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3-(Ethoxycarbonyl)-1-(5-methyl-5-(nitrosooxy)hexyl)pyridin-1-ium cation: A green alternative to *tert*-butyl nitrite for synthesis of nitro-group-containing arenes and drugs at room temperature

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ABSTRACT

Due to their remarkable properties, task-specific ionic liquids have turned out to be progressively popular over the last few years in the field of green organic synthesis. Herein, for the first time, we report that a new task-specific nitrite-based ionic liquid such as 3-(ethoxycarbonyl)-1-(5-methyl-5-(nitrosooxy)hexyl)pyridin-1-ium bis(trifluoromethanesulfonyl)imides (**TS-N-IL**) derived from biodegradable ethyl nicotinate indeed acted as an efficient and eco-friendly reagent for the synthesis of highly valuable nitroaromatic compounds and drugs including nitroxynil, tolcapone, niclofolan, flutamide, niclosamide and nitrazepam. The bridging of an ionic liquid with nitrite group not only increases the yield and rate of direct C–N bond formation reaction but also allows easy product separation and recyclability of a byproduct. Nonvolatile nature, easy synthesis, merely stoichiometric need and mildness are a portion of the extra focal points of **TS-N-IL** while contrasted with *tert*-butyl nitrite an outstanding and highly-flammable reagent utilized largely in organic synthesis.

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Introduction

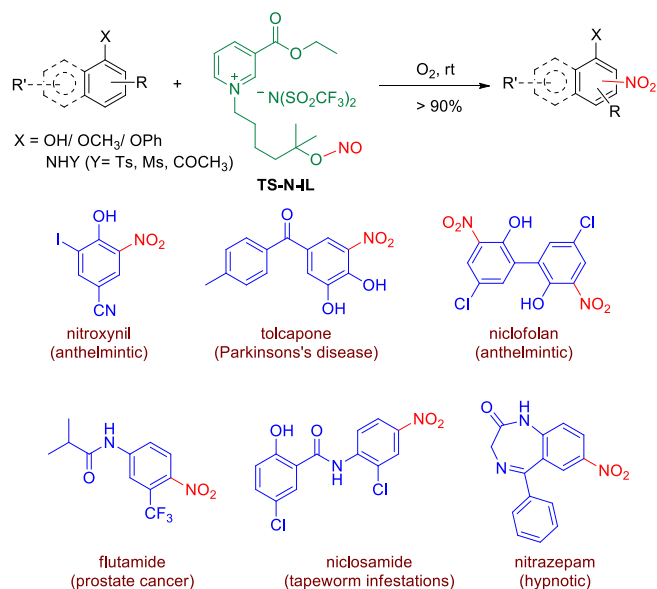
Nitro compounds [1] are highly valuable and versatile building blocks used to a great extent for the preparation of dyes, explosives, fertilizers, perfumes, plastics and so on. Numerous nitro compounds are also biologically active that are used as drugs and diagnostic aids [1]. Over the quite a long while, various synthetic strategies have been portrayed for their preparation [2]. Among these, in the course of the most recent decade, a significantly utilized methodology employs *tert*-butyl nitrite (TBN) as a radical nitrating agent [3]. Despite works in acid- and additive-free conditions [3], TBN remains associated with many obstacles; for example, extremely flammable (flash point: $-10\text{ }^{\circ}\text{C}$), highly volatile (bp: $59\text{--}62\text{ }^{\circ}\text{C}$), required large quantity (2–5 equivalence) and on inward breath show harmful impacts on the cardiovascular systems and focal nervous systems (see: hazard statements and signal word for TBN) [1–3]. Moreover, in large-scale reactions, one of the TBN's byproducts, i.e., *tert*-butanol entangles the product separation and poses crucial ecological concerns [3]. As an outcome, the advancement of a practical and environmentally benign derivative would supplant TBN is a challenging area for investigation.

Ionic liquids are low flammable, non-volatile, possess excellent thermal- and chemical stabilities, have great solvating capability, exhibit wide liquid range and simplicity of recycling [4]. They are additionally known to have influences on the reaction rate, selectivity, etc. [4a]. After their successful use in various chemical and enzymatic reactions, Davis and coworkers [5] presented an idea of task-specific ionic liquids (TSILs) in which a functional group is covalently tethered to the cation or anion of the ionic fluid to carry not only as a solvent but also as reagent and/or catalyst in the chemical reactions [6]. Afterwards, a few TSILs were created and utilized as solvents and reagents or catalysts in Diels-Alder reactions [7], Friedel-Crafts reactions [8], transition metal-catalyzed reactions [9] and so forth. Nevertheless, to the best of our knowledge, the use of a task-specific ionic liquid in general and a task-specific nitrite-based ionic liquid [10] in particular for the synthesis of nitro-group-containing arenes and drugs has not yet been accounted.

In continuation of our ongoing works on the utilization of ionic fluids in organic synthesis [11], herein, for the first time; we report that a new task-specific nitrite-based ionic liquid such as 3-(ethoxycarbonyl)-1-(5-methyl-5-(nitrosooxy)hexyl)pyridin-1-ium bis(trifluoromethanesulfonyl)imides (**TS-N-IL**, Scheme 1) derived from biodegradable ethyl nicotinate in fact acted as an efficient and eco-friendly reagent for the synthesis of exceptionally important nitroaromatic compounds and drugs including nitroxynil,

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Scheme 1. A general strategy for the synthesis of nitro-group-containing arenes and drugs using a novel task-specific nitrite-based ionic liquid (TS-N-IL) reported in this paper. At the bottom is provided the chemical structure of drugs synthesized using TS-N-IL.

tolcapone, niclofolan, flutamide, niclosamide and nitrazepam (Scheme 1). Nonvolatile nature, easy synthesis, merely stoichiometric need and mildness are few advantages of TS-N-IL while contrasted with *tert*-butyl nitrite a well-known and a toxic reagent utilized in organic synthesis.

Results and discussion

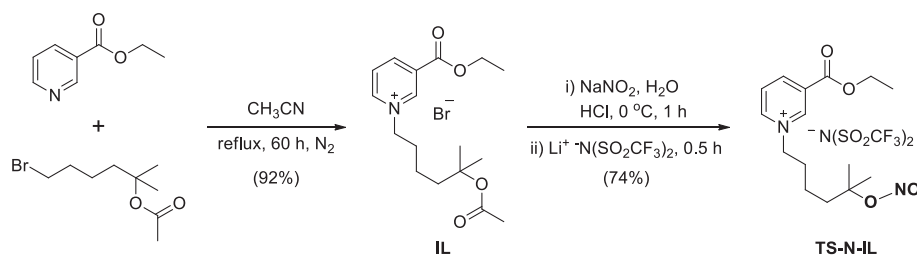
The nitrite functionalized ionic liquid, i.e., TS-N-IL was prepared in three steps by i) alkylation of ethyl nicotinate with 6-bromo-2-methylhexan-2-yl acetate at reflux temperature, ii) nitrification of resultant ionic liquid (IL, Scheme 2) with aqueous NaNO₂ and HCl at 0 °C and iii) anion exchange with lithium trifluoromethylsulfonamide, cf. Scheme 2. The synthesized TS-N-IL was characterized by FT-IR, NMR, TGA, DSC and elemental analysis, cf. Electronic Supporting Information (ESI). The IR spectra of TS-N-IL exhibit an intense peak at 1643 cm⁻¹ corresponding to the asymmetrical stretching of nitrite ester group, peaks between 1636–1489 cm⁻¹ and 1418–1396 cm⁻¹, respectively, are due to C=C multiple bond stretching and aromatic C=N vibrations. The aromatic and alkyl C-H stretching frequencies appear in the ranges of 3150–3080 and 3000–2865 cm⁻¹, respectively. Additionally, the sharp peak shows the carbonyl stretching frequency of the ester at 1710 cm⁻¹. TGA curve of TS-N-IL measured under argon atmosphere showed an initial ~6% weight loss near to ~74 °C due to the removal of NO and was followed by a shouldering from 140 to 290 °C with maximum decomposition of organic moiety. DSC

profile of TS-N-IL measured under argon atmosphere exhibited endotherm at 74 °C possibly due to the loss of NO group. These results recommended that TS-N-IL is nonvolatile and stable up to 150 °C. Therefore, TS-N-IL is expected to decrease potential exposure and known toxicity during use, while compared to TBN has a low flash- and boiling points.

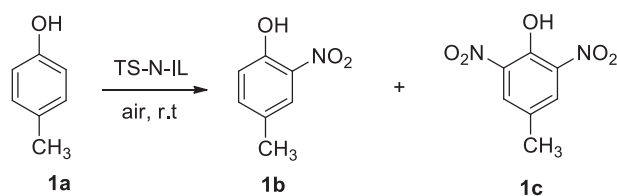
Later, we investigated the nitrating capacity of novel TS-N-IL (Scheme 2). A reaction of 4-methylphenol (**1a**, 1 equiv.) and TS-N-IL (2.0 equiv.) under an open-air atmosphere at room temperature, after stirring the reaction mixture for 2 h, afforded the expected 4-methyl-2-nitrophenol (**1b**) in quantitative yield (Table 1 and entry 1). The product was characterized by melting point and NMR spectroscopy (ESI), which are in close agreement with the literature reports [3]. The bisnitrated product (4-methyl-2,6-dinitrophenol, **1c**) was possibly watched if the substrate was left under the reaction conditions until well after the beginning material was completely devoured, and then just in little amounts (Table 1 and entry 2). The use of acetonitrile, DMF, etc., as an additional solvent; the reaction continued at a slower rate (Table 1 and entries 3–6). Reaction under oxygen-free conditions is relatively sluggish (Table 1 and entry 7). Additionally, an endeavor to increase the reaction rate by raising the temperature to 50 °C got failed (Table 1 and entries 8–9). With regard to the optimal amount of TS-N-IL, the reaction in the presence of 1.3 equivalents gave the best outcomes (Table 1 and entries 10–13). Also, no discernible 4-methyl-2,6-dinitrophenol (**1c**) emerged even after 6 h with the usage of 1.3 equiv., of TS-N-IL, cf. Table 1 and entry 14. Thence, the optimized reaction conditions were as follows: **1a** (1.0 equiv.) and TS-N-IL (1.3 equiv.) under an open air atmosphere at room temperature for 2 h.

Next, we treated a series of phenols with TS-N-IL and the results are compiled in Table 2. We found that under optimized reaction conditions (Table 1), TS-N-IL was compelling at changing over phenol and its derivatives into corresponding C-nitro compounds in good yield (Table 2). At the point when both *ortho* and *para* positions are available (Table 2 and entries 2 and 3), a mixture of mononitrated regioisomers was acquired. It very well may be seen from the proportion of **2b** and **2b'** and **3b** and **3b'** that the *para*-isomer is more effectively created than the *ortho*-isomer. Nevertheless, phenol with substituent just in the *para*-position (**1a**, **4a** and **5a**) solely afforded corresponding *ortho*-nitro product (**1b**, **4b** and **5b**) in quantitative yield. Also, salicylic acid (**6a**), 2-naphthol (**7a**) and 6-bromo-2-naphthol (**8a**) under the optimized conditions afforded the expected nitro compounds **6b**, **7b** and **8b**, respectively, in good yield (Table 2). These outcomes demonstrated that an electronic effect on the substituted group played not significant role in the reaction, which precludes the possibility of an electrophilic substitution reaction [3].

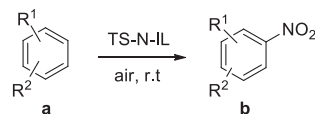
Encouraged by these results, we then directed our concentration toward the nitration of amides using TS-N-IL as a reagent. A reaction of 4-methyl-*N*-phenylbenzenesulfonamide (**9a**) with TS-N-IL under the same experimental conditions (Table 1) utilized for nitration of phenols resulted in incomplete conversion. Viz.,



Scheme 2. The synthetic route to task-specific nitrite-based ionic liquid (TS-N-IL).

Table 1Selected results of optimization of reaction conditions for TS-N-IL-mediated nitration.^a

Entry	Equivalents of TS-N-IL used	Solvent ^b	Temperature (°C)	Time (h)	Yield (%) of 1b ^c
1	2	—	25	2	96
2	2	—	25	6	78 ^d
3	2	CH ₃ CN	25	2	63
4	2	DMF	25	2	88
5	2	THF	25	2	71
6	2	Acetone	25	2	52
7	2	—	25	12	≈23 ^e
8	2	—	50	1	74
9	2	—	50	1.5	94
10	1.7	—	25	1.5	95
11	1.3	—	25	2	94
12	1.0	—	25	4	82
13	3.0	—	25	1	95
14	1.3	—	25	6	94 ^f

^a Unless specified otherwise, all reactions were carried with 0.5 mmol of **1a** and TS-N-IL under open air atmosphere.^b Solvents were distilled prior to use.^c Isolated yield.^d 4-Methyl-2,6-dinitrophenol (**1c**) was obtained in 16% yield.^e A reaction performed under N₂ atmosphere.^f 4-Methyl-2,6-dinitrophenol (**1c**) was detected in trace.**Table 2**Nitration of different classes of arenes using TS-N-IL as a nitrating reagent.^a

Entry	Substrate	Product	Time (h)	Yield (%) ^b
1	<chem>Cc1ccc(O)cc1</chem> 1a	<chem>Cc1ccc(O)c([N+](=O)[O-])c1</chem> 1b	2	96
2	<chem>Oc1ccccc1</chem> 2a	<chem>Oc1ccc([N+](=O)[O-])cc1</chem> 2b	2	78
		<chem>Oc1ccccc1[N+](=O)[O-]</chem> 2b'		14
3	<chem>Cc1ccc(O)cc1</chem> 3a	<chem>Cc1ccc(O)c([N+](=O)[O-])c1</chem> 3b	2	63
		<chem>Cc1ccc(O)c([N+](=O)[O-])c1</chem> 3b'		34
4	<chem>COc1ccc(O)cc1</chem> 4a	<chem>COc1ccc(O)c([N+](=O)[O-])c1</chem> 4b	2	95

(continued on next page)

Table 2 (continued)

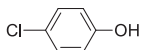
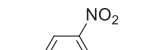
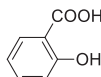
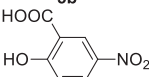
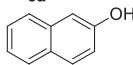
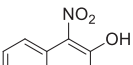
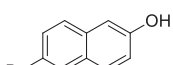
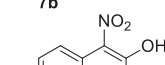
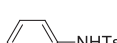
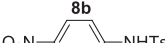
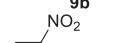
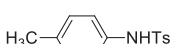
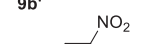
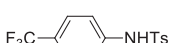
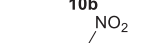
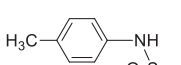
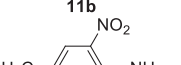
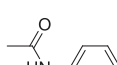
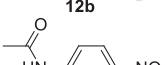
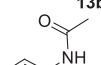



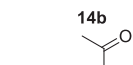
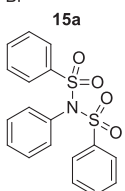
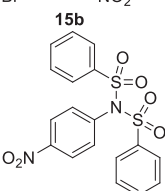
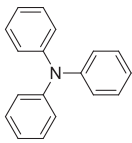
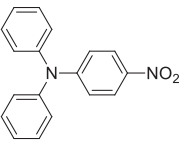
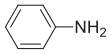
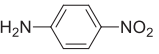
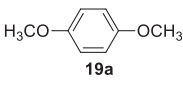
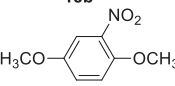
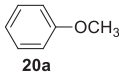
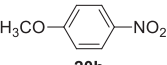
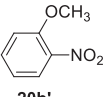
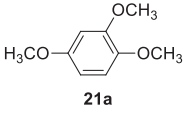
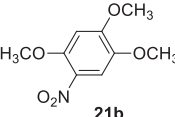
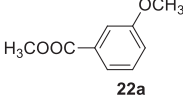
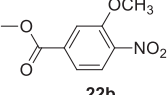
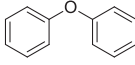
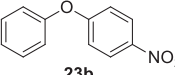
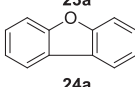
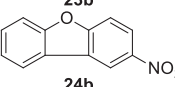
Entry	Substrate	Product	Time (h)	Yield (%) ^b
5	 5a	 5b	2	94
6	 6a	 6b	2	89
7	 7a	 7b	2	92
8	 8a	 8b	2	96
9	 9a	 9b	5	72
		 9b'		19
10	 10a	 10b	5	93
11	 11a	 11b	5	89
12	 12a	 12b	5	90
13	 13a	 13b	6	71
		 13b'		22
14	 14a	 14b	6	94
15	 15a	 15b	6	88
16	 16a	 16b	12	ND

Table 2 (continued)

Entry	Substrate	Product	Time (h)	Yield (%) ^b
17			3	89
18			2	<5
19			2	97
20		 	2	74 20
21			2	93
22			2	88
23			2	95
24			2	96

^a Unless specified otherwise, all reactions were carried with 1.0 mmol of arenes and 1.3 mmol of **TS-N-IL** under open air atmosphere at room temperature.

^b Isolated yield. ND; not detected. Ts: -SO₂C₆H₄CH₃.

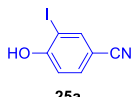
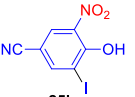
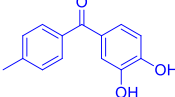
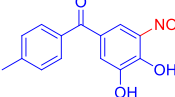
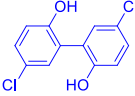
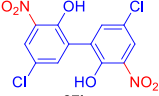
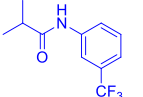
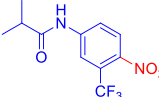
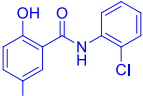
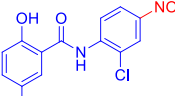
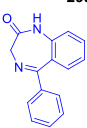
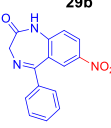
substrate **9a** in part changed over into a regioisomeric mixture of mononitrated derivatives **9b** and **9b'**, respectively, in 46% and 11% yields. Conversions were improved significantly by dragging out the reaction time from 2 h to 5 h (Table 2, entry 9): the combined yields of **9b** and **9b'** surpassed 90% at ambient conditions. As opposed to the phenols, running the nitration of amides at elevated temperature (50–60 °C) had no negative impact on the product outcome while diminishing reaction time from 5 h to 3 h. In this way, both in room- and elevated temperatures, an assortment of substituted amides **9a–15a** (Table 2 and entries 9–15) were underwent nitration in good yield and a variety of common functional groups very much endured under the reaction conditions employed. Nevertheless, an attempt at nitrating tertiary sulfonamide (**16a**) was ineffective. Likewise, nitration of aniline (**18a**) brought about the complex mixtures at ambient conditions.

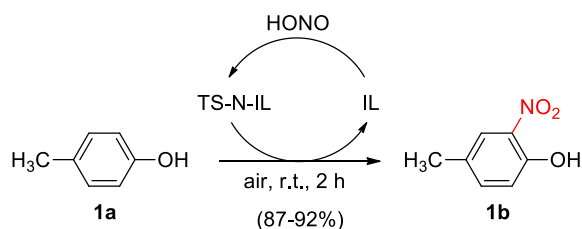
A while later, the nitration of electron-rich arenes (Table 2) by TS-N-IL was explored. A reaction of 1,4-dimethoxybenzene (**19a**, 1 equiv.) and TS-N-IL (1.3 equiv.) under an open-air atmosphere at room temperature, after stirring the reaction mixture for 2 h, afforded the expected 4-methoxy-2-nitrophenol (**19b**) in quantitative yield (>95%). On increasing the reaction temperature to 50 °C, this conversion somewhat decreased to 91%. Indeed, even no nitro-substituted product was seen when the reaction was performed at 90 °C. Therefore, we treated a series of electron-rich arenes (**19a–24a**) with TS-N-IL at room temperature. Fortunately, fantastic out-

comes were watched for anisole (**20a**), 1,2,4-trimethoxybenzene (**21a**), methyl 3-methoxybenzoate (**22a**), diphenyl ether (**23a**) and dibenzo[*b,d*]furan (**24a**) afforded products (**20b–24b**) in quantitative yields (Table 2). In addition, as like phenols (**2a** and **3a**) and amides (**9a** and **13a**), the nitration of anisole (**20a**) gave a mixture of mononitrated regioisomers (**20b** and **20b'**) with *para*-isomer as a noteworthy product.

To probe the tactic utility of TS-N-IL, synthesis of a variety of nitro-group-containing drugs were investigated. For instance, nitroxynil (**25b**) is an anthelmintic drug utilized for treatment against adult worms of bunostomum, haemonchus, and oesophagostomum in cattle and sheep [12]. A traditional method to introduce nitro group into 4-hydroxy-3-iodobenzonitrile (**25a**) was electrophilic nitration by concentrated nitric acid, with only 58% yield and different unfortunate results through over-oxidation and -CN group hydrolysis were reported [12]. In contrast, TS-N-IL was observed to be a viable nitro source and offered a millimoles scale synthesis of nitroxynil (**25b**, 91%) under mild conditions (Table 3 and entry 1) at room temperature. Moreover, other nitro-group-containing drugs such as tolcapone (**26b**) [13], niclofolan (**27b**) [14], flutamide (**28b**) [15], niclosamide (**29b**) [16] and nitrazepam (**30b**) [17] were likewise prepared in moderate to good yields utilizing TS-N-IL as a nitrating agent under acid-free conditions. Thus, a mild and highly efficient synthesis of different classes of nitro arenes and drugs has been accomplished by using a novel

Table 3
The synthesis of nitro-group-containing drugs using TS-N-IL as a nitro source at room temperature.^a

Entry	Substrate	Product	Time	Yield (%) ^b
1			2	91
2			2	67 ^c
3			2	93
4			5	69 ^c
5			5	48 ^c
6			5	88

^a Unless specified otherwise, all reactions were carried with 1.0 mmol of arenes and 1.3 mmol of TS-N-IL under open air atmosphere at room temperature.^b Isolated yield.^c Dinitrated product such as 5-chloro-N-(2-chloro-4-nitrophenyl)-2-hydroxy-3-nitrobenzamide also detected in 29% yield.**Scheme 3.** An illustration for IL recovery and reuse in the form of TS-N-IL for synthesis of 4-methyl-2-nitrophenol (**1b**) from 4-methylphenol (**1a**) at ambient conditions.

TS-N-IL as nitrating reagent under solvent-free condition at room temperature. Also, substituents such as halogens, ethers, amines, amides, phenols and carboxyls were well tolerated with TS-N-IL and can be used for further modifications.

The by-product, i.e., **IL** (Scheme 2) formed in the TS-N-IL-mediated nitration reaction(s) displays poor-miscibility in a wide range of solvents including acetonitrile, hexane, diethyl ether and ethyl acetate. Hence, after completion of the nitration reaction, **IL** was recovered easily by removing nitro compounds by extraction using ethyl acetate as a solvent. The recovered **IL** was washed with excess of ethyl acetate, dried under vacuum for 12 h and reconverted into TS-N-IL by nitrosation, cf. Schemes 2 and 3. The nitration reaction of 4-methylphenol (**1a**) using TS-N-IL synthesized from recovered **IL** also worked effectively and afforded 4-methyl-2-nitrophenol (**1b**) in 92% yield. In this manner, for four cycles, **IL** was over and over recovered; treated with nitrous acid and utilized for nitration of **1a**. Indeed, in each cycle (Scheme 3)

expected nitro compound was isolated in 87–92% yield, demonstrating that **IL** can therefore easily be reused without degradation. Moreover, **IL** could be recovered with a high recuperation (>90%) in each cycle.

Conclusion

In contrast to TBN, a novel TS-N-IL has observed to be nonvolatile, less flammable, required only stoichiometric amount, highly efficient, good functional group tolerance, affords mononitration products exclusively, and stable up to 150 °C. In addition, the byproduct (**IL**) is reusable and immiscible with molecular solvents that disentangle the workup procedure and increase the product yield due to absence of watery workup. Moreover, nicconate-based ionic fluids are known to degrade within 7 days of being treated with waste water organisms. Henceforth, **IL** and TS-N-IL employed here is expected to biodegrade under mild conditions. Therefore, we believe that TS-N-IL would draw in interests of academic and industries for the synthesis of nitro-group-containing arenes and drugs under a green protocol.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data (general aspects, procedure, experimental characterization data and copy of spectra) to this article can be found online at <https://doi.org/10.1016/j.tetlet.2019.151529>.

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