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Potassium 4-Iodylbenzenesulfonate (PIBS): An Efficient Recyclable Hypervalent Iodine Reagent for Iodo-functionalization of Alkenes, Alkynes and Ketones

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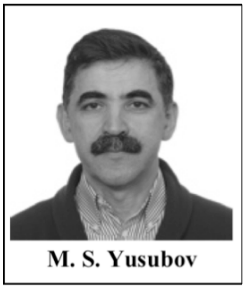

M. S. Yusubov

Abstract: Potassium 4-iodylbenzenesulfonate (PIBS) is a thermally stable and water soluble hypervalent iodine oxidant particularly useful as a recyclable reagent for oxidative iodination of alkenes, alkynes and ketones. This reagent can be effectively recovered from the reaction mixture by treatment of the aqueous layer with Oxone at 60 °C followed by filtration of the precipitate.

Keywords: Iodination, iodine, iodoketones, alkyl iodides, iodomethoxylation, hypervalent iodine.

INTRODUCTION

Compounds of polyvalent iodine have recently emerged as versatile and environmentally benign reagents for various synthetically important oxidative transformations [1-19]. Particularly important are the applications of hypervalent iodine reagents, such as, (diacetoxyiodo)benzene or derivatives of benziodoxole, in oxidative iodination reactions. For example, various aryl iodides can be conveniently prepared by iodination of arenes in the presence of organoiodine(III) or organoiodine(V) oxidants [20-28]. However, despite their importance, the common hypervalent iodine(III) and iodine(V) reagents (*e.g.*, diacetoxyiodobenzene or 2-iodoxybenzoic) have a serious disadvantage with respect to the principles of Green Chemistry since they are normally used as the non-recyclable, stoichiometric reagents.

Recently, we reported the preparation and X-structural study of potassium 4-iodylbenzenesulfonate (PIBS, Fig. **1**) and demonstrated potential utility of this compound as a recyclable reagent for preparation of aryl iodides *via* oxidative iodination of arenes [29].

In the present communication we report the use of PIBS as an efficient and recyclable reagent for iodination of alkenes, alkynes and ketones leading to the corresponding aliphatic iodides. Aliphatic organoiodine compounds are important building blocks in synthetic organic chemistry; however, only a limited number of methods of direct I-Csp^3 bond formation are available. For example, α-iodoketones, are important building blocks in organic synthesis [30]. Previously reported methods for the preparation of α-iodoketones commonly employ oxidative iodination of carbonyl compounds using such inconvenient and environmentally harmful reagents as selenium dioxide [31], mercury(II) chloride [32], or ceric(IV) ammonium nitrate [33]. Therefore, the development of a convenient and environmentally benign procedure for the synthesis of α-iodoketones and other aliphatic iodides is an important goal.

PIBS PIBS-H

Fig. (1). Potassium 4-iodylbenzenesulfonate (PIBS) and its reduced form potassium 4-iodobenzenesulfonate (PIBS-H).

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RESULTS AND DISCUSSION

We have found that PIBS in the presence of I_2 in MeOH is an effective reagent for iodomethoxylation of alkenes and alkynes. These reactions proceed under mild conditions with the ratio of substrate:reagent 3:1 for alkenes and 2:1 for alkynes and afford respective products of iodomethoxylation in high yields (Table **1**). Furthermore, the reduced form of PIBS, potassium 4-iodobenzenesulfonate (PIBS-H, Fig. **1**), can be easily extracted from the reaction mixture using water as a "green" solvent. Pure PIBS can be regenerated in 67% yields by simple treatment of aqueous PIBS-H with Oxone as an environmentally benign oxidant. Hence, in contrast with other hypervalent iodine compounds, recycling of PIBS is a very simple and environmentally friendly procedure. For example, recovery of the previously reported recyclable reagents, 3-iodosylbenzoic acid and 3-(dichloroiodo)benzoic acid, requires the anion exchange resin (IRA 900; hydroxide form) and subsequent steps of regeneration from the polymer surface [34, 35] Recycling of another recyclable reagent, 4,4'-bis(dichloroiodo)biphenyl, involves the use of the environmentally unsafe chlorine as reagent and chlorinated solvents [35, 37].

Our procedure for iodomethoxylation of alkenes allows simple and environmentally sustainable synthesis of important products **3** in high yields (Table **1**). Previously known methods for the preparation of β-iodoethers **3** were based on the reactions of alkenes with non-recyclable reagents: *N*-iodosuccinimide [38-40], dichloroiodoisocyanuric acid [41], triiodoisocyanuric acid [42] *N*-iodosaccharin [43], ICl [44], I_2 [45], *t*-butyl or methyl hypoiodites [46], $I(Py)_2BF_4$ [47], iodide/iodate [48], I_2-H_2O_2 [49], AgOTf [50], Ce (IV) salts [51], thallium salts [52,53], Pb (IV) salts [54], Cu (II) salts [55, 56], and Hg (II) salts [57].

Various alkyl- or aryl substituted and cyclic alkenes were used as substrates for iodomethoxylation (Scheme **1**). In all cases the reaction was complete in 20 min with full conversion of alkene (monitoring by GC-MS). After reaction completion, CH_2Cl_2 and H_2O were added, which resulted in the formation of two layers, with PIBS and PIBS-H dissolved in the aqueous phase. Pure products **3** were isolated from the organic layer after evaporation of solvent, and PIBS was recovered from the reaction mixture by treatment of the aqueous layer with Oxone at 60 °C followed by filtration of the precipitate.

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Table 1. Oxidative iodination of alkenes and alkynes with I_2/PIBS.

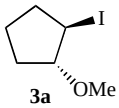
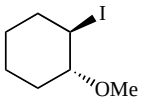
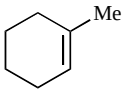
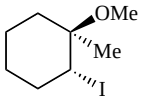
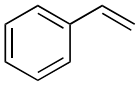
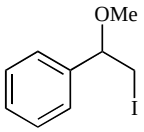
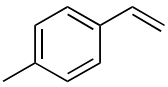
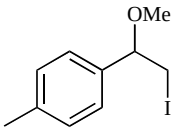
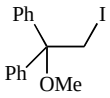
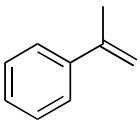
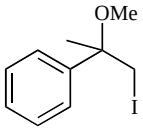
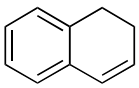
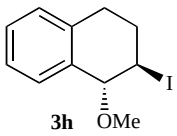
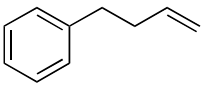
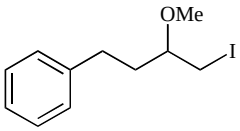
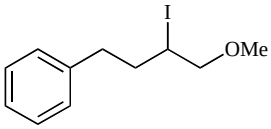
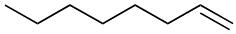
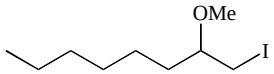
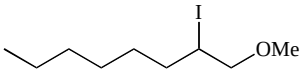
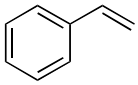
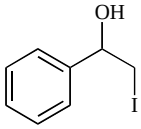
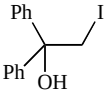
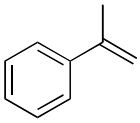
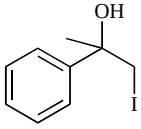
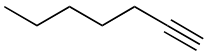
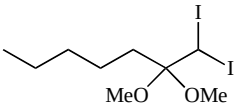
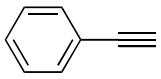
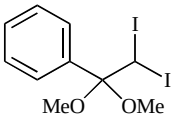
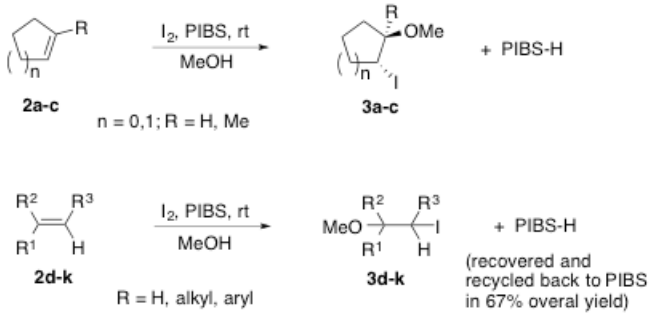
Entry	Starting Material	Products	Time (h)	Yield (%)
1	 **2a**	 **3a**	0.3	72
2	 **2b**	 **3b**	0.3	89
3	 **2c**	 **3c**	0.3	83
4	 **2d**	 **3d**	0.3	94
5	 **2e**	 **3e**	0.3	86
6	 **2f**	 **3f**	0.3	92
7	 **2g**	 **3g**	0.3	85
8	 **2h**	 **3h**	2	78
9	 **2i**	 **3i**  **3i'** (3:1 ratio)	0.25	56

Table 1. contd…

Entry	Starting Material	Products	Time (h)	Yield (%)
10	 **2j**	 **3j**  **3j'** (3:1 ratio)	0.3	92
11	 **2d**	 **4a**	0.5	80
12	 **2f**	 **4b**	0.5	90
13	 **2g**	 **4c**	0.5	85
14	 **5a**	 **6a**	2	64
15	 **5b**	 **6b**	2	74



Scheme 1. Iodomethoxylation of alkenes with PIBS.

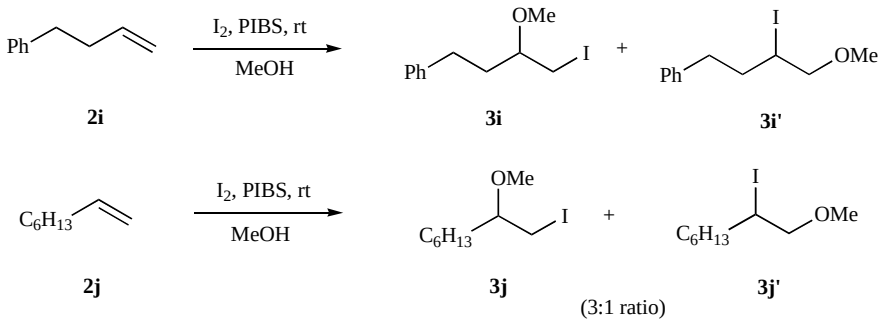
The reaction affords products with the expected *anti*-stereoselectivity *via* intermediate formation of bridged iodonium intermediates. The Markovnikov-type regioselectivity of this addition (Scheme **1**) is explained by the selective attack of a nucleophile (MeOH) on the more substituted carbon of the cyclic iodonium ion. In the initial step of the reaction, iodine is oxidized by PIBS to the respective electrophilic intermediates, I^+ or CH_3OI, followed by their addition to the double bonds.

The iodomethoxylation of cycloalkenes proceeds at room temperature to afford respective products in 80-89% preparative yield. The NMR-pure products were obtained by evaporation of solvent from organic layer and did not require addition purification.

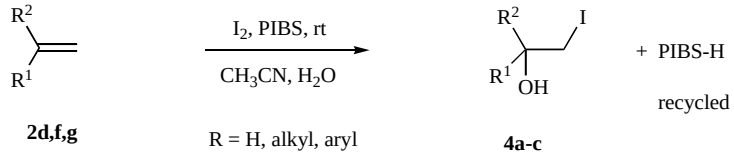
The iodomethoxylation of 4-phenyl-1-butene **2j** and 1-octene **2k** proceeds with a lower regioselectivity and gives an inseparable mixture of Markovnikov and anti-Markovnikov adducts in 3:1 ratio, respectively (Scheme **2**).

When methanol is replaced with water, PIBS reacts with alkenes to form the respective iodohydrins in high yields (Scheme **3**). This reaction proceeds under mild conditions and the desirable products can be easily separated from PIBS-H and unreacted PIBS by standard aqueous work-up.

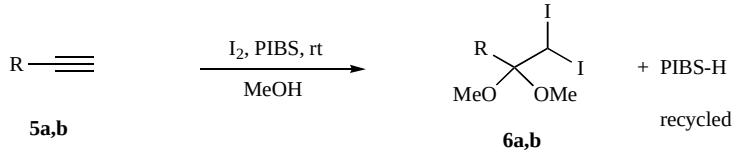
Reactions of PIBS with alkynes **5** lead to α,α-diiodoacetals **6** (Scheme **4**), which are important intermediates in organic synthesis. Thus, phenylacetylene **5b** reacts with equimolar quantities of iodine



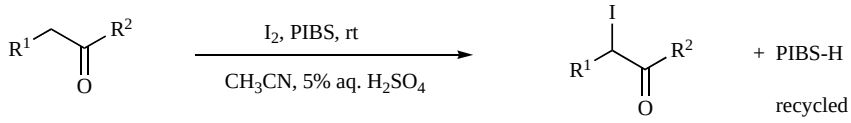
Scheme 2. Iodomethoxylation of 4-phenyl-1-butene **2j** and 1-octene **2k**.



Scheme 3. Iodohydroxylation of alkenes with PIBS.



Scheme 4. Iodomethoxylation of alkynes with PIBS.



Scheme 5. Oxidative iodination of ketones.

and PIBS to give respective diiodoacetal **6b** in 78% yield (Table **1**, entry 16).

The reaction procedure was as following: PIBS was added to the solution of iodine in MeOH in equimolar quantities under stirring at room temperature. In 10-20 min PIBS dissolved and the mixture color has become light yellow. The resulting active species of electrophilic iodine synthesized *in situ* by this procedure were further added to phenylacetylene in minimal volume of MeOH and then the mixture was cooled in darkness to –10 °C (in a freezer) for 2 hours. The precipitated rhombic crystals were filtered, washed by cold methanol, and stored at low temperature no longer than 10 days. Diidoacetal **6a** was extremely unstable under daylight and at room temperature.

Iodoketones are key intermediates in the synthesis of various functional derivatives of carbonyl compounds [30]. At the same time the high sensitivity to light is a substantial drawback of iodoketones. Recently, we have found that *m*-iodosylbenzoic acid and its derivatives are efficient reagents for oxidative iodination of ketones, and the reduced form of these reagents, *m*-iodobenzoic acid, can be easily recovered from the reaction mixture by treatment with anionic exchange resin [49]. With reference to our previous research, we have developed a facile and convenient method for α-iodination of ketones **7a-g** to iodoketones **8a-g** by I_2 and PIBS in acetonitrile at 60 °C for 0.5-1 hour in the presence of catalytic quantities of sulfuric acid (Scheme **5** and Table **2**).

In the case of substrates **7a** and **7b** the final product mixture contained mono- (**8a,b**) and diiodo (**9a,b**) derivatives (Table **2**, entries 1 and 2). At the same time only monoiodo derivatives in high yields (66-67%) were obtained by the iodination of cyclohexanone **7c** and acetophenone **7d** (Table **2**, entries 3 and 4). The final iodoketones **8c,d** rapidly decomposed in the presence of light, so quick isolation is needed.

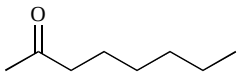
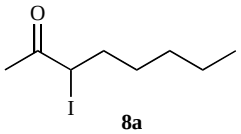
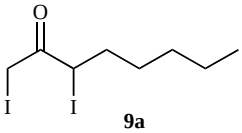
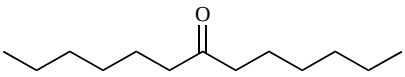
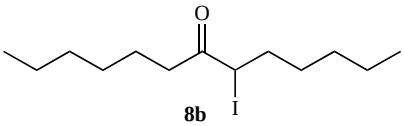
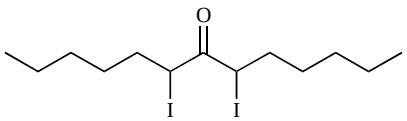
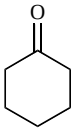
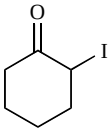
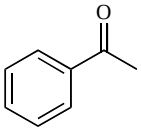
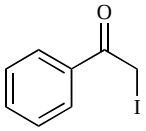
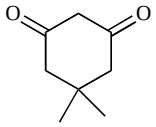
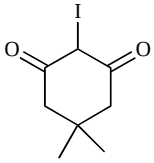
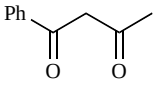
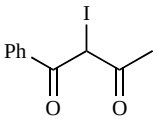
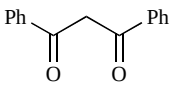
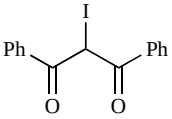
The iodination of 1,3-diketones (**7e-g**) proceeded at room temperature in excellent yield of 83-93%. The reaction of 1-phenyl-1,3-butandione (**7f**) in acetonitrile proceeded non-selectively and affording two products. Only when dichloromethane was used as solvent, we achieved the desired selectivity and monoiodo derivative (**8f**) was obtained in 83% yield.

The advantage of PIBS as an oxidant is due the easiness of product separation using water as a green solvent. The final aqueous-methanol solution of PIBS-H was treated with Oxone to afford PIBS in 67% yield. A minimum quantity of water should be used during oxidation to achieve complete formation of PIBS. The relatively low regeneration of PIBS-H to PIBS is explained by partial solubility of PIBS in water, which results in some product losses during filtration.

EXPERIMENTAL SECTION

General: All commercial reagents were ACS reagent grade and used without further purification. All other reagents and solvents

Table 2. Oxidative iodination of ketones with I_2/PIBS.

Entry	Starting Material	Products	Time (h)	Yield (%)
1	 **7a**	 **8a**  **9a**	1	68
2	 **7b**	 **8b**  **9b**	1	81
3	 **7c**	 **8c**	1	66
4	 **7d**	 **8d**	1	85
	 **7e**	 **8e**	0.5	75
6	 **7f**	 **8f**	0.5	83
7	 **7g**	 **8g**	0.5	93

were of commercial quality from freshly opened containers. All melting points were determined in an open capillary tube with a Mel-temp II® melting point apparatus. NMR spectra were recorded on a Varian UNITY INOVA 500 MHz NMR spectrometer at 500 MHz (^{1}H NMR), 125 MHz (^{13}C NMR); Bruker 300 MHz at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR) and 200 MHz at 200 MHz (^{1}H NMR), 50 MHz (^{13}C NMR); chemical shifts are reported in parts per million (ppm). GC-MS analysis was carried out with a HP 5890A Gas Chromatograph using a 5970 Series mass selective detector. High resolution mass spectra (HRMS) were obtained on a Water LCT Premier spectrometer with micromass MS software using electrospray ionization (ESI). Analytical thin-layer chromatography was performed using precoated silica gel 60 F254 plates (MERCK, Darmstadt) and the spots were visualized with UV light at 254 nm.

Preparation of 4-Iodobenzensulfonic Acid (PIBS-H): Concentrated sulfuric acid (50 mL, 80 g, 0.82 mol) was added to iodobenzene (20 mL, 36.4 g, 0.178 mol) under stirring, and the reaction mixture was heated to 50 °C. The stirring was continued at 50–60 °C for 30 h; the color of the reaction mixture became pink after about 3 h. Then the reaction mixture was stirred with hexane (20 mL) for 5 min in order to remove unreacted iodobenzene; the hexane layer was separated and discarded. The sulfuric acid layer was extracted with small portions of boiling chloroform (total 100 mL) by removing the upper layer (solution of product in $CHCl_3$) with a pipette. The chloroform solution was concentrated to a small volume, and crystals of product were filtered, washed with hexane, and dried in vacuum. Yield of PIBS-H: 48.0 g (95%), m.p. 65–67 °C (ref. [29]: m.p. 66-68 °C). ^{1}H NMR (500 MHz, D_2O): δ 7.89 (dd, J = 8.5, 2.0 Hz, 2H, Ar), 7.52 (dd, J = 8.5, 1.5 Hz, 2H, Ar). Lit. NMR [29]: ^{1}H NMR (500 MHz, D_2O): δ 7.90 (dd, J = 8.5, 2.0 Hz, 2H, Ar),7.52 (dd, J = 8.5, 1.5 Hz, 2H, Ar). ^{13}C NMR (125 MHz, D_2O): δ 97.7 (C4), 127.0 (C2), 138.0 (C3) 142.0 (C1).

Preparation of Potassium 4-Iodylbenzenesulfonate (PIBS): 4-Iodobenzenesulfonic acid (1) (2.840 g, 10 mmol) was added to a solution of Oxone (15.35 g, 25 mmol) in water (10 mL) with stirring at 60 °C. The reaction mixture was left overnight, then cooled to room temperature. After 1 h at rt, the precipitate was filtered and washed two times with water (2x5 mL). The solid was dried in vacuum to give 3.400 g (96%) of PIBS as white powder; m.p. 278–280 °C (recrystallized from water; explodes at m.p.) (ref. [29]: m.p. 278–280 °C). ^{1}H NMR (500 MHz, D_2O): δ 8.13 (m, 2H$_{arom}$), 8.14 (m, 2H$_{arom}$). Lit. NMR [29]: ^{1}H NMR (500 MHz, D_2O): δ 8.14 (m, C_6H_4). ^{13}C NMR (125 MHz, D_2O): δ 127.3 (C2), 127.6 (C3), 147.1 (C1)), 151.9 (C4).

General procedure for iodomethoxylation. Alkene 2 (1.0 mmol) was added to a mixture of iodine (140 mg, 0.55 mmol) and PIBS (106 mg, 0.3 mmol) in MeOH (1.0 mL) and the reaction mixture was stirred at room temperature for 20 min (the reactions were monitored by GC-MS). Then, dichloromethane (3.0 mL) and H_2O (3.0 mL) were added and organic layer was separated. The organic solution was washed with 5% aqueous solution of $Na_2S_2O_3$ (3.0 mL), then with water (5.0 mL), and dried with Na_2SO_4. The solution was concentrated under reduced pressure to afford pure methoxyiodides as judged by NMR-spectroscopy.

The iodohydroxylation was carried out similarly except that MeCN–H_2O (5:1, 0.5 mL) was employed as solvent instead of MeOH and the molar ratio alkene:PIBS:iodine was 1.0:0.3:0.55.

1-Iodo-2-methoxycyclopentane (**3a**) [55]. oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (m, 1H), 1.81 (m, 2H), 2.06 (m, 2H), 2.23 (m, 1H), 3.36 (s, OCH_3), 4.09 (m, 1H), 4.26 (m, 1H). Lit. NMR [58] for (-)-2-Iodocyclopentanol (**1S,2R**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.61–1.54 (m, 1H), 1.84–1.78 (m, 2H), 2.15–2.01 (m, 2H), 2.39–2.32 (m, 1H), 4.05–4.01 (m, 1H), 4.45–4.42 (m, 1H). ^{13}C NMR could not be obtained for **3a** due to fast decomposition of the sample on storage.

***trans*-1-Iodo-2-methoxycyclohexane** (**3b**) [36]. oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (m, 2H), 1.59 (m, 2H), 1.81 (m, 1H), 1.95 (m, 1H), 2.18 (m, 1H), 2.41 (m, 1H), 3.25 (ddd, 1H, J = 8.2, 8.2, 4.0 Hz), 3.41 (s, OCH_3), 4.06 (ddd, 1H, J = 9.8, 8.1, 4.2). Lit. [36] ^{1}H NMR (200 MHz, CCl_4-$CDCl_3$–3 : 1, TMS): δ 3.16 (ddd, 1H, J = 8.2, 8.2, 4.0 Hz), 3.31 (s, OCH_3), 3.99 (ddd, 1H, J = 9.8, 8.1, 4.2 Hz). ^{13}C NMR (50 MHz, CCl_4 - $CDCl_3$ – 3:1, TMS) δ, 23.1 (C5), 26.4 (C4), 29.6 (C6), 34.2 (C1), 36.8 (C3), 56.6 (OCH_3), 83.3 (C2). MS (EI) *m/z* (%) 240 (<1), 127 (6), 113 (100), 82 (100).

2-iodo-1-methoxy-1-methylcyclohexane (**3c**) [36]. oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (s, 3H, CH_3), 1.59 (m, 2H), 1.63 (m, 2H), 1.70 (m, 1H), 1.98 (m, 2H), 2.32 (m, 1H), 3.23 (s, OCH_3), 4.37 (dd, 1H, J = 9.9, 4.8). Lit. NMR [36]: ^{1}H NMR (200 MHz, CCl_4-$CDCl_3$–3 : 1, TMS): δ 1.27 (s, CH_3), 3.15 (s, OCH_3), 4.29 (dd, 1H, J = 8.2, 4.0). ^{13}C NMR (50 MHz, CCl_4-$CDCl_3$ – 3 : 1, TMS): δ 21.0 (C4), 23.4 (C5), 25.6 (CH_3), 32.5 (C3), 35.3 (C6), 41.4 (C1), 48.6 (OCH_3), 75.3 (C2). MS (EI) *m/z* (%) 254 (1), 127 (31), 97 (34), 95 (37), 85 (54), 71 (63), 57 (100), 43 (85). HRMS: Calcd. for $C_8H_{15}IO$: 254.01694; Found: 254.01840.

2-odo-1-methoxy-1-phenylethane (**3d**) [44]. yield 96% as oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.26 (m, 2H, CH_2), 3.34 (s, 3H, OCH_3), 4.30 (dd, 1H, J= 5.4, 7.5 Hz), 7.26 (m, 5H$_{arom}$). Lit. NMR [36]: ^{1}H NMR (400 MHz, CCl_4-$(CD_3)_2CO$- 3 : 1, TMS): δ 3.21 (s, 3H, OCH_3), 3.23 (m, 2H, CH_2), 4.21 (dd, 1H, J = 5.0, 8.0 Hz), 7.26–7.34 (m, 5H$_{arom}$). ^{13}C NMR (125 MHz, CCl_4-$(CD_3)_2CO$ - 3:1) δ 10.1 (C1), 56.9 (OCH_3), 83.6 (C2), 126.5 (C2$^{/}$), 128.2 (C4$^{/}$), 128.5 (C3$^{/}$), 140.0 (C1$^{/}$). MS (EI) *m/z* (%) 262 (<1), 135 (14), 121 (100), 104 (10), 103 (9), 91 (10), 77(13); $[M]^+$ found = 261.98537, $C_9H_{11}IO$ requires 261.98564.

2-Iodo-1-methoxy-1-(4-methylphenyl)ethane (3e) [48]. yield 86% as oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.30 (s, 3H, OCH_3), 3.35 (m, 2H, CH_2), 4.28 (dd, 1H, J= 4.8, 7.5 Hz), 7.20 (m, 4H$_{arom}$). Lit NMR [60]: for 2-Iodo-1-(4-methylphenyl) ethanol: ^{1}H NMR ($CDCl_3$-TMS): δ 2.31 (s, 3H, CH_3), 2.67 (br s, 1H), 3.32– 3.38 (t, 2H, t, J = 4.4), 4.69 –4.75 (1H, q, J ¼ 4.4), 7.09–7.23 (4H, m, J ¼ 7.2). MS (EI) *m/z* (%) 262 (<1), 135 (14), 121 (100), 104 (10), 103 (9), 91 (10), 77(13). ^{13}C NMR could not be obtained for 3e due to fast decomposition of the sample on storage.

2-Iodo-1-methoxy-1,1-diphenylethane (**3f)** [36]. m.p. 85–86 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.12 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2), 7.19 (t, 2H$_{arom}$) 7.24 (t, 4H$_{arom}$), 7.37 (d, 4H$_{arom}$).). Lit. NMR [36]: ^{1}H NMR (500 MHz, CCl_4-$CDCl_3$ – 3 : 1, TMS): δ 3.12 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2), 7.21 (t, 2H$_{arom}$) 7.27(t, 4H$_{arom}$), 7.34 (d, 4H$_{arom}$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.39 (C1), 50.0 (OCH_3), 80.5 (C2), 127.1 (C4$^{/}$), 127.3(C2$^{/}$), 128.0 (C3$^{/}$), 142.9 (C1$^{/}$). HRMS (*m/z*): Calcd. for $C_{15}H_{15}IO$: 338.01694. Found: 338.01713.

1-Iodo-2-methoxy-2-phenylpropane (**3g**) [34]. oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64 (s, 3H, CH_3), 3.07 (s, 3H, OCH_3), 3.37 (d, 1Ha, J =10.8 Hz), 3.44 (d, 1H$_b$, J = 10.8 Hz), 7.22-7.35 (m, 5H$_{arom}$). Lit. NMR [36]: ^{1}H NMR (500 MHz, CCl_4-$CDCl_3$ – 3 : 1, TMS): δ 1.69 (s, 3H, CH_3), 3.11 (s, 3H, OCH_3), 3.37 (d, 1H$_a$, J . 10.0), 3.46 (d, 1H$_b$, J = 10.0 Hz), 7.25 (t, 1H$_{arom}$) 7.32(t, 2H$_{arom}$), 7.37 (d, 2H$_{arom}$). ^{13}C NMR (125 MHz, CCl_4-$CDCl_3$ – 3 : 1, TMS) δ 19.6 (C1), 23.9 (C3), 51.1 (OCH_3), 76.9 (C2), 126.3 (C4$^{/}$), 127.7 (C2$^{/}$), 128.4 (C3$^{/}$), 141.5 (C1$^{/}$). MS (EI) *m/z* (%) 276 (<1), 261 (<1), 149 (14), 148 (49), 135 (75), 118 (74), 105 (57), 91 (63), 77 (58). HRMS (m/z): Calcd. for $C_{10}H_{13}IO$: 276.00129. Found: 276.00142.

2-Iodo-1-methoxy-1,2,3,4-tetrahydronaphthalene (**3h**) [58]. Oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.26 (m, 1H), 2.32 (m, 1H), 2.80-3.03 (m, 2H), 3.50 (s, 3H, OCH_3), 4.57 (d, 1H, J =3.3 Hz), 4.78 (m, 1H), 7.14-7.30 (m, 5H$_{arom}$). Lit. NMR [61]: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.27 (m, 1H), 2.32 (m, 1H), 2.82 (m, 1H),

2.97 (m, 1H), 3.50 (s, 3H, OCH_3), 4.58 (d, 1H, *J* =3.6 Hz), 4.74 (m, 1H), 7.14-7.30 (m, $5H_{arom}$). ^{13}C NMR could not be obtained for **3i** due to fast decomposition of the sample on storage.

1-iodo-2-methoxy-4-phenylbutan (**3i**) [35]. oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.83 (m, 2H, C^3H_2), 2.62 (m, 2H, C^4H_2), 2.94 (m, 1H, $C^2\underline{H}$), 3.20 (m, 2H, C^1H_2), 3.27 (s, 3H, OCH_3), 7.12 - 7.25(m, $5H_{arom}$). Lit. NMR [35]: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.87 (m, 2 H, C^3H_2), 2.63 (m, 2 H, C^4H_2), 2.95 (m, 1 H, C^2H), 3.21 (m, 2 H, C^1H_2), 3.32 (s, 3 H, OCH_3), 7.12–7.25(m, 5 H_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.0 (C1), 31.2 (C4), 36.3 (C3), 56.9 (OCH_3), 78.5 (C2), 125.8 ($C4^/$), 126.1 ($C2^/$); 128.3 ($C3^/$), 142.1 ($C1^/$). Calcd. for $C_{11}H_{15}IO$: C, 45.54%; H, 5.21%; I, 43.74; Found: C 45.35%, H 5.34%, I 43.47%. MS (EI) *m/z* (%) 290 (<1), 185 (19), 163 (18), 131 (100), 117 (10), 105 (8), 91 (69), 77 (6), 58 (8).

2-iodo-1-methoxy-4-phenylbutan (**3i'**): Oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.89 (m, 2H, C^3H_2), 2.93 (m, 2H, C^4H_2), 3.29 (s, 3H, OCH_3), 3.32 (m, 1H, $C^2\underline{H}$), 4.04 (m, 2H, C^1H_2), 7.12 - 7.25(m, $5H_{arom}$). Lit. NMR [35]: ^1H NMR (300 MHz, $CDCl_3$): δ = 2.05 (m, 2 H, C^3H_2), 2.81 (m, 2 H, C^4H_2), 3.29 (s, 3 H, OCH_3), 3.58 (m, 2 H, C^2H), 4.05 (m, 1 H, C^1H), 7.12–7.25(m, 5 H_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 33.1 (C1), 35.1 (C4), 37.9 (C3), 58.5 (OCH_3), 78.1 (C1), 125.8 ($C4^/$); 126.1 ($C2^/$), 128.4 ($C3^/$), 142.1 ($C1^/$). Calcd. for $C_{11}H_{15}IO$: C, 45.54%; H, 5.21%; I, 43.74; Found: C 45.35%, H 5.34%, I 43.47%. MS (EI) *m/z* (%) 290 (6), 131 (100), 115 (5), 105 (6), 91 (44), 77 (3), 65 (8), 45 (11).

1-iodo-2-methoxyoctane (**3j**) [36]. Oil. ^1H NMR (500 MHz, CCl_4-$CDCl_3$ – 3:1, TMS): δ 0.84 (m, 3H, C^8H_3), 1.24 (m, 8H, $C^{4-7}H_2$), 1.50 (m, 2H, C^3H_2), 2.95 (m, 1H, C^1H), 3.16 (s, 3H, OCH_3), 3.29 (m, 2H, C^2H_2). Lit. NMR [62]: ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 0.70-1.03 (m, 3H, C^8H_3), 1.09-1.52 (m, 10H, $C^{3-7}H_2$), 3.0 (m, 1H, C^1H), 3.29 (d, 2H, C^2H, J = 4.0 Hz), 3.41 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.9 (C1), 14.0 (C8), 22.5 (C7), 25.0 (C4), 29.1 (C5), 31.6 (C6), 34.1 (C3), 56.8 (OCH_3), 79.8 (C2). MS (EI) *m/z* (%) 270 (<1), 239 (1), 185 (85), 129 (100), 127 (<1), 97 (33), 69 (17), 55 (42), 43 (26), 41 (23). HRMS (m/z): Calcd. for $C_9H_{19}IO$. 254.04824; Found: 270.04820.

2-iodo-1-methoxyoctane (**3j'**) [36]. Oil. ^1H NMR (500 MHz CCl_4-$CDCl_3$ – 3:1, TMS): δ 0.76 (m, 3H, C^8H_3), 1.30 (m, 8H, $C^{4-7}H_2$), 1.50 (m, 2H, C^3H_2), 2.48 (m, 1H, C^1H), 3.30 (s, 3H, OCH_3), 3.59 (m, 1H, C^2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ, м.д.): 14.1 (C8), 22.6 (C7), 25.0 (C4), 29.3 (C5), 31.8 (C6), 33.1 (C2), 36.2 (C3), 58.3 (OCH_3), 78.1 (C1). MS (EI) *m/z* (%) 270 (<1), 239 (1), 143 (21), 111 (19), 69 (100), 55 (42), 45 (48). HRMS (m/z): Calcd. for $C_9H_{19}IO$: 254.04824; Found: 270.04820.

2-Iodo-1-phenylethanol (4a) [36]. Oil. ^1H NMR (300 MHz, $CDCl_3$): δ 2.61 (s, 1H, OH), 3.40-3.52 (m, 2H), 4.83 (d, 1H, *J* = 7.8 Hz), 7.35 (m, $5H_{arom}$). Lit. NMR [36]: ^1H NMR (200 MHz, CCl_4-$CDCl_3$– 3 : 1, TMS): δ 3.31 (s, 1H, OH), 3.37 (m, 2H, H-2), 4.73 (dd, 1H, *J* = 4.1, 8.2 Hz), 7.30 (s, $5H_{arom}$) ^{13}C NMR (50 MHz, CCl_4-$CDCl_3$ – 3 : 1): δ 14.6 (C1), 73.7 (C2), 125.6 ($C2^/$), 128.07 ($C4^/$), 128.3 ($C4^/$), 141.2 ($C1^/$).

2-Iodo-1,1-diphenylethanol (**4b**) [36]. Oil. ^1H NMR (300 MHz,$(CD_3)_2CO$): δ 4.16 (s, 2H, CH_2-OH), 5.44 (s, 1H, OH), 7.32 (m, $2H_{arom}$) 7.39 (m, $4H_{arom}$), 7.52 (d, $4H_{arom}$). Lit. NMR [36]: ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 4.18 (s, 2H, CH_2-OH), 5.47 (s, 1H, OH), 7.33 (m, $2H_{arom}$) 7.39 (m, $4H_{arom}$), 7.54 (d, $4H_{arom}$). ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ 21.90 (C1), 114.67 (C2), 127.1 ($C4^/$), 128.9 ($C2^/$), 129.2 ($C3^/$) , 146.1 ($C1^/$).

1-Iodo-2-phenylpropan-2-ol (**4c**) [36]. Oil. ^1H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ 1.70 (s, 3H, CH_3), 2.94 (s, 1H, OH), 3.64 (d, $1H_a$, *J* = 12.5 Hz), 3.67 (d, $1H_b$, *J* = 12.5 Hz), 7.33 (m, $1H_{arom}$) 7.53 (m, $2H_{arom}$), 7.57 (d, $2H_{arom}$). Lit. NMR [36]: ^1H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ 1.70 (s, 3H, CH_3), 2.96 (s, 1H, OH), 3.63 (d, $1H_a$, *J* = 12.5 Hz), 3.67 (d, $1H_b$, *J* = 12.5 Hz), 7.33 (m, $1H_{arom}$) 7.54 (m, $2H_{arom}$), 7.56 (d, $2H_{arom}$). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS): δ 23.86 (C1), 29.40 (C3), 72.79 (C2), 126.0 ($C4^/$), 127.7 ($C2^/$), 128.8 ($C3^/$), 146.2 ($C1^/$).

1,1-Diiodo-2,2-dimethoxyhexane (**6a**) [34]. Oil. ^1H NMR (500 MHz, $CDCl_3$) : δ 0.96 (t, 3H, CH_3), 1.39 (m, 4H, CH_2), 2.05 (t, 2H, CH_2), 3.36 (s, 6H, CH_3O) 5.42 (s, 1H, CI_2H); Lit. NMR [34]: ^1H NMR (500 MHz, $CDCl_3$) : δ 0.96 (t, 3H, CH_3), 1.33–1.46 (m, 4H, CH_2), 2.05 (t, 2H, CH_2), 3.34 (s, 6H, CH_3O) 5.41 (s, 1H, CI_2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -15.3 ($C1_2$), 12.1 (C6), 21.7 (C4), 26.5 (C5), 33.8 (C3), 50.5 (OCH_3), 99.0 (C2).

1,1-Diiodo-2,2-dimethoxyethyl-2-phenylethane (6b) [34]. colorless solid: mp 84–86 °C (decomp.); ^1H NMR (300 MHz, $CDCl_3$): δ 3,35 (s, 6H, OCH_3), 5.59 (s, 1H), 7.38 (m, $3H_{arom}$), 7.69 (m, $2H_{arom}$); Lit NMR [34]: ^1H NMR (300 MHz, $CDCl_3$): δ 3,45 (s, 6H, OCH_3), 5.87 (s, 1H), 7.38-7.41 (m, $3H_{arom}$), 7.69 (m, $2H_{arom}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ -19.5 (C1), 49.3 (OCH_3), 97.8 (C2), 125.7 ($C2^/$), 127.5 ($C4^/$), 128.1 ($C3^/$), 133.8 ($C1^/$).

General Procedure for Oxidative Iodination of Ketones 7a–b

A ketone (1.0 mmol) and MeCN (2 mL) were placed in a light-protected flask and then H_2SO_4 (5%, 0.5 mL), I_2 (0.14 g, 0.55 mmol), and PIBS (0.106 g, 0.3 mmol) were added with stirring. The mixture was stirred at 60 °C for 1 h (the reactions were monitored by GC-MS and by TLC hexane-ethylacetate 5:1). Then the mixture was cooled to 0 °C and CH_2Cl_2 (3.0 mL) and H_2O (3.0 mL) were added and organic layer was separated. The organic solution was washed with 5% aqueous solution of $Na_2S_2O_3$ (3.0 mL), then with water (5.0 mL), and dried with Na_2SO_4. The solution was concentrated under reduced pressure to afford the NMR-pure product **8**.

Iodoacetophenone 8d [62]. m.p. 32-34°C (0.209 g, 85%) ^1H NMR (300 MHz, $CDCl_3$): δ 4.36 (c, 2H, CH_2I), 7.54 (d, $2H_{arom}$, *J* = 7.2 Hz), 7.62 (m, $1H_{аром}$), 8.0 (d, $2H_{аром}$, *J* = 7.2 Hz). Lit NMR [63]: ^1H NMR (300 MHz, $CDCl_3$): δ 1H NMR (300 MHz, $CDCl_3$): δ = 4.31 (s, 2H), 7.43-7.59 (m, 3H), 7.91-8.0 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 1.7 (C2), 128.7 ($C3^/$), 130.0 ($C2^/$), 133.2 ($C4^/$), 134.0 ($C1^/$), 192.8 (C1).

3-Iodooctan-2-one (8a) and 1,3-diiodooctan-2-one (9a) 1.2:1 [63]. Oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88-0.90 (m, 6H, CH_3), 1.29-1.41 (m, 18H, CH_2), 1.90-1.98 (m, 4H, CI-C$\underline{H}_2$), 2.40 (s, 3H, CH_3-CO), 3.83 (d, 2H, IC$\underline{H}_a$, *J* = 9.6 Hz), 4.35 (d, 2H, IC$\underline{H}_b$, *J* = 9.6 Hz), 4.44 (t, –CHI-C(O)–), *J* = 7.5 Hz), 4.94 (t, *J* = 7.5 Hz, 1H, –CHI-C(O)–). Lit. NMR [62]: for **3**-iodooctan-2-one**:** ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.23-1.35 (m, 4H), 1.58-1.71 (m, 2H), 1.89 (d, 3H, *J* = 7.5 Hz), 2.54-2.67 (m, 1H), 2.80-2.94 (m, 1H), 4.62 (q, 1H, *J* = 6.8 Hz); for 1,3-diiodooctan-2-one: ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84-0.93 (m, 3H), 1.27-1.38 (m, 6H), 1.92-2.07 (m, 2H), 3.85 (d, 1H, *J* = 9.8 Hz), 4.36 (d, 1H, *J* = 9.8 Hz), 4.95 (t, 1H, *J* = 7.5 Hz).

6-Iodotridecan-7-one (8b) and 6,8-diiodotridecan-7-one (9b) 10:1 [63]. White, less stable solid. ^1H NMR (300 MHz, $CDCl_3$): δ 0.89-0.90 (m, 6H, CH_3), 1.29-1.42 (m, 14H, CH_2), 1.57-1.65 (m, 2H, CH_2), 1.88-1.96 (m, 2H, CH_2), 2.57-2.67 (m, 1H, CH_a), 2.73-2.84 (m, 1H, CH_b), 4.44 (t, *J* = 7.5 Hz, –CHI-C(O)–)), 4.97 (t, *J* = 7.5 Hz, 1H, –CHI-C(O)–). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9 (C1, C13 for **9a** and **9b**), 22.2 (C2 for **9a**, C2,C12 for **9b**), 22.3 (C9 for **9a**), 24.1 (C12 for **9a**), 28.7 (C4 for **9a** and **9b**), 29.0 (C10 for **9a** and **9b**), 30.1 (C6 for **9b**), 31.0 (C3 for **9a** and **9b**), 31.5 (C11 for **9a**), 32.9 (C6 for **9a**), 34.0 (C5 for **9a**), 34.2 (C5, C8 for **9b**), 38.9 (C8 for **9a**), 196.8 (C7 for **9b**), 205.4 (C7 for **9a**).

2-Iodocyclohexanone (8c) [63]. Oil. ^1H NMR (500 MHz, $CDCl_3$): δ 1.56-1.75 (m, 2 H, CH_2), 1.96-2.14 (m, 4 H, 2 CH_2), 2.34 (m, 2 H, CH_2), 4.65 (m, 1 H, CHI). Lit NMR [64]: ^1H NMR (500 MHz, $CDCl_3$): δ 1.58–1.77 (m, 2H, CH_2), 1.98–2.17 (m, 4H, CH_2), 2.35 (m, 2H, CH_2), 4.68 (m, 1H, CHI).

2-Iodo-5,5-dimethylcylohexane-1,3-dione (8e). m.p. 162-165 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.04 (s, 6H, CH_3), 1.10

(s, 3H, CH_3, enol form), 1.12 (s, 3H, CH_3, enol form), 2.53 (s, 4H), 3.33 (s, 1H). Lit NMR [65]: (400 MHz, $CDCl_3$): δ 0.85 (s, 3H, ax.CH_3), 1.19 (s, 3H, eq.CH_3), 2.38 (dd, 2H, *J* = 1.4, 14.6Hz), 3.38 (d, 2H, *J* = 14.6 Hz), 4.75 (t, 1H, *J* = 1.8 Hz).

2-Iodo-1-phenylbutane-1,3-dione (8f) [65]. Light-sensitive unstable solid. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 2.56 (s, 3H, CH_3), 2.60 (s, 3 H, CH_3, enol form), 5.95 (s, 1H, CHI), 7.49 (m, 2 H_{arom}), 7.63 (t, *J* = 7.5 Hz, 1 H_{arom}), 7.97 (d, *J* = 7.5 Hz, 2 H_{arom}). Lit. NMR [66]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H, CH_3), 5.98 (s, 1H), 7.47 (t, 2H, *J* = 8 Hz), 7.61 (t, 1H, *J* = 8 Hz), 7.96 (d, J = 8 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.6 (CH_3), 129.2 (C3′), 129.3 (C2′), 133.6 (C4′), 135.2 (C1′), 198.9 (C=O).

2-Iodo-1,3-diphenylpropane-1,3-dione (8g) [65]. m.p. 104-106 °C (lit. 105-106 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.94 (s, 1H, CHI), 7.47 (t, 4H_{arom}, *J* = 8.0 Hz), 7.59 (t, 2H_{arom}, *J* = 7.0Hz,), 7.99 (m, 4H_{arom}). Lit. NMR [66]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (s, 1H), 7.46 (t, 4H, *J* = 8 Hz), 7.59 (t, 2H, *J* = 7 Hz), 7.98 (m, 4 H).

CONCLUSION

In conclusion, potassium 4-iodylbenzenesulfonate (PIBS) is a convenient, recyclable hypervalent iodine oxidant particularly useful as a reagent for oxidative iodination of alkenes, alkynes and ketones. This reagent can be effectively recovered from the reaction mixture by treatment of the aqueous layer with Oxone at 60 °C followed by filtration of the precipitate.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's web site along with the published article.

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