Intramolecular Carbolithiation of Allyl *o*-Lithioaryl Ethers: A New Enantioselective Synthesis of Functionalized 2,3-Dihydrobenzofurans

José Barluenga,*[a] Francisco J. Fañanás,[a] Roberto Sanz,[b] and César Marcos[b]

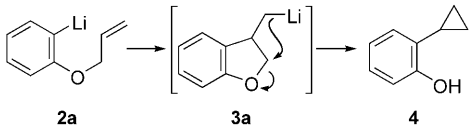
Abstract: A new and easy method for the diastereoselective synthesis of 3-functionalized 2,3-dihydrobenzofuran derivatives from allyl 2-bromoaryl ethers is described. The key step of this transformation involves an intramolecular carbolithiation reaction of allyl 2-lithioaryl ethers. The substituents in both the allyl and the aryl moieties play an important and decisive role in stopping the reaction at the benzofuran thus avoiding a γ-elimination reaction. Finally, this process is amenable to the synthesis of enantiomerically enriched compounds by using (−)-sparteine as a chiral inductor.

Keywords: (−)-sparteine · 2,3-dihydrobenzofurans · allyl aryl ethers · enantioselectivity · intramolecular carbolithiation · synthetic methods

Introduction

The intramolecular carbolithiation of carbon−carbon double bonds is now a common process in the generation of cyclic compounds, and it is particularly well suited for the creation of five-membered rings through a 5-*exo*-*trig* cyclization process.[1] In this context, unsaturated aryllithium compounds undergo carbometalation reactions to yield indanes,[2] benzofurans,[3] indoles,[4] indolines,[5] and isoquinolines.[6] Enantioselective reactions of this kind[7] can be carried out by starting with an enantiomerically enriched secondary lithium derivative in those cases in which the cyclization reaction is fast enough to avoid epimerization.[8] Moreover, enantiofacially selective cycloisomerization of an achiral olefinic organolithium can be achieved by performing the carbolithiation reaction in the presence of a bidentate chiral ligand like (−)-sparteine.[9] On the other hand, 2,3-dihydrobenzofuran (coumaran) is a basic skeleton found in a number of biologically interesting compounds. For example, one group of neolignans[10] possesses the dihydrobenzofuran moiety with a *trans*-stereochemistry.[11] Many of the procedures used in the construction of dihydrobenzofurans involve the radical cyclization of an aryl radical onto a double bond and so general functionalization is not always possible and, more importantly, ring closure to afford 2,3-dihydrobenzofurans is not enantioselective and not completely diastereoselective.[12] Moreover, an interesting study of the intramolecular carbolithiation of allyl 2-lithiophenyl ether (**2a**) has been published by Bailey and Punzalan (Scheme 1).[13] The main product of this reaction is 2-cyclopropylphenol (**4**) which is proposed to be formed by an intramolecular 5-*exo* carbolithiation reaction, which gives the lithiated dihydrobenzofuran (**3a**), followed by an 1,3-elimination process.

Inspired by this work and in connection with our interest in this field,[14] we have investigated the possibility of accessing dihydrobenzofuran derivatives through a carbolithiation reaction analogous to that described in Scheme 1. To this end, it was necessary to find the appropriate conditions to avoid the γ-elimination reaction referred to above. Hence, we report herein the stereoselective carbolithiation of allyl *o*-lithioaryl ethers to afford 2,3-dihydrobenzofuran derivatives. This process is amenable to the synthesis of enantiomerically enriched products.



Scheme 1. Tandem carbolithiation/1,3-elimination reactions of allyl 2-lithiophenyl ether **2a**.

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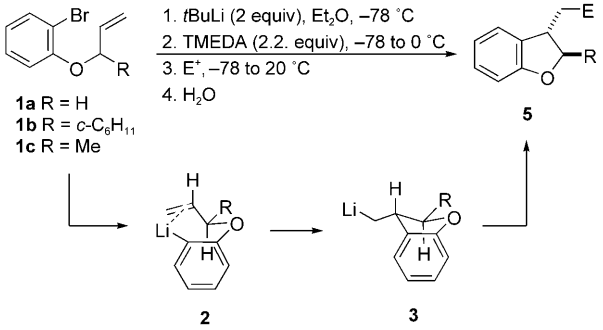
Results and Discussion

Intramolecular carbolithiation of allyl 2-lithiophenyl ether: First, we treated allyl 2-bromophenyl ether **1a** with *tert*-butyllithium (2 equiv) in diethyl ether at −78 °C to afford allyl 2-lithiophenyl ether **2a**, which is stable at this temperature. Addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (2.2 equiv) to the solution of intermediate **2a**, followed by warming to −20 °C and reaction with different electrophiles gave rise, after hydrolysis, to the functionalized dihydrobenzofuran derivatives **5a**,**b** in yields of around 30% along with 2- cyclopropylphenol **4** (ca. 20%) (Scheme 2 and Table 1, entries 1 and 2). Moreover, in these cases around 40% of phenol was generated as a result of a competitive



Scheme 2. *trans*-2,3-Dihydrobenzofuran derivatives **5** from allyl 2-bromophenyl ethers **1** through intramolecular carbolithiation of organolithium compounds **2**.

S_N2' cleavage of the allyl moiety by the excess *t*BuLi used in the bromine/lithium exchange reaction.[15] We concluded that the 1,3-elimination process is not slow enough compared with the carbolithiation reaction and therefore it is not possible to obtain selectively the dihydrobenzofuran derivatives **5**.

2,3-Disubstituted-2,3-dihydrobenzofurans by intramolecular carbolithiation of 1-substituted-2-propenyl 2-lithiophenyl ethers: With the purpose of minimizing the γ-elimination reaction, we considered that this process could be avoided in the presence of a substituent in the α-position of the allyl moiety and so the reactions of the readily available ethers **1b,c** were investigated. Ether **1b** was prepared by the Mitsunobu reaction between 2-bromophenol and 1-cyclohexyl-2-propyn-1-ol and subsequent partial hydrogenation, whilst **1c** was synthesized by a Williamson ether synthesis between 2-bromophenol and ethyl 2-bromopropionate followed by diisobutylaluminum hydride (DIBAL) reduction and Wittig methylenation. Thus, treatment of ethers **1b,c** with *t*BuLi in diethyl ether at −78 °C, further addition of TMEDA at the same temperature, and warming to 0 °C afforded, after reaction with different electrophiles, the corresponding functionalized *trans*-2,3-dihydrobenzofurans **5c–h** in good yields and with total diastereoselectivity[16] (Scheme 2 and Table 1, entries 3–8).

Table 1. Synthesis of dihydrobenzofuran derivatives **5**.

Entry	Ether[a]	R	E^+	Product	E	Yield [%][b]
1	**1a**	H	PhNCO	**5a**	PhNHCO	34[c]
2	**1a**	H	Ph_2S_2	**5b**	PhS	29[d]
3	**1b**	*c*-C_6H_{11}	D_2O	**5c**	D	70
4	**1b**	*c*-C_6H_{11}	TMSCl	**5d**	TMS	64
5	**1b**	*c*-C_6H_{11}	Ph_2S_2	**5e**	PhS	80
6	**1b**	*c*-C_6H_{11}	Et_2CO	**5f**	Et_2COH	73
7	**1c**	Me	H_2O	**5g**	H	74
8	**1c**	Me	Ph_2CO	**5h**	Ph_2COH	65
9	(*R*)-**1c**[e]	Me	H_2O	(2*R*,3*S*)-**5g**	H	77[f]
10	(*R*)-**1c**[e]	Me	Ph_2CO	(2*R*,3*S*)-**5h**	Ph_2COH	69[f]

[a] For the synthesis of the starting ethers, see the Experimental Section. [b] Yield of isolated product based on the starting ether **1**. [c] 2-Cyclopropylphenol **4** (18%) and phenol (38%) were also obtained. [d] 2-Cyclopropylphenol **4** (20%) and phenol (40%) were also obtained. [e] An *ee* of 96% was determined by HPLC. [f] An *ee* of 96% was determined by HPLC.

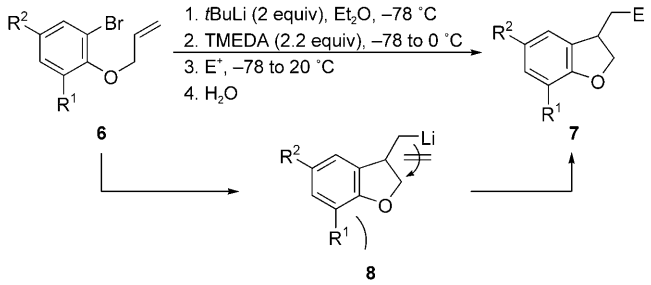
It is very interesting to note that this carbolithiation reaction is completely diastereoselective, since only the *trans* diastereoisomer was obtained. This fact can be explained by assuming that the cyclization reaction takes place via a transition state with the same geometric disposition as intermediate **2**, which resembles a chair-like cyclohexane.[17] The stereocontrol is attributed to steric interactions that favour a geometry in which the substituent preferentially occupies a pseudoequatorial position. And so, for the case shown in Scheme 2, one would predict that the formation of the *trans* isomer of 3-lithiomethyl-2-substituted-2,3-dihydrobenzofuran **3** would be predominant. In fact, it can be deduced from the exclusive formation of functionalized heterocycles **5** that this diastereoisomer was indeed formed (Scheme 2).

With this result in mind, we reasoned that if the starting ether was nonracemic the resulting dihydrobenzofuran derivative would be obtained enantioselectively. So, when (*R*)-**1c**, prepared by the condensation of 2-bromophenol with (*S*)-ethyl lactate under Mitsunobu conditions[18] and subsequent DIBAL reduction and Wittig methylenation, was allowed to react under the conditions indicated in Scheme 2, *trans*-dihydrobenzofuran derivatives (2*R*,3*S*)-**5g,h** were obtained in good yields and with total transference of chirality

Abstract in Spanish: *Se describe un método nuevo y sencillo para la síntesis diastereoselectiva de derivados de 2,3-dihidrobenzofurano funcionalizados en la posición 3 a partir de alil 2-bromoaril éteres. El paso clave de esta transformación implica una reacción de carbolitiación intramolecular de alil 2-litioaril éteres. La presencia de sustituyentes tanto en el resto alílico como en el arílico desempeña un papel decisivo e importante para poder detener la reacción en el estadio de benzofurano, evitando así la reacción de γ-eliminación. Finalmente, este proceso puede ser aplicado a la síntesis de compuestos enantioméricamente enriquecidos mediante el uso de (−)-esparteína como inductor quiral.*

(Table 1, entries 9 and 10). It is remarkable that this is the first enantioselective synthesis of *trans*-2,3-dimethyl-2,3-dihydrobenzofuran.

3-Functionalized-2,3-dihydrobenzofurans by intramolecular carbolithiation of allyl 2-lithio-6-substituted phenyl ethers: Owing to the effect of a substituent in the position adjacent to the oxygen atom, we decided to study the outcomes of this kind of carbometallation reaction with allyl aryl ethers in which the aromatic ring possesses different substituents. Surprisingly, we found that when simple 2-propenyl ethers **6**, substituted at the 6-position of the aryl moiety, were treated under the same conditions as those shown in Scheme 2, functionalized 2,3-dihydrobenzofurans **7** were generated in moderate-to-good yields (Scheme 3 and Table 2). We tentatively proposed that the substituent at the 6-position could exert a stereoelectronic effect that inhibits the 1,3-elimination process in the intermediate organolithium **8**. Although we carried out all the reactions in the temperature range of −78 to 0 °C, we also observed that ether **6a**, with the bulky *tert*-butyl group as R^1, undergoes the carbolithiation reaction at a lower temperature (over −60 °C) than ether **6b** (over −40 °C) with R^1 = Me, whereas the nonsubstituted ether **1a** cyclizes at an even higher temperature (over −20 °C). This fact could be due to the steric effect of the substituent that forces the allyl group to be close to the lithium atom in the organolithium intermediates. A similar effect could also be responsible for the inhibition of the subsequent 1,3-elimination process.



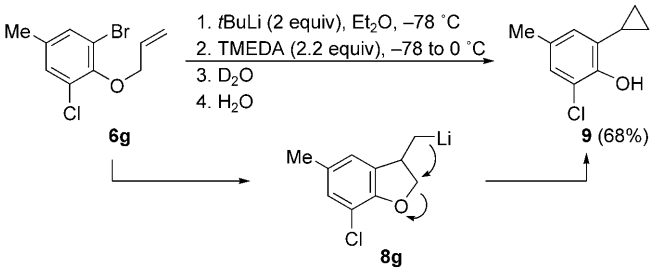
Scheme 3. Formation of dihydrobenzofuran derivatives **7** from 6-substituted aryl ethers **6**.

Table 2. Synthesis of dihydrobenzofuran derivatives **7**.

Ether	R^1	R^2	E^+	Product	E	Yield [%][a]
6a	*t*Bu	Me	D_2O	**7a**	D	73
6a	*t*Bu	Me	Ph_2CO	**7b**	Ph_2COH	73
6a	*t*Bu	Me	$Br(CH_2)_2Br$	**7c**	Br	63
6a	*t*Bu	Me	PhNCO	**7d**	PhNHCO	61
6b	Me	Me	D_2O	**7e**	D	62
6b	Me	Me	Ph_2CO	**7f**	Ph_2COH	66
6b	Me	Me	Ph_2S_2	**7g**	PhS	65
6b	Me	Me	$Br(CH_2)_2Br$	**7h**	Br	66
6c	TMS	Me	D_2O	**7i**	D	75
6c	TMS	Me	PhNCO	**7j**	PhNHCO	75
6c	TMS	Me	Bu_3SnCl	**7k**	Bu_3Sn	69
6c	TMS	Me	$Br(CH_2)_2Br$	**7l**	Br	75
6d	TMS	H	H_2O	**7m**	H	70
6d	TMS	H	PhNCO	**7n**	PhNHCO	70
6d	TMS	H	Bu_3SnCl	**7o**	Bu_3Sn	73
6d	TMS	H	Ph_2S_2	**7p**	PhS	79
6d	TMS	H	Me_2SO_4	**7q**	Me	67
6e	*i*-Pr	H	Ph_2CO	**7r**	Ph_2COH	78
6f	Me	Cl	Ph_2S_2	**7s**	PhS	59

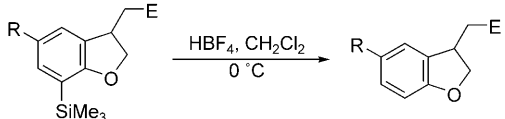
[a] Yield of isolated product based on starting ether **6**.

The different behavior of the regioisomeric allyl ethers **6f** and **6g**, in which the methyl and chlorine substituents at the 4- and 6-positions are interchanged, is remarkable. Whereas **6f** (R^1 = Me, R^2 = Cl) efficiently gave dihydrobenzofuran derivative **7s** in 59% yield (Table 2), the regioisomer **6g** (R^1 = Cl, R^2 = Me) led, under the same reaction conditions, exclusively to *o*-cyclopropylphenol derivative **9** in 68% yield (Scheme 4). Although the carbolithiation reactions of the organolithium intermediates derived from **6f** and **6g** are slower at 0 °C than the cyclization reactions of the organolithiums derived from **6a–e** (1 h for **6f** and 3 h for **6g**), the different outcomes of these reactions could be attributed to an increase in the electron-withdrawing effect of the chlorine atom in intermediate **8g** (Scheme 4) relative to **8f**, which in turn would decrease the electron density on the oxygen atom and thus favor the γ-elimination process.



Scheme 4. Formation of *o*-cyclopropylphenol derivative **9** from 6-chloro-substituted aryl ether **6g**.

Interestingly, ethers **6c,d** with trimethylsilyl groups at the 6-position behave as synthetic equivalents of the parent ether **1a** because the trimethylsilyl group can be removed under mild conditions with HBF_4 in dichloromethane at 0 °C (Scheme 5). In this way, functionalized 2,3-dihydrobenzofuran derivatives **5i,j** and **7t,u**, which have no substituents at the 2- and 7-positions of the benzofuran moiety, can be syn-



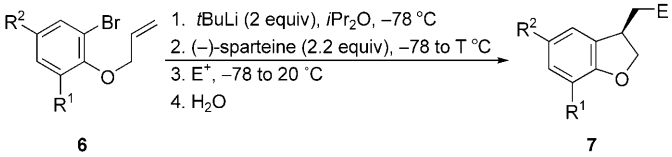
	R	E	Yield [%]
7t	Me	D	75
7u	Me	$SnBu_3$	83
5i	H	H	84
5j	H	$SnBu_3$	90

Scheme 5. Protodesilylation of 7-trimethylsilyl-substituted 2,3-dihydrobenzofurans **7i,k,m,o**.

thesized in good yields, avoiding the careful control of the temperature and the low yields obtained with ether **1a**.

Enantioselective synthesis of 3-functionalized-2,3-dihydrobenzofurans: Having developed an efficient methodology for the diastereoselective synthesis of 2,3-dihydrobenzofuran derivatives we next turned our attention to the possibility of carrying out this reaction enantioselectively by conducting the carbolithiation reaction in the presence of a bidentate chiral ligand such as (−)-sparteine.[9] First, we carried out several experiments with ether **6b** and determined that, under the same reaction conditions, diisopropyl ether was the most effective solvent with which to obtain high enantioselectivity and chemical yield. We did not observe significant change in the *ee* values when a less polar solvent such as hexane was used, but lower chemical yields were obtained. Accordingly, we carried out a set of experiments with ethers **6a–e** in diisopropyl ether using (−)-sparteine in the second step and at the lowest temperature at which the carbolithiation reaction proceeds to obtain the best enantioselectivity possible. The results of these experiments are summarized in Table 3.

Table 3. Enantioselective synthesis of dihydrobenzofurans **7**.

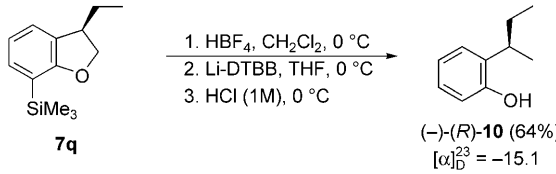


6 **7**

Ether	R^1	R^2	T [°C]	E^+	Product	E	Yield [%][a]	*ee* [%][b]
6a	*t*Bu	Me	−65	Ph_2CO	**7b**	Ph_2COH	64	84
6a	*t*Bu	Me	−65	PhNCO	**7d**	PhNHCO	58	86
6b	Me	Me	−40	D_2O	**7e**	D	47	79
6b	Me	Me	−40	Ph_2CO	**7f**	Ph_2COH	60	77
6b	Me	Me	−40	Ph_2S_2	**7g**	PhS	61	80
6c	TMS	Me	−50	PhNCO	**7j**	PhNHCO	56	80
6d	TMS	H	−50	PhNCO	**7n**	PhNHCO	68	82
6d	TMS	H	−50	Me_2SO_4	**7q**	Me	76	81[c]
6e	*i*-Pr	H	−60	Ph_2CO	**7r**	Ph_2COH	66	87

[a] Yield of isolated product based on starting ether **6**. [b] The *ee* values were assayed by HPLC using mixtures of hexane/2-propanol. [c] The *ee* value was determined from the specific rotation of the transformed (−)-2-*sec*-butylphenol compared with the literature value.[19]

The absolute configuration of the stereogenic center of the major enantiomer was unequivocally determined by chemical correlation of the 2,3-dihydrobenzofuran **7q** with the known (−)-(*R*)-2-*sec*-butylphenol **10**.[19] Thus, protodesilylation of 2,3-dihydrobenzofuran **7q** with HBF_4 followed by reductive ring opening with Li/4,4′-di-*tert*-butylbiphenyl (DTBB)[20] afforded, after hydrolysis, 2-*sec*-butylphenol **10** in 64% yield (Scheme 6). The measure of the specific rotation of **10** {$[\alpha]_D^{23} = -15.1$; $[\alpha]_D^{23}$(lit.)[19] $= -18.6$} allowed the unequivocal assignment of the absolute configuration of the stereogenic center as *R*. We assume the same configuration for all the examples shown in Table 3. Note that the enantio-



7q

(−)-(*R*)-**10** (64%)
$[\alpha]_D^{23} = -15.1$

Scheme 6. Chemical correlation of 3-ethyl-7-trimethylsilyl-2,3-dihydrobenzofuran **7q** with (−)-(*R*)-2-*sec*-butylphenol.

facial selectivity in these cyclization reactions is the same as that reported for the asymmetric carbolithiation of *N*-allyl-2-lithioanilines, which affords (*R*)-lithiomethylindolines.[9a,b]

Conclusions

In summary, we have developed an effective and general method for the synthesis of 2,3-dihydrobenzofuran derivatives based on an intramolecular carbolithiation reaction of *o*-lithioaryl ethers. Note that this process supposes the first example in which the carbolithiation reaction can be stopped at the 2,3-dihydrobenzofuran stage by appropriate selection of the ether moiety. Moreover, and in marked contrast to the previously published synthesis of dihydrobenzofuran derivatives by radical cyclization reactions, the strategy described herein allows the enantioselective and totally diastereoselective preparation of this kind of heterocycle. Current investigations are focused on the application of this methodology to the preparation of biologically active compounds in which 2,3-dihydrobenzofuran is the basic molecular framework.

Experimental Section

General: All reactions were carried out under nitrogen in oven-dried glassware with magnetic stirring. Temperatures are reported as bath temperatures. Diethyl ether, diisopropyl ether, and THF were continuously refluxed and freshly distilled from sodium under nitrogen. TMEDA and (−)-sparteine were refluxed over potassium under nitrogen using benzophenone as indicator and distilled at reduced pressure. Solvents used in extraction and purification were distilled prior to use. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Merck) and compounds were visualized with UV light (254 nm) or iodine. Flash column chromatography was carried out on silica gel 60, 230–400 mesh (Merck). Melting points were obtained on a Büchi-Tottoli apparatus using open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-400 (400 MHz; 101 MHz), Varian Mercury-plus 300 (300 MHz; 75 MHz) or Varian Gemini VXR-200 (200 MHz; 50 MHz) spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with the residual solvent resonance used as the internal standard ($CHCl_3$: $\delta_H = 7.26$ ppm; $\delta_C = 76.95$ ppm; [D_6]DMSO: $\delta_H = 2.54$ ppm; $\delta_C = 40.15$ ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double doublet, td: triplet of doublets, t: triplet, q: quartet, dq: double quartet, m: multiplet), coupling constants (J in Hz), and integration. Low-resolution electron-impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 5987A or Micromass Autospec spectrometer and only the molecular ions and/or base peaks in the spectra are given. High-resolution mass spectrometry was carried out on a Micromass Au-

tospec spectrometer. Elemental analyses were performed with Perkin Elmer and LECO elemental analysers. Enantiomer ratios were determined by chiral HPLC analysis using a Hewlett Packard Series 1100 with G1315A detector and a Chiralcel OD-H column (25×0.46 cm, Daicel Chem. Ind.) in comparison with the authentic racemic products. Optical rotations were measured on a Perkin Elmer 241 polarimeter ($c=1$, 10 mg mL^{-1}); $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. All commercially available reagents were used without further purification unless otherwise indicated and were purchased from Aldrich Chemical Co. and Acros Organics. *t*BuLi was used as a 1.5 M solution in pentane. Ether **1a** was prepared as described in our previous report.[14c]

Procedure for the synthesis of 2-bromophenyl 1-cyclohexyl-2-propenyl ether (1b)

Preparation of 1-cyclohexyl-2-propynol: A solution of cyclohexanecarboxaldehyde (5.60 g, 50 mmol) in THF (20 mL) was added dropwise to a solution of 0.5 M ethynylmagnesium bromide in THF (100 mL, 50 mmol) at 0 °C. After stirring for an additional 1 h at room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate (3×30 mL) and the combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by column chromatography (hexane/ethyl acetate, 7:1) afforded 1-cyclohexyl-2-propynol (6.42 g, 93 %) as a colorless oil. $R_f=0.17$ (hexane/ethyl acetate, 7:1); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=4.13$–4.08 (m, 1H), 2.48 (s, 1H), 2.42 (d, $J=2.2$ Hz, 1H), 1.85–1.59 (m, 5H), 1.56–1.46 (m, 1H), 1.27–0.96 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta=83.9$, 73.3, 66.7, 43.7, 28.3, 27.8, 26.2, 25.7, 25.6 ppm ppm; LRMS (70 eV, EI): *m*/*z* (%): 138 (1) $[M]^+$, 55 (100).

Preparation of 2-bromophenyl 1-cyclohexyl-2-propynyl ether: A solution of diisopropyl azodicarboxylate (6.06 g, 30 mmol) in THF (10 mL) was added dropwise to a solution of 2-bromophenol (5.19 g, 30 mmol), 1-cyclohexyl-2-propynol (4.14 g, 30 mmol), and PPh_3 (7.86 g, 30 mmol) in THF (40 mL) at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was quenched with water and extracted with ethyl acetate (3×15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography (hexane/ethyl acetate, 40:1) to afford 2-bromophenyl 1-cyclohexyl-2-propynyl ether (5.63 g, 64 %) as a pale yellow solid. M.p. 34–36 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.54$ (dd, $J=7.9$, 1.6 Hz, 1H), 7.29–7.23 (m, 1H), 7.13 (dd, $J=8.3$, 1.4 Hz, 1H), 6.88–6.83 (m, 1H), 4.54 (dd, $J=5.8$, 2.1 Hz, 1H), 2.50 (d, $J=2.1$ Hz, 1H), 2.09–1.78 (m, 5H), 1.76–1.68 (m, 1H), 1.41–1.15 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta=154.0$, 133.2, 128.1, 122.3, 115.0, 112.7, 80.5, 75.7, 73.3, 42.6, 28.4, 28.2, 26.2, 25.8, 25.7 ppm; LRMS (70 eV, EI): *m*/*z* (%): 294 (4) $[M+2]^+$, 292 (4) $[M]^+$, 209 (100).

*Preparation of 2-bromophenyl 1-cyclohexyl-2-propenyl ether (**1b**)*: A suspension of palladium (5% on calcium carbonate, 0.39 g) in hexane (3 mL) was added to a solution of 2-bromophenyl 1-cyclohexyl-2-propynyl ether (4.40 g, 15 mmol) and quinoline (0.56 mL, 3.89 mmol) in hexane (20 mL). The mixture was stirred under hydrogen (1 atm) at room temperature until the reaction had gone to completion, which was monitored by GC–MS. The mixture was filtered through a pad of Celite to remove the catalyst and then hexane was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate, 100:1) to afford **1b** (3.45 g, 78 %) as a colorless oil. $R_f=0.48$ (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.51$ (dd, $J=7.9$, 1.6 Hz, 1H), 7.20–7.14 (m, 1H), 6.86 (dd, $J=8.3$, 1.3 Hz, 1H), 6.81–6.75 (m, 1H), 5.89–5.79 (m, 1H), 5.27–5.17 (m, 2H), 4.40 (t, $J=6.1$ Hz, 1H), 2.02–1.94 (m, 1H), 1.86–1.63 (m, 5H), 1.35–1.10 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta=154.8$, 135.9, 133.1, 127.9, 121.4, 117.5, 115.2, 112.9, 84.6, 42.6, 28.7, 28.2, 26.4, 26.1, 26.0 ppm; LRMS (70 eV, EI): *m*/*z* (%): 296 (1) $[M+2]^+$, 294 (1) $[M]^+$, 81 (100); elemental analysis calcd (%) for $C_{15}H_{19}BrO$: C 61.03, H 6.49; found: C 61.09, H 6.46.

Procedure for the synthesis of 2-bromophenyl 3-buten-2-yl ether (1c)

Preparation of ethyl 2-(2-bromophenoxy)propanoate: 2-Bromophenol (3.46 g, 20 mmol) and ethyl 2-bromopropanoate (3.62 g, 10 mmol) were dissolved in acetone (50 mL). Potassium carbonate (2.76 g, 20 mmol) was added to the solution and the resulting mixture was refluxed for 24 h. Then the mixture was cooled to room temperature and concentrated to about 5 mL. Water was added and the mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford the corresponding ester (4.80 g, 88 %) which was used in the next reaction step without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.52$ (dd, $J=7.9$, 1.6 Hz, 1H), 7.21–7.15 (m, 1H), 6.86–6.81 (m, 1H), 6.79 (dd $J=8.2$, 1.3 Hz, 1H), 4.73 (q, $J=6.9$ Hz, 1H), 4.24–4.14 (m, 2H), 1.66 (d, $J=6.9$ Hz, 3H), 1.22 (t, $J=7.2$ Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta=171.4$, 154.1, 133.4, 128.2, 122.8, 114.7, 112.8, 73.9, 61.2, 18.3, 13.9 ppm; LRMS (70 eV, EI): *m*/*z* (%): 274 (38) $[M+2]^+$, 272 (38) $[M]^+$, 199 (100).

Preparation of 2-(2-bromophenoxy)propanal: A solution of DIBAL-H (15 mL of a 1.0 M solution in hexane, 15 mmol) was added dropwise through a syringe to a solution of ethyl 2-(2-bromophenoxy)propanoate (4.10 g, 15 mmol) in CH_2Cl_2 (40 mL) at −78 °C. The resulting solution was stirred for an additional 3 h at this temperature prior to quenching with MeOH and the mixture was allowed to warm to room temperature. Water was then added and the reaction mixture was filtered through a pad of Celite and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography (hexane/ethyl acetate, 7:1) to give the title compound (2.92 g, 85 %) as a colorless oil. $R_f=0.29$ (hexane/ethyl acetate, 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=9.76$ (d, $J=1.8$ Hz, 1H), 7.56 (dd, $J=7.9$, 1.6 Hz, 1H), 7.25–7.19 (m, 1H), 6.91–6.86 (m, 1H), 6.80 (dd, $J=8.2$, 1.4 Hz, 1H), 4.62 (dq, $J=6.9$, 1.8 Hz, 1H), 1.52 (d, $J=6.9$ Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta=201.6$, 153.8, 133.7, 128.4, 123.2, 115.1, 113.1, 79.4, 15.4 ppm; LRMS (70 eV, EI): *m*/*z* (%): 230 (86) $[M+2]^+$, 228 (87) $[M]^+$, 63 (100).

*Procedure for the synthesis of 2-bromophenyl 3-buten-2-yl ether (**1c**)*: A solution of LDA, obtained by addition of *n*BuLi (6.0 mL of a 2.5 M solution in hexane, 15 mmol) to a solution of diisopropylamine (2.10 mL, 15 mmol) in THF (5 mL), was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (5.36 g, 15 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for an additional 1.5 h at 0 °C and a solution of 2-(2-bromophenoxy)propanal (2.29 g, 10 mmol) in THF (10 mL) was added dropwise at 0 °C. The suspension was then allowed to warm to room temperature and stirred for an additional 10 h. Water was added and the mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography (hexane/ethyl acetate, 100:1) to give **1c** (1.27 g, 56 %) as a colorless oil. $R_f=0.43$ (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.53$ (d, $J=8.0$ Hz, 1H), 7.24–7.18 (m, 1H), 6.92 (d, $J=8.3$ Hz, 1H), 6.84–6.79 (m, 1H), 5.99–5.88 (m, 1H), 5.29 (dd, $J=17.2$, 1.2 Hz, 1H), 5.18 (dd, $J=10.5$, 1.2 Hz, 1H), 4.81 (quintet, $J=6.3$ Hz, 1H), 1.50 (d, $J=6.3$ Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta=154.3$, 138.5, 133.2, 128.0, 121.9, 115.9, 115.8, 113.2, 76.3, 21.2 ppm; LRMS (70 eV, EI): *m*/*z* (%): 228 (7) $[M+2]^+$, 226 (7) $[M]^+$, 172 (100); elemental analysis calcd (%) for $C_{10}H_{11}BrO$: C 52.89, H 4.88; found: C 52.86, H 4.90.

Procedure for the synthesis of the starting ether (*R*)-1c

Preparation of (R)-ethyl 2-(2-bromophenoxy)propanoate: The title compound was prepared from 2-bromophenol and (*S*)-ethyl lactate under Mitsunobu conditions following the procedure described in the literature.[18] HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH=90:10, flow rate=0.8 mL min^{-1}, $\lambda=210$ nm): $t_R=5.84$ (minor), 7.06 (major) min.

*Procedure for the synthesis of (R)-2-bromophenyl 3-buten-2-yl ether [(R)-**1c**]*: The title compound was prepared from (*R*)-ethyl 2-(2-bromophenoxy)propanoate by the same procedure (DIBAL reduction and Wittig olefination) as described above for the synthesis of the racemic ether. HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH=99.5:0.5, flow rate=0.8 mL min^{-1}, $\lambda=210$ nm): $t_R=16.45$ (minor), 21.68 (major) min.

General procedure for the synthesis of starting ethers 6a–g: 2-Bromo-6-*tert*-butyl-4-methylphenol, 2-bromo-4,6-dimethylphenol, 2-bromo-4-chloro-6-methylphenol, and 2-bromo-6-chloro-4-methylphenol were pre-

pared by bromination of commercially available 2-*tert*-butyl-4-methylphenol, 2,4-dimethylphenol, 4-chloro-2-methylphenol, and 2-chloro-4-methylphenol with bromine in CH_2Cl_2. 2-Bromo-6-isopropylphenol was prepared by bromination of 2-isopropylphenol with $Br_2/tBuNH_2$.[21] 2-Bromo-4-methyl-6-trimethylsilylphenol and 2-bromo-6-trimethylsilylphenol were prepared by treatment of the corresponding *O*-trimethylsilyl ether of 2,6-dibromo-4-methylphenol and 2,6-dibromophenol with *n*BuLi.[22] The corresponding 2-bromophenol (25 mmol) and allyl bromide (4.24 g, 35 mmol) were dissolved in acetone (50 mL), potassium carbonate (3.46 g, 25 mmol) was added to the solution, and the resulting mixture was refluxed for 24 h. Then the mixture was cooled to room temperature and concentrated to about 5 mL. Water was added and the mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate, 100:1) to afford the corresponding ethers **6**.

2-Bromo-6-*tert*-butyl-4-methylphenyl 2-propenyl ether (6a): Reaction of 2-bromo-6-*tert*-butyl-4-methylphenol (6.09 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL), followed by workup as described above, yielded **6a** (5.59 g, 79%) as a colorless oil. R_f=0.59 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.25 (s, 1H), 7.07 (s, 1H), 6.19–6.08 (m, 1H), 5.50 (dq, J=17.2, 1.6 Hz, 1H), 5.30 (dq, J=10.6, 1.6 Hz, 1H), 4.57 (dt, J=5.2, 1.6 Hz, 2H), 2.27 (s, 3H), 1.38 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=152.5, 144.7, 134.1, 133.4, 132.1, 127.4, 117.9, 117.0, 73.3, 35.4, 30.8, 20.7 ppm; LRMS (70 eV, EI): m/z (%): 284 (11) $[M+2]^+$, 282 (11) $[M]^+$, 162 (100); HRMS (EI): calcd for $C_{14}H_{19}BrO$: 282.0619; found: 282.0620; elemental analysis calcd (%) for $C_{14}H_{19}BrO$: C 59.37, H 6.76; found: C 59.43, H 6.73.

2-Bromo-4,6-dimethylphenyl 2-propenyl ether (6b): Reaction of 2-bromo-4,6-dimethylphenol (5.03 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL) followed by workup as described above yielded **6b** (4.88 g, 81%) as a colorless oil. R_f=0.34 (hexane/ethyl acetate, 25:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.19 (s, 1H), 6.91 (s, 1H), 6.13 (ddt, J=17.1, 10.4, 5.7 Hz, 1H), 5.43 (dq, J=17.1, 1.4 Hz, 1H), 5.26 (dq, J=10.4, 1.4 Hz, 1H), 4.40 (dt, J=5.7, 1.4 Hz, 2H), 2.27 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=151.9, 134.8, 133.6, 132.7, 131.2, 130.9, 117.7, 117.0, 73.5, 20.4, 17.0 ppm; LRMS (70 eV, EI): m/z (%): 242 (34) $[M+2]^+$, 240 (34) $[M]^+$, 199 (100); HRMS (EI): calcd for $C_{11}H_{13}BrO$: 240.0150; found: 240.0148; elemental analysis calcd (%) for $C_{11}H_{13}BrO$: C 54.79, H 5.43; found: C 54.75, H 5.41.

2-Bromo-4-methyl-6-trimethylsilylphenyl 2-propenyl ether (6c): Reaction of 2-bromo-4-methyl-6-trimethylsilylphenol (6.48 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL) followed by workup as described above yielded **6c** (5.54 g, 74%) as a colorless oil. R_f=0.49 (hexane/ethyl acetate, 30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.39 (s, 1H), 7.13 (s, 1H), 6.17–6.06 (m, 1H), 5.47 (dq, J=17.3, 1.6 Hz, 1H), 5.29 (dq, J=10.6, 1.6 Hz, 1H), 4.50 (dt, J=5.3, 1.6 Hz, 2H), 2.29 (s, 3H), 0.30 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=157.8, 135.3, 135.0, 134.8, 133.4, 117.2, 116.4, 73.9, 20.4, −0.3 ppm; LRMS (70 eV, EI): m/z (%): 300 (14) $[M+2]^+$, 298 (14) $[M]^+$, 177 (100); HRMS (EI) calcd for $C_{13}H_{19}BrOSi$: 298.0389; found: 298.0393.

2-Bromo-6-trimethylsilylphenyl 2-propenyl ether (6d): Reaction of 2-bromo-6-trimethylsilylphenol (6.13 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL) followed by workup as described above yielded **6d** (5.49 g, 77%) as a colorless oil. R_f=0.57 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.56 (dd, J=7.9, 1.6 Hz, 1H), 7.35 (dd, J=7.5, 1.6 Hz, 1H), 6.98 (dd, J=7.9, 7.5 Hz, 1H), 6.17–6.06 (m, 1H), 5.48 (dq, J=17.3, 1.6 Hz, 1H), 5.30 (dq, J=10.6, 1.6 Hz, 1H), 4.53 (dt, J=5.3, 1.6 Hz, 1H), 0.30 (s. 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=160.1, 135.6, 135.1, 134.4, 133.3, 125.2, 117.2, 116.8, 73.8, −0.3 ppm; LRMS (70 eV, EI): m/z (%): 286 (4) $[M+2]^+$, 284 (3) $[M]^+$, 269 (100); elemental analysis calcd (%) for $C_{12}H_{17}BrOSi$: C 50.53, H 6.01; found: C 50.59, H 5.98.

2-Bromo-6-isopropylphenyl 2-propenyl ether (6e): Reaction of 2-bromo-6-isopropylphenol (5.38 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL) followed by workup as described above yielded **6e** (5.23 g, 82%) as a colorless oil. R_f=0.57 (hexane/ethyl acetate, 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.38 (dd, J=7.8, 1.6 Hz, 1H), 7.20 (dd, J=7.8, 1.6 Hz, 1H), 6.98 (t, J=7.8 Hz, 1H), 6.15 (ddt, J=17.2, 10.4, 5.6 Hz, 1H), 5.46 (dq, J=17.2, 1.5 Hz, 1H), 5.29 (dq, J=10.4, 1.5 Hz, 1H), 4.45 (dt, J=5.6, 1.5 Hz, 2H), 3.36 (sept., J=7.0 Hz, 1H), 1.22 (d, J=7.0 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=153.0, 144.2, 133.4, 130.7, 125.8, 125.5, 117.6, 117.5, 74.4, 27.1, 23.7 ppm; LRMS (70 eV, EI): m/z (%): 256 (73) $[M+2]^+$, 254 (74) $[M]^+$, 41 (100); HRMS (EI) calcd for $C_{12}H_{15}BrO$: 254.0306; found: 254.0308; elemental analysis calcd (%) for $C_{12}H_{15}BrO$: C 56.49, H 5.93; found: C 56.52, H 5.97.

2-Bromo-4-chloro-6-methylphenyl 2-propenyl ether (6f): Reaction of 2-bromo-4-chloro-6-methylphenol (5.54 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL) followed by workup as described above yielded **6f** (5.43 g, 83%) as a white solid. M.p. 36–38°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.37 (dq, J=2.6, 0.6 Hz, 1H), 7.09 (dq, J=2.6, 0.6 Hz, 1H), 6.11 (ddt, J=17.2, 10.4, 5.8 Hz, 1H), 5.42 (dq, J=17.2, 1.5 Hz, 1H), 5.28 (dq, J=10.4, 1.5 Hz, 1H), 4.40 (dt, J=5.8, 1.5 Hz, 2H), 2.28 (t, J=0.6 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=153.0, 134.6, 133.1, 130.3, 130.0, 129.3, 118.2, 117.8, 73.7, 16.8 ppm; LRMS (70 eV, EI): m/z (%): 264 (8) $[M+4]^+$, 262 (36) $[M+2]^+$, 260 (28) $[M]^+$, 221 (100); HRMS (EI) calcd for $C_{10}H_{10}BrClO$: 259.9604; found: 259.9608.

2-Bromo-6-chloro-4-methylphenyl 2-propenyl ether (6g): Reaction of 2-bromo-6-chloro-4-methylphenol (5.54 g, 25 mmol), K_2CO_3 (3.46 g, 25 mmol), and allyl bromide (4.24 g, 35 mmol) in acetone (50 mL) followed by workup as described above yielded **6g** (5.36 g, 82%) as a colorless oil. R_f=0.37 (hexane/ethyl acetate, 30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dq, J=2.1, 0.7 Hz, 1H), 7.12 (dq, J=2.1, 0.7 Hz, 1H), 6.15 (ddt, J=17.2, 10.4, 5.9 Hz, 1H), 5.43 (dq, J=17.2, 1.5 Hz, 1H), 5.27 (dq, J=10.4, 1.5 Hz, 1H), 4.51 (dt, J=5.9, 1.5 Hz, 2H), 2.26 (t, J=0.7 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=149.7, 135.8, 133.0, 132.2, 130.0, 128.6, 118.5, 118.2, 74.1, 20.3 ppm; LRMS (70 eV, EI): m/z (%): 264 (12) $[M+4]^+$, 262 (55) $[M+2]^+$, 260 (42) $[M]^+$, 221 (100); HRMS (EI) calcd for $C_{10}H_{10}BrClO$: 259.9604; found 259.9598.

Procedure for the carbolithiation of ether 1a: Preparation of 2-cyclopropylphenol (4) and 2,3-dihydrobenzofuran derivatives 5a and 5b: A solution of ether **1a** (213 mg, 1 mmol) in diethyl ether (10 mL) cooled in a dry ice/acetone bath at −78°C was treated with *t*BuLi (1.33 mL, 2 mmol) and the reaction mixture was stirred for 15 min at this temperature. TMEDA (0.33 mL, 2.2 mmol) was added to the resulting solution at −78°C and the reaction mixture was stirred for an additional 30 min at this temperature. The resulting mixture was allowed to warm to −20°C and stirred overnight at this temperature. Then the corresponding electrophile (PhNCO or Ph_2S_2, 1.1 mmol) was added at −78°C. Stirring was continued for 30 min at this temperature and then for 5 h at room temperature before the hydrolysis with water. The mixture was extracted with ethyl acetate (3×10 mL) and the combined organic layers were washed with 1M HCl (2×10 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate).

2-Cyclopropylphenol (4): The spectral data of **4** were in total agreement with those previously reported.[14c]

(2,3-Dihydrobenzofuran-3-yl)-*N*-phenylacetamide (5a): Ether **1a** (213 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of phenyl isocyanate (131 mg, 1.1 mmol) and workup as described above yielded **5a** (86 mg, 34%) as a pale yellow solid. M.p. 128–130°C (lit.[23] 132–133°C); ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ=10.02 (s, 1H), 7.65–7.56 (m, 2H), 7.33–7.17 (m, 3H), 7.13–6.98 (m, 2H), 6.85–6.72 (m, 2H), 4.68 (t, J=9.0 Hz, 1H), 4.24 (dd, J=9.0, 6.6 Hz, 1H), 3.92–3.81 (m, 1H), 2.83 (dd, J=15.2, 5.9 Hz, 1H), 2.61 (dd, J=15.2, 8.8 Hz, 1H) ppm; ^{13}C NMR ([D$_6$]DMSO, 101 MHz): δ=170.1, 160.1, 139.7, 130.8, 129.4, 128.9, 125.2, 123.9, 121.0, 119.8, 109.9, 76.9, 42.1, 38.7 ppm; LRMS (70 eV, EI): m/z (%): 253 (88) $[M]^+$, 134 (100); HRMS (EI) calcd for $C_{15}H_{15}NO_2$: 253.1102; found: 253.1099.

3-Phenylthiomethyl-2,3-dihydrobenzofuran (5b):[12f] Ether **1a** (213 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA

(0.33 mL, 2.2 mmol). Addition of diphenyl disulfide (237 mg, 1.1 mmol) and workup as described above yielded **5b** (70 mg, 29%) as a colorless oil. R_f=0.40 (hexane/ethyl acetate, 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.42–7.37 (m, 2H), 7.34–7.29 (m, 2H), 7.27–7.20 (m, 2H), 7.18–7.13 (m, 1H), 6.90–6.84 (m, 1H), 6.82–6.79 (m, 1H), 4.62 (t, J=9.1 Hz, 1H), 4.45 (dd, J=9.1, 5.5 Hz, 1H), 3.68–3.57 (m, 1H), 3.32 (dd, J=13.0, 5.0 Hz, 1H), 3.01 (dd, J=13.0, 9.7 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.9, 135.4, 129.8, 129.0, 128.8, 126.5, 124.5, 120.4, 109.7, 76.0, 41.5, 38.8 ppm; LRMS (70 eV, EI): m/z (%): 242 (95) $[M]^+$, 77 (100); HRMS (EI) calcd for $C_{15}H_{14}OS$: 242.0765; found: 242.0766.

General procedure for the carbolithiation of ethers 1b,c and 6: Preparation of 2,3-dihydrobenzofuran derivatives 5c–h, 7a—s, and 2-chloro-6-cyclopropyl-4-methylphenol (9): A solution of the corresponding starting ether **1b,c** or **6** (1 mmol) in diethyl ether (10 mL) cooled in a dry ice/acetone bath at −78°C was treated with *t*BuLi (1.33 mL, 2 mmol) and the reaction mixture was stirred for 15 min at this temperature. TMEDA (0.33 mL, 2.2 mmol) was added to the resulting solution at −78°C and the reaction mixture was stirred for an additional 30 min at this temperature. The mixture was allowed to warm to 0°C and then stirred for an additional 15 min for ethers **1b,c** and **6a–e**, 1 h for ether **6f**, and 3 h for ether **6g**. The corresponding electrophile (1.1 mmol) was added to the solution at −78°C and stirring was continued for 30 min at this temperature and then for 5 h at room temperature prior to the addition of water. The mixture was extracted with ethyl acetate (3×10 mL) and the combined organic layers were washed with 1 M HCl (2×10 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

(*R,*S**)-2-Cyclohexyl-3-deuteriomethyl-2,3-dihydrobenzofuran (5c)**: Ether **1b** (295 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of deuterium oxide (excess) and workup as described above yielded **5c** (152 mg, 70%) as a white solid. M.p. 38–40°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.17–7.10 (m, 2H), 6.90–6.84 (m, 1H), 6.82–6.76 (m, 1H), 4.08 (t, J=6.9 Hz, 1H), 3.31 (q, J=6.9 Hz, 1H), 2.02–1.94 (m, 1H), 1.88–1.61 (m, 5H), 1.38–1.09 (m, 7H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.1, 132.3, 127.8, 123.6, 119.8, 108.9, 94.9, 42.5, 39.1, 28.4, 28.3, 26.4, 26.0, 25.8, 20.2 (t, J=19.6 Hz) ppm; LRMS (70 eV, EI): m/z (%): 217 (14) $[M]^+$, 122 (100); HRMS (EI) calcd for $C_{15}H_{19}DO$: 217.1576; found: 217.1580.

(*R,*S**)-2-Cyclohexyl-3-trimethylsilylmethyl-2,3-dihydrobenzofuran (5d)**: Ether **1b** (295 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of chlorotrimethylsilane (120 mg, 1.1 mmol) and workup as described above yielded **5d** (185 mg, 64%) as a colorless oil. R_f=0.60 (hexane/ethyl acetate, 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.11–7.06 (m, 2H), 6.84–6.79 (m, 1H), 6.76–6.73 (m, 1H), 4.14 (t, J=5.3 Hz, 1H), 3.34 (q, J=6.0 Hz, 1H), 1.85–1.62 (m, 5H), 1.58–1.46 (m, 1H), 1.30–1.04 (m, 5H), 1.00 (d, J=6.5 Hz, 2H), 0.03 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.1, 133.3, 127.7, 124.0, 119.8, 108.9, 94.6, 42.7, 40.8, 29.4, 27.3, 26.4, 26.2, 25.9, 24.6, −0.5 ppm; LRMS (70 eV, EI): m/z (%): 288 (21) $[M]^+$, 73 (100); HRMS (EI) calcd for $C_{18}H_{28}OSi$: 288.1909; found: 288.1911.

(*R,*S**)-2-Cyclohexyl-3-phenylthiomethyl-2,3-dihydrobenzofuran (5e)**: Ether **1b** (295 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of diphenyl disulfide (237 mg, 1.1 mmol) and workup as described above yielded **5e** (260 mg, 80%) as a colorless oil. R_f=0.27 (hexane/ethyl acetate, 30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.44–7.39 (m, 2H), 7.37–7.30 (m, 3H), 7.27–7.16 (m, 2H), 6.91–6.86 (m, 1H), 6.86–6.82 (m, 1H), 4.45 (dd, J=6.0, 4.5 Hz, 1H), 3.49–3.43 (m, 1H), 3.29 (dd, J=12.8, 5.5 Hz, 1H), 3.10 (dd, J=12.8, 8.6 Hz, 1H), 1.89–1.52 (m, 6H), 1.30–1.02 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.5, 135.9, 129.1, 129.0, 128.9, 128.7, 126.1, 124.5, 119.9, 109.2, 91.7, 43.7, 42.5, 39.5, 28.4, 27.5, 26.2, 25.9, 25.7 ppm; LRMS (70 eV, EI): m/z (%): 324 (35) $[M]^+$, 83 (100); elemental analysis calcd (%) for $C_{21}H_{24}OS$: C 77.73, H 7.46; found: C 77.70, H 7.47.

(*R,*S**)-3-(2-Cyclohexyl-2,3-dihydrobenzofuran-3-ylmethyl)-3-pentanol (5f)**: Ether **1b** (295 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of 3-pentanone (95 mg, 1.1 mmol) and workup as described above yielded **5f** (221 mg, 73%) as a colorless oil. R_f=0.18 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.17–7.14 (m, 1H), 7.11–7.05 (m, 1H), 6.83–6.78 (m, 1H), 6.76–6.71 (m, 1H), 4.43 (t, J=4.4 Hz, 1H), 3.38–3.32 (m, 1H), 1.83–1.47 (m, 12H), 1.35–0.98 (m, 6H), 0.94–0.85 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.3, 132.1, 127.7, 124.3, 119.8, 108.7, 93.9, 74.9, 45.4, 42.2, 40.0, 31.6, 30.7, 29.8, 26.6, 26.3, 26.2, 25.9, 8.0, 7.6 ppm; LRMS (70 eV, EI): m/z (%): 302 (12) $[M]^+$, 161 (100); HRMS (EI) calcd for $C_{20}H_{30}O_2$: 302.2246; found: 302.2244.

(*R,*S**)-2,3-Dimethyl-2,3-dihydrobenzofuran (5g)**:[16] Ether **1c** (227 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of water (excess) and workup as described above yielded **5g** (110 mg, 74%) as a colorless oil. R_f=0.34 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.15–7.09 (m, 2H), 6.89–6.84 (m, 1H), 6.79–6.75 (m, 1H), 4.35 (dq, J=8.4, 6.3 Hz, 1H), 3.11–3.02 (m, 1H), 1.49 (d, J=6.3 Hz, 3H), 1.32 (d, J=6.9 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.0, 132.4, 127.9, 123.6, 120.2, 109.3, 87.2, 43.8, 20.0, 17.9 ppm; LRMS (70 eV, EI): m/z (%): 148 (62) $[M]^+$, 133 (100); HRMS (EI) calcd for $C_{10}H_{12}O$: 148.0888; found: 148.0891.

(*R,*S**)-2-(2-Methyl-2,3-dihydrobenzofuran-3-yl)-1,1-diphenylethanol (5h)**: Ether **1c** (227 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of benzophenone (200 mg, 1.1 mmol) and workup as described above yielded **5g** (215 mg, 65%) as a white solid. M.p. 132–134°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.51–7.23 (m, 10H), 7.13–7.07 (m, 1H), 7.04 (d, J=7.4 Hz, 1H), 6.85–6.79 (m, 1H), 7.23 (d, J=8.0 Hz, 1H), 4.61–4.54 (m, 1H), 3.10–3.04 (m, 1H), 2.75–2.65 (m, 2H), 2.21 (s, 1H), 1.16 (d, J=6.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=158.7, 147.0, 146.4, 131.6, 128.3, 128.0, 127.3, 127.1, 126.1, 124.6, 120.1, 109.3, 86.5, 78.4, 48.6, 44.8, 20.6 ppm; LRMS (70 eV, EI): m/z (%): 330 (75) $[M]^+$, 75 (100); elemental analysis calcd (%) for $C_{23}H_{22}O_2$: C 83.60, H 6.71; found: C 83.54, H 6.72.

(2*R*,3*S*)-5g: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH=99.8:0.2, flow rate=0.8 mL min^{-1}, λ=290 nm): t_R=8.94 (minor), 9.95 (major) min.

(2*R*,3*S*)-5h: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH=90:10, flow rate=0.8 mL min^{-1}, λ=210 nm): t_R=11.37 (minor), 15.06 (major) -min.

7-*tert*-Butyl-3-deuteriomethyl-5-methyl-2,3-dihydrobenzofuran (7a): Ether **6a** (283 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of deuterium oxide (excess) and workup as described above yielded **7a** (150 mg, 73%) as a colorless oil. R_f=0.48 (hexane/ethyl acetate, 25:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.97 (s, 1H), 6.93 (s, 1H), 4.73 (t, J=8.5 Hz, 1H), 4.10 (t, J=8.5 Hz, 1H), 3.58–3.48 (m, 1H), 2.39 (s, 3H), 1.45 (s, 9H), 1.39–1.35 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=155.5, 132.7, 132.5, 129.1, 125.2, 121.9, 77.8, 36.2, 33.9, 29.3, 21.0, 18.7 (t, J=19.5 Hz) ppm; LRMS (70 eV, EI): m/z (%): 205 (28) $[M]^+$, 190 (100); HRMS (EI) calcd for $C_{14}H_{19}DO$: 205.1576; found: 205.1573.

2-(7-*tert*-Butyl-5-methyl-2,3-dihydrobenzofuran-3-yl)-1,1-diphenylethanol (7b): Ether **6a** (283 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of benzophenone (200 mg, 1.1 mmol) and workup as described above yielded **7b** (282 mg, 73%) as a colorless oil. R_f=0.28 (hexane/ethyl acetate, 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.57–7.47 (m, 4H), 7.44–7.29 (m, 6H), 6.95 (s, 1H), 6.87 (s, 1H), 4.44 (t, J=9.0 Hz, 1H), 4.00 (t, J=9.0 Hz, 1H), 3.56–3.46 (m, 1H), 3.00 (dd, J=14.1, 2.1 Hz, 1H), 2.64 (dd, J=14.1, 10.3 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 1H), 1.41 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=155.5, 147.0, 146.3, 132.4, 131.5, 129.0, 128.3, 128.2, 127.2, 127.0, 126.0, 125.9, 125.3, 121.8, 78.0, 77.6, 47.1, 37.8, 33.8, 29.2, 21.0 ppm; LRMS (70 eV, EI): m/z (%): 386 (52) $[M]^+$, 355 (100); HRMS (EI) calcd for $C_{27}H_{30}O_2$: 386.2246; found: 386.2245.

3-Bromomethyl-7-*tert*-butyl-5-methyl-2,3-dihydrobenzofuran (7c): Ether **6a** (283 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of 1,2-dibromoethane (207 mg, 1.1 mmol) and workup as described above yielded **7c** (178 mg, 63%) as a white solid. M.p. 65–67°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.96 (s, 1H), 6.91 (s, 1H), 4.64 (t, J=9.2 Hz, 1H), 4.46 (dd, J=9.2, 5.3 Hz, 1H), 3.84–3.75 (m, 1H), 3.65 (dd, J=10.0, 4.4 Hz, 1H), 3.40 (t, J=10.0 Hz, 1H), 2.32 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=156.0, 133.2, 129.5, 127.9, 126.7, 122.4, 75.3, 44.7, 35.2, 33.9, 29.2, 21.0 ppm; LRMS (70 eV, EI): m/z (%): 284 (55) $[M+2]^+$, 282 (59) $[M]^+$, 267 (100);

elemental analysis calcd (%) for $C_{14}H_{19}BrO$: C 59.37, H 6.76; found: C 59.44, H 6.79.

2-(7-*tert*-Butyl-5-methyl-2,3-dihydrobenzofuran-3-yl)-*N*-phenylacetamide (7d): Ether **6a** (283 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of phenyl isocyanate (131 mg, 1.1 mmol) and workup as described above yielded **7d** (197 mg, 61%) as a white solid. M.p. 132–134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69 (s, 1H), 7.51–7.45 (m, 2H), 7.33–7.27 (m, 2H), 7.15–7.09 (m, 1H) 6.93 (s, 1H), 6.85 (s, 1H), 4.68 (t, J = 9.1 Hz, 1H), 4.27 (dd, J = 9.1, 5.7 Hz, 1H), 3.94–3.84 (m, 1H), 2.74 (dd, J = 15.0, 5.7 Hz, 1H), 2.59 (dd, J = 15.0, 8.8 Hz, 1H), 2.27 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 169.5, 155.5, 137.4, 132.8, 129.7, 129.4, 128.9, 125.9, 124.4, 122.2, 120.1, 75.8, 42.5, 38.5, 33.9, 29.2, 20.9 ppm; LRMS (70 eV, EI): *m*/*z* (%): 323 (18) $[M]^+$, 135 (100); elemental analysis calcd (%) for $C_{21}H_{25}NO_2$: C 77.98, H 7.79, N 4.33; found: C 78.03, H 7.74, N 4.35.

3-Deuteriomethyl-5,7-dimethyl-2,3-dihydrobenzofuran (7e): Ether **6b** (241 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of deuterium oxide (excess) and workup as described above yielded **7e** (101 mg, 62%) as a colorless oil. R_f = 0.22 (hexane/ethyl acetate, 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.80 (s, 1H), 6.76 (s, 1H), 4.66 (t, J = 8.7 Hz, 1H), 4.04 (dd, J = 8.7, 7.6 Hz, 1H), 3.54–3.45 (m, 1H), 2.27 (s, 3H), 2.18 (s, 3H), 1.30–1.26 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 155.8, 131.5, 129.7, 129.6, 121.6, 119.0, 78.2, 36.7, 20.7, 18.9 (t, J = 19.5 Hz), 15.0 ppm; LRMS (70 eV, EI): *m*/*z* (%): 163 (74) $[M]^+$, 147 (100); HRMS (EI) calcd for $C_{11}H_{13}DO$: 163.1106; found: 163.1110.

2-(5,7-Dimethyl-2,3-dihydrobenzofuran-3-yl)-1,1-diphenylethanol (7f): Ether **6b** (241 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of benzophenone (200 mg, 1.1 mmol) and workup as described above yielded **7f** (227 mg, 66%) as a colorless oil. R_f = 0.21 (hexane/ethyl acetate, 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56–7.29 (m, 10H), 6.84–6.81 (m, 2H), 4.42 (t, J = 9.0 Hz, 1H), 4.02 (t, J = 9.0 Hz, 1H), 3.58–3.48 (m, 1H), 2.97 (dd, J = 14.1, 2.1 Hz, 1H), 2.62 (dd, J = 14.1, 10.3 Hz, 1H), 2.39 (s, 1H), 2.34 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 155.7, 147.0, 146.2, 130.3, 129.8, 129.3, 128.2, 128.1, 127.2, 126.9, 126.0, 125.9, 121.5, 118.9, 77.9, 77.8, 47.2, 38.2, 20.6, 15.0 ppm; LRMS (70 eV, EI): *m*/*z* (%): 344 (17) $[M]^+$, 146 (100); HRMS (EI) calcd for $C_{24}H_{24}O_2$: 344.1776; found: 344.1776.

5,7-Dimethyl-3-phenylthiomethyl-2,3-dihydrobenzofuran (7g): Ether **6b** (241 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of diphenyl disulfide (237 mg, 1.1 mmol) and workup as described above yielded **7g** (176 mg, 65%) as a colorless oil. R_f = 0.21 (hexane/ethyl acetate, 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48–7.43 (m, 2H), 7.40–7.34 (m, 2H), 7.30–7.24 (m, 1H), 6.95 (s, 1H), 6.86 (s, 1H), 4.66 (t, J = 9.0 Hz, 1H), 4.49 (dd, J = 9.0, 5.7 Hz, 1H), 3.70–3.61 (m, 1H), 3.38 (dd, J = 12.9, 4.8 Hz, 1H), 3.03 (dd, J = 12.9, 9.9 Hz, 1H), 2.34 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 156.1, 135.5, 130.5, 129.5, 128.9, 128.2, 126.2, 122.1, 119.3, 75.7, 41.8, 38.5, 20.6, 15.0 ppm; LRMS (70 eV, EI): *m*/*z* (%): 270 (28) $[M]^+$, 147 (100); HRMS (EI) calcd for $C_{17}H_{18}OS$: 270.1078; found: 270.1076.

3-Bromomethyl-5,7-dimethyl-2,3-dihydrobenzofuran (7h): Ether **6b** (241 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of 1,2-dibromoethane (207 mg, 1.1 mmol) and workup as described above yielded **7h** (159 mg, 66%) as a colorless oil. R_f = 0.33 (hexane/ethyl acetate, 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.87 (s, 1H), 6.84 (s, 1H), 4.64 (t, J = 9.2 Hz, 1H), 4.45 (dd, J = 9.2, 5.3 Hz, 1H), 3.87–3.79 (m, 1H), 3.63 (dd, J = 10.0, 4.6 Hz, 1H), 3.39 (t, J = 10.0 Hz, 1H), 2.28 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 156.4, 131.1, 129.7, 126.6, 122.2, 119.7, 75.6, 45.1, 35.1, 20.6, 15.0 ppm; LRMS (70 eV, EI): *m*/*z* (%): 242 (4) $[M+2]^+$, 240 (4) $[M]^+$, 147 (100); elemental analysis calcd (%) for $C_{11}H_{13}BrO$: C 54.79, H 5.43; found: C 54.84, H 5.40.

3-Deuteriomethyl-5-methyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7i): Ether **6c** (299 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of deuterium oxide (excess) and workup as described above yielded **7i** (166 mg, 75%) as a colorless oil. R_f = 0.52 (hexane/ethyl acetate, 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.12–7.07 (m, 2H), 4.73 (t, J = 8.7 Hz, 1H), 4.10 (dd, J = 8.7, 7.8 Hz, 1H), 3.61–3.51 (m, 1H), 2.41 (s, 3H), 1.42–1.38 (m, 2H), 0.40 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 162.8, 133.2, 130.8, 128.9, 125.5, 119.2, 77.9, 36.0, 20.8, 18.7 (t, J = 19.5 Hz), −1.2 ppm; LRMS (70 eV, EI): *m*/*z* (%): 221 (97) $[M]^+$, 75 (100); HRMS calcd for $C_{13}H_{19}DOSi$: 221.1346; found: 221.1342.

2-(5-Methyl-7-trimethylsilyl-2,3-dihydrobenzofuran-3-yl)-*N*-phenylacetamide (7j): Ether **6c** (299 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of phenyl isocyanate (131 mg, 1.1 mmol) and workup as described above yielded **7j** (255 mg, 75%) as a white solid. M.p. 130–132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (s, 1H), 7.54–7.45 (m, 2H), 7.35–7.26 (m, 2H), 7.16–7.09 (m, 1H), 7.04 (s, 1H), 6.99 (s, 1H), 4.66 (t, J = 9.2 Hz, 1H), 4.24 (dd, J = 9.2, 5.8, 1H), 3.96–3.85 (m, 1H), 2.73 (dd, J = 15.2, 6.2, 1H), 2.60 (dd, J = 15.2, 8.5, 1H), 2.27 (s, 3H), 0.30 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.5, 162.7, 137.4, 133.9, 129.1, 128.9, 127.9, 125.9, 124.4, 120.1, 119.7, 75.9, 42.5, 38.3, 20.7, −1.3 ppm; LRMS (70 eV, EI): *m*/*z* (%): 339 (28) $[M]^+$, 135 (100); elemental analysis calcd (%) for $C_{20}H_{25}NO_2Si$: C 70.75, H 7.42, N 4.13; found: C 70.67, H 7.38, N 4.09.

5-Methyl-3-tributylstannylmethyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7k): Ether **6c** (299 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of tributyltin chloride (358 mg, 1.1 mmol) and workup as described above yielded **7k** (351 mg, 69%) as a colorless oil. R_f = 0.43 (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.08–7.03 (m, 2H), 4.71 (t, J = 8.3 Hz, 1H), 4.01 (t, J = 8.3 Hz, 1H), 3.85–3.70 (m, 1H), 2.39 (s, 3H), 1.64–1.34 (m, 13H), 1.20 (dd, J = 13.2, 9.2 Hz, 1H), 1.03–0.81 (m, 15H), 0.38 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 162.6, 133.1, 132.4, 128.9, 125.5, 119.2, 78.9, 39.9, 29.2, 27.4, 20.8, 14.5, 13.7, 9.3, −1.2 ppm; LRMS (70 eV, EI): *m*/*z* (%): 453 (53) $[M-C_4H_9]^+$, 179 (100); elemental analysis calcd (%) for $C_{25}H_{46}OSiSn$: C 58.94, H 9.10; found: C 58.85, H 9.04.

3-Bromomethyl-5-methyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7l): Ether **6c** (299 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of 1,2-dibromoethane (207 mg, 1.1 mmol) and workup as described above yielded **7l** (224 mg, 75%) as a white solid. M.p. 26–28 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11–7.06 (m, 2H), 4.64 (t, J = 9.3 Hz, 1H), 4.44 (dd, J = 9.3, 5.4 Hz, 1H), 3.87–3.78 (m, 1H), 3.66 (dd, J = 10.0, 4.6 Hz, 1H), 3.42 (t, J = 10.0 Hz, 1H), 2.33 (s, 3H), 0.32 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 163.1, 134.7, 129.2, 126.1, 126.0, 120.2, 75.4, 44.6, 35.1, 20.7, −1.3 ppm; LRMS (70 eV, EI): *m*/*z* (%): 300 (100) $[M+2]^+$, 298 (92) $[M]^+$; HRMS (EI) calcd for $C_{13}H_{19}BrOSi$: 298.0389; found: 298.0390.

3-Methyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7m): Ether **6d** (285 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of water (excess) and workup as described above yielded **7m** (144 mg, 70%) as a colorless oil. R_f = 0.56 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26–7.19 (m, 2H), 6.91 (t, J = 7.3 Hz, 1H), 4.69 (t, J = 8.5 Hz, 1H), 4.07 (t, J = 8.5 Hz, 1H), 3.60–3.49 (m, 1H), 1.37 (d, J = 6.9 Hz, 3H), 0.34 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.8, 132.9, 130.7, 124.8, 119.9, 119.7, 77.8, 36.1, 19.1, −1.2 ppm; LRMS (70 eV, EI): *m*/*z* (%): 206 (38) $[M]^+$, 75 (100); HRMS calcd for $C_{12}H_{18}OSi$: 206.1127; found: 206.1129.

2-(7-Trimethylsilyl-2,3-dihydrobenzofuran-3-yl)-*N*-phenylacetamide (7n): Ether **6d** (285 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of phenyl isocyanate (131 mg, 1.1 mmol) and workup as described above yielded **7n** (228 mg, 70%) as a white solid. M.p. 129–131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (s, 1H), 7.51–7.43 (m, 2H), 7.33–7.23 (m, 3H), 7.19–7.08 (m, 2H), 6.86 (t, J = 7.3 Hz, 1H), 4.68 (t, J = 9.1 Hz, 1H), 4.24 (dd, J = 9.1, 5.8 Hz, 1H), 3.98–3.88 (m, 1H), 2.72 (dd, J = 15.1, 6.2 Hz, 1H), 2.59 (dd, J = 15.1, 8.5 Hz, 1H), 0.32 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.5, 164.7, 137.4, 133.7, 128.9, 127.7, 125.2, 124.5, 120.2, 120.1, 75.8, 42.5, 38.2, −1.3 ppm; LRMS (70 eV, EI): *m*/*z* (%): 325 (13) $[M]^+$, 135 (100); elemental analysis calcd (%) for $C_{19}H_{23}NO_2Si$: C 70.11, H 7.12, N 4.30; found: C 70.17, H 7.18, N 4.25.

3-Tributylstannylmethyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7o): Ether **6d** (285 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of tributyltin chloride (358 mg, 1.1 mmol) and workup as described above yielded **7o** (361 mg, 73%) as a colorless oil. R_f=0.69 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.21–7.14 (m, 2H), 6.87 (t, J=7.3 Hz, 1H), 4.65 (t, J=8.5 Hz, 1H), 3.94 (t, J=8.5 Hz, 1H), 3.79–3.68 (m, 1H), 1.56–1.25 (m, 13H), 1.12 (dd, J=13.2, 9.3 Hz, 1H), 0.95–0.72 (m, 15H), 0.30 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=164.5, 132.8, 132.3, 124.8, 120.0, 119.7, 78.7, 39.9, 29.1, 27.4, 14.5, 13.7, 9.3, −1.2 ppm; LRMS (70 eV, EI): m/z (%): 439 (59) $[M-C_4H_9]^+$, 179 (100).

3-Phenylthiomethyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7p): Ether **6d** (285 mg, 1 mmol) was treated with *t*BuLi (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of diphenyl disulfide (237 mg, 1.1 mmol) and workup as described above yielded **7p** (248 mg, 79%) as a colorless oil. R_f=0.39 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.51–7.46 (m, 2H), 7.42–7.26 (m, 5H), 6.96 (t, J=7.3 Hz, 1H), 4.67 (t, J=9.2 Hz, 1H), 4.49 (dd, J=9.2, 5.9 Hz, 1H), 3.73–3.64 (m, 1H), 3.41 (dd, J=12.9, 5.1 Hz, 1H), 3.08 (dd, J=12.9, 9.7 Hz, 1H), 0.40 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=164.9, 135.5, 133.8, 129.6, 128.9, 127.5, 126.3, 125.4, 120.1, 120.0, 75.3, 41.1, 38.6, −1.3 ppm; LRMS (70 eV, EI): m/z (%): 314 (46) $[M]^+$, 191 (100); HRMS (EI) calcd for $C_{18}H_{22}OSSi$: 314.1161; found: 314.1157.

3-Ethyl-7-trimethylsilyl-2,3-dihydrobenzofuran (7q): Ether **6d** (285 mg, 1 mmol) was treated with *tBu*Li (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of dimethyl sulfate (139 mg, 1.1 mmol) and workup as described above yielded **7q** (148 mg, 67%) as a colorless oil. R_f=0.43 (hexane/ethyl acetate, 20:1); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.26–7.20 (m, 2H), 6.90 (t, J=7.3 Hz, 1H), 4.64 (t, J=8.9 Hz, 1H), 4.22 (dd, J=8.9, 6.5 Hz, 1H), 3.43–3.31 (m, 1H), 1.93–1.78 (m, 1H) 1.71–1.55 (m, 1H), 1.03 (t, J=7.5 Hz, 3H), 0.33 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ=165.0, 133.0, 129.4, 125.3, 119.7, 119.6, 75.9, 43.0, 27.6, 11.5, −1.3 ppm; LRMS (70 eV, EI): m/z (%): 220 (86) $[M]^+$, 163 (100); HRMS (EI) calcd for $C_{13}H_{20}OSi$: 220.1283; found: 220.1285.

2-(7-Isopropyl-2,3-dihydrobenzofuran-3-yl)-1,1-diphenylethanol (7r): Ether **6e** (255 mg, 1 mmol) was treated with *tBu*Li (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of benzophenone (200 mg, 1.1 mmol) and workup as described above yielded **7r** (279 mg, 78%) as a colorless oil. R_f=0.42 (hexane/ethyl acetate, 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.51–7.26 (m, 10H), 7.03 (d, J=7.5 Hz, 1H), 6.97 (d, J=7.5 Hz, 1H), 6.85 (t, J=7.5 Hz, 1H), 4.41 (t, J=9.0 Hz, 1H), 4.00 (t, J=9.0 Hz, 1H), 3.57–3.47 (m, 1H), 3.08 (sept., J=7.0 Hz, 1H), 2.95 (dd, J=14.0, 2.0 Hz, 1H), 2.62 (dd, J=14.0, 10.3 Hz, 1H), 2.22 (s, 1H), 1.27–1.21 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=157.0, 147.0, 146.2, 130.6, 130.4, 128.3, 128.2, 127.2, 127.0, 126.0, 125.9, 124.8, 121.0, 120.2, 78.0, 77.9, 47.3, 38.2, 28.0, 22.3, 22.2 ppm; LRMS (70 eV, EI): m/z (%): 358 (30) $[M]^+$, 327 (100); HRMS (EI) calcd for $C_{25}H_{26}O_2$: 358.1933; found: 358.1930.

5-Chloro-7-methyl-3-(phenylthiomethyl)-2,3-dihydrobenzofuran (7s): Ether **6f** (262 mg, 1 mmol) was treated with *tBu*Li (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Addition of diphenyl disulfide (237 mg, 1.1 mmol) and workup as described above yielded **7s** (172 mg, 59%) as a pale yellow solid. M.p. 39–41 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.42–7.37 (m, 2H), 7.35–7.29 (m, 2H), 7.27–7.21 (m, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 4.62 (t, J=9.2 Hz, 1H), 4.46 (dd, J=9.2, 5.7 Hz, 1H), 3.64–3.55 (m, 1H), 3.28 (dd, J=13.1, 5.1 Hz, 1H), 2.98 (dd, J=13.1, 9.5 Hz, 1H), 2.17 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=156.9, 135.0, 129.9, 129.8, 129.6, 129.0, 126.6, 124.6, 121.8, 121.2, 76.1, 41.7, 38.5, 15.0 ppm; LRMS (70 eV, EI): m/z (%): 292 (14) $[M+2]^+$, 290 (35) $[M]^+$, 167 (100); elemental analysis calcd (%) for $C_{16}H_{15}ClOS$: C 66.08, H 5.20; found: C 65.99, H 5.13.

2-Chloro-6-cyclopropyl-4-methylphenol (9): Ether **6g** (262 mg, 1 mmol) was treated with *tBu*Li (1.33 mL, 2 mmol) and TMEDA (0.33 mL, 2.2 mmol). Workup as described above yielded **9** (124 mg, 68%) as a colorless oil. R_f=0.38 (hexane/ethyl acetate, 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.95 (s, 1H), 6.60 (s, 1H), 5.58 (s, 1H), 2.21 (s, 3H), 2.10–2.03 (m, 1H), 0.98–0.93 (m, 2H), 0.69–0.64 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=147.9, 130.3, 130.0, 126.4, 125.4, 119.1, 20.4, 9.8, 7.1 ppm; LRMS (70 eV, EI): m/z (%): 184 (34) $[M+2]^+$, 182 (100) $[M]^+$; HRMS (EI) calcd for $C_{10}H_{11}ClO$: 182.0498; found: 182.0496.

General procedure for the protodesilylation of 2,3-dihydrobenzofuran derivatives 7i,k,m,o: Preparation of 2,3-dihydrobenzofuran derivatives 5i,j and 7t,u: A solution of the 7-trimethylsilyl-2,3-dihydrobenzofuran **7i,k,m,o** (0.5 mmol) in CH_2Cl_2 (5 mL) at 0 °C was treated with HBF_4 (0.083 mL of a 54 wt.% solution in diethyl ether, 0.6 mmol) and the reaction mixture was stirred for 2 h at this temperature prior to the addition of water. The organic layer was washed with a saturated aqueous $NaHCO_3$ solution and the mixture was extracted with ethyl acetate (3× 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

3-Deuteriomethyl-5-methyl-2,3-dihydrobenzofuran (7t): Reaction of 2,3-dihydrobenzofuran **7i** (111 mg, 0.5 mmol) and HBF_4 (0.083 mL, 0.6 mmol) in CH_2Cl_2 (5 mL) followed by workup as described above yielded **7t** (56 mg, 75%) as a colorless oil. R_f=0.20 (hexane/ethyl acetate, 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.99 (s, 1H), 6.94 (d, J=8.1 Hz, 1H), 6.71 (d, J=8.1 Hz, 1H), 4.68 (t, J=8.6 Hz, 1H), 4.07 (dd, J=8.6, 7.6 Hz, 1H), 3.57–3.47 (m, 1H), 2.33 (s, 3H), 1.34–1.30 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=157.5, 132.1, 129.6, 128.2, 124.3, 108.8, 78.4, 36.4, 20.7, 18.8 (t, J=19.6 Hz) ppm; LRMS (70 eV, EI): m/z (%): 149 (72) $[M]^+$, 133 (100); HRMS (EI) calcd for $C_{10}H_{11}DO$: 149.0950; found: 149.0955.

5-Methyl-3-tributylstannylmethyl-2,3-dihydrobenzofuran (7u): Reaction of 2,3-dihydrobenzofuran **7k** (255 mg, 0.5 mmol) and HBF_4 (0.083 mL, 0.6 mmol) in CH_2Cl_2 (5 mL) followed by workup as described above yielded **7u** (181 mg, 83%) as a colorless oil. R_f=0.47 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.95 (s, 1H), 6.89 (d, J=8.2 Hz, 1H), 6.66 (d, J=8.2 Hz, 1H), 4.63 (t, J=8.5 Hz, 1H), 3.94 (dd, J=8.5, 7.4 Hz, 1H), 3.73–3.62 (m, 1H), 2.29 (s, 3H), 1.50–1.23 (m, 13H), 1.08 (dd, J=13.2, 9.5 Hz, 1H), 0.92–0.73 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=157.3, 133.8, 129.6, 128.1, 124.3, 108.9, 79.5, 40.3, 29.1, 27.4, 20.8, 14.6, 13.6, 9.3 ppm; LRMS (70 eV, EI): m/z (%): 381 (100) $[M-C_4H_9]^+$; elemental analysis calcd (%) for $C_{22}H_{38}OSn$: C 60.43, H 8.76; found: C 60.35, H 8.71.

3-Methyl-2,3-dihydrobenzofuran (5i):[12f] Reaction of 2,3-dihydrobenzofuran **7m** (103 mg, 0.5 mmol) and HBF_4 (0.083 mL, 0.6 mmol) in CH_2Cl_2 (5 mL) followed by workup as described above yielded **5i** (57 mg, 84%) as a colorless oil. R_f=0.29 (hexane/ethyl acetate, 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.21–7.17 (m, 1H), 7.16–7.13 (m, 1H), 6.94–6.88 (m, 1H), 6.85–6.82 (m, 1H), 4.71 (t, J=8.6 Hz, 1H), 4.10 (dd, J=8.6, 7.5 Hz, 1H), 3.62–3.51 (m, 1H), 1.36 (d, J=6.9 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.5, 132.1, 127.8, 123.7, 120.3, 109.3, 78.3, 36.3, 19.2 ppm; LRMS (70 eV, EI): m/z (%): 134 (66) $[M]^+$, 119 (100); HRMS (EI) calcd. for $C_9H_{10}O$: 134.0732; found: 134.0730.

3-Tributylstannylmethyl-2,3-dihydrobenzofuran (5j): Reaction of 2,3-dihydrobenzofuran **7o** (248 mg, 0.5 mmol) and HBF_4 (0.083 mL, 0.6 mmol) in CH_2Cl_2 (5 mL)followed by workup as described above yielded **5j** (190 mg, 90%) as a colorless oil. R_f=0.45 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.18–7.14 (m, 1H), 7.13–7.08 (m, 1H), 6.90–6.84 (m, 1H), 6.80–6.76 (m, 1H), 4.66 (t, J=8.5 Hz, 1H), 3.99 (t, J=8.5 Hz, 1H), 3.82–3.66 (m, 1H), 1.57–1.25 (m, 13H), 1.13 (dd, J=13.2, 9.5 Hz, 1H), 0.97–0.77 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ=159.4, 133.8, 127.7, 123.6, 120.4, 109.4, 79.3, 40.2, 29.1, 27.3, 14.6, 13.6, 9.2; elemental analysis calcd (%) for $C_{21}H_{36}OSn$: C 59.60, H 8.57; found: C 59.66, H 8.51.

General procedure for the enantioselective carbolithiation of ethers 6: Preparation of enantioenriched 2,3-dihydrobenzofuran derivatives 7b,d–g,j,n,q,r: A solution of the corresponding starting ether **6** (1 mmol) in diisopropyl ether (10 mL) cooled in a dry ice/acetone bath at −78 °C was treated with *t*BuLi (1.33 mL, 2 mmol) and the reaction mixture was stirred for 15 min at this temperature. (−)-Sparteine (0.50 mL, 2.2 mmol) was added to the resulting solution at −78 °C and the reaction mixture was stirred for an additional 30 min at this temperature. The mixture was allowed to warm to −65 °C for ether **6a**, −40 °C for ether **6b**, −50 °C for ethers **6c,d**, and −60 °C for ether **6e** and then stirred at this temperature overnight. The corresponding electrophile (1.1 mmol) at −78 °C was

added to the solution and stirring was continued for 30 min at this temperature and for 5 h at room temperature prior to the addition of water. The mixture was extracted with ethyl acetate (3×10 mL) and the combined organic layers were washed with 1 M HCl (2×10 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography. The physical and spectroscopic data of the resulting dihydrobenzofuran derivatives have been reported above and the *ee* values were determined by HPLC (except for **7q**).

7b: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 96:4, flow rate = 0.8 mL min^{-1}, λ = 210 nm): t_R = 9.59 (minor), 20.64 (major) min.

7d: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 90:10, flow rate = 0.8 mL min^{-1}, λ = 210 nm): t_R = 15.19 (major), 25.47 (minor) min.

7e: HPLC (Daicel Chiralcel OD-H, hexane, flow rate = 0.8 mL min^{-1}, λ = 290 nm): t_R = 12.33 (major), 14.02 (minor) min.

7f: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 96:4, flow rate = 0.8 mL min^{-1}, λ = 210 nm): t_R = 15.54 (minor), 24.21 (major) min.

7g: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 99.5:0.5, flow rate = 0.8 mL min^{-1}, λ = 210 nm): t_R = 40.62 (minor), 52.48 (major) min.

7j: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 90:10, flow rate = 0.8 mL min^{-1}, λ = 210 nm): t_R = 14.06 (major), 21.98 (minor) min.

7n: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 90:10, flow rate = 0.8 mL min^{-1}, λ = 254 nm): t_R = 14.89 (major), 21.61 (minor) min.

7q: Ether **6d** (4.28 g, 15 mmol) in diisopropyl ether (40 mL) was treated with *t*BuLi (20 mL, 30 mmol) and (−)-sparteine (7.6 mL, 33 mmol). Addition of dimethyl sulfate (2.14 g, 17 mmol) and workup as described above yielded **7q** (2.51 g, 76%) as a colorless oil. The *ee* (81%) was determined by comparing the specific rotation of the transformed (−)-2-*sec*-butylphenol ($[\alpha]_D^{23} = -15.1$) with the literature value ($[\alpha]_D^{23} = -18.6$).[19]

7r: HPLC (Daicel Chiralcel OD-H, hexane/2-PrOH = 90:10, flow rate = 0.8 mL min^{-1}, λ = 290 nm): t_R = 13.61 (minor), 14.87 (major) min.

Procedure for the transformation of 7q into (−)-2-*sec*-butylphenol (10): Preparation of 3-ethyl-2,3-dihydrobenzofuran: 3-Ethyl-2,3-dihydrobenzofuran was prepared from 7-trimethylsilyl-2,3-dihydrobenzofuran **7q** following the general procedure for protodesilylation as described above for 2,3-dihydrobenzofuran derivatives **7i,k,m,o**. Reaction of **7q** (2.20 g, 10 mmol) and HBF_4 (1.65 mL, 12 mmol) in CH_2Cl_2 (20 mL) and workup as described above yielded 3-ethyl-2,3-dihydrobenzofuran[12f] (1.32 g, 89%) as a colorless oil. R_f = 0.43 (hexane/ethyl acetate, 10:1); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.23–7.11 (m, 2H), 6.92–6.88 (m, 2H), 4.66 (t, J = 8.9 Hz, 1H), 4.25 (dd, J = 8.9, 6.3 Hz, 1H), 3.46–3.39 (m, 1H), 1.91–1.75 (m, 1H), 1.70–1.55 (m, 1H), 1.00 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.9, 130.8, 128.0, 124.3, 120.2, 109.3, 76.5, 43.2, 27.6, 11.3 ppm; LRMS (70 eV, EI): *m*/*z* (%): 148 (48) $[M]^+$, 119 (100).

Preparation of 2-*sec*-butylphenol (10): A mixture of lithium (29 mg, 4.2 mmol) and 4,4′-di-*tert*-butylbiphenyl (DTBB) (1.12 g, 4.2 mmol) in THF (5 mL) was stirred for 4 h at 0 °C. 3-Ethyl-2,3-dihydrobenzofuran (296 mg, 2 mmol) was added and the resulting mixture was stirred for an additional 6 h at 0 °C. The reaction was carefully quenched with 1 M HCl at the same temperature and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 10:1) to afford the title compound (216 mg, 72%) as a colorless oil. Spectral data of the obtained product were in total agreement with those corresponding to a commercial sample. The *ee* (81%) was determined by comparing its specific rotation ($[\alpha]_D^{23} = -15.1$) with the literature value ($[\alpha]_D^{23} = -18.6$).[19]

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