Chiral Hypervalent Organo-Iodine(III) Compounds

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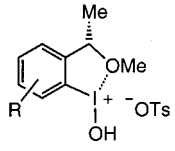
A series of *ortho*-substituted chiral hypervalent iodine reagents has been synthesized utilizing a zirconium-mediated iodoacylation reaction, which was followed by a stereoselective reduction, methylation, and an oxidation/ligand-exchange sequence. The evaluation of these new compounds as stereoselective electrophilic reagents towards alkenes and ketones is reported. Enantioselectivities as high as 65% have been achieved in the dioxytosylation of styrene and of up to 40% in the oxytosylation of propiophenone. X-ray structure analysis and ab initio calculations on a hypervalent iodine salt have been used to develop a model for rationalizing the stereoselectivities in these reactions with chiral hypervalent iodine reagents. In this model, high enantiomeric excess in the reaction correlates with the relative population of a conformation in which a methyl group on the asymmetric carbon atom is in the axial position. This work provides new opportunities for the synthesis of new and more efficient chiral hypervalent iodine reagents for stereoselective synthesis.

Introduction

Hypervalent iodine compounds have found broad application in organic chemistry and are frequently used in synthesis.[1−5] The investigation of their efficacy as oxidants and as electrophilic reagents, and the development of new reactions of such species is of current interest. They are of high synthetic potential by virtue of the fact that they are nonmetallic oxidation and oxygenation reagents, thus circumventing the problem of toxicity associated with many of the transition metals commonly used for carrying out such reactions. Using the commercially available hydroxy(tosyloxy)iodobenzene (Koser's reagent), alkenes can be dioxytosylated, ketones can be α-oxytosylated, and sulfides can be converted into sulfoxides.[6−8] In some reactions employing hypervalent iodine reagents, products with new stereocenters are generated. Until recently, only very few chiral hypervalent iodine compounds had been reported and hence reactions with these compounds are very rare.[9−18]

We have developed the synthesis of a series of chiral hypervalent iodine compounds of type **1** and have reported their use in stereoselective reactions with alkenes and ketones.[19,20] It was shown previously that the placement of a chiral moiety *ortho* to the iodine atom on the aromatic ring results in compounds that react selectively with alkenes.[19] These investigations showed a 1-methoxyethyl substituent to give the highest degree of selectivity achieved to date and therefore this substituent has also been utilized in the present study. Likewise, the placement of a second substituent *ortho* to the iodine atom was found to further increase the selectivity in the additions of these reagents to alkenes.[20] In order to explore the scope of this selectivity, a number of *ortho*-alkyloxy-, *ortho*-alkyl-, and *ortho*-aryl-substituted compounds have been synthesized.

Many details of the reaction mechanism, in particular with respect to the chiral induction, are still unclear. Herein, we report our progress in the synthesis and evaluation of new reagents according to a generally applicable procedure. In addition, we present ab initio calculations aimed at rationalizing the chiral induction by reagents of type **1**. These results might be useful in the further optimization of chiral reagents, leading to more efficient stereoselective reactions.



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Results and Discussion

Synthesis

The synthetic strategy for obtaining the new chiral hypervalent iodine reagents described herein is based on a simple, four-step sequence. The requisite aryl halide was subjected to a zirconium-mediated reaction with acetonitrile and iodine to give the corresponding iodoaryl methyl ketones. Stereoselective reduction then generated the chiral alcohols, which were easily methylated and oxidized to the required

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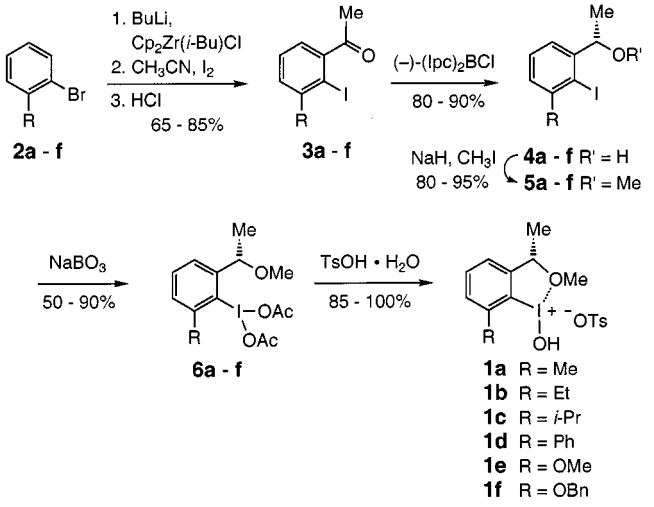
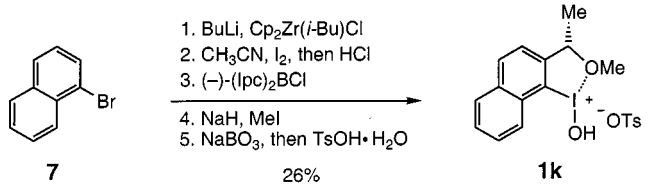
iodine(III) compounds. This strategy proved very effective in generating a host of differently substituted compounds in high yields and with excellent asymmetric induction.

Hypervalent iodine reagents bearing an *ortho* substituent were synthesized from the corresponding substituted halides as shown in Scheme 1. Lithiation of the bromobenzene derivatives **2** and reaction with (isobutyl)zirconocene chloride,[21] followed by treatment with acetonitrile and iodine gave the required acylation products **3** in good yields. Asymmetric reduction of the iodo ketones **3** with (−)-*B*-chlorodiisopinocampheylborane [(−)-(Ipc)$_2$BCl] [22−24] gave excellent yields of the benzylic alcohols **4** with very high enantioselectivities (94−99% *ee*). Subsequent methylation of the resulting secondary alcohols with sodium hydride and methyl iodide proved facile. This was followed by oxidation with sodium perborate tetrahydrate in glacial acetic acid to give the diacetoxyiodo compounds **6**.[25] Ligand exchange with toluenesulfonic acid monohydrate furnished compounds **1a**−**1f** in good yields. These compounds were found to be unstable and were therefore generated in situ prior to reaction with styrene or propiophenone. Additionally, 1-bromonaphthalene (**7**) was subjected to the above reaction sequence to give **1k** in 26% overall yield (Scheme 2).

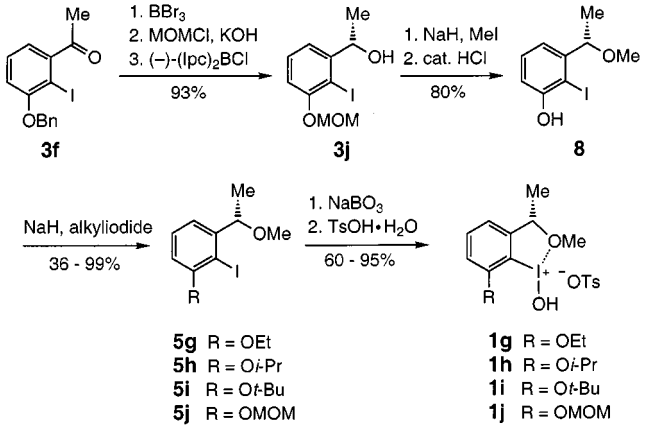


Scheme 1. Synthesis of chiral hypervalent iodine compounds of type **1**



Scheme 2. Synthesis of chiral hypervalent iodine compound **1k**

Hypervalent iodine reagents bearing an *ortho*-alkyloxy substituent were synthesized in a similar fashion from the corresponding protected *ortho*-hydroxy compound **3f**, as shown in Scheme 3. 2-Bromophenol was protected as the benzyl ether[26] and subjected to the reaction sequence with acetonitrile and iodine to give iodo ketone **3f** in good yield. Debenzylation and re-protection[27] of the phenol as an MOM ether, followed by stereoselective reduction with (−)-(Ipc)$_2$BCl, gave the enantiomerically pure chiral alcohol **3j** after recrystallization. After methylation, the MOM ether was cleaved using a catalytic amount of hydrochloric acid and the resulting phenol derivative **8** was treated with sodium hydride and the appropriate alkyl halides to give the desired *ortho*-alkyloxy iodo compounds **5g**−**5j**. The *tert*-butyl ether **5i** was synthesized in low yield (36%) by reaction of **8** with *tert*-butyl 2,2,2-trichloroacetimidate and boron trifluoride−diethyl ether.[28]



Scheme 3. Synthesis of chiral *ortho*-alkyloxy-substituted hypervalent iodine compounds **1g**−**1j**

Perborate oxidation of the *ortho*-alkyloxy iodo compounds **5** in glacial acetic acid gave moderate to good yields of the diacetoxyiodo compounds, which were converted into the final hydroxy(tosyloxy)iodo compounds **1g**−**1j** by means of a ligand-exchange reaction with toluenesulfonic acid monohydrate. These compounds also proved to be unstable and were thus generated in situ during the reactions with styrene and propiophenone. NMR analysis of the crude reaction mixtures indicated a 60−95% conversion into the desired hydroxy(tosyloxy)iodine(III) reagents **1**, with the material balance being accounted for by unchanged iodine(I) compound **5**.

Reactions

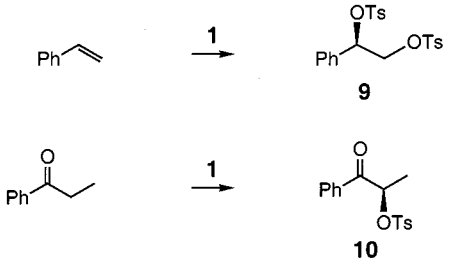
Reactions of the hypervalent iodine reagents **1a**−**1k** with alkenes and ketones were carried out using styrene and propiophenone as representative substrates.[29] The results of the enantioselective dioxytosylation of styrene and the α-oxytosylation of propiophenone (Scheme 4) are given in Table 1. This evaluation of the chiral hypervalent iodine reagents shows that increasing the size of the *ortho* substituent from R = H through R = Me (**1a**) to R = Et (**1b**) results in an increased selectivity in the dioxytosylation of styrene. The unsubstituted reagent yielded the product **9** with 33% *ee*,[19] whereas using **1a** and **1b**, **9** was obtained with 47% and 65% *ee*, respectively. Likewise, the *ortho*-methoxy compound gave an *ee* of 52% in the dioxytosylation of styrene.[20] A similar trend is seen in the oxytosylation of propiophenone, where an increase in selectivity is also

Table 1. Enantioselectivity in the dioxytosylation of styrene and in the α-oxytosylation of propiophenone

Compound	R	**9** [*ee*][a]	**10** [*ee*][a]
1a	Me	47%	[b]
1b	Et	65%	40%
1c	*i*Pr	48%	[b]
1d	Ph	13%	[b]
1e	OMe	52%	28%
1f	OBn	35%	29%
1g	OEt	30%	14%
1h	O*i*Pr	28%	17%
1i	O*t*Bu	34%	11%
1j	OMOM	43%	15%
1k	Naphthyl	36%	[b]

[a] All reactions were carried out at −30 °C. Enantiomeric excesses were determined by HPLC using a Chiralcel OD column. − [b] Not determined.

observed on going from **1e** to **1b** (Table 1). This is suggestive of a cooperative effect between the *ortho* substituent and the chiral moiety. However, further increases in steric bulk at the *ortho* position indicate a limit to the size/selectivity trend. For example, in the *ortho*-alkyl series, maximum selectivity is observed for the *ortho*-ethyl compound **1b**, with lower selectivity being observed for reagents **1** bearing both smaller and larger substituents. The marked reduction in selectivity seen with the phenyl-substituted compound **1d** can be attributed to unfavorable π-stacking interactions between the substituent and the phenyl ring of the substrate.



Scheme 4. Reactions of chiral hypervalent iodine compounds **1**

In the *ortho*-alkyloxy series, all the alkyloxy compounds **1e**−**1j** give roughly the same selectivity in the reaction with styrene, with the methoxy substituent giving the best result. No significant relationship between the size of the alkyloxy group and the selectivity can be seen. This could in part be due to the formation of a hydrogen bond between the ether oxygen atom and the hydroxy group on the iodine atom. This would minimize the steric effect of the alkyloxy substituent on the iodine atom by forcing the alkyloxy substituent away from the iodine atom. Such a hydrogen bond was found in the structures of **1e**−**1j** generated by the ab initio calculations described in the next section. Likewise, only a weak correlation is seen between the polarity of the *ortho* substituent and the selectivity, with alkyl compounds being slightly more selective than the corresponding alkyloxy compounds.

Computational Studies

We performed computational studies on the hypervalent iodine compounds in order to obtain further insight into the origin of the observed stereoselectivities and to provide a structural basis for further optimizations of these compounds. We started our computational studies from the previously published X-ray structure of **1l**.[20] The T-shaped structure, which stems from the stereoelectronic requirements of a three-center four-electron system, is a typical feature of hypervalent iodine compounds[30] and is also found in **1l**. In contrast to Koser's reagent, the two oxygen atoms nearest to the iodine atom in the present system are the oxygen atom of the hydroxy group (I−OH: 1.94 Å) and the methoxy oxygen atom (I−OMe: 2.47 Å). Thus, the tosylate oxygen atom of Koser's reagent is replaced by the methoxy oxygen atom of **1l**. The three sulfonate oxygen atoms are even further away from the iodine atom (I−OTs: 2.82 Å, 3.40 Å, 4.43 Å). Because of the ionic character of compounds **1**, the interaction with the tosylate group can be considered as being purely electrostatic and calculations have been performed starting from the X-ray data of **1l** neglecting the tosylate counterion.[20]

Relatively few computational studies of hypervalent iodine compounds have hitherto appeared in the literature,[31−36] hence accounts of the performances of different computational methods and indications for the choice of basis sets are limited. We chose the B3LYP hybrid density functional,[37] which has evolved in recent years as an accurate and computationally efficient method for the calculation of organic molecules.[38,39] For the basis set, we used the LANL2DZ effective core potential.[40] All calculations were performed using the Gaussian 94 and Gaussian 98 series of programs.[41]

We started our studies with a validation of the computational methodology through comparison of the calculated structure with the known X-ray structure of **1l**. As shown in Figure 1, the key geometrical parameters of the experimental and computed structures are in good agreement. The I−OMe distance (X-ray: 2.47 Å) is calculated as 2.39 Å, while the I1−C2−C3 angle (X-ray: 116.1°) is calculated as 117.6°.

Having validated this computational method, we proceeded to use it to calculate the structures **11** without the tosylate counterion. We found the oxygen atom of the chiral moiety to be oriented towards the iodine atom. Additionally, the T-shaped structure around the iodine atom was found to be preserved in all these molecules. Despite the presence of an additional methoxy group in **11m**, the geometry around the iodine atom is virtually identical to that in **11l**, which has no additional substituent, and no interference with the chiral moiety is observed.

For **11e**, which bears a methoxy group in the second *ortho* position, a hydrogen bond between the proton of the hydroxy group at the iodine atom and the oxygen atom of the methoxy group with an O−H distance of 1.8 Å is calculated. Because of this additional attraction, the distance between the oxygen atom of the chiral side chain (O5) and

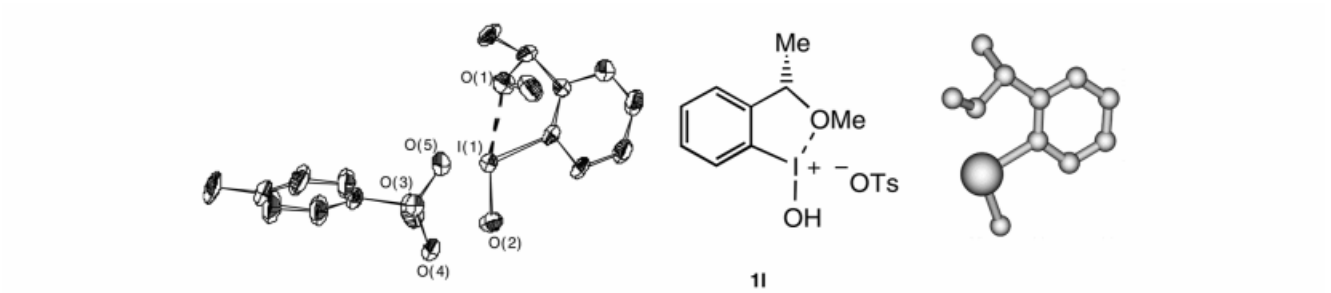
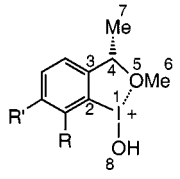


Figure 1. X-ray structure of **11l** and the calculated structure of the corresponding cation

the iodine atom (I1) is greater (2.47 Å) than that in **11m** or **11l** (2.39 Å). Moreover, when compared to the situation in **11m** or **11l**, the stereogenic carbon atom of **11e** is twisted out of the aromatic plane. This is reflected in a larger dihedral angle D1 (see Table 2). As a result of this torsion, the methyl group C7 resides in a pseudoaxial position in relation to the five-membered ring containing the iodine atom and the oxygen atom of the chiral side chain. In addition to the electronic effects, the substituent R in the second *ortho* position to the iodine atom also exerts an influence on the chiral moiety through steric interactions, leading to the higher selectivities seen in Table 1. Therefore, other substituents were introduced in this position. In all structures with the second *ortho* position to the iodine atom occupied by a substituent (**11a**−**11d**, Figure 2), the dihedral angle D1 is larger than that in **11l**.

Table 2. Selected calculated distances and angles for structures **11**

Structure	**11a**	**11b**	**11e-ax**	**11l**	**11m**
I1−O5	2.42 Å	2.40 Å	2.47 Å	2.39 Å	2.39 Å
I1−O8	2.04 Å	2.04 Å	2.03 Å	2.03 Å	2.03 Å
I1−C2−C3	113.6°	112.7°	118.1°	117.5°	117.4°
D1: C7−C4−O5−I1	83.2°	84.9°	84.3°	103.1°	103.7°
D2: O5−I1−C2−C3	−19.6°	−16.1°	−18.3°	−7.7°	−7.6°



11a R = Me R' = H
11b R = Et R' = H
11c R = *i*-Pr R' = H
11d R = Ph R' = H
11e R = OMe R' = H
11k R, R' = -CH=CH–CH=CH-
11l R = H R' = H
11m R = H R' = OMe

Figure 2. Structures **11** without the tosylate counterion

The differences in geometry of the optimized structures **11a**−**11d** with the methyl group C7 in a pseudoaxial position are too small to be meaningful and cannot be the reason for the observed difference in selectivity. Therefore, we focussed our attention on the structures and relative energy differences of low-energy conformers of **11a**−**11d** and **11l** having the methyl group C7 either in a pseudoaxial (**11l-ax**) or in a pseudoequatorial (**11l-eq**) orientation. The relative energy difference between the conformers provides their relative population according to the Boltzmann distribution. In **11l-ax**, with the methyl group C7 in a pseudoaxial position, the dihedral angle D1 is 103.1°. The optimization of **11l-eq** with the methyl group in a pseudoequatorial position did not show a new local minimum and **11l-ax** was again obtained. However, compounds **11a**−**11e** and **11k** did show local minima for both the pseudoequatorial (D1: 168.3−174.9°) and the pseudoaxial (D1: 81.5−85.3°) oriented methyl group. In the case of **11k**, this new equatorial conformation was in fact 2.1 kcal/mol lower in energy than the starting axial conformation.

Optimization of **11b** (R = Et) and **11c** (R = *i*Pr) gave two additional local minima as a result of the rotation of R. The energy differences between all these conformers are summarized in the Supporting Information. As shown in Figure 3, the facial discrimination of structure **11b** is higher with the methyl group in a pseudoaxial position than it is with this group in a pseudoequatorial position.

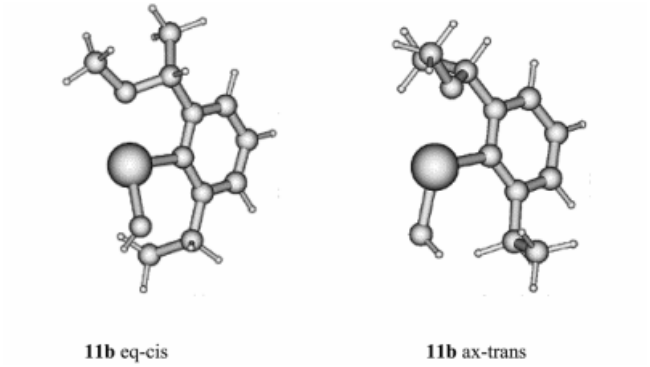


Figure 3. Pseudoequatorial and pseudoaxial positions of the methyl group C7 in **11b**

In all the structures other than **11k**, the pseudoaxial orientation of the methyl group is energetically favored. The reason for this can be deduced by analyzing the computed structures of **11a-eq**−**11e-eq** with a pseudoequatorial methyl group C7. The interatomic distance between C6 and C7 is only about 3.0 Å, bringing the hydrogen atoms in these positions into van der Waals contact. This steric repulsion might provide an explanation for the favored pseudoaxial orientation. Another reason might be the preferred arrangement of the T-shaped structure of hypervalent compounds.[30] The T-shaped structure of the molecule creates steric hindrance with the additional substituent R, which, in some cases, can lead to a lower energy conformer with a pseudoequatorial methyl group C7, as seen with **11k**.

In the dioxytosylation of styrene with **1k**, in which the methyl group is preferentially equatorial, an *ee* of just 36%

is observed, while with **1b**, which has the most favored axial position of C7, an *ee* of 65% is achieved (Table 1). This is in good agreement with the preferred orientations of the methyl group C7 calculated for **11k** and **11b**. However, compound **1d** gives only a low enantiomeric excess in the dioxytosylation of styrene. This was surprising at first glance, but the reaction with vinylcyclohexane to give 1-cyclohexyl-1,2-ditosyloxyethane shows that **1d** is indeed able to discriminate between the faces of double bonds quite well (44% *ee*). The lower selectivity seen in the dioxytosylation of styrene is probably due to an additional π-stacking interaction between the phenyl ring of the substrate and the phenyl substituent of **1d**.

Conclusion

In summary, we have presented a new, rapid synthesis for the generation of a large number of new chiral hypervalent iodine reagents. Evaluation of these new reagents by their reactions with styrene and propiophenone has indicated that enantioselectivities are improved by the presence of an *ortho* substituent, but that there is a limit to this improvement. Additionally, we have been able to show that B3LYP calculations on structures **11** can be used to rationalize the observed stereoselectivities in the dioxytosylation of styrene with the corresponding reagents **1**. Therefore, such calculations could be used in the future for the development of new chiral hypervalent iodine compounds. However, the proposed model is still limited because only structures of type **11** have been calculated and compared. In future, calculations on the intermediates and the transition states will have to be performed. Until new calculations and additional experimental efforts aimed at elucidating the mechanism of the dioxytosylation of alkenes are provided, the proposed model offers a powerful tool for the evaluation of these reagents and may be refined with new experimental data. Further investigations aimed at probing the effects of substituents on the selectivities of these reagents are ongoing.

Experimental Section

General Remarks: All reactions were performed under argon in anhydrous solvents. − ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, with samples in $CDCl_3$ solution using TMS as an internal standard. Melting points are uncorrected. − All starting materials (**2a**, **2b**, **2c**, **2d**, **2e**, **7**) are commercially available and were used without further purification. Compound **2f**[26] was synthesized according to the literature procedure.

General Procedures

GP1:[21] In a 200-mL Schlenk flask, zirconocene dichloride (3.51 g, 12 mmol) was dissolved in THF (70 mL) and *tert*-butyllithium (10.5 mmol, 6.55 mL of a 1.6 M solution in hexane) was added at −78 °C. The brown solution was allowed to warm to room temperature; the yellow precipitate dissolved and after 1 h the solution was cooled to −78 °C once more. In a second flask, the bromobenzene derivative (12.0 mmol) was dissolved in THF (20 mL) and *n*-butyllithium (12.0 mmol, 7.5 mL of a 1.6 M solution in hexane) was added at −78 °C. After the solution in the first flask had been recooled to −78 °C, it was slowly transferred to the second flask by means of a cannula. After 1 h at −50 °C, acetonitrile (0.53 mL, 10 mmol) was added, the flask was sealed, and the reaction mixture was heated to 65 °C for 18 h. After cooling to room temperature, a solution of iodine (6.35 g, 25 mmol) in THF (25 mL) was added and the resulting mixture was stirred for a further 7 h. After hydrolysis with 1 M HCl (20 mL) and stirring for 5 h, the mixture was extracted with saturated aq. Na_2SO_3 solution (5 × 25 mL). The organic phase was washed with water, dried with $MgSO_4$, and concentrated in vacuo.

GP2: Chiral reductions of acetophenone derivatives with (−)-*B*-chlorodiisopinocampheylborane were carried out as described previously.[22] A solution of the acetophenone derivative in THF was added to a solution of 1.1 equiv. of (−)-*B*-chlorodiisopinocampheylborane in THF (1.0 M) at −25 °C. After the reaction (15−25 h), the solution was allowed to warm to room temperature and the solvent was removed. The residue was dissolved in diethyl ether and diethanolamine (2.2 equiv.) was added. After stirring for 2 h at room temperature, the mixture was filtered through Celite and concentrated in vacuo.

GP3: Sodium hydride (10 mmol) (55−65% in oil) was washed with pentane (4 ×) and then suspended in DMF (12 mL). After cooling to 0 °C, a solution of the alcohol or phenol (2.5 mmol) in DMF (6 mL) was added. After stirring for 15 min at room temperature, the mixture was cooled to 0 °C and methyl iodide (355 mg, 2.5 mmol) was added. After a further 3 h at room temperature, water was carefully added. The resulting mixture was extracted with *tert*-butyl methyl ether (2 ×), and the combined organic phases were washed with brine (3 ×), dried with $MgSO_4$, and concentrated in vacuo.

GP4:[25] A 0.1 M solution of an aryl iodide in glacial acetic acid was heated to 50−75 °C and then sodium perborate tetrahydrate (10 equiv.) was slowly added. The reaction mixture was stirred for 3−4 h. The conversion was monitored by TLC. After completion of the reaction, the mixture was quickly extracted with a small volume of dichloromethane (2 ×). The combined extracts were dried with $MgSO_4$ and the solvent was removed in vacuo. The diacetoxyiodo derivatives could be purified either by washing with pentane or by dissolving the crude product in acetonitrile and washing with pentane.

GP5: The (diacetoxyiodo)benzene derivative was dissolved in acetonitrile (ca. 0.9 M). To this solution, exactly 1 equiv. of *para*-toluenesulfonic acid monohydrate in acetonitrile (0.4 M) was added. After stirring for 1 h, the solvent was removed in vacuo. Some of the products were found to be unstable and were therefore characterized only by NMR spectroscopy.

(*S*)-(Hydroxy)[2-(1-methoxyethyl)-6-methylphenyl](4-methylphenylsulfonato-κ*O*)iodine (1a): GP5; 90% (62 mg) yield; purification not possible. − ^{1}H NMR ($CDCl_3$): δ = 1.47 (d, 3 H, *J* = 6.3 Hz), 2.35 (s, 3 H), 2.77 (s, 3 H), 3.21 (s, 3 H), 4.76 (q, 1 H, *J* = 5.8 Hz), 7.1 (m, 1 H), 7.1 (m, 2 H), 7.38 (m, 2 H), 7.54 (m, 2 H).

(*S*)-(Hydroxy)[2-ethylphenyl-6-(1-methoxyethyl)](4-methylphenylsulfonato-κ*O*)iodine (1b): GP5; purification not possible. − ^{1}H NMR ($CDCl_3$): δ = 1.20−1.50 (m, 6 H), 2.35 (s, 3 H), 3.04 (q, *J* = 7.4 Hz, 2 H), 3.25 (s, 3 H), 4.70−4.80 (m, 1 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 7.20−7.45 (m, 3 H), 7.62 (d, *J* = 8.2 Hz, 2 H), 9.37 (s, 1 H, OH).

(*S*)-(Hydroxy)[2-(1-methoxyethyl)-6-(1-methylethyl)phenyl](4-methylphenylsulfonato-κ*O*)iodine (1c): GP5; purification not possible. − ^{1}H NMR ($CDCl_3$): δ = 1.10−1.50 (m, 9 H), 2.34 (s, 3 H), 3.25 (s, 3 H), 3.35 (m, 1 H), 4.80 (m, 1 H), 7.10−7.60 (m, 7 H).

(*S*)-[3-(1-Methoxyethyl)-1,1′-biphenyl-2-yl)]hydroxy(4-methylphenylsulfonato-κ*O*)iodine (1d): GP5; purification not possible. − ^{1}H NMR ($CDCl_3$): δ = 1.49 (d, *J* = 6.4 Hz, 3 H), 2.37 (s, 3 H), 3.05−3.30 (m, 3 H), 4.60−4.75 (m, 1 H), 7.18 (d, *J* = 8 Hz, 2 H), 7.20−7.80 (m, 8 H), 7.64 (d, *J* = 8.2 Hz, 2 H), 10.06 (s, 1 H, OH).

(*S*)-(Hydroxy)[2-(1-methoxyethyl)-6-methoxyphenyl](4-methylphenylsulfonato-κ*O*)iodine (1e): Described in ref.[20]

(*S*)-[2-(Benzyloxy)-6-(1-methoxyethyl)phenyl](hydroxy)(4-methylphenylsulfonato-κ*O*)iodine (1f): GP5; generation in situ.

(*S*)-[2-Ethoxy-6-(1-methoxyethyl)phenyl](hydroxy)(4-methylphenylsulfonato-κ*O*)iodine (1g): GP5; generation in situ.

(*S*)-(Hydroxy)[2-(1-methoxyethyl)-6-(1-methylethyloxy)phenyl](4-methylphenylsulfonato-κ*O*)iodine (1h): GP5; generation in situ.

(*S*)-[2-(1,1-Dimethylethoxy)-6-(1-methoxyethyl)phenyl](hydroxy)(4-methylphenylsulfonato-κ*O*)iodine (1i): GP5; generation in situ.

(*S*)-(Hydroxy)[2-(1-methoxyethyl)-6-(methoxymethoxy)phenyl](4-methylphenylsulfonato-κ*O*)iodine (1j): GP5; generation in situ.

(*S*)-(Hydroxy)[2-(1-methoxyethyl)naphthalen-1-yl](4-methylphenylsulfonato-κ*O*)iodine (1k): GP5; generation in situ.

2-Iodo-3-methylacetophenone (3a): GP1; 39% (1.02 g) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:10); yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 2.48 (s, 3 H, $COCH_3$), 2.85 (s, 3 H, CH_3), 7.06 (m, 1 H, 4-H arom.), 7.27 (dd, 2 H, *J* = 1.3 Hz, *J* = 5.3 Hz, 3-, 5-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 29.0 (q, CH_3), 30.1 (q, $CO\mathit{C}H_3$), 96.8 (s, arom. C-2), 124.1 (d, arom. C), 128.0 (d, arom. C), 130.8 (d, arom. C), 142.9 (s, arom. C-1 or C-3), 147.2 (s, arom. C-1 or C-3), 204.0 (s, $\mathit{C}OCH_3$). − IR (KBr): $\tilde{\nu}$ = 3045, 2976, 2961, 1704, 1567, 1433, 1396, 1652, 1275, 1174, 1126, 1012, 783, 718 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 260 (66), 245 (100), 217 (28), 90 (35), 63 (14). − HRMS: calcd. for C_9H_9IO 259.9698; found 259.9704 [M^+].

3-Ethyl-2-iodoacetophenone (3b): GP1; 52% (1.42 g) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:10); yellow solid. − ^{1}H NMR ($CDCl_3$): δ = 1.22 (t, 3 H, *J* = 7.5 Hz, $CH_2C\mathit{H}_3$), 2.59 (s, 3 H, $COCH_3$), 2.80 (q, 2 H, *J* = 7.5 Hz, $C\mathit{H}_2CH_3$), 7.05 (dd, 1 H, *J* = 1.9 Hz, *J* = 7.1 Hz, 3- or 5-H arom.), 7.25 (dd, 1 H, *J* = 1.9 Hz, *J* = 7.7 Hz, 3- or 5-H arom.), 7.31 (t, 1 H, *J* = 7.4 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 14.5 (q, $CH_2\mathit{C}H_3$), 30.3 (q, $CO\mathit{C}H_3$), 34.5 (t, $\mathit{C}H_2CH_3$), 95.8 (s, arom. C-2), 124.1 (d, arom. C-6), 128.3 (d, arom. C-5), 129.5 (d, arom. C-4), 147.7 (s, arom. C-1 or C-3), 147.8 (s, arom. C-1 or C-3), 204.3 (s, $\mathit{C}OCH_3$). − IR (KBr): $\tilde{\nu}$ = 3062, 2967, 2931, 2872, 1704, 1568, 1455, 1407, 1352, 1269, 1175, 1128, 1098, 1009, 796, 722 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 274 (72), 259 (100), 104 (41), 103 (13), 77 (12). − HRMS: calcd. for $C_{10}H_{11}IO$ 273.9855; found 273.9861 [M^+].

2-Iodo-3-(1-methylethyl)acetophenone (3c): GP1; 31% (580 mg) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:10); yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 1.24 [d, 6 H, *J* = 6.8 Hz, $CH(C\mathit{H}_3)_2$], 2.59 (s, 3 H, $COCH_3$), 3.5 (q, 1 H, *J* = 6.8 Hz, $C\mathit{H}Me_2$), 7.03 (dd, 1 H, *J* = 1.9 Hz, *J* = 7.2 Hz, 5-H arom.), 7.27 (dd, 1 H, *J* = 1.9 Hz, *J* = 7.8 Hz, 3-H arom.), 7.3 (t, 1 H, *J* = 7.5 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 23.0 [q, $CH(\mathit{C}H_3)_2$], 30.5 (d, $\mathit{C}HMe_2$), 38.0 (q, $CO\mathit{C}H_3$), 96.3 (s, arom. C-2), 124.1 (d, arom. C), 126.9 (d, arom. C), 128.5 (d, arom. C), 148.1 (s, arom. C-1 or C-3), 151.6 (s, arom. C-1 or C-3), 204.7 (s, $\mathit{C}OMe$). − IR (KBr): $\tilde{\nu}$ = 3056, 2963, 2867, 1704, 1465, 1352, 1273, 1182, 1106, 1005, 793, 726 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 288 (74), 273 (100), 217 (11), 147 (9), 131 (11), 117 (12). − HRMS: calcd. for $C_{10}H_{13}IO$ 288.0011; found 288.0011 [M^+].

2-Iodo-3-phenylacetophenone (3d): GP1; 56% (1.80 g) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:50 → 1:10); colorless crystals, m.p. 103−106 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.64 (s, 3 H, $COCH_3$), 7.21 (dd, 1 H, *J* = 1.9 Hz, *J* = 7.4 Hz, H arom.), 7.30 (m, 3 H, H arom.), 7.42 (m, 4 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 30.3 (q, $CO\mathit{C}H_3$), 94.4 (s, arom. C-2), 125.4 (d), 127.9 (d), 128.0 (d, 2 C), 128.1 (d), 129.4 (d, 2 C), 130.8 (d), 144.1 (s), 147.9 (s, arom. C-1), 148.3 (s, arom. C-3), 204.2 (s, $\mathit{C}OCH_3$). − IR (KBr): $\tilde{\nu}$ = 3052, 1706, 1442, 1413, 1396, 1352, 1298, 1276, 1183, 1124, 1010, 809, 765, 701 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 323 (21), 322 (91), 308 (22), 307 (100), 165 (12), 153 (25), 152 (77), 151 (22), 126 (10), 76 (19). − HRMS: calcd. for $C_{14}H_{11}IO$ 321.9855; found 321.9857 [M^+].

3-(Benzyloxy)-2-iodoacetophenone (3f): GP1; 65% (2.38 g) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:10); brown crystals, m.p. 53−55 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.60 (s, 3 H, $COCH_3$), 5.18 (s, 2 H, CH_2), 6.87−6.93 (m, 2 H, H arom.), 7.25−7.42 (m, 4 H, H arom.), 7.49−7.51 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 30.1 (q, $CO\mathit{C}H_3$), 71.2 (t, CH_2), 83.8 (s, arom. C-2), 113.6 (d), 119.7 (d), 127.0 (d, 2 C), 128.0 (d), 128.6 (d, 2 C), 129.5 (d), 136.1 (s), 148.0 (s), 157.3 (s), 203.3 (s, $\mathit{C}OCH_3$). − IR (KBr): $\tilde{\nu}$ = 3060, 3029, 2913, 2867, 1696, 1560, 1498, 1449, 1423, 1387, 1272, 1240, 1044, 1029, 785, 751, 737, 697 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 353 [M^+ + H] (4), 352 (19), 225 (3), 181 (2), 119 (3), 91 (100), 65 (13), 43 (13), 39 (4). − $C_{15}H_{13}IO_2$ (352.17): calcd. C 51.16, H 3.72, O 9.09; found C 50.89, H 3.93, O 8.94.

(*S*)-1-[2-Iodo-3-(methoxymethoxy)phenyl]ethanol (3j): GP2; 58% (1.65 g) yield, 95% *ee*;[42] after recrystallization (*tert*-butyl methyl ether/pentane) 99% *ee*; colorless crystals, m.p. 50−51 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.45 [d, 3 H, *J* = 6.3 Hz, $CH(OH)C\mathit{H}_3$], 2.25 (d, 1 H, *J* = 3.0 Hz, OH), 3.51 (s, 3 H, OCH_3), 5.17 [dq, 1 H, *J* = 6.4 Hz, *J* = 3.1 Hz, $C\mathit{H}$(OH)Me], 5.24 (s, 2 H, CH_2), 6.96 (dd, 1 H, *J* = 7.8 Hz, *J* = 1.7 Hz, 3- or 5-H arom.), 7.22 (dd, 1 H, *J* = 7.7 Hz, *J* = 1.7 Hz, 3- or 5-H arom.), 7.29 (t, 1 H, *J* = 7.8 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 23.5 [q, $CH(OH)\mathit{C}H_3$], 56.4 (q, OCH_3), 73.9 [d, $\mathit{C}H$(OH)Me], 90.9 (s, arom. C-2), 95.1 (t, CH_2), 113.6 (d, arom. C-6), 119.7 (d, arom. C-4), 129.5 (d, arom. C-5), 149.6 (s, arom. C-3), 155.5 (s, arom. C-1). − IR (KBr): $\tilde{\nu}$ = 3332, 3070, 2975, 2929, 2897, 2824, 1932, 1850, 1773, 1590, 1566, 1468, 1453, 1444, 1425, 1369, 1253, 1150, 1073, 1026, 916, 784, 716, 737 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 309 [M^+ + H] (5), 308 (36), 277 (4), 263 (5), 246 (54), 136 (5), 91 (6), 77 (5), 65 (7), 63 (6), 45 (100), 43 (12), 39 (6).

(*S*)-1-(2-Iodo-3-methylphenyl)ethanol (4a): GP2; 72% (400 mg) yield, 94% *ee*;[43] purification by flash chromatography on silica gel (dichloromethane); colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.44 [d, 3 H, *J* = 6.4 Hz, $CH(OH)C\mathit{H}_3$], 2.47 (s, 3 H, CH_3), 5.17 [q, 1 H, *J* = 6.3 Hz, $C\mathit{H}$(OH)Me], 7.15 (dd, 1 H, *J* = 1.2 Hz, *J* = 7.4 Hz, 3- or 5-H arom.), 7.24 (t, 1 H, *J* = 7.5 Hz, 4-H arom.), 7.34 (dd, 1 H, *J* = 1.3 Hz, *J* = 7.6 Hz, 3- or 5-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 23.6 [q, $CH(OH)\mathit{C}H_3$], 26.9 (q, CH_3), 74.3 [d, $\mathit{C}H$(OH)Me], 104.7 (s, arom. C-2), 123.4 (d, arom. C), 128.2 (d, arom. C), 128.8

(d, arom. C), 141.9 (s, arom. C-3), 148.2 (s, arom. C-1). − IR (KBr): $\tilde{\nu}$ = 3334, 3046, 2972, 2923, 1459, 1402, 1367, 1113, 1068, 1003, 783 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 262 (47), 247 (100), 119 (16), 92 (70), 91 (35), 65 (11). − HRMS: calcd. for $C_9H_{11}IO$ 261.9855; found 261.9860 [M^+]. − $[\alpha]_D^{25}$ = −46.4 (*c* = 1.205, $CHCl_3$).

(*S*)-1-(3-Ethyl-2-iodophenyl)ethanol (4b): GP2; 86% (950 mg) yield, 95% *ee*;[44] purification by flash chromatography on silica gel (dichloromethane); colorless oil. − ^1H NMR ($CDCl_3$): δ = 1.21 (t, 3 H, *J* = 7.5 Hz, CH_2CH_3), 1.45 [d, 3 H, *J* = 6.3 Hz, CH(OH)CH_3], 2.27 (br., 1 H, OH), 3.37 (q, 2 H, *J* = 7.5 Hz, CH_2CH$_3$), 5.20 [dq, 1 H, *J* = 2.2 Hz, *J* = 6.3 Hz, C*H*(OH)CH$_3$], 7.13 (dd, 1 H, *J* = 1.7 Hz, *J* = 7.4 Hz, 3- or 5-H arom.), 7.27 (t, 1 H, *J* = 7.4 Hz, 4-H arom.), 7.36 (dd, 1 H, *J* = 1.7 Hz, *J* = 7.7 Hz, 3- or 5-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 14.6 (q, CH_2CH_3), 23.7 [q, CH(OH)*C*H$_3$], 35.3 (t, *C*H_2CH$_3$), 74.5 [d, *C*H(OH)CH$_3$], 104.1 (s, arom. C-2), 123.8 (d, arom. C), 127.7 (d, arom. C), 128.5 (d, arom. C), 146.9 (s, arom. C), 148.3 (s, arom. C). − IR (KBr): $\tilde{\nu}$ = 3346, 3061, 2968, 2929, 2871, 1572, 1456, 1413, 1368, 1338, 1110, 1070, 1004, 910, 839, 796, 724 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 276 (58), 262 (15), 261 (100), 106 (52), 105 (14), 91 (27), 77 (14). − HRMS: calcd. for $C_{10}H_{13}IO$ 276.0011; found 276.0018 [M^+]. − $[\alpha]_D^{25}$ = −43.5 (*c* = 1.135, $CHCl_3$).

(*S*)-1-[2-Iodo-3-(1-methylethyl)phenyl]ethanol (4c): GP2; 68% (238 mg) yield, > 99% *ee*;[44] purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:10); colorless oil. − ^1H NMR ($CDCl_3$): δ = 1.23 [t, 6 H, *J* = 6.5 Hz, CH(CH_3)$_2$], 1.44 [d, 3 H, *J* = 6.3 Hz, CH(OH)CH_3], 2.57 (br., 1 H, OH), 3.37 (sept, 1 H, *J* = 6.8 Hz, C*H*Me$_2$), 5.21 [q, 1 H, *J* = 6.3 Hz, C*H*(OH)Me], 7.14 (dd, 1 H, *J* = 1.8 Hz, *J* = 7.6 Hz, 3- or 5-H arom.), 7.29 (t, 1 H, *J* = 7.6 Hz, 4-H arom.), 7.39 (dd, 1 H, *J* = 1.9 Hz, *J* = 7.7 Hz, 3- or 5-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 23.1 (q, CH_3), 23.4 (q, CH_3), 23.7 (q, CH_3), 38.6 (d, *C*HMe$_2$), 74.8 [d, *C*H(OH)Me], 104.9 (s, arom. C-2), 124.3 (d, arom. C), 125.2 (d, arom. C), 128.6 (d, arom. C), 148.4 (s, arom. C-1 or C-3), 150.7 (s, arom. C-1 or C-3). − IR (KBr): $\tilde{\nu}$ = 3347, 3063, 2964, 2929, 2863, 1456, 1409, 1365, 1103, 1069, 1001, 794, 726 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 290 (61), 275 (100), 257 (12), 233 (11), 130 (16), 105 (14), 91 (17), 77 (14), 43 (53). − HRMS: calcd. for $C_{11}H_{15}IO$ 290.0168; found 290.0167 [M^+]. − $[\alpha]_D^{25}$ = −44.0 (*c* = 0.835, $CHCl_3$).

(*S*)-1-(2-Iodo-1,1′-biphenyl-3-yl)ethanol (4d): GP2; 81% (1.135 g) yield, 95% *ee*;[45] purification by flash chromatography on silica gel (dichloromethane); colorless crystals, m.p. 108−110 °C. − ^1H NMR ($CDCl_3$): δ = 1.50 [d, 3 H, *J* = 6.3 Hz, CH(OH)CH_3], 2.35 (br., 1 H, OH), 5.23 [dq, 1 H, *J* = 1.9 Hz, *J* = 6.3 Hz, C*H*(OH)Me], 7.18 (dd, 1 H, *J* = 1.8 Hz, *J* = 7.4 Hz, 5-H arom.), 7.25 (m, 2 H, H arom.), 7.39 (m, 4 H, H arom.), 7.54 (dd, 1 H, *J* = 1.7 Hz, *J* = 7.7 Hz, 3-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 23.8 [q, CH(OH)*C*H$_3$], 74.6 [d, *C*H(OH)Me], 102.4 (s, arom. C-2), 125.0 (d, arom. C), 127.5 (d, arom. C), 127.8 (d, 2 C, arom. C), 128.2 (d, arom. C), 129.0 (d, 2 C, arom. C), 129.4 (d, arom. C), 145.4 (s, arom. C), 147.7 (s, arom. C-1 or C-3), 148.7 (s, arom. C-1 or C-3). − IR (KBr): $\tilde{\nu}$ = 3585, 3437, 2977, 1450, 1360, 1334, 1278, 1243, 1171, 1124, 1098, 1065, 1000, 904, 806, 756, 731, 697 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 325 (17), 324 (85), 310 (20), 309 (100), 182 (43), 181 (34), 180 (13), 179 (16), 178 (19), 155 (15), 154 (67), 153 (34), 152 (55), 151 (17), 76 (17). − HRMS: calcd. for $C_{14}H_{13}IO$ 324.0011; found 324.0009 [M^+]. − $[\alpha]_D^{25}$ = − 47.4 (*c* = 0.99, $CHCl_3$).

(*S*)-1-[3-(Benzyloxy)-2-iodophenyl]ethanol (4f): GP2; 67% (856 mg) yield, 99% *ee*[46] after recrystallization (pentane); colorless crystals, m.p. 71−72 °C. − ^1H NMR ($CDCl_3$): δ = 1.45 [d, 3 H, *J* = 6.4 Hz, CH(OH)CH_3], 2.23 (d, 1 H, *J* = 2.8 Hz, OH), 5.13 (s, 2 H), 5.18 [dq, 1 H, *J* = 6.3 Hz, *J* = 2.9 Hz, C*H*(OH)Me], 6.75 (dd, 1 H, *J* = 7.9 Hz, *J* = 1.5 Hz, H arom.), 7.18 (dd, 1 H, *J* = 7.7 Hz, *J* = 1.4 Hz, H arom.), 7.24−7.52 (m, 6 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 23.5 [q, CH(OH)*C*H$_3$], 71.1 (t, CH_2), 73.9 [d, *C*H(OH)Me], 90.5 (s, arom. C-2), 111.5 (d, arom. C-6), 118.9 (d, arom. C-4), 127.0 (d, 2 C), 127.8 (d), 128.5 (d, 2 C), 129.4 (d, arom. C-5), 136.5 (s), 149.6 (s, arom. C-3), 156.6 (s, arom. C-1). − IR (KBr): $\tilde{\nu}$ = 3294, 3063, 3034, 2970, 1587, 1564, 1497, 1469, 1450, 1371, 1262, 1047, 1028, 1014, 779, 745, 730, 713 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 355 [M^+ + H] (8), 354 (35), 246 (9), 227 (3), 91 (100), 77 (4), 65 (17), 45 (1), 37 (4).

(*S*)-2-Iodo-1-(1-methoxyethyl)-3-methylbenzene (5a): GP3; 92% (303 mg) yield; no purification necessary; colorless oil. − ^1H NMR ($CDCl_3$): δ = 1.37 [d, 3 H, *J* = 6.3 Hz, CH(OMe)CH_3], 2.47 (s, 3 H, CH_3), 3.24 (s, 3 H, OCH_3), 4.68 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 7.15 (m, 1 H, H arom.), 7.24 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.6 [q, CH(OMe)*C*H$_3$], 29.6 (q, CH_3), 56.6 (q, OCH_3), 83.5 [d, *C*H(OMe)Me], 105.5 (s, arom. C-2), 123.6 (d, arom. C), 128.3 (d, arom. C), 128.8 (d, arom. C), 141.9 (s, arom. C-3), 146.1 (s, arom. C-1). − IR (KBr): $\tilde{\nu}$ = 3046, 2976, 2926, 2819, 1447, 1403, 1369, 1342, 1312, 1240, 1205, 1114, 1061, 1005, 840, 784, 745, 719 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 276 (16), 261 (100), 245 (9), 118 (10), 91 (16). − HRMS: calcd. for $C_{10}H_{13}IO$ 276.0011; found 276.0021 [M^+]. − $[\alpha]_D^{25}$ = −76.1 (*c* = 1.50, $CHCl_3$).

(*S*)-1-Ethyl-2-iodo-3-(1-methoxyethyl)benzene (5b): GP3; quant. (725 mg) yield; no purification necessary; colorless oil. − ^1H NMR ($CDCl_3$): δ = 1.22 (t, 3 H, *J* = 7.5 Hz, CH_2CH_3), 1.38 [d, 3 H, *J* = 6.3 Hz, CH(OCH$_3$)CH_3], 2.80 (q, 2 H, *J* = 7.5 Hz, CH_2CH$_3$), 3.24 (s, 3 H, OCH_3), 4.69 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.13 (dd, 1 H, *J* = 2.6 Hz, *J* = 6.7 Hz, 3- or 5-H arom.), 7.24−7.28 (m, 2 H, 4-H and 3- or 5-H arom.)]. − ^{13}C NMR ($CDCl_3$): δ = 14.6 (q, CH_2CH_3), 22.7 [q, CH(OMe)*C*H$_3$], 35.2 (t, *C*H_2CH$_3$), 56.6 (q, OCH_3), 83.7 [d, *C*H(OMe)Me], 104.9 (s, arom. C-2), 123.9 (d, arom. C-4), 127.6 (d, arom. C-5), 128.5 (d, arom. C-6), 146.2 (s, arom. C-1 or C-3), 146.9 (s, arom. C-1 or C-3). − IR (KBr): $\tilde{\nu}$ = 3061, 2971, 2930, 2820, 1572, 1455, 1413, 1370, 1346, 1113, 1062, 1004, 797, 726 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 290 (24), 276 (19), 275 (100), 259 (10), 105 (11), 91 (9). − HRMS: calcd. for $C_{11}H_{15}IO$ 290.0168; found 290.0168 [M^+]. − $[\alpha]_D^{25}$ = −82.3 (*c* = 1.72, $CHCl_3$).

(*S*)-2-Iodo-1-(1-methoxyethyl)-3-(1-methylethyl)benzene (5c): GP3; 83% (156 mg) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:20); colorless oil. − ^1H NMR ($CDCl_3$): δ = 1.23 [dd, 6 H, *J* = 1.9 Hz, *J* = 6.9 Hz, CH(CH_3)$_2$], 1.38 [d, 3 H, *J* = 6.3 Hz, CH(OMe)CH_3], 3.25 (s, 3 H, OCH_3), 3.38 (sept, 1 H, *J* = 6.8 Hz, C*H*Me$_2$), 4.71 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.15 (dd, 1 H, *J* = 2.4 Hz, *J* = 6.9 Hz, H arom.), 7.28 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.7 (q, CH_3), 23.2 (q, CH_3), 23.3 (q, CH_3), 38.6 (d, *C*HMe$_2$), 56.7 (q, OCH_3), 84.0 [d, *C*H(OMe)Me], 105.8 (s, arom. C-2), 124.4 (d, arom. C), 125.2 (d, arom. C), 128.6 (d, arom. C), 146.2 (s, arom. C-1 or C-3), 150.8 (s, arom. C-1 or C-3). − IR (KBr): $\tilde{\nu}$ = 3057, 2964, 2927, 2820, 1574, 1455, 1410, 1369, 1329, 1205, 1110, 1061, 1002, 866, 795, 728 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 304 (12), 290 (18), 289 (100), 273 (6), 147 (9), 131 (7), 130 (6), 119 (8), 117 (9), 115 (9), 91 (11). − HRMS: calcd. for $C_{12}H_{17}IO$ 304.0324; found 304.0323 [M^+]. − $[\alpha]_D^{25}$ = −80.3 (*c* = 0.93, $CHCl_3$).

(*S*)-2-Iodo-3-(1-methoxyethyl)-1,1′-biphenyl (5d): GP3; 95% (843 mg) yield; no purification necessary; colorless crystals, m.p.

75−78 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.42 [d, 3 H, *J* = 6.4 Hz, CH(OMe)C*H*$_3$], 3.30 (s, 3 H, OCH_3), 4.72 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.19 (dd, 1 H, *J* = 2.3 Hz, *J* = 6.9 Hz, 5-H arom.), 7.28 (dd, 1 H, *J* = 2.1 Hz, *J* = 7.8 Hz, 3-H arom.), 7.28 (m, 1 H, H arom.), 7.40 (m, 5 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.7 [q, CH(OMe)*C*H$_3$], 56.8 (q, OCH_3), 83.8 [d, *C*H(OMe)Me], 103.1 (s, arom. C-2), 125.1 (d, arom. C), 127.5 (d, arom. C), 127.8 (d, 2 C, arom. C), 128.2 (d, arom. C), 129.0 (d, arom. C), 129.4 (d, 2 C, arom. C), 145.4 (s, arom. C), 146.9 (s, arom. C-1 or C-3), 147.7 (s, arom. C-1 or C-3). − IR (KBr): ṽ = 3056, 2972, 2927, 2820, 1451, 1399, 1366, 1228, 1207, 1109, 1056, 1003, 802, 762, 731, 703 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 338 (33.4), 324 (25), 232 (100), 180 (16), 178 (14), 165 (16), 152 (24). − HRMS: calcd. for $C_{15}H_{15}IO$ 338.0168; found 338.0174 [M^+]. − $[\alpha]_D^{25}$ = −82.6 (*c* = 1.20, $CHCl_3$).

(*S*)-1-(Benzyloxy)-2-iodo-3-(1-methoxyethyl)benzene (5f): GP3; 80% (696 mg) yield; purification by flash chromatography on silica gel (dichloromethane); colorless crystals, m.p. 67−70 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.38 [d, 3 H, *J* = 6.4 Hz, CH(OMe)C*H*$_3$], 3.24 (s, 3 H, OCH_3), 4.70 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 5.14 (s, 2 H, CH_2), 6.76 (dd, 1 H, *J* = 8.1 Hz, *J* = 1.3 Hz, H arom.), 7.07 (dd, 1 H, *J* = 7.7 Hz, *J* = 1.3 Hz, H arom.), 7.22−7.42 (m, 4 H, H arom.), 7.51−7.53 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.5 [q, CH(OMe)*C*H$_3$], 56.7 (q, OCH_3), 71.0 (t, CH_2), 83.0 [d, *C*H(OH)Me], 91.4 (s, arom. C-2), 111.2 (d, arom. C-4), 119.1 (d, arom. C-6), 127.0 (d, 2 C), 127.8 (d), 128.5 (d, 2 C), 129.4 (d, arom. C-5), 136.5 (s), 147.7 (s, arom. C-1), 156.7 (s, arom. C-3). − IR (KBr): ṽ = 3064, 3024, 2990, 2980, 2910, 2879, 2823, 1942, 1873, 1859, 1815, 1774, 1752, 1686, 1654, 1584, 1564, 1498, 1380, 1365, 1267, 1116, 904, 789 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 369 [M^+ + H] (8), 368 (35), 353 (3), 246 (14), 241 (1), 209 (7), 91 (100), 77 (3), 65 (12), 59 (3), 37 (3). − $C_{16}H_{17}IO_2$ (368.21): calcd. C 52.19, H 4.65, O 8.69; found C 52.00, H 4.73, O 8.70.

(*S*)-1-Ethoxy-2-iodo-3-(1-methoxyethyl)benzene (5g): Starting material: **8**. GP3 (using ethyl iodide instead of methyl iodide); 99% (83 mg) yield; no purification necessary; colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.37 [d, 3 H, *J* = 6.4 Hz, CH(OCH$_3$)C*H*$_3$], 1.50 (t, 3 H, *J* = 7.0 Hz, OCH$_2$C*H*$_3$), 3.24 (s, 3 H, OCH_3), 4.06−4.13 (m, 2 H, OC*H*$_2$CH$_3$), 4.68 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 6.71 [dd, 1 H, *J* = 8.0 Hz, *J* = 1.3 Hz, 3- or 5-H arom.), 7.05 (dd, 1 H, *J* = 7.8 Hz, *J* = 1.3 Hz, 3- or 5-H arom.), 7.28 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 14.8 (q, OCH$_2$*C*H$_3$), 22.5 [q, CH(OMe)*C*H$_3$], 56.7 (q, OCH_3), 65.0 (t, O*C*H$_2$CH$_3$), 83.1 [d, *C*H(OMe)Me], 91.4 (s, arom. C-2), 110.8 (d, arom. C-4), 118.7 (d, arom. C-6), 129.4 (d, arom. C-5), 147.5 (s, arom. C-1), 157.1 (s, arom. C-3). − IR (KBr): ṽ = 2984, 2932, 2825, 1586, 1566, 1456, 1392, 1372, 1345, 1315, 1283, 1263, 1155, 1113, 1054, 1011, 959, 871, 833, 693 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 307 [M^+ + H] (9), 306 (58), 291 (100), 276 (6), 263 (24), 248 (7), 247 (7), 149 (8), 120 (19), 91 (13), 77 (9), 65 (8), 59 (18), 43 (9), 39 (2).

(*S*)-2-Iodo-1-(1-methoxyethyl)-3-(1-methylethoxy)benzene (5h): Starting material: **8**. GP3 (using isopropyl iodide instead of methyl iodide); 93% (108 mg) yield; no purification necessary; colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.37 [d, 3 H, *J* = 6.3 Hz, CH(OCH$_3$)C*H*$_3$], 1.40−1.42 [m, 6 H, OCH(C*H*$_3$)$_2$], 3.24 (s, 3 H, OCH_3), 4.57 (sept, 1 H, *J* = 6.1 Hz, OC*H*Me$_2$), 4.68 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 6.72 (dd, 1 H, *J* = 8.1 Hz, *J* = 1.3 Hz, 3- or 5-H arom.), 7.03 (dd, 1 H, *J* = 7.7 Hz, *J* = 1.4 Hz, 3- or 5-H arom.), 7.27 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.08 [q, OCH(*C*H$_3$)$_2$], 22.12 [q, OCH(*C*H$_3$)$_2$], 22.5 [q, CH(OMe)*C*H$_3$], 56.7 (q, OCH_3), 72.1 (d, O*C*HMe$_2$), 83.2 [d, *C*H(OMe)Me], 93.1 (s, arom. C-2), 112.6 (d, arom. C-6), 118.7 (d, arom. C-4), 129.2 (d, arom. C-5), 147.7 (s, arom. C-3), 156.3 (s, arom. C-1). − IR (KBr): ṽ = 2981, 2932, 2825, 1584, 1566, 1457, 1385, 1373, 1345, 1315, 1281, 1262, 1114, 1060, 1009, 980, 897, 855, 834, 821, 690 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 321 [M^+ + H] (5), 320 (39), 305 (2), 278 (31), 263 (100), 248 (8), 247 (10), 120 (16), 91 (10), 77 (6), 65 (7), 59 (15), 43 (18), 39 (5).

(*S*)-1-(1,1-Dimethylethoxy)-2-iodo-3-(1-methoxyethyl)benzene (5i): Starting material: **8**; synthesized according to ref.[28]; 36% (71 mg) yield; colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.37 [d, 3 H, *J* = 6.4 Hz, CH(OCH$_3$)C*H*$_3$], 1.49 [s, 9 H, C(CH$_3$)$_3$], 3.24 (s, 3 H, OCH_3), 4.67 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 7.00 (dd, 1 H, *J* = 7.9 Hz, *J* = 1.6 Hz, 3- or 5-H arom.), 7.11 (dd, 1 H, *J* = 7.7 Hz, *J* = 1.4 Hz, 3- or 5-H arom.), 7.24 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.5 [q, CH(OMe)*C*H$_3$], 29.2 [q, C(*C*H$_3$)$_3$], 56.6 (q, OCH_3), 81.3 (s, *C*Me$_3$), 83.4 [d, *C*H(OMe)Me], 99.2 (s, arom. C-2), 119.8 (d, arom. C-4 or C-6), 120.5 (d, arom. C-4 or C-6), 128.7 (d, arom. C-5), 147.6 (s, arom. C-1), 155.7 (s, arom. C-3). − IR ($CHCl_3$): ṽ = 2983, 2932, 2825, 1567, 1455, 1415, 1392, 1369, 1344, 1315, 1264, 1162, 1113, 1059, 1012, 957, 919, 895, 862, 834, 821, 689 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 334 [M^+] (4), 319 (8), 278 (60), 263 (100), 248 (8), 247 (12), 231 (13), 152 (3), 137 (6), 120 (14), 91 (9), 77 (6), 65 (6), 59 (13), 57 (22), 41 (11), 39 (6).

(*S*)-2-Iodo-1-(1-methoxyethyl)-3-(methoxymethoxy)benzene (5j): GP3; 90% (1.54 g) yield; no purification necessary; yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 1.38 [d, 3 H, *J* = 6.4 Hz, CH(OMe)C*H*$_3$], 3.25 (s, 3 H, OCH_3), 3.53 (s, 3 H, arom. OCH_3), 4.67 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 5.25 (s, 2 H, CH_2), 6.98 (dd, 1 H, *J* = 8.0 Hz, *J* = 1.4 Hz, 3- or 5-H arom.), 7.11 (dd, 1 H, *J* = 7.8 Hz, *J* = 1.4 Hz, 3- or 5-H arom.), 7.29 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.5 [q, CH(OMe)*C*H$_3$], 56.4 (q, OCH_3), 56.7 (q, OCH_3), 83.0 [d, *C*H(OMe)Me], 91.8 (s, arom. C-2), 95.0 (t, CH_2), 113.4 (d, arom. C-6), 119.9 (d, arom. C-4), 129.4 (d, arom. C-5), 147.5 (s, arom. C-3), 155.6 (s, arom. C-1). − IR (KBr): ṽ = 3005, 2983, 2932, 2827, 1587, 1567, 1460, 1442, 1254, 1154, 1108, 1084, 1018, 990 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 323 [M^+ + H] (10), 322 (46), 307 (19), 291 (10), 277 (17), 246 (54), 134 (5), 120 (11), 104 (8), 91 (12), 77 (9), 65 (8), 63 (8), 59 (14), 45 (100), 43 (8), 39 (6).

(*S*)-Bis(acetato-*O*)[2-(1-methoxyethyl)-6-methylphenyl]iodine (6a): GP4; 88% (132 mg) yield; yellow solid. − ^{1}H NMR ($CDCl_3$): δ = 1.47 [d, 3 H, *J* = 6.4 Hz, CH(OMe)C*H*$_3$], 1.95 (s, 3 H, OCOCH$_3$), 1.96 (s, 3 H, OCOCH$_3$), 2.76 (s, 3 H, CH_3), 3.23 (s, 3 H, OCH_3), 4.73 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.43 (dd, 1 H, *J* = 1.9 Hz, *J* = 6.9 Hz, 3- or 5-H arom.), 7.49 (dd, 1 H, *J* = 2.2 Hz, *J* = 7.9 Hz, 3- or 5-H arom.), 7.54 (t, 1 H, *J* = 7.3 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.2 (q, 2 C, OCO*C*H$_3$), 24.0 [q, CH(OMe)*C*H$_3$], 27.0 (q, CH_3), 56.8 (q, OCH_3), 83.1 [d, *C*H(OMe)Me], 125.0 (d, arom. C), 130.1 (d, arom. C), 130.8 (s, arom. C-1), 133.1 (d, arom. C), 141.0 (s, arom. C-6), 145.6 (s, arom. C-2), 176.2 (s, O*C*OMe), 176.6 (s, O*C*OMe).

(*S*)-Bis(acetato-*O*)[2-ethyl-6-(1-methoxyethyl)phenyl]iodine (6b): GP4; 81% (112 mg) yield; colorless solid, m.p. 97−100 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.34 (t, 3 H, *J* = 7.5 Hz, CH$_2$C*H*$_3$), 1.48 [d, 3 H, *J* = 6.3 Hz, CH(OMe)C*H*$_3$], 1.95 (s, 3 H, OCOCH$_3$), 1.96 (s, 3 H, OCOCH$_3$), 3.05 (q, 2 H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 3.23 (s, 3 H, OCH_3), 4.74 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 7.44 (dd, 1 H, *J* = 2.0 Hz, *J* = 7.3 Hz, 3- or 5-H arom.), 7.52 (dd, 1 H, *J* = 2.0 Hz, *J* = 7.7 Hz, 3- or 5-H arom.), 7.60 (t, 1 H, *J* = 7.4 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 15.2 (q, CH$_2$*C*H$_3$), 20.2 (q, OCO*C*H$_3$), 20.3 (q, OCO*C*H$_3$), 24.0 [q, CH(OMe)*C*H$_3$], 33.6 (t,

CH_2CH_3), 56.7 (q, OCH_3), 83.3 [d, *C*H(OMe)Me], 125.2 (d, arom. C-5), 128.8 (d, arom. C-4), 130.6 (s, arom. C-1), 133.2 (d, arom. C-3), 145.5 (s, arom. C-2 or C-6), 146.0 (s, arom. C-2 or C-6), 176.2 (s, O*C*OMe), 176.5 (s, O*C*OMe). − $[\alpha]_D^{25}$ = −87.8 (*c* = 0.95, $CHCl_3$).

(*S*)-Bis(acetato-*O*)[2-(1-methoxyethyl)-6-(1-methylethyl)-phenyl]iodine (6c): GP4; inseparable from **5c**; colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.35 [dd, 6 H, *J* = 1.9 Hz, *J* = 6.8 Hz, CH(CH_3)$_2$], 1.48 [d, 3 H, *J* = 6.5 Hz, CH(OMe)CH_3], 1.95 (s, 3 H, OCOCH_3), 1.96 (s, 3 H, OCOCH_3), 3.24 [s, 3 H, CH(OCH_3)Me], 3.40 (sept, 1 H, *J* = 6.7 Hz, C*H*Me$_2$), 4.76 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.46 (dd, 1 H, *J* = 1.8 Hz, *J* = 7.4 Hz, 3- or 5-H arom.), 7.54 (dd, 1 H, *J* = 1.8 Hz, *J* = 7.6 Hz, 3- or 5-H arom.), 7.62 (t, 1 H, *J* = 7.5 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.2 (q), 24.0 (q), 24.1 (q), 24.4 (q), 39.0 (d, *C*HMe$_2$), 56.8 (q, OCH_3), 83.6 [d, *C*H(OMe)Me], 125.7 (d, arom. C), 126.8 (d, arom. C), 131.4 (s, arom. C-1), 133.2 (s, arom. C), 145.4 (s, arom. C-2), 150.3 (s, arom. C-6), 176.3 (s, O*C*OMe), 176.5 (s, O*C*OMe).

(*S*)-Bis(acetato-*O*)[3-(1-methoxyethyl)-1,1′-biphenyl-2-yl]iodine (6d): GP4; 92% (248 mg) yield, inseparable from **5d**; colorless solid. − ^{1}H NMR ($CDCl_3$): δ = 1.52 [d, 3 H, *J* = 6.3 Hz, CH(OMe)CH_3], 1.90 (s, 3 H, COCH_3), 1.93 (s, 3 H, COCH_3), 3.28 [s, 3 H, CH(OCH_3)Me], 4.76 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.37−7.50 (m, 6 H, H arom.), 7.69 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.18 (q), 20.23 (q), 24.0 [q, CH(OMe)*C*H$_3$], 56.9 (q, OCH_3), 83.3 [d, *C*H(OMe)Me], 126.1 (d, arom. C), 128.1 (d, arom. C), 128.6 (d, arom. C), 129.0 (d, arom. C), 129.6 (s, arom. C-1), 130.0 (d, arom. C), 132.6 (d, arom. C), 142.7 (s), 145.4 (s, arom. C-2 or C-6), 146.7 (s, arom. C-2 or C-6), 176.0 (s, O*C*OMe), 176.7 (s, O*C*OMe). − $[\alpha]_D^{25}$ = −69.1 (*c* = 0.63, $CHCl_3$).

(*S*)-Bis(acetato-*O*)[2-(benzyloxy)-6-(1-methoxyethyl)phenyl]iodine (6f): GP4; 87% yield (determined by NMR), inseparable from **5f**; colorless solid. − ^{1}H NMR ($CDCl_3$): δ = 1.48 [d, 3 H, *J* = 6.4 Hz, CH(OMe)CH_3], 1.939 (s, 3 H, COCH_3), 1.942 (s, 3 H, COCH_3), 3.24 [s, 3 H, CH(OCH_3)Me], 4.73 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 5.28 (s, 2 H, CH_2), 7.07 (dd, 1 H, *J* = 8.2 Hz, *J* = 1.1 Hz, H arom.), 7.28 (dd, 1 H, *J* = 7.9 Hz, *J* = 1.1 Hz, H arom.), 7.45−7.33 (m, 5 H, H arom.), 7.55 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.3 (q, 2 C), 23.7 [q, CH(OMe)*C*H$_3$], 56.8 (q, OCH_3), 71.6 (t, CH_2), 82.4 [d, *C*H(OMe)Me], 112.2 (d, arom. C), 117.7 (s, arom. C), 119.7 (d, arom. C), 126.9 (d, 2 C, arom. C), 128.2 (d, arom. C), 128.7 (d, 2 C, arom. C), 134.5 (d, arom. C), 135.6 (s, arom. C-2), 147.1 (s, arom. C-6), 154.9 (s, arom. C), 176.6 (s, O*C*OMe), 176.7 (s, O*C*OMe).

(*S*)-Bis(acetato-*O*)[2-ethoxy-6-(1-methoxyethyl)phenyl]iodine (6g): GP4; 69% yield (determined by NMR), inseparable from **5g**; yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 1.46−1.50 [m, 6 H, OCH$_2$CH_3 and CH(OMe)CH_3], 1.94 (s, 3 H, OCOCH_3), 1.95 (s, 3 H, OCOCH_3), 3.23 (s, 3 H, OCH_3), 4.19−4.26 (m, 2 H, OCH_2CH$_3$), 4.70 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 7.03 (dd, 1 H, *J* = 8.2 Hz, *J* = 1.3 Hz, 3- or 5-H arom.), 7.26 (dd, 1 H, *J* = 7.8 Hz, *J* = 1.3 Hz, 3- or 5-H arom.), 7.57 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 14.5 (q, OCH$_2$*C*H$_3$), 20.3 (q, 2 C, OCO*C*H$_3$), 23.8 [q, CH(OMe)*C*H$_3$], 56.8 (q, OCH_3), 65.9 (t, O*C*H$_2$CH$_3$), 82.4 [d, *C*H(OMe)Me], 111.9 (d, arom. C-5), 119.3 (d, arom. C-3), 129.4 (s, arom. C-1), 134.5 (d, arom. C-4), 147.0 (s, arom. C-2 or C-6), 155.3 (s, arom. C-2 or C-6), 176.5 (s, O*C*OMe), 176.7 (s, O*C*OMe). − IR ($CHCl_3$): $\tilde{\nu}$ = 2988, 2934, 2827, 1715, 1646, 1588, 1567, 1461, 1366, 1275, 1111, 1051, 1007, 909, 871 cm^{-1}.

(*S*)-Bis(acetato-*O*)[2-(1-methoxyethyl)-6-(1-methylethoxy)-phenyl]iodine (6h): GP4; 69% yield (determined by NMR), inseparable from **5g**; yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 1.42 [t, 6 H, *J* = 6.3 Hz, OCH(CH_3)$_2$], 1.47 [d, 3 H, *J* = 6.5 Hz, CH(OMe)CH_3], 1.94 (s, 3 H, OCOCH_3), 1.95 (s, 3 H, OCOCH_3), 3.24 (s, 3 H, OCH_3), 4.66−4.79 [m, 2 H, C*H*(OMe)Me and OC*H*Me$_2$], 7.03 (dd, 1 H, *J* = 8.5 Hz, *J* = 1.2 Hz, 3- or 5-H arom.), 7.23 (dd, 1 H, *J* = 7.8 Hz, *J* = 1.2 Hz, 3- or 5-H arom.), 7.56 (t, 1 H, *J* = 8.0 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.3 (q, 2 C, OCO*C*H$_3$), 21.8 [q, OCH(*C*H$_3$)$_2$], 21.9 [q, OCH(*C*H$_3$)$_2$], 23.8 [q, CH(OMe)*C*H$_3$], 56.8 (q, OCH_3), 72.8 (d, O*C*HMe$_2$), 82.5 [d, *C*H(OMe)Me], 112.7 (d, arom. C-3), 119.0 (d, arom. C-5), 129.2 (s, arom. C-1), 134.4 (d, arom. C-4), 147.1 (s, arom. C-6), 154.4 (s, arom. C-2), 176.5 (s, O*C*OMe), 176.6 (s, O*C*OMe).

(*S*)-Bis(acetato-*O*)[2-(1,1-dimethylethoxy-6-(1-methoxyethyl)-phenyl]iodine (6i): GP4; 47% yield; yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 1.47 [d, 3 H, *J* = 6.4 Hz, CH(OMe)CH_3], 1.55 [s, 9 H, C(CH_3)$_3$], 1.95 (s, 3 H, OCOCH_3), 1.96 (s, 3 H, OCOCH_3), 3.24 (s, 3 H, OCH_3), 4.69 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 7.28 (d, 2 H, *J* = 8.1 Hz, 3- and 5-H arom.), 7.52 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.3 (q, 2 C, OCO*C*H$_3$), 23.7 [q, CH(OMe)*C*H$_3$], 29.0 [q, 3 C, C(*C*H$_3$)$_3$], 56.8 (q, OCH_3), 82.5 (s, *C*Me$_3$), 82.7 [d, *C*H(OMe)Me], 117.9 (d, arom. C-5), 120.0 (d, arom. C-3), 123.4 (s, arom. C-1), 133.7 (d, arom. C-4), 147.1 (s, arom. C-2), 153.7 (s, arom. C-6), 176.4 (s, O*C*OMe), 176.6 (s, O*C*OMe).

(*S*)-Bis(acetato-*O*)[2-(methoxymethoxy)-6-(1-methoxyethyl)-phenyl]iodine (6j): GP4; 83% yield, colorless crystals. − ^{1}H NMR ($CDCl_3$): δ = 1.48 [d, 3 H, *J* = 6.4 Hz, CH(OMe)CH_3], 1.947 (s, 3 H, OCOCH_3), 1.953 (s, 3 H, OCOCH_3), 3.24 (s, 3 H, OCH_3), 3.53 (s, 3 H, CH$_2$OCH_3), 4.72 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 5.32 (d, 1 H, *J* = 6.9 Hz, CH_2), 5.35 (d, 1 H, *J* = 7.1 Hz, CH_2), 7.29−7.34 (m, 2 H, 3- and 5-H arom.), 7.58 (t, 1 H, *J* = 8.0 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 20.2 (q, 2 C, OCO*C*H$_3$), 23.7 [q, CH(OMe)*C*H$_3$], 56.5 (q, OCH_3), 56.8 (q, OCH_3), 82.4 [d, *C*H(OMe)Me], 95.1 (t, CH_2), 114.0 (d, arom. C-5), 118.2 (s, arom. C-1), 120.4 (d, arom. C-3), 134.5 (d, arom. C-4), 146.8 (s, arom. C-2), 153.7 (s, arom. C-6), 176.8 (s, O*C*OMe), 177.0 (s, O*C*OMe).

3-Hydroxy-2-iodoacetophenone:[47] Compound **3f** (4.13 g, 11.7 mmol) was dissolved in CH_2Cl_2 (150 mL) and a solution of BBr_3 (1.55 mL, 16.1 mmol) in CH_2Cl_2 (20 mL) was slowly added (over 20 min) at −70 °C. After 30 min, water (50 mL) was added and after stirring for a further 60 min, the organic solvent was removed in vacuo. The aqueous phase was extracted with *tert*-butyl methyl ether (4 × 30 mL) and then the combined organic phases were extracted with 1 N aq. NaOH (3 × 20 mL). After acidification of the combined aqueous extracts with 2 N HCl, extraction with *tert*-butyl methyl ether and subsequent evaporation the solvent gave the product; 93% (2.87 g), colorless crystals, m.p. 93−97 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.82 (s, 3 H, CH_3), 5.95 (s, 1 H, OH), 7.10−7.15 (m, 2 H), 7.29 (t, 1 H, *J* = 8.1 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 29.2 (q, CH_3), 83.7 (s, arom. C-2), 117.4 (d, arom. C-4 or C-6), 121.0 (d, arom. C-4 or C-6), 129.7 (d, arom. C-5), 143.7 (s, arom. C-3), 155.7 (s, arom. C-1), 201.1 (s, CO). − IR (KBr): $\tilde{\nu}$ = 3192, 3080, 3050, 3000, 2911, 1673, 1589, 1567, 1453, 1418, 1358, 1324, 1294, 1233, 1175, 1015, 892, 782 cm^{-1}. − MS (EI, 70 eV): *m/z* (%) = 263 [M$^+$ + H] (8), 262 (81), 247 (100), 219 (14), 191 (3), 92 (23), 63 (5), 43 (6), 39 (1).

2-Iodo-3-(methoxymethoxy)acetophenone:[48] Powdered KOH (1.27 g, 19.3 mmol) was suspended in CH_3CN (25 mL) and a solution of 3-hydroxy-2-iodoacetophenone (2.68 g, 10.2 mmol) in CH_3CN (15 mL) was added. After 1 h, methoxymethyl chloride (1.0 mL, 13.2 mmol) was slowly added. After stirring for a further

2.5 h, water (25 mL) was added. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 25 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. Quantitative yield (3.21 g), light-brown oil. − ^{1}H NMR ($CDCl_3$): δ = 2.60 (s, 3 H, $COCH_3$), 3.52 (s, 3 H, OCH_3), 5.27 (s, 2 H, CH_2), 6.97 (dd, 1 H, *J* = 7.5 Hz, *J* = 1.3 Hz), 7.11 (dd, 1 H, *J* = 8.3 Hz, *J* = 1.3 Hz), 7.32 (t, 1 H, *J* = 7.9 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 30.0 (q, CH_3), 56.5 (q, OCH_3), 84.1 (s, arom. C-2), 95.0 (t, CH_2), 115.8 (d, arom. C-4 or C-6), 120.5 (d, arom. C-4 or C-6), 129.5 (d, arom. C-5), 147.8 (s, arom. C-3), 156.2 (s, arom. C-1), 203.6 (s, CO). − IR (KBr): $\tilde{\nu}$ = 3006, 2960, 2935, 2852, 2830, 1701, 1564, 1458, 1443, 1420, 1355, 1284, 1263, 1156, 1082, 1019, 968, 922 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 307 [M^+ + H] (7), 306 (44), 276 (5), 275 (7), 261 (7), 179 (2), 119 (5), 75 (6), 63 (10), 45 (100), 43 (27), 39 (2).

(*S*)-2-Iodo-3-(1-methoxyethyl)phenol (8): Compound **5j** (1.36 g, 4.22 mmol) was dissolved in MeOH (25 mL) and treated with conc. HCl (0.5 mL). After stirring for 75 min at 55 °C, the solvent was removed in vacuo and the residue was redissolved in *tert*-butyl methyl ether (40 mL). After washing with water (2 × 15 mL), the organic phase was extracted with 1 N aq. NaOH (3 × 15 mL). After acidification of the combined aqueous extracts with 2 N HCl, extraction with *tert*-butyl methyl ether (3 × 20 mL), drying of the extracts with $MgSO_4$, and evaporation the solvent gave the product. Recrystallization from *tert*-butyl methyl ether/pentane gave 89% (1.05 g) yield; colorless crystals, m.p. 119−121 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.38 [d, 3 H, *J* = 6.4 Hz, CH(OMe)CH_3], 3.25 (s, 3 H, OCH_3), 4.51 [q, 1 H, *J* = 6.4 Hz, C*H*(OMe)Me], 5.50 (s, 1 H, OH), 6.94 (dd, 1 H, *J* = 7.9 Hz, *J* = 1.5 Hz, 3- or 5-H arom.), 6.99 (dd, 1 H, *J* = 7.7 Hz, *J* = 1.4 Hz, 3- or 5-H arom.), 7.25 (t, 1 H, *J* = 7.8 Hz, 4-H arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.4 [q, CH(OMe)*C*H_3], 56.7 (q, OCH_3), 83.2 [d, *C*H(OMe)Me], 90.4 (s, arom. C-2), 113.9 (d, arom. C-4), 118.6 (d, arom. C-6), 129.9 (d, arom. C-5), 146.4 (s, arom. C-1), 154.5 (s, arom. C-3). − IR (KBr): $\tilde{\nu}$ = 3164, 2972, 2910, 2832, 1935, 1856, 1778, 1685, 1571, 1458, 1438, 1374, 1362, 1324, 1291, 1219, 1094, 1050, 1010, 988, 936, 841, 796 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 279 [M^+ + H] (7), 278 (45), 263 (100), 248 (18), 247 (15), 151 (5), 120 (21), 108 (7), 91 (13), 77 (9), 65 (11), 63 (10), 59 (21), 43 (11), 39 (10). − $C_9H_{11}IO_2$ (278.09): calcd. C 38.87, H 3.99, O 11.51; found C 39.24, H 3.98, O 11.74.

1-(1-Iodonaphthalen-2-yl)ethanone: 1-Bromonaphthalene was used in GP1. 61% (1.80 g) yield, pale-brown solid. − ^{1}H NMR ($CDCl_3$): δ = 2.66 (s, 3 H, $COCH_3$), 7.26 (d, 1 H, *J* = 8.3 Hz), 7.47−7.62 (m, 2 H), 7.73 (dd, 1 H, *J* = 8.0 Hz, *J* = 1.4 Hz), 7.80 (d, 1 H, *J* = 8.3 Hz), 8.23 (d, 1 H, *J* = 8.4 Hz). − ^{13}C NMR ($CDCl_3$): δ = 30.3 (q, CO*C*H_3), 95.9 (s, arom. C-1), 123.1 (d), 127.5 (d), 128.3 (d), 128.5 (d), 129.3 (d), 132.8 (d), 133.7 (s), 134.1 (s), 145.5 (s, arom. C-2), 204.5 (s, CO). − IR ($CHCl_3$): $\tilde{\nu}$ = 3125, 2975, 2937, 2850, 2250, 1785, 1485, 1350 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 296 (80), 281 (100), 253 (32), 141 (11), 126 (59), 115 (6), 74 (9), 63 (6), 43 (17). − HRMS: calcd. for $C_{12}H_9IO$ 295.9698; found 295.9700 [M^+].

(*S*)-1-(1-Iodonaphthalen-2-yl)ethanol: GP2; 84% (1.52 g) yield; orange oil; 97% *ee*.[49] − ^{1}H NMR ($CDCl_3$): δ = 1.52 [d, 3 H, *J* = 6.4 Hz, CH(OH)CH_3], 2.38 (d, 1 H, *J* = 2.2 Hz, OH), 5.47 [dq, 1 H, *J* = 6.3 Hz, *J* = 2.5 Hz, C*H*(OH)CH_3], 7.44−7.57 (m, 2 H), 7.68 (d, 1 H, *J* = 8.6 Hz), 7.75 (d, 1 H, *J* = 8.0 Hz), 7.81 (d, 1 H, *J* = 8.5 Hz), 8.25 (d, 1 H, *J* = 7.8 Hz). − ^{13}C NMR ($CDCl_3$): δ = 23.7 (q, CH_3), 75.1 [d, *C*H(OH)Me], 102.1 (s), 123.7 (d), 126.2 (d), 127.6 (d), 128.1 (d), 129.2 (d), 132.6 (d), 133.7 (s), 134.3 (s), 146.4 (s). − IR ($CHCl_3$): $\tilde{\nu}$ = 3602, 3400, 3065, 2977, 2925, 2250 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 298 (99), 283 (100), 155 (16), 141 (12), 128 (90), 115 (7), 86 (12), 77 (9), 43 (38). − HRMS: calcd. for $C_{12}H_{11}IO$ 297.9855; found 297.9860 [M^+]. − $[\alpha]_D^{25}$ = −56.0 (*c* = 0.30, $CHCl_3$).

(*S*)-1-Iodo-2-(1-methoxyethyl)naphthalene: GP3; 87% (1.28 g) yield; purification by flash chromatography on silica gel (*tert*-butyl methyl ether/pentane, 1:5); colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.47 [d, 3 H, *J* = 7.0 Hz, CH(OMe)CH_3], 3.27 (s, 3 H, OCH_3), 4.98 [q, 1 H, *J* = 6.3 Hz, C*H*(OMe)Me], 7.48−7.62 (m, 3 H), 7.78 (d, 1 H, *J* = 8.0 Hz), 7.84 (d, 1 H, *J* = 8.0 Hz), 8.27 (d, 1 H, *J* = 9.0 Hz). − ^{13}C NMR ($CDCl_3$): δ = 22.5 (q, CH_3), 56.8 (q, OCH_3), 84.3 [d, *C*H(OMe)Me], 103.6 (s), 123.9 (d), 126.5 (d), 127.7 (d), 128.3 (d), 129.5 (d), 132.7 (d), 134.0 (s), 134.6 (s), 144.6 (s). − IR ($CHCl_3$): $\tilde{\nu}$ = 2960, 2930, 2855, 2330, 2250, 1460, 1366 cm^{-1}. − MS (EI, 70 eV): *m*/*z* (%) = 312 (38), 297 (100), 282 (10), 154 (19), 141 (7), 126 (12), 76 (5), 59 (5), 43 (6). − HRMS: calcd. for $C_{13}H_{13}IO$ 312.0011; found 312.0008 [M^+]. − $[\alpha]_D^{25}$ = −77.1 (*c* = 0.69, $CHCl_3$).

(*S*)-Bis(acetato-*O*)[2-(1-methoxyethyl)naphthalen-1-yl]iodine: GP4; 81% (560 mg) yield; inseparable from (*S*)-1-iodo-2-(1-methoxyethyl)naphthalene; yellow oil. − ^{1}H NMR ($CDCl_3$): δ = 1.57 [d, 3 H, *J* = 6.4 Hz, CH(OH)CH_3)], 1.89 (s, 3 H, $COCH_3$), 1.90 (s, 3 H, $COCH_3$), 3.26 (s, 3 H, OCH_3), 4.98 [q, 1 H, *J* = 6.3 Hz, C*H*(OH)CH_3], 7.50−8.30 (m, 6 H). − ^{13}C NMR ($CDCl_3$): δ = 20.1 (q, OCO*C*H_3), 20.2 (q, OCO*C*H_3), 23.8 [q, CH(OMe)*C*H_3], 56.9 (q, OCH_3), 84.0 [d, *C*H(OMe)Me], 103.5 (s), 124.0 (d), 127.5 (d), 128.2 (d), 128.9 (d), 129.3 (d), 130.5 (s), 131.6 (s), 134.0 (d), 144.9 (s), 176.5 (s, O*C*OMe), 176.6 (s, O*C*OMe).

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