.3 Hz, 1H), 4.10–4.27 (m, 2 × 1H), 6.70 (d, $J$ = 7.5 Hz, 1H), 7.01–7.05 (m, 1H), 7.17–7.42 (m, 2 × 12H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 147.3 (d, $J_{C-P}$ = 3.0 Hz), 146.9 (d, $J_{C-P}$ = 4.8 Hz), 140.8, 140.7, 140.6, 140.5, 140.4, 135.7, 135.5, 134.5 (d, $J_{C-P}$ = 6.8 Hz), 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.3, 127.2, 127.0, 126.8, 126.7, 126.6, 126.3, 126.2, 126.1, 126.0, 56.5 (d, $J_{C-P}$ = 22.0 Hz), 55.7 (d, $J_{C-P}$ = 22.0 Hz), 36.6 (d, $J_{C-P}$ = 29.1 Hz), 36.5 (d, $J_{C-P}$ = 27.3 Hz), 35.9 (d, $J_{C-P}$ = 23.4 Hz), 35.3 (d, $J_{C-P}$ = 25.5 Hz), 26.1

(d, $J_{C-P}$ = 6.5 Hz), 25.4 (d, $J_{C-P}$ = 8.8 Hz); $^{31}$P NMR (202 MHz, $CDCl_3$) $\delta$ 61.0, 59.2.

### 4.7. Compound **16**

Inside a nitrogen filled glovebox compound **15** (6.74 mg, 0.027 mmol) was weighed into a flask. DMAP (0.77 mg, 6.2 μL) and (*S*)-MTPA-Cl (10 μl, 62 μL) were then added. Pyridine (120 μL) was added via a syringe and the solution was stirred at r.t. for 16 h. The resulting product was taken up in EtOAc (20 mL) and washed with sat. $NaHCO_3$ (2 × 10 mL) and $NH_4Cl$ (2 × 10 mL) solutions and brine (2 × 10 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvents were evaporated in vacuo to yield the title compound. The enantiomeric excess was determined by HPLC [CHIRALCEL OD-H, 0.025% *i*-PrOH/hexane, 1 mL/min]. $^1$H NMR ($CDCl_3$) $\delta$ *7.52–7.48* (m, 4H), 7.39–7.36 (m, 6H), 5.75–5.67 (m, 2.5H), 5.61–5.55 (m, 0.5H), 0.27 (s, 6H).

### 4.8. General procedure for allylboration of aldehydes

Inside a nitrogen filled glovebox compound **3** (51.3 mg, 0.15 mmol) was weighed into a vial [28]. 1,2-Dichlorobenzene (500 μL) and aldehyde (1.5 mmol) were then added and the vial was capped. Heating was performed outside the glovebox in a microwave reactor. 1-Methoxynapthalene (23.7 mg, 0.15 mmol) and 2 mL of water were then added and the mixture stirred for 15 min. $Et_2O$ (10 mL) was added and the phases separated. The water phase was then repeatedly extracted with $Et_2O$ (3 × 10 mL) and the combined organic phases dried over $MgSO_4$, filtered, the solvents were evaporated and a $^1$H NMR spectrum was recorded. The crude product was then dried under vacuum to remove remaining 1,2-dichlorobenzene. Purification was performed using gradient chromatography yielding the products as colorless oils.

#### 4.8.1. Compound **23a**

Compound **23a** was purified on alumina (activity grade II) using gradient of 1–5% EtOAc in hexane. Yield 75%, major + minor isomer (5 h r × n time). Major and minor isomer were then separated on silica using a gradient of 2–5% EtOAc in hexane. Major isomer: $^1$H NMR ($CDCl_3$) $\delta$ 0.39 (s, 3H), 0.51 (s, 3H), 1.35–1.50 (m, 1H), 1.70–1.90 (m, 1H), 1.83 (d, *J* = 8.9 Hz, 1H), 1.95–2.30 (m, 3H) 2.43–2.55 (m, 1H), 4.89 (d, *J* = 8.9 Hz,1H), 5.18–5.30 (m, 1H), 5.97–6.10 (m, 1H), 6.70–6.88 (m, 2H), 7.10–7.22 (m, 3H), 7.58–7.70 (m, 3H), 7.87–7.98 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ *−4.6, −2.9,* 20.5, 26.2, 26.6, 42.4, 75.0, 124.2, 124.8, 126.4, 127.8, 128.1, 129.0, 133.1, 134.0, 138.5, 144.7. Anal. Calc. for $C_{21}H_{26}$Osi: C, 78.21; H, 8.13. Found: C, 78.11; H, 8.09%.

Minor isomer: $^1$H NMR ($CDCl_3$) $\delta$ 0.41 (s, 3H), 0.44 (s, 3H), 1.49 (d, *J* = 4.9 Hz, 1H), 1.50–1.56 (m, 1H), 1.78–1.90 (m, 2H), 1.92–2.12 (m, 2H), 2.61–2.67 (m, 1H), 4.37 (dd, *J* = 10.0, 4.9 Hz, 1H), 4.97–5.02 (m, 1H), 5.54–5.61 (m, 1H), 7.19–7.39 (m, 8H), 7.59–7.68 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ *−2.9, −1.9,* 21.4, 25.7, 26.3, 44.6, 76.2, 126.9, 127.6, 127.8, 128.28, 128.33, 128.6, 129.4, 133.8, 141.2, 143.7.

#### 4.8.2. Compound **23b**

Compound **23b** was purified on alumina (activity grade II) using a gradient of 1–10% $Et_2O$ in hexane. Yield 67%, major isomer (91:9 d.r.). Major isomer: $^1$H NMR ($CDCl_3$) $\delta$ 0.33 (s, 3H), 0.37 (s, 3H), 0.79–0.85 (t, *J* = 7.1 Hz, 3H), 1.02–1.42 (m, 8H), 1.65–1.75 (m, 1H), 1.92–2.16 (m, 3H), 2.20–2.26 (m, 1H), 3.60–3.68 (m, 1H), 5.67–5.78 (m, 1H), 5.99–6.08 (m, 1H), 7.29–7.40 (m, 3H), 7.49–7.59 (m, 2H). $^{13}$C NMR$CDCl_3$) $\delta$ *−3.99, −3.29,* 14.0, 20.6, 22.5, 26.3, 26.8, 28.2, 36.9, 39.6, 74.2, 125.3, 127.8, 128.8, 132.7, 133.8, 138.9. Anal. Calc. for $C_{19}H_{30}$OSi: C, 75.43; H, 10.00. Found: C, 75.32; H, 9.88%.

#### 4.8.3. Compound **23c**

Compound **23c** was purified on silica gel using a gradient of 2–5% $Et_2O$ in hexane. Yield 20%, major isomer. $^1$H NMR ($CDCl_3$) $\delta$ 0.41 (s, 3H), 0.43 (s, 3H), 1.35–1.42 (m, 1H), 1.70–1.76 (m, 1H), 1.84 (d, *J* = 9.7 Hz, 1H), 1.92–2.18 (m, 3H), 2.71–2.80 (m, 1H), 4.87 (d, *J* = 9.6 Hz, 1H), 5.44–5.51 (m, 1H), 6.00 (dt, *J* = 3.2, 0.9 Hz, 1H), 6.03–6.10 (m, 1H), 6.27 (dd, *J* = 3.20, 1.82 Hz, 1H), 7.27–7.30 (m, 1H), 7.32–7.40 (m, 3H), 7.52–7.61 (m, 2H). Spectrum contains around 24% of the minor isomer.

#### 4.8.4. Compound **23d**

Compound **23d** was purified on silica gel using gradient of 5–40% DCM in hexane. Yield 82%, major (maj) + minor (min) isomer (65:35 d.r.). $^1$H NMR ($CDCl_3$) $\delta$ 0.38 (s, 3H, maj), 0.42 (s, 3H, min), 0.44 (s, 3H, min), 0.51 (s, 3H, maj), 1.18–1.59 (m, overlapping), 1.71–2.28 (m, overlapping), 2.40–2.48 (m, 1H, maj), 2.53–2.65 (m, 1H, min), 4.36 (dd, *J* = 10.0, 4.1 Hz, 1H, min), 4.84 (d, *J* = 8.8 Hz, 1H, maj), 4.99 (ddt, *J* = 10.0, 4.3, 2.1 Hz, 1H, min), 5.18–5.28 (m, 1H, maj), 5.56–5.64 (m, 1H, min), 6.02–6.12 (m, 1H, maj), 6.63–6.78 (m, 2H, maj), 6.81–6.91 (m, 2H, maj), 6.92–7.03 (m, 2H, min), 7.13–7.22 (m, 2H, min), 7.30–7.68 (m, overlaping), 7.78–7.82 (m, 1H, min). $^{13}$C NMR ($CDCl_3$) $\delta$ *−4.80* (maj), −2.90 (min), −2.76 (maj), −1.86 (min), 20.5 (maj), 21.3 (min), 24.8 (maj), 25.7 (min), 26.1 (maj), 26.3 (min), 26.4 (maj), 42.5 (maj), 44.7 (min), 74.5 (maj), 75.5 (min), 114.5 (maj), 114.6 (maj), 114.9 (min), 115.1 (min), 123.9 (maj), 126.3 (maj), 126.4 (maj), 127.77 (min), 127.84 (maj), 128.1 (maj), 128.42 (min), 128.49 (min), 128.53 (min), 128.66 (min), 129.1 (maj), 129.2 (min), 133.5 (maj), 133.9 (d, $^2J_{C-F}$ = 25.4 Hz, maj), 134.1 (d, $^2J_{C-F}$ = 23.6, min), 138.4 (maj), 139.5 (d, $^3J_{C-F}$ = 3.1 Hz, min), 140.4 (d, $^3J_{C-F}$ = 3.1 Hz, maj), 141.0 (min), 161.5 (d, $^1J_{C-F}$ = 244.3 Hz, maj), 162.8 (d, $^1J_{C-F}$ = 245.4 Hz, min).

#### 4.8.5. Compound **23e**

Compound **23e** was purified on silica gel using a gradient of 11–50% DCM in hexane. Yield 66%, major + minor isomer. Major isomer: $^1$H NMR ($CDCl_3$) $\delta$ 0.33 (s, 3H), 0.37 (s, 3H), 0.52 (app. qd, *J* = 12.2, 3.8 Hz, 1H), 0.76 (app. qd, *J* = 12.5, 3.3 Hz, 1H), 1.04 (d, *J* = 9.5 Hz, 1H), 1.06–1.34 (m, 6H), 1.39–1.49 (m, 1H), 1.52–1.61 (m, 2H), 1.63–1.77 (m, 2H), 1.89–2.18 (m, 4H), 2.45–2.50 (m, 1H), 3.27 (app t, *J* = 9.0 Hz, 1H), 5.63–5.70 (m, 1H), 5.99–6.07 (m, 1H), 7.32–7.39 (m, 3H), 7.50–7.57 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ *−3.9, −3.3,* 20.6, 25.9, 26.1, 26.2, 26.3, 26.7, 29.3, 29.6, 36.1, 42.6, 78.7, 125.5, 127.7, 128.8, 132.6, 133.85, 138.94. Anal. Calc. for $C_{21}H_{32}$OSi: C, 76.77; H, 9.82. Found: C, 76.65; H, 9.77%.

Minor isomer: $^1$H NMR ($CDCl_3$) $\delta$ 0.30 (s, 3H), 0.34 (s, 3H), 0.78 (d, *J* = 7.2 Hz, 1H), 0.83–1.90 (m, 14H), 1.93–2.11 (m, 2H), 2.30–2.37 (m, 1H), 3.20–3.27 (m, 1H), 5.63–5.67 (m, 1H), 5.68–5.75 (m, 1H), 7.32–7.38 (m, 3H), 7.52–7.58 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ *−2.4, −2.3,* 21.0, 24.4, 25.4, 26.4, 26.70, 26.76, 26.82, 31.2, 39.0, 40.1, 127.9, 128.6, 128.8, 129.6, 133.8, 141.4. Signal from RCH(OH)Cy obscured by residual solvent peak.

#### 4.8.6. Compound **23f**

Compound **23f** was purified on silica gel using a gradient of 0–10% $Et_2O$ in hexane. Yield 29%, major isomer. $^1$H NMR ($CDCl_3$) $\delta$ 0.38 (s, 3H), 0.53, (s, 3H), 1.40–1.51 (m, 1H), 1.77–1.88 (m, 1H), 1.91 (d, *J* = 9.0 Hz, 1H), 1.96–2.12 (m, 2H), 2.13–2.27 (m, 1H), 2.43–2.50 (m, 1H), 4.88 (d, *J* = 9.0 Hz, 1H), 5.12–5.19 (m, 1H), 6.04–6.12 (m, 1H), 6.76–6.82 (m, 2H), 7.39–7.48 (m, 5H), 7.61–7.66 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ *−5.0, −2.7,* 20.4, 26.1, 26.4, 42.4, 74.5, 123.4, 124.2 (q, $^1J_{C-F}$ = 271.7 Hz), 124.7 (q, $^3J_{C-F}$ = 3.7 Hz), 125.2, 128.2, 128.7 (q, $^3J_{C-F}$ = 32.3 Hz), 129.2, 133.96, 134.00, 138.3, 148.8.

## Acknowledgments

This work was supported by the Swedish Research Council and by the Carl Trygger Foundation. We are grateful to Dr Nina Kann and Dr Magnus Johansson for generous gifts of ligands **18** and **19**. We would also like to thank Mr. Michael Holzwarth for his effort on the allylboration reactions and Dr. Zoltan Szabo for running NOESY spectra.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.08.029.

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[28] Compound **3** can be weighed and handled outside the glovebox without the use of schlenck techniques. As it slowly decomposes in air we chose to store and handle it inside the glovebox.