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Catalytic Enantioselective α-Oxysulfonylation of Ketones Mediated by Iodoarenes

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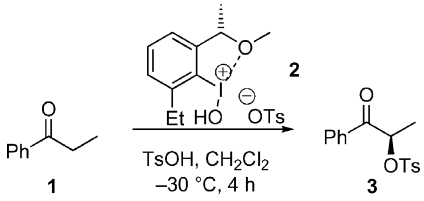
The α-oxysulfonylation of ketones catalysed by enantio enriched iodoarenes using *m*CPBA as stoichiometric oxidant is reported to give useful synthetic intermediates in good yield and modest enantioselectivity. We believe this to be the first report of an enantioselective organocatalytic reaction involving hypervalent iodine reagents which should open up a new field for enantioselective organocatalysis of oxidation reactions.

Introduction

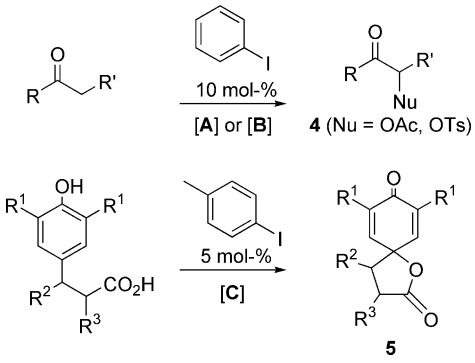
The past three decades have revealed the use of hypervalent iodine compounds as very versatile and mild oxidation and oxygenation reagents[1–7] replacing toxic and heavy metal-containing reagents, thus providing more environmental friendly reaction conditions. They can also be employed as electrophilic reagents e.g. for functionalisations of alkenes and subsequent halolactonisations,[8] dioxytosylations[9] or α-oxytosylations.[10] For these reactions, mostly hypervalent iodine compounds bearing two heteroatom ligands on iodine(III) as well as their polymer-supported derivatives are used. Due to the high interest in enantioselective reactions, employment of enantiomerically enriched hypervalent iodine compounds has been investigated recently, e.g. α-oxytosylation of ketones.[11–13] In this manner, synthetically valuable tosylates such as **3** can be obtained in up to 40% *ee* (Scheme 1).

In this reaction, the Koser-type iodane **2** has to be used in stoichiometric amounts. On the other hand, a range of enantiomerically pure iodine compounds of various types has been synthesized but remained untested, because oxidation to the respective aryl λ^3-iodanes has been unsuccessful so far.



Scheme 1. Enantioselective α-oxytosylation of propiophenone.

Recently, the catalytic use of iodine compounds has been developed.[8,14–17] First investigations in iodocatalysis were undertaken by Fujita and co-workers with anodic gem-difluorination of thiodiketals mediated by aryl iodides.[18] *m*CPBA is a potent oxidation reagent in the synthesis of λ^3-iodane compounds. Ochiai and co-workers successfully employed *m*CPBA as stoichiometric chemical oxidant in



Scheme 2. First catalytic reactions using iodoarene as catalysts. [**A**] *m*CPBA (2 equiv.), $BF_3{\cdot}OEt_2$ (3 equiv.), AcOH, room temp., 43–63% yield, Nu = OAc; [**B**] *m*CPBA (1.1 equiv.), *p*-TsOH (1.1 equiv.), MeCN, 50 °C, 63–88% yield, Nu = OTs; [**C**] *m*CPBA (1.5 equiv.), CF_3CO_2H (1 equiv.), CH_2Cl_2, room temp., 66–91% yield.

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the first catalytic α-acetoxylation of phenones.[15] The reaction was conducted using iodobenzene as catalyst and acetic acid as nucleophile in presence of $BF_3{\cdot}Et_2O$ and water leading to functionalised ketones **4** (Scheme 2). Kita et al. reported that only 5 mol-% iodotoluene[19] are used together with 1.5 equiv. *m*CPBA and 1 equiv. trifluoroacetic acid to achieve the spirocyclization to lactones **5** in 66–91% yield (Scheme 2).[16]

Based on these results, we recently reported the first catalytic use of enantiomerically pure iodoarenes in asymmetric reactions[20] which opened the possibility to employ a wide range of enantiomerically pure iodoarenes with very different structural features as catalysts. Very recently, Kita et al. reported a highly enantioselective spirocyclization using an aryliodide with a spirobiindane moiety.[21]

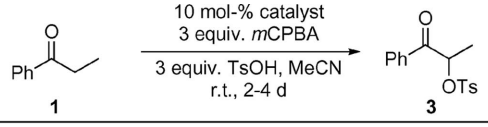
Results and Discussion

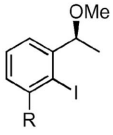
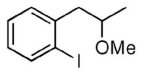
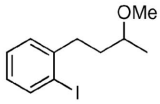
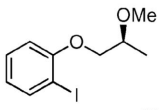
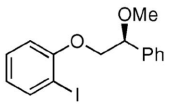
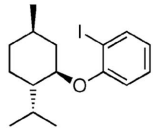
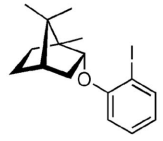
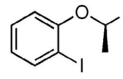
We herein report the synthesis of enantiomerically enriched α-oxysulfonylated phenones using chiral iodoarenes as catalysts. The reaction using stoichiometric iodanes can usually be performed at –30 °C to maximise enantioselectivity,[11] but at this temperature the reactions employing catalytic amounts of iodoarenes and *m*CPBA as the stoichiometric oxidant proceed very slowly, consistent with the results of Togo.[17] This suggests that the formation of the hydroxy(tosyloxy)iodoarene could be the rate-determining step in the catalytic cycle. Therefore, the reactions were conducted at room temperature for 2–4 days using commercial 70–77% wet *m*CPBA as the stoichiometric oxidant since we found no difference in the reactivity compared to dry *m*CBPA. Acetonitrile was used since we observed highest reaction rates and cleanest products with this solvent.[20] Initially, *p*-toluenesulfonic acid was used as the nucleophile and clean reactions with propiophenone **1** to give tosylate **3** were observed. Most of the reactions described herein were conducted using small amounts of reagents (0.1–0.2 mmol), leading to sometimes poor yields compared to conversions achieved due to loss during work-up and purification.

Various chiral ethers bearing iodoarene moieties have been synthesized and the results in the catalytic oxytosylation of propiophenone are summarised in Table 1.

Interesting trends regarding enantioselectivities were observed from these results. The addition of a substituent to the 6-position of the aromatic ring resulted in an increase in the enantioselectivity when catalysts **7**–**9** were employed, an ethyl substituent yielding highest selectivities (entry 2). When the ether moiety was shifted further away from the iodine, a decrease of enantioselectivity (entries 5 and 6) was observed, only the diether derivative **13** with a phenylethyl ether moiety resulted in moderate selectivity (entry 8). Other ethers of 2-iodophenol with various terpene-derived chiral moieties bearing no additional heteroatom resulted in almost no enantioselectivity. The existence of an additional heteroatom in the chiral moiety, which is able to coordinate to the iodine atom, seems to be a very important feature of these catalysts.

Table 1. Enantiomerically pure ethers as catalysts in the α-oxytosylation of propiophenone **1**.



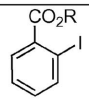
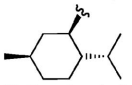
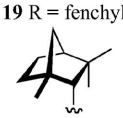
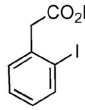
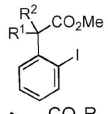
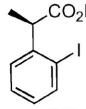
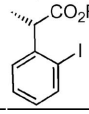
Entry	Catalyst	% Conv.[a]	**3** % *ee*[b] (abs. config.)	**3** % Yield
1	 **6** R = H	71	12 (*R*)	68
2	**7** R = Et	62	27 (*R*)	59
3	**8** R = OBn	50	25 (*R*)	48
4	**9** R = O*t*Bu	9	3 (*R*)	n.d.
5	 (–)-**10**[c]	76	3 (*R*)	n.d.
6	 (+)-**11**[c]	66	2 (*S*)	n.d.
7	 **12**	91	3 (*R*)	n.d.
8	 **13**	75	25 (*R*)	65
9	 **14**	97	1 (*R*)	n.d.
10	 **15**	63	0	n.d.
11	 **16**	22	4 (*R*)	n.d.

[a] Determined by ^{1}H NMR analysis of the crude reaction product. [b] Determined by HPLC. [c] Absolute configuration of iodoarene unknown. n.d. = not determined.

We therefore synthesized the chiral esters **17**–**31** as a new class of iodine catalysts. Many of these compounds are available through simple esterifications using enantiomerically pure alcohols such as (–)-borneol, (–)-menthol and (–)-fenchol as detailed in the experimental part. The results of the catalytic reactions are shown in Table 2.

When terpene esters derived from 2-iodobenzoic acid were used as catalysts, conversions and enantiomeric excesses were quite poor. Due to the close proximity of the bulky ester moiety of **17**–**19** to the iodine atom, the iodine centre might be hindered for an approach of the oxidising

Table 2. Enantiomerically pure esters as catalysts in the α-oxytosylation of propiophenone **1**.

Entry	Catalyst	% Conv.[a]	**3** % *ee*[b] (abs. config.)	**3** % Yield
1	 **17** R = bornyl	8	1 (*S*)	8
2	**18** R = menthyl	8	3 (*S*)	6
3	 **19** R = fenchyl	n.d.	1 (*S*)	5
4	 **20** R = Me	99	-	n.d.
5	 **21** R = bornyl	n.d.	6 (*S*)	60
6	**22** R = menthyl	100	0	78
7	**23** R = fenchyl	100	0	84
8	 **24** R^1 = H, R^2 = Me	95	24 (*S*)	72
9	**25** R^1 = H, R^2 = Et	95	23 (*S*)	83
10	**26** R^1 = H, R^2 = Bn	n.d.	6 (*S*)	65
11	**27** R^1 = Me, R^2 = *n*Pr	75	8 (*R*)	24
12	 **28** R = bornyl	45	23 (*S*)	n.d.
13	**29** R = menthyl	n.d.	15 (*S*)	73
14	**30** R = fenchyl	100	26 (*S*)	n.d.
15	 **31** R = bornyl	46	21 (*R*)	n.d.
16	**32** R = menthyl	100	39 (*R*)	42
17	**33** R = fenchyl	n.d.	29 (*R*)	67

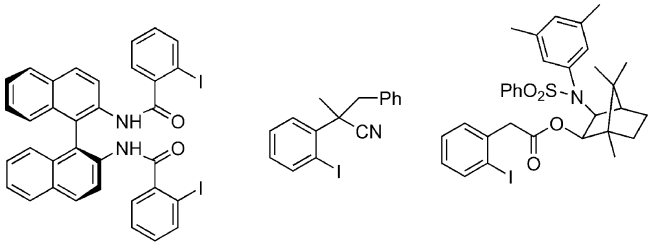
[a] Determined by ^{1}H NMR analysis of the crude reaction product. [b] Determined by HPLC. n.d. = not determined.

agents which results in poor conversions. This assumption is supported by the fact that esters **21**–**23**, with an additional carbon atom in the side chain, resulted in excellent conversions. Here, the bulky terpene moiety is shifted further away from the iodine atom. Secondly, methyl ester **20** also gave good conversions; the methyl moiety is too small to interfere with the oxidation of the iodine atom.

However, an elongation of the side chain by one methylene moiety resulted in better conversions and yields, but still poor selectivities when borneyl ester **21** (entry 5) was employed and in racemic products when menthyl or fenchyl esters **22** and **23** (entries 6 and 7) were used. The introduction of stereogenic centres in the benzylic position of such reagents has already been successful as shown with the synthesis and use of compound **2** (Scheme 1). Alkylation of the prochiral benzylic carbon atom in **21**–**23** could achieve an increase of the enantioselectivity in the α-oxytosylation, since the chiral centre would be closer to the iodine moiety. Different substituted methyl esters **24**–**27** were prepared in order to determine the optimal nature of the substituent (entries 8–11). Conversions achieved with these catalysts were generally high. Highest enantioselectivities could be obtained using catalyst **24** with a methyl substituent. Esters **25**–**27** equipped with more hindered substituents or with even two substituents resulted in lower enantioselectivities.

Based on these results, methyl substituents were introduced into esters **21**–**23** by alkylation. The resulting diastereomers were separated by preparative HPLC. The absolute configuration of ester **32** has been determined by ester cleavage and comparison to literature.[22] Based on the absolute configurations (*S*) of the products **3**, the absolute configurations of esters **31** and **33** are assumed to be identical to **32**. When catalysts **28**–**33** were employed, an increase of enantioselectivity up to 39% was observed for the menthyl ester **32**. On the other hand, its diastereomer **29** resulted in a product with only 15% *ee*. Without the additional methyl substituent in the benzylic position, the ester can rotate freely and no selectivity is observed. The methyl substituent might then force the ester into a certain conformation with the chiral terpene substituent leading to additional interactions. This results in lower selectivities (15% *ee*, entry 13), or in a matched scenario, to higher selectivities (39% *ee*, entry 16) compared to the methyl ester **24** (24% *ee*, entry 8). These facts again demonstrate the importance of a chiral moiety in the *ortho*-position to the iodine.

In order to investigate the influence of a nitrogen atom as potential coordination site to the iodine atom, several amide catalysts were prepared. Binaphthyl derivative **34** resulted in very poor yields and selectivities. The nitrogen atom in nitrile **35** seems to coordinate less efficiently to the iodine and is a reactive catalyst in the synthesis of **3** (95% conversion), but the selectivity obtained is low (7% *ee*). Compound **36**, based on a chiral alcohol developed by Helmchen and co-workers,[23] containing both, an ester moiety as well as a nitrogen atom, failed as catalyst; no conversion was observed (Figure 1).



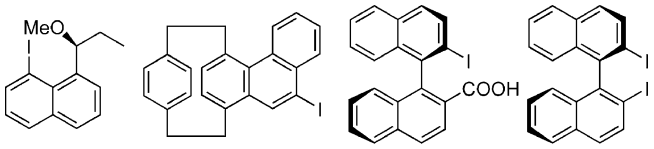
34 **35** **36**

Figure 1. Nitrogen-containing iodoarene catalysts.

The fact, that disubstituted esters and nitriles as catalysts result in poor enantiomeric excess, only confirms the crucial influence of small substituents in the side chain, as observed previously.[12]

Several other naphthalene-derived iodine compounds have been prepared and investigated. Iodoarenes **37**–**40** are compounds we could not previously investigate in reactions shown in Scheme 1 because they could not be converted to stable λ^3-iodanes. Reaction using **37** as catalyst failed, the paracyclophane derivative **38** led to good conversion (75%), but only produced racemic **3**. The reason for the synthetic efforts to prepare optically pure **38** was the impossibility to oxidize iodoparacyclophane to a hypervalent iodine derivative. A Heck-reaction of 4-bromo-[2.2]-paracyclophane[24]

with styrene produced 4-styryl-[2.2]-paracyclophane,[25] which was then photochemically isomerised to 1,4-phenanthreno-[2.2]-paracyclophane,[24] brominated[26] and the bromine finally excanged to iodine to give **38**. The binaphthyl derivative **39** was less reactive than **40** (Figure 2), probably due to an intramolecular coordination with the carboxylic acid moiety. Catalyst **40** generated **3** in 79% yield with 12% *ee* (*S*).

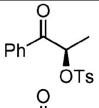
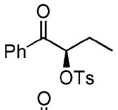
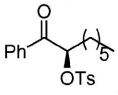
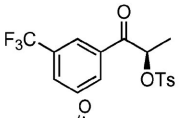
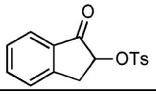


37 **(+)-38** **39** **40**

Figure 2. Naphthalene- and phenanthrene-based iodoarene catalysts.

A range of aryl alkyl ketones were investigated using ether **7** as catalyst (Table 3). The reactions were conducted under the reaction conditions described above. All selected substrates gave good yields and similar selectivities, therefore propiophenone was used for all further investigations.

Table 3. α-Oxytosylation of aryl alkyl ketones using catalyst **7**.

Entry	Product		% Yield	% *ee*[a]
1		**3**	78	27
2		**41**	66	24
3		**42**	86	27
4		**43**	70	28
5		**44**	79	21

[a] Determined by HPLC.

In a next series of experiments, the nature of the nucleophile was examined. A range of sterically variable sulfonic acids was employed and some results are summarised in Table 4. Methanesulfonic acid was used as the least sterically hindered reagent to yield product **45**. Conversions were generally much lower than conversions of reactions using *p*TsOH, whereas enantioselectivities decreased only little. Surprisingly, menthyl ester **18** was not active as a catalyst. The use of benzenesulfonic acid in these reactions led to similar results as obtained with *p*-toluenesulfonic acid.

Table 4. α-Oxysulfonylation of propiophenone using different catalysts.

Entry	Catalyst	% *ee* of **45**[a]	% Conv.[b]	% *ee* of **46**[a]	% Conv.[b]
1	**14**	5	85	0	50
2	**15**	2	13	0	33
3	**16**	4	89	2	20
4	**18**	n.d.	0	n.d.	<5
5	**24**	23	33	23	89
6	**25**	18	5	22	98
7	**29**	15	n.d.	18	100
8	**32**	31	39	29	15

[a] Determined by HPLC. [b] Determined by ^{1}H NMR analysis of the crude reaction product. n.d. = not determined.

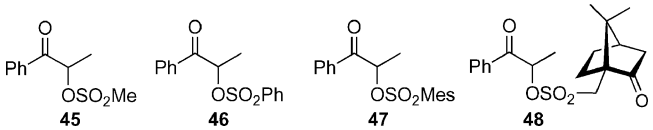
Mesitylenesulfonic acid was used as a sterically congested nucleophile yielding ketone **47**. Catalyst **18** failed to give any product. In opposition to previous results, catalyst **29** led to a product with higher enantioselectivity alongside moderate conversion whereas its diastereomer **32** showed excellent conversion but low selectivity again suggesting the cooperative effect of a chirally-matched catalyst. Also, reactions catalysed by the fenchyl-derived catalyst **30** were conducted, resulting in only moderate selectivity and conversion.

Chiral sulfonic acids such as camphorsulfonic acid could lead to increased selectivities. As shown in Table 5, this was indeed the case; the use of (1*S*)-(–)-10-camphorsulfonic acid as nucleophile increased the diastereomeric excess of **48** to up to 44% when the reaction was catalysed by catalyst **32** (entry 5). The diastereomer **29** as well as catalyst **30** resulted in low selectivities. Catalysts **18** and **24** failed to give product **48** (Figure 3).

Table 5. α-Oxysulfonylation of propiophenone using bulky nucleophiles.

Entry	Catalyst	% *ee* of **47**[a]	% Conv.[b] (% yield)	% *de* of **48**[a]	% Conv.[b] (% yield)
1	**18**	–	0	–	0
2	**24**	–	–	–	0
3	**29**	29	20	26	71
4	**30**	22	10	25	43
5	**32**	11	100 (33)	44	67 (24)

[a] Determined by HPLC, absolute configuration unknown. [b] Determined by ^{1}H NMR analysis of the crude reaction product.

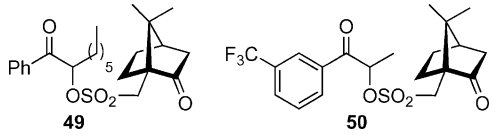


45 **46** **47** **48**

Figure 3. Use of other sulfonic acids as nucleophiles. Mes: 2,4,6-trimethylphenyl.

Also (1*R*)-(+)-10-camphorsulfonic acid was used as a nucleophile with **29** and **32** as catalysts in order to investigate the influence of the opposite enantiomer nucleophile. The conversions are high, but the diastereoselectivies obtained are 18% (for **29**) and 34% (for **32**) and therefore lower than with (–)-camphorsulfonic acid.

Based on the results obtained so far, menthyl ester catalyst **32** achieved highest enantioselectivities was employed in reactions with (–)-camphorsulfonic acid using other promising ketones such as **43** and **44** under the conditions described above. Unexpectedly, enantioselectivities and yields were inferior to the results achieved with propiophenone and the compounds **49** and **50** only obtained with 16% and 26% *de*, respectively (Figure 4).

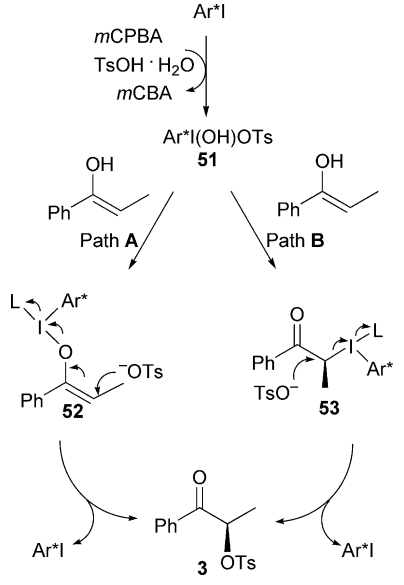


49 **50**

Figure 4. α-Oxytosylation using (–)-camphorsulfonic acid as nucleophile.

In all reactions described above the iodine atom was always covalently bound to an aromatic moiety in the catalyst. To our best knowledge, the only alkyl iodides, which can be oxidised to λ^3-iodanes are fluorinated iodine compounds.[27–31] Iodoalkanes containing a very small alkane moiety cannot be isolated as hypervalent compounds due to their instability. We investigated methyliodide and iodoacetonitrile as possible catalysts. The reaction using methyl iodide as catalyst gave only a conversion of 18% and iodoacetonitrile none at all. On the other hand, both compounds were also used in catalytic amounts in the respective acetoxylation reaction using the reaction conditions established by Ochiai and co-workers,[15] resulting in 99% conversion for both compounds.

Two possible mechanisms are discussed (Scheme 3). The enol tautomer of propiophenone reacts with the Koser-type iodane **51** generated in situ from the iodoarene (path **A**) and a subsequent S_N2'-type attack of the tosylate to **52** replaces the iodine moiety. The facile reduction of λ^3-iodane to an iodine(I) compound in the reductive elimination step



Scheme 3. Possible mechanisms of the α-oxytosylation of propiophenone.

forms the driving force for this reaction.[32,33] Another mechanistic possibility is the hypervalent iodine atom to be attacked by the double bond electrons of the enol tautomer to form **53** with subsequent S_N2-type replacement by the tosylate (path **B**). The chiral moiety in this reaction path is closer to the newly formed stereocentre than in **52**. This might suggest path **B** to take place; concordant to the mechanism proposed by Moriarty.[34]

In this reaction, substitution of the hyper-leaving group by *m*-chlorobenzoate rather than by the tosylate does not occur in our work as well as that of Togo.[17] Also, enolisation of product **3** resulting in racemisation, which is vital take place in reagent **1** in order to proceed the reaction, has not been monitored. To ensure this fact, enriched product **3** was resubmitted to the reaction conditions described above; no change of enantioenrichment was observed. The results obtained fortify the suggestion that a rigid five-membered ring is formed in the intermediate hypervalent species based on oxygen-containing catalysts. The chiral centre is fixed in position due to coordination to the iodine atom, yielding in high enantioselectivities. If this interaction cannot be achieved, free rotation of the chiral moiety is possible resulting in poor enantioselectivities.

Conclusions

In conclusion, we have established and improved the enantioselective oxysulfonylation of ketones catalysed by enantiomerically pure iodoarenes. α-Sulfonyloxylated ketones are obtained in good yields as well as in promising enantiomeric excesses. Best results were achieved, when esters containing two chiral centres were used as catalysts and (–)-camphorsulfonic acid as a chiral sulfonic acid used as nucleophile.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 or Bruker Avance 500BB against an internal deuterium lock. Melting points are uncorrected. IR measurements were taken using a Perkin–Elmer 1600 FTIR spectrometer or on a Bruker Alpha-E FTIR Spectrometer as a liquid film. Low resolution mass spectrometry was carried out using a Varian Saturn 2 GC-MS. Flash chromatography was carried out using Fisher Silica Gel (35–70 mesh). Preparative thin-layer chromatography was carried out using Merck silica gel 60 F254 on glass plates. All solvents used were dried and purified by standard methods. Reactions requiring the exclusion of air were carried out under an atmosphere of argon in oven dried glassware.

General Procedures (GP)

GP1. Etherification of 1-Fluoro-2-nitrobenzene:[35] In a dry flask 2.2 equiv. of sodium hydride (60% in mineral oil) were washed with hexane to remove the mineral oil and then dried by flushing with argon. The resulting powder was suspended in dry THF. Then 1.0 equiv. of 1-fluoro-2-nitrobenzene in THF were added drop wise at 0 °C. Subsequently, 2.2 equiv. of an alcohol were added and the mixture was refluxed overnight. The mixture was washed with NH_4Cl solution (aqueous, satd.), extracted with CH_2Cl_2 and dried

with $MgSO_4$. After evaporation of the solvents, the product was purified by column chromatography.

GP2. Hydrogenation of Nitroarenes:[36] In a flask under argon atmosphere, the respective nitroaryl ether was dissolved in MeOH. Then Pd/C (10%) was then added and the mixture was stirred vigorously in a hydrogen atmosphere until the reaction was completed. The mixture was then filtered through SiO_2 and the solvent was evaporated; the crude product was used without further purification.

GP3. Iodination of Amines:[37] To a mixture of an amine (1 equiv.) in water and H_2SO_4 a solution of sodium nitrite (1.2 equiv.) was added slowly at 0 °C and the mixture was stirred for 3 d. After reaction completion the excess nitrous acid was quenched by the addition of urea. An aqueous solution of KI (1.2 equiv.) was added and the mixture was stirred for 3 h at 50 °C. To the resulting mixture an aqueous solution of $Na_2S_2O_3$ was added. The mixture was extracted with diethyl ether, washed with 1M NaOH to pH 5, washed with brine and dried with $MgSO_4$. Evaporation of the solvent afforded the crude product.

GP4. Synthesis of Esters: 2-Iodobenzoyl chloride (1 equiv.) and an alcohol (1.5 equiv.) were stirred together with *p*-TsOH (5 mol-%) in acetonitrile at 80 °C for 1–3 d. After reaction completion, the mixture was cooled to room temperature and poured into aqueous saturated $NaHCO_3$ and extracted with CH_2Cl_2 (3×). The combined organic layers were dried with $MgSO_4$ and solvent was removed. The crude product was purified by flash chromatography (petroleum ether:diethyl ether, 4:1).

GP5. Synthesis of Esters: 2-Iodophenylacetic acid (1 equiv.), an alcohol (1.5 equiv.) and *p*-TsOH (5 mol-%) were stirred at room temperature in CH_2Cl_2 for 1–3 d. After reaction completion, the mixture was poured into aqueous saturated $NaHCO_3$ and extracted with CH_2Cl_2 (3×). The combined organic layers were dried with $MgSO_4$ and solvent was removed. The crude product was purified by flash chromatography (petroleum ether/diethyl ether, 4:1).

GP6. Alkylation of Esters and Nitriles:[38] To a freshly prepared LDA solution was added dropwise a solution of the respective ester or nitrile (1 equiv.) in dry THF at –78 °C and stirred for 30 min at this temperature. The alkylhalogenide (1.2 equiv.) was added dropwise and the mixture was stirred at room temperature for 2–3 h. After reaction completion, the mixture was poured into aqueous saturated NH_4Cl and extracted with CH_2Cl_2 (3×). The combined organic layers were dried with $MgSO_4$ and solvent was removed. The crude product was purified by flash chromatography (petroleum ether/diethyl ether, 4:1).

GP7. α-Oxysulfonylation of Ketones: A ketone (1 equiv.), an organoiodine catalyst (10 mol-%), *m*CBPA (2.3–3 equiv.) and a sulfonic acid (3 equiv.) were stirred at room temperature for 2–4 d. After reaction completion, the mixture was poured into aqueous saturated $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3×). Then, the organic layers were poured into aqueous saturated $NaHCO_3$ and extracted with CH_2Cl_2 (3×). The combined organic layers were dried with Na_2SO_4 and solvent was removed. The crude product was purified by flash chromatography (petroleum ether/diethyl ether, 4:1) or preparative TLC (petroleum ether/diethyl ether, 2:1).

2-{[(4-Methylphenyl)sulfonyl]oxy}-1-phenyl-1-propanone (3): Synthesis according to GP7 from propiophenone (45 mg, 0.33 mmol), catalyst **32** (12 mg, 0.03 mmol, 10 mol-%), *m*CPBA (172 mg, 1 mmol) and *p*-toluenesulfonic acid (190 mg, 1 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). Yield 42% (43 mg, 0.14 mmol). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.90–7.85 (m, 2 H, arom.), 7.78–7.73 (m, 2 H, arom.), 7.59 (tt, J = 2.2, 7.4 Hz, 1 H, arom.), 7.49–7.42 (m, 2 H, arom.), 7.28–7.25 (m, 2 H, arom.), 5.79 (q, J = 6.9 Hz, 1 H, 2-C*H*), 2.41 (s, 3 H, 16-CH_3), 1.60 (d, J = 6.9 Hz, 3 H, 1-CH_3) ppm. HPLC conditions: Chiracel OB-H column, hexane/2-propanol, 40:60, 0.5 mL/min, 40 °C, t_R = 18.1 min (*R*), 21.6 min (*S*).[39]

1-(2-Iodophenyl)-2-propanol: Synthesized from 1-(2-iodophenyl)-propan-2-one.[40] Methylmagnesium iodide (372 mg, 2.24 mmol) was added dropwise over 5 min to a solution of 2-iodophenyl acetaldehyde (550 mg, 2.24 mmol) in dry diethyl ether (4 mL) under Ar at –10 °C. After 1.5 h, aq. satd. ammonium chloride (5 mL) was added to the stirred solution. The aqueous phase was washed with dichloromethane (2 × 10 mL) and the organic layers combined and dried with $MgSO_4$. The solvent was removed under vacuum to yield a light yellow oil. The product was purified by column chromatography, (petroleum ether/diethyl ether, 1:1). Yield 97% (568 mg, 2.18 mmol) HPLC conditions: Chiracel OD column, hexane/2-propanol, 99:1, 3 mL/min, 10 °C, t_R = 145.1 min (–)-enantiomer, 165.5 min (+)-enantiomer. Enantiomer 2 (R_f = 165.5 min): $[\alpha]_D$ = 21.3 (c = 0.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.78 (dd, J = 1.2, 8.0 Hz, 1 H, arom. H), 7.39 (m, 2 H, arom. H), 6.96 (dt, J = 1.2, 7.9 Hz, 1 H, arom. H), 4.14 (m, 1 H, C*H*OH), 2.92 (m, 2 H, CH_2), 1.55 (s, 1 H, O*H*), 1.34 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 141.4 (C-2), 139.8 (C-6), 130.9 (C-5), 128.4 (C-3), 128.4 (C-4), 101.2 (C-1), 67.7 (C-8), 49.9 (C-7), 23.0 (C-9) ppm. IR (neat): $\tilde{\nu}$ = 3199 (OH), 1124 (CO) cm^{-1}. MS (ES$^+$): *m*/*z* (%) = 262 (4) [M]$^+$, 218 (45), 105 (5), 91 (100), 45 (47). HRMS: calcd. for $C_9H_{11}IO{\cdot}NH_4^+$ 280.0193, found 280.0195.

(+)-1-Iodo-2-(2-methoxypropyl)benzene (10): Sodium hydride (53 mg, 2.22 mmol) (55–65% in oil) was washed with pentane (4 × 1 mL) and then suspended in dimethylformamide (3 mL). After cooling to 0 °C, a solution of (+)-1-(2-iodophenyl)-2-propanol (193 mg, 0.74 mmol) in dimethylformamide (2 mL) was added. After stirring for 15 minutes at room temperature, the mixture was cooled to 0 °C and methyl iodide (355 mg, 2.5 mmol) was added. After a further 3 hours at room temperature, water (5 mL) was carefully added. The resulting mixture was extracted with *tert*-butyl methyl ether (2 × 5 mL), and the combined organic phases were washed with brine (3 × 5 mL), dried with $MgSO_4$, and concentrated under reduced pressure to yield a yellow oil. The product was purified by column chromatography (hexane/ethyl acetate, 4:1). Yield 97% (198 mg, 0.72 mmol). HPLC conditions: Chiracel OD-H column, hexane/2-propanol, 99:1, 0.5 mL/min, 22 °C, t_R = 8.4 min (–)-enantiomer, 9.9 min (+)-enantiomer. $[\alpha]_D$ = 41.2 (c = 0.12, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.74 (dd, J = 1.2, 7.6 Hz, 1 H, arom. H), 7.18 (m, 2 H, arom. H), 6.81 (dt, J = 7.9, 1.2 Hz, 1 H, arom. H), 3.55 (m, 1 H, C*H*OCH$_3$), 3.28 (s, 3 H, OCH_3), 2.98 (dd, J = 13.6, 6.5 Hz, 1 H, ArC*H*H), 2.67 (dd, J = 13.5, 6.6 Hz, 2 H, ArCH*H*), 1.10 (d, J = 6.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 140.7 (C-2), 138.4 (C-6), 130.1 (C-5), 127.1 (C-3), 127.0 (C-4), 100.3 (C-1), 55.5 (C-8), 49.1 (C-10), 28.7 (C-7), 18.0 (C-9) ppm. IR (neat): $\tilde{\nu}$ = 2820, 1469, 1366, 1169, 1122, 1089, 1010, 907, 751, 717 cm^{-1}. MS (ES+): *m*/*z* (%) = 276 (16) [M]$^+$, 217 (34), 105 (9), 91 (100), 58 (37). HRMS: calcd. for $C_{10}H_{13}IO$ 276.112, found 276.1115 [M + H]$^+$.

4-(2-Iodophenyl)-2-butanone:[41] Synthesized according to ref.[40]: A mixture of 2-iodobenzyl chloride (3.0 g, 11.9 mmol), 2,4-pentanedione (1.35 mL, 13.1 mmol) and potassium carbonate (1.65 g, 12 mmol) in ethanol (30 mL) was heated to reflux and stirred for 24 hours. The solvent was removed under vacuum and the residue partitioned between diethyl ether (10 mL) and water (10 mL). The organic layer was dried with $MgSO_4$ and concentrated under vac-

uum to yield a brown oil. Purification by column chromatography (petroleum ether/diethyl ether, 4:1) to give a pale yellow oil. Yield 84%, (4.41 g, 16.1 mmol). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.84 (d, J = 7.7 Hz, 1 H, arom. H), 7.29 (m, 2 H, arom. H), 6.93 (dt, J = 1.3, 6.9 Hz, 1 H, arom. H), 3.03 (t, J = 7.7 Hz, 2 H, ArCH_2), 2.78 (t, J = 7.7 Hz, 2 H, O =CCH_2), 2.20 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 207.5 (C-9), 143.6 (C-2), 139.6 (C-6), 129.7 (C-5), 128.6 (C-5), 128.1 (C-4), 100.3 (C-1), 43.7 (C-7), 34.8 (C-8), 30.1 (C-10) ppm.

4-(2-Iodophenyl)-2-butanol: 1-(2-Iodophenyl)butan-3-one (2.00 g, 7.30 mmol) was added dropwise over 2 min to a stirred suspension of sodium borohydride (152 mg, 4.02 mmol) in ethanol (20 mL) under argon at room temperature. The resulting solution was heated to reflux with stirring. After 3 hours, the solution was removed from the oil bath, cooled to room temperature and quenched with water (10 mL) and acetic acid (3 mL). The resulting mixture was concentrated under vacuum, and the residue partitioned between ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL), the organic fractions combined, dried with $MgSO_4$ and the solvent removed under reduced pressure, to yield the alcohol as a yellow oil. Purification was performed using column chromatography (petroleum ether/diethyl ether, 3:1) to give a pale yellow oil. Yield 97% (1.96 g, 7.1 mmol). The racemate has been reported.[42] HPLC conditions: Chiracel OD semi-preparative column, hexane/2-propanol, 93:7, 4.5 mL/min, 15 °C, t_R = 25.1 min (–)-enantiomer, 32.5 min (+)-enantiomer. $[\alpha]_D$ = +9.25 (c = 1.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.74 (dd, J = 1.1, 7.6 Hz, 1 H, arom. H), 7.19 (m, 2 H, arom. H), 6.92 (dt, J = 1.3, 6.6 Hz, 1 H, arom. H), 3.81 (m, 1 H, CH_2CHOMe), 2.80 (ddd, J = 6.9, 9.6, 13.7 Hz, 1 H, ArCH_2), 2.70 (ddd, J = 6.9, 9.6, 13.7 Hz, 1 H, ArCH_2), 1.67 (m, 2 H, CHCH_2), 1.43 (s, 1 H, OH), 1.20 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 144.6 (C-2), 139.5 (C-6), 127.8 (C-4), 129.5 (C-3), 128.5 (C-5), 100.6 (C-1), 67.5 (C-9), 39.6 (C-7), 37.1 (C-8), 23.6 (C-10) ppm. IR (neat): $\tilde{\nu}$ = 3371, 2922, 1463, 1377, 1155, 1010, 741, 720 cm^{-1}. MS (ES$^+$): m/z (%) = 276 (16) [M$^+$], 258 (52), 231 (12), 217 (67), 107 (79), 91 (100), 58 (37). HRMS: calcd. for $C_{10}H_{13}IO{\cdot}NH_4^+$ 294.0349, found 294.0353.

(+)-1-Iodo-2-(3-methoxybutyl)benzene (11): Sodium hydride (261 mg, 10.9 mmol) (55–65% in oil) was washed with pentane (4 × 2 mL) and then suspended in dimethylformamide (10 mL). After cooling to 0 °C, a solution of (+)-4-(2-iodophenyl)-2-butanol (1.00 g, 3.62 mmol) in dimethylformamide (5 mL) was added. After stirring for 15 min at room temperature, the mixture was cooled to 0 °C and methyl iodide (514 mg, 3.62 mmol) was added. After a further 3 h at room temperature, water (20 mL) was carefully added. The resulting mixture was extracted with *tert*-butyl methyl ether (2 × 15 mL), and the combined organic phases were washed with brine (3 × 10 mL), dried with $MgSO_4$, and concentrated under reduced pressure to yield a yellow coloured oil. Purification was performed using column chromatography (hexane/ethyl acetate, 3:1) to give a pale yellow oil. Yield 96% (1.01 g, 3.48 mmol). HPLC conditions: Chiracel OD-H column, hexane/2-propanol, 95:5, 0.5 mL/min, 20 °C, t_R = 8.9 min (–)-enantiomer, 13.0 min (+)-enantiomer. $[\alpha]_D$ = +53 (c = 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.74 (dd, J = 1.2, 7.9 Hz, 1 H, arom. H), 7.20 (dt, J = 1.8, 7.6 Hz, 1 H, arom. H), 7.15 (dd, J = 1.8, 7.6 Hz, 1 H, arom. H), 6.80 (dt, J = 1.2, 7.9 Hz, 1 H, arom. H), 3.38 (s, 3 H, OCH_3), 3.19 (dq, J = 6.4, 12.4 Hz, 1 H, CH), 2.73 (ddd, J = 6.4, 10.0, 13.4 Hz, 1 H, ArCH_2), 2.69 (ddd, J = 5.6, 10.2, 13.4 Hz, 1 H, ArCH_2), 1.72–1.60 (m, 2 H, CHCH_2), 1.14 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.3 (C-2), 139.9 (C-6), 129.9 (C-3), 128.7 (C-5), 128.1 (C-4), 100.9 (C-1), 76.4 (C-11), 56.4 (C-9), 37.5 (C-7), 37.0 (C-8), 19.4 (C-10) ppm. IR (neat): $\tilde{\nu}_{max}$ = (= 3059), 2924, 2819, 1586, 1465, 1434, 1372, 1169, 1137, 1094, 1010, 911, 747, 716 cm^{-1}. MS (ES$^+$): m/z (%) = 291 (31) [M$^+$], 290 (100), 278 (64), 217 (67), 107 (79), 91 (100), 58 (37), 258 (21), 217 (9), 131 (20), 104, (7), 91 (23), 59 (100). HRMS: calcd. for $C_{11}H_{15}IO{\cdot}H^+$: 291.0240, found 291.0239.

(*S*)-1-(2-Iodophenoxy)-2-propanol:[43] K_2CO_3 (1.70 g, 12 mmol) and 2-iodophenol (660 mg, 3 mmol) were dissolved in DMF (5 mL), and the mixture was refluxed for 1 hour. (*S*)-(–)-Propylene oxide (240 μL, 3.3 mmol) was added and the reaction was allowed to proceed at 60 °C until completion (48 h). The reaction was quenched with aqueous NH_4Cl (30 mL) and extracted with diethyl ether (2 × 30 mL). The aqueous layer was acidified with 10% HCl (5 mL) and extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The product was purified by flash column chromatography through silica (hexane/ethyl acetate, 6:1). The product (pale yellow oil) was obtained in 70% yield (584 mg, 2.1 mmol) with <5% of the minor regioisomer [(*S*)-1-(2-iodophenoxy)-1-propanol, determined by ^{1}H NMR]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (dd, J = 1.6, 7.8 Hz, 1 H), 7.11 (dt, J = 1.6, 7.8 Hz, 1 H), 6.62 (dd, J = 1.2, 8.2 Hz, 1 H), 6.56 (dt, J = 1.3, 7.6 Hz, 1 H), 4.09 (m, 1 H, CHOH), 3.79 (dd, J = 3.7, 9.1 Hz, 1 H, CHH), 3.67 (dd, J = 7.0, 9.1 Hz, 1 H, CHH), 3.10 (s, 1 H, OH), 1.19 (d, J = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.0, 139.3, 129.7, 123.1, 112.7, 87.0, 74.6, 66.1, 19.1 ppm.

(*S*)-2-Iodo-1-(2-methoxypropoxy)benzene (12): NaH (60% dispersion in oil, 300 mg, 7.5 mmol) was washed with hexane (3 × 10 mL) and suspended in DMF (5 mL). (*S*)-1-(2-Iodophenoxy)-2-propanol (2.0 mmol) was dissolved in 2 mL of DMF and added dropwise. The reaction mixture was allowed to stir at room temperature for 45 min. Methyl iodide (380 μL, 6.0 mmol) was added and the reaction was allowed to proceed until completion (3–4 h). Water was added dropwise to the flask until effervescence ceased (2–5 mL), then excess was added (10–15 mL total). The crude product was extracted with diethyl ether (3 × 20 mL). The organic layers were combined and dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The product was purified by flash column chromatography through silica, using hexane/ethyl acetate, 10:1. The pure product, a pale yellow oil, was obtained in 90% yield (525 mg, 1.8 mmol). $[\alpha]_D$ = –5.69 (c = 27.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (dd, J = 8.0, 1.5 Hz, 1 H, 9-CH), 7.27 (dt, J = 7.4,4 Hz, 1 H, 7-CH), 6.80 (dd, J = 7.0, 1.1 Hz, 1 H, 5-CH), 6.70 (dt, J = 7.5, 1.4 Hz, 1 H, 6-CH), 4.03 (dd, J = 5.9, 5.5 Hz, 1 H, 3-CH_b), 3.88 (dd, J = 5.1, 4.8 Hz, 1 H, 3-CH_a), 3.79 (m, 1 H, J = 6.3, 1.5, 2-CH), 3.50 (s, 3 H, OCH_3), 1.31 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.1, 139.2, 129.4, 122.4, 112.1, 86.3, 72.6, 75.2, 57.4, 17.0 ppm. IR: $\tilde{\nu}$ = 2974, 2929, 2877, 2822, 1581, 1467, 1437, 1242, 1116, 745 cm^{-1}. MS (EI): m/z (%) = 283 (82), 255 (100), 225 (43), 199 (49), 171 (15), 159 (9), 127 (60), 89 (12). HRMS: calcd. for $C_{10}H_{14}IO_2$ 293.0039, found 293.0034.

1-{[(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl]oxy}-2-nitrobenzene: Following GP1, sodium hydride (496 mg, 15.9 mmol) in THF (10 mL) were stirred with 1-fluoro-2-nitrobenzene (1.02 g, 762 μL, 7.22 mmol) and L-menthol (2.48 g, 15.9 mmol). Yield 94% (1.9 g, 6.86 mmol), yellow oil. $[\alpha]_D$ = –69.9 (c = 2.89, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.76 (dd, J = 8.1, 1.7 Hz, 1 H, 2-CH), 7.51–7.44 (m, 1 H, 3-CH), 7.08 (d, J = 8.3 Hz, 1 H, 4-CH), 6.99–6.92 (m, 1 H, 5-CH), 4.20 (dt, J = 4.1, 10.5 Hz, 1 H, 7-CH), 2.25–2.17 (m, 1 H, 13-CH), 2.14–2.09 (m, 1 H, menthyl), 1.77–1.69 (m, 2 H, menthyl), 1.64–1.57 (m, 1 H, menthyl), 1.53–1.43 (m, 1

H, menthyl), 1.16–1.04 (m, 2 H, menthyl), 1.03–0.95 (m, 1 H, menthyl), 0.92 (d, J = 7.2 Hz, 3 H, 14′-CH_3), 0.91 (d, J = 6.4 Hz, 3 H, 14-CH_3), 0.74 (d, J = 6.8 Hz, 3 H, 15-CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 151.9, 133.9, 125.8, 119.9, 115.4, 79.6, 47.9, 40.0, 34.6, 31.8, 26.1, 23.8, 22.4, 21.1, 16.7 ppm. IR (KBr): $\tilde{\nu}$ = 2955 (s), 2861 (w), 1608 (m), 1525 (s), 1478 (w), 1349 (m), 1279 (m), 1249 (w), 744 (w) cm^{-1}. MS (EI): m/z (%) = 277 (1), 153 (7), 139 (27), 138 (50), 97 (16), 83 (100), 81 (26), 55 (37). HRMS: calcd. for $C_{16}H_{23}NO_3$ 277.1672, found 277.1672.

2-Amino-1-{[(1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl]-oxy}benzene: According to GP2, 1-{[(1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl]oxy}-2-nitrobenzene (250 mg, 0.90 mmol) was dissolved in methanol (40 mL). After the addition of Pd/C (10%) catalyst (8 mg) the mixture was stirred under the atmosphere of hydrogen for 5.5 h. After filtration, the crude product (207 mg, 0.84 mmol, 93%) was used without further purification. $[\alpha]_D$ = –90.4 (c = 0.35, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (d, J = 7.5 Hz, 1 H, 5-CH), 6.81–6.70 (m, 3 H, arom.), 4.09 (dt, J = 10.5, 3.9 Hz, 1 H, 7-CH), 3.81 (s, 2 H, NH_2), 2.34–2.25 (m, 1 H, menthyl), 2.23–2.17 (m, 1 H, menthyl), 1.80–1.72 (m, 2 H, menthyl), 1.60–1.53 (m, 1 H, menthyl), 1.51–1.41 (m, 1 H, menthyl), 1.19–1.08 (m, 1 H, menthyl), 1.06–1.00 (m, 1 H, menthyl), 0.95 (d, J = 7.0 Hz, 3 H, 14′-CH_3), 0.93 (d, J = 6.5 Hz, 3 H, 14-CH_3), 0.95–0.91 (m, 1 H, menthyl), 0.83 (d, J = 6.9 Hz, 3 H, 15-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 137.8, 121.2, 118.8, 115.8, 113.5, 78.2, 48.5, 40.9, 35.0, 31.8, 26.5, 24.0, 22.6, 21.3, 17.1 ppm. IR (KBr): $\tilde{\nu}$ = 3473 (w), 3376 (w), 2955 (w), 1603 (s), 1501 (s), 1453 (m), 1280 (m), 1016 (m), 741 (s) cm^{-1}. MS (EI): m/z (%) = 248 (1), 110 (9), 109 (100), 108 (12), 81 (13), 80 (40), 55 (32), 43 (53). HRMS: calcd. for $C_{16}H_{24}NO{\cdot}H^+$ 248.2009, found 248.2011.

2-Iodo-1-{[(1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl]-oxy}benzene (14): GP3: To a suspension of 2-amino-1-{[(1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl]oxy}benzene (280 mg, 1.13 mmol) in H_2O and concd. H_2SO_4 (1 mL), a solution of $NaNO_2$ (94 mg, 1.36 mmol) was added at 0 °C. This mixture was stirred for 90 hours; ensuring temperature was maintained below 0 °C. Finally, an aqueous solution of KI (226 mg, 1.36 mmol) was added and stirred at 50 °C for 2 hours. The reaction was then quenched with satd. NH_4Cl (10 mL), extracted with CH_2Cl_2 and dried with Na_2SO_4 to give a brown oil. Yield 54% (219 mg, 0.61 mmol). $[\alpha]_D$ = –69.0 (c = 0.58, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, J = 6.2, 1.6 Hz, 1 H, 2-CH), 7.30–7.24 (m, 1 H, 4-CH), 6.82 (dd, J = 8.3, 0.7 Hz, 1 H, 3-CH), 6.58 (dt, J = 7.5, 1.2 Hz, 1 H, 5-CH), 4.09 (dt, J = 10.0, 5.0 Hz, 1 H, 7-CH), 2.28–2.35 (m, 1 H, menthyl), 2.14–2.10 (m, 1 H, menthyl), 1.77–1.71 (m, 2 H, menthyl), 1.67–1.61 (m, 1 H, menthyl), 1.51–1.43 (m, 1 H, menthyl), 1.16–1.05 (m, 2 H, menthyl), 0.93 (d, J = 7.1 Hz, 3 H, 14′-CH_3), 0.93 (d, J = 6.6 Hz, 3 H, 14-CH_3), 0.95–0.88 (m, 1 H, menthyl), 0.76 (d, J = 7.0 Hz, 3 H, 15-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.2, 139.9, 129.6, 122.3, 113.3, 88.3, 79.2, 48.2, 40.5, 34.8, 31.8, 26.4, 23.9, 22.5, 21.2, 16.9 ppm. IR (neat): $\tilde{\nu}$ = 2950 (s), 2869 (s), 1582 (m), 1465 (s), 1379 (w), 1277 (m), 1237 (s), 1181 (w), 1155 (w), 1115 (w), 1100 (w), 1039 (w), 1013 (m), 744 (m) cm^{-1}. MS (EI): m/z (%) = 358 (29), 220 (74), 151 (9), 138 (100), 123 (17), 95 (42), 83 (50), 81 (46), 55 (34). HRMS: calcd. for $C_{16}H_{23}IO$ 358.0788, found 358.0788.

(1*R*,2*S*,4*S*)-1,7,7-Trimethyl-2-[(2-nitrophenyl)oxy]bicyclo[2.2.1]heptane: According to GP1 NaH (224 mg, 5.59 mmol) was stirred with 1-fluoro-2-nitrobenzene (358 mg, 2.54 mmol) and (–)-borneol (862 mg, 5.6 mmol). After purification by flash column chromatography, the product was obtained as a yellow oil in 90% yield (630 mg, 2.3 mmol). $[\alpha]_D$ = –93.4 (c = 1.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (dd, J = 8.1, 1.6 Hz, 1 H, 2-CH), 7.49–7.45 (m, 1 H, arom.), 6.96 (t, J = 7.7 Hz, 1 H, arom.), 6.92 (d, J = 8.7 Hz, 1 H, 5-CH), 4.45–4.40 (m, 1 H, 7-CH), 2.44–2.37 (m, 1 H, bornyl), 2.32–2.25 (m, 1 H, bornyl), 1.82–1.73 (m, 2 H, bornyl), 1.41–1.25 (m, 2 H, borneyl), 1.16 (dd, J = 13.4, 3.2 Hz, 1 H, bornyl), 0.95 (s, 6 H, 13,13′-CH_3), 0.93 (s, 3 H, 14-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 133.9, 125.6, 119.5, 115.4, 85.1, 49.9, 47.6, 45.2, 36.7, 27.8, 26.8, 19.7, 19.0, 13.6 ppm. IR (KBr): $\tilde{\nu}$ = 2947 (m), 2873 (m), 1609 (s), 1578 (m), 1522 (s), 1356 (s), 1281 (s), 1164 (m), 1115 (m), 1022 (m), 991 (m), 868 (m), 831 (m), 738 (s) cm^{-1}. MS (EI): m/z (%) = 275 (3), 153 (5), 138 (10), 137 (100), 95 (32), 81 (71), 69 (14), 41 (10). HRMS: calcd. for $C_{16}H_{21}NO_3$ 275.1516, found 275.1518.

(1*R*,2*S*,4*S*)-2-[(2-Aminophenyl)oxy]-1,7,7-trimethylbicyclo[2.2.1]-heptane: According to GP2, (1*R*,2*S*,4*S*)-1,7,7-trimethyl-2-[(2-nitrophenyl)oxy]bicyclo[2.2.1]heptane (250 mg, 0.91 mmol) was dissolved in methanol (40 mL). After the addition of Pd/C catalyst (8 mg) the mixture was stirred under the hydrogen atmosphere for 5.5 h. After filtration the crude product (213 mg, 0.87 mmol, 96%) was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76–6.71 (m, 2 H, arom.), 6.69–6.65 (m, 2 H, arom.), 4.36–4.32 (m, 1 H, 7-CH), 2.42–2.33 (m, 1 H, bornyl), 2.24–2.17 (m, 1 H, bornyl), 1.82–1.71 (m, 2 H, bornyl), 1.44–1.35 (m, 1 H, bornyl), 1.32–1.25 (m, 1 H, borneyl), 1.16 (dd, J = 13.4, 3.2 Hz, 1 H, bornyl), 0.95 (s, 6 H, 15,15′-CH_3), 0.92 (s, 3 H, 13-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.6, 136.6, 120.7, 118.5, 115.1, 112.5, 83.1, 49.7, 47.6, 45.2, 37.1, 28.0, 27.2, 19.8, 19.0, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3466 (w), 3379 (w), 2984 (w), 3872 (w), 1602 (s), 1503.8 (s), 1454 (s), 1387 (m), 1362 (m), 1283 (w), 1275 (s), 1220 (s), 1146 (s), 1108 (m), 1016 (m), 738 (s) cm^{-1}. MS (ESI): m/z (%) = 254 (4), 137 (7), 109 (46), 108 (25), 95 (19), 81 (52), 80 (100), 69 (21), 67 (26), 65 (20), 53 (43), 43 (25), 41 (78). HRMS: calcd. for $C_{16}H_{23}NO{\cdot}H^+$ 246.1852, found 246.1852.

(1*R*,2*S*,4*S*)-2-[(2-Iodophenyl)oxy]-1,7,7-trimethylbicyclo[2.2.1]heptane (15): According to GP3 (1*R*,2*S*,4*S*)-1,7,7-trimethyl-2-[(2-aminophenyl)oxy]bicyclo[2.2.1]heptane (280 mg, 1.02 mmol) was stirred with $NaNO_2$ (84 mg, 1.22 mmol) and KI (203 mg, 1.36 mmol). After work-up, (317.0 mg, 0.71 mmol) product were obtained (70% yield) as a red-brown oil. $[\alpha]_D$ = –25.0 (c = 0.11, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, J = 8.2, 1.6 Hz, 1 H, 2-CH), 7.28–7.22 (m, 1 H, arom.), 6.65 (d, J = 7.8 Hz, 1 H, 5-CH), 4.38–4.32 (m, 1 H, 7-CH), 2.52–2.44 (m, 1 H, bornyl), 2.42–2.34 (m, 1 H, bornyl), 1.83–1.73 (m, 2 H, bornyl), 1.43–1.36 (m, 1 H, bornyl), 1.33–1.28 (m, 1 H, bornyl), 1.13 (dd, J = 13.4, 3.2 Hz, 1 H, bornyl), 0.98 (s, 3 H, 14-CH_3), 0.94 (s, 3 H, 13′-CH_3), 0.93 (s, 3 H, 13-CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 157.7, 139.6, 129.6, 122.2, 113.2, 87.5, 84.7, 50.2, 47.8, 45.5, 36.9, 28.2, 27.6, 20.1, 19.3, 14.2 ppm. IR (neat): $\tilde{\nu}$ = 3059 (w), 2947 (s), 2877 (m), 1576 (m), 1464 (s), 1389 (w), 1369 (w), 1278. (m), 1248 (s), 1137 (m), 1111 (w), 1049 (m), 1023 (m), 891 (w), 846 (w), 744 (s) cm^{-1}. MS (EI): m/z (%) = 356 (21), 220 (14), 153 (9), 138 (12), 137 (100), 136 (27), 121 (7), 81 (84), 77 (21), 69 (18), 44 (10), 41 (15). HRMS: calcd. for $C_{16}H_{21}IO$ 356.0632, found 356.0630.

2-Nitrophenyl (*R*)-1-Phenylethyl Ether:[44] 1-Fluoro-2-nitrobenzene (526 mg, 3.72 mmol) and (*R*)-1-phenylethanol (500 mg, 4.09 mmol) were dissolved in dry THF (10 mL) under argon and cooled to 0 °C. A solution of potassium bis(trimethylsilyl)amide (0.5 M in toluene, 8.19 mL, 4.09 mmol) was added dropwise. The mixture was stirred for 4 h and warmed up to room temp. The reaction was quenched with satd. NH_4Cl, extracted with CH_2Cl_2 and dried with $MgSO_4$. Evaporation of the solvents afforded 862 mg (3.54 mmol, 95%) of the product as a yellow oil. $[\alpha]_D$ = –86.2 (c = 0.48, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, J = 8.1, 1.7 Hz, 1 H, 2-CH), 7.25–7.10 (m, 6 H, arom.), 6.82–6.73 (m, 2 H, arom.), 5.28 (q, J = 6.4 Hz, 1 H, 7-CH), 1.53 (d, J = 6.4 Hz, 3 H, 8-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 140.0, 131.7, 127.0, 125.1, 124.8, 123.7, 123.5, 118.4, 114.5, 76.1, 21.9 ppm. IR (neat): $\tilde{\nu}$ = 3568 (w), 3435 (w), 3035 (m), 2975 (m), 2928 (m), 1955 (w), 1889 (w), 1816 (w), 1604 (s), 1526 (s), 1483 (s), 1447 (m), 1356 (s), 1278 (s), 1254 (s), 1163 (m), 745 (s), 697 (s), 667 (m), 606 (m) cm^{-1}. MS (ES): m/z (%) = 261 (11), 231 (2), 214 (100), 198 (3), 138 (5), 122 (55), 110 (65), 94 (16), 80 (6), 52 (12), 44 (10). HRMS: calcd. for $C_{14}H_{13}NO_3{\cdot}NH_4^+$ 261.1234, found 261.1232.

2-Aminophenyl (*R*)-1-Phenylethyl Ether: According to GP2, 2-nitrophenyl (*R*)-1-phenylethyl ether (943 mg, 3.88 mmol) was dissolved in MeOH (50 mL). After addition of Pd/C (10%) catalyst (8 mg) the mixture was stirred under hydrogen atmosphere for 4 h. After filtration the crude product (784 mg, 3.68 mmol, 95%) was used without further purification. $[\alpha]_D$ = –7.3 (c = 0.13, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.32–7.15 (m, 5 H, arom.), 6.66–6.45 (m, 4 H, arom.), 5.22 (q, J = 6.4 Hz, 1 H, 7-CH), 1.58 (d, J = 6.4 Hz, 3 H, 8-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.9, 143.6, 137.1, 128.9, 127.8, 125.8, 121.6, 118.7, 115.6, 114.2, 76.8, 24.7 ppm. IR (KBr): $\tilde{\nu}$ = 1599 (s), 1500 (s), 1453 (s), 1366 (m), 1267 (s), 1215 (s), 1139 (m), 1081 (s), 1005 (m), 738 (s), 697 (s) cm^{-1}. MS (EI): m/z (%) = 214 (88), 196 (3), 122 (34), 109 (43), 94 (100), 84 (38), 72 (53). HRMS: calcd. for $C_{14}H_{15}NO{\cdot}H^+$ 214.1226, found 214.1223.

2-Iodophenyl (*R*)-1-Phenylethyl Ether (16): 2-Aminophenyl (*R*)-1-phenylethyl ether (75 mg, 0.31 mmol) in H_2O (0.5 mL) and concd. HCl (0.11 mL) was treated with a solution of $NaNO_2$ (25 mg, 0.36 mmol) in H_2O (0.1 mL) at 0 °C for 40 min. The reaction mixture was slowly transferred into a solution of KI (61 mg) in H_2O (0.15 mL) at 0 °C. The reaction mixture was then stirred 5 min at room temp., 15 min at 45 °C and 15 min at 80 °C. Then the mixture was cooled to 0 °C and quenched with aqueous $Na_2S_2O_3$ (1 M). The aqueous phase was extracted with ethyl acetate, washed with brine and the solvent was evaporated under reduced pressure to yield the product in 54% (62 mg, 0.19 mmol) as a deep red oil. $[\alpha]_D$ = –37.2 (c = 0.04, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.71–7.63 (m, 1 H, 13-CH), 7.41–7.15 (m, 5 H, arom.), 7.13–6.82 (m, 2 H, arom.), 6.73–6.52 (m, 1 H, arom.), 5.28 (q, J = 6.4 Hz, 1 H, 7-CH), 1.61 (d, J = 6.4 Hz, 3 H, 8-CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 139.5, 129.7, 129.1, 127.6, 125.7, 122.5, 120.9, 115.9, 114.2, 87.7, 39.9, 24.5 ppm. IR (neat): $\tilde{\nu}$ = 3062 (w), 3011 (w), 2980 (m), 2920 (w), 1582 (m), 1470 (s), 136 (w), 1241 (s), 1071 (m), 1016 (m), 930 (w), 823 (w), 752 (s), 699 (m) cm^{-1}.

(2*S*)-*endo*-Bornyl 2-Iodobenzoate (17): Synthesis according to GP4 from 2-iodobenzoyl chloride (138 mg, 0.9 mmol) and (–)-borneol (358 mg, 1.34 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 94% (324 mg, 0.84 mmol), colourless oil. $[\alpha]_D$ = –22.1 (c = 2.72, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (dd, J = 7.9, 1.1 Hz, 1 H, 15-CH), 7.79 (dd, J = 7.8, 1.7 Hz, 1 H, 12-CH), 7.41 (td, J = 7.6, 1.2 Hz, 1 H, 13-CH), 7.17–7.13 (m, 1 H, 14-CH), 5.14 (ddd, J = 9.9, 5.7, 1.3 Hz, 1 H, 2-CH), 2.53–2.47 (m, 1 H, bornyl), 2.13–2.07 (m, 1 H, bornyl), 1.83–1.77 (m, 1 H, bornyl), 1.74 (t, J = 4.6 Hz, 1 H, bornyl), 1.41–1.27 (m, 2 H, bornyl), 1.19 (dd, J = 13.9, 3.5 Hz, 1 H, bornyl), 0.96 (s, 3 H, 10′-CH_3), 0.94 (s, 3 H, 8-CH_3), 0.91 (s, 3 H, 10-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.3, 141.6, 136.2, 132.7, 131.1, 128.2, 94.3, 82.2, 49.4, 48.4, 45.3, 37.1, 28.4, 27.8, 20.1, 19.3, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 2956 (s), 2873 (m), 2342 (w), 1722 (s), 1580 (m), 1457 (m), 1427 (m), 1374 (w), 1291 (s), 1244 (s), 1131 (s), 1043 (m), 1000 (m), 973 (w), 738 (s) cm^{-1}. MS (EI): m/z (%) = 384 (13), 231 (100), 203 (31), 136 (68), 109 (55), 93 (47), 76 (25). HRMS: calcd. for $C_{17}H_{21}IO_2$ 384.0581, found 384.0576.

(2*R*,4*R*,7*S*)-Menthyl 2-Iodobenzoate (18): Synthesis according to GP4 from commercially available 2-iodobenzoyl chloride (2.46 g, 9.24 mmol) and L-menthol (2.17 g, 13.85 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 98% (3.5 g, 9.06 mmol), colourless oil. $[\alpha]_D$ = –45.4 (c = 0.48, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (dd, J = 7.9, 1.1 Hz, 1 H, 15-C), 7.74 (dd, J = 7.8, 1.7 Hz, 1 H, 12-C), 7.40 (td, J = 7.6, 1.2 Hz, 1 H, 13-C), 7.14 (td, J = 7.5, 1.7 Hz, 1 H, 14-C), 4.97 (td, J = 10.9, 4.4 Hz, 1 H, 2-CH), 2.21–2.15 (m, 1 H, menthyl), 2.06–1.96 (m, 1 H, menthyl), 1.76–1.69 (m, 2 H, menthyl), 1.59–1.51 (m, 2 H, menthyl), 1.19–1.07 (m, 2 H, menthyl), 0.95 (d, J = 6.9 Hz, 3 H,9′-CH_3), 0.92 (d, J = 7.0 Hz, 3 H, 9-CH_3), 0.97–0.88 (m, 1 H, menthyl), 0.82 (d, J = 6.9 Hz, 3 H, 10-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 141.5, 136.4, 132.6, 130.8, 128.2, 94.2, 76.3, 47.5, 41.2, 34.6, 31.9, 26.7, 23.7, 22.4, 21.2, 16.6 ppm. IR (neat): $\tilde{\nu}$ = 2954 (s), 2860 (m), 1719 (s), 1284 (s), 1249 (s), 1126 (m), 1090 (m), 1038 (w), 1008 (m), 955 (w), 738 (s) cm^{-1}. MS (EI): m/z (%) = 386 (100), 380 (5), 371 (4), 330 (10), 321 (12), 305 (3), 293 (3), 274 (3). HRMS: calcd. for $C_{17}H_{23}IO_2$ 386.0737, found 386.0737.

(2*R*)-*endo*-Fenchyl 2-Iodobenzoate (19): Synthesis according to GP4 from commercially available 2-iodobenzoyl chloride (325 mg, 1.22 mmol) and (+)-(1*R*)-*endo*-fenchyl alcohol (125 mg, 0.81 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 88% (274 mg, 0.71 mmol), colourless oil. $[\alpha]_D$ = 16.3 (c = 2.46, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, J = 7.9 Hz, 1 H, 15-CH), 7.81 (dd, J = 7.8, 1.7 Hz, 1 H, 12-CH), 7.39 (td, J = 7.6, 0.8 Hz, 1 H, 13-CH), 7.14 (td, J = 7.6, 1.3 Hz, 1 H, 14-CH), 4.62 (d, J = 1.9 Hz, 1 H, 2-CH), 1.90–1.84 (m, 1 H, fenchyl), 1.76–1.74 (m, 1 H, fenchyl), 1.74–1.70 (m, 1 H, fenchyl), 1.66–1.63 (m, 1 H, fenchyl), 1.53–1.43 (m, 1 H, fenchyl), 1.23 (dd, J = 10.4, 1.1 Hz, 1 H, fenchyl), 1.20 (s, 3 H, 10′-CH_3), 1.14 (s, 3 H, 10-CH_3), 1.18–1.10 (m, 1 H, fenchyl), 0.87 (s, 3 H, 8-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 141.6, 135.9, 132.6, 130.9, 128.1, 94.4, 88.0, 48.8, 48.7, 41.8, 40.1, 30.0, 27.1, 26.1, 20.7, 19.9 ppm. IR (neat): $\tilde{\nu}$ = 3413 (m), 2935 (m), 2869 (m), 2358 (w), 1713 (s), 1579 (w), 1463 (m), 1291 (s), 1269 (s), 1135 (m), 1108 (m), 1030 (w), 985 (w), 780 (m), 741 (s) cm^{-1}. MS (EI): m/z (%) = 384 (6), 231 (100), 203 (31), 153 (37), 136 (70), 81 (71). HRMS: calcd. for $C_{17}H_{21}IO_2$ 384. 0581, found 384.0578.

(3*S*)-*endo*-Bornyl 2-(2-Iodophenyl)acetate (21): Synthesis according to GP5 from 2-iodophenylacetic acid (1.04 g, 3.98 mmol) and (–)-borneol (0.92 g, 5.97 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 99% (1.57 g, 3.94 mmol), colourless oil. $[\alpha]_D$ = –24.2 (c = 0.53, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, J = 8.5, 0.9 Hz, 1 H, 16-CH), 7.35–7.28 (m, 2 H, arom.), 7.00–6.92 (m, 1 H, arom.), 4.89 (ddd, J = 9.9, 5.5, 1.3 Hz, 1 H, 3-CH), 3.81 (s, 2 H, 1-CH_2), 2.40–2.27 (m, 1 H, bornyl), 1.80–1.61 (m, 3 H, bornyl), 1.28–1.09 (m, 2 H, bornyl), 1.02 (dd, J = 13.8, 3.4 Hz, 1 H, bornyl), 0.88 (s, 3 H, 11′-CH_3), 0.84 (s, 3 H, 11-CH_3), 0.79 (s, 3 H, 9-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 139.8, 138.6, 130.9, 129.1, 128.7, 101.4, 81.1, 49.2, 48.1, 47.1, 45.2, 37.0, 28.3, 27.3, 20.0, 19.2, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3059 (w), 2956 (s), 2871 (m), 1730 (s), 1467 (m), 1448 (m), 1434 (m), 1335 (m), 1303 (w), 1251 (s), 1218 (s), 1152 (s), 1110 (m), 1016 (s), 738 (m) cm^{-1}. MS (EI): m/z (%) = 417 (14), 416 (100), 290 (41), 154 (16), 137 (84), 121 (15), 108 (45), 95 (55), 81 (32). HRMS: calcd. for $C_{18}H_{27}INO_2$ 416.1081, found 416.1084.

(3*R*,5*R*,8*S*)-Menthyl 2-(2-Iodophenyl)acetate (22): Synthesis according to GP5 from 2-iodophenylacetic acid (2.92 g, 11.13 mmol) and L-menthol (2.61g, 16.7 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 95% (4.24 g, 10.6 mmol), colourless oil. $[\alpha]_D$ = –42.1 (*c* = 1.17, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.8 Hz, 1 H, 16-C*H*), 7.36–7.21 (m, 2 H, arom.), 6.99–6.92 (m, 1 H, arom.), 4.71 (td, *J* = 4.4, 10.9 Hz, 1 H, 3-C*H*), 3.77 (s, 2 H, 1-CH_2), 1.99–2.10 (m, 1 H, menthyl), 1.91–1.77 (m, 1 H, menthyl), 1.74–1.60 (m, 2 H, menthyl), 1.53–1.43 (m, 1 H, menthyl), 1.42–1.25 (m, 2 H, menthyl), 1.01 (t, *J* = 11.9 Hz, 2 H, menthyl), 0.90 (d, *J* = 6.6 Hz, 3 H, 10′-CH_3), 0.86 (d, *J* = 6.9 Hz, 3 H, 10-CH_3), 0.73 (d, *J* = 6.9 Hz, 3 H, 11-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 139.8, 138.4, 130.9, 129.1, 128.7, 101.4, 75.3, 50.6, 47.0, 41.1, 34.6, 31.8, 26.6, 23.8, 22.4, 21.2, 16.8 ppm. IR (neat): $\tilde{\nu}$ = 3376 (m), 2929 (s), 2861 (s), 2346 (w), 1729 (s), 1585 (w), 1452 (s), 1370 (m), 1248 (m), 1219 (m), 1166 (m), 1038 (m), 1021 (m), 986 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 418 (22), 292 (63), 273 (29), 156 (45), 136 (70), 108 (22), 91 (100), 81 (87), 58 (49). HRMS: calcd. for $C_{18}H_{29}INO_2$ 418.1237, found 418.1241.

(3*R*)-*endo*-Fenchyl 2-(2-Iodophenyl)acetate (23): Synthesis according to GP5 from 2-iodophenylacetic acid (1.01 g, 3.86 mmol) and (1*R*)-*endo*-(+)-fenchyl alcohol (0.89 g, 5.79 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 60% (0.914 g, 2.3 mmol), colourless oil. $[\alpha]_D$ = 13.9 (*c* = 0.53, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.9 Hz, 1 H, 16-C*H*), 7.35–7.29 (m, 2 H, arom.), 7.01–6.91 (m, 1 H, arom.), 4.38 (d, *J* = 1.9 Hz, 1 H, 3-C*H*), 3.85 (s, 2 H, 1-CH_2), 1.68 (d, *J* = 3.7 Hz, 1 H, fenchyl), 1.62–1.52 (m, 3 H, fenchyl), 1.46–1.35 (m, 1 H, fenchyl), 1.15 (dd, *J* = 1.3, 10.1 Hz, 1 H, fenchyl), 1.07 (s, 3 H, 10′-CH_3), 1.02 (s, 3 H, 10-CH_3), 0.92–1.03 (m, 1 H, fenchyl), 0.72 (s, 3 H, 9-CH_3) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 171.2, 139.8, 138.5, 131.0, 129.1, 128.7, 101.4, 87.3, 48.7, 48.6, 46.9, 41.7, 39.9, 30.0, 26.9, 26.1, 20.6, 19.8 ppm. IR (neat): $\tilde{\nu}$ = 3424 (w), 3057 (w), 2857 (s), 2868 (m), 2358 (w), 1729 (s), 1585 (w), 1563 (w), 1468 (m), 1335 (m), 1252 (s), 1213 (s), 1157 (s), 1102 (w), 1035 (s), 1007 (s), 802 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 416 (14), 290 (100), 154 (30), 137 (73), 106 (27). HRMS: calcd. for $C_{18}H_{27}INO_2$ 416.1081, found 416.1080.

Methyl (2-Iodophenyl)acetate:[45] Synthesis according to GP5 from 2-iodophenylacetic acid (8.4 g, 32.1 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 91% (8.1 g, 29.3 mmol), yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 7.9, 1.0 Hz, 1 H, 2-C*H*), 7.19 (m, 2 H, 4-, 5-C*H*), 6.86 (td, *J* = 7.5, 1.8 Hz, 1 H, 3-C*H*), 3.71 (s, 2 H, 7-CH_2), 3.61 (s, 3 H, 9-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.1, 139.7, 137.9, 130.8, 129.1, 128.6, 101.2, 52.4, 46.3 ppm.

Methyl 2-(2-Iodophenyl)propionate (24): Synthesis according to GP6 from methyl 2-iodophenylacetate (3.51 g, 12.63 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 75% (2.78 g, 9.5 mmol), yellow oil. Enantiomer 1 (R_f = 24.5 min): $[\alpha]_D$ = –70.7 (*c* = 0.65, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 7.9, 1.1 Hz, 1 H, 9-C*H*), 7.31 (td, *J* = 7.5, 0.9 Hz, 1 H, 7-C*H*), 7.20 (dd, *J* = 7.8, 1.4 Hz, 1 H, 6-C*H*), 6.95 (td, *J* = 7.7, 1.9 Hz, 1 H, 8-C*H*), 4.11 (q, *J* = 7.1 Hz, 1 H, 3-C*H*), 3.68 (s, 3 H, 1-CH_3), 1.45 (d, *J* = 7.1 Hz, 3 H, 4-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 143.9, 140.1, 129.1, 129.1, 127.8, 101.3, 52.5, 49.9, 18.6 ppm. IR (neat): $\tilde{\nu}$ = 3436 (br), 2966 (w), 2919 (w), 2343 (w), 1737 (s), 1649 (m), 1549 (m), 1467 (m), 1431 (m), 1331 (w), 1261 (m), 1202 (w), 1085 (m), 1008 (m), 7901 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 290 (2), 231 (28), 163 (99), 104 (100), 103 (70), 77 (44), 59 (64). HRMS: calcd. for $C_{10}H_{11}O_2I{\cdot}NH_4^+$ 308.0142, found 308.0142. HPLC conditions: Chiracel OD-H column, hexane/2-propanol, 99:1, 0.5 mL/min, 10 °C, t_R = 24.5 min (–)-enantiomer, 27.5 min (+)-enantiomer.

Methyl 2-(2-Iodophenyl)butyrate (25): Synthesis according to GP6 from methyl 2-iodophenylacetate (3.2 g, 11.61 mmol) and ethyl iodide (2.35 mg, 15.1 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 95% (3.35 g, 11 mmol), yellow oil. Enantiomer 1 (R_f = 24.5 min): $[\alpha]_D$ = –58.5 (*c* = 0.94, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.9 Hz, 1 H, 10-C*H*), 7.40–7.19 (m, 2 H, arom.), 7.00–6.83 (m, 1 H, arom.), 3.95 (t, *J* = 7.8 Hz, 1 H, 3-C*H*), 3.65 (s, 3 H, 1-CH_3), 2.13–1.91 (m, 1 H, 4-CH_B), 1.87–1.65 (m, 1 H, 4-CH_A), 0.91 (t, *J* = 7.4 Hz, 3 H, 5-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 144.4, 140.1, 129.1, 128.9, 128.1, 102.2, 56.7, 52.4, 27.2, 12.4 ppm. IR (neat): $\tilde{\nu}$ = 3433 (br), 2936 (w), 2350 (w), 1729 (s), 1464 (m), 1430 (m), 1345 (w), 1306 (w), 1261 (w), 1199 (m), 1165 (m), 1007 (m), 742 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 322 (48), 196 (100), 194 (23), 168 (63) 52 (74). HRMS: calcd. for $C_{11}H_{13}O_2I{\cdot}NH_4^+$ 322.0298, found 322.0300. HPLC conditions: Chiracel OD column, hexane/2-propanol, 99:1, 0.5 mL/min, 10 °C, t_R = 21.6 min (–)-enantiomer, 24.9 min (+)-enantiomer.

Methyl 2-Benzyl-2-(2-iodophenyl)acetate (26): Synthesis according to GP6 from methyl 2-iodophenylacetate (278 mg, 1 mmol) and benzyl bromide (206 mg, 1.21 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 91% (332 mg, 0.91 mmol), yellow oil. Enantiomer 1 (R_f = 36.2 min): $[\alpha]_D$ = –72.1 (*c* = 0.72, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 1.2, 7.9 Hz, 1 H, 15-C*H*), 7.47 (dd, *J* = 1.6, 7.8 Hz, 1 H, 12-C*H*), 7.28 (td, *J* = 1.2, 7.5 Hz, 1 H, 13-C*H*), 7.27–7.08 (m, 5 H, 6,7,8,9,10-C*H*), 6.88 (td, *J* = 1.6, 7.5 Hz, 1 H, 14-C*H*), 4.39 (dd, *J* = 5.8, 9.4 Hz, 1 H, 3-C*H*), 3.63 (s, 3 H, 1-CH_3), 3.32 (dd, *J* = 9.3, 13.7 Hz, 1 H, 4-CH_B), 3.03 (dd, *J* = 5.7, 13.7 Hz, 1 H, 4-CH_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 141.8, 140.2, 138.9, 128.7, 129.5, 129.4, 129.1, 128.2, 126.8, 101.8, 57.2, 52.5, 39.9 ppm. IR (neat): $\tilde{\nu}$ = 3037 (w), 2943 (w), 1731 (s), 14956 (w), 1455 (w), 1431 (m), 1349 (w), 1214 (m), 1161 (m), 1008 (m), 750 (m), 691 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 384 (10), 258 (100), 256 (65), 108 (73), 91 (97). HRMS: calcd. for $C_{16}H_{15}O_2I{\cdot}NH_4^+$ 384.0455, found 384.0459. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 99:1, 3 mL/min, 10 °C, t_R = 36.2 min (–)-enantiomer, 39.8 min (+)-enantiomer.

Methyl 2-(2-Iodophenyl)-2-propylpropionate (27): Synthesis according to GP6 from **24** (2.75 g, 9.5 mmol) and 1-propyl iodide (2.1 g, 12.4 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 54% (1.71 g, 5.13 mmol), yellow oil. Enantiomer 2 (R_f = 33.5 min): $[\alpha]_D$ = 8.1 (*c* = 0.85, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 1.1, 7.8 Hz, 1 H, 12-C*H*), 7.36–7.31 (m, 2 H, arom.), 6.94–6.90 (m, 1 H, arom.), 3.70 (s, 3 H, 1-CH_3), 2.35–2.29 (m, 1 H, 4-CH_B), 1.98–1.90 (m, 1 H, 4-CH_A), 1.62 (s, 3 H, 7-CH_3), 1.23–1.15 (m, 1 H, 5-CH_B), 0.92–0.82 (m, 4 H, 5-CH_A and 6-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.2, 145.5, 142.3, 128.6, 128.4, 128.2, 98.6, 53.6, 52.8, 39.6, 25.1, 18.0, 14.9 ppm. IR (neat): $\tilde{\nu}$ = 3440 (br), 2933 (m), 1729 (s), 1644 (w), 1459 (m), 1430 (m), 1374 (w), 1233 (m), 1132 (m), 1008 cm^{-1}. (m), 743 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 350 (35), 224 (62), 222 (32), 182 (100), 58 (19). HRMS: calcd. for $C_{13}H_{17}O_2I{\cdot}NH_4^+$ 350.0611, found 350.0614. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 99:1, 3 mL/min, 10 °C, t_R = 28.1 min (–)-enantiomer, 33.5 min (+)-enantiomer.

(4*S*)-*endo*-Bornyl (2*R*)-2-(2-Iodophenyl)propionate (28): Synthesis according to GP6 from **21** (649.0 mg, 1.63 mmol). The product was purified by flash column chromatography (petroleum ether:diethyl ether, 4:1). Yield 41% (276 mg, 0.67 mmol), colourless oil. $[\alpha]_D$ = –24.1 (c = 2.26, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (dd, J = 1.2, 7.9 Hz, 1 H, 17-C*H*), 7.33–7.27 (m, 2 H, arom.), 6.95–6.92 (m, 1 H, arom.), 4.86 (ddd, J = 1.2, 5.5, 9.9 Hz, 1 H, 4-C*H*), 4.14 (q, J = 7.2 Hz, 1 H, 2-C*H*), 2.36–2.25 (m, 1 H, bornyl), 1.69–1.64 (m, 2 H, bornyl), 1.49 (d, J = 7.2 Hz, 3 H, 1-CH_3), 1.21–1.10 (m, 2 H, bornyl), 1.01 (dd, J = 3.4, 13.7 Hz, 1 H, bornyl), 0.86 (s, 3 H, 12′-CH_3), 0.81 (s, 3 H, 12-CH_3), 0.83–0.80 (m, 1 H, bornyl), 0.63 (s, 3 H, 10-CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 174.1, 143.9, 139.7, 128.9, 128.7, 127.6, 101.5, 80.6, 49.8, 48.9, 47.8, 44.9, 36.6, 28.0, 27.1, 19.7, 18.9, 17.9, 13.5 ppm. IR (Neat): $\tilde{\nu}$ = 2930 (m), 2852 (w), 2354 (w), 1702 (m), 1594 (m), 1448 (m), 1359 (m), 1218 (m), 1195 (s), 1181 (s), 1120 (w), 1099 (w), 1067 (w), 1016 (m), 922 (m), 814 (m), 757 (m) cm^{-1}. MS (EI): m/z (%) = 430 (34), 318 (35), 304 (53), 137 (100). HRMS: calcd. for $C_{19}H_{25}IO_2{\cdot}NH_4^+$ 430.1237, found 430.1241. HPLC conditions: preparative Chiracel OD column, 98/1 hexane/2-propanol, 3 mL/min, 10 °C, t_R = 29.0 min.

(4*R*,6*R*,9*S*)-Menthyl (2*R*)-2-(2-Iodophenyl)propionate (29): Synthesis according to GP6 from **22** (317.6 mg, 0.793 mmol) and methyl iodide (146.5 mg, 1.03 mmol). The product was purified by flash column chromatography (petroleum ether/diethyl ether, 4:1). Yield 90% (297 mg, 0.71 mmol), colourless oil. $[\alpha]_D$ = –73.4 (c = 2.53, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, J = 0.9, 7.6 Hz, 1 H, 17-C*H*), 7.32–7.27 (m, 2 H, 14-, 15-C*H*), 6.94–6.91 (m, 1 H, 16-C*H*), 4.61 (td, J = 4.4, 10.9 Hz, 1 H, 4-C*H*), 4.08 (q, J = 7.1 Hz, 1 H, 2-C*H*), 2.07–2.00 (m, 1 H, menthyl), 1.69–1.62 (m, 1 H, menthyl), 1.62–1.57 (m, 1 H, menthyl), 1.46 (d, J = 7.2 Hz, 3 H, 1-CH_3), 1.35–1.24 (m, 2 H, menthyl), 1.04–0.92 (m, 2 H, menthyl), 0.90 (d, J = 6.5 Hz, 3 H, 12-CH_3), 0.88–0.79 (m, 2 H, menthyl), 0.71 (d, J = 7.0 Hz, 3 H, 11′-CH_3), 0.56 (d, J = 6.9 Hz, 3 H, 11-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 144.1, 139.9, 129.0, 128.8, 127.8, 101.7, 75.2, 50.1, 47.3, 41.1, 34.6, 31.7, 26.1, 23.6, 22.4, 20.9, 18.2, 16.4 ppm. IR (neat): $\tilde{\nu}$ = 2952 (m), 2920 (s), 2849 (m), 2356 (w), 1728 (s), 1462 (m), 1371 (w), 1258 (m), 1203 (w), 1174 (m), 1086 (m) cm^{-1}. MS (EI): m/z (%) = 432 (4), 307 (18), 306 (100), 287 (74), 105 (10). HRMS: calcd. for $C_{19}H_{27}IO_2{\cdot}NH_4^+$ 432.1394, found 432.1393. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 98:2, 3 mL/min, 10 °C, t_R = 23.2 min.

(4*R*)-*endo*-Fenchyl (2*R*)-2-(2-Iodophenyl)propionate (30): Synthesis according to GP6 from **23** (542 mg, 1.36 mmol). The product was purified by flash column chromatography (petroleum ether/diethyl ether, 4:1). Yield 89% (497 mg, 1.21 mmol), colourless oil. $[\alpha]_D$ = –41.1 (c = 0.93, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, J = 1.1, 7.7 Hz, 1 H, 17-C*H*), 7.35–7.29 (m, 2 H, arom.), 6.95–6.91 (m, 1 H, arom.), 4.33 (d, J = 1.9 Hz, 1 H, 4-C*H*), 4.20 (q, J = 7.2 Hz, 1 H, 2-C*H*), 1.65–1.62 (m, 2 H, fenchyl), 1.62–1.56 (m, 1 H, fenchyl), 1.55–1.53 (m, 1 H, fenchyl), 1.51 (d, J = 7.2 Hz, 3 H, 1-CH_3), 1.40–1.33 (m, 1 H, fenchyl), 1.13 (dd, J = 1.4, 10.2 Hz, 1 H,fenchyl), 1.04 (s, 3 H, 11′-CH_3), 1.03 (s, 3 H, 11-CH_3), 1.01–0.97 (m, 1 H, fenchyl), 0.46 (s, 3 H, 10-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.5, 139.9, 129.0, 128.8, 128.1, 127.9, 101.9, 87.0, 50.1, 48.8, 48.7, 41.6, 39.9, 30.0, 27.0, 26.1, 20.3, 19.8, 18.3 ppm. IR (neat): $\tilde{\nu}$ = 3056 (w), 2959 (s), 2919 (s), 2868 (m), 1731 (s), 1585 (w), 1563 (w), 1469 (m), 1433 (w), 1242 (w), 1206 (m), 1180 (m), 1125 (w), 1083 (w) cm^{-1}. MS (EI): m/z (%) = 431 (6), 430 (32), 305 (11), 304 (61), 154 (56), 137 (100), 81 (28). HRMS: calcd. for $C_{19}H_{25}IO_2{\cdot}NH_4^+$ 430.1237, found 430.1240. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 98:2, 3 mL/min, 10 °C, t_R = 24.5 min.

(4*S*)-*endo*-Bornyl (2*S*)-2-(2-Iodophenyl)propionate (31): $[\alpha]_D$ = 16.5 (c = 0.66, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (dd, J = 1.3, 7.8 Hz, 1 H, 17-C*H*), 7.33–7.27 (m, 2 H, arom.), 6.93–6.90 (m, 1 H, arom.), 4.86–4.82 (ddd, J = 1.0, 5.6, 9.8 Hz, 1 H, 4-C*H*), 4.13 (q, J = 7.2 Hz, 1 H, 2-C*H*), 2.39–2.28 (m, 1 H, bornyl), 1.76–1.70 (m, 1 H, bornyl), 1.66–1.59 (m, 2 H, bornyl), 1.49 (d, J = 7.2 Hz, 3 H, 1-CH_3), 1.22–1.16 (m, 2 H, bornyl), 1.01–0.95 (dd, J = 3.4, 13.7 Hz, 1 H, bornyl), 0.87 (s, 3 H, 10-CH_3), 0.83 (s, 3 H, 12′-CH_3), 0.82 (s, 3 H, 12-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 143.9, 139.7, 128.9, 128.7, 127.6, 102.1, 80.6, 49.7, 48.9, 47.8, 44.9, 36.6, 27.9, 27.2, 19.7, 18.9, 17.9, 13.5 ppm. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 98:2, 3 mL/min, 10 °C, t_R = 24.9 min.

(4*R*,6*R*,9*S*)-Menthyl (2*S*)-2-(2-Iodophenyl)propionate (32): $[\alpha]_D^{23}$ = –20.9 (c = 3.04, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, J = 1.2, 7.9 Hz, 1 H, 17-C*H*), 7.34–7.27 (m, 2 H, 14-,15-C*H*), 6.95–6.90 (m, 1 H, 16-C*H*), 4.68 (td, J = 4.4, 10.9 Hz, 1 H, 4-C*H*), 4.12 (q, J = 7.2 Hz, 1 H, 2-C*H*), 1.94–1.88 (m, 1 H, menthyl), 1.88–1.83 (m, 1 H, menthyl), 1.69–1.56 (m, 2 H, menthyl), 1.47 (d, J = 6.4 Hz, 3 H, 1-CH_3), 1.35–1.24 (m, 1 H, menthyl), 1.04–0.92 (m, 2 H, menthyl), 0.88 (d, J = 8.3 Hz, 3 H, 11′-CH_3), 0.86 (d, J = 7.8 Hz, 3 H, 11-CH_3), 0.88–0.79 (m, 2 H, menthyl), 0.76 (d, J = 6.8 Hz, 3 H, 12-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.9, 144.1, 139.9, 129.0, 128.8, 127.8, 101.6, 75.2, 50.1, 47.3, 41.1, 34.6, 31.7, 26.1, 23.6, 22.4, 20.9, 18.2, 16.4 ppm. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 98:2, 3 mL/min, 10 °C, t_R = 19.5 min.

(4*R*)-*endo*-Fenchyl (2*S*)-2-(2-Iodophenyl)propionate (33): $[\alpha]_D$ = 34.4 (c = 1.43, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, J = 1.1, 7.7 Hz, 1 H,17-C*H*), 7.35–7.28 (m, 2 H, arom.), 6.96–6.93 (m, 1 H, arom.), 4.35 (d, J = 1.9 Hz, 1 H, 4-C*H*), 4.22 (q, J = 7.2 Hz, 1 H, 2-C*H*), 1.69–1.56 (m, 3 H, fenchyl), 1.55–1.53 (m, 1 H, fenchyl), 1.52 (d, J = 7.2 Hz, 3 H, 1-CH_3), 1.42–1.33 (m, 1 H, fenchyl), 1.13 (dd, J = 1.4, 10.2 Hz, 1 H, fenchyl), 1.09 (s, 3 H, 10-CH_3), 0.96–0.90 (m, 1 H, fenchyl), 0.83 (s, 3 H, 11′-CH_3), 0.78 (s, 3 H, 11-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.7, 139.9, 128.9, 128.7, 127.9, 101.6, 87.1, 50.1, 48.7, 48.6, 41.6, 39.7, 29.9, 26.9, 26.1, 20.7, 19.6, 18.2 ppm. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 98:2, 3 mL/min, 10 °C, t_R = 22.5 min.

***N*,*N*′-(1*S*)-[1,1′-Binaphthalene]-2,2′-diylbis(2-iodobenzamide) (34):** 2-Iodobenzoyl chloride (308 mg, 1.16 mmol) and (*S*)-(–)-1,1′-binaphthyl-2,2′-diamine (110 mg, 0.39 mmol) were stirred in CH_2Cl_2 (6 mL) at room temperature for 2 d. After completion of the reaction, the mixture was poured into aqueous saturated $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and solvent was removed. The crude product was purified by flash chromatography (petroleum ether/diethyl ether, 4:1). Yield 92% (264 mg, 0.36 mmol), white powder. $[\alpha]_D$ = 8.1 (c = 0.85, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.56 (d, J = 8.9 Hz, 2 H, arom.), 8.10 (d, J = 9.0 Hz, 2 H, arom.), 7.97 (d, J = 8.2 Hz, 2 H, arom.), 7.70 (d, J = 7.9 Hz, 2 H, arom.), 7.49–7.46 (m, 2 H, arom.), 7.36–7.30 (m, 2 H, arom.), 7.20–7.15 (m, 4 H, arom.), 6.97 (td, J = 1.6, 7.6 Hz, 2 H, arom.), 6.92 (dd, J = 1.5, 7.6 Hz, 2 H, arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.5, 141.5, 140.3, 135.1, 132.9, 132.1, 131.8, 130.5, 128.8, 128.6, 128.5, 127.9, 126.3, 125.7, 122.6, 110.4, 92.6 ppm. IR (neat): $\tilde{\nu}$ = 3456 (m), 3078 (w), 3021 (m), 2357 (w), 1818 (w), 1668 (w), 1595 (m), 1490 (s), 1452 (s), 1332 (w), 1158 (m), 1073 (s), 1029 (m), 983 (m), 961 (s) cm^{-1}. MS (EI): m/z (%) = 745 (100), 686 (15),

680 (9). HRMS: calcd. for $C_{34}H_{23}I_2N_2O_2$ 744.9849, found 744.9877.

2-(2-Iodophenyl)propionitrile: Synthesis according to GP6 from 2-iodophenylacetonitrile (8.21 g, 33.8 mmol) and methyl iodide (7.19 g, 50.7 mmol). The product was purified by flash column chromatography (petroleum ether/diethyl ether, 4:1). Yield 97% (8.43 g, 32.8 mmol), yellow oil. Enantiomer 1 (R_f = 50.9 min): $[\alpha]_D$ = –31.2 (c = 2.33, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, J = 1.5, 8.0 Hz, 1 H, 8-C*H*), 7.61 (dd, J = 1.7, 7.6 Hz, 1 H, 5-C*H*), 7.42 (td, J = 1.1, 7.5 Hz, 1 H, 6-C*H*), 7.03 (td, J = 1.5, 7.6 Hz, 1 H, 7-C*H*), 4.24 (q, J = 7.5 Hz, 1 H, 2-C*H*), 1.60 (d, J = 7.1 Hz, 3 H, 3-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 130.2, 129.7, 128.0, 123.5, 121.6, 98.8, 36.6, 21.0 ppm. IR (neat): $\tilde{\nu}$ = 2938 (s), 2925 (s), 2840 (s), 2352 (w), 1731 (m), 1465 (s), 1434 (m), 1375 (w), 1269 (w), 1009 (s), 755 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 257 (100), 242 (39), 128 (53), 103 (32). HRMS: calcd. for C_9H_8IN 256.9702, found 256.9690. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 98:2, 3 mL/min, 10 °C, t_R = 50.9 min (–)-enantiomer, 54.5 min (+)-enantiomer.

2-Benzyl-2-(2-iodophenyl)propionitrile (35): Synthesis according to GP6 from 2-iodophenyl-methylacetonitrile (685 mg, 2.67 mmol) and benzyl bromide (684 mg, 4 mmol). The product was purified by flash column chromatography (petroleum ether/diethyl ether, 4:1). Yield 91% (839 mg, 2.43 mmol), yellow oil. Enantiomer 2 (R_f = 80.9 min): $[\alpha]_D$ = 8.5 (c = 0.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.9 Hz, 1 H, 15-C*H*), 7.20–7.15 (m, 2 H, arom.), 7.14–7.10 (m, 3 H, arom.), 7.06–7.02 (m, 2 H, arom.), 6.91–6.84 (m, 1 H, arom.), 3.60 (d, J = 13.6 Hz, 1 H, 4-CH_B), 3.17 (d, J = 13.6 Hz, 1 H, 4-CH_A), 1.78 (s, 3 H, 3-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 138.9, 135.2, 130.6, 129.9, 129.1, 128.8, 128.4, 127.6, 122.6, 95.7, 45.2, 43.6, 25.4 ppm. IR (neat): $\tilde{\nu}$ = 3318 (m), 2926 (s), 2360 (w), 2246 (w), 1693 (w), 1495 (m), 1454 (s), 1375 (w), 1078 (w), 1009 (w), 855 (m), 824 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 365 (96), 347 (2), 315 (4), 254 (5), 237 (100), 222 (3), 108 (6). HRMS: calcd. for $C_{16}H_{18}IN_2$ 365.0509, found 365.0509. HPLC conditions: semi-preparative Chiracel OD column, hexane/2-propanol, 99:1, 3 mL/min, 10 °C, t_R = 75.3 min, 80.9 min.

***N*-(3,5-Dimethylphenyl)-*N*-[(1*S*,2*R*,3*S*,4*R*)-3-hydroxy-4,7,7-trimethylbicyclo[2.2.1]hept-2-yl]benzenesulfonamide:**[22] 3-[(3,5-Dimethylphenyl)amino]isoborneol was synthesized according to literature.[22] A mixture of 3-[(3,5-dimethylphenyl)amino]isoborneol (2.00 g, 7.3 mmol), benzenesulfonic acid chloride (3.90 g, 21.9 mmol) and pyridine (1.73 g, 2.1 mmol) in acetonitrile was stirred for 3 d at room temperature. The reaction mixture was quenched in aq. satd. $NaHCO_3$, then extracted with CH_2Cl_2 (3 × 20 mL), dried with $MgSO_4$ to give a white powder. Yield 65% (1.96 g, 4.75 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (tt, J = 1.1, 7.3 Hz, 1 H, 20-C*H*), 7.51–7.50 (m, 2 H, 18-C*H*, 22-C*H*), 7.46–7.43 (m, 2 H, 19-C*H*, 21-C*H*), 6.98 (s, 1 H, 12-C*H*), 6.90 (s, 1 H, 14- or 10-C*H*), 5.83 (s, 1 H, 10- or 14-C*H*), 3.76 (d, J = 2.7 Hz, 1 H, 1-C*H*), 3.54 (d, J = 6.2 Hz, 1 H, 6-C*H*), 2.28 (s, 3 H, 16-CH_3), 2.10 (s, 3 H, 15-CH_3), 1.64–1.58 (m, 2 H, cyclohexyl), 1.51–1.45 (m, 1 H, CH_2), 1.22–1.17 (m, 1 H, CH_2), 0.99 (s, 3 H, 8′-CH_3), 0.97 (s, 3 H, 8-CH_3), 0.97–0.92 (m, 1 H, CH_2), 0.57 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 139.2, 135.9, 133.4, 132.1, 130.1, 129.3, 128.6, 82.9, 69.6, 50.2, 49.3, 47.3, 33.5, 28.3, 22.1, 21.4, 12.2 ppm. MS (EI): *m*/*z* (%) = 414 (69), 274 (100), 160 (23), 122 (28). HRMS: calcd. for $C_{24}H_{32}NO_3S$ 414.2097, found 414.2100.

***N*-Phenylsulfonylamino-*N*-(3,5-dimethylphenyl)-*N*-isobornyl 2-Iodophenylacetate (36):** A mixture of *N*-(3,5-dimethylphenyl)-*N*-[(1*S*,2*R*,3*S*,4*R*)-3-hydroxy-4,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-benzenesulfonamide (110 mg, 0.27 mmol), 2-iodophenylacetic acid (202 mg, 0.8 mmol), 1,3-dicyclohexylcarbodiimide (165 mg, 0.81 mmol) and 4-(dimethylamino)pyridine (98 mg, 0.81 mmol) with acetonitrile (10 mL) was stirred for 2 d at 60–80 °C. After work-up using aq. satd. $NaHCO_3$ and CH_2Cl_2 (4 × 20 mL) and drying over $MgSO_4$, the product was purified by column chromatography (petroleum ether/diethyl ether, 4:1) to give a white cloudy/green solid. Yield 61% (108 mg, 0.16 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, J = 1.1, 7.9 Hz, 1 H, 2-C*H*), 7.60 (tt, J = 1.2, 7.4 Hz, 1 H, 28-C*H*), 7.52–7.50 (m, 2 H, 26-, 30-C*H*), 7.46–7.42 (m, 2 H, 27-, 29-C*H*), 7.32 (dt, J = 1.1, 7.4 Hz, 1 H, 4-C*H*), 7.24 (dd, J = 1.7, 7.6 Hz, 1 H, 5-C*H*), 6.99 (s, 1 H, 20-C*H*), 6.97 (dt, J = 1.6, 7.6 Hz, 1 H, 3-C*H*), 6.90 (s, 1 H, 22- or 18-C*H*), 5.84 (s, 1 H, 18- or 22-C*H*), 3.98 (s, 2 H, 7-CH_2), 3.76 (d, J = 2.7 Hz, 1 H, 9-C*H*), 3.54 (d, J = 6.2 Hz, 1 H, 14-C*H*), 2.28 (s, 3 H, 24-CH_3), 2.10 (s, 3 H, 23-CH_3), 1.64–1.59 (m, 2 H, CH_2), 1.51–1.45 (m, 1 H, CH_2), 1.23–1.16 (m, 1 H, CH_2), 0.99 (s, 3 H, 16′-CH_3), 0.97 (s, 3 H, 16-CH_3), 0.97–0.92 (m, 1 H, *CH*), 0.57 (s, 3 H, 15-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.9, 139.2, 138.3, 137.1, 135.9, 133.4, 132.2, 131.4, 130.1, 129.3, 129.2, 128.8, 128.6, 128.3, 101.7, 82.9, 69.6, 54.9, 50.2, 49.3, 47.3, 33.5, 28.3, 22.1, 21.4, 12.2 ppm. IR (KBr): $\tilde{\nu}$ = 2355, 2332 cm^{-1}.

13-Iodo-[2.2](1,4)phenanthrenoparacyclophane (38):[46,47] 5-Bromo-[2.2](1,4)phenanthrenoparacyclophane (310 mg, 0.71 mmol) was dissolved in dry DMF (20 mL) and iodine (1.8 g, 7.1 mmol), potassium iodide (1.1 g, 7.02 mmol) and nickel-powder (412 mg, 7.1 mmol) were added to the solution and refluxed in argon atmosphere. After 4 h the mixture was separated from unused nickel, and diluted with water and the phases were separated. The aqueous phase was extracted several times with CH_2Cl_2 and the combined organic phases were washed with a small portion of brine and dried with $MgSO_4$ and purified by flash column chromatography to give the product in 96% yield (295 mg, 0.68 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.42 (dd, J = 1.3, 8.0 Hz, 1 H, 8-C*H*), 8.31 (s, 1 H, 14-C*H*), 8.20 (dd, J = 1.5, 8.2 Hz, 1 H, 11-C*H*), 7.63–7.56 (m, 2 H, 9-C*H*, 10-C*H*), 6.98 (d, J = 7.5 Hz, 1 H, 17-C*H*), 6.78 (d, J = 7.4 Hz, 1 H, 18-C*H*), 6.57 (dd, J = 1.7, 7.9 Hz, 2 H, 21-C*H*), 6.53 (dd, J = 1.7, 7.9 Hz, 1 H, 20-C*H*), 5.93 (dd, J = 1.8, 7.8 Hz, 1 H, 23-C*H*), 5.29 (dd, J = 1.6, 7.8 Hz, 1 H, 24-C*H*), 4.27 (ddd, J = 4.8, 8.5, 14.0 Hz, 1 H, 1-CH_AH), 3.82–3.76 (m, 1 H, 4-CH_AH), 3.40 (ddd, J = 6.5, 8.6, 14.8 Hz, 1 H, 1-CHH_B), 3.29–3.22 (m, 1 H, 3-CHH_B), 3.04 (ddd, J = 7.1, 14.5, 17.7 Hz, 2 H, 3-CH_AH, 4-CHH_B), 2.92 (ddd, J = 4.8, 8.8, 13.5 Hz, 1 H, 2-CHH_B), 2.74 (ddd, J = 6.3, 8.5, 14.3 Hz, 1 H, 2-CH_AH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.1, 138.2, 136.8, 136.4, 136.3, 135.4, 135.2, 133.5, 132.8, 132.5, 132.4, 131.5, 132.0, 133.0, 128.8, 128.7, 127.5, 126.7, 130.0, 98.0, 38.8, 35.1 34.9, 33.6 ppm. MS (EI): *m*/*z* (%) = 434 (3), 329 (20), 307 (9), 203 (100), 202 (85), 104 (48), 78 (21). HRMS: calcd. for $C_{24}H_{19}I$ 434.0526, found 434.0529. HPLC conditions: Chiracel OD column, hexane/2-propanol, 90:10, 0.5 mL/min, 254 nm, 22 °C, t_R = 12.4 min, 17.3 min. Enantiomer 1 (t_R = 12.4 min): $[\alpha]_D^{22}$ = –180 (c = 0.245, $CHCl_3$). Enantiomer 2 (t_R = 17.3 min): $[\alpha]_D^{22}$ = 187 (c = 0.205, $CHCl_3$).

1-Oxo-1-phenylbutan-2-yl 4-Methylbenzenesulfonate (41): Synthesis according to GP7 from butyrophenone (74 mg, 0.5 mmol), catalyst **7** (15 mg, 0.05 mmol), *m*CBPA (77%, 356 mg, 1.5 mmol) and *p*-toluenesulfonic acid (300 mg, 1.5 mmol) yielding 105 mg (0.33 mmol, 66%) **41** as colorless solid. m.p. 79–85 °C. $[\alpha]_D$ = 3.69 (c = 1.73, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.8 Hz, 2 H), 7.66 (d, J = 8.3 Hz, 2 H), 7.51 (t, J = 7.4 Hz, 1 H), 7.47 (t, J = 8.1 Hz, 2 H), 7.17 (d, J = 8.1 Hz, 2 H), 5.48 (dd, J = 5.0, 7.9 Hz, 1 H), 2.32 (s, 3 H), 1.93–1.85 (m, 2 H), 0.90 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 144.0,

133.1, 132.7, 132.1, 128.7, 127.7, 127.6, 127.0, 81.5, 25.2, 20.6, 8.5 ppm. IR (NaCl): $\tilde{\nu}$ = 1699, 1386, 1158, 828, 763, 661 cm^{-1}. HRMS (ESI-H^+): calcd. for $C_{17}H_{19}O_4S$ 319.1004, found 319.0990. HPLC conditions: Chiracel OB-H, 40 °C, 0.5 mL/min, hexane/2-propanol, 60:40, t_R = 15.1 minutes (major), 17.9 (minor).

1-Oxo-1-phenyloctan-2-yl 4-Methylbenzenesulfonate (42):[48] Synthesis according to GP7 from 1-phenyl-1-octanone (102 mg, 0.5 mmol), catalyst **7** (15 mg, 0.05 mmol), *m*CBPA (77%, 356 mg, 1.5 mmol) and *p*-toluenesulfonic acid (300 mg, 1.5 mmol) yielding 160 mg (0.43 mmol, 86%) **42** as colorless solid. m.p. 56–59 °C. $[\alpha]_D$ = 13.71 (*c* = 1.62, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 1.2, 7.9 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.51 (t, *J* = 8.0 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 5.51 (dd, *J* = 5.6, 7.6 Hz, 1 H), 2.32 (s, 3 H), 1.83–1.77 (m, 2 H), 1.48–1.32 (m, 1 H), 1.30–1.18 (m, 1 H), 1.17–1.04 (m, 6 H), 0.79 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 195.1, 145.0, 134.1, 133.8, 133.3, 129.7, 128.8, 128.7, 128.6, 81.4, 32.7, 31.4, 28.5, 25.0, 22.5, 21.7, 14.1 ppm. HPLC conditions: Chiracel OB-H, 40 °C, 0.5 mL/min, hexane/2-propanol, 60:40, t_R = 13.2 minutes (major), 15.8 (minor).

1-[3-(Trifluoromethyl)phenyl]-1-oxobutan-2-yl 4-Methylbenzenesulfonate (43): Synthesis according to GP7 from 1-[3-(trifluoromethyl)phenyl]-1-butanone (101 mg, 0.5 mmol), catalyst **7** (15 mg, 0.05 mmol), *m*CBPA (77%, 356 mg, 1.5 mmol) and *p*-toluenesulfonic acid (300 mg, 1.5 mmol) yielding 130 mg (0.35 mmol, 70%) **43** as colorless solid. m.p. 92–94 °C. $[\alpha]_D$ = 6.83 (*c* = 2.53, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.8 Hz, 1 H), 8.02 (s, 1 H), 7.76 (d, *J* = 7.6 Hz, 1 H), 7.65 (d, *J* = 6.8 Hz, 2 H), 7.54 (t, *J* = 7.8 Hz, 1 H), 6.99 (d, *J* = 7.0 Hz, 2 H), 5.63 (q, *J* = 7.0 Hz, 1 H), 2.34 (s, 3 H), 1.55 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 144.3, 133.2, 132.0, 131.0, 130.0 (q, *J* = 33 Hz), 129.1, 128.8, 128.4, 126.9, 124.7, 122.5 (q, *J* = 272 Hz), 76.6, 20.6, 17.5 ppm. IR (NaCl): $\tilde{\nu}$ = 1704, 1385, 1156, 829, 762, 665 cm^{-1}. LRMS (EI+): *m*/*z* (%) = 372 (2) [$M^{\cdot+}$], 328 (5), 281 (2), 199 (22), 174 (100), 155 (20), 119 (10), 91 (21). HRMS (EI+) calcd. for $C_{17}H_{15}F_3O_4S$ 372.0643, found 372.0633. HPLC conditions: Chiracel OB-H, 40 °C, 0.5 mL/min, hexane/2-propanol, 60:40, t_R = 15.3 minutes (major), 16.8 (minor).

2,3-Dihydro-1-oxo-1*H*-inden-2-yl 4-Methylbenzenesulfonate (44):[49] Synthesis according to GP7 from 1-indanone (66 mg, 0.5 mmol), catalyst **7** (15 mg, 0.05 mmol), *m*CBPA (77%, 356 mg, 1.5 mmol) and *p*-toluenesulfonic acid (300 mg, 1.5 mmol) yielding 120 mg (0.39 mmol, 79%) **44** as colorless solid. m.p. 97–102 °C. $[\alpha]_D$ = 31.58 (*c* = 1.21, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.3 Hz, 2 H), 7.76 (d, *J* = 8.3 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.41–7.32 (m, 4 H), 5.05 (dd, *J* = 4.6, 8.0 Hz, 1 H), 3.57 (dd, *J* = 8.0, 17.2 Hz, 1 H), 3.19 (dd, *J* = 4.6, 17.2 Hz, 1 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 150.3, 145.7, 136.8, 134.0, 133.5, 130.3, 128.8, 128.6, 127.1, 125.1, 78.6, 34.3, 22.1 ppm. HPLC conditions: Chiracel OB-H, 40 °C, 0.5 mL/min, hexane/2-propanol, 60:40, t_R = 27.4 minutes (minor), 30.5 (major).

2-(Methylsulfonyl)propiophenone (45):[50] Synthesis according to GP7 from propiophenone (107 mg, 0.8 mmol), an organoiodine catalyst (10 mol-%), *m*CBPA (77%, 413 mg, 1.84 mmol) and 2-methanesulfonic acid (230 mg, 2.39 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.96–7.92 (m, 2 H, 3-C*H*), 7.67–7.60 (m, 1 H, 5-C*H*), 7.54–7.48 (m, 2 H, 4-C*H*), 6.06 (q, *J* = 7.0 Hz, 1 H, 2-C*H*), 3.14 (s, 3 H, 6-CH_3), 1.67 (d, *J* = 7.0 Hz, 3 H, 1-CH_3) ppm. HPLC conditions: Chiracel OB-H column, hexane/2-propanol, 40:60, 0.5 mL/min, 40 °C, t_R = 22.5 min, 24.9 min.

2-(Phenylsulfonyl)propiophenone (46): Synthesis according to GP7 from propiophenone (50 mg, 0.37 mmol), an organoiodine catalyst (10 mol-%), *m*CBPA (77%, 193 mg, 0.86 mmol) and benzenesulfonic acid (177 mg, 1.12 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.90–7.86 (m, 4 H, arom.), 7.65–7.56 (m, 2 H, arom.), 7.52–7.43 (m, 4 H, arom.), 5.83 (q, *J* = 6.9 Hz, 1 H, 2-C*H*), 1.61 (d, *J* = 6.9 Hz, 3 H, 1-CH_3) ppm. HPLC conditions: Chiracel OB-H column, hexane/2-propanol, 40:60, 0.5 mL/min, 40 °C, t_R = 15.8 min, 18.8 min.

2-(Mesitylsulfonyl)propiophenone (47): Synthesis according to GP7 from propiophenone (46 mg, 0.34 mmol), an organoiodine catalyst (10 mol-%), *m*CBPA (77%, 178 mg, 0.79 mmol) and 2-mesitylenesulfonic acid (243 mg, 1.03 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.90–7.85 (m, 2 H, 3-C*H*), 7.58 (tt, *J* = 1.3, 7.4 Hz, 1 H, 5-C*H*), 7.48–7.41 (m, 2 H, 4-C*H*), 6.90 (s, 2 H, 7-C*H*), 5.74 (q, *J* = 6.9 Hz, 1 H, 2-C*H*), 2.59 (s, 6 H, 6-CH_3), 2.27 (s, 3 H, 8-CH_3), 1.59 (d, *J* = 6.9 Hz, 3 H, 1-CH_3) ppm. HPLC conditions: Chiracel AD column, hexane/2-propanol, 70:30, 0.5 mL/min, 10 °C, t_R = 10.9 min, 12.6 min.

2-(Camphorsulfonyl)propiophenone (48):[51] Synthesis according to GP7 from propiophenone (33 mg, 0.25 mmol), an organoiodine catalyst (10 mol-%), *m*CBPA (77%, 128 mg, 0.57 mmol) and (1*S*)-(+)- or (1*R*)-(–)-10-camphorsulfonic acid (173 mg, 0.74 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.98–7.96 (m, 1 H, 3-C*H*, arom.), 7.94 (t, *J* = 1.5 Hz, 1 H, arom.), 7.62 (tt, *J* = 1.3, 7.4 Hz, 1 H, 15-C*H*), 7.54–7.47 (m, 2 H, 14,16-C*H*), 6.06 (q, *J* = 6.9 Hz, 1 H 2-C*H*), 6.07 (q, *J* = 6.9 Hz, 1 H, 2-C*H* for other diastereomer), 3.75 (d, *J* = 15.0 Hz, 1 H, 3-CH_B) (3.67, *J* = 15.1 Hz for other diastereomer), 3.21 (d, *J* = 15.0 Hz, 1 H, 3-CH_A) (δ =3.19 ppm, *J* = 15.1 Hz for other diastereomer), 2.35–2.32 (m, 2 H, camphor), 2.13–2.01 (m, 2 H, camphor), 1.97 (d, 2 H, *J* = 4.5 Hz, camphor) (δ =1.90 ppm, *J* = 4.6 Hz for other diastereomer), 1.68 (d, 3 H, *J* = 7.0 Hz, 1-CH_3) (δ =1.66 ppm for other diastereomer), 1.47–1.38 (m, 1 H, camphor), 1.08 (s, 3 H, 11′-CH_3) (δ =1.12 ppm for other diastereomer), 0.87 (s, 3 H, 11-CH_3) ppm. HPLC conditions: Chiracel AD column, hexane/2-propanol 70:30, 0.5 mL/min, 10 °C, t_R = 21.8 min, 28.0 min.

2-(Camphorsulfonyl)octaphenone (49): Synthesis according to GP7 from octanophenone (82 mg, 0.4 mmol), catalyst **32** (16.6 mg, 0.04 mmol), *m*CBPA (77%, 208 mg, 0.92 mmol) and (1*S*)-(+)-10-camphorsulfonic acid (280 mg, 1.2 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). The diastereomers could not be separated by TLC. Yield 23% (40 mg, 0.09 mmol). $[\alpha]_D$ = 17.0 (*c* = 1.75, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.97–7.93 (m, 2 H, 16,20-C*H*), 7.64–7.50 (m, 3 H, 17,18,19-C*H*), 5.98–5.90 (m, 1 H, 7-C*H*), 3.66 (d, *J* = 15.1 Hz, 1 H, 8-CH_B), 3.22 (d, *J* = 15.1 Hz, 1 H, 8-CH_A), 2.58–0.83 (m, 26 H, 12-C*H*, 2,3,4,5,6,11,13,14-CH_2, 1,16,16′-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 214.3, 195.7, 134.8, 134.3, 129.3, 128.9, 128.8, 58.5, 49.4, 48.3, 43.2, 42.8, 33.0, 32.9, 31.8, 28.9, 27.3, 25.2, 22.8, 20.2, 20.0 ppm. IR (neat): $\tilde{\nu}$ = 3427 (s), 2960 (s), 2923 (s), 2860 (m), 2360 (w), 1741 (s), 1697 (s), 1597 (w), 1447 (m), 1358 (s), 1252 (w), 1225 (m), 1175 (s), 930 (m), 769 (m), 697 (m) cm^{-1}. MS (nano-ES): *m*/*z* (%) = 250 (2), 222 (100), 170 (25), 120 (15), 105 (32), 94 (13), 72 (11), 58 (35), 44 (57). HRMS: calcd. for $C_{24}H_{34}O_5{\cdot}NH_4^+$ 452.2465, found 452.2465. HPLC conditions: Chiracel AD column, hexane/2-propanol, 70:30, 0.5 mL/min, 10 °C, t_R = 19.7 min (minor), 21.5 min (major).

2-(Camphorsulfonyl)-*m*-(trifluoromethyl)propiophenone (50): Synthesis according to GP7 from *m*-trifluoromethylpropiophenone

(78 mg, 0.39 mmol), catalyst **32** (16.2 mg, 0.039 mmol), *m*CPBA (77%, 200 mg, 1.23 mmol) and (1*S*)-(+)-10-camphorsulfonic acid (269 mg, 1.6 mmol); purification by preparative TLC (diethyl ether/petroleum ether, 1:2). Yield 19% (31.8 mg, 0.074 mmol). $[a]_D$ = 26.5 (c = 1.2, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, 3-C*H*), 8.15 (d, J = 7.8 Hz, 1 H, 7-C*H*), 7.88 (d, J = 7.4 Hz, 1 H, 5-C*H*), 7.66 (t, J = 7.8 Hz, 1 H, 6-C*H*), 6.01 (q, J = 6.9 Hz, 1 H, 2-C*H*) (6.02, J = 6.9 Hz for other diastereomer), 3.68 (d, J = 14.9 Hz, 1 H, 8-CH_B), 3.18 (d, J = 15.2 Hz, 1 H, 8-CH_A), 2.52–2.32 (m, 2 H, camphor), 2.14–2.02 (m, 2 H, camphor), 1.68 (d, J = 6.9 Hz, 3 H, 1-CH_3), 1.97–1.47 (m, 3 H, camphor), 1.12 (s, 3 H, 16′-CH_3), 1.09 (s, 3 H, 16-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.1, 193.3, 133.5, 130.9, 130.8, 129.3, 128.6, 124.5, 57.1, 48.0, 47.0, 41.8, 41.5, 28.7, 25.9, 24.0, 18.7, 18.6, 17.5 ppm. IR (neat): $\tilde{\nu}$ = 3475 (m), 2968 (s), 2921 (s), 2354 (w), 1747 (s), 1711 (s), 1605 (m), 1440 (m), 1363 (s), 1328 (s), 1257 (m), 1210 (s), 1169 (s), 1128 (s), 1074 (s), 1016 (m), 927 (s), 809 (m) cm^{-1}. MS (nano-ES): m/z (%) = 450 (7), 202 (12), 173 (37), 153 (15), 108 (14), 72 (16), 52 (60), 44 (100). HRMS: calcd. for $C_{20}H_{23}O_5S{\cdot}NH_4^+$ 450.1557, found 450.1561. HPLC conditions: Chiracel AD column, hexane/2-propanol, 70:30, 0.5 mL/min, 10 °C, t_R = 16.4 min (major), 20.6 min (minor).

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