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N-Heterocyclic carbene–Pd(II) complex derived from proline for the Mizoroki–Heck reaction in water

Yi-Qiang Tang [a], Chun-Yan Chu [a], Lei Zhu [a], Bin Qian [b], Li-Xiong Shao [a,*]

[a] College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Wenzhou, Zhejiang Province 325035, People's Republic of China
[b] Oujiang College, Wenzhou University, Chashan University Town, Wenzhou, Zhejiang Province 325035, People's Republic of China

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ABSTRACT

N-Heterocyclic carbene–Pd(II) complex **1** derived from proline was found to be an efficient catalyst in the Mizoroki–Heck reaction of aryl bromides and iodides performed in water. The reactions can tolerate various functional groups in the substrates and all gave the corresponding coupling products in good to high yields.

1. Introduction

Palladium-catalyzed Mizoroki–Heck coupling reaction, sharing the 2010 Nobel Prize, is a powerful and versatile method for arylation and vinylation of olefins.[1] During the past decades, most efficient Mizoroki–Heck reactions reported were carried out in organic solvents with phosphine-based compounds as the ancillary ligand. In order to overcome the toxicity of organic solvents and the toxicity, air and/or moisture-sensitivity of phosphine-based ligands, many efforts have been made to find out alternative ligands and clean solvents.[2,3] Compared to toxic and volatile organic solvents, water, as a non-toxic, non-flammable and the most environmentally friendly solvent, had attracted much attention in organic synthesis.[3] On the other hand, in contrast to phosphine-based ligands, *N*-heterocyclic carbenes (NHCs), as excellent σ-donors and weaker π-acceptors, can produce stable NHC–metal complexes with strong NHC–metal bonds, which usually exhibits higher stability in the solid state and even in solution than phosphine-based ligands.[4] Although NHC–metal complexes have attracted much attention in the carbon–carbon and carbon–heteroatom bond formation reactions performed in routine organic solvents, their applications in pure water were rarely reported.[5] Recently, we have developed some NHC–metal complexes derived from proline and found them to be efficient catalysts in carbon–carbon bond formations performed in water.[6] For instance, NHC–Pd(II) complexes derived from *N*-benzyl proline were proved to be good catalysts in the room temperature Suzuki–Miyaura coupling reaction of aryl iodides and bromides carried out in pure water.[6c] These results prompted us to further investigate the applications of these complexes in other carbon–carbon bond formation reactions. In continuing research, we found that NHC–Pd(II) complex **1** (Fig. 1) derived from *N*-benzyl proline was also a favourable catalyst for the Mizoroki–Heck reaction of aryl iodides and bromides performed in pure water. Herein, we wish to report these results in detail.

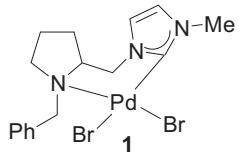

Fig. 1. NHC–Pd(II) complex **1** derived from proline.

2. Results and discussion

Initial examinations were carried out using bromobenzene **2a** (1.0 mmol) and acrylic acid **3a** (1.5 equiv) as the substrates, NHC–Pd(II) complex **1** (1.0 mol %) as the catalyst, H_2O (2.0 mL) as

* Corresponding author. Tel./fax: +86 577 86689300; e-mail addresses: Shaolix@wzu.edu.cn, shaolix@163.com (L.-X. Shao).

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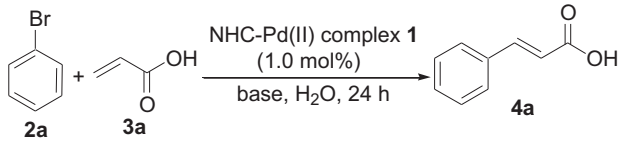
the solvent at 100 °C to find out the best base (Table 1, entries 1–9). As can be seen from Table 1, the best result was obtained with KO^{t}Bu as the base and the corresponding coupling product **4a** can be achieved in 91% yield (entry 3). The yield can be further increased to 96% at elevated temperature (120 °C) (entry 10).

Table 1
Optimization for the NHC–Pd(II) complex **1** catalyzed reaction of bromobenzene **2a** with acrylic acid **3a**



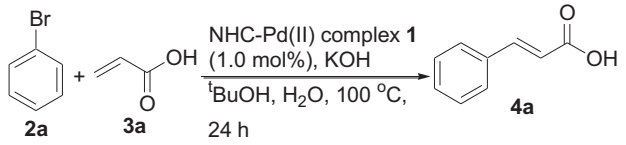
Entry[a]	Base	Yield[b] (%)
1	NaO^{t}Bu	47
2	KOH	42
3	KO^{t}Bu	91
4	NaOH	55
5	K_2CO_3	17
6	Na_2CO_3	10
7	$KHCO_3$	13
8	$KF·2H_2O$	<5
9	$K_3PO_4·3H_2O$	12
10[c]	KO^{t}Bu	96

[a] Otherwize specified, all reactions were carried out using **2a** (1.0 mmol), **3a** (1.5 mmol), base (3.0 equiv), **1** (1.0 mol %) in H_2O (2.0 mL) at 100 °C for 24 h.
[b] Isolated yields.
[c] The temperature is 120 °C.

It is conceivable that the base KO^{t}Bu will rapidly hydrolyze to KOH and ^{t}BuOH under the identical reaction conditions. Further studies showed that ^{t}BuOH was essential for the reactions with KOH as the base, which clearly illustrated the differences between the results using KOH and ^{t}BuOK as the base, respectively (Table 2).

So the optimal reaction conditions were then established as using NHC–Pd(II) complex **1** (1.0 mol %) as the catalyst, KO^{t}Bu (3.0 equiv) as the base, H_2O (2.0 mL) as the solvent at the temperature of 100 or 120 °C.

Table 2
NHC–Pd(II) complex **1** catalyzed reaction of bromobenzene **2a** with acrylic acid **3a** using KOH as the base in the presence of different amount of ^{t}BuOH

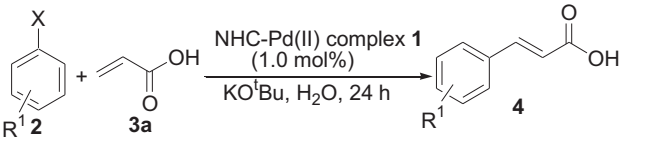


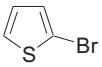
Entry[a]	^{t}BuOH (equiv)	Yield[b] (%)
1	0	42
2	1.0	88
3	2.0	96
4	5.0	98

[a] All reactions were carried out using **2a** (1.0 mmol), **3a** (1.5 mmol), KOH (3.0 equiv), **1** (1.0 mol %) in H_2O (2.0 mL) in the presence of the listed amount of ^{t}BuOH at 100 °C for 24 h.
[b] Isolated yields.

To survey the generality of this NHC–Pd(II) complex **1** catalyzed Mizoroki–Heck reaction performed in water, we next investigated the reactions of a variety of aryl bromides and iodides **2** with acrylic acid **3a** under the identical conditions (Table 3). As can be seen from Table 3, all reactions took place smoothly to give the coupling products **4** in good to excellent yields in most cases. Substituents on the aryl bromides have some effect on the reactions. For instance, it seems that aryl bromides with electron-donating groups, such as 4-MeO (**2b**), 4-Me (**2c**) and 3-MeO (**2d**) gave better yields (entries 1–3). On the contrary, aryl bromides with electron-poor groups, such as 4-Cl (**2e**) and 4-F (**2f**) gave inferior results (entries 4 and 5). Only moderate yield of product **4g** was obtained when strongly electron-withdrawing group-substituted 4-nitrophenyl bromide **2g** was used as the substrate (entry 6). Heteroaryl bromides, such as 2-bromothiophene **2k** and 3-bromothiophene **2l** were also proved to be suitable reaction partners to give the corresponding products **4h** and **4i** in reasonable yields, respectively (entries 10 and 11). In addition, aryl iodides showed better reactivity in these Mizoroki–Heck reactions to give products **4** in excellent yields, with no differences between the substituents on the aryl rings (entries 7–9).

Table 3
NHC–Pd(II) complex **1** catalyzed reactions of aryl bromides and iodides **2** with acrylic acid **3a**

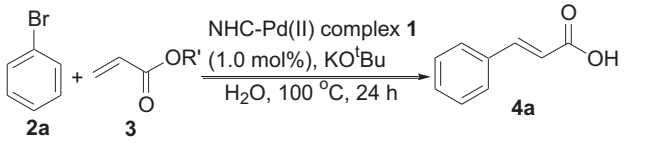


Entry[a]	**2** (R^1/X)	Yield[b] (%)
1	**2b** (4-MeO/Br)	**4b**, 83
2	**2c** (4-Me/Br)	**4c**, 99
3	**2d** (3-MeO/Br)	**4d**, 96
4	**2e** (4-Cl/Br)	**4e**, 77
5	**2f** (4-F/Br)	**4f**, 80
6	**2g** (4-NO_2/Br)	**4g**, 54
7	**2h** (H/I)	**4a**, 92
8	**2i** (4-MeO/I)	**4b**, 95
9	**2j** (4-F/I)	**4f**, 95
10	**2k** 	**4h**, 49
11	**2l** 	**4i**, 50

[a] All reactions were carried out using **2** (1.0 mmol), **3a** (1.5 mmol), KO^{t}Bu (3.0 equiv), **1** (1.0 mol %) in H_2O (2.0 mL) at 120 °C (for bromide) or 100 °C (for iodide) for 24 h.
[b] Isolated yields.

The reactions of bromobenzene **2a** with some acrylate esters, such as acrylate methyl ester **3b**, ethyl ester **3c** and *n*-butyl ester **3d** were also investigated under the similar conditions. The reactions can be performed at 100 °C to give product **4a**, the coupling-hydrolyzed product, in good to excellent yields in all cases (Table 4). Maybe the high solubility of product **4a** in H_2O accelerates the hydrolysis of the coupling products, the esters, resulting cinnamic acid **4a** as the sole product.

Table 4
NHC–Pd(II) complex **1** catalyzed reactions of bromobenzene **2** with acrylate esters **3**

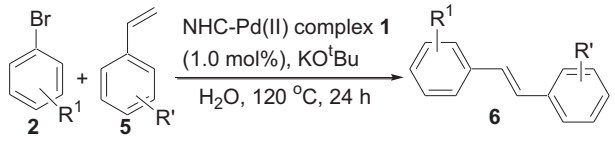


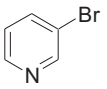
Entry[a]	**3** (R′)	Yield[b] (%)
1	**3b** (Me)	89
2	**3c** (Et)	94
3	**3d** (^{n}Bu)	97

[a] All reactions were carried out using **2a** (1.0 mmol), **3** (1.5 mmol), KO^{t}Bu (3.0 equiv), **1** (1.0 mol %) in H_2O (2.0 mL) at 100 °C for 24 h.
[b] Isolated yields.

Furthermore, the reactions between aryl bromides **2** and a kind of styrenes were also carried out under the identical conditions. As can be seen from Table 5, all reactions can give the corresponding coupling products **6** in moderate to high yields, despite the electron-rich or poor, or sterically hindered substituents on the aryl rings of both of aryl bromides and styrenes. The reaction between 3-bromopyridine **2o** and styrene **5a** also works well to give product **6j** in 84% yield (entry 10).

Table 5
NHC–Pd(II) complex **1** catalyzed reactions of aryl bromides **2** with styrenes **5**



Entry[a]	**2** (R^1)	**3** (R')	Yield[b] (%)
1	**2a** (H)	**5a** (H)	**6a**, 90
2	**2b** (4-MeO)	**5a**	**6b**, 80
3	**2c** (4-Me)	**5a**	**6c**, 69
4	**2d** (3-MeO)	**5a**	**6d**, 88
5	**2e** (4-Cl)	**5a**	**6e**, 80
6	**2f** (4-F)	**5a**	**6f**, 86
7	**2g** (4-NO2)	**5a**	**6g**, 85
8	**2m** (2-Me)	**5a**	**6h**, 90
9	**2n** (4-Ac)	**5a**	**6i**, 81
10	**2o** 	**5a**	**6j**, 84
11	**2b**	**5b** (4-Me)	**6k**, 92
12	**2g**	**5b**	**6l**, 75
13	**2b**	**5c** (4-Cl)	**6m**, 80
14	**2g**	**5c**	**6n**, 85

[a] All reactions were carried out using **2** (1.0 mmol), **5** (1.5 mmol), KO^{t}Bu (3.0 equiv), **1** (1.0 mol %) in H_2O (2.0 mL) at 120 °C for 24 h.
[b] Isolated yields.

In further investigations, we found that NHC–Pd(II) complex **1** showed no catalytic activity towards aryl chlorides under the identical reaction conditions. In addition, we found that when enone, such as 1-phenyl-propenone was used as the substrate, the reaction became disordered and no desired product can be obtained.

3. Conclusion

In summary, NHC–Pd(II) complex **1** derived from proline showed good to excellent catalytic activities upon Mizoroki–Heck reaction performed in water, with aryl bromides and iodides as the electrophilic partners. We, for the first time, systematically investigated the NHC–Pd complex catalyzed Mizoroki–Heck reactions performed in pure water. The complex is air- and moisture stable and can be stored under air for several months.

4. Experimental section

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-300 or 500 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard or in DMSO-d_6; *J*-values are in hertz. Commercially obtained reagents were used without further purification. Flash column chromatography was carried out using Huanghai 300–400 mesh silica gel at increased pressure.

4.2. Experimental procedures

*4.2.1. General procedure for the NHC–Pd(II) complex **1**-catalyzed Mizoroki–Heck reaction.* (*If olefin is acrylic acid*) Under N_2 atmosphere, acrylic acid **3a** (1.5 mmol), KO^{t}Bu (3.0 equiv) and H_2O (2.0 mL) were added into a seal tube and the mixture was stirred at room temperature for 10 min. Then NHC–Pd(II) complex **1** (1.0 mol %) and aryl halides **2** (1.0 mmol) were added. The mixture was stirred vigorously at 120 °C (for bromides) or 100 °C (for iodides) for 24 h. After cooling to room temperature, HCl (4 M) was dropped into the reaction mixture to reach a pH of 1, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the pure product.

(*If olefin is acrylate esters*) Under N_2 atmosphere, NHC–Pd(II) complex **1** (1.0 mol %), KO^{t}Bu (3.0 equiv) and H_2O (2.0 mL) were added into a seal tube, then acrylate esters **3** (1.5 mmol) and aryl bromides **2** (1.0 mmol) were added. The mixture was stirred vigorously at 100 °C for 24 h. After cooling to room temperature, HCl (4 M) was dropped into the reaction mixture to reach a pH of 1, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the pure product.

(*If olefin is styrenes*) Under N_2 atmosphere, NHC–Pd(II) complex **1** (1.0 mol %), KO^{t}Bu (3.0 equiv) and H_2O (2.0 mL) were added into a seal tube, then styrenes (1.5 mmol) and aryl bromides **2** (1.0 mmol) were added. The mixture was stirred vigorously at 120 °C for 24 h. After cooling to room temperature, the solvent was extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the pure product.

*4.2.1.1. Compound **4a**[7].* A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 6.47 (d, *J*=16.0 Hz, 1H), 7.41–7.43 (m, 3H, Ar), 7.55–7.57 (m, 2H, Ar), 7.80 (d, *J*=16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.2, 128.4, 129.0, 130.7, 134.1, 147.1, 171.8.

*4.2.1.2. Compound **4b**[7].* A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 3.85 (s, 3H, OMe), 6.32 (d, *J*=16.0 Hz, 1H), 6.92 (d, *J*=9.0 Hz, 2H, Ar), 7.51 (d, *J*=9.0 Hz, 2H, Ar), 7.74 (d, *J*=16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.4, 114.4, 114.6, 126.8, 130.1, 146.7, 161.8, 172.1.

*4.2.1.3. Compound **4c**[7].* A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 2.39 (s, 3H, Me), 6.41 (d, *J*=16.0 Hz, 1H), 7.21 (d, *J*=8.0 Hz, 2H, Ar), 7.45 (d, *J*=8.0 Hz, 2H, Ar), 7.77 (d, *J*=16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.5, 116.1, 128.4, 129.7, 131.3, 141.3, 147.1, 172.1.

*4.2.1.4. Compound **4d**[8].* A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 3.84 (s, 3H, OMe), 6.44 (d, *J*=16.0 Hz, 1H), 6.97 (dd, *J*=8.0, 2.5 Hz, 1H, Ar), 7.07 (s, 1H), 7.15 (d, *J*=8.0 Hz, 1H, Ar), 7.51 (dd, J_1=J_2=8.0 Hz, 1H, Ar), 7.76 (d, *J*=16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.3, 113.1, 116.7, 117.5, 121.1, 130.0, 135.4, 147.0, 159.9, 172.1.

*4.2.1.5. Compound **4e**[8].* A white solid. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.55 (d, *J*=16.0 Hz, 1H), 7.46 (d, *J*=8.0 Hz, 2H, Ar), 7.58 (d, *J*=16.0 Hz, 1H, Ar), 7.74 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 120.0, 128.9, 129.9, 133.2, 134.8, 142.6, 167.3.

*4.2.1.6. Compound **4f**[7].* A white solid. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.49 (d, *J*=16.0 Hz, 1H), 7.24 (dd, J_1=J_2=8.5 Hz, 2H, Ar), 7.59 (d, *J*=16.0 Hz, 1H), 7.76 (dd, J_1=5.5 Hz, J_2=8.5 Hz, 2H, Ar). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 115.9 (d, J_{C-F}=22.5 Hz), 119.0 (d,

J_{C-F}=2.5 Hz), 130.5 (d, J_{C-F}=8.75 Hz), 130.9 (d, J_{C-F}=3.75 Hz), 142.7, 163.1 (d, J_{C-F}=246.25 Hz), 167.4.

4.2.1.7. Compound ***4g***[7]. A yellow solid. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.74 (d, J=16.0 Hz, 1H), 7.69 (d, J=16.0 Hz, 1H), 7.97 (d, J=8.5 Hz, 2H, Ar), 8.23 (d, J=8.5 Hz, 2H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 123.5, 123.9, 129.3, 140.7, 141.4, 148.0, 166.9.

4.2.1.8. Compound ***4h***[9]. A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 6.25 (d, J=15.6 Hz, 1H), 7.08 (dd, J=5.1, 3.6 Hz, 1H, Ar), 7.31 (d, J=3.6 Hz, 1H, Ar), 7.43 (d, J=5.1 Hz, 1H, Ar), 7.89 (d, J=15.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 116.8, 125.2, 127.2, 129.0, 137.3, 140.4, 172.0.

4.2.1.9. Compound ***4i***[10]. A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 6.27 (d, J=15.6 Hz, 1H), 7.32–7.38 (m, 2H, Ar), 7.56 (d, J=1.5 Hz, 1H, Ar), 7.77 (d, J=15.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.9, 128.2, 129.3, 131.6, 139.2, 139.3, 171.7.

4.2.1.10. Compound ***6a***[11]. A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.11 (s, 2H), 7.25 (t, J=7.5 Hz, 2H, Ar), 7.36 (dd, J_1=J_2=7.5 Hz, 4H, Ar), 7.52 (d, J=7.5 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.5, 127.6, 128.66, 128.70, 137.3.

4.2.1.11. Compound ***6b***[11]. A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 3.83 (s, 3H, OMe), 6.90 (d, J=8.5 Hz, 2H, Ar), 6.98 (d, J=16.0 Hz, 1H), 7.07 (d, J=16.0 Hz, 1H), 7.23 (t, J=7.5 Hz, 1H, Ar), 7.34 (t, J=7.5 Hz, 2H, Ar), 7.45–7.50 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.3, 114.1, 126.2, 126.6, 127.2, 127.7, 128.2, 128.6, 130.2, 137.7, 159.3.

4.2.1.12. Compound ***6c***[11]. A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 2.36 (s, 3H, Me), 7.05 (d, J=16.0 Hz, 1H), 7.14 (d, J=16.0 Hz, 1H), 7.17 (d, J=8.0 Hz, 2H, Ar), 7.24 (t, J=7.5 Hz, 1H, Ar), 7.33 (t, J=8.0 Hz, 2H, Ar), 7.41 (d, J=8.0 Hz, 2H, Ar), 7.50 (d, J=7.5 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 126.37, 126.41, 127.4, 127.7, 128.61, 128.62, 129.4, 134.5, 137.48, 137.50.

4.2.1.13. Compound ***6d***[11]. A yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 3.85 (s, 3H, OMe), 6.82 (d, J=7.5 Hz, 1H), 7.05–7.12 (m, 4H), 7.25–7.29 (m, 2H), 7.36 (t, J=7.5 Hz, 2H, Ar), 7.51 (d, J=7.5 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.3, 111.8, 113.3, 119.3, 126.5, 127.7, 128.6, 128.7, 129.6, 137.3, 138.8, 159.9.

4.2.1.14. Compound ***6e***[11]. A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.05 (d, J=16.5 Hz, 1H), 7.09 (d, J=16.5 Hz, 1H), 7.26–7.38 (m, 5H, Ar), 7.44 (d, J=8.5 Hz, 2H, Ar), 7.51 (d, J=7.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 126.5, 127.4, 127.6, 127.9, 128.7, 128.8, 129.3, 133.2, 135.9, 137.0.

4.2.1.15. Compound ***6f***[11]. A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.00–7.09 (m, 4H), 7.26 (t, J=7.5 Hz, 1H, Ar), 7.36 (dd, J_1=J_2=7.5 Hz, 2H, Ar), 7.46–7.50 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 115.6 (d, J_{C-F}=21.7 Hz), 115.6, 126.4, 127.5, 127.7, 128.0 (d, J_{C-F}=8.0 Hz), 128.5 (d, J_{C-F}=2.3 Hz), 128.7, 133.5 (d, J_{C-F}=3.3 Hz), 137.2, 162.33 (d, J_{C-F}=247.6 Hz).

4.2.1.16. Compound ***6g***[12]. A yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.15 (d, J=16.0 Hz, 1H), 7.28 (d, J=16.0 Hz, 1H), 7.34–7.42 (m, 3H, Ar), 7.56 (d, J=8.0 Hz, 2H, Ar), 7.64 (d, J=8.5 Hz, 2H, Ar), 8.22 (d, J=8.5 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 124.2, 126.3, 126.9, 127.0, 128.8, 128.9, 133.3, 136.2, 143.9, 146.8.

4.2.1.17. Compound ***6h***[11]. A pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 2.43 (s, 3H, Me), 7.00 (d, J=16.5 Hz, 1H), 7.05–7.38 (m, 7H), 7.52 (d, J=7.5 Hz, 2H, Ar), 7.59 (d, J=7.5 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.9, 125.4, 126.2, 126.55, 126.57, 127.5, 127.6, 128.7, 130.0, 130.4, 135.8, 136.4, 137.7.

4.2.1.18. Compound ***6i***[11]. A white solid. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 2.61 (s, 3H, Me), 7.14 (d, J=16.0 Hz, 1H), 7.23 (d, J=16.0 Hz, 1H), 7.30 (t, J=7.5 Hz, 1H, Ar), 7.38 (t, J=7.5 Hz, 2H, Ar), 7.54 (d, J=7.5 Hz, 2H, Ar), 7.59 (d, J=8.0 Hz, 2H, Ar), 7.96 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.6, 126.5, 126.8, 127.5, 128.3, 128.8, 128.9, 131.5, 136.0, 136.7, 142.0, 197.5.

4.2.1.19. Compound ***6j***[13]. A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.07 (d, J=16.5 Hz, 1H), 7.18 (d, J=16.5 Hz, 1H), 7.27–7.33 (m, 2H, Ar), 7.38 (t, J=7.2 Hz, 2H, Ar), 7.53 (d, J=7.2 Hz, 2H, Ar), 7.83 (d, J=7.8 Hz, 1H, Ar), 8.49 (dd, J=4.8, 1.5 Hz, 1H, Ar), 8.73 (d, J=2.1 Hz, 1H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.5, 124.9, 126.7, 128.2, 128.8, 130.8, 132.6, 133.0, 136.7, 148.5.

4.2.1.20. Compound ***6k***[14]. A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.35 (s, 3H, Me), 3.83 (s, 3H, OMe), 6.89 (d, J=8.7 Hz, 2H), 6.98 (d, J=8.4 Hz, 2H, Ar), 7.15 (d, J=7.8 Hz, 2H, Ar), 7.39 (d, J=8.1 Hz, 2H), 7.44 (d, J=8.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 55.3, 114.1, 126.2, 126.6, 127.3, 127.6, 129.3, 130.4, 134.9, 137.0, 159.2.

4.2.1.21. Compound ***6l***[15]. A yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.38 (s, 3H, Me), 7.09 (d, J=16.5 Hz, 1H), 7.19–7.28 (m, 3H, Ar+C=CH), 7.45 (d, J=7.8 Hz, 2H, Ar), 7.61 (d, J=9.0 Hz, 2H, Ar), 8.21 (d, J=9.0 Hz, 2H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 124.1, 125.3, 126.7, 127.0, 129.6, 133.3, 133.5, 139.0, 144.1, 146.6.

4.2.1.22. Compound ***6m***[16]. A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 6.88–6.93 (m, 3H, Ar+C=CH), 7.03 (d, J=16.2 Hz, 1H), 7.30 (d, J=8.4 Hz, 2H, Ar), 7.41 (d, J=9.0 Hz, 2H, Ar), 7.44 (d, J=9.0 Hz, 2H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 114.2, 125.3, 127.4, 127.8, 128.8, 128.9, 129.8, 132.7, 136.2, 159.5.

4.2.1.23. Compound ***6n***[17]. A yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.11 (d, J=16.5 Hz, 1H), 7.17 (d, J=16.5 Hz, 1H), 7.37 (d, J=8.4 Hz, 2H, Ar), 7.48 (d, J=8.4 Hz, 2H, Ar), 7.63 (d, J=9.0 Hz, 2H, Ar), 8.23 (d, J=9.0 Hz, 2H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ 124.2, 126.89, 126.93, 128.2, 129.1, 131.9, 134.6, 134.7, 143.5, 147.0.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.10.033. These data include MOL files and InChiKeys of the most important compounds described in this article.

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