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Bulky *N*-Heterocyclic-Carbene-Coordinated Palladium Catalysts for 1,2-Addition of Arylboron Compounds to Carbonyl Compounds

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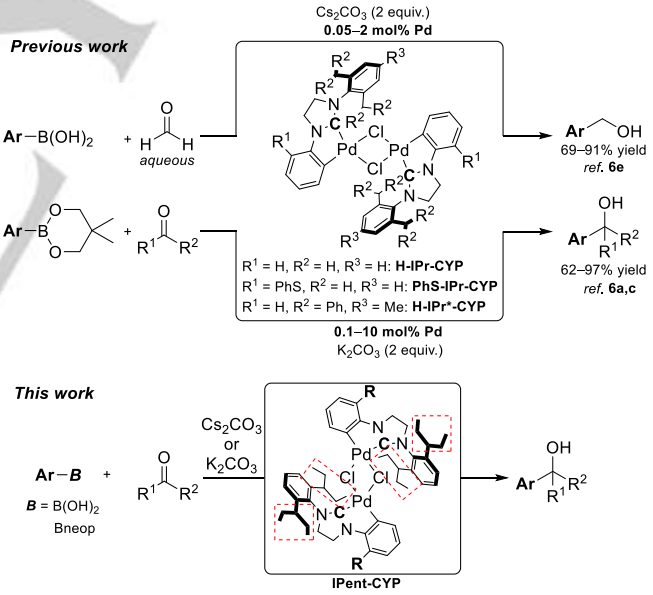
‡ Responsible for X-ray crystal structure determination

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

Abstract: The synthesis of primary, secondary, and tertiary alcohols by the 1,2-addition of arylboronic acids or boronates to carbonyl compounds, including unactivated ketones, using novel bulky yet flexible *N*-heterocyclic carbene (NHC)-coordinated 2,6-di(pentan-3-yl)aniline (IPent)-based cyclometallated palladium complexes (CYPs) as catalysts is reported. The PhS-IPent-CYP-catalyzed reactions are efficient at low catalyst loadings (0.02–0.3 mol% Pd), and the exceptional catalytic activity for 1,2-addition is attributed to the steric bulk of the NHC ligand. These reactions can yield a wide range of functionalized benzylic alcohols that are difficult to synthesize by classical protocols using highly active organomagnesium or lithium reagents.

Introduction

Benzylic alcohols are one of the most important moieties found in various bioactive compounds and their intermediates.[1] 1,2-Addition of carbon nucleophiles to carbonyl compounds is the most popular approach for the synthesis of benzylic alcohols because it can provide a range of primary, secondary, and tertiary alcohols.[2] Although typical carbon nucleophiles such as organomagnesium[2h] and lithium[2d] compounds have high reactivities for such addition reactions, they have the disadvantages of poor functional group tolerance and air/moisture sensitivity. In contrast to the traditional Grignard reaction, the transition-metal-catalyzed Grignard-type reaction using moisture- and air-stable arylboronic acids as carbon nucleophiles tolerates a broad range of functional groups and yields various functionalized benzylic alcohols.[3–8] Therefore, numerous transition metal catalysts for the 1,2-addition of arylboron compounds to carbonyl compounds have been explored. Although 1,2-addition to aldehydes is commonly realized, very few catalysts have also promoted 1,2-addition to unactivated ketones. Furthermore, only rhodium[4f,k] and nickel[5b,d,e,h] catalysts have been used for intermolecular addition reactions to unactivated ketones in recent years.



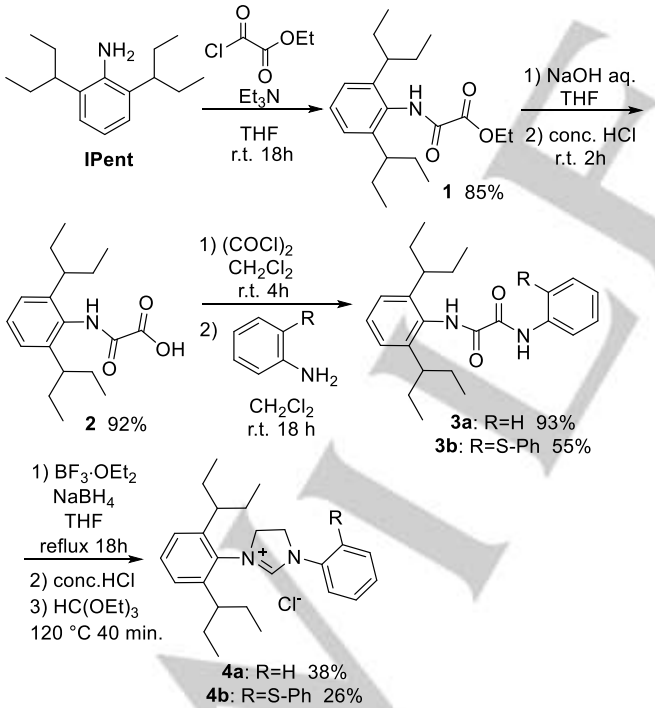
Scheme 1. NHC-coordinated CYPs catalyzed 1,2-addition of arylboron compounds to carbonyl compounds.

In our laboratory, we have focused on catalysis by cyclometallated palladium complexes (CYPs). Most recently, we have demonstrated that PhS-IPr-CYP exhibits remarkable catalytic activity for intermolecular 1,2-addition reactions to various carbonyl compounds, including unactivated ketones, at lower catalyst loading than those required for Rh and Ni catalysts (Scheme 1).[6a,c] It is well known that the effect of *N*-heterocyclic carbene (NHC) ligands on palladium catalysis is strongly related to their steric bulk, with increased flexible steric bulk leading to more effective catalysis.[9,10] Thus, a reasonable increase in the bulkiness due to the 2,6-diisopropylphenyl

groups on IPr-CYPs has the potential to further improve the catalytic activity for 1,2-addition reactions. In fact, H-IPr*-CYP with highly hindered and less flexible 2,6-bis(diphenylmethyl)-4-methylphenyl groups shows better catalytic activity than H-IPr-CYP but lower catalytic activity than PhS-IPr-CYP.[6c] Based on these results, we have focused on the 2,6-di(penta-3-yl)phenyl group, which is more flexible than the 2,6-bis(diphenylmethyl)-4-methylphenyl group and bulkier than the 2,6-diisopropylphenyl group. Here, we report the synthesis of bulky yet flexible 2,6-di(penta-3-yl)aniline (IPent)-based NHC-coordinated CYPs (IPent-CYPs) and their catalytic behavior for the 1,2-addition of arylboron compounds to carbonyl compounds.

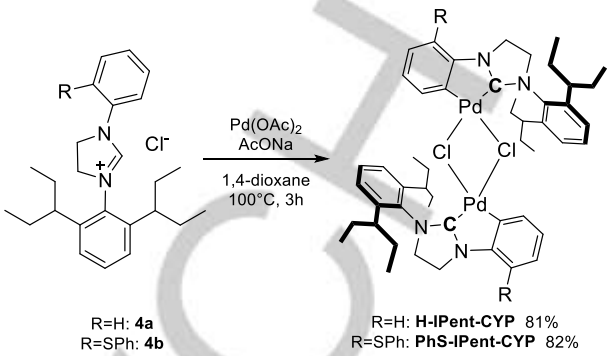
Results and Discussion

Nolan and co-workers have reported a bulky imidazolium chloride (IPent·HCl), which is readily available via the cyclization of the corresponding diimine using paraformaldehyde under acidic conditions.[10i] In contrast, Organ and co-workers have reported that its saturated analogue is unobtainable using a typical procedure involving the cyclization of the corresponding diamine using orthoformate ester. The synthesis of sterically demanding imidazolinium salts needed Tf_2O as a strong dehydration reagent for the dehydrative cyclization of *N*-formyl *N*,*N*'-diarylethylenediamine under strong acidic conditions using TfOH.[11] However, IPent-based unsymmetrical 1,3-diarylimidazolinium chlorides **4** were synthesized via a typical procedure in moderate yields (Scheme 2).



Scheme 2. Synthesis of IPent-based imidazolinium salts **4**.

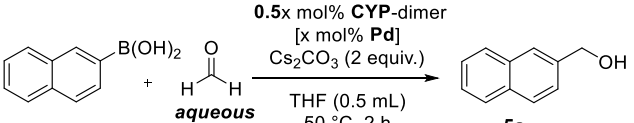
In the same manner as described in our previous report,[6d] H-IPent-CYP and PhS-IPent-CYP were prepared from $Pd(OAc)_2$ and corresponding imidazolinium salts **4** (Scheme 3). High-resolution FAB mass spectroscopy revealed that both complexes are μ-chloro-bridged dimers, similar to IPr-CYPs. For PhS-IPent-CYP, the structure was also clearly revealed by X-ray crystallographic analysis.[12]



Scheme 3. Synthesis of IPent-CYPs from IPent based imidazolinium salts **4** and $Pd(OAc)_2$

First, the IPent-CYP and IPr-CYP catalysts were compared by examining the NHC-CYP-catalyzed 1,2-addition of 2-naphthalenylboronic acid to aqueous formaldehyde, as summarized in Table 1. H-IPr-CYP and PhS-IPr-CYP have previously been reported to have good catalytic activity (turnover number (TON) up to 960) at 70 °C.[6d] However, their activities declined under the current mild conditions, and the corresponding alcohol was afforded in low yields (entries 1 and 2). In contrast, H-IPent-CYP and PhS-IPent-CYP strongly promoted the reaction under the same mild conditions, providing the desired product in satisfactory yields (entries 3 and 4). Although H-IPr*-CYP and H-IPent-CYP exhibited poor catalytic activity at only 0.03 mol% catalyst loading, PhS-IPent-CYP showed excellent catalytic activity at this catalyst loading, achieving a TON of 3200 (entries 5–7).

Table 1. Survey of CYP-catalyzed 1,2-addition of 2-naphthalenylboronic acid to aqueous formaldehyde.

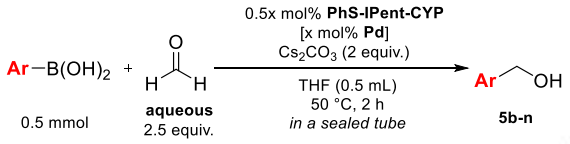


entry	catalyst	x	Yield (%)[a]
1	H-IPr-CYP	0.05	26
2	PhS-IPr-CYP	0.05	29
3	H-IPent-CYP	0.05	96
4	PhS-Ipent-CYP	0.05	97
5	H-IPr*-CYP	0.03	8
6	H-IPent-CYP	0.03	20[b]
7	PhS-Ipent-CYP	0.03	96[b]

[a] Isolated yield. [b] 1 mmol of 2-naphthalenylboronic acid, 2.5 mmol of formaldehyde and 2.0 mmol of Cs_2CO_3 were used in the reactions.

The scope of the PhS-IPent-CYP-catalyzed hydroxymethylation of various (hetero)arylboronic acids and esters using aqueous formaldehyde is summarized in Table 2. 1-Naphthaleneboronic acid, which is slightly sterically crowded, showed reactivity similar to that of 2-naphthaleneboronic acid (entry 1). Arylboronic acids bearing electron-donating groups like methoxy or poor electron-withdrawing groups like chloro, bromo, and ethoxycarbonyl were smoothly converted to the corresponding benzylalcohols in 83–93% yields at a low catalyst loading of 0.03 mol% (entries 2–6). In contrast, substrates bearing reactive and strong electron-withdrawing functional groups such as formyl, nitro, and cyano required the use of 0.05 mol% PhS-IPent-CYP (entries 7–9). Further, heteroarylboronic acids such as 2,6-dimethoxy-3-pyridyl-, 2-benzofuranyl-, and 2-benzothiophenylboronic acid were easily converted to the desired products at a catalyst loading of 0.03 mol% (entries 10–12). However, the reaction of substrates bearing cyano or pyridyl groups, which coordinate strongly to palladium complexes, required a higher temperature of 70 °C (entries 9 and 10).

Table 2. PhS-IPent-CYP-catalyzed hydroxymethylation of arylboronic acids to aqueous formaldehyde.



Entry	Ar	5	x (mol%)	Yield (%)[a]
1	1-naphthyl	**b**	0.03	87
2	4-methoxyphenyl	**c**	0.03	84
3	2-methoxy	**d**	0.03	93
4	4-chlorophenyl	**e**	0.03	86
5	4-bromophenyl	**f**	0.03	83
6	4-(ethoxycarbonyl)phenyl	**g**	0.03	90
7	4-formyl-3-methoxyphenyl	**h**	0.05	80
8	3-nitrophenyl	**i**	0.05	93
9[b,c]	3-cyanophenyl	**j**	0.05	81
10[c]	2,6-dimethoxy-3-pyridyl	**k**	0.03	83
11	2-benzofuranyl	**l**	0.03	81
12[d]	2-benzo[b]thiophenyl	**m**	0.03	86

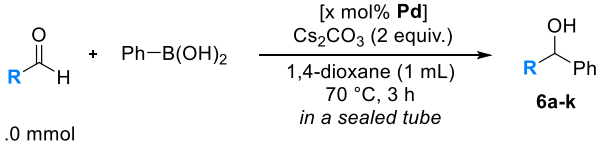
[a] Isolated yield. [b] 2-Me-THF was used instead of THF. [c] The reaction was carried out at 70 °C. [d] CsF was used instead of Cs_2CO_3.

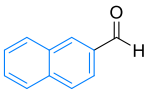
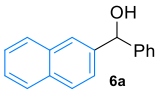
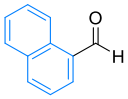
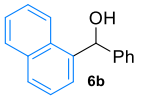
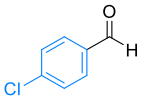
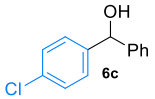
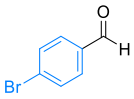
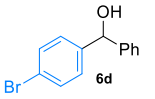
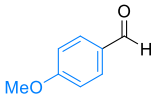
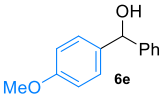
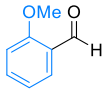
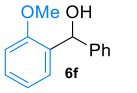
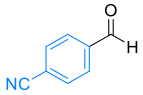
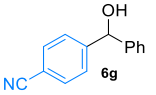
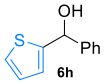
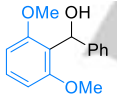
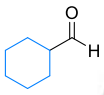
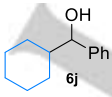
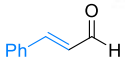
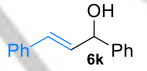
PhS-IPent-CYP also exhibited excellent catalytic activity for the 1,2-addition of phenylboronic acid to aldehydes other than formaldehyde, as summarized in Table 3. Slightly electron-poor or neutral aryl aldehydes such as naphthaldehydes and 4-chlorobenzaldehyde easily reacted at a catalyst loading of 0.025 mol% (entries 1, 5 and 6). Phenylboronic acid neopentyl glycol ester reacted with 2-naphthaldehyde to give as excellent a yield as phenylboronic acid, whereas phenylboronic acid pinacol ester and 2,4,6-triphenylboroxine were not suitable for the catalytic reaction. The results show the 1,2-addition reaction to aldehydes would rather not occur in the absence of water (entries 1–4). Unfortunately, the reaction with 4-bromobenzaldehyde afforded a complex mixture of several diarylmethanols, including desired **6d**, 4-phenylbenzhydrol, and other compounds, as detected by crude ^{1}H NMR (entry 7). Although methoxybenzaldehydes, which are electron-rich aryl aldehydes, required a catalyst loading of 0.05 mol%, the reactions proceeded smoothly regardless of the position of the methoxy group (entries 8 and 9). The phenylation of aldehydes containing coordinating atoms such as N or S also proceeded in excellent yields (entries 10 and 11). A sterically hindered 2,6-disubstituted benzaldehyde, an aliphatic aldehyde, and alkenyl aldehyde were also converted to the corresponding alcohols in good yields (entries 12–14).

The 1,2-addition reactions of arylboronic acids to 2-naphthaldehyde are summarized in Table 4. 2-Naphthalene boronic acid, sterically hindered 1-naphthaleneboronic acid, electron-rich 4-methylphenylboronic acid, and slightly electron-poor 4-chlorophenylboronic acid reacted at a catalyst loading of 0.025 mol%, giving the corresponding products in excellent yields (entries 1–4). Interestingly, 4-bromophenylboronic acid was smoothly transformed to corresponding alcohols. Although the bromine atom on 4-bromobenzaldehyde was very reactive because electron-withdrawing groups like the formyl group on the aryl halide facilitate oxidative addition, that on 4-bromophenylboronic acid remained nearly intact, with byproducts such as (4-biphenyl)(2-naphthyl)methanol formed in less than 3% yield (entry 5). The reactions of arylboronic acids substituted with electron-withdrawing fluoro, trifluoromethyl, and methoxycarbonyl groups and that of 2-thiopheneboronic acid required a catalyst loading of exceeding 0.05 mol% (entries 6–9).

We also examined the PhS-IPent-CYP-catalyzed 1,2-addition of arylboronates to unactivated ketones under the optimized conditions previously determined with PhS-IPr CYP[6a] (Table 5). The PhS-IPent-CYP-catalyzed reaction provided triphenylmethanol **7a** from benzophenone and phenylboronate in 96% yield at a catalyst loading of 0.2 mol% (entry 1). Notably, the catalytic activity of PhS-IPent-CYP was more than 25 times higher than that of PhS-IPr-CYP for this addition reaction. PhS-IPent-CYP exhibited good catalytic activity even with a catalytic loading of 0.1 mol% and showed superior catalytic activity to H-IPent-CYP (entry 2). Phenylboronic acid was not suitable for the 1,2-addition to benzophenone (entry 3). 2-Acetonaphthone and dialkyl ketones such as acetone and *N*-Boc-4-piperidone also reacted at lower catalyst loadings to give the desired products in satisfactory yields (entries 4–6). Although acetone, which is the simplest ketone, required a catalyst loading of 0.1 mol%, the reaction proceeded under mild conditions, which is advantageous owing to the low boiling point of acetone. Methoxyphenylboronates bearing strong electron-donating groups were efficiently converted to the corresponding tertiary alcohols (entries 7 and 8). Even reactions with arylboronates bearing strong electron-withdrawing groups such as fluoro, trifluoromethyl, methoxycarbonyl, and nitro proceeded with catalyst loadings of only 0.04–0.3 mol% (entries 9–12). Moreover, the TON achieved with PhS-IPent-CYP was approximately 100 times greater than that achieved with PhS-IPr-CYP in the reaction of 4-trifluoromethylphenylboronate.

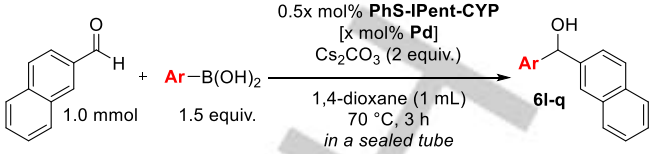
Table 3. PhS-IPent-CYP-catalyzed phenylation of aldehydes.

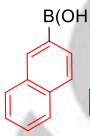
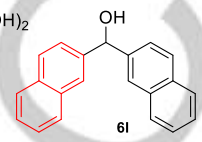
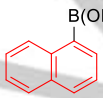
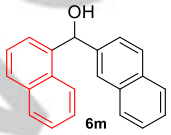
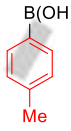
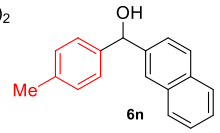
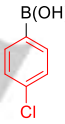
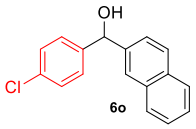
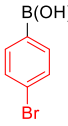
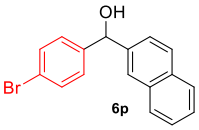
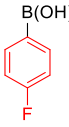
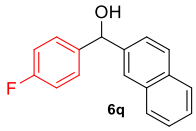
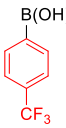
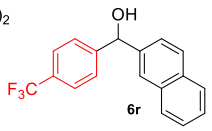
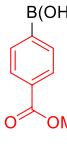
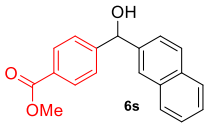


Entry	Aldehyde	Product **6**	x (mol%)	Yield (%)[a]
1		 **6a**	0.025	95
2[b]			0.025	92
3[c]			0.025	30
4[d]			0.025	18
5		 **6b**	0.025	95
6		 **6c**	0.025	97
7		 **6d**	0.025	C.M.[e]
8		 **6e**	0.05	81
9		 **6f**	0.05	91
10		 **6g**	0.05	98
11		 **6h**	0.075	96
12[b]		 **6i**	0.1	76
13[f]		 **6j**	0.2	96
14[b,g]		 **6k**	0.1	96

[a] Isolated yield. [b] Phenylboronic acid neopentyl glycol ester was used instead of phenylboronic acid. [c] Phenylboronic acid pinacol ester was used instead of phenylboronic acid. [d] 2,4,6-Triphenylboroxine was used instead of phenylboronic acid. [e] Complex mixture. [f] CsF was used instead of Cs_2CO_3 and the reaction was carried for 18 h. [g] The reaction was carried out at 100 °C.

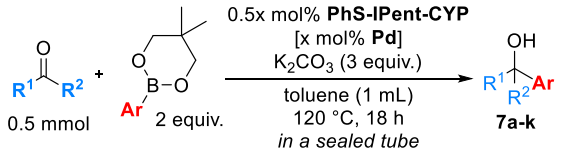
Table 4. PhS-IPent-CYP-catalyzed 1,2-addition of arylboronic acids to 2-naphthaldehyde.

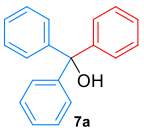
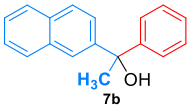
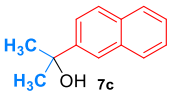
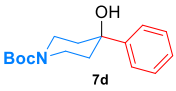
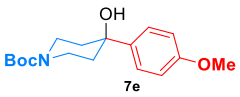
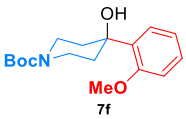
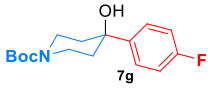
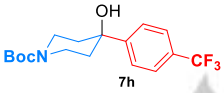
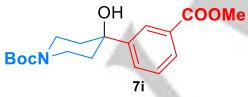
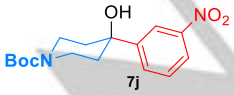


Entry	Arylboronic acid	Product **6**	x (mol%)	Yield (%)[a]
1		 **6l**	0.025	93
2		 **6m**	0.025	93
3		 **6n**	0.025	95
4		 **6o**	0.025	84
5		 **6p**	0.05	90
6		 **6q**	0.075	93
7		 **6r**	0.075	99
8		 **6s**	0.05	91
9		**6t**	0.075	98

[a] Isolated yield.

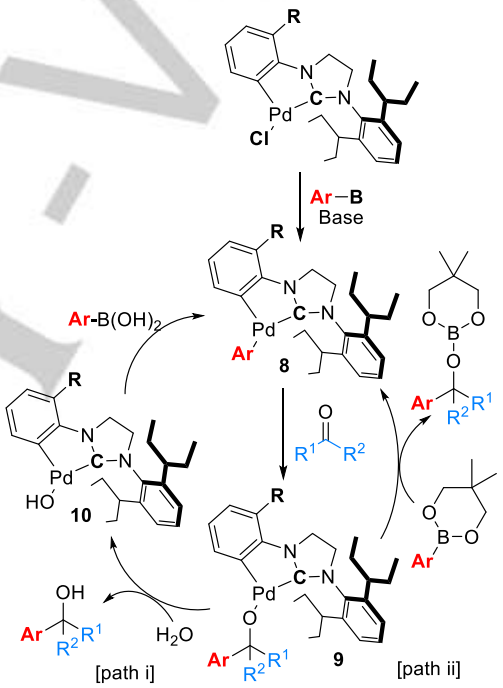
Table 5. PhS-IPent-CYP catalyzed 1,2-addition of arylboronates to unactivated ketones.



Entry	Product **6**	x (mol%)	Yield (%)[a]
1		0.2	96 (90)[b]
2		0.1	82 (58)[c]
3	**7a**	0.2	6[d]
4	 **7b**	0.05	99
5	 **7c**	0.1	97[e]
6	 **7d**	0.02	98
7	 **7e**	0.02	96
8	 **7f**	0.02	92
9	 **7g**	0.04	97
10	 **7h**	0.1	85 (62)[f]
11	 **7i**	0.1	93
12	 **7j**	0.3	90

[a] Isolated yield. [b] PhS-IPr-CYP (5 mol% Pd) was used instead of PhS-IPent-CYP.[6a] [c] H-IPent-CYP (0.1 mol% Pd) was used instead of PhS-IPent-CYP. [d] Phenylboronic acid was used instead of phenylboronic acid neopentyl glycol ester. [e] The reaction was carried out with 0.5 mmol of 2-naphthalene boronate at 50 °C and acetone (0.5 mL) was used instead of toluene. [f] PhS-IPr-CYP (6 mol% Pd) was used instead of PhS-IPent-CYP.[6a]

A possible catalytic cycle is proposed on the basis of previous reports on addition reactions using arylboron compounds (Scheme 4). After *m*-chloro-bridged PhS-IPent-CYP is converted to monomeric arylpalladium intermediate **8** through the transmetallation of an arylboronic acid or boronate, an aryl group is inserted in the carbonyl compound to form alkoxypalladium **9**. The results show that the addition to formaldehyde proceed even in the presence of water, whereas the addition to aldehydes and ketones proceed smoothly in the absence of water. Therefore, two pathways for the regeneration of arylpalladium **8** can be suggested. One possible pathway is the hydrolysis of alkoxypalladium **9** followed by a transmetallation with an arylboronic acid (path i). The other path is the direct transmetallation of alkoxypalladium **9** with an arylboronate (path ii).



Scheme 4. Possible catalytic cycle.

Conclusion

In conclusion, we developed IPent-CYPs with bulky NHC ligands as catalysts for the 1,2-addition of aryl- and heteroarylboron compounds to aldehydes and ketones. Compared to IPr-CYPs, which bear isopropyl groups, IPent-CYPs bearing flexible and bulky 3-pentyl groups showed exceptional catalytic activity and enabled the synthesis of a wide range of versatile functionalized primary, secondary, and tertiary alcohols using extremely small amounts of catalyst.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Brucker DPX-300 (300.13 MHz) or AVANCE III 400 spectrometer (400.15 MHz)

at ambient temperature. High-resolution mass spectra were taken with a JEOL MStaion JMS-700 or Orbitrap ThermoFisher Exactive ion trap mass spectrometer. Melting points were recorded on a Yanaco MP-S3. Commercially available organic and inorganic compounds were used without purification. H-IPr*-CYP[6c] was prepared according to the literature procedures. For the procedure nd the characterization data of IPent-CYP, see Supporting Information.

General Procedure for CYP-Catalyzed Hydroxymethylation of Arylboronic Acids (Table 1 and 2). CYP (0.63–0.125 μmol (Pd: 0.125–0.25 μmol)), (hetero)arylboronic acid (0.50 mmol) and Cs_2CO_3 or CsF (1.0 mmol) were charged in a 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon. This sequence was repeated five times. Then THF (0.5 mL) and 37 wt% formaldehyde in H_2O (102 mg, formaldehyde 1.25 mmol) were added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The test tube was placed into an oil bath preheated at 50 °C. After the reaction mixture was stirred for 2 h and cooled to room temperature. The obtained crude was purified by passing it through a silica gel column with a hexane / ethyl acetate eluent.

Naphthalen-2-ylmethanol (5a).[6e] Using 2-naphthalenboronic acid (86.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 μmol), the product was obtained in 97% yield (77.0 mg, 0.487 mmol) as a white solid. mp: 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 1.91 (s, 1H), 4.88 (s, 2H), 7.48–7.55 (m, 3H), 7.82–7.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) : *δ* 65.5, 125.2, 125.5, 125.9, 126.2, 127.7, 127.9, 128.4, 133.0, 1334, 138.3.

Naphthalen-1-ylmethanol (5b).[6e] Using 1-naphthalenboronic acid (86.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 87% yield (68.5 mg, 0.433 mmol) as a white solid. mp: 61–63 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.43 (s, 1H), 5.08 (s, 2H), 7.82–8.14 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 63.5, 123.7, 125.3, 125.5, 125.9, 126.3, 128.5, 128.7, 131.2, 133.8, 136.3.

(4-Merhoxyphenyl) methanol (5c).[6e] Using 4-methoxyphenylboronic acid (76.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 84% yield (58.3 mg, 0.422 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.48 (s, 1H), 3.81 (s, 3H), 4.58 (s, 2H) 6.88–6.91 (m, 2H), 7.27–7.29 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$, ppm): *δ* 55.3, 64.8, 113.9, 128.6, 133.2, 159.1.

(2-Merhoxyphenyl) methanol (5d).[6e] Using (2-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 93% yield (64.4 mg, 0.466 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.49 (s, 1H) 3.89 (s, 3H), 4.71 (s, 2H),6.88–7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 55.3, 62.2, 110.2, 120.7, 128.8, 129.0, 129.1, 157.5.

(4-Chlorophenyl) methanol (5e).[6e] Using (4-chlorophenyl)boronic acid (78.2 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 86% yield (61.2 mg, 0.429 mmol) as a white solid. mp: 71–73 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.80 (s, 1H) 4.59 (s, 2H),7.22–7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 64.3, 128.3, 133.3, 139.2, 162.3.

(4-Bromophenyl) methanol (5f).[6e] Using (4-bromophenyl)boronic acid (100.4 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 83% yield (77.6 mg, 0.415 mmol) as a white solid. mp: 76–79 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.49 (s, 1H) 3.89 (s, 3H), 4.71 (s, 2H),6.88–7.35 (m, 4H); ^{13}C NMR (75MHz, $CDCl_3$, ppm): *δ* 64.4, 121.4, 128.6, 131.6, 139.7.

Ethyl 4-(hydroxymethyl)benzoate (5g).[6e] Using (4-(ethoxycarbonyl)-phenyl)boronic acid (97.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 μmol), the product was obtained in 90% yield (81.2 mg, 0.451 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 1.39 (t, *J* = 7.1 Hz, 3H), 2.91 (s, 1H), 4.35 (q, *J* = 6.4 Hz, 2H), 4.72 (d, *J* = 4.6 Hz, 2H) 7.40 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 14.3, 61.0, 64.4, 126.4, 129.4, 129.7, 146.2, 166.7.

4-(Hydroxymethyl)-2-methoxybenzaldehyde (5h).[6e] Using (4-formyl-3-methoxyphenyl)boronic acid (89.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 μmol), the product was obtained in 80% yield (66.6 mg, 0.401 mmol) as a white solid. mp: 46–48 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 3.29 (s, 1H), 3.90 (s, 3H), 4.57 (s, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 10.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 55.8, 63.9, 111.9, 124.3, 127.0, 133.5, 135.1, 161.3, 190.1.

(3-Nitrophenyl)methanol (5i).[6e] Using (3-nitrophenyl)boronic acid (83.5 mg, 0.50 mmol), cesium fluoride (152 mg, 1.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 μmol), the product was obtained in 93% yield (71.2 mg, 0.465 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.79 (s, 1H), 4.79 (s, 2H), 7.48–7.54 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.20 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 63.8, 121.4, 122.4, 129.4, 132.7, 143.0, 148.3.

3-(Hydroxymethyl)benzonitrile (5j).[6e] The reaction was carried out at 70 °C using (3-cyanophenyl)boronic acid (73.5 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol), PhS-IPent-CYP (0.15 mg, 0.12 μmol) and 2-methyltetrahydrofuran (0.5 mL) as a solvent. The product was obtained in 81% yield (53.8 mg, 0.404 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.85 (t, *J* = 5.4 Hz, 1H), 4.71 (d, *J* = 5.1 Hz, 2H), 7.41–7.49 (m, 1H), 7.52–7.61 (m, 2H), 7.63–7.66 (m, 1H), 7.80–7.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) : *δ* 63.7, 112.2, 118.9, 129.3, 130.1, 131.1, 131.2, 142.5.

(2,6-Dimethoxypyridin-3-yl)methanol (5k).[6e] The reaction was carried out at 70 °C using 2,6-Dimethoxypyridine-3-boronic acid (91.5 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol). The product was obtained in 83% yield (70.1 mg, 0.414 mmol) as a white solid. mp: 57–59°C ; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.46 (s, 1H), 3.90 (s, 3H) 3.96 (s, 3H), 4.55 (s, 2H), 6.26 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 55.3, 53.6, 60.3, 100.3, 114.1, 140.3, 160.3, 162.6.

Benzofuran-2-ylmethanol (5l).[6e] Using benzofuran-2-ylboronic acid (81.0 mg, 0.50 mmol), cesium carbonate (326 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 81% yield (69.3 mg, 0.405 mmol) as a yellow liquid.^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 3.43 (brm, 1H), 4.74 (d, *J* = 3.9 Hz, 2H), 6.61 (s, 1H), 7.23–7.34 (m, 2H), 7.46–7.57 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 57.9, 104.1, 111.3, 121.2, 122.9, 124.4, 128.2, 155.1, 156.6.

Benzo[b]thiophen-2-ylmethanol (5m).[6e] Using benzo[b]thiophen-2-ylboronic acid (89.0 mg, 0.50 mmol), cesium fluoride (152 mg, 1.00 mmol) and PhS-IPent-CYP (0.08 mg, 0.07 μmol), the product was obtained in 86% yield (70.2 mg, 0.428 mmol) as a light yellow liquid.; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): *δ* 2.44 (s, 1H), 4.91 (s, 2H), 7.20 (s, 1H), 7.30–7.41 (m, 2H), 7.71–7.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): *δ* 60.8, 121.5, 122.5, 123.6, 124.3, 124.4, 139.6, 140.0, 144.8.

General Procedure for PhS-IPent-CYP-Catalyzed 1,2-Addition of Arylboronic Acids to Aldehydes (Table 3 and 4). PhS-IPent-CYP (0.125–0.50 μmol (Pd: 0.25–1.0 μmol)), aldehyde (1.0 mmol), (hetero)arylboronic acid (1.50 mmol) and Cs_2CO_3 (2.0 mmol) were charged in a 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon. This sequence was repeated

five times. Then 1,4-dioxane (1.0 mL) was added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The test tube was placed into an oil bath preheated at 70 °C. After the reaction mixture was stirred for 3 h and cooled to room temperature. The obtained crude was purified by passing it through a silica gel column with a hexane / ethyl acetate eluent.

Naphthalen-2-yl(phenyl)methanol (6a).[6d] Using a mixture of Phenylboronic acid (183 mg, 1.50 mmol), 2-Naphthaldehyde (156 mg, 1.00 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 95 % yield (221.9 mg, 0.947 mmol) as a white solid. mp: 86–87°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.96 (brd, 3.0 Hz, 1H), 5.96 (d,2.1 Hz, 1H), 7.32–7.52 (m, 6H), 7.53–7.61 (m, 2H), 7.18–7.95 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 76.4, 125.2, 125.4, 126.2, 126.4, 127.0, 127.8, 128.0, 128.4, 128.5, 128.7, 133.1, 133.5, 141.5, 143.9.

Naphthalen-1-yl(phenyl)methanol (6b).[6d] Using phenylboronic acid (183 mg, 1.50 mmol), 1-naphthaldehyde (156 mg, 1.00 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 95 % yield (222.1 mg, 0.948 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.63 (s, 1H), 6.52 (s, 1H), 7.28–7.56 (m, 8H), 7.66 (d, J = 7.0 Hz, 1H), 7.81–7.96 (m, 2H), 8.03–8.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 73.6, 124.1, 124.7, 125.4, 125.7, 126.2, 127.1, 127.7, 128.5, 128.6, 128.8, 130.8, 134.0, 139.0, 143.2.

4-Chlorophenyl(phenyl)methanol (6c).[6d] Using phenylboronic acid (183 mg, 1.50 mmol), 4-chlorobenzaldehyde (141 mg, 1.00 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 97 % yield (212.1 mg, 0.973 mmol) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.18 (s, 1H), 5.71 (s, 1H) 7.28–7.40 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 75.5, 126.6, 127.9, 128.0, 128.6, 128.7, 133.3, 142.3, 143.4.

4-Methoxyphenyl(phenyl)methanol (6e).[6d] Using phenylboronic acid (183 mg, 1.50 mmol), *p*-anisaldehyde (136 mg, 1.00 mmol), cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.31mg, 0.25 µmol), the product was obtained in 81% yield (173.6 mg, 0.811 mmol) as a white solid. mp:64–66°C;^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.89 (s, 1H), 3.81 (s, 3H), 5.76 (s, 1H), 6.88–6.92 (m, 2H), 7.28–7.42 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 55.3, 75.7, 113.9, 126.5, 127.4, 128.0, 128.5, 136.3, 144.2, 159.0.

(2-Methoxyphenyl)(phenyl)methanol (6f).[6d] Using Phenylboronic acid (183 mg, 1.50 mmol), *o*-Anisaldehyde (136 mg, 1.00 mmol) cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.31mg, 0.25 µmol), the product was obtained in 91 % yield (194.2 mg, 0.907 mmol) as a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.43–3.47 (m, 1H), 3.82 (s, 3H), 6.15 (d, J=5.3 Hz, 1H), 6.93–7.06 (m, 2H), 7.31–7.50 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 55.5, 71.9, 110.85, 120.9, 126.7, 127.2, 127.8, 128.3, 128.8, 132.2, 143.6, 156.7.

4-(Hydroxyl(phenyl)methyl)benzonitrile (6g).[6d] Using phenylboronic acid (183 mg, 1.50 mmol), 4-cyanobenzaldehyde (131 mg, 1.00 mmol), cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.31 mg, 0.25 µmol), the product was obtained in 98 % yield (205.1 mg, 0.983 mmol) as a white solid. mp:68–69°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.48(d, J = 3.6 Hz, 1H), 5.79 (d, J = 3.5 Hz, 1H) 7.27–7.39 (m, 5H), 7.45–7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 75.4, 110.8, 119.0, 126.8, 127.1, 128.2, 128.8, 132.3, 142.9, 149.3.

Phenyl(thiophen-2-yl)methanol (6h).[6d] Using phenylboronic acid (183 mg, 1.50 mmol), 2-thiophencarboxaldehyde (112 mg, 1.00 mmol), cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.46 mg, 0.38 µmol), the product was obtained in 96 % yield (182.6 mg, 0.959 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.96 (d, J = 3.9 Hz, 1H), 5.83 (d, J = 3.6 Hz, 1H), 7.02 (dd, J = 5.0 Hz, 1H), 7.17 (m, 1H), 7.29–7.41 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 72.8, 121.7, 126.2, 126.5, 126.6, 127.8, 128.6, 143.4, 145.4.

(2,6-Dimethoxyphenyl)(phenyl)methanol (6i).[7m] Using 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (285 mg, 1.50 mmol), 2,6-dimethoxybenzaldehyde (166 mg, 1.00 mmol), cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.61 mg, 0.50 µmol), the product was obtained in 76 % yield (185.5 mg, 0.760 mmol) as a white solid. mp: 88–89°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.80 (s, 6H), 4.48 (d, J = 11.8 Hz, 1H), 6.44 (d, J = 11.7 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 7.23–7.38 (m, 4H), 7.44–7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 55.9, 68.6, 104.7, 119.6, 125.7, 126.6, 128.0, 129.0, 144.9, 157.8.

Cyclohexyl(phenyl)methanol (6j).[6d] The reaction was carried out for 18 h using phenylboronic acid (183 mg, 1.50 mmol), cyclohexanecarboxaldehyde (112 mg, 1.00 mmol), cesium fluoride (304 mg, 2.00 mmol) and PhS-IPent-CYP (1.22 mg, 1.00 µmol), the product was obtained in 96 % yield (183.1 mg, 0.962 mmol) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.91–1.43 (m, 6H), 1.59–2.04 (m, 5H), 2.31 (d, J = 2.6 Hz, 1H), 4.35–4.37 (m, 1H), 7.28–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 25.9, 26.0, 26.3, 28.7, 29.2, 44.8, 79.2, 126.5, 127.2, 128.0, 143.5.

(*E*)-1,3-Diphenylprop-2-en-1-ol (6k).[4n] The reaction was carried out at 100 °C using 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (285 mg, 1.50 mmol), *trans*-cinnamaldehyde (132 mg, 1.00 mmol), cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.61 mg, 0.50 µmol), the product was obtained in 96 % yield (202.7 mg, 0.964 mmol) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.39 (d, J = 3.6 Hz 1H), 5.41 (dd, J = 3.6 Hz, 6.5 Hz, 1H), 6.43 (dd, J = 6.5 Hz, 15.8 Hz, 1H), 6.72 (d, J = 15.9 Hz 1H), 7.26–7.50 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 75.1, 126.4, 126.7, 127.8, 127.9, 128.6, 128.7, 130.6, 131.6, 136.6, 142.8.

Di(naphthalene-2-y)methanol (6l).[6d] Using a mixture of 2-naphthaldehyde (156 mg, 1.00 mmol), 2-naphthaleneboronic acid (258 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 93% yield (263.7 mg, 0.927 mmol) as a white solid. mp:110–112°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.93 (s, 1H), 5.93 (s, 1H), 7.31–7.42 (m, 6H), 7.64–7.78 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 76.5, 125.0, 125.4, 126.1, 126.3, 127.8, 128.2, 128.5, 133.0, 133.4, 141.1.

Naphthalen-1-yl(naphthalen-2-yl)methanol (6m).[6d] Using a mixture of 2-naphthaldehyde (156 mg, 1.00 mmol), 1-naphthaleneboronic acid (258 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 93% yield (264.2 mg, 0.929 mmol) as a white solid. mp:107–109°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.52 (s, 1H), 6.71 (s, 1H), 7.28–7.92 (m, 14 H) ; ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 73.7, 124.0, 125.0, 125.2, 125.4, 125.7, 125.7, 126.1, 126.2, 126.3, 127.7, 128.2, 128.3, 128.7, 128.8, 130.9, 133.0, 133.3, 134.0, 138.7, 140.6.

Naphthalen-2-yl(p-tolyl)methanol (6n).[6d] Using a mixture of 2-naphthaldehyde (156 mg, 1.00 mmol), 4-Methylphenylboronic acid (204 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 95% yield (236.1 mg, 0.951 mmol) as a white solid. mp:91–92°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.42 (s, 3H), 2.83 (m, 1H), 5.96 (m, 1H), 7.22 (d, J =8.0 Hz, 2H), 7.35 (d, J =8.0 Hz, 2H), 7.46–7.57 (m, 3H), 7.83–7.93 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.2, 76.2, 124.9, 125.0, 126.0, 126.2, 126.8, 127.8, 128.2, 128.3, 129.3, 132.9, 133.4, 137.4, 140.9, 141.4.

(4-Chlorophenyl)(naphthalene-2-yl)methanol (6o).[6d] Using a mixture of 2-naphthaldehyde (156 mg, 1.00 mmol), 4-Chlorophenylboronic acid (210 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.15 mg, 0.12µmol), the product was obtained in 84% yield (224.6 mg, 0.838 mmol) eluent yielded 224.6 mg of the title compound

(83 % yield) as a yellow liquid.; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.16 (d, J = 3.6 Hz, 1H), 5.85 (d, J = 3.6 Hz, 1H), 7.28–7.39 (m, 5H), 7.53–7.58 (m, 2H), 7.80–7.88 (m, 4H) ; ^{13}C NMR(75 MHz, $CDCl_3$, ppm): δ 75.7, 124.7, 125.3, 126.3, 126.4, 127.8, 128.1, 128.2, 128.6, 128.7, 133.0, 133.3, 133.4, 140.7, 142.1.

(4-Bromophenyl)(naphthalene-2-yl)methanol (6p). Using 2-naphthaldehyde (156 mg, 1.00 mmol), 4-bromophenylboronic acid (301 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.32 mg, 0.25 µmol), the product was obtained in 90% yield (281.7 mg, 0.898 mmol) as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.75 (s, 1H), 5.89 (s, 1H), 7.25–7.29 (m, 2H), 7.38 (dd, J = 8.5 Hz, 1H) 7.45–7.57 (m, 4H), 7.80–7.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 75.7, 121.6, 124.6, 125.3, 126.3, 126.4, 127.8, 128.1, 128.4, 128.6, 131.6, 133.0, 133.2, 140.6, 142.6; HRMS (APCI) *m/z*: $[M]^+$ calcd. For $C_{17}H_{13}OBr$: 312.0144. Found: 312.0138.

(4-Fluorophenyl)(naphthalene-2-yl)methanol (6q).[6d] Using 2-naphthaldehyde (156 mg, 1.00 mmol), 4-fluorophenylboronic acid (234 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.46 mg,0.37 µmol), the product was obtained in 93% yield (234.8 mg, 0.931 mmol) as a white solid.mp: 67–68°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.69 (d, J = 26.4 Hz, 1H), 5.83 (d, J = 10.1 Hz, 1H), 7.05 (t, J = 8.7 Hz, 1H), 7.31–7.42 (m, 4H), 7.57–7.60 (m, 2H), 7.82–7.92(m, 4H) ; ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 75.6, 115.4 (d, J = 21.3 Hz), 124.8, 125.2, 126.3, 126.5, 127.9, 128.2, 128.5 (d, J = 5.9 Hz), 128.6, 133.0, 133.4, 139.5 (d, J = 3.0 Hz), 141.1, 162.3 (d, J = 244.2 Hz); ^{19}F NMR(377MHz, $CDCl_3$, ppm): δ -114.6.

Naphthalen-2-yl(4-(trifluoromethyl)phenyl)methanol (6r). Using 2-naphthaldehyde (156 mg, 1.00 mmol), 4-(Trifluoromethyl)phenylboronic acid (284 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.46 mg, 0.37 µmol), the product was obtained in 99 % yield (299.3 mg, 0.990 mmol) as a white solid. mp 101–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.74 (m, 1H), 6.00 (m, 1H), 7.39–7.63 (m, 7H), 7.82–7.88 (m, 4H) ; ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 75.9, 124.2 (q, J = 270 Hz), 124.5, 125.5 (q, J = 3.9 Hz), 125.5, 126.4, 126.5, 126.8, 127.8, 128.1, 128.8, 129.7 (q, J = 32.2 Hz), 133.1, 133.2, 140.4, 147.3; ^{19}F NMR(377MHz, $CDCl_3$, ppm): δ -62.3; HRMS (APCI) *m/z*: $[M]^+$ calcd. For $C_{18}H_{13}OF_3$: 302.0913. Found: 302.0911.

Methyl 4-(hydroxy(naphthalen-2-yl)methyl)benzoate (6s). Using 2-naphthaldehyde (156 mg, 1.00 mmol), 4-(methoxycarbonyl)phenylboronic acid (270 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.32 mg, 0.25 µmol), the product was obtained in 91 % yield (266.0 mg, 0.910 mmol) as a coloreless liquid.^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.73 (s, 1H), 3.88 (s, 3H), 5.91 (s, 1H), 7.36–7.51 (m, 5H), 7.76–7.83 (m, 4H), 7.94–7.97 (m, 2H) ; ^{13}C NMR(75 MHz, $CDCl_3$, ppm): δ 52.2, 75.9, 124.7, 125.5, 126.2, 126.4, 126.5, 127.8, 128.1, 128.6, 129.1, 129.8, 133.0, 133.3, 140.7, 148.8, 167.2; HRMS (APCI) *m/z*: $[M]^+$ calcd. For $C_{19}H_{16}O_3$: 292.1094. Found: 292.1091.

Naphthalen-2-yl(thiophen-3-yl)methanol (6t).[6d] Using 2-naphthaldehyde (156 mg, 1.00 mmol), 3-thiopheneboronic acid (192 mg, 1.50 mmol),cesium carbonate (652 mg, 2.00 mmol) and PhS-IPent-CYP (0.46 mg, 0.37 µmol), the product was obtained in 98% yield (235.0 mg, 0.978 mmol) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.13 (s, 1H), 5.97 (s, 1H), 7.04 (d, J = 4.9 Hz, 1H), 7.21 (s, 1H), 7.30 (dd, J = 3.0 Hz, 4.8 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.55–7.58 (m, 2H), 7.83–7.91(m, 4H); ^{13}C NMR(75 MHz, $CDCl_3$, ppm): δ 72.9, 122.0, 124.5, 125.1, 126.1, 126.3, 126.3, 126.7, 127.8, 128.2, 128.4, 133.1, 133.4, 140.8, 145.3.

General Procedure for PhS-IPent-CYP-Catalyzed 1,2-Addition of Arylboronates to Ketones (Table 5). PhS-IPent-CYP (0.05–0.5 µmol (Pd: 0.1–1.0 µmol)), ketone (0.5 mmol), arylboronate (1.0 mmol) and K_2CO_3 (1.5 mmol) were charged in a 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon. This sequence was repeated five times. Then toluene (1.0 mL) was added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The test tube was placed into an oil bath preheated at 120 °C. After the reaction mixture was stirred for 18 h and cooled to room temperature. The obtained crude was purified by passing it through a silica gel column with a hexane / ethyl acetate eluent.

Triphenylmethanol (7a).[5d] Using benzophenone (91 mg, 0.50 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (190 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.61 mg, 0.50 µmol), the product was obtained in 96% yield (125.0 mg, 0.480 mmol) as a white solid.mp: 161–163°C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.87 (s, 1H), 7.28–7.38 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 82.0, 127.3, 127.9, 146.9.

1-(Naphthalen-2-yl)-1-phenylethan-1-ol (7b).[5d] Using 1-(naphthalen-2-yl)ethanone (85.0 mg, 0.50 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (190 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.15 mg, 0.12 µmol), the product was obtained in 99% yield (123.6 mg, 0.498 mmol) as a colorless liquid.^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.13 (s, 3H), 2.67 (s, 1H), 7.36–7.45 (m, 3H), 7.51–7.62 (m, 5 H), 7.84–7.96 (m, 3H), 8.09 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 30.8, 76.4, 123.8, 125.1, 126.1, 126.2, 127.1, 127.6, 128.1, 128.3, 128.4, 132.5, 133.1, 133.9, 145.3, 147.8.

2-(Naphthalen-2-yl)propan-2-ol (7c).[13] 5,5-dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane (240 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.31 mg, 0.25 µmol) were charged in a 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon. This sequence was repeated five times. Then acetone (0.5 mL, 11 mmol) was added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The test tube was placed into an oil bath preheated at 50 °C. After the reaction mixture was stirred for 18 h and cooled to room temperature. The product was obtained in 97% yield (90.1 mg, 0.484 mmol) as a white solid. mp 62–63°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.71 (s, 6H), 2.00 (s, 1H), 7.49–7.52 (m, 2H), 7.63–7.66 (m, 1H), 7.85–7.89 (m, 3 H), 7.97 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 22.0, 72.7, 122.4, 123.6, 125.8, 126.1, 127.5, 128.0, 128.2, 132.3, 133.2, 146.5; HRMS (APCl) *m/z*: $[M]^+$ calcd. For $C_{13}H_{14}O$: 186.1039. Found: 186.1037.

***tert*-Butyl 4-hydroxy-4-phenylpiperidine-1-carboxylate (7d).**[5d] Using *tert*-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (190 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.06 mg, 0.06 µmol), the product was obtained in 98% yield (135.3 mg, 0.488 mmol) as a white solid.mp 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.48 (s, 9H), 1.69–1.75 (m, 2H), 1.92–2.03 (m, 2H), 2.30 (s, 1H),3.24 (brs, 2H), 4.00 (d, J = 12.2 Hz, 2H), 7.24–7.36 (m, 3 H), 7.46–7.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 28.5, 38.0, 40.1, 71.4, 79.6, 124.5, 127.1, 128.4, 148.2, 154.9.

***tert*-Butyl 4-hydroxy-4-(4-methoxyphenyl)piperidine-1-carboxylate (7e).**[5d] Using *tert*-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (220 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.06 mg, 0.06 µmol), the product was obtained in 96 % yield (146.9 mg, 0.478 mmol) as a colorless liquid.^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.46 (s, 9H), 1.70 (d, J = 12.2 Hz , 2H), 1.87–1.95 (m, 2H), 2.36 (s, 1H), 3.22 (brs, 2H), 3.78 (s, 3H), 3.95 (d, J = 10.9 Hz , 2 H), 6.85–6.88 (m, 2H), 7.36–7.39 (m, 2H) ; ^{13}C NMR(75 MHz, $CDCl_3$, ppm): δ 28.5, 38.1, 39.7, 55.2, 70.9, 79.5, 113.6, 125.8, 140.4, 154.9, 158.6.

***tert*-Butyl 4-hydroxy-4-(2-methoxyphenyl)piperidine-1-carboxylate (7f).**[5d] Using *tert*-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50

mmol), 2-(2-methoxyphenyl)-5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (220 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.06 mg, 0.06 µmol), the product was obtained in 92 % yield (140.9 mg, 0.458 mmol) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.47 (s, 9H), 1.94–1.97 (m, 4H), 3.30 (brs, 2H), 3.87 (s, 3H), 4.00 (brs, 2H), 4.08 (brs, 1H), 6.91–6.97 (m, 2H), 7.21–7.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 28.5, 35.9, 39.5, 55.3, 71.3, 79.2, 111.4, 121.1, 125.5, 128.4, 134.7, 155.0, 157.1.

***tert*-Butyl 4-(4-fluorophenyl)-4-hydroxypiperidine-1-carboxylate (7g).**[5d] Using *tert*-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50 mmol), 2-(4-fluorophenyl)-5,5-dimethyl-1,3-2-dioxaborinane(208 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.12 mg, 0.09 µmol), the product was obtained in 97 % yield (143.9 mg, 0.487 mmol) as a white solid; mp 105–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.43 (s, 9H), 1.68 (d, J = 12.7 , 2H), 1.84–1.93 (m, 2H), 2.81 (s, 1H), 3.19 (brs, 2H), 3.93 (d, J = 12.5 , 2H), 6.96–7.03 (m, 2H), 7.39–7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 28.4, 38.1, 39.7, 70.9, 79.7, 115.0 (d, J = 21.1 Hz), 126.3 (d, J = 7.9 Hz), 144.2 (d, J = 3.0 Hz), 154.9, 161.8 (d, J = 244 Hz);^{19}F NMR (376MHz, $CDCl_3$, ppm): δ -114.0.

***tert*-Butyl 4hydroxy-4-(4-(trifluoromethyl)phenyl)piperidine-1-carboxylate (7h).**[5d] Using *tert*-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50 mmol), 5,5-dimethyl-2-(-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (258 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.31 mg, 0.25 µmol), the product was obtained in 85 % yield (147.5 mg, 0.427 mmol) as a white solid; 146–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.46 (s, 9H), 1.71 (d, J = 12.4 Hz, 2H), 1.91–2.00 (m, 2H), 2.67 (s, 1H), 3.20 (brs, 2H), 4.01 (d, J = 12.0 Hz, 2H), 7.61 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 28.4, 37.9, 39.7, 71.4, 79.8, 124.1 (q, J = 270 Hz), 125.1, 125.3 (q, J = 3.7 Hz), 129.3 (q, J = 32.2 Hz), 152.2, 154.9;^{19}F NMR(376MHz, $CDCl_3$, ppm): δ -62.5.

***tert*-butyl 4-hydroxy-4-(3-methoxycarbonyl)phenyl)piperidine-1-carboxylate (7i).** Using *tert*-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50 mmol), methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate(248 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.31 mg, 0.25 µmol), the product was obtained in 93 % yield (156.2 mg, 0.466 mmol) as a white solid. mp 119–120 °C;^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.44 (s, 9H), 1.71(d, J = 12.6 Hz, 2H), 1.90–2.00 (m, 2H), 2.81 (s, 1H), 3.22 (brs, 2H), 3.86 (s, 3H), 3.98 (d, J = 12.1 Hz, 2H), 7.39 (t, J = 7.8 Hz, 1H), 7.68 (m, 1H), 7.88 (m, 1H), 8.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 28.4, 38.0, 40.0, 52.1, 71.3, 79.6, 125.8, 128.3, 128.5, 129.3, 130.1, 148.8, 154.8, 167.1; FTMS (APCl) *m/z*: $[M-H]^+$ calcd. For $C_{18}H_{24}O_5N$:334.1660. Found: 334.1668.

***tert*-butyl 4-hydroxy-4-(3-nitrophenyl)piperidine-1-carboxylate (7j).** Using a mixture of tert-butyl 4-oxopiperidine-1-carboxylate (100 mg, 0.50 mmol), 5,5-dimethyl-2-(3-nitrophenyl)-1,3-2-dioxaborinane (235 mg, 1.00 mmol), potassium carbonate (207 mg, 1.50 mmol) and PhS-IPent-CYP (0.91 mg, 0.74 µmol), the product was obtained in 90 % yield (144.3 mg, 0.448 mmol) as a yellow liquid.;^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.39 (s, 9H), 1.71 (d, J = 12.7, 2H), 1.90–1.97 (m, 2H), 3.21 (brs, 2H), 3.57 (s, 1H) 3.95–3.99 (m, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.78 (m, 1H), 8.03 (m, 1H), 8.36 (t, J = 2.0 , 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 28.4, 37.9, 39.7, 71.2, 79.9, 120.0, 122.0, 129.3, 131.1, 148.2, 150.9, 154.8; FTMS (APCl) *m/z*: $[M-H]^+$ calcd. For $C_{16}H_{21}O_5N_2$:321.1456. Found: 321.1461.

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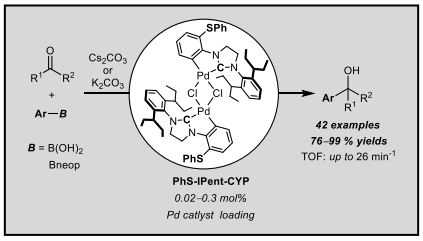

Organopalladium catalysis: The *N*-heterocyclic carbene (NHC)-coordinated IPent-based cyclometallated palladium complexes (IPent-CYPs) was synthesized and used as the catalyst for the 1,2-addition of arylboron compounds to various carbonyl compounds including unactivated ketones. Bulky yet flexible IPent-CYPs had excellent catalytic performance in this reaction, far superior to that of bulky and less flexible IPr*-CYP.