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PAPER

Synthesis of (*Z*)-3-aryloxy-acrylonitriles, (*E*)-3-aryloxy-acrylonitriles and 3-cyanobenzofurans through the sequential reactions of phenols with propiolonitriles†

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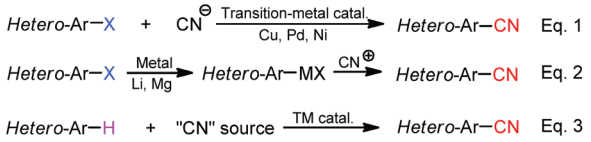
A Na_2CO_3-promoted addition of phenols to propiolonitriles generated (*Z*)-3-aryloxy-acrylonitriles in nearly quantitative yields with exclusively *Z*-isomers, and a DABCO-promoted addition reaction of phenols with propiolonitriles afforded mainly (*E*)-3-aryloxy-acrylonitriles with high yields. The obtained (*E*)-3-aryloxy-acrylonitriles underwent intramolecular cyclization to give 3-cyanobenzofurans in good yields through palladium-catalyzed direct C–H bond functionalization.

Introduction

Aromatic nitriles, especially heteroaromatic cyanide units, are important structural motifs frequently found in a variety of biologically active compounds, agrochemicals, dyes, materials and natural products.[1] Moreover, they are also versatile building blocks, as well as starting materials for the synthesis of a number of their corresponding derivatives, such as acids, esters, amides, amines, aldehydes, and so forth by modern organic synthesis[2] through simple and easy transformations.[3]

The classic synthetic protocols for the synthesis of heteroaromatic cyanides *via* cyanating reactions of heteroaromatic compounds are the Rosenmund–von Braun method and the Sandmeyer reaction.[4] However, there are some drawbacks, such as stoichiometric amount of cuprous cyanide required, harsh reaction conditions used and laborious isolation of products needed in the reactions. In recent years, transition-metal-catalyzed cyanation of heteroaromatic halides with metal cyanides, acetone cyanohydrin, TMSCN, and $K_4Fe(CN)_6$ (Scheme 1, eqn (1)),[5] and electrophilic cyanation of metalated heteroaromatics using cyano electrophiles (Scheme 1, eqn (2))[6] have attracted much attention. However, pre-functionalized substrates are required.

Most recently, the direct cyanation of heteroarenes as well as chelation-assisted reactions, such as Pd-catalyzed cyanation of C–H bonds of 2-arylpyridines,[7] Pd-catalyzed cyanation of C–H bonds of indoles,[8] Cu-catalyzed cyanation of heterocycle C–H bonds,[9] and Cu-catalyzed cyanation of 2-arylpyridine and indole C–H bonds (Scheme 1, eqn (3))[10] have been reported in the literature. Nevertheless, the requirement of the chelation group in some cases would limit the substrate scope.



Scheme 1 Synthesis of heteroaromatic cyanides.

However, compared to the direct cyanation of pyridines,[11a] thiophenols,[11b,d] indole, substituted indoles, and pyrroles,[8,11b–d] 2-phenylpyridines,[7,10] and benzoxazole, benzothiazole, benzimidazole, caffeine, and triazoles,[9] introduction of a cyano functionality into the 3-position of benzofuran ring, an electron-rich heteroaromatic ring, is more difficult. When using transition-metal-catalyzed cyanation of heteroaromatic halides (Scheme 1, eqn (1)) or electrophilic cyanation of metalated heteroaromatics (Scheme 1, eqn (2)), the requisite 3-halo benzofurans are not easily prepared *via* the general halogenation of benzofurans.[12] In addition, the direct cyanation of benzofurans at the 3-position is also rare.[8a,13]

In our continuing efforts on organic transformations through C–H functionalizations and preparation of heteroaromatic cyanides,[14] herein we report that a Na_2CO_3-promoted addition of phenols to propiolonitriles generated (*Z*)-3-aryloxy-acrylonitriles in nearly quantitative yields with exclusively *Z*-isomers, and a DABCO-promoted addition reaction of phenols with propiolonitriles afforded mainly (*E*)-3-aryloxy-acrylonitriles with high yields. The obtained (*E*)-3-aryloxy-acrylonitriles underwent intramolecular cyclization to afford the corresponding

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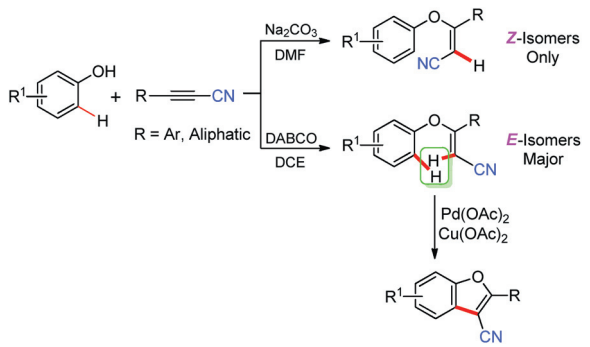


Scheme 2 Synthesis of (*Z*)-3-aryloxy-acrylonitriles, (*E*)-3-aryloxy-acrylonitriles and 3-cyanobenzofurans.

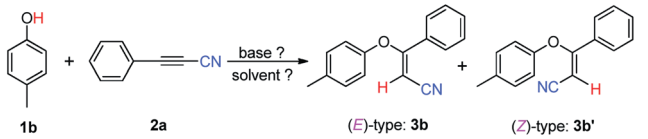
3-cyanobenzofurans in good yields through a palladium-catalyzed direct C–H bond functionalization (Scheme 2).

Results and discussion

Firstly, our exploration was focused on the optimization of reaction conditions for the model addition of 4-methylphenol (**1b**) to 3-phenylpropiolonitrile (**2a**). Table 1 shows that the base plays an important role in the reaction,[15] and base is essential in the model reaction (Table 1, entry 1). When 1 equiv of Na_2CO_3 or K_2CO_3 was used as a base, the model reaction proceeded smoothly in DMF at room temperature (25 °C) and generated the corresponding addition product **3b** + **3b′** in 97, or 91% yield, with 100% *Z*-isomer **3b′** (Table 1, entries 2 and 3). On the other hand, organic base DABCO (1,4-diazabicyclo[2.2.2]octane, 1 equiv) could promote the model reaction with increasing product yield of **3b** + **3b′** (up to 96%) and *E*-isomer (**3b**) ratio (*E* : *Z* = **3b** : **3b′** = 85 : 15) in $ClCH_2CH_2Cl$ at 45 °C (Table 1, entries 11–19). Fortunately, the mixture of a pair of *Z*- and *E*-isomers could be separated and isolated by chromatography on a silica column. However, only a trace amount of **3b** + **3b′** was isolated when Et_3N, Ph_3N, DBU (1,8-diazabicycloundec-7-ene), or DMAP (4-dimethylaminopryidine) was used as a base in $ClCH_2CH_2Cl$ at 45 °C (Table 1, entries 20–23).

A variety of phenols and propiolonitriles were examined for the extension of the addition reaction. As can be seen from Table 2, when the reaction of various substituted phenols and 3-aryl(aliphatic)-propiolonitriles was performed under Na_2CO_3/DMF/20–25 °C reaction conditions, the corresponding addition products were isolated in almost quantitative yields with *Z*-isomers as the sole ones (Table 2, entries 1–19). An obvious *ortho*-position effect of 3-arylpropiolonitrile was observed (Table 2, entry 20). Under DABCO/$ClCH_2CH_2Cl$/45 °C reaction conditions, the phenols also exhibited high reactivity to 3-phenylpropiolonitrile and the corresponding addition products were obtained in excellent yields with the ratios of *E* : *Z* in the range of 93 : 7 to 74 : 26 (Table 2, entries 1′–13′). However, the *E* : *Z* ratio of the product obtained using phenol with an electron-withdrawing group at the *para*-position, was greater than that of the phenol without substitution, or with an electron-donating group (Table 2, entries 9′–11′ *vs.* 1′–8′, 12′, and 13′). The addition of α-naphthalenol to 3-phenylpropiolonitrile generated **3n** + **3n′** in 96% yield with 70 : 30 (*E* : *Z*) ratio (Table 2, entry 14′). The

Table 1 Optimization of the reaction conditions for the addition of 4-methylphenol (**1b**) to 3-phenylpropiolonitrile (**2a**)[a]



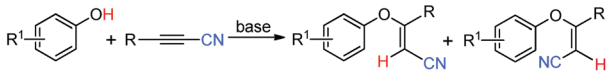
Entry	Base (equiv)	Solvent	Temp. (°C)	Yield[b] (**3b** + **3b′**) (%)	*E* : *Z* ratio
1	—	DMF	rt	0	0 : 0
2	K_2CO_3 (1.0)	DMF	rt	91	0 : 100
3	Na_2CO_3 (1.0)	DMF	rt	97	0 : 100
4	Na_2CO_3 (0.5)	DMF	rt	48	0 : 100
5	Na_2CO_3 (1.5)	DMF	rt	97	0 : 100
6	Na_2CO_3 (1.0)	DMAc	rt	94	0 : 100
7	Na_2CO_3 (1.0)	$(CH_2Cl)_2$	rt	15	0 : 100
8	Na_2CO_3 (1.0)	CH_3CN	rt	32	0 : 100
9	Na_2CO_3 (1.0)	C_2H_5OH	rt	53	10 : 90
10	Na_2CO_3 (1.0)	DMF	100	97	12 : 88
11	DABCO (1.0)	DMF	rt	49	34 : 66
12	DABCO (1.0)	CH_2Cl_2	rt	36	58 : 42
13	DABCO (1.0)	$(CH_2Cl)_2$	rt	53	86 : 14
14	DABCO (1.0)	C_2H_5OH	rt	34	33 : 67
15	DABCO (1.0)	CH_3CN	rt	17	0 : 100
16	DABCO (1.0)	$(CH_2Br)_2$	rt	0/0	0 : 0
17	DABCO (1.0)	$(CH_2Cl)_2$	45	96	85 : 15
18	DABCO (1.0)	$(CH_2Cl)_2$	65	91	75 : 25
19	DABCO (0.5)	$(CH_2Cl)_2$	45	49	85 : 15
20	Et_3N (1.0)	$(CH_2Cl)_2$	45	Trace	—
21	Ph_3N (1.0)	$(CH_2Cl)_2$	45	Trace	—
22	DBU (1.0)	$(CH_2Cl)_2$	45	Trace	—
23	DMAP (1.0)	$(CH_2Cl)_2$	45	Trace	—

[a] Reaction conditions: 4-methylphenol (**1b**, 1.1 mmol), 3-phenylpropiolonitrile (**2a**, 1.0 mmol), solvent (2.0 mL), base (amount in Table 1) at the temperature indicated in Table 1, 12 h. [b] Isolated yield. DMF = *N*,*N*-dimethylformamide, DMAc = *N*,*N*-dimethylacetamide, rt = 20–25 °C.

reactions of 4-methylphenol with 3-(4-*tert*-butylphenyl)-, 3-(4-methoxyphenyl)- and 3-(4-chlorophenyl)-propiolonitriles proceeded well and generated the corresponding products in good yields with the ratios of *E* : *Z*from 85 : 15 to 77 : 23 (Table 2, entries 15′–17′). It is important to note that 3-aliphatic propiolonitriles, such as non-2-ynenitrile and hept-2-ynenitrile also reacted with 4-methylphenol to generate the corresponding products in good yields and good regio- and stereoselectivity (Table 2, entries 18′ and 19′). However, no desired product was found when 4-methylphenol reacted with 3-(2-methylphenyl)-propiolonitrile (Table 2, entry 20′). X-ray crystallographic analysis of **3j** confirmed its structure[16] and showed that the dihedral angel of the phenol ring and vinyl plane is 77.78°.

With the addition products (*E*)-3-aryloxy-acrylonitriles and (*Z*)-3-aryloxy-acrylonitriles in our hands, transformation of them into the corresponding 3-cyanobenzofurans was examined *via* palladium-catalyzed direct C–H bond activation. The results are summarized in Table 3. Firstly, the effect of solvent on the model reaction of **3b** was investigated, and a significant solvent effect was observed. Dioxane was found to be the best among the solvents tested (Table 3, entries 1–7). The effect of palladium catalytic systems was also examined, and the results indicated that $Pd(OAc)_2$–PPh_3 system displayed the highest reactivity

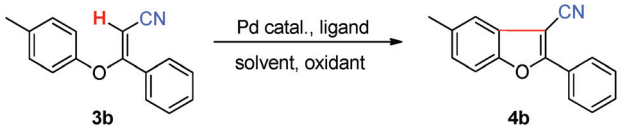
Table 2 Base-promoted addition reactions of phenols to propiolonitriles[a,b]



Entry	R^1	R	Yield[c] (**3** + **3′**) (%)	*E* : *Z* ratio
1	H	C_6H_5	**3a** + **3a′**, 99	0 : 100
1′			**3a** + **3a′**, 96	85 : 15
2	*p*-CH_3	C_6H_5	**3b** + **3b′**, 99	0 : 100
2′			**3b** + **3b′**, 97	83 : 17
3	*m*-CH_3	C_6H_5	**3c** + **3c′**, 98	0 : 100
3′			**3c** + **3c′**, 94	81 : 19
4	*o*-CH_3	C_6H_5	**3d** + **3d′**, 93	0 : 100
4′			**3d** + **3d′**, 89	78 : 22
5	*p*-C_2H_5	C_6H_5	**3e** + **3e′**, 98	0 : 100
5′			**3e** + **3e′**, 91	83 : 17
6	*p*-(*i*-C_3H_7)	C_6H_5	**3f** + **3f′**, 99	0 : 100
6′			**3f** + **3f′**, 93	84 : 16
7	*p*-(*t*-C_4H_9)	C_6H_5	**3g** + **3g′**, 97	0 : 100
7′			**3g** + **3g′**, 95	80 : 20
8	*p*-CH_3O	C_6H_5	**3h** + **3h′**, 95	0 : 100
8′			**3h** + **3h′**, 94	74 : 26
9	*p*-Cl	C_6H_5	**3i** + **3i′**, 99	0 : 100
9′			**3i** + **3i′**, 95	91 : 9
10	*p*-NO_2	C_6H_5	**3j** + **3j′**, 99	0 : 100
10′			**3j** + **3j′**, 98	93 : 7
11	*p*-C_6H_5CO	C_6H_5	**3k** + **3k′**, 96	0 : 100
11′			**3k** + **3k′**, 94	90 : 10
12	*m*,*m*-$(CH_3)_2$	C_6H_5	**3l** + **3l′**, 99	0 : 100
12′			**3l** + **3l′**, 93	80 : 20
13	*p*-Cl-*m*-CH_3	C_6H_5	**3m** + **3m′**, 96	0 : 100
13′			**3m** + **3m′**, 91	87 : 13
14	*α*-naphthyl	C_6H_5	**3n** + **3n′**, 96	0 : 100
14′			**3n** + **3n′**, 96	70 : 30
15	*p*-CH_3	*p*-(*t*-C_4H_9)C_6H_4	**3o** + **3o′**, 97	0 : 100
15′			**3o** + **3o′**, 91	82 : 18
16	*p*-CH_3	*p*-$CH_3OC_6H_4$	**3p** + **3p′**, 95	0 : 100
16′			**3p** + **3p′**, 90	77 : 23
17	*p*-CH_3	*p*-ClC_6H_4	**3q** + **3q′**, 98	0 : 100
17′			**3q** + **3q′**, 92	85 : 15
18	*p*-CH_3	*n*-C_6H_{13}	**3r** + **3r′**, 93	0 : 100
18′			**3r** + **3r′**, 85	80 : 20
19	*p*-CH_3	*n*-C_4H_9	**3s** + **3s′**, 91	0 : 100
19′			**3s** + **3s′**, 82	81 : 19
20	*p*-CH_3	*o*-$CH_3C_6H_4$	**3t** + **3t′**, 62	0 : 100
20′			**3t** + **3t′**, 0	—

[a] For entries 1–20: phenol (**1**, 1.1 mmol), propiolonitrile (**2**, 1.0 mmol), Na_2CO_3 (1.0 mmol), DMF (2.0 mL) at room temperature, 12 h. [b] For entries 1′–20′: phenol (**1**, 1.1 mmol), propiolonitrile (**2**, 1.0 mmol), DABCO (1.0 mmol), DCE (2.0 mL) at 45 °C, 12 h. [c] Isolated yields.

Table 3 Optimization of the reaction conditions for palladium-catalyzed intramolecular cyclization of (*E*)-3-phenyl-3-(*p*-tolyloxy)-acrylonitrile (**3b**)[a]

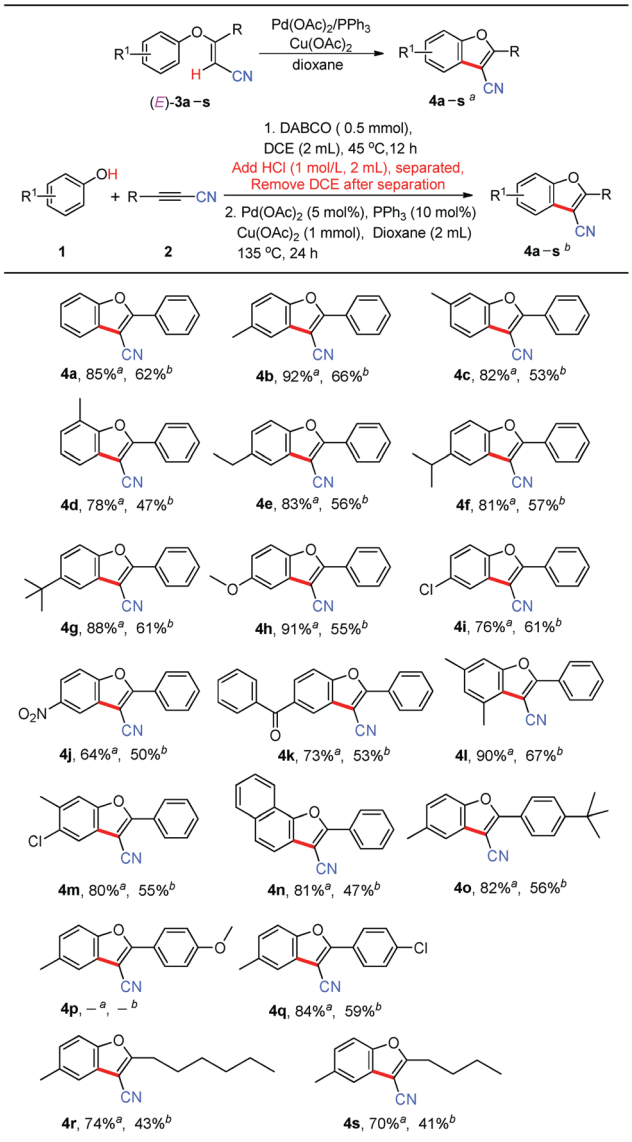


Entry	Pd catal.	Ligand	Solvent	Oxidant	Yield[b] (%)
1	$Pd(OAc)_2$	PPh_3	DMF	$Cu(OAc)_2$	81
2	$Pd(OAc)_2$	PPh_3	DMAc	$Cu(OAc)_2$	74
3	$Pd(OAc)_2$	PPh_3	*i*-PrOH	$Cu(OAc)_2$	0
4	$Pd(OAc)_2$	PPh_3	DMSO	$Cu(OAc)_2$	13
5	$Pd(OAc)_2$	PPh_3	NMP	$Cu(OAc)_2$	27
6	$Pd(OAc)_2$	PPh_3	Toluene	$Cu(OAc)_2$	18
7	$Pd(OAc)_2$	PPh_3	Dioxane	$Cu(OAc)_2$	92
8	$Pd(OAc)_2$	dppf	Dioxane	$Cu(OAc)_2$	47
9	$Pd(OAc)_2$	dppe	Dioxane	$Cu(OAc)_2$	54
10	$Pd(OAc)_2$	P*n*-Bu_3	Dioxane	$Cu(OAc)_2$	68
11	$Pd(OAc)_2$	—	Dioxane	$Cu(OAc)_2$	61
12	$Pd(PPh_3)_2Cl_2$	—	Dioxane	$Cu(OAc)_2$	81
13	$Pd(CH_3CN)_2Cl_2$	—	Dioxane	$Cu(OAc)_2$	73
14	$Pd(PPh_3)_4$	—	Dioxane	$Cu(OAc)_2$	58
15	$Pd(PCy_3)_2Cl_2$	—	Dioxane	$Cu(OAc)_2$	67
16	$Pd(OAc)_2$	PPh_3	Dioxane	$Cu(OTf)_2$	59
17	$Pd(OAc)_2$	PPh_3	Dioxane	$CuCl_2$	0
18	$Pd(OAc)_2$	PPh_3	Dioxane	$CuBr_2$	0
19	$Pd(OAc)_2$	PPh_3	Dioxane	$CuSO_4$	0
20	$Pd(OAc)_2$	PPh_3	Dioxane	Ag_2O	17
21	$Pd(OAc)_2$	PPh_3	Dioxane	$K_2S_2O_8$	0
22	$Pd(OAc)_2$	PPh_3	Dioxane	TBHP	0
23	$Pd(OAc)_2$	PPh_3	Dioxane	O_2	0

[a] Reaction conditions: (*E*)-3-phenyl-3-(*p*-tolyloxy)acrylonitrile (**3b**, 1.0 mmol), Pd catalyst (5.0 mol%), ligand (10.0 mol%) if necessary, solvent (2.0 mL), oxidant (2.0 mmol) at 130 °C, 16 h. [b] Isolated yield. DMF = *N*,*N*-dimethylformamide, DMAc = *N*,*N*-dimethylacetamide, DMSO = dimethyl sulfoxide, NMP = *N*-methyl-2-pyrrolidone, dppf = 1,1′-bis(diphenylphosphino)ferrocene, dppe = 1,2-bis(diphenylphosphino)ethane, TBHP = *tert*-butyl hydroperoxide.

(Table 3, entries 8–15). The oxidant also played an important role in the reaction. $Cu(OAc)_2$ was found to be the best among the oxidants examined (Table 3, entries 16–23). So, the optimized reaction conditions were found to be $Pd(OAc)_2$–PPh_3–$Cu(OAc)_2$–dioxane at 130 °C for 16 h. It should be noted that when (*Z*)-3-aryloxy-acrylonitrile **3b′** was used as a substrate under the same reaction conditions, no desired cyclization product was detected, and starting material was unchanged and recovered.

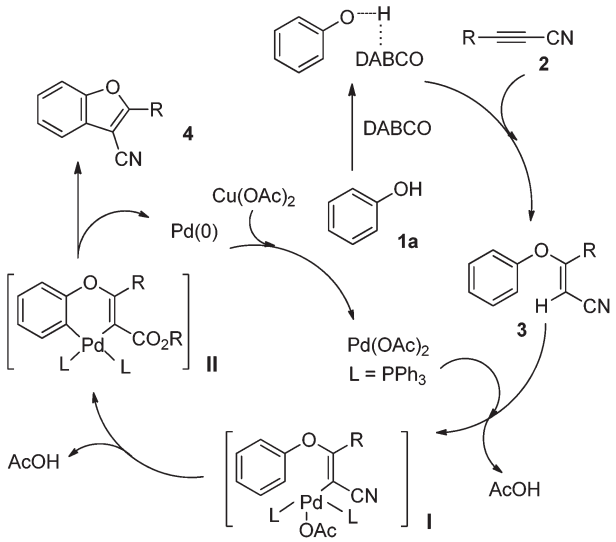
Under the optimized cyclization reaction conditions, (*E*)-3-aryloxy-3-substituted acrylonitriles **3a–o** and **3q–s**, underwent palladium-catalyzed intramolecular cyclization well *via* the direct C–H bond activation to afford the desired 3-cyanobenzofurans, **4a–o** and **4q–s**. As can be seen from Scheme 3, substrates **3** derived from 3-phenylpropiolonitrile and phenols with an electron-donating or electron-withdrawing group were able to make the reaction proceed smoothly, and afforded the corresponding products **4a–k** in 64–92% yields. The yields of products from substrates prepared from phenols with electron-donating groups were greater than those from substrates prepared from phenols with electron-withdrawing groups (Scheme 3, **4a–h** *vs.* **4i–k**). It should be noted that the reaction could tolerate an *ortho*-substituted group (**4d**). When two positions of phenol were occupied with Me/Me or Cl/Me groups, good yields of **4l** and **4m** were obtained. Substrate **3n** from α-naphthalenol also generated **4n** in 81% yield. When substrates **3o** and **3q** from 4-methylphenol and 3-(4-*tert*-butylphenyl)-propiolonitrile and 3-(4-chlorophenyl)-propiolonitrile also underwent the reaction, 82, and 84% yields of **4o** and **4q** were obtained. It is worth noting that only 6-substituted-3-cyanobenzofuran isomers (**4c**, **4l** and **4m**) were observed when substrates were prepared from 3-substituted phenols with propiolonitrile. The reactions of **3r** and **3s** also underwent the cyclization to generate **4r** and **4s** in 74 and 70% yields, respectively. However, when **3p** was used as substrate, no desired cyclization product **4p** was isolated. It is important to note that the reactions of **3i–k** in DMF were superior to those in dioxane.



[a] Isolated yields under reaction conditions: (*E*)-3-aryloxy-acrylonitrile (**3**, 1.0 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.10 mmol), Cu(OAc) (2.0 mmol), dioxane (2.0 mL) at 130 °C for 16 h. [b] Isolated yields under reaction conditions: phenol (**1**, 1.1 mmol), propiolonitrile (**2**, 1.0 mmol), DABCO (1.0 mmol), DCE (2.0 mL) at 45 °C, 12 h, then HCl (1 mol/L, 2 mL) was added, DCE was removed after separation, and then $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.10 mmol), Cu(OAc) (2.0 mmol), dioxane (2.0 mL) at 130 °C for 16 h. For **4i–k**, DMF (2.0 mL) was used instead of dioxane (2.0 mL) as solvent.

Scheme 3 Palladium-catalyzed synthesis of 3-cyanobenzofurans.

To simplify the procedure and increase the novelty of this study, we tried to develop a one-pot procedure for benzofuran preparation directly from alkynes and propiolonitriles, instead of sequential operation and avoiding isolation of the intermediate vinyl derivatives. However, no satisfactory results were obtained by using one-pot procedures for benzofuran preparation directly from alkynes and propiolonitriles. To our delight, when the reaction of phenol with propiolonitrile in the presence of DABCO was neutralized with HCl (1.0 mol L^{-1}, aq.) after the addition



Scheme 4 Proposed reaction mechanism.

reaction to remove DABCO *via* a simple separation, it was possible to proceed with the intramolecular cyclization of 3-aryloxy-acrylonitriles, providing comparable total yields of desired products (Scheme 3). It is important to note that this procedure eliminated the column chromatographic separation of the mixture of (*Z*)-3-aryloxy-acrylonitriles and (*E*)-3-aryloxy-acrylonitriles.

A possible reaction mechanism is proposed in Scheme 4. First, an intermolecular nucleophilic addition of phenol to propiolonitrile promoted by DABCO generated (*E*)-3-aryloxy-acrylonitrile (**3**) with good regio- and stereo-selectivity.[15,17] Subsequently, the formed **3** reacted with $Pd(OAc)_2$ to form a vinylpalladium intermediate **I** through electrophilic palladation *via* C–H activation of the vinyl proton,[18] which underwent intramolecular electrophilic aromatic palladation *via* C–H activation of the aromatic hydrogen to give an intermediate **II**.[19] Carbon–carbon bond formation *via* reductive elimination of **II**, afforded the corresponding product 3-cyanobenzofuran (**4**) and Pd^0. And finally, the oxidation of Pd^0 by the oxidant $Cu(OAc)_2$ regenerated the Pd^{II} species to complete the catalytic cycle. Moreover, the structure of product **4j** was further confirmed by X-ray crystallography.[20]

Conclusion

In conclusion, a series of organic transformations of simple phenols and propiolonitriles was developed, including (1) a Na_2CO_3-promoted addition of phenols to propiolonitriles generating (*Z*)-3-aryloxy-acrylonitriles in almost quantitative yields with exclusively *Z*-isomers; (2) a DABCO-promoted addition reaction of phenols to propiolonitriles affording mainly (*E*)-3-aryloxy-acrylonitriles with high yields; (3) a palladium-catalyzed intramolecular cyclization of (*E*)-3-aryloxy-acrylonitriles giving 3-cyanobenzofurans in good yields through direct C–H bond functionalization. It provides a novel, efficient and practical approach to (*Z*)-3-aryloxy-acrylonitriles, (*E*)-3-aryloxy-acrylonitriles and 3-cyanobenzofurans under mild reaction conditions.

Experimental section

All the chemicals and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR, ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

Typical procedure for Na_2CO_3-promoted addition reaction of phenol to propiolonitrile

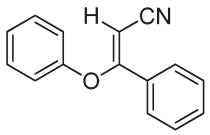
Under an air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with 4-methylphenol (1.1 mmol), 3-phenylpropiolonitrile (1.0 mmol), Na_2CO_3 (1.0 mmol) and DMF (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in air bath at room temperature for 12 h. After the reaction was completed, it was diluted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give (*Z*)-3-phenyl-3-(*p*-tolyloxy)acrylonitrile (**3b′**) in 99% yield.

Typical procedure for DABCO-promoted addition reaction of phenol to propiolonitrile

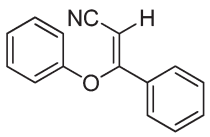
Under an air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with 4-methylphenol (1.1 mmol), 3-phenylpropiolonitrile (1.0 mmol), DABCO (1.0 mmol) and $ClCH_2CH_2Cl$ (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 45 °C for 12 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give (*Z*)-3-phenyl-3-(*p*-tolyloxy)acrylonitrile (**3b′**) and (*E*)-3-phenyl-3-(*p*-tolyloxy)-acrylonitrile (**3b**).

Typical procedure for palladium-catalyzed intramolecular cyclization of (*E*)-3-aryloxy-acrylonitrile

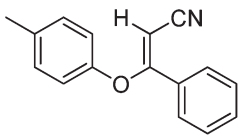
Under an air atmosphere, a sealable reaction tube equipped with a magnetic stirrer bar was charged with (*E*)-3-phenyl-3-(*p*-tolyloxy)acrylonitrile (**3b**, 1.0 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.10 mmol), $Cu(OAc)_2$ (2.0 mmol) and dioxane (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 130 °C for 16 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give 5-methyl-2-phenylbenzofuran-3-carbonitrile, **4b**, in 92% yield.



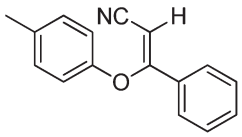
(*E*)-3-Phenoxy-3-phenylacrylonitrile, 3a. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–8.00 (m, 2H), 7.56–7.45 (m, 5H), 7.33–7.29 (m, 1H), 7.16–7.14 (m, 2H), 4.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.63, 153.28, 131.83, 131.49, 130.29, 128.52, 127.94, 126.26, 121.01, 117.90, 75.05. IR (KBr, cm^{-1}): 2215 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{15}H_{11}NO$: 221.0841, Found: 221.0840.



(*Z*)-3-Phenoxy-3-phenylacrylonitrile, 3a′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.47–7.43 (m, 1H), 7.41–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.14–7.10 (m, 1H), 7.06–7.03 (m, 2H), 5.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.29, 155.61, 132.05, 131.39, 129.66, 128.84, 126.83, 124.11, 118.03, 115.07, 81.83. IR (KBr, cm^{-1}): 2218 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{15}H_{11}NO$: 221.0841, Found: 221.0842.

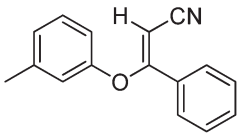


(*E*)-3-Phenyl-3-(*p*-tolyloxy)acrylonitrile, 3b. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.6 Hz, 2H), 7.57–7.50 (m, 3H), 7.26 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 7.6 Hz, 2H), 4.55 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.98, 151.07, 136.13, 132.02, 131.47, 130.80, 128.55, 127.98, 120.81, 118.12, 74.63, 20.84. IR (KBr, cm^{-1}): 2215 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{16}H_{13}NO$: 235.0997, Found: 235.0992.

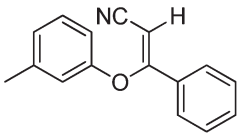


(*Z*)-3-Phenyl-3-(*p*-tolyloxy)acrylonitrile, 3b′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 2H), 7.46–7.36 (m, 3H), 7.10 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 5.37 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.66, 153.50, 133.86, 132.39, 131.34, 130.15, 128.84, 126.91, 118.07, 115.18, 81.03, 20.67. IR (KBr, cm^{-1}): 2219 ($\nu_{C\equiv N}$). HRMS (EI)

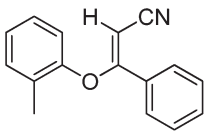
([M]$^+$) Calcd for $C_{16}H_{13}NO$: 235.0997, Found: 235.1001.



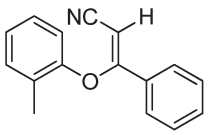
(*E*)-3-Phenyl-3-(*m*-tolyloxy)acrylonitrile, 3c. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–8.00 (m, 2H), 7.57–7.50 (m, 3H), 7.37–7.33 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.97–6.94 (m, 2H), 4.57 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.69, 153.25, 140.66, 131.93, 131.42, 129.94, 128.49, 127.91, 127.02, 121.54, 118.01, 117.92, 74.81, 21.21. IR (KBr, cm^{-1}): 2215 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{13}NO$: 235.0997, Found: 235.0998.



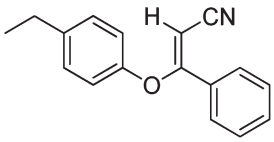
(*Z*)-3-Phenyl-3-(*m*-tolyloxy)acrylonitrile, 3c′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 2H), 7.47–7.43 (m, 1H), 7.41–7.37 (m, 2H), 7.20–7.16 (m, 1H), 6.94–6.89 (m, 2H), 6.83–6.80 (m, 1H), 5.43 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.29, 155.59, 139.91, 132.13, 131.33, 129.28, 128.81, 126.77, 124.89, 118.58, 115.13, 114.88, 81.76, 21.28. IR (KBr, cm^{-1}): 2218 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{13}NO$: 235.0997, Found: 235.0999.



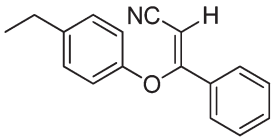
(*E*)-3-Phenyl-3-(*o*-tolyloxy)acrylonitrile, 3d. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.04 (m, 2H), 7.58–7.52 (m, 3H), 7.35–7.29 (m, 2H), 7.26–7.22 (m, 1H), 7.08–7.06 (m, 1H), 4.41 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.74, 151.19, 131.96, 131.82, 131.50, 130.07, 128.55, 127.83, 127.80, 126.61, 121.32, 118.07, 73.45, 15.67. IR (KBr, cm^{-1}): 2215 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{13}NO$: 235.0997, Found: 235.0999.



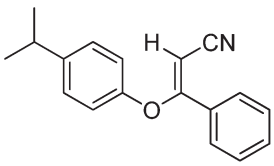
(*Z*)-3-Phenyl-3-(*o*-tolyloxy)acrylonitrile, 3d′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.61 (m, 2H), 7.51–7.47 (m, 1H), 7.44–7.41 (m, 2H), 7.28–7.26 (m, 1H), 7.15–7.09 (m, 2H), 6.87–6.85 (m, 1H), 5.33 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.35, 153.56, 132.55, 131.42, 131.33, 128.89, 128.85, 126.97, 126.52, 125.01, 118.31, 114.75, 78.42, 16.04. IR (KBr, cm^{-1}): 2213 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{13}NO$: 235.0997, Found: 235.0994.



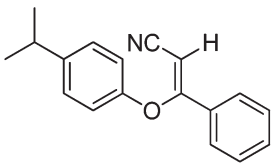
(*E*)-3-(4-Ethylphenoxy)-3-phenylacrylonitrile, 3e. White solid, m.p. 48–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (m, 2H), 7.57–7.49 (m, 3H), 7.29 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 4.57 (s, 1H), 2.70 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.77, 151.04, 142.27, 131.89, 131.32, 129.48, 128.39, 127.84, 120.73, 117.96, 74.49, 28.07, 15.40. IR (KBr, cm^{-1}): 2214 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO$: 249.1154, Found: 249.1153.



(*Z*)-3-(4-Ethylphenoxy)-3-phenylacrylonitrile, 3e′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.47–7.43 (m, 1H), 7.41–7.37 (m, 2H), 7.15–7.12 (m, 2H), 6.98–6.94 (m, 2H), 5.40 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.52, 153.59, 140.05, 132.23, 131.28, 128.89, 128.78, 126.83, 117.89, 115.14, 81.31, 27.95, 15.45. IR (KBr, cm^{-1}): 2218 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO$: 249.1154, Found: 249.1152.

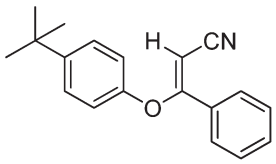


(*E*)-3-(4-*iso*-Propylphenoxy)-3-phenylacrylonitrile, 3f. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–8.01 (m, 2H), 7.57–7.50 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 4.58 (s, 1H), 3.02–2.92 (m, 1H), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.82, 151.12, 146.98, 131.97, 131.38, 128.46, 128.12, 127.90, 120.77, 118.03, 74.55, 33.50, 23.90. IR (KBr, cm^{-1}): 2211 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{18}H_{17}NO$: 263.1310, Found: 263.1307.

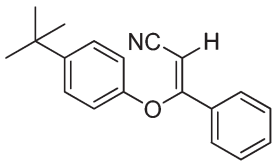


(*Z*)-3-(4-*iso*-Propylphenoxy)-3-phenylacrylonitrile, 3f′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.47–7.36 (m, 3H), 7.18–7.14 (m, 2H), 6.98–6.94 (m, 2H), 5.41 (s, 1H), 2.93–2.83 (m, 1H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.46, 153.63, 144.63, 132.24, 131.29, 128.80, 127.48, 126.83, 117.75, 115.14, 81.57, 33.27, 23.93. IR

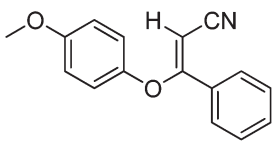
(KBr, cm^{-1}): 2219 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{18}H_{17}NO$: 263.1310, Found: 263.1309.



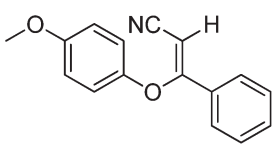
(*E*)-3-(4-*tert*-Butylphenoxy)-3-phenylacrylonitrile, 3g. White solid, m.p. 102–104 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03–8.01 (m, 2H), 7.57–7.47 (m, 5H), 7.08–7.05 (m, 2H), 4.58 (s, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.82, 150.91, 149.33, 132.02, 131.43, 128.51, 127.94, 127.15, 120.45, 118.07, 74.62, 34.50, 31.31. IR (KBr, cm^{-1}): 2213 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{19}H_{19}NO$: 277.1467, Found: 277.1473.



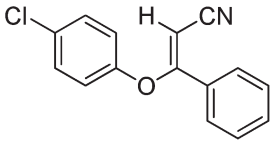
(*Z*)-3-(4-*tert*-Butylphenoxy)-3-phenylacrylonitrile, 3g′. White solid, m.p. 79–81 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 2H), 7.47–7.39 (m, 3H), 7.34–7.30 (m, 2H), 6.98–6.94 (m, 2H), 5.42 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.41, 153.40, 146.87, 132.23, 131.31, 128.82, 126.83, 126.47, 117.28, 115.14, 81.86, 34.19, 31.29. IR (KBr, cm^{-1}): 2219 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{19}H_{19}NO$: 277.1467, Found: 277.1469.



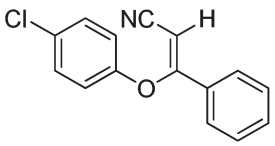
(*E*)-3-(4-Methoxyphenoxy)-3-phenylacrylonitrile, 3h. White solid, m.p. 62–64 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00–7.98 (m, 2H), 7.57–7.49 (m, 3H), 7.07–7.04 (m, 2H), 6.99–6.96 (m, 2H), 4.53 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.28, 157.61, 146.59, 132.00, 131.48, 128.54, 127.96, 122.05, 118.15, 115.24, 74.35, 55.61. IR (KBr, cm^{-1}): 2210 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{16}H_{13}NO_2$: 251.0946, Found: 251.0949.



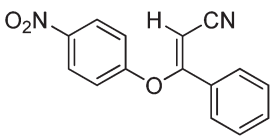
(*Z*)-3-(4-Methoxyphenoxy)-3-phenylacrylonitrile, 3h′. White solid, m.p. 71–73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.47–7.37 (m, 3H), 7.01–6.97 (m, 2H), 6.85–6.82 (m, 2H), 5.31 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.99, 156.36, 149.19, 132.44, 131.29, 128.78, 126.89, 119.65, 115.14, 114.59, 79.76, 55.48. IR (KBr, cm^{-1}): 2205 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{16}H_{13}NO_2$: 251.0946, Found: 251.0948.



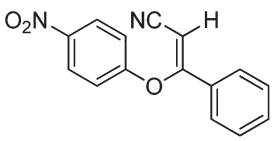
(*E*)-3-(4-Chlorophenoxy)-3-phenylacrylonitrile, 3i. White solid, m.p. 76–78 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H), 7.57–7.49 (m, 3H), 7.44–7.41 (m, 2H), 7.10–7.06 (m, 2H), 4.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.21, 151.82, 131.63, 131.59, 131.45, 130.37, 128.57, 127.92, 122.32, 117.46, 75.83. IR (KBr, cm^{-1}): 2212 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{15}H_{10}NOCl$: 255.0451, Found: 255.0452.



(*Z*)-3-(4-Chlorophenoxy)-3-phenylacrylonitrile, 3i′. White solid, m.p. 53–55 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.48–7.44 (m, 1H), 7.41–7.37 (m, 2H), 7.27–7.24 (m, 2H), 6.97–6.93 (m, 2H), 5.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.96, 154.24, 131.64, 129.72, 129.22, 129.00, 126.83, 119.14, 114.88, 82.77. IR (KBr, cm^{-1}): 2219 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{15}H_{10}NOCl$: 255.0451, Found: 255.0450.

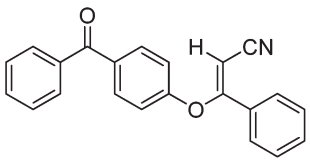


(*E*)-3-(4-Nitrophenoxy)-3-phenylacrylonitrile, 3j. White solid, m.p. 87–89 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.32–8.28 (m, 2H), 7.92–7.89 (m, 2H), 7.57–7.48 (m, 3H), 7.25–7.22 (m, 2H), 4.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.41, 158.88, 144.84, 132.08, 130.65, 128.89, 128.06, 126.14, 120.60, 116.66, 80.05. IR (KBr, cm^{-1}): 2213 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd for $C_{15}H_{10}N_2O_3$: 266.0691, Found: 266.0692.

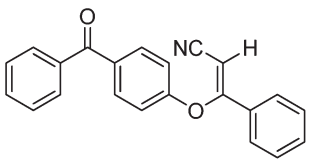


(*Z*)-3-(4-Nitrophenoxy)-3-phenylacrylonitrile, 3j′. White solid, m.p. 78–80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.21–8.17 (m, 2H), 7.54–7.47 (m, 3H), 7.44–7.39 (m, 2H), 7.12–7.08 (m, 2H), 5.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.77, 160.40, 143.49, 132.16, 130.64, 129.28, 126.57, 125.94, 117.35, 114.43, 85.27. IR (KBr, cm^{-1}): 2224 ($\nu_{C\equiv N}$). HRMS (EI) ($[M]^+$) Calcd

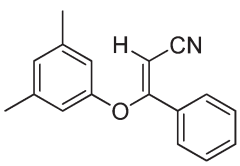
for $C_{15}H_{10}N_2O_3$: 266.0691, Found: 266.0689.



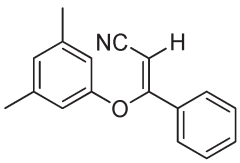
(*E*)-3-(4-Benzoylphenoxy)-3-phenylacrylonitrile, 3k. White solid, m.p. 118–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.81–7.79 (m, 2H), 7.64–7.60 (m, 1H), 7.54–7.49 (m, 5H), 7.22 (d, J = 8.4 Hz, 2H), 4.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.99, 171.43, 156.83, 137.04, 135.02, 132.56, 132.43, 131.72, 131.25, 129.77, 128.64, 128.30, 127.97, 120.40, 117.23, 77.45. IR (KBr, cm^{-1}): 2212 ($\nu_{C\equiv N}$), 1653 ($\nu_{C=O}$). HRMS (EI) ([M]$^+$) Calcd for $C_{22}H_{15}NO_2$: 325.1103, Found: 325.1104.



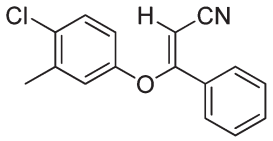
(*Z*)-3-(4-Benzoylphenoxy)-3-phenylacrylonitrile, 3k′. White solid, m.p. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.73 (m, 4H), 7.59–7.54 (m, 3H), 7.48–7.44 (m, 3H), 7.41–7.37 (m, 2H), 7.10–7.06 (m, 2H), 5.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.16, 167.30, 158.95, 137.37, 132.91, 132.28, 132.24, 131.77, 131.21, 129.70, 129.06, 128.18, 126.66, 116.97, 114.77, 84.22. IR (KBr, cm^{-1}): 2216 ($\nu_{C\equiv N}$), 1657 ($\nu_{C=O}$). HRMS (EI) ([M]$^+$) Calcd for $C_{22}H_{15}NO_2$: 325.1103, Found: 325.1106.



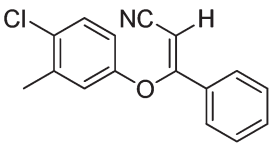
(*E*)-3-(3,5-Dimethylphenoxy)-3-phenylacrylonitrile, 3l. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–7.99 (m, 2H), 7.57–7.50 (m, 3H), 6.95 (s, 1H), 6.77 (s, 2H), 4.58 (s, 1H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.75, 153.25, 140.25, 132.05, 131.38, 128.48, 127.90, 127.89, 118.51, 118.13, 74.62, 21.14. IR (KBr, cm^{-1}): 2215 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO$: 249.1154, Found: 249.1158.



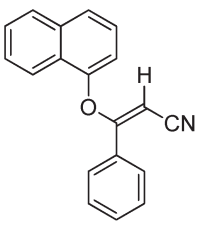
(*Z*)-3-(3,5-Dimethylphenoxy)-3-phenylacrylonitrile, 3l′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 2H), 7.47–7.37 (m, 3H), 6.75 (s, 1H), 6.66 (s, 2H), 5.42 (s, 1H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.30, 155.65, 139.49, 132.31, 131.31, 128.82, 126.77, 125.81, 115.54, 115.19, 81.77, 21.23. IR (KBr, cm^{-1}): 2214 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO$: 249.1154, Found: 249.1155.



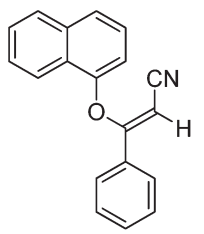
(*E*)-3-(4-Chloro-3-methylphenoxy)-3-phenyl-acrylonitrile, 3m. White solid, m.p. 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.96 (m, 2H), 7.57–7.48 (m, 3H), 7.41 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 6.93–6.90 (m, 1H), 4.59 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.33, 151.64, 138.51, 131.73, 131.59, 131.56, 130.55, 128.54, 127.90, 123.27, 119.61, 117.60, 75.49, 20.14. IR (KBr, cm^{-1}): 2213 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{12}NOCl$: 269.0607, Found: 269.0612.



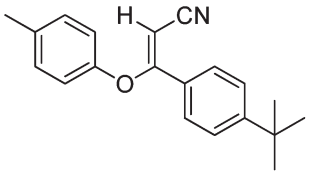
(*Z*)-3-(4-Chloro-3-methylphenoxy)-3-phenyl-acrylonitrile, 3m′. White solid, m.p. 51–53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.53 (m, 2H), 7.48–7.37 (m, 3H), 7.22 (d, J = 8.8 Hz, 1H), 6.92 (d, J = 2.8 Hz, 1H), 6.78–6.75 (m, 1H), 5.46 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.96, 154.07, 137.70, 131.71, 131.56, 129.86, 129.33, 128.94, 126.78, 120.08, 116.32, 114.98, 82.70, 20.19. IR (KBr, cm^{-1}): 2219 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{12}NOCl$: 269.0607, Found: 269.0605.



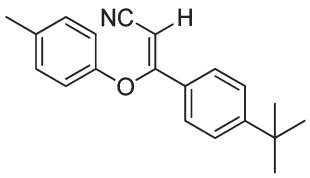
(*E*)-3-(Naphthalen-1-yloxy)-3-phenylacrylonitrile, 3n. White solid, m.p. 80–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.0 Hz, 2H), 7.97–7.93 (m, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.61–7.51 (m, 6H), 7.27 (d, J = 7.2 Hz, 1H), 4.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.36, 148.97, 135.00, 131.75, 131.66, 128.70, 128.24, 127.92, 127.02, 127.01, 126.56, 126.00, 125.68, 120.99, 117.85, 117.55, 75.17. IR (KBr, cm^{-1}): 2212 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{19}H_{13}NO$: 271.0997, Found: 271.1001.



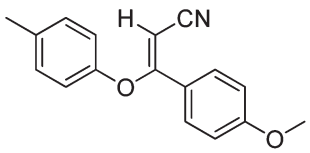
(*Z*)-3-(Naphthalen-1-yloxy)-3-phenylacrylonitrile, 3n′. White solid, m.p. 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39–8.37 (m, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.65–7.58 (m, 5H), 7.46–7.42 (m, 1H), 7.37–7.27 (m, 3H), 6.86 (d, J = 7.6 Hz, 1H), 5.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.36, 151.35, 134.61, 132.00, 131.51, 128.94, 127.91, 126.85, 126.46, 125.66, 125.20, 124.24, 121.28, 114.99, 112.35, 82.01. IR (KBr, cm^{-1}): 2218 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{19}H_{13}NO$: 271.0997, Found: 271.0995.



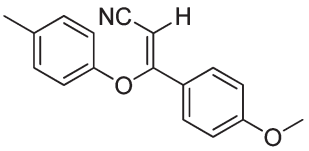
(*E*)-3-(4-*tert*-Butylphenyl)-3-(*p*-tolyloxy)acrylonitrile, 3o. White solid, m.p. 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 4.52 (s, 1H), 2.40 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.84, 154.89, 151.04, 135.90, 130.68, 129.10, 127.67, 125.42, 120.75, 118.29, 73.81, 34.84, 30.98, 20.74. IR (KBr, cm^{-1}): 2210 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{20}H_{21}NO$: 291.1623, Found: 291.1626.



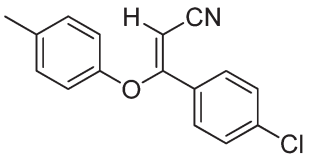
(*Z*)-3-(4-*tert*-Butylphenyl)-3-(*p*-tolyloxy)acrylonitrile, 3o′. White solid, m.p. 76–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.37 (s, 1H), 2.31 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.56, 155.02, 153.69, 133.63, 130.13, 129.44, 126.60, 125.83, 117.87, 115.39, 80.38, 34.88, 31.00, 20.68. IR (KBr, cm^{-1}): 2221 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{20}H_{21}NO$: 291.1623, Found: 291.1622.



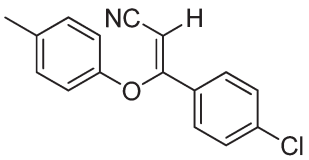
(*E*)-3-(4-Methoxyphenyl)-3-(*p*-tolyloxy)acrylonitrile, 3p. White solid, m.p. 54–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.01–6.99 (m, 4H), 4.45 (s, 1H), 3.88 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.64, 161.98, 151.17, 135.95, 130.72, 129.72, 124.34, 120.83, 115.02, 113.83, 72.94, 55.38, 20.82. IR (KBr, cm^{-1}): 2212 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO_2$: 265.1103, Found: 265.1105.



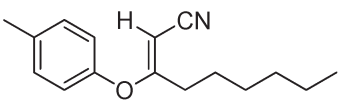
(*Z*)-3-(4-Methoxyphenyl)-3-(*p*-tolyloxy)acrylonitrile, 3p′. White solid, m.p. 39–41 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.92–6.86 (m, 4H), 5.29 (s, 1H), 3.82 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.33, 161.98, 153.70, 133.44, 130.06, 128.54, 124.44, 117.71, 114.18, 114.16, 79.45, 55.30, 20.58. IR (KBr, cm^{-1}): 2216 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO_2$: 265.1103, Found: 265.1102.



(*E*)-3-(4-Chlorophenyl)-3-(*p*-tolyloxy)acrylonitrile, 3q. White solid, m.p. 89–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 4.56 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.56, 150.73, 137.41, 136.19, 130.76. 130.32, 129.25, 128.72, 120.64, 117.73, 74.83, 20.74. IR (KBr, cm^{-1}): 2210 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{12}NOCl$: 269.0607, Found: 269.0610.

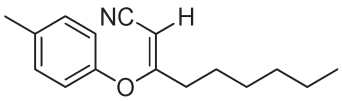


(*Z*)-3-(4-Chlorophenyl)-3-(*p*-tolyloxy)acrylonitrile, 3q′. White solid, m.p. 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.35 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.55, 153.20, 137.55, 134.23, 130.24, 129.92, 129.16, 128.16, 118.11, 115.01, 81.07, 20.67. IR (KBr, cm^{-1}): 2219 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{12}NOCl$: 269.0607, Found: 269.0606.

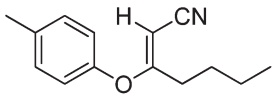


(*E*)-3-(*p*-Tolyloxy)-non-2-enenitrile, 3r. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H), 6.89–6.86 (m, 2H), 4.15 (s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.79–1.72 (m, 2H), 1.47–1.42 (m, 2H), 1.38–1.33 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.96, 150.60, 136.02, 130.61, 120.75, 117.86, 74.17, 33.09, 31.37, 28.46, 26.84, 22.42, 20.76, 13.96. IR (KBr, cm^{-1}): 2217 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{21}NO$: 243.1623,

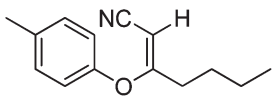
Found: 243.1626.



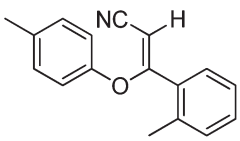
(*Z*)-3-(*p*-Tolyloxy)-non-2-enenitrile, 3r′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, J = 8.0 Hz, 2H), 6.95–6.92 (m, 2H), 4.67 (s, 1H), 2.35 (s, 3H), 2.23 (t, J = 7.6 Hz, 2H), 1.51–1.45 (m, 2H), 1.30–1.22 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.29, 151.62, 135.03, 130.08, 119.92, 115.19, 77.29, 32.94, 31.22, 28.32, 26.39, 22.30, 20.72, 13.87. IR (KBr, cm^{-1}): 2220 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{21}NO$: 243.1623, Found: 243.1624.



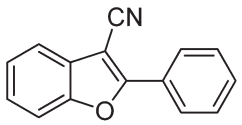
(*E*)-3-(*p*-Tolyloxy)-hept-2-enenitrile, 3s. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 7.6 Hz, 2H), 4.15 (s, 1H), 2.66 (t, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.78–1.71 (m, 2H), 1.53–1.44 (m, 2H), 1.00 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.00, 150.63, 136.07, 130.64, 120.79, 117.91, 74.21, 32.87, 29.01, 22.02, 20.80, 13.75. IR (KBr, cm^{-1}): 2217 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{14}H_{17}NO$: 215.1310, Found: 215.1307.



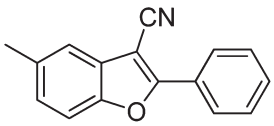
(*Z*)-3-(*p*-Tolyloxy)-hept-2-enenitrile, 3s′. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 4.66 (s, 1H), 2.36 (s, 3H), 2.23 (t, J = 7.6 Hz, 2H), 1.52–1.45 (m, 2H), 1.34–1.27 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.32, 151.64, 135.09, 130.12, 119.96, 115.23, 77.23, 32.73, 28.56, 21.85, 20.78, 13.60. IR (KBr, cm^{-1}): 2220 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{14}H_{17}NO$: 215.1310, Found: 215.1311.



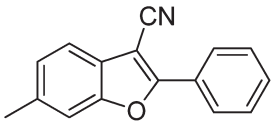
(*Z*)-3-(*o*-Tolyl)-3-(*p*-tolyloxy)acrylonitrile, 3t′. White solid, m.p. 43–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 1H), 7.29–7.26 (m, 1H), 7.21–7.17 (m, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 4.97 (s, 1H), 2.39 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.45, 152.17, 136.24, 133.88, 132.19, 130.86, 130.48, 129.83, 129.72, 125.83, 118.70, 115.20, 82.88, 20.54, 20.10. IR (KBr, cm^{-1}): 2212 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{15}NO$: 249.1154, Found: 249.1158.



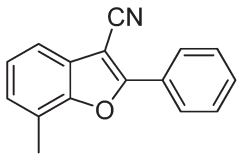
2-Phenylbenzofuran-3-carbonitrile, 4a. White solid, m.p. 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.18 (m, 2H), 7.72–7.70 (m, 1H), 7.58–7.50 (m, 4H), 7.44–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.57, 153.22, 131.13, 129.10, 127.72, 127.15, 126.40, 126.34, 124.63, 119.84, 114.25, 111.65, 88.01. IR (KBr, cm^{-1}): 2222 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{15}H_9NO$: 219.0684, Found: 219.0687.



5-Methyl-2-phenylbenzofuran-3-carbonitrile, 4b. White solid, m.p. 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.17 (m, 2H), 7.56–7.49 (m, 4H), 7.45 (d, J = 8.4 Hz, 1H), 7.23–7.21 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.59, 151.75, 134.54, 131.01, 129.10, 127.94, 127.66, 127.28, 126.38, 119.61, 114.44, 111.18, 87.75, 21.31. IR (KBr, cm^{-1}): 2222 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{11}NO$: 233.0841, Found: 233.0844.

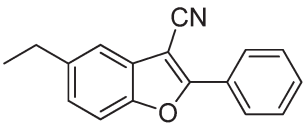


6-Methyl-2-phenylbenzofuran-3-carbonitrile, 4c. White solid, m.p. 114–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.14 (m, 2H), 7.55–7.51 (m, 4H), 7.34 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.02, 153.64, 137.02, 130.88, 129.06, 127.92, 126.25, 126.04, 124.61, 119.29, 114.49, 111.77, 87.82, 21.74. IR (KBr, cm^{-1}): 2225 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{11}NO$: 233.0841, Found: 233.0842.

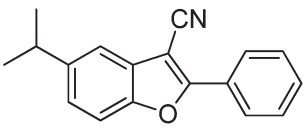


7-Methyl-2-phenylbenzofuran-3-carbonitrile, 4d. White solid, m.p. 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.19 (m, 2H), 7.58–7.52 (m, 4H), 7.30–7.27 (m, 1H), 7.22–7.20 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.21, 152.33, 131.03, 129.09, 127.93, 127.29, 126.73, 126.38, 124.69, 122.08, 117.26, 114.48, 88.24, 14.81. IR (KBr, cm^{-1}): 2220 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{11}NO$: 233.0841, Found:

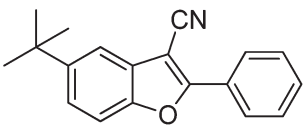
233.0845.



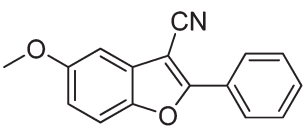
5-Ethyl-2-phenylbenzofuran-3-carbonitrile, 4e. White solid, m.p. 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.18 (m, 2H), 7.57–7.47 (m, 5H), 7.27–7.24 (m, 1H), 2.80 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.66, 151.89, 141.10, 131.02, 129.12, 127.97, 127.32, 126.71, 126.39, 118.43, 114.51, 111.31, 87.91, 28.77, 15.99. IR (KBr, cm^{-1}): 2222 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{17}H_{13}NO$: 247.0997, Found: 247.0999.



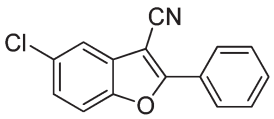
5-(*iso*-Propyl)-2-phenylbenzofuran-3-carbonitrile, 4f. White solid, m.p. 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.17 (m, 2H), 7.56–7.47 (m, 5H), 7.30–7.27 (m, 1H), 3.12–3.01 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.60, 151.85, 145.78, 130.96, 129.06, 127.91, 127.19, 126.32, 125.43, 116.89, 114.50, 111.28, 87.95, 34.08, 24.27. IR (KBr, cm^{-1}): 2224 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{18}H_{15}NO$: 261.1154, Found: 261.1151.



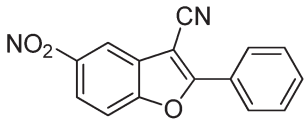
5-(*tert*-Butyl)-2-phenylbenzofuran-3-carbonitrile, 4g. White solid, m.p. 55–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21–8.18 (m, 2H), 7.71–7.70 (m, 1H), 7.57–7.51 (m, 3H), 7.50–7.49 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.67, 151.58, 148.15, 130.98, 129.09, 127.96, 126.91, 126.35, 124.41, 116.08, 114.59, 111.00, 88.15, 34.93, 31.65. IR (KBr, cm^{-1}): 2225 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{19}H_{17}NO$: 275.1310, Found: 275.1307.



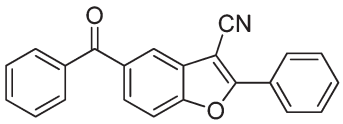
5-Methoxy-2-phenylbenzofuran-3-carbonitrile, 4h. White solid, m.p. 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.14 (m, 2H), 7.55–7.50 (m, 3H), 7.44 (d, J = 9.2 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 7.00–6.97 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.99, 157.26, 148.10, 131.00, 129.07, 127.92, 127.86, 126.27, 115.68, 114.42, 112.34, 101.40, 88.07, 55.85. IR (KBr, cm^{-1}): 2225 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{11}NO_2$: 249.0790, Found: 249.0791.



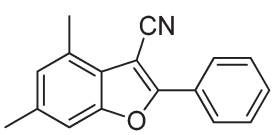
5-Chloro-2-phenylbenzofuran-3-carbonitrile, 4i. White solid, m.p. 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18–8.16 (m, 2H), 7.67 (d, J = 2.0 Hz, 1H), 7.56–7.54 (m, 3H), 7.51–7.49 (m, 1H), 7.39–7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.86, 151.62, 131.61, 130.59, 129.23, 128.52, 127.31, 126.75, 126.56, 119.55, 113.61, 112.75, 87.66. IR (KBr, cm^{-1}): 2224 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{15}H_8NOCl$: 253.0294, Found: 253.0292.



5-Nitro-2-phenylbenzofuran-3-carbonitrile, 4j. White solid, m.p. 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 2.4 Hz, 1H), 8.33–8.31 (m, 1H), 8.18–8.15 (m, 2H), 7.70 (d, J = 9.2 Hz, 1H), 7.58–7.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.41, 155.55, 145.17, 132.28, 129.33, 127.67, 126.64, 126.46, 122.04, 116.17, 112.72, 112.31, 88.55. IR (KBr, cm^{-1}): 2228 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{15}H_8N_2O_3$: 264.0535, Found: 264.0538.

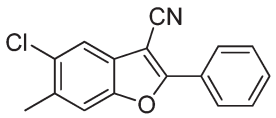


5-Benzoyl-2-phenylbenzofuran-3-carbonitrile, 4k. White solid, m.p. 127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21–8.18 (m, 2H), 8.13 (d, J = 1.2 Hz, 1H), 7.96–7.94 (m, 1H), 7.83–7.81 (m, 2H), 7.68–7.62 (m, 2H), 7.57–7.51 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.45, 163.02, 155.13, 137.31, 134.51, 132.59, 131.67, 129.89, 129.22, 128.56, 128.40, 127.15, 127.00, 126.53, 122.48, 113.60, 111.75, 88.42. IR (KBr, cm^{-1}): 2229 ($\nu_{C\equiv N}$), 1655 ($\nu_{C=O}$). HRMS (EI) ([M]$^+$) Calcd for $C_{22}H_{13}NO_2$: 323.0946, Found: 323.0952.

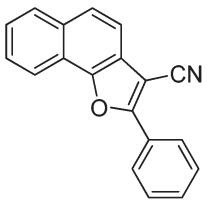


4,6-Dimethyl-2-phenylbenzofuran-3-carbonitrile, 4l. White solid, m.p. 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18–8.15 (m, 2H), 7.56–7.50 (m, 3H), 7.18 (s, 1H), 6.92 (s, 1H), 2.71 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.12, 153.74, 136.78, 131.14, 130.73, 129.03, 128.12, 127.15, 126.27, 122.93, 115.98, 109.32, 87.31, 21.60, 17.79. IR (KBr, cm^{-1}): 2221 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for

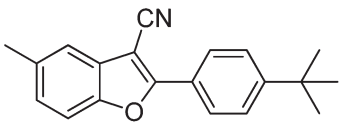
$C_{17}H_{13}NO$: 247.0997, Found: 247.1001.



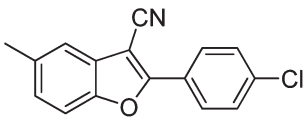
5-Chloro-6-methyl-2-phenylbenzofuran-3-carbonitrile, 4m. White solid, m.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.08 (m, 2H), 7.58 (s, 1H), 7.52–7.49 (m, 3H), 7.37 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.92, 151.77, 134.81, 131.27, 131.07, 129.10, 127.37, 126.29, 126.07, 119.47, 113.73, 113.19, 87.22, 20.89. IR (KBr, cm^{-1}): 2226 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{10}NOCl$: 267.0451, Found: 267.0452.



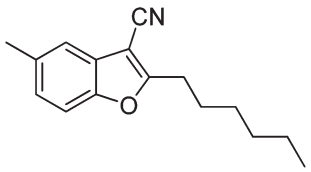
2-Phenylnaphtho[1,2-*b*]furan-3-carbonitrile, 4n. White solid, m.p. 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 8.20–8.18 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.64–7.60 (m, 2H), 7.57–7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.41, 148.92, 132.04, 130.73, 129.08, 128.51, 127.92, 127.13, 126.22, 126.01, 125.46, 123.13, 120.50, 119.74, 117.07, 114.31, 88.97. IR (KBr, cm^{-1}): 2225 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{19}H_{11}NO$: 269.0841, Found: 269.0843.



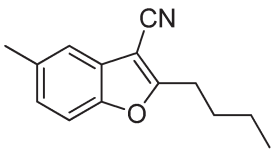
2-(4-*tert*-Butylphenyl)-5-methylbenzofuran-3-carbonitrile, 4o. White solid, m.p. 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.44 (s, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 2.47 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.70, 154.48, 151.48, 134.24, 127.26, 127.21, 126.08, 125.93, 125.02, 119.32, 114.47, 110.99, 86.89, 34.91, 30.97, 21.20. IR (KBr, cm^{-1}): 2221 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{20}H_{19}NO$: 289.1467, Found: 289.1472.



2-(4-Chlorophenyl)-5-methylbenzofuran-3-carbonitrile, 4q. White solid, m.p. 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 2H), 7.47–7.40 (m, 4H), 7.20 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.17, 151.65, 137.03, 134.69, 129.35, 127.90, 127.42, 127.02, 126.26, 119.58, 114.14, 111.15, 87.99, 21.29. IR (KBr, cm^{-1}): 2223 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{10}NOCl$: 267.0451, Found: 267.0452.



2-Hexyl-5-methylbenzofuran-3-carbonitrile, 4r. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.17–7.14 (m, 1H), 2.95 (t, J = 7.2 Hz, 2H), 2.47 (s, 3H), 1.86–1.78 (m, 2H), 1.42–1.32 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.70, 152.03, 134.07, 126.59, 125.99, 119.30, 113.58, 110.97, 90.26, 31.27, 28.64, 28.16, 27.40, 22.41, 21.24, 13.96. IR (KBr, cm^{-1}): 2229 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{16}H_{19}NO$: 241.1467, Found: 241.1471.



2-Butyl-5-methylbenzofuran-3-carbonitrile, 4s. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 2.96 (t, J = 7.2 Hz, 2H), 2.47 (s, 3H), 1.84–1.77 (m, 2H), 1.48–1.39 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.73, 152.05, 134.12, 126.63, 126.00, 119.33, 113.65, 111.00, 90.29, 29.50, 27.90, 22.15, 21.28, 13.61. IR (KBr, cm^{-1}): 2229 ($\nu_{C\equiv N}$). HRMS (EI) ([M]$^+$) Calcd for $C_{14}H_{15}NO$: 213.1154, Found: 213.1151.

Acknowledgements

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Notes and references

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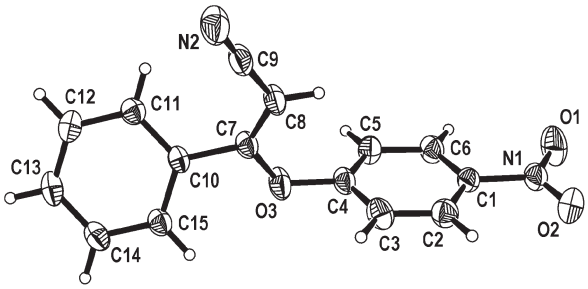

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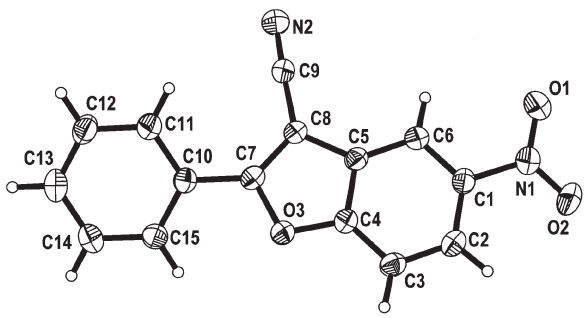

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