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Asymmetric Synthesis of γ-Lactones through Koga Amine-Controlled Addition of Enediolates to α,β-Unsaturated Sulfoxonium Salts

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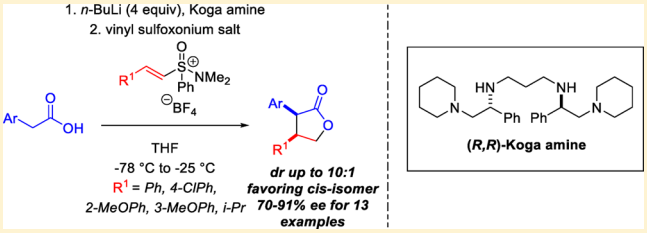
Supporting Information

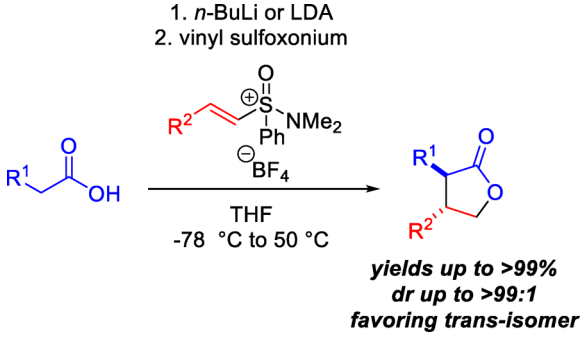
ABSTRACT: A chiral Koga amine-controlled asymmetric synthesis of *cis*-γ-lactones through a formal [3 + 2] cycloaddition of enediolates with α,β-unsaturated sulfoxonium salts is described. The desired structural motif was formed in moderate to good yields (50−71% for 13 examples), with good to very good diastereoselectivity (dr 5:1 to 10:1 for 20 examples), favoring the *cis*-isomer, and good to excellent enantioselectivity (70−91% ee for 13 examples).



INTRODUCTION

The development of methods facilitating the asymmetric synthesis of γ-lactones has attracted attention from many research groups due to their intriguing biological activity and their potential as synthetic intermediates.[1,2] Notwithstanding the recent achievements of the Johnson group in developing an elegant catalytic asymmetric approach to 4,5-substituted γ-lactones, enantioselective approaches to γ-lactones are often characterized by limitations in substitution patterns accommodated, inconvenient/unwieldy procedures, or variable levels of asymmetric induction.[1,2] Indeed enantioselective entries to 3,4-substituted, especially α-arylsubstituted, γ-lactones have been rare.[2d] We recently reported a diastereoselective and convergent method for the assembly of 3,4-substituted γ-lactones through the reaction of lithium enediolates with α,β-unsaturated sulfoxonium salts (Scheme 1).[3a] The desired product was obtained with excellent diastereoselectivity in most cases, with the *trans*-isomer being favored as the major isomer. Given the prevalence of γ-lactone or γ-lactone-derived motifs in natural products, we were motivated to develop an asymmetric variant of our diastereoselective methodology.[1]

Scheme 1. Our Previous Work



We were attracted to the idea of utilizing chiral amine ligands as a means of controlling enantioselectivity in the desired reaction manifold.[4] Interestingly, Zakarian's group had described the use of chiral Koga amine ligands in the enantioselective alkylation of enediolates, and more recently in the conjugate addition of enediolates to acrylates.[5] Inspired by Zakarian's work, we proceeded to evaluate the use of chiral Koga amine ligands in the addition of enediolates to α,β-unsaturated sulfoxonium salts. Herein, we describe the results of our study which demonstrate that chiral Koga amine ligands can be used to affect an interesting switch in product diastereoselectivity (to the *cis*-isomer), as well as facilitate an enantioselective entry to 3,4-disubstituted γ-lactones.

RESULTS AND DISCUSSION

We began our studies by investigating the reaction of 2-methoxyphenylacetic acid **1a** with phenyl-substituted sulfoxonium salt **2a** at −78 °C, using *n*-BuLi as the base for enediolate generation and chiral Koga amines **4**−**7** (Table 1).[5−7] Sulfoxonium salt **2a** and all related racemic salts in this study were prepared by procedures previously described by Johnson and co-workers, while enantioenriched salts were prepared through an additional step, involving a resolution procedure described by Gais and co-workers.[6,7]

The reaction conditions previously developed by us for the diastereoselective synthesis of *trans*-γ-lactones proved ineffective in the context of developing an asymmetric variant (Table 1, entry 1).[3a] Specifically, the use of excess carboxylic acid derived enediolate (2 equiv) and an elevated quench temperature proved counterproductive for satisfactory yield (trace) (Table 1, entry 1). In addition, the use of excess mole equivalents of sulfoxonium salt proved ineffective here. Investigation of conditions described by Zakarian's group for

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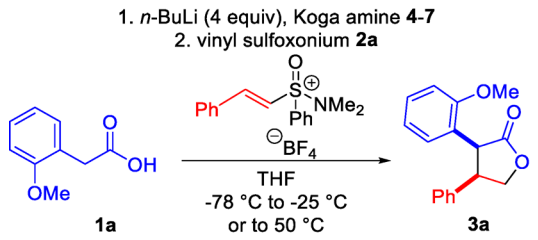
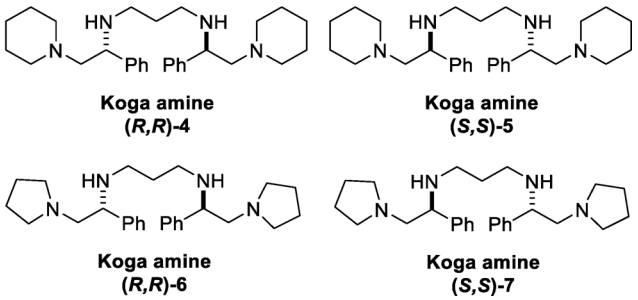
Table 1. Optimization of Enantioselective [3 + 2] Cycloaddition of Enediolates with Sulfoxonium Salts





entry	chiral amine[a]	reaction conditions (°C for temp)	quench	quench temp (°C)	% yield[b]	dr[c]	% ee[d]
1	**4**	−78 for 4 h → rt o/n	HCl (0.1 M)	50	trace		
2	**4**	−78 for 1 h → −25 for 12 h	HCl (0.1 M)	−25	43	13:1	74
3	**5**	−78 for 1 h → −25 for 12 h	HCl (0.1 M)	−25	41	10:1	68
4	**6**	−78 for 1 h → −25 for 12 h	HCl (0.1 M)	−25	43	10:1	52
5	**7**	−78 for 1 h → −25 for 12 h	HCl (0.1 M)	−25	28	nd	46
6	**4**	−78 for 1 h → −25 for 1 h	HCl (0.1 M)	−25	30	7:1	78
7	**4**	−78 for 1 h → −25 for 5 min	HCl (0.1 M)	−25	51	6:1	72
8[e]	**4**	−78 for 1 h → −25 for 5 min	HCl (0.1 M)	−25	60	6:1	78
9[e]	**4**	**−78 for 1 h → −25 for 5 min**	**AcOH**	**-25**	**63**	**6:1**	77
10[e,f]	none	−78 for 1 h → −25 for 5 min	AcOH	−25	61	1:1	18

[a]Reaction conditions: 1.03 equiv of Koga amine **4**−**7** and 1.0 equiv of (±)-**2a**. [b]% yield = isolated yield for both diastereomers. [c]dr determined by GC−MS or ^{1}H NMR analysis. [d]ee determined by chiral HPLC analysis. [e]Enediolate generated over 30 min. Entries 1−7 involved 15 min enediolate generation. [f](*R*)-**2a** was used. (3*R*,4*S*)-**3b** formed as major enantiomer of *cis*-isomer.

asymmetric alkylations also proved unsuccessful (36%, dr 1:1).[5] However, keeping the reaction at −25 °C, rather than warming up to room temperature, prior to quenching led to improved yield and diastereoselectivity (Table 1, entries 2 and 3). Limiting the amount of time at −25 °C to 5 min (instead of 1−12 h) gave significantly improved product yield (entry 7 vs entry 2).

Adjusting enediolate generation time to 30 min from 15 min contributed to a further elevation in yield of **3a** (entry 8). The acidity of the quenching agent was also an important consideration—acetic acid afforded a slightly superior yield compared to dilute HCl (entry 9 vs entry 8). Pyrrolidine-substituted Koga amines (**6** and **7**) resulted in significantly lower levels of enantioselectivity (entries 4 and 5). Ultimately, it was found that the reaction gave optimal yield, diastereoselectivity, and enantiomeric excess of the desired γ-lactone **3a** when the enediolate reactant (1 equiv), generated through treatment of the carboxylic acid (1 equiv) and Koga amine **4** (1.03 equiv) with *n*-BuLi (4 equiv), was added to **2a** (1 equiv) in THF at −78 °C. Keeping the reaction at −78 °C for 1 h, followed by warming the reaction to −25 °C for 5 min, and quenching the reaction at −25 °C with glacial acetic acid provided best results (entry 9).

When enantioenriched **2a** (rather than racemate) was used as substrate, in the absence of any Koga amine, the desired product **3a** was obtained in a modest ee of 18% (entry 10). Nonetheless, this result opened up the possibility of investigating a match of chirality between that of the Koga amine and that of the sulfoxonium salt (Table 2).[8] Interestingly, in all experiments conducted in the presence of Koga amines **4**−**7**, the *cis*-isomer of lactone **3a** was favored (as determined by comparison of NMR data with that for *trans*-**3a** and X-ray crystal structure analysis of recrystallized lactone **3g**).[3a] In addition, the absolute stereochemistry of **3a** was determined to be (3*S*,4*R*) by analogy with the assignment for **3g** (see CIF file for **3g** in the Supporting Information).

The scope with respect to both acid and sulfoxonium salt structure was then systematically evaluated (Table 2). A variety of acids, including those possessing electron-donating (e.g., MeO or Me) or electron-withdrawing substituents (e.g., F) at the 2-position on the aryl ring, were tolerated well for all vinyl sulfoxonium salts investigated. Other aryl-substituted α,β-unsaturated sulfoxonium salts also worked well, with R^2 = 4-ClPh providing the desired lactones in good yields (entries 19−21), and with only slightly lower diastereoselectivity and enantioselectivity relative to the styrenyl salt (entries 1−3). The presence of a more electron-donating and sterically demanding 2-MeOPh substituent at the β-position led to lower reaction efficiency (yields: 30−40%), but with retention of good diastereoselectivity and enantioselectivity (entries 16 and 17) compared to the styrenyl examples (entries 1 and 3). Alkyl-substitution at the β-position also led to a moderate yield of the desired γ-lactone, albeit with good diastereoselectivity and enantioselectivity (entry 22). Overall, good to very good diastereoselectivity favoring formation of the *cis*-diastereomer as the major isomer was achieved in most cases (dr 5:1 to 10:1 for 20 examples).

An intriguing aspect of our studies was the finding that, when enantioenriched sulfoxonium salts were employed in combination with the appropriate enantiomer of Koga amine (**4** or **5**), a significant amplification of asymmetric induction could be obtained through a match of the chirality associated with the sulfoxonium salt and that of the chiral amine.[8] This improvement in enantioselectivity ranged from 10% to 21% ee compared to the result obtained with a racemic sulfoxonium salt, e.g., an increase from 77% to 91% ee for entries 1 and 2, and from 64% to 85% ee for entries 19 and 20. In the future, improvements in enantioselectivity may be achieved through

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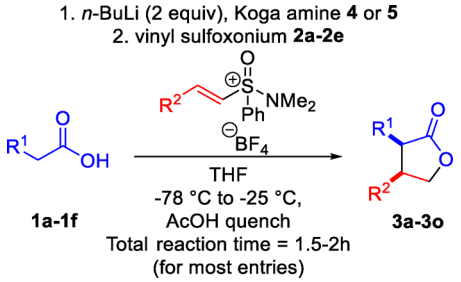
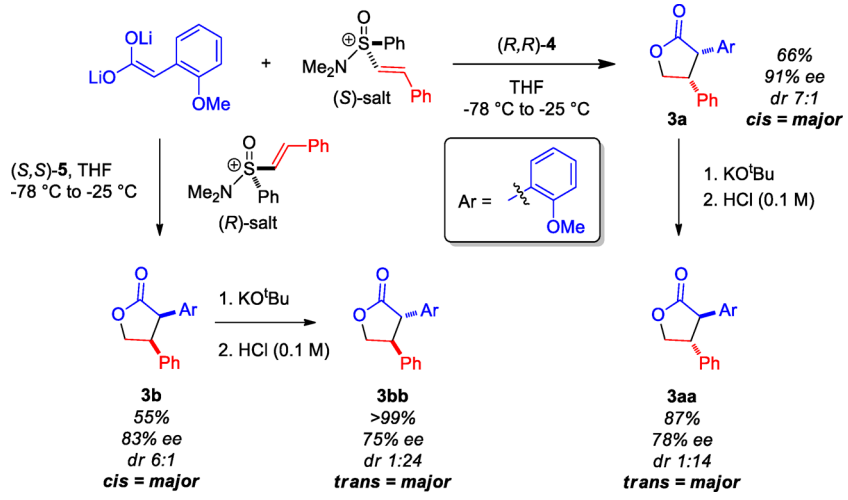
Table 2. Substrate Scope of Enantioselective γ-Lactone Formation[a]



entry	chiral amine	sulfoxonium salt	R^1	R^2	% yield[b]	dr[c]	% ee[d]	product
1	**4**	(±)-**2a**	2-MeOPh	Ph	63	6:1	77	**3a**
2	**4**	(*S*)-**2a**	2-MeOPh	Ph	66	7:1	91	**3a**
3	**5**	(±)-**2a**	2-MeOPh	Ph	41	10:1	68	**3b**
4	**5**	(*R*)-**2a**	2-MeOPh	Ph	55	4:1 (6:1)[e]	78 (83)[e]	**3b**
5	**4**	(±)-**2a**	2-MePh	Ph	66	6:1	70	**3c**
6	**4**	(*S*)-**2a**	2-MePh	Ph	50	5:1	82	**3c**
7	**5**	(*R*)-**2a**	2-MePh	Ph	48	5:1	76	**3d**
8	**4**	(±)-**2a**	Ph	Ph	65	5:1	76	**3e**
9	**4**	(*S*)-**2a**	Ph	Ph	45	4:1	81	**3e**
10	**4**	(±)-**2a**	1-Naph	Ph	67	8:1	50	**3f**
11	**4**	(*S*)-**2a**	1-Naph	Ph	64	5:1	53	**3f**
12	**5**	(±)-**2a**	1-Naph	Ph	45	7:1	50	**3g**
13	**5**	(*R*)-**2a**	1-Naph	Ph	58	6:1	61	**3g**
14	**4**	(*S*)-**2a**	2-FPh	Ph	50	5:1	78	**3h**
15	**5**	(*R*)-**2a**	2-FPh	Ph	56	4:1	72	**3i**
16	**4**	(±)-**2b**	2-MeOPh	2-MeOPh	34	7:1	75	**3j**
17	**5**	(±)-**2b**	2-MeOPh	2-MeOPh	31	7:1	68	**3k**
18	**4**	(±)-**2c**	2-MeOPh	3-MeOPh	46	7:1	nd	**3l**
19	**4**	(±)-**2d**	2-MeOPh	4-ClPh	71	5:1	64	**3m**
20	**4**	(*S*)-**2d**	2-MeOPh	4-ClPh	55	6:1	85	**3m**
21	**5**	(±)-**2d**	2-MeOPh	4-ClPh	58	5:1	57	**3n**
22[f]	**4**	(±)-**2e**	2-Naph	*i*-Pr	39	7:1	80	**3o**

[a]Reaction conditions: 1.03 equiv of Koga amine **4** or **5** and 1.0 equiv of **2**. [b]% yield = isolated yield for both diastereomers. [c]dr determined by GC–MS analysis. [d]ee determined by chiral HPLC analysis. [e]Reaction carried out on 1 mmol scale. [f]Using procedure of Table 1, entry 1 (ref 3a).

Scheme 2. Asymmetric Synthesis of All Stereoisomers of 3a



careful modification of substituents at the sulfur center on the sulfoxonium salt as well as on the Koga amine.

The synthetic potential of the methodology was demonstrated by the facile conversion of enantioenriched **3a** and **3b** into the corresponding *trans*-isomers (**3aa** and **3bb**) through employment of an isomerization procedure (Scheme 2). In this way, all four stereoisomers of the γ-lactone could be readily accessed with good to excellent diastereoselectivity (dr 6:1 to 24:1) and good to excellent enantioselectivity (75–91% ee).

X-ray crystal structure analysis of **3g** revealed that its major diastereomer is the *cis*-isomer (see CIF file for **3g** in the Supporting Information). By analogy, the relative stereo-

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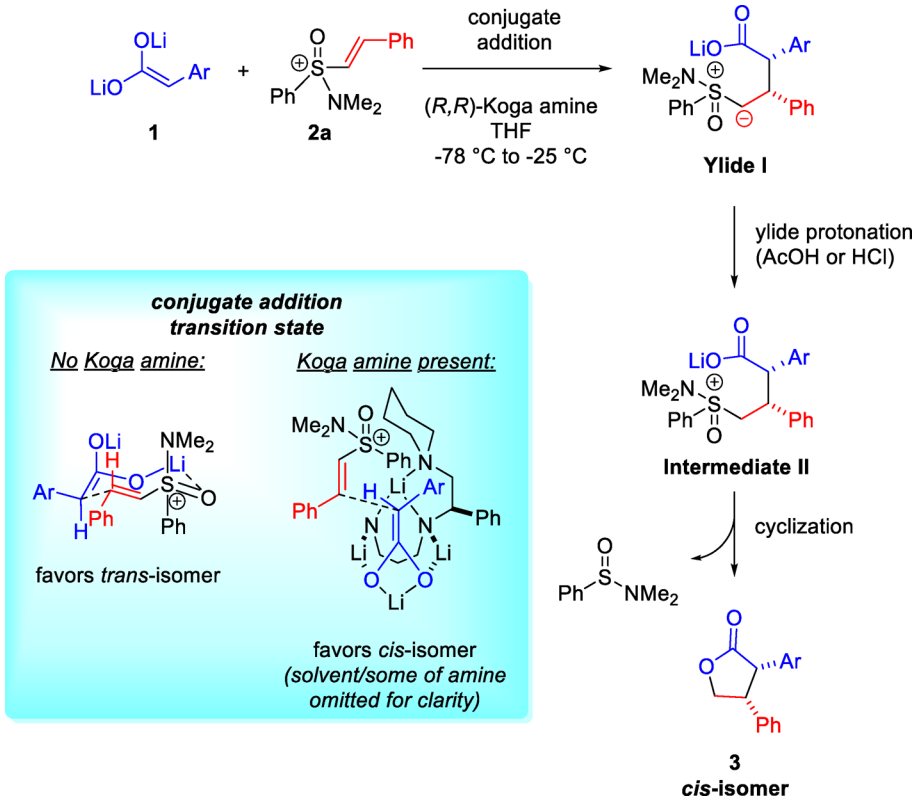
Scheme 3. Proposed Reaction Mechanism



chemistry of all other lactones (**3a**–**3o**) produced by the Koga amine-controlled reaction was assigned to be *cis*. In addition, the absolute stereochemistry of **3g** was revealed to be (3*R*,4*S*). By analogy, the lactone products **3a**–**3o** of all (*S*)-Koga amine **5**-controlled reactions were assigned the (3*R*,4*S*)-configuration, while the products of all (*R*)-Koga amine **4**-controlled reactions were assigned the (3*S*,4*R*)-configuration. The major diastereomer of **3aa** and **3bb** was confirmed to be *trans* by comparison of their GC–MS and ^{1}H NMR data with those for starting materials, *cis*-**3a** and *cis*-**3b**, respectively, and with previously prepared *trans*-**3aa**.[3a]

Reaction Mechanism. We propose that the reaction proceeds through a conjugate addition-ylide protonation–cyclization mechanism (Scheme 3). Ylide intermediate **I** is formed through conjugate addition of lithium enediolate **1** to the *β*-position of vinyl sulfoxonium **2a**.[5] Protonation of ylide **I** by added acetic acid leads to the formation of intermediate **II**, followed by cyclization, providing access to *γ*-lactone **3**. The dramatic change in the sense of diastereoselectivity to favor the *cis*-isomer, in contrast to our earlier studies (in the absence of Koga amine), may be explained by the conjugate addition step proceeding through an open antiperiplanar transition state (see inset of Scheme 3).[3a,9] This differs from our previously proposed transition state for the reaction conducted in the absence of Koga amine where a closed transition state, involving lithium chelation of the sulfoxonium oxygen and enediolate, leads to the *trans*-isomer dominating (Scheme 3).[3a] The use of equilibrating conditions (−78 °C to rt overnight, heating to 50 °C, and 2 equiv of enediolate) and quenching at an elevated temperature (50 °C) could also explain the pronounced *trans*-selectivity of our previously reported system.[3a] In contrast, the low temperature (−78 to −25 °C) at which the present reaction is conducted and quenched, the use of only 1 equiv of enediolate, and the short reaction time (1.5–2 h) limit the possibility of intermediates or *cis*-**3** undergoing equilibration.

CONCLUSION

In conclusion, we report that the Koga amine-controlled reaction of lithium enediolates with vinyl sulfoxonium salts provides a convenient, diastereoselective, and enantioselective route to *cis*-*γ*-lactones. Future studies will focus on the development of a catalytic asymmetric variant of the reported reaction and other [3 + 2] cycloadditions.

EXPERIMENTAL SECTION

General. All reactions were carried out in flame-dried glassware under a nitrogen atmosphere using standard inert atmosphere techniques unless otherwise stated. THF was freshly distilled from a sodium benzophenone ketyl still under nitrogen prior to use.[10] Acetone was distilled from $CaSO_4$. 2-Phenylacetic acid, 2-methoxyphenylacetic acid, 2-methylphenylacetic acid, 1-naphthylacetic acid, 2-fluorophenylacetic acid, 2-naphthylacetic acid, 2-methoxybenzaldehyde, methylphenyl sulfoxide, sodium azide, formaldehyde, formic acid, trimethyloxonium tetrafluoroborate, (1*S*)-(+)-10-camphorsulfonic acid, (1*R*)-(−)-10-camphorsulfonic acid, and *n*-butyllithium (2.5 M in hexane) were purchased and used as received. Benzaldehyde, 3-methoxybenzaldehyde, and isobutyraldehyde were purchased and distilled prior to use. 4-Chlorobenzaldehyde was washed with $NaHCO_3$ (satd.), extracted into ether, and crystallized. Iatrobeads (neutral silica, 60 *μ*M particle size) and TLC plates (UV254, 250 *μ*M) were used as received. Ethenyl sulfoximine precursors and sulfoxonium salts **2a**–**2e** were prepared as previously described by the groups of Johnson and Gais.[6,7] Koga amines (*R*,*R*)-**4**, (*S*,*S*)-**5**, (*R*,*R*)-**6**, and (*S*,*S*)-**7** were synthesized by previously reported methods.[5]

NMR spectra were recorded on a 200 spectrometer (200 MHz for ^{1}H and 50 MHz for ^{13}C) and 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). NMR chemical shifts were reported relative to

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TMS (0 ppm) for ^{1}H and to $CDCl_3$ (77.23 ppm) for ^{13}C spectra. High-resolution mass spectra were obtained on an Accurate Mass Q-TOF LC-MS instrument with ESI as ionization method. Low-resolution mass spectra were recorded on a GC−MS instrument equipped with a mass selective detector, and using a GC column (30 m, 0.25 mm ID). IR spectra were recorded on an IR spectrometer. Optical rotations were measured on an automatic polarimeter in dichloromethane at 598 nm. Chiral high performance liquid chromatography analysis (chiral HPLC) was performed using OD-H or AD-H columns (0.46 cm × 25 cm) on an HPLC instrument attached with a diode array detector (deuterium lamp, 190−600 nm) with HPLC-grade isopropanol and hexanes as the eluting solvents. Enantiomeric excesses were determined at λ = 254 or 225 nm (details given for each compound). Diastereoselectivity for γ-lactone formation was determined by GC−MS analysis of the crude product.

Method A for Preparation of γ-Lactones. Two 10 mL flame-dried flasks were equipped with septa and stir bars. One was charged with α,β-unsaturated sulfoxonium salt **2** (0.25 mmol, 1.0 equiv) and the other with the Koga tetraamine **4** or **5** (115.5 mg, 0.258 mmol, 1.03 equiv) and arylacetic acid (0.25 mmol, 1.0 equiv). Both were placed under high vacuum for 30 min and subjected to vacuum/nitrogen fill cycles (×3). The salt was suspended in THF (1.0 mL), and the tetraamine and arylacetic acid were dissolved in THF (3.0 mL). The acid and amine solution was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexane, 0.4 mL, 1.00 mmol, 4.0 equiv) was added dropwise. The solution was stirred for 30 min. The two flasks were immersed in a dry ice/acetone bath (−78 °C) and cooled for 5 min. A cannula was bridged across the two flasks, and the nitrogen line was removed from the enediolate flask. The enediolate flask was pressurized with a syringe and dry nitrogen to transfer the enediolate complex to the α,β-unsaturated sulfoxonium salt suspension. THF (0.5 mL) was used to rinse the flask and cooled for a minute before a second transfer was performed. The reaction was stirred for 1 h at −78 °C, and then placed in a −25 °C isopropanol/cryocool bath for 5 min, before quenching with glacial acetic acid (0.1 mL). The flask was swirled by hand in the bath 4 or 5 times until the color was white and immediately extracted into ethyl acetate (30 mL), using additional portions to rinse the flask. The mixture was washed vigorously with HCl (1 M, 10 mL), brine (10 mL), $NaHCO_3$ (10 mL), and brine (10 mL). Ethyl acetate (30 mL) was brought through each wash 2 more times for a total of ∼100 mL of ethyl acetate collected. The collected organics were dried over $MgSO_4$ and filtered through cotton. The crude product was concentrated to an oil/solid and quickly purified over neutral silica (10 g), eluting with 8% EtOAc:hexane to prevent isomerization and decomposition. Note: The crude product was observed to isomerize to the *trans*-isomer when left at the crude stage overnight (at room temperature), or when left to stir for an hour after quenching.

Method B for Preparation of γ-Lactones. Two 10 mL flame-dried flasks were equipped with septa and stir bars. One was charged with α,β-unsaturated sulfoxonium salt **2** (0.27 mmol, 1.1 equiv) and the other with tetraamine **4** or **5** (115.5 mg, 0.258 mmol, 1.03 equiv) and arylacetic acid (0.25 mmol, 1.0 equiv). Both flasks were placed under high vacuum for 30 min and filled with N_2. The salt was suspended in THF (0.5 mL), and the tetraamine and arylacetic acid were dissolved in THF (1.5 mL). The flask containing the acid and amine was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexane, 0.4 mL, 1.00 mmol, 4.0 equiv) was added dropwise. The solution was stirred for 30 min. The two flasks were immersed in a dry ice/acetone bath (−78 °C) and cooled for 5 min. A cannula was bridged across the two flasks, and the nitrogen line was removed from the enediolate flask. The enediolate flask was pressurized with a syringe and dry nitrogen to transfer the enediolate complex to the α,β-unsaturated sulfoxonium salt suspension. THF (0.5 mL) was used to rinse the flask and cooled for a minute before a second transfer. The reaction was stirred for 1 h at −78 °C, and then placed in a −25 °C isopropanol/cryocool bath for 16 h, before quenching with HCl (0.1 M, ∼5 mL). The product was extracted into ethyl acetate (30 mL), using excess to rinse the flask. The product mixture was washed vigorously with HCl (1 M, 10 mL), brine (10 mL), $NaHCO_3$ (10 mL), and brine (10 mL) in that order, saving each wash. Ethyl acetate (30 mL) was brought through each wash 2 more times for a total of ∼100 mL of ethyl acetate collected. The collected organics were dried with $MgSO_4$ and filtered through cotton. The crude product was concentrated to an oil/solid and quickly purified over neutral silica (10 g), eluting with 8% EtOAc:hexane.

Method C for Preparation of γ-Lactones. One 10 mL flame-dried flask equipped with a septum and a stir bar was charged with tetraamine **4** or **5** (115.5 mg, 0.258 mmol, 1.03 equiv) and arylacetic acid (0.25 mmol, 1.0 equiv). The α,β-unsaturated sulfoxonium salt (0.27 mmol, 1.1 equiv) was added to another 10 mL flame-dried flask, and the flask was fitted with a septum. Both flasks were placed under high vacuum for 30 min and filled with N_2. The salt was dissolved in THF (0.4 mL), and the tetraamine and arylacetic acid were dissolved in THF (1.7 mL). The flask containing the acid and amine was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexane, 0.4 mL, 1.00 mmol, 4.0 equiv) was added dropwise to the solution. The solution was stirred for 15 min. The enediolate flask was immersed in a dry ice/acetone bath and cooled for 5 min to −78 °C. A syringe was used to transfer the α,β-unsaturated sulfoxonium salt solution, still at room temperature, over 10 min to the enediolate solution. The reaction was stirred for 4 h at −78 °C and allowed to warm to room temperature overnight. The next morning, the reaction was heated to 50 °C for 30 min and quenched with HCl (0.1 M, ∼5 mL). The product mixture was extracted with dichloromethane (3 × 10 mL), using excess to rinse the flask. The collected organics were washed with HCl (1 M, 10 mL) and brine (10 mL), dried with Na_2SO_4, and filtered through cotton. The crude product was concentrated to an oil/solid and quickly purified over neutral silica (10 g), eluting with 8% EtOAc:hexane.

Isomerization Procedure. The lactone (1 equiv) was placed in a flame-dried flask fitted with a septum and a stir bar. THF (0.11 M) was added, and the reaction cooled to 0 °C. KO^{t}Bu (1 M in hexane, 0.25 equiv) was added dropwise, and the mixture was heated to 50 °C for 30 min. The reaction was quenched with HCl (0.1 M, ∼5 mL) added dropwise, and extracted into dichloromethane. The mixture was purified by column chromatography using neutral silica, eluting with 8% EtOAc:hexane to yield the pure *trans*-lactone. Chiral HPLC analysis was carried out using an AD-H column, eluting with 95:5 hexane:isopropanol system at 1.5 mL/min.

*(3S,4R)-3-(2-Methoxyphenyl)-4-phenyldihydrofuran-2(3H)-one (**3a**).* The reaction was performed following Method A using sulfoxonium salt (±)-**2a**, (*R*)-Koga amine **4**, and 2-methoxyphenylacetic acid **1a**. **3a** was isolated as a colorless oil (42.3 mg, 63%) with a dr = 6:1 as determined by GC−MS analysis of the isolated product. HPLC analysis: 77% ee [Daicel Chiralpak OD-H column; 1.0 mL/min; solvent system: 5% isopropanol in hexane; retention time: 25.3 min (major), 41.3 min (minor)]; IR (thin film): 1770, 1495, 754 706 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.11−7.06 (m, 4H), 6.87−6.84 (m, 2H), 6.75−6.64 (m, 3H), 4.74−4.66 (m, 2H), 4.57 (d, J = 8.9 Hz, 1H), 4.08 (ddd, J = 8.9, 6.6, 4.6 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.2, 157.2 137.9, 130.3, 128.8, 128.3, 127.9, 127.3, 122.4, 120.5, 110.2, 71.8, 55.4, 46.4, 46.3; MS (EI 70 eV): 268, 223, 193, 165, 148, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_3^+$: 269.1178; found: 269.1167.

*(−)-(3S,4R)-3-(2-Methoxyphenyl)-4-phenyldihydrofuran-2(3H)-one (**3a**).* The reaction was performed following Method A using sulfoxonium salt (*S*)-**2a**, (*R*)-Koga amine **4**, and 2-methoxyphenylacetic acid **1a**. (−)-**3a** was isolated as a colorless oil (44.0 mg, 66%) with a dr = 7:1 as determined by GC−MS analysis of the crude. HPLC analysis: 91% ee [Daicel Chiralpak OD-H column; 1.0 mL/min; solvent system: 5% isopropanol in hexane; retention time: 24.3 min (major), 39.4 min (minor)]; $[\alpha]_D^{23}$ = −255.2 (c = 2.21, CH_2Cl_2); IR (thin film): 1768, 1495, 753, 705 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.12−7.06 (m, 4H), 6.87−6.84 (m, 2H), 6.75−6.64 (m, 3H), 4.74−4.66 (m, 2H), 4.57 (d, J = 8.9 Hz, 1H), 4.08 (ddd, J = 9.0, 6.6, 4.6 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.2, 157.2 137.9, 130.3, 128.8, 128.3, 127.9, 127.3, 122.4, 120.6, 110.2, 71.8, 55.4, 46.4, 46.4; MS (EI

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J. Org. Chem. 2017, 82, 606−615

70 eV): 268, 223, 193, 165, 148, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_3^+$: 269.1178; found: 269.1171.

*(+)-(3R,4S)-3-(2-Methoxyphenyl)-4-phenyldihydrofuran-2(3H)-one (**3b**).* The reaction was performed following Method B using sulfoxonium salt (±)-**2a**, (*S*)-Koga amine **5**, and 2-methoxyphenylacetic acid **1a**. (+)-**3b** was isolated as a colorless oil (41.0 mg, 41%) with a dr = 10:1 as determined by GC−MS analysis of the crude. HPLC analysis: 68% ee [Daicel Chiralpak OD-H column; 1.0 mL/min; solvent system: 5% isopropanol in hexane; retention time: 23.8 min (minor), 36.9 min (major)]; $[\alpha]_D^{23\,°C}$ = +123.1 (c = 1.80, CH_2Cl_2); IR (thin film): 1768, 1495, 753, 705 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.12−7.06 (m, 4H), 6.87−6.84 (m, 2H), 6.75−6.64 (m, 3H), 4.74−4.66 (m, 2H), 4.57 (d, J = 8.9 Hz, 1H), 4.08 (ddd, J = 8.9, 6.6, 4.6 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.2, 157.2 137.9, 130.3, 128.8, 128.3, 127.9, 127.3, 122.4, 120.5, 110.2, 71.8, 55.4, 46.4, 46.3; MS (EI 70 eV): 268, 223, 193, 165, 148, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_3^+$: 269.1178; found: 269.1172.

*(3R,4S)-3-(2-Methoxyphenyl)-4-phenyldihydrofuran-2(3H)-one (**3b**).* The reaction was performed following Method A using sulfoxonium salt (*R*)-**2a**, (*S*)-Koga amine **5**, and 2-methoxyphenylacetic acid **1a**. **3b** was isolated as a colorless oil (36.6 mg, 55%) with a dr = 4:1 as determined by GC−MS analysis of the crude. HPLC analysis: 78% ee [Daicel Chiralpak OD-H column; 1.0 mL/min; solvent system: 5% isopropanol in hexane; retention time: 25.7 min (minor), 40.1 min (major)]; IR (thin film): 1768, 1495, 753, 705 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.12−7.06 (m, 4H), 6.87−6.84 (m, 2H), 6.75−6.64 (m, 3H), 4.74−4.67 (m, 2H), 4.57 (d, J = 8.9 Hz, 1H), 4.08 (ddd, J = 9.0, 6.6, 4.6 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.2, 157.2 137.9, 130.3, 128.8, 128.3, 127.9, 127.3, 122.4, 120.6, 110.2, 71.8, 55.4, 46.4, 46.4; MS (EI 70 eV): 268, 223, 193, 165, 148, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_3^+$: 269.1178; found: 269.1173.

*(3S,4R)-3-(2-Methylphenyl)-4-phenyldihydrofuran-2(3H)-one (**3c**).* The reaction was performed following Method A, quenching with HCl (0.1 M) instead of acetic acid, using sulfoxonium salt (±)-**2a**, (*R*)-Koga amine **4**, and 2-methylphenylacetic acid **1b**. **3c** was isolated as a colorless oil (41.5 mg, 66%) with a dr = 6:1 as determined by GC−MS analysis of the crude. HPLC analysis: 70% ee [Daicel Chiralpak AD-H column; 1.5 mL/min; solvent system: 1% isopropanol in hexane; retention time: 15.0 min (minor), 17.4 min (major)]; IR (thin film): 1770, 1494, 1024, 757, 704 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.14−6.93 (m, 6H), 6.81−6.78 (m, 2H), 6.75−6.73 (m, 1H), 4.74−4.64 (m, 2H), 4.39 (d, J = 8.9 Hz, 1H), 4.05 (ddd, J = 8.9, 6.6, 5.6 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.3, 137.0, 136.7, 132.0, 130.3, 129.0, 128.5, 128.2, 127.7, 126.1, 71.6, 48.9, 46.7, 19.8; MS (EI 70 eV): 252, 207, 193, 178, 132, 104, 91 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_2^+$: 253.1229; found: 253.1225.

*(3S,4R)-3-(2-Methylphenyl)-4-phenyldihydrofuran-2(3H)-one (**3c**).* The reaction was performed following Method A using sulfoxonium salt (*S*)-**2a**, (*R*)-Koga amine **4**, and 2-methylphenylacetic acid **1b**. **3c** was isolated as a colorless oil (31.6 mg, 50%) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 82% ee [Daicel Chiralpak AD-H column; 1.5 mL/min; solvent system: 1% isopropanol in hexane; retention time: 15.0 min (minor), 17.5 min (major)]; IR (thin film): 1771, 1496, 1024, 757, 704 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.14−6.94 (m, 6H), 6.80−6.78 (m, 2H), 6.75−6.73 (m, 1H), 4.74−4.64 (m, 2H), 4.39 (d, J = 8.6 Hz, 1H), 4.05 (ddd, J = 8.6, 6.6, 5.6 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.3, 137.0 136.7, 132.0, 130.3, 129.0, 128.5, 128.2, 127.7, 126.1, 71.6, 48.9, 46.7, 19.8; MS (EI 70 eV): 252, 207, 193, 178, 132, 104, 91 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_2^+$: 253.1229; found: 253.1228.

*(3R,4S)-3-(2-Methylphenyl)-4-phenyldihydrofuran-2(3H)-one (**3d**).* The reaction was performed following Method A using sulfoxonium salt (*R*)-**2a**, (*S*)-Koga amine **5**, and 2-methylphenylacetic acid **1b**. **3d** was isolated as a colorless oil (30.4 mg, 48%) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 76% ee [Daicel Chiralpak AD-H column; 1.5 mL/min; solvent system: 1% isopropanol in hexane; retention time: 15.2 min (major), 17.9 min (minor)]; IR (thin film): 1767, 1022, 754, 703 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.14−6.94 (m, 6H), 6.80−6.78 (m, 2H), 6.74−6.73 (m, 1H), 4.74−4.65 (m, 2H), 4.39 (d, J = 8.9 Hz, 1H), 4.05 (ddd, J = 8.9, 6.6, 5.6 Hz, 1H), 2.08 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.3, 137.0 136.7, 132.0, 130.3, 129.0, 128.5, 128.2, 127.7, 126.1, 71.6, 48.9, 46.7, 19.8; MS (EI 70 eV): 252, 207, 193, 178, 132, 104, 91 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_2^+$: 253.1229; found: 253.1224.

*(3S,4R)-3,4-Diphenyldihydrofuran-2(3H)-one (**3e**).* The reaction was performed following Method A using sulfoxonium salt (±)-**2a**, (*R*)-Koga amine **4**, and phenylacetic acid **1c**. **3e** was isolated as a white solid (38.9 mg, 65%, mp 140−142 °C) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 76% ee [Daicel Chiralpak OD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 19.0 min (major), 29.1 min (minor)]; IR (thin film): 1764, 1038, 710, 698 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.15−7.08 (m, 6H), 6.86−6.81 (m, 4H), 4.75−4.68 (m, 2H), 4.25 (d, J = 8.5 Hz, 1H), 4.00 (ddd, J = 8.5, 6.1, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.6, 137.0 133.3, 129.6, 128.6, 128.4, 128.1, 127.6, 127.5, 71.5, 52.2, 48.0; MS (EI 70 eV): 238, 193, 179, 118, 104, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{16}H_{15}O_2^+$: 239.1072; found: 239.1066.

*(3S,4R)-3,4-Diphenyldihydrofuran-2(3H)-one (**3e**).* The reaction was performed following Method A using sulfoxonium salt (*S*)-**2a**, (*R*)-Koga amine **4**, and phenylacetic acid **1c**. **3e** was isolated as a white solid (26.8 mg, 45%, mp 136−138 °C) with a dr = 4:1 as determined by GC−MS analysis of the crude. HPLC analysis: 81% ee [Daicel Chiralpak OD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 18.7 min (major), 28.4 min (minor)]; IR (thin film): 1767, 1039, 697 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.15−7.09 (m, 6H), 6.86−6.80 (m, 4H), 4.74−4.67 (m, 2H), 4.25 (d, J = 8.5 Hz, 1H), 4.00 (ddd, J = 8.5, 6.1, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.7, 137.0 133.2, 129.6, 128.6, 128.4, 128.1, 127.6, 127.5, 71.5, 52.2, 48.0; MS (EI 70 eV): 238, 193, 179, 118, 104, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{16}H_{15}O_2^+$: 239.1072; found 239.1071.

*(−)-(3S,4R)-3-(Naphthalen-1-yl)-4-phenyldihydrofuran-2(3H)-one (**3f**).* The reaction was performed following Method A quenching with HCl (0.1 M) using sulfoxonium salt (±)-**2a**, (*R*)-Koga amine **4**, and 1-naphthylacetic acid **1d**. (−)-**3f** was isolated as a white solid (47.4 mg, 67%, mp 139−140 °C) with a dr = 8:1 as determined by GC−MS analysis of the crude. HPLC analysis: 50% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 15.4 min (major), 24.1 min (minor)]; $[\alpha]_D^{23\,°C}$ = −354.1 (c = 1.43, CH_2Cl_2); IR (thin film): 1771, 1145, 703 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.86 (d, J = 8.2 Hz, 1H), 7.80−7.78 (m, 1H), (d, J = 8.2 Hz, 1H), 7.50−7.42 (m, 2H), 7.20−6.89 (m, 4H), 6.99−6.89 (m, 4H), 6.67−6.65 (m, 2H), 5.02 (d, J = 8.6 Hz, 1H), 4.87−4.76 (m, 2H), 4.26−4.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 137.4, 133.6, 132.2, 129.3, 129.2, 128.3, 128.2, 127.6, 127.4, 126.5, 125.6, 125.2, 122.5, 71.7, 48.2, 47.2; MS (EI 70 eV): 288, 243, 229, 168, 153, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{20}H_{17}O_2^+$: 289.1229; found: 289.1224.

*(−)-(3S,4R)-3-(Naphthalen-1-yl)-4-phenyldihydrofuran-2(3H)-one (**3f**).* The reaction was performed following Method A, quenching with HCl (0.1 M), using sulfoxonium salt (*S*)-**2a**, (*R*)-Koga amine **4**, and 1-naphthylacetic acid **1d**. **3f** was isolated as a white solid (46.0 mg, 64%, mp 138−139 °C) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 53% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 15.0 min (major), 23.5 min (minor)]; IR (thin film): 1766, 1143, 702 cm^{-1}; ^1H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.85 (d, J = 8.3 Hz, 1H), 7.79−7.77 (m, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.49−7.41 (m, 2H), 7.19−7.15 (m, 1H), 6.98−6.88

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(m, 4H), 6.66−6.64 (m, 2H), 5.01 (d, J = 8.6 Hz, 1H), 4.86−4.75 (m, 2H), 4.25−4.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 137.4, 133.6, 132.2, 129.3, 129.2, 128.3, 128.2, 127.6, 127.4, 126.5, 125.6, 125.3, 122.5, 71.7, 48.2, 47.2; MS (EI 70 eV): 288, 243, 229, 168, 153, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{20}H_{17}O_2^+$: 289.1229; found: 289.1224.

*(+)-(3R,4S)-3-(Naphthalen-1-yl)-4-phenyldihydrofuran-2(3H)-one (**3g**).* The reaction was performed following Method A, quenching with HCl (0.1 M), using sulfoxonium salt (±)-**2a**, (*S*)-Koga amine **5**, and 1-naphthylacetic acid **1d**. (+)-**3g** was isolated as a white solid (32.3 mg, 45%, mp 133−135 °C) with a dr = 7:1 as determined by GC−MS analysis of the crude. 15.2 mg of the major isomer was crystallized from isopropanol to >99% optical purity as shown by chiral HPLC analysis. X-ray crystal analysis determined the stereochemistry of the major isomer to be (3*R*,4*S*) (see CIF file for **3g** in the Supporting Information); HPLC analysis: 50% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 15.1 min (minor), 23.6 min (major)]; $[\alpha]_D^{24}$ = +69.7 (c = 0.67, CH_2Cl_2); IR (thin film): 1770, 1146, 703 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.86 (d, J = 8.4 Hz, 1H), 7.80−7.77 (m, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.50−7.42 (m, 2H), 7.20−7.16 (m, 1H), 6.99−6.89 (m, 4H), 6.67−6.65 (m, 2H), 5.02 (d, J = 8.6 Hz, 1H), 4.88−4.76 (m, 2H), 4.27−4.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 137.4, 133.7, 132.2, 129.3, 129.2, 128.4, 128.2, 127.6, 127.5, 126.5, 125.7, 125.3, 122.5, 71.8, 48.3, 47.2; MS (EI 70 eV): 288, 243, 168, 153, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{20}H_{17}O_2^+$: 289.1229; found: 289.1221.

*(+)-(3R,4S)-3-(Naphthalen-1-yl)-4-phenyldihydrofuran-2(3H)-one (**3g**).* The reaction was performed following Method A using sulfoxonium salt (*R*)-**2a**, (*S*)-Koga amine **5**, and 1-naphthylacetic acid **1d**. **3g** was isolated as a white solid (41.6 mg, 58%, mp 139−140 °C) with a dr = 6:1 as determined by GC−MS analysis of the crude. HPLC analysis: 61% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 15.3 min (minor), 24.3 min (major)]; IR (thin film): 1768, 1145, 702 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.86 (d, J = 8.4 Hz, 1H), 7.80−7.78 (m, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.50−7.42 (m, 2H), 7.20−7.16 (m, 1H), 7.00−6.89 (m, 4H), 6.67−6.65 (m, 2H), 5.02 (d, J = 8.6 Hz, 1H), 4.88−4.77 (m, 2H), 4.27−4.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 137.4, 133.7, 132.2, 129.3, 129.2, 128.4, 128.2, 127.6, 127.5, 126.5, 125.7, 125.3, 122.5, 71.8, 48.3, 47.2; MS (EI 70 eV): 288, 243, 168, 153, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{20}H_{17}O_2^+$: 289.1229; found: 289.1220.

*(3S,4R)-3-(2-Fluorophenyl)-4-phenyldihydrofuran-2(3H)-one (**3h**).* The reaction was performed following Method A using sulfoxonium salt (*S*)-**2a**, (*R*)-Koga amine **4**, and 2-fluorophenylacetic acid **1e**. **3h** was isolated as a clear oil (32.1 mg, 50%) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 78% ee [Daicel Chiralpak OD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 14.1 min (major), 18.4 min (minor)]; IR (thin film): 1770, 1493, 1455, 754, 697 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.13−7.08 (m, 4H), 6.94−6.89 (m, 3H), 6.84−6.74 (m, 2H), 4.81−4.73 (m, 2H), 4.57 (d, J = 8.7 Hz, 1H), 4.11−4.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 175.8, 161.2 (d, J = 244 Hz, 1C), 137.6, 130.8 (d, J = 3 Hz, 1C), 129.4 (d, J = 8 Hz, 1C), 128.7, 127.7, 127.7, 124.1 (d, J = 3 Hz, 1C), 121.1 (d, J = 14 Hz, 1C), 114.9 (d, J = 21 Hz, 1C), 71.9, 46.5, 45.5 (d, J = 3 Hz, 1C); MS (EI 70 eV): 256, 211, 197, 136, 108, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{16}H_{14}FO_2^+$: 257.0978; found: 257.0969.

*(3R,4S)-3-(2-Fluorophenyl)-4-phenyldihydrofuran-2(3H)-one (**3i**).* The reaction was performed following Method A using sulfoxonium salt (*R*)-**2a**, (*S*)-Koga amine **5**, and 2-fluorophenylacetic acid **1e**. **3i** was isolated as a clear oil (35.7 mg, 56%) with a dr = 4:1 as determined by GC−MS analysis of the crude. HPLC analysis: 72% ee [Daicel Chiralpak OD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 13.9 min (minor), 17.8 min (major)]; IR (thin film): 1768, 1493, 1455, 755, 704 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.14−7.08 (m, 4H), 6.94−6.89 (m, 3H), 6.84−6.74 (m, 2H), 4.81−4.73 (m, 2H), 4.57 (d, J = 8.7 Hz, 1H), 4.11−4.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 175.8, 161.1 (d, J = 244 Hz, 1C), 137.5, 130.8 (d, J = 4 Hz, 1C), 129.4 (d, J = 9 Hz, 1C), 128.7, 127.7, 127.7, 124.1 (d, J = 4 Hz, 1C), 121.0 (d, J = 14 Hz, 1C), 115.0 (d, J = 21 Hz, 1C), 71.9, 46.5, 45.5 (d, J = 2 Hz, 1C); MS (EI 70 eV): 256, 211, 197, 136, 108, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{16}H_{14}FO_2^+$: 257.0978; found: 257.0966.

*(−)-(3S,4R)-3,4-Bis(2-methoxyphenyl)dihydrofuran-2(3H)-one (**3j**).* The reaction was performed following Method A using sulfoxonium salt (±)-**2b**, (*R*)-Koga amine **4**, and 2-methoxyphenylacetic acid **1a**. (−)-**3j** was isolated as a clear oil (25.5 mg, 34%) with a dr = 7:1 as determined by GC−MS analysis of the crude. HPLC analysis: 75% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 2% isopropanol in hexane; retention time: 32.6 min (major), 45.3 min (minor)]; $[\alpha]_D^{24}$ = −202.4 (c = 0.17, CH_2Cl_2); IR (thin film): 1770, 1493, 1455, 754, 697 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.08−7.02 (m, 2H), 6.96 (dd, J = 7.6, 1.6 Hz, 1H), 6.81 (dd, J = 7.8, 1.7 Hz, 1H), 6.73 (dt, J = 7.5, 1.0 Hz, 1H), 6.66−6.62 (m, 2H), 6.55 (d, J = 8.2 Hz, 1H), 4.69−4.67 (m, 2H), 4.53 (d, J = 9.7 Hz, 1H), 4.47−4.41 (m, 1H), 3.72 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.8, 157.4, 157.3, 130.3, 128.6, 128.5, 127.9, 126.7, 123.1, 120.3, 120.1, 110.0, 109.8, 71.0, 55.4, 55.0, 45.4, 40.5; MS (EI 70 eV): 298, 280, 223, 148, 119, 91 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{18}H_{19}O_4^+$: 299.1283; found: 299.1278.

*(+)-(3R,4S)-3,4-Bis(2-methoxyphenyl)dihydrofuran-2(3H)-one (**3k**).* The reaction was performed following Method A using sulfoxonium salt (±)-**2b**, (*S*)-Koga amine **5**, and 2-methoxyphenylacetic acid **1a**. (+)-**3k** was isolated as a clear oil (23.0 mg, 31%) with a dr = 7:1 as determined by GC−MS analysis of the crude. HPLC analysis: 68% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 2% isopropanol in hexane; retention time: 33.8 min (minor), 46.6 min (major)]; $[\alpha]_D^{24}$ = +22.8 (c = 0.80, CH_2Cl_2); IR (thin film): 1768, 1494, 1462, 750 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.08−7.02 (m, 2H), 6.96 (dd, J = 7.6, 1.6 Hz, 1H), 6.81 (dd, J = 7.9, 1.7 Hz, 1H), 6.73 (dt, J = 7.5, 1.0 Hz, 1H), 6.66−6.62 (m, 2H), 6.55 (dd, J = 8.2, 0.6 Hz, 1H), 4.69−4.67 (m, 2H), 4.53 (d, J = 9.7 Hz, 1H), 4.47−4.41 (m, 1H), 3.72 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.8, 157.4, 157.3, 130.3, 128.5, 128.5, 127.9, 126.7, 123.0, 120.2, 120.1, 110.0, 109.8, 71.0, 55.4, 55.0, 45.4, 40.5; MS (EI 70 eV): 298, 280, 223, 148, 119, 91m/z; $(M + H)^+$ HRMS m/z calcd for $C_{18}H_{19}O_4^+$: 299.1283; found: 299.1283.

*(−)-(3S,4R)-3-(2-Methoxyphenyl)-4-(3-methoxyphenyl)dihydrofuran-2(3H)-one (**3l**).* The reaction was performed following Method B, but left to stir for 72 h at −25 °C instead of overnight, using sulfoxonium salt (±)-**2c**, (*R*)-Koga amine **4**, and 2-methoxyphenylacetic acid **1a**. (−)-**3l** was isolated as a yellow oil (34.6 mg, 46%) with a dr = 7:1 as determined by GC−MS analysis of the crude; $[\alpha]_D^{24}$ = −87.3 (c = 1.79, CH_2Cl_2); IR (thin film): 1770, 1495, 1463, 1251, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.13−7.09 (m, 1H), 7.03−6.99 (m, 1H), 6.79−6.77 (m, 1H) 6.73−6.61 (m, 2H), 6.62 (dd, J = 8.2, 2.1 Hz, 1H), 6.50 (d, J = 7.6 Hz, 1H), 6.34 (s, 1H), 4.72−4.64 (m, 2H), 4.55 (d, J = 8.8 Hz, 1H), 4.05 (ddd, J = 8.9, 6.7, 4.8 Hz, 1H), 3.71 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.2, 159.5, 157.3, 139.4, 130.3, 129.3, 128.9, 122.5, 120.6, 120.3, 113.5, 113.1, 110.3, 71.8, 55.5, 55.3, 46.4; MS (EI 70 eV): 298, 253, 223, 148, 121, 91 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{18}H_{19}O_4^+$: 299.1283; found: 299.1275.

*(3S,4R)-4-(4-Chlorophenyl)-3-(2-methoxyphenyl)dihydrofuran-2(3H)-one (**3m**).* The reaction was performed following Method A using sulfoxonium salt (±)-**2d**, (*R*)-Koga amine **4**, and 2-methoxyphenylacetic acid **1a**. **3m** was isolated as a clear oil (53.5 mg, 71%) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 64% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 2% isopropanol in hexane; retention time: 30.1 min (major), 32.6 min (minor)]; IR (thin film): 1773, 1494, 1247, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.14−7.10 (m, 1H), 7.06−7.03 (m, 2H), 6.80−6.76 (m, 3H), 6.72−6.69 (m,

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J. Org. Chem. 2017, 82, 606−615

2H), 4.69 (dd, J = 9.4, 6.8 Hz, 1H), 4.60 (dd, J = 9.4, 4.6 Hz, 1 H), 4.54 (d, J = 8.9 Hz, 1 H), 4.06 (ddd, J = 8.9, 6.8, 4.6 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 157.1, 136.4, 133.1, 130.2, 129.2, 129.0, 128.4, 122.1, 120.7, 110.3, 71.5, 55.4, 46.3, 45.7; MS (EI 70 eV): 302, 257, 223, 165, 148, 121, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{16}ClO_3^+$: 303.0788; found: 303.0777.

*(3S,4R)-4-(4-Chlorophenyl)-3-(2-methoxyphenyl)dihydrofuran-2(3H)-one (**3m**).* The reaction was performed following Method A using sulfoxonium salt (*S*)-**2d**, (*R*)-Koga amine **4**, and 2-methoxyphenylacetic acid **1a**. **3m** was isolated as a clear oil (41.9 mg, 55%) with a dr = 6:1 as determined by GC−MS analysis of the crude. HPLC analysis: 85% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 2% isopropanol in hexane; retention time: 29.6 min (major), 32.1 min (minor)]; IR (thin film): 1771, 1494, 1246, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.15−7.10 (m, 1H), 7.06−7.03 (m, 2H), 6.80−6.76 (m, 3H), 6.73−6.69 (m, 2H), 4.70 (dd, J = 9.4, 6.8 Hz, 1H), 4.61 (dd, J = 9.4, 4.6 Hz, 1 H), 4.54 (d, J = 8.9 Hz, 1 H), 4.06 (ddd, J = 8.9, 6.8, 4.6 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 157.1, 136.4, 133.1, 130.2, 129.2, 129.1, 128.4, 122.1, 120.8, 110.3, 71.5, 55.4, 46.3, 45.8; MS (EI 70 eV): 302, 257, 223, 165, 148, 121, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{16}ClO_3^+$: 303.0788; found: 303.0779.

*(3R,4S)-4-(4-Chlorophenyl)-3-(2-methoxyphenyl)dihydrofuran-2(3H)-one (**3n**).* The reaction was performed following Method A using sulfoxonium salt (±)-**2d**, (*S*)-Koga amine **5**, and 2-methoxyphenylacetic acid **1a**. **3n** was isolated as a clear oil (44.2 mg, 58%) with a dr = 5:1 as determined by GC−MS analysis of the crude. HPLC analysis: 57% ee [Daicel Chiralpak AD-H column; 1 mL/min; solvent system: 2% isopropanol in hexane; retention time: 30.2 min (minor), 32.6 min (major)]; IR (thin film): 1770, 1493, 1245, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.15−7.10 (m, 1H), 7.06−7.03 (m, 2H), 6.80−6.76 (m, 3H), 6.73−6.69 (m, 2H), 4.70 (dd, J = 9.4, 6.8 Hz, 1H), 4.60 (dd, J = 9.4, 4.6 Hz, 1 H), 4.54 (d, J = 8.9 Hz, 1 H), 4.06 (ddd, J = 8.9, 6.8, 4.6 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 176.8, 157.1, 136.4, 133.1, 130.2, 129.2, 129.1, 128.4, 122.1, 120.8, 110.3, 71.5, 55.4, 46.3, 45.8; MS (EI 70 eV): 302, 257, 223, 165, 148, 121, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{16}ClO_3^+$: 303.0788; found: 303.0784.

*(+)-(3R,4R)-4-Isopropyl-3-(naphthalen-2-yl)dihydrofuran-2(3H)-one (**3o**).* The reaction was performed following Method C using sulfoxonium salt (±)-**2e**, (*R*)-Koga amine **4**, and 2-naphthylacetic acid **1f**. (+)-**3o** was isolated as a white solid (24.8 mg, 39%, mp 118−120 °C) with a dr = 7:1 as determined by GC−MS analysis of the crude. HPLC analysis: 80% ee [Daicel Chiralpak OD-H column; 1 mL/min; solvent system: 10% isopropanol in hexane; retention time: 14.5 min (minor), 20.2 min (major)]; $[\alpha]_D^{23\,°C}$ = +23.9 (c = 0.51, CH_2Cl_2); IR (thin film): 1769, 1011, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.85−7.80 (m, 3H), 7.72 (d, J = 1.3 Hz, 1H), 7.51−7.48 (m, 2H), 7.30 (dd, J = 8.5, 1.9 Hz, 1H), 4.54−4.52 (m, 1H), 4.32 (t, J = 9.5 Hz, 1H), 4.00 (d, J = 8.7 Hz, 1H), 2.61 (d, J = 9.4 Hz, 1H), 1.38−1.27 (m, 1H), 0.09 (d, J = 6.5 Hz, 3H), 0.79 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 178.0, 133.6, 132.8, 131.8, 128.8, 128.5, 128.1, 127.8, 126.9, 126.7, 126.5, 70.9, 49.8, 48.5, 26.9, 21.8; MS (EI 70 eV): 254, 186, 167, 141, 69 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{19}O_2^+$: 255.1385; found: 255.1376.

*(3R,4R)-3-(2-Methoxyphenyl)-4-phenyldihydrofuran-2(3H)-one (**3aa**).* The reaction was performed following the isomerization procedure using (−)-(3*S*,4*R*)-3-(2-methoxyphenyl)-4-phenyldihydrofuran-2(3*H*)-one **3a** (42.8 mg, 0.16 mmol). **3aa** was isolated as a colorless oil (37.4 mg, 87%), with a dr = 1:14 (favoring the *trans*-isomer), as determined by chiral HPLC analysis of the purified product. HPLC analysis: 78% ee [Daicel Chiralpak AD-H column; 1.5 mL/min; solvent system: 5% isopropanol in hexane; retention time: 15.7 min (major), 19.2 min (minor)]; $[\alpha]_D^{23\,°C}$ = −146.5 (c = 0.55, CH_2Cl_2); IR (thin film): 1774, 1496, 755, 699 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.34−7.19 (m, 6H), 7.01 (dd, J = 7.5, 1.7 Hz, 1H), 6.90−6.85 (m, 2H), 4.76−4.72 (m, 1H), 4.38−4.29 (m, 1H), 4.03−3.94 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.0, 157.4 138.8, 131.0, 129.5, 129.2, 127.8, 127.4, 124.7, 121.2, 111.8, 72.4, 55.8, 50.8, 48.6; MS (EI 70 eV): 268, 223, 193, 165, 148, 115, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_3^+$: 269.1178; found: 269.1167.

*(3S,4S)-3-(2-Methoxyphenyl)-4-phenyldihydrofuran-2(3H)-one (**3bb**).* The reaction was performed following the isomerization procedure using (+)-(3*R*,4*S*)-3-(2-methoxyphenyl)-4-phenyldihydrofuran-2(3*H*)-one **3b** (27.4 mg, 0.10 mmol). **3bb** was isolated as a colorless oil (27.4 mg, >99%) with a dr = 1:24 (favoring the *trans*-isomer) as determined by GC−MS analysis of the crude. The HPLC analysis: 75% ee [Daicel Chiralpak AD-H column; 1.5 mL/min; solvent system: 5% isopropanol in hexane; retention time: 15.4 min (minor), 18.6 min (major)]; $[\alpha]_D^{23\,°C}$ = +175.0 (c = 2.74, CH_2Cl_2); IR (thin film): 1771, 1495, 754, 699 cm^{-1}; ^{1}H (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 7.33−7.19 (m, 6H), 7.01 (dd, J = 7.5, 1.7 Hz, 1H), 6.91−6.85 (m, 2H), 4.75−4.71 (m, 1H), 4.37−4.28 (m, 1H), 4.02−3.94 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 177.0, 157.4, 138.8, 130.9, 129.5, 129.1, 127.8, 127.4, 124.7, 121.1, 111.7, 72.4, 55.8, 50.8, 48.6; MS (EI 70 eV): 268, 223, 193, 165, 148, 115, 91, 77 m/z; $(M + H)^+$ HRMS m/z calcd for $C_{17}H_{17}O_3^+$: 269.1178; found: 269.1175.

General Procedure for Preparation of Ethenyl-Sulfoxonium Salts. *2-(N,N-Dimethyl-S-phenylsulfonimidoyl)-1-Substituted Ethenyl Tetrafluoroborate.* Ethenyl sulfoximines were prepared as previously described by the groups of Johnson and Gais.[6,7] The appropriate ethenyl sulfoximine (~5 mmol, 1 equiv) was dissolved in dichloromethane (16.6 mL, 0.3 M) and cooled to 0 °C. $Me_3O^+BF_4^-$ (1.1−1.8 equiv) was added all at once, and the reaction was stirred vigorously for 4 h. The reaction was analyzed by TLC (20% EtOAc:hexane) for consumption of starting material and quenched with deionized water (~30 mL) if complete. If not complete, the reaction was stirred at room temperature overnight. After quenching, the organic layer was collected and the aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organics were dried with sodium sulfate and filtered. For crystallization: To minimize exposure to water, vapor liquid diffusion was carried out by placing a beaker containing the crude dichloromethane solution inside a screw cap chamber filled with ether, to give a final mixture of ether:-dichloromethane (2:1). The crystallization was allowed to proceed over several days. The crystals were then collected by decanting the filtrate and drying under high vacuum. Amorphous solids would oil out of solution and were dried under high vacuum to yield a foam which could be ground into a powder. Oils were placed under reduced pressure (rotovap) and heated to 50 °C for ~6 h and then placed in a vacuum desiccator overnight.

*(Dimethylamino)-phenyl-(2-phenylvinyl)-oxosulfonium Fluoroborate ((±)-**2a**).* Performed at (5.10 g, 19.7 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h, and then warmed to room temperature overnight. Isolated as white crystals (5.45 g, 77%, mp 131−132 °C).[6c] IR (thin film): 1054 (BF stretch), 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.34−8.32 (m, 2H), 7.98 (d, J = 15.1 Hz, 1H), 7.90−7.79 (m, 6H), 7.56−7.46 (m, 3H), 3.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 154.0, 137.2, 134.2, 131.6, 131.0, 130.9, 130.3, 129.8, 129.4, 115.7, 38.0; (M^+) HRMS m/z calcd for $C_{16}H_{18}NOS^+$: 272.1109; found: 272.1110.

*(S,E)-(Dimethylamino)-phenyl-(2-phenylvinyl)-oxosulfonium Fluoroborate ((S)-**2a**).* Performed at (1.94 g, 7.0 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h. Isolated as a hygroscopic white amorphous solid, which resisted crystallization (1.69 g, 67%). $[\alpha]_D^{24\,°C}$ = −1.32 (c = 7.65, CH_2Cl_2); IR (thin film): 1055 (BF stretch), 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.34−8.32 (m, 2H), 7.99 (d, J = 15.1 Hz, 1H), 7.90−7.79 (m, 6H), 7.56−7.46 (m, 3H), 3.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 154.0, 137.2, 134.2, 131.6, 131.0, 130.9, 130.3, 129.8, 129.4, 115.7, 38.0; (M^+) HRMS m/z calcd for $C_{16}H_{18}NOS^+$: 272.1109; found: 272.1113.

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J. Org. Chem. 2017, 82, 606−615

*(R,E)-(Dimethylamino)-phenyl-(2-phenylvinyl)-oxosulfonium Fluoroborate ((R)-**2a**).* Performed at (1.91 g, 6.9 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h. Isolated as a hygroscopic white amorphous solid, which resisted crystallization (2.19 g, 88%). $[\alpha]_D^{24\circ C}$ = +4.35 (*c* = 6.85, CH_2Cl_2);[6c] IR (thin film): 1057 (BF stretch), 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.34−8.32 (m, 2H), 7.98 (d, *J* = 15.08 Hz, 1H), 7.90−7.79 (m, 6H), 7.57−7.46 (m, 3H), 3.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 154.0, 137.2, 134.2, 131.6, 131.0, 130.9, 130.3, 129.8, 129.4, 115.7, 38.0; (M^+) HRMS *m*/*z* calcd for $C_{16}H_{18}NOS^+$: 272.1109; found: 272.1111.

*(Dimethylamino)-phenyl-(2-methoxyphenyl-2-vinyl)-oxosulfonium Fluoroborate ((±)-**2b**).* Performed at (1.88 g, 6.56 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h, and then warmed to room temperature overnight. A portion of (±)-**2b** was crystallized by dissolving in minimal hot EtOAc and adding to ether (50 mL), open to air. The resulting solid was dissolved in minimal dichloromethane, dried with sodium sulfate, and recrystallized through vapor liquid diffusion of ether into dichloromethane to yield a pale yellow solid (1.97 g, >95%, 25% recrystallized, mp 123−124 °C). IR (thin film): 1051 (BF stretch), 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.35−8.32 (m, 2H), 8.07−7.98 (m, 2H), 7.87−7.77 (m, 3H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53−7.49 (m, 1H), 7.04 (*t*, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 3.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 160.4, 149.0, 136.8, 135.9, 133.4, 131.5, 130.8, 129.4, 121.4, 120.1, 115.6, 111.7, 56.1, 37.9; (M^+) HRMS *m*/*z* calcd for $C_{17}H_{20}NO_2S^+$: 302.1215; found: 302.1212.

*(Dimethylamino)-phenyl-(3-methoxyphenyl-2-vinyl)-oxosulfonium Fluoroborate ((±)-**2c**).* Performed at (1.45 g, 5.0 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h, and then warmed to room temperature overnight. Isolated as yellow crystals (1.55 g, 80%, mp 164−165 °C). IR (thin film): 1057 (BF stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.34−8.31 (m, 2H), 8.01 (d, *J* = 15.0 Hz, 1H), 7.91−7.79 (m, 4H), 7.49−7.48 (m, 1H), 7.37−7.33 (m, 1H), 7.24−7.22 (m, 1H), 7.11−7.08 (m, 1H), 3.92 (*s*, 3H), 3.14 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 160.8, 154.0, 137.2, 132.2, 131.6, 130.5, 130.3, 129.4, 124.7, 122.4, 115.5, 112.4, 56.1, 38.0; (M^+) HRMS *m*/*z* calcd for $C_{17}H_{20}NO_2S^+$: 302.1215; found: 302.1208.

*(Dimethylamino)-phenyl-(4-chlorophenyl-2-vinyl)-oxosulfonium Fluoroborate ((±)-**2d**).* Performed at (1.75 g, 6.0 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h, and then warmed to room temperature overnight. Isolated as pale yellow crystals (1.93 g, 78%, mp 174−175 °C). IR (thin film): 1032 (BF stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.33−8.31 (m, 2H), 8.00 (d, *J* = 15.1 Hz, 1H), 7.90−7.75 (m, 6H), 7.47−7.45 (m, 2H), 3.14 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 152.4, 140.6, 137.3, 132.1, 131.6, 130.2, 130.0, 129.4, 129.4, 116.3, 38.0; (M^+) HRMS *m*/*z* calcd for $C_{16}H_{17}ClNOS^+$: 306.0719; found: 306.0718.

*(S,E)-(Dimethylamino)-phenyl-(4-chlorophenyl-2-vinyl)-oxosulfonium Fluoroborate ((S)-**2d**).* Performed at (2.28 g, 7.8 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h, and then warmed to room temperature overnight. Isolated as a hygroscopic pale yellow amorphous solid, which resisted crystallization (2.38 g, 78%); $[\alpha]_D^{24\circ C}$ = +47.9 (*c* = 3.05, CH_2Cl_2); IR (thin film): 1032 (BF stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.32−8.30 (m, 2H), 8.00 (d, *J* = 15.1 Hz, 1H), 7.92−7.75 (m, 6H), 7.46−7.44 (m, 2H), 3.14 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 152.4, 140.6, 137.3, 132.1, 131.6, 130.2, 130.1, 129.5, 129.4, 116.3, 38.0; (M^+) HRMS *m*/*z* calcd for $C_{16}H_{17}ClNOS^+$: 306.0719; found: 306.0718.

*(R,E)-(Dimethylamino)-phenyl-(4-chlorophenyl-2-vinyl)-oxosulfonium Fluoroborate ((R)-**2d**).* Performed at (2.34 g, 8.0 mmol) scale using 1.8 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h, and then warmed to room temperature overnight. Isolated as a hygroscopic pale yellow amorphous solid, which resisted crystallization (2.35 g, 75%); $[\alpha]_D^{24\circ C}$ = −27.4 (*c* = 2.58, CH_2Cl_2); IR (thin film): 1032 (BF stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.33−8.31 (m, 2H), 8.00 (d, *J* = 15.1 Hz, 1H), 7.89−7.75 (m, 6H), 7.47−7.45 (m, 2H), 3.14 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 152.4, 140.6, 137.3, 132.1, 131.7, 130.2, 130.1, 129.5, 129.4, 116.3, 38.0; (M^+) HRMS *m*/*z* calcd for $C_{16}H_{17}ClNOS^+$: 306.0719; found: 306.0715.

*(Dimethylamino)-phenyl-(2-isopropylvinyl)-oxosulfonium Fluoroborate ((±)-**2e**).* Performed at (1.25 g, 5.6 mmol) scale using 1.1 equiv of $Me_3O^+BF_4^-$, stirred at 0 °C for 4 h. Isolated as a clear yellow oil (1.83 g, >95%). Occasionally, a plug column was used to purify by removing impurities with ether, and collecting the pure salt using dichloromethane. IR (thin film): 1031 (BF stretch), 947 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) for the major diastereomer: δ 8.27−8.24 (m, 2H), 7.93−7.88 (m, 1H), 7.83−7.79 (m, 2H), 7.42−7.32 (m, 2H), 3.09 (s, 6H), 2.89−2.81 (m, 1H), 1.18 (dd, *J* = 12.0, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major diastereomer: δ 166.4, 137.3, 131.6, 129.8, 129.4, 37.9, 32.7, 20.8, 20.8; (M^+) HRMS *m*/*z* calcd for $C_{13}H_{20}NOS^+$: 238.1266; found: 238.1266.

Determination of Relative and Absolute Stereochemistry. **3g**, from an (*S*)-Koga amine **5**-controlled reaction, was crystallized from isopropanol to provide a sample suitable for X-ray crystallographic analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02622.

Spectroscopic data, and chromatograms for all new compounds (PDF)

X-ray crystallographic data for **3g** (CIF)

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Notes

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