Synthesis of Highly Enantioenriched Sulfonimidoyl Fluorides and Sulfonimidamides by Stereospecific SuFEx Reaction

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Sulfonimidamides present exciting opportunities as chiral isosteres of sulfonamides, with potential for additional directional interactions. Here we present the first modular enantioselective synthesis of sulfonimidamides, including the first stereoselective synthesis of enantioenriched sulfonimidoyl fluorides, and studies on their reactivity. A new route to sulfonimidoyl fluorides is presented from solid bench-stable, NBoc-sulfinamide salt building blocks. Enantioenriched arylsulfonimidoyl fluorides are shown to be readily racemized by fluoride ions. Conditions are developed which trap fluoride, and enable the stereospecific reaction of sulfonimidoyl fluorides with primary and secondary amines (100% es) generating sulfonimidamides with up to 99% ee. Aryl and alkyl sulfonimidoyl fluoride reagents are suitable for mild late stage functionalization reactions, exemplified by coupling with a selection of complex amines in marketed drugs.

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Synthesis of Highly Enantioenriched Sulfonimidoyl Fluorides and Sulfonimidamides by Stereospecific SuFEx Reaction

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Abstract

Sulfonimidamides present exciting opportunities as chiral isosteres of sulfonamides, with potential for additional directional interactions. Here we present the first modular enantioselective synthesis of sulfonimidamides, including the first stereoselective synthesis of enantioenriched sulfonimidoyl fluorides, and studies on their reactivity. A new route to sulfonimidoyl fluorides is presented from solid bench-stable, NBoc-sulfonamide salt building blocks. Enantioenriched arylsulfonimidoyl fluorides are shown to be readily racemized by fluoride ions. Conditions are developed which trap fluoride, and enable the stereospecific reaction of sulfonimidoyl fluorides with primary and secondary amines (100% es) generating sulfonimidamides with up to 99% ee. Aryl and alkyl sulfonimidoyl fluoride reagents are suitable for mild late stage functionalization reactions, exemplified by coupling with a selection of complex amines in marketed drugs.

Directional interactions are crucial to the development of active ingredients in pharmaceutical and agrochemical products. Inclusion of chiral moieties can increase complementarity and hence potency and selectivity of a compound for a biological target.^[1] In contrast to sulfones and sulfonamides, their chiral aza-analogues, sulfoximines and sulfonimidamides (Fig 1a), have been underrepresented in the life sciences despite their beneficial chemical properties.^[2,3] They have high chemical and metabolic stability, and can improve physicochemical properties of a molecule, such as increased solubility, with the introduction of both hydrogen bond donor and acceptor capabilities for NH-derivatives.^[4,5] It is notable that sulfoximines have appeared in several new S(VI) clinical candidates as single enantiomers (Fig 1b).^[6,7,8] Sulfonimidamides are less developed in drug discovery, but present similar potential advantages.^[9] However, to date there are no general methods available to prepare these in enantioenriched form.

Similarly, sulfonyl fluorides have been developed by Sharpless as click reagents in sulfur-fluorine exchange (SuFEx) reactions, and are used increasingly as biological probes.^[10,11] To date, application of the chiral sulfonimidoyl fluoride derivatives as biological probes is limited,^[10a,11c] but presents interesting potential for improved specific directional interactions.

Methods for the synthesis of sulfonimidamides have developed significantly in recent years including powerful NH transfer methods.^[12] A valuable disconnection for divergent synthesis is formation of the S–N bond, by coupling an electrophilic S-source with amines.^[13,14] Several methods proceed via the sulfonimidoyl chloride, including recent powerful methods developed by Chen^[15] and Willis (Fig 1c).^[16] However, sulfonimidoyl chlorides are typically unstable and decompose under basic, aqueous or reductive conditions, requiring *in situ* generation and amine coupling.^[5] Alternative sulfonimidoyl reagents have been developed as more stable sulfonimidamide precursors.^[17-19] Sharpless has used SOF₄ gas to generate stable N-aryl sulfonimidoyl fluoride reagents which were reacted with pyrrolidine or lithium amide reagents (Fig 1d).^[20] It is notable that none of the methods described to date have been amenable to the preparation of enantioenriched derivatives.^[21]

S(VI) Aza-analogues

a) S(VI) Aza-analogues introduce of a new chiral sulfur centre

b) New S(VI) clinical candidates

c) Routes to sulfonimidamides with substitution at sulfur

d) Sulfonimidoyl fluorides as sulfonimidamide precursors

e) This route

Figure 1. Structure of sulfoximine and sulfonimidamide groups and S(VI) clinical candidates with asymmetric sulfur centres. Synthetic routes to access sulfonimidamides typically rely on sulfonimidoyl chloride precursors, alternative sulfonimidoyl-X species, and this work as a new way to access enantioenriched sulfonimidoyl fluorides and sulfonimidamides.

Enantioenriched sulfonimidoyl fluorides have been unknown until very recently. Zuilhof isolated the first example of an enantioenriched sulfonimidoyl fluoride, generated by the reaction of a racemic sulfonimidoyl chloride with KF, followed by separation of the enantiomers by chiral HPLC.^[22] Notably these reagents reacted with phenols in the presence of DBU, without requiring silylation, but underwent racemisation ascribed to the base. Using sodium phenolate provided enantioenriched sulfonimidates in a rapid reaction.

Here we describe a method to prepare highly enantioenriched sulfonimidoyl fluorides from bench-stable sulfinamide salts, and their use in the synthesis of a diverse range of enantioenriched sulfonimidamides by stereospecific SuFEx reaction (Fig 1e). The first stereocontrolled synthesis of sulfonimidoyl fluorides is reported. Fluoride ions are demonstrated to cause racemization of the sulfonimidoyl fluorides, which is avoided by fluoride trapping. The mild coupling reagents allow the use of neutral primary and secondary amines, and the methodology is exemplified in the functionalization of amine containing drug compounds, showing the potential for its use to rapidly prepare novel chemical entities and diverse chemical libraries.^[23] A readily removed NBoc-protecting

group on the imide nitrogen is employed, which also increased the electrophilicity of the sulfonimidoyl fluoride.

By analogy with sulfonyl fluorides, we envisaged a new route to sulfonimidoyl fluorides through fluorination of sulfinamide salts.^[24,25] Initially, racemic *p*-tolyl sulfinamide salt **1a** was prepared from the corresponding NBoc-sulfoximine by elimination of acrylate (see SI). Pleasingly, sulfonimidoyl fluoride **2a** was formed in high yield and excellent purity using Selectfluor, after a simple aqueous workup (Scheme 1a, Procedure A). Furthermore, we developed conditions for the reaction **2a** with 11 examples of primary and secondary amines (Procedure B; e.g. piperidine, 77% yield **3a** in Scheme 1a. See SI for further examples).

Scheme 1. A new route to sulfonimidamides via sulfonimidoyl fluorides was developed, however racemization was observed in both fluorination and amine coupling steps, understood to be from sulfonimidoyl fluoride racemization. For details on Procedures A & B, see SI. For 1d, reactions were performed on a 0.1 mmol scale in THF (0.3 M) at rt for 3 h. Retained ee given by %ee(*R*)-2a product/%ee(*R*)-2a SM.

While this route demonstrated the proof of concept, a key aim for this project was in the development of an efficient strategy to enantioenriched sulfonimidamides. The corresponding enantioenriched salt (**S**)-**1a** was formed from commercial (*S*)-(+)-*p*-toluenesulfinamide (**S**)-**4** (Table 1; (**S**)-**4** to (**S**)-**1a**). However, when using the enantioenriched sulfinamide salt, a significant loss of ee occurred in both fluorination and coupling steps (Scheme 1b). Monitoring the reduction of ee over the course of the SuFEx reaction showed sulfonimidoyl fluoride (**R**)-**2a** rapidly racemized (Scheme 1c, see SI for additional data). Sulfonimidamide (**R**)-**3a** retained a low ee and was proven to be configurationally stable under the reaction conditions.

We proposed that degenerate nucleophilic attack of fluoride ions in solution on the sulfonimidoyl fluoride center was causing the racemization (Scheme 1d). To explore this hypothesis, two fluoride ion sources, TBAF and KF, were added to the sulfonimidoyl fluoride (**R**)-**2a** in THF at rt for 3 h. In the absence of a soluble fluoride ion source (Entry 1), a small amount of racemization occurred, presumably as a result of elimination of fluoride ions from the starting material. A soluble fluoride source (TBAF, Entry 2) caused the complete racemization of the sulfonimidoyl fluoride whereas the highly insoluble, inorganic KF did not release fluoride ions into solution and may, in fact, have complexed with F⁻ present to prevent racemization (Entry 3).^[26,27]

This directed us to examine fluoride trapping strategies (See SI). Firstly, in the fluorination step, changing the solvent to ethanol, being polar and protic, resulted in full preservation of ee.

However, the yield of the fluorination was much reduced, presumably from the protonation of the sulfinamide salt causing reduced nucleophilicity of the sulfur center. The introduction of potassium acetate as a soluble inorganic base resulted in an increased yield for this step with no loss of ee (Table 1, (**S**)-1a to (**R**)-2a).

Preventing racemization of the sulfonimidoyl fluoride in the amine coupling step required more extensive optimization (Table 1, (**R**)-2a–(**R**)-3a). A selection of trapping additives was examined (Entries 2-6). A typical organic fluoride ion scavenger, TMS-Cl shut down the reactivity and resulted in almost complete recovery of starting material. The addition of water resulted in an increased yield, however, there was only a small increase in es observed. Soluble inorganic salts were investigated to precipitate insoluble fluoride salts.^[26] Adding KBr was not beneficial, whereas LiCl gave complete preservation of ee. The use of more soluble LiBr resulted in complete preservation of ee and an increase in yield. Changing the solvent had a lesser effect on ee than in the fluorination step and alcohol solvents caused a significant amount of sulfonimide formation (Entries 7-8). However, changing the solvent to MeCN resulted in an increased yield (Entry 9), and when combined with LiBr resulted in the formation of an enantioenriched sulfonimidamide in excellent yield (Entry 10).

Table 1. Optimization of amine coupling for retention of ee and yield

Entry	Solvent	Additive	Yield (%) ^a			% es ^c
			(R)-2a	(R)-3a	Total ^b	
1	THF	-	30	52	82	8
2	THF	TMS-Cl	75	1	76	n.d.
3	THF	H ₂ O	6	77	83	26
4	THF	KBr	33	44	77	13
5	THF	LiCl	11	31	42	>99
6	THF	LiBr	19	56	75	>99
7	EtOH	-	-	33	33	45
8	<i>i</i> PrOH	-	6	66	72	29
9	MeCN	-	9	73	82	28
10	MeCN	LiBr	-	96	96	>99
11	MeCN	Lil	-	87	87	>99

^a Reactions performed on 0.1 mmol scale. ^aYields determined by ¹H-NMR using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses. ^b Sum of preceding two columns. ^c es, enantiospecificity, given by %ee(**R**)-3a/%ee(**R**)-2a. For details on Procedure C, see SI.

With the optimized conditions in hand, the amine scope of the reaction was explored (Scheme 2). Pleasingly, both primary and secondary amines were suitable in this reaction with complete enantiospecificity in all cases. Aliphatic, benzylic and allylic amines were all coupled in good yields ((**R**)-3b–(**R**)-3g). Acyclic and cyclic secondary amines reacted in excellent yields ((**R**)-

3h–(R)-3l). Ketones and *gem*-difluoro substituents were all well tolerated on the amine substrate ((**R**)-**3m**–(**R**)-**3n**). Chemoselective reactivity was observed with 6-piperidinol to form sulfonimidamide (**R**)-**3o** without significant competing sulfonimide formation. Finally, more highly functionalized piperidines and piperazine heterocycles were coupled in good yield under the mild conditions ((**R**)-**3p**–(**R**)-**3s**), including the drug desipramine. Treating (**R**)-**2a** with both enantiomers of α -methylbenzylamine gave different single diastereomer products ((**R**)-**3t** and (**R**)-**3u**).

Scheme 2. Amine scope using the *p*-tolyl sulfonamide salt. Reactions performed on 0.25 mmol scale. Coupling reaction performed using (**R**)-**2a** (95–99% ee) with no loss of ee in this step.

Sulfonimidamide (**R**)-**3h** was determined to be (*R*)-stereochemistry by single crystal X-ray diffraction analysis (Scheme 3; CCDC 1991431). This indicates inversion in the substitution reaction.

Nucleophilic substitution with inversion at the sulfur center has precedent with sulfonimidoyl chlorides and sulfonimidates,^[14,21,28] and more recently in the nucleophilic attack of phenols on sulfonimidoyl fluorides.^[22] Fluorination is presumed to occur with retention of the configuration similar to prior studies on chlorination (*S* changing to *R* due to priority change).^[29]

Scheme 3. From the commercially available (*S*)-enantiomer of the sulfonamide salt building block, the fluorination-amine coupling sequence was proven to occur with overall inversion of the sulfur centre from crystal structure analysis, rationalized to occur in the amine coupling step.

To exemplify a general approach to enantioenriched sulfonamides, we targeted 4-bromophenylsulfonimidoyl fluoride (**R**)-**2b**, exploiting enantioselective sulfoxide oxidation as the asymmetric step (Scheme 4).

Scheme 4. Preparation enantioenriched 4-bromophenyl sulfonimidamides. Ligand 1 = (*S*)-(-)-2-(*N*-3,5-diiodosalicyliden)amino-3,3-dimethyl-1-butanol. Stereochemistry of **8** assigned based on prior literature.^[30] Suzuki conditions = PhB(OH)₂ (1.5 equiv), K₂CO₃ (2 equiv), Pd(dtbpf)Cl₂ (10 mol%), MeCN:H₂O (1:1, 0.2 M), 80 °C, 2 h.

Catalytic enantioselective oxidation of sulfide **7** gave sulfoxide **8** in 68% yield and 99% ee (*S*).^[30] Rh-catalyzed NBoc transfer to form the sulfoximine (**S**)-**9**,^[31] which has been shown to occur with retention of ee, and elimination of methyl acrylate from gave the bench-stable sulfonamide salt (**S**)-**1b**. The elimination occurred with preservation of ee, as indicated by re-protonation of a sample of the salt. This provides a new approach to enantioenriched sulfonamide salts. Treatment of (**S**)-**1b**

with Selectfluor gave fluoride (**(R)**-**2b**) with 92% ee. Reaction of (**(R)**-**2b**) with amines gave high yields and maintained high ee (**(R)**-**3v**–(**(R)**-**3x**). Using the enantiopure drug compound duloxetine yielded a single diastereoisomer product (**(R)**-**3y**). Moreover, the 4-bromophenyl substituent of (**(R)**-**3x**) was shown to be a suitable handle for further derivatization, as exemplified in a Suzuki–Miyaura cross-coupling to give enantioenriched biphenyl derivative (**(R)**-**10**).

Moreover, additional racemic aryl and alkyl sulfinamide salts **1c–1h** were prepared (See SI). These were converted to new sulfonimidoyl fluorides **2c–2h** with Selectfluor and coupled with piperidine to form a collection of NBoc-protected sulfonimidamides (**3z–3aj**, Scheme 5). Electron-rich methoxyphenyl (**3ab**), and electron-poor pyridine derivatives (**3ac**) were successfully employed. Alkyl sulfinamide salts were also successfully converted to piperidine sulfonimidamides **3ad** and **3ae**. Procedure A (DMF) was more suitable for the fluorination step with the alkyl derivatives. The SuFEx reaction with methylsulfonimidoyl fluoride **2h** was demonstrated with several amines, including the marketed drugs primaquine, desipramine and amoxapine (**3ah–3aj**).

Scheme 5. Scope of varying sulfinamide salt building blocks in fluorination and SuFEx amine coupling reactions. For reaction conditions and equivalents, see SI. a) Procedure A; b) Procedure B; c) Procedure C; d) Procedure D. e) Competing S_NAr reactivity gave reduced yield of **3aa**.

Finally, the NBoc protecting-group was readily removed on both tertiary and secondary enantioenriched sulfonimidamide substrates with TFA in CH_2Cl_2 (Scheme 6). Treating (**(R)**-**3a**) and (**(R)**-**3f**) with TFA effected deprotection with no racemization to give NH-sulfonimidamides (**(R)**-**11**) and (**(R)**-**12**).

Scheme 6. NBoc-deprotection of primary and secondary sulfonimidamide. Sample of (**(R)**-**3f**) used had 98% ee, with NBoc-deprotection occurring with complete preservation of ee.

In conclusion, we have reported a new, practical method to access sulfonimidamides from bench-stable sulfonamide salt building blocks by a SuFEx reaction of sulfonimidoyl fluorides. We describe the first facile route to enantioenriched sulfonimidamides, which are currently underrepresented in the life sciences. Moreover, the stereocontrolled synthesis of enantioenriched sulfonimidoyl fluorides is reported for the first time. Similar to the achiral sulfonyl fluorides, we see great potential for enantioenriched sulfonimidoyl fluorides as novel warheads for chemical biology and molecular pharmacology. Our synthetic methodology has a broad substrate scope of sulfonamide salt starting materials and both primary and secondary amines are suitable coupling partners for the SuFEx reaction to access a diverse array of sulfonimidamides. The methodology can be applied to the late stage functionalization of drug molecules all in good to excellent yields, which has the potential to accelerate the preparation of novel chemical entities and diverse chemical libraries.

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References

- [1] D. Saha, A. Kharbanda, W. Yan, N. R. Lakkaniga, B. Frett and H. Y. Li, *J. Med. Chem.*, **2020**, 63, 441.
- [2] a) P. K. Chinthakindi, T. Naicker, N. Thota, T. Govender, H. G. Kruger and P. I. Arvidsson, *Angew. Chem. Int. Ed.*, **2017**, 56, 4100. b) F. Sehgelmeble et al., *ChemMedChem*, **2012**, 7, 396. c) F. Izzo, M. Schäfer, P. Lienau, U. Ganzer, R. Stockman and U. Lücking, *Chem. Eur. J.*, **2018**, 24, 9295.
- [3] a) U. Lücking, *Org. Chem. Front.*, **2019**, 6, 1319. b) U. Lücking, *Angew. Chem. Int. Ed.*, **2013**, 52, 9399. c) J. A. Sirvent and U. Lücking, *ChemMedChem*, **2017**, 12, 487.
- [4] a) M. Frings, C. Bolm, A. Blum and C. Gnam, *Eur. J. Med. Chem.*, **2017**, 126, 225. b) H. J. Lim, W. H. Lee and S. J. Park, *Molecules*, **2019**, 24, 3451.
- [5] C. Gnam, A. Jeanguenat, A. C. Dutton, C. Grimm, D. P. Kloer and A. J. Crossthwaite, *Bioorg. Med. Chem. Lett.*, **2012**, 22, 3800.
- [6] a) A. Min et al., *Mol. Cancer Ther.*, **2017**, 16, 566. b) K. M. Foote et al., *J. Med. Chem.*, **2018**, 61, 9889; c) F. P. Vendetti, A. Lau, S. Schamus, T. P. Conrads, M. J. O'Connor, C. J. Bakkenist, *Oncotarget*, **2015**, 6, 44289.
- [7] a) U. Lücking, et al., *ChemMedChem*, **2013**, 8, 1067. b) U. Lücking et al., *ChemMedChem*, **2017**, 12, 1776.
- [8] U. Lücking et al., *Cancer Res.*, **2017**, 77, 984.
- [9] G. C. Nandi and P. I. Arvidsson, *Adv. Synth. Catal.*, **2018**, 360, 2976.
- [10] a) J. Dong, L. Krasnova, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2014**, 53, 9430. b) F. Liu, H. Wang, S. Li, G. A. L. Bare, X. Chen, C. Wang, J. E. Moses, P. Wu and K. B. Sharpless, *Angew. Chem. Int. Ed.*, **2019**, 58, 8029. c) Z. Liu, J. Li, S. Li, G. Li, K. B. Sharpless and P. Wu, *J. Am. Chem. Soc.*, **2018**, 140, 2919. d) For recent reviews, see: P. K. Chinthakindi and P. I. Arvidsson, *Eur. J. Org. Chem.*, **2018**, 2018, 3648. e) A. S. Barrow, C. J. Smedley, Q. Zheng, S. Li, J. Dong and J. E. Moses, *Chem. Soc. Rev.*, **2019**, 48, 4731.
- [11] a) L. H. Jones and J. W. Kelly, *RSC Med. Chem.*, **2020**, 11, 10. b) A. Narayanan and L. H. Jones, *Chem. Sci.*, **2015**, 6, 2650. c) H. Mukherjee, J. Debreczeni, J. Breed, S. Tentarelli, B. Aquila, J. E. Dowling, A. Whitty and N. P. Grimster, *Org. Biomol. Chem.*, **2017**, 15, 9685.

- [12] a) F. Izzo, M. Schäfer, R. Stockman and U. Lücking, *Chem. Eur. J.*, **2017**, 23, 15189. b) E. L. Briggs, A. Tota, M. Colella, L. Degennaro, R. Luisi and J. A. Bull, *Angew. Chem. Int. Ed.*, **2019**, 58, 14303. c) J. Bull, L. Degennaro and R. Luisi, *Synlett*, **2017**, 28, 2525.
- [13] H. Takei, I. Watanabe and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **1965**, 38, 1989.
- [14] C. R. Johnson, E. U. Jonsson, A. Wambsgans and C. C. Bacon, *J. Org. Chem.*, **1979**, 44, 2061.
- [15] Y. Chen and J. Gibson, *RSC Adv.*, **2015**, 5, 4171.
- [16] T. Q. Davies, A. Hall and M. C. Willis, *Angew. Chem. Int. Ed.*, **2017**, 56, 14937.
- [17] S. V. Zasukha, V. M. Timoshenko, A. A. Tolmachev, V. O. Pivnytska, O. Gavrylenko, S. Zherish, Y. Shermolovich and O. O. Grygorenko, *Chem. Eur. J.*, **2019**, 25, 6928.
- [18] M. Bremerich, C. M. Conrads, T. Langletzt and C. Bolm, *Angew. Chem. Int. Ed.*, **2019**, 58, 19014.
- [19] For preparation and use of sulfonimidoyl fluorides from the corresponding chlorides using KF, see: a) C. R. Johnson, K. G. Bis, J. H. Cantillo, N. A. Meanwell, M. F. D. Reinhard, J. R. Zeller and G. P. Vonk, *J. Org. Chem.*, **1983**, 48, 1. b) R. Kowalczyk, A. J. F. Edmunds, R. G. Hall, C. Bolm, *Org. Lett.* **2011**, 13, 768. c) J. Guo, C. Kuang, J. Rong, L. Li, C. Ni and J. Hu, *Chem. Eur. J.*, **2019**, 25, 7259. d) For a CF₃ reagent: M. Wright, C. Martínez-Lamenca, J. E. Leenaerts, P. E. Brennan, A. A. Trabanco and D. Oehlich, *J. Org. Chem.*, **2018**, 83, 9510.
- [20] B. Gao, S. Li, P. Wu, J. E. Moses and K. B. Sharpless, *Angew. Chem. Int. Ed.*, **2018**, 57, 1939.
- [21] For a single example via the sulfonimidoyl chloride, see: C. Worch, I. Atodiresei, G. Raabe and C. Bolm, *Chem. Eur. J.*, **2010**, 16, 677.
- [22] D. Liang, D. E. Streefkerk, D. Jordaan, J. Wagemakers, J. Baggerman, H. Zuilhof, *Angew. Chem. Int. Ed.* **2020**, 59, 7494.
- [23] M. Moir, J. J. Danon, T. A. Reekie and M. Kassiou, *Expert Opin. Drug Discov.*, **2019**, 14, 1137.
- [24] A. L. Tribby, I. Rodríguez, S. Shariffudin and N. D. Ball, *J. Org. Chem.*, **2017**, 82, 2294.
- [25] A. T. Davies, J. M. Curto, S. W. Bagley and M. C. Willis, *Chem. Sci.*, **2017**, 8, 1233.
- [26] a) N. Xin, Y. Sun, M. He, C. J. Radke and J. M. Prausnitz, *Fluid Phase Equilib.*, **2018**, 461, 1. b) D. A. Wynn, M. M. Roth, B. D. Pollard, *Talanta*, **1984**, 31, 1036.
- [27] This is an alternative hypothesis to Zuilhof who proposed the participation of DBU in the racemisation of the sulfonimidoyl fluorides. (For related proposed amine involvement in sulfonyl fluorides, see: V. Gembus, F. Marsais and V. Levacher, *Synlett*, **2008**, 1463.) However, their experimental results would also be consistent with our hypothesis as the improved ee using the sodium phenolate over the corresponding phenol may be attributed to the formation of NaF, removing fluoride ions from solution and preventing racemisation of the sulfonimidoyl fluoride.
- [28] a) M. Reggelin and C. Zur, *Synthesis*, **2000**, 2000, 1. b) M. Reggelin and B. Junker, *Chem. Eur. J.*, **2001**, 7, 1232.
- [29] Nucleophilic attack of the S(IV) species to form sulfonimidoyl chlorides is known to occur with retention of the configuration of the sulfur center. a) E. U. Jonsson and C. R. Johnson, *J. Am. Chem. Soc.*, **1971**, 93, 5308. b) M. R. Jones and D. J. Cram, *J. Am. Chem. Soc.*, **1974**, 96, 2183.
- [30] C. Drago, L. Caggiano and R. F. W. Jackson, *Angew. Chem. Int. Ed.*, **2005**, 44, 7221.
- [31] M. Zenzola, R. Doran, R. Luisi and J. A. Bull, *J. Org. Chem.*, **2015**, 80, 6391.

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SUPPORTING INFORMATION

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Extended References from Manuscript

- [2b] F. Sehgelmeble, J. Janson, C. Ray, S. Rosqvist, S. Gustavsson, L. I. Nilsson, A. Minidis, J. Holenz, D. Rotticci, J. Lundkvist and P. I. Arvidsson, *ChemMedChem*, **2012**, 7, 396.
- [6a] A. Min, S.-A. Im, H. Jang, S. Kim, M. Lee, D. K. Kim, Y. Yang, H.-J. Kim, K.-H. Lee, J. W. Kim, T.-Y Kim, D.-Y. Oh, J. Brown, M. J. O'Connor, Y.-J. Bang, *Mol. Cancer Ther.*, **2017**, 16, 566.
- [6b] K. M. Foote, J. W. M. Nissink, T. McGuire, P. Turner, S. Guichard, J. W. T. Yates, A. Lau, K. Blades, D. Heathcote, R. Odedra, G. Wilkinson, Z. Wilson, C. M. Wood and P. J. Jewsbury, *J. Med. Chem.*, **2018**, 61, 9889.
- [7a] U. Lücking, R. Jautelat, M. Krüger, T. Brumby, P. Lienau, M. Schäfer, H. Briem, J. Schulze, A. Hillisch, A. Reichel, A. M. Wengner and G. Siemeister, *ChemMedChem*, **2013**, 8, 1067.
- [7b] U. Lücking, A. Scholz, P. Lienau, G. Siemeister, D. Kosemund, R. Bohlmann, H. Briem, I. Terebesi, K. Meyer, K. Prella, K. Denner, Ulf Bömer, M. Schäfer, K. Eis, R. Valencia, S. Ince, F. von Nussbaum, D. Mumberg, K. Ziegelbauer, B. Klebl, A. Choidas, P. Nussbaumer, M. Baumann, C. Schultz-Fademrecht, G. Rührter, J. Eickhoff, M. Brands, *ChemMedChem*, **2017**, 12, 1776
- [8] U. T. Luecking, A. Scholz, D. Kosemund, R. Bohlmann, H. Briem, P. Lienau, G. Siemeister, I. Terebesi, K. Meyer, K. Prella, R. Valencia, S. Ince, F. von Nussbaum, D. Mumberg, K. Ziegelbauer and M. Brands, in *Cancer Chemistry*, American Association for Cancer Research, **2017**, 77, 984.

General Experimental Conditions

All non-aqueous reactions were run under an inert atmosphere (argon) with flame-dried glassware, using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, CH₂Cl₂, DMF, MeCN, EtOH and toluene) or used as supplied. Reactions for the scope optimisation were carried out in sealed Biotage microwave vials.

Flash chromatography was performed using 230–400 mesh silica, with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glassbacked silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and stained with aqueous potassium permanganate solution or a ninhydrin solution in reagent stain.

Nuclear magnetic resonance spectra were recorded on 400 MHz spectrometers. The frequency used to record the NMR spectra is given in each assignment and spectrum (¹H NMR at 400 MHz; ¹³C NMR at 101 MHz; ¹⁹F NMR at 377 MHz). Chemical shifts for ¹H NMR spectra are recorded in parts per million with the residual protic solvent resonance as the internal standard (chloroform: δ = 7.26 ppm, D₂O: δ = 4.79 ppm). Data is reported as follows: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, m = multiplet and br = broad], coupling constant (in Hz), integration and assignment). ¹³C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million with the residual protic solvent resonance as the internal standard (¹³CDCl₃: δ = 77.2 ppm). Assignments of ¹H and ¹³C spectra were based upon the analysis of δ_{H} and J values, as well as DEPT, COSY and HSQC experiments where appropriate. For clarity NMR spectra are displayed as follows unless this would obscure signals: ¹H NMR spectra are displayed between 10.0 ppm and 0.0 ppm; ¹³C NMR spectra are displayed between 210 ppm and 0 ppm.

IR spectra were recorded as solids or neat liquids on an Agilent Cary 630 FTIR spectrometer and are reported in wavenumbers (cm⁻¹) to the nearest integer.

High-resolution mass spectrometry (HRMS) analyses were performed using electrospray ion source (ESI). This was performed using a Waters LCT Premier equipped with an ESI source operated in positive ion mode. The software used was MassLynx 4.1. This software does not account for the electron and all the calibrations/references are calculated accordingly, i.e. [M+H]⁺ is detected and the mass is calibrated to output [M+H]. In the cases where this software is used we report the HRMS as [M+H].

All melting points were determined in open glass capillaries and are uncorrected.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

Observed optical rotation (α') was measured at the indicated temperature (T °C) and were converted to the corresponding specific rotations $[\alpha]_{\text{D}}$ in deg cm² g⁻¹, concentration (c) in g per 100 mL.

HPLC analyses were carried out on an Agilent 1260 Infinity Series system, employing Daicel Chiracel columns.

Structures of Additional Compounds in SI

General Procedures

General Procedure A: Synthesis of racemic sulfonimidoyl fluorides

Selectfluor (1.32 g, 3.75 mmol, 1.5 equiv) was added to a solution of sulfinamide salt **1a-b**, **S4b-g** (2.5 mmol, 1 equiv) in DMF (13 mL, 0.2 M) at 0 °C and warmed to 25 °C for 18 h. H₂O (25 mL) was added and the aqueous mixture extracted with EtOAc (3 × 25 mL). The combined organic layers were dried (Na₂SO₄), filtered and the solvent removed under reduced pressure to give the racemic sulfonimidoyl fluorides **2a-h** which was typically used with no further purification.

General Procedure B: Synthesis of racemic sulfonimidamides

Amine (0.50 mmol, 2.0 equiv.) and triethylamine (70 µL, 0.50 mmol, 2.0 equiv) were added to a stirred solution sulfonimidoyl fluoride **2a-h** (0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. The resulting residue was then purified by silica flash column chromatography as described for each entry to yield the sulfonimidamides **3a-3aj**.

General Procedure C: Synthesis of enantioenriched sulfonimidoyl fluorides

Selectfluor (0.71 g, 2.0 mmol, 2 equiv) were added to a stirred solution of sulfinamide salt **1a-b**, **S4b-g** (1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (3 × 40 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. Typically, no further purification was required giving sulfonimidoyl fluoride **2a-h**.

General Procedure D: Synthesis of enantioenriched sulfonimidamides

Amine (0.50 mmol, 2.0 equiv.) and triethylamine (70 µL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2a-h** (0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2.0 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. The resulting residue was then purified by silica flash column chromatography as described for each entry to yield the sulfonimidamides **3a-aj**.

Initial route to racemic sulfonimidamides using Procedures A and B

Reactions were performed on a 0.25 mmol scale. In each case, the racemic material was remade in their enantioenriched form using General Procedures B & D. The experimental and analytical data are given later in the Amine Scope section of the SI (p S15)

Synthesis of enantioenriched sulfinamide salt ((S)-1a)

tert-Butyl (*p*-tolylsulfinyl)carbamate ((S)-5)

Prepared according to a literature procedure.^[1] *n*-BuLi (1.52 M in hexanes, 10.6 mL, 16.1 mmol, 2.5 equiv) was added dropwise to a stirred solution of (S)-*p*-toluenesulfinamide (1.0 g, 6.4 mmol, 1 equiv) in THF (8 mL, 0.8 M) at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 10 min followed by the addition of di-*tert*-butyl carbamate (1.70 g, 7.8 mmol, 1.2 equiv) in THF (5 mL, 1.5 M) and warmed to rt for 3 h. At $0\text{ }^\circ\text{C}$, the reaction mixture was quenched with NH_4Cl solution (sat. aq., 10 mL) and diluted with CH_2Cl_2 (10 mL). The mixture was extracted with CH_2Cl_2 ($5 \times 15\text{ mL}$) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by recrystallisation (3:1 hexane/EtOAc) gave sulfinamide (S)-5 as a white solid (1.03 g, 62%, >99% ee). mp = $90\text{--}92\text{ }^\circ\text{C}$. IR (film)/ cm^{-1} 3116, 3064, 2971, 2922, 2814, 1703 (C=O), 1595, 1490, 1331, 1156, 1100, 898, 809. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.9\text{ Hz}$, 2H, $2 \times \text{Ar-H}$), 7.32 (d, $J = 7.9\text{ Hz}$, 2H, $2 \times \text{Ar-H}$), 2.41 (s, 3H, Ar- CH_3), 1.49 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 152.7 (C=O), 142.5 (Ar- C_q), 140.7 (Ar- C_q), 130.1 ($2 \times \text{Ar-C}$), 124.8 ($2 \times \text{Ar-C}$), 83.6 ($\text{C}(\text{CH}_3)_3$), 28.2 ($\text{C}(\text{CH}_3)_3$), 21.5 (Ar- CH_3). $[\alpha]_D^{21} = +80$ (c 0.1, CHCl_3). HPLC Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1} , $35\text{ }^\circ\text{C}$, UV detection wavelength: 260 nm, ((S)-5) retention time: 22 min. Analytical data (NMR) in agreement with those reported in the literature.^[2]

(rac)-5 HPLC Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1} , $35\text{ }^\circ\text{C}$, UV detection wavelength: 260 nm, retention times: 22 & 24 min.

Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((S)-1a)

NaH (60% in oil, 52 mg, 1.23 mmol, 1.05 equiv) was added portionwise to sulfinamide (S)-5 (300 mg, 1.23 mmol, 1 equiv) in THF (13 mL, 0.1 M) and stirred for 1 h at rt. The reaction mixture was quenched with MeOH (0.1 mL, 0.1 mmol, 0.05 equiv) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt (S)-1a (340 mg, 1.23 mmol, quant, >99% ee) as a white solid. mp = $233\text{--}234\text{ }^\circ\text{C}$. IR (film)/ cm^{-1} 3086, 3049, 2922, 2960, 1642 (C=O), 1580, 1480, 1241, 1152, 1021, 798. ^1H NMR (400 MHz, D_2O) δ 7.54 (d, $J = 8.2\text{ Hz}$, 2H, $2 \times \text{Ar-H}$), 7.35 (d, $J = 8.2\text{ Hz}$, 2H, $2 \times \text{Ar-H}$), 2.37 (s, 3H, Ar- CH_3), 1.41 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, D_2O) δ 165.9 (C=O), 143.2 (Ar- C_q), 141.7 (Ar- C_q), 129.6 ($2 \times \text{Ar-C}$), 124.7 ($2 \times \text{Ar-C}$), 79.6 ($\text{C}(\text{CH}_3)_3$), 27.8 ($\text{C}(\text{CH}_3)_3$), 20.5 (Ar- CH_3). HRMS (ESI) m/z Calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_3\text{S}$ [M] $^-$: 254.0844; Found: 254.0851. $[\alpha]_D^{21} = +56$ (c 1.0, H_2O).

Determination of ee from reprotonation. The minimum MeOH ($\sim 0.1\text{ mL}$) was added to a sample of (S)-1a ($\sim 1\text{ mg}$) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide (S)-5.

Applying the racemic conditions to enantioenriched starting materials

When General Procedures A and B were applied to enantioenriched material, racemisation occurs at both steps in the synthesis.

tert-Butyl (fluoro(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-2a)

Reaction performed according to General Procedure A. Selectfluor (1.15 g, 3.25 mmol, 1.5 equiv) was added to a solution of sulfinamide salt (**S**)-1a (600 mg, 2.16 mmol, >99% ee, 1 equiv) in DMF (10.8 mL) at 0 °C and warmed to 25 °C for 18 h. H₂O (25 mL) was added and the aqueous mixture extracted with EtOAc (3 × 25 mL). The combined organic layers were dried (MgSO₄), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride (**R**)-2a (585 mg, 98%, 81% ee) as a colourless oil. IR (film)/cm⁻¹ 2982, 2933, 1700 (C=O), 1595, 1454, 1327, 1141, 1096, 813, 678. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.40 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 2.48 (s, 3H, Ar-CH₃), 1.53 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 152.7 (C=O), 147.1 (Ar-C_q), 130.8 (d, *J* = 20.9 Hz, Ar-C_q), 130.2 (2 × Ar-C), 128.3 (2 × Ar-C), 82.7 (C(CH₃)₃), 28.0 (C(CH₃)₃), 21.9 (Ar-CH₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 68.8. HRMS (ESI) *m/z* Calcd for C₁₂H₁₇NO₃SF [M+H]⁺: 274.0913; Found: 274.0924.

(**R**)-2a [α]_D²¹ = +9 (c 5.0, CHCl₃). HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm, retention time: 13 & 14 min.

tert-Butyl (oxo(piperidin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3a)

Reaction performed according to General Procedure B. Piperidine (49 μ L, 0.50 mmol) and triethylamine (70 μ L, 0.50 mmol) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-2a (68.3 mg, 0.25 mmol) in THF (0.83 mL) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 15% EtOAc/pentane) afforded sulfonimidamide (**R**)-3a (64.8 mg, 77%, 8% ee) as a white solid; mp = 137–139 °C. *R*_f 0.40 (15% EtOAc in pentane). IR (film)/cm⁻¹ 2974, 2937, 2855, 1677 (C=O), 1595, 1454, 1364, 1275, 1156, 1092, 932, 816. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 7.31 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 3.10–3.06 (m, 4H, 2 × NCH₂), 2.42 (s, 3H, Ar-CH₃), 1.66–1.59 (m, 4H, 2 × NCH₂CH₂), 1.45–1.41 (m, 2H, NCH₂CH₂CH₂), 1.46–1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.8 (C=O), 143.8 (Ar-C_q), 133.4 (Ar-C_q), 129.8 (2 × Ar-C), 127.9 (2 × Ar-C), 80.1 (C(CH₃)₃), 46.7 (2 × NCH₂), 28.2 (C(CH₃)₃), 25.3 (2 × NCH₂CH₂), 23.7 (NCH₂CH₂CH₂), 21.6 (Ar-CH₃). HRMS (SI) *m/z* Calcd for C₁₇H₂₇N₂O₃S [M+H]⁺: 339.1742; Found: 339.1728.

(**R**)-3a [α]_D²¹ = –18 (c 0.5, CHCl₃). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm, retention time: 17 & 21 min.

Determination of ee and conversion along the timescale of the reaction

Sulfonimidoyl fluoride **(R)-2a** (273 mg, 1 mmol) was subjected to General Procedure B with the initial addition of 1,3,5-trimethoxybenzene (169 mg, 1 mmol). Aliquots (~50 μ L) were removed from the sealed reaction vial at the timepoints given below and the sample was split and concentrated for preparation of ^1H -NMR and HPLC samples. Yields were determined using 1,3,5-trimethoxybenzene as the internal standard in the ^1H -NMR. %ee of the crude samples were obtained by HPLC analysis on both the **(R)-2a** and **(R)-3a** column conditions.

Time (h)	(R)-2a		(R)-3a	
	Yield (%)	%ee	Yield (%)	%ee
0.00	100	100	0	-
0.33	73	52	8	64
0.67	70	20	13	56
1	71	4	14	38
1.5	50	0	29	18
2	52	0	27	15
2	44	0	37	10
3	42	0	35	10
4	37	0	43	9
5	28	0	45	8
6	23	0	53	8
8	17	0	58	8
10	7	0	69	7
24	0	0	72	6
48	0	0	73	6

HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm, retention time: 13 & 14 min.

Entry	Fluoride Ion Source	Retained ee of (R)-2a (%)
1	-	93
2	TBAF	0
3	KF	99

Retained ee given by %ee(*R*)-2a product/%ee(*R*)-2a Starting material

Optimisation of Synthesis of Enantioenriched Sulfonimidoyl Fluoride (*R*)-2a

Entry	Solvent	Base	Yield (%) ^a			(R)-2a ee (%)
			Protonated (S)-1a	(R)-2a	Total ^b	
1	DMF	-	-	74	74	81-95
2	THF	-	19	30	49	68
3	MeCN	-	14	59	73	79
4	Et ₂ O	-	16	52	68	85-99
5	<i>i</i> PrOH	-	19	59	78	79
6	CH ₂ Cl ₂	-	22	59	81	68
7	Hexane	-	22	57	79	44
8	EtOH	-	23	46	69	>99
9	EtOH	K ₂ CO ₃	14	58	72	n.d.
10	EtOH	NaOAc	9	71	80	>99
11	EtOH	KOAc	2	80	82	>99
12	EtOH	NEt ₃	72	trace	72	n.d.
13 ^c	EtOH	KOAc	-	[98]	98	>99

Reactions performed on a 0.1 mmol scale. ^aConversion determined by ¹H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parenthesis. ^bSum of two preceding columns.

^cReaction performed on a 1.2 mmol scale.

Optimisation of Synthesis of Enantioenriched Sulfonimidamide (*R*)-3a

Entry	Solvent	Additive	Yield (%) ^a			% es ^c
			(<i>R</i>)-2a	(<i>R</i>)-3a	Total ^b	
1	THF	-	30	52	82	8
2	THF	TMS-Cl	75	1	76	n.d.
3	THF	KBr	33	44	77	13
4	THF	LiCl	11	31	42	>99
5	THF	H ₂ O	6	77	83	26
6	THF	LiBr	19	56	75	>99
7	EtOH	-	-	33	33	45
8	<i>t</i> BuOH	-	18	54	72	38
9	<i>i</i> PrOH	-	6	66	72	29
10	MeCN	-	9	73	82	28
11	MeCN	LiBr	-	96	96	>99
12	MeCN	LiI	-	87	87	>99
13	MeCN	Li ₂ CO ₃	-	60	60	96

Reactions performed on a 0.1 mmol scale. ^aConversion determined by ¹H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parenthesis. ^bSum of two preceding columns. ^ces, enantiospecificity, given by %ee(*R*)-3a/ %ee(*R*)-2a

Experimental and Characterisation Data: Amine scope with (*R*)-2a (Scheme 2)

tert-Butyl (fluoro(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-2a)

Reaction performed according to General Procedure C. Selectfluor (0.71 g, 2.0 mmol, 2 equiv) were added to a stirred solution of sulfinamide salt (**S**)-1a (0.29 g, 1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (3 × 40 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. No further purification was required giving sulfonymidoyl fluoride (**R**)-2a (0.29 g, quant., >99% ee) as a colourless viscous oil. IR (film)/cm⁻¹ 2982, 2933, 1700 (C=O), 1595, 1454, 1327, 1141, 1096, 813, 678. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.40 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 2.48 (s, 3H, Ar-CH₃), 1.53 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 152.7 (C=O), 147.1 (Ar-C_q), 130.8 (d, *J* = 20.9 Hz, Ar-C_q), 130.2 (2 × Ar-C), 128.3 (2 × Ar-C), 82.7 (C(CH₃)₃), 28.0 (C(CH₃)₃), 21.9 (Ar-CH₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 68.8. HRMS (ESI) *m/z* Calcd for C₁₂H₁₇NO₃SF [M+H]⁺: 274.0913; Found: 274.0924. [α]_D²¹ = +9 (c 5.0, CHCl₃). HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm, retention time: 13 & 14 min.

Synthesis of racemic sample for HPLC analysis performed according to General Procedure A, see p. S10: Selectfluor (533 g, 1.51 mmol, 1.5 equiv) was added to a solution of sulfinamide salt (**rac**)-1a (250 mg, 1.00 mmol) in DMF (5.00 mL) at 0 °C and warmed to 25 °C for 16 h. H₂O (10 mL) was added and the aqueous mixture extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (MgSO₄), filtered and the solvent removed under reduced pressure to give sulfonymidoyl fluoride (**rac**)-2a (116 mg, 48%) as a colourless oil with characterisation data in accordance with the above.

tert-Butyl (oxo(piperidin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3a)

Reaction performed according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonymidoyl fluoride (**R**)-2a (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 20% EtOAc/pentane) afforded sulfonymidamide (**R**)-3a (81.3 mg, 96%, >99% ee) as a white solid. mp = 137–139 °C. *R*_f 0.40 (15% EtOAc in pentane). IR (film)/cm⁻¹ 2974, 2937, 2855, 1677 (C=O), 1595, 1454, 1364, 1275, 1156, 1092, 932, 816. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 7.30 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 3.07 (m, 4H, 2 × NCH₂), 2.41 (s, 3H, Ar-CH₃), 1.61 (p, *J* = 5.7 Hz, 4H, 2 × NCH₂CH₂), 1.49–1.41 (m, 2H, NCH₂CH₂CH₂), 1.39 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.9 (C=O), 143.8 (Ar-C_q), 133.4 (Ar-C_q), 129.8 (2 × Ar-C), 127.9 (2 × Ar-C), 80.1 (C(CH₃)₃), 46.7 (2 × NCH₂), 28.2 (C(CH₃)₃), 25.3 (2 × NCH₂CH₂), 23.7 (NCH₂CH₂CH₂), 21.6 (Ar-CH₃). HRMS (ESI) *m/z* Calcd for C₁₇H₂₇N₂O₃S [M+H]⁺: 339.1742; Found: 339.1728. [α]_D²¹ = -18 (c 0.5, CHCl₃). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm, ((*R*)-3a) retention time: 21 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B, see p. S10, to afford sulfonimidamide (**rac**)-**3a** (64.8 mg, 77%) as a white solid with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm, ((**rac**)-**3a**) retention time: 17 & 21 min.

tert-Butyl (R)-((butylamino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3b)

Reaction performed according to General Procedure D. Butylamine (50 μL, 0.50 mmol,

2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution

of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3b** (66.2 mg, 81%, 99% ee) as a white solid. mp = 135–137 °C. R_f 0.32 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3068, 2960, 2930, 2870, 1681 (C=O), 1454, 1275, 1163, 1118, 902, 813. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 7.30 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 6.87 (s, 1H, NH), 2.98–2.93 (m, 1H, NCHH), 2.77–2.69 (m, 1H, NCHH), 2.42 (s, 3H, Ar-CH₃), 1.51–1.42 (m, 2H, NCH₂CH₂), 1.35 (s, 9H, C(CH₃)₃), 1.28–1.22 (m, 2H, CH₂CH₃), 0.83 (t, *J* = 7.3 Hz, 3H, CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.1 (C=O), 143.8 (Ar-C_q), 135.8 (Ar-C_q), 129.7 (2 × Ar-C), 128.1 (2 × Ar-C), 80.1 (C(CH₃)₃), 41.0 (NCH₂), 31.4 (NCH₂CH₂), 28.1 (C(CH₃)₃), 21.6 (Ar-CH₃), 19.8 (CH₂CH₃), 13.6 (CH₂CH₃). HRMS (ESI) *m/z* Calcd for C₁₆H₂₇N₂O₃S [M+H]⁺: 327.1742; Found: 327.1739. [α]_D²¹ = +42 (c 1.0, CHCl₃). HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, ((**R**)-**3b**) retention time: 21 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3b** (53.0 mg, 65%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, (**rac**)-**3b** retention times: 21 & 23 min.

tert-Butyl (R)-((benzylamino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3c)

Reaction performed according to General Procedure D. Benzylamine (50 μL, 0.50 mmol,

2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution

of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg,

0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3c** (70.2 mg, 78%, 99% ee) as a white solid. mp = 62–63 °C. R_f 0.39 (10% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3064, 2978, 2930, 2840, 1677, 1454, 1249, 1152, 1115, 1059, 906, 865, 787, 731, 697, 671. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.33–7.29 (m, 2H, 2 × Ar-H), 7.28–7.26 (m, 2H, 2 × Ar-H), 7.25–7.19 (m, 3H, 3 × Ar-H), 6.43 (s, 1H, NH), 4.22 (d, *J* = 13.8 Hz, 1H, NHCHH), 3.94 (d, *J* = 13.8 Hz, 1H, NHCHH), 2.43 (s, 3H, Ar-CH₃), 1.40 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.8 (C=O), 144.6 (Ar-C_q), 136.3 (Ar-C_q), 136.0 (Ar-C_q), 130.3 (2 × Ar-C), 129.2 (2 × Ar-C), 128.5 (2 × Ar-C), 128.45 (2 × Ar-C), 128.42 (Ar-C), 81.0 (C(CH₃)₃), 46.1 (NHCH₂), 28.6 (C(CH₃)₃), 22.0 (Ar-CH₃). HRMS (ESI) *m/z* Calcd for C₁₉H₂₅N₂O₃S [M+H]⁺: 361.1586; Found: 361.1593. [α]_D²³ = +88 (c 0.5, CHCl₃). HPLC Conditions:

Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. ((*R*)-**3c**) Retention time: 41 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide (*rac*)-**3c** (~10 mg) with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. ((*R*)-**3c**) Retention times: 37 & 42 min.

tert-Butyl (*R*)-((allylamino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((*R*)-3d**)**

Reaction performed according to General Procedure D. Allylamine (37 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3d** (45.9 mg, 60%, 98% ee) as a white solid. mp = 95–96 °C. *R*_f 0.21 (10% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3071, 2978, 2930, 1681, 1595, 1453, 1278, 1159, 1118, 1092, 1062, 924, 813. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.31 (d, *J* = 7.9 Hz, 2H, 2 × Ar–H), 5.74 (ddt, *J* = 17.1, 10.3, 5.8 Hz, 1H, NCH₂CH), 5.21 (dd, *J* = 17.1, 1.3 Hz, 1H, NHCH₂CHCHH), 5.11 (dd, *J* = 10.2, 1.3 Hz, 1H, NHCH₂CHCHH), 3.62 (ddt, *J* = 15.0, 5.6, 1.6 Hz, 1H, NHCHH), 3.42 (ddt, *J* = 14.9, 6.0, 1.5 Hz, 1H, NHCHH), 2.42 (s, 3H, Ar–CH₃), 1.37 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.2 (C=O), 144.1 (Ar–C_q), 135.8 (Ar–C_q), 132.8 (NHCH₂CH=CH₂), 129.9 (2 × Ar–C), 128.1 (2 × Ar–C), 118.0 (NHCH₂CH=CH₂), 80.5 (C(CH₃)₃), 44.1 (NHCH₂), 28.2 (C(CH₃)₃), 21.7 (Ar–CH₃). HRMS (ESI) *m/z* Calcd for C₂₀H₂₈N₅O₃S [M+H]⁺: 418.1913; Found: 418.1899. [α]_D²³ = +40 (c 0.5, CHCl₃). HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm, (**R**)-**3d** retention times 23 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide (*rac*)-**3d** (~10 mg) with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm, (*rac*)-**3d** retention times 23 & 26 min.

tert-Butyl (*R*)-(((cyclopropylmethyl)amino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((*R*)-3e**)**

Reaction performed according to General Procedure D. Cyclopropylmethanamine (44 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried

LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3e** (50.0 mg, 62%, 95% ee) as a white solid. mp = 124–126 °C. *R*_f 0.26 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3086, 2974, 2926, 2873, 1674 (C=O), 1595, 1454, 1252, 1156, 1111, 1044, 809, 731. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.1 Hz, 2H, 2 × Ar–H), 7.30 (d, *J* = 8.1 Hz, 2H, 2 × Ar–H), 6.56 (s, 1H, NH), 2.89 (dd, *J* = 12.8, 7.0 Hz, 1H, NHCHH), 2.62 (dd, *J* = 12.8, 7.3 Hz, 1H, NHCHH), 2.42 (s, 3H, Ar–CH₃), 1.37 (s, 9H, C(CH₃)₃), 0.95–0.86 (m, 1H, NHCH₂CH), 0.50–0.41 (m, 2H, 2 × CHCHH), 0.16–0.05 (m, 2H, 2 × CHCHH). ¹³C NMR (101 MHz, CDCl₃) δ 157.2 (C=O), 143.9 (Ar–C_q), 135.9 (Ar–C_q), 129.8 (2 × Ar–C),

128.1 (2 × Ar-C), 80.3 (C(CH₃)₃), 46.6 (NCH₂), 28.2 (C(CH₃)₃), 21.7 (Ar-CH₃), 10.7 (NCH₂CH), 3.9 (1 × CHCH₂), 3.6 (1 × CHCH₂). HRMS (ESI) *m/z* Calcd for C₁₆H₂₅N₂O₃S [M+H]⁺: 325.1586; Found: 325.1590. [α]²¹_D = +29 (c 1.0, CHCl₃). HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 280 nm, (**R**)-**3e** retention time 26 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3e** (34.1 mg, 65%) as a yellow solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 280 nm, (**rac**)-**3e** retention times 26 & 28 min.

tert-Butyl (R)-((cyclobutylamino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3f)

Reaction performed according to General Procedure D. Cyclobutylamine (43 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3f** (61.9 mg, 76%, >99% *ee*) as a white solid. mp = 131–133 °C. *R*_f 0.18 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3068, 2978, 2870, 1674, 1595, 1450, 1390, 1275, 1245, 1141, 1096, 973, 906, 857, 731. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 7.29 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 6.77 (s, 1H, NH), 3.75–3.59 (m, 1H, NHCH), 2.41 (s, 3H, Ar-CH₃), 2.30–2.22 (m, 1H, 1 × NHCHCHH), 2.11–2.00 (m, 1H, 1 × NHCHCHH), 1.89–1.77 (m, 2H, 2 × NHCHCHH), 1.66–1.49 (m, 2H, NHCHCH₂CH₂), 1.36 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.3 (C=O), 143.9 (Ar-C_q), 136.7 (Ar-C_q), 129.7 (2 × Ar-C), 128.0 (2 × Ar-C), 80.4 (C(CH₃)₃), 46.9 (NHCH), 32.0 (1 × NHCHCH₂), 31.3 (1 × NHCHCH₂), 28.2 (C(CH₃)₃), 21.7 (Ar-CH₃), 15.4 (NHCHCH₂CH₂). HRMS (ESI) *m/z* Calcd for C₁₆H₂₅N₂O₃S [M+H]⁺: 325.1586; Found: 325.1587. [α]²¹_D = +48 (c 0.8, CHCl₃). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm, (**R**)-**3f** retention time: 15 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3f** (44.0 mg, 54%) as a white solid with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm, (**rac**)-**3f** retention times: 15 & 18 min.

tert-Butyl (R)-((cyclohexylamino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3g)

Reaction performed according to General Procedure D. Cyclohexylamine (57 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3g** (60.8mg, 68%, 97% *ee*) as a white solid. mp = 124–125 °C. *R*_f 0.32 (10% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2933, 2855, 1741, 1684, 1453, 1368, 1278, 1162 1096, 1021, 931, 909, 861, 813, 671. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.30 (d, *J* = 7.8 Hz, 2H, 2 × Ar-H),

6.03 (d, $J = 7.5$ Hz, 1H, NH), 3.19–3.02 (m, 1H, NHCH), 2.43 (s, 3H, Ar-CH₃), 2.04–1.97 (m, 1H, 1 × NHCHCHH), 1.76–1.63 (m, 1H, 1 × NHCHCHH), 1.55–1.45 (m, 2H, 2 × NHCHCHH), 1.40 (s, 9H, C(CH₃)₃), 1.36–1.22 (m, 2H, 2 × NHCHCH₂CHH), 1.20–1.04 (m, 4H, 2 × NCHCH₂CHH & NCHCH₂CH₂CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 157.5 (C=O), 143.9 (Ar-C_q), 137.2 (Ar-C_q), 129.8 (2 × Ar-C), 128.0 (2 × Ar-C), 80.4 (C(CH₃)₃), 51.6 (NHCH), 34.6 (1 × NHCHCH₂), 33.4 (1 × NHCHCH₂), 28.3 (C(CH₃)₃), 25.3 (2 × NCHCH₂CH₂), 24.7 (NCHCH₂CH₂CH₂), 21.7 (Ar-CH₃). HRMS (ESI) m/z Calcd for C₁₈H₂₉N₂O₃S [M+H]⁺: 353.1899; Found: 353.1906. $[\alpha]^{23}_D = +42$ (c 0.5, CHCl₃). HPLC conditions: Chiralpak IF column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, (**R**)-**3g** retention times 24 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide (**rac**)-**3g** (~10 mg) with characterisation data in accordance with the above. HPLC conditions: Chiralpak IF column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, (**rac**)-**3g** retention times 19 & 24 min.

tert-Butyl (R)-((dimethylamino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3h)

Reaction performed according to General Procedure D. Dimethylamine hydrochloride (41 mg, 0.50 mmol, 2.0 equiv) and triethylamine (140 μL, 1.00 mmol, 4.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 20% EtOAc/pentane) afforded sulfonimidamide (**R**)-**3g** (64.2 mg, 86%, 96% ee) as a white solid. mp = 115–116 °C. *R*_f 0.16 (20% EtOAc in pentane). IR (film)/cm⁻¹ 3027, 2974, 2922, 2878, 1692, 1592, 1476, 1390, 1275, 1156, 1040, 943, 820, 775. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, $J = 8.3$ Hz, 2H, 2 × Ar-H), 7.32 (d, $J = 8.2$ Hz, 2H, 2 × Ar-H), 2.75 (s, 6H, N(CH₃)₂), 2.42 (s, 3H, Ar-CH₃), 1.40 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.7 (C=O), 144.0 (Ar-C_q), 132.6 (Ar-C_q), 129.8 (2 × Ar-C), 127.9 (2 × Ar-C), 80.3 (C(CH₃)₃), 37.8 (N(CH₃)₂), 28.2 (C(CH₃)₃), 21.6 (Ar-CH₃). HRMS (ESI) m/z Calcd for C₁₄H₂₃N₂O₃S [M+H]⁺: 299.1429; Found: 299.1437. $[\alpha]^{21}_D = -28$ (c 1.0, CHCl₃). HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**R**)-**3g** retention time: 25 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3g** (56.9 mg, 74%) as a colourless oil with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**3g** retention times: 23 & 25 min.

tert-Butyl (R)-((benzyl(methyl)amino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3i)

Reaction performed according to General Procedure D. *N*-methyl benzylamine (65 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3i** (50.4 mg, 54%, 99% ee) as a white solid. mp = 95–97 °C. *R*_f = 0.28 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2971, 2926, 1666, 1450, 1282, 1248, 1148, 1085, 992, 936, 895, 816, 753. ¹H NMR (400 MHz,

CDCl_3) δ 7.87 (d, J = 8.1 Hz, 2H, 2 $\times$ Ar-H), 7.38 (d, J = 8.1 Hz, 2H, 2 $\times$ Ar-H), 7.36–7.27 (m, 5H, 5 $\times$ Ar-H), 4.41 (d, J = 14.1 Hz, 1H, NCHH), 4.17 (d, J = 14.0 Hz, 1H, NCHH), 2.67 (s, 3H, NCH₃), 2.47 (s, 3H, Ar-CH₃), 1.47 (s, 9H, C(CH₃)₃). ^{13}C NMR (101 MHz, CDCl_3) δ 157.0 (C=O), 144.4 (Ar-C_q), 136.1 (Ar-C_q), 134.5 (Ar-C_q), 130.2 (2 $\times$ Ar-C), 129.1 (2 $\times$ Ar-C), 128.9 (2 $\times$ Ar-C), 128.3 (Ar-C), 128.2 (2 $\times$ Ar-C), 80.7 (C(CH₃)₃), 54.2 (NCH₂), 34.7 (NCH₃), 28.6 (C(CH₃)₃), 22.0 (Ar-CH₃). HRMS (APCI) m/z Calcd for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 375.1737; Found: 375.1735. $[\alpha]^{23}_{\text{D}} = -12$ (c 1, CHCl_3). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. (**R**)-**3i** retention time: 33 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3i** (56.9 mg, 61%) as a colourless oil with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. (**rac**)-**3i** retention times: 21 & 33 min.

tert-Butyl (R)-((3,4-dihydroisoquinolin-2(1H)-yl)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3j)

Reaction performed according to General Procedure D. 1,2,3,4-tetrahydroisoquinoline (63 μL , 0.50 mmol, 2.0 equiv) and triethylamine (70 μL , 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 20% EtOAc in pentane) afforded sulfonimidamide (**R**)-**3j** (90.3 mg, 93%, 97% ee) as a pale-yellow oil. R_f 0.36 (20% EtOAc in pentane). IR (film)/cm⁻¹ 2974, 2930, 1670 (C=O), 1595, 1495, 1364, 1249, 1152, 951, 895, 727. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 8.4 Hz, 2H, 2 $\times$ Ar-H), 7.31 (d, J = 8.1 Hz, 2H, 2 $\times$ Ar-H), 7.14–7.10 (m, 2H, 2 $\times$ Ar-H), 7.08–7.00 (m, 2H, 2 $\times$ Ar-H), 4.41–4.32 (m, 2H, NCH₂), 3.55 (dt, J = 11.7, 5.7 Hz, 1H, NCHH), 3.40 (dt, J = 17.7, 5.9 Hz, 1H, NCHH), 2.92–2.88 (m, 2H, NCH₂CH₂), 2.40 (s, 3H, Ar-CH₃), 1.40 (s, 9H, C(CH₃)₃). ^{13}C NMR (101 MHz, CDCl_3) δ 156.6 (C=O), 144.1 (Ar-C_q), 133.5 (Ar-C_q), 133.2 (Ar-C_q), 131.8 (Ar-C_q), 129.8 (2 $\times$ Ar-C), 128.8 (Ar-C), 127.9 (2 $\times$ Ar-C), 126.8 (Ar-C), 126.4 (Ar-C), 126.4 (Ar-C), 80.4 (C(CH₃)₃), 47.4 (NCH₂), 43.5 (NCH₂CH₂), 29.0 (NCH₂CH₂), 28.1 (C(CH₃)₃), 21.6 (Ar-CH₃). HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 387.1742; Found: 387.1747. $[\alpha]^{23}_{\text{D}} = 0$ (c 1.0, CHCl_3). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**R**)-**3j** retention times: 33 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3j** (65.3 mg, 68%) as a colourless oil with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**3j** retention times: 26 & 33 min.

tert-Butyl (R)-(oxo(pyrrolidin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3k)

Reaction performed according to General Procedure D. Pyrrolidine (42 μL , 0.50 mmol, 2.0 equiv) and triethylamine (70 μL , 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed

under reduced pressure. Purification by flash column chromatography (SiO_2 , 5% Et_2O in CH_2Cl_2) afforded sulfonimidamide **(R)-3k** (75.7 mg, 93%, 97% ee) as a white solid. mp = 129–131 °C. R_f 0.25 (5% Et_2O in CH_2Cl_2). IR (film)/ cm^{-1} 3068, 2975, 2926, 2866, 1674 (C=O), 1595, 1457, 1275, 1156, 1059, 887, 727. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.3 Hz, 2H, 2 $\times$ Ar–H), 7.29 (d, J = 8.3 Hz, 2H, 2 $\times$ Ar–H), 3.32–3.19 (m, 4H, 2 $\times$ NCH_2), 2.40 (s, 3H, Ar– CH_3), 1.82–1.76 (m, 4H, 2 $\times$ NCH_2CH_2), 1.38 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 156.9 (C=O), 143.7 (Ar– C_q), 134.3 (Ar– C_q), 129.8 (2 $\times$ Ar–C), 127.7 (2 $\times$ Ar–C), 80.0 ($\text{C}(\text{CH}_3)_3$), 47.9 (2 $\times$ NCH_2), 28.1 ($\text{C}(\text{CH}_3)_3$), 25.4 (2 $\times$ NCH_2CH_2), 21.6 (Ar– CH_3). HRMS (ESI) m/z Calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 325.1586; Found: 325.1594. $[\alpha]^{21}_D = -9$ (c 1.0, CHCl_3). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1} , 35 °C, UV detection wavelength: 260 nm, **(R)-3k** retention times: 20 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide **(rac)-3k** (51.5 mg, 64%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1} , 35 °C, UV detection wavelength: 250 nm, **(rac)-3k** retention times: 19 & 20 min.

tert-Butyl (R)-(morpholino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3l)

Reaction performed according to General Procedure D. Morpholine (50 μL , 0.50 mmol, 2.0 equiv) and triethylamine (70 μL , 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **(R)-2a** (69 mg, 0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 5% Et_2O in CH_2Cl_2) afforded sulfonimidamide **(R)-3l** (74.9 mg, 88%, >99% ee) as a white solid. R_f 0.21 (5% Et_2O in CH_2Cl_2). mp = 136–138 °C. IR (film)/ cm^{-1} 2974, 2859, 1677 (C=O), 1595, 1464, 1278, 1159, 1115, 939, 816. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 8.3 Hz, 2H, 2 $\times$ Ar–H), 7.33 (d, J = 8.1 Hz, 2H, 2 $\times$ Ar–H), 3.72–3.70 (m, 4H, 2 $\times$ OCH_2), 3.09–3.08 (m, 4H, 2 $\times$ NCH_2), 2.43 (s, 3H, Ar– CH_3), 1.39 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 156.5 (C=O), 144.4 (Ar– C_q), 132.1 Ar– C_q , 130.0 (2 $\times$ Ar–C), 128.0 (2 $\times$ Ar–C), 80.5 ($\text{C}(\text{CH}_3)_3$), 66.2 (2 $\times$ OCH_2), 45.8 (2 $\times$ NCH_2), 28.1 ($\text{C}(\text{CH}_3)_3$), 21.7 (Ar– CH_3). HRMS (ESI) m/z Calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 341.1535; Found: 341.1540. $[\alpha]^{21}_D = -11$ (c 1.0, CHCl_3). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1} , 35 °C, UV detection wavelength: 250 nm, **(R)-3l** retention time: 31 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide **(rac)-3l** (66.2 mg, 78%) as a white solid with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1} , 35 °C, UV detection wavelength: 250 nm, **(rac)-3l** retention time: 25 & 31 min.

tert-Butyl (R)-(oxo(4-oxopiperidin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3m)

Reaction performed according to General Procedure D. 4-piperidone hydrochloride salt (78 mg, 0.50 mmol, 2.0 equiv) and triethylamine (140 μL , 1.00 mmol, 4.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **(R)-2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h.

The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **(R)-3m** (30.4 mg, 35%, 97% ee) as a white solid. mp = 145–146 °C. R_f 0.28 (10% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2974, 2926, 2870, 1718, 1670, 1595, 1368, 1341, 1274, 1252, 1156, 1111, 924, 816, 764, 708, 667. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.34 (d, *J* = 7.7 Hz, 2H, 2 × Ar–H), 3.57–3.46 (m, 4H, 2 × NCH₂), 2.53 (t, *J* = 6.2 Hz, 4H, 2 × NCH₂CH₂), 2.44 (s, 3H, Ar–CH₃), 1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 206.2 (C=O), 156.9 (C=O), 144.9 (Ar–C_q), 134.0 (Ar–C_q), 130.5 (2 × Ar–C), 128.1 (2 × Ar–C), 81.1 (C(CH₃)₃), 45.9 (NCH₂), 41.1 (NCH₂CH₂), 28.5 (C(CH₃)₃), 22.0 (Ar–CH₃). HRMS (ESI) *m/z* Calcd for C₁₇H₂₅N₂O₄S [M+H]⁺: 353.1535; Found: 353.1527. [α]_D²³ = 0 (c 0.2, CHCl₃). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm. **(R)-3m** retention times: 43 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide **(rac)-3m** (~10 mg) with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm. **(rac)-3m** retention times: 37 & 43 min.

***tert*-Butyl (R)-((4,4-difluoropiperidin-1-yl)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3n)**

Reaction performed according to General Procedure D. 4,4-difluoropiperidine (61 mg, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **(R)-2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **(R)-3n** (70.0 mg, 75%, 99% ee) as a white solid. mp = 152–154 °C. R_f 0.80 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2978, 2870, 1670, 1364, 1249, 1148, 1118, 1036, 996, 913, 865, 816, 768, 708. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.34 (d, *J* = 7.7 Hz, 2H, 2 × Ar–H), 3.29 (dd, *J* = 12.8, 6.5 Hz, 4H, 2 × NCH₂), 2.44 (s, 3H, Ar–CH₃), 2.06 (td, *J* = 13.4, 6.5 Hz, 4H, 2 × NCH₂CH₂), 1.41 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.8 (C=O), 144.8 (Ar–C_q), 133.8 (Ar–C_q), 130.4 (2 × Ar–C), 128.0 (2 × Ar–C), 81.0 (C(CH₃)₃), 43.4 (t, *J* = 5.7 Hz, NCH₂), 34.0 (t, *J* = 23.9 Hz, (NCH₂CH₂), 28.6 (C(CH₃)₃), 22.0 (Ar–CH₃). ¹⁹F NMR (377 MHz, CDCl₃) δ -99.2. HRMS (ESI) *m/z* Calcd for C₁₇H₂₅F₂N₂O₃S [M+H]⁺: 375.1554; Found: 375.1548. [α]_D²³ = -6 (c 1, CHCl₃). HPLC conditions: Chiralpak IB column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(R)-3n** retention times 10 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide **(rac)-3n** (~10 mg) with characterisation data in accordance with the above. HPLC conditions: Chiralpak IB column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(rac)-3n** retention times 10 & 12 min.

***tert*-Butyl (R)-((4-hydroxypiperidin-1-yl)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3o)**

Reaction performed according to General Procedure D. Triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **(R)-2a** (69 mg, 0.25 mmol, 1 equiv), 4-piperidinol (51 mg, 0.50 mmol, 2.0 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was

removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **(R)-3o** (50.0 mg, 56%, 99% ee) as a viscous oil. *R*_f 0.11 (5% MeOH in CH₂Cl₂). IR (film)/cm⁻¹ 3433, 2978, 2930, 2866, 1670, 1454, 1388, 1252, 1156, 1088, 1036, 917, 865, 813, 731, 667. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.30 (d, *J* = 7.8 Hz, 2H, 2 × Ar-C), 3.75 (tt, *J* = 7.5, 3.7 Hz, 1H, CHOH), 3.45–3.29 (m, 2H, 2 × NCHH), 2.97–2.91 (m, 2H, 2 × NCHH), 2.41 (s, 3H, Ar-CH₃), 2.08 (bs, 1H, OH), 1.93–1.82 (m, 2H, 2 × NCH₂CHH), 1.67–1.53 (m, 2H, 2 × NCH₂CHH), 1.37 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.1 (C=O), 144.3 (Ar-C_q), 133.7 (Ar-C_q), 130.2 (2 × Ar-C), 128.1 (2 × Ar-C), 80.6 (C(CH₃)₃), 66.3 (CHOH), 43.3 (NCH₂), 33.7 (NCH₂CH₂), 28.5 (C(CH₃)₃), 21.9 (Ar-CH₃). HRMS (ESI) *m/z* Calcd for C₁₇H₂₇N₂O₄S [M+H]⁺: 355.1692; Found: 355.1691. [α]_D²³ = -4 (c 1, CHCl₃). HPLC conditions: Chiralpak IA column, 85:15 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, **(R)-3o** retention time: 13 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide **(rac)-3o** (~10 mg) with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 85:15 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, **(rac)-3o** retention times: 11 & 13 min.

***tert*-Butyl (R)-4-(*N*-(*tert*-butoxycarbonyl)-4-methylphenylsulfonimidoyl)piperazine-1-carboxylate ((R)-3p)**

Reaction performed according to General Procedure D. 1-Boc piperazine (93 mg, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **(R)-2a** (69 mg, 0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 20% EtOAc/pentane) afforded sulfonimidamide **(R)-3p** (79.0 mg, 74%, 97% ee) as a white solid. mp = 136–138 °C. *R*_f 0.26 (20% EtOAc in pentane). IR (film)/cm⁻¹ 2974, 2930, 2863, 1692, 1595, 1464, 1364, 1249, 1159, 1126, 932, 865, 731. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 7.32 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 3.47 (t, *J* = 5.1 Hz, 4H, 2 × NCH₂), 3.09–3.01 (m, 4H, 2 × NCH₂), 2.41 (s, 3H, Ar-CH₃), 1.39 (s, 9H, C(CH₃)₃), 1.38 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.5 (C=O), 154.3 (C=O), 144.3 (Ar-C_q), 132.6 (Ar-C_q), 130.0 (2 × Ar-C), 127.9 (2 × Ar-C), 80.5 (C(CH₃)₃), 80.5 (C(CH₃)₃), 45.7 (4 × NCH₂), 28.4 (C(CH₃)₃), 28.1 (C(CH₃)₃), 21.6 (ArCH₃). HRMS (ESI) *m/z* Calcd for C₂₁H₃₄N₃O₅S [M+H]⁺: 440.2219; Found: 440.2227. [α]_D²¹ = -6 (c 1.0, CHCl₃). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(R)-3p** retention time: 30 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide **(rac)-3p** (81.2 mg, 74%) as a white solid with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(rac)-3p** retention times: 27 & 30 min.

tert-Butyl (R)-(oxo(4-(pyrimidin-2-yl)piperazin-1-yl)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3q)

Reaction performed according to General Procedure D. 1-(2-pyrimidinyl)piperazine (70 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3q** (72.1 mg, 69%, >99% ee) as a white solid. mp = 193–196 °C. *R*_f 0.25 (10% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3019, 2978, 2874, 1740, 1681, 1588, 1551, 1491, 1450, 1364, 1260, 1159, 954, 913. ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 4.7 Hz, 2H, 2 $\times$ Ar-H), 7.76 (d, *J* = 8.4 Hz, 2H, 2 $\times$ Ar-H), 7.35 (d, *J* = 8.0 Hz, 2H, 2 $\times$ Ar-H), 6.52 (t, *J* = 4.7 Hz, 1H, Ar-H), 3.94 (dd, *J* = 6.0, 4.3 Hz, 4H, 2 $\times$ NCH₂), 3.19 (m, 4H, NCH₂), 2.44 (s, 3H, Ar-CH₃), 1.43 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 161.3 (Ar-C_q), 157.8 (C=O), 156.6 (2 $\times$ Ar-C), 144.2 (Ar-C_q), 132.6 (Ar-C_q), 130.0 (2 $\times$ Ar-C), 127.9 (2 $\times$ Ar-C), 110.6 (Ar-C), 80.5 (C(CH₃)₃), 45.8 (2 $\times$ NCH₂), 43.2 (2 $\times$ NCH₂), 28.2 (C(CH₃)₃), 21.6 (Ar-CH₃). HRMS (ESI) *m/z* Calcd for C₂₀H₂₈N₅O₃S [M+H]⁺: 418.1913; Found: 418.1905. [α]_D²³ = 0 (c 1, CHCl₃). HPLC Conditions: Chiralpak IB column, 97:3 *n*hexane:PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. (**R**)-**3q** retention times: 33 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide (**rac**)-**3q** (~10 mg) with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IB column, 97:3 *n*hexane:PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. (**rac**)-**3q** retention times: 33 & 38 min.

tert-Butyl (R)-((4-(6-fluorobenzo[d]isoxazol-3-yl)piperidin-1-yl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3r)

Reaction performed according to General Procedure D. 6-Fluoro-3-(4-piperidinyl)benzisoxazole (110 mg, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under

reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3r** (88.4 mg, 75%, 98% ee) as a pale-yellow oil. *R*_f 0.27 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2974, 2930, 2855, 1737, 1670, 1614, 1446, 1271, 1148, 1111, 1044, 924, 839, 796, 731, 667. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H, 2 $\times$ Ar-H), 7.61 (dd, *J* = 8.8, 5.1 Hz, 1H, Ar-H), 7.35 (d, *J* = 8.0 Hz, 2H, 2 $\times$ Ar-H), 7.24 (dd, *J* = 8.4, 2.1 Hz, 1H, Ar-H), 7.06 (td, *J* = 8.8, 2.1 Hz, 1H, Ar-H), 4.06 (dd, *J* = 12.2, 1.9 Hz, 1H, NCHH), 3.87 (dd, *J* = 12.1, 1.9 Hz, 1H, NCHH), 3.12 (p, *J* = 7.7 Hz, 1H, NCH₂CH₂CH), 2.90–2.79 (m, 1H, NCHH), 2.72 (ddd, *J* = 12.1, 8.3, 6.1 Hz, 1H, NCHH), 2.45 (s, 3H, Ar-CH₃), 2.12 (tt, *J* = 8.8, 4.6 Hz, 4H, 2 $\times$ NCH₂CH₂), 1.43 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 164.8 (d, *J* = 280 Hz, Ar-C_q), 164.3 (Ar-C_q), 160.4 (C=N), 156.6 (C=O), 134.0 (Ar-C_q), 130.3 (2 $\times$ Ar-C), 128.2 (2 $\times$ Ar-C), 125.5 (Ar-C_q), 122.7 (*J* = 11 Hz, Ar-C), 117.3 (Ar-C_q), 113.2 (d, *J* = 25 Hz, Ar-C), 97.9 (d, *J* = 27 Hz, Ar-C), 80.8 (C(CH₃)₃), 46.8 (NCH₂), 45.3 (NCH₂), 34.1 (NCH₂CH₂CH), 30.3 (1 $\times$ NCH₂CH₂), 30.0 (1 $\times$ NCH₂CH₂), 28.6 (C(CH₃)₃), 22.0 (Ar-CH₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 109.0. HRMS (ESI) *m/z* Calcd for C₂₄H₂₉N₃O₄SF [M+H]⁺: 474.1863; Found:

474.1861. $[\alpha]^{23}_D = +20$ (c 0.5, CHCl_3). HPLC conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. (**R**)-**3r** retention time: 36 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D on a 0.1 mmol scale to afford the sulfonimidamide (**rac**)-**3r** (~10 mg) with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. (**rac**)-**3r** retention times: 23 & 36 min.

tert-Butyl (R)-(((3-(10,11-dihydro-5H-dibenzo[*b,f*]azepin-5-yl)propyl)(methyl)amino)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3s)

Prepared according to General Procedure D. Desipramine hydrochloride (151 mg, 0.50 mmol, 2.0 equiv) and triethylamine (140 μL, 1.00 mmol, 4.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 20% Et_2O in CH_2Cl_2) afforded sulfonimidamide (**R**)-**3s** (96.8 mg, 75%, 98% ee) as a colourless oil. R_f 0.17 (20% EtOAc in pentane). IR (film)/cm⁻¹ 3060, 2974, 2922, 1670, 1595, 1487, 1454, 1390, 1249, 1152, 910, 865, 731. ¹H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.3$ Hz, 2H, 2 × Ar-H), 7.22 (d, $J = 8.3$ Hz, 2H, 2 × Ar-H), 7.15–7.10 (m, 4H, 4 × Ar-C), 7.08 (d, $J = 7.4$ Hz, 2H, 2 × Ar-H), 6.95–6.91 (m, 2H, 2 × Ar-H), 3.72 (t, $J = 6.6$ Hz, 2H, NCH_2), 3.29–3.17 (m, 2H, NCH_2), 3.15 (s, 4H, 2 × Ar- CH_2), 2.69 (s, 3H, NCH_3), 2.40 (s, 3H, Ar- CH_3), 1.79–1.74 (m, 2H, NCH_2CH_2), 1.42 (s, 9H, $\text{C}(\text{CH}_3)_3$). ¹³C NMR (101 MHz, CDCl_3) δ 156.7 (C=O), 148.1 (2 × Ar- C_q), 143.7 (Ar- C_q), 134.7 (Ar- C_q), 134.4 (2 × Ar- C_q), 130.0 (2 × Ar-C), 129.7 (2 × Ar-C), 127.6 (2 × Ar-C), 126.5 (2 × Ar-C), 122.7 (2 × Ar-C), 119.9 (2 × Ar-C), 80.1 ($\text{C}(\text{CH}_3)_3$), 47.8 (NCH_2), 47.6 (NCH_2), 34.7 (NCH_3), 32.2 (2 × Ar- CH_2), 28.2 ($\text{C}(\text{CH}_3)_3$), 25.9 (NCH_2CH_2), 21.6 (Ar- CH_3). HRMS (ESI) m/z Calcd for $\text{C}_{30}\text{H}_{38}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 520.2634; Found: 520.2622. $[\alpha]^{21}_D = +8$ (c 1.0, CHCl_3). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 290 nm, (**R**)-**3s** retention time: 30 min.

Synthesis of racemic sample for HPLC analysis prepared according to General Procedure B to afford sulfonimidamide (**rac**)-**3s** (77.7 mg, 60%) as a colourless oil with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 290 nm, (**rac**)-**3s** retention times: 22 & 30 min.

tert-Butyl ((R)-oxo(((S)-1-phenylethyl)amino)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate ((R)-3t)

Prepared according to General Procedure D. (S)-1-phenylethan-1-amine (64 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 5% Et_2O in CH_2Cl_2) afforded sulfonimidamide (**R**)-**3t** (42 mg, 45%) as a single diastereomer as a colourless oil. R_f 0.24 (5% Et_2O in CH_2Cl_2). IR (film)/cm⁻¹ 3083, 2978, 1673, 1453, 1367, 1278, 1162, 1118. ¹H NMR (400 MHz, CDCl_3) δ 7.58

(d, $J = 8.4$ Hz, 2H, 2 $\times$ Ar-H), 7.15–7.07 (m, 5H, 5 $\times$ Ar-C), 7.03–6.96 (m, 2H, 2 $\times$ Ar-H), 6.55 (d, $J = 4.7$ Hz, 1H, NH), 4.47–4.44 (m, 1H, NHCH), 2.34 (s, 3H, Ar-CH₃), 1.57 (d, $J = 6.8$ Hz, 3H, CHCH₃), 1.41 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.3 (C=O), 143.5 (Ar-C_q), 141.3 (Ar-C_q), 136.0 (Ar-C_q), 129.3 (2 $\times$ Ar-C), 128.4 (2 $\times$ Ar-C), 127.8 (2 $\times$ Ar-C), 127.4 (Ar-C), 126.2 (2 $\times$ Ar-C), 80.4 (C(CH₃)₃), 52.6 (NHCH), 28.1 (C(CH₃)₃), 24.1 (CH(CH₃)), 21.4 (Ar-CH₃). HRMS (APCI +p) m/z : Calcd for C₂₀H₂₇N₂O₃S [M+H]⁺: 375.1737; Found: 375.1737. [α]_D²³ = +4 (c 1.0, CDCl₃).

tert-Butyl ((R)-oxo(((R)-1-phenylethyl)amino)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3u)

Prepared according to General Procedure D. (R)-1-phenylethan-1-amine (64 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (69 mg, 0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3u** (40 mg, 43%) as a single diastereomer as a colourless oil. R_f 0.28 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3063, 2978, 1677, 1453, 1367, 1274, 1159, 1118, 969, 909. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, $J = 8.4$ Hz, 2H, 2 $\times$ Ar-H), 7.34–7.25 (m, 7H, 7 $\times$ Ar-C), 6.58 (s, 1H, NH), 4.43 (q, $J = 6.9$ Hz, 1H, NHCH), 2.45 (s, 3H, Ar-CH₃), 1.39 (s, 9H, C(CH₃)₃), 1.30 (d, $J = 6.9$ Hz, 3H, CHCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 157.0 (C=O), 143.9 (Ar-C_q), 142.3 (Ar-C_q), 136.8 (Ar-C_q), 129.6 (2 $\times$ Ar-C), 128.6 (2 $\times$ Ar-C), 127.9 (2 $\times$ Ar-C), 127.6 (Ar-C), 126.2 (2 $\times$ Ar-C), 80.3 (C(CH₃)₃), 52.4 (NHCH), 28.1 (C(CH₃)₃), 23.0 (CHCH₃), 21.5 (Ar-CH₃). HRMS (APCI +p) m/z : Calcd for C₂₀H₂₇N₂O₃S [M+H]⁺: 375.1737; Found: 375.1725. [α]_D²³ = +39 (c 1.0, CDCl₃).

Crystal Structure Data for (R)-3h**(R)-3h**

The absolute structure of **(R)-3h** was unambiguously determined by use of the Flack parameter [$x = -0.035(17)$].

Figures

Figure S 1: The crystal structure of (R)-3h.

Preparation of enantioenriched 4-bromophenyl derivatives (Scheme 4)

Methyl 3-((4-bromophenyl)thio)propanoate (7)

Methyl acrylate (2.00 mL, 22.0 mmol, 1.1 equiv) and sodium acetate (247 mg, 3.0 mmol, 0.15 equiv) were added to 4-bromobenzenethiol (3.78 g, 20.0 mmol, 1 equiv) in $\text{THF}:\text{H}_2\text{O}$ (1:1, 67 mL) and stirred at 25°C for 18 h. Aqueous NaHCO_3 (50 mL) was added and the aqueous mixture was extracted with EtOAc (3×60 mL) and washed with brine (60 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give sulfide **7** (5.08, 92%) as a white solid. mp = $52\text{--}54^\circ\text{C}$. R_f 0.18 (5% Et_2O in pentane). IR (film)/ cm^{-1} 2997, 2950, 2844, 1737, 1474, 1435, 1359, 1245, 1217, 1195, 1172, 1092, 1008, 811. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.6$ Hz, 2H, $2 \times \text{Ar-H}$), 7.23 (d, $J = 8.6$ Hz, 2H, $2 \times \text{Ar-H}$), 3.68 (s, 3H, OCH_3), 3.15 (t, $J = 7.4$ Hz, 2H, SCH_2), 2.62 (t, $J = 7.4$ Hz, 2H, SCH_2CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5 (C=O), 134.6 (Ar-C_q), 132.2 ($2 \times \text{Ar-C}$), 131.8 ($2 \times \text{Ar-C}$), 120.8 (Ar-C_q), 52.0 (OCH_3), 34.2 (SCH_2), 29.3 (SCH_2CH_2). Analytical data (NMR) in agreement with those reported in the literature.^[3]

Methyl 3-((4-bromophenyl)sulfinyl)propanoate (8)

Prepared according to a literature procedure.^[4,5] A solution of $\text{VO}(\text{acac})_2$ (16 mg, 0.06 mmol, 1 mol%) in CHCl_3 (1.5 mL) was added dropwise to a solution of (*S,E*)-2-(((1-hydroxy-3,3-dimethylbutan-2-yl)imino)methyl)-4,6-diiodophenol (42 mg, 0.09 mmol, 1.5 mol%) in CHCl_3 (1.5 mL) and stirred at 25°C for 30 min. Sulfide **7** (1.65 g, 6.0 mmol, 1.0 equiv) and CHCl_3 (3 mL) were added and the reaction mixture cooled to 0°C . H_2O_2 (30% in H_2O , 736 μL , 7.2 mmol, 1.2 equiv) was added dropwise and the mixture left to vigorously stir at 0°C for 72 h. Sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (30 mL) was added and the aqueous mixture was extracted with CHCl_3 (3×30 mL) and washed with brine (40 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (40% EtOAc in pentane) afforded sulfoxide **(S)-8** (1.19 g, 68%, 99% ee) as a white solid. mp = $79\text{--}80^\circ\text{C}$. R_f 0.23 (40% EtOAc in pentane). IR (film)/ cm^{-1} 3050, 2997, 2948, 2916, 2846, 1728, 1571, 1472, 1435, 1415, 1388, 1239, 1170, 1131, 1060, 1034, 1005, 893, 826, 762, 732, 718. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.5$ Hz, 2H, $2 \times \text{Ar-H}$), 7.49 (d, $J = 8.6$ Hz, 2H, $2 \times \text{Ar-H}$), 3.67 (s, 3H, OCH_3), 3.23 (ddd, $J = 13.2, 8.2, 6.8$ Hz, 1H, SCHH), 2.94 (ddd, $J = 13.4, 8.0, 5.7$ Hz, 1H, SCHH), 2.84 (ddd, $J = 17.2, 8.1, 6.8$ Hz, 1H, SCH_2CHH), 2.56 (ddd, $J = 17.2, 8.2, 5.7$ Hz, 1H, SCH_2CHH). ^{13}C NMR (101 MHz, CDCl_3) δ 171.6 (C=O), 142.2 (Ar-C_q), 132.7 ($2 \times \text{Ar-C}$), 125.8 (Ar-C_q), 125.8 ($2 \times \text{Ar-C}$), 52.3 (SCH_2), 51.3 (OCH_3), 26.1 (SCH_2CH_2). HRMS (Voltage EI+) m/z Calcd for $\text{C}_{10}\text{H}_{11}\text{O}_3\text{SBr}$ $[\text{M}+\text{H}]^+$: 289.9612;

Found: 289.9607. $[\alpha]^{23}_D = -98$ (c 1.0, CHCl_3). HPLC conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**S**)-**8** retention time: 19 min.

Synthesis of racemic sample for HPLC analysis prepared by *m*CPBA oxidation to afford sulfoxide (**rac**)-**8** (5.09 g, 87%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**8** retention times: 19 & 21 min.

Methyl 3-(4-bromo-*N*-(*tert*-butoxycarbonyl)phenylsulfonyl)propanoate ((**S**)-**9**)

Prepared according to a literature procedure.^[6] Magnesium oxide (659 mg, 16.4 mmol, 4 equiv), *tert*-butyl carbamate (720 mg, 6.2 mmol, 1.5 equiv), $\text{PhI}(\text{OAc})_2$ (1.98 g, 6.2 mmol, 1.5 equiv) and $\text{Rh}_2(\text{OAc})_4$ (45 mg, 0.10 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide (**S**)-**8** (1.19 g, 4.1 mmol, 1 equiv) in CH_2Cl_2 (40 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At rt, the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (25% EtOAc in pentane) afforded sulfoximine (**S**)-**9** (1.45 g, 87%, 99% ee) as a white solid. mp = 83–84 °C. R_f 0.15 (25% EtOAc in pentane). mp = 100–101 °C. IR (film)/cm⁻¹ 2978, 1740 (C=O), 1699, 1669, 1390, 1274, 1252, 1155, 1110. ¹H NMR (400 MHz, CDCl_3) δ 7.82–7.78 (m, 2H, 2 × Ar-H), 7.77–7.73 (m, 2H, 2 × Ar-H), 3.76–3.65 (m, 1H, SCHH), 3.63 (s, 3H, OCH₃), 3.58 (dd, J = 6.3, 5.5 Hz, 1H, SCHH), 2.81 (qdd, J = 17.3, 8.9, 6.2 Hz, 2H, SCH_2CH_2), 1.38 (s, 9H, $\text{C}(\text{CH}_3)_3$). ¹³C NMR (101 MHz, CDCl_3) δ 170.0 (C=O), 157.3 (C=O), 136.0 (Ar-C_q), 133.0 (Ar-C_q), 129.6 (2 × Ar-C), 129.4 (2 × Ar-C), 81.0 ($\text{C}(\text{CH}_3)_3$), 52.4 (OCH₃), 51.6 (SCH₂), 27.9 ($\text{C}(\text{CH}_3)_3$), 27.1 (SCH_2CH_2). HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_5\text{S}_2\text{Br}$ $[\text{M}+\text{H}]^+$: 408.0303; Found: 408.0296. $[\alpha]^{23}_D = +44$ (c 1.0, CHCl_3). HPLC conditions: Chiralpak IA column, 93:7 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**R**)-**9** retention time: 22 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfoximine (**rac**)-**9** (6.24 g, 95%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 93:7 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**9** retention times: 22 & 37 min.

Sodium ((4-bromophenyl)sulfinyl)(*tert*-butoxycarbonyl)amide ((**S**)-**1b**)

5 M NaOH in MeOH (718 μL , 3.6 mmol, 1.05 equiv) was added to sulfoximine (**S**)-**9** (1.39 g, 3.4 mmol, 1.0 equiv) at 25 °C in CH_2Cl_2 (25 mL, 0.1 M) and the reaction was stirred for 1 h. The suspension was then filtered to collect the white precipitate, which was washed with CH_2Cl_2 (100 mL). Excess solvent was then removed under reduced pressure to afford sulfinamide salt (**S**)-**1b** as a white solid (1.05 g, 90%, 99% ee). mp = 227–229 °C. IR (film)/cm⁻¹ 2981, 1640, 1468, 1390, 1271, 1162, 998, 834, 760; ¹H NMR (400 MHz, D_2O) δ 7.71–7.65 (m, 2H, 2 × Ar-H), 7.56–7.50 (m, 2H, 2 × Ar-H), 1.40 (s, 9H, $\text{C}(\text{CH}_3)_3$). ¹³C NMR (101 MHz, D_2O) δ 165.9 (C=O), 145.6 (Ar-C_q), 132.0 (2 × Ar-C), 126.5 (2 × Ar-C), 124.6 (Ar-C_q), 79.7 ($\text{C}(\text{CH}_3)_3$), 27.7 ($\text{C}(\text{CH}_3)_3$). HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_3\text{SBr}$ $[\text{M}]^-$: 317.9800; Found: 317.9806. Further characterisation was carried out after washing ~20 mg with sat. aq. NH_4Cl solution. Sulfinamide: $[\alpha]^{23}_D = +88$ (c 1.0, CDCl_3). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**S**)-**1b** retention time: 20 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfinamide salt **(rac)-1b** (786 mg, 89%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(rac)-1b** retention times: 18 & 20 min.

tert-Butyl ((4-bromophenyl)fluoro(oxo)-λ⁶-sulfaneylidene)carbamate ((R)-2b)

Prepared according to General Procedure C. Selectfluor (850 mg, 2.4 mmol, 2.0 equiv) was added to a stirred solution of sulfinamide salt **(S)-1b** (411 mg, 1.2 mmol, 1.0 equiv) and potassium acetate (235 mg, 2.4 mmol, 2.0 equiv) in ethanol (6.0 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (5 × 15 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. No further purification was required giving sulfonylimidoyl fluoride **(R)-2b** (175 mg, quant, 92% ee) as a colourless oil. IR (film)/cm⁻¹ 3093, 2982, 1707, 1573, 1331, 1252, 1148, 1069, 1010, 909, 857, 756. ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.94 (m, 2H, 2 × Ar–H), 7.79–7.74 (m, 2H, 2 × Ar–H), 1.53 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 151.7 (C=O), 132.5 (2 × Ar–C), 132.3 (Ar–C_q), 130.8 (Ar–C_q), 129.2 (2 × Ar–C), 82.7 (C(CH₃)₃), 27.5 (C(CH₃)₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 69.8. [α]_D²³ = –15 (c 1.7, CDCl₃). HPLC conditions: Chiralpak IA column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(R)-2b** retention time: 11 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfonylimidoyl fluoride **(rac)-2b** (175 mg, quant.) as a colourless oil with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, **(rac)-2b** retention times: 10 & 11 min.

tert-Butyl (R)-((benzylamino)(4-bromophenyl)(oxo)-λ⁶-sulfaneylidene)carbamate ((R)-3v)

Prepared according to General Procedure D. Benzylamine (55 μL, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonylimidoyl fluoride **(R)-2b** (85 mg, 0.25 mmol, 1.0 equiv) and LiBr (43 mg, 0.50 mmol, 2.0 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 2% Et₂O in CH₂Cl₂) afforded sulfonylimidamide **(R)-3v** (66 mg, 62%, 92% ee) as a white solid. *R*_f = 0.23 (2% Et₂O in CH₂Cl₂); mp = 154–156 °C. IR (film)/cm⁻¹ 3086, 1684, 1572, 1282, 1159, 1088, 909; ¹H NMR (400 MHz, CDCl₃) δ 7.79–7.75 (m, 2H, 2 × Ar–H), 7.63–7.60 (m, 2H, 2 × Ar–H), 7.30–7.25 (m, 3H, 3 × Ar–C), 7.23–7.17 (m, 2H, 2 × Ar–H), 6.89 (s, 1H, NH), 4.25 (d, *J* = 14.1 Hz, 1H, NHCHH), 3.99 (d, *J* = 14.1 Hz, 1H, NHCHH), 1.38 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.8 (C=O), 138.0 (Ar–C_q), 135.6 (Ar–C_q), 132.3 (2 × Ar–C), 129.4 (2 × Ar–C), 128.7 (2 × Ar–C), 128.2 (Ar–C_q), 128.0 (3 × Ar–C), 80.9 (C(CH₃)₃), 45.5 (NHCH₂), 28.0 (C(CH₃)₃). HRMS (ESI) *m/z*: Calcd for C₁₈H₂₂N₂O₃SBr [M+H]⁺: 425.0535; Found: 425.0531. [α]_D²³ = +6 (c 0.5, CH₂Cl₂). HPLC conditions: Chiralpak ID column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, **(R)-3v** retention time: 15 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfonimidamide (**rac**)-**3v** (20 mg, 47%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak ID column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm, (**rac**)-**3v** retention times: 15 & 20 min.

tert-Butyl (R)-((allylamino)(4-bromophenyl)(oxo)- λ^6 -sulfaneylidene)carbamate ((R)-3w)

Prepared according to General Procedure D. Allylamine (38 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2b** (85 mg, 0.25 mmol, 1.0 equiv) and LiBr (43 mg, 0.50 mmol, 2.0 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3w** (70 mg, 75%, 90% ee) as a white solid. *R*_f = 0.31 (5% Et₂O in CH₂Cl₂); mp = 86–88 °C. IR (film)/cm⁻¹ 3243, 2981, 1677, 1572, 1390, 1282, 1159, 1088, 905; ¹H NMR (400 MHz, CDCl₃) δ 7.84–7.81 (m, 2H, 2 $\times$ Ar–H), 7.70–7.66 (m, 2H, 2 $\times$ Ar–H), 6.36 (s, 1H, NH), 5.73 (dddd, *J* = 17.1, 10.2, 6.1, 5.5 Hz, 1H, NCH₂CH), 5.22 (dq, *J* = 17.1, 1.5 Hz, 1H, NCH₂CHCHH), 5.15 (dq, *J* = 10.2, 1.3 Hz, 1H, NCH₂CHCHH), 3.68 (dd, *J* = 15.1, 5.5 Hz, 1H, NCHH), 3.46 (dd, *J* = 15.0, 6.1 Hz, 1H, NCHH), 1.41 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.7 (C=O), 138.0 (Ar–C_q), 132.4 (2 $\times$ Ar–C), 132.3 (NCH₂CH), 129.5 (2 $\times$ Ar–C), 128.2 (Ar–C_q), 118.2 (NCH₂CHCH₂), 80.8 (C(CH₃)₃), 43.9 (NCH₂), 28.0 (C(CH₃)₃). HRMS (ESI) *m/z*: Calcd for C₁₄H₂₀N₂O₃SBr [M+H]⁺: 375.0378; Found: 375.0380. [α]_D²³ = +8 (c 0.5, CH₂Cl₂). HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**R**)-**3w** retention time: 20 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfonimidamide (**rac**)-**3w** (18 mg, 48%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**3w** retention times: 20 & 29 min.

tert-Butyl ((4-bromophenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate ((R)-3x)

Prepared according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2b** (85 mg, 0.25 mmol, 1.0 equiv) and LiBr (43 mg, 0.50 mmol, 2.0 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 2% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**3x** (88 mg 87%, 90% ee) as a white solid. *R*_f = 0.36 (2% Et₂O in CH₂Cl₂); mp = 171–172 °C. IR (film)/cm⁻¹ 2974, 2937, 2855, 1674, 1572, 1275, 1151, 931, 745; ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.71 (m, 2H, 2 $\times$ Ar–H), 7.69–7.65 (m, 2H, 2 $\times$ Ar–H), 3.20–3.05 (m, 4H, 2 $\times$ NCH₂), 1.67–1.59 (m, 4H, 2 $\times$ NCH₂CH₂), 1.51–1.44 (m, 2H, NCH₂CH₂CH₂), 1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.4 (C=O), 135.8 (Ar–C_q), 132.3 (2 $\times$ Ar–C), 129.2 (2 $\times$ Ar–C), 127.9 (Ar–C_q), 80.4 (C(CH₃)₃), 46.6 (2 $\times$ NCH₂), 28.0 (C(CH₃)₃), 25.2 (2 $\times$ NCH₂CH₂), 23.5 (NCH₂CH₂CH₂). HRMS (ESI) *m/z*: Calcd for C₁₆H₂₄N₂O₃SBr [M+H]⁺: 403.0691; Found: 403.0703. [α]_D²³ = –8 (c 0.5, CH₂Cl₂). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**R**)-**3x** retention time: 24 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfonimidamide (**rac**)-**3x** (~20mg, 50%) as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**3x** retention times: 16 & 24 min.

tert-Butyl ((R)-(4-bromophenyl)(methyl((S)-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)amino)(oxo)-λ⁶-sulfaneylidene)carbamate ((R)-3y)

Prepared according to General Procedure D. Duloxetine Hydrochloride (167 mg, 0.50 mmol, 2.0 equiv) and triethylamine (140 μL, 1.0 mmol, 4.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride (**R**)-**2a** (85 mg, 0.25 mmol, 1.0 equiv) and LiBr (43 mg, 0.50 mmol, 2.0 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) followed by (SiO₂, 10% acetone in pentane) afforded sulfonimidamide (**R**)-**3y** (124 mg, 80%) as a single diastereomer as a white solid. *R_f* 0.15 (10% acetone in pentane). mp = 57–60 °C. IR (film)/cm⁻¹ 2978, 1744, 1673, 1572, 1461, 1394, 1263, 1151, 1088, 775. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (dd, *J* = 6.9, 3.0 Hz, 1H, Ar–H), 7.82–7.76 (m, 1H, Ar–H), 7.70 (d, *J* = 8.6 Hz, 2H, 2 × Ar–H), 7.56–7.46 (m, 4H, 4 × Ar–C), 7.41 (d, *J* = 8.2 Hz, 1H, Ar–H), 7.32–7.24 (m, 1H, Ar–H), 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H, Ar–H), 7.10 (d, *J* = 3.4 Hz, 1H, Ar–H), 6.94 (dd, *J* = 5.0, 3.5 Hz, 1H, Ar–H), 6.83 (d, *J* = 7.7 Hz, 1H, Ar–H), 5.74 (dd, *J* = 8.3, 4.3 Hz, 1H, OCHAr), 3.52 (ddd, *J* = 13.7, 8.2, 5.3 Hz, 1H, NCHH), 3.37 (dt, *J* = 14.2, 7.4 Hz, 1H, NCHH), 2.87 (s, 3H, NCH₃), 2.51 (dtd, *J* = 13.5, 8.0, 5.2 Hz, 1H, NCH₂CHH), 2.40–2.28 (m, 1H, NCH₂CHH), 1.45 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.3 (C=O), 152.8 (Ar–C_q), 144.3 (Ar–C_q), 136.6 (Ar–C_q), 134.5 (Ar–C_q), 132.3 (2 × Ar–C), 128.9 (2 × Ar–C), 128.0 (Ar–C_q), 127.6 (Ar–C), 126.7 (Ar–C), 126.3 (Ar–C), 125.9 (Ar–C_q), 125.7 (Ar–C), 125.3 (Ar–C), 124.98 (Ar–C), 124.97 (Ar–C), 121.8 (Ar–C), 120.9 (Ar–C), 107.0 (Ar–C), 80.5 (C(CH₃)₃), 73.4 (OCHAr), 47.0 (NCH₂), 37.4 (NCH₃), 35.4 (NCH₂CH₂), 28.1 (C(CH₃)₃). HRMS (ESI) *m/z*: Calcd for C₂₉H₃₁N₂O₄S₂BrNa [M+Na]⁺: 637.0815; Found: 637.0806. [α]_D²³ = +10 (c 0.5, CH₂Cl₂).

tert-Butyl (R)-([1,1'-biphenyl]-4-yl(oxo)(piperidin-1-yl)-λ⁶-sulfaneylidene)carbamate ((R)-10)

Prepared according to a literature procedure.^[7] Sulfonimidamide (**R**)-**3x** (40 mg, 0.10 mmol, 1 equiv), phenylboronic acid (18 mg, 0.15 mmol, 1.5 equiv), potassium carbonate (28 mg, 0.20 mmol, 2 equiv) and 1,1'-bis(di-*tert*-butylphosphino)ferrocene palladium dichloride (6.5 mg, 0.01 mmol, 10 mol%) was added to a glass vial with MeCN:H₂O (1:1, 500 μL, 0.2 M) and was degassed before being stirred and heated to 80 °C for 2 h. The reaction mixture was quenched with aq. sat. NH₄Cl (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (3 × 10 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO₂, 3% Et₂O in CH₂Cl₂) afforded sulfonimidamide (**R**)-**10** (37 mg, 91%, 90% ee) as a colourless oil. *R_f* 0.38 (3% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2974, 2937, 2855, 1669, 1595, 1453, 1394, 1248, 1148, 928, 760. ¹H NMR (400 MHz, CDCl₃) δ 7.95–7.90 (m, 2H, 2 × Ar–H), 7.76–7.70 (m, 2H, 2 × Ar–H), 7.64–7.60 (m, 2H, 2 × Ar–H), 7.52–7.46 (m, 2H, 2 × Ar–H), 7.45–7.39 (m, 1H, Ar–H), 3.17 (q, *J* = 4.9 Hz, 4H, 2 × NCH₂), 1.67 (p, *J* = 5.6 Hz, 4H, 2 × NCH₂CH₂), 1.52–1.46 (m, 2H, NCH₂CH₂CH₂), 1.43 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.7 (C=O), 145.7 (Ar–C_q), 139.2 (Ar–

C_q), 135.1 (Ar–C_q), 129.0 (2 × Ar–C), 128.5 (Ar–C), 128.2 (2 × Ar–C), 127.6 (2 × Ar–C), 127.3 (2 × Ar–C), 80.1 (C(CH₃)₃), 46.6 (2 × NCH₂), 28.1 (C(CH₃)₃), 25.2 (2 × NCH₂CH₂), 23.6 (NCH₂CH₂CH₂). [α]²³_D = –7 (c 1.0, CDCl₃). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{–1}, 35 °C, UV detection wavelength: 250 nm, (**R**)-**10** retention time: 32 min.

Synthesis of racemic sample for HPLC analysis prepared by using the above procedure to afford sulfonimidamide (**rac**)-**10** (~10 mg) as a colourless oil with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{–1}, 35 °C, UV detection wavelength: 250 nm, (**rac**)-**10** retention times: 27 & 32 min.

Experimental Data for Racemic Sulfinamide Salts (S4b-f)

Synthesis of sulfinamide salts

Thiol Alkylation

Methyl 3-(tolylthio)propanoate (S1a)

Methyl acrylate (2.00 mL, 22.1 mmol) and sodium acetate (247 mg, 3.02 mmol) were added to 4-methylbenzene-1-thiol (2.50 g, 20.1 mmol) in THF:H₂O (1:1, 67 mL) and stirred at 25 °C for 18 h. Aqueous NaHCO₃ (50 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 60 mL) and washed with brine (60 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure to give sulfide **S1a** (4.25, quant.) as a colourless oil. IR (film)/cm⁻¹ 3019, 2952, 1737 (C=O), 1491, 1435, 1353, 1193, 1241, 1092, 1017, 980, 805. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 7.11 (d, *J* = 7.9 Hz, 2H, 2 × Ar-H), 3.67 (s, 3H, OCH₃), 3.11 (t, *J* = 7.4 Hz, 2H, SCH₂), 2.60 (t, *J* = 7.4 Hz, 2H, SCH₂CH₂), 2.32 (s, 3H, Ar-CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 172.3 (C=O), 136.9 (Ar-C_q), 131.3 (Ar-C_q), 131.1 (2 × Ar-C), 129.8 (2 × Ar-C), 51.8 (OCH₃), 34.3 (SCH₂), 29.8 (SCH₂CH₂), 21.1 (Ar-CH₃). Analytical data (NMR) in agreement with those reported in the literature.^[8]

Methyl 3-(phenylthio)propanoate (S1b)

Methyl acrylate (269 μL, 3.0 mmol, 1.0 equiv) and sodium acetate (37 mg, 0.45 mmol, 0.15 equiv) were added to benzenethiol (306 μL, 3.0 mmol, 1.0 equiv) in THF:H₂O (1:1, 10 mL) and stirred at 25 °C for 18 h. Aqueous NaHCO₃ (50 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (5% EtOAc in pentane) afforded sulfide **S1b** (498 mg, 72%) as a colourless oil. R_f 0.25 (5% EtOAc in pentane). IR (film)/cm⁻¹ 2951, 1733 (C=O), 1583, 1481, 1437, 1356, 1243, 1171, 1024, 737, 690. ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.35 (m, 2H, 2 × Ar-H), 7.35–7.25 (m, 2H, 2 × Ar-H), 7.24–7.18 (m, 1H, Ar-H), 3.68 (s, 3H, OCH₃), 3.17 (t, *J* = 7.4 Hz, 2H, SCH₂), 2.63 (t, *J* = 7.4 Hz, 2H, SCH₂CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 172.2 (C=O), 135.1 (Ar-C_q), 130.1 (Ar-C), 129.0 (2 × Ar-C), 126.6 (2 × Ar-C), 51.9 (OCH₃), 34.2 (SCH₂), 29.1 (SCH₂CH₂). Analytical data (NMR) in agreement with those reported in the literature.^[9]

Methyl 3-((4-fluorophenyl)thio)propanoate (S1c)

Methyl acrylate (1.81 mL, 20 mmol, 1.0 equiv) and sodium acetate (247 mg, 3.00 mmol, 0.15 equiv) were added to the 4-fluorobenzenethiol (2.13 mL, 20 mmol, 1 equiv) in THF:H₂O (67 mL, 1:1) and stirred at 25 °C and monitored by TLC. Aqueous NaHCO₃ (50 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 60 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated under reduced pressure to give sulfide **S1c** (3.59 g, 84%) as a yellow oil which was

used without further purification. IR (film)/cm⁻¹ 2952, 1733 (C=O), 1588, 1491, 1435, 1357, 1219, 1156, 1088, 980, 820. ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.36 (m, 2H, 2 × Ar–H), 7.02–6.98 (m, 2H, 2 × Ar–H), 3.66 (s, 3H, OCH₃), 3.09 (t, *J* = 7.4 Hz, 2H, SCH₂), 2.58 (t, *J* = 7.4 Hz, 2H, SCH₂CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 172.2 (C=O), 162.3 (d, ¹*J*_{C-F} = 247 Hz, Ar–C_q), 133.5 (d, ³*J*_{C-F} = 8.1 Hz, 2 × Ar–C), 130.1 (d, ⁴*J*_{C-F} = 3.1 Hz, Ar–C_q), 116.3 (d, ²*J*_{C-F} = 21.9 Hz, 2 × Ar–C), 51.9 (OCH₃), 34.3 (SCH₂), 30.5 (SCH₂CH₂). ¹⁹F NMR (377 MHz, CDCl₃) δ -114.6– -114.7 (m, 1F, Ar–F). Analytical data (NMR) in agreement with those reported in the literature.^[10]

Methyl 3-((4-methoxyphenyl)thio)propanoate (**S1d**)

Methyl acrylate (1.81 mL, 20 mmol, 1.0 equiv) and sodium acetate (247 mg, 3.00 mmol, 0.15 equiv) were added to the 4-methoxybenzenethiol (2.13 mL, 20 mmol, 1 equiv) in THF:H₂O (67 mL, 1:1) and stirred at 25 °C and monitored by TLC. Aqueous NaHCO₃ (50 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 60 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated under reduced pressure to give the corresponding sulfide **S1d** (3.76 g, 83%) as an orange oil which was used without further purification. IR (film)/cm⁻¹ 3001, 2952, 2837, 1733 (C=O), 1592, 1491, 1461, 1357, 1241, 1170, 1029, 980, 824. ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.33 (m, 2H, 2 × Ar–H), 6.86–6.81 (m, 2H, 2 × Ar–H), 3.78 (s, 3H, OCH₃), 3.65 (s, 3H, OCH₃), 3.03 (t, *J* = 7.4 Hz, 2H, SCH₂), 2.56 (t, *J* = 7.4 Hz, 2H, SCH₂CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 172.3 (C=O), 159.4 (Ar–C_q), 134.2 (2 × Ar–C), 125.1 (2 × Ar–C), 114.7 (Ar–C_q), 55.3 (Ar–OCH₃), 51.7 (COOCH₃), 34.4 (SCH₂), 31.1 (SCH₂CH₂). Analytical data (NMR) in agreement with those reported in the literature.^[11]

Methyl 3-(pyridin-2-ylthio)propanoate (**S1e**)

Prepared according to a literature procedure.^[12] Methyl 3-bromopropionate (2.6 mL, 24 mmol, 1.2 equiv) was added to a stirred solution of 2-mercaptopyridine (2.22 g, 20 mmol, 1 equiv) and NEt₃ (4.16 mL, 30 mmol, 1.5 equiv) in acetonitrile (10 mL, 2 M) and heated under reflux to 85 °C for 24 h. At rt the reaction mixture was concentrated under reduced pressure. Purification by flash column chromatography (10% EtOAc in pentane) afforded sulfide **S1e** (3.11 g, 15.8 mmol, 79%) as a pale-yellow oil. *R*_f 0.33 (10% EtOAc in pentane). IR (film)/cm⁻¹ 3049, 2997, 2952, 1737 (C=O), 1580, 1454, 1412, 1357, 1249, 1108, 984, 760, 723. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (ddd, *J* = 5.0, 1.9, 1.0 Hz, 1H, Ar–H), 7.46 (ddd, *J* = 8.1, 7.3, 1.9 Hz, 1H, Ar–H), 7.16 (dt, *J* = 8.1, 1.1 Hz, 1H, Ar–H), 6.97 (ddd, *J* = 7.3, 4.9, 1.1 Hz, 1H, Ar–H), 3.70 (s, 3H, OCH₃), 3.43 (t, *J* = 7.1 Hz, 2H, SCH₂), 2.79 (t, *J* = 7.1 Hz, 2H, SCH₂CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 172.7 (C=O), 158.3 (Ar–C_q), 149.6 (Ar–C), 136.0 (Ar–C), 122.5 (Ar–C), 119.6 (Ar–C), 51.9 (OCH₃), 34.7 (SCH₂), 25.0 (SCH₂CH₂). Analytical data (NMR) in agreement with those reported in the literature.^[12]

Methyl 3-(isopropylthio)propanoate (**S1f**)

2-iodopropane (3.6 mL, 36 mmol, 2 equiv) was added to methyl 3-sulfanylpropanoate (2.0 mL, 18 mmol, 1 equiv) and K₂CO₃ (2.99 g, 22 mmol, 1.2 equiv) in acetone (90 mL, 0.2 M) at 25 °C and stirred for 24 h. The reaction mixture was quenched with 1 M K₂CO₃ (50 mL) and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO₂, 10% Et₂O in pentane) afforded sulfide **S1f** (5.09 g, 84%) as a colourless oil. *R*_f 0.30 (10% Et₂O in pentane). IR (film)/cm⁻¹ 2960, 2930, 2870, 1737

(C=O), 1439, 1357, 1244, 1170, 1051, 1021, 980. ^1H NMR (400 MHz, CDCl_3) δ 3.69 (s, 3H, OCH_3), 2.94 (p, J = 6.7 Hz, 1H, SCH), 2.80 (td, J = 7.4, 0.7 Hz, 2H, SCH_2), 2.63–2.56 (m, 2H, SCH_2CH_2), 1.26 (d, J = 6.7 Hz, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 172.6 (C=O), 51.9 (OCH_3), 35.1 (SCH), 34.9 (SCH_2), 25.6 (SCH_2CH_2), 23.4 ($\text{CH}(\text{CH}_3)_2$). HRMS (ESI) m/z Calcd for $\text{C}_7\text{H}_{15}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 163.0793; Found: 163.0791.

Methyl 3-(methylthio)propanoate (**S1g**)

Iodomethane (5.6 mL, 90 mmol, 2 equiv) was added to methyl 3-sulfanylpropanoate (5.0 mL, 45 mmol, 1 equiv) and K_2CO_3 (7.46 g, 54 mmol, 1.2 equiv) in acetone (200 mL, 0.2 M) at 25 °C and stirred for 24 h. The reaction mixture was quenched with 1 M K_2CO_3 (100 mL) and extracted with CH_2Cl_2 (3 $\times$ 200 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 , 5% Et_2O in pentane) afforded sulfide **S1g** (5.09 g, 84%) as a colourless oil. **Note: due to the volatility of the product, removal of solvent was carried out at pressures no less than 200 mbar at 25 °C** R_f 0.25 (5% Et_2O in pentane). IR (film)/ cm^{-1} 2952, 2918, 1733 (C=O), 1435, 1357, 1245, 1144, 1021. ^1H NMR (400 MHz, CDCl_3) δ 3.70 (s, 3H, OCH_3), 2.78–2.75 (m, 2H, SCH_2), 2.64–2.61 (m, 2H, SCH_2CH_2), 2.12 (s, 3H, SCH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 172.6 (C=O), 51.9 (OCH_3), 34.4 (SCH_2), 29.2 (SCH_2CH_2), 15.6 (SCH_3). Analytical data (NMR) in agreement with those reported in the literature.^[13]

Sulfide Oxidation

Methyl 3-(*p*-tolylsulfinyl)propanoate (**S2a**)

*m*CPBA (3.30 g, 19.1 mmol, 1 equiv) was added portionwise to sulfide **S1a** (4.02 g, 19.1 mmol, 1 equiv) in CH_2Cl_2 (100 mL, 0.2 M) at 0 °C and stirred for 2 hr. The reaction mixture was quenched with 1 M K_2CO_3 (100 mL) and the aqueous mixture was extracted with CH_2Cl_2 (3 $\times$ 80 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford sulfoxide **S2a** (3.97 g, 92%) as a pale-yellow oil. IR (film)/ cm^{-1} 2952, 2922, 1733 (C=O), 1595, 1494, 1439, 1358, 1234, 1170, 1085, 1040, 977, 809. ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 8.2 Hz, 2H, 2 $\times$ Ar-H), 7.36–7.28 (m, 2H, 2 $\times$ Ar-H), 3.65 (s, 3H, OCH_3), 3.20 (ddd, J = 13.3, 8.6, 6.7 Hz, 1H, SCHH), 2.94 (ddd, J = 13.3, 8.5, 5.7 Hz, 1H, SCHH), 2.81 (ddd, J = 17.2, 8.5, 6.6 Hz, 1H, SCH_2CHH), 2.53 (ddd, J = 17.2, 8.6, 5.7 Hz, 1H, SCH_2CHH), 2.41 (s, 3H, Ar- CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 171.8 (C=O), 141.8 (Ar- C_q), 139.7 (Ar- C_q), 130.1 (2 $\times$ Ar-C), 124.2 (2 $\times$ Ar-C), 52.2 (OCH_3), 51.3 (SCH_2), 26.1 (SCH_2CH_2), 21.5 (Ar- CH_3). Analytical data (NMR) in agreement with those reported in the literature.^[14]

Methyl 3-(phenylsulfinyl)propanoate (**S2b**)

*m*CPBA (131 mg, 0.76 mmol, 1 equiv) was added portionwise to sulfide **S1b** (150 mg, 0.76 mmol, 1 equiv) in CH_2Cl_2 (5 mL, 0.2 M) at 0 °C and stirred for 2 h. The reaction mixture was quenched with 3 M KOH (15 mL) and the aqueous mixture was extracted with CH_2Cl_2 (3 $\times$ 15 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (50% EtOAc in pentane) afforded sulfoxide **S2b** (113 mg, 70%) as a colourless oil. R_f 0.17 (50% EtOAc in pentane). IR (film)/ cm^{-1} 3316, 3054, 2949, 2901, 1721 (C=O), 1591, 1440, 1197, 1183, 819, 756. ^1H NMR (400 MHz, CDCl_3) δ 7.67–7.60 (m, 2H, 2 $\times$ Ar-H), 7.58–7.48 (m, 3H, 3 $\times$ Ar-H), 3.67 (s, 3H, OCH_3), 3.25 (ddd, J = 13.4, 8.5, 6.7 Hz, 1H, SCHH), 2.97 (ddd, J =

13.3, 8.3, 5.7 Hz, 1H, SCHH), 2.85 (ddd, $J = 17.2, 8.4, 6.7$ Hz, 1H, SCH₂CHH), 2.57 (ddd, $J = 17.2, 8.5, 5.7$ Hz, 1H, SCH₂CHH). ¹³C NMR (101 MHz, CDCl₃) δ 171.8 (C=O), 143.0 (Ar-C_q), 131.3 (Ar-C), 129.4 (2 $\times$ Ar-C), 124.1 (2 $\times$ Ar-C), 52.3 (OCH₃), 51.2 (SCH₂), 26.1 (SCH₂CH₂). Analytical data (NMR) in agreement with those reported in the literature.^[15]

Methyl 3-((4-fluorophenyl)sulfinyl)propanoate (S2c)

*m*CPBA (2.83 g, 16.4 mmol, 1 equiv) was added portionwise to sulfide **S1c** (3.50 g, 16.4 mmol, 1 equiv) in CH₂Cl₂ (80 mL, 0.2 M) at 0 °C and stirred for 4 hr. The reaction mixture was quenched with 1 M K₂CO₃ (100 mL) and the aqueous mixture was extracted with CH₂Cl₂ (3 $\times$ 80 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure to afford sulfoxide **S2c** (3.76 g, quant.) as a pale-yellow oil. *R*_f 0.20 (50% EtOAc in pentane). IR (film)/cm⁻¹ 2997, 2952, 1773 (C=O), 1588, 1491, 1439, 1357, 1219, 1174, 1219, 1044, 977, 835, 749. ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.53 (m, 2H, 2 $\times$ Ar-H), 7.24–7.19 (m, $J = 8.5$ Hz, 2H, 2 $\times$ Ar-H), 3.64 (s, 3H, OCH₃), 3.25–3.15 (m, 1H, SCHH), 2.93 (ddd, $J = 13.7, 7.9, 6.0$ Hz, 1H, SCHH), 2.85–2.77 (m, 1H, SCH₂CHH), 2.59–2.50 (m, 1H, SCH₂CHH). ¹³C NMR (101 MHz, CDCl₃) δ 171.6 (C=O), 164.5 (d, ¹*J*_{C-F} = 251.9 Hz, Ar-F), 138.5 (Ar-C_q), 126.4 (d, ³*J*_{C-F} = 8.8 Hz, 2 $\times$ Ar-C), 116.8 (d, ²*J*_{C-F} = 22.6 Hz, 2 $\times$ Ar-C), 52.3 (OCH₃), 51.5 (SCH₂), 26.0 (SCH₂CH₂). ¹⁹F{¹H} NMR (377 MHz, CDCl₃) δ -108.3 (1F, Ar-F). HRMS (ESI) *m/z* Calcd for C₁₀H₁₂O₃SF [M+H]⁺: 231.0491; Found: 231.0481.

Methyl 3-((4-methoxyphenyl)sulfinyl)propanoate (S2d)

*m*CPBA (2.83 g, 16.4 mmol, 1 equiv) was added portionwise to sulfide **S1d** (3.70 g, 16.4 mmol, 1 equiv) in CH₂Cl₂ (80 mL, 0.2 M) at 0 °C and stirred for 4 hr. The reaction mixture was quenched with 1 M K₂CO₃ (100 mL) and the aqueous mixture was extracted with CH₂Cl₂ (3 $\times$ 80 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure to afford sulfoxide **S2d** (3.91 g, 99%) as a yellow oil. *R*_f 0.14 (50% EtOAc in pentane). IR (film)/cm⁻¹ 2952, 2840, 1733 (C=O), 1595, 1495, 1461, 1357, 1245, 1170, 1025, 828, 753. ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.42 (m, 2H, 2 $\times$ Ar-H), 6.93–6.90 (m, 2H, 2 $\times$ Ar-H), 3.73 (s, 3H, OCH₃), 3.53 (s, 3H, OCH₃), 3.06 (ddd, $J = 13.4, 8.5, 6.8$ Hz, 1H, SCHH), 2.90–2.81 (m, 1H, SCHH), 2.67 (ddd, $J = 17.2, 8.5, 6.8$ Hz, 1H, SCH₂CHH), 2.43 (ddd, $J = 17.2, 8.5, 5.9$ Hz, 1H, SCH₂CHH). ¹³C NMR (101 MHz, CDCl₃) δ 171.4 (C=O), 161.9 (Ar-C_q), 133.5 (Ar-C_q), 125.7 (2 $\times$ Ar-C), 114.7 (2 $\times$ Ar-C), 55.4 (Ar-OCH₃), 51.9 (COOCH₃), 51.03 (SCH₂), 25.89 (SCH₂CH₂). HRMS (ESI) *m/z* Calcd for C₁₁H₁₅O₄S [M+H]⁺: 243.0691; Found: 243.0691.

Methyl 3-(pyridin-2-ylsulfinyl)propanoate (S2e)

*m*CPBA (2.62 g, 15.2 mmol, 1 equiv) was added portionwise to sulfide **S1e** (3.00 g, 15.2 mmol, 1 equiv) in CH₂Cl₂ (80 mL, 0.2 M) at 0 °C and stirred for 4 hr. The reaction mixture was quenched with 1 M K₂CO₃ (100 mL) and the aqueous mixture was extracted with CH₂Cl₂ (3 $\times$ 80 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure to afford sulfoxide **S2e** (1.97 g, 9.3 mmol, 61%) as a pale yellow oil. *R*_f 0.26 (2% MeOH in CH₂Cl₂). IR (film)/cm⁻¹ 3049, 2993, 2952, 1733 (C=O), 1576, 1424, 1356, 1238, 1174, 1084, 1036, 771. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (ddd, $J = 4.7, 1.7, 1.0$ Hz, 1H, Ar-H), 8.00–7.87 (m, 2H, 2 $\times$ Ar-H), 7.39 (ddd, $J = 7.1, 4.7, 1.7$ Hz, 1H, Ar-H), 3.65 (s, 3H, OCH₃), 3.50 (ddd, $J = 13.6, 9.3, 6.1$ Hz, 1H, SCHH), 3.20

(ddd, $J = 13.7, 9.2, 5.9$ Hz, 1H, SCHH), 2.86 (ddd, $J = 17.1, 9.2, 6.1$ Hz, 1H, SCH₂CHH), 2.45 (ddd, $J = 17.0, 9.3, 5.9$ Hz, 1H, SCH₂CHH). ¹³C NMR (101 MHz, CDCl₃) δ 171.7 (C=O), 163.9 (Ar–C_q), 150.0 (Ar–C), 138.1 (Ar–C), 124.9 (Ar–C), 120.4 (Ar–C), 52.3 (CH₃), 48.1 (SCH₂), 25.6 (SCH₂CH₂). Analytical data (NMR) in agreement with those reported in the literature.^[12]

Methyl 3-(isopropylsulfinyl)propanoate (S2f)

mCPBA (2.56 g, 14.8 mmol, 1 equiv) was added portionwise to sulfide **S1f** (2.40 g, 14.8 mmol, 1 equiv) in CH₂Cl₂ (75 mL, 0.2 M) at 0 °C and stirred for 2 hr. The reaction mixture was quenched with 1 M K₂CO₃ (100 mL) and the aqueous mixture was extracted with CH₂Cl₂ (3 × 80 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure to afford sulfoxide **S2f** (1.63 g, 62%) as a pale-yellow oil. R_f 0.11 (60% EtOAc in pentane). IR (film)/cm⁻¹ 2960, 2874, 1737 (C=O), 1439, 1364, 1234, 1040, 977, 828. ¹H NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H, OCH₃), 3.03–2.91 (m, 1H, SCH(CH₃)₂), 2.91–2.74 (m, 4H, 2 × CH₂), 1.33 (d, $J = 6.9$ Hz, 3H, 1 × CH(CH₃)₂), 1.28 (d, $J = 6.9$ Hz, 3H, 1 × CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 172.2 (C=O), 52.3 (OCH₃), 51.0 (SCH₂), 43.6 (CH(CH₃)₂), 27.4 (SCH₂CH₂), 15.9 (1 × CH(CH₃)₂), 15.0 (1 × CH(CH₃)₂). HRMS (APCI) m/z Calcd for C₇H₁₄O₃S [M+H]⁺: 179.0742; Found: 179.0736.

Methyl 3-(methanesulfinyl)propanoate (S2g)

mCPBA (4.49 g, 26.0 mmol, 1 equiv) was added portionwise to sulfide **S1g** (3.47 g, 26.0 mmol, 1 equiv) in CH₂Cl₂ (130 mL, 0.2 M) at 0 °C and stirred for 1 hr. The reaction mixture was quenched with 1 M K₂CO₃ (100 mL) and the aqueous mixture was extracted with CH₂Cl₂ (3 × 80 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure to afford sulfoxide **S2g** (3.09 g, 79%) as a colourless oil. *Note: volatility was observed under pressures of >1 mbar* IR (film)/cm⁻¹ 3000, 2956, 1730 (C=O), 1439, 1364, 1241, 1178, 1029, 943, 827. ¹H NMR (400 MHz, CDCl₃) δ 3.72 (s, 3H, OCH₃), 3.06 (ddd, $J = 13.0, 8.2, 7.1$ Hz, 1H, SCHH), 2.94–2.87 (m, 1H, SCHH), 2.87–2.80 (m, 2H, SCH₂CH₂), 2.59 (s, 3H, SCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 171.9 (C=O), 52.4 (OCH₃), 49.0 (SCH₂), 38.9 (SCH₂CH₂), 26.9 (SCH₃). Analytical data (NMR) in agreement with those reported in the literature.^[13]

NBoc-transfer

Methyl 3-(N-(tert-butoxycarbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3a)

Prepared according to a literature procedure.^[6] Magnesium oxide (3.24 g, 80.4 mmol, 4 equiv), *tert*-butyl carbamate (3.53 g, 30.2 mmol, 1.5 equiv), PhI(OAc)₂ (9.71 g, 30.2 mmol, 1.5 equiv) and Rh₂(OAc)₄ (0.22 g, 0.5 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2a** (4.20 g, 20.1 mmol, 1 equiv) in CH₂Cl₂ (200 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (50% EtOAc in pentane) afforded sulfoximine **S3a** (4.39 g, 19.4 mmol, 97%) as a white solid. mp = 83–84 °C. R_f 0.34 (50% EtOAc in pentane). IR (film)/cm⁻¹ 2978, 1740 (C=O), 1670 (C=O), 1439, 1364, 1274, 1252, 1156, 894 ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, $J = 8.4$ Hz, 2H, 2 × Ar–H), 7.37 (d, $J = 8.4$ Hz, 2H, 2 × Ar–H), 3.69 (ddd, $J = 14.3, 9.5, 6.0$ Hz, 1H, SCHH), 3.61 (s, 3H, OCH₃), 3.55 (ddd, $J = 14.2, 9.3, 6.0$ Hz, 1H, SCHH), 2.89–2.67 (m, 2H, SCH₂CH₂), 2.46 (s, 3H, Ar–CH₃), 1.37 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 170.3 (C=O), 157.7 (C=O), 145.2 (Ar–C_q), 133.8 (Ar–C_q), 130.5 (2 ×

Ar-C), 128.3 (2 × Ar-C), 80.8 (C(CH₃)₃), 52.5 (OCH₃), 51.9 (Ar-CH₃), 28.1 (C(CH₃)₃), 27.4 (CH₂), 21.8 (CH₂). HRMS (ESI) *m/z* Calcd for C₁₆H₂₅NO₅S [M+H]⁺: 342.1370; Found: 342.1375.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)propanoate (**S3b**)

Prepared according to a literature procedure.^[6] Magnesium oxide (71 mg, 1.8 mmol, 4 equiv), *tert*-butyl carbamate (77 mg, 0.66 mmol, 1.5 equiv), PhI(OAc)₂ (213 mg, 0.66 mmol, 1.5 equiv) and Rh₂(OAc)₄ (4.9 mg, 0.011 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2b** (94 mg, 0.44 mmol, 1 equiv) in CH₂Cl₂ (4.4 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (50% EtOAc in pentane) afforded sulfoximine **S3b** (114 mg, 80%) as a colourless oil. *R*_f 0.43 (50% EtOAc in pentane). IR (film)/cm⁻¹ 2987, 2940, 1738 (C=O), 1666, 1447, 1408, 1367, 1215, 1153, 1133, 872, 740. ¹H NMR (400 MHz, CDCl₃) δ 8.00–7.93 (m, 2H, 2 × Ar-H), 7.73–7.67 (m, 1H, Ar-H), 7.65–7.58 (m, 2H, 2 × Ar-H), 3.73 (ddd, *J* = 14.4, 9.4, 6.0 Hz, 1H, SCHH), 3.63 (s, 3H, OCH₃), 3.61–3.54 (m, 1H, SCHH), 2.92–2.72 (m, 2H, SCH₂CH₂), 1.37 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 170.3 (C=O), 157.5 (C=O), 137.1 (Ar-C_q), 134.1 (Ar-C), 129.8 (2 × Ar-C), 128.2 (2 × Ar-C), 80.9 (C(CH₃)₃), 52.5 (OCH₃), 51.8 (CH₂), 28.1 (C(CH₃)₃), 27.4 (CH₂). HRMS (ESI) *m/z* Calcd for C₁₅H₂₂NO₅S [M+H]⁺: 328.1219; Found: 328.1213.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-4-fluorophenylsulfonimidoyl)propanoate (**S3c**)

Prepared according to a literature procedure.^[6] Magnesium oxide (2.63 g, 65.2 mmol, 4 equiv), *tert*-butyl carbamate (2.87 g, 24.5 mmol, 1.5 equiv), PhI(OAc)₂ (7.87 g, 24.5 mmol, 1.5 equiv) and Rh₂(OAc)₄ (0.18 g, 0.4 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2c** (3.76 g, 16.3 mmol, 1 equiv) in CH₂Cl₂ (162 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (30% EtOAc in pentane) afforded sulfoximine **S3c** (3.63 g, 64%) as a viscous yellow oil. *R*_f 0.22 (30% EtOAc in pentane). IR (film)/cm⁻¹ 2978, 1737 (C=O), 1666 (C=O), 1588, 1491, 1364, 1275, 1226, 1144, 895, 835, 731. ¹H NMR (400 MHz, CDCl₃) δ 7.96–7.89 (m, 2H, 2 × Ar-H), 7.29–7.23 (m, 2H, 2 × Ar-H), 3.74–3.65 (m, 1H, SCHH), 3.60 (s, 3H, OCH₃), 3.59–3.53 (m, 1H, SCHH), 2.78 (ddd, *J* = 15.5, 8.9, 6.3 Hz, 2H, SCH₂CH₂), 1.35 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 170.1 (C=O), 166.0 (d, ¹*J*_{C-F} = 257.2 Hz, Ar-F), 157.3 (C=O), 132.7 (Ar-C_q), 131.0 (d, ³*J*_{C-F} = 9.6 Hz, 2 × Ar-C), 117.1 (d, ²*J*_{C-F} = 22.8 Hz, 2 × Ar-C), 80.9 (C(CH₃)₃), 52.4 (OCH₃), 51.8 (CH₂), 28.0 (CH₂), 27.2 (C(CH₃)₃). ¹⁹F{¹H} NMR (377 MHz, CDCl₃) δ -103.0 (1F, Ar-F). HRMS (ESI) *m/z* Calcd for C₁₅H₂₁NO₅SF [M+H]⁺: 346.1124; Found: 346.1130.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-4-methoxyphenylsulfonimidoyl)propanoate (**S3d**)

Prepared according to a literature procedure.^[6] Magnesium oxide (2.60 g, 64.4 mmol, 4 equiv), *tert*-butyl carbamate (2.84 g, 24.2 mmol, 1.5 equiv), PhI(OAc)₂ (7.80 g, 24.2 mmol, 1.5 equiv) and Rh₂(OAc)₄ (0.18 g, 0.4 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2d** (3.90 g, 16.1 mmol, 1 equiv) in CH₂Cl₂ (161 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (60% Et₂O in Hexane) afforded sulfoximine **S3d** (3.62 g, 63%) as a pale pink solid. mp = 93–95 °C. *R*_f 0.12 (60% Et₂O in Hexane). IR (film)/cm⁻¹ 2974, 1737 (C=O),

1666 (C=O), 1592, 1498, 1364, 1245, 1148, 1107, 891, 731. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.8 Hz, 2H, 2 $\times$ Ar-H), 7.02 (d, J = 8.8, 2H, 2 $\times$ Ar-H), 3.87 (s, 3H, OCH_3), 3.69–3.63 (m, 1H, SCHH), 3.59 (s, 3H, OCH_3), 3.57–3.51 (m, 1H, SCHH), 2.79–2.71 (m, 2H, SCH_2CH_2), 1.36 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3 (C=O), 164.1 (Ar-C_q), 157.7 (C=O), 130.4 (2 $\times$ Ar-C), 127.6 (Ar-C_q), 115.0 (2 $\times$ Ar-C), 80.6 ($\text{C}(\text{CH}_3)_3$), 55.9 (OCH_3), 52.4 (OCH_3), 52.0 (CH_2), 28.1 (CH_2), 27.5 ($\text{C}(\text{CH}_3)_3$). HRMS (ESI) m/z Calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_6\text{S}$ $[\text{M}+\text{H}]^+$ 358.1324; Found: 358.1340.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)pyridine-2-sulfonimidoyl)propanoate (**S3e**)

Prepared according to a literature procedure.^[6] Magnesium oxide (1.48 g, 36.8 mmol, 4 equiv), *tert*-butyl carbamate (1.62 g, 13.8 mmol, 1.5 equiv), $\text{PhI}(\text{OAc})_2$ (4.44 g, 13.8 mmol, 1.5 equiv) and $\text{Rh}_2(\text{OAc})_4$ (0.10 g, 0.2 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2e** (1.97 g, 9.2 mmol, 1 equiv) in CH_2Cl_2 (92 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (1% MeOH in CH_2Cl_2) afforded sulfoximine **S3e** (0.97 g, 64%) as a pale yellow oil. R_f 0.14 (1% MeOH in CH_2Cl_2). IR (film)/ cm^{-1} 3056, 2978, 1737 (C=O), 1700, 1662 (C=O), 1580, 1429, 1364, 1275, 1230, 1148, 895, 864, 764. ^1H NMR (400 MHz, CDCl_3) δ 8.71 (ddd, J = 4.7, 1.7, 0.8 Hz, 1H, Ar-H), 8.20 (dt, J = 7.9, 1.0 Hz, 1H, Ar-H), 7.98 (td, J = 7.8, 1.7 Hz, 1H, Ar-H), 7.55 (ddd, J = 7.7, 4.7, 1.1 Hz, 1H, Ar-H), 3.98–3.79 (m, 2H, SCH_2CH_2), 3.62 (s, 3H, OCH_3), 2.91 (ddd, J = 17.3, 8.9, 6.3 Hz, 1H, SCHH), 2.76 (ddd, J = 17.3, 9.1, 6.3 Hz, 1H, SCHH), 1.33 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3 (C=O), 157.5 (C=O), 155.8 (Ar-C_q), 150.3 (Ar-C), 138.3 (Ar-C), 127.5 (Ar-C), 124.4 (Ar-C), 80.8 ($\text{C}(\text{CH}_3)_3$), 52.4 (OCH_3), 47.8 (CH_2), 28.0 ($\text{C}(\text{CH}_3)_3$), 27.2 (CH_2). HRMS (ESI) m/z Calcd for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$ 329.1171; Found: 329.1168.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)propan-2-ylsulfonimidoyl)propanoate (**S3f**)

Prepared according to a literature procedure.^[6] Magnesium oxide (1.45 g, 36.4 mmol, 4 equiv), *tert*-butyl carbamate (1.60 g, 13.7 mmol, 1.5 equiv), $\text{PhI}(\text{OAc})_2$ (4.40 g, 13.7 mmol, 1.5 equiv) and $\text{Rh}_2(\text{OAc})_4$ (0.10 g, 0.2 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2f** (1.62 g, 9.1 mmol, 1 equiv) in CH_2Cl_2 (91 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT, the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (50% EtOAc in pentane) afforded sulfoximine **S3f** (1.15 g, 43%) as a white solid. mp = 93–94 °C. R_f 0.30 (50% EtOAc in pentane). IR (film)/ cm^{-1} 2982, 1737 (C=O), 1655 (C=O), 1364, 1279, 1249, 1156, 1092, 1054, 891, 848. ^1H NMR (400 MHz, CDCl_3) δ 3.79–3.69 (m, 4H, $\text{CH}(\text{CH}_3)_3$ and OCH_3), 3.69–3.51 (m, 2H, SCH_2), 2.98 (ddd, J = 8.1, 6.8, 4.0 Hz, 2H, SCH_2CH_2), 1.52–1.44 (m, 15H, $\text{C}(\text{CH}_3)_3$ and $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 171.2 (C=O), 158.8 (C=O), 80.5 ($\text{C}(\text{CH}_3)_3$), 54.3 ($\text{CH}(\text{CH}_3)_2$), 52.6 (OCH_3), 43.2 (CH_2), 28.3 ($\text{C}(\text{CH}_3)_3$), 27.2 (CH_2), 15.8 (1 $\times$ $\text{CH}(\text{CH}_2)_2$), 15.7 (1 $\times$ $\text{CH}(\text{CH}_2)_2$). HRMS (ESI) m/z Calcd for $\text{C}_{12}\text{H}_{24}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$ 294.1375; Found: 294.1381.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-*S*-methylsulfonimidoyl)propanoate (**S3g**)

Prepared according to a literature procedure.^[6] Magnesium oxide (2.58 g, 64 mmol, 4 equiv), *tert*-butyl carbamate (2.81 g, 24 mmol, 1.5 equiv), $\text{PhI}(\text{OAc})_2$ (7.73 g, 24 mmol,

1.5 equiv) and $\text{Rh}_2(\text{OAc})_4$ (0.18 g, 0.4 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S2g** (2.46 g, 16 mmol, 1 equiv) in CH_2Cl_2 (160 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (50% EtOAc in pentane) afforded sulfoximine **S3g** (3.39 g, 14.0 mmol, 87%) as a pale-yellow oil. R_f 0.28 (50% EtOAc in pentane). IR (film)/ cm^{-1} 2978, 2933, 1737 (C=O), 1655 (C=O), 1439, 1364, 1275, 1250, 1152, 992, 861, 790. ^1H NMR (400 MHz, CDCl_3) δ 3.78 (dd, J = 14.3, 7.1 Hz, 1H, SCHH), 3.74 (s, 3H, OCH_3), 3.65 (dt, J = 14.4, 7.2 Hz, 1H, SCHH), 3.24 (s, 3H, SCH_3), 3.10–2.86 (m, 2H, SCH_2CH_2), 1.48 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 170.9 (C=O), 158.5 (C=O), 80.9 ($\text{C}(\text{CH}_3)_3$), 52.7 (OCH_3), 49.5 (CH_2), 40.8 (CH_2), 28.3 ($\text{C}(\text{CH}_3)_3$), 27.7 (SCH_3). HRMS (ESI) m/z Calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 266.1060; Found: 266.1062.

Elimination to Sulfinamide Salt

Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((*rac*)-1a)

NaH (60% in oil, 526 mg, 13.1 mmol) was added to sulfoximine **S3a** (4.28 g, 12.5 mmol) in THF (125 mL) at 25 °C and stirred for 3 h. The reaction was quenched with MeOH (25 μL) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt (**rac**)-1a (3.46 g, quant. yield) as a white solid. The data was identical to that shown for (**S**)-1a above.

Sodium (*tert*-butoxycarbonyl)(phenylsulfinyl)amide (**S4b**)

NaH (60 % in oil, 137 mg, 3.44 mmol, 1.05 equiv) was added to a stirred solution of sulfoximine **S3b** (1.07 g, 3.27 mmol, 1.0 equiv) in anhydrous THF (33 mL, 0.1 M) at 25 °C and stirred for 1 h. MeOH (100 mL) was added and the solvent removed under reduced pressure. The resulting precipitate was washed with hexane (50 mL) and collected by filtration to afford the sulfinamide salt **S4b** as a white solid (852 mg, 99%). mp = 238–240 °C. IR (film)/ cm^{-1} 3344, 2978, 1631 (C=O), 1582, 1268, 1155, 1004, 993, 829, 747, 697. ^1H NMR (400 MHz, D_2O) δ 7.63 (dd, J = 6.7, 3.0 Hz, 2H, 2 $\times$ Ar-H), 7.54–7.47 (m, 3H, 3 $\times$ Ar-H), 1.39 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, D_2O) δ 165.9 (C=O), 146.1 (Ar- C_q), 130.9 (Ar-C), 129.0 (2 $\times$ Ar-C), 124.6 (2 $\times$ Ar-C), 79.6 ($\text{C}(\text{CH}_3)_3$), 27.7 ($\text{C}(\text{CH}_3)_3$). HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3\text{S}$ $[\text{M}]^-$: 240.0694; Found: 240.0704.

Sodium (*tert*-butoxycarbonyl)((4-fluorophenyl)sulfinyl)amide (**S4c**)

NaH (60% in oil, 442 mg, 11.0 mmol, 1.05 equiv) was added to sulfoximine **S3c** (3.60 g, 10.5 mmol, 1 equiv) in THF (100 mL) at 25 °C and stirred for 3 h. The reaction was quenched with MeOH (25 μL) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **S4c** (1.91 g, 65%) as a white solid. mp = 162–164 °C. IR (film)/ cm^{-1} 2982, 2933, 1644 (C=O), 1588, 1484, 1453, 1394, 1275, 1219, 1167, 999, 895, 831, 794, 761. ^1H NMR (400 MHz, D_2O) δ 7.72–7.62 (m, 2H, 2 $\times$ Ar-H), 7.25 (t, J = 8.9 Hz, 2H, 2 $\times$ Ar-H), 1.41 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, D_2O) δ 165.7 (C=O), 163.9 (d, $^1J_{\text{C-F}}$ = 247.8 Hz, Ar- C_q), 127.1 (d, $^3J_{\text{C-F}}$ = 9.3 Hz, 2 $\times$ Ar-C), 126.5 (Ar- C_q), 116.1 (d, $^2J_{\text{C-F}}$ = 23.5 Hz, 2 $\times$ Ar-C), 79.8 ($\text{C}(\text{CH}_3)_3$), 27.8 ($\text{C}(\text{CH}_3)_3$). ^{19}F NMR (377 MHz, CD_3OD) δ -114.03 (1F, Ar-F). HRMS (ESI) m/z Calcd for $\text{C}_{11}\text{H}_{13}\text{FNO}_3\text{S}$ $[\text{M}]^-$: 258.0600; Found: 258.0594.

Sodium (*tert*-butoxycarbonyl)((4-methoxyphenyl)sulfinyl)amide (S4d)

NaH (60% in oil, 425 mg, 10.6 mmol, 1.05 equiv) was added to sulfoximine **S3d** (3.61 g, 10.1 mmol, 1 equiv) in THF (100 mL) at 25 °C and stirred for 3 h. The reaction was quenched with MeOH (25 μ L) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **S4d** (2.69 g, 91%) as a white solid. mp = 219–220 °C. IR (film)/cm⁻¹ 2982, 2933, 1633 (C=O), 1595, 1491, 1457, 1252, 1159, 1081, 1033, 999, 832. ¹H NMR (400 MHz, D₂O) δ 7.61 (d, J = 8.9 Hz, 2H, 2 $\times$ Ar–H), 7.09 (d, J = 8.9 Hz, 2H, 2 $\times$ Ar–H), 3.86 (s, 3H, OCH₃), 1.41 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, D₂O) δ 165.6 (C=O), 160.9 (Ar–C_q), 138.3 (Ar–C_q), 126.6 (2 $\times$ Ar–C), 114.5 (2 $\times$ Ar–C), 79.6 (C(CH₃)₃), 55.5 (OCH₃), 27.8 (C(CH₃)₃). HRMS (ESI) m/z Calcd for C₁₂H₁₆NO₄S [M]⁻: 270.0800; Found: 270.0804.

Sodium (*tert*-butoxycarbonyl)(pyridin-2-ylsulfinyl)amide (S4e)

NaH (60% in oil, 370 mg, 9.2 mmol, 1.05 equiv) was added to sulfoximine **S3e** (3.02 g, 8.8 mmol, 1 equiv) in THF (90 mL) at 25 °C and stirred for 24 h. The reaction was quenched with MeOH (25 μ L) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **S4e** (2.64 g, quant) as a white solid. mp = 191–194 °C. IR (film)/cm⁻¹ 3015, 2978, 2933, 1629 (C=O), 1573, 1454, 1368, 1290, 1156, 1085, 999, 835, 798, 760. ¹H NMR (400 MHz, D₂O) δ 8.53 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H, Ar–H), 8.02 (td, J = 7.8, 1.7 Hz, 1H, Ar–H), 7.87 (dt, J = 8.0, 1.1 Hz, 1H, Ar–H), 7.52 (ddd, J = 7.7, 4.9, 1.2 Hz, 1H, Ar–H), 1.41 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, D₂O) δ 166.2 (C=O), 164.9 (Ar–C_q), 148.9 (Ar–C), 139.3 (Ar–C), 125.7 (Ar–C), 119.6 (Ar–C), 79.9 (C(CH₃)₃), 27.7 (C(CH₃)₃). HRMS (ESI) m/z Calcd for C₁₀H₁₃N₂O₃S [M]⁻: 241.0647; Found: 241.0641.

Sodium (*tert*-butoxycarbonyl)(isopropylsulfinyl)amide (S4f)

NaH (60% in oil, 164 mg, 4.1 mmol, 1.05 equiv) was added to sulfoximine **S3f** (1.15 g, 3.9 mmol, 1 equiv) in THF (40 mL) at 25 °C and stirred for 24 h. The reaction was quenched with MeOH (25 μ L) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **S4f** (1.06 g, quant.) as a white solid. mp = 199–200 °C. IR (film)/cm⁻¹ 2930, 2986, 2870, 1606 (C=O), 1464, 1297, 1256, 1170, 1074, 988, 905, 746, 664. ¹H NMR (400 MHz, CD₃OD) δ 2.51–2.44 (m, 1H, SCH), 1.39 (s, 9H, C(CH₃)₃), 1.17 (d, J = 7.0 Hz, 3H, 1 $\times$ CH(CH₃)₂), 1.11 (d, J = 7.0 Hz, 3H, 1 $\times$ CH(CH₃)₂). ¹³C NMR (101 MHz, MeOD) δ 167.2 (C=O), 78.4 (C(CH₃)₃), 54.1 (CH(CH₃)₂), 29.3 (C(CH₃)₃), 16.7 (1 $\times$ CH(CH₃)₂), 16.3 (1 $\times$ CH(CH₃)₂). HRMS (ESI) m/z Calcd for C₈H₁₆NO₃S [M]⁻: 206.0851; Found: 206.0847.

Sodium (*tert*-butoxycarbonyl)(methylsulfinyl)amide (S4g)

NaH (60% in oil, 0.34 g, 8.4 mmol, 1.05 equiv) was added to sulfoximine **S3g** (2.16 g, 8.0 mmol, 1 equiv) in THF (0.1 M) at 25 °C and stirred for 2 h. The reaction was quenched with MeOH (20 μ L) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **S4g** (1.44 g, 7.2 mmol, 90%) as a white solid. mp = 183–188 °C. IR (film)/cm⁻¹ 2974, 2930, 1610 (C=O), 1364, 1286, 1163, 999, 835, 756. ¹H NMR (400 MHz, D₂O) δ 2.40 (s,

3H, SCH₃), 1.38 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, D₂O) δ 79.4 (C(CH₃)₃), 40.6 (SCH₃), 27.7 (C(CH₃)₃). HRMS (ESI) *m/z* Calcd for C₆H₁₂NO₃S [M]⁺: 178.0538; Found: 178.0542.

Synthesis of Sulfonimidoyl Fluorides (2c-2h)

tert-Butyl (fluoro(oxo)(phenyl)-λ⁶-sulfaneylidene)carbamate (2c)

Prepared according to General Procedure A. Selectfluor (81 mg, 0.23 mmol, 1.5 equiv) was added to a solution of sulfinamide salt **S4b** (40 mg, 0.15 mmol) in DMF (0.75 mL, 0.2 M) at 0 °C and warmed to 25 °C for 18 h. H₂O (25 mL) was added and the aqueous mixture extracted with EtOAc (3 × 25 mL). The combined organic layers were dried (Na₂SO₄), filtered and the solvent removed under reduced pressure. Purification by flash column chromatography (SiO₂, 10% EtOAc in pentane) afforded sulfonimidoyl fluoride **2c** (21 mg, 54%) as a colourless oil. *R*_f 0.51 (20% EtOAc in pentane). IR (film)/cm⁻¹ 2980, 1726 (C=O), 1700, 1325, 1249, 1140, 1095, 744, 697. ¹H NMR (400 MHz, CDCl₃) δ 8.16–8.07 (m, 2H, 2 × Ar–H), 7.81–7.73 (m, 1H, Ar–H), 7.68–7.57 (m, 2H, 2 × Ar–H), 1.54 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 152.3 (d, *J* = 2.8 Hz, C=O), 135.4 (Ar–C), 133.9 (d, *J* = 21.4 Hz, Ar–C_q), 129.5 (2 × Ar–C), 128.1 (2 × Ar–C), 82.7 (C(CH₃)₃), 27.9 (C(CH₃)₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 68.54. Analytical data (NMR) in agreement with those reported in the literature.^[16]

tert-Butyl (fluoro(4-fluorophenyl)(oxo)-λ⁶-sulfaneylidene)carbamate (2d)

Prepared according to General Procedure C. Selectfluor (0.71 g, 2.0 mmol, 2 equiv) was added to a stirred solution of sulfinamide salt **S4c** (0.28 g, 1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (3 × 40 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. No further purification was required giving sulfonimidoyl fluoride **2d** (0.25 g, 88%) as a colourless viscous oil. IR (film)/cm⁻¹ 3109, 2981, 2937, 1700, 1588, 1495, 1371, 1271, 1238, 1141, 1014, 910, 839, 731, 682. ¹H NMR (400 MHz, CDCl₃) δ 8.21–8.13 (m, 2H, 2 × Ar–H), 7.32 (dd, *J* = 9.2, 7.9 Hz, 2H, 2 × Ar–H), 1.55 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 166.9 (d, ¹*J*_{C–F} = 259.9 Hz, Ar–C_q), 152.6 (C=O), 131.7 (d, ³*J*_{C–F} = 10.1 Hz, 2 × Ar–C), 131.1 (Ar–C_q), 117.5 (d, ²*J*_{C–F} = 25.5 Hz, 2 × Ar–C), 83.0 (C(CH₃)₃), 28.0 (C(CH₃)₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 70.1 (S–F), -99.5 (Ar–F).

tert-Butyl (fluoro(4-methoxyphenyl)(oxo)-λ⁶-sulfaneylidene)carbamate (2e)

Prepared according to General Procedure C. Selectfluor (0.71 g, 2.0 mmol, 2 equiv) were added to a stirred solution of sulfinamide salt **S4d** (0.29 g, 1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (3 × 40 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. No further purification was required giving sulfonimidoyl fluoride **2e** (0.29 g, quant.) as a colourless viscous oil. IR (film)/cm⁻¹ 2982, 2937, 1700, 1595, 1498, 1461, 1320, 1245, 1141, 1096, 1021, 910, 835, 805, 708. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 9.1 Hz, 2H, 2 × Ar–H), 7.04 (d, *J* = 9.1 Hz, 2H, 2 × Ar–H), 3.91 (s, 3H, OCH₃), 1.52 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ

165.3 (Ar-C_q), 152.8 (C=O), 130.8 (2 × Ar-C), 114.9 (2 × Ar-C), 110.1 (Ar-C_q), 82.6 (C(CH₃)₃), 56.1 (OCH₃), 28.1 (C(CH₃)₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 69.9.

tert-Butyl (fluoro(oxo)(pyridin-2-yl)-λ⁶-sulfaneylidene)carbamate (2f)

Prepared according to General Procedure A. Selectfluor (527 mg, 1.5 mmol, 1.5 equiv) was added to a stirred solution of sulfinamide salt **S4e** (0.26 g, 1.0 mmol, 1 equiv) in DMF (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with EtOAc (5 × 15 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by column chromatography (SiO₂, 100% CH₂Cl₂) gave sulfonimidoyl fluoride **2f** (177 mg, 68%) as an amorphous solid. R_f 0.19 (20% EtOAc in pentane). IR (film)/cm⁻¹ 3094, 2982, 2937, 1726, 1481, 1580, 1491, 1368, 1334, 1275, 1252, 1144, 1043, 991, 973, 857, 760. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 5.5 Hz, 1H, Ar-H), 8.23 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.03 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.71–7.65 (m, 1H, Ar-H), 1.52 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 150.8 (Ar-C), 138.7 (Ar-C), 129.1 (Ar-C), 124.0 (Ar-C), 83.2 (C(CH₃)₃), 27.98 (C(CH₃)₃). ¹⁹F NMR (377 MHz, CDCl₃) δ 58.0.

tert-Butyl (fluoro(isopropyl)(oxo)-λ⁶-sulfaneylidene)carbamate (2g)

Prepared according to General Procedure C. Selectfluor (0.71 g, 2.0 mmol, 2 equiv) was added to a stirred solution of sulfinamide salt **S4f** (0.26 g, 1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (5 × 15 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. No further purification was required giving sulfonimidoyl fluoride **2g** (0.19 g, 0.86 mmol, 86%) as a white solid.

Alternatively, prepared according to General Procedure A. Selectfluor (0.71 g, 2.0 mmol, 2 equiv) was added to a stirred solution of sulfinamide salt **S4f** (0.26 g, 1.0 mmol, 1 equiv) in DMF (5 mL, 0.2 M) at 0 °C and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH₂Cl₂ (10 mL). The mixture was extracted with CH₂Cl₂ (5 × 15 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated under reduced pressure. No further purification was required giving sulfonimidoyl fluoride **2g** (0.20 g, 0.90 mmol, 90%) as a white solid.

mp = 62–65 °C. IR (film)/cm⁻¹ 3440, 3388, 3340, 1737, 1670, 1621, 1488, 1454, 1379, 1215, 752. ¹H NMR (400 MHz, CDCl₃) δ 3.72 (hept, *J* = 6.8 Hz, 1H, SCH), 1.56 (m, 6H, CH(CH₃)₂), 1.50 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 153.1 (C=O), 82.6 (C(CH₃)₃), 55.4 (d, *J* = 12.6 Hz, CH(CH₃)₂), 28.1 (C(CH₃)₃), 16.7 (1 × CH(CH₃)₂), 16.5 (1 × CH(CH₃)₂). ¹⁹F NMR (377 MHz, CDCl₃) δ 41.3

tert-Butyl (fluoro(methyl)(oxo)-λ⁶-sulfaneylidene)carbamate (2h)

Prepared according to General Procedure A. Selectfluor (1.32 g, 3.74 mmol, 1.5 equiv) was added to a solution of sulfinamide salt **S4g** (500 mg, 2.49 mmol, 1 equiv) in DMF (13 mL, 0.2 M) at 0 °C and warmed to 25 °C for 18 h. H₂O (25 mL) was added and the aqueous mixture extracted with EtOAc (3 ×

25 mL). The combined organic layers were dried (MgSO_4), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **2h** (233 mg, 47%) as a colorless oil. IR (film)/ cm^{-1} 2937, 2981, 1692 (C=O), 1319, 1252, 1141, 984, 909, 857, 782. ^1H NMR (400 MHz, CDCl_3) δ 3.43 (d, $^3J_{\text{H-F}} = 4.8$ Hz, 3H, SCH₃), 1.50 (s, 9H, C(CH₃)₃). ^{13}C NMR (101 MHz, CDCl_3) δ 82.9 (C(CH₃)₃), 39.6 (d, $^2J_{\text{C-F}} = 19.5$ Hz, SCH₃) 28.0 (C(CH₃)₃). ^{19}F NMR (377 MHz, CDCl_3) δ 62.66.

Synthesis of Racemic Sulfonimidamides (3z-aj)

tert-Butyl (oxo(phenyl)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3z)

Prepared according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2c** (65 mg, 0.25 mmol, 1.0 equiv) and LiBr (43 mg, 0.50 mmol, 2.0 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 1% Et₂O in CH₂Cl₂) afforded sulfonimidamide **3z** (60 mg, 74%) as a white solid. R_f = 0.12 (1% Et₂O in CH₂Cl₂); mp = 95–97 °C. IR (film)/cm⁻¹ 2974, 2937, 2855, 1673, 1446, 1364, 1249, 1148, 928. ¹H NMR (400 MHz, CDCl₃) δ 7.88–7.82 (m, 2H, 2 $\times$ Ar–H), 7.62–7.56 (m, 1H, Ar–H), 7.55–7.49 (m, 2H, 2 $\times$ Ar–H), 3.11 (td, J = 5.0, 3.2 Hz, 4H, 2 $\times$ NCH₂), 1.63 (p, J = 5.8 Hz, 4H, 2 $\times$ NCH₂CH₂), 1.48–1.41 (m, 2H, NCH₂CH₂CH₂), 1.39 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.5 (C=O), 136.5 (Ar–C_q), 132.7 (Ar–C), 128.9 (2 $\times$ Ar–C), 127.6 (2 $\times$ Ar–C), 80.1 (C(CH₃)₃), 46.6 (2 $\times$ NCH₂), 28.0 (C(CH₃)₃), 25.2 (2 $\times$ NCH₂CH₂), 23.5 (NCH₂CH₂CH₂). HRMS (ESI) m/z : Calcd for C₁₆H₂₅N₂O₃S [M+H]⁺: 325.1586; Found: 325.1596.

tert-Butyl ((4-fluorophenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3aa)

Prepared according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2d** (69 mg, 0.25 mmol, 1 equiv) and LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **3aa** (41.5 mg, 48%) as a white solid. mp = 137–138 °C. R_f 0.48 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 3071, 2975, 2937, 2855, 1674, 1588, 1491, 1365, 1275, 1152, 1096, 932, 865, 821. ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.84 (m, 2H, 2 $\times$ Ar–H), 7.24–7.15 (m, 2H, 2 $\times$ Ar–H), 3.12 (m, 4H, 2 $\times$ NCH₂), 1.64 (p, J = 5.7 Hz, 2H, 2 $\times$ NCH₂CH₂), 1.52–1.43 (m, 2H, NCH₂CH₂CH₂), 1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 165.3 (d, ¹ J_{C-F} = 258 Hz, Ar–C_q), 156.6 (C=O), 132.9 (Ar–C_q), 130.6 (d, ³ J_{C-F} = 8.9 Hz, 2 $\times$ Ar–C), 116.4 (d, ² J_{C-F} = 22.5 Hz, 2 $\times$ Ar–C), 80.4 (C(CH₃)₃), 46.8 (2 $\times$ NCH₂), 28.2 (C(CH₃)₃), 25.4 (NCH₂CH₂), 23.7 (NCH₂CH₂CH₂). ¹⁹F NMR (377 MHz, CDCl₃) δ -105.2. HRMS (ESI) m/z Calcd for C₁₆H₂₄FN₂O₃S [M+H]⁺: 343.1492; Found: 343.1489.

tert-Butyl ((4-methoxyphenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3ab)

Prepared according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2e** (72 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **3ab** (77.8 mg, 88%) as a white solid. mp = 115–117 °C. R_f 0.45 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2975, 2937, 2851, 1670, 1595, 1495, 1454, 1364, 1245, 1148, 1092, 1047, 924, 835, 805, 723. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.9 Hz, 2H, 2 $\times$ Ar–H), 6.98 (d, J = 9.0 Hz, 2H, 2 $\times$ Ar–H), 3.87 (s, 3H, OCH₃), 3.09 (m, 4H, 2 $\times$ NCH₂), 1.63 (p, J = 5.6 Hz, 4H, 2 $\times$ NCH₂CH₂), 1.49–1.43 (m, 2H, NCH₂CH₂CH₂), 1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 163.2 (Ar–C_q), 156.9 (C=O), 130.1 (2 $\times$ Ar–C), 127.8 (Ar–C_q), 114.3 (2 $\times$ Ar–C),

80.1 ($C(CH_3)_3$), 55.8 (OCH_3), 46.7 ($2 \times NCH_2$), 28.3 ($C(CH_3)_3$), 25.4 ($2 \times NCH_2CH_2$), 23.8 ($NCH_2CH_2CH_2$). HRMS (ESI) m/z Calcd for $C_{17}H_{27}N_2O_4S$ $[M+H]^+$: 355.1692; Found: 355.1689.

***tert*-Butyl (oxo(piperidin-1-yl)(pyridin-2-yl)- λ^6 -sulfaneylidene)carbamate (3ac)**

Prepared according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2f** (65 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 5% Et_2O in CH_2Cl_2) afforded sulfonimidamide **3ac** (69 mg, 84%) as a white solid. R_f 0.14 (2% Et_2O in CH_2Cl_2). mp = 123–124 °C. IR (film)/ cm^{-1} 2974, 2940, 2855, 1700, 1364, 1278, 1151, 1051, 939. 1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.7 Hz, 1H, Ar–H), 8.08 (d, J = 7.9 Hz, 1H, Ar–H), 7.91 (t, J = 7.7 Hz, 1H, Ar–H), 7.48 (t, J = 7.6 Hz, 1H, Ar–H), 3.38–3.34 (m, 4H, $2 \times NCH_2$), 1.67–1.62 (m, 4H, $2 \times NCH_2CH_2$), 1.55–1.46 (m, 2H, $NCH_2CH_2CH_2$), 1.39 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 ($C=O$), 156.5 (Ar– C_q), 149.6 (Ar–C), 137.8 (Ar–C), 126.4 (Ar–C), 124.0 (Ar–C), 80.1 ($C(CH_3)_3$), 47.3 ($2 \times NCH_2$), 28.0 ($C(CH_3)_3$), 25.4 ($2 \times NCH_2CH_2$), 23.7 ($NCH_2CH_2CH_2$). HRMS (APCI +p) m/z : Calcd for $C_{15}H_{24}N_3O_3S$ $[M+H]^+$: 326.1533; Found: 326.1542.

***tert*-Butyl (isopropyl(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3ad)**

Prepared according to General Procedure D. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2g** (56 mg, 0.25 mmol, 1 equiv) and flame-dried LiBr (43 mg, 0.50 mmol, 2 equiv) in MeCN (0.83 mL, 0.3 M) at RT and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 20% EtOAc in pentane) afforded sulfonimidamide **3ad** (23 mg, 32%) as a white solid. R_f 0.25 (1% Et_2O in CH_2Cl_2). mp = 72–74 °C. IR (film)/ cm^{-1} 2929, 2855, 1666, 1453, 1278, 1237, 1162, 1043, 939. 1H NMR (400 MHz, $CDCl_3$) δ 3.44–3.22 (m, 5H, $CH(CH_3)_2 + 2 \times NCH_2$), 1.68–1.60 (m, 6H, $2 \times NCH_2CH_2$ and $NCH_2CH_2CH_2$), 1.49 (s, 9H, $C(CH_3)_3$), 1.42 (d, J = 6.8 Hz, 3H, $1 \times CH(CH_3)_2$), 1.32 (d, J = 6.9 Hz, 3H, $1 \times CH(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6 ($C=O$), 79.7 ($C(CH_3)_3$), 54.5 ($CHCH_3$), 47.4 ($2 \times NCH_2$), 28.2 ($C(CH_3)_3$), 25.8 ($2 \times NCH_2CH_2$), 23.9 ($NCH_2CH_2CH_2$), 16.2 ($1 \times CH(CH_3)_2$), 15.7 ($1 \times CH(CH_3)_2$). HRMS (ESI) m/z : Calcd for $C_{13}H_{27}N_2O_3S$ $[M+H]^+$: 291.1742; Found: 291.1732.

***tert*-Butyl (methyl(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3ae)**

Prepared according to General Procedure B. Piperidine (50 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2h** (50 mg, 0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2 , 50% EtOAc/pentane) afforded sulfonimidamide **3ae** (53.4 mg, 81%) as a white solid. mp = 63–64 °C. R_f 0.29 (50% EtOAc in pentane). IR (film)/ cm^{-1} 2930, 2855, 1662 ($C=O$), 1595, 1457, 1249, 1279, 1204, 1148, 1066, 981, 924, 820. 1H NMR (400 MHz, $CDCl_3$) δ 3.34–3.18 (m, 4H, $2 \times NCH_2$), 2.97 (s, 3H, SCH_3), 1.70–1.60 (m, 4H, $2 \times NCH_2CH_2$), 1.59–1.51 (m, 2H, $NCH_2CH_2CH_2$), 1.45 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 ($C=O$), 80.1 ($C(CH_3)_3$), 46.8 ($2 \times NCH_2$), 38.7 (SCH_3), 28.2 ($C(CH_3)_3$), 25.6 ($2 \times NCH_2CH_2$), 23.8 ($NCH_2CH_2CH_2$). HRMS (APCI) m/z Calcd for $C_{11}H_{22}N_2O_3S$ $[M+H]^+$: 263.1424; Found: 263.1421.

tert-Butyl (methyl(morpholino)(oxo)- λ^6 -sulfaneylidene)carbamate (3af)

Prepared according to General Procedure B. Morpholine (44 μ L, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2h** (50 mg, 0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 50% EtOAc/pentane) afforded sulfonimidamide **3af** (53.7 mg, 81%) as a white solid. mp = 96–97 °C. *R*_f 0.31 (50% EtOAc in pentane). IR (film)/cm⁻¹ 2863, 2974, 2930, 1666 (C=O), 1453, 1368, 1279, 1245, 1156, 1111, 1069, 939, 865, 790, 723. ¹H NMR (400 MHz, CDCl₃) δ 3.76 (t, *J* = 4.6 Hz, 4H, 2 $\times$ OCH₂), 3.35–3.20 (m, 4H, 2 $\times$ NCH₂), 3.01 (s, 3H, SCH₃), 1.45 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.4 (C=O), 80.3 (C(CH₃)₃), 66.2 (2 $\times$ OCH₂), 45.9 (2 $\times$ NCH₂), 37.9 (SCH₃), 27.9 (C(CH₃)₃). HRMS (ESI) *m/z* Calcd for C₁₀H₂₀N₂O₄S [M+H]⁺: 265.1230; Found: 265.1222.

tert-Butyl 4-(*N*-(tert-butoxycarbonyl)-*S*-methylsulfonimidoyl)piperazine-1-carboxylate (3ag)

Prepared according to General Procedure B. 1-Boc piperazine (93 mg, 0.50 mmol, 2.0 equiv) and triethylamine (70 μ L, 0.50 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2h** (50 mg, 0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 60% EtOAc/pentane) afforded sulfonimidamide **3ag** (66.3 mg, 73%) as a white solid. mp = 126–127 °C. *R*_f 0.19 (60% EtOAc in pentane). IR (film)/cm⁻¹ 2978, 2933, 2870, 1696 (C=O), 1457, 1420, 1368, 1282, 1249, 1163, 1125, 691, 931. ¹H NMR (400 MHz, CDCl₃) δ 3.54 (bs, 4H, 2 $\times$ NCH₂), 3.29 (tq, *J* = 12.1, 6.6, 5.8 Hz, 4H, 2 $\times$ NCH₂), 3.02 (s, 3H, SCH₃), 1.47 (s, 9H, C(CH₃)₃), 1.46 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.6 (C=O), 154.3 (C=O), 80.6 (C(CH₃)₃), 80.5 (C(CH₃)₃), 45.8 (2 $\times$ NCH₂), 38.7 (2 $\times$ NCH₂), 28.4 (C(CH₃)₃), 28.2 (C(CH₃)₃). HRMS (ESI) *m/z* Calcd for C₁₅H₂₉N₃O₅SNa [M+Na]⁺: 363.1726; Found: 363.1730.

tert-Butyl (((4-((6-methoxyquinolin-8-yl)amino)pentyl)amino)(methyl)(oxo)- λ^6 -sulfaneylidene)carbamate (3ah)

Prepared according to General Procedure B. Primaquine bisphosphate (227 mg, 0.50 mmol, 2.0 equiv) and triethylamine (210 μ L, 1.50 mmol, 6.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2h** (49 mg, 0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **3ah** (49 mg, 58%) as a 1:1 mixture of diastereomers as a colourless oil. *R*_f 0.14 (10% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2970, 2933, 1666, 1617, 1520, 1386, 1282, 1162, 977, 824, 790. ¹H NMR (400 MHz, CDCl₃) δ 8.53 (dd, *J* = 4.3, 1.7 Hz, 2H, Ar-H_{a+b}), 7.92 (dd, *J* = 8.3, 1.7 Hz, 2H, Ar-H_{a+b}), 7.31 (dd, *J* = 8.2, 4.2 Hz, 2H, Ar-H_{a+b}), 6.34 (d, *J* = 2.5 Hz, 2H, Ar-H_{a+b}), 6.28 (t, *J* = 2.4 Hz, 2H, Ar-H_{a+b}), 5.99 (d, *J* = 8.5 Hz, 2H, NH_{a+b}), 5.70 (s, 2H, NH_{a+b}), 3.89 (s, 6H, OCH_{3(a+b)}), 3.68–3.59 (m, 2H, NCH_{a+b}), 3.16 (s, 4H, NCH_{2(a+b)}), 3.11 (d, *J* = 1.6 Hz, 6H, SCH_{3(a+b)}), 1.79–1.67 (m, 8H, 2 $\times$ CH_{2(a+b)}), 1.46 (s, 18H, C(CH_{3(a+b)})₃), 1.31 (d, *J* = 6.4 Hz, 6H, CH_{3(a+b)}). ¹³C NMR (101 MHz, CDCl₃) δ 159.3 (Ar-C_{q(a+b)}), 157.7 (C=O)_{a+b}, 144.8 (Ar-C_{q(a+b)}), 144.3 (Ar-C)_{a+b}, 135.2 (Ar-C_{q(a+b)}), 134.8 (Ar-C)_{a+b}, 129.8 (Ar-C_{q(a+b)}), 121.9 (Ar-C)_{a+b}, 96.8 (Ar-C)_{a+b}, 91.7 (Ar-C)_{a+b}, 80.4 (C(CH₃)_{3(a+b)}), 55.2 (OCH_{3(a+b)}), 47.7 (NCH_{2(a+b)}), 47.6 (NCH_{2(a+b)}), 42.4 (NCH)_{a/b}, 42.3 (NCH)_{a/b}, 41.0 (SCH_{3(a+b)}).

33.6 (CH₂)_{a/b}, 33.5 (CH₂)_{a/b}, 28.1 (C(CH₃)₃)_{a+b}, 26.5 (CH₂)_{a/b}, 26.4 (CH₂)_{a/b}, 20.6 (CHCH₃)_{a+b}. HRMS (ESI) *m/z*: Calcd for C₂₁H₃₃N₄O₄S [M+H]⁺: 437.2223; Found: 437.2225.

tert-Butyl (((3-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)propyl)(methyl)amino)(methyl)(oxo)-λ⁶-sulfaneylidene)carbamate (3ai)

Prepared according to General Procedure B. Desipramine hydrochloride (151 mg, 0.50 mmol, 2.0 equiv) and triethylamine (210 μL, 1.50 mmol, 6.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2h** (49 mg, 0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under

reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **3ai** (79.2 mg, 71%) as a colourless oil. *R_f* 0.35 (50% EtOAc in pentane). IR (film)/cm⁻¹ 3060, 2974, 2930, 1666 (C=O) 1595, 1487, 1274, 1244, 1156, 910, 862, 731. ¹H NMR (400 MHz, CDCl₃) δ 7.15–7.09 (m 6H, 6 × Ar–H), 6.96–6.87 (m, 2H, 2 × Ar–H), 3.81 (t, *J* = 6.5 Hz, 2H, NCH₂), 3.36 (dt, *J* = 14.2, 7.2 Hz, 1H, NCHH), 3.24 (dt, *J* = 14.1, 7.1 Hz, 1H, NCHH), 3.17 (s, 4H, 2 × Ar–CH₂), 2.81 (s, 3H, SCH₃), 2.77 (s, 3H, NCH₃), 1.86 (dtd, *J* = 8.4, 7.4, 6.7, 4.2 Hz, 2H, NCH₂CH₂), 1.46 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 156.8 (C=O), 148.0 (2 × Ar–C_q), 134.4 (2 × Ar–C_q), 130.1 (2 × Ar–C), 126.6 (2 × Ar–C), 122.9 (2 × Ar–C), 119.9 (2 × Ar–C), 80.2 (C(CH₃)₃), 47.9 (NCH₂), 47.5 (NCH₂), 39.5 (SCH₃), 34.9 (NCH₃), 32.3 (2 × Ar–CH₂), 28.3 (C(CH₃)₃), 26.3 (NCH₂CH₂). HRMS (ESI) *m/z* Calcd for C₂₄H₃₃N₃O₃S [M+H]⁺: 444.2330; Found: 444.2321.

tert-Butyl ((4-(2-chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)piperazin-1-yl)(methyl)(oxo)-λ⁶-sulfaneylidene)carbamate (3aj)

Prepared according to General Procedure B. Amoxipine (157 mg, 0.50 mmol, 2.0 equiv) and triethylamine (70 μL, 1.00 mmol, 2.0 equiv) were added to a stirred solution of sulfonimidoyl fluoride **2h** (49 mg, 0.25 mmol, 1 equiv) in THF (0.83 mL, 0.3 M) at RT and warmed to 80 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 5% Et₂O in CH₂Cl₂) afforded sulfonimidamide **3aj**

(45 mg, 45%) as a colourless oil. *R_f* 0.26 (5% Et₂O in CH₂Cl₂). IR (film)/cm⁻¹ 2978, 2929, 1669, 1602, 1558, 1472, 1282, 1252, 1162, 954. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar–H), 7.31 (d, *J* = 2.6 Hz, 1H, Ar–H), 7.20 (d, *J* = 8.6 Hz, 1H, Ar–H), 7.17–7.08 (m, 3H, 3 × Ar–H), 7.06–7.00 (m, 1H, Ar–H), 3.65 (s, 4H, 2 × NCH₂), 3.45 (s, 4H, 2 × NCH₂), 3.06 (s, 3H, SCH₃), 1.49 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.3 (Ar–C_q), 158.4 (Ar–C_q), 156.5 (C=O), 151.7 (Ar–C_q), 139.6 (Ar–C_q), 132.9 (Ar–C), 130.5 (Ar–C_q), 128.7 (Ar–C), 127.1 (Ar–C), 125.8 (Ar–C), 125.1 (Ar–C), 124.6 (Ar–C_q), 122.8 (Ar–C), 120.1 (Ar–C), 80.5 (C(CH₃)₃), 47.1 (2 × NCH₂), 45.5 (2 × NCH₂), 38.4 (SCH₃), 28.1 (C(CH₃)₃). HRMS (ESI) *m/z*: Calcd for C₂₃H₂₈N₄O₄SCl [M+H]⁺: 491.1520; Found: 491.1511.

Experimental Procedures for NBoc-deprotection

(*R*)-1-(4-Methylphenylsulfonimidoyl)piperidine ((*R*)-11)

Trifluoroacetic acid (46 μ L, 0.6 mmol, 10 equiv) was added to sulfonimidamide (**(*R*)-3a**) (20 mg, 0.06 mmol, 1 equiv) in CH_2Cl_2 (0.3 mL, 0.2 M) at 0 $^\circ\text{C}$, and stirred at RT for 4 h. The reaction mixture was quenched with NaHCO_3 (5 mL), water (10 mL) was added and then diluted with CH_2Cl_2 (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3×20 mL), and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 , 30% EtOAc in pentane) afforded NH-sulfonimidamide (**(*R*)-11**) (12.5 mg, 89%, >99% ee) as a white solid. mp = 83–84 $^\circ\text{C}$. R_f 0.10 (30% EtOAc in pentane). IR (film)/ cm^{-1} 3280, 2937, 2851, 1595, 1491, 1454, 1252, 1133, 1072, 1043, 977, 917, 816, 701. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 8.4 Hz, 2H, $2 \times \text{Ar-H}$), 7.29 (d, J = 8.1 Hz, 2H, $2 \times \text{Ar-H}$), 2.96 (t, J = 5.5 Hz, 4H, $2 \times \text{NCH}_2$), 2.42 (s, 3H, Ar- CH_3), 1.66–1.56 (m, 4H, $2 \times \text{NCH}_2\text{CH}_2$), 1.41–1.31 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 142.9 (Ar- C_q), 133.3 (Ar- C_q), 129.4 ($2 \times \text{Ar-C}$), 128.2 ($2 \times \text{Ar-C}$), 48.1 ($2 \times \text{NCH}_2$), 25.8 ($2 \times \text{NCH}_2\text{CH}_2$), 23.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 21.6 (Ar- CH_3). Characterisation data (NMR) in accordance with literature.^[17] $[\alpha]^{23}_D = -8$ (c 0.5, CHCl_3). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min $^{-1}$, 35 $^\circ\text{C}$, UV detection wavelength: 250 nm. (**(*R*)-11** retention time: 44 min.

Synthesis of racemic sample for HPLC analysis prepared according to the above procedure to afford sulfonimidamide (**(rac)-11**) as a white solid with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min $^{-1}$, 35 $^\circ\text{C}$, UV detection wavelength: 250 nm, (**(rac)-11** retention times: 28 & 44 min.

(*R*)-*N*-Cyclobutyl-4-methylbenzenesulfonimidamide ((*R*)-12)

Trifluoroacetic acid (54 μ L, 0.8 mmol, 10 equiv) was added to sulfonimidamide (**(*R*)-3f**) (23 mg, 0.08 mmol, 1 equiv) in CH_2Cl_2 (700 μ L, 0.1 M) at 0 $^\circ\text{C}$, and stirred at RT for 4 h. The reaction mixture was quenched with NaHCO_3 (5 mL), water (10 mL) was added and then diluted with CH_2Cl_2 (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3×20 mL), and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 , 20% Et $_2\text{O}$ in CH_2Cl_2) afforded NH-sulfonimidamide (**(*R*)-12**) (13 mg, 84%, 98% ee) as a colourless oil. R_f 0.19 (20% Et $_2\text{O}$ in CH_2Cl_2). IR (film)/ cm^{-1} 3254, 2974, 2944, 2870, 1446, 1244, 1133, 1010, 816. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.4 Hz, 2H, $2 \times \text{Ar-H}$), 7.28 (d, J = 8.0 Hz, 2H, $2 \times \text{Ar-H}$), 3.84–3.74 (m, 1H, NCH), 2.42 (s, 3H, Ar CH_3), 2.15–1.97 (m, 2H, $2 \times \text{NCHCHH}$), 1.79–1.51 (m, 4H, $2 \times \text{NCHCHH} + \text{CH}_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 142.8 (Ar- C_q), 139.0 (Ar- C_q), 129.5 ($2 \times \text{Ar-C}$), 127.2 ($2 \times \text{Ar-C}$), 48.6 (NCH), 31.9 ($1 \times \text{NCHCH}_2$), 31.8 ($1 \times \text{NCHCH}_2$), 21.4 (Ar- CH_3), 15.0 ($\text{NCHCH}_2\text{CH}_2$). HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{17}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 225.1062; Found: 225.1062. $[\alpha]^{23}_D = -46$ (c 0.13, CHCl_3). HPLC Conditions: Chiralpak IA column, 85:15 *n*hexane:*i*PrOH, flow rate: 1 mL min $^{-1}$, 35 $^\circ\text{C}$, UV detection wavelength: 250 nm. (**(*R*)-12** retention time: 11 min.

Synthesis of racemic sample for HPLC analysis prepared according to the above procedure to afford sulfonimidamide (**(rac)-12**) as a colourless oil with characterisation data in accordance with the above. HPLC

Conditions: Chiralpak IA column, 85:15 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm, (***rac***)-**12** retention times: 11 & 16 min.

X-Ray Crystallography Supplementary Data

Manuscript: Synthesis of Highly Enantioenriched Sulfonimidamides by Stereospecific SuFEx Reaction of Sulfonimidoyl Fluorides with Amines

Authors: Stephanie Greed, Edward L. Briggs, Fahima I.M. Idris, Andrew J.P. White, Ulrich Lücking, and James A. Bull

The X-ray crystal structure of (*R*)-3h

Crystal data for (*R*)-3h: C₁₄H₂₂N₂O₃S, *M* = 298.39, triclinic, *P*1 (no. 1), *a* = 6.2313(4), *b* = 8.2793(5), *c* = 8.8044(6) Å, α = 117.174(7), β = 100.944(5), γ = 93.245(5)°, *V* = 391.37(5) Å³, *Z* = 1, *D*_c = 1.266 g cm⁻³, μ (Cu-K α) = 1.917 mm⁻¹, *T* = 173 K, colourless blocks, Agilent Xcalibur PX Ultra A diffractometer; 2737 independent measured reflections (*R*_{int} = 0.0246), *F*² refinement,^[X1,X2] *R*₁(obs) = 0.0300, *wR*₂(all) = 0.0798, 2681 independent observed absorption-corrected reflections [*|F*_o| > 4 σ (*|F*_o)], completeness to θ_{full} (67.7°) = 99.9%, 188 parameters. The absolute structure of (*R*)-3h was unambiguously determined by use of the Flack parameter [*x* = -0.035(17)]. CCDC 1991431.

References

- [X1] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.
[X2] SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

Figures

Figure S 2: The crystal structure of (*R*)-3h (50% probability ellipsoids).

References

- [1] C. Worch, I. Atodiresei, G. Raabe, C. Bolm, *Chem. Eur. J.* **2010**, *16*, 677–683.
- [2] M. Steurer, C. Bolm, *J. Org. Chem.* **2010**, *75*, 3301–3310.
- [3] C. B. W. Phippen, J. K. Beattie, C. S. P. McErlean, *Chem. Commun.* **2010**, *46*, 8234–8236.
- [4] C. Drago, E.-J. Walker, L. Caggiano, R. F. W. Jackson, *Org. Synth.* **2009**, *86*, 121–129.
- [5] C. Drago, L. Caggiano, R. F. W. Jackson, *Angew. Chem. Int. Ed.* **2005**, *44*, 7221–7223.
- [6] M. Zenzola, R. Doran, R. Luisi, J. A. Bull, *J. Org. Chem.* **2015**, *80*, 6391–6399.
- [7] N. Pemberton, H. Graden, E. Evertsson, E. Bratt, M. Lepistö, P. Johannesson, P. H. Svensson, *ACS Med. Chem. Lett.* **2012**, *3*, 574–578.
- [8] C. H. Rosa, M. L. B. Peixoto, G. R. Rosa, B. Godoi, F. Z. Galetto, M. G. M. D'Oca, M. Godoi, *Tetrahedron Lett.* **2017**, *58*, 3777–3781.
- [9] J. Li, X. Bi, H. Wang, J. Xiao, *Phosphorus, Sulfur Silicon Relat. Elem.* **2014**, *189*, 1873–1881.
- [10] W. Guo, G. Lv, J. Chen, W. Gao, J. Ding, H. Wu, *Tetrahedron* **2010**, *66*, 2297–2300.
- [11] F. Rajabi, S. Razavi, R. Luque, *Green Chem.* **2010**, *12*, 786–789.
- [12] L. Zong, X. Ban, C. W. Kee, C.-H. Tan, *Angew. Chem. Int. Ed.* **2014**, *53*, 11849–11853.
- [13] N. P. Crouch, R. M. Adlington, J. E. Baldwin, M.-H. Lee, C. H. MacKinnon, *Tetrahedron* **1997**, *53*, 6993–7010.
- [14] H. Cui, W. Wei, D. Yang, Y. Zhang, H. Zhao, L. Wang, H. Wang, *Green Chem.* **2017**, *19*, 3520–3524.
- [15] H. L. Yue, M. Klussmann, *Synlett* **2016**, *27*, 2505–2509.
- [16] H. Mukherjee, J. Debreczeni, J. Breed, S. Tentarelli, B. Aquila, J. E. Dowling, A. Whitty, N. P. Grimster, *Org. Biomol. Chem.* **2017**, *15*, 9685–9695.
- [17] F. Izzo, M. Schäfer, R. Stockman, U. Lücking, *Chem. Eur. J.* **2017**, *23*, 15189–15193.

^1H and ^{13}C -NMR Spectra

***tert*-Butyl (*p*-tolylsulfinyl)carbamate ((*S*)-5)**

Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-1a)

***tert*-Butyl (fluoro(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-2a)**

tert-Butyl (oxo(piperidin-1-yl)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3a)

tert-Butyl (R)-((butylamino)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3b)

tert-Butyl (R)-((benzylamino)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3c)

tert-Butyl (R)-((allylamino)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3d)

***tert*-Butyl (*R*)-(((cyclopropylmethyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3e)**

tert-Butyl (R)-((cyclobutylamino)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3f)

***(R)*-3g**

¹H NMR (400 MHz, CDCl₃)

Chemical structure of ***(R)*-3g** is shown above the spectrum:

CC1=CC=C(C=C1)S(=O)(=O)N(C2CCCCC2)C3CCCCC3

¹H NMR spectrum (400 MHz, CDCl₃) data:

Chemical Shift (ppm)	Integration
7.84, 7.82	1.97
7.31, 7.29	2.01
6.04	1.05
1.16, 2.96, 1.19, 1.12, 2.65, 8.80, 2.00, 3.30	1.16, 2.96, 1.19, 1.12, 2.65, 8.80, 2.00, 3.30

tert-Butyl (*R*)-((dimethylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3h)

tert-Butyl (*R*)-((benzyl(methyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3i)

tert-Butyl (R)-((3,4-dihydroisoquinolin-2(1H)-yl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3j)

tert-Butyl (R)-(oxo(pyrrolidin-1-yl)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3k)

tert-Butyl (R)-(morpholino(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3I)

tert-Butyl (R)-(oxo(4-oxopiperidin-1-yl)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3m)

tert-Butyl (R)-((4,4-difluoropiperidin-1-yl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3n)

tert-Butyl (R)-((4-hydroxypiperidin-1-yl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3o)

***tert*-Butyl (*R*)-4-(*N*-(*tert*-butoxycarbonyl)-4-methylphenylsulfonimidoyl)piperazine-1-carboxylate
(*R*)-3p**

tert-Butyl (R)-(oxo(4-(pyrimidin-2-yl)piperazin-1-yl)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3q)

tert-Butyl (R)-((4-(6-fluorobenzo[d]isoxazol-3-yl)piperidin-1-yl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3r)

tert-Butyl (*R*)-(((3-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)propyl)(methyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3s)

tert-Butyl ((R)-oxo(((S)-1-phenylethyl)amino)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3t)

tert-Butyl ((R)-oxo((R)-1-phenylethyl)amino)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3u)

Methyl 3-((4-bromophenyl)thio)propanoate (7)

Methyl 3-((4-bromophenyl)sulfinyl)propanoate (8)

Methyl 3-(4-bromo-*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)propanoate ((*S*)-9)

Sodium ((4-bromophenyl)sulfinyl)(*tert*-butoxycarbonyl)amide ((S)-1b)

tert-Butyl ((4-bromophenyl)fluoro(oxo)- λ^6 -sulfaneylidene)carbamate ((*R*)-2b)

tert-Butyl (R)-((benzylamino)(4-bromophenyl)(oxo)- λ^6 -sulfaneylidene)carbamate ((R)-3v)

tert-Butyl (R)-((allylamino)(4-bromophenyl)(oxo)- λ^6 -sulfaneylidene)carbamate ((R)-3w)

tert-Butyl ((4-bromophenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3x)

***tert*-Butyl ((*R*)-(4-bromophenyl)(methyl((*S*)-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)amino)(oxo)- λ^6 -sulfaneylidene)carbamate ((*R*)-3y)**

tert-Butyl (R)-([1,1'-biphenyl]-4-yl(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate ((R)-10)

Methyl 3-(tolylthio)propanoate (S1a)

Methyl 3-(phenylthio)propanoate (S1b)

Methyl 3-((4-fluorophenyl)thio)propanoate (S1c)

Methyl 3-((4-methoxyphenyl)thio)propanoate (S1d)

Methyl 3-(pyridin-2-ylthio)propanoate (S1e)

Methyl 3-(isopropylthio)propanoate (S1f)

Methyl 3-(methylthio)propanoate (S1g)

Methyl 3-(*p*-tolylsulfinyl)propanoate (S2a)

Methyl 3-(phenylsulfinyl)propanoate (S2b)

Methyl 3-((4-fluorophenyl)sulfinyl)propanoate (S2c)

Methyl 3-((4-methoxyphenyl)sulfinyl)propanoate (S2d)

Methyl 3-(pyridin-2-ylsulfinyl)propanoate (S2e)

Methyl 3-(isopropylsulfinyl)propanoate (S2f)

Methyl 3-(methanesulfinyl)propanoate (S2g)

Methyl 3-(N-(tert-butoxycarbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3a)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)propanoate (S3b)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-4-fluorophenylsulfonimidoyl)propanoate (S3c)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-4-methoxyphenylsulfonimidoyl)propanoate (S3d)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)pyridine-2-sulfonimidoyl)propanoate (S3e)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)propan-2-ylsulfonimidoyl)propanoate (S3f)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-*S*-methylsulfonyl)propanoate (S3g)

Sodium (*tert*-butoxycarbonyl)(phenylsulfinyl)amide (S4b)

Sodium (*tert*-butoxycarbonyl)((4-fluorophenyl)sulfinyl)amide S4c

Sodium (*tert*-butoxycarbonyl)((4-methoxyphenyl)sulfinyl)amide (S4d)

Sodium (*tert*-butoxycarbonyl)(pyridin-2-ylsulfinyl)amide (S4e)

Sodium (*tert*-butoxycarbonyl)(isopropylsulfinyl)amide (S4f)

Sodium (*tert*-butoxycarbonyl)(methylsulfinyl)amide (S4g)

tert-Butyl (fluoro(oxo)(phenyl)- λ^6 -sulfaneylidene)carbamate (2c)

***tert*-Butyl (fluoro(4-fluorophenyl)(oxo)- λ^6 -sulfaneylidene)carbamate (2d)**

***tert*-Butyl (fluoro(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)carbamate (2e)**

tert-Butyl (fluoro(oxo)(pyridin-2-yl)- λ^6 -sulfaneylidene)carbamate (2f)

tert-Butyl (fluoro(isopropyl)(oxo)- λ^6 -sulfaneylidene)carbamate (2g)

tert-Butyl (fluoro(methyl)(oxo)- λ^6 -sulfaneylidene)carbamate (2h)

tert-Butyl (oxo(phenyl)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3z)

***tert*-Butyl ((4-fluorophenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3aa)**

tert-Butyl ((4-methoxyphenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3ab)

***tert*-Butyl (oxo(piperidin-1-yl)(pyridin-2-yl)- λ^6 -sulfaneylidene)carbamate (3ac)**

tert-Butyl (isopropyl(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3ad)

tert-Butyl (methyl(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate (3ae)

tert-Butyl (methyl(morpholino)(oxo)- λ^6 -sulfaneylidene)carbamate (3af)

***tert*-Butyl 4-(*N*-(*tert*-butoxycarbonyl)-*S*-methylsulfonimidoyl)piperazine-1-carboxylate (3ag)**

tert-Butyl (((4-((6-methoxyquinolin-8-yl)amino)pentyl)amino)(methyl)(oxo)- λ^6 -sulfaneylidene)carbamate (3ah)

***tert*-Butyl (((3-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)propyl)(methyl)amino)(methyl)(oxo)- λ^6 -sulfaneylidene)carbamate (3ai)**

tert-Butyl ((4-(2-chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)piperazin-1-yl)(methyl)(oxo)- λ^6 -sulfaneylidene)carbamate (3aj)

(R)-1-(4-Methylphenylsulfonimidoyl)piperidine ((R)-11)

(R)-N'-Cyclobutyl-4-methylbenzenesulfonimidamide ((R)-12)

HPLC Data

HPLC Data

***tert*-Butyl (*p*-tolylsulfinyl)carbamate ((*S*)-5)**

Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-5

Signal 1: DAD1 A, Sig=250, 10 Ref=360, 100

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.808	BB	0.8231	1568.53638	27.10690	49.7337
2	24.483	BB	0.9969	1585.33215	22.31392	50.2663

Total s : 3153.86853 49.42082

(*S*)-5

$[\alpha]_D^{21} = +80$ (c 0.1, CHCl₃).

Signal 1: DAD1 A, Sig=250, 10 Ref=360, 100

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.068	BB	0.9253	1221.97766	18.72633	100.0000

Total s : 1221.97766 18.72633

ee > 99%

***tert*-Butyl (fluoro(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-2a)**

Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-2a

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.074	BB	0.2726	1481.25183	83.62629	49.9140
2	14.306	BB	0.3176	1486.35461	71.18559	50.0860

Totals : 2967.60645 154.81188

(*R*)-2a

$[\alpha]_D^{21} = +9$ (c 5.0, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.294	BV	0.2625	78.58254	4.71449	0.3559
2	14.000	VB	0.3970	2.20035e4	830.72552	99.6441

Totals : 2.20821e4 835.44002

ee > 99%

***tert*-Butyl (*R*)-(oxo(piperidin-1-yl)(*p*-tolyl- λ^6 -sulfaneylidene)carbamate ((*R*)-3a)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm.

(*rac*)-(3a)

Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.698	BB	0.3925	130.26352	4.92661	50.1539
2	21.711	BB	0.4862	129.46416	3.89039	49.8461

Totals : 259.72768 8.81699

(*R*)-(3a)

$[\alpha]_D^{21} = -18$ (c 0.5, CHCl₃).

Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.465	MM	0.3392	5.06887	2.49059e-1	0.2228
2	21.196	BB	0.5707	2269.86426	59.28167	99.7772

Totals : 2274.93313 59.53072

ee > 99%

***tert*-Butyl (*R*)-((butylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3b)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm.

(*rac*)-(3b)

Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.304	BB	0.5260	887.74835	25.88978	49.9281
2	23.101	BB	0.5633	890.30682	24.08071	50.0719

Totals : 1778.05518 49.97049

(*R*)-(3b)

$[\alpha]^{21}_D = +42$ (c 1.0, CHCl₃).

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.768	BB	0.5266	1584.74768	45.46916	99.3530
2	23.529	MM	0.4161	10.32006	4.13375e-1	0.6470

Totals : 1595.06774 45.88253

ee = 99%

***tert*-Butyl (*R*)-((benzylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3c)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3c)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.900	BB	1.0203	1.27760e4	184.40756	49.7300
2	41.966	BB	1.3526	1.29147e4	131.17830	50.2700

Totals : 2.56908e4 315.58586

(*R*)-(3c)

$[\alpha]^{23}_D = +88$ (c 0.5, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.971	MM	0.8366	33.02581	6.57922e-1	0.6327
2	41.234	BB	1.1786	5186.88770	65.16691	99.3673

Totals : 5219.91351 65.82483

ee = 99%

***tert*-Butyl (*R*)-((allylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3d)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 270 nm.

(*rac*)-(3d)

Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.167	BB	0.5364	338.05084	9.03798	50.3426
2	25.526	BB	0.5708	333.45023	8.09127	49.6574

Totals : 671.50107 17.12926

(*R*)-(3d)

$[\alpha]_D^{23} = +40$ (c 0.5, CHCl₃).

Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.111	BB	0.5258	684.38165	18.49214	99.1628
2	25.722	MM	0.5570	5.77836	1.72910e-1	0.8372

Totals : 690.16001 18.66505

ee = 98%

***tert*-Butyl (*R*)-(((cyclopropylmethyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3e)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 280 nm.

(rac)-(3e)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.929	BB	0.6237	1115.89270	26.91534	50.0552
2	27.963	BB	0.6729	1113.43213	24.46601	49.9448

Totals : 2229.32483 51.38135

(*R*)-(3e)

$[\alpha]^{21}_D = +29$ (c 1.0, CHCl₃).

Signal 5: DAD1 E, Sig=280,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.715	BB	0.7456	2133.07471	39.90491	97.3256
2	28.469	MM	0.6996	58.61450	1.39648	2.6744

ee = 95%

***tert*-Butyl (*R*)-((cyclobutylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3f)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm.

(*rac*)-(3f)

Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.322	BB	0.3697	307.63245	12.64949	50.1173
2	18.378	BB	0.4523	306.19284	10.25480	49.8827

Totals : 613.82529 22.90428

(*R*)-(3f)

$[\alpha]_D^{21} = +48$ (c 0.8, CHCl₃).

Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.256	BB	0.4059	1500.06885	56.10583	99.5933
2	18.350	MM	0.3520	6.12579	2.90021e-1	0.4067

Totals : 1506.19464 56.39585

ee > 99%

***tert*-Butyl (*R*)-((cyclohexylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3g)**

Conditions: Chiralpak IF column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm.

(*rac*)-(3g)

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.708	BB	0.4301	213.50233	7.23872	50.5042
2	24.406	BB	0.4724	209.23958	5.67202	49.4958

Totals : 422.74191 12.91074

(*R*)-(3g)

$[\alpha]_D^{21} = +42$ (c 0.5, CHCl₃).

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.616	MP	0.4110	10.25777	4.15939e-1	1.2543
2	24.202	BB	0.5475	807.56189	21.34123	98.7457

Totals : 817.81966 21.75717

ee = 97%

***tert*-Butyl (*R*)-((dimethylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3h)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3h)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.967	BB	0.5220	1830.77698	52.61246	49.8946
2	24.693	BB	0.5691	1838.50952	48.41205	50.1054

Totals : 3669.28650 101.02451

(*R*)-(3h)

$[\alpha]_D^{21} = -28$ (c 1.0, CHCl₃)

Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.430	BB	0.4528	167.01021	5.34144	2.1583
2	24.730	BB	0.6141	7570.95605	180.96532	97.8417

Totals : 7737.96626 186.30676

ee = 96%

***tert*-Butyl (*R*)-((benzyl(methyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3i)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3i) **(*R*)-(3i)**

$[\alpha]_D^{23} = -12$ (c 1, CHCl₃).

ee = 99%

***tert*-Butyl (*R*)-((3,4-dihydroisoquinolin-2(1*H*)-yl)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3j)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3j)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.098	BB	0.6530	7382.16113	170.54291	50.0445
2	32.947	BB	0.8578	7369.01855	126.83379	49.9555

Totals : 1.47512e4 297.37669

(*R*)-(3j)

$[\alpha]_D^{23} = 0$ (c 1.0, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.869	BB	0.5728	270.96118	6.65785	1.4398
2	33.283	BB	0.9275	1.85491e4	293.42993	98.5602

Totals : 1.88200e4 300.08778

ee = 97%

***tert*-Butyl (*R*)-(oxo(pyrrolidin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3k)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 260 nm.

(*rac*)-(3k)

Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.580	BV	0.4467	2058.69604	70.07999	49.6798
2	19.953	VB	0.4841	2085.23169	65.02983	50.3202

Totals : 4143.92773 135.10983

(*R*)-(3k)

$[\alpha]_D^{21} = -9$ (c 1.0, CHCl₃).

Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.002	BB	0.3669	74.11945	2.85495	1.6924
2	20.045	BB	0.4906	4305.41699	131.28296	98.3076

Totals : 4379.53644 134.13790

ee = 97%

***tert*-Butyl (*R*)-(morpholino(oxo(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3I)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3I)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.298	BB	0.5799	373.90707	9.28350	49.8459
2	31.147	BB	0.6895	376.21826	7.78965	50.1541

Totals : 750.12534 17.07315

(*R*)-(3I)

$[\alpha]^{23}_D = -11$ (c 1.0, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.638	MM	0.4908	11.85784	4.02664e-1	0.2452
2	31.015	BB	0.7408	4824.73779	97.24724	99.7548

Totals : 4836.59563 97.64990

ee > 99%

***tert*-Butyl (*R*)-(oxo(4-oxopiperidin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3m)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm.

(*rac*)-(3m)

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.303	BB	0.9859	1279.99353	16.16244	53.3272
2	43.695	BB	1.0028	1120.27039	13.38072	46.6728

Totals : 2400.26392 29.54317

(*R*)-(3m)

$[\alpha]^{23}_D = 0$ (c 0.2, CHCl₃).

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.238	MM	0.9614	74.80834	1.29684	1.4650
2	42.851	BB	1.3254	5031.48389	49.26838	98.5350

Totals : 5106.29223 50.56522

ee = 97%

***tert*-Butyl (*R*)-((4,4-difluoropiperidin-1-yl)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3n)**

Conditions: Chiralpak IB column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3n)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.193	BB	0.2356	460.88104	29.60700	49.3914
2	12.269	BB	0.2806	472.23984	25.20912	50.6086

Totals : 933.12088 54.81612

(*R*)-(3n)

$[\alpha]^{23}_D = -6$ (c 1, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.157	BB	0.2463	2060.77588	126.33929	98.9847
2	12.375	BB	0.2460	21.13705	1.08157	1.0153

Totals : 2081.91293 127.42087

ee = 98%

***tert*-Butyl (*R*)-((4-hydroxypiperidin-1-yl)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3o)**

Conditions: Chiralpak IA column, 85:15 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm.

(*rac*)-(3o)

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.809	BB	0.3085	297.77713	14.44385	50.0692
2	13.226	BB	0.3574	296.95435	12.05329	49.9308

Totals : 594.73148 26.49714

(*R*)-(3o)

$[\alpha]^{23}_D = -4$ (c 1, CHCl₃).

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.851	MM	0.3270	6.67761	3.40398e-1	0.4953
2	13.166	BB	0.3669	1341.47754	55.71297	99.5047

Totals : 1348.15515 56.05337

ee = 99%

***tert*-Butyl (*R*)-4-(*N*-(*tert*-butoxycarbonyl)-4-methylphenylsulfonimidoyl)piperazine-1-carboxylate ((*R*)-3p)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3p)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.005	BB	0.7199	898.88306	18.66262	49.8027
2	29.963	BB	0.7678	906.00513	17.16478	50.1973

Totals : 1804.88818 35.82741

(*R*)-(3p)

$[\alpha]_D^{21} = -6$ (c 1.0, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.188	MM	0.7131	29.50145	6.89538e-1	1.6876
2	29.957	BB	0.8091	1718.63159	32.28175	98.3124

Totals : 1748.13304 32.97128

ee = 97%

***tert*-Butyl (*R*)-(oxo(4-(pyrimidin-2-yl)piperazin-1-yl)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3q)**

Conditions: Chiralpak IB column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3q)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.129	BB	1.2832	1748.99963	16.28195	50.8502
2	37.599	BB	1.4582	1690.51697	13.71306	49.1498

Totals : 3439.51660 29.99501

(*R*)-(3q)

$[\alpha]_D^{23} = 0$ (c 1, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.712	BB	1.4899	5410.35449	47.17966	99.5737
2	39.058	MM	1.3907	23.16299	2.77596e-1	0.4263

Totals : 5433.51748 47.45725

ee > 99%

***tert*-Butyl (*R*)-((4-(6-fluorobenzo[d]isoxazol-3-yl)piperidin-1-yl)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3r)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-(3r)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.011	BB	0.6102	1826.53259	45.32460	50.1203
2	36.371	BB	0.9385	1817.76233	27.38116	49.8797

Totals : 3644.29492 72.70576

(*R*)-(3r)

$[\alpha]_D^{23} = +20$ (c 0.5, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.255	MM	0.5510	7.72514	2.33659e-1	0.8118
2	36.375	BB	0.8939	943.83289	14.60569	99.1882

Totals : 951.55803 14.83935

ee = 98%

tert-Butyl (R)-(((3-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)propyl)(methyl)amino)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)carbamate ((R)-3s)

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 290 nm.

(rac)-(3s)

Signal 8: DAD1 H, Sig=290,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.781	BB	0.5561	2224.52295	61.19504	50.0466
2	29.482	BB	0.8284	2220.38013	39.46446	49.9534

Totals : 4444.90308 100.65950

(R)-(3s)

$[\alpha]_D^{23} = +8$ (c 1.0, CHCl₃).

Signal 8: DAD1 H, Sig=290,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.150	MM	0.5800	5.17081	1.48593e-1	1.1202
2	30.390	BB	0.7305	456.44647	8.36694	98.8798

Totals : 461.61729 8.51553

ee = 98%

Methyl 3-((4-bromophenyl)sulfinyl)propanoate ((S)-8)

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm. Retention times: 19 & 21 min.

(rac)-8

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.053	BB	0.4091	1772.47925	66.46956	49.9404
2	20.705	BB	0.4420	1776.70703	61.69768	50.0596

Totals : 3549.18628 128.16724

(S)-8

$[\alpha]^{23}_D = -98$ (c 1.0, CHCl₃)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.153	MM	0.5728	2.73200e4	794.92761	99.5233
2	21.059	MM	0.4381	130.86740	4.97806	0.4767

Totals : 2.74509e4 799.90567

ee = 99%

Methyl (S)-3-(4-bromo-N-(tert-butoxycarbonyl)phenylsulfonimidoyl)propanoate ((S)-9)

Conditions: Chiralpak IA column, 93:7 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(rac)-9

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.001	BB	0.5177	292.65317	7.17716	51.1008
2	36.838	BB	0.7778	280.04456	4.25531	48.8992

Totals : 572.69772 11.43247

(S)-9

$[\alpha]^{23}_D = +44$ (c 1.0, CHCl₃)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.792	BB	0.6193	6407.31689	153.39117	99.5667
2	37.041	MM	0.9987	27.88206	4.65299e-1	0.4333

Totals : 6435.19896 153.85647

ee = 99%

Sodium (S)-((4-Bromophenyl)sulfinyl)(*tert*-butoxycarbonyl)amide ((S)-1b)

The ee of the sulfinamide salt was tested by reprotonation to the sulfinamide *tert*-Butyl (S)-((4-bromophenyl)sulfinyl)carbamate. For experimental conditions see experimental data for (S)-1a.

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(rac)-*tert*-Butyl ((4-bromophenyl)sulfinyl)carbamate

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.540	BB	0.5101	2789.14917	83.83952	50.0487
2	20.780	BB	0.5762	2783.71631	74.80299	49.9513

Totals : 5572.86548 158.64250

(S)-*tert*-Butyl ((4-bromophenyl)sulfinyl)carbamate

$[\alpha]^{23}_D = +88$ (c 1.0, CDCl₃)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.584	MM	0.4719	11.06724	3.90911e-1	0.4186
2	20.794	BB	0.5750	2633.01880	70.30122	99.5814

Totals : 2644.08604 70.69213

ee = 99%

***tert*-Butyl (*R*)-((4-bromophenyl)fluoro(oxo)- λ^6 -sulfaneylidene)carbamate ((*R*)-2b)**

Conditions: Chiralpak IA column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-2b

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.961	BB	0.2623	2229.76563	128.59897	50.0398
2	12.041	BB	0.2921	2226.22266	113.86397	49.9602

Totals : 4455.98828 242.46294

(*S*)-2b

$[\alpha]_D^{23} = -15$ (c 1.7, CDCl₃)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.796	MM	0.2715	426.70654	26.19217	4.1100
2	11.663	MM	0.3022	9955.47168	549.06299	95.8900

Totals : 1.03822e4 575.25516

ee = 92%

***tert*-Butyl (*R*)-((benzylamino)(4-bromophenyl)(oxo)- λ^6 -sulfaneylidene)carbamate (*(R)*-3v)**

Conditions: Chiralpak ID column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 254 nm.

(rac)-3v

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.289	BB	0.4308	1897.99060	66.13738	49.9878
2	19.880	BB	0.6643	1898.91638	40.85403	50.0122

Totals : 3796.90698 106.99141

(*R*)-3v

$[\alpha]^{23}_D = +6$ (c 0.5, CH₂Cl₂)

Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.389	BB	0.4214	703.08716	24.45546	95.9608
2	20.290	MM	1.0244	29.59464	4.81516e-1	4.0392

Totals : 732.68180 24.93698

ee = 92%

***tert*-Butyl (*R*)-((allylamino)(4-bromophenyl)(oxo)- λ^6 -sulfaneylidene)carbamate ((*R*)-3w)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-3w

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.086	BB	0.5924	1710.61499	42.06887	50.7446
2	29.582	BB	0.7395	1660.41260	30.10318	49.2554

Totals : 3371.02759 72.17204

(*R*)-3w

$[\alpha]^{23}_D = +8$ (c 0.5, CH₂Cl₂)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.922	BB	0.5810	3122.61719	77.67725	94.8143
2	29.492	MM	0.9223	170.78593	3.08615	5.1857

Totals : 3293.40312 80.76340

ee = 90%

***tert*-Butyl (*R*)-((4-bromophenyl)(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate ((*R*)-3x)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-3x

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.040	BB	0.4242	2639.59253	95.57035	50.0593
2	24.784	BB	0.6478	2633.33691	60.26088	49.9407

Totals : 5272.92944 155.83123

(*R*)-3x

$[\alpha]^{23}_D = -8$ (c 0.5, CH₂Cl₂)

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.207	MM	0.4393	155.29939	5.89220	4.9157
2	24.968	BB	0.6367	3003.94165	68.35349	95.0843

Totals : 3159.24104 74.24569

ee = 90%

***tert*-Butyl (*R*)-([1,1'-biphenyl]-4-yl(oxo)(piperidin-1-yl)- λ^6 -sulfaneylidene)carbamate ((*R*)-10)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-10

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.894	BB	0.7426	3461.90698	68.61781	49.9489
2	32.744	BB	0.8816	3468.99438	57.19546	50.0511

Totals : 6930.90137 125.81327

(*R*)-10

$[\alpha]^{23}_D = -7$ (c 1.0, CDCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.045	BB	0.6254	763.23010	15.26192	4.1086
2	32.483	MM	1.0390	1.78133e4	285.74695	95.8914

Totals : 1.85765e4 301.00886

ee = 92%

1-(4-Methylphenylsulfonimidoyl)piperidine ((*R*)-11)

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(*rac*)-11

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.974	BB	0.5747	1665.61560	43.70134	49.7831
2	44.100	BB	0.9287	1680.12842	25.17134	50.2169

Totals : 3345.74402 68.87268

(*R*)-11

$[\alpha]^{23}_D = -8$ (c 0.5, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.456	MM	0.4303	10.69019	4.14060e-1	0.2128
2	43.921	BB	1.0525	5011.75488	65.80835	99.7872

Totals : 5022.44507 66.22241

ee > 99%

(R)-N'-Cyclobutyl-4-methylbenzenesulfonimidamide ((R)-12)

Conditions: Chiralpak IA column, 85:15 *n*hexane:*i*PrOH, flow rate: 1 mL min⁻¹, 35 °C, UV detection wavelength: 250 nm.

(rac)-12

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.432	BB	0.3197	658.97382	30.53941	50.2113
2	16.453	BB	0.4416	653.42694	21.93403	49.7887

Totals : 1312.40076 52.47344

(R)-12

$[\alpha]^{23}_D = -46$ (c 0.13, CHCl₃).

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.376	BB	0.3356	2437.28149	107.06171	99.1757
2	16.693	MM	0.5273	20.25801	6.40252e-1	0.8243

Totals : 2457.53950 107.70197

ee = 98%

SI Sulfonimidamides chemrxiv.pdf (17.32 MiB)

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