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2-Iodoxybenzoic Acid Tosylates: the Alternative to Dess-Martin Periodinane Oxidizing Reagents

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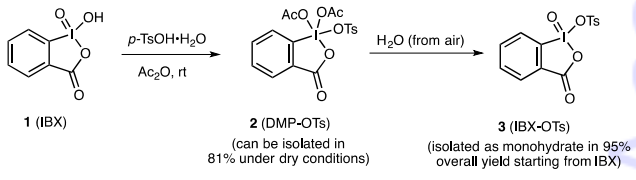
Abstract. Two powerful hypervalent iodine(V) oxidants, DMP-OTs (1-tosyloxy-1,1-diacetoxy-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one) and IBX-OTs (1-tosyloxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one) show high reactivity in the oxidation of structurally complex primary and secondary alcohols, which are highly functionalized polyketide or terpene fragments or steroids. The yields of the corresponding carbonyl compounds are even higher for protocol that uses pyridine as additive. The oxidations proceed very fast at room temperature leaving the protective groups and π-systems intact and affording the corresponding carbonyl compounds in good to excellent yields. Moreover, IBX-OTs is an efficient reagent for the oxidative dehydrogenation of steroidal alcohols to the corresponding enones.

Keywords: Iodine; Oxidation; Alcohols; Synthetic methods; Terpenoids

Introduction

Oxidizing reagents are essential constituents of synthetic organic methodology.[1] Selective oxidation of a hydroxyl group to carbonyl often represents a key step in total synthesis of complex natural products. Hypervalent iodine compounds have emerged as versatile and environmentally benign oxidizing reagents.[2] Particularly useful hypervalent iodine oxidants are 2-iodoxybenzoic acid (IBX) and the product of its acetylation Dess-Martin periodinane (DMP), which are now employed extensively in organic synthesis as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds as well as for a variety of other synthetically useful oxidative transformations.[3] IBX and DMP are mild oxidants with a relatively low reactivity towards some substrates. In particular, oxidations of primary alcohols with these reagents often require elevated temperatures or extended periods of time, which is undesirable in the reactions with sensitive substrates. There is a clear need in the development of more powerful but still selective oxidizing reagents.

Recently, we have reported the preparation and structural study of new tosylate derivatives of IBX, namely, the tosylate derivative of DMP (DMP-OTs, **2**) and the tosylate derivative of IBX (IBX-OTs, **3**).[4] These compounds are prepared by simple treatment of IBX (**1**) with TsOH•H_2O in acetic anhydride at room temperature (Scheme 1).



Scheme 1. Preparation of tosylate derivatives of IBX.

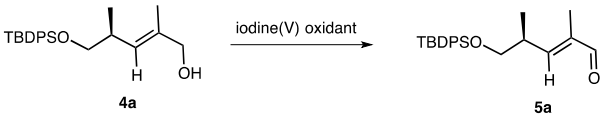
Preliminary studies[4] have shown that tosylate **3** has a higher reactivity toward alcohols compared with IBX or DMP. In particular, we have found that the oxidation of simple primary alcohols (1-octanol and substituted benzyl alcohols) with 1 equiv of IBX-OTs **3** in general is complete within 3-10 min at room temperature with a quantitative conversion to the respective carbonyl compounds.[4] We explain the

enhanced reactivity of compound **3** compared to the DMP or IBX by the electron-withdrawing properties of the tosylate substituent and consequently the higher electrophilicity of the central iodine atom. In the present paper, we have investigated the applicability of the tosylate derivatives of IBX to the oxidation of structurally complex alcohols, some of which serve as key intermediates in total syntheses of terpenes and polyketide antibiotics.[5-8]

Results and Discussion

We have initially investigated the oxidation of known allylic alcohol **4a**[5] as a model substrate for optimizing the reaction conditions that are applicable in natural product synthesis (Table 1).

Table 1. Optimization and comparison studies for iodine(V)-promoted oxidations of (*S*,*E*)-5-((tert-butyldiphenylsilyl)oxy)-2,4-dimethylpent-2-en-1-ol 4a.[a]



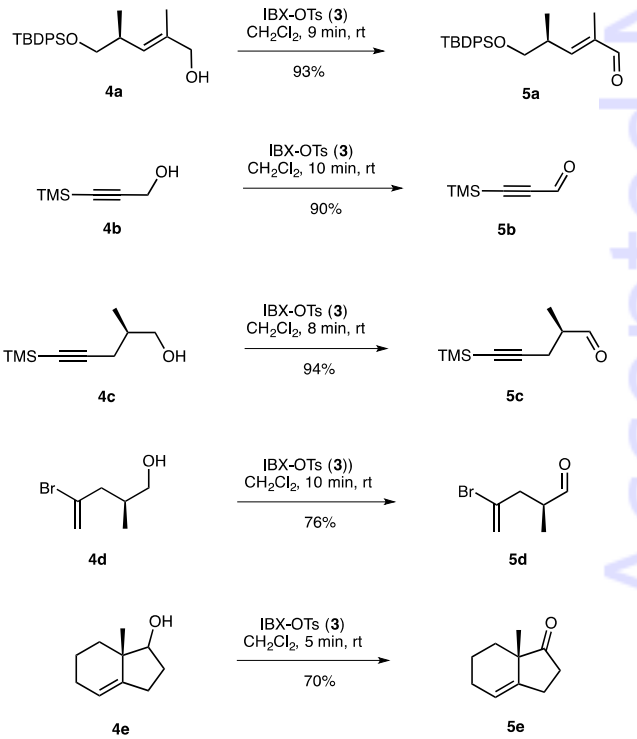
4a **5a**

Entry	Conditions	Ratio reagent/ substrate	Solvent	Conversion (%)[b]
1	**3**, rt, 3 min	1.06	CH_2Cl_2	96
2	**3**, rt, 3 min	1.06	CH_3CN	94
3	**3**, rt, 3 min	1.06	DMSO	72
4	**3**, rt, 3 min	1.06	EtOAc	32
5	**3**, pyridine, rt, 3 min	1.06	CH_2Cl_2	96
6	**2**, rt, 3 min	1.1	CH_2Cl_2	100
7	**2**, pyridine, rt, 3 min	1.1	CH_2Cl_2	100
8	DMP, rt, 3 min	1.1	CH_2Cl_2	63
9	DMP, rt, 3 min	1.1	CH_3CN	64
10	IBX, rt, 10 min	1.1	CH_2Cl_2	0
11	$PhI(OAc)_2$-TEMPO, rt, 10 min	1.2	CH_2Cl_2	6

[a] For detailed procedures, see Experimental Section. [b] Determined by ^1H NMR spectroscopy.

A stoichiometric amount of IBX-OTs **3** was able to almost quantitatively transform alcohol **4a** into aldehyde **5a**[5] at room temperature within 3 minutes. Consequently, we carried out a series of oxidations in different solvents or with other hypervalent iodine reagents and terminated the reaction after three minutes by adding aqueous solutions of $NaHSO_3$ and $NaHCO_3$ and diethyl ether to the reaction mixture. Only in the case of the reagent systems IBX (**1**) and (diacetoxyiodo)benzene (DIB)/TEMPO the reaction was terminated after 10 minutes as no transformation could be detected by TLC after three minutes (entries 10 and 11). The new iodine(V) reagents **2** and **3** turned out to be very powerful oxidants in dichloromethane and in selected cases also in acetonitrile. Pyridine can be used as an additive (entries 5 and 7). Both reagents demonstrate superior oxidation properties compared to DMP, the most prominent oxidant in natural product synthesis (entries 8 and 9). IBX (**1**) itself as well as the common reagent system DIB/TEMPO[9] are inefficient under the conditions employed (entries 10 and 11). Likewise, a physical mixture of IBX and $TsOH•H_2O$ is inactive due to insolubility of both components in dichloromethane. A physical mixture of DMP with $TsOH•H_2O$ has low stability and inconsistent reactivity.

Next, we extended the scope of the oxidation property of IBX-OTs monohydrate **3** to several structurally complex alcohols **4a-e** (Scheme 2). These alcohols contain an olefinic double bond or an alkyne moiety. While alcohols **4a** and **4b**[6] yield aldehydes that are conjugated with a π-system, the oxidation of alcohols **4c** and **4d** yields aldehydes **5c** and **5d** that contain an isolated π-system,[6] in case of **5d** bearing a vinyl bromide. Finally, a secondary alcohol **4e**[10] was also included into this series of oxidations. The oxidations proceeded extremely rapidly and within 10 minutes the transformation went to completion leaving the π-systems intact and isolated yields were generally good to excellent.



Scheme 2. Oxidation of alcohols **4a-4e** using IBX-OTs **3** (isolated yields are shown).

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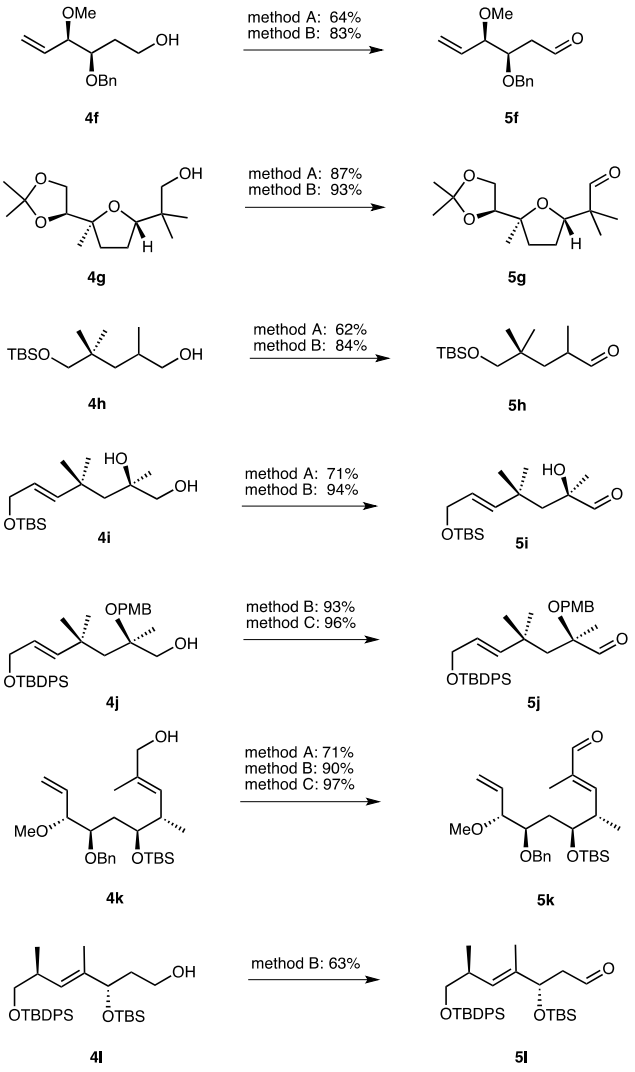
In a second series of oxidations we extended the reactions to other natural product fragments testing different methods (Scheme 3).

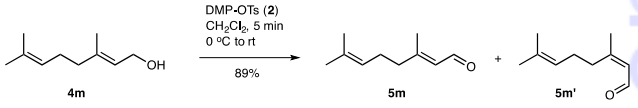


Method A: **3** was added to a mixture of **4** and pyridine in CH_2Cl_2, rt, 0.2-12 h
Method B: **3** was mixed with pyridine in CH_2Cl_2, evaporated, and then **4** in CH_2Cl_2 was added, rt, 0.5 h
Method C: **2** was mixed with pyridine in CH_2Cl_2, evaporated, and then **4** in CH_2Cl_2 was added, rt, 0.5 h

Scheme 3. Oxidation of alcohols **4f-4l** using IBX-OTs/pyridine or DMP-OTs/pyridine (isolated yields are shown).

In the initial experiments (Table 1), we have shown that both IBX-OTs **3** and DMP-OTs **2** demonstrate strong oxidative reactivity towards alcohols. During the optimizations we observed that their high reactivity is not affected when a base like pyridine is added in stoichiometric amount.[11] Mildly basic conditions can be important in oxidations of acid sensitive natural products and advanced synthetic intermediates, and therefore we decided to further explore the reactivity of structurally complex alcohols **4f-l**. In these studies, we selected compounds **4f-l**, advanced synthetic intermediates in the total synthesis of the two polyketides ansamitocin[5] (alcohols **4k** and **4l**) and the elansolids[7] (alcohols **4h-4j**) as well as diterpene tonantzitlolone[6] (alcohol **4g**) using three following procedures. Method A: IBX-OTs **3** was added to a mixture of **4** and pyridine in CH_2Cl_2 at room temperature. Method B: IBX-OTs **3** was mixed with pyridine in CH_2Cl_2 and evaporated to give an oily complex, which was then mixed with alcohol **4** in CH_2Cl_2. Method C: DMP-OTs **2** was mixed with pyridine in CH_2Cl_2 and evaporated to give an oily complex,[11b] which was then mixed with alcohol **4** in CH_2Cl_2. All these oxidations proceeded quickly at room temperature affording the corresponding oxidation products in good to excellent yields. In general, the yields were higher for protocols that use preformed complexes IBX-OTs/Py or DMP-OTs/Py (methods B and C). Compared to IBX-OTs **3**, DMP-OTs **2** affords the oxidation products in slightly higher yields; however, IBX-OTs is a practically more convenient reagent because of its higher stability to moisture.

Substrates **4a-l** represent the very expensive and difficult to obtain synthons available only in submillimolar quantities. In order to test the applicability of reagents **2** and **3** on a larger scale, we performed oxidation of a common natural alcohol, geraniol **5m**, in a millimolar quantity. We have found that the reaction of geraniol with IBX-OTs **3** was excessively exothermic leading to a complex mixture of products. In contrast, the reaction of geraniol with DMP-OTs **2** in the presence of pyridine selectively produced the expected citral as an inseparable mixture of *E*- and *Z*-isomers **5m** and **5m'** (1.0 : 0.4 ratio) isolated by column chromatography in 89% yield (Scheme 4). This result is similar to the chromium(VI)-mediated oxidations of geraniol,[12] however, our reaction conditions are milder and the product yield is significantly higher.



Scheme 4. Oxidation of geraniol **4m** on millimolar scale using DMP-OTs/pyridine.

Finally, we studied the oxidation of several steroidal alcohols **4n-4p** using IBX-OTs as oxidant (Scheme 5). The reactions of steroidal alcohols **4n-4p** with 1 equiv IBX-OTs in CH_2Cl_2 (procedure 1, Scheme 5) selectively afforded the corresponding ketones **5n-5p** in 70-89% isolated yields. For steroids **4o** and **4p** containing hydroxyl in the A ring at position 4, this oxidation was also accompanied in part with desaturation of one or both α, β -positions of the keto group yielding enones **5o'** and **5p'** as well as dienone **5o"**. The preparative yields of enones **5o'**, **5o"** and **5p'** can be improved by using excess IBX-

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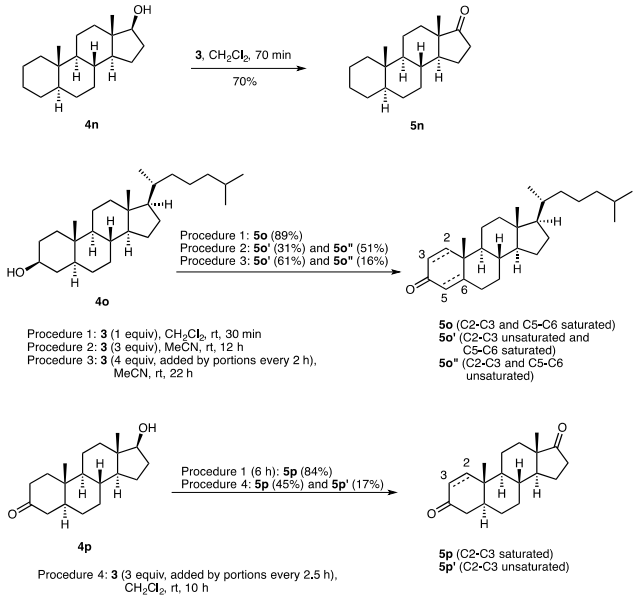
OTs in acetonitrile at room temperature (procedures 2-4, Scheme 5). This result is in agreement with the oxidative dehydrogenation of steroidal alcohols **4n** and **4o** to the corresponding enones **5o'**, **5o"** and **5p'** using IBX at 65-85 °C (DMSO, 24-48 h) reported by Nicolaou.[13] In contrast to the Nicolaou's work, the oxidations of **4o** and **4p** with IBX-OTs smoothly proceed in acetonitrile at room temperature, however, the isolated yields of enones **5o'**, **5o"** and **5p'** are slightly lower.



Scheme 5. Oxidation of steroids **4n-4p** (isolated yields are shown).

Conclusion

In summary, we have demonstrated that DMP-OTs **2** and IBX-OTs **3** are superior reagents for the oxidation of structurally complex alcohols, which serve as key intermediates in total syntheses of terpenes and polyketide antibiotics. The oxidations proceed extremely rapidly at room temperature leaving the protective groups and π-systems intact and affording the corresponding carbonyl compounds in good to excellent yields. In general, the yields of the corresponding oxidation products are higher for protocol that uses pyridine as additive. Compared to IBX-OTs **3**, DMP-OTs **2** generally affords the oxidation products in slightly higher yields; however, IBX-OTs is practically more convenient reagent because of its higher stability to moisture. Moreover, IBX-OTs **3** is an efficient reagent for the oxidative dehydrogenation of steroidal alcohols to the corresponding enones.

Experimental Section

General experimental remarks

2-Iodobenzoic acid, *p*-toluenesulfonic acid and other common reagents and solvents were from commercial sources and used without further purification from freshly opened containers. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to tetramethylsilane. Mass spectra (EI) were obtained at 70 eV or LCT (ESI). Analytical thin-layer chromatography was performed using precoated silica gel plates and the spots were visualized with UV light at 254 nm or by staining with H_2SO_4/2,4-dinitrophenylhydrazine or H_2SO_4/4-methoxybenzaldehyde in ethanol. Alcohols **4** were prepared according to known procedures or obtained from commercial sources: Alcohols **4b**, **4n** and **4o**[14] are commercially available. Substrates **4a** and **4l** were prepared according to Frenzel *et al*. starting from methyl (*R*)-(−)-3-hydroxy-2-methylpropionate.[5b] Alcohols **4c** and **4d** were prepared from **4b** according to known procedures from the Kirschning group.[6d] Substrate **4e** was prepared according to Beckmann *et al*. starting from Hajos-Wiechert ketone.[10] Alcohols **4f** and **4k** were obtained following a multistep procedure which started from acrolein and allyl methyl ether.[5a] Compound **4g** was prepared from methyl geranoate in several steps[6d] and **4h** is available from methyl (R)-(−)-3-hydroxy-2-methylpropionate.[7b] Finally, alcohol **4i** was synthesized from methyl isobutyrate and 1-{[(2-(chloromethyl)allyl)oxy]methyl}-4-methoxybenzene.[8] IBX (**1**) was prepared by oxidation of 2-iodobenzoic acid with Oxone.[15] IBX-OTs monohydrate (**3**) was prepared by treating IBX with *p*-TsOH•H_2O in acetic anhydride according to the published procedure.[4]

***1-Tosyloxy-1,1-diacetoxy-1H-1λ^5-benzo[d][1,2]iodoxol-3-one (DMP-OTs, 2)*; modified procedure**.[4] A mixture of IBX **1** (1.68 g, 6.0 mmol), *p*-TsOH•H_2O (3.42 g, 18.0 mmol), and acetic anhydride (20 mL) was magnetically stirred at room temperature. A formation of clear, colorless solution was observed after 40 min of stirring and then a white, microcrystalline precipitate started to form. After stirring the mixture for additional 4 h, the precipitate was filtered and washed on filter in dry atmosphere with a mixture of Et_2O/Ac_2O = 20:1 (20 mL) and dried in vacuum at room temperature during 6 h to give 2.60 g (81%) of DMP-OTs **2**, as a white, microcrystalline solid. Mp: 99-100 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.16 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.91 (s, 6H).

Optimization and comparison studies for iodine(V)-promoted oxidations of (*S*,*E*)-5-((*tert*-butyldiphenylsilyl)oxy)-2,4-dimethylpent-2-en-1-ol 4a (Table 1).

*Oxidation with IBX-OTs **3** (Table 1, entries 1-4):* To a solution of **4a** (37 mg, 0.1 mmol) in 1.0 mL of the appropriate solvent (see Table 1), IBX-OTs•H_2O **3** (48 mg, 0.106 mmol) was added and was stirred 3 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^{1}H NMR spectra (see Supporting Information for actual NMR spectra).

*Oxidation with IBX-OTs **3** in the presence of pyridine (Table 1, entry 5):* To a solution of **4a** (37 mg, 0.1 mmol) and pyridine (8 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL), IBX-OTs **3** (48 mg, 0.11 mmol) was added and the mixture was stirred 3 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^{1}H NMR spectra (see Supporting Information for actual NMR spectra).

*Oxidation with DMP-OTs **2** (Table 1, entry 6):* To a solution of **4a** (37 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL), DMP-OTs **2** (59 mg, 0.11 mmol) was added and the mixture was stirred 3 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^1H NMR spectra (see Supporting Information for actual NMR spectra).

*Oxidation with DMP-OTs **2** in the presence of pyridine (Table 1, entry 7):* To a solution of **4a** (37 mg, 0.1 mmol) and pyridine (8 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL), DMP-OTs **2** (59 mg, 0.11 mmol) was added and the mixture was stirred 3 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^1H NMR spectra (see Supporting Information for actual NMR spectra).

Oxidation with DMP (Table 1, entries 8 and 9): To a solution of **4a** (37 mg, 0.1 mmol) 1.0 mL of the appropriate solvent (see Table 1), DMP (47 mg, 0.11 mmol) was added and the mixture was stirred 3 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^1H NMR spectra (see Supporting Information for actual NMR spectra).

*Oxidation with IBX **1** (Table 1, entry 10):* To a solution of **4a** (37 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL), IBX **1** (31 mg, 0.11 mmol) was added and the mixture was stirred 10 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^1H NMR spectra (see Supporting Information for actual NMR spectra).

Oxidation with $PhI(OAc)_2$-TEMPO (Table 1, entry 11): To a solution of **4a** (37 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL), $PhI(OAc)_2$ (39 mg, 0.12 mmol) and TEMPO (3.2 mg, 0.02 mmol) were added and the mixture was vigorously stirred 10 min at rt. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. Conversion of alcohol to aldehyde was controlled by ^1H NMR spectra (see Supporting Information for actual NMR spectra).

General Experimental Procedure for Oxidation of Alcohols by IBX-OTs 3 (Scheme 2). To a solution of alcohol **4** (0.1-0.35 mmol) in CH_2Cl_2 (1-3 mL), IBX-OTs **3** (1.05-1.2 equiv) was added under stirring at room temperature. Reaction mixture was stirred 5-10 min (see Table 2; monitored by TLC and GC-MS). Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The analytically pure product **5** was isolated by filtration of reaction mixture through a short silica gel column using dichloromethane as eluent.

*(S,E)-5-((tert-butyldiphenylsilyl)oxy)-2,4-dimethylpent-2-enal (**5a**).* Following the general procedure, the reaction of alcohol **4a** (87 mg, 0.236 mmol) with IBX-OTs **3** (120 mg, 0.265 mmol) in CH_2Cl_2 (2.2 mL) afforded product **5a** as an oil (81 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.66-7.64 (m, 4H), 7.47-7.37 (m, 6H), 6.29 (dd, *J* = 9.6 Hz, 1.6 Hz, 1H), 3.69-3.65 (m, 1H), 3.62-3.58 (m, 1H), 2.98-2.90 (m, 1H), 1.73 (s, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 157.3, 139.4, 135.75, 135.7, 133.6, 133.56, 129.9, 129.87, 129.84, 67.7, 36.5, 27.0, 19.4, 16.2, 9.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{30}O_2NaSi$ 389.1913; Found: 389.1909.

*3-(Trimethylsilyl)propynal (**5b**).* Following the general procedure, the reaction of alcohol **4b** (44 mg, 0.35 mmol) with IBX-OTs **3** (169 mg, 0.37 mmol) in CH_2Cl_2 (2.2 mL) afforded product **5b** as an oil (39 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.16 (s, 1H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 103.2, 102.3, 0.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_6H_{10}ONaSi$ 149.0399; Found: 149.0391.

*3(R)-2-methyl-5-(trimethylsilyl)pent-4-ynal (**5c**).* Following the general procedure, the reaction of alcohol **4c** (42.5 mg, 0.25 mmol) with IBX-OTs **3** (135 mg, 0.30 mmol) in CH_2Cl_2 (2.5 mL) afforded product **5c** as an oil (39.5 mg, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.7 (d, *J* = 0.8 Hz, 1H), 2.57-2.51 (m, 2H), 2.51-2.35 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 103.5, 87.2, 45.3, 21.3, 13.2, 0.14. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{16}ONaSi$ 191.0868; Found: 191.0868.

*(S)-4-bromo-2-methylpent-4-enal (**5d**).* Following the general procedure, the reaction of alcohol **4d** (24 mg, 0.134 mmol) with IBX-OTs **3** (66.7 mg, 0.147 mmol) in CH_2Cl_2 (1.2 mL) afforded product **5d** as an oil (18 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$-TMS): δ 9.64 (d, *J* = 0.8 Hz, 1H), 5.59-5.58 (m, 1H), 5.43 (m, 1H), 2.86-2.80 (m, 1H), 2.74-2.68 (m, 1H), 2.35-2.29 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2, 131.1, 119.4, 44.6, 42.1, 12.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for C_6H_9BrONa 198.9734; Found: 198.9719.

*(7aS)-7a-methyl-2,3,5,6,7,7a-hexahydro-1H-inden-1-one (**5e**).* Following the general procedure, the reaction of alcohol **4e** (53 mg, 0.35 mmol) with IBX-OTs **3** (174 mg, 0.385 mmol) in CH_2Cl_2 (2 mL) afforded product **5e** as a volatile oil (37 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.55 (dd, *J* = 6 Hz, 2.8 Hz, 1H), 2.70-2.61 (m, 1H), 2.54-2.44 (m, 2H), 2.24-2.14 (m, 1H), 2.08-1.92 (m, 2H), 1.78-1.58 (m, 3H), 1.32-1.24 (m, 1H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.3, 141.7, 120.7, 47.5, 37.0, 28.9, 27.1, 24.8, 22.0, 18.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}ONa$ 173.0942; Found: 173.0941.

General Experimental Procedures for Oxidation of Alcohols by IBX-OTs or DMP-OTs in the presence of Pyridine (Scheme 3).

General Method A: To a solution of alcohol **4** (0.1-0.3 mmol) and pyridine (1.2 equiv) in CH_2Cl_2 (1-3 mL), IBX-OTs **3** (1.11-1.5 equiv) was added and the mixture was stirred at rt. The reaction was monitored by TLC and GC-MS until full disappearance of the alcohol. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The analytically pure product **5** was isolated by filtration of reaction mixture through a short silica gel column using dichloromethane as eluent.

General Method B: IBX-OTs **3** (1.2 equiv) was mixed with pyridine (1.2 equiv) in CH_2Cl_2 (1-2 mL) and the solvent was immediately evaporated. To the resulting oily residue, a solution of alcohol **4** (0.1 mmol) in CH_2Cl_2 (1 mL) was added and the mixture was stirred at rt. The reaction was monitored by TLC and GC-MS until full disappearance of the alcohol. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by

Na_2SO_4 and solvent removed in vacuum. The analytically pure product **5** was isolated by filtration of reaction mixture through a short silica gel column using dichloromethane as eluent.

*(3R,4R)-3-(benzyloxy)-4-methoxyhex-5-enal (**5f**).* *Method A:* the reaction of alcohol **4f** (70 mg, 0.297 mmol) with IBX-OTs **3** (203 mg, 0.45 mmol) and pyridine (28 mg, 0.35 mmol) in CH_2Cl_2 (3 mL) after stirring for 3 h afforded product **5f** as an oil (45 mg, 64%). *Method B:* the reaction of IBX-OTs **3** (122 mg, 0.27 mmol) with pyridine (22 mg, 0.275 mmol) followed by addition of alcohol **4f** (58 mg 0.246 mmol) in CH_2Cl_2 (2 mL) after stirring for 0.5 h afforded product **5f** as an oil (44 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.29-7.21 (m, 5H), 5.74-5.65 (m, 1H), 5.28-5.22 (m, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.01-3.97 (m, 1H), 3.69-3.66 (m, 1H), 3.23 (s, 3H), 2.62-2.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 138.2, 134.4, 128.5, 128.1, 127.9, 119.5, 83.9, 76.0, 73.2, 57.0, 45.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_3Na$ 257.1154; Found: 257.1156.

*2-((2S,5S)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-5-methyltetrahydrofuran-2-yl)-2-methylpropanal (**5g**).* *Method A:* the reaction of alcohol **4g** (52 mg, 0.201 mmol) with IBX-OTs **3** (96 mg, 0.212 mmol) and pyridine (18 mg, 0.215 mmol) in CH_2Cl_2 (2 mL) after stirring for 25 min afforded product **5g** as an oil (45 mg, 87%). *Method B:* the reaction of IBX-OTs **3** (95 mg, 0.21 mmol) with pyridine (17 mg, 0.21 mmol) followed by addition of alcohol **4g** (39.5 mg 0.152 mmol) in CH_2Cl_2 (1 mL) after stirring for 20 min afforded product **5g** as an oil (39 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 4.08-4.03 (m, 2H), 3.98-3.95 (m, 1H), 2.02-1.92 (m, 2H), 1.76-1.63 (m, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.10 (s,3H), 1.05 (s, 3H), 1.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ .206.6, 109.5, 84.2, 83.5, 81.2, 66.1, 48.9, 33.9, 27.0, 26.4, 25.2, 22.7, 19.5, 16.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{24}O_4Na$ 279.1572; Found: 279.1569.

*5-((tert-butyldimethylsilyl)oxy)-2,4,4-trimethylpentanal (**5h**).* *Method A:* the reaction of alcohol **4h** (52 mg, 0.201 mmol) with IBX-OTs **3** (135 mg, 0.299 mmol) and pyridine (24 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) after stirring for 2 h afforded product **5h** as an oil (32 mg, 62%). *Method B:* the reaction of IBX-OTs **3** (79 mg, 0.175 mmol) with pyridine (15 mg, 0.18 mmol) followed by addition of alcohol **4h** (39.5 mg 0.152 mmol) in CH_2Cl_2 (1 mL) after stirring for 30 min afforded product **5h** as an oil (33 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 3.22 (s, 2H), 2.46-2.37 (m, 1H), 1.85 (dd, *J* = 14.4 Hz, 8.0 Hz, 1H), 1.18 (dd, *J* = 14.4 Hz, 3.6 Hz, 1H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.84 (s, 3H), 0.83 (s, 3H), 0.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 71.3, 42.9, 39.8, 35.8, 26.0, 25.0, 24.7, 18.4, 16.6, -5.4, -5.43. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{30}O_2NaSi$ 281.1913; Found: 281.1913.

*5-((tert-butyldimethylsilyl)oxy)-2,4,4-trimethylpentanal (**5i**).* *Method A:* the reaction of alcohol **4i** (63 mg, 0.208 mmol) with IBX-OTs **3** (113 mg, 0.25 mmol) and pyridine (20 mg, 0.25 mmol) in CH_2Cl_2 (2 mL) after stirring for 2 h afforded product **5i** as an oil (44 mg, 71%). *Method B:* the reaction of IBX-OTs **3** (68 mg, 0.15 mmol) with pyridine (11 mg, 0.15 mmol) followed by addition of alcohol **4i** (37 mg 0.122 mmol) in CH_2Cl_2 (1 mL) after stirring for 30 min afforded product **5i** as an oil (34.5 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 5.63-5.59 (m, 1H), 5,46-5.41 (m, 1H), 4.11 (d, *J* = 4.8 Hz, 2H), 1.94 (d, *J* = 14.8 Hz, 1H), 1.85 (d, *J* = 14.8 Hz, 1H), 1.20 (s, 3H), 1.08 (s, 3H), 1.02 (s, 3H), 0.91 (d, *J* = 16 Hz, 9H), 0.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.4, 139.8, 127.2, 79.0, 63.8, 35.9, 29.5, 28.2, 26.1, 26.0, 25.8, 18.6, -3.4, -5.0, -5.03. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{32}O_3NaSi$ 323.2018; Found: 323.2017.

*(R,E)-7-((tert-butyldiphenylsilyl)oxy)-2-((4-methoxybenzyl)oxy)-2,4,4-trimethylhept-5-enal (**5j**).* *Method B:* the reaction of IBX-OTs **3** (106 mg, 0.234 mmol) with pyridine (19 mg, 0.235 mmol) followed by addition of alcohol **4j** (80 mg 0.213 mmol) in CH_2Cl_2 (2 mL) after stirring for 30 min afforded product **5j** as an oil (74 mg, 93%). *Method C:* DMP-OTs **2** (36.4 mg, 0.068 mmol) was mixed with pyridine (5.5 mg, 0.068 mmol) in CH_2Cl_2 (1 mL) and the solvent was immediately evaporated. To the resulting oily residue, a solution of alcohol **4j** (23.8 mg 0.063 mmol) in CH_2Cl_2 (1 mL) was added and the mixture was stirred at rt for 30 min. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The analytically pure product **5j** was isolated by filtration of reaction mixture through a short silica gel column using dichloromethane as eluent. The quantitative conversion of substrate **4j** to the product **5j** was confirmed by ^{1}H NMR (see Supporting Information for actual spectra). Product **5j** was isolated as an oil (22.6 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1H), 7.69-7.67 (m, 4H), 7.44-7.35 (m, 6H), 7.28-7.26 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.67-5.62 (m, 1H), 5.48-5.41 (dt, *J* = 15.6 Hz, 5.2 Hz, 1H), 4.42 (dd, *J* = 29.2 Hz, 10.8 Hz, 2H), 4.14 (dd, *J* = 5.2 Hz, 1.6 Hz, 2H), 3.79 (s, 3H), 1.85 (dd, *J* = 18 Hz, 14.8 Hz, 2H), 1.58-1.51 (m, 1H), 1.33 (s, 3H), 1.09-1.04 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 159.2, 141.3, 135.7, 134.0, 130.7, 129.7, 128.9, 127.7, 125.3, 113.9, 83.7, 65.7, 64.9, 55.4, 50.2, 35.8, 29.8, 28.8, 26.9, 20.5, 19.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{44}O_4NaSi$ 567.2907; Found: 567.2905.

*(4S,5S,7R,8R,E)-7-(benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-8-methoxy-2,4-dimethyldeca-2,9-dienal (**5k**).* *Method A:* the reaction of alcohol **4k** (45 mg, 0.1 mmol) with IBX-OTs **3** (50 mg, 0.11 mmol) and pyridine (9 mg, 0.115 mmol) in CH_2Cl_2 (1 mL) after stirring for 12 h afforded product **5k** as an oil (32 mg, 71%). *Method B:* the reaction of IBX-OTs **3** (95 mg, 0.21 mmol) with pyridine (17 mg, 0.215 mmol) followed by addition of alcohol **4k** (90 mg 0.2 mmol) in CH_2Cl_2 (2 mL) after stirring for 30 min afforded product **5k** as an oil (80 mg, 90%). *Method C:* DMP-OTs **2** (54 mg, 0.1 mmol) was mixed with pyridine (8.7 mg, 0.11 mmol) in CH_2Cl_2 (1 mL) and the solvent was immediately evaporated. To the resulting oily residue, a solution of alcohol **4k** (41 mg 0.09 mmol) in CH_2Cl_2 (1 mL) was added and the mixture was stirred at rt for 30 min. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The analytically pure product **5k** was isolated by filtration of reaction mixture through a short silica gel column using dichloromethane as eluent. The quantitative conversion of substrate **4k** to the product **5k** was confirmed by ^{1}H NMR (see Supporting Information for actual spectra). Product **5k** was isolated as an oil (39 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 7.31-7.26 (m, 5H), 6.36 (dd, *J* = 9.6 Hz, 1.2 Hz, 1H), 5.78-5.69 (m, 1H), 5.33-5.26 (m, 2H), 4.75 (d, *J* = 8.8 Hz, 1H), 4.53 (d, *J* = 8.8, 1H), 3.82-3.78 (m, 1H), 3.70-3.67 (m, 1H), 3.55-3.50 (m, 1H), 3.30 (s, 1H), 2.82-2.77 (m, 1H), 1.88-1.81 (m, 1H), 1.61 (d, *J* = 1.2 Hz, 3H), 1.99 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.76, 158.3, 138.8, 138.1, 135.0, 128.4, 127.9, 127.7, 119.0, 84.7, 77.9, 72.9, 71.6, 56.9, 38.1, 36.0, 26.0, 18.2, 13.6, 9.5, -3.9, -4.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{42}O_4NaSi$ 469.2750; Found: 469.2750.

*(3S,6S,E)-3-((tert-butyldimethylsilyl)oxy)-7-((tert-butyldiphenylsilyl)oxy)-4,6-dimethylhept-4-enal (**5l**).* *Method B:* the reaction of IBX-OTs **3** (50 mg, 0.11 mmol) with pyridine (9 mg, 0.115 mmol) followed by addition of alcohol **4l** (53 mg 0.1 mmol) in CH_2Cl_2 (1 mL) after stirring for 30 min afforded product **5l** as an oil (33 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.67-7.64 (m, 5H), 7.40-7.37 (m, 7H), 5.31 (d, *J* = 9.2 Hz, 1H), 4.46 (dd, *J* = 8.4 Hz, 4 Hz, 1H), 3.53-3.49 (m, 1H), 3.46-3.40 (m, 1H), 2.64-2.54 (m, 1H), 2.41-2.36 (m, 1H), 1.54

(d, *J* = 1.2 Hz, 3H), 1.05 (s, 9H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.83 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 136.5, 135.75, 135.7, 134.0, 129.7, 129.68, 129.2, 127.7, 73.8, 68.3, 50.3, 35.1, 27.0, 25.8, 19.4, 18.2, 17.4, 12.0, -4.4., -5.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{48}O_3NaSi$ 547.3040; Found: 547.3039.

Oxidation of geraniol 4m on a millimolar scale (Scheme 4).

DMP-OTs **2** (590 mg, 1.1 mmol) was added to a solution of geraniol **4m** (154 mg, 1.0 mmol) and pyridine (90 mg, 1.14 mmol) in CH_2Cl_2 (6 mL) at 0 °C and the mixture was stirred for 5 min (the reaction was monitored by TLC and GC-MS until full disappearance of geraniol). Then Et_2O (5 mL), petroleum ether (5 mL) and aqueous solutions of $NaHSO_3$ (5%, 5 mL) and $NaHCO_3$ (5%, 5 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The analytically pure product was isolated as an inseparable mixture of *E*- and *Z*-isomers **5m** and **5m'** (1.0 : 0.4 ratio) by filtration of reaction mixture through a short silica gel column using petroleum ether as eluent; oil (135 mg, 89%); ^{1}H NMR and ^{13}C NMR (see Supporting Information) identical to the spectra of commercially available sample of citral.

Oxidation of Steroids 4m-4o by IBX-OTs 3 (Scheme 5).

General Procedure 1: To a solution of steroid **4** (0.1-0.2 mmol) in CH_2Cl_2 (1-2 mL), IBX-OTs **3** (1.05-1.2 equiv) was added under stirring at room temperature. Reaction mixture was stirred 0.5-6 h (see Table 4; monitored by TLC and GC-MS). Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The analytically pure product **5** was isolated by filtration of reaction mixture through a short silica gel column using petroleum ether-ethyl acetate (9:1, 4:1) as eluent.

*(5R,8R,9S,10S,13S,14S)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (**5n**).* Following the general Procedure 1, the reaction of 5□□androstan□□□□□ol **4n** (42 mg, 0.152 mmol) with IBX-OTs **3** (82 mg, 0.186 mmol) in CH_2Cl_2 (2 mL) afforded product **5n** as a white solid (37 mg, 70%), mp 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45-2.38 (m, 1H), 2.07-2.00 (m, 1H), 1.94-1.88 (m, 1H), 1.79-1.74 (m, 2H), 1.67-1.64 (m, 3H), 1.55-1.44 (m, 4H), 1.29-1.17 (m, 8H), 1.06-1.04 (m, 1H), 0.98-0.87 (m, 2H), 0.84 (s, 3H), 0.79 (s, 3H), 0.73-0.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.7, 55.0, 51.7, 48.0, 47.2, 38.8, 36.6, 36.0, 35.2, 31.8, 31.1, 29.1, 28.9, 26.9, 22.3, 21.9, 20.2, 14.0, 12.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{30}ONa$ 297.2194; Found: 297.2199.

*(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-3H-cyclopenta[a]phenanthren-3-one (**5o**).* Following the general Procedure 1, the reaction of 5α-cholestane-3β-ol **4o** (84 mg, 0.216 mmol) with IBX-OTs **3** (90 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) afforded product **5o** as a white solid (69 mg, 89%), mp 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42-2.35 (m, 1H), 2.31-2.22 (m, 2H), 2.10-1.96 (m, 3H), 1.84-1.82 (m, 1H), 1.71-1.67 (m, 1H), 1.59-1.48 (m, 5H), 1.49-1.25 (m, 10H), 1.09-1.02 (m, 7H), 1.00 (s, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 1.6 Hz, 3H), 0.85 (d, *J* = 2 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4, 56.42, 56.4, 53.9, 46.9, 44.9, 42.7, 40.0, 39.6, 38.7, 38.4, 36.3, 35.9, 35.8, 35.5, 31.9, 29.1, 28.4, 28.2, 24.4, 24.0, 22.7, 21.6, 18.8, 12.2, 11.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{47}O$ 387.3627; Found: 387.3617.

*(5S,8R,9S,10S,13S,14S)-10,13-dimethyltetradecahydro-3H-cyclopenta[a]phenanthrene-3,17(2H)-dione (**5p**).* Following the general Procedure 1, the reaction of 5α-cholestane-17β-ol-3-one **4p** (60 mg, 0.207 mmol) with IBX-OTs **3** (94 mg, 0.207 mmol) in CH_2Cl_2 (2 mL) afforded product **5p** as a white solid 50 mg (84%), mp 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48-2.24 (m, 4H), 2.13-1.90 (m, 4H), 1.85-1.81 (m, 2H), 1.71-1.48 (m, 4H), 1.43-1.25 (m, 6H), 1.05-0.96 (m, 4H), 0.88 (s, 3H), 0.82-0.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.1, 211.8, 54.01, 51.4, 47.9, 46.7, 44.7, 38.6, 38.2, 36.0, 35.9, 35.1, 31.6, 30.7, 28.8, 21.9, 20.8, 13.9, 11.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{28}O_2Na$ 311.1987; Found: 311.1985.

Oxidative Dehydrogenation of 5α-cholestane-3β-ol 4o (Scheme 5).

Procedure 2: To a solution of steroid **4o** (55 mg, 0.142 mmol) in CH_3CN (2 mL), IBX-OTs **3** (203 mg, 0.45 mmol) was added and stirred for 10 h. Then additional IBX-OTs **3** (68 mg, 0.15 mmol) was added and the stirring was continued for 2 h. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The resulting oil was separated by column chromatography to afford product **5o'** (17 mg, 31%) and product **5o"** (28 mg, 51%) isolated as white solids.

Procedure 3: To a solution of steroid **4o** (39 mg, 0.1 mmol) in CH_3CN (3 mL), IBX-OTs **3** (48 mg, 0.106 mmol) was added and stirred for 10 h. Then additional IBX-OTs **3** (136 mg, 0.3 mmol) was added by portions in the course of 2 h and the stirring was continued for 10 h. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The resulting oil was separated by column chromatography to afford product **5o'** (23 mg, 61%) and product **5o"** (6 mg, 16%) isolated as white solids.

*(1S,2R,10S,11S,14R,15R)-14-[(R)-1,5-Dimethylhexyl]-2,15-dimethyltetracyclo[8.7.0.0^{2,7}.0^{11,15}]heptadeca-3,6-dien-5-one (**5o'**);* mp 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 10 Hz, 1H), 5.84 (d, *J* = 10 Hz, 1H), 2.4-2.32 (m, 1H), 2.23-2.17 (m, 1H), 2.03 (dt, *J* = 12.8 Hz, 3.2 Hz, 1H), 1.94-1.78 (m, 2H), 1.7 (dt, *J* = 13.2 Hz, 3.6 Hz, 2H), 1.56-1.32 (m, 9H), 1.17-1.04 (m, 9H), 0.99 (s, 4H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.85 (dd, *J* = 6.8 Hz, 2 Hz, 7H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 158.8, 127.5, 56.5, 56.3, 50.1, 44.4, 42.8, 41.2, 40.0, 39.6, 39.1, 36.3, 35.9, 35.8, 31.5, 28.4, 28.2, 27.8, 24.3, 24.0, 23.0, 22.7, 18.8, 13.1, 12.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{44}ONa$ 407.3290; Found: 407.3290.

*(1S,2S,7S,10R,11S,15S)-2,15-Dimethyltetracyclo[8.7.0.0^{2,7}.0^{11,15}]heptadecane-5,14-dione (**5o"**);* mp 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 10 Hz, 1H), 6.22 (dd, *J* = 10 Hz, 2 Hz, 1H), 6.06 (t, *J* = 1.6 Hz, 1H), 2.43-2.35 (m, 1H), 2.31-2.26 (m, 1H), 1.99-1.94 (m, 1H), 1.91-1.72 (m, 2H), 1.63-1.41 (m, 6H) 1.32-1.19 (m, 4H), 1.16 (s, 3H), 1.11-0.90 (m, 9H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.79 (dd, *J* = 6.4 Hz, 1.6 Hz, 6H), 0.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 169.7, 156.2, 127.6, 123.9, 56.2, 55.6, 52.5, 43.8, 42.8, 39.64, 39.62, 36.2, 35.9, 35.7, 33.8, 33.1, 28.3, 28.2, 24.5, 24.0, 23.0, 22.96, 22.7, 18.8, 18.7, 12.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{43}O$ 383.3314; Found: 383.3315.

Oxidative Dehydrogenation of 5α-cholestane-17β-ol-3-on 4p (Scheme 5).

Procedure 4: To a solution of steroid **4p** (58.5 mg, 0.2 mmol) in CH_2Cl_2 (3 mL), IBX-OTs **3** was added 3

times every 2.5 h by portions (3 x 90.5 mg, total 0.6 mmol) and the stirring was continued for 10 h. Then Et_2O (3 mL) and aqueous solutions of $NaHSO_3$ (5%, 1 mL) and $NaHCO_3$ (5%, 3 mL) were added and the mixture was vigorously stirred 5 min. Organic layer was separated, dried by Na_2SO_4 and solvent removed in vacuum. The resulting oil was separated by column chromatography to afford product **5p** (26 mg, 45%) and product **5p'** (10 mg, 17%) isolated as white solids.

*(5S,8R,9S,10R,13S,14S)-10,13-dimethyl-5,6,7,8,9,10,11,12,13,14,15,16-dodecahydro-3H-cyclopenta[a]phenanthrene-3,17(4H)-dione (**5p'**);* mp 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 10. Hz, 1H), 5.87 (d, *J* = 10 Hz, 1H), 2.50-2.42 (m, 1H), 2.39-2.34 (m, 1H), 2.27-2.21 (m, 1H), 2.13-2.04 (m, 1H), 1.98-1.83 (m, 4H), 1.67-1.59 (m, 2H), 1.57-1.43 (m, 4H), 1.36-1.30 (m, 2H), 1.08-1.01 (m, 5H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.6, 200.0, 157.9, 127.8, 51.4, 50.2, 48.0, 44.4, 41.0, 39.2, 35.9, 35.4, 31.6, 30.3, 27.5, 21.8, 20.7, 14.0, 13.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{26}O_2Na$ 309.1830; Found: 309.1824.

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FULL PAPER

2-Iodoxybenzoic Acid Tosylates: the Alternative to Dess-Martin Periodinane Oxidizing Reagents

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