Pd-tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) complex catalyzed acylodeboronation of arylboronic acids with benzoyl chloride or acetic anhydride

Jinli Zhang, Zixing Han, Junmiao Li, and Yangjie Wu*

The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou, 450052, P. R. China
E-mail: wyj@zzu.edu.cn

DOI: http://dx.doi.org/10.3998/ark.5550190.p007.750

Abstract

The palladium-tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) complex, in the form of $[NaL]^+$ $[PdCl_3]^-$, exhibited high catalytic efficiency for the acylodeboronation reaction of arylboronic acids with benzoyl chloride or acetic anhydride, producing the corresponding ketones in good to excellent yields under mild reaction conditions. Various arylboronic acids, benzoyl chlorides and acetic anhydrides were tolerated in this method. Moreover, a typical method for synthesis of acetyl aryl ketones was obtained.

Keywords: **T**etraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate), palladium catalyst, aryl ketone, carbonylation

Introduction

Due to the wide occurrence of aryl ketone moiety in a large number of biologically active compounds[1], natural products,[2] cosmetics,[3] pharmaceutical, fragrance, dye, agrochemicals and functional material industries as well as in organic synthesis,[4] considerable efforts have been made for its synthesis. Aromatic ketones can be effectively prepared by palladium catalyzed carbonylation reaction of acyl chlorides with boronic acid.[5-7] Such method can avoid the restrictions of the regioselectivity limitation of *para* position (traditional Friedel-Crafts acylation[8]), using of toxic carbon monoxide and the formation of biaryl side products (carbonylative Suzuki-Miyaura cross-coupling[9]), the requirement of directing group (carbonylative C-H activation[10]), harsh reaction conditions (oxidation of benzyl alcohols[11] and addition of organometallic reagents to carboxylic derivatives or nitriles[12]) and incompatibility with electron-deficient groups etc.[7,13-15]

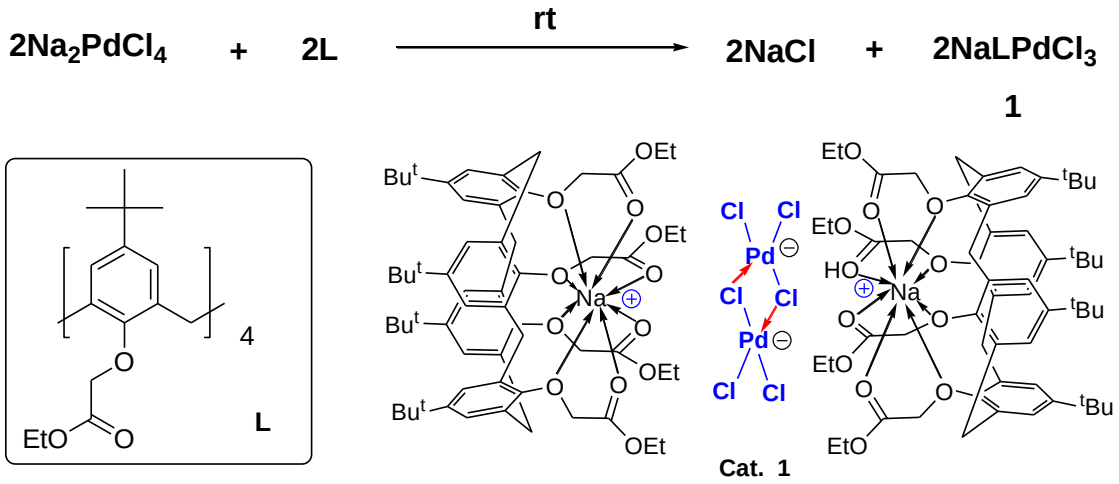
However, there are still some limitations for the synthesis of aliphatic acyl phenone using aliphatic acyl chloride or acetic anhydride as acyl reagent, especially for the synthesis of various acetophenone from acetic chloride or anhydride.[5c,5f,6g,7a] The coupling between phenylboronic acid and acetic anhydride were scatteredly reported[5c,5f,6d] and only Gooben[5f] obtained satisfactory results. Thus, it is challenging to develop catalytic carbonylation of aliphatic acyl chloride or acetic anhydride with high efficiency.

Nowadays, calixarenes are emerging as a versatile family of ancillary ligands in a variety of catalytic processes.[16] For example, calixarenes bearing phosphines or NHCs functional groups have been reported to exhibit notably high catalytic activities in transition metal catalyzed C-C bond formation reactions.[17] In addition, calix[4]aryl acetates showed remarkably high sodium ion affinity and selectivity owing to the "size fitting effect".[18a-18c] Recently, our group reported the synthesis of a kind of tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) and its catalytic activity in Suzuki cross-coupling reaction.[18d] In this paper, we wish to report the palladium-tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) complex catalyzed acylodeboronation reaction of arylboronic acids with benzoyl chloride or acetic anhydride respectively for the easy preparation of aryl ketones. To the best of our knowledge, this is the first report on the coupling of carboxylic anhydride or acyl chloride catalyzed by 0.5% catalyst loading of palladium complex based on tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate).

Results and Discussion

Synthesis of the catalyst and its characterization

Tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) (**L**) was synthesized according to the general procedure.[19] Palladium complex was obtained according to the literature and characterized by X-ray[18d] analysis.



Scheme 1. Synthesis of catalyst **1**.

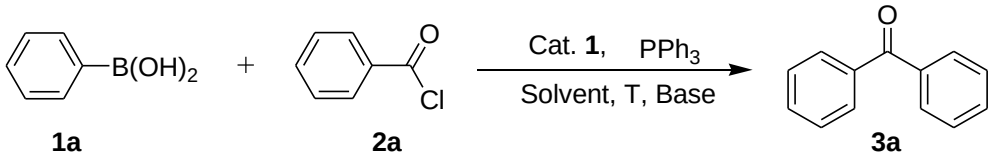
The red solid of **L** was obtained in a 65% yield. mp >280 °C (dec). NMR spectra: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.07 (8H, s), 4.48-4.43 (16H, m), 4.26 (4H, d, *J* 12.2 Hz), 3.37 (4H, d, *J* 12.2 Hz), 1.47 (12H, t, *J* 7.1 Hz), 1.11 (36H, s). ^{13}C NMR: δ 171.0, 149.6, 148.2, 134.3, 125.7, 73.2, 62.4, 34.0, 31.2, 29.8, 14.4. As shown in Scheme 1, the $Na_2Pd_2Cl_6$ complex with tetraethyl tetra-*t*-butyl-calixarene-tetra(oxyacetate) shows clearly a "cone" structure.

Catalytic survey

Studies on acylodeboronation reaction of arylboronic acid with benzoyl chloride

The coupling reaction of phenyl boronic acid and benzoyl chloride was chosen as a model reaction (Table 1) to test the reactivity of Cat. **1**. To compare the catalytic activities, $Pd(OAc)_2$ and $PdCl_2$ were used under the same reaction conditions, and relatively lower yields were obtained respectively (entries 2-5). Yamamoto's and Goossen's studies have showed that the phosphine ligands played key roles in the successful execution of the reactions.[20] Gratifyingly, the carbonylation coupling proceeded smoothly and gave benzophenone in 68% isolated yield when Cat. **1** was used as a catalyst in the presence of PPh_3 and K_3PO_4 in toluene at 90 °C under air (Table 1, entry 7). These results indicated that the combination of tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) and PPh_3 promoted the procedure of acylodeboronation. Inspired by these results, we then screened the bases and reaction temperatures by using 0.5 mol% Cat. **1**. The carbonylation yield as high as 95% was obtained when the reaction was conducted at 70 °C under air (entry 10), which was much higher than the yields obtained by $Pd(PPh_3)_4$.[5c,7a] Under the proper reaction conditions, other phosphine ligands were also applied and gave lower carbonylation yields (entries 11-14). Cat. **1** showed slight catalytic activities under lower temperature and concentration (entries 15-16). The results showed that the "size fitting effect" between tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) and palladium anion played key roles for the reaction (entry 18).

Table 1. Study on acylodeboronation reaction of phenyl boronic acid with benzoyl chloride



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

Entry[a]	Catalyst	Bases	T, °C	Time, h	Yield % [b]
1	--	K_3PO_4	90	12	Trace
	Na_2PdCl_4+PPh_3	K_3PO_4	90	12	<5
2	$Pd(OAc)_2$	K_3PO_4	90	12	50
3	$Pd(OAc)_2$+PPh_3	K_3PO_4	90	12	31
4	$PdCl_2$	K_3PO_4	90	12	16
5	$PdCl_2$+PPh_3	K_3PO_4	90	12	35
6	Cat. **1**	K_3PO_4	90	12	Trace

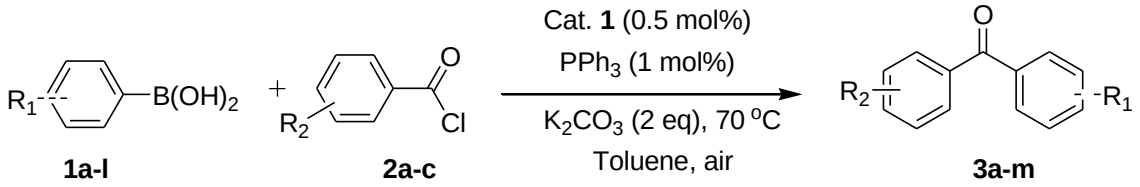
Table 1. Continued

Entry[a]	Catalyst	Bases	T, °C	Time, h	Yield % [b]
7	Cat. **1**+PPh_3	K_3PO_4	90	12	68
8	Cat. **1**+PPh_3	K_2CO_3	90	12	98
9	Cat. **1**+PPh_3	Na_2CO_3	90	12	Trace
10	**Cat. 1+PPh_3**	**K_2CO_3**	**70**	**12**	**95**
11	$Pd(OAc)_2$+dppe	K_2CO_3	70	12	56
12	$Pd(OAc)_2$+dppf	K_2CO_3	70	12	48
13	$PdCl_2$+dppe	K_2CO_3	70	12	77
14	$PdCl_2$+dppf	K_2CO_3	70	12	71
15	Cat. **1**+PPh_3	K_2CO_3	40	12	38
16	Cat. **1**+PPh_3	K_2CO_3	70	12	76[c]
17	Cat. **1**+PPh_3	K_2CO_3	70	12	92[d]
18 [e]	L+ NaCl + $PdCl_2$	K_2CO_3	70	12	-

[a] benzoyl chloride (1.0 mmol), phenyl boronic acid (0.5 mmol), base (1.0 mmol), complex **1** (0.5 mol%, 3.1 mg), PPh_3 (0.01 mmol) and toluene (2.0 mL), 70 °C. [b] isolated yields. [c] 0.25 mol% complex **1** was used and the acylodeboronation yield was determined by GC analysis using **3a** as internal standard substances. [d] 1 mol% complex **1** was used and the acylodeboronation yield was determined by GC analysis using **3a** as internal standard substances. [e] tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) **L** (0.005 mmol), NaCl (0.005 mmol), $PdCl_2$(0.005 mmol), and the acylodeboronation yield could not be repeated (20-60%).

With the standard conditions in hand, we then examined the scope and limitation of **Cat. 1** in the acylodeboronation reaction. Various arylboronic acids and benzoyl chloride were applied to this system (Table 2, entries 1-14). The results listed in Table 2 showed that this catalytic system tolerated various functional groups, such as CH_3, CH_3O, Br, Cl, F, CHO, and CH_3CO. Both electron-rich and electron-deficient arylboronic acids could provide the desired products in moderate to excellent yields (Table 2, entries 1-10). 1-Naphthyl and 2-thienyl boronic acids also reacted smoothly with benzoyl chloride, yielding the corresponding aryl ketones in 89% and 95% yields, respectively (Table 2, entries 11-12). Some ketones, such as **3b, 3f, 3i** and **3j**, usually difficult to obtain from traditional Friedel-Crafts methods by using benzoyl chloride as substrate,[8] were produced successfully with moderate to good yields in this protocol (Table 2, entries 2, 6, 9, 10).

Table 2. Complex **1** catalyzed acylodeboronation reaction of arylboronic acids with benzoyl chloride



1a-l **2a-c** **3a-m**

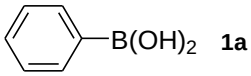
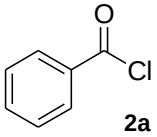
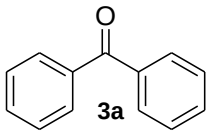
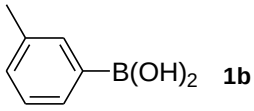
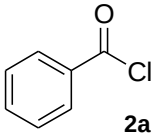
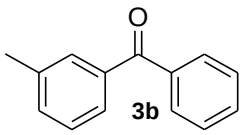
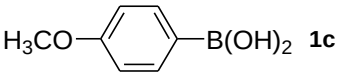
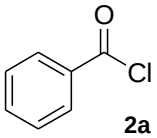
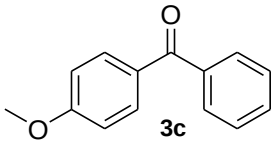
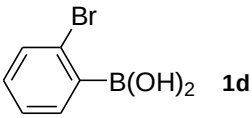
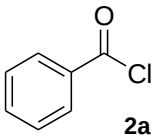
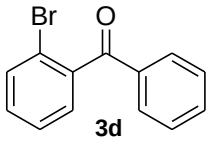
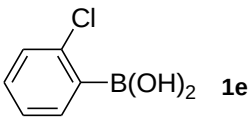
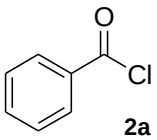
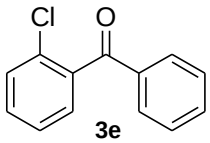
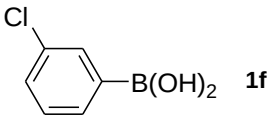
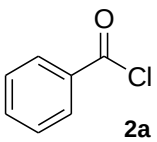
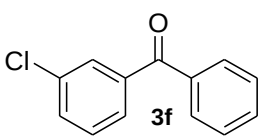
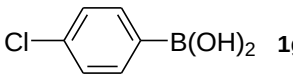
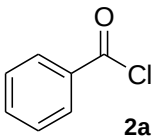
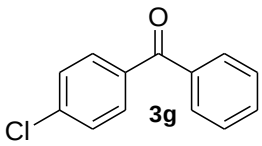
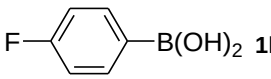
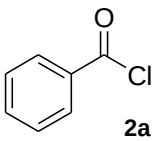
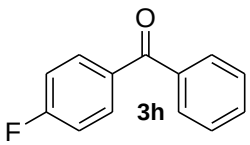
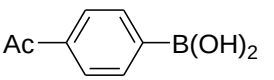
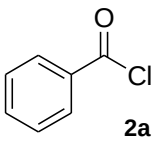
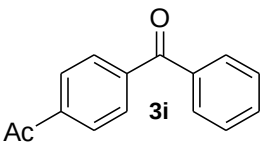
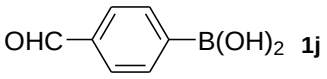
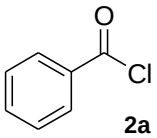
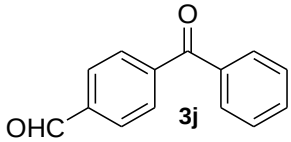
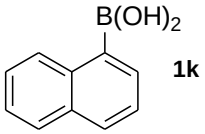
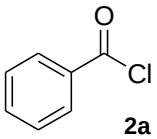
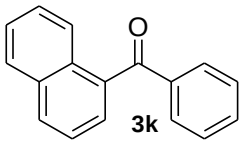
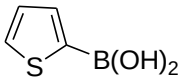
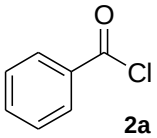
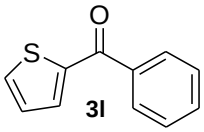
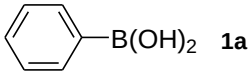
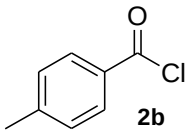
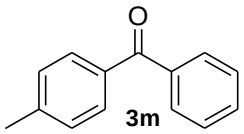
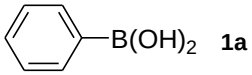
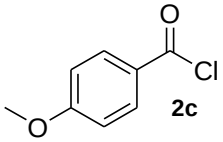
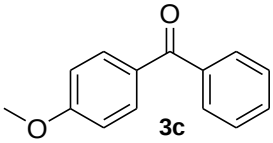
Entry[a]	Arylboronic acids	Benzoyl chlorides	Products	Yield, %[b]
1	 **1a**	 **2a**	 **3a**	95
2	 **1b**	 **2a**	 **3b**	84
3	 **1c**	 **2a**	 **3c**	90
4	 **1d**	 **2a**	 **3d**	90
5	 **1e**	 **2a**	 **3e**	93
6	 **1f**	 **2a**	 **3f**	75
7	 **1g**	 **2a**	 **3g**	73
8	 **1h**	 **2a**	 **3h**	78
9	 **1i**	 **2a**	 **3i**	67

Table 2. Continued

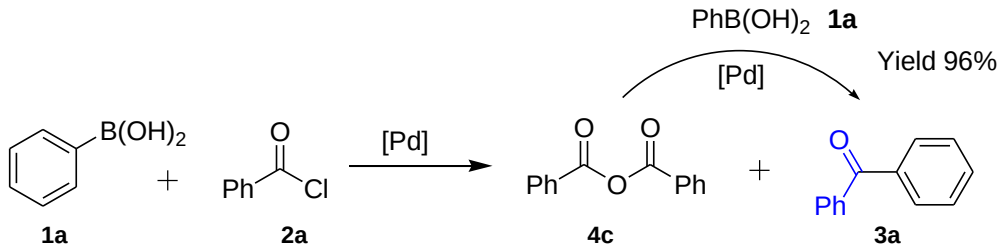
Entrya	Arylboronic acids	Benzoyl chlorides	Products	Yield, % b
10	 **1j**	 **2a**	 **3j**	62
11	 **1k**	 **2a**	 **3k**	89
12	 **1l**	 **2a**	 **3l**	95
13	 **1a**	 **2b**	 **3m**	84
14	 **1a**	 **2c**	 **3c**	88

[a] reaction conditions: benzoyl chloride (1.0 mmol), arylboronic acid (0.5 mmol), base (1.0 mmol), complex 1 (0.5 mol%), PPh_3 (0.01 mmol) and toluene (2.0 mL), 70 °C, 12h. [b] isolated yields.

Studies on the acylodeboronation reaction of arylboronic acid with acetic anhydride

When Na_2CO_3 was used as base (Table 1, entry 9), trace amount of benzophenone was observed. Benzoic acid anhydride was obtained as main product (determined by GC analysis). Treating the obtained benzoic acid anhydride with phenylboronic acid (new added), the desired benzophenone was isolated in 96% yield. These results revealed that the formation of ketone may proceed *via* the intermediate of benzoic acid anhydride, and Cat. **1** was also an efficient catalyst for the carbonylation reaction of arylboronic acid with acid anhydride (Scheme 2).

Acetophenone derivatives are useful intermediates in industry as well as in organic synthesis. Carbonylation reaction of acetyl chloride or anhydride with boronic acid could also be used for its synthesis. Bandgar [6g] has reported the reaction of arylboronic acid with benzoyl chloride by using $PdCl_2$ as catalyst and Na_2CO_3 as base. But the catalyst loading is high (3.3%) and the coupling between acetyl chloride with boronic acid remains unsuccessful [6g,7a] or only in moderate yields.[5c] Also the coupling between acetic anhydride with arylboronic acid has been reported by Gooben [5f] by using $Pd(OAc)_2$ as catalyst, expensive P(*p*-MeOPh)$_3$ as ligand, and excess of arylboronic acid.

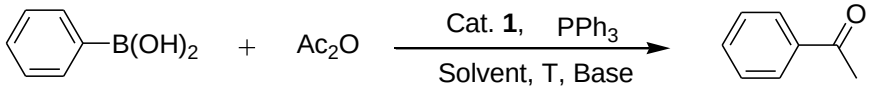


Na_2CO_3	Air	Major		Trace
	N_2	1	:	5
K_3PO_4	Air	1	:	4.5
K_2CO_3	Air	Trace		Major

Scheme 2. Study on the effect of Na_2CO_3 as base for acylodeboronation reaction of phenylboronic acid with benzoic acid chloride.

We then choose acetic anhydride as reagent to test the reactivity of Cat.**1**. Initially, the cross-coupling reaction conditions of phenylboronic acid with acetic anhydride were screened (listed in Table 3). The best yield of 85% was obtained when $KHCO_3$ was used as base in toluene at 110 °C under nitrogen (Table 3, entry 6).

Tabel 3. Study on acylodeboronation reaction of phenyl boronic acid with acetic anhydride



Entry[a]	Catalyst	Solvent	Base	T, °C	Time, h	Gas	Yield, %[b]
1	Cat. **1**+PPh_3	Toluene	K_2CO_3	70	12	Air	15
2	Cat. **1**+PPh_3	Toluene	K_2CO_3	70	12	N_2	48
3	Cat. **1**+PPh_3	Toluene	K_2CO_3	110	3	N_2	67
4	Cat. **1**+PPh_3	Toluene	K_3PO_4	110	3	N_2	42
5	Cat. **1**+PPh_3	Toluene	Na_2CO_3	110	3	N_2	40
6	**Cat. 1**+PPh_3	**Toluene**	**$KHCO_3$**	**110**	**3**	**N_2**	**85**
7	Cat. **1**+PPh_3	Toluene	$NaHCO_3$	110	3	N_2	17
8	$PdCl_2$+PPh_3	Toluene	Na_2CO_3	110	3	N_2	52
9	$PdCl_2$+dppe	Toluene	$KHCO_3$	110	3	N_2	Trace
10	$PdCl_2$+dppf	Toluene	$KHCO_3$	110	3	N_2	Trace
11	$Pd(OAc)_2$+ PPh_3	Toluene	$KHCO_3$	110	3	N_2	40
12	$Pd(OAc)_2$+dppe	Toluene	$KHCO_3$	110	3	N_2	Trace
13	$Pd(OAc)_2$+dppf	Toluene	$KHCO_3$	110	3	N_2	Trace
14	Cat. **1**	Toluene	$KHCO_3$	110	3	N_2	Trace

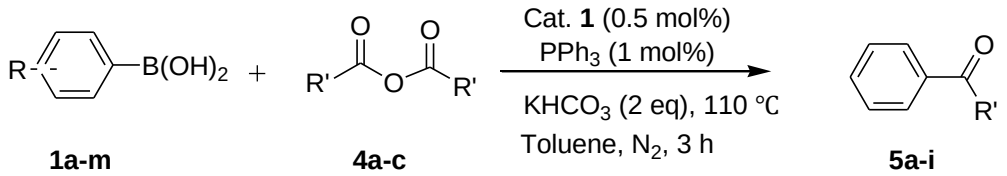
Table 3. Continued

Entry[a]	Catalyst	Solvent	Base	T, °C	Time, h	Gas	Yield, % [b]
15	Cat. **1**+PPh_3	THF	$KHCO_3$	60	3	N_2	77
16	Cat. **1**+PPh_3	DMF	$KHCO_3$	110	3	N_2	Trace
17[c]	L +NaCl+ $PdCl_2$	Toluene	$NaHCO_3$	110	3	N_2	-

[a] acetic anhydride (1.0 mmol), arylboronic acid (0.5 mmol), base (1.0 mmol), complex **1** (0.5 mol%), PPh_3 (0.01 mmol) and solvent (2.0 mL). [b] isolated yields. [c] yields could not be repeated (20-40%).

Under the optimal conditions, the scope of arylboronic acids and anhydrides for this acylodeboronation transformation was investigated. As shown in Table 4, the carbonylation yields were influenced by electron effect. Arylboronic acids with electron-rich groups such as CH_3 or CH_3O, as well as 1-naphthyl motif could be coupled with acetic anhydride in moderate to good yields (Table 4, entries 1-5). When arylboronic acids bearing electron-deficient groups were applied, moderate yields were still obtained (Table 4, entries 6-8). Other kinds of anhydrides were also applied, yielding the corresponding ketones in lower yields (Table 4, entries 9-10).

Table 4. Complex **1** catalyzed acylodeboronation reaction of arylboronic acids with acetic anhydride



1a-m **4a-c** **5a-i**

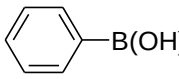
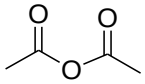
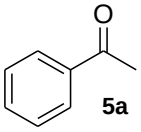
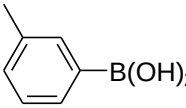
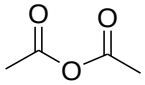
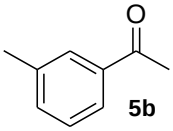
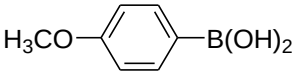
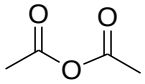
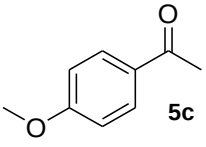
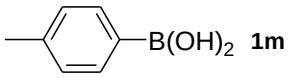
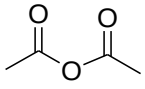
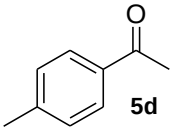
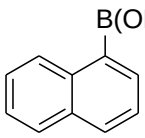
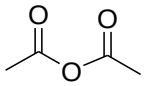
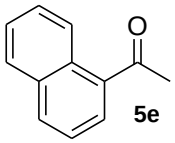
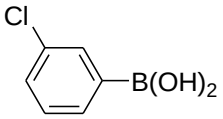
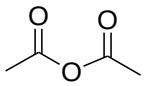
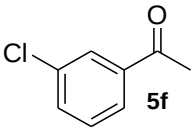
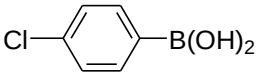
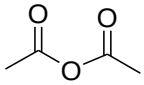
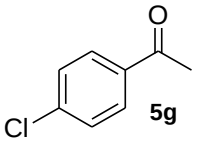
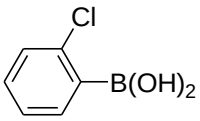
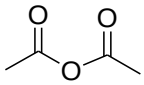
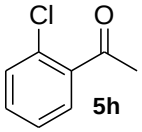
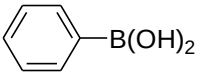
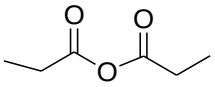
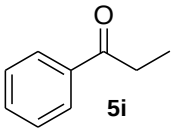
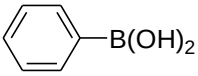
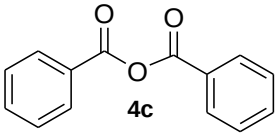
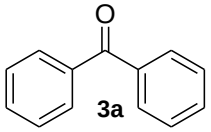
Entry[a]	Arylboronic acids	Anhydrides	Products	Yield, % [b]
1	 **1a**	 **4a**	 **5a**	85
2	 **1b**	 **4a**	 **5b**	76
3	 **1c**	 **4a**	 **5c**	69
4	 **1m**	 **4a**	 **5d**	79

Table 4. Continued

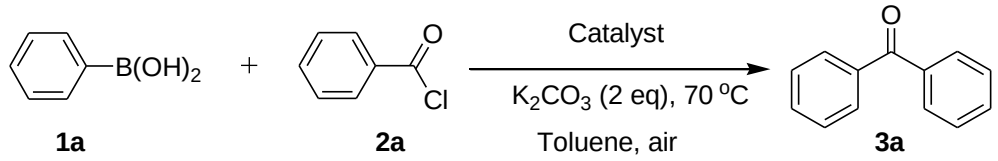
Entry[a]	Arylboronic acids	Anhydrides	Products	Yield, % [b]
5	 **1k**	 **4a**	 **5e**	89
6	 **1f**	 **4a**	 **5f**	62
7	 **1g**	 **4a**	 **5g**	61
8	 **1e**	 **4a**	 **5h**	59
9	 **1a**	 **4b**	 **5i**	56
10	 **1a**	 **4c**	 **3a**	59 (96 [c])

[a] reaction conditions: acetic anhydride (1.0 mmol), arylboronic acid (0.5 mmol), base (1.0 mmol), complex **1** (0.5 mol%), PPh_3 (0.01 mmol) and toluene (2.0 mL), 110 °C, 3 h. [b] isolated yields. [c] Na_2CO_3 was used as base.

Mechanistic study

In order to provide evidence that the enhanced yields using Cat. **1** were not due to the use of a Na_2PdCl_4 instead of $Pd(OAc)_2$ or $PdCl_2$, the carbonylation reaction of benzoyl chloride with phenylboronic acid was conducted by using the mixture of Na_2PdCl_4 pre-catalyst and triphenylphosphine. It is clear that the high catalytic efficiency were attributed to the "size fitting effect" between tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) **L** and palladium anion (Table 5, entries 1-4). Furthermore, a investigation on the catalytic activity of Na_2PdCl_4 with different phosphine ligands such as PPh_3, dppe or dppf was undertaken to clarify the role of tetraethyl *p*-tert-butyl-calix[4]aryl tetraacetate (**L**) in the formation of the catalytically active species (Table 5, entries 5-7). Na_2PdCl_4 with the mixture of **L** and different phosphine as ligands showed slightly lower activity under the same reaction conditions. Except the ligand dppe, the mixture of Na_2PdCl_4, **L** and PPh_3 or dppf resulted in the homo-coupling of phenylboronic acid.

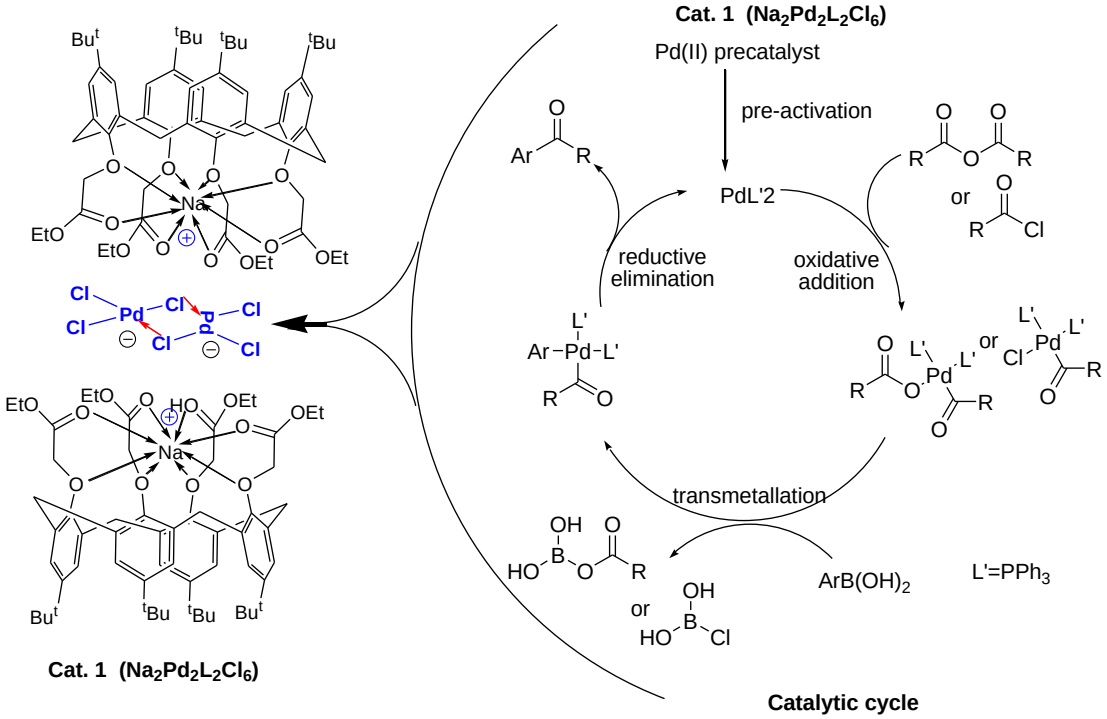
Table 5. Studies on the role of tetraethyl tetra-*t*-butylcalixarenetetra(oxyacetate) **L**



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

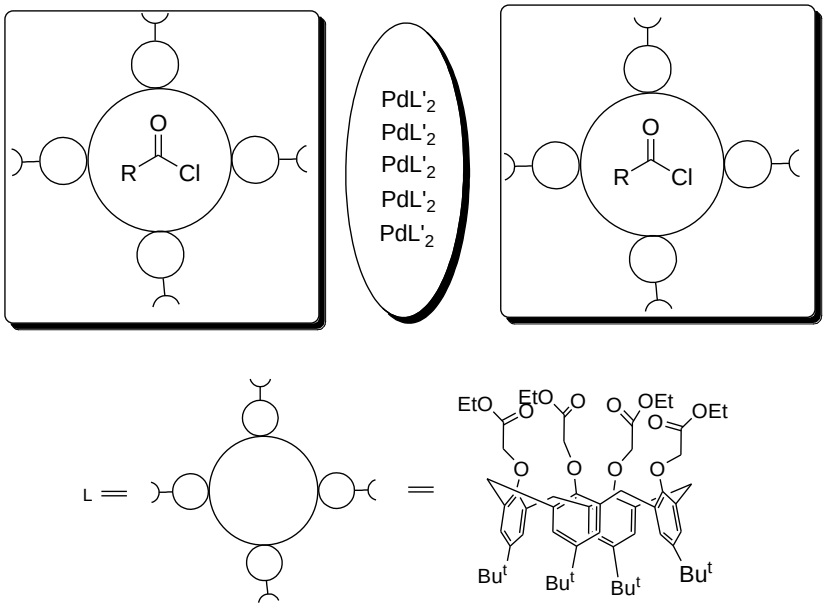
Entry[a]	Catalyst	Yiled % of **3a** [b]
1	Cat.1+PPh_3	98
2	Na_2PdCl_4+PPh_3	65
3	$PdCl_2$+PPh_3	81
4	$Pd(OAc)_2$+ PPh_3	82
5	Na_2PdCl_4+L+PPh_3	10 [c]
6	Na_2PdCl_4+L+dppe	78
7	Na_2PdCl_4+L+dppf	15 [c]

[a] benzoyl chloride (1.0 mmol), phenyl boronic acid (0.5 mmol), K_2CO_3 (1.0 mmol), complex **1** (0.5 mol%), tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) **L** (0.005 mmol), NaCl (0.005 mmol), $PdCl_2$ (0.005 mmol), $Pd(OAc)_2$ (0.005 mmol), phosphine ligand (0.01 mmol) and toluene (2.0 mL), 70 °C, 24 h. [b] GC yields by using **3a** as internal standard substances. [c] the side product (~70% GC yield) was determined by using biphenyl as internal standard substances.



Scheme 3. Possible mechanism.

Based on the ligature and results obtained above, a possible reaction mechanism was proposed as outlined in Scheme 3. Firstly, Pre-activation of Cat.**1** generated the active palladium catalyst PdL'_2 in the anion of $Pd_2Cl_6^-$. We hypothesized that the active palladium catalyst covered on the anion as shown in Scheme 4. The benzoyl chloride **2a** was transported one by one through the cage of tetraethyl tetra-t-butylcalixarene-tetra(oxyacetate) **L** to access the active palladium catalyst from two side (Scheme 4). Fast oxidative addition gave the intermediate. After the completion of transmetallation of phenylboronic acid **1a**, the catalytic cycle was finished followed by the reductive elimination finally.



Scheme 4. The role of the tetraethyl *p*-tert-butyl-calix[4]aryl tetraacetate.

It is reliable that the catalytic cycle was finished in the anion part of $Pd_2Cl_6^-$ since the biphenyl was observed as main product when the ligand **L** was mixed with **1a** and **2a** (Table 5, entry 5). We resumed that the efficiency of Pd-tetraethyl tetra-*t*-butylcalixarene-tetra (oxyacetate) complex in the carbonylation reaction could be attributed to its surface properties, and its capacity to bind strongly to benzoyl chloride into its hydrophobic pocket, which enhanced the ability to interact with the reagents and palladium (Scheme 4).[18d]

Conclusions

In summary, Pd-tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) complex, in the form of $[NaL]^+[PdCl_3]^-$, catalyzed cross-coupling reactions of various arylboronic acids with benzoyl chloride or acetic anhydride were successfully achieved with low catalyst loading of 0.5 mol%. This protocol has the advantages of straightforward, easy handling and cheap substrates as

coupling partner. Most important, the advantage of high functional group tolerance made this method possible to obtain several acetophenones difficult to access by traditional Friedel-Crafts reaction. Moreover, this study provides a particular method to synthesize methyl aryl ketones by acetylation using acylodeboronation reactions.

Experimental Section

General. Melting points were measured on a XT-5 microscopic apparatus. GC analyses were performed on Agilent 4890D gas chromatograph. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard.

Palladium complex based on a tetraethyl tetra-*t*-butylcalixarene-tetra(oxyacetate) was synthesized according to the literature.[3d] All solvents were tried by the standard methods. The chemicals were reagent grade and used without further treatment.

General procedure for the acylodeboronation reaction of arylboronic acids with benzoyl chloride. A 5 mL flask charged with benzoyl chloride (1.0 mmol), arylboronic acid (0.5 mmol), K_2CO_3 (1.0 mmol), complex **1** (0.5 mol%, 3.1 mg), PPh_3 (0.01 mmol, 1.3 mg) and toluene (2.0 mL) was put into a preheated 70 ^{o}C oil bath for an appropriate period of time under air. After the reaction was finished, the reaction mixture was cooled to room temperature, filtered through a short silica column and washed with ethyl acetate. Then the combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography (eluent: ethylacetate/petroleum ether). All the products were known compounds and characterized by comparing mp, ^{1}H NMR and ^{13}C NMR spectra with literature.

Benzophenone (3a, Table 2, entry 1). White solid, mp 47-48 ^{o}C (lit.[21] 47-49 ^{o}C). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.81-7.78 (m, 4H), 7.59-7.54 (m, 2H), 7.49-7.45 (m, 4H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 196.7, 137.4, 132.3, 129.9, 128.1.

3-Methyl-benzophenone (3b, Table 2, entry 2). Light yellow oil [22]. ^{1}H NMR (400 Mz, $CDCl_3$):δ 7.79-7.77 (m, 2H), 7.62 (s, 1H), 7.57-7.54 (m, 2H), 7.47-7.44 (m, 2H), 7.37-7.34 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 Mz, $CDCl_3$): δ196.8, 138.0,137.6, 137.5, 133.4, 132.2, 130.3, 130.0, 128.4, 128.1, 127.2, 21.2.

4-Methoxybenzophenone (3c, Table 2, entry 3 and entry 14). White solid, mp 59-60 ^{o}C (lit.[23] 61-62 ^{o}C). ^{1}H NMR (400 Mz, $CDCl_3$):δ 7.83-7.80 (m, 2H), 7.76-7.73 (m, 2H), 7.54-7.45 (m, 3H), 6.96-6.93 (m, 2H), 3.86 (s, 3 H). ^{13}C NMR (100 Mz, $CDCl_3$): δ195.4,163.0, 138.1, 132.4, 131.7, 130.0, 129.6, 128.0,113.4, 55.34.

2-bromobenzophenone (3d, Table 2, entry 4). light yellow oil [24]. ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.80-7.78 (m, 2H), 7.62-7.56 (m, 2H), 7.45. ^{13}C NMR (100 Mz, $CDCl_3$): δ 195.7, 140.5, 136.0, 133.7, 133.1, 131.1,130.1, 128.8, 128.5, 127.1, 119.4.

2-Chlorobenzophenone (3e, Table 2, entry 5). White solid, mp 42-43 ºC (lit.[10b] 43-45 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.79-7.77 (m, 2 H), 7.55-7.53 (m, 1 H), 7.44-7.38 (m, 4 H), 7.31-7.23 (m, 2 H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 195.4, 138.4, 136.3, 133.6, 131.1, 131.0,130.0, 129.0, 128.5, 126.6.

3-Chlorobenzophenone (3f, Table 2, entry 6). White solid, mp 81-83 ºC (lit.[25]. 84 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.79-7.77 (m, 3H), 7.66-7.64 (m, 1H), 7.59-7.50 (m, 2H), 7.48-7.46 (m, 2H), 7.43-7.40 (m, 1H). ^{13}C NMR (100 Mz, $CDCl_3$): δ195.0, 139.1, 136.8, 134.4, 132.7, 132.2, 130.1, 129.9, 129.7, 129.5, 128.5, 128.3, 128.0.

4-Chlorobenzophenone (3g, Table 2, entry 7). White solid, mp 73-74 ºC (lit.[26] 73-74 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.77-7.73 (m, 4H),7.58-7.56 (m, 1H), 7.51-7.45 (m, 4H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 195.3, 138.7, 137.0, 135.7, 132.5, 131.1, 129.8, 128.5, 128.2.

4-Fluoro-benzophenone (3h, Table 2, entry 8). White solid, mp 48-49 ºC (lit.[27] 47-49 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.85-7.75 (m, 4H), 7.58-7.45 (m, 3H), 7.16-7.12 (m, 2H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 195.1, 166.5, 164.0, 137.3, 133.7, 133.6, 132.6, 132.5, 132.3, 130.0, 128.5, 128.2, 115.9, 115.2.

4-Acetobenzophenone (3i, Table 2, entry 9). White solid, mp 83-84 ºC (lit.[28] 83-84 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.87-7.85 (m, 2H), 7.82-7.79 (m, 2H), 7.62-7.50 (m, 3H), 2.67 (s, 3H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 197.5, 195.9, 141.1, 139.4, 136.7, 133.8, 130.1, 130.0, 128.5, 128.3, 26.8.

4-Formyl-benzophenone (3j, Table 2, entry 10). White solid, mp 57-59 ºC (lit.[29] 58-60 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 10.1(s, 1H), 7.95-7.92 (m, 2H), 7.91-7.89 (m, 2H), 7.81-7.79 (m, 2H), 7.62-7.58 (m, 1H), 7.52-7.44 (m, 2H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 195.6, 191.6, 142.4, 138.3, 133.0, 130.1, 129.7, 129.2, 128.4.

1-Benzoylnaphthalene (3k, Table 2, entry 11). White solid, mp 74-75 ºC (lit.[30] 74-76 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 8.10-8.08 (m, 1H), 7.94 (d, *J* 8.4 Hz, 1H), 7.93-7.82 (m, 3H), 7.53-7.38 (m, 7H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 197.9, 138.2, 136.2, 133.6, 133.2, 131.2, 130.8, 130.3, 128.7, 128.4, 127.7, 127.2, 126.4, 125.6, 124.3.

2-Benzoylthiophene (3l, Table 2, entry 12). White solid, mp 54-55 ºC (lit.[31] 56-57 ºC). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.85-7.87 (m, 2H), 7.72-7.71 (m, 1H), 7.64-7.63 (m, 1H), 7.61-7.58 (m, 1H), 7.50-7.48 (m, 2H), 7.16-7.14 (m, 1H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 188.1, 143.5, 138.0, 134.8, 134.2, 132.2, 130.0, 129.0, 128.3, 127.9.

4-Methyl-benzophenone (3m, Table 2, entry 13). light yellow oil[32]. ^{1}H NMR (400 Mz, $CDCl_3$): δ 8.10-8.08 (d, *J* 8.0 Hz, 2H), 7.79-7.71 (d, *J* 7.6 Hz, 2H), 7.59-7.55 (m, 1H), 7.20 (m, 5 H), 2.43 (s, 3 H); ^{13}C NMR (100 Mz, $CDCl_3$): δ196.5, 165.3, 151.0, 144.4, 143.3, 132.2, 130.3, 130.2, 130.0, 129.5, 129.3, 129.0, 128.2, 126.8, 125.8, 121.8, 21.7.

General procedure for the acylodeboronation reaction of arylboronic acids with acetic anhydride. A 5 mL flask charged with acetic anhydride (1.0 mmol), arylboronic acid (0.5 mmol), $KHCO_3$ (1.0 mmol), complex **1** (0.5 mol%, 3.1 mg), PPh_3 (0.01 mmol, 1.3 mg) and toluene (2.0 mL) was evacuated and backfilled with N_2 for three times before the reaction was put into a preheated 110 ºC oil bath. After the reaction was finished in 3h, the reaction mixture

was cooled to room temperature, filtered through a short silica column and washed with ethyl acetate. Then the combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography (eluent: ethylacetate/petroleum ether). All the products were known compounds and characterized by comparing mp, ^{1}H NMR and ^{13}C NMR spectra with literature.

Acetophenone (5a, Table 4, entry 1). Light yellow oil[33] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.97-7.94 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.45 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 198.5, 137.6, 133.5, 129.0, 128.7, 26.9.

3-Methylacetophenone (5b, Table 4, entry 2). Light yellow oil[14] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.76-7.73 (m, 2H), 7.35-7.33 (m, 2H), 2.60 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 198.4, 138.3, 137.1, 133.8, 128.7, 128.4, 125.5, 26.6, 21.3.

4-Methoxyacetophenone (5c, Table 4, entry 3). Light yellow oil[33] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.91 (d, *J* 8.80 Hz, 2H), 6.93 (d, *J* 8.80 Hz, 2H), 3.84 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 196.7, 163.5, 130.5, 130.3, 113.6, 55.4, 26.3.

4-Methylacetophenone (5d, Table 4, entry 4). Light yellow oil[33] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.84 (d, *J* 8.04 Hz, 2H), 7.23 (d, *J* 8.04 Hz, 2H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 197.8, 143.8, 134.7, 129.2, 128.4, 26.5, 21.6.

1-Acetonaphthone (5e, Table 4, entry 5). Light yellow oil[33] ^{1}H NMR (400 Mz, $CDCl_3$): δ 8.74 (d, *J* 8.60 Hz, 1H), 7.85 (m, 3H), 7.57 (m, 1H), 7.45 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 201.8, 135.4, 134.0, 133.0, 130.2, 128.7, 128.4, 128.0, 126.4, 126.0, 124.3, 30.0.

3-Chloroacetophenon (5f, Table 4, entry 6). light yellow oil [34] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.93-7.92 (m, 1H), 7.84-7.82 (m, 1H), 7.55-7.53 (m, 1H), 7.43-7.39 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 196.7, 138.6, 134.9, 133.0, 129.9, 128.4, 126.4, 26.6.

4-Chloroacetophenone (5g, Table 4, entry 7). light yellow oil[34] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.88 (d, *J* 8.8 Hz, 2H), 7.42 (d, *J* 8.8 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 196.8, 139.5, 135.4, 129.7, 129.4, 128.9, 122.9, 26.5.

2-Chloroacetophenone (5h, Table 4, entry 8). Llight yellow oil[34] ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.56-7.54 (m, 1H), 7.41-7.31 (m, 3 H), 2.65 (s, 3H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 200.4, 139.1, 132.0, 131.2, 130.6, 129.4, 126.9, 30.7.

1-phenylpropan-1-one (5i, Table 4, entry 9). Light yellow oil[33] ^{1}H NMR (400 Mz, $CDCl_3$): δ 8.00-7.96 (m, 1H), 7.56-7.44 (m, 2H), 7.09-7.07 (m, 2H), 3.0 (m, 2H), 1.22-1.24 (m, 3H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 198.5, 137.6, 133.5, 129.0, 128.7, 26.9.

Acknowledgements

We are grateful to the National Science Foundation of China (Project 21102132, 21172200, 20772114) and the Innovation Fund for Outstanding Scholar of Henan Province (Project 0621001100) for the financial support given to this research.

References

1. (a) Nabuurs, S. B.; Wagener, M.; Vlieg, J. *J. Med. Chem.* 2007, 50, 6507.
http://dx.doi.org/10.1021/jm070593p
PMid:18031000
(b) Tang, G.; Nikolovska-Coleska, Z.; Qiu, S.; Yang, C.; Guo, J.; Wang, S. *J. Med. Chem.* 2008, 51, 717.
http://dx.doi.org/10.1021/jm701358v
PMid:18237106
2. (a) Li, J.; Jiang, Y.; Tu, P.-F. *J. Nat. Prod.* 2005, 68, 1802.
http://dx.doi.org/10.1021/np050347l
PMid:16378382
(b) Deng, Y.; Chin, Y. W.; Chai, H.; Keller, W. J.; Kinghorn, A. D. *J. Nat. Prod*. 2007, 70, 2049.
http://dx.doi.org/10.1021/np070501z
PMid:18076142
(c) Baggett, S.; Mazzola, E. P.; Kennelly, E. J. *Stud. Nat. Prod. Chem.* 2005, 32, 721.
http://dx.doi.org/10.1016/S1572-5995(05)80067-5
3. (a) Dobashi, Y.; Ohkatsu, Y.; *Polym. Degrad. Stab.* **2008**, *93*, 436.
http://dx.doi.org/10.1016/j.polymdegradstab.2007.11.011
(b) Calafat, A. M.; Wong, L. Y.; Ye, X.; Reidy, J. A.; Needham, L. L. *Environ. Health Perspect*. **2008**, *116*, 893.
http://dx.doi.org/10.1289/ehp.11269
PMid:18629311 PMCid:245315
(c) Nohynek, G. J.; Schaefer, H. *Regul. Toxicol. Pharmacol*. **2001**, *33*, 285.
http://dx.doi.org/10.1006/rtph.2001.1476
PMid:11407932
4. (a) Franck, H. G.; Stadelhofer, J. W. *Industrial Aromatic Chemistry*; Springer: Berlin, 1988.
http://dx.doi.org/10.1007/978-3-642-73432-8
(b) Roberts, S. M.; Poignant, G. *Catalysts for Fine Chemical Synthesis*, Vol.1: Hydrolysis, Oxidation and Reduction; Wiley-VCH: Weinheim, 2002.
(c) Surburg, H.; Panten, J. *Common Fragrance and Flavor Materials*, 5th Ed.; Wiley-VCH: Weinheim, Germany, 2006.
http://dx.doi.org/10.1002/3527608214
(d) Romines, K. R.; Freeman, G. A.; Schaller, L.T.; Cowan, J. R.; Gonzales, S. S.; Tidwell J. H.; Andrews, C. W.; Stammers, D. K.; Hazen, R. J.; Ferris, R. G.; Short, S. A.; Chan, J. H.; Boone, L. R. *J. Med. Chem.* **2006**, *49*, 727.
http://dx.doi.org/10.1021/jm050670l
PMid:16420058
(e) Masson, P. J.; Coup, D.; Millet, J.; Brown, N. L. *J. Biol. Chem*. **1994**, *270*, 2662.

(f) De Kimpe, N.; Keppens, M.; Fonck, G. *Chem. Commun*. **1996**, 635.
http://dx.doi.org/10.1039/cc9960000635

5. (a) Negishi, E.; Yosida, T. *J. Org. Chem.* 1975, 40, 1676.
(b) Cho, C. S.; Uemara, S. *J. Organomet. Chem.* **1993**, *443*, 253.
(c) Haddach, M.; McCarthy, J. R. *Tetrahedron Lett.* **1999**, *40*, 3109.
(d) Bumagin, N. A. *Tetrahedron. Lett.* **1999**, *40*, 3057.
http://dx.doi.org/10.1016/S0040-4039(99)00364-0
(e) Chen, H. *Org. Lett.* **2000**, *2*, 1649.
http://dx.doi.org/10.1021/ol000013h
PMid:10880192
(f) Gooben, L. J.; Ghosh, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 3458.
http://dx.doi.org/10.1002/1521-3773(20010917)40:18<3458::AID-ANIE3458>3.0.CO;2-0
(g) Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 371.
http://dx.doi.org/10.1246/bcsj.74.371
(h) Wang, J.; Zhang, Y.; Fu, Y. *Bull. Chem. Soc. Jpn* **2002**, *75*, 1381.
http://dx.doi.org/10.1246/bcsj.75.1381
(i) Urawa, Y.; Ogura, K. *Tetrahedron Lett.* **2003**, *44*, 271.
http://dx.doi.org/10.1016/S0040-4039(02)02501-7
(j) Eddarir, S.; Cotelle, N.; Rolando C. *Tetrahedron. Lett.* **2003**, *44*, 5359.
http://dx.doi.org/10.1016/S0040-4039(03)01140-7

6. (a) Tatamidani, H.; Chatani, N. *J. Org. Chem.* **2004**, *69*, 5615.
http://dx.doi.org/10.1021/jo0492719
PMid:15307730
(b) Tatamidani, H.; Kakiuchi, F.; Chatani, N. *Org. Lett.* **2004**, *6*, 3597.
http://dx.doi.org/10.1021/ol048513o
PMid:15387557
(c) Liebeskind L. S. *J. Org. Chem.* **2004**, *69*, 3554.
http://dx.doi.org/10.1021/jo049964p
PMid:15132570
(d) Xin, B.; Zhang, Y.; Cheng, K. *J. Org. Chem.* **2006**, *71*, 5725.
http://dx.doi.org/10.1021/jo060749d
PMid:16839154
(e) Nishihara, A.; Inoue, Y.; Fujisawa, M.; Takagi, K. *Synlett* **2005**, 2309.
http://dx.doi.org/10.1055/s-2005-872661
(f) Gooben, L. J.; Koley, D.; Thiel, W. *J. Am. Chem. Soc.* **2005**, *127*, 11102.
http://dx.doi.org/10.1021/ja052435y
PMid:16076218
(g) Bandgar, B. P.; Patil, A. V. *Tetrahedron Lett*. **2005**, *46*, 7627.
http://dx.doi.org/10.1016/j.tetlet.2005.08.111

7. (a) Polackova, V.; Toma, S.; Augustinova I. *Tetrahedron* **2006**, *62*, 11675. http://dx.doi.org/10.1016/j.tet.2006.09.055
(b) Liu, G.; Cai, M. *Catal. Commun.* **2007**, *8*, 251. http://dx.doi.org/10.1016/j.catcom.2006.06.015
(c) Xin, B.; Cheng, K. *Synthesis* **2007**, 1970.
(d) Kekeli, E. K.; Xu, H.; Wolf, C. *Tetrahedron Lett.* **2008**, *49*, 5773. http://dx.doi.org/10.1016/j.tetlet.2008.07.115
(e) Maddali, L. N. R.; Varadhachari, V.; Priyabrata, D. *Tetrahedron Lett.* **2010**, *51*, 4975. http://dx.doi.org/10.1016/j.tetlet.2010.07.074
(f) Zhang, L.; Wu, J. L.; Shi, L. J.; Xia, C. G.; Li, F. W. *Tetrahedron Lett.* **2011**, *52*, 3897. http://dx.doi.org/10.1016/j.tetlet.2011.05.079
8. (a) Olah, G. A.; *Friedel-Crafts Chemistry*; Wiley: New York, 1973.
(b) Song, C. E.; Shim, W. H.; Roh, E. J.; Choi, J. H. *Chem. Commun.* **2000**, 1695. http://dx.doi.org/10.1039/b005335j
(c) Furstner, A.; Voigtlander, D.; Schrader, W.; Giebel, D.; Reetz, M. T. *Org. Lett.* **2001**, *3*, 417. http://dx.doi.org/10.1021/ol0069251 PMid:11428028
(d) Ross, J.; Xiao J. *Green Chem.* **2002**, *4*, 129. http://dx.doi.org/10.1039/b109847k
(e) Gmouh, S.; Yang, H.; Vaultier, M. *Org. Lett.* **2003**, *5*, 2219. http://dx.doi.org/10.1021/ol034529n PMid:12816413
(f) Fillion, E.; Fishlock, D.; Wilsily, A.; Goll, J.M. *J. Org. Chem.* **2005**, *70*, 1316. http://dx.doi.org/10.1021/jo0483724 PMid:15704966
9. (a) Cai, M.; Zheng, G.; Zha, L.; Peng, J. *Eur. J. Org. Chem.* **2009**, *10*, 1585. http://dx.doi.org/10.1002/ejoc.200801253
(b) Khedkar, M. V.; Tambade, P.J.; Qureshi, Z. S.; Bhanage, B. M. *Eur. J. Org. Chem*. **2010**, *36*, 6981. http://dx.doi.org/10.1002/ejoc.201001134
(c) O'Keefe, B. M.; Simmons, N.; Martin, S. F. *Org. Lett.* **2008**, *10*, 5301.
(d) Ahmed, M. S. M.; Mori, A. *Org. Lett.* **2003**, *5*, 3057. http://dx.doi.org/10.1021/ol035007a PMid:12916980
(e) Liang, B.; Huang, M.; You, Z.; Xiong, Z.; Lu, K.; Fathi, R.; Chen, J.; Yang, Z. *J. Org. Chem.* **2005**, *70*, 6097. http://dx.doi.org/10.1021/jo050498t PMid:16018709

(f) Peng, C.; Cheng, J.; Wang, J. *J. Am. Chem. Soc.* **2007**, *129*, 8708.
http://dx.doi.org/10.1021/ja073010+
PMid:17589999
(g) Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Shim, E.; Lee, M. *J. Org. Chem.* **2004**, *69*, 4852.
http://dx.doi.org/10.1021/jo0495790
PMid:15230616
10. (a) Bensari, A.; Zaveri, N. T. *Synthesis* **2003**, 267.
(b) Chan, C. W.; Zhou, Z.; Chan, A. S. C.; Yu, W. Y. *Org. Lett.* **2010**, *12*, 3926.
http://dx.doi.org/10.1021/ol101618u
PMid:20704334
(c) Jia, X.; Zhang, S.; Wang, W.; Luo, F.; Cheng, J.; *Org. Lett.* **2009**, *11*, 3120.
http://dx.doi.org/10.1021/ol900934g
PMid:19552400
(d) Kochi, T.; Urano, S.; Seki, H.; Mizushima, E.; Sato, M.; Kakiuchi, F. *J. Am. Chem. Soc.* 2009, *131*, 2792.
http://dx.doi.org/10.1021/ja8097492
PMid:19209853
(e) Xiao, F.; Shuai, Q.; Zhao, F.; Basle, O.; Deng, G.; Li, C. J. *Org. Lett.* **2011**, *13*,1614.
http://dx.doi.org/10.1021/ol200017a
PMid:21355624
(f) Zhang, L.; Ang, G. Y.; Chiba, S. *Org. Lett.* **2011**, *13*, 1622.
http://dx.doi.org/10.1021/ol200425c
PMid:21381689
g) Yang, Y.; Chen, L.; Zhang, Z.; Zhang, Y. *Org. Lett.* **2011**, *13*, 1342. (
http://dx.doi.org/10.1021/ol200025k
PMid:21332150
h) Wu, X. F.; Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 7316.
http://dx.doi.org/10.1002/anie.201003895
PMid:20740517
11. (a) Wu, S.; Ma, H.; Lei, Z. *Tetrahedron* **2010**, *66*, 8641.
http://dx.doi.org/10.1016/j.tet.2010.09.035
(b) Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett. 2006*, *8*, 693.
http://dx.doi.org/10.1021/ol052830t
PMid:16468744
(c) Guan, B.; Xing, D.; Cai, G.; Wan, X.; Yu, N.; Fang, Z.; Yang, L.; Shi, Z. *J. Am. Chem. Soc.* 2005, *127*, 18004.
http://dx.doi.org/10.1021/ja055398j
PMid:16366542

12. (a) Wong, Y. C.; Parthasarathy, K.; Cheng, C. H. *Org. Lett.* **2010**, *12*, 1736.
http://dx.doi.org/10.1021/ol1003252
PMid:20334426
(b) Zhao, B. W.; Lu, X. Y. *Tetrahedron Lett.* **2006**, *47*, 6765.
http://dx.doi.org/10.1016/j.tetlet.2006.07.074
(c) Yu, A.; Li, J.; Cui, M.; Wu, Y. *Synlett* **2007**, 3063.
(d) Lindh, J.; Sjoberg, P. J. R.; Larhed, M. *Angew. Chem. In. Ed.* **2010**, *49*, 7733.
(e) Takemiya, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 4800.
13. (a) Álvarez-Bercedo, P.; Flores-Gaspar, A.; Correa, A.; Martin, R. *J. Am. Chem. Soc***. 2010**, *132*, 466.
http://dx.doi.org/10.1021/ja909811t
PMid:20038097
(b) Ruan J.; Saidi O.; Iggo J.A.; Xiao J. *J. Am. Chem. Soc*. **2008**, *130*,10510.
http://dx.doi.org/10.1021/ja804351z
PMid:18636731
14. (a) Liu, S.; Berry, N.; Thomson, N.; Pettman, A.; Hyder, Z.; Mo, J.; Xiao, J. *J. Org. Chem.* 2006, 71, 7467.
http://dx.doi.org/10.1021/jo0609632
PMid:16958544
(b) Mo, J.; Xiao, J.; *Angew. Chem. Int. Ed.* 2006, 45, 4152.
http://dx.doi.org/10.1002/anie.200600799
PMid:16718713
(c) Mo, J.; Xu, L.; Xiao, J. *J. Am. Chem. Soc.* **2005**, 127, 751.
http://dx.doi.org/10.1021/ja0450861
PMid:15643901
(d) Ruan, J.; Li, X.; Saidi, O.; Xiao, J. *J. Am. Chem. Soc***. 2008**, *130*, 2424.
http://dx.doi.org/10.1021/ja0782955
PMid:18232688
(e) Hansen, A. L.; Skydstrup, T. J. Org. Chem. 2005, 70, 5997.
http://dx.doi.org/10.1021/jo050669u
PMid:16018696
(f) Tivola, P. B.; Deagostino, A.; Prandi, C.; Venturello, P. *Org. Lett.* **2002**, *4*,1275.
http://dx.doi.org/10.1021/ol0255817
(g) Tsubouchi, A.; Onishi, K.; Takeda, T. *J. Am. Chem. Soc*. **2006**, *128*,14268.
http://dx.doi.org/10.1021/ja0658822
PMid:17076495
15. Al-Masum, M.; Ng, E.; Wai, M. C. *Tetrahedron Lett.* **2011**, *52*, 1008.
http://dx.doi.org/10.1016/j.tetlet.2010.12.085

16. Homden, D. M.; Redshaw, C. *Chem. Rev*. **2008**, *108*, 5086.
http://dx.doi.org/10.1021/cr8002196
PMid:18956902
17. (a) Itagaki, M.; Suzukamo, G.; Nomura, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 79.
http://dx.doi.org/10.1246/bcsj.71.79
(b) Monnereau, L.; Semeril, D.; Matt, D.; Toupet, L.; Motac, A. J. *Adv. Synth. Catal.* **2009**, *351*, 1383.
http://dx.doi.org/10.1002/adsc.200800759
18. (a) Ohto, K.; Ishibashi, H.; Kawakita, H.; Inoue, K.; Oshima T. J. *Incl. Phenom. Macrocycl. Chem.* **2009**, *65*, 111.
http://dx.doi.org/10.1007/s10847-009-9639-1
(b) Chang, S. K.; Cho, I. *J. Chem. Soc., Perkin Trans.* **1986**, 211.
(c) McKervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B.; Harris, S. *J. Chem. Soc., Chem. Commun.* **1985**, 388.
(d) Mu, B.; Li, J. Y.; Han, Z. X.; Wu, Y. J. *J. Organomet. Chem.* **2012**, *700*, 117.
http://dx.doi.org/10.1016/j.jorganchem.2011.11.024
19. Zhou, Z. X.; Xing, Y. J.; Lu, K.; Wu, Y. J. *Chin. Chem. Lett*. **1998**, *9*, 1067.
20. (a) Kakino, R.; Narahashi, H.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn* **2002**, *75*, 1333.
http://dx.doi.org/10.1246/bcsj.75.1333
(b) Goossen, L. J.; Ghosh, K. Eur. *J. Org. Chem.* **2002**, *19*, 3254.
http://dx.doi.org/10.1002/1099-0690(200210)2002:19<3254::AID-EJOC3254>3.0.CO;2-6
21. Blicke, F. F.; Schulmann, E. L. *J. Am. Chem. Soc.* **1954**, *76*, 1226.
http://dx.doi.org/10.1021/ja01634a006
22. Brown, H. C.; Young, H. L. *J. Org. Chem.* **1957**, *22*, 719.
http://dx.doi.org/10.1021/jo01358a001
23. Kulp, S. S.; McGee, M. J. *J. Org. Chem*.**1983**, *48*, 4097.
http://dx.doi.org/10.1021/jo00170a044
24. Lerebours, R.; Camacho-Soto, A.; Wolf, C. *J. Org. Chem.* **2005**, *70*, 8601.
http://dx.doi.org/10.1021/jo051257o
PMid:16209619
25. Clark, M. T.; Hendley, E. C.; Neville, O. K. *J. Am. Chem. Soc.* **1955**, *77*, 3280.
http://dx.doi.org/10.1021/ja01617a038
26. Greene, F. D.; Gilman, R. V.; James, C. C.; Richard, D. G. *J. Org. Chem.* **1960**, *25*, 1790.
http://dx.doi.org/10.1021/jo01080a031
27. Morley, J. O. *Synthesis* **1977**, 54.
http://dx.doi.org/10.1055/s-1977-24276
28. Zelinski, R. P.; Turnquest, B. W.; Martin, E. C. *J. Am. Chem. Soc*. **1951**, *73*, 5521.
http://dx.doi.org/10.1021/ja01156a001

29. Suhana, H.; Srinivasan, P.C. *Synth. Commun.* **2003**, *33*, 3097.
http://dx.doi.org/10.1081/SCC-120023419
30. Henry, R. H.; Nunn, L. G. J. *J. Org. Chem.***1947**, *12*, 540.
http://dx.doi.org/10.1021/jo01168a008
31. Rao, M. L. N.; Venkattesh, V.; Banerjee, D. *Tetrahedron* **2007**, *63*, 12917.
http://dx.doi.org/10.1016/j.tet.2007.10.047
32. Wu, S.; Ma, H.; Lei, Z. *Tetrahedron* **2010**, *66*, 8641.
http://dx.doi.org/10.1016/j.tet.2010.09.035
33. Ruan, J.; Iggo, J. A.; Berry, N. G.; Xiao, J. *J. Am. Chem. Soc*. **2010**, *132*, 16689.
http://dx.doi.org/10.1021/ja1081926
PMid:21028842
34. Horton, W. J.; Robertson, D. E. *J. Org. Chem.* **1960**, *25*, 1016.
http://dx.doi.org/10.1021/jo01076a039

