Iron(III)-mediated Oxy-sulfonylation of enamides with sodium and lithium sulfinates

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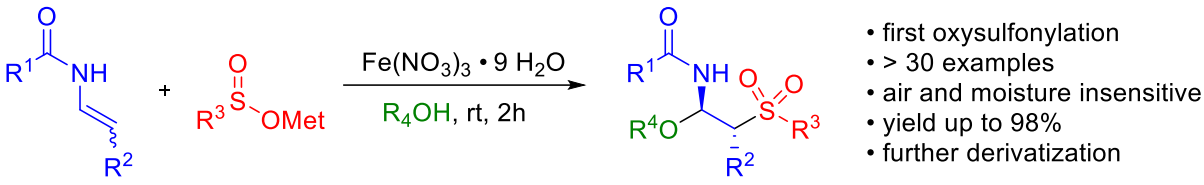


Abstract

An iron-mediated vicinal difunctionalization of enamides and enecarbamates with sulfinic acid salts and alcohols is described. This reaction proceeds under mild conditions and furnishes the oxy-sulfonylated products in moderate to excellent yields. Moreover, the direct incorporation of sulfur dioxide into the sulfonylated products via organolithium chemistry has been achieved. The formed *N*-*O*-acetals are competent acylimine precursors. Their utilization as building block for the synthesis of biologically relevant β-amidosulfones is described as well.

Introduction:

Molecules bearing sulfonyl-derived functional groups, such as sulfones or sulfonamides, play an important role in organic chemistry and are widely used in various fields.[1,2] Among the different classes of sulfonyl-derived functional groups, sulfones are of particular interest. They display intriguing chemical and physical properties as well as interesting biological activities. Sulfones, which are often considered as chemical chameleons[3], are versatile building blocks in organic synthesis. The sulfone motif can be found in various molecules with different applications ranging from agrochemcials and functional materials to active pharmaceutical ingredients.[2-4] Traditional approaches for the construction of sulfones include Friedel-Crafts type reactions of arenes with sulfonyl chlorides[5], the oxidation of sulfides and sulfoxides[6], addition reactions of sulfonyl radicals to alkenes and alkynes[7] or the electrophilic trapping of sulfinic acid salts[8,9]. In the last ten years novel approaches based on the direct incorporation of sulfur dioxide[10, 11] or the functionalization of C-H bonds[12,13] have emerged as attractive and more sustainable alternatives.

Among the different types of sulfones, the β-amidosulfone motif represents an important scaffold. β-Amidosulfones are versatile building blocks for the synthesis of alkaloids[14], carbohydrates[15] or amino acids[16] and this structural unit can be found in various pharmaceuticals. Selected examples are cystemustine[17], a potential cure for glioma and melanoma, the MDM2 Inhibitor AMG 232[18], the benzodiazepine Elfazepam[19], or the PDE4 inhibitor Apremilast[20], which is used for the treatment of psoarisis (Figure 1).

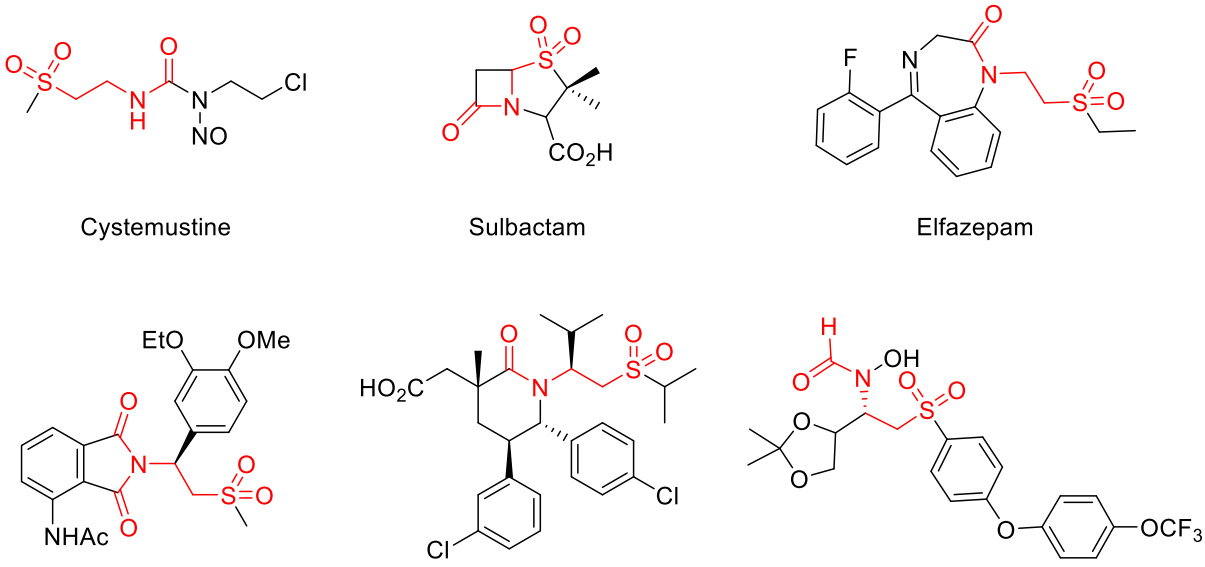


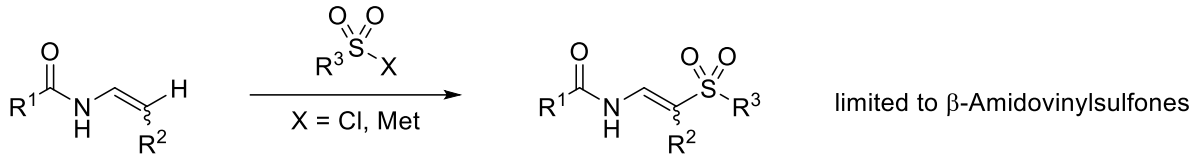
Figure 1 Biologically active β-amidosulfones

In the last years several groups have reported different methods for the synthesis of β-amidovinyl sulfones via a direct C-H-sulfonylation of enamides (Scheme 1a).[21, 22] These amidovinyl sulfones are useful molecules for the construction of the β-amido sulfone structure. However, an additional step for the synthesis of the desired product is necessary.

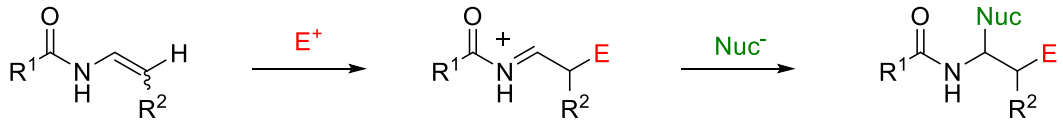
Enamides are versatile building blocks and the direct di-functionalization (Scheme 1b) of these electron-rich olefins gives rise to various highly functionalized scaffolds.[23, 24] Although various methods for the amino- and halo-oxygenation[25] as well as the dioxygenation[26] of enamides and enecarbamates have been described, there is so far, to the best of our knowledge, no analogous oxysulfonylation. Such a process would provide an alternative, highly modular access to the β-amido sulfone unit.

Herein we report an iron-mediated oxysulfonylation of enamides using sodium or lithium sulfinates and alcohols. This novel method gives access to a new class of β-amidosulfones. A further diversification of the obtained products is described as well.

a.) Previous work



b.) Typical reactivity of enamides

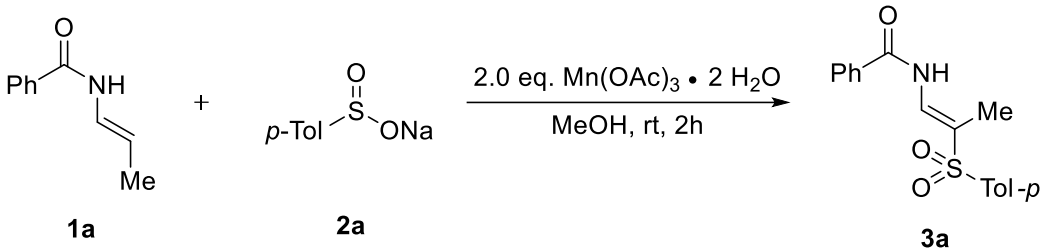


Scheme 1 Previous and typical reactivity of enamides. E^+ = electrophile; Nuc^- = Nucleophile.

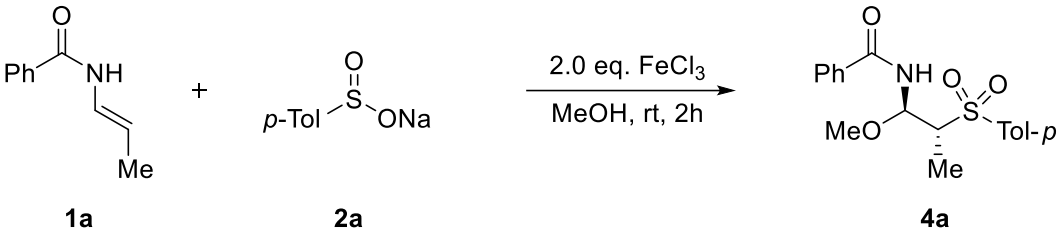
Results and Discussion

During our investigations on the $Mn(OAc)_3$-promoted C-H-sulfonylation of enamides[22], we made an interesting observation (Scheme 2). Whereas the reaction of *p*-toluenesulfinate **2a** with the (*E*)-configured enamide **1a** in MeOH in the presence of $Mn(OAc)_3$ afforded the (*E*)-vinyl sulfone **3a** in 84% yield, the formation of the oxysulfonylation product **4a** with incorporation of MeOH was observed in the presence of $FeCl_3$.

a.) Previous work



b.) This work

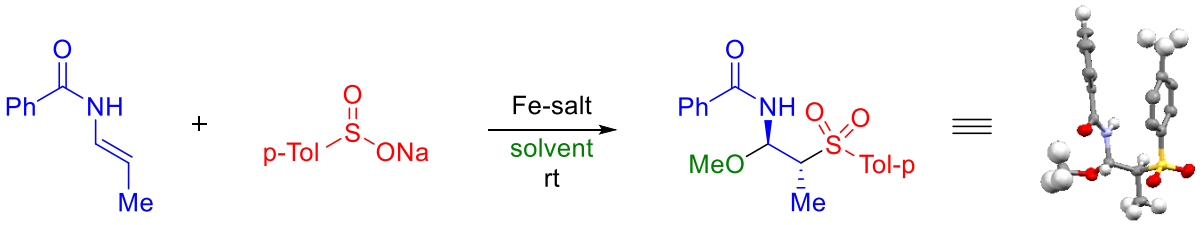


Scheme 2 Previous manganese-mediated C-(sp2) functionalisation and a unprecedented iron-mediated oxysulfonylation. The diastereomeric ratio(dr) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.

Since the direct oxysulfonylation of enamides has not been reported so far, we decided to further investigate this interesting transformation. As mentioned above, the reaction in the presence of anhydrous $FeCl_3$ afforded β-amidosulfone **4a** in 45% yield and a diastereomeric ratio of approx. 4:1 (entry 1). The structure of the major diastereomer could be unambiguously assigned by single X-ray crystallography.[27] The use of $FeCl_3 \cdot 6H_2O$ led to an improved yield of 64% (entry 2). No product formation was observed in the presence of iron(II) chloride (entry 3). In the presence of $Fe(ClO_4)_3$ only 24% of the desired product could be isolated (entry 4). Surprisingly, the use of $Fe(NO_3)_3 \cdot 9\ H_2O$ led the rapid formation of amidosulfone **4a** in 91% yield within only two hours at room temperature (entry 5). The use of iron salts bearing more strongly coordinating anions, such as $Fe(acac)_3$, has a detrimental effect on the reaction (entry 6). Two equivalents of the iron(III) salt are necessary for an efficient transformation. Decreasing the amount of $Fe(NO_3)_3 \cdot 9\ H_2O$ to only one equivalent led to almost complete shutdown of the reaction (entry 7). All our attempts to substitute $Fe(NO_3)_3 \cdot 9\ H_2O$ at least partially with a cooxidant, such as $NaIO_4$ or IBX, did not afford the desired product in acceptable yields (entry 8). In contrast, lowering the amount of the sulfinate salt did only slightly affect the isolated yield (entry 9 & 10). Typically, all reactions were performed without any effort the exclude air or moisture. Interestingly, a control reaction performed under an atmosphere of nitrogen afforded the amidosulfone **4a** in only 66% yield, indicating a positive effect of oxygen on the reaction efficiency.

MeOH is the solvent of choice for this transformation. The use of other solvents together with only 20 equivalents of MeOH led to the formation of product **4a** in low to moderate yields (entry 11). Slightly acidic conditions seem to be optimal for this process. The addition of any buffering or basic additive, e.g. NaOAc, led to a sharp decrease in the isolated yield (entry 13).

Table 1: Optimization of the reaction conditions



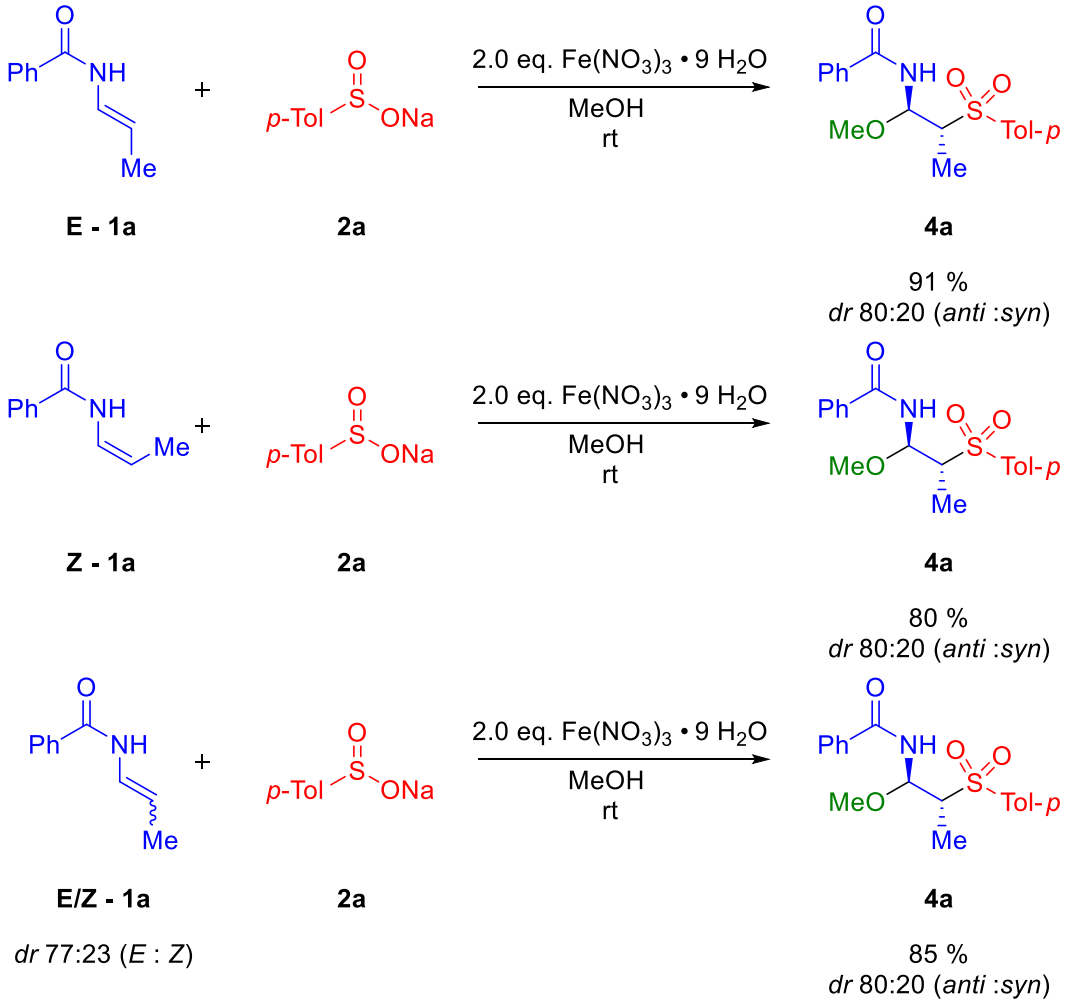
1a **2a** **4a**

Entry	Mediator (equiv)	Additiv (equiv)	Solvent	Time (h)	Yield[a]	*dr*[b]
1	$FeCl_3$ (2.0)	-	MeOH	24	45%	78:22
2	$FeCl_3 \cdot 6\ H_2O$ (2.0)	-	MeOH	24	64 %	76:24
3	$FeCl_2 \cdot 4\ H_2O$ (2.0)	-	MeOH	24	-	-
4	$Fe(ClO_4)_3 \cdot H_2O$ (2.0)	-	MeOH	24	32%	42:58
5	**$Fe(NO_3)_3 \cdot 9\ H_2O$ (2.0)**	**-**	**MeOH**	**2**	**91%**	**80:20**
6	$Fe(acac)_3$ (2.0)	-	MeOH	24	-	-
7	$Fe(NO_3)_3 \cdot 9\ H_2O$ (1.0)	-	MeOH	24	7%	80:20
8	$Fe(NO_3)_3 \cdot 9H_2O$ (1.0)	$NaIO_4$ (4.0), IBX (4.0	MeOH	24	0-55%	-
9[c]	$Fe(NO_3)_3 \cdot 9H_2O$ (2.0)	-	MeOH	2	75%	80:20
10[d]	$Fe(NO_3)_3 \cdot 9H_2O$ (2.0)	-	MeOH	2	71%	80:20
11[e]	$Fe(NO_3)_3 \cdot 9H_2O$ (2.0)	-	MeOH	2	66 %	61:39
12	$Fe(NO_3)_3 \cdot 9H_2O$ (2.0)	MeOH (20)	DCM, EtOAc, Aceton, THF, MeCN	2	20 – 50%	
13	$Fe(NO_3)_3 \cdot 9H_2O$ (2.0)	NaOAc (2.0)	MeOH	2	23 %	75:25

Reaction conditions unless otherwise specified: Oxidant (2.0 equiv.), sulfinate salt (2.0 equiv.), solvent (2 mL), 2 h, rt. [a] Overall isolated yield after column chromatography. [b] the diastereomeric ratio(*dr*) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up. [c] 1.5 equiv. of the sulfinate salt were used. [d] 1.1 equiv. of the sulfinate salt were used. [e] under nitrogen atmosphere. Structure of **4a** in the solid state (Aromatic H atoms omitted for clarity).

In the next step we investigated the reaction of the corresponding (*Z*)-configured enamide **1a** under the optimized reaction conditions (Scheme 2). Interestingly the desired β-amidosulfone **4a** could be obtained in 80% yield and a similar diastereomeric ratio of 4:1. A mixture of both configurational isomers of the enamide afforded amidosulfone **4a** in 85% yield with no changes in the observed diastereoselectivity. This reactivity allows for a considerable simplification of our method in terms of practicability. The nickel-catalyzed isomerization of allylamides **5a**, one of the most efficient approaches for the preparation of the required enamides, typically affords a difficult-to-separate

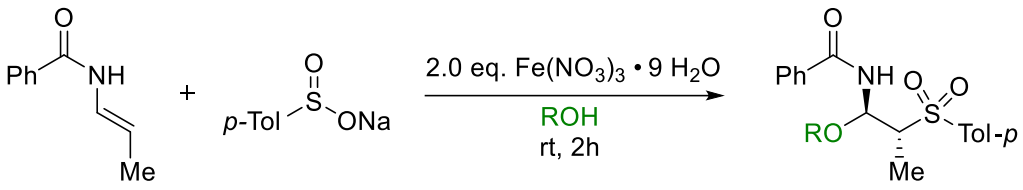
mixture of the (*E*)- and the (*Z*)-enamide.[28] Since the configuration of the enamide double bond does not significantly affect the outcome of the oxysulfonylation reaction, these (*E*/*Z*)-mixtures could be used directly for all further investigations.



Scheme 3 Reactivity of different geometrical isomers in the oxy-sulfonylation. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.

With the optimized reactions conditions at hand, we started to explore the substrate scope of this process.

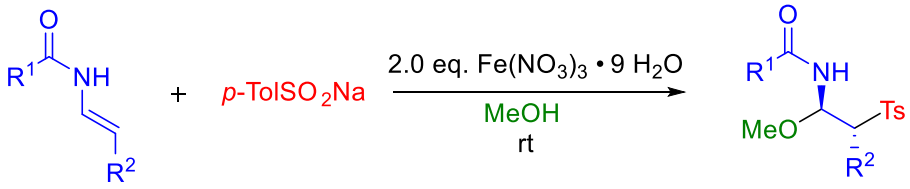
At first, reactions with different alcohols were investigated. Replacement of MeOH as solvent with other aliphatic alcohols, such as EtOH or *i*PrOH, delivered the expected β-amidosulfones **4b** & **4c** in slightly lower yields of 53% and 31% and a comparable *diastereomeric ratio* of 4:1 (Scheme 4). Fluorinated alcohols such as trifluoroethanol or 1,1,1,3,3,3-hexafluoroisopropan-2-ol (HFIP), proved to be not suitable for this reaction.



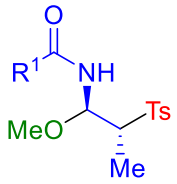
1a **2a** **4**

4b R = Et 53% *dr* 80:20
4c R = *i*Pr 31% *dr* 81:19
4d R = CF_3CH_2 -% (*decomposition*)
4e R = $(CF_3)_2CH$ -% (*decomposition*)

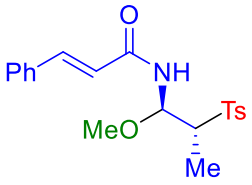
Scheme 4: Scope of alcohols. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^1H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.



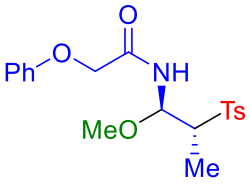
1 **2a** **4**



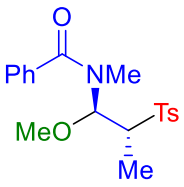
4f R^1 = *p*-Tol 64% *dr* 81:19
4g R^1 = Mesityl 63% *dr* 62:38
4h R^1 = 4-MeO-Ph 68% *dr* 80:20
4i R^1 = 4-F-Ph 62% *dr* 81:19
4j R^1 = 4-CF_3-Ph 61% *dr* 80:20
4k R^1 = 2-Thienyl 68% *dr* 83:17
4l R^1 = *t*Bu 72% *dr* 88:12
4m R^1 = $PhCH_2$ 70% *dr* 62:38



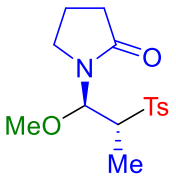
4n 62% *dr* 64:36



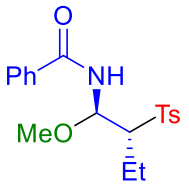
4o 70% *dr* 65:35



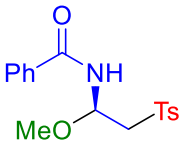
4p 40% *dr* >98:2



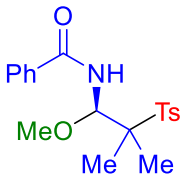
4q 60% *dr* 89:11



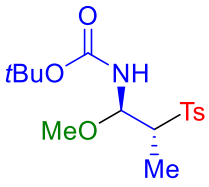
4r 77% *dr* 75:25



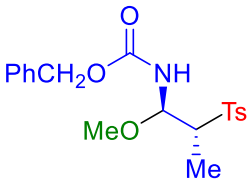
4s 67%



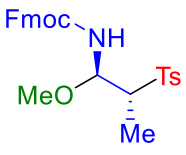
4t 43%



4u 40% *dr* 46:54



4v 44% *dr* 45:55



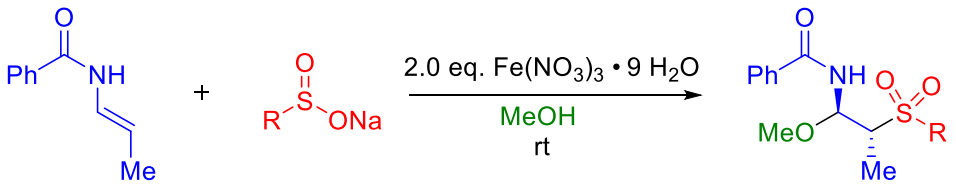
4w 43% *dr* 48:52

Scheme 5 Substrate scope with (E/Z)-mixture of enamide and enecarbamates. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.

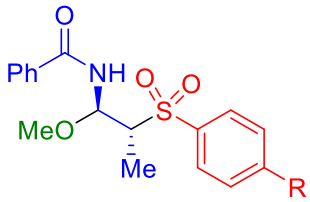
Subsequently we studied the oxysulfonylation of different enamides (Scheme 5). Various benzamide-derived enamides bearing both, electron donating and electron withdrawing groups provided the amidosulfones **4f**-**i** in 61 – 68% yield with similar diastereomeric ratios. Furthermore, reactions of heteroaryl- or alkylamide-derivatives afforded the compounds **4k**-**m** in 68 – 72% yield. Olefins or oxygen-substituents in the enamide side-chain were tolerated and the corresponding products **4n** and **4o** could be isolated in 62% and 70% yield with a decreased diastereoselectivity of 1.8:1.

In contrast to the previous reports on the C-H-sulfonylation of enamides, this transformation is less sensitive towards structural modifications on the enamide core. Our protocol is suitable for tertiary enamides without a free N-H-functionality, providing the sulfonylated *N*,*O*-acetals **4p** and **4q** in 40% and 60%. Modification of the olefin-moiety is also possible and the ethyl- as well as the un- or disubstituted products **4r**-**t** could be accessed in 43-77% yield. Moreover, encearbamates are suitable starting materials for this reaction. Although the desired *N*-protected β-aminosulfones **4u**-**w** were only formed in 40-44% yield and a diastereomeric ratio of roughly 1:1, the introduction of common Boc, Cbz, or Fmoc-protecting groups can be highly useful for subsequent transformations.

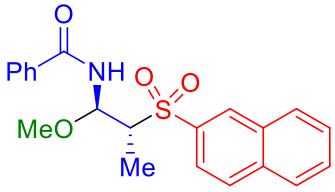
Next, we investigated reactions of different sulfinic acid sodium salts (Scheme 6). Aromatic sulfinates bearing different functional groups performed satisfactorily under the standard reaction conditions, affording the β-amidosulfones **6a**-**h** in 48-68% yield. Both electron-withdrawing (**6d** & **6h**) or electron-donating (**6b** & **6c**) as well as halogen-substituents **6f** & **6g** were well tolerated. Only in the case of the 2-naphthyl sulfinic acid sodium salt, the desired amidosulfone **6i** was obtained in only 22% yield. To our delight the methylsulfone **6j** could be synthesized in 54% with a diastereoselectivity of 6:1 from the corresponding methyl sulfinate **2k**. Unfortunately, reactions with heteroaromatic sulfinates, e.g. pyridine sulfinate **2l**, or sodium trifluoromethane sulfinate **2m** did not afforded the desired products. In these cases, only the MeOH-addition product **7** was obtained.



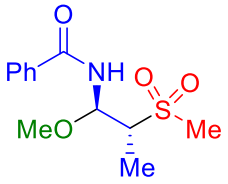
1a **2** **6**



6a R = H 68% *dr* 80:20
6b R = *t*Bu 68% *dr* 81:19
6c R = MeO 51% *dr* 81:19
6d R = NO_2 48% *dr* 79:21
6e R = F 61% *dr* 79:21
6f R = Cl 59% *dr* 80:20
6g R = Br 52% *dr* 80:20
6h R = CF_3 64% *dr* 79:21

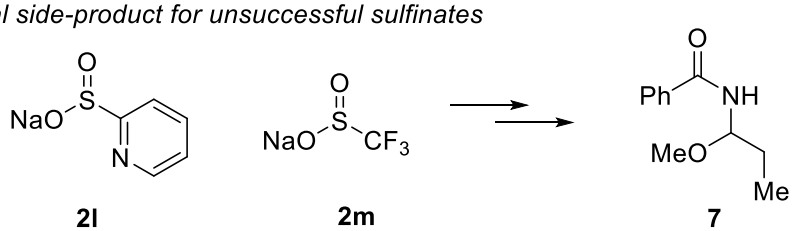


6i 22% *dr* 79:21



6j 54% *dr* 86:14

typical side-product for unsuccessful sulfinates

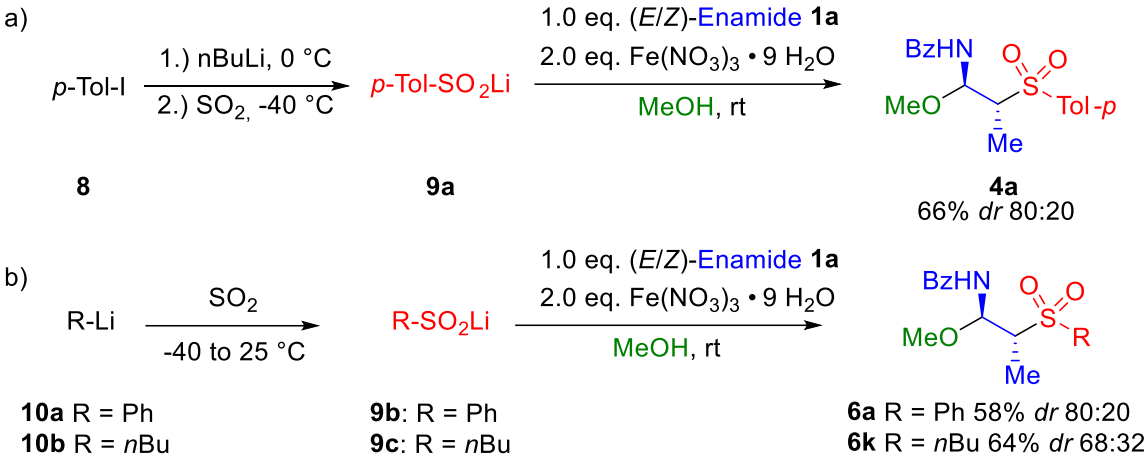


2l **2m** **7**

Scheme 6: Scope of different sodium sulfinic acid sulfonates. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.

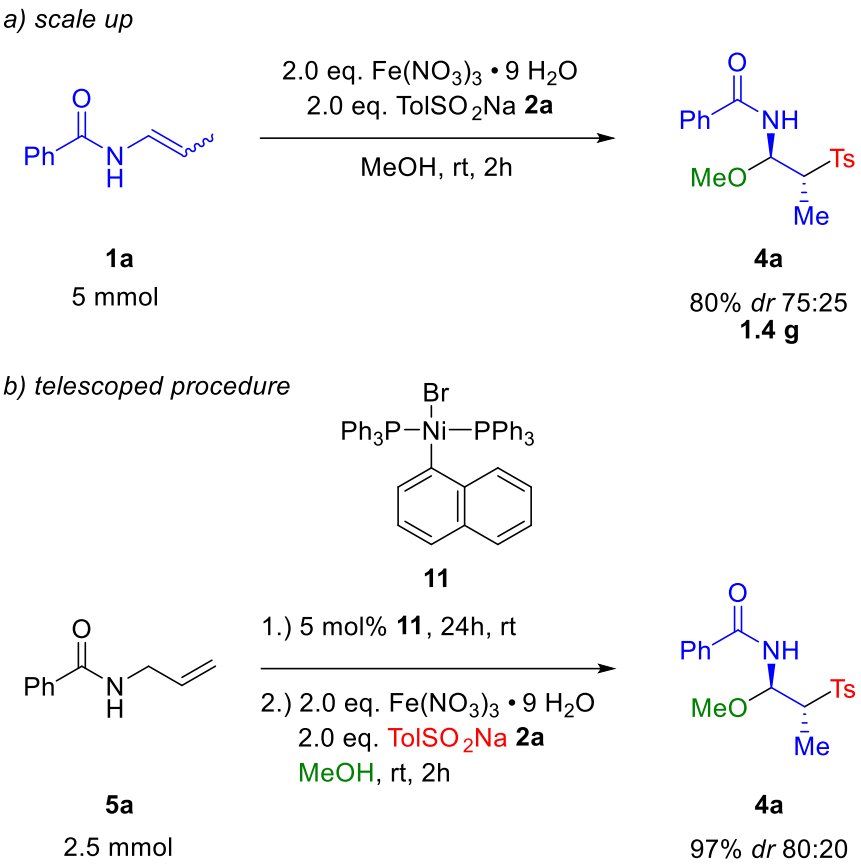
A common drawback of all methods based on sulfinic acid sodium salts is their limited commercial availability. One approach to circumvent this problem is the use of the corresponding lithium salts. Lithium sulfinates can be easily accessed by the reaction of organolithium compounds with sulfur dioxide.[24, 29] In order to explore their potential utilization, we synthesized several lithium sulfinates. Lithium *p*-toluene sulfinate **9a** was prepared in two steps from the 4-iodotoluene **8** via lithium-halide exchange and trapping with sulfur dioxide (Scheme 7a). The sulfinic acid salts **9b** and **9c** could be prepared from sulfur dioxide and the commercially available reagents phenyllithium **10a** and *n*-butyllithium **10b**. To our delight, all three crude lithium sulfinates **9a**-**c** are suitable starting materials for our oxysulfonylation process. The desired amidosulfones were obtained in 58-68% yield with a *dr* of 4:1 for the arylsulfones **4a** and **6a** and 2:1 for the alkylsulfone **6k**. These results exemplify, that the

β-amidosulfone scaffold can be accessed from simple building blocks and sulfur dioxide via classical organolithium chemistry.



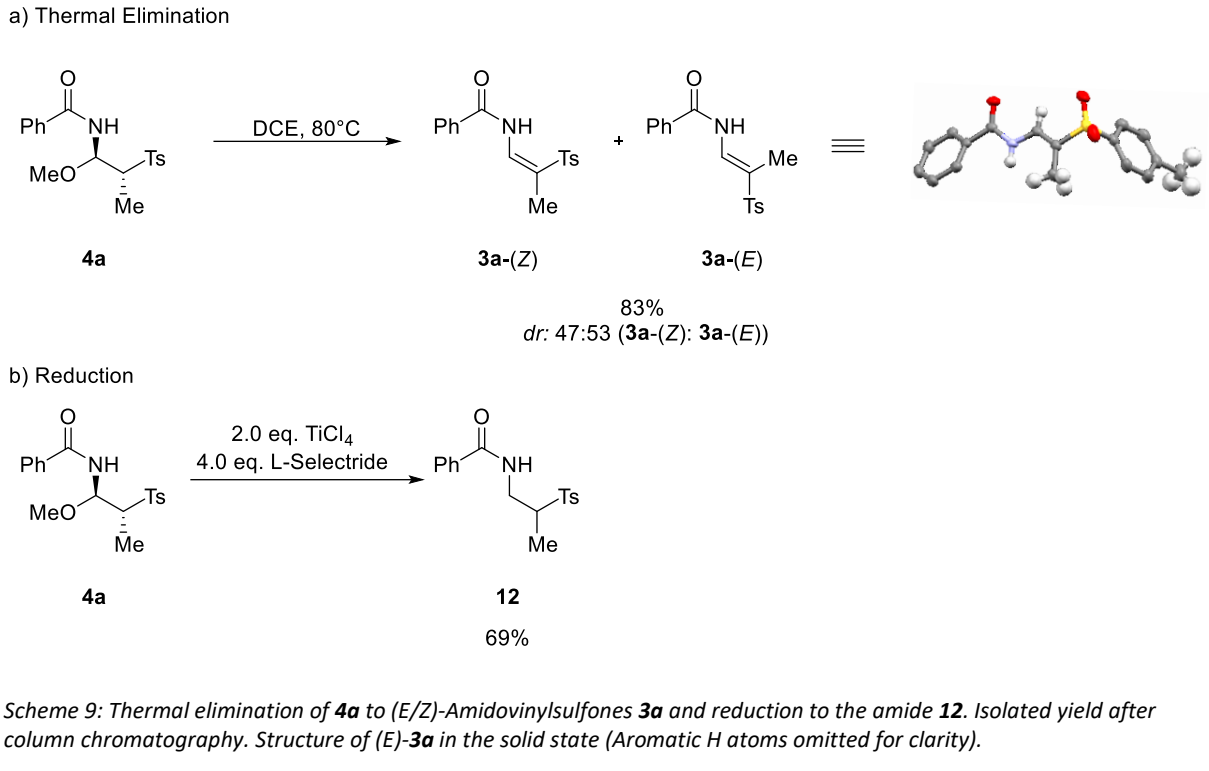
Scheme 7: Preparation of lithium sulfinates and the addition to enamides. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.

Since the formed *N*,*O*-acetals are stable acylimine precursors, we decided to investigate further transformations exploiting the labile hemiaminal functionality using **4a** as model compound. In order to study this reactivity, we needed access to substantial amounts of **4a** (Scheme 8). Gratifyingly, the reaction of a (*E*/*Z*)-mixture of enamide **1a** with *p*-toluenesulfinate **2a**, performed on a 5 mmol scale, afforded 1.4 g of the desired product **4a** (80% yield). In order to provide a more direct approach to the *N*,*O*-acetal **4a**, we studied a one-pot transformation of the parent allylamide **5a**. After the nickel-catalyzed isomerization of allylamide **5a**, the formed (*E*/*Z*)-mixture of enamide **1a** was not isolated. Instead, sulfinate **2a** and $Fe(NO_3)_3 \cdot 9\ H_2O$ were directly added to the reaction mixture, affording the desired *N*,*O*-acetal **4a** in 97% overall yield. This telescoped one-pot process offers a simple and fast access to various β-amido sulfones of type **4**.



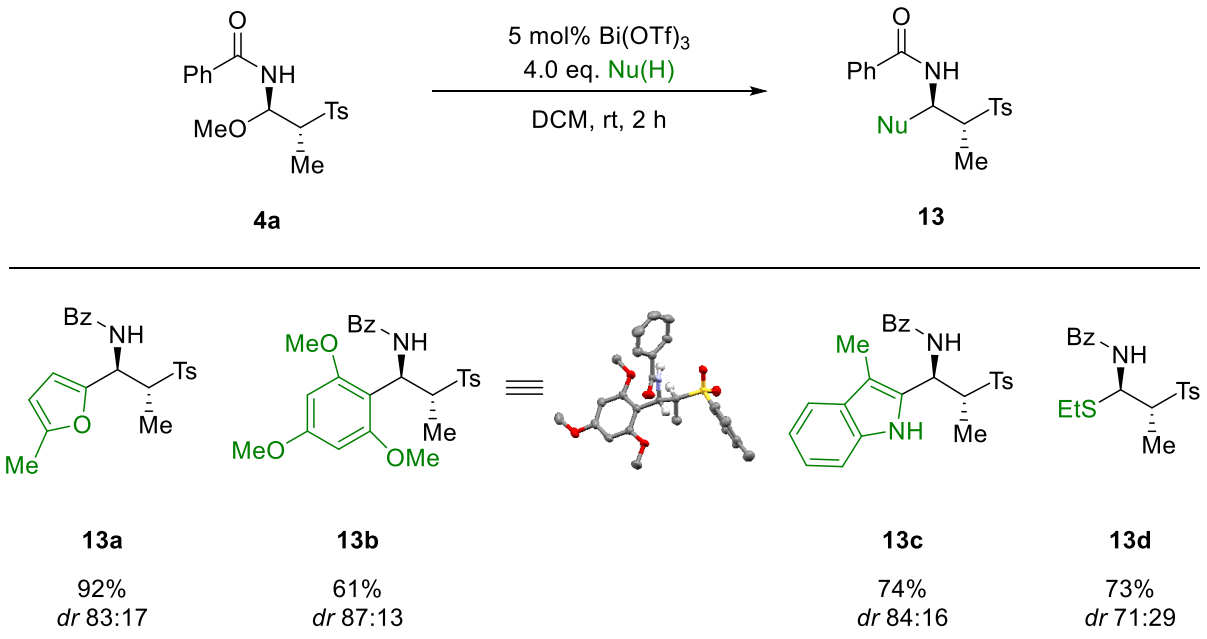
*Scheme 8 Synthesis of ß-amidosulfones **4a** on a large scale and via a one-pot-isomerisation-oxysulfonylation process. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up.*

With sufficient quantities of **4a** in hand, we started to investigate further transformations based on the labile hemiaminal functionality (Scheme 9). Although treatment of **4a** with a base did not lead to any reaction, simple heating in DCE afforded a mixture 1.1:1 mixture of the (*E*)- and the (*Z*)-amidovinylsulfone **3a** in 83% overall yield.[27] Reduction of **4a** with L-Selectride in the presence of $TiCl_4$ afforded amide **12** in 69% yield.



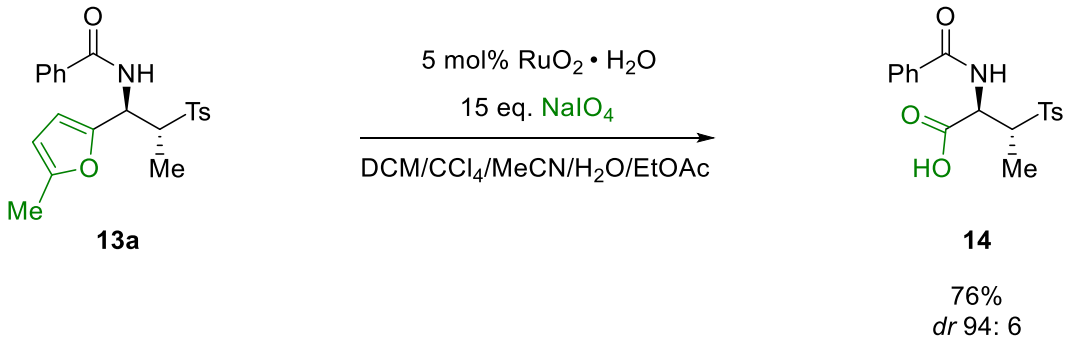
*Scheme 9: Thermal elimination of **4a** to (E/Z)-Amidovinylsulfones **3a** and reduction to the amide **12**. Isolated yield after column chromatography. Structure of (E)-**3a** in the solid state (Aromatic H atoms omitted for clarity).*

Interestingly, *N*,*O*-acetal **4a** underwent efficient reactions with different electronrich (hetero)arenes in the presence of 5 mol% $Bi(OTf)_3$[30,31] leading to the formation of the three amidoalkylation products **13a**-**d** in 61-92 % yield (Scheme 10). In all cases, the shown *anti*-diastereomer was formed as major isomer with a high degree of diastereoselectivity. The relative configuration of the major diastereomer of **13b** could be assigned unambiguously by single X-ray crystallography.[27] Reaction with ethanethiol afforded the *N*,*S*-acetal **13d** in 73% yield.



*Scheme 10 Reactivation of the acylimine with $Bi(OTf)_3$. Isolated yield after column chromatography. The diastereomeric ratio(dr) was determined by ^1H NMR spectroscopic analysis of the crude reaction mixture after aqueous work up. Structure of **13b** in the solid state (Aromatic and methyl H atoms omitted for clarity).*

The amidoalkylation products **13a-d** represent interesting molecular scaffolds and can be useful building blocks for the synthesis of biologically active targets. For instance, the oxidative cleavage of the furan residue in compound **13a** provided the α-amino-acid derivative **14** in 76% yield with retention of stereochemistry (scheme 11).

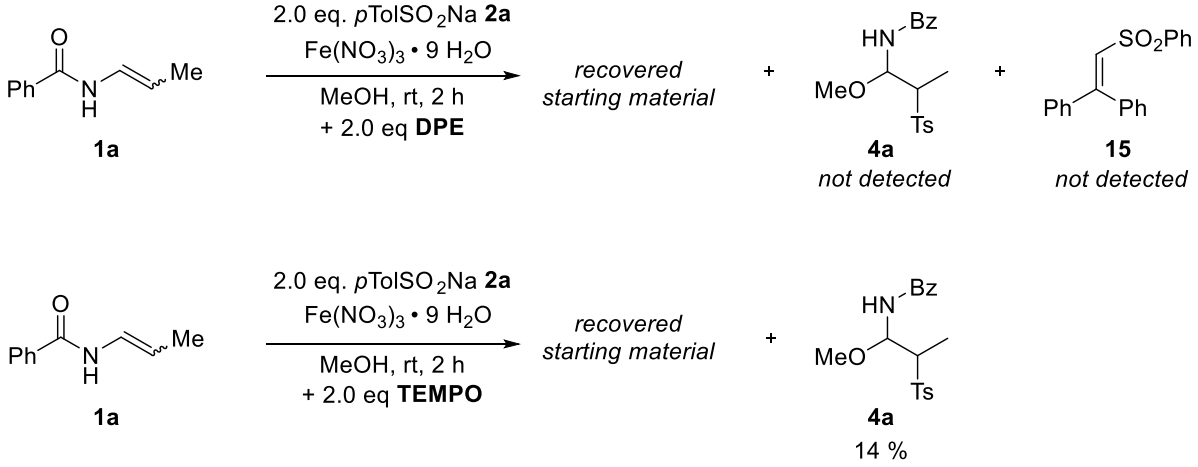


*Scheme 11 Preparation of sulfonated α-amino-acid derivative **14**. Isolated yield after column chromatography.*

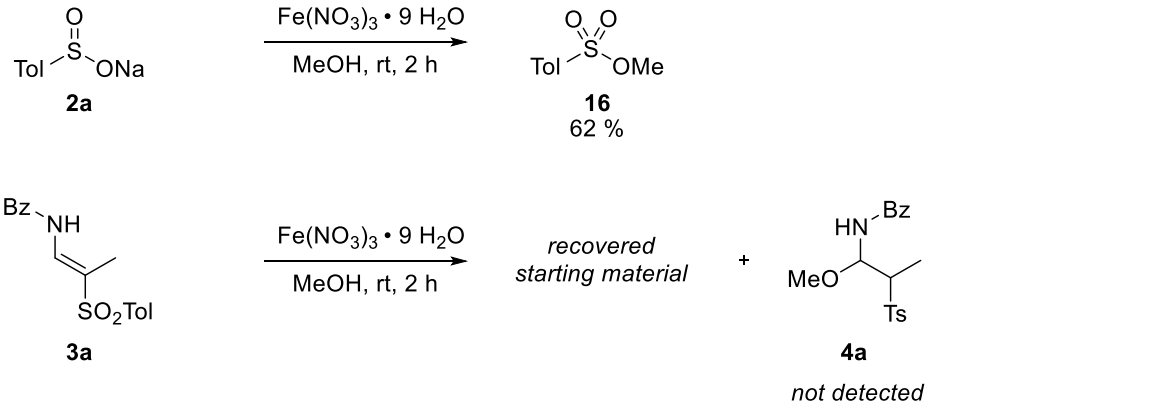
In order to gain some more insights into the reaction mechanism, a series of control experiments was performed. The addition of radical inhibitors such as DPE (1,1-diphenylethylene) or TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) led to a significantly reduced yields or a complete shutdown of the reaction, indicating the involvement of radical processes. However, no trapping products such as **15**, a common product in reactions involving sulfonyl radicals, could be detected via ^1H NMR or MS.

Interestingly the reaction of sulfinate salt **2a** with $Fe(NO_3)_3 \cdot 9\ H_2O$ in MeOH in the absence of an enamide afforded the sulfonic acid ester **16** in 62% yield. Such products are typically formed from highly electrophilic, cationic sulfonyl species.[32] As the incorporation of MeOH into the final product of type **4** could also occur in a secondary acid-catalyzed addition to an initially formed amidovinyl sulfone, we treated vinyl sulfone **3a** with MeOH in the presence of 2 equivalents of $Fe(NO_3)_3 \cdot 9\ H_2O$. No product formation was observed in this case and the enamide could be recovered almost quantitatively after two hours.

a) radical inhibitors

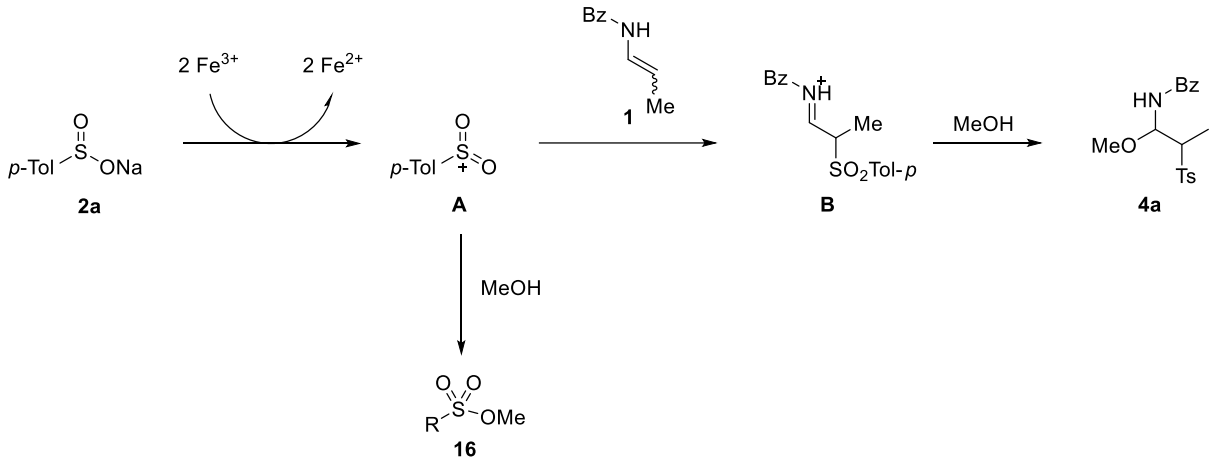


b) further mechanistic studies



Scheme 12 Mechanistic experiments.

Based on these results and previous studies on the radical C-H-sulfonylation of enamides, we assume a ionic reaction mechanism as shown in scheme 13 is. First, the sulfinate is oxidized to the cationic sulfur species **A**. This highly electrophilic species adds to the nucleophilic enamide, furnishing the acyliminium ion **B**. This reactive intermediate is immediately trapped by MeOH. In the absence of the enamide, a direct reaction of **A** with MeOH leads to the formation of the sulfonate **16** (Scheme 13).



Scheme 13 Proposed reaction mechanism.

Conclusion

In summary, we have developed the first vicinal oxysulfonylation of enamides and enecarbamates with sulfinic acid salts and alcohols. This highly modular 3-component transformation enables the facile preparation of β-amidosulfones, an important scaffold in pharmacologically relevant structures. The reaction proceeds readily at room temperature and tolerates a variety of functional groups, including carbamate protecting groups on the nitrogen. This process is amendable to the gram-scale synthesis of the amidosulfone products. A telescoped isomerization-oxysulfonylation process starting from the corresponding allylamides provides a fast access to the β-amidosulfone unit from simple starting materials. The use of readily available organolithium reagents enables a construction of the sulfonyl moiety in the amidosulfone products directly from sulfur dioxide. The resulting *N*,*O*-acetals are competent acylimine-precursors and their reactivity can be exploited for the synthesis of different amidosulfone scaffolds. Mechanistic studies indicate an ionic reaction pathway.

Experimental methods

Reactions. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR.

Chromatography Column chromatography was performed with Silica 60 (0.04-0.063 mm, 230-400 mesh) and the specified solvent mixture. Thin layer chromatography was performed on aluminum sheets coated with SiO_2 (TLC silica gel 60 F_{254}). The spots were visualized by ultraviolet light, iodine, cerium ammonium molybdate (CAM) or vanillin.

Solvents Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. Solvents for column chromatography were technical standard.

Materials. All starting materials obtained from commercial sources were used without further purification.

SO_2 (sulfur dioxide, purity 3.8) was used directly without further purification. **SO_2 is a toxic and corrosive gas! It should be handled with care only in a well-ventilated fume-hood with the necessary precaution!** All reactions were performed with a defined amount of liquid SO_2. Therefore, SO_2 was condensed into a dry and Ar-filled Schlenk-flask, cooled to -78 °C. Because of its high heat of evaporation, liquid and cooled SO_2 can be easily handled, measured and transferred with syringes. For small-scale reactions, we recommend this procedure.

Enamides **1a**-**n** & **1q**-**s** were synthesized from the corresponding *N*-allylamides via the isomerization-protocol of Halli *et al.*[28]

All sulfinic acids sodium salts were either obtained from different providers or prepared from the corresponding sulfonyl chlorides using reported procedures.[33]

Anhydrous $Bi(OTf)_3$ was obtained from different providers and used directly. No special precautions were taken to avoid exposure of $Bi(OTf)_3$ to moisture. Therefore, we cannot rule out the formation of $Bi(OTf)_3 \cdot xH_2O$ during storage. However, no changes in catalytic activity and yield even upon prolonged storage (>1 year) were observed. Therefore, the amount of $Bi(OTf)_3$ used is always calculated on anhydrous $Bi(OTf)_3$. The actual catalyst loading for particular reactions might be slightly lower, depending on the batch quality and storage time.

Analytical Data and Instrumentation

NMR spectroscopy Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon spectra (^{13}C NMR) were recorded at, 400 MHz (^{1}H), 101 MHz (^{13}C) and 376 MHz (^{19}F), respectively. Chemical shifts are reported as δ - values relative to the residual $CDCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C). Coupling constants (*J*) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets dqd = doublet of quartets of doublets.

Melting points. Melting points are reported uncorrected.

Mass spectrometry. Mass spectra (MS) were measured using electrospray ionization (ESI) techniques. High resolution mass spectra (HRMS) were measured using electron ionization mass spectroscopy (EI-MS-TOF). Since the prepared *N*,*O*-Acetals are inherently unstable the elimination of the alcohol moiety was observed in HRMS measurements.

Infrared spectroscopy. Infrared spectra (IR) of neat substances were recorded on a FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm^{-1}).

Diastereomeric ratio. The diastereomeric ratios (*dr*) were determined by ^{1}H-NMR analysis of the unpurified product after aqueous workup and after isolation via column chromatography.
A diastereomeric ratio of *dr* > 98:2 indicates that no other isomer was observed by ^{1}H NMR. Minor diastereomers were in most cases not fully characterized. In some cases, no minor isomers could be isolated after column chromatography, although their formation was observed via NMR analysis of the crude reaction mixture. Presumably, small amounts of the side products were lost during column chromatography.

Preparation and Analytical Data

Synthesis of *N*,*O*-acetals **4** from sodium sulfinates.

Typical procedure 1: An oven-dried, 10 mL tube was charged with a magnetic stirring bar, enamide (1.0 equiv., 0.2 mmol), sulfinate salt (2.0 equiv., 0.4 mmol) and the alcohol (2 mL). $Fe(NO_3)_3$·9 H_2O (162 mg, 2.0 equiv., 0.4 mmol) was added and the tube was closed with a rubber septum. The resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (as judged by thin layer chromatography), saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification of the crude residue by flash column chromatography afforded the analytically pure product.

Synthesis of compound **4a**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) and recrystallisation from toluene/cyclohexane afforded the analytically pure sulfone **4a** as colorless crystalls (63 mg, 0.18 mmol, 91%, isolated *dr* 98: 2; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 53-67°C. R_f (*n*-hexane:EtOAc = 7:3) 0.2. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 7.97 – 7.87 (m, 2H), 7.85 – 7.74 (m, 3H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.66 – 5.46 (m, 1H), 3.62 (qd, *J* = 7.2, 4.0 Hz, 1H), 3.24 (s, 3H), 2.44 (s, 3H), 1.43 (d, *J* = 7.3 Hz, 3H). *(Peaks only for major diastereomer).* ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.7, 144.9, 137.1, 133.3, 132.4, 129.6, 128.9, 127.4, 81.3, 62.6, 55.9, 21.8, 10.9. *(Peaks only for major diastereomer).* HRMS (EI) m/z calcd for $C_{17}H_{17}NO_3S$ 315.0929 $[M\text{-}MeOH]^+$, found 315.0924 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm^{-1}): 2937 (w), 1652 (m), 1598 (w),

1517 (m), 1487 (m), 1350 (w), 1286 (m), 1192 (w), 1135 (s), 1073 (s), 910 (m), 844 (w), 814 (m), 802 (m), 725(m).

5-mmol reaction: An oven-dried, 100 mL roundbottom flask was charged with a magnetic stirring bar, (*E*/*Z*)-Enamide derivative **1a** (806 mg, 1.0 equiv., 5.0 mmol, *E*:*Z* = 76:24), sulfinate salt **2a** (1.78 g, 2.0 equiv., 10.0 mmol) in methanol (50 mL). $Fe(NO_3)_3 \cdot 9\ H_2O$ (4.04 g, 2.0 equiv., 10.0 mmol) was added and the flask was closed with a rubber septum. The resulting mixture was stirred at room temperature for 3 h. Upon completion of the reaction (as judged by thin layer chromatography), saturated aqueous NH_4Cl (50 mL) was added (***Note:*** on bigger scales an additional washing step with saturated aqueous NH_4Cl is recommended to avoid the accumulation of inorganic salts in the organic phase). The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (50 mL). The aqueous phase was extracted with dichloromethane (3x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification by flash column chromatography (*n*-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4a** as a colorless foam (1.40 g, 4.02 mmol, 80%, isolated *dr* 75: 25; *dr* of the crude mixture 76: 24 as determined by ^1H NMR analysis of the unpurified product after aqueous workup).
*Analytical data match those of **4a**.*

Synthesis of compound **4b**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in ethanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (*n*-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4b** as a colorless oil (38 mg, 0.105 mmol, 53%, isolated *dr* 79: 21; *dr* of the crude mixture 80: 20 as determined by ^1H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.26. ^1H NMR (*400 MHz, $CDCl_3$*) δ 8.25 (d, *J* = 9.7 Hz, 1H; *minor-diastereomer*), 7.88 (dd, *J* = 5.5, 3.1 Hz, 3H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.62 (ddd, *J* = 9.3, 5.9, 3.3 Hz, 1H), 3.73 – 3.31 (m, 3H), 2.43 (s, 3H), 1.47 (d, *J* = 7.3 Hz, 3H; *major-diastereomer*), 1.42 (d, *J* = 7.1 Hz, 3H; *minor-diastereomer*), 1.05 (t, *J* = 7.0 Hz, 3H; *minor-diastereomer*), 0.88 (t, *J* = 7.0 Hz, 3H; *major-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.6, 144.7, 137.5, 133.3, 132.3, 129.4, 129.0, 128.9, 127.3, 79.8, 64.1, 62.7, 21.7, 14.7, 10.6. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 167.1, 145.0, 135.2, 133.5, 132.3, 130.0, 129.3, 128.8, 127.4, 79.5, 64.8, 64.6, 21.8, 14.8, 13.1. MS (ESI): m/z calcd for $C_{19}H_{22}NO_4S^-$ 360.1 $[M-H]^-$, found 360.0 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{17}H_{17}NO_3S$ 315.0929 $[M-EtOH]^+$, found 315.0937 $[M-EtOH]^+$. IR ($\tilde{\nu}$ in cm^{-1}): 3335 (w), 2978 (w), 1650, 1598 (w), 1581 (w), 1517 (m), 1487 (m), 1453 (m), 1286 (s), 1138 (s), 1068 (s), 845 (m), 801 (m), 713 (m), 693 (m), 663 (m).

Synthesis of compound **4c**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in isopropanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4c** as a colorless oil (23 mg, 0.062 mmol, 31%, isolated *dr* 79: 21; *dr* of the crude mixture 81: 19 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.44. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.35 (d, *J* = 9.6 Hz, 1H; *minor-diastereomer*), 7.93 – 7.69 (m, 5H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.72 (dd, *J* = 9.6, 4.0 Hz, 1H; *major-diastereomer*), 5.68 (dd, *J* = 9.8, 2.1 Hz, 1H; *minor-diastereomer*), 3.89 – 3.71 (m, 1H), 3.60 (qd, *J* = 7.2, 4.1 Hz, 1H; *major-diastereomer*), 3.42 (qd, *J* = 7.0, 2.1 Hz, 1H; *minor-diastereomer*), 2.44 (s, 3H; *minor-diastereomer*), 2.43 (s, 3H; *major-diastereomer*), 1.47 (d, *J* = 7.3 Hz, 3H; *major-diastereomer*), 1.38 (d, *J* = 7.1 Hz, 3H; *minor-diastereomer*), 1.05 (dd, *J* = 6.0, 4.4 Hz, 1H; *minor-diastereomer*), 0.96 (d, *J* = 6.0 Hz, 3H; *major-diastereomer*), 0.89 (d, *J* = 6.2 Hz, 3H; *major-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.4, 144.5, 137.9, 133.5, 132.3, 129.4, 128.9, 128.9, 127.3, 77.8, 69.8, 63.2, 23.0, 21.7, 21.2, 10.7. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 167.0, 144.9, 135.1, 133.6, 132.2, 130.3, 129.2, 128.9, 127.4, 77.6, 70.0, 65.3, 23.2, 21.8, 21.1, 13.4. MS (ESI): m/z calcd for $C_{20}H_{24}NO_4S^-$ 374.2 $[M-H]^-$, found 374.1 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{17}H_{17}NO_3S$ 315.0929 $[M-C_3H_7OH]^+$, found 315.0948 $[M- C_3H_7OH]^+$. IR (ATR, ν in cm^{-1}): 3359 (w), 2975 (w), 1647, 1598 (w), 1581 (w), 1518 (m), 1486 (m), 1451 (m), 1380 (w), 1286 (s), 1136 (s), 1079(s), 1048 (s), 929 (w), 814 (m), 713 (m), 669 (m).

Synthesis of compound **4f**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1b** (35 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 76:24), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4f** as a colorless solid (46 mg, 0.128 mmol, 64%, isolated *dr* 81: 19; *dr* of the crude mixture 81: 19 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 57-92 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 7.82 – 7.73 (m, 5H), 7.36 – 7.27 (m, 4H), 5.60 – 5.53 (m, 1H), 3.61 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.43 – 3.39 (m, 1H; *minor-diastereomer*), 3.33 (s, 3H; *minor-diastereomer*), 3.23 (s, 3H; *major-diastereomer*), 2.43 (d, *J* = 6.5 Hz, 6H), 1.42 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.6, 144.8, 143.0, 137.2, 130.4, 129.6, 129.6, 128.9, 127.4, 81.3, 62.6, 55.9, 21.8, 21.7, 10.9. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 167.2, 145.0, 142.9, 135.5, 130.5, 129.7, 129.5, 129.0, 127.4, 81.3, 64.5, 56.4, 21.8, 21.7, 12.9. MS (ESI): m/z calcd for $C_{19}H_{23}NaNO_4S^+$ 384.1 $[M+Na]^+$, found 384.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_3S$ 329.1086 $[M-MeOH]^+$, found 329.1100 $[M-MeOH]^+$. IR (ATR, ν in

400 cm^{-1}): 3345 (w), 2931 (w), 1649 (m), 1612 (m), 1524 (m), 1494 (m), 1453 (m), 1349 (w), 1286 (s), 1187
401 (m), 1133 (s), 1072 (s), 1018 (m),952 (m), 815 (m), 748 (m), 664 (m).
402
403 Synthesis of compound **4g**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1c** (41 mg, 1.0
404 equiv., 0.2 mmol, *E*:*Z* = 17:83), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The
405 reaction was stirred at room temperature for 2 h. Purification by flash column chromatography
406 (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4g** as a colorless solid (49 mg,
407 0.125 mmol, 63%, isolated *dr* 62: 38; *dr* of the crude mixture 62: 38 as determined by ^{1}H NMR analysis
408 of the unpurified product after aqueous workup). m.p. 181-203 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.24. ^{1}H
409 NMR (*400 MHz, $CDCl_3$*) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 3.1 Hz, 3H), 5.74 –
410 5.66 (m, 1H *major-diastereomer*), 5.60 – 5.54 (m, 1H *minor-diastereomer*), 3.57 (qd, *J* = 7.2, 3.2 Hz, 1H),
411 3.43 (s, 3H), 3.34 (s, 3H), 2.45 (s, 3H), 2.37 (s, 2H), 2.34 (s, 4H), 2.28 (s, 3H), 1.42 (d, *J* = 7.3 Hz, 3H). ^{13}C
412 NMR (*101 MHz, $CDCl_3$*) δ 171.2, 170.9, 145.0, 144.8, 139.0, 139.0, 137.0, 135.7, 134.3, 134.3, 134.1,
413 134.1, 129.6, 129.0, 128.6, 81.1, 80.8, 64.5, 62.8, 56.9, 56.5, 21.8, 21.2, 19.7, 19.6, 12.9, 10.3. MS (ESI):
414 m/z calcd for $C_{21}H_{27}NO_4SNa^+$ 412.2 $[M+Na]^+$, found 412.1 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{20}H_{23}NO_3S$
415 357.1399 $[M-MeOH]^+$, found 357.1417 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 2922 (w), 1636 (m), 1611 (m),
416 1522 (m), 1454 (m), 1376 (w), 1287 (s), 1183 (m), 1130 (s), 1026 (s), 1075 (s), 1054 (s), 949 (w), 815
417 (m), 726 (s), 665 (m).
418
419 Synthesis of compound **4h**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1d** (38 mg, 1.0
420 equiv., 0.2 mmol, *E*: *Z* = 74:26), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The
421 reaction was stirred at room temperature for 2 h. Purification by flash column chromatography
422 (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4h** as a colorless foam (51 mg,
423 0.136 mmol, 68%, isolated *dr* 79: 21; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis
424 of the unpurified product after aqueous workup). m.p. 51-78 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.12. ^{1}H
425 NMR (*400 MHz, $CDCl_3$*) δ 8.12 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 7.89 – 7.84 (m, 2H), 7.78 (dd, *J* =
426 8.4, 2.1 Hz, 2H), 7.74 (d, *J* = 9.6 Hz, 1H; *major-diastereomer*), 7.33 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.8 Hz,
427 2H), 5.60 – 5.51 (m, 1H), 3.87 (s, 3H), 3.62 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.43 – 3.37 (m,
428 1H; *minor-diastereomer*), 3.33 (s, 3H; *minor-diastereomer*), 3.23 (s, 3H; *major-diastereomer*), 2.44 (s,
429 3H), 1.42 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.2, 163.0, 144.8,
430 137.2, 129.6, 129.3, 128.9, 125.5, 114.1, 81.3, 62.6, 55.9, 55.6, 21.8, 11.0. ^{13}C NMR (*101 MHz, $CDCl_3$*;
431 *minor-diastereomer*) δ 166.8, 162.9, 145.1, 135.5, 129.7, 129.6, 129.3, 128.9, 125.6, 114.1, 81.3, 64.6,
432 56.4, 55.6, 13.0, 8.5. MS (ESI): m/z calcd for $C_{19}H_{23}NO_5SNa^+$ 400.1 $[M+Na]^+$, found 400.0 $[M+Na]^+$. HRMS
433 (EI) m/z calcd for $C_{18}H_{19}NO_4S$ 345.1035 $[M-MeOH]^+$, found 345.1035 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}):

2931 (w), 1650 (m), 1605 (m), 1527 (m), 1493 (m), 1351 (w), 1288 (m), 1251 (s), 1177 (m), 1135 (s), 1073 (s), 1025 (m), 952 (m), 843 (m), 814 (m), 767 (m), 733 (m), 666 (w).

Synthesis of compound **4i**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1e** (36 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 75:25), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4i** as a colorless foam (45 mg, 0.123 mmol, 62%, isolated *dr* 80: 20; *dr* of the crude mixture 81: 19 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 109-127 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.19. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.19 (d, *J* = 9.8 Hz, 1H), 7.90 (ddd, *J* = 5.2, 4.2, 2.7 Hz, 2H), 7.81 (d, *J* = 9.7 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 5.58 – 5.48 (m, 1H), 3.61 (qd, *J* = 7.2, 4.1 Hz, 1H), 3.44 – 3.37 (m, 1H), 3.33 (s, 3H), 3.23 (s, 3H), 2.43 (s, 3H), 1.41 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 166.6, 165.3 (d, *J* = 253.1 Hz), 144.9, 137.0, 129.80 (d, *J* = 9.1 Hz), 129.6, 129.6, 128.9, 116.0 (d, *J* = 21.9 Hz), 81.4, 62.5, 56.0, 21.8, 11.0. ^{13}C NMR (*101 MHz, $CDCl_3$; minor-diastereomer*) δ 166.2, 165.3 (d, *J* = 253.0 Hz), 145.1, 135.3, 129.7, 129.6, 129.5 (d, *J* = 3.1 Hz), 128.9, 116.0 (d, *J* = 21.7 Hz), 81.3, 64.4, 56.5, 21.8, 12.9. ^{19}F NMR (*376 MHz, $CDCl_3$*) δ -106.90 (tt, *J* = 8.4, 5.3 Hz; *major-diastereomer*), -107.00 (tt, *J* = 8.4, 5.2 Hz; *minor-diastereomer*). MS (ESI): m/z calcd for $C_{18}H_{20}NO_4SFNa^+$ 388.1 $[M+Na]^+$, found 388.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{17}H_{16}NO_3SF$ 333.0835 $[M-MeOH]^+$, found 333.0849 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 2939 (w), 1650 (m), 1602 (m), 1526 (m), 1493 (s), 1350 (m), 1286 (m), 1229 (m), 1133 (s), 1073 (s), 1014 (m), 962 (m), 851 (m), 815 (m), 764 (m), 732 (m), 665 (m).

Synthesis of compound **4j**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1f** (50 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 55:45), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4j** as a colorless foam (51 mg, 0.123 mmol, 61%, isolated *dr* 80: 20; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 129-141 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.24. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.33 (d, *J* = 9.8 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 9.5 Hz, 1H), 7.77 (t, *J* = 8.3 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.56 (dt, *J* = 9.7, 3.4 Hz, 1H), 3.63 (qd, *J* = 7.2, 4.1 Hz, 1H), 3.42 (td, *J* = 6.8, 4.5 Hz, 1H), 3.35 (s, 3H), 3.25 (s, 2H), 2.45 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 166.5, 166.0, 145.3, 145.0, 137.0, 136.7, 136.6, 136.6, 135.2, 134.2, 134.1 (q, *J* = 32.8 Hz), 133.8, 129.7, 129.7, 129.6, 128.9, 127.9, 127.8, 126.0 (dd, *J* = 7.4, 3.6 Hz), 123.7 (d, *J* = 272.6 Hz), 81.6, 81.4, 64.4, 62.4, 56.7, 56.1, 21.8, 13.0, 11.2. ^{19}F NMR (*376 MHz, $CDCl_3$*) δ -63.0 (s; *minor-diastereomer*), -63.0 (s; *major-diastereomer*). MS (ESI): m/z calcd for $C_{19}H_{20}NO_4SF_3Na^+$ 438.1 $[M+Na]^+$,

found 338.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{18}H_{17}NO_3S\ F_3$383.0820 $[M\text{-}MeOH]^+$, found 383.0803 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm^{-1}): 3323 (w), 2933 (w), 1659 (m), 1533 (m), 1510 (m), 1451 (m), 1364 (w), 1325 (m), 1298 (s), 1140 (m), 1111 (s), 1064 (s), 1014 (m), 966 (m), 860 (m), 850 (m), 816 (m), 774 (m), 738 (m), 682 (m), 665 (m).

Synthesis of compound **4k**: Prepared according to TP1 from (*E*/*Z*)-Enamide derivative **1g** (33 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 69:31), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4k** as a colorless foam (48 mg, 0.136 mmol, 68%, isolated *dr* 83: 17; *dr* of the crude mixture 83: 17 as determined by ^1H NMR analysis of the unpurified product after aqueous workup). m.p. 145-148 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.19. ^1H NMR (*400 MHz, $CDCl_3$*) δ 8.05 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 7.81 – 7.74 (m, 2H), 7.66 (d, *J* = 9.6 Hz, 1H; *major-diastereomer*), 7.61 (dd, *J* = 4.7, 1.9 Hz, 1H), 7.55 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.56 – 5.45 (m, 1H), 3.59 (qd, *J* = 7.2, 4.1 Hz, 1H; *major-diastereomer*), 3.39 (dd, *J* = 7.2, 2.6 Hz, 1H; *minor-diastereomer*), 3.33 (s, 3H; *major-diastereomer*), 3.24 (s, 3H; *major-diastereomer*), 2.43 (s, 3H), 1.41 (dd, *J* = 7.2, 3.9 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 162.3, 144.9, 138.1, 137.0, 131.4, 129.6, 128.9, 128.0, 81.2, 62.5, 56.0, 21.8, 10.8. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 161.9, 145.1, 138.3, 135.4, 131.4, 129.5, 128.9, 128.0, 81.2, 64.4, 56.5, 21.8, 12.9. MS (ESI): m/z calcd for $C_{16}H_{19}NO_4S_2Na^+$ 376.1 $[M+Na]^+$, found 376.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{15}H_{15}NO_3S_2$ 321.0493 $[M\text{-}MeOH]^+$, found 321.0512 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm^{-1}): 3228 (w), 3091 (w), 2931 (w), 2836 (w), 1616 (m), 1532 (m), 1509 (m), 1451 (m), 1420 (m), 1361 (m), 1285 (s),1251 (m), 1197 (w), 1119 (s), 1131 (s), 1074 (s), 1038 (m), 945 (m), 863 (w), 801 (m), 729 (s), 665 (m).

Synthesis of compound **4l**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1h** (28 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 91:9), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4l** as a colorless oil (47 mg, 0.144 mmol, 72%, isolated *dr* 89: 11; *dr* of the crude mixture 88: 12 as determined by ^1H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 16.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 5.37 (dd, *J* = 9.7, 3.9 Hz, 1H; *major-diastereomer*), 5.33 (dd, *J* = 9.8, 2.7 Hz, 1H; *minor-diastereomer*), 3.52 (qd, *J* = 7.2, 3.9 Hz, 1H; *major-diastereomer*), 3.33 – 3.25 (m, 1H; *minor-diastereomer*), 3.24 (s, 3H; *minor-diastereomer*), 3.14 (s, 3H; *major-diastereomer*), 2.44 (s, 3H; *minor-diastereomer*), 1.33 (dd, *J* = 7.3, Hz,

3H), 1.29 – 1.24 (m, 9H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 179.6, 144.8, 137.2, 129.6, 128.9, 80.8, 62.4, 55.6, 39.3, 27.6, 21.8, 10.8. MS (ESI): m/z calcd for $C_{16}H_{25}NO_4SNa^+$ 350.1 $[M+Na]^+$, found 350.1 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{15}H_{21}NO_3S$ 295.1242 $[M-MeOH]^+$, found 295.1234 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1})**:** 3364 (w), 2957 (w), 1658 (m), 1598 (w), 1502 (m), 1454 (m), 1366 (w), 1302 (m), 1287 (m), 1239 (m), 1183 (m), 1136 (s),1074 (s), 955 (w),879 (m), 814 (m), 744 (m), 714 (m), 680 (w), 665 (w).

Synthesis of compound **4m**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1i** (35 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 60:40), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4m** as a colorless oil (51 mg, 0.141 mmol, 70%, isolated *dr* 63: 37; *dr* of the crude mixture 62: 38 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.43 – 7.28 (m, 7H), 7.00 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 6.70 (d, *J* = 9.4 Hz, 1H; *major-diastereomer*), 5.35 (dd, *J* = 9.7, 4.0 Hz, 1H; *major-diastereomer*), 5.31 (dd, *J* = 10.0, 3.0 Hz, 1H; *minor-diastereomer*), 3.64 (s, 2H), 3.40 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.23 – 3.16 (m, 4H; *minor-diastereomer*), 3.11 (s, 3H; *major-diastereomer*), 2.43 (d, *J* = 3.1 Hz, 3H), 1.28 (d, *J* = 7.2 Hz, 3H; *minor-diastereomer*), 1.21 (d, *J* = 7.2 Hz, 3H; *major-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$ major-diastereomer*) δ 171.9, 144.8, 136.7, 134.4, 129.6, 129.5, 129.3, 129.0, 127.7, 80.6, 62.5, 55.8, 44.2, 21.8, 10.3. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 171.5, 144.9, 136.7, 134.4, 129.6, 129.5, 129.4, 129.3, 127.7, 80.6, 64.0, 56.3, 44.2, 21.8, 11.9. MS (ESI): m/z calcd for $C_{19}H_{23}NO_4SNa^+$ 384.1 $[M+Na]^+$, found 384.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_3S$ 329.1086 $[M-MeOH]^+$, found 329.1090 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3312 (w), 2938 (w), 1658 (m), 1597 (w), 1516 (m), 1495 (m), 1454 (m), 1357 (w), 1299 (m), 1287 (m), 1138 (s), 1073 (s), 931 (w), 814 (m), 728 (m).

Synthesis of compound **4n**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1j** (37 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 48:52), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4n** as a colorless solid (46 mg, 0.124 mmol, 62%, isolated *dr* 64: 36; *dr* of the crude mixture 64: 36 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 70-78 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.14. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 7.78 (dd, *J* = 8.2, 3.1 Hz, 2H), 7.72 – 7.65 (m, 1H), 7.54 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.45 (d, *J* = 10.0 Hz, 1H), 7.40 (d, *J* = 4.7 Hz, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 9.7 Hz, 1H), 6.48 (dd, *J* = 15.7, 3.7 Hz, 1H), 5.53 (dd, *J* = 9.8, 4.0 Hz, 1H; *major-diastereomer*), 5.49 (dd, *J* = 10.0, 2.5 Hz,

1H; *minor-diastereomer*), 3.56 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.37 (dd, *J* = 7.1, 2.6 Hz, 1H; *minor-diastereomer*), 3.32 (s, 3H; *minor-diastereomer*), 3.22 (s, 3H; *major-diastereomer*), 2.44 (s, 3H), 1.41 (dd, *J* = 7.2, 1.8 Hz, 3H). ^{13}C NMR (*101 MHz, CDCl$_3$*) δ 166.5, 166.1, 145.1, 144.8, 143.0, 142.9, 137.1, 135.5, 134.6, 134.6, 130.3, 130.3, 129.7, 129.6, 129.6, 129.1, 129.0, 128.2, 120.2, 120.0, 80.9, 80.9, 64.5, 62.6, 56.4, 55.9, 21.8, 12.9, 10.7. MS (ESI): m/z calcd for $C_{20}H_{23}NO_4SNa^+$ 396.1 $[M+Na]^+$, found 396.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{19}H_{19}NO_3S$ 341.1086 $[M-MeOH]^+$, found 341.1100 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3305 (w), 2933 (w), 1661 (m), 1626 (m), 1599 (m), 1517 (m), 1450 (m), 1353 (m), 1287 (m), 1207 (m), 1185 (m), 1139 (s), 1072 (s), 977 (m), 814 (m), 747 (m), 665 (w).

Synthesis of compound **4o**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1k** (38 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 55:45), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4o** as a low melting solid (53 mg, 0.141 mmol, 70%, isolated *dr* 65: 35; *dr* of the crude mixture 65: 35 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.12. ^{1}H NMR (*400 MHz, CDCl$_3$*) δ 8.15 (d, *J* = 10.6 Hz, 1H; *minor-diastereomer*), 7.77 (d, *J* = 9.8 Hz, 1H; *major-diastereomer*), 7.70 (dd, *J* = 17.2, 8.2 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.08 – 7.01 (m, 1H), 7.00 – 6.94 (m, 2H), 5.48 (dd, *J* = 9.8, 4.0 Hz, 1H; *major-diastereomer*), 5.41 (dd, *J* = 10.2, 3.2 Hz, 1H; *minor-diastereomer*), 4.58 – 4.49 (m, 2H), 3.47 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.31 (d, *J* = 19.6 Hz, 1H; *minor-diastereomer*), 3.25 (s, *J* = 4.3 Hz, 3H; *minor-diastereomer*), 3.18 (s, 3H; *major-diastereomer*), 2.40 (s, 3H), 1.37 (d, *J* = 7.2 Hz, 3H; *minor-diastereomer*), 1.30 (d, *J* = 7.2 Hz, 3H; *major-diastereomer*). ^{13}C NMR (*101 MHz, CDCl$_3$*) δ 169.2, 169.0, 157.2, 157.1, 144.9, 144.8, 136.7, 135.7, 129.9, 129.5, 129.5, 129.4, 128.9, 122.4, 122.3, 114.8, 114.8, 80.2, 80.0, 67.0, 63.9, 62.5, 58.7, 56.4, 56.0, 21.7, 11.9, 10.0, 8.4. MS (ESI): m/z calcd for $C_{19}H_{22}NO_5S^-$ 376.1 $[M-H]^-$, found 376.2 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_4S$ 345.1035 $[M-MeOH]^+$, found 345.1039 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3350 (w), 2932 (w), 1682 (m), 1598 (m), 1512 (m), 1493 (m), 1288 (m), 1236 (m), 1139 (s), 1078 (s), 816 (m), 751 (m), 690 (m).

Synthesis of compound **4p**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1l** (35 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 60:40), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4p** as a colorless oil (29 mg, 0.080 mmol, 40%, isolated *dr* >98: 2; *dr* of the crude mixture >98: 2 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.18. ^{1}H NMR (*400 MHz, CDCl$_3$*) δ 7.89 – 7.28 (m, 9H), 5.81 (d, *J* = 8.6 Hz, 1H), 3.55 – 3.48 (m, 1H), 3.33 – 3.10 (m, 3H), 2.89 (s, 3H), 2.43 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (*101 MHz, CDCl$_3$*) δ 173.1, 145.1, 136.3, 133.7, 130.1,

129.9, 129.8, 128.6, 127.3, 82.1, 60.7, 55.9, 31.1, 21.8, 12.6. MS (ESI): m/z calcd for $C_{19}H_{26}NO_4SNa^+$ 384.1 $[M+Na]^+$, found 384.1 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_3S$ 329.1086 $[M-MeOH]^+$, found 329.1080 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 2939 (w), 1641 (s), 1597 (m), 1446 (m), 1395 (m), 1344 (m), 1303 (s), 1290 (s), 1189 (m), 1138 (s), 1073 (s), 1049 (s), 1023 (s), 952 (m), 815 (m), 723 (m), 699 (s), 659 (m).

Synthesis of compound **4q**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1m** (25 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 100:0), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4q** as a colorless oil (37 mg, 0.120 mmol, 60%, isolated *dr* 90: 10; *dr* of the crude mixture 89: 11 as determined by ^1H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.14. ^1H NMR (*400 MHz, $CDCl_3$*) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.30 (d, *J* = 7.5 Hz, 1H; *minor-diastereomer*), 5.22 (d, *J* = 8.5 Hz, 1H; *major-diastereomer*), 3.45 – 3.26 (m, 3H), 3.17 (s, 3H; *major-diastereomer*), 3.05 (s, 3H; *minor-diastereomer*), 2.47 – 2.35 (m, 5H), 1.99 – 1.84 (m, 2H), 1.36 (d, *J* = 7.0 Hz, 3H; *major-diastereomer*), 1.27 (d, *J* = 7.3 Hz, 3H; *minor-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 176.5, 145.1, 134.2, 129.8, 129.5, 80.8, 60.7, 55.8, 42.0, 31.5, 21.8, 18.3, 11.9. MS (ESI): m/z calcd for $C_{15}H_{21}NO_4SNa^+$ 334.1 $[M+Na]^+$, found 334.2 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{15}H_{21}NO_4S$ 311.1191 $[M]^+$, found 311.1208 $[M]^+$. IR (ATR, ν in cm^{-1}): 2935 (w), 1692 (s), 1596 (w), 1494 (w), 1454 (w), 1406 (m), 1285 (m), 1259 (m), 1202 (m), 1138 (s), 1076 (s), 958 (m), 911 (w), 818 (m), 801 (m), 741 (m).

Synthesis of compound **4r**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1n** (35 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 89:11), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4r** as a colorless foam (56 mg, 0.155 mmol, 77%, isolated *dr* 75: 25; *dr* of the crude mixture 75: 25 as determined by ^1H NMR analysis of the unpurified product after aqueous workup). m.p. 97-108°C. R_f (*n*-hexane:EtOAc = 7:3) 0.28. ^1H NMR (*400 MHz, $CDCl_3$*) δ 8.57 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 8.18 (d, *J* = 9.9 Hz, 1H; *major-diastereomer*), 7.95 – 7.87 (m, 2H), 7.83 – 7.75 (m, 2H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.84 – 5.58 (m, 1H), 3.45 (dd, *J* = 8.7, 4.4 Hz, 1H; *major-diastereomer*), 3.34 (s, 3H; *minor-diastereomer*), 3.22 – 3.18 (m, 1H; *minor-diastereomer*), 3.17 (s, 3H; *major-diastereomer*), 2.43 (s, 3H), 2.25 – 2.15 (m, 1H; *major-diastereomer*), 1.93 – 1.86 (m, 1H; *minor-diastereomer*), 1.80 – 1.65 (m, 1H), 1.08 (dd, *J* = 13.1, 5.6 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.6, 144.6, 138.4, 133.2, 132.4, 129.4, 128.9, 128.7, 127.3, 79.7, 68.5, 55.5, 21.7, 18.9, 12.2. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-*

diastereomer) δ 167.2, 145.0, 135.8, 133.3, 133.2, 132.3, 129.7, 129.4, 128.8, 78.7, 70.9, 56.4 , 20.9, 11.7, 8.3. MS (ESI): m/z calcd for $C_{19}H_{22}NO_4S^-$ 360.1 $[M-H]^-$, found 360.2 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_3S$ 329.1086 $[M-MeOH]^+$, found 329.1094 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3366 (w), 2942 (w), 1667 (m), 1600 (w), 1518 (m), 1489 (m), 1358 (w), 1280 (s), 1187 (w), 1137 (s), 1100 (m), 1065 (s), 1036 (m), 974 (m), 813 (m), 714 (m), 681 (m), 665 (w).

Synthesis of compound **4s**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1o** (32 mg, 1.0 equiv., 0.2 mmol), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4s** as a colorless foam (45 mg, 0.135 mmol, 67%). m.p. 139-142 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.14. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 7.83 (dd, *J* = 11.7, 7.9 Hz, 4H), 7.62 (d, *J* = 9.5 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.70 (dt, *J* = 9.3, 4.5 Hz, 1H), 3.68 (dd, *J* = 14.7, 5.1 Hz, 1H), 3.52 (dd, *J* = 14.7, 3.9 Hz, 1H), 3.29 (s, 3H), 2.43 (s, 3H).^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.3, 145.2, 137.5, 133.3, 132.4, 129.9, 128.9, 128.4, 127.4, 60.0, 56.1, 21.8. HRMS (EI) m/z calcd for $C_{16}H_{15}NO_3S$ 301.0773 $[M-MeOH]^+$, found 301.0787 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3267 (m), 2934 (m), 1641 (s), 1601 (m), 1581 (m), 1529 (s), 1490 (w), 1404 (w), 1362 (w), 1300 (s), 1179 (w), 1101 (s), 1082 (s), 1034 (m), 959 (m), 871 (w), 852 (w), 804 (m), 781 (m).

Synthesis of compound **4t**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1p** (35 mg, 1.0 equiv., 0.2 mmol), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4t** as a colorless foam (31 mg, 0.086 mmol, 43%). m.p. 55-68°C. R_f (*n*-hexane:EtOAc = 7:3) 0.32. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.17 (d, *J* = 9.9 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.53 – 7.46 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.36 (d, *J* = 10.0 Hz, 1H), 3.27 (s, 3H), 2.44 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.7, 144.8, 135.3, 133.4, 132.3, 130.7, 129.1, 128.9, 127.4, 85.4, 66.3, 56.2, 21.8, 21.8, 19.7. HRMS (EI) m/z calcd for $C_{19}H_{23}NO_4S$ 361.1348 $[M]^+$, found 361.1369 $[MH]^+$. IR (ATR, ν in cm^{-1}): 3329 (w), 2941 (w), 1659 (m), 1598 (w), 1513 (m), 1485 (m), 1460 (m), 1344 (m), 1283 (s), 1124 (s), 1094 (s), 1073 (s), 1051 (s), 814 (m), 714 (m), 690 (m).

Synthesis of compound **4u**: Prepared according to TP1 from (*E*/*Z*)-Enecarbamate derivative **1q** (31 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 42:58), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography

(n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4u** as a colorless oil (27 mg, 0.079 mmol, 40%, isolated *dr* 57: 43; *dr* of the crude mixture 44: 56 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.1, 4.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.01 (d, *J* = 10.2 Hz, 1H; *major-diastereomer*), 5.72 (d, *J* = 9.9 Hz, 1H; *minor-diastereomer*), 5.12 (dd, *J* = 10.2, 3.8 Hz, 1H; *minor-diastereomer*), 5.02 (dd, *J* = 10.5, 3.1 Hz, 1H; *major-diastereomer*), 3.47 – 3.38 (m, 1H; *minor-diastereomer*), 3.37 – 3.30 (m, 1H; *minor-diastereomer*), 3.24 (s, 3H; *minor-diastereomer*), 3.18 (s, 3H; *minor-diastereomer*), 2.43 (s, 3H), 1.46 (d, *J* = 2.7 Hz, 9H), 1.36 (dd, *J* = 7.0, 3.6 Hz, 3H). ^{13}C NMR (*101 MHz, CDCl$_3$*) δ 155.4, 155.4, 144.8, 144.6, 136.8, 135.7, 129.5, 129.5, 129.1, 82.5, 82.2, 80.4, 80.4, 64.3, 63.1, 55.7, 55.4, 28.4, 28.8, 21.8, 11.9, 10.2. MS (ESI): m/z calcd for $C_{16}H_{25}NO_5SNa^+$ 366.1 $[M+Na]^+$, found 366.1 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{15}H_{21}NO_4S$ 311.1191 $[M-MeOH]^+$, found 311.1173 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3350 (w), 2980 (w), 1705 (m), 1597 (w), 1495 (m), 1455 (m), 1366 (m), 1300 (m), 1286 (m), 1247 (m),1140 (s), 1074 (s), 1008 (m), 916 (m), 853 (w), 815 (m), 728 (m), 664 (m).

Synthesis of compound **4v**: Prepared according to TP1 from (*E*/*Z*)-Enamide derivative **1r** (38 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 42:58), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4v** as a colorless oil (33 mg, 0.087 mmol, 44%, isolated *dr* 55: 45; *dr* of the crude mixture 45: 55 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.26. ^{1}H NMR (*400 MHz, CDCl$_3$*) δ 7.73 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.27 (d, *J* = 10.2 Hz, 1H), 5.99 (d, *J* = 9.9 Hz, 1H), 5.24 – 5.07 (m, 3H), 3.43 (dd, *J* = 6.8, 4.0 Hz, 1H), 3.35 (dd, *J* = 7.1, 3.1 Hz, 1H), 3.27 (s, 1H), 3.20 (s, 2H), 2.43 (s, 3H), 1.35 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (*101 MHz, CDCl$_3$*) δ 156.1, 144.9, 144.7, 136.6, 136.2, 136.1, 135.6, 129.5, 129.5, 129.0, 128.7, 128.4, 128.3, 128.2, 83.0, 82.7, 67.3, 67.2, 64.2, 63.0, 55.9, 55.6, 21.8, 11.7, 10.1. MS (ESI): m/z calcd for $C_{19}H_{23}NO_5SNa^+$ 400.1 $[M+Na]^+$, found 400.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_4S$ 345.1035 $[M-MeOH]^+$, found 345.1050 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3335 (w), 2945 (w), 1722 (s), 1708 (s), 1597 (w), 1514 (m), 1454 (m), 1303 (m), 1287 (m), 1229 (m), 1140 (s), 1075 (s), 1016 (m), 964 (m), 915 (m), 817 (m), 732 (m), 698 (m), 665 (w).

Synthesis of compound **4w**: Prepared according to TP1 from (*E*/*Z*)-Enecarbamate derivative **1s** (56 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 54:46), sulfinate salt **2a** (71 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4w** as a colorless foam (40 mg, 0.086 mmol, 43%, isolated *dr* 52: 48; *dr* of the crude mixture 48: 52 as determined by ^{1}H NMR analysis

of the unpurified product after aqueous workup). m.p. 66-82 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.28. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 7.77 (d, *J* = 7.4 Hz, 4H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.41 (s, 2H), 7.33 (t, *J* = 6.8 Hz, 5H), 6.27 (d, *J* = 10.5 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 5.15 (ddd, *J* = 24.0, 10.2, 3.3 Hz, 1H), 4.52 – 4.37 (m, 2H), 4.24 (dt, *J* = 10.1, 5.1 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.39 – 3.33 (m, 1H), 3.24 (s, 1H), 3.17 (s, 2H), 2.43 (s, 4H), 1.36 (dd, *J* = 6.9, 4.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 156.1, 144.8, 143.7, 141.5, 129.6, 129.5, 129.1, 127.9, 127.3, 125.2, 120.2, 83.2, 82.9, 67.2, 64.3, 63.0, 55.9, 55.6, 47.3, 21.8, 11.9, 10.4. MS (ESI): m/z calcd for $C_{26}H_{27}NO_5SNa^+$ 488.2 $[M+Na]^+$, found 487.8 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{26}H_{27}NO_5S^+$ 465.1610 $[M]^+$, found 465.1620 $[M]^+$. IR (ATR, ν in cm^{-1}): 3329 (w), 2946 (w), 1724 (m), 1597 (w), 1511 (m), 1449 (m), 1287 (m), 1226 (m), 1194 (m), 1140 (s), 1075 (s), 1017 (m), 958 (m), 815 (m), 758 (m), 738 (s), 658 (w).

Synthesis of compound **6a**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2b** (66 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6a** as a colorless oil (46 mg, 0.136 mmol, 68%, isolated *dr* 80: 20; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.16. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.18 (d, *J* = 9.9 Hz, 1H; *minor-diastereomer*), 7.97 – 7.87 (m, 4H), 7.83 (d, *J* = 9.6 Hz, 1H; *major-diastereomer*), 7.68 – 7.61 (m, 1H), 7.60 – 7.46 (m, 5H), 5.66 – 5.52 (m, 1H), 3.67 (qd, *J* = 7.3, 3.9 Hz, 1H; *major-diastereomer*), 3.44 (tt, *J* = 7.0, 3.6 Hz, 1H; *minor-diastereomer*), 3.34 (s, 3H; *minor-diastereomer*), 3.21 (s, 3H; *major-diastereomer*), 1.45 (dd, *J* = 7.2, 2.5 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$; major-diastereomer*) δ 167.7, 140.3, 133.8, 133.2, 132.4, 129.0, 129.0, 128.8, 127.4, 81.3, 62.5, 55.9, 10.8 ppm. ^{13}C-NMR (*101 MHz, $CDCl_3$, minor-diastereomer*): δ 167.3, 138.4, 134.0, 133.4, 132.4, 129.7, 129.7,128.9, 127.4, 81.3, 64.6, 56.5, 13.0 ppm. MS (ESI): m/z calcd for $C_{17}H_{18}NO_4S^-$ 332.4 $[M-H]^-$, found 332.0 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{16}H_{15}NO_3S$ 301.0773 $[M-MeOH]^+$, found 301.0790 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3335 (w), 2936 (w), 1649 (m), 1603 (w), 1581 (w), 1515 (m), 1486 (m), 1446 (m), 1351 (w), 1288 (m), 1196 (w), 1136 (s), 1070 (s), 999 (m), 956 (m), 844 (m), 802 (w), 768 (w), 736 (m), 715 (m), 688 (m).

Synthesis of compound **6b**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2c** (88 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6b** as a colorless foam (53 mg, 0.136 mmol, 68%, isolated *dr* 83: 17; *dr* of the crude mixture 81: 19 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 144-154 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.29. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.17 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 7.90 (d, *J* = 7.3 Hz, 2H), 7.82 (d, *J*

= 8.5 Hz, 3H), 7.62 – 7.44 (m, 5H), 5.60 (dt, *J* = 9.7, 3.7 Hz, 1H), 3.64 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.47 – 3.39 (m, 1H; *minor-diastereomer*), 3.36 (s, 3H; *minor-diastereomer*), 3.24 (s, 3H; *major-diastereomer*), 1.45 (d, *J* = 7.0 Hz, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.7, 157.8, 137.1, 133.3, 132.4, 129.0, 129.0, 128.7, 127.4, 126.0, 81.4, 62.5, 56.0, 31.2, 11.0. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 167.3, 158.0, 135.4, 133.4, 132.4, 129.5, 129.0, 128.9, 127.4, 126.0, 81.3, 64.5, 56.5, 35.4, 13.0. MS (ESI): m/z calcd for $C_{21}H_{27}NO_4SNa^+$ 412.2 $[M+Na]^+$, found 412.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{20}H_{23}NO_3S$ 357.1399 $[M-MeOH]^+$, found 357.1417 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3337 (w), 2938 (w), 1648 (s), 1593 (w), 1524 (s), 1491 (m), 1450 (m), 1364 (m), 1303 (s), 1291 (s), 1265 (m), 1143 (s), 1096 (m), 1071 (s), 965 (m), 842 (m), 831 (m), 804 (w), 761 (m), 701 (s), 667 (m).

Synthesis of compound **6c**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2d** (78 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6c** as a colorless foam (37 mg, 0.102 mmol, 51%, isolated *dr* 81: 19; *dr* of the crude mixture 81: 19 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 56-58°C. R_f (*n*-hexane:EtOAc = 7:3) 0.1. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.20 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 7.89 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 3H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 5.64 – 5.50 (m, 1H), 3.86 (s, 3H), 3.59 (qd, *J* = 7.2, 4.2 Hz, 1H; *major-diastereomer*), 3.40 (dd, *J* = 7.1, 2.5 Hz, 1H; *minor-diastereomer*), 3.33 (s, 3H; *minor-diastereomer*), 3.25 (s, 3H; *major-diastereomer*), 1.42 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.7, 163.9, 133.3, 132.4, 131.9, 131.1, 128.9, 127.3, 114.1, 81.3, 62.7, 56.0, 55.8, 11.0. ^{13}C NMR (*101 MHz, $CDCl_3$; minor-diastereomer*) δ 167.3, 164.0, 133.4, 132.3, 132.1, 131.4, 128.8, 127.2, 114.1, 81.2, 64.5, 56.5, 55.8, 12.9. MS (ESI): m/z calcd for $C_{18}H_{20}NO_5S^-$ 362.1 $[M-H]^-$, found 362.2 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{17}H_{17}NO_4S$ 331.0878 $[M-MeOH]^+$, found 331.0886 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3335 (w), 2940 (w),1652 (m), 1595 (m), 1518 (m),1488 (m), 1292 (m), 1260 (s), 1183 (w), 1135 (s), 1073 (s), 1024 (m), 835 (m), 804 (m), 733 (m).

Synthesis of compound **6d**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2e** (84 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6d** as a light yellow foam (36 mg, 0.095 mmol, 48%, isolated *dr* 79: 21; *dr* of the crude mixture 79: 21 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 150-165 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.13. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.41 – 8.32 (m, 2H), 8.16 – 8.05 (m, 2H), 7.99 (d, *J* = 10.1 Hz, 1H;

minor-diastereomer), 7.89 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 9.7 Hz, 1H; *major-diastereomer*), 7.63 – 7.54 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 5.65 (dd, *J* = 9.9, 3.7 Hz, 1H; *major-diastereomer*), 5.58 (dd, *J* = 10.0, 2.7 Hz, 1H; *minor-diastereomer*), 3.74 (qd, *J* = 7.3, 3.8 Hz, 1H; *major-diastereomer*), 3.54 (qd, *J* = 7.2, 2.8 Hz, 1H; *minor-diastereomer*), 3.30 (s, 3H; *minor-diastereomer*), 3.17 (s, 3H; *major-diastereomer*), 1.53 (d, *J* = 7.3 Hz, 2H; *major-diastereomer*), 1.48 (d, *J* = 7.2 Hz, 3H; *minor-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$)* δ 167.8, 150.8, 146.6, 133.0, 132.7, 130.3, 129.1, 127.3, 124.0, 80.9, 63.0, 55.8, 10.0. ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.3, 151.0, 146.6, 133.1, 132.6, 131.4, 129.0, 127.4, 123.9, 81.0, 65.4, 56.4, 13.1. MS (ESI): m/z calcd for $C_{17}H_{18}N_2O_6SNa^+$ 401.1 $[M+Na]^+$, found 401.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{16}H_{14}N_2O_5S$ 346.0623 $[M\text{-}MeOH]^+$, found 346.0642 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm^{-1}): 3331 (m), 2932 (w), 1651 (m), 1603 (w), 1580 (w), 1520 (s), 1489 (m), 1348 (m), 1297 (s), 1265 (m), 1190 (w), 1133 (m), 1098 (m), 1070 (s), 967 (m), 854 (m), 802 (w), 758 (m), 742 (m), 720 (m), 701 (m).

Synthesis of compound **6e**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2f** (73 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6e** as a colorless oil (43 mg, 0.122 mmol, 61%, isolated *dr* 80: 20; *dr* of the crude mixture 79: 21 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.7 Hz, 1H; *minor-diastereomer*), 7.98 – 7.85 (m, 4H), 7.80 (d, *J* = 9.5 Hz, 1H; *major-diastereomer*), 7.56 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.20 (dd, *J* = 12.0, 5.0 Hz, 2H), 5.60 (dd, *J* = 9.7, 3.8 Hz, 1H; *major-diastereomer*), 5.55 (dd, *J* = 9.9, 2.6 Hz, 1H; *minor-diastereomer*), 3.64 (qd, *J* = 7.2, 3.9 Hz, 1H; *major-diastereomer*), 3.44 (qd, *J* = 7.1, 2.6 Hz, 1H; *minor-diastereomer*), 3.31 (s, 3H; *minor-diastereomer*), 3.21 (s, 3H; *major-diastereomer*), 1.51 – 1.41 (m, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.7, 165.9 (d, *J* = 256.3 Hz), 136.3 (d, *J* = 3.2 Hz), 133.2, 132.5, 131.8 (d, *J* = 9.6 Hz), 128.9, 127.3, 116.2 (d, *J* = 22.7 Hz), 81.2, 62.8, 55.9 (s), 10.6 (s). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.3, 166.1 (d, *J* = 256.8 Hz), 134.3 (d, *J* = 3.2 Hz), 133.3, 132.7 (d, *J* = 9.6 Hz), 132.4, 128.9, 127.3, 116.1 (d, *J* = 22.6 Hz), 81.2, 64.8, 56.4, 13.0. ^{19}F NMR (*376 MHz, $CDCl_3$*) δ -103.1 – -103.2 (m, *minor-diastereomer*), -103.4 – -103.6 (m; *major-diastereomer*). MS (ESI): m/z calcd for $C_{17}H_{18}NO_4SFNa^+$ 374.1 $[M+Na]^+$, found 374.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{16}H_{14}NO_3SF$ 429.2173 $[M\text{-}MeOH]^+$, found 429.2169 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm^{-1}): 3336 (w), 2937 (w), 1649 (m), 1590 (m), 1517 (m), 1489 (m), 1350 (w), 1311 (m), 1287 (s), 1230 (m), 1198 (w), 1134 (s), 1071 (s), 961 (w), 837 (m), 819 (m), 691 (m), 671 (m), 709 (m).

Synthesis of compound **6f**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2g** (79 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography

(n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6f** as a colorless foam (43 mg, 0.117 mmol, 59%, isolated *dr* 80: 20; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 109 – 137 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.26. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.12 (d, *J* = 9.7 Hz, 1H; *minor-diastereomer*), 7.96 – 7.82 (m, 4H), 7.78 (d, *J* = 9.7 Hz, 1H; *major-diastereomer*), 7.58 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.47 (m, 4H), 5.61 (dd, *J* = 9.8, 3.8 Hz, 1H; *major-diastereomer*), 5.56 (dd, *J* = 9.9, 2.5 Hz, 1H; *minor-diastereomer*), 3.65 (qd, *J* = 7.3, 3.9 Hz, 1H; *major-diastereomer*), 3.45 (ddd, *J* = 16.4, 9.5, 6.7 Hz, 1H; *minor-diastereomer*), 3.33 (s, 3H, *minor-diastereomer*), 3.22 (s, 3H; *major-diastereomer*), 1.47 (d, *J* = 7.3 Hz, 3H; *major-diastereomer*), 1.44 (d, *J* = 7.2 Hz, 3H; *minor-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$; major-diastereomer*) δ 167.7, 140.6, 139.0, 133.1, 132.5, 130.4, 129.2, 129.0, 127.3, 81.2, 62.8, 55.9, 10.5. ^{13}C NMR (*101 MHz, $CDCl_3$; minor-diastereomer*) δ 167.3, 140.9, 136.8, 133.3, 132.5, 131.4, 129.2, 129.0, 127.4, 81.2, 64.9, 56.5, 13.1. MS (ESI): m/z calcd for $C_{17}H_{18}NO_4SNaCl^+$ 390.83 $[M+Na]^+$, found 390.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{16}H_{14}NO_3SCl$ 335.0383 $[M\text{-}MeOH]^+$, found 335.0398 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm^{-1}): 3325 (w), 2925 (w), 1649 (s), 1603 (w), 1580 (m), 1522 (s), 1491 (m), 1474 (m), 1450 (m), 1366 (m), 1353 (m), 1308 (s), 1280 (m), 1262 (m), 1189 (w), 1137 (m), 1069 (s), 1011 (m), 964 (m), 932 (m), 834 (m), 817 (m), 801 (m), 765 (m), 694 (m), 672 (w), 665 (w).

Synthesis of compound **6g**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2h** (97 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6g** as a colorless foam (43 mg, 0.102 mmol, 52%, isolated *dr* 79: 21; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 57-65 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.27. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.11 (d, *J* = 10.0 Hz, 1H-*minor-diastereomer*), 7.88 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.77 (dt, *J* = 9.0, 2.1 Hz, 3H), 7.71 – 7.64 (m, 2H), 7.58 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 5.61 (dd, *J* = 9.8, 3.8 Hz, 1H *major-diastereomer*), 5.59 (ddd, *J* = 12.5, 9.9, 3.2 Hz, 1H *minor-diastereomer*), 5.56 (dd, *J* = 9.9, 2.5 Hz, 1H *major-diastereomer*), 3.65 (qd, *J* = 7.3, 3.8 Hz, 1H *major-diastereomer*), 3.52 – 3.35 (m, 1H *minor-diastereomer*), 3.32 (s, 3H *minor-diastereomer*), 3.22 (s, 3H *major-diastereomer*), 1.47 (d, *J* = 7.3 Hz, 3H *major-diastereomer*), 1.44 (d, *J* = 7.2 Hz, 3H *minor-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$ major-diastereomer*) δ 167.7, 139.5, 133.1, 132.5, 132.2, 130.5, 129.2, 129.0, 127.3, 81.2, 62.8, 55.9, 10.5. ^{13}C NMR (*101 MHz, $CDCl_3$ minor-diastereomer*) δ 167.3, 137.4, 133.3, 132.5, 132.2, 131.4, 129.5, 129.0, 127.4, 81.2, 64.9, 56.5, 13.1. MS (ESI): m/z calcd for $C_{17}H_{17}NO_4SBr^-$ 411.3 $[M\text{-}H]^-$, found 409.9 $[M\text{-}H]^-$. HRMS (EI) m/z calcd for $C_{16}H_{14}NO_3SBr$ 380.9857 $[M\text{-}MeOH]^+$, found 380.9879 $[M\text{-}MeOH]^+$. IR (ATR, ν in cm-1): 3275, 2925 (w), 1646, 1604, 1574, 1523,

1489, 1389, 1363, 1311, 1274, 1190, 1139, 1103, 1065, 1036, 1009, 961, 926, 844, 825, 800, 754, 724, 692, 668.

Synthesis of compound **6h**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2i** (93 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6h** as a colorless foam (51 mg, 0.127 mmol, 64%, isolated *dr* 79: 21; *dr* of the crude mixture 79: 21 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 109 - 127 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.28. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.83 – 7.74 (m, 3H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 5.64 (dd, *J* = 9.8, 3.8 Hz, 1H; *major-diastereomer*), 5.58 (dd, *J* = 10.0, 2.6 Hz, 1H; *minor-diastereomer*), 3.71 (qd, *J* = 7.3, 3.8 Hz, 1H; *major-diastereomer*), 3.50 (ddd, *J* = 14.5, 7.4, 2.9 Hz, 1H; *minor-diastereomer*), 3.32 (s, 3H; *minor-diastereomer*), 3.19 (s, 3H; *major-diastereomer*), 1.50 (d, *J* = 7.3 Hz, 3H; *major-diastereomer*), 1.46 (d, *J* = 7.2 Hz, 3H; *minor-diastereomer*). ^{13}C NMR (*101 MHz, $CDCl_3$*;*major-diastereomer*) δ 167.8, 144.3, 133.1, 132.6, 130.6, 129.5, 129.0, 128.9, 127.3, 126.0 (dd, *J* = 7.2, 3.5 Hz), 81.1, 62.8, 55.8, 10.3.(no peaks for the minor diastereomer could be observed in the ^{13}C NMR in this case) ^{19}F NMR (*376 MHz, $CDCl_3$*) δ -63.1 (s, *major-diastereomer*), -63.2 (s, *minor-diastereomer*). MS (ESI): m/z calcd for $C_{18}H_{18}NO_4SF_3Na^+$ 424.1 $[M+Na]^+$, found 424.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{17}H_{14}NO_3SF_3$ 369.0646 $[M-MeOH]^+$, found 369.0634 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3334 (w), 2936 (w), 1648 (m), 1603 (w), 1581 (w), 1523 (m), 1491 (m), 1455 (w), 1404 (w), 1355 (w), 1318 (s), 1293 (s), 1126 (s), 1102 (m), 1074 (m), 1059 (s), 1017 (m), 969 (m), 843 (m), 787 (m), 748 (m), 721 (m), 699 (s), 666 (m).

Synthesis of compound **6i**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2j** (86 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **6i** as a colorless foam (17 mg, 0.044 mmol, 22%, isolated *dr* 79: 21; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 80-86 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.22. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.48 (s, 1H), 8.23 (d, *J* = 9.9 Hz, 1H; *minor-diastereomer*), 8.02 – 7.95 (m, 2H), 7.94 – 7.82 (m, 5H), 7.72 – 7.54 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 5.62 (td, *J* = 9.8, 3.2 Hz, 1H), 3.75 (qd, *J* = 7.2, 4.0 Hz, 1H; *major-diastereomer*), 3.53 (qd, *J* = 7.1, 2.5 Hz, 1H; *minor-diastereomer*), 3.34 (s, 1H; *minor-diastereomer*), 3.20 (s, 3H; *major-diastereomer*), 1.48 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.7, 137.2, 135.4, 133.2, 132.4, 132.2, 130.7, 129.6, 129.4, 129.0, 128.9, 128.1, 127.7, 127.4, 123.6, 81.3, 62.7, 55.9, 10.9. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 167.3, 135.5, 135.3, 133.4, 132.4, 132.1, 131.7, 129.7, 129.4, 129.0, 128.9, 128.1, 127.8, 127.4, 124.2, 81.3, 64.7, 56.5, 13.0.

MS (ESI): m/z calcd for $C_{21}H_{21}NO_4SNa^+$ 406.1 $[M+Na]^+$, found 406.0 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{20}H_{17}NO_3S$ 351.0929 $[M-MeOH]^+$, found 351.0947 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3332 (w), 2936 (w), 1648 (m), 1517 (m), 1486 (m), 1454 (m), 1347 (m), 1299 (s), 1196 (w), 1140 (s), 1122 (s), 1068 (s), 947 (m), 855 (m), 815 (m), 752 (m), 690 (m), 659 (m).

Synthesis of compound **6j**: Prepared according to TP1 from (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **2k** (41 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) and recrystallisation from toluene/cyclohexane afforded the analytically pure sulfone **6j** as a low melting solid (29 mg, 0.11 mmol, 54%, isolated *dr* >98: 2; *dr* of the crude mixture 86: 14 as determined by ^1H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.1. ^1H NMR (*400 MHz, $CDCl_3$*) δ 8.04 (d, *J* = 9.7 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.70 (dd, *J* = 10.0, 3.4 Hz, 1H), 3.54 (qd, *J* = 7.3, 3.4 Hz, 1H), 3.45 (s, 3H), 3.16 (s, 3H), 1.42 (d, *J* = 7.3 Hz, 3H). (peaks listed only for the major diastereomer) ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.9, 133.0, 132.5, 128.9, 127.3, 80.8, 60.8, 56.3, 44.4, 9.1. (peaks listed only for the major diastereomer) MS (ESI): m/z calcd for $C_{12}H_{17}NO_4SNa^+$ 294.1 $[M+Na]^+$, found 293.9 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}NO_3S$ 239.0616 $[M-MeOH]^+$, found 239.0621 $[M-MeOH]^+$. IR (ATR, ν in cm^{-1}): 3349 (w), 2934 (w), 1648 (m), 1580 (w), 1518 (m), 1486 (m), 1349 (w), 1288 (s), 1196 (w), 1120 (m), 1073 (s), 959 (m), 847 (m), 801 (w), 764 (m), 712 (m), 691 (m).

Synthesis of compound **7**: Prepared according to TP1 from (*E*/*Z*)-Enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sulfinate salt **1m** (88 mg, 2.0 equiv., 0.4 mmol) in methanol (2 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure *N*,*O*-Acetale **7** as a colorless solid (30 mg, 0.157 mmol, 79%). m.p. 61 – 65 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.38. ^1H NMR (*400 MHz, $CDCl_3$*) δ 7.80 (dt, *J* = 3.5, 2.4 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.50 – 7.43 (m, 2H), 6.23 (d, *J* = 7.9 Hz, 1H), 5.33 – 5.24 (m, 1H), 3.42 (s, 3H), 1.92 – 1.61 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 167.7, 134.2, 132.0, 128.9, 127.1, 83.0, 56.2, 29.0, 9.3. MS (ESI): m/z calcd for $C_{11}H_{15}NO_2Na^+$ 216.1 $[M+Na]^+$, found 216.1 $[M+Na]^+$. IR (ATR, ν in cm^{-1}): 3227 (w), 2935 (w), 1635 (s), 1605 (m), 1579 (m), 1540 (s), 1489 (m), 1470 (m), 1445 (m), 1364 (w), 1320 (m), 1298 (m), 1260 (m), 1198 (m), 1143 (m), 1096 (s), 1047 (m), 1027 (m), 1014 (m), 939 (m), 920 (m), 842 (m), 808 (m), 765 (w), 707 (s), 693 (s), 666 (m).
Analytical data match those reported in the literature.[34]

Synthesis of compound **4a** from lithium sulfinate **9a**: A solution of 1-iodo-4-methylbenzene **8a** (1.6 g, 7.5 mmol, 1.0 equiv) in Et_2O (15 mL) was treated with nBuLi (2.9 mL, 2.58 M in hexane, 7.5 mmol, 1.0

equiv) dropwise at 0 °C (ice bath cooling). The mixture was allowed to stir at 0 °C for 30 min. After cooling to -40 °C, liquid SO_2 (0.5 mL, 25 mmol, 3.3 equiv) was added and the reaction mixture was allowed to warm to 25 °C for 90 min. The resulting suspension was filtered. The obtained solid was washed with EtOAc (3x 30 mL) and DCM (3x 30 mL) to give sulfinate **9a** as a colorless solid solid (870 mg, 72%). The crude sulfinate was used without further purification in the next step.

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, lithiumsulfinate **9a** (65 mg, 2.0 equiv, 0.4 mmol), (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23) and methanol (2 mL). $Fe(NO_3)_3 \cdot 9\,H_2O$ (162 mg, 2.0 equiv., 0.4 mmol) was added and the tube was closed with a rubber septum. The resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (as judged by thin layer chromatography), saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification of the crude residue by flash column chromatography afforded the analytically pure product as a colorless foam (46 mg, 0.132 mmol, 66% isolated *dr* 80: 20; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). *Analytical data match those of **4a** prepared from the corresponding sodium sulfinate.*

Synthesis of compound **6a** from lithium sulfinate **9b**: A dry, N_2-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with phenyllithium (14.6 mL, 23 mmol, 1.55 M solution in Et_2O, 1.0 equiv) and cooled to −40 °C. At this temperature, liquid SO_2 (0.5 mL, 25 mmol, 1.1 equiv) was added and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and coevaporated two times with DCM (150 mL) to afford the solid benzenesulfinic lithium salt **9b** (4.3 g). This procedure affords sulfinate **9b** sufficiently pure for the following transformation.

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, lithiumsulfinate **9b** (65 mg, 2.0 equiv, 0.4 mmol), (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23) and methanol (2 mL). $Fe(NO_3)_3 \cdot 9\,H_2O$ (162 mg, 2.0 equiv., 0.4 mmol) was added and the tube was closed with a rubber septum. The resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (as judged by thin layer chromatography), saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification of the crude residue by flash column chromatography afforded the analytically pure product as a colorless oil (39 mg, 0.117 mmol, 58%, isolated *dr* 80: 20; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). *Analytical data match those of **6a** prepared from the corresponding sodium sulfinate.*

Synthesis of compound **6k** from lithium sulfinate **9c**: A dry, N_2-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with nBuLi (1.63 mL, 3.8 mmol, 2.34 M) and THF (5 mL), then cooled to −40 °C. At this temperature, liquid SO_2 (0.5 mL, 25 mmol) was added and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and coevaporated two times with CH_2Cl_2 (150 mL) to afford the solid lithium salt **9c** (500 mg), which can be used directly for the next step.

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, the obtained lithiumsulfinate **9c** (65 mg, 2.0 equiv, 0.4 mmol), (*E*/*Z*)-enamide derivative **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23) and methanol (2 mL). $Fe(NO_3)_3 \cdot 9\ H_2O$ (162 mg, 2.0 equiv., 0.4 mmol) was added and the tube was closed with a rubber septum. The resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (as judged by thin layer chromatography TLC), saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification of the crude residue by flash column chromatography afforded the analytically pure product as a colorless oil (40 mg, 0.128 mmol, 64% isolated *dr* 71: 29; *dr* of the crude mixture 68: 32 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). R_f (*n*-hexane:EtOAc = 7:3) 0.22. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.24 (d, *J* = 9.8 Hz, 1H; *minor-diastereomer*), 8.16 (d, *J* = 9.8 Hz, 1H; *major-diastereomer*), 7.91 – 7.82 (m, 2H), 7.53 (ddd, *J* = 7.3, 6.1, 4.4 Hz, 1H), 7.49 – 7.42 (m, 2H), 5.66 (dd, *J* = 10.0, 3.3 Hz, 1H; *major-diastereomer*), 5.58 (dd, *J* = 9.8, 2.7 Hz, 1H; *minor-diastereomer*), 3.55 (qd, *J* = 7.3, 3.3 Hz, 1H; *major-diastereomer*), 3.44 (s, 3H; *minor-diastereomer*), 3.42 (s, 3H; *major-diastereomer*), 3.33 – 3.16 (m, 2H), 3.13 – 3.05 (m, 1H; *minor-diastereomer*), 1.95 – 1.76 (m, 2H), 1.60 (d, *J* = 7.3 Hz, 3H; *minor-diastereomer*), 1.54 – 1.44 (m, 2H), 1.40 (d, *J* = 7.3 Hz, 3H; *major-diastereomer*), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*; *major-diastereomer*) δ 167.9, 133.0, 132.4, 128.9, 127.3, 81.0, 58.5, 56.2, 56.1, 23.9, 21.9, 13.7, 9.1. ^{13}C NMR (*101 MHz, $CDCl_3$*; *minor-diastereomer*) δ 167.2, 133.2, 132.3, 128.8, 127.3, 80.8, 63.5, 56.8, 52.0, 22.4, 22.0, 13.8, 13.0. MS (ESI): m/z calcd for $C_{15}H_{22}NO_4S^-$ 312.1 $[M\text{-}H]^-$, found 312.1 $[M\text{-}H]^-$. HRMS (EI) m/z calcd for $C_{14}H_{20}NO_3S^+$ 282.1158 $[M\text{-}MeO]^+$, found 282.11640 $[M\text{-}MeO]^+$. IR (ATR, ν in cm^{-1}): 3348 (w), 2959 (w), 1661 (m), 1582 (w), 1516 (m), 1488 (m), 1463 (m), 1352 (m), 1285 (m), 1264 (s), 1194 (m), 1117 (s), 1094 (s), 1071 (s), 949 (w), 845 (m), 801 (w), 706 (m), 687 (m).

Telescoped processed for the synthesis of **4a:** An oven-dried, 25 mL round bottom flask was charged with a magnetic stirring bar, $Ni(PPh_3)_2$[NaphthylBr] **11** (100 mg, 5 mol%, 0.5 mmol) and MeOH (10 mL) and capped with a rubber septum. The resulting suspension was degassed by slowly bubbling nitrogen

through the mixture for 15 min with simultaneous sonication in an ultrasound bath. Then *N*-allylamide **5a** (400 mg, 1.0 equiv., 2.5 mmol) was added at room temperature under vigorous stirring. The reaction mixture was stirred for 24 h time. After complete conversion of the allylamide (as judged by thin layer chromatography), sulfinate salt **2a** (890 mg, 2.0 equiv., 5.0 mmol) and $Fe(NO_3)_3 \cdot 9\ H_2O$ (2.02 g, 2.0 equiv., 5.0 mmol) were added to the reaction mixture. The resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (as judged by thin layer chromatography), saturated aqueous NH_4Cl (20 mL) was added. The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with dichloromethane (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification by flash column chromatography (*n*-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **4a** as a colorless foam (843 mg, 2.4 mmol, 97%, isolated *dr* 80: 20; *dr* of the crude mixture 80: 20 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). *Analytical data match those of **4a**.*

Synthesis of **3** via thermal elimination of **4a**: An oven-dried, 10 mL screw cap glass tube with a PP-cap was charged with a magnetic stirring bar, sulfone **4a** (35 mg, 1.0 equiv., 0.1 mmol) and dichloroethane (1 mL). The reaction mixture was stirred at 80 °C for 20 h. After cooling to room temperature saturated aqueous $NaHCO_3$ (3 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Purification by flash column chromatography (*n*-hexane/EtOAc) afforded the (*E*)- and (*Z*)-β-amidovinylsulfones **3** as a colorless solid (26 mg, 0.083 mmol, 83%, isolated *dr* 53: 47; (**3**-(*E*): **3**-(Z)) *dr* of the crude mixture 53: 47 (**3**-(*E*): **3**-(Z)); as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). Separation of both isomers by column chromatography was possible.

3-(*E*) : R_f (*n*-hexane:EtOAc = 7:3) 0.22. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.29 (d, *J* = 11.7 Hz, 1H), 7.85 – 7.72 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 1H), 1.89 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 144.1, 137.0, 133.2, 132.5, 131.4, 129.9, 129.2, 128.1, 127.5, 118.5, 21.7, 10.7. Analytical data match those reported in the literature. Crystals of (*E*)-**3** suitable for X-Ray could be obtained by slow evaporation from ethylacetate.

3-(*Z*): m.p. 159 – 164 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.53. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 11.00 (d, *J* = 11.4 Hz, 1H), 8.02 – 7.93 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.87 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 164.1, 145.0, 136.6,

133.1, 132.2, 130.8, 130.1, 129.2, 127.8, 127.6, 113.2, 21.8, 16.1. MS (ESI): m/z calcd for $C_{17}H_{17}NO_3SNa^+$ 338.1 $[M+Na]^+$, found 338.2 $[M+Na]^+$. HRMS (EI) m/z calcd for $C_{17}H_{17}NO_3S$ 315.0929 $[M]^+$, found 315.0940 $[M]^+$. IR (ATR, ν in cm^{-1}): 3350 (m), 2924 (w), 1688 (m), 1641 (s), 1476 (m), 1287 (s), 1128 (s), 1073 (m), 944 (m), 875 (m), 806 (m), 711 (s), 688 (s), 668 (m).

Synthesis of **12**: A flame dried and argon flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with *N*,*O*-acetal **4a** (87 mg, 0.25 mmol, 1.0 equiv), 2.5 mL DCM and cooled to -50 °C. $TiCl_4$ (55 µl, 0.5 mmol 2.0 equiv) was added and the reaction was stirred for 15 min. Then L-Selectride (1 mL, 1 mmol, 4.0 equiv; 1M in THF) was added dropwise. The reaction was allowed to warm to rt overnight. After TLC showed complete consumption of the starting material, saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. Column chromatography (*n*-hexane:EtOAc = 9:1→4:1→7:3→1:1) afforded the desired amide **12** as a colorless solid (55 mg, 0.17 mmol, 69%). R_f (*n*-hexane:EtOAc = 7:3) 0.12. ^{1}H NMR (*400 MHz, CDCl$_3$*) δ 7.83 – 7.74 (m, 4H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.20 (s, 1H), 3.94 (ddd, *J* = 14.9, 6.5, 3.2 Hz, 1H), 3.85 – 3.67 (m, 1H), 3.36 (pd, *J* = 7.1, 3.2 Hz, 1H), 2.45 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (*101 MHz, CDCl$_3$*) δ 167.5, 145.5, 133.9, 133.9, 131.9, 130.2, 128.9, 128.8, 127.1, 59.7, 39.4, 21.8, 12.7. Analytical data match those reported in the literature.[19]

Nucleophilic trapping of *N*,*O*-acetyl **4a**

Typical procedure 2: An oven-dried, 10 mL screw cap glass tube with a PP-cap was charged with a magnetic stirring bar, *N*,*O*-acetal **4a** (1.0 equiv.), $Bi(OTf)_3$ (5 mol%) and 1 ml Dichloromethane. Then the nucleophile (4.0 equiv.) was added and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (as judged by thin layer chromatography), the reaction mixture was diluted with EtOAc and filtered through a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc and the solvent was evaporated under reduced pressure. Purification of the crude residue by flash column chromatography afforded the analytically pure product.

Synthesis of compound **13a:** Prepared according to TP2 from sulfone **4a** (35 mg, 1.0 equiv., 0.1 mmol), $Bi(OTf)_3$ (7 mg, 5 mol %., 0.01 mmol) and 2-methylfuran (72 µL, 1.0 equiv., 0.4 mmol) in DCM (1 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc) afforded the analytically pure sulfone **13a** as a colorless oil (74 mg, 0.185 mmol, 92%, isolated *dr* 83: 17; *dr* of the crude mixture 83: 17 as determined by ^{1}H NMR analysis of the unpurified

product after aqueous workup). m.p. 142 – 147 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.32. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 8.01 – 7.83 (m, 2H), 7.77 – 7.66 (m, 1H), 7.61 – 7.44 (m, 5H), 7.29 (d, *J* = 8.2 Hz, 1H, *minor-diastereomer*), 7.23 (d, *J* = 8.2 Hz, 2H, *major-diastereomer*), 6.15 (d, *J* = 3.0 Hz, 1H, *minor-diastereomer*), 6.06 (d, *J* = 3.0 Hz, 1H *major-diastereomer*), 5.87 (d, *J* = 3.0 Hz, 1H, *minor-diastereomer*), 5.73 (d, *J* = 2.3 Hz, 1H *major-diastereomer*), 5.63 (dd, *J* = 8.4, 3.2 Hz, 1H, *minor-diastereomer*), 5.49 (dd, *J* = 8.4, 5.7 Hz, 1H *major-diastereomer*), 4.04 – 3.92 (m, 1H *major-diastereomer*), 3.66 (dd, *J* = 7.3, 3.5 Hz, 1H, *minor-diastereomer*), 2.40 (s, 3H), 2.16 (s, 1H, *minor-diastereomer*), 1.97 (s, 3H, *major-diastereomer*), 1.49 (t, *J* = 6.2 Hz, 1H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 166.9, 151.9, 148.6, 144.6, 135.4, 133.8, 132.1, 129.7, 128.9, 128.5, 127.4, 108.8, 106.5, 61.2, 49.5, 21.7, 13.3, 12.4. MS (ESI): m/z calcd for $C_{22}H_{22}NO_4S^-$ 396.1 [M-H]-, found 396.1 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{17}H_{17}NO_3S$ 315.0929 $[M-C_5H_6OH]^+$, found 315.0925 $[M+H]^+$. IR (ATR, ν in cm^{-1}): 3284 (m), 2936 (m), 1636 (m), 1542 (m), 1492 (m), 1447 (m), 1307 (s), 1291 (s), 1216 (m), 1184 (m), 1135 (s), 1083 (m), 1023 (m), 852 (w), 802 (m), 785 (m), 719 (m), 696 (m).

Synthesis of compound **13b:** Prepared according to TP2 from sulfone **4a** (35 mg, 1.0 equiv., 0.1 mmol), $Bi(OTf)_3$ (3.3 mg, 5mol%, 5.0 µmol) and 2,4,6-trimethoxybenzene (38 mg, 4.0 equiv., 0.4 mmol) in DCM (1 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) afforded the analytically pure sulfone **13b** as a colorless solid (30 mg, 0.061 mmol, 61%, isolated *dr* 87: 13; *dr* of the crude mixture 87: 13 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 76 – 83 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.08. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.74 – 7.70 (m, *J* = 7.1 Hz, 2H), 7.47 – 7.35 (m, 4H), 7.30 – 7.24 (m, 2H), 6.07 (s, 2H), 5.94 (t, *J* = 9.8 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.79 (s, 6H), 3.75 (s, 3H), 2.34 (s, 3H), 1.11 (d, *J* = 7.1 Hz, 3H). *(Peaks only for major diastereomer)* ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 165.6, 161.1, 158.8, 144.5, 135.0, 134.6, 131.2, 129.7, 129.3, 128.5, 127.2, 108.5, 91.3, 62.6, 56.2, 55.4, 45.4, 21.7, 13.4. *(Peaks only for major diastereomer)* MS (ESI): m/z calcd for $C_{26}H_{28}NO_6S^-$ 482.2 $[M-H]^-$, found 482.4 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{26}H_{29}NO_3S$ 483.1716 $[M]^+$, found 483.1699 $[M]^+$. IR (ATR, ν in cm^{-1}): 3393 (w), 2931 (m), 1653 (m), 1592 (m), 1526 (m), 1489 (m), 1455 (m), 1418 (m), 1287 (m), 1204 (m), 1115 (s), 953 (m), 856 (w), 801 (m), 724 (m), 694 (m).

Synthesis of compound **13c:** Prepared according to TP2 from sulfone **4a** (35 mg, 1.0 equiv., 0.1 mmol), $Bi(OTf)_3$ (3.3 mg, 0.05 equiv., 5.0 µmol) and 3-methylindole (53 mg, 4.0 equiv., 0.4 mmol) in DCM (1 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) and recrystallisation from toluene/cyclohexane afforded the analytically pure sulfone **13c** as colorless needles (33 mg, 0.074 mmol, 74%, isolated *dr* >98: 2 *dr* of the crude mixture 84 16 as determined by ^{1}H NMR analysis of the unpurified product after

aqueous workup). m.p. 109 – 116 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.23. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 9.49 (s, 1H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.45 (dt, *J* = 31.4, 7.1 Hz, 5H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.13 (m, *J* = 12.5, 8.1 Hz, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.35 (t, *J* = 8.0 Hz, 1H), 4.50 (dq, *J* = 14.4, 7.1 Hz, 1H), 2.30 (d, *J* = 4.5 Hz, 6H), 1.12 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 168.9, 145.1, 135.6, 135.3, 133.8, 132.1, 131.2, 129.9, 128.7, 128.3, 128.3, 127.3, 122.6, 119.4, 119.0, 111.4, 109.6, 60.4, 49.2, 21.7, 13.4, 9.0. MS (ESI): m/z calcd for $C_{26}H_{25}N_2O_3S^-$ 445.2 $[M-H]^-$, found 445.3 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{26}H_{26}N_2O_3$ 446.1664 $[M]^+$, found 446.1670 $[M]^+$.IR (ATR, ν in cm^{-1}): 3347 (w), 2921 (w), 1634 (m), 1525 (m), 1488 (m), 1458 (m), 1286 (s), 1137 (s), 1082 (m), 906 (m), 813 (m), 731 (m).

Synthesis of compound **13d:** Prepared according to TP2 from sulfone **4a** (35 mg, 1.0 equiv., 0.1 mmol), $Bi(OTf)_3$ (3.3 mg, 0.05 equiv., 5.0 µmol) and ethanethiol (29 µL, 4.0 equiv., 0.4 mmol) in DCM (1 mL). The reaction was stirred at room temperature for 2 h. Purification by flash column chromatography (n-hexane/EtOAc+0.2 vol% NEt_3) and recrystallisation from toluene/cyclohexan afforded the analytically pure sulfone **13d** as a colorless foam (28 mg, 0.073 mmol, 73%, isolated *dr* 98: 2; *dr* of the crude mixture 71: 29 as determined by ^{1}H NMR analysis of the unpurified product after aqueous workup). m.p. 53– 57 °C. R_f (*n*-hexane:EtOAc = 7:3) 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.30 (m, 3H), 5.66 (dd, *J* = 9.5, 4.7 Hz, 1H), 3.66 (qd, *J* = 7.1, 4.8 Hz, 1H), 2.75 – 2.55 (m, 2H), 2.45 (s, 3H), 1.45 (d, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 166.8, 145.5, 135.5, 133.4, 132.3, 130.1, 129.0, 128.9, 127.3, 63.8, 55.4, 26.4, 21.9, 14.7, 13.9. MS (ESI): m/z calcd for $C_{19}H_{22}NO_3S_2^-$ 376.1 $[M-H]^-$, found 376.3 $[M-H]^-$. HRMS (EI) m/z calcd for $C_{17}H_{17}NO_3S$ 315.0929 $[M-C_2H_5SH]^+$, found 315.0937 $[M- C_2H_5SH]^+$.IR (ATR, ν in cm^{-1}): 3349 (w), 2934 (w), 1648 (m), 1580 (w), 1518 (m), 1486 (m), 1349 (w), 1288 (s), 1196 (w), 1120 (m), 1073 (s), 959 (m), 847 (m), 801 (w), 764 (m), 712 (m), 691 (m).

Synthesis of compound **14:** A 25 mL round bottom flask was charged with a magnetic stirring bar, $NaIO_4$ (802 mg, 15.0 equiv., 3.75 mmol), CCl_4 (1.3 mL), MeCN (1.3 mL), H_2O (2.0mL) and EtOAc (0.8 mL). $RuO_2{\cdot}H_2O$ (1.4 mg, 5 mol%, 12.5 µmol) was added and the resulting suspension stirred for 1h. Then sulfone **13a** (99.4 mg, 1.0 equiv., 0.25 mmol) in DCM; (1.5 mL) was added and the resulting mixture was stirred at room temperature for 24 h. Upon completion of the reaction (as judged by thin layer chromatography), the reaction mixture was acidified with 1N $NaHSO_4$ (pH = 1) and filtered through a short plug of celite. The plug was rinsed with additional DCM and the solvent was washed with brine and three times with an aqueous $NaHCO_3$ (50 mL). The aqueous phase was again carefully acidified with 1N $NaHSO_4$ to pH = 1 and then extracted three times with EtOAc (50mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced

pressure to afforded the analytically pure product as a colorless foam (69 mg, 0.19 mmol, 76%, isolated *dr* 94: 6). m.p. 67– 75 °C. R_f (DCM: MeOH = 9:1) 0.4. ^{1}H NMR (*400 MHz, $CDCl_3$*) δ 10.19 (s, 1H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 24.1, 8.1 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.21 (dd, *J* = 8.8, 3.5 Hz, 1H), 4.12 – 4.00 (m, 1H), 2.39 (s, 3H), 1.40 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (*101 MHz, $CDCl_3$*) δ 172.9, 168.3, 145.7, 134.6, 133.0, 132.4, 130.1, 128.8, 128.8, 127.5, 60.7, 53.5, 21.7, 13.1. MS (ESI): m/z calcd for $C_{18}H_{19}NO_5S$ 360.4 $[M-H]^+$, found 360.3 $[M-H]^+$. HRMS (EI) m/z calcd for $C_{18}H_{19}NO_5S$ 361.0984 $[M]^+$, found 361.0996 $[M]^+$. IR (ATR, ν in cm^{-1}): 3341 (w), 3062 (w), 2928 (w), 1735 (m), 1640 (m), 1600 (w), 1579 (m), 1526 (w), 1489 (m), 1452 (w), 1286 (s), 1139 (s), 1084 (m), 816(w), 710 (m).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: .

NMR spectra and X-ray crystal structures (PDF)

X-ray data for compounds **3a-(*E*), 4a** and **13b** (ZIP)

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Notes

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