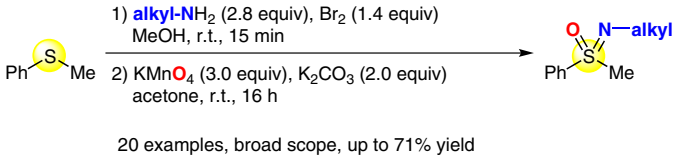
Synthesis C. A. Dannenberg et al. Paper

Direct Access to *N*-Alkylsulfoximines from Sulfides by a Sequential Imidation/Oxidation Procedure

Carl Albrecht Dannenberg
Vincent Bizet*
Carsten Bolm*

Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
carsten.bolm@oc.rwth-aachen.de



Received: 09.03.2015
Accepted: 14.03.2015
Published online: 16.04.2015
DOI: 10.1055/s-0034-1380536; Art ID: ss-2015-z0151-op

Abstract Synthetically relevant *N*-alkyl-substituted sulfoximines are directly prepared from sulfides by an unprecedented one-pot imidation/oxidation sequence. In situ generated *N*-bromoalkylamines serve as readily accessible imidating agents leading to *N*-alkylsulfiliminium bromides that are subsequently oxidized providing the corresponding *N*-alkylsulfoximines. In this manner, gram quantities of the products can be obtained in a short period of time avoiding the use of toxic and cumbersome to handle alkylating reagents.

Key words sulfoximine, imidation, oxidation, synthetic method, sulfide

Since their discovery, sulfoximines have been widely studied and applied in asymmetric synthesis and catalysis,[1,2] medicinal chemistry,[3–5] and crop protection.[6] An important structural feature of these sulfur reagents is the sulfoximine nitrogen because its functionalization allows fine-tuning of the molecular properties of the target compounds related to, for example, LADME,[7] bioactivity, and/or solubility. For a number of recent applications, NH- and *N*-cyanosulfoximines proved to be the structures of choice. For instance, BAY 1000394 (**1**)[3,4a–c] and AZD6738 (**2**)[4d] are potent kinase inhibitors, currently in phase 1 clinical trials, and sulfoxaflor (**3**) is a commercial insecticide (Figure 1).[6] Recently, Goldberg and co-workers (AstraZeneca) emphasized the improved solubility of *N*-methylsulfoximines in water compared to NH-sulfoximines and their sulfone analogues.[8] In their study, the *N*-methylsulfoximines proved superior to the others combining a higher solubility with equivalent isolipophilicity of the corresponding sulfone. Noteworthy is also that sulfoximines can be chiral adding an extra point of diversity compared to isosteric sulfones.

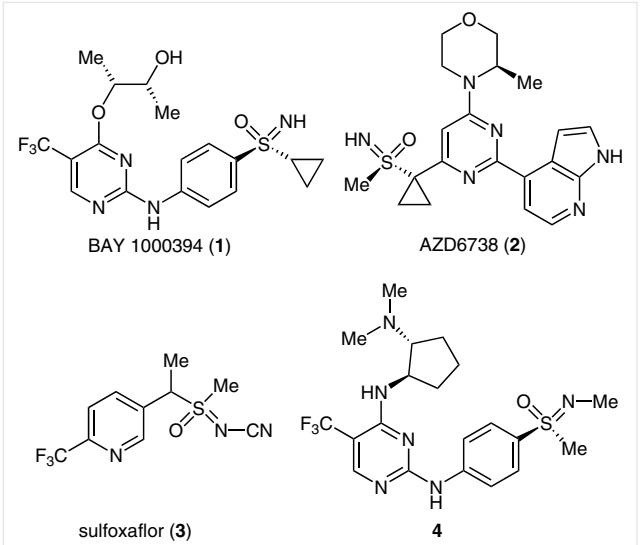


Figure 1 Relevant bioactive sulfoximines

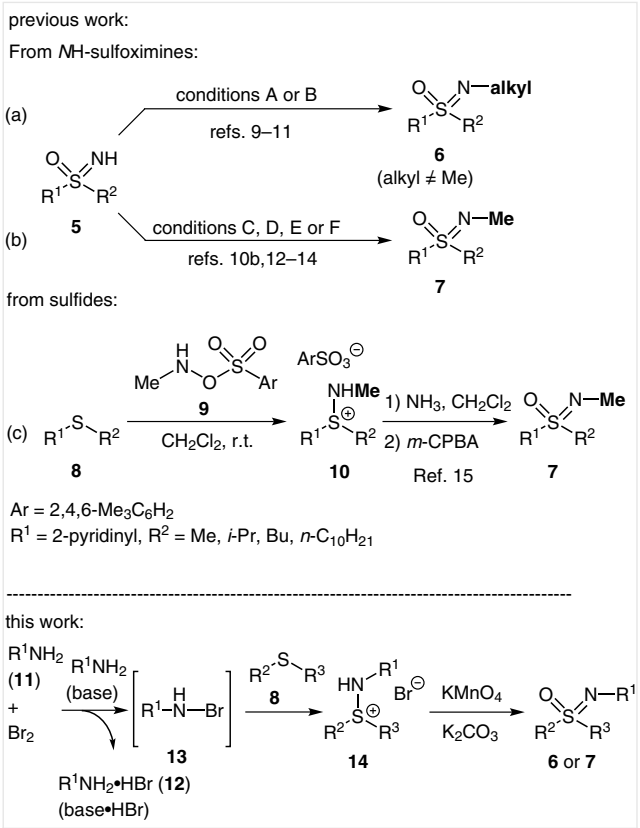
With respect to *N*-methylsulfoximines this attribute proved to be important in a recent work by Walker and co-workers (Pfizer), who found that the *N*-methylsulfoximine **4** (with *S*-configuration at sulfur) had equipotent inhibitory activity on proline-rich tyrosine kinase 2 as its sulfone analogue showing a significantly reduced hERG liability.[5a]

Motivated by the synthetic relevance of N-alkylated sulfoximines **6** and **7**, various approaches for their preparation have been developed (Scheme 1, a–c). Most of them, however, have severe synthetic drawbacks as they require preformed NH-sulfoximines **5**, multi-step synthetic sequences, and highly reactive reagents such as strong bases and toxic alkylating agents. For example, N-alkylated derivatives **6** have been prepared by a two-step protocol involving an initial N-acylation of **5** with an acyl halide followed

by reduction of the resulting N-acylated intermediate with borane.[9] Although the latter transformation is well established, it can be problematic in reactions performed on larger scale due to the instability of the reducing agent. A direct introduction of the *N*-alkyl substituent requires the use of a (toxic) alkyl halide in combination with a strong base such as butyllithium or an alkali metal hydride and a phase-transfer catalyst under strictly anhydrous conditions,[10] or, alternatively, a super-basic system consisting of KOH in DMSO.[11] As long as the substrates are base-tolerant and the alkyl halides can be handled, these direct alkylations might be the methods of choice. Generally, *N*-methyl derivatives **7** are accessed differently (Scheme 1, b). Most common for the preparation of these compounds are reductive amidations of NH-sulfoximines **5** with a mixture of formaldehyde and formic acid under Eschweiler–Clark conditions. After reflux for several days, many N-methylated products can be obtained in good yields.[12] The use of methyl transfer agents such as methyl iodide,[10b] trimethyloxonium tetrafluoroborate[12d,13] or 'magic methyl' (methyl fluorosulfate)[14] allows the reduction of the reaction time and the temperature. Although appealing at first glance, it is noteworthy that these conditions are unsuitable for acid-sensitive substrates, and furthermore, the pronounced toxicities of the latter mentioned alkylating agents render such methylations unattractive in scaled-up processes.

To the best of our knowledge, there is only a single report on the direct sulfide-to-*N*-methylsulfoximine conversion.[15] It involves sulfide imidation with *N*-methyl-*O*-mesitylsulfonylhydroxylamine (**9**)[16,17] leading to sulfonium arylsulfonates **10** and subsequent oxidation of **10** with *m*-CPBA to *N*-methylsulfoximines **7** (Scheme 1, c). Unfortunately, only four products with a rather specific substitution pattern [derived from 2-(alkylthio)pyridines] have been prepared in this manner, and the yields were unsatisfying (38% over two steps at best).

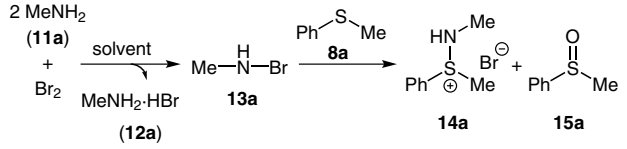
Considering the importance of N-alkylated sulfoximines **6** and **7** in the aforementioned biomedical applications and their general relevance in synthesis we wondered about a direct access of such compounds starting from sulfides **8** utilizing straightforward reagents under easy to perform experimental conditions. A particular need was recognized in the synthesis of *N*-methylsulfoximines **7**. Primary alkylamines **11** were identified as ideal sources for the envisaged imidation process. Hence, for the preparation of **7**, simple methylamine (**11a**) was regarded as the reagent of choice. In the light of the mass spectrometry work by Cook and co-workers,[18] we hypothesized that the activation of the amine could be achieved by treatment with bromine leading to *N*-bromoalkylamines **13**. Reaction of **13** with the sulfide **8** would then lead to the alkylsulfiliminium bromides **14**.[19] Oxidations of **14** should then lead to the desired N-alkylated sulfoximines **6**. Starting from methylamine, *N*-methylsulfoximines **7** could easily be accessed. To our delight, this hypothesized pathway proved applicable (Scheme 1, bottom). Using a combination of $MeNH_2$ (**11a**, 2.8 equiv) and Br_2 (1.4 equiv) in methanol at room temperature led to full conversion of thioanisole (**8a**) in only 15 minutes with *N*-methylsulfiliminium bromide (**14a**) and sulfoxide **15a** being the only products (formed in a 92:8 ratio as determined by ^1H NMR spectroscopy; Table 1, entry 1).[20] Attempts to avoid the formation of **15a** by lowering the temperature to 0 °C (entry 2), modifying the substrate/reagent ratios (entries 3 and 4), or changing the solvent (entries 5–9) remained unsuccessful. In all cases, sulfoxide **15a** was observed as a by-product in considerable amounts. An important observation was made during the solvent screening. While MeOH could be replaced by EtOH or H_2O without significantly affecting the product formation and the **14a**/**15a** ratio (entries 5 and 6), use of 2,2,2-trifluoroethanol led to a selectivity change providing sulfoxide **15a** as the main product (entry 7). In CH_2Cl_2 the ratio of **14a**/**15a** was 54:46, and in acetone neither of the two products was observed (entries 8 and 9, respectively). Noticeably, in the latter two solvents a precipitate formed upon mixing of $MeNH_2$ and Br_2, and this solid was identified as



Scheme 1 Synthetic routes to *N*-alkylsulfoximines **6** and **7**. *Reagents and conditions*: A) 1. RCOCl, DMAP (cat.), pyridine or Et_3N, CH_2Cl_2, 2. HBX_2, CH_2Cl_2; B) BuLi, MH (+ PTC) or KOH in DMSO, alkyl halide; C) H_2CO, HCO_2H, H_2O, reflux; D) NaH, MeI, DMF; E) $Me_3O^+BF_4^-$, CH_2Cl_2; F) FSO_2OMe, MeCN.

methylammonium bromide (**12a**). In the subsequent optimization of the process, the low solubility of **12a** in acetone proved beneficial because it allowed the separation of the products **14** from the ammonium salts **12**. Thus, for solubility reasons the initial sulfur imidation (with $MeNH_2$ and Br_2) was performed in MeOH, where all reagents and intermediates dissolved. Then, the polar, protic solvent was removed under vacuum and acetone was added leading to a solution of **14a** and crystals of **12a**, which could be removed by filtration. The obtained *N*-methylsulfiliminium salt **14a** was stable for a few days at –20 °C, but decomposed readily at room temperature.[21] As a final note, bromine could not be replaced by iodine.

Table 1 Screening of the Reaction Parameters[a]



Entry	Solvent	Ratio of **14a**/**15a**[b]
1	**MeOH**	**92:8**
2[c]	MeOH	85:15
3[d]	MeOH	80:20
4[e]	MeOH	85:15
5	EtOH	90:10
6	H_2O	80:20
7	2,2,2-trifluoroethanol	25:75
8	CH_2Cl_2	54:46
9	acetone	n.r.[f]

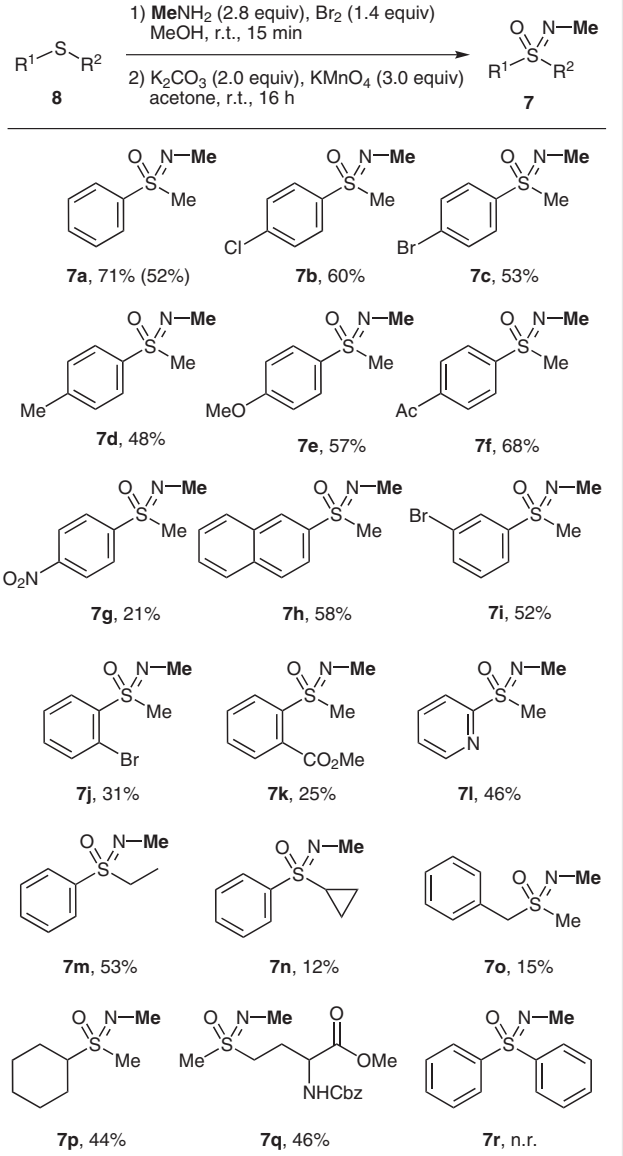
[a] The reactions were carried out on a 0.5 mmol scale with 2.8 equiv of $MeNH_2$ (**11a**) and 1.4 equiv of Br_2 at r.t.
[b] Determined by ^1H NMR spectroscopy.
[c] The reaction was carried out at 0 °C.
[d] Use of 2.0 equiv of $MeNH_2$ (**11a**) and 1.0 equiv of Br_2.
[e] Use of 4.0 equiv of $MeNH_2$ (**11a**) and 2.0 equiv of Br_2.
[f] n.r. = no reaction.

Next, we focused on the oxidation step to convert *N*-alkylsulfiliminium salts **14** to their corresponding sulfoximine derivatives **6** and **7**. Following the initial work described above, **14a** was selected as a representative substrate. While attempts to use sodium hypochlorite or hydrogen peroxide as oxidants remained unsuccessful, **7a** was obtained by oxidation of **14a** with *m*-CPBA. However, knowing about the potential hazards of this peracid we were delighted to find that $KMnO_4$ could also be applied. In combination with K_2CO_3, it provided **7a** in 71% yield after 16 hours at room temperature (for additional information, see Supporting Information). Noteworthy is also that this transformation proceeded in acetone, which allowed a direct use of the aforementioned sulfiliminium salt solution after removal of **12a** representing an operational advantage over the alternative oxidation procedures. Reducing the reaction time from 16 hours to just 2 hours led to a decrease in the yield of **7a** (64%). Presumably due to the instability of **14a** the product yield could not be further increased. As main by-products sulfide **8a** and sulfoxide **15a** were detected.

For the investigation of the substrate scope, diversely substituted sulfides **8a**–**r** were subjected to the optimized reaction conditions for both steps (sulfide imidation with $MeNH_2/Br_2$ and subsequent sulfiliminium salt oxidation with $KMnO_4/K_2CO_3$; Scheme 2). In general, *para*- and *meta*-substituted aryl methyl sulfides **8b**–**i** with both electron-donating and -withdrawing groups on the arene reacted well providing the corresponding *N*-methylsulfoximines **7b**–**i** in moderate to good yields (up to 68%). The only exception was sulfoximine **7g**, which was obtained in only 21% yield due to the low solubility of the starting material (sulfide **8g**) in methanol. Electronic effects of the aryl substituents had no apparent influence on the substrate reactivities and product yields. Presumably, steric hindrance led to the slightly lower yields in the conversions of *ortho*-substituted aryl methyl sulfides **8j** and **8k** affording sulfoximines **7j** and **7k** in 31 and 25% yield, respectively. Applying the reaction sequence on methyl 2-pyridinyl sulfide (**8l**) gave sulfoximine **7l** in 46% yield illustrating that the process was superior to the existing technology providing the same product.[15] Further variations of sulfide structure revealed that also other substituent combinations were tolerated. The results, however, varied. For example, whereas *S*-ethyl phenyl sulfide led to **7m** in good yield (53%), preparation of the analogous *S*-cyclopropyl derivative **7n** and *N*,*S*-dimethyl-*S*-benzylsulfoximine (**7o**) proved more difficult (12% and 15% yield, respectively). Dialkyl-substituted sulfides **8p** and **8q** reacted well leading to **7p** and **7q** in 44 and 46% yield, respectively. The latter product is of particular interest because it is a protected NMe analogue of methionine sulfoximine (MSO), which is a potent inhibitor of the γ-glutamylcysteine synthetase, an essential enzyme in the glutathione biosynthesis.[2d]

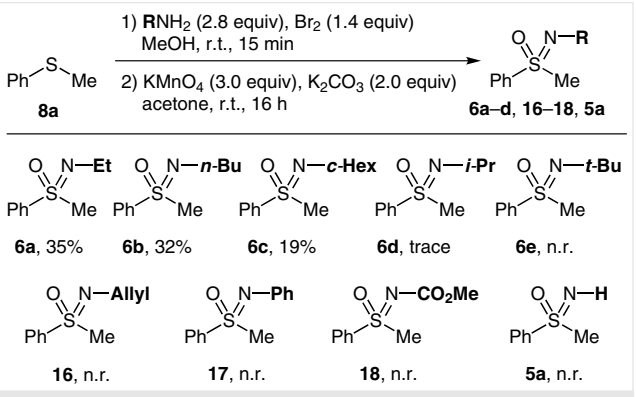
Diphenyl sulfide (**8r**) did not react, which was in line with earlier observations.[22] The scalability of the process was demonstrated in a conversion of sulfide **8a** on a 10 mmol scale, which gave *N*-methylsulfoximine **7a** in 52% yield.

Encouraged by these results we wondered about using other amines in direct conversions of sulfides into N-substituted sulfoximines **6**. In order to allow a comparison to the data obtained in reactions with methylamine, methyl phenyl sulfide (**8a**) was used as the substrate. Pleasingly, such transformations proved possible, but unfortunately, the substrate range was rather limited, and the yields remained comparably low. For example, using ethylamine instead of methylamine afforded *N*-ethylsulfoximine **6a** in 35% yield (Scheme 3) as compared to 72% yield in the preparation of



Scheme 2 Scope of the NMe sulfoximine synthesis (performed on a 1.0 mmol scale). The yield of **7a** shown in parentheses resulted from a reaction on a 10 mmol scale.

N-methyl analogue **7a** (Scheme 2). Applying *n*-butylamine and cyclohexylamine gave sulfoximines **6b** and **6c** in 32 and 19% yield, respectively. Although these yields were low, the overall synthetic value of the process was regarded high considering the multi-step alternative providing the same products. Attempts to prepare N-substituted sulfoximines **6d**, **6e**, and **16**–**18** were unsuccessful providing the products in only trace amounts at best (Scheme 3). Most likely, the more pronounced stereoelectronic effects of the R groups (as, for example, in *tert*-butylamine, aniline, or methyl carbamate) were responsible for the low reactivity of the intermediates. Finally, ammonia was tested as the amino component, but also in this case, no product (**5a**) was observed.



Scheme 3 Scope of the sulfoximine synthesis

In conclusion, we have developed a new direct route to *N*-methyl- and other *N*-alkylsulfoximines by an unprecedented imidation/oxidation sequence starting from sulfides. In contrast to most other synthetic methods leading to the same products, the process avoids the intermediacy of NH-sulfoximines, which are often cumbersome to prepare. Using simple reagents under mild conditions at room temperature various products can be accessed within a short period of time.

Unless otherwise stated, the starting materials were commercially available and used as received. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded either on Varian V-NMRS 600, Varian V-NMRS 400 or Varian Mercury 300 spectrometer, in $CDCl_3$. Chemical shifts (δ) are given in ppm relative to TMS and calibrated to residual $CHCl_3$. Coupling constants (*J*) are reported in Hz and standard coupling patterns are used. IR spectra were recorded on a PerkinElmer FT-IR Spectrum 100 as KBr pellets or neat liquids; wave numbers are given in cm^{-1}. Mass spectra were recorded on a Finnigan SSQ 7000 spectrometer [electron ionization (EI), 70 eV] and peaks are listed according to their *m*/*z* values. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer with positive ion mode. Elemental analyses were performed on an ElementarVario EL instrument. Melting points were measured with a Büchi Melting Point B-540 apparatus. Flash column chromatography was performed with Merck silica gel 60 (35–70 mesh). Reactions were monitored by TLC on silica gel 60 F254 coated on aluminum sheets from Merck with detection by UV light and/or staining solutions ($KMnO_4$). Preparative HPLC was carried out on Varian, Kromasil-RP-18 250 × 30 mm, MeOH–H_2O; 12 mL/min, 51 bar, 254 nm, SD-1 PumpeProstar 320 UV-Detector for compounds **7g**, **7k**, and **7n** after column chromatography.

N,*S*-Dimethyl-*S*-phenylsulfiliminium Bromide (14a)

A 100 mL round-bottomed flask, equipped with a magnetic stir bar, was charged with MeOH (50 mL) and $MeNH_2$ (**11a**, 33% in EtOH, 3.5 mL, 28.0 mmol, 2.8 equiv). Subsequently, Br_2 (0.72 mL, 14.0 mmol, 1.4 equiv) was added dropwise and the reaction mixture was stirred vigorously for 5 min. Afterwards, thioanisole (**8a**; 1.2 mL, 10 mmol,

1.0 equiv) was added and the mixture was stirred for another 10 min. After full consumption of **8a**, the solvent was removed under reduced pressure. The residue was taken up in acetone (30 mL) and filtered over filter paper. The filtrate was concentrated under reduced pressure until ca. 10 mL, which was then added dropwise to cold Et_2O (200 mL) under vigorous stirring to form a milky solution. After ca. 30 min, the solution became completely clear along with the formation of an oily off-white precipitate sticking all around the flask. The solvent was carefully removed keeping the precipitate in the flask. The oily residue was dried under high vacuum to give **14a**, which was used without further purification; yield: 2.0 g (85%); viscous yellow oil.

IR (ATR): 3860 (vw), 3741 (vw), 3428 (m), 3051 (vs), 2912 (m), 2822 (m), 2742 (vw), 2660 (vw), 2549 (vw), 2317 (s), 2110 (m), 1997 (w), 1924 (w), 1772 (vw), 1691 (w), 1580 (w), 1441 (vs), 1320 (m), 1152 (w), 1070 (vs), 974 (vs), 840 (w), 751 (vs), 684 (vs) cm^{-1}.

^1H NMR (600 MHz, CD_3OD): δ = 8.00–7.99 (m, 2 H), 7.84–7.81 (m, 1 H), 7.78–7.76 (m, 2 H), 4.85 (s, 1 H), 3.49 (s, 3 H), 2.68 (s, 3 H).

^{13}C NMR (151 MHz, CD_3OD): δ = 135.4, 131.8, 129.8, 129.7, 29.6, 28.0.

MS (ESI): *m*/*z* (%) = 154 (51), 139 (24), 124 (100), 107 (28).

N-Alkylsulfoximines 6 *and N*-Methylsulfoximines 7 from Sulfides 8; General Procedure

A 50 mL round-bottomed flask, equipped with a magnetic stir bar was charged with MeOH (6 mL) and an alkylamine **11** (2.8 mmol, 2.8 equiv) for the synthesis of **6** and methylamine (**11a**; 33% in EtOH, 360 µL, 2.8 mmol, 2.8 equiv) for the synthesis of **7**. Subsequently, bromine (80 µL, 1.4 mmol, 1.4 equiv) was added dropwise. The reaction mixture was stirred vigorously for 5 min. Afterwards, sulfide **8** (1.0 mmol, 1.0 equiv) was added and the mixture was stirred for another 10 min. The reaction progress was monitored by TLC. After full consumption of **8**, the solvent was removed under reduced pressure. The residue was taken up in acetone (25 mL) and filtered over filter paper. The filtrate was concentrated under reduced pressure to ca. 10 mL. After the addition of K_2CO_3 (276.4 mg, 2.0 mmol, 2.0 equiv) and $KMnO_4$ (474.1 mg, 3.0 mmol, 3.0 equiv), the mixture was stirred for 16 h at r.t. Then, the solvent was removed under reduced pressure, the mixture was diluted with CH_2Cl_2 (20 mL), and the CH_2Cl_2 layer was washed with distilled H_2O (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The product was purified by column chromatography (silica gel, eluent: *n*-pentane–EtOAc) to yield *N*-alkylsulfoximine **6** or *N*-methylsulfoximine **7**.

N-Ethyl-*S*-methyl-*S*-*phenylsulfoximine* (6a)

Eluent: *n*-pentane–EtOAc (2:1) to EtOAc; yield: 64 mg (35%); colorless oil.

IR (ATR): 3396 (vw), 3061 (vw), 2968 (m), 2925 (w), 2855 (w), 2681 (vw), 2327 (vw), 2103 (vw), 1992 (vw), 1920 (vw), 1737 (vw), 1641 (vw), 1583 (vw), 1475 (vw), 1445 (m), 1408 (vw), 1375 (vw), 1292 (w), 1226 (vs), 1136 (vs), 1088 (s), 988 (s), 865 (vw), 814 (w), 775 (m), 743 (vs), 689 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 2 H), 7.57–7.47 (m, 3 H), 3.02 (s, 3 H), 2.98–2.90 (m, 1 H), 2.81–2.73 (m, 1 H), 1.11 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.6, 132.8, 129.4, 128.7, 45.2, 38.5, 18.3.

MS (EI, 70 eV): *m*/*z* (%) = 184 (6), 183 ([M^+], 11), 170 (5), 169 (9), 168 (100), 142 (7), 141 (78), 140 (7), 126 (10), 125 (24), 124 (13), 97 (11), 92 (6), 91 (5), 78 (9), 77 (24), 65 (5), 63 (6), 51 (16).

HRMS (ESI): *m*/*z* [M^+ + H] calcd for $C_9H_{14}NOS$: 184.07906; found: 184.07928.

N-Butyl-*S*-methyl-*S*-*phenylsulfoximine* (6b)

Eluent: *n*-pentane–EtOAc (2:1) to EtOAc; yield: 68 mg (32%); yellow oil.

IR (ATR): 3821 (vw), 3401 (w), 3064 (vw), 2928 (s), 2863 (s), 2674 (vw), 2323 (w), 2097 (w), 1994 (vw), 1913 (vw), 1658 (w), 1581 (vw), 1531 (vw), 1447 (s), 1411 (w), 1368 (vw), 1311 (w), 1232 (vs), 1132 (vs), 1085 (vs), 976 (vs), 863 (w), 782 (m), 742 (vs), 688 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.87–7.83 (m, 2 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 2 H), 3.03 (s, 3 H), 2.92–2.87 (m, 1 H), 2.74–2.69 (m, 1 H), 1.51–1.45 (m, 2 H), 1.33–1.23 (m, 2 H), 0.81 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.7, 132.8, 129.4, 128.7, 45.2, 43.6, 35.0, 20.4, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 212 ([M^+], 4), 169 (5), 168 (66), 142 (8), 141 (100), 140 (7), 126 (12), 125 (34), 124 (15), 97 (13), 91 (5), 78 (11), 77 (26), 63 (6), 51 (7).

HRMS (ESI): *m*/*z* [M^+ + H] calcd for $C_{11}H_{18}NOS$: 212.11036; found: 212.11043.

N-Cyclohexyl-*S*-*methyl*-*S*-phenylsulfoximine (6c)

Eluent: *n*-pentane–EtOAc (2:1) to EtOAc; yield: 45 mg (19%); colorless oil.

IR (ATR): 3854 (vw), 3400 (w), 3063 (vw), 3011 (vw), 2925 (vs), 2852 (s), 2663 (vw), 2335 (vw), 2088 (vw), 1992 (vw), 1919 (vw), 1735 (vw), 1654 (vw), 1582 (vw), 1532 (vw), 1445 (s), 1410 (w), 1366 (w), 1316 (w), 1230 (vs), 1131 (vs), 1083 (s), 1018 (vw), 971 (s), 889 (w), 839 (vw), 787 (m), 742 (vs), 689 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.92–7.89 (m, 2 H), 7.60–7.56 (m, 1 H), 7.55–7.51 (m, 2 H), 3.03 (s, 3 H), 2.86–2.80 (m, 1 H), 1.89–1.85 (m, 1 H), 1.69–1.61 (m, 3 H), 1.49–1.45 (m, 1 H), 1.40–1.34 (m, 1 H), 1.32–1.26 (m, 1 H), 1.16–1.06 (m, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.9, 132.8, 129.3, 128.7, 54.3, 45.8, 37.7, 36.5, 25.7, 25.6, 25.4.

MS (EI, 70 eV): *m*/*z* (%) = 328 (3), 240 (6), 239 (18), 238 (100), 237 ([M^+ + H], 43), 236 (20), 195 (7), 194 (57), 141 (5), 125 (3), 97 (3), 91 (2), 77 (3).

HRMS (ESI): *m*/*z* [M^+ + H] calcd for $C_{13}H_{20}NOS$: 238.12601; found: 238.12653.

N,*S*-Dimethyl-*S*-*phenylsulfoximine* (7a)

Eluent: EtOAc; yield: 120 mg (71%); colorless oil.

IR (ATR): 3882 (vw), 3195 (m), 3062 (s), 2921 (s), 2314 (vw), 2098 (vw), 1999 (vw), 1912 (vw), 1672 (vs), 1446 (s), 1369 (w), 1312 (m), 1236 (vs), 1149 (s), 1093 (m), 967 (m), 847 (w), 751 (vs), 687 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.92–7.88 (m, 2 H), 7.64–7.60 (m, 1 H), 7.59–7.55 (m, 2 H), 3.08 (s, 3 H), 2.65 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.9, 133.0, 129.6, 128.9, 45.1, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 172 (5), 171 (11), 170 ([M^+], 100), 169 (23), 168 (14), 156 (9), 154 (42), 141 (10), 140 (6), 125 (10), 106 (19), 97 (6), 77 (17), 51 (9).

HRMS (ESI): *m*/*z* [M⁺ + H] calcd for $C_8H_{12}NOS$: 170.06341; found: 170.06325.

***N*,*S*-Dimethyl-*S*-(4-*chlorophenyl*)sulfoximine (7b)**

Eluent: *n*-pentane–EtOAc (1:1) to EtOAc; yield: 65 mg (32%); colorless oil.

IR (ATR): 3561 (vw), 3202 (vw), 3069 (vw), 2916 (w), 2804 (vw), 2296 (vw), 2096 (vw), 1923 (vw), 1670 (s). 1575 (m), 1471 (m), 1393 (w), 1313 (w), 1237 (vs), 1146 (vs), 1086 (vs), 971 (vs), 833 (vs), 768 (vs) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 3.07 (s, 3 H), 2.64 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.8, 137.5, 130.4, 130.0, 45.2, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 206 (7), 205 (10), 204 (23), 203 ([M⁺], 26), 190 (11), 188 (27), 177 (6), 175 (18), 174 (6), 161 (11), 160 (10), 159 (33), 158 (8), 143 (8), 142 (34), 141 (8), 140 (100), 139 (7), 138 (5), 133 (6), 131 (14), 128 (9), 127 (6), 126 (13), 125 (6), 113 (14), 112 (11), 111 (40), 108 (10), 105 (9), 104 (5), 99 (10), 85 (6), 77 (12), 75 (47), 74 (13), 73 (6), 63 (19), 61 (6), 61 (7), 50 (20), 34 (5).

HRMS (ESI): *m*/*z* [M⁺ + H] calcd for $C_8H_{11}ClNOS$: 204.02444; found: 204.02406.

***N*,*S*-Dimethyl-*S*-(4-bromophenyl)*sulfoximine* (7c)**

Eluent: *n*-pentane–EtOAc (1:1) to EtOAc; yield: 131 mg (53%); white solid; mp 59–60 °C.

IR (ATR): 3197 (vw), 2915 (m), 2807 (w), 2283 (vw), 2087 (vw), 1922 (vw), 1671 (m), 1569 (m), 1464 (m), 1383 (m), 1314 (w), 1227 (vs), 1145 (vs), 1081 (vs), 968 (vs), 826 (vs), 756 (vs) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.73 (m, 2 H), 7.72–7.68 (m, 2 H), 3.06 (s, 3 H), 2.64 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.1, 132.9, 130.5, 128.3, 45.2, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 255 (5), 251 (11), 250 (93), 249 (59), 248 (100), 247 ([M⁺], 51), 246 (13), 236 (6), 235 (7), 234 (66), 233 (6), 232 (57), 221 (10), 220 (6), 219 (11), 218 (7), 205 (18), 204 (10), 203 (18), 202 (6), 187 (8), 186 (80), 185 (10), 184 (79), 172 (6), 157 (10), 155 (10), 105 (7), 76 (6), 75 (7), 63 (5), 50 (6).

HRMS (ESI): *m*/*z* [M⁺ + H] calcd for $C_8H_{11}BrNOS$: 247.97429; found: 247.97392.

***N*,*S*-Dimethyl-*S*-(4-methylphenyl)*sulfoximine* (7d)**

Eluent: EtOAc; yield: 88 mg (48%); colorless oil.

IR (ATR): 3399 (vw), 2919 (w), 2804 (vw), 2364 (vw), 2089 (vw), 1925 (vw), 1660 (vw), 1595 (w), 1408 (w), 1313 (w), 1234 (vs), 1142 (vs), 1100 (vs), 971 (vs), 815 (s), 759 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 7.9 Hz, 2 H), 3.05 (s, 3 H), 2.62 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.9, 135.7, 130.3, 128.9, 45.2, 29.6, 21.6.

MS (EI, 70 eV): *m*/*z* (%) = 184 (6), 183 ([M⁺], 23), 168 (19), 155 (14), 140 (5), 139 (27), 138 (5), 121 (10), 120 (100), 119 (5), 118 (5), 108 (6), 107 (7), 105 (6), 93 (5), 92 (14), 91 (63), 89 (10), 79 (7), 78 (8), 77 (19), 65 (32), 63 (17), 51 (6).

HRMS (ESI): *m*/*z* [M⁺ + H] calcd for $C_9H_{14}NOS$: 184.07906; found: 184.07875.

***N*,*S*-Dimethyl-*S*-(4-methoxyphenyl)*sulfoximine* (7e)**

Eluent: EtOAc; yield: 114 mg (57%); colorless oil.

IR (ATR): 3555 (vw), 2925 (w), 2568 (vw), 2299 (vw), 2084 (vw), 1906 (vw), 1737 (w), 1588 (s), 1489 (m), 1309 (m), 1237 (vs), 1139 (vs), 1098 (vs), 1020 (s), 971 (s), 836 (vs), 764 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 2 H), 7.05–7.01 (m, 2 H), 3.88 (s, 3 H), 3.06 (s, 3 H), 2.64 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.4, 131.0, 130.0, 114.8, 55.8, 45.5, 29.6.

MS (EI, 70 eV): *m*/*z* (%) = 201 (2), 200 (12), 199 ([M⁺], 30), 184 (14), 171 (8), 156 (5), 155 (35), 139 (5), 137 (8), 136 (100), 123 (10), 121 (13), 108 (11), 95 (5), 92 (12), 77 (14), 64 (6), 63 (11).

HRMS (ESI): *m*/*z* [M⁺ + H] calcd for $C_9H_{14}NO_2S$: 200.07398; found: 200.07355.

***N*,*S*-Dimethyl-*S*-(4-acetylphenyl)*sulfoximine* (7f)**

Eluent: EtOAc; yield: 144 mg (68%); white solid; mp 72 °C.

IR (ATR): 3566 (vw), 3360 (vw), 3281 (vw), 3091 (vw), 3055 (vw), 2996 (w), 2962 (vw), 2914 (w), 2880 (w), 2801 (vw), 2637 (vw), 2298 (vw), 2175 (vw), 2081 (vw), 1945 (vw), 1841 (vw), 1684 (vs), 1573 (w), 1393 (s), 1360 (m), 1319 (vw), 1224 (vs), 1145 (vs), 1096 (s), 962 (vs), 835 (s), 778 (vs), 742 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.14–8.11 (m, 2 H), 8.01–7.97 (m, 2 H), 3.10 (s, 3 H), 2.67 (s, 3 H), 2.65 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.0, 140.5, 129.4, 129.3, 128.2, 44.9, 29.7, 27.1.

MS (EI, 70 eV): *m*/*z* (%) = 213 (11), 212 (77), 211 ([M⁺], 52), 210 (9), 198 (11), 197 (11), 196 (100), 183 (16), 182 (11), 167 (18), 152 (11), 149 (6), 148 (54), 132 (7), 121 (5), 106 (7), 105 (6), 104 (5), 91 (9), 76 (5).

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.85; H, 6.15; N, 6.63.

***N*,*S*-Dimethyl-*S*-(4-nitrophenyl)*sulfoximine* (7g)**

Eluent: *n*-pentane–EtOAc (1:1); yield: 45 mg (21%); yellow solid; mp 128 °C.

IR (ATR): 3104 (w), 3055 (vw), 2995 (vw), 2919 (m), 2810 (vw), 2635 (vw), 2450 (vw), 2289 (vw), 2207 (vw), 2164 (vw), 2093 (vw), 2007 (vw), 1945 (vw), 1821 (vw), 1707 (vw), 1604 (w), 1518 (vs), 1468 (m), 1402 (vw), 1345 (vs), 1229 (vs), 1146 (vs), 1081 (vs), 990 (vs), 966 (s), 856 (vs), 770 (vs), 736 (vs), 682 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.41–8.38 (m, 2 H), 8.10–8.06 (m, 2 H), 3.11 (s, 3 H), 2.63 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.6, 145.4, 130.2, 124.8, 44.8, 29.6.

MS (EI, 70 eV): *m*/*z* (%) = 215 (19), 214 ([M⁺], 38), 213 (6), 201 (6), 200 (10), 199 (100), 186 (14), 170 (6), 153 (14), 151 (14), 150 (11), 140 (10), 105 (22), 104 (5), 92 (7), 76 (9), 75 (6), 63 (7), 50 (7).

HRMS (ESI): *m*/*z* [M⁺ + H] calcd for $C_8H_{11}N_2O_3S$: 215.04849; found: 215.04849.

***N*,*S*-Dimethyl-*S*-(2-naphthyl)*sulfoximine* (7h)**

Eluent: EtOAc; yield: 55 mg (58%); colorless oil.

IR (ATR): 3863 (vw), 3390 (w), 3014 (w), 2915 (w), 2803 (w), 2311 (w), 2093 (w), 1995 (vw), 1918 (vw), 1713 (vw), 1587 (w), 1501 (vw), 1455 (w), 1409 (w), 1341 (w), 1235 (vs), 1141 (vs), 975 (s), 845 (s), 755 (vs) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.45 (s, 1 H), 7.95 (dd, *J* = 12.5, 8.4 Hz, 2 H), 7.89 (d, *J* = 8.1 Hz, 1 H), 7.80 (dd, *J* = 8.6, 1.6 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.57 (t, *J* = 6.9 Hz, 1 H), 3.11 (s, 3 H), 2.64 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 135.7, 135.0, 132.7, 130.6, 129.7, 129.2, 128.9, 127.9, 127.5, 123.5, 44.9, 29.6.

MS (EI, 70 eV): *m*/*z* (%) = 221 (3), 220 ([M$^+$], 10), 219 (37), 204 (11), 191 (8), 175 (25), 157 (12), 156 (100), 147 (12), 144 (5), 141 (5), 129 (17), 128 (33), 127 (72), 126 (10), 115 (31), 101 (6), 77 (9), 63 (9).

HRMS (ESI): *m*/*z* [M$^+$ + H] calcd for $C_{12}H_{14}NOS$: 220.07906; found: 220.07895.

N,*S*-Dimethyl-*S*-(3-bromophenyl)*sulfoximine* (7i)

Eluent: *n*-pentane–EtOAc (1:1); yield: 129 mg (52%); yellow oil.

IR (ATR): 3408 (vw), 2914 (m), 2809 (w), 2305 (vw), 1737 (m), 1568 (w), 1410 (m), 1238 (vs), 1134 (vs), 973 (vs), 855 (m), 777 (vs) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04–8.02 (m, 1 H), 7.82–7.79 (m, 1 H), 7.74–7.72 (m, 1 H), 7.45–7.42 (m, 1 H), 3.07 (s, 3 H), 2.63 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.1, 136.1, 131.8 131.1, 127.4, 123.7, 45.1, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 251 (10), 250 (89), 249 (37), 248 (100), 247 ([M$^+$], 31), 246 (11), 235 (5), 234 (54), 232 (52), 221 (8), 219 (8), 205 (7), 203 (7), 186 (20), 185 (7), 184 (22), 183 (6), 157 (15), 155 (13), 108 (8), 105 (14), 104 (7), 96 (8), 92 (5), 77 (9), 76 (25), 75 (27), 74 (13), 69 (5), 63 (18), 61 (5), 50 (19).

HRMS (ESI): *m*/*z* [M$^+$ + H] calcd for $C_8H_{11}BrNOS$: 247.97392; found: 247.97415.

N,*S*-Dimethyl-*S*-(2-bromophenyl)*sulfoximine* (7j)

Eluent: *n*-pentane–EtOAc (3:1) to EtOAc; yield: 77 mg (31%); white solid; mp 79 °C.

IR (ATR): 3840 (vw), 3405 (m), 2924 (m), 2662 (vw), 2320 (vw), 2206 (vw), 2104 (vw), 1908 (vw), 1733 (s), 1550 (vs), 1428 (s), 1374 (s), 1240 (vs), 1141 (s), 1094 (vs), 957 (m), 903 (m), 836 (m), 754 (vs), 690 (vs) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (dd, *J* = 7.9, 1.7 Hz, 1 H), 7.74 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.50 (td, *J* = 7.7, 1.2 Hz, 1 H), 7.42 (td, *J* = 7.7, 1.7 Hz, 1 H), 3.25 (s, 3 H), 2.58 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 137.7, 135.6, 134.1, 133.8, 128.4, 121.0, 42.6, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 251 (10), 250 (96), 249 (36), 248 (100), 247 ([M$^+$], 29), 246 (9), 234 (50), 232 (48), 221 (9), 220 (7), 219 (9), 218 (7), 205 (10), 204 (5), 203 (10), 186 (32), 185 (5), 184 (36), 183 (6), 157 (17), 155 (19), 153 (16), 139 (8), 138 (16), 125 (18), 120 (5), 109 (7), 108 (25), 106 (8), 105 (51), 104 (28), 97 (11), 96 (42), 95 (8), 92 (17), 91 (30), 89 (6), 85 (9), 83 (13), 82 (6), 81 (8), 78 (16), 77 (57), 76 (68), 75 (84), 74 (41), 70 (10), 69 (20), 65 (15), 64 (13), 63 (84), 61 (16), 60 (9), 57 (6), 55 (6), 51 (18), 50 (69), 48 (8), 47 (11), 46 (6), 45 (12).

HRMS (ESI): *m*/*z* [M$^+$ + H] calcd for $C_8H_{11}BrNOS$: 247.97392; found: 247.97412.

Methyl 2-(*N*,*S*-Dimethylsulfonimidoyl)*benzoate* (7k)

Eluent: *n*-pentane–EtOAc (1:1); yield: 57 mg (25%); colorless oil.

IR (ATR): 3609 (vw), 3379 (vw), 3188 (vw), 3016 (vw), 2950 (w), 2879 (vw), 2806 (vw), 2329 (vw), 2174 (vw), 2095 (vw), 1990 (vw), 1729 (vs), 1663 (w), 1590 (vw), 1567 (vw), 1432 (s), 1288 (vs), 1242 (vs), 1150 (vs), 1111 (vs), 1056 (s), 959 (s), 854 (m), 829 (w), 776 (vs), 747 (vs) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97–7.94 (m, 1 H), 7.61 (m, 2 H), 7.56–7.53 (m, 1 H), 3.91 (s, 3 H), 3.23 (s, 3 H), 2.57 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.7, 137.3, 134.7, 132.9, 130.8, 130.8, 129.1, 53.2, 45.0, 29.6.

MS (EI, 70 eV): *m*/*z* (%) = 228 (20), 227 ([M$^+$], 13), 212 (17), 200 (5), 199 (39), 198 (29), 196 (18), 184 (8), 183 (86), 169 (5), 168 (10), 167 (100), 166 (6), 165 (6), 164 (6), 153 (18), 152 (54), 148 (10), 137 (6), 136 (7), 135 (10), 133 (11), 132 (50), 125 (10), 121 (13), 120 (15), 119 (5), 118 (6), 109 (11), 108 (9), 106 (6), 105 (55), 104 (48), 97 (8), 96 (19), 95 (6), 92 (45), 91 (13), 79 (8), 78 (11), 77 (55), 76 (42), 75 (11), 74 (12), 70 (5), 69 (6), 65 (7), 64 (10), 63 (31), 59 (7), 51 (9), 50 (22).

HRMS (ESI): *m*/*z* [M$^+$ + Na] calcd for $C_{10}H_{13}NO_3S$ + Na: 250.05084; found: 250.05064.

N,*S*-Dimethyl-*S*-(2-pyridinyl)*sulfoximine* (7l)

Eluent: EtOAc; yield: 78 mg (46%); colorless oil.

IR (ATR): 3847 (vw), 3420 (m), 2916 (m), 2804 (vw), 2694 (vw), 2296 (m), 2092 (m), 1996 (vw), 1916 (w), 1742 (w), 1643 (vw), 1569 (m), 1423 (s), 1315 (vw), 1236 (vs), 1149 (vs), 1103 (vs), 974 (s), 854 (m), 766 (vs), 689 (vw) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.76 (m, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 7.94 (td, *J* = 7.7, 1.2 Hz, 1 H), 7.53–7.47 (m, 1 H), 3.23 (s, 3 H), 2.66 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.5, 150.6, 137.9, 126.6, 123.6, 41.1, 29.7.

MS (EI, 70 eV): *m*/*z* (%) = 171 ([M$^+$], 2), 155 (4), 142 (20), 127 (7), 124 (16), 107 (10), 96 (9), 95 (7), 93 (4), 92 (6), 80 (22), 79 (37), 78 (100), 76 (6), 75 (5), 67 (12), 63 (8), 52 (15), 51 (53), 47 (5).

Anal. Calcd for $C_7H_{10}N_2OS$: C, 49.39; H, 5.92; N, 16.46. Found: C, 49.24; H, 5.96; N, 16.32.

N-Methyl-*S*-ethyl-*S*-*phenylsulfoximine* (7m)

Eluent: *n*-pentane–EtOAc (1:1) to EtOAc; yield: 97 mg (53%); colorless oil.

IR (ATR): 3827 (vw), 3408 (w), 3062 (vw), 2932 (w), 2878 (w), 2804 (w), 2666 (vw), 2321 (vw), 2099 (w), 2000 (vw), 1920 (vw), 1741 (vw), 1646 (vw), 1580 (vw), 1447 (s), 1233 (vs), 1142 (vs), 981 (vw), 927 (vw), 859 (vs), 771 (s), 728 (vs), 689 (s) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85–7.81 (m, 2 H), 7.62–7.58 (m, 1 H), 7.57–7.53 (m, 2 H), 3.19–3.09 (m, 2 H), 2.66 (s, 3 H), 1.21 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 137.0, 133.0, 129.7, 129.5, 50.9, 29.6, 7.5.

MS (EI, 70 eV): *m*/*z* (%) = 184 (12), 183 ([M$^+$], 7), 155 (12), 154 (21), 126 (11), 125 (24), 109 (20), 108 (6), 107 (89), 106 (60), 105 (26), 97 (21), 94 (13), 91 (6), 79 (11), 78 (50), 77 (100), 76 (5), 65 (10), 61 (7), 60 (8), 51 (48).

HRMS (ESI): *m*/*z* [M$^+$ + H] calcd for $C_9H_{14}NOS$: 184.07906; found: 184.07909.

N-Methyl-*S*-cyclopropyl-*S*-*phenylsulfoximine* (7n)

Eluent: *n*-pentane–EtOAc (1:1) to EtOAc; yield: 23 mg (12%); colorless oil.

IR (ATR): 3573 (vw), 3394 (vw), 3059 (vw), 3014 (vw), 2915 (w), 2875 (w), 2804 (w), 2663 (vw), 2329 (vw), 2097 (w), 1990 (vw), 1908 (vw), 1733 (vw), 1640 (vw), 1581 (vw), 1444 (s), 1305 (w), 1242 (vs), 1186 (m), 1145 (vs), 1109 (s), 1082 (s), 997 (vw), 887 (vs), 857 (vs), 760 (s), 724 (vs), 689 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.76 (m, 2 H), 7.59–7.46 (m, 3 H), 2.65 (s, 3 H), 2.55–2.43 (m, 1 H), 1.46–1.38 (m, 1 H), 1.08–0.97 (m, 2 H), 0.82–0.73 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.2, 132.7, 129.4, 129.0, 32.9, 29.9, 5.8, 4.9.

MS (EI, 70 eV): *m*/*z* (%) = 197 (6), 196 (38), 195 (44), 194 ([M$^+$], 22), 167 (8), 166 (5), 154 (13), 147 (10), 126 (8), 125 (51), 118 (6), 117 (19), 116 (11), 115 (13), 109 (15), 107 (29), 106 (100), 105 (13), 104 (5), 97 (33), 94 (8), 91 (6), 87 (5), 85 (34), 83 (49), 79 (13), 78 (23), 77 (81), 76 (5), 65 (9), 61 (6), 53 (5), 51 (40), 50 (15), 49 (5), 48 (10), 47 (15).

HRMS (ESI): *m*/*z* [M$^+$ + Na] calcd for $C_{10}H_{13}NOS$ + Na: 218.06101; found: 218.06102.

N,S-Dimethyl-*S*-*benzylsulfoximine* (7o)

Eluent: *n*-pentane–EtOAc (1:1) to EtOAc; yield: 27 mg (15%); colorless oil.

IR (ATR): 3868 (vw), 3393 (w), 2918 (m), 2806 (w), 2323 (w), 2091 (w), 1896 (w), 1652 (w), 1454 (m), 1413 (m), 1314 (w), 1232 (vs), 1117 (vs), 976 (m), 843 (m), 774 (m), 699 (m) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.35 (m, 5 H), 4.32 (s, 2 H), 2.85 (s, 3 H), 2.70 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 130.7, 129.8, 129.1, 128.9, 59.5, 38.4, 29.6.

MS (EI, 70 eV): *m*/*z* (%) = 183 ([M$^+$], 1), 168 (3), 92 (7), 91 (100), 89 (5), 65 (21), 63 (9).

HRMS (ESI): *m*/*z* [M$^+$ + Na] calcd for $C_9H_{13}NOS$ + Na: 206.06101; found: 206.06139.

N,S-Dimethyl-*S*-*cyclohexylsulfoximine* (7p)

Eluent: EtOAc; yield: 77 mg (44%); colorless oil.

IR (ATR): 3530 (w), 2928 (vs), 2865 (s), 2804 (w), 2323 (vw), 2089 (w), 1993 (vw), 1644 (vw), 1450 (m), 1227 (vs), 1131 (vs), 958 (m), 849 (s), 752 (vw), 694 (w) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.88 (tt, *J* = 12.3, 3.4 Hz, 1 H), 2.76 (s, 3 H), 2.73 (s, 3 H), 2.25–2.16 (m, 2 H), 1.88 (d, *J* = 13.5 Hz, 2 H), 1.68 (d, *J* = 13.0 Hz, 1 H), 1.48–1.37 (m, 2 H), 1.30–1.22 (m, 2 H), 1.19–1.11 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 62.5, 34.7, 29.2, 26.6, 26.5, 25.6, 25.6, 25.2.

MS (EI, 70 eV): *m*/*z* (%) = 176 ([M$^+$], 10), 145 (5), 94 (24), 93 (23), 83 (27), 79 (6), 78 (47), 77 (5), 67 (10), 63 (139), 55 (100), 54 (5), 53 (13), 47 (5).

HRMS (ESI): *m*/*z* [M$^+$ + H] calcd for $C_8H_{18}NOS$: 176.11036; found: 176.10951.

Methyl 2-{[(Benzyloxy)carbonyl]amino}-4-(*N,S-dimethylsulfonimidoyl*)butanoate (7q)

Eluent: EtOAc; yield: 158 mg (46%); viscous colorless oil.

IR (ATR): 3855 (vw), 3319 (w), 2943 (m), 2807 (vw), 2641 (vw), 2320 (w), 2082 (w), 1717 (vs), 1529 (s), 1446 (m), 1223 (vs), 1148 (vs), 1047 (vs), 853 (m), 744 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.12 (m, 5 H), 6.22 (dd, *J* = 41.1, 7.9 Hz, 1 H), 5.05 (s, 2 H), 4.40 (s, 1 H), 3.69 (s, 3 H), 3.19–2.99 (m, 2 H), 2.80 (s, 3 H), 2.69 (s, 3 H), 2.39–2.27 (m, 1 H), 2.20–2.07 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 171.6, 156.1, 136.0, 128.5, 128.2, 128.2, 128.1, 128.1, 67.1, 52.7, 52.6, 52.5, 49.9, 38.6, 38.4, 29.0, 28.9, 26.1, 26.0.

MS (EI, 70 eV): *m*/*z* (%) = 343 (1), 342 ([M$^+$], 2), 250 (2), 249 (3), 158 (10), 146 (2), 120 (2), 114 (11), 111 (2), 107 (3), 97 (3), 94 (9), 92 (9), 91 (100), 85 (2), 83 (3), 79 (2), 78 (10), 71 (3), 65 (4), 57 (4).

HRMS (ESI): *m*/*z* [M$^+$ + H] calcd for $C_{15}H_{23}N_2O_5S$: 343.13222; found: 343.13278.

Acknowledgment

V.B. thanks the Alexander von Humboldt foundation for a postdoctoral fellowship. We also thank Prof. Dr. M. Rueping and C. Vermeeren for performing preparative high-performance liquid chromatography.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380536.

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