JOC The Journal of Organic Chemistry

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Tobias Hokamp, and Thomas Wirth

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01315 • Publication Date (Web): 09 Jun 2019

Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Structurally Defined α-Tetralol-Based Chiral Hypervalent Iodine Reagents

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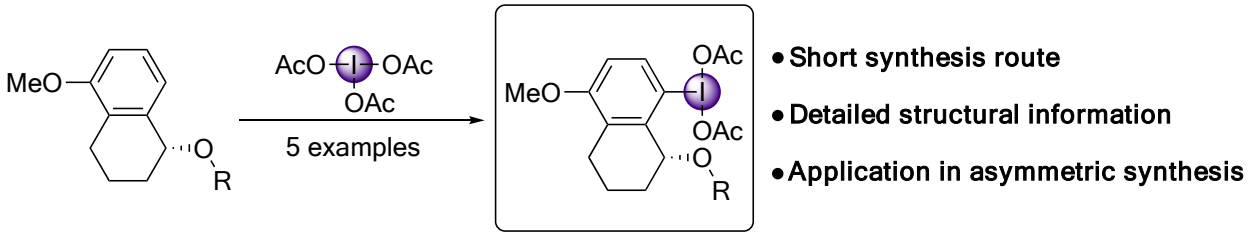
Abstract

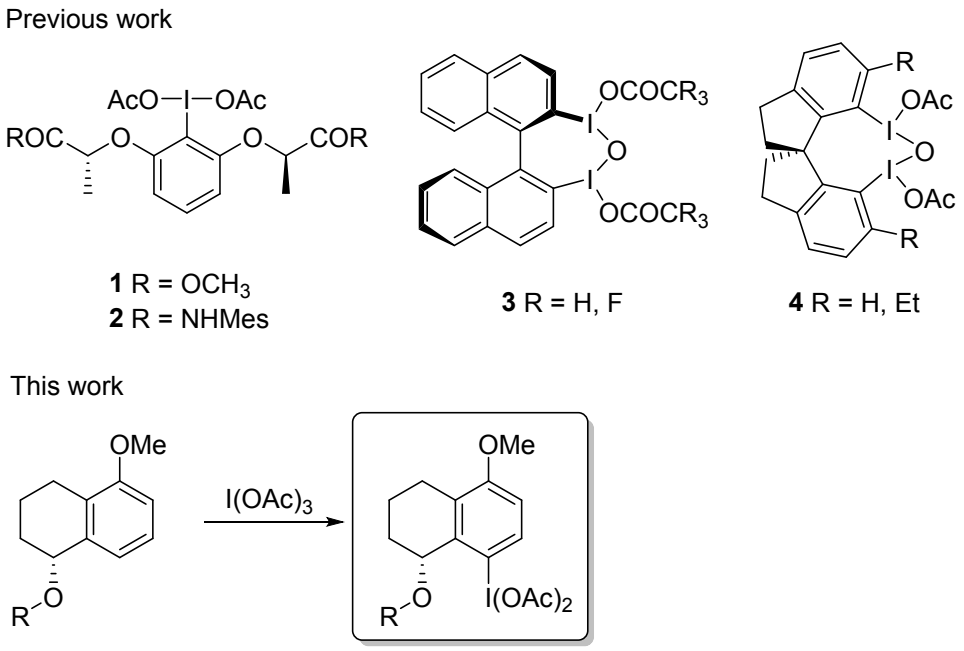
A novel class of chiral hypervalent iodine reagents containing an α-tetralol-scaffold is being introduced. Iodine triacetate is employed in a key-step as highly selective and efficient iodinating reagent for a short and convenient synthesis of iodine(III) derivatives. Solid state X-ray analyses offer valuable structural information while reactivities and stereoselectivities are investigated in three model reactions.



Tetralol-based hypervalent iodine reagents

Introduction

Chiral hypervalent iodine compounds are powerful tools in synthetic organic chemistry as they have contributed to a variety of novel chemical transformations.[1] As mild, versatile and environmentally benign reagents they found application in stereoselective reactions such as α-functionalization of carbonyl compounds,[2] alkene functionalization,[3] phenolic oxidation,[4] oxidation of sulfides[5] and rearrangement reactions.[6] A huge variety of chiral hypervalent organoiodine reagents have been reported over the past two decades. Examples include the lactic acid based reagent **1**[7] and the amide derivative **2**.[4c,8] Furthermore, chirality was introduced through the incorporation of binaphthyl backbones **3**[9] or through a rigid spirocyclic backbone as in **4**.[4a]



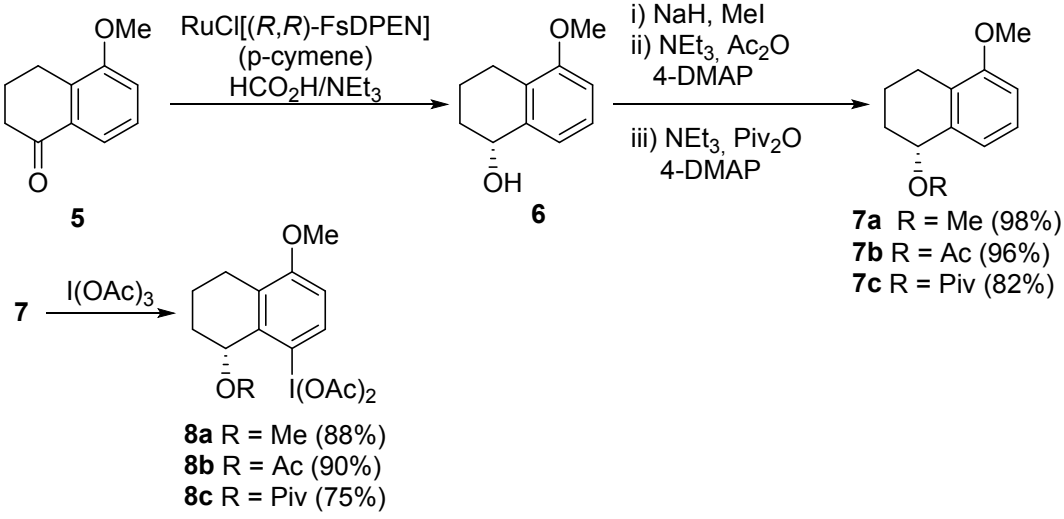
Scheme 1: Top: An overview of chiral hypervalent iodine reagents. Bottom: Synthesis of novel tetralol-based chiral hypervalent iodine reagents.

This work addresses the synthesis of hypervalent iodine reagents containing a chiral α-tetralol scaffold (Scheme 1). Here, the chiral center is located in a rigid ring system close to the iodine-center, similar to the corresponding selenium-derivatives, which have been successfully employed.[10] As this class of hypervalent iodine reagents has not been reported so far, defined structural information of those compounds is highly desirable in order to get insight into their possible reactivities.

Results and Discussion

As a key step for the synthesis we aimed to apply iodine triacetate [$I(OAc)_3$] as iodinating agent, which has demonstrated excellent selectivities and yields in our previous studies on the direct conversion of non-iodinated arenes into (diacetoxyiodo)arenes.[11] For a selective iodination in the 8-position, a methoxy-substituent has been implemented as a directing group in the 4-position. This key step will reduce the number of steps for the synthesis of iodinated tetralol-derivatives compared to know routes for similar reagents.[12]

Initially, 5-methoxy-1-tetralone (**5**) was stereoselectively reduced to (*R*)-**6** using a chiral ruthenium catalyst (Scheme 2).[13] Alcohol **6** was obtained in >99% *ee* and excellent yield (94%) and was the starting point for the synthesis of a range of tetralol-based hypervalent iodine reagents. The absolute configuration of **6** was determined by a solid-state x-ray structure.[14] For the first examples of hypervalent iodine compounds based on a tetralol-scaffold, different substituents were introduced yielding **7a-c**. To our delight, direct conversion to the desired hypervalent iodine reagents **8a-c** in good to excellent yield (75-90%) was achieved by simple reaction of **7a-c** with iodine triacetate.

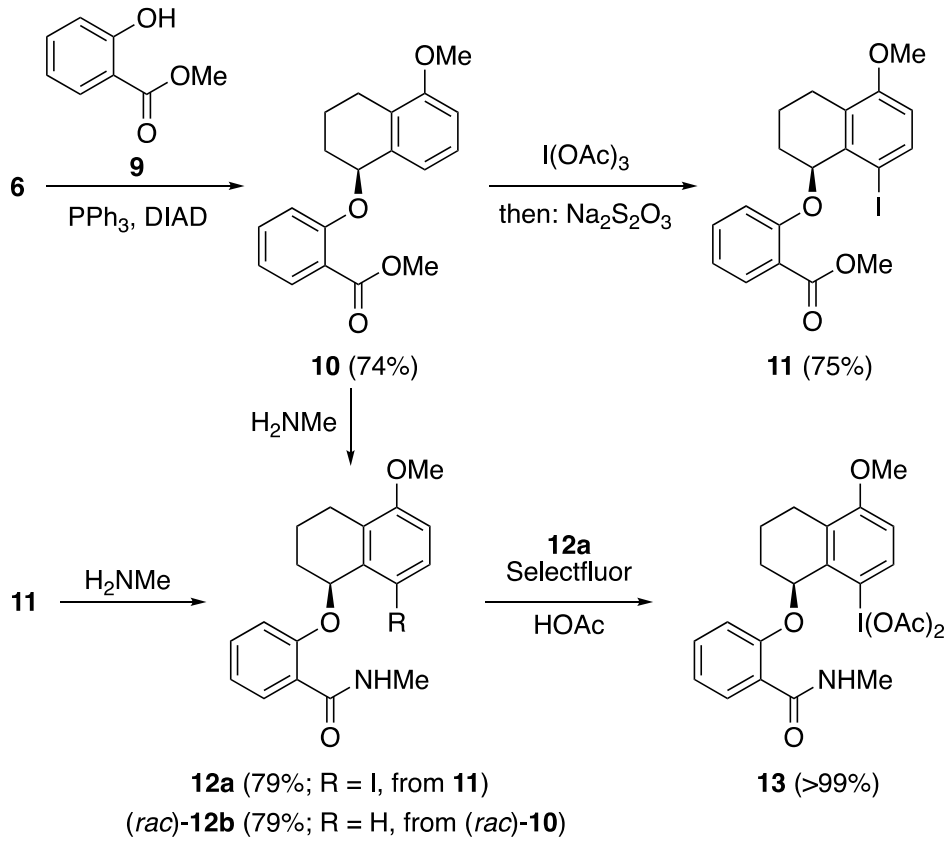


Scheme 2: Synthesis of tetralol-based hypervalent iodine reagents **8a-c** by using $I(OAc)_3$ as a key step.

The effect of amide-containing substituents was studied in the next step. As reported by Ishihara and Muñiz,[3c,4c-d] the amide NH groups of **2** engage in hydrogen bonding with the acetoxy groups located at the central iodine atom.

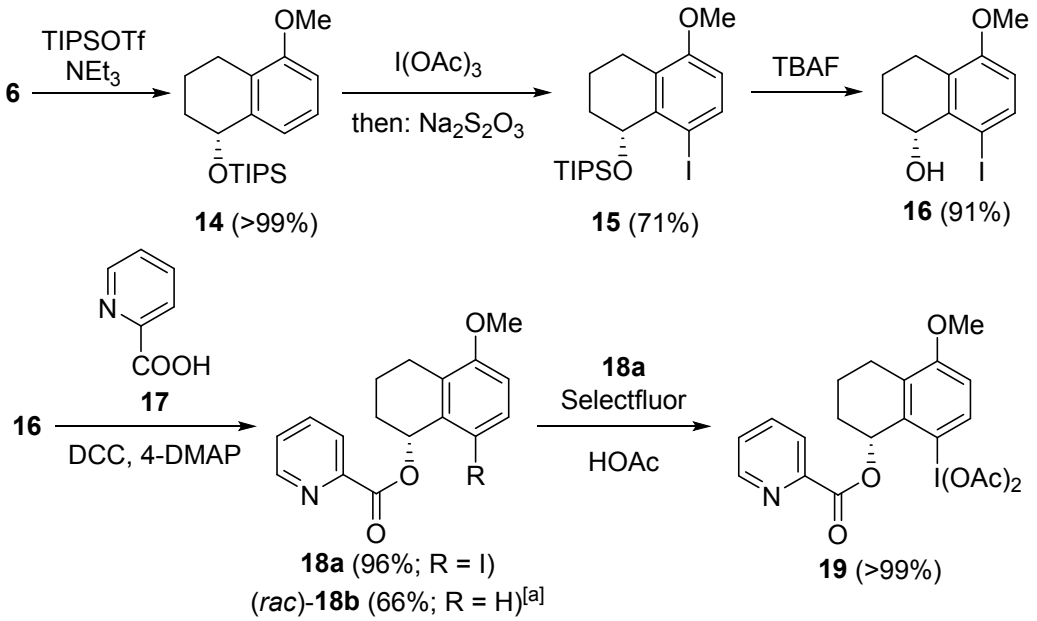
A convenient way for the introduction of an amide-containing substituent was the installation of *N*-methylsalicylamide through a Mitsunobu reaction to reach **13** as final product after treatment with iodine triacetate. However, an alternative pathway had to be chosen as the direct synthesis of **13** from **12b** afforded mainly **12a** and minor quantities of **13**. Hence, methyl salicylate (**9**) was introduced first *via* Mitsunobu-reaction to give **10** in good yields (74%), which was then selectively iodinated to **11** in 75% yield (Scheme 3). Amide **12a** was synthesized after

treating **11** with methylamine (79% yield) and oxidation of **12a** with Selectfluor® in presence of acetic acid provided the amide-containing tetralol-based hypervalent iodine reagent **13** in quantitative yield.



Scheme 3: Synthesis of the tetralol-based hypervalent iodine reagent **13**.

As a next step, a pyridine-containing substituent was introduced to the chiral center. It is well known that pyridine-derivatives are suitable ligands for iodine(III) reagents, as they have the ability to coordinate to the iodine-center.[15] Therefore, we planned to esterify **6** with picolinic acid (**17**). However, as in case for the synthesis of **13**, reaction of iodine triacetate with **18b** led to the formation of **18a** and small amounts of **19**. Hence, **6** was first protected with a triisopropylsilyl group to give **14** in quantitative yield (Scheme 4). Iodination by using iodine triacetate (**15**, 71% yield) and deprotection gave **16** in excellent yield (91%). Picolinic acid (**17**) was introduced by Steglich-esterification yielding **18** (96%), which was then oxidized by Selectfluor® in presence acetic acid to give **19** in quantitative yield.



Scheme 4: Synthesis of the pyridine-containing tetralol-based hypervalent iodine reagent **19**. [a] prepared *via* Steglich esterification from **6**.

First structural information of this novel class of tetralol-based iodine(III) reagents was obtained by solid state structural analysis of **8a** (Figure 1).[14] As expected for hypervalent iodine(III) compounds of type $ArIL_2$ with Ar being an aryl moiety and L a ligand containing heteroatom (O, N, halogen), **8a** has a trigonal bipyramidal geometry with the acetate ligands in the axial position and the aryl moiety occupying the equatorial position. The two acetate ligands form, together with the iodine atom, a nearly linear three-center-four-electron (3c-4e) hypervalent bond with an angle of 167.3° and a distance of 2.170 Å for I(1)-O(1) and 2.144 Å for I(1)-O(3), respectively.[16] The I(1)-O(5) distance is with 3.451 Å as long as the sum of the van der Waal's radii of I (1.98 Å) and O (1.52 Å) and therefore no interaction between both atoms is being observed.[17] The hypervalent bond [O(1)-I(1)-O(3)] is perpendicular to the aromatic ring.

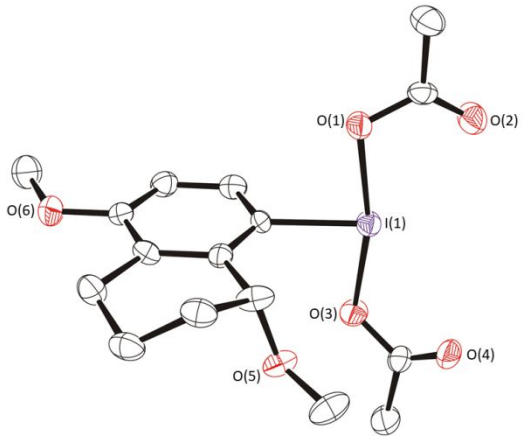


Figure 1: X-ray structures of iodine(III) reagent **8a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

By the introduction of a pivaloyl substituent as a more bulky group than a methoxy-substituent (**8c**), the hypervalent I(1)-C(1) bond rotates so that the hypervalent bond [O(4)-I(1)-O(6)] is no longer perpendicular to the aromatic ring as it was the case in **8a** (Figure 2).[14] The dihedral angle in **8c** between C(2)-C(1)-I(1)-O(1) is with 111.7° greater than the torsion in **8a** (90.1°). Additionally, no interaction between the iodine center and the substituent can be observed, as the distance between I(1)-O(6) is 3.831 Å while the distance between I(1)-O(5) is 3.540 Å long.

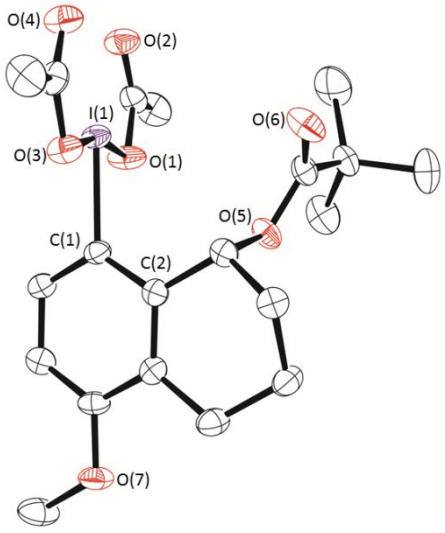


Figure 2: X-ray structures of iodine(III) reagent **8c**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Interestingly, the introduction of an amide substituent in hypervalent iodine compound **13** did not lead to any formation of hydrogen bonds between the acetoxy groups and the amide NH group in the solid state but between NH and O(5) (2.004 Å, Figure 3).[14]

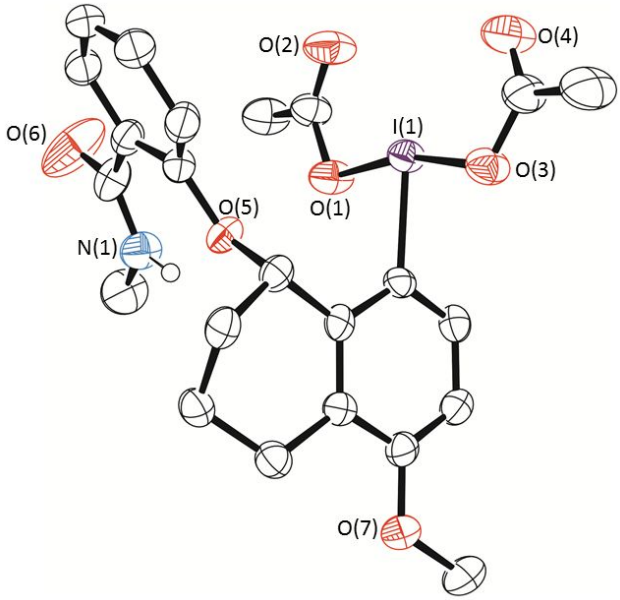


Figure 3: X-ray structures of iodine(III) reagent **13**. Hydrogen atoms are omitted for clarity with the exception of the amide proton. Thermal ellipsoids are shown at 50% probability.

More surprisingly, in case of **19**, no coordination of the pyridine nitrogen to the iodine center can be observed (distance of N(1)-I(1): 4.766 Å) although pyridine is known for its ability to coordinate to hypervalent iodine reagents (Figure 4).[14,15]

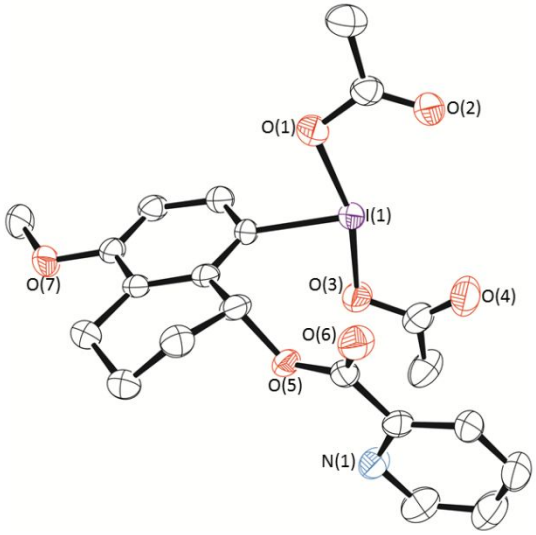
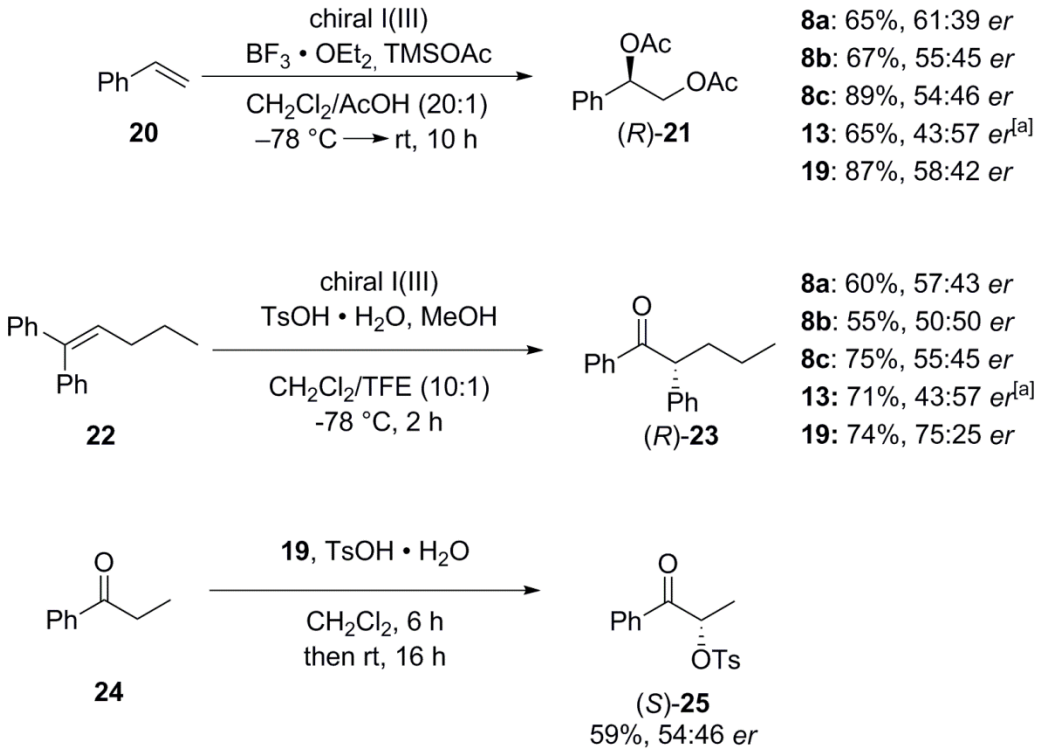


Figure 4: X-ray structures of iodine(III) reagent **19**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Moreover, ^{1}H and $^{13}C\{^{1}H\}$ NMR analysis for all described hypervalent iodine reagents reveals a hindered rotation of the I(1)-C bond as the acetate protons and carbons of both ligands show different chemical environment.

After having achieved valuable information regarding the structures of tetralol-based hypervalent iodine reagents, the focus was directed towards the reactivity and the stereocontrol of those reagents. Therefore, the well-known diacetoxylation of styrene **20**[3e] and the oxidative rearrangement of **22**[6b] (Scheme 5) were carried out. Both reactions furnished similar yields for all hypervalent iodine reagents. Diacetoxylated product (*R*)-**21** was obtained in 65% yield using **8a** and in 67% yield using **8b**. Reagent **8c** and **19** provided (*R*)-**21** in very good yield (89% and 87%, respectively), while **13** gave (*S*)-**21** in good yield (65%). The use of all five hypervalent iodine reagents furnished rearranged product (*R*)-**23** in yields between 55% (using **8b**) and 75% yield (using **8c**). However, the stereoselectivities in the diacetoxylation of **20** remained mainly little (up to 61:39 *er*). Furthermore, the oxidative rearrangement provided mainly low enantiomeric ratios between 50:50 *er* by the use of **8b** and 57:43 *er* when **8a** and **13** were applied. Interestingly, the enantiomeric ratio could be increased to 75:25 *er* in presence of **19**. Thus, reagent **19** was further investigated in the α-tosylation of propiophenone **24**. However, (*S*)-**25** was obtained in good yield (59%) but poor stereoselectivity (54:46 *er*). Those

results are surprising, as hypervalent iodine reagents containing amide- or pyridine substituents have been very successfully employed in stereoselective reactions.[3c,4c-d,15g]



Scheme 5: Stereoselective diacetoxylation and rearrangement using different tetralol-based hypervalent iodine reagents. Yields are reported and enantiomeric ratios are determined by chiral HPLC. [a] (*S*)-isomer was the major isomer.

Conclusion

In summary, we have introduced a novel class of chiral hypervalent iodine reagents containing a tetralol-scaffold, which can be directly synthesized by using iodine triacetate as iodinating reagent. Valuable structural information was received by solid-state X-ray analysis. Furthermore, the reactivities and stereoselectivities were investigated in three model reactions.

Experimental Section

Reactions involving air and moisture sensitive reagents were carried out in flame dried glass wares under a dry nitrogen. A dry, nitrogen-filled glove box from MBraun was used for the storage of moisture sensitive hypervalent iodine reagents. Solvents used in reactions were dried according to standard procedures. Reagents were purchased from Acros Organics, Alfa Aesar GmbH & Co. KG, Fisher Scientific, FluoroChem, Merck KGAA and Sigma Aldrich GmbH. Styrene was distilled prior to use by a Büchi GKR-50 Kugelrohr apparatus. All other reagents obtained from commercial sources were used as received. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 298 K on a Bruker DPX 300, Bruker DPX 400 or a Bruker DPX 500. All resonances are reported relative to TMS. Spectra were calibrated relative to solvents' residual proton and carbon chemical shifts. Coupling constants (J) are reported in Hz. TLC was performed to monitor the reactions using precoated aluminium sheets of Merck silica gel 60 F254 (0.20 m), and detection of compounds was performed under UV light (254 nm) or by staining with a solution of $KMnO_4$. Flash column chromatography was performed using Merck silica gel 60 (40-63 µm) to purify products applying nitrogen pressure of about 0.2 bar or on a Biotage Isolera Four using Biotage cartridges SNAP Ultra 10 g, SNAP Ultra 25 g, SNAP Ultra 50 g and SNAP Ultra 100 g. HRMS were measured by the EPSRC Mass Spectrometry Facility in Swansea University on a Waters Xevo G2-S and on a Thermo Scientific LTQ Orbitrap XL or at Cardiff University on a Waters LCT Premier XE. Ions were generated by Electrospray Ionization (ES), Electron Ionization (EI), Nanospray Ionization (NSI), Atmospheric Sample Analysis Probe (ASAP) or Chemical Ionization (CI). Melting points were determined with a Gallenkamp variable heater and are not corrected. Infrared spectra were recorded on a Shimadzu FTIR Affinity-1S spectrometer. HPLC was performed on an Agilent Technologies 1260 Infinity Quaternary LC system. Separation was performed using Lux 5 µm Cellulose-1, LC Column (250 x 4.6 mm) or YMC Chiral Amylose-C S-5µm (25 cm). Optical rotations were measured with a SCHMIDT + HAENSCH UniPol L polarimeter.

Iodine triacetate I(OAc)$_3$. Following a reported procedure,[11] ground iodine (2.5 g, 10 mmol, 1.0 equiv.), acetic acid (3.5 mL, 61 mmol, 6.1 equiv.) and acetic anhydride (7.0 mL, 74 mmol, 7.4 equiv.) were added to a flame-dried *Schlenk* tube under nitrogen. The solution was cooled

to –40 °C and fuming nitric acid (≥99.5%, 2.7 mL, 65 mmol, 6.5 equiv.) was added while stirring. Afterwards, the solution was allowed to warm to room temperature and stirred for 2 hours protected from light. All volatiles were then removed *in vacuo* and **4** was obtained as pale yellow solid in 94% (5.60 g, 18.4 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.19 (s, 9H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 180.3, 19.8 ppm. The spectroscopic data agree with the literature.[11]

*(R)-5-Methoxy-1,2,3,4-tetrahydro-1-naphthol (**6**)*. 5-Methoxy-1-tetralone **5** (1.76 g, 10.0 mmol) and RuCl[(*R*,*R*)-FsDPEN](p-cymene) (356 mg, 0.450 mmol, 4.5 mol%, 90% purity) were dissolved in dry DMF (100 mL) in a flame-dried *Schlenk* flask under nitrogen atmosphere. After stirring the resulting solution for 10 minutes at room temperature, formic acid trimethylamine complex (5:2, 4.1 mL, 50 mmol, 5.0 equiv.) was added. The reaction mixture was then stirred at room temperature for 4 days. Afterwards, the reaction was quenched with water (150 mL) and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 80:20) to afford **6** as colorless solid in 94% (1.67 g, 9.40 mmol) yield. A sample was recrystallized from ethyl acetate/*n*-hexane at room temperature. Colorless crystals of **6** were obtained suitable for X-ray diffraction.[14] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 8.1, 0.7 Hz, 1H), 4.76 (t, *J* = 4.4 Hz, 1H), 3.83 (s, 3H), 2.80 – 2.71 (m, 1H), 2.60 – 2.51 (m, 1H), 2.00 – 1.73 (m, 5H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ = 157.1, 140.2, 126.6, 126.2, 120.7, 108.8, 68.3, 55.5, 31.8, 23.1, 18.2 ppm. The spectroscopic data agree with the literature.[18] HPLC-analysis: YMC Chiral Amylose-C S-5µm (25 cm), *n*-hexane/i-PrOH = 60:40, 1.0 mL/min, 254 nm t_R (major) = 5.0 min, t_R (minor) = 5.4 min, >99:1 *er*.

*(R)-1,5-Dimethoxy-1,2,3,4-tetrahydronaphthalene (**7a**)*. **6** (178 mg, 1.00 mmol) was dissolved in dry THF (8 mL) under nitrogen atmosphere. The reaction mixture was cooled to 0 °C and NaH (80 mg, 2.0 mmol, 2.0 equiv., 60% dispersion in mineral oil) was added portionwise. After the turbid mixture had been stirred for 1 h at 0 °C, methyl iodide (125 µL, 2.00 mmol, 2.0 equiv.)

was added and the solution was stirred for 13 h at room temperature. The reaction mixture was then quenched with aqueous KOH solution (10%, 10 mL). After extraction with EtOAc (3 x 10 mL), the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10) to afford **7a** as colorless solid in 98% (188 mg, 0.980 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.31 (t, *J* = 4.7 Hz, 1H), 3.82 (s, 3H), 3.45 (s, 3H), 2.76 (dt, 1H, *J* = 17.6, 5.7 Hz), 2.62 – 2.50 (m, 1H), 2.06 – 1.92 (m, 2H), 1.90 – 1.80 (m, 1H), 1.78 – 1.70 (m, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 157.2, 137.9, 126.6, 126.1, 121.6, 108.9, 76.9, 56.3, 55.5, 27.1, 23.0, 18.0 ppm. $[\alpha]_D^{20}$ = +19.5 (c = 0.44, $CHCl_3$). The spectroscopic data agree with the literature.[19]

*(R)-5-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl acetate (**7b**)*. **6** (178 mg, 1.00 mmol) was dissolved in triethylamine (2.0 mL, 14 mmol, 14 equiv.) and acetic anhydride (284 µL, 3.00 mmol, 3.0 equiv.). 4-(Dimethylamino)-pyridine (12 mg, 0.10 mmol, 10 mol%) was then added and the reaction mixture was stirred at room temperature for 3 h. After completion of the reaction, the solution was diluted with methanol (10 mL) and concentrated under reduced pressure. The residue was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10) to afford **7b** as colorless oil in 96% (211 mg, 0.960 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 5.99 (t, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 2.83 (dt, *J* = 9.0, 5.0 Hz, 1H), 2.58 – 2.49 (m, 1H), 2.08 (s, 3H), 2.01 – 1.88 (m, 3H), 1.87 – 1.78 (m, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 170.9, 157.2, 135.8, 127.2, 126.6, 121.5, 109.3, 70.1, 55.5, 28.7, 22.9, 21.7, 18.2 ppm. $[\alpha]_D^{20}$ = +121.5 (c = 0.40, $CHCl_3$). The spectroscopic data agree with the literature.[20]

*(R)-5-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl pivalate (**7c**)*. **6** (232 mg, 1.30 mmol) was dissolved in triethylamine (2.6 mL, 18 mmol, 14 equiv.) and pivalic anhydride (791 µL, 3.90 mmol, 3.0 equiv.). 4-(Dimethylamino)-pyridine (16 mg, 0.13 mmol, 10 mol%) was then

added and the reaction mixture was stirred at room temperature for 14 h. Afterwards, the solution was diluted with methanol (10 mL) and concentrated under reduced pressure. The residue was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10) to afford **7c** as colorless solid in 82% (280 mg, 1.07 mmol) yield. M.p.: 66 – 70 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.94 (t, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 2.83 – 2.78 (m, 1H), 2.61 – 2.52 (m, 1H), 2.00 – 1.78 (m, 4H), 1.21 (s, 9H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 178.3, 157.0, 136.2 127.1, 126.4, 121.1, 108.9, 69.8, 55.4, 38.9, 28.7, 27.2, 23.0, 18.4 ppm. HRMS (ESP): *m/z* = 285.1467 calcd. for $C_{16}H_{22}O_3Na^+$ $[M+Na]^+$, found: 285.1469. IR (neat): 1708, 1477, 1469, 1438, 1396, 1340, 1250, 1146, 1070, 1058, 977, 918, 777, 721, 706 cm^{-1}. $[\alpha]_D^{20}$ = +61.0 (c = 0.40, $CHCl_3$).

General Procedure 1 for the Synthesis of Hypervalent Iodine Reagents 8. Iodine triacetate (1.00 mmol, 304 mg) was dissolved in glacial acetic acid (2.0 mL). The arene (1.00 mmol, 1.0 equiv.) was added subsequently and the reaction mixture was stirred at room temperature for 4 h. Next, all volatiles were removed and the residue was washed with dry *n*-hexane:Et_2O (10:1, 3 x 10 mL) to obtain the pure product.

*(R)-8-(Diacetoxyiodo)-1,5-dimethoxy-1,2,3,4-tetrahydronaphthalene (**8a**)*. **7a** (192 mg, 1.00 mmol, 1.0 equiv.) was reacted according to general procedure 1 to give **8a** as colorless solid in 88% (384 mg, 0.880 mmol) yield. A sample was recrystallized from CH_2Cl_2/*n*-hexane at -40 °C. Colorless crystals of 8a were obtained suitable for X-ray diffraction.[14] M.p.: 124 – 128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.7 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 4.50 (t, *J* = 3.1 Hz, 1H), 3.87 (s, 3H), 3.49 (s, 3H), 2.92 – 2.84 (m, 1H), 2.46 – 2.31 (m, 2H), 2.00 (s, 3H), 1.96 (s, 3H), 1.94 – 1.86 (m, 1H), 1.83 – 1.75 (m, 1H), 1.62 (tt, *J* = 13.7, 3.3 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 176.8, 176.4, 160.5, 138.6, 137.7, 130.7, 118.4, 110.9, 76.8, 56.5, 55.8, 25.0, 23.6, 20.5, 20.4, 16.3 ppm. HRMS (EI): *m/z* = 376.0166 calcd. for $C_{14}H_{17}O_4I^+$ $[M\text{-}OAc\text{-}H]^+$,

found: 376.0165. IR (neat): 1641, 1566, 1458, 1360, 1339, 1252, 1188, 1078, 1047, 1007, 912, 821, 802, 665 cm^{-1}. $[\alpha]_D^{20}$ = –63.1 (c = 0.40, $CHCl_3$).

*(R)-8-(Diacetoxyiodo)-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl acetate (**8b**)*. **7b** (220 mg, 1.00 mmol, 1.0 equiv.) was reacted according to general procedure 1 to give **8b** as colorless solid in 90% (418 mg, 0.880 mmol) yield. M.p.: 129 – 131 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.10 (t, *J* = 2.5 Hz, 1H), 3.89 (s, 3H), 3.01 – 2.92 (m, 1H), 2.50 – 2.38 (m, 1H), 2.33 – 2.23 (m, 1H), 2.06 (s, 3H), 1.96 (s, 3H), 1.96 (s, 3H), 1.92 – 1.81 (m, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 176.5, 176.4, 169.9, 160.7, 138.1, 136.2, 131.7, 118.0, 111.7, 71.2, 56.0, 28.4, 23.6, 21.2, 20.5, 20.5, 16.8 ppm. HRMS (CI): *m/z* = 364.0404 calcd. for $C_{13}H_{19}NO_3I^+$ $[M\text{-}2OAc+NH_4]^+$, found: 364.0405. IR (neat): 1728, 1647, 1566, 1462, 1437, 1366, 1261, 1227, 1103, 1070, 1007, 984, 912, 808, 729, 667, 606 cm^{-1}. $[\alpha]_D^{20}$ = +9.5 (c = 0.42, $CHCl_3$).

*(R)-8-(Diacetoxyiodo)-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl pivalate (**8c**)*. **7c** (262 mg, 1.00 mmol, 1.0 equiv.) was reacted according to general procedure 1 to give **8c** as colorless solid in 75% (380 mg, 0.750 mmol) yield. A sample was recrystallized from CH_2Cl_2/*n*-hexane at -40 °C. Colorless crystals of **8c** were obtained suitable for X-ray diffraction.[14] M.p.: 124 – 128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.08 (d, *J* = 2.6 Hz, 1H), 3.90 (s, 3H), 3.01 – 2.93 (m, 1H), 2.49 – 2.39 (m, 1H), 2.25 – 2.18 (m, 1H), 1.98 (s, 3H), 1.91 (s, 3H), 1.89 – 1.78 (m, 2H), 1.77 – 1.70 (m, 1H), 1.19 (s, 9H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 177.4 (C), 176.6, 176.6, 160.5, 137.7, 136.3, 131.8, 117.3, 111.6, 70.0, 55.9, 39.0, 28.1, 27.1, 23.7, 20.7, 20.6, 16.6 ppm. HRMS (NSI): *m/z* = 447.0663 calcd. for $C_{18}H_{24}O_5I^+$ $[M–OAc]^+$, found: 447.0654. IR (neat): 1724, 1643, 1568, 1466, 1362, 1261, 1138, 1105, 1069, 1013, 978, 920, 820, 665, 615 cm^{-1}. $[\alpha]_D^{20}$ = –107.0 (c = 0.42, $CHCl_3$).

*Methyl (S)-2-((5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)benzoate (**10**)*. **6** (445 mg, 2.50 mmol), methyl salicylate (405 µL, 3.13 mmol, 1.3 equiv.) and triphenylphosphine (825 mg, 3.13 mmol, 1.3 equiv.) were dissolved in dry THF (7 mL) under nitrogen atmosphere. The

reaction mixture was cooled to 0 °C and diisopropyl azodicarboxylate (652 µL, 3.13 mmol, 1.3 equiv.) was added dropwise. After 1 h at 0 °C, the mixture was warmed up to room temperature and stirred for 18 h. The solvent was removed under reduced pressure and Et_2O (20 mL) was added. Triphenylphosphine oxide, which precipitated, was removed by filtration and the filtrate was concentrated under vacuum. The crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 95:5) to afford **10** as white solid in 74% (578 mg, 1.85 mmol) yield. M.p.: 48 – 52 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 2H), 7.04 – 7.00 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.39 (t, *J* = 5.4 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.83 (dt, *J* = 17.8, 6.1 Hz, 1H), 2.63 (m, 1H), 2.17 – 2.07 (m, 2H), 2.06 – 1.97 (m, 1H), 1.85 – 1.76 (m, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 167.3, 157.7, 157.1, 136.8, 133.1, 131.6, 126.7, 126.2, 123.0, 121.3, 121.0, 117.0, 109.1, 76.7, 55.5, 52.1, 28.2, 23.0, 18.4 ppm. HRMS (ESP): *m/z* = 335.1259 calcd. for $C_{19}H_{20}O_4Na^+$ $[M+Na]^+$, found: 335.1259. IR (neat): 1728, 1597, 1450, 1300, 1240, 1182, 1163, 1128, 1080, 1012, 977, 777, 754, 729, 662 cm^{-1}. $[\alpha]_D^{20}$ = –29.0 (c = 0.41, $CHCl_3$).

*Methyl (S)-2-((8-iodo-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)benzoate (**11**)*. Iodine triacetate (1.7 mmol, 0.52 mg) was dissolved in glacial acetic acid (3.5 mL) in a flame-dried *Schlenk* tube under nitrogen atmosphere. **10** (1.7 mmol, 0.53 g) was added subsequently and the reaction mixture was stirred at room temperature for 10 h. Next, the reaction mixture was quenched with saturated aqueous solution of $Na_2S_2O_3$ (10 mL), extracted with CH_2Cl_2 (3 x 10 mL), washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (*n*-hexane:EtOAc = 95:5) to afford **11** as pale yellow solid in 75% (559 mg, 1.28 mmol) yield. M.p.: 114 – 117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 8.6 Hz, 1H), 5.52 – 5.49 (m, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 2.98 (dd, *J* = 18.0, 5.4 Hz, 1H), 2.41 (ddd, *J* = 18.3, 12.4, 6.3 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.12 – 2.00 (m, 1H), 1.80 – 1.72 (m, 1H), 1.66 (tt, *J* = 14.0, 3.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 167.1, 157.6, 157.1, 137.1, 137.1, 133.0, 131.7, 130.7, 122.0, 120.2, 114.4, 111.6, 92.2, 76.2, 55.6, 51.9, 27.1, 23.6, 16.7 ppm. HRMS

(ESP): *m/z* = 439.0406 calcd. for $C_{19}H_{20}O_4I^+$ $[M+H]^+$, found: 439.0408. IR (neat): 1728, 1597, 1580, 1485, 1452, 1339, 1296, 1238, 1209, 1196, 1082, 1069, 981, 934, 802, 754, 731 cm^{-1}. $[\alpha]_D^{20}$ = –60.3 (c = 0.40, $CHCl_3$).

*(S)-2-((8-iodo-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-N-methylbenzamide (**12a**)*. **11** (526 mg, 1.20 mmol) was dissolved in a flame-dried *Schlenk* tube under nitrogen atmosphere in CH_2Cl_2 (2.0 mL) and methylamine (7.5 mL, 60 mmol, 50 equiv., 8 M in ethanol). The reaction mixture was stirred at room temperature for 21 h. Afterwards, all volatiles were removed under reduced pressure and the crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 80:20) to afford **12a** as colorless solid in 79% (0.42 g, 0.95 mmol) yield. M.p.: 138 – 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.63 (br, 1H), 7.49 – 7.43 (m, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 5.58 – 5.54 (m, 1H), 3.85 (s, 3H), 3.02 – 2.95 (m, 1H), 2.73 (d, *J* = 4.8 Hz, 3H), 2.47 – 2.38 (m, 2H), 1.87 – 1.68 (m, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 166.2, 157.6, 155.9, 137.6, 136.4, 132.6, 132.5, 130.6, 122.7, 121.3, 113.3, 111.9, 91.4, 77.0, 55.7, 26.9, 26.5, 23.4, 17.0 ppm. HRMS (ESP): *m/z* = 438.0566 calcd. for $C_{19}H_{21}NO_3I^+$ $[M+H]^+$, found: 438.0572. IR (neat): 3408, 1643, 1599, 1541, 1460, 1435, 1294, 1252, 1219, 1161, 1101, 1067, 1013, 982, 904, 804, 723, 644 cm^{-1}. $[\alpha]_D^{20}$ = –65.4 (c = 0.39, $CHCl_3$).

*2-((5-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-N-methylbenzamide (**12b**)*. (*Rac*)-**10** (234 mg, 0.750 mmol) was dissolved in a flame-dried *Schlenk* tube under nitrogen atmosphere in CH_2Cl_2 (1.0 mL) and methylamine (4.7 mL, 38 mmol, 50 equiv., 8 M in ethanol). The reaction mixture was stirred at room temperature for 21 h. Afterwards, all volatiles were removed under reduced pressure and the crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 80:20) to afford **12b** as colorless solid in 79% (184 mg, 0.590 mmol) yield. M.p.: 99 – 103 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.88 (br, 1H), 7.50 – 7.40 (m, 1H), 7.22 – 7.14 (m, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.52 (t, *J* = 4.8 Hz, 1H), 3.86 (s, 3H), 2.86 (dt, *J* = 17.8, 5.7 Hz, 1H), 2.77 (d, *J* = 4.8 Hz, 3H), 2.67 – 2.57 (m, 1H), 2.21 – 2.12 (m, 1H), 2.12 – 2.03 (m, 1H), 2.00 – 1.90 (m, 1H), 1.90 –

1.80 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 166.0, 157.2, 156.5, 135.9, 132.6, 132.5, 126.8, 126.8, 123.1, 121.7, 120.9, 114.6, 109.5, 76.6, 55.5, 28.1, 26.4, 22.8, 18.5 ppm. HRMS (ESP): *m/z* = 334.1419 calcd. for $C_{19}H_{21}NO_3Na^+$ $[M+Na]^+$, found: 334.1427. IR (neat): 3402, 1647, 1597, 1535, 1472, 1409,1344, 1294, 1252, 1219, 1159, 1101, 1067, 1008, 976, 924, 777, 754, 727, 644 cm^{-1}.

*(S)-8-(Diacetoxyiodo)-2-((5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-N-methylbenzamide (**13**)*. **12a** (307 mg, 0.700 mmol) was dissolved in CH_3CN (12 mL) and glacial acetic acid (4 mL) under nitrogen atmosphere. Selectfluor® was added subsequently and the resulting suspension was stirred at room temperature for 3 h. After completion of the reaction, solvents were removed under vacuum and the product was dissolved in $CHCl_3$. After filtration under nitrogen atmosphere, the filtrate was concentrated under reduced pressure to afford **13** as yellow solid in >99% (389 mg, 0.700 mmol) yield. A sample was recrystallized from CH_2Cl_2/*n*-hexane at -40 °C. Colorless crystals of **13** were obtained suitable for X-ray diffraction.[14] M.p.: 140 – 144 °C. ^1H NMR (500 MHz, $CDCl_3$): *δ* = 8.22 (d, *J* = 8.7 Hz, 1H), 8.12 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.45 (m, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.06 – 6.02 (m, 1H), 3.95 (s, 3H), 3.02 (dd, *J* = 17.5, 3.2 Hz, 1H), 2.74 (d, *J* = 4.8 Hz, 3H), 2.51 – 2.36 (m, 2H), 1.99 (s, 3H), 1.88 – 1.74 (m, 3H), 1.72 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 176.7, 176.2, 166.2, 160.8, 153.8, 138.1, 136.3, 133.0, 132.7, 131.4, 123.2, 122.0, 119.0, 112.9, 111.8, 73.9, 56.0, 26.7, 26.2, 23.6, 20.6, 20.0, 16.8 ppm. HRMS (NSI): *m/z* = 438.0561 calcd. for $C_{19}H_{21}NO_3I^+$ $[M–2OAc+H]^+$, found: 438.0553. IR (neat): 3410, 1645, 1599, 1566, 1464, 1362, 1259, 1217, 1101, 1065, 1007, 980, 932, 802, 754, 665 cm^{-1}. $[\alpha]_D^{20}$ = +25.0 (c = 0.40, $CHCl_3$).

*(R)-Triisopropyl((5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)silane (**14**)*. **6** (0.54 g, 3.0 mmol) was dissolved in a flame-dried *Schlenk* tube under nitrogen atmosphere in CH_2Cl_2 (7.0 mL) and triethylamine (0.63 mL, 4.5 mmol, 1.5 equiv.). The solution was cooled to 0 °C and triisopropylsilyl trifluoromethanesulfonate (0.81 mL, 3.0 mmol, 1.0 equiv.) was added. The reaction mixture was then warmed up to room temperature and stirred for 20 h. After

completion of the reaction, all volatiles were removed under vacuum and the crude mixture was purified by flash column chromatography (*n*-hexane) to afford **14** as colorless oil in >99% (1.00 g, 3.00 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 – 7.11 (m, 2H), 6.72 (d, *J* = 7.8 Hz 1H), 4.92 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.81 (s, 3H), 2.72 – 2.56 (m, 2H), 2.08 – 1.92 (m, 2H), 1.87 – 1.78 (m, 1H), 1.77 – 1.66 (m, 1H), 1.21 – 1.14 (m, 3H), 1.14 – 1.07 (m, 18H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 157.0, 141.5, 126.0, 125.9, 120.3, 108.2, 69.7, 55.5, 32.8, 23.1, 19.0, 18.5, 18.4, 13.0 ppm. HRMS (ESP): *m/z* = 333.2250 calcd. for $C_{20}H_{33}O_2Si^+$ $[M–H]^+$, found: 333.2263. IR (neat): 2940, 2864, 1585, 1470, 1436, 1258, 1101, 1080, 1067, 1003, 881, 812, 772, 675, 652 cm^{-1}. $[\alpha]_D^{20}$ = –19.5 (c = 0.41, $CHCl_3$).

*(R)-((8-Iodo-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)triisopropylsilane (**15**)*. A solution of iodine triacetate (3.0 mmol, 0.91 g) in glacial acetic acid (6.0 mL) in a flame-dried *Schlenk* tube under nitrogen atmosphere was transferred to a second *Schlenk* tube under nitrogen atmosphere which contained **14** (3.00 mmol, 1.00 g). The solution was stirred at room temperature for 15 h and the reaction was then quenched by addition of saturated aqueous solution of $Na_2S_2O_3$ (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 10 mL), washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (*n*-hexane) to afford **15** as pale yellow solid in 71% (981 mg, 2.13 mmol) yield. M.p.: 60 – 64 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.6 Hz, 1H), 6.52 (d, *J* = 8.6 Hz, 1H), 5.04 (t, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 2.90 – 2.82 (m, 1H), 2.51 (ddd, *J* = 17.5, 10.1, 7.2 Hz, 1H), 2.18 – 2.07 (m, 2H), 1.74 – 1.59 (m, 2H), 1.33 – 1.23 (m, 3H), 1.11 (d, *J* = 7.5 Hz, 9H), 1.06 (d, *J* = 7.5 Hz, 9H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 157.6, 141.7, 137.0, 129.4, 111.2, 91.0, 72.7, 55.6, 32.0, 22.6, 18.8, 18.7, 16.3, 13.6 ppm. HRMS (ESP): *m/z* = 286.9933 calcd. for $C_{11}H_{12}OI^+$ $[M–OTIPS]^+$, found: 286.9940. IR (neat): 2940, 2862, 1570, 1458, 1433, 1381, 1366, 1325, 1296, 1251, 1201, 1182, 1155, 1089, 1070, 1026, 1001, 957, 883, 862, 812, 793, 716, 679, 627, 613 cm^{-1}. $[\alpha]_D^{20}$ = –34.8 (c = 0.39, $CHCl_3$).

*(R)-8-Iodo-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**16**)*. **15** (842 mg, 1.83 mmol) was dissolved in THF (10 mL), followed by the addition of tetrabutylammonium fluoride (5.4 mL,

5.4 mmol, 3.0 equiv., 1 M solution in THF). The solution was stirred at room temperature for 1 h and then concentrated *in vacuo*. The residue was then quenched with saturated aqueous solution of NH_4Cl (20 mL), extracted with EtOAc (3 x 20 mL), washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10) to afford **16** as colorless solid in 91% (508 mg, 1.67 mmol) yield. M.p.: 88 – 93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.6 Hz, 1H), 6.54 (d, *J* = 8.6 Hz, 1H), 4.83 – 4.77 (m, 1H), 3.80 (s, 3H), 2.89 (dd, *J* = 18.0, 5.3 Hz, 1H), 2.41 – 2.29 (m, 2H), 2.21 – 2.13 (m, 1H), 1.98 – 1.86 (m, 1H), 1.84 – 1.76 (m, 1H), 1.75 – 1.65 (m, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 157.9, 140.3, 137.2, 129.7, 111.4, 91.0, 70.1, 55.7, 30.6, 23.7, 16.7 ppm. HRMS (CI): *m/z* = 302.9882 calcd. for $C_{11}H_{12}O_2I^+$ $[M–H]^+$, found: 302.9885. IR (neat): 3410, 1568, 1458, 1435, 1337, 1294, 1247, 1201, 1179, 1155, 1096, 1065, 1011, 980, 907, 799, 754, 731, 650 cm^{-1}. $[\alpha]_D^{20}$ = +50.3 (c = 0.40, $CHCl_3$).

*(R)-8-Iodo-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl picolinate (**18a**)*. **16** (456 mg, 1.50 mmol) was dissolved in a flame-dried *Schlenk* tube under nitrogen atmosphere in CH_2Cl_2 (15 mL). After cooling the solution to 0 °C, dicyclohexylcarbodiimide (400 mg, 1.94 mmol, 1.3 equiv.), 4-(dimethylamino)-pyridine (187 mg, 1.53 mmol, 1.0 equiv.) and picolinic acid (221 mg, 1.80 mmol, 1.2 equiv.) were added. The solution was then warmed up to room temperature and stirred for 3 h. The resulting suspension was diluted with Et_2O and filtered through celite. The filtrate was concentrated under vacuum and the crude product was purified by flash column chromatography (*n*-hexane:EtOAc = 70:30) to afford **18a** as colorless solid in 96% (586 mg, 1.43 mmol) yield. M.p.: 140 – 144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 4.6 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 6.60 (d, *J* = 8.6 Hz, 1H), 6.14 – 6.09 (m, 1H), 3.83 (s, 3H), 2.97 (m, 1H), 2.50 – 2.39 (m, 2H), 1.91 – 1.81 (m, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 164.3, 157.6, 150.2, 148.4, 137.4, 136.9, 136.0, 131.2, 126.8, 125.3, 111.9, 91.6, 75.0, 55.7, 28.7, 23.7, 17.2 ppm. HRMS (ESP): *m/z* = 410.0253 calcd. for $C_{17}H_{17}NO_3I^+$ $[M+H]^+$, found: 410.0250. IR (neat): 1711, 1572, 1456, 1435, 1337, 1325, 1296, 1283, 1244, 1206, 1182, 1123, 1011, 995, 976, 895, 799, 746, 702, 681, 652, 619 cm^{-1}. $[\alpha]_D^{20}$ = +81.5 (c = 0.27, $CHCl_3$).

*5-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl picolinate (**18b**)*. (*Rac*)-**6** (267 mg, 1.50 mmol) was dissolved in a flame-dried *Schlenk* tube under nitrogen atmosphere in CH_2Cl_2 (15 mL). After cooling the solution to 0 °C, dicyclohexylcarbodiimide (400 mg, 1.94 mmol, 1.3 equiv.), 4-(dimethylamino)-pyridine (187 mg, 1.53 mmol, 1.0 equiv.) and picolinic acid (221 mg, 1.80 mmol, 1.2 equiv.) were added. The solution was then warmed up to room temperature and stirred for 3 h. The resulting suspension was diluted with Et_2O and filtered through celite. The filtrate was concentrated under vacuum and the crude product was purified by flash column chromatography (*n*-hexane:EtOAc = 70:30) to afford **18b** colorless solid in 74% (315 mg, 1.11 mmol) yield. M.p.: 48 – 52 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 – 8.75 (m, 1H), 8.10 – 8.05 (m, 1H), 7.79 (td, *J* = 7.7, 1.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.33 (t, *J* = 4.5 Hz, 1H), 3.83 (s, 3H), 2.86 (dt, *J* = 17.9, 5.3 Hz, 1H), 2.66 – 2.54 (m, 1H), 2.20 – 1.98 (m, 3H), 1.95 – 1.84 (m, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 164.8, 157.2, 150.2, 148.6, 137.0, 135.4, 127.3, 126.8, 126.6, 125.3, 121.6, 109.4, 71.8, 55.5, 28.8, 22.9, 18.5 ppm. HRMS (ESP): *m/z* = 284.1287 calcd. for $C_{17}H_{18}NO_3^+$ $[M+H]^+$, found: 284.1297. IR (neat): 1705, 1585, 1472, 1437, 1351, 1302, 1287, 1263, 1244, 1180, 1125, 1103, 1065, 885, 877, 792, 777, 750, 705, 640, 617 cm^{-1}.

*(R)-8-(Diacetoxyiodo)-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl picolinate (**19**)*. **18a** (450 mg, 1.10 mmol) was dissolved in CH_3CN (20 mL) and glacial acetic acid (6.6 mL) under nitrogen atmosphere. Selectfluor® was added subsequently and the resulting suspension was stirred at room temperature for 4 h. After completion of the reaction, solvents were removed under vacuum and the product was dissolved in $CHCl_3$. After filtration under nitrogen atmosphere, the filtrate was concentrated under reduced pressure to afford **19** as yellow solid in >99% (580 mg, 1.10 mmol) yield. A sample was recrystallized from CH_2Cl_2/*n*-hexane at -40 °C. Colorless crystals of **8a** were obtained suitable for X-ray diffraction.[14] M.p.: 62 – 66 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.75 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.14 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.50 (t, *J* = 2.8 Hz, 1H), 3.91 (s, 3H), 3.07 – 2.97 (m, 1H), 2.57 – 2.40 (m, 2H), 1.97 (s, 3H),

2.02 – 1.82 (m, 3H), 1.43 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 176.4, 176.1, 164.0, 160.7, 150.0, 148.1, 138.1, 137.0, 135.9, 132.0, 127.0, 125.7, 118.4, 111.8, 72.7, 56.0, 28.6, 23.7, 20.5, 19.8, 16.9 ppm. HRMS (CI): *m/z* = 468.0302 calcd. for $C_{19}H_{19}NO_5I^+$ $[M\text{-}OAc]^+$, found: 468.0304. IR (neat): 1717, 1647, 1568, 1464, 1437,1362, 1287, 1263, 1125, 1069, 978, 916, 812, 731, 667 cm^{-1}. $[\alpha]_D^{20}$ = –56.3 (c = 0.40, $CHCl_3$).

General Procedure 2 for the Stereoselective Diacetoxylation of Styrene 20. In analogy to a procedure of Fujita *et al.*,[3e] the hypervalent iodine reagent (0.200 mmol, 1.25 equiv.) and styrene **20** (18 µL, 0.16 mmol) were dissolved in CH_2Cl_2 (1.6 mL) in the presence of glacial acetic acid (80 µL) and trimethylsilyl acetate (80 µL, 0.53 mmol, 3.3 equiv.) in a flame-dried *Schlenk* tube under nitrogen atmosphere. The solution was cooled to –78 °C. Boron trifluoride diethyl etherate (40 µL, 0.32 mmol, 2.0 equiv.) was added to the solution, which was then warmed up to room temperature over 10 h. H_2O (5 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10).

*(R)-1-Phenylethane-1,2-diyl diacetate (**(R)-21**)*. **7a** (87 mg, 0.200 mmol, 1.3 equiv.) was reacted according to general procedure 2 to give (*R*)-**21** as pale yellow oil in 65% (23 mg, 0.10 mmol) yield. **7b** (93 mg, 0.200 mmol, 1.3 equiv.) was reacted according to general procedure 2 to give (*R*)-**21** as pale yellow oil in 67% (24 mg, 0.11 mmol) yield. **7c** (101 mg, 0.200 mmol, 1.3 equiv.) was reacted according to general procedure 2 to give (*R*)-**21** as pale yellow oil in 89% (32 mg, 0.14 mmol) yield. **19** (105 mg, 0.200 mmol, 1.3 equiv.) was reacted according to general procedure 2 to give (*R*)-**21** as pale yellow oil in 87% (31 mg, 0.14 mmol) yield. In order to determine the enantiomeric ratio of **21**, the products were converted into the corresponding diols. HPLC-analysis: Lux® 5 µm Cellulose-1, LC Column (250 x 4.6 mm), *n*-hexane/i-PrOH = 95:5, 0.7 mL/min, 209 nm, t_R (major) = 29.4 min, t_R (minor) = 32.5 min, up to 61:39 *er*.

*(S)-1-Phenylethane-1,2-diyl diacetate (**(S)-21**)*. **13** (111 mg, 0.200 mmol, 1.3 equiv.) was reacted according to general procedure 2 to give (*S*)-**21** as pale yellow oil in 65% (23 mg, 0.10 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 – 7.30 (m, 5H), 6.02 (dd, *J* = 8.0, 3.9 Hz, 1H), 4.33 (dd, *J* = 11.9, 3.9 Hz, 1H), 4.29 (dd, *J* = 11.9, 8.0 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 170.8, 170.2, 136.6, 128.8, 128.7, 126.8, 73.5, 66.2, 21.2, 20.9 ppm. The spectroscopic data agree with the literature.[3c] In order to determine the enantiomeric ratio of **21**, the products were converted into the corresponding diols. HPLC-analysis: Lux® 5 µm Cellulose-1, LC Column (250 x 4.6 mm), *n*-hexane/i-PrOH = 95:5, 0.7 mL/min, 209 nm, t_R (minor) = 28.9 min, t_R (major) = 33.5 min, 57:43 *er*.

General Procedure 3 for the Oxidative Rearrangement of 22. The hypervalent iodine reagent (0.20 mmol, 1.2 equiv.) was dissolved in CH_2Cl_2:trifluoroethanol (10:1 v/v, 1.5 mL) and methanol (24 µL, 0.60 mmol, 3.3 equiv.). The solution was cooled to -78 °C, 1,1-diphenylpentane **22** (40 mg, 0.18 mmol) and TsOH • H_2O (48 mg, 0.25 mmol, 1.3 equiv.) were added subsequently and the reaction mixture was stirred at -78 °C for 2 h. The reaction was then quenched with aqueous saturated $Na_2S_2O_3$ (5 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10).

*(R)-1,2-Diphenyl-1-pentanone ((R)-**23**)*. **7a** (87 mg, 0.20 mmol, 1.2 equiv.) was reacted according to general procedure 3 to give (*R*)-**23** as colorless solid in 60% (26 mg, 0.12 mmol) yield. **7b** (93 mg, 0.20 mmol, 1.2 equiv.) was reacted according to general procedure 3 to give (*R*)-**23** as colorless solid in 55% (24 mg, 0.10 mmol) yield. **7c** (101 mg, 0.200 mmol, 1.2 equiv.) was reacted according to general procedure 3 to give (*R*)-**23** as colorless solid in 75% (32 mg, 0.14 mmol) yield. **19** (105 mg, 0.200 mmol, 1.2 equiv.) was reacted according to general procedure 3 to give (*R*)-**23** as colorless solid in 74% (32 mg, 0.13 mmol) yield. HPLC-analysis: YMC Chiral Amylose-C S-5µm (25 cm), *n*-hexane/i-PrOH = 99.5:0.5, 1.0 mL/min, 243 nm t_R (minor) = 9.1 min, t_R (major) = 12.7 min, up to 75:25 *er*.

*(S)-1,2-Diphenyl-1-pentanone ((S)-**23**)*. **13** (111 mg, 0.200 mmol, 1.2 equiv.) was reacted according to general procedure 3 to give (*S*)-**23** as colorless solid in 71% (31 mg, 0.13 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 4H), 7.11 (t, *J* = 7.0 Hz, 1H), 4.48 (t, *J* = 7.2 Hz, 1H), 2.14 – 2.03 (m, 1H), 1.79 – 1.68 (m, 1H), 1.32 – 1.11 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 200.2, 140.0, 137.2, 132.9, 129.0, 128.8, 128.6, 128.4, 127.1, 53.6, 36.3, 21.0, 14.2 ppm. The spectroscopic data agree with the literature.[6b] HPLC-analysis: YMC Chiral Amylose-C S-5µm (25 cm), *n*-hexane/i-PrOH = 99.5:0.5, 1.0 mL/min, 243 nm t_R (major) = 8.4 min, t_R (minor) = 10.4 min, 57:43 *er*.

*(2S)-2-[(4-Methylbenzenesulfonyl)oxy]-1-phenylpropan-1-one ((S)-**25**)*. **19** (105 mg, 0.200 mmol, 1.3 equiv.) and *p*-TsOH • H_2O (95 mg, 0.40 mmol, 2.5 equiv.) were dissolved in CH_2Cl_2 (2 mL) and the resulting solution was stirred for 30 minutes. Afterwards, the solution was cooled to -40 °C and propiophenone **24** (21 µL, 0.16 mmol) was added. After having stirred at this temperature for 3 h, the solution was warmed up to room temperature over 10 h. The reaction was then quenched with aqueous saturated $Na_2S_2O_3$ (5 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (*n*-hexane:EtOAc = 90:10) to give (*S*)-**25** as colorless oil in 59% (29 mg, 0.094 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.85 (m, 2H), 7.77 – 7.72 (m, 2H), 7.62 – 7.56 (m, 1H), 7.49 – 7.42 (m, 2H), 7.29 – 7.25 (m, 2H), 5.78 (q, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 1.60 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 195.0, 145.1, 134.0, 133.8, 133.6, 129.9, 128.9, 128.9, 128.1, 77.5, 21.8, 18.9 ppm. The spectroscopic data agree with the literature.[21] HPLC-analysis: YMC Chiral Amylose-C S-5µm (25 cm), *n*-hexane/i-PrOH = 85:15, 0.7 mL/min, 226 nm t_R (minor) = 15.8 min, t_R (major) = 17.5 min, 54:46 *er*.

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all synthesized compounds **6**-**8**, **10**-**16**, **18**, **19**, **21**, **23** and **25**; chiral HPLC chromatograms of **6**, **21**, **23** and **25**; X-ray crystal data of compounds **6**, **8a**, **8c**, **13** and **19**.

Acknowledgments

We thank the Fonds der Chemischen Industrie (TH) and the School of Chemistry, Cardiff University for financial support.

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