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Benzimidazole-based palladium–*N*-heterocyclic carbene: a useful catalyst for C–C cross-coupling reaction at ambient condition

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ABSTRACT

A convenient way for the synthesis of benzimidazole-based Pd–*N*-heterocyclic carbene complex and its structural characterization are described. The complex efficiently catalyzes Suzuki cross-coupling reaction in a wide variety of substrates including heteroaromatic system at ambient condition. The catalyst is also effective for multi Suzuki cross-coupling reaction. In addition, the catalyst is equally active toward C–C cross-coupling reaction between acid chloride and arylboronic acid, giving the desired ketones in high yield.

1. Introduction

Transition metal catalyzed C–C cross-coupling reaction is an indispensable tool for the construction of C–C bond, which plays an important role in fine chemical synthesis, medicinal chemistry, natural product synthesis as well as in the field of nanotechnology.[1] After isolation of stable *N*-heterocyclic carbene (NHC) by Arduengo et al. in 1991,[2a] it has led to numerous applications in the field of transition metal catalysis and has turned out to be a potentially active ligating agent.[2] Use of *N*-heterocyclic carbenes, as nucleophiles in organo catalytic reactions has also been well established.[3] Despite the existence of several families of stable carbenes, only imidazole based carbenes and their metal complexes have found numerous applications so far.[4] A common facet of all those NHC–metal complexes are having bulky substituents, specially adamentyl,[5,7b] aryl,[6] cyclohexyl,[7] *tert*-butyl,[8] etc. in 1,3 position of imidazole ring. Bulky group often plays several important roles viz., it assists to from strong σ-bond with metals, which results in high stability of the metal complex and it also facilitates the catalytic performances.[9,7b] It is very rare where normal alkyl chain is used instead of bulky group specifically for NHC–metal complexation. Few reports are available in the literature where the presence of Pd–NHC complex with *N*-alkyl substituted imidazole has been detected as reactive intermediate, which catalyzes organic transformations in ionic liquid media.[10] Benzimidazole-based NHC–metal complexes have recently been prepared instead of imidazole to accomplish high level of activity in Pd-catalyzed cross-coupling reactions.[11,12] Most importantly, the catalytic activity of benzimidazolidine NHCs can be tuned by simply introducing different functional group specifically at the 5 and 6 positions of the benzimidazole moeity.[11a,b] It is anticipated that an enormous modification will make it more competent moiety. In the last few years, a number of benzimidazole-based palladium–NHC catalysts have been developed but those findings have limited applications in organic synthesis.[11,12] Recent work by Huynh et al.[12a] and Metallions et al.[12b] on benzimidazole backbone palladium complexes require harsh conditions for catalyzing C–C cross-coupling reactions. It opens up the scope of stumbling onto more efficient and economic catalysts capable of catalyzing a reaction in mild condition. Herein, we report the synthesis of a new air stable benzimidazole-based Pd–NHC complex, an efficient, economic catalyst for a broad variety of C–C cross-coupling at ambient condition.

2. Result and discussion

Butyl propyl benzimidazolium bromide was synthesized in approximately quantitative yield and was recrystallized from ethyl acetate.[13] The solid salt was then refluxed with $Pd(OAc)_2$ in acetonitrile for 10 h. Depending on the ratio of the reagents (palladium salt and the ionic liquid), we have isolated two different products catalysts A and B (Figs. 1 and 2). The structures are well characterized by single crystal X-ray crystallography. Catalyst A is

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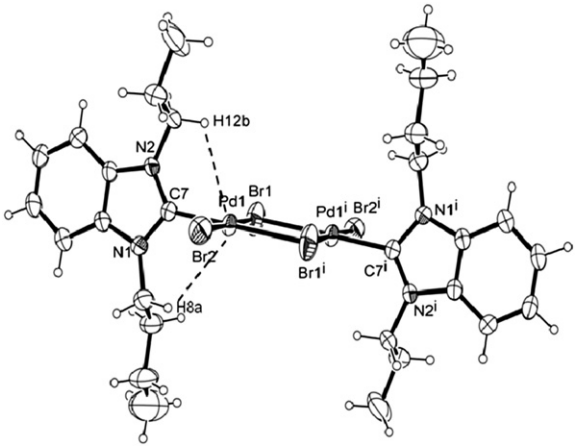


Fig. 1. Catalyst A.

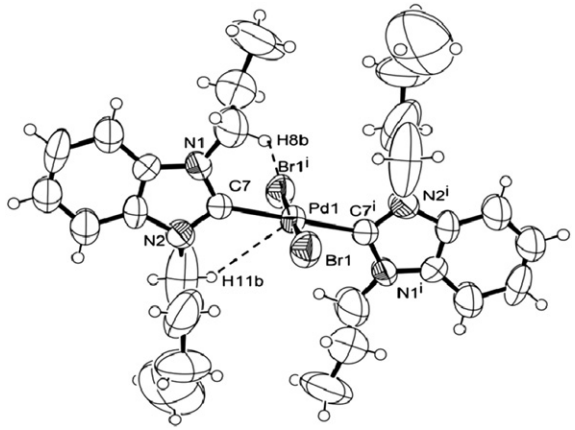


Fig. 2. Catalyst B.

crystallized in triclinic crystal system with *P*-1 space group while catalyst B has been crystallized in monoclinic crystal system with $P2_1/c$ space group. The catalysts display different structural features. Catalyst A is binuclear Pd(II) complex while catalyst B is a mononuclear Pd(II), whereas Pd(II) shows essentially square-planar geometry in both the structures. The structural feature of the catalyst A shows the bridged structure with two bromine as the bridging atoms that bridge two Pd(II) centers [Pd(II)···Pd(II) distance is 3.556 Å]. The carbon atom of NHC ligand has been organometallically coordinated to Pd(II) centers with Pd–C bond distance of 1.960 Å. The bond between Pd(II) and the bridging Br atom that is trans to NHC ligand is relatively elongated to some extent and this could be due to the trans effect of NHC ligand. It is also noteworthy, that the C–H protons (α-hydrogen atoms) of the alkyl groups are oriented toward the Pd(II) center resulting in relatively short C–H···Pd distances of 2.887 and 2.868 Å, respectively. The distances are typical to the preagostic interactions involving d^8 systems. The origin of preagostic interactions is not clear however, it may involve weak overlap of the filled d_{z^2} or d_{xz} orbital of the metal center with the C–H σ bond electrons. Catalyst B is mononuclear with essentially square-planar geometry around Pd(II) center. The palladium center is coordinated by two carbene and two bromo ligands. Two NHC ligands are trans to each other with C–Pd(II)–C angle of 180°.

With these novel Pd catalysts in hand, we envisioned to apply them in the construction of C–C bond via cross-coupling reaction. We commenced our studies using catalyst A for Suzuki coupling reaction where 4-iodotoluene and phenylboronic acid were selected as model coupling partners for optimizing the reaction. We started the reaction in toluene and the low conversion of desired product prompted us to look for the suitable solvent for this reaction. A screening of different solvents was then carried out to find the best condition. The detailed optimization results are summarized in Table 1. Solvents like dioxane, acetonitrile, ethanol, and water were found unsuitable for this reaction. A mixture of acetone/water proved to be the best solvent combination, which leads to the desired product in 97% yield within 45 min at ambient condition (Table 1, entry 4).

Table 1
Screening of solvent for catalyst A in Suzuki cross-coupling reaction[a]

Entry	Solvent (4 mL)	Time (h)	Yield[b] (%)
1	Toluene	1.00	40
2	Dioxane	3.00	78
3	Acetonitrile	3.00	66
4	*Acetone/water (1:1)*	*0.75*	*97*
5	Water[c]	1.50	40
6	Ethanol/water (1:1)	1.00	60

[a] Reaction conditions: 4-iodotoluene(1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), catalyst A (1 mol %, 0.0096 g), room temperature.
[b] Isolated yield after column chromatography.
[c] TBAB of 1 equiv was used.

After the optimization of Suzuki reaction with catalyst A, we sought to check the catalytic performance of catalyst B as well. We considered similar reaction between 4-iodoanisole and phenylboronic acid with same palladium content under optimized condition and corresponding results are given in Table 2 (entries

Table 2
Catalyst screening and loading experiment[a]

Entry	Catatyst	Catalyst loading (mol %)	Pd-content (mol %)	Time (h)	Yield[b] (%)
1	*A*	*1.0*	*1.99*	*1.0*	*98*
2	A	0.5	0.995	1.5	87
3	B	1.0	0.995	1.5	40
4	B	1.0	0.995	5.0	84
5	$Pd(OAc)_2$	2.0	2.0	1.0	69
6	$PdCl_2$	2.0	2.0	1.0	57
7	$Pd_2(dba)_3$	1.0	2.0	1.0	78

[a] Reaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol).
[b] Isolated yield after column chromatography.

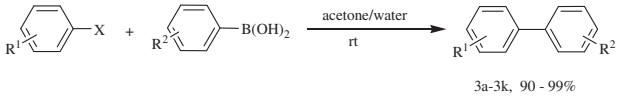
2 and 3). It is noteworthy that catalyst A is much more effective compared to catalyst B. This is plausibly because catalyst A under the reaction condition undergoes dissociation to form monomer units (Pd–NHC) and this facilitates the oxidative coupling, the most important step for such cross-coupling reactions. In order to find the minimum concentration of the catalyst required for efficient catalytic activity, we again chose a reaction between 4-iodoanisole and phenylboronic acid as the model case. Yield of the product decreases on decreasing the amount of catalyst in a fixed period of reaction. But the yield of the product increases by increasing the reaction time in case of both the catalysts (Table 2, entries 2 and 4). It has been found that the minimum concentration of catalyst A for effective coupling is 1 mol %. In order

to compare the catalytic efficiency of our newly developed Pd–NHC catalyst with commercially available Pd salts like $Pd(OAc)_2$, $PdCl_2$, and $Pd_2(dba)_3$, we performed the same reaction under similar condition without altering palladium content. The results are shown in Table 2 (entries 5 and 6) where the yields of the corresponding coupled products are obtained in the range of 57–78%.

With the optimized conditions in hand, we probed the scope of Suzuki reaction of different mono aryl halides with different arylboronic acids (Table 3). Notably, both electron deficient as well as electron rich aryl halides provided the desired coupled products in excellent yield. Iodo and bromo aryl halides underwent this coupling reaction very smoothly. Several active functional groups such as $-NH_2$, $-COCH_3$, $-CN$, $-Cl$, $-F$ remain dormant and allow selective Suzuki coupling (Table 3, entries 8, 9, 15, 11, and 6, respectively). On the other hand, sterically hindered aryl halides (Table 3, entries 4 and 6) also result in the desired coupled product in excellent yield. In addition, 3-tolylboronic acids, 4-formylphenylboronic acid were also successfully coupled to form the corresponding substituted biphenyl without any side reaction (Table 3, entries 14 and 15). We also attempted the cross-coupling reaction of activated aryl chloride but in this case we only have the marginal successes (Table 3, entries 16–18).

Suzuki coupling for heteroaromatic system often needs harsh condition compared to aromatic system. We explored the possibility of the application of the catalyst in heteroaromatic systems. And accordingly, we made an attempt to carry out the Suzuki reaction at our optimized condition but the yield of the desired product was not satisfactory (it lies between 40 and 50% even after continuing the reaction for 48 h). To overcome this shortcoming, we increased the reaction temperature to 40 °C and the results are summarized in Table 4. Bromo pyridine, pyrimidine, and quinoline all underwent smooth reaction. 3-Tolylboronic acid as well as electron deficient 4-fluorophenylboronic acid also resulted in the desired product in 82 and 96% yields (Table 4, compounds **4d** and **4e**), respectively.

Table 3
Suzuki cross-coupling reaction of mono aryl halides[a]



3a-3k, 90 - 99%

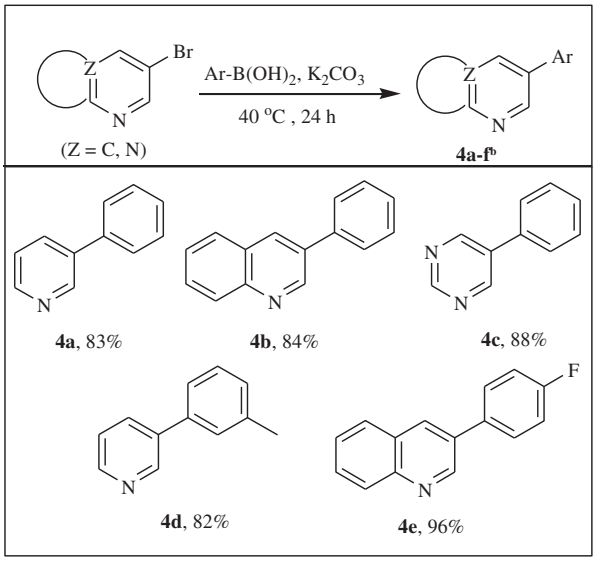
Entry	R^1	R^2	X	Time (min)	Yield[b] (%)	Product
1	H	H	I	45	98	3a
2	4-CH_3	H	I	45	97	3b
3	4-OCH_3	H	I	60	98	3c
4	2-CH_3	H	I	45	93	3d
5	3-CH_3	H	I	45	96	3e
6	2-F	H	I	60	97	3f
7	3-Cl	H	I	60	96	3g
8	4-NH_2	H	I	45	98	3h
9	4-$COCH_3$	H	Br	45	98	3i
10	3-CH_3	H	Br	60	90	3e
11	3-Cl	H	Br	60	91	3g
12	4-OCH_3	H	Br	60	98	3c
13	H	H	Br	60	99	3a
14	3-CH_3	3-CH_3	Br	60	90	3j
15	4-CN	4-CHO	Br	60	98	

Table 3 (*continued*)

Entry	R^1	R^2	X	Time (min)	Yield[b] (%)	Product
16	4-$COCH_3$	H	Cl	24 h	NR	
17[c]	4-$COCH_3$	H	Cl	24 h	NR	
18[d]	4-$COCH_3$	H	Cl	24 h	47	3i

[a] Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), catalyst A (1 mol %), room temperature.
[b] Isolated yield after column chromatography purification.
[c] Reaction was carried out at 70 °C.
[d] DMF/water (1:1) was used as solvent and the reaction was carried out at 90 °C.

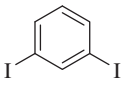
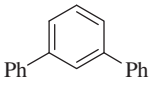
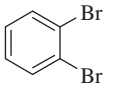
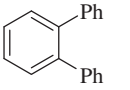
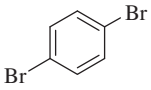
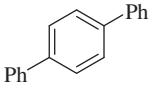
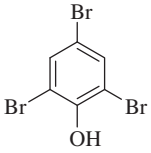
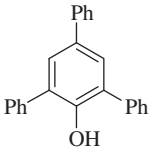
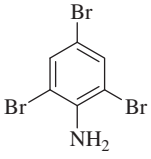
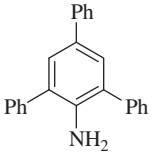
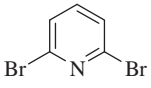
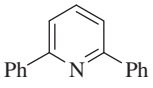
Table 4
Suzuki cross-coupling of heteroaryl halides[a,b]



[a] Reaction conditions: heteroaryl halide (1 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), catalyst A (1 mol %).
[b] Isolated yield after column chromatography purification.

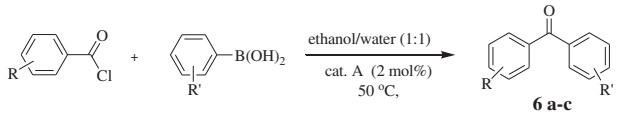
To expand the scope of the catalyst, we ventured to use it for polyarylation and the results are summarized in Table 5. Initially, we started with 1,3-diiodobenzene, which results in the corresponding *m*-terphenyl with 92% yield within 1.5 h at ambient condition. But in case of bromo compounds the reaction time is longer as iodide is a better leaving group compared to bromide. 1,2-Dibromobenezene results in the formation of *o*-terphenyl in 60%, which may be due to the steric hindrance on the other hand 1,4-dibromobenzene accomplished *p*-terphenyl in 90% yield. 2,4,6-Tribromo phenol and aniline required longer time and yielded the desired products in 50 and 60%, respectively (Table 5, entries 4 and 5). Surprisingly, 2,6-dibromopyridine also underwent the reaction smoothly resulting in 2,6-diphenylpyridine in 90% yield at 40 °C. Reactions of acid chloride with arylboronic acid for the synthesis of aryl ketones with the catalyst A were studied next.

Table 5
Multi Suzuki cross-coupling reaction in one step[a]

Entry	Haloarene	Time (h)	Product	Yield[b] (%)
1		1.5	 **5a**	92
2		5	 **5b**	60
3		5	 **5c**	90
4		24	 **5d**	50
5		24	 **5e**	60
6[c]		24	 **5f**	90

[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol for each halide), K_2CO_3 (2 mmol for each halide), catalyst A (1 mol %), room temperature.
[b] Isolated yield after column chromatography purification.
[c] Reaction was carried out at 40 °C.

After successful demonstration of the Suzuki coupling reaction, we further proceeded to find other suitable applications of the catalyst A and accordingly made an attempt to use our catalyst for aryl ketone synthesis from acid chloride. Very recently Zhang et al.[14] used ionically tagged benzimidazole–Pd(II) complex for similar reactions but reported prolong reaction time (12 h at 60 °C). In our system, treatment of acid chloride with boronic acid in mixed solvent (ethanol/water) at 50 °C in presence of the catalyst A resulted in the desired ketone in high yield within a couple of hours and corresponding results are displayed in Scheme 1. It has been found that the presence of an electron withdrawing group in phenylboronic acid (Scheme 1, compound **6b**) highly accelerated the reaction and resulted in 96% yield of the corresponding aryl ketone within 2 h.

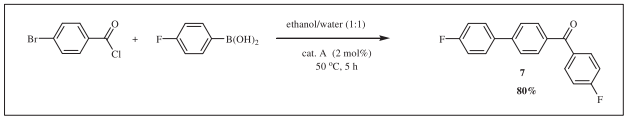


		Time	Yield[b]	Product
R = H	R' = H	5 h	80 %	**6a**
R = 4-F	R' = 4-F	2 h	96 %	**6b**
R = 2-Cl	R' = H	5 h	78 %	**6c**

[a] Reaction conditions: arylacid chloride (1.2 mmol), arylboronic acid (1 mmol), K_2CO_3 (2 mmol). [b] Isolated yield after column chromatography purification.

Scheme 1. Cross-coupling reaction of acid chlorides with arylboronic acids.[a]

In order to expand these promising initial results, we were tempted to perform two reactions in one pot. For that purpose we had designed an experiment attempting to consecutive couplings with different functional groups in one-pot reaction. Indeed, we were successful in consecutive one-pot coupling of 4-bromo benzoylchloride with 4-fluorophenylboronic acid leading to the formation of the double coupled product in 80% yield (Scheme 2).



Scheme 2. Two different cross-couplings in one pot.

3. Conclusion

In summary, we introduced benzimidazole-based Pd–NHC, a new air stable versatile catalyst, which efficiently catalyzed C–C cross-coupling reaction at ambient conditions in a wide variety of substrates. Our reaction conditions offer selective cross-coupling, which may often be a useful tool in synthetic chemistry. Studies aimed at further scope of the catalyst with regard to different kinds of related reactions are in active pursuit in our laboratories.

4. Experimental section

4.1. General methods

Unless stated otherwise, all reagents such as palladium acetate, arylboronic acid, aryl halides, potassium carbonate, benzimidazole, alkyl halides, and solvents were used as received from commercial suppliers. NMR spectra were recorded on 300 MHz spectrometer at 298 K and calibrations were done on the basis of solvent residual peak. Mass spectra were performed using ion trap mode. Elemental analysis were done in varioEL CHNS. Products were isolated using column chromatography on silica gel (60–120 mesh) and a mixture of petroleum ether (60–80 °C)/ethyl acetate was used as an eluent. Reaction progress was monitored by silica gel TLC.

4.2. Preparation of Pd–NHC (catalyst A and catalyst B)

4.2.1. Catalyst A. To a solution of *n*-butyl propyl benzimidazolium bromide (0.297 g, 1 mmol) in acetonitrile (20 mL) was added palladium acetate (0.224 g, 1 mmol) and the mixture was refluxed (85 °C) for 12 h. After cooling, the mixture was filtered through a Celite-bed and the resulting yellow filtrate was concentrated (3 mL) under reduced pressure. Diethyl ether (15 mL) was added slowly to the filtrate to get orange crystals of the catalyst A. The catalyst was then filtered off and dried under vacuum (0.395 g, 74%).

4.2.2. Catalyst B. In the case of preparation of the catalyst B, similar procedure was adopted except the stoichiometric quantities of *n*-butyl propyl benzimidazolium bromide and palladium acetate. In this case, the stoichiometric ratios (2:1) were used. The catalyst B was isolated as yellow crystals and the yield was 85%.

4.3. General procedure of Suzuki reaction

A mixture of aryl halide (1 mmol), arylboronic acid (1.2 mmol), catalyst A (1 mol %, 0.0096 g), K_2CO_3 (2 mmol), and (1:1) acetone/water mixed solvent (3 mL) were taken in 25 mL round bottom flask and the mixture was stirred at room temperature (40 °C for heteroaryl halides) until the completion of reaction (required time given in Tables 3–5). The reaction mixture was then diluted with water (20 mL) and extracted three times with dichloromethane (3×10 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After that it was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether (60–80 °C) and ethyl acetate were as the eluent.

4.4. General procedure for unsymmetrical ketone synthesis

Catalyst A (18 mg, 2 mol %), K_2CO_3 (276 mg, 2 mmol), and (1:1) ethanol/water mixed solvent (3 mL) were taken in a 25 mL round bottom flask and then benzoylchloride (1.2 mmol) and arylboronic acid (1 mmol) were introduced into it. The resulting mixture was immersed in a preheated oil bath at 50 °C for requisite reaction time as given in Scheme 1. After completion of reaction, water (20 mL) was added to it and the mixture was extracted with diethyl ether (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Finally the crude product was purified by column chromatography using silica gel.

4.5. Spectral analysis of compounds

4.5.1. Catalyst A. Isolated as orange solid. Found: C, 34.86; H, 4.11; N, 5.75. $C_{28}H_{40}Br_4N_4Pd_2$ requires C, 34.85; H, 4.18; N, 5.81%. R_f (25% EtOAc/PET) 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.43 (m, 4H), 7.29–7.33 (m, 4H), 5.30 (m, 8H), 2.17–2.30 (m, 8H), 1.59–1.69 (m, 4H), 1.12–1.21 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 134.5, 134.4, 123.4, 110.6, 50.5, 48.8, 31.3, 22.9, 20.4, 13.9, 11.7. The crystal data of catalyst A have been deposited at Cambridge Crystallographic Centre. The CCDC reference number is *871899*.

4.5.2. Catalyst B. Isolated as yellow solid. Found: C, 47.96; H, 5.69; N, 7.84. $C_{28}H_{40}Br_2N_4Pd$ requires C, 48.12; H, 5.77; N, 8.02%. R_f (25% EtOAc/PET) 0.67; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.33 (m, 4H), 7.16–7.20 (m, 4H), 4.69–4.77 (m, 8H), 2.15–2.26 (m, 8H), 1.46–1.55 (m, 4H), 0.99–1.11 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.1, 134.7, 134.6, 122.6, 110.4, 50.0, 48.3, 31.9, 23.2, 20.7, 14.0, 11.9. The crystal data of catalyst B have been deposited at Cambridge Crystallographic Centre. The CCDC reference number is *871898*.

*4.5.3. Biphenyl (**3a**).*[15] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.70 (m, 4H), 7.49–7.56 (m, 4H), 7.40–7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 128.8, 127.3, 127.2.

*4.5.4. 4-Methylbiphenyl (**3b**).*[16] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.58 (m, 9H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 138.3, 137.0, 129.5, 128.7, 127.2, 127.0, 126.8, 21.1.

*4.5.5. 4-Methoxybiphenyl (**3c**).*[17] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.59 (m, 4H), 7.42–7.47 (m, 2H), 7.27–7.35 (m, 1H), 7.00 (d, 2H, J=2.4 Hz), 3.87 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 140.8, 133.8, 128.7, 128.2, 126.7, 126.66, 114.2, 55.3.

*4.5.6. 2-Methylbiphenyl (**3d**).*[17] Isolated as colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.57 (m, 5H), 7.38–7.45 (m, 4H), 2.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 141.4, 135.5, 130.5, 129.9, 129.3, 128.2, 127.4, 126.9, 125.9, 20.6.

*4.5.7. 3-Methylbiphenyl (**3e**).*[18] Isolated as colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J=8.7 Hz, 2H), 7.52 (m, 4H), 7.43 (m, 2H), 7.26 (d, J=7.2 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 141.3, 138.4, 128.9, 128.80, 128.78, 128.2, 128.1, 127.3, 124.4, 21.6.

*4.5.8. 2-Fluorobiphenyl (**3f**).*[19] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.57 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 159.8 (J_{CF}=246 Hz, CF), 135.8 (C_6H_5), 130.8 (J_{CF}=3.6 Hz, CH), 129.2 (C_6H_5), 129.0 (J_{CF}=3 Hz, CH), 128.9 (C_6H_5), 128.7 (C_6H_5), 128.4 (C_6H_5), 127.4 (J_{CF}=36 Hz, C_6H_5F), 124.3 (J_{CF}=3.6 Hz, CH), 116.1 (J_{CF}=22.5 Hz, CH).

*4.5.9. 3-Chlorobiphenyl (**3g**).*[20] Isolated as colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.65 (m, 3H), 7.35–7.53 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 139.8, 134.7, 130.1, 129.0, 128.0, 127.4, 127.3, 127.2, 125.4.

*4.5.10. 4-Aminobiphenyl (**3h**).*[21] Isolated as pale yellow solid, ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.43–7.46 (m, 2H), 7.27–7.31 (m, 4H), 7.09–7.14 (m, 1H), 6.59–6.53 (m, 2H), 5.15 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.8, 141.2, 129.1, 128.00, 127.7, 126.1, 125.8, 114.8.

*4.5.11. 4-Acetylbiphenyl (**3i**).*[19] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J=8.4 Hz, 2H), 7.61–7.69 (m, 4H), 7.45 (m, 3H), 2.63 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 145.7, 139.8, 135.8, 128.92, 128.89, 128.20, 127.24, 127.19, 26.6.

*4.5.12. 3,3′-Dimethylbiphenyl (**3j**).*[22] Isolated as colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.48 (m, 6H), 7.23 (d, J=7.2, 2H), 2.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 138.3, 128.9, 128.0, 127.98, 124.3, 21.6.

*4.5.13. 4-Cyano-4′-formylbiphenyl (**3k**).*[23] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.99 (d, J=7.8 Hz, 2H), 7.72–7.79 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 144.9, 144.1, 136.1, 132.8, 130.5, 128.1, 127.9, 118.6, 112.1.

*4.5.14. 3-Phenylpyridine (**4a**).*[24] Isolated as yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, J=2.4 Hz, 1H), 8.58 (dd, J=4.8 Hz, 1.5 Hz), 7.86 (m, 1H), 7.55–7.58 (m, 3H), 7.32–7.49 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 148.3, 137.8, 136.7, 134.4, 129.1, 128.1, 127.2, 123.6.

*4.5.15. 3-Phenylquinoline (**4b**).*[25] Isolated as yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.25 (m, 1H), 8.14 (d, J=8.4 Hz, 1H),

7.82 (d, J=8.1 Hz, 1H), 7.66–7.71 (m, 3H), 7.49–7.56 (m, 3H), 7.38–7.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 147.3, 137.8, 136.0, 133.8, 133.2, 129.4, 129.2, 128.1, 128.0, 127.8, 127.4, 127.0.

*4.5.16. 5-Phenylpyrimidine (**4c**).*[26] Isolated as colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.93 (s, 2H), 7.44–7.58 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 154.1, 134.4, 134.1, 129.5, 129.1, 127.0.

*4.5.17. 3-(3-Methyl-phenyl)-pyridine (**4d**).*[24] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, J=1.5 Hz, 1H), 8.62 (dd, J=5.1, 1.5, 1H), 7.90–7.91 (m, 1H), 7.83–7.87 (m, 1H), 7.17–7.36 (m, 4H), 2.36 (s, 3H).

*4.5.18. 3-(4-Flurophenyl)-quinoline (**4e**).*[25] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (d, J=2.1, 1H), 8.33 (d, J=2.1, 1H), 8.21 (d, J=8.4, 1H), 7.71–7.80 (m, 1H), 7.60–7.71 (m, 4H), 7.23–7.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 161.4, 149.0 (J_{CF}=3.3 Hz), 146.5, 134.1, 133.7 (J_{CF}=7.4 Hz), 133.4, 133.0, 129.9, 129.5, 129.1 (J_{CF}=8 Hz), 128.7, 128.0 (J_{CF}=3.9 Hz), 127.2 (J_{CF}=26.70 Hz), 116.3 (J_{CF}=21.5 Hz).

*4.5.19. 1,3-Diphenylbenzene (**5a**).*[27] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (m, 1H), 7.65 (dd, J=8.4, 1.5, 4H), 7.55–7.61 (m, 2H), 7.54 (t, 1H), 7.46–7.49 (m, 3H), 7.44 (t, 1H), 7.35–7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 141.2, 129.2, 128.8, 127.4, 127.3, 126.2, 126.1.

*4.5.20. 1,2-Diphenylbenzene(**5b**).*[27] Isolated as pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.42 (m, 6H), 7.14–7.21 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 140.6, 130.6, 129.9, 127.8, 127.4, 126.42.

*4.5.21. 1,4-Diphenylbenzene (**5c**).*[27] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.70 (m, 8H), 7.49 (t, J=7.2 Hz, 4H), 7.27–7.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.

*4.5.22. 2,4,6-Triphenylphenol (**5d**).*[27] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.66 (m, 8H), 7.42–7.58 (m, 6H), 7.32–7.37 (m, 3H), 5.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 140.5, 137.6, 133.8, 129.4, 129.1, 128.9, 128.8, 128.6, 127.8, 126.9, 126.8.

*4.5.23. 2,4,6-Triphenylaniline (**5e**).*[28] Isolated as pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.7.60 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 140.3, 139.7, 131.1, 129.4, 128.9, 128.7, 128.4, 128.3, 127.4, 126.4, 126.39.

*4.5.24. 2,6-Diphenylpyridine (**5f**).*[29] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22–8.27 (m, 4H), 7.81 (m, 1H), 7.70 (d, 2H), 7.48–7.59 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 139.5, 137.5, 129.0, 128.7, 127.0, 118.6.

*4.5.25. Benzophenone (**6a**).*[30] Isolated as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.68 (m, 4H), 7.51–7.45 (m, 2H), 7.40–7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 136.5, 131.4, 129.0, 127.2.

*4.5.26. Bis(4-fluorophenyl)methanone (**6b**).* Isolated as white solid; observed melting point 107–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.84 (m, 4H), 7.14–7.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 167.1, 163.7, 133.7, 132.8, 132.6, 132.5, 115.7, 115.4; HRMS (EI^+): $[M]^+$, found 218.0547. $C_{13}H_8F_2O$ requires 218.0543.

*4.5.27. (2-Chlorophenyl)-phenyl-methanone (**6c**).* Isolated as colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83–7.85 (d, J=7.8 Hz, 2H), 7.60–7.65 (t, J=7.5 Hz, 1H), 7.46–7.51 (m, 4H), 7.38–7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 138.5, 136.4, 133.7, 131.3, 131.1, 130.2, 130.1, 129.1, 128.6, 126.7. HRMS (EI^+): $[M]^+$, found 216.0331. $C_{13}H_9ClO$ requires 216.0342.

*4.5.28. (4-Fluorobiphenyl)-(4-fluorophenyl)-methanone (**7**).* Isolated as white solid; observed melting point 143–145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.81 (m, 4H), 7.49–7.58 (m, 4H), 7.057.11 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 167.1, 164.6, 163.7, 161.4, 144.3, 136.1, 136.0, 133.8, 132.7, 132.6, 131.0, 130.6, 130.2, 129.0, 128.9, 126.9, 116.1, 115.8, 115.7, 115.4. HRMS (EI^+): $[M]^+$, found 294.0859. $C_{19}H_{12}F_2O$ requires 294.0856.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.10.055.

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