Synthesis of Schiff bases from substitute aromatic aldehydes and 2-(4-aminophenyl)acetonitrile catalysed by 3,5-difluoroarylboronic acid

Zhiping Du, Tianhua Shen, Haibo Dang, Zhenfang Fu and Qingbao Song*

College of Chemical Engineering and Material Science, Zhejiang University of Technology, Hangzhou, 310032, P. R. China

A simple efficient method for synthesis of Schiff bases in good yields from aromatic aldehydes and 2-(4-aminophenyl)acetonitrile catalysed by 3,5-difluoroarylboric acid at room temperature for 2 hours is reported.

Keywords: Schiff bases, 3,5-difluoroaryllboronic acid, aromatic aldehydes, 2-(4-aminophenyl) acetonitrile

In recent years, the synthesis of Schiff base compounds has attracted much interest among organic chemists. Schiff bases have played a very important role in medical biology,[1,2] functional materials,[3] catalysis chemistry[4] and coordination chemistry[5] in the few past decades, especially in asymmetric catalytic reactions. Schiff bases are frequently used as ligands in some organic synthesis reactions such as asymmetric sulfoxidation,[6] Suzuki-Miyaura[7] and enantioselective Henry reaction[8] (Fig. 1). These reactions catalysed by chiral Schiff bases provided high *ee* values. In the past, various catalysts such as TiO_2,[9] $MgSO_4$,[10,11] $NbCl_5$,[12] Pt,[13] ionic liquids,[14] CaO,[15] molecular sieves,[16] clay,[17] P_2O_5/SiO_2,[18] P_2O_5/Al_2O_3,[19] dioxane/AcOH[20] and boric acid[21] were successfully used to synthesise Schiff bases. At the same time, some other reaction techniques appeared, for instance, ultrasound irradiation[22], microwave irradiation[23,24] and solvent-free reaction[25]. However, syntheses of Schiff bases usually suffer from high reaction temperatures, long reaction times and low yields. Therefore, improvement of these reactions is required.

To our knowledge, boronic acid, ferrocenic boronic acid or substituted arylboronic acids have not been studied as catalysts for the synthesis of Schiff bases. In this paper, we report our research on substituted arylboronic acids as catalysts for the synthesis of Schiff bases. We found that 3,5-difluoroarylboric acid was an efficient catalyst for the synthesis of Schiff bases. Under mild conditions, 18 new compounds were synthesised.

Results and discussion

We optimised the reaction conditions in terms of catalysts, loading of catalysts, solvents and reaction times. 4-Chlorobenzaldehyde was selected as the model substrate. Ethanol was initially used as the solvent. The results are summarised in Table 1. Initially, we combined 4-chlorobenzaldehyde **1** (1.5 mmol) and 2-(4-aminophenyl)acetonitrile **2** (1.5 mmol) together without catalyst and 52% yield (entry 1) was obtained. When we used boric acid as the catalyst, the yield rose to 60% (entry 2). Then we added phenylboronic acid (0.015 mmol) as the catalyst to improve the reaction, and the desired **4a** was obtained in 79% yield (entry 3). Arylboronic acids with electron-donating groups showed higher yields (entries 4 and 5). It is noteworthy that ideal yields were obtained when the reaction was carried out using arylboronic acids with electron-withdrawing groups (entries 6–8). To our surprise, 3,5-difluoroarylboric acid promoted the yield to 96% (entry 6). The results above indicated that the electronic effect of substituted arylboronic acid affected the yield of the present reaction. At the same time, we examined naphthalen-1-ylboronic acid (**3h**), 1,1′-ferrocenediboronic acid (**3i**) and 2-thienylboronic acid (**3j**) (entries 9–11), all of which were not as efficient as 3,5-difluorophenylboronic acid (entry 6). The effects of catalyst's loading were tested (entries 12–14) and the most appropriate loading of catalyst was found to be 1 mol % (entry 6). We found that ethanol was the most suitable solvent by selecting solvents (entries 6 and 15–18). Finally, the effect of reaction time was studied (entries 19–21) and the most suitable reaction time was 2 hours (entry 6). On the basis of these investigations, the preferred reaction conditions are aromatic aldehydes: amine: 3,5-difluoroarylboric acid = 1: 1: 0.01 in ethanol (5 mL) at room temperature for 2 hours.

With the optimised conditions in hand, a variety of new Schiff bases were synthesised in good yields, as shown in Table 2. We found that aromatic aldehydes with electron-withdrawing substituents gave higher yields than those with electron-donating substituents.

In summary, we have developed a simple and efficient method for the synthesis of Schiff bases from substituted aromatic aldehydes and 2-(4-aminophenyl)acetonitrile catalysed by 3,5-difluoroarylboric acid at room temperature. This process may be useful in medical biology and asymmetric chemistry.

Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer, using $CDCl_3$ as solvent (500 MHz for ^{1}H or 126 MHz for ^{13}C, respectively). IR spectra (KBr) were recorded on a NEXUS FI/IR spectrometer. Melting points were taken on Büchi M-560. Mass spectra (MS) were carried out on VARIAN1200 and measured by the EI method. M^+ values quoted for ^{35}Cl and ^{79}Br where appropriate. The reaction mixture was monitored by TLC on silica gel plates (60 F-254). Microanalyses were performed on a LECO CHNS-932 Elemental Analyser. All boronic acids were purchased from the Aladdin (Shanghai, China) chemical company.

*Synthesis of Schiff bases (**4a**–**r**); general procedure*

A mixture of 2-(4-aminophenyl)acetonitrile (1.5 mmol), an aldehyde (1.5 mmol), 3,5-difluoroarylboric acid (0.015 mmol) and anhydrous ethanol (5 mL) was stirred in a reaction flask for 2 hours. The reaction mixture was monitored by TLC. After completion, the reaction mixture was filtered, washed with ether, and recrystallised from anhydrous ethanol. The structures and yield of the products are given in Table 2.

2-(4-(4-Chlorobenzylideneamino)phenyl)acetonitrile (**4a**)*:* White solid; IR (film) 2246, 1619 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 151.6, 137.7, 134.5, 130.9, 130.0, 129.5, 129.1, 128.9, 128.8, 127.6, 121.6, 117.80, 115.4, 23.2; MS *m/z* 254 (M^+). Anal. Calcd for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 70.60; H, 4.19; N, 10.87%.

2-(4-(2-Nitrobenzylideneamino)phenyl)acetonitrile (**4b**): A yellow solid; IR (film) 2249, 1610 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.31 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.07–8.12 (m, 1H), 7.77 (t,

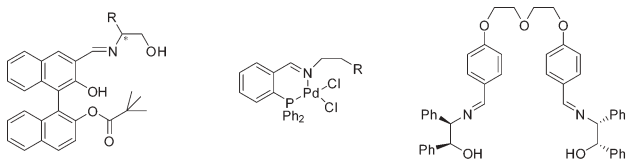
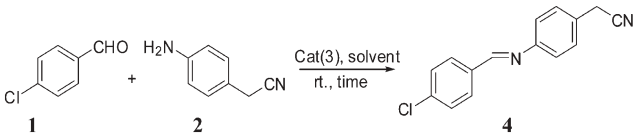


Fig. 1 Schiff bases in asymmetric catalytic reactions.

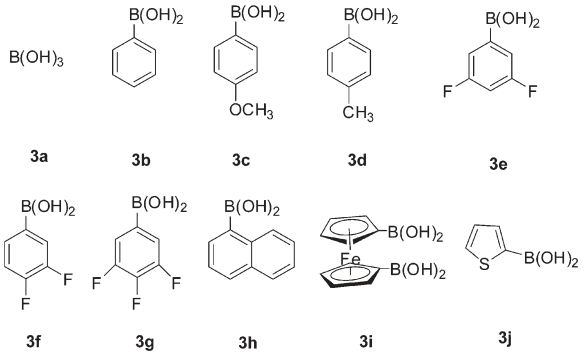
* Correspondent. E-mail: qbsong@zjut.edu.cn

Table 1 Optimisation for synthesis of Schiff bases[a]



1 2 4

Catalyst:



3a 3b 3c 3d 3e 3f 3g 3h 3i 3j

Entry	Catalyst	Solvent	Time/h	Yield/%[b]
1	None	EtOH	2	52
2	**3a**	EtOH	2	60
3	**3b**	EtOH	2	79
4	**3c**	EtOH	2	77
5	**3d**	EtOH	2	75
6	**3e**	EtOH	2	96
7	**3f**	EtOH	2	90
8	**3g**	EtOH	2	84
9	**3h**	EtOH	2	65
10	**3i**	EtOH	2	61
11	**3j**	EtOH	2	83
12[c]	**3e**	EtOH	2	78
13[d]	**3e**	EtOH	2	95
14[e]	**3e**	EtOH	2	95
15	**3e**	MeOH	2	89
16	**3e**	CH_2Cl_2	2	30
17	**3e**	THF	2	21
18	**3e**	Toluene	2	10
19	**3e**	EtOH	1	72
20	**3e**	EtOH	3	95
21	**3e**	EtOH	4	93

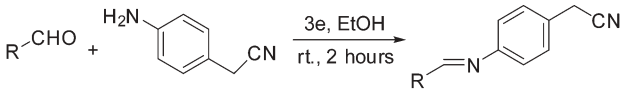
[a]Reaction conditions: **1** (1.5 mmol), **2** (1.5 mmol), **3e** (0.015 mmol), Solvent (5 mL), rt.
[b]Isolated yield.
[c]Reaction conditions: **1** (1.5 mmol), **2** (1.5 mmol), **3e** (0.0075 mmol), Solvent (5 mL), rt.
[d]Reaction conditions: **1** (1.5 mmol), **2** (1.5 mmol), **3e** (0.03 mmol), Solvent (5 mL), rt.
[e]Reaction conditions: **1** (1.5 mmol), **2** (1.5 mmol), **3e** (0.075 mmol), Solvent (5 mL), rt.

J = 7.6 Hz, 1H), 7.62–7.69 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.28–7.32 (m, 2H), 3.81 (s, 2H); ^{13}C NMR (126 MHz, CDCl3) δ 156.5, 151.0, 149.4, 133.6, 131.4, 130.9, 129.8, 129.6, 128.9, 128.4, 124.6, 121.9, 117.7, 115.5, 23.3; MS *m/z* 265 (M^+). Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.75; H, 4.04; N, 15.72%.

2-(4-(3-Nitrobenzylideneamino)phenyl)acetonitrile (**4c**): Yellow solid; IR (film) 2246, 1625 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74–8.77 (m, 1H), 8.55 (s, 1H), 8.33–8.35 (m, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.24–7.31 (m, 2H), 3.81 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 150.7, 148.7, 137.6, 134.2, 129.8, 128.9, 128.9, 128.3, 125.7, 123.4, 121.6, 117.7, 115.4, 23.2; MS *m/z* 265 (M^+). Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.84; H, 4.12; N, 15.79%.

2-(4-(2-(Trifluoromethyl)benzylideneamino)-phenyl)acetonitrile (**4d**): White solid; IR (film) 2245, 1623 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.2 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.40

Table 2 Synthesis of Schiff bases via 3,5-difluoroarylboric acid cascade process[a]



5 2 4a–r

Entry	R	Product	Yield/%[b]	M.p./°C
1	4-ClC_6H_4	**4a**	95	106–108
2	2-$NO_2C_6H_4$	**4b**	90	115–117
3	3-$NO_2C_6H_4$	**4c**	91	116–117
4	2-$CF_3C_6H_4$	**4d**	87	70–71
5	4-BrC_6H_4	**4e**	85	109–111
6	4-FC_6H_4	**4f**	90	98–100
7	3-ClC_6H_4	**4g**	92	76–78
8	2,4-$Cl_2C_6H_4$	**4h**	84	102–104
9	2-ClC_6H_4	**4i**	83	88–90
10	3,4-$(CH_3O)_2C_6H_4$	**4j**	75	96–98
11	2,5-$(CH_3O)_2C_6H_4$	**4k**	80	108–110
12	4-$CH_3C_6H_4$	**4l**	79	122–124
13	3-OH-4-$CH_3C_6H_4$	**4m**	81	127–129
14	4-Pyridyl	**4n**	71	125–127
15	3,5-$(CH_3O)_2C_6H_4$	**4o**	78	104–106
16	2-Naphthyl	**4p**	68	130–132
17	4-$OHCC_6H_4$	**4q**	82	205–207
18	4-$CH_3OC_6H_4$	**4r**	80	107–109

[a]Reaction conditions: **3e** (0.015 mmol), **2** (1.5 mmol), **5** (1.5 mmol), EtOH (5 mL), rt., 2 hours.
[b]Isolated yield.

(d, *J* = 8.3 Hz, 2H), 7.24–7.27 (m, 2H), 3.80 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 151.5, 133.9, 133.6, 132.1, 130.9, 129.1, 128.9, 128.5, 128.1, 125.8, 125.8, 121.7, 117.7, 115.5, 23.2; MS *m/z* 288 (M^+). Anal. Calcd for $C_{16}H_{11}F_3N_2$: C, 66.66; H, 3.85; N, 9.720. Found: C, 66.55; H, 3.72; N, 9.58%.

2-(4-(2-Bromobenzylideneamino)phenyl)acetonitrile (**4e**): White solid; IR (film) 2247, 1619 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 151.5, 134.9, 132.4, 132.1, 130.9, 130.2, 128.9, 128.8, 127.6, 126.2, 121.5, 117.8, 115.4, 23.2; MS *m/z* 299 (M^+). Anal. Calcd for $C_{15}H_{11}BrN_2$: C, 60.22; H, 3.71; N, 9.36. Found: C, 60.06; H, 3.64; N, 9.26%.

2-(4-(2-Fluorobenzylideneamino)phenyl)acetonitrile (**4f**): White solid; IR (film) 2244, 1598 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.91 – 7.95 (m,2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.17–7.23 (m,4H), 3.79 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 151.74, 132.4, 132.4, 130.9, 130.9, 128.9, 128.8, 127.4, 121.5, 117.8, 116.1, 115.9, 115.4, 23.2; MS *m/z* 238 (M^+). Anal. Calcd for $C_{15}H_{11}FN_2$: C, 75.62; H, 4.65; N, 11.76. Found: C, 75.51; H, 4.54; N, 11.69%.

2-(4-(3-Chlorobenzylideneamino)phenyl)acetonitrile (**4g**): White solid; IR (film) 2247, 1623 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.95 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.46–7.50 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 151.4, 137.7, 135.1, 131.5, 130.0, 128.9, 128.9, 128.4, 127.8, 127.2, 121.6, 117.8, 115.5, 23.2; MS *m/z* 254 (M^+). Anal. Calcd for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 70.62; H, 4.32; N, 10.88%.

2-(4-(2,4-Dichlorobenzylideneamino)phenyl)acetonitrile (**4h**): White solid; IR (film) 2246, 1582 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 12.3 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 3H), 7.24–7.29 (m, 2H), 3.80 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 151.4, 137.9, 136.6, 131.6, 129.9, 129.8, 129.6, 128.9, 128.1, 127.8, 121.8, 117.7, 115.5, 23.3; MS *m/z* 288 (M^+). Anal. Calcd for $C_{15}H_{10}Cl_2N_2$: C, 62.31; H, 3.49; N, 9.69. Found: C, 62.15; H, 3.46; N, 9.62%.

2-(4-(2-Chlorobenzylideneamino)phenyl)acetonitrile (**4i**): White solid; IR (film) 2251, 1618 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.25 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.42–7.49 (m, 2H), 7.39 (dd, *J* = 9.2, 3.3 Hz, 3H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 151.7, 136.2, 133.0, 132.4, 130.0, 128.9, 128.8, 128.6, 127.8, 127.2, 121.8, 117.8, 115.4, 23.2; MS *m/z* 254

(M^+). Anal. Calcd for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 70.68; H, 4.25; N, 10.90%.

2-(4-(3,4-Dimethoxybenzylideneamino)phenyl)acetonitrile (**4j**): White solid; IR (film) 2240, 1582 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.18–7.25 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 152.3, 152.2, 149.6, 129.3, 128.9, 128.7, 126.9, 124.6, 121.6, 117.9, 115.4, 110.6, 109.1, 56.0, 56.0, 23.2; MS *m/z* 280 (M^+). Anal. Calcd for $C_{17}H_{16}O_2N_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.77; H, 5.68; N, 9.89%.

2-(4-(2,5-Dimethoxybenzylideneamino)phenyl)acetonitrile (**4k**): White solid; IR (film) 2244, 1594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.70 (d, *J* = 2.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.94 (dd, *J* = 17.9, 9.1 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 154.4, 153.9, 128.9, 128.7, 127.1, 123.5, 121.8, 120.3, 117.9, 115.5, 113.4, 112.9, 110.5, 56.3, 55.9, 23.2; MS *m/z* 280 (M^+). Anal. Calcd for $C_{17}H_{16}O_2N_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.78; H, 5.65; N, 9.90%.

2-(4-(4-Methylbenzylideneamino)phenyl)acetonitrile (**4l**): Yellow solid: IR (film) 2245, 1617 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 152.2, 142.2, 133.5, 129.8, 129.7, 129.6, 128.9, 128.8, 127.1, 121.6, 119.3, 117.9, 115.5, 23.2, 21.6; MS *m/z* 234 (M^+). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.95; H, 5.91; N, 11.82%.

*2-(4-(3-Hydroxy-4-methylbenzylideneamino)phenyl)acetonitrile (***4m**): Yellow solid: IR (film) 2270, 1587 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.73 (s, 1H), 3.98 (s, 3H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 152.1, 149.6, 146.1, 129.9, 128.9, 128.7, 126.9, 122.5, 121.6, 117.9, 115.5, 113.9, 110.4, 56.1, 23.2; MS *m/z* 266 (M^+). Anal. Calcd for $C_{16}H_{14}O_2N_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.08; H, 5.22; N, 10.40%.

2-(4-(Pyridine-4-ylmethyleneamino)phenyl)acetonitrile (**4n**): A yellow solid: IR (film) 2248, 1595 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.8 Hz, 2H), 8.46 (s, 1H), 7.76 (d, *J* = 5.9 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 3.80 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 151.2, 150.8, 150.5, 150.5, 142.5, 128.9, 128.5, 122.4, 121.6, 121.6, 117.7, 115.4, 23.2; MS *m/z* 221 (M^+). Anal. Calcd for $C_{14}H_{11}N_3$: C, 75.98; H, 5.01; N, 18.99. Found: C, 75.88; H, 4.94; N, 18.89%.

2-(4-(3,5-Dimethoxybenzylideneamino)phenyl)acetonitrile (**4o**): Yellow solid: IR (film) 2244, 1594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.69 (d, *J* = 3.2 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.05 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 154.4, 153.9, 128.9, 128.7, 127.1, 123.5, 121.8, 120.4, 117.9, 115.4, 113.4, 112.9, 110.5, 56.3, 55.9, 23.2; MS *m/z* 280 (M^+). Anal. Calcd for $C_{17}H_{16}O_2N_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.76; H, 5.64; N, 9.87%.

2-(4-(Naphthalen-2-ylmethyleneamino)phenyl)acetonitrile (**4p**): White solid: IR (film) 2245, 1618 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.23 (s, 1H), 8.16–8.19 (m, 1H), 7.95 (t, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.54–7.62 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 3.80 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 152.0, 135.2, 133.7, 133.1, 131.5, 129.1, 128.9, 128.8, 128.7, 128.0, 127.7, 127.4, 126.7, 123.9, 121.6, 117.9, 115.5, 23.2; MS *m/z* 270 (M^+). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.30; H, 5.11; N, 10.22%.

2-(4-(4-Hydroxybenzylideneamino)phenyl)acetonitrile (**4q**): Yellow solid: IR (film) 2252, 1579 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.15 (s, 1H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, d-DMSO) δ 160.7, 160.2, 151.3, 132.0, 130.7, 128.9, 128.6, 128.0, 127.4, 121.3, 119.3, 115.8, 115.6, 114.1, 21.9; MS *m/z* 236 (M^+). Anal. Calcd for $C_{15}H_{12}ON_2$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.09; H, 5.00; N, 11.70%.

2-(4-(4-Methoxybenzylideneamino)phenyl)acetonitrile (**4r**):Yellow solid: IR (film) 2247, 1601 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.86 (dd, *J* = 8.7, 4.4 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.90 (d, *J* = 6.7 Hz, 3H), 3.78 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 160.2, 152.2, 132.0, 130.7, 129.0, 128.9, 128.7, 126.9, 121.6, 117.9, 115.4, 114.3, 114.3, 55.4, 23.2; MS *m/z* 250 (M^+). Anal. Calcd for $C_{16}H_{14}ON_2$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.63; H, 5.47; N, 11.02%.

Electronic Supplementary Information

Spectra of the products have been deposited in the ESI available through stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

This work was financially supported by the National Science Foundation of Zhejiang Province (LY12B02016) and the State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology (P. R. China).

Received 10 December 2012; accepted 22 February 2013
Paper 1201670 doi: 10.3184/174751913X13647468553118
Published online: 15 May 2013

References

1 Y. Zhang, B. Zou, K. Wang, Y. Pan, H. Liang, X. Yi and H. Wang, *Med. Chem. Res*., 2012, **21**, 1341.
2 N. Zhang, Y.-h. Fan, Z. Zhang, J. Zuo, P.-f. Zhang, Q. Wang, S.-b. Liu and C.-j. Bi, *Inorg. Chem. Commun*., 2012, **22**, 68.
3 M. Ruf, W.S. Durfee and C.G. Pierpont, *Chem. Commun*., 2004, 1022.
4 V.J. Mayani, S.H.R. Abdi, R.I. Kureshy, N.-u. Kahn, H. Das and H.C. Bajaj, *J. Org. Chem*., 2010, **75**, 6191.
5 P. Seth, L.K. Das, M.G.B. Drew and A. Ghosh, *Eur. J. Inorg. Chem.*, 2012, 2232.
6 Y.-C. Jeong, Y. D. Huang, S. Choi and K.-H. Ahn, *Tetrahedron Asymmetry*, 2005, **16**, 3497.
7 T. Mahamo, M.M. Mogorosi, J.R. Moss, S.F. Mapolie, J.C. Slootweg, K. Lammertsma and G.S. Smith, *J. Organomet. Chem.*, 2012, **703**, 34.
8 M. Çolak, T. Aral, H. Hoşgören and N. Demirel, *Tetrahedron Asymmetry*, 2007, **18**, 1129.
9 M. Hosseini-Sarvari, *Chinese Chem. Lett.*, 2011, **22**, 547-550.
10 D. Blanco-Ania, P.H.H. Hermkens, L.A.J.M. Sliedregt, H.W. Scheeren and F.P.J.T. Rutjes, *Tetrahedron*, 2009, **65**, 5393.
11 A.K. Chakraborti, S. Bhagat and S. Rudrawar, *Tetrahedron Lett.*, 2004, **45**, 7641.
12 L.C. da Silva-Filho, V. Lacerda Jr, M.G. Constantina and G.V.J. da Silva, *Synthesis*, 2008, 2527.
13 L. Hu, X. Cao, D. Ge, H. Hong, Z. Guo, L. Chen, X. Sun, J. Tang, J. Zheng, J. Lu and H. Gu, *Chem. A Eur. J.*, 2011, **17**, 14283.
14 M.C. Law, T.W. Cheung, K.-Y. Wong and T.H. Chan, *J. Org. Chem*, 2007, **72**, 923.
15 M. Gopalakrishnan, P. Sureshkumar, V. Kanagarajan and J. Thanusu, *Res. Chem. Intermed.*, 2007, **33**, 541.
16 C.K.Z. Andrade, S.C.S. Takada, L.M. Alves, J.P. Rodrigues, P.A.Z. Suarez, R.F. Brandao and V.C.D. Soares, *Synlett*, 2004, 2135.
17 R.S. Varma, R. Dahiya and S. Kumar, *Tetrahedron Lett.*, 1997, **38**, 2039.
18 H. Naeimi, H. Sharghi, F. Salimi and K. Rabiei, *Heteroatom Chemistry*, 2008, **19**, 43.
19 H. Naeimi, F. Salimi and K. Rabiei, *J. Mol. Catal. A: Chem.*, 2006, **260**, 100.
20 P.A. Kerneghan, S.D. Halperin, D.L. Bryce and K.E. Maly, *Canad. J. Chem.*, 2011, **89**, 577.
21 B.T. Cho and S.K. Kang, *Tetrahedron*, 2005, **61**, 5725.
22 K.P. Guzen, A.S. Guarezemini, A.T.G. Órfão, R. Cella, C.M.P. Pereira and H.A. Stefani, *Tetrahedron Lett.*, 2007, **48**, 1845.
23 M. Gopalakrishnan, P. Sureshkumar, V. Kanagarajan, J. Thanusu and R. Govindaraju, *J. Chem. Res.*, 2005, **5**, 299.
24 R.S. Varma and R. Dahiya, *Synlett*, 1997, 1245.
25 P.C. Andrews, A.C. Peatt and C.L. Raston, *Tetrahedron Lett.*, 2004, **45**, 243.