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Deadly KCN and pricey metal free track for accessing β-ketonitriles employing mild reaction conditions

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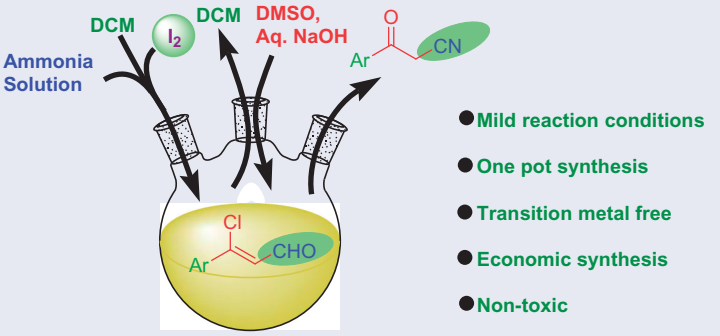
ABSTRACT

A one pot synthesis of β-ketonitriles from readily accessible 3-chloropropenals using economically benign iodine, aqueous ammonia and sodium hydroxide solution, employing mild reaction conditions have been described. This report presents a convenient, inexpensive, highly toxic-matter-free and eco-friendly approach for β-ketonitriles.

GRAPHICAL ABSTRACT



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KEYWORDS
Aqueous ammonia; iodine; β-ketonitriles; 3-methoxypropenenitrile; one-pot; transition metal free

Introduction

β-Ketonitriles are extremely versatile and valuable synthetic intermediates for the synthesis of a wide variety of biologically and pharmacologically active heterocycles including pyrazoles,[1] isoxazoles,[2] thiazoles,[3] imidazoles,[4] furans,[5,6] pyrroles,[6] thiophenes,[7] 2-pyridones,[8] pyrazolopyrimidines,[9] 1,2,3-triazoles,[10] benzothiazoles,[11] imidazo[1,2-a]pyridines,[12] dihydropyridazines,[6] etc. (Figure 1.) as well as many drugs targeting different therapeutic areas such as anti-HIV,[13] anti-inflammatory,[14] antidepressants[15] etc. Further, β-ketonitriles can be converted to benzochromenes,[16] dioxaprollenes,[17] 1-naphthols,[18] and β-hydroxy nitriles.[19] β-Hydroxy nitriles, obtained by enantioselective reduction of the carbonyl group of β-ketonitriles,

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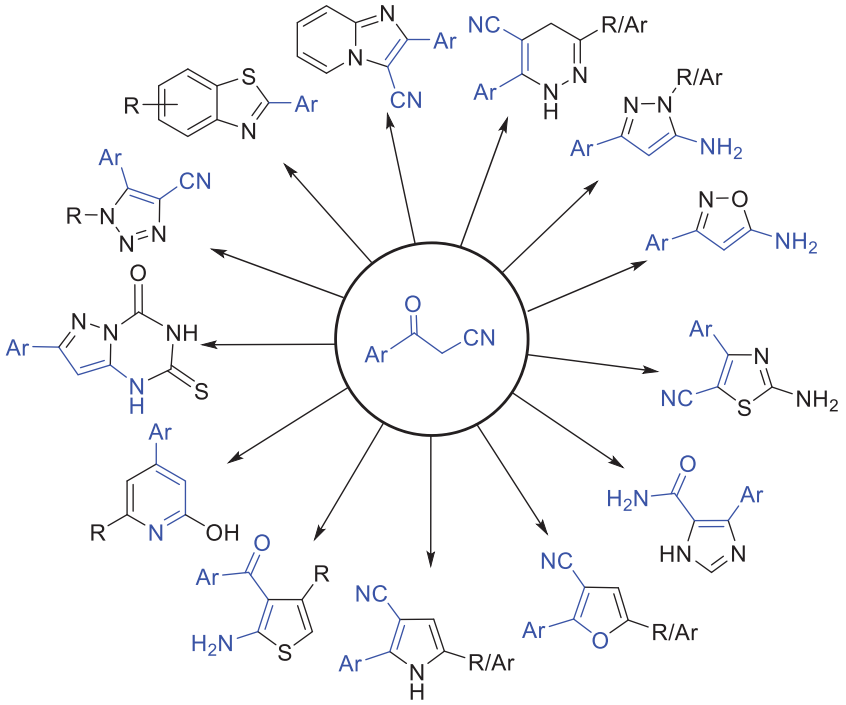
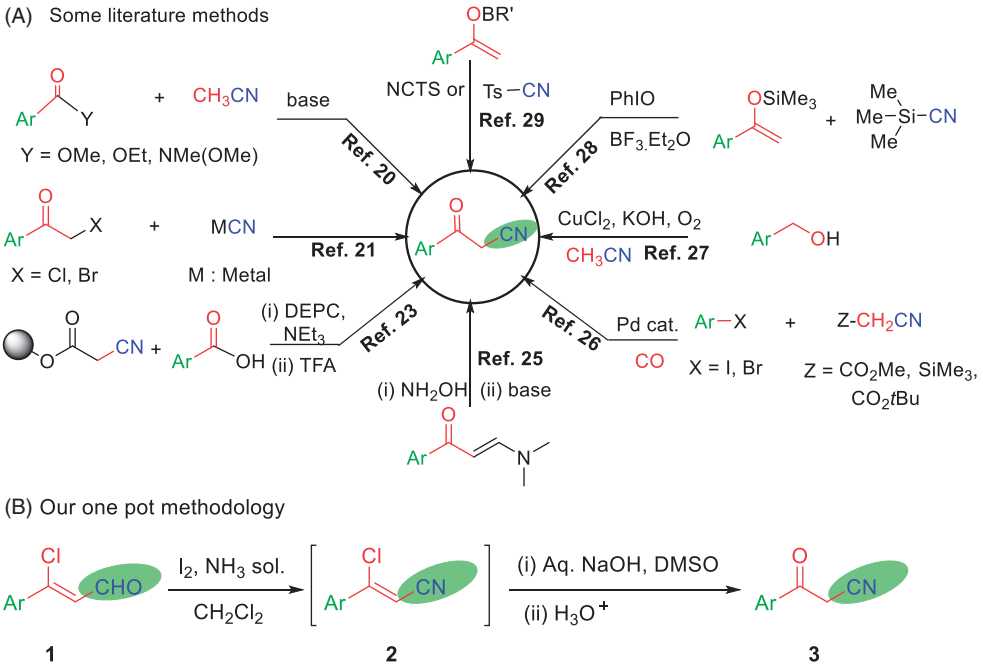


Figure 1. General synthetic utility of β-ketonitriles in synthesis of heterocyclic compounds.

can be further converted to optically pure β-hydroxy carboxylic acids and their derivatives which are other very important precursors in organic chemistry.

Consequently, continuous efforts have understandably been devoted for developing efficient approaches for the synthesis of β-ketonitriles. Conventional methods of their synthesis involve the condensation of acetonitrile with excess of various esters or amides in presence of strong base,[20] reaction of α-haloketones with highly toxic metal cyanides,[21] such as KCN and reaction of cyclic enamines with toxic cyanogen chloride (Cl–CN).[22] Beside these, some other methods of their synthesis include C-acylation of resin bound cynoacetate,[23] indium-mediated coupling of bromoacetonitriles with aromatic aryl cyanides,[24] conversion of enaminones via isoxazoles,[25] Pd-catalyzed carbonylation of aryl halides (–I, –Br)[26] and copper-catalyzed oxidative coupling of aromatic alcohols with acetonitrile.[27] Recently some more methods involving cyanation of silyl enolates using hypervalent-iodine along with trimethylsilyl cyanide (TMSCN) as cyanating reagent[28] and boron enolates using either N-cyano-N-phenyl-p-toluenesulfonamide (NCTS) or TsCN as a cyanating reagent have been reported[29] (Scheme 1A).

All the aforestated methods suffer from certain serious drawbacks/bottlenecks: (1) Some methods use toxic metal cyanides (KCN or NaCN) or Cl-CN either in the direct synthesis or at any stage during synthesis of reagents e.g. TMSCN, TsCN; (2) Some protocols use costly metals e.g. Pd, In, Mo etc. while others use costly reagents like trimethylsilyl acetonitriles which give rise to cost issues besides making these methods unfavorable for commercial applications; (3) Some methods use comparatively less stable substrates, or their reagent synthesis increases the number of steps in overall synthesis. Mainly tedious experimental procedures and use of highly toxic chemicals limit the



Scheme 1. Methods of synthesis of β-ketonitriles.

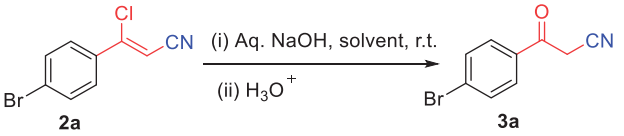
applicability of these methods to well established laboratories and well-trained manpower rendering these methods unsuitable for undergraduate students' labs. Thus, development of a convenient synthetic method for β-ketonitriles that uses inexpensive and nontoxic reagents under aqueous condition is still highly desired.

In previous work, our research group reported, economic and eco-friendly, transition metal-free synthesis of propynenitriles and 3-chloropropenenitriles starting from 3-chloropropenals.[30] Considering the fact that propynenitriles are good substrates for nucleophilic addition reactions, it was conceived that conversion of propynenitriles to β-ketonitriles can be achieved via nucleophilic addition of water followed by tautomerization. After numerous failed attempts, we developed a simple, inexpensive, toxic matter free, novel, one pot protocol for the synthesis of β-ketonitriles **3** starting from 3-chloropropenals **1**. The reaction initiates with transformation of formyl group to nitrile by treatment of iodine and aqueous ammonia in dichloromethane solvent followed by treatment with aqueous base in DMSO solvent in one pot (Scheme 1B). Use of common lab chemicals such as iodine, aqueous ammonia and sodium hydroxide as a base in overall conversion increases its significance making it suitable for any undergraduate lab.

Results and discussion

Conversion of 3-chloropropenals **1** to isolable intermediate, 3-chloropropenenitriles **2** was reported earlier by our group.[30] Optimization studies were initiated taking one of the intermediates; (Z)-3-(4-bromophenyl)-3-chloropropenenitrile (**2a**) as reactant

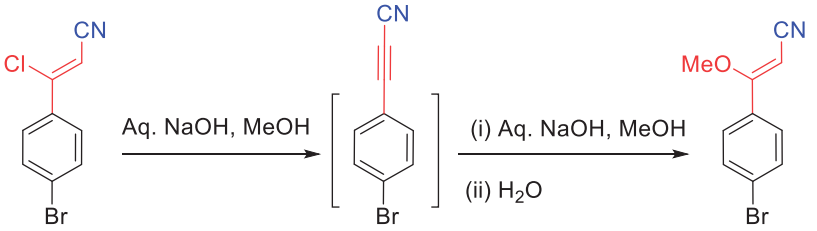
Table 1. Optimization of Solvent and Base Equivalents[a].



2a 3a

Entry	Solvent	Aq. NaOH (%)	Time	Yield (%)[b]
1	MeOH	10	20 min–24 h	Up[c] (91)
2	*t*-Butanol	10	4 h	62
3	THF	10	15 min	**4a** (88)
4	THF	10	30 h	Mixture
5	*p*-Dioxane	10	12 h	Mixture
6	CH_3CN	10	6 h	Mixture
7	DMF	10	8 h	Mixture
8	DME	10	4 h	Mixture
9	Acetone	10	12 h	42
10	DMSO	10	15 min	66
11	DMSO	15	10 min	71
12	**DMSO**	**20**	**4 min**	**77**
13	DMSO	25	4 min	74

[a]Reaction conditions: **2a** (1.00 mmol), Aq. NaOH (1 mL). [b]Isolated yield. [c]Undesired product.
Bold indicates the reaction conditions for obtaining best results.



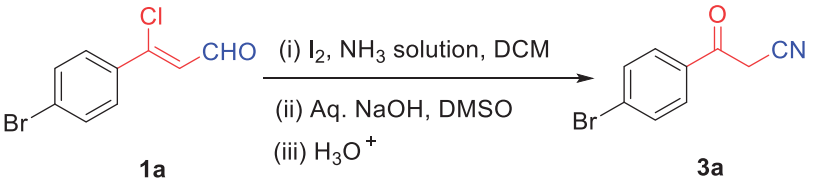
2a 4a 5

Scheme 2. Synthesis of undesired product **5**. Reaction conditions: **2a** (1.00 mmol), Aq. NaOH (1 mL, 10%), MeOH (10 mL)

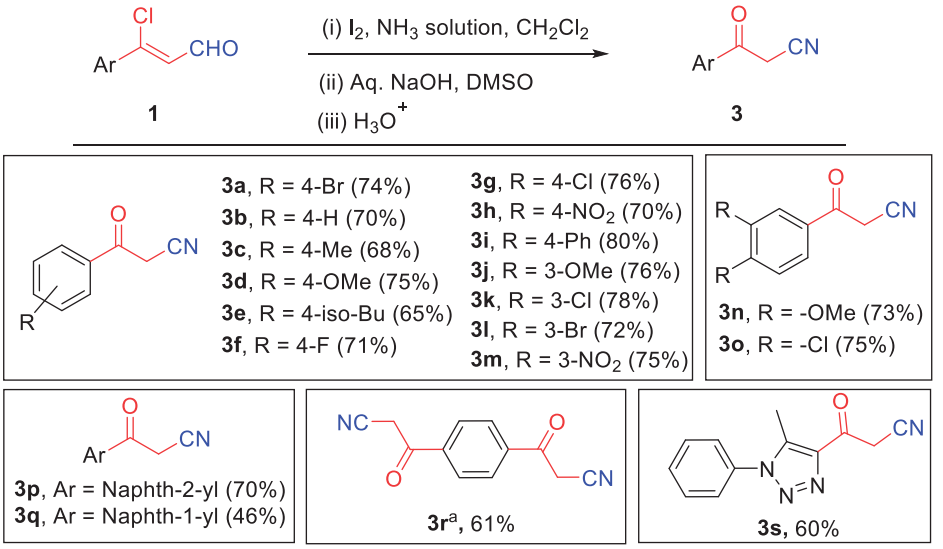
because it could be obtained conveniently from 4-bromoacetophenone as solid in high yield. For obtaining *β*-ketonitrile **3a**, reactant **2a** was treated with sodium hydroxide as base in various solvents as described in Table 1.

Initially, polar protic solvent, methanol was screened and we were pleased to observe a single spot that was different from reactant as seen in thin layer chromatography (TLC) within 20 min (Table 1, entry 1). However, rigorous analysis of ^{1}H and ^{13}C NMR along with 2D-NMR spectra suggested the formation of undesired Z-alkene **5**, the structure of which was confirmed as (Z)-3-(4-bromophenyl)-3-methoxypropenenitrile **5** (Scheme 2; see Supporting Information (SI) for complete details). Next, we stirred the reaction mixture for 24 h under aforestated reaction conditions but no further reaction was observed. This led to the conclusion that polar protic solvent undergoes nucleophilic addition reaction with propynenitrile intermediate **4a** formed by elimination of HCl from reactant **2a** in presence of NaOH base (Scheme 2).

After that *t*-butanol was selected as solvent for the reaction since it is bulkier and weaker nucleophile than methanol. Surprisingly desired product **3a** was obtained in acceptable amount in *t*-butanol, even though poor solubility of reactant **2a** in solvent at

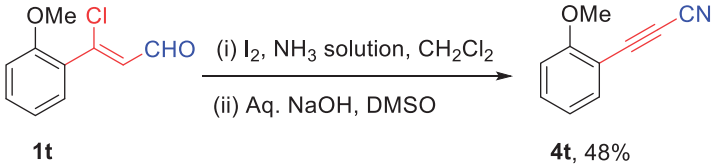


Scheme 3. One pot synthesis of target product (**3a**). Reaction conditions: 3-Chloropropenal **1a** (3.0 mmol), I_2 (3.0 mmol), ammonia solution (4 mL), DCM (20 mL), Aq. NaOH (3 mL, 20%), DMSO (15 mL) at r.t.

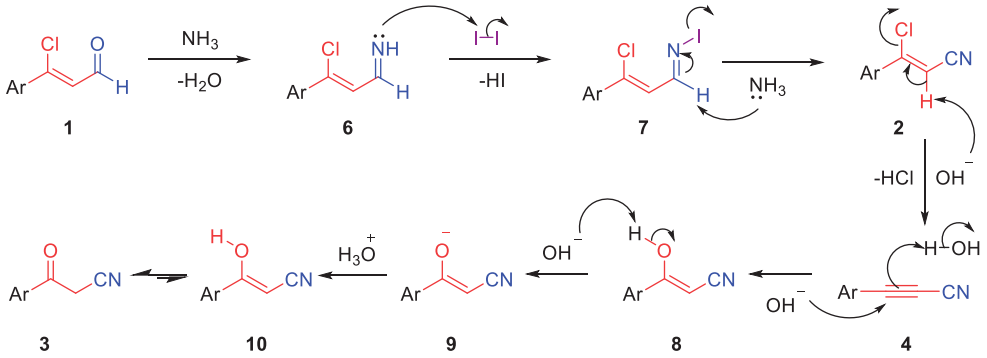


Scheme 4. Synthesis of various β-ketonitriles **3** from 3-chloropropenals **1**. Reaction conditions: 3-Chloropropenals **1** (3.0 mmol), I_2 (3.0 mmol), ammonia solution (4 mL), DCM (20 mL), Aq. NaOH (3 mL, 20%), DMSO (15 mL) at r.t. [a]2 equiv. of reagents were used.

room temperature remained an issue (Table 1, entry 2). In order to overcome the issues arising in protic solvents, we turned our attention toward polar aprotic solvents and reaction in THF led to formation of propynenitrile **4a** within 15 min (Table 1, entry 3),[30] however prolonged stirring even for 30 h at room temperature resulted into mixture of products instead of desired product **3a** (Table 1, entry 4).Similarly, reactions in *p*-dioxane, CH_3CN, DMF and DME solvents afforded mixture of products (Table 1, entries 5, 6, 7 and 8). Use of acetone resulted into desired product **3a**, nevertheless the procedure suffered from poor conversion (42%, Table 1, entry 9). After many futile attempts, desired product **3a** was obtained in substantial amount at room temperature in DMSO solvent (Table 1, entry 10). Yield was further improved by normalizing of equivalents of base along with reaction time optimization (Table 1, entries 11, 12, and 13). Best results were obtained by using DMSO solvent and 20% of aqueous NaOH base (Table 1, entry 12). Finally, our target was to convert two step procedure of synthesis of β-ketonitriles **3** starting from 3-chloropropenals **1** in one pot manner which was achieved by treating 3-chloropropenal with I_2 and ammonia in DCM followed by



Scheme 5. Formation of propynenitrile **4t** in case of *ortho* substituted derivative **1t**. Reaction conditions: 3-Chloropropenal **1t** (3.0 mmol), I_2 (3.0 mmol), ammonia solution (4 mL), DCM (20 mL), Aq. NaOH (3 mL, 20%), DMSO (15 mL) at r.t.



Scheme 6. Proposed mechanism.

evaporation of DCM solvent on a rotary evaporator and reacting the residual mass with aqueous NaOH in DMSO solvent (Scheme 3). Poor solubility of residual solid in *t*-butanol made it less attractive option for the one pot reaction. It is pertinent to mention here that various 3-chloropropenals **1** were easily synthesized from commercially available substituted acetophenones under Vilsmeier Haack reaction conditions[31].

With the optimized reaction conditions in hand, the substrate scope for synthesis of variety of *β*-ketonitriles using differently substituted 3-chloropropenals **1** was examined. Interestingly substrates bearing electron donating as well as electron withdrawing groups at *para* and *meta* positions at phenyl ring afforded corresponding *β*-ketonitriles in high yields with equal ease (Scheme 4).

On the other hand, substrate incorporating *ortho* methoxy substituents at phenyl ring (**1t**) resulted into corresponding propynenitrile product **4t** probably due to slow reaction caused by steric effect of *ortho* substituent to incoming nucleophile (Scheme 5).

However, the isosteric *ortho* substituted derivatives e.g. 1-naphthyl (**1q**) and 1,2,3-triazole ring containing derivative (**1 s**) resulted into desired products **3q** and **3 s** in relatively low yields upon recrystallization.

On the basis of results of above substrate studies, literature review and earlier report from our group,[30] a plausible reaction pathway was proposed as shown in Scheme 6. Conversion of 3-chloropropenals **1** to corresponding 3-chloropropenenitriles **2** is parallel to general mechanism for the conversion of aldehydes into nitriles. Iodine acts as an oxidizing agent and reaction proceeds via formation of N-iodoaldemine **7** which upon removal of HI under basic conditions of aqueous ammonia results in

3-chloropropenenitriles **2**. Thereafter, NaOH in DMSO solvent eliminates HCl from 3-chloropropenenitrile **2** to form propynenitrile **4** which is subsequently attacked by hydroxyl group nucleophilically to afford enolnitrile intermediate **8**. This intermediate **8** is further attacked by NaOH base to generate enolate intermediate **9** which upon acidic work up and tautomerization results into *β*-ketonitrile **3**.

Conclusion

In conclusion, a convenient, inexpensive, eco-friendly and toxic-matter-free one pot synthesis of *β*-ketonitriles **3** from 3-chloropropenals **1** have been developed, employing mild reaction conditions with the use of I_2, aqueous ammonia and NaOH reagents. This method is so handy that it can be easily used by undergraduate students in a frugal lab. In addition, development of new and simple method for *β*-ketonitriles may open new avenues to explore expeditious synthesis of novel pharmacologically potent compounds, natural products and drugs.

Experimental section

Materials and general methods

All the commercially available chemicals were used without further purification. All the solvents were dried and/or purified according to standard procedures prior to use. All the reactions were monitored by TLC on TLC silica gel on F_{254} aluminum plates using a mixture of chloroform and methanol as eluent while visualization was achieved by UV lamp. Melting points were determined in open capillaries in an electrical melting point apparatus and are uncorrected. IR spectra were recorded on ABB MB 3000 DTGS IR instrument. ^{1}H NMR spectra were recorded on 400 MHz, while ^{13}C NMR spectra were registered at 100 MHz, using deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6) as solvent, and tetramethylsilane (TMS) as internal standard at room temperature. Chemical shifts are reported as δ values in parts per million (ppm) downfield from TMS. High resolution mass spectra were obtained from a MicroMass ESI-TOF MS spectrometer. Multiplicities are described as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), triplet of triplet (tt), multiplet (m), exchangeable proton (ex) for NMR assignments and strong (s), medium (m), broad (br) for IR assignments. The coupling constants are expressed in hertz (Hz).

General procedure for the synthesis of β-ketonitriles 3

To a solution of 3-chloropropenal (**1**, 3.0 mmol) in 20 mL of dichloromethane, added molecular iodine (3.0 mmol) in one lot and allowed to stir for 3–5 minutes. Then 4 mL of 30% aqueous ammonia solution was added to reaction mixture and stirred further for 45 minutes. Slight excess of iodine was neutralized with few drops of aqueous sodium thiosulfate solution and organic layer was evaporated under reduced pressure. DMSO (15 mL) was added to solid mass left followed by addition of 3 mL of aqueous NaOH (20%) maintaining the equilibrium temperature, 25 °C by using water bath. Reaction was monitored by TLC. After completion of reaction (3–10 minutes), reaction

mixture was poured into ice cold water and neutralized with dilute HCl. Solid product was filtered, dried and recrystallized with minimum amount of ethanol.

3-(4-Bromophenyl)-3-oxopropanenitrile (3a)

Yield 74 %; yellow solid; Lit. m. p. 158-162 °C,[26a] Obs. m. p. 152–154 °C; IR(KBr) (ν, cm^{-1}): 2947, 2924 (C–H stretch), 2214 (C≡N stretch), 1690 (C=O stretch); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81–7.78 (m, 2H, Ar), 7.70–7.67 (m, 2H, Ar), 4.06 (s, 2H, $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 133.0, 132.6, 130.3, 129.9, 113.4, 29.4.

Supplemental data (full experimental detail, copies of H-H COSY, HSQC, ROESY and DEPT-135 spectra of compound **5** as well as ^{1}H and ^{13}C NMR spectra for compounds **5**, **3a-3s**, **4t**) can be accessed on the publisher's website.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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