Synthesis, characterisation and photophysical properties of α,β-diaryl-acrylonitrile derivatives

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α,β-Diarylacrylonitrile derivatives can be prepared by two different routes: (1) the intermolecular condensation of the same arylacetonitriles (2) the condensation of arylaldehydes and arylacetonitriles with a catalytic amount of $NaOCH_3$ at room temperature. Several α,β-diarylacrylonitrile derivatives have been synthesised in this paper and characterised. The UV-vis absorption and photoluminescent (PL) spectra of the products were investigated.

Keywords: arylacetonitrile, arylaldehyde, α,β-diarylacrylonitrile, intermolecular condensation, photophysical property

The biaryl unit is a useful group in many classes of natural products[1,2] and α,β-diarylacrylonitriles are of considerable economic interest since nitriles serve as versatile intermediates in the synthesis of variety of products such as perfumes, sex pheromones, vitamin A and pigments.[3,4] Many approaches to synthesis of these compounds have been reported.[2-10] Niederl and Ziering described the synthesis and estrogenic character of a number of alkoxy cyanostilbenes.[5] John and co-workers reported the direct conversion of carbonyl compounds into α, β-unsaturated nitriles in the presence of nitriles.[6] Russel and Hunziker studied the condensation of substituted phenylacetic acids and aromatic aldehydes in refluxing acetic anhydride in the presence of triethylamine.[8] Furthermore, a mild and efficient route to prepare phenanthrane derivatives using an intramolecular biaryl oxidative coupling of stilbenes by vanadium oxytrichloride was reported by Huang and coworkers.[2] Motokura *et al* studied ruthenium-grafted hydrotalcite as a multifunctional catalyst for the direct α-alkylation of nitriles with primary alcohols.[9] Buskley and Rapoport reported the condensation of nitriles and aldehydes using NaOEt at reflux in ethanol.[10] However, in previous syntheses of diarylacrylonitriles, either a base and solvent or expensive reagents were used.

In our previous work, we studied the synthesis and photophysical properties of some tertiary arylamines.[11-15] We now report two different synthetic routes to α, β-diarylarylonitrile derivatives and their photophysical properties.

Under optimised conditions, arylacetonitriles undergo intermolecular condensation in the presence of $NaNH_2$ giving α,β-diarylarylonitrile derivatives (see Scheme 1). We have found that 3,4-dimethoxyphenylacetonitrile and 4-methoxyphenylacetonitrile can form diarylacrylonitriles at reflux temperture in toluene, but reaction does not take place at room temperature. Phenylacetonitrile and 4-chlorophenylacetonitrile give diarylacrylonitriles at room temperature while the yields of the products were very poor at reflux temperature as demonstrated in Table 1.

Table 1 Products, conditions and yields of the reactions

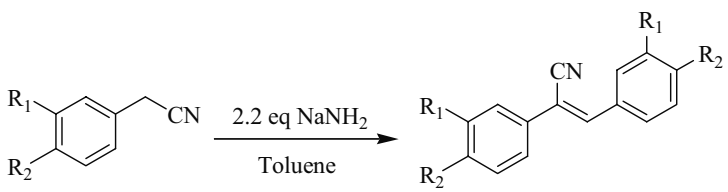
Entry	R^1	R^2	R^3	R^4	Temp. /°C	Time /h	Yield[a] /%
2a	OMe	OMe	OMe	OMe	Reflux	20	82[b]
2b	H	OMe	H	OMe	Reflux	6	50[b]
2c	H	H	H	H	r.t.	6	70[b]
2c	H	H	H	H	Reflux	6	30[b]
2d	H	Cl	H	Cl	r.t.	6	45[b]
2d	H	Cl	H	Cl	Reflux	6	20[b]
2b	H	OMe	H	OMe	r.t.	2	92[c]
2c	H	H	H	H	r.t.	1	95[c]
2d	H	Cl	H	Cl	r.t.	1	97[c]
2e	OMe	OMe	H	H	r.t.	2	94[c]
2f	H	Cl	H	H	r.t.	1	97[c]
2g	H	OMe	H	H	r.t.	2	93[c]
2h	H	H	H	OMe	r.t.	2	94[c]
2i	OMe	OMe	H	OMe	r.t.	3	92[c]
2j	H	Cl	H	OMe	r.t.	1	94[c]
2k	H	H	H	Cl	r.t.	1	95[c]
2l	OMe	OMe	H	Cl	r.t.	2	94[c]
2m	H	OMe	H	Cl	r.t.	2	95[c]
2n	H	NO_2	H	H	r.t.	1	90[c]

[a]Isolated yields; [b]Method 1; [c]Method 2.

The condensation of arylaldehydes and arylacetonitriles gives α,β-diarylarylonitrile derivatives with $NaOCH_3$ in ethanol. The results are shown in Scheme 2 and Table 1. The products were obtained in high to quantitative yields in short reaction times compared to the first method.

All products were obtained as single stereoisomers, and identified using IR, ^{1}H NMR, ^{13}C NMR, mass spectra and elemental analysis as appropriate. The formation of a single (*Z*)-isomer was established by TLC and ^{1}H NMR measurements.

Further experiments on preparation of such derivatives are shown in Scheme 3 and Table 2. Naphthaldehyde replaced benzaldehyde and reacted with arylacetonitriles to afford several new compounds.



2a-d

R_1 = OMe; H; R_2 = OMe, H, Cl

Scheme 1

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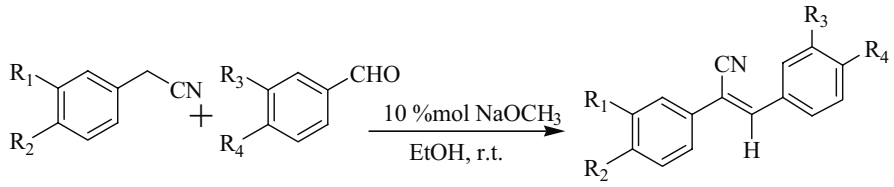
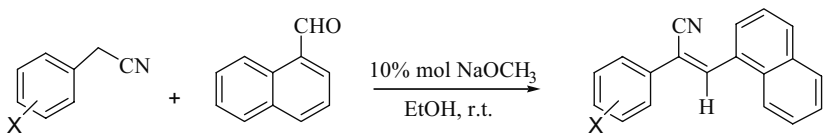


2b-n

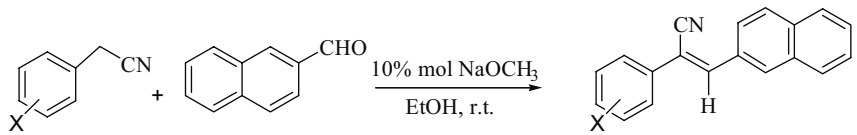
R_1 =OMe, H; R_2 =OMe, H, Cl, NO_2

R_3 =OMe, H; R_4 =OMe, H, Cl

Scheme 2



X= H; *p*-Cl, *p*-Br, *p*-NO2; *m*-NO_2 **3a-e**



X= H; *p*-Cl, *p*-Br, *p*-NO2; *m*-NO_2 **3f-j**

Scheme 3

In order to investigate their photophysical properties, the UV-vis and photoluminescent (PL) spectra of compounds in CH_2Cl_2 solution and the solid state were recorded. The spectroscopic data are summarised in Tables 3 and 4.

The lowest UV-vis absorption maxima in CH_2Cl_2 solution appear in the region of 315–369 nm and are assigned to the π–π^* transitions of the compounds. All these compounds emit light strongly in the solution and in the solid state. They exhibit emission with λ_{max} in the range of 390–490 nm in CH_2Cl_2 and 399–529 nm in the solid state. The emission peaks of the compounds in the solid state show red shifts 10–80 nm from the peaks in CH_2Cl_2 solution except for **2k**, indicating intermolecular interactions in their solid states.

As Table 4 shows, replacement of the H atom in **3a** by a more powerful electron-acceptor group, such as Cl, Br and NO_2, gives compounds (**3b, 3c, 3d, 3e**), which have emission at much longer wavelengths. The compound (**3i**) shows a considerable red-shift with emission at 518 nm.

Table 2 Reaction conditions and yields of α,β-diarylacrylonitrile derivatives (**3a–j**)

Entry	X	Time/h	Yield/%
3a	H	2	82
3b	*p*-Cl	1	88
3c	*p*-Br	1	90
3d	*p*-NO_2	1	89
3e	*m*-NO_2	1	87
3f	H	1.5	86
3g	*p*-Cl	1	90
3h	*p*-Br	1	88
3i	*p*-NO_2	1	91
3j	*m*-NO_2	1	89

Table 3 Photophysical properties of compounds (**2a–n**)

Entry	$^a\lambda_{max}^{abs}$/nm	$^b\lambda_{max}^{em}$/nm	$^c\lambda_{max}^{em}$/nm
2a	360,226	441	500
2b	346,239	426	468
2c	315,232	390	399
2d	323,236	398	431
2e	345,275,240	445	463
2f	319,233	395	438
2g	322,236	414	470
2h	323,238	420	432
2i	352,242,227	440	468
2j	343,239	443	527
2k	323,235	458	410
2l	353,280,241	448	471
2m	339,238	421	439
2n	338,227	430	437

[a]Maximum absorption wavelength in CH_2Cl_2 solution; [b]Maximum emission wavelength in CH_2Cl_2 solution; [c]Maximum emission wavelength in the solid state.

Table 4 Photophysical properties of compounds (**3a–j**)

Entry	$^a\lambda_{max}^{abs}$/nm	$^b\lambda_{max}^{em}$/nm	$^c\lambda_{max}^{em}$/nm
3a	341,232	420	481
3b	345,232	431	498
3c	348,231	437	484
3d	369,297,232	464	529
3e	350,296,232	456	497
3f	334,281,241	412	432
3g	338,282,242	420	423
3h	336,282,243	418	424
3i	353,264,237	490	518
3j	330,279,232	453	500

[a]Maximum absorption wavelength in CH_2Cl_2 solution; [b]Maximum emission wavelength in CH_2Cl_2 solution; [c]Maximum emission wavelength in the solid state.

Experimental

Chemicals were purchased from Aldrich. Thin layer chromatography (TLC) on commercial plates of silica gel GF_{254} was used to monitor the progress of the reactions. Yields refer to isolated products after purification. Melting points were determined on a YANACO melting point apparatus and are uncorrected. Infrared(IR) spectra were taken on a Nicolet 230 FT-IR spectrophotometer. ^{1}H NMR or ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance 500 DMX and 400 DMX spectrometers using TMS as internal standard. Elemental analysis was carried out on an Eager 200 instrument. Mass spectra were obtained from a Bruker Esquire 3000 plus instrument. Uv-vis spectra were recorded on a Hitachi U-3300 spectrophotometer and photoluminescence (PL) spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer.

Typical procedure for synthesis of α, β-*diarylacrylonitrile derivatives*

Method 1: The arylacetonitrile (10 mmol) was added to one portion of $NaNH_2$ (22 mmol) in toluene (25 mL). The reaction mixture was stirred for an appropriate time at room temperature or at reflux temperature. Some toluene was added to dissolve the material and this solution was then worked with H_2O (30 mL) 3 times. After drying over Na_2SO_4, filtration and removal of solvents the crude product was purified by washing with small portions of cold acetone or by column chromatography on silica gel using acetic ether/hexane as eluent.

Method 2: To a solution of the arylacetonitrile (10 mmol) and the aromatic aldehyde (10 mmol) in EtOH (absolute, 20 mL) was added in one portion 1 mmol $NaOCH_3$. The reaction mixture was stirred for an appropriate time at room temperature, filtered and washed with small portions of cold EtOH to afford the products.

(Z)-2,3-bis(3,4-dimethoxyphenyl)acrylonitrile (**2a**): M.p. 154–155 °C (lit.,[16] 155–156 °C); IR υ_{max} (KBr)/cm^{-1}: 3001, 2936, 2208, 1605, 1516, 1262, 1026; ^{1}H NMR(400 MHz, $CDCl_3$) δ_H: 7.68 (d, J = 1.5 Hz, 1 H), 7.35 (d, J = 1.9 Hz, 2 H), 7.24–7.22 (m, 1 H), 7.13 (d, J = 0.8 Hz, 1 H), 6.93–6.90 (m, 2 H), 3.97 (s, 3 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.93 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ: 151.06 (C), 149.94 (C), 149.44 (C), 149.19 (C), 140.62 (CH), 127.86 (C), 127.08 (C), 124.18 (CH), 118.99 (CH), 118.97 (C), 111.47 (CH), 111.11 (CH), 110.88 (CH), 108.82 (CH), 108.74 (C), 56.24 (CH_3), 56.23 (CH_3), 56.19 (CH_3), 56.17 (CH_3). MS: *m/z*: Calcd for $C_{19}H_{19}NO_4$ 325.4. Found: 325.1.

(Z)-2,3-bis(4-methoxyphenyl)acrylonitrile (**2b**): M.p. 106–107 °C (lit.,[5] 108 °C); IR υ_{max}(KBr)/cm^{-1}: 3002, 2963, 2838, 2213, 1605, 1514, 1254, 1176, 1024; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.86 (d, J = 4.2 Hz, 2 H), 7.59 (d, J = 4.4 Hz, 2 H), 7.36(s, 1 H), 6.97 (dd, J = 3.6 Hz, J = 4.6 Hz, 4 H), 3.87 (d, J = 3.6 Hz, 6 H).

(Z)-2,3-diphenylacrylonitrile (**2c**): M.p. 49–50 °C (lit.[17], 49–51 °C); IR υ_{max}(KBr)/cm^{-1}: 3055, 3032, 2219, 1492, 1447, 1020; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.88 (d, J = 3.5 Hz, 2 H), 7.67 (d, J = 3.6 Hz, 2 H), 7.54 (s, 1 H), 7.49–7.38 (m, 6 H).

(Z)-2,3-bis(4-chlorophenyl)acrylonitrile (**2d**): M.p. 107–108 °C (lit.,[17] 108.5–109 °C); IR υ_{max}(KBr)/cm^{-1}: 3043, 2226, 1593, 1495, 1095, 1016; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.83(d, J = 4.4 Hz, 2 H), 7.61 (d, J = 4.4 Hz, 2 H), 7.46–7.42 (m, 5 H).

(Z)-2-(3,4-dimethoxyphenyl)-3-phenylacrylonitrile (**2e**): M.p. 85–86 °C (lit.,[5] 87 °C); IR υ_{max}(KBr)/cm^{-1}: 3002, 2954, 2834, 2222, 1601, 1512, 1265, 1252, 1148, 1024; ^{1}H NMR(400 MHz, $CDCl_3$) δ_H: 7.86 (dd, J = 0.8 Hz, J = 3.5 Hz, 2 H), 7.45 (dd, J = 3.7 Hz, J = 1.5 Hz, 4 H), 7.28–7.26 (m, 1 H), 7.15 (d, J = 1 Hz, 1 H), 6.92 (d, J = 4.2 Hz, 1 H), 3.96 (s, 3 H), 3.93 (s, 3 H).

2-(4-chlorophenyl)-3-phenylacrylontrile (**2f**): M.p. 110–111 °C (lit.,[18] 110–110 °C); IR υ_{max}(KBr)/cm^{-1}: 3056, 2218, 1598, 1495, 1095, 1013; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 7.76 (d, J = 4.7 Hz, 2 H), 7.61 (d, J = 4.3 Hz, 2 H), 7.51 (s, 1 H), 7.48–7.41 (m, 5 H).

(Z)-2-(4-methoxyphenyl)-3-phenylacrylonitrile (**2g**): M.p. 92–93 °C (lit.[5], 94 °C); IR υ_{max}(KBr)/cm^{-1}: 3004, 2948, 2834, 2215, 1606, 1509, 1257, 1180, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.87 (d, J = 3.4 Hz, 2 H), 7.62 (d, J = 4.6 Hz, 2 H), 7.47–7.42 (m, 4 H), 6.97 (d, J = 4.4 Hz, 2 H), 3.86 (s, 3 H).

(Z)-3-(4-methoxyphenyl)-2-phenylacrylonitrile (**2h**): M.p. 91–92 °C (lit.,[18] 92.5–93.5 °C); IR υ_{max}(KBr)/cm^{-1}: 3014, 2844, 2209, 1603, 1512, 1256, 1182; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.90 (d, J = 4.4 Hz, 2 H), 7.66 (d, J = 3.6 Hz, 2 H), 7.47–7.42 (m, 3 H), 7.38 (d, J = 3.8 Hz, 1 H), 6.99 (d, J = 4.6 Hz, 2 H), 3.88 (s, 3 H).

(Z)-2-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)acrylonitrile (**2i**): M.p. 129–131 °C (lit.,[5] 129 °C); IR υ_{max}(KBr)/cm^{-1}: 3006, 2967, 2212, 1605, 1513, 1256, 1177, 1150; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.87 (d, J = 4.4 Hz, 2 H), 7.37 (s, 1 H), 7.23 (d, J = 4.2 Hz, 1 H), 7.13 (s, 1 H), 6.98 (d, J = 4.2 Hz, 2 H), 6.91 (d, J = 4.2 Hz, 1 H), 3.96 (s, 3 H), 3.93 (s, 3 H), 3.87 (s, 3 H).

(Z)-2-(4-chlorophenyl)-3-(4-methoxyphenyl)acrylonitrile (**2j**): M.p. 110–111 °C (lit.,[18] 108.5–109 °C); IR υ_{max}(KBr)/cm^{-1}: 3014, 2967, 2839, 2214, 1605, 1594, 1512, 1266, 1176, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.89 (d, J = 4.4 Hz, 2 H), 7.59 (d, J = 4.4 Hz, 2 H), 7.42 (dd, J = 4.8 Hz, J = 4.4 Hz, 3 H), 6.99 (d, J = 4.6 Hz, 2 H), 3.88 (s, 3 H).

(Z)-3-(4-chlorophenyl)-2-phenylacrylonitrile(**2k**):M.p.109–110 °C (lit.,[18] 110–110.5 °C); IR υ_{max}(KBr)/cm^{-1}: 3047, 3009, 2218, 1601, 1516, 1019; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.83 (d, J = 4.2 Hz, 2 H), 7.67 (d, J = 3.6 Hz, 2 H), 7.49–7.41 (m, 6 H).

(Z)-3-(4-chlorophenyl)-2-(3,4-dimethoxyphenyl)acrylonitrile (**2l**): M.p. 115–116 °C (lit.,[5] 115 °C); IR υ_{max}(KBr)/cm^{-1}: 3057, 3030, 2218, 1588, 1492, 1091; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 7.81 (d, J = 4.4 Hz, 2 H), 7.43 (d, J = 4.6 Hz, 2 H), 7.38 (s, 1 H), 7.26 (t, J = 2.2 Hz, J = 1.0 Hz, 1 H), 7.14 (d, J = 1.0 Hz, 1 H), 6.92 (d, J = 4.2 Hz, 1 H), 3.96 (s, 3 H), 3.93 (s, 3H).

(Z)-3-(4-chlorophenyl)-2-(4-methoxyphenyl)acrylonitrile (**2m**): M.p. 109–110 °C (lit.,[18] 108.5–109 °C); IR υ_{max}(KBr)/cm^{-1}: 3010, 2938, 2832, 2219, 1605, 1511, 1095; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.79 (d, J = 4.4 Hz, 2 H), 7.60 (d, J = 4.4 Hz, 2 H), 7.42 (d, J = 4.4 Hz, 2 H), 7.37 (s, 1 H), 6.96 (d, J = 4.4 Hz, 2 H), 3.86 (s, 3 H).

(Z)-2-(4-nitrophenyl)-3-phenylacrylonitrile (**2n**): M.p. 176–177 °C (lit.,[19] 175–176 °C); IR υ_{max}(KBr)/cm^{-1}: 3029, 2220, 1606, 1594, 1513, 1342, 1209, 1114; ^{1}H NMR(400 MHz, $CDCl_3$)δ_H: 8.34–8.32 (m, 2 H), 7.96–7.94 (m, 2 H), 7.88–7.86 (m, 2 H), 7.70 (s, 1 H), 7.52 (dd, J = 1.6 Hz, J = 1.4 Hz, 3H).

(Z)-3-(naphthalen-l-yl)-2-phenylacrylonitrile (**3a**): M.p. 108–109 °C (lit.,[18] 110–110.5 °C); IR υ_{max}(KBr)/cm^{-1}: 3042, 2214, 1590, 1507, 1448, 778, 757, 678; ^{1}H NMR(400 MHz, $CDCl_3$)δ_H: 8.29(s, 1H), 8.10 (d, J = 7.2 Hz, 1H),7.97(m, 3H), 7.79 (d, J = 7.6 Hz, 2H), 7.59 (m, J = 8.0 Hz, 3H), 7.51 (m, 3H).

(Z)-2-(4-chlorophenyl)-3-(naphthalen-l-yl)acrylonitrile (**3b**): M.p. 173–174 °C (lit.,[18] 174–175 °C); IR υ_{max}(KBr)/cm^{-1}: 3042, 2218, 1594, 1490, 1407, 1095, 824, 778; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (s, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.94 (m, 3H), 7.71 (d, J = 8.8 Hz, 2H), 7.58 (m, 3H), 7.47 (d, J = 8.8 Hz, 2H).

(Z)-2-(4-bromophenyl)-3-(naphthalen-l-yl)acrylonitrile (**3c**): M.p. 179–180 °C (lit.[20]); IR υ_{max}(KBr)/cm^{-1}: 3063, 2218, 1594, 1511, 1486, 1070, 824, 778; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 8.28 (s,1H), 8.09 (d, J = 7.2 Hz, 1H), 7.94 (m, J = 8.0 Hz 3H), 7.60 (m, 7H).

(Z)-3-(naphthalen-l-yl)-2-(4-nitrophenyl)acrylonitrile (**3d**): M.p. 191–192 °C (lit.[21]); IR υ_{max}(KBr)/cm^{-1}: 3071, 2214, 1594, 1569, 1515, 1344, 853, 778, 749; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 8.50 (s, 1H), 8.36 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 7.2 Hz, 1H) 7.95 (m, 5H), 7.61 (m, 3H).

(Z)-3-(naphthalen-l-yl)-2-(3-nitrophenyl)acrylonitrile (**3e**): M.p. 170–171 °C; IR υ_{max}(KBr)/cm^{-1}: 3076, 2218, 1594, 1577, 1523, 1353, 774, 732; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.64 (s, 1H), 8.45 (s, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.14(m, 2H), 7.99 (m, 3H), 7.71 (t, J = 8.0 Hz, 1H),7.62 (m, 3H). Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33. Found: C, 75.72; H, 4.19; N, 9.22%.

(Z)-3-(naphthalene-2-yl)-2-phenylacrylonitrile (**3f**): M.p. 117–118 °C (lit.[22]); IR υ_{max}(KBr)/cm^{-1}: 3059, 2210, 1590, 1494, 1448, 820, 745, 683; ^{1}H NMR(400 MHz, $CDCl_3$) δ_H: 8.29 (s, 1H), 8.10 (d, J = 8.8 Hz, 1H), 7.89 (m, J = 8.0 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.69 (s, 1H), 7.52 (s, 2H),7.54 (m, 2H), 7.46 (m, 3H).

(Z)-2-(4-chlorophenyl)-3-(naphthalen-2-yl)acrylonitrile (**3g**): M.p. 169–171 °C; IR υ_{max}(KBr)/cm^{-1}: 3046, 2222, 1598, 1490, 1465, 1103, 828, 741; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 8.27 (s, 1H), 8.08 (d, J = 10.4 Hz, 1H), 7.88 (m, J = 8.4 Hz, 2H), 7.64 (t, J = 3.6 Hz, 1H), 7.57 (t, J = 7.2 Hz, 3H), 7.53 (d, J = 6.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H). Anal. Calcd for $C_{19}H_{12}ClN$: C, 78.76; H, 4.17; N, 4.83. Found: C, 78.64; H, 4.30; N, 4.75%.

(Z)-2-(4-bromophenyl)-3-(naphthalen-2-yl)acrylonitrile (**3h**): M.p. 169–171 °C; IR υ_{max}(KBr)/cm^{-1}: 3051, 2214, 1606, 1581, 1561, 1492, 1078, 824, 745; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 8.29 (s, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.0 Hz 2H), 7.87 (d, J = 7.6 Hz, 1H),7.67 (s, 1H), 7.59 (s, 6H). Anal. Calcd for $C_{19}H_{12}BrN$: C, 68.28; H, 3.62; N, 4.19. Found: C, 68.26; H, 3.62; N, 4.19%.

(Z)-3-(naphthalen-2-yl)-2-(4-nitrophenyl)acrylonitrile (**3i**): M.p. 209–210 °C (lit.[21]); IR υ_{max}(KBr)/cm^{-1}: 3055, 2210, 1606, 1586, 1511, 1340, 853, 745; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 8.36 (t, J = 6.0 Hz, 3H),8.16 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 3.2 Hz, 2H), 7.91 (d, J = 8.8 Hz, 3H), 7.85 (s, 1H), 7.60 (m, 2H).

(Z)-3-(naphthalen-2-yl)-2-(3-nitrophenyl)acrylonitrile (**3j**): M.p. 209–210 °C; IR υ_{max}(KBr)/cm^{-1}: 3076, 2218, 1594, 1577, 1523, 1353, 891, 774; ^{1}H NMR (400 MHz, $CDCl_3$)δ_H: 8.60 (s, 1H), 8.37 (s, 1H),

8.29 (d, J = 8.0 Hz, 1H), 8.15 (t, J = 7.6 Hz, 1H),8.08 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H) 7.84 (s, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.60 (m, 2H). Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33. Found: C, 75.87; H, 4.15; N, 9.26%.

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