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Cu-catalyzed debrominative cyanation of *gem*-dibromoolefins: a facile access to α,β-unsaturated nitriles

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An efficient catalytic route for the synthesis of α,β-unsaturated nitriles from easily accessible *gem*-dibromoolefins has been developed. The method utilized inexpensive reagents such as Cu_2O as catalyst, L-proline as ligand and NaCN as cyanide source to afford α,β-unsaturated nitriles in high yields (62-86%). Deuterium exchange study has shown that one of the bromide atoms of *gem*-dibromoolefins exchanges with cyanide while the other with deuterium atom.

α,β-Unsaturated nitriles are a ubiquitous structural unit frequently found in natural products and act as a valuable synthetic intermediates for pharmaceuticals, agrochemicals, dyes and functional materials.[1] They also serve as a synthetic precursor for the transformation to a variety of functional group such as amides, ester, ketone, amine and alcohols.[2] The compact nature of the nitrile moiety, as well as its hydrogen bond accepting ability, and metabolic stability has made it an important functional group in medicinal chemistry research. Some of the representative examples of pharmaceutical agents which comprise a α,β-unsaturated nitrile group includes IDX899 and rilpivirine, the potent anti-HIV nonnucleoside reverse transcriptase inhibitors; entacapone, a drug for Parkinson's disease ; and CC-5079, the anticancer agent (Fig. 1).[3] Therefore, the development of newer methods for their facile access is of significant interest among organic chemists. A number of synthetic routes to α,β-unsaturated nitriles are known such as amide dehydrogenation reaction,[4] Wittig/Horner-Wadsworth-Emmons[5] or Peterson olefination,[6] carbocyanation of alkynes,[7] cyanation of alkenyl halides[8] and oxidative transformation of the corresponding aldehydes,[9] amines,[10] amides,[11] alcohols,[12] azides,[13] and hydrozones.[14] Although some of these methods are attractive, they suffer from certain limitations of using extreme conditions, poor yields and expensive reagents. Therefore, the development of convenient and user-friendly procedure for the synthesis of α,β-unsaturated nitriles by using inexpensive reagents and from easily accessible starting material is highly desirable.

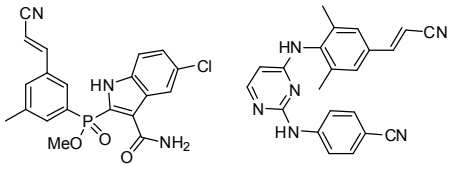

Fig.1 Representative examples of pharmaceuticals containing α,β-unsaturated nitrile group.

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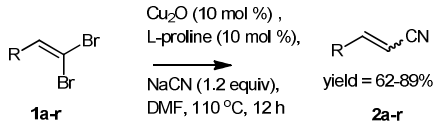
†Electronic supplementary information (ESI) available: Experimental procedure, characterization data, ^1H and ^{13}C NMR spectra.

The chemistry of *gem*-dibromoolefins (**1a-r**), was almost confined to the synthesis of terminal alkynes through Corey-Fuchs reaction.[15] Recently, versatility of *gem*-dibromoolefins have been exploited in the synthesis of various carbocycles and heterocycles such as indoles,[16] benzofuran,[17] benzothiophenes,[18] isocoumarins[19] and other heterocycles[20] through metal catalyzed tandem coupling reaction (Suzuki, Sonogashira, Heck or Ullmann type) or C-H activation. In addition the versatility of *gem*-dibromoolefins in metal catalyzed cross coupling reactions with alkynes, vinylalanes and organoboranes, tin, magnesium and zinc compounds to give highly stereoselective synthesis of trisubstituted alkenes[21] by prudent selection of coupling partner has been exploited. To the best of our knowledge, a direct method of synthesis of α,β-unsaturated nitriles



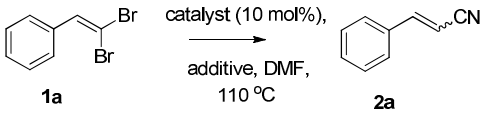
R = aryl, alkenyl, hetroaryl

Scheme 1. Cu_2O catalyzed synthesis of α,β-unsaturated nitriles from *gem*-dibromoolefins

utilizing *gem*-dibromoolefins as precursor remains elusive in literature. In continuation of our studies on Cu-mediated/catalyzed development of newer synthetic methodologies,[22] herein we report a novel Cu_2O catalyzed synthesis of α,β-unsaturated nitriles from *gem*-dibromoolefins (**Scheme 1**).

In our initial study, (2,2-dibromovinyl)benzene (**1a**) was treated with CuCN (3 equiv) in DMF at 150 °C, which gave the corresponding cinnamonitrile (**2a**) in 21% yield with *E*/*Z* ratio 4.5/1 (Table 1, entry 1). The yield of **2a** was, however, significantly improved to 57% when L-proline (**L1**) was used as promoter in combination with CuCN in DMF at 120 °C (entry 2).[23] In order to provide a catalytic process, we have carried out the cyanation reaction with copper (I) oxide as a catalyst, NaCN as CN source. Thus, by using Cu_2O (10 mol%) along with NaCN (1.1 equiv), **2a** was obtained in low yield (24%, entry 3). In order to improve the yield and selectivity, a series of N-based ligands [L-proline (**L1**), 1,10- phenanthroline (**L2**), N,N-dimethylethylenediamine (**L3**) and 1,2-ethylenediamine (**L4**)] were screened along with Cu_2O (entry 4-7). After several experimentations, it was thus found that a combination of (2,2-dibromovinyl)benzene, NaCN, copper (I) oxide (10 mol%), L-proline (L1, 10 mol%) in DMF at 110 °C for 12 h was the best optimized condition in achieving **2a** in high yield (81%, entry 4), however, significant improvement in selectivity was not observed. Replacing the solvent (dioxane, toluene) or CN source ($K_4[Fe(CN)_6]$ or TMSCN) had a deleterious effect on the conversion (entry 4,8). Also lowering Cu_2O concentration (5 mol%) afforded

Table 1: Cu_2O-catalyzed synthesis of cinnamonitrile **2a**: optimization studies[a]



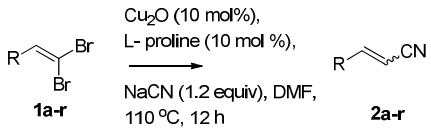
1a **2a**

no.	Catalyst	ligand/ additive (10 mol %)	CN source (equiv)	yield (%)[b]
1	--	-	CuCN (3)	21[c]
2	--	**L1** (1 equiv)	CuCN (2.2)	57[d]
3	Cu_2O	--	NaCN	24
4	Cu_2O	**L1**	NaCN (1.1)	81(43[e] trace[f])
5	Cu_2O	**L2**	NaCN (1.1)	68
6	Cu_2O	**L3**	NaCN (1.1)	41
7	Cu_2O	**L4**	NaCN (1.1)	26
8	Cu_2O	KI	$K_4[Fe(CN)_6]$ (0.5)	trace[g]
9	Cu_2O	**L1**	TMSCN	trace
10	CuI	**L1**	NaCN (1.1)	76
11	CuBr	**L1**	NaCN (1.1)	68
12	CuCl	**L1**	NaCN (1.1)	66
13	CuCN	**L1**	NaCN (1.1)	54

[a](2,2-dibromovinyl)benzene (3 mmol), catalyst (10 mol%), ligand (10 mol%), solvent 10 mL, 12 h. [b]isolated yield after column chromatographic purification. [c] temp. 150 °C. [d]temp. 120 °C. [e]5 mol% Cu_2O was used. [f]toluene and dioxane were used separately. [g]DMF:H_2O was used (1:1).

2a in low yields (43%). The result was also inferior when the catalyst was changed to CuX (X = Br, Cl, I or CN) (entry 10-13).

Table 2: Cu_2O catalyzed synthesis of substituted α,β- unsaturated nitriles (**2a-r**): substrate scope[a]



1a-r **2a-r**

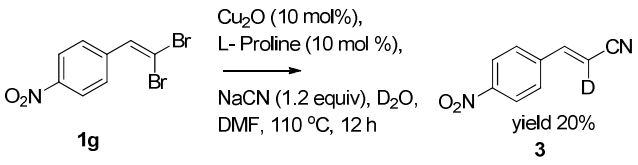
No.	substrates (**1a-r**) (**R**)	yield (%)[b]	*E*/*Z*[c]
a	phenyl	84	4.5:1
b	4-OMe- phenyl	86	1.2:1
c	4-F- phenyl	80	1.2:1
d	4-Cl- phenyl	82	E only
e	4-MeS- phenyl	89	2:1
f	4-CF_3- phenyl	82	1.2:1
g	4-NO_2- phenyl	79	4:1
h	2-NO_2- phenyl	84	3:1
i	4-Me- phenyl	86	2:1
j	2-thienyl	79	2:1
k	2-furyl	84	2:1
l	cinnamyl	76	1.2:1
m	3,4-$(OMe)_2$-benzyl	74	E only[d]
n	ferrocenyl	71	3:1
o	2-Br-5-OMe- phenyl	74	3:1[e]
p	2-Br-4,5-$(OMe)_2$- phenyl	62	4:1[e]
q	2-Br-3,4,5 -$(OMe)_3$- phenyl	72	3:1[e]
r	2- Br-3,5-$(OMe)_2$- phenyl	74	4:1[e]

[a] reaction conditions: *gem*-dibromoolefin (3 mmol), NaCN (3.3 mmol), Cu_2O (10 mol%), L-proline (10 mol%), DMF, 110 °C, 12 h; [b] isolated yield after column chromatographic purification. [c] determined from ^1H NMR. [d] C=C isomerized to β,γ- (benzylic) position; [e] Br on the aromatic nucleus was also exchanged with CN.

With the optimized conditions in hand [Cu_2O (10 mol%), L-proline (10 mol%), NaCN (1.2 equiv, DMF, 110 °C], we then investigated the generality of this copper (I) oxide catalyzed debrominative cyanation of *gem*-dibromoolefins **1a-r** (Table 2). The starting materials **1a-r** are readily prepared from the corresponding commercially available aldehydes *via* the

Ramirez procedure.[24] The substrates bearing different substitutions like halogen, alkyl, alkoxy, nitro, thio etc group on the aromatic nucleus were well tolerated under the reaction conditions and the *E* and *Z* substituted α,β- unsaturated nitriles (**2a-r**) were isolated in good yields. In case of *p*-chlorocinnamonitrle **2d** we observed as a single *E* isomer. In addition to the aryl group, the reaction also proceeded equally well with different *gem*-dibromoolefins including heteroaryl- and alkenyl substituted alkenes. Interestingly, when 4-(3,3-dibromoallyl)-1,2-dimethoxybenzene **1m** was subjected under standarized condition we observed the isomerized product ie. β,γ-unsaturated nitrile as a single *E* isomer. Intriguingly, (2,2-dibromovinyl)ferrocene (**1n**) performed well, under the optimized condition to generate the expected product in 71% yield. In all cases we observed thermodynamic stable *E* as the major product with ratio varing from 1.2:1 to 100:0. However, in case of aliphatic *gem*-dibromoolefins we observed the complex reaction mixture, which may be a limitation of this catalytic process.

In order to gain insight into the mechanistic details of the reaction, *p*-nitrodibromoalkene **1g** was treated with Cu_2O (10 mol %), L-proline (10 mol %), NaCN (1.2 equiv), D_2O (2 equiv) in DMF at 110 °C for 12 h that resulted in α-deuterated *p*-nitrocinnamonitrile **3** (Scheme 2). Based on this deuterated study, a probable mechanism for debrominative coupling reaction has been proposed. First L-proline interacts with Cu_2O to generate a proline-Cu (I) complex **A**.[25] The oxidative addition of dibromoolefins to Cu (I) species then produces intermediate **B** which subsequently undergoes nucleophilic displacement with NaCN to generate intermediate **C**. Reductive elimination of intermediate **C** produces bromo cyano olefin **D** with the liberation of catalytic complex **A**. Bromo cyano olefin **D** again undergoes subsequent oxidative addition with Cu (I) complex **A** to generate intermediate **E** which on protonation facilitates the formation of α,β-unsaturated nitriles (Figure 2).



Scheme 2 Deuterium exchange experiment

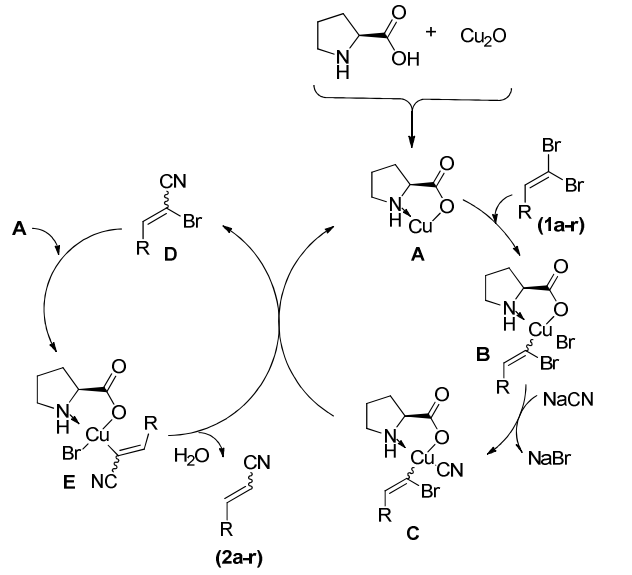


Fig. 2. Proposed catalytic cycle for debrominative cyanation of *gem*-dibromoolefins

In conclusion, we have developed an efficient catalytic process for the synthesis of α,β-unsaturated nitriles from *gem*-dibromoolefins using Cu (I) oxide as catalyst, L-proline as ligand, and NaCN as cyanide source. The eassy accessible starting materials, broad reaction scope and using cheap commercially available reagents makes this method of high significance in organic synthesis.

Acknowledgements

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Experimental Section

1. General

Solvents were purified and dried by standard procedures before use; petroleum ether of boiling range 60–80 °C was used. Melting points are uncorrected. Infrared spectra were recorded on Shimadzu FTIR-8400 spectrometer. The wave numbers (n) of recorded IR-signals are quoted in cm−1. ^1H and ^{13}C NMR were recorded on Bruker AV-200, AV-400 and AV-500 NMR spectrometers, respectively. Purification was done using column chromatography (230−400 mesh).

Note: sodium cyanide is "highly toxic" and must be handled with care.

2. General experimental procedure for the preparation of α,β-unsaturated nitriles (2a-r):

To a stirred solution of *gem*-dibromoolefins **1a-r** (3 mmol) in dry DMF (15 mL) was added NaCN (3.3 mmol), Cu_2O (0.3 mmol) and *L*-proline (0.3 mmol). The entire reaction mixture was heated to 110 °C while being stirred under N_2 for 12 h (monitored by TLC). The reaction mixture was then cooled to room temperature and excess cyanide was quenched with aq. $NaClO_2$, diluted with water (10 mL) and EtOAc (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The aqueous layer after extraction was poured into aq. $KMnO_4$ solution to quench excess NaCN and then disposed off. The combined organic extracts were washed with brine, dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to give crude products which were purified by column chromatography [silica gel (230-400 mesh) and petroleum ether: EtOAc (7:3) as an eluent

to afford the corresponding α,β-unsaturated nitriles (**2a-r**) in 62-89% yield.

3. General experimental procedure for the preparation of α-deuterated p-nitro cinnamonitrile 3:

To a stirred solution of 1-(2,2-dibromovinyl)-4-nitrobenzene (1 mmol) in dry DMF (5 mL) was added NaCN (1.1 mmol), Cu_2O (0.1 mmol), *L*-proline (0.1 mmol) and D_2O (1 mmol). The entire reaction mixture was heated to 120 °C while being stirred under N_2 for 12 h (monitored by TLC). The reaction mixture was then cooled to room temperature and excess cyanide was quenched with aq. $NaClO_2$, diluted with water (10 mL) and EtOAc (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The aqueous layer after extraction was poured into aq. $KMnO_4$ solution to quench excess NaCN and then disposed off. The combined organic extracts were washed with brine, dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to give crude products which were purified by column chromatography [silica gel (230-400 mesh) and petroleum ether: EtOAc (7:3) as an eluent to afford the corresponding α-deuterated p-nitro cinnamonitrile **3** in 20% yield.

4. Spectroscopic Data:

Cinnamonitrile (2a): Yield: 84% (0.325 g, 2.52 mmol); Colourless liquid; IR ($CHCl_3$, cm^{-1}): υ_{max} 856, 1247, 1560, 1591, 2211; unseparable mixture of *E*/*Z* (4.5/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.88 (d, *J* = 16.7 Hz, 1H), 7.40 (d, *J* = 16.7 Hz, 1H), 7.42-7.45 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 96.0, 117.8, 127.2, 128.9, 131.0, 133.4, 150.2; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.44 (d, *J* = 12.1 Hz, 1H), 7.11 (d, *J* = 12.1 Hz, 1H), 7.41-7.49 (m, 3H), 7.78-7.82 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 94.9, 117.8, 128.1, 128.7, 128.8, 129.2, 130.7, 133.4, 148.3; Analysis: C_9H_7N requires C, 83.69; H, 5.46; N, 10.84; Found: C, 83.56; H, 5.34; N, 10.31 %.

3-(4-methoxyphenyl)acrylonitrile (2b): Yield: 86% (0.410 g, 2.58 mmol); White solid; mp. 53-54°C;[26] IR ($CHCl_3$, cm^{-1}): υ_{max} 1089, 1299, 1514, 1589, 2218; unseparable mixture of *E*/*Z* (1.2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.70 (d, *J* = 16.5 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 16.5 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.1, 93.2, 114.3, 118.3, 128.8, 130.7, 149.6, 161.8; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.28 (d, *J* = 12.1 Hz, 1H), 6.89 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 12.1 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.1, 91.6, 114.1, 117.6, 126.1, 126.3, 130.7, 147.7, 161.4; Analysis: $C_{10}H_9NO$ requires C, 75.45; H, 5.70; N, 8.8; O, 10.05; Found: C, 83.56; H, 5.34; N, 8.03%.

3-(4-fluorophenyl)acrylonitrile (2c): Yield: 80% (0.353 g, 2.4 mmol); White solid; mp. 40-42°C;[26] IR ($CHCl_3$, cm^{-1}): υ_{max} 690, 1080, 1260, 1505, 1621, 2225; unseparable mixture of *E*/*Z* (1.2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (d, *J* = 16.6 Hz, 1H), 7.05-7.11 (m, 2H), 7.36 (d, *J* = 16.6 Hz, 1H), 7.41-7.44 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 96.2, 115.5, 115.9, 127.3, 127.8, (d, *J* = 8.1 Hz), 133.9 (d, *J* = 3.3 Hz), 162 (d, *J*, 247.7); *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.43 (d, *J* = 12.3 Hz, 1H), 7.08 (d, *J* = 12.3 Hz, 1H), 7.13-7.17 (m, 2H), 7.79-7.86 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 96.2, 115.5, 115.9, 127.3, 127.8, (d, *J* = 8.1 Hz), 133.9 (d, *J* = 3.3 Hz), 162 (d, *J*, 247.7) Analysis: C_9H_6FN requires C, 73.46; H, 4.11; F, 12.91; N, 9.52; Found: C, 73.35; H, 4.01; N, 9.13%.

(*E*)-3-(4-chlorophenyl)acrylonitrile (2d): Yield: 82% (0.410 g, 2.58 mmol); White solid; mp. 83-84 °C; IR ($CHCl_3$, cm^{-1}): υ_{max} 956, 1107, 1601, 1624, 2217; *E* isomer ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.86 (d, *J* = 16.6 Hz, 1H), 7.34 (d, *J* = 16.6 Hz, 1H), 7.38 (s, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 97.1, 117.6, 128.4, 129.3, 131.9, 137.2, 148.8; Analysis: C_9H_6ClN requires C, 66.06; H, 3.70; Cl, 21.67; N, 8.56; Found: C, 66.42; H, 3.31; N, 8.25%.

3-(4-(methylthio)phenyl)acrylonitrile (2e): Yield: 89% (0.467 g, 2.67 mmol); gum; IR ($CHCl_3$, cm^{-1}): υ_{max} 856, 1023, 1247, 1560, 1591, 2211; unseparable mixture of *E*/*Z* (2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 3H), 5.80 (d, *J* = 16.6 Hz, 1H), 7.23 (d, *J* = 16.6 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.7, 94.7, 118.1, 125.5, 127.4, 129.6, 143.1, 149.4; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 3H), 5.36 (d, *J* = 12 Hz, 1H), 7.03 (d, *J* = 12 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.6, 93.3, 117.3, 125.3, 129.1, 129.7, 142.9, 147.6; Analysis: $C_{10}H_9NS$ requires C, 68.53; H, 5.18; N, 7.99; S, 18.30; Found: C, 68.39; H, 5.04; N, 7.72%.

3-(4-(trifluoromethyl)phenyl)acrylonitrile (2f): Yield: 82% (0.484 g, 2.46 mmol); White solid; mp. 83-84°C;[26] IR ($CHCl_3$, cm^{-1}): υ_{max} 1220, 1299, 1514, 1589, 2218; unseparable mixture of *E*/*Z* (1.2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.98 (d, *J* = 16.6 Hz, 1H), 7.44 (d, *J* = 16.6 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 99.2, 117.2, 126 (q, *J* = 3.6 Hz), 127.5, 129.1, 132 (q, *J* = 14.6 Hz), 136.6, 148.5; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.60 (d, *J* = 12.1 Hz, 1H), 7.18 (d, *J* = 12.1 Hz, 1H), 7.72 (d, *J* = 6.6 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 97.9, 116.4, 120.8, 125.7 (q, *J* = 3.6 Hz), 129.1, 132.3 (q, *J* = 15 Hz), 136.6, 146.8; Analysis: $C_{10}H_6F_3N$ requires C, 60.92; H, 3.07; F, 28.91; N, 7.10; Found: C, 60.52; H, 3.03; N, 7.01%.

3-(4-nitrophenyl)acrylonitrile (2g): Yield: 79% (0.484 g, 2.46 mmol); Separable *E*/*Z* (4/1) isomers; *E* isomer: Yellow solid; mp. 203-204 °C; IR ($CHCl_3$, cm^{-1}): υ_{max} 889, 1344, 1524, 1621, 2225; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.05 (d, *J* = 16.6 Hz, 1H), 7.47 (d, *J* = 16.6 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 101.6, 116.7, 124.4, 128.1, 139.2, 147.6; *Z* isomer: Yellow solid; mp. 200-201 °C; IR ($CHCl_3$, cm^{-1}): υ_{max} 883, 1374, 1531, 1591, 2217 ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.75 (d, *J* = 11.6 Hz, 1H), 7.32 (d, *J* = 11.6 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 8.14(d, *J* = 8.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 99.2, 117.0, 122.2, 127.3, 141.3, 146.1, 147.6, 134.2, 146.3, 147.2; Analysis: $C_9H_6N_2O_2$ requires C, 62.07; H, 3.47; N, 16.09; O, 18.37; Found: C, 61.92; H, 3.16; N, 16.16%.

3-(2-nitrophenyl)acrylonitrile (2h): Yield: 84% (0.438 g, 2.52 mmol); Separable *E*/*Z* (3/1) isomers; *E* isomer: Yellow solid; mp. 91-92 °C; IR ($CHCl_3$, cm^{-1}): υ_{max} 891, 1201, 1366, 1567, 1605, 2216; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.73 (d, *J* = 16.4 Hz, 1H), 7.56-7-76 (m, 3H), 7.96 (d, *J* = 16.4 Hz, 1H), 8.14 (dd, *J* = 7.7, 1.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 101.7, 116.7, 125.3, 128.7, 129.7, 131.2, 133.9, 146.4, 147.6; *Z* isomer: Yellow solid; mp. 86-87 °C; IR ($CHCl_3$, cm^{-1}): υ_{max} 824, 1199, 1354, 1561, 1643, 2217; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.73 (d, *J* = 11.7 Hz, 1H), 7.61-7.90 (m, 3H), 7.73 (d, *J* = 11.7 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 100.2, 115.7, 125.2, 129.5, 130.6, 130.9, 134.2, 146.3, 147.2; Analysis: $C_9H_6N_2O_2$ requires C, 62.07; H, 3.47; N, 16.09; O, 18.37;Found: C, 62.15; H, 3.29; N, 16.05%.

3-(p-tolyl)acrylonitrile (2i): Yield: 86% (0.369 g, 2.58 mmol); gum; IR ($CHCl_3$, cm^{-1}): υ_{max} 1090, 1215, 1297, 1455, 1517, 2219; unseparable mixture of *E*/*Z* (2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.80 (d, *J* = 16.7 Hz, 1H), 7.22 (d, *J* = 16.7 Hz, 1H), 7.31-7.39 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 95.0, 118.3, 127.3, 129.7, 130.8, 141.7, 150.3; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.36 (d, *J* = 12.1 Hz, 1H), 7.05 (d, *J* = 12.1 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 93.6, 118.3, 128.9, 127.3, 129.7, 130.8, 141.7, 148.4; Analysis: $C_{10}H_9N$ requires C, 83.88; H, 6.34; N, 9.78; Found: C, 83.16; H, 6.42; N, 9.66%.

3-(thiophen-2-yl)acrylonitrile (2j): Yield: 79% (0.320 g, 2.37 mmol); gum; IR ($CHCl_3$, cm^{-1}): υ_{max} 886, 927, 1037, 1290, 1488, 1503, 2218; unseparable mixture of *E*/*Z* (2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.64 (d, *J* = 16.4 Hz, 1H), 7.04-7.07 (m, 1H), 7.24-7.26 (m, 1H), 7.39-7.42 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 94.4, 117.7, 128.3, 129.1, 131.1, 138.3, 142.5; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.26 (d, *J* = 11.7 Hz, 1H), 7.09-7.13 (m, 1H), 7.23 (d, *J* = 11.7 Hz, 1H), 7.50-7.57 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 91.7, 117.3, 127.6, 130.1, 132.2, 137.6, 140.5; Analysis: C_7H_5NS requires C, 62.19; H, 3.73; N, 10.36; S, 23.72; Found: C, 62.05; H, 3.63; N, 10.16%.

3-(furan-2-yl)acrylonitrile (2k): Yield: 84% (0.300 g, 2.52 mmol); Pale yellow oil; IR ($CHCl_3$, cm^{-1}): υ_{max} 975, 1117, 1234, 1601, 1623, 2217; unseparable mixture of *E*/*Z* (2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.76 (d, *J* = 16.2 Hz, 1H), 6.48-6.50 (m, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 7.10 (d, *J* = 16.2 Hz, 1H), 7.49 (d, *J* = 1.5Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 93.9, 112.6, 115.2, 117.2, 135.9, 145.3, 150.1 *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.23 (d, *J* = 12.0 Hz, 1H), 6.53-6.55 (m, 1H), 6.94 (d, *J* = 12.0 Hz, 1H), 7.03-7.07 (m, 1H), 7.57 (d, *J* = 2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 91.5, 112.5, 115.4, 126.7, 134.8, 144.9, 150.0; Analysis: C_7H_5NO requires C, 70.58; H, 4.23; N, 11.76; O, 13.43; Found: C, 70.35; H, 4.11; N, 11.48%.

(4E)-5-phenylpenta-2,4-dienenitrile (2l): Yield: 76% (0.353 g, 2.27 mmol); Colourless liquid; IR ($CHCl_3$, cm^{-1}): υ_{max} 767, 856, 1237, 1555, 2211; unseparable mixture of *E*/*Z* (1.2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.42 (d, *J* = 15.8 Hz, 1H), 6.80-6.87 (m, 2H), 7.07-7.15 (m, 1H), 7.34-7.40 (m, 3H), 7.46-7.48 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 98.4, 118.1, 125.4, 127.6, 129.6, 129.7, 135.3, 141.6, 150.1; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.24 (d, *J* = 10.5 Hz, 1H), 6.90-7.01 (m, 2H), 7.19-7.29 (m, 1H), 7.34-7.42 (m, 3H), 7.44-7.52 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 96.7, 116.4, 124.2, 127.4, 128.9, 129.6, 129.7, 135.2, 141.3, 149.1; Analysis: $C_{11}H_9N$ requires C, 85.13; H, 5.85; N, 9.03; Found: C, 85.06; H, 5.73; N, 8.96%.

(E)-4-(3,4-dimethoxyphenyl)but-3-enenitrile (2m): Yield: 74% (0.451 g, 2.22 mmol); Colourless liquid IR ($CHCl_3$, cm^{-1}): υ_{max} 1089, 1210, 1289, 1504, 1579, 2218; *E* isomer ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.19 (td, *J* = 5.7, 1.3 Hz, 2H), 3.81 (s, 3H), 3.82 (s, 3H), 5.76-5.90 (m, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.71-6.84 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.4, 55.6, 108.8, 111.0, 114.5, 117.1, 119.5, 128.5, 134.1, 148.9; Analysis: $C_{12}H_{13}NO_2$ requires C, 70.92; H, 6.45; N, 6.89; O, 15.74; Found: C, 70.56; H, 6.31; N, 6.25%.

3-(ferrocenyl)acrylonitrile (2n): Yield: 71% (0.504 g, 2.13 mmol); brownish liquid; IR ($CHCl_3$, cm^{-1}): υ_{max} 1142, 1334, 1514, 1621, 2223; unseparable mixture of *E*/*Z* (1.2/1) isomers; *E* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.17 (s, 5H), 4.43 (s, 4H), 5.42 (d, *J* = 16.4 Hz, 1H), 7.25 (d, *J* = 16.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 68.1, 69.8, 71.3, 78.0, 91.9, 118.8, 151.6; *Z* distinct signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.19 (s, 5H), 4.46 (s, 4H), 5.17 (d, *J* = 11.6 Hz, 1H), 6.95 (d, 11.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 68.1, 69.9, 71.2, 77.9, 90.4, 118.4, 144.8; Analysis: $C_{13}H_{11}FeN$ requires C, 65.86; H, 4.68; Fe, 23.56; N, 5.91; Found: C, 65.56; H, 4.43; N, 5.85%.

2-(2-cyanovinyl)-4-methoxybenzonitrile (2o): Yield: 74% (0.408 g, 2.22 mmol); Separable *E*/*Z* (3/1) isomers; *E* isomer: White solid; mp. 128-129 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 547, 709, 767, 833, 856, 1023, 1247, 1597, 2211; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.07 (d, *J* = 16.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.53 Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 7.62 (d, *J* = 16.5 Hz, 1H), 7.64 (d, 8.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.8, 99.9, 104.9, 112.2, 116.1, 116.8, 117.8, 134.5, 137.7, 144.0, 162.9; *Z* isomer: White solid; mp. 111-112 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 657, 711, 840, 872, 1027, 1317, 1547, 2215; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.94 (s, 3H), 5.70 (d, *J* = 12.1 Hz, 1H), 7.01 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.49 (d, *J* = 12.1 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.86 (d, J = 2.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.7, 101.6, 104.1, 111.9, 116.6, 116.8, 135.2, 137.7, 145.5, 162.9; Analysis: $C_{11}H_8N_2O$ requires C, 71.73; H, 4.38; N, 15.21; O, 8.69; Found: C, 71.52; H, 4.16; N, 15.09%.

2-(2-cyanovinyl)-4,5-dimethoxybenzonitrile (2p): Yield: 62% (0.398 g, 1.86 mmol); Separable *E*/*Z* (4/1) isomers; *E* isomer: White solid; mp. 135-136 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 886, 927, 960, 1037, 1290, 1488, 1503, 2223; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.95 (s, 3H), 3.98 (s, 3H), 5.98 (d, *J* = 16.5 Hz, 1H), 7.01 (s, 1H), 7.09 (s, 1H), 7.65 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 54.3, 93.7, 102.2, 106.7, 112.6, 115.1, 116.1, 128.2, 142.9, 149.2, 150.8; *Z* isomer: White solid; mp. 123-124 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 829, 931, 957, 1034, 1251, 1472, 1523, 2219^{1}H NMR (200 MHz, $CDCl_3$) δ 3.96 (s, 3H), 4.02 (s, 3H), 5.60 (d, *J* = 12.1 Hz, 1H), 7.10 (s, 1H), 7.46 (d, *J* = 12.1 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 56.3, 96.9, 106.0, 109.6, 114.1, 116.8, 130.3, 143.6, 150.9, 152.6; Analysis: $C_{12}H_{10}N_2O_2$ requires C, 67.28; H, 4.71; N, 13.08; found: C, 67.79; H, 4.12; N, 13.46%.

6-(2-cyanovinyl)-2,3,4-trimethoxybenzonitrile (2q): Yield: 72% (0.527 g, 2.16 mmol); Separable *E*/*Z* (3/1) isomers; *E* isomer: White solid; mp. 151-152 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 791, 845, 964, 1052, 1239, 1412, 1472, 1533, 1664, 2217; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.91 (s, 3H), 3.96 (s, 3H), 4.06, (s, 3H), 6.03 (d, *J* = 16.5 , 1H), 7.81 (s, 1H), 7.59 (d, *J* = 16.5, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 56.3, 61.1, 61.7, 100.3, 104.6, 114.1, 116.9, 132.2, 143.6, 145.3, 155.8, 157.4; *Z* isomer: White solid; mp. 138-139 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 783, 941, 1056, 1241, 1416, 1534, 1605, 2211; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.93 (s, 3H), 4.00 (s, 3H), 4.07, (s, 3H), 5.64 (d, *J* = 12.2 , 1H), 7.44 (d, *J* = 12.2 , 1H), 7.71 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 56.4, 61.5, 61.8, 98.4, 101.1, 106.5, 114.1, 116.6, 132.0, 143.5, 143.7, 155.9, 157.3; Analysis: $C_{13}H_{12}N_2O_3$ requires C, 63.93 ; H, 4.95 ; N, 11.47; found: requires C, 63.71 ; H, 4.51 ; N, 11.22

2-(2-cyanovinyl)-4,6-dimethoxybenzonitrile (2r): Yield: 74% (0.475 g, 2.22 mmol); Separable *E*/*Z* (4/1) isomers; *E* isomer: Yellow solid; mp. 135-136 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 964, 1107, 1244, 1301, 1624, 2217; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.94 (s, 3H), 6.09 (d, *J* = 16.5 , 1H), 6.52 (s, 1H), 6.64 (s, 1H), 7.61, (d, *J* = 16.5 , 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.9, 56.3, 94.6, 100.1, 101.9, 103.2, 114.4, 116.7, 138.7, 145.8, 163.6, 164.2; *Z* isomer: Yellow solid; mp. 121-122 ^oC; IR ($CHCl_3$, cm^{-1}): υ_{max} 941, 1105, 1213, 1654, 2219; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.94 (s, 3H), 5.72 (d, *J* = 12.1 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 54.3, 93.7, 102.2, 106.8, 112.6, 115.1, 116.1, 128.3, 142.9, 149.2, 150.1; Analysis: $C_{12}H_{10}N_2O_2$ requires C, 67.28 ; H, 4.71 ; N, 13.08; found: requires C, 67.61 ; H, 4.42 ; N, 13.15.

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