Sulfoxides as Stereochemical Controllers in Intermolecular Heck Reactions

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Abstract: The study of a variety of substituted sulfoxides as chiral auxiliaries in intermolecular Heck reactions of sulfinyldihydrofurans and sulfinylcyclopentenes with different iodoarenes is reported. In the presence of $[Pd(OAc)_2]/Ag_2CO_3$ and a bidentate phosphine ligand, synthetically useful yields and asymmetric inductions were obtained. By far the best diastereoselectivities were obtained by the use of the palladium-coordinating *o*-(*N*,*N*-dimethylamino)phenylsulfinyl group. By final removal of the chiral auxiliary, these sulfoxide-stereocontrolled asymmetric Heck processes were applied to the enantioselective synthesis of 1-aryl-substituted and 1,3-diaryl-substituted dihydrofurans and cyclopentenes.

Keywords: asymmetric synthesis · cyclopentenes · dihydrofurans · Heck reaction · sulfoxides

Introduction

Since its discovery in the late 1960s, the palladium-catalyzed arylation and alkenylation of olefins (the Heck reaction) has become one of the most versatile and widely used metal-catalyzed method for C–C bond formation.[1] Among other factors, the high versatility of this reaction relies on the availability of the starting substrates (usually alkenes and organic halides or triflates), its broad substrate generality, and its high functional group compatibility. Currently, a very important challenge to provide even more improvements in the synthetic usefulness of this reaction is the development of highly efficient asymmetric versions.[2] Most precedents of asymmetric Heck reactions have been performed with the use of catalytic amounts of enantiopure chiral ligands, specially bidentate ligands, such as BINAP or (phosphinoaryl)oxazolines.[2, 3]

Despite the inherent conceptual and practical appeal of an approach based on chiral catalysts, it is surprising that the alternative stoichiometric chiral auxiliary approach, presumably less substrate-dependent, has been seldom considered.[4] In this field, we reasoned that the amply demonstrated capability of the sulfinyl group to act as an efficient stereochemical controller in key traditional C–C bond-forming reactions,[5] such as Michael additions and Diels–Alder cycloadditions, could also be extended to transition metal mediated reactions.[6] Herein we report in detail on appropriately substituted sulfoxides that act as efficient chiral auxiliaries in intermolecular asymmetric Heck reactions of cyclic alkenes.[7]

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Results and Discussion

Synthesis and Heck reactions of sulfinyldihydrofurans and sulfinylcyclopentenes: To explore the reactivity of cyclic α,β-unsaturated sulfoxides in Heck reactions we undertook the synthesis of a variety of racemic sulfinyldihydrofurans and sulfinylcyclopentenes that have very different substituents at the sulfur atom in terms of steric size, electronic character, and potential palladium-coordinating properties (Scheme 1). The arylsulfinyl dihydrofurans **1**–**4** were readily prepared in two steps from 2,3-dihydrofuran by sulfenylation with the corresponding aryl methyl sulfoxide under Pummerer reaction conditions[8] and further oxidation of the thioether (*meta*-chloroperoxybenzoic acid (MCPBA)). To test a bulky alkyl sulfoxide, the *tert*-butylsulfinyl dihydrofuran **5** was synthesized from α-bromo-γ-butyrolactone by initial nucleophilic substitution with sodium *tert*-butyl thiolate, reduction of the lactone to the hemiacetal moiety with diisobutylaluminum hydride (DIBAL-H), and formal dehydration (Scheme 1). Concerning the cyclopentene series, the *p*-tolylsulfinyl and *tert*-butylsulfinyl cyclopentenes **6** and **7** were readily prepared by direct sulfinylation of cyclopentenyllithium with methyl *p*-tolylsulfinate or *tert*-butyl thiosulfinate,[9] respectively. Finally, the potentially palladium-coordinating aminophenylsulfinyl cyclopentene **8** was prepared in two steps by sulfenylation of

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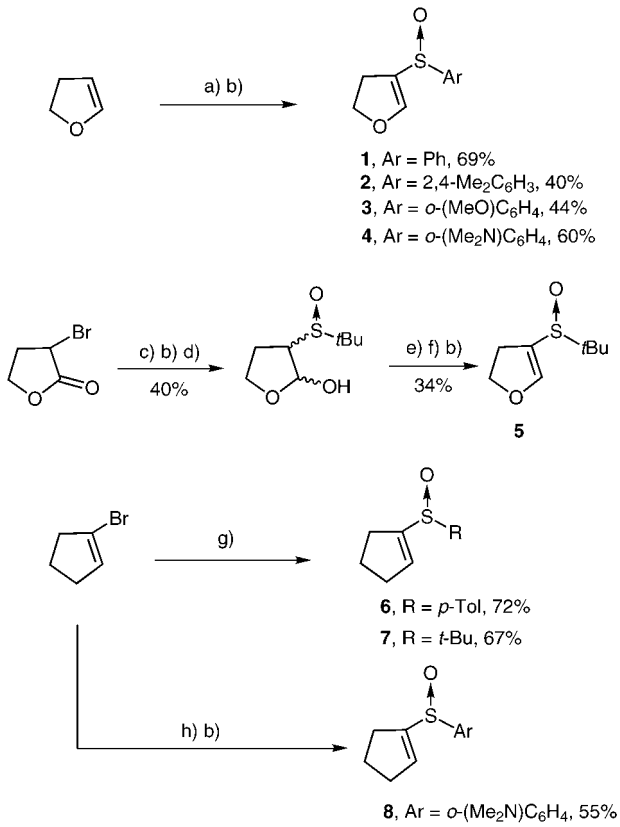


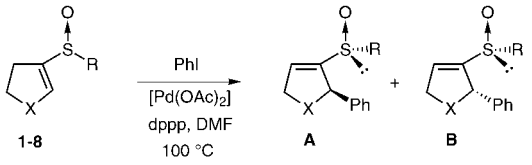
Scheme 1. Synthesis of racemic sulfinyldihydrofurans and cyclopentenes **1**–**8**. a) 1) ArSOMe, $(CF_3CO)_2O$, CH_2Cl_2, −78 °C, 2) Et_3N, −78 °C; b) MCPBA, CH_2Cl_2, −78 °C; c) NaS*t*Bu, DMF, RT; d) DIBAL-H, THF, −78 °C; e) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 0 °C; f) PhSeH, $BF_3 \cdot Et_2O$, CH_2Cl_2, 0 °C; g) 1) *n*BuLi, THF, −78 °C; 2) *t*BuSOS*t*Bu or *p*TolSOOMe, THF, −78 °C; h) 1) *n*BuLi, THF, −78 °C; 2) Ar-S-S-Ar, THF, −78 °C. DMAP = 4-dimethylaminopyridine.

cyclopentenyl-lithium with the corresponding disulfide and subsequent oxidation with MCPBA.

With the α,β-unsaturated sulfoxides **1**–**8** in hand, we studied their Heck reactions with excess iodobenzene.[10] After extensive experimentation, we found that while complex mixtures of sulfinylated and nonsulfinylated compounds were obtained in the presence of common bases, such as Et_3N, diisopropylethylamine (DIPEA), proton sponge, or K_2CO_3 in DMF at 100 °C, a clean reaction was observed with the use of Ag_2CO_3 as the base. As a second and less determinant factor, bidentate phosphine ligands, such as 1,3-bis(diphenylphosphanyl)propane (dppp) or 1,1′-bis(diphenylphosphanyl)ferrocene (dppf), tended to be somewhat more efficient than monodentate ligands (PPh_3, $P(o\text{Tol})_3$, or $AsPh_3$). Typical optimized experimental conditions were: PhI (3 equiv), $[Pd(OAc)_2]$ (10 mol %), dppp (10 mol %), Ag_2CO_3 (2 equiv) in DMF at 100 °C (Table 1).

Abstract in Spanish: *Se ha abordado el estudio de una amplia variedad de sulfóxidos como auxiliares quirales en reacciones de Heck intermoleculares de sulfinildihidrofuranos y sulfinilciclopentenos con yodoarenos. Elevados rendimientos e inducciones asimétricas apreciables se obtuvieron utilizando [Pd(OAc)$_2$] como catalizador, Ag_2CO_3 como base y una fosfina bidentada como ligando. Con gran diferencia, las mejores diastereoselectividades se obtuvieron utilizando un sulfóxido con capacidad para coordinarse con el átomo de paladio: el grupo o-(N,N-dimetilamino)fenilsulfinilo. Tras eliminación final del auxiliar quiral, estas reacciones de Heck asimétricas controladas por el grupo sulfinilo se han aplicado a la síntesis enantioselectiva de dihidrofuranos y ciclopentenos 1-aril y 1,3-diarilsustituidos.*

Table 1. Heck reaction of α,β-unsaturated sulfoxides **1**–**8** with iodobenzene.[a]



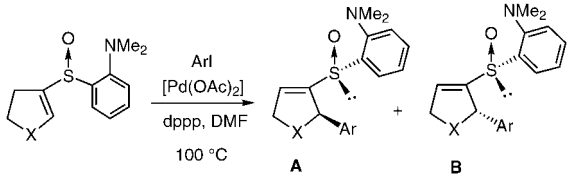
Sulfoxide	X	R	Product	**A**:**B** ratio[b]	Yield [%][c]
1	O	Ph	**9**	77:23	68
2	O	2, 4-$Me_2C_6H_3$	**10**	78:22	80
3	O	*o*-(MeO)C_6H_4	**11**	75:25	47
4	O	*o*-(Me_2N)C_6H_4	**12**	6:94	80
5	O	*t*Bu	–	–[d]	–
6	CH_2	*p*Tol	**13**	60:40	62
7	CH_2	*t*Bu	–	–[d]	–
8	CH_2	*o*-(Me_2N)C_6H_4	**14**	8:92	76

[a] Reaction conditions: PhI (3 equiv), $[Pd(OAc)_2]$ (10 mol %), dppp (10 mol %), Ag_2CO_3 (200 mol %), DMF, 100 °C. [b] Determined by ^{1}H NMR spectroscopy on the crude mixture. [c] In purified products after flash chromatography. [d] Complex mixture of products.

Under these conditions, except for the *tert*-butylsulfinyl derivatives **5** and **7** which proved to be much less reactive and afforded complex mixtures of products after long reaction times, the rest of the substrates led to the corresponding Heck products in reasonable to good yields (47–80 %). Taking into account the usually scant reactivity of trisubstituted alkenes in intermolecular Heck reactions,[11] note the efficiency of these sulfinylated cycloalkenes as well as the absence of products resulting in a final isomerization of the double bond.[12] However, the most interesting outcome of these reactions is the dependence of the stereoselectivity on the substitution at the sulfoxide. The reaction of the aryl sulfoxides **1**–**3** and **6** was uniformly and moderately stereoselective in favor of the **A** isomer, regardless of the steric bulk of the sulfoxide. On the contrary, the Heck reaction of the sulfoxides that contain a *o*-(*N*,*N*-dimethylamino)phenyl group (**4** and **8**) occurred with much higher stereoselectivity and, outstandingly, with opposite stereocontrol (the **B** isomer was the major product).

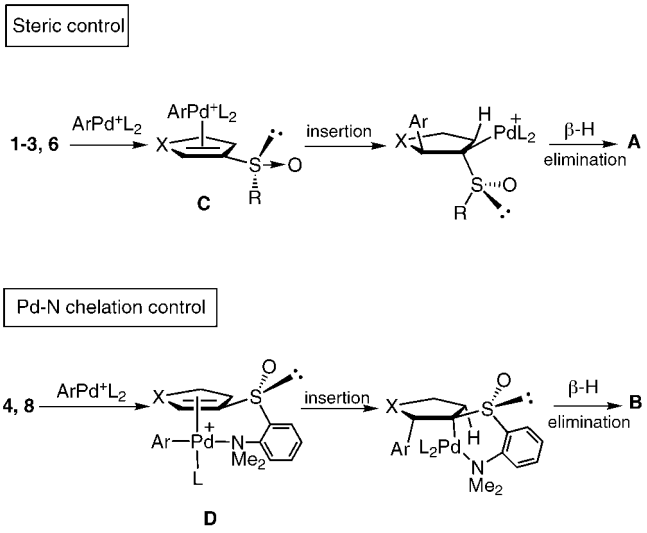
To investigate the scope of the Heck arylations of optimal sulfoxides **4** and **8**, both electron-poor and electron-rich iodoarenes were studied (entries 1–9, Table 2). The reaction is quite general and affords the corresponding Heck products (**12**–**21**) in moderate to good isolated yields (45–86 %). Interestingly, these reactions led predominantly to the **B** isomer, with observed **A**:**B** ratios ranging from 25:75 to 6:94. The only exception to this general trend was the behavior of the *ortho*-substituted iodoarene (entry 9, Table 2), which afforded an equimolecular mixture of **A** and **B** isomers.

Table 2. Heck reaction of aminosulfoxides **4** and **8** with iodoarenes.[a]



Entry	Sulfoxide	X	Ar	Product	**A**:**B** ratio[b]	Yield [%][c]
1	**4**	O	Ph	**12**	6:94	80
2	**8**	CH_2	Ph	**14**	8:92	76
3	**4**	O	*p*-(MeO)C_6H_4	**15**	14:86	55
4	**8**	CH_2	*p*-(MeO)C_6H_4	**16**	25:75	77
5	**4**	O	*p*-(NO_2)C_6H_4	**17**	6:94	64
6	**8**	CH_2	*p*-(NO_2)C_6H_4	**18**	12:88	83
7	**4**	O	*p*-(CO_2Me)C_6H_4	**19**	7:93	45
8	**4**	O	3-Me-4-MeO-C_6H_3	**20**	15:85	86
9	**4**	O	2,4-$(MeO)_2C_6H_3$	**21**	50:50	47

[a] Reaction conditions as indicated in Table 1. [b] Determined by ^{1}H NMR spectroscopy on the crude mixture. [c] In purified products after flash chromatography.



Scheme 2. Mechanistic hypothesis for the stereoselectivity of the Heck reaction.

The configurational assignment of stereoisomers **A** and **B** was first established by NMR studies (and later confirmed by chemical correlations). In particular, the chemical shifts of H2 and H4 were found to be excellent diagnostic criteria (Figure 1). Thus, H4 appears to be significantly more deshielded in isomers **A** than in isomers **B** ($\delta\delta$H4(**A** – **B**) = 0.1 – 0.5 ppm, $CDCl_3$), whereas the opposite behavior is observed for H2 ($\delta\delta$H2(**A** – **B**) = 0.1 – 0.5 ppm, $CDCl_3$). These important spectroscopic effects might be explained on the basis of the highly deshielding effect induced by the sulfinylic oxygen on its hydrogen in 1,3-parallel relationship:[13] H4 in isomers **A** and H2 in isomers **B** in their presumed most stable conformations around the C–S bond, thus avoiding important 1,3-parallel interactions between substituents at sulfur and at C2 (Figure 1).

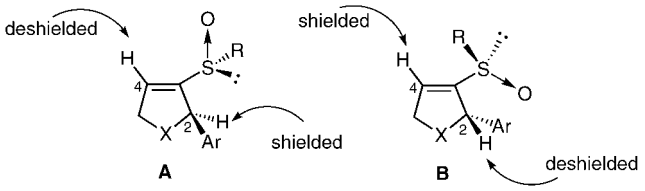


Figure 1. ^{1}H NMR criteria for the stereochemical assignment of **A** and **B** isomers. $\delta\delta$H4(**A** – **B**) = 0.1 – 0.5 ppm, $CDCl_3$; $\delta\delta$H2(**A** – **B**) = 0.1 – 0.5 ppm, $CDCl_3$.

As a mechanistic hypothesis, we speculate that the opposite stereochemical behavior of the *o*-(dimethylamino)phenyl sulfoxides **4** and **8**, compared to the rest of aryl sulfoxides, could be caused by the ability of the nitrogen to chelate the palladium atom in the key π-alkenyl palladium complex, to give in this case a chelation-controlled reaction[14] instead of a sterically controlled process (Scheme 2). Thus, after oxidative addition, the coordination of the intermediate cationic arylpalladium species $[ArPdL_2]^+$ with the double bond of vinyl sulfoxides **1** – **3** and **6** would preferably occur from the least hindered face,[15] namely that opposite the R group, to give complex **C**. Further insertion on the upper face of the double bond and *β*-hydrogen elimination would explain the formation of **A** as the major isomer. On the other hand, in the case of the sulfoxides **4** and **8**, the plausible coordination of $[ArPdL_2]^+$ to the dimethylamino moiety would lead to the amino complex **D**[16], which would intramolecularly direct the insertion of the aryl group on the bottom face of the double bond to afford the isomer **B** after the final *β*-hydrogen elimination step. In agreement with this proposal, the pronounced drop of **B** stereoselectivity observed in the reaction with the bulky *ortho*-substituted iodoarene (entry 9, Table 2), compared to *meta*- and *para*-substituted substrates (entries 1 – 8), could be caused by the greater difficulty to attain the required sterically congested π-complex **D** (see Scheme 2) with palladium – nitrogen coordination.

Once it had been demonstrated that the *o*-(dimethylamino)phenylsulfinyl group can act as an efficient stereochemical controller in intermolecular diastereoselective Heck reactions, and taking into account that the Heck products are new examples of *α*,*β*-unsaturated sulfoxides, we envisaged the possibility of the use of these compounds as substrates for a second Heck reaction. Thus, the dihydrofurans **12B** and **15B** and the cyclopentenes **14** (**A**:**B** = 8:92) and **16** (**A**:**B** = 20:80) were treated with different iodoarenes (Ar^2I) under quite similar palladium-catalyzed conditions ($[Pd(OAc)_2]$ (10 mol %), dppp or dppf (10 mol %), Ag_2CO_3 (200 mol %), DMF, 100 °C), although longer reaction times were employed (usually 20 – 24 h instead of 1 – 6 h) (Table 3).

Outstandingly, a single 1,3-diarylated stereoisomer **F** was detected and isolated in all cases (products **22** – **29**, 50 – 84 % yield after chromatographic purification). In full agreement with these results, when the palladium-catalyzed reaction of **4** and **8** with excess iodobenzene was monitored by thin-layer chromatography until disappearance of the corresponding monosubstituted Heck products **12** and **14**, the 1,3-diphenyl-substituted dihydrofuran **22** and cyclopentene **25** were isolated in 55 % and 81 % yield, respectively, as single isomers (Scheme 3). The stereochemical assignment of the products **F**

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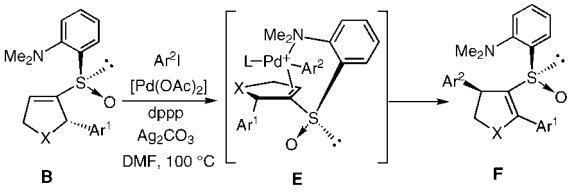
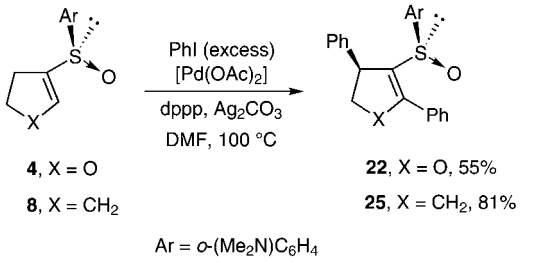
Table 3. Second Heck reaction with iodoarenes.[a]



Entry	Sulfoxide	X	Ar^1	Ar^2	Product	Yield [%][b]
1[c]	**12B**	O	Ph	Ph	**22**	83
2	**12B**	O	Ph	*p*-(MeO)C_6H_4	**23**	69
3[c]	**12B**	O	Ph	*p*-(NO_2)C_6H_4	**24**	84[d]
4	**14B**[e]	CH_2	Ph	Ph	**25**	75
5	**14B**[e]	CH_2	Ph	*p*-(MeO)C_6H_4	**26**	80
6[c]	**15B**	O	*p*-(MeO)C_6H_4	Ph	**27**	78
7	**15B**	O	*p*-(MeO)C_6H_4	*p*-(MeO)C_6H_4	**28**	70
8	**16B**[f]	CH_2	*p*-(MeO)C_6H_4	Ph	**29**	50

[a] Reaction conditions as indicated in Table 1. [b] In pure product after flash chromatography. [c] Reaction carried out in the presence of dppf instead of dppp. [d] Conversion yield. [e] Sulfoxide **14** was used as a 8:92 mixture of **A** + **B** isomers. [f] Sulfoxide **16** was used as a 20:80 mixture of **A** + **B** isomers.

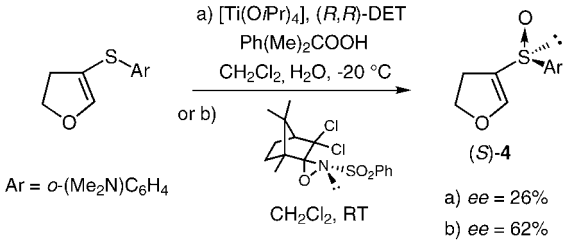


Scheme 3. Double Heck reaction of α,β-unsaturated sulfoxides **4** and **8**.

could not be unambiguously established by NMR methods, but was rigorously proved by X-ray diffraction[17] in the case of dihydrofuran **24** and cyclopentene **25**. This excellent diastereoselectivity could again be explained invoking a chelation control exerted by the *o*-(dimethylamino)phenylsulfinyl group (intermediate **E**), which in this case could be reinforced by the steric effects associated with aryl substitution at the initially formed stereogenic carbon. In agreement with the critical importance of the Pd–N coordination in the stereochemical control of the Heck reaction of *o*-(dimethylamino)-phenylsulfoxides, the Heck reaction of the phenylsulfinyl dihydrofuran **9B** with iodobenzene occurred with poor stereoselectivity to afford a 2:1 mixture of the corresponding 1,3-diphenyl-substituted diastereomers.

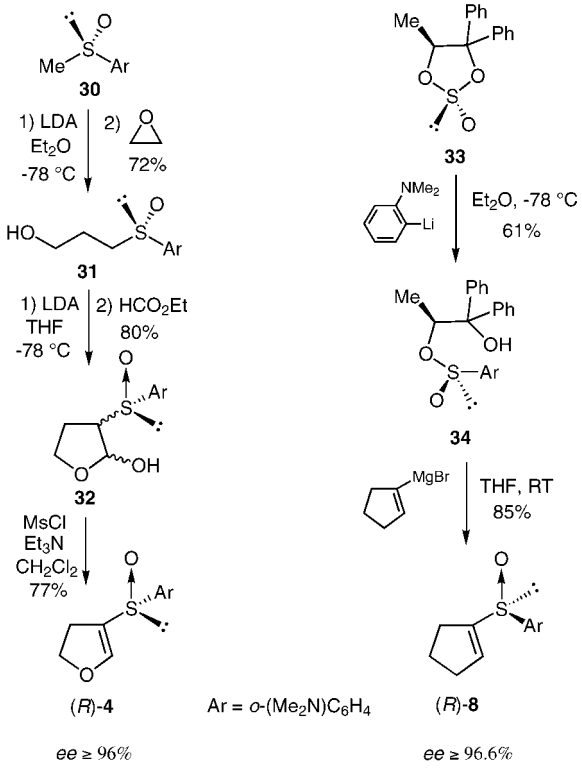
Application in asymmetric synthesis: To apply these highly diastereoselective sulfur-mediated Heck reactions in asymmetric synthesis, three issues had to be addressed: 1) the synthesis of the starting sulfoxides **4** and **8** in enantiomerically pure form, 2) the confirmation that the Heck reactions take place without previous racemization at the sulfur center, and 3) the final elimination of the chiral auxiliary.

As the most direct potential approach to the enantioselective synthesis of dihydrofuran **4**, we studied first the asymmetric oxidation of its thioether precursor (Scheme 4). Unfortunately, both the treatment with [Ti(O*i*Pr)$_4$]/(*R*,*R*)-diethyl tartrate ((*R*,*R*)-DET)/cumene hydroperoxide under Kagan's conditions[18] for enantioselective oxidation of sulfides and the oxidation with Davis' chiral oxaziridine[19] afforded (*S*)-**4** with low or moderate optical purity (enantiomeric excess (*ee*) = 26% and 62%, respectively, measured by ^{1}H NMR in the presence of [Pr(hfc)$_3$] (hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate).



Scheme 4. Attempts of enantioselective synthesis of **4** by asymmetric oxidation.

As a second alternative, we undertook the enantioselective synthesis of **4** and **8** with enantiomerically pure sulfur compounds as starting materials. Different synthetic approaches were developed for the preparation of (*R*)-**4** and (*R*)-**8** (Scheme 5). In the case of (*R*)-**4** the synthesis starts with the readily available (*S*)-*o*-(*N*,*N*-dimethylamino)phenyl methyl sulfoxide[20][(*S*)-**30**]. Its deprotonation with lithium diisopropylamide (LDA; Et_2O, $-78\,^\circ C$) and further reaction with ethylene oxide afforded the γ-hydroxysulfoxide (*S*)-**31** (72%). Subsequent treatment with LDA (2 equiv, THF, $-78\,^\circ C$) and addition of ethyl formate gave the hemiacetal **32** as a mixture of stereoisomers at C2 and C3 (80% yield).

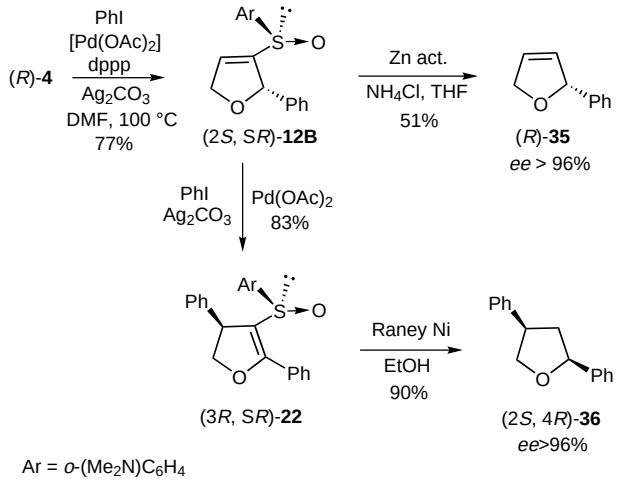


Scheme 5. Synthesis of enantiopure (*R*)-**4** and (*R*)-**8**.

Finally, dehydration of **32** with MsCl/Et_3N gave the required dihydrofuran (*R*)-**4** in 77% yield and with very high optical purity (*ee* > 96%, ^{1}H NMR, [Pr(hfc)$_3$]).

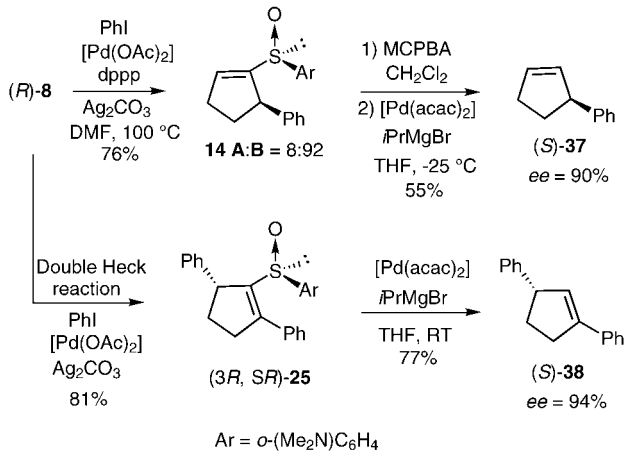
On the other hand, the enantiopure sulfinylcyclopentene (*R*)-**8** was readily prepared in two steps by application of Kagan's procedure for the synthesis of enantiopure sulfoxides based on two successive sulfur-nucleophilic substitutions from the commercially available sulfite **33**.[21] The reaction of enantiopure **33** with *o*-(*N*,*N*-dimethylamino)phenyllithium (generated in situ by treatment of the corresponding iodide with *n*BuLi) in diethyl ether at −78 °C, gave the sulfinate **34** as the major product (61% yield). Unexpectedly, the reaction of **34** with cyclopentenyllithium afforded (*R*)-**8** with an enantiomeric excess of 88%; this indicates that a certain racemization at sulfur had occurred. Interestingly, this loss of optical purity was completely suppressed when the reaction was performed with the Grignard reagent of 1-bromocyclopentene (THF, RT), which led to the required cyclopentenylsulfoxide (*R*)-**8** in high yield (85%) and enantiomeric purity (*ee* = 96.6%, HPLC, Chiralcel OD column).

The application of (*R*)-**4** and (*R*)-**8** to the enantioselective synthesis of aryl- and 1,3-diaryl-substituted dihydrofurans and cyclopentenes is shown in Scheme 6 and Scheme 7, respectively.



Scheme 6. Synthesis of dihydrofuran (*R*)-**35** and tetrahydrofuran (2*S*,4*R*)-**36**.

Heck reaction of (*R*)-**4** with iodobenzene under the optimized reaction conditions and further chromatographic purification afforded (2*S*,S*R*)-**12B** (77% yield; note: in the nomenclature used in this paper the nonitalic S in the stereochemical descriptor indicates the sulfur atom). Its desulfinylation with activated powdered zinc[22] yielded the known (*R*)-2-phenyl-2,5-dihydrofuran ((*R*)-**35**, *ee* > 96%), whose optical rotation was identical to that previously reported.[12e] It is worth noting that this chemical correlation proves the stereochemical assignments previously established by NMR and also demonstrates that sulfoxide (*R*)-**4** is configurationally stable under the experimental conditions of the Heck reaction. On the other hand, the second Heck reaction of (2*S*,S*R*)-**12B** with iodobenzene yielded (3*R*,S*R*)-**22** (83%), which was transformed in one-step into enantiopure



Scheme 7. Synthesis of cyclopentenes (*S*)-**37** and (*S*)-**38**.

(2*S*,4*R*)-2,4-diphenyltetrahydrofuran[23] ((2*S*,4*R*)-**36**, 90%, *ee* > 96%, ^{1}H NMR, [Pr(hfc)$_3$]) by direct hydrogenation and C−S cleavage with Raney-Ni (EtOH, RT).

In a similar way, by controlling the progress of the Heck reaction of (*R*)-**8** with iodobenzene, either the monosubstituted Heck product **14** (**A**:**B** = 8:92) or the disubstituted Heck product **25** were isolated in very high optical purities (*ee* = 97% for **25**, HPLC, Chiralcel OD column). After some experimentation,[24] we found that in these cases the most suitable method for the cleavage of the chiral auxiliary was the palladium-catalyzed reductive desulfurization in the presence of a bulky Grignard reagent[25] ([Pd(acac)$_2$] (5 mol%), *i*PrMgBr (300 mol%), THF). Thus, oxidation of sulfoxides **14** to the corresponding sulfone (MCPBA) and desulfonylation with [Pd(acac)$_2$]/*i*PrMgBr gave (*S*)-3-phenylcyclopentene[12e] [(*S*)-**37**] (55% yield, *ee* = 90%, GC Cyclosilb column). Under quite similar palladium-catalyzed reductive conditions (3*R*,S*R*)-**25** afforded (*S*)-1,3-diphenylcyclopentene [(*S*)-**38**] (77%, *ee* = 94%, HPLC, Chiralpak AS column) (Scheme 7).

Conclusions

We have shown that the sulfinyl group is able to act as a stereochemical controller in intermolecular Heck arylations and double Heck arylations of sulfinyl cycloalkenes. High reactivities and synthetically useful diastereoselectivities were achieved by the use of the potentially palladium chelating *o*-(*N*,*N*-dimethylamino)phenylsulfinyl group. Interestingly, the procedure based on the use of this unprecedented type of palladium-coordinating aryl-substituted sulfoxide seems to be very general with respect to both the alkene (cyclopentene or dihydrofuran) and the substitution at the iodoarene. Moreover, as the enantiomerically pure sulfinylcycloalkenes **4** and **8** are readily available, and suitable methods for the final removal of the sulfoxide have been developed, this overall chiral auxiliary-based procedure constitutes an alternative to the use of chiral bidentate ligands in asymmetric Heck reactions.

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Experimental Section

Melting points are uncorrected; ^{1}H NMR were acquired at 200 or 300 MHz, ^{13}C NMR were acquired at 50 or 75 MHz (indicated in each case). Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass spectra (MS) and high resolution mass spectra (HRMS) were determined at an ionizing voltage of 70 eV. Reactions were usually carried out under a dry argon atmosphere in anhydrous solvents. THF and diethyl ether were distilled from sodium benzophenone under argon. CH_2Cl_2 and ethyl formate were distilled from P_2O_5. Flash column chromatography was performed on silica gel (Merck-60, 230–400 mesh).

Synthesis of (±)-4-arylsulfinyl-2,3-dihydrofurans 1–4: Trifluoroacetic anhydride (9.9 mL, 70 mmol) was added to a solution of methyl aryl sulfoxide (14.0 g, 76 mmol) in dry CH_2Cl_2 (120 mL) at $-78\,^\circ$C, and the solution was stirred for 15 min. 2,3-Dihydrofuran (5.3 g, 70 mmol) was added to this mixture and the reaction was stirred at $-78\,^\circ$C for 15 min. Triethylamine (35 mL) was added at the same temperature, the mixture was slowly warmed to room temperature and stirred for 24 h. The reaction mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:20) to afford the corresponding sulfenyldihydrofuran (10.9 g, 65%).

A solution of MCPBA (23 mmol) in CH_2Cl_2 was added dropwise to a cooled solution ($-78\,^\circ$C) of the sulfenyldihydrofuran (5.0 g, 23 mmol) in CH_2Cl_2 (75 mL). The reaction was monitored by TLC until the starting sulfide had disappeared. A saturated solution of Na_2SO_3 (10 mL), followed by a saturated solution of $NaHCO_3$ (30 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 ($2\times$ 100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography.

4-(Phenylsulfinyl)-2,3-dihydrofuran (1): Yield 69%; m.p. 57–58 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.61-7.39$ (m, 5H), 7.09 (t, $J = 1.6$ Hz, 1H), 4.60–4.36 (m, 2H), 2.94 (dddd, $J = 14.0$, 9.7, 8.1, 2.1 Hz, 1H), 2.20 (dddd, $J = 14.0$, 10.7, 9.1, 1.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 153.2, 141.6, 128.8, 127.6, 122.9, 117.9, 71.1, 23.1; MS (EI): m/z (%): 194 ([M^+], 8), 178 (5), 146 (100), 117 (44), 77 (33); elemental analysis calcd (%) for $C_{10}H_{10}O_2S$: C 61.83, H 5.19, S 16.50; found: C 61.67, H 4.98, S 16.42.

4-[(2,4-Dimethyl)phenylsulfinyl]-2,3-dihydrofuran (2): Yield 40%; m.p. 51–52 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.00 (s, 1H), 7.00 (t, $J = 1.7$ Hz, 1H), 4.58–4.36 (m, 2H), 2.93 (dddd, $J = 14.0$, 11.1, 7.5, 1.7 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 2.15 (dddd, $J = 14.0$, 11.0, 9.1, 1.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 153.2, 141.7, 137.1, 134.2, 131.6, 127.4, 124.3, 118.0, 72.5, 24.9, 21.1, 17.9; MS (EI): m/z (%): 222 ([M^+], 10), 205 (13), 174 (100), 105 (29), 91 (35), 77 (33); elemental analysis calcd (%) for $C_{12}H_{14}O_2S$: C 64.84, H 6.35, S 14.42; found: C 64.22, H 6.21, S 14.45.

4-(2-Methoxyphenylsulfinyl)-2,3-dihydrofuran (3): Yield 44%; m.p. 121–123 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.84$ (dd, $J = 7.8$, 1.8 Hz, 1H), 7.41 (dt, $J = 8.1$, 2.5 Hz, 1H), 7.15 (dt, $J = 7.5$, 0.9 Hz, 1H), 7.00 (t, $J = 1.7$ Hz, 1H), 6.90 (dd, $J = 8.4$, 0.8 Hz, 1H), 4.5–4.38 (m, 2H), 3.83 (s, 3H), 2.91 (dddd, $J = 15.6$, 12.3, 7.7, 1.7 Hz, 1H), 2.20 (dddd, $J = 15.7$, 11.3, 9.6, 1.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 155.2$, 152.6, 131.8, 129.6, 125.5, 121.0, 117.9, 110.7, 72.2, 55.6, 24.9; MS (EI): m/z (%): 224 ([M^+], 6), 208 (8), 176 (100), 147 (11), 108 (11), 77 (21); elemental analysis calcd (%) for $C_{11}H_{12}O_3S$: C 58.91, H 5.39, S 14.29; found: C 58.43, H 5.12, S 14.34.

4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2,3-dihydrofuran (4): Yield 60%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.91$ (dd, $J = 7.8$, 1.8 Hz, 1H), 7.41 (dt, $J = 7.6$, 1.7 Hz, 1H), 7.25 (dt, $J = 7.3$, 1.4 Hz, 1H), 7.13 (dd, $J = 8.0$, 1.3 Hz, 1H), 7.00 (t, $J = 1.9$ Hz, 1H), 4.55–4.33 (m, 2H), 2.86 (dddd, $J =$ 13.9, 11.0, 7.5, 2.0 Hz, 1H), 2.69 (s, 6H), 2.10 (dddd, $J = 13.9$, 11.1, 9.4, 2.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 152.7$, 151.01, 136.3, 131.4, 125.6, 123.9, 120.0, 118.3, 72.2, 44.7, 25.2; MS (EI): m/z (%): 237 ([M^+], 9), 220 (95), 150 (100), 136 (36), 91 (40), 77 (39); HRMS (EI): m/z calcd for $C_{12}H_{15}NO_2S$: 237.0828; found: 237.0823; elemental analysis calcd (%) for $C_{12}H_{15}NO_2S$: C 60.73, H 6.37, N 5.90, S 13.51; found: C 60.29, H 6.60, N 5.85, S 13.85.

Synthesis of 4-(*tert*-butylsulfinyl)-2,3-dihydrofuran (5)

3-(*tert*-Butylsulfenyl)-4,5-dihydro-2-furanone: α-Bromo-γ-butyrolactone (1.0 g, 6.06 mmol) was added to a solution of sodium *tert*-butyltiolate (747 mg, 6.70 mmol) in DMF (15 mL) at room temperature. The mixture was stirred at room temperature for 12 h. The mixture was diluted with Et_2O (30 mL) and washed with H_2O (2×20 mL). The organic layer was dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:1) to afford the sulfenylfuranone (537 mg, 51%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.30$ (m, 2H), 3.55 (dd, $J = 8.4$, 6.0 Hz, 1H), 2.70 (m, 1H), 2.22 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.4$, 66.4, 44.4, 38.7, 32.4, 31.0.

3-(*tert*-Butylsulfinyl)-4,5-dihydro-2-furanone: Oxidation of the previously obtained sulfenylfuranone (500 mg, 2.87 mmol) with MCPBA as described for the synthesis of sulfoxides **1**–**4** afforded the corresponding sulfinylfuranone (544 mg, 99%). M.p. 82–83 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 4.44 (t, $J = 7.0$ Hz, 2H), 3.61 (dd, $J = 10.2$, 5.9 Hz, 1H), 3.00 (m, 1H), 2.36 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 174.4$, 68.1, 55.7, 53.2, 23.0, 19.3; MS (EI): m/z (%): 134 ([$M^+ - t$Bu], 25), 86 (33), 57 (tBu, 100); elemental analysis calcd (%) for $C_8H_{14}O_3S$: C 50.50, H 7.42, S 16.85; found: C 50.84, H 7.38, S 17.34.

4-(*tert*-Butylsulfinyl)-2,3-dihydrofuran (5): DIBAL-H in hexane (1M, 3.4 mL, 3.4 mmol) was added to a solution of the previously obtained sulfinylfuranone (430 mg, 2.26 mmol) in THF (6 mL) at $-78\,^\circ$C under an Ar atmosphere. After the mixture had been stirred for 1 h, HCl was added (10%, 10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2×15 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated to afford the corresponding mixture of hemiacetals (347 mg, 80%).

Ac_2O (340 μL, 3.60 mmol), Et_3N (750 μL, 5.4 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (catalytic amount) were added to a solution of these hemiacetals (347 mg, 80%) in dry CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred at room temperature for 1 h. NH_4Cl (15 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 ($2\times$ 10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated to afford a mixture of acetates (359 mg, 85%).

Benzeneselenol (262 μL, 2.13 mmol) was added to a solution of these acetates (359 mg, 1.53 mmol) in dry CH_2Cl_2 (15 mL) cooled at $-78\,^\circ$C under an Ar atmosphere. The mixture was stirred at 0 °C for 16 h. NaOH (1M, 10 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated to afford a mixture of selenides.

A solution of MCPBA (1.50 mmol) in CH_2Cl_2 was added to a solution of this mixture of selenides in CH_2Cl_2 (10 mL) at $-78\,^\circ$C. After 1 h, solutions of saturated Na_2SO_3 (10 mL) and saturated $NaHCO_3$ (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (AcOEt) to afford **5** (115 mg, 40% from the acetates). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.86$ (t, $J = 1.8$ Hz, 1H), 4.58 (dt, $J = 8.2$, 1.7 Hz, 2H), 3.08 (dddd, $J = 14.0$, 10.2, 8.6, 1.7 Hz, 1H), 2.84 (dddd, $J = 14.2$, 11.0, 9.1, 2.0 Hz, 1H), 1.28 (s, 9H).

1-(*p*-Tolylsulfinyl)cyclopentene (6): *n*BuLi (2.5M, 1.42 mL, 3.40 mmol) was added to a solution of 1-bromocyclopentene (0.50 g, 3.40 mmol) in THF (10 mL) at $-78\,^\circ$C. After the mixture had been stirred for 1.5 h at $-78\,^\circ$C, a solution of methyl *p*-toluenesulfinate (0.91 g, 3.09 mmol) in THF (10 mL) was added and the reaction mixture was kept at $-78\,^\circ$C for 1 h and was then poured into water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:1) to afford **6** (0.46 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.44$ and 7.25 (AA′BB′ system, m, 4H), 6.51 (s, 1H), 2.47 (m, 2H), 2.37(s, 3H), 2.08 (m, 2H), 1.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.7$, 141.0, 139.3, 137.8, 129.7, 124.5, 32.8, 27.9, 22.9, 21.3; MS (EI): m/z (%): 206 ([M^+], 31), 190 (14), 157 (39), 143 (100), 123 (75), 84 (56), 65 (47).

1-(*tert*-Butylsulfinyl)cyclopentene (7): *n*BuLi (2.5M, 1.42 mL, 3.40 mmol) was added to a solution of 1-bromocyclopentene (0.50 g, 3.40 mmol) in THF (10 mL) at $-78\,^\circ$C. After the mixture had been stirred for 1.5 h at $-78\,^\circ$C, a solution of (±)-*tert*-butyl-*tert*-butanethiosulfinate (0.44 g, 3.09 mmol) in THF (10 mL) was added, and the reaction was kept at

$-78\,^{\circ}C$ for 1 h. The reaction mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:1) to afford **7** (0.26 g, 67%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=6.33$ (m, 1H), 2.52 (m, 4H), 2.01(m, 2H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.4$, 139.2, 55.3, 32.6, 31.6, 23.9, 23.4; MS (EI): m/z (%): 172 ([M^+], 0.6), 116 (97), 86 (49), 84 (75), 67 (100), 57 (65).

1-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]cyclopentene (8): *n*BuLi (2.5 M, 5.7 mL, 14.22 mmol) was added to a solution of 1-bromocyclopentene (2.41 g, 16.41 mmol) in THF (120 mL) at $-78\,^{\circ}C$. After the mixture had been stirred for 1.5 h at $-78\,^{\circ}C$, a solution of 2-(*N*,*N*-dimethylamino)-phenyl disulfide (3.37 g, 10.94 mmol) in THF (220 mL) was added and the reaction was kept at $-78\,^{\circ}C$ for 1 h. The reaction mixture was poured into water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. Oxidation of the resulting sulfenyl cyclopentene with MCPBA, as described for the synthesis of sulfoxide **7**, afforded **8** (1.75 g, 68%). M.p. 52–53 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.85$ (dd, $J=1.6$, 7.5 Hz, 1H), 7.40 (dt, $J=1.6$, 7.5 Hz, 1H), 7.23 (dt, $J=1.1$, 7.53 Hz, 1H), 7.11 (dd, $J=1.1$, 7.0 Hz, 1H), 6.47 (m, 1H), 2.69 (s, 6H), 2.45 (m, 3H), 1.98 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.6$, 146.9, 137.2, 131.4 (2C), 125.6, 124.2, 120.0, 44.9, 32.9, 28.4, 23.1; elemental analysis calcd (%) for $C_{13}H_{17}NOS$: C 66.34, H 7.28, N 5.95, S 13.63; found: C 66.43, H 7.05, N 5.71, S 13.49.

General procedure for the Heck reactions of sulfinyldihydrofurans and cyclopentenes with iodoarenes: In a two-necked round-bottom flask were sequentially added at room temperature the corresponding α,β-unsaturated sulfoxide (2.2 mmol), iodoarene (6.6 mmol), silver carbonate (4.4 mmol), palladium acetate (0.22 mmol), dppp (or dppf) (0.22 mmol), and dry DMF (50 mL). The reaction mixture was degassed and stirred vigorously at 100 °C under argon. The reaction was monitored by TLC until the starting sulfoxide had disappeared (2–48 h). The mixture was then cooled to room temperature, diluted with diethyl ether (50 mL), and washed with water (2×30 mL). The organic layer was dried ($MgSO_4$) and evaporated. The residue was analyzed by ^1H NMR spectroscopy to determine the A:B ratio and was purified by flash chromatography (the eluents and yields are indicated below for each case).

2-Phenyl-3-(phenylsulfinyl)-2,5-dihydrofuran (9): Eluent: ethyl acetate/hexane (1:1). Yield 68%.

*Isomer **A** (2R*,SR*)*: M.p. 79–80 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=$ 7.51–7.13 (m, 10H), 6.87 (q, $J=1.8$ Hz, 1H), 5.27 (ddd, $J=5.8$, 3.9, 2.0 Hz, 1H), 5.06 (ddd, $J=14.3$, 5.9, 1.8 Hz, 1H), 4.85 (ddd, $J=14.3$, 4.0, 1.8 Hz, 1H); ^{13}C NMR: (75 MHz): $\delta=147.9$, 141.2, 138.5, 131.7, 130.9, 129.2, 128.8, 128.5, 127.3, 125.1, 86.0, 75.5; elemental analysis calcd (%) for $C_{16}H_{14}0_2S$: C 71.11, H 5.18, S 11.85; found: C 70.92, H 5.37, S 11.88

*Isomer **B** (2S*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$)(significant signals): $\delta=$ 6.54 (q, $J=1.9$ Hz, 1H), 5.80 (ddd, $J=5.9$, 4.3, 2.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=147.5$, 141.6, 138.5, 132.6, 131.1, 128.7, 128.4, 128.2, 127.0, 124.8, 86.3, 74.8; MS (EI): m/z: 270 ([M^+], 2), 253 (100), 144 (31), 125 (9), 115 (77), 105 (29), 91 (27), 77 (35).

3-(2,4-Dimethylphenylsulfinyl)-2-phenyl-2,5-dihydrofuran (10): Eluent: ethyl acetate/hexane (1:4). Yield 80%.

*Isomer **A** (2R*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.51$ (d, $J=8.1$ Hz, 1H), 7.35–7.05 (m, 6H), 6.97 (br s, 1H), 6.89 (q, $J=1.9$ Hz, 1H), 5.21 (ddd, $J=5.8$, 3.9, 1.9 Hz, 1H), 5.04 (ddd, $J=14.1$, 5.6, 1.7 Hz, 1H), 4.89 (ddd, $J=$ 14.1, 3.8, 1.7 Hz, 1H), 2.37 (s, 3H), 2.10 (s, 3H).

*Isomer **B** (2S*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$) (significant signals): $\delta=$ 6.30 (q, $J=1.8$ Hz, 1H), 5.82 (ddd, $J=5.9$, 3.9, 1.7 Hz, 1H). Mixture **A** + **B**; MS (EI): m/z (%): 298 ([M^+], 11), 281 (97), 154 (17), 144 (32), 137 (43), 105 (100), 91 (78), 77 (68); HRMS (EI): m/z calcd for $C_{18}H_{18}O_2S$: 298.1027; found: 298.1029.

3-(2-Methoxyphenylsulfinyl)-2-phenyl-2,5-dihydrofuran (11): Eluent: ethyl acetate/hexane (1:2). Yield 47%.

*Isomer **A** (2R*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.57$ (dd, $J=8.1$, 1.6 Hz, 1H), 7.36 (dt, $J=8.6$, 1.6 Hz, 1H), 7.30–7.13 (m, 5H), 7.01 (dt, $J=$ 7.6, 0.9 Hz, 1H), 6.84 (q, $J=1.7$ Hz, 1H), 6.80 (dd, $J=7.1$, 0.7 Hz, 1H), 5.65 (ddd, $J=5.5$, 3.4, 1.8 Hz, 1H), 4.97 (ddd, $J=14.4$, 5.8, 1.7 Hz, 1H), 4.81 (ddd, $J=14.2$, 3.4, 1.8 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=155.6$, 147.2, 139.4, 132.5, 131.8, 129.5, 128.5, 128.4, 127.1, 125.4, 121.7, 110.6, 86.0, 75.0, 55.4.

*Isomer **B** (2S*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$)(significant signals): $\delta=$ 7.62 (dd, $J=9.5$, 1.7 Hz, 1H), 6.67 (dd, $J=8.5$, 0.7 Hz, 1H), 6.56 (q, $J=$ 1.7 Hz, 1H), 5.78 (ddd, $J=5.8$, 3.9, 2.0 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) (significant signals): $\delta=148.0$, 138.8, 133.2, 127.4, 125.9, 121.4, 110.5, 86.7; MS(EI) (m/z): 300 ([M^+], 7), 283 (96), 252 (31), 144 (35), 115 (100), 91 (32), 77 (74); HRMS (EI): m/z calcd for $C_{17}H_{16}O_3S$: 300.0820; found: 300.0821.

3-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-2-phenyl-2,5-dihydrofuran (12): Eluent: ethyl acetate/hexane (1:2). Yield 80%.

*Isomer **B** (2S*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.70$ (dd, $J=7.8$, 1.7 Hz, 1H), 7.40 (dt, $J=7.6$, 1.6 Hz, 1H), 7.30–7.13 (m, 6H), 7.03 (dd, $J=$ 7.9, 1.1 Hz, 1H), 6.30 (q, $J=2.0$ Hz, 1H), 5.76 (ddd, $J=5.9$, 4.3, 2.1 Hz, 1H), 4.92 (ddd, $J=14.5$, 5.4, 1.6 Hz, 1H), 4.77 (ddd, $J=14.5$, 5.4, 1.6 Hz, 1H), 2.56 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.3$, 146.4, 138.9, 135.2, 132.7, 131.9, 128.3, 128.1, 127.2, 126.2, 123.8, 119.6, 86.7, 74.6, 44.4; MS (EI): m/z (%): 313 ([M^+], 4), 296 (79), 190 (47), 150 (100), 120 (21), 91 (51), 77 (53); elemental analysis calcd (%) for $C_{18}H_{19}NO_2S$: C 68.98, H 6.11, N 4.47, S 10.23; found: C 68.97, H 6.34, N 4.33, S 10.68. (2*S*,*SR*)-**12 B** (obtained from (*R*)-**4**): $[\alpha]_D^{25}=-162.5$ ($c=1.0$, $CHCl_3$) (*ee* $\geq$ 96%, determined by ^1H NMR, (*R*)-2,2,2-trifluoro-1-(9-antryl)ethanol).

*Isomer **A** (2R*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.69$ (dd, $J=8.1$, 1.6 Hz, 1H), 7.38 (dt, $J=7.5$, 1.8 Hz, 1H), 7.33–7.18 (m, 5H), 7.12 (dt, $J=$ 7.5, 1.1 Hz, 1H), 7.05 (dd, $J=8.1$, 1.1 Hz, 1H), 6.82 (q, $J=1.6$ Hz, 1H), 5.57 (ddd, $J=5.9$, 3.8, 2.1 Hz, 1H), 4.95 (ddd, $J=14.0$, 5.4, 1.6 Hz, 1H), 4.80 (ddd, $J=14.0$, 3.2, 1.6 Hz, 1H), 2.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.6$, 148.2, 139.3, 136.2, 132.2, 131.5, 128.6, 128.4, 127.2, 125.7, 124.3, 119.6, 86.3, 75.0, 44.9; elemental analysis calcd (%) for $C_{18}H_{19}NO_2S$: C 68.98, H 6.11, N 4.47, S 10.23; found: C 68.79, H 6.06, N 4.38, S 9.96.

2-(*p*-Tolylsulfinyl)-3-phenyl-1-cyclopentene (13): Eluent: ethyl acetate/hexane (2:1). Yield 62%.

*Isomer **A** (3R*,SR*)*: ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.32-7.12$ (m, 6H), 7.07–6.99 (m, 3H), 7.30–7.13 (m, 5H), 6.79 (m, 1H), 3.48 (m, 1H),2.87–2.44 (m, 3H), 2.38 (s, 3H), 2.09–1.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)(mixture **A** + **B**): $\delta=151.1$, 150.8, 142.5, 142.4, 141.8, 139.3, 138.3, 138.0, 135.6, 135.3, 129.8, 129.5, 128.6, 128.3, 127.6, 127.4, 126.7, 126.4, 125.4, 125.2, 50.1, 50.0, 36.0, 25.2, 31.7, 31.5, 21.4, 21.3; MS (EI): m/z (%): 282 ([M^+], 54), 266 (71), 234 (76), 141 (88), 128 (95), 115 (100), 91 (94), 65 (53).

*Isomer **B** (3S*,SR*)*: ^1H NMR (300 MHz, $CDCl_3$) (significant signals): $\delta=$ 6.38 (m, 1H), 4.03 (m, 1H).

2-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-3-phenyl-1-cyclopentene (14): Eluent: ethyl acetate/CH_2Cl_2 (1:8). Yield 76%.

*Isomer **B** (3R*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.72$ (dd, $J=1.6$, 8.0 Hz, 1H), 7.37 (dt, $J=1.6$, 7.53 Hz, 1H), 7.00–7.25 (m, 7H), 6.10 (m, 1H), 4.09 (m, 1H), 2.36–2.72 (m, 9H), 1.98 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.5$, 150.0, 142.8, 137.9, 136.3, 131.5, 128.1, 127.5, 127.1, 126.4, 123.7, 119.3, 50.2, 44.5, 35.3, 31.4; MS (EI): m/z (%): 311 ([M^+], 9), 294 (100), 176 (17), 152 (43), 143 (34), 120 (17), 91 (41), 77 (25); HRMS (EI): m/z calcd for $C_{19}H_{21}NOS$: 311.1343; found: 311.1341. (3*R*,*SR*)-**14 B** (*de* = 84%) (obtained from (*R*)-**8**): $[\alpha]_D^{25}=+143.3$ ($c=1$, $CHCl_3$).

*Isomer **A** (3S*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$) (significant signal): $\delta=$ 6.81 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=152.2$, 150.7, 143.0, 137.2, 136.2, 131.7, 128.2, 127.5, 127.1, 125.9, 123.5, 119.0, 49.7, 44.7, 35.8, 31.4.

3-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2-(4-methoxyphenyl)-2,5-dihydrofuran (15): Eluent: ethyl acetate/hexane (2:3). Yield 55%.

*Isomer **B** (2S*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.68$ (dd, $J=7.7$, 1.6 Hz, 1H), 7.39 (dt, $J=7.6$, 1.6 Hz, 1H), 7.21–7.02 (m, 5H), 6.80 (d, $J=$ 8.6 Hz, 1H), 6.31 (q, $J=1.7$ Hz, 1H), 5.67 (ddd, $J=5.9$, 4.1, 2.0 Hz, 1H), 4.87 (ddd, $J=14.6$, 5.8, 1.7 Hz, 1H), 4.70 (ddd, $J=14.6$, 4.1, 1.9 Hz, 1H), 3.79 (s, 3H), 2.60 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=159.7$, 151.4, 146.3, 135.4, 133.1, 131.9, 131.1, 128.8, 126.4, 123.9, 119.6, 113.5, 86.4, 74.4, 55.2, 44.6; MS (EI): m/z (%): 343 ([M^+], 7), 326 (94), 190 (44), 176 (18), 150 (100), 120 (9), 107 (7), 91 (34).

*Isomer **A** (2R*,SR*)*: ^1H NMR (200 MHz, $CDCl_3$) significant signals: $\delta=$ 6.80 (q, $J=1.8$ Hz, 1H), 5.55 (ddd, $J=5.6$, 3.6, 1.9 Hz, 1H), 3.79 (s, 3H), 2.56 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.7$, 151.6, 148.1, 136.1, 132.0, 131.4, 128.5, 128.4, 127.3, 125.6, 124.1, 119.5, 113.6, 85.8, 55.2, 44.9.

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2-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3-(4-methoxyphenyl)-1-cyclopentene (16): Eluent: ethyl acetate/CH_2Cl_2 (1:8). Yield 77%.

Isomer ***B*** *(3R*,SR*)*: ^{1}H NMR (200 MHz): $\delta = 7.73$ (dd, $J = 1.6$, 8.1 Hz, 1H), 7.40 (dt, $J = 1.6$, 8.1 Hz, 1H), 7.18 (dt, $J = 1.6$, 8.1 Hz, 1H), 7.08–7.00 (m, 3H), 6.80–6.72 (m, 2H), 6.07 (q, $J = 2.15$ Hz, 1H), 4.05 (m, 1H), 3.79 (s, 3H), 2.62 (s, 6H), 2.35–2.60 (m, 3H), 1.90 (m, 1H); ^{13}C NMR (75 MHz): $\delta = 158.2$, 151.5, 150.2, 137.8, 136.5, 135.0, 131.5, 128.6, 126.6, 123.9, 119.4, 113.6, 55.2, 49.6, 44.7, 35.4, 31.4; MS (EI): *m*/*z* (%): 341 ([M^+], 8), 324 (83), 176 (20), 152 (81), 150 (100), 120 (15), 91 (38), 77 (27); HRMS (EI): *m*/*z* calcd for $C_{20}H_{23}NO_2S$: 341.1449; found: 341.1458.

Isomer ***A*** *(3S*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$) (significant signal): $\delta =$ 6.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.4$, 146.7, 138.5, 137.9, 132.2, 129.3, 126.4, 125.0, 124.6, 120.7, 119.9, 114.5, 55.9, 45.6, 33.6, 29.2, 23.9.

3-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2-(4-nitrophenyl)-2,5-dihydrofuran (17): Eluent: ethyl acetate/hexane (1:2). Yield 64%.

Isomer ***B*** *(2S*,SR*)*: M.p. 120–121 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 8.13 (d, $J = 8.8$ Hz, 2H), 7.62 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.43 (dt, $J = 7.6$, 1.6 Hz, 1H), 7.30 (d, $J = 8.9$ Hz, 2H), 7.19 (dt, $J = 7.6$, 1.1 Hz, 1H), 7.10 (dd, $J = 8.0$, 0.9 Hz, 1H), 6.55 (q, $J = 1.9$ Hz, 1H), 5.67 (ddd, $J = 5.8$, 3.8, 1.8 Hz, 1H), 4.98 (ddd, $J = 14.9$, 5.9, 1.6 Hz, 1H), 4.82 (ddd, $J = 14.8$, 3.9, 1.7 Hz, 1H), 2.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.4$, 147.8, 146.4, 145.4, 135.0, 134.5, 132.3, 128.2, 126.4, 124.1, 123.4, 119.8, 85.6, 75.2, 44.7; MS (EI): *m*/*z* (%): 358 ([M^+], 4), 341 (100), 190 (48), 150 (97), 120 (22), 91 (43); elemental analysis calcd (%) for $C_{18}H_{18}N_2O_4S$: C 60.32, H 5.06, N 7.82, S 8.95; found: C 60.15, H 5.03, N 7.62, S 8.98.

2-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3-(4-nitrophenyl)-1-cyclopentene (18): Eluent: ethyl acetate/CH_2Cl_2 (1:8). Yield 83%.

Isomer ***B*** *(3R*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.06$ (m, 2H), 7.62 (dd, $J = 1.6$, 7.5 Hz, 1H), 7.40 (dt, $J = 1.6$, 7.5 Hz, 1H), 7.24–7.12 (m, 3H), 7.04 (dd, $J = 1.6$, 7.5 Hz, 1H), 6.48 (q, $J = 2.1$ Hz, 1H), 3.97 (m, 1H), 2.63 (s, 6H), 2.72–2.48 (m, 3H), 1.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) (mixture **A** + **B**): $\delta = 151.4$, 151.2, 151.0, 150.8, 148.1, 146.5, 140.7, 139.1, 135.7, 131.7, 131.6, 128.3, 127.8, 127.6, 126.0, 125.4, 123.8, 123.7, 123.3, 123.1, 119.5, 119.2, 49.8, 44.6, 44.5, 35.2, 35.0, 31.6, 31.5; MS (EI): *m*/*z* (%): 356 ([M^+], 3), 340 (41), 339 (96), 176 (23), 152 (24), 150 (100), 91 (40), 77 (73); HRMS (EI): *m*/*z* calcd for $C_{19}H_{20}N_2O_2S$: 356.1210; found: 356.1194.

Isomer ***A*** *(3S*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$) (significant signal): $\delta =$ 6.70 (m, 1H).

3-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2-(4-methoxycarbonylphenyl)-2,5-dihydrofuran (19): Eluent: ethyl acetate/hexane (1:1). Yield 45%.

Isomer ***B*** *(2S*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.95$ (d, $J = 8.2$ Hz, 2H), 7.66 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.40 (dt, $J = 7.6$, 1.7 Hz, 1H), 7.25 (d, $J =$ 8.3 Hz, 2H), 7.17 (dt, $J = 7.5$, 1.1 Hz, 1H), 7.02 (dd, $J = 7.7$, 1.1 Hz, 1H), 6.35 (q, $J = 1.8$ Hz, 1H), 5.75 (ddd, $J = 5.9$, 3.8, 1.6 Hz, 1H), 4.94 (ddd, $J = 14.6$, 5.9, 1.7 Hz, 1H), 4.79 (ddd, $J = 14.6$, 4.0, 1.8 Hz, 1H), 3.91 (s, 3H), 2.55 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 174.7$, 151.4, 146.3, 144.2, 135.3, 133.3, 132.2, 130.1, 129.5, 127.3, 126.4, 124.0, 119.7, 86.3, 75.0, 52.1, 44.6; MS (EI): *m*/*z* (%): 371 ([M^+], 2), 354 (49), 203 (6), 190 (31), 150 (100), 136 (30), 120 (17), 91 (26); HRMS (EI): *m*/*z* calcd for $C_{20}H_{21}NO_4S$: 371.1191; found: 371.1185; elemental analysis calcd (%) for $C_{20}H_{21}NO_4S$: C 64.67, H 5.70, N 3.77, S 8.63; found: C 64.34, H 6.04, N 3.75, S 8.25.

Isomer ***A*** *(2R*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$) (significant signals): $\delta =$ 6.82 (q, $J = 1.8$ Hz, 1H), 5.65 (ddd, $J = 5.6$, 3.4, 1.9 Hz, 1H), 3.91 (s, 3H), 2.60 (s, 6H).

3-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2-(4-methoxy-3-methylphenyl)-2,5-dihydrofuran (20): Eluent: ethyl acetate/hexane (1:3). Yield 86%.

Isomer ***B*** *(2S*,SR*)*: M.p. 80–83 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.71$ (dd, $J = 7.8$, 1.7 Hz, 1H), 7.38 (dt, $J = 7.6$, 1.7 Hz, 1H), 7.20 (dt, $J = 7.5$, 0.9 Hz, 1H), 7.04–6.98 (m, 2H), 6.87 (d, $J = 2.0$ Hz, 1H), 6.71 (d, $J =$ 8.3 Hz, 1H), 6.30 (q, $J = 1.8$ Hz, 1H), 5.68 (ddd, $J = 5.8$, 4.1, 2.0 Hz, 1H), 4.88 (ddd, $J = 14.5$, 5.8, 1.7 Hz, 1H), 4.72 (ddd, $J = 14.6$, 4.1, 1.8 Hz, 1H), 3.81 (s, 3H), 2.61 (s, 6H), 2.14 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 157.8, 151.5, 146.4, 135.4, 132.7, 131.9, 130.4, 129.7, 126.4, 126.2, 123.8, 119.5, 109.3, 86.5, 74.2, 55.2, 44.6, 16.2; MS (EI): *m*/*z* (%): 357 ([M^+], 5), 340 (56), 190 (34), 150 (100), 91 (39), 77 (27); elemental analysis calcd (%) for $C_{20}H_{23}NO_3S$: C 67.20, H 6.49, N 3.92, S 8.97; found: C 67.19, H 6.67, N 3.60, S 8.80.

Isomer ***A*** *(2R*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.66$ (dd, $J = 7.7$, 1.6 Hz, 1H), 7.36 (dt, $J = 7.6$, 1.6 Hz, 1H), 7.10 (dt, $J = 7.6$, 1.2 Hz, 1H), 7.10–7.00 (m, 2H), 6.92 (d, $J = 2.1$ Hz, 1H), 6.80 (q, $J = 1.7$ Hz, 1H), 6.72 (d, $J = 8.3$ Hz, 1H), 5.53 (ddd, $J = 5.6$, 3.4, 1.8 Hz, 1H), 4.93 (ddd, $J = 14.3$, 5.8, 1.8, 1H), 4.75 (ddd, $J = 14.2$, 3.6, 1.7 Hz, 1H), 3.80 (s, 3H), 2.60 (s, 6H), 2.15 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 158.0$, 151.7, 148.1, 136.3, 132.0, 131.3, 130.9, 129.5, 126.6, 125.9, 125.7, 124.1, 119.5, 109.6, 86.0, 74.7, 55.3, 44.9, 16.2; HRMS (EI): *m*/*z* calcd for $C_{20}H_{23}NO_3S$: 357.1399; found: 357.1392.

3-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2-(2,4-dimethoxyphenyl)-2,5-dihydrofuran (21): Eluent: ethyl acetate/hexane (2:3). Yield 47%.

Isomer ***B*** *(2S*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.65$ (dd, $J = 7.8$, 1.7 Hz, 1H), 7.35 (dt, $J = 7.6$, 1.6 Hz, 1H), 7.11 (dt, $J = 7.5$, 1.1 Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 1H), 7.01 (dd, $J = 8.1$, 1.0 Hz, 1H), 6.37 (m, 2H), 6.10 (ddd, $J = 5.8$, 3.8, 1.9 Hz, 1H), 4.81 (ddd, $J = 14.5$, 5.7, 1.7 Hz, 1H), 4.71 (ddd, $J =$ 14.4, 3.8, 1.8 Hz, 1H), 3.80 (s, 3H) 3.70 (s, 3H), 2.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 161.0$, 158.3, 151.5, 145.8, 135.6, 133.8, 131.7, 129.6, 126.3, 123.8, 119.6, 104.0, 98.2, 80.7, 74.1, 55.3, 55.2, 44.7; MS (EI): *m*/*z* (%): 373 ([M^+], 4), 356 (58), 205 (40), 190 (36), 165 (49), 150 (100), 136 (22), 120 (19), 91 (31), 77 (25); HRMS (EI): *m*/*z* calcd for $C_{20}H_{23}NO_4S$: 373.1348; found: 373.1351.

Isomer ***A*** *(2R*,SR*)*: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.71$ (dd, $J = 7.9$, 1.6 Hz, 1H), 7.37 (d, $J = 7.5$, 1.7 Hz, 1H), 7.22 (d, $J = 8.2$ Hz, 1H), 7.13 (dt, $J = 7.6$, 1.1 Hz, 1H), 7.04 (dt, $J = 8.0$, 1.0 Hz, 1H), 6.80 (q, $J = 1.9$ Hz, 1H), 6.45 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.38 (d, $J = 2.4$ Hz, 1H), 5.91 (ddd, $J = 5.5$, 3.3, 2.1 Hz, 1H), 4.85 (ddd, $J = 14.0$, 7.5, 1.7 Hz, 1H), 4.72 (ddd, $J = 14.0$, 3.3, 1.6 Hz, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 2.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 160.9$, 158.2, 151.4, 146.7, 136.1, 131.7, 130.1, 129.3, 125.1, 124.3, 119.7, 119.4, 103.7, 98.2, 80.4, 74.2, 55.1, 55.0, 44.4; HRMS (EI): *m*/*z* calcd for $C_{20}H_{23}NO_4S$: 373.1348; found: 373.1341.

(3*R,S*R**)-4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3,5-diphenyl-2,3-dihydrofuran (22)**: Eluent: ethyl acetate/hexane (1:4). Yield 83%; m.p. 112–113 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.04$ (m, 2H), 7.61 (dd, $J = 7.8$, 1.9 Hz, 1H), 7.56–7.47 (m, 3H), 7.42 (dd, $J = 7.5$, 1.9 Hz, 1H), 7.32–7.06 (m, 7H), 4.61 (dd, $J = 10.2$, 9.1 Hz, 1H), 4.30 (dd, $J = 9.1$, 6.2 Hz, 1H), 3.61 (dd, $J = 10.3$, 6.2 Hz, 1H), 2.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.1$, 150.6, 142.1, 136.5, 131.1, 130.6, 129.0, 128.6, 128.3, 127.6, 127.0, 126.5, 123.3, 119.5, 114.5, 78.9, 49.4, 44.4; MS (EI): *m*/*z* (%): 389 ([M^+], 11), 372 (65), 152 (73), 120 (12), 77 (61); elemental analysis calcd (%) for $C_{24}H_{23}NO_2S$: C 74.01, H 5.96, N 3.60, S 8.22; found: C 73.74, H 5.88, N 3.28, S 8.49. (3*R*,S*R*)-**22** (obtained from (2*S*,S*R*)-**12B**): $[\alpha]_D^{25} = -118$ ($c = 1.0$, $CHCl_3$).

(3*R,S*R**)-4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3-(4-methoxyphenyl)-5-phenyl-2,3-dihydrofuran (23)**: Eluent: ethyl acetate/hexane (1:4). Yield 69%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.01$ (m, 2H), 7.58 (dd, $J = 7.5$, 1.6 Hz, 1H), 7.53–7.45 (m, 3H), 7.41 (dd, $J = 7.5$, 1.6 Hz, 1H), 7.15 (t, $J =$ 7.5 Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 6.80 (d, $J = 8.6$ Hz, 2H), 4.58 (dd, $J =$ 10.3, 8.9 Hz, 1H), 4.26 (dd, $J = 9.1$, 6.4 Hz, 1H), 3.79 (s, 3H), 3.56 (dd, $J =$ 10.2, 6.3 Hz, 1H), 2.48 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.0$, 158.6, 150.6, 136.5, 134.2, 131.1, 130.6, 129.1, 128.6, 128.3, 126.6, 123.3, 119.5, 114.6, 113.7, 79.0, 55.1, 48.8, 44.2.

(3*R,S*R**)-4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3-(4-nitrophenyl)-5-phenyl-2,3-dihydrofuran (24)**: Eluent: ethyl acetate/hexane (1:4). Yield 46% (84% in converted yield); m.p. 119–121 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.12$ (d, $J = 8.1$ Hz, 2H), 8.04–7.99 (m, 2H), 7.58 (dt, $J = 7.6$, 1.7 Hz, 1H), 7.58–7.49 (m, 3H), 7.45 (dt, $J = 7.5$, 1.6 Hz, 1H), 7.28 (d, $J =$ 8.6 Hz, 2H), 7.17 (t, $J = 7.4$ Hz, 2H), 4.64 (dd, $J = 9.6$, 9.4 Hz, 1H), 4.28 (dd, $J = 9.3$, 5.6 Hz, 1H), 3.71 (dd, $J = 10.2$, 5.7 Hz, 1H), 2.47 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 165.3$, 150.7, 149.8, 146.9, 136.3, 131.4, 131.0, 128.5, 128.3, 126.1, 123.6, 123.4, 119.8, 114.0, 78.0, 49.0, 44.1; MS (EI): *m*/*z* (%): 434 ([M^+], 8), 417 (66), 150 (62), 120 (15), 105 (100), 77 (63); elemental analysis calcd (%) for $C_{24}H_{22}N_2O_4S$: C 66.34, H 5.10, N 6.45, S 7.38; found: C 66.03, H 4.90, N 6.24, S 7.00.

Crystal structure data for $C_{24}H_{22}N_2O_4S$ [(3*R,S*R**)-24]**: Crystal size 0.15 × 0.50 × 0.30 mm, monoclinic, space group *C*2/*c*, $a = 35.163(3)$, $b = 6.7788(5)$, $c = 22.205(2)$ Å, $\beta = 124.160(5)°$, $V = 4379.8(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.318$ Mg m^{-3}, $\mu = 1.590$ mm^{-1}, $2\theta_{max} = 114.26°$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, $2\theta/\omega$ scans, $T = 296$ K, absorption correction: none, 2942 reflections collected, 2459 independent. Refinement on F^2 for 2942 reflections and 283 parameters gave $R1 = 0.0521$ and $wR2 = 0.1384$ for $I > 2\sigma(I)\mu$ Residual electron density $-0.268 < \Delta\rho < 0.259$ e Å^{-3}. S, O, N,

and C atoms were refined with anisotropic thermal displacements parameters and the H atoms with isotropic parameters. The structure was solved and refined with SHELX-97.[26]

(3*R,S*R**)-2-[2-(*N*,*N*-Dimethylamino)phenylsulfinyl]-1,3-diphenyl-1-cyclopentene (25)**: Eluent: ethyl acetate/hexane (1:6). Yield 75%; m.p. 160–161 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.78$ (dd, $J = 8.1$ Hz, 2H), 7.52–7.35 (m, 5H), 7.27–7.15 (m, 4H), 7.12–6.98 (m, 3H), 3.47 (m, 1H), 2.95 (m, 2H), 2.47 (s, 6H), 2.32 (m, 1H), 1.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.7$, 150.8, 143.7, 140.1, 136.7, 135.4, 131.0, 128.7, 128.4, 128.3, 127.9, 127.7, 126.7, 126.3, 123.5, 119.3, 52.3, 44.2, 36.5, 34.7; MS (EI): *m*/*z* (%): 387 ([M^+], 6), 370 (100), 266 (6), 233 (17), 217 (39), 150 (62), 120 (10), 91 (55), 77 (23); elemental analysis calcd (%) for $C_{25}H_{25}NOS$: C 77.49, H 6.51, N 3.62, S 8.26; found: C 77.24, H 6.47, N 3.23, S 7.89. (3*R*,S*R*)-**25** (obtained from (*R*)-**8**): $[\alpha]_D^{25} = +204.2$ ($c = 1.0$, $CHCl_3$); HPLC: *ee* = 97.7% (Chiralcel OD column; hexane/2-propanol 90:10; 0.5 mL min^{-1}, 220 nm; (3*R*,S*R*)-**25** = 10.3 min, (3*S*,S*S*)-**25** = 6.9 min).

Crystal structure data for $C_{25}H_{25}NOS$ [(3*R*,S*R*)-25]: Crystal size 0.17 × 0.25 × 0.25 mm, monoclinic, space group $P2_1$, $a = 8.431(2)$, $b = 14.141(3)$, $c = 8.867(2)$ Å, $\beta = 102.19(2)^\circ$, $V = 1033.3(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.245$ Mg m^{-3}, $\mu = 1.492$ mm^{-1}, $2\theta_{max} = 114.28^\circ$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, $2\theta/\omega$ scans, $T = 296$ K, absorption correction: none, 1595 reflections collected, 1583 independent. Refinement on F^2 for 1595 reflections and 254 parameters gave $R1 = 0.0328$ and $wR2 = 0.1055$ for $I > 2\sigma(I)\mu$. Absolute structure parameter (Flack) = 0.01(2). Residual electron density $-0.185 < \Delta\rho < 0.273$ e Å^{-3}. S, O, N and C atoms were refined with anisotropic thermal displacements parameters and the H atoms with isotropic parameters. The structure was solved and refined with SHELX-97.[26]

(3*R,S*R**)-2-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3-(4-methoxyphenyl)-1-phenyl-1-cyclopentene (26)**: Eluent: ethyl acetate/hexane (1:4). Yield 80%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.81–7.70$ (m, 2H), 7.52–7.35 (m, 5H), 7.09 (m, 2H), 6.93 (m, 2H), 6.77 (m, 2H), 3.79 (s, 3H), 3.42 (tq, $J = 2.1$, 5.4 Hz, 1H), 2.92 (tq, $J = 2.1$, 6.5 Hz, 2H), 2.44 (s, 6H), 2.26 (m, 1H), 1.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.0$, 155.5, 150.7, 140.0, 136.5, 135.7, 135.3, 130.9, 128.6, 128.2 (2C), 128.1, 126.7, 123.4, 119.3, 113.2, 55.0, 51.4, 44.1, 36.3, 34.7; MS (EI): *m*/*z* (%): 417 ([M^+], 33), 400 (100), 263 (26), 247 (78), 152 (34), 150 (72), 121 (29), 91 (48), 77(29); HRMS (EI): *m*/*z* calcd for $C_{26}H_{27}NO_2S$: 417.1751; found: 417.1762.

(3*R,S*R**)-4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-5-(4-methoxyphenyl)-3-phenyl-2,3-dihydrofuran (27)**: Eluent: ethyl acetate/hexane (1:2). Yield 78%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.99$ (d, $J = 8.9$ Hz, 2H), 7.60 (dd, $J = 8.2$, 1.8 Hz, 1H), 7.41 (dt, $J = 7.6$, 1.7 Hz, 1H), 7.31–7.06 (m, 7H), 7.00 (d, $J = 9.0$ Hz, 2H), 4.57 (dd, $J = 10.1$, 9.1 Hz, 1H), 4.28 (dd, $J = 9.0$, 5.9 Hz, 1H), 3.88 (s, 3H), 3.57 (dd, $J = 10.2$, 5.9 Hz, 1H), 2.51 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.1$, 161.5, 150.6, 142.4, 136.5, 131.1, 130.3, 128.3, 127.6, 127.0, 126.6, 123.3, 121.5, 119.5, 113.7, 112.9, 78.7, 55.3, 49.5, 44.2.

(3*R,S*R**)-4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-3,5-bis-(4-methoxyphenyl)-2,3-dihydrofuran (28)**: Eluent: ethyl acetate/hexane (1:4). Yield 70%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.99$ (d, $J = 9.0$ Hz, 2H), 7.60 (dd, $J = 7.9$, 1.8 Hz, 1H), 7.40 (dt, $J = 7.6$, 1.7 Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 4.54 (dd, $J = 10.2$, 9.1 Hz, 1H), 4.23 (dd, $J = 9.1$, 6.0 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.53 (dd, $J = 10.1$, 6.1 Hz, 1H), 2.51 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 164.9$, 161.4, 158.5, 150.6, 136.6, 134.5, 131.0, 130.3, 128.6, 126.7, 123.2, 121.6, 119.5, 113.7, 113.0, 78.8, 55.3, 55.1, 48.8, 44.2.

(3*R,S*R**)-2-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-1-(4-methoxyphenyl)-3-phenyl-1-cyclopentene (29)**: Eluent: ethyl acetate/hexane (1:4). Yield 50%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.78–7.72$ (m, 2H), 7.46–7.33 (m, 2H), 7.27–7.14 (m, 3H), 7.12–7.05 (m, 2H), 6.95–7.04 (m, 4H), 3.88 (s, 3H), 3.45 (tq, $J = 1.1$, 5.4 Hz, 1H), 2.92 (tc, $J = 1.6$, 6.5 Hz, 2H), 2.48 (s, 6H), 2.26 (m, 1H), 1.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 160.0$, 155.2, 150.7, 143.8, 138.4, 136.6, 130.9, 129.8, 127.8, 127.6, 126.7, 126.4, 126.2, 123.4, 119.3, 113.5, 55.2, 52.2, 44.2, 36.3, 34.5; MS (EI): *m*/*z* (%): 417 ([M^+], 22), 400 (100), 263 (33), 247 (76), 152 (33), 150 (83), 121 (26), 91 (49), 77(27); HRMS (EI): *m*/*z* calcd for $C_{26}H_{27}NO_2S$: 417.1762; found: 417.1744.

(*S*)-2-(*N*,*N*-dimethylamino)phenyl methyl sulfoxide [(*S*)-30]: 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl(−)-(*S*)-methanesulfinate[20] (2.93 g, 9.1 mmol) in toluene (30 mL) was added to a solution of *o*-$(Me_2N)C_6H_4$-MgI (27.3 mmol, 3 equiv) in diethyl ether (30 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Saturated NH_4Cl (100 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:1) to afford (*S*)-**30** (1.28 g, 77%). $[\alpha]_D^{25} = -250.3$ ($c = 1$, $CHCl_3$) (*ee* ≥ 96%, ^{1}H NMR, (*R*)-2,2,2-trifluoro-1-(9-antryl)ethanol); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.88$ (dd, $J = 9.7$, 2.1 Hz, 1H), 7.43 (dt, $J = 7.5$, 1.6 Hz, 1H), 7.28 (dt, $J = 7.5$, 2.2 Hz, 1H), 7.14 (dd, $J = 9.1$, 1.1 Hz, 1H), 2.76 (s, 3H), 2.71 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.8$, 139.6, 130.8, 123.8, 123.2, 119.3, 43.9, 41.1.

(*S*)-3-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-1-propanol [(*S*)-31]: LDA in THF (0.5 M, 6.2 mL, 3.09 mmol) at −78 °C under argon was added to a solution of (*S*)-**30** (472 mg, 2.58 mmol) in dry diethyl ether (16 mL). The solution was stirred for 30 min and then ethylene oxide (5 mL) was added at −78 °C. The reaction mixture was slowly warmed to −10 °C and then kept at this temperature for 1 h. Saturated NH_4Cl solution (25 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (ethyl acetate) to give (*S*)-**31** (420 mg, 72%). $[\alpha]_D^{25} = -301.5$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.82$ (dd, $J = 7.5$, 1.6 Hz, 1H), 7.43 (dt, $J = 7.5$, 1.6 Hz, 1H), 7.28 (dt, $J = 7.5$, 1.1 Hz, 1H), 7.15 (dd, $J = 8.1$, 1.1 Hz, 1H), 3.66 (br t, $J = 5.4$ Hz, 2H), 3.40 (br s, 1H, OH), 3.20 (m, 1H), 3.00 (m, 1H), 2.69 (s, 6H), 1.87 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 150.2$, 136.5, 131.0, 124.4, 123.9, 119.6, 60.1, 50.6, 44.1, 25.0; MS (FAB): *m*/*z* (%): 228 ([M^++1], 100).

(*R*)-4-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-2,3-dihydrofuran [(*R*)-4]: (*S*)-**31** (400 mg, 1.76 mmol) was dissolved in THF (12 mL), the solution was cooled to −78 °C under argon, and LDA in THF (0.5 M, 10.6 mL, 5.29 mmol) was added. After 30 min at −78 °C, ethyl formate (570 mL, 7.05 mmol) was added, and the reaction mixture was stirred at this temperature for 2 h. A saturated aqueous solution of NH_4Cl (30 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (ethyl acetate/CH_2Cl_2 1:2) to give the lactols **32** as a mixture of stereoisomers (358 mg, 80%). This mixture of lactols (328 mg, 1.29 mmol) was dissolved in CH_2Cl_2 (14 mL). The solution was cooled at 0 °C under argon and MsCl (200 mL, 2.57 mmol) and Et_3N (720 mL, 5.16 mmol) were sequentially added. The reaction mixture was stirred at 0 °C for 1 h. Saturated aqueous NH_4Cl (30 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:1) to give (*R*)-**4** (215 mg, 77%). $[\alpha]_D^{25} = -221.7$ ($c = 0.95$, $CHCl_3$) (*ee* ≥ 96%, ^{1}H NMR, [Pr(hfc)$_3$]).

(2*S*,S*S*)-1,1-Diphenyl-1,2-dihydroxypropyl-2-*O*-[2-(*N*,*N*-dimethylamino)-phenyl sulfinate (34): *n*BuLi (2.5 M, 2.2 mL, 5.47 mmol) was added under argon to a solution of *N*,*N*-dimethyl-2-iodoaniline (1.26 g, 5.11 mmol) in dry Et_2O (63 mL), cooled at −78 °C. This solution was slowly added to a solution of sulfite **33** (1.0 g, 3.65 mmol) in Et_2O/THF (13:1, 14 mL). The reaction was monitored by TLC until **33** had disappeared. The mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:7) to afford (2*S*,S*S*)-**34** (870 mg, 61%). $[\alpha]_D^{25} = -141.8$ ($c = 1$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.95$ (dd, $J = 1.6$, 8.0 Hz, 1H), 7.53–7.08 (m, 14H), 5.15 (q, $J = 5.9$ Hz, 1H), 2.50 (s, 6H), 1.46 (d, $J = 5.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.9$, 144.6, 143.2, 140.0, 133.1, 129.9, 127.8, 127.7, 127.2, 126.8, 124.6, 124.4, 83.4, 80.5, 45.5, 18.4; MS (EI): *m*/*z* (%): 395 ([M^+], 9), 183 (52), 169 (50), 152 (19), 136 (19), 120 (29), 105 (100), 91 (10), 77 (69); HRMS (EI): *m*/*z* calcd for $C_{23}H_{24}NO_3S$: 395.1521; found: 395.1537.

(*R*)-1-[2-(*N*,*N*-dimethylamino)phenylsulfinyl]-1-cyclopentene [(*R*)-8]: The sulfinate (2*S*,S*S*)-**34** (200 mg, 0.51 mmol) in THF (15 mL) was slowly added under argon to a solution of 1-cyclopentenylmagnesium bromide (1.16 mmol) in THF (8 mL) at room temperature. The reaction was stirred at room temperature for 1 h. The mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:5) to afford (*R*)-**8** (102 mg, 85%). $[\alpha]_D^{25} = +190$ ($c = 1$, $CHCl_3$); HPLC: *ee* = 96.6% (Chiralcel OD column; hexane/2-

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propanol 97:3; 0.5 mL min^{-1}, $\lambda = 254$ nm; (*R*)-**8** = 25.1 min; (*S*)-**8** = 27.1 min)

(*R*)-2-Phenyl-2,5-dihydrofuran [(*R*)-35]:[12e] Activated zinc (1.30 g) and saturated aqueous NH_4Cl solution (5 mL) were added to a solution of (2*S*,5*R*)-**12B** (106 mg, 0.34 mmol) in THF (5 mL). The mixture was stirred vigorously at room temperature under argon. The progress of the reaction was monitored by TLC. CH_2Cl_2 (20 mL) was added after 4 h. The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (20 mL), dried (Na_2SO_4), and evaporated. Flash chromatography (ethyl acetate/hexane 1:10) of the residue gave (*R*)-**35** (25 mg, 51 %). $[\alpha]_D^{25} = +282.0$ (c = 0.50, $CHCl_3$) ($ee \geq 96$ %, ^{1}H NMR, [Pr(hfc)$_3$]); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.23-7.39$ (m, 5H), 6.03 (ddt, $J = 6.0$, 2.2, 1.6 Hz, 1H), 5.88 (ddt, $J = 6.0$, 2.4, 1.6 Hz, 1H), 5.76–5.82 (m, 1H), 4.87 (ddt, $J = 12.9$, 6.1, 1.6 Hz, 1H), 4.76 (dddd, $J = 12.9$, 4.1, 2.4, 1.6 Hz, 1H).

(2*S*,4*R*)-2,4-Diphenyltetrahydrofuran [(2*S*,4*R*)-36]:[23] A solution of (3*R*,5*R*)-**22** (130 mg, 0.33 mmol) in EtOH (5 mL) was added at 0 °C to a suspension of Raney-Ni in EtOH (5 mL) and under a hydrogen atmosphere (1 atm). The reaction was monitored by TLC. After 20 h at 0 °C the reaction was filtered over celite and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:30) to give (2*S*,4*R*)-**36** (68 mg, 90 %). $[\alpha]_D^{25} = -52.4$ ($c = 1.40$, $CHCl_3$) ($ee \geq 96$ %, ^{1}H NMR, [Pr(hfc)$_3$]); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.47-7.20$ (m, 10H), 5.08 (dd, $J = 10.2$, 5.7 Hz, 1H), 4.37 (t, $J = 8.4$ Hz, 1H), 4.03 (t, $J = 8.4$ Hz, 1H), 3.65 (m, 1H), 2.77 (m, 1H), 2.02 (q, $J = 10.5$ Hz, 1H).

(*S*)-3-Phenyl-1-cyclopentene [(*S*)-37]:[12e] MCPBA (70 %, 181 mg, 0.72 mmol) in CH_2Cl_2 (7 mL) was added to a solution of **14A**,**B** (8:92) (150 mg, 0.48 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred vigorously at 25 °C. After 4 h, saturated Na_2SO_3 (20 mL) and saturated aqueous $NaHCO_3$ (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was dissolved in THF (10 mL), degassed, and cooled at −25 °C under argon. Then [Pd(acac)$_2$] (4.86, 0.02 mmol) (acac = acetylacetonate) and *i*PrMgBr (0.9 M, 1.26 mL, 1.11 mmol) were added successively. After the mixture had been stirred for 2 h at −25 °C, saturated aqueous NH_4Cl (2 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (hexane) to give (*S*)-**32** (69 mg, 55 %). $[\alpha]_D^{25} = -190$ ($c = 1$, $CHCl_3$) ($ee = 90$ %, GC, Cyclosib column); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.28$ (m, 2H), 7.18 (m, 3H), 5.94 (dq, $J = 2.2$, 5.7 Hz, 1H), 5.77 (dq, $J = 2.2$, 5.7 Hz, 1H), 3.89 (m, 1H), 2.44 (m, 3H), 1.73 (m, 1H).

(*S*)-1,3-Diphenylcyclopentene [(*S*)-38]: [Pd(acac)$_2$] (2.80 mg, 0.01 mmol) and *i*PrMgBr (0.9 M, 750 μL, 0.66 mmol) were added to a solution of **25** (83 mg, 0.22 mmol) in THF (5 mL), degassed at room temperature under argon. The mixture was stirred for 1.5 h at room temperature and saturated aqueous NH_4Cl (2 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (hexane) to give (*S*)-**38** (37 mg, 77 %). $[\alpha]_D^{25} = +204$ ($c = 1$, $CHCl_3$); HPLC: $ee = 94$ % (Chiralpak AS column; hexane; 0.3 mL min^{-1}, $\lambda = 254$ nm; (*S*)-**38** = 16.3 min, (*R*)-**38** = 18.1 min); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.50$ (m, 2H), 7.40–7.12 (m, 8H), 6.23 (q, $J = 2.0$ Hz, 1H), 4.08 (tq, $J = 4.1$, 8.9 Hz, 1H), 2.84 (m, 2H), 2.57 (tq, $J = 4.5$, 8.5 Hz, 1H), 1.92 (tq, $J = 6.9$, 9.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.4$, 136.3, 129.3, 128.5, 128.4, 128.1, 127.8, 127.3, 126.2, 125.8, 51.9, 34.1, 33.1; MS (EI): *m*/*z* (%): 220 ([M^+], 92), 143 (36), 91 (44), 77 (19).

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[10] Incomplete reactions were always observed with an equimolecular amount of iodobenzene. On the other hand, other electrophiles, such as bromobenzene and phenyltriflate, were also used in these Heck reactions. However, these electrophiles were much less reactive than iodobenzene; they gave low conversions and therefore very poor yields of Heck products.

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[12] Dihydrofurans and cyclopentenes are very prone to undergo double-bond isomerization in Heck reactions. For some asymmetric Heck reactions of dihydrofurans and cyclopentenes, see, for instance: a) S. R. Gilbertson, Z. Fu, D. Xie, *Tetrahedron Lett.* **2001**, *42*, 365; b) A. J. Hennessy, Y. M. Malone, P. J. Guiry, *Tetrahedron Lett.* **2000**, *41*, 2261; c) Y. Hashimoto, Y. Horie, M. Hayashi, K. Saigo, *Tetrahedron: Asymmetry* **2000**, *11*, 2205; d) C. G. Hartung, K. Köhler, M. Beller, *Org. Lett.* **1999**, *1*, 709; e) O. Loiseleur, M. Hayashi, N. Schmees, A. Pfaltz, *Synthesis* **1997**, 1338; f) K. K. Hii, T. D. W. Claridge, J. M. Brown, *Angew. Chem.* **1997**, *109*, 1033; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 984; g) S. Hillers, S. Sartori, O. Reiser, *J. Am. Chem. Soc.* **1996**, *118*, 2087; h) O. Loiseleur, P. Meier, P. A. Pfaltz, *Angew. Chem.* **1996**, *108*, 218; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 200.

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[14] For Pd–N coordinated complexes in Heck reactions of acyclic nitrogen-containing vinyl ethers, see: a) M. Larhed, C. Andersson, A. Hallberg, *Tetrahedron* **1994**, *50*, 285; b) C. Andersson, J. Larsson, A. Hallberg, *J. Org. Chem.* **1990**, *55*, 5757; c) K. Olofsson, H. Sahlin, M. Larhed, A. Hallberg, *J. Org. Chem.* **2001**, *66*, 544.

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