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Practical one-pot transformation of electron-rich aromatics into aromatic nitriles with molecular iodine and aq NH_3 using Vilsmeier–Haack reaction

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ABSTRACT

Various electron-rich aromatics could be efficiently transformed into the corresponding aromatic nitriles in good to moderate yields by treatment with DMF and $POCl_3$, followed by the reaction with molecular iodine or 1,3-diiodo-5,5-dimethylhydantoin (DIH) in aq NH_3. Some of less reactive aromatics, such as anisole, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, and mesitylene, could be also transformed into the corresponding aromatic nitriles in good to moderate yields using *N*-methylformanilide and $O(POCl_2)_2$, followed by the reaction with molecular iodine in aq NH_3. Moreover, propiophenone derivatives could be successfully transformed into the corresponding β-chlorocinnamonitriles by the reaction with DMF and $POCl_3$, followed by the reaction with molecular iodine and aq NH_3. These reactions are novel metal-free one-pot methods for the preparation of aromatic nitriles from electron-rich aromatics and β-chlorocinnamonitriles from propiophenones.

1. Introduction

Aromatic nitriles are important synthetic transformation precursors because they can be easily transformed into amides, esters, primary amines, carboxylic acids, and nitrogen-containing heterocycles, such as tetrazoles and oxazoles, and are also used as synthetic intermediates for agrochemicals, pharmaceuticals, and functional materials.[1] Practically, Citalopram hydrobromide® (treatment of alcohol dependency), Periciazine® (anti-psychotic drug), Fadrozole® (oncolytic drug), and Letrozole® (breast cancer therapy) are pharmaceutically important aromatic nitriles, and 4-cyano-4′-pentylbiphenyl is a typical liquid crystal material.[2] The most typical methods for the preparation of aromatic nitriles are the dehydration of aromatic primary amides[3,4] with $SOCl_2$, TsCl/Py, P_2O_5, $POCl_3$, $COCl_2$, $(EtO)_3P/I_2$, Ph_3P/CCl_4, $(COCl)_2$/DMSO, $(CH_2O)_n/HCO_2H$, $(CF_3SO_2)_2O/Et_3N$, or Bu_2SnO, the condensation of carboxylic acids with NH_3/silica gel or NH_3/ethyl polyphosphate, the reaction of esters with Me_2AlNH_2,[4] and the Sandmeyer reaction of aromatic diazonium ion with toxic CuCN.[4,5] On the other hand, recently, the direct transformation of aromatic bromides into the corresponding aromatic nitriles has been actively studied with CuCN in *N*,*N*-dimethylformamide (DMF) at 153 °C (the Rosenmund–von Braun reaction),[6a] $Pd(OAc)_2$•$K_4[Fe(CN)_6]$ at 120 °C,[6b] Pd•(binaphthyl)$P(Bu^t)_2$•$Zn(CN)_2$•Zn at 80–95 °C,[6c] $Pd_2(dba)_3$•$Zn(CN)_2$•DPPF at 80–120 °C,[6d] $Pd(tmhd)_2$•$K_4[Fe(CN)_6]$ at 80 °C,[6e] $Zn(CN)_2$•$Pd_2(dba)_3$ at 100 °C,[6f] Pd/C•CuI•$K_4[Fe(CN)_6]$•$3H_2O$ at 130–140 °C,[6g] CuI•alkylimidazole•Pd/C•CuI•$K_4[Fe(CN)_6]$ at 140–180 °C,[6h] $Zn(CN)_2$•$Pd_2(dba)_3$•dppf•Zn•$ZnBr_2$ at 95 °C,[6i] CuO•Pd•$K_4[Fe(CN)_6]$ at 120 °C,[6j] $K_4Fe(CN)_6$•CuI/microwave,[6k] $Pd(OAc)_2$•$Cu(OAc)_2$• $K_4[Fe(CN)_6]$ at 130 °C,[6l] Pd/C•dppf•$Zn(CN)_2$ at 100–120 °C,[6m] Pd•*t*-Bu_3P•NaCN at 70 °C,[6n] $Pd(dba)_2$• $K_4[Fe(CN)_6]$•*t*-BuOK at 50 °C,[6o] $Pd\{C_6H_4[CH_2N(CH_2Ph)_2]\}(\mu\text{-}Br)_2$•$K_4[Fe(CN)_6]$ at 130 °C,[6p] and $Pd(Ph_3P)_4$•$K_4[Fe(CN)_6]$ at 85 °C,[6q] all of which require toxic metal cyanides. The direct cyanation of aromatics containing a 2-pyridyl group via C–H bond cleavage with $Cu(OAc)_2$•TMSCN[7a] and $Pd(OAc)_2$•CuBr•CuCN[7b] at 130 °C, the cyanation of indoles at 3-position with $Pd(OAc)_2$•$Cu(OAc)_2$•$K_4[Fe(CN)_6]$,[6l] the cyanation of benzothiazole with CuCN•phenanthroline•I_2•NaCN•*t*-BuOLi at 110 °C,[7c] and the cyanation of indoles and aromatics bearing a 2-pyridyl group with FeI_2•CuCN•$PhI(OAc)_2$,[7d] all of which require toxic metal cyanides as well, were reported. In addition, the cyanation of aromatics bearing a 2-pyridyl group with $Pd(OAc)_2$•$CuBr_2$•DMF at 130 °C,[8a] the cyanation of aromatic bromides and iodides in the presence of $Cu(OAc)_2$ in DMF at 150 °C,[8b] and the cyanation of indoles at 3-position with $Pd(OAc)_2$•$CuBr_2$•$FeCl_2$•DMF at 130 °C,[8c] under cyanide-free conditions were reported. Moreover, the metal-free cyanation of indoles and pyrroles with $PhI(O_2CCF_3)_2$ and TMSCN in the presence of BF_3•Et_2O[9a] and $GaCl_3$-catalyzed cyanation of electron-rich aromatics with BrCN[9b] were also reported. However, most of the methods mentioned above required toxic transition metals and/or cyanides. Thus, a transition-metal-free and cyanide-free, and therefore environmentally benign and economical approach for the transformation of aromatics into the corresponding aromatic nitriles is greatly required. To the best of our knowledge,

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studies on the one-pot transformation of aromatics into the corresponding aromatic nitriles using less toxic reagents are extremely limited. Typical methods are the reaction of electron-rich aromatics with chlorosulfonylisocyanate to form *N*-chlorosulfonyl amides and the subsequent treatment with DMF to provide aromatic nitriles, together with the evolution of SO_3 and HCl,[10a,b] and the reaction of indoles or pyrroles with triphenylphospine–thiocyanogen (TPPT).[10c] Another method reported by us recently is the reaction of methoxybenzenes and fluorobenzenes with *n*-BuLi and subsequently DMF, followed by the reaction with molecular iodine and aq NH_3.[11]

Here, as part of our ongoing studies on the use of molecular iodine for organic synthesis,[12] we would like to report one-pot transformation of aromatics into the corresponding aromatic nitriles and related reactions as a full paper.[13]

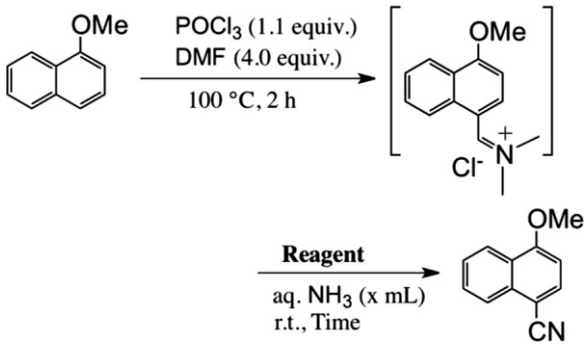
2. Results and discussion

The Vilsmeier–Haack reaction is an efficient method for the transformation of electron-rich aromatics into the corresponding aromatic aldehydes using $POCl_3$ and DMF.[14,15] Based on this reaction and our previous study on the use molecular iodine for the transformation of benzylic halides and benzylic alcohols into aromatic nitriles,[12i–l] we recently reported a one-pot transformation of electron-rich aromatics into the corresponding aromatic nitriles using $POCl_3$ and DMF, followed by the reaction with molecular iodine and aq NH_3.[13] To further extend the application of this novel metal-free and cyanide-free introduction of a cyano group into aromatics, the details and limitations of the reaction were studied.

As the first step, 1-methoxynaphthalene (6 mmol) was treated with $POCl_3$ (1.1 equiv) and DMF (4.0 equiv) at 100 °C for 2 h to form *N*,*N*-dimethyliminium salt quantitatively. Then, molecular iodine and aq NH_3 (28–30%) were added to the formed *N*,*N*-dimethyliminium salt at room temperature as the second step, as shown in Table 1 (entries 1–5). Optimization studies indicated that treatment of the *N*,*N*-dimethyliminium salt with molecular iodine (2.0 equiv) and aq NH_3 (12 mL) for 3 h at room temperature gave 4-methoxy-1-cyanonaphthalene in 99% yield (entry 5). When molecular iodine was not added to the *N*,*N*-dimethyliminium salt at the second step, 4-methoxy-1-cyanonaphthalene was not obtained at all and instead, 4-methoxy-1-naphthaldehyde was obtained quantitatively (entry 6). On the other hand, when *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), and 1,3-diiodo-5,5-dimethylhydantoin (DIH) were used instead of molecular iodine, NCS did not work at all, NBS gave 4-methoxy-1-cyanonaphthalene in moderate yield, and NIS and DIH showed high reactivity to provide 4-methoxy-1-cyanonaphthalene in good yields (entries 7–10).

Thus, the use of molecular iodine or iodine-containing reagents, such as NIS and DIH, is the key to furnish 4-methoxy-1-cyanonaphthalene in good yields. Here, DIH has two N–I bonds and therefore, it works as 2 equiv of molecular iodine. Based on these results, various electron-rich aromatics, such as 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, 1,2,3-trimethoxybenzene, 1-methoxynaphthalene, 2-methoxynaphthalene, 1,5-dimethoxynaphthalene, and *N*,*N*-dimethylaniline, were treated with $POCl_3$ and DMF, followed by the reaction of molecular iodine (2.0 equiv) or DIH (1.0 equiv), and aq NH_3 (12 mL) at room temperature for 3 h to provide the corresponding aromatic nitriles in good yields with high regioselectivity, as shown in Table 2 (entries 1–8). There is little difference in the yields of aromatic nitriles between molecular iodine and DIH. The same treatment of heteroaromatics, such as indole, *N*-methylindole, *N*-methylcarbazole, thiophene, 2-decylthiophene, and 2-decylfuran, gave also the corresponding heteroaromatic nitriles in good to moderate yields with high regioselectivities (entries 9–11, 13–15). Treatment of *N*-benzylpyrrole with $POCl_3$ and DMF, followed by the reaction with molecular iodine or DIH, and aq NH_3 gave two regioisomers, *N*-benzyl-2-cyanopyrrole and *N*-benzyl-3-cyanopyrrole, in good yields; in this case, the former nitrile was the major product (entry 12). Meanwhile, the same treatment of benzothiophene and benzofuran did not generate the corresponding heteroaromatic nitriles at all. Then, less reactive aromatics, such as anisole, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, and mesitylene, for the Vilsmeier–Haack reaction were used as substrates for the present reaction. Anisole, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, and mesitylene did not react with $POCl_3$ and DMF effectively and therefore, the corresponding aromatic nitriles were formed in extremely low yields, as shown in Table 3 (Method **A**, entries 1, 4, 7, 16). However, when anisole, 1,2-dimethoxybenzene, and 1,4-dimethoxybenzene were treated with $O(POCl_2)_2$ and *N*-methylformanilide (NMFA) (Method **B**) at 100 °C for 10–13 h in the first step,[15] and then, molecular iodine and aq NH_3 were added to the reaction mixture, 1-cyano-4-methoxybenzene, 1-cyano-3,4-dimethoxybenzene, and 1-cyano-2,5-dimethoxybenzene were furnished in good yields with high regioselectivities, respectively (entries 2, 5, 8). Treatment of 1,2,3-trimethoxybenzene and anthracene with $POCl_3$ and DMF (Method **A**), followed by the reaction with molecular iodine and aq NH_3 gave the corresponding aromatic nitriles in moderate yields, while the same reactions with $O(POCl_2)_2$ and NMFA, followed by the reaction with molecular iodine and aq NH_3 gave 1-cyano-2,3,4-trimethoxybenzene and 9-cyanoanthracene in good yields with high regioselectivities, respectively, (entries 10, 11, 13, 14). This is due to the formation of highly electrophilic iminium species from the reaction of NMFA and $O(POCl_2)_2$. Treatment of 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, anthracene, and mesitylene with $(CF_3SO_2)_2O$ and DMF,[16]

Table 1
Optimization of the second-step reaction for one-pot transformation of 1-methoxynaphthalene into 1-cyano-4-methoxynaphthalene



Entry	Reagent	Aq NH_3 (*x* ml)	Time (h)	Yield (%)
1	I_2 (1.1 equiv)	6	3	41
2	I_2 (1.1 equiv)	6	18	38
3	I_2 (1.1 equiv)	12	3	66
4	I_2 (1.5 equiv)	12	3	71
5	I_2 (2.0 equiv)	12	3	99
6	—	12	3	0
7	NCS (2.0 equiv)	12	3	Trace
8	NBS (2.0 equiv)	12	3	43
9	NIS (2.0 equiv)	12	3	89
10	DIH (1.25 equiv)	12	3	89

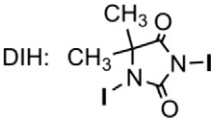
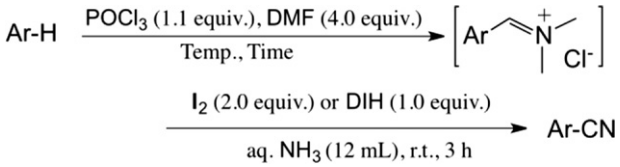
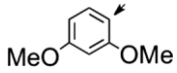
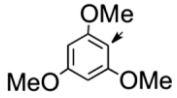
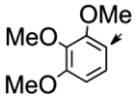
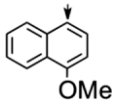
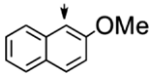
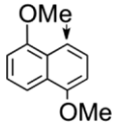
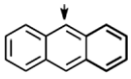
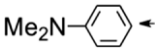
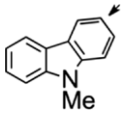
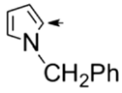
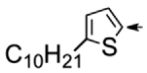
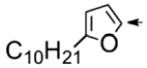


Table 2
One-pot transformation of aromatics into aromatic nitriles



Entry	Ar–H	Temp (°C)	Time (h)	Yield (%)	
				I_2	DIH
1		40	3	74	92
2		40	3	99	99
3		100	4	59	67
4		100	2	99	89[a]
5		100	6	90	90[a]
6		80	4	91	99[a]
7		100	10	67	—
8		80	2	86	86[a]
9		rt	3	81	65
10		40	3	99	92
11		100	1	99	98[a]
12		40	1	87 (α:β=72:15)	86 (α:β=62:24)
13		80	4	45	54
14		80	2	76	81
15		80	2	91	81
16		100	6	0	—

[a] DIH (1.25 equiv) was used.

followed by the reaction with molecular iodine and aq NH_3 generated the corresponding aromatic nitriles in moderate yields, respectively, (entries 6, 9, 15, 17). However, the introduction of a cyano group into naphthalene, benzothiophene, and benzofuran with methods **A**–**C** did not succeed because the introduction of the *N*,*N*-dimethyliminium group to the aromatics (the first step) did not occur.

When the previous method[11] and the present method were compared in terms of the introduction of a cyano group into 1,3-dimethoxybenzene and *N*-methylindole, the complementary introduction of the cyano group could be achieved, as shown in Scheme 1.

Thus, when 1,3-dimethoxybenzene and *N*-methylindole were treated with $POCl_3$ and DMF, followed by the reaction with molecular iodine and aq NH_3, 1-cyano-2,4-dimeth oxybenzene and *N*-methyl-3-cyanoindole were obtained in good yields with high regioselectivities, respectively. On the other hand, when 1,3-dimethoxybenzene and *N*-methylindole were treated with *n*-BuLi and subsequently DMF, followed by the reaction with molecular iodine and aq NH_3, 2-cyano-1,3-dimethoxybenzene and *N*-methyl-2-cyanoindole were obtained in good yields with high regioselectivities, respectively.

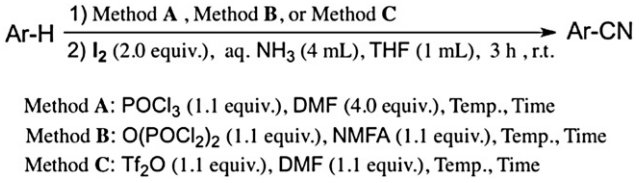
Then, as a synthetic application of the present method, aromatic ketones were used as the substrate. When propiophenone was treated with $POCl_3$ (1.6 equiv) and DMF (1.6 equiv) at 60 °C for 3 h, β-chloro-α-methylcinnamonitrile was obtained in 93% yield with *E*/*Z*=83/17 ratio. Based on this result, *p*-methylpropiophenone, *p*-methoxypropiophenone, *p*-chloropropiophenone, *p*-fluoropropiophenone, *n*-nonanophenone, α-tetralone, and 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one were treated with $POCl_3$ and DMF, followed by the reaction with molecular iodine and aq NH_3 to provide the corresponding β-chlorocinnamonitrile derivatives in good yields, respectively, as shown in Table 4.

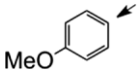
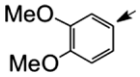
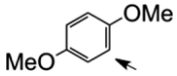
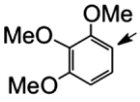
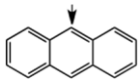
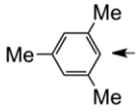
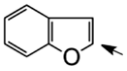
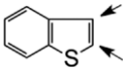
A plausible reaction mechanism for the one-pot transformation of electron-rich aromatics into aromatic nitriles is proposed, as shown in Scheme 2. The initial step involves the Vilsmeier–Haack reaction to form aromatic *N*,*N*-dimethyliminium salt (**a**). Once aromatic *N*,*N*-dimethyliminium salt (**a**) is formed, it reacts smoothly with aq NH_3 to form the corresponding aromatic imine (**b**), which further reacts with molecular iodine to generate the corresponding aromatic *N*-iodoimine (**c**). Once *N*-iodoimine (**c**) is formed, elimination of HI rapidly occurs in aq NH_3 to provide the corresponding aromatic nitrile.

3. Conclusion

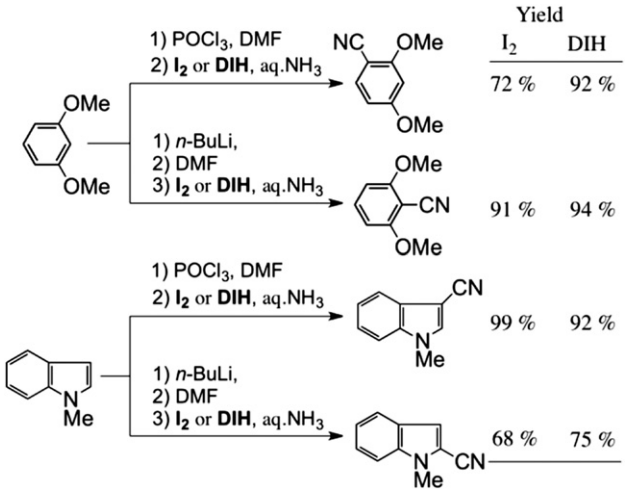
In conclusion, various electron-rich aromatics, such as 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, 1-methoxynaphthalene, 2-methoxynaphthalene, 1,5-dimethoxynaphthalene, anthracene, *N*,*N*-dimethylaniline, indole, 2-decylthiophene,

Table 3
One-pot transformation of aromatics into aromatic nitriles with modefied Vilsmeier–Haack reaction



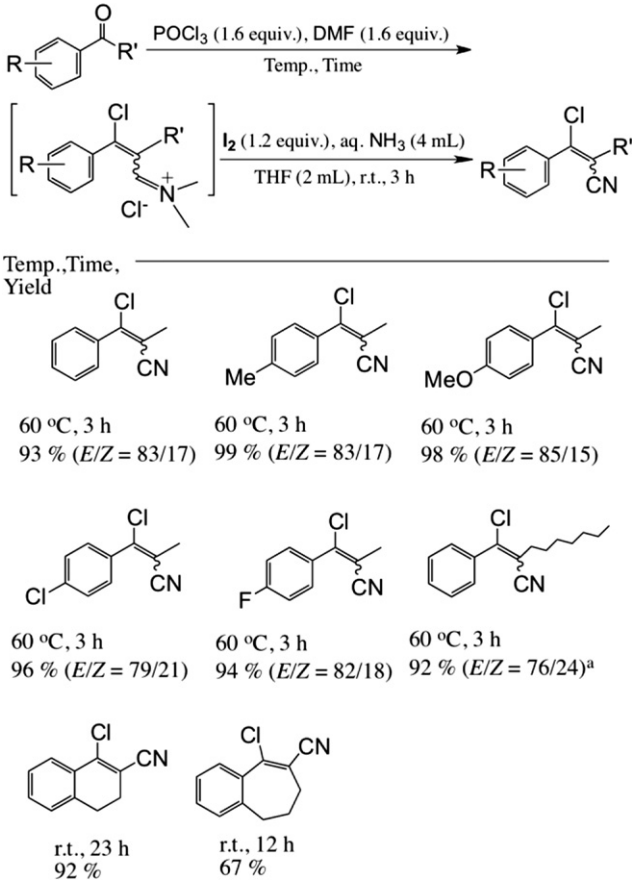
Entry	Ar–H	Method	Temp (°C)	Time (h)	Yield (%)
1		A	100	10	11
2		B	100	13	69
3		C	100	13	19
4		A	100	5	11 (35)[a]
5		B	100	10	92
6		C	100	10	53
7		A	100	6	0 (98)[a]
8		B	100	10	71 (19)[a]
9		C	100	10	32 (39)[a]
10		A	100	4	59
11		B	100	12	82
12		C	100	12	78 (8)[a]
13		A	100	10	67
14		B	100	10	99
15		C	100	10	32 (41)[a]
16		A	100	5	0 (62)[a]
17		C[b]	120–130	65	52
18		A	90	8	0 (76)[a]
19		C	100	20	0 (39)[a]
20		A	100	6	12
21		B	100	13	24
22		C	100	13	24
23		A	100	6	0
24		B	100	13	35[c]
25		C	100	13	4 (49)[a]

[a] Yield of starting material.
[b] Tf_2O (2.2 equiv) and DMF (2.2 equiv) were used.
[c] Ratio of α:β was 45:55.



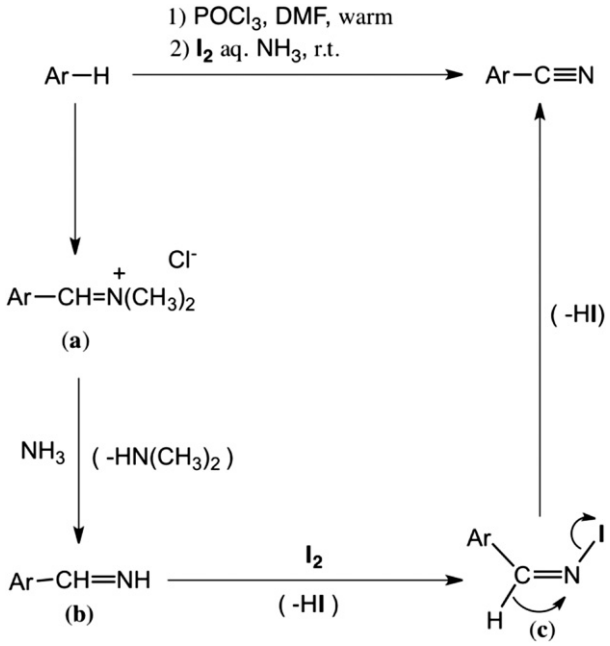
Scheme 1. Complementary one-pot introduction of cyano group with (1) $POCl_3$/DMF, (2) I_2/aq NH_3 system and (1) *n*-BuLi, (2) DMF, (3) I_2/aq. NH_3 system.

Table 4
One-pot transformation of alkyl aryl ketones into β-chlorocinnamonitrile derivatives



[a] *E*/*Z* ratio was decided by ^{1}H-NMR analysys.

2-decylfuran, and pyrrole, could be smoothly transformed into the corresponding aromatic nitriles and heteroaromatic nitriles in good yields, respectively, by treatment with $POCl_3$ and DMF, followed by the reaction with molecular iodine in aq NH_3. However, the introduction of cyano group to less reactive aromatics, such as benzothiophene, benzofuran, naphthalene, and benzene, did not



Scheme 2. Reaction mechanism for nitrile from aromatics.

succeed, because the corresponding aromatic *N*,*N*-dimethyliminium salts were not formed from these aromatics with a $POCl_3$ and DMF system and a NMFA and $O(POCl_2)_2$ system, respectively. The same treatment of propiophenones with $POCl_3$ and DMF, followed by the reaction with molecular iodine and aq NH_3 gave the corresponding β-chlorocinnamonitrile derivatives in good yields, respectively. The present reactions are novel metal-free one-pot transformations of electron-rich aromatics and propiophenones into the corresponding aromatic nitriles and β-chlorocinnamonitriles. The advantages of the present reaction are operational simplicity, low cost, low toxicity, and easy availability of reaction materials. Therefore, we believe the present reactions are useful and environmentally benign methods for the preparation of aromatic nitriles from aromatics and β-chlorocinnamonitriles from propiophenones.

4. Experimental section

4.1. General

^1H NMR spectra were recorded with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in parts per million downfield from TMS in δ units. Mass spectra were recorded on JMS-HX110, MS-T100GCV, and Thermo LTQ Orbtrap spectrometers. IR spectra were measured with a JASCO FT-IR4100 spectrometer. Melting points were determined on a YAMATO Melting Point electrothermal apparatus MP-21 in open capillary tubes and are uncorrected. Kieselgel 60 F254 was used for TLC, Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography, and Wakogel B-5F was used for preparative *p*-TLC.

4.2. Typical experimental procedure for the transformation of aromatics into aromatic nitriles with I_2 and aq NH_3 using the Vilsmeier–Haack reaction

To a flask containing 1,3,5-trimethoxybenzene (1009.1 mg, 6 mmol) were added $POCl_3$ (1011.9 mg, 6.6 mmol) and DMF (1754.1 mg, 24 mmol) at 0 °C. After being stirred for 3 h at 40 °C, I_2 (3045.7 mg, 12 mmol) and aq NH_3 (12 mL, 28–30%) were added to the reaction mixture. The obtained mixture was stirred for 3 h at rt. After the reaction, the mixture was poured into aq satd Na_2SO_3 solution and extracted with $CHCl_3$ (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated to provide almost pure 2,4,6-trimethoxybenzonitrile (1156.1 mg) in 99% yield. If necessary, it was recrystallized from a mixture of hexane and EtOAc (1:1).

4.3. Typical experimental procedure for the transformation of aromatics into aromatic nitriles with DIH and aq NH_3 using the Vilsmeier–Haack reaction

To a flask containing 1,3,5-trimethoxybenzene (1009.1 mg, 6 mmol) were added $POCl_3$ (1011.9 mg, 6.6 mmol) and DMF (1754.1 mg, 24 mmol) at 0 °C. After being stirred for 3 h at 40 °C, DIH (2279.5 mg, 6 mmol) and aq ammonia (12 mL, 28–30%) were added to the reaction mixture. The obtained mixture was stirred for 3 h at rt. After the reaction, the mixture was poured into aq satd Na_2SO_3 solution and extracted with $CHCl_3$ (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated to provide almost pure 2,4,6-trimethoxybenzonitrile (1156.1 mg) in 99% yield. If necessary, it was recrystallized from a mixture of hexane and EtOAc (1:1).

4.4. Typical experimental procedure for transformation of 1,2-dimethoxybenzene to 3,4-dimethoxybenzonitrile with I_2 and aq NH_3 using NMFA and $O(POCl_2)_2$ system

To an ice cooled solution of *N*-methylformanilide (2.2 mmol) was added dropwise diphosphoryl chloride (2.2 mmol). The solution was stirred for 30 min at 0 °C, and then 1,2-dimethoxybenzene (276.3 mg, 2 mmol) in DMF (1.0 mL) was added dropwise. After being stirred for 10 h at 100 °C, I_2 (1015.2 mg, 4 mmol), aq NH_3 (4 mL, 28–30%) and THF (1 mL) were added to the reaction mixture. The obtained mixture was stirred for 3 h at rt. After the reaction, the mixture was poured into aq satd Na_2SO_3 solution and extracted with $CHCl_3$ (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated. The product was purified by flash short column chromatography (Hexane:AcOEt=3:1) to afford 3,4-dimethoxybenzonitrile as a white solid in 92% yield.

4.5. Typical experimental procedure for conversion of mesityrene to 2,4,6-trimethylbenzonitrile with I_2 and aq NH_3 using $(Tf)_2O$ and DMF system

To an ice cooled solution of DMF (4.4 mmol) was added dropwise Tf_2O (4.4 mmol) in a screw-capped glass vial (10 mL). The solution was stirred for 0.5 h at 0 °C.Then, 1,3,5-trimethylbenzene (240.4 mg, 2 mmol) in DMF (1.0 ml) was added dropwise. After being stirred for 65 h at 120–130 °C, I_2 (1015.2 mg, 4 mmol), aq NH_3 (4 mL, 28–30%), and THF (1 mL) were added to the reaction mixture, and the obtained mixture was stirred for 3 h at rt. After the reaction, the mixture was poured into aq satd Na_2SO_3 solution and extracted with $CHCl_3$ (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated. The product was purified by flash short column chromatography (Hexane:AcOEt=9:1) to give 2,4,6-trimethylbenzonitrile as a white solid in 52% yield.

4.5.1. 2,4-Dimethoxybenzonitrile. Mp 93–94 °C (commercial, mp 93–94 °C); IR (Nüjol) 2219 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3H), 3.90 (s, 3H), 6.46 (s, 1H), 6.51 (d, *J*=8.5 Hz, 1H), 7.48 (d, *J*=8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 55.9, 93.8, 98.4, 105.7, 116.9, 134.8, 162.8, 164.6.

4.5.2. 2,4,6-Trimethoxybenzonitrile. Mp 139–140 °C (commercial, mp 143–145 °C); IR (Nüjol) 2212 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):

δ 3.86 (s, 3H), 3.89 (s, 6H), 6.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.0, 83.7, 90.2, 114.6, 163.6, 165.3.

4.5.3. 2,3,4-Trimethoxybenzonitrile. Mp 55–56 °C (commercial, mp 56–57 °C); IR (Nüjol) 2226 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 3.92 (s, 3H), 4.06 (s, 3H), 6.70 (d, *J*=8.7 Hz, 1H), 7.29 (d, *J*=8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.1, 60.9, 61.6, 98.9, 107.4, 116.4, 128.6, 141.7, 155.7, 157.9.

4.5.4. 4-Methoxy-1-cyanonaphthalene. Mp 100–102 °C (commercial, mp 100–102 °C); IR (Nüjol) 2213 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (s, 3H), 6.84 (d, *J*=8.2 Hz, 1H), 7.59 (t, *J*=8.2 Hz, 1H), 7.69 (t, *J*=8.2 Hz, 1H), 7.86 (d, *J*=8.2 Hz, 1H), 8.17 (d, *J*=8.2 Hz, 1H), 8.32 (d, *J*=8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.0, 101.9, 103.3, 118.5, 122.7, 124.8, 125.1, 126.7, 128.9, 133.4, 134.0, 159.3.

4.5.5. 2-Methoxy-1-cyanonaphthalene. Mp 96–97 °C (lit.[17] mp 95–96 °C); IR (Nüjol) 2211 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (s, 3H), 7.28 (d, *J*=8.7 Hz, 1H), 7.45 (t, *J*=8.0 Hz, 1H), 7.64 (t, *J*=8.0 Hz, 1H), 7.83 (d, *J*=8.0 Hz, 1H), 8.04 (d, *J*=8.7 Hz, 1H), 8.09 (d, *J*=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5, 95.0, 111.9, 115.7, 123.9, 125.0, 127.9, 128.4, 129.1, 133.4, 135.0, 161.5.

4.5.6. 4,8-Dimethoxy-1-cyanonaphthalene. Mp 126–129 °C; IR (Nüjol) 2211 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (s, 6H), 6.85 (d, *J*=8.2 Hz, 1H), 6.99 (d, *J*=7.7 Hz, 1H), 7.47 (t, *J*=7.7 Hz, 1H), 7.86 (d, *J*=8.2 Hz, 1H), 7.89 (d, *J*=7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.9, 98.3, 103.9, 107.5, 114.8, 120.8, 124.9, 126.7, 126.8, 136.2, 154.6, 158.8; HRMS (ESI) $[M]^+$, calcd for $C_{13}H_{11}O_2N$=213.0784, found=213.0780.

4.5.7. 9-Cyanoanthracene. Mp 173–175 °C (commercial, mp 173–177 °C); IR (Nüjol) 2212 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (t, *J*=8.5 Hz, 2H), 7.73 (t, *J*=8.5 Hz, 2H), 8.09 (d, *J*=8.5 Hz, 2H), 8.43 (d, *J*=8.5 Hz, 2H), 8.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.4, 117.2, 125.2, 126.3, 128.9 (2C), 130.6, 132.7, 133.3.

4.5.8. 4-(N,N-Dimethyamino)benzonitrile. Mp 74–75 °C (commercial, mp 75 °C); IR (Nüjol) 2210 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (s, 6H), 6.64 (d, *J*=9.1 Hz, 2H), 7.47 (d, *J*=9.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 97.2, 111.3, 120.7, 133.3, 152.4.

4.5.9. 3-Cyanoindole. Mp 177–179 °C (commercial, mp 179–182 °C); IR (Nüjol) 2227 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.20–7.29 (m, 2H), 7.56 (d, *J*=8.0 Hz, 1H), 7.64 (d, *J*=8.0 Hz, 1H), 8.24 (s, 1H), 12.20 (br, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): 84.3, 113.0, 116.4, 118.4, 121.7, 123.4, 126.8, 134.5, 135.2.

4.5.10. N-Methyl-3-cyanolindole. Mp 60–61 °C (lit.[18] mp 60.5–61.5 °C); IR (Nüjol) 2219 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (s, 3H), 7.25 (t, *J*=6.4 Hz, 1H), 7.28–7.35 (m, 2H), 7.44 (s, 1H), 7.68 (d, *J*=7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.2, 84.5, 110.1, 115.8, 119.1, 121.7, 123.4, 127.3, 135.4, 135.6.

4.5.11. 9-Methyl-9H-carbazole-3-carbonitrile. Mp 90–92 °C (lit.[19] mp 91–93 °C); IR (Nüjol) 2212 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.31 (t, *J*=7.8 Hz, 1H), 7.37 (d, *J*=8.6 Hz, 1H), 7.42 (d, *J*=8.0 Hz, 1H), 7.55 (t, *J*=8.0 Hz, 1H), 7.66 (d, *J*=8.6 Hz, 1H), 8.04 (d, *J*=7.8 Hz, 1H), 8.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.9, 101.0, 108.7, 108.8, 120.1, 120.3, 120.4, 121.3, 122.4, 124.6, 126.9, 128.4, 141.1, 142.0.

4.5.12. 2-Cyano-N-benzylpyrrole. Oil; IR (neat) 2215 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (s, 2H), 6.19 (dd, *J*=2.9, 2.7 Hz, 1H), 6.80–6.86 (m, 2H), 7.18 (d, *J*=7.4 Hz, 2H), 7.31–7.38 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 104.0, 109.9, 113.7, 120.2, 126.6, 127.3, 128.3, 128.9, 135.9; HRMS(FAB) $[M+H]^+$, calcd for $C_{12}H_{11}N_2$=183.0922, found=183.0927.

4.5.13. 3-Cyano-N-benzylpyrrole. Oil; IR (neat) 2224 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.06 (s, 2H), 6.44 (d, *J*=1.7 Hz, 1H), 6.65 (s, 1H), 7.11–7.17 (m, 3H), 7.33–7.41 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.0, 104.6, 112.5, 119.0, 122.3, 127.3, 128.1, 128.4, 129.0, 135.8; HRMS(FAB) $[M+H]^+$, calcd for $C_{12}H_{11}N_2$=183.0922, found=183.0927.

4.5.14. 2-Cyanothiophene. Oil (commercial, oil); IR (neat) 2222 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (dd, *J*=5.2, 3.7 Hz, 1H), 7.62 (d, *J*=5.2 Hz, 1H), 7.64 (d, *J*=3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.8, 114.1, 127.6, 132.5, 137.3.

4.5.15. 5-Decylthiophene-2-carbonitrile. Oil; IR (neat) 2218 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.1 Hz, 3H), 1.23–1.38 (m, 14H), 1.67 (quintet, *J*=7.5 Hz, 2H), 2.83 (t, *J*=7.5 Hz, 2H), 6.78 (d, *J*=3.6 Hz, 1H), 7.43 (d, *J*=3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.5, 28.8, 29.0, 29.1, 29.3, 29.6, 29.9, 31.2, 31.7, 106.6, 114.3, 124.7, 137.4, 154.2; HRMS (FAB) $[M+H]^+$, calcd for $C_{15}H_{24}NS$=250.1629, found=250.1636.

4.5.16. 5-Decylfuran-2-carbonitrile. Oil; IR (neat) 2229 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.0 Hz, 3H), 1.21–1.38 (m, 14H), 1.65 (quintet, *J*=7.1 Hz, 2H), 2.66 (t, *J*=7.1 Hz, 2H), 6.11 (d, *J*=3.4 Hz, 1H), 6.99 (d, *J*=3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 27.5, 28.1, 28.9, 29.1, 29.2, 29.4, 29.5, 31.8, 106.9, 111.9, 123.0, 124.2, 162.5; HRMS (FAB) $[M+H]^+$, calcd for $C_{15}H_{24}NO$=234.1858, found=234.1861.

4.5.17. 4-Methoxybenzonitrile. Mp 54–55 °C (commercial, mp 57–59 °C); IR (Nüjol) 2216 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.95 (d, *J*=8.9 Hz, 2H), 7.59 (d, *J*=8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 103.8, 114.7, 119.2, 133.9, 162.8.

4.5.18. 3,4-Dimethoxybenzonitrile. Mp 65–67 °C (commercial, mp 68–70 °C); IR (Nüjol) 2223 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 3.94 (s, 3H), 6.90 (d, *J*=8.4 Hz, 1H), 7.08 (d, *J*=2.0 Hz, 1H), 7.29 (dd, *J*=8.4 Hz, *J*=2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.92, 55.94, 103.7, 111.1, 113.7, 119.1, 126.3, 149.0, 152.7.

4.5.19. 2,5-Dimethoxybenzonitrile. Mp 79–82 °C (commercial, mp 81–85 °C); IR (Nüjol) 2224 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.89 (s, 3H), 6.91 (d, 1H, *J*=9.0), 7.05–7.11 (m, 2H), ^{13}C NMR (400 MHz, $CDCl_3$) δ 48.9, 49.3, 94.7, 105.5, 109.3, 110.5, 113.8, 146.1, 148.7.

4.5.20. 2,4,6-Trimethylbenzonitrile. Mp 50–51 °C (lit.[12l] mp 54–55 °C); IR (Nüjol) 2218 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.47 (s, 6H), 6.92 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 20.6, 21.5, 110.2, 117.6, 128.1, 141.9, 142.7.

4.6. Typical experimental procedure for transformation of propiophenone to β-chloro-α-methyl–cinnamonitrile

Propiophenone (268.4 mg, 2 mmol) was added to $POCl_3$ (490.7 mg, 3.2 mmol) and DMF (233.9 mg, 3.2 mmol) at 0 °C. After being stirred for 3 h at 60 °C, I_2 (609.1 mg, 2.4 mmol), aq NH_3 (4 mL, 28–30%) and THF (2 mL) were added to the reaction mixture. The obtained mixture was stirred for 3 h at rt. After the reaction, the mixture was poured into aq satd Na_2SO_3 solution and extracted with $CHCl_3$ (3×20 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated. The product was purified by flash short column chromatography (Hexane:AcOEt=12:1) to afford (*E*)-β-chloro-α-methylcinnamonitrile as a white solid in 77% yield, and

(*Z*)-β-chloro-α-methyl−cinnamonitrile as a colorless oil in 16% (83:17, *E*/*Z* ratio).

4.6.1. (E)-β-Chloro-α-methylcinnamonitrile. Oil; IR (neat) 1606, 2216 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.20 (s, 3H), 7.37−7.45 (m, 3H), 7.58−7.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 106.8, 118.1, 128.37, 128.41, 130.6, 135.9, 149.5; HRMS (ESI) $[M+Na]^+$, calcd for $C_{10}H_8NClNa$=200.0237, found=200.0240.

4.6.2. (Z)-β-Chloro-α-methylcinnamonitrile. Oil; IR (neat) 1616, 2219 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.01 (s, 3H), 7.35−7.39 (m, 2H), 7.40−7.47 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5, 108.6, 117.8, 128.4, 128.6, 130.3, 135.0, 149.6; HRMS (ESI) $[M+Na]^+$, calcd for $C_{10}H_8NClNa$=200.0237, found=200.0240.

4.6.3. (E)-β-Chloro-α-methyl-p-methylcinnamonitrile. Mp 39−42 °C; IR (Nüjol) 1606, 2215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.39 (s, 3H), 7.23 (d, *J*=7.9 Hz, 2H), 7.28 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6. 21.4. 107.9. 118.0. 128.5. 129.2. 132.1. 140.8. 145.4; HRMS (ESI) $[M+Na]^+$, calcd for $C_{11}H_{10}NClNa$=214.0394, found=214.0394.

4.6.4. (Z)-β-Chloro-α-methyl-p-methylcinnamonitrile. Oil; IR (neat) 1608, 2218 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.39 (s, 3H), 7.23 (d, *J*=7.9 Hz, 2H), 7.52 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 21.4, 106.0, 118.5, 128.4, 129.1, 133.2, 141.1, 149.9; HRMS (ESI) $[M+Na]^+$, calcd for $C_{11}H_{10}NClNa$=214.0394, found=214.0397.

4.6.5. (E)-β-Chloro-α-methyl-p-methoxycinnamonitrile. Mp 74−75 °C; IR (Nüjol) 1604, 2212 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.39 (s, 3H), 7.23 (d, *J*=7.9 Hz, 2H), 7.52 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 21.4, 106.0, 118.5, 128.4, 129.1, 133.2, 141.1, 149.9; HRMS (ESI) $[M+Na]^+$, calcd for $C_{11}H_{10}ONClNa$=230.0343, found=230.0339. (NOE of aromatic group based on Me group; 0.19%).

4.6.6. (Z)-β-Chloro-α-methyl-p-methoxycinnamonitrile. Oil; IR (neat) 1604, 2213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 3.85 (s, 3H), 6.94 (d, *J*=8.8 Hz, 2H), 7.34 (d, *J*=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 55.4, 107.2, 113.9, 118.2, 127.1, 130.3, 145.2, 161.0; HRMS (ESI) $[M+Na]^+$, calcd for $C_{11}H_{10}ONClNa$=230.0343, found=230.0344. (NOE of aromatic group based on Me group; 1.13%).

4.6.7. (E)-β-Chloro-α-methyl-p-chlorocinnamonitrile. Mp 75−78 °C; IR (Nüjol) 1591, 2212 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 3H), 7.41 (d, *J*=8.6 Hz, 2H), 7.57 (d, *J*=8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 107.5, 118.0, 128.8, 129.8, 134.4, 136.8, 148.3; HRMS (APCI) $[M+H]^+$, calcd for $C_{10}H_8NCl_2$=212.0028, found=212.0030.

4.6.8. (Z)-β-Chloro-α-methyl-p-chlorocinnamonitrile. Oil; IR (neat) 1592, 2221 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 7.33 (d, *J*=8.6 Hz, 2H), 7.57 (d, *J*=8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.6, 109.2, 117.5, 128.9, 129.9, 133.3, 136.5, 143.8; HRMS (APCI) $[M+H]^+$, calcd for $C_{10}H_8NCl_2$=212.0028, found=212.0033.

4.6.9. (E)-β-Chloro-α-methyl-p-fluorocinnamonitrile. Mp 66−69 °C; IR (Nüjol) 1604, 2212 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 3H), 7.12 (t, *J*=8.6 Hz, 2H), 7.60−7.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 107.1, 115.7 (d, J_{C-F}=21.6 Hz), 118.1, 130.7 (d, J_{C-F}=8.4 Hz), 132.1 (d, J_{C-F}=3.6 Hz), 148.4, 163.8 (d, J_{C-F}=251.9 Hz); HRMS (APCI) $[M+H]^+$, calcd for $C_{10}H_8NClF$=196.0324, found=196.0325. (NOE of aromatic group based on Me group; 0.14%).

4.6.10. (Z)-β-Chloro-α-methyl-p-fluorocinnamonitrile. Oil; IR (neat) 1602, 2220 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 7.14 (t, *J*=8.6 Hz, 2H), 7.37−7.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.6, 108.9, 115.8 (d, J_{C-F}=21.6 Hz), 117.7, 130.7 (d, J_{C-F}=8.4 Hz), 131.0 (d, J_{C-F}=3.6 Hz), 144.0, 163.4 (d, J_{C-F}=251.9 Hz); HRMS (ESI) $[M+H]^+$, calcd for $C_{10}H_8NClF$=196.0324, found=196.0327. (NOE of aromatic group based on Me group; 0.82%).

4.6.11. (E)-β-Chloro-α-heptylcinnamonitrile. Oil; IR (neat) 1595, 2215 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J*=7.2 Hz, 3H), 1.25−1.48 (m, 8H), 1.68 (quintet, *J*=7.5 Hz, 2H), 2.57 (t, *J*=7.7 Hz, 2H), 7.40−7.44 (m, 3H), 7.59−7.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 27.3, 28.86, 28.91, 31.7, 32.7, 112.6, 117.7, 128.45, 128.51, 130.6, 136.2, 148.8; HRMS (ESI) $[M+Na]^+$, calcd for $C_{16}H_{20}NClNa$=284.1176, found=284.1164.

4.6.12. (Z)-β-Chloro-α-heptylcinnamonitrile. Oil; IR (neat) 1677, 2218 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, *J*=7.2 Hz, 3H), 1.15−1.41 (m, 8H), 1.59 (quintet, *J*=7.5 Hz, 2H), 2.26 (t, *J*=7.7 Hz, 2H), 7.33−7.37 (m, 2H), 7.42−7.45 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 28.3, 28.6, 28.7, 31.56, 31.68, 114.9, 117.1, 128.3, 128.6, 130.2, 135.4, 144.8; HRMS (APCI) $[M+H]^+$, calcd for $C_{16}H_{21}NCl$=262.1357, found=262.1355.

4.6.13. 1-Chloro-3,4-dihydronaphthalene-2-carbonitrile. Mp 54−55 °C ; IR (Nüjol) 1605, 2212 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.63−2.67 (m, 2H), 2.91−2.95 (m, 2H), 7.19 (d, *J*=6.2 Hz, 1H), 7.30−7.38 (m, 2H), 7.69 (d, *J*=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 26.8, 107.9, 117.3, 126.1, 127.3, 127.7, 130.3, 131.1, 136.4, 143.4; HRMS (ESI) $[M+H]^+$, calcd for $C_{11}H_9NCl$=190.0418, found=190.0418.

4.6.14. 3-Chloro-4-cyano-1,3-benzocycloheptadiene. Oil; IR (neat) 1604, 2214 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.20 (t, *J*=7.0 Hz, 2H), 2.28 (q, *J*=6.8 Hz, 2H), 2.68 (t, *J*=7.0 Hz, 2H), 7.24−7.26 (m, 1H), 7.34−7.38 (m, 2H), 7.55−7.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 31.4, 34.1, 111.4, 117.7, 126.8, 128.5, 129.1, 130.7, 135.6, 140.4, 145.2; HRMS (ESI) $[M+H]^+$, calcd for $C_{12}H_{11}NCl$=204.0575, found=204.0579.

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