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Addition reaction of arylboronic acids to aldehydes and α,β-unsaturated carbonyl compounds catalyzed by conventional palladium complexes in the presence of chloroform

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ABSTRACT

Arylboronic acids react with aldehydes and α,β-unsaturated carbonyl compounds in the presence of a base and a catalytic amount of a palladium(0) complex with chloroform, affording the corresponding addition products in good yields, and chiral benzhydrol was obtained with up to 43% e.e. using (*S,S*)-bppm as a ligand. General palladium complexes have no catalytic activity without chloroform. Because chloroform is essential for this reaction, these reactions would be promoted by dichloromethylpalladium(II) species.

1. Introduction

Carbon–carbon bond formation reactions using transition metal catalyst are very important methods in organic synthesis. Organoboron reagents have low toxicity and are practically useful for carbon–carbon bond formations with various electrophiles in the presence of several kinds of transition metals [1]. The most typical example is the Miyaura–Suzuki reaction: Palladium- or nickel-catalyzed carbon–carbon bond formation reaction with organoborons and organohalides [1,2]. As other typical examples, rhodium-catalyzed addition reactions to α,β-unsaturated carbonyl compounds, [3] aldehydes, [4] ketones [5] and *N*-arylsulfonyl aldimines [6] with organoboron reagents have been developed. In the last few years, various groups have reported the use of a cheaper metal than the Rh, such as nickel [7] or palladium [8] catalyst, for 1,4-addition of α,β-unsaturated carbonyl compounds with organoborons. Additionally, copper [9], palladium [10] and nickel [11] catalyzed 1,2-addition of organoboron compounds to aldehydes, ketones, imines and nitriles have been developed very recently. However, these addition reactions with organoboron compounds by metals other than Rh are still under development.

We have already demonstrated in communications that the addition of chloroform makes conventional palladium compounds active as a catalyst for the 1,2-addition of arylboronic acids to aldehydes [8a] and 1,4-addition to α,β-unsaturated carbonyl compounds [10b]. Herein, we report the entire results of the addition of arylboronic acids to aldehydes, α,β-unsaturated carbonyl compounds, and α,β-unsaturated nitriles catalyzed by palladium(0) phosphine complexes in the presence of base and a catalytic amount of chloroform (Scheme 1).

2. Results and discussion

Palladium-catalyzed addition of phenylboronic acid to 4-cyanobenzaldehyde was examined, and summarized in Table 1, which shows effects of palladium precursors together with phosphine ligands. $Pd_2(dba)_3 \cdot CHCl_3$ as a palladium(0) precursor catalyzed the 1,2-addition reaction in the presence of PPh_3. Interestingly, the yields of the 1,2-addition products decreased with the increase of the amount of PPh_3 (Table 1, entries 1–4). Bidentate phosphines with small bite angles such as dppe, dppp and dppb were not or less effective (Table 1, entries 5–7). However, bidentate phosphines with large bite angles such as dppf, (*R*)-binap, (*S,R*)-bppfa and (*S,S*)-bppm were effective for the 1,2-addition reaction. (Table 1, entries 8–11). Chiral bidentate phosphines such as (*R*)-binap and (*S,R*)-bppfa were not effective for asymmetric induction of this reaction (Table 1, entries 9 and 10). On the other hand, the bidentate ligand (*S,S*)-bppm derived from proline was moderately effective, and the monodentate ligand (*R*)-mop showed lower selectivity (respectively, 43% e.e., 16% e.e., Table 1, entries 11 and 12). Noteworthy

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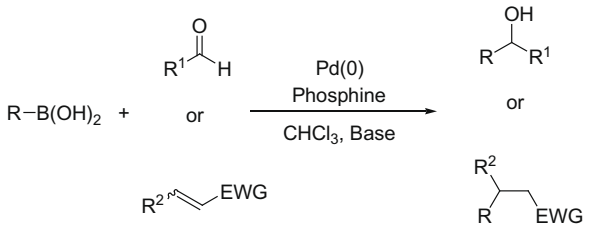
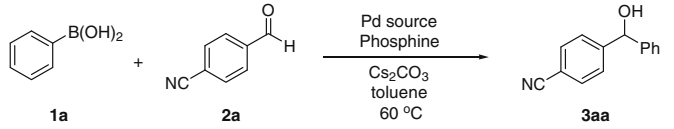


Scheme 1.

Table 1
Survey of Pd catalysts on 1,2-addition reaction of phenylboronic acid to 4-cyanobenzaldehyde.



1a **2a** **3aa**

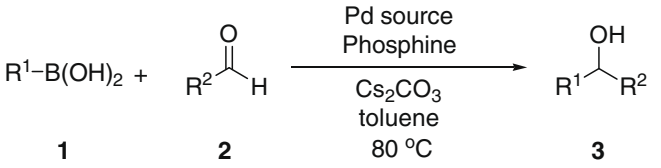
Entry[a]	Pd source	Ligand [mol%]	Yield [%][b]
1	$Pd_2(dba)_3 \cdot CHCl_3$	PPh_3 (5)	95 (94)[c]
2	$Pd_2(dba)_3 \cdot CHCl_3$	PPh_3 (10)	84
3	$Pd_2(dba)_3 \cdot CHCl_3$	PPh_3 (11)	43
4	$Pd_2(dba)_3 \cdot CHCl_3$	PPh_3 (15)	2
5	$Pd_2(dba)_3 \cdot CHCl_3$	dppe (5)	0 (0)[d]
6	$Pd_2(dba)_3 \cdot CHCl_3$	dppp (5)	0 (42)[d]
7	$Pd_2(dba)_3 \cdot CHCl_3$	dppb (5)	52
8	$Pd_2(dba)_3 \cdot CHCl_3$	dppf (5)	75
9	$Pd_2(dba)_3 \cdot CHCl_3$	(*R*)-binap (5)	89[e]
10	$Pd_2(dba)_3 \cdot CHCl_3$	(*S*)-(*R*)-bppfa (5)	86[e]
11	$Pd_2(dba)_3 \cdot CHCl_3$	(*S*,*S*)-bppm (5)	64[f]
12	$Pd_2(dba)_3 \cdot CHCl_3$	(*R*)-mop (5)	72[g]
13	$Pd_2(dba)_3$	PPh_3 (5)	0 (95)[h]
14	$Pd(dba)_2$	PPh_3 (5)	0 (97)[h]
15	$[PdCl(\pi\text{-}C_3H_5)]_2$	PPh_3 (5)	0 (92)[h]
16	$Pd(OAc)_2$	PPh_3 (10)	0 (98)[h]
17	$Pd(acac)_2$	PPh_3 (10)	0 (82)[h]
18[i]	$Pd(acac)_2$	PPh_3 (5)	0
19	$PdCl_2(CH_3CN)_2$	PPh_3 (5)	0 (92)[h]
20	$Pd(PPh_3)_4$	none	0

[a] The reaction was carried out with phenylboronic acid (2.0 mmol), 4-cyanobenzaldehyde (1.0 mmol), Cs_2CO_3 (1.0 mmol) and Pd source (5 mol%) in 2.0 mL of toluene at 60 °C for 24 h.
[b] Yields were relative to an internal standard by ^1H NMR spectroscopy.
[c] Yield of product isolated by silica gel column chromatography, based on 4-cyanobenzaldehyde.
[d] The reactions were carried out at 80 °C.
[e] Corresponding alcohol was racemate.
[f] Enantiomeric excess was 43%.
[g] Enantiomeric excess was 16%.
[h] Chloroform (0.01 mL) was added.
[i] $Cu(BF_4)_2 \cdot 6H_2O$ (20 mol%) was added.

is that no other palladium(II) complexes as well as palladium(0) complex precursors favor the 1,2-addition reaction without $CHCl_3$ (Table 1, entries 13–20), although the addition reaction proceeds smoothly by adding a catalytic amount of chloroform (Table 1, entries 13–17, and 19). When other polyhalomethanes such as CH_2Cl_2, CCl_4, $CHBr_3$ and $CHBrCl_2$ had been used instead of $CHCl_3$, the yields of the addition product were lower than using $CHCl_3$.

Results of the reaction of aldehydes with arylboronic acids are summarized in Table 2. Remarkable electronic effects both in aldehydes and arylboronic acids are shown in the reaction. That is, electron-withdrawing aldehydes and arylboronic acids with a donating group reacted smoothly (Table 2, entries 1–3 and, 11–13). On the other hand, electron-rich aldehydes were converted to biarylmethanols in lower yields (Table 2, entries 6 and 8), although additions to ortho-substituted electron-rich aldehydes such as 2-anisaldehyde and 2-tolaldehyde proceeded smoothly

Table 2
Pd-catalyzed 1,2-addition of various aldehydes and arylborobic acids.



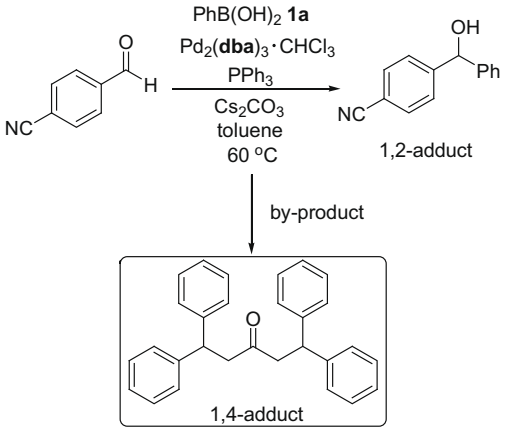
1 **2** **3**

Entry[a]	R^1-$B(OH)_2$, R^1=	Aldehyde, R^2=	Yield (%)[b]
1	Ph (**1a**)	4-$CF_3C_6H_4$ (**2b**)	**3ab**, 99
2	**1a**	4-MeOC(O)C_6H_4 (**2c**)	**3ac**, 88
3	**1a**	4-FC_6H_4 (**2d**)	**3ad**, 84
4	**1a**	Ph (**2e**)	**3ae**, 73
5	**1a**	2-Naphthyl (**2f**)	**3af**, 70
6	**1a**	4-MeC_6H_4 (**2g**)	**3ag**, 58
7	**1a**	2-MeC_6H_4 (**2h**)	**3ah**, 70
8	**1a**	4-$MeOC_6H_4$ (**2i**)	**3ai**, 56
9	**1a**	2-$MeOC_6H_4$ (**2j**)	**3aj**, 75
10	**1a**	EtOC(O) (**2k**)	**3ak**, 48
11	4-$MeOC_6H_4$ (**1b**)	**2f**	**3bf**, 86
12	2-$MeOC_6H_4$ (**1c**)	**2f**	**3cf,** 87
13	4-MeC_6H_4 (**1d**)	**2f**	**3df,** 84
14	4-FC_6H_4 (**1e**)	**2f**	**3ef,** 52
15	2-FC_6H_4 (**1f**)	**2f**	<1
16	4-NCC_6H_4 (**1g**)	**2f**	<1
17	**1e**	4-NCC_6H_4 (**2a**)	**3ea,** 71
18	**1f**	**2a**	**3fa,** 75

[a] The reaction was carried out with aldehyde (1.0 mmol), arylboronic acid (2.0 mmol), Cs_2CO_3 (1.0 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.025 mmol), and PPh_3 (0.05 mmol) in 2.0 mL of toluene at 80 °C for 24 h.
[b] Yield of product isolated by silica gel column chromatography, based on aldehyde.

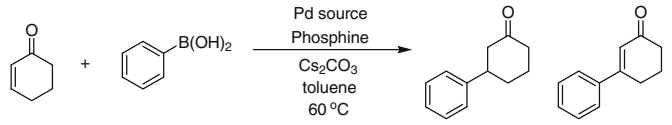
(Table 2, entries 7 and 9). Electron-deficient arylboronic acids reacted slowly to electron-normal aromatic aldehyde such as 2-naphthaldehyde (Table 2, entries 14–16), but the reaction was facilitated with electron-withdrawing aldehyde such as 4-cyanobenzaldehyde (Table 2, entries 17 and 18).

When the 1,2-addition was examined with $Pd_2(dba)_3 \cdot CHCl_3$, we obtained 1,4-adduct of phenylboronic acid to dba as by-product (Scheme 2). Therefore, we have employed this catalyst system for 1,4-addition reaction of arylboronic acids to α,β-unsaturated carbonyl compounds. Palladium-catalyzed addition of phenylboronic acid to 2-cyclohexenone was examined at 60 °C, and the results are summarized in Table 3. $Pd_2(dba)_3 \cdot CHCl_3$ has excellent catalytic activity, although palladium(0) complex precursors and neutral palladium(II) complex, such as $Pd(dba)_2$, $Pd(OAc)_2$, and $PdCl_2(CH_3CN)_2$, have no catalytic activity in the absence of



Scheme 2.

Table 3
Survey of Pd catalysts on 1,4-addition reaction of phenylboronic acid to 2-cyclohexenone.



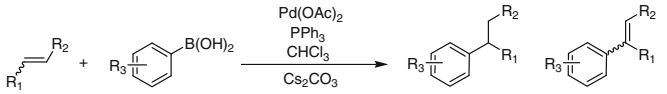
Entry[a]	Pd source (mol%)	Ligand (mol%)	Yield (%)[c,d]
1	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	PPh_3 (6)	>99[e]
2	$Pd(OAc)_2$ (5)	PPh_3 (10)	0 (>99[f], 97[g], 82[h])
3	$PdCl_2(CH_3CN)_2$ (5)	PPh_3 (5)	0 (>99)[f]
4	$Pd(dba)_2$ (5)	PPh_3 (5)	0 (>99)[f]
5	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	PPh_3 (12)	43
6	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	PPh_3 (24)	< 3
7	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	dppe (6)	0
8	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	dppp (6)	3
9	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	dppb (6)	5
10	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	dppf (6)	18
11[b]	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	PPh_3 (6)	>99

[a] Reactions were carried out at 60 °C for 24 h in the presence of 2-cyclohexenone (1.0 mmol), phenylboronic acid (2.0 mmol), palladium complex (3 or 5 mol%), phosphine (5, 6, 12 or 24 mol%) and Cs_2CO_3 (1.0 mmol) in toluene 2 mL.
[b] A catalytic amount of Cs_2CO_3 (0.2 mmol) was used.
[c] Determined by ^1H NMR spectroscopy.
[d] Heck-type product **6aa** was not determined by ^1H NMR.
[e] Yield of product isolated by silica gel column chromatography, based on 2-cyclohexenone.
[f] Reactions were carried out at 80 °C, and $CHCl_3$ (0.01 mL) was added.
[g] Reactions were carried out at 80 °C, and $CHBr_3$ (0.01 mL) was added.
[h] Reactions were carried out at 80 °C, and $CHBrCl_2$ (0.01 mL) was added.

chloroform. However, palladium complexes, such as $Pd(OAc)_2$, $Pd(dba)_2$ and $PdCl_2(CH_3CN)_2$, catalyzed 1,4-addition smoothly in the presence of a catalytic amount of chloroform and PPh_3 (Table 3, entries 1–4). The yields of the 1,4-addition products decreased with the increase of triphenylphosphine, and bidentate phosphines such as dppe, dppp, dppb and dppf were less effective (Table 3, entries 5–10). In addition, the reaction proceeded smoothly even using a catalytic amount of Cs_2CO_3 (Table 3, entry 11).

Results of the reaction of several α,β-unsaturated carbonyl compounds with arylboronic acids are summarized in Table 4. The palladium-catalyzed addition of electron-rich arylboronic acids such as 4-tolylboronic acid and 4-methoxyphenylboronic acid to 2-cyclohexenone reacted smoothly as well as phenylboronic acid (Table 4, entries 1 and 2). On the other hand, ortho-substituted or electron-deficient arylboronic acids such as 2-methoxyphenylboronic acid, 4-fluorophenylboronic acid, 4-cyanophenylboronic acid, and 4-trifluoromethylphenylboronic acid

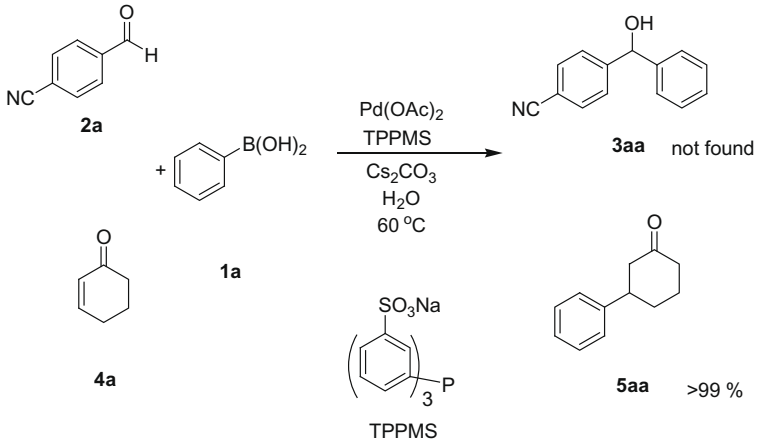
Table 4
Pd-catalyzed 1,4-addition of various olefines and arylborobic acids.



Entry[a]	$ArB(OH)_2$, R_3 =	α,β-Unsaturated enones	Yield (%)[b,c]
1	4-MeO (**1b**)	2-Cyclohexenone **4a**	**5ba**, 96
2	4-Me (**1d**)	**4a**	**5da**, >99
3	4-F (**1e**)	**4a**	**5ea**, 83
4	4-NC (**1g**)	**4a**	**5ga**, 54
5	2-MeO (**1j**)	**4a**	**5ja**, 56 (89)[d]
6	4-F_3C (**1k**)	**4a**	**5ka**, 70
7	H (**1a**)	2-Cyclopentenone (**4b**)	**5ab**, >99
8	**1a**	2-Cycloheptenone (**4c**)	**5ac**, >99
9	**1a**	(*E*)-Chalcone (**4d**)	**5ad**, >99
10	**1a**	Benzalacetone (**4e**)	**5ae**, 89
11	**1a**	(*E*)-4-Hexen-3-one (**4f**)	**5af**, 91
12	**1a**	3-Hepten-2-one (**4g**)	**5ag**, 92
13	**1a**	5-Methyl-3-hexen-2-one (**4h**)	**5ah**, 80
14[e]	**1a**	Crotonaldehyde (**4i**)	**5ai**, 91
15[e]	**1a**	(*E*)-2-Hexenal (**4j**)	**5aj**, 90
16	**1a**	Cinnamaldehyde (**4k**)	**5ak**, 68
17[f]	**1a**	Methyl crotonate (**4l**)	**5al**, 51 (**6al**, 3)
18[g]	**1a**	**4l**	**5al**, 87 (**6al**, 2)
19[g]	**1a**	Methyl 2-penteonate (**4m**)	**5am**, 67 (**6am**, 2)
20	**1a**	2-pentenenitrile (**4n**)	**5an**, 64 (**6an**, 7)
21[h]	**1a**	**4n**	**5an**, 79 (**6an**, 2)

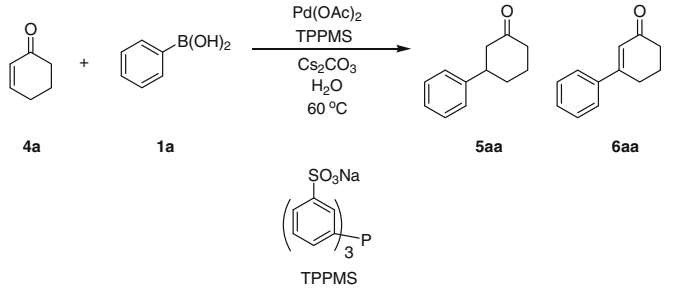
[a] Reactions were carried out at 80 °C for 24 h in the presence of α,β-unsaturated enone (1.0 mmol), arylboronic acid (2.0 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), Cs_2CO_3 (1.0 mmol) and chloroform (0.01 mL) in toluene 2 mL.
[b] Yield of product isolated by silica gel column chromatography, based on enone.
[c] Heck-type product **6** was determined by ^1H NMR.
[d] Reaction was carried out for 40 h.
[e] Reactions were carried out for 16 h.
[f] Reactions were carried out in THF 2 mL.
[g] Reactions were carried out in THF/H_2O = 1.6 mL/0.4 mL.
[h] H_2O (0.02 mL) was added.

reacted slowly to 2-cyclohexenone (Table 4, entries 3–6). The 1,4-addition of phenylboronic acid proceeded smoothly to several cyclic and acyclic α,β-unsaturated carbonyl compounds except bulky β-substituted enone, such as 5-methyl-3-hexen-2-one (Table 4, entries 7–13). When α,β-unsaturated aldehydes were used for this addition, we obtained only 1,4-adduct without accompanying a 1,2-adduct (Table 4, entries 14–16). α,β-Unsaturated carbonyl ester and nitrile were also arylated to give the 1,4-adduct in good yield accompanied with Heck-type product in low yield. Addition of water to the reaction improved the ratio of 1,4-adduct/Heck-type product (Table 4, entries 17–21).



Scheme 3.

Table 5
Pd-catalyzed 1,4-addition in water and reuse of the aquas phase for the reaction.



Cycle[a]	Yield (%)[c]
1	>99
2[b]	>99
3[b]	>99
4[b]	80
5[b]	8[d]

[a] Reactions were carried out at 60 °C for 24 h in the presence of 2-cyclohexenone (1.0 mmol), phenylboronic acid (1.5 mmol), $Pd(OAc)_2$ (5 mol%), tppms (10 mol%), $CHCl_3$ (0.01 mL) and Cs_2CO_3 (0.2 mmol) in degassed H_2O 5 mL.
[b] The aqueous catalyst solution from the previous cycle was used after degassing operation.
[c] Isolated yield.
[d] Determined by ^1H NMR.

Metal-catalyzed reactions in aqueous media are very attractive for being environmentally friendly. [12] We demonstrated 1,2- and 1,4-additions in water using tppms as a ligand. As shown in Scheme 3, the 1,2-addition to 4-cyanobenzaldehyde did not occur in water, however, the 1,4-addition proceeded smoothly as well as the reaction in toluene. Thus, we confirmed the water phase after this reaction was able to be recycled (Table 5). The aqueous catalyst solution was able to be recycled up to three times without again adding catalyst source such as $Pd(OAc)_2$, tppms, Cs_2CO_3 and $CHCl_3$ (Table 5, Cycles 1–4). However, the fourth recycling of the aqueous catalyst solution was impossible (Table 5, Cycle 5). When the catalyst is reused, the degassing operation of the aqueous solution is necessary. If this operation was omitted, the homo-coupling of arylboronic acid occurred preferentially, rather than the 1,4-addition reaction.

In 2001, Cole-Hamilton et al. reported that 1,2-addition to the formyl group in 4-chlorobenzaldehyde of phenylboronic acid with palladacycle **7** proceeded [10a]. From the result, we thought that the catalytically active species of these addition reactions was carbon binding phosphine-palladium complexes, such as dichloromethylpalladium(II)-phosphine **8**, which might be generated from phosphine coordinated palladium(0) complex with chloroform. Therefore, we examined the catalytic activity of Herrmann's complex chloro(dichloromethyl)bis(triphenylphosphine)palladium(II) (**9**), [13] which was prepared from $Pd(PPh_3)_4$ with chloroform (Scheme 4). This complex catalyzed this reaction as well. Very recently, Hu et al. reported these reactions were catalyzed by several carbon binding phosphine–palladium complexes such as palladacycles **10**–**12** in good yield (Fig. 1) [10f,g], and independently we reported a similar study using optically active palladacycle **10b** [8f,14].

We propose the catalytic cycle of this reaction in Scheme 5. At first, dichloromethyl coordinating palladium(II)–phosphine intermediate **13** is generated by oxidative addition of chloroform to coordinated palladium(0)–phosphine complex, and dichloromethylpalladium(II) intermediate **13** produces a hydroxypalladium(II) species **14** by counter anion exchange. Then, the transmetalation between arylboronic acid and the hydroxyl palladium(II) species **14** occurs to generate an arylpalladium(II) intermediate **15**, and

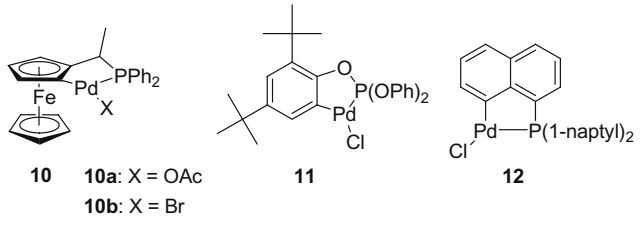
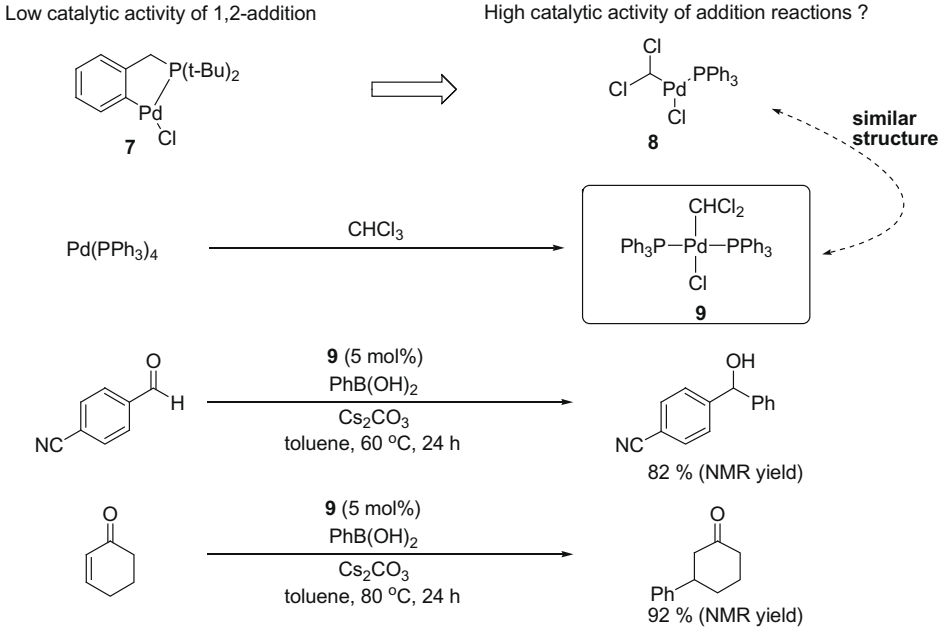
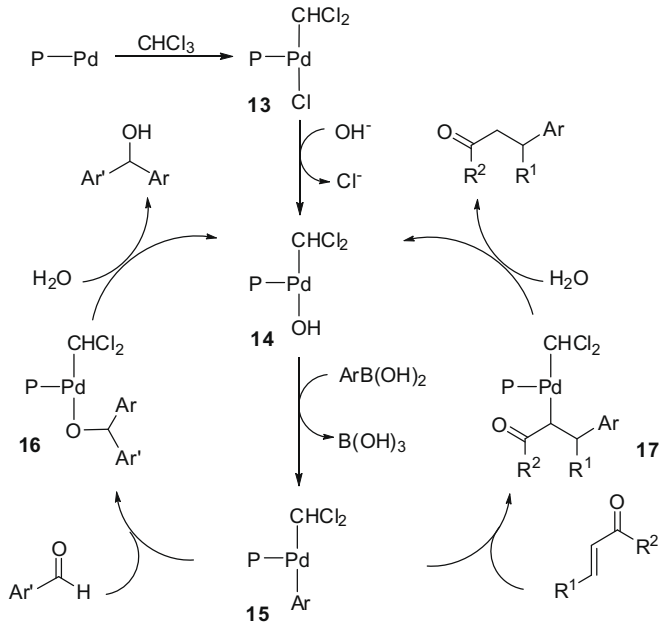


Fig. 1. Usuable palladacycle catalysts on these addition reactions.



Scheme 4.



Scheme 5.

the insertion of the aldehyde or the enone into the carbon–palladium bond affords a corresponding alkoxypalladium **16** or a C-bound enolate **17**. Alkoxypalladium **16** or palladium enolate **17** is hydrolyzed to give the corresponding alcohol or carbonyl compound, and then the hydroxypalladium(II) species **14** is regenerated.

3. Conclusion

In conclusion, we have disclosed the use of the carbon-bound palladium(II)–phosphine catalyst, such as dichloromethylpalladium(II)–phosphine intermediate that was generated from palladium(0)–phosphine complex with chloroform, for the addition reactions to aldehydes or α,β-unsaturated carbonyl compounds and α,β-unsaturated nitriles using arylboronic acids. Furthermore, when using tppms as a ligand, 1,4-addition proceeded smoothly in water, and the aqueous phase was able to be recycled up to three times.

Now, we are investigating an asymmetric version of these reactions with organopalladium complexes such as optically active palladacycles [8f] or palladium(0) complex with a chiral monodantate phosphine like (*S,S*)-bppm in the presence of chloroform. [6b,14] Further applications and development of the catalytic system are underway.

4. Experiment

4.1. General

All reactions were carried out under an argon atmosphere by standard Schlenk techniques. All organic and inorganic compounds are commercially available, and are used without purification. All solvents were dried by standard methods and distilled under argon. Nuclear magnetic resonance spectra were measured on a Varian MERCURY plus300-4N spectrometer (1H: 300 MHz, 13C: 75 MHz, 19F: 282 MHz). IR spectra were measured on a Shimadzu IR-408 spectrometer. Exact mass spectrometry was performed on a JEOL JMS-700 (FAB-MS, matrix: *m*-NBA, reference: PEG-400). All substrates are commercially available and are used without purification. Some alcohols produced,**3ae, 3ag, 3ah, 3ai, 3ak**, were identified compared with authentic samples purchased.

4.2. 1,2-Addition of arylboronic acid to aldehyde in the presence of Pd precursor, phosphine, and $CHCl_3$

This is a typical procedure for 1,2-addition of arylboronic acid to aldehyde. In a 80-mL Schlenk tube were placed $Pd_2(dba)_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol), 4-cyanobenzaldehyde (131.1 mg, 1.0 mmol), phenylboronic acid (243.9 mg, 2.0 mmol), cesium carbonate (325.8 mg, 1.0 mmol), and toluene (2 mL). The resulting solution was stirred at 60 °C for 24 h., and then the product was extracted with CH_2Cl_2. The analytically pure alcohol was obtained by chromatography on silica gel. When other aldehydes and arylboronic acid were used, usually the reaction was carried out at 80 °C.

4.3. 1,4-Addition of arylboronic acid to enone in the presence of Pd precursor, phosphine, and $CHCl_3$

This is a typical procedure for 1,4-addition of arylboronic acid to enone. In a 80-mL Schlenk tube were placed $Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol), 2-cyclohexen-1-one (96.1 mg, 1.0 mmol), phenylboronic acid (243.9 mg, 2.0 mmol), cesium carbonate (325.8 mg, 1.0 mmol), and toluene (2 mL). The resulting solution was stirred at 60 °C for 24 h., and then the product was extracted with CH_2Cl_2. The analytically pure ketone was obtained by chromatography on silica gel. When other enones and arylboronic acid were used, usually the reaction was carried out at 80 °C for 24–40 h.

4.4. 4-Cyanophenyl(phenyl)methanol (***3aa***) [15]

^{1}H NMR ($CDCl_3$): δ 2.63 (brs, 1H, −O*H*), 5.82 (s, 1H, −C*H*OH), 7.24–7.42 (m, 5H, -*Ar*), 7.49–7.58 (m, 4H, -*Ar*), ^{13}C NMR ($CDCl_3$) δ 75.9, 111.3, 119.1, 126.9, 127.2, 128.5, 129.1, 132.5, 143.0, 149.1.

4.5. Phenyl(4-trifluoromethylphenyl)methanol (***3ab***) [16]

^{1}H NMR ($CDCl_3$): δ 2.42 (d, *J* = 2.7 Hz, 1H, −O*H*), 5.84 (d, *J* = 2.1 Hz, 1H, –C*H*OH), 7.25–7.34 (m, 5H, -*Ar*), 7.12–7.49 (dd, *J* = 18.9, 8.1, 4H, -*Ar*), ^{13}C NMR ($CDCl_3$): δ 75.7, 124.0 (d, *J* = 273.0 Hz, −CF_3), 125.2, 1253, 126.5, 128.0, 128.6, 129.8 (d, *J* = 32.0 Hz, –*C*–CF), 142.9, 147.3.

4.6. 4-Methoxycarbonylphenyl(phenyl)methanol (***3ac***) [17]

^{1}H NMR ($CDCl_3$): δ 2.86 (brs, 1H, −O*H*), 3.85 (s, 3H, −OCH_3), 5.80 (s, 1H, −C*H*OH), 7.24–7.31 (m, 5H, -*Ar*), 7.41 (d, *J* = 8.1 Hz, 2H, -*Ar*), 7.94 (d, *J* = 8.1 Hz, 2H, -*Ar*); ^{13}C NMR (75 MHz) δ 52.1, 75.7, 126.1, 126.5, 127.7, 128.5, 128.9, 129.6, 143.1, 148.6, 166.8.

4.7. 4-Fluorophenyl(phenyl)methanol (***3ad***) [18]

^{1}H NMR ($CDCl_3$): δ 2.70 (brs, 1H, –O*H*), 5.66 (s, 1H, –O*H*), 6.90–6.98 (m, 2H, -*Ar*), 7.18–7.31 (m, 7H, -*Ar*); ^{13}C NMR (75 MHz): δ 75.8, 115.5 (d, *J* = 21.1 Hz, –*C*–CF), 126.7, 127.9, 128.5 (d, *J* = 8.0 Hz, –C–C–CF), 128.8, 139.8 (d, *J* = 3.5 Hz, –*C*–C–C–CF), 143.8, 162.3 (d, *J* = 243.8 Hz, –CF); ^{19}F NMR (282 MHz) δ −115.2.

4.8. Benzhydrol (***3ae***)

^{1}H NMR ($CDCl_3$) δ 2.18 (brs, 1H, −O*H*), 5.83 (s, 1H, −C*H*OH), 7.22–7.39 (m, 10H, -*Ar*); ^{13}C NMR (75 MHz) δ 76.2, 126.4, 127.5, 128.4, 143.6.

*4.9. Phenyl(2-naphthyl)methanol (**3af**) [19]*

^{1}H NMR ($CDCl_3$): δ 2.36 (brs, 1H, –O*H*), 5.98 (s, 1H, –O*H*), 7.23–7.49 (m, 8H, -*Ar*), 7.76–7.88 (m, 4H, -*Ar*); ^{13}C NMR (75 MHz) δ 76.7, 125.0, 125.2, 126.2, 126.4, 126.9, 127.9, 128.3, 128.5, 128.8, 133.1, 133.4, 141.3, 143.8.

*4.10. 4-Methylphenyl(phenyl)methanol (**3ag**)*

^{1}H NMR ($CDCl_3$): δ 2.21 (brs, 1H, –O*H*), 2.32 (s, 3H, –CH_3), 5.79 (s, 1H, –C*H*OH), 7.11–7.38 (m, 9H, -*Ar*); ^{13}C NMR (75 MHz) δ 21.5, 76.4, 126.65, 126.72, 127.6, 128.6, 129.4, 137.5, 141.1, 144.1.

*4.11. 2-Methylphenyl(phenyl)methanol (**3ah**)*

^{1}H NMR ($CDCl_3$): δ 2.16 (brs, 1H, –O*H*), 2.24 (s, 3H, –CH_3), 5.98 (s, 1H, –C*H*OH), 7.11–7.31 (m, 8H, -*Ar*), 7.48–7.51 (m, 1H, -*Ar*); ^{13}C NMR (75 MHz) δ 19.8, 73.7, 126.3, 126.5, 127.3, 127.7, 127.8, 128.7, 130.7, 135.6, 141.6, 143.0.

*4.12. 4-Methoxyphenyl(phenyl)methanol (**3ai**)*

^{1}H NMR ($CDCl_3$) δ 2.34 (brs, 1H, –O*H*), 3.75 (s, 3H, –OCH_3), 5.74 (s, 1H, –C*H*OH), 6.83 (d, *J* = 8.4, 2H, -*Ar*), 7.20–7.35 (m, 7H, -*Ar*); ^{13}C NMR (75 MHz) δ 55.6, 76.1, 114.1, 126.6, 127.6, 128.1, 128.6, 136.4, 144.2, 159.2

*4.13. 2-Methoxyphenyl(phenyl)methanol (**3aj**) [20]*

^{1}H NMR δ 3.14 (brs, 1H, –O*H*), 3.73 (s, 3H, –OCH_3), 6.01 (s, 1*H*, –C*H*OH), 6.81–6.92 (m, 2H, -*Ar*), 7.19–7.36 (m, 7H, -*Ar*); ^{13}C NMR (75 MHz) δ 55.3, 71.9, 110.5, 120.6, 126.3, 126.9, 127.6, 127.9, 128.5, 131.8, 143.1, 156.4.

*4.14. Ethyl mandelate (**3ak**)*

^{1}H NMR ($CDCl_3$): δ 1.19 (t, *J* = 7.2 Hz, 3H, –OCH$_2$CH_3), 3.61 (brs, 1H, –O*H*), 4.08–4.28 (m, 2H, –OCH_2CH$_3$), 5.13 (s, 1H, –C*H*OH), 7.26–7.42 (m, 5H, -*Ar*); ^{13}C NMR (75 MHz) δ 14.0, 62.1, 126.3, 128.1, 128.3, 138.2, 173.3.

4.15. 4-Methoxyphenyl(2-naphthyl)methanol (3bf)[21]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 1H, –O*H*), 3.79 (s, 3H, –OCH_3), 5.94 (s, 1H, –C*H*OH), 6.86 (d, *J* = 8.7, 2H, -*Ar*), 7.25–7.49 (m, 5H, -*Ar*), 7.77–7.89 (m, 4H, -*Ar*); ^{13}C NMR (75 MHz) δ 55.3, 75.8, 113.8, 124.6, 124.6, 125.8, 126.0, 127.5, 127.9, 128.0, 128.1, 132.6, 133.1,135.8, 141.1, 158.9.

*4.16. 2-Methoxyphenyl(2-naphthyl)methanol (**3cf**) [10b]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.14 (brs, 1H, –O*H*), 3.78 (s, 3H, –CH_3), 6.21 (d, *J* = 4.2, 1H, –C*H*OH), 6.86–6.94 (m, 2H, -*Ar*), 7.21–7.27 (m, 2H, -*Ar*), 7.39–7.48 (m, 3H, -*Ar*), 7.75–7.85 (m, 4H, -*Ar*); ^{13}C NMR (75 MHz) δ 55.3, 72.1, 110.6, 120.6, 124.7, 124.8, 125.4, 125.7, 127.4, 127.6, 127.80, 127.84, 128.6, 131.6, 132.5, 133.0, 140.4, 156.5.

*4.17. 4-Methylphenyl(2-naphthyl)methanol (**3df**) [22]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.26 (brs, 1H, –O*H*), 2.32 (s, 3H, –CH_3), 5.95 (s, 1H, –C*H*OH), 7.13 (d, *J* = 8.2 Hz, 2H, -*Ar*), 7.23–7.29 (m, 2H, -*Ar*), 7.29–7.48 (m, 3H, -*Ar*), 7.75–7.87 (m, 4H, -*Ar*); ^{13}C NMR (75 MHz) δ 21.5, 76.5, 125.0, 125.1, 126.1, 126.4, 126.9, 127.9, 128.3, 128.5, 129.5, 133.1, 133.5, 137.6, 141.0, 141.5.

*4.18. 4-Fluorophenyl(2-naphthyl)methanol (**3ef**) [23]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.47 (d, *J* = 2.1 Hz, 1H, –O*H*), 5.92 (d, *J* = 2.1 Hz, 1H, –C*H*OH), 6.96–7.02 (m, 2H, -*Ar*), 7.31–7.37 (m, 3H, -*Ar*), 7.42–7.49 (m, 2H, -*Ar*), 7.75–7.82 (m, 4H, -*Ar*); ^{13}C NMR (75 MHz) δ 75.7, 115.2 (d, *J* = 21.8 Hz, –C–CF), 124.5, 124.9, 126.0, 126.2, 127.6, 127.9, 128.3 (d, *J* = 9.2 Hz, –C–C–CF), 128.4, 132.8, 133.1, 139.2 (d, *J* = 2.9 Hz, –C–C–C–CF),140.7, 162.0 (d, *J* = 243.8 Hz, –CF); ^{19}F NMR (282 MHz) δ *−115.0.*

*4.19. 4-Cyanophenyl(4-fluorophenyl)methanol (**3ea**) [24]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.49 (brs, –O*H*), 5.84 (s, 1H, –C*H*OH), 7.00–7.05 (m, 2H, -*Ar*), 7.25–7.32 (m, 2H, -*Ar*), 7.54 (dd, *J* = 30.9 and 8.1 Hzs, 4H, -*Ar*); ^{13}C NMR (75 MHz) δ 75.2, 111.5, 116.0 (d, *J* = 21.2 Hz, 2C, –C–CF),118.9, 128.6 (d, *J* = 8.6 Hz, 2C, –C–C–CF), 132.5, 138.8, 148.8, 162.6 (d, *J* = 245.5 Hz, 1C, –CF); ^{19}F NMR (282 MHz) δ *−113.9.*

*4.20. 4-Cyanophenyl(2-fluorophenyl)methanol (**3fa**) [25]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.68 (brs, –O*H*), 6.16 (s, 1H, –C*H*OH), 7.00–7.60 (m, 8H, -*Ar*); ^{13}C NMR (75 MHz) δ 69.5, 111.5, 115.8 (d, *J* = 21.7 Hz, 1C, –C–CF), 119.0, 124.9 (d, *J* = 3.4 Hz, 1C, –C–C–CF), 127.1, 127.8 (d, *J* = 3.5 Hz, 1C, –C–C–CF), 129.9, 130.2 (d, *J* = 16.1 Hz, 1C, –C–CF), 132.5, 148.1, 161.6 (d, *J* = 244.9 Hz, 1C, –CF); ^{19}F NMR (282 MHz) δ *−118.6.*

*4.21. 3-Phenylcyclohexanone (**5aa**) [26]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.70–1.92 (m, 2H), 2.07–2.19 (m, 2H), 2.32–2.63 (m, 4H), 2.95–3.06 (m, 1H, –C*H*Ar), 7.19–7.24 (m, 3H, -*Ar*), 7.29–7.34 (m, 2H, -*Ar*) ^{13}C NMR (75 MHz) δ 25.9, 33.1, 41.5, 49.2, 126.8, 126.9, 128.9, 144.5, 211.0.

*4.22. 3-Phenylcyclopentanone (**5ab**) [26]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.88–2.02 (m, 1H), 2.19–2.47 (m, 4H), 2.63 (dd, *J* = 18.6 and 7.5 Hzs, 1H), 3.32–3.44 (m, 1H, –C*H*Ar), 7.18–7.23 (m, 3H, -*Ar*), 7.29–7.33 (m, 2H, -*Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.5, 39.2, 42.5, 46.1, 126.9, 128.8, 143.2, 218.5.

*4.23. 3-Phenylcycloheptanone (**5ac**) [26]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.44–1.57 (m, 1H), 1.64–1.79 (m, 2H), 1.95–2.12 (m, 3H), 2.59–2.66 (m, 3H), 2.88–2.97 (m, 2H), 7.15–7.21 (m, 3H, -*Ar*), 7.26–7.31 (m, 2H, -*Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.5, 29.6, 39.5, 43.0, 44.3, 51.5, 126.6, 128.8, 128.9, 147.1, 213.5.

*4.24. 1,3,3-Triphenyl-1-propanone (**5ad**) [26]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.70 (d, *J* = 7.2 Hz, 2H, –COCH_2), 4.81 (t, *J* = 7.2 Hz, 1H, –C*H*Ar), 7.10–7.26 (m, 10H, -*Ar*), 7.34–7.50 (m, 3H, -*Ar*), 7.87–7.90 (m, 2H, -*Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 45.1, 46.4, 126.6, 128.0, 128.2, 128.8, 128.9, 133.4, 137.2, 144.4, 198.1.

*4.25. 4,4-Diphenyl-2-butanone (**5ae**) [27]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 3H, –COCH_3), 3.17 (d, *J* = 7.5 Hz, 2H, –COCH_2), 4.58 (t, *J* = 7.5 Hz, 1H, –C*H*Ar), 7.13–7.29 (m, 10H, -*Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.0, 46.4, 50.0, 126.7, 128.0, 128.8, 144.1, 206.9.

*4.26. 5-Phenyl-3-hexanone (**5af**) [28]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (t, J = 7.2 Hz, 3H, –$COCH_2CH_3$), 1.24 (d, J = 6.9 Hz, 3H, –CH(Ar)CH_3), 2.21–2.38 (m, 2H, –CH_2CH_3), 2.57–2.74 (m, 2H, –$COCH_2$), 3.25–3.37 (m, 1H, –*CH*Ar), 7.13–7.29 (m, 5H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.0, 22.3, 35.8, 37.0, 51.3, 126.4, 127.0, 128.7, 146.4, 210.4.

*4.27. 4-Phenyl-2-heptanone (**5ag**) [26]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, J = 7.2 Hz, 3H, –CH_2CH_3), 1.08–1.22 (m, 2H, –CH_2CH_3), 1.49–1.60 (m, 2H, –$CH_2CH_2CH_3$), 1.98 (s, 3H, –$COCH_3$), 2.65–2.76 (m, 2H, –$COCH_2$), 3.12 (q, J = 7.2 Hz, 1H, –*CH*Ar), 7.12–7.18 (m, 3H, *-Ar*), 7.23–7.28 (m, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.4, 20.9, 31.0, 39.0, 41.4, 51.3, 126.5, 127.6, 128.6, 144.7, 208.0.

*4.28. 5-Methyl-4-phenyl-2-hexanone (**5ah**) [29]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.74 (d, J = 6.9 Hz, 3H, –$CHCH_3$), 0.93 (d, J = 6.6 Hz, 3H, –$CHCH_3$), 1.79–1.86 (m, 1H, –*CH*CH_3), 1.95 (s, 3H, –$COCH_3$), 2.77–2.79 (m, 2H, –CH_2CO), 2.88–2.95 (m, 1H, –*CH*Ar), 7.11–7.18 (m, 3H, *-Ar*), 7.22–7.27 (m, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 21.1, 30.9, 33.6, 47.9, 48.3, 126.4, 128.3, 128.4, 143.4, 208.3.

4.29. 3-Phenylbutanal (5ai) [26]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (d, J = 6.9 Hz, 3H, –CH_3), 2.60–2.79 (m, 2H, –CH_2CHO), 3.30–3.41 (m, 1H, –*CH*Ar), 7.17–7.32 (m, 5H, *-Ar*), 9.69 (t, J = 2.1 Hz, 1H, –*CH*O); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 34.6, 52.0, 126.7, 127.0, 128.8, 145.6, 201.9.

*4.30. 3-Phenylhexanal (**5aj**) [26]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, J = 7.2 Hz, 3H, –CH_3), 1.11–1.24 (m, 2H, –CH_2CH_3), 1.56–1.63 (m, 2H, –CH_2CHAr), 2.67 (dd, J = 2.1 and 1.8 Hzs, –CH_2CHO), 3.16 (q, J = 1.8 Hz, 1H, –*CH*Ar), 7.13–7.30 (m, 5H, *-Ar*), 9.61 (t, J = 2.1 Hz, 1H, –*CH*O); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3, 20.8, 39.1, 40.2, 50.9, 126.7, 127.6, 128.8, 144.1, 202.0.

4.31. 3,3-Diphenylpropanal (5ak)[26]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.10 (dd, J = 7.8 and 1.8 Hzs, 2H, –CH_2CHO), 4.58 (t, J = 7.8 Hz, 1H, –*CH*Ar), 7.12–7.28 (m, 10H, *-Ar*), 9.56 (t, J = 1.8 Hz, 1H, –*CH*O); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 45.3, 49.7, 126.9, 127.9, 128.9, 143.5, 200.1.

*4.32. Methyl 3-phenylbutanoate (**5al**) [30]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (d, J = 6.9 Hz, 3H, –CH_3), 2.53–2.70 (m, 2H, –CH_2CHAr), 3.25–3.37 (m, 1H, –*CH*Ar), 3.64 (s, 3H, –OCH_3), 7.19–7.35 (m, 5H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.1, 36.8, 43.0, 51.9, 126.6, 126.9, 128.7, 145.8, 172.9.

*4.33. Methyl 3-phenylpentanoate (**5am**) [31]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (t, J = 7.2 Hz, 3H, –CH_3), 1.54–1.75 (m, 2H, –CH_2CH_3), 2.52–2.67 (m, 2H, –CH_2CO), 2.95–3.05 (m, 1H, –*CH*Ar), 3.55 (s, 3H, –OCH_3), 7.13–7.29 (m, 5H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.3, 29.4, 41.6, 44.2, 51.7, 126.6, 127.6, 128.5, 144.0, 173.0.

*4.34. 3-Phenylpentanenitrile (**5an**) [32]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 ((t, J = 7.2 Hz, 3H, –CH_3), 1.68–1.93 (m, 2H, –CH_2CH_3), 2.57 (t, J = 7.2 Hz, 2H, –CH_2CN), 2.78–2.85 (m, 1H, –*CH*Ar), 7.16–7.34 (m, 5H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.2, 25.1, 28.3, 44.2, 118.9, 127.4, 127.5, 129.0, 141.8.

*4.35. 3-(4-Methoxyphenyl)cyclohexanone (**5ba**) [33]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ *1.69–1.86* (m, 2H), 2.01–2.15 (m, 2H), 2.29–2.58 (m, 4H), 2.89–2.98 (m, 1H, –*CH*Ar), 3.76 (s, 3H, –OCH_3), 6.82–6.87 (m, 2H, *-Ar*), 7.09–7.14 (m, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.8, 33.3, 41.5, 44.3, 49.5, 55.5, 114.2, 127.7, 136.7, 158.3, 211.2.

*4.36. 3-(4-Methylphenyl)cyclohexanone (**5da**) [29]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.69–1.82 (m, 2H), 2.00–2.13 (m, 2H), 2.30 (s, 3H, –CH_3), 2.32–2.56 (m, 4H), 2.89–2.96 (m, 1H, –*CH*Ar), 7.06–7.12 (m, 4H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 25.9, 33.2, 41.5, 44.7, 49.4, 126.6, 129.6, 136.3, 141.6, 211.1.

*4.37. 3-(4-Fluorophenyl)cyclohexanone (**5ea**) [34]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.72–1.88 (m, 2H), 2.04–2.18 (m, 2H), 2.31–2.59 (m, 4H), 2.94–3.03 (m, 1H, –*CH*Ar), 6.99 (m, 2H, *-Ar*), 7.13–7.19 (m, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.7, 33.2, 41.4, 44.3, 49.4, 115.6 (d, J = 21.1 Hz, 2C, –C–CF), 128.2 (d, J = 8.0 Hz, 2C, –C–C–CF), 140.2, 161.6 (d, J = 262.6 Hz, 1C, –CF), 210.8; ^{19}F NMR ($CDCl_3$, 282 MHz) δ *−116.5.*

*4.38. 4-(3-Oxocyclohexyl)benzonitrile (**5ga**) [35]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.77–1.95 (m, 2H), 2.08–2.21 (m, 2H), 2.35–2.61 (m, 4H), 3.04–3.14 (m, 1H, –*CH*Ar), 7.35 (d, J = 8.4 Hz, 2H, *-Ar*), 7.62 (d, J = 8.1 Hz, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.6, 32.5, 41.3, 44.9, 48.4, 110.7, 119.0,127.7, 132.7, 149.7, 210.0.

*4.39. 3-(2-Methoxyphenyl)cyclohexanone (**5ja**) [36]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.76–2.12 (m, 4H), 2.33–2.55 (m, 4H), 3.34–3.45 (m, 1H, –*CH*Ar), 3.78 (s, 3H, –CH_3), 6.82–6.94 (m, 2H *–Ar*), 7.14–7.21 (m, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.9, 31.3, 38.3, 41.7, 48.0, 55.5, 110.7, 120.8, 126.7, 127.7, 132.6, 156.8, 211.9.

*4.40. 3-(4-Trifluoromethylphenyl)cyclohexanone (**5ka**) [29]*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.75–1.94 (m, 2H), 2.07–2.20 (m, 2H), 2.33–2.62 (m, 4H), 3.03–3.13 (m, 1H, –*CH*Ar), 7.34 (d, J = 8.1 Hz, 2H, *-Ar*), 7.57 (d, J = 8.1 Hz, 2H, *-Ar*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.7, 32.8, 41.3, 44.8, 48.7, 124.3 (q, J = 270.1 Hz, 1C, –CF_3), 125.7 (q, J = 4.0 Hz, 2C, –C–C–CF_3), 127.1, 129.1 (q, J = 32.0 Hz, 1C, –C–CF_3), 148.4, 210.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ *−62.9.*

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