

## Simple One-Pot Conversion of Alcohols into Nitriles

Hiroyuki Shimojo, Katsuhiko Moriyama, Hideo Togo\*

Graduate School of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan  
Fax +81(43)2902792; E-mail: togo@faculty.chiba-u.jp

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**Abstract:** Various benzylic and primary alcohols were efficiently converted into the corresponding nitriles in good yields at room temperature by treatment with *tert*-butyl hypochlorite, diiodine, or 1,3-diiodo-5,5-dimethylhydantoin in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), followed by treatment with diiodine and aqueous ammonia. The nitriles were obtained in good yields and high purities simply by extraction of the reaction mixture with chloroform and subsequent removal of the solvent.

**Key words:** nitriles, alcohols

Nitriles are very useful and important intermediates in synthetic organic chemistry,<sup>1</sup> because they are readily converted into many biologically important heterocyclic compounds, such as oxazoles,<sup>2a-c</sup> thiazoles,<sup>2d,e</sup> tetrazoles,<sup>2f-i</sup> [1,2,3]triazolo[1,5-*c*]pyrimidines,<sup>2j</sup> and imidazoles.<sup>2k</sup> Nitriles can be prepared by the condensation of carboxylic acids with 4-toluenesulfonamide and phosphorus pentachloride at 200 °C,<sup>3a</sup> with ammonia and silica gel at 500 °C,<sup>3b</sup> or with ammonia and ethyl polyphosphate at 80 °C,<sup>3c</sup> among other methods. However, the most typical methods for the preparation of nitriles are the reaction of an alkyl halide with a toxic metal cyanide to give a one-carbon-homologated aliphatic nitrile and the dehydration of a primary amide to give an aliphatic or aromatic nitrile with the same number of carbon atoms.<sup>3d</sup> In the latter reaction, a primary amide or aldoxime is dehydrated with thionyl chloride, 4-toluenesulfonyl chloride and pyridine, phosphorus pentoxide, phosphoryl chloride, phosgene, triethyl phosphite and diiodine, or triphenylphosphine and carbon tetrachloride;<sup>3d</sup> alternatively, a primary amide can be dehydrated with a metal complex, such as a rhenium(VII) oxo complex.<sup>3e</sup>

Primary amines can be converted oxidatively into the corresponding nitriles by treatment with silver(II) oxide,<sup>4a</sup> lead(IV) acetate,<sup>4b-c</sup> cobalt peroxide,<sup>4f</sup> nickel peroxide,<sup>4g</sup> sodium persulfate, tetrabutylammonium persulfate with metals,<sup>4h-k</sup> sodium hypochlorite,<sup>4l-n</sup> potassium ferricyanide,<sup>4o</sup> copper(I) or copper(II) compounds with oxygen,<sup>4p-s</sup> ruthenium(III) chloride or related ruthenium reagents,<sup>4t-x</sup> iodosylbenzene,<sup>4y</sup> or trichloroisocyanuric acid and (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO).<sup>4z</sup> However, there are only a few reports on the direct oxidative conversion of alcohols into nitriles by a one-pot procedure. One-pot methods that have been reported involve

the use of potassium persulfate in the presence of a catalytic amount of nickel(II) sulfate in aqueous sodium hydroxide,<sup>5a</sup> treatment with ammonium bicarbonate and tetrabutylammonium persulfate in the presence of a catalytic amount of copper(II) formate–nickel(II) formate (1:1) in a solution of potassium chloride in aqueous 2-propanol,<sup>5b</sup> or treatment with manganese(IV) oxide, ammonia, and magnesium sulfate in tetrahydrofuran–2-propanol for benzylic and cinnamyl alcohols.<sup>5c</sup> Direct oxidative conversions of alcohols into the corresponding nitriles by using a ruthenium hydroxide–alumina catalyst in aqueous ammonia at 6 atm and 120 °C,<sup>5d</sup> a manganese(IV) oxide and oxygen (0.85 MPa) system with ammonia gas (0.5 MPa) at 100 °C,<sup>5e</sup> or a copper(I) iodide–bipyridyl–TEMPO catalyst system with oxygen and aqueous ammonia at room temperature<sup>5f</sup> have also been reported recently.

Previously, we reported the direct conversion of alcohols into nitriles by treatment with diiodine and aqueous ammonia at 60 °C. The conversion of benzylic alcohols required several hours, and that of primary alcohols required nearly 24 hours.<sup>6</sup> This method is very useful for the transition-metal-free direct preparation of nitriles from alcohols with the same number of carbon atoms, especially benzylic alcohols. It is not, however, suitable for the conversion of alcohols bearing carbon–carbon double bonds, because of the addition of iodine to the double bond. Nor is it suitable for conversion of compounds such as 2-phenylethanol, because the nitrile that is formed is iodinated at 60 °C. Thus, neither the treatment of dec-9-en-1-ol (1 mmol) with diiodine (5 equiv) in aqueous ammonia (28–30%, 4 mL) for 24 hours at 60 °C (Scheme 1, eq 1) nor the treatment of 2-phenylethanol (1 mmol) with diiodine (3 equiv) in aqueous ammonia (3 mL) for 24 hours at 60 °C (Scheme 1, eq 2) gave the corresponding nitrile. Treatment of cinnamyl alcohol (1 mmol) with diiodine (3 equiv) in aqueous ammonia (3 mL) for 5.5 hours at 60 °C gave cinnamonitrile in 46% yield only, as a result of the Michael-type addition of ammonia to cinnamonitrile under these reaction conditions (Scheme 1, eq 3).

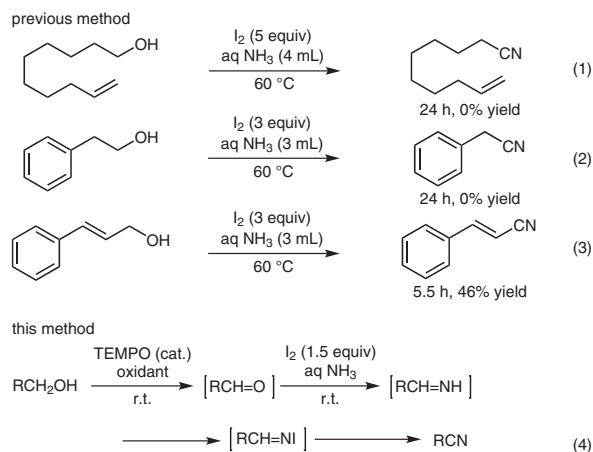
Here, as part of our basic study on diiodine and related iodine reagents for organic synthesis,<sup>7</sup> we would like to report a mild and efficient one-pot conversion of benzylic alcohols or primary alcohols into the corresponding nitriles by using *tert*-butyl hypochlorite, diiodine, or 1,3-diiodo-5,5-dimethylhydantoin (DIH; 1,3-diiodo-5,5-dimethylimidazolidine-2,4-dione) in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl radical (TEMPO), followed by treatment with diiodine and aque-

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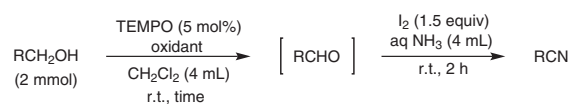
**Scheme 1** Conversion of alcohols into nitriles by using molecular iodine and aqueous ammonia

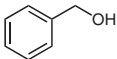
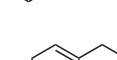
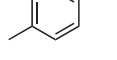
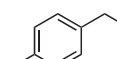
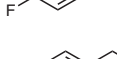
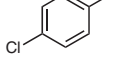
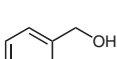
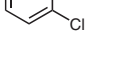
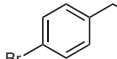
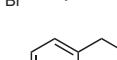
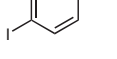
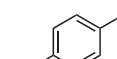
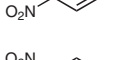
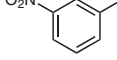


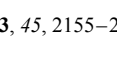

ous ammonia at room temperature (Scheme 1, eq 4). This reaction is based on the well-known fact that *N*-oxoammonium salts derived from nitroxyl radicals, such as

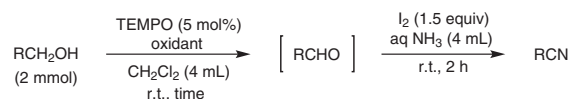
TEMPO, promote the oxidation of primary alcohols to the corresponding aldehydes effectively under mild conditions.<sup>8</sup>

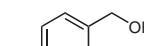
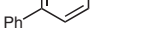
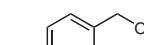
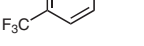

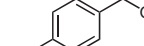

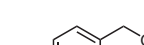
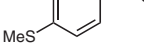

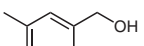
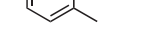
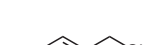
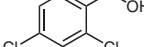

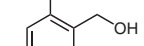
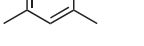

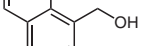
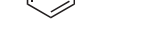

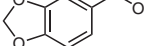


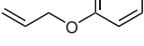
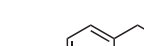
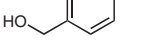
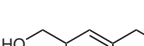
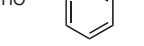

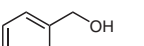
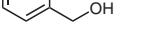

Thus, *tert*-butyl hypochlorite (1.1 equiv) as an oxidant was added to a mixture of benzyl alcohol (2.0 mmol) and TEMPO (5 mol%, 0.05 equiv) in dichloromethane, and the mixture was stirred for one hour at room temperature under argon. Diiodine (1.5 equiv) and 28–30% aqueous ammonia (4 mL) were then added. The resulting mixture was stirred for two hours then poured into saturated aqueous sodium sulfite and extracted with chloroform. After removal of the solvent from the organic layer, benzonitrile was obtained in 95% yield and 99% purity (Table 1, entry 1). Thus, the nitrile was obtained in good yield and high purity by simple extraction of the reaction mixture with chloroform and subsequent removal of the solvent. When diiodine was used instead of *tert*-butyl hypochlorite in the first step with the same procedure and conditions, benzonitrile was obtained in 76% yield after purification (entry 2).

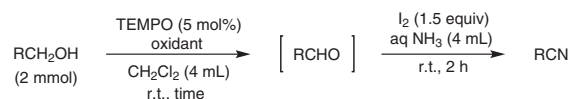
**Table 1** Simple Transformation of Alcohols into Nitriles

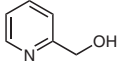
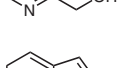
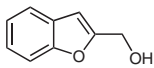
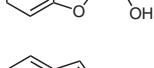
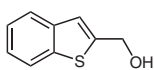
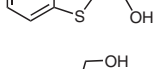
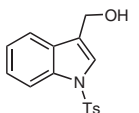
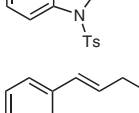
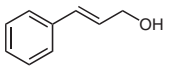
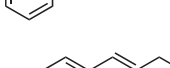
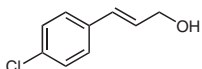
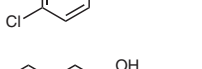
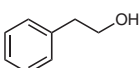
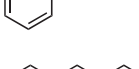
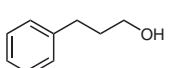
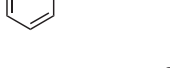
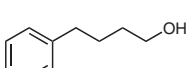

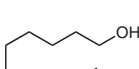
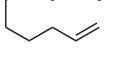
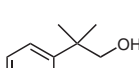
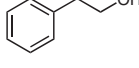
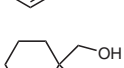
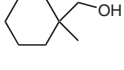


Entry	RCH <sub>2</sub> OH	Oxidant (equiv)	Time (h)	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>
1		<i>t</i> -BuOCl (1.1)	1	95	99
2		I <sub>2</sub> (1.1)	1	76	–
3		<i>t</i> -BuOCl (1.5)	0.5	99	99
4		I <sub>2</sub> (1.5)	0.5	99	99
5		<i>t</i> -BuOCl (1.3)	1	93	93
6		I <sub>2</sub> (1.3)	1	99	99
7		<i>t</i> -BuOCl (1.5)	1	95	99
8		I <sub>2</sub> (1.5)	1	99	99
9		<i>t</i> -BuOCl (1.5)	0.5	99	99
10		I <sub>2</sub> (1.5)	0.5	95	92
11		<i>t</i> -BuOCl (1.5)	1	99	99
12		I <sub>2</sub> (1.5)	1	99	85
13		<i>t</i> -BuOCl (1.5)	2	99	99
14		I <sub>2</sub> (1.5)	2	99	99
15		<i>t</i> -BuOCl (1.3)	2	95	99
16		I <sub>2</sub> (1.3)	2	99	99
17		<i>t</i> -BuOCl (1.5)	1	99	99
18		I <sub>2</sub> (1.5)	1	99	99

**Table 1** Simple Transformation of Alcohols into Nitriles (continued)

Entry	RCH <sub>2</sub> OH	Oxidant (equiv)	Time (h)	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>
19		<i>t</i> -BuOCl (1.2)	2	99	99
20		I <sub>2</sub> (1.2)	2	99	99
21		<i>t</i> -BuOCl (1.1)	1	99	99
22		I <sub>2</sub> (1.1)	1	99	99
23		<i>t</i> -BuOCl (1.5)	1	51 (49) <sup>c</sup>	–
24		I <sub>2</sub> (1.5)	1	0	–
25		DIH (1.1)	0.5	99	99
26		I <sub>2</sub> (1.5)	0.5	0	–
27		DIH (1.5)	0.5	93 (7) <sup>d</sup>	–
28		<i>t</i> -BuOCl (1.5)	0.5	99	99
29		I <sub>2</sub> (1.5)	0.5	99	99
30		DIH (1.5)	0.5	99	99
31		<i>t</i> -BuOCl (1.5)	1	99	99
32		I <sub>2</sub> (1.5)	1	70	–
33 <sup>e</sup>		I <sub>2</sub> (2.0)	0.5	9	–
34 <sup>e</sup>		DIH (2.0)	0.5	99	96
35 <sup>e</sup>		<i>t</i> -BuOCl (2.0)	1	99	92
36 <sup>e</sup>		I <sub>2</sub> (2.0)	1	99	99
37 <sup>e</sup>		DIH (1.1)	2	99	99
38 <sup>e,f</sup>		<i>t</i> -BuOCl (3.0)	0.5	11 (89) <sup>g</sup>	–
39 <sup>e,f</sup>		I <sub>2</sub> (1.5)	0.5	0	–
40 <sup>e,f</sup>		DIH (1.1)	0.5	99	99
41		I <sub>2</sub> (1.3)	1	trace	–
42		DIH (1.3)	1	97	82
43 <sup>h</sup>		<i>t</i> -BuOCl (3.0)	0.5	99	99
44 <sup>h</sup>		I <sub>2</sub> (3.0)	0.5	38	–
45 <sup>h</sup>		<i>t</i> -BuOCl (3.0)	0.5	99	99
46 <sup>h</sup>		I <sub>2</sub> (3.0)	0.5	56	–
47 <sup>f,h,i</sup>		<i>t</i> -BuOCl (3.0) <sup>j</sup>	1.5	0 (96) <sup>k</sup>	75
48 <sup>f,h,i</sup>		I <sub>2</sub> (3.0) <sup>j</sup>	0.5	0 (0) <sup>k</sup>	–
49 <sup>f,h,i</sup>		DIH (2.2) <sup>l</sup>	0.5	0 (92) <sup>k</sup>	85
50 <sup>e</sup>		I <sub>2</sub> (1.3)	1	0	–
51 <sup>e</sup>		DIH (1.3)	1	99	99

**Table 1** Simple Transformation of Alcohols into Nitriles (continued)

Entry	RCH <sub>2</sub> OH	Oxidant (equiv)	Time (h)	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>
52		<i>t</i> -BuOCl (1.5)	1	99	99
53		I <sub>2</sub> (1.5)	1	80	–
54 <sup>f</sup>		I <sub>2</sub> (1.5)	1	99	99
55 <sup>f</sup>		DIH (1.5)	1	99	99
56 <sup>e,f</sup>		I <sub>2</sub> (1.5)	0.5	99	83
57 <sup>e,f</sup>		DIH (1.5)	0.5	92	99
58 <sup>f</sup>		I <sub>2</sub> (1.5)	1	trace	–
59 <sup>f</sup>		DIH (1.5)	1	99	99
60		I <sub>2</sub> (1.1) <sup>m</sup>	0.5	0	–
61		DIH (1.1) <sup>m</sup>	0.5	95	96
62 <sup>i</sup>		I <sub>2</sub> (1.5) <sup>m</sup>	1	28	–
63 <sup>i</sup>		DIH (1.5) <sup>m</sup>	1	99	99
64 <sup>f</sup>		I <sub>2</sub> (1.1) <sup>n</sup>	0.5	99	99
65 <sup>f</sup>		DIH (1.1) <sup>n</sup>	0.5	99	99
66 <sup>f</sup>		I <sub>2</sub> (1.1) <sup>n</sup>	1	99	99
67 <sup>f</sup>		DIH (1.1) <sup>n</sup>	1	52	–
68 <sup>f</sup>		I <sub>2</sub> (1.1) <sup>n</sup>	1	99	96
69 <sup>f</sup>		DIH (1.1) <sup>n</sup>	1	47	–
70 <sup>f</sup>		I <sub>2</sub> (1.1) <sup>n</sup>	1	99	97
71 <sup>f</sup>		DIH (1.1) <sup>n</sup>	1	47	–
72 <sup>e</sup>		I <sub>2</sub> (2.0)	2	0	–
73 <sup>e</sup>		DIH (2.0)	2	98	99
74 <sup>e</sup>		I <sub>2</sub> (2.0)	1	0	–
75 <sup>e</sup>		DIH (2.0)	1	99	99

<sup>a</sup> Isolated yield of pure compound.<sup>b</sup> Purity of the nitrile after extraction with CHCl<sub>3</sub> and removal of the solvent.<sup>c</sup> Yield of 1-chloro-4-methoxybenzene.<sup>d</sup> Yield of 4-(methanesulfonyl)benzotrile.<sup>e</sup> I<sub>2</sub> and aq NH<sub>3</sub> were added, and then the mixture was stirred for 3 h.<sup>f</sup> The oxidant was added at 0 °C then the mixture was warmed to r.t.<sup>g</sup> Yield of 6-chloro-1,3-benzodioxole-5-carbonitrile.<sup>h</sup> I<sub>2</sub> (3 equiv) and aq NH<sub>3</sub> (8 mL) were added.<sup>i</sup> I<sub>2</sub> and aq NH<sub>3</sub> were added at 0 °C then the mixture was warmed to r.t.<sup>j</sup> TEMPO (0.5 equiv) was used.<sup>k</sup> Yield of phthalide [2-benzofuran-1(3*H*)-one].<sup>l</sup> TEMPO (0.4 equiv) was used.<sup>m</sup> TEMPO (0.1 equiv) was used.<sup>n</sup> TEMPO (0.2 equiv) was used.

Having identified the optimal conditions for treatment with *tert*-butyl hypochlorite or diiodine in the first step of the reaction, we applied this treatment to a series of substituted benzyl alcohols and to 1-naphthylmethanol. Oxidation with *tert*-butyl hypochlorite or diiodine in the presence of TEMPO, followed by the treatment with diiodine and aqueous ammonia gave the corresponding aromatic nitriles in good yields and high purities by simple extraction of the reaction mixture with chloroform and subsequent removal of the solvent (entries 3–22, 28, 29, 31, 32, 35, and 36); an exception was the reaction of (2,4-dichlorophenyl)methanol with diiodine in the first step (entry 32).

Similar treatment of (4-methoxyphenyl)methanol with *tert*-butyl hypochlorite in the first step under the optimized conditions gave 4-methoxybenzonitrile in only 51% yield together with 1-chloro-4-methoxybenzene in 49% yield (entry 23); likewise, 1,3-benzodioxol-5-ylmethanol gave 1,3-benzodioxole-5-carbonitrile (piperonylnitrile) in 11% yield together with 6-chloro-1,3-benzodioxole-5-carbonitrile in 89% yield (entry 38). In the former reaction, 1-chloro-4-methoxybenzene was formed through *ipso*-substitution of the electron-rich benzylic alcohol by the chloronium ion derived from *tert*-butyl hypochlorite. In the latter reaction, the alcohol was initially chlorinated on the aromatic ring by *tert*-butyl hypochlorite, with subsequent oxidative cyanation. Moreover, treatment of (4-methoxyphenyl)methanol or 1,3-benzodioxol-5-ylmethanol with diiodine in the first step under the optimized conditions did not give the corresponding nitriles at all (entries 24 and 39, respectively). Thus, diiodine is not a sufficiently strong oxidant to permit TEMPO-catalyzed oxidation of electron-rich benzylic alcohols.

To suppress the *ipso*-substitution and chlorination of the aromatic ring by *tert*-butyl hypochlorite, we used DIH as an oxidant. DIH is a weaker oxidant than *tert*-butyl hypochlorite, but a stronger one than diiodine; however, it has the disadvantage of being rather expensive. Treatment of (4-methoxyphenyl)methanol with DIH (1.1 or 1.5 equiv) in the presence of TEMPO (0.05 equiv), followed by the treatment with diiodine (1.5 equiv) and aqueous ammonia (4 mL) under the optimized conditions gave 4-methoxybenzonitrile in 99% yield and high purity (entry 25). Similarly, [4-(methylsulfanyl)phenyl]methanol gave 4-(methylsulfanyl)benzonitrile in 93% yield together with 7% of 4-(methanesulfinyl)benzonitrile (entry 27), whereas 1,3-benzodioxol-5-ylmethanol gave 1,3-benzodioxole-5-carbonitrile in 99% yield and high purity (entry 40). These nitriles were again isolated in good yields and high purities by simple extraction of the reaction mixture with chloroform and subsequent removal of the solvent.

Similar treatment of 2,4,6-trimethylbenzyl alcohol with DIH gave the corresponding aromatic nitrile in good yield and high purity (entry 34), whereas the corresponding reaction with diiodine in the first step did not work well (entry 33). [4-(Allyloxy)phenyl]methanol, which contains an olefinic group, on treatment with DIH in the presence of

TEMPO under the optimized conditions gave 4-(allyloxy)benzonitrile in good yield and high purity (entry 42), whereas the use of diiodine in the first step did not give the nitrile as a result of the low oxidizing ability of the reagent (entry 41); the same reaction with *tert*-butyl hypochlorite also failed because the reagent added across the olefinic double bond. Treatment of 1,4- or 1,3-bis(hydroxymethyl)benzene with *tert*-butyl hypochlorite (3.0 equiv) in the presence of TEMPO, followed by the reaction with diiodine (3.0 equiv) and aqueous ammonia (4 mL), gave terephthalonitrile and isophthalonitrile, respectively, in good yields and high purities (entries 43 and 45, respectively), whereas the corresponding reaction of 1,2-bis(hydroxymethyl)benzene with *tert*-butyl hypochlorite or DIH in the first step gave the corresponding phthalide **D** exclusively in good yield (entries 47 and 49).

In the case of electron-rich heteroarylmethanols, DIH was used to suppress *ipso*-substitution of the aromatic ring. Thus, treatment of 2-thienylmethanol, benzofuran-2-ylmethanol, 1-benzothien-2-ylmethanol, and [1-tosyl-1*H*-indol-3-yl]methanol with DIH in the presence of TEMPO, followed by treatment with diiodine and aqueous ammonia under the optimized conditions, gave the corresponding nitriles in good yields and high purities (entries 51, 55, 57, and 59, respectively); the corresponding reactions of benzofuran-2-ylmethanol and 1-benzothien-2-ylmethanol with diiodine in the first step also gave the corresponding nitriles in good yields and high purity (entries 54 and 56), whereas the reaction failed with 2-thienylmethanol and [1-tosyl-1*H*-indol-3-yl]methanol (entries 50 and 58). On the other hand, *tert*-butyl hypochlorite could be efficiently used to oxidize electron-deficient pyridin-3-ylmethanol to give 3-cyanopyridine in good yield and high purity (entry 52).

The reaction of cinnamyl alcohol or 4-chlorocinnamyl alcohol with DIH in the presence of TEMPO, followed by treatment with diiodine and aqueous ammonia under the same conditions also gave the corresponding cinnamionitriles in good yields and high purity (entries 61 and 63, respectively), whereas diiodine was not an effective oxidant for these compounds.

Finally, we examined the reaction of aliphatic primary alcohols such as 2-phenylethanol, 3-phenylpropan-1-ol, 4-phenylbutan-1-ol, 2-methyl-2-phenylpropan-1-ol, and  $\alpha$ -methylcyclohexylmethanol with DIH or diiodine in the presence of TEMPO, followed by treatment with diiodine and aqueous ammonia under the optimized conditions. 2-Phenylethanol gave phenylacetonitrile in good yield and high purity when DIH or diiodine was used in the first step (entries 64 and 65). Diiodine was a more effective oxidant than DIH for 3-phenylpropan-1-ol and 4-phenylbutan-1-ol, giving 3-phenylpropanenitrile and 4-phenylbutanenitrile, respectively, in good yields and high purity (entries 66–69). For 2-methyl-2-phenylpropan-1-ol and  $\alpha$ -methylcyclohexylmethanol, which are neopentyl-type alcohols, the use of DIH in the first step gave the best results, and diiodine did not work at all (entries 72–75). Moreover, dec-9-en-1-ol, which contains an olefin group, on

treatment with diiodine in the presence of TEMPO under the optimized conditions, gave dec-9-enitrile in good yield (entry 70); DIH was not effective in this reaction as a result its addition reaction with the olefin group (entry 71). With cinnamyl alcohols or aliphatic primary alcohols, when *tert*-butyl hypochlorite was used in the first step instead of diiodine or DIH, yields of the corresponding nitriles were very low as a result of addition to the olefinic groups in the first case or the occurrence of side reactions in the second.

In summary, we have developed a metal-free one-pot method for the conversion of various primary alcohols into the corresponding nitriles by using *tert*-butyl hypochlorite, diiodine, or DIH in the presence of TEMPO, followed by treatment with diiodine and aqueous ammonia. For effective one-pot conversion of alcohols into nitriles, we recommend the use of *tert*-butyl hypochlorite or diiodine as the oxidant in the first step of the reaction for various benzylic alcohols; the use of DIH for electron-rich benzylic alcohols [such as (4-methoxyphenyl)methanol, 1,3-benzodioxol-5-ylmethanol, benzothiophen-2-methanol, or benzofuran-2-methanol], cinnamyl alcohols, or neopentyl-type alcohols; and the use of diiodine for long-chain primary alcohols or olefinic alcohols. The reaction proceeds through a TEMPO-catalyzed oxidation of the alcohol by *tert*-butyl hypochlorite, diiodine, or DIH to give the corresponding aldehyde. This reacts with diiodine and aqueous ammonia to give the corresponding nitrile through elimination of hydrogen iodide from the resulting *N*-iodoimine at room temperature (Scheme 1, eq 4).<sup>6</sup> However, reasons for differences in the reactivities of *tert*-butyl hypochlorite, diiodine, and DIH in the TEMPO-catalyzed oxidations of benzylic and primary alcohols to the corresponding aromatic or aliphatic nitriles via aldehyde intermediates are still not clear.

In conclusion, various benzylic alcohols and primary alcohols, including those containing olefinic groups, were efficiently converted into the corresponding nitriles in good yields at room temperature by oxidation with *tert*-butyl hypochlorite, diiodine, or DIH in the presence of TEMPO, followed by treatment with diiodine and aqueous ammonia. The nitriles were obtained in high purity simply by extraction of the reaction mixture with chloroform and subsequent removal of the solvent. We believe that, because of the simple experimental procedures, the reaction will be very useful for the direct preparation of various aromatic and aliphatic nitriles from benzylic or primary alcohols under mild conditions.

Melting points were determined with a Yamato MP-21 melting-point apparatus. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL JNM-ECS400 and JNM-ECA500 spectrometers. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from TMS. Mass spectra were recorded on JMS T100GCV and Thermo LTQ Orbitrap XL spectrometers. Merck silica gel 60F<sub>254</sub> was used for TLC. Where necessary, nitriles were purified by column chromatography on silica gel 60 (Kanto Kagaku Co.)

#### Conversion of Benzyl Alcohol into Benzonitrile with *tert*-Butyl Hypochlorite; Typical Procedure

*t*-BuOCl (238.9 mg, 2.2 mmol) was added to a mixture of BnOH (216.3 mg, 2.0 mmol) and TEMPO (15.6 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) at r.t. under argon, and the mixture was stirred at r.t. until the alcohol was consumed (1 h). I<sub>2</sub> (761.4 mg, 3 mmol) and 28–30% aq NH<sub>3</sub> (4 mL) were added at r.t., and the mixture was stirred for 2 h then poured into sat. aq Na<sub>2</sub>SO<sub>3</sub> (20 mL) and extracted with CHCl<sub>3</sub> (3 × 20 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered. Removal of the solvent under reduced pressure gave PhCN as a colorless oil; yield: 195.9 mg (95%). The purity was estimated by <sup>1</sup>H NMR spectroscopy.

IR (neat): 2228 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.48 (t, *J* = 7.9 Hz, 2 H), 7.63 (t, *J* = 7.9 Hz, 1 H), 7.69 (d, *J* = 7.9 Hz, 2 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 111.96, 118.34, 128.67, 131.68, 132.32.

#### Conversion of (4-Tolyl)methanol into 4-Methylbenzonitrile with Diiodine; Typical Procedure

I<sub>2</sub> (761.4 mg, 3.0 mmol) was added to a mixture of (4-tolyl)methanol (244.3 mg, 2.0 mmol) and TEMPO (15.6 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) at r.t. under argon, and the mixture was stirred at r.t. until the alcohol was consumed (0.5 h). I<sub>2</sub> (761.4 mg, 3 mmol) and 28–30% aq NH<sub>3</sub> (4 mL) were added at r.t., and the resulting mixture was stirred for 2 h then poured into sat. aq Na<sub>2</sub>SO<sub>3</sub> (20 mL) and extracted with CHCl<sub>3</sub> (3 × 20 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered. Removal of the solvent under reduced pressure gave 4-methylbenzonitrile as a white solid; yield 232.0 mg (99%); mp 28 °C (commercial sample; mp 27 °C).

IR (neat): 2228 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.42 (s, 3 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.53, 108.98, 118.84, 129.53, 131.73, 143.38.

#### Conversion of (4-Methoxyphenyl)methanol into 4-Methoxybenzonitrile with DIH; Typical Procedure

DIH (835.8 mg, 2.2 mmol) was added to a mixture of (4-methoxyphenyl)methanol (276.3 mg, 2.0 mmol) and TEMPO (15.6 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) at r.t. under argon, and the mixture was stirred at r.t. until the alcohol was consumed (1 h). I<sub>2</sub> (761.4 mg, 3 mmol) and 28–30% aq NH<sub>3</sub> (4 mL) were added at r.t., and the resulting mixture was stirred at r.t. for 2 h then poured into sat. aq Na<sub>2</sub>SO<sub>3</sub> (20 mL) and extracted with CHCl<sub>3</sub> (3 × 20 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered. Removal of the solvent under reduced pressure gave 4-methoxybenzonitrile as a white solid; yield: 263.6 mg (99%); mp 58 °C (commercial sample; mp 60 °C). The purity was estimated by <sup>1</sup>H NMR.

IR (neat): 2215 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.86 (s, 3 H), 6.95 (d, *J* = 8.9 Hz, 2 H), 7.59 (d, *J* = 8.9 Hz, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 55.52, 103.96, 114.73, 119.21, 133.97, 162.82.

Most of the nitriles prepared in this study are commercially available and they were identified by comparison with authentic samples.

#### 4-Fluorobenzonitrile

White solid; yield: 225.3 mg (93%); mp 35–37 °C (commercial sample; mp 34 °C).

IR (neat): 2234 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.18 (t, *J* = 8.8 Hz, 2 H), 7.69 (dd, 2 H, *J*<sub>H-H</sub> = 8.8 Hz, *J*<sub>H-F</sub> = 5.2 Hz).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 108.66 (d,  $J$  = 3.6 Hz), 116.98 (d,  $J$  = 22.7 Hz), 118.14, 134.81 (d,  $J$  = 9.5 Hz), 165.14 (d,  $J$  = 254.0 Hz).

#### 4-Chlorobenzonitrile

White solid; yield: 261.4 mg (95%); mp 88 °C (commercial sample); mp 92 °C.

IR (neat): 2224  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47 (d,  $J$  = 8.8 Hz, 2 H), 7.61 (d,  $J$  = 8.8 Hz, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 110.72, 117.91, 129.64, 133.32, 139.50.

#### 2-Chlorobenzonitrile

White solid; yield: 272.4 mg (99%); mp 44–45 °C (commercial sample); mp 43–46 °C.

IR (neat): 2229  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.38 (t,  $J$  = 7.7 Hz, 1 H), 7.53 (t,  $J$  = 7.7 Hz, 1 H), 7.54 (d,  $J$  = 7.7 Hz, 1 H), 7.68 (d,  $J$  = 7.7 Hz, 1 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 113.14, 115.82, 127.08, 129.89, 133.81, 133.86, 136.62.

#### 4-Bromobenzonitrile

White solid; yield: 360.4 mg (99%); mp 108–110 °C (commercial sample); mp 113 °C.

IR (neat): 2224  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.53 (d,  $J$  = 8.4 Hz, 2 H), 7.63 (d,  $J$  = 8.4 Hz, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 111.24, 118.03, 128.01, 132.63, 133.39.

#### 4-Iodobenzonitrile

Pale-yellow solid; yield: 453.5 mg (99%); mp 119–120 °C (commercial sample); mp 127 °C.

IR (neat): 2226  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.37 (d,  $J$  = 8.5 Hz, 2 H), 7.85 (d,  $J$  = 8.5 Hz, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 100.27, 111.74, 118.20, 133.14, 138.51.

#### 4-Nitrobenzonitrile

Pale-yellow solid; yield: 281.4 mg (95%); mp 141–143 °C (commercial sample); mp 147 °C.

IR (neat): 2232  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.89 (d,  $J$  = 8.9 Hz, 2 H), 8.37 (d,  $J$  = 8.9 Hz, 2 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 116.77, 118.30, 124.26, 133.44, 150.00.

#### 3-Nitrobenzonitrile

Pale-yellow solid; yield: 293.3 mg (99%); mp 111 °C (commercial sample); mp 114–117 °C.

IR (neat): 2236  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.74 (t,  $J$  = 8.1 Hz, 1 H), 8.00 (dd,  $J$  = 1.4, 8.1 Hz, 1 H), 8.49 (dd,  $J$  = 1.4, 8.1 Hz, 1 H), 8.54 (t,  $J$  = 1.4 Hz, 1 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 114.09, 116.48, 127.19, 127.49, 130.62, 137.56, 148.19.

#### Biphenyl-4-carbonitrile

White solid; yield: 354.9 mg (99%); mp 83–84 °C (commercial sample); mp 87 °C.

IR (neat): 2225  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.40–7.46 (m, 1 H), 7.48 (t,  $J$  = 7.1 Hz, 2 H), 7.59 (d,  $J$  = 7.1 Hz, 2 H), 7.69 (d,  $J$  = 8.6 Hz, 2 H), 7.73 (d,  $J$  = 8.6 Hz, 2 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 110.91, 118.92, 127.21, 127.72, 128.64, 129.09, 132.58, 139.17, 145.67.

#### 4-(Trifluoromethyl)benzonitrile

White solid; yield: 338.8 mg (99%); mp 37–38 °C (commercial sample); mp 37 °C.

IR (neat): 2235  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77 (d,  $J$  = 8.4 Hz, 2 H), 7.81 (d,  $J$  = 8.4 Hz, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 116.01, 117.38, 123.00 (q,  $J$  = 274.0 Hz), 126.13 (q,  $J$  = 3.83 Hz), 132.64, 134.50 (q,  $J$  = 33.5 Hz).

#### 4-(Methylsulfanyl)benzonitrile

White solid; yield: 277.5 mg (93%); mp 61–62 °C (commercial sample); mp 61–63 °C.

IR (neat): 2220  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.51 (s, 3 H), 7.27 (d,  $J$  = 8.6 Hz, 2 H), 7.54 (d,  $J$  = 8.6 Hz, 2 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.56, 107.49, 118.85, 125.35, 132.04, 145.99.

#### 2,5-Dimethylbenzonitrile

Colorless oil; yield: 259.7 mg (99%); oil (commercial sample); mp 13–14 °C.

IR (neat): 2227  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.33 (s, 3 H), 2.49 (s, 3 H), 7.19 (d,  $J$  = 8.1 Hz, 1 H), 7.27 (d,  $J$  = 8.1 Hz, 1 H), 7.39 (s, 1 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.82, 20.51, 112.41, 118.23, 130.00, 132.59, 133.46, 135.94, 138.74.

#### 2,4-Dichlorobenzonitrile

White solid; yield: 340.6 mg (99%); mp 58–59 °C (commercial sample); mp 61 °C.

IR (neat): 2233  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.38 (dd,  $J$  = 8.3, 1.8 Hz, 1 H), 7.55 (d,  $J$  = 1.8 Hz, 1 H), 7.62 (d,  $J$  = 8.3 Hz, 1 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 111.69, 115.07, 127.69, 130.11, 134.43, 137.65, 139.92.

#### 2,4,6-Trimethylbenzonitrile

White solid; yield: 143.7 mg (99%, starting from 1 mmol of the alcohol); mp 48 °C (commercial sample); mp 52–53 °C.

IR (neat): 2215  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.32 (s, 3 H), 2.48 (s, 6 H), 6.93 (s, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.44, 21.41, 110.12, 117.46, 128.05, 141.78, 142.68.

#### 1-Naphthonitrile

Pale-yellow oil; yield: 151.6 mg (99%, starting from 1 mmol of the alcohol); commercial sample; mp 36–38 °C.

IR (neat): 2222  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52 (dd,  $J$  = 7.4, 7.8 Hz, 1 H), 7.62 (td,  $J$  = 7.4, 1.1 Hz, 1 H), 7.70 (td,  $J$  = 7.8, 1.1 Hz, 1 H), 7.89–7.94 (m, 2 H), 8.08 (d,  $J$  = 7.8 Hz, 1 H), 8.24 (d,  $J$  = 7.4 Hz, 1 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 109.91, 117.59, 124.70, 124.87, 127.33, 128.37, 128.44, 132.10, 132.39, 132.67, 133.06.

**1,3-Benzodioxole-5-carbonitrile**

White solid; yield: 291.3 mg (99%); mp 89–90 °C (commercial sample; mp 94 °C).

IR (neat): 2219 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.07 (s, 2 H), 6.87 (d, *J* = 8.1 Hz, 1 H), 7.04 (d, *J* = 1.7 Hz, 1 H), 7.22 (dd, *J* = 8.1, 1.7 Hz, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 102.17, 104.88, 109.08, 111.34, 118.85, 128.7, 147.98, 151.49.

**4-(Allyloxy)benzonitrile**

White solid; yield: 308.8 mg (97%); mp 43–44 °C (lit.<sup>9</sup> 43–46 °C).

IR (neat): 2216 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.59 (dt, *J* = 5.2, 1.3 Hz, 2 H), 5.34 (dq, *J* = 10.4, 1.3 Hz, 1 H), 5.42 (dq, *J* = 13.0, 1.3 Hz, 1 H), 5.99–6.08 (m, 1 H), 6.96 (d, *J* = 8.9 Hz, 2 H), 7.58 (d, *J* = 8.9 Hz, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 68.96, 104.05, 115.41, 118.45, 119.15, 132.03, 133.93, 161.80.

**Terephthalonitrile**

White solid; yield: 253.7 mg (99%); mp 217 °C (commercial sample; mp 223–230 °C).

IR (neat): 2231 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.80 (s, 4 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 116.69, 116.98, 132.76.

**Isophthalonitrile**

White solid; yield: 253.7 mg (99%); mp 156 °C (commercial sample; mp 162 °C).

IR (neat): 2234 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.66 (t, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 8.2 Hz, 2 H), 7.96 (s, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 114.15, 116.56, 130.31, 135.39, 135.97.

**Thiophene-2-carbonitrile**

Colorless oil; yield: 216.1 mg (99%).

IR (neat): 2221 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.14 (dd, *J* = 3.7, 5.2 Hz, 1 H), 7.63 (dd, *J* = 5.2, 1.1 Hz, 1 H), 7.64 (dd, *J* = 1.1, 3.7 Hz, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 109.39, 113.86, 127.32, 132.35, 137.09.

**Pyridine-3-carbonitrile**

Pale-yellow solid; yield: 206.1 mg (99%); mp 46–48 °C (commercial sample; mp 50 °C).

IR (neat): 2231 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.46 (dd, *J* = 7.9, 5.1 Hz, 1 H), 7.99 (dt, *J* = 7.9, 1.6 Hz, 1 H), 8.84 (dd, *J* = 5.1, 1.6 Hz, 1 H), 8.91 (d, *J* = 1.6 Hz, 1 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 101.87, 116.40, 123.40, 139.04, 152.22, 152.76.

**1-Benzofuran-2-carbonitrile**

Pale-yellow solid; yield: 141.7 mg (99%, starting from 1 mmol of the alcohol); mp 33–34 °C (lit.<sup>10</sup> oil).

IR (neat): 2230 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.37 (t, *J* = 7.4 Hz, 1 H), 7.46 (s, 1 H), 7.49–7.58 (m, 2 H), 7.68 (d, *J* = 7.7 Hz, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 111.59, 111.84, 118.27, 122.35, 124.33, 125.24, 127.04, 128.22, 155.42.

**1-Benzothiophene-2-carbonitrile**

Pale-yellow oil; yield: 292.9 mg (92%); (commercial sample; mp 24–28 °C).

IR (neat): 2234 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.45–7.55 (m, 2 H), 7.84–7.89 (m, 3 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 109.59, 114.42, 122.31, 125.23, 125.68, 127.82, 134.94, 137.38, 141.22.

**1-Tosyl-1*H*-indole-3-carbonitrile**

Pale-yellow solid; yield: 293.4 mg (99%, starting from 1 mmol of the alcohol); mp 157–158 °C (lit.<sup>6b</sup> 155–157).

IR (neat): 2234 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.38 (s, 3 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.4 Hz, 1 H), 7.70 (d, *J* = 7.4 Hz, 1 H), 7.83 (d, *J* = 8.7 Hz, 2 H), 8.00 (d, *J* = 7.4 Hz, 1 H), 8.09 (s, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.67, 93.68, 113.45, 113.78, 120.28, 124.77, 126.51, 127.21, 128.33, 130.37, 133.12, 133.67, 134.14, 146.35.

**(2*E*)-3-Phenylacrylonitrile**

Colorless oil; yield: 245.4 mg (95%); (commercial sample; mp 18–20 °C).

IR (neat): 2216 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 5.89 (d, *J* = 16.6 Hz, 1 H), 7.38–7.47 (m, 6 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 96.10, 117.90, 127.10, 128.86, 130.97, 133.24, 150.34.

**(2*E*)-3-(4-Chlorophenyl)acrylonitrile**

White solid; yield: 323.9 mg (99%); mp 83–84 °C (lit.<sup>11</sup> 84–86 °C).

IR (neat): 2236.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.86 (d, *J* = 16.8 Hz, 1 H), 7.35 (d, *J* = 16.8 Hz, 1 H), 7.38 (br s, 4 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 96.91, 117.74, 128.46, 129.35, 131.87, 137.19, 149.05.

**Phenylacetoneitrile**

Colorless oil; yield: 232.0 mg (99%).

IR (neat): 2252 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.75 (s, 2 H), 7.30–7.42 (m, 5 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 23.21, 117.49, 127.49, 127.60, 128.70, 129.48.

**3-Phenylpropanenitrile**

Colorless oil; yield: 257.1 mg (98%).

IR (neat): 2247 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.61 (t, *J* = 7.5 Hz, 2 H), 2.95 (t, *J* = 7.5 Hz, 2 H), 7.22–7.29 (m, 3 H), 7.34 (t, *J* = 7.0 Hz, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 19.29, 31.50, 119.09, 127.17, 128.21, 128.81, 138.00.

**4-Phenylbutanenitrile**

Colorless oil; yield: 246.8 mg (85%).

IR (neat): 2245 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.00 (quint, *J* = 7.1 Hz, 2 H), 2.30 (t, *J* = 7.1 Hz, 2 H), 2.77 (t, *J* = 7.1 Hz, 2 H), 7.16–7.25 (m, 3 H), 7.31 (t, *J* = 7.0 Hz, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 16.30, 26.84, 34.29, 119.43, 126.43, 128.38, 128.59, 139.65.



**Dec-9-enenitrile**

Colorless oil; yield: 299.5 mg (99%).

IR (neat): 2245 cm<sup>-1</sup>.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.25–1.45 (m, 8 H), 1.66 (quint, *J* = 7.4 Hz, 2 H), 2.05 (dtt, *J* = 7.0, 6.8, 1.5 Hz, 2 H), 2.33 (t, *J* = 7.4 Hz, 2 H), 4.94 (ddt, *J* = 10.4, 2.0, 1.5 Hz, 1 H), 5.00 (ddt, *J* = 17.0, 2.0, 1.5 Hz, 1 H), 5.80 (ddt, *J* = 10.4, 17.0, 7.0 Hz, 1 H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 17.04, 25.27, 28.52, 28.65, 33.59, 114.27, 119.76, 138.83.HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>18</sub>N: 152.1434; found: 152.1434.**2-Methyl-2-phenylpropanenitrile**Colorless oil; yield: 284.6 mg (98%); (lit.<sup>11</sup> oil).IR (neat): 2237 cm<sup>-1</sup>.<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.73 (s, 6 H), 7.31 (t, *J* = 7.3 Hz, 1 H), 7.39 (dd, *J* = 7.3, 8.0 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 29.11, 37.11, 124.48, 125.00, 127.73, 128.88, 141.37.**1-Methylcyclohexanecarbonitrile**Colorless oil; yield: 243.9 mg (99%); (lit.<sup>12</sup> oil).IR (neat): 2232 cm<sup>-1</sup>.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.08–1.27 (m, 3 H), 1.32 (s, 3 H), 1.53–1.76 (m, 5 H), 1.93 (d, *J* = 13.4 Hz, 2 H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 23.15, 25.01, 27.35, 34.41, 37.25, 124.60.**Acknowledgment**

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