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New chiral hypervalent iodine(V) compounds as stoichiometric oxidants

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ABSTRACT

The synthesis and application of some new hypervalent iodine compounds bearing chiral and achiral ester motives derived from easily accessible starting materials is presented. The oxidation is carried out using dimethyldioxirane as an oxidant providing the desired compounds in moderate to high yields. A crystal structure analysis for one iodine(V) derivative is investigated. The λ^5-iodanes are applied as stoichiometric reagents in the oxidation of thioanisole to phenylmethyl sulfoxide, benzyl alcohol to benzaldehyde, and *meso*-hydrobenzoine to benzaldehyde, benzyl, and benzoin.

1. Introduction

Pentavalent iodine compounds have proven to be mild oxidizing agents.[1] The iodyl (IO_2^+)-moiety is isoelectronic to ozone and, therefore, it is likely that reactions employing iodyl compounds proceed via a comparable mechanism. Iodylarenes are usually polymeric and cannot be dissolved in ordinary solvents.[1c,2] They are thermally stable unless heated in the absence of solvents: melting points usually are explosion points.[3]

The first iodyl compound, $PhIO_2$, was synthesized by Willgerodt in 1900.[4] Usually, iodylarenes are prepared by treatment of iodoarenes with strong oxidants such as peracetic acid,[5] sodium hypochlorite,[6] peroxymonosulfates[7] or diacetyl peroxide.[8] One of the best known iodine(V) compounds is the well-established and widely used Dess–Martin periodinane (DMP).[9] The advantage of DMP is the enhanced stability as well as safety since iodoxybenzoic acid was experienced to be explosive under excessive heating or impact.[3] Cyclic iodylarenes possess an enhanced stability because the pentavalent iodine atom is part of a five-membered ring; non-cyclic iodylarenes have been reported to have explosive properties.[10]

Some years ago, the synthesis and employment of IBX[1f] as well as the corresponding IBX-esters[11] and IBX amides[12] has been reported. These esters belong to a new class of pentavalent iodine compounds with a pseudo-benziodoxole structure and have been employed successfully in oxidizing alcohols to the respective carbonyl derivatives in excellent yields of 95–100%.[13] The ester moiety in these IBX reagents can be derived from chiral moieties such as menthol or borneol. A variety of alcohols was oxidized by pentavalent iodine compounds bearing ester moieties in the presence of TFA, KBr or BF_3-etherate.[14] As an example, benzaldehyde was obtained exclusively when benzyl alcohol was stirred together with KBr as catalyst in chloroform at 50 °C.[14] IBX amides oxidized successfully primary and secondary alcohols to the corresponding aldehydes and ketones without the presence of an acid, in contrast to non-cyclic iodylarenes such as iodylbenzene ($PhIO_2$). Iodylbenzene only reacts after appropriate activation such as stirring in DMSO, since the strong intermolecular bonding between the iodine atom and an oxygen atom occupies the coordination site at the iodine atom necessary for reactions.[1f,15] After the reaction using pentavalent iodine compounds bearing chiral amides in the side chain, the remaining alcohol showed some enantioenrichment of 9%, when 1-phenylethanol was oxidized in $CDCl_3$ at room temperature over a time period of 18 h.[12]

A range of differently substituted iodoarenes can be oxidized with suitable oxidants to obtain λ^5-iodane derivatives. These hypervalent iodine compounds can then be used in different oxidations or functionalizations.

2. Results and discussion

Some hypervalent (2-iodosylphenyl)acetic acid derivatives bearing a stereocenter in the benzylic position have been prepared recently.[16] As iodyl compounds are usually prepared by direct oxidation of the corresponding iodoarenes with strong oxidizing agents, we investigated different oxidants such as sodium periodate,[17] potassium bromate,[18] sodium hypochlorite,[6] oxone,[19] and dimethyldioxirane (DMDO).[20] Iodoarenes are initially oxidized to

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the corresponding iodosylarenes, which then disproportionate to iodylarenes either at room temperature or at elevated temperatures[21] or under metal catalysis.[22]

The starting materials for the iodosylarenes **2a**–**i** were synthesized by esterification of either (2-iodophenyl)acetic acid or 2-iodobenzoyl chloride (**1a**, **1f**–**h**) and subsequent deprotonation in benzylic position and reaction with alkylhalogenides to gain access to **1b** and **1c**.[23] A secondary alkyl moiety was introduced, applying the same method, to obtain compounds **1d**–**e**.[23]

Skulski and co-workers have developed a synthetic method toward iodyl compounds using sodium periodate in water under reflux in good yields (up to 91%).[17] This method was applied to the disubstituted ester **1d**. Unfortunately the ^{1}H NMR analysis of the crude product showed only traces of the desired iodane. The oxidation of iodoarene **1d** with potassium bromate and sulfuric acid under heating for about 4 h returned only starting material.[18] The mono- and disubstituted methylesters **1b** and **1d** have also been treated with oxone[16,19] in an aqueous solution at elevated temperatures. In both reactions, only starting material was isolated after work-up. For the oxidation with sodium hypochlorite,[6] (2-iodophenyl)acetic acid was employed as starting material, but could not be oxidized under these conditions; starting material was recovered. Compound **1d** could also not be oxidized with this method, the starting material was recovered. Only **1i** could be oxidized with sodium hypochlorite to the corresponding iodyl compound **2i** in 60% yield.

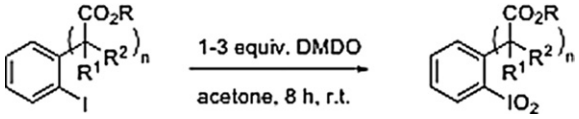
Dimethyldioxirane (DMDO) has been used in the past to oxidize iodoarenes to λ^3- and λ^5-iodanes.[20] DMDO was prepared according to a procedure developed by Murray and Singh from acetone, oxone, $NaHCO_3$, and water.[24] Concentrations of DMDO solutions are generally low,[25] 0.07–0.09 M are reported. This is probably due to the high volatility and inherent instability of the oxidant. In order to achieve optimum yields, extra care and constant vigilance was taken with regards to the sealing of the reaction apparatus as well as to efficient stirring of the reaction mixture using an overhead stirrer. The product mixture of DMDO in acetone has to be stored at −20 °C.

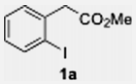
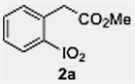
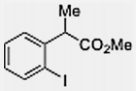
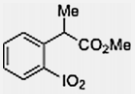
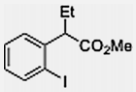
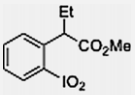
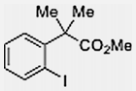
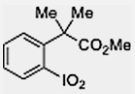
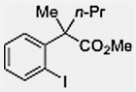
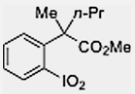
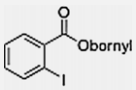
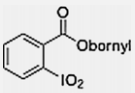
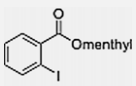
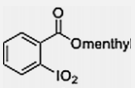
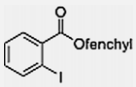
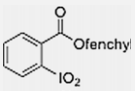
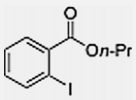
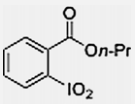
A range of iodoarenes was oxidized using a freshly prepared solution of DMDO in acetone. The oxidation of methylester **1d** in the presence of acetic acid in the DMDO-reaction mixture was supposed to result in the corresponding (diacetoxy)iodo derivative as described earlier.[20] However, the addition of acetic acid did not make any difference and the corresponding iodyl compound was formed as confirmed by ^{1}H NMR spectroscopy (low-field shift of the aromatic *ortho*-proton to $\delta \approx 8.0$ ppm), ^{13}C NMR (absence of the characteristic C–I signal around δ=95 ppm), IR (strong peak at 769 cm^{-1}), and mass spectrometry. Therefore, all reactions were performed without the addition of acetic acid (Table 1). After reaction completion, the solvent was evaporated to give colorless solids; remains of starting materials were removed by washing with diethyl ether. Yields achieved ranged from promising 44% for **2a** (Table 1, entry 1) to excellent 99% for compound **2i** (Table 1, entry 8).

Not all iodyl derivatives could be fully characterized due to the sometimes very small amounts of iodoarenes and not achieving full reaction conversion or also due to the possibility of decomposition of the iodyl compounds.

The solubility properties of hypervalent iodine compounds have generally been found to be low in many organic solvents.[1c,2] The analysis of the crystal structures of iodosyl and iodyl compounds can explain their poor solubility properties, which are caused by strong secondary I–O bonds forming a polymer. The effects of the latter have been investigated thoroughly in the past.[21b] The solubility of the iodyl compounds **2a**–**i** is dependent on structural features: methylesters with only one or no substituent did not dissolve in solvents other than dimethylsulfoxide (Table 1, entries 1–3), whereas esters with two or bulkier alkyl substituents as well as all iodoarenes with a terpene moiety were easily dissolved in chloroform or dichloromethane and therefore offering the possibility of mild reaction conditions when used as oxidizing reagents.

Table 1
Synthesis of iodylarenes **2**



Entry	Ar–I	Product Ar–IO_2	Yield [%]
1	 **1a**	 **2a**	44
2	 ***rac*-1b**	 ***rac*-2b**	67
3	 ***rac*-1c**	 ***rac*-2c**	63
4	 **1d**	 **2d**	74
5	 ***rac*-1e**	 ***rac*-2e**	98
6	 **1f**	 **2f**	54
7	 **1g**	 **2g**	64
8	 **1h**	 **2h**	99
9[a]	 **1i**	 **2i**	60

[a] Synthesized using 2 equiv NaOCl in AcOH/CH_2Cl_2 at rt, 3 days.

Although being a fairly stable compound, a crystal structure was obtained of the dimethyl-substituted iodylarene **2d** (Fig. 1).[26] A similar distance between the iodine atom and the ester oxygen has been found in **2d** (2.611–2.933 Å) and some IBX-esters.[11] Also, intermolecular secondary I···O bonding interactions have been detected. The interaction distance from the iodine atom to iodyl oxygen atoms of neighboring molecules has been found to range from 2.654–3.100 Å. The angle of the 3c4e-bond of O10–I3–O9 has been found to be 101.5(2)°.

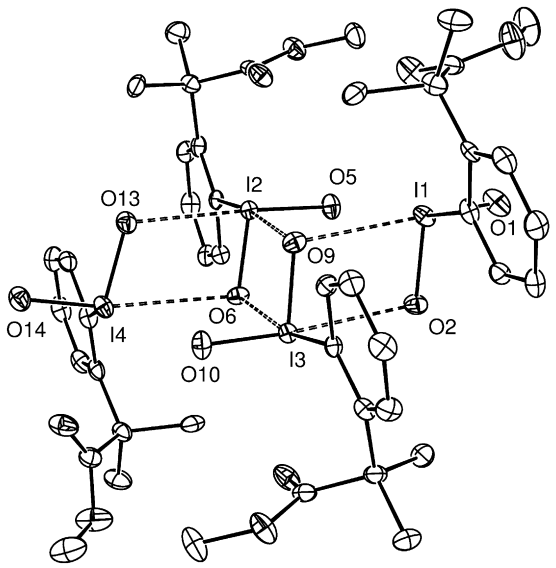


Figure 1. Crystal structure analysis of **2d** indicating secondary interactions.

Bonding features discovered in **2d** are very similar to the ones obtained from the IBX-esters.[11] The distances between the iodine atom and the ester oxygens range between 2.6 and 3.1 Å, distances to other iodyl–oxygen moieties are between 2.6 and 2.9 Å. Likewise, **2d** can be dissolved in commonly used solvents such as dichloromethane and chloroform.

Unlike DMP or IBX, iodyl compounds **2a**–**i** have not been found to be explosive, neither when scratched with a spatula nor on impact. When heated above 150 °C, combustion has been observed for some iodylarenes, but in most cases only melting or degradation under discoloration has been observed.

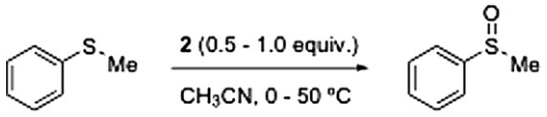
To test possible reactions with compounds **2a**–**i**, thioanisole was oxidized to phenylmethyl sulfoxide. About 0.5–1.0 equiv of the oxidant was used in order to determine the minimum amount necessary for a full conversion. The reactions were conducted by stirring in acetonitrile at 0 °C to improve enantioselectivity, but then had to be heated up to 50 °C, since conversions were too small (Table 2). In order to examine the dissolving behavior and oxidation ability of iodylarenes **2a**–**i**, the reactions were performed without addition of TFA (trifluoroacetic acid), which supports the dissolving. With enantiomerically pure iodylarenes stereoselective reactions have been carried out. In some cases, the sulfoxides were contaminated with impurities, which could not be removed by preparative TLC and a determination of the enantiomeric excess was not possible.

Initially two reactions were conducted using 1 equiv of mono- and disubstituted methylesters *rac*-**2b** and *rac*-**2e** (Table 2, entries 2 and 5) resulting in complete conversions. For the following reactions, the amount of oxidant was reduced: 0.8 equiv of achiral ester **2a** also resulted in complete conversion (Table 2, entry 1), whereas the use of 0.7 equiv seems to be sufficient only for some reactions (Table 2, entries 4, 6, and 7). The mono-substituted methylesters *rac*-**2c** led to good conversions of 94% (Table 2, entry 3). The difference of the conversion was high, when terpene esters with a shorter side chain were used: complete conversion was achieved using the bornyl ester **2f** (Table 2, entry 6), whereas only 19% were observed from the use of the respective fenchylester **2h** (Table 2, entry 7). Only 0.5 equiv of methylester *rac*-**2b** achieved a moderate 57% conversion (Table 2, entry 3). The employment of 1 equiv of FIBX resulted in excellent conversion of 99% and 90% yield (Table 2, entry 8).[27]

If 1 equiv of oxidant is used, usually excellent conversions were achieved; the use of lower amounts gave mixed results with no clear trends being observed. In case of 0.7 equiv, already small structural differences seem to result in dramatic changes of conversions, e.g., the introduction of a methyl group at the benzylic position in the *ortho* side chain. The enantiomeric excess for the reaction with **2h** could not be determined due to overlapping signals with **1h**.

IBX was employed in the oxidation of primary and secondary alcohols at room temperature in dimethylsulfoxide by Frigerio and Santagostino.[28] In order to investigate the oxidation properties of iodylarenes described here, a range of reagents was employed as oxidants in the oxidation of benzyl alcohol (Table 3). All reactions were conducted in dichloromethane or in acetonitrile at room temperature or at elevated temperature with 1 equiv of an iodyl derivative.

Table 2
Oxidation of thioanisole **3** to phenylmethyl sulfoxide **4**

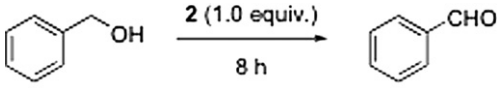


3 **4**

Entry	Equiv	Iodylarene	Conversion %[a]	**4** ee[c] [%]
1	0.8	**2a**	99	—
2	1.0	*rac*-**2b**	99	—
3	0.5	*rac*-**2b**	57	—
4	0.7	*rac*-**2c**	94	—
5	1.0	*rac*-**2e**	99	—
6	0.7	**2f**	99	0
7	0.7	**2h**	19	[d]
8	1.0	FIBX	99 (90)[b]	—

[a] Determined by ^{1}H NMR and HPLC.
[b] Yield.
[c] Determined by HPLC on a chiral column (Chiracel OD).
[d] Determination was not possible.

Table 3
Oxidation of benzyl alcohol to benzaldehyde



5 **6**

Entry	Solvent	Temp	Equiv TFA	Iodylarene	Conversion[a] %
1	CH_2Cl_2	rt	—	**2a**	11
2	CH_2Cl_2	Reflux	1.0	**2a**	51
3	CH_2Cl_2	rt	—	*rac*-**2b**	35
4	CH_2Cl_2	Reflux	1.0	*rac*-**2c**	100
5	CH_2Cl_2	rt	—	**2d**	2
6	CH_2Cl_2	Reflux	—	**2d**	51
7	CH_3CN	Reflux	—	**2i**	0.2

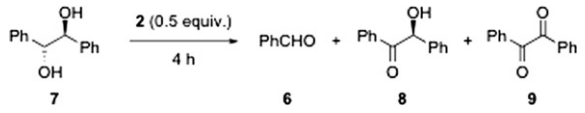
[a] Determined by ^{1}H NMR.

The employment of the unsubstituted methylester **2a** resulted in only small conversion of 11% if stirred at room temperature. The addition of trifluoroacetic acid (TFA) and heating improved the conversion to moderate 51% (Table 3, entries 1 and 2). Moderate 35% conversion was achieved with the methylated ester *rac*-**2b** at room temperature in absence of TFA (Table 3, entry 3). Ethyl ester *rac*-**2c** achieved complete conversion by refluxing in presence of TFA (Table 3, entry 4). The importance of heating the reaction mixture was again shown in the reaction of the disubstituted iodylarene **2d** firstly at room temperature resulting in only 2% conversion, which was improved to 51% conversion simply by

heating (Table 3, entries 5 and 6). On the other hand, the iodyl derivative **2i** resulted in no conversion, even though the reaction mixture was refluxed overnight (Table 3, entry 7).

In the following reaction series, some iodylarenes were tested as suitable oxidants for the enantioselective oxidation of *meso*-hydrobenzoin.[29] For this purpose, diol **7** was stirred together with the iodylarene in dichloromethane or acetonitrile at room temperature or elevated temperatures with or without trifluoroacetic acid (TFA) (Table 4). Only benzaldehyde **6** was recovered from the reaction conducted at 65 °C using **2a** as oxidant without TFA (Table 4, entry 1); at 40 °C and in the presence of 1 equiv a 1:2 mixture of **6** and **8** was detected (Table 4, entry 2). If TFA was added to the reaction mixture and stirred at room temperature only benzil **8** was found (Table 4, entry 3). A product mixture with similar ratios was observed, when methyl- and ethyl-substituted methylesters *rac*-**2b** and *rac*-**2c** were employed in refluxing dichloromethane in the presence of TFA (Table 4, entries 4 and 5). On the other hand, the employment of FIBX as oxidant at room temperature without TFA resulted in a product mixture of **6** (30%) and benzoin **9** (70%) (Table 4, entry 6).[27] Compound **9** was not detected in any other oxidation reaction.

Table 4
Oxidation of *meso*-hydrobenzoin using iodylarenes with and without TFA



7 6 8 9

Entry	Solvent	Temperature [°C]	Equiv TFA	Iodyl-arene	Yield **6**[a] [%]	Yield **8**[a] [%]	Yield **9**[a] [%]
1	CH_3CN	Reflux	—	**2a**	100	—	—
2	CH_3CN	40	1.0	**2a**	32	68	—
3	CH_3CN	20	1.0	**2a**	—	100	—
4	CH_2Cl_2	Reflux	1.0	*rac*-**2b**	32	68	—
5	CH_2Cl_2	Reflux	1.0	*rac*-**2c**	35	65	
6	CH_3CN	20	—	FIBX	30 (20)[b]	—	70 (64)[b]

[a] Determined by ^1H NMR.
[b] Yield.

It is obvious that the temperature as well as the presence of TFA takes crucial influence on the products observed. Apart from the reaction employing FIBX as oxidant, product mixtures of benzaldehyde and benzil were found, the latter being the major fraction, when the product mixtures where heated in presence of TFA. Only reactions either being heated or conducted in presence of TFA at room temperature resulted in either benzaldehyde or benzil. When FIBX was employed at room temperature without TFA, the major fraction of the reaction mixture was the originally desired product **9**. These results suggest the oxidation strength of iodylarenes synthesized in this project to be greater than the one of FIBX, since only compounds resulting from over-oxidation of *meso*-hydrobenzoin were observed.

Iodylarene **2a** was also employed in oxidation reactions of secondary alcohols, such as cyclopentanol and 2,3-butanediol together with TFA in dichloromethane at 40 °C, but only starting material was recovered from these reactions.

3. Conclusion

Several commonly used oxidation methods have been applied to iodoarenes. The desired λ^5-iodanes could be synthesized and isolated in good to excellent yields. These iodylarenes were subsequently employed as oxidants for different substrates, in order to determine their oxidative potential. Sulfides like thioanisole, primary alcohols, such as benzyl alcohol and secondary alcohols such as *meso*-hydrobenzoin were oxidized successfully to the respective sulfoxides, aldehydes, and ketones. However, even though the iodylarenes employed in the oxidation of thioanisole were enantiomerically pure, the enantiomeric excess could not be determined. A crystal structure analysis for **2d** was obtained and analyzed.

4. Experimental part

4.1. General

Air-insensitive reactions were conducted in loosely covered vials. Inert reactions were conducted under an atmosphere of argon in oven dried glassware. A Büchi GKR-50 Kugelrohr distillation apparatus was employed for Kugelrohr distillations. Dichloromethane was dried over calcium hydride, THF, and diethyl ether over sodium and benzophenone. All other high purity solvents and also all chemicals used were purchased from Sigma–Aldrich, Alfa Aesar, Fluka or Acros. NMR spectroscopy was performed on Bruker DPX 500, DPX 400 or Bruker DPX 250. The chemical shifts δ are given in parts per million relative to tetramethylsilane. Coupling constants J are given in Hertz. The multiplicity of signals is designated: s=singlet, d=doublet, t=triplet, q=quartet, dt=doublet of triplets, td=triplet of doublets, sex=sextet, m=multiplet. Mass spectroscopic measurements have been performed on Waters LCR Premier XE—tof. High resolution mass spectrometry for some compounds was carried out by EPSRC Swansea. Gas Chromatography Mass Spectrometry was collected on a Perkin–Elmer 8700, beta-column. High Pressure Liquid Chromatography was done on Shimadzu Class VP. Analytical chiral columns (0.46 cm×25 cm) were used for separation of enantiomers (Chiracel OB, OB-H, OD-H, AD) at solvent flow rates of 0.5 mL/min; for preparative separations of enantiomers a chiral preparative Chiracel OD column (2 cm×25 cm) was used, the solvent flow rate was 3 mL/min. IR spectra were collected on a Perkin–Elmer 1600 series FTIR. Wave numbers are quoted in cm^{-1}; samples were measure either neat or as KBr disc. Melting points were measured on a Gallenkamp variable heater and are uncorrected.

4.2. General procedures (GP)

4.2.1. GP 1: alkylation in benzylic position. To a freshly prepared LDA solution (1.8 mmol, 1.2 equiv) was added dropwise a solution of the respective iodoarene ester (1.5 mmol, 1 equiv) in dry THF at −78 °C and stirred for 30 min at this temperature. Then the alkylhalogenide (1.8 mmol, 1.2 equiv) was added dropwise and the mixture was stirred at room temperature for 2–3 h. After reaction completion, the mixture was poured into aqueous saturated NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3×8 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed after filtration. If the ester was alkylated twice, the procedure was repeated with the crude reaction mixture without further purification. The crude product was purified by flash chromatography (petroleum ether–diethyl ether 4:1).

4.2.2. GP 2: oxidation using DMPO. An iodoarene was stirred in a solution of DMDO (1–3 equiv, depending on reaction progress) in acetone at room temperature for 8 h. After reaction completion, the solvent was evaporated and the resulting solid washed with diethyl ether.

4.2.3. GP 3: oxidation using NaOCl. CH_2Cl_2 was added to a vigorously stirred suspension of an iodoarene (1 equiv, 0.5 mmol) and a 4% aq sodium hypochlorite solution (2 mL) and then acetic acid (0.5 mL) was added dropwise during 10 min at room temperature. The resulting mixture was stirred overnight. The reaction mixture was then extracted with CH_2Cl_2 (5×10 mL). The combined extracts were washed with aqueous saturated $NaHCO_3$ solution (6 mL),

dried over $MgSO_4$. The solvent was evaporated under reduced pressure after filtration to afford the crude product.

4.2.3.1. 2-Methyl-(2-iodophenyl)propionic acid methylester ***1d***. Synthesis according to GP 1 from **1a** (338 mg, 1.20 mmol) and methyl iodide (208 mg, 1.50 mmol). After work-up and solvent evaporation, the procedure was repeated. The product was purified by flash column chromatography (petrol ether:diethyl ether 4:1). Yield: 75% (274 mg, 900 μmol), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.63 (s, 6H, 4,5-CH_3), 3.67 (s, 3H, 1-CH_3), 6.79 (td, 1H, J=7.8, 2.2 Hz, 9-CH), 7.33–7.43 (m, 2H, 7,8-CH), 7.77 (dd, 1H, J=7.8, 1.2 Hz, 10-CH) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=26.6 (4,5-C), 49.4 (3-C), 52.2 (1-C), 98.6 (11-C), 126.3, 127.3, 129.6, 132.9, 145.9 (6-C), 176.3 (2-C) ppm. Material was used directly in oxidation reaction.

4.2.3.2. (2-Iodoxyphenyl)acetic acid methylester ***2a***. Synthesis according to GP 2 **1a** (190 mg, 690 μmol) was stirred in a solution of DMDO in acetone (65.7 mM, 21.0 mL, 1.38 mmol, 2 equiv) for 8 h at room temperature. Yield 44% (94.2 mg, 306 μmol), colorless solid. Decomposition point: 141–142 °C. IR (KBr) (ν): 3374.3 (m) (H_2O), 2922.6 (m), 1699.5 (s), 1673.0 (m), 1439.1 (s), 1358.2 (s), 1278.1 (s), 1250.6 (s), 1160.9 (s), 989.3 (s), 786.3 (s), 755.5 (s) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ=3.73 (s, 3H, 9-CH_3), 4.24 (s, 2H, 7-CH_2), 7.40 (d, 1H, J=7.5 Hz, 5-CH), 7.52 (t, 1H, J=7.4 Hz, 3- or 4-CH), 7.61 (t, 1H, J=7.6 Hz, 3- or 4-CH), 7.99 (d, 1H, J=7.8 Hz, 2-CH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ=38.6 (7-C), 53.2 (9-C), 127.7, 129.1, 132.3, 132.4, 134.0 (6-C), 151.1 (1-C), 173.6 (8-C) ppm. m/z (EI)=276.0 (5), 231.8 (5), 216.9 (33), 149.0 (100), 121.0 (46), 90.0 (53), 63.0 (32). Molecular peak could not be obtained. HRMS (ESI): found $[M+H]^+$ 308.9619, $C_9H_{10}O_4I$ requires 308.9618.

4.2.3.3. (±)-2-(2-Iodoxyphenyl)propionic acid methylester rac- ***2b***. According to GP 2 *rac*-**1b** (200 mg, 690 μmol) was stirred in a solution of DMDO in acetone (65.7 mM, 21.0 mL, 1.38 mmol, 2 equiv) for 8 h at room temperature. Yield: 67% (150 mg, 465 μmol) colorless solid. Mp 158 °C. IR (KBr) (ν): 3448.6 (m) (H_2O), 3060.0 (s), 2947.7 (m), 1734.7 (m), 1457.9 (s), 1432.9 (m), 1282.4 (s), 1263.6 (s), 1204.8 (s), 1115.6 (m), 1078.0 (s), 724.6 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.56 (d, 3H, J=7.0 Hz, 4-CH_3), 3.67 (s, 3H, 1-CH_3), 4.67 (q, 1H, J=7.0 Hz, 3-CH), 7.46 (dd, 1H, J=7.2, 1.5 Hz, 6-CH), 7.54–7.60 (m, 2H, 7,8-CH), 8.07 (dd, 1H, J=7.5, 1.8 Hz, 9-CH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ=18.7 (4-C), 49.7 (3-C), 53.0 (1-C), 128.2, 128.9, 129.5, 132.6, 140.0 (5-C), 151.2 (10-C), 174.4 (2-C) ppm. m/z (ESI)=509.0 (2), 413.3 (7), 391.3 (52), 345.0 (26), 323.0 (100), 319.0 (68), 305.0 (21), 161.1 (10). HRMS (ESI): $[M+H]^+$ found 322.9778, $C_{10}H_{12}O_4I$ requires 322.9775.

4.2.3.4. (±)-1-Ethyl-1-(2-iodoxyphenyl)acetic acid methylester rac- ***2c***. According to GP 3 *rac*-**1c** (208 mg, 684 μmol) was stirred in a solution of DMDO in acetone (54.0 mM, 12.0 mL, 648 μmol, 1.06 equiv) for 24 h at room temperature. Yield: 63% (144 mg, 428 μmol), colorless solid. Combustion point: 166 °C. IR (KBr) (ν): 2969.8 (m), 2945.3 (m), 2875.8 (s), 1734.2 (m), 1470.0 (s), 1431.9 (s), 1318.1 (s), 1263.6 (s), 1245.8 (s), 1203.9 (s), 1155.6 (m), 734.3 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ=0.88 (t, 3H, J=7.3 Hz, 5-CH_3), 1.83–1.92 (m, 1H, 4-CH_A), 2.09–2.18 (m, 1H, 4-CH_B), 3.61 (s, 3H, 1-CH_3), 4.25 (dd, 1H, J=8.4, 6.5 Hz, 3-CH), 7.41 (dd, 1H, J=6.2, 1.3 Hz, aromatic), 7.48–7.54 (m, 3H, aromatic), 8.03–8.05 (m, 1H, 10-CH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ=11.8 (5-C), 24.7 (4-C), 49.5 (3-C), 52.0 (1-C), 124.9, 128.1, 128.2, 131.7, 137.2 (6-C), 150.7 (11-C), 172.9 (2-C) ppm. m/z (ESI)=391.3 (3), 359.0 (9), 337.0 (100), 333.0 (11), 303.0 (4), 175.1 (6). HRMS (ESI): $[M+H]^+$ found 336.9934, $C_{11}H_{14}O_4I$ requires 336.9931.

4.2.3.5. 1,1-Dimethyl-1-(2-iodoxyphenyl)acetic acid methylester ***2d***. According to GP 2 **1d** (622 mg, 2.05 mmol) was stirred in a solution of DMDO in acetone (69.0 mM, 60 mL, 4.09 mmol, 2 equiv) together with acetic acid (258 μL, 4.50 mmol, 2.2 equiv) for 24 h at room temperature. Yield: 74% (507 mg, 1.51 mmol), colorless solid. Decomposition point: 150 °C. IR (neat) (ν): 3417.5 (m) (H_2O), 2965.6 (m), 1699.5 (s), 1458.4 (s), 1433.3 (m), 1282.7 (s), 1252.6 (s), 1152.1 (s), 1101.9 (m), 976.4 (m), 850.9 (m), 775.5 (s), 740.4 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.77 (s, 6H, 4,5-CH_3), 3.82 (s, 3H, 1-CH_3), 7.49–7.55 (m, 3H, 7,8,9-CH), 8.37 (d, 1H, J=7.5 Hz, 10-CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=29.1 (4,5-C), 47.2 (3-C), 54.5 (1-C), 127.5, 127.6, 129.7, 133.0, 142.6 (6-C), 150.1 (11-C), 180.5 (2-C) ppm. m/z (ESI)= 337.0 (6), 322.0 (45), 305.0 (3), 196.1 (100), 177.0 (7), 119.1 (4), 52.1 (41), 44.1 (8). Exact mass within error limits could not be determined.

4.2.3.6. (±)-2-(2-Iodoxyphenyl)-2-propylpropionic acid methylester rac- ***2e***. According to GP 2 *rac*-**1e** (83.9 mg, 218 μmol) was stirred in a solution of DMDO in acetone (53.2 mM, 4.1 mL, 218 μmol, 1 equiv) for 8 h at room temperature. Yield: 54% (48.8 mg, 117 μmol), colorless solid. Decomposition point: 153 °C. IR (KBr) (ν): 3434.6 (m), 3053.1 (w), 2944.1 (s), 2856.9 (m), 1709.0 (s), 1469.2 (m), 1452.8 (s), 1431.0 (s), 1371.1 (w), 1294.8 (m), 1267.5 (s), 1245.7 (s), 1202.1 (m), 1136.7 (s), 1076.8 (m), 973.2 (m), 929.6 (w), 853.3 (w), 771.6 (s), 722.5 (s), 586.3 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.91 (t, 3H, 6-CH_3), 1.08–1.13 (m, 1H, 5-CH_A), 1.21–1.28 (m, 1H, 5-CH_B), 1.75 (s, 3H, 7-CH_3), 2.02–2.15 (m, 2H, 4-CH_2), 3.87 (s, 3H, 1-CH_3), 7.49 (dd, 1H, J=7.9, 1.4 Hz, 9-CH), 7.59 (td, 1H, J=7.9, 1.4 Hz, 10- or 11-CH), 7.67 (td, 1H, J=7.2, 1.4 Hz, 10- or 11-CH), 8.45 (dd, 1H, J=8.0, 1.4 Hz, 12-CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.5 (6-C), 18.5 (5-C), 25.2 (7-C), 45.3 (4-C), 51.3 (1-C), 54.5 (3-C), 127.5, 128.4, 129.9, 133.2, 133.7 (8-C), 141.3 (13-C), 180.8 (2-C) ppm. m/z (ESI)=729.0 (100), 365.0 (79), 331.0 (1), 232.0 (3), 205.1 (64). HRMS (ESI): $[M+H]^+$ found 365.0235, $C_{13}H_{18}O_4I$ requires 365.0250.

4.2.3.7. 2-Iodoxyphenyl-1-(1S)-endo-bornylether ***2f***. According to GP 2 **1f** (83.9 mg, 218 μmol) was stirred in a solution of DMDO in acetone (53.2 M, 4.1 mL, 218 μmol, 1 equiv) for 8 h at room temperature. Yield: 54% (48.8 mg, 117 μmol). Mp 150 °C. $[\alpha]_D^{25}$ −2.0 (c 0.205, DMSO). IR (KBr) (ν): 3434.6 (m), 3053.1 (w), 2955.0 (s), 2867.8 (m), 2355.5 (w), 1725.4 (m), 1681.8 (s), 1583.7 (m), 1458.3 (m), 1376.6 (m), 1311.2 (s), 1251.2 (m), 1142.2 (s), 1109.5 (s), 1038.6 (m), 1016.8 (m), 973.2 (m), 886.0 (w), 771.6 (s), 744.3 (s), 678.9 (m), 635.3 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.91 (s, 3H, 10-CH_3), 0.93 (s, 3H, 8-CH_3), 0.96 (s, 3H, 10′-CH_3), 1.17 (dd, 1H, J=13.9, 3.5 Hz, bornyl), 1.27–1.34 (m, 1H, bornyl), 1.42–1.48 (m, 1H, bornyl), 1.73–1.86 (m, 2H, bornyl), 2.01–2.13 (m, 1H, bornyl), 2.47–2.53 (m, 1H, bornyl), 5.17–5.22 (m 1H, 2-CH), 7.72 (t, 1H, J=7.5 Hz, 14-CH), 7.95–8.00 (m, 1H, 13-CH), 8.13 (d, 1H, J=7.6 Hz, 12-CH), 8.50 (d, 1H, J=7.8 Hz, 15-CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.0 (8-C), 19.2 (10- or 10′-C), 20.0 (10′- or 10-C), 27.6, 28.3, 37.0, 45.2, 48.4, 49.7, 84.8 (2-C), 123.2, 125.2, 127.3, 130.8, 133.2 (11-C), 135.5 (16-C), 168.8 (17-C) ppm. m/z (ESI)=480.0 (30), 417.0 (9), 384.9 (3), 343.9 (6), 321.9 (100), 304.9 (22), 263.9 (16), 232.0 (5), 213.0 (4). HRMS (ESI): $[M+H]^+$ found 417.0554, $C_{17}H_{22}O_4I$ requires 417.0563.

4.2.3.8. 2-Iodoxybenzoic acid (2R,4R,7R)-menthylester ***2g***. According to GP 2 **1g** (65.4 mg, 169 μmol) was stirred in a solution of DMDO in acetone (54.5 M, 3.1 mL, 169 μmol, 1 equiv) for 8 h at room temperature. Yield: 64% (45.1 mg, 108 μmol), colorless solid. Decomposition point: 180 °C. $[\alpha]_D^{25}$ +20.0 (c 0.10, DMSO). IR (KBr) (ν): 2965.0 (m), 2924.0 (m), 2876.3 (m), 1607.4 (m), 1562.5 (s), 1438.2 (s), 1340.8 (m), 832.1 (m), 742.0 (s), 695.2 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.79 (d, 3H, J=6.9 Hz, 10-CH_3), 0.82–0.88 (m, 1H, menthyl), 0.93 (d, 3H, J=7.0 Hz, 9-CH_3), 0.95 (d, 3H, J=6.9 Hz, 9′-CH_3), 1.12–1.18 (m, 1H, menthyl), 1.21 (t, 1H, J=6 Hz, menthyl), 1.54–1.65 (m, 2H, menthyl), 1.74–1.79 (m, 2H, menthyl), 1.86–1.93 (m, 1H, menthyl), 2.15–2.22 (m, 1H, menthyl), 5.05 (td, 1H, J=11.1, 4.6 Hz, 2-CH), 7.76 (td, 1H, J=7.5, 1.0 Hz, 14-C), 8.00 (td, 1H, J=7.5, 1.3 Hz, 13-C), 8.14 (dd, 1H, J=7.6, 1.2 Hz, 12-C), 8.53 (d, 1H, J=7.9 Hz,

15-C) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=16.9 (10-C), 21.0 (9- or 9′-C), 22.2 (9′- or 9-C), 23.9, 26.9, 31.9, 34.3, 40.9, 47.5, 79.5 (2-C), 125.1, 130.8, 133.5, 135.5, 139.5 (11-C), 147.7 (16-C), 167.8 (1-C) ppm. *m*/*z* (ESI)=482.1 (79), 419.1 (24), 384.9 (12), 343.9 (48), 321.9 (100), 305.9 (54), 288.9 (48), 264.9 (40), 247.9 (38), 232.0 (4), 213.0 (6). HRMS (ESI): $[M+H]^+$ found 419.1711, $C_{17}H_{24}O_4I$ requires 419.1719.

4.2.3.9. 2-Iodoxybenzoic acid (2R)-endo-fenchylester ***2h****.* According to GP 2 **1h** (73.7 mg, 192 μmol) was stirred in a solution of DMDO in acetone (53.9 mM, 3.6 mL, 192 μmol, 1 equiv) for 8 h at room temperature. Yield: 99% (79.3 mg, 190 μmol), colorless solid. Mp 163 °C. $[\alpha]_D^{25}$ +24.0 (*c* 0.20, DMSO). IR (KBr) (ν): 3439.5 (m), 3064.0 (w), 2954.9 (s), 2871.5 (m), 2363.5 (w), 2322.6 (w), 1725.4 (m), 1681.8 (s), 1583.7 (m), 1458.3 (m), 1365.7 (m), 1340.0 (s), 1300.3 (s), 1136.8 (s), 1109.5 (s), 1033.2 (m), 984.1 (m), 967.8 (m), 771.6 (s), 738.9 (s), 640.8 (m), 613.5 (m) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.84 (s, 3H, 8-CH_3), 1.12 (s, 3H, 10-CH_3), 1.20 (s, 3H, 10′-CH_3), 1.20–1.28 (m, 1H, fenchyl), 1.30 (dd, 1H, *J*=10.5, 1.4 Hz, fenchyl), 1.51–1.58 (m, 1H, fenchyl), 1.66–1.71 (m, 1H, fenchyl), 1.74–1.82 (m, 2H, fenchyl), 1.85–1.91 (m, 1H, fenchyl), 4.70 (d, 1H, *J*=1.1 Hz, 2-CH), 7.74 (td, 1H, *J*=7.5, 1.0 Hz, 14-CH), 7.98 (td, 1H, *J*=7.8, 1.3 Hz, 13-CH), 8.15 (dd, 1H, *J*=7.6, 1.3 Hz, 12-CH), 8.51 (dd, 1H, *J*=7.9, 0.8 Hz, 15-CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=19.8 (8-C), 20.5, 26.0, 27.1, 29.9, 40.4, 41.7, 48.5, 49.1, 90.7 (2-C), 125.2, 127.1, 130.6, 133.3, 135.5 (11-C), 146.3 (16-C), 168.7 (1-C) ppm. *m*/*z* (ESI)=480.1 (100), 417.1 (19), 384.9 (9), 343.9 (47), 321.9 (46), 305.9 (20), 264.9 (19), 247.9 (13), 165.1 (2). HRMS (ESI): $[M+H]^+$ found 417.0553, $C_{17}H_{22}O_4I$ requires 417.0563.

4.2.3.10. 2-Iodoxybenzoic acid propylester ***2i****.* According to GP 3 **1j** (58.0 mg, 200 μmol) was stirred together with NaOCl (2.0 mL) and acetic acid (200 μL) in CH_2Cl_2 (8 mL) at room temperature for 3 days. Yield: 60% (38.8 mg, 120 μmol), colorless solid. Decomposition point: 186 °C. IR (ν): 3417.5 (w) (H_2O), 2965.6 (w), 1679.4 (m), 1584.0 (w), 1463.5 (w), 1393.2 (w), 1302.8 (m), 1142.1 (w), 1112.0 (w), 750.4 (m) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.02 (t, 3H, *J*=7.4 Hz, 1-CH_3), 1.82 (sex, 2H, *J*=7.1 Hz, 2-CH_2), 4.33 (t, 2H, *J*=6.7 Hz, 3-CH_2), 7.66 (t, 1H, *J*=7.5 Hz, 7- or 8-CH), 7.92 (t, 1H, *J*=7.4 Hz, 7- or 8-CH), 8.09 (d, 1H, *J*=7.2 Hz, 6-CH), 8.43 (d, 1H, *J*=7.9 Hz, 9-CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=10.7 (1-C), 22.1 (2-C), 69.0 (3-C), 125.2, 126.8, 130.6, 132.2, 135.3 (5-C), 149.9 (10-C), 168.4 (4-C) ppm. *m*/*z* (ESI)=322.9 (100), 321.9 (26), 305.9 (12), 280.9 (9), 264.9 (6), 202.1 (3). HRMS (ESI): $[M+H]^+$ found 322.9776, $C_{10}H_{12}O_4I$ requires 322.9780.

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