ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2014, **1**, 1123

Received 31st July 2014,
Accepted 5th September 2014

DOI: 10.1039/c4qo00218k

rsc.li/frontiers-organic

Palladium(II)-catalyzed direct conversion of allyl arenes into alkenyl nitriles†

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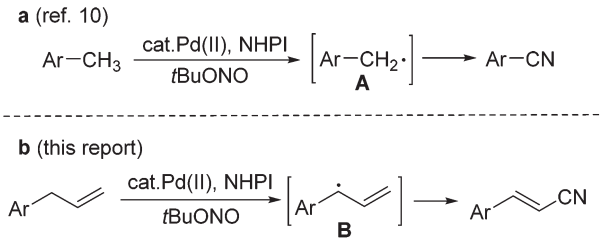
A mild palladium-catalyzed ammoxidation approach, which leads to the formation of the C≡N triple bond in an allyl group, has been developed to directly convert allylarenes into alkenyl nitriles.

Introduction

Alkenyl nitriles are both unique structural units in organic synthesis and versatile building blocks of natural products, agricultural chemicals, pharmaceuticals, and dyes.[1] Due to their important applications in various fields, efforts have been devoted to the development of efficient synthetic methods for this type of nitrile compound.[2] However, most of the methods so far developed are based on functional group transformations or addition reactions. To the best of our knowledge, there is only one case in which a Fe-catalyzed direct conversion of the allyl derivatives into the corresponding unsaturated nitriles was reported.[3,4] Qin and Jiao have demonstrated the oxidative C–H bond transformation of allyl arenes or alkenes into the corresponding nitriles, with Me_3SiN_3 as the nitrogen source and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as the oxidant.[4] The allyl radical generated through single-electron-transfer is proposed as the key step intermediate in this transformation. This allylic C–H bond transformation is related to the recent studies on the transition-metal-catalyzed direct allylic C–H functionalization of terminal alkenes, which has emerged as a powerful strategy in organic synthesis.[5–9]

On the other hand, we have recently reported a direct synthesis of aromatic nitriles from the methyl arenes with $Pd(OAc)_2$ and *N*-hydroxyphthalimide (NHPI) as the catalysts, and *tert*-butyl nitrite (*t*BuONO, TBN) as the nitrogen source.[10] Benzyl radical **A** is proposed as the key intermediate in the reaction (Scheme 1a). As the continuation of our interest in the development of novel cyanation methods,[11] we further conceived that a similar allyl radical **B** should also be generated in a similar catalytic system, and a direct conversion of terminal alkenes into alkenyl nitriles might be achieved. Herein, we report a Pd-catalyzed direct transformation of allyl arenes into the corresponding alkenyl nitriles, using *tert*-butyl nitrite as both the nitrogen source and oxidant. The reaction proceeds under mild conditions, affording moderate to good yields of alkenyl nitriles (Scheme 1b).



Scheme 1 $Pd(OAc)_2$-catalyzed cyanation of methyl arenes and allyl arenes.

Results and discussion

Similar to our previous study,[10] the investigation began with evaluation of the direct transformation of 1-allylbenzene **1a** into the corresponding cinnamonitrile **2a** under oxidative conditions (Table 1). In the absence of an additive, the reaction of **1a** catalyzed by 10 mol% of $Pd(OAc)_2$ with *tert*-butyl nitrite at 60 °C in DCE or THF gave only a trace amount of **2a** (entries 1 and 2), whereas the reaction in 1,4-dioxane and acetonitrile produced **2a** in 14% and 26% yield, respectively (entries 3 and 4). Gratifyingly, **2a** was formed in 62% yield in the presence of *N*-hydroxyphthalimide (NHPI) as an additive in a catalytic amount (30 mol%) with 5 mol% of $Pd(OAc)_2$ (entry 5). The reaction could be optimized using 10 mol% of $Pd(OAc)_2$ at 50 °C (entry 6). We also examined another carbon radical producing catalyst *N*,*N*′,*N*″-trihydroxyisocyanuric acid (THICA) as an additive.[12] The reaction afforded **2a**, *albeit* in diminished

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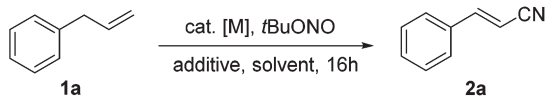
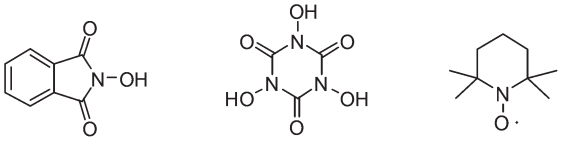
†Electronic supplementary information (ESI) available: Preparation of substrates, characterization data, ^1H, ^{13}C NMR, MS and IR spectra. See DOI: 10.1039/c4qo00218k

Table 1 Optimization of reaction conditions[a]



Entry	Cat. (mol%)	TBN (equiv.)	Additive (mol%)	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$ (10)	3	None	DCE	Trace
2	$Pd(OAc)_2$ (10)	3	None	THF	Trace
3	$Pd(OAc)_2$ (10)	3	None	Dioxane	14
4	$Pd(OAc)_2$ (10)	3	None	MeCN	26
5	$Pd(OAc)_2$ (5)	3	NHPI (30)	MeCN	62
6	**$Pd(OAc)_2$ (10)**	**2**	**NHPI (30)**	**MeCN**	**80**
7	$Pd(OAc)_2$ (10)	2	THICA (10)	MeCN	56
8	$Pd(OAc)_2$ (10)	2	TEMPO (30)	MeCN	26
9	$PdCl_2(MeCN)_2$ (10)	2	NHPI (20)	MeCN	11
10	$Cu(OAc)_2$ (10)	2	NHPI (20)	MeCN	Trace
11	CuCl (10)	2	NHPI (20)	MeCN	Trace
12	$Fe(OAc)_2$ (10)	2	NHPI (20)	MeCN	Trace

[a] The reaction conditions: **1a** (0.3 mmol), catalyst, additive, and *tert*-butyl nitrite (TBN) in a dry solvent with stirring under N_2 for 16 h. [b] Isolated yields. NHPI: *N*-hydroxyphthalimide; THICA: *N*,*N*′,*N*″-trihydroxyisocyanuric acid. TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy.

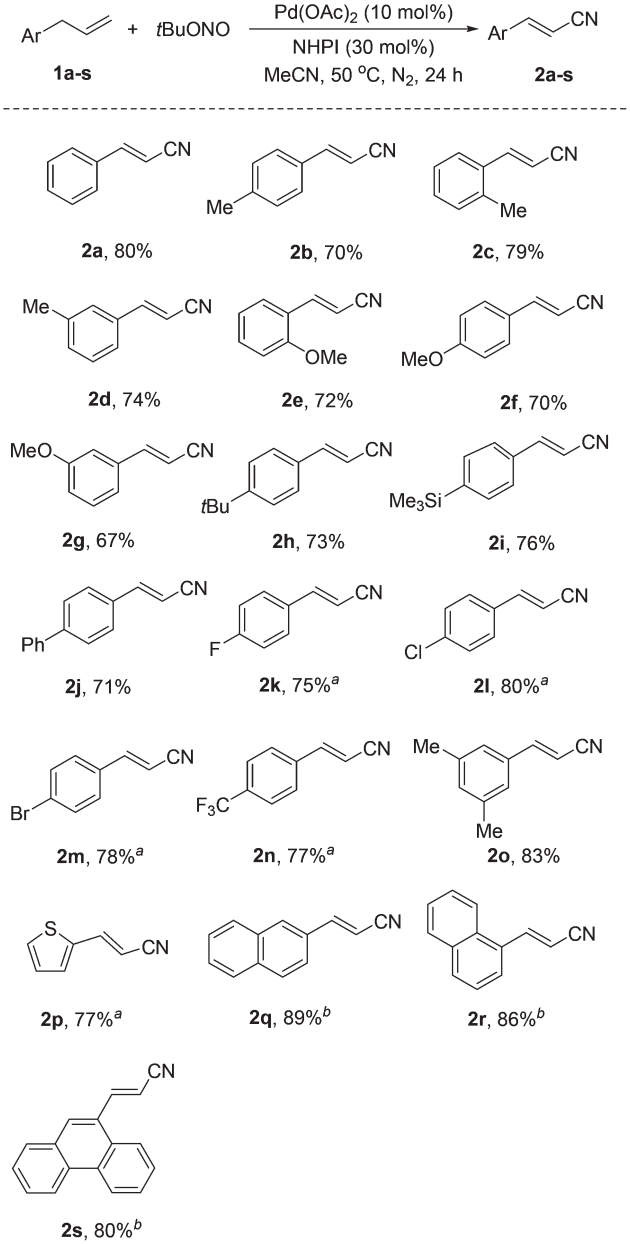


yield. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) has also been examined as an additive, however the reaction only gives **2a** in 26% yield (entry 8). Other metal catalysts, including $PdCl_2(MeCN)_2$, $Cu(OAc)_2$, CuCl and $Fe(OAc)_2$, have also been examined but they only afforded a very low yield or a trace amount of the product **2a** (entries 9–12).

With the optimized reaction conditions, various allylarenes were investigated with 10 mol% $Pd(OAc)_2$ and 30 mol% NHPI as a co-catalyst system (Scheme 2). Electron-donating substituents, such as Me and OMe, at the *para*, *meta*, and *ortho* positions of the arene group did not affect the reaction, affording the corresponding alkenyl nitriles in 67–83% yields (**2b–h**, **2o**). Remarkably, some sensitive substituents or functional groups, such as trimethylsilyl (TMS), Cl and Br, were tolerated well in this transformation (**2h**, **2l**, **2m**). Substrates substituted with electron-withdrawing groups, such as F and CF_3, also worked well and afforded the desired products in moderate yields (**2k**, **2n**).

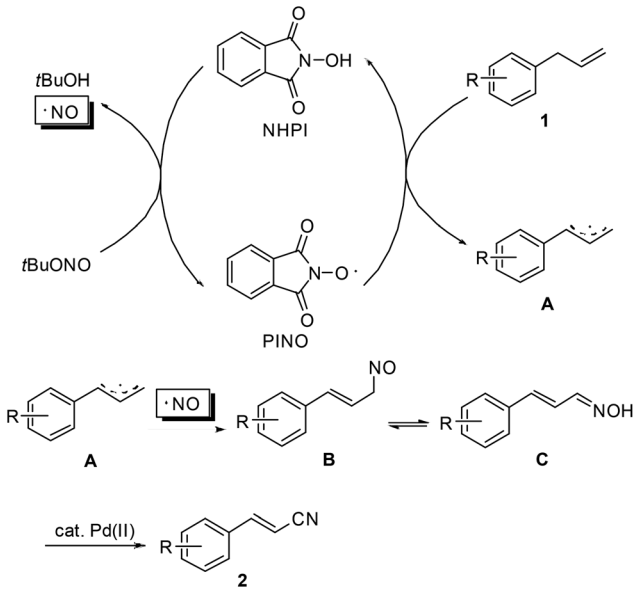
It is noteworthy that this reaction also worked with a heteroaryl-substituted propene, 1-allyl-2-thiophene (**1p**), giving **2p** in 77% yield. In addition, polycyclic aromatic-substituted propenes were also successfully converted into the corresponding alkenyl nitriles in good yields (**2q–s**).

Similar to the transformation of methyl arenes into aromatic nitriles,[10] a plausible mechanism is proposed as shown in Scheme 3. Initially, as an oxidant, *tert*-butyl nitrite reacts



Scheme 2 Scope of the Pd-catalyzed direct conversion of allylarenes into alkenyl nitriles. If not otherwise noted, the reaction conditions are as following: **1a–s** (0.3 mmol), *tert*-butyl nitrite (0.6 mmol), $Pd(OAc)_2$ (0.03 mmol), and NHPI (0.09 mmol) in MeCN (1.5 mL) at 50 °C under N_2 for 24 h. Yields of isolated products are given. [a]*tert*-Butyl nitrite (2.5 equiv.) was used. [b]*tert*-Butyl nitrite (3.0 equiv.) was used.

with NHPI to generate the active phthalimide *N*-oxyl radical (PINO). The *tert*-butyl nitrite itself decomposes into an NO radical and 2-methyl-2-propanol.[13] Then, allyl arene **1** undergoes single-electron-transfer (SET) oxidation with PINO to produce the corresponding allyl radical **A**. Subsequently, radical recombination of the NO radical with **A** occurs to form intermediate **B**. Upon isomerization of **B** to aldoxime **C**, Pd-$(OAc)_2$-catalyzed dehydration of **C** finally leads to the desired nitrile product **2**.[14] To substantiate this mechanistic hypo-



Scheme 3 Proposed mechanism.

thesis, we have carried out the reaction of **1a** under the standard conditions but in the absence of the $Pd(OAc)_2$ catalyst. The reaction gave a complex mixture, from which oxime **C** along with the corresponding cinnamaldehyde can be identified by GC-MS.

In conclusion, we have developed a novel Pd(II)-catalyzed direct synthesis of alkenyl nitriles from the corresponding allyl arenes under mild conditions using *tert*-butyl nitrite as the nitrogen source and inexpensive NHPI as the co-catalyst. Notably, in this transformation, three C–H bonds are cleaved to form one C≡N bond. This reaction offers a novel method for the synthesis of biologically and medicinally important alkenyl nitriles.

Experimental section

General

All the palladium-catalyzed reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled under a nitrogen atmosphere prior to use. 1,4-Dioxane and THF were dried over Na with the benzophenone-ketyl intermediate as an indicator. Acetonitrile and 1,2-dichloroethane were dried over CaH_2. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with a Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. LRMS were obtained on an Agilent 5975C inert 350 EI mass spectrometer. HRMS were obtained on a Bruker Apex IV FTMS by ESI or a GCT CA127 Micronass UK by EI. All reactions were carried out in dry sealed tubes under an atmosphere of nitrogen. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The starting materials **1a–o** and **1q–s** were prepared from the corresponding aryl bromide according to a previously reported literature.[7d] **1p** was prepared from thiophene according to a previously reported literature.[15]

General procedure for Pd(II)-catalyzed reaction

Under a nitrogen atmosphere, allylbenzene **1a** (36 mg, 0.3 mmol), *tert*-butylnitrite (65 mg, 0.6 mmol, 2.0 equiv.), NHPI (16 mg, 0.09 mmol, 0.3 equiv.) and $Pd(OAc)_2$ (7 mg, 0.03 mmol, 0.1 equiv.) in MeCN (1.5 mL) were stirred at 50 °C for 16 h. After cooling, the reaction was diluted with CH_2Cl_2 (2 mL) and the resulting mixture was filtered, and the filtrate was concentrated. Purification by column chromatography of the mixture gave pure **2a** as light yellow oil (31 mg, 80%).[4] ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.46 (m, 6H), 5.88 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 133.5, 131.2, 129.1, 127.3, 118.1, 96.3.

***trans*-4-Methylcinnamonitrile (2b).** The general procedure gave pure **2b** as a white solid (30 mg, 70% yield).[4] ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, J = 16.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.81 (d, J = 16.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.4, 141.7, 130.8, 129.8, 127.3, 118.4, 95.0, 21.4.

***trans*-2-Methylcinnamonitrile (2c).** The general procedure gave pure **2c** as light yellow oil (34 mg, 79% yield).[4] ^1H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, J = 16.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.30–7.34 (m, 1H), 7.21–7.26 (m, 2H), 5.80 (d, J = 16.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.4, 137.2, 132.5, 131.0, 130.9, 126.5, 125.5, 118.3, 97.1, 19.5.

***trans*-3-Methylcinnamonitrile (2d).** The general procedure gave **2d** as light yellow oil (32 mg, 74% yield).[4] ^1H NMR ($CDCl_3$, 400 MHz) δ 7.37 (d, J = 16.4 Hz, 1H), 7.24–7.32 (m, 4H), 5.86 (d, J = 16.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 138.9, 133.5, 132.0, 129.0, 127.9, 124.5, 118.2, 96.0, 21.2.

***trans*-2-Methoxylcinnamonitrile (2e).** The general procedure gave pure **2e** as yellow oil (34 mg, 72% yield).[16] ^1H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, J = 16.8 Hz, 1H), 7.37–7.41 (m, 2H), 6.92–6.99 (m, 2H), 6.06 (d, J = 16.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.3, 146.5, 132.3, 128.9, 122.6, 120.8, 119.0, 111.3, 97.0, 55.6.

***trans*-4-Methoxylcinnamonitrile (2f).** The general procedure gave pure **2f** as a white solid (33 mg, 70% yield).[4] ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 16.4 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 5.71 (d, J = 16.4 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.0, 150.0, 129.0, 126.3, 118.7, 114.5, 93.3, 55.4.

***trans*-3-Methoxylcinnamonitrile (2g).** The general procedure gave pure **2g** as light yellow oil (31 mg, 67% yield). ^1H NMR ($CDCl_3$, 400 MHz). δ 7.30–7.37 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.95–6.99 (m, 2H), 3.83 (s, 3H), 5.86 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 150.4, 134.8, 130.1, 119.9, 118.0, 116.8, 112.4, 96.6, 55.3; IR (neat): ν = 2921, 2849, 2217, 1620, 1599, 1578, 1489, 1456, 1433, 1279, 1246, 1171, 1159, 1049, 965, 825, 779, 686 cm^{-1}; EI-MS: m/z (%) 159.1 (M^+, 100);

HRMS *m*/*z* (ESI) calcd for $C_{10}H_{10}NO$ $(M + H)^+$: 160.0757, found 160.0752.

***trans*-4-(*tert*-Butyl)cinnamonitrile (2h).** The general procedure gave pure **2h** as yellow oil (41 mg, 73% yield).[17] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.44 (m, 5H), 5.83 (d, J = 16.4 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.9, 150.4, 130.8, 127.2, 126.1, 118.4, 95.2, 35.0, 31.1.

***trans*-4-(Trimethylsilyl)cinnamonitrile (2i).** The general procedure gave pure **2i** as yellow oil (46 mg, 76% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, J = 8.0 Hz, 2H), 7.38–7.43 (m, 3H), 5.90 (d, J = 16.8 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 145.1, 134.0, 133.7, 126.4, 118.2, 96.4, −1.34; IR (neat): ν = 2958, 2218, 1619, 1398, 1249, 1106, 969, 858, 838, 800, 683 cm^{-1}; EI-MS: *m*/*z* (%) 201.1 (M^+, 100); HRMS *m*/*z* (ESI) calcd for $C_{12}H_{16}NSi$ $(M + H)^+$ 202.1047, found 202.1045.

***trans*-4-Phenylcinnamonitrile (2j).** The general procedure gave pure **2j** as a white solid (44 mg, 71% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59–7.63 (m, 4H), 7.37–7.51 (m, 6H), 5.88 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.0, 143.9, 139.6, 132.2, 128.9, 128.1, 127.8, 127.6, 127.0, 118.2, 95.9; IR (neat): ν = 2216, 1618, 1604, 1486, 1409, 1006, 854, 814, 977, 761, 692 cm^{-1}; EI-MS: *m*/*z* (%) 205.1 (M^+, 100); HRMS *m*/*z* (ESI) calcd for $C_{15}H_{12}N$ $(M + H)^+$ 206.0964, found 206.0961.

***trans*-4-Fluorocinnamonitrile (2k).** The general procedure gave pure **2k** as a yellow solid (33 mg, 75% yield).[17] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.47 (m, 2H), 7.37 (d, J = 16.8 Hz, 1H), 7.08–7.26 (m, 2H), 5.81 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.4 (d, J = 251.6 Hz), 149.2, 129.8 (d, J = 3.2 Hz), 129.4 (d, J = 8.7 Hz), 117.9, 116.4 (d, J = 22.2 Hz), 96.1.

***trans*-4-Chlorocinnamonitrile (2l).** The general procedure gave pure **2l** as a light yellow solid (39 mg, 80% yield)[4] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33–7.39 (m, 5H), 5.8 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.1, 137.3, 132.0, 129.4, 128.5, 117.8, 97.0.

***trans*-4-Bromocinnamonitrile (2m).** The general procedure gave pure **2m** as a yellow solid (49 mg, 78% yield).[18] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 16.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 5.88 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.2, 132.4, 128.7, 125.6, 117.8, 97.1.

***trans*-4-(Trifluoromethyl)cinnamonitrile (2n).** The general procedure gave pure **2n** as a white solid (46 mg, 77% yield).[3] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 16.8 Hz, 1H), 5.99 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.8, 136.7, 132.7 (q, J = 32.6 Hz), 127.6, 126.1 (q, J = 3.8 Hz), 123.6 (q, J = 270.7 Hz), 117.3, 99.2.

***trans*-3,5-(Dimethyl)cinnamonitrile (2o).** The general procedure gave pure **2o** as a white solid (39 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (d, J = 16.4 Hz, 1H), 7.05–7.07 (m, 3H), 5.84 (d, J = 16.8 Hz, 1H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9, 138.7, 133.4, 133.0, 125.2, 118.3, 95.7, 21.1; IR (neat): ν = 3019, 2921, 2361, 2330, 2217, 1619, 1601, 1442, 1302, 1166, 1038, 967, 855, 815 cm^{-1}; EI-MS: *m*/*z* (%) 157.1 (M^+, 100); HRMS *m*/*z* (ESI) calcd for $C_{11}H_{12}N$ $(M + H)^+$ 158.0964, found 158.0960.

***trans*-3-(Thiophen-2-yl)acrylonitrile (2p).** The general procedure gave pure **2p** as yellow oil (31 mg, 77% yield).[4] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, J = 16.4 Hz, 1H), 7.42 (d, J = 5.2 Hz, 1H), 7.24–7.26 (m, 1H), 7.07–7.09 (dd, J = 5.2, 3.6 Hz, 1H), 5.65 (d, J = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.7, 138.4, 131.2, 129.2, 128.3, 118.0, 94.4.

***trans*-3-(Naphthalen-2-yl)acrylonitrile (2q).** The general procedure gave pure **2q** as a white solid (48 mg, 89% yield).[4] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83–7.87 (m, 4H), 7.52–7.56 (m, 4H), 5.97 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 134.5, 133.1, 131.0 129.6, 129.0, 128.7, 127.8, 127.8, 127.1, 122.2, 118.3, 96.3.

***trans*-3-(Naphthalen-1-yl)acrylonitrile (2r).** The general procedure gave pure **2r** as a white solid (46 mg, 86% yield).[19] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, J = 16.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.88–7.96 (m, 2H), 7.48–7.68 (m, 4H), 5.98 (d, J = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.9, 133.6, 131.5, 130.9, 130.7, 128.9, 127.4, 126.6, 125.4, 124.7, 122.8, 118.2, 98.8.

***trans*-3-(Phenanthren-9-yl)acrylonitrile (2s).** The general procedure gave pure **2s** as a white solid (55 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62–8.71 (m, 2H), 8.15 (d, J = 16.4 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.82–7.88 (m, 2H), 7.60–7.72 (m, 4H), 5.99 (d, J = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.6, 131.2, 130.7, 130.4, 130.0, 129.3, 129.1, 128.2, 127.3, 127.2, 127.2, 126.5, 123.8, 123.3, 122.6, 118.0, 99.3; IR (neat): ν = 2924, 2215, 1605, 1494, 1450, 1245, 1148, 959, 820, 750, 722, 669, 656 cm^{-1}; EI-MS: *m*/*z* (%) 229.1 (M^+, 100); HRMS *m*/*z* (ESI) calcd for $C_{17}H_{12}N$ $(M + H)^+$ 230.0964, found 230.0960.

Acknowledgements

The project was supported by the 973 Program (no. 2015CB856602) and the National Nature Science Foundation of China (grant 21272010 and 21332002).

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