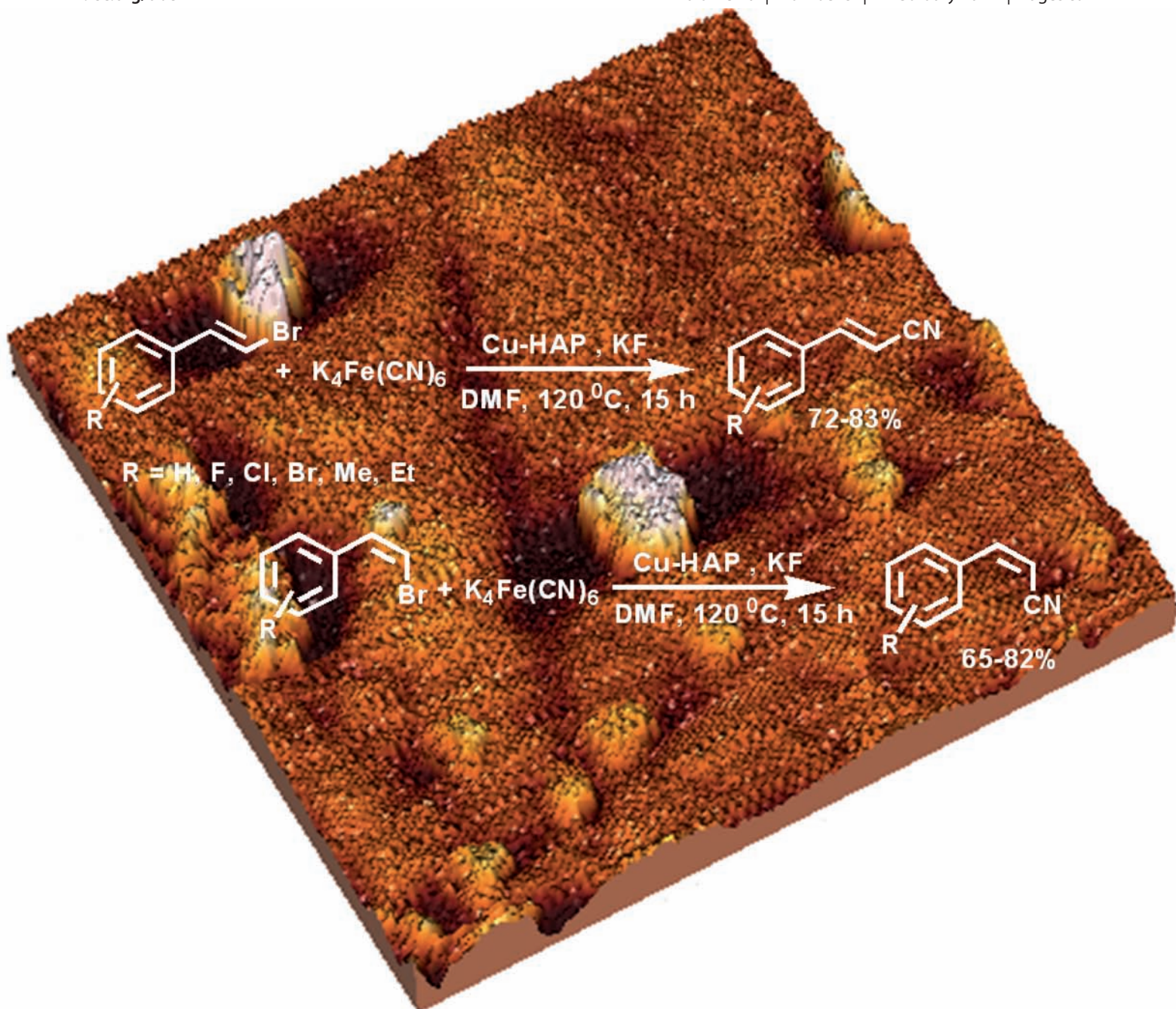


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# Hydroxyapatite-supported Cu(I)-catalysed cyanation of styrenyl bromides with $K_4[Fe(CN)_6]$ : an easy access to cinnamitriles†

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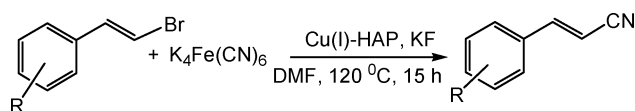
An efficient cyanation of styrenyl bromides by  $K_4[Fe(CN)_6]$  has been achieved under the catalysis of hydroxyapatite-supported copper(I) producing a variety of functionalized cinnamitriles in high yields. The stereochemistry of the styrenyl double bond is preserved during the process providing the same stereoisomer of product.

## Introduction

Heterogeneous supported metal salts have received tremendous attention in catalysis as these substances offer ease of separation and reusability of the catalyst, metal contaminant free products, improved efficiency compared to their homogeneous counterparts.<sup>1</sup> Hydroxyapatite, a Ca–phosphate complex, is found to be one of the active heterogeneous supports capable of accommodating a variety of metals and metal salts.<sup>2</sup> Recently, we demonstrated the application of hydroxyapatite supported Pd(II) catalyst for an efficient coupling of diiodoalkenes and conjugated alkenes<sup>3</sup> and this prompted us to explore impregnation of other inexpensive and benign metal salts with hydroxyapatite to find more useful applications.

The cyanation is an important reaction as nitriles are valuable intermediates in organic synthesis and –CN group can be transformed to a broad spectrum of functionalities.<sup>4</sup> The  $\alpha,\beta$ -unsaturated nitriles particularly cinnamitriles are very useful synthons possessing aromatic ring, double bond and nitrile functionality for further manipulation.<sup>5</sup> Thus, various methods have been developed for the synthesis of cinnamitriles.<sup>6</sup> The commonly used classical methods involve dehydration of cinnamamides or cinnamaloximes,<sup>6a</sup> and Wittig-type reactions using cyanoalkylphosphate.<sup>6b</sup> Both of these processes have serious limitations with regard to use of toxic and hazardous reagents<sup>6a</sup> and large amount of waste generation.<sup>6b</sup> Another approach is oxidative reaction of cinnamylalcohol and cinnamaldehyde and ammonia in air under high pressure using Ru catalyst.<sup>6c</sup> The Pd-catalysed Mizoroki–Heck reaction of acrylonitrile with aryl halides also produced cinnamitriles, although this reaction entails waste salts.<sup>6d</sup> Recently, better modification of this re-

action has been demonstrated using benzene and acrylonitrile in presence of  $Pd(OAc)_2/HPMoV$  catalyst under oxygen.<sup>6e</sup> The use of a large volume of hazardous benzene and acrylonitrile is not acceptable in a green context. The more straightforward approach is the transition metal catalysed cyanation of styrenyl halides.<sup>7</sup> These processes include reaction of styrenyl halides with  $[(C_2H_5)_3(CH_3)N]_3Co(CN)_5$  in acetonitrile,<sup>7a</sup>  $Zn(CN)_2/Pd(PPh_3)_4$  in DMF under microwave irradiation,<sup>7b</sup>  $K_4Fe(CN)_6$  catalysed by  $PdCl_2$  in ionic liquid under microwave irradiation.<sup>7c</sup> However, these procedures involve highly toxic metal cyanides,<sup>7a,7b</sup> and lack general applicability.<sup>7</sup> More significantly, none of these reactions<sup>6,7</sup> are stereoselective and produce a mixture of *cis* and *trans* stereoisomers in varying amounts. In addition, reactions of *cis*-styrenyl halides are not addressed adequately. Our primary objective is to develop a convenient method using a benign cyanating agent and catalyst and address the issue of stereochemistry involving both *cis* and *trans*-styrenyl halides. Thus, we report here the cyanation of styrenyl bromides with  $K_4Fe(CN)_6$  catalysed by hydroxyapatite-supported copper iodide (Scheme 1).



Scheme 1 Cyanation of styrenyl bromides.

## Results and discussion

The catalyst was prepared by stirring a slurry of hydroxyapatite and CuI in aqueous acetone at 60 °C for 48 h. Filtration of the solid material followed by washing with acetone and drying provided the Cu(I)-HAP catalyst. The Cu content was determined to be 0.3237 mmol g<sup>-1</sup> by ICP-MS (Inductively Coupled Plasma Mass Spectroscopy). The Energy Dispersive Spectra (EDS) of this material showed the presence of both calcium and copper (Fig. 1). The X-ray Photoelectron Spectroscopic (XPS) study exhibited a peak of Cu 2p<sub>3/2</sub> at 934.2 eV with no satellite peak indicating Cu in the +1 oxidation state (Fig. 2a).<sup>8</sup> The Field Emission

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† Electronic supplementary information (ESI) available: <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all products listed in Tables 2 and 3. See DOI: 10.1039/c1ob06467c

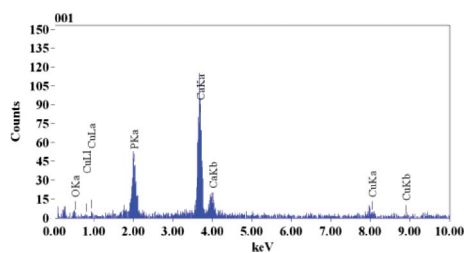


Fig. 1 EDX spectra of Cu(I)-HAP.

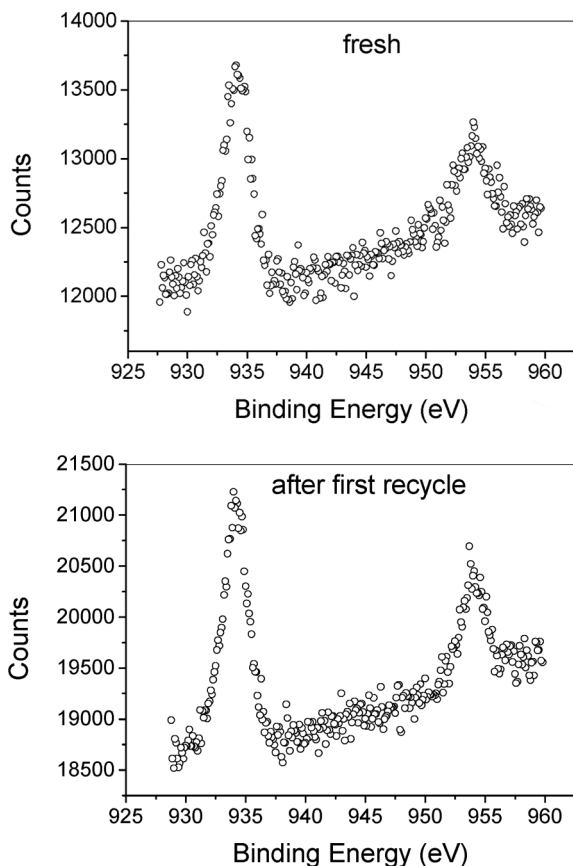


Fig. 2 XPS study of fresh catalyst (a) XPS study of recycled catalyst.

Scanning Electron Microscope (FESEM) image (Fig. 3) and Atomic Force Microscopy (AFM) (Fig. 4) showed the morphology of the catalyst.

To standardise the reaction conditions we carried out several experiments for a representative reaction of styrenyl bromide and  $K_4Fe(CN)_6$  in the presence of Cu(I)-HAP under different

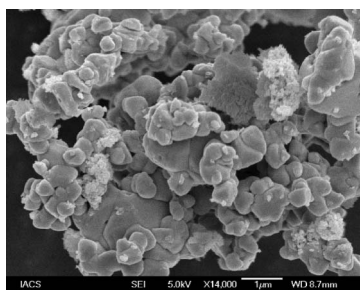
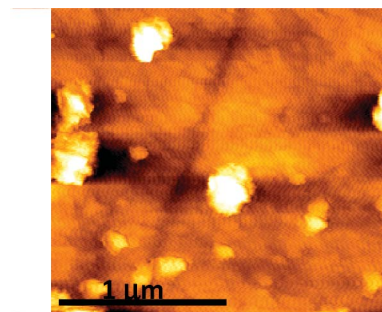
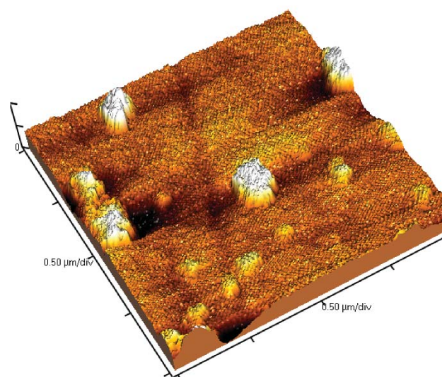


Fig. 3 SEM image of the Cu-HAP catalyst.



(a)



(b)

Fig. 4 AFM image of Cu(I)-HAP catalyst (b) AFM topological image of the catalyst.

Table 1 Standardisation of reaction conditions

Entry	Additive	Solvent	$T/^\circ\text{C}$	Time (h)	Yield (%)
1	$\text{Na}_2\text{CO}_3$	DMF	120	12	45
2	$\text{K}_3\text{PO}_4$	DMF	120	12	52
3	KF	DMF	120	12	70
4 <sup>a</sup>	<b>KF</b>	<b>DMF</b>	<b>120</b>	<b>15</b>	<b>82</b>
5	KF	DMF	120	20	82
6	KF	THF	75	15	42
7	KF	Toluene	110	15	35
8	KF	$\text{H}_2\text{O}$	100	15	—
9 <sup>b</sup>	KF	DMF	120	15	15
10 <sup>c</sup>	KF	DMF	120	15	21
11	—	DMF	120	15	45

<sup>a</sup> The bold mark signifies the best conditions. <sup>b</sup> Reaction was carried out in absence of Cu(I)-HAP. <sup>c</sup> Reaction was carried out with CuI alone.

conditions with variation of additive, solvent and temperature. It was found that best result was obtained using KF in DMF at  $120^\circ\text{C}$  in 15 h (Table 1, entry 4). Other bases such as  $\text{Na}_2\text{CO}_3$  and  $\text{K}_3\text{PO}_4$  and solvents like THF, toluene and water were not very effective. In absence of Cu(I)-HAP the progress of the reaction was not at all significant (15% yield, Table 1, entry 9). Using CuI alone the reaction did not proceed effectively (21% yield, Table 1, entry 10). The reaction was also not very effective in absence of KF (Table 1, entry 11).

Thus, in a typical experimental procedure, a mixture of (*E*)- $\beta$ -bromostyrene,  $K_4Fe(CN)_6$ , KF and Cu(I)-HAP in DMF was

heated with stirring at 120 °C under argon for a required period of time (TLC). Standard workup followed by purification by column chromatography provided the product.

Several diversely substituted styrenyl bromides underwent cyanation by this procedure to produce the corresponding cinnamionitriles. The results are reported in Table 2. The (*E*) and (*Z*) isomer of each styrenyl bromide was subjected to this reaction. The (*E*)-styrenyl bromides produced (*E*)-cinnamionitriles and (*Z*)-isomers led to (*Z*)-products exclusively. We did not find a mixture of product isomers in any reaction except one where (*Z*)-2-methylstyrenyl bromide led to a mixture of (*E*) and (*Z*) cinnamionitriles in 23:77 ratio (Table 2, entry 14). However, the corresponding (*E*)-styrenyl bromide provided the (*E*)-product selectively (Table 2, entry 13). A possible rationale may be more steric hindrance in (*Z*)-isomer leading to (*E*) and (*Z*) mixture in the product. However, it is notable that 2-substituted styrenyl bromides participated in this cyanation reaction without any difficulty. The substitution with halo groups such as F, Cl, Br is compatible with this procedure.

This procedure is also applicable to cyanation of aryl iodides to the corresponding aryl nitriles which are important class of compounds.<sup>11</sup> The results are summarized in Table 3. Although, several methods are available for the preparation of aryl nitriles,<sup>12</sup> this method makes an alternative useful addition.

The reactions are in general very clean and high yielding. The pure products are obtained by simple column chromatography and no ligand or additive is required for this reaction. We are not aware of any previous general methods for Cu-catalysed cyanation of styrenyl halides. However, we found only one report of cyanation of  $\beta$ -bromostyrene using stoichiometric CuCN at an elevated temperature of 202 °C.<sup>6e</sup> The most significant feature of our procedure is achievement of exclusive stereoselectivity of products. A comparison of results with similar cyanation reactions of styrenyl halides by other procedures substantiated our claim as illustrated in Table 4. The catalyst was recycled for four cycles with gradual decrease in yield of the product (Table 5). This might be due to the formation of a coating on the catalyst surface (Table 5) which possibly reduces its activity. Furthermore, we also observed considerable leaching of the catalyst (Cu content in the fresh catalyst: 0.3237 mmol g<sup>-1</sup> and in the recovered one after 4th cycle: 0.2430 mmol g<sup>-1</sup>). This also contributes to the reduced catalytic activity.

Regarding the reaction pathway we propose an oxidative addition of styrenyl bromide/aryl iodide (ArX) to Cu(I)-HAP generating a Cu(III) complex<sup>20,12a</sup> **A** which undergoes transmetalation with K<sub>4</sub>Fe(CN)<sub>6</sub> to provide a transient Cu(III) intermediate **B**. This ultimately leads to the product, ArCN *via* reductive elimination of Cu(III) to Cu(I) as outlined in Scheme 2. It may be assumed that KF helps release of CN<sup>-</sup> ion probably *via* interaction of F<sup>-</sup> ion on the Fe centre. The XPS analysis of the regenerated catalyst shows the oxidation state of copper as Cu(I) supporting our proposition (Fig. 2b).

## Conclusion

In conclusion, we have developed a simple and efficient procedure for cyanation of styrenyl bromides to the corresponding cinnamionitriles with K<sub>4</sub>Fe(CN)<sub>6</sub> catalysed by hydroxyapatite supported CuI. The (*E*) and (*Z*) styrenyl bromides provide the corresponding

**Table 2** Synthesis of cinnamionitriles

Entry	Substrate	Product	Yield (%) <sup>a</sup>	Ref.
1			82	9
2			78	9
3			83	6b
4			76	6b
5			80	9
6			68	9
7			80	10
8			79	10
9			81	9
10			82	9
11			78	—
12			75	—
13			72	9
14			65	9

(*E*:*Z* = 23:77)

<sup>a</sup> Yields refer to those of purified isolated products characterised by spectroscopic data (IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR).

(*E*) and (*Z*) cinnamionitriles as sole products. In addition to excellent stereoselectivity, simple operation and good yields, this procedure is an attractive one for the synthesis of cinnamionitriles due to the absence of ligand and additive, easy recovery and

**Table 3** Synthesis of aryl nitriles

Ar-I + K <sub>4</sub> Fe(CN) <sub>6</sub> $\xrightarrow[\text{DMF, 120 } ^\circ\text{C, 15 h}]{\text{Cu(I)-HAP, KF}}$ Ar-CN				
Entry	Substrate	Product	Yield (%) <sup>a</sup>	Ref.
1			84	13
2			78	14
3			81	14
4			84	15
5			82	14
6			72	15
7			74	16
8			82	17
9			80	17
10			80	17
11			82	18
12			84	15
13			75	19
14			80	13
15			75	13
16			71	13

<sup>a</sup> Yields refer to those of purified isolated products characterised by spectroscopic data (IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR).

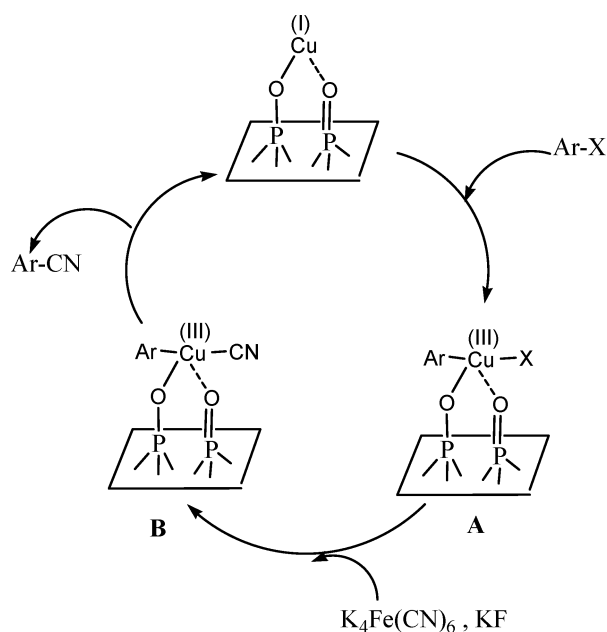
**Table 4** Comparison of results with similar cyanation reaction

Entry	Substrate	Result		
		PdCl <sub>2</sub> , DMEDA, [bmim]BF <sub>4</sub> <sup>7c</sup>	[Co(CN) <sup>3-</sup> ] <sup>7a</sup>	Cu(I)-HAP (our method)
1		Yield 74% E/Z = 8:1	Yield 75% E/Z = 24:1	Yield 82% E = 100%
2		Yield 71% E/Z = 1:2	Yield 75% E/Z = 28:47	Z = 100%
3		Yield 65% E/Z = 17:1	—	Yield 80% E = 100%
4		Yield 63% E/Z = 1:4	—	Yield 68% Z = 100%

**Table 5** Recyclability of catalyst

No. of cycles	Yield (%)	Amount of catalyst recovered after each cycle (mg) <sup>a</sup>
1	82	112
2	75	121
3	69	136
4	50	145

<sup>a</sup> Starting amount of fresh catalyst was 100 mg.



**Scheme 2** Plausible mechanism.

reusability of the catalyst for a number of runs and the use of a benign cyanating agent. To the best of our knowledge this is the

first report of copper-catalysed synthesis of cinnamionitriles from styrenyl bromides.

## Experimental

IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids on a FT-8300 Shimadzu spectrometer. NMR spectra were recorded on Bruker 500 MHz and 300 MHz spectrometers for  $^1\text{H}$  NMR and at 125 MHz and 75 MHz for  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$  solutions.

### Preparation of Cu(I)-HAP catalyst

Hydroxyapatite [HAP,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] was prepared following a reported procedure.<sup>21</sup>

Hydroxyapatite (1 g) was stirred with CuI (0.38 g, 2 mmol) in acetone–water (25 mL, 24 : 1) for 48 h. The slurry was filtered and the residue was washed with acetone and dried overnight (12 h) at 100 °C in an oven to furnish Cu(I)-HAP catalyst (Cu content as measured by ICP-MS is 0.3237 mmol g<sup>-1</sup>).

### Representative experimental procedure for the cyanation of (*E*)- $\beta$ -bromostyrene (Table 2, entry 1)

A mixture of (*E*)- $\beta$ -bromostyrene (183 mg, 1 mmol),  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  (422 mg, 1 mmol), anhydrous KF (72 mg, 1.2 mmol) and Cu(I)-HAP catalyst (100 mg, 3.2 mol%) in DMF (4 mL) was heated with stirring at 120 °C under argon for 15 h (TLC). The reaction mixture was filtered to separate the solid catalyst which was used for successive cycles. The filtrate was extracted with  $\text{Et}_2\text{O}$  (4  $\times$  15 mL). The extract was washed with water, brine and then dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent left the crude product which was purified by column chromatography over silica gel (60–120 mesh) (hexane/ether 94 : 6) to provide pure (*E*)-cinnamionitrile (106 mg, 82%) as a pale yellow oil, IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3059, 3028, 2218, 1620, 1577, 1492, 1446, 1273, 1207, 1180.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  5.86 (d,  $J = 16.5$  Hz, 1H), 7.35–7.44 (m, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  96.3, 118.1, 127.4 (2C), 129.1 (2C), 131.2, 133.5, 150.5. These data are in good agreement with the reported values.<sup>9</sup>

This procedure was followed for the reactions of all styrenyl bromides listed in Table 2 and aryl iodides in Table 3. All of these products except two (Table 2, entries 11 and 12) are known and have been identified by comparison of their spectroscopic data (IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) with those reported (references in Table 2 and 3). The unknown compounds (Table 2, entries 11 and 12) were characterised properly by their spectroscopic data as follows.

### (*E*)-4-Ethylcinnamionitrile (Table 2, entry 11)

Pale yellow oil, IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3209, 3055, 3024, 2466, 2932, 2874, 2359, 2342, 2216, 1618, 1607, 1566, 1508, 1458, 1420.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.24 (t,  $J = 7.6$  Hz, 3H), 2.68 (q,  $J = 7.6$  Hz, 2H), 5.81 (d,  $J = 16.7$  Hz, 1H), 7.22–7.24 (m, 2H), 7.33–7.38 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  15.3, 28.8, 95.1, 118.5, 127.5 (2C), 128.7 (2C), 131.1, 148.1, 150.6. HRMS Cald. for  $\text{C}_{11}\text{H}_{11}\text{NNa}^+$  ( $\text{M}^+ + \text{Na}$ ): 180.0789, Found 180.0788.

### (*Z*)-4-Ethylcinnamionitrile (Table 2, entry 12)

Pale yellow oil, IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3064, 2966, 2932, 2897, 2874, 2212, 1609, 1562, 1510, 1452, 1421, 1319, 1230, 1175.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.25 (t,  $J = 7.5$  Hz, 3H), 2.69 (q,  $J = 7.5$  Hz, 2H), 5.37 (d,  $J = 12.5$  Hz, 1H), 7.09 (d,  $J = 12.5$  Hz, 1H), 7.26 (d,  $J = 8$  Hz, 2H), 7.73 (d,  $J = 8$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  15.2, 28.9, 93.8, 117.6, 128.4 (2C), 129.2 (2C), 131.2, 147.8, 148.6. HRMS Cald. for  $\text{C}_{11}\text{H}_{11}\text{NNa}^+$  ( $\text{M}^+ + \text{Na}$ ): 180.0789, Found 180.0788.

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